

## Supporting Information

### “On-Water” Defluorophosphorylation of Trifluoromethylated Enones with Phosphine Oxides

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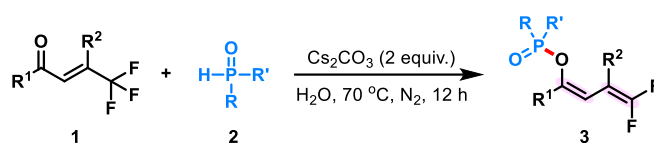
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## General information

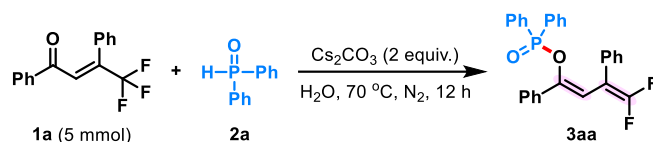
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under N<sub>2</sub> atmosphere using undistilled solvent. Melting points were recorded on an electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. <sup>1</sup>H, <sup>19</sup>F, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on Bruker Avance or Joel 400 MHz spectrometers. The chemical shifts ( $\delta$ ) are reported in ppm and coupling constants ( $J$ ) in Hz. High resolution mass spectra (HRMS) were obtained on a Waters Q-TOF Premier Spectrometer (ESI or EI Source). Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

## General procedure for the synthesis of (Z)-4,4-difluoro-1-arylbuta-1,3-dien-1-yl phosphinates 3



A solution of  $\beta$ -trifluoromethylated enone **1**<sup>[1]</sup> (0.3 mmol), phosphine oxide **2** (0.45 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) in H<sub>2</sub>O (3.5 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 12 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1~6/1) as eluent to afford the pure products **3**.

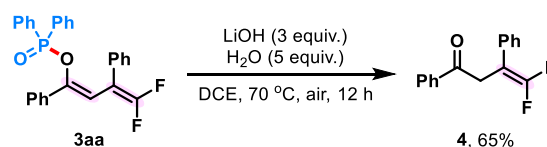
## General procedure for the scaled-up synthesis of product 3aa



A solution of (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one **1a** (1.38 g, 5 mmol), diphenylphosphine oxide **2a** (1.52 g, 7.5 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (3.26 g, 10 mmol) in H<sub>2</sub>O (60 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 12 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (60 mL) and extracted with EtOAc (60 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1~6/1) as eluent to afford the pure product **3a** (1.46 g, 64% yield).

## Further transformation of product 3aa

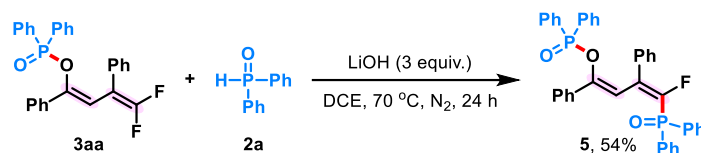
### a) Dephosphorylation of product 3aa



A solution of (*Z*)-4,4-difluoro-1,3-diphenylbuta-1,3-dien-1-yl diphenylphosphinate **3aa** (137.5 mg,

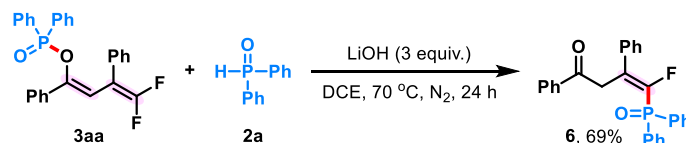
0.3 mmol), LiOH (21.6 mg, 0.9 mmol), and H<sub>2</sub>O (27.0 mg, 1.5 mmol) in DCE (2 mL) was stirred at 70 °C (oil bath) under air for 12 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1) as eluent to afford the pure product **4** (50.7 mg, 65% yield).

#### b) Phosphorylation of product **3aa**



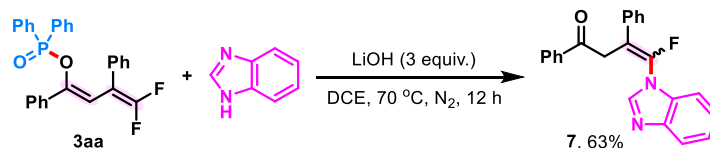
A solution of (*Z*)-4,4-difluoro-1,3-diphenylbuta-1,3-dien-1-yl diphenylphosphinate **3aa** (137.5 mg, 0.3 mmol), diphenylphosphine oxide **2a** (151.6 mg, 0.75 mmol), and LiOH (21.6 mg, 0.9 mmol) in DCE (2 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 24 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (4/1~1/1) as eluent to afford the pure product **5** (104.6 mg, 54% yield).

#### c) Synthesis of product **6**



A solution of (*Z*)-4,4-difluoro-1,3-diphenylbuta-1,3-dien-1-yl diphenylphosphinate **3aa** (137.5 mg, 0.3 mmol), diphenylphosphine oxide **2a** (75.8 mg, 0.375 mmol), and LiOH (21.6 mg, 0.9 mmol) in DCE (2 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 24 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1~6/1) as eluent to afford the pure product **6** (91.8 mg, 69% yield).

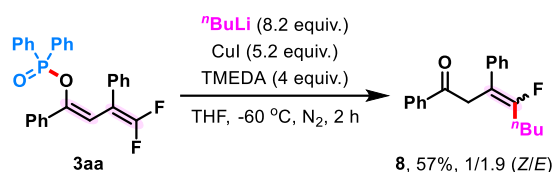
#### d) Synthesis of product **7**



A solution of (*Z*)-4,4-difluoro-1,3-diphenylbuta-1,3-dien-1-yl diphenylphosphinate **3aa** (137.5 mg, 0.3 mmol), 1*H*-benzo[*d*]imidazole (88.6 mg, 0.75 mmol), and LiOH (21.6 mg, 0.9 mmol) in DCE (2 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 12 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate

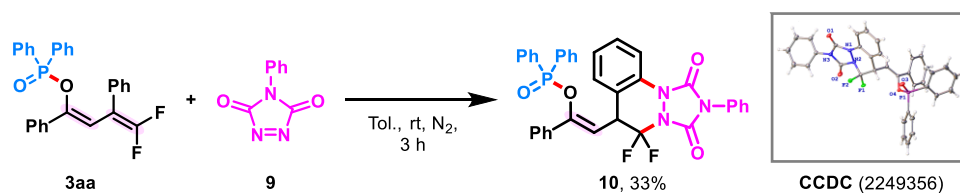
(10/1~6/1) as eluent to afford the pure product **7** (67.4 mg, 63% yield, *Z/E* = 4/3).

### e) Synthesis of product **8**



A solution of (*Z*)-4,4-difluoro-1,3-diphenylbuta-1,3-dien-1-yl diphenylphosphinate **3aa** (137.5 mg, 0.3 mmol), <sup>n</sup>BuLi (2.5 M in hexane, 1 mL, 2.5 mmol), CuI (297.1 mg, 1.56 mmol), and TMEDA (139.4 mg, 1.2 mmol) in THF (5 mL) was stirred at -60 °C under N<sub>2</sub> for 2 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1) as eluent to afford the pure product **8** (48.8 mg, 55% yield, *Z/E* = 1/1.9).

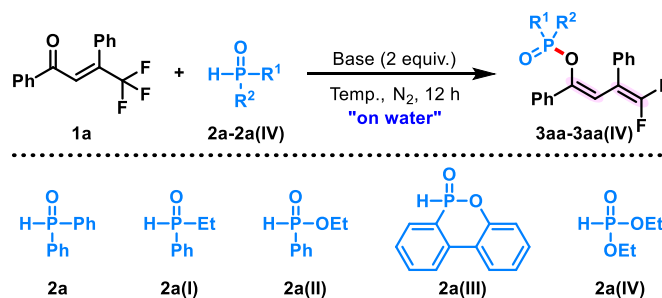
### f) Synthesis of product **10**



A solution of (*Z*)-4,4-difluoro-1,3-diphenylbuta-1,3-dien-1-yl diphenylphosphinate **3aa** (45.8 mg, 0.1 mmol) and **9** (26.3 mg, 0.15 mmol) in toluene (2 mL) was stirred at room temperature under N<sub>2</sub> for 3 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (6/1~4/1) as eluent to afford the pure product **10** (20.7 mg, 33% yield).

## Optimization of reaction conditions

**Table S1.** Optimization of reaction conditions in water<sup>a</sup>



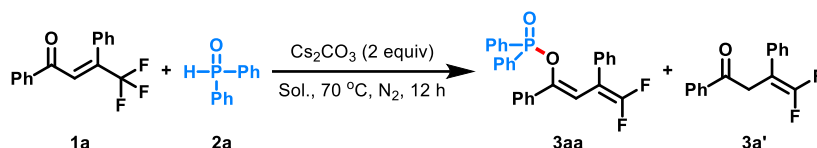
Entry	<b>2</b> (x equiv)	Base	Temp. (°C)	Yield of <b>3aa-3aa(IV)</b> (%) <sup>b</sup>
1	<b>2a</b> (2.5)	CS <sub>2</sub> CO <sub>3</sub>	70	56 (52) <sup>c</sup>



2	<b>2a(I)</b> (2.5)	Cs <sub>2</sub> CO <sub>3</sub>	70	0
3	<b>2a(II)</b> (2.5)	Cs <sub>2</sub> CO <sub>3</sub>	70	0
4	<b>2a(III)</b> (2.5)	Cs <sub>2</sub> CO <sub>3</sub>	70	0
5	<b>2a(IV)</b> (2.5)	Cs <sub>2</sub> CO <sub>3</sub>	70	0
6	<b>2a</b> (2.5)	K <sub>3</sub> PO <sub>4</sub>	70	55
7	<b>2a</b> (2.5)	LiOH	70	7
8	<b>2a</b> (2.5)	NaOAc	70	30
9	<b>2a</b> (2.5)	Et <sub>3</sub> N	70	40
10	<b>2a</b> (2.5)	NaOH	70	29
11	<b>2a</b> (2.5)	Cs <sub>2</sub> CO <sub>3</sub>	40	16 (trace) <sup>d</sup>
12	<b>2a</b> (2.5)	Cs <sub>2</sub> CO <sub>3</sub>	100	25 (10) <sup>d</sup>
13	<b>2a</b> (2.0)	Cs <sub>2</sub> CO <sub>3</sub>	70	61
<b>14</b>	<b>2a (1.5)</b>	<b>Cs<sub>2</sub>CO<sub>3</sub></b>	<b>70</b>	<b>63 (62)<sup>c</sup></b>
15	<b>2a</b> (1.0)	Cs <sub>2</sub> CO <sub>3</sub>	70	53
16	<b>2a</b> (1.5)	Cs <sub>2</sub> CO <sub>3</sub>	70	61 <sup>e</sup>
17	<b>2a</b> (1.5)	Cs <sub>2</sub> CO <sub>3</sub>	70	61 <sup>f</sup>
18	<b>2a</b> (1.5)	Cs <sub>2</sub> CO <sub>3</sub>	70	61 <sup>g</sup>
19	<b>2a</b> (1.5)	Cs <sub>2</sub> CO <sub>3</sub>	70	61 <sup>h</sup>

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2** (0.3-0.75 mmol), and base (0.6 mmol) in H<sub>2</sub>O (3.5 mL) at 40-100 °C (oil bath) under N<sub>2</sub> for 12 h. <sup>b</sup> Yields were determined by <sup>19</sup>F NMR analysis with 4-chlorobenzotrifluoride (0.1 mmol) as an internal standard. <sup>c</sup> Isolated yield. <sup>d</sup> Yield of byproduct 4,4-difluoro-1,3-diphenylbut-3-en-1-one. <sup>e</sup> In water (2 mL). <sup>f</sup> In water (1 mL). <sup>g</sup> For 24 h. <sup>h</sup> Cs<sub>2</sub>CO<sub>3</sub> (2.5 equiv) was used.

**Table S2.** Optimization of reaction solvents in the presence of Cs<sub>2</sub>CO<sub>3</sub><sup>a</sup>



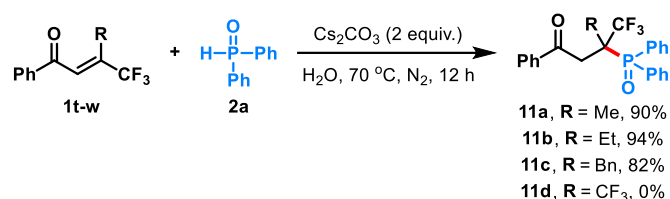
Entry	Solvent (x mL)	Yield of <b>3aa</b> (%) <sup>b</sup>	Yield of <b>3a'</b> (%) <sup>b</sup>
1	MeCN (1)	0	53
2	MeCN (3.5)	0	57
3	MeCN (6)	0	50
4	EtOH (3.5)	0	3
5	DMSO (1)	0	0
6	DMSO (3.5)	0	0
7	DMSO (6)	0	0
8	DMF (3.5)	0	7
9	THF (1)	0	60
10	THF (3.5)	0	82
11	THF (6)	0	83
12	EtOAc (3.5)	0	72
13	Toluene (1)	0	76
14	Toluene (3.5)	11	64

15	Toluene (6)	3	78
16	NMP (3.5)	0	11
17	DMA (3.5)	0	17

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (0.6 mmol) in solvent (1-6 mL) at 70 °C under N<sub>2</sub> for 12 h. <sup>b</sup> Yields were determined by <sup>19</sup>F NMR analysis with 4-chlorobenzotrifluoride (0.1 mmol) as an internal standard.

### Mechanistic studies

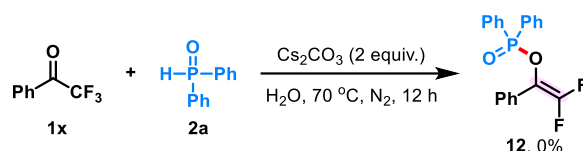
#### a) The influence of substituent (R) on the reaction of trifluoromethylated enone



A solution of trifluoromethylated enone **1t-w** (0.3 mmol), diphenylphosphine oxide **2a** (91.0 mg, 0.45 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) in H<sub>2</sub>O (3.5 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 12 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1~5/1) as eluent to afford the pure products **11a-d** (0-94% yields).

*This result suggested that the substituent adjacent to the trifluoromethyl group has a dramatic influence on the reaction selectivity.*

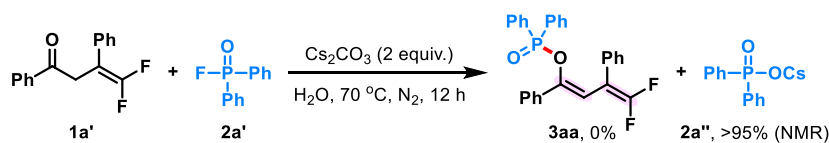
#### b) The reaction of 2,2,2-trifluoro-1-phenylethan-1-one (**1x**) with **2a**



A solution of 2,2,2-trifluoro-1-phenylethan-1-one **1x** (52.2 mg, 0.3 mmol), diphenylphosphine oxide **2a** (91.0 mg, 0.45 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) in H<sub>2</sub>O (3.5 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 12 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. No desired product **12** was observed.

