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Note

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Synthesis of Organophosphorus Compounds through Copper-Catalyzed Annulation Involving C−O and C−P Bond Formation

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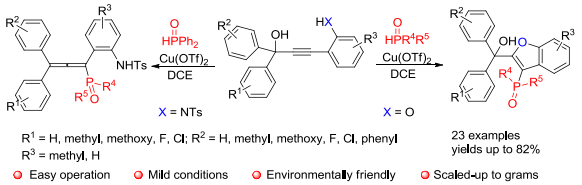


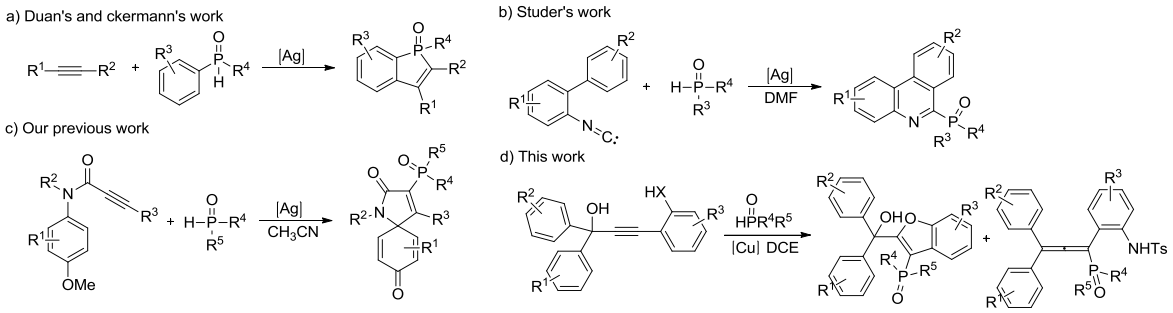
ABSTRACT:

A novel Copper (II) trifluoromethanesulfonate-catalyzed, high-efficiency, and atom-economical synthesis of valuable organophosphorus compounds via cascade annulation of propargylic alcohols with diphenylphosphine oxide is described. This protocol, which has good functional-group compatibility and insensitivity to an ambient atmosphere, provides a simple and direct pathway to the products organophosphorus compounds in good yields under mild conditions. The method could be efficiently scaled up to gram scale, thus highlighting a potential application of this methodology.

Organophosphorus compounds, as an important class of organic products, have received considerable attention from the synthetic community because they have broad applications in the field of material science,[1] medicinal chemistry,[2] organic synthesis,[3] natural products,[4] and ligand chemistry.[5] In light of their importance, the construction of C(sp^2)−P bond is one of the most important and fundamental reactions to synthesize the organophosphorus compounds. The classical synthetic strategies for the formation of C−P bond rely on the transition-metal catalyzed cross-coupling reactions and reactions of phosphines reagents with an electrophilic C(sp^2)-(pseudo)halides.[6] An Ag-mediated C−H/P−H functionalization method to construct benzo[*b*]-phosphole oxides by employing arylphosphine oxides and internal alkynes as the

substrates was disclosed by the Duan group and Ackermann group independently. (Scheme 1a).[7] In the meantime, Studer and coworkers reported a novel protocol for the synthesis of 6-phosphorylated phenanthridines starting from readily available 2-isocyanobiphenyls and the commercially available diphenylphosphine oxides (Scheme 1b).[8] Recently, our group also developed an Ag-catalyzed cascade difunctionalization of *N*-(p-methoxyaryl)-propiolamides with diphenylphosphine oxides to regiospecifically generate a large amount of phosphorylated azadecenones (Scheme 1c).[9] In spite of much attention have been paid toward the C−P bond construction and various utilized routes have been investigated and established, the development of new reliable synthetic strategy for the formation of C−P bond from easy preparation starting materials is still attractive yet challenging task.

Scheme 1. Summary of previous studies and our new anticipation toward organophosphorus compounds



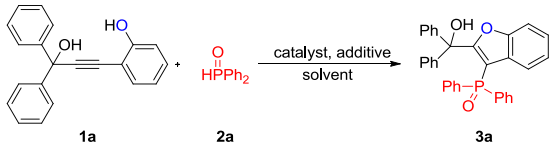
Recently, the rapid development of transition-metal-catalyzed cascade cycloaddition of propargylic alcohols with various nucleophiles or electrophiles provides a new and powerful synthetic strategy to synthesize meritorious heterocycles, carbocycles, and bridged rings. Propargylic alcohols, due to its high reactivity and lower cost, have extensively been used as organic synthons for the construction of different compounds such as indoles,[10] indenes,[11] furans,[12] pyridines,[13] azoles,[14] and azepines.[15] Stimulated by these fascinating research and our continuing interest on the transformation of propargylic alcohols, we herein report a facile copper-catalyzed cycloaddition of propargylic alcohols with diphenylphosphine oxides, which

enables atom-economy and environmental sustainability synthesis of organophosphorus compounds under base-free, ligand-free conditions (Scheme 1d).

Initially, our investigation focused on the reaction of alkynol substrate **1a** with diphenylphosphine oxide **2a** to optimize the reaction conditions. To our delight, in the presence of 20 mol % of $Y(OTf)_3$ as catalyst in toluene at 60 °C for 6 h under an air atmosphere, the expected product **3a** was obtained in a yield of 37% (Table 1, entry 1). The structure of product **3a** was further confirmed by NMR spectroscopy and X-ray crystal diffraction analysis (see the Supporting Information). Subsequently, examination of several catalysts indicated that $Cu(OTf)_2$ was optimal, which furnished 42% yield of the product (entries 2−5). A subsequent survey on the effect of temperature indicated that 90°C was the most favored temperature for this transformation (entries 6−8). To advance the process further, we further optimized the cascade reaction by adding additives. The desired product was obtained in 78% yield in the presence of 50 mol % of Ag_2CO_3 (entries 9−11). The loading of catalyst was investigated, yet, decreasing the amount of $Cu(OTf)_2$ to 15 mol % slightly reduced the yield to 71% (entries 12−13). Other solvents such as CH_3CN, DCE, CH_3NO_2, and THF were further evaluated, indicating that DCE was the optimal choice for this transformation and could increase the product yield up to 75% (entries 14−17). Ultimately, the optimal conditions for the generation of **3a** were settled as **1a** (1.2 equiv.), diphenylphosphine oxide **2a** (0.1 mmol) in the presence of $Cu(OTf)_2$ (15 mol %) and Ag_2CO_3 (0.5 equiv.) in DCE (2.0 mL) at 90°C for 6 h.

