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Boron-Catalyzed *N*-Alkylation of Arylamines and Arylamides with Benzylic Alcohols

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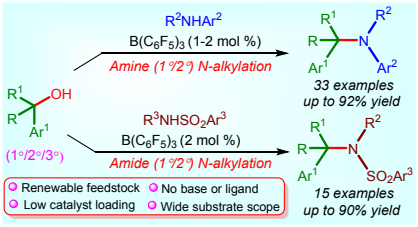


ABSTRACT: A sustainable boron-based catalytic approach for chemoselective *N*-alkylation of primary and secondary aromatic amines and amides with primary, secondary, and tertiary benzylic alcohols have been presented. The metal-free protocol operates at low catalyst loading, tolerates several functional groups and generates H_2O as the sole by-product. Preliminary mechanistic studies were performed to demonstrate the crucial role of boron catalyst for the activation of the intermediate dibenzyl ether and to identify the rate-determining step.

INTRODUCTION

The *N*-alkylation of amines through carbon-nitrogen bond formation[1] has become an efficient approach for the construction of a plethora of *N*-alkyl amines, which are essential motifs in pharmaceuticals, agrochemicals, and natural products (Figure 1a).[2] Among the state-of-the-art synthetic methods, the traditional protocols involved a non-catalytic reaction of amines with alkyl halides, tosylates or triflates, which are limited due to their toxicity, poor chemoselectivity, over-alkylation, and generation of stoichiometric waste.[3] In comparison to the classical approach, the more appealing strategies for C–N bond formation involved transition-metal-catalyzed reductive amination of carbonyl compounds,[4] hydroamination of alkenes and alkynes,[5] borrowing hydrogen methodologies using alcohols or amines.[1b,6]

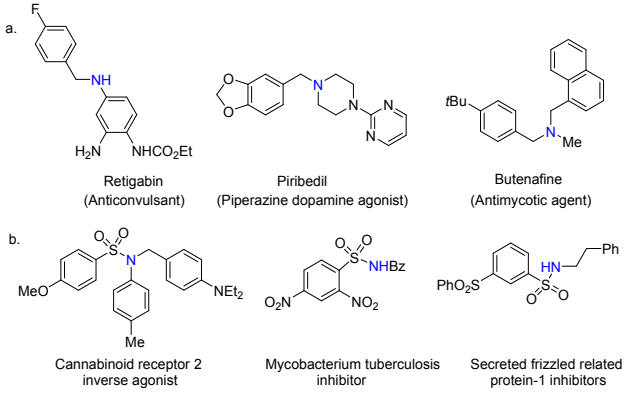
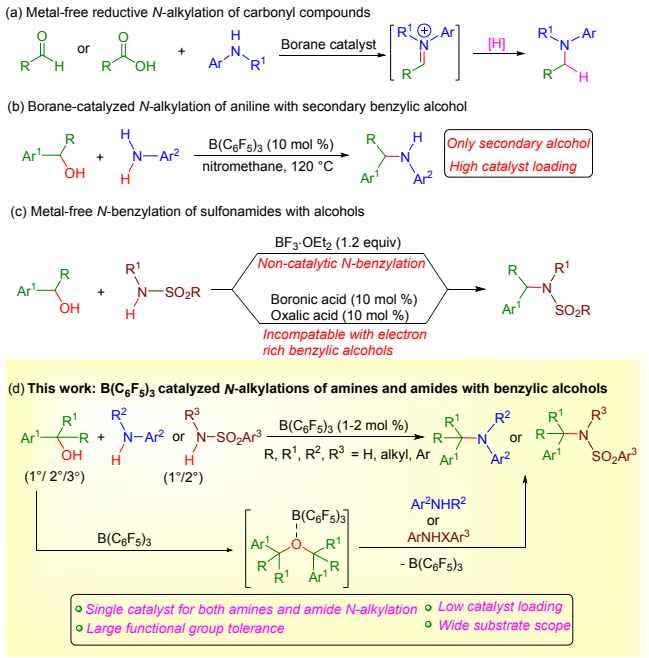


Figure 1. Selected bioactive *N*-alkylated (a) amines, and (b) sulfonamides

Similar to *N*-alkylamines, the *N*-alkyl amides has also attracted much attention due to their extensive applications in pharmaceutical, biological, and chemical industry.[7] In particular, the *N*-alkyl sulfonamides, a sub-class of amide are commonly employed as cannabinoid receptor 2 inverse agonist,[8] inhibitors of *Mycobacterium* tuberculosis[9] and secreted frizzled-related protein-1 (sFRP-1) inhibitors (Figure 1b).[10] Due to the several limitations of classical approaches for the synthesis of *N*-alkyl sulfonamides,[11] the widely accepted methodologies involve borrowing hydrogen catalysis in the presence of transition metal[12] and Lewis-[13] or Brønsted-acid[14] catalyzed direct substitution of alcohol by nitrogen nucleophiles. Despite the development of these remarkable atom economical processes, often their green credentials are somehow limited due to the use of (i) toxic noble metals, (ii) capricious ligands and bases, (iii) high reaction temperature, (iv) the use of excess amines or alcohols, (v) highly reactive and non-renewable feedstock. Nevertheless, with the increasing trend to follow up the principles of green chemistry, it is highly attractive to develop a metal-free green and sustainable chemical process for *N*-alkylation reaction using renewable resources.[15]

In recent years, the main group element boron has emerged as an alternative catalyst due to their excellent reactivity and selectivity for a wide range of transformations.[16-11] Recently, the boron-catalyzed hydroamination of alkynes,[17] and reductive *N*-alkylation of amines with carbonyls in the presence of H_2 or hydrosilanes (Scheme 1a) have been demonstrated for the diversification of amines.[18] Conversely, in the pursuit of more sustainable developments, the use of widely available primary alcohols as alkylating agent under metal-free conditions remain unexplored.[19] While the manuscript in preparation, Chan et al. reported $B(C_6F_5)_3$-

catalyzed *N*-alkylation of anilines with secondary alcohols (Scheme 1b). The reaction proceeded in nitromethane solvent *via* the intermediacy of a carbocation in the presence of higher loading of catalyst.[20] However, the formation of a carbocation from primary alcohols is challenging,[21] and the scope of primary alcohols with amines under metal and base free conditions have not been explored to date. As the carbocations generated from primary alcohols are strong Lewis acid, the alkylation should occur selectively at the nitrogen site of the anilines that requires less reorganization evergy.[21c] Besides, the *N*-benzylation of sulfonamide with alcohols under metal-free conditions could only be achieved either in a non-catalytic pathway using more than stoichiometric boron reagent[22] or in the presence of a catalytic combination of boric acid/oxalic acid where electron-rich benzylic alcohols are not productive (Scheme 1c).[23] In continuation of our recent finding of the catalytic transformation of aromatic amines in the presence of $B(C_6F_5)_3$-catalyst,[24] herein we report a boron-catalyzed *N*-alkylation of aromatic amines and amides with primary and hindered benzylic alcohols (Scheme 1d). The reaction operates at a catalyst loading of 1-2 mol% and tolerates functional groups like carbonyl, cyano, carboxylic acid, halogens, nitro, etc. and produces water as the sole by-product thereby making the process highly environmentally benign.

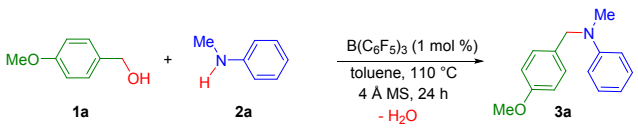


Scheme 1. Boron-catalyzed *N*-alkylation of amines and amides.

RESULTS AND DISCUSSION

At the onset of our study, the *N*-alkylation reaction of *p*-anisyl alcohol **1a** with *N*-methyl aniline **2a** was investigated (Table 1). To our delight, the *N*-alkylated product **3a** was detected in 92% NMR yield by employing 1 mol% of $B(C_6F_5)_3$ at 110 °C in toluene after 24 h in the presence of 4Å molecular sieve (entry 1). The yield dramatically reduced on moving from a non-polar to a polar solvent (entries 2-4) and in acetonitrile, no reaction was observed (entry 5). A lower yield was obtained when the temperature was reduced to 90 °C (entry 6), whereas at a slightly higher temperature (120 °C) the yield reduced to 90% (entry 7). The observed yield remains almost similar even after 2 mol% catalyst loading (entry 8) but decreased significantly when 0.5 mol% of catalyst was used (entry 9). Other boron catalysts were not efficient for this reaction (entries 10-11). A controlled reaction confirmed that molecular sieve has a crucial role in the improvement of product yield (entry 12).

