Regiodivergent Approach to α- and β-(Arylthio)alkenylphosphane Oxides and Sulfides: Aminophosphanes as Synthetic Auxiliaries

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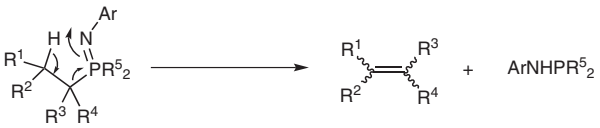
Abstract: β-(Arylthio)ethenylphosphane oxides and sulfides are easily prepared by nucleophilic addition of thiophenols to the C≡C bond of the respective *P*,*P*-diphenyl-*P*-phenylethynyl P(V) derivatives. The regioisomeric α-(arylthio) analogues can be also prepared, starting from the same activated alkynes, by sequential nucleophilic addition of aminophosphanes and thiophenols. In these latter cases, aminophosphanes, which are recovered at the end of the processes, act just as synthetic auxiliaries for modulating the regiochemical outcome of the global thiophenol addition.

Key words: alkynes, aminophosphanes, nucleophilic additions, phosphorus, regioselectivity

A few examples of nucleophilic additions to the C≡C bond of some classes of *P*-alkynyl derivatives, such as phosphane oxides and sulfides, phosphonates, and thiophosphonates, have been described up to now.[1] The regiochemical results of these reactions are in agreement with the electron-withdrawing character of these P(V) functionalities, which play the role of activating groups in such processes.

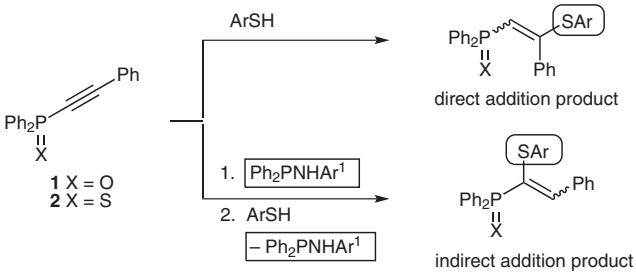
We have reported that aminophosphanes[2] $R^1{}_2PNHR^2$ are excellent nucleophilic species in reactions with reactive alkyl halides,[3] and carbon–carbon double[4] and triple[5] bonds. In all these reactions the aminophosphanes experience regioselective alkylation at the P atom and, consequently, they behave as synthetic equivalents of iminophosphide anions $[R^1{}_2P{=}NR^2]^-$ or, in other words, as iminophosphoranyl synthons. We have also shown that Michael-type additions of nucleophiles to the C=C bond of *P*-alkenyl iminophosphoranes are easy processes facilitated by the electron-withdrawing characteristics of the iminophosphoranyl group.[4,6] Additionally, we have recently demonstrated that some *P*-alkyl iminophosphoranes bearing hydrogen atoms on the β-carbon atom may easily experience β-elimination reactions of aminophosphane units (Scheme 1) yielding alkenes.[5]

On the basis of an adequate combination of these precedents, we reasoned that aminophosphanes might be useful synthetic auxiliaries[7] in indirect additions of nucleophiles to activated alkynes, as far as a three-step sequence consisting of aminophosphane addition to the alkyne, further addition of a nucleophile to the resulting *P*-alkenyl iminophosphorane, and final β-elimination of the aminophosphane auxiliary, could be succesfully achieved. Such synthetic strategy would allow the preparation of the alternative regioisomers to those derived from the direct addition of the same nucleophile.



Scheme 1 β-Elimination of aminophosphane units in *P*-alkyl iminophosphoranes

Here we present the results obtained when aminophosphanes are utilized as synthetic auxiliaries in the addition of thiophenols to the triple carbon–carbon bonds of *P*,*P*-diphenyl-*P*-phenylethynylphosphane oxide **1** and sulfide **2** (Scheme 2).



