

B(OH)₃-Catalyzed Dual Friedel-Crafts Type Reaction of Anilines and Aldehydes to Access Di- or Triarylmethanes (TRAMs)

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The catalytic influences of boric acid have been introduced on dual Friedel-Crafts reaction between arylamines and aldehydes to install the Csp³-center that leads to the formation of *di*- or *tri*-substituted methanes. The described reaction conditions have directed the transformation to favor the *para-para* substitution pattern to deliver the major products rather than the corresponding *ortho-para* functionalization process. The devised transformation was examined by DFT calculation, which shows

the favorable activation energy of transition states (TS) for the generation of highly substituted molecular scaffolds. The method was applicable over diversely substituted aldehydes and arylamines to afford the final products in excellent yields (60-92%) and selectivity. The proposed mechanism is supported by suitable control experiments, GC-MS studies, and DFT calculations.

Introduction

The C–C bond-forming reactions play a significant role in accessing a plethora of bioactive molecules and useful pharmaceutical intermediates.^[1-2] Among these processes, the classical Friedel-Crafts reaction remains attractive to such C–C bond-forming reactions, which have been well explored in the diverse fields of chemistry.^[2] This strategy has also been extended for the synthesis of triarylmethanes and their allied structures due to their notable biological and pharmacophoric properties.^[3] These “*small but smart*” scaffolds are found abundantly in natural products^[4] and act as key intermediates in synthesis,^[5] dyes,^[6] fluorescent probes,^[7] as anti-fungal agents

in commercial fish hatcheries,^[8] photochromic agents,^[9] medicinal chemistry,^[10] material sciences,^[11] and host-guest chemistry.^[12] The derivatives of triarylmethanes were also witnessed as anti-tubercular, anti-viral, anti-oxidant, anti-fungal, anti-cancer, and anti-inflammatory agents.^[13] Owing to their immense applications, several protocols have been reported for the synthesis of triarylmethanes (TRAMs) over the past few decades by addressing the drawbacks of previous methods.^[14]

Most of these chemical transformations were realized using the Friedel-Crafts reaction of electron-rich aldehydes with arenes and anilines. Several synthetic tools were employed to prepare triarylmethanes that involve a multistep Friedel-Crafts alkylation promoted/catalyzed by Brønsted or Lewis acids such as FeCl₃/Ac₂O,^[15] TfOH,^[16] I₂,^[17] AuCl₃,^[18] [Ir(COD)Cl]₂-SnCl₄,^[19] *ortho*-benzenedisulfonimide,^[20] Bi₂(SO₄)₃/TMSCl,^[21] perfluorinated sulfonic acid resin (Nafion-H),^[22] montmorillonite,^[23] and ZnBr₂/SiO₂.^[24]

In recent times, Afonso and co-workers have described the synthesis of TRAMs by using Yb(OTf)₃-catalyzed reaction conditions at high pressure (Scheme 1a).^[3a] In 2021, Sirion group reported a BAILs (Brønsted Acidic Ionic Liquids)-catalyzed approach towards the synthesis of aniline and phenol-based triarylmethanes (Scheme 1b).^[14a-b] Moreover, Pan and co-workers have designed an AgOTf-catalyzed Friedel-Crafts reaction of anilines and glyoxylates to access diarylmethanes (Scheme 1c).^[14c]

However, the scope of these methods was hindered by the special requirements of the designed catalysts concerning cost, availability, and their precaution in handling.^[14] To overcome these drawbacks, we aspired to employ an inexpensive and environmentally friendly catalyst such as boric acid^[25] towards the synthesis of *di*-/*tri*-substituted methanes using the Friedel-Crafts reaction between arylamines and aldehydes.

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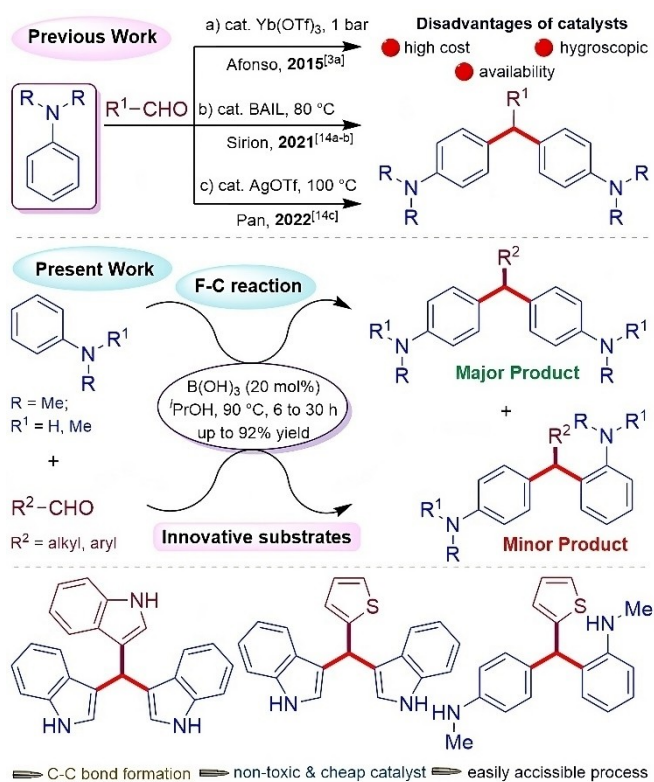
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Scheme 1. Strategies for the synthesis of triarylmethanes by Friedel-Crafts reaction.

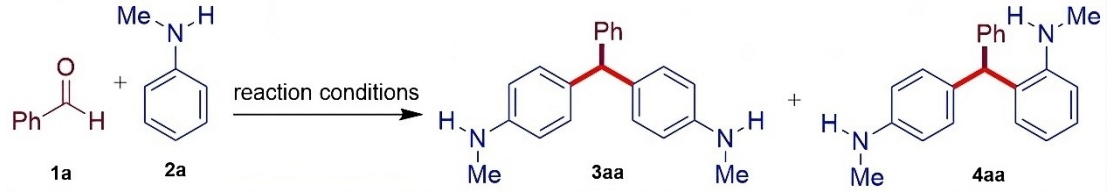
Results and Discussion

To design an efficient method for the synthesis of a diverse range of triarylmethanes, we commenced with our screening experiments by considering benzaldehyde (**1a**) and *N*-methylaniline (**2a**) as model substrates (Table 1). To initiate the experimental studies, the Brønsted acids (H₂SO₄, HCl) or Lewis acids (AlCl₃, Cu(OTf)₂, Fe(NO₃)₂, I₂, B(OH)₃) were examined for this transformation at 90 °C in isopropanol as the solvent for 24 hours (Table 1, entries 1–7). The performed reactions lead to the formation of two different regioisomers of *tri*-arylmethanes in which the corresponding *para-para* isomer **3aa** was identified as the major product and *ortho-para* isomer **4aa** remained as the minor product (Table 1, entries 1–7). In the case of H₂SO₄, the transformation resulted in the formation of product **3aa** in 46% yield and the **4aa** was observed in 12% yield (entry 1); whereas, the HCl leads to a single isomer **3aa** in rather low yield (17%) (entry 2). The Lewis acids, AlCl₃ and Cu(OTf)₂ revealed moderate efficiency in obtaining molecule **3aa** in yields ranging from 60–68% and **4aa** in yields 10–13%, respectively (entries 3–4). The reaction with Fe(NO₃)₃ resulted in trace amounts of **3aa** and **4aa** (entry 5); whereas the reaction with molecular iodine directed this transformation towards the formation of product **3aa** in 41% and **4aa** in 9% yields (entry 6). It was evident from the tested catalysts that the catalytic amounts of B(OH)₃ could lead to the selective formation of regioisomer **3aa** in higher proportion by suppressing the formation of product **4aa**. Hence, the catalytic amounts

