Synthesis X.-L. Wang et al. Paper

Synthesis of α,β-Unsaturated Phosphine Sulfides

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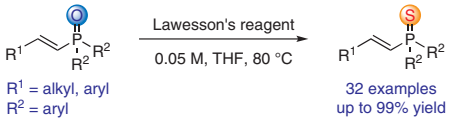

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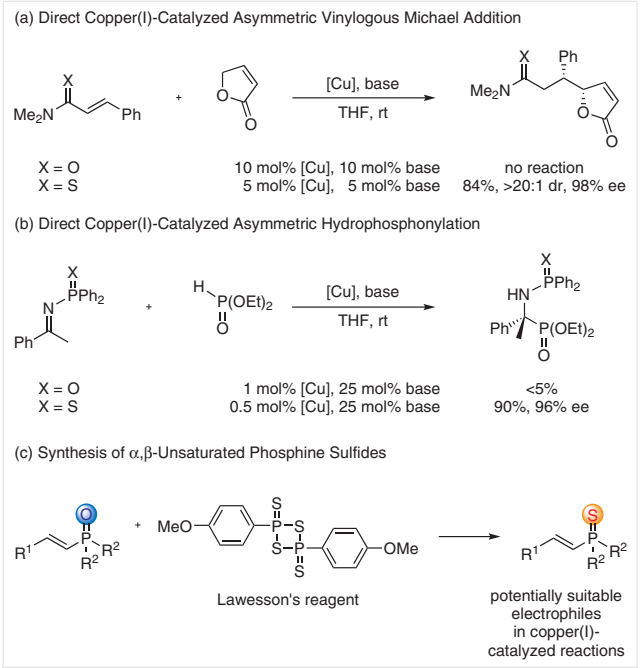
Abstract α,β-Unsaturated phosphine sulfides may exhibit different reactivity from α,β-unsaturated phosphine oxides toward nucleophilic addition and thus may find new applications in copper(I)-catalyzed asymmetric reactions. Herein, various α,β-unsaturated phosphine sulfides were prepared in moderate to excellent yields from the parent α,β-unsaturated phosphine oxides with Lawesson's reagent. The reaction enjoys a broad substrate scope and tolerates a variety of functional groups.

Key words phosphine oxides, phosphine sulfides, thionation, Lawesson's reagent, thiocarbonyl compounds

'Soft' thiocarbonyl compounds may show different reactivities from the parent and 'hard' carbonyl compounds in asymmetric catalysis with soft metal catalysts.[1] Thioamides have been reported as wonderful enolizable substrates in direct asymmetric aldol, Mannich, and Michael reactions with copper(I) catalysts.[2] However, the parent amides were hard to enolize under the same reaction conditions and did not react with aldehydes, imines, and α,β-unsaturated compounds to give the target products. Moreover, α,β-unsaturated thioamides have served as powerful electrophiles and enabled various challenging asymmetric reactions in the presence of copper(I) catalysts.[3] For example, the addition of crotonolactone to an α,β-unsaturated amide was found to be extremely difficult while the reaction with an α,β-unsaturated thioamide proceeded efficiently to give the adduct in 84% yield with >20:1 dr and 98% ee (Scheme 1a).[3g]

N-Thiophosphinoyl ketimines also allowed unprecedented copper(I)-catalyzed asymmetric nucleophilic additions.[4,5] In 2013, Shibasaki, Kumagai, and co-workers reported a copper(I)-catalyzed asymmetric addition of dialkyl phosphite to *N*-thiophosphinoyl ketimines (Scheme 1b).[5c] It is noteworthy that an *N*-phosphinoyl ketimine was inert in the presence of the copper(I) catalyst, which resulted in significantly low yield. However, an *N*-thiophosphinoyl ketimine reacted with diethyl phosphite smoothly to afford the product in 90% yield with 96% ee. Analogously, it is very reasonable to envision that α,β-unsaturated phosphine sulfides would find their application in asymmetric reactions with copper(I) catalysts. Here, we would like to report a method for the efficient preparation of an array of α,β-unsaturated phosphine sulfides from the parent α,β-unsaturated phosphine oxides with Lawesson's reagent.



Scheme 1 Application of an α,β-unsaturated thioamide and *N*-thiophosphinoyl ketimine as efficient electrophiles in copper(I)-catalyzed asymmetric reactions

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2,4-Bis(4-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide was named Lawesson's reagent (LR) due to Professor Lawesson's profound contributions for systematic study on the application of this reagent in organic chemistry.[6] LR is a mild and convenient thionating agent for ketones, esters, and amides, which allows the preparation of thioketones, thioesters, and thioamides in good yields.[7] Furthermore, LR has been employed in the synthesis of various heterocyclic compounds containing sulfur atom(s).[8] LR shows advantages over other classical thionating reagents (such as P_4S_{10}), such as commercial availability, easy handling, and relatively high yield in the thionation. The thionation mechanism with LR has been supported both experimentally[9] and computationally.[10] Recently, new applications of LR in organic synthesis have emerged.[11]

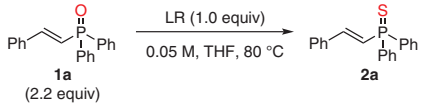
The use of LR to transform P=O to P=S has been previously studied.[12] The reaction was generally carried out in refluxing toluene and good conversion can be accomplished without affecting some functional groups such as imide, amide, lactam, and ester. However, substrates bearing an α,β-unsaturated moiety remain unexplored. Moreover, α,β-unsaturated phosphine sulfides might give some unexpected new reactions in which the parent α,β-unsaturated phosphine oxides might not be applied, especially in the presence of soft copper(I) catalysts.[13] Therefore, there is a need to investigate such a thionation reaction with LR, which transforms α,β-unsaturated phosphine oxides to the corresponding α,β-unsaturated phosphine sulfides (Scheme 1c). Reported approaches toward the synthesis of α,β-unsaturated phosphine sulfides include the addition of secondary phosphine chalcogenides to alkynes,[14] Wittig olefination,[15] and the sulfidation of α,β-unsaturated phosphines, which were generated by the hydrophosphination of alkynes.[16] Compared to the above-reported examples, our method with LR represents an easy and straightforward methodology with a broad substrate scope and good tolerance of functional groups.

