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Highly regio- and stereoselective palladium-catalyzed allene bifunctionalization cascade via π-allyl intermediate

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ABSTRACT

We report a palladium-catalyzed allene bifunctionalization reaction that forms C–C and either C–O or C–N bonds in one pot with excellent regio- and stereoselectivity. Carboxylic acids, amides, and hydroxide are all suitable nucleophiles. Organoboronic acid acts as hydroxide transfer reagent. An intermediate π-allyl palladium complex was isolated, which yields improved catalytic performance as well as evidence of the origin of stereoselectivity. A derivatization study emphasizes the utility of the functionalized allylic products.

1. Introduction

Polysubstituted allyl compounds are important building blocks in organic synthesis, and are common structural motifs in natural products.[1] Transition metal-catalyzed nucleophilic allylic substitution is a rapid process to construct polysubstituted allyl compounds.[2] The palladium catalyzed Tsuji–Trost reaction has been developed into a powerful tool for this transformation in recent years.[3] The π-allyl palladium intermediates are essential to the formation of allylic substitution products; such π-allyl palladium species have been thoroughly studied and reviewed by organometallic chemists.[4] Allenes possess two adjacent C=C double bonds, and can be used to construct π-allyl metal complexes with participation of electrophiles such as aryl halides. Subsequent nucleophilic substitution yields the polysubstituted allyl products.[5]

In most reports of palladium-catalyzed allene bifunctionalization reactions, the allene substituent R is an electron donating group such as alkyl/aryl, or a weak electron withdrawing group (EWG) such as carboxylic acid, ester or amide (eq. 1, Scheme 1).[5c,5d] Savic et al. demonstrated that heteroatom-based nucleophiles such as acetate could be employed in the bifunctionalization cascade, yielding allyl acetate products[9b] (eq. 2, Scheme 1). However, selectivity problems hampered further applications of this method.

Reports of nucleophilic substitution reactions utilizing allenes bearing strong EWG (such as sulfone, phosphonate and phosphine oxide) are still scarce.[6] Boronic acids are commonly used to construct C–C bonds via the transmetallation step in Suzuki-Miyaura coupling reactions.[7,8] However, examples of boronic acid employed as hydroxide source to construct C–O bonds are uncommon.[9] Herein we report a new series of palladium-catalyzed allene bifunctionalization reactions which generate substituted allylic alcohols, esters and amides employing boronic acid, carboxylic acids and amides, respectively as nucleophiles (eq. 3, Scheme 1). We observe good regioselective control and pure (*Z*)-selectivity of the double bond geometry. We isolated a possible intermediate π-allyl palladium complex and used it as catalyst, which improved the efficiency of the reaction.

2. Results and discussion

In the cascade reaction involving phenylsulfonyl allene **1a** and phenyl iodide **2a**, different palladium sources, boronic acids, phosphine ligands, and bases were screened in order to find optimal reaction conditions (Table 1). For purification purposes, the allyl alcohol product was protected using imidazole/TBSCl.[10] Optimal conditions (**entry 1**, Table 1) resulted in a 64% isolated

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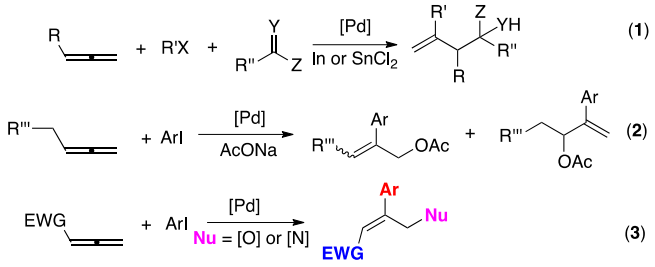
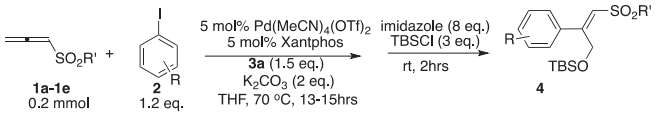


Scheme 1. Cascade reaction pathway involving allenes.

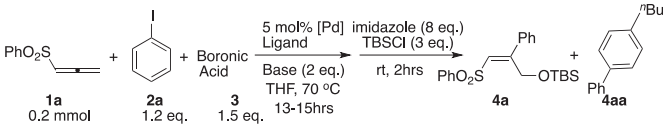


4a, R = H, R' = Ph (64%)
4b, R = 4-Me, R' = Ph (57%)
4c, R = 4-F, R' = Ph (54%)
4d, R = 4-Cl, R' = Ph, (53%)
4e, R = 4-Br, R' = Ph, (52%)
4f, R = 4-^{t}Bu, R' = Ph, (73%)
4g, R = 3-Me, R' = Ph, (59%)
4h, R = 3-Cl, R' = Ph, (50%)
4i, R = 3-OMe, R' = Ph, (50%)
4j, R = 3,5-dimethyl, R' = Ph, (56%)
4k, R = H, R' = 4-MePh (**1b**), (66%)
4l, R = H, R' = 4-OMePh (**1c**), (57%)
4m, R = H, R' = 4-BrPh (**1d**), (35%)

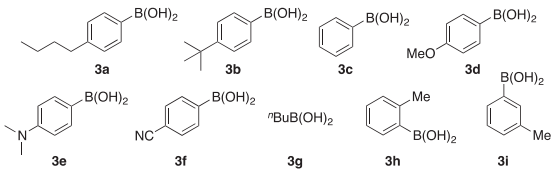
Scheme 2. Substrate scope.

yield of desired product **4a**, but we were unable to completely suppress the biphenyl product **4aa** formed by the direct C-C coupling of phenyl iodide **2a** and boronic acid **3a**. For the palladium source, $[Pd(MeCN)_4](OTf)_2$ outperformed its counterparts $Pd_2(dba)_3$ and $Pd(OAc)_2$ (**entries 1**–**3**, Table 1). Arylboronic acids of varying structure were also screened (entries **4**–**9**, Table 1); use of *ortho* methyl-substituted phenyl boronic acid (**3h**) yielded only a trace amount of desired product **4a**, and *meta*-methylphenyl boronic acid (**3i**) gave 26% isolated yield of **4a** (entries **10**–**11**, Table 1). The optimal boronic acid was *p*-*n*-butylphenylboronic acid (**3a**). Screening different phosphine ligands (entries **12**–**17**, Table 1) revealed Xantphos to be the preferred choice. The success of Xantphos may be attributed to its wide bite angle and rigid carbon skeleton, which can help to increase the ability of Pd to bind the C–C double bond of the functionalized allene substrates.[11] Changing the base from potassium carbonate to KF or K_3PO_4 did not lead to improved yields (entries **18**–**19**, Table 1).

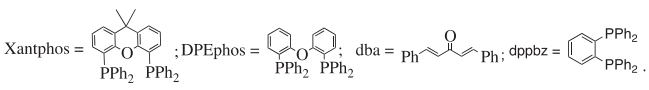
Table 1
Optimization of palladium catalyzed cascade reaction.



Entry	[Pd]/5 mol%	[P]/10 mol%	Boronic acids **3**	Base	**4a**[a] (%)	**4aa** (%)
	[Pd]/[P] = 1:2					
1	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3a**	K_2CO_3	64	26
2	$Pd_2(dba)_3$	Xantphos	**3a**	K_2CO_3	28	–
3	$Pd(OAc)_2$	Xantphos	**3a**	K_2CO_3	9	–
4	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3b**	K_2CO_3	46	–
5	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3c**	K_2CO_3	26	–
6	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3d**	K_2CO_3	49	–
7	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3e**	K_2CO_3	trace	–
8	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3f**	K_2CO_3	25	–
9	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3g**	K_2CO_3	trace	–
10	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3h**	K_2CO_3	trace	–
11	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3i**	K_2CO_3	26	–
12	$[Pd(MeCN)_4](OTf)_2$	PPh_3	**3a**	K_2CO_3	trace	34
13	$[Pd(MeCN)_4](OTf)_2$	dppe	**3a**	K_2CO_3	trace	trace
14	$[Pd(MeCN)_4](OTf)_2$	dppp	**3a**	K_2CO_3	trace	18
15	$[Pd(MeCN)_4](OTf)_2$	dppf	**3a**	K_2CO_3	trace	6
16	$[Pd(MeCN)_4](OTf)_2$	dppbz	**3a**	K_2CO_3	trace	trace
17	$[Pd(MeCN)_4](OTf)_2$	DPEphos	**3a**	K_2CO_3	trace	25
18	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3a**	KF	26	–
19	$[Pd(MeCN)_4](OTf)_2$	Xantphos	**3a**	K_3PO_4	trace	–
20	$[Pd(MeCN)_4](OTf)_2$	Xantphos	THF/H_2O (3:0.1/mL)	K_2CO_3	Complicated	–



THF was dried by sodium/benzophenone and used in glove box (O_2 < 0.1 ppm and H_2O < 0.1 ppm).
[a] There is no need to purify the allyl alcohol precursor. Isolated yield of two steps were shown. -TBS = -$SiMe_2(^tBu)$; -OTf = -SO_2CF_3;



