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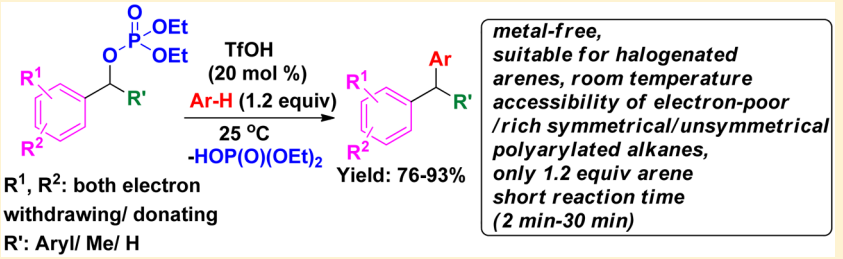
Benzylic Phosphates in Friedel–Crafts Reactions with Activated and Unactivated Arenes: Access to Polyarylated Alkanes

Gangaram Pallikonda and Manab Chakravarty*

Department of Chemistry, Birla Institute of Technology and Sciences, Pilani Hyderabad Campus, Jawahar nagar, Shameerpet Mandal, Hyderabad, Telangana 500078, India

Supporting Information



ABSTRACT: Easily reachable electron-poor/rich primary and secondary benzylic phosphates are suitably used as substrates for Friedel–Crafts benzylation reactions with only 1.2 equiv activated/deactivated arenes (no additional solvent) to access structurally and electronically diverse polyarylated alkanes with excellent yields and selectivities at room temperature. Specifically, diversely substituted di/triarylmethanes are generated within 2–30 min using this approach. A wide number of electron-poor polyarylated alkanes are easily accomplished through this route by just tuning the phosphates.

The Friedel–Crafts (FC) benzylation reaction[1] is one of the traditional synthetic protocols for polyarylated alkanes, a valuable structural motif in the field of pharmaceutical, biological, and material sciences.[2,3] The low reactivity, selectivity, and limitation for only electron-rich substrates and the need for harsh reaction conditions, including hazardous solvents/reagents, are the potential drawbacks for this route. The beneficial alternative source for functionalized polyarylated alkanes includes metal-catalyzed cross-coupling reactions.[4] Although these are all certainly remarkable processes, the major concerns are the necessity of solvents, expensive transition metals and their toxicities,[5] long duration, elevated temperature (60–140 °C), and special care for moisture/air sensitive organometallic reagents. Therefore, being much more economical, improvements of the FC reactions are still a priority.[1e] In this aspect, the practices of using different kinds of electrophilic species, such as benzyl alcohols,[6a,b,h] acetates,[6c] halides,[6d] ethers,[6e] *N*-sulfonyl aldimines or sulphonamido sulfones,[6f] and silyl ethers[6g] are attractive. Recently, significant advances in the FC reaction have been achieved using primary benzylic hydroxamates at moderate temperature by Bode et al.[7] Nevertheless, most of these methods are limited to the synthesis of mainly diarylalkanes in the presence of excess activated (majorly) arenes or solvents along with the aforementioned drawbacks. Being poor nucleophiles, arenes tend to undergo reactions only under heating and excess stoichiometry of arenes. Hence, such FC benzylation reactions only at rt are sporadically reported in the literature.[6a,d,g,h]

Therefore, with our current interest,[8] we present here both secondary and primary benzylic phosphates as easily accessible and unique substrates for the FC benzylation reactions to predominantly access electronically and structurally diverse triarylmethanes along with diaryl-ethanes and methanes at rt within a short duration using only 1.2 equiv of both activated or deactivated arenes. Moreover, in the literature, primary benzylic phosphates were known to be used in transition metal-catalyzed cross-coupling route to generate mainly diarylmethanes in the presence of solvents at 60–100 °C.[9] Notably, efforts to access diphenylethane via Suzuki–Miyaura cross coupling were unsuccessful by starting from secondary benzylic phosphate.[9a] In the very recent report, the cross-coupling of benzylic phosphate with bromobenzene was considered challenging due to the poor electrophilicity of phosphates.[9f] Indeed, the synthetic approach for diarylethanes and triarylmethanes using secondary benzylic phosphates is almost undeveloped.[9e] It is highly pertinent to note the pioneering work by Johnson et al. with a completely different target where α-aryl-α-ketophosphonates[10a] and α-hydroxy-β-phosphonyloxy esters[10b] were successfully used in (excess) acid-mediated nucleophilic substitution reactions to access a variety of α,α-diaryl ketones and α-hydroxy esters, respectively. However, only limited arenes in excess quantities were explored for these reactions in chlorinated solvent, and the minimum reaction duration was 1 h. Even though C–O and P–O bond cleavage for phosphate monoesters was extensively studied previously under both

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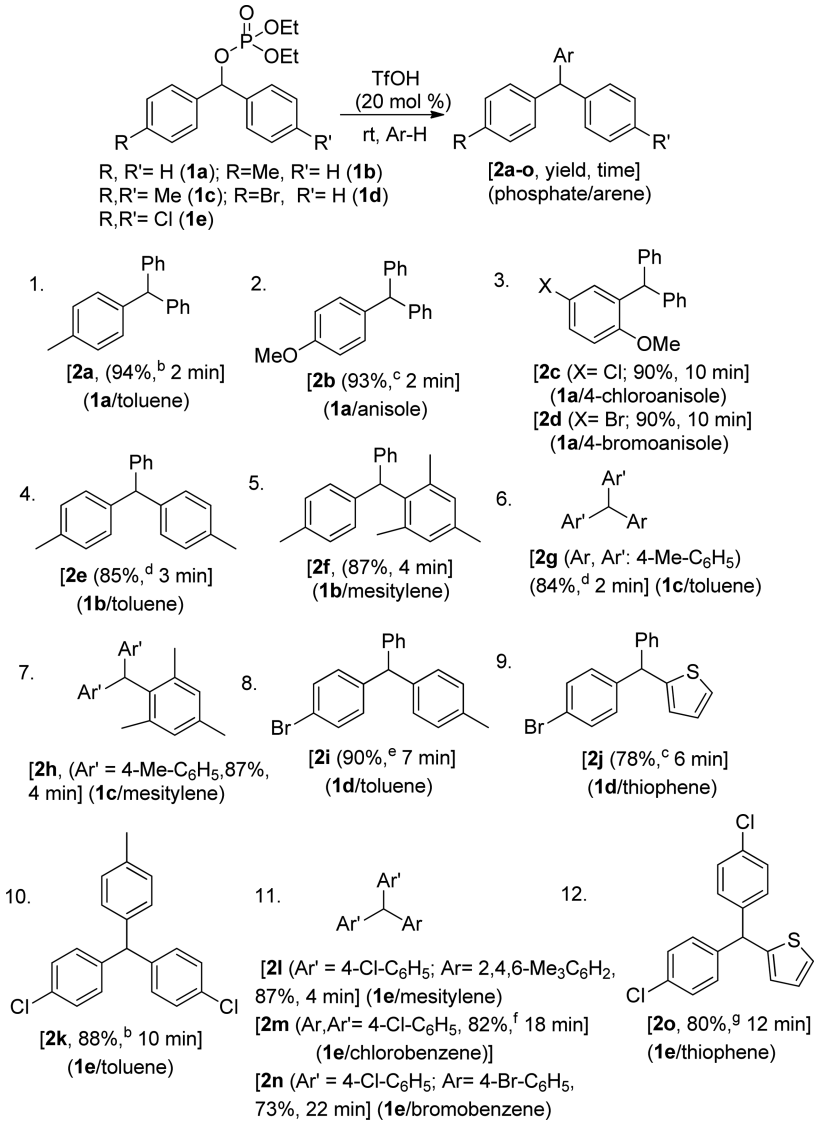
Table 1. List of Triarylmethanes Synthesized Using Phosphates[a]



