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Benzylation of arenes with benzyl halides synergistically promoted by in situ generated superacid boron trifluoride monohydrate and tetrahaloboric acid

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ABSTRACT

To examine the assembly methodology of diarylmethanes, a benzylation of (hetero)arenes with benzyl halides has been developed and various diarylmethanes were furnished with yields of up to 98% and regioselectivities of up to >99%. The complexation of the by-product halogen hydride with $BF_3 \cdot OEt_2$ generated the Bronsted acid $BF_3 \cdot HX$ (HBF_3X, X=Cl or Br) in situ to synergistically promote the benzylation.

1. Introduction

Diarylmethanes are notably important fragments in supramolecules such as calixarene, cryptophane, and pillar[*n*]arene[1] and in drugs such as beclobrate, avrainvilleol, and papaverine.[2] Many cross-coupling strategies are used to synthesize these fragments, such as Negishi reactions of benzyl halides with arylzinc reagents,[3] Suzuki–Miyaura reactions of benzyl reagents or diarylmethyl carbonates with organoboron reagents,[4] and the benzylation of aromatic sulfinic acid sodium salts with benzyl chlorides.[5] As an alternative protocol, the direct Friedel–Crafts benzylation of (hetero)arenes provides an efficient method to construct diarylmethanes through the transformation of an unactivated C–H bond, which involves aluminum, iron, scandium, hafnium, platinum, lanthanum, and gold metal salts.[6,7]

BF_3 is a commonly used Lewis acid that has strong interactions with numerous ligands such as carbon, nitrogen, oxygen, fluorine, phosphorus, and sulfur, to form many of coordinate compounds.[8] $BF_3 \cdot OEt_2$ is an adduct of BF_3 and Et_2O through a donor–acceptor bonding[9] and is capable to effectively participate in a series of synthetic mechanisms such as alkylation,[10a,b] cyclization,[10c,e] rearrangement,[10f] and coupling reactions.[10g] Among these mechanisms, two general reactions of $BF_3 \cdot OEt_2$ were suggested (Fig. 1): (1) In the catalytic reaction, $BF_3 \cdot OEt_2$ exhibits the strong Lewis acidity and high catalytic activity without any additive, and only a catalytic amount is required;[10b,d,f] (2) in the second reaction, the stoichiometric amount of $BF_3 \cdot OEt_2$ and the addition of H_2O or a moist atmosphere are often required to form the superacid $BF_3 \cdot H_2O$ in situ[11] and $BF_3 \cdot OEt_2$ exhibits Bronsted acidity.[10e,11c,12] In our former work, the Lewis acidity of $BF_3 \cdot OEt_2$ promoted the synthesis of bis(indolyl)methanes,[10b] and the Bronsted acidity of the superacid $BF_3 \cdot H_2O$ effectively promoted the benzylation of arenes with benzyl ethers or benzyl alcohols.[12f,g] Here, we report the benzylation of (hetero)arene with benzyl halides, which was promoted by a synergistic nonmetal $BF_3 \cdot H_2O/BF_3 \cdot HX$ system.

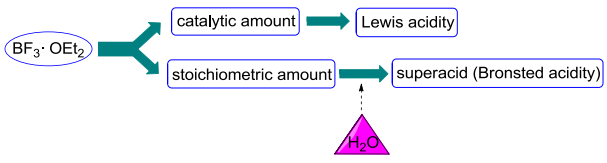

Fig. 1. Bifunction of $BF_3 \cdot OEt_2$.

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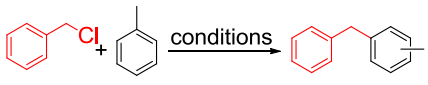
0040-4020/

2. Results and discussion

First, we investigated the effect of different conditions on the model reaction, and the results are shown in Table 1. Without H_2O, 1.5 equiv of $BF_3{\cdot}OEt_2$ exhibits low reactivity, and the desired product was obtained in 23% yield with a regioselectivity of 50:42:8 in N_2 using anhydrous toluene, which indicates that $BF_3{\cdot}OEt_2$ is a low-efficiency promoter for this transformation (entry 1). The addition of 0.2 equiv of H_2O is beneficial for the formation of $BF_3{\cdot}H_2O$ (maximum to 0.2 equiv) to increase the yield to 64% (entry 2). Upon increasing the amount of H_2O to 0.4 equiv (maximum to 0.4 equiv of $BF_3{\cdot}H_2O$), the target product was obtained with excellent yield (92%, *p*-/*o*-/*m*-=52:42:6, entry 3). It is noteworthy that 0.4 equiv of $BF_3{\cdot}OEt_2$ with 0.4 equiv of H_2O only resulted in a yield of 66% (entry 4), which indicates that 0.4 equiv of the superacid $BF_3{\cdot}H_2O$ is inadequate for this transformation, and $BF_3{\cdot}HX$ (X=Cl),[13] which originates from the initially released by-product hydrohalide (HX), efficiently promotes this reaction. However, when the amount of H_2O was increased to 0.6 equiv, the product yield dramatically decreased (34%) (entry 5). Compared to entry 1, the reactions of $BF_3{\cdot}OEt_2$ result in good yield under open-flask conditions with anhydrous toluene or by using undistilled toluene in a protective atmosphere (entries 6 and 7), and the best yield of 92% was obtained with a regioselectivity of 53:41:6 when unpretreated toluene was used under the open-flask conditions (entry 8). Throughout the investigations, traces of residual water in air or toluene are favorable for this reaction. Other boron species, such as H_3BO_3 and HBF_4, were also screened in this reaction. When H_3BO_3 was used as the boron reagent, no benzylation product was detected (entry 9). The tetrahaloboric acid HBF_4 exhibits high reactivity and results in a 90% yield with a regioselectivity of 49:44:7 under N_2 protection using distilled toluene (entry 10).

