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Benzylation of Arenes with Benzyl Halides under Promoter-Free and Additive-Free Condition

Xinqiang Cheng,[a] Jiankai Shan,[b] Xinzhe Tian,[a] Yun-Lai Ren*[a] and Yanyan Zhu*[b]

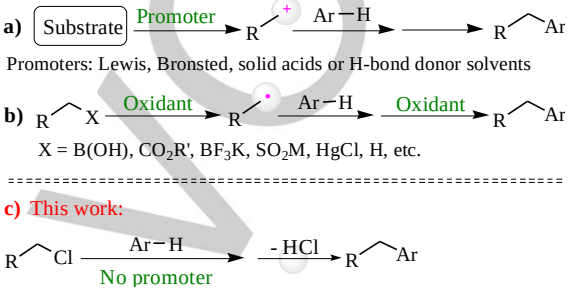
Abstract: It was found that benzyl chlorides and bromides could directly react with electron-rich arenes, which provided an example of promoter-free and additive-free benzylation of arenes. A variety of benzyl chlorides and bromides were reacted with benzene rings to give the targeted products in low to high yields. The present condition tolerated the vinyl group of the substrates. Preliminary mechanistic investigation suggests that the present reactions possibly proceed via an autocatalytic mechanism pathway.

Introduction

Alkylation of arenes plays an important role in modern organic synthesis[1-3] because it can serve as a powerful tool for the formation of C(sp^2)–C(sp^3) bonds.[4a-d] As a result, a great deal of attention has been paid to this class of reactions, and several strategies have been developed. One is Friedel–Crafts reactions based on the formation of a strong electrophile with a pronounced C^+ character (Scheme 1a).[1-3] In general, Friedel–Crafts alkylation reactions with alkyl halides, olefins and so on require stoichiometric quantity of Lewis,[5a] Brønsted[5b,c] or solid acids.[6] In addition, some strong hydrogen bonding donor solvents such as hexafluoro-isopropanol, trifluoroacetic acid and 2,2,2-trifluoroethanol have been recently used to activate the C-X bonds[7,8] and other Friedel–Crafts type reactions.[9]

Another strategy for alkylation of arenes relies on the transition metal-catalyzed activation of the C-H bonds on the aromatic rings.[10] For instance, arenes can be benzylated via Ru- or Rh-catalyzed C−H activation with the assistance of several proximal directing groups.[11]

Recently, radical oxidative couplings are emerging as an interesting strategy for alkylation of arenes where the alkylation reagents are required to be oxidized into the alkyl radicals (Scheme 1b).[12,2c] For example, the radical alkylation of a variety of arenes with alkylboronic acids[13] has been reported. At the same time, alkanes,[12a] trifluoroborates,[14] sulfinates,[15] alkylmercury halides,[16] carboxylic acid[12b,17] and their derivatives have been used to form the alkyl radical coupling partners for the alkylation. In addition, Trahanovsky and co-workers have reported a base-promoted radical alkylation of arenes with alkyl halides as the alkylating reagent,[18] in which $(Bu_3Sn)_2$ was used as the radical initiator for the alkyl radical, and the substrates were limited to several special arenes.



Scheme 1. Alkylation of arenes.

Clearly, the above-mentioned processes rely on the presence of various promoters or additive.[12-18] By comparison, a promoter- and additive-free process is a more attractive goal from environmental and economic perspectives.[19a] Thus we have attempted to actualize this goal, and found that benzyl chlorides and bromides could directly react with electron-rich arenes, which provided an example of promoter-free and additive-free alkylation of arenes (Scheme 1c).

Results and Discussion

Our initial study aimed at the reactivity of benzyl chloride toward mesitylene. When the reaction mixture was stirred at 140 °C for 20 h, the targeted product was obtained in a GC yield as high as 86% (Table 1, entry 1), along with a small amount of 3,5-dimethylbenzyl chloride by-product. In addition, the methyl in mesitylene underwent the oxidation to give a small amount of 3,5-dimethylbenzaldehyde as the by-product, which was possibly due to the presence of oxygen in the reaction system.[19b-d] Indeed, a larger amount of oxidation by-product was observed when the air in the reaction tube was replaced by oxygen gas (Table 1, entries 2-6). Thus we performed the reaction under argon atmosphere to inhibit the formation of the by-product (Table 1, entry 7). As we expected, hardly any products from the oxidation of the methyl group were observed under the oxygen-free condition, which promoted us to carry out all the following reactions under argon atmosphere.

Further studies were undertaken to obtain higher yield and more generally practical reaction conditions, and the results were shown in Table 1. It was found that the present reaction was highly dependent on the reaction temperature (Table 1, entries 7-12). 140 °C allowed the reaction to proceed smoothly with a complete conversion, and the desired product was obtained in 91% yield (Table 1, entry 7), while the reaction at 60 °C gave the targeted product in only 2% yield (Table 1, entry 11).

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Sometimes, the decrease of the temperature to 120, 100, or 80 °C allowed the reaction to proceed with good results (Table 1, entries 8-10), but the reproducibility of these experimental results was not high according to our parallel experiments, so 140 °C was ascertained as the optimum temperature. Next, the effect of the solvent on the reaction was investigated. The results revealed that the use of the reactant (mesitylene) as the solvent was required (Table 1, entry 7 vs entries 13-15), and the addition of any other solvents resulted in poor results related to the conversion and the yield.

