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Studies on highly regio- and stereoselective fluorohydroxylation reaction of 3-aryl-1,2-allenyl phosphine oxides with Selectfluor

Guangke He, Chunling Fu *, Shengming Ma *

Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027, Zhejiang, PR China

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ABSTRACT

The fluorohydroxylation of allenyl phosphine oxides with Selectfluor in commercial MeCN without prior treatment or a mixed solvent of anhydrous MeCN (refluxed over CaH_2 and distilled before use) and 7.0 equiv of H_2O or $MeNO_2/H_2O$=10/1 afforded 2-fluoro-3-hydroxy-1(*E*)-alkenyl diphenyl phosphine oxides in moderate yields with very high regio- and stereoselectivities. The *E*-stereoselectivity is believed to be controlled by the phosphine oxide functionality. In the reaction of 3-(4-methoxyphenyl)-1,2-propadienyl diphenyl phosphine oxide, further fluorination on the electron-rich phenyl ring was also observed.

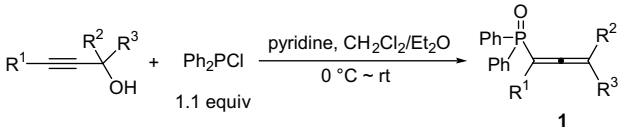
1. Introduction

Organofluorine compounds are playing a great role in pharmaceuticals owing to their unique physical and biological properties.[1,2] Similarly, organophosphorous compounds also show synthetic potential.[3a–g] It is well known that monofluorination towards organic molecules is not easy.[4] Recently, we observed that electrophilic reaction of some allenes provides an efficient pathway for the monofluorination, for example, β-fluorolactonization of 1,2-allenoic acids[5] and fluorohydroxylation of 3-aryl-1,2-allenes.[6] As a part of our research program aimed at exploring novel synthetic methodology for producing mono-fluorinated compounds, the electrophilic fluorination of 1,2-allenylic phosphine oxides is of interest to us. In this paper we wish to disclose a highly regio- and stereoselective protocol of fluorohydroxylation reaction of 3-aryl-1,2-allenylic phosphine oxides.

2. Results and discussion

It is well known that 3-aryl-1,2-allenylic diphenyl phosphine oxides **1** can be easily prepared from the reaction of corresponding propargylic alcohols with Ph_2PCl.[7] Thus, the starting materials used in this studies were synthesized accordingly (Table 1). On the other hand, among all kinds of electrophilic fluorination reagents, Selectfluor (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo-[2.2.2]octane-bis(tetrafluoroborate) is an effective one because of its availability, reliability, and mildness.[8–10]

Table 1
Synthesis of 3-aryl-1,2-allenylic diphenyl phosphine oxides (**1**)[7]



1

Entry	R^1	R^2	R^3	Isolated yield of **1** (%)
1	H	Me	Ph	63 (**1a**)
2	H	Et	Ph	55 (**1b**)
3	H	Ph	Ph	54 (**1c**)
4	*n*-C_4H_9	Me	Ph	45 (**1d**)
5	Ph	Me	Ph	51 (**1e**)
6	H	H	Ph	75 (**1f**)
7[a]	H	H	4-$NO_2C_6H_4$	69 (**1g**)
8	H	H	4-FC_6H_4	58 (**1h**)
9	H	H	4-ClC_6H_4	52 (**1i**)
10	H	H	3-ClC_6H_4	68 (**1j**)
11	H	H	2-ClC_6H_4	46 (**1k**)
12	H	H	4-MeC_6H_4	44 (**1l**)
13	*n*-C_4H_9	H	Ph	62 (**1m**)
14	Ph	H	Ph	54 (**1n**)
15	H	H	4-$MeOC_6H_4$	20 (**1o**)

[a] The reaction was conducted at −40 °C.

According to our previous experimental results on the electrophilic reaction of allenes,[5,6,11–14] MeCN/H_2O was a good solvent system for electrophilic addition reactions of allenes. When a mixture of MeCN/H_2O (10:1) was used as the solvent, 3-phenylbuta-1,2-dienyl diphenyl phosphine oxide **1a** reacted with 1.5 equiv of Selectfluor at 80 °C to give 2-fluoro-3-hydroxy-3-phenyl-1(*E*)-butenyl diphenyl phosphine oxide *E*-**2a** in moderate yield together with the formation of 2-fluoro-3-phenylbuta-1(*E*),3-

* Corresponding authors.
E-mail addresses: fucl@zju.edu.cn (C. Fu), masm@mail.sioc.ac.cn (S. Ma).

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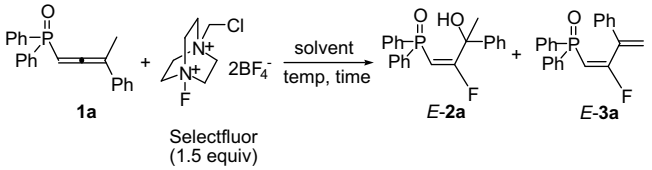
dienyl diphenyl phosphine oxide *E*-**3a** (entry 1, Table 2). Obviously, the ratio of *E*-**2a**/*E*-**3a** was not satisfactory. Considering the hydroxyl group in *E*-**2a** was formed from the water in the reaction medium, more water was added, however, the yield of *E*-**2a** and the ratio of *E*-**2a**/*E*-**3a** were essentially the same (entries 2–3, Table 2). The reaction in pure H_2O afforded the products in much lower yields with an *E*-**2a**/*E*-**3a** ratio of 95:5 (entry 4, Table 2). Furthermore, the selectivity was not very much improved by conducting the reaction at 60 °C or even lower (entries 5–6, Table 2). Surprisingly, the fluorohydroxylation reaction in commercial MeCN without prior treatment afforded *E*-**2a** exclusively in 66% isolated yield, indicating that the trace amount of water in MeCN is just enough for this transformation (entry 7, Table 2). In fact, it was found that the reaction proceeded smoothly in anhydrous MeCN (refluxed over CaH_2 and distilled before use) in the presence of 7 equiv of H_2O (entry 8, Table 2). Suitable amount of water is providing the hydroxyl group in the product *E*-**2a**.

Table 2
Fluorohydroxylation of 3-phenylbuta-1,2-dienyl diphenyl phosphine oxide (**1a**) with Selectfluor[a]



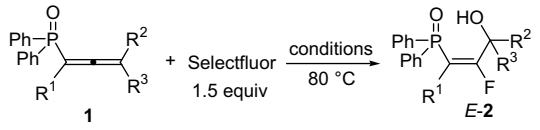
Entry	MeCN/H_2O	Temp (°C)	Time (h)	NMR yield of *E*-**2a** and *E*-**3a** (%)[b]	Ratio of *E*-**2a**/*E*-**3a**[c]
1	10/1	80	2.0	80	92/8
2	5/1	80	1.5	85	91/9
3	3/1	80	4.0	83	92/8
4	0/1	80	51.0	57	95/5
5	10/1	60	6.0	78	91/9
6	10/1	40	10.0	81	90/10
7	1/0[d]	80	2.0	71 (66)	>99/1
8	1/0[e]	80	2.0	66 (64)	>99/1

[a] The reaction was carried out using 0.2 mmol of **1a**, 0.3 mmol of Selectfuor, 2.3 mL of solvent.
[b] NMR yield based on **1a** using CH_2Br_2 as the internal standard.
[c] The ratio of *E*-**2a**/*E*-**3a** was determined by ^1H NMR analysis of the crude product.
[d] Commercial MeCN was used without prior treatment.
[e] Anhydrous MeCN was used together with 7 equiv H_2O.

Having established the optimized fluorohydroxylation conditions **A** (entry 7, Table 1) and conditions **B** (entry 8, Table 1), attention was paid to study the scope and the limitation of the present method. For 3,3-disubstituted 1,2-allenylic diphenyl phosphine oxides, the yields ranged from 62 to 86% (entries 1–6, Table 3); for fully substituted substrates, the reaction could also proceed smoothly (entries 7–10, Table 3). In addition, it was observed that if the phenyl at the 3-position was replaced with a vinyl or ethyl group, the yield was rather low. Thus, the existence of an aryl group at 3-position in the starting materials is necessary.

When 3-phenyl-1,2-propadienyl diphenyl phosphine oxide **1f** was subjected to the above conditions, the NMR yield of fluorohydroxylation product *E*-**2f** was only 58%. Any other adjustments referring to the ratio of MeCN/H_2O had no obvious influence even with 3.0 equiv of Selectfluor (entries 1–5, Table 4), which prompted us to screen other solvents. Surprisingly, when $MeNO_2$ was used in place of MeCN, the fluorohydroxylation reaction was remarkably improved to form the expected product *E*-**2f** in 88% NMR yield (62% isolated) (entry 7, Table 4). In

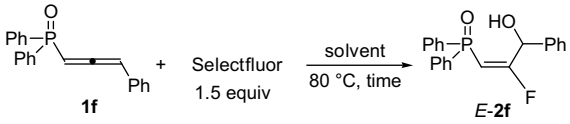
Table 3
Fluorohydroxylation of differently substituted 1,2-propadienyl diphenyl phosphine oxides **1** with Selectfluor



Entry	R^1	R^2	R^3	Conditions[a]	Time (h)	Isolated yield of *E*-**2** (%)
1	H	Me	Ph (**1a**)	A	2.0	66 (**2a**)
2	H	Me	Ph (**1a**)	B	2.0	64 (**2a**)
3	H	Et	Ph (**1b**)	A	3.0	62 (**2b**)
4	H	Et	Ph (**1b**)	B	3.0	70 (**2b**)
5	H	Ph	Ph (**1c**)	A	2.0	78 (**2c**)
6	H	Ph	Ph (**1c**)	B	3.0	85 (**2c**)
7	n-C_4H_9	Me	Ph (**1d**)	A	15.0	66 (**2d**)
8	n-C_4H_9	Me	Ph (**1d**)	B	14.0	74 (**2d**)
9	Ph	Me	Ph (**1e**)	A	12.0	70 (**2e**)
10	Ph	Me	Ph (**1e**)	B	16.0	75 (**2e**)

[a] *Conditions A*. The reaction was carried out using 0.3 mmol of **1**, 0.45 mmol of Selectfluor, 3.5 mL of commercial MeCN. *Conditions B*. The reaction was carried out using 0.2 mmol of **1**, 0.3 mmol of Selectfluor, 2.25 mL of anhydrous MeCN (refluxed over CaH_2) and 7.0 equiv of H_2O in the atmosphere of N_2.