Table 1
Benzylation of toluene with benzylchloride under different conditions[a]



1a 2a 3aa

Entry	Boron source	Toluene	Atmosphere	H_2O (equiv)	Yield[b] (%) (ratio)[c]
1	$BF_3{\cdot}OEt_2$	Dry	N_2	—	23 (50:42:8)
2	$BF_3{\cdot}OEt_2$	Dry	N_2	0.2	64 (49:43:8)
3	$BF_3{\cdot}OEt_2$	Dry	N_2	0.4	92 (52:42:6)
4[d]	$BF_3{\cdot}OEt_2$	Dry	N_2	0.4	66 (48:44:8)
5	$BF_3{\cdot}OEt_2$	Dry	N_2	0.6	34 (51:43:6)
6	$BF_3{\cdot}OEt_2$	Dry	Air	—	78 (50:44:6)
7	$BF_3{\cdot}OEt_2$	Undistilled	N_2	—	74 (52:42:6)
8	$BF_3{\cdot}OEt_2$	Undistilled	Air	—	92 (53:41:6)
9	H_3BO_3	Undistilled	Air	—	0
10[e]	HBF_4	Dry	N_2	—	90 (49:44:7)

[a] Reaction conditions: (chloromethyl)benzene (1.0 mmol), toluene (2.0 mL), H_2O (specified), boron source (1.5 equiv), 2 h, reflux (120 °C of oil bath).
[b] Isolated yield.
[c] Isomer ratios of *p*-/*o*-/*m*-determined by ^{13}C NMR.
[d] $BF_3{\cdot}OEt_2$ (0.4 equiv) was used.
[e] For optimal conditions, see Supplementary data.

After exploring the reaction conditions, our interest focused on the effect of substituting benzyl halide in the Friedel–Crafts reaction with undistilled arenes (Table 2). Throughout the investigations, the substitutions of benzyl donors with electron-donating and electron-withdrawing groups slightly inhibited the reaction and resulted in low yields, and those with neutral groups provided better reactivities under the optimal reaction conditions. The model reaction resulted in a 92% isolated yield (entry 1). Benzyl bromide reacted with toluene, which exhibited high reactivity, and the desired product was obtained in excellent yield (entry 2). The reaction with *para*-methyl-substituted benzyl bromide **1c** proceeded effectively (entry 3). The substrates that included with electron-withdrawing substituents, such as F and Cl also worked well and produced the corresponding halo-substituted diphenylmethanes, which were readily further functionalized (entries 4 and 5). No benzylation product was detected with the nitro, cyano, and ester groups as substituents on benzyl donors. When (1-bromoethyl)benzene **1f** was used, the benzylation reaction generated the product in 89% yield (entry 6). Other arenes such as **2b** and **2c** were surveyed and reacted with **1g**, and the products **3gb** and **3gc** were obtained in 71% and 32% yields, respectively, both of which can readily be converted into the drug beclobrate (entries 7 and 8).[14] To our delight, our method is also suitable for ferrocene, which yields a mono-substituted product in 21% yield (entry 9). High regioselectivities (>87%) and excellent yields (>90%) were detected when the (halo-methylene)dibenzenes **1h** and **1i** were used (entries 10 and 11). Compared to **1i**, 1-chloro-4-(chloro(phenyl)methyl)-benzene **1j** generated the corresponding product with slightly lower yield and regioselectivity for the *para* regioisomer, which supported the effect of the electron-withdrawing group (entry 11).

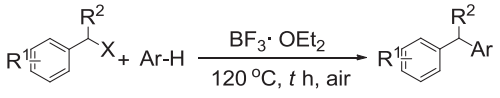
Then, a series of reactions of (hetero)arenes with (bromomethylene)dibenzene were tested, where the reactivities and regioselectivities were investigated (Table 3). Ferrocene was a compatible substrate, which generates the mono-substituted product in 38% yield (entry 1). The desired product **3he** was obtained in 92% yield with a regioselectivity of 92% (entry 2). *m*-Xylene and *p*-xylene produced **3hf** and **3hg** in 83% and 84% yields, respectively (entries 3 and 4). The reaction worked well with **2h** and **2i**, which were effectively transformed into the triphenylmethane derivatives with good yields (entries 5 and 6). Ethylbenzene **2j** was converted into the corresponding product in 70% yield with a regioselectivity greater than 99% (entry 7). The reaction with benzene produced triphenylmethane in lower yield (entry 8). Stoichiometric naphthalene dissolved in DCM served as a highly reactive substrate and gave the corresponding product in 72% yield with a regioselectivity of 66% (entry 9). Interestingly, the resulting α-diphenylmethylated naphthalene **3hl** was readily separated via recrystallization from the mixing benzylation product of **2l**, and the structure of **3hl** was confirmed using X-ray crystallographic analysis (Fig. 2).[15] Heteroarene such as thiophene was also tolerated and generated the product with 80% yield (entry 10).

A plausible synergistic scheme is considered for a synergistic promotion model for **1a** (Scheme 1). In the presence of 0.4 equiv of water, the precursor $BF_3{\cdot}OEt_2$ (0.4 equiv), which is a low-efficiency promoter for benzylation (Table 1, entry 1), is maximally transformed into 0.4 equiv of superacid $BF_3{\cdot}H_2O$,[11] which only results in a yield of 66% (Table 1, entry 4) with the successive production of the by-product HCl via the cleavage of the C–Cl bond of **1a**. Ligand-exchange occurs between $BF_3{\cdot}OEt_2$ and HCl and subsequently generates the by-product complex $BF_3{\cdot}HCl$[13] (HBF_3Cl, which is structurally similar to HBF_4), which acts as an efficient synergistic promoter to generate target product **3aa**.