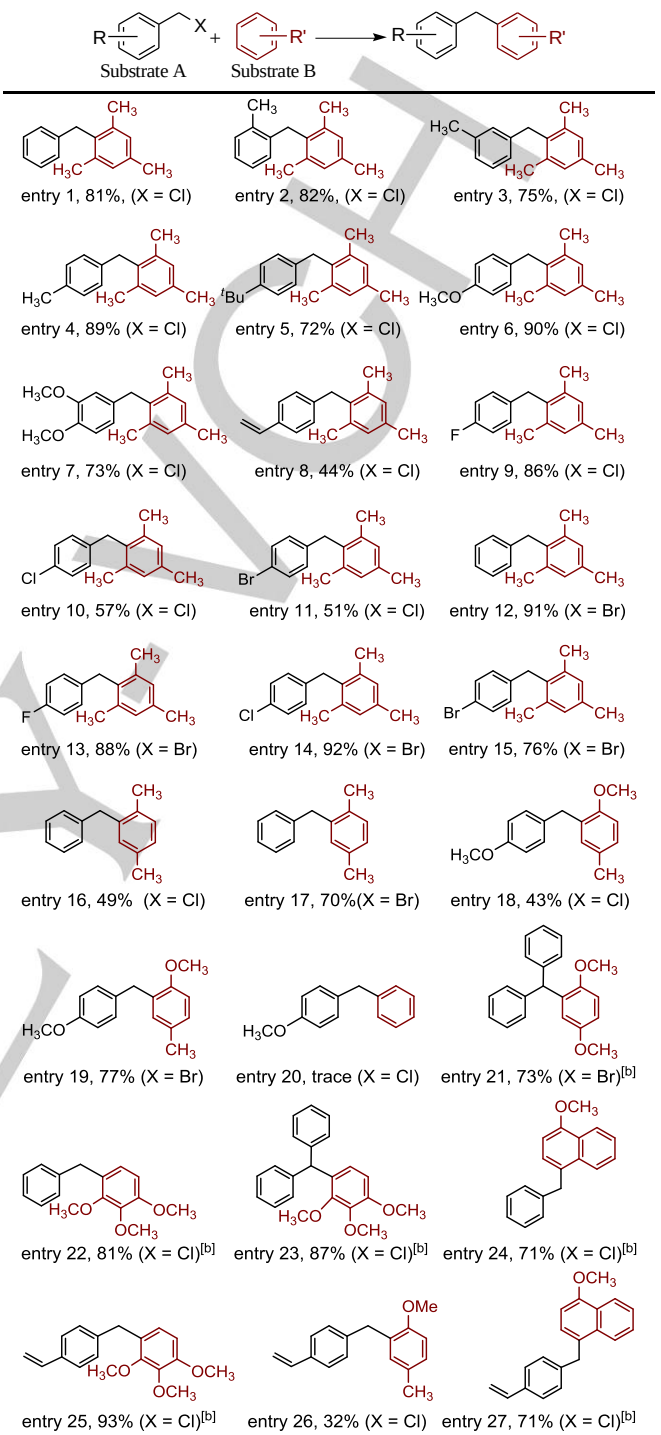
Table 1. Benzylation of mesitylene under various conditions.[a]

Entry	Solvent	Ambience[b]	T [°C]	Yield [%][c]
1	mesitylene	air	140	86
2	mesitylene	O_2	140	79
3	mesitylene	O_2[d]	140	67
4	mesitylene	O_2[d]	140	63
5	mesitylene	O_2[d]	140	65
6	mesitylene	O_2[d]	140	58
7	mesitylene	Ar	140	91
8	mesitylene	Ar	120	87
9	mesitylene	Ar	100	80
10	mesitylene	Ar	80	75
11	mesitylene	Ar	60	2
12	mesitylene	Ar	40	trace
13	cyclohexane/ mesitylene[e]	Ar	140	5
14	CH_3CN/ mesitylene[e]	Ar	140	6
15	CCl_4/ mesitylene[e]	Ar	140	19

[a] Reaction conditions: 0.5 mmol benzyl chloride, 2 mL solvent, 20 h. [b] 1 atm. [c] Determined by GC. [d] The pressure of O_2 was respectively 0.5 MPa (entry 3), 1 MPa (entry 4), 2 MPa (entry 5) and 4 MPa (entry 6). [e] The volume ratio of the two was 1:1.

With the optimal conditions in hand, a variety of representative benzyl halides were used to explore the scope and limitation of the new methodology. As shown in Table 2, the present reaction was compatible with various groups, e.g. alkyl, alkoxy, fluoro, bromo, and chloro group (Table 2, entries 2-11). Even the highly reactive vinyl substituent was also tolerated (Table 2, entries 8 and 25-27). Generally, all the electron-donating group-substituted benzyl chlorides were good substrates, and the reactions gave the targeted products in 72-90% isolated yields (Table 2, entries 2-7). For example, a complete coversion and 90% isolated yield were observed in the case of 4-methoxybenzyl chloride (Table 2, entry 6). Surprisingly, among the test benzyl chlorides with the electron-withdrawing groups, only 4-fluorobenzyl chloride provided a satisfying result, and the targeted product was obtained in an isolated yield as high as 86% (Table 2, entry 9), while 4-chlorobenzyl chloride and 4-bromobenzyl chloride underwent the present transformation in 57% and 51% yields (Table 2, entries 10 and 11), respectively. By comparison, the chloro or bromo group-substituted benzyl bromides[20] was found to give higher yields (Table 2, entry 13-15).

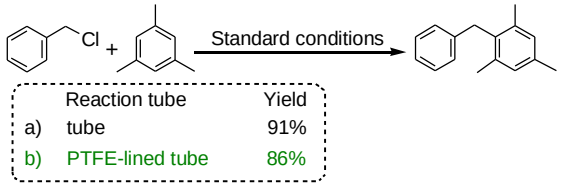
Table 2. Benzylation of mesitylene with benzyl chlorides or bromides.[a]



[a] Reaction condition A: 0.5 mmol benzyl halide, 2mL Substrate B, 20 h, 140 °C, all the yields were the isolated yields. [b] Reaction condition B: 0.5 mmol benzyl halide, 2 mmol Substrate B, 1 mL cyclohexane, 20 h, 140 °C, all the yields were the isolated yields.

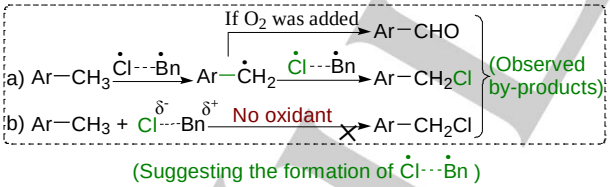
Subsequently, we evaluated the reactivity of various benzene rings under the optimized conditions, and the results were listed in Table 2 (entries 16-27). Electron-rich benzene rings in mesitylene, *para*-xylene and 4-methylanisole were reactive toward benzyl chlorides and bromides (Table 2, entries 16-19 and 21-27), but no targeted product was observed in the case of electron-deficient or electron-neutral benzene rings of

chlorobenzene and benzene (Table 2, entry 20). These results indicated that the presence of the strong electron-donating substituent group had a positive effect on the reactivity of benzene rings. When 4-methylanisole was used as the substrate, the benzylation reaction selectively occurred at the *ortho*-position with regard to the methoxy group (Table 2, entries 18 and 19), although this position had a larger steric hindrance than the position ortho to the methyl group.[21] In addition, we tried the benzylation of 1,4-dimethoxybenzene with benzyl chloride under the standard condition (Condition A in Table 2), and the targeted product was obtained in a high GC yield (83%), but it was difficult to isolate the product due to higher boiling and melting point of this substrate. Thus we had to reduce the used amount of the substrate by an addition of the solvent like cyclohexane (Condition B in Table 2). As shown as Table 2 (entries 21-25 and 27), such a condition allowed a series of benzene rings in 1,2,3-trimethoxybenzene, 1,4-dimethoxybenzene and 1-methoxynaphthalene to be smoothly benzylated to give the products in 71-93% yields.



