Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Supporting Information

Base-Promoted Regio- and Diastereoselective Synthesis of Tri- and Tetra-substituted Homoallenyl Phosphine Oxides via Alkynyl Enones

Shaochan Zhou, Haotian Zou, Xianqiang Huang, Jialin Qi,* and Zhenghu Xu*

qijl25@163.com

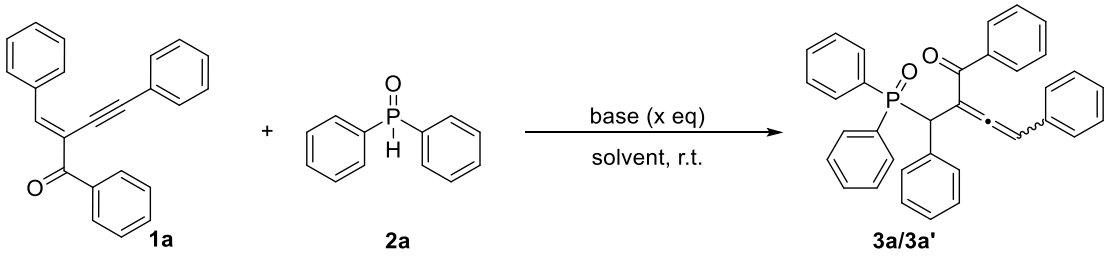
CONTENT:

1. General Information

Unless otherwise noted, analytic grade solvents were used for the chromatography and all the reagents were obtained commercially and used without further purification. All reactions were performed under nitrogen atmosphere. Column chromatography was performed with silica gel (100-200 mesh) as the stationary phase. Reactions were monitored by TLC. Solvents were dried with CaH_2. All NMR spectra were recorded on Bruker-500 MHz spectrometer. The chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz respectively. HRMS were measured on the Q-TOF6510 instruments.

2.Optimization of Reaction Condition

Table S1. Optimization of hydrophosphinylation reaction conditions[a]

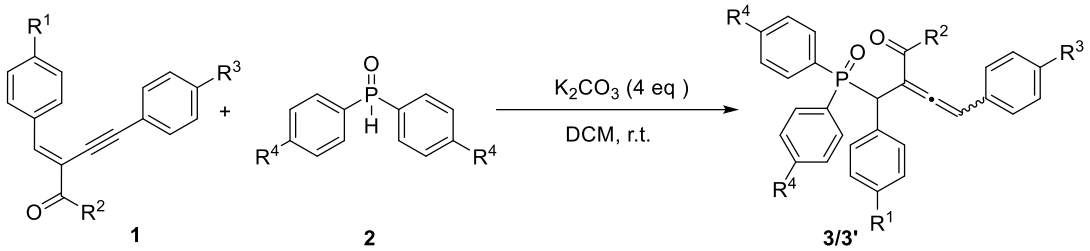


Entry	**2a**(eq)	Base(x eq)	Solvent	Time(h)	Yield/%[b]	dr(**3a**/**3a'**)[c]
1	4	-	DCM	26	30(25)	50:50
2	4	Et_3N(4 eq)	DCM	26	68	67:33
3	4	DIPEA(4 eq)	DCM	26	77	67:33
4	4	Cs_2CO_3(4 eq)	DCM	26	-	-
5	4	Cy_2NH (4 eq)	DCM	26	84	50:50
6	4	NaH(2 eq)	DCM	26	-	-
7	4	LiH(4 eq)	DCM	26	75	50:50
8	4	KOH(4 eq)	DCM	26	73	50:50
9	4	$Ca(OH)_2$(4 eq)	DCM	26	34	50:50
10	4	K_2CO_3(4 eq)	DCM	26	96(92)	88:12
11	2	K_2CO_3(2 eq)	DCM	26	67	56:44