Table 1. Optimization for *N*-alkylation of secondary aryl amines.[a]



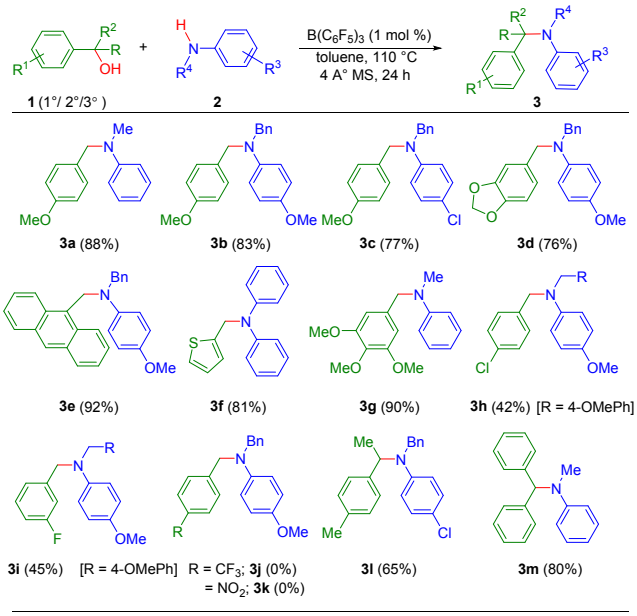
1a 2a 3a

entry	deviation from standard condition	yield (%)[b]
1	none	92 (88)[c]
2	benzene	75
3	chlorobenzene	56
4	1,4-dioxane	12
5	acetonitrile	n.r.
6	90 °C temperature	58
7	120 °C temperature	90
8	2 mol % $B(C_6F_5)_3$	93
9	0.5 mol % $B(C_6F_5)_3$	63
10	1 mol % BPh_3	n.r.
11	5 mol % BF_3•Et_2O	33
12	without 4Å MS	78

[a] Reaction conditions: **1a** (0.375 mmol), **2a** (0.25 mmol), $B(C_6F_5)_3$ (1 mol %), and 4Å molecular sieve (30 mg) in 0.5 mL of solvent for 24h at appropriate temperature. [b] NMR yield using mesitylene as an internal standard. [c] Yield obtained after column purification. n.r. = no reaction.

With the optimized conditions in hand, the scope for the *N*-alkylation reaction of secondary aromatic amines with primary and secondary alcohols was examined (Table 2). When *p*-anisyl alcohol **1a** was reacted with *N*-benzyl anilines having electron-donating (-OMe) and withdrawing (-Cl) groups, the corresponding *N*-alkylated compounds **3b** and **3c** have obtained in 83% and 77% yields, respectively. Similarly, the piperonyl alcohol and 9-anthracene methanol smoothly afforded **3d** (76%) and **3e** (92%). The heteroaryl alcohol and trimethoxy substituted benzyl alcohol were also furnished **3f** and **3g** in high to excellent yields. In contrast, benzyl alcohols having moderate electron-withdrawing substituents (Cl, F) on the aromatic rings delivered **3h** and **3i** in moderate yields, and the presence of strong electron-withdrawing $-CF_3$ or $-NO_2$ groups completely shut down the reaction, thus indicating a strong electronic influence of the ring substituent on its reactivity, *vide infra*. Importantly, the hindered secondary alcohols with different secondary amines were also equally useful under the optimized reaction condition to give **3l** and **3m** in 65-80% yields.

Table 2. $B(C_6F_5)_3$-catalyzed *N*-alkylation of secondary anilines with benzylic alcohols.[a]

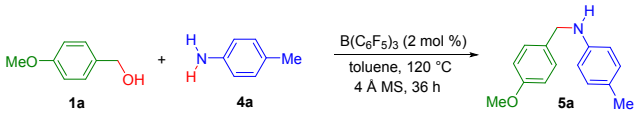


[a]Reaction condition: Table 1, entry 1. Yields are given in parenthesis.

Subsequently, we have realized the challenge associated with the selective mono-alkylation of primary amines with primary alcohols. The difficulty lies not only in the generation of the primary electrophile but also in the selectivity step as the product secondary amine has higher nucleophilicity than the starting aniline.[21] To best of our knowledge, selective mono-alkylation of aniline with primary alcohol is unknown under metal-free conditions.

To test the viability of selective mono-alkylation of primary amines with primary alcohols, alcohol **1a**, and aniline **4a** were selected as the model substrates (Table 3). When the **1a** and **4a** were treated under the optimized condition of Table 1, only 62% yield of **5a** was observed (entry 1). Pleasingly, with 2 mol% of catalyst loading, the yield was improved to 84% (entry 2). Further increase in catalyst loading or reaction temperature leads to lower yields of **5a** with the formation of bis-alkylated products (entries 3-4). Besides, the use of excess amine was not adequate to improve the yield of **5a** (entry 5).

Table 3. Optimization for monoalkylation of aniline with primary alcohol.[a]



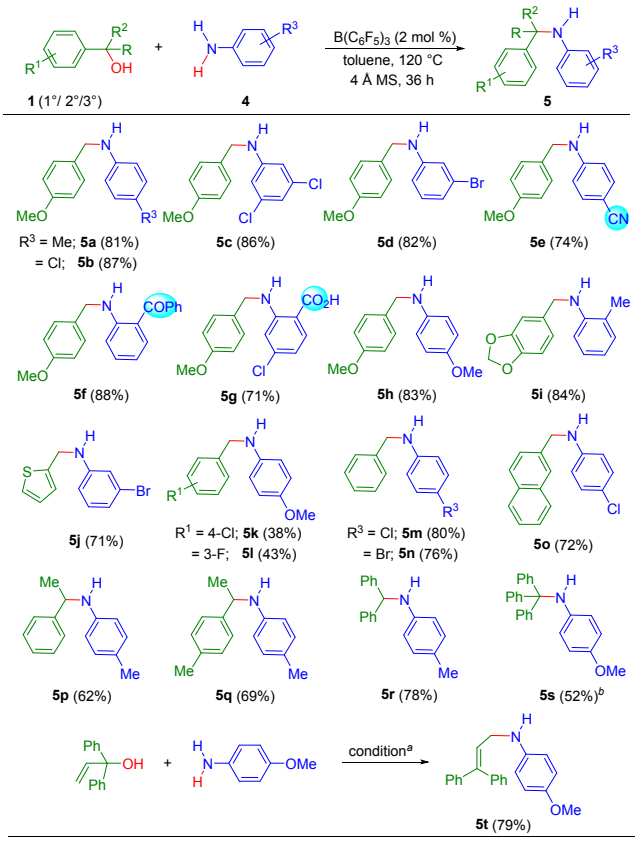
entry	deviation from standard condition	yield (%)[b]
1	Table 1, entry 1	62
2	none	84 (81)[c]
3	3 mol % $B(C_6F_5)_3$	73[d]
4	130 °C temperature	70[d]
5	1.0 equiv **1a** and 1.5 equiv **4a**	51

[a] Reaction conditions: **1a** (0.375 mmol), **4a** (0.25 mmol), $B(C_6F_5)_3$ (2 mol %), and 4Å molecular sieve (30 mg) in 0.5 mL of toluene. [b] NMR yield using mesitylene as an internal standard. [c] Yield after column purification. [d] Bis-alkylated product also detected in 10% NMR yield.

After finding the optimum condition, we have then explored the scope for selective mono-alkylation of anilines **4** with different benzylic alcohols **1,** and results are summarized in Table 4. To note, in all cases studied, the formation of the bis-alkylated product was not observed. The reaction of **1a** with halo substituted anilines delivered mono-alkylated compounds **5b-d** in 82-87% yields. It is noteworthy to mention that the benzylamines having carboxyl or cyano groups are present in many bioactive compounds,[2a,25] and, in general, these functional groups are often sensitive under reductive alkylation conditions in the presence of H_2 or hydrosilane.[10] Pleasingly, the reaction of **1a** with aromatic amines **4e-g** having substituents like -CN, -COPh and -COOH could readily be tolerated under the present reaction conditions to give desired compound **5e-g** in 71-84% yields. The *p*-OMe substituted electron-rich aniline was also alkylated with **1a** to yield **5h** (83%).

Similarly, the ortho substituent on aniline did not affect the formation of **5i** (84%). The heteroaryl alcohol showed good reactivity to produce **5j** in 71% yield. Halogen substituents on the alcohol coupling partner were also tolerated to deliver **5k** and **5l** in moderate yields. The parent benzyl and naphthyl alcohols underwent the alkylation reaction smoothly to afford the targeted products **5m-o** in good yields. Notably, the secondary alcohols were also equally useful under this condition to furnish **5p-r** in 62-78% yields. Similarly, the hindered tertiary alcohol provided **5s** in 52% yield at lower reaction temperature. Interestingly, for tertiary alcohol having a vinyl group attached to the 3° carbon center, migration of the double bond took place to deliver the linear allyl amine **5t** in 79% yield.

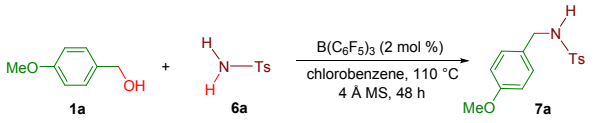
Table 4. $B(C_6F_5)_3$-catalyzed selective mono-*N*-alkylation of anilines with benzylic alcohols.[a]



[a] Reaction condition: Table 3, entry 2. Yields are given in parenthesis. [b]Reaction temperature 80 °C.

Further, we are interested to extend the scope for this metal-free C-N coupling protocol for the *N*-alkylation of amides. To our delight, with 1 mol% of $B(C_6F_5)_3$ loading, the monoalkylation of *p*-toluenesulfonamide **6a** with *p*-methoxybenzyl alcohol **1a** afforded **7a** in 37% yield (Table 5, entry 1). When the reaction time was prolonged to 48 h the yield of the monoalkylated product was increased to 60% (entry 2). The yield could be improved (entry 3) by applying 2 mol% of $B(C_6F_5)_3$ at 110 °C. Although, a further increase in catalyst loading or reaction temperature leads to decrease in product yield of **7a** with the formation of bis-alkylated product (entries 4-5). Gratifyingly, yield of **7a** was improved to 93% when chlorobenzene was used as solvent (entry 6). However, detrimental effect was observed as benzene or 1,4-dioxane were used as solvent (Table 5, entries 7-8). The change in stoichiometry between **1a** and **6a** does not significantly alter the yield (entry 9).