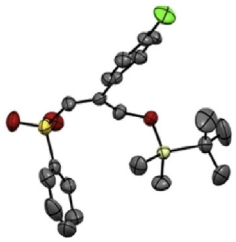
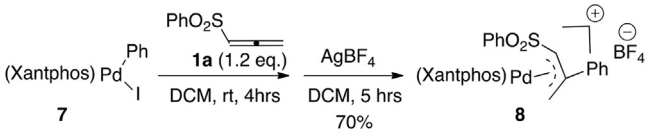
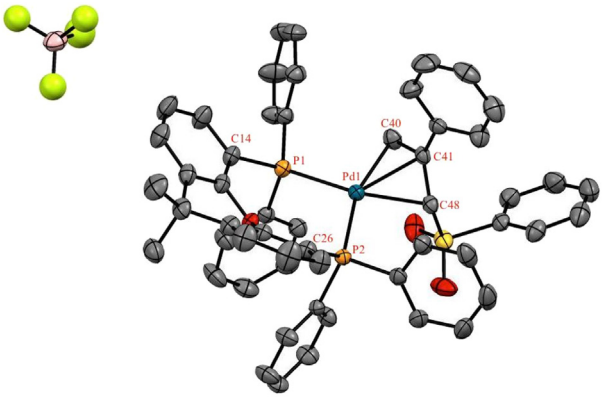


Fig. 1. ORTEP drawing of **4d** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.



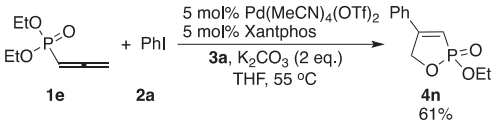


Scheme 3. The ORTEP drawing of complex **8** with 50% thermal ellipsoids. Hydrogen atoms and co-crystallized solvent are omitted for clarity. There is one disordered component of BF_4 counter anion shown in the crystal structure. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.3779(6), Pd(1)–P(2) 2.3733(6), Pd(1)–C(40) 2.212(3), Pd(1)–C(41) 2.193(2), Pd(1)–C(48) 2.154(2); P(1)–Pd(1)–P(2) 106.88(2); P(1)–Pd(1)–C(41) 126.75(6), P(2)–Pd(1)–C(41) 125.52(6), C(14)-P(1)-Pd(1) 125.68(8), C(26)-P(2)-Pd(1) 119.15(8).

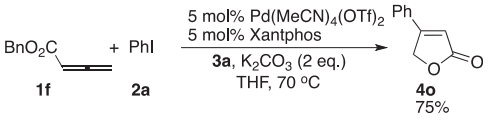
To address the origin of the hydroxide nucleophile, we performed control experiments using either water or boroxine[12] in place of organoboronic acid. These experiments did not result in product formation (entry **20**, Table 1 and see SI for further detail).

With the optimized reaction conditions in hand, we studied the scope with respect to the aryl iodide **2** (Scheme 2). For the *para* (**2b-2f**) and *meta* (**2g-2i**) substituted phenyl iodide substrates, the cascade reaction furnishes the desired products (**4b-4i**) with moderate to good combined isolated yields. Carbon-halogen functionalities on the phenyl ring remained intact (**4d**, **4e**), which indicates the potential to build more complicated molecules via cross coupling reactions. The (*Z*) geometry of the C—C double bond of **4d** was confirmed by X-ray crystallography (Fig. 1). The highest yield (73%) can be reached when 4-*t*-butyl phenyl iodide is used as substrate (**4f**). We also tested other substituents R′ on the sulfone (**4k-4m**, Scheme 3). For R' = Me, the yield of corresponding product **4k** is similar to **4a**; the electron donating group R' = OMe decreased the yield (**4l**), and when the electron withdrawing group R' = Br was used, the yield dropped to 35% (**4m**).

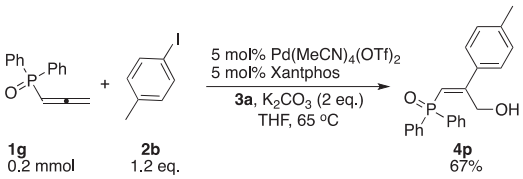
Allenes containing other types of functional groups were used, such as the phosphonate **1e** and the ester **1f**. The cascade reaction afforded the cyclic products **4n**[13] (61%) and **4o**[14] (75%) (eqs. 1 and 2). Their formation can be rationalized as the intramolecular nucleophilic substitution reaction of the OH group (formed in the first step of cascade reaction) with the phosphonate substituent due to their mutually *cis* orientation. However, when the phosphonate group was replaced by a phosphine oxide group (**1g**), the cyclization was inhibited, and allylic alcohol **4p** forms in 67% yield (eq. 3). The solid-state structure of **4p** was confirmed by X-ray crystallography (see full detail in SI).



(1)



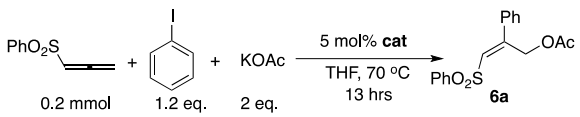
(2)



(3)

In all cases, the allene's EWG and the aryl halide's aryl group are oriented *trans* to each other in the olefin products, which is similar to the orientation of π-allyl palladium complexes we isolated before.[15,16]

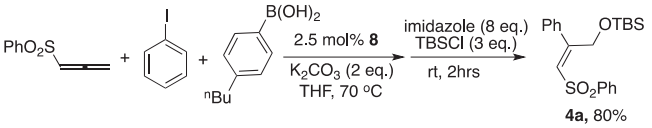
Therefore, we hypothesized that the reaction pathway involves a π-allyl palladium intermediate. To investigate this hypothesis, the complex (Xantphos)PdPhI, **7**,[17] was reacted with allene **1a** (Scheme 3). After iodide abstraction with $AgBF_4$ was carried out in CH_2Cl_2, the *cis*-π-allyl palladium complex **8** was isolated as light yellow solid in 70% yield. The structure of **8** was confirmed by X-ray crystallography (Scheme 3). The coordination geometry at palladium is best described as distorted square planar, with the two phosphorus donors and the η^3-allyl fragment comprising the coordination sphere. The two phosphorus atoms are *cis* to each other with a bite angle (P-Pd-P) of 106.9°, which occurs within the calculated flexible bite angle range of Xantphos (97-135°).[17] The distances between the two phosphorus atoms and the palladium center are 2.378 and 2.373 Å. The distance between the metal center and the allyl moiety is in the range of 2.15–2.21 Å, which is similar to analogues in the literature.[17c] The *trans* configuration between the sulfone substituent on the terminal carbon of the allene and the phenyl group on the central carbon of the allene is evident in the crystal structure.[15] This *trans* orientation is maintained after nucleophilic substitution in the final coupling product. Complex **8** can be used as an effective catalyst in the cascade



cat:	Yield of **6a** (%)
$Pd(MeCN)_4(OTf)_2$/Xantphos	39
$Pd(dba)_2$ /Xantphos	48
Complex **8**	66
Complex **7**	64

Scheme 4. Catalyst screening for the multicomponent reaction using KOAc as nucleophile.

reaction with higher isolated yield (80%) and lower catalyst loading (2.5 mol%, eq. 4) compared to $[Pd(MeCN)_4](OTf)_2$, which suggests that the π-allyl palladium complex **8** is a possible intermediate in this cascade reaction. The stoichiometric reaction of complex **8** with boronic acid and potassium carbonate was also conducted, and yielded the desired product **4a** with 36% yield in the presence of phenyl iodide. (see SI for full detail).[18]

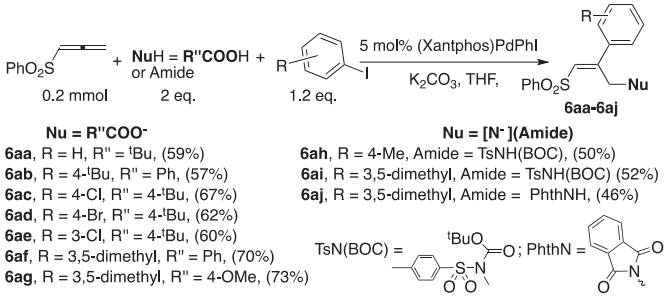


(4)

In order to expand the nucleophile scope in the cascade reaction, we investigated the viability of carboxylates as coupling partners. When potassium acetate was reacted with sulfonyl allene **1a** and phenyl iodide **2a** under our $[Pd(MeCN)_4](OTf)_2$/Xantphos coupling conditions, desired allylic acetate **6a** formed in 39% isolated yield (Scheme 4). Improvement of the yield to 64% or 66% was achieved by employing precatalysts **7** or **8**, respectively. Given the similar catalytic performance of **7** and **8**, we used the more stable and easily available complex **7** as catalyst to study the substrate scope of aryl iodides and nucleophiles (Scheme 5).

