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One-Step Synthesis of Triphenylphosphonium Salts from (Het)arylmethyl Alcohols

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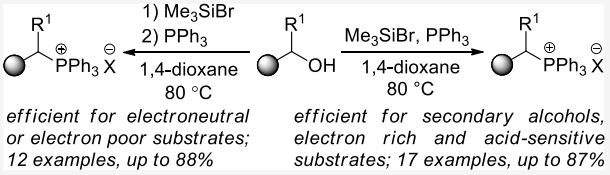
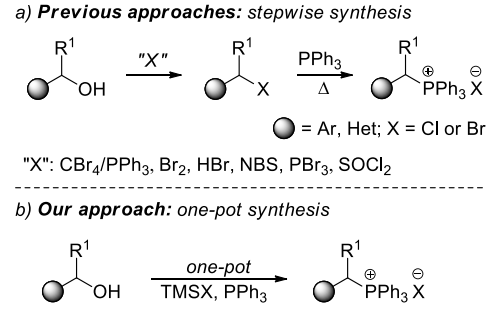
ABSTRACT: Two approaches for the synthesis of substituted phosphonium salts from easily available benzyl alcohols and their heterocyclic analogs have been developed. The developed protocols are complementary: the direct mixing of alcohol, trimethylsilyl bromide, and triphenylphosphine in 1,4-dioxane followed by heating at 80 °C was found to be more efficient for acid-sensitive substrates, such as salicyl or furfuryl alcohols as well as secondary benzyl alcohols, while a *one-pot* procedure including sequential addition of trimethylsilyl bromide and triphenylphosphine gave higher yields for benzyl alcohols bearing electroneutral or electron-withdrawing substituents.



Phosphonium salts are an important class of organic compounds that are intensively used in both laboratory and industry. For example, they have been applied for the development of solar cells,[1] corrosion inhibitors,[2] lubricants,[3] supercapacitors,[4] and various ionic liquids.[5] Moreover, phosphonium salts are widely used in modern synthetic practice as key starting reagents for the Wittig reaction, which is a powerful tool for the construction of the C=C bond,[6] arylating[7] and alkylating[8] agents, phase-transfer catalysts for asymmetric transformations,[9] etc.

Phosphonium salts are typically obtained via reaction of phosphines with appropriate organic halides, which are aggressive and uncomfortable to work with, the more reactive ones being more irritating. That is why the development of other methods for phosphine alkylation with stable and safe precursors has been an important challenge for many years. The most attractive approach for the solution to this problem is the use of alcohols which can be transformed into phosphonium salts by two-step procedures including alcohol-to-halide transformation with various halogenation reagents (PBr_3,[10] NBS,[11] Br_2,[12] HBr,[13] CBr_4/PPh_3,[14] $SOCl_2$,[15] etc.) followed by phosphine alkylation (Scheme 1). However, some problems, such as (1) the application of aggressive halogenating agents, (2) the isolation and purification of irritating, allergenic, and often carcinogenic organic halides, and (3) the increased formation of waste products remain unsolved. It is also important that the use of harsh bromination conditions does not allow involvement of sensitive starting materials and is often accompanied by low selectivity of halogenation. Therefore, the development of mild protocols for the synthesis of various phosphonium salts from stable and easy to handle precursors is an important and urgent task.[16]

Scheme 1. Previous Approaches and Concept of This Work



Herein, we report two advantageous protocols for the synthesis of phosphonium salts based on the reaction of substituted alcohols with triphenylphosphine and halosilanes.

We began our investigation by searching for a mild bromination reagent. Halosilanes were chosen, as they are abundant and easy to handle halogenating agents.[17] We found that the treatment of starting benzyl alcohol **1a** in 1,4-dioxane with trimethylsilyl bromide (TMSBr) with heating (80 °C, 8 h) smoothly afforded the benzyl bromide. We assumed that the intermediate benzyl bromide does not need to be isolated from the reaction mixture since the formed byproducts will not interfere with the formation of the phosphonium salt **2a**. Indeed, the product **2a** was obtained in 84% yield upon

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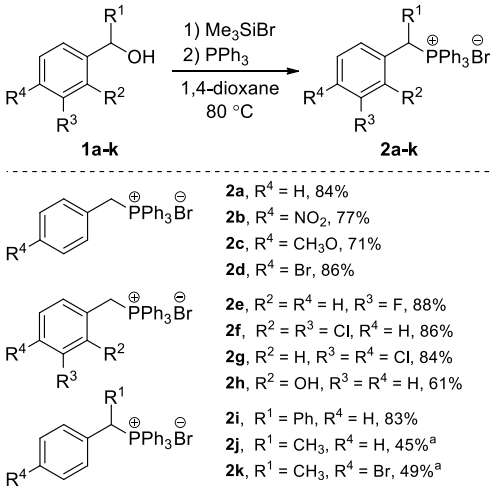
addition of PPh_3 followed by heating the reaction mixture at 80 °C for 12 h.

We found that by using this *one-pot* protocol the benzyl alcohols **1a−g**, containing several functionalities in the aromatic ring, such as alkoxy, hydroxy, halogen, and nitro groups, could be converted to the desired phosphonium salts **2a−g** in high yields (Scheme 2). The slightly reduced yield of

Scheme 2. Scope of the *One-Pot* Protocol for the Synthesis of Phosphonium Salts 2



[a]Equal amounts of the corresponding styrenes were also formed.

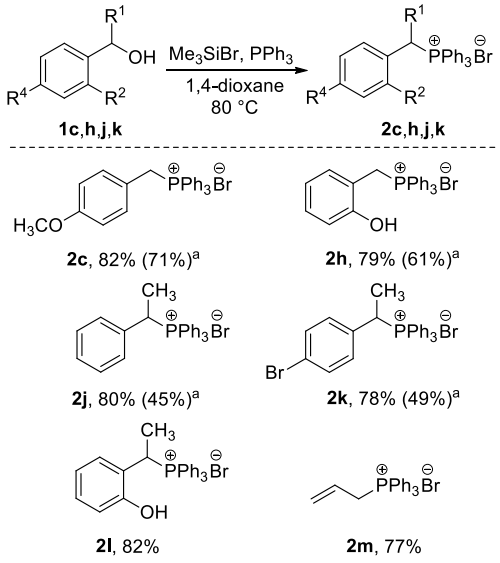
2h was presumably explained by the partial dehydration of starting salicyl alcohol **1h** with generation of highly reactive *o*-quinone methide, which is involved in diverse side processes.