of B(OH)₃ were considered for further optimization studies. Next, with the aim towards exclusive formation of the product **3aa**, a reaction of **1a** and **2a** was carried out in different solvent systems (entries 8–13). It was found that the reactions in MeCN, EtOH, and 1,2-DCE furnished the regioisomer **3aa** in yields ranging from 50–68% (entries 8–10); whereas, THF, CHCl₃ and DMF as solvents resulted in trace amounts of product **3aa** (entries 11–13). Among the tested solvents, the isopropanol delivered the best yield (70%) of **3aa** (entry 7). At last, we have tested the effects of reaction time on the yields of product **3aa** to realize the slight enhancement (up to 75%) in yields in 12 hours of reaction time (entries 14–16). Having performed a substantial screening of the reaction conditions, it was perceived that the highest yield (75%) of **3aa** and **4aa** (15%) were obtained when the reaction of benzaldehyde (**1a**) and *N*-methylaniline (**2a**) was carried out using 20 mol% of B(OH)₃ in isopropanol (iPrOH) as solvent at 90 °C for 12 hours (Table 1, entry 15).

After realizing the best-optimized reaction conditions, we have illustrated the scope of the invented process over a wide range of aromatic aldehydes **1** with *N*-methylaniline (**2a**) to access the diversely substituted *tri*-arylmethanes **3** as the major products and **4** as the minor products (Scheme 2). The aromatic aldehydes **1b–f** embedded with electron-donating functional groups (–OMe, –OH) delivered the desired products **3ba–fa** in higher yields (60–75%); whereas the minor products **4ba–fa** were obtained in yields ranging from 5–15%. Further, *di*- and *tri*-substituted aldehydes were subjected to the developed reaction conditions to obtain the *para-para* isomers **3ga–ha** in 65–68% yields with high selectivity. In these cases, the formation of corresponding *ortho-para* isomers **4ga–ha** was completely suppressed. These observations could be associated with the steric effects arising due to the presence of adjacent substituents that restrict *ortho-para* bond formation. On the other hand, the aromatic aldehydes embedded with electron-deficient functional groups (–Cl, –Br, –NO₂) were reacted under these reaction conditions to witness the higher selectivity towards the formation of *para-para* isomers **3ia–ma** in yields ranging from 61–91% yields. From the above outcomes, it was perceived that the presence of electron-deficient groups governs the selectivity towards the formation of *para-para* isomers **3** over *ortho-para* isomers **4**. Nevertheless, the aromatic aldehydes **1n–o** with electron-withdrawing groups (–CN, –Br) substituted at *ortho*-position lead to the generation of *para-para* isomers **3na** (Scheme 2) and **3oa** in (Scheme 3) in 62–71% yields, along with the generation of minor *ortho-para* products **4na–oa** in 9–15% yields. To demonstrate the practical application of the designed process, a gram scale synthesis was performed. The reaction conditions afforded the desired *para-para* bonded *tri*-arylmethane **3ma** as a single product in 90% yield (3.1 g), with un-identification of *ortho-para* bonded *tri*-arylmethane **4ma** (Scheme 2).

Next, the scope of this developed method was expanded using polycyclic aromatic aldehydes **1p–r** and aliphatic aldehydes **1s–t** to furnish *di*-/*tri*-substituted methanes **3** and **4**. It was found that the aldehydes **1p–q** directed the selective formation of **3pa–qa** in 66–68% yields with complete suppres-

Table 1. Optimization of the reaction between benzaldehyde (**1a**) and *N*-methylaniline (**2a**).^[a]

Entry	Catalyst (mol %)	Reaction conditions	% Yield 3aa ^[b]	% Yield 4aa ^[b]
1	H ₂ SO ₄ (20)	ⁱ PrOH, 90 °C, 24 h	46	12
2	HCl (20)	ⁱ PrOH, 90 °C, 24 h	17	–
3	AlCl ₃ (20)	ⁱ PrOH, 90 °C, 24 h	60	10
4	Cu(OTf) ₂ (20)	ⁱ PrOH, 90 °C, 24 h	68	13
5	Fe(NO ₃) ₃ (20)	ⁱ PrOH, 90 °C, 24 h	Traces	Traces
6	I ₂ (20)	ⁱ PrOH, 90 °C, 24 h	41	9
7	B(OH) ₃ (20)	ⁱ PrOH, 90 °C, 24 h	70	15
8	B(OH) ₃ (20)	MeCN, 90 °C, 24 h	50	8
9	B(OH) ₃ (20)	EtOH, 90 °C, 24 h	65	12
10	B(OH) ₃ (20)	DCE, 90 °C, 24 h	68	15
11	B(OH) ₃ (20)	THF, 90 °C, 24 h	Traces	Traces
12	B(OH) ₃ (20)	CHCl ₃ , 90 °C, 24 h	Traces	Traces
13	B(OH) ₃ (20)	DMF, 90 °C, 24 h	Traces	Traces
14	B(OH) ₃ (20)	ⁱ PrOH, 90 °C, 18 h	72	13
15	B(OH) ₃ (20)	ⁱ PrOH, 90 °C, 12 h	75	15
16	B(OH) ₃ (20)	ⁱ PrOH, 90 °C, 6 h	52	11

^[a] Unless otherwise mentioned, all reactions were performed using 1.0 mmol of **1a**, and 3.0 mmol of **2a** in 1.5 mL solvent. ^[b] Isolated yields.