Alkyl and aryl carboxylic acids are successful nucleophiles in the cascade; in the presence of a variety of aryl halides, the catalytic cascade reaction yields products **6aa-6ag** with 57–73% isolated yields. Commonly used Tosyl- and Phth-protected amide (TsNH(BOC), PhthNH) were also employed as nitrogen-containing nucleophiles to produce allylic amides **6ah-6aj** with moderate yields. Single crystals of **6ai** were obtained and analyzed by X-ray crystallography, which confirmed that the sulfonyl group and the aryl group are oriented *trans* to each other in the allylic amide product (Fig. 2). Removal of the Phth-group allows access to the free allylic amine.[19]

To demonstrate the utility of our allene bifunctionalization method, we subjected one of the products to a derivatization study, namely allylic silyl ether **4a** (Scheme 6). The free alcohol **5a** can be obtained with 91% isolated yield under KF-promoted Si-O cleavage with the assistance of TMSCl as Lewis acid.[20] The allylic halide compound **5b** was formed with 83% isolated yield under PPh_3/DDQ assisted C-O cleavage.[21] Allylic acetate **6a** can be obtained as well from alcohol **5a** with 95% yield via a standard acetylation pathway. The allylic acetate **6a** can be employed as a useful building block to form C–C, C–N or C–C double bonds under different conditions. Reaction with C-nucleophilic reagent di-*tert*-butyl propanedioate yields the C-C coupling product **6b**[22] in 68% isolated yield. When **6a** was subjected to catalytic borylation, unexpected C–C double bond migration occurred to yield product **6c** instead of the desired allylic boronate.[23] C-N coupling of **6a** with aniline[24] proceeded smoothly



Scheme 5. Substrate scope for different nucleophiles containing carboxylic acids and amides.

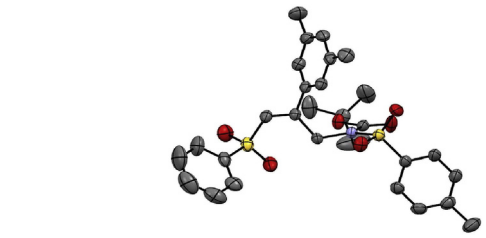
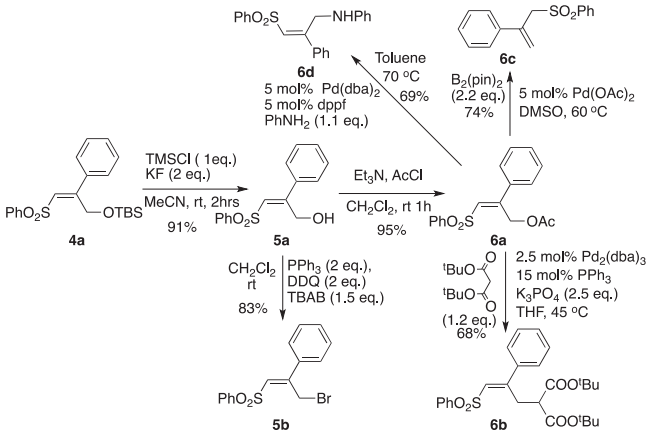
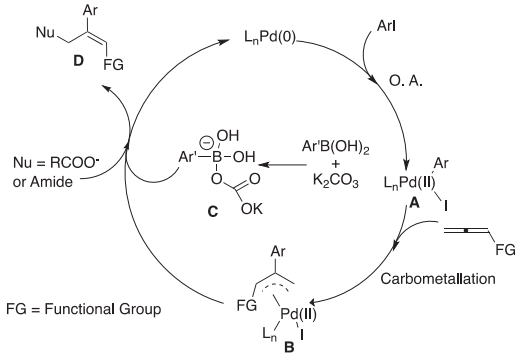


Fig. 2. ORTEP drawing of **6ai** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.



Scheme 6. Derivatization studies of allylic silyl ether **4a**.



Scheme 7. Proposed catalytic cycle.

under the influence of Pd/dppf cocatalysts: product **6d** formed in 69%.

Based on the observations above, the reaction mechanism is proposed in Scheme 7. Pd(0) reacts with aryl iodide via oxidative addition to produce Pd(II) intermediate **A**. Subsequently, carbometallation of the allene occurs to form the π-allyl palladium(II) intermediate **B**, which can be trapped by different **Nu**s via nucleophilic attack on the terminal allene carbon, which results in release of the coupling product **D** and regeneration of Pd(0). Hydroxide delivery from organoboronic acid (Nu = $^-$OH) can be explained by nucleophilic attack of the "ate complex" **C**, which is produced by the reaction of boronic acid with base.[9a] The exclusive *trans* orientation between the allene substituent and the aryl group on the central carbon can be attributed to the strong electron withdrawing ability of the functional group on the allene.[15]

3. Conclusion

In summary, the palladium-catalyzed cascade reaction of aryl iodides and functionalized allenes was demonstrated, which produced (*Z*)-allylic alcohol compounds with pure steroselectivity. The putative intermediate π-allyl palladium complex can be trapped by several kinds of nucleophiles to form C–O or C–N bonds. Organoboronic acids were used to form the C–OH bond and promote the completion of the catalytic cycle. The utility of the allylic acetate products was shown in a derivatization study. Our results show that useful building blocks can be easily produced by this cascade methodology. We would like to expand this reactivity to other sensitive substrates. The corresponding research is under development in our lab.

4. Experimental section

4.1. General information

Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates, glass. Visualization on TLC was achieved by the use of UV light (254 nm). Flash column chromatography was undertaken on silica gel (300–400 mesh). The purity of nitrogen gas is 99.999%. Air sensitive liquid and solutions were manipulated by using glove box and dry solvents. The catalytic reactions were performed under a nitrogen atmosphere either in a glove box (Delix, China) or in sealed thick glass tubes purchased from Synthware Company (BeiJing). THF, benzene and deuterated benzene were distilled from Na metal under nitrogen protected solvent purification system obtained from Synthware Company. Unless otherwise stated, all commercial reagents were used without additional purification. Proton nuclear magnetic resonance spectra were recorded on Brucker Avance 600 MHz, Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak ($CHCl_3$ in $CDCl_3$: 7.24 ppm; C_6H_6 in C_6D_6: 7.16 ppm). Carbon 13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was recorded on Brucker Avance 151 MHz and was fully decoupled by broad band decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.23 ppm of chloroform-d and 128.39 ppm of C_6D_6. Phosphorus 31 nuclear magnetic resonance spectroscopy (^{31}P NMR) was recorded on Brucker Avance 243 MHz and phosphoric acid was used as external standard. Infrared (IR) spectra were recorded on Thermo Scientific Nicolet iS50. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorptions are reported. High resolution mass spectra were obtained by using Thermo Scientific Q Exactive (API or ESI as ion source) Melting points was measured using RD-II manufactured by Tianjin optical instrument factory.

4.2. General procedure for the palladium catalyzed cascade reaction to produce compounds 4 (Scheme 2)

In an N_2-filled glove box with oxygen and water levels ≤0.1 ppm, to an oven-dried screw-capped vial was added $[Pd(MeCN)_4](OTf)_2$ (5.3 mg, 5 mol%), Xantphos (5.5 mg, 5 mol%), K_2CO_3 (55 mg, 2 eq.), boronic acids **3a** (53 mg, 1.5 eq.) and THF (3 mL), then allene **1a** (36 mg, 0.2 mmol) and aryl iodide **2** (0.24 mmol, 1.2 eq.) were also added to the suspension. The joint position between the vial and cap was sealed with electrical tape to and the vial was heated to 70 °C with stirring using an aluminum heating plate outside of the glove box for 13–15 h. The reaction was monitored by TLC (Hexane/Ethyl acetate = 2:1) to show that the allyl alcohol precursor had formed completely. Then, imidazole (8 eq. 108 mg) and TBSCl (3 eq. 90 mg) were added into the vial under air and stirred for another 2 h at room temperature, which was monitored by TLC (Hexane/Ethyl acetate = 7:1) as well to confirm that the formation of TBS protected allyl alcohol **4a** was complete. Then product was isolated and purified by short column chromatography (Hexane/Ethyl acetate = 20:1) to yield pure **4**.

4.2.1. {[(2Z)-3-(benzenesulfonyl)-2-phenylprop-2-en-1-yl]oxy}(tert-butyl)dimethylsilane (**4a**)

Eluent: Hexane/Ethyl acetate. White solid (50 mg, 64%), Melting point 48–49 °C, ^1H NMR (600 MHz, C_6D_6) δ 7.93 (2H, d, J = 6 Hz), 7.11–6.95 (8H, m), 6.41 (1H, s), 5.27 (2H, s), 0.79 (9H, s), 0.03 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 155.69, 143.27, 138.14, 133.38, 129.80, 129.64, 128.95, 128.70, 128.43, 127.93, 58.89, 26.18, 18.60, −4.87; IR (film, cm^{-1}): 2924, 1470, 1303, 1287, 1174, 1144, 1082, 837; HRMS (ESI+): Calcd for $C_{21}H_{29}O_3SSi$ $[M+H]^+$: 389.16012; Found: 389.15999.

