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

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The doping of an organic backbone with boron and nitrogen has recently garnered significant attention in the scientific community. In this context, the incorporation of borazine moieties into molecular scaffolds has imparted unique (opto)electronic properties that differ substantially from those of their all-carbon analogs. Despite their promising characteristics and potential applications in materials science, their broader use is hampered by synthetic challenges. Specifically, the synthesis of borazine-containing compounds often necessitates strictly controlled anhydrous conditions, prolonged reaction times, and the use of hazardous starting materials and solvents. To address these limitations, we have developed an efficient and more environmentally friendly catalytic protocol for the synthesis of *B*,*B*′,*B*″-tri(aryl)borazines, avoiding the use of both metals and solvents. By exploiting microwave-assisted heating, we optimized the reaction conditions, significantly reducing reaction times while using triflic anhydride as a sub-stoichiometric promoter and minimizing the amount of hexamethyldisilazane (HMDS) without compromising yield or product integrity. The optimized reaction conditions, to the best of our knowledge, enabled the efficient synthesis of a diverse array of substrates for the first time, providing a promising foundation for further investigation into their potential applications in advanced materials development.

Green foundation

1. We have defined a protocol to address the issues related to the synthesis of borazine-containing compounds that often necessitate critical conditions and established a catalytic protocol operating under solvent-free and microwave-assisted heating conditions.
2. Beyond the use of boronates as a safer, milder boron source compared to BCl_3, the adoption of MW and solvent-free conditions led to significant benefits, including a lower *E*-factor and improved EcoScale values.
3. This protocol enriches the synthetic repertoire for borazine chemistry and opens new avenues for further functionalization of *N*–H borazines in a sustainable manner.

Introduction

Back in 2005, the groundbreaking studies of S. Yamaguchi and C. M. Che, respectively, on the synthesis of hexa-arylborazines (HABs) and *B*,*B*′,*B*″-tri(aryl)borazines, turned the spotlight on their importance for optoelectronic applications.[1,2] Borazines, the “valence isomers of benzene,” are six-membered heterocycles with alternating B and N atoms.[3] Due to the polarity of the B–N bond, caused by an unequal electron sharing between boron and nitrogen, borazines show an increase in the HOMO–LUMO gap and reduced aromaticity compared to their pure carbon analogs.[4,5] These differences are mainly reflected in exceptional optical applications, among others. In addition to optoelectronic applications, borazine-based (molecular) materials are among the ideal candidates for developing sustainable catalysts for metal-free chemical transformations, such as the use of hexamethyl borazine as a recyclable trifluoromethylation reagent,[6] as well as borazine-doped nanocarbon-based catalysts for the sustainable production of vinyl chloride.[7]

Over the years, further developments have expanded the applications of these molecular entities across various fields,[8–10] including their use in the synthesis of boron nitride (hBN) and hybrid boron carbon nitride (BCN),[11] in metal and covalent organic frameworks (MOFs and COFs, respectively),[12–14] polymers and ceramics,[15] and for doping of nanographene.[16]

Although we can now produce a wide range of HABs in a waste-minimized continuous flow process,[17–19] the existing

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synthetic protocols for their *B*,*B*′,*B*″-aryl substituted counterparts, despite their remarkable chemical stability compared to *N*,*N*′,*N*″-tri(aryl)borazines and potential applications in organic light-emitting devices (OLEDs),[2] are yet to be updated to enable the synthesis of a broader range of aryl groups and more eco-friendly production routes.

To the best of our knowledge, only a few reported methods require high reaction temperatures and long reaction times to exclusively synthesize *B*,*B*′,*B*″-tri(phenyl)borazine (Fig. 1).

The first synthesis of B-aryl substituted borazines was reported by Nöth *et al.* in 1974.[20] In particular, *B*,*B*′,*B*″-tri(phenyl)borazine was obtained in 36% yield after 36 hours, using benzene, a well-known human carcinogen, as the reaction medium, *via* the reaction of dichlorophenylborane with hexamethylcyclotrisilazane (HMCS). A similar procedure was further conducted by Gruzinova and co-workers, where the same molecule was obtained in 40% yield, starting from 2,4,6-triphenylboroxine and HMCS.[21]