[a]Reaction conditions: **1** (1 equiv), ArH (1.2 equiv) [e.g., **1a** (1.56 mmol), toluene (1.87 mmol), and TfOH (0.31 mmol)]; only for **2j** was 1,2-dichloroethane (DCE, 3 mL) used; regioisomeric (*p*/*o*) ratio (determined by ^{1}H NMR). [b]Ratio of 85:15. [c]Ratio of 87:13. [d]Ratio of 83:17. [e]Ratio of 84:16. [f]Ratio of 74:26. [g]Ratio of 92:8.

acidic and photochemical conditions,[11] surprisingly, these were not explored to date to accomplish polyarylated alkanes. More importantly, the route described herein can expediently afford electron-poor polyarylated methanes efficiently, which is not an expected outcome from the traditional FC benzylation reactions. Thus, one of the major drawbacks in the synthesis of electron-deficient polyarylated alkanes via the FC route has been circumvented using the electron-poor phosphates as a source of electrophiles that are comfortably prepared through phospha-Brook rearrangement (highly favorable for electron-poor systems). A much cleaner, economical, and less cumbersome process has been demonstrated by using a catalytic amount of triflic acid (TfOH) as a replacement of traditional metal chlorides.

Our recent protocol via *n*-BuLi triggered phospha-Brook rearrangement has made both electron-poor/rich primary and secondary benzylic phosphates easily reachable.[8d] Being mainly interested in triarylmethanes, we kept our focus on the FC-type benzylation reactions of the most inexpensive secondary benzylic phosphate **1a** with toluene (only 1.2 equiv) at rt to obtain desired product **2a** (entry 1, Table 1) under key reaction parameters, such as the variety of acid catalysts in different quantities and reaction times (Table S1). As the formation of the desired compound was satisfactory at rt, we could avoid the need for excess volatile arenes. In some cases, the formation of ether $Ph_2HC-O-CHPh_2$ was also observed as expected.[6g] Although there were many choices for the selection of Lewis or protic acids, the catalytic amount of TfOH (20 mol %, entry 9, Table S1) was selected for all of the reactions to afford desired products efficiently within a few minutes at rt. Moreover, TfOH was reported to be suitable for the FC reactions in the literature.[1f] Phosphate **1a** reacted with both anisole as well as nonactivated, halogenated anisoles to synthesize functionalized triarylmethanes **2b**−**d** in excellent yields and regioselectivity within 2−10 min (entries 2 and 3, Table 1).

In fact, halogenated compounds **2c** and **2d** could be utilized for further derivatization through well-known metal-catalyzed C−C or C−N coupling reactions.[12] The other electronically

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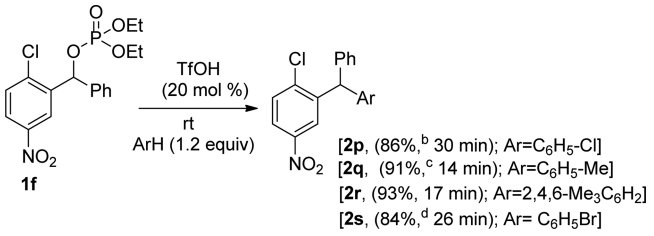
different phosphates **1b−e** are used to access a wide range of triarylmethanes. We have experienced the instability of mainly electron-rich secondary benzylic phosphates **1b** and **c** that tend to form diaryl alcohols or ethers during the purification through column chromatography (SiO_2). However, without purification, both of these phosphates are successfully used in the benzylation reactions to generate **2e−h** (entries 4−7, Table 1) appreciably within 2−4 min. Notably, both unsymmetrical and symmetrical crowded triarylmethanes **2f** and **2h** are completely new and synthesized comfortably using this approach at rt. Further, we have extended the scope of this route by using stable phosphates **1d** and **1e**, where benzylation of **1d** afforded the synthetically unexplored triarylmethanes **2i** and **2j** satisfactorily (entries 8 and 9, Table 1), and electronically diverse triarylmethanes **2k−o** (entries 10−12, Table 1) were generated conveniently within 6−22 min from a benzylation reaction of **1e**. It is worth noting that being weakly inactive groups, syntheses of such electronically deactivated triarylmethanes **2i−o** are considerably challenging using the traditional FC route.

Next, we moved toward the benzylation reaction of much electron-poorer, easily synthesized, inexpensive, and stable phosphate **1f** that afforded unsymmetrical triarylmethanes **2p−s** within 30 min (Scheme 1) in a similar fashion. These highly

Scheme 1. Reactions of Phosphate 1f with Arenes including Chlorobenzene with Regioisomeric Ratios Determined by ^{1}H NMR

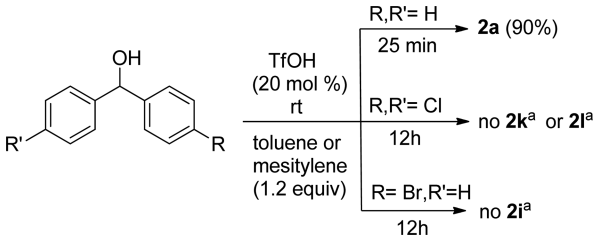


[b]Ratio *p/o*, 74:26. [c]Ratio *p/o/m*, 82:14:4. [d]Ratio *p/o/m*, 83:12:5.

functionalized unsymmetrical triarylmethanes **2p−s** are completely new and challenging to achieve within this short reaction time at rt.[13] Thus, these reactions offer a time-saving path to obtain a large number of unsymmetrical and electron-poor triarylmethanes in a simple, economic, and convenient manner.

