JOC*Note*

Zwitterionic Phosphonium Sulfonates as Easily Phase-Separable Ion-Tagged Wittig Reagents

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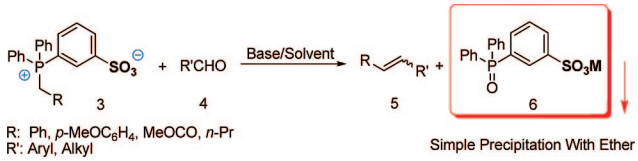
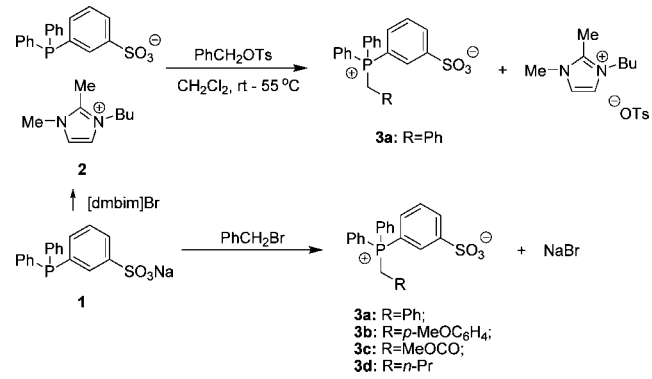


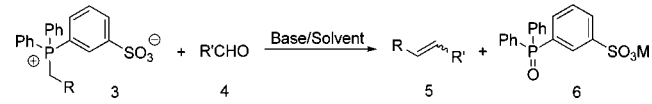
Zwitterionic phosphonium sulfonates **3**, conveniently derived from TPPMS (**1**), can be used as Wittig reagents in solution. The excess reagents and byproduct TPPMSO (**6**) can be easily separated from the product alkenes by simple precipitation with a less polar solvent. The alkenes thus obtained were often sufficiently pure without chromatographic purification. A one-pot protocol for the synthesis of α,β-unsaturated esters has been developed and appears to be convenient.

In the past few decades, considerable efforts have been devoted toward the development of supports to bind catalysts, reagents, or scavengers to facilitate the purification process after a synthetic reaction. Following the success of Merrifield peptide synthesis,[1] insoluble solid polymer resin was soon used as a support for reagents and catalysts.[2,3] Recent efforts have been directed toward the use of soluble polymers[4−6] or fluorous-phase synthesis[7] to restore the homogeneous reaction conditions. In these cases, the phase separation depends on the difference in the molecular weight of the support from the product or on the affinity of the fluorous tag for fluorous solvents. Recently, the use of ion tag as soluble support for organic synthesis has been explored.[8,9] phase separation depends on the differential solubility of the ionic moiety in polar versus nonpolar solvents.

SCHEME 1. Synthesis of Zwitterionic Phosphonium Sulfonates



SCHEME 2. Wittig Reactions of Zwitterionic Phosphonium Sulfonates 3a−d



The Wittig reaction is an important reaction in organic synthesis. The separation of the product alkene from the byproduct triphenylphosphine oxide (Ph_3PO) is a classical problem, requiring tedious chromatography or recrystallization. To overcome this problem, polymer-bound[10] or fluorous-tagged[11] phosphines have been developed. We report here our study on the use of ion-tagged Wittig reagents.

Most ion tag-supported reagents used imidazolium[8] or phosphonium[9] ions as the support. Because the sodium salt of triphenylphosphine-*m*-sulfonate (TPPMS, **1**) is used industrially,[12] we first examined the ionic salt 1,2-dimethyl-3-butylimidazolium triphenylphosphine-*m*-sulfonate (**2**), prepared from the reaction of **1** with 1,2-dimethyl-3-butylimidazolium bromide. Reaction of **2** with benzyl tosylate gave the zwitterionic phosphonium salt **3a** together with 1,2-dimethyl-3-butylimidazolium tosylate. It became obvious to us that the imidazolium moiety is redundant as the same zwitterionic compound **3a** can be prepared from **1** and benzyl bromide (Scheme 1). Compounds **3b−d** were prepared similarly from the corresponding bromides.[13]