Scheme 2 Regiodivergent direct and indirect (by using aminophosphanes as synthetic auxiliaries) addition of thiophenols to alkynes **1** and **2**

We first tested the direct addition approach by reacting the phosphane oxide **1**[8] and sulfide **2**[9] with thiophenols in the presence of a catalytic amount (0.2 equiv) of potassium hexamethyldisilazide (KHMDS), in toluene under reflux for 12 hours, to give the β-(arylthio)ethenylphosphane oxides **3** and sulfides **4**, respectively (Scheme 3, Table 1). These products were isolated as mixtures of *Z*- and *E*-stereoisomers, and only in one case these two isomers could be efficiently separated by chromatographic purification on silica gel which was previously deactivated with triethylamine (5% in hexane).[10] As it has been found in other nucleophilic additions to the C≡C bond of electron-deficient alkynes,[11] the reactions leading to **3** and **4** are totally regioselective, the nucleophilic part of the reagents adding to the carbon atom which is in the β-position to the phosphorus atom.

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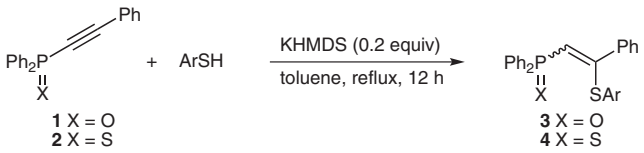


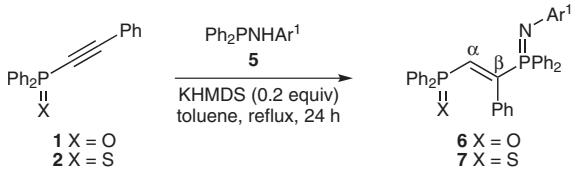
Scheme 3 Synthesis of β-(arylthio)ethenylphosphane oxides **3** and sulfides **4**

Table 1 β-(Arylthio)ethenylphosphane Oxides **3** and Sulfides **4**

Product	X	Ar	Ratio *Z*/*E*[a]	Isolated yields (%)	
				Z-Isomer	*E*-Isomer
3a	O	Tol	58:42	90[b]	
3b	O	PMP	66:33	51	25
4a	S	Tol	62:38	75[b]	
4b	S	PMP	58:42	72[b]	

[a] As determined by ^{1}H NMR spectra of the final reaction mixtures.
[b] Global yield, *Z*- and *E*-isomers not separated.

We then approached the indirect addition route by refluxing toluene solutions of the oxide **1** and sulfide **2** with a number of aminophosphanes **5** for 24 hours in the presence of the same catalytic amount of KHMDS. The expected iminophosphoranyl phosphane oxides **6** and sulfides **7** were, respectively, obtained in good yields (Scheme 4, Table 2).[12] It is worth noting that these nucleophilic additions proceeded with total regio- and diastereoselectivity, affording exclusively the *E*-isomers.



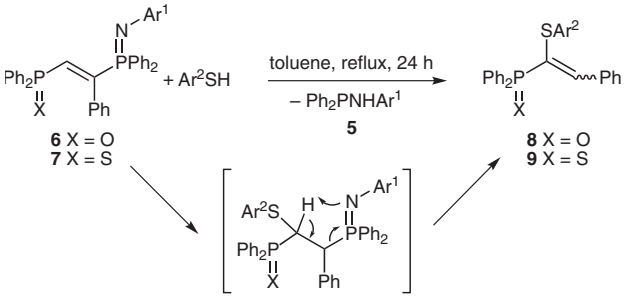
Scheme 4 Aminophosphane additions to alkynes **1** and **2**

Table 2 (*E*)-β-(Iminophosphoranyl)phosphane Oxides **6** and Sulfides **7**

Product	X	Ar[1]	Isolated yields (%)
6a	O	Tol	65
6b	O	PMP	78
6c	O	4-BrC_6H_4	88
7a	S	Tol	90
7b	S	PMP	81
7c	S	4-BrC_6H_4	83