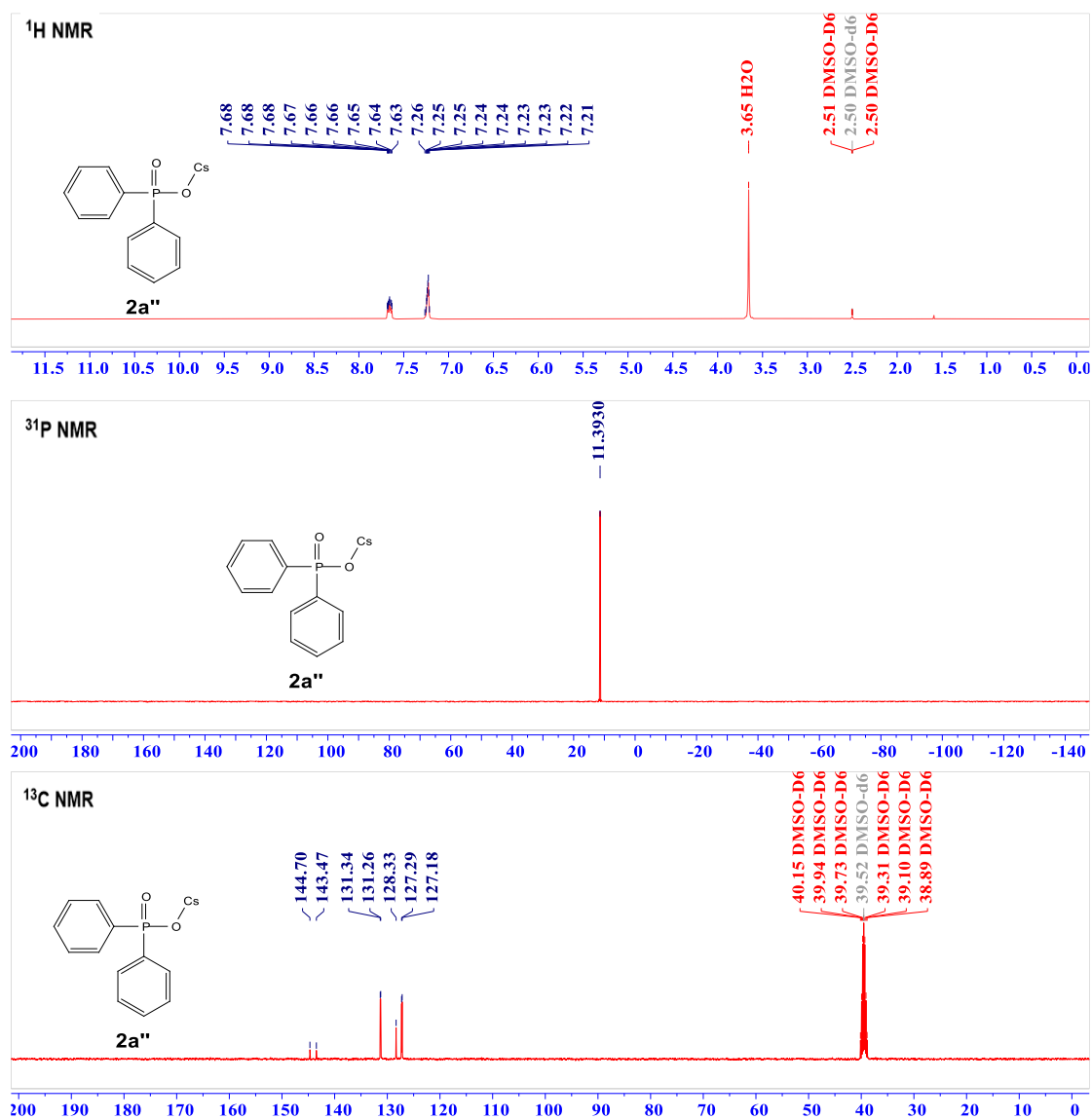
*This result suggested that the alkenyl moiety in the trifluoromethylated enone was important for the success of the present defluorophosphorylation.*

#### c) The reaction of **1a'** with **2a'** under standard conditions

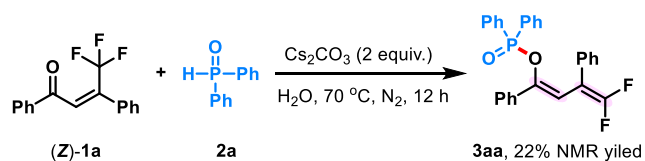


A solution of 4,4-difluoro-1,3-diphenylbut-3-en-1-one (77.5 mg, 0.3 mmol, **1a'**), diphenylphosphinic fluoride (79.3 mg, 0.36 mmol, **2a'**), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) in H<sub>2</sub>O (3.5 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 12 h. No desired product **3aa** was detected.

The residue was then directly analyzed by NMR. 95% NMR yield of cesium diphenylphosphinate **2a''** was determined by <sup>31</sup>P NMR analysis of residue using triphenylphosphine oxide as an internal standard.



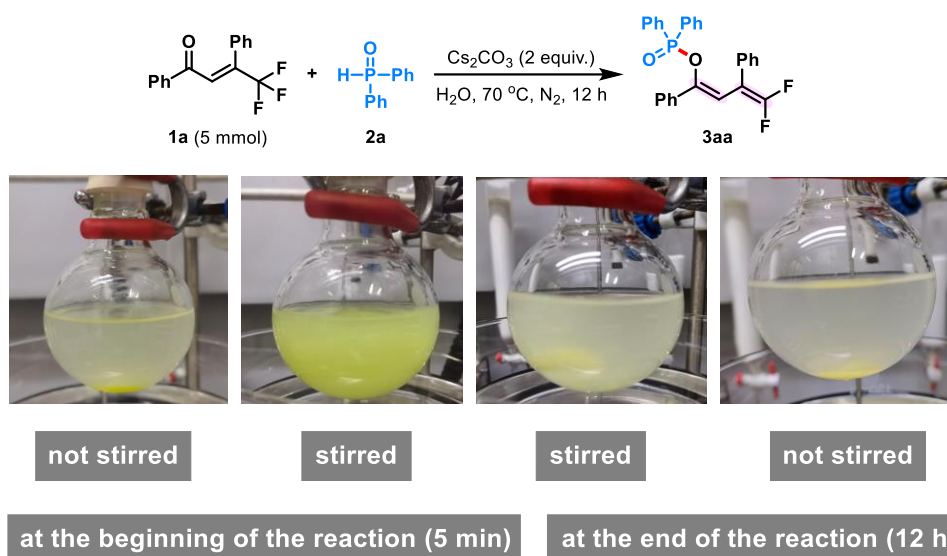
#### d) The reactivity of Z-trifluoromethylated enone (**Z**)-**1a**



A solution of (**Z**)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one (**Z**)-**1a** (82.9 mg, 0.3 mmol), diphenylphosphine oxide **2a** (91.0 mg, 0.45 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) in H<sub>2</sub>O

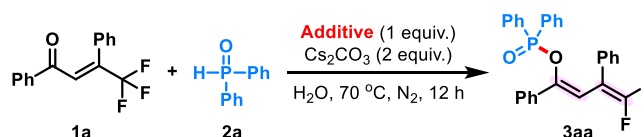
(3.5 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 12 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The yield of product **3aa** was determined by <sup>19</sup>F NMR analysis with 4-chlorobenzotrifluoride (0.1 mmol) as an internal standard. This result suggested that the configuration of the trifluoromethylated enone has a critical effect on the reaction performance. Low yield is presumably attributed to the competitive relationship between carbonyl group and trifluoromethyl group in the Z-trifluoromethylated enone for the formation of hydrogen bond with water.

### e) The heterogeneity of the reaction



The heterogeneity of the reaction was observed during the scaled-up synthesis of product **3aa**.

### f) The influence of different additives on the reaction

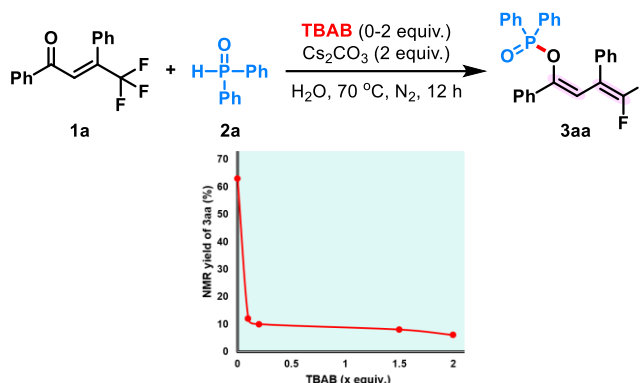


Entry	Additive	3aa (%)
1	<i>n</i> Bu <sub>4</sub> NBr	4
2	<i>n</i> Bu <sub>4</sub> NHSO <sub>4</sub>	8
3	18-crown-6	49
4	BF <sub>3</sub> ·Et <sub>2</sub> O	29
5	HFIP	13
6	<i>N</i> -methylacetamide	32

A solution of (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one **1a** (82.9 mg, 0.3 mmol), diphenylphosphine oxide **2a** (91.0 mg, 0.45 mmol), additive (0.3 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) in H<sub>2</sub>O (3.5 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 12 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The yields of product **3aa** were determined by <sup>19</sup>F NMR analysis with 4-chlorobenzotrifluoride (0.1 mmol) as an internal standard.

These results suggested that the unique properties at the macroscopic phase boundary between water and insoluble reactants, such as hydrophobic effect and hydrogen-bonding interaction, were involved in the formation of **3aa**.

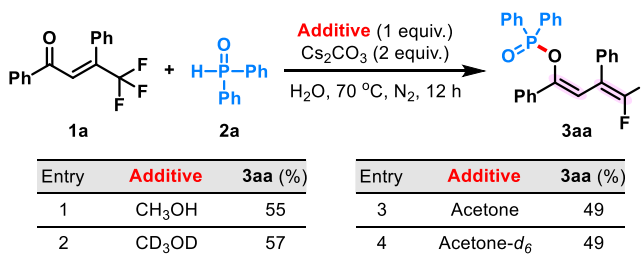
### g) The influence of TBAB on the reaction



A solution of (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one **1a** (82.9 mg, 0.3 mmol), diphenylphosphine oxide **2a** (91.0 mg, 0.45 mmol), TBAB (0-0.6 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) in H<sub>2</sub>O (3.5 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 12 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The yields of product **3aa** were determined by <sup>19</sup>F NMR analysis with 4-chlorobenzotrifluoride (0.1 mmol) as an internal standard.

These results suggested that hydrogen-bonding interaction at the macroscopic phase boundary between water and insoluble reactants accelerated the reaction.

### h) The isotropic effect of additives on the reaction



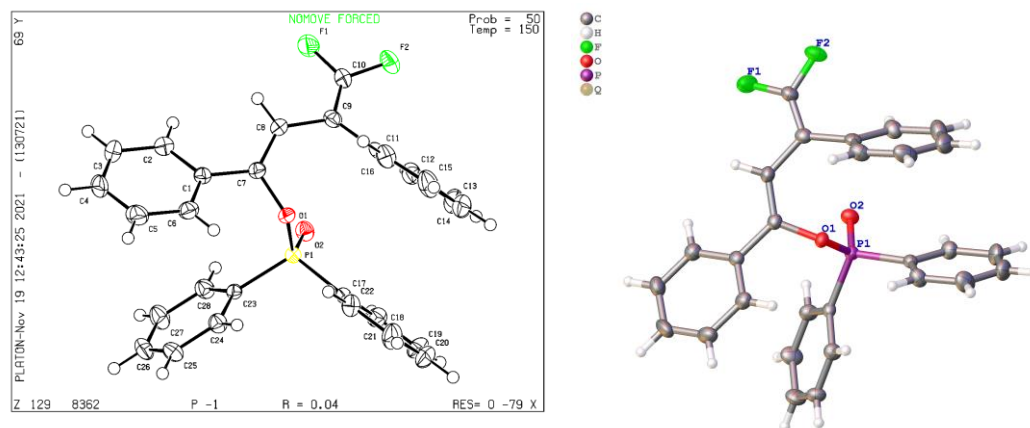
A solution of (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one **1a** (82.9 mg, 0.3 mmol), diphenylphosphine oxide **2a** (91.0 mg, 0.45 mmol), additive (0.3 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) in H<sub>2</sub>O (3.5 mL) was stirred at 70 °C (oil bath) under N<sub>2</sub> for 12 h. The reaction was then quenched by saturated NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The yield of product **3aa** was determined by <sup>19</sup>F NMR analysis with 4-chlorobenzotrifluoride (0.1 mmol) as an internal standard.

Finally, no obvious isotropic effect was observed when CH<sub>3</sub>OH/CD<sub>3</sub>OD and acetone/acetone-*d*<sub>6</sub> with different H<sup>+</sup> ion conjugation abilities were used as additives.

## The X-ray crystal structure of products 3aa and 10

The single crystals were grown from the mixed solution of DCM and EtOAc (v/v = 1:3) by slowly evaporating the above solvents at room temperature.

### (Z)-4,4-Difluoro-1-phenylbuta-1,3-dien-1-yl diphenylphosphinate (3aa):



CCDC number: 2131663

**Table S3 Crystal data and structure refinement for product 3aa.**

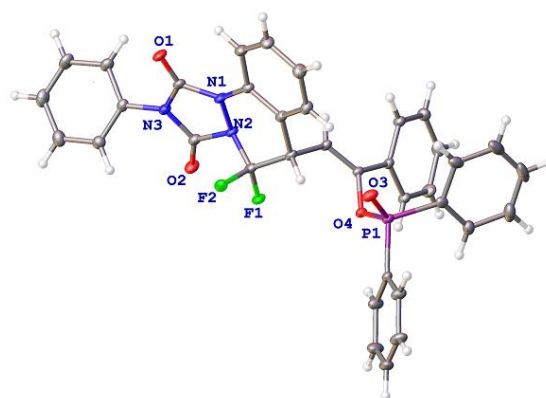
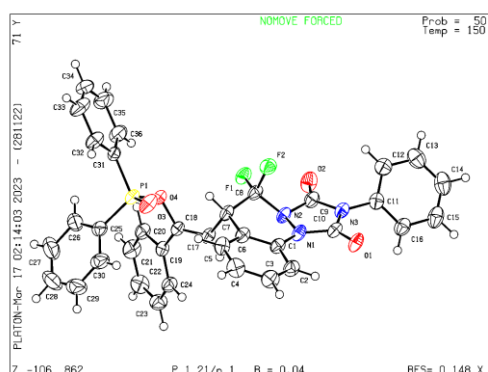
Identification code	<b>3aa</b>
Empirical formula	C <sub>28</sub> H <sub>21</sub> F <sub>2</sub> O <sub>2</sub> P
Formula weight	458.42
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.1385(4)
b/Å	11.7600(8)
c/Å	17.0258(11)
α/°	104.208(6)
β/°	96.087(5)
γ/°	103.597(6)
Volume/Å <sup>3</sup>	1140.47(14)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.335
μ/mm <sup>-1</sup>	0.160
F(000)	476.0
Crystal size/mm <sup>3</sup>	0.14 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.854 to 50
Index ranges	-7 ≤ h ≤ 7, -13 ≤ k ≤ 13, -20 ≤ l ≤ 17
Reflections collected	7518
Independent reflections	4016 [R <sub>int</sub> = 0.0266, R <sub>sigma</sub> = 0.0506]

Data/restraints/parameters	4016/0/298
Goodness-of-fit on $F^2$	1.047
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0428$ , $wR_2 = 0.0947$
Final R indexes [all data]	$R_1 = 0.0559$ , $wR_2 = 0.1041$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.34/-0.39

### Crystal structure determination of [product 3aa]

**Crystal Data** for  $C_{28}H_{21}F_2O_2P$  ( $M = 458.42 \text{ g/mol}$ ): triclinic, space group P-1 (no. 2),  $a = 6.1385(4) \text{ \AA}$ ,  $b = 11.7600(8) \text{ \AA}$ ,  $c = 17.0258(11) \text{ \AA}$ ,  $\alpha = 104.208(6)^\circ$ ,  $\beta = 96.087(5)^\circ$ ,  $\gamma = 103.597(6)^\circ$ ,  $V = 1140.47(14) \text{ \AA}^3$ ,  $Z = 2$ ,  $T = 149.99(10) \text{ K}$ ,  $\mu(\text{Mo K}\alpha) = 0.160 \text{ mm}^{-1}$ ,  $D_{\text{calc}} = 1.335 \text{ g/cm}^3$ , 7518 reflections measured ( $3.854^\circ \leq 2\theta \leq 50^\circ$ ), 4016 unique ( $R_{\text{int}} = 0.0266$ ,  $R_{\text{sigma}} = 0.0506$ ) which were used in all calculations. The final  $R_1$  was 0.0428 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1041 (all data).

### (Z)-2-(5,5-Difluoro-1,3-dioxo-2-phenyl-2,3,5,6-tetrahydro-1H-[1,2,4]triazolo[1,2-a]cinnolin-6-yl)-1-phenylvinyl diphenylphosphinate (10):



CCDC number: 2249356

### Table S4 Crystal data and structure refinement for product 10.

Identification code	<b>10</b>
Empirical formula	$C_{36}H_{26}F_2N_3O_4P$
Formula weight	633.57
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	13.6060(3)
$b/\text{\AA}$	16.1758(4)
$c/\text{\AA}$	14.0833(3)
$\alpha/^\circ$	90
$\beta/^\circ$	98.198(2)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	3067.89(12)

Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.372
$\mu/\text{mm}^{-1}$	1.286
F(000)	1312.0
Crystal size/ $\text{mm}^3$	$0.16 \times 0.13 \times 0.1$
Radiation	Cu K $\alpha$ ( $\lambda = 1.54184$ )
2 $\Theta$ range for data collection/ $^\circ$	8.374 to 148.334
Index ranges	$-16 \leq h \leq 16, -19 \leq k \leq 18, -17 \leq l \leq 12$
Reflections collected	12151
Independent reflections	6063 [ $R_{\text{int}} = 0.0279, R_{\text{sigma}} = 0.0358$ ]
Data/restraints/parameters	6063/0/416
Goodness-of-fit on $F^2$	1.025
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0417, wR_2 = 0.1071$
Final R indexes [all data]	$R_1 = 0.0475, wR_2 = 0.1131$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.34/-0.38

### Crystal structure determination of [10]

**Crystal Data** for  $\text{C}_{36}\text{H}_{26}\text{F}_2\text{N}_3\text{O}_4\text{P}$  ( $M = 633.57$  g/mol): monoclinic, space group  $P2_1/n$  (no. 14),  $a = 13.6060(3)$   $\text{\AA}$ ,  $b = 16.1758(4)$   $\text{\AA}$ ,  $c = 14.0833(3)$   $\text{\AA}$ ,  $\beta = 98.198(2)^\circ$ ,  $V = 3067.89(12)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $T = 149.99(10)$  K,  $\mu(\text{Cu K}\alpha) = 1.286$   $\text{mm}^{-1}$ ,  $D_{\text{calc}} = 1.372$   $\text{g/cm}^3$ , 12151 reflections measured ( $8.374^\circ \leq 2\Theta \leq 148.334^\circ$ ), 6063 unique ( $R_{\text{int}} = 0.0279$ ,  $R_{\text{sigma}} = 0.0358$ ) which were used in all calculations. The final  $R_1$  was 0.0417 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1131 (all data).