We showed also that the developed protocol was suitable for the synthesis of *sec*-alkyl triphenylphosphonium salts. In particular, using benzhydrol **1i**, the corresponding salt was obtained in a high yield. Nevertheless, in the case of α-methylbenzyl alcohols **1j,k** the desired products **2j,k** were formed in moderate yield, while the formation of an equal amount of the corresponding styrenes was also observed.

The formation of styrenes as side products in the reactions of **1j,k** can be explained by the intermediacy of a secondary benzyl cation during the alcohol to alkyl bromide transformation. Presumably, in a nonpolar solvent, the bromide ion exists predominantly in bound form that lowers its reactivity. This problem is absent for neutral phosphines which are known to be a highly nucleophilic species.[18] Based on these considerations, we assumed that the target phosphonium salts can be synthesized via direct attack of triphenylphosphine on the Me_3SiBr-activated alcohol by adding trimethylsilyl bromide to the mixture of alcohol and phosphine. Indeed, the target salts **2j,k** were obtained in high yields and the formation of side styrenes was not observed (Scheme 3).

In addition, we showed that this protocol was more efficient for alcohols **1c,h**, producing the salts **2c,h** in 82% and 79% yields, while using the *one-pot* procedure, these products were obtained in 71% and 61% yields, respectively. It is noteworthy, that α-methyl-2-hydroxybenzyl alcohol **1l** was transformed into the corresponding phosphonium salt **2l** in high yield despite **1l** being both a secondary alcohol and prone to the formation of *ortho*-quinone methide. Moreover, under these conditions allyl alcohol **1m** produced phosphonium salt **2m** in very good yield. It should be noted that the use of the developed protocol for

Scheme 3. Synthesis of Phosphonium Bromides 2



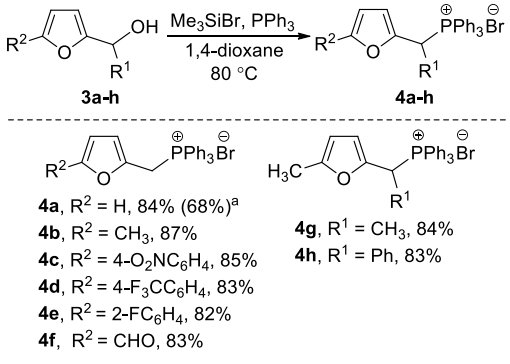
[a]One-pot protocol yields are given in parentheses.

the synthesis of phosphonium salts **2** bearing electron-withdrawing substituents is associated with some peculiarities. Namely, in reactions of halogen-containing starting materials, we observed slightly decreased yields of the desired salts, while alcohol **1b** with a highly electron-deficient nitro group afforded the desired product **2b** in trace amount only.

Next, we proceeded in the synthesis of various furfurylphosphonium salts using the developed protocols. It should be noted that the synthesis of substituted furfuryl phosphonium salts is a challenging task due to the high acidic sensitivity of furan derivatives, including furfuryl alcohols.[19] As a result, the common halogenating reagents (PBr_3, HBr, Br_2/PPh_3) afford furfuryl bromides in moderate to good yields.[20] In addition, the purification and storage of the intermediate furfuryl bromides is complicated by its autocatalytic degradation and very irritating nature.[21]

Therefore, we investigated a *one-pot* procedure and found that the sequential treatment of solution of furfuryl alcohol **3a** in 1,4-dioxane at 80 °C with Me_3SiBr and PPh_3 led to the desired phosphonium salt **4a** in 68% yield. However, the best result was achieved when a mixture of furfuryl alcohol **3a**, Me_3SiBr, and PPh_3 was heated at 80 °C in 1,4-dioxane (Scheme 4). The lower yield of the phosphonium salt **4a** in the

Scheme 4. Synthesis of Furfurylphosphonium Bromides 4



[a]One-pot protocol yield is given in parentheses.

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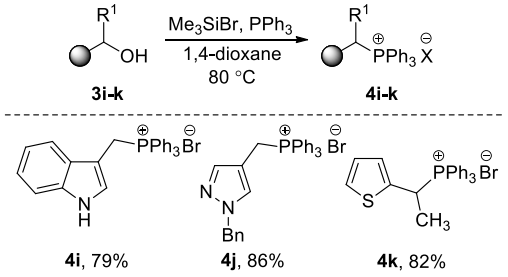
one-pot synthesis is presumably associated with the partial decomposition of furfuryl bromide during the slow second step of **4a** synthesis (6 h).

Using the found reaction conditions, we synthesized a series of furfurylphosphonium salts **4a−h** (Scheme 4). Namely, 5-methyl- and 5-aryl-substituted furfuryl alcohols **3b−e**, 5-(hydroxymethyl)furfural **3f**, and α-methyl- and α-phenylfurfuryl alcohols **3g,h** were smoothly converted to the corresponding phosphonium salts **4** in 82−87% yields.

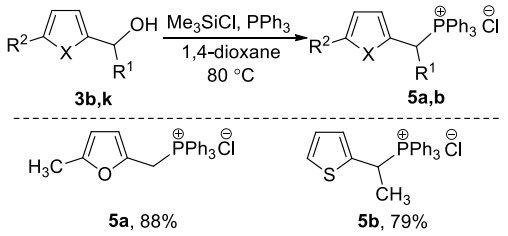
Moreover, we showed that other heterocycle-substituted alcohols, such as indol-3-yl- **1i**, *N*-benzylpyrazol-4-yl- **1j**, and α-phenyl-2-thienylmethanol **1k**, could be efficiently converted to the corresponding phosphonium salts **2i−k** (Scheme 5).

Scheme 5. Synthesis of (Hetarylmethyl)phosphonium Bromides 4



Next, we tested Me_3SiCl as a halogenating agent and found that the developed protocol allowed for obtaining phosphonium chlorides **5a,b** in high yields from the corresponding alcohols **3b,k** (Scheme 6).