Careful scrutiny of the NMR data of compounds **6** and **7**, paying particular attention to the values of the $^3J_{HP}$, $^3J_{CP}$, and $^3J_{PP}$ coupling constants, allowed us the unambiguous assignment of their *E*-geometries. For example, in their ^{1}H NMR spectra the value of $^3J_{HP}$ for the α-proton is close to 21 Hz, coincident with other reports of *cis* $^3J_{HP}$ coupling constants in *P*-vinyliminophosphoranes[12] and analogous bis(sulfides) and bis(oxides).[13] In addition, in their ^{13}C NMR spectra, the quaternary *ipso* carbon of the *C*-phenyl group appears coupled with phosphorus with a coupling constant $^3J_{CP}$ = 8.4–8.9 Hz, which is in the typical range of *cis* $^3J_{CP}$ values of comparable structures.[13,14] The values of the $^3J_{PP}$ coupling constants in their ^{31}P NMR spectra, close to 46 Hz, are in agreement with typical values found for compounds bearing two P(V) atoms placed in relative *trans* disposition of a carbon–carbon double bond.[13b,15]

Fortunately, the following two steps of the planned synthetic strategy, namely the addition of thiophenols and the further β-elimination of aminophosphane, occurred in a single experimental step when species **6** and **7** were reacted with thiophenols in toluene at reflux, yielding the α-(arylthio)ethenylphosphane oxides **8** and sulfides **9** (Scheme 5, Table 3).[16]



Scheme 5 Synthesis of α-(arylthio)ethenylphosphane oxides **8** and sulfides **9**.

Delightfully, these one-pot addition–elimination processes occur in a completely regioselective manner giving rise to compounds **8** and **9** resulting from the introduction of the ArS group at the α-carbon of the ethenyl fragment, whereas the alternative regioisomers **3** and **4** were not detected in the final reaction mixtures. This result is apparently determined by the regiocontrol operating in the thiophenol addition step, in which the P=N function controls the conjugate addition whereas the P=X (X = O, S) one is a mere spectator. This fact could be attributed to the easy accessibility of the nucleophile to the less substituted carbon atom of the C=C bond, as well as to the preactivation of the thiophenol by the interaction between its acidic proton and the basic N center of the iminophosphoranyl fragment.

Previously unknown α-(arylthio)ethenylphosphane oxides **8** and sulfides **9** were so obtained in fair to good yields (Table 3). Although we carried out the reaction of each thiophenol with several, differently Ar[1]-substituted reactants **6** or **7**, we could not determine a general trend concerning which Ar[1] group would give rise to the best yield of products. Whereas the detailed study of the stereochemical course of these processes and its rational explanation are out of the bounds of this synthetic publication, it is worth noting that phosphane oxides **8** were obtained

Table 3 α-(Arylthio)ethenylphosphane Oxides **8** and Sulfides **9**

Entry	Product	X	Ar[1]	Ar[2]	Ratio *Z*/*E*[a]	Isolated yields (%)	
						Z-Isomer	*E*-Isomer
1	**8a**	O	Tol	Tol	87:13	80	12
2	**8a**	O	PMP	Tol	93:7	70	6
3	**8a**	O	4-BrC_6H_4	Tol	74:26	68	25
4	**8b**	O	Tol	PMP	58:42	44	32
5	**8b**	O	PMP	PMP	58:42	43	24
6	**8b**	O	4-BrC_6H_4	PMP	57:43	50	39
7	**9a**	S	Tol	Tol	100:0	30	-
8	**9a**	S	PMP	Tol	100:0	43	-
9	**9a**	S	4-BrC_6H_4	Tol	100:0	56	-
10	**9b**	S	Tol	PMP	100:0	58	-
11	**9b**	S	PMP	PMP	100:0	37	-
12	**9b**	S	4-BrC_6H_4	PMP	100:0	64	-

[a] As determined by integration in the ^{1}H NMR spectra of the final reaction mixtures. Each isomer was unequivocally identified according to the values of the $^3J_{HP}$ and $^3J_{CP}$ coupling constants shown by their β-H and phenyl C-*ipso* atoms, respectively, in the ^{1}H NMR and ^{13}C NMR spectra.