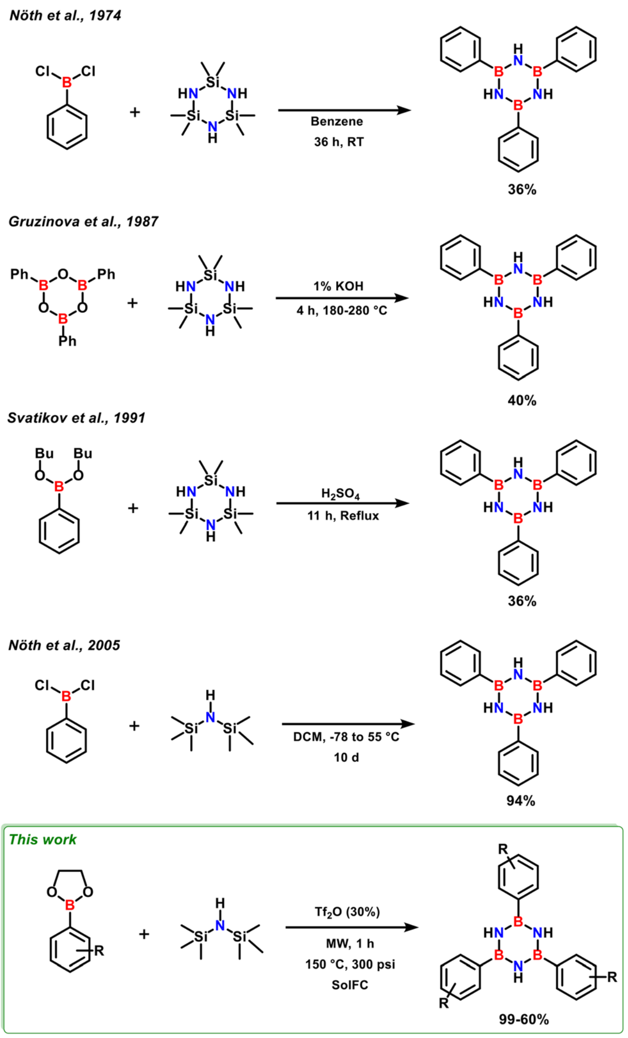


Fig. 1 Advancements in the synthesis methods for *B*,*B*′,*B*″-tri(phenyl)borazine over the years. SolFC: solvent-free conditions.

A few years later, Svatikov and co-workers studied the acid-catalyzed synthesis of *B*,*B*′,*B*″-tri(phenyl)borazine from dibutyl phenylborate, highlighting limited progress when using HMCS (36% yield).[22]

Finally, in 2005, Nöth *et al.* successfully synthesized the desired *B*,*B*′,*B*″-tri(phenyl)borazine using dichlorophenylborane and hexamethyldisilazane (HMDS), achieving an excellent yield of 98%. However, this significant accomplishment is overshadowed by the lengthy 10-day reaction time required at 55 °C to complete the transformation.[23]

Given this context and considering the recent statement from the European Commission that energy production and use contribute over 75% of the EU's greenhouse gas emissions, developing safer and less energy-intensive synthetic protocols is crucial for advancing the decarbonization of the European energy system.[24] In this context, with the aim of developing a functional-group-compatible and green-inspired synthetic protocol, we report herein a solvent- and metal-free Lewis acid-catalyzed synthesis of *B*,*B*′,*B*″-tri(aryl)borazines.

We therefore decided to develop a metal-free procedure and compare it with metal-free protocols to prevent metal coordination of the borazine –NH functionality and the well-known challenges associated with removing metal contamination, which can significantly complicate purification and negatively impact the overall efficiency and ecological balance of the process.

Employing microwave-assisted organic synthesis (MAOS) and substituting boron halides with cyclic boronic acid esters (boronates) collectively offer advantages from both synthetic and environmental perspectives.

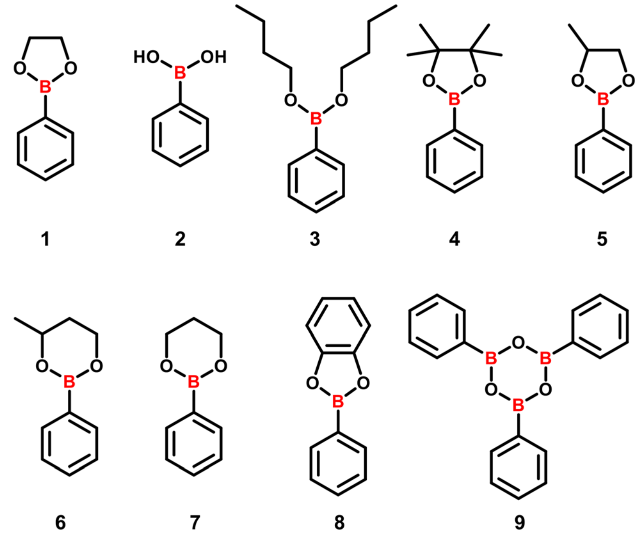
Following appropriate optimization of all the reaction parameters, a broad library of functionalized *B*,*B*′,*B*″-tri(aryl)borazines was synthesized with high yields and short reaction times. The use of tailored boronic esters allows for precise functionalization of the aryl moiety, facilitating potential late-stage functionalization and further development of novel applications.

Results and discussion

Boron and nitrogen source screening

Method development was initiated by investigating various boron and nitrogen sources, evaluated based on Lewis acidity/basicity, thermodynamic stability, structural flexibility (boron-site pyramidalization), intrinsic safety, and ease of preparation. The objective was mainly to facilitate the formation of the B·N Lewis adduct as the initial step in B–N bond formation while minimizing the formation of linear oligomeric $(B–N)_n$ species, thereby efficiently promoting borazine ring formation.[25,26]

Boronate candidates (Scheme 1), compared to boron halides, are considerably less hazardous and more stable, although the higher Lewis acidity of boron halides, such as R-BCl_2, offers a greater ability to form the borazine ring. On the other hand, when boronic esters are compared with boronic acids, they show a lower tendency for self-conden-



Scheme 1 Boron sources considered for the synthesis of *B*,*B*′,*B*″-tri(aryl)borazines.

