Unified Synthesis of Multiply Arylated Alkanes by Catalytic Deoxygenative Transformation of Diarylketones

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ABSTRACT: A deoxygenative transformation of diarylketones leading to multiply arylated alkanes was developed. Diarylketones were reacted with diphenylphosphine oxide resulting in a *phospha*-Brook rearrangement, followed by palladium-catalyzed cross-couplings or a Friedel–Crafts type alkylation to afford the corresponding multiply arylated alkanes. A variety of diarylketones can be converted to multiply arylated alkanes such as diarylmethanes, tetraarylethanes, and triarylmethanes by reduction, dimerization, and arylation in one pot. Furthermore, a one-pot conversion from arylcarboxylic acids to diarylmethanes and tetraarylethanes, and a synthesis of tetraarylmethane and triphenylethane using sequential coupling reactions are also presented.

■ INTRODUCTION

Multiply arylated alkanes are widely used as pharmaceuticals, natural products, and organic materials (Figure 1A). A diarylmethane such as tofogliflozin is a representative motif among multiply arylated alkanes.[1] A triarylmethane such as (+)-securidane A and a tetraarylethane such as Raptinal are also known bioactive products.[2,3] CDP-840, a phosphodiesterase(PDE)-IV inhibitor,[4] is classified as a triarylethane, and COF-102, known as a covalent organic framework, has a tetraarylmethane skeleton.[5] Since these are important structures, the synthesis of multiply arylated alkanes has long been investigated.[6-10] Particularly recently, excellent catalytic and efficient syntheses of these alkanes have been reported using readily available building blocks and state-of-the-art methodologies (Figure 2B). For example, diarylmethanes are generally synthesized from benzyl electrophiles, but recently, a direct coupling from benzyl alcohol, which is a readily available starting material, has been reported. Shu and coworkers discovered a nickel-catalyzed direct cross-coupling of benzylic alcohols with aryl triflates in the presence of DMO (dimethyl oxalate) to afford the corresponding diarylmethanes.[11] Masarwa and coworkers reported a unique synthetic method of triarylmethanes from aldehydes:[12] an aldehyde was mixed with an arene and triphenylphosphine in the presence of TfOH to generate a diarylphosphonium salt, followed by another arene in one pot to furnish the corresponding triarylmethane. This simple operation allowed for a one-pot synthesis of triarylmethanes from aldehydes, but this method is limited to the use of electron-rich arenes. Li's group reported a deoxygenative dimerization from diaryl ketones, inspired by a classical Wolff–Kishner type of diarylmethane synthesis.[13] This is an excellent method that can synthesize diaryl ketones in two steps (2 pots) through the formation of hydrazine as an intermediate. Moran's group then developed a one-pot synthesis of triarylethanes from aryl epoxides.[14] A ring-opening reaction of the epoxide by an electron-rich arene was followed by a Friedel–Crafts type alkylation of the resulting diarylethanol with

another electron-rich arene via a phenonium intermediate. Although this method appears to be a classical synthetic method, a variety of electron-rich triarylethanes can be prepared. Walsh and coworkers demonstrated a straightforward synthesis of tetraarylmethanes from diarylmethanes.[15] After deprotonation of the diarylmethane with a base (KOt-Bu), two further arenes can be introduced by palladium-catalyzed C–H arylations with aryl chlorides. A variety of tetraarylmethanes can be synthesized, although an electron-deficient heteroarene (a pyridine moiety) is required for one of the aromatic rings of the diarylmethane. While various syntheses of multiply arylated alkanes have been reported, thus far, there is no unified synthetic protocol from the same starting materials.

Meanwhile, recent attention has been focused on the deoxygenative transformation of aromatic carbonyls, which has been extensively studied by the Li group and others.[16] Regarding this field of research, we have also developed a deoxygenative C–P bond formation of aromatic esters (Figure 1C).[17] In this reaction, an aromatic ester reacts with phosphine oxide in the presence of a palladium catalyst to give an acylphosphine oxide species as the intermediate. The intermediate has a highly electron-deficient carbonyl, thus a nucleophilic attack of the phosphine oxide to the carbonyl occurs, followed by a [1,2]-*phospha*-Brook rearrangement and reduction of the carbon–oxygen bond using a palladium catalyst and sodium formate (HCO$_2$Na) as a mild reductant to afford the corresponding deoxygenative products. Based on this mechanism, we envisioned that this reaction could be utilized as a unified synthesis of multiply arylated alkanes from diarylketones (Figure 1D).