as mixtures of *Z*- and *E*-isomers, in which *Z* is always the major component, with *Z*/*E* ratios ranging from 57:43 (entry 6) to 93:7 (entry 2). In contrast, phosphane sulfides **9** were isolated as single *Z*-isomers, although in lower yields. In the crude reaction mixtures leading to these latter compounds, we could detect phosphinothioic amides Ar^{1}NHP(*S*)Ph$_2$ in variable amounts, that most probably are the result of a sulfur-atom transfer from sulfides **9** to the aminophosphanes **5** originated in those reactions. Such sulfur transfer, which has been shown to be feasible from phosphorus atoms to more nucleophilic ones,[17] can account for the lower yields in sulfides **9** when compared with oxides **8**.

We also attempted to carry out the indirect addition sequence in a one-pot manner. Thus, alkynylphosphane oxide (**1**) was reacted with *N*-4-tolylamino-*P*,*P*-diphenylphosphane (1 equiv) and KHMDS (0.2 equiv) in refluxing toluene. After 24 hours, 4-methoxythiophenol (1 equiv) was added into the reaction flask and refluxing continued for 12 hours. The ^{1}H NMR and ^{31}P NMR analysis showed that the major components of the final reaction mixture were those resulting from the indirect addition process [86% yield, (*Z*)-**8b**/(*E*)-**8b** = 87:13] although accompanied by a minor amount of the direct thiophenol addition isomers [14% yield, (*Z*)-**3b**/(*E*)-**3b** = 66:34].

Finally we tested a one-pot process in which the aminophosphane auxiliary was used in substoichiometric amounts. When an equimolecular mixture of **1** and 4-methoxythiophenol was refluxed in toluene solution for 24 hours in the presence of only 0.2 equiv of *N*-4-tolylamino-*P*,*P*-diphenylphosphane, the main products were also (*Z*)-**8b**/(*E*)-**8b** (66%, 77:23 ratio), although the conversion was only 76%.

α-(Arylthio)alkenylphosphane oxides and sulfides have been scarcely reported in the chemical literature. To our knowledge, only the syntheses of 1-(phenylthio)vinyldiphenylphosphane oxide, from its saturated analogue,[18] and (*Z*)-1-(phenylthio)crotyldiphenylphosphane oxide, obtained from allyldiphenylphosphane oxide,[19] have been disclosed.

In summary, we have developed a convenient method for modulating the regiochemistry of thiophenol additions to the C≡C bond of *P*,*P*-diphenyl-*P*-phenylethynylphosphane oxide and sulfide, which allows the regiodivergent approach to the α- and β-addition products. Whereas the base-mediated addition of thiophenols led to the expected β-(arylthio)ethenyl derivatives, the addition of aminophosphanes to the β-carbon of the alkyne, and its easy removal after the further thiophenol addition are the key points for the success of the indirect addition mode leading to the α-substituted products. We hope these results may stimulate the search for new applications of aminophosphanes as auxiliary reagents in other addition reactions.