We commenced with the thionation of **1a** in the presence of LR (Table 1). Considering the unpleasant smell from LR, **1a** was used in 2.2 equivalents to obtain a full conversion of LR. At room temperature, several common solvents were screened, including THF, MeCN, MeOH, DME, toluene, DCM, and DMF. The reaction in THF, MeCN, DME, or toluene generated product **2a** in about 20% yield. With DME as the solvent, the chemical yield increased as the reaction temperature was increased. At 80 °C, **2a** was obtained in 82% yield. The same tendency was observed for the reaction in THF. Product **2a** was isolated in 89% yield at 80 °C (entry 13). Therefore, THF was chosen as the best solvent and the best reaction temperature was set as 80 °C.

With the optimized reaction conditions in hand, the substrate scope of α,β-unsaturated phosphine oxides was investigated (Scheme 2). As for β-aryl-substituted α,β-unsaturated phosphine oxides, substrates with electron-withdrawing groups (including halide, trifluoromethyl, and cyano) at the *para*-position generally gave high yields (**2b–f**) while the products (**2g** and **2h**) with electron-donating groups (including methyl and methoxy) were isolated in moderate yields. Substrates with a halogen atom at the *meta*-position were accepted to generate the products (**2i** and **2j**) in moderate yields. It is interesting to note that the sterically congested *ortho*-bromo-substituted substrate gave the product in quantitative yield (**2k**). The reaction conditions were also applicable to heteroaromatic substrates, furnishing the corresponding products (**2l–q**) in good to excellent yields.

As for β-alkyl-substituted α,β-unsaturated phosphine oxides, both linear and cyclic alkyls were well tolerated to afford the corresponding products (**2r–t**) in high yields. Remarkably, thionation of the substrate with a bulky *tert*-butyl group at the β-position proceeded nicely, in 83% yield (**2u**). Moreover, an α,β,γ,δ-unsaturated phosphine oxide was successfully transformed to the corresponding sulfide in synthetically useful yield (**2v**). Particularly noteworthy is product **2w**, possessing a TMS substituent at the β-position, which allows further structure elaboration. The alkyls bearing functional groups (including sulfonate, chloride, benzyl ether, and sulfonamide) were well tolerated without disturbing the target thionation reaction (**2x–ab**). Lastly, substrates with various aryl groups (including *p*-tolyl, *p*-fluorophenyl, 2-naphthyl, and 2-furanyl) on the phosphine center

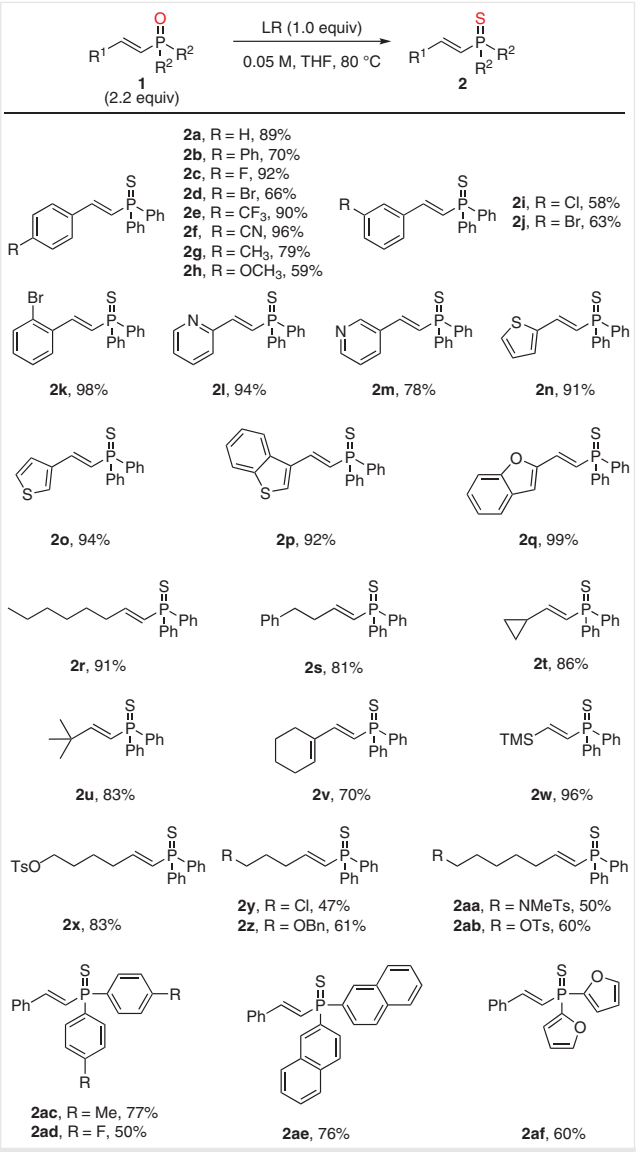
Table 1 Optimization of the Reaction Conditions[a]



1a (2.2 equiv) **2a**

Entry	Solvent	Temp (°C)	Yield (%)[b]
1	THF	rt	26
2	MeCN	rt	23
3	MeOH	rt	–
4	DME	rt	29
5	toluene	rt	19
6	DCM	rt	8
7	DMF	rt	–
8	DME	40	36
9	DME	60	73
10	DME	80	82
11	THF	40	34
12	THF	60	43
13	THF	80	96 (89)[c]

[a] Reaction conditions: **1a** (0.22 mmol), LR (0.10 mmol).
[b] Determined by ^{1}H NMR analysis of the crude reaction mixture using $MeNO_2$ as an internal standard.
[c] Isolated yield.



Scheme 2 Substrate scope of α,β-unsaturated phosphine oxides. *Reagents and conditions*: **1** (2.2 mmol), LR (1.0 mmol), THF (20 mL); isolated yields.

were tested. To our joy, these substrates smoothly underwent the thionation to deliver the products in moderate yields (**2ac–af**).

In summary, a synthetic pathway for the preparation of α,β-unsaturated phosphine sulfides has been developed, which employs α,β-unsaturated phosphine oxides and Lawesson's reagent as starting materials. Generally, the α,β-unsaturated phosphine sulfides were isolated in moderate to excellent yields under mild reaction conditions. The present reaction enjoys a broad substrate scope. Aryls, heteroaryls, simple alkyls, and functionalized alkyls are well accepted at the β-position. Hopefully, these α,β-unsaturated phosphine sulfides will find applications in copper(I)-catalyzed asymmetric reactions.