### DFT calculation results

#### Computational details:

All calculations were performed using Gaussian 16, Revision A.03 package.<sup>[2]</sup> All of the reactants, intermediates, transition states, and products were optimized by the DFT with the M06-2X functional.<sup>[3]</sup> For geometry optimizations and frequency calculations, BS-I basis set system was employed. In BS-I, we employed LANL2DZ basis sets for Cs atom and 6-31+G(d) basis sets for H, C, O, F, and P. All the stationary structures were characterized with no imaginary frequency and the transition state structures (TSs) were characterized with a single imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed on all the TSs. The solvent effect of water was evaluated through the SMD method,<sup>[4]</sup> in which a better basis system BS-II was used. In BS-II, we employed SDD basis set for Cs with effective core potentials, 6-311++G(d,p) basis sets for H, C, O, F, and P. All reported energies are free energies at a concentration of 1 M and a temperature of 298.15 K

#### Cartesian coordinates of the optimized structures:

##### 1a

E = -990.707115236 a.u.

O 1

O                    -3.80001100      1.60774500      2.05412600



C	-4.56956100	1.64719500	1.11603700
C	-5.02210600	0.40770000	0.41442600
C	-5.74566200	0.46743200	-0.78080300
C	-4.68495100	-0.83423000	0.96444700
C	-6.13226900	-0.70809300	-1.42180600
H	-5.99747100	1.42936000	-1.22015200
C	-5.07714800	-2.00539200	0.32716100
H	-4.11638800	-0.85658500	1.88909600
C	-5.80101800	-1.94268900	-0.86624200
H	-6.68961900	-0.65974300	-2.35207600
H	-4.82000700	-2.96889800	0.75632000
H	-6.10536600	-2.85887000	-1.36368800
C	-5.13371000	2.95883100	0.64464700
H	-6.21788800	3.04224500	0.61786800
C	-4.37554000	4.00367600	0.30071500
C	-2.89436600	3.97172800	0.18070700
C	-2.29910600	2.97403500	-0.59961600
C	-2.08355900	4.91532000	0.82069700
C	-0.91520100	2.90964400	-0.72831800
H	-2.92774000	2.25100700	-1.11456900
C	-0.69858500	4.84738300	0.69102400
H	-2.53102400	5.68872800	1.43571200
C	-0.11137600	3.84717400	-0.08190800
H	-0.46637500	2.13048800	-1.33672900
H	-0.07689900	5.57726100	1.20043100
H	0.96879700	3.79930900	-0.18121700
C	-5.05247900	5.30023200	-0.07902300
F	-4.66731500	5.71123500	-1.29778000
F	-4.74735500	6.28888800	0.78315500
F	-6.39135600	5.20325500	-0.09910100

### 3aa

E = -1770.54727465 a.u.

0 1

O	-4.81567400	0.06828700	1.42569800
C	-3.67852700	0.17997000	0.63812300
C	-2.94205900	1.45287800	0.80276900
C	-1.56760600	1.53756000	0.54437600
C	-3.60952200	2.58602800	1.28524900
C	-0.88194400	2.73061600	0.75239600
H	-1.02315900	0.65684800	0.21647900
C	-2.92086500	3.77568600	1.50010100
H	-4.67024700	2.52317900	1.50683500
C	-1.55456600	3.85390700	1.23329400

H	0.18523300	2.77687300	0.55640500
H	-3.45254900	4.64132200	1.88434400
H	-1.01521800	4.78015000	1.40748700
C	-3.32817500	-0.81796000	-0.18880500
H	-2.44693500	-0.66168600	-0.80270200
C	-4.00984600	-2.10825600	-0.33249800
C	-5.45273700	-2.31614800	-0.02438900
C	-6.41624300	-1.50437900	-0.63441800
C	-5.86212800	-3.31584700	0.86004700
C	-7.76836200	-1.70143100	-0.37515200
H	-6.09556000	-0.71459500	-1.30961200
C	-7.21890500	-3.51260300	1.11921200
H	-5.11176700	-3.91456000	1.36798100
C	-8.17385000	-2.70957400	0.50212500
H	-8.50812700	-1.06639100	-0.85474400
H	-7.52593600	-4.28559500	1.81788100
H	-9.22921100	-2.85711300	0.71305500
C	-3.30039700	-3.13003500	-0.81450000
F	-3.76044300	-4.34353000	-1.05364600
F	-2.01712000	-3.06784300	-1.13909000
P	-4.68503900	-0.64255800	2.90294400
O	-3.83877600	-1.86282600	2.94718900
C	-6.42950400	-0.88388200	3.27267000
C	-7.43378300	-0.10678700	2.68931300
C	-6.75995200	-1.89454800	4.18141500
C	-8.76702400	-0.33532000	3.02478800
H	-7.17338200	0.65240800	1.95703300
C	-8.09353800	-2.12131000	4.51040700
H	-5.97144800	-2.51057500	4.60648300
C	-9.09567700	-1.33958100	3.93404400
H	-9.54938700	0.26127000	2.56488400
H	-8.35215000	-2.91028500	5.21016700
H	-10.13609100	-1.51884400	4.18964600
C	-4.03481700	0.69639200	3.93016500
C	-4.84925700	1.71490800	4.43219200
C	-2.64738500	0.76360600	4.09322700
C	-4.27516100	2.80688200	5.08025400
H	-5.92916300	1.65861700	4.31634900
C	-2.07620600	1.86296200	4.72892400
H	-2.02701200	-0.04140900	3.70732500
C	-2.88949500	2.88550900	5.21792400
H	-4.90789300	3.59642000	5.47484900
H	-0.99777200	1.92360100	4.83959800
H	-2.44272500	3.74317900	5.71253200

**I2**

E = -1966.65848961 a.u.

0 1

P	0.16334200	-0.00127300	-0.31856600
O	0.39123700	1.44260700	0.25893500
C	1.12984200	-0.03086700	-1.90014300
C	1.02448500	-1.09920700	-2.79840300
C	1.85535700	1.10012600	-2.28068400
C	1.65699500	-1.05314700	-4.03909100
H	0.42466700	-1.96980700	-2.53456200
C	2.48212700	1.15562100	-3.52573700
H	1.89674700	1.94175500	-1.59310800
C	2.38572200	0.07962100	-4.40787400
H	1.57157900	-1.89238100	-4.72455800
H	3.04247100	2.04243500	-3.81220400
H	2.87096700	0.12297600	-5.37912800
C	1.22014100	-1.10382300	0.74968300
C	1.91893100	-0.57285300	1.84024800
C	1.18804600	-2.49692600	0.59691100
C	2.56994400	-1.41039400	2.74977400
H	1.96121000	0.50707700	1.96792300
C	1.84105700	-3.33647500	1.49667900
H	0.63363200	-2.93495600	-0.23304000
C	2.53085200	-2.79411300	2.58409100
H	3.11447800	-0.97974800	3.58661300
H	1.80668700	-4.41365900	1.35658800
H	3.03415700	-3.44648000	3.29199400
Cs	-1.09942800	1.94005300	2.76128700
O	-2.94197700	1.67412700	0.39465900
C	-2.92072200	1.02890900	-0.64481800
C	-2.21654100	1.51705600	-1.86109200
C	-2.06755700	0.71949100	-3.00262000
C	-1.63958300	2.79162500	-1.82915800
C	-1.35922900	1.19464900	-4.10173500
H	-2.45741300	-0.29433600	-3.02079100
C	-0.94305700	3.26953400	-2.93231400
H	-1.72851600	3.38276100	-0.92416900
C	-0.80246000	2.47221900	-4.06925900
H	-1.21878900	0.55958900	-4.97070600
H	-0.49015000	4.25583400	-2.90028100
H	-0.23730300	2.83631100	-4.92229100
C	-3.70944600	-0.24268600	-0.74101400
H	-4.19762800	-0.44458200	-1.69009300

C	-3.88537600	-1.10404100	0.26405600
C	-3.25779600	-1.07372100	1.61792600
C	-3.93651700	-0.54410400	2.72063600
C	-2.01374300	-1.68443500	1.80160500
C	-3.37122500	-0.62824500	3.99327100
H	-4.90715400	-0.07770700	2.57821300
C	-1.43666700	-1.74971000	3.07092000
H	-1.49570200	-2.10423600	0.94673000
C	-2.12183700	-1.23051100	4.17020300
H	-3.91316700	-0.23526700	4.84915900
H	-0.45920000	-2.21303000	3.18818300
H	-1.68946300	-1.30337200	5.16452500
C	-4.76207900	-2.31494900	0.03803100
F	-5.77007500	-2.34892300	0.92977100
F	-4.06613600	-3.45468500	0.19159400
F	-5.31552200	-2.35053100	-1.18311400
O	1.60435700	3.02688000	1.92422100
H	1.34075400	2.45827000	1.14458400
H	2.43872300	3.45524500	1.69791700

## TS1-2

E = -1966.65646749 a.u.

0 1

P	0.27671600	0.04995900	-0.10147000
O	0.78664400	1.30680600	0.69657000
C	1.16048600	0.16791200	-1.73044200
C	1.24577600	-0.90429200	-2.62833200
C	1.64821000	1.41622500	-2.12695000
C	1.81647100	-0.73646900	-3.88778800
H	0.87685700	-1.88677700	-2.33651100
C	2.21177200	1.59008400	-3.39231300
H	1.58376200	2.24377900	-1.42437900
C	2.29739100	0.51631600	-4.27706200
H	1.89096400	-1.58272000	-4.56625000
H	2.58775400	2.56688600	-3.68732200
H	2.74113300	0.64950500	-5.26003000
C	1.19799100	-1.40923600	0.58834900
C	2.32197500	-1.23222800	1.40065200
C	0.72853800	-2.70944700	0.36679100
C	2.97576000	-2.32936600	1.95987700
H	2.67875800	-0.22179200	1.58560600
C	1.38370900	-3.81212200	0.91585100
H	-0.17084700	-2.86140700	-0.23116200
C	2.51057900	-3.62271900	1.71557600

H	3.85154500	-2.17847900	2.58583700
H	1.00731100	-4.81477800	0.73156800
H	3.01872700	-4.47751700	2.15283700
Cs	-1.31271300	2.49227900	2.41410300
O	-3.15458700	1.67003000	0.15808700
C	-2.90615000	0.91065800	-0.77098400
C	-2.27687600	1.40845200	-2.02657400
C	-1.80939500	0.54623100	-3.02549300
C	-2.14394700	2.79211700	-2.19522700
C	-1.22405600	1.06053300	-4.17754100
H	-1.84920600	-0.53038800	-2.88757500
C	-1.55995200	3.30537700	-3.34736800
H	-2.51182200	3.45163800	-1.41533300
C	-1.10064400	2.43879500	-4.34063500
H	-0.83245700	0.38410200	-4.93032100
H	-1.45919700	4.37929400	-3.47234800
H	-0.63020000	2.83691500	-5.23495200
C	-3.33457000	-0.52201000	-0.71208100
H	-3.56583100	-1.00309200	-1.65710300
C	-3.46121700	-1.23227900	0.41254600
C	-3.16618500	-0.80043700	1.80906200
C	-4.10777300	-0.06787800	2.54015400
C	-1.97933400	-1.21087500	2.42664200
C	-3.86752200	0.24530200	3.87700300
H	-5.02538600	0.25156400	2.05528300
C	-1.73377900	-0.88271800	3.76116100
H	-1.24537500	-1.78233900	1.86657400
C	-2.68055500	-0.16404600	4.49104600
H	-4.61259000	0.79792400	4.44243500
H	-0.80317500	-1.19807300	4.22375800
H	-2.49862300	0.07066000	5.53620400
C	-3.91130800	-2.67262400	0.30933000
F	-5.00256800	-2.88874600	1.06491200
F	-2.95814800	-3.51418400	0.74835000
F	-4.21742200	-3.04448500	-0.94259600
O	1.62801000	2.21537700	3.00244400
H	1.53137700	1.78912500	2.10516300
H	2.57224300	2.27926700	3.18874600

## II

E = -1966.65729884 a.u.

0 1

P	-0.13552900	-1.74569400	2.15912900
O	0.02878000	-0.21841500	2.52922500

C	0.30602400	-1.84505600	0.34825700
C	-0.09077600	-2.95106800	-0.41435700
C	1.01307600	-0.81665100	-0.28536700
C	0.23982400	-3.04718400	-1.76696300
H	-0.67276700	-3.74299400	0.05781200
C	1.34451500	-0.90832600	-1.63725200
H	1.31069300	0.05588800	0.29392800
C	0.96124200	-2.02417500	-2.38209200
H	-0.07550300	-3.91334500	-2.34365200
H	1.89850700	-0.10383400	-2.11540500
H	1.20845900	-2.08784800	-3.43841000
C	1.43988100	-2.50672600	2.80224900
C	1.90263500	-3.76013300	2.38150600
C	2.14106300	-1.84301300	3.81455700
C	3.04622800	-4.32449200	2.94063000
H	1.37200700	-4.29782400	1.59785100
C	3.28838100	-2.40591400	4.37785900
H	1.77551400	-0.87895900	4.16169300
C	3.74612300	-3.64739800	3.94174700
H	3.39586300	-5.29329600	2.59364700
H	3.82240000	-1.87495700	5.16207300
H	4.63795700	-4.08769500	4.37866400
Cs	-0.78194800	2.54922600	2.10390100
O	-2.05597700	1.12152500	-0.20899700
C	-2.27052100	0.04709500	-0.75680800
C	-1.96853200	-0.12221400	-2.21197100
C	-2.42695900	-1.20601400	-2.96844500
C	-1.19842700	0.86805600	-2.83515700
C	-2.11834900	-1.29686000	-4.32441300
H	-3.03460900	-1.98401000	-2.51904700
C	-0.88095300	0.77244700	-4.18338500
H	-0.84168700	1.69982000	-2.23625400
C	-1.34141300	-0.31349800	-4.93150400
H	-2.48209100	-2.14022900	-4.90321300
H	-0.27174500	1.53854100	-4.65356800
H	-1.09433200	-0.39097400	-5.98636700
C	-2.82476500	-1.12011300	-0.02282900
H	-2.78096500	-2.07144300	-0.53721500
C	-3.28489100	-1.12650400	1.23834700
C	-3.51235000	0.03276400	2.14253800
C	-4.33351500	1.08765900	1.72390000
C	-2.97543900	0.05361000	3.43613200
C	-4.61168100	2.15050600	2.57902600
H	-4.75501800	1.06760600	0.72291900

C	-3.26223200	1.11667800	4.29359800
H	-2.31106500	-0.74203100	3.75410300
C	-4.08043900	2.16440200	3.87158100
H	-5.25917400	2.95580400	2.24467300
H	-2.84436800	1.11817000	5.29626300
H	-4.31483600	2.98171900	4.54811300
C	-3.84246200	-2.44508600	1.75204100
F	-5.19182400	-2.41320100	1.66581200
F	-3.54866300	-2.68742200	3.03185500
F	-3.43360000	-3.50253800	1.03703700
O	2.01903700	1.44644200	2.33965900
H	2.91910400	1.10917600	2.43600500
H	1.40418700	0.65536200	2.44118000

### TS1-2'

E = -1890.24207678 a.u.

0 1

P	0.15440800	-0.93086800	-0.19334200
O	0.03966800	-0.81692200	1.35041300
C	1.36033300	0.41254600	-0.67406800
C	1.11095400	1.27471600	-1.74538900
C	2.48603200	0.64418800	0.13183200
C	1.96689600	2.34972200	-2.00977800
H	0.23758400	1.11268300	-2.37399700
C	3.34131900	1.71258900	-0.12782900
H	2.67937700	-0.02996600	0.96555800
C	3.07821400	2.57263500	-1.20019900
H	1.76092000	3.01197300	-2.84636300
H	4.21999000	1.87194700	0.49238900
H	3.74474500	3.40566100	-1.40577500
C	1.19480600	-2.40881100	-0.55466400
C	1.66321800	-2.67474000	-1.84739000
C	1.44643900	-3.32655100	0.46820700
C	2.38888400	-3.83344900	-2.10952800
H	1.46729800	-1.96389700	-2.65000200
C	2.17070500	-4.49061100	0.20439900
H	1.07103600	-3.10867200	1.46540800
C	2.64289400	-4.74574200	-1.08200500
H	2.75795700	-4.02829300	-3.11289900
H	2.36594800	-5.19987600	1.00438000
H	3.20581700	-5.65195000	-1.28699400
Cs	-0.23820800	2.08301800	2.00139300
O	-2.16709600	1.29943600	-0.13630900
C	-2.32596900	0.25339100	-0.77295700

C	-2.31136100	0.30480200	-2.27872300
C	-2.07339600	-0.81185300	-3.08966900
C	-2.54428900	1.54570700	-2.87807800
C	-2.06709200	-0.68376000	-4.47463700
H	-1.83825600	-1.77246200	-2.63989600
C	-2.54265800	1.67313600	-4.26613900
H	-2.72005500	2.40536800	-2.23879500
C	-2.30218000	0.55898400	-5.06756300
H	-1.86560700	-1.55292600	-5.09358900
H	-2.72829100	2.64188000	-4.72085500
H	-2.29391400	0.65580200	-6.14925400
C	-2.76901800	-1.01323100	-0.13498700
H	-2.90987800	-1.84949000	-0.80924400
C	-2.99881300	-1.22384700	1.17380100
C	-2.95863000	-0.25162500	2.29944900
C	-3.77259300	0.88764100	2.28165200
C	-2.16694500	-0.50109500	3.42986300
C	-3.78312300	1.77189200	3.35941300
H	-4.39160600	1.08122000	1.41121900
C	-2.19014200	0.37593900	4.51432500
H	-1.50125300	-1.35686700	3.43049200
C	-2.99548600	1.51630000	4.48417200
H	-4.42321500	2.64909700	3.32885000
H	-1.57660800	0.16447500	5.38597300
H	-3.02161100	2.19170200	5.33497000
C	-3.38605600	-2.62438800	1.58936600
F	-4.49570500	-2.61558100	2.35601500
F	-2.42564900	-3.22582800	2.31871700
F	-3.64049900	-3.43603500	0.54993900

## II'

E = -1890.24283963 a.u.