Table 5. Optimization for monoalkylation of sulfonamide with benzyl alcohol.[a]

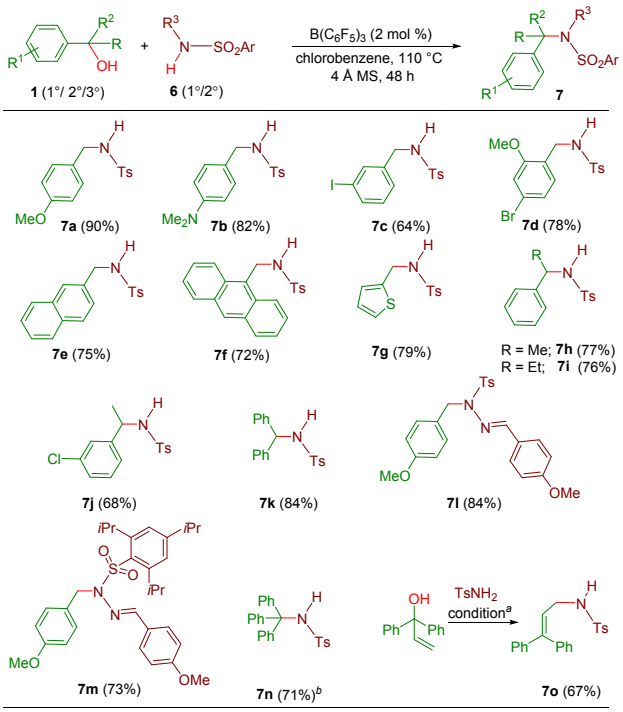


entry	deviation from standard condition	yield (%)[b]
1	$B(C_6F_5)_3$ (1 mol %)	37
2	$B(C_6F_5)_3$ (1 mol %), 48 h	60
3	in toluene solvent	81
4	$B(C_6F_5)_3$ (3 mol %), in toluene solvent	71[c]
5	in toluene solvent at 120 °C	73[c]
6	none	93 (90)[d]
7	in benzene solvent	80
8	in 1,4-dioxane solvent	45
9	1.0 equiv **1a** and 1.2 equiv **6a**	91

[a] Reaction conditions: **1a** (0.25 mmol), **6a** (0.25 mmol), $B(C_6F_5)_3$ (2 mol %), and 4Å molecular sieve (30 mg) in 0.5 mL of chlorobenzene. [b] NMR yield using mesitylene as an internal standard. [c] Bis-alkylated product also detected in 15% NMR yield. [d] Yield after column purification.

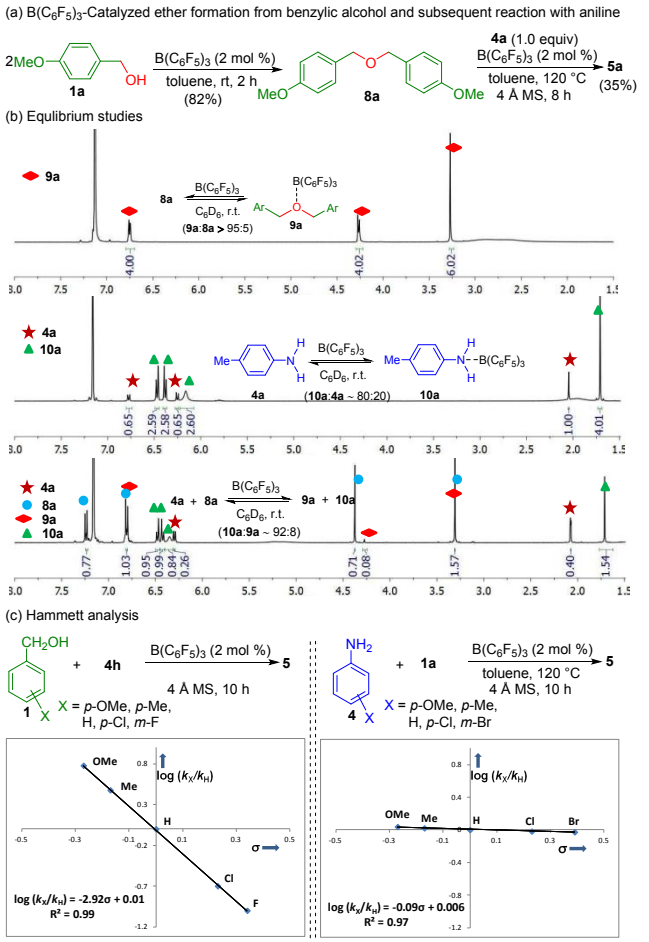
With the optimum conditions in hand, we have explored the scope and limitation of the boron catalyzed alkylations of amides. Initially, differently substituted alcohols were reacted with *p*-toluenesulfonamide **6a**, and the results were summarized in Table 6. To note in all cases studied bis-alkylated product was not detected. Benzyl alcohols with different substituents at *o*-, *m*-, or *p*-position readily reacted with **6a** to furnish **7b-d** in 64-82% yields. Similarly, the naphthyl, anthracenyl and thiophenyl methanol produced the *N*-alkylated sulfonamide **7e-g** in 72-79% yields. The reaction could also be extended to secondary alcohols, and the products 7**h-k** were obtained in moderate to excellent yields. The *N*-sulfonyl hydrazones can also be alkylated selectively at the sp^3 nitrogen with **1a** to afford **7l** and **7m** in 84% and 73% yields, respectively. The hindered trityl alcohol also reacted at slightly higher temperature in DCE solvent to yield **7n** (71%) and similar migration of double bond also observed for the vinyl group containing tertiary alcohol to selectively afford the linear amide **7o** in 67% yield.

Table 6. $B(C_6F_5)_3$-catalyzed selective mono-*N*-alkylation of amides with benzylic alcohols.[a]



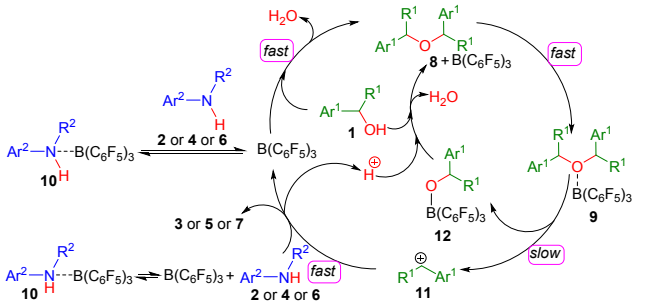
[a]Reaction condition: Table 5, entry 6. Yields are given in parenthesis. [b]In DCE solvent at 120 °C.

In order to probe the mechanistic cycle for the metal-free *N*-alkylation reaction, several experimental pieces of evidence have been depicted in Scheme 2. At first, when benzyl alcohol **1a** was stirred in toluene at room temperature in the presence of boron-catalyst, dibenzyl ether **8a** was formed in 82% yield (Scheme 2a). To see whether **8a** is an intermediate in the catalytic cycle or not, the stoichiometric reaction of **4a** with **8a** afforded **5a** in 35% yield after 8 h under the standard conditions (Scheme 2a). Again, the stoichiometric reaction of **8a** and $B(C_6F_5)_3$ in C_6D_6 at room temperature lead to the formation of **9a** ($B(C_6F_5)_3$ adduct of **8a**) in **9a**:**8a** > 95:5 ratio (Scheme 2b). Whereas, in our recent report,[24] we have studied the equilibrium between **4a** and **10a** ($B(C_6F_5)_3$ adduct of **4a**) to give **10a**:**4a** 80:20 (Scheme 2b). Also, a mixture of **4a**, **8a**, and $B(C_6F_5)_3$ in benzene showed **10a**:**9a** 92:8 (Scheme 2b). The above equilibrium studies highlight the reversibility of the Lewis acid-base adduct of $B(C_6F_5)_3$ with aniline and dibenzyl ether intermediate, and availability of the catalyst for alcohol activation. Further, the Hammett correlation study was performed to examine the electronic effect of arene substituents on both the alcohols and anilines (Scheme 2c). After varying the electronic groups on the aryl-ring of **1**, a large $\rho = -2.92$ was found which probably indicates the accumulation of positive charge on the benzylic carbon of alcohol in the rate-determining step (RDS). In contrast, an insignificant electronic influence of the substituents on the aromatic ring of aniline **2** was observed ($\rho = -0.09$).



Scheme 2. Mechanistic studies for the $B(C_6F_5)_3$-catalyzed *N*-alkylation reaction.

Based upon the above experimental results and previous reports,[13a,26] a plausible reaction mechanism is shown in Scheme 3. At first, amine forms a reversibly Lewis adduct **10** with $B(C_6F_5)_3$.[24] Alcohol **1** in the presence of $B(C_6F_5)_3$ catalyst quickly delivers dibenzyl ether **8**, which could furnish an adduct **9** with $B(C_6F_5)_3$ through the oxygen center. Later, the adduct **9** could break into carbocation **11** and intermediate **12** in a rate-limiting step. However, an alternative reaction path for the formation of carbocation **11** directly from alcohol in the presence of Lewis acid cannot be ruled out.[14c,20] The carbocation **11** could then be intercepted instantaneously by the aniline **2** or **4** or amide **6** to affords *N*-alkylated products **3** or **5** or **7** with the regeneration of $B(C_6F_5)_3$ catalyst. The intermediate **12**, on the other hand immediately transforms into **8** in the presence of **1**.



Scheme 3. Proposed mechanism for borane-catalyzed *N*-alkylation.

CONCLUSION

In summary, we have developed a metal-free protocol for catalytic *N*-alkylation of primary and secondary aromatic amines and amides with readily available benzylic alcohols under mild conditions. This method is useful for direct functionalization of amines and amides even in the presence of sensitive functional groups like cyano, carboxylic acid, and carbonyl that are often difficult to survive under metal-catalyzed reductive amination process. Mechanistic experiments suggest the formation of an ether adduct which decomposes to the product in the rate-determining step. This protocol could show future perspectives for the development of amine functionalization in a green and sustainable pathway.