For establishing the role of phosphate as an electrophile, a few of the above-mentioned reactions were repeated using the corresponding diarylmethanols in place of phosphates as shown in Scheme 2. Although compound **2a** was obtained successfully

Scheme 2. Reactions of Diarylmethanols with Arenes[a]

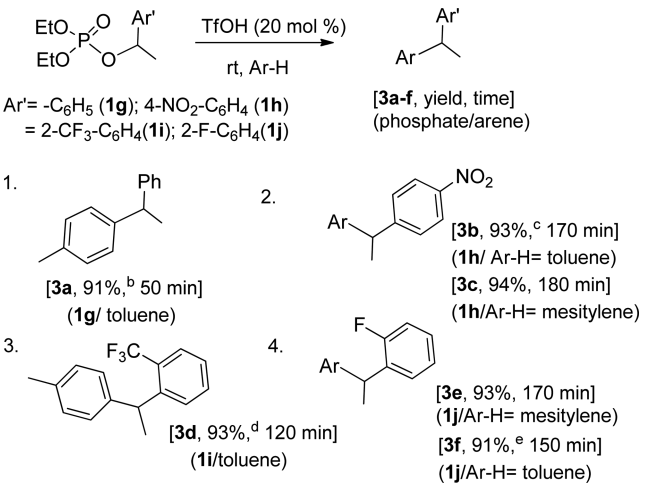


[a]No reaction at rt, but upon heating at 60 °C for 6 h, the respective ether formation was observed.

within 25 min [longer reaction time in comparison to phosphate], the halogen-substituted triarylmethanes, such as **2k−l** or **2i**, were not reachable by starting with these unfunctionalized diarylmethanols. Under similar conditions, compounds **2p−s** were also not formed even after 12 h when (2-chloro-5-nitrophenyl)(phenyl)methanol was treated with arenes. Thus, the necessity of phosphate as a leaving group is very important for this strategy.

As synthesis of diarylethane from the Pd-catalyzed cross-coupling reaction of **1g** with $PhB(OH)_2$ was unfruitful,[9a] we attempted to synthesis such alkanes by starting with conveniently synthesized electronically diverse secondary benzylic phosphates **1g−j**. To our delight, the expected diarylethanes **3a−f** (Table 2) were generated appreciably at

Table 2. List of Synthesized Diarylethanes Using Phosphates[a]



[a]Reaction conditions: **1** (1 equiv), ArH (1.2 equiv) [e.g., **1g** (1.94 mmol), toluene (2.32 mmol and TfOH (0.39 mmol)]; regioisomeric ratio (*p/o*) (determined by ^{1}H NMR). [b]Ratio of 83:17. [c]Ratio of 67:33. [d]Ratio of 82:18. [e]Ratio of 86:14.

rt, although the reaction time was somewhat longer (50−180 min). This reflects that these phosphates are comparatively less reactive toward the arenes under similar reaction conditions [TfOH (20 mol %)/rt, 1.2 equiv of arenes]. Although only toluene or mesitylene were chosen as arenes, the phosphates **1h−j** are significantly electron-poor systems due to the presence of a strong deactivating group, such as $-NO_2$, -F, or $-CF_3$. The required timings for the synthesis of **3b−f** indicate that the reactivities of the phosphates **1h−j** are very much comparable to each other. The electron-poor, structurally diverse diarylethanes **3c−f** are unknown in the literature and most likely difficult to access through the FC route by using other electrophilic species. Therefore, these phosphates have opened a new door as an electrophile to access such electron-poor diarylethanes successfully. Highly relevant compounds (diarylalkanes) are synthesized by Lei et al. by $ZnCl_2$-mediated benzylation of secondary benzyltrifluoroacetate with highly air sensitive arylzinc reagent using toluene as solvent at 50 °C for 24 h.[4c]

Although the syntheses of diarylmethanes are very well established,[1e,6] we planned to examine the approachability of diarylmethanes using a few limited primary benzylic phosphates **1k−n** under these reaction conditions. The diarylmethanes bearing weakly activated (**4a−c**) and deactivated (**4d−e**)

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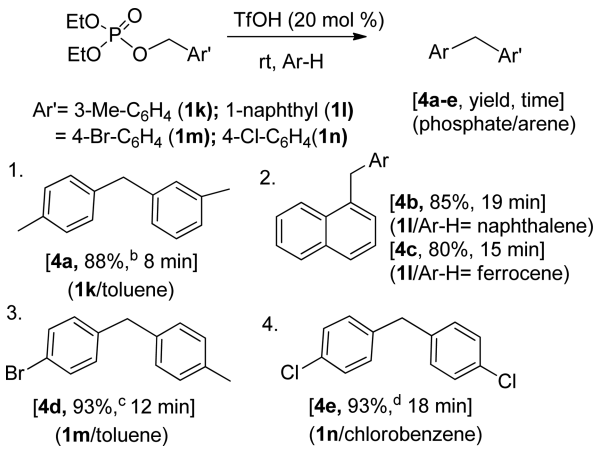
benzene rings were conveniently synthesized at rt within 8−18 min (Table 3), and hence, these phosphates are essentially

Table 3. List of Synthesized Diarylmethanes Using Phosphates[a]



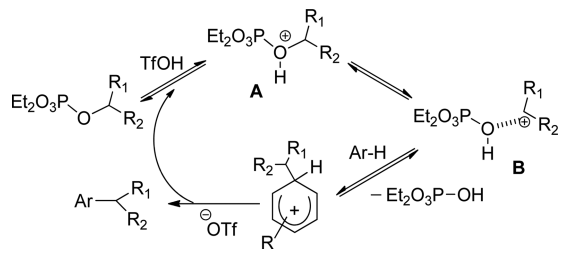
[a]Reaction conditions: **1** (1 equiv), Ar′H (1.2 equiv) [e.g., **1k** (1.94 mmol), toluene (2.32 mmol), and TfOH (0.39 mmol)] only for **4b** and **c**. DCE (3 mL) was used; regioisomeric ratio (*p*/*o*) (determined by ^{1}H NMR). [b]Ratio of 62:38. [c]Ratio of 61:39. [d]Ratio of 64:36.

efficient substrates for the synthesis of a variety of diarylmethanes. 1-Naphthylphosphate **1l** was recently used for the Pd-catalyzed cross-coupling reaction to produce the polycyclic diarylmethanes,[9e] and inspired by these outcomes, useful polycyclic di(1-naphthylmethane) **4b**[14] was synthesized in pure isomeric form (entry 2, Table 3). In addition, we could also conveniently synthesize diarylmethane **4c** in which ferrocene was connected with 1-naphthalene (entry 2, Table 3).

We could not separate some of these polyarylated alkanes in pure isomeric form from the regioisomeric mixture due to the minute difference in polarity for these isomers that are highly nonpolar in nature.

On the basis of experimental results and related literature reports,[10] these reactions presumably proceed via a carbocationic intermediate as shown in Scheme 3. The formation of

Scheme 3. Plausible Reaction Mechanism for the FC Reactions of Benzylic Phosphates



products with strongly deactivating substituents can apparently be justified by the formation of relatively stable species of type **B** through **A**. There is no considerable solvent effect to stabilize intermediate **B**. However, a strong ion-dipole interaction between the cation and phosphate (leaving group) may lead to an improvement in the optimum stability of **B** to facilitate the FC-type benzylation reactions of such electrophiles with deactivating group(s) as well as unactivated arenes within a short period of time.