0 1

P	0.14813500	-1.22116200	-0.39828500
O	-0.15909400	-0.97353900	1.11623600
C	1.34246600	0.17795600	-0.80152000
C	0.95268400	1.20175500	-1.67091600
C	2.53890300	0.33379700	-0.08351700
C	1.71987300	2.36464400	-1.80678900
H	0.02980400	1.09694100	-2.23904400
C	3.31052000	1.48707000	-0.21474800
H	2.85550900	-0.46144000	0.59041800
C	2.89572600	2.51228400	-1.07316400
H	1.39903500	3.14989700	-2.48647900



H	4.23996900	1.58788700	0.34054600
H	3.49708600	3.41114200	-1.17917100
C	1.39220000	-2.59522700	-0.41993900
C	2.04633100	-2.97344200	-1.59864500
C	1.63884400	-3.31203500	0.75305700
C	2.94574300	-4.03637900	-1.60119100
H	1.85574800	-2.42370700	-2.52013700
C	2.53553300	-4.38307800	0.75226100
H	1.11857400	-3.01069000	1.65972900
C	3.19133100	-4.74623400	-0.42276500
H	3.45490100	-4.31594100	-2.51984800
H	2.72167700	-4.93570200	1.66974100
H	3.88837300	-5.57962400	-0.42470100
Cs	-0.06472100	1.90367400	1.81440300
O	-2.24617000	1.40268000	-0.20407300
C	-2.56877200	0.42884900	-0.87738200
C	-2.60671000	0.55093000	-2.37179000
C	-2.43404800	-0.54119800	-3.22996500
C	-2.79366200	1.82860300	-2.91075300
C	-2.45094600	-0.35237300	-4.60910800
H	-2.22553800	-1.52608100	-2.82374700
C	-2.82320100	2.01327100	-4.28994000
H	-2.91454300	2.66799500	-2.23265400
C	-2.65062100	0.92182800	-5.14129800
H	-2.29659300	-1.20025000	-5.26931800
H	-2.97923600	3.00615800	-4.70114800
H	-2.66612700	1.06401900	-6.21789900
C	-3.00065800	-0.85873800	-0.27944600
H	-3.23719900	-1.64733700	-0.98236500
C	-3.08899700	-1.14361600	1.03062500
C	-2.93057800	-0.24046200	2.20103200
C	-3.69152400	0.93075900	2.29066400
C	-2.08686600	-0.58740700	3.26614800
C	-3.59529900	1.75752200	3.40880000
H	-4.35542800	1.19616200	1.47362300
C	-2.00347600	0.23325000	4.39031800
H	-1.46033400	-1.46748100	3.17886400
C	-2.75274500	1.40916700	4.46617200
H	-4.19421600	2.66210800	3.46202200
H	-1.34887800	-0.04980800	5.21013200
H	-2.69307200	2.04097100	5.34811000
C	-3.48013100	-2.56236800	1.39926800
F	-4.51798000	-2.56327800	2.25951800
F	-2.47813700	-3.22402800	1.99954400

F	-3.85322200	-3.29958300	0.34178800
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### I3

E = -1890.25355233 a.u.

0 1

O	-4.41665600	0.04333500	0.97064100
C	-5.44171900	0.86168100	0.81142600
C	-6.58124100	0.31109300	-0.06325000
C	-7.75673400	1.01201300	-0.36532900
C	-6.44525100	-1.00144800	-0.52124200
C	-8.78417700	0.39840400	-1.08077600
H	-7.90052000	2.03381600	-0.02385500
C	-7.46666900	-1.61196000	-1.24733100
H	-5.52739700	-1.52245600	-0.26893300
C	-8.64583500	-0.91908700	-1.52037500
H	-9.69367400	0.95282600	-1.29540600
H	-7.34699600	-2.63542800	-1.59276900
H	-9.44721700	-1.39574500	-2.07768800
C	-5.15566300	2.30208100	0.44185200
H	-6.02891900	2.90209900	0.20069300
C	-3.98368300	2.95467200	0.46487700
C	-2.61779400	2.40775300	0.69657400
C	-2.12901400	1.36309000	-0.10114100
C	-1.76766600	2.97727700	1.65436100
C	-0.82914800	0.89222000	0.06729000
H	-2.78923500	0.91222200	-0.83307000
C	-0.46340900	2.50562000	1.82194200
H	-2.13014700	3.78591500	2.28096200
C	0.01137300	1.46166100	1.02871700
H	-0.46685700	0.08486100	-0.56304600
H	0.18271000	2.96609500	2.56432400
H	1.03167600	1.10600700	1.14381400
C	-4.00962400	4.44077500	0.19859500
F	-3.05372800	4.81251400	-0.67426700
F	-3.78546400	5.16075600	1.32736500
F	-5.17808700	4.88090000	-0.29396200
P	-6.13270200	1.08940200	2.63971200
O	-4.97548500	1.44170900	3.55623200
C	-6.85475500	-0.51148100	3.15385700
C	-7.83719700	-1.22180500	2.45041300
C	-6.35821900	-1.04230300	4.35064700
C	-8.29876800	-2.44447900	2.93577200
H	-8.24527500	-0.83764400	1.52047000
C	-6.82314300	-2.26390500	4.83480400

H	-5.62046300	-0.46898500	4.90678000
C	-7.79214400	-2.96986300	4.12358000
H	-9.05577500	-2.98741400	2.37733200
H	-6.43679600	-2.65984000	5.76995000
H	-8.15631600	-3.92292400	4.49638600
C	-7.44761000	2.34646300	2.77841600
C	-8.81553200	2.07036300	2.68835400
C	-7.02132400	3.67337100	2.92683800
C	-9.74441800	3.10934900	2.73245200
H	-9.16353600	1.04606400	2.58960200
C	-7.95075000	4.70967800	2.96477600
H	-5.95830900	3.88296800	3.02003100
C	-9.31382300	4.42889400	2.86408600
H	-10.80531800	2.88612300	2.66613100
H	-7.61097900	5.73519200	3.07563500
H	-10.03928700	5.23662800	2.89483300
Cs	-2.52620100	-0.20177100	3.11375100

#### TS3-4

E = -1890.22883905 a.u.

0 1

O	-4.73137300	0.54169200	1.85554800
C	-5.71921800	1.13676700	0.99551900
C	-6.39444800	0.18911200	0.06676300
C	-7.29335400	0.61828000	-0.92564700
C	-6.14339300	-1.18576600	0.17996800
C	-7.94206000	-0.29892400	-1.74600800
H	-7.49022800	1.67792000	-1.06635900
C	-6.78290700	-2.10047400	-0.65470600
H	-5.45624500	-1.52807600	0.94706400
C	-7.69319500	-1.66652900	-1.61551200
H	-8.63817000	0.05836400	-2.49982700
H	-6.57615300	-3.16118100	-0.54092000
H	-8.19878100	-2.38020400	-2.25896600
C	-5.41766900	2.47164600	0.47195200
H	-6.29728900	3.04588100	0.18926000
C	-4.23339300	3.12019500	0.39534300
C	-2.89388900	2.50376600	0.50132000
C	-2.70104300	1.18065700	0.06577200
C	-1.77162600	3.22177200	0.95170700
C	-1.43978300	0.59052300	0.10580900
H	-3.54647600	0.62141900	-0.32298600
C	-0.50877000	2.63050700	0.98784200
H	-1.88314100	4.25246700	1.27323900

C	-0.33548000	1.30987700	0.56914200
H	-1.31730000	-0.42916700	-0.24853700
H	0.34423500	3.21164800	1.32746900
H	0.65169400	0.85636000	0.57708200
C	-4.25581900	4.58937100	0.07449100
F	-3.37459000	4.91331800	-0.89535400
F	-3.91743000	5.35179800	1.14595200
F	-5.45627600	5.02821200	-0.33213200
P	-5.99906300	1.12573200	2.92611900
O	-5.12502400	1.40944500	4.14813700
C	-6.95157400	-0.41307100	3.17276400
C	-8.18993200	-0.67943600	2.58366000
C	-6.37795900	-1.37408400	4.00987600
C	-8.83410800	-1.89343000	2.81350800
H	-8.65294900	0.05188000	1.92821600
C	-7.01684900	-2.59114400	4.23829900
H	-5.43223300	-1.14874200	4.49664400
C	-8.24690300	-2.85389600	3.63580100
H	-9.79230400	-2.09086200	2.34193400
H	-6.56175300	-3.32982200	4.89236700
H	-8.74919500	-3.80082200	3.81207800
C	-7.26217700	2.49108000	3.07918300
C	-8.21923900	2.72103300	2.08471200
C	-7.26716700	3.30475700	4.21694900
C	-9.17334300	3.72663400	2.22664000
H	-8.21958600	2.11121600	1.18347700
C	-8.21228800	4.32153700	4.35705700
H	-6.51843000	3.12527000	4.98138800
C	-9.16904200	4.53221000	3.36545100
H	-9.91225100	3.88779500	1.44657900
H	-8.20200000	4.95041700	5.24321900
H	-9.90503300	5.32367400	3.47527200
Cs	-2.32691700	0.88875000	3.61821800

#### I4

E = -1890.26321761 a.u.

0 1

O	-5.05604600	0.59883800	1.62271800
C	-5.67967400	0.78547900	0.36270200
C	-6.42905600	-0.37492200	-0.14916200
C	-7.50220200	-0.21561700	-1.04189300
C	-6.10705100	-1.67429100	0.27095500
C	-8.22849800	-1.31405600	-1.48808900
H	-7.78828400	0.78103500	-1.36759700

C	-6.84119500	-2.77176800	-0.17000000
H	-5.28061400	-1.81884500	0.96117400
C	-7.90767000	-2.60060900	-1.05116500
H	-9.05983900	-1.16284300	-2.17114100
H	-6.57751600	-3.76601200	0.18021200
H	-8.48250800	-3.45621700	-1.39247900
C	-5.43930100	1.93174000	-0.32402400
H	-6.03098500	2.02780800	-1.23456300
C	-4.54843400	3.01404400	-0.01004900
C	-3.17173000	2.85635800	0.36457200
C	-2.55745000	1.57391200	0.47603900
C	-2.30593000	3.96821200	0.60091600
C	-1.22614200	1.42241400	0.84351200
H	-3.13909200	0.68831500	0.24812600
C	-0.97455500	3.80111700	0.96441500
H	-2.68393600	4.97796000	0.48508300
C	-0.41294900	2.52826400	1.12021000
H	-0.81179000	0.41840200	0.90145600
H	-0.36070900	4.68592200	1.11939500
H	0.63153200	2.40435200	1.38839700
C	-5.00724800	4.35747100	-0.40917500
F	-4.29235900	4.96591300	-1.39716000
F	-4.98026400	5.27545700	0.61670000
F	-6.29351000	4.35815200	-0.84147100
P	-5.82981400	0.60891100	3.04947900
O	-4.82579200	0.30976800	4.12112200
C	-7.17356200	-0.58659200	3.00088700
C	-8.36480100	-0.33640600	2.31291900
C	-6.96364900	-1.81801100	3.62624500
C	-9.32818100	-1.33501800	2.21653800
H	-8.52997800	0.62456100	1.83101100
C	-7.93704800	-2.81109400	3.53726200
H	-6.03773600	-1.98708800	4.16939200
C	-9.11113100	-2.57251800	2.82459800
H	-10.24186200	-1.15225700	1.65959200
H	-7.77716800	-3.77100000	4.01903900
H	-9.86294700	-3.35222200	2.74337200
C	-6.54064900	2.25975300	3.32189700
C	-7.05201800	3.10027200	2.32592000
C	-6.55333100	2.68898300	4.65872200
C	-7.54549600	4.36019500	2.66178200
H	-7.04637400	2.78803900	1.28842500
C	-7.05415400	3.94621600	4.99001700
H	-6.16852800	2.02884200	5.43261200

C	-7.54576900	4.78500500	3.98873600
H	-7.91194700	5.01243400	1.87522500
H	-7.06448200	4.26840100	6.02721700
H	-7.92866500	5.76882300	4.24369800
Cs	-2.92080300	2.67336700	3.71751500

## I6

E = -1890.24957734 a.u.

0 1

O	-4.87326200	0.12229300	1.43157700
C	-3.70812700	0.15357900	0.65428000
C	-2.81954000	1.30535000	0.92417000
C	-1.42666600	1.18706800	0.83224400
C	-3.36250600	2.54110400	1.30534700
C	-0.59962600	2.27375700	1.10930100
H	-0.98729000	0.23102800	0.55755600
C	-2.53727300	3.62275500	1.59093000
H	-4.44092100	2.64413600	1.38397400
C	-1.15060200	3.49428400	1.49576400
H	0.47818300	2.16130600	1.03483600
H	-2.97775000	4.56931100	1.89097900
H	-0.50583000	4.33796000	1.72286900
C	-3.49052600	-0.74140900	-0.33097700
H	-2.60632500	-0.51867300	-0.92349500
C	-4.21543600	-1.91991300	-0.77419000
C	-5.41916100	-2.52167200	-0.13727400
C	-6.59348700	-1.79296300	0.08433300
C	-5.39152300	-3.88348000	0.20545200
C	-7.70599800	-2.40145800	0.66144500
H	-6.63228300	-0.74434600	-0.19706200
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H	-8.60821600	-1.82024700	0.83338800
H	-6.47228500	-5.54242300	1.04153900
H	-8.53300500	-4.21614900	1.47697800
C	-3.65035700	-2.61486400	-1.79148300
F	-4.23928800	-3.59105600	-2.42464700
F	-2.42286000	-4.21906900	-0.76710000
F	-2.58552300	-2.21121400	-2.44405800
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C	-6.60806700	-0.55283100	3.27676700
C	-7.53691300	0.34314900	2.73450100

C	-7.03899800	-1.63006000	4.05200400
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H	-6.30951200	-2.33732200	4.43670100
C	-9.32463000	-0.90648200	3.76775800
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H	-8.73934500	-2.65258000	4.88440000
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C	-4.41622000	3.17868900	4.97369500
H	-6.05721200	2.09414900	4.10631700
C	-2.26138600	2.08679100	4.90202000
H	-2.22908200	0.14015600	3.97539200
C	-3.05107600	3.18097200	5.25593100
H	-5.03435800	4.02306400	5.26360300
H	-1.19832700	2.08662800	5.12283300
H	-2.60288400	4.03366700	5.75754800
Cs	-2.10398400	-3.37356700	1.80799100

### TS5-6

E = -1890.24957342 a.u.

0 1

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H	-0.98228000	0.22151700	0.55316700
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## I5

E = -1890.26950345 a.u.

0 1

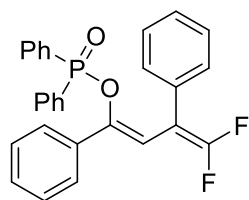
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H	-7.09919700	1.17290700	2.00986900
C	-8.55755900	-1.47335000	4.44371200
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C	-2.76976700	0.95842000	4.24517700

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H	-1.06780100	2.05378800	4.96815700
H	-2.42010200	3.99250400	5.72844200
Cs	-2.61118600	-3.63220200	1.97891400

### Characterization data for products



#### **(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl diphenylphosphinate (3aa):**

Yield = 62% (84.6 mg). White solid. M.p. 84.7–85.3 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

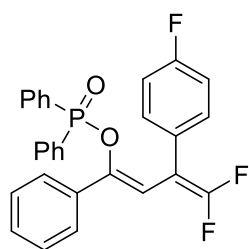
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.55-7.48 (m, 5H), 7.47-7.40 (m, 3H), 7.34-7.28 (m, 5H), 7.27-7.22 (m, 7H), 6.01-5.94 (m, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -79.49 (d, *J* = 19.4 Hz, 1F), -87.05 (d, *J* = 19.4 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.20 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 153.4 (t, *J* = 293.6 Hz), 149.8-148.6 (m), 135.6, 132.2 (t, *J* = 4.2 Hz), 132.1 (d, *J* = 1.6 Hz), 131.5 (d, *J* = 10.6 Hz), 130.6 (d, *J* = 137.3 Hz), 128.8, 128.6 (t, *J* = 4.1 Hz), 128.1, 128.1, 128.0 (d, *J* = 5.3 Hz), 127.1, 126.5, 107.9-107.5 (m), 90.2 (t, *J* = 19.5 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>28</sub>H<sub>22</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 459.1320, found: 459.1315.



