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Acetic Acid Mediated Sulfonylation of Allenylphosphine Oxides: Divergent Synthesis of Bifunctionalized 1,3-Butadienes and Allenes

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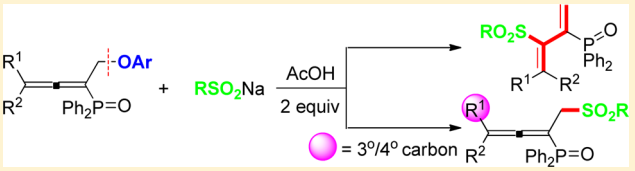
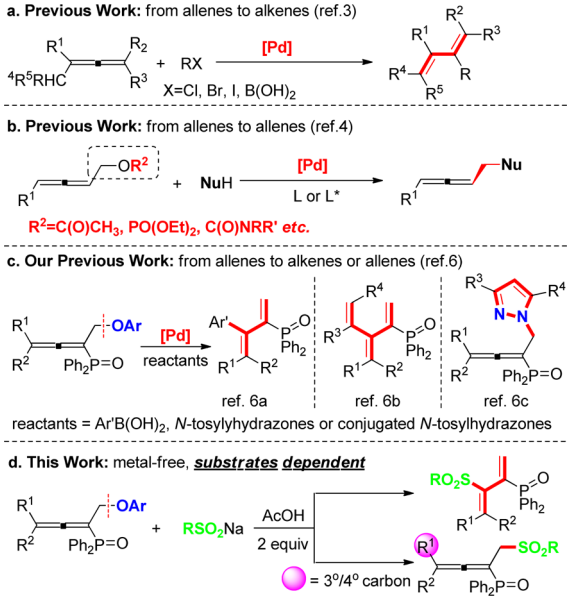
Supporting Information

ABSTRACT: An acetic acid-mediated sulfonylation of allenylphosphine oxides with sodium sulfinates is disclosed. This new methodology involves tandem (Ar)O−C(sp^3) bond cleavage and C(sp^2)/C(sp^3)−SO_2 formation toward divergent synthesis of sulfonyl- and phosphinyl-bifunctionalized 1,3-butadienes or allenes, depending on the substitution at the terminal carbon atoms of allenylphosphine oxides. The reaction mechanism is explained via an acid-accelerated synergistic process.



Allenes have been extensively investigated in organic transformations for expedient construction of potentially bioactive naturally occurring or synthetic compounds.[1] As a result, allene chemistry has evolved into a hot research topic within recent years. It is well-known that the introduction of electron-withdrawing substituents on allenes, most often with ester to keto functions, will differentiate electron density of cumulated double bonds, thereby simplifying regio- and stereoselectivity control in most documented reactions.[2] In the presence of transition metals, in general, electrophiles or nucleophiles will link with the central carbon atom to produce alkene derivatives (Scheme 1a).[3] Alternatively, the reactions maintain the allene skeleton provided that the starting allenes possess electron-deficient leaving groups at the α-position[4] (Scheme 1b). Nevertheless, studies on allenylphosphine oxides, a type of representative electron-deficient allenes, have been comparably underdeveloped so far.[5,6] In this regime, recently, our group has, however, advanced the palladium-catalyzed couplings of allenylphosphine oxides with arylboronic acids, *N*-tosylhydrazones, or conjugated *N*-tosylhydrazones to afford phosphinyl 1,3-butadienes,[6a] phosphinyl [3]dendralenes,[6b] and pyrazole−methylene-substituted allenes,[6c] respectively (Scheme 1c). Mechanistically, the formation of these unsaturated hydrocarbons was initiated by the palladium-catalyzed cleavage of an electron-rich (Ar)O−C(sp^3) bond, which was deemed as a challenging issue among transition-metal catalysis.[7] The high demand of green and sustainable chemistry spurs us to develop an alternative protocol in a metal-free manner. We envisioned that acid-mediated cleavage of the (Ar)O−C(sp^3) bond and synergistic sulfonylation would provide unprecedented sulfonyl and phosphinyl bifunctionalized adducts.

Scheme 1. Transformation of Allenes to Alkenes (a) or Allenes (b), Our Previous Work on Allenylphosphine Oxides (c), and This Work (d)



Sulfone functionalities have attracted tremendous attention owing to their wide existence in ubiquitous materials,[8] agrochemicals,[9] and medicines[10] and, most importantly, to organic chemists as synthetic building blocks in potential bioactive molecules.[11] As such, considerable achievements have

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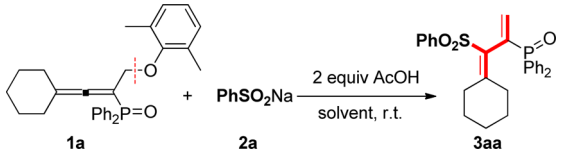
been documented regarding the C−S bond formation.[12] Among these, C(sp^2)−SO_2 formations were enabled through oxidative coupling with either transition-metal catalysis, synthetic oxidants, or photoredox catalysis, etc.[13] Nevertheless, the sulfonylation of allenes is rather rare to date.[14] For instance, in 2016, Lei's group developed a highly regio- and stereoselective oxy-sulfonylation of aryl- or ester-substituted allenes under air to access 2-sulfonyl allylic alcohols.[14a] In the same year, Miao and co-workers revealed an acetic acid-mediated nucleophilic addition of sodium sulfinates to "ketone activated" allenes, in which β- and γ-adducts (monoalkenes) could be efficiently tuned by solvents.[14b] Herein, as our continuing explorations on allene chemistry and C−X bond formation,[6,15] we disclose an acetic acid mediated tandem (Ar)O−C(sp^3) bond cleavage of allenylphosphine oxides and C(sp^2)/C(sp^3)−SO_2 formation toward bifunctionalized 1,3-butadienes or allenes, depending on the terminal substitutions of the starting allenes (Scheme 1d).

The optimization of reaction conditions was initiated with allenylphosphine oxide (**1a**),[16] sodium benzenesulfinate (**2a**), and 2 equiv of acetic acid in THF for 24 h. For a preliminary result, the sulfonylation product, (3-cyclohexylidene-3-(phenyl sulfonyl)prop-1-en-2-yl)diphenylphosphine oxide (**3aa**), was isolated with 53% yield (entry 2, Table 1), whereas no product was formed without using acid as an additive (entry 1, Table 1). Systematic sovlent screenings revealed that the couplings proceeded smoothly in various organic solvents, especially in 1,4-dioxane and nonprotic polar solvents (entries 6−9). Notably, protic sovlents, including ethanol and water, unambiguously inhibited the sulfonylation (entries 10 and 11). To our delight, with DMSO as sovlent, the isolated yield of **3aa** could be improved to 92% within a shorter time of 11 h as well (entry 12, 14); however, catalytic amounts of acetic acid led to a substainitial yield decrease to 36%. Other acids, such as sulfuric acid, *p*-TsOH, PivOH, TfOH, boronic acid, and benzoic acid, were inactive and did not enable the transformation, thus leaving the starting material intact (entries 15−20), but formic acid and boron trifluoride−diethyl etherate afforded the adduct in moderate yields (entries 21 and 22). Further efforts to improve the yields with higher temperature led to a slight decrease in the yield of **3aa** (entry 23).