With the optimized conditions established, the substrate scope of this transformation of diphenylphosphine oxides **2** with various propargylic alcohols **1** was then investigated. As shown in Scheme 2, a variety of alkynols bearing electron-rich groups (Me, OMe, **3a−3e**) and electron-deficient groups (F, Cl, Ph, **3f−3i**) at any position of the aryl ring (R^1 or R^2) were compatible with the cascade annulation reaction, giving the corresponding products **3a−3i** with yields ranging from 32% to 78%. It is worth noting that halo-substituted organophosphorus

Table 1. Optimization of the reaction conditions of **1a** with diphenylphosphine oxide [a, b]



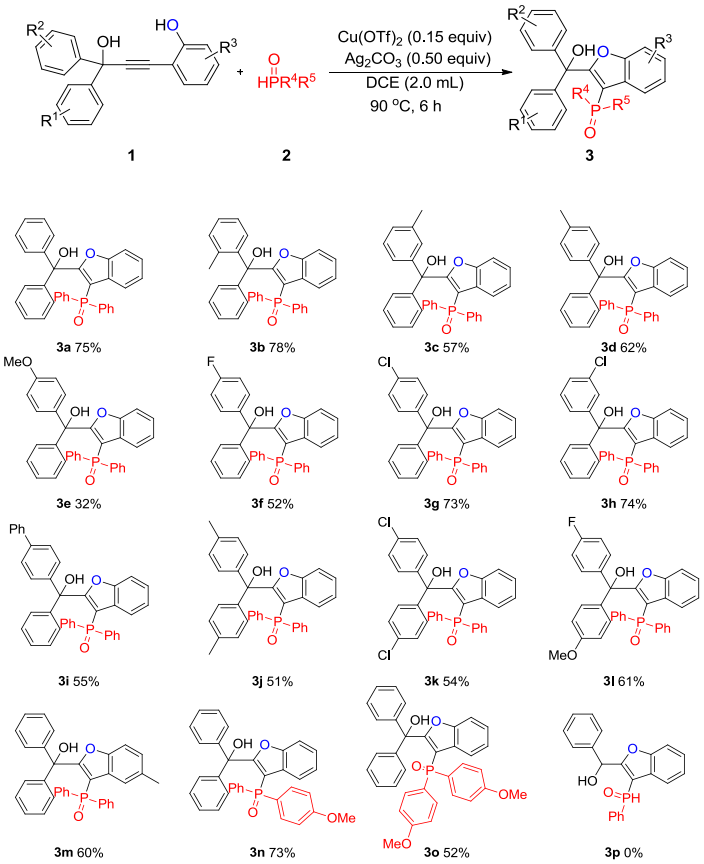
1a 2a 3a

entry	catalyst (mol %)	additive (50 mol %)	solvent	temp (℃)	yield (%)[b]
1	$Y(OTf)_3$ (20)	/	$PhCH_3$	60	37
2	$Yb(OTf)_3$ (20)	/	$PhCH_3$	60	22
3	$Bi(OTf)_3$ (20)	/	$PhCH_3$	60	29
4	$Zn(OTf)_2$ (20)	/	$PhCH_3$	60	34
5	$Cu(OTf)_2$ (20)	/	$PhCH_3$	60	42
6	$Cu(OTf)_2$ (20)	/	$PhCH_3$	80	45
7	$Cu(OTf)_2$ (20)	/	$PhCH_3$	90	61
8	$Cu(OTf)_2$ (20)	/	$PhCH_3$	100	52
9	$Cu(OTf)_2$ (20)	AgOAc	$PhCH_3$	90	65
10	$Cu(OTf)_2$ (20)	Ag_2CO_3	$PhCH_3$	90	78
11	$Cu(OTf)_2$ (20)	CF_3COOAg	$PhCH_3$	90	28
12	$Cu(OTf)_2$ (10)	Ag_2CO_3	$PhCH_3$	90	61
13	$Cu(OTf)_2$ (15)	Ag_2CO_3	$PhCH_3$	90	71
14	$Cu(OTf)_2$ (15)	Ag_2CO_3	CH_3CN	90	52
15	**$Cu(OTf)_2$ (15)**	**Ag_2CO_3**	**DCE**	**90**	**75**
16	$Cu(OTf)_2$ (15)	Ag_2CO_3	CH_3NO_2	90	16
17	$Cu(OTf)_2$ (15)	Ag_2CO_3	THF	90	43

[a]Unless otherwise noted, all reactions were performed with **1a** (1.2 equiv.) and diphenylphosphine oxide **2a** (0.1 mmol) in solvent (2.0 mL) for 6 h. [b]Yields are given for isolated products.

compounds could be further utilized for C−C or C−N bond formation (**3f**−**3h**). Symmetrical propargylic alcohols **1j** and **1k** were tested, and they proceeded smoothly in the annulation to furnish the corresponding products **3j** and **3k** in 51 and 54% yields, illustrating that the electronic effect of substituents on the phenyls (R^1 and R^2) is not evident for this transformation. Indeed, propargylic alcohol **1l** with two different substituents methoxy group and F also efficiently furnish the expected product **3l** in 61% yield. Next, we sought to investigate the scope with respect to the diphenylphosphine oxide **2**, H-phosphine oxides such as **2n** and **2o** were suitable substrates for this transformation, and the corresponding products **3n** and **3o** were obtained in 73% and 52% yields, respectively. Unfortunately, secondary propargylic alcohol 2-(3-hydroxy-3-phenylprop-1-yn-1-yl)phenol **1p** was not compatible with

Scheme 2 Transformation of propargylic alcohols to benzofuran-3-yldiphenylphosphine oxides *a*, *b*

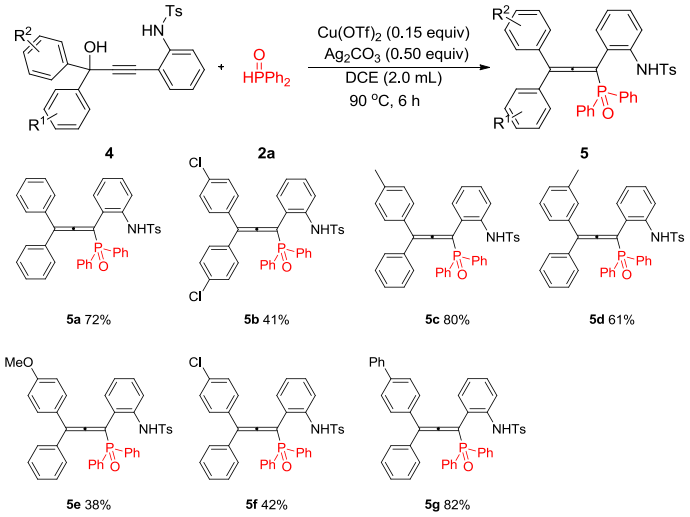


[a]Unless otherwise noted, all reactions were performed with **1** (1.2 equiv.) and **2** (0.1 mmol) in the presence of $Cu(OTf)_2$ (15 mol %), Ag_2CO_3 (0.5 equiv.) in DCE (2.0 mL) at 90 °C for 6 h. [b]Yields are given for isolated products.

the reaction under the standard conditions due to the fact that only a aryl group is difficult to stabilize the intermediate **A** generated by the substrate alkynol **1** (see Scheme 5).