#### **(Z)-4,4-Difluoro-3-(4-fluorophenyl)-1-phenylbuta-1,3-dien-1-yl diphenylphosphinate (3ba):**

Yield = 57% (81.3 mg). White solid. M.p. 114.5–116.1 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

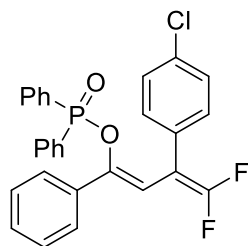
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.58-7.49 (m, 4H), 7.48-7.39 (m, 4H), 7.34-7.26 (m, 4H), 7.24-7.16 (m, 5H), 6.95-6.86 (m, 2H), 6.00 (q, *J* = 2.9 Hz, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -80.31 (d, *J* = 20.9 Hz, 1F), -87.55 (d, *J* = 20.9 Hz, 1F), -114.44 (s, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 30.94 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 161.7 (d, *J* = 246.6 Hz), 153.4 (t, *J* = 293.7 Hz), 149.3-148.8 (m), 135.4, 132.1 (d, *J* = 2.8 Hz), 131.3 (d, *J* = 10.4 Hz), 131.3, 130.6-130.3 (m), 130.0, 128.8, 128.1, 128.0 (d, *J* = 2.0 Hz), 126.4, 114.9 (d, *J* = 21.7 Hz), 107.9-107.6 (m), 89.8 (t, *J* = 19.7 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>28</sub>H<sub>21</sub>F<sub>3</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 477.1226, found: 477.1223.



**(Z)-3-(4-Chlorophenyl)-4,4-difluoro-1-phenylbuta-1,3-dien-1-yl diphenylphosphinate (3ca):**

Yield = 44% (64.4 mg). White solid. M.p. 105.1–106.5 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

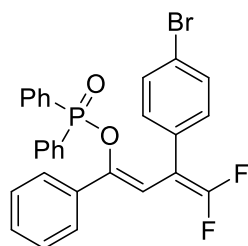
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.52-7.47 (m, 3H), 7.47-7.40 (m, 5H), 7.33-7.27 (m, 4H), 7.24-7.15 (m, 7H), 6.01 (q,  $J$  = 2.8 Hz, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -79.53 (d,  $J$  = 18.0 Hz, 1F), -86.80 (d,  $J$  = 17.9 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.11 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 153.5 (t,  $J$  = 295.4 Hz), 149.4-148.9 (m), 135.4, 132.9, 132.1 (d,  $J$  = 2.9 Hz), 131.3 (d,  $J$  = 10.6 Hz), 130.7 (t,  $J$  = 4.3 Hz), 130.5 (d,  $J$  = 136.6 Hz), 130.1 (t,  $J$  = 3.9 Hz), 129.8, 128.2, 128.1, 128.0 (d,  $J$  = 2.9 Hz), 126.3, 107.8-107.0 (m), 89.9 (t,  $J$  = 20.0 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>28</sub>H<sub>21</sub>ClF<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 493.0930, found: 493.0926.



**(Z)-3-(4-Bromophenyl)-4,4-difluoro-1-phenylbuta-1,3-dien-1-yl diphenylphosphinate (3da):**

Yield = 50% (81.2 mg). White solid. M.p. 103.6–105.2 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

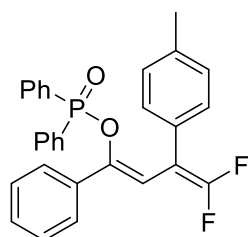
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.51-7.47 (m, 2H), 7.47-7.41 (m, 6H), 7.36-7.27 (m, 6H), 7.24-7.18 (m, 3H), 7.14-7.08 (m, 2H), 6.02 (q,  $J$  = 2.7 Hz, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -79.36 (d,  $J$  = 17.9 Hz, 1F), -86.73 (d,  $J$  = 17.9 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.15 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 153.5 (t,  $J$  = 296.4 Hz), 149.4-149.0 (m), 135.3, 132.2 (d,  $J$  = 3.4 Hz), 131.3 (d,  $J$  = 10.6 Hz), 131.2, 130.4 (d,  $J$  = 137.2 Hz), 130.4 (t,  $J$  = 3.9 Hz), 128.9, 128.2, 128.0, 128.0, 126.3, 121.1, 107.7-107.0 (m), 90.0 (t,  $J$  = 19.7 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>28</sub>H<sub>21</sub>BrF<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 537.0425, found: 537.0428.



**(Z)-4,4-Difluoro-1-phenyl-3-(*p*-tolyl)buta-1,3-dien-1-yl diphenylphosphinate (3ea):**

Yield = 50% (71.4 mg). Yellow oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

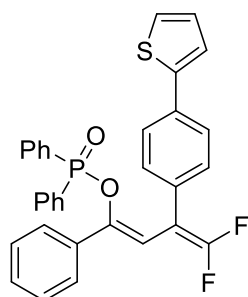
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.52-7.47 (m, 5H), 7.47-7.41 (m, 3H), 7.33-7.27 (m, 4H), 7.26-7.21 (m, 3H), 7.16-7.06 (m, 4H), 5.97 (q, *J* = 3.1 Hz, 1H), 2.34 (s, 3H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -80.25 (d, *J* = 20.9 Hz, 1F), -87.64 (d, *J* = 20.9 Hz, 1F) ppm.

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ = 31.23 ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.4 (t, *J* = 295.2 Hz), 149.6-148.5 (m), 136.9, 135.7, 132.1 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 10.6 Hz), 130.5 (d, *J* = 137.7 Hz), 129.2 (t, *J* = 4.0 Hz), 128.9, 128.8, 128.6 (t, *J* = 3.9 Hz), 128.1 (d, *J* = 4.8 Hz), 128.0, 126.5, 108.2-107.8 (m), 90.2 (t, *J* = 18.8 Hz), 21.2 ppm.

HRMS (*m/z*): calcd for C<sub>29</sub>H<sub>24</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 473.1476, found: 473.1476.



**(Z)-4,4-Difluoro-1-phenyl-3-(4-(thiophen-2-yl)phenyl)buta-1,3-dien-1-yl diphenylphosphinate (3fa):**

Yield = 56% (90.6 mg). Yellow solid. M.p. 136.0–137.1 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

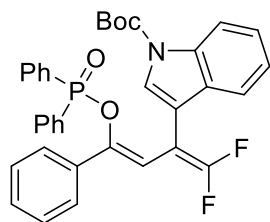
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.53-7.49 (m, 5H), 7.49-7.44 (m, 3H), 7.41-7.35 (m, 2H), 7.32-7.30 (m, 1H), 7.30-7.28 (m, 1H), 7.27-7.22 (m, 9H), 7.09 (dd, *J* = 5.3, 3.4 Hz, 1H), 6.03 (q, *J* = 2.7 Hz, 1H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -79.27 (d, *J* = 18.1 Hz, 1F), -86.60 (d, *J* = 17.9 Hz, 1F) ppm.

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ = 31.30 ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.6 (t, *J* = 294.2 Hz), 149.5-149.0 (m), 143.8, 135.5, 133.1, 132.1 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 10.6 Hz), 131.3 (t, *J* = 4.4 Hz), 130.5 (d, *J* = 137.3 Hz), 129.1 (t, *J* = 4.1 Hz), 128.9, 128.1 (d, *J* = 13.4 Hz), 128.1, 128.1, 126.4, 125.5, 124.9, 123.1, 107.7-107.2 (m), 90.2 (t, *J* = 19.5 Hz) ppm.

HRMS (*m/z*): calcd for C<sub>32</sub>H<sub>24</sub>F<sub>2</sub>O<sub>2</sub>PS [M+H]<sup>+</sup> 541.1197, found: 541.1197.



**tert-Butyl (Z)-3-(4-((diphenylphosphoryl)oxy)-1,1-difluoro-4-phenylbuta-1,3-dien-2-yl)-1H-indole-1-carboxylate (3ga):**

Yield = 57% (102.5 mg). Red oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

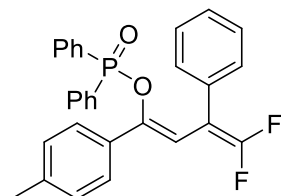
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.19-8.01 (m, 1H), 7.55 (dd,  $J$  = 7.9, 0.9 Hz, 1H), 7.40-7.32 (m, 6H), 7.32-7.24 (m, 5H), 7.22-7.16 (m, 6H), 7.15-7.12 (m, 1H), 6.22 (q,  $J$  = 2.9 Hz, 1H), 1.63 (s, 9H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -81.55 (d,  $J$  = 16.4 Hz, 1F), -85.06 (s, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 30.45 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 154.1 (t,  $J$  = 293.1 Hz), 149.1, 148.4-147.7 (m), 135.6, 135.0, 131.9 (d,  $J$  = 3.4 Hz), 131.1 (d,  $J$  = 10.6 Hz), 130.4 (d,  $J$  = 136.6 Hz), 129.6 (d,  $J$  = 3.4 Hz), 128.6, 128.0 (d,  $J$  = 4.3 Hz), 127.8, 126.3, 125.3, 124.2, 122.7, 120.0, 115.1, 111.5 (t,  $J$  = 3.4 Hz), 107.5 (d,  $J$  = 5.8 Hz), 84.1 (t,  $J$  = 22.1 Hz), 83.5, 28.1 ppm.

**HRMS (m/z):** calcd for C<sub>35</sub>H<sub>31</sub>F<sub>2</sub>NO<sub>4</sub>P [M+H]<sup>+</sup> 598.1953, found: 598.1957.



**(Z)-4,4-Difluoro-3-phenyl-1-(p-tolyl)buta-1,3-dien-1-yl diphenylphosphinate (3ha):**

Yield = 39% (54.9 mg). White solid. M.p. 129.6–131.2 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

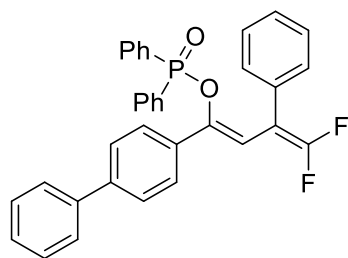
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.54-7.46 (m, 4H), 7.45-7.38 (m, 4H), 7.33-7.25 (m, 6H), 7.25-7.19 (m, 3H), 7.11-7.02 (m, 2H), 5.92 (q,  $J$  = 3.3 Hz, 1H), 2.30 (s, 3H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -79.51 (d,  $J$  = 19.4 Hz, 1F), -87.24 (d,  $J$  = 19.5 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.10 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 153.4 (t,  $J$  = 294.6 Hz), 149.9-149.1 (m), 138.9, 132.8, 132.3 (t,  $J$  = 4.3 Hz), 132.0 (d,  $J$  = 2.9 Hz), 131.5 (d,  $J$  = 10.6 Hz), 130.6 (d,  $J$  = 137.8 Hz), 128.7, 128.5 (t,  $J$  = 4.1 Hz), 128.1 (d,  $J$  = 2.4 Hz), 127.9, 127.0, 126.4, 106.8-106.5 (m), 90.2 (t,  $J$  = 20.0 Hz), 21.2 ppm.

**HRMS (m/z):** calcd for C<sub>29</sub>H<sub>24</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 473.1476, found: 473.1477.



**(Z)-1-([1,1'-Biphenyl]-4-yl)-4,4-difluoro-3-phenylbuta-1,3-dien-1-yl diphenylphosphinate (3ia):**

Yield = 68% (108.4 mg). White solid. M.p. 103.9–104.1 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

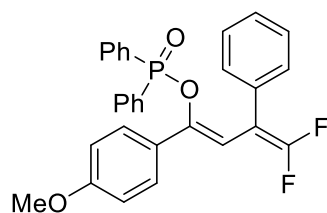
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.62-7.53 (m, 5H), 7.53-7.46 (m, 5H), 7.45-7.38 (m, 4H), 7.35-7.22 (m, 10H), 6.04 (q,  $J$  = 3.0 Hz, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -79.26 (d,  $J$  = 19.4 Hz, 1F), -86.92 (d,  $J$  = 19.4 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.49 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 153.4 (t,  $J$  = 295.3 Hz), 149.2-148.7 (m), 141.5, 140.3, 134.5, 132.2 (t,  $J$  = 4.3 Hz), 132.1 (d,  $J$  = 2.9 Hz), 131.5 (d,  $J$  = 10.6 Hz), 130.5 (d,  $J$  = 137.8 Hz), 128.7, 128.6 (t,  $J$  = 3.9 Hz), 128.1, 128.0, 127.4, 127.1, 126.9, 126.8, 126.7, 107.8-107.4 (m), 90.3 (t,  $J$  = 19.5 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>34</sub>H<sub>26</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 535.1633, found: 535.1630.



**(Z)-4,4-Difluoro-1-(4-methoxyphenyl)-3-phenylbuta-1,3-dien-1-yl diphenylphosphinate (3ja):**

Yield = 61% (90.0 mg). White solid. M.p. 136.4–136.8 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

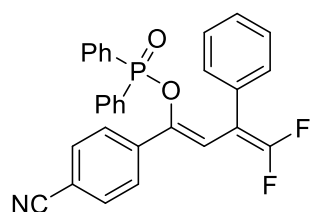
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.53-7.48 (m, 3H), 7.47-7.39 (m, 5H), 7.32-7.25 (m, 6H), 7.25-7.20 (m, 3H), 6.81-6.75 (m, 2H), 5.84 (q,  $J$  = 3.3 Hz, 1H), 3.76 (s, 3H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -79.69 (d,  $J$  = 20.9 Hz, 1F), -87.41 (d,  $J$  = 20.9 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.10 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 160.0, 153.3 (t,  $J$  = 294.8 Hz), 149.5-149.0 (m), 132.4 (t,  $J$  = 4.6 Hz), 132.0 (d,  $J$  = 2.9 Hz), 131.4 (d,  $J$  = 10.6 Hz), 130.6 (d,  $J$  = 137.7 Hz), 128.5 (t,  $J$  = 4.1 Hz), 128.1, 128.1, 128.0, 127.9, 127.0, 113.4, 106.2-105.4 (m), 90.1 (t,  $J$  = 19.6 Hz), 55.1 ppm.

**HRMS (m/z):** calcd for C<sub>29</sub>H<sub>24</sub>F<sub>2</sub>O<sub>3</sub>P [M+H]<sup>+</sup> 489.1426, found: 489.1428.



**(Z)-1-(4-Cyanophenyl)-4,4-difluoro-3-phenylbuta-1,3-dien-1-yl diphenylphosphinate (3ka):**

Yield = 61% (89.0 mg). White solid. M.p. 151.4–152.7 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~4/1).

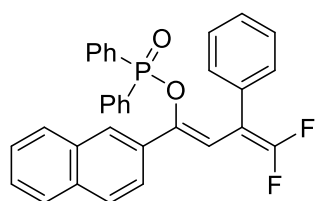
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.65-7.58 (m, 2H), 7.56-7.52 (m, 2H), 7.51-7.42 (m, 6H), 7.36-7.25 (m, 7H), 7.21-7.16 (m, 2H), 6.14 (q, *J* = 3.0 Hz, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ = -78.47 (d, *J* = 16.4 Hz, 1F), -85.84 (d, *J* = 16.4 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):** δ = 32.56 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 153.6 (t, *J* = 294.8 Hz), 147.3-146.9 (m), 140.0, 132.4 (d, *J* = 2.9 Hz), 131.9, 131.6 (t, *J* = 4.2 Hz), 131.4 (d, *J* = 10.6 Hz), 130.0 (d, *J* = 137.3 Hz), 128.6 (t, *J* = 3.9 Hz), 128.3 (d, *J* = 5.8 Hz), 128.2, 127.4, 126.8, 118.5, 112.1, 111.2-110.3 (m), 90.2 (t, *J* = 19.1 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>29</sub>H<sub>21</sub>F<sub>2</sub>NO<sub>2</sub>P [M+H]<sup>+</sup> 484.1272, found: 484.1277.