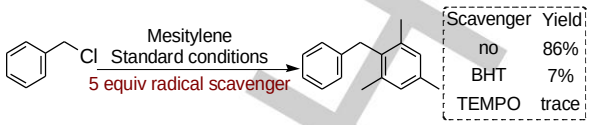
Scheme 2. Effect of the reaction vessel on the reaction (for the standard conditions, see Condition A in Table 2).

It was possible that the present transformation was being induced by Lewis acid metal impurities in the reaction system.[22] To rule out this possibility, we analysed the reaction system using inductively coupled plasma mass spectroscopy (ICP-MS), but no detectable amount of metal impurities was observed. Maybe the inner wall of the reaction tube played the role of the promoter for the reaction, but this possibility was also ruled out based on our experimental results: a change of the reaction tube from glassware to a new polytetrafluoroethylene (PTFE)-lined tube had no significant effect on the reaction (Scheme 2a vs 2b). By all appearance, all the experimental results above confirmed the reliability of our conclusion that the present reaction was promoter-free.



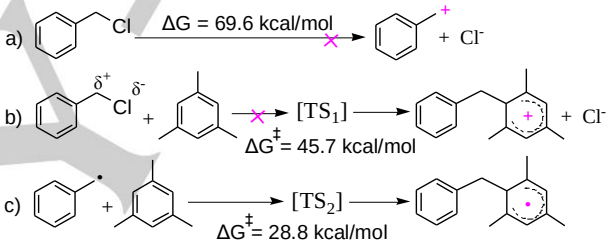
Scheme 3. Possible mechanism pathways for the chlorination.

Afterwards, our attention was turned to the investigation on the reaction mechanism. In any case, it was observed that methyl group of mesitylene underwent the chlorination[23,24] to give 3,5-dimethyl-benzyl chloride by-product (Scheme 3). Obviously, this by-product should be formed via one of the two kinds of pathways based on previous literatures:[23,24] One involved the chlorine radical (Scheme 3a),[23] and the other required the presence of strong oxidants (Scheme 3b).[24] Actually, the latter mechanistic pathway should be excluded because there was no any strong oxidant in our reaction system. Thus it was reasonable that the chlorine radical was formed in our reaction system based on the observed chlorination by-product (Scheme 3a). In addition, the addition of the radical scavengers such as 2,6-di^{t}butyl-4-methylphenol (BHT) and TEMPO[25] resulted in a dramatic decrease in the yield of the targeted product (Scheme 4), which revealed that the preferential pathway involved the radicals.



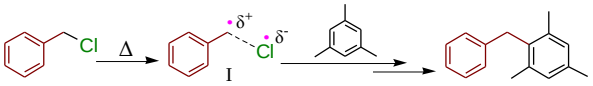
Scheme 4. Effect of the radical scavengers on the reaction (for the standard conditions, see Condition A in Table 2).

Indeed, the following results from our DFT calculation suggest that the ion-type mechanism should be excluded. (1) Based on our calculation, the present reaction condition does not allow more than 33.5 kcal/mol energy barrier to be overcome, while the heterolytic cleavage energy of the C-Cl bond in benzyl chloride is as high as 69.6 kcal/mol (Scheme 5a), revealing that the heterolytic cleavage does not occur under our condition. (2) The direct reaction between benzyl chloride and the benzene ring requires a transition state (TS_1) with as high as 45.7 kcal/mol energy barrier (Scheme 5b), which suggests that this ion-type mechanism pathway is also unreasonable.



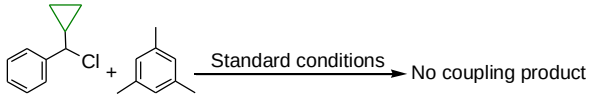
Scheme 5. Results from our DFT calculation (for TS_1 and TS_1, see Scheme S4 and S5 in the supporting information).

It is noteworthy that the alkyl radicals are a kind of weakly nucleophilic radicals (Scheme 5c),[13] thus the radical-type mechanism[26] is not consistent with our experimental results that electron-rich arenes were preferentially benzylated over electron-deficient arenes. However, this can be rationalized by assuming that the homolytic cleavage of the C-Cl bond is incomplete in the present reaction, and the resulting benzyl radical (see Transition state I in Scheme 6) has a cationic and electrophilic characteristic due to an electron-withdrawing inductive effect of the Cl atom.



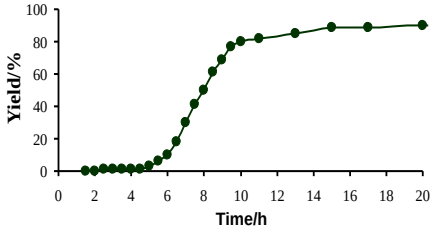
Scheme 6. The benzylation via the incomplete homolytic cleavage of the C-Cl bond.

Subsequently, a radical clock experiment with the benzyl chloride bearing a cyclopropyl group was performed to confirm the existence of the benzylic radical[26d] (Scheme 7). Strangely, the substrate bearing a cyclopropyl group was less reactive, which could not confirm the existence of the benzylic radical.



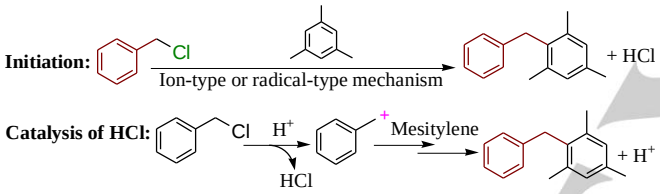
Scheme 7. Radical clock experiment (for the standard conditions, see Condition A in Table 2).

The benzylation with benzyl chloride would give HCl as the by-product. Presumably the resulting HCl played a role of the catalyst for the continuing Friedel–Crafts reaction based on previous literatures.[5,6] Indeed, the reaction displayed an induction period and a sigmoid kinetic profile characteristic of autocatalytic systems (Scheme 8),[3a,7] which suggests that the reaction is an autocatalytic process.