In conclusion, easy access of electron-poor/rich primary and secondary benzylic phosphates via favorable phospha-Brook rearrangement has opened a new entry to access structurally and electronically diverse polyarylated alkanes at room temperature in excellent yields and selectivities via the Friedel−Crafts benzylation reactions. This reaction was operated in the presence of triflic acid as catalyst using only 1.2 equiv of activated or deactivated arenes (including haloarenes) at room temperature. No additional solvents were entertained. Moreover, the reaction was complete within 2−30 min to access di- and triarylmethanes, and thus, this method offers a time-saving approach toward these alkanes.

EXPERIMENTAL SECTION

General Comments. Organic extracts were dried over anhydrous sodium sulfate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (100−200 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F254 (0.25 mm). ^{1}H, ^{13}C, and ^{31}P NMR spectra (^{1}H, 400 or 500 MHz; ^{13}C, 101 or 126 MHz; ^{31}P, 162 or 201 MHz) were recorded using a 400 or 500 MHz spectrometer in $CDCl_3$ with shifts referenced to $SiMe_4$ (δ = 0) or 85% H_3PO_4 (δ = 0). IR spectra were recorded on an FT-IR spectrophotometer. Melting points were determined using a local hot-stage melting point apparatus and are uncorrected. Phosphates are prepared using our developed procedures.[8d] Phosphates **1b**, **1c**, and **1f** were freshly prepared and used without further purification or isolation.

General Procedure for Synthesis of Polyarylated Methanes from Phosphates. Trifluoromethanesulfonic acid (0.027 mL, 0.31 mmol) was added dropwise to a solution of phosphate **1a** (0.500 g, 1.56 mmol) and toluene (0.198 mL, 1.87 mmol) at room temperature, and the mixture was stirred until the phosphate disappeared (by TLC). The reaction was quenched with water, and the required compounds were extracted with EtOAc (3 × 25 mL). The combined organic layer was washed with brine, dried with Na_2SO_4, and then evaporated under reduced pressure. The residue was purified with flash column chromatography (EtOAc/hexane = ∼1:99) to give triarylmethane **2a**. Unless otherwise stated, all other triaryl/diaryl methanes and diarylethanes are synthesized using similar molar quantities (quantities are mentioned with respect to 0.500 g of phosphate) of the respective phosphates in a manner similar to the synthesis of **2a**. In the case of solid arenes, such as naphthalene and ferrocene, 1,2-dichloroethane (DCE, 3 mL) was used, and dichloromethane was used for the extraction followed by purification through column chromatography. ***Caution!*** *DCE is currently considered a potential cancer-inducing agent.*

Spectroscopic Data for Triarylmethanes. *(p-Tolylmethylene)-dibenzene (**2a**).*[6h] The reaction mixture was stirred for 2 min to form a viscous liquid; yield 94% (0.38 g). The other regioisomer (*ortho*) was also present in 15% along with this sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3H), 5.71 (s, 1H), 7.26−7.30 (m, 2H), 7.32−7.35 (m, 6H), 7.39−7.43 (m, 2H), 7.44−7.46 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.2, 56.5, 126.3, 128.4, 129.1, 129.4, 129.5, 135.9, 141.0, 144.2.

*((4-Methoxyphenyl)methylene)dibenzene (**2b**).*[6h] The reaction mixture was stirred for 2 min using anisole (0.203 mL, 1.87 mmol) to form a viscous liquid; yield 93% (0.39 g). The other regioisomer (*ortho*) was also present in 13% along with this sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 5.56 (s, 1H), 6.87−6.89 (m, 2H), 7.07−7.09 (m, 2H), 7.16−7.18 (m, 4H), 7.26−7.28 (m, 2H), 7.32−7.35 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.2, 56.1, 113.7, 126.3, 128.3, 129.4, 130.4, 136.2, 144.3, 158.1.

*((4-Chloro-2-methoxyphenyl)methylene)dibenzene (**2c**).*[15] The reaction mixture was stirred for 10 min using 4-chloroanisole (0.229 mL, 1.87 mmol) to form a white solid; mp 118−120 °C (lit 120 °C);[3] yield 90% (0.43 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 5.94 (s, 1H), 6.84 (d, J = 8.7 Hz, 1H), 6.89 (d, J = 2.1 Hz, 1H), 7.13−7.15 (m, 4H), 7.21−7.23 (m, 1H), 7.27−7.28 (m, 2H), 7.31−7.35 (m, 4H);

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J. Org. Chem. 2016, 81, 2135−2142

^{13}C NMR (101 MHz, $CDCl_3$) δ 49.6, 55.9, 111.9, 125.4, 126.4, 127.4, 128.4, 129.4, 130.2, 134.7, 143.1, 155.8.

((4-Bromo-2-methoxyphenyl)methylene)dibenzene (**2d**).[16] The reaction mixture was stirred for 10 min using 4-bromoanisole (0.234 mL, 1.87 mmol) to form a white solid; mp 128−130 °C (lit 133 °C);[4b] yield 90% (0.49 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 5.94 (s, 1H), 6.79 (d, J = 8.8 Hz, 1H), 7.02−7.03 (m, 1H), 7.13−7.15 (m, 4H), 7.25−7.31 (m, 2H), 7.34−7.38 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 49.6, 55.8, 112.5, 112.9, 126.4, 128.3, 129.4, 130.4, 133.0, 135.1, 143.1, 156.3.

4,4′-(Phenylmethylene)bis(methylbenzene) (**2e**).[13a] Trifluoromethanesulfonic acid (0.026 mL, 0.29 mmol), phosphate **1b** (0.500 g, 1.49 mmol), and toluene (0.19 mL, 1.79 mmol) were used. The reaction mixture was stirred for 3 min to form a viscous liquid; yield 85% (0.34 g). The other regioisomer (*ortho*) was also present in 17% along with this sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 6H), 5.58 (s, 1H), 7.06−7.12 (m, 4H), 7.29−7.38 (m, 7H), 7.35−7.38 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.1, 56.1, 126.2, 128.3, 129.1, 129.3, 129.4, 135.7, 141.1, 144.3.

1,3,5-Trimethyl-2-(phenyl(p-tolyl)methyl)benzene (**2f**). Trifluoromethanesulfonic acid (0.026 mL, 0.29 mmol), phosphate **1b** (0.500 g, 1.49 mmol), and mesitylene (0.25 mL, 1.79 mmol) were used. The reaction mixture was stirred for 4 min to form a viscous liquid; yield 87% (0.39g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20 (s, 6H), 2.47 (s, 3H), 2.51 (s, 3H), 6.16 (s, 1H), 7.04 (s, 2H), 7.19−7.20 (m, 2H), 7.26−7.36 (m, 4H), 7.37−7.41 (m, 1H), 7.43−7.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.0, 21.2, 22.2, 50.8, 125.9, 128.3, 129.1, 129.4 (merged with other signal), 130.3, 135.5, 136.1, 137.4, 137.7, 139.4, 143.1; LC/MS m/z 300 $[M]^+$. Anal. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.76; H, 8.15.