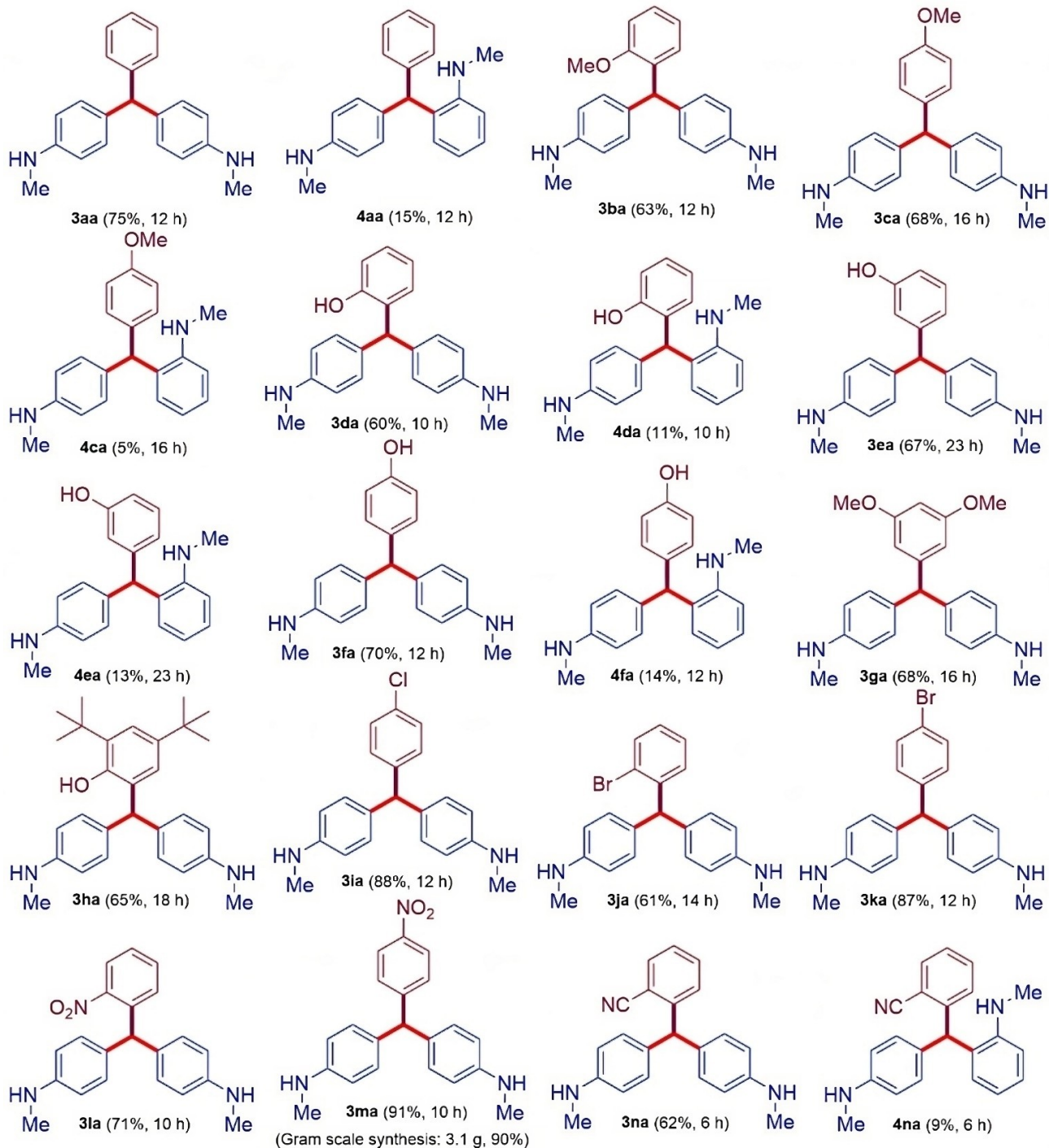
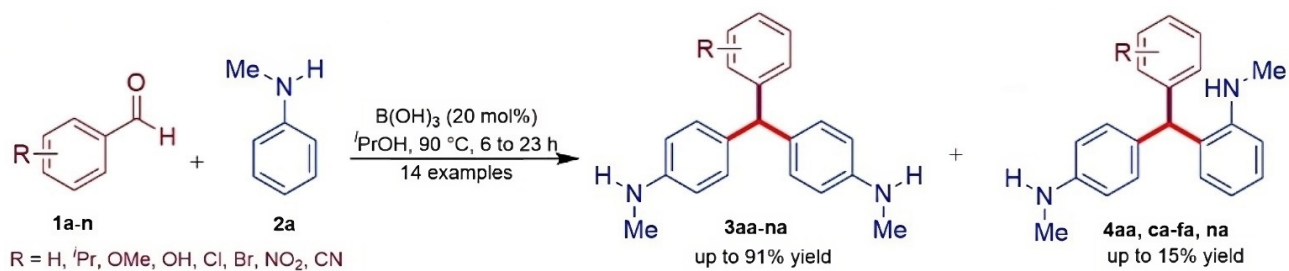
sion of the formation of molecules **4pa–qa**. The exception to this trend could be associated with the bulkier aldehyde **1r** which resulted in a mixture of *para-para* product **3ra** in 67% yield and *ortho-para* product **4ra** in 14% yield. The probable reason for this outcome might be governed by the electronic factors of the aromatic aldehyde and the stabilization of oxo-carbocation **B**, and the stability of intermediate **J**. It was also observed that in comparison to monocyclic aromatic and heteroaromatic aldehydes, the present transformation requires a longer reaction time when polycyclic aromatic aldehydes are employed in this transformation. Nevertheless, the exceptions were found with the aldehydes **1e**, **1h**, **1v**, **1w**, **1z** for which the reaction required a longer time for the complete conversion. The described reaction conditions were found suitable for aliphatic aldehyde **1s** to access the *tri*-substituted methane **3sa** in 65% yield and high selectivity towards *para-para* regioisomers was identified. Interestingly, the paraformaldehyde (**1t**) was tolerated considerably under these reaction conditions to deliver *di*-aryl-substituted methane **3ta** (60%) and **4ua** (9%) in adequate yields and selectivity (Scheme 3).

Next, the suitability of the described process was investigated by employing the *hetero*-aromatic aldehydes **1u–z**, **a'–b'**. The pyridine aldehydes **1u–y** exhibited excellent reactivity and selectivity towards *para-para* bond formation to obtain *tri*-arylmethanes **3ua–ya** in 76–90% yields with un-identification of corresponding *ortho-para* bonded *tri*-arylmethanes **4ua–ya**.