Scheme 8. Benzylation of mesitylene with benzyl chloride (for the reaction conditions, see Condition A in Table 2).

According to the above-mentioned observations, a autocatalytic mechanism pathway is proposed and shown in Scheme 9. At the present stage, the mechanism of the initiation step can not be clarified. Perhaps the initiation step involves an incomplete homolytic cleavage of the C-Cl bond shown in Scheme 6,[27,28] or an ion-type mechanism.[5,6]



Scheme 9. Proposed mechanism pathways for the benzylation.

Conclusions

In conclusion, a promoter-free and additive-free method was developed for the benzylation of benzenes with benzyl halides. A variety of benzyl chlorides and bromides were reacted with benzene rings to afford the targeted products in low to high yields. This provides a method for the synthesis of many 1,1-diarylmethanes and 1,1,1-triarylmethanes that often occur as the useful structural motifs in natural products or bioactive molecules.[4] Interestingly, the present condition tolerated the vinyl group of the substrates. Preliminary mechanistic investigation suggests that the present reactions possibly proceed via an autocatalytic mechanism pathway where the resulting HCl plays a role of the catalyst for the continuing reaction. These findings may be helpful for chemists to develop new, economical and green methods for the alkylation or functionalization of arenes under catalyst-free, promoter-free and additive-free condition.

Experimental Section

General: ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 500 or 400 MHz instrument with chemical shifts reported in ppm relative to the internal standard tetramethylsilane. Gas chromatography analyses were performed on a Varian CP-3800 instrument with a FID detector and a CP-WAX 57CB FS capillary chromatographic column (25 m × 0.32 mm). GC-MS spectra were recorded on an Agilent 7890/5973N gas chromatography-mass spectrometry instrument. Data are reported as follows: m/z, % relative intensity, and possible fragment.

Typical procedure for the benzylation of arenes with benzyl halides:

Reaction condition A: To a dried about 40 mL tube equipped with a magnetic stirring, 0.5 mmol benzyl halide and 2 mL substituted benzene were added under Ar atmosphere. The reaction tube was sealed with a septum and placed in a constant-temperature oil bath set at 140 ^{o}C to perform the reaction for 20 h. Once the reaction time was reached, the mixture was cooled to room temperature. The products were purified by silica gel column chromatography on silica gel (200-300 mesh) using EtOAc/petroleum ether as the eluent, and identified by ^{1}H-NMR and ^{13}C-NMR.

Reaction condition B: To a dried about 40 mL tube equipped with a magnetic stirring, 0.5 mmol benzyl halide, 2 mmol substituted benzene and 1 mL cyclohexane were added under Ar atmosphere. The reaction tube was sealed with a septum and placed in a constant-temperature oil bath set at 140 ^{o}C to perform the reaction for 20 h. Once the reaction time was reached, the mixture was cooled to room temperature. The products were purified by silica gel column chromatography on silica gel (200-300 mesh) using EtOAc/petroleum ether as the eluent, and identified by ^{1}H-NMR and ^{13}C-NMR.

Computational details: Using the Gaussian 09 program, all theoretical calculations were carried out at the M06-2X/6-31G (d) level in mesitylene with the SMD continuum model at 413.15 K. And the corresponding vibrational frequencies were calculated at the same level to take account of free energy contributions. What has been confirmed is that all the reactants, intermediates, and products have no imaginary frequencies whereas each transition state has only one imaginary frequency. Furthermore, the intrinsic reaction coordinate (IRC) calculations were also performed at the same level to ensure that the transition states led to the expected reactants and products. The single-point energies of the optimized structures were then refined at the M06-2X/6-311++G (2df, 2pd) level of theory in the solvent (mesitylene) with the SMD continuum model at 413.15 K. And all energies reported in this article include the zero-point vibrational energy (ZPVE) correction.

The spectroscopic data of the isolated products:

Phenyl-(2,4,6-trimethylphenyl)methane[29a] (Table 2, entries 1 and 12): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.32 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 2H), 6.99 (s, 2H), 4.12 (s, 2H), 2.39 (s, 3H), 2.30 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 140.2, 137.1, 135.7, 133.9, 129.0, 128.4, 127.9, 125.7, 34.8, 21.0, 20.2.

(2-Methylphenyl)-(2,4,6-trimethylphenyl)methane[29b] (Table 2, entry 2): White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.17 (d, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.90 (s, 2H), 6.50 (d, *J* = 7.7 Hz, 2H), 3.86 (s, 2H), 2.41 (s, 3H), 2.30 (s, 3H), 2.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 140.0, 137.2, 136.3, 135.6, 133.6, 129.7, 128.9, 126.3, 126.1, 125.7, 32.0, 21.0, 19.9, 19.8.

(3-Methylphenyl)-(2,4,6-trimethylphenyl)methane[29b] (Table 2, entry 3): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.10 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.88 (s, 2H), 6.85 (s, 1H), 6.78 (d, *J* = 7.3 Hz, 1H), 3.97 (s, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 2.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 140.1, 137.9, 137.1, 135.6, 133.9, 128.9, 128.7, 128.3, 126.5, 124.9, 34.7, 21.5, 21.0, 20.2.

(4-Methylphenyl)-(2,4,6-trimethylphenyl)methane[29a] (Table 2, entry 4): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.02 (d, 2H, *J* =

7.9 Hz), 6.89 (d, 2H, *J* = 7.9 Hz), 6.87 (s, 2H), 3.97 (s, 2H), 2.28 (s, 6H), 2.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 137.1, 137.0, 135.6, 135.1, 134.1, 129.1, 128.9, 127.8, 34.3, 21.0, 20.96, 20.2.

(4-^{t}Butylphenyl)-(2,4,6-trimethylphenyl)methane[29a] (Table 2, entry 5): White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.32 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.96 (s, 2H), 4.05 (s, 2H), 2.36 (s, 3H), 2.29 (s, 6H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 148.4, 137.0, 135.6, 134.2, 128.9, 127.6, 125.2, 34.3, 34.26, 31.5, 21.0, 20.2.

(4-Methoxyphenyl)-(2,4,6-trimethylphenyl)methane[8] (Table 2, entry 6): White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.98 (d, *J* = 8.4 Hz, 2H), 6.94 (s, 2H), 6.83–6.85 (m, 2H), 4.01 (s, 2H), 3.81 (s, 3H), 2.35 (s, 3H), 2.27 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 157.7, 137.0, 135.6, 134.2, 132.1, 128.9, 128.8, 113.8, 55.3, 33.8, 20.9, 20.1.