To extend the applicability of this reaction, we sought to investigate the scope of various substituted 3-(2-aminophenyl)-1,1-diphenylprop-2-yn-1-ols **4** with diphenylphosphine oxide **2a** (Scheme 3). Symmetrical propargylic alcohols **4a** and **4b** reacted with diphenylphosphine oxide smoothly with moderate to good yields. For the unsymmetrical substituted propargylic alcohols containing either electron-donating (Me, OMe, **4c−4e**) or electron-withdrawing groups (Cl, Ph, **4f−4g**), the reactions proceeded smoothly to provide the desired products in 38−82% yields.

Scheme 3. Transformation of propargylic alcohols to diphenyl(propa-1,2-dien-1-yl)phosphine oxides [a, b]

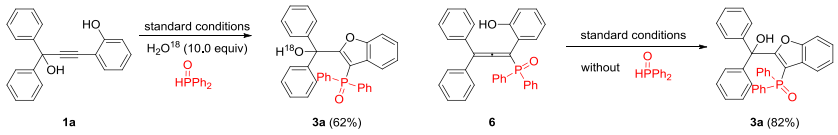


[a]Unless otherwise noted, all reactions were performed with **4** (1.2 equiv.) and **2a** (0.1 mmol) in the presence of $Cu(OTf)_2$ (15 mol %), Ag_2CO_3 (0.5 equiv.) in DCE (2.0 mL) at 90 °C for 6 h. [b]Yields are given for isolated products.

A noteworthy advantage of the cascade annulation reaction was that this transformation could be efficiently scaled up to gram under the optimal conditions, thus highlighting a potential application of this methodology in synthetic industry

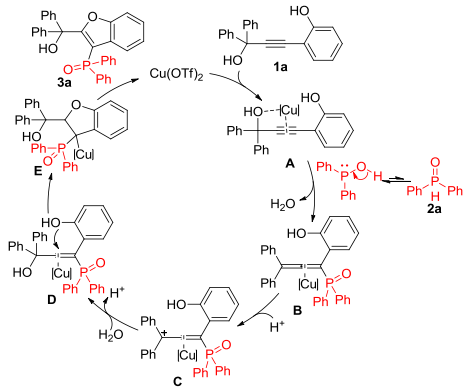
To gain insight into the novel transformation, additional mechanistic studies have been conducted (Scheme 4). When 10.0 equivalent $H_2{}^{18}O$ was added into the reactions under the standard conditions, the corresponding product **3a** containing ^{18}O was obtained in 62% yield, thus indicating that the hydroxy of the desired product **3a** is from the substrate propargylic alcohol **1a**. Furthermore, when the compound **6** (see the Supporting Information) was investigated under the optimal conditions without diphenylphosphine oxide, the expected product **3a** was obtained in 82% yield, this result suggested that the compound **6** was the intermediate in this novel transformation.

Scheme 4. Verification experiments for the mechanism



On the basis of previously published literature and the above experimental results,[16-17] a plausible mechanism is depicted in Scheme 5. Initially, the coordination of Lewis acid $Cu(OTf)_2$ to the propargyl alcohol **1a** led to intermediate **A**, which could undergo a subsequent intermolecular attack of the Ph_2OP anion to produce the stabilized allenic intermediate **B**. The protonation of intermediate **B** affords intermediate **C**. Subsequent nucleophilic attack of H_2O onto the intermediate **C** forms intermediate **D**. Then, the intramolecular nucleophilic addition of intermediate **D** to the carbenium ion site produces intermediate **E**. Finally, the desired product **3a** is afforded with release of a proton and the regenerated catalyst.

Scheme 5. Proposed mechanism for the formation of organophosphorus compounds.



CONCLUSIONS

In summary, a novel Copper (II) trifluoromethanesulfonate-catalyzed cascade cycloaddition of propargylic alcohols with substituted diphenylphosphine oxides has been developed, furnishing the benzofuran-3-yldiphenylphosphine oxides and diphenyl(propa-1,2-dien-1-yl)phosphine oxides with good yields in a simple, high-efficiency way. This protocol demonstrates a facile and atom-economical access to the organophosphorus compound derivatives, which acts as an important skeleton in a number of natural products and bioactive molecules. The good functional group tolerance and operational simplicity of our developed reaction system are to be ranked among the most versatile and efficient alternatives for the synthesis of organophosphorus compound scaffolds.

EXPERIMENTAL SECTION

General Remarks: Column chromatography was carried out on silica gel. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$. ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), q (quartet) or m (multiplet). Copies of their ^{1}H NMR and ^{13}C NMR spectra are provided in the Supporting Information. High-resolution mass spectra were measured on Orbitrap Elite with electrospray ionization mode (ESI^{+}). Solvents were dried under standard method. Commercially available reagents were used with further purification. DCE was distilled immediately before use from CaH.

General procedure for the synthesis of (2-(hydroxydiphenylmethyl)benzofuran-3-yl)diphenylphosphine oxide (3a)

The reaction of propargylic alcohol **1a** (1.2 equiv.), diphenylphosphine oxide **2a** (0.1 mmol), $Cu(OTf)_2$ (15 mol %) and Ag_2CO_3 (0.5 equiv.) in DCE (2.0 mL) was conducted at 90 °C under an air atmosphere. The reaction was completed within 6.0 h by TLC monitoring. The resulting mixture was cooled down to room temperature and then diluted with ethyl acetate (2 × 10 mL), washed with a saturated aqueous solution of brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was further purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5:1) to afford 37.5 mg of **3a**.

General procedure for the synthesis of (1-(2-hydroxyphenyl)-3,3-diphenylpropa-1,2-dien-1-yl)diphenylphosphine oxide (6)

The reaction of propargylic alcohol **1a** (0.1 mmol), diphenylphosphine oxide **2a** (2.0 equiv.), $Cu(OTf)_2$ (15 mol %) and in THF (2.0 mL) was conducted at 40 °C under an air atmosphere. The reaction was completed within 2.0 h by TLC monitoring. The resulting mixture was cooled down to room temperature and then diluted with ethyl acetate (2 × 10 mL), washed with a saturated aqueous solution of brine, dried over Na_2SO_4, and evaporated under reduced

pressure. The residue was further purified by chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford 35.1 mg of **6** (72.5%).