sation, a fundamental prerogative for B–N condensation, and enhanced Lewis acidity.[27,28] This property can be attributed, among other reasons, to the molecule's geometry. Specifically, boronic esters present a higher sp^3 hybridized character compared to sp^2 hybridized boron in boronic acids, a feature that might facilitate the planar-to-pyramidal shift that occurs upon B–N complexation.[29–31]

Another critical point that must not be overlooked is the boronic ester's inherent stability and steric hindrance. Finch and Lockhart's 1962 study reported that, as the size of a cyclic boronate increases, the formation of a boronate–amine adduct occurs more slowly, resulting in greater instability.[26] This is a direct consequence of the intrinsic stability of cyclic boronates. In fact, as the boronate ring size increases from five- to six-membered, the electron-donating effect becomes more pronounced, reducing the Lewis acidity of the boron center. This, in turn, decreases the overall reactivity of the boronic ester. In contrast, a five-membered boronate will be more reactive, allowing the formation of an irreversible B–N bond, because it can release internal strain by adopting a tetrahedral boron configuration, which, as previously specified, increases the corresponding Lewis acidity. Steric hindrance also plays a non-marginal role. Boronates with highly substituted rings are more sterically hindered and less susceptible to B–N adduct formation.

Regarding the selection of nitrogen sources, the range of choices is narrower than that for boron. Like boronates, the nitrogen-containing molecule must be capable of participating in the cyclocondensation reaction while also being compatible with the boron-based partner. Aminosilanes such as hexamethyldisilazane (HMDS, **10**) and hexamethylcyclotrisilazane (HMCS) are the most promising candidates for synthesizing *B*,*B*′,*B*″-aryl substituted borazines, based on previously reported procedures.

The higher boiling point of HMCS can be beneficial as it promotes thermal cleavage of the silicon–nitrogen bond. However, the harsh conditions can shift the reaction toward the formation of poly(iminoborane)s and boroxazine rather than borazine.[22] Given these considerations, commercially available HMDS (**10**) was chosen as its nitrogen counterpart.

The experimental results shown in Table 1, conducted under conventional heating, align with the previously mentioned hypothesis, confirming through entries 5 and 11 the preference for five-membered over six-membered ring boronates (32% *vs.* 15% isolated yield, respectively).

Boronic acid **2** (entry 6), acyclic boronic ester **3** (entry 7), and boroxine **9** (entry 13) did not prove to be suitable starting materials for our purposes. The latter two, in particular, despite having been reported as viable substrates to access *B*,*B*′,*B*″-tri(phenyl)borazine (**11**), failed to react under our screening conditions. This could be attributed to the lower temperature adopted (150 °C *vs.* the reported 180–280 °C) and the absence of a catalyst (0.3% conc. H_2SO_4 and 1% KOH, respectively).[21,22]

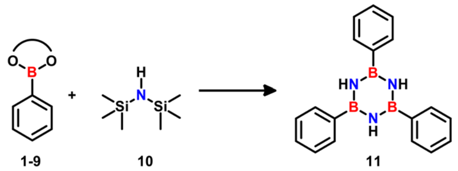
The scenario with the catechol-based boronic ester **8** (entry 12) is somewhat different. Although its Lewis acidity is higher compared to other boronates,[32] which is reflected in the acceptable yield obtained, the reduced O-to-B-π-donation makes it more susceptible to nucleophilic attack, even by water.[33]

As a result, 2-phenyl-1,3,2-dioxaborolane (**1**) was identified as the most reactive boronic ester, offering not only increased safety and stability but also a straightforward, adaptable preparation method for various substituents.

Catalyst/activator screening and reaction parameter optimization

After determining the most suitable starting materials, our focus shifted to developing an efficient synthetic protocol for accessing *B*,*B*′,*B*″-tri(aryl)borazines. The first aspect taken into

Table 1 Screening of the boron source[a]



Entry	Boron source	10 (mL)	*T* (°C)	*t* (h)	Isolated yield (%)
1	**1**	0.21	110	24	0
2	**1**	0.21	110	72	0
3	**1**	0.21	150	72	0
4	**1**	1.3	150	72	13
5	**1**	3	150	72	32
6	**2**	3	150	72	0
7	**3**	3	150	72	Traces
8	**4**	3	150	72	10
9	**5**	3	150	72	Traces
10	**6**	3	150	72	0
11	**7**	3	150	72	15
12	**8**	3	150	72	19
13	**9**	3	150	72	0

[a] Reaction conditions: **1–9** (1 mmol).

consideration involved refining the reaction time and heating method. Initially, the highest isolated yield was achieved under conventional heating for 72 hours at 150 °C, yielding 32% of the corresponding borazine.

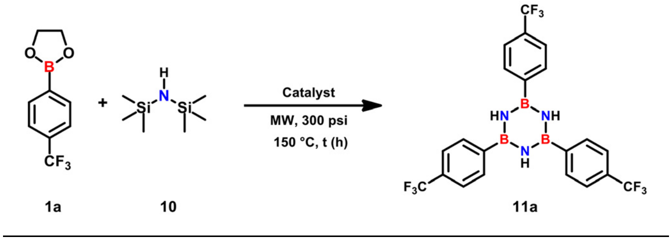
Aiming for a greener and less energy-demanding procedure, we investigated transitioning to microwave-assisted organic synthesis (MAOS), a non-conventional heating technology with well-documented benefits.[34] Indeed, microwave irradiation offers considerable time and energy savings by enabling selective dielectric heating. This allows for the replacement of traditional solvents with greener alternatives or, when feasible, the establishment of solvent-free procedures.

