

7.9; N, 5.2. Found: C, 62.7; H, 7.9; N, 5.1.

(1*R*,2*R*)- and (1*R*,2*S*)-9-(*tert*-butoxycarbonyl)-2-(methoxycarbonyl)-9-azabicyclo[4.2.1]non-3-ene (19, R = OCH₃) were obtained (along with their respective γ,δ -unsaturated isomers) by treatment of the iodo acids with excess potassium *tert*-butoxide (300 mol %) in DMA (0.1 M) at 125 °C according to the dehydrohalogenation procedure described above. After 3 h the reaction mixtures were cooled to 0 °C, calcined K₂CO₃ (500 mol %) and iodomethane (300 mol %) were added, and stirring was continued at room temperature for 90 min. Aqueous workup followed by

LPC (3/17 EtOAc/hexanes) gave 18 and 19 (R = OCH₃) in a combined 72% yield.

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Vinylphosphonium Salts: Stereoselective Palladium-Catalyzed Vinylation of Triphenylphosphine with Vinyl Triflates

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The reaction of vinyl triflates with a slight excess of triphenylphosphine and 1–3 mol % Pd(PPh₃)₄ in refluxing THF results in the formation of the corresponding vinyltriphenylphosphonium triflate salts in good yield. A wide variety of salts, including cyclic ones, can be prepared. Unlike past syntheses of these compounds, pure stereoisomeric starting triflates stereoselectively yield stereoisomeric products. The current synthesis is especially useful for the preparation of *Z* isomers.

Vinylphosphonium salts^{1–3} are useful for cycloadditions,^{4–8} for Michael additions, for the synthesis of heterocyclic compounds,^{9–12} and as reagents in a variety of other transformations.^{13,14} Unfortunately, the syntheses of vinylphosphonium salts have been limited to mixtures of isomers, or at best the *E* isomers, exclusively.¹⁵ As a result, studies of the Michael additions and, more importantly, [2 + 4] cycloaddition⁴ reactions have only been carried out to a very limited degree and most extensively with the parent salt (vinyltriphenylphosphonium bromide), available commercially as Schweizer's reagent.¹⁶

Previously used syntheses include additions of triphenylphosphine to allyl bromide followed by base-cata-

lyzed prototropic rearrangement,⁹ additions to alkynylphosphonium salts,¹¹ and, most recently, the oxidative elimination of phenyl selenoxide from cyclic alkyl phenyl selenides.⁵ As we recently reported in preliminary form, a wide variety of vinylphosphonium salts can now be synthesized stereoselectively by the palladium-catalyzed coupling of vinyl triflates with triphenylphosphine.¹⁷ The most beneficial aspect of this synthesis is that the previously unavailable *Z* isomers of the salts can be obtained in good yield. Herein we report the full details of this novel, new synthesis of vinylphosphonium species.

Results and Discussion

Attempts to synthesize stable (σ -vinyl)palladium(II) species using vinyl triflates and tetrakis(triphenylphosphine)palladium(0) resulted in the formation of the vinylphosphonium salts as the only isolable organic species. It was then established that this reaction could be carried out with catalytic quantities of palladium(0).

Interaction of vinyl triflates¹⁸ 1–5 with a slight excess of triphenylphosphine and 1–3 mol % of tetrakis(triphenylphosphine)palladium(0) in refluxing THF resulted in the corresponding vinylphosphonium salts 6–10 in 62–90% isolated yields (eq 1). Reaction of triflate 1 with 1.05 equiv of PPh₃ and 3 mol % Pd(PPh₃)₄ at 66 °C for 6 h gave 6 in 89% isolated yield. Crystallization of salts 6, 8, and 9 is rapid upon addition of hexanes or pentane, whereas compounds 7 and 10 crystallized only after extended periods of time at low temperatures. Passing the crude solutions through a plug of unactivated florisil before adding the alkanes facilitates crystallization. Alternatively,

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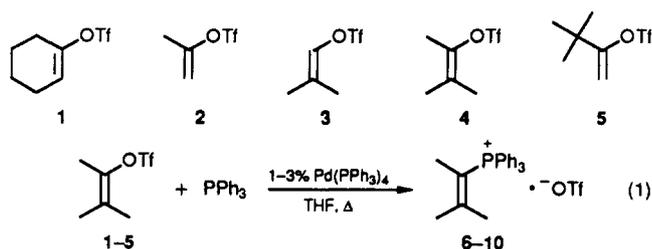
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use of 1 mol % catalyst rather than 3 mol % (relative to starting triflate) or titration of the oils with Et₂O also aid in crystallization.