With the optimal conditions in hands, we evaluated the nature of sodium sulfinates that could participate in the sulfonylation of allenylphosphine oxide (**1a**). As depicted in Table 2, a series of sodium arylsulfinates showed tolerance with electron-donating or electron-withdrawing substituents, with good to excellent yields of adducts isolated ranging from 71 to 92%. Here, the X-ray structure of **3aa** clearly demonstrated the existence of a sulfonyl group and spatial alignment of the double bonds.[17] It is worth mentioning that the yields were remarkably sensitive to the electron property of substitutions

Table 1. Reaction Condition Optimization[a]

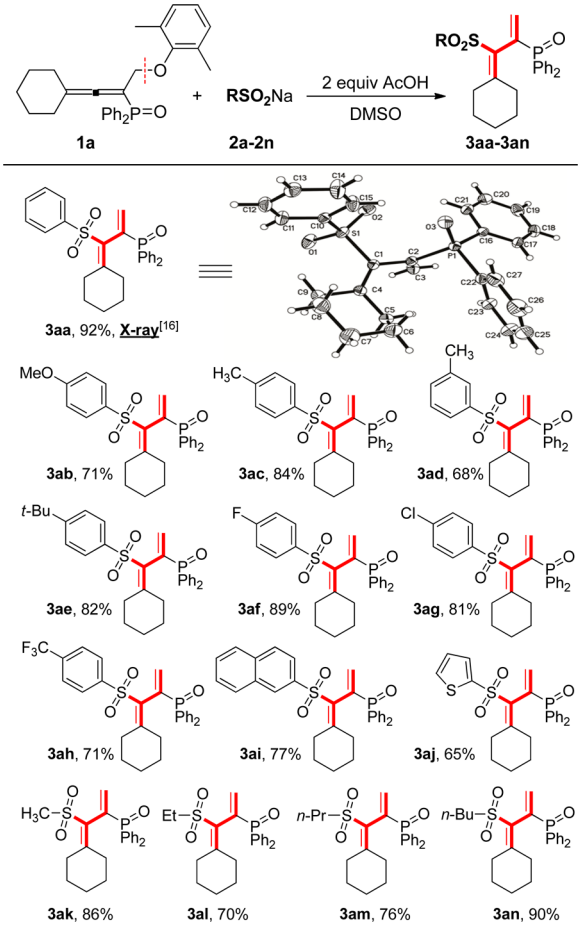


1a 2a 3aa

entry	acid	solvent	yield of **3aa**[b] (%)
1		THF	NR
2	AcOH	THF	53
3	AcOH	$CHCl_3$	21
4	AcOH	CH_3CN	55
5	AcOH	toluene	29
6	AcOH	DMF	80
7	AcOH	1,4-dioxane	90
8	AcOH	NMP	87
9	AcOH	sulfolane	85
10	AcOH	H_2O	NR
11	AcOH	EtOH	trace
12	AcOH	DMSO	92
13[c]	AcOH	DMSO	36
14[d]	**AcOH**	**DMSO**	**92**
15	H_2SO_4	DMSO	NR
16	*p*-TsOH	DMSO	NR
17	PivOH	DMSO	NR
18	TfOH	DMSO	NR
19	$B(OH)_3$	DMSO	NR
20	PhCOOH	DMSO	NR
21	HCOOH	DMSO	40
22	$BF_3{\cdot}Et_2O$	DMSO	56
23[e]	AcOH	DMSO	88

[a]Reaction conditions: allenylphosphine oxide (**1a**, 0.20 mmol), sodium benzenesulfinate (**2a**, 0.40 mmol), acid (2.0 equiv), solvent (1 mL), rt, 24 h. [b]Isolated yields. NR = no reaction. [c]20% mmol of AcOH was used. [d]11 h. [e]50 °C.

Table 2. Substrate Scopes of Sodium Sulfinates[a]



[a]Reaction conditions: allenylphosphine oxide (**1a**, 0.20 mmol), sodium sulfinate (**2a**−**n**, 0.40 mmol), acetic acid (2.0 equiv), DMSO (1 mL), rt, 11 h, isolated yields.

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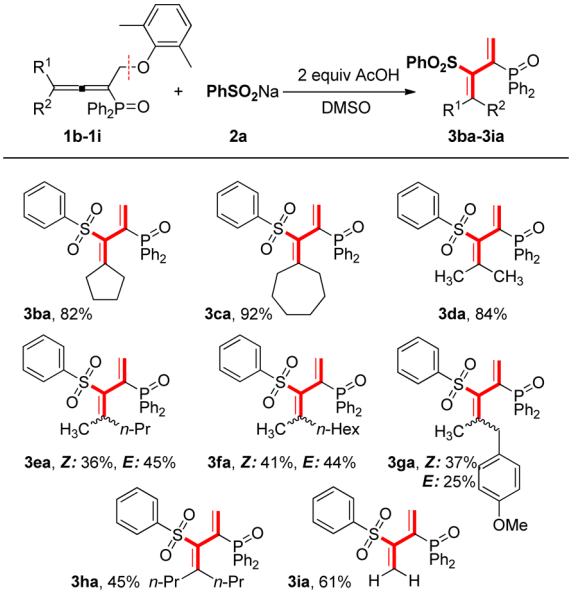
on the phenyl moiety, in which strong electron-donating (*p*-methoxy) and electron-withdrawing (*p*-trifluoromethyl) groups impaired the coupling efficiency comparatively, with yields dropped to around 70% (**3ab**, **3ah**). This transformation exhibited sensitivity to *meta*-substitution as well, furnishing 68% yield of **3ad** with *m*-methyl-substituted compound (**2d**) as substrate. Sodium naphthalene-2-sulfinate and thienyl-2-sulfonate were also reliable substrates under the standard conditions, affording the products (**3ai**, **3aj**) in medium yields of 77% and 65%, respectively. Moreover, sodium alkylsulfinates bearing C1−C4 chains all exemplified the generality of this sulfonylation (**3ak**−**an**).

Subsequently, the scope of allenylphosphine oxides was investigated by altering the substitutions at terminal carbon atoms. Besides cyclohexyl substitution, cyclopentyl and cycloheptyl substituents gave comparable yields of the corresponding adducts (**3ba**, **3ca**). Substrates with acyclic alkyl groups and no substitutents (**2i**) were proven to be reactive with sodium benzenesulfinate, generating the bifunctionalized 1,3-butadienes in 45−85% yields (Table 3). Note that the variation of R^1 and

Table 3. Reactivity of Allenylphosphine Oxides[a]

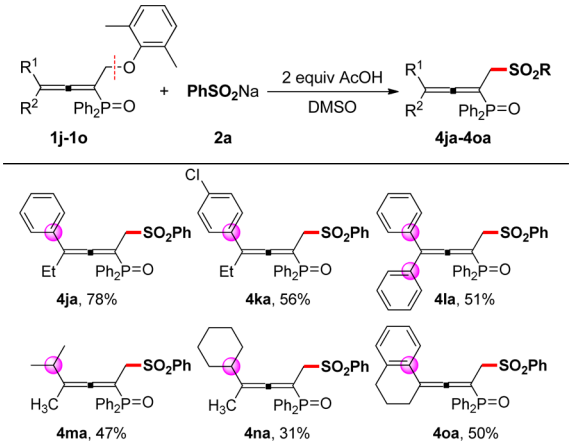


[a]Reaction conditions: allenylphosphine oxide (**1b**−**i**, 0.20 mmol), sodium benzenesulfinate (**2a**, 0.40 mmol), acetic acid (2.0 equiv), DMSO (1 mL), rt, 11 h, isolated yields, *Z*/*E* configurations were determined by NOESY experiments.

R^2 would produce stereodiversity in products. For instance, with terminal methyl and *n*-propyl substitutions, *Z*- and *E*-isomers (**3ea**) were isolated with a combined yield of 81%, along with a slight *E*-preference (*E*/*Z* = 1/0.8). However, the stereopreferences were not regular while expanding to other ones (**3fa**, **3ga**). Quite interestingly, the reaction pathway was fortuitously changed with the allenylphosphine oxides (**1j**−**o**) bearing terminal tertiary or quaternary carbon centers at the α-positions. As listed in Table 4, acceptable to good yields of sulfonylated phosphinyl allenes (**4**) were obtained, presenting a series of novel tetrasubstituted allenes. The regiodivergent phenomena might be the combination effect of steric hindrance and stabilization of distal substituents to intermediates.