4.2.2. {[(2Z)-3-(benzenesulfonyl)-2-(4-methylphenyl)prop-2-en-1-yl]oxy}(tert-butyl)dimethylsilane (**4b**)

Eluent Hexane/Ethyl acetate. White solid (46 mg, 57%), Melting point 64–66 °C, ^1H NMR (600 MHz, C_6D_6) δ 7.97–7.92 (2H, m), 7.09 (2H, d, J = 6 Hz), 6.98–6.93 (3H, m), 6.85 (2H, d, J = 6 Hz), 6.49 (1H, s), 5.30 (2H, s), 2.03 (3H, s), 0.83 (9H, s), 0.07 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 155.49, 143.48, 139.99, 135.26, 133.28, 129.61, 129.48, 128.68, 128.43, 127.90, 58.81, 26.24, 21.46, 18.65, −4.82; IR (film, cm^{-1}): 2929, 1316, 1140, 1106, 812, 788, 688; HRMS (ESI^+): Calcd for $C_{22}H_{31}O_3SSi^+$ $[M+H]^+$: 403.17577; Found: 403.17579.

4.2.3. {[(2Z)-3-(benzenesulfonyl)-2-(4-fluorophenyl)prop-2-en-1-yl]oxy}(tert-butyl)dim-ethylsilane (**4c**)

Eluent Hexane/Ethyl acetate. White solid (44 mg, 54%), Melting point 82–83 °C, ^1H NMR (600 MHz, C_6D_6) δ 7.95–7.91 (2H, m), 6.99–6.93 (3H, m), 6.89–6.84 (2H, m), 6.67–6.62 (2H, m), 6.30 (1H, s), 5.20 (2H, s), 0.79 (9H, s), 0.02 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 164.90, 163.25, 154.38, 143.20, 133.95 (d, J = 3 Hz), 133.44, 130.42 (d, J = 7.5 Hz), 129.65, 128.84, 127.93, 115.67 (d, J = 7.5 Hz), 58.76, 26.14, 18.56, −4.90; ^{19}F NMR (564.6 MHz, C_6D_6) δ −111.47 (s); IR (film, cm^{-1}): 2850, 1599, 1507, 1305, 1163, 1142, 829, 772; HRMS (ESI^+): Calcd for $C_{21}H_{28}FO_3SSi^+$ $[M+H]^+$: 407.15070; Found: 407.15066.

4.2.4. {[(2Z)-3-(benzenesulfonyl)-2-(4-chlorophenyl)prop-2-en-1-yl]oxy}(tert-butyl)di-methylsilane (**4d**)

Eluent Hexane/Ethyl acetate. White solid (45 mg, 53%), Melting point 112–113 °C; ^1H NMR (600 MHz, C_6D_6) δ 7.92 (2H, d, J = 6 Hz), 6.99–6.94 (5H, m), 6.81 (2H, d, J = 6 Hz), 6.30 (1H, s), 5.18 (2H, s), 0.79 (9H, s), 0.02 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 154.20, 143.06, 136.43, 135.93, 133.51, 129.80, 129.68, 129.24, 128.91, 128.68, 127.95, 58.69, 26.14, 18.64, −4.90; IR (film, cm^{-1}): 2855, 1597, 1489, 1142, 1082, 809, 687; HRMS (ESI^+): Calcd for $C_{21}H_{28}ClO_3SSi^+$ $[M+H]^+$: 423.12114 [Cl^{35}], 425.11819 [Cl^{37}]; Found: 423.12084 [Cl^{35}], 425.11727 [Cl^{37}].

4.2.5. {[(2Z)-3-(benzenesulfonyl)-2-(4-bromophenyl)prop-2-en-1-yl]oxy}(tert-butyl)di-methylsilane (**4e**)

Eluent Hexane/Ethyl acetate. White solid (48 mg, 52%), Melting point 83–85 °C; ^1H NMR (600 MHz, C_6D_6) δ 7.91 (2H, d, J = 6 Hz), 7.13 (2H, d, J = 6 Hz), 6.95–6.93 (3H, m), 6.73 (2H, d, J = 6 Hz), 6.29 (1H, s), 5.18 (2H, s), 0.79 (9H, s), 0.01 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 154.26, 143.05, 136.90, 133.49, 131.89, 130.01, 129.66, 129.25, 128.68, 127.95, 124.24, 58.66, 26.07, 18.58, −4.91; IR (film, cm^{-1}): 2855, 1598, 1485, 1141, 1125, 853, 790; HRMS (ESI^+): Calcd for $C_{21}H_{28}BrO_3SSi^+$ $[M+H]^+$: 467.07063 [Br^{79}], 469.06858 [Br^{81}]; Found: 467.07039 [Br^{79}], 469.06806 [Br^{81}].

*4.2.6. {[(2Z)-3-(benzenesulfonyl)-2-(4-tert-butylphenyl)prop-2-en-1-yl]oxy}(tert-butyl)-dimethylsilane **(4f)***

Eluent Hexane/Ethyl acetate. Colorless oil (65 mg, 73%); ^{1}H NMR (600 MHz, C_6D_6) δ 7.98–7.95 (2H, m), 7.18–7.12 (4H, m), 7.01–6.97 (3H, m), 6.51 (1H, s), 5.30 (2H, s), 1.15 (9H, s), 0.82 (9H, s), 0.06 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 155.47, 153.13, 143.47, 135.37, 133.32, 129.63, 128.68, 128.30, 127.92, 125.72, 58.92, 34.95, 31.53, 26.22, 18.66, −4.81; IR (neat, cm^{-1}): 2961, 1598, 1300, 1148, 1112, 857, 755; HRMS (ESI^+): Calcd for $C_{25}H_{37}O_3SSi^+$ $[M+H]^+$: 445.22272; Found: 445.22280.

*4.2.7. {[(2Z)-3-(benzenesulfonyl)-2-(3-methylphenyl)prop-2-en-1-yl]oxy}(tert-butyl)di-methylsilane **(4g)***

Eluent Hexane/Ethyl acetate. Colorless oil (48 mg, 59%); ^{1}H NMR (600 MHz, C_6D_6) δ 7.96–7.93 (2H, m), 7.04–6.94 (6H, m), 6,90–6.86 (1H, m), 6.48 (1H, s), 5.28 (2H, s), 2.02 (3H, s), 0.81 (9H, s), 0.04 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 155.84, 143.35, 138.21, 138.19, 133.37, 130.62, 129.63, 129.11, 128.86, 128.69, 127.93, 125.60, 59.00, 26.20, 21.54, 18.63, −4.86; IR (neat, cm^{-1}): 2855, 1599, 1305, 1254, 1147, 1083, 834, 811; HRMS (ESI^+): Calcd for $C_{22}H_{31}O_3SSi^+$ $[M+H]^+$: 403.17577; Found: 403.17595.

*4.2.8. {[(2Z)-3-(benzenesulfonyl)-2-(3-chlorophenyl)prop-2-en-1-yl]oxy}(tert-butyl)di-methylsilane **(4h)***

Eluent Hexane/Ethyl acetate. Colorless oil (42 mg, 50%); ^{1}H NMR (600 MHz, C_6D_6) δ 7.90 (2H, d, J = 6 Hz), 7.25 (1H, s), 7.01–6.93 (4H, m), 6.76 (1H, d, J = 6 Hz), 6.68 (1H, t, J = 6 Hz), 6.30 (1H, s), 5.15 (2H, s), 0.79 (9H, s), 0.00 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 154.07, 142.90, 139.96, 134.71, 133.54, 129.98, 129.82, 129.68, 128.71, 127.96, 126.44, 58.85, 26.13, 18.54, −4.97; IR (neat, cm^{-1}): 2855, 1471, 1446, 1306, 1254, 1147, 1083, 775, 686; HRMS (ESI^+): Calcd for $C_{21}H_{28}ClO_3SSi^+$ $[M+H]^+$: 423.12114 [Cl^{35}], 425.11819 [Cl^{37}]; Found: 423.12107 [Cl^{35}], 425.11755 [Cl^{37}].

*4.2.9. {[(2Z)-3-(benzenesulfonyl)-2-(3-methoxyphenyl)prop-2-en-1-yl]oxy}(tert-butyl)di-methylsilane **(4i)***

Eluent Hexane/Ethyl acetate. Colorless oil (42 mg, 50%); ^{1}H NMR (600 MHz, C_6D_6) δ 7.93 (2H, d, J = 6 Hz), 6.98–6.91 (5H, m), 6.75 (1H, d, J = 6 Hz), 6.70 (1H, d, J = 6 Hz), 6.50 (1H, s), 5.26 (2H, s), 3.26 (3H, s), 0.82 (9H, s), 0.05 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 160.32, 155.43, 143.22, 139.78, 133.37, 129.82, 129.63, 129.25, 127.94, 120.70, 115.69, 114.04, 59.05, 55.17, 26.23, 18.56, −4.86; IR (neat, cm^{-1}): 2928, 1575, 1485, 1289, 1170, 835, 776; HRMS (ESI^+): Calcd for $C_{22}H_{31}O_4SSi^+$ $[M+H]^+$: 419.17068; Found: 419.17075.