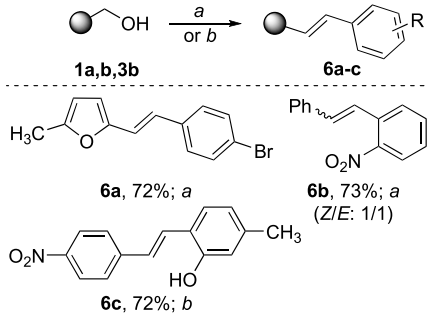
Scheme 6. Synthesis of Phosphonium Chlorides 5a,b



Finally, we compared the developed protocols with related method based on the use of triphenylphosphine hydrobromide.[22] We found that these methods produced the desired benzyltriphenylphosphonium bromides **2c,d** containing the electron-donating methoxy group and bromine atom, respectively, as well as furfuryl phosphonium bromide **4b** in similar yields (84−86% using $Ph_3P{\cdot}HBr$). However, when 4-nitrobenzyl alcohol **1b** was used, the yield of the desired salt **2b** dramatically dropped to 5% when triphenylphosphine hydrobromide was applied. The obtained results are in a good agreement with the literature data, which describe that $PPh_3{\cdot}HBr$ under mild conditions reacts only with alcohols that generate stable carbocations.[23] In addition, the disadvantages of $PPh_3{\cdot}HBr$ include the impossibility of using secondary (and, presumably, tertiary) alcohols, since in this case dehydration occurs predominantly.[22,23]

Most often, phosphonium salts are synthesized for further application as key starting compounds for the Wittig olefination; therefore, we decided to realize the synthesis of a substituted alkenes. Initially, we synthesized the phosphonium salts **4b** and **2a**, and then we added 4-bromobenzaldehyde or 2-nitrobenzaldehyde and NaOMe to the resulting reaction mixture and isolated the desired alkenes **6a,b** in 72% or 73% yield respectively (Scheme 7). Moreover, we

Scheme 7. Synthesis of Substituted Styrenes 6a−c[a]



[a](a) Me_3SiBr, PPh_3, 1,4-dioxane, 80 °C, then aldehyde, NaOMe 1,4-dioxane, 5 °C → rt; (b) Me_3SiBr, 1,4-dioxane, 80 °C, then PPh_3 1,4-dioxane, 80 °C, then aldehyde, NaOMe, 1,4-dioxane, 5 °C → rt.

synthesized stilbene **6c** in good yield via sequential treatment of starting 4-nitrobenzyl alcohol **1b** with Me_3SiBr in 1,4-dioxane under heating, then with PPh_3, and finally with 4-methylsalicylaldehyde and NaOMe. The obtained results demonstrates the attractiveness of the developed protocols not only for the synthesis of various phosphonium salts but also for the preparation of substituted styrenes.

In conclusion, we have developed two environment- and user-friendly protocols for the synthesis of substituted phosphonium salts. The first one is designed for the transformation of various benzyl alcohols and hetarylmethanols into the corresponding phosphonium salts. Another protocol allows phosphonium salts to be obtained from the sensitive starting compounds, such as furfuryl or salicyl alcohols. Both developed protocols are based on the reaction of starting alcohols, trialkylhalosilanes, and triphenylphosphine in 1,4-dioxane upon heating. The developed protocols complement each other and allow for the synthesis of a wide range of phosphonium salts, including those containing electron-withdrawing groups. Finally, we have performed a *one-pot* synthesis of an alkene via preparation of phosphonium salt and subsequent Wittig olefination, which highlights the practical importance of the developed protocol for synthetic needs.

EXPERIMENTAL SECTION

General Information. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance III HD 400 (400 MHz for ^1H and 100 MHz for ^{13}C NMR) spectrometer at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, ^1H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; [D_6] DMSO, ^1H: δ = 2.50 ppm, ^{13}C: δ = 39.52 ppm). Coupling constants (J) are given in Hertz. Splitting patterns of an apparent multiplets associated with an averaged coupling constants were designated as s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet), dd (doublet of doublets), and br (broadened). High-resolution mass measurements were carried out using a Bruker UHR-TOF Maxis (Electro Spray Ionization/Time of Flight) mass spectrometer. GC/MS analysis was performed on a Thermo Trace 1300. Melting points were determined with a Stuart SMP 30. Column chromatography was performed on silica gel Macherey Nagel (40−63 μm). All the reactions were carried out using freshly distilled and dry solvents from solvent stills. The starting benzyl alcohols **1a−l**, allyl alcohol **1m**, furfuryl alcohols **3a,b,f**,

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and (1*H*-indol-3-yl)methanol **3i** are commercially available substances. The starting furfuryl alcohols **3c−e,g,h**, (1-benzyl-1*H*-pyrazol-4-yl)methanol **3j** and 1-(thiophen-2-yl)ethan-1-ol **3k** were obtained according to the described procedures.[24]

General Procedure for the *One-Pot* Synthesis of Phosphonium Salts 2. To a solution of benzyl alcohol **1** (10 mmol) in 1,4-dioxane (20 mL) bromotrimethylsilane (1.58 mL, 12 mmol) was added dropwise, and the resulting mixture was stirred at 80 °C for 10−24 h. Upon full conversion of the starting alcohol **1** (GC/MS control), PPh_3 was added, and the reaction mixture was stirred for an additional 4−8 h at 80 °C. The reaction mixture was cooled to 5−10 °C, and the formed precipitate was filtered, washed with 1,4-dioxane, and dried in air. The products were recrystallized from EtOH.

*Benzyltriphenylphosphonium Bromide (**2a**).*[25] Yield: 3.64 g, 84%; white solid, mp 298−300 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97−7.85 (m, 3H), 7.81−7.63 (m, 12H), 7.35−7.25 (m, 1H), 7.26−7.18 (m, 2H), 6.99 (d, J = 7.1 Hz, 2H), 5.25 (d, J = 15.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 135.1 (d, J = 2.8 Hz, 3C), 134.0 (d, J = 9.9 Hz, 6C), 130.8 (d, J = 5.6 Hz, 2C), 130.1 (d, J = 12.4 Hz, 6C), 128.8 (d, J = 3.1 Hz, 2C), 128.3 (d, J = 3.6 Hz), 128.0 (d, J = 8.7 Hz), 117.8 (d, J = 85.5 Hz, 3C), 28.1 (d, J = 47.3 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{25}H_{22}P^+$ 353.1454; found 353.1457.

*(4-Nitrobenzyl)triphenylphosphonium Bromide (**2b**).*[26] Yield: 3.68 g, 77%; yellow solid, mp 273−275 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.10 (d, J = 8.2 Hz, 2H), 7.97−7.88 (m, 3H), 7.83−7.69 (m, 12H), 7.29 (dd, J = 8.2, 2.1 Hz, 2H), 5.52 (d, J = 16.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 147.3 (d, J = 4.3 Hz), 136.2 (d, J = 8.6 Hz), 135.3 (d, J = 2.7 Hz, 3C), 134.1 (d, J = 10.1 Hz, 6C), 132.1 (d, J = 5.4 Hz, 2C), 130.2 (d, J = 12.6 Hz, 6C), 123.8 (d, J = 3.0 Hz, 2C), 117.3 (d, J = 86.0 Hz, 3C), 28.0 (d, J = 47.0 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{25}H_{21}PNO_2^+$ 398.1304; found 398.1317.