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(10) **Representative Experimental Procedure and Spectral Data for Compounds 3**
A solution of *P*,*P*-diphenyl-*P*-phenylethynylphosphane oxide (**1**, 0.3 g, 1 mmol), 4-methoxythiophenol (0.21 g, 1.5 mmol), and KHMDS (0.5 M soln in toluene, 0.4 mL, 0.2 mmol) in toluene (20 mL) was refluxed for 12 h under a nitrogen atmosphere. Then the solvent was removed under reduced pressure, and the residue was purified by chromatography on deactivated silica gel (5% Et_3N in hexane) with EtOAc–hexane 1:1 (v/v) and then EtOAc to yield a mixture of *Z*- and *E*-isomers; R_f = 0.5 (EtOAc). The subsequent fractional crystallization allowed the separation of the two isomers.
(*Z*)-*P*,*P*-Diphenyl-*P*-[2-phenyl-2-(4-methoxyphenylthio)]ethenylphosphane Oxide (*Z*-3b)
White needles (from CH_2Cl_2–Et_2O), mp 196–197 °C. IR (Nujol): 1589, 1544, 1491, 1439, 1246, 1181, 1119, 739, 719, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.63 (s, 3 H, OCH_3), 6.51 (d, 2 H, $^3J_{HH}$ = 8.9 Hz, H_{Ar}), 6.53 (d, 1 H, $^2J_{HP}$ = 20.0 Hz, CHP), 6.88 (d, 2 H, $^3J_{HH}$ = 8.9 Hz, H_{Ar}), 7.16–7.19 (m, 3 H, Ph), 7.38–7.45 (m, 2 H, Ph), 7.46–7.51 (m, 6 H, Ph_2), 7.87–7.94 (m, 4 H, Ph_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.08 (OCH_3), 114.08, 122.41 (d, $^1J_{CP}$ = 104.5 Hz, P*C*H=C), 123.18 (quaternary), 128.04, 128.48, 128.50 (d, $^3J_{CP}$ = 12.2 Hz, C_m), 129.26, 131.19 (d, $^2J_{CP}$ = 9.8 Hz, C_o), 131.50 (d, $^4J_{CP}$ = 2.8 Hz, C_p), 134.35 (d, $^1J_{CP}$ = 106.7 Hz, C_i), 134.4, 139.03 (d, $^3J_{CP}$ = 14.4 Hz, quaternary), 159.20 (d, $^2J_{CP}$ = 1.0 Hz, PCH=*C*), 161.28 (quaternary). ^{31}P NMR (121 MHz, $CDCl_3$): d = 19.90. MS (EI): *m/z* = 443 (10) $[M + 1]^+$, 442 (10) $[M]^+$, 201 (100). Anal. Calcd for $C_{27}H_{23}O_2PS$ (442.51): C, 73.28; H, 5.24. Found: C, 73.41; H, 5.10.
(*E*)-*P*,*P*-Diphenyl-*P*-[2-phenyl-2-(4-methoxyphenylthio)]ethenylphosphane Oxide (*E*-3b)
White needles (from CH_2Cl_2), mp 119–120 °C. IR (Nujol): 1588, 1554 1492, 1439, 1247, 1176, 1167, 1116, 703, 691 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 5.78 (d, 1 H, $^2J_{HP}$ = 15.2 Hz, CHP), 6.95 (d, 2 H, $^3J_{HH}$ = 9.0 Hz, H_{Ar}), 6.99–7.11 (m, 3 H), 7.17–7.30 (m, 7 H), 7.37–7.50 (m, 5 H), 7.55 (d, 2 H, $^3J_{HH}$ = 9.0 Hz, H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.53 (OCH_3), 113.50 (d, $^1J_{CP}$ = 104.6 Hz, P*C*H=C), 115.51, 121.23 (quaternary), 128.10 (d, $^3J_{CP}$ = 12.1 Hz, C_m), 128.22, 129.23 (d, $^4J_{CP}$ = 1.2 Hz,), 129.39, 130.81 (d, $^2J_{CP}$ = 9.5 Hz, C_o), 130.88 (d, $^4J_{CP}$ = 2.7 Hz, C_p), 133.69 (d, $^1J_{CP}$ = 106.6 Hz, C_i), 136.86 (d, $^3J_{CP}$ = 6.5 Hz, quaternary), 137.41, 161.12 (quaternary), 164.79 (d, $^2J_{CP}$ = 4.7 Hz, PCH=*C*). ^{31}P NMR (121 MHz, $CDCl_3$): d = 17.90. MS (EI): *m/z* = 443 (11) $[M + 1]^+$, 442 (28) $[M]^+$, 201 (100). Anal. Calcd for $C_{27}H_{23}O_2PS$ (442.51): C, 73.28; H, 5.24. Found: C, 73.39; H, 5.38.