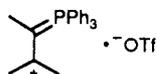
Compounds 6–10 are generally isolated in high purity (~98% directly from the reaction mixture) as microcrystalline solids, although they are slightly colored due to palladium impurities. They can then be recrystallized from warm THF/hexanes, giving pure products. Phosphonium salts 6–10 are colorless or light yellow and have been fully characterized by microanalysis or fast atom bombardment mass spectroscopy (FAB), IR, and NMR (¹H, ¹³C, and ³¹P).

The IR spectra clearly show the products to be ionic with the presence of absorptions at 1267 ± 5 and 635 ± 5 cm⁻¹, which are assigned to the antisymmetric stretching modes of the sulfonyl group in ionic triflates.¹⁹ The corresponding absorptions for the covalently bonded triflates (e.g., starting triflates) appear near 645, 1215, and 1421 cm⁻¹. The vinyl C=C stretching mode is too weak to be observed even in extremely concentrated KBr samples due to the abundance of other absorptions.

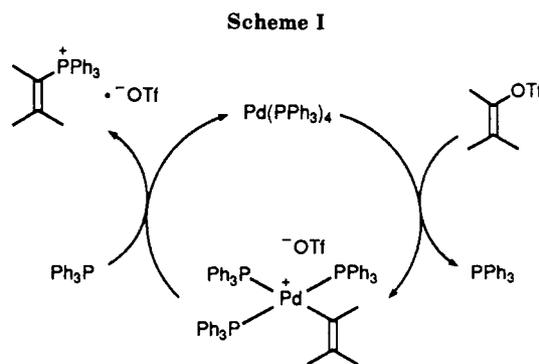
The NMR spectra of compounds 6–10 are very simple, and all significant resonances can easily be assigned. The stereochemical integrity of the product salts was supported by examination of coupling constants in the ¹H and ¹³C{¹H} spectra. It has been established that both ³J_{PC} and ⁴J_{PH} for trans substituents are greater than those which are cis.²⁰

The ³¹P{¹H} spectra display an expected singlet the chemical shifts of which range from 27.5 for 13E (vide infra) to 11.7 ppm for 8 in CDCl₃. The chemical shifts of these phosphonium salts are generally sensitive to steric compression (in agreement with Schweizer²⁰) and sterically hindered salts display resonances which are shifted upfield from their less hindered analogues.

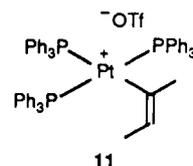
The ¹³C{¹H} spectra exhibit extensive and large phosphorus-carbon coupling. The resonances for all compounds can easily be assigned, and nearly all appear as doublets. The most significant feature of these spectra is the large variations in chemical shifts of the α- and β-vinyl carbons. In cases where an α-alkyl substituent (e.g., 2-propenyltriphenylphosphonium triflate, 7) is present, the chemical shifts for the α- and β-carbons are 126 and 142 ppm, respectively. In the case of (2-methylpropenyl)triphenylphosphonium triflate (8), the α-carbon is shifted upfield by 23 ppm to 103 ppm, and the β-carbon is shifted downfield by 30 ppm to 172 ppm relative to the 2-propenyl case (7). These variations have been attributed²⁰ to the increased contribution of the resonance form shown below.