General procedure for the synthesis of 1[18]

Ethynylmagnesium bromide (0.5 mol/L in THF, 24 mL, 1.2 equiv) was added dropwise into a stirred solution of benzophenone (10 mmol, 1.82 g) in THF (35 mL) under argon. The mixture was allowed to stir for 4h at room temperature. After the completion of the reaction determined by TLC, the reaction mixture was quenched by addition of an aqueous saturated solution of NH_4Cl (35 mL) and extracted with ethyl acetate (2×50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting material 1,1-diphenylprop-2-yn-1-ol was directly used for the next step without further purification.

$Pd(PPh_3)_2Cl_2$ (56.1 mg, 0.08 mmol, 1 mol %) and CuI (30.6 mg, 0.16mmol, 2 mol %) were sequentially added to a stirred solution of 1,1-diphenylprop-2-yn-1-ol (8 mmol, 1.67 g) in triethylamine (30 mL) under argon at room temperature. The mixture was allowed to stir for 10 min. Then tert-butyl(2-iodophenoxy)dimethylsilane (3.48 g, 10.4 mmol, 1.3 equiv) was added. The mixture was allowed to stir overnight. The resulting mixture was poured into an aqueous saturated solution of NH_4Cl (30 mL) and the product was extracted with ethyl acetate (2×40 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 10:1) to give 3-(2-((tert-butyldimethylsilyl)oxy) phenyl)-1,1-diphenylprop-2-yn-1-ol.

Tetrabutylammonium fluoride (1.57 g, 6 mmol, 1.2 equiv) was added to a stirred solution of 3-(2-((tert-butyldimethylsilyl)oxy)phenyl)-1,1-diphenylprop-2-yn-1-ol (2.07 g, 5 mmol) in THF (25 mL) at room temperature for 30 min. After the completion of the reaction determined by TLC, the reaction mixture was quenched by addition of water (10 mL) and extracted with ethyl acetate (2×30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4,

and concentrated under reduced pressure. The crude material was purified by column chromatography (silica gel, petroleum ether/ethyl acetate/dichloromethane, 10:1:1) to give the pure product 2-(3-hydroxy-3,3-diphenylprop-1-yn-1-yl)phenol **1a**.

General procedure for the synthesis of 4[18]

$Pd(PPh_3)_2Cl_2$ (56.1 mg, 0.08 mmol, 1 mol %) and CuI (30.6 mg, 0.16 mmol, 2 mol %) were sequentially added to a stirred solution of 1,1-diphenylprop-2-yn-1-ol (8 mmol, 1.67 g) in triethylamine (30 mL) under argon at room temperature. The mixture was allowed to stir for 10 min. Then 2-iodoaniline (2.1 g, 9.6 mmol, 1.2 equiv) was added. The mixture was allowed to stir overnight. The resulting mixture was poured into an aqueous saturated solution of NH_4Cl (35 mL) and the product was extracted with ethyl acetate (2×50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate/triethylamine, 100:10:1) to give 3-(2-aminophenyl)-1,1-diphenylprop-2-yn-1-ol.

TsCl (1.24 g, 6.5 mmol, 1.3 equiv) was added portion-wise to a solution of 3-(2-aminophenyl)-1,1-diphenylprop-2-yn-1-ol 3-(2-aminophenyl)-1,1-diphenylprop-2-yn-1-ol (1.5 g, 5 mmol) in CH_2Cl_2 (25 mL) and pyridine (1.6 mL, 20 mmol, 4.0 equiv) under 0 °C. The mixture was then warmed to room temperature and allowed to stir for 4 h. After the completion of the reaction determined by TLC, the mixture was concentrated in vacuo, and the residue was extracted with ethyl acetate (2×30 mL). The combined organic layers were washed with HCl (aq, 5%, 20 mL) and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate/triethylamine, 100:5:1) to give N-(2-(3-hydroxy-3,3-diphenylprop-1-yn-1-yl)phenyl)-4-methylbenzenesul fonamide **4a**.

Characterization data of 3a–6

(2-(hydroxydiphenylmethyl)benzofuran-3-yl)diphenylphosphine oxide (3a):

The resultant residue was purified by flash silica gel column chromatography to afford **3a** as a yellow solid (37.5 mg, 75%); m.p. 146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.71 (s, 1H), 7.57–7.52 (m, 6H), 7.42–7.37 (m, 5H), 7.32–7.30 (m, 4H), 7.24–7.21 (m, 7H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 172.7, 172.5, 153.5, 153.3, 144.9, 132.4, 132.4, 131.9, 131.8, 131.7, 130.8, 128.7, 128.6, 128.5, 128.3, 127.7, 127.6, 127.3, 124.7, 123.7, 121.0, 112.0, 106.9, 105.8, 79.2. IR (KBr) 3060, 2926, 1667, 1597, 1488, 1444, 1267, 1241, 1168, 1122, 910, 870, 751, 698cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{25}O_3PNa$ 523.1434; found 523.1432.

(2-(hydroxy(phenyl)(o-tolyl)methyl)benzofuran-3-yl)diphenylphosphine oxide (3b):

The resultant residue was purified by flash silica gel column chromatography to afford **3b** as a yellow liquid (40.2 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$): 8.64 (s, 1H), 7.69–7.64 (m, 2H), 7.59–7.55 (m, 1H), 7.47–7.44 (m, 3H), 7.42–7.41 (m, 2H), 7.39–7.37 (m, 3H), 7.35–7.32 (m, 2H), 7.26–7.23 (m, 4H), 7.20–7.18 (m, 1H), 7.16–7.11 (m, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.97–6.93 (m, 1H), 6.67–6.61 (m, 2H), 2.15 (s, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 173.2, 173.1, 153.3, 153.2, 144.7, 142.7, 138.5, 132.5, 132.5, 132.3, 132.2, 132.0, 131.8, 131.7, 131.6, 131.5, 130.7, 128.8, 128.7, 128.6, 128.5, 128.5, 128.3, 127.8, 127.3, 127.3, 124.7, 124.7, 123.7, 121.0, 112.0, 106.4, 105.2, 80.1, 21.0. IR (KBr) 3061, 1596, 1525, 1442, 1267, 1244, 1168, 1121, 1062, 872, 746, 698, 653 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{27}O_3PNa$ 537.1590; found 537.1586.