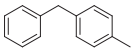
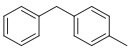
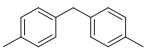
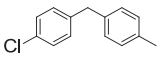
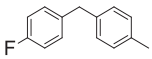
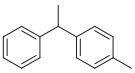
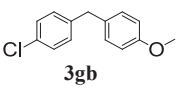
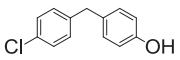
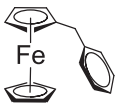
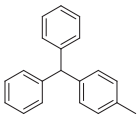
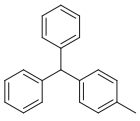
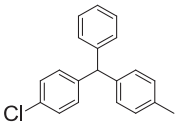
3. Conclusions

In conclusion, a synergistic metal-free system of $BF_3{\cdot}H_2O$/$BF_3{\cdot}HX$-promoted benzylation of (hetero)arenes with benzylhalides has been developed, and various diarylmethanes were furnished with yields of up to 98% and regioselectivities above 99%. Moreover, a plausible synergistic scheme was introduced to interpret the observed reactivities.

Table 2
Investigation of benzyl halides with arenes[a]

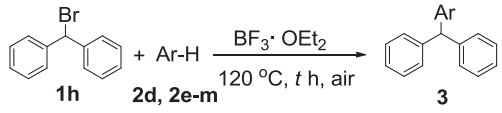


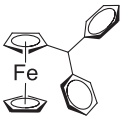
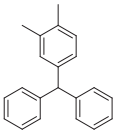
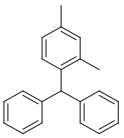
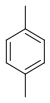
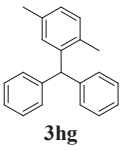
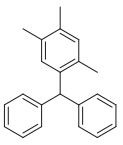
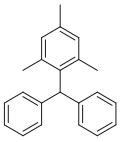
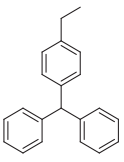
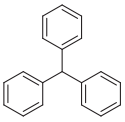
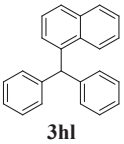
1a-i **2a-d** **3**

Entry	**1** (R^1, R^2, X)	**2**	Major product	*t* (h)	Yield[b] (%) (ratio)[c]
1	**1a** (H, H, Cl)	 **2a**	 **3aa**	2	92 (53:41:6)
2	**1b** (H, H, Br)	 **2a**	 **3ba**	2	98 (51:42:7)
3	**1c** (4-Me, H, Br)	 **2a**	 **3ca**	5	67 (62:32:6) [88 (60:35:5)][d]
4	**1d** (4-Cl, H, Br)	 **2a**	 **3da**	10	71 (51:40:9) [88 (51:41:8)][d]
5	**1e** (4-F, H, Br)	 **2a**	 **3ea**	5	75 (51:42:7) [95 (52:40:8)][d]
6	**1f** (H, Me, Cl)	 **2a**	 **3fa**	6	89 (84:12:4)
7	**1g** (**4**-Cl, H, Br)	 **2b**	 **3gb**	10	71 (>99)
8[e]	**1g** (**4**-Cl, H, Br)	 **2c**	 **3gc**	10	18 (>99)
9[e]	**1b** (H, H, Br)	 **2d**	 **3bd**	6	21 (–)
10	**1h** (H, Ph, Br)	 **2a**	 **3ha**	5	93 (86:14)
11	**1i** (H, Ph, Cl)	 **2a**	 **3ia**	5	90 (92:8)
12	**1j** (4-Cl, Ph, Cl)	 **2a**	 **3ja**	5	85 (85:12:3)

[a] Reaction conditions: benzylation agents (1.0 mmol), toluene (2.0 mL), $BF_3{\cdot}OEt_2$ (1.5 equiv), reflux (120 °C of oil bath) in air.
[b] Isolated yield.
[c] Isomer ratios of *p*-/*o*-/*m*-determined by ^{13}C NMR.
[d] H_2O (0.4 equiv), N_2 atmosphere.
[e] Benzyl halide (1.0 mmol), arene (4.0 mmol), DCM (2.0 mL), reflux (120 °C of oil bath), in air.

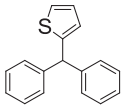
Table 3
Exploration of the scope of arenes with (bromomethylene)dibenzene[a]



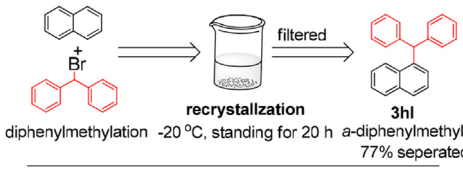
Entry	2	Major product	*t* (h)	Yield[b] (%) (ratio)[c]
1[d]	 **2d**	 **3hd**	10	38 (–)
2	 **2e**	 **3he**	5	92 (4-/3-=92:8)
3	 **2f**	 **3hf**	5	83 (4- >99%)
4	 **2g**	 **3hg**	5	84 (–)
5	 **2h**	 **3hh**	5	98 (5-/6-=66:34)[d]
6	 **2i**	 **3hi**	5	83 (–)
7	 **2j**	 **3hj**	5	70 (*p*- >99%)
8[e]	 **2k**	 **3hk**	10	18 (–)
9[d]	 **2l**	 **3hl**	5	72 (α-/β-=66:34)