Mechanistic Considerations. A catalytic cycle for this new reaction is shown in Scheme I. Stille and Scott^{21,22}

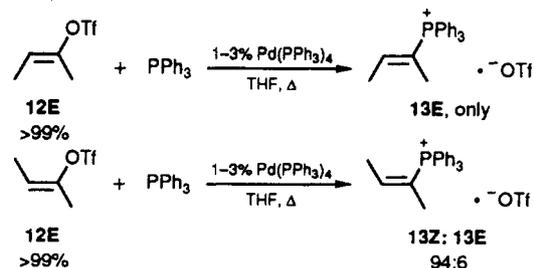


propose oxidative addition of vinyl triflates to palladium in the initial step of vinylic cross-coupling reactions. Oxidative addition to low-valent group eight transition metals has recently been shown by us to likely occur by initial formation of a π-complex followed by stereoselective rearrangement to a (σ-vinyl)M(II) species.²³ An X-ray structure of the platinum analogue of this type of intermediate (11) was recently reported by us.²³



Stereochemistry. It is well-known that palladium-catalyzed coupling reactions very often yield products in which the stereochemistry of the starting materials is retained in the products.²⁴ To examine the selectivity of the present coupling reaction, we investigated the reactions of two pairs of stereoisomeric vinyl triflates: 12E and 12Z ((E)-2-butenyl triflate) and (Z)-2-butenyl triflate) and 14E and 14Z ((E)-2-phenylpropenyl triflate and (Z)-2-phenylpropenyl triflate). Triflates 12E and 12Z were prepared as a 35:65 mixture, respectively, by addition of triflic acid to 2-butyne.²⁵ The isomers were then separated by preparatory GC. Triflates 14Z and 14E were obtained as a 75:25 mixture from reaction of *d,l*-2-phenylpropionaldehyde, triflic anhydride, and a hindered base; they were separated by preparatory HPLC. Individual isomers were characterized by comparison with previous work.²⁶

Each individual isomer was reacted with 1.05 equiv of PPh₃ and 1–3 mol % Pd(PPh₃)₄, and the mixture was refluxed in THF for 3 h. The crude product mixtures were then concentrated and analyzed by both ¹H and ³¹P NMR spectroscopy. Reaction of (E)-2-butenyl triflate 12E yielded *only* the (E)-2-buten-2-yltriphenylphosphonium triflate 13E in greater than 99% isomeric purity. Reaction



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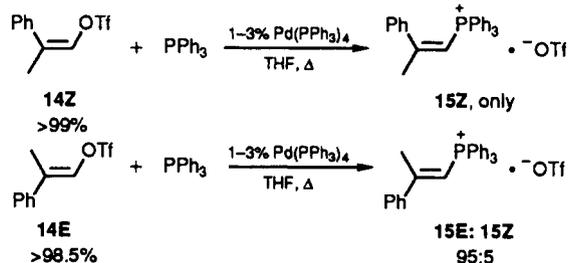
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of the *Z* isomer, **12Z**, under the same conditions yielded a 94:6 (*Z:E*) mixture. By using similar conditions, reactions with triflates **14E** and **14Z** were also carried out and again analyzed before any workup. Triflate **14Z** yielded only **15Z** (greater than 99% isomeric purity), while **14E** provided a 95:5 mixture of **15E** and **15Z**.



The origin of the slight degree of isomerization in these two examples is not clear at this point. One possibility is that there is β -hydride elimination from the initially formed π -olefin complex yielding $(\text{Ph}_3\text{P})_3\text{PdH}^+$ and 2-butyne followed by readdition of the palladium hydride to the acetylene.²³ This does not, however, explain the isomerization of the (*E*)-2-phenylpropen-1-yltriphenylphosphonium salt which has no hydrogens β to the triflate moiety.

Conclusions

We have presented a new and useful preparation of a variety of vinylphosphonium salts via a simple new procedure utilizing readily available vinyl triflates, triphenylphosphine, and palladium(0) catalyst. This represents a single-step synthesis whereby the vinylphosphonium salts can be obtained in good isolated yield with a high degree of stereoselectivity; it is especially advantageous for the preparation of *Z* isomers which were previously inaccessible.

This new synthesis provides the opportunity for further studies on stereoselective [2 + 4] cycloaddition reactions, thereby providing a useful extension of the current use of the parent as a ketene synthon.