The substrate-dependent reaction pathways are quite interesting and distinct from those of our previous studies,

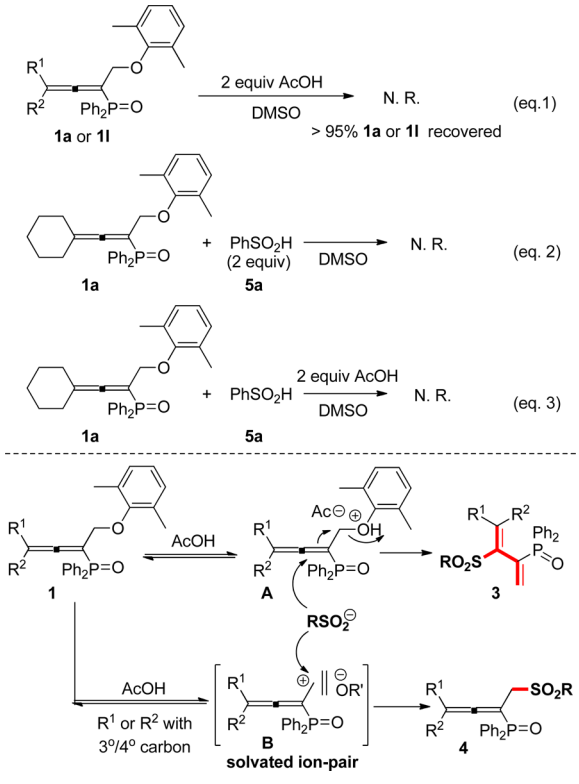
Table 4. Reactivity of Allenylphosphine Oxides Bearing Terminal Tertiary or Quaternary Carbon Centres[a]



[a]Reaction conditions: allenylphosphine oxide (**1j**−**o**, 0.20 mmol), sodium benzenesulfinate (**2a**, 0.40 mmol), acetic acid (2.0 equiv), DMSO (1 mL), rt, 48 h, isolated yields.

which enlightened us to explore the reaction mechanism.[18] First, **1a** and **1l** were applied independently in the absence of sodium benzenesulfinate (**2a**) under the standard conditions. More than 95% of the starting materials were recovered, without observation of the (Ar)O−C(sp^3) bond cleavage (eq 1, Scheme 2). Taking into account that benzenesulfinic acid could be a reactive intermediate, control experiments with benzenesulfinic acid with or without acetic acid were conducted in DMSO, respectively. The pK_a values of benzenesulfinic acid and acetic acid,[19] together with the results shown in eqs 2 and 3, rule out the in situ generation of benzenesulfinic acid and the

Scheme 2. Control Experiments and Plausible Mechanism



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possibility of an electrophile.[12e] On the basis of the experimental observations and previous reports,[14b] a mechanism is proposed in Scheme 2. The aryl ether moiety is reversibly protonated upon the treatment of acetic acid. On one hand, for substrates without terminal tertiary or quaternary carbons, sodium sulfinates attack the central carbon of intermediate **A**, synergistically releasing the 2,6-dimethylphenol group to finalize product **3**. On the other hand, a "stabilized" solvated ion pair (**B**) might form predominantly when substrates bearing terminal tertiary or quaternary carbons are used, and subsequent nucleophilic attack on cationic carbon will lead to the allene products (**4**).

In conclusion, an acetic acid mediated sulfonylation of allenylphosphine oxides with sodium sulfinates is disclosed. This new methodology involves tandem (Ar)O−C(sp^3) bond cleavage and C(sp^2)/C(sp^3)−SO_2 formation toward divergent synthesis of sulfonyl and phosphinyl bifunctionalized 1,3-butadienes or allenes, depending on the endmost substitutions of allenylphosphine oxides. Mechanistic studies reveal that the (Ar)O−C(sp^3) bond cleavage by acetic acid is reversible; thus, C(sp^2)/C(sp^3)−SO_2 formation occurs synergistically. We expect this new and operationally simple protocol to provide novel scaffolds for building potential bioactive compounds.

EXPERIMENTAL SECTION

General Methods. Solvents and reagents were reagent grade and used without purification unless otherwise noted. Anhydrous solvents were obtained as follows: THF, 1,4-dioxane, and toluene were dried by distillation from sodium and benzophenone; $CHCl_3$, DMF, and DMSO were redistilled over CaH_2. All reactions were carried out in oven-dried glassware under oxygen unless otherwise specified. Column chromatography was performed using silica gel (300−400 mesh). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ operating at 400, 100, and 162 MHz in the presence of tetramethylsilane (TMS) as an internal standard and are reported in ppm (δ). Coupling constants are reported in hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; and br, broad.

Synthetic Procedures: General Procedure for Acetic Acid Mediated Sulfonylation of Allenylphosphine Oxides (3 or 4). *(3-Cyclohexylidene-3-(phenylsulfonyl)prop-1-en-2-yl)-diphenylphosphine Oxide (**3aa**).* In a 5 mL flask were dissolved allenylphosphine oxide (**1a**, 88 mg, 0.2 mmol), sodium benzenesulfinate (**2a**, 66 mg, 0.4 mmol), and acetic acid (24 mg, 0.4 mmol) in 1 mL of DMSO. The reaction mixture was stirred at room temperature for 11 h until complete consumption of **1a** as monitored by TLC. The resulting mixture was diluted with ethyl acetate and washed with saturated NaCl aqueous solution. The organic layer was collected and concentrated. The resulting crude product was purified by column chromatography [eluent: 1:1 (v/v) of ethyl acetate/petroleum ether] to furnish **3aa** as an off-white solid (86 mg, 92% yield): mp 87.9−89.5 °C; TLC (R_f = 0.20, PET/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99−7.97 (m, 2H), 7.96−7.87 (m, 4H), 7.56−7.43 (m, 9H), 6.19 (d, J = 1.5 Hz, 1H), 6.12 (d, J = 19.1 Hz, 1H), 2.52−2.44 (m, 2H), 2.19−2.05 (m, 2H), 1.52−1.29 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1 (d, J = 4.8 Hz), 143.3, 140.4 (d, J = 93.8 Hz), 137.1 (d, J = 10.0 Hz), 132.7, 132.5 (d, J = 59.8 Hz), 132.4 (d, J = 6.6 Hz), 132.1, 132.0 (d, J = 2.6 Hz), 128.9, 128.3 (dd, J = 25.2, 12.2 Hz), 127.4, 35.5, 31.9, 28.1, 27.1, 25.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{27}H_{28}O_3PS$ 463.1497, found 463.1483; IR (film) ν 2918, 2850, 1624, 1588, 1436, 1300, 1198, 1141, 755, 722, 691 cm^{-1}.

*(3-Cyclohexylidene-3-((4-methoxyphenyl)sulfonyl)prop-1-en-2-yl)diphenylphosphine oxide (**3ab**):* yellow solid; mp 99.8−100.7 °C (70 mg, 71% yield); TLC (R_f = 0.33, PET/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.88 (m, 6H), 7.59−7.46 (m, 6H), 6.92 (d, J = 8.8 Hz, 2H), 6.17 (d, J = 6.7 Hz, 1H), 6.10 (d, J = 27.8 Hz, 1H), 3.85 (s, 3H), 2.57−2.48 (m, 2H), 2.18−2.14 (m, 1H), 2.04 (d, J = 12.3 Hz, 1H), 1.48−1.29 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 159.1 (d, J = 4.9 Hz), 140.7 (d, J = 93.8 Hz), 136.8 (d, J = 10.2 Hz), 134.9, 132.9 (d, J = 6.6 Hz), 132.7 (d, J = 9.9 Hz), 132.1 (d, J = 9.5 Hz), 131.9 (d, J = 7.7 Hz), 129.8, 128.3 (dd, J = 24.7, 12.2 Hz), 114.0, 55.6, 35.4, 31.7, 28.1, 27.3, 25.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9 (s); HRMS (ESI) ([M + Na]$^+$) calcd for $C_{28}H_{29}NaO_4PS$ 515.1422, found 515.1408; IR (film) ν 3060, 2925, 2852, 1592, 1497, 1437, 1311, 1294, 1258, 1192, 1137, 1115, 1085, 1024, 835, 802, 744, 693 cm^{-1}.

*(3-Cyclohexylidene-3-tosylprop-1-en-2-yl)diphenylphosphine oxide (**3ac**):* yellow solid; mp 112.9−114.3 °C (80 mg, 84% yield); TLC (R_f = 0.28, PET/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.89 (m, 4H), 7.80 (d, J = 8.2 Hz, 2H), 7.59−7.45 (m, 6H), 7.24 (d, J = 8.1 Hz, 2H), 6.18 (d, J = 12.1 Hz, 1H), 6.11 (d, J = 33.1 Hz, 1H), 2.57−2.45 (m, 2H), 2.40 (s, 3H), 2.20−2.16 (m, 1H), 2.08 (s, 1H), 1.49−1.30 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (d, J = 4.9 Hz), 143.5, 140.6 (d, J = 93.9 Hz), 140.2, 137.0 (d, J = 9.9 Hz), 132.7 (d, J = 9.8 Hz), 132.1 (d, J = 9.6 Hz), 132.04 (d, J = 2.5 Hz), 131.96 (d, J = 2.8 Hz), 129.5, 128.3 (dd, J = 26.6, 12.3 Hz), 127.5, 35.5, 31.7, 28.1, 27.2, 25.6, 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{28}H_{30}O_3PS$ 477.1653, found 477.1641; IR (film) ν 2954, 2920, 2849, 1630, 1591, 1455, 1438, 1298, 1288, 1196, 1180, 1138, 1116, 918, 815, 726, 700 cm^{-1}.