Tri-p-tolylmethane (**2g**).[17] Trifluoromethanesulfonic acid (0.025 mL, 0.28 mmol), phosphate **1c** (0.500 g, 1.43 mmol), and toluene (0.18 mL, 1.72 mmol) were used. The reaction mixture was stirred for 2 min to form a viscous liquid; yield 84% (0.34 g). The other regioisomer (*ortho*) was also present in 17% along with this sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 9H), 5.62 (s, 1H), 7.18 (d, J = 8.0 Hz, 6H), 7.25 (d, J = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.2, 55.9, 129.1, 129.4, 135.8, 141.5.

4,4′-(Mesitylmethylene)bis(methylbenzene) (**2h**). Trifluoromethanesulfonic acid (0.025 mL, 0.28 mmol), phosphate **1c** (0.500 g, 1.43 mmol), and mesitylene (0.24 mL, 1.72 mmol) were used. The reaction mixture was stirred for 4 min to form a white solid; mp 88−90 °C; yield 87% (0.39 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16, (s, 6H), 2.43 (s, 3H), 2.47 (s, 6H), 6.09 (s, 1H), 6.99 (s, 2H), 7.13−7.15 (m, 4H), 7.20−7.22(m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.9, 21.1, 22.1, 50.4, 128.9, 129.3, 130.2, 135.4, 135.9, 137.5, 137.7, 139.8. Anal. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.29; H, 8.58.

1-Bromo-4-(phenyl(p-tolyl)methyl)benzene (**2i**). Trifluoromethanesulfonic acid (0.022 mL, 0.25 mmol), phosphate **1d** (0.500 g, 1.25 mmol), and toluene (0.159 mL, 1.51 mmol) were used for this reaction. The reaction mixture was stirred for 7 min to form a viscous liquid; yield 90% (0.38 g). The other regioisomer (*ortho*) was also present in 16% along with this sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 5.54 (s, 1H), 7.05−7.07 (m, 4H), 7.16−7.18 (m, 4H), 7.29−7.31 (m, 1H), 7.34−7.38 (m, 2H), 7.46 (d, J = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.1, 55.9, 120.3, 126.5, 128.4, 129.2, 129.3, 129.4, 131.2, 131.4, 136.1, 140.4, 143.3, 143.6; LC/MS m/z 336 $[M]^+$, 338 $[M+2]^+$. Anal. Calcd for $C_{20}H_{17}Br$: C, 71.23; H, 5.08. Found: C, 71.15; H, 5.14.

2-((4-Bromophenyl)(phenyl)methyl)thiophene (**2j**). Trifluoromethanesulfonic acid (0.022 mL, 0.25 mmol), phosphate **1d** (0.500 g, 1.25 mmol), and thiophene (0.12 mL, 1.51 mmol) were used. The reaction mixture was stirred for 6 min to form a viscous liquid; yield 78% (0.32 g). The other regioisomer was also present in 13% along with this sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (s, 1H), 6.72−6.73 (m, 1H), 6.97−6.99 (m, 1H), 7.12−7.14 (m, 2H), 7.22−7.25 (m, 3H), 7.29−7.31 (m, 1H), 7.33−7.37 (m, 2H), 7.45−7.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 51.6, 120.7, 124.8, 126.5, 126.7, 126.9, 128.6, 128.8, 130.6, 131.5, 142.9, 143.2, 147.2; LC/MS m/z 328 $[M]^+$. Anal. Calcd for $C_{17}H_{13}BrS$: C, 62.01; H, 3.98. Found: C, 62.15; H, 3.92.

4,4′-(p-Tolylmethylene)bis(chlorobenzene) (**2k**). Trifluoromethanesulfonic acid (0.022 mL, 0.25 mmol), phosphate **1e** (0.500 g, 1.28 mmol), and toluene (0.163 mL, 1.54 mmol) were used. The reaction mixture was stirred for 10 min to form a viscous liquid; yield 88% (0.37 g). The other regioisomer (*ortho*) was also present in 15% along with this sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 5.49 (s, 1H), 6.99−7.02 (m, 2H), 7.06−7.08 (m, 4H), 7.15−7.17 (m, 2H), 7.29−7.32 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.1, 55.1, 128.6, 129.2, 129.3, 130.7, 132.4, 136.4, 139.9, 142.2; LC/MS m/z 325 $[M^+ - 1]$. Anal. Calcd for $C_{20}H_{16}Cl_2$: C, 73.40; H, 4.93. Found: C, 73.31; H, 4.87.

4,4′-(Mesitylmethylene)bis(chlorobenzene) (**2l**).[18] Trifluoromethanesulfonic acid (0.022 mL, 0.25 mmol), phosphate **1e** (0.500 g, 1.28 mmol), and mesitylene (0.216 mL, 1.54 mmol) were used. The reaction mixture was stirred for 4 min to form a gummy solid; yield 87% (0.39g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 6H), 2.33 (s, 3H), 5.94 (s, 1H), 6.91 (s, 2H), 7.05 (d, J = 8.4 Hz, 4H), 7.28−7.29 (d, J = 8.4 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.8, 21.9, 49.9, 128.4, 130.4, 130.6, 131.9, 136.1, 136.6, 137.4, 140.6.

Tris(4-chlorophenyl)methane (**2m**).[19] Trifluoromethanesulfonic acid (0.022 mL, 0.25 mmol), phosphate **1e** (0.500 g, 1.28 mmol), and chlorobenzene (0.156 mL, 1.54 mmol) were used to form a gummy liquid. The reaction mixture was stirred for 18 min to yield 82% (0.36 g). The other isomer (*ortho*) was also present (26%) with this sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 (s, 1H), 7.04−7.06 (m, 6H), 7.30−7.33 (m, 6H); other peaks appeared at δ 5.95 (s), 6.90−6.95 (m), 7.12−7.14 (m), 7.23−7.25 (m), 7.38−7.45 (m) for the minor isomer. ^{13}C NMR (101 MHz, $CDCl_3$) δ 54.9, 128.7, 130.6, 132.7, 141.5; other peaks appeared at δ 52.2, 126.9, 128.3, 128.4, 128.8, 129.9, 130.1, 130.2, 130.8, 132.6, 140.6 for the minor isomer.

4,4′-((4-Bromophenyl)methylene)bis(chlorobenzene) (**2n**). Trifluoromethanesulfonic acid (0.023 mL, 0.26 mmol), phosphate **1e** (0.500 g, 1.28 mmol), and bromobenzene (0.162 mL, 1.54 mmol) were used. The reaction mixture was stirred for 22 min to form a gummy liquid; yield 73% (0.36 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (s, 1H), 7.05 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.5 Hz, 4H), 7.34−7.37 (m, 4H), 7.49−7.52 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.1, 120.9, 128.8, 130.7, 131.1, 131.8, 132.8, 141.4, 142.0. Anal. Calcd for $C_{19}H_{13}BrCl_2$: C, 58.20; H, 3.34. Found: C, 58.36; H, 3.41.