EXPERIMENTAL SECTION

General Information

All reactions were performed under a dry and oxygen free argon atmosphere by using Schlenk techniques or in a glovebox under argon atmosphere. ^1H, ^{13}C NMR, ^{11}B ($BF_3.OEt_2$ reference) and ^{19}F ($CFCl_3$ reference) spectra were recorded on a Bruker-AVANCE500 or JEOL-ECS400 spectrometer. The ^1H NMR and ^{13}C NMR chemical shifts were presented relative to tetramethylsilane (TMS) or residual solvent peak as an internal standard. Mass spectral analyses were done in Bruker micrOTOF-Q II Spectrometer. Perkin–Elmer FT–IR Spectrometer was used for FT-IR spectra. Dry solvents were freshly prepared and degassed by freeze-pump-thaw cycles, prior to use. Anilines, benzylic alcohols, amides, boron compounds and other chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, Acros Organics, and Avra Synthesis and used without further purification. Secondary aryl amines were prepared according to the previous report.[27]

Representative procedure for $B(C_6F_5)_3$-catalyzed *N*-alkylation of secondary aromatic amines 2 with benzylic alcohols 1.

30 mg of activated 4Å molecular sieve (powdered) was taken in an oven dried 15 mL Schlenk tube. Benzyl alcohol **1a** (51.8 mg, 0.375 mmol, 1.5 equiv), *N*-methylaniline **2a** (26.8 mg, 0.25 mmol, 1.0 equiv), and $B(C_6F_5)_3$ catalyst (1.3 mg, 0.0025 mmol, 1 mol %) dissolved in 0.5 mL of toluene was then added in that tube under argon. The solution was then stirred at 110 °C (oil bath temperature) for 24 h under argon atmosphere. Upon completion, the solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford **3a** as colorless liquid.

N-(4-Methoxybenzyl)-N-methylaniline ***(3a)***.[28] Analytical TLC on silica gel, 100:0 hexane/ethylacetate R_f = 0.50; Yield 88% (50 mg, 0.22 mmol). ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.21-7.16 (m, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.3 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 4.43 (s, 2H), 3.75 (s, 3H), 2.94 (s, 3H). ^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 158.6, 149.9, 130.9, 129.1, 128.0, 116.5, 114.0, 112.5, 56.0, 55.3, 38.3. IR (neat / cm^{-1}): 3026, 2945, 1601, 1538, 1336, 1224, 1034, 857, 683. HRMS (ESI^+): calculated for $C_{15}H_{17}NONa$ $[M + Na]^+$: 250.1208; found: 250.1215.

N-Benzyl-4-methoxy-N-(4-methoxybenzyl)aniline ***(3b)***. Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.40; Yield 83% (69.2 mg, 0.2075 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 3H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.56 (s, 2H), 4.53 (s, 2H), 3.83 (s, 3H), 3.77 (s, 3H). ^{13}C{^1H} NMR (126 MHz,

$CDCl_3$) δ 158.5, 151.7, 143.9, 139.0, 130.8, 128.5, 128.1, 126.9, 126.7, 114.8, 114.7, 113.9, 55.7, 55.2, 55.0, 54.6. IR (neat / cm^{-1}): 2938, 2830, 1595, 1234, 1157, 1033, 838, 698. HRMS (ESI^+): calculated for $C_{22}H_{23}NO_2Na$ $[M + Na]^+$: 356.1626; found: 356.1620.

N-Benzyl-4-chloro-N-(4-methoxybenzyl)aniline ***(3c)***. Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.60; Yield 77% (65.0 mg, 0.1925 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 8.1 Hz, 2H), 4.62 (s, 2H), 4.59 (s, 2H), 3.82 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.7, 147.7, 138.2, 129.9, 129.0, 128.7, 127.8, 127.0, 126.6, 121.5, 114.1, 113.8, 55.3, 54.3, 53.9. IR (neat / cm^{-1}): 3064, 3030, 2852, 1598, 1506, 1448, 1400, 1321, 1319, 1178, 1093, 816, 731, 693. HRMS (ESI^+): calcd for $C_{21}H_{20}ClNONa$ $[M + Na]^+$: 360.1131; found 360.1130.

N-(Benzo[d][1,3]dioxol-5-ylmethyl)-N-benzyl-4-methoxyaniline ***(3d)***. Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.35; Yield 76% (65.9 mg, 0.19 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 5H), 6.82 – 6.69 (m, 7H), 5.94 (s, 2H), 4.54 (s, 2H), 4.47 (s, 2H), 3.75 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 151.8, 147.9, 146.4, 143.7, 138.9, 132.9, 128.5, 127.0, 126.8, 119.9, 114.9, 114.7, 108.2, 107.5, 100.9, 55.7, 55.1, 55.0. IR (neat / cm^{-1}): 3028, 2900, 2832, 1515, 1488, 1443, 1243, 1039, 937, 812, 736, 697. HRMS (ESI^+): calcd for $C_{22}H_{21}NO_3Na$ $[M + Na]^+$: 370.1419, found 370.1421.

N-(Anthracen-9-ylmethyl)-N-benzyl-4-methoxyaniline ***(3e)***. Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.50; Yield 92% (92.8 mg, 0.23 mmol). ^1H NMR (400 MHz, CHLOROFORM-D) δ 8.41 (s, 1H), 8.25 (d, *J* = 9.4 Hz, 2H), 8.02 – 7.93 (m, 2H), 7.47 – 7.38 (m, 4H), 7.09 – 7.00 (m, 5H), 6.93 – 6.84 (m, 4H), 5.34 (s, 2H), 4.18 (s, 2H), 3.80 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-D) δ 152.7, 144.6, 139.8, 131.5, 131.3, 129.0, 128.8, 127.9, 127.1, 126.2, 125.9, 124.9, 124.6, 117.0, 114.7, 55.6, 52.9, 47.8. IR (neat / cm^{-1}): 3053, 2931, 2832, 1511, 1452, 1244, 1038, 813, 731. HRMS (ESI^+): calcd for $C_{29}H_{25}NONa$ $[M + Na]^+$: 426.1834, found 426.1845.

N-Phenyl-N-(thiophen-2-ylmethyl)aniline ***(3f)***. Analytical TLC on silica gel, 100:0 hexane/ethylacetate R_f = 0.40; Yield 81% (53.7 mg, 0.2025 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.9 Hz, 4H), 7.16 (d, *J* = 5.0 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 4H), 7.02 – 6.90 (m, 4H), 5.12 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.6, 142.8, 129.3, 126.7, 124.7, 124.1, 121.7, 121.0, 51.8. IR (neat / cm^{-1}): 3060, 3030, 1594, 1501, 1453, 1367, 1105, 1030, 748, 730, 696. HRMS (ESI^+): calcd for $C_{17}H_{15}NSNa$ $[M + Na]^+$: 288.0823, found 288.0821.

N-Methyl-N-(3,4,5-trimethoxybenzyl)aniline ***(3g)***. Analytical TLC on silica gel, 19:5 hexane/ethylacetate R_f = 0.30; Yield 90% (64.7 mg, 0.225 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.48 (s, 2H), 4.46 (s, 2H), 3.85 (s, 3H), 3.81 (s, 6H), 3.00 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 153.4, 150.0, 136.7, 134.9, 129.1, 116.8, 112.7, 103.4, 60.8, 57.2, 56.0, 38.4. IR (neat / cm^{-1}): 3060, 3029, 1598, 1502, 1454, 1106, 751, 730, 696. HRMS (ESI^+): calcd for $C_{17}H_{21}NO_3Na$ $[M + Na]^+$: 310.1419, found 310.1422.

N-(4-Chlorobenzyl)-4-methoxy-N-(4-methoxybenzyl)aniline ***(3h)***. Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.30; Yield 42% (38.6 mg, 0.105 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.17 (t, *J* = 8.2 Hz, 4H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 8.9 Hz, 2H), 4.46 (s, 4H), 3.80 (s, 3H), 3.74 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.6, 152.0, 143.6, 137.6, 132.4, 130.5, 128.6, 128.4, 128.2, 115.2, 114.7, 113.9, 55.7, 55.2, 54.8, 54.4. IR (neat / cm^{-1}): 2933, 2834, 1611, 1515, 1489, 1244, 1173, 1035, 810. HRMS (ESI^+): calculated for $C_{22}H_{22}ClNO_2Na$ $[M + Na]^+$: 390.1237; found: 390.1229.

N-(3-Fluorobenzyl)-4-methoxy-N-(4-methoxybenzyl)aniline ***(3i)***. Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.25; Yield 45% (38.6 mg, 0.105 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.00 – 6.89 (m, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 4.49 (s, 4H), 3.80 (s, 3H), 3.74 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.2 (d, *J* = 245.9 Hz), 158.6, 152.0, 143.6, 142.1 (d, *J* = 6.5 Hz), 130.5, 130.0 (d, *J* = 8.2 Hz), 128.2, 122.5 (d, *J* = 2.3 Hz), 115.0, 114.7, 114.0, 113.8 (d, *J* = 18.1 Hz), 113.6 (d, *J* = 17.4 Hz), 55.7, 55.2, 54.9, 54.6. IR (neat / cm^{-1}): 2938, 2834, 1617, 1520, 1177, 1036, 812, 786, 689. HRMS (ESI^+): calcd for $C_{22}H_{22}FNO_2Na$ $[M + Na]^+$: 374.1532, found 374.1536.