(3,4-Dimethoxyphenyl)-(2,4,6-trimethylphenyl)methane[8] (Table 2, entry 7): White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.93 (s, 2H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.67 (d, *J* = 1.8 Hz, 1H), 6.50 (td, J_1 = 8.2 Hz, J_2 = 1.0 Hz, 1H), 4.00 (s, 2H), 3.86 (d, *J* = 9.1 Hz, 6H), 2.33 (s, 3H), 2.26 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 1148.9, 147.1, 137.0, 135.6, 133.9, 132.7, 128.9, 119.4, 111.5, 111.2, 55.9, 55.8, 34.2, 20.9, 20.1.

(4-Vinylphenyl)-(2,4,6-trimethylphenyl)methane[8] (Table 2, entry 8): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.35 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.97 (s, 2H), 6.74 (dd, J_1 = 17.6 Hz, J_2= 10.9 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.25 (d, *J* = 10.9 Hz, 1H), 4.08 (s, 2H), 2.37 (s, 3H), 2.28 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 139.9, 137.0, 136.7, 135.8, 135.2, 133.7, 129.0, 128.1, 126.3, 113.0, 34.5, 21.0, 20.2.

(4-Fluorophenyl)-(2,4,6-trimethylphenyl)methane[29a] (Table 2, entries 9 and 13): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.03–7.06 (m, 2H), 6.98–7.02 (m, 4H), 4.06 (s, 2H), 2.38 (s, 3H), 2.28 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 162.2, 160.3, 137.0, 135.9, 135.7, 135.68, 133.7, 129.2, 129.15, 129.1, 115.2, 115.1, 33.9, 20.96, 20.1.

(4-Chlorophenyl)-(2,4,6-trimethylphenyl)methane[29a] (Table 2, entries 10 and 14): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.23 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.94 (s, 2H), 4.0 (s, 2H), 2.34 (s, 3H), 2.23 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 138.6, 136.9, 136.0, 133.3, 131.4, 130.4, 129.2, 129.0, 128.5, 34.1, 20.9, 20.1.

(4-Bromophenyl)-(2,4,6-trimethylphenyl)methane[29c] (Table 2, entries 11 and 15): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.39 (d, *J* = 8.4 Hz, 2H), 6.92–6.95 (m, 4H), 4.0 (s, 2H), 2.35 (s, 3H), 2.23 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 139.2, 137.0, 136.0, 133.2, 131.4, 129.6, 129.0, 119.5, 34.2, 21.0, 20.1.

Phenyl-(2,5-dimethylphenyl)methane[29d] (Table 2, entries 16 and 17): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.37 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 4.06 (s, 2H), 2.39 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 140.7, 138.8, 135.4, 133.5, 130.9, 130.3, 128.8, 128.4, 127.2, 126.0, 39.5, 21.1, 19.3.

(4-Methoxyphenyl)-(2-methoxy-5-methylphenyl)methane[29e] (Table 2, entries 18 and 19): Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.19 (d, *J* = 8.7 Hz, 2H), 7.03 (dd, J_1 = 8.2 Hz, J_2 = 1.8 Hz, 1H), 6.93 (d, *J* = 1.9 Hz, 1H), 6.88 (d, *J* = 9.6 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 1H), 3.94 (s, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 157.8, 155.3, 133.3, 131.0, 129.9, 129.86, 129.7, 127.6, 113.7, 110.5, 55.6, 55.3, 35.0, 20.5.

1-Benzhydryl-2,5-dimethoxybenzene[29f] (Table 2, entry 21): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.13–7.32 (m, 10H); 6.85 (d, *J* =8.8 Hz, 1H), 6.77 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 6.51 (d, *J* = 3.2 Hz, 1H), 5.94 (s, 1H), 3.70 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 153.4, 151.6, 143.7, 134.1, 129.5, 128.2, 126.1, 117.5, 111.9, 111.1, 56.4, 55.6, 49.8.

1,2,3-Trimethoxy-4-benzylbenzene[29g] (Table 2, entry 22): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.19–7.33 (m, 5 H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 2H), 3.91 (s, 3H), 3.87 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 152.4, 151.9, 142.4, 141.5, 128.8, 128.3, 127.4, 125.9, 124.5, 107.2, 60.8, 56.0, 35.8.

1,2,3-Trimethoxy-4-benzhydrylbenzene[29f] (Table 2, entry 23): White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.37 (t, *J* = 7.5 Hz, 4H), 7.26–7.31 (m, 6H), 6.78 (dd, J_1 = 15.0 Hz, J_2= 9.0 Hz, 2H), 6.03 (s, 1H), 3.99 (s, 3H), 3.89 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 152.5, 151.9, 144.2, 142.5, 130.8, 129.6, 128.4, 126.3, 124.6, 106.9, 60.7, 60.6, 55.9, 50.2.

1-Methoxy-4-benzylnaphthalene[29a] (Table 2, entry 24): White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.42–8.44 (m, 1H), 8.00–8.02 (m, 1H), 7.54-7.56 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.29 (dd, J_1 = 7.5 Hz, J_2= 4.5 Hz, 4H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.47 (s, 2H), 4.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 154.6, 141.2, 133.0, 128.8, 128.6, 128.5, 127.3, 126.6, 126.1, 126.0, 125.0, 124.3, 122.6, 103.4, 55.5, 38.72.

1,2,3-Trimethoxy-4-(4-vinylbenzyl)benzene[29g] (Table 2, entry 25): White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.38 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.74 (dd, J_1 = 17.5 Hz, J_2= 11.0 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 5.76 (d, *J* = 17.5 Hz, 1H), 5.24 (d, *J* = 11 Hz, 1H), 3.97 (s, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 3.81(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 152.5, 151.9, 142.5, 141.3, 136.7, 135.3, 129.0, 127.2, 126.3, 124.5, 113.0, 107.2, 60.77, 60.75, 56.0, 35.6.