*4.2.10. {[(2Z)-3-(benzenesulfonyl)-2-(3,5-dimethylphenyl)prop-2-en-1-yl]oxy}(tert-butyl)-dimethylsilane **(4j)***

Eluent Hexane/Ethyl acetate; Colorless oil (47 mg, 56%); ^{1}H NMR (600 MHz, C_6D_6) δ 7.98–7.94 (2H, m), 6.96 (3H, s), 6.88 (2H, s), 6.71 (1H, s), 6.54 (1H, s), 5.30 (2H, s), 2.04 (6H, s), 0.77 (9H, s), 0.05 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 155.99, 143.45, 138.23, 138.08, 133.29, 131.59, 129.62, 128.74, 127.92, 126.31, 59.11, 26.21, 21.48, 18.65, −4.85; IR (neat, cm^{-1}): 2885, 1595, 1306, 1254, 1147, 1101, 1083, 835, 776; HRMS (ESI^+): Calcd for $C_{23}H_{33}O_3SSi^+$ $[M+H]^+$: 417.19142; Found: 417.19104.

*4.2.11. {[(2Z)-3-(4-methylbenzenesulfonyl)-2-phenylprop-2-en-1-yl]oxy}tert-butyldi-methyl silane **(4k)***

Eluent Hexane/Ethyl acetate; White solid (53 mg, 66%), Melting point 92–93 °C; ^{1}H NMR (600 MHz, C_6D_6) δ 7.88 (2H, d, J = 6 Hz), 7.12 (2H, d, J = 6 Hz), 7.05–6.97 (3H, m), 6.83 (2H, d, J = 6 Hz), 6.46 (1H, s), 5.30 (2H, s), 1.90 (3H, s), 0.80 (9H, s), 0.04 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 155.14, 144.34, 140.46, 138.23, 130.34, 129.74, 129.38, 128.71, 128.43, 128.08, 58.88, 26.20, 21.54, 18.61, −4.85; IR (neat, cm^{-1}): 2854, 1598, 1313, 1299, 1139, 1078, 809, 781; HRMS (ESI^+): Calcd for $C_{22}H_{31}O_3SSi^+$ $[M+H]^+$: 403.17577; Found: 403.17565.

*4.2.12. {[(2Z)-3-(4-methoxybenzenesulfonyl)-2-phenylprop-2-en-1-yl]oxy}tert-butyldi-methylsilane **(4l)***

Eluent Hexane/Ethyl acetate; White solid (48 mg, 57%), Melting point 56–58 °C; ^{1}H NMR (600 MHz, C_6D_6) δ 7.91 (2H, d, J = 6 Hz), 7.14 (2H, d, J = 6 Hz), 7.05–6.98 (3H, m), 6.56 (2H, d, J = 6 Hz), 6.48 (1H, s), 5.33 (2H, s), 3.11 (3H, s), 0.81 (9H, s), 0.07 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 163.94, 154.55, 138.55, 134.97, 130.25, 129.76, 129.67, 128.70, 128.44, 114.97, 58.89, 55.40, 26.21, 18.62, −4.82; IR (neat, cm^{-1}): 2928, 1594, 1497, 1257, 1141, 1084, 831, 776; HRMS (ESI^+): Calcd for $C_{22}H_{31}O_4SSi^+$ $[M+H]^+$: 419.17068; Found: 419.17058.

*4.2.13. {[(2Z)-3-(4-bromobenzenesulfonyl)-2-phenylprop-2-en-1-yl]oxy}(tert-butyl)dime-thylsilane **(4m)***

Eluent Hexane/Ethyl acetate; White solid (33 mg, 35%), Melting point 52–53 °C; ^{1}H NMR (600 MHz, C_6D_6) δ 7.56 (2H, d, J = 6 Hz), 7.11 (2H, d, J = 6 Hz), 7.06 (2H, d, J = 6 Hz), 7.03–6.98 (3H, m), 6.31 (1H, s), 5.20 (2H, s), 0.79 (9H, s), 0.02 (6H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 156.15, 142.03, 138.13, 132.91, 129.98, 129.45, 128.77, 128.68, 58.85, 26.15, 18.59, −4.90; IR (neat, cm^{-1}): 2932, 1601, 1574, 1306, 1146, 1084, 1009; HRMS (ESI^+): Calcd for $C_{21}H_{28}BrO_3SSi^+$ $[M+H]^+$: 467.07063 [Br^{79}], 469.06858 [Br^{81}]; Found: 467.07063 [Br^{79}], 469.06832 [Br^{81}].

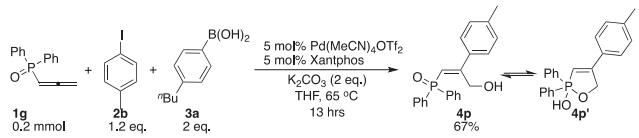
*4.2.14. 2-Ethoxy-4-phenyl-2,5-dihydro-1,2-oxaphosphole 2-oxide **(4n**, eq. 1)*[13]

The title compound was prepared according to the general procedure and there is no need to add imidazole/TBSCl for the synthesis of cyclic products. Eluent Hexane/Ethyl acetate; White solid (27 mg, 61%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43–7.38 (m, 5H), 6.34 (1H, d, J (PH) = 30 Hz), 5.13–5.02 (2H, m), 4.13 (2H, q, J = 6 Hz), 1.33 (3H, t, J = 6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.35 (d, J(PC) = 21 Hz), 131.53 (d, J(PC) = 21 Hz), 131.19, 129.30, 126.05, 108.84 (d, J(PC) = 171 Hz), 70.27 (d, J(PC) = 9 Hz), 63.34 (d, J(PC) = 6 Hz), 16.63; ^{31}P NMR (243 MHz, $CDCl_3$) δ 43.72 (s).

*4.2.15. 4-Phenyl-2,5-dihydrofuran-2-one (**4o**, eq. 2)*[14]

The title compound was prepared according to the general procedure and there is no need to add imidazole/TBSCl for the synthesis of cyclic products. Eluent: Hexane/Ethyl acetate; White Solid (27 mg, 75%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51–7.42 (5H, m), 6.35 (1H, s), 5.20 (2H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.05, 164.11, 131.96, 129.80, 129.47, 126.62, 113.18, 71.19; IR (neat, cm^{-1}): 3500, 1597, 1443, 1301, 1174, 1082, 1033, 836, 771; HRMS (ESI^+): Calcd for $C_{15}H_{15}O_3S^+$ $[M+H]^+$: 275.07364; Found: 275.07338.

*4.2.16. (2Z)-3-(diphenylphosphoroso)-2-phenylprop-2-en-1-ol (**4p,** eq. 3)*



The procedure was the same as the general procedure above. The amount of boronic acid **3a** was increased to 2 eq. and the reaction temperature was decreased to 65 °C to obtain higher yield. The solid phase of product contains **4p** confirmed by X-ray crystallography (see SI for detail), however, both **4p** and **4p'** exist in the solution phase, the ratio of them is confirmed as 6.43:1 (**4p**/**4p'**) by

the integration of ^{31}P NMR in $CDCl_3$. Eluent: Hexane/Ethyl acetate; White Solid (47 mg, 67%); Melting Point: 122–123 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.75 (4H, t, *J(PH)* = 12 Hz), 7.55–7.43 (6H, m), 7.36 (2H, d, *J* = 6 Hz), 7.15 (2H, d, *J* = 6 Hz), 6.31 (*minor isomer*, 0.09 H, d, *J(PH)* = 24 Hz), 6.29 (1H, d, *J(PH)* = 24 Hz), 5.75 (1H, br s), 4.72 (2H, s), 2.33 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.38 (minor isomer), 164.25, 140.99 (minor isomer, d, *J(PC)* = 16.5 Hz), 139.67, 138.00 (d, *J(PC)* = 16.5 Hz), 133.88, 133.73 (minor isomer), 133.17, 133.02 (minor isomer), 132.18 (minor isomer, d, *J(PC)* = 3.0 Hz), 132.12 (d, *J(PC)* = 3.0 Hz), 131.30, 131.24, 129.49, 129.44 (minor isomer), 128.96 (minor isomer), 128.93, 128.88 (minor isomer), 128.85, 128.81 (minor isomer), 126.64 (minor isomer), 126.57, 119.50 (minor isomer, d, *J(PC)* = 100.5 Hz), 118.44 (d, *J(PC)* = 100.5 Hz), 63.54 (minor isomer, d, *J(PC)* = 6.0 Hz), 63.45 (d, *J(PC)* = 6.0 Hz), 21.37; ^{31}P NMR (243 MHz, $CDCl_3$) δ 23.99 (major isomer, s), 23.86 (minor isomer, s), *the ratio of major isomer and minor isomer is confirmed by the integration of ^{31}P NMR as* **6.43:1**; IR (film, cm^{-1}): 3365, 1594, 1456, 1170, 1071, 851, 822, 751; HRMS (ESI^+): Calcd for $C_{22}H_{22}O_2P+$ $[M+H]^+$: 349.13519; Found: 349.13530.