*(4-Methoxybenzyl)triphenylphosphonium Bromide (**2c**).*[25] Yield: 3.28 g, 71%; white solid, mp 248−250 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.96−7.85 (m, 3H), 7.79−7.63 (m, 12H), 6.91 (dd, J = 8.5, 2.1 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 5.18 (d, J = 15.1 Hz, 2H), 3.68 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 159.1 (d, J = 3.7 Hz), 135.0 (d, J = 2.6 Hz, 3C), 134.0 (d, J = 9.8 Hz, 6C), 132.0 (d, J = 5.3 Hz, 2C), 130.1 (d, J = 12.3 Hz, 6C), 119.1 (d, J = 8.6 Hz), 117.9 (d, J = 85.1 Hz, 3C), 114.2 (d, J = 2.8 Hz, 2C), 55.1, 27.4 (d, J = 46.6 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{26}H_{24}OP^+$ 383.1559; found 383.1567.

*(4-Bromobenzyl)triphenylphosphonium Bromide (**2d**).* Yield: 4.38 g, 86%; white solid, mp 233−235 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.91−7.85 (m, 3H), 7.81−7.63 (m, 12H), 7.44 (d, J = 8.0 Hz, 2H), 6.96 (dd, J = 8.0, 2.2 Hz, 2H), 5.32 (d, J = 15.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 135.1 (d, J = 2.7 Hz, 3C), 134.0 (d, J = 9.9 Hz, 6C), 132.9 (d, J = 5.5 Hz, 2C), 131.7 (d, J = 3.0 Hz, 2C), 130.1 (d, J = 12.5 Hz, 6C), 127.5 (d, J = 8.6 Hz), 121.8 (d, J = 4.8 Hz), 117.6 (d, J = 85.6 Hz, 3C), 27.5 (d, J = 46.9 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{25}H_{21}PBr^+$ 431.0559; found 431.0564.

*(3-Fluorobenzyl)triphenylphosphonium Bromide (**2e**).*[27] Yield: 3.96 g, 88%; white solid, mp 312−314 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.95−7.89 (m, 3H), 7.82−7.68 (m, 12H), 7.30 (dd, J = 14.5, 7.6 Hz, 1H), 7.22−7.05 (m, 1H), 6.88 (d, J = 7.5 Hz, 1H), 6.79 (d, J = 9.9 Hz, 1H), 5.34 (d, J = 15.9 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.7 (dd, J = 244.8, 3.7 Hz), 135.2 (d, J = 2.8 Hz, 3C), 134.0 (d, J = 10.0 Hz, 6C), 130.8 (dd, J = 5.1, 3.2 Hz), 130.7 (d, J = 8.4 Hz), 130.1 (d, J = 12.5 Hz, 6C), 127.0 (dd, J = 5.5, 2.7 Hz), 117.7 (dd, J = 22.4, 5.6 Hz, 3C), 117.6 (d, J = 85.7 Hz), 115.2 (dd, J = 20.6, 3.7 Hz), 27.7 (d, J = 46.4 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{25}H_{21}PF^+$ 371.1359; found 371.1365.

*(2,3-Dichlorobenzyl)triphenylphosphonium Bromide (**2f**).* Yield: 4.31 g, 86%; white solid, mp 268−270 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97−7.89 (m, 3H), 7.84−7.61 (m, 13H), 7.34−7.25 (m, 1H), 7.20 (d, J = 7.5 Hz, 1H), 5.33 (d, J = 15.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 135.4 (d, J = 2.8 Hz, 3C), 134.0 (d, J = 10.1 Hz, 6C), 133.2 (d, J = 6.2 Hz), 132.7 (d, J = 3.5 Hz), 131.0 (d, J = 4.2 Hz, 2C), 130.2 (d, J = 12.6 Hz, 6C), 128.8 (d, J = 8.5 Hz), 128.5 (d, J = 3.4 Hz), 116.9 (d, J = 85.7 Hz, 3C), 27.5 (d, J = 48.6 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{25}H_{20}PCl_2^+$ 421.0674; found 421.0681.

*(3,4-Dichlorobenzyl)triphenylphosphonium Bromide (**2g**).* Yield: 4.21 g, 84%; white solid, mp 311−313 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.96−7.88 (m, 3H), 7.81−7.71 (m, 12H), 7.54 (d, J = 8.2 Hz, 1H), 7.13 (br s, 1H), 7.07 (d, J = 8.2 Hz, 1H), 5.39 (d, J = 15.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) 135.2 (d, J = 2.7 Hz, 3C), 134.1 (d, J = 10.0 Hz, 6C), 132.7 (d, J = 5.4 Hz), 131.2 (d, J = 4.5 Hz), 131.1 (d, J = 3.7 Hz), 130.9, 130.8 (d, J = 3.1 Hz) 130.2 (d, J = 12.5 Hz, 6C), 129.2 (d, J = 8.5 Hz), 117.3 (d, J = 85.8 Hz, 3C), 27.1 (d, J = 47.2 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{25}H_{20}PCl_2^+$ 421.0674; found 421.0681.

*(2-Hydroxybenzyl)triphenylphosphonium Bromide (**2h**).* Yield: 2.73 g, 61%; white solid, mp 246−248 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.79 (s, 1H), 7.92−7.83 (m, 3H), 7.77−7.62 (m, 12H), 7.17−7.04 (m, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 6.66−6.55 (m, 1H), 4.94 (d, J = 14.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 156.1 (d, J = 5.5 Hz), 134.9 (d, J = 2.7 Hz, 3C), 133.9 (d, J = 9.8 Hz, 6C), 131.6 (d, J = 5.2 Hz), 129.9 (d, J = 12.3 Hz, 6C), 129.8 (d, J = 3.5 Hz), 119.0 (d, J = 3.1 Hz), 118.4 (d, J = 85.1 Hz, 3C), 115.5 (d, J = 2.8 Hz), 113.7 (d, J = 8.7 Hz), 23.2 (d, J = 48.5 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{25}H_{22}PO^+$ 369.1403; found 369.1409.