Lawesson's reagent was obtained from Meryer Chemical. The solvents were purchased as anhydrous solvents from Energy Chemical. α,β-Unsaturated phosphine oxides were prepared according to reported procedures.[17] NMR spectra were acquired on an Agilent 400 or Bruker 400 instrument operating at 400, 101, 376, and 162 MHz for ^{1}H, ^{13}C, ^{19}F, and ^{31}P, respectively. For ^{1}H NMR, chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard. For ^{13}C NMR, chemical shifts are reported in the scale relative to NMR solvent ($CDCl_3$: δ 77.0 ppm) as an internal reference. For ^{19}F NMR, chemical shifts are reported in δ ppm referenced to an external $CFCl_3$ standard. For ^{31}P NMR, chemical shifts are reported in δ ppm referenced to an external H_3PO_4 (85%) standard. Multiplicities are reported using the standard abbreviations. Mass spectra (ESI) were measured on an Agilent Technologies 1100 Series LC-MS system. High-resolution mass spectra (ESI) were measured on a Thermo Scientific LTQ FT Ultra FT-MS instrument. IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer. Melting points were detected on a Büchi Melting Point M-565 apparatus.

(*E*)-Diphenyl(styryl)phosphine Sulfide (2a); Typical Procedure for the Thionation of α,β-Unsaturated Phosphine Oxides

α,β-Unsaturated phosphine oxide **1a** (669 mg, 2.2 mmol, 2.2 equiv) and Lawesson's reagent (404 mg, 1 mmol, 1.0 equiv) were dissolved in anhydrous THF (20 mL). The resulting yellow solution was refluxed at 80 °C for 12 h. Then, it was cooled to room temperature. The solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc/hexane, 1:4) to provide pure product **2a**.

White solid; yield: 570 mg (89%); mp 107–110 °C.

IR (film): 3054, 2924, 1605, 1574, 1479, 1435, 1103, 979, 847, 712 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.78 (m, 4 H), 7.67–7.41 (m, 9 H), 7.38–7.37 (m, 3 H), 6.96 (dd, *J* = 21.1, 16.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.87 (d, *J* = 6.1 Hz), 134.98 (d, *J* = 19.4 Hz), 133.36 (d, *J* = 87.3 Hz), 131.52 (d, *J* = 2.9 Hz), 131.46 (d, *J* = 10.7 Hz), 130.09, 128.83, 128.66 (d, *J* = 12.6 Hz), 127.96 (d, *J* = 1.1 Hz), 119.65 (d, *J* = 86.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.16.

MS (ESI): *m*/*z* $[M + H]^+$ = 321.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{17}PS$: 321.0861; found: 321.0862.

(*E*)-(2-([1,1′-Biphenyl]-4-yl)vinyl)diphenylphosphine Sulfide (2b)

White solid; yield: 555 mg (70%); mp 145–148 °C.

IR (film): 3053, 3028, 1602, 1485, 1435, 1130, 982, 709 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.79 (m, 4 H), 7.69–7.55 (m, 7 H), 7.55–7.41 (m, 8 H), 7.40–7.32 (m, 1 H), 6.99 (dd, *J* = 21.1, 16.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.38 (d, *J* = 6.0 Hz), 142.83, 140.10, 133.95 (d, *J* = 19.5 Hz), 133.42 (d, *J* = 87.0 Hz), 131.54 (d, *J* = 3.2 Hz), 131.49 (d, *J* = 10.6 Hz), 128.88, 128.68 (d, *J* = 12.6 Hz), 128.48 (d, *J* = 1.1 Hz), 127.82, 127.47, 127.03, 119.50 (d, *J* = 86.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.24.

MS (ESI): m/z $[M + H]^+$ = 397.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{21}PS$: 397.1174; found: 397.1172.

(*E*)-(4-Fluorostyryl)diphenylphosphine Sulfide (2c)

White solid; yield: 622 mg (92%); mp 122–123 °C.

IR (film): 3053, 2924, 1599, 1507, 1438, 1228, 1103, 981, 798, 711 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.78 (m, 4 H), 7.62–7.40 (m, 9 H), 7.03 (t, J = 8.6 Hz, 2 H), 6.90 (dd, J = 20.8, 16.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.69 (d, J = 251.0 Hz), 146.58 (d, J = 6.4 Hz), 133.31 (d, J = 87.3 Hz), 131.61 (d, J = 2.9 Hz), 131.43 (d, J = 10.7 Hz), 131.17 (d, J = 3.2 Hz), 129.88 (dd, J = 8.4, 1.1 Hz), 128.72 (d, J = 12.5 Hz), 119.42 (dd, J = 86.4, 2.4 Hz), 115.94 (d, J = 21.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –109.94.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.13.

MS (ESI): m/z $[M + H]^+$ = 339.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{16}FPS$: 339.0767; found: 339.0762.

(*E*)-(4-Bromostyryl)diphenylphosphine Sulfide (2d)

White solid; yield: 525 mg (66%); mp 146–148 °C.

IR (film): 3080, 3053, 1605, 1586, 1485, 1435, 1103, 981, 849, 713 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.79 (m, 4 H), 7.58–7.44 (m, 9 H), 7.41–7.39 (m, 2 H), 6.96 (dd, J = 20.6, 16.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.46 (d, J = 6.1 Hz), 133.92 (d, J = 19.5 Hz), 133.16 (d, J = 87.3 Hz), 132.04, 131.61 (d, J = 3.0 Hz), 131.44 (d, J = 10.8 Hz), 129.38, 128.70 (d, J = 12.5 Hz), 124.29, 120.68 (d, J = 85.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.09.

MS (ESI): m/z $[M + H]^+$ = 399.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{16}BrPS$: 398.9964; found: 398.9966.

(*E*)-Diphenyl(4-(trifluoromethyl)styryl)phosphine Sulfide (2e)

White solid; yield: 699 mg (90%); mp 149–151 °C.