Experimental Section

General Data. Uncorrected melting points were obtained with a Mel-Temp capillary melting point apparatus. Analytical gas chromatography was performed on a Hewlett-Packard 5711A flame ionization detector GC equipped with a Hewlett-Packard 3380A integrator and a 0.0125 in. \times 8 ft QF-1 on 80/100 Chromosorb W analytical column. NMR spectra were recorded on a Varian XL-300 spectrometer, and chemical shifts are reported in CDCl_3 relative to residual CHCl_3 (^1H) at 7.24 ppm, the CDCl_3 triplet (^{13}C) at 77.0 ppm, and external 85% H_3PO_4 (^{31}P) at 0.00 ppm. All ^1H NMR data were recorded at 300 MHz, ^{13}C spectra were broadband ^1H decoupled and recorded at 75 MHz, and ^{31}P spectra were broadband ^1H decoupled and recorded at 121 MHz. The purity of all the compounds was judged to be greater than 95% by melting point and ^1H and ^{13}C spectral determinations. IR spectra were recorded in cm^{-1} as KBr pellets on a Mattson Polariscop spectrometer with 4 cm^{-1} resolution. High-resolution mass spectra were recorded on VG Micromass 7070E double-focusing high-resolution spectrometer operating at 5 kV with a VG Analytical 2000 data system.

Materials. All vinyl triflates were prepared in greater than 98.5% isomeric purity (NMR and Analytical GC) by known methods.¹⁸ (*E*)- and (*Z*)-2-phenylpropenyl triflates were separated by preparatory HPLC using a 21.4 mm i.d. Rainin 83-121-C column on a Varian 5000 liquid chromatograph equipped with a UV-100 detector. The isomers were eluted with hexane (Omnisolve, HPLC grade) and monitored at 272 nm. (*E*)- and (*Z*)-2-butenyl triflates were separated by preparatory GC using a Varian Aerograph A-90P GC equipped with a $1/4$ in. \times 20 ft 15%

QF-1 preparative column. Acetylenes were purchased from Farhan laboratories and used as received. Triphenylphosphine was purchased from Aldrich and recrystallized from hexane. Tetrakis(triphenylphosphine)palladium(0) was prepared from PdCl_2 according to an established method.²⁷ Solvents were either reagent grade or were purified by known methods.²⁸ Tetrahydrofuran was freshly distilled from sodium and diphenyl ketone, hexane was acid washed and distilled from CaH_2 , and CDCl_3 was purchased from Cambridge Isotopes and used as received. Silica gel (60–200 μm) was purchased from Davison Chemical and florisil (100–200 mesh) was purchased from J. T. Baker; each was used unactivated.

General Procedure for Preparation of Vinyltriphenylphosphonium Triflates: Cyclohexenyltriphenylphosphonium Triflate (6). Cyclohexenyl triflate (0.1176 g, 0.511 mmol) was placed in 5.0 mL of freshly distilled THF. Triphenylphosphine (0.1474 g, 0.562 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0130 g, 0.0112 mmol) were added, and the mixture was heated to reflux for 6 h. The solution was then cooled to room temperature, 5.0 mL of hexane was added, and the solution placed in the freezer (-15°C) for 8 h. The crude product was collected by vacuum filtration on a Hirsch funnel and washed with cold THF followed by hexane. The product (0.3346 g, 89%) was then dried in vacuo and determined to be $\sim 99\%$ pure by ^1H and ^{31}P NMR without further recrystallization: mp $246\text{--}247^\circ\text{C}$; IR (KBr) 3060 w, 2941 w, 1612 m, 1586 m, 1481 m, 1434 s, 1270 s, 1221 s, 1190 s, 1104 s, 1029 s, 993 s, 937 m, 911 m, 749 s, 732 m, 720 s, 689 s, 632 s; ^1H NMR δ 1.75 (m, 4 H), 2.18 (m, 2 H), 2.45 (m, 2 H), 6.71 (dm, $^3J_{\text{PH}} = 23 \text{ Hz}$, 1 H), 7.50–7.85 (aromatics, 15 H); ^{31}P NMR δ 23.8 (s); ^{13}C NMR δ 20.3 (s), 21.9 (d, $J_{\text{PC}} = 8.4 \text{ Hz}$), 26.4 (d, $J_{\text{PC}} = 8.5 \text{ Hz}$), 27.8 (d, $J_{\text{PC}} = 15 \text{ Hz}$), 116.7 (d, $^1J_{\text{PC}} = 89 \text{ Hz}$), 118.7 (d, $^1J_{\text{PC}} = 78 \text{ Hz}$), 130.5 (d, $^3J_{\text{PC}} = 13 \text{ Hz}$), 134.0 (d, $^2J_{\text{PC}} = 9.7 \text{ Hz}$), 135.3 (s), 155.9 (d, $^2J_{\text{PC}} = 7.8 \text{ Hz}$); exact mass (FAB, HRMS) calcd 343.16156, found 343.16147. Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{PF}_3\text{SO}_3$: C, 60.97; H, 4.91; P, 6.29. Found: C, 60.88; H, 5.00; P, 6.23.