Diarylketones are inexpensive, readily available basic chemicals that can also be generated from aryl carboxylic acids, acid chlorides, and esters in a single step by palladium-catalyzed cross-coupling.[18] In general, diarylketones have an electron-deficient carbonyl, and phosphine oxide is able to attack the carbonyl, which would then undergo a [1,2]-*phospha*-Brook rearrangement to produce diarylphosphinates.
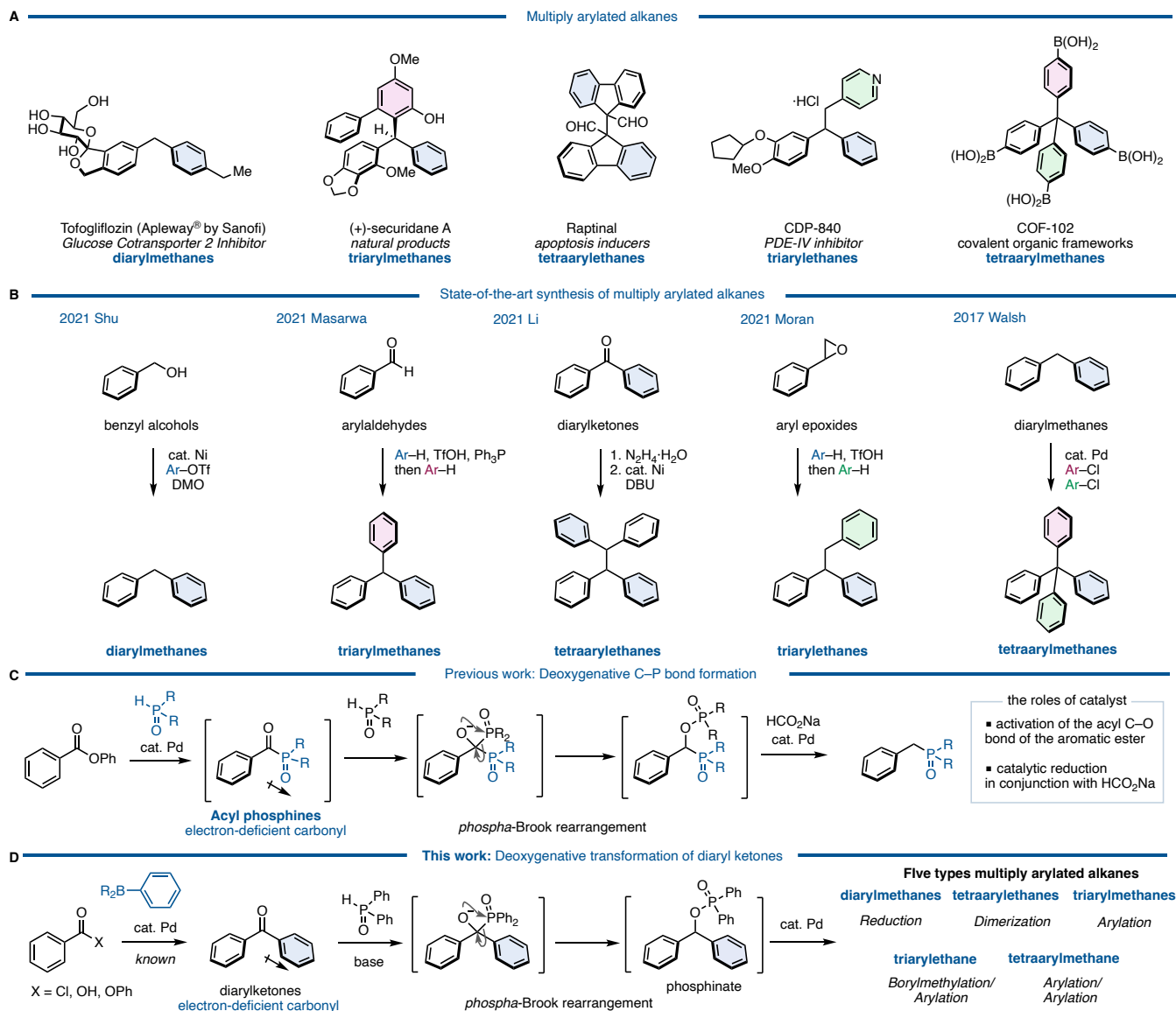
Figure 1. (A) Multiply arylated alkanes in pharmaceuticals, natural products, and organic materials. (B) State-of-the-art synthesis of multiply arylated alkanes. (C) Deoxygenative C–P bond formation of aromatic esters. (D) Deoxygenative transformation of diarylketones.

Since this phosphinate would be a common synthetic intermediate similar to (pseudo)halogenated diarylmethane, we hypothesized that it could be transformed to diarylmethanes by reduction, tetraarylethanes by dimerization, and triarylmethanes by arylation. Furthermore, a homologation of the intermediate by diborylmethane, followed by arylation would afford triarylethanes, and tetraarylmethanes would be synthesized by arylation of triarylmethanes. Herein, we report a deoxygenative transformation of diarylketones with diphenyl phosphine oxide by using a palladium catalyst and HCO$_2$Na, leading to five different types of multiply arylated arenes in one-pot.

■ RESULTS AND DISCUSSION

Discovery and screening of optimal conditions for the synthesis of diarylmethanes and tetraarylethanes by deoxygenative transformations.

Following our previous work on deoxygenative C–P bond formation,[17] benzophenone (**1**) and diphenylphosphine oxide (1.5 equiv) with 5.0 mol % PdCl$_2$, 10 mol % dcype (1,2-

bis(dicyclohexylphosphino)ethane), and sodium formate (HCO$_2$Na, 1.5 equiv) as a hydrogen source in 1,2-dimethoxyethane (DME) at 150 °C for 12 h were used as the initial conditions. As a result, these conditions successfully gave the desired diphenylmethane (**2A**) in 10% yield along with the unexpected tetraphenylethane (**3A**) in 4% yield. After extensive optimization of the reaction conditions (see the Supporting Information for details), we identified the optimal conditions for **2A**. To our delight, when the conditions were changed to PdCl$_2$/PPh$_3$ as a catalyst and Cs$_2$CO$_3$ (2.0 equiv), HCO$_2$Na (2.0 equiv) in DMSO at 150 °C for 1 h, the yield of **2A** significantly improved to 93% and no **3A** was observed (Table 1, entry 1).

Next, control experiments were undertaken. The palladium salt is essential for this reaction, because without it, the reaction furnished the "half-reduced" diphenylmethanol (**2A'**), and the starting material **1** was also recovered (Table 1, entry 2). Without the ligand, the yield was lower (Table 1, entry 3), and diphenylphosphine oxide was critical (Table 1, entry 4). The reaction can proceed without the base, but the yield of **2A** and the selectivity for **2A** and **3A** was significantly decreased (Table 1, entry 5). The reaction resulted in

further decreasing product yields without HCO$_2$Na (Table 1, entry 6). Although this reaction is typically performed at 150 °C, it can proceed at 100 °C with only a slight decrease in yield of **2A**. (Table 1, entry 7). We then examined various conditions to improve the yield of **3A** and found that simply changing the solvent to DME, and decreasing the amount of Cs$_2$CO$_3$ (0.4 equiv) significantly improves the yield of **3A**. Finally, by extending the reaction time to 12 h, we succeeded in preferentially producing **3A** in 76% yield (Table 1, entry 7, and see the Supporting Information for details).