(2-(hydroxy(phenyl)(m-tolyl)methyl)benzofuran-3-yl)diphenylphosphine oxide (3c):

The resultant residue was purified by flash silica gel column chromatography to afford **3c** as a yellow solid (29.3 mg, 57%); m.p. 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.67 (s, 1H), 7.57 (s, 1H), 7.55–7.52 (m, 5H), 7.41–7.37 (m, 5H), 7.33–7.30 (m, 2H), 7.24–7.20 (m, 4H), 7.14 (s, 1H), 7.12–7.08 (m, 1H), 7.06–6.98 (m, 3H), 6.57 (d, *J* = 8.0 Hz, 1H), 2.21 (s, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 172.8, 172.7, 153.5, 153.3, 144.9, 137.2, 132.4, 132.3, 132.3, 132.0, 131.9, 131.8, 131.7, 131.7, 131.6, 130.9, 130.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.1, 128.1,

127.6, 127.5, 127.3, 124.8, 124.6, 123.7, 121.0, 112.0, 106.8, 105.7, 79.2, 21.5. IR (KBr) 3397, 2922, 1740, 1605, 1518, 1446, 1263, 1130, 1075, 1026, 750, 699cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{34}H_{28}O_3P$ 515.1771; found 515.1771.

(2-(hydroxy(phenyl)(p-tolyl)methyl)benzofuran-3-yl)diphenylphosphine oxide (3d):

The resultant residue was purified by flash silica gel column chromatography to afford **3d** as a yellow solid (31.9 mg, 62%); m.p. 146-148 °C;^{1}H NMR (400 MHz, $CDCl_3$): 8.63 (s, 1H), 7.56–7.51 (m, 6H), 7.40–7.36 (m, 5H), 7.33–7.31 (m, 2H), 7.23–7.19 (m, 5H), 7.17 (s, 1H), 7.01–6.97 (m, 3H), 6.55 (d, *J* = 8.0 Hz, 1H), 2.30 (s, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 172.9, 172.8, 153.4, 153.3, 145.0, 142.1, 136.9, 132.4, 132.3, 132.3, 132.2, 132.1, 131.9, 131.8, 131.7, 130.9, 130.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 127.6, 127.6, 127.5, 127.3, 124.6, 123.7, 121.0, 112.0, 106.8, 105.7, 79.1, 21.0. IR (KBr) 3059, 2922, 1731, 1647, 1606, 1513, 1442, 1265, 1241, 1169, 1125, 1071, 750, 697cm^{-1}. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{34}H_{27}O_3PNa$ 537.1590; found 537.1588.

(2-(hydroxy(4-methoxyphenyl)(phenyl)methyl)benzofuran-3-yl)diphenylphosphine oxide (3e):

The resultant residue was purified by flash silica gel column chromatography to afford **3e** as a yellow solid (17.2 mg, 32%); m.p. 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.61 (s, 1H), 7.58–7.51 (m, 6H), 7.43–7.37 (m, 5H), 7.32–7.29 (m, 2H), 7.23–7.19 (m, 6H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 173.0, 172.9, 158.8, 153.5, 153.3, 145.1, 137.3, 132.4, 132.0, 132.0, 131.8, 131.8, 131.7, 130.9, 130.9, 128.8, 128.7, 128.7, 128.6, 128.4, 127.6, 127.6, 127.3, 124.6, 123.7, 121.0, 113.0, 112.0, 106.8, 105.7, 78.9, 55.2. IR (KBr) 3123, 2924, 1607, 1510, 1441, 1302, 1249, 1170, 1122, 1065, 912, 750, 698cm^{-1}. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{34}H_{27}O_4PNa$ 553.1539; found 553.1538.

(2-((4-fluorophenyl)(hydroxy)(phenyl)methyl)benzofuran-3-yl)diphenylphosphine oxide (3f):

The resultant residue was purified by flash silica gel column chromatography to afford **3f** as a yellow solid (26.8 mg, 52%); m.p. 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.75 (s, 1H), 7.59–7.50 (m, 6H), 7.44–7.36 (m, 5H), 7.30–7.26 (m, 4H), 7.24–7.20 (m, 4H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 1H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 172.4, 172.2, 163.3, 160.8, 153.4, 153.3, 144.7, 140.7, 140.7, 132.5, 132.5, 132.4, 131.8, 131.7, 131.7, 131.6, 131.6, 130.7, 130.6, 129.4, 129.3, 128.7, 128.7, 128.6, 128.6, 128.4, 128.3, 127.7, 127.5, 127.4, 124.8, 123.8, 121.0, 114.5, 114.3, 111.9, 107.1, 105.9, 78.8. IR (KBr) 3397, 2922, 2852, 1733, 1601, 1506, 1442, 1227, 1161, 1127, 1074, 751, 697, 553cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{25}FO_3P$ 519.1520; found 519.1517.

(2-((4-chlorophenyl)(hydroxy)(phenyl)methyl)benzofuran-3-yl)diphenylphosphine oxide (3g):

The resultant residue was purified by flash silica gel column chromatography to afford **3e** as a yellow solid (38.7 mg, 73%); m.p. 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.77 (s, 1H), 7.58–7.50 (m, 6H), 7.43–7.37 (m, 5H), 7.30–7.28 (m, 2H), 7.25–7.21 (m, 6H), 7.15–7.13 (m, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 172.1, 172.0, 153.4, 153.3, 144.4, 143.5, 133.2, 132.5, 132.5, 132.4, 131.8, 131.7, 131.7, 131.6, 131.5, 130.7, 130.5, 129.0, 128.7, 128.6, 128.4, 128.3, 127.7, 127.7, 127.5, 127.4, 124.8, 123.9, 121.0, 112.0, 107.2, 106.1, 78.7. IR (KBr) 3061, 2924, 1525, 1487, 1441, 1267, 1245, 1168, 1121, 1015, 752, 698, 657, 553cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{24}ClO_3PNa$ 557.1044; found 557.1048.