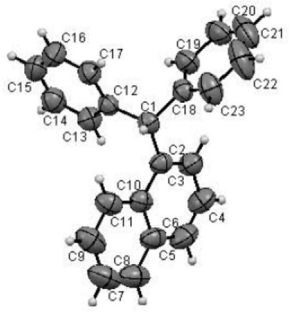
(*continued on next page*)

Table 3 (*continued*)

Entry	2	Major product	*t* (h)	Yield[b] (%) (ratio)[c]
10[e]	 **2m**	 **3hm**	2	80 (2-/3-=93:7)

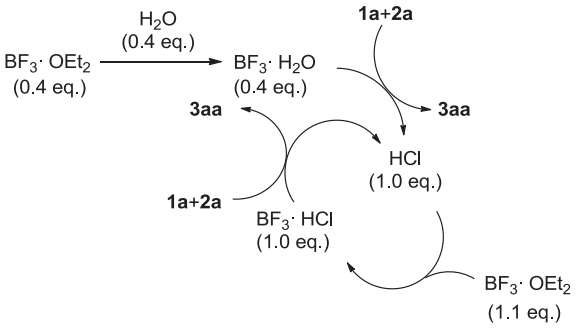
[a] Reaction conditions: (bromomethylene)dibenzene (1.0 mmol), arene (2.0 mL), and $BF_3{\cdot}OEt_2$ (1.5 equiv), 120 °C, in air.
[b] Isolated yield.
[c] Isomer ratios determined by ^{13}C NMR.
[d] (Bromomethylene)dibenzene (1.0 mmol), arene (4.0 mmol), DCM (2.0 mL), reflux (120 °C of oil bath), in air.
[e] Reflux (120 °C of oil bath), in air.





3hl

Fig. 2. Simple operation to separate the α-diphenylmethylation product **3hl** and the X-ray structure.



Scheme 1. Proposed synergistic promotion scheme of benzylation.

4. Experimental section

4.1. General information

The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 500/125 MHz spectrometer at 20–25 °C. ^{11}H NMR chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS, δ=0.00 ppm) as the internal standard. The data of ^1H NMR were reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constant (*J* values) in hertz (Hz), and integration. ^{13}C NMR spectra were reported in parts per million (ppm) using solvent $CDCl_3$ (δ=77.2 ppm)

as an internal standard. All the reagents used were of analytical grade, purchased locally and used without any purification unless otherwise specified. Column chromatography was performed using silica gel, and analytical thin-layer chromatography (TLC), which was used to monitor the reactions was performed on silica gel plates.

Toluene distillation: toluene purchased from chemical supplier was firstly dried over 4 Å molecular sieve for 1 week, and then transferred to distillation apparatus under nitrogen protection. Na slice was added, and after reflux for half a day, dry toluene was collected for use.

4.2. Typical procedure for the benzylation of toluene with benzyl chloride

To a 50 mL round flask filled with toluene (2 mL) were added benzyl chloride **1a** (126.6 mg, 1.0 mmol) and $BF_3 \cdot OEt_2$ (188.8 μL, 1.5 mmol) in the atmosphere. Then, the reaction mixture was refluxed in oil bath of 120 °C and the stirring was turned on. After 2 h, the stirring stopped, reaction mixture was cooled to room temperature, and the toluene was removed to get thick residue under reducing pressure. The resulting residue was purified by flash column chromatography on silica gel column using petroleum ether as eluant to afford a colorless oil product (160.4 mg, 92% yield).

*4.2.1. 1-Benzyl-4-methylbenzene (prepared by benzyl chloride) (**3aa**).* Colorless liquid, 167.4 mg, yield: 92%, *p*-/*o*-/*m*-=53:41:6; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27–7.23 (m, 3.3H), 7.18–7.05 (m, 11.2H), 7.00–6.97 (m, 0.4H), 3.97 (s, 1.4H), 3,93 (s, 2H), 2.30 (s, 3H), 2.23 (s, 2H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 141.6 (*p*), 140.6 (*o*), 139.1 (*o*), 138.2 (*p*), 136.8 (*o*), 135.7 (*p*), 130.5 (*o*), 130.1 (*o*), 129.9 (*m*), 129.3 (*p*), 129.04 (*p*), 129.0 (*p*), 128.9 (*o*), 128.6 (*p*), 128.5 (*o*), 127.0 (*m*), 126.6 (*o*), 126.2 (*p*), 126.1 (*o*), 42.1 (*m*), 41.7 (*p*), 39.6 (*o*), 21.6 (*m*), 21.2 (*p*), 19.8 (*o*). IR: ν 700, 728, 1321, 1452, 1493, 1516, 1597, 2915, 3027, 3063 cm^{-1}.

*4.2.2. 1-Benzyl-4-methylbenzene (prepared by benzyl bromide) (**3ba**).* Colorless liquid, 178.6 mg, yield: 98%, *p*-/*o*-/*m*-=51:42:7; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26–7.23 (m, 3.3H), 7.17–7.05 (m, 11.1H), 7.00–6.97 (m. 0.4H), 3.97 (s, 1.4H), 3,92 (s, 2H), 2.30 (s, 3H), 2.22 (s, 2H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 141.6 (*p*), 140.6 (*o*), 139.1 (*o*), 138.2 (*p*), 136.8 (*o*), 135.7 (*p*), 130.5 (*o*), 130.1 (*o*), 129.9 (*m*), 129.3 (*p*), 129.04 (*p*), 129.0 (*p*), 128.9 (*o*), 128.6 (*p*), 128.5 (*o*), 127.0 (*m*), 126.6 (*o*), 126.2 (*p*), 126.1 (*o*), 42.1 (*m*), 41.7 (*p*), 39.6 (*o*), 21.6 (*m*), 21.2 (*p*), 19.8 (*o*). IR: ν 700, 728, 1321, 1452, 1493, 1516, 1597, 2915, 3027, 3063 cm^{-1}.