Table 1. Variations from standard conditions.[a]
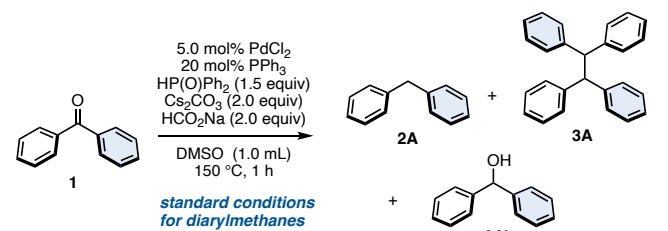
entry	variations[b]	1/%	2A/%	3A/%	2A'/%
1	none	0	93	0	0
2	w/o PdCl$_2$	35	0	0	44
3	w/o PPh$_3$	14	56	0	15
4	w/o HP(O)Ph$_2$	86	0	0	12
5	w/o Cs$_2$CO$_3$	27	31	12	28
6	w/o HCO$_2$Na	64	13	4	14
7	100 °C	4	83	0	0
8[c]	DME, 12 h	0	13	76	0

[a] Conditions; **1** (0.20 mmol), PdCl$_2$ (5.0 mol %), PPh$_3$ (20 mol %), Cs$_2$CO$_3$ (2.0 equiv), HCO$_2$Na (1.5 equiv), DMSO (1.0 mL), 150 °C, 1 h. Yields were determined by ^{1}H NMR analysis. [b] Variations from standard conditions. [c] Cs$_2$CO$_3$ (0.4 equiv) was used.

Substrate scope for diarylmethanes and tetraarylethanes.

Under these optimized conditions, the substrate scope of diaryl-ketones was investigated (Scheme 1). Changing one of phenyl groups of the benzophenone (**1**) to a naphthyl or a *meta*-tolyl group also afforded diarylmethanes **2B** and **2C** in moderate yields. Biphenyl group worked as well (**2D**), however, installing a methoxy group at the *para*-position of the biphenyl decreased the yield (**2E**) even after increasing the amounts of catalysts, since this resulted in a lot of accompanying diarylmethanol (54% yield). The low yield was caused by the failure of the Pd/HCO$_2$Na reduction of the phosphinate formed by the *phospha*-Brook rearrangement due to the electron-donating group. As a result, the phosphinate was hydrolyzed after quenching by water, resulting in the alcohol. Fluorinated diarylketones gave the corresponding diarylmethanes **2F** and **2G** in moderate yields. Diarylketones with an alkyne, bis-trifluoromethyl groups, or dimethoxy groups were tolerated to furnish the corresponding diarylmethanes **2H**–**2J**. When the phenyl group of **1** was replaced by heteroaromatics such as pyridine or quinoline, the corresponding diarylmethanes **2K**–**2N** were obtained in good to high yields. Even for cyclic ketones, the corresponding diarylmethanes **2O**–**2S** were afforded, regardless of the
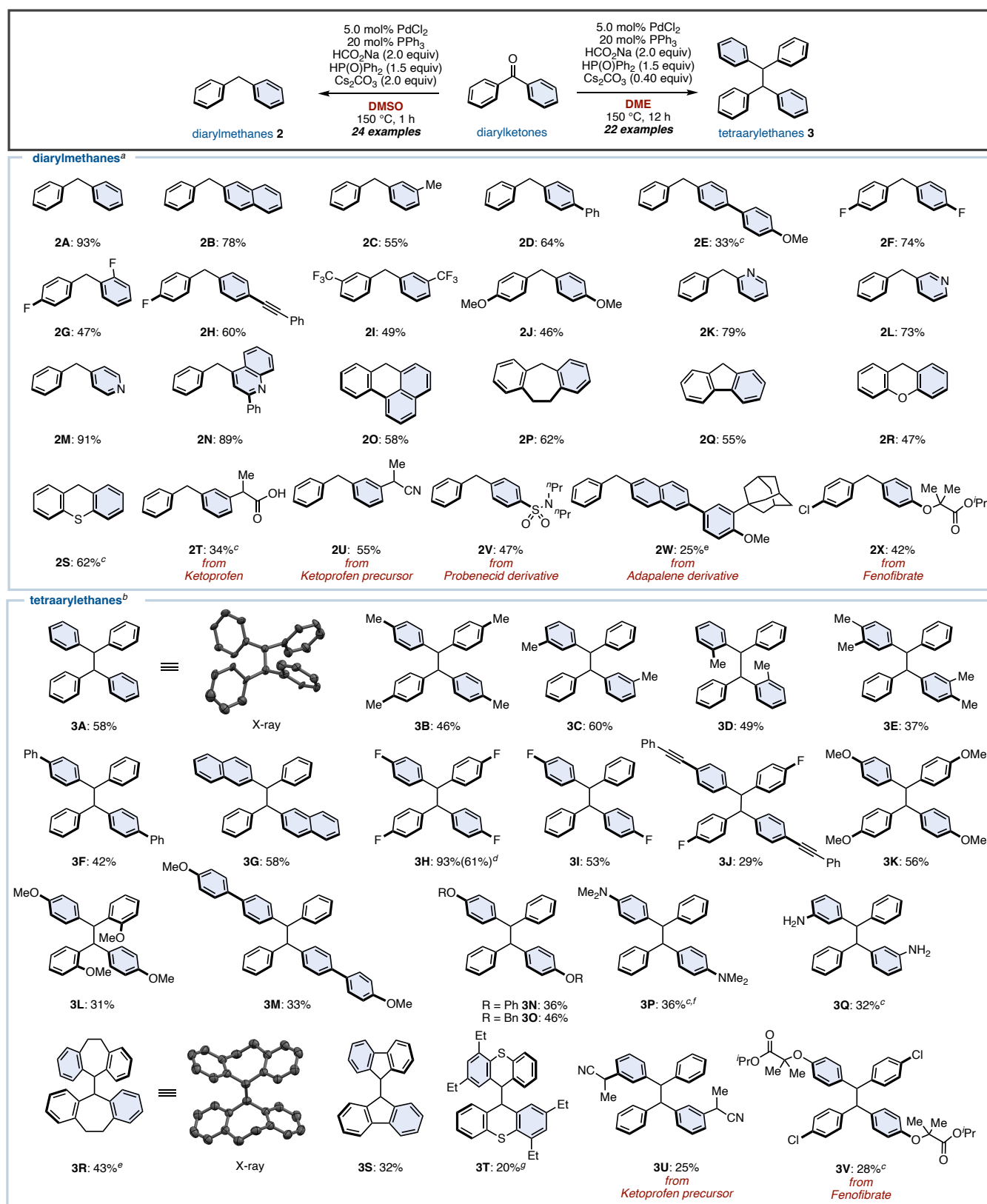
ring size or the presence of heteroatoms. We also attempted this reaction with ketoprofen as well as its precursor, giving the corresponding diarylmethanes **2T** and **2U**. Additionally, diarylketones, which can be readily derivatized in one step from carboxylic-acid-containing drugs such as probenecid and adapalene, successfully converted to the corresponding diarylmethanes **2V** and **2W**, albeit in low yields. Fenofibrate, which is a well-known pharmaceutical, succeeded in giving product **2X** in a moderate yield.