Table 4
Screening of reaction conditions for the reaction of 3-phenylpropa-1,2-dienyl diphenyl phosphine oxide (**1f**) with Selectfluor[a]



Entry	Solvent	Time (h)	NMR yield of *E*-**2f** (%)[b]
1	MeCN	23.5	58
2	MeCN/H_2O=20/1	24.0	63
3	MeCN/H_2O=10/1	11.0	68
4[c]	MeCN/H_2O=10/1	11.5	60
5	MeCN/H_2O=5/1	13.0	40
6	DMF/H_2O=10/1	54.5	32
7	$MeNO_2$/H_2O=10/1	20.0	88 (62)
8[d]	$MeNO_2$/H_2O=10/1	24.0	55
9[e]	$MeNO_2$/H_2O=10/1	33.0	69

[a] The reaction was carried out using 0.2 mmol of **1f**, 0.3 mmol of Selectfluor, 2.2 mL of solvent.
[b] NMR yield based on **1f** using CH_2Br_2 as the internal standard.
[c] Using 3.0 equiv of Selectfluor.
[d] Using 1.2 equiv of Selectfluor.
[e] The reaction was conducted at 60 °C.

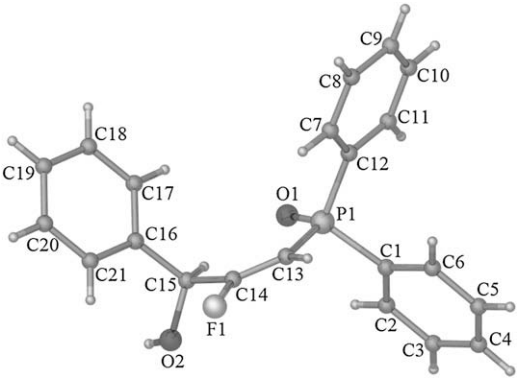
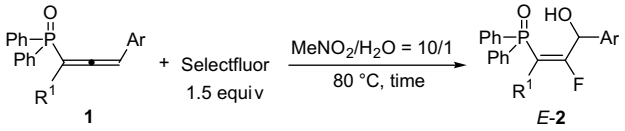


Figure 1. ORTEP representation of *E*-**2f**.

addition, the transformation is less efficient with a less amount of Selectfluor or at lower temperature (entries 8–9, Table 4). The regio- and stereochemical issue was further confirmed by X-ray diffraction study of *E*-**2f** (Fig. 1).[15]

Next, the scope for the differently substituted aryl group at the 3-position was explored. By comparing the results listed in entries 4–6 of Table 5, it was concluded that the steric effect of the substituents on the aryl group is not serious. When there is a strong electron-withdrawing substituent on the benzene ring, such as nitro group, the transformation was complete requiring 2.5 equiv of Selectfluor producing *E*-**2g** in only 33% yield (entry 2, Table 5). In addition to H, both C_4H_9 and phenyl group may be introduced to the 1-position of the starting 3-aryl-1,2-allenyl phosphine oxides (entries 8–9, Table 5).

Table 5
Fluorohydroxylation of 3-aryl substituted 1,2-propadienyl diphenyl phosphine oxides **1** with Selectfluor[a]



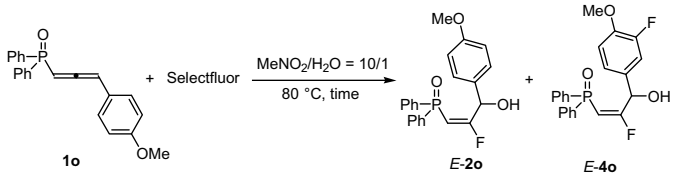
Entry	R^1	Ar	Time (h)	Isolated yield of *E*-**2** (%)
1	H	C_6H_5 (**1f**)	20.0	62 (**2f**)
2[b]	H	4-$NO_2C_6H_4$ (**1g**)	28.0	33 (**2g**)
3	H	4-FC_6H_4 (**1h**)	10.0	72 (**2h**)
4	H	4-ClC_6H_4 (**1i**)	12.0	56 (**2i**)
5[c,d]	H	3-ClC_6H_4 (**1j**)	24.0	50 (**2j**)
6	H	2-ClC_6H_4 (**1k**)	33.0	56 (**2k**)
7[e]	H	4-MeC_6H_4 (**1l**)	25.0	63 (**2l**)
8[c,d]	*n*-C_4H_9	C_6H_5 (**1m**)	24.0	59 (**2m**)
9[d]	C_6H_5	C_6H_5 (**1n**)	12.5	67 (**2n**)

[a] The reaction was carried out using 0.3 mmol of **1f**–**n**, 0.45 mmol of Selectfluor, 3.0 mL of $MeNO_2$, and 0.3 mL of H_2O.
[b] 2.5 equiv of Selectfluor were used.
[c] 2.0 equiv of Selectfluor were used.
[d] The pure product was obtained by means of recrystallization after chromatography on silica gel (see Supplementary data for detailed information).
[e] The reaction temperature was 40 °C.

For 3-(4-methoxyphenyl)propa-1,2-dienyl diphenyl phosphine oxide **1o**, the reaction afforded not only the normal product *E*-**2o** but also the double fluorinated *E*-**4o** under the optimized conditions **B** (entry 1, Table 6) and it is difficult to separate these two products by flash column chromatography on silica gel. After trial and error, we observed that by employing 0.9 equiv of Selectfluor at rt the reaction afforded *E*-**2o** highly selectively with an *E*-**2o**/*E*-**4o** ratio as high as 97:3 (entry 4, Table 6); in addition, *E*-**4o** can also be obtained as the only product by using 3.5 equiv of Selectfluor (entry 5, Table 6). Furthermore, the transformation from *E*-**2o** to *E*-**4o** can also be realized when employing 2.2 equiv Selectfluor (Eq. 1). The position of the fluorine atom in the methoxy-substituted phenyl ring was also confirmed by X-ray diffraction study (Fig. 2).[16]

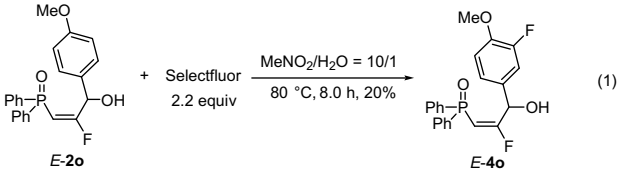
On the basis of previous results,[17] a plausible mechanism was proposed: firstly, the fluorinonium intermediate **3** is afforded by the interaction of the relatively electron-rich carbon-carbon double bond in allene **1** with F^+. Subsequently, a five-membered cyclic intermediate **4** is formed via neighboring group paticipation of the oxygen atom of the diphenyl phosphine oxide functionality. Finally, water molecule attacks the positively charged phosphorous atom to cleave the P–O bond, forming the final product *E*-**2** (Scheme 1).

Table 6
Fluorohydroxylation of 3-(4-methoxyphenyl)-1,2-propadienyl diphenyl phosphine oxide **1o** with different amount of Selectfluor[a]



Entry	Selectfluor (equiv)	Time (h)	NMR yield of *E*-**2o** and *E*-**4o** (%)[b]	Ratio of *E*-**2o**/*E*-**4o**[c]
1	1.5	7.0	38	65/35
2	2.5	5.0	41	29/71
3	3.0	8.0	43	8/92
4[d]	0.9	8.0	69 (45)[e]	97/3
5	3.5	8.0	25 (14)[e]	0/100

[a] The reaction was carried out using 0.3 mmol of **1o**, Selectfluor (0.9–3.5 equiv), 3.0 mL of $MeNO_2$, and 0.3 mL of H_2O.
[b] *E*-**2o** and *E*-**4o** can not be separated by flash column chromatography.
[c] The ratio of *E*-**2o**/*E*-**4o** was determined by ^1H NMR analysis after purification of the crude product by flash column chromatography on silica gel.
[d] The reaction was carried out at rt.
[e] Isolated yields.