*4.2.3. Di-p-tolylmethane (**3ca**).* Colorless liquid, 131.5 mg, yield: 67%, *p*-/*o*-/*m*-=62:32:6; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.16–7.12 (m, 1.7H), 7.09–7.05 (m, 8.9H), 7.00 (d, *J*=5.0 Hz, 1.2H), 3.94 (s, 1H), 3.90 (s, 2H), 2.30 (s, 7.6H), 2.24 (s, 1.5H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 139.4 (*o*), 138.5 (*p*), 137.5 (*o*), 136.8 (*o*), 135.6 (*p*), 135.5 (*o*), 130.4 (*o*), 130.0 (*o*), 129.29 (*p*), 129.25 (*o*), 129.0 (*p*), 128.8 (*o*), 126.5 (*o*), 126.1 (*o*), 41.3 (*p*), 39.2 (*o*), 21.2 (*p*), 19.8 (*o*). IR: ν 793, 800, 1012, 1121, 1323, 1443, 1494, 1507, 2920, 2996, 3022, 3046 cm^{-1}.

*4.2.4. 1-Chloro-4-(4-methylbenzyl)benzene (**3da**).* Colorless liquid, 153.8 mg, yield: 71%, *p*-/*o*-/*m*-=51:40:9; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24–7.22 (m, 3.8H), 7.19–7.13 (m, 2.3H), 7.10–7.09 (m, 4H), 7.07–7.01 (m, 3.5H), 6.97–6.95 (m, 0.3H), 3.94 (s, 1.5H), 3.90 (s, 2H), 2.31 (s, 3.1H), 2.21 (s, 2.1H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 140.6 (*m*), 140.1 (*p*), 139.9 (*m*), 139.0 (*o*), 138.5 (*o*), 138.3 (*m*), 137.7 (*p*), 136.7 (*o*), 136.0 (*p*), 131.95 (*p*), 131.86 (*o*), 130.6 (*o*), 130.4 (*m*), 130.4 (*p*), 130.2 (*o*), 130.0 (*o*), 129.8 (*m*), 129.4 (*p*), 128.9 (*o*), 128.69 (*p*), 128.66 (*p*), 127.2 (*m*), 126.9 (*o*), 126.3 (*o*), 126.0 (*m*), 41.4 (*m*), 41.0 (*p*), 39.0 (*o*), 21.6 (*m*), 21.2 (*o*), 19.8 (*p*). IR: ν 742, 795, 1014, 1087, 1334, 1406, 1451, 1493, 1521, 2921, 2971, 3022, 3044 cm^{-1}.

*4.2.5. 1-Fluoro-4-(4-methylbenzyl)benzene (**3ea**).* Colorless liquid, 150.2 mg, yield: 75%, *p*-/*o*-/*m*-=51:42:7; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.15–7.04 (m, 13.9H), 6.96–6.93 (m, 5H), 3.94 (s, 2H), 3.89 (s, 2.9H), 2.31 (s, 4.4H), 2.22 (s, 3H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 162.5 (d, *J*=8.8 Hz) (*p*), 160.5 (d, *J*=8.6 Hz) (*o*), 138.9 (*o*), 138.1 (*p*), 137.3 (*p*), 136.7 (*o*), 136.2 (*o*), 135.9 (*p*), 130.6 (*o*), 130.4 (d, *J*=7.5 Hz) (*p*), 130.2 (d, *J*=7.6 Hz) (*o*), 130.0 (*o*), 129.8 (*m*), 129.4 (*p*), 128.9 (*p*), 128.6 (*m*), 127.1 (*m*), 126.8 (*o*), 126.2 (*o*), 126.0 (*m*), 115.4 (*o*), 115.2 (*p*), 41.2 (*m*), 40.8 (*p*), 39.8 (*o*), 21.6 (*m*), 21.2 (*p*), 19.8 (*o*). IR: ν 739, 812, 843, 1157, 1216, 1434, 1462, 1510, 1602, 2859, 2926, 3016, 3043 cm^{-1}.

*4.2.6. 1-Methyl-4-(1-phenylethyl)benzene (**3fa**).* Colorless liquid, 174.2 mg, yield: 89%, *p*-/*o*-/*m*-=84:12:4, ^{1}H NMR ($CDCl_3$, 500 MH) δ 7.27–7.25 (m, 2.6H), 7.22–7.21 (m, 2.4H), 7.18–7.16 (m, 1.6H), 7.09 (m, 4.2H), 4.31 (m, 0.1H), 4.12–4.10 (m, 1H), 2.30 (s, 3.1H), 2.23 (s, 0.5H), 1.62 (m, 3.5H), 1.53 (m, 0.6H). ^{13}C NMR (125 MHz, $CDCl_3$, major product) δ 146.7, 143.5, 135.5, 129.1, 128.3, 127.7, 127.6, 126.0, 44.4, 22.0, 21.0. IR: ν 697, 756, 823, 1019, 1021, 1451, 1494, 1513, 1597, 2875, 2923, 2965, 3024, 3058 cm^{-1}.

*4.2.7. 1-Chloro-4-(4-methoxybenzyl)benzene (**3gb**).* White solid, 164.8 mg, yield: 71%, *p*- >99%; ^{1}H NMR ($CDCl_3$, 500 MH) δ 7.23 (d, *J*=8.0 Hz, 2H), 7.09 (d, *J*=8.5 Hz, 2H), 7.07 (d, *J*=8.5 Hz, 2H), 6.83 (d, *J*=8.5 Hz, 2H), 3.88 (s, 2H), 3.78 (s, 3H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 158.2, 140.1, 132.7, 131.8, 130.2, 129.9, 128.6, 114.0, 55.3, 40.4. IR: ν 795, 854, 1014, 1042, 1092, 1173, 1244, 1454, 1488, 1513, 1611, 2830, 2844, 2954, 3030, 3002 cm^{-1}.