**(Z)-4,4-Difluoro-1-(naphthalen-2-yl)-3-phenylbuta-1,3-dien-1-yl diphenylphosphinate (3la):**

Yield = 56% (85.9 mg). White solid. M.p. 161.8–162.9 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

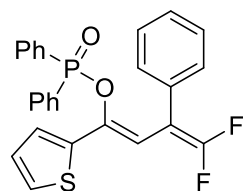
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.92 (d, *J* = 2.2 Hz, 1H), 7.81-7.76 (m, 1H), 7.75-7.70 (m, 1H), 7.69-7.65 (m, 1H), 7.64-7.60 (m, 1H), 7.59-7.51 (m, 4H), 7.49-7.41 (m, 4H), 7.35-7.27 (m, 9H), 6.15 (q, *J* = 3.0 Hz, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ = -79.27 (d, *J* = 19.4 Hz, 1F), -86.98 (d, *J* = 19.4 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):** δ = 31.27 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 153.5 (t, *J* = 295.7 Hz), 149.5-149.0 (m), 133.3, 132.9, 132.7, 132.3 (t, *J* = 4.2 Hz), 132.1 (d, *J* = 3.4 Hz), 131.5 (d, *J* = 10.6 Hz), 130.8 (d, *J* = 137.3 Hz), 128.7 (t, *J* = 3.9 Hz), 128.5, 128.2, 128.1, 127.8, 127.5, 127.2, 126.6, 126.3, 126.2, 123.8, 109.0-107.7 (m), 90.5 (t, *J* = 19.4 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>32</sub>H<sub>24</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 509.1476, found: 509.1474.



**(Z)-4,4-Difluoro-3-phenyl-1-(thiophen-2-yl)buta-1,3-dien-1-yl diphenylphosphinate (3ma):**

Yield = 61% (84.9 mg). Yellow solid. M.p. 128.2–130.1 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.60-7.51 (m, 4H), 7.48-7.42 (m, 2H), 7.36-7.29 (m, 4H), 7.29-7.26 (m, 2H), 7.25-7.22 (m, 2H), 7.22-7.16 (m, 3H), 6.90 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.98 (q, *J* = 2.7 Hz, 1H) ppm.

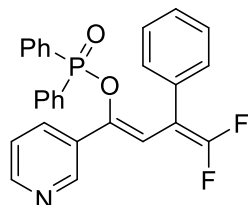
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ = -78.51 (d, *J* = 17.2 Hz, 1F), -86.48 (d, *J* = 17.5 Hz, 1F) ppm.



**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.94 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 153.4 (t,  $J$  = 295.0 Hz), 144.0-143.5 (m), 138.8, 132.2 (d,  $J$  = 2.5 Hz), 132.0 (t,  $J$  = 4.0 Hz), 131.5 (d,  $J$  = 10.6 Hz), 130.4 (d,  $J$  = 137.8 Hz), 128.6 (t,  $J$  = 3.9 Hz), 128.2, 128.1 (d,  $J$  = 2.9 Hz), 127.5, 127.4, 127.2, 126.1, 107.1-106.1 (m), 90.2 (t,  $J$  = 19.5 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>26</sub>H<sub>20</sub>F<sub>2</sub>O<sub>2</sub>PS [M+H]<sup>+</sup> 465.0884, found: 465.0882.



**(Z)-4,4-Difluoro-3-phenyl-1-(pyridin-3-yl)buta-1,3-dien-1-yl diphenylphosphinate (3na):**

Yield = 43% (59.9 mg). Yellow solid. M.p. 80.1–82.0 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~1/1).

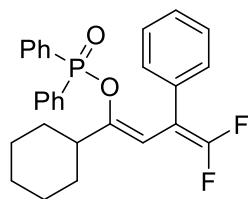
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.68 (d,  $J$  = 2.4 Hz, 1H), 8.50 (dd,  $J$  = 4.8, 1.6 Hz, 1H), 7.90-7.85 (m, 1H), 7.54-7.42 (m, 6H), 7.36-7.26 (m, 7H), 7.25-7.18 (m, 3H), 6.04 (q,  $J$  = 3.1 Hz, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -78.89 (d,  $J$  = 17.9 Hz, 1F), -86.33 (d,  $J$  = 17.9 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 32.29 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 153.7 (t,  $J$  = 295.1 Hz), 149.4, 147.1, 146.6-146.1 (m), 134.4, 132.4 (d,  $J$  = 3.4 Hz), 131.9, 131.8 (t,  $J$  = 3.5 Hz), 131.5 (d,  $J$  = 10.6 Hz), 130.1 (d,  $J$  = 137.3 Hz), 128.6 (t,  $J$  = 3.9 Hz), 128.3 (d,  $J$  = 6.3 Hz), 128.2, 127.4, 122.9, 109.9-109.4 (m), 90.1 (t,  $J$  = 19.4 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>27</sub>H<sub>21</sub>F<sub>2</sub>NO<sub>2</sub>P [M+H]<sup>+</sup> 460.1272, found: 460.1270.



**(Z)-1-Cyclohexyl-4,4-difluoro-3-phenylbuta-1,3-dien-1-yl diphenylphosphinate (3oa):**

Yield = 51% (71.4 mg). Yellow oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

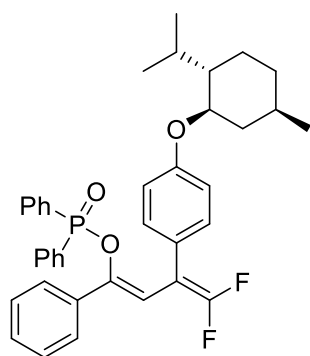
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.55-7.48 (m, 4H), 7.47-7.42 (m, 2H), 7.35-7.29 (m, 4H), 7.27-7.22 (m, 3H), 7.20-7.15 (m, 2H), 5.26 (q,  $J$  = 2.7 Hz, 1H), 2.59-2.47 (m, 1H), 2.11-1.99 (m, 2H), 1.78-1.62 (m, 3H), 1.28-1.13 (m, 5H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -80.78 (d,  $J$  = 22.4 Hz, 1F), -88.59 (d,  $J$  = 22.8 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 29.64 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 157.8-157.2 (m), 153.2 (t,  $J$  = 293.6 Hz), 132.7 (t,  $J$  = 4.1 Hz), 132.1 (d,  $J$  = 2.9 Hz), 131.4 (d,  $J$  = 10.6 Hz), 131.1 (d,  $J$  = 137.9 Hz), 128.3 (t,  $J$  = 3.8 Hz), 128.2, 128.1 (d,  $J$  = 3.4 Hz), 126.9, 103.3-102.8 (m), 89.6 (t,  $J$  = 18.5 Hz), 43.4, 31.4, 26.1, 25.9 ppm.

**HRMS (m/z):** calcd for C<sub>28</sub>H<sub>28</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 465.1789, found: 465.1788.



**(Z)-4,4-Difluoro-3-(4-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)-1-phenylbuta-1,3-dien-1-yl diphenylphosphinate (3pa):**

Yield = 57% (104.3 mg). Yellow oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

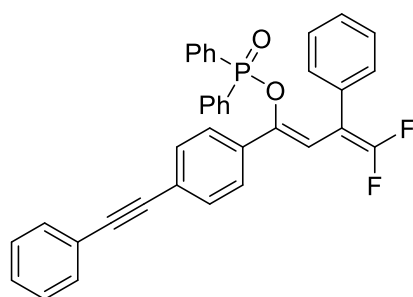
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.60-7.52 (m, 6H), 7.48-7.41 (m, 2H), 7.36-7.27 (m, 7H), 7.19-7.13 (m, 2H), 6.89-6.82 (m, 2H), 5.95 (dt,  $J$  = 4.0, 2.5 Hz, 1H), 4.67 (q,  $J$  = 2.7 Hz, 1H), 2.18-2.08 (m, 1H), 1.87-1.69 (m, 4H), 1.68-1.56 (m, 1H), 1.14-1.00 (m, 3H), 0.98 (d,  $J$  = 6.7 Hz, 3H), 0.91 (d,  $J$  = 6.6 Hz, 3H), 0.87 (d,  $J$  = 6.5 Hz, 3H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -80.76 (d,  $J$  = 19.8 Hz, 1F), -88.13 (d,  $J$  = 19.4 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.16 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 157.4, 153.1 (t,  $J$  = 293.5 Hz), 149.4-149.1 (m), 135.7, 132.1 (d,  $J$  = 2.9 Hz), 131.6 (d,  $J$  = 10.6 Hz), 130.7 (d,  $J$  = 137.8 Hz), 129.7 (t,  $J$  = 4.1 Hz), 128.8, 128.1 (d,  $J$  = 5.3 Hz), 128.0, 126.5, 123.8 (t,  $J$  = 4.3 Hz), 115.1, 108.0, 89.6 (t,  $J$  = 19.7 Hz), 73.0, 47.7, 37.5, 34.9, 29.2, 26.2, 24.7, 22.2, 21.0, 20.9 ppm.

**HRMS (m/z):** calcd for C<sub>38</sub>H<sub>40</sub>F<sub>2</sub>O<sub>3</sub>P [M+H]<sup>+</sup> 613.2678, found: 613.2684.



**(Z)-4,4-Difluoro-3-phenyl-1-(4-(phenylethynyl)phenyl)buta-1,3-dien-1-yl diphenylphosphinate (3qa):**

Yield = 58% (97.6 mg). White solid. M.p. 167.9–169.1 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.54-7.51 (m, 4H), 7.51-7.47 (m, 4H), 7.47-7.38 (m, 4H), 7.36-7.28 (m, 8H), 7.28-7.21 (m, 4H), 6.04 (q,  $J$  = 3.3 Hz, 1H) ppm.

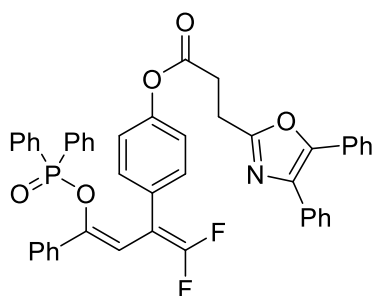
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -79.11 (d,  $J$  = 19.4 Hz, 1F), -86.69 (d,  $J$  = 19.9 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.58 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 153.5 (t,  $J$  = 295.2 Hz), 148.8-148.3 (m), 135.4, 132.2 (d,  $J$  = 2.9 Hz), 132.2 (t,  $J$  = 4.1 Hz), 131.6, 131.5, 131.3, 130.5 (d,  $J$  = 137.3 Hz), 128.7 (t,  $J$  = 3.9 Hz),

128.4, 128.3, 128.2 (d,  $J = 4.3$  Hz), 128.1, 127.2, 126.4, 123.7, 123.1, 108.8-108.2 (m), 90.7, 90.4 (t,  $J = 19.9$  Hz), 89.1 ppm.

**HRMS (m/z):** calcd for  $C_{36}H_{26}F_2O_2P$   $[M+H]^+$  559.1633, found: 559.1632.



**(Z)-4-(4-((Diphenylphosphoryl)oxy)-1,1-difluoro-4-phenylbuta-1,3-dien-2-yl)phenyl 3-(4,5-diphenyloxazol-2-yl)propanoate (3ra):**

Yield = 58% (131.5 mg). Yellow oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~3/1).

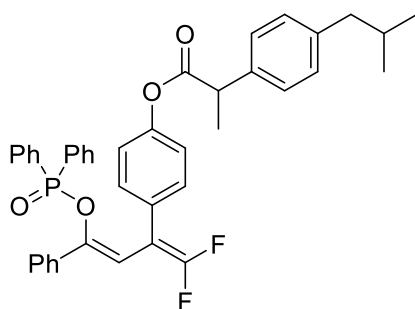
**$^1H$  NMR (400 MHz,  $CDCl_3$ ):**  $\delta = 7.69$ – $7.63$  (m, 2H),  $7.62$ – $7.57$  (m, 2H),  $7.56$ – $7.48$  (m, 6H),  $7.45$ – $7.37$  (m, 4H),  $7.36$ – $7.27$  (m, 9H),  $7.27$ – $7.24$  (m, 2H),  $7.22$ – $7.18$  (m, 2H),  $7.04$ – $6.98$  (m, 2H),  $6.01$ – $5.94$  (m, 1H),  $3.33$  (t,  $J = 7.5$  Hz, 2H),  $3.20$  (t,  $J = 7.1$  Hz, 2H) ppm.

**$^{19}F$  NMR (376 MHz,  $CDCl_3$ ):**  $\delta = -79.16$  (d,  $J = 19.4$  Hz, 1F),  $-86.67$  (d,  $J = 19.4$  Hz, 1F) ppm.

**$^{31}P$  NMR (162 MHz,  $CDCl_3$ ):**  $\delta = 31.42$  ppm.

**$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):**  $\delta = 170.5$ ,  $161.4$ ,  $150.4$  (t,  $J = 293.4$  Hz),  $149.5$ ,  $149.5$ – $149.3$  (m),  $145.5$ ,  $135.5$ ,  $135.1$ ,  $132.2$  (d,  $J = 2.9$  Hz),  $131.7$  (d,  $J = 108.4$  Hz),  $131.4$  (d,  $J = 10.6$  Hz),  $130.0$  (t,  $J = 4.4$  Hz),  $129.8$ ,  $129.6$  (t,  $J = 3.8$  Hz),  $128.9$ ,  $128.8$ ,  $128.6$ ,  $128.5$ ,  $128.5$ ,  $128.2$ ,  $128.1$ ,  $128.1$ ,  $127.8$ ,  $126.4$ ,  $126.4$ ,  $121.2$ ,  $107.9$ – $106.5$  (m),  $89.6$  (t,  $J = 20.2$  Hz),  $31.1$ ,  $23.4$  ppm.

**HRMS (m/z):** calcd for  $C_{46}H_{35}F_2NO_5P$   $[M+H]^+$  750.2215, found: 750.2220.



**(Z)-4-(4-((Diphenylphosphoryl)oxy)-1,1-difluoro-4-phenylbuta-1,3-dien-2-yl)phenyl 2-(4-isobutylphenyl)propanoate (3sa):**

Yield = 67% (134.0 mg). Yellow oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

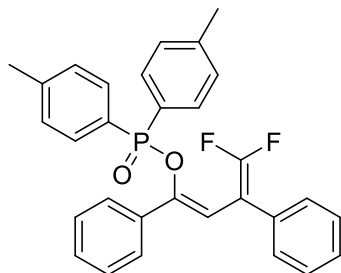
**$^1H$  NMR (400 MHz,  $CDCl_3$ ):**  $\delta = 7.54$ – $7.45$  (m, 6H),  $7.43$ – $7.37$  (m, 2H),  $7.36$ – $7.32$  (m, 2H),  $7.31$ – $7.23$  (m, 7H),  $7.20$ – $7.16$  (m, 4H),  $6.94$ – $6.88$  (m, 2H),  $5.97$  (q,  $J = 3.4$  Hz, 1H),  $3.96$  (q,  $J = 7.1$  Hz, 1H),  $2.49$  (d,  $J = 7.1$  Hz, 2H),  $1.95$ – $1.82$  (m, 1H),  $1.63$  (d,  $J = 7.1$  Hz, 3H),  $0.92$  (d,  $J = 6.6$  Hz, 6H) ppm.

**$^{19}F$  NMR (376 MHz,  $CDCl_3$ ):**  $\delta = -79.45$  (d,  $J = 19.4$  Hz, 1F),  $-86.87$  (d,  $J = 19.4$  Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.33 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 173.0, 153.4 (t,  $J$  = 297.7 Hz), 149.8, 149.6–149.1 (m), 140.8, 137.2, 135.5, 132.6 (d,  $J$  = 2.9 Hz), 131.4 (d,  $J$  = 10.1 Hz), 130.5 (d,  $J$  = 137.7 Hz), 129.7 (t,  $J$  = 4.2 Hz), 129.6, 129.5, 129.5, 128.9, 128.1 (d,  $J$  = 2.5 Hz), 127.2, 126.4, 121.0, 107.6, 89.7 (t,  $J$  = 19.7 Hz), 45.2, 45.0, 30.2, 22.4, 18.5 ppm.

**HRMS (m/z):** calcd for C<sub>41</sub>H<sub>38</sub>F<sub>2</sub>O<sub>4</sub>P [M+H]<sup>+</sup> 663.2470, found: 663.2471.



**(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl di-*p*-tolylphosphinate (3ab):**

Yield = 57% (83.0 mg). Yellow oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

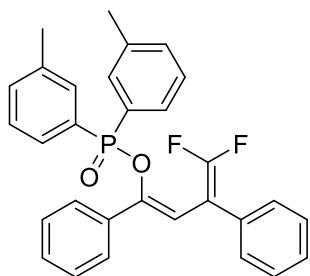
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.59-7.53 (m, 2H), 7.45-7.37 (m, 4H), 7.33-7.27 (m, 6H), 7.25-7.21 (m, 2H), 7.14-7.08 (m, 4H), 6.00-5.93 (m, 1H), 2.33 (s, 6H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -79.33 (d,  $J$  = 19.4 Hz, 1F), -86.96 (d,  $J$  = 19.6 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 32.42 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 153.4 (t,  $J$  = 295.6 Hz), 149.8-149.3 (m), 142.6 (d,  $J$  = 2.9 Hz), 135.8, 132.3 (t,  $J$  = 4.3 Hz), 131.5 (d,  $J$  = 11.1 Hz), 128.8, 128.8, 128.7, 128.5 (t,  $J$  = 4.1 Hz), 128.0 (d,  $J$  = 2.0 Hz), 127.5 (d,  $J$  = 140.3 Hz), 126.8, 126.5, 108.0-106.9 (m), 90.1 (t,  $J$  = 19.5 Hz), 21.5 ppm.

**HRMS (m/z):** calcd for C<sub>30</sub>H<sub>26</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 487.1633, found: 487.1637.