IR (film): 3054, 1613, 1574, 1479, 1435, 1323, 1167, 1066, 982, 850, 804, 713 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.78 (m, 4 H), 7.69–7.57 (m, 5 H), 7.54–7.43 (m, 6 H), 7.11 (dd, J = 20.4, 16.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.00 (d, J = 6.2 Hz), 138.28 (d, J = 20.2 Hz), 132.90 (d, J = 87.4 Hz), 131.76 (d, J = 2.9 Hz), 131.46 (q, J = 32.6 Hz), 131.45 (d, J = 10.7 Hz), 128.80 (d, J = 12.6 Hz), 128.17, 125.78 (q, J = 3.8 Hz), 123.84 (q, J = 272.3 Hz), 123.05 (d, J = 84.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.76.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.92.

MS (ESI): m/z $[M + H]^+$ = 389.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{16}F_3PS$: 389.0735; found: 389.0731.

(*E*)-4-(2-(Diphenylphosphorothioyl)vinyl)benzonitrile (2f)

White solid; yield: 662 mg (96%); mp 156–157 °C.

IR (film): 3053, 2226, 1603, 1480, 1435, 1102, 981, 852, 718 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.75 (m, 4 H), 7.67–7.46 (m, 11 H), 7.12 (dd, J = 20.0, 16.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.39 (d, J = 6.4 Hz), 139.11 (d, J = 19.4 Hz), 132.64 (d, J = 87.7 Hz), 132.60, 131.83 (d, J = 2.9 Hz), 131.43 (d, J = 10.7 Hz), 128.82 (d, J = 12.6 Hz), 128.39, 124.36 (d, J = 83.5 Hz), 118.37, 113.12.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.83.

MS (ESI): m/z $[M + H]^+$ = 346.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{16}NPS$: 346.0814; found: 346.0812.

(*E*)-(4-Methylstyryl)diphenylphosphine Sulfide (2g)

White solid; yield: 528 mg (79%); mp 131–133 °C.

IR (film): 3051, 3022, 1607, 1567, 1478, 1435, 1103, 983, 712 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.75 (m, 4 H), 7.57 (dd, J = 23.0, 16.6 Hz, 1 H), 7.51–7.38 (m, 8 H), 7.16 (d, J = 7.9 Hz, 2 H), 6.90 (dd, J = 21.3, 16.6 Hz, 1 H), 2.33 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.90 (d, J = 6.1 Hz), 140.48, 133.57 (d, J = 87.1 Hz), 132.30 (d, J = 19.5 Hz), 131.53, 131.46 (d, J = 8.4 Hz), 129.60, 128.68 (d, J = 12.4 Hz), 127.99, 118.27 (d, J = 87.1 Hz), 21.49.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.30.

MS (ESI): m/z $[M + H]^+$ = 335.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{19}PS$: 335.1018; found: 335.1016.

(*E*)-(4-Methoxystyryl)diphenylphosphine Sulfide (2h)

White solid; yield: 413 mg (59%); mp 173–175 °C.

IR (film): 3052, 2930, 2358, 1601, 1571, 1479, 1462, 1435, 1255, 1102, 982, 710 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.78 (m, 4 H), 7.61–7.40 (m, 9 H), 6.93–6.86 (m, 2 H), 6.78 (dd, J = 21.2, 16.6 Hz, 1 H), 3.83 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.17, 147.50 (d, J = 6.4 Hz), 133.74 (d, J = 87.2 Hz), 131.50, 131.39, 129.57, 128.59 (d, J = 12.5 Hz), 127.84 (d, J = 19.6 Hz), 116.53 (d, J = 88.3 Hz), 114.21, 55.38.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.40.

MS (ESI): m/z $[M + H]^+$ = 351.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{19}OPS$: 351.0967; found: 351.0965.

(*E*)-(3-Chlorostyryl)diphenylphosphine Sulfide (2i)

White solid; yield: 411 mg (58%); mp 111–113 °C.

IR (film): 3053, 1607, 1563, 1478, 1307, 1182, 1103, 980, 743 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.77 (m, 4 H), 7.60–7.43 (m, 8 H), 7.42–7.37 (m, 1 H), 7.35–7.24 (m, 2 H), 6.99 (dd, J = 20.5, 16.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.20 (d, J = 6.3 Hz), 136.79 (d, J = 19.6 Hz), 134.85, 133.07 (d, J = 87.5 Hz), 131.64 (d, J = 3.0 Hz), 131.45 (d, J = 10.7 Hz), 130.11, 129.92, 128.72 (d, J = 12.6 Hz), 127.51, 126.36, 121.66 (d, J = 85.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.94.

MS (ESI): m/z $[M + H]^+$ = 355.

HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{16}ClPS$: 355.0472; found: 355.0470.

(*E*)-(3-Bromostyryl)diphenylphosphine Sulfide (2j)

White solid; yield: 501 mg (63%); mp 134–136 °C.

IR (film): 3053, 2924, 1606, 1561, 1476, 1435, 1307, 1103, 980, 823, 713 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.75 (m, 4 H), 7.69 (s, 1 H), 7.60–7.41 (m, 9 H), 7.25 (t, *J* = 7.8 Hz, 1 H), 6.98 (dd, *J* = 20.5, 16.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.09 (d, *J* = 6.2 Hz), 137.06 (d, *J* = 19.4 Hz), 133.06 (d, *J* = 87.4 Hz), 132.83, 131.65 (d, *J* = 3.0 Hz), 131.45 (d, *J* = 10.8 Hz), 130.43, 130.39, 128.73 (d, *J* = 12.6 Hz), 126.83, 122.98, 121.70 (d, *J* = 85.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.94.

MS (ESI): *m*/*z* $[M + H]^+$ = 399.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{16}BrPS$: 398.9966; found: 398.9965.

(*E*)-(2-Bromostyryl)diphenylphosphine Sulfide (2k)

White solid; yield: 780 mg (98%); mp 131–133 °C.

IR (film): 3057, 3019, 1600, 1583, 1482, 1462, 1103, 981, 712 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.74 (m, 5 H), 7.59 (d, *J* = 7.9 Hz, 1 H), 7.53 (dd, *J* = 8.0, 1.3 Hz, 1 H), 7.54–7.39 (m, 6 H), 7.31–7.22 (m, 1 H), 7.18–7.12 (m, 1 H), 6.92 (dd, *J* = 20.7, 16.7 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.95 (d, *J* = 7.2 Hz), 135.00 (d, *J* = 19.5 Hz), 133.33, 132.71 (d, *J* = 86.9 Hz), 131.72 (d, *J* = 3.0 Hz), 131.61 (d, *J* = 10.7 Hz), 131.05, 128.74 (d, *J* = 12.6 Hz), 128.03 (d, *J* = 1.6 Hz), 127.74, 124.95 (d, *J* = 1.0 Hz), 123.70 (d, *J* = 84.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.30.