*4.2.8. 2-(p-Tolylmethylene)dibenzene (prepared by (bromomethylene)dibenzene) (**3ha**).* Light yellow liquid, 240.2 mg, yield: 93%, *p*-/*o*-=86:14. ^{1}H NMR ($CDCl_3$, 500 MHz, major product) δ 7.26 (t, *J*=7.0 Hz, 4H), 7.19 (t, *J*=7.0 Hz, 2H), 7.11 (d, *J*=7.5 Hz, 4H), 7.08 (d, *J*=8.0 Hz, 2H), 7.01 (d, *J*=8.0 Hz, 2H), 5.51 (s, 1H), 2.31 (s, 3H). ^{13}C NMR: ($CDCl_3$, 125 MHz, major product) δ 144.3, 141.1, 136.0, 129.6, 129.5, 129.2, 128.4, 126.4, 56.7, 21.2. IR: ν 605, 697, 756, 1437, 1496, 1504, 1594, 3024, 3058 cm^{-1}.

*4.2.9. 2-(p-Tolylmethylene)dibenzene (prepared by (chloromethylene)dibenzene) (**3ia**).* Light yellow liquid, 232.5 mg, yield: 90%, *p*-/*o*-=92:8; ^{1}H NMR ($CDCl_3$, 500 MHz, major product) δ 7.26 (t, *J*=7.0 Hz, 4H), 7.19 (t, *J*=7.0 Hz, 2H), 7.11 (d, *J*=7.5 Hz, 4H), 7.08 (d, *J*=8.0 Hz, 2H), 7.01 (d, *J*=8.0 Hz, 2H), 5.51 (s, 1H), 2.31 (s, 3H). ^{13}C NMR: ($CDCl_3$, 125 MHz, major product) δ 144.3, 141.1, 136.0, 129.6, 129.5, 129.2, 128.4, 126.4, 56.7, 21.2. IR: ν 605, 697, 756, 1437, 1496, 1504, 1594, 3024, 3058 cm^{-1}.

*4.2.10. 1-Chloro-4-(phenyl(p-tolyl)methyl)benzene (**3ja**).* Colorless liquid, 248.9 mg, yield: 85%, *p*-/*o*-/*m*-=85:12:3; ^{1}H NMR ($CDCl_3$, 500 MHz, major product) δ 7.28–7.20 (m, 5H), 7.15–7.14 (m, 0.5H), 7.08 (s, 4H), 7.03 (d, *J*=7.5 Hz, 2H), 6.97 (d, *J*=7.0 Hz, 2H), 5.47 (s, 1H), 2.31 (s, 3H). ^{13}C NMR: ($CDCl_3$, 125 MHz, major product) δ 143.8, 142.9, 140.6, 136.3, 132.2, 131.1, 130.9, 129.5, 129.4, 129.3, 128.6, 126.6, 56.0, 21.2. IR (KBr): ν 700, 748, 798, 809, 846, 1014, 1090, 1407, 1449, 1491, 1510, 1597, 2873, 2921, 3027, 3061,3088 cm^{-1}.

*4.2.11. ((3,4-Dimethylphenyl)methylene)dibenzene (**3he**).* Colorless liquid, 250.6 mg, yield: 92%, 4-/3-=92:8; ^{1}H NMR ($CDCl_3$, 500 MHz, major product) δ 7.27 (t, *J*=6.0 Hz, 4H), 7.20 (t, *J*=6.5 Hz, 2H), 7.12 (d, *J*=7.0 Hz, 4H), 7.04 (d, *J*=6.0 Hz, 1H), 6.91 (s, 1H), 6.82 (d, *J*=7.0 Hz, 1H), 5.48 (s, 1H), 2.23 (s, 3H), 2.19 (s, 3H). ^{13}C NMR: ($CDCl_3$, 125 MHz, major product) δ 144.4, 141.5, 136.6, 134.6, 130.1, 129.7, 129.6, 128.4, 127.0, 126.3, 56.7, 20.0, 19.5. IR: ν 697, 734, 750, 1443, 1494, 1597, 2875, 2915, 2965, 3007, 3055 cm^{-1}.

*4.2.12. ((2,4-Dimethylphenyl)methylene)dibenzene (**3hf**).* Colorless liquid, 226.1 mg, yield: 83%, 4- >99%; ^{1}H NMR ($CDCl_3$, 500 MHz, major product) δ 7.26 (t, *J*=6.5 Hz, 4H), 7.20 (t, *J*=6.5 Hz, 2H), 7.05 (d, *J*=6.5 Hz, 4H), 6.99 (s, 1H), 6.90 (d, *J*=7.0 Hz, 1H), 6.69 (d, *J*=7.0 Hz,

1H), 5.63 (s, 1H), 2.29 (s, 3H), 2.17 (s, 3H). ^{13}C NMR: ($CDCl_3$, 125 MHz, major product) δ 143.7, 139.5, 136.5, 135.9, 131.4, 129.7, 129.5, 128.4, 126.5, 126.3, 53.3, 21.0, 19.9. IR: ν 703, 731, 756, 1454, 1496, 1600, 2921, 3021, 3058, 3080 cm^{-1}.