*(3-Cyclohexylidene-3-(m-tolylsulfonyl)prop-1-en-2-yl)-diphenylphosphine oxide (**3ad**):* yellow solid; mp 105.9−107.1 °C (65 mg, 68% yield); TLC (R_f = 0.31, PET/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95−7.88 (m, 4H), 7.74−7.72 (m, 2H), 7.57−7.45 (m, 6H), 7.32 (d, J = 5.2 Hz, 2H), 6.19 (d, J = 6.7 Hz, 1H), 6.12 (d, J = 27.6 Hz, 1H), 2.57−2.45 (m, 2H), 2.38 (s, 3H), 2.21 (dd, J = 11.5, 7.5 Hz, 1H), 2.10 (d, J = 14.2 Hz, 1H), 1.52 (dd, J = 14.7, 7.1 Hz, 1H), 1.44 (dd, J = 10.6, 4.8 Hz, 3H), 1.36−1.31 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1 (d, J = 4.8 Hz), 143.1, 140.5 (d, J = 93.5 Hz), 139.0 (s), 137.1 (d, J = 10.0 Hz), 133.5, 132.7 (d, J = 9.8 Hz), 132.2, 132.1, 132.0 (d, J = 2.6 Hz), 131.9 (d, J = 2.6 Hz), 128.3 (dd, J = 28.0, 12.2 Hz), 128.1 (d, J = 126.1 Hz), 124.6, 35.5, 31.8, 28.1, 27.2, 25.6, 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0 (s); HRMS (ESI) ([M + Na]$^+$) calcd for $C_{28}H_{29}NaO_3PS$ 499 .1473, found 499.1472; IR (film) ν 2963, 2916, 2853, 1628, 1591, 1453, 1437, 1298, 1290, 1193, 1177, 1145, 1117, 1084, 927, 836, 728, 698 cm^{-1}.

*(3-((4-tert-Butylphenyl)sulfonyl)-3-cyclohexylideneprop-1-en-2-yl)diphenylphosphine oxide (**3ae**):* white solid; mp 143.1−143.6 °C (85 mg, 82% yield); TLC (R_f = 0.24, PET/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93−7.85 (m, 6H), 7.55−7.43 (m, 8H), 6.18 (d, J = 2.5 Hz, 1H), 6.11 (d, J = 23.7 Hz, 1H), 2.57−2.46 (m, 2H), 2.20−2.04 (m, 2H), 1.52−1.35 (m, 6H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (d, J = 4.8 Hz), 156.4, 140.5 (d, J = 93.7 Hz), 140.1, 137.0 (d, J = 10.0 Hz), 132.7 (d, J = 9.9 Hz), 132.1 (d, J = 9.6 Hz), 132.0 (d, J = 2.7 Hz), 131.9, 128.3 (dd, J = 27.3, 12.2 Hz), 127.3, 125.8, 35.5, 35.1, 31.8, 31.1, 28.1, 27.2, 25.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{31}H_{36}O_3PS$ 519.2123, found 519.2109; IR (film) ν 3053, 2961, 2918, 2852, 1624, 1591, 1435, 1300, 1291, 1194, 1178, 1143, 1115, 1105, 1083, 766, 754, 725, 694 cm^{-1}.

*(3-Cyclohexylidene-3-((4-fluorophenyl)sulfonyl)prop-1-en-2-yl)-diphenylphosphine oxide (**3af**):* yellow solids;mp 78.2−78.8 °C (85 mg, 89% yield); TLC (R_f = 0.36, PET/EA = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 8.6, 5.2 Hz, 2H), 7.94−7.85 (m, 4H), 7.61−7.47 (m, 6H), 7.14 (t, J = 8.6 Hz, 2H), 6.17 (t, J = 28.7 Hz, 2H), 2.47 (t, J = 5.2 Hz, 2H), 2.15−2.05 (m, 2H), 1.50−1.39 (m, 5H), 1.28−1.19 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0 (d, J = 254.9 Hz), 160.2, 140.0 (d, J = 94.0 Hz), 139.4 (d, J = 2.9 Hz), 137.2 (d, J = 10.5 Hz), 132.6 (d, J = 10.0 Hz), 132.12 (d, J = 2.6 Hz), 132.05, 132.0 (d, J = 3.5 Hz), 130.5 (d, J = 9.4 Hz), 128.4 (dd, J = 21.3, 12.2 Hz), 116.0 (d, J = 22.5 Hz), 35.5, 32.0, 28.2, 27.2, 25.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{27}H_{27}FO_3PS$ 481.1403, found 481.1392; IR (film) ν 3038, 2933, 2854, 1625, 1590, 1497, 1437, 1308, 1291, 1267, 1195, 1179, 1139, 1116, 1083, 925, 838, 727, 699 cm^{-1}.

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*(3-((4-Chlorophenyl)sulfonyl)-3-cyclohexylideneprop-1-en-2-yl)-diphenylphosphine oxide (**3ag**):* white solid; mp 95.9−96.6 °C (80 mg, 81% yield); TLC (R_f = 0.35, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.2 Hz, 2H), 7.92−7.83 (m, 4H), 7.59−7.40 (m, 8H), 6.15 (dd, J = 30.8, 28.7 Hz, 2H), 2.47 (d, J = 5.9 Hz, 2H), 2.15−2.05 (m, 2H), 1.50−1.39 (m, 5H), 1.25−1.22 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5 (d, J = 4.7 Hz), 141.9, 139.9 (d, J = 93.9 Hz), 139.1, 137.3 (d, J = 10.3 Hz), 132.6 (d, J = 10.0 Hz), 132.12 (d, J = 2.7 Hz), 132.05, 132.0, 129.2, 129.1, 128.4 (dd, J = 22.4, 12.2 Hz), 35.5, 32.1, 28.2, 27.2, 25.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9 (s); HRMS (ESI) ([M + H] $^+$) calcd for $C_{27}H_{27}ClO_3PS$ 497.1107, found 497.1093; IR (film) ν 3011, 2932, 2855, 1625, 1584, 1480, 1397, 1306, 1297, 1197, 1142, 1084, 826, 766, 728, 698 cm^{-1}.

*(3-Cyclohexylidene-3-((4-(trifluoromethyl)phenyl)sulfonyl)prop-1-en-2-yl)diphenylphosphine oxide (**3ah**):* yellow liquid (75 mg, 71% yield); TLC (R_f = 0.35, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.0 Hz, 2H), 7.92−7.83 (m, 4H), 7.72 (d, J = 8.1 Hz, 2H), 7.61−7.47 (m, 6H), 6.25 (d, J = 39.2 Hz, 1H), 6.12 (d, J = 17.6 Hz, 1H), 2.52−2.42 (m, 2H), 2.12 (d, J = 15.6 Hz, 2H), 1.55 (s, 1H), 1.45 (s, 4H), 1.27 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, J = 4.7 Hz), 146.9, 140.0, 139.1, 137.6 (d, J = 10.5 Hz), 132.5 (d, J = 10.1 Hz), 132.2 (d, J = 2.6 Hz), 132.01, 131.99 (d, J = 13.3 Hz), 128.5 (dd, J = 21.7, 12.2 Hz), 128.1, 125.9 (d, J = 3.5 Hz), 35.6, 32.2, 28.2, 27.2, 26.9, 25.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{28}H_{27}F_3O_3PS$ 531.1371, found 531.1357; IR (film) ν 3056, 2983, 1438, 1323, 1264, 1175, 1143, 1062, 909, 732, 704 cm^{-1}.