(1)

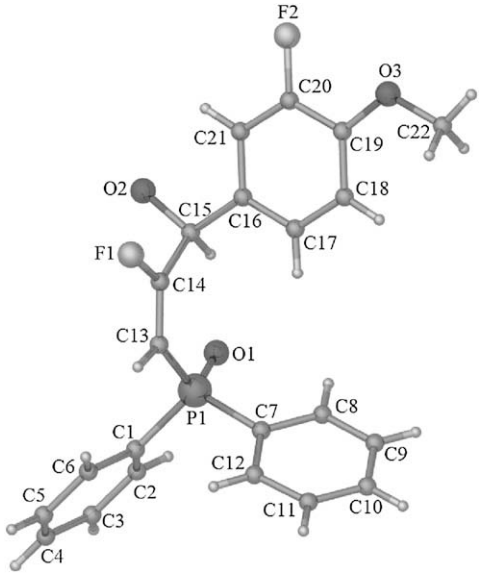
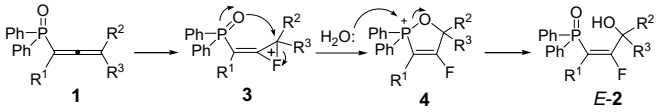


Figure 2. ORTEP representation of *E*-**4o**.



Scheme 1. The proposed mechanism.

3. Conclusions

In conclusion, we have developed a method for the synthesis of 3-aryl-2-fluoro-3-hydroxy-1(*E*)-alkenyl diphenyl phosphine oxides

with high regio- and stereoselectivity from the readily available 3-aryl-1,2-allenyl phosphine oxides and Selectfluor. The stereoselectivity is controlled by the neighboring group participation of the diphenyl phosphine oxide functionality as observed in our laboratory.[17] Further studies are underway in our laboratory.

4. Experimental

4.1. Starting materials

Known compounds **1c** and **1f** were prepared according to the published procedure.[7] New compounds **1a**–**1b**, **1d**–**1e**, and **1g**–**1o** were also prepared according to this procedure.[7] Select fluor (95%) was purchased from YouLong Chemicals in China. In other cases, select fluor was ordered from Alfa Aesar. Due to the coupling between ^{13}C, ^{31}P, and ^{19}F, the ^{13}C NMR spectra are very complicated, however, these spectra are provided in Supplementary data.

*4.1.1. 3-Phenylbuta-1,2-dienyl diphenyl phosphine oxide (**1a**)*

4.1.1.1. Typical procedure I. To an oven-dried three-necked round-bottom flask were subsequently added 2-phenylbut-3-yn-2-ol (1.4643 g, 10 mmol), pyridine (0.96 mL, d=0.9831 g/mL, 0.94 g, 11.9 mmol), and 10 mL of Et_2O. After the mixture was cooled to 0 °C with an ice-salt bath, a solution of diphenylphosphinous chloride (2.00 mL, d=1.204 g/mL, 2.41 g, 10.9 mmol) in 11 mL of CH_2Cl_2 was added dropwise at 0 °C with stirring within 1 h. After being kept for 1 h at this temperature, the reaction mixture was allowed to warm up naturally to room temperature and stirred at this temperature for 7 h. The solution was then poured into a flask containing smashed ice and the aqueous layer was then extracted with 30×3 mL of CH_2Cl_2. The combined organic layer was washed with 20 mL of brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, chromatography on silica gel (eluent: dichloromethane/ethyl acetate=10:1 to 5:1) of the crude product afforded **1a** (2.0732 g, 63%) as a white solid: mp 79.5–80.5 °C (Et_2O/CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.81–7.69 (m, 4H), 7.54–7.35 (m, 6H), 7.32–7.25 (m, 2H), 7.25–7.16 (m, 3H), 6.19–6.12 (m, 1H), 1.93 (dd, J_1=6.2 Hz, J_2=3.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.0 (d, J_{pc}=1.9 Hz), 133.8 (d, J_{pc}=86.5 Hz), 133.7 (d, J_{pc}=89.8 Hz), 131.8 (d, J_{pc}=2.3 Hz), 131.7, 131.3 (d, J_{pc}=10.5 Hz), 128.4 (d, J_{pc}=1.4 Hz), 128.2 (d, J_{pc}=1.4 Hz), 127.4, 125.7 (d, J_{pc}=2.2 Hz), 103.1 (d, J_{pc}=13.9 Hz), 87.6 (d, J_{pc}=103.3 Hz), 15.7 (d, J_{pc}=6.7 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.3; MS (EI, 70 eV) m/z (%) 331 (M^++1, 10), 330 (M^+, 50), 201 (100); IR ν (KBr, cm^{-1}) 3055, 2924, 1936, 1595, 1494, 1437, 1347, 1198, 1119, 1103, 1068. Anal. Calcd for $C_{22}H_{19}OP$: C, 79.98; H, 5.80. Found: C, 79.89; H, 5.88.

The following compounds were prepared according to Typical procedure I.

*4.1.2. 3-Phenylpenta-1,2-dienyl diphenyl phosphine oxide (**1b**)*

The reaction of 3-phenylpent-1-yn-3-ol (1.6058 g, 10 mmol), pyridine (0.96 mL, d=0.9831 g/mL, 0.94 g, 11.9 mmol), and Ph_2PCl (2.00 mL, d=1.204 g/mL, 2.41 g, 10.9 mmol) in a mixed solvent (11 mL of CH_2Cl_2 and 10 mL of Et_2O) afforded **1b** (1.8842 g, 55%) as a yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80–7.67 (m, 4H), 7.54–7.34 (m, 6H), 7.34–7.16 (m, 5H), 6.23 (q, J=3.6 Hz, 1H), 2.39–2.13 (m, 2H), 0.93 (d, J=7.4 Hz, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.4; MS (EI, 70 eV) m/z (%) 345 (M^++1, 3), 344 (M^+, 18), 201 (100); IR ν (neat, cm^{-1}) 3056, 2968, 2933, 2875, 1935, 1596, 1494, 1449, 1437, 1357, 1309, 1229, 1199, 1120, 1104, 1071; HRMS calcd for $C_{23}H_{21}OP$: 344.1330. Found: 344.1335.

*4.1.3. 2-Phenylocta-2,3-dien-4-yl diphenyl phosphine oxide (**1d**)*

The reaction of 2-phenyloct-3-yn-2-ol (1.6205 g, 8 mmol), pyridine (0.78 mL, d=0.9831 g/mL, 0.77 g, 9.7 mmol), and Ph_2PCl (1.60 mL, d=1.204 g/mL, 1.93 g, 8.7 mmol) in a mixed solvent (9 mL of CH_2Cl_2 and 10 mL of Et_2O) afforded **1d** (1.4010 g, 45%) as a colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76–7.63 (m, 4H), 7.52–7.10 (m, 11H), 2.48–2.32 (m, 2H), 1.83 (d, J=6.6 Hz, 3H), 1.63–1.48 (m, 2H), 1.42–1.24 (m, 2H), 0.85 (t, J=7.4 Hz, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 30.9; MS (EI, 70 eV) m/z (%) 387 (M^++1, 5), 386 (M^+, 16), 201 (100); IR ν (neat, cm^{-1}) 3056, 2956, 2928, 2859, 1931, 1597, 1494, 1460, 1437, 1369, 1195, 1117, 1101, 1067, 1027; HRMS calcd for $C_{26}H_{27}OP$: 386.1800. Found: 386.1808.

*4.1.4. 1,3-Diphenylbuta-1,2-dienyl diphenyl phosphine oxide (**1e**)*

The reaction of 2,4-diphenybut-3-yn-2-ol (1.7846 g, 8.0 mmol), pyridine (0.78 mL, d=0.9831 g/mL, 0.77 g, 9.7 mmol), and Ph_2PCl (1.60 mL, d=1.204 g/mL, 1.93 g, 8.7 mmol) in a mixed solvent (9 mL of CH_2Cl_2 and 10 mL of Et_2O) afforded **1e** (1.6770 g, 51%) as a colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79–7.65 (m, 6H), 7.48–7.12 (m, 14H), 1.85 (d, J=6.0 Hz, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 31.0; MS (EI, 70 eV) m/z (%) 407 (M^++1, 15), 406 (M^+, 48), 205 (100); IR ν (neat, cm^{-1}) 3056, 2922, 1924, 1596, 1493, 1437, 1357, 1195, 1118, 1102, 1067, 1027; HRMS calcd for $C_{28}H_{23}OP$: 406.1487. Found: 406.1476.

*4.1.5. 3-(4-Fluorophenyl)propa-1,2-dienyl diphenyl phosphine oxide (**1h**)*

The reaction of 1-(4-fluorophenyl)prop-2-yn-1-ol (1.5085 g, 10.0 mmol), pyridine (0.96 mL, d=0.9831 g/mL, 0.94 g, 11.9 mmol), and Ph_2PCl (2.00 mL, d=1.204 g/mL, 2.41 g, 10.9 mmol) in a mixed solvent (11 mL of CH_2Cl_2 and 10 mL of Et_2O) afforded **1h** (1.9396 g, 58%) as a white solid: mp 124.5–125.8 °C (acetone/dichloromethane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.84–7.70 (m, 4H), 7.56–7.36 (m, 6H), 7.14–7.06 (m, 2H), 6.99–6.90 (m, 2H), 6.36–6.21 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.8 (t, J=2.0 Hz), 162.12 (d, J_{pc}=246.2 Hz), 162.10 (d, J_{pc}=246.1 Hz), 132.8 (d, J_{pc}=7.4 Hz), 131.97 (d, J_{pc}=3.8 Hz), 131.93 (d, J_{pc}=2.3 Hz), 131.4 (d, J_{pc}=8.1 Hz), 131.2 (d, J_{pc}=9.4 Hz), 131.1 (d, J_{pc}=9.5 Hz), 128.5–128.3 (m, 1C), 128.3 (d, J_{pc}=2.6 Hz), 127.1 (dd, J_1=7.0 Hz, J_2=3.5 Hz), 115.6 (dd, J_1=22.4 Hz, J_2=1.7 Hz), 95.3 (d, J_{pc}=13.1 Hz), 89.9 (d, J_{pc}=100.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −113.6 (d, J_{PF}=2.5 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.7 (d, J_{FP}=3.4 Hz); MS (EI, 70 eV) m/z (%) 335 (M^++1, 12), 334 (M^+, 50), 201 (100); IR ν (KBr, cm^{-1}) 3078, 3051, 2979, 2954, 1939, 1594, 1505, 1437, 1221, 1186, 1155, 1123, 1106. Anal. Calcd for $C_{21}H_{16}FOP$: C, 75.44; H, 4.82. Found: C, 75.09; H, 4.99.