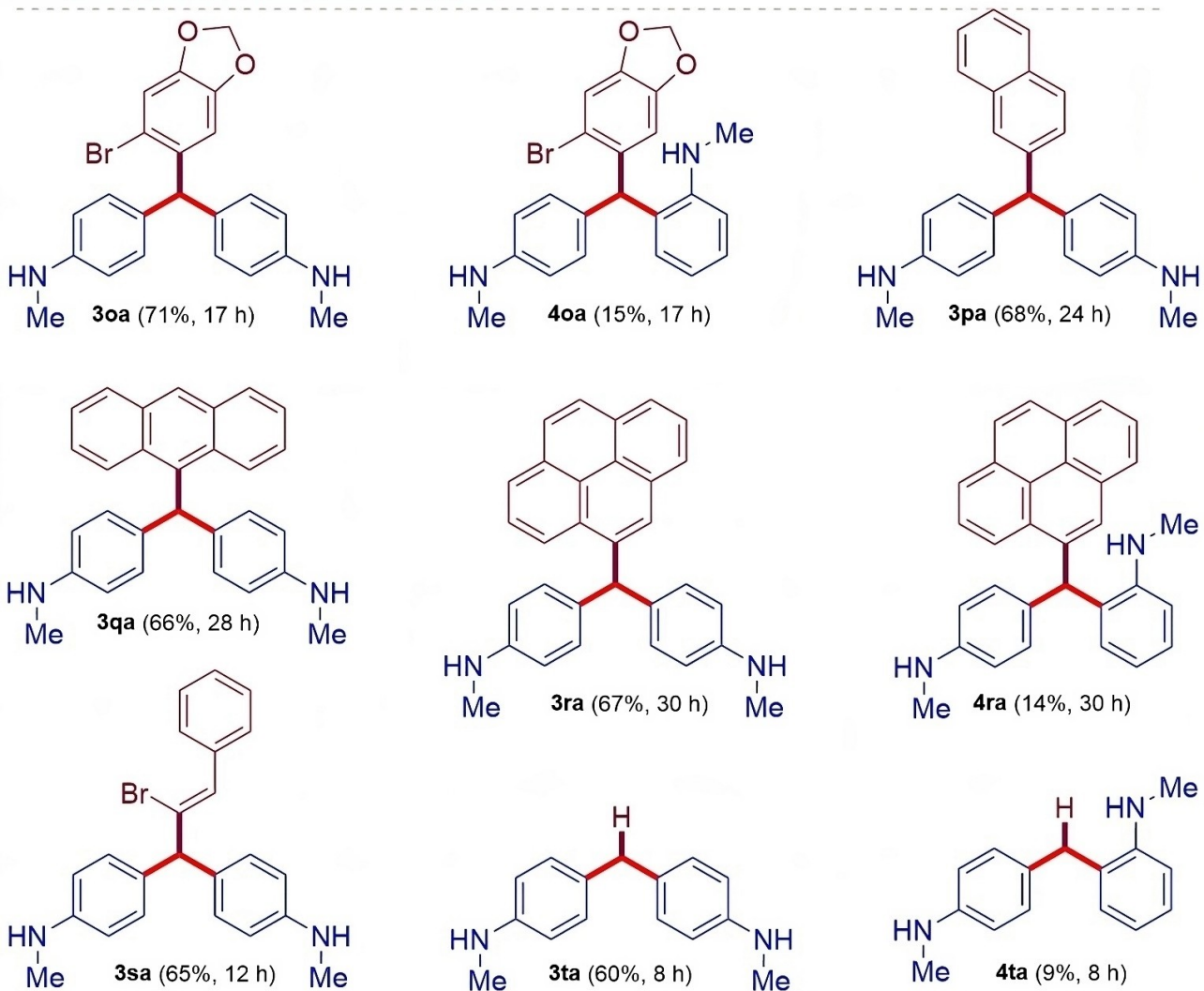
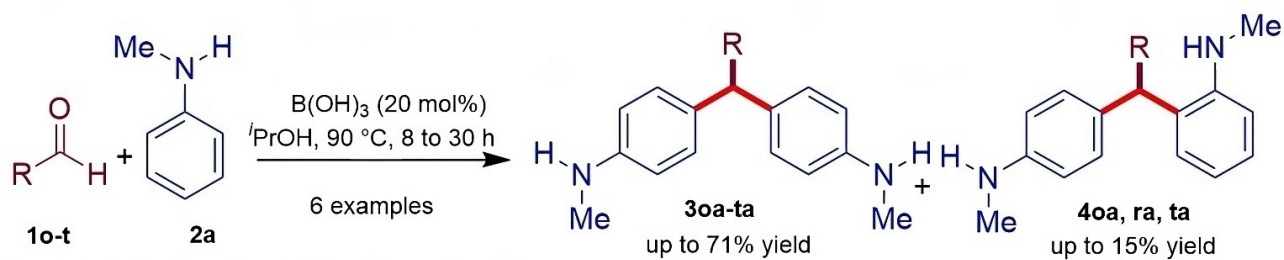
The quinoline aldehyde **1z** has also revealed similar selectivity in giving **3za** in 66% yield. In contrast, the isoquinoline aldehyde **1a'** and thiophene aldehyde **1b'** provided the products **3a'a–b'a** in 62–67% yields and **4a'a–b'a** in 7–17% yields (Scheme 4).

The feasibility of this protocol was then extended towards the *di*-substituted anilines and differently substituted aldehydes. The optimized reaction conditions were applied to aromatic/*hetero*-aromatic aldehydes **1a**, **i**, **o**, **x**, **c'** in combination with *N,N*-dimethylaniline (**2b**) to obtain *para-para* bonded *tri*-arylmethanes **3ab**, **ib**, **ob**, **xb**, **c'b** in 63–72% yields as the major products and *ortho-para* bonded *tri*-arylmethanes **4ab**, **ib**, **ob**, **xb**, **c'b** in traces amounts (Scheme 5). The reaction selectivity was drastically enhanced by changing the substrate *N*-methylaniline (**2a**) to *N,N*-dimethylaniline (**2b**). This outcome was attributed to the electron-rich nature of an aniline ring, which activates the aromatic ring at *para*-position for nucleophilic approach over carbonyl carbon of an aldehyde.

To further evaluate the scope of the developed process, we aspired to screen different aniline analogs such as indole under the reaction conditions. To our surprise, the reactions of aldehydes **1l**, **o**, **b'–c'** and indoles **5a–b** furnish *tri*-arylmethanes **6la**, **la**, **b'a–c'b** in 70–92% yields (Scheme 6). The evidence of the exclusive formation of a single isomer in all cases is accredited to the selective activation of the indole ring at the 3rd position.



Scheme 2. Scope of aromatic aldehydes **1** for the synthesis of *tri*-arylmethanes.