The Wittig reaction of **3a** with various carbonyl compounds was evaluated in different base/solvent conditions (Scheme 2), and the results are summarized in Table 1. While NaOH in water was able to effect the reaction between **3a** and 4-nitrobenzaldehyde (**4a**) in good yield; NaOH in methanol was generally more effective for all aldehydes tested. The separation of the

(1) Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149.
(2) (a) Guillier, F.; Orain, D.; Bradley, M. *Chem. Rev.* **2000**, *100*, 2091. (b) James, I. W. *Tetrahedron* **1999**, *55*, 4855. (c) Ley, S. V.; Baxendale, I. R. *Chem. Rec.* **2002**, *2*, 377.
(3) Smith, C. D.; Baxendale, I. R.; Tranmer, G. K.; Baumann, M.; Smith, S. C.; Lwethwaite, R. A.; Ley, S. V. *Org. Biomol. Chem.* **2007**, *5*, 1562.
(4) Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345.
(5) Toy, P. H.; Janda, K. D. *Acc. Chem. Res.* **2000**, *33*, 546.
(6) Charette, A. B.; Boezio, A. A.; Janes, M. K. *Org. Lett.* **2000**, *2*, 3777.
(7) (a) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72. (b) Studer, A.; Hadida, S.; Ferritto, S. Y.; Kim, P. Y.; Jeger, P.; Wipf, P.; Curran, D. P. *Science* **1997**, *275*, 823. For reviews, see: (c) Zhang, W. *Tetrahedron* **2003**, *59*, 4475; *Chem. Rev.* **2004**, *104*, 2531.
(8) (a) Fraga-Dubreuil, J.; Bazureau, J. P. *Tetrahedron Lett.* **2001**, *42*, 6097. (b) Miao, W.; Chan, T. H. *Org. Lett.* **2003**, *5*, 5003. (c) Miao, W.; Chan, T. H. *Acc. Chem. Res.* **2006**, *39*, 897.
(9) (a) Poupon, J.-C.; Boezio, A. A.; Charette, A. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 1415. (b) Stazi, F.; Marcoux, D.; Poupon, J.-C.; Latassa, D.; Charrette, A. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 5011.
(10) Bolli, M. H.; Ley, S. V. *J. Chem. Soc. Perkin Trans. 1* **1998**, 2243, and references cited therein.
(11) Galante, A.; Lhoste, P.; Sinou, D. *Tetrahedron Lett.* **2001**, *42*, 5425.
(12) (a) Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* **1995**, *502*, 177. (b) Baricelli, P. J.; Baricelli, D.; Lujano, E.; Melean, L. G.; Borusiak, M.; Lopez-Linares, F.; Bastidas, L. J.; Rosales, M. *J. Mol. Catal. A* **2007**, *271*, 180.
(13) While NaBr was formed in the formation of **3**, its presence appeared to be innocuous as it had no significant influence to the Wittig reaction.

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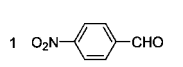
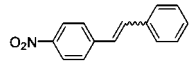
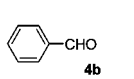
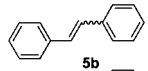
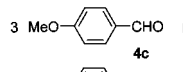
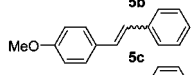
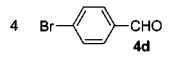
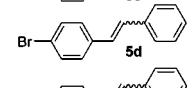
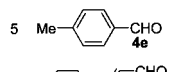
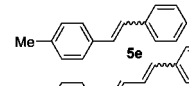
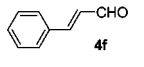
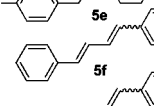
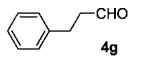
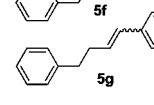
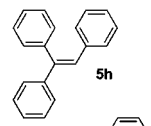
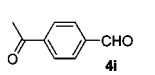
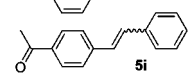
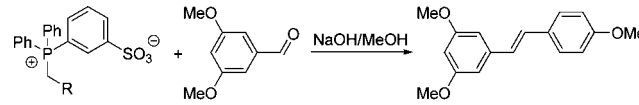
TABLE 1. Wittig Reactions of 3a with Various Aldehydes