*4.1.6. 3-(4-Chlorophenyl)propa-1,2-dienyl diphenyl phosphine oxide (**1i**)*

The reaction of 1-(4-chlorophenyl)prop-2-yn-1-ol (2.1640 g, 13 mmol), pyridine (1.25 mL, d=0.9831 g/mL, 1.23 g, 15.6 mmol), and Ph_2PCl (2.60 mL, d=1.204 g/mL, 3.13 g, 14.2 mmol) in a mixed solvent (14 mL of CH_2Cl_2 and 13 mL of Et_2O) afforded **1i** (2.3597 g, 52%) as a white solid: mp 159.3–160.0 °C (Et_2O/CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.84–7.70 (m, 4H), 7.57–7.37 (m, 6H), 7.26–7.20 (m, 2H), 7.06 (d, J=8.1 Hz, 2H), 6.32 (dd, J_1=6.6 Hz, J_2=2.1 Hz, 1H), 6.25 (dd, J_1=10.5 Hz, J_2=6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.9 (d, J_{pc}=1.3 Hz), 133.4 (d, J_{pc}=2.1 Hz), 132.7 (d, J_{pc}=8.6 Hz), 132.1 (d, J_{pc}=2.7 Hz), 132.0 (d, J_{pc}=2.7 Hz), 131.3 (d, J_{pc}=10.3 Hz), 131.2 (d, J_{pc}=9.9 Hz), 130.6 (d, J_{pc}=113.8 Hz), 130.5 (d, J_{pc}=111.5 Hz), 128.9 (d, J_{pc}=1.4 Hz), 128.43 (d, J_{pc}=12.5 Hz), 128.40 (d, J_{pc}=12.5 Hz), 128.1 (d, J_{pc}=2.2 Hz), 95.4 (d, J_{pc}=13.1 Hz), 90.1 (d, J_{pc}=100.7 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.7; MS (EI, 70 eV) m/z (%) 353 (M^+ (^{37}Cl)+1, 3), 352 (M^+ (^{37}Cl), 13), 351 (M^+ (^{35}Cl)+1, 10), 350 (M^+ (^{35}Cl), 36), 201 (100); IR ν (KBr, cm^{-1}) 3057, 2983, 2952, 1940, 1488, 1436, 1414, 1186, 1121, 1105, 1091, 1012. Anal. Calcd for $C_{21}H_{16}ClOP$: C, 71.90; H, 4.60. Found: C, 71.90; H, 4.60.

*4.1.7. 3-(3-Chlorophenyl)propa-1,2-dienyl diphenyl phosphine oxide (**1j**)*

The reaction of 1-(3-chlorophenyl)prop-2-yn-1-ol (1.3371 g, 8.0 mmol), pyridine (0.75 mL, d=0.9831 g/mL, 0.74 g, 9.3 mmol), and

Ph_2PCl (1.60 mL, d=1.204 g/mL, 1.93 g, 8.7 mmol) in a mixed solvent (9 mL of CH_2Cl_2 and 8 mL of Et_2O) afforded **1j** (1.9008 g, 68%) as a white solid: mp 83.7–85.0 °C (Et_2O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.83–7.71 (m, 4H), 7.56–7.38 (m, 6H), 7.23–7.13 (m, 2H), 7.11–6.96 (m, 2H), 6.34 (dd, J_1=6.6 Hz, J_2=2.1 Hz, 1H), 6.23 (dd, J_1=10.8 Hz, J_2=6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.8 (d, J_{pc}=1.4 Hz), 134.4 (d, J_{pc}=1.5 Hz), 133.0 (d, J_{pc}=41.9 Hz), 132.9 (d, J_{pc}=43.7 Hz), 132.1 (d, J_{pc}=3.0 Hz), 132.0 (d, J_{pc}=1.7 Hz), 131.2 (d, J_{pc}=9.5 Hz), 131.1 (d, J_{pc}=9.6 Hz), 129.8, 128.5, 128.3, 127.7 (d, J_{pc}=1.2 Hz), 126.7 (d, J_{pc}=2.1 Hz), 125.0 (d, J_{pc}=2.1 Hz), 95.3 (d, J_{pc}=13.4 Hz), 90.2 (d, J_{pc}=100.4 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.8; MS (EI, 70 eV) m/z (%) 353 (M^+ (^{37}Cl)+1, 3), 352 (M^+ (^{37}Cl), 12), 351 (M^+ (^{35}Cl)+1, 9), 350 (M^+ (^{35}Cl), 34), 201 (100); IR ν (KBr, cm^{-1}) 3055, 2943, 1941, 1593, 1569, 1475, 1437, 1370, 1262, 1189, 1162, 1118, 1080. Anal. Calcd for $C_{21}H_{16}ClOP$: C, 71.90; H, 4.60. Found: C, 71.95; H, 4.64.

4.1.8. 3-(2-Chlorophenyl)propa-1,2-dienyl diphenyl phosphine oxide (**1k**)

The reaction of 1-(2-chlorophenyl)prop-2-yn-1-ol (2.1653 g, 13 mmol), pyridine (1.25 mL, d=0.9831 g/mL, 1.23 g, 15.6 mmol), and Ph_2PCl (2.60 mL, d=1.204 g/mL, 3.13 g, 14.2 mmol) in a mixed solvent (14 mL of CH_2Cl_2 and 13 mL of Et_2O) afforded **1k** (2.1188 g, 46%) as a white solid: mp 83.5–84.5 °C (Et_2O/ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.84–7.71 (m, 4H), 7.57–7.36 (m, 6H), 7.32–7.20 (m, 2H), 7.19–7.08 (m, 2H), 6.73 (dd, J_1=11.0 Hz, J_2=6.8 Hz, 1H), 6.33 (dd, J_1=6.6 Hz, J_2=1.8 Hz, 1H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.9; MS (EI, 70 eV) m/z (%) 353 (M^+ (^{37}Cl)+1, 2), 352 (M^+ (^{37}Cl), 9), 351 (M^+ (^{35}Cl)+1, 8), 350 (M^+ (^{35}Cl), 30), 201 (100); IR ν (KBr, cm^{-1}) 3064, 3020, 3005, 2923, 1941, 1590, 1568, 1476, 1438, 1367, 1277, 1186, 1156, 1120, 1109, 1047, 1035. Anal. Calcd for $C_{21}H_{16}ClOP$: C, 71.90; H, 4.60. Found: C, 71.94; H, 4.45.

4.1.9. 3-(4-Methylphenyl)propa-1,2-dienyl diphenyl phosphine oxide (**1l**)

The reaction of 1-(4-methylphenyl)prop-2-yn-1-ol (1.3563 g, 9.29 mmol), pyridine (0.90 mL, d=0.9831 g/mL, 0.88 g, 11.2 mmol), and Ph_2PCl (1.90 mL, d=1.204 g/mL, 2.29 g, 10.4 mmol) in a mixed solvent (11 mL of CH_2Cl_2 and 10 mL of Et_2O) afforded **1l** (1.3399 g, 44%) as a white solid: mp 129.8–130.8 °C (Et_2O/ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.83–7.71 (m, 4H), 7.54–7.35 (m, 6H), 7.07 (d, J=8.4 Hz, 2H), 7.03 (d, J=8.7 Hz, 2H), 6.32–6.20 (m, 2H), 2.30 (s, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.0; MS (EI, 70 eV) m/z (%) 331 (M^++1, 15), 330 (M^+, 61), 201 (100); IR ν (KBr, cm^{-1}) 3052, 2949, 1939, 1511, 1483, 1437, 1367, 1220, 1210, 1187, 1169, 1121, 1102, 1070, 1018. Anal. Calcd for $C_{22}H_{19}OP$: C, 79.98; H, 5.80. Found: C, 80.02; H, 5.82.