Next, we examined the substrate scope for the synthesis of tetraarylethanes **3** using the standard conditions (Table 1, entry 8). Benzophenone (**1**) gave 1,1,2,2-tetraphenylethane (**3A**) in 58% isolated yield, and the structure of **3A** was assigned by X-ray crystallographic analysis. Mono- or di-tolylmethanones with methyl groups in the *para*-, *meta*-, or *ortho*-positions, as well as xy-lylmethanone smoothly generated the corresponding tetraarylethanes **3B**–**3E**. Diarylketones bearing biphenyl and naphthyl groups afforded the corresponding tetraarylethanes **3F** and **3G** in moderate yields. Note that when unsymmetrical diarylketones are used, the resulting tetraarylethanes **3** become a mixture of diastereomers with a ratio of almost 1:1. A ketone with bis-4-fluorophenyl groups reacted well to give the desired product **3H** in a high yield, and this reaction also proceeds on gram scale (61% yield). In contrast, reactions with a mono-fluorophenyl group gave **3I** and **3J** in moderate to low yields. Diarylketones with methoxy, alkoxy, dimethylamino, and NH$_2$ groups were tolerated to furnish the corresponding tetraarylethanes **3K**–**3Q**. In the case of low yields, the corresponding diarylmethanes and the diarylmethanols were obtained as by-products. Cyclic ketones such as dibenzosu-berone did not progress at all under our standard conditions. Therefore, we re-optimized the reaction and found that tributyl phosphine was effective as a ligand to give **3R** in 51% yield (the structure of **3R** was assigned by X-ray crystallographic analysis). However, the reaction conditions were ineffective with other cyclic ketones (**3S** and **3T**). Ketoprofen precursor and fenofibrate were applicable to this reaction as well (**3U** and **3V**).

Studies for elucidation of the reaction mechanism.

We hypothesize the reaction mechanism as follows: 1) the diaryl-ketone starting material could be converted to a diarylphosphinate via a *phospha*–Brook rearrangement; 2) then, reduction and dimer-ization by a Pd/HCO$_2$Na catalytic system would lead to diarylme-thanes and tetraarylmethanes. However, their precise mechanisms and requirements for adequate conditions are not known. Therefore, we performed additional control experiments to elucidate the reaction mechanism for the synthesis of diarylmethane **2** and tetraarylethane **3** (Figure 2). When benzophenone (**1**) was reacted with diphenylphosphine oxide in the presence of Cs$_2$CO$_3$ as a base without Pd/HCO$_2$Na, phosphinate **4A** was obtained quantitatively (Figure 2A). Although stoichiometric amounts of metal carbonates (Cs$_2$CO$_3$ or K$_2$CO$_3$) are not required, the reaction did not proceed at all without the addition of metal carbonates. These results indicate that the base is critical for the formation of phosphinate **4A**, but that high temperatures (150 °C), a palladium catalyst, and HCO$_2$Na are not required (see the Supporting Information for details).

Scheme 1. Substrate scope[a]

Reaction conditions (top box):

Left arrow to **diarylmethanes 2**: 5.0 mol% PdCl₂, 20 mol% PPh₃, HCO₂Na (2.0 equiv), HP(O)Ph₂ (1.5 equiv), Cs₂CO₃ (2.0 equiv), **DMSO**, 150 °C, 1 h, *24 examples*

Center: **diarylketones**

Right arrow to **tetraarylethanes 3**: 5.0 mol% PdCl₂, 20 mol% PPh₃, HCO₂Na (2.0 equiv), HP(O)Ph₂ (1.5 equiv), Cs₂CO₃ (0.40 equiv), **DME**, 150 °C, 12 h, *22 examples*

diarylmethanes[a]

2A: 93%
2B: 78%
2C: 55%
2D: 64%
2E: 33%[c]
2F: 74%

2G: 47%
2H: 60%
2I: 49%
2J: 46%
2K: 79%
2L: 73%

2M: 91%
2N: 89%
2O: 58%
2P: 62%
2Q: 55%
2R: 47%

2S: 62%[c]
2T: 34%[c] *from Ketoprofen*
2U: 55% *from Ketoprofen precursor*
2V: 47% *from Probenecid derivative*
2W: 25%[e] *from Adapalene derivative*
2X: 42% *from Fenofibrate*

tetraarylethanes[b]