(2-((3-chlorophenyl)(hydroxy)(phenyl)methyl)benzofuran-3-yl)diphenylphosphine oxide (3h):

The resultant residue was purified by flash silica gel column chromatography to afford **3h** as a yellow solid (39.5 mg, 74%); m.p. 86-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.81 (s, 1H), 7.60–7.49 (m, 6H), 7.44–7.39 (m, 5H), 7.33–7.32 (m, 1H), 7.30–7.28 (m, 2H), 7.24–7.18 (m, 6H), 7.16–7.14 (m, 1H), 7.04–7.00 (m, 1H), 6.58 (d, *J* = 8.0 Hz, 1H). ^{13}C{H} NMR (100 MHz, $CDCl_3$):

δ 171.8, 171.6, 153.4, 153.3, 146.9, 144.3, 133.7, 132.6, 132.5, 132.5, 132.4, 131.7, 131.7, 131.6, 131.6, 128.9, 128.8, 128.7, 128.7, 128.6, 127.8, 127.6, 127.6, 127.4, 126.0, 124.9, 123.9, 121.0, 112.0, 107.3, 106.1, 78.8. IR (KBr) 3063, 1592, 1526, 1471, 1441, 1267, 1245, 1167, 1121, 1062, 871, 750, 698, 653cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{25}ClO_3P$ 535.1224; found 535.1222.

(2-([1,1'-biphenyl]-4-yl(hydroxy)(phenyl)methyl)benzofuran-3-yl)diphenylphosphine oxide (3i):

The resultant residue was purified by flash silica gel column chromatography to afford **3i** as a yellow solid (31.7 mg, 55%); m.p. 46-48 °C ^{1}H NMR (400 MHz, $CDCl_3$): 8.75 (s, 1H), 7.58–7.52 (m, 7H), 7.51–7.48 (m, 1H), 7.44–7.40 (m, 7H), 7.38–7.32 (m, 7H), 7.25–7.22 (m, 4H), 7.03–6.99 (m, 1H), 6.58 (d, *J* = 8.0 Hz, 1H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 172.7, 172.5, 153.4, 144.7, 144.1, 140.9, 140.0, 132.4, 132.4, 132.3, 132.3, 131.8, 131.7, 131.7, 131.6, 128.7, 128.7, 128.6, 128.5, 128.5, 128.0, 127.7, 127.6, 127.4, 127.2, 127.1, 126.4, 124.7, 123.8, 121.0, 112.0, 107.0, 105.9, 79.1. IR (KBr) 3060, 2852, 1597, 1524, 1486, 1442, 1266, 1167, 1121, 1064, 750, 698, 650, 548cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{39}H_{29}O_3PNa$ 599.1747; found 599.1747.

(2-(hydroxydi-p-tolylmethyl)benzofuran-3-yl)diphenylphosphine oxide (3j):

The resultant residue was purified by flash silica gel column chromatography to afford **3j** as a yellow solid (26.8mg, 51%); m.p. 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.54 (s, 1H), 7.56–7.51 (m, 6H), 7.42–7.36 (m, 5H), 7.22–7.17 (m, 5H), 7.01–6.97 (m, 5H), 6.52 (d, *J* = 8.0 Hz, 1H), 2.30 (s, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 173.2, 173.1, 153.4, 153.3, 142.1, 136.8, 132.2, 132.2, 132.1, 131.8, 131.7, 131.0, 129.0, 128.6, 128.5, 128.3, 127.5, 124.5, 123.6, 120.9, 112.0, 106.8, 105.6, 79.0, 21.1. IR (KBr) 3135, 2857, 1587, 1514, 1440, 1245, 1170, 1121, 1071, 698, 650, 580, 553cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{35}H_{30}O_3P$ 529.1927; found 529.1927.

(2-(bis(4-chlorophenyl)(hydroxy)methyl)benzofuran-3-yl)diphenylphosphine oxide (3k):

The resultant residue was purified by flash silica gel column chromatography to afford **3k** as a yellow solid (31.0 mg, 54%); m.p. 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.80 (s, 1H), 7.59–7.54 (m, 3H), 7.53–7.51 (m, 2H), 7.49 (s, 1H), 7.44–7.39 (m, 5H), 7.25 (s, 1H), 7.22–7.20 (m, 4H), 7.16–7.14 (m, 4H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 171.6, 171.4, 153.3, 153.2, 143.0, 133.5, 132.6, 132.5, 131.7, 131.6, 131.5, 130.4, 128.9, 128.8, 128.7, 128.4, 128.2, 127.9, 125.0, 124.0, 121.0, 112.0, 107.6, 106.4, 78.3. IR (KBr) 3080, 2924, 1525, 1488, 1439, 1267, 1245, 1167, 1121, 1095, 828, 751, 579cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{24}Cl_2O_3P$ 569.0835; found 569.0833.

(2-((4-fluorophenyl)(hydroxy)(4-methoxyphenyl)methyl)benzofuran-3-yl)diphenylphosphine oxide (3l):

The resultant residue was purified by flash silica gel column chromatography to afford **3l** as a yellow solid (33.4 mg, 61%); m.p. 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.65 (s, 1H), 7.58–7.51 (m, 6H), 7.44–7.38 (m, 5H), 7.28–7.27 (m, 1H), 7.25–7.24 (m, 1H), 7.23–7.20 (m, 1H), 7.19–7.17 (m, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 172.7, 172.6, 163.3, 160.9, 158.9, 153.4, 153.3, 140.9, 137.1, 132.5, 132.4, 132.4, 132.4, 131.9, 131.8, 131.7, 131.7, 131.6, 130.8, 129.4, 129.3, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 124.8, 123.8, 121.0, 114.5, 114.3, 113.1, 112.0, 107.0, 105.8, 78.5, 55.2. IR (KBr) 3438, 2925, 1607, 1507, 1439, 1249, 1166, 1121, 1069, 833, 751, 698, 650, 581 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{26}FO_4PNa$ 571.1445; found 571.1443.

(2-(hydroxydiphenylmethyl)-5-methylbenzofuran-3-yl)diphenylphosphine oxide (3m):

The resultant residue was purified by flash silica gel column chromatography to afford **3m** as a colourless liquid (30.9 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$): 8.63 (s, 1H), 7.69–7.63 (m, 2H), 7.60–7.56 (m, 1H), 7.48–7.45 (m, 3H), 7.43–7.42 (m, 2H), 7.39–7.36 (m, 3H), 7.35–7.33 (m, 2H), 7.26–7.24 (m, 4H), 7.16–7.13 (m, 2H), 7.03–6.99 (m, 1H), 6.97–6.93 (m, 1H), 6.67–6.65 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 2.15 (s, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 173.3, 173.1,

153.4, 153.3, 144.7, 142.7, 138.5, 132.5, 132.5, 132.3, 132.2, 132.0, 131.9, 131.8, 131.8, 131.6, 131.5, 130.7, 128.8, 128.7, 128.6, 128.5, 128.5, 127.8, 127.4, 127.3, 124.7, 124.7, 123.7, 121.0, 112.0, 106.4, 105.3, 80.1, 21.0. IR (KBr) 3061, 1595, 1442, 1267, 1244, 1168, 1121, 1062, 873, 747, 698, 653, 558 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{27}O_3PNa$ 537.1590; found 537.1591.