4.1.10. 1-Phenylhepta-1,2-dien-3-yl diphenyl phosphine oxide (**1m**)

The reaction of 1-phenylhept-2-yn-1-ol (1.8828 g, 10 mmol), pyridine (0.96 mL, d=0.9831 g/mL, 0.94 g, 11.9 mmol), and Ph_2PCl (2.00 mL, d=1.204 g/mL, 2.41 g, 10.9 mmol) in a mixed solvent (11 mL of CH_2Cl_2 and 10 mL of Et_2O) afforded **1m** (2.3002 g, 62%) as a white solid: mp 78.6–79.6 °C (*n*-hexane/ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.82–7.65 (m, 4H), 7.54–7.14 (m, 9H), 7.12–7.04 (m, 2H), 6.12 (dt, J_1=11.1 Hz, J_2=3.2 Hz, 1H), 2.53–2.28 (m, 2H), 1.63–1.47 (m, 2H), 1.44–1.27 (m, 2H), 0.83 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.1 (d, J_{pc}=6.9 Hz), 132.5 (d, J_{pc}=4.0 Hz), 131.77 (d, J_{pc}=2.7 Hz), 131.76 (d, J_{pc}=101.3 Hz), 131.66 (d, J_{pc}=2.9 Hz), 131.5 (d, J_{pc}=13.9 Hz), 131.4 (d, J_{pc}=103.3 Hz), 131.3 (d, J_{pc}=14.0 Hz), 128.5 (d, J_{pc}=1.2 Hz), 128.2 (d, J_{pc}=7.8 Hz), 128.0 (d, J_{pc}=6.7 Hz), 127.3 (d, J_{pc}=1.7 Hz), 126.5 (d, J_{pc}=2.3 Hz), 102.9 (d, J_{pc}=97.5 Hz), 97.2 (d, J_{pc}=13.5 Hz), 30.4 (d, J_{pc}=5.0 Hz), 27.7 (d, J_{pc}=6.2 Hz), 22.2, 13.7; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 29.7; MS (EI, 70 eV) m/z (%) 373 (M^++1, 4), 372 (M^+, 16), 201 (100); IR ν (KBr, cm^{-1}) 3057, 2957, 2929, 2858, 1932, 1597, 1497, 1458, 1437, 1195, 1118, 1101, 1070, 1025. Anal. Calcd for $C_{25}H_{25}OP$: C, 80.62; H, 6.77. Found: C, 80.63; H, 6.75.

4.1.11. 1,3-Diphenylpropa-1,2-dienyl diphenyl phosphine oxide (**1n**)

The reaction of 1,3-diphenylprop-2-yn-1-ol (2.0776 g, 10 mmol), pyridine (0.96 mL, d=0.9831 g/mL, 0.94 g, 11.9 mmol), and Ph_2PCl (2.00 mL, d=1.204 g/mL, 2.41 g, 10.9 mmol) in a mixed solvent (12 mL of CH_2Cl_2 and 10 mL of Et_2O) for 13 h afforded **1n** (2.1243 g, 54%) as a white solid: mp 152.6–153.1 °C (*n*-hexane/dichloromethane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.84–7.64 (m, 6H), 7.49–7.16 (m, 12H), 7.15–7.07 (m, 2H), 6.29 (d, J=10.8 Hz, 1H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 29.7; MS (EI, 70 eV) m/z (%) 393 (M^++1, 18), 392 (M^+, 62), 201 (100); IR ν (KBr, cm^{-1}) 3077, 3053, 3024, 2970, 1929, 1596, 1491, 1457, 1437, 1381, 1317, 1192, 1178, 1120, 1099, 1072, 1030. Anal. Calcd for $C_{27}H_{21}OP$: C, 82.64; H, 5.39. Found: C, 82.71; H, 5.37.

4.1.12. 3-(4-Methoxyphenyl)propa-1,2-dienyl diphenyl phosphine oxide (**1o**)

The reaction of 1-(4-methoxylphenyl)prop-2-yn-1-ol (1.6253 g, 10 mmol), pyridine (0.96 mL, d=0.9831 g/mL, 0.94 g, 11.9 mmol), and Ph_2PCl (2.00 mL, d=1.204 g/mL, 2.41 g, 10.9 mmol) in a mixed solvent (11 mL of CH_2Cl_2 and 10 mL of Et_2O) afforded **1o** (0.6880 g, 20%) as a yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.83–7.72 (m, 4H), 7.54–7.38 (m, 6H), 7.10–7.05 (m, 2H), 6.84–6.78 (m, 2H), 6.31–6.21 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.2 (d, J_{pc}=1.3 Hz), 159.2 (d, J_{pc}=1.5 Hz), 132.4 (d, J_{pc}=106.1 Hz), 132.2 (d, J_{pc}=106.1 Hz), 131.91 (d, J_{pc}=3.2 Hz), 131.88 (d, J_{pc}=1.6 Hz), 131.3 (d, J_{pc}=9.7 Hz), 131.2 (d, J_{pc}=9.7 Hz), 128.4, 128.3, 128.2 (d, J_{pc}=2.4 Hz), 123.2 (d, J_{pc}=7.8 Hz), 114.2 (d, J_{pc}=1.4 Hz), 95.8 (d, J_{pc}=13.1 Hz), 89.6 (d, J_{pc}=102.6 Hz), 55.2; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.9; MS (EI, 70 eV) m/z (%) 347 (M^++1, 18), 346 (M^+, 70), 201 (100); IR ν (neat, cm^{-1}) 3056, 2956, 2935, 2836, 1934, 1606, 1511, 1463, 1437, 1376, 1295, 1251, 1174, 1120, 1103, 1029; HRMS calcd for $C_{22}H_{19}O_2P$: 346.1123. Found: 346.1133.

4.1.13. 3-(4-Nitrophenyl)propa-1,2-dienyl diphenyl phosphine oxide (**1g**)

To an oven-dried three-necked round-bottom flask was added 1-(4-nitrophenyl)prop-2-yn-1-ol (0.3549 g, 2.0 mmol) and pyridine (0.20 mL, d=0.9831 g/mL, 0.20 g, 2.5 mmol), and 2.0 mL of Et_2O. After the mixture was cooled to −40 °C, a solution of diphenylphosphinous chloride (0.40 mL, d=1.204 g/mL, 0.48 g, 2.2 mmol) in 2.5 mL of CH_2Cl_2 was added dropwise at this temperature with stirring within 20 min. After the reaction mixture was stirred for additional 11 h at −40 °C, the resulting solution was then poured into a flask containing smashed ice and the aqueous layer was extracted with 20×3 mL of CH_2Cl_2. The combined organic layer was washed with 10 mL of brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, chromatography on silica gel (eluent: dichloromethane/ethyl acetate=10/1) of the crude product afforded **1g** (0.4980 g, 69%) as a white solid: mp 155.2–156.3 °C (Et_2O/dichloromethane); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16–8.06 (m, 2H), 7.85–7.69 (m, 4H), 7.59–7.37 (m, 6H), 7.31–7.21 (m, 2H), 6.47–6.31 (m, 2H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.4; MS (EI, 70 eV) m/z (%) 362 (M^++1, 7), 334 (M^+, 25), 201 (100); IR ν (KBr, cm^{-1}) 3058, 2922, 1934, 1593, 1511, 1489, 1434, 1338, 1226, 1182, 1123, 1105. Anal. Calcd for $C_{21}H_{16}NO_3P$: C, 69.80; H, 4.46; N, 3.88. Found: C, 69.91; H, 4.46; N, 3.87.

4.2. Reaction of 3-aryl-1,2-allenyl phosphine oxides 1a–1e with Selectfluor

4.2.1. 2-Fluoro-3-hydroxy-3-phenyl-1(E)-butenyl diphenyl phosphine oxide (E-**2a**)

4.2.1.1. Typical procedure II (conditions A). To a solution of **1a** (66.9 mg, 0.2 mmol) in 2.3 mL of MeCN was added Selectfluor (106.3 mg, 0.3 mmol) at room temperature. Then the resulting mixture was

stirred at 80 °C. After complete consumption of the starting material as monitored by TLC (eluent: petroleum ether/ethyl acetate=2:1), the mixture was quenched with 5 mL of H_2O, extracted with 20×3 mL of diethyl ether, washed with 5 mL of brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and flash chromatography on silica gel (petroleum ether/ethyl acetate=5:2) afforded *E*-**2a** (48.9 mg, 66%) as a white solid: mp 102.3–103.2 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.68 (m, 2H), 7.60–7.44 (m, 9H), 7.44–7.35 (m, 2H), 7.35–7.21 (m, 3H), 5.69 (dd, J_1=28.1 Hz, J_2=12.2 Hz, 1H), 1.79 (d, J=3.3 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.8 (d, J_{PF}=41.7 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.9 (d, J_{FP}=42.3 Hz); MS (EI, 70 eV) *m*/*z* (%) 367 (M^++1, 4), 366 (M^+, 15), 351 (100); IR ν (KBr, cm^{-1}) 3168, 3059, 2989, 2937, 1630, 1600, 1493, 1438, 1370, 1311, 1296, 1213, 1175, 1122, 1086, 1063, 1028. Anal. Calcd for $C_{22}H_{20}FO_2P$: C, 72.12; H, 5.50. Found: C, 72.20; H, 5.60.

4.2.1.2. Typical procedure III (conditions B). To a dried Schlenk tube were added anhydrous MeCN (2.25 mL), H_2O (24.5 mg, 1.4 mmol), and **1a** (66.0 mg, 0.2 mmol) subsequently under a nitrogen atmosphere at room temperature. Selectfluor (111.6 mg, 0.3 mmol, 95%) was then added to the reaction mixture at rt. Then the resulting mixture was stirred at 80 °C for 2 h. After complete consumption of the starting material as monitored by TLC (eluent: petroleum ether/ethyl acetate=2:1), the mixture was quenched with 5 mL of H_2O, extracted with 20×3 mL of diethyl ether, washed with 5 mL of brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and flash chromatography on silica gel (petroleum ether/ethyl acetate=5:2) afforded *E*-**2a** (47.2 mg, 64%) as a white solid.