MS (ESI): *m*/*z* $[M + H]^+$ = 399.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{16}BrPS$: 398.9966; found: 398.9962.

(*E*)-Diphenyl(2-(pyridin-2-yl)vinyl)phosphine Sulfide (2l)

White solid; yield: 604 mg (94%); mp 130–133 °C.

IR (film): 3052, 3003, 1579, 1469, 1435, 1309, 1102, 979, 859, 712 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.64–8.58 (m, 1 H), 7.88–7.79 (m, 4 H), 7.73–7.64 (m, 3 H), 7.51–7.36 (m, 7 H), 7.23 (dd, *J* = 7.6, 4.7 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.87, 152.67, 149.98, 146.61 (d, *J* = 6.9 Hz), 137.02, 133.15 (d, *J* = 87.5 Hz), 131.57 (d, *J* = 2.9 Hz), 131.42 (d, *J* = 10.7 Hz), 128.68 (d, *J* = 12.5 Hz), 124.50 (d, *J* = 46.7 Hz), 124.40 (d, *J* = 84.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.75.

MS (ESI): *m*/*z* $[M + H]^+$ = 322.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{16}NPS$: 322.0814; found: 322.0809.

(*E*)-Diphenyl(2-(pyridin-3-yl)vinyl)phosphine Sulfide (2m)

White solid; yield: 501 mg (78%); mp 135–138 °C.

IR (film): 3051, 2956, 1654, 1607, 1584, 1479, 1435, 1102, 980, 851, 713 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.76 (s, 1 H), 8.59 (d, *J* = 4.7 Hz, 1 H), 7.90–7.77 (m, 5 H), 7.68–7.44 (m, 7 H), 7.32 (dd, *J* = 8.1, 4.8 Hz, 1 H), 7.09 (dd, *J* = 20.3, 16.7 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.79, 149.46, 144.17 (d, *J* = 6.5 Hz), 134.37, 132.82 (d, *J* = 87.5 Hz), 131.74 (d, *J* = 3.1 Hz), 131.43 (d, *J* = 10.7 Hz), 130.67 (d, *J* = 19.1 Hz), 128.77 (d, *J* = 12.6 Hz), 123.68, 122.51 (d, *J* = 84.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.96.

MS (ESI): *m*/*z* $[M + H]^+$ = 322.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{16}NPS$: 322.0814; found: 322.0810.

(*E*)-Diphenyl(2-(thiophen-2-yl)vinyl)phosphine Sulfide (2n)

White solid; yield: 593 mg (91%); mp 106–108 °C.

IR (film): 3072, 3019, 1636, 1598, 1479, 1243, 1102, 998, 819, 713 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.65 (m, 5 H), 7.51–7.39 (m, 6 H), 7.31 (d, *J* = 5.0 Hz, 1 H), 7.19 (d, *J* = 3.6 Hz, 1 H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1 H), 6.72 (dd, *J* = 20.3, 16.3 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.51 (d, *J* = 22.2 Hz), 140.40 (d, *J* = 7.4 Hz), 133.41 (d, *J* = 87.7 Hz), 131.59 (d, *J* = 3.0 Hz), 131.42 (d, *J* = 10.8 Hz), 130.37, 128.72 (d, *J* = 12.6 Hz), 128.26, 128.11, 117.94 (d, *J* = 87.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.97.

MS (ESI): *m*/*z* $[M + H]^+$ = 327.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{15}PS_2$: 327.0426; found: 327.0421.

(*E*)-Diphenyl(2-(thiophen-3-yl)vinyl)phosphine Sulfide (2o)

White solid; yield: 613 mg (94%); mp 117–119 °C.

IR (film): 3072, 3053, 1602, 1573, 1478, 1297, 1102, 978, 832, 743 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (m, 4 H), 7.58 (dd, *J* = 22.6, 16.5 Hz, 1 H), 7.51–7.38 (m, 7 H), 7.29 (m, 2 H), 6.76 (dd, *J* = 21.3, 16.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.40 (d, *J* = 6.4 Hz), 138.22 (d, *J* = 20.9 Hz), 133.42 (d, *J* = 87.2 Hz), 131.57 (d, *J* = 3.0 Hz), 131.46 (d, *J* = 10.7 Hz), 128.70 (d, *J* = 12.5 Hz), 127.68, 126.97, 125.31, 118.96 (d, *J* = 87.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.29.

MS (ESI): *m*/*z* $[M + H]^+$ = 327.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{15}PS_2$: 327.0426; found: 327.0421.

(*E*)-(2-(Benzo[*b*]thiophen-3-yl)vinyl)diphenylphosphine Sulfide (2p)

White solid; yield: 691 mg (92%); mp 163–165 °C.

IR (film): 3063, 3016, 1601, 1479, 1434, 1103, 830, 979, 713 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.77 (m, 7 H), 7.70 (s, 1 H), 7.52–7.29 (m, 8 H), 7.06 (dd, *J* = 21.6, 16.7 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.48, 139.68 (d, *J* = 6.5 Hz), 137.03, 133.43 (d, *J* = 87.3 Hz), 132.23 (d, *J* = 20.6 Hz), 131.64 (d, *J* = 3.0 Hz), 131.51 (d, *J* = 10.7 Hz), 128.77 (d, *J* = 12.4 Hz), 127.75 (d, *J* = 1.8 Hz), 125.07, 124.94, 123.03, 121.99, 120.24 (d, *J* = 85.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.56.

MS (ESI): *m*/*z* $[M + H]^+$ = 377.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{17}PS_2$: 377.0582; found: 377.0579.

(*E*)-(2-(Benzo[*b*]furan-2-yl)vinyl)diphenylphosphine Sulfide (2q)

White solid; yield: 713 mg (99%); mp 120–122 °C.