N-Benzyl-4-chloro-N-(1-(p-tolyl)ethyl)aniline ***(3l)***. Analytical TLC on silica gel, 100:0 hexane/ethylacetate R_f = 0.30; Yield 65% (54.6 mg, 0.1625 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.19 (m, 5H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.19 (q, *J* = 7.0 Hz, 1H), 4.50 (d, *J* = 17.4 Hz, 1H), 4.39 (d, *J* = 17.4 Hz, 1H), 2.35 (s, 3H), 1.59 (d, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.8, 139.6, 139.3, 136.7, 129.3, 128.8, 128.4, 126.7, 126.6, 126.4, 121.9, 115.4, 57.2, 50.3, 21.0, 18.7. IR (neat / cm^{-1}): 3026, 2976, 2924, 1597, 1497, 1449, 1245, 805, 731. HRMS (ESI^+): calcd for $C_{22}H_{22}ClNNa$ $[M + Na]^+$: 358.1338, found 358.1351.

N-Benzhydryl-N-methylaniline ***(3m)***: Analytical TLC on silica gel, 49:1 hexane/ethylacetate R_f = 0.60; Yield 80% (54.7 mg, 0.20 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.27 (m, 12H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.31 (s, 1H), 2.86 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 150.2, 140.7, 129.1, 128.7, 128.4, 127.2, 116.8, 113.0, 67.0, 34.5. IR (neat / cm^{-1}): 3061, 3026, 1598, 1504, 1319, 1105, 990, 748, 699. HRMS (ESI^+): calcd for $C_{20}H_{19}NNa$ $[M + Na]^+$: 296.1415, found 296.1410.

Representative procedure for $B(C_6F_5)_3$-catalyzed *N*-alkylation of Primary aromatic amines 4 with benzylic alcohols 1.

30 mg of powdered 4Å molecular sieve was taken in an oven dried 15 mL Schlenk tube. In that tube, benzyl alcohol **1a** (51.8 mg, 0.375 mmol, 1.5 equiv), aniline **4a** (26.8 mg, 0.25 mmol, 1.0 equiv), $B(C_6F_5)_3$ catalyst (2.5 mg, 0.005 mmol, 2 mol %) and toluene (0.5 mL) were added under argon and the tube was sealed, stirred at 120 °C (oil bath temperature) for 36 h. Upon completion, the solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography using hexane/ethylacetate as eluent to afford **5a** as colorless liquid.

N-(4-Methoxybenzyl)-4-methylaniline ***(5a)***.[29] Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.50; Yield 81% (46.0 mg, 0.2025 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.24 (s, 2H), 3.81 (s, 4H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.8, 146.0, 131.6, 129.7, 128.8, 126.7, 114.0, 113.0, 55.3, 48.1, 20.4. IR (neat / cm^{-1}): 2963, 2839, 1611, 1513, 1242, 1179,

1028, 814. HRMS (ESI$^+$): calcd for $C_{15}H_{17}NONa$ [M + Na]$^+$: 250.1208, found 250.1211.

4-Chloro-N-(4-methoxybenzyl)aniline (***5b***).[30] Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.40; Yield 87% (53.9 mg, 0.2175 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.0 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 4.21 (s, 2H), 3.97 (brs, 1H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.0, 146.7, 130.9, 129.0, 128.7, 122.0, 114.1, 113.9, 55.3, 47.8. IR (neat / cm^{-1}): 3413, 2957, 2932, 2836, 1601, 1505, 1512, 1247, 1177, 1034, 815, 506. HRMS (ESI$^+$): calcd for $C_{14}H_{14}ClNONa$ [M + Na]$^+$: 270.0662, found 270.0670.

3,5-Dichloro-N-(4-methoxybenzyl)aniline (***5c***): Analytical TLC on silica gel, 49:1 hexane/ethylacetate R_f = 0.35; Yield 86% (60.6 mg, 0.2150 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 9.3 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.65 (s, 1H), 6.46 (s, 2H), 4.19 (d, *J* = 5.1 Hz, 2H), 4.09 (brs, 1H), 3.80 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.1, 149.6, 130.0, 128.8, 117.2, 114.2, 111.0, 55.3, 47.4. IR (neat / cm^{-1}): 2933, 2836, 1593, 1511, 1452, 1247, 1177, 1114, 820, 799. HRMS (ESI$^+$): calcd for $C_{14}H_{13}Cl_2NONa$ [M + Na]$^+$: 304.0272; found 304.0269.

3-Bromo-N-(4-methoxybenzyl)aniline (***5d***). Analytical TLC on silica gel, 49:1 hexane/ethylacetate R_f = 0.40; Yield 82% (59.8 mg, 0.205 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.78 (s, 1H), 6.53 (d, *J* = 8.2 Hz, 1H), 4.23 (s, 2H), 4.01 (brs, 1H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.0, 149.4, 130.7, 130.5, 128.8, 123.3, 120.2, 115.4, 114.1, 111.5, 55.3, 47.6. IR (neat / cm^{-1}): 3411, 3000, 2931, 2835, 1595, 1511, 1418, 1359, 1323, 1301, 1245, 1174, 1102, 1067, 1033, 985, 809, 762, 682, 518. HRMS (ESI$^+$): calcd for $C_{14}H_{14}BrNONa$ [M + Na]$^+$: 314.0156; found 314.0162.

4-((4-Methoxybenzyl)amino)benzonitrile (***5e***). Analytical TLC on silica gel, 49:1 hexane/ethylacetate R_f = 0.40; Yield 74% (44.1 mg, 0.185 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 4.55 (brs, 1H), 4.27 (d, *J* = 5.3 Hz, 2H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.1, 151.1, 133.6, 129.7, 128.6, 120.4, 114.2, 112.3, 98.8, 55.2, 46.9. IR (neat / cm^{-1}): 2997, 2935, 2832, 2222, 1518, 1249, 1172, 1036, 811. HRMS (ESI$^+$): calculated for $C_{15}H_{14}N_2ONa$ [M + Na]$^+$: 261.1004; found: 261.1012.

(2-((4-Methoxybenzyl)amino)phenyl)(phenyl)methanone (***5f***). Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.50; Yield 88% (69.8 mg, 0.22 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (brs, 1H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.57 – 7.42 (m, 4H), 7.41 – 7.29 (m, 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.57 (t, *J* = 7.5 Hz, 1H), 4.45 (d, *J* = 5.4 Hz, 2H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 199.3, 158.8, 151.5, 140.4, 135.4, 134.9, 130.7, 130.5, 129.0, 128.4, 128.0, 117.4, 114.1, 114.0, 111.9, 55.2, 46.4. IR (neat / cm^{-1}): 2931, 2830, 1725, 1615, 1585, 1513, 1242, 1032, 818, 783. HRMS (ESI$^+$): calcd for $C_{21}H_{19}NO_2Na$ [M + Na]$^+$: 340.1313; found 340.1301.

4-Chloro-2-((4-methoxybenzyl)amino)benzoic acid (***5g***). Analytical TLC on silica gel, 4:1 hexane/ethylacetate R_f = 0.30; Yield 71% (51.8 mg, 0.1775 mmol). ^{1}H NMR (500 MHz, THF-d_8) δ 8.43 (brs, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 1.7 Hz, 1H), 6.51 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.35 (d, *J* = 5.1 Hz, 2H), 3.74 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, THF-d_8) δ 170.4, 160.3, 153.2, 141.2, 134.4, 131.6, 129.3, 115.4, 115.0, 112.0, 110.2, 55.5, 47.1. IR (neat / cm^{-1}): 3046, 2997, 2933, 2834, 1709, 1611, 1515, 1244, 1173, 1034, 809. HRMS (ESI$^+$): calcd for $C_{15}H_{14}ClNO_3Na$ [M + Na]$^+$: 314.0560; found 314.0575.

4-Methoxy-N-(4-methoxybenzyl)aniline (***5h***).[30] Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.40; Yield 83% (50.5 mg, 0.2075 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 4.21 (s, 2H), 3.78 (m, 7H). ^{13}C{^{1}H} ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 158.8, 152.1, 142.5, 131.6, 128.8, 114.9, 114.1, 114.0, 55.8, 55.3, 48.7. IR (neat / cm^{-1}): 3010, 2997, 1588, 1534, 1230, 1101, 1035, 780. HRMS (ESI$^+$): calcd for $C_{15}H_{17}NO_2Na$ [M + Na]$^+$: 266.1157; found 266.1149.

N-(Benzo[d][1,3]dioxol-4-ylmethyl)-2-methylaniline (***5i***): Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.50; Yield 84% (50.6 mg, 0.21 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 2H), 6.90 (s, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.70 (t, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 2H), 4.30 (s, 2H), 3.83 (brs, 1H), 2.18 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.9, 146.7, 145.9, 133.4, 130.0, 127.1, 121.9, 120.6, 117.2, 110.0, 108.3, 108.0, 101.0, 48.1, 17.5. IR (neat / cm^{-1}): 3000, 2933, 2835, 1513, 1488, 1244, 1172, 1034, 811. HRMS (ESI$^+$): calcd for $C_{15}H_{15}NO_2Na$ [M + Na]$^+$: 264.1000, found 264.1005.

3-Bromo-N-(thiophen-2-ylmethyl)aniline (***5j***). Analytical TLC on silica gel, 100:0 hexane/ethylacetate R_f = 0.50; Yield 71% (47.6 mg, 0.1775 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 1H), 7.04 – 6.69 (m, 3H), 6.91 – 6.78 (m, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 4.49 (s, 2H), 4.11 (brs, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.8, 142.0, 130.5, 126.9, 125.3, 124.8, 123.2, 120.8, 115.7, 111.8, 43.2. IR (neat / cm^{-1}): 2933, 2830, 1594, 1455, 1360, 1033, 748, 694. HRMS (ESI$^+$): calcd for $C_{11}H_{10}BrNSNa$ [M + Na]$^+$: 289.9615, found 289.9610.