*4.2.2. 2-Fluoro-3-hydroxy-3-phenyl-1(E)-butenyl diphenyl phosphine oxide (E-**2a**) and 2-fluoro-3-phenylbuta-1(E), 3-dienyl diphenyl phosphine oxide (E-**3a**)*

To a solution of **1a** (67.8 mg, 0.2 mmol) in 2.0 mL of MeCN were subsequently added 0.2 mL of H_2O and Selectfluor (105.7 mg, 0.3 mmol) at room temperature. Then the resulting mixture was stirred at 80 °C. After complete consumption of the starting material as monitored by TLC (eluent: Et_2O/ethyl acetate=10:1), the mixture was quenched with 8 mL of H_2O, extracted with 20×3 mL of diethyl ether, washed with 5 mL of brine, and dried over anhydrous Na_2SO_4. Filtration and evaporation afforded the crude product, which was analyzed by ^{1}H NMR study to show an *E*-**2a**/*E*-**3a** ratio of 92:8. Flash chromatography on silica gel (petroleum ether/ethyl acetate=5:2 to 1:1) afforded *E*-**2a** (45.1 mg, 60%) and *E*-**3a** (3.9 mg, 5.5%). *E*-**3a**: colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.69 (m, 4H), 7.47–7.32 (m, 6H), 7.29–7.21 (m, 3H), 7.21–7.11 (m, 2H), 6.18 (dd, J_1=23.1 Hz, J_2=9.9 Hz, 1H), 6.04 (d, J=3.0 Hz, 1H), 5.68 (d, J=1.5 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.0 (d, J_{PF}=38.4 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 18.0 (d, J_{FP}=38.3 Hz); MS (EI, 70 eV) *m*/*z* (%) 349 (M^++1, 24), 348 (M^+, 100); IR ν (neat, cm^{-1}) 3056, 2926, 2854, 1627, 1575, 1496, 1438, 1332, 1311, 1193, 1119, 1103, 1071, 1028; HRMS calcd for $C_{22}H_{18}FOP$: 348.1079. Found: 348.1080.

The following compounds were prepared according to Typical Procedure II (conditions A) and Typical Procedure III (conditions B) respectively.

*4.2.3. 2-Fluoro-3-hydroxy-3-phenyl-1(E)-pentenyl diphenyl phosphine oxide (E-**2b**)*

4.2.3.1. Conditions A. The reaction of **1b** (103.9 mg, 0.3 mmol) and Selectfluor (159.4 mg, 0.45 mmol) in 3.5 mL of MeCN at 80 °C for 3 h afforded *E*-**2b** (70.9 mg, 62%) as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81–7.70 (m, 2H), 7.59–7.44 (m, 9H), 7.43–7.21 (m, 5H), 5.73 (dd, J_1=29.0 Hz, J_2=12.2 Hz, 1H), 2.29–2.13 (m, 1H), 2.08–1.88 (m, 1H), 0.98 (t, J=7.4 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −65.2 (d, J_{PF}=42.0 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.9 (d, J_{FP}=43.7 Hz); MS (EI, 70 eV) *m*/*z* (%) 381 (M^++1, 0.2), 380 (M^+, 0.3), 351 (100); IR ν (neat, cm^{-1}) 3164, 3059, 2970, 2937, 2878, 1630, 1600, 1492, 1438, 1173, 1122, 1087, 1069; HRMS calcd for $C_{23}H_{22}FO_2P$: 380.1341. Found: 380.1349.

4.2.3.2. Conditions B. The reaction of **1b** (69.1 mg, 0.2 mmol) and Selectfluor (111.7 mg, 0.3 mmol, 95%) in anhydrous MeCN (2.25 mL) and H_2O (26.4 mg, 1.4 mmol) at 80 °C for 3 h afforded *E*-**2b** (53.8 mg, 70%) as a colorless liquid.

*4.2.4. 2-Fluoro-3-hydroxy-3,3-diphenyl-1(E)-propenyl diphenyl phosphine oxide (E-**2c**)*

4.2.4.1. Conditions A. The reaction of **1c** (77.8 mg, 0.20 mmol) and Selectfluor (107.5 mg, 0.30 mmol) in 2.3 mL of CH_3CN at 80 °C for 2 h afforded *E*-**2c** (66.4 mg, 78%) as a white solid: mp 143.5–144.0 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75–7.63 (m, 5H), 7.59–7.50 (m, 2H), 7.50–7.41 (m, 4H), 7.41–7.33 (m, 4H), 7.33–7.25 (m, 6H), 5.92 (dd, J_1=27.2 Hz, J_2=12.2 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −56.4 (d, J_{PF}=38.4 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.7 (d, J_{FP}=38.8 Hz); MS (EI, 70 eV) *m*/*z* (%) 429 (M^++1, 32), 428 (M^+, 100); IR ν (KBr, cm^{-1}) 3160, 3059, 3002, 1631, 1492, 1449, 1437, 1163, 1157, 1118, 1093, 1063, 1031. Anal. Calcd for $C_{27}H_{22}FO_2P$: C, 75.69; H, 5.18. Found: C, 75.70; H, 5.25.

4.2.4.2. Conditions B. The reaction of **1c** (79.0 mg, 0.20 mmol) and Selectfluor (112.5 mg, 0.30 mmol, 95%) in anhydrous MeCN (2.25 mL) and H_2O (25.3 mg, 1.4 mmol) at 80 °C for 3 h afforded *E*-**2c** (73.3 mg, 85%) as a white solid.

*4.2.5. 3-Fluoro-2-hydroxy-2-phenyl-3(E)-octen-4-yl diphenyl phosphine oxide (E-**2d**)*

4.2.5.1. Conditions A. The reaction of **1d** (115.8 mg, 0.3 mmol) and Selectfluor (168.2 mg, purity: 95%, 0.45 mmol) in 3.5 mL of MeCN at 80 °C for 15 h afforded *E*-**2d** (83.1 mg, 66%) as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.73–7.63 (m, 2H), 7.62–7.54 (m, 1H), 7.54–7.44 (m, 5H), 7.41–7.32 (m, 4H), 7.32–7.24 (m, 2H), 7.24–7.17 (m, 1H), 2.08–1.88 (m, 2H), 1.76 (d, J=4.5 Hz, 3H), 1.00–0.82 (m, 3H), 0.82–0.63 (m, 1H), 0.57 (t, J=7.1 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −66.7 (d, J_{PF}=32.7 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 35.4 (d, J_{FP}=32.4 Hz); MS (EI, 70 eV) *m*/*z* (%) 423 (M^++1, 3), 422 (M^+, 8), 407 (100); IR ν (neat, cm^{-1}) 3146, 3059, 2957, 2937, 2871, 1620, 1493, 1437, 1171, 1140, 1119, 1098, 1072, 1060, 1028; HRMS calcd for $C_{26}H_{28}FO_2P$: 422.1811. Found: 422.1811.

4.2.5.2. Conditions B. The reaction of **1d** (76.9 mg, 0.2 mmol) and Selectfluor (112.1 mg, 0.3 mmol, 95%) in anhydrous MeCN (2.25 mL) and H_2O (25.7 mg, 1.4 mmol) at 80 °C for 14 h afforded *E*-**2d** (62.1 mg, 74%) as a colorless liquid.

*4.2.6. 2-Fluoro-3-hydroxy-1,3-diphenyl-1(E)-butenyl diphenyl phosphine oxide (E-**2e**)*

4.2.6.1. Conditions A. The reaction of **1e** (122.1 mg, 0.3 mmol) and Selectfluor (160.1 mg, 0.45 mmol) in 3.5 mL of MeCN at 80 °C for 12 h afforded *E*-**2e** (92.6 mg, 70%) as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.67–7.16 (m, 15H), 7.15–6.99 (m, 3H), 6.72–6.63 (m, 2H), 1.86 (d, J=4.2 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −61.5 (d, J_{PF}=20.0 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 32.5 (d, J_{FP}=21.1 Hz); MS (EI, 70 eV) *m*/*z* (%) 443 (M^++1, 3), 442 (M^+, 7), 427 (100); IR ν (neat, cm^{-1}) 3145, 3059, 2987, 2937, 1614, 1493, 1437, 1369, 1312, 1227, 1198, 1166, 1119, 1098, 1070, 1029; HRMS calcd for $C_{28}H_{24}FO_2P$: 442.1498. Found: 442.1490.

4.2.6.2. Conditions B. The reaction of **1e** (75.7 mg, 0.19 mmol) and Selectfluor (104.5 mg, 0.285 mmol, 95%) in anhydrous MeCN (2.25 mL) and H_2O (23.1 mg, 1.33 mmol) at 80 °C for 16 h afforded *E*-**2e** (61.6 mg, 75%) as a colorless liquid.

4.3. Reaction of 3-aryl-1,2-allenyl phosphine oxides (1f–1o) and *E*-2o with Selectfluor

*4.3.1. 2-Fluoro-3-hydroxy-3-phenyl-1(E)-propenyl diphenyl phosphine oxide (E-**2f**)*

4.3.1.1. Typical procedure IV. To a solution of **1f** (62.9 mg, 0.20 mmol) in 2 mL of $MeNO_2$ was added 0.2 mL of H_2O. Then Selectfluor (105.6 mg, 0.30 mmol) was subsequently added at room temperature and the resulting mixture was stirred at 80 °C. After complete consumption of the starting material as monitored by TLC (eluent: *n*-hexane/ethyl acetate=3:2), the mixture was quenched with 5 mL of H_2O, extracted with diethyl ether (20×3 mL), washed with 5 mL of brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and flash chromatography on silica gel (dichloromethane/ethyl acetate=10:1 to 5:1) afforded *E*-**2f** (43.3 mg, 62%) as a white solid: mp 179.8–180.3 °C (*n*-hexane/acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.67 (m, 2H), 7.67–7.37 (m, 10H), 7.37–7.23 (m, 3H), 6.75 (dd, J_1=9.0 Hz, J_2=0.9 Hz, 1H), 5.73 (dd, J_1=25.8 Hz, J_2=13.2 Hz, 1H), 5.67 (dd, J_1=15.0 Hz, J_2=8.7 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −70.0 (d, J_{PF}=40.6 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.0 (d, J_{FP}=40.8 Hz); MS (EI, 70 eV) *m*/*z* (%) 353 (M^++1, 3), 352 (M^+, 13), 201 (100); IR ν (KBr, cm^{-1}) 3314, 3058, 3016, 1661, 1599, 1491, 1454, 1437, 1290, 1279, 1191, 1124, 1108, 1086, 1050, 1026. Anal. Calcd for $C_{21}H_{18}FO_2P$: C, 71.59; H, 5.15. Found: C, 71.46; H, 5.20.