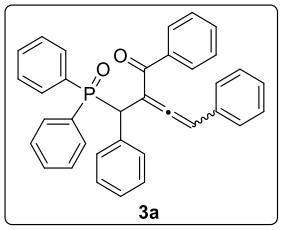
12	2	K_2CO_3(4 eq)	DCM	26	85	80:20
13	3	K_2CO_3(3 eq)	DCM	26	69	57:43
14	3	K_2CO_3(4 eq)	DCM	26	84	80:20
15	4	K_2CO_3(2 eq)	DCM	26	81	75:25
16	4	K_2CO_3(4 eq)	THF	26	34	25:75
17	4	K_2CO_3(4 eq)	CHCN	26	96	67:33
18	4	K_2CO_3(4 eq)	Toluene	26	6 4	67:33
19	4	K_2CO_3(4 eq)	DCM	1	30	50:50
20	4	K_2CO_3(4 eq)	DCM	2	39	50:50
21	4	K_2CO_3(4 eq)	DCM	4	42	50:50
22	4	K_2CO_3(4 eq)	DCM	6	85	57:43
23	4	K_2CO_3(4 eq)	DCM	9	86	77:23
24	4	K_2CO_3(4 eq)	DCM	12	87	81:19
25	4	K_2CO_3(4 eq)	DCM	16	88	82:18
26	4	K_2CO_3(4 eq)	DCM	21	90	83:17
27	4	K_2CO_3(4 eq)	DCM	23	92	84:16
28	4	K_2CO_3(4 eq)	DCM	28	94	67:33
29	4	K_2CO_3(4 eq)	DCM	31	93	60:40
30	4	K_2CO_3(4 eq)	DCM	36	92	61:39
31	4	K_2CO_3(4 eq)	DCM	42	91	61:39

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (y eq), base (x eq), and solvent (2 mL), at room temperature. [b] Combined yields of the two diastereomers (**3a** and **3a'**) and determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. Combined isolated for all isomers was indicated in parentheses. [c] Determined by ^{1}H NMR analysis of the crude reaction mixtures.

3. Preparation and Characterization of Trisubstituted Allenes 3



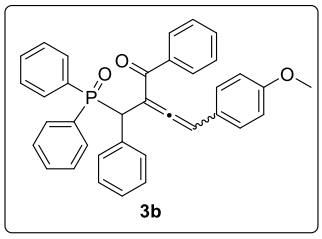
A mixture of enynones **1** (0.2 mmol), diarylphosphine oxides **2** (0.8 mmol) and K_2CO_3 (0.8 mmol, 4 eq) in DCM (2 mL) was stirred at room temperature for 26 h under the atmosphere of nitrogen. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered and evaporated under reduced pressure and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 10/1 to 3/1) to afford the desired product **3** and **3'**.



3a, yield: 87% , 88/12 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.02 – 7.94 (m, 2H), 7.64 – 7.52 (m, 4H), 7.40 – 7.34 (m, 5H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.32 – 7.24 (m, 8H), 7.22 – 7.15 (m, 3H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.53 (d, *J* = 5.8 Hz, 1H), 5.37 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.73 (d, *J* = 6.3 Hz), 193.23 (d, *J* = 5.04 Hz), 137.22, 135.36 (d, *J* = 5.04 Hz), 132.19 (dd, *J* = 32.13, 99.54 Hz), 132.20, 131.78 (d, *J* = 2.52 Hz), 130.98 (dd, *J* = 8.82, 47.88 Hz), 131.39 (d, *J* = 2.52 Hz), 130.38 (d, *J* = 6.3 Hz), 128.68, 128.58 (d, *J* = 12.6 Hz), 128.29, 128.23, 128.21, 128.01 (d, *J* = 27.72 Hz), 127.63, 127.28, 107.77 (d, *J* = 3.78 Hz), 101.61 (d, *J* = 2.52 Hz), 44.33 (d, *J* = 68.04 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.43. HRMS (ESI, m/z) calcd for $C_{35}H_{27}O_2P[M+H]^+$ 511.1821, found 511.1828.