*(Diphenylmethyl)triphenylphosphonium Bromide (**2i**).*[28] Yield: 4.22 g, 83%; white solid, mp 236−238 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.95−7.83 (m, 3H), 7.79−7.61 (m, 12H), 7.39−7.26 (m, 11H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 135.2 (d, J = 2.7 Hz, 3C), 134.6 (d, J = 9.3 Hz, 6C), 133.4 (d, J = 3.8 Hz, 2C), 130.3 (d, J = 6.8 Hz, 4C), 130.1 (d, J = 12.2 Hz, 6C), 129.2 (4C), 128.9 (d, J = 1.7 Hz, 2C), 117.8 (d, J = 82.4 Hz, 3C), 45.0 (d, J = 43.3 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{31}H_{26}P^+$ 429.1767; found 429.1776.

*(1-Phenylethyl)triphenylphosphonium Bromide (**2j**).*[29] Yield: 2.01 g, 45%; white solid, mp 230−232 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.96−7.84 (m, 3H), 7.82−7.65 (m, 12H), 7.37−7.30 (m, 1H), 7.30−7.22 (m, 2H), 7.00 (d, J = 7.5 Hz, 2H), 5.88 (dq, J = 14.3, 7.0 Hz, 1H), 1.71 (dd, J = 18.8, 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 135.0 (d, J = 2.7 Hz, 3C), 134.3 (d, J = 9.3 Hz, 6C), 133.7 (d, J = 5.2 Hz), 130.2 (d, J = 12.1 Hz, 6C), 129.7 (d, J = 5.8 Hz, 2C), 128.9 (d, J = 3.3 Hz), 128.8 (d, J = 2.2 Hz, 2C), 117.2 (d, J = 82.6 Hz, 3C), 33.9 (d, J = 43.6 Hz), 16.7. HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{26}H_{24}P^+$ 367.1610; found 367.1616.

*[1-(4-Bromophenyl)ethyl]triphenylphosphonium Bromide (**2k**).* Yield: 2.58 g, 49%; white solid, mp 218−220 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 77.95−7.88 (m, 3H), 7.80−7.72 (m, 12H), 7.49 (d, J = 8.2 Hz, 2H), 6.94 (dd, J = 8.2, 1.9 Hz, 2H), 5.88 (dq, J = 14.7, 7.2 Hz, 1H), 1.69 (dd, J = 18.7, 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 135.2 (d, J = 2.8 Hz, 3C), 134.3 (d, J = 9.3 Hz, 6C), 133.1 (d, J = 5.2 Hz), 131.8 (d, J = 2.8 Hz, 4C), 130.3 (d, J = 12.2 Hz, 6C), 122.3 (d, J = 4.0 Hz), 116.9 (d, J = 82.8 Hz, 3C), 33.2 (d, J = 44.1 Hz), 16.5. HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{26}H_{23}PBr^+$ 445.0715; found 445.0719.

General Procedure for the Synthesis of Phosphonium Salts 2,4. To a solution of alcohol **1** or **3** (10 mmol) in 1,4-dioxane (20 mL) were added bromotrimethylsilane (1.58 mL, 12 mmol) and PPh_3 (2.62 g, 10 mmol). The resulting mixture was stirred at 80 °C for 4−24 h until the starting alcohol was entirely consumed (GC/MS control). The reaction mixture was cooled to 5−10 °C, and the formed precipitate was filtered off, washed with 1,4-dioxane, and dried in air. The products were recrystallized from EtOH.

*(4-Methoxybenzyl)triphenylphosphonium Bromide (**2c**).*[25] Yield: 3.80 g, 82%. All spectral data are consistent with those described above.

*(2-Hydroxybenzyl)triphenylphosphonium Bromide (**2h**).* Yield: 3.54 g, 79%. All spectral data are consistent with those described above.

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*(1-Phenylethyl)triphenylphosphonium Bromide (**2j**).*[29] Yield: 3.56 g, 80%. All spectral data are consistent with those described above.

*[1-(4-Bromophenyl)ethyl]triphenylphosphonium Bromide (**2k**).* Yield: 4.10 g, 78%. All spectral data are consistent with those described above.

*[1-(2-Hydroxyphenyl)ethyl]triphenylphosphonium Bromide (**2l**).* Yield: 3.80 g, 82%; white solid, mp 158−160 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.13 (s, 1H), 7.93−7.88 (m, 3H), 7.75−7.69 (m, 6H), 7.68−7.60 (m, 6H), 7.21−7.11 (m, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.61−6.59 (m, 1H), 6.51 (d, J = 8.2 Hz, 1H), 5.47 (dq, J = 14.5, 7.3 Hz, 1H), 1.73 (dd, J = 18.6, 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.3 (d, J = 6.1 Hz), 135.0 (d, J = 2.8 Hz, 3C), 134.2 (d, J = 9.3 Hz, 6C), 130.1 (d, J = 12.1 Hz, 6C), 129.2 (d, J = 4.8 Hz), 119.6 (d, J = 5.0 Hz), 119.4 (d, J = 2.4 Hz), 117.6 (d, J = 82.4 Hz, 3C), 115.8 (d, J = 2.0 Hz), 66.4, 28.1 (d, J = 45.6 Hz), 16.7. HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{26}H_{24}PO^+$ 383.1559; found 383.1565.

*Triphenyl(prop-2-en-1-yl)phosphonium Bromide (**2m**).*[30] Yield: 2.95 g, 77%; white solid, mp 225−227 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.95−7.88 (m, 3H), 7.86−7.75 (m, 12H), 5.84−5.63 (m, 1H), 5.46−5.29 (m, 2H), 4.65 (dd, J = 16.7, 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 135.0 (d, J = 2.9 Hz, 3C), 133.8 (d, J = 10.0 Hz, 6C), 130.2 (d, J = 12.5 Hz, 6C), 125.0 (d, J = 13.4 Hz), 124.5 (d, J = 9.7 Hz), 118.2 (d, J = 85.8 Hz, 3C), 26.5 (d, J = 49.5 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{21}H_{20}P^+$ 303.1297; found 303.1298.

*(Furan-2-ylmethyl)triphenylphosphonium Bromide (**4a**).*[31] Yield: 3.55 g, 84%; beige solid, mp 274−276 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.93−7.89 (m, 3H), 7.82−7.65 (m, 12H), 7.59 (br s, 1H), 6.41 (br s, 1H), 6.16 (t, J = 3.2 Hz, 1H), 5.47 (d, J = 14.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 144.1 (d, J = 4.3 Hz), 141.8 (d, J = 11.0 Hz), 135.2 (d, J = 3.5 Hz, 3C), 133.8 (d, J = 10.5 Hz, 6C), 130.1 (d, J = 12.8 Hz, 6C), 117.9 (d, J = 86.1 Hz, 3C), 112.1 (d, J = 8.4 Hz), 111.4 (d, J = 3.8 Hz), 22.8 (d, J = 50.9 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{23}H_{20}OP^+$ 343.1246; found 343.1248.