Entry	Aldehyde	Product	Base/Solvent	Yield (%) (E:Z)
1	 **4a**	 **5a**	NaOH/MeOH	> 95 (1.1 : 1.0)
			NaOH/ H_2O	> 95 (1.6 : 1.0)
			LiHMDS /THF	91 (2.4 : 1.0)
			LiHMDS /DCM	88 (1.8 : 1.0)
			K_2CO_3/MeOH	83 (1.2 : 1.0)
			K_2CO_3/iPrOH	0
2	 **4b**	 **5b**	NaOH/MeOH	> 95 (1.7 : 1.0)
			NaOH/ H_2O	83 (3.6 : 1.0)
3	 **4c**	 **5c**	NaOH/MeOH	83 (1.1 : 1.0)
			NaOH/ H_2O	trace
4	 **4d**	 **5d**	NaOH/MeOH	> 95 (1.2 : 1.0)
5	 **4e**	 **5e**	NaOH/MeOH	> 95 (2.0 : 1.0)
6	 **4f**	 **5f**	NaOH/MeOH	> 95 (2.3 : 1.0)
7	 **4g**	 **5g**	NaOH/MeOH	78 (1.2 : 1.0)
8	Benzophenone **4h**	 **5h**	LiHMDS /THF	20
			NaOH/MeOH	0
9	 **4i**	 **5i**	NaOH/MeOH	> 95 (1.1 : 1.0)

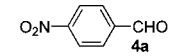
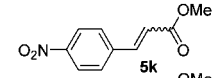
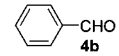
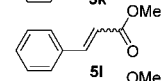
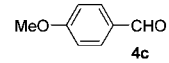
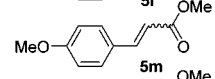
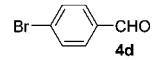
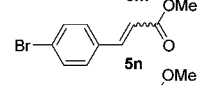
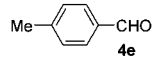
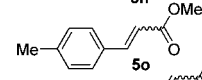
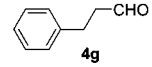
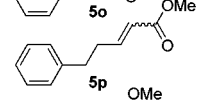
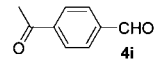
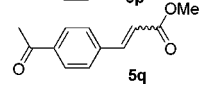
SCHEME 3. Synthesis of Methylated Resveratrol



3b: R=*p*-MeOPh

5j, 90% yield
E:Z=3.5 :1.0

TABLE 2. Wittig Reactions of 3c with Various Aldehydes[a]

Entry	Aldehyde	Product	Yield (%) (E:Z)
1	 **4a**	 **5k**	> 95 (2.6 : 1.0)
2	 **4b**	 **5l**	> 95 (2.8 : 1.0)
3	 **4c**	 **5m**	> 95 (2.6 : 1.0)
4	 **4d**	 **5n**	> 95 (2.6 : 1.0)
5	 **4e**	 **5o**	> 95 (3.2 : 1.0)
6	 **4g**	 **5p**	> 95 (1.7 : 1.0)
7	 **4i**	 **5q**	> 95 (2.7 : 1.0)

[a] Base/solvent: K_2CO_3/MeOH.

product alkenes **5** from the byproduct phosphine oxide **6** (TPPMSO) was very easy. After the reaction was completed, a less polar solvent such as diethyl ether was added to the reaction mixture to allow precipitation of the phosphine oxide **6**. After simple filtration, the organic layer was then free of **3a** and **6**, as evident from the absence of signal in the ^{31}P NMR. In most cases, the product alkene **5** needed no further purification on the basis of their ^1H NMR. Under such conditions, *trans*-cinnamic aldehyde (entry 6) was converted to the corresponding diene in high yield, and aliphatic aldehyde such as hydrocinnamaldehyde (entry 7) also worked well. There was no reaction at all between **3a** and ketones such as benzophenone (entry 8), acetophenone, cyclohexanone, or acetone in MeOH/NaOH and the ketones were recovered quantitatively. This reaction has therefore a high selectivity for aldehydes. Thus, 4-acetylbenzaldehyde (**4i**) reacted with **3a** chemoselectively (entry 9) in quantitative yield. Using compound **3b** and 3, 5-dimethoxybenzaldehyde under the same reaction conditions, the methylated resveratrol **5j** was obtained in 90% yield (Scheme 3). Methylated resveratrol **5j** had been converted to the bioactive resveratrol.[14]