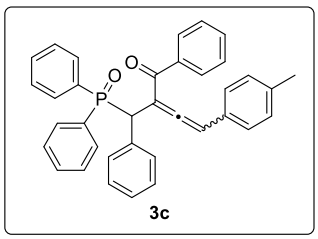
3a', (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.01 – 7.92 (m, 2H), 7.68 – 7.57 (m, 4H), 7.44 – 7.40 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 3H), 7.32 – 7.27 (m, 3H), 7.19 – 7.11 (m, 8H), 6.96 – 6.90 (m, 2H), 6.64 (d, *J* = 5.5 Hz, 1H), 5.35 (d, *J* = 7.8 Hz,

1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.74 (d, *J* = 7.56 Hz), 192.79 (d, *J* = 3.78 Hz), 137.31, 135.82 (d, *J* = 3.78 Hz), 132.40 (dd, *J* = 7.56, 98.28 Hz), 132.15, 131.62 (dd, *J* = 2.52, 32.76 Hz), 131.34 (d, *J* = 2.52 Hz), 131.08 (d, *J* = 8.82 Hz), 130.23 (d, *J* = 6.30 Hz), 128.62 (d, *J* = 5.04 Hz), 128.52 (d, *J* = 11.34 Hz), 128.43, 128.27 (d, *J* = 11.34 Hz), 128.00, 127.64 (d, *J* = 12.60 Hz), 127.29, 108.64 (d, *J* = 3.78 Hz), 101.93 (d, *J* = 2.52 Hz), 43.94 (d, *J* = 69.30 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 30.02; HRMS (ESI, m/z) calcd for $C_{35}H_{27}O_2P[M+H]^+$511.1821, found 511.1824.



3b

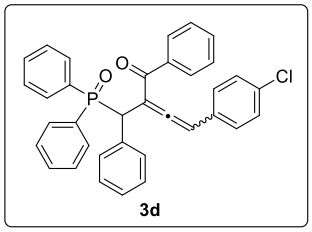
3b, yield: 99%, 88/12 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.94 – 7.87 (m, 2H), 7.55 – 7.46 (m, 4H), 7.30 – 7.26 (m, 5H), 7.26 – 7.22 (m, 1H), 7.21 – 7.14 (m, 5H), 7.12 – 7.09 (m, 3H), 7.00 (t, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.40 (d, *J* = 6.0 Hz, 1H), 5.31 (d, *J* = 7.8 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 216.77 (d, *J* = 6.3 Hz), 192.23 (d, *J* = 5.04 Hz), 158.47 , 124.75 (dd, *J* = 15.12, 2919.42 Hz), 134.47 (d, *J* = 5.04 Hz), 131.63 (d, *J* = 23.94 Hz), 131.05, 130.08 (dd, *J* = 56.70 , 221.76 Hz), 130.52 (dd, *J* = 2.52, 49.14 Hz), 130.24 (dd, *J* = 8.82, 61.74 Hz), 128.11 (d, *J* = 119.70 Hz), 127.22 (d, *J* = 153.72 Hz), 127.51 (d, *J* = 11.34 Hz), 126.89 (d, *J* = 69.30 Hz), 127.07, 126.19, 123.00 (d, *J* = 1.26 Hz), 113.17 (d, *J* = 16.38 Hz), 106.65 (d, *J* = 37.80 Hz), 100.05 (d, *J* = 2.52 Hz), 54.29, 43.24 (d, *J* = 68.04 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.44. HRMS (ESI, m/z) calcd for $C_{36}H_{29}O_3P[M+H]^+$ 541.1927, found 541.1928.



3c

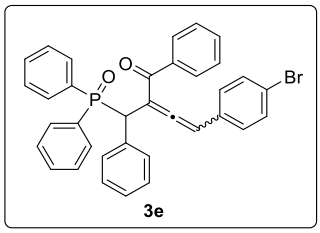
3c, yield: 90%, 87/13 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.04 – 7.94 (m, 2H), 7.61 – 7.55 (m, 4H), 7.41 – 7.35 (m, 5H), 7.31 – 7.23 (m, 4H),

7.18 (dd, *J* = 7.8, 1.7 Hz, 5H), 7.13 – 7.06 (m, 4H), 6.50 (d, *J* = 6.0 Hz, 1H), 5.37 (d, *J* = 7.9 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.89 (d, *J* = 6.3 Hz), 193.29 (d, *J* = 5.04 Hz), 137.81, 137.30, 135.47, 132.67, (d, *J* = 31.50 Hz), 132.10, 131.14 (dd, *J* = 5.67, 221.76 Hz), 131.74, 131.28 (dd, *J* = 8.82, 12.74 Hz), 131.35 (d, *J* = 0.24 Hz), 130.39 (d, *J* = 6.30 Hz), 128.47 (dd, *J* = 10.71, 21.72 Hz), 128.44 (d, *J* = 5.04 Hz), 128.60, 128.19, 128.31 (d, *J* = 26.46 Hz), 127.23, 107.72 (d, *J* = 2.54 Hz), 101.46 (d, *J* = 1.26 Hz), 44.28 (d, *J* = 69.30 Hz), 21.35. ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.31. HRMS (ESI, m/z) calcd for $C_{36}H_{29}O_2P[M+H]^+$ 525.1978, found 525.1981.