2-(Bis(4-chlorophenyl)methyl)thiophene (**2o**). Trifluoromethanesulfonic acid (0.028 mL, 0.25 mmol), phosphate **1e** (0.500 g, 1.28 mmol), and thiophene (0.123 mL, 1.55 mmol) were used. The reaction mixture was stirred for 12 min to form a viscous liquid; yield 80% (0.32 g). The other regioisomer was also present in 8% along with this sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.7 (s, 1H), 6.74−6.75 (m, 1H), 7.00 (m, 1H), 7.01−7.02 (m, 4H), 7.18−7.19 (m, 1H), 7.33−7.36 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 50.9, 125.1, 126.7, 126.8, 128.7, 130.2, 132.9, 141.9, 146.7; LC/MS m/z 318 $[M]^+$, 320 $[M + 2]^+$, 322 $[M + 4]^+$. Anal. Calcd for $C_{17}H_{12}Cl_2S$: C, 63.96; H, 3.79; S, 10.04. Found: C, 64.36; H, 4.10; S, 10.03.

1-Chloro-2-((4-chlorophenyl) (phenyl)methyl)-4-nitrobenzene (**2p**). Trifluoromethanesulfonic acid (0.022 mL, 0.25 mmol), phosphate **1f** (0.500 g, 1.25 mmol), and chlorobenzene (0.152 mL, 1.50 mmol) were used. The reaction mixture was stirred for 30 min to form a light yellow solid; mp 108−110 °C; yield 86% (0.38g). The other regioisomer was also present in 26% along with this sample. IR (KBr, cm^{-1}) 1519, 1342; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (s, 1H), 7.03−7.10 (m, 4H), 7.33−7.39 (m, 5H), 7.61 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 2.8 Hz, 1H), 8.10 (dd, J = 8.0 Hz, 2.8 Hz, 1H); peaks appeared at δ 6.31 (s), 6.87−6.89 (m), 7.23−7.28 (m), 7.44−7.47 (m), 7.62 (d, J = 8.7 Hz), 7.76 (d, J = 2.8 Hz), 8.09−8.13 (m) for other isomers. ^{13}C NMR (101 MHz, $CDCl_3$) δ 52.9, 123.0, 125.7, 127.5, 128.9, 129.6, 130.1, 130.6, 130.7, 134.6, 140.5, 141.4, 141.8, 146.6, 146.7; peaks at δ 50.9, 125.3, 127.1, 128.8, 128.9, 129.3, 129.5, 130.7, 130.8, 133.1, 139.1, 139.2, 139.5, 142.7, 143.3 were observed for other isomers. Anal. Calcd for $C_{19}H_{13}Cl_2NO_2$: C, 63.71; H, 3.66; N, 3.91. Found: C, 63.85; H, 3.61; N, 3.86.

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*1-Chloro-4-nitro-2-(phenyl(p-tolyl)methyl)benzene (**2q**).* Trifluoromethanesulfonic acid (0.022 mL, 0.25 mmol), phosphate **1f** (0.500 g, 1.25 mmol), and toluene (0.159 mL, 1.50 mmol) were used. The reaction mixture was stirred for 14 min to form a white solid; mp 90−92 °C; yield 91% (0.38g); other regioisomers were observed with the ratio (*p/o/m* 82:14:4) in this sample. IR (KBr, cm^{-1}) 1516, 1343, 1046; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 5.85 (s, 1H), 6.87 (d, J = 8.1 Hz, 2H), 6.97 (d, J = 12 Hz,2H), 7.04 (d, J = 8.1 Hz, 2H), 7.19−7.25 (m, 3H), 7.45 (d, J = 5.0 Hz, 1H), 7.76 (d, J = 2.8 Hz, 1H), 7.94−7.96 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.1, 53.5, 122.7, 125.7, 126.2, 129.3, 129.5, 129.6, 130.6, 130.9, 137.9, 139.5, 141.4, 141.5, 144.1, 146.6; the other peaks appeared at δ 19.7, 50.6, 122.8, 125.8, 127.1, 127.3, 127.5, 128.7, 128.8, 128.9, 129.2, 136.6, 136.9, 141.2, 143.7 due to other isomers. Anal. Calcd for $C_{20}H_{16}ClNO_2$: C, 71.11; H, 4.77; N, 4.15. Found: C, 71.22; H, 4.71; N, 4.23.

*2-((2-Chloro-5-nitrophenyl) (phenyl)methyl)-1,3,5-trimethylbenzene (**2r**).* Trifluoromethanesulfonic acid (0.022 mL, 0.25 mmol), phosphate **1f** (0.500 g, 1.25 mmol), and mesitylene (0.21 mL, 1.50 mmol) were used. The reaction mixture was stirred for 17 min to form a light yellow solid; mp 126−128 °C; yield 93% (0.42g). IR (KBr, cm^{-1}) 1596, 1512, 1343; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 6H), 2.33 (s, 3H), 6.17 (s, 1H), 6.92 (s, 2H), 7.02 (d, J = 8.8 Hz, 2H), 7.28−7.36 (m, 3H), 7.61 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 2.4 Hz, 1H), 8.12 (dd, J = 8.0 Hz, 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.9, 22.0, 49.8, 122.7, 126.5, 126.8, 128.7 (merged with other carbon), 130.4, 130.6, 134.4, 136.9, 137.3, 140.2, 142.1, 142.9, 146.7. Anal. Calcd for $C_{22}H_{20}ClNO_2$: C, 72.22; H, 5.51; N, 3.83. Found: C, 72.15; H, 5.58; N, 3.79.

*2-((4-Bromophenyl) (phenyl)methyl)-1-chloro-4-nitrobenzene (**2s**).* The reaction mixture was stirred for 26 min to form a light yellow gummy solid; yield 84% (0.42g); other regioisomers with the ratio (*p/o/m* 83:12:5) were observed in this sample. IR (KBr, cm^{-1}) 1523, 1345, 1046; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (s, 1H), 6.96 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.32−7.39 (m, 3H), 7.47 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 2.8 Hz, 1H), 8.11 (dd, J = 8.0, 2.8 Hz, 1H); other isomers appeared at δ 5.78 (s, 0.06H), 6.25 (s. 0.15H), 6.85−6.87 (m, 0.16H), 7.17−7.21 (m, 0.16H), 7.30−7.432 (m), 7.60 (d, J = 8.8 Hz), 7.63−7.65 (m, 0.16H), 7.72 (d, J = 2.8 Hz, 0.16H), 8.07−8.12 (m, 0.16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 52.9, 121.2, 122.9, 125.6, 127.4, 128.9, 129.2, 130.8, 131.0, 131.9, 140.0, 140.3, 141.4, 143.2, 146.6; the other minor peaks at δ 123.3, 125.3, 127.6, 128.6, 128.9, 129.6, 133.6, 139.3, 140.7 appeared due to other isomers. Anal. Calcd for $C_{19}H_{13}BrClNO_2$: C, 56.67; H, 3.25; N, 3.48. Found: C, 56.73; H, 3.21; N, 3.52.