(2-(hydroxydiphenylmethyl)benzofuran-3-yl)(4-methoxyphenyl)(phenyl)phosphine oxide (3n):

The resultant residue was purified by flash silica gel column chromatography to afford **3n** as a yellow solid (38.9 mg, 73%); m.p. 102-104 °C; ^1H NMR (400 MHz, $CDCl_3$): 8.81 (s, 1H), 7.56–7.54 (m, 1H), 7.53–7.44 (m, 4H), 7.39–7.36 (m, 3H), 7.34–7.32 (m, 2H), 7.31–7.29 (m, 2H), 7.24–7.23 (m, 3H), 7.21–7.20 (m, 4H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.91–6.88 (m, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 172.4, 172.2, 162.8, 162.8, 153.4, 153.3, 145.0, 145.0, 133.8, 133.6, 132.3, 132.2, 132.2, 131.7, 131.6, 131.2, 128.6, 128.5, 128.5, 128.4, 127.6, 127.5, 127.3, 124.6, 123.6, 123.1, 122.0, 121.1, 114.3, 114.2, 111.9, 107.3, 106.1, 79.2, 55.3. IR (KBr) 3063, 1597, 1502, 1446, 1298, 1261, 1122, 1059, 1027, 800, 751, 699, 665 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{27}O_4PNa$ 553.1539; found 553.1538.

(2-(hydroxydiphenylmethyl)benzofuran-3-yl)bis(4-methoxyphenyl)phosphine oxide (3o):

The resultant residue was purified by flash silica gel column chromatography to afford **3o** as a yellow solid (29.1 mg, 52%); m.p. 108-110 °C; ^1H NMR (400 MHz, $CDCl_3$): 8.91 (s, 1H), 7.49–7.43 (m, 4H), 7.38–7.36 (m, 1H), 7.33–7.31 (m, 4H), 7.24–7.22 (m, 6H), 7.20–7.18 (m, 1H), 7.04–7.00 (m, 1H), 6.89–6.87 (m, 4H), 6.66 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 6H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 172.1, 171.9, 162.7, 162.7, 153.4, 153.3, 145.1, 133.7, 133.6, 128.6, 128.5, 127.6, 127.6, 127.2, 124.5, 123.6, 123.5, 122.3, 121.1, 114.2, 114.1, 111.9, 107.6, 106.5, 79.2, 55.3. IR (KBr) 3442, 2840, 1597, 1501, 1448, 1296, 1259, 1156, 1120, 1059, 1026, 802, 751, 701, 551 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{35}H_{30}O_5P$ 561.1825; found 561.1824.

N-(2-(1-(diphenylphosphoryl)-3,3-diphenylpropa-1,2-dien-1-yl)phenyl)-4-methylbenzenesulfonamide (5a):

The resultant residue was purified by flash silica gel column chromatography to afford **5a** as a colourless liquid (46.0 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$): 10.90 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.69–7.64 (m, 4H), 7.44–7.40 (m, 2H), 7.35–7.30 (m, 10H), 7.29–7.28 (m, 1H), 7.20–7.18 (m, 1H), 7.12–7.08 (m, 1H), 7.05–7.04 (m, 4H), 7.02–7.00 (m, 2H), 6.96–6.93 (m, 1H), 2.27 (s, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 212.2, 212.1, 142.8, 138.2, 137.0, 134.1, 134.0, 132.3, 132.3, 131.9, 131.8, 131.7, 131.6, 130.6, 129.5, 129.4, 129.3, 128.6, 128.5, 128.4, 128.3, 128.3, 127.3, 124.4, 121.5, 111.8, 111.6, 102.6, 101.7, 21.4. IR (KBr) 3436, 3058, 1630, 1596, 1492, 1440, 1379, 1335, 1160, 1120, 1091, 730, 697, 544 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{40}H_{32}NO_3PSNa$ 660.1733; found 660.1731.

N-(2-(3,3-bis(4-chlorophenyl)-1-(diphenylphosphoryl)propa-1,2-dien-1-yl)phenyl)-4-methylbenzenesulfonamide (5b):

The resultant residue was purified by flash silica gel column chromatography to afford **5b** as a colourless liquid (28.9 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$): 10.81 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.68–7.63 (m, 4H), 7.49–7.45 (m, 2H), 7.34–7.32 (m, 8H), 7.29–7.27 (m, 1H), 7.15–7.10 (m, 4H), 6.97–6.95 (m, 5H), 2.35 (s, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 211.6, 143.0, 138.7, 137.1, 134.5, 132.6, 132.6, 132.2, 132.2, 131.7, 131.6, 130.3, 129.6, 129.6, 129.5, 129.2, 129.0, 128.6, 128.5, 127.2, 125.3, 124.7, 122.2, 109.9, 103.6, 102.7, 21.5. IR (KBr) 3439, 2924, 1925, 1637, 1490, 1438, 1335, 1160, 1120, 1092, 732, 700, 660, 547cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{40}H_{30}Cl_2NO_3PSNa$ 728.0953; found 728.0950.

N-(2-(1-(diphenylphosphoryl)-3-phenyl-3-(p-tolyl)propa-1,2-dien-1-yl)phenyl)-4-methylbenzenesulfonamide (5c):

The resultant residue was purified by flash silica gel column chromatography to afford **5c** as a colourless liquid (52.2 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): 10.91 (s, 1H), 7.79 (d, *J* = 8.4Hz, 2H), 7.69–7.64 (m, 4H), 7.43–7.42 (m, 2H), 7.38–7.36 (m, 1H), 7.33–7.30 (m, 7H), 7.20–7.14

(m, 3H), 7.12–7.08 (m, 1H), 7.04–7.02 (m, 2H), 7.00–6.98 (m, 2H), 6.96–6.92 (m, 3H), 2.38 (s, 3H), 2.27 (s, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 212.4, 212.3, 142.8, 138.2, 137.0, 134.3, 132.3, 132.3, 131.9, 131.9, 131.7, 131.6, 131.1, 131.0, 130.7, 130.6, 129.6, 129.6, 129.3, 129.3, 128.6, 128.5, 128.4, 128.3, 128.2, 127.3, 125.2, 125.2, 124.3, 121.4, 111.7, 111.6, 102.7, 101.4, 21.4, 21.2. IR (KBr) 3437, 1924, 1633, 1492, 1440, 1335, 1160, 1093, 935, 698, 550 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{41}H_{34}NO_3PSNa$ 674.1889; found 674.1888.