3d

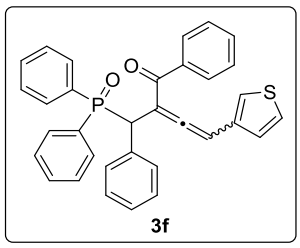
3d, yield: 68%, 85/15 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.00 – 7.94 (m, 2H), 7.60 – 7.50 (m, 4H), 7.42 – 7.38 (m, 3H), 7.35 – 7.30 (m, 4H), 7.29 – 7.16 (m, 9H), 7.10 (t, *J* = 7.7 Hz, 2H), 6.50 (d, *J* = 5.9 Hz, 1H), 5.35 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.71 (d, *J* = 6.30 Hz), 192.99 (d, *J* = 5.04 Hz), 137.14, 135.20 (d, *J* = 5.04 Hz), 133.71, 132.03 (dd, *J* = 15.12, 99.54 Hz), 132.33, 131.15 (dd, *J* = 2.52, 180.18 Hz), 131.48, 131.46, 131.39, 130.63 (dd, *J* = 8.82, 88.2 Hz), 129.28 (d, *J* = 69.30 Hz), 128.68 (d, *J* = 11.34 Hz), 128.15 (d, *J* = 109.62 Hz), 128.28, 128.20 (d, *J* = 12.06 Hz), 127.37 (d, *J* = 1.26 Hz), 108.01 (d, *J* = 3.78 Hz), 100.62 (d, *J* = 1.26 Hz), 44.25 (d, *J* = 63.00 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.66. HRMS (ESI, m/z) calcd for $C_{35}H_{26}ClO_2P[M+H]^+$ 545.1432, found 545.1436.



3e

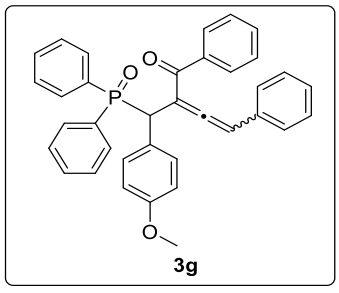
3e, yield: 90%, 89/11 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.99 – 7.92 (m, 2H), 7.61 – 7.52 (m, 4H), 7.47 – 7.38 (m, 5H), 7.34 – 7.32 (m, 4H),

7.26 (s, 2H), 7.20 – 7.16 (m, 5H), 7.11 (t, J = 7.6 Hz, 2H), 6.48 (d, J = 5.8 Hz, 1H), 5.34 (d, J = 7.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.72 (d, J = 6.30 Hz), 192.95, 137.17, 135.20 (d, J = 5.04 Hz), 132.51, 132.33, 131.91 (d, J = 3.78 Hz), 131.85, 131.19 (dd, J = 8.82, 56.70 Hz), 130.28 (d, J = 5.04 Hz), 129.75, 128.67 (d, J = 11.34 Hz), 128.56, 128.19 (d, J = 12.60 Hz), 128.14, 127.71, 127.35, 121.92, 108.07 (d, J = 3.78 Hz), 100.68 (d, J = 2.52 Hz), 44.24 (d, J = 69.30 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.58. HRMS (ESI, m/z) calcd for $C_{35}H_{26}BrO_2P[M+H]^+$ 589.0927, found 589.0939.