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(12) **Representative Experimental Procedure and Spectral Data for Compounds 6**
A solution of *P*,*P*-diphenyl-*P*-phenylethynylphosphane oxide (**1**, 0.3 g, 1 mmol), *P*,*P*-diphenyl-*P*-(4-tolylamino)-phosphane (0.44 g, 1.5 mmol), and KHMDS (0.5 M soln in toluene, 0.4 mL, 0.2 mmol) in anhyd toluene (20 mL) was refluxed for 24 h under a nitrogen atmosphere. Then, the solvent was removed under reduced pressure, and the residue was purified by chromatography on deactivated silica gel (5% Et_3N in hexane) with EtOAc–hexane 1:1 (v/v) and then EtOAc to yield **6a** as orange prisms (from CH_2Cl_2–Et_2O), mp 153–155 °C. IR (Nujol): 1505, 1439, 1331, 1181, 1119, 722, 706, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, CH_3), 6.82–6.86 (m, 6 H, H_{Ar} and Ph), 6.93–6.99 (m, 3 H, H_{Ar} and Ph), 7.17–7.26 (m, 4 H, Ph_2), 7.29–7.45 (m, 12 H, Ph_2), 7.63 (t, 1 H, $^2J_{HP}$ = $^3J_{HP}$ = 21.2 Hz, CH), 7.64–7.69 (m, 4 H, Ph_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.74 (CH_3), 124.06 (d, $^3J_{CP}$ = 18.5 Hz, C_2-Ar), 127.35, 128.06 (d, $^5J_{CP}$ = 1.2 Hz, C_4-Ph), 128.26 (d, $^3J_{CP}$ = 12.1 Hz, C_m), 128.47 (d, $^3J_{CP}$ = 12.1 Hz, C_m), 128.87 (d, $^1J_{CP}$ = 102.5 Hz, C_i), 129.55, 129.60, 130.77 (d, $^2J_{CP}$ = 9.7 Hz, C_o), 131.30 (d, $^4J_{CP}$ = 2.7 Hz, C_p), 131.92 (d, $^4J_{CP}$ = 2.4 Hz, C_p), 132.80 (d, $^2J_{CP}$ = 9.2 Hz, C_o), 133.12 (d, $^1J_{CP}$ = 105.4 Hz, C_i), 134.00 (t, $^2J_{CP}$ = $^3J_{CP}$ = 8.9 Hz, quaternary, C_1-Ph), 137.90 [dd, $^1J_{CP}$ = 87.6 Hz, $^2J_{CP}$ = 5.4 Hz, P*C*H = CP], 147.97 (d, $^2J_{CP}$ = 2.0 Hz, quaternary, C_1-Ar), 152.62 [d, $^1J_{CP}$ = 65.6 Hz, PCH=*C*P], C_4-Ar not observed. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 4.39 (d, $^3J_{PP}$ = 45.4 Hz, P=N), 18.03 (d, $^3J_{PP}$ = 45.4 Hz, P=O). MS (EI): *m/z* = 594 (13) $[M + 1]^+$, 593 (28) $[M]^+$, 291 (100). Anal. Calcd for $C_{39}H_{33}NOP_2$ (593.20): C, 78.91; H, 5.60; N, 2.36. Found: C, 79.04; H, 5.46; N, 2.26.

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(16) **Representative Experimental Procedure and Spectral Data for Compounds 8**
A solution of **6a** (0.78 g, 1.32 mmol) and 4-methoxythiophenol (0.21 g, 1.5 mmol) in anhyd toluene (20 mL) was refluxed for 12 h under a nitrogen atmosphere. Then, the solvent was removed under reduced pressure, and the residue was purified by chromatography on deactivated silica gel (5% Et_3N in hexane) with EtOAc–hexane 1:1 (v/v) and then EtOAc.