3-(4-Vinylbenzyl)-4-methoxytoluene [29g] (Table 2, entry 26): Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.31 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.98 (dd, J_1 = 8.3 Hz, J_2 = 1.8 Hz, 1H), 6.87 (d, *J* = 1.9 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.68 (dd, J_1 = 17.6 Hz, J_2 = 10.9 Hz, 1H), 5.68 (dd, J_1 = 17.6 Hz, J_2 = 1.0 Hz, 1H), 5.17 (dd, J_1 = 10.9 Hz, J_2 = 0.9 Hz, 1H), 3.92 (s, 2H), 3.77 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 155.3, 141.0, 136.8, 135.2, 131.1, 129.7, 129.3, 129.1, 127.7, 126.2, 112.9, 110.5, 55.6, 35.6, 20.5.

1-Methoxy-4-(4-vinylbenzyl)naphthalene[29a] (Table 2, entry 27):

Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.36-8.38 (m, 1H), 7.94-7.96 (m, 1H), 7.50-7.52 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.73 (dd, J_1 = 17.6 Hz, J_2 = 10.9 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 4.41 (s, 2H), 4.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 154.6, 140.9, 136.7, 135.4, 132.9, 128.9, 128.4, 127.2, 126.6, 126.3, 126.1, 125.0, 124.2, 122.6, 113.1, 103.4, 55.5, 38.5

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[1] For recent representative literatures, see: a) M. R. Porter, R. M. Shaker, C. Calcanas, J. J. Topczewski, *J. Am. Chem. Soc.* **2018**, *140,* 1211–1214; b) S. Nakamura, T. Furukawa, T. Hatanakac, Y. Funahashic, *Chem. Commun.* **2018**, *54*, 3811–3814; c) N. G. Schmidt, T. Pavkov-Keller, N. Richter, B. Wiltschi, K. Gruber, W.

Kroutil, *Angew. Chem. Int. Ed.* **2017**, *56*, 7615–7619; d) D. V. Patil, S. W. Kim, Q. H. Nguyen, H. Kim, S. Wang, T. Hoang, S. Shin, *Angew. Chem. Int. Ed.* **2017**, *56*, 3670–3674; e) V. D. Vuković, E. Richmond, E. Wolf, J. Moran, *Angew. Chem. Int. Ed.* **2017**, *56*, 3085–3089; f) J. X. Fang, L. S. Li, C. Yang, J. P. Chen, G. J. Deng, H. Gong, *Org. Lett.* **2018**, *20*, 7308–7311; g) J. Y. Zhang, Y. Yang, J. X. Fang, G. J. Deng, H. Gong, *Chem. Asian J.* **2017**, *12*, 2524–2527.

[2] For selected reviews, see: a) Z. Sadiq, M. Iqbal, E. A. Hussain, S. Naz, *J. Mol. Liq.* **2018**, *255*, 26–42; b) G. Sartori, R. Maggi, *Chem. Rev.* **2011**, *111*, 181–214; c) W. R. Bowman, J. M. D. Storey, *Chem. Soc. Rev.* **2007**, *36*, 1803–1822.

[3] a) S. L. You, Q. Cai, M. Zenga, *Chem. Soc. Rev.* **2009**, *38*, 2190–2201; b) F. Forster, T. T. Metsänen, E. Irran, P. Hrobárik, M. Oestreich, *J. Am. Chem. Soc.* **2017**, *139*, 16334–16342; c) P. Li, J. J. Zhao, L. J. Shi, J. Wang, X. D. Shi, F. W. Li, *Nat. Commun.* **2018**, *9*, 1972; d) M. Horvat, M. Jereb, J. Iskra, *Eur. J. Org. Chem.* **2018**, 3837–3843; e) M. Dryzhakov, J. Moran, *ACS Catal.* **2016**, *6*, 3670−3673; f) M. Jereb, K. Gosak, *Org. Biomol. Chem.* **2015**, *13*, 3103–3115; g) S. Ogoshi, H. Nakashima, K. Shimonaka, H. Kurosawa, *J. Am. Chem. Soc.* **2001**, *123*, 8626–8627; h) M. De Rosa, A. Soriente, *Eur. J. Org. Chem.* **2010**, 1029–1032. i) S. Tuengpanya, C. Chantana, U. Sirion, W. Siritanyong, K. Srisook, J. Jaratjaroonphong, *Tetrahedron*, **2018**, *74*, 4373-4380; j) J. Jaratjaroonphong, S. Tuengpanya, S. Ruengsangtongkul, *J. Org. Chem.* **2015**, 80, 559–5673; k) J. Jaratjaroonphong, S. Tuengpanya, R. Saeeng, S. Udompong, K. Srisook, *Eur. J. Med. Chem.* **2014**, *83*, 561-5684; l) J. Jaratjaroonphong, S. Krajangsri, V. Reutrakul, *Tetrahedron Lett.* **2012**, *53*, 2476–24795; m) J. Jaratjaroonphong, S. Sathalalai, P. Techasauvapak, V. Reutrakul, *Tetrahedron Lett.* **2009**, *50*, 6012–6015.

[4] a) H. D. Hao, D. Trauner, *J. Am. Chem. Soc.* **2017**, *139*, 4117–4122; b) T. Yildiz, *Synthetic Commun.* **2017**, *48*, 2177–2188; c) T. Yildiz, H. B. Kucuk, *RSC Adv.* **2017**, *7*, 16644–16649; d) O. V. Maltsev, I. P. Beletskaya, S. G. Zlotin, *Russ. Chem. Rev.* **2011**, *80*, 1067–1113; e) J. Noei, A. R. Khosropour, Tetrahedron Lett. 2013, 54, 9–11; f) M. Yoshikawa, H. Kamisaki, J. Kunitomo, H. Oki, H. Kokubo, A. Suzuki, T. Ikemoto, K. Nakashima, N. Kamiguchi, A. Harada, H. Kimura, T. Taniguchi, *Bioorg. Med. Chem.* **2015**, *23*, 7138–7149; g) Y. L. Ren, M. Tian, X. Z. Tian, Q. Wang, H. T. Shang, J. J. Wang, Z. C. Zhang, *Catal. Commun.* **2014**, *52*, 36–39; h) Y. L. Ren, Z. F. Liu, S. B. He, S. Zhao, J. J. Wang, R. Q. Niu, W. P. Yin, *Org. Process Res. Dev.* **2009**, *13*, 764–768.

[5] a) G. A. Olah, Ed. *Friedel-Crafts Chemistry*, Wiley: New York, **1973**; b) G. A. Olah, Ed. *Friedel-crafts and related reactions*, Wiley: New York, **1963**; c) P. L. Manna, C. Talotta, G. Floresta, M. De Rosa, A. Soriente, A. Rescifina, C. Gaeta, P. Neri, *Angew. Chem. Int. Ed.* **2018**, *57*, 5423–5428.