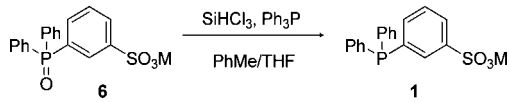
With the more acidic compound **3c**, potassium carbonate could be used to effect the Wittig reaction. As shown in Table 2, various aromatic and aliphatic aldehydes were converted to the corresponding alkenes **5** in excellent yields. Ketones, such as benzophenone, acetophenone, cyclohexanone, and acetone, were found to be unreactive under the conditions and were recovered quantitatively. 4-acetylbenzaldehyde (**4i**) reacted with **3c** to give the alkene **5q** in excellent yield, demonstrating high chemoselectivity. Again, the separation of the product alkenes **5** from the byproduct phosphine oxide **6** (TPPMSO) was achieved by adding diethyl ether to allow precipitation of the phosphine oxide **6**. Furthermore, it was not necessary to prepare the phosphonium salt **3c** as a separate step in this reaction. By simply mixing TPPMS (**1**), methyl bromoacetate, potassium carbonate, and the aldehyde **4** together in methanol and stirring the mixture at room temperature, the α,β-unsaturated ester **5** was obtained in excellent yield with high purity containing little byproduct according to their ^1H NMR without chromatography (see the Supporting Information). This one-pot reaction appears to be as convenient as the well established Horner−Wadsworth−Emmons (HWE) modification.[15] On the other hand, the HWE reaction is stereoselective in giving the thermodynamically more stable *E*-α,β-unsaturated esters, whereas the present reaction gives a mixture of *E*- and *Z*-isomers. This lack of stereoselectivity could be useful if the *Z*-isomer is the desired product or if a mixture of stereoisomers is required for the biological activity.[16] Furthermore, the mixture of stereoisomers could be isomerized to the thermodynamically more stable *E*-isomer.[17]We demonstrated this ease of conversion with the synthesis of *E*-**5l**. After the one-pot reaction of TPPMS, methyl bromoacetate and benzaldehyde was completed, the phosphine oxide **6** was removed by filtration as before. The crude product

(14) Several syntheses of **5j** using the classical Wittig reaction of the corresponding triphenylphosphonium salt of **3b** have been reported. The reaction required strong base (*n*-BuLi or *t*-BuOK) in THF at low temperature and had yields ranging from 60% to 92% with *E*/*Z* ratios between 1:1 and 1:2.8. (a) Ali, M. A.; Kondo, K.; Tsuda, Y. *Chem. Pharm. Bull.* **1992**, *40*, 1130–6. (b) Zhang, W.; Go, M. L. *Eur. J. Med. Chem.* **2007**, *42*, 841. (c) Petitt, G. R.; Grealish, M. P.; Jung, M. K.; Hamel, E.; Petitt, R. K.; Chapuis, J. C.; Schmidt, J. M. *J. Med. Chem.* **2002**, *45*, 2534. (d) Yu, J.; Gaunt, M. J.; Spencer, J. B. *J. Org. Chem.* **2002**, *67*, 4624.

(15) Kurti, L., Czako, B., Eds. *Strategic Applications of Named Reactions in Organic Synthesis*; Elsevier Academic Press: Burlington, MA, 2005; pp 212−3, and references cited therein.

(16) See, for example: Chan, T. H.; Koumaglo, K. *Tetrahedron Lett.* **1986**, *27*, 883.

SCHEME 4. Reduction of TPPMSO (6)



was dissolved in THF and 25 mol % of diphenyl disulfide[16] was added and the mixture was refluxed overnight to give pure *E*-**5l**.