Spectroscopic Data for Diarylethanes. *1-Methyl-4-(1-phenylethyl)benzene (**3a**).*[6g] Trifluoromethanesulfonic acid (0.034 mL, 0.39 mmol), phosphate **1g** (0.500 g, 1.94 mmol) and toluene (0.246 mL, 2.32 mmol) were used. The reaction mixture was stirred for 50 min viscous liquid; yield 91% (0.34 g). The other regioisomer (*ortho*) was also present in 17% along with this sample. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (d, J = 7.2 Hz, 3H), 2.38 (s, 3H), 4.20 (q, J ∼7.0 Hz, 1H), 7.17−7.18 (m, 3H), 7.19−7.20 (m, 1H), 7.23−7.24 (m, 1H), 7.29−7.30 (m, 2H), 7.33−7.37 (m, 2H); other peaks at δ 1.67−1.69 (m), 2.31 (s), 4.40 (q, J = 7.0 Hz), 7.16 (br), 7.24 (br), 7.37 (br) were due to minor isomer. ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.0, 21.9, 44.4, 125.9, 127.5, 127.6, 128.4, 129.1, 135.5, 143.5, 146.7; other isomer peaks appeared at δ 19.8, 22.2, 41.0, 125.8, 126.1, 126.14, 126.7, 127.7, 128.3, 130.4, 136.1, 143.9, 146.3.

*1-Methyl-4-(1-(4-nitrophenyl)ethyl)benzene (**3b**).*[20] Trifluoromethanesulfonic acid (0.029 mL, 0.33 mmol), phosphate **1h** (0.500 g, 1.65 mmol), and toluene (0.209 mL, 1.98 mmol) were used. The reaction mixture was stirred for 170 min to form a viscous liquid; yield 93% (0.37 g); isolated as a mixture of regioisomers 67:33 (*p/o*). The peaks due to other isomers were not separable by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (d, J = 7.2 Hz, 3H), 1.66 (d, J = 7.2 Hz, 1.5H), 2.23 (s, 1.5 H), 2.35 (s, 3H), and 4.24 (q, J = 7.2 Hz, 1H), 4.44 (q, J = 7.2 Hz, 0.5H), 7.10−7.27 (m, 5H), 7.27−7.28 (m, 1H), 7.32−7.34 (m, 1H), 7.38−7.40 (m, 2H), 8.14−8.17 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.0, 21.6, 44.4, 123.7, 127.4, 128.4, 129.4, 130.7, 136.3, 141.6, 154.4; other regioisomer peaks are observed at δ 19.8, 21.8, 41.1, 124.6, 126.4, 126.6, 126.8, 127.5, 128.4, 128.8, 136.0, 142.2, 154.1.

*1,3,5-Trimethyl-2-(1-(4-nitrophenyl)ethyl)benzene (**3c**).* Trifluoromethanesulfonic acid (0.029 mL, 0.33 mmol), phosphate **1h** (0.500 g, 1.65 mmol), and mesitylene (0.276 mL, 1.98 mmol) were used. The reaction mixture was stirred for 180 min to form a yellow solid; mp 172−174 °C; yield 94% (0.41 g). IR (KBr, cm^{-1}) 1523, 1448, 1344. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (d, J = 7.2 Hz, 3H), 2.15 (s, br, 6H), 2.32 (s, 3H), 4.72 (q, J ∼7.2 Hz, 1H), 6.9 (s, 2H), 7.38 (d, J = 9.0 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 16.9, 20.8, 21.1, 38.3, 123.4, 127.7, 130.3, 136.2, 136.3, 138.7, 145.9, 153.8. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.86; H, 7.06; N, 5.28.

*1-(1-(p-Tolyl)ethyl)-2-(trifluoromethyl)benzene (**3d**).* Trifluoromethanesulfonic acid (0.027 mL, 0.31 mmol), phosphate **1i** (0.500 g, 1.53 mmol), and toluene (0.19 mL, 1.84 mmol) were used. The reaction mixture was stirred for 120 min to form a viscous liquid; yield 93% (0.37 g). The other regioisomer (*ortho*) was also present in 18% along with this sample. Other isomer signals were not separable. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (d, J ∼7.1 Hz, 3H), 2.40 (s, 3H), 4.80 (q, J ∼7.0 Hz, 1H), 7.18−7.21 (m, 2H), 7.25−7.27 (m, 2H), 7.32−7.35 (m, 2H), 7.47−7.50 (m, 1H), 7.72 (d, J = 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.0, 22.2, 39.1 (q, J = 1.8 Hz), 125.6 (q, J = 5.9 Hz), 125.9, 126.5 (q, J = 35.0 Hz), 127.6, 127.1 (q, J = 259.1 Hz), 129.1, 129.8, 132.1, 135.8, 142.1, 146.5 (d, J = 1.3 Hz). Anal. Calcd for $C_{16}H_{15}F_3$: C, 72.71; H, 5.72. Found: C, 72.81; H, 5.65.

*2-(1-(2-Fluorophenyl)ethyl)-1,3,5-trimethylbenzene (**3e**).* Trifluoromethanesulfonic acid (0.032 mL, 0.36 mmol), phosphate **1j** (0.500 g, 1.81 mmol), and mesitylene (0.303 mL, 2.17 mmol) were used. The reaction mixture was stirred for 170 min to form a white solid; yield 93% (0.40 g); mp 98−100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (d, J = 7.4 Hz, 3H), 2.53 (s, 6H), 2.58 (s, 3H), 5.08 (q, J = 7.3 Hz, 1H), 7.14 (s, 2H), 7.21−7.26 (m, 1H), 7.39−7.49 (m, 2H), 7.72−7.74 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 17.3, 21.0, 21.3, 34.3 (d, J = 1.5 Hz), 115.5 (d, J = 1.5 Hz), 123.7 (d, J = 3.5 Hz), 127.7 (d, J = 8.2 Hz), 129.2 (d, J = 4.8 Hz), 130.5, 132.4 (d, J = 13.7 Hz), 135.6, 136.3 138.9, 161.8 (d, J = 245.2 Hz). Anal. Calcd for $C_{17}H_{19}F$: C, 84.26; H, 7.90. Found: C, 84.38; H, 8.04.