3f

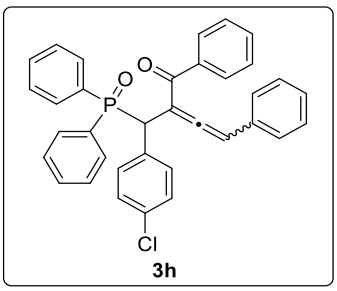
3f, yield: 52%, 67/33 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.62 – 7.55 (m, 4H), 7.40 – 7.23 (m, 11H), 7.23 – 7.07 (m, 6H), 6.57 (d, J = 6.4 Hz, 1H), 5.37 (d, J = 7.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.36 (d, J = 6.30 Hz), 192.93, 137.14, 135.51 (d, J = 5.04 Hz), 132.52 (d, J = 21.42 Hz), 132.26 (d, J = 2.52 Hz), 132.19, 131.60 (dd, J = 3.78, 49.14 Hz), 131.25 (dd, J = 8.82, 71.82 Hz), 130.33 (d, J = 6.30 Hz), 128.74, 128.56 (d, J = 11.34 Hz), 127.92 (d, J = 80.64 Hz), 128.14, 127.43, 127.25, 126.06, 124.02, 106.87 (d, J = 3.78 Hz), 96.00 (d, J = 2.52 Hz), 44.21 (d, J = 68.04 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.58. HRMS (ESI, m/z) calcd for $C_{33}H_{25}O_2PS$ $[M+H]^+$ 517.1386, found 517.1383.



3g

3g, yield: 68%, 90/10 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.99 – 7.94 (m, 2H), 7.62 – 7.57 (m, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.39 – 7.33 (m, 6H),

7.30 – 7.24 (m, 8H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 2H), 6.52 (d, *J* = 5.8 Hz, 1H), 5.33 (d, *J* = 8.0 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.58 (d, *J* = 75.60 Hz), 193.25 (d, *J* = 50.40 Hz), 158.81, 137.24, 132.36 (dd, *J* = 37.80, 99.54 Hz), 132.17, 131.83, 132.37 (dd, *J* = 35.28, 98.28 Hz), 131.48 (d, *J* = 16.38 Hz), 131.46, 131.05 (d, *J* = 88.20 Hz), 128.67, 128.35 (dd, *J* = 12.60, 42.84 Hz), 128.27, 128.85, 127.61, 127.33 (d, *J* = 50.40 Hz), 113.68, 108.06 (d, *J* = 37.80 Hz), 101.56 (d, *J* = 25.20 Hz), 55.13, 43.72 (d, *J* = 25.20 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.39. HRMS (ESI, m/z) calcd for $C_{36}H_{29}O_3P[M+H]^+$ 541.1927, found 541.1927.

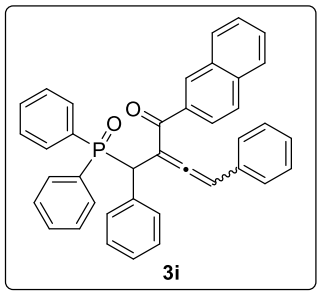


3h

3h, yield: 51%, 67/33 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.95 – 7.82 (m, 2H), 7.56 – 7.51 (m, 2H), 7.46 – 7.42 (m, 2H), 7.31 – 7.26 (m, 6H), 7.23 – 7.18 (m, 8H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.45 (d, *J* = 5.9 Hz, 1H), 5.28 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.51 (d, *J* = 6.30 Hz), 193.02 (d, *J* = 5.04 Hz), 137.04, 134.09 (d, *J* = 5.04 Hz), 132.61 (dd, *J* = 1.26, 178.92 Hz), 132.33 (d, *J* = 37.80 Hz), 132.33, 131.66, 131.61, 131.20 (dd, *J* = 8.82, 63.00 Hz), 128.75, 128.67 (d, *J* = 25.20 Hz), 128.58, 128.43, 128.40, 128.31, 128.05, 127.68, 107.55 (d, *J* = 3.78 Hz), 101.80 (d, *J* = 2.52 Hz), 43.67 (d, *J* = 68.04 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.15. HRMS (ESI, m/z) calcd for $C_{35}H_{26}ClO_2P[M+H]^+$ 545.1432, found 545.1431.