*4.2.13. ((2,5-Dimethylphenyl)methylene)dibenzene (**3hg**).* Colorless liquid, 230.3 mg, yield: 84%; ^{1}H NMR ($CDCl_3$, 500 MH) δ 7.27–7.20 (m, 6H), 7.06–7.05 (m, 5H), 6.95 (d, J=7.0 Hz, 1H), 6.62 (s, 1H), 5.64 (s, 1H), 2.20 (s, 3H), 2.16 (s, 3H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 143.7, 142.2, 135.2, 133.6, 130.5, 130.3, 129.8, 128.4, 127.2, 126.3, 53.6, 21.4, 19.7. IR: ν 610, 697, 745, 854, 1373, 1446, 1491, 1597, 2853, 2915, 3055, 3078 cm^{-1}.

*4.2.14. ((2,4,5-Trimethylphenyl)methylene)dibenzene (**3hh**).* White solid, 280.1 mg, yield: 98%, 5-/6-=66:34; ^{1}H NMR ($CDCl_3$, 500 MHz, major product) δ 7.27 (t, J=7.5 Hz, 4H), 7.20 (t, J=6.5 Hz, 2H), 7.06 (d, J=7.0 Hz, 4H), 6.94 (s, 1H), 6.56 (s, 1H), 5.61 (s, 1H), 2.20 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H). ^{13}C NMR: ($CDCl_3$, 125 MHz, major product) δ 143.9, 139.8, 134.5, 133.8, 133.7, 132.0, 130.9, 129.8, 128.4, 126.3, 53.4, 19.7, 19.5, 19.4. IR (KBr): ν 702, 728, 748, 1445, 1496, 1602, 2862,3005, 3022, 3064 cm^{-1}.

*4.2.15. (Mesitylmethylene)dibenzene (**3hi**).* White solid, 237.2 mg, yield: 83%; ^{1}H NMR ($CDCl_3$, 500 MH) δ 7.26 (t, J=6.5 Hz, 4H), 7.19 (t, J=6.0 Hz, 2H), 7.09 (d, J=7.0 Hz, 4H), 6.85 (s, 2H), 5.99 (s, 1H), 2.28 (s, 3H), 1.99 (s, 6H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 142.7, 137.7, 137.2, 136.2, 130.3, 129.5, 128.3, 126.1, 51.2, 22.2, 21.0. IR (KBr): ν 619, 714, 739, 812, 1446, 1491, 1600, 2859, 2915, 3019, 3043 cm^{-1}.

*4.2.16. ((4-Ethylphenyl)methylene)dibenzene (**3hj**).* White solid, 190.7 mg, yield: 70%, *p*- >99%; ^{1}H NMR ($CDCl_3$, 500 MHz, major product) δ 7.27 (t, J=7.0 Hz, 4H), 7.20 (t, J=7.0 Hz, 2H), 7.12–7.11 (m, 6H), 7.02 (d, J=7.0 Hz, 2H), 5.52 (s, 1H), 2.62 (quart, J=7.5 Hz, 2H), 1.22 (t, J=7.5 Hz, 3H). ^{13}C NMR: ($CDCl_3$, 125 MHz, major product) δ 144.3, 142.3, 141.3, 129.6, 129.5, 128.4, 127.9, 126.4, 56.7, 28.6, 15.7. IR (KBr): ν 605, 694, 751, 1412, 1454, 1494, 1510, 1597, 2867, 2926, 2963, 3022, 3061 cm^{-1}.

*4.2.17. Triphenylmethane (**3hk**).* White solid, 44.1 mg, yield: 18%; ^{1}H NMR ($CDCl_3$, 500 MH) δ 7.27 (t, J=7.5 Hz, 6H), 7.20 (t, J=7.5 Hz, 3H), 7.11 (d, J=7.5 Hz, 6H), 5.55 (s, 1H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 144.1, 129.6, 128.5, 126.5, 57.0. IR (KBr): ν 605, 700, 736, 759, 1437, 1448, 1496, 1600, 2851, 2929, 3016, 3052, 3077 cm^{-1}.

*4.2.18. 2-Benzhydrylthiophene (**3hm**).* White solid, 200.1 mg, yield: 80%, 2-/3-=93:7; ^{1}H NMR ($CDCl_3$, 500 MHz, major product) δ 7.30 (t, J=6.5 Hz, 4H), 7.24–7.21 (m, 7H), 6.93 (s, 1H), 6.69 (s, 1H), 5.68 (s, 1H). ^{13}C NMR: ($CDCl_3$, 125 MHz, major product) δ 148.1, 144.0, 129.0, 128.6, 126.9, 126.7, 126.5, 52.3. IR (KBr): ν 622, 700, 759, 1031, 1076, 1227, 1431, 1446, 1494, 1603, 3022, 3058, 3100 cm^{-1}.

4.3. Typical procedure for the benzylation of (hetero)arenes using DCM as solvent

To a 50 mL round flask, (bromomethylene)dibenzene (247.1 mg, 1.0 mmol) and naphthalene (512.8 mg, 4.0 mmol) were dissolved in 2 mL of DCM. Then, $BF_3{\cdot}OEt_2$ (188.8 μL, 1.5 mmol) was added. The resulting reaction mixture was transferred into an oil bath of 120 °C and refluxed for 5 h in the atmosphere. After completion of the reaction, reaction mixture was cooled to room temperature and the solvent was removed by vacuum rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel column using petroleum ether as eluant to afford **3hl** as a white solid product (212.1 mg, 72% yield).