IR (film): 3054, 2925, 1613, 1573, 1471, 1435, 1325, 1104, 968, 816, 716 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (m, 4 H), 7.62 (dd, *J* = 24.2, 16.2 Hz, 1 H), 7.55 (d, *J* = 7.8 Hz, 1 H), 7.50–7.40 (m, 7 H), 7.30 (t, *J* = 7.7 Hz, 1 H), 7.26–7.12 (m, 2 H), 6.85 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.40, 152.75 (d, *J* = 21.7 Hz), 134.84 (d, *J* = 7.7 Hz), 133.33 (d, *J* = 87.8 Hz), 131.66 (d, *J* = 3.0 Hz), 131.41 (d, *J* = 10.8 Hz), 128.77 (d, *J* = 12.6 Hz), 128.37 (d, *J* = 1.4 Hz), 126.40, 123.39, 122.02, 120.46 (d, *J* = 86.2 Hz), 111.27, 110.48.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.81.

MS (ESI): *m*/*z* $[M + H]^+$ = 361.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{17}OPS$: 361.0810; found: 361.0805.

(*E*)-(Oct-1-en-1-yl)diphenylphosphine Sulfide (2r)

Colorless oil; yield: 597 mg (91%).

IR (film): 3054, 2629, 1617, 1480, 1436, 1103, 1053, 972, 717 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.70 (m, 4 H), 7.51–7.37 (m, 6 H), 6.92–6.79 (m, 1 H), 6.35 (dd, *J* = 24.2, 16.2 Hz, 1 H), 2.32 (tdd, *J* = 8.4, 5.9, 1.9 Hz, 2 H), 1.52–1.45 (m, 2 H), 1.37–1.23 (m, 6 H), 0.91–0.83 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.96 (d, *J* = 3.5 Hz), 133.60 (d, *J* = 86.2 Hz), 131.339 (d, *J* = 3.0 Hz), 131.338 (d, *J* = 10.5 Hz), 128.53 (d, *J* = 12.5 Hz), 121.71 (d, *J* = 84.7 Hz), 34.14 (d, *J* = 17.9 Hz), 31.53, 28.84, 27.94 (d, *J* = 1.4 Hz), 22.55, 14.08.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.69.

MS (ESI): *m*/*z* $[M + H]^+$ = 329.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{25}PS$: 329.1487; found: 329.1483.

(*E*)-Diphenyl(4-phenylbut-1-en-1-yl)phosphine Sulfide (2s)

Colorless oil; yield: 564 mg (81%).

IR (film): 3054, 2923, 1615, 1480, 1435, 1335, 1102, 971, 780 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (m, 4 H), 7.48–7.32 (m, 6 H), 7.29–7.16 (m, 3 H), 7.13 (d, *J* = 7.1 Hz, 2 H), 6.89–6.70 (m, 1 H), 6.26 (dd, *J* = 23.6, 16.3 Hz, 1 H), 2.80 (t, *J* = 7.4 Hz, 2 H), 2.68–2.57 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.23 (d, *J* = 3.7 Hz), 140.65, 133.32 (d, *J* = 86.3 Hz), 131.40 (d, *J* = 10.6 Hz), 131.36 (d, *J* = 3.4 Hz), 128.56 (d, *J* = 7.9 Hz), 128.55, 128.48, 126.14, 123.07 (d, *J* = 84.2 Hz), 35.69 (d, *J* = 18.0 Hz), 34.16 (d, *J* = 1.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.70.

MS (ESI): *m*/*z* $[M + H]^+$ = 349.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{21}PS$: 349.1174; found: 349.1170.

(*E*)-(2-Cyclopropylvinyl)diphenylphosphine Sulfide (2t)

White solid; yield: 489 mg (86%); mp 120–123 °C.

IR (film): 3052, 2925, 1669, 1617, 1573, 1479, 1100, 977, 796, 711 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (m, 4 H), 7.49–7.39 (m, 6 H), 6.47–6.24 (m, 2 H), 1.77–1.69 (m, 1 H), 0.97–0.88 (m, 2 H), 0.71–0.58 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.19 (d, *J* = 5.4 Hz), 133.93 (d, *J* = 86.8 Hz), 131.28 (d, *J* = 10.7 Hz), 131.28 (d, *J* = 2.9 Hz), 128.52 (d, *J* = 12.5 Hz), 117.71 (d, *J* = 88.0 Hz), 16.34 (d, *J* = 23.2 Hz), 8.67 (d, *J* = 1.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.45.

MS (ESI): *m*/*z* $[M + H]^+$ = 285.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{17}PS$: 285.0861; found: 285.0858.

(*E*)-(3,3-Dimethylbut-1-en-1-yl)diphenylphosphine Sulfide (2u)

White solid; yield: 498 mg (83%); mp 118–119 °C.

IR (film): 3050, 3006, 1662, 1609, 1586, 1480, 1435, 1101, 984, 828, 746, 710 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (m, 4 H), 7.52–7.38 (m, 6 H), 6.88 (dd, *J* = 23.8, 16.5 Hz, 1 H), 6.25 (dd, *J* = 23.7, 16.5 Hz, 1 H), 1.12 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.26 (d, *J* = 2.7 Hz), 133.48 (d, *J* = 86.2 Hz), 131.06 (d, *J* = 10.5 Hz), 131.05 (d, *J* = 2.9 Hz), 128.28 (d, *J* = 12.3 Hz), 116.62 (d, *J* = 84.8 Hz), 34.94 (d, *J* = 15.9 Hz), 28.54 (d, *J* = 1.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.35.

MS (ESI): *m*/*z* $[M + H]^+$ = 301.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{21}PS$: 301.1174; found: 301.1171.

(*E*)-(2-(Cyclohex-1-en-1-yl)vinyl)diphenylphosphine Sulfide (2v)

White solid; yield: 454 mg (70%); mp 139–141 °C.

IR (film): 3052, 2928, 1628, 1584, 1480, 1435, 1102, 981, 712 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (m, 4 H), 7.45 (m, 6 H), 7.14 (dd, *J* = 22.8, 16.4 Hz, 1 H), 6.22 (dd, *J* = 22.0, 16.4 Hz, 1 H), 6.11 (m, 1 H), 2.19 (m, 4 H), 1.68 (m, 2 H), 1.60 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.26 (d, *J* = 5.7 Hz), 138.20 (d, *J* = 1.4 Hz), 135.12 (d, *J* = 19.6 Hz), 133.85 (d, *J* = 86.6 Hz), 131.40 (d, *J* = 10.7 Hz), 131.29 (d, *J* = 3.0 Hz), 128.52 (d, *J* = 12.3 Hz), 115.01 (d, *J* = 88.4 Hz), 26.29, 24.49, 22.09, 22.05.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.38.