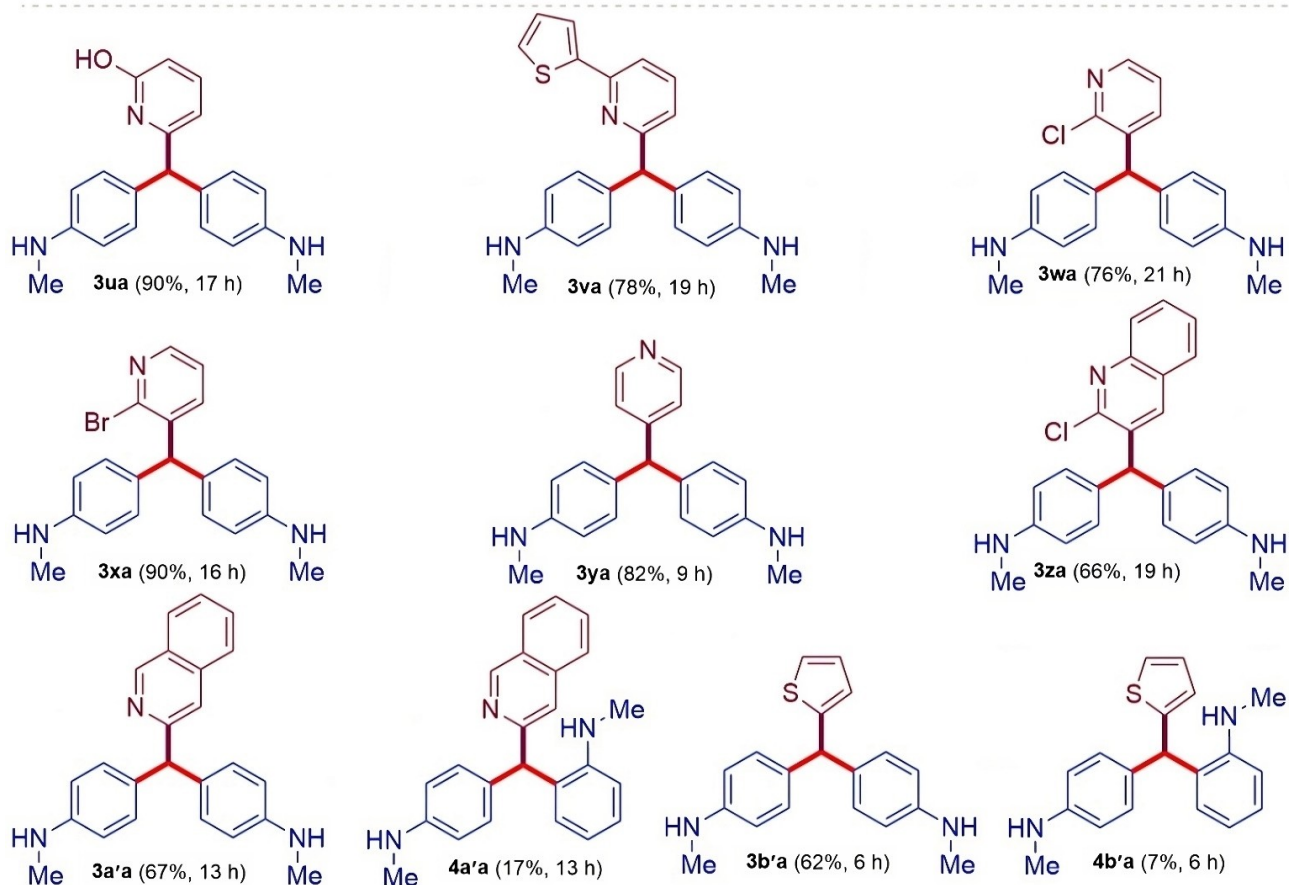
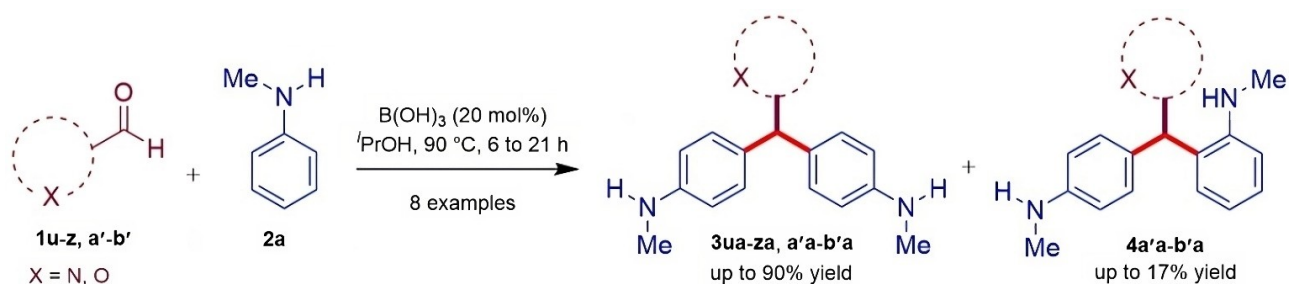


Scheme 3. Further scope of aldehydes **1** for the synthesis of triarylmethanes **3–4**.

After establishing a considerable substrate scope for the developed process, we aimed to depict a plausible reaction mechanism for the synthesis of *tri*-arylmethanes. To pursue this objective, we have chosen to evaluate the reaction process with the aid of GC-MS analysis and DFT studies. Further insights into the reaction mechanism were acquired by monitoring the course of the reaction of **1c** and **2a** under the standard reaction conditions at a regular interval of 1 hour. According to the obtained gas chromatography-mass spectrometry (GC-MS) data, the reaction process involves the formation of intermediates **B**

($[M]^+ = 198.06$), **C** ($[M + Na]^+ = 327.35$), **D** ($[M + Na]^+ = 118$), **E** ($[M]^+ = 226.12$), **I** ($[M + Na]^+ = 191.22$) and **K** ($[M]^+ = 333.19$) through which the product **3ca** ($[M]^+ = 332.52$) can be obtained (details of mass spectra are given in Figure S3, SI).

Further, the DFT studies^[26] were carried out to substantiate the observations made by GC-MS investigations in formulating a feasible reaction mechanism. The obtained DFT calculations (Figure S1–S2, SI) were found to be in good agreement with the observations drawn from GC-MS experiments. Based on the

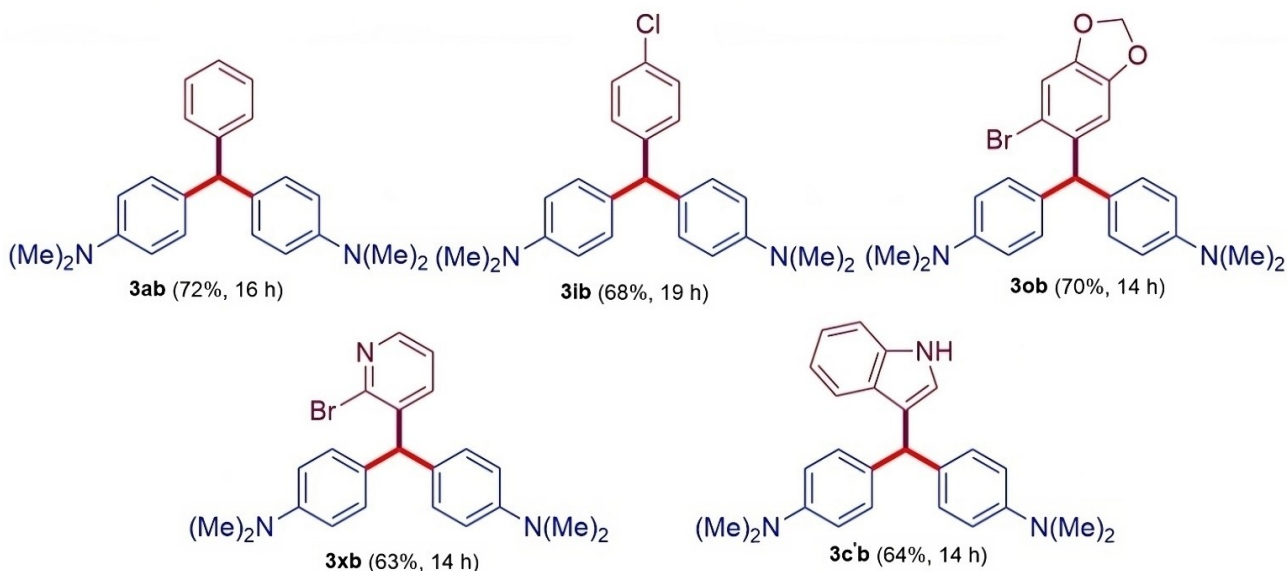
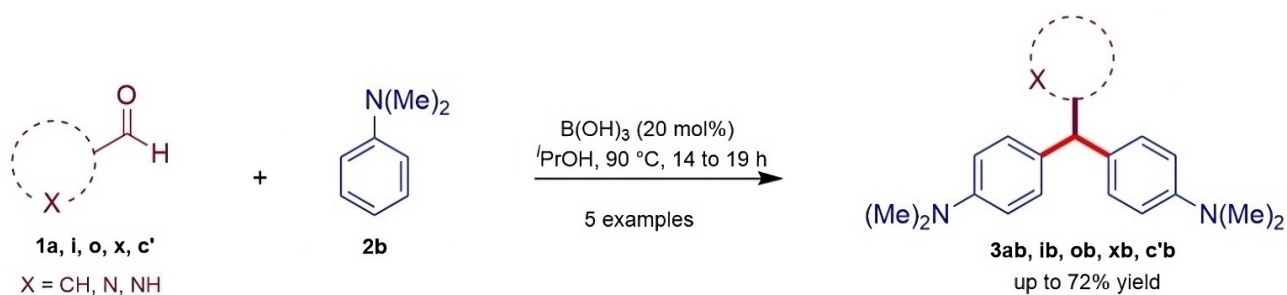