*[(5-Methylfuran-2-yl)methyl]triphenylphosphonium Bromide (**4b**).*[32] Yield: 3.80 g, 87%; beige solid, mp 215−217 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97−7.93 (m, 3H), 7.82−7.64 (m, 12H), 6.05 (t, J = 3.4 Hz, 1H), 6.00 (br s, 1H), 5.38 (d, J = 14.5 Hz, 2H), 2.04 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 152.6 (d, J = 4.0 Hz), 139.6 (d, J = 11.3 Hz), 135.1 (d, J = 2.8 Hz, 3C), 133.8 (d, J = 10.1 Hz, 6C), 130.1 (d, J = 12.5 Hz, 6C), 118.0 (d, J = 85.8 Hz, 3C), 112.9 (d, J = 8.3 Hz), 107.3 (d, J = 3.2 Hz), 23.0 (d, J = 50.4 Hz), 13.0. HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{24}H_{22}OP^+$ 357.1403; found 357.1396.

*{[5-(4-Nitrophenyl)furan-2-yl]methyl}]triphenylphosphonium Bromide (**4c**).* Yield: 4.56 g, 85%; yellow solid, mp 286−288 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.20 (d, J = 8.8 Hz, 2H), 8.01−7.88 (m, 3H), 7.84−7.72 (m, 12H), 7.47 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 2.9 Hz, 1H), 6.53 (t, J = 3.4 Hz, 1H), 5.64 (d, J = 15.1 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 151.7 (d, J = 3.9 Hz), 146.1, 144.4 (d, J = 12.1 Hz), 135.3 (d, J = 2.7 Hz, 3C), 135.0 (d, J = 2.0 Hz), 133.9 (d, J = 10.2 Hz, 6C), 130.2 (d, J = 12.6 Hz, 6C), 124.4 (2C), 124.7 (2C), 117.9 (d, J = 86.0 Hz, 3C), 115.2 (d, J = 8.3 Hz), 111.4 (d, J = 3.1 Hz), 23.5 (d, J = 50.5 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{29}H_{23}NO_3P^+$ 464.1410; found 464.1428.

*({5-[4-(Trifluoromethyl)phenyl]furan-2-yl}methyl)triphenylphosphonium Bromide (**4d**).*[29] Yield: 4.70 g, 83%; white solid, mp 258−260 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98−7.91 (m, 3H), 7.83−7.73 (m, 12H), 7.70 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 3.0 Hz, 1H), 6.49 (t, J = 3.4 Hz, 1H), 5.61 (d, J = 15.0 Hz, 2H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 152.1 (d, J = 3.6 Hz), 143.2 (d, J = 12.0 Hz), 135.2 (d, J = 2.7 Hz, 3C), 133.9 (d, J = 10.2 Hz, 6C), 132.9, 130.2 (d, J = 12.6 Hz, 6C), 127.6 (q, J = 31.8 Hz), 125.8 (q, J = 3.6 Hz, 2C), 124.1 (q, J = 271.8 Hz, 2C), 123.6, 118.0 (d, J = 86.0 Hz, 3C), 114.7 (d, J = 8.3 Hz), 109.6 (d, J = 3.0 Hz), 23.4 (d, J = 50.4 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{30}H_{23}F_3OP^+$ 487.1433; found 487.1451.

*{[5-(2-Fluorophenyl)furan-2-yl]methyl}triphenylphosphonium Bromide (**4e**).* Yield: 4.23 g, 82%; white solid, mp 258−260 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.99−7.87 (m, 3H), 7.85−7.71 (m, 12H), 7.38−7.21 (m, 2H), 7.19−7.09 (m, 1H), 7.96−7.86 (m, 1H), 6.78 (br s, 1H), 6.47 (t, J = 3.4 Hz, 1H), 5.60 (d, J = 15.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.6 (d, J = 249.8 Hz), 147.8 (t, J = 3.2 Hz), 142.3 (d, J = 11.3 Hz), 135.2 (d, J = 2.8 Hz, 3C), 133.9 (d, J = 10.2 Hz, 6C), 130.1 (d, J = 12.6 Hz, 6C), 129.5 (d, J = 8.3 Hz), 125.2 (d, J = 2.3 Hz), 124.7 (d, J = 3.0 Hz), 117.9 (d, J = 86.0 Hz, 3C), 117.2 (dd, J = 12.0, 1.9 Hz), 116.2 (d, J = 21.0 Hz), 114.6 (d, J = 8.5 Hz), 111.3 (dd, J = 10.9, 2.9 Hz), 23.2 (d, J = 50.2 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{29}H_{23}FOP^+$ 437.1465; found 437.1476.

*[(5-Formylfuran-2-yl)methyl]triphenylphosphonium Bromide (**4f**).*[33] Yield: 4.74 g, 83%; yellow solid, mp 261−263 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.43 (s, 1H), 7.99−7.87 (m, 3H), 7.82−7.70 (m, 12H), 7.45 (d, J = 3.1 Hz, 1H), 6.48 (t, J = 3.1 Hz, 1H), 5.69 (d, J = 15.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 177.8, 152.7 (d, J = 1.5 Hz), 148.8 (d, J = 10.9 Hz), 135.3 (d, J = 1.2 Hz, 3C), 133.8 (d, J = 10.4 Hz, 6C), 130.2 (d, J = 12.7 Hz, 6C), 124.1 (d, J = 2.7 Hz), 117.5 (d, J = 88.2 Hz, 3C), 114.9 (d, J = 7.8 Hz), 23.3 (d, J = 50.8 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{24}H_{20}O_2P^+$ 371.1195; found 371.1202.

*[1-(5-Methylfuran-2-yl)ethyl]triphenylphosphonium Bromide (**4g**).* Yield: 3.78 g, 84%; beige solid, mp 172−173 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.93−7.87 (m, 3H), 7.83−7.72 (m, 12H), 6.15 (t, J = 3.6 Hz, 1H), 6.01 (d, J = 3.0 Hz, 1H), 5.97 (dq, J = 14.2, 7.2 Hz, 1H), 2.02 (d, J = 2.0 Hz, 3H), 1.61 (dd, J = 18.2, 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 152.7 (d, J = 3.8 Hz), 144.3 (d, J = 8.8 Hz), 135.0 (d, J = 2.9 Hz, 3C), 134.1 (d, J = 9.5 Hz, 6C), 130.1 (d, J = 12.2 Hz. 6C), 117.4 (d, J = 82.9 Hz, 3C), 112.4 (d, J = 7.9 Hz), 107.2 (d, J = 2.9 Hz), 28.9 (d, J = 46.7 Hz), 14.1−13.0 (d, J = 1.2 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{25}H_{24}OP^+$ 371.1559; found 371.1545.