*(3-Cyclohexylidene-3-(naphthalen-2-ylsulfonyl)prop-1-en-2-yl)-diphenylphosphine oxide (**3ai**):* white solid; mp 163.9−164.5 °C (79 mg, 77% yield); TLC (R_f = 0.22, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.00−7.87 (m, 8H), 7.64−7.44 (m, 8H), 6.22 (d, J = 4.9 Hz, 1H), 6.15 (d, J = 16.1 Hz, 1H), 2.60−2.51 (m, 2H), 2.24−2.06 (m, 2H), 1.53−1.30 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5 (d, J = 4.9 Hz), 140.9, 140.2, 140.0, 137.3 (d, J = 10.1 Hz), 134.9, 132.7 (d, J = 9.8 Hz), 132.2, 132.1 (d, J = 6.9 Hz), 132.0, 129.5, 129.2, 128.8, 128.7, 128.3 (dd, J = 30.5, 12.2 Hz), 127.9, 127.3, 122.8, 35.6, 31.9, 28.1, 27.3, 25.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9 (s); HRMS (ESI) ([M + H] $^+$) calcd for $C_{31}H_{30}O_3PS$ 513.1653, found 513.1641; IR (film) ν 3057, 2930, 2854, 1617, 1592, 1433, 1295, 1196, 1179, 1140, 1125, 1112, 1068, 965, 853, 756, 745, 724, 691 cm^{-1}.

*(3-Cyclohexylidene-3-(thiophene-2-ylsulfonyl)prop-1-en-2-yl)-diphenylphosphine oxide (**3aj**):* yellow solid; mp 135.7−136.8 °C (61 mg, 65% yield); TLC (R_f = 0.28, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93−7.84 (m, 4H), 7.66 (d, J = 2.9 Hz, 1H), 7.59−7.44 (m, 7H), 7.01 (t, J = 4.3 Hz, 1H), 6.16 (t, J = 28.1 Hz, 2H), 2.73−2.65 (m, 2H), 2.22 (d, J = 13.2 Hz, 1H), 2.07 (t, J = 8.9 Hz, 1H), 1.45 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1 (d, J = 4.8 Hz), 144.4, 140.7 (d, J = 93.7 Hz), 137.0 (d, J = 9.8 Hz), 133.6, 132.7 (d, J = 9.7 Hz), 132.6, 132.2 (d, J = 9.7 Hz), 132.1 (d, J = 2.7 Hz), 132.0 (d, J = 2.3 Hz), 128.3 (dd, J = 26.7, 12.2 Hz), 127.4, 35.7, 32.0, 28.1, 27.4, 25.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9 (s); HRMS (ESI) ([M + H] $^+$) calcd for $C_{25}H_{26}O_3PS_2$ 469.1061, found 469.1048; IR (film) ν 3042, 2920, 2851, 1623, 1589, 1435, 1403, 1305, 1197, 1180, 1136, 1115, 1099, 1014, 754, 727, 698 cm^{-1}.

*(3-Cyclohexylidene-3-(methylsulfonyl)prop-1-en-2-yl)-diphenylphosphine oxide (**3ak**):* yellow liquid (69 mg, 86% yield); TLC (R_f = 0.23, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.78 (m, 4H), 7.60−7.43 (m, 6H), 6.10 (d, J = 40.4 Hz, 1H), 5.91 (d, J = 18.0 Hz, 1H), 3.10 (s, 3H), 2.73 (t, J = 5.8 Hz, 2H), 2.09−1.93 (m, 2H), 1.78−1.60 (m, 2H), 1.53−1.48 (m, 2H), 1.31−1.28 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4 (d, J = 5.4 Hz), 136.2 (d, J = 10.8 Hz), 133.3 (d, J = 5.7 Hz), 132.6 (d, J = 10.5 Hz), 132.3, 132.21 (d, J = 103.7 Hz), 132.16, 128.5 (dd, J = 12.1, 7.9 Hz), 43.8, 35.2, 32.1, 28.3, 28.0, 25.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.7 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{22}H_{26}O_3PS$ 401.1340, found 401.1328; IR(film) ν 3058, 2927, 2854, 1622, 1590, 1436, 1297, 1192, 1175, 1133, 1116, 1098, 959, 774, 725, 695 cm^{-1}.

*(3-Cyclohexylidene-3-(ethylsulfonyl)prop-1-en-2-yl)diphenylphosphine oxide (**3al**):* white solid; mp 141.3−142.5 °C (58 mg, 70% yield); TLC (R_f = 0.23, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.80 (m, 4H), 7.60−7.44 (m, 6H), 6.13 (d, J = 40.2 Hz, 1H), 5.95 (d, J = 18.0 Hz, 1H), 3.37 (dq, J = 14.8, 7.5 Hz, 1H), 3.00 (dq, J = 14.5, 7.4 Hz, 1H), 2.78−2.68 (m, 2H), 2.15−2.00 (m, 2H), 1.76−1.60 (m, 2H), 1.57−1.47 (m, 2H), 1.43−1.35 (m, 2H), 1.32 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, J = 5.2 Hz), 139.9 (d, J = 94.7 Hz), 136.5 (d, J = 10.7 Hz), 132.7, 132.4 (d, J = 37.5 Hz), 132.14, 132.08 (d, J = 2.8 Hz), 128.5 (t, J = 11.8 Hz), 49.8, 35.5, 32.2, 28.3, 28.2, 25.8, 5.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.5 (s); HRMS (ESI) ([M + H] $^+$) calcd for $C_{23}H_{28}O_3PS$ 415.1497, found 415.1486; IR (film) ν 3049, 2933, 1622, 1593, 1432, 1300, 1190, 1176, 1131, 1116, 953, 756, 729, 720, 699 cm^{-1}.

*(3-Cyclohexylidene-3-(propylsulfonyl)prop-1-en-2-yl)-diphenylphosphine oxide (**3am**):* white solid; mp 89.3−89.96 °C (65 mg, 76% yield); TLC (R_f = 0.21, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.81 (m, 4H), 7.60−7.45 (m, 6H), 6.13 (d, J = 40.3 Hz, 1H), 5.95 (d, J = 18.1 Hz, 1H), 3.20−3.13 (m, 1H), 2.93−2.84 (m, 1H), 2.81−2.66 (m, 2H), 2.21−2.14 (m, 1H), 2.10−2.04 (m, 1H), 1.87−1.78 (m, 2H), 1.76−1.62 (m, 2H), 1.59−1.36 (m, 4H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, J = 5.4 Hz), 139.7 (d, J = 94.7 Hz), 136.6 (d, J = 10.8 Hz), 132.7 (d, J = 10.2 Hz), 132.24, 132.15, 132.1 (d, J = 2.7 Hz), 128.5 (t, J = 12.7 Hz), 57.1, 35.5, 32.2, 28.3, 28.2, 25.8, 14.8, 13.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.6 (s); HRMS (ESI) ([M + H] $^+$) calcd for $C_{24}H_{30}O_3PS$ 429.1653, found 429.1642; IR (film) ν 3057, 2931, 2855, 1620, 1590, 1437, 1308, 1192, 1175, 1125, 999, 917, 726, 694 cm^{-1}.

*(3-(Butylsulfonyl)-3-cyclohexylideneprop-1-en-2-yl)-diphenylphosphine oxide (**3an**):* yellow liquid (79 mg, 90% yield); TLC (R_f = 0.23, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.80 (m, 4H), 7.58−7.43 (m, 6H), 6.12 (d, J = 40.3 Hz, 1H), 5.94 (d, J = 18.1 Hz, 1H), 3.23−3.16 (m, 1H), 2.97−2.88 (m, 1H), 2.80−2.65 (m, 2H), 2.22−2.04 (m, 2H), 1.79−1.62 (m, 4H), 1.53−1.32 (m, 6H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (d, J = 5.3 Hz), 139.7 (d, J = 94.8 Hz), 136.6 (d, J = 10.8 Hz), 132.6, 132.5 (d, J = 51.7 Hz), 132.13, 132.07 (d, J = 2.7 Hz), 128.4 (t, J = 8.1 Hz), 55.2, 35.5, 32.2, 28.3, 28.1, 25.8, 22.9, 21.8, 13.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.5 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{25}H_{32}O_3PS$ 443.1810, found 443.1800; IR (film) ν 2930, 2855, 1615, 1590, 1437, 1297, 1268, 1194, 1126, 1116, 1099, 769, 724, 694 cm^{-1}.