Scheme 4. Scope of hetero-aromatic aldehydes **1** for the synthesis of tri-arylmethanes **3-4**.

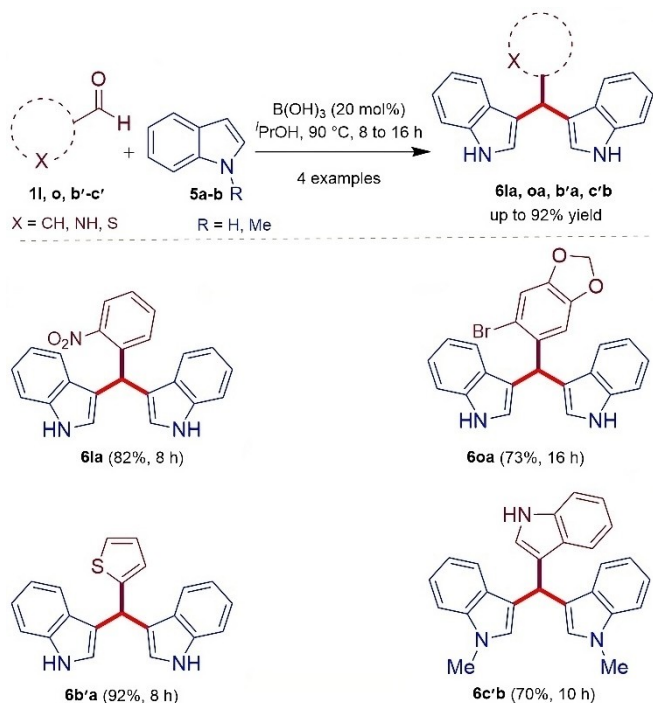
above-mentioned experimental and literature^[3a,13,27] evidence, a plausible reaction mechanism was drawn (Scheme 7).

According to the proposed mechanism, the starting material **1c** reacts with the catalyst B(OH)_3 (**A**) to form an intermediate **B** ($[\text{M}]^+ = 198.0$) through a transition state **TS-I**. The activation energy for the formation of intermediate **B** is 10.77 kcal/mol, which is energetically highly favorable. The intermediate **B** undergoes nucleophilic addition with compound **2a** to form the intermediate **C** ($[\text{M}]^+ = 305.14$, $[\text{M} + \text{Na}]^+ = 327.54$) through a transition state **TS-II**. The activation energy for the formation of intermediate **C** was elevated to 7.61 kcal/mol. Subsequent elimination of tetrahydroxyborate (**D**) ($[\text{M}]^+ = 78.02$, $[\text{M} + \text{K}]^+ = 118$) from intermediate **C** leads to the formation of imine intermediate **E** ($[\text{M}]^+ = 226.12$, $[\text{M} + \text{K}]^+ = 265.21$) though a transition state **TS-III**. The generation of intermediate **E** requires a high amount of activation energy (65.17 kcal/mol) as the

elimination of intermediate **D** takes place during the process. Next, the imine intermediate **E** undergoes nucleophilic addition with compound **2a** at the *para*-position to attain the possible intermediate **F**. The nucleophilic approach occurs through a transition state **TS-IV** with a lowered activation energy of 22.87 kcal/mol. The rearomatization of intermediate **F** takes place through a transition state **TS-V** with an activation energy of 32.90 kcal/mol to generate the intermediate **G**. The intermediate **H** can be obtained by the co-ordination of intermediate **G** with B(OH)_3 through a transition state **TS-VI** and activation energy of 21.58 kcal/mol. Next, the intermediate **H** undergoes an intramolecular rearrangement, and the subsequent elimination of intermediate **I** ($[\text{M}]^+ = 167.98$, $[\text{M} + \text{Na}]^+ = 191.22$) leads to the formation of intermediate **J** via the transition state **TS-VII** with an activation energy of 14.11 kcal/mol. Then, the intermediate **I** undergoes dissociation of *N*-



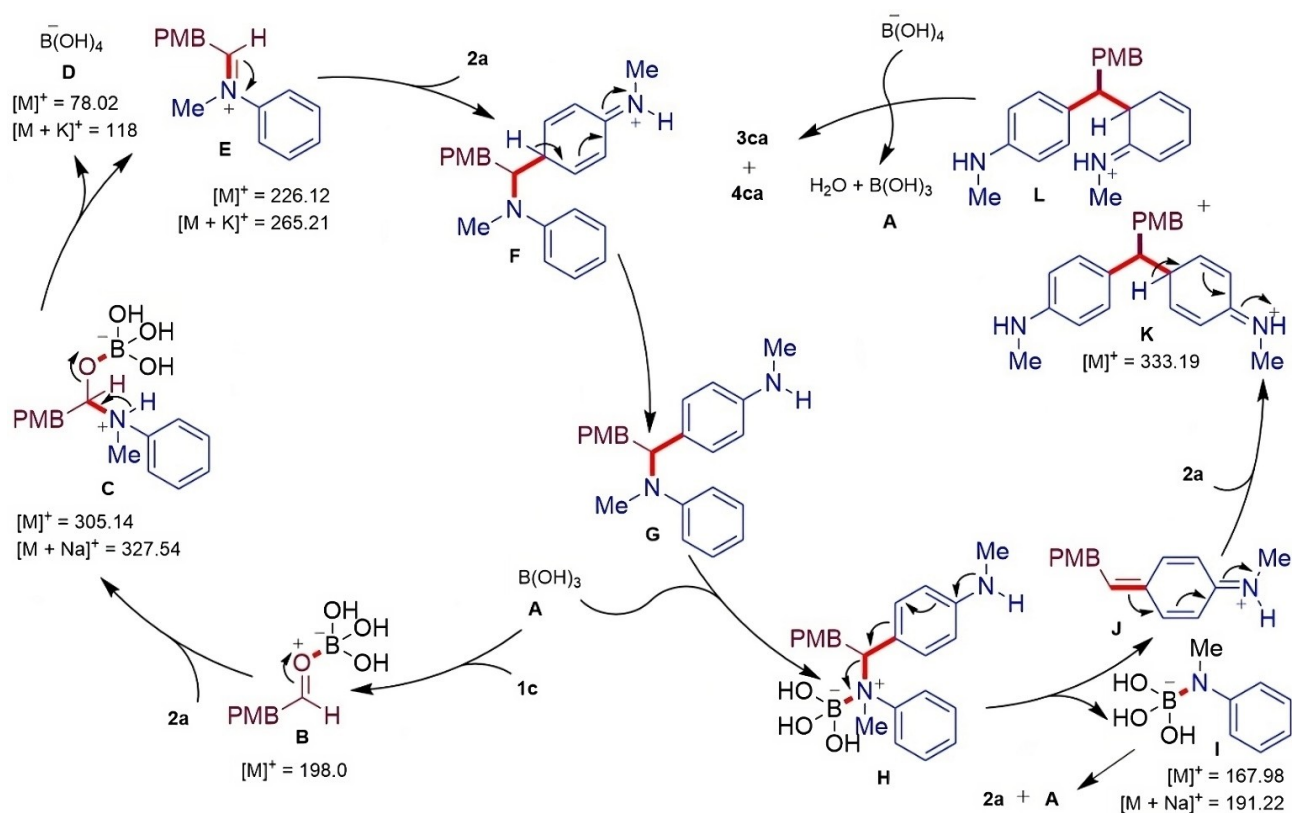
Scheme 5. Scope of aldehydes **1** and *N,N*-dimethylaniline (**2b**) for the synthesis of *tri*-arylmethanes **3–4**.