MS (ESI): *m*/*z* $[M + H]^+$ = 325.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{21}PS$: 325.1174; found: 325.1171.

(*E*)-Diphenyl(2-(trimethylsilyl)vinyl)phosphine Sulfide (2w)

White solid; yield: 607 mg (96%); mp 154–156 °C.

IR (film): 3053, 2956, 1478, 1436, 1248, 1053, 988, 837, 717 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.71 (m, 4 H), 7.51–7.42 (m, 6 H), 7.37–7.28 (m, 1 H), 6.93 (dd, *J* = 31.7, 19.5 Hz, 1 H), 0.16 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.29 (d, *J* = 5.5 Hz), 136.54 (d, *J* = 69.4 Hz), 132.94 (d, *J* = 84.1 Hz), 131.48 (d, *J* = 10.6 Hz), 131.44 (d, *J* = 2.6 Hz), 128.61 (d, *J* = 12.3 Hz), −1.66.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.70.

MS (ESI): *m*/*z* $[M + H]^+$ = 317.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{21}PSSi$: 317.0944; found: 317.0942.

(*E*)-6-(Diphenylphosphorothioyl)hex-5-en-1-yl 4-Methylbenzenesulfonate (2x)

Colorless oil; yield: 780 mg (83%).

IR (film): 3053, 2925, 1597, 1480, 1436, 1356, 1099, 932, 813, 711 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.68 (m, 6 H), 7.54–7.39 (m, 6 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 6.85–6.72 (m, 1 H), 6.35 (dd, *J* = 23.7, 16.2 Hz, 1 H), 4.02 (t, *J* = 6.2 Hz, 2 H), 2.43 (s, 3 H), 2.35–2.23 (m, 2 H), 1.71–1.65 (m, 2 H), 1.60–1.48 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.44 (d, *J* = 3.7 Hz), 144.84, 133.34 (d, *J* = 86.5 Hz), 132.87, 131.43 (d, *J* = 3.0 Hz), 131.32 (d, *J* = 10.6 Hz), 129.87, 128.59 (d, *J* = 12.5 Hz), 127.84, 122.60 (d, *J* = 84.1 Hz), 70.03, 33.21 (d, *J* = 18.0 Hz), 28.29, 23.93 (d, *J* = 1.5 Hz), 21.65.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.62.

MS (ESI): *m*/*z* $[M + H]^+$ = 471.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{27}O_3PS_2$: 471.1212; found: 471.1208.

(*E*)-(5-Chloropent-1-en-1-yl)diphenylphosphine Sulfide (2y)

Colorless oil; yield: 301 mg (47%).

IR (film): 3073, 2989, 1621, 1586, 1479, 1435, 1306, 1102, 975, 818, 710 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.70 (m, 4 H), 7.53–7.39 (m, 6 H), 6.92–6.79 (m, 1 H), 6.45 (dd, *J* = 23.6, 16.2 Hz, 1 H), 3.54 (t, *J* = 6.4 Hz, 2 H), 2.56–2.44 (m, 2 H), 2.06–1.85 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.54 (d, *J* = 3.9 Hz), 133.35 (d, *J* = 86.6 Hz), 131.46 (d, *J* = 3.0 Hz), 131.30 (d, *J* = 10.6 Hz), 128.62 (d, *J* = 12.5 Hz), 123.38 (d, *J* = 83.9 Hz), 44.10, 31.11 (d, *J* = 18.3 Hz), 30.64 (d, *J* = 1.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.48.

MS (ESI): *m*/*z* $[M + H]^+$ = 321.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{18}ClPS$: 321.0628; found: 321.0624.

(*E*)-(5-(Benzyloxy)pent-1-en-1-yl)diphenylphosphine Sulfide (2z)

White solid; yield: 478 mg (61%); mp 39–42 °C.

IR (film): 3054, 3005, 1633, 1574, 1479, 1362, 1102, 976, 808, 710 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.67 (m, 4 H), 7.53–7.37 (m, 6 H), 7.37–7.22 (m, 5 H), 6.94–6.81 (m, 1 H), 6.37 (dd, *J* = 23.9, 16.2 Hz, 1 H), 4.47 (s, 2 H), 3.49 (t, *J* = 6.2 Hz, 2 H), 2.45 (m, 2 H), 1.85–1.78 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.05 (d, *J* = 3.8 Hz), 138.33, 133.49 (d, *J* = 86.5 Hz), 131.36 (d, *J* = 2.9 Hz), 131.35 (d, *J* = 10.7 Hz), 128.55 (d, *J* = 12.3 Hz), 128.38, 127.59 (two peaks overlap), 122.28 (d, *J* = 84.7 Hz), 72.96, 69.24, 30.79 (d, *J* = 18.2 Hz), 28.18 (d, *J* = 1.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.64.

MS (ESI): *m*/*z* $[M + H]^+$ = 393.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{25}OPS$: 393.1436; found: 393.1431.

(*E*)-*N*-(7-(Diphenylphosphorothioyl)hept-6-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (2aa)

Colorless oil; yield: 497 mg (50%).

IR (film): 3053, 2931, 1614, 1596, 1436, 1338, 1120, 933, 814, 712 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (m, 4 H), 7.65 (d, *J* = 8.3 Hz, 2 H), 7.54–7.39 (m, 6 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 6.91–6.78 (m, 1 H), 6.37 (dd, *J* = 24.1, 16.2 Hz, 1 H), 2.96 (t, *J* = 7.1 Hz, 2 H), 2.68 (s, 3 H), 2.42 (s, 3 H), 2.38–2.28 (m, 2 H), 1.52 (m, 4 H), 1.42–1.34 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.40 (d, *J* = 3.6 Hz), 143.23, 134.38, 133.48 (d, *J* = 86.3 Hz), 131.36 (d, *J* = 3.0 Hz), 131.35 (d, *J* = 10.7 Hz), 129.62, 128.57 (d, *J* = 12.3 Hz), 127.36, 122.03 (d, *J* = 84.6 Hz), 49.86, 34.60, 34.00 (d, *J* = 17.9 Hz), 27.53, 27.31, 26.04, 21.50.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.71.