*(3-Cyclopentylidene-3-(phenylsulfonyl)prop-1-en-2-yl)-diphenylphosphine oxide (**3ba**):* yellow liquid (74 mg, 82% yield); TLC (R_f = 0.33, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.83 (m, 4H), 7.79 (d, J = 8.0 Hz, 2H), 7.58−7.42 (m, 9H), 6.13 (d, J = 17.6 Hz, 1H), 6.04 (d, J = 38.6 Hz, 1H), 2.71−2.34(m, 3H), 2.06−2.01 (m, 1H), 1.68−1.62 (m, 2H), 1.49 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, J = 4.8 Hz), 141.3, 140.7 (d, J = 93.9 Hz), 137.7 (d, J = 9.7 Hz), 133.0, 132.0 (d, J = 2.6 Hz), 130.2 (d, J = 7.8 Hz), 128.8, 128.4, 128.3, 127.9, 36.7, 32.9, 26.7, 25.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.2 (s); HRMS (ESI) ([M + Na]$^+$) calcd for $C_{26}H_{25}NaO_3PS$ 471.1160, found 471.1149; IR (film) ν 3053, 2959, 2920, 1625, 1588, 1436, 1302, 1181, 1140, 1115, 721, 690 cm^{-1}.

*(3-Cycloheptylidene-3-(phenylsulfonyl)prop-1-en-2-yl)-diphenylphosphine oxide (**3ca**):* white solid; mp 127.5−129.3 °C (90 mg, 92% yield); TLC (R_f = 0.32, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.5 Hz, 2H), 7.95−7.90 (m, 4H), 7.60−7044 (m, 9H), 6.20 (d, J = 0.9 Hz, 1H), 6.13 (d, J = 19.6 Hz, 1H), 2.73−2.67 (m, 1H), 2.45−2.40 (m, 2H), 2.33−2.28 (m, 1H), 1.52−1.28 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (d, J = 5.0 Hz), 142.9, 140.8 (d, J = 93.7 Hz), 137.2 (d, J = 10.0 Hz), 134.7 (d, J = 6.5 Hz), 132.8 (d, J = 5.7 Hz), 132.4 (d, J = 51.3 Hz), 132.0, 131.9 (d, J = 2.5 Hz), 128.9, 128.3 (dd, J = 26.5, 12.2 Hz), 127.7, 36.2, 32.4, 28.7, 26.3, 26.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1 (s); HRMS (ESI) ([M + Na] $^+$) calcd for $C_{28}H_{29}NaO_3PS$ 499.1473, found 499.1460; IR (film) ν 3392, 3184, 2917, 2848, 1645, 1586, 1469, 1435, 1300, 1197, 1139, 1113, 757, 719, 691 cm^{-1}.

*(4-Methyl-3-(phenylsulfonyl)penta-1,3-dien-2-yl)diphenylphosphine oxide (**3da**):* yellow solids; mp 139.0−139.9 °C (71 mg, 84% yield); TLC (R_f = 0.23, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.88 (m, 6H), 7.58−7.43 (m, 9H), 6.17 (d, J = 4.2 Hz, 1H), 6.10 (d, J = 25.4 Hz, 1H), 1.99 (d, J = 1.9 Hz, 3H), 1.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4 (d, J = 4.8 Hz), 142.3, 140.8 (d, J =

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93.9 Hz), 137.5 (d, J = 10.0 Hz), 134.8 (d, J = 7.0 Hz), 132.8, 132.6 (d, J = 9.8 Hz), 132.14, 132.05, 128.9, 128.4 (dd, J = 29.6, 12.1 Hz), 127.6, 26.2, 22.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.4 (s); HRMS (ESI) ([M + H] $^+$) calcd for $C_{24}H_{24}O_3PS$ 423.1184, found 423.1169; IR (film) ν 3062, 2918, 2850, 1628, 1592, 1436, 1302, 1197, 1140, 1115, 1083, 752, 722, 691 cm $^{-1}$.

*(Z)-(4-Methyl-3-(phenylsulfonyl)hepta-1,3-dien-2-yl)diphenylphosphine oxide (**3ea-Z**):* yellow liquid (32 mg, 36% yield); TLC (R_f = 0.28, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2H), 7.95−7.86 (m, 4H), 7.61−7.52 (m, 5H), 7.49−7.45 (m, 4H), 6.19 (d, J = 18.3 Hz, 1H), 6.11 (d, J = 3.0 Hz, 1H), 2.22−2.15 (m, 1H), 1.90 (d, J = 2.6 Hz, 3H), 1.36−1.18 (m, 3H), 0.66 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2 (d, J = 4.8 Hz), 142.5, 140.2 (d, J = 93.8 Hz), 137.5 (d, J = 10.2 Hz), 135.2 (d, J = 6.4 Hz), 132.6 (d, J = 10.0 Hz), 132.5 (d, J = 70.4 Hz), 132.04, 132.01, 128.9, 128.4 (dd, J = 29.9, 12.2 Hz), 127.8, 40.8, 21.0, 19.5, 13.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0 (s); HRMS (ESI) ([M + H]$^+$) Calcd for $C_{26}H_{28}O_3PS$: 451.1497, found 451.1485; IR (film) ν 3058, 2961, 2929, 2871, 1620, 1589, 1436, 1300, 1195, 1142, 1114, 1097, 1084, 751, 721, 690 cm^{-1}.

*(E)-(4-Methyl-3-(phenylsulfonyl)hepta-1,3-dien-2-yl)diphenylphosphine oxide (**3ea-E**):* white solid; mp 106.1−107.2 °C (41 mg, 45% yield); TLC (R_f = 0.20, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.89 (m, 6H), 7.58−7.45 (m, 9H), 6.18 (d, J = 17.7 Hz, 1H), 6.03 (d, J = 38.4 Hz, 1H), 2.62−2.55 (m, 1H), 2.20−2.13 (m, 1H), 1.83 (s, 3H), 1.25−1.15 (m, 1H), 1.12−0.99 (m, 1H), 0.73 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 142.8, 141.5 (d, J = 93.4 Hz), 137.1 (d, J = 9.7 Hz), 134.8 (d, J = 7.3 Hz), 132.9, 132.6 (d, J = 9.9 Hz), 132.2 (d, J = 9.7 Hz), 132.0, 128.9, 128.3 (dd, J = 28.5, 12.3 Hz), 127.6, 37.1, 23.5, 21.1, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.3 (s); IR (film) ν 3079, 2957, 2923, 2869, 1609, 1588, 1444, 1434, 1312, 1304, 1290, 1167, 1116, 763, 724, 694 cm^{-1}.

*(Z)-(4-Methyl-3-(phenylsulfonyl)deca-1,3-dien-2-yl)diphenylphosphine oxide (**3fa-Z**):* yellow liquid (40 mg, 41% yield); TLC (R_f = 0.30, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.8 Hz, 2H), 7.94−7.86 (m, 4H), 7.61−7.52 (m, 5H), 7.49−7.45 (m, 4H), 6.19 (d, J = 22.9 Hz, 1H), 6.11 (s, 1H), 2.24−2.16 (m, 1H), 1.90 (d, J = 2.5 Hz, 3H), 1.33−1.16 (m, 5H), 1.13−1.05 (m, 2H), 1.03−0.91 (m, 2H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4 (d, J = 5.0 Hz), 142.5, 140.2 (d, J = 93.7 Hz), 137.4 (d, J = 10.3 Hz), 135.0 (d, J = 6.2 Hz), 132.8, 132.6 (d, J = 10.1 Hz), 132.1, 132.0, 128.9, 128.4 (dd, J = 27.8, 12.2 Hz), 127.8, 39.0, 31.5, 29.2, 27.6, 22.5, 19.6, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{29}H_{34}O_3PS$ 493.1966, found 493.1955; IR (film) ν 3058, 2955, 2927, 2855, 1621, 1589, 1482, 1436, 1301, 1188, 1142, 1114, 750, 722, 691 cm^{-1}.

*(E)-(4-Methyl-3-(phenylsulfonyl)deca-1,3-dien-2-yl)diphenylphosphine oxide (**3fa-E**):* yellow liquid (43 mg, 44% yield); TLC (R_f = 0.18, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.89 (m, 6H), 7.60−7.45 (m, 9H), 6.19 (d, J = 17.7 Hz, 1H), 6.04 (d, J = 38.4 Hz, 1H), 2.61−2.55 (m, 1H), 2.23−2.13 (m, 1H), 1.83 (s, 3H), 1.25−1.20 (m, 2H), 1.13 (d, J = 22.0 Hz, 5H), 0.94−0.91 (m, 1H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (d, J = 4.9 Hz), 142.9, 141.5 (d, J = 93.4 Hz), 137.1 (d, J = 9.5 Hz), 134.6 (d, J = 6.8 Hz), 132.9, 132.6 (d, J = 9.7 Hz), 132.2 (d, J = 9.7 Hz), 132.0, 128.9, 128.3 (dd, J = 28.5, 12.2 Hz), 127.6, 35.4, 31.5, 29.5, 27.8, 23.6, 22.5, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.4 (s); IR (film) ν 3058, 2926, 2851, 1644, 1619, 1588, 1437, 1303, 1196, 1423, 1115, 749, 723, 690 cm^{-1}.