[6] a) Z. C. Wang, L. Wang, Z. Zhou, Y. Y. Zhang, H. T. Li, C. Stampfl, C. H. Liang, J. Huang, *J. Phys. Chem. C* **2017**, *121*, 15248−15255; b) A. K. Siwek, M. Ahrens, M. Feist, T. Braun, E. Kemnitz, *ChemCatChem* **2017**, *9*, 839–845; c) H. X. Miao, W. M. Zhang, S. F. Hu, J. H. Ma, R. F. Li, *Catal. Commun.* **2016**, *78*, 68–70.

[7] P. A. Champagne, Y. Benhassine, J. Desroches, J. F. Paquin, *Angew. Chem. Int. Ed.* **2014**, *53*, 13835–13839.

[8] M. Hofmann, N. Hampel, T. Kanzian, H. Mayr, *Angew. Chem. Int. Ed.* **2004**, *43*, 5402–5405.

[9] a) V. D. Vukovic, E. Richmond, E. Wolf, J. Moran, *Angew. Chem. Int. Ed.* **2017**, *56*, 3085–3089; b) R. J. Tang, T. Milcent, B. Crousse, *J. Org. Chem.* **2018**, *83*, 14001−14009; c) G. C. Liu, B. Xu, *Tetrahedron Lett.* **2018**, *59*, 869–872; d) J.-D. Hamel, M. Beaudoin, M. Cloutier, J.-F. Paquin, *Synlett* **2017**, *28*, 2823–2828; e) W. Ji, Y. A. Liu, X. Liao, *Angew. Chem. Int. Ed.* **2016**, *55*, 13286–13289; f) R. H. Vekariya, J. Aubé, *Org. Lett.* **2016**, *18*, 3534−3537; g) J. Desroches, P. A. Champagne, Y. Benhassine, J.-F. Paquin, *Org. Biomol. Chem.* **2015**, *13*, 2243–2246; h) H. F. Motiwala, R. H. Vekariya, J. Aubé, *Org. Lett.* **2015**, *17*, 5484−5487;

[10] a) G. Li, X. Ma, C. Jia, Q. Han, Y. Wang, J. Wang, L. Yu, S. Yang, *Chem. Commun.* **2017**, *53*, 1261−1264; b) Z. Ruan, S.-K. Zhang, C. Zhu, P. N. Ruth, D. Stalke, L. Ackermann, *Angew. Chem., Int. Ed.* **2017**, *56*, 2045−2049; c) Z.-Y. Li, L. Li, Q.-L. Li, K. Jing, H. Xu, G.-W. Wang, *Chem. Eur. J.*, **2017**, *23*, 3285−3290; d) S. Warratz, D. J. Burns, C. Zhu, K. Korvorapun, T. Rogge, J. Scholz, C. Jooss, D. Gelman, L. Ackermann, *Angew. Chem. Int. Ed.* **2017**, *56*, 1557−1560; e) T. Kamei, *J. Syn. Org. Chem. Jpn.* **2012**, *70*, 756−757.

[11] a) J. Li, S. Arratz, D. Zell, S. De Sarkar, E. E. Ishikawa, L. Ackermann, *J. Am. Chem. Soc.* **2015**, *137*, 13894−13901; b) B. B. Li, D. Z. Li, J. Y. Zhang, D. Q. Shi, Y. S. Zhao, *ACS Catal.* **2017**, *7*, 4138−4143; c) M. Z. Lu, C. Q. Wang, S. J. Song, T. P. Loh, *Org. Chem. Front.* **2017**, *4*, 303–307.

[12] a) J. R. Zhang, L. Xu, Y. Y. Liao, J. C. Deng, R. Y. Tang, *Chin. J. Chem.* **2017**, *35*, 271–279; b) Y. J. Li, L. Ge, M. T. Muhammad, H. L. Bao, *Synthesis* **2017**, *49*, 5263–5284.

[13] a) L. Z. Zhang, Z. Q. Liu, *Org. Lett.* **2017**, *19*, 6594−6597; b) S. Castro, J. J. Fernández, F. J. Fañanás, R. Vicente, F. Rodríguez, *Chem. - Eur. J.* **2016**, *22*, 9068–9071; c) G.-X. Li, C. A. Morales-Rivera, Y. Wang, F. Gao, G. He, P. Liu, G. Chen, *Chem. Sci.* **2016**, *7*, 6407–6412; d) M. Tobisu, K. Koh, T. Furukawa, N. Chatani, *Angew. Chem. Int. Ed.* **2012**, *51*, 11363–11366.

[14] a) G. A. Molander, V. Colombel and V. A. Braz, *Org. Lett.* **2011**, *13*, 1852–1855; b) M. Presset, N. Fleury-Bregeot, D. Oehlrich, F. Rombouts, G. A. Molander, *J. Org. Chem.* **2013**, *78*, 4615–4619.

[15] a) Y. Fujiwara, J. A. Dixon, F. O'Hara, E. D. Funder, D. D. Dixon, R. A. Rodriguez, R. D. Baxter, B. Herle, N. Sach, M. R. Collins, Y. Ishihara, P. S. Baran, *Nature* **2012**, *492*, 95−99.

[16] G. A. Russell, P. Chen, B. H. Kim, R. Rajaratnam, *J. Am. Chem. Soc.* **1997**, *119*, 8795−8801.

[17] a) F. Yu, T. Wang, H. Zhou, Y. J. Li, X. H. Zhang, H. L. Bao, *Org. Lett.* **2017**, *19*, 6538−6541; b) W. M. Zhao, X. L. Chen, J. W. Yuan, L. B. Qu, L. K. Duan, Y. F. Zhao, *Chem. Commun.* **2014**, *50*, 2018−2020; c) S. Lu, Y. Gong, D. Zhou, *J. Org. Chem.* **2015**, *80*, 9336−9341; d) J. Yang, J. Zhang, L. Qi, C. Hu, Y. Chen, *Chem. Commun.* **2015**, *51*, 5275−5278; e) K. R. Babu, N. Zhu, H. Bao, *Org. Lett.* **2017**, *19*, 46−49; f) D. A. DiRocco, K. Dykstra, S. Krska, P. Vachal, D. V. Conway, M. Tudge, *Angew. Chem. Int. Ed.* **2014**, *53*, 4802−4806; g) D. G. Wang, J. X/ Fang, G. J. Deng, H. Gong, *ACS Sustain. Chem. Eng.* **2017**, *5*, 6398-6403; h) K. Sun, S. J. Li, X. L. Chen, Y. Liu, X. Q. Huang, D. H. Wei, L. B. Qu, Y. F. Zhao, B. Yu, *Chem. Commun.* **2019**, *55*, 2861–2864; i) H. Hu, X. L. Chen, K. Sun, J. C. Wang, Y. Liu, H. Liu, B. Yu, Y. Q. Sun, L. B. Qu, Y, F. Zhao, *Org. Chem. Front.* **2018**, *5*, 2925–2929.