3h', (Colorless oil.) ^{1}H NMR (500 MHz, CDCl3) δ (ppm) 7.97 – 7.93 (m, 2H), 7.67 –7.62 (m, 2H), 7.55 – 7.52 (m, 2H), 7.44 – 7.41 (m, 3H), 7.35 – 7.30 (m, 6H), 7.20 – 7.12 (m, 6H), 7.11 – 7.07 (m, 3H), 6.91 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.64 (d, *J* = 5.3 Hz, 1H), 5.32 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.55 (d, *J* = 6.30 Hz), 192.62 (d, *J* = 5.04 Hz), 137.16, 134.53 (d, *J* = 5.04 Hz), 133.36, 132.26, 131.25

(dd, J = 2.52, 148.68 Hz), 131.51 (d, J = 6.30 Hz), 131.13 (dd, J = 8.82, 36.54 Hz), 128.68, 128.62, 128.56, 128.50 (d, J = 8.82 Hz), 128.33 (d, J = 7.56 Hz), 128.19, 127.74, 127.69, 127.50, 108.45 (d, J = 3.78 Hz), 102.15 (d, J = 1.26 Hz), 43.29 (d, J = 68.04 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.65. HRMS (ESI, m/z) calcd for $C_{35}H_{26}ClO_2P$[M+H]+ 545.1432, found 545.1431.

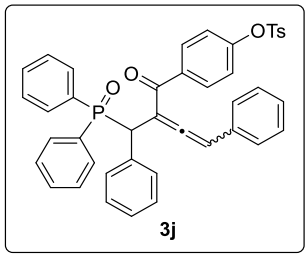


3i

3i, yield: 59%, 67/33 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.05 – 8.00 (m, 2H), 7.80 (s, 1H), 7.69 – 7.65 (m, 1H), 7.44 – 7.61 (m 5H), 7.56 – 7.52 (m, 1H), 7.46 – 7.46 (m, 3H), 7.39 – 7.34 (m, 3H), 7.33 – 7.24 (m, 7H), 7.22 – 7.18 (m, 4H), 6.53 (d, J = 6.4 Hz, 1H), 5.41 (d, J = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.00 (d, J = 6.30 Hz), 193.04 (d, J = 5.04 Hz), 135.57 (d, J = 3.78 Hz), 135.19, 133.88, 132.53 (d, J = 25.20 Hz), 131.73 (dd, J = 2.52, 69.30 Hz), 131.75 (d, J = 22.68 Hz), 131.81, 131.78, 131.32 (dd, J = 8.82, 69.30 Hz), 131.46 (d, J = 2.52 Hz), 130.65, 130.41 (d, J = 6.30 Hz), 129.15, 128.75, 128.59, 128.57, 128.50, 128.27, 127.79 (d, J = 18.90 Hz), 127.98, 127.31, 125.50 (d, J = 201.60 Hz), 107.64 (d, J = 3.78 Hz), 101.56 (d, J = 2.52 Hz), 44.44 (d, J = 69.30 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.55. HRMS (ESI, m/z) calcd for $C_{39}H_{29}O_2P$[M+H]$^+$ 561.1978, found 561.1984.

3i', (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.03 – 7.93 (m, 2H), 7.85 (s, 1H), 7.75 – 7.58 (m, 6H), 7.50 – 7.48 (m, 1H), 7.48 – 7.34 (m, 7H), 7.33 – 7.28 (m, 2H), 7.20 – 7.13 (m, 6H), 7.04 – 6.93 (m, 2H), 6.63 (d, J = 5.2 Hz, 1H), 5.39 (d, J = 7.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.52 (d, J = 6.30 Hz), 192.63 (d, J = 5.04 Hz), 135.77 (d, J = 3.78 Hz), 135.14, 134.25, 132.45 (dd, J = 8.82, 98.28 Hz), 131.77 (d, J = 2.52 Hz), 131.50 (d, J = 2.52 Hz), 131.46, 131.24 (dd, J = 8.82, 36.54 Hz), 130.37, 130.31, 130.26, 129.17, 128.63, 128.59, 128.50, 128.47, 127.93 (dd, J =

12.6, 86.94 Hz), 128.04 (d, *J* = 5.04 Hz), 127.72, 127.33, 126.44, 124.76, 108.58 (d, *J* = 3.78 Hz), 101.81 (d, *J* = 2.52 Hz), 44.15 (d, *J* = 69.30 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 30.08. HRMS (ESI, m/z) calcd for $C_{39}H_{29}O_2P[M+H]^+$ 561.1978, found 561.1985.