N-(4-Chlorobenzyl)-4-methoxyaniline (***5k***).[30] Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.40; Yield 38% (26.1 mg, 0.095 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (s, 4H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.59 (d, *J* = 8.9 Hz, 2H), 4.27 (s, 2H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.3, 142.1, 138.2, 132.7, 128.70, 128.65, 114.9, 114.1, 55.7, 48.5. IR (neat / cm^{-1}): 3063, 3032, 1601, 1498, 1319, 816, 730. HRMS (ESI$^+$): calcd for $C_{14}H_{14}ClNONa$ [M + Na]$^+$: 270.0662, found 270.0670.

N-(3-Fluorobenzyl)-4-methoxyaniline (***5l***).[31] Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.35; Yield 43% (24.9 mg, 0.1075 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 13.9, 7.7 Hz, 1H), 7.17 – 7.10 (m, 2H), 6.97 (t, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.31 (s, 2H), 3.86 (brs, 1H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.1 (d, *J* = 246.0 Hz), 152.3, 142.6 (d, *J* = 6.9 Hz), 142.0, 130.0 (d, *J* = 8.2 Hz), 122.8 (d, *J* = 2.8 Hz), 114.9, 114.2 (d, *J* = 21.4 Hz), 114.1, 113.9 (d, *J* = 21.1 Hz), 55.7, 48.6. IR (neat / cm^{-1}): 2997, 2831, 1589, 1514, 1179, 917, 685. HRMS (ESI$^+$): calcd for $C_{14}H_{14}FNONa$ [M + Na]$^+$: 254.0957, found 254.0952.

N-Benzyl-4-chloroaniline (***5m***).[32] Analytical TLC on silica gel, 49:1 hexane/ethylacetate R_f = 0.50; Yield 80% (43.5 mg, 0.2 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.47 (m, 4H), 7.43 – 7.40 (m, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 4.43 (s, 2H), 4.18 (brs, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.6, 138.9, 129.0, 128.7, 127.4, 127.3, 122.1, 113.9, 48.3. IR (neat / cm^{-1}): 3063, 3028, 1601, 1502, 1450, 1323, 1175, 1120, 1089, 817, 734, 700. HRMS (ESI$^+$):

calcd for $C_{13}H_{12}ClNNa$ [M + Na]$^+$: 240.0556, found 240.0547.

N-Benzyl-4-bromoaniline (***5n***).[33] Analytical TLC on silica gel, 49:1 hexane/ethylacetate R_f = 0.50; Yield 76% (49.8 mg, 0.19 mmol). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.35 – 7.34 (m, 4H), 7.31 – 7.27 (m, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.50 (d, *J* = 8.6 Hz, 2H), 4.29 (s, 2H), 4.07 (brs, 1H). ^{13}C{^{1}H} NMR (101 MHz, CHLOROFORM-D) δ 147.0, 138.8, 131.9, 128.7, 127.3, 114.4, 109.1, 48.2. IR (neat / cm^{-1}): 3064, 3030, 2857, 1598, 1500, 1322, 1179, 1068, 810, 730, 694. HRMS (ESI$^+$): calcd for $C_{13}H_{12}BrNNa$ [M + Na]$^+$: 284.0051, found 284.0042.

4-Chloro-N-(naphthalen-2-ylmethyl)aniline (***5o***).[34] Analytical TLC on silica gel, 49:1 hexane/ethylacetate R_f = 0.10; Yield 72% (49.8 mg, 0.18 mmol). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.82 – 7.77 (m, 4H), 7.47 – 7.43 (m, 3H), 7.09 (d, *J* = 8.9 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 4.45 (s, 2H), 4.16 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.7, 136.4, 133.5, 132.8, 129.1, 128.5, 127.73, 127.70, 126.2, 125.9, 125.9, 125.5, 122.2, 114.0, 48.6. IR (neat / cm^{-1}): 3429, 3054, 2963, 1599, 1504, 1402, 1313, 1262, 1178, 1095, 855, 813, 750, 621. HRMS (ESI$^+$): calcd for $C_{17}H_{14}ClNNa$ [M + Na]$^+$: 290.0712, found 290.0720.

4-Methyl-N-(1-phenylethyl)aniline (***5p***).[35] Analytical TLC on silica gel, 49:1 hexane/ethylacetate R_f = 0.40; Yield 62% (32.8 mg, 0.155 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 5H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.52 (d, *J* = 8.3 Hz, 2H), 4.54 (q, *J* = 6.7 Hz, 1H), 3.97 (brs, 1H), 2.27 (s, 3H), 1.58 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.4, 145.0, 129.5, 128.6, 126.7, 126.3, 125.8, 113.4, 53.6, 25.0, 20.3. IR (neat / cm^{-1}): 2938, 2834, 1615, 1588,1518, 1250, 819, 783. HRMS (ESI$^+$): calcd for $C_{15}H_{17}NNa$ [M + Na]$^+$: 234.1259, found 234.1245.

4-Methyl-N-(1-(p-tolyl)ethyl)aniline (***5q***). Analytical TLC on silica gel, 99:1 hexane/ethylacetate R_f = 0.35; Yield 69% (38.9 mg, 0.1725 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 8.1 Hz, 2H), 4.51 (q, *J* = 6.6 Hz, 1H), 3.94 (brs, 1H), 2.40 (s, 3H), 2.27 (s, 3H), 1.56 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.1, 142.4, 136.2, 129.5, 129.2, 126.2, 125.7, 113.4, 53.3, 25.0, 21.0, 20.3. IR (neat / cm^{-1}): 2949, 2831, 1615, 1584, 1513, 1246, 1037, 822, 782. HRMS (ESI$^+$): calcd for $C_{16}H_{19}NNa$ [M + Na]$^+$: 248.1415; found 248.1407.

N-Benzhydryl-4-methylaniline (***5r***).[28] Analytical TLC on silica gel, 100:0 hexane/ethylacetate R_f = 0.30; Yield 78% (53.3 mg, 0.195 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.36 (m, 8H), 7.33 (d, *J* = 6.9 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 2H), 6.55 (d, *J* = 7.0 Hz, 2H), 5.55 (s, 1H), 4.19 (brs, 1H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.1, 143.1, 129.6, 128.7, 127.4, 127.2, 126.8, 113.5, 63.3, 20.3. IR (neat / cm^{-1}): 2997, 2934, 2834, 1615, 1584, 1513, 1241, 1032, 783. HRMS (ESI$^+$): calcd for $C_{20}H_{19}NNa$ [M + Na]$^+$: 296.1415; found 296.1417.

4-Methoxy-N-tritylaniline (***5s***).[20] Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.50; Yield 52% (47.5 mg, 0.13 mmol). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.39 – 7.27 (m, 6H), 7.28 – 7.24 (m, 6H), 7.22 – 7.18 (m, 3H), 6.50 (d, *J* = 8.9 Hz, 2H), 6.30 (d, *J* = 8.9 Hz, 2H), 4.75 (brs, 1H), 3.63 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, CHLOROFORM-D) δ 151.7, 145.5, 140.0, 129.2, 127.8, 126.7, 117.2, 113.7, 71.6, 55.4. IR (neat / cm^{-1}): 3026, 2999, 1510, 1490, 1447, 1247, 1237, 1034, 820, 701. HRMS (ESI$^+$): calcd for $C_{26}H_{23}NONa$ [M + Na]$^+$: 388.1677; found 388.1670.

N-(3,3-diphenylallyl)-4-methoxyaniline (***5t***). Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.20; Yield 79% (62.3 mg, 0.1975 mmol). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.41 – 7.34 (m, 4H), 7.28 – 7.19 (m, 7H), 6.76 (d, *J* = 9.0 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 6.19 (t, *J* = 6.6 Hz, 1H), 3.79 (d, *J* = 6.7 Hz, 2H), 3.73 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, CHLOROFORM-D) δ 152.2, 144.0, 142.1, 142.0, 139.3, 129.7, 128.5, 128.3, 128.1, 127.5, 126.6, 126.5, 114.8, 114.4, 55.8, 44.2. IR (neat / cm^{-1}): 2929, 1634, 1511, 1234, 1032, 818, 755, 699. HRMS (ESI$^+$): calcd for $C_{22}H_{21}NONa$ [M + Na]$^+$: 338.1521; found 338.1519.

Large scale synthetic procedure for B(C_6F_5)$_3$-catalyzed *N*-benzylation of *p*-toluidine (4a) with *p*-methoxybenzyl alcohol (1a).

In an oven dried 100 mL Schlenk tube 300 mg of powdered 4Å molecular sieve was taken. In that tube, benzyl alcohol **1a** (518.1 mg, 03.75 mmol, 1.5 equiv), aniline **4a** (267.9 mg, 2.5 mmol, 1.0 equiv), $B(C_6F_5)_3$ catalyst (25.6 mg, 0.05 mmol, 2 mol %) and toluene (50 mL) were added under argon and the tube was sealed, stirred at 120 °C (oil bath temperature) for 48 h. Upon completion, the solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography using hexane/ethylacetate as eluent to afford **5a** in 76% yield (431.5 mg, 1.9 mmol).

Representative procedure for B(C_6F_5)$_3$-catalyzed *N*-alkylation of amide 6 with benzylic alcohol 1.