To assess the effectiveness of microwave irradiation, we performed a reaction between **1a** and HMDS (**10**) and benchmarked it against conventional heating. The microwave-assisted protocol delivered a comparable yield to that previously obtained under conventional heating (Table 1, entry 5), while significantly reducing the reaction time to 5 hours (Table 2, entry 1).

A catalytic system was explored to increase the reaction rate further. Inspired by previously reported procedures,[22] we first tested 30 mol% H_2SO_4 while reducing the reaction time to 3 h, but this did not lead to satisfactory results. Therefore, we screened other known Lewis acids that might compensate for the lower acidity of boronic esters compared to boron halides.

Different strong Lewis acids, such as BBr_3, BCl_3, $AlCl_3$, or $FeCl_3$ (Table 2, entries 3–6), were explored without obtaining satisfactory results. At this stage, selecting an acid with a lower Hammett acidity (H_0) value was crucial. Since sulfuric acid was the only catalyst that yielded moderate results, we turned to a superacid, such as triflic acid (TfOH).

Table 2 Screening of acidic catalysts and activators under MW irradiation[a]



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

[a] Reaction conditions: **1a** (1 mmol), **10** (3 mL), 150 °C.

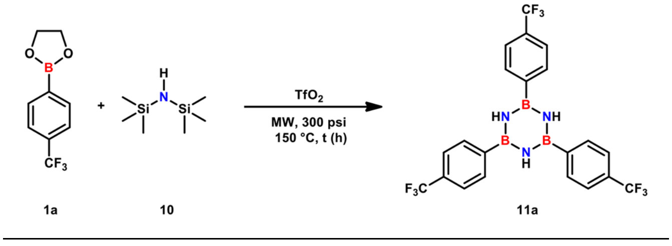
The enhanced acidity of TfOH resulted in a higher isolated yield of 49% (Table 2, entry 8), confirming the need for a stronger acid catalyst.

On the other hand, the N–Si bond cleavage in HMDS can also be promoted by using an acidic catalyst. In fact, several triflate-based catalysts have been reported to facilitate reactions involving the desilylation of HMDS.[35,36] Among these, metal triflates are frequently employed due to the Lewis acid–base interactions between the electrophilic metallic center and the basic N. However, as our study targets avoiding the use of solvents, and since HMDS (**10**) works as a solvent-like excess reagent, we hypothesized that the use of such metal salts could increase the system's heterogeneity. The lack of solubility could impede mass transfer or lead to inconsistent heating profiles, ultimately compromising the reaction outcome.

To address this issue, we replaced the metal triflates by testing their different liquid counterparts, such as trimethylsilyl trifluoromethanesulfonate (TMSOTf), a strong Lewis acid known to catalyze carbohydrate silylation,[37] *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf), and triflic anhydride (Tf_2O). The latter, confirming our hypothesis, gave the best results, yielding a good 75% isolated yield after 3 h of irradiation at 150 °C (Table 2, entry 11).

After identifying the optimal reaction temperature and Tf_2O as the best activator, we focused on optimizing the remaining parameters (Table 3) to improve the reaction yield. Initially, increasing the concentration by reducing the amount of HMDS (**10**) resulted in an 8% increase in yield (Table 3, entry 1). This improvement showed that controlling the amount of HMDS (**10**) directly influences the reaction outcome. Building on this, we investigated reducing the reaction time to 2 hours, which yielded results comparable to those achieved with a longer duration (83% *vs.* 82%, Table 3, entries 1 and 2). By further reducing the reaction time to 1.5 hours, we observed a 61% yield (Table 3, entry 3).

Table 3 Reaction time and quantity of HMDS optimization[a]



Entry	Tf_2O (mol%)	10 (mL)	t (h)	Isolated yield (%)
Control	30	3	3	75
1	30	2	3	83
2	30	2	2	82
3	30	2	1.5	61
4	30	1	1.5	98
5	30	1	1	98
6	30	1	0.5	60
7	15	1	1	32
8	60[b]	1	1	Traces

[a] Reaction conditions: **1a** (1 mmol). [b] TfOH was used instead of Tf_2O.

Building on the effects observed with reduced quantity of HMDS (**10**), we further reduced its volume to 1 mL while maintaining a reaction time of 1.5 hours. We also confirmed that performing the reaction under more concentrated conditions was advantageous, maximizing the isolated yield to an excellent 98% (Table 3, entry 4). A further reduction in reaction time led to a linear increase in isolated yield, with 1 hour identified as the optimal duration for complete conversion (Table 3, entry 5).

Finally, to complete the optimization stage, the Tf_2O amount was modulated. As reported in entry 7, reducing its quantity to 15 mol% resulted in a significant decrease in the isolated yield.

To gain further insight into the process, we investigated whether the active species is represented by triflic anhydride or triflic acid, the latter potentially formed *via* hydrolysis of Tf_2O. To this end, a control experiment under the optimized conditions using 60 mol% TfOH was conducted, which proved ineffective and afforded negligible conversion to the desired product, with only a trace yield (Table 3, entry 8).