[18] C. Wang, G. A. Russell, W. S. Trahanovsky, *J. Org. Chem.* **1998**, *63*, 9956−9959.

[19] a) N. Fukuda, T. Kajiwara, T. Katou, K. Majima, T. Ikemoto, *Synlett* **2013**, *24*, 1438–1442; b) E. Gaster, S. Kozuch, D. Pappo, *Angew. Chem. Int. Ed.* **2017**, *56*, 5912–5915; c) Y. Y. Shan, M. Lai, R. Li, Z. Y. Wu, M. Q. Zhao, *Asian J. Org. Chem.* **2017**, *6*, 1715–1718; d) Y. L. Ren, B. Y. Wang, X. Z. Tian, S. Zhao, J. J. Wang, *Tetrahedron Lett.* **2015**, *56*, 6452–6455; e) Y. L. Ren, H. T. Shang, J. J. Wang, X. Z. Tian, S. Zhao, Q. Wang, F. W. Li, *Adv. Synth. Catal.* **2013**, *355*, 3437–3442; f) F. P. Ren, X. Z. Tian, Y. L. Ren, S. Zhao, J. J. Wang, B. Zhao, *Catal. Commun.* **2017**, *101*, 98–101.

[20] a) S. P. Maj, D. N. R. Rao, M. C. R. Symons, *J. Chem. Soc., Faraday Trans. I* **1984**, *80*, 2767–2775; b) Q. Liu, H. Yi, J. Liu, Y. H. Yang, X. Zhang, Z. Q. Zeng, A. W. Lei, *Chem. Eur. J.* **2013**, *19*, 5120–5126.

[21] Z. C. Miao, J. Zhou, J. P. Zhao, D. D. Liu, X. Bi, L. J. Chou, S. P. Zhuo, *Appl. Surf. Sci.* **2017**, *411*, 419–430.

[22] S. L. Buchwald, C. Bolm, *Angew. Chem. Int. Ed.* **2009**, *48*, 5586–5588.

[23] a) M. A. Short, J. M. Blackburn, J. L. Roizen, *Angew. Chem. Int. Ed.* **2018**, *57*, 296–299; b) R. Thapa, J. Brown, T. Balestri, R. T. Taylor, *Tetrahedron Lett.* **2014**, *55*, 6743–6746.

[24] a) A. Podgorsek, M. Zupan, J. Iskra, *Angew. Chem. Int. Ed.* **2009**, *48*, 8424–8450; b) A. Podgorsek, S. Stavber, M. Zupan, J. Iskra, *Tetrahedron* **2009**, *65*, 4429–4439.

[25] a) M. S. Oderinde, A. Varela-Alvarez, B. Aquila, D. W. Robbins, J. W. Johannes, *J. Org. Chem.* **2015**, *80*, 7642−7651; b) H. Q. Wang, Z. Wang, H. C. Huang, J. J. Tan, K. Xu, *Org. Lett.* **2016**, *18*, 5680−5683.

[26] a) F. L. Jin, Y. Z. Zhong, X. Zhang, H. C. Zhang, Q. Zhao, W. Han, *Green Chem.* **2016**, *18*, 2598–2603; b) Y. Li, M. Lai, Z. Y. Wu, M. Q.

Zhao, M. Y. Zhang, *ChemistrySelect* **2018**, *3*, 5588–5592; c) V. Jouikov, J. Simonet, *Electrochem. Commun.* **2010**, *12*, 331–334; d) D. Kumar, S. P. de Visser, P. K. Sharma, S. Cohen, S. Shaik, *J. Am. Chem. Soc.* **2004**, *126*, 1907–1920.

[27] a) M. L. Tsao, C. M. Hadad, M. S. Platz, *J. Am. Chem. Soc.* **2003**, *125*, 8390–8399; b) M. L. Poutsma, *Science* **1967**, *157*, 997–1005.

[28] a) G. S. Bapat, A. Fischer, G. N. Henderson, S. Raymahasay, *J. Chem. Soc. Chem. Commun.* **1983**, 119–120; b) B. D. Peter, C. J. Bernice, *J. Chem. Soc. Perkin Trans. 2: Phys. Org. Chem.* **1981**, 42–48.

[29] a) H. Sun, B. Li, S. J. Chen, J. Li, R. M. Hua, *Tetrahedron* **2007**, *63*, 10185–10188; b) T. J. Davies, R. V. H. Jones, W. E. Lindsell, C. Miln, P. N. Preston, *Tetrahedron Lett.* **2002**, *43*, 487–488; c) X. B. Mo, J. Yakiwchuk, J. Dansereau, J. A. McCubbin, D. G. Hall, *J. Am. Chem. Soc.* **2015**, *137*, 9694−9703; d) Y. Li, Y. Xiong, X. M. Li, X. G. Ling, R. F. Huang, X. H. Zhang, J. C. Yang, *Green Chem.* **2014**, *16*, 2976–2981; e) T. Kobayashi, S. M. Rahman, *Synth. Commun.* **2003**, *33*, 3997–4003; f) H. S. P. Rao, A. V. B. Rao, *Beilstein J. Org. Chem.* **2016**, *12*, 496–504; g) T. E. Storr, C. J. Teskey, M. F. Greaney, *Chem. Eur. J.* **2016**, *22*, 18169–18178.

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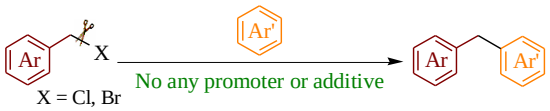

It was found that benzyl chlorides and bromides could directly react with electron-rich arenes, which provided an example of promoter- and additive-free benzylation of arenes.

C-C bond formation

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Benzylation of Arenes with Benzyl Halides under Promoter-Free and Additive-Free Condition