3A: 58% ≡ X-ray
3B: 46%
3C: 60%
3D: 49%
3E: 37%

3F: 42%
3G: 58%
3H: 93% (61%)[d]
3I: 53%
3J: 29%
3K: 56%

3L: 31%
3M: 33%
3N: R = Ph, 36%
3O: R = Bn, 46%
3P: 36%[c,f]
3Q: 32%[c]

3R: 43%[e] ≡ X-ray
3S: 32%
3T: 20%[g]
3U: 25% *from Ketoprofen precursor*
3V: 28%[c] *from Fenofibrate*

Conditions; [a]**1** (0.40 mmol), diphenylphosphine oxide (1.5 equiv), PdCl₂ (5.0 mol %), PPh₃ (20 mol %), HCO₂Na (2.0 equiv), Cs₂CO₃ (2.0 equiv), DMSO (1.0 mL), 150 °C, 1 h. [b]**1** (0.40 mmol), diphenylphosphine oxide (1.5 equiv), PdCl₂ (5.0 mol %), PPh₃ (20 mol %), HCO₂Na (2.0 equiv), Cs₂CO₃ (0.40 equiv), DME (1.0 mL), 150 °C, 12 h. [c]PdCl₂ (10 mol %), PPh₃ (40 mol %) were used. [d]6.0 mmol scale. [e]P[n]Bu₃ (20 mol %), K₂CO₃ (2.0 equiv), MeCN, 12 h. [f]Isolated as an acetamide by treating with Ac₂O. [g]20 mol % MePPh₂, K₂CO₃ (2.0 equiv), MeCN, 12 h.

Next, we attempted the diphenylmethane (**2A**) synthesis from phosphinate **4A** under our optimal conditions without addition of Cs$_2$CO$_3$ (Figure 2B). Surprisingly, the desired diphenylmethane **2A** was obtained in only 6% yield, and ketone **1** was obtained as the major product (entry 1). The addition of Cs$_2$CO$_3$ slightly improved the yield of **2A** (12%), but increased the yield of alcohol **2A'** as well, which is an effect of phosphinate **4A** being partially hydrolyzed (entry 2). Without the addition of the palladium catalyst, **2A** was not produced at all and was completely converted to ketone **1** (entry 3). It was finally realized that the desired diphenylmethane **2A** was obtained in 53% by adding diphenylphosphine oxide and Cs$_2$CO$_3$ (entry 4). In the absence of HCO$_2$Na (entry 5), the yield of **2A** decreased, but the yield increased for alcohol **2A'** and ketone **1**. The existing equilibrium between ketone **1** and phosphinate **4A** in DMSO suggests that reduction might be proceeding as soon as the phosphinate **4A** is produced by the Pd/HCO$_2$Na catalytic system.

Additional control experiments for the synthesis of tetraphenylethane **3A** from phosphinate **4A** were performed (Figure

2C). Phosphinate **4A** in DME in the presence of PdCl$_2$/PPh$_3$ and HCO$_2$Na gave the desired tetraphenylethane **3A** in 57% yield, along with 7% diphenylmethane **2A** as a byproduct. This result is mostly consistent with the results from ketone **1**, but the requirements were further elaborated. Without the addition of a palladium catalyst or HCO$_2$Na, the reaction hardly proceeded (entries 2 and 3). Furthermore, an excess amount of Cs$_2$CO$_3$ was found to inhibit the dimerization reaction (entry 4). Hence, the amount of Cs$_2$CO$_3$ in the dimerization of **1** was kept minimal (0.40 equiv, see Scheme 1).