Scheme 6. Synthesis of indole-embedded *tri*-arylmethanes **6**.

methylaniline (**2a**) to regenerate B(OH)_3 back to the catalytic cycle. Further, the intermediate **J** can undergo nucleophilic addition with *N*-methylaniline (**2a**) in two ways leading to the formation of two different intermediates **K** and **L**. The intermediate **K** can be formed from **J** by the nucleophilic addition of compound **2a** at the *para*-position via the transition state **TS-VIIIA** with an activation energy of 12.33 kcal/mol. Similarly, the intermediate **L** can also be formed by the nucleophilic addition of compound **2a** at the *ortho*-position via the transition state **TS-VIIIB** with an activation energy of 14.19 kcal/mol. Subsequent aromatization of intermediate **K** and **L** in the presence of B(OH)_4^- furnished the desired products **3ca** and **4ca** respectively. The formation of product **3ca** from the intermediate **K** proceeds through a transition state **TS-IXA** with an activation energy of 11.26 kcal/mol, which is energetically highly favored and hence, displayed the greater selectivity. The activation energy for the formation of the **4ca** via transition state **TS-IXB** from intermediate **L** is 33.87 kcal/mol.

After establishing several aspects of this developed strategy, authors were surprised that the scope of this transformation is limited to the *N*-protected anilines. This observation was validated by carrying out the reaction between benzaldehyde (**1a**) and aniline **7a** in the presence of 20 mol% of B(OH)_3 in *i*PrOH as solvent at 90 °C for 12 hours, which resulted in no conversion of both starting materials. The reason behind the

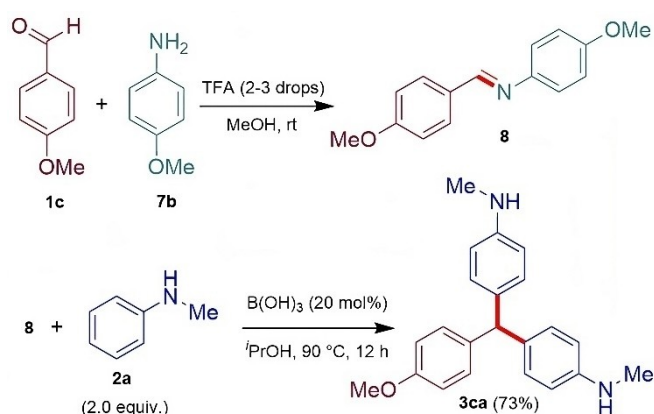


Scheme 7. Proposed reaction mechanism for the synthesis of *tri*-arylmethanes **3 ca** and **4 ca**.

incompetence of *N*-unprotected anilines to act as nucleophiles in the synthesis of *di*-/*tri*-substituted methanes could be associated with the low electron density in the *para*-position of the aromatic ring. Hence, the participation of a second aniline moiety in the formation of intermediate **F** via a dual Friedel-Crafts-type approach may be prohibited. The inactivity of aniline (**7 a**) guided us to elucidate an alternative hypothesis to analyze the outcomes of this method. In this protocol, the imine derivative **8** was prepared by the reaction between 4-methoxy benzaldehyde (**1 c**) and anisidine (**7 b**), which was then exposed to the developed reaction conditions under the influences of *N*-methylaniline (**2 a**). Interestingly, it was noticed that the operated transformation delivered the corresponding triarylmethane **3 ca** (73%), in which the aromatic residues of aldehyde **1 c** and *N*-methylaniline (**2 a**) were intact; whereas, the anisidine (**7 b**) residue in the intermediate **8** has shoved off during the reaction to derive the final product (Scheme 8).

Conclusions

In summary, a robust, cost-effective boric acid-catalyzed dual Friedel-Crafts reaction has been demonstrated for the synthesis of *di*-/*tri*-substituted methanes. The developed protocol provides direct access to symmetric and unsymmetric *tri*-arylmethanes by utilizing diversely substituted aldehydes and *N*-substituted anilines/indoles. The described reaction conditions



Scheme 8. Synthesis of *tri*-arylmethane **3 ca** using presynthesized aldimine intermediate **8**.

were successful in delivering the *tri*-arylmethanes in moderate to excellent yields and selectivity. The designed process was comprehensively supported using GC-MS and DFT studies.

Supporting Information

The authors have cited additional references within the Supporting Information.^[3,14a-b]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Friedel-Crafts Reaction · B(OH)₃ catalysis · Tertiary Csp³-Center · Diarylmethanes · Triarylmethanes (TRAMs)