**(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl di-*m*-tolylphosphinate (3ac):**

Yield = 62% (90.8 mg). Yellow oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.55-7.49 (m, 2H), 7.39 (d,  $J$  = 13.1 Hz, 2H), 7.33-7.25 (m, 7H), 7.24-7.18 (m, 7H), 5.99-5.93 (m, 1H), 2.24 (s, 6H) ppm.

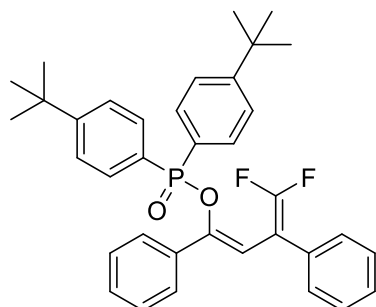
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -79.34 (d,  $J$  = 19.9 Hz, 1F), -86.89 (d,  $J$  = 19.2 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 32.01 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 153.5 (t,  $J$  = 294.5 Hz), 149.6-149.2 (m), 137.9 (d,  $J$  = 13.5 Hz), 135.7, 132.9 (d,  $J$  = 2.9 Hz), 132.3 (t,  $J$  = 4.3 Hz), 131.9 (d,  $J$  = 10.6 Hz), 130.6 (d,  $J$  = 136.8 Hz), 128.8, 128.7, 128.6, 128.5 (t,  $J$  = 3.9 Hz), 128.0, 127.9, 127.1, 126.5, 107.7-107.4 (m), 90.1 (t,

$J = 19.3$  Hz), 21.2 ppm.

**HRMS (m/z):** calcd for  $C_{30}H_{26}F_2O_2P$   $[M+H]^+$  487.1633, found: 487.1637.



**(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl bis(4-(tert-butyl)phenyl)phosphinate (3ae):**

Yield = 35% (60.2 mg). White solid. M.p. 173.4–173.8 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

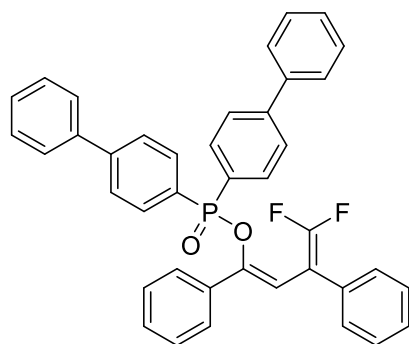
**$^1H$  NMR (400 MHz,  $CDCl_3$ ):**  $\delta = 7.55$ -7.50 (m, 2H), 7.49-7.41 (m, 4H), 7.33-7.28 (m, 4H), 7.28-7.20 (m, 8H), 6.00-5.92 (m, 1H), 1.27 (s, 18H) ppm.

**$^{19}F$  NMR (376 MHz,  $CDCl_3$ ):**  $\delta = -79.44$  (d,  $J = 19.4$  Hz, 1F),  $-86.93$  (d,  $J = 19.4$  Hz, 1F) ppm.

**$^{31}P$  NMR (162 MHz,  $CDCl_3$ ):**  $\delta = 32.04$  ppm.

**$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):**  $\delta = 155.4$  (d,  $J = 2.9$  Hz), 153.4 (t,  $J = 294.5$  Hz), 149.5-149.0 (m), 135.9, 132.4 (t,  $J = 4.1$  Hz), 131.4 (d,  $J = 10.6$  Hz), 128.7, 128.6 (t,  $J = 3.7$  Hz), 128.0 (d,  $J = 4.8$  Hz), 127.6 (d,  $J = 139.0$  Hz), 127.0, 126.4, 125.1, 124.9, 107.8-107.1 (m), 90.3 (t,  $J = 20.0$  Hz), 34.8, 30.9 ppm.

**HRMS (m/z):** calcd for  $C_{36}H_{38}F_2O_2P$   $[M+H]^+$  571.2572, found: 571.2569.



**(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl di([1,1'-biphenyl]-4-yl)phosphinate (3af):**

Yield = 36% (65.7 mg). White solid. M.p. 123.5–125.1 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

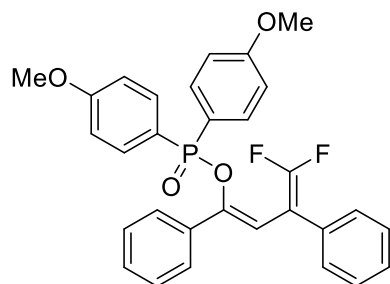
**$^1H$  NMR (400 MHz,  $CDCl_3$ ):**  $\delta = 7.66$ -7.60 (m, 4H), 7.60-7.52 (m, 10H), 7.50-7.44 (m, 4H), 7.43-7.38 (m, 2H), 7.32-7.22 (m, 8H), 6.06-6.01 (m, 1H) ppm.

**$^{19}F$  NMR (376 MHz,  $CDCl_3$ ):**  $\delta = -79.28$  (d,  $J = 19.4$  Hz, 1F),  $-86.71$  (d,  $J = 19.4$  Hz, 1F) ppm.

**$^{31}P$  NMR (162 MHz,  $CDCl_3$ ):**  $\delta = 31.41$  ppm.

**$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):**  $\delta = 153.5$  (t,  $J = 295.6$  Hz), 149.6-149.2 (m), 145.0, 144.9, 139.9, 135.7, 132.3 (t,  $J = 4.2$  Hz), 132.1 (d,  $J = 11.1$  Hz), 129.9, 128.9, 128.9, 128.6 (t,  $J = 3.9$  Hz), 128.2 (d,  $J = 5.3$  Hz), 128.1, 127.2, 127.2, 126.9 (d,  $J = 14.0$  Hz), 126.6, 108.0-107.6 (m), 90.3 (t,  $J = 19.1$  Hz) ppm.

**HRMS (m/z):** calcd for C<sub>40</sub>H<sub>30</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 611.1946, found: 611.1949.



**(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl bis(4-methoxyphenyl)phosphinate (3ag):**

Yield = 50% (78.4 mg). Yellow solid. M.p. 87.4–88.2 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~4/1).

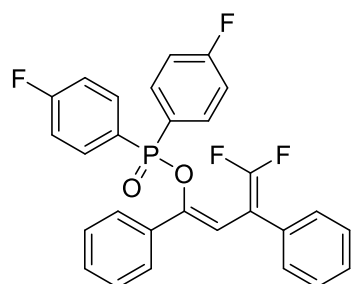
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.58-7.50 (m, 2H), 7.47-7.38 (m, 4H), 7.31-7.21 (m, 8H), 6.82-6.75 (m, 4H), 5.96-5.92 (m, 1H), 3.78 (s, 6H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ = -79.30 (d, *J* = 19.4 Hz, 1F), -86.82 (d, *J* = 19.4 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):** δ = 32.24 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 162.5 (d, *J* = 2.9 Hz), 153.5 (t, *J* = 294.5 Hz), 149.7-149.3 (m), 135.9, 133.4 (d, *J* = 12.0 Hz), 132.4 (t, *J* = 4.8 Hz), 128.5 (t, *J* = 4.1 Hz), 128.1 (d, *J* = 4.3 Hz), 127.9 (d, *J* = 176.6 Hz), 126.5, 123.0, 121.6, 113.7, 113.5, 108.0-106.8 (m), 90.2 (t, *J* = 18.7 Hz), 55.2 ppm.

**HRMS (m/z):** calcd for C<sub>30</sub>H<sub>26</sub>F<sub>2</sub>O<sub>4</sub>P [M+H]<sup>+</sup> 519.1531, found: 519.1531.



**(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl bis(4-fluorophenyl)phosphinate (3ah):**

Yield = 51% (75.1 mg). White solid. M.p. 120.9–121.6 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

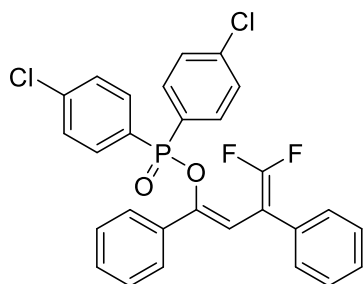
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.50-7.42 (m, 6H), 7.31-7.24 (m, 8H), 7.01-6.94 (m, 4H), 6.00 (q, *J* = 3.1 Hz, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ = -79.57 (d, *J* = 19.4 Hz, 1F), -86.76 (d, *J* = 19.4 Hz, 1F), -105.60 (p, *J* = 7.4 Hz, 2F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):** δ = 29.08 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 165.1 (dd, *J* = 254.1, 3.6 Hz), 153.6 (t, *J* = 294.0 Hz), 149.4-148.9 (m), 135.4, 134.1 (d, *J* = 9.2 Hz), 134.0 (d, *J* = 9.2 Hz), 132.1 (t, *J* = 4.1 Hz), 129.1, 128.6 (t, *J* = 3.9 Hz), 128.2 (d, *J* = 10.6 Hz), 127.3, 126.5, 126.5 (dd, *J* = 126.5, 3.4 Hz), 115.6 (dd, *J* = 21.7, 14.9 Hz), 108.5-107.4 (m), 90.3 (t, *J* = 20.2 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>28</sub>H<sub>20</sub>F<sub>4</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 495.1132, found: 495.1128.



**(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl bis(4-chlorophenyl)phosphinate (3ai):**

Yield = 56% (89.2 mg). White solid. M.p. 135.8–137.3 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

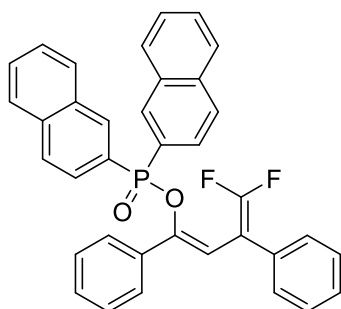
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.49-7.44 (m, 2H), 7.41-7.34 (m, 4H), 7.31-7.23 (m, 12H), 6.00 (q, *J* = 3.3 Hz, 1H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -79.41 (d, *J* = 19.1 Hz, 1F), -86.53 (d, *J* = 19.4 Hz, 1F) ppm.

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ = 28.98 ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.6 (t, *J* = 293.8 Hz), 149.4-148.6 (m), 139.0 (d, *J* = 3.9 Hz), 135.3, 132.9 (d, *J* = 11.6 Hz), 132.0 (t, *J* = 4.0 Hz), 129.1, 128.7 (d, *J* = 139.1 Hz), 128.7, 128.5, 128.5, 128.2 (d, *J* = 9.2 Hz), 127.3, 126.5, 108.1-107.9 (m), 90.2 (t, *J* = 19.1 Hz) ppm.

HRMS (m/z): calcd for C<sub>28</sub>H<sub>20</sub>Cl<sub>2</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 527.0541, found: 527.0543.



**(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl di(naphthalen-2-yl)phosphinate (3aj):**

Yield = 67% (111.9 mg). White solid. M.p. 120.4–122.3 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

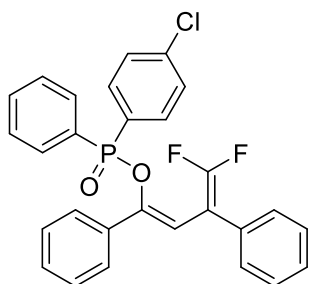
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.22 (d, *J* = 14.6 Hz, 2H), 7.79-7.73 (m, 5H), 7.72 (d, *J* = 3.8 Hz, 1H), 7.58-7.52 (m, 5H), 7.52-7.45 (m, 3H), 7.24-7.18 (m, 3H), 7.16-7.06 (m, 5H), 6.01-5.95 (m, 1H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -79.13 (d, *J* = 19.4 Hz, 1F), -86.42 (d, *J* = 19.4 Hz, 1F) ppm.

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ = 31.53 ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.4 (t, *J* = 294.2 Hz), 149.8-149.2 (m), 135.6, 134.7 (d, *J* = 2.9 Hz), 133.7 (d, *J* = 10.1 Hz), 132.1, 132.0 (t, *J* = 4.3 Hz), 132.0, 128.9, 128.9, 128.3 (t, *J* = 4.1 Hz), 128.1 (d, *J* = 10.1 Hz), 128.0, 127.9, 127.9, 127.8 (d, *J* = 137.2 Hz), 127.6, 127.1, 126.6 (d, *J* = 20.2 Hz), 126.2 (d, *J* = 11.1 Hz), 107.7, 90.2 (t, *J* = 19.7 Hz) ppm.

HRMS (m/z): calcd for C<sub>36</sub>H<sub>26</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 559.1633, found: 559.1637.



**(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl (4-chlorophenyl)(phenyl)phosphinate (3ak):**

Yield = 51% (75.9 mg). White solid. M.p. 105.0–106.0 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

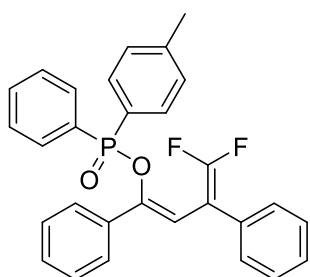
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.53-7.42 (m, 5H), 7.42-7.35 (m, 2H), 7.34-7.22 (m, 12H), 5.99 (q, *J* = 3.0 Hz, 1H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -79.45 (d, *J* = 19.4 Hz, 1F), -86.76 (d, *J* = 19.2 Hz, 1F) ppm.

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ = 30.08 ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.5 (t, *J* = 296.0 Hz), 149.4-149.0 (m), 138.7 (d, *J* = 3.4 Hz), 135.5, 132.9 (d, *J* = 11.6 Hz), 132.3 (d, *J* = 2.9 Hz), 132.1 (t, *J* = 4.6 Hz), 131.4 (d, *J* = 10.6 Hz), 130.2 (d, *J* = 138.1 Hz), 129.8, 129.0, 128.5 (t, *J* = 3.4 Hz), 128.5, 128.3 (d, *J* = 8.2 Hz), 128.2 (d, *J* = 9.1 Hz), 128.1, 127.2, 126.5, 108.0-107.7 (m), 90.2 (t, *J* = 19.0 Hz) ppm.

HRMS (m/z): calcd for C<sub>28</sub>H<sub>21</sub>ClF<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 493.0930, found: 493.0934.



**(Z)-4,4-Difluoro-1,3-diphenylbuta-1,3-dien-1-yl phenyl(*p*-tolyl)phosphinate (3al):**

Yield = 59% (84.0 mg). Yellow oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.58-7.48 (m, 4H), 7.46-7.37 (m, 3H), 7.33-7.24 (m, 10H), 7.12 (dd, *J* = 8.1, 3.6 Hz, 2H), 6.01-5.95 (m, 1H), 2.34 (s, 3H) ppm.

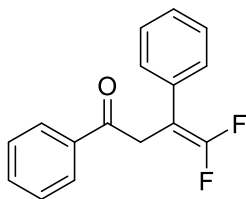
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -79.42 (d, *J* = 19.4 Hz, 1F), -87.00 (d, *J* = 19.3 Hz, 1F) ppm.

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ = 31.82 ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.4 (t, *J* = 292.7 Hz), 149.6-149.1 (m), 142.7 (d, *J* = 2.9 Hz), 135.7, 132.3 (t, *J* = 4.3 Hz), 132.0 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 25.2 Hz), 131.5 (d, *J* = 3.9 Hz), 130.8 (d, *J* = 136.8 Hz), 128.9, 128.8, 128.7, 128.5 (t, *J* = 4.1 Hz), 128.1, 128.0, 127.9 (t, *J* = 7.2 Hz), 127.1, 126.5, 107.8-107.2 (m), 90.2 (t, *J* = 19.5 Hz), 21.5 ppm.

HRMS (m/z): calcd for C<sub>29</sub>H<sub>24</sub>F<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 473.1476, found: 473.1476.





**4,4-Difluoro-1,3-diphenylbut-3-en-1-one (4):**

Yield = 65% (50.7 mg). White solid. M.p. 66.7–68.4 °C.

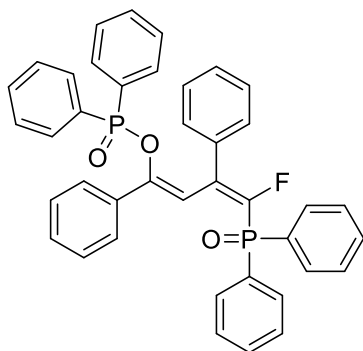
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 100/1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.00-7.93 (m, 2H), 7.60-7.53 (m, 1H), 7.49-7.43 (m, 2H), 7.34-7.28 (m, 4H), 7.27-7.20 (m, 1H), 4.06 (t,  $J$  = 2.2 Hz, 2H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -87.94 (d,  $J$  = 37.3 Hz, 1F), -88.98 (d,  $J$  = 37.2 Hz, 1F) ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 195.3 (t,  $J$  = 2.7 Hz), 154.7 (dd,  $J$  = 292.4, 288.0 Hz), 136.2, 133.5, 133.4, 128.7, 128.5, 128.1, 128.0 (t,  $J$  = 3.6 Hz), 127.4, 87.1 (dd,  $J$  = 21.7, 17.3 Hz), 38.3 (d,  $J$  = 2.4 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>16</sub>H<sub>13</sub>F<sub>2</sub>O [M+H]<sup>+</sup> 259.0929, found: 259.0934.