2-Propen-2-yltriphenylphosphonium Triflate (7). Prepared by general procedure with 2-propenyl triflate (0.8732 g, 4.593 mmol), triphenylphosphine (1.0001 g, 3.813 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.1762 g, 0.154 mmol). In addition, the solvent was removed from the mixture under reduced pressure, and the oil was eluted through a plug of florisil with THF to facilitate crystallization. After addition of hexane and collection by vacuum filtration, the crude product was recrystallized from THF/hexane, yielding 1.1906 g (69%) of pure product: mp $117\text{--}118^\circ\text{C}$; IR (KBr) 3060 w, 1611 vw, 1586 m, 1482 m, 1438 s, 1265 vs, 1221 s, 1145 s, 1107 s, 1029 s, 993 s, 971 m, 850 w, 751 s, 735 s, 722 s, 709 s, 688 s, 632 s; ^1H NMR δ 2.20 (d, br s, $^3J_{\text{PH}} = 14 \text{ Hz}$, 3 H), 5.99 (d, br s, $^3J_{\text{PH}} = 24 \text{ Hz}$, 1 H), 6.72 (dm, $^3J_{\text{PH}} = 48 \text{ Hz}$, 1 H), 7.6–7.9 (aromatics, 15 H); ^{31}P NMR δ 25.7 (s); ^{13}C NMR δ 20.6 (d, $^2J_{\text{PC}} = 12 \text{ Hz}$), 116.1 (d, $^1J_{\text{PC}} = 88 \text{ Hz}$), 126.3 (d, $^1J_{\text{PC}} = 73 \text{ Hz}$), 130.6 (d, $^3J_{\text{PC}} = 12 \text{ Hz}$), 134.0 (d, $^2J_{\text{PC}} = 10 \text{ Hz}$), 135.5 (s), 141.8 (d, $^2J_{\text{PC}} = 9.1 \text{ Hz}$); exact mass (FAB, HRMS) calcd 303.13026, found 303.12986. Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{PF}_3\text{SO}_3$: C, 58.41; H, 4.46; P, 6.85. Found: C, 58.06; H, 4.47; P, 7.43.