*(Z)-(5-(4-Methoxyphenyl)-4-methyl-3-(phenylsulfonyl)penta-1,3-dien-2-yl)diphenylphosphine oxide (**3ga-Z**):* yellow liquid (39 mg, 37% yield); TLC (R_f = 0.30, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2H), 7.95 (dd, J = 12.0, 7.6 Hz, 2H), 7.85 (dd, J = 11.5, 7.7 Hz, 2H), 7.60−7.50 (m, 5H), 7.48−7.45 (m, J = 7.6 Hz, 4H), 6.95 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.5 Hz, 2H), 6.26 (d, J = 39.0 Hz, 1H), 6.15 (d, J = 17.7 Hz, 1H), 3.78 (s, 3H), 3.61 (d, J = 14.8 Hz, 1H), 3.24 (d, J = 14.9 Hz, 1H), 1.79 (d, J = 2.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 154.4, 142.3, 140.2 (d, J = 93.5 Hz), 137.9 (d, J = 10.3 Hz), 136.6, 132.6 (d, J = 9.9 Hz), 132.4 (d, J = 95.9 Hz), 132.1, 132.0, 129.8, 129.2, 128.9, 128.4 (dd, J = 23.7, 12.2 Hz), 127.8, 114.0, 55.2, 43.3, 19.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.4 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{31}H_{30}O_4PS$: 529.1602, found 529.1591; IR (film) ν 2952, 2919, 2849, 1645, 1610, 1510, 1436, 1301, 1247, 1179, 1141, 1134, 1028, 813, 722, 690 cm^{-1}.

*(E)-(5-(4-Methoxyphenyl)-4-methyl-3-(phenylsulfonyl)penta-1,3-dien-2-yl)diphenylphosphine oxide (**3ga-E**):* yellow solids; mp 138.9−139.8 °C (26 mg, 25% yield); TLC (R_f = 0.18, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.89 (m, 5H), 7.60−7.44 (m, 10H), 6.83 (d, J = 8.6 Hz, 2H), 6.74 (d, J = 8.6 Hz, 2H), 6.20 (d, J = 17.7 Hz, 1H), 6.10 (d, J = 38.2 Hz, 1H), 3.95 (d, J = 14.4 Hz, 1H), 3.79 (s, 3H), 3.58 (d, J = 14.3 Hz, 1H), 1.73 (d, J = 1.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 155.0 (d, J = 4.8 Hz), 142.6, 141.6 (d, J = 93.3 Hz), 137.2 (d, J = 9.5 Hz), 136.4 (d, J = 6.9 Hz), 133.0, 132.6 (d, J = 9.9 Hz), 132.2 (d, J = 9.6 Hz), 132.0, 130.0, 129.0, 128.9, 128.4 (dd, J = 17.9, 12.3 Hz), 127.8, 113.9, 55.3, 39.4, 23.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.2 (s); IR (film) ν 2918, 2848, 1608, 1580, 1510, 1435, 1290, 1173, 1140, 1137, 1034, 953, 810, 760, 721, 687 cm^{-1}.

*Diphenyl(3-(phenylsulfonyl)-4-propylhepta-1,3-dien-2-yl)phosphine oxide (**3ha**):* yellow solids; mp 126.8−128.3 °C (43 mg, 45% yield); TLC (R_f = 0.21, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−7.97 (m, 4H), 7.93−7.88 (m, 2H), 7.61−7.44 (m, 9H), 6.16 (d, J = 17.7 Hz, 1H), 5.98 (d, J = 38.4 Hz, 1H), 2.69−2.63 (m, 1H), 2.37−2.29 (m, 1H), 2.07−2.00 (m, 1H), 1.94−1.87 (m, 2H), 1.40−1.26 (m, 2H), 1.24−1.12 (m, 2H), 0.97−0.87 (m, 1H), 0.74−0.69 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5 (d, J = 4.8 Hz), 143.0 0, 141.1 (d, J = 93.3 Hz), 137.0 (d, J = 9.8 Hz), 134.8 (d, J = 6.8 Hz), 132.9, 132.7 (d, J = 9.9 Hz), 132.2 (d, J = 9.7 Hz), 132.0 (d, J = 2.7 Hz), 128.9, 128.3 (dd, J = 27.4, 12.2 Hz), 127.7, 37.4, 34.0, 21.5, 21.4, 14.3, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.5 (s); HRMS (ESI) ([M + H] $^+$) calcd for $C_{28}H_{32}O_3PS$: 479.1810, found 479.1793; IR (film) ν 3059, 2965, 2919, 2874, 2819, 1646, 1613, 1470, 1438, 1297, 1287, 1195, 1142, 754, 722, 694 cm^{-1}.

*Diphenyl(3-(phenylsulfonyl)buta-1,3-dien-2-yl)phosphine oxide (**3ia**):* yellow liquid (50 mg, 61% yield); TLC (R_f = 0.30, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.55−7.47 (m, 8H), 7.43−7.38 (m, 4H), 6.85 (d, J = 40.3 Hz, 1H), 6.60 (s, 2H), 5.80 (d, J = 20.9 Hz, 1H); ^{13}C NMR δ 143.9 (d, J = 10.6 Hz), 138.4, 136.4 (d, J = 7.6 Hz), 134.5 (d, J = 91.4 Hz), 133.6, 132.3 (d, J = 2.8 Hz), 131.8 (d, J = 9.8 Hz), 130.6, 129.9 (d, J = 3.7 Hz), 129.6, 128.9 (d, J = 43.0 Hz), 128.6 (d, J = 1.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.9 (s); HRMS (ESI) ([M + Na]$^+$) calcd for $C_{22}H_{19}NaO_3PS$ 417.0690, found 417.0679; IR (film) ν 3395, 3058, 2920, 2849, 1587, 1482, 1446, 1437, 1304, 1179, 1147, 1117, 1077, 744, 717, 688 cm^{-1}.

*Diphenyl(4-phenyl-1-(phenylsulfonyl)hexa-2,3-dien-2-yl)phosphine oxide (**4ja**):* yellow liquid (78 mg, 78% yield); TLC (R_f = 0.15, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.5 Hz, 2H), 7.67−7.50 (m, 6H), 7.47−7.38 (m, 5H), 7.35−7.28 (m, 5H), 7.22 (d, J = 7.3 Hz, 2H), 4.33−4.23 (m, 2H), 2.27−2.04 (m, 2H), 0.80 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.8, 139.3, 133.9 (d, J = 6.3 Hz), 133.7, 132.1 (d, J = 2.8 Hz), 131.59, 131.59 (d, J = 19.2 Hz), 130.7 (d, J = 20.8 Hz), 129.1, 128.6, 128.3 (dd, J = 12.4, 10.1 Hz), 128.2, 128,0 126.7 (d, J = 2.1 Hz), 113.3 (d, J = 13.4 Hz), 90.5 (d, J = 102.3 Hz), 53.7 (d, J = 10.3 Hz), 23.4 (d, J = 5.1 Hz), 11.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.1 (s); HRMS (ESI) ([M + H]$^+$) Calcd for $C_{30}H_{28}O_3PS$: 499.1497, found 499.1484; IR (film) ν 3057, 2963, 2916, 2849, 1927, 1589, 1494, 1447, 1438, 1309, 1188, 1141, 1084, 875, 724, 689 cm^{-1}.