This implies that triflic anhydride (Tf_2O) leads to the formation of the active species under our developed conditions.

The scope and limitations of our protocol were therefore investigated by expanding the substrate scope under the optimized reaction conditions (Table 3, entry 5) to several aryl decorated 2-aryl-1,3,2-dioxaborolanes (**11–11r**).

The method developed here proved to be highly efficient, achieving excellent yields across a wide range of both electron-withdrawing and electron-donating substituted substrates. However, no discernible trend was observed in the product yields of the previously mentioned decorated boronates (Scheme 2).

Two critical factors were instead identified as non-negligible in this reaction: the solubility of both the boronic ester and the final product, and the steric hindrance near the boron atom.

Isolated product yields significantly declined with increased steric bulk adjacent to the boron, particularly with *ortho*-substituents. Specifically, a 96% yield was achieved with *ortho*-positioned fluorine (**11p**), whereas larger substituents led to no product formation (**11q** and **11r**).

As is well known, incorporating boron and nitrogen in the *para* position of polycyclic aromatic hydrocarbons (PAHs) can tailor the HOMO–LUMO gap due to their opposite resonance effects. This proves to be a crucial step for tuning opto-electronic properties of materials.[2,38]

To explore novel frameworks in this field, product **11f** was synthesized.

Environmental sustainability assessment

To underscore the impact of the work presented here, we evaluated the environmental benefits of our established procedure for the synthesis of B,B',B''-tri(phenyl)borazine (**11**), as there are direct literature examples available for comparison.

We focused specifically on the comparison of procedures not involving the use of metal catalysts, which can complicate the isolation processes, and the impact of metal should also be considered in terms of cost and toxicity.

Initially, we focused on the *E*-factor, a key metric that quantifies the environmental impact of a synthetic protocol by measuring the mass ratio of waste to the desired product.[39]

As illustrated in Fig. 2, our method showed a significantly lower *E*-factor (29.1), underscoring its enhanced sustainability in terms of waste generation compared to other reported protocols (see Table SI-2 for further details).

Several improvements contributed to these green achievements. Above all, the absence of a reaction medium is definitely the parameter that most positively affects the *E*-factor. Performing the reaction without solvents, due to the use of HMDS (**10**) as both a reactant and the reaction medium, drastically minimized process-associated waste compared to the reference methods. These, in contrast, use large volumes of dangerous and toxic solvents (benzene, dichloromethane, diethyl ether, and hexane) both during the reaction and, particularly, in the purification stages.[20–23]

In particular, by substituting these solvents in the purification step with a safer alternative such as heptane and, at the same time, reducing the volume required, we developed an innovative isolation method that achieved the lowest *E*-factor value among known procedures.

Another key aspect contributing to the excellent waste minimization of our procedure is the elimination of metal catalysts or additives. This also avoids the need for energy- and solvent-intensive, time-consuming purification steps, which would otherwise increase the overall environmental impact of the protocol described.

As stated above, the *E*-factor focuses solely on the waste produced and, based on its amount, assigns a numerical value indicating the less impactful route (the lower the waste, the lower the *E*-factor score, the greener the procedure). However, this metric fails to provide insights into productivity, technical setups used across procedures and alternative materials that offer safer and more cost-effective options than the commonly used ones.

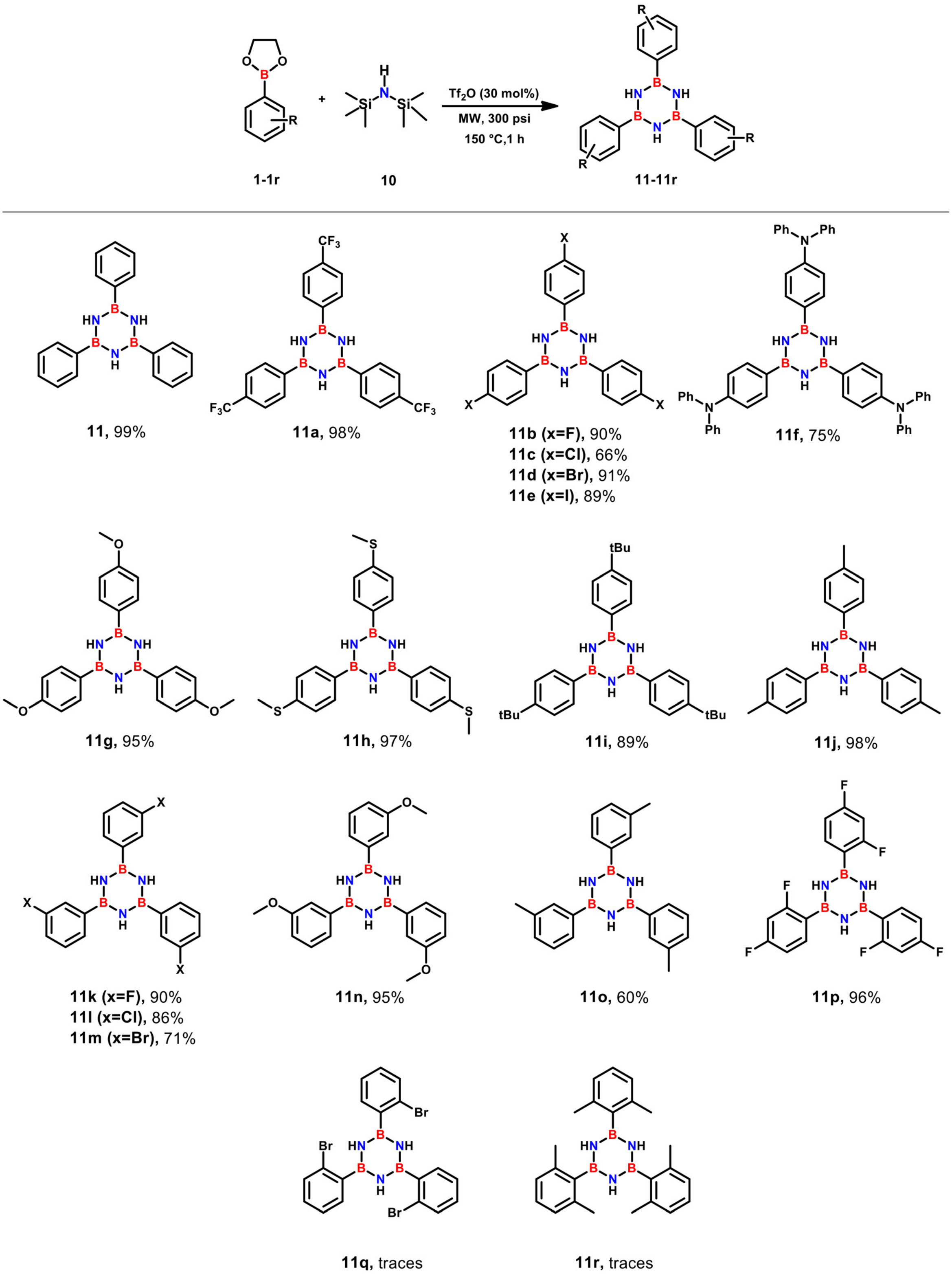
Simple and fast tools that consider these parameters include the space–time yield (STY) and EcoScale.