(2-Methyl-1-propen-1-yl)triphenylphosphonium Triflate (8). 2-Methyl-1-propenyl triflate (0.1186 g, 0.5808 mmol), triphenylphosphine (0.1600 g, 0.610 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0201 g, 0.0174 mmol) were used in the general procedure. The product was then recrystallized from THF/hexane, yielding 0.2934 g (71%): mp $188\text{--}190^\circ\text{C}$; IR (KBr) 3070 w, 3003 w, 1610 s, 1585 vw, 1480 m, 1435 s, 1265 s, 1140 s, 1103 s, 1027 s, 740 s, 714 s, 688 s, 630 s; ^1H NMR δ 1.70 (dd, $^4J_{\text{PH}} = 2.6 \text{ Hz}$, $^3J_{\text{HH}} = 1.0 \text{ Hz}$, 3 H), 2.32 (m, 3 H), 6.18 (d, $^2J_{\text{PH}} = 23 \text{ Hz}$, 1 H), 7.50–7.80 (aromatics, 15 H); ^{31}P NMR δ 11.7 (s); ^{13}C NMR δ 24.7 (d, $^3J_{\text{PC}} = 7.6 \text{ Hz}$), 29.8 (d, $^3J_{\text{PC}} = 19 \text{ Hz}$), 102.7 (d, $^1J_{\text{PC}} = 90 \text{ Hz}$, vinyl), 119.4 (d, $^1J_{\text{PC}} = 90 \text{ Hz}$, ipso), 130.6 (d, $^3J_{\text{PC}} = 13 \text{ Hz}$), 133.3 (d, $^2J_{\text{PC}} = 11 \text{ Hz}$), 135.0 (d, $^4J_{\text{PC}} = 3.1 \text{ Hz}$), 172.4 (d, $^2J_{\text{PC}} = 1.4 \text{ Hz}$); exact mass (FAB, HRMS) calcd 317.14591, found 317.14465. Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{PF}_3\text{SO}_3$: C, 59.22; H, 4.75; P, 6.64. Found: C, 58.80; H, 4.88; P, 6.48.

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(3-Methyl-2-buten-2-yl)triphenylphosphonium Triflate (9). Prepared by the general procedure with 3-methyl-2-butenyl triflate (0.1061 g, 0.4840 mmol), triphenylphosphine (0.1396 g, 0.5324 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0168 g, 0.0145 mmol). The crude product was then recrystallized from THF/hexane, yielding 0.2102 g (90%) of colorless needles: mp 159–160 °C; IR (KBr) 3059 w, 3000 w, 2920 w, 1608 s, 1586 m, 1482 m, 1435 s, 1270 vs, 1145 s, 1100 s, 1025 s, 992 s, 845 s, 755 s, 720 s, 690 s, 630 s; ^1H NMR δ 1.64 (m, 3 H), 1.81 (dm, $^3J_{\text{PH}} = 17$ Hz, 3 H), 2.22 (m, 3 H), 7.60–7.80 (aromatics, 15 H); ^{31}P NMR δ 21.1 (s); ^{13}C NMR δ 18.8 (d, $^2J_{\text{PC}} = 14$ Hz), 24.8 (d, $^3J_{\text{PC}} = 14$ Hz), 28.2 (d, $^3J_{\text{PC}} = 10$ Hz), 107.2 (d, $^1J_{\text{PC}} = 81$ Hz), 119.3 (d, $^1J_{\text{PC}} = 87$ Hz), 130.6 (d, $^3J_{\text{PC}} = 13$ Hz), 133.7 (d, $^2J_{\text{PC}} = 9.8$ Hz), 134.9 (d, $^4J_{\text{PC}} = 2.6$ Hz), 163.1 (d, $^2J_{\text{PC}} = 7.9$ Hz); exact mass (FAB, HRMS) calcd 331.16156; found 331.16004.

(2,2-Dimethyl-3-buten-3-yl)triphenylphosphonium Triflate (10). 2,2-Dimethyl-3-butenyl triflate (0.1737 g, 0.7480 mmol), triphenylphosphine (0.2158 g, 0.8227 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0086 g, 0.0075 mmol) were used in the general procedure. The product was recrystallized from THF/hexane, yielding 0.2663 g (72%) of colorless needles: mp 155–156 °C; IR (KBr) 3094 w, 2969 m, 2932 w, 1472 w, 1446 s, 1439 m, 1280 vs, 1263 vs, 1227 m, 1168 m, 1158 m, 1144 s, 1103 m, 1034 s, 768 w, 639 w; ^1H NMR δ 1.11 (s, 9 H), 6.00 (d, $^3J_{\text{PH}} = 24$ Hz, 1 H), 6.90 (d, $^3J_{\text{PH}} = 50$ Hz, 1 H), 7.70–7.90 (aromatics, 15 H); ^{31}P NMR δ 26.9 (s); ^{13}C NMR δ 30.9 (d, $^3J_{\text{PC}} = 3.7$ Hz), 38.8 (d, $^2J_{\text{PC}} = 9.5$ Hz), 118.7 (d, $^1J_{\text{PC}} = 86$ Hz, ipso), 130.5 (d, $^3J_{\text{PC}} = 12$ Hz), 134.4 (d, $^2J_{\text{PC}} = 10$ Hz), 135.3 (d, $^4J_{\text{PC}} = 2.9$ Hz), 139.9 (d, $^1J_{\text{PC}} = 62$ Hz), 141.6 (d, $^2J_{\text{PC}} = 9.9$ Hz); exact mass (FAB, HRMS) calcd 345.17721, found 345.17740.