Furthermore, the following crossover experiment was performed to confirm whether dimerization of the phosphinate **4A** or crosscoupling with the diphenylketone (**1**)/diphenylmethane (**2A**) occurs (Figure 2D). To this end, phosphinate **4A** was reacted under our standard conditions for dimerization with diaryl ketone **5** or diarylmethane **2Y** (1.0 equiv of each), respectively. If a crossover reaction had occurred, **3A'** would have been detected in addition to **3A**, however **3A'** was not detected at all. These results suggest that a dimerization reaction of phosphinate **4A** is proceeding.
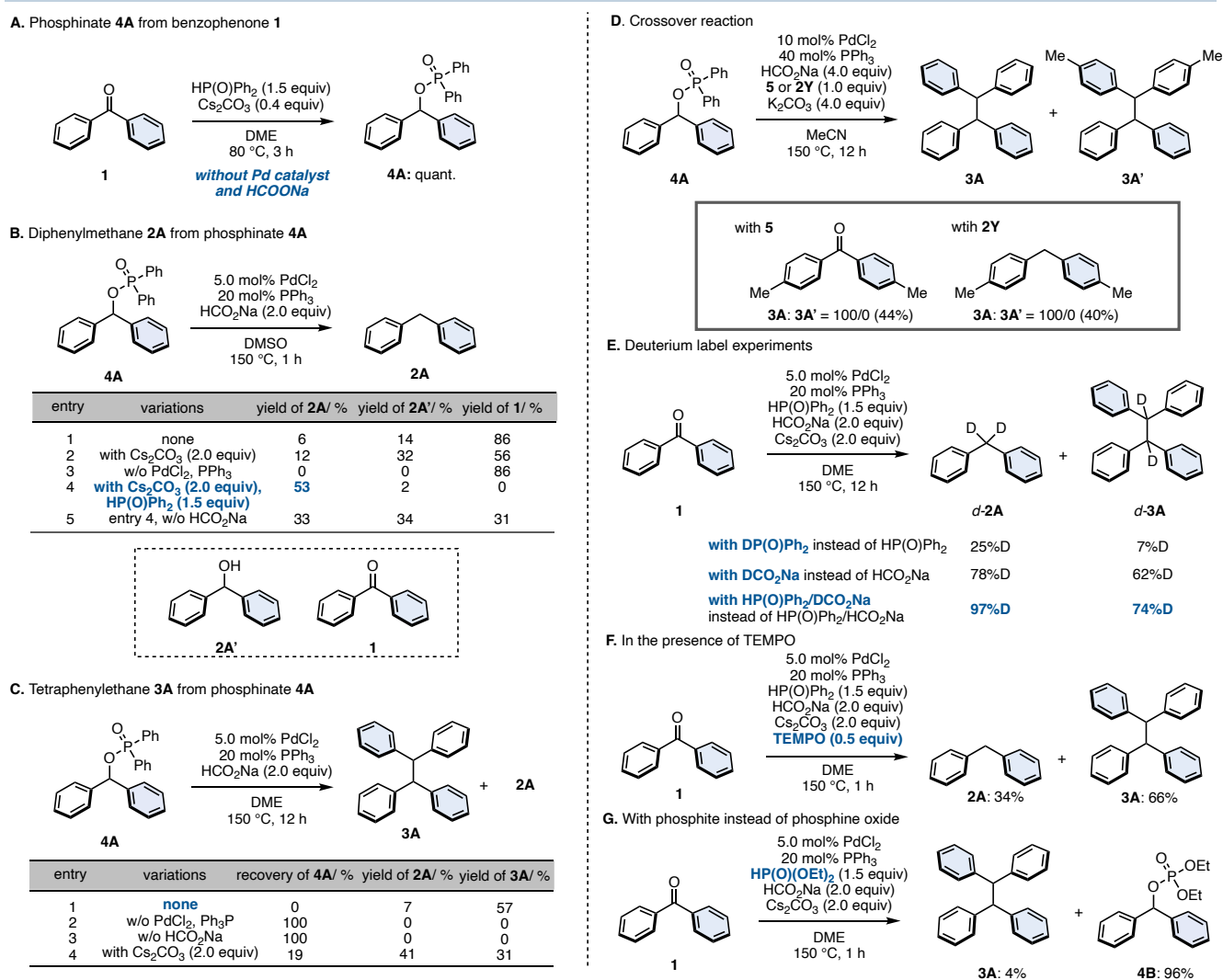

Figure 2. (A) Phosphinate **4A** from benzophenone(**1**). (B) Diphenylmethane **2A** from phosphinate **4A**. (C) Tetraphenylethane **3A** from phosphinate **4A**. (D) Crossover reaction. Numbers in the parentheses are yields of **3A**. (E) Deuterium labeling experiments. (F) Standard conditions with TEMPO as a radical scavenger. (G) With phosphite instead of phosphine oxide.

Moreover, deuterium labeling experiments were conducted (Figure 2E). Under optimal conditions for **2A** synthesis, deuterated diphenylphosphine oxide (DP(O)Ph$_2$) was added instead of diphenylphosphine oxide to afford *d*-**2A** (25% D) and *d*-**3A** (7% D). When DCO$_2$Na was used instead of HCO$_2$Na, this led to a dramatic increase in the deuterated ratio of *d*-**2A** (78% D) and *d*-**3A** (62% D). Finally, both deuterated agents were combined to give **2A** (97% D) and **3A** (74% D). These results suggest that HCO$_2$Na works as a hydrogen source in this reaction.

We also attempted this reductive transformation under a radical scavenger (Figure 2F): in the presence of TEMPO, the reaction gave both **2A** and **3A**. This result confirmed that these reactions do not proceed through a radical pathway. Lastly, the same reaction was attempted using diethyl phosphite instead of diphenylphosphine oxide (Figure 2G). This is because generally the *phospha*–Brook rearrangement is almost exclusively reported for phosphite esters.[19] When this reaction was performed with diethyl phosphite, the phosphate ester **4B** was obtained in 96% yield, but the desired tetraphenylethane **3A** was formed in small amounts. Thus, the reaction proved to be effective only with diphenylphosphine oxide.

Synthesis of Triarylmethanes.

Next, we considered that the phosphinate is a (pseudo)halide, and that triarylmethane could be synthesized by screening for appropriate conditions. To the best of our knowledge, Friedel–Crafts-type arylations or cross-couplings of phosphite have been reported,[20,21] but there is no report for phosphinates thus far. As a result of our investigation, we found the following two reaction conditions for the one-pot synthesis of triarylmethane from diarylketones (Scheme 2).

For electron-rich aromatic rings, Friedel–Crafts-type reaction conditions were effective. Benzophenone (**1**) was reacted with diphenyl phosphine oxide (1.5 equiv) and Cs$_2$CO$_3$ (0.40 equiv) in DME at 80 °C for 3 h to generate phosphinate **4A** *in situ*, followed by the addition of toluene, thiophene, or mesitylene with TfOH (2.0 equiv) at room temperature for 2 min to give the corresponding triarylmethanes **6A**–**6C** in moderate yields. Although small amounts of positional isomers were produced when generating **6A** and **6B**, triarylmethanes can be synthesized rapidly from benzophenone (**1**) without the use of metal catalysts. Not only benzophenone (**1**), but also an unsymmetrical diaryl ketone, a cyclic diaryl ketone, and a diarylketone with substituents such as a chlorine and an ester could be converted to the corresponding triarylmethanes **6D**–**6F** in moderate yields. When an aromatic ring with an electron-withdrawing substituent was used as the substrate, a Suzuki–Miyaura-type coupling reaction was effective. Similarly, after the preparation of phosphinate **4A**, the corresponding triarylmethanes were formed simply by adding arylboronic acid (1.5 equiv), Pd(OAc)$_2$ (10 mol%), and P(*p*-tolyl)$_3$ (40 mol%) to the reaction vessel and stirring at 150°C for 1 h. In addition to triarylmethanes **6G**–**6I** with trifluoromethyl, cyano, and ester groups, triarylmethanes **6J**–**6L** with methoxy, phenyl, and phenoxy groups at the *para* position of the aromatic ring could be synthesized.