*(4-(4-Chlorophenyl)-1-(phenylsulfonyl)hexa-2,3-dien-2-yl)diphenylphosphine oxide (**4ka**):* yellow liquid (60 mg, 56% yield); TLC (R_f = 0.12, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.9 Hz, 2H), 7.66−7.60 (m, 4H), 7.58−7.54 (m, 1H), 7.52−7.49 (m, 1H), 7.46−7.38 (m, 5H), 7.36−7.32 (m, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 4.31−4.19 (m, 2H), 2.25−2.14 (m, 1H), 2.10−2.04 (m, 1H), 0.80 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.4 (d, J = 4.1 Hz), 139.2, 133.81, 133.77 (d, J = 1.2 Hz), 132.4 (d, J = 6.4 Hz), 132.2 (t, J = 2.7 Hz), 131.6, 131.5 (d, J = 20.8 Hz), 130.5 (d, J = 16.0 Hz), 129.1, 128.7, 128.4 (dd, J = 12.4, 8.8 Hz), 128.1, 127.9 (d, J = 2.0 Hz), 112.4 (d, J = 13.3 Hz), 91.1 (d, J =

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101.3 Hz), 53.6 (d, J = 10.1 Hz), 23.4 (d, J = 5.0 Hz), 11.8 (d, J = 1.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.2 (s); HRMS (ESI) ([M + H]$^+$) Calcd for $C_{30}H_{27}ClO_3PS$ 533.1107, found 533.1092; IR (film) ν 3058, 2923, 1927, 1589, 1490, 1446, 1437, 1309, 1184, 1141, 1118, 1085, 832, 723, 690 cm^{-1}.

*(4,4-Diphenyl-1-(phenylsulfonyl)buta-2,3-dien-2-yl)diphenylphosphine oxide (**4la**):* white solids; mp 138.3−139.4 °C (56 mg, 51% yield); TLC (R_f = 0.13, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.8 Hz, 2H), 7.54 (dd, J = 12.1, 7.7 Hz, 4H), 7.47 (t, J = 7.3 Hz, 3H), 7.36−7.24 (m, 12H), 6.99 (d, J = 7.3 Hz, 4H), 4.32 (d, J = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.1 (d), 138.4, 134.0 (d, J = 6.1 Hz), 133.5, 132.2 (d, J = 2.6 Hz), 131. Six (d, J = 9.9 Hz), 131.3, 130.3, 128.9, 128.6, 128.5, 128.4 (dd, J = 14.1, 8.3 Hz), 114.8 (d, J = 13.6 Hz), 90.8 (d, J = 99.3 Hz), 53.6 (d, J = 9.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.7 (s); HRMS (ESI) ([M + Na]$^+$) calcd for $C_{34}H_{27}NaO_3PS$ 569.1316, found 569.1317; IR (film) ν 3056, 2935, 2913, 2844, 1928, 1589, 1493, 1450, 1437, 1311, 1192, 1144, 1115, 1079, 833, 724, 695 cm^{-1}.

*(4,5-Dimethyl-1-(phenylsulfonyl)hexa-2,3-dien-2-yl)diphenylphosphine oxide (**4ma**):* yellow solid; mp 96.3−96.9 °C (42 mg, 47% yield); TLC (R_f = 0.13, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 2H), 7.70−7.65 (m, 4H), 7.61 (t, J = 7.4 Hz, 1H), 7.56−7.44 (m, 8H), 4.18−4.07 (m, 2H), 2.05−1.97 (m, 1H), 1.54 (d, J = 5.9 Hz, 3H), 0.75 (d, J = 6.8 Hz, 3H), 0.68 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3 (d, J = 5.6 Hz), 139.5, 133.6, 132.0 (d, J = 2.5 Hz), 131.8 (d, J = 9.7 Hz), 131.7 (d, J = 9.7 Hz), 129.1, 128.3 (t, J = 11.1 Hz), 128.2, 110.8 (d, J = 13.0 Hz), 86.9 (d, J = 107.2 Hz), 53.6 (d, J = 10.9 Hz), 31.9 (d, J = 4.7 Hz), 20.4 (d, J = 2.0 Hz), 20.3 (d, J = 2.8 Hz), 15.1 (d, J = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.7 (s); HRMS (ESI) ([M + H] $^+$) calcd for $C_{26}H_{28}O_3PS$ 451.1497, found 451.1488; IR (film) ν 3056, 2953, 2922, 2851, 1941, 1588, 1484, 1447, 1437, 1308, 1180, 1139, 1117, 857, 720, 692 cm^{-1}.

*(4-Cyclohexyl-1-(phenylsulfonyl)penta-2,3-dien-2-yl)diphenylphosphine oxide (**4na**):* yellow liquid (30 mg, 31% yield); TLC (R_f = 0.14, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 2H), 7.71−7.59 (m, 5H), 7.56−7.41 (m, 8H), 4.14 (qd, J = 14.9, 8.8 Hz, 2H), 1.89 (s, 1H), 1.65−1.59 (m, 3H), 1.55 (d, J = 5.9 Hz, 3H), 1.38 (d, J = 12.3 Hz, 2H), 1.16−1.06 (m, 2H), 1.03−0.95 (m, 1H), 0.85−0.75 (m, 1H), 0.58−0.48 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.8 (d, J = 5.8 Hz), 139.5, 132.7 (d, J = 180.7 Hz), 132.0 (d, J = 2.8 Hz), 131.9, 131.7 (d, J = 9.7 Hz), 129.0, 128.3 (dd, J = 15.5, 12.3 Hz), 128.2, 110.2 (d, J = 13.2 Hz), 86.8 (d, J = 107.2 Hz), 53.7 (d, J = 11.1 Hz), 41.4 (d, J = 4.6 Hz), 30.6 (d, J = 1.8 Hz), 30.5 (d, J = 2.8 Hz), 26.2 (d, J = 2.5 Hz), 25.9, 15.4 (d, J = 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{29}H_{32}O_3PS$ 491.1810, found 491.1799; IR (film) ν 3058, 2925, 2851, 1943, 1588, 1482, 1447, 1437, 1309, 1185, 1140, 1118, 1085, 910, 725, 690 cm^{-1}.

*(1-(3,4-Dihydronaphthalen-1(2H)-ylidene)-3-(phenylsulfonyl)-prop-1-en-2-yl)diphenylphosphine oxide (**4oa**):* yellow solids; mp 124.3−125.7 °C (51 mg, 50% yield); TLC (R_f = 0.13, PET/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 2H), 7.71 (dd, J = 12.1, 7.7 Hz, 2H), 7.63 (dd, J = 12.1, 7.7 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.52−7.32 (m, 8H), 7.22 (d, J = 7.5 Hz, 1H), 7.16−7.08 (m, 2H), 7.04 (d, J = 7.3 Hz, 1H), 4.30 (d, J = 8.8 Hz, 2H), 2.72−2.64 (m, 1H), 2.60−2.53 (m, 1H), 2.49−2.41 (m, 1H), 2.09−2.01 (m, 1H), 1.75−1.66 (m, 1H), 1.38−1.30 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.3 (d, J = 4.1 Hz), 139.1, 136.9, 132.9 (d, J = 160.8 Hz), 131.63, 131.63 (d, J = 19.3 Hz), 130.9 (d, J = 53.7 Hz), 129.2, 129.1, 128.4 (dd, J = 12.4, 4.3 Hz), 128.2, 128.1 (d, J = 6.6 Hz), 128.0, 126.2, 107.2 (d, J = 13.5 Hz), 90.6 (d, J = 103.3 Hz), 53.5 (d, J = 10.2 Hz), 29.4, 27.4 (d, J = 5.1 Hz), 22.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.0 (s); HRMS (ESI) ([M + H]$^+$) calcd for $C_{31}H_{28}O_3PS$ 511.1497, found 511.1484; IR (film) ν 3057, 2923, 2849, 1927, 1588, 1489, 1446, 1436, 1308, 1180, 1140, 1118, 1084, 910, 857, 722, 690 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00813.

Compound characterization data, ORTEP/crystallographic data for **3aa**, and ^{1}H, ^{13}C, ^{31}P NMR and HR-MS spectra for all new compounds (PDF)

X-ray data for compound **3aa** (CIF)

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Notes

The authors declare no competing financial interest.

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(16) Substrates with 2,6-dimethyl substitution were chosen for its solid state and operationally simplicity; see details in our previous study (ref 6a).

(17) CCDC 1538139 (**3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(18) The possibility of radical mechanism was ruled out by employing TEMPO as a radical scavenger or AIBN as a radical accelerator.

(19) The pK_a values of benzenesulfinic acid and acetic acid in DMSO are 7.1 and 12.3, respectively. See also: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463.

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