The first metric expresses process performance in terms of product generation, related to reaction volume and time ($g\ L^{-1}\ h^{-1}$).

As illustrated in Fig. 2, our process proved to be the most efficient among those reported in the literature (see Table SI-3 for further details), achieving an impressive 85.16 $g\ L^{-1}\ h^{-1}$. This result is largely attributed to the brief reaction time (1 h) and the lack of a reaction solvent, which significantly restricts the reaction volume.

Regarding the EcoScale, it is a web tool designed to define the green quality of a synthetic procedure, which takes into account not only the benignity of reagents, additives, solvents, and catalysts but also the costs, the experimental methodologies, and the new technologies employed.[40]

As shown in Fig. 3, our procedure, yielding an EcoScale value of 66, is the least impactful among the methods con-



Scheme 2 Substrate scope of the triflic anhydride-catalyzed synthesis of *B*,*B*′,*B*′′-tri(aryl)borazines **11–11r**. Reaction conditions: **1–1r** (1 mmol) and **10** (1 mL).

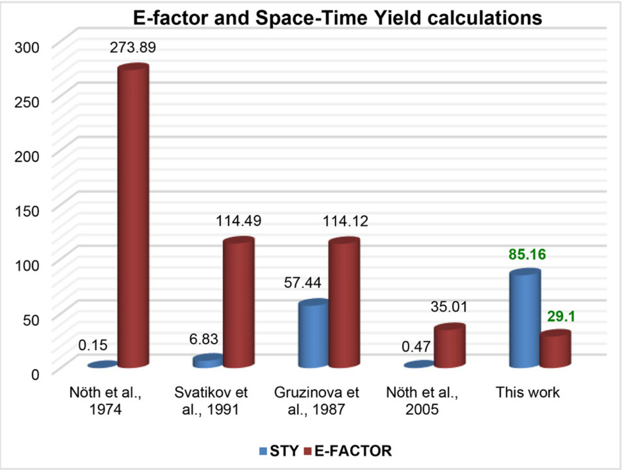


Fig. 2 *E*-factor and Space–Time Yield (STY) value comparison.

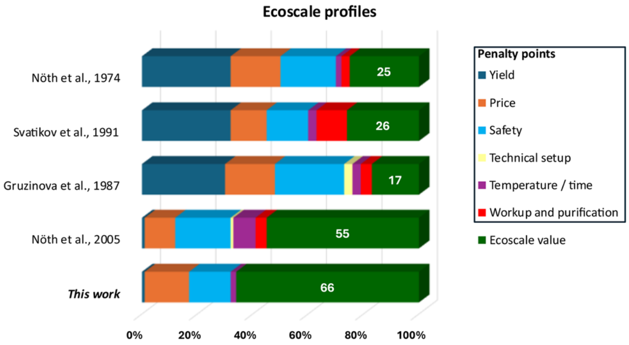


Fig. 3 EcoScale profile of the developed protocol compared with the literature references. The EcoScale values (green bars) are calculated as 100 minus the penalty point assigned for each of the parameters considered.