- [1] a) D. Chaturvedi, N. C. Barua, *Curr. Org. Synth.* **2012**, *9*, 17–30; b) R. S. Menon, A. T. Biju, V. Nair, *Chem. Soc. Rev.* **2015**, *44*, 5040–5052; c) T. Wdowik, D. Gryko, *ACS Catal.* **2022**, *12*, 6517–6531 and references cited therein.
- [2] a) B. M. Trost, I. Fleming, G. Pattenden, in *Comprehensive Organic Synthesis*, (eds) Friedel-Crafts Alkylations (Pergamon Press, Oxford, 1991); b) C. Friedel, J. M. Crafts, *J. Chem. Soc.* **1877**, *32*, 725–791; c) V. D. Vuković, E. Richmond, E. Wolf, J. Moran, *Angew. Chem. Int. Ed.* **2017**, *5*, 3085–3089; d) Q. Qin, Y. Xie, P. E. Floreancig, *Chem. Sci.* **2018**, *9*, 8528–8534; e) H. T. Ang, J. P. G. Rygus, D. G. Hall, *Org. Biomol. Chem.* **2019**, *17*, 6007–6014; f) J. Khan, A. Tyagi, N. Yadav, R. Mahato, C. K. Hazra, *J. Org. Chem.* **2021**, *86*, 17833–17847; g) S. Singh, N. Vodnala, C. K. Hazra, *J. Org. Chem.* **2022**, *87*, 10044–10053 and references cited therein.
- [3] a) R. F. A. Gomes, J. A. S. Coelho, R. F. M. Frade, A. F. Trindade, C. A. M. Afonso, *J. Org. Chem.* **2015**, *80*, 10404–10411; b) N. Mibu, K. Yokomizo, M. Uyeda, K. Sumoto, *Chem. Pharm. Bull.* **2003**, *11*, 1325–1327; c) P. Wang, J. Kozlowski, M. Cushman, *J. Org. Chem.* **1992**, *57*, 3861–3866.
- [4] a) A. R. D. Bindal, J. T. Golab, J. A. Katzenellenbogen, *J. Am. Chem. Soc.* **1990**, *112*, 7861–7868; b) L. Bai, N. Masukawa, M. Yamaki, S. Takagi, *Phytochemistry* **1998**, *47*, 1637–1640; c) C. Jin, R. G. Michetich, M. Daneshlab, *Phytochemistry* **1999**, *50*, 505–508; d) B. Zhou, D. X. Liu, X. J. Yuan, J. Y. Li, Y. C. Xu, J. Li, Y. Li, J. M. Yue, *Research* **2018**, *2018*, 2674182; e) S. A. Snyder, S. P. Breazzano, A. G. Ross, Y. Lin, A. L. Zografos, *J. Am. Chem. Soc.* **2009**, *131*, 1753–1765.
- [5] a) D. Likhatchev, L. Alexandrova, M. Tlenkopatchev, R. Vilar, R. Vera-Graziano, *J. Appl. Polym. Sci.* **1995**, *57*, 37–44; b) C. Hamciuc, I. D. Carja, E. Hamciuc, T. VladBubulac, M. Ignat, *Polym. Adv. Technol.* **2013**, *24*, 258–265; c) R. J. Kamel, M. A. Mutar, F. S. Khlewee, *Int. J. Res. Pharm. Sci.* **2019**, *10*, 1936–1941.
- [6] a) R. Muthyala, A. R. Katritzky, X. Lan, *Dyes Pigm.* **1994**, *25*, 303–324; b) C. P. Dong, S. Kodama, A. Uematsu, A. Nomoto, M. Ueshima, A. Ogawa, *J. Org. Chem.* **2017**, *82*, 12530–12538; c) M. Irie, *J. Am. Chem. Soc.* **1983**, *105*, 2078–2079.
- [7] a) A. C. Bhasikuttan, J. Mohanty, W. M. Nau, H. Pal, *Angew. Chem.* **2007**, *119*, 4198–4200; b) Y. Urano, M. Kamiya, K. Kanda, T. Ueno, K. Hirose, T. Nagano, *J. Am. Chem. Soc.* **2005**, *127*, 4888–4894; c) M. Beija, C. A. M. Afonso, J. M. G. Martinho, *Chem. Soc. Rev.* **2009**, *38*, 2410–2433.
- [8] R. A. Schnick, *Prog. Fish-Cult.* **1988**, *50*, 190–196.
- [9] D. F. Duxbury, *Chem. Rev.* **1993**, *93*, 381–433.
- [10] V. Nair, S. Thomas, S. C. Mathew, K. G. Abhilash, *Tetrahedron* **2006**, *62*, 6731–6747.
- [11] a) N. Batina, M. Kunitake, K. J. Itaya, *Electroanal. Chem.* **1996**, *405*, 245–250; b) W. Haiss, R. J. Nichols, J. K. Sass, *Surf. Sci.* **1997**, *388*, 141–149; c) D. Fisher, W. R. Caseri, G. J. Hahner, *J. Colloid Interface Sci.* **1998**, *198*, 337–346.
- [12] E. V. Ganin, V. Ven-Dzvu, *Russ. J. Gen. Chem.* **2003**, *73*, 1320–1321.
- [13] M. Nibu, K. Yokomizo, M. Uyeda, K. Sumoto, *Chem. Pharm. Bull.* **2005**, *53*, 1171–1174.
- [14] a) N. Ponpao, W. Senapak, R. Saeeng, J. Jaratjaroonphong, U. Sirion, *RSC Adv.* **2021**, *11*, 22692–22709 and references cited therein; b) S. Rinkam, W. Senapak, S. Watchasit, R. Saeenga, U. Sirion, *Synlett.* **2022**, *33*, 1383–1390; c) W. Li, D. Wang, X. Liang, Z. Jin, S. Zhou, G. Chen, Y. Pan, *Org. Lett.* **2022**, *24*, 3086–3091.
- [15] Z. Li, Z. Duan, J. Kang, H. Wang, L. Yu, Y. Wu, *Tetrahedron* **2008**, *64*, 1924–1930.
- [16] a) S. Salto, T. Ohwada, K. Shudo, *J. Org. Chem.* **1996**, *61*, 8089–8093; b) M. Wilsdorf, D. Leichnitz, H. U. Reissig, *Org. Lett.* **2013**, *15*, 2494–2497.
- [17] J. Jaratjaroonphong, S. Sathalalai, P. Techasavapak, V. Reutrakul, *Tetrahedron Lett.* **2009**, *50*, 6012–6015.
- [18] V. Nair, K. G. Abhilash, N. Vidya, *Org. Lett.* **2005**, *7*, 5857–5859.
- [19] J. Choudhury, S. Podder, S. Roy, *J. Am. Chem. Soc.* **2005**, *127*, 6162–6163.
- [20] M. Barbero, S. Cadamuro, S. Dugghera, C. Magistris, P. Venturello, *Org. Biomol. Chem.* **2011**, *9*, 8393–8399.
- [21] C. R. Liu, M. B. Li, C. F. Yang, S. K. Tian, *Chem. Commun.* **2008**, 1249–1251.
- [22] S. G. K. Prakash, G. Fogassy, G. A. Olah, *Catal. Lett.* **2010**, *138*, 155–159.
- [23] a) N. Kaur, D. Kishore, *J. Chem. Pharm. Res.* **2012**, *4*, 991–1015; b) A. Jha, A. C. Garade, M. Shirai, C. V. Rode, *Appl. Clay Sci.* **2013**, *74*, 141–146.
- [24] M. Kodomari, M. Nagamatsu, M. Akaike, T. Aoyama, *Tetrahedron Lett.* **2008**, *49*, 2537–2540.
- [25] H. M. Meshram, N. N. Rao, G. S. Kumar, *Synth. Commun.* **2010**, *40*, 3496–3500.
- [26] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, Montgomery, {Jr.}, J. A., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision C.01, Gaussian Inc. Wallingford CT, **2016**.
- [27] R. K. Mylavarapu, G. C. M. Kondaiah, N. Kolla, R. Veeramalla, P. Koilkonda, A. Bhattacharya, R. Bandichhor, *Org. Process Res. Dev.* **2007**, *11*, 1065–1068.