With the less acidic phosphonium salt **3d**, stronger base was required to effect the Wittig reaction. Using lithium hexamethyldisilazide in THF, **3d** reacted with 4-nitrobenzaldehyde (**1a**) to give 1-(4-nitrophenyl)pent-1-ene (**5r**) in 90% isolated yield with $E/Z = 2.1{:}1.0$. Again, the separation of the product alkene from the byproduct phosphine oxide was achieved by ether precipitation.

A key issue is whether the recovered TPPMSO (**6**) can be recycled back to the phosphine sulfonate **1**. Normally, triphenylphosphine oxide is reduced to the corresponding phosphine with either (1) trichlorosilane ($SiHCl_3$) in combination with or without triethylamine or (2) $LiAlH_4$ or its derivative such as alane.[18] In the present case, considerable difficulties were met in the reduction of TPPMSO, presumably because of the electron withdrawing effect of the sulfonate group. $SiHCl_3$, $SiHCl_3/NEt_3$, $SiHCl_3/PhNMe_2$ in toluene, xylene, and PhCN were tried, and all gave poor conversion (about 10−20% with 1 equiv of reduction reagent, based on the integrated signals in ^{31}P NMR of the crude product). If excess reducing reagent was used, the conversion was increased somewhat but never reached more than 50% and the product became complicated. $LiAlH_4$, $LiAlH_4/CeCl_3$ systems were also examined, and they did not offer any improvement. Wyatt et al. reported[19] the use of alane generated in situ from $LiAlH_4$ and H_2SO_4. Curran et al. had used a similar reagent, an alane−*N*,*N*-dimethylamine complex, for reduction of fluorous phosphine oxide.[20] In our hands, none of these alane reagents were suitable as they all gave poor yield of **1**. Finally, Spencer et al. recently reported the quantitative reduction of arylphosphine oxides by using $SiHCl_3$ in combination with triphenylphosphine as oxygen acceptor.[21] The addition of triphenylphosphine allows the reduction to be performed under milder conditions even for very electron deficient phosphine oxides. This method was found to work for TPPMSO (**6**) giving TPPMS (**1**) in excellent yield (Scheme 4). The reaction mixture was quenched by NaOH solution followed by addition of methanol. The solid silica gel derived from hydrolysis of the chlorosilanes was removed by filtration. The filtrate was concentrated and washed with ether. The TPPMS (**1**) was obtained as white solid, identical with the authentic compound. Triphenylphosphine was easily recovered from the ether solution. In this respect, the drawback mentioned by Spencer[20] regarding the difficulty of separating triphenylphospine from the product arylphosphine is avoided because of the insolubility of TPPMS in ether.

In conclusion, we have demonstrated that zwitterionic phosphonium sulfonates **3**, conveniently derived from TPPMS (**1**), can be used as Wittig reagents. The excess reagents and byproduct TPPMSO (**6**) can be easily separated from the product alkenes by simple precipitation with a less polar solvent such as ether. The alkene products thus obtained were often sufficiently pure according to their ^1H NMR spectra to require no chromatographic purification. The sulfonate moiety is robust toward strongly basic conditions and resists reduction by silanes and alanes. The TPPMSO (**6**) can be recycled back to TPPMS (**1**) in high yield.

Recently, the development of supported reagents for the facilitation of the purification of organic reaction products is questioned partly due to the fact that most of the reagents reported in the literature are not commercially available and require multistep synthetic sequences for their preparation. This drawback limits the general practicability of these supported reagents. In our method, the TPPMS is commercially available and also can be prepared from TPP by one step. Relative to the polymer-supported Wittig reagent,[10] because of the low nominal molecular weight of the sulfonate group (SO_3, MW = 80) relative to that of most polymer support (MW ≥ 2000), the loading capacity of the ion tag is much higher. Relative to the fluorous Wittig reagents,[11] the zwitterionic phosphonium sulfonates are easily prepared and their Wittig reactions can be conducted in a range of common solvents instead of perfluoro solvents. While the use of water-soluble phosphonium salts with carboxylic acid or phenol group for Wittig reactions had been previously explored, it met with limited success.[22] The Wittig reaction appeared to be confined to benzyl-containing phosphonium bromides and there was no demonstration of the recycling of the product phosphine oxides.[21] It is our belief that the current approach is a considerable improvement over these related strategies. Finally, the one-pot protocol for the synthesis of α,β-unsaturated esters appears to be convenient.