Table 4 STY and SHS for the purification solvents adopted both in this work and in the reference procedures

	Solvent	STY	SHS (∑ Ω)
Gruzinova et al. (1987)[21]	Benzene	57.44	1005.586
Nöth et al. (2005)[23]	Diethyl ether	0.47	485.531
Svatikov et al. (1991)[22]	Hexane	6.83	8.849
Nöth et al. (1974)[20]	Hexane	0.15	8.849
This work	Heptane	85.16	7.402

sidered (see Table SI-4), confirming the findings from the *E*-factor calculations.

In particular, the limited reaction time (1 h),the increased reaction rate and conversion mediated by MW irradiation, in addition to a safer isolation procedure, proved to be crucial factors for the significant sustainability enhancement.

An additional sustainability assessment was taken into account when selecting the purification solvent. As previously explained, the *E*-factor was used to evaluate the waste produced; with the STY, we assessed process productivity; and by calculating the EcoScale, we provided a clear view of the overall process greenness. Actually, we have not yet focused on one of the principal upgrades we provided, that is the use of a more benign solvent, *i.e.*, heptane, in contrast to those (hexane, benzene, and diethyl ether) used by its literature reference counterparts, which, alongside dipolar aprotic solvents, are among the most toxic and hazardous for both human health and the environment.[41] To quantify this benefit, we calculated the Safety/Hazard Score (SHS) proposed by Andraos,[42] which considers the intrinsic toxicological profile and the operational chemical-associated risk of an input material or process.

The final SHS value was derived by considering a wide selection of impact categories Ω (CGP: corrosiveness potential as a gas; CLP: corrosiveness potential as a liquid; FP: flammability potential; OBP: oxygen balance potential; XVP: explosive vapour potential; OELP: occupational exposure limit potential; SDP: skin dose potential; and RPP: risk phrase potential), with their sum ($\sum\Omega$) providing the overall safety/hazard score.

The SHS related to heptane is lower (7.402) than the others, confirming its higher safety (Table 4). As detailed in Table SI-5, the lower magnitude of this value is mainly dependent on heptane's limited OELP, SDP, and RPP categories, which, in contrast, significantly impact benzene, diethyl ether, and hexane, respectively.

Conclusions

In conclusion, we developed an optimized synthetic protocol for the synthesis of *B*,*B*′,*B*″-tri(aryl)borazines, achieving notable efficiency and environmental benefits. Our evaluation of alternative boron and nitrogen sources identified 2-phenyl-1,3,2-dioxaborolane (**1**) and hexamethyldisilazane (**10**) as the ideal reagents. The application of microwave-assisted organic synthesis, along with triflic anhydride as a strong Lewis acid activator, significantly enhanced product yields while drastically reducing reaction times. Moreover, the use of HMDS (**10**) as both a reactant and the reaction medium, combined with the avoidance of metal-based catalysts or additives, enabled a streamlined work-up process that led to a considerably lower *E*-factor compared to existing methods, underscoring the limited environmental impact of the developed protocol, as confirmed by the EcoScale value.

The versatility of our method was further demonstrated by its compatibility with various functional groups, enabling the synthesis of valuable borazine derivatives. Overall, this work enriches the synthetic repertoire in borazine chemistry and highlights the importance of establishing more environmentally benign processes and practices in chemical research and development.

Author contributions

E. C.: writing – review & editing, writing – original draft, methodology, and data curation. F. C.: writing – review & editing, methodology, and investigation. A. N. K.: methodology and investigation. D. M.: methodology and investigation. F. H.: methodology and investigation. L. V.: writing – review & editing, writing – original draft, supervision, funding acquisition, and conceptualization.

Conflicts of interest

There are no conflicts to declare.

Data availability

Supplementary information (SI): experimental procedures, characterization data (^{1}H-NMR, ^{13}C-NMR, ^{11}B-NMR and ^{19}F-NMR), and the *E*-factor, Space–Time Yield (STY), EcoScale, and Safety/Hazard Score (SHS) calculations. See DOI: https://doi.org/10.1039/d6gc01222a.