The following compounds were prepared according to Typical procedure IV.

*4.3.2. 2-Fluoro-3-hydroxy-3-(4-nitrophenyl)-1(E)-propenyl diphenyl phosphine oxide (E-**2g**)*

The reaction of **1g** (71.5 mg, 0.2 mmol) and Selectfluor (186.7 mg, purity: 95%, 0.5 mmol) in 2.0 mL of $MeNO_2$ and 0.2 mL of H_2O at 80 °C for 28 h afforded *E*-**2g** (25.8 mg, 33%) as a white solid: mp 161.0–161.2 °C (Et_2O/dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18–8.08 (m, 2H), 7.78–7.47 (m, 10H), 7.46–7.35 (m, 2H), 7.14 (d, J=8.4 Hz, 1H), 5.99 (dd, J_1=17.9 Hz, J_2=8.3 Hz, 1H), 5.76 (dd, J_1=25.4 Hz, J_2=13.1 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −71.3 (d, J_{PF}=38.9 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.8 (d, J_{FP}=39.4 Hz); MS (EI, 70 eV) *m*/*z* (%) 398 (M^++1, 5), 397 (M^+, 15), 201 (100); IR ν (KBr, cm^{-1}) 3237, 2927, 2854, 1649, 1596, 1519, 1437, 1342, 1180, 1124, 1104, 1070. Anal. Calcd for $C_{21}H_{17}FNO_4P$: C, 63.48; H, 4.31; N, 3.53. Found: C, 63.37; H, 4.29; N, 3.40.

*4.3.3. 2-Fluoro-3-hydroxy-3-(4-fluorophenyl)-1(E)-propenyl diphenyl phosphine oxide (E-**2h**)*

The reaction of **1h** (100.5 mg, 0.30 mmol) and Selectfluor (159.9 mg, 0.45 mmol) in 3.0 mL of $MeNO_2$ and 0.3 mL of H_2O at 80 °C for 10 h afforded *E*-**2h** (80.2 mg, 72%) as a white solid: mp 127.2–127.8 °C (acetone/dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76–7.35 (m, 12H), 7.02–6.90 (m, 2H), 6.86 (d, J=8.1 Hz, 1H), 5.85 (dd, J_1=17.1 Hz, J_2=8.1 Hz, 1H), 5.69 (dd, J_1=25.2 Hz, J_2=13.2 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.0 (d, J_{PF}=41.2 Hz), −114.4; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.3 (d, J_{FP}=40.9 Hz); MS (EI, 70 eV) *m*/*z* (%) 371 (M^++1, 1), 370 (M^+, 4), 202 (100); IR ν (KBr, cm^{-1}) 3321, 3077, 3018, 1657, 1602, 1507, 1437, 1294, 1228, 1191, 1155, 1123, 1107, 1067. Anal. Calcd for $C_{21}H_{17}F_2O_2P$: C, 68.11; H, 4.63. Found: C, 68.19; H, 4.66.

*4.3.4. 2-Fluoro-3-hydroxy-3-(4-chlorophenyl)-1(E)-propenyl diphenyl phosphine oxide (E-**2i**)*

The reaction of **1i** (105.8 mg, 0.30 mmol) and Selectfluor (159.8 mg, 0.45 mmol) in 3.0 mL of $MeNO_2$ and 0.3 mL of H_2O at 80 °C for 12 h afforded *E*-**2i** (65.0 mg, 56%) as a white solid: mp 168.4–168.6 °C (*n*-hexane/dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74–7.33 (m, 12H), 7.28–7.18 (m, 2H), 6.94 (d, J=7.8 Hz, 1H), 5.91 (dd, J_1=18.5 Hz, J_2=7.7 Hz, 1H), 5.68 (dd, J_1=25.4 Hz, J_2=13.4 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.8 (d, J_{PF}=41.5 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.3 (d, J_{FP}=40.8 Hz); MS (EI, 70 eV) *m*/*z* (%) 371 (M^+ (^{37}Cl)−OH, 3), 370 (M^+ (^{37}Cl)−H_2O or M^+ (^{35}Cl)+1−OH, 2), 369 (M^+ (^{35}Cl)+1−H_2O or M^+ (^{35}Cl)−OH or M^+ (^{37}Cl)+1−HF, 12), 368 (M^+ (^{37}Cl)−HF or M^+ (^{35}Cl)−H_2O, 37), 367 (M^+ (^{35}Cl)+1−HF, 44), 366 (M^+ (^{35}Cl)−HF, 100); IR ν (KBr, cm^{-1}) 3270, 3073, 3016, 2929, 2858, 1660, 1486, 1437, 1302, 1192, 1169, 1122, 1107, 1058, 1015. Anal. Calcd for $C_{21}H_{17}ClFO_2P$: C, 65.21; H, 4.43. Found: C, 64.85; H, 4.57.

*4.3.5. 2-Fluoro-3-hydroxy-3-(3-chlorophenyl)-1(E)-propenyl diphenyl phosphine oxide (E-**2j**)*

The reaction of **1j** (70.3 mg, 0.20 mmol) and Selectfluor (148.9 mg, purity: 95%, 0.40 mmol) in 2.0 mL of $MeNO_2$ and 0.2 mL of H_2O at 80 °C for 24 h afforded *E*-**2j** (38.5 mg, 50%) as a white solid: mp 172.0–172.5 °C (*n*-hexane/dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.67 (m, 2H), 7.67–7.39 (m, 9H), 7.38–7.32 (m, 1H), 7.27–7.18 (m, 2H), 6.89 (dd, J_1=8.4 Hz, J_2=0.9 Hz, 1H), 5.78 (dd, J_1=17.0 Hz, J_2=8.3 Hz, 1H), 5.73 (dd, J_1=25.4 Hz, J_2=13.1 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −71.0 (d, J_{PF}=39.8 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.7 (d, J_{FP}=38.2 Hz); MS (EI, 70 eV) *m*/*z* (%) 388 (M^+ (^{37}Cl), 2), 386 (M^+ (^{35}Cl), 7), 202 (100); IR ν (KBr, cm^{-1}) 3225, 1667, 1594, 1438, 1426, 1302, 1184, 1134, 1121, 1108, 1045. Anal. Calcd for $C_{21}H_{17}ClFO_2P$: C, 65.21; H, 4.43. Found: C, 65.31; H, 4.40.

*4.3.6. 2-Fluoro-3-hydroxy-3-(2-chlorophenyl)-1(E)-propenyl diphenyl phosphine oxide (E-**2k**)*

The reaction of **1k** (106.0 mg, 0.30 mmol) and Selectfluor (159.0 mg, 0.45 mmol) in 3.0 mL of $MeNO_2$ and 0.3 mL of H_2O at 80 °C for 33 h afforded *E*-**2k** (65.5 mg, 56%) as a white solid: mp 148.0–148.7 °C (*n*-hexane/dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.64 (m, 5H), 7.63–7.41 (m, 6H), 7.35–7.17 (m, 3H), 6.84 (d, J=7.5 Hz, 1H), 6.09 (dd, J_1=13.7 Hz, J_2=7.7 Hz, 1H), 5.85 (dd, J_1=24.9 Hz, J_2=13.2 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −69.1 (d, J_{PF}=40.3 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.4 (d, J_{FP}=38.9 Hz); MS (EI, 70 eV) *m*/*z* (%) 370 (M^+ (^{37}Cl)−H_2O or M^+ (^{35}Cl)+1−OH, 0.1), 369 (M^+ (^{35}Cl)+1−H_2O or M^+ (^{35}Cl)−OH or M^+ (^{37}Cl)−F, 2), 368 (M^+ (^{37}Cl)−HF or M^+ (^{35}Cl)−H_2O, 10), 367 (M^+ (^{35}Cl)+1−HF, 13), 366 (M^+ (^{35}Cl)−HF, 34), 331 (100); IR ν (KBr, cm^{-1}) 3214, 1664, 1466, 1438, 1313, 1289, 1186, 1129, 1120, 1099, 1064, 1030. Anal. Calcd for $C_{21}H_{17}ClFO_2P$: C, 65.21; H, 4.43. Found: C, 64.93; H, 4.62.