Experimental Section

Typical Procedure for Preparation of Phosphonium Salts 3a−d. A mixture of TPPMS (1, 728 mg, 2 mmol) and a slight excess of the corresponding bromide (2.4 mmol) was stirred at 50 °C overnight. Ether was added, and the precipitate was filtered to give the target phosphonium salts as white solid.

3a. ^1H NMR (400 MHz, DMSO-d_6): δ 8.05 (d, $J = 7.2$ Hz, 1H), 7.91−7.83 (m, 3H), 7.76−7.58 (m, 10H), 7.28−7.19 (m, 3H), 6.96 (d, $J = 7.2$ Hz, 2H), 5.19 (d, $J = 16$ Hz, 2H). ^{31}P NMR (81 MHz, DMSO-d_6): δ 23.3 (s). HRMS: *m*/*z* calcd for $C_{25}H_{22}PO_3S^+$ 433.1022, found 433.1025.

3b. ^1H NMR (400 MHz, DMSO-d_6): δ 8.05 (d, $J = 7.2$ Hz, 1H), 7.91−7.60 (m, 13H), 6.88 (d, $J = 7.2$ Hz, 2H), 6.78 (d, $J = 7.2$ Hz, 2H), 5.11 (d, $J = 14.8$ Hz, 2H), 3.67 (s, 3H). ^{31}P NMR (81 MHz, DMSO-d_6): δ 23.7 (s). HRMS: *m*/*z* calcd for $C_{26}H_{24}PO_4S^+$ 463.1127, found 463.1125.

3c. ^1H NMR (400 MHz, DMSO-d_6): δ 8.06−7.72 (m, 14H), 5.40 (d, $J = 14.4$ Hz, 2H), 3.59 (s, 3H). ^{31}P NMR (81 MHz, DMSO-d_6): δ 25.4 (s). HRMS *m*/*z* calcd for $C_{21}H_{20}PO_5S^+$ 433.0764, found 433.0767.

3d. ^1H NMR (400 MHz, DMSO-d_6): δ 8.05 (d, $J = 7.6$ Hz, 1H), 7.91−7.73 (m, 13H), 3.06 (m, 2H), 1.47 (m, 4H), 0.87 (t, $J = 6.4$ Hz, 3H). ^{31}P NMR (81 MHz, DMSO-d_6): δ 23.3 (s). HRMS: *m*/*z* calcd for $C_{22}H_{24}PO_3S^+$ 399.1178, found 399.1181.

Typical Procedure for Wittig Reactions Using Phosphonium Salts 3a and 3b. To phosphonium salt **3a** or **3b** (0.2 mmol)

(17) For examples of *Z*- to *E*-isomerization, see: (a) Miyata, O.; Shinada, T.; Ninomiya, I.; Naito, T. *Synthesis* **1990**, 1123. (b) Baag, M.; Kar, A.; Argade, N. P. *Tetrahedron* **2003**, *59*, 6489. (c) Kim, I. S.; Dong, G. R.; Jung, Y. H. *J. Org. Chem.* **2007**, *72*, 5424.

(18) Leyva, A.; Garcia, H.; Corma, A. *Tetrahedron* **2007**, *63*, 7097.

(19) (a) Bootle-Wilbraham, A.; Head, S.; Longstaff, J.; Wyatt, P. *Tetrahedron Lett.* **1999**, *40*, 5267. (b) Griffin, S.; Heath, L.; Wyatt, P. *Tetrahedron Lett.* **1998**, *39*, 4405.

(20) Dandapani, S.; Curran, D. P. *Tetrahedron* **2002**, *58*, 3855.

(21) Wu, H.-C.; Yu, J.-Q.; Spencer, J. B. *Org. Lett.* **2004**, *6*, 4675.