*[1-(5-Methylfuran-2-yl)(phenyl)methyl]triphenylphosphonium Bromide (**4h**).*[34] Yield: 4.25 g, 83%; beige solid, mp 210−212 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96−7.86 (m, 3H), 7.79−7.66 (m, 6H), 7.60−7.47 (m, 6H), 7.44−7.37 (m, 1H), 7.36−7.30 (m, 2H), 7.28−7.15 (m, 3H), 6.26 (t, J = 3.2 Hz, 1H), 6.10 (br s, 1H), 2.10 (s, 3H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.3 (d, J = 3.3 Hz), 143.2 (d, J = 7.9 Hz), 135.3 (d, J = 2.8 Hz, 3C), 134.5 (d, J = 9.4 Hz, 6C), 130.6(d, J = 6.0 Hz, 2C), 130.5, 130.0 (d, J = 12.3 Hz, 6C), 129.4(d, J = 2.8 Hz), 129.1 (d, J = 1.6 Hz, 2C), 117.1 (d, J = 82.6 Hz, 3C), 113.5 (d, J = 7.8 Hz), 107.5, 41.3 (d, J = 44.3 Hz), 13.1. HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{30}H_{26}OP^+$ 433.1716; found 433.1730.

*(1H-Indol-3-ylmethyl)triphenylphosphonium Bromide (**4i**).* Yield: 3.72 g, 79%; beige solid, mp 263−265 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.24 (s, 1H), 7.85 (t, J = 7.0 Hz, 3H), 7.78−7.63 (m, 12H), 7.33 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 6.84 (t, J = 7.4 Hz, 1H), 6.77 (t, J = 7.4 Hz, 1H), 5.28 (d, J = 13.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 135.4, 134.8 (d, J = 2.8 Hz, 3C), 134.0 (d, J = 9.7 Hz, 6C), 131.5 (d, J = 9.8 Hz), 130.0 (d, J = 12.2 Hz, 6C), 128.8 (d, J = 11.6 Hz), 121.6, 118.9, 118.6 (d, J= 84.7 Hz, 3C), 118.4, 111.6, 99.2 (d, J = 8.6 Hz), 20.0 (d, J = 48.6 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{27}H_{23}PN^+$ 392.1563; found 392.1568.

*[(1-Benzyl-1H-pyrazol-4-yl)methyl]triphenylphosphonium Bromide (**4j**).* Yield: 4.40 g, 86%; white solid, mp 236−237 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.93−7.84 (m, 3H), 7.77−7.62 (m, 12H), 7.38 (d, J = 2.2 Hz, 1H), 7.36−7.20 (m, 3H), 7.06 (d, J = 6.6 Hz, 2H), 7.00 (s, 1H), 5.24 (s, 2H), 5.09 (d, J = 14.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 139.8 (d, J = 4.2 Hz), 137.1, 135.0 (d, J = 2.7 Hz, 3C), 133.8 (d, J = 9.8 Hz, 6C), 131.1 (d, J = 5.5 Hz), 130.1 (d, J = 12.4 Hz, 6C), 128.5, 127.7, 127.4 (2C), 118.1 (d, J = 85.4 Hz, 3C), 106.3 (d, J = 7.6 Hz), 54.7, 18.7 (d, J = 50.3 Hz). HRMS (ESI$^+$) m/z: [M − Br]$^+$ Calcd for $C_{29}H_{26}PN_2^+$ 433.1828; found 433.1835.

*(1-Thiophen-2-ylethyl)triphenylphosphonium Bromide (**4k**).*[35] Yield: 3.71 g, 82%; white solid, mp 165−167 °C; ^{1}H NMR (400

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MHz, DMSO-d_6): δ 7.99−7.85 (m, 3H), 7.87−7.70 (m, 12H), 7.53 (br d, J = 4.3 Hz, 1H), 7.01−6.94 (m, 1H), 6.85 (br s, 1H), 6.45 (dq, J = 14.2, 7.0 Hz, 1H), 1.71 (dd, J = 18.1, 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 135.3 (d, J = 6.5 Hz), 135.4 (d, J = 2.8 Hz, 3C), 134.3 (d, J = 9.3 Hz, 6C), 130.2 (d, J = 12.2 Hz, 6C), 129.5 (d, J = 7.6 Hz), 127.8 (d, J = 3.9 Hz), 127.1 (d, J = 2.8 Hz), 117.0 (d, J = 82.8 Hz, 3C), 30.4 (d, J = 46.4 Hz), 18.0. HRMS (ESI^+) m/z: $[M - Br]^+$ Calcd for $C_{24}H_{22}PS^+$ 373.1174; found 373.1178.

General Procedure for the Synthesis of Phosphonium Salts 5a,b. To a solution of alcohol **3b**,**k** (10 mmol) in 1,4-dioxane (20 mL) were added chlorotrimethylsilane (1.52 mL, 12 mmol) and PPh_3 (2.62 g, 10 mmol). The resulting mixture was stirred at 80 °C for 4−6 h until the starting alcohol was entirely consumed (GC/MS control). The reaction mixture was cooled to 5−10 °C, and the formed precipitate was filtered off, washed with 1,4-dioxane, and dried in air. The products were recrystallized from EtOH.

*[(5-Methylfuran-2-yl)methyl]triphenylphosphonium Chloride (**5a**).* Yield: 3.57 g, 88%; white solid, mp 242−245 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 7.94−7.86 (m, 3H), 7.80−7.66 (m, 12H), 6.04 (t, J = 3.4 Hz, 1H), 6.00 (br s, 1H), 5.40 (d, J = 14.4 Hz, 2H), 2.04 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 152.7 (d, J = 4.0 Hz), 139.8 (d, J = 11.4 Hz), 135.1 (d, J = 2.9 Hz, 3C), 133.9 (d, J = 10.1 Hz, 6C), 130.1 (d, J = 12.5 Hz, 6C), 118.1 (d, J = 85.7 Hz, 3C), 112.9 (d, J = 8.3 Hz), 107.3 (d, J = 3.2 Hz), 23.0 (d, J = 50.4 Hz), 13.1. HRMS (ESI^+) m/z: $[M - Cl]^+$ Calcd for $C_{24}H_{22}OP^+$ 357.1403; found 357.1408.