4.3. Procedure for isolation of complex 8 and its catalytic reactivity (Scheme 3 and eq. 4)

4.3.1. Procedure for isolation of complex **8** (Scheme 3)

In glove box, to an oven-dried screw-capped vial was added complex **7** (0.033 mmol, 30 mg), CH_2Cl_2 (3 mL) to get yellow solution. Then allene compound **1a** (7.2 mg, 1.2 eq.) dissolved in 1 mL of CH_2Cl_2 was added slowly into the stirred solution above. The color of the reaction mixture changed to deep red immediately. After 4 h, silver tetrafluoroborate (6.4 mg, 1 eq.) was added into the reaction solution and the color changed to yellow slowly with brown precipitate generated at the same time. After stirring for another 5 h at room temperature, the suspension was worked up first by filtration The filtrate was concentrated to *ca*. 0.5 mL, then diethyl ether (5 mL) was added to afford the yellow precipitate. The solid was collected and was washed with diethyl ether (2 mL × 3). After drying, light yellow solid was obtained. Yellow solid (25 mg, 70%); ^1H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, 1H, *J(PH)* = 12 Hz), 7.64 (d, 1H, *J(PH)* = 12 Hz), 7.60–7.49 (m, 8H), 7.48–7.43 (m, 7H), 7.42–7.34 (m, 5H), 7.31 (t, 2H, *J* = 6 Hz), 7.23–7.14 (m, 6H), 6.92–6.85 (m, 4H), 6.65 (t, 2H, *J* = 6 Hz), 5.32 (d, 1H, *J* = 6 Hz), 4.98 (br s, 1H), 3.97 (br s, 1H), 1.81 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.26 (d, *J(PC)* = 7.6 Hz), 154.98 (d, *J(PC)* = 7.6 Hz), 140.67 (d, *J(PC)* = 3.0 Hz), 134.86 (d, *J(PC)* = 3.0 Hz), 134.66, 134.56 (d, *J(PC)* = 3.0 Hz), 133.57 (d, *J(PC)* = 13.6 Hz), 132.96 (d, *J(PC)* = 13.6 Hz), 132.8 (d, *J(PC)* = 9.0 Hz), 132.73, 132.62 (d, *J(PC)* = 24.1 Hz), 132.81 (d, *J(PC)* = 12.1 Hz), 132.01, 131.73, 131.31 (d, *J(PC)* = 3.0 Hz), 130.13 (d, *J(PC)* = 9.0 Hz), 129.80 (d, *J(PC)* = 12.1 Hz), 129.65 (d, *J(PC)* = 9.0 Hz), 129.66, 129.15, 129.00 (d, *J(PC)* = 7.6 Hz), 128.93 (d, *J(PC)* = 7.6 Hz), 127.92 (d, *J(PC)* = 43.8 Hz), 126.96, 126.67 (d, *J(PC)* = 43.8 Hz), 125.72 (d, *J(PC)* = 7.6 Hz), 125.39 (d, *J(PC)* = 7.6 Hz), 118.16 (d, *J(PC)* = 45.3 Hz), 115.79 (d, *J(PC)* = 45.3 Hz), 90.61 (d, *J(PC)* = 40.77 Hz), 77.66 (t, *J(PC)* = 33.22 Hz), 36.39, 30.85, 25.11; ^{31}P NMR (243 MHz, $CDCl_3$) δ 5.03 (d, *J (PP)* = 29.2 Hz), −0.15 (d, *J(PP)* = 29.2 Hz); Elemental analysis calcd for $[C_{54}H_{45}BF_4O_3P_2PdS+2\ CH_2Cl_2]$: C, 56.10; H, 4.12. Found: C, 56.63; H, 4.41.

4.3.2. Procedure for catalytic reactivity of complex **8** (eq. 4)

In an N_2-filled glove box with oxygen and water levels ≤0.1 ppm, to an oven-dried screw-capped vial was added complex **8** (5.4 mg, 2.5 mol%), K_2CO_3 (55 mg, 2 eq.), boronic acid **3a** (53 mg, 1.5 eq.) and THF (3 mL), then allene **1a** (36 mg, 0.2 mmol) and phenyl iodide **2a** (0.24 mmol, 49 mg, 1.2 eq.) were also added to the suspension. The joint position between the vial and cap was sealed with electrical tape and the vial was heated to 70 °C with stirring using an aluminum heating plate outside of the glove box for 13 h. The reaction was monitored by TLC (Hexane/Ethyl acetate = 2:1). Upon completion of the reaction, imidazole (8 eq. 108 mg) and TBSCl (3 eq. 90 mg) were added into the vial under air and stirred for another 2 h at room temperature. This protection step was also monitored by TLC (Hexane/Ethyl acetate = 7:1) to confirm completion of the formation of the TBS-protected allyl alcohol **4a**. The product was isolated and purified by short column chromatography (Hexane/Ethyl acetate = 20:1) to yield pure product of **4a** (62 mg, 80%). NMR data for this material was the same as above.

4.4. General procedure for substrate scope employing different nucleophiles containing carboxylic acids and amides (Schemes 4 and 5)

In an N_2-filled glove box with oxygen and water levels ≤0.1 ppm, to an oven-dried screw-capped vial were added (Xantphos)Pd(Ph)I (8.8 mg, 5 mol%), K_2CO_3 (55 mg, 0.4 mmol, 2.0 eq.), carboxylic acid or amide (0.4 mmol, 2.0 eq.) and THF (3 mL), then allene **1a** (36 mg, 0.2 mmol) and Aryl iodide **2** (0.24 mmol, 1.2 eq.) were also added to the suspension. The joint position between the vial and cap was sealed with electrical tape and the reaction vial was heated to 70 °C with stirring using an aluminum heating plate outside of the glove box for 13 h. The reaction was monitored by TLC (Hexane/Ethyl acetate = 5:1) The product was isolated and purified by column chromatography (Hexane/Ethyl acetate = 20:1–10:1) to yield pure product.

4.4.1. (2Z)-3-(benzenesulfonyl)-2-phenylprop-2-en-1-yl acetate (**6a**)

The KOAc (39 mg, 0.4 mmol, 2 eq.) was used directly; Eluent: Hexane/Ethyl acetate (10:1); Colorless oil (41 mg, 64%); The NMR data is matched with above.

4.4.2. (2Z)-3-(benzenesulfonyl)-2-phenylprop-2-en-1-yl-2,2-dimethyl-propanoate (**6aa**)

Eluent: Hexane/Ethyl acetate (20:1); White solid (42 mg, 59%); Melting Point: 90–91 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 8.00 (2H, d, *J* = 6 Hz), 7.63 (1H, t, *J* = 6 Hz), 7.56 (2H, t, *J* = 6 Hz), 7.35–7.29 (3H, m), 7.25 (2H, d, *J* = 6 Hz), 6.50 (1H, s), 5.63 (2H, s), 0.90 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.76, 152.15, 141.42, 136.54, 133.83, 130.05, 129.62, 129.61, 128.73, 127.69, 127.46, 59.11, 38.73, 26.94; IR (film, cm^{-1}): 3037, 1730, 1601, 1306, 1133, 1081763, 746; HRMS (ESI^+): Calcd for $C_{20}H_{26}NO_4S^+$ $[M+NH_4]^+$: 376.15771; Found: 376.15770.

4.4.3. (2Z)-3-(benzenesulfonyl)-2-(4-tert-butylphenyl)prop-2-en-1-yl benzoate (**6ab**)

Eluent: Hexane/Ethyl acetate (20:1); Oil (49 mg, 57%); ^1H NMR (600 MHz, $CDCl_3$) δ 8.00 (2H, d, *J* = 6 Hz), 7.79 (2H, d, *J* = 6 Hz), 7.56 (1H, t, *J* = 6 Hz), 7.50–7.47 (3H, m), 7.35 (4H, s), 7.33 (2H, t, *J* = 6 Hz), 6.71 (1H, s), 5.81 (2H, s), 1.25 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.02, 153.90, 150.04, 141.60, 133.76, 133.70, 133.26, 130.22, 129.83, 129.66, 129.54, 128.41, 127.63, 126.97, 125.96, 59.52, 34.91, 31.23; IR (film, cm^{-1}): 2961, 1717, 1265, 1146, 1025, 997; HRMS (ESI^+): Calcd for $C_{26}H_{30}NO_4S^+$ $[M+NH_4]^+$: 452.18901; Found: 452.18888.