*1-Fluoro-2-(1-(p-tolyl)ethyl)benzene (**3f**).* Trifluoromethanesulfonic acid (0.032 mL, 0.36 mmol), phosphate **1j** (0.500 g, 1.81 mmol), and toluene (0.23 mL, 2.17 mmol) were used.The reaction mixture was stirred for 150 min to form a viscous liquid; yield 91% (0.35 g). The other regioisomer (*ortho*) was also present in 14% along with this sample. The signals in ^{1}H NMR for the minor isomer were merged with the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (d, J = 7.0 Hz, 0.48 H minor isomer), 2.00 (d, J = 7.2 Hz, 3H), 2.62 (s, 0.48H minor isomer), 2.68 (s, 3H), 4.87 (q, J ∼7.2 Hz, 1H), 5.06 (q, J = 7.2 Hz, 0.16H), 7.32−7.42 (m, 2.5H), 7.46−7.50 (m, 3H), 7.54−7.59 (m, 3.6H), 7.69−7.70 (m, 0.2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.1, 21.3, 37.6 (d, J = 2.6 Hz), 115.7 (d, J = 22.5 Hz), 124.4 (d, J = 3.6 Hz), 127.8, 127.9 (d, J = 8.2 Hz), 128.8 (d, J = 4.5 Hz), 129.5, 133.9 (d, J = 14.4 Hz), 135.9, 142.4, 160.9 (d, J = 245.4 Hz). Peaks at δ 19.7, 21.0, 34.1 (d, J = 2.6 Hz), 115.4 (d, J = 22.3 Hz), 124.4 (d, J = 3.6 Hz), 126.5 (d, J = 28.8 Hz), 126.8, 127.8 (d, J = 3.8 Hz), 128.8 (d, J = 245.4 Hz), 129.4, 130.83, 130.84, 133.9 (d, J = 14.4 Hz), 136.4, 143.1 appeared for the other isomer. Anal. Calcd for $C_{15}H_{15}F$: C, 84.08; H, 7.06. Found: C, 84.23; H, 7.12.

Spectroscopic Data for Diarylmethanes. *1-Methyl-3-(4-methylbenzyl)benzene (**4a**).*[9e] Trifluoromethanesulfonic acid (0.034 mL, 0.39 mmol), phosphate **1k** (0.500 g, 1.94 mmol), and toluene (0.246 mL, 2.32 mmol) were used. The reaction mixture was stirred for 8 min to form a viscous liquid; yield 88% (0.33 g). The other regioisomer (*ortho*) was also present in 38% along with this sample. Some signals for both isomers were not clearly distinguished. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53, 2.58, 2.586, 2.59 (4s, 9.6H), 4.18 (s, 2H), 4.22 (s, 1.2H minor), 7.20−7.29 (m, 4.8H), 7.34−7.39 (m, 4H), 7.395−7.47 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 19.9 (minor), 21.3, 21.69, 21.7 (minor), 41.8, 126.1, 126.2, 126.3, 126.7, 126.9, 127.0, 128.5, 128.6, 129.0, 129.4, 129.8, 129.9, 130.2, 130.5, 135.7, 136.8, 138.1, 138.2, 138.5, 139.3, 140.6, 141.6.

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Di(naphthalen-1-yl)methane (**4b**).[21] Trifluoromethanesulfonic acid (0.03 mL, 0.34 mmol), phosphate **1l** (0.500 g, 1.70 mmol), and naphthalene (0.26 g, 2.04 mmol) were used. The reaction mixture was stirred for 19 min; yield 85% (0.38 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.9 (s, 2H), 7.13 (d, J = 7.1 Hz, 2H), 7.37−7.40 (m, 2H), 7.51−7.54 (m, 4H), 7.81 (d, J = 8.2 Hz, 2H), 7.94−7.96 (m, 2H), 8.07−8.09 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 35.7, 123.9, 125.6, 125.7, 126.1, 127.1, 127.14, 128.8, 132.2, 133.8, 136.2.

(Naphthalen-1-ylmethyl)ferrocene (**4c**).[22] Trifluoromethanesulfonic acid (0.03 mL, 0.34 mmol), phosphate **1l** (0.500 g, 1.70 mmol), and ferrocene (0.379 g, 2.04 mmol) were used. The reaction mixture was stirred for 15 min to form an orange solid; mp: 98−100 °C; yield 80% (0.44 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (m, 2H), 4.17 (m, 2H), 4.19 (s, 5H),4.21 (s, 2H), 7.29−7.3 (m, 1H), 7.4−7.43 (m,1H), 7.51−7.55(m, 2H), 7.74−7.76 (m, 1H), 7.87−7.89 (m, 1H), 8.12−8.14 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 33.2, 67.1, 67.4, 68.8, 69.1, 123.9, 125.5, 125.54, 125.8, 126.1, 126.8, 128.7, 131.9, 133.7, 137.8. This compound was isolated with 90% purity.

1-Bromo-4-(4-methylbenzyl)benzene (**4d**).[9c] Trifluoromethanesulfonic acid (0.027 mL, 0.31 mmol), phosphate **1m** (0.500 g, 1.55 mmol), and toluene (0.197 mL, 1.86 mmol) were used. The reaction mixture was stirred for 12 min to form a viscous liquid; yield 93% (0.37 g). The other regioisomer (*ortho*) was also present in 39% along with this sample. Some signals for both the isomers were not separable. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 2.1H minor), 2.46 (s, 3H), 4.01 (s, 2H), 4.05 (s, 1.4H minor), 7.10−7.13 (m, 1.6H), 7.16−7.19 (m, 4H), 7.23−7.25 (m, 2H), 7.29−7.31 (m, 2H), 7.50−7.53 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 19.8 (minor), 21.2, 39.0 (minor), 41.0, 119.9, 120.0, 126.3, 126.8, 128.9, 129.4, 130.0, 130.58, 130.6, 130.8, 131.59, 131.6, 135.9, 136.7, 137.5, 138.4, 139.5, 140.6.

Bis(4-chlorophenyl)methane (**4e**).[7] Trifluoromethanesulfonic acid (0.027 mL, 0.31 mmol), phosphate **1n** (0.500 g, 1.79 mmol), and chlorobenzene (0.217 mL, 2.16 mmol) were used. The reaction mixture was stirred for 18 min to form a viscous liquid; yield 93% (0.39 g). The other regioisomer (*ortho*) was also present in 36% along with this sample. Some signals for both the isomers were not separable. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 2H), 4.11 (s, 1.12 H minor), 7.12 (d, J = 8.4 Hz, 4H), 7.29 (d, J = 8.4H, 4H), 7.14−7.24 (m, 2.8H), 7.28−7.31 (m, 0.9H), 7.33−7.43 (m, 1.36H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 40.6, 128.7, 130.2, 132.2, 139.0; peaks at δ 38.6, 126.5, 126.9, 127.9, 128.6, 129.7, 130.3, 130.9, 132.18, 138.0, 138.2 were observed for other isomers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02441.

Spectral data for all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: manabchakravarty@gmail.com.

Notes

The authors declare no competing financial interest.

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