*(1-Thiophen-2-ylethyl)triphenylphosphonium Chloride (**5b**).* Yield: 3.22 g, 79%; white solid, mp 162−164 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 7.94−7.87 (m, 3H), 7.85−7.70 (m, 12H), 7.53 (br d, J = 4.3 Hz, 1H), 7.02−6.95 (m, 1H), 6.82 (br s, 1H), 6.44 (dq, J = 14.2, 7.0 Hz, 1H), 1.71 (dd, J = 18.1, 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 135.9 (d, J = 6.4 Hz), 135.6 (d, J = 2.8 Hz, 3C), 134.8 (d, J = 9.3 Hz, 6C), 130.7 (d, J = 12.2 Hz, 6C), 130.0 (d, J = 7.4 Hz), 128.3 (d, J = 3.9 Hz), 127.6 (d, J = 3.0 Hz), 117.6 (d, J = 82.8 Hz, 3C), 30.8 (d, J = 46.7 Hz), 18.5. HRMS (ESI^+) m/z: $[M - Cl]^+$ Calcd for $C_{24}H_{22}PS^+$ 373.1174; found 373.1187.

General Procedure for the Alternative Synthesis of Phosphonium Salts 2b−d,4b. To a solution of alcohol **1b−d** or **3b** (10 mmol) in 1,4-dioxane (20 mL) was added PPh_3·HBr (3.77 g, 11 mmol). The resulting mixture was stirred at 80 °C for 4−24 h until the starting alcohol was entirely consumed (GC/MS control). The reaction mixture was cooled to 5−10 °C, and the formed precipitate was filtered off, washed with 1,4-dioxane, and dried on air. The products were recrystallized from EtOH.

*(4-Nitrobenzyl)triphenylphosphonium Bromide (**2b**).*[26] Yield: 0.24 g, 5%. All spectral data are consistent with those described above.

*(4-Methoxybenzyl)triphenylphosphonium Bromide (**2c**).*[25] Yield: 3.98 g, 86%. All spectral data are consistent with those described above.

*(4-Bromobenzyl)triphenylphosphonium Bromide (**2d**).* Yield: 4.35 g, 85%. All spectral data are consistent with those described above.

*[(5-Methylfuran-2-yl)methyl]triphenylphosphonium Bromide (**4b**).*[32] Yield: 3.67 g, 84%. All spectral data are consistent with those described above.

General Procedure for the Synthesis of Styrenes 6. To a solution of alcohol **1a** or **3b** (10 mmol) in 1,4-dioxane (20 mL) were added bromotrimethylsilane (1.58 mL, 12 mmol) and PPh_3 (2.62 g, 10 mmol). The resulting mixture was stirred at 80 °C for 6−8 h. The reaction mixture was cooled to 5 °C, and then 4-bromobenzaldehyde or 2-nitrobenzaldehyde (10 mmol) and NaOMe (0.43 mL, 13 mmol, 3 M) were added. The resulting mixture was stirred for 12 h at room temperature, quenched with water, and extracted with ethyl acetate (3 × 25 mL). The combined organic fractions dried with anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The product was purified by column chromatography on silica gel using the mixture of petroleum ether/ethyl acetate (9:1) as an eluent and recrystallized from a suitable solvent.

*2-[(E)-2-(4-Bromophenyl)ethenyl]-5-methylfuran (**6a**).*[36] Yield: 1.88 g, 72%; pale-yellow solid, mp 91−92 °C (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 16.2 Hz, 1H), 6.81 (d, J = 16.2 Hz, 1H), 6.26 (d, J = 3.1 Hz, 1H), 6.03 (d, J = 3.1 Hz, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 152.7, 151.5, 136.4, 131.8 (2C), 127.7 (2C), 124.2, 120.9, 117.4, 110.7, 108.1, 13.9. HRMS (ESI^+) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}BrO^+$ 263.0066; found 263.0063.

*1-Nitro-2-styrylbenzene (**6b**).*[37] Yield: 1.64 g (isolated as a Z/E-mixture in 1/1 ratio), 73%; pale orange oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13−8.06 (m, 1H), 7.97 (dd, J = 8.2, 1.2 Hz, 1H), 7.77 (dd, J = 7.8, 0.8 Hz, 1H), 7.61 (d, J = 15.8 Hz, 1H), 7.61−7.52 (m, 3H), 7.44−7.36 (m, 5H), 7.35−7.26 (m, 2H), 7.19−7.15 (m, 3H), 7.10 (d, J = 15.8 Hz, 1H), 7.07−7.05 (m, 2H), 6.90 (d, J = 12.1 Hz, 1H), 6.78 (d, J = 12.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.3, 148.1, 136.6, 136.0, 134.0, 133.8, 133.2 (2C), 133.1, 132.4, 131.9, 129.2 (2C), 128.9 (2C), 128.7, 128.4 (2C), 128.3, 128.2, 128.0, 127.6, 127.2 (2C), 126.6, 124.9, 124.8, 123.6. HRMS (ESI^+) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{11}NNaO_2^+$ 248.0682; found 248.0678.

Synthesis of (*E*)-5-Methyl-2-(4-nitrostyryl)phenol (6c). To a solution of benzyl alcohol **1b** (1.53 g, 10 mmol) in 1,4-dioxane (20 mL) bromotrimethylsilane (1.58 mL, 12 mmol) was added dropwise, and the resulting mixture was stirred at 80 °C for 8 h. Upon full conversion of the starting alcohol **1b** (GC/MS control), PPh_3 was added, and the reaction mixture was stirred for an additional 4 h at 80 °C. The reaction mixture was cooled to 5 °C, and then 4-methylsalicylaldehyde (1.36 g, 10 mmol) and NaOMe (0.43 mL, 13 mmol, 3M) were added. The resulting mixture was stirred for 12 h at room temperature, quenched with water, and extracted with ethyl acetate (3 × 25 mL). The combined organic fractions were dried with anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The product was purified by column chromatography on silica gel using the mixture of petroleum ether/ethyl acetate (9:1) as an eluent and recrystallized from a mixture of ethyl acetate/petroleum ether. Yield: 1.84 g, 72%; pale orange solid, mp 163−165 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 16.4 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.15 (d, J = 16.4 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 6.63 (br. s, 1H), 5.17 (br. s, 1H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.6, 146.6, 144.8, 140.6, 128.1, 127.5, 126.8 (2C), 126.2, 124.3 (2C), 122.4, 121.0, 116.9, 21.4. HRMS (ESI^+) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{13}NNaO_3^+$ 278.0788; found 278.0784.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00733.

Copies of ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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