(Z)-2-Buten-2-yltriphenylphosphonium Triflate (13Z). Prepared by the general procedure with (Z)-2-butenyl triflate (0.1148 g, 0.5624 mmol), triphenylphosphine (0.1623 g, 0.6186 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0195 g, 0.0169 mmol). The product was then recrystallized from THF/hexane, yielding 0.1639 g (62%) based on starting triflate: mp 178–179 °C; IR (KBr) 3067 w, 1626 m, 1443 s, 1271 s, 1222 s, 1172 s, 1147 s, 1108 s, 1029 s, 997 s, 846 m, 758 s, 723 s, 702 s, 637 s; ^1H NMR δ 1.54 (m, 3 H), 1.95 (dt, $^3J_{\text{PH}} = 14$ Hz, $^1J_{\text{HH}} = 1.5$ Hz, 3 H), 7.27 (dq, $J_{\text{PH}} = 37$ Hz, $^3J_{\text{HH}} = 6.1$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, 1 H), 7.50–7.90 (aromatics, 15 H); ^{31}P NMR δ 18.3 (s); ^{13}C NMR δ 19.9 (d, $^3J_{\text{PC}} = 9.1$ Hz), 24.1 (d, $^2J_{\text{PC}} = 14$ Hz), 114.7 (d, $^1J_{\text{PC}} = 74$ Hz, vinyl), 117.9 (d, $^1J_{\text{PC}} = 87$ Hz, ipso), 130.7 (d, $^3J_{\text{PC}} = 13$ Hz), 133.8 (d, $^2J_{\text{PC}} = 10$ Hz), 135.2 (d, $^4J_{\text{PC}} = 3.0$ Hz), 153.2 (d, $^2J_{\text{PC}} = 7.9$ Hz, vinyl).

(E)-2-Buten-2-yltriphenylphosphonium Triflate (13E). (E)-2-Butenyl triflate (0.1203 g, 0.6290 mmol), triphenylphosphine (0.1817 g, 0.6928 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0218 g, 0.0126 mmol) were used in the general procedure. The product was then recrystallized from THF/hexane, yielding 0.2006 g (73%): mp 131–132 °C; IR (KBr) 3064 w, 3011 w, 1614 m, 1438 s, 1268 vs, 1225 m, 1147 s, 1109 s, 1031 s, 997

m, 753 s, 745 s, 719 s, 691 s, 636 vs; ^1H NMR δ 2.05 (m, 6 H), 6.50 (m, 1 H), 7.56–7.80 (aromatics, 15 H); ^{31}P NMR δ 27.5 (s); ^{13}C NMR δ 15.3 (d, $J_{\text{PC}} = 12$ Hz), 16.5 (d, $J_{\text{PC}} = 17$ Hz), 116.5 (d, $^1J_{\text{PC}} = 81$ Hz), 117.1 (d, $^1J_{\text{PC}} = 89$ Hz), 130.6 (d, $^3J_{\text{PC}} = 13$ Hz), 134.1 (d, $^2J_{\text{PC}} = 10$ Hz), 135.3 (d, $^4J_{\text{PC}} = 3.2$ Hz), 154.5 (d, $^2J_{\text{PC}} = 11$ Hz); exact mass (FAB, HRMS) calcd 317.14591, found 317.14525.