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References

1 A. Wakamiya, T. Ide and S. Yamaguchi, *J. Am. Chem. Soc.*, 2005, **127**, 14859–14866.
2 I. H. T. Sham, C.-C. Kwok, C.-M. Che and N. Zhu, *Chem. Commun.*, 2005, 3547.
3 K. Ota and R. Kinjo, *Chem. – Asian J.*, 2020, **15**, 2558–2574.
4 Y. Wu, X. Yan, Z. Liu, T. Lu, M. Zhao, J. Xu and J. Wang, *Chem. – Eur. J.*, 2024, e202403369.
5 R. Islas, E. Chamorro, J. Robles, T. Heine, J. C. Santos and G. Merino, *Struct. Chem.*, 2007, **18**, 833–839.
6 J. B. Geri and N. K. Szymczak, *J. Am. Chem. Soc.*, 2017, **139**, 9811–9814.
7 C. Chen, Z. Shen, Y. Zhu, F. Wang, B. Jiang and H. Qi, *RSC Adv.*, 2021, **11**, 183–191.
8 D. Marchionni, S. Basak, A. N. Khodadadi, A. Marrocchi and L. Vaccaro, *Adv. Funct. Mater.*, 2023, 2303635.
9 D. Marchionni, A. Nazari Khodadadi, E. Cela, F. Huang and L. Vaccaro, *Adv. Synth. Catal.*, 2024, **366**, 494–501.
10 D. Marchionni, D. Gernini, A. Nazari Khodadadi, E. Cela, F. Huang and L. Vaccaro, *Green Chem.*, 2024, **26**, 7752–7758.
11 Y. Kubota, K. Watanabe, O. Tsuda and T. Taniguchi, *Science*, 2007, **317**, 932–934.
12 F. Fasano, J. Dosso, C. G. Bezzu, M. Carta, F. Kerff, N. Demitri, B. Su and D. Bonifazi, *Chem. – Eur. J.*, 2021, **27**, 4124–4133.
13 T. E. Reich, K. T. Jackson, S. Li, P. Jena and H. M. El-Kaderi, *J. Mater. Chem.*, 2011, **21**, 10629.
14 K. T. Jackson, T. E. Reich and H. M. El-Kaderi, *Chem. Commun.*, 2012, **48**, 8823.
15 N. Han, S. Wang, A. K. Rana, S. Asif, J. J. Klemeš, A. Bokhari, J. Long, V. K. Thakur and X. Zhao, *Renewable Sustainable Energy Rev.*, 2022, **170**, 112910.
16 D. Marinelli, F. Fasano, B. Najjari, N. Demitri and D. Bonifazi, *J. Am. Chem. Soc.*, 2017, **139**, 5503–5519.
17 A. N. Khodadadi, E. Cela, D. Marchionni, F. Huang, F. Ferlin and L. Vaccaro, *Green Chem.*, 2024, **26**, 7059–7066.
18 A. N. Khodadadi, E. Cela, H. Mosaffa, F. Huang, D. Marchionni and L. Vaccaro, *Green Synth. Catal.*, 2025, S2666554925000456.
19 F. Campana, K. Zhou, J. A. Yunda, A. N. Khodadadi, D. Bonifazi, S. Melinte and L. Vaccaro, *Chem. Eng. J.*, 2025, **504**, 158822.
20 H. Nöth, W. Tinhof and T. Taeger, *Chem. Ber.*, 1974, **107**, 3113–3120.
21 E. A. Gruzinova, M. Yu. Svatikov, G. V. Kotrelev and A. A. Zhdanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1059–1060.
22 M. Yu. Svatikov, E. A. Gruzinova and G. V. Kotrelev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1494–1496.
23 H. Nöth and A. Troll, *Eur. J. Inorg. Chem.*, 2005, 3524–3535.
24 Energy and the Green Deal, https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal/energy-and-green-deal_en, (accessed October 23, 2024).
25 H. Shi, C. Shen, J. Hu, J. Zhang and J. Xie, *Ceram. Int.*, 2021, **47**, 6068–6076.
26 A. Finch and J. C. Lockhart, *J. Chem. Soc.*, 1962, 3723.
27 A. Adamczyk-Woźniak, M. Jakubczyk, P. Jankowski, A. Sporzyński and P. M. Urbański, *J. Phys. Org. Chem.*, 2013, **26**, 415–419.
28 N. Fujita, S. Shinkai and T. D. James, *Chem. – Asian J.*, 2008, **3**, 1076–1091.
29 T. D. James and S. Shinkai, in *Host-Guest Chemistry*, ed. S. Penadés, Springer Berlin Heidelberg, Berlin, Heidelberg, 2002, vol. 218, pp. 159–200.
30 D. G. Hall, in *Boronic Acids*, ed. D. G. Hall, Wiley, 1st edn, 2005, pp. 1–99.
31 A. Lopalco, V. J. Stella and W. H. Thompson, *Eur. J. Pharm. Sci.*, 2018, **124**, 10–16.
32 A. Adamczyk-Woźniak, M. Jakubczyk, A. Sporzyński and G. Żukowska, *Inorg. Chem. Commun.*, 2011, **14**, 1753–1755.
33 C. P. Manankandayalage, D. K. Unruh and C. Krempner, *Dalton Trans.*, 2020, **49**, 4834–4842.

34 C. O. Kappe, *Angew. Chem., Int. Ed.*, 2004, **43**, 6250–6284.

35 C.-K. Chan, Y.-H. Chung and C.-C. Wang, *RSC Adv.*, 2022, **12**, 8263–8273.

36 M. Maier, J. Klopf, C. Glasmacher, F. Fantuzzi, J. Bachmann, O. Ayhan, A. Koner, B. Engels and H. Helten, *Chem. Commun.*, 2022, **58**, 4464–4467.

37 A. A. Joseph, V. P. Verma, X. Liu, C. Wu, V. M. Dhurandhare and C. Wang, *Eur. J. Org. Chem.*, 2012, 744–753.

38 T. Hatakeyama, K. Shiren, K. Nakajima, S. Nomura, S. Nakatsuka, K. Kinoshita, J. Ni, Y. Ono and T. Ikuta, *Adv. Mater.*, 2016, **28**, 2777–2781.

39 R. A. Sheldon, *Green Chem.*, 2023, **25**, 1704–1728.

40 K. Van Aken, L. Strekowski and L. Patiny, *Beilstein J. Org. Chem.*, 2006, **2**, 3.

41 G. Quaglia, F. Campana, L. Latterini and L. Vaccaro, *ACS Sustainable Chem. Eng.*, 2022, **10**, 9123–9130.

42 J. Andraos, *Org. Process Res. Dev.*, 2013, **17**, 175–192.