*4.3.1. 4-(4-Chlorobenzyl)phenol (**3gc**).* Light yellow solid, 70.8 mg, yield: 32%, *p*- >99%; ^{1}H NMR ($CDCl_3$, 500 MH) δ 7.24 (d, J=7.0 Hz, 2H), 7.09 (d, J=8.0 Hz, 2H), 7.02 (d, J=8.0 Hz, 2H), 6.75 (d, J=7.5 Hz, 2H), 4.71 (s, 1H), 3.87 (s, 2H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 154.2, 140.2, 133.0, 132.0, 130.3, 130.2, 128.7, 115.6, 40.5. IR (KBr): ν 548, 809, 1011, 1087, 1104, 1224, 1435, 1446, 1485, 1507, 1597, 2830, 2811, 2828, 3041, 3057, 3422 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{11}ClO$ $[M+H]^+$ 218.0498, found 218.0418.

*4.3.2. Benzylferrocene (**3bd**).* Orange solid, 58.0 mg, yield: 21%, ^{1}H NMR ($CDCl_3$, 500 MH) δ 7.28–7.25 (m, 2H), 7.18–7.17 (m, 3H), 4.12–4.12 (m, 5H), 4.09–4.08 (m, 4H), 3.69 (s, 2H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 141.8, 128.6, 128.4, 126.1, 88.1, 68.8, 67.7, 53.6, 36.22. IR (KBr): ν 490, 720, 801, 821, 1034, 1025, 1106, 1429, 1443, 1491, 2887, 2926, 3021, 3072, 3439 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{16}Fe$ $[M+H]^+$ 276.0601, found 276.0602.

*4.3.3. Diphenylmethylferrocene (**3hd**).* Orange solid, 133.8 mg, yield: 38%; ^{1}H NMR ($CDCl_3$, 500 MH) δ 7.27–7.24 (m, 4H), 7.18–7.16 (m, 6H), 5.14 (s, 1H), 4.15–4.14 (m, 4H), 3.99 (s, 5H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 154.2, 128.9, 128.2, 126.3, 91.8, 69.0, 68.9, 67.8, 52.0. IR (KBr): ν 515, 630, 703, 725, 809, 826, 1000, 1025, 1106, 1449, 1491, 1600, 2990, 3016, 3103, 3442 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{20}Fe$ $[M+H]^+$ 352.0914, found 352.0903.

*4.3.4. 1-Benzhydrylnaphthalene (**3hl′**).* White solid, 212.0 mg, yield: 72%, α-/β-=66:34; ^{1}H NMR ($CDCl_3$, 500 MH) δ8.00 (d, J=8.0 Hz, 1H), 7.87 (d, J=8.0 Hz, 1H), 7.82–7.80 (m, 0.4H), 7.78–7.75 (m, 1.3H), 7.73–7.71 (m, 0.5H), 7.50–7.35 (m, 4.5H), 7.33–7.26 (m, 6.4H), 7.25–7.22 (m, 2.8H), 7.18 (d, J=7.0 Hz 1.7H), 7.14 (d, J=7.5 Hz, 4H), 6.97 (d, J=7.5 Hz, 1H), 6.30 (s, 1H), 6.23 (s, 1H), 5.73 (s, 0.4H). ^{13}C NMR: ($CDCl_3$, 125 MHz) δ 143.9 (α-), 141.7 (β-), 140.1 (α-), 134.1 (α-), 133.6 (β-), 132.3 (β-), 132.1 (α-), 129.9 (α-), 129.8 (β-), 128.9 (β-), 128.6 (α-), 128.3 (β-), 128.1 (α-), 128.0 (β-), 127.8 (α-), 127.7 (β-), 127.5 (α-), 126.6 (α-), 126.3 (α-), 126.2 (β-), 125.8 (β-), 125.6 (α-), 125.4 (α-), 124.5 (α-), 57.1 (β-), 53.3 (α-). IR (KBr): ν 613, 720, 778, 791, 811, 1390, 1446, 1491, 1594, 3027, 3058, 3083 cm^{-1}.

4.4. Typical procedure for control experiment under nitrogen

To a 50 mL three-necked bottle filled with distilled toluene (2 mL), benzyl chloride **1a** (126.6 mg, 1.0 mmol), $BF_3{\cdot}OEt_2$ (188.8 μL, 1.5 mmol), and water (7.2 μL, 0.4 mmol) were added under nitrogen atmosphere. Reaction mixture was refluxed in oil bath of 120 °C for 2 h. After completion of the reaction, reaction mixture was cooled to room temperature and toluene was removed by vacuum rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel column using petroleum ether as eluant to afford a colorless oil product (163.1 mg, 92% yield).

4.5. Procedure for separation of α-diphenylmethylation product

To a 50 mL round flask, the mixing product **3hl′** (50 mg) was dissolved in 0.5 mL of dichloromethane and petroleum ether (2.5 mL) was dropped slowly. Then, the mixture was transferred into −20 °C. After standing for 20 h, white crystals appeared, the mother solvent was poured out to obtain α-diphenylmethylated naphthalene **3hl** (38.4 mg, 77% yield).

*4.5.1. 1-Benzhydrylnaphthalene (after recrystallization) (**3hl**).* White solid, 25.4 mg, yield 77%; ^{1}H NMR ($CDCl_3$, 500 MH) δ 8.00 (d, J=7.5 Hz, 1H), 7.86 (d, J=8.0 Hz, 1H), 7.76 (d, J=8.0 Hz, 1H), 7.46–7.35 (m, 3H), 7.29 (t, J=7.5 Hz, 4H), 7.24 (t, J=6.5 Hz, 2H), 7.13 (d, J=7.5 Hz,

4H), 6.95 (d, J=7.5 Hz, 1H), 6.23 (s, 1H). IR (KBr): ν 614, 717, 784, 813, 1390, 1446, 1491, 1594, 3027, 3083 cm^{-1}.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.01.037.

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14. The procedure for synthesis of beclobrate, see Supplementary data.
15. CCDC 961203 (**3hl**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.