(*Z*)-*P*,*P*-Diphenyl-*P*-[2-phenyl-1-(4-methylphenylthio)]ethenylphosphane Oxide (*Z*-8b)

R_f = 0.7 (EtOAc); white prisms (from CH_2Cl_2–Et_2O), mp 126–127 °C. IR (Nujol): 1589, 1493, 1434, 1298, 1246, 1201, 723, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3 H, OCH_3), 6.45 (d, 2 H, $^3J_{HH}$ = 8.9 Hz, H_{Ar}), 6.72 (d, 2 H, $^3J_{HH}$ = 8.9 Hz, H_{Ar}), 7.31–7.38 (m, 7 H, Ph_2 and Ph), 7.44–7.47 (m, 2 H, Ph), 7.78–7.81 (m, 4 H, Ph_2), 7.88–7.90 (m, 2 H, Ph), 8.27 (d, 1 H, $^3J_{HP}$ = 17.3 Hz, CHP). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.26 (OCH_3), 114.34, 124.63 (d, $^3J_{CP}$ = 1.5 Hz, quaternary, C_1-Ar), 125.37 (d, $^1J_{CP}$ = 97.1 Hz, P*C*=CH), 128.22 (d, $^3J_{CP}$ = 2.1 Hz, C_m), 128.38, 129.72, 130.25, 130.42 (d_{right}, C_i), 130.77, 131.87 (d, $^4J_{CP}$ = 2.8 Hz, C_p), 132.38 (d, $^2J_{CP}$ = 9.7 Hz, C_o), 134.58 (d, $^3J_{CP}$ = 15.7 Hz, quaternary, C_1-Ph), 152.14 (d, $^2J_{CP}$ = 13.7 Hz, PC=*C*H), 158.25 (quaternary). ^{31}P NMR (162 MHz, $CDCl_3$): d = 28.30. MS (EI): *m/z* = 443 (23) [M + 1]$^+$, 442 (66) [M]$^+$, 303 (100). Anal. Calcd for $C_{27}H_{23}O_2PS$ (442.51): C, 73.28; H, 5.24. Found: C, 73.15; H, 5.32.

(*E*)-*P*,*P*-Diphenyl-*P*-[2-phenyl-2-(4-methoxyphenylthio)]ethenylphosphane Oxide (*E*-8b)

R_f = 0.55 (EtOAc); colourless oil. IR (Nujol): 1593, 1491, 1291, 1246, 1176, 1115, 722, 694 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, OCH_3), 6.83 (d, 2 H, $^3J_{HH}$ = 8.8 Hz, H_{Ar}), 7.01–7.03 (m, 3 H), 7.24 (d, 1 H, $^3J_{HP}$ = 48.2 Hz, CHP), 7.29–7.33 (m, 6 H, Ph_2), 7.37–7.42 (m, 4 H, Ph), 7.72–7.77 (m, 4 H, Ph_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.42 (OCH_3), 115.19, 124.11 (d, $^3J_{CP}$ = 5.0 Hz, quaternary, C_1-Ar), 127.67, 128.07 (d, $^3J_{CP}$ = 12.2 Hz, C_m), 128.28, 129.73, 131.66 (d, $^4J_{CP}$ = 3.0 Hz, C_p), 131.92 (d, $^2J_{CP}$ = 9.3 Hz, C_o), 131.97 (d, $^1J_{CP}$ = 89.8 Hz, P*C*=CH), 132.23 (d, $^1J_{CP}$ = 106.2 Hz, C_i), 135.12, 135.52 (d, $^3J_{CP}$ = 5.0 Hz, quaternary, C_1-Ph), 146.26 (d, $^2J_{CP}$ = 7.4 Hz, PC=*C*H), 160.13 (quaternary). ^{31}P NMR (121 MHz, $CDCl_3$): δ = 25.39. MS (EI): *m/z* = 442 (10) [M]$^+$, 105 (100). Anal. Calcd for $C_{27}H_{23}O_2PS$ (442.51): C, 73.28; H, 5.24. Found: C, 73.16; H, 5.32.

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