Synthetic utility and applications of this method.

Finally, the synthetic utility and applications of this method were investigated (Scheme 3). As mentioned in the introduction, diaryl ketones can be readily prepared from aromatic carboxylic acids. Therefore, we demonstrated a one-pot diarylme-

thane/tetraarylethane synthesis from aryl carboxylic acids (Scheme 3A). The reaction of benzoic acid with phenylboronic acid and Boc$_2$O in the presence of a palladium catalyst gave benzophenone (**1**) via a mixed acid anhydride.[18a] When **1** was subjected directly to the diverging conditions of Scheme 1 without isolation in one-pot, diphenylmethane (**2A**) and tetraphenylmethane (**3A**) were successfully synthesized in 70% and 43% yields from benzoic acid, respectively.

Scheme 2. Synthesis of triarylmethanes.
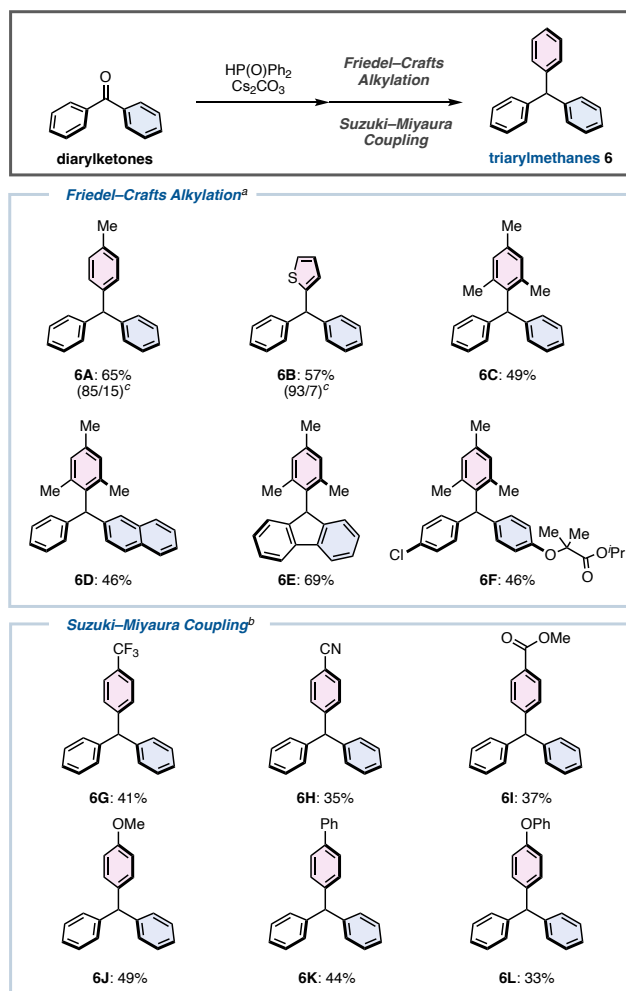
Conditions: [a]diarylketone (0.40 mmol), diphenylphosphine oxide (1.5 equiv), Cs$_2$CO$_3$ (0.40 equiv), DME (2.0 mL), 80 °C, 3 h; then arene (1.0 mL), TfOH (2.0 equiv), RT, 2 min. [b]Diarylketone (0.40 mmol), diphenylphosphine oxide (1.2 equiv), Cs$_2$CO$_3$ (2.0 equiv), 1,4-dioxane (2.0 mL), 150 °C, 1 h; then arylboronic acid (1.5 equiv), Pd(OAc)$_2$ (10 mol%), P(*p*-tolyl)$_3$ (40 mol%), 150 °C, 1 h. [c]The ratio of isomers (*para*/*ortho*-position (**6A**) or C2/C3 position (**6B**)) is shown in parentheses.

We also attempted a deoxygenative allylation of diarylketones (Scheme 3B). After phosphinate formation by a *phospha*–Brook rearrangement of naphthalen-2-yl(*p*-tolyl)methanone (**7**), allyltrifluoroborate with palladium catalyst/**L1** led to benzyl substitution to form allyldiarylmethane **8** in 52% yield. In contrast, the use of naphthalen-2-yl(phenyl)methanone (**9**), which is a demethyl form of **7**, afforded diarylmethane **10**, which substituted at the *para*-position of the phenyl group. Diarylmethane **10** was likely formed

from a π-benzyl palladium complex by a dearomatizing allylation reaction.[22]

Next, an intramolecular dimerization was carried out (Scheme 3C). Applying the reaction conditions from the tetraarylethane synthesis to compound **11**, which is essentially two diphenylketones linked together, the diphosphinate intermediate **12** becomes diphenylphenanthrene **13** as the coupling and subsequent autooxidation proceeds. Oxidation of **13** with DDQ in the presence of TfOH gave dibenzo[*g,p*]chrysene **14** in good yield. This method has the potential to be used in the synthesis of various polycyclic aromatic hydrocarbons (PAHs).

Furthermore, the *phospha*–Brook rearrangement can be used to make diarylmethane from aromatic aldehydes (Scheme 3D). For example, diphenylphosphine oxide and a base are applied to 2-naphthaldehyde (**15**) to form the corresponding phosphinate, followed by an sp³ Suzuki–Miyaura-type coupling with phenyl-

boronic acid to afford diarylmethane **2B** in moderate yield. Since aromatic aldehydes are also inexpensive and readily available, a variety of diarylmethanes may be synthesized in a practical fashion.