((E)-2-Phenyl-1-propen-1-yl)triphenylphosphonium Triflate (15E). (E)-2-Phenyl-1-propenyl triflate (0.1010 g, 0.3794 mmol), triphenylphosphine (0.1090 g, 0.4173 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0044 g, 0.0038 mmol) were used in the general procedure. After 3 h of reflux, the solution was cooled to room temperature and the solvent was removed under reduced pressure. The mixture was then passed through 5 g of unactivated silica gel with THF as the eluent. The solvent was again removed under reduced pressure, and the solid was dissolved in a minimum of CHCl_3 . This was then titrated with dry diethyl ether, yielding 0.1263 g of the (E)-phosphonium salt (63%). Recrystallization from THF/hexane yielding 0.0859 g (43% overall) of pure E isomer: mp 183–185 °C; IR (KBr) 3086 w, 3065 m, 3022 m, 1592 s, 1568 s, 1438 vs, 1384 m, 1266 vs, 1224 s, 1150 s, 1110 s, 1031 vs, 821 s, 752 s, 721 s, 690 s, 637 vs; ^1H NMR δ 2.14 (d, $^4J_{\text{PH}} = 2.4$ Hz, 3 H), 6.53 (d, $^2J_{\text{PH}} = 20$ Hz, 1 H), 7.40–7.90 (aromatics, 20 H); ^{31}P NMR δ 13.5 (s); ^{13}C NMR δ 22.9 (d, $^3J_{\text{PC}} = 7.7$ Hz), 103.1 (d, $^1J_{\text{PC}} = 91$ Hz, vinyl), 119.2 (d, $^1J_{\text{PC}} = 90$ Hz, ipso), 126.6 (s), 129.0 (s), 130.8 (d, $^3J_{\text{PC}} = 13$ Hz), 131.5 (s), 133.2 (d, $^2J_{\text{PC}} = 11$ Hz), 135.2 (d, $^4J_{\text{PC}} = 3.0$ Hz), 139.4 (d, $^3J_{\text{PC}} = 18$ Hz), 168.5 (s).

((Z)-2-Phenyl-1-propen-1-yl)triphenylphosphonium Triflate (15Z). Prepared by the general procedure with (Z)-2-phenyl-1-propenyl triflate (0.070 g, 0.263 mmol), triphenylphosphine (0.0759 g, 0.289 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0030 g, 0.0026 mmol). The solid was then recrystallized from THF/hexane, yielding 0.0961 g (69%) of a colorless microcrystalline solid: mp 155–156 °C; IR (KBr) 3064 w, 1610 m, 1592 m, 1439 s, 1266 vs, 1224 s, 1159 s, 1147 s, 1109 s, 1033 s, 839 w, 768 s, 754 w, 712 m, 703 m, 697 m, 687 m; ^1H NMR δ 2.61 (t, $^4J_{\text{HH}} = 1.0$ Hz, 3 H), 6.71–7.05 (m, $^2J_{\text{PH}} = 21$ Hz, aromatic and vinyl, 6 H), 7.45–7.70 (aromatics, 15 H); ^{31}P NMR δ 12.2 (s); ^{13}C NMR δ 31.4 (d, $^3J_{\text{PC}} = 17$ Hz), 103.9 (d, $^1J_{\text{PC}} = 90$ Hz, vinyl), 119.5 (d, $^1J_{\text{PC}} = 90$ Hz, ipso), 126.2 (s), 128.3 (s), 129.0 (s), 130.0 (d, $^3J_{\text{PC}} = 13$ Hz), 133.4 (d, $^2J_{\text{PC}} = 10$ Hz), 134.4 (d, $^4J_{\text{PC}} = 2.9$ Hz), 138.0 (d, $^3J_{\text{PC}} = 6.9$ Hz), 172.2 (s); exact mass (FAB, HRMS) calcd 379.16156; found 379.16180.

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Supplementary Material Available: ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for title compounds 6–10, 13, and 15 are available (18 pages). Ordering information is given on any current masthead page.