4.4.4. (2Z)-3-(Benzenesulfonyl)-2-(4-chlorophenyl)prop-2-en-1-yl-4-tert-butylbenzoate (**6ac**)

Eluent: Hexane/Ethyl acetate (15:1); White solid (63 mg, 67%); Melting Point: 61–62 °C;^1H NMR (600 MHz, $CDCl_3$) δ 8.02 (2H, d, *J* = 6 Hz), 7.72 (2H, d, *J* = 6 Hz), 7.61 (1H, t, *J* = 6 Hz), 7.55 (2H, t,

J = 6 Hz), 7.35 (2H, d, J = 6 Hz), 7.32 (2H, d, J = 6 Hz), 7.29 (2H, d, J = 6 Hz), 6.62 (1H, s), 5.81 (2H, s), 1.28 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.96, 157.21, 149.74, 141.22, 136.42, 135.15, 133.96, 130.93, 129.70, 129.69, 129.22, 128.68, 127.79, 126.61, 125.56, 59.26, 35.28, 31.24; IR (film, cm^{-1}): 2962, 1717, 1307, 1266, 1147, 1083, 1012; HRMS (ESI^+): Calcd for $C_{26}H_{29}ClNO_4S^+$ $[M+NH_4]^+$: 486.15003 [Cl^{35}], 488.14708 [Cl^{37}]; Found: 486.15019 [Cl^{35}], 488.14643 [Cl^{37}].

4.4.5. (2Z)-3-(Benzenesulfonyl)-2-(4-bromophenyl)prop-2-en-1-yl-4-tert-butylbenzoate **(6ad)**

Eluent: Hexane/Ethyl acetate (15:1); White solid (64 mg, 62%); Melting Point: 62–64 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (2H, d, J = 6 Hz), 7.72 (2H, d, J = 6 Hz), 7.61 (1H, t, J = 6 Hz), 7.54 (2H, t, J = 6 Hz), 7.44 (2H, d, J = 6 Hz), 7.35 (2H, d, J = 6 Hz), 7.24 (2H, d, J = 6 Hz), 6.63 (1H, s), 5.81 (2H, s), 1.28 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.94, 157.19, 149.77, 141.17, 135.61, 133.96, 132.16, 130.94, 129.69, 129.68, 128.88, 127.78, 126.58, 125.55, 124.71, 59.20, 35.26, 31.23; IR (film, cm^{-1}): 2961, 1716, 1608, 1266, 773, 721; HRMS (ESI^+): Calcd for $C_{26}H_{29}BrNO_4S^+$ $[M+NH_4]^+$: 530.09952 [Br^{79}], 532.09747 [Br^{81}]; Found: 530.09878 [Br^{79}], 532.09643 [Br^{81}].

4.4.6. (2Z)-3-(Benzenesulfonyl)-2-(3-chlorophenyl)prop-2-en-1-yl-4-tert-butylbenzoate **(6ae)**

Eluent: Hexane/Ethyl acetate (15:1); Oil (56 mg, 60%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (2H, d, J = 6 Hz), 7.72 (2H, d, J = 6 Hz), 7.62 (1H, t, J = 6 Hz), 7.55 (2H, t, J = 6 Hz), 7.38–7.29 (4H, m), 7.27–7.25 (2H, m), 6.63 (1H, s), 5.81 (2H, s), 1.28 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.93, 157.16, 149.50, 140.06, 138.58, 134.91, 134.01, 131.55, 130.19, 129.70, 127.82, 127.45, 126.61, 125.53, 59.39, 35.26, 31.23; IR (film, cm^{-1}): 2962, 1717, 1608, 853, 719; HRMS (ESI^+): Calcd for $C_{26}H_{29}ClNO_4S^+$ $[M+NH_4]^+$: 486.15003 [Cl^{35}], 488.14708 [Cl^{37}]; Found: 486.15022 [Cl^{35}], 488.14635 [Cl^{37}].

4.4.7. (2Z)-3-(Benzenesulfonyl)-2-(3,5-dimethylphenyl)prop-2-en-1-yl benzoate **(6af)**

Eluent: Hexane/Ethyl acetate (20:1); Oil (57 mg, 70%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (2H, d, J = 6 Hz), 7.80 (2H, d, J = 6 Hz), 7.58 (1H, t, J = 6 Hz), 7.54–7.46 (3H, m), 7.34 (2H, t, J = 6 Hz), 6.99 (2H, s), 6.97 (1H, s), 6.65 (1H, s), 5.79 (2H, s), 2.25 (6H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ166.06, 150.88, 141.56, 138.55, 136.74, 133.74, 133.27, 132.00, 130.38, 129.82, 129.71, 129.57, 128.45, 127.69, 125.04, 59.8, 21.39; IR (film, cm^{-1}): 2918, 1717, 1599, 1308, 1263, 1146; HRMS (ESI^+): Calcd for $C_{24}H_{26}NO_4S^+$ $[M+NH_4]^+$: 424.15771; Found: 424.15760.

4.4.8. (2Z)-3-(Benzenesulfonyl)-2-(3,5-dimethylphenyl)prop-2-en-1-yl-4-methoxybenzo-ate **(6ag)**

Eluent: Hexane/Ethyl acetate (20:1); Oil (64 mg, 73%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (2H, d, J = 6 Hz), 7.75 (2H, d, J = 6 Hz), 7.58 (1H, t, J = 6 Hz), 7.51 (2H, t, J = 6 Hz), 6.98 (2H, s), 6.97 (1H, s), 6.81 (2H, d, J = 6 Hz), 6.64 (1H, s), 5.75 (2H, s), 3.80 (3H, s), 2.24 (6H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.76, 163.64, 151.17, 141.60, 138.50, 136.80, 133.70, 131.95, 131.89, 130.24, 129.55, 127.68, 125.05, 122.06, 113.70, 59.53, 55.57, 21.39; IR (film, cm^{-1}): 2918, 1711, 1604, 1252, 1146, 1025; HRMS (ESI^+): Calcd for $C_{25}H_{28}NO_5S^+$ $[M+NH_4]^+$: 454.16827; Found: 454.16823.

4.4.9. tert-Butyl-N-[(2Z)-3-(benzenesulfonyl)-2-(4-methylphenyl)-prop -2-en-1-yl]-N-(4-methylbenzenesulfonyl) carbamate **(6ah)**

Eluent: Hexane/Ethyl acetate (20:1); White solid (54 mg, 50%); Melting Point: 69–70 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (2H, d, J = 6 Hz), 7.61 (1H, t, J = 6 Hz), 7.54 (2H, t, J = 6 Hz), 7.52 (2H, t, J = 6 Hz), 7.21 (2H, t, J = 6 Hz), 7.18 (2H, t, J = 6 Hz), 7.11 (2H, t, J = 6 Hz), 6.25 (1H, s), 5.63 (2H, s), 2.39 (3H, s), 2.33 (3H, s), 1.21 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.09, 150.85, 144.48, 141.43, 139.76, 136.99, 133.65, 129.43, 129.37, 129.21, 128.50, 128.04, 127.92, 127.79, 127.48, 84.92, 44.8, 27.85, 21.77, 21.48; IR (film, cm^{-1}): 2979, 1723, 1292, 1144, 1084; HRMS (ESI^+): Calcd for $C_{28}H_{35}N_2O_6S_2^+$ $[M+NH_4]^+$: 559.19310; Found: 559.19346.

4.4.10. tert-Butyl-N-[(2Z)-3-(Benzenesulfonyl)-2-(3,5-dimethylphenyl) prop-2-en-1-yl]-N-(4-methylbenzenesulfonyl) carbamate **(6ai)**

Eluent: Hexane/Ethyl acetate (20:1); White solid (58 mg, 52%); Melting Point: 163–165 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (2H, d, J = 6 Hz), 7.61 (1H, t, J = 6 Hz), 7.55 (2H, t, J = 6 Hz), 7.47 (2H, t, J = 6 Hz), 7.16 (2H, d, J = 6 Hz), 6.98 (1H, s), 6.91 (2H, s), 6.26 (1H, s), 5.62 (2H, s), 2.38 (3H, s), 2.24 (6H, s), 1.20 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.40, 150.89, 144.42, 141.50, 138.18, 137.15, 136.92, 133.67, 131.18, 129.46, 129.37, 128.04, 127.83, 127.54, 125.73, 84.83, 44.81, 27.85, 21.79, 21.36; IR (film, cm^{-1}): 2917, 1734, 1347, 1161, 1083; HRMS (ESI^+): Calcd for $C_{29}H_{37}N_2O_6S_2^+$ $[M+NH_4]^+$: 573.20875; Found: 573.20906.

4.4.11. 2-[(2Z)-3-(Benzenesulfonyl)-2-(3,5-dimethylphenyl)prop-2-en-1-yl]-2,3-dihydro-1H-isoindole-1,3-dione **(6aj)**

Eluent: Hexane/Ethyl acetate (20:1); White solid (40 mg, 46%); Melting Point: 168–170 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (2H, d, J = 6 Hz), 7.70–7.67 (2H, m), 7.61 (1H, t, J = 6 Hz), 7.63–7.58 (4H, m), 6.83 (2H, s), 6.81 (1H, s), 6.44 (1H, s), 5.47 (2H, s), 2.14 (6H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.73, 152.24, 141.32, 138.32, 136.40, 134.14, 133.78, 131.81, 131.68, 129.52, 129.16, 127.90, 124.86, 123.41, 35.85, 21.23; IR (film, cm^{-1}): 3017, 1770, 1715, 751, 715; HRMS (ESI^+): Calcd for $C_{25}H_{25}N_2O_4S^+$ $[M+NH_4]^+$: 449.15295; Found: 449.15215.