Finally, we attempted to synthesize triarylethanes and tetraarylmethanes from diarylketones (Scheme 3E and 3F). The coupling reaction of **9** with diborylmethane (1.5 equiv) underwent *phospha*-Brook rearrangement, followed by palladium catalyst and base to afford diarylethylboronate **15**. A one-pot alkyl-Suzuki–Miyaura type coupling with phenylboronic acid was carried out without isolation of **15**, and then triarylethanes **16** were successfully produced in 37% yield from diarylketone **9**. Furthermore, after subjecting benzophenone (**1**) to the reaction conditions of Scheme 2 for the synthesis of triarylmethane, the resulting triphenylmethane **17** was treated with benzofuran, DDQ and catalytic Sc(OTf)₃ to give tetraarylmethane **18**.[10a] The structure of tetraarylmethane **18** was determined by X-ray crystallography.

Scheme 3. Synthetic utility and applications of decarbonylative transformation of diarylketones.
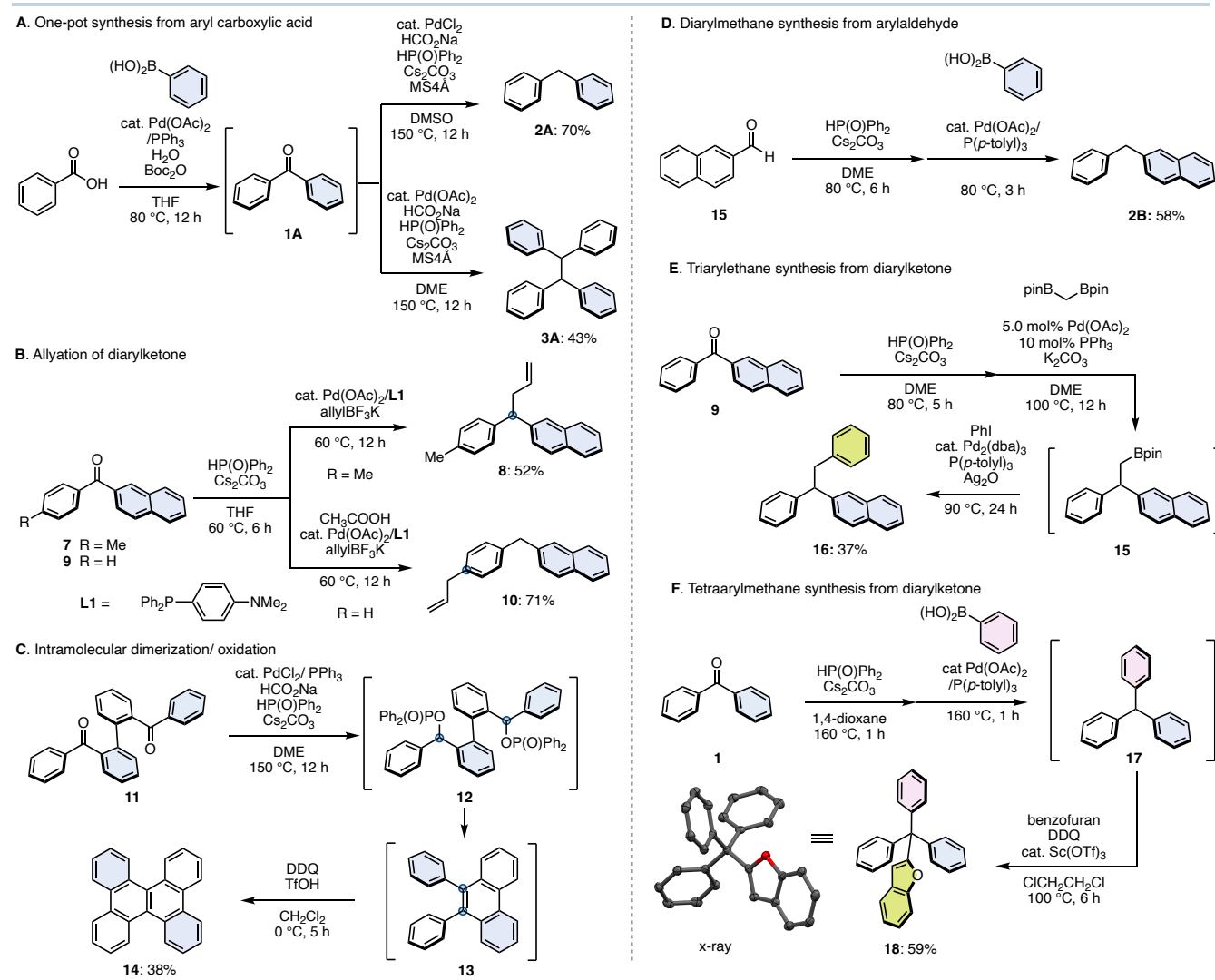
■ CONCLUSION

In summary, we developed a unified synthesis of multiply arylated alkanes from diarylketones. The key for this reaction is the ready generation of diarylphosphinates from diarylketones with diphenylphosphine oxide *via* a *phospha*-Brook rearrangement.

Using this method, we have succeeded in synthesizing five different types of multiply arylated alkanes from diarylketones in a single step (one-pot). Expanding the range of nucleophiles for diarylphosphinates including enantioselective transformations is currently undergoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available.
Experimental procedures and spectroscopic data for compounds including ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra (PDF)

Accession Codes

CCDC 2121107 (**3A**), 2121108 (**3R**), and 2159413 (**18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

No competing financial interests have been declared.

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diarylketones → phosphinates → 63 examples

- **Diarylketones**: inexpensive, readily available common starting material
- **Five-types multiply arylated alkanes**: same protocol for the syntheses of diarylmethanes, tetraarylethanes, triarylmethanes, triarylethane, and tetraarylmethane
- **Phospha-Brook Rearrangement**: preparation (pseudo)halides in situ w/o metal cat.