MS (ESI): *m*/*z* $[M + H]^+$ = 498.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{27}H_{32}NO_2PS_2$: 498.1685; found: 498.1681.

(*E*)-7-(Diphenylphosphorothioyl)hept-6-en-1-yl 4-Methylbenzenesulfonate (2ab)

White solid; yield: 581 mg (60%); mp 38–40 °C.

IR (film): 3053, 2934, 1597, 1435, 1175, 1101, 949, 711 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.67 (m, 6 H), 7.45 (m, 6 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 6.81 (ddt, *J* = 22.7, 16.2, 6.6 Hz, 1 H), 6.35 (dd, *J* = 24.0, 16.2 Hz, 1 H), 4.00 (t, *J* = 6.4 Hz, 2 H), 2.42 (s, 3 H), 2.28 (m, 2 H), 1.67–1.60 (m, 2 H), 1.48–1.40 (m, 2 H), 1.38–1.30 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.11 (d, *J* = 3.7 Hz), 144.79, 133.86, 132.98 (d, *J* = 4.3 Hz), 131.41 (d, *J* = 2.9 Hz), 131.31 (d, *J* = 10.7 Hz), 129.87, 128.59 (d, *J* = 12.3 Hz), 127.81, 122.18 (d, *J* = 84.5 Hz), 70.33, 33.82 (d, *J* = 18.0 Hz), 28.55, 27.31 (d, *J* = 1.5 Hz), 24.98, 21.66.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.62.

MS (ESI): *m*/*z* $[M + H]^+$ = 485.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{29}O_3PS_2$: 485.1373; found: 485.1366.

(*E*)-Styryl(di-*p*-tolyl)phosphine Sulfide (2ac)

White solid; yield: 536 mg (77%); mp 117–119 °C.

IR (film): 3022, 2919, 1599, 1497, 1102, 979, 709 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.63 (m, 4 H), 7.61–7.47 (m, 3 H), 7.41–7.30 (m, 3 H), 7.29–7.21 (m, 4 H), 6.93 (dd, *J* = 20.9, 16.7 Hz, 1 H), 2.38 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.24 (d, *J* = 5.8 Hz), 141.98 (d, *J* = 2.9 Hz), 135.11 (d, *J* = 19.3 Hz), 131.49 (d, *J* = 11.1 Hz), 130.16 (d, *J* = 89.6 Hz), 129.96, 129.39 (d, *J* = 13.0 Hz), 128.81, 127.92, 120.27 (d, *J* = 86.5 Hz), 21.52.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.64.

MS (ESI): *m*/*z* $[M + H]^+$ = 349.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{21}PS$: 349.1174; found: 349.1171.

(*E*)-Bis(4-fluorophenyl)(styryl)phosphine Sulfide (2ad)

White solid; yield: 356 mg (50%); mp 101–103 °C.

IR (film): 3060, 2924, 1647, 1575, 1495, 1395, 1175, 979, 828, 711 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.69 (m, 4 H), 7.63–7.48 (m, 3 H), 7.39 (dd, *J* = 4.9, 1.9 Hz, 3 H), 7.16 (m, 4 H), 6.91 (dd, *J* = 21.4, 16.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.83 (dd, *J* = 253.8, 3.3 Hz), 148.26 (d, *J* = 6.1 Hz), 134.70 (d, *J* = 19.5 Hz), 133.87 (dd, *J* = 12.5, 8.8 Hz), 130.35, 129.16 (dd, *J* = 90.5, 3.4 Hz), 128.91, 128.01, 119.19 (d, *J* = 88.0 Hz), 116.07 (dd, *J* = 21.6, 13.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –107.21.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.74.

MS (ESI): *m*/*z* $[M + H]^+$ = 357.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{15}F_2PS$: 357.0673; found: 357.0669.

(*E*)-Di(naphthalen-2-yl)(styryl)phosphine Sulfide (2ae)

White solid; yield: 639 mg (76%); mp 199–201 °C.

IR (film): 3052, 2923, 1651, 1604, 1590, 1500, 1338, 1081, 979, 859, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (dd, *J* = 15.7, 1.5 Hz, 2 H), 7.91–7.80 (m, 6 H), 7.80–7.66 (m, 3 H), 7.53 (m, 6 H), 7.40–7.31 (m, 3 H), 7.14 (dd, *J* = 21.3, 16.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.28 (d, *J* = 6.1 Hz), 135.05 (d, *J* = 19.5 Hz), 134.53 (d, *J* = 2.6 Hz), 133.28 (d, *J* = 10.8 Hz), 132.59 (d, *J* = 13.9 Hz), 130.43 (d, *J* = 87.5 Hz), 130.22, 128.97, 128.92, 128.69 (d, *J* = 12.2 Hz), 128.28, 128.10 (d, *J* = 1.1 Hz), 127.85, 127.08, 126.50 (d, *J* = 11.4 Hz), 119.46 (d, *J* = 86.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.70.

MS (ESI): *m*/*z* $[M + H]^+$ = 421.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{28}H_{21}PS$: 421.1174; found: 421.1170.

(*E*)-Di(furan-2-yl)(styryl)phosphine Sulfide (2af)

White solid; yield: 360 mg (60%); mp 97–98 °C.

IR (film): 3125, 3024, 1605, 1575, 1494, 1209, 1173, 1053, 978, 850, 740 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.60 (m, 3 H), 7.59–7.53 (m, 2 H), 7.38 (m, 3 H), 7.15 (m, 2 H), 7.02 (dd, *J* = 23.1, 16.7 Hz, 1 H), 6.51 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.48 (d, *J* = 7.3 Hz), 148.46 (d, *J* = 7.7 Hz), 147.40 (d, *J* = 125.9 Hz), 134.78 (d, *J* = 21.4 Hz), 130.34, 128.83, 128.11, 121.89 (d, *J* = 21.5 Hz), 116.66 (d, *J* = 96.5 Hz), 111.18 (d, *J* = 9.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 7.52.

MS (ESI): *m*/*z* $[M + H]^+$ = 301.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{13}O_2PS$: 301.0447; found: 301.0443.

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Supporting Information

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