In an oven dried 15 mL Schlenk tube 30 mg of powdered 4Å molecular sieve was taken. Benzyl alcohol **1a** (34.5 mg, 0.25 mmol, 1.0 equiv), amide **6a** (42.8 mg, 0.25 mmol, 1.0 equiv), $B(C_6F_5)_3$ catalyst (2.5 mg, 0.005 mmol, 2 mol %) and chlorobenzene (0.5 mL) were then added under argon. The tube was sealed, stirred at 110 °C (oil bath temperature) for 48 h. Upon completion, the solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography to afford **7a**.

N-(4-Methoxybenzyl)-4 methylbenzenesulfonamide (***7a***).[36] Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.35; Yield 90% (65.6 mg, 0.225 mmol). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 4.98 (t, *J* = 6.0 Hz, 1H), 4.01 (d, *J* = 6.1 Hz, 2H), 3.73 (s, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, CHLOROFORM-D) δ 159.1, 143.3, 136.8, 129.6, 129.2, 128.3, 127.1, 113.9, 55.2, 46.6, 21.4. IR (neat / cm^{-1}): 2933, 2867, 1599, 1462, 1410, 1235, 1098, 987, 828, 663. HRMS (ESI$^+$): calcd for $C_{15}H_{17}NO_3SNa$ [M + Na]$^+$: 314.0827; found 314.0820.

N-(4-(Dimethylamino)benzyl)-4-methylbenzenesulfonamide (***7b***). Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.20; Yield 82% (62.4 mg, 0.205 mmol). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 4.46 (t, *J* = 5.6 Hz, 1H), 4.01 (d, *J* = 5.8 Hz, 2H), 2.92 (s, 6H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.4, 143.3, 137.0, 129.7, 129.0, 127.2, 123.6, 112.5, 47.0, 40.5, 21.5. IR (neat / cm^{-1}): 2922, 2804, 1616, 1524, 1327, 1159, 1094, 810, 661. HRMS (ESI$^+$): calcd for $C_{16}H_{20}N_2O_2SNa$ [M + Na]$^+$: 327.1143; found 327.1135.

N-(3-Iodobenzyl)-4-methylbenzenesulfonamide (***7c***). Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.45; Yield 64% (62.0 mg, 0.16 mmol). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.43 (s, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 4.66 (d, *J* = 5.7 Hz, 1H), 4.07 (d, *J* = 6.3 Hz, 2H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (126

MHz, $CDCl_3$) δ 143.8, 138.6, 137.0, 136.9, 136.8, 130.3, 129.8, 127.13, 127.06, 94.4, 46.5, 21.6. IR (neat / cm^{-1}): 2922, 2850, 1641, 1634, 1323, 1153, 658. HRMS (ESI^+): calcd for $C_{14}H_{14}INO_2SNa$ $[M + Na]^+$: 409.9688; found 409.9675.

*N-(4-Bromo-2-methoxybenzyl)-4-methylbenzenesulfonamide (**7d**)*. Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.25; Yield 78% (72.2 mg, 0.195 mmol). ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.93 (s, 2H), 6.81 (s, 1H), 5.08 (t, *J* = 6.5 Hz, 1H), 4.09 (d, *J* = 6.6 Hz, 2H), 3.72 (s, 3H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-D) δ 157.7, 143.3, 137.2, 130.9, 129.4, 127.0, 123.5, 113.8, 55.5, 43.4, 21.5. IR (neat / cm^{-1}): 2927, 2856, 1595, 1489, 1462, 1400, 1329, 1160, 1030, 814, 730, 663. HRMS (ESI^+): calcd for $C_{15}H_{16}BrNO_3SNa$ $[M + Na]^+$: 391.9932; found 391.9931.

*4-Methyl-N-(naphthalen-2-ylmethyl)benzenesulfonamide (**7e**)*.[12a] Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.45; Yield 75% (58.3 mg, 0.1875 mmol). ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.77 – 7.74 (m, 4H), 7.59 (s, 2H), 7.47 – 7.44 (m, 2H), 7.31 – 7.27 (m, 4H), 4.68 (t, *J* = 6.2 Hz, 2H), 4.28 (d, *J* = 6.3 Hz, 4H), 2.40 (s, 5H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 143.6, 137.0, 133.6, 133.2, 132.9, 129.7, 128.6, 127.73, 127.66, 127.2, 126.7, 126.4, 126.2, 125.6, 47.5, 21.5. IR (neat / cm^{-1}): 2922, 2855, 1629, 1603, 1323, 1162, 813, 733. HRMS (ESI^+): calcd for $C_{18}H_{17}NO_2SNa$ $[M + Na]^+$: 334.0878; found 334.0865.

*N-(Anthracen-9-ylmethyl)-4-methylbenzenesulfonamide(**7f**)*. Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.40; Yield 72% (65.1 mg, 0.18 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.00 – 7.97 (m, 2H), 7.96 – 7.92 (m, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.45 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.06 (d, *J* = 5.4 Hz, 2H), 4.54 (s, 1H), 2.50 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, CDCl3) δ 143.7, 136.4, 131.4, 130.2, 129.8, 129.2, 128.7, 127.5, 126.8, 125.9, 125.2, 123.2, 39.5, 21.6. (s). IR (neat / cm^{-1}): 2922, 2850, 1633, 1336, 1158, 1094, 729, 670. HRMS (ESI^+): calcd for $C_{22}H_{19}NO_2SNa$ $[M + Na]^+$: 384.1034; found 384.1023.

*4-Methyl-N-(thiophen-2-ylmethyl)benzenesulfonamide (**7g**)*.[37] Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.35; Yield 79% (52.8 mg, 0.1975 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 5.0 Hz, 1H), 6.90 – 6.87 (m, 1H), 6.86 (d, *J* = 3.1 Hz, 1H), 4.67 (s, 1H), 4.34 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 143.7, 138.9, 136.8, 129.8, 127.2, 126.9, 126.5, 125.8, 42.1, 21.5. IR (neat / cm^{-1}): 2918, 2850, 1599, 1421, 1323, 1157, 1090, 1039, 813, 665. HRMS (ESI^+): calcd for $C_{12}H_{13}NO_2S_2Na$ $[M + Na]^+$: 290.0285; found 290.0280.

*4-Methyl-N-(1-phenylethyl)benzenesulfonamide (**7h**)*.[38] Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.40; Yield 77% (53.0 mg, 0.1925 mmol). ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.15 (m, 5H), 7.12 – 7.09 (m, 2H), 5.16 (s, 1H), 4.46 (p, *J* = 7.0 Hz, 1H), 2.38 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-D) δ 143.1, 142.0, 137.6, 129.4, 128.5, 127.4, 127.0, 126.1, 53.6, 23.5, 21.4. IR (neat / cm^{-1}): 3033, 2978, 2927, 1599, 1497, 1455, 1327, 1162, 1090, 962, 814, 665. HRMS (ESI^+): calcd for $C_{15}H_{17}NO_2SNa$ $[M + Na]^+$: 298.0878; found 298.0865.

*4-Methyl-N-(1-phenylpropyl)benzenesulfonamide (**7i**)*.[39] Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.40;Yield 76% (55.0 mg, 0.19 mmol). ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.36 (s, 1H), 7.25 (d, *J* = 2.7 Hz, 2H), 7.20 (s, 2H), 7.11 – 7.08 (m, 2H), 4.82 (d, *J* = 6.9 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 1.96 – 1.77 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.9, 142.9, 140.7, 137.7, 129.3, 128.4, 127.4, 127.1, 126.5, 59.8, 30.6, 21.4, 10.4. IR (neat / cm^{-1}): 2922, 2855, 1599, 1455, 1319, 1310, 1162, 670. HRMS (ESI^+): calcd for $C_{16}H_{19}NO_2SNa$ $[M + Na]^+$: 312.1034; found 312.1031.

*N-(1-(3-Chlorophenyl)ethyl)-4-methylbenzenesulfonamide (**7j**)*. Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.40; Yield 68% (52.7 mg, 0.17 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 4.8 Hz, 2H), 7.05 – 7.01 (m, 1H), 6.98 (s, 1H), 5.42 (s, 1H), 4.47 – 4.39 (m, 1H), 2.38 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.0, 143.3, 137.4, 134.2, 129.7, 129.4, 127.4, 127.0, 126.4, 124.4, 53.2, 23.4, 21.4. IR (neat / cm^{-1}): 2978, 2927, 1598, 1576, 1435, 1327, 1161, 1092, 965, 814, 665. HRMS (ESI^+): calcd for $C_{15}H_{16}ClNO_2SNa$ $[M + Na]^+$: 332.0488; found 332.0495.

*N-Benzhydryl-4-methylbenzenesulfonamide (**7k**)*.[40] Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.30; Yield 84% (70.9 mg, 0.21 mmol). ^1H NMR (500 MHz, THF) δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.45 (s, 1H), 7.17 – 7.08 (m, 11H), 5.59 (s, 1H), 2.59 – 2.24 (m, 1H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, THF) δ 143.1, 142.9, 140.8, 130.0, 129.1, 128.7, 128.0, 127.9, 62.1, 21.5. IR (neat / cm^{-1}): 3058, 2986, 2922, 1599, 1493, 1450, 1162, 936, 810. HRMS (ESI^+): calcd for $C_{20}H_{19}NO_2SNa$ $[M + Na]^+$: 360.1034; found 360.1022.

*N-(4-Methoxybenzyl)-N′-(4-methoxybenzylidene)-4-methylbenzenesulfonohydrazide (**7l**)*. Analytical TLC on silica gel, 4:1 hexane/ethylacetate R_f = 0.30; Yield 84% (89.1 mg, 0.21 mmol). ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.71 (s, 1H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.83 (dd, *J* = 8.9, 2.2 Hz, 4H), 4.63 (s, 2H), 3.77 (d, *J* = 12.3 Hz, 6H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-D) δ 161.4, 159.0, 150.7, 143.9, 134.2, 129.5, 129.2, 128.6, 128.3, 127.6, 126.6, 55.3, 55.2, 52.5, 21.6. IR (neat / cm^{-1}): 2927, 2838, 1607, 1510, 1353, 1247, 1166, 1030, 742, 657. HRMS (ESI^+): calcd for $C_{23}H_{24}N_2O_4SNa$ $[M + Na]^+$: 447.1354; found 447.1362.