(22) The sulfonate group is more robust than, for example, the carboxylic acid group to reduction by alane or silane. See: (a) Russell, M. G.; Warren, S. *Tetrahedron Lett.* **1998**, *39*, 7995. (b) Russell, M. G.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 505.

suspended in methanol (1 mL) was added NaOH (0.25 mmol). After 5 min, the appropriate aldehyde (0.2 mmol) was added. The mixture was stirred at room temperature overnight. Ether (3 mL) was added to precipitate **6**. After filtration, the filtrate was evaporated to give the alkene product **5**.

The alkenes **5a**−**j** (Table 1 and Scheme 3) are known compounds: **5a**;[23] **5b**−**e**;[24] **5f**;[25] **5g**;[26] **5i**;[27] **5j**.[28] They were properly characterized and found to be in agreement with literature reports.

Typical Procedure for Wittig Reaction Using Phosphonium Salt 3c. Method 1. To phosphonium salt **3c** (104 mg, 0.2 mmol) suspended in methanol (1 mL) was added K_2CO_3 (0.25 mmol). After 5 min, the appropriate aldehyde (4, 0.2 mmol) was added. The reaction mixture was stirred at room temperature overnight. Ether (3 mL) was added to precipitate **6**. After filtration, the filtrate was evaporated to give the alkene product **5**.

Method 2. TPPMS (**1**, 73 mg, 0.2 mmol), methyl bromoacetate (31 mg, 0.2 mmol), K_2CO_3 (0.25 mmol), and the appropriate aldehyde (**4**, 0.2 mmol) were all added to methanol (1 mL) and the mixture stirred overnight. The reaction was worked up as above to give alkene product **5**.

The alkenes **5k**−**q** (Table 2) are known compounds: **5k**−**n**;[29] **5o**;[30] **5p**;[31] **5q**.[32]

Isomerization for the synthesis of *E*-5l. A mixture of *E*- and *Z*-**5l** was prepared according to method 2. After addition of ether and filtration to remove the precipitated **6**, the filtrate was concentrated and the crude product dissolved in anhydrous THF (2 mL). Diphenyl disulfide (11 mg, 25 mol%) was added, and the mixture was refluxed under argon overnight. NMR showed that the isomerization was completed. The mixture was purified by chromatography to give the pure *E*-**5l** in 90% yield.

Typical Procedure for Wittig Reaction Using Phosphonium Salt 3d. To phosphonium salt **3d** (100 mg, 0.2 mmol) suspended in THF (1 mL) was added LiHMDS (0.2 mmol in THF). After 5 min, the appropriate aldehyde (0.2 mmol) was added. The reaction mixture was stirred at room temperature overnight. Ether (3 mL) was added to give precipitate. The mixture was filtered, and the filtrate was evaporated to give corresponding alkene product **5r**, with properties in agreement with literature report.[33]

Reduction of TPPMSO (6) Using Trichlorosiland and Triphenylphosphine. In a 50 mL pressure tube, the phosphine oxide **6** (200 mg, 0.52 mmol) and triphenylphosphine (274 mg, 1.05 mmol) were suspended in toluene (10 mL) under argon atmosphere. To the mixture was added trichlorosilane (1 mL, 10 mmol) at room temperature. The mixture was stirred at 110 °C overnight. The mixture was cooled to ambient temperature. The mixture was quenched with NaOH (2 mL, 20 wt %), and MeOH (25 mL) was added subsequently. The mixture was filtrated by a thin pad of Celite. The liquid phase was concentrated, and MeOH (25 mL) was added again. The solution was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was washed with ether (3 × 20 mL) to give the TPPMS (**1**) as white solid (170 mg, 90% yield).

TPPMS (**1**): ^{1}H NMR (400 MHz, CD_3OD) δ 7.85−7.81 (m, 2H), 7.43−7.39 (m, 1H), 7.37−7.26 (m, 11H); ^{31}P NMR (81 MHz, CD_3OD) δ −4.07 (s).

TPPMSO (**6**): ^{1}H NMR (400 MHz, CD_3OD) δ 8.13−8.07 (m, 2H), 7.81−7.75 (m, 1H), 7.69−7.62 (m, 7H), 7.58−7.53 (m, 4H); ^{31}P NMR (81 MHz, CD_3OD) 32.6 (s).

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Supporting Information Available: Copies of NMR spectra of reagents and product alkenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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