*4.3.7. 2-Fluoro-3-hydroxy-3-(4-methylphenyl)-1(E)-propenyl diphenyl phosphine oxide (E-**2l**)*

The reaction of **1l** (66.2 mg, 0.20 mmol) and Selectfluor (106.0 mg, 0.30 mmol) in 2.0 mL of $MeNO_2$ and 0.2 mL of H_2O at 40 °C for 25 h afforded *E*-**2l** (46.4 mg, 63%) as a white solid: mp 184.0–184.6 °C (acetone/dichloromethane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77–7.69 (m, 2H), 7.68–7.59 (m, 2H), 7.58–7.40 (m, 6H), 7.38 (d, J=8.0 Hz, 2H), 7.12 (d, J=8.5 Hz, 2H), 6.63 (d, J=9.0 Hz, 1H), 5.70 (dd, J_1=26.0 Hz, J_2=13.0 Hz, 1H), 5.64 (dd, J_1=14.3 Hz, J_2=9.3 Hz, 1H), 2.32 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −70.7 (d, J_{PF}=40.6 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.7 (d, J_{FP}=41.2 Hz); MS (EI, 70 eV) *m*/*z* (%) 367 (M^++1, 2), 366 (M^+, 7), 202 (100); IR ν (KBr, cm^{-1}) 3328, 3017, 2922, 1654, 1512, 1437, 1295, 1193, 1133, 1122, 1106, 1070, 1024. Anal. Calcd for $C_{22}H_{20}FO_2P$: C, 72.12; H, 5.50. Found: C, 71.72; H, 5.62.

*4.3.8. 2-Fluoro-1-hydroxy-1-phenyl-2(E)-hept-2-en-3-yl diphenyl phosphine oxide (E-**2m**)*

The reaction of **1m** (74.9 mg, 0.20 mmol) and Selectfluor (149.6 mg, purity: 95%, 0.40 mmol) in 2.0 mL of $MeNO_2$ and 0.2 mL of H_2O

at 80 °C for 21 h afforded *E*-**2m** (48.1 mg, 59%) as a white solid: mp 149.3–149.7 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80–7.67 (m, 2H), 7.66–7.48 (m, 6H), 7.48–7.39 (m, 4H), 7.36–7.22 (m, 3H), 6.00–5.84 (m, 2H), 2.15–1.82 (m, 2H), 1.06–0.84 (m, 3H), 0.84–0.67 (m, 1H), 0.56 (t, J=6.9 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −79.6 (d, J_{PF}=33.6 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 33.5 (d, J_{FP}=32.7 Hz); MS (EI, 70 eV) m/z (%) 390 (M^+-H_2O, 46), 201 (100); IR ν (KBr, cm^{-1}) 3345, 3061, 2954, 2869, 1653, 1494, 1454, 1436, 1231, 1184, 1171, 1136, 1119, 1101, 1044, 1029. Anal. Calcd for $C_{25}H_{26}FO_2P$: C, 73.51; H, 6.42. Found: C, 73.50; H, 6.49.

4.3.9. 2-Fluoro-3-hydroxy-1,3-diphenyl-1(E)-propenyl diphenyl phosphine oxide (E-**2n**)

The reaction of **1n** (78.6 mg, 0.20 mmol) and Selectfluor (105.5 mg, 0.30 mmol) in 2.0 mL of $MeNO_2$ and 0.2 mL of H_2O at 80 °C for 12.5 h afforded *E*-**2n** (57.9 mg, 67%) as a white solid: mp 192.8–194.1 °C (*n*-hexane/dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76–7.62 (m, 2H), 7.61–7.50 (m, 3H), 7.50–7.20 (m, 10H), 7.17–6.95 (m, 3H), 6.71 (d, J=7.5 Hz, 2H), 6.38 (d, J=7.8 Hz, 1H), 6.08 (dd, J_1=20.9 Hz, J_2=8.0 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.3 (d, J_{PF}=21.4 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 30.8 (d, J_{FP}=21.4 Hz); MS (EI, 70 eV) m/z (%) 409 (M^++1−HF, 12), 408 (M^+−HF, 45), 202 (100); IR ν (KBr, cm^{-1}) 3282, 3060, 1641, 1491, 1437, 1218, 1186, 1175, 1118, 1101, 1083, 1055. Anal. Calcd for $C_{27}H_{22}FO_2P$: C, 75.69; H, 5.18. Found: C, 75.48; H, 5.29.

4.3.10. 2-Fluoro-3-hydroxy-3-(3-fluoro-4-methoxylphenyl)-1(E)-propenyl diphenyl phosphine oxide (E-**4o**)

The reaction of **1o** (104.0 mg, 0.30 mmol) and Selectfluor (391.7 mg, purity: 95%, 1.05 mmol) in 3.0 mL of $MeNO_2$ and 0.3 mL of H_2O at 80 °C for 9.5 h afforded *E*-**4o** (16.8 mg, 14%) as a white solid: mp 192.5–194.2 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81–7.42 (m, 10H), 7.26–7.14 (m, 2H), 6.96–6.83 (m, 1H), 6.72 (d, J=8.7 Hz, 1H), 5.74 (dd, J_1=25.8 Hz, J_2=12.6 Hz, 1H), 5.57 (dd, J_1=14.0 Hz, J_2=8.9 Hz, 1H), 3.87 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −69.9 (d, J_{PF}=40.3 Hz), −134.7; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.0 (d, J_{FP}=40.8 Hz); MS (EI, 70 eV) m/z (%) 401 (M^++1, 1), 400 (M^+, 6), 202 (100); IR ν (KBr, cm^{-1}) 3280, 3021, 2938, 2843, 1657, 1513, 1438, 1430, 1310, 1272, 1215, 1177, 1138, 1121, 1112, 1059, 1026. Anal. Calcd for $C_{22}H_{19}F_2O_3P$: C, 66.00; H, 4.78. Found: C, 65.93; H, 4.96.

4.3.11. 2-Fluoro-3-hydroxy-3-(4-methoxyphenyl)-1(E)-propenyl diphenyl phosphine oxide (E-**2o**)

To a solution of **1o** (103.3 mg, 0.30 mmol) in 3.0 mL of $MeNO_2$ was added 0.3 mL of H_2O. Then Selectfluor (101.2 mg, 0.27 mmol, purity: 95%) was subsequently added at room temperature and the resulting mixture was stirred at rt for 42 h. The mixture was quenched with 5 mL of H_2O, extracted with diethyl ether (20×3 mL), washed with 5 mL of brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and flash chromatography on silica gel (petroleum ether/ethyl acetate=3:2) afforded *E*-**2o** and *E*-**4o** as a mixture (46.8 mg, 45%, *E*-**2o**/*E*-**4o**=**97**/**3**). *E*-**2o**: white solid, mp 162.3–164.0 °C (*n*-hexane/dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.37 (m, 12H), 6.89–6.79 (m, 2H), 6.62 (dd, J_1=8.9 Hz, J_2=0.8 Hz, 1H), 5.70 (dd, J_1=26.1 Hz, J_2=13.2 Hz, 1H), 5.66 (dd, J_1=14.9 Hz, J_2=8.9 Hz, 1H), 3.78 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −70.5 (d, J_{PF}=40.6 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.7 (d, J_{FP}=40.8 Hz); MS (EI, 70 eV) m/z (%) 382 (M^+, 7); IR ν (KBr, cm^{-1}) 3275, 3022, 2837, 1656, 1606, 1508, 1437, 1299, 1249, 1179, 1168, 1122, 1105, 1063, 1033. Anal. Calcd for $C_{22}H_{20}FO_3P$: C, 69.11; H, 5.27. Found: C, 69.03; H, 5.36.

4.3.12. 2-Fluoro-3-hydroxy-3-(3-fluor-4-methoxyphenyl)-1(E)-propenyl diphenyl phosphine oxide (E-**4o**)

Following Typical procedure IV, the reaction of *E*-**2o** (117.4 mg, *E*-**2o**/*E*-**4o**=97.5:2.5, 0.3 mmol) and Selectfluor (246.7 mg, 0.66 mmol, purity: 95%) in 3.0 mL of $MeNO_2$ and 0.3 mL of H_2O at 80 °C for 10 h afforded *E*-**4o** (23.7 mg, 20%) as a solid.

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Supplementary data

The ^{1}H, ^{13}C, and ^{31}P spectra for all the new compounds are included in Supplementary data. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.07.009.

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15. Crystal data of *E*-**2f**: $C_{21}H_{18}FO_2P$, *MW*=352.32, Monoclinic, space group $P2_1/n$, Final *R* indices [$I>2\sigma(I)$], *R*1=0.0315, *wR*$_2$=0.0797, *R* indices (all data) *R*1=0.0335, *wR*$_2$=0.0816, *a*=9.2910(5) Å, *b*=9.8723 (5) Å, *c*=19.8349 (10) Å, α=90°, β=93.2510(10)°, γ=90°, *V*=1816.40 (16) Å^3, *T*=123(2) K, *Z*=4, reflections collected/unique: 20,447/3190 (R_{int}=0.0219), number of observations [$>2\sigma(I)$] 2990, parameters: 226. The Cambridge database file is CCDC-707615.
16. Crystal data of *E*-**4o**: $C_{22}H_{19}F_2O_3P$, *MW*=400.34, Monoclinic, space group *C*2/*c*, Final *R* indices [$I>2\sigma(I)$], *R*1=0.0524, *wR*$_2$=0.1444, *R* indices (all data) *R*1=0.0641, *wR*$_2$=0.1574, *a*=18.3812(3) Å, *b*=10.6050 (2) Å, *c*=20.9534 (4) Å, α=90°, β=105.9890(10)°, γ=90°, *V*=3926.49 (12) Å^3, *T*=296(2) K, *Z*=8, reflections collected/unique: 22,661/3462 (R_{int}=0.0290), number of observations [$>2\sigma(I)$] 2798, parameters: 241. The Cambridge database file is CCDC-707616.
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