*2,4,6-Triisopropyl-N-(4-methoxybenzyl)-N′-(4-methylbenzylidene)benzenesulfonohydrazide (**7m**)*. Analytical TLC on silica gel, 19:1 hexane/ethylacetate R_f = 0.25; Yield 73% (95.0 mg, 0.1825 mmol). ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.43 (s, 1H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.18 (s, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.13 (s, 2H), 4.26 (dq, *J* = 13.6, 6.8 Hz, 2H), 3.77 (s, 3H), 2.90 (dq, *J* = 13.7, 6.9 Hz, 1H), 2.28 (s, 3H), 1.30 – 1.25 (m, 18H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-D) δ 158.9, 153.3, 151.7, 141.7, 139.7, 131.7, 129.0, 128.2, 127.0, 126.8, 123.7, 114.3, 55.2, 47.9, 34.2, 29.9, 24.9, 23.6, 21.3. IR (neat / cm^{-1}): 2960, 2931, 2867, 1615, 1599, 1514, 1459, 1247, 1166, 903, 733, 581. HRMS (ESI^+): calcd for $C_{31}H_{40}N_2O_3SNa$ $[M + Na]^+$: 543.2657; found 543.2667.

*4-Methyl-N-tritylbenzenesulfonamide (**7n**)*. Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.30; Yield 71% (73.4 mg, 0.1775 mmol). ^1H NMR (400 MHz, CHLOROFORM-D) δ 7.33 – 7.28 (m, 6H), 7.19 – 7.13 (m, 9H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 5.76 (brs, 1H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 143.2, 142.1, 139.4, 129.2, 128.80, 127.7, 127.1, 126.5, 72.6, 21.4. IR (neat / cm^{-1}): 2920, 1636, 1597, 1494, 1400, 1316,

1160, 1152, 1023, 697. HRMS (ESI^+): calcd for $C_{26}H_{23}NO_2SNa$ $[M + Na]^+$: 436.1347; found 436.1365.

*N-(3,3-Diphenylallyl)-4-methylbenzenesulfonamide (**7o**)*. Analytical TLC on silica gel, 9:1 hexane/ethylacetate R_f = 0.20; Yield 67% (60.9 mg, 0.1675 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.22 (m, 8H), 7.12 – 6.99 (m, 4H), 5.91 (t, *J* = 7.0 Hz, 1H), 4.46 – 4.45 (m, 1H), 3.66 (t, *J* = 6.5 Hz, 2H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.5, 143.4, 141.2, 138.4, 137.1, 129.7, 129.5, 128.4, 128.2, 127.8, 127.7, 127.4, 127.2, 123.2, 42.4, 21.5. IR (neat / cm^{-1}): 2921, 1598, 1443, 1321, 1158, 1092, 758, 701. HRMS (ESI^+): calcd for $C_{22}H_{21}NO_2SNa$ $[M + Na]^+$: 386.1191; found 386.1185.

Reaction procedure for $B(C_6F_5)_3$-catalyzed formation of dibenzyl ether 8a from alcohol 1a.

In a 15 mL Schlenk tube alcohol **1a** (51.8 mg, 0.375 mmol) and $B(C_6F_5)_3$ catalyst (3.8 mg, 0.0075 mmol, 2 mol %) were dissolved in 0.5 mL of toluene. Then the solution was stirred at room temperature under argon atmosphere for 2 h. The solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography to obtain **8a** as a colorless liquid in 82% yield (39.7 mg, 0.1538 mmol).

*4,4'-(Oxybis(methylene))bis(methoxybenzene) (**8a**)*.[41] ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.48 (s, 2H), 3.82 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.2, 130.5, 129.4, 113.8, 71.4, 55.3. GCMS. calcd for $C_{20}H_{19}N$: (m/z) = 258.13; found 258.13.

Procedure for $B(C_6F_5)_3$-catalyzed reaction of dibenzyl ether 8a with aniline 4a.

In a 15 mL Schlenk tube 10 mg of powdered 4Å molecular sieve was taken. Next, ether **8a** (37.7 mg, 0.15 mmol), aniline **4a** (16.1 mg, 0.15 mmol and $B(C_6F_5)_3$ catalyst (1.5 mg, 0.003 mmol, 2 mol %) in 0.25 mL of toluene was added. Then the solution was stirred at 120 °C (oil bath temperature) under argon atmosphere for 8 h. The solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography to obtain **5a** as a colorless liquid in 35% yield (11.9 mg, 0.0525 mmol).

Recation procedure for equilibrium studies in between 8a and 9a ($B(C_6F_5)_3$ adduct of 8a).

In a J-Young NMR tube, ether **8a** (2.6 mg, 0.01 mmol) was dissolved in 0.6 mL of benzene-d_6 under argon and ^1H NMR was measured at room temperature. Now, 5.1 mg of $B(C_6F_5)_3$ (0.01 mmol) was added to the NMR tube and after 1h at room temperature the reaction mixture was analyzed by 1H NMR again to obtain **9a**:**8a** > 95:5.

Now the solvent was evaporated by taking the reaction mixture from the NMR tube to a round bottom flask under argon. The crude residue was washed with cold hexane (1 mL) to get **9a**.

9a. ^1H NMR (500 MHz, C_6D_6) δ 7.18 (d, *J* = 8.6 Hz, 4H), 6.78 (d, *J* = 8.6 Hz, 4H), 4.30 (d, *J* = 8.4 Hz, 4H), 3.30 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 160.3, 148.4 (d, *J* = 241.3 Hz), 140.7 (d, *J* = 251.7 Hz), 137.6 (d, *J* = 246.7 Hz), 130.2, 130.1, 114.4, 71.7, 54.9. ^{19}F NMR (471 MHz, C_6D_6) δ -134.42 (dd, *J* = 23.2, 7.3 Hz), -155.65 (t, *J* = 20.7 Hz), -163.05 (td, *J* = 23.7, 8.7 Hz). $^{11}B\{1H\}$ NMR[42] (161 MHz, C_6D_6) δ 1.5. HRMS (ESI^+): calculated for $C_{34}H_{19}BF_{15}O_3$ $[M + H]^+$: 771.1188; found: 771.1207.

Procedure for equilibrium studies in between 4a and 10a ($B(C_6F_5)_3$ adduct of 4a).

In a J-Young NMR tube, aniline **4a** (1.1 mg, 0.01 mmol) was dissolved in 0.6 mL of benzene-d_6 under argon and ^1H NMR was measured at room temperature. Now, 5.1 mg of $B(C_6F_5)_3$ (0.01 mmol) was added to the NMR tube and after 1h at room temperature the reaction mixture was analyzed by ^1H NMR again to obtain **10a**:**4a** 80:20.

Recation procedure for equilibrium studies in a mixture of 4a, 8a and $B(C_6F_5)_3$.

In a J-Young NMR tube, ether **8a** (2.6 mg, 0.01 mmol), aniline **4a** (2.7 mg, 0.016 mmol) and $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol) were dissolved in 0.6 mL of benzene-d_6 under argon. After 1h at room temperature the reaction mixture was analyzed by ^1H NMR again to obtain **10a**:**9a** 92:8.

Experimental procedure for Hammett analysis by varying alcohol with aniline.

In five different 15 mL Schlenk tubes, *p*-anisidine (30.8 mg, 0.25 mmol, 1.0 equiv), $B(C_6F_5)_3$ catalyst (2.5 mg, 0.005 mmol, 2 mol %) were added with 30 mg of 4Å molecular sieve. Next, 0.5 mL toluene solution of alcohol *p*-methoxybenzyl alcohol, *p*-methybenzyl alcohol, benzyl alcohol, *p*-chlorobenzyl alcohol and *m*-fluorobenzyl alcohol (0.375 mmol, 1.5 equiv) was slowly added in the five different Schlenk tubes respectively. Now, the Schlenk tubes containing the reaction mixture were heated at 120 °C (oil bath temperature) for 10 h under argon. The solvent was removed under reduced pressure and the corresponding NMR yield of *N*-alkylated product from Schlenk tube 1-5 was found as 60%, 30%, 10%, 2% and 1%, respectively (average of three independent runs). The ratio of the reaction rate was determined from the ratio of the yields of corresponding product to draw Hammett plot.

Experimental procedure for Hammett analysis by varying aniline with an alcohol.

In five different 15 mL Schlenk tubes, *p*-anisidine, *p*-toluidine, aniline, *p*-chloroaniline and *m*-bromoaniline (0.25 mmol, 1.0 equiv) was dissolved in 0.5 mL toluene. Now, $B(C_6F_5)_3$ catalyst (2.5 mg, 0.005 mmol, 2 mol %), *p*-methoxybenzyl alcohol (51.8 mg, 0.375 mmol, 1.5 equiv) and 30 mg of 4Å molecular sieve were added in each of the five different Schlenk tubes. Now, the Schlenk tubes containing the reaction mixture were heated at 120 °C (oil bath temperature) for 10 h under argon. The solvent was removed under reduced pressure and the yield of the corresponding *N*-alkylated product was found as 60%, 58%, 55%, 53% and 52%, respectively (average of three independent runs). The ratio of the reaction rate was determined from the ratio of the yields of corresponding product to draw Hammett plot.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
NMR spectra (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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