N-(2-(1-(diphenylphosphoryl)-3-phenyl-3-(m-tolyl)propa-1,2-dien-1-yl)phenyl)-4-methylbenzenesulfonamide (5d):

The resultant residue was purified by flash silica gel column chromatography to afford **5d** as a colourless liquid (39.4 mg, 61%); ^1H NMR (400 MHz, $CDCl_3$): 10.85 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.71–7.64 (m, 4H), 7.44–7.43 (m, 2H), 7.36–7.30 (m, 8H), 7.23–7.17 (m, 2H), 7.15–7.08 (m, 2H), 7.07–7.05 (m, 2H), 7.01–6.99 (m, 2H), 6.96–6.93 (m, 1H), 6.84–6.82 (m, 2H), 2.34 (s, 3H), 2.28 (s, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 212.3, 212.2, 142.8, 138.3, 138.3, 137.0, 134.3, 134.2, 133.9, 133.9, 132.3, 131.8, 131.7, 131.7, 131.6, 129.3, 129.1, 128.6, 128.5, 128.3, 128.2, 127.3, 125.6, 125.5, 124.4, 121.5, 21.4, 21.4. IR (KBr) 3438, 1923, 1630, 1491, 1440, 1379, 1335, 1160, 1119, 1092, 732, 698, 545 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{41}H_{35}NO_3PS$ 652.2070; found 652.2065.

N-(2-(1-(diphenylphosphoryl)-3-(4-methoxyphenyl)-3-phenylpropa-1,2-dien-1-yl)phenyl)-4-methylbenzenesulfonamide (5e):

The resultant residue was purified by flash silica gel column chromatography to afford **5e** as a colourless liquid (25.2 mg, 38%); ^1H NMR (400 MHz, $CDCl_3$): 10.88 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.69–7.64 (m, 4H), 7.45–7.41 (m, 2H), 7.34–7.31 (m, 8H), 7.19–7.17 (m, 1H), 7.13–7.09 (m, 1H), 7.05–7.02 (m, 4H), 6.98–6.95 (m, 3H), 6.89–6.86 (m, 2H), 3.84 (s, 3H), 2.29 (s, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 212.5, 159.7, 142.8, 138.3, 137.0, 132.3, 131.9, 131.8, 131.7, 129.7, 129.7, 129.4, 128.6, 128.5, 128.5, 128.4, 128.3, 127.3, 124.4, 121.5, 114.1, 55.4, 21.5. IR (KBr) 3437, 1634, 1509, 1440, 1335, 1251, 1159, 1093, 1030, 935, 730, 698, 551cm^{-1}.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{41}H_{34}NO_4PSNa$ 690.1838; found 690.1835.

N-(2-(3-(4-chlorophenyl)-1-(diphenylphosphoryl)-3-phenylpropa-1,2-dien-1-yl)phenyl)-4-methylbenzenesulfonamide (5f):

The resultant residue was purified by flash silica gel column chromatography to afford **5f** as a colourless liquid (28.5 mg, 42%); ^1H NMR (400 MHz, $CDCl_3$): 10.86 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.69–7.64 (m, 4H), 7.46–7.43 (m, 2H), 7.38–7.36 (m, 2H), 7.33–7.29 (m, 8H), 7.16–7.12 (m, 2H), 7.09–7.07 (m, 2H), 7.05–7.03 (m, 2H), 6.98–6.95 (m, 3H), 2.31 (s, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 211.9, 211.9, 142.9, 138.5, 137.0, 134.2, 133.8, 132.5, 132.5, 131.8, 131.7, 131.7, 131.6, 131.6, 129.6, 129.6, 129.5, 129.4, 128.8, 128.8, 128.6, 128.5, 128.4, 128.4, 127.2, 124.6, 121.9, 110.8, 110.7, 103.1, 102.2, 21.5. IR (KBr) 3439, 3060, 1923, 1595, 1490, 1440, 1269, 1235, 1160, 1120, 1093, 1016, 732, 699, 660 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{40}H_{31}ClNO_3PSNa$ 694.1343; found 694.1340.

N-(2-(3-([1,1'-biphenyl]-4-yl)-1-(diphenylphosphoryl)-3-phenylpropa-1,2-dien-1-yl)phenyl)-4-methylbenzenesulfonamide (5g):

The resultant residue was purified by flash silica gel column chromatography to afford **5g** as a colourless liquid (59.2 mg, 82%); ^1H NMR (400 MHz, $CDCl_3$): 10.92 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.72–7.66 (m, 4H), 7.64–7.58 (m, 4H), 7.47–7.42 (m, 4H), 7.38–7.36 (m, 4H), 7.34–7.31 (m, 5H), 7.22–7.20 (m, 1H), 7.13–7.10 (m, 5H), 7.02–7.00 (m, 2H), 6.98–6.94 (m, 1H), 2.26 (s, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 212.3, 212.3, 142.8, 141.0, 140.2, 138.3, 137.0, 134.1, 133.0, 132.9, 132.4, 131.9, 131.9, 131.8, 131.7, 131.7, 131.6, 130.5, 129.6, 129.4, 129.3, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 127.6, 127.3, 127.0, 125.2, 124.4, 121.5, 111.5, 111.4, 102.8, 101.8, 21.4. IR (KBr) 3434, 3058, 1630, 1598, 1489, 1440, 1378, 1234, 1160, 1120, 731, 697, 661, 546 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{46}H_{36}NO_3PSNa$ 736.2046; found 736.2046.

(1-(3-hydroxyphenyl)-3,3-diphenylpropa-1,2-dien-1-yl)diphenylphosphine oxide (6):

The resultant residue was purified by flash silica gel column chromatography to afford **6** as a

yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): 10.72 (s, 1H), 7.69–7.64 (m, 4H), 7.46–7.42 (m, 2H), 7.32–7.30 (m, 10H), 7.24–7.22 (m, 1H), 7.17–7.13 (m, 1H), 7.03–7.01 (m, 4H), 6.97–6.94 (m, 1H), 6.79 (t, J = 7.6 Hz, 1H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 213.0, 212.9, 155.7, 155.7, 134.1, 134.1, 132.5, 132.5, 131.8, 131.7, 131.6, 131.6, 130.4, 130.3, 129.3, 128.6, 128.5, 128.4, 128.2, 128.2, 128.1, 120.1, 119.5, 111.6, 111.5, 103.4, 102.4.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H and ^{13}C NMR spectra for all products (PDF)

X-ray crystallographic data for product **3a** and **6** (CIF)

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Notes

The authors declare no competing financial interest

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