**(1Z,3E)-4-(Diphenylphosphoryl)-4-fluoro-1,3-diphenylbuta-1,3-dien-1-yl diphenylphosphinate (5):**

Yield = 54% (104.6 mg). White solid. M.p. 215.1–216.3 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 4/1~1/1).

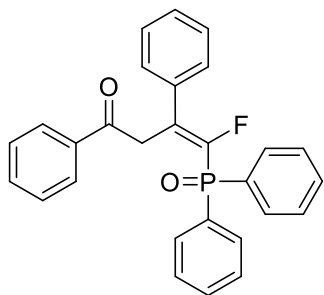
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.95-7.85 (m, 4H), 7.60-7.53 (m, 2H), 7.53-7.44 (m, 5H), 7.43-7.35 (m, 4H), 7.33-7.26 (m, 3H), 7.26-7.18 (m, 6H), 7.17-7.08 (m, 7H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -117.90 (d,  $J$  = 83.4 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.15, 22.83 (d,  $J$  = 84.5 Hz) ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 149.6 (t,  $J$  = 8.5 Hz), 136.0, 134.4 (dd,  $J$  = 17.5, 10.4 Hz), 133.8 (d,  $J$  = 8.2 Hz), 132.3 (d,  $J$  = 3.4 Hz), 131.9, 131.8, 131.7, 131.4 (d,  $J$  = 10.6 Hz), 130.7 (d,  $J$  = 108.4 Hz), 130.0 (d,  $J$  = 137.0 Hz), 129.7 (d,  $J$  = 4.3 Hz), 128.5 (d,  $J$  = 12.6 Hz), 128.5, 128.0, 127.8, 127.7 (d,  $J$  = 1.8 Hz), 127.6, 126.5, 110.1 ppm.

**HRMS (m/z):** calcd for C<sub>40</sub>H<sub>32</sub>FO<sub>3</sub>P<sub>2</sub> [M+H]<sup>+</sup> 641.1805, found: 641.1799.



**(E)-4-(Diphenylphosphoryl)-4-fluoro-1,3-diphenylbut-3-en-1-one (6)**

Yield = 69% (91.8 mg). Yellow oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

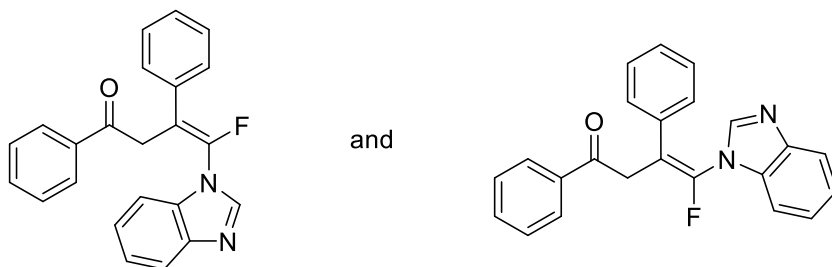
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.04-7.95 (m, 2H), 7.92-7.82 (m, 4H), 7.61-7.55 (m, 2H), 7.53-7.46 (m, 5H), 7.44-7.36 (m, 4H), 7.36-7.25 (m, 3H), 5.00 (s, 2H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -115.67 (d, *J* = 84.9 Hz, 1F) ppm.

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ = 23.53 (d, *J* = 86.7 Hz) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 196.5, 149.8 (dd, *J* = 275.5, 128.1 Hz), 136.6, 136.0 (dd, *J* = 8.4, 3.0 Hz), 133.4 (dd, *J* = 19.3, 7.7 Hz), 133.0, 132.5 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 10.6 Hz), 130.3 (d, *J* = 108.9 Hz), 128.6, 128.5, 128.4, 128.3, 128.2 (d, *J* = 3.4 Hz), 128.0 (d, *J* = 3.9 Hz), 40.2 ppm.

HRMS (m/z): calcd for C<sub>28</sub>H<sub>23</sub>FO<sub>2</sub>P [M+H]<sup>+</sup> 441.1414, found: 441.1409.



**(Z)-4-(1H-benzo[d]imidazol-1-yl)-4-fluoro-1,3-diphenylbut-3-en-1-one (7) and (E)-4-(1H-benzo[d]imidazol-1-yl)-4-fluoro-1,3-diphenylbut-3-en-1-one (7')**

Yield = 63% (67.4 mg; *Z/E* = 4/3). Colourless oil.

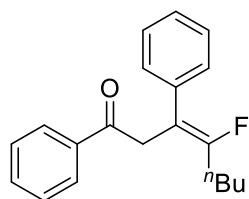
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (7 and its isomer 7'): δ = 8.14 (s, 0.4H), 8.07-8.05 (m, 0.6H), 8.05-8.02 (m, 0.6H), 7.85-7.78 (m, 1.4H), 7.78-7.72 (m, 1H), 7.66-7.55 (m, 2H), 7.55-7.49 (m, 2H), 7.45-7.28 (m, 4H), 7.15-7.09 (m, 1.8H), 7.05-6.98 (m, 1.2H), 4.40 (d, *J* = 3.0 Hz, 1.2H), 3.94 (d, *J* = 1.5 Hz, 0.8H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) (7 and its isomer 7'): δ = -89.22 (s, 0.43F), -90.41 (s, 0.57F) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (7 and its isomer 7'): δ = 195.7 (d, *J* = 4.0 Hz), 194.9 (d, *J* = 2.9 Hz), 145.0, 144.4, 143.0, 142.7, 142.6 (d, *J* = 3.4 Hz), 142.4 (d, *J* = 2.9 Hz), 142.3, 141.8, 136.2, 135.8, 135.0 (d, *J* = 3.9 Hz), 134.2 (d, *J* = 3.3 Hz), 133.7, 133.6, 133.0, 133.0, 128.8, 128.7, 128.6, 128.4, 128.3 (d, *J* = 3.9 Hz), 128.2, 128.1, 128.1, 127.5 (d, *J* = 3.4 Hz), 124.6, 124.5, 123.7, 123.5, 120.7, 120.4, 113.3 (d, *J* = 23.6 Hz), 112.3 (d, *J* = 26.0 Hz), 111.2, 110.7, 41.1, 40.9 ppm.

HRMS (m/z): calcd for C<sub>23</sub>H<sub>18</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> 357.1398, found: 357.1394.



**(Z)-4-Fluoro-1,3-diphenylbut-3-en-1-one (8):**

Yield = 36% (31.6 mg). Yellow oil.

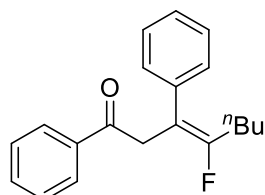
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 100/1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.97–7.93 (m, 2H), 7.58–7.52 (m, 1H), 7.47–7.41 (m, 2H), 7.32–7.27 (m, 2H), 7.26–7.22 (m, 1H), 7.21–7.17 (m, 2H), 4.10 (d,  $J$  = 2.7 Hz, 2H), 2.25 (dt,  $J$  = 23.2, 7.5 Hz, 2H), 1.57–1.48 (m, 2H), 1.35–1.25 (m, 2H), 0.84 (t,  $J$  = 7.3 Hz, 3H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -105.29 (t,  $J$  = 23.1 Hz, 1F) ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 196.9 (d,  $J$  = 1.8 Hz), 159.6 (d,  $J$  = 255.3 Hz), 138.4 (d,  $J$  = 8.7 Hz), 136.7, 133.0, 129.0 (d,  $J$  = 2.9 Hz), 128.5, 128.3, 128.2, 127.1, 112.8 (d,  $J$  = 18.8 Hz), 40.9 (d,  $J$  = 6.7 Hz), 28.9 (d,  $J$  = 27.5 Hz), 28.6, 22.0, 13.8 ppm.

**HRMS (m/z):** calcd for C<sub>20</sub>H<sub>22</sub>FO [M+H]<sup>+</sup> 297.1649, found: 297.1643.



**(E)-4-Fluoro-1,3-diphenylbut-3-en-1-one (8'):**

Yield = 19% (17.2 mg). Yellow oil.

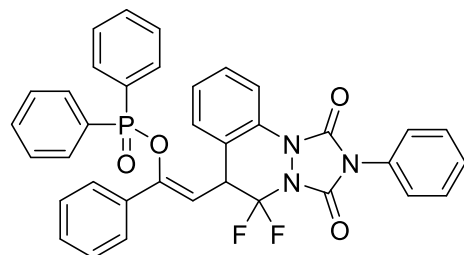
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 100/1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.95–7.90 (m, 2H), 7.59–7.54 (m, 1H), 7.47–7.41 (m, 2H), 7.33–7.28 (m, 4H), 7.24–7.18 (m, 1H), 4.02 (s, 2H), 2.35 (dt,  $J$  = 23.2, 7.6 Hz, 2H), 1.64–1.55 (m, 2H), 1.45–1.35 (m, 2H), 0.92 (t,  $J$  = 7.3 Hz, 3H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -105.29 (t,  $J$  = 23.1 Hz, 1F) ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 196.5 (d,  $J$  = 3.3 Hz), 159.0 (d,  $J$  = 255.8 Hz), 137.4, 136.6, 133.2, 128.6, 128.5 (d,  $J$  = 3.4 Hz), 128.1, 128.1, 126.8, 110.9 (d,  $J$  = 17.3 Hz), 41.6 (d,  $J$  = 5.8 Hz), 29.4 (d,  $J$  = 28.4 Hz), 28.5, 22.3, 13.9 ppm.

**HRMS (m/z):** calcd for C<sub>20</sub>H<sub>22</sub>FO [M+H]<sup>+</sup> 297.1649, found: 297.1650.



**(Z)-2-(5,5-Difluoro-1,3-dioxo-2-phenyl-2,3,5,6-tetrahydro-1H-[1,2,4]triazolo[1,2-a]cinnolin-6-yl)-1-phenylvinyl diphenylphosphinate (10):**

Yield = 33% (20.7 mg; using 0.1 mmol **3aa**). Yellow oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~4/1).

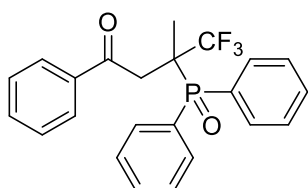
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.35 (d,  $J$  = 8.4 Hz, 1H), 7.94–7.83 (m, 2H), 7.75–7.65 (m, 2H), 7.61–7.51 (m, 6H), 7.49–7.37 (m, 5H), 7.36–7.29 (m, 4H), 7.28–7.20 (m, 2H), 7.19–7.13 (m, 2H), 5.58–5.50 (m, 1H), 5.26 (td,  $J$  = 11.0, 7.2 Hz, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -83.81 (dd,  $J$  = 189.2, 7.5 Hz, 1F), -90.57 (dd,  $J$  = 189.2, 11.9 Hz, 1F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 32.04 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 151.7, 151.6, 147.3, 146.0, 135.0, 132.7 (dd,  $J$  = 21.0, 3.1 Hz), 131.8 (d,  $J$  = 10.6 Hz), 131.6 (d,  $J$  = 10.6 Hz), 130.7 (d,  $J$  = 9.9 Hz), 130.4 (d,  $J$  = 55.4 Hz), 129.3, 129.2, 128.9 (d,  $J$  = 3.4 Hz), 128.6 (d,  $J$  = 13.5 Hz), 128.3 (d,  $J$  = 13.5 Hz), 128.1, 126.5, 126.1, 125.6, 121.0, 117.2 (t,  $J$  = 261.7 Hz), 115.9, 110.0–109.8 (m), 43.6–42.8 (m) ppm.

**HRMS (m/z):** calcd for C<sub>36</sub>H<sub>27</sub>F<sub>2</sub>N<sub>3</sub>O<sub>4</sub>P [M+H]<sup>+</sup> 634.1702, found: 634.1705.



**3-(Diphenylphosphoryl)-4,4,4-trifluoro-3-methyl-1-phenylbutan-1-one (11a):**

Yield = 90% (112.7 mg). White solid. M.p. 121.6–122.5 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~6/1).

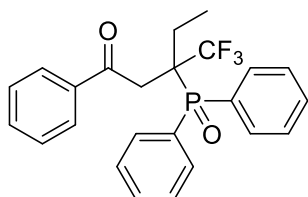
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.15–8.00 (m, 4H), 7.89–7.82 (m, 2H), 7.60–7.46 (m, 7H), 7.45–7.38 (m, 2H), 3.62 (dd,  $J$  = 15.3, 9.1 Hz, 1H), 3.36 (dd,  $J$  = 15.2, 8.9 Hz, 1H), 1.76 (d,  $J$  = 15.0 Hz, 3H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -63.47 (d,  $J$  = 2.7 Hz, 3F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.18 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 196.3 (d,  $J$  = 10.6 Hz), 137.5, 133.2, 132.5, 132.4 (d,  $J$  = 3.4 Hz), 132.3 (d,  $J$  = 6.3 Hz), 129.4 (dd,  $J$  = 95.3, 10.1 Hz), 128.6 (d,  $J$  = 5.3 Hz), 128.4 (d,  $J$  = 16.9 Hz), 127.0 (q,  $J$  = 283.4 Hz), 49.7 (dd,  $J$  = 61.4, 24.8 Hz), 36.2, 15.5 ppm.

**HRMS (m/z):** calcd for C<sub>23</sub>H<sub>21</sub>F<sub>3</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 417.1226, found: 417.1224.



**3-(Diphenylphosphoryl)-1-phenyl-3-(trifluoromethyl)pentan-1-one (11b):**

Yield = 94% (121.3 mg). White solid. M.p. 120.1–121.5 °C.

Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1~6/1).

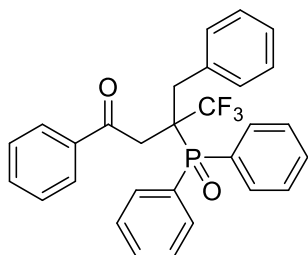
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.11–8.04 (m, 2H), 8.03–7.96 (m, 2H), 7.92–7.83 (m, 2H), 7.59–7.38 (m, 9H), 3.90 (dd,  $J$  = 16.6, 7.8 Hz, 1H), 3.55 (dd,  $J$  = 16.6, 13.3 Hz, 1H), 2.50–2.29 (m, 2H), 1.04 (t,  $J$  = 7.4 Hz, 3H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -61.13 (s, 3F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 31.57 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 196.0 (d,  $J$  = 8.2 Hz), 137.5, 133.1, 132.4 (d,  $J$  = 8.7 Hz), 132.1 (dd,  $J$  = 6.9, 3.4 Hz), 132.0 (d,  $J$  = 7.3 Hz), 130.3 (dd,  $J$  = 130.0, 93.9 Hz), 128.4 (dd,  $J$  = 11.5, 9.7 Hz), 128.3 (d,  $J$  = 45.4 Hz), 127.0 (q,  $J$  = 283.6 Hz), 54.0 (dd,  $J$  = 59.7, 23.1 Hz), 33.3, 22.2, 9.0 (d,  $J$  = 5.8 Hz) ppm.

**HRMS (m/z):** calcd for C<sub>24</sub>H<sub>23</sub>F<sub>3</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 431.1382, found: 431.1382.



**3-Benzyl-3-(diphenylphosphoryl)-4,4,4-trifluoro-1-phenylbutan-1-one (11c):**

Yield = 82% (121.4 mg). White solid. M.p. 158.2–159.3 °C.

Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1~6/1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.15–8.06 (m, 2H), 8.00 (dd,  $J$  = 11.5, 7.9 Hz, 2H), 7.78 (d,  $J$  = 6.5 Hz, 2H), 7.56–7.46 (m, 4H), 7.43–7.36 (m, 5H), 7.19 (s, 5H), 4.31 (dd,  $J$  = 14.1, 7.9 Hz, 1H), 3.91 (dd,  $J$  = 17.6, 5.6 Hz, 1H), 3.56 (dd,  $J$  = 14.0, 5.5 Hz, 1H), 3.21 (dd,  $J$  = 23.6, 17.6 Hz, 1H) ppm.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -60.25 (s, 3F) ppm.

**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):**  $\delta$  = 29.73 ppm.

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 195.9 (d,  $J$  = 3.0 Hz), 136.9, 134.9 (d,  $J$  = 11.6 Hz), 133.1, 132.3 (d,  $J$  = 8.7 Hz), 132.2 (d,  $J$  = 7.9 Hz), 131.9 (d,  $J$  = 1.2 Hz), 131.0 (dd,  $J$  = 103.8, 97.1 Hz), 130.8, 128.2 (d,  $J$  = 25.5 Hz), 128.1 (d,  $J$  = 22.6 Hz), 128.0 (d,  $J$  = 33.7 Hz), 127.0, 126.8 (q,  $J$  = 284.8 Hz), 55.1 (dd,  $J$  = 57.8, 21.7 Hz), 36.2, 34.3 ppm.

**HRMS (m/z):** calcd for C<sub>29</sub>H<sub>25</sub>F<sub>3</sub>O<sub>2</sub>P [M+H]<sup>+</sup> 493.1539, found: 493.1544.

## Reference

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# $^1\text{H}$ , $^{19}\text{F}$ , $^{31}\text{P}$ , and $^{13}\text{C}$ NMR spectra of products