4.5. General procedure for the study of allylic alcohol derivation to synthesize compounds (**5a-5b, 6a-6d**, Scheme 6)

4.5.1. (2Z)-3-(benzenesulfonyl)-2-phenylprop-2-en-1-ol **(5a)**

To an oven-dried screw-capped vial was added **4a** (0.2 mmol, 77 mg), KF (23 mg, 2 eq.) and MeCN (3 mL), then TMSCl (21 mg, 1 eq.) was added into the white suspension. The mixture was stirred at room temperature and monitored by TLC (Hexane/Ethyl acetate = 2/1). After completion of the reaction, all of the volatiles were removed by rotary evaporation and the residue was purified by column chromatography to yield pure product **5a** as white solid (50 mg, 91%). Melting point: 82–83 °C; ^{1}H NMR (600 MHz, C_6D_6) δ 7.86–7.82 (2H, m), 7.05–7.03 (2H, m), 7.01–6.88 (6H, m), 6.40 (1H, s), 4.76 (2H, d, J = 6 Hz), 2.98 (1H, br s); ^{13}C NMR (150 MHz, C_6D_6) δ 156.04, 142.71, 138.87, 133.52, 130.09, 130.07, 129.69, 129.13, 128.68, 127.92, 127.63, 60.29; IR (neat, cm^{-1}): 3500, 1597, 1443, 1301, 1174, 1082, 1033, 836, 771; HRMS (ESI^+): Calcd for $C_{15}H_{15}O_3S^+$ $[M+H]^+$: 275.07364; Found: 275.07338.

4.5.2. [(1Z)-1-(benzenesulfonyl)-3-bromoprop-1-en-2-yl] benzene **(5b)**

To an oven-dried screw-capped vial was added **5a** (0.1 mmol, 27 mg), PPh_3 (52 mg, 2 eq.), DDQ (45 mg, 2 eq.) and CH_2Cl_2 (3 mL) followed by addition of TBAB (96 mg, 1.5 eq.). The mixture was stirred at room temperature and monitored by TLC (Hexane/Ethyl acetate = 2/1). After completion of the reaction, volatiles were removed by rotary evaporation and the residue was purified by column chromatography to yield pure product **5b** as colorless oil (28 mg, 83%). ^{1}H NMR (600 MHz, C_6D_6) δ 8.00–7.97 (2H, m), 6.99–6.92 (4H, m), 6.91–6.84 (4H, m), 6.34 (1H, s), 4.79 (2H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 150.32, 142.28, 137.73, 133.71, 130.40, 130.24, 129.71, 129.19, 128.68, 127.40, 25.09; IR (neat, cm^{-1}): 1597, 1445, 1304, 1083, 806; HRMS (ESI^+): Calcd for $C_{15}H_{14}BrO_2S^+$ $[M+H]^+$: 336.98924[Br^{79}], 338.98719[Br^{81}]; Found: 336.98928

[Br^{79}], 338.98725[Br^{81}].

4.5.3. (2Z)-3-(benzenesulfonyl)-2-phenylprop-2-en-1-yl acetate (6a)

To an oven-dried screw-capped vial was added **5a** (0.35 mmol, 97 mg), Et_3N (42 mg, 1.2 eq.) and CH_2Cl_2 (3 mL) followed by slow addition of AcCl (30 mg, 1.1 eq.). The mixture was stirred at room temperature and monitored by TLC (Hexane/Ethyl acetate = 2/1). After completion of the reaction, volatiles were removed by rotary evaporation and the residue was purified by column chromatography to yield pure product **6a** as colorless oil (108 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (2H, d, J = 6 Hz), 7.63 (1H, t, J = 6 Hz), 7.56 (2H, t, J = 6 Hz), 7.39–7.28 (5H, m), 6.57 (2H, s), 5.58 (2H, s), 1.86 (3H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 170.47, 150.85, 141.38, 136.61, 133.86, 130.47, 130.27, 129.60, 128.91, 127.69, 127.28, 59.20, 20.74; IR (neat, cm^{-1}): 1738, 1604, 1445, 1306, 1227; HRMS (ESI^+): Calcd for $C_{17}H_{16}NaO_4S^+$ $[M+Na]^+$: 339.06615; Found: 339.06637.

4.5.4. 2-[(2E)-3-(benzenesulfonyl)-2-phenylprop-2-en-1-yl]-1,3-di-tert-butyl propanedioate (6b)

To an oven-dried screw-capped vial was added $Pd_2(dba)_3$ (0.0025 mmol, 2.5 mol%, 2.8 mg), PPh_3 (0.015 mmol, 15 mol%, 3.9 mg), **6a** (0.10 mmol, 31 mg), K_3PO_4 (53 mg, 2.5 eq.), and dry THF (2 mL) followed by slow addition of di-*tert*-butyl propanedioate (52 mg, 1.2 eq.) solution in dry THF (1 mL). The mixture was stirred at 45 °C and monitored by TLC (Hexane/Ethyl acetate = 7/1). After completion of the reaction, all of the volatiles were removed by rotary evaporation and the residue was purified by column chromatography to yield pure product **6b** as white solid (32 mg, 68%). Melting point 91–92 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 6 Hz), 7.59 (1H, t, J = 6 Hz), 7.52 (2H, t, J = 6 Hz), 7.35–7.27 (5H, m), 6.39 (1H, s), 3.60 (2H, d, J = 6 Hz), 3.31 (1H, t, J = 6 Hz), 1.31 (18H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.78, 154.95, 141.97, 139.02, 133.53, 129.99, 129.86, 129.47, 128.94, 127.66, 127.34, 81.99, 53.33, 28.71, 27.91; IR (film, cm^{-1}): 1740, 1718, 1366, 1274, 1146; HRMS (ESI^+): Calcd for $C_{26}H_{32}NaO_6S^+$ $[M+H]^+$: 495.18118; Found: 495.18149.

4.5.5. [3-(Benzenesulfonyl)prop-1-en-2-yl]benzene (6c)[20]

To an oven-dried screw-capped vial was added $Pd(OAc)_2$ (0.005 mmol, 5 mol%, 1.1 mg), **6a** (0.10 mmol, 31 mg), $B_2(pin)_2$ (0.22 mmol, 2.2 eq., 56 mg) and degassed DMSO (2 mL). The mixture was stirred at 60 °C and monitored by TLC (Hexane/Ethyl acetate = 7/1). After completion of the reaction, water (3 mL) was added into the mixture and extracted with ether (3 mL × 3), the organic phase was collected and washed with brine (5 mL). Ether was removed by rotary evaporation and the residue was purified by column chromatography to yield pure product **6c** as white solid (19 mg, 74%). ^{1}H NMR (600 MHz, C_6D_6) δ 7.64 (2H, d, J = 6 Hz), 7.11–7.07 (2H, m), 7.01–6.96 (3H, m), 6.87 (1H, t, J = 6 Hz), 6.79 (2H, t, J = 6 Hz), 5.28 (1H, s), 4.93 (1H, s), 3.86 (2H, s); ^{13}C NMR (150 MHz, C_6D_6) δ 139.97, 139.76, 137.63, 133.35, 129.27, 129.03, 128.83, 126.96, 121.62, 62.18.

4.5.6. N-[(2Z)-3-(benzenesulfonyl)-2-phenylprop-2-en-1-yl]aniline (6d)

To an oven-dried screw-capped vial was added $Pd_2(dba)_3$ (0.00375 mmol, 2.5 mol%, 4.3 mg), dppf (0.0075 mmol, 5 mol%, 4.0 mg), **6a** (0.15 mmol, 48 mg), aniline (0.165 mmol, 1.1 eq., 15.4 mg) and dry toluene (2 mL). The mixture was stirred at 70 °C and monitored by TLC (Hexane/Ethyl acetate = 7/1). After completion of the reaction, volatiles were removed by rotary evaporation and the residue was purified by column chromatography to yield pure product **6d** as solid (36 mg, 69%). Melting point 137–138 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 6 Hz), 7.63 (1H, t, J = 6 Hz), 7.54 (2H, t, J = 6 Hz), 7.37–7.30 (5H, m), 7.11 (2H, t, J = 6 Hz), 6.71 (1H, t, J = 6 Hz), 6.63 (1H, s), 6.54 (2H, d, J = 6 Hz), 4.67 (2H, s), 3.82 (1H, br, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.50, 147.40, 141.72, 138.03, 133.78, 130.23, 130.16, 129.62, 129.36, 129.06, 127.59, 127.07, 118.47, 113.75, 42.65; IR (film, cm^{-1}): 3383, 1601, 1506, 1297, 1133; HRMS (ESI^+): Calcd for $C_{21}H_{20}NO_2S^+$ $[M+H]^+$: 350.12093; Found: 350.12115.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2017.08.021.

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