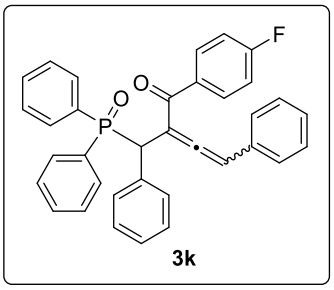


3j

3j, yield: 50%, 61/39 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.97 – 7.90 (m, 2H), 7.64 – 7.59 (m, 2H), 7.57 – 7.52 (m, 4H), 7.45 – 7.39 (m, 3H), 7.33 – 7.23 (m, 5H), 7.21 – 7.09 (m, 8H), 6.90 (d, *J* = 3.9 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 5.6 Hz, 1H), 5.29 (d, *J* = 7.9 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.79 (d, *J* = 6.30 Hz), 191.45 (d, *J* = 6.30 Hz), 152.15, 145.54, 135.90, 135.62 (d, *J* = 5.04 Hz), 131.98, 131.68 (dd, *J* = 2.52, 28.98 Hz), 131.18 (dd, *J* = 8.82, 31.50 Hz), 129.95 (d, *J* = 59.22 Hz), 130.12, 128.71, 128.45 (d, *J* = 31.50 Hz), 128.49, 128.46, 128.39, 128.33 (d, *J* = 1.26 Hz), 127.54, 127.36, 121.65, 108.75 (d, *J* = 3.78 Hz), 102.19 (d, *J* = 2.52 Hz), 43.93 (d, *J* = 68.04 Hz), 21.68. ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.33. HRMS (ESI, m/z) calcd for $C_{42}H_{33}O_5PS[M+Na]^+$ 703.1679, found 703.1738.

3j', (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.93 – 7.87 (m, 2H), 7.63 – 7.57 (m, 2H), 7.56 – 7.51 (m, 5H), 7.42 – 7.39 (m, 3H), 7.36 – 7.32 (m, 1H), 7.30 – 7.23 (m, 6H), 7.17 – 7.14 (m, 3H), 7.13 (s, 1H), 7.12 – 7.09 (m, 4H), 6.92 – 6.85 (m, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 5.6 Hz, 1H), 5.26 (d, *J* = 7.8 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.78 (d, *J* = 6.30 Hz), 191.44 (d, *J* = 5.04 Hz), 152.16, 145.53, 135.90, 135.63 (d, *J* = 3.78 Hz), 131.99, 131.68 (dd, *J* = 2.52, 27.72 Hz), 131.19 (dd, *J* = 8.82, 31.50 Hz), 130.24, 129.93 (d, *J* = 57.96 Hz), 130.12, 128.71, 128.45 (d, *J* = 37.76 Hz), 128.49, 128.46, 128.39, 128.22 (d, *J* = 2.52 Hz), 127.54, 127.36, 121.65, 121.57, 108.76 (d, *J* = 3.78 Hz), 102.19 (d, *J* = 2.52 Hz), 44.93

(d, J = 68.04 Hz), 21.67. ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.81. HRMS (ESI, m/z) calcd for $C_{42}H_{33}O_5PS[M+Na]^+$ 703.1679, found 703.1738.

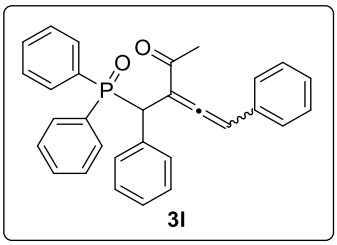


3k

3k, yield: 48%, 67/33 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.03 – 7.92 (m, 2H), 7.62 – 7.55 (m, 4H), 7.42 – 7.38 (m, 2H), 7.77 – 7.35 (m, 3H), 7.35 – 7.30 (m, 5H), 7.29 – 7.25 (m, 3H), 7.19 (d, J = 7.5 Hz, 3H), 6.75 (t, J = 8.7 Hz, 2H), 6.54 (d, J = 6.1 Hz, 1H), 5.34 (d, J = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.29 (d, J = 6.30 Hz), 191.66 (d, J = 3.78 Hz), 166.18 (d, J = 2.52 Hz), 135.30 (d, J = 5.04 Hz), 132.49 (dd, J = 2.52, 204.12 Hz), 132.50 (d, J = 5.04 Hz), 132.62 (dd, J = 3.78, 45.36 Hz), 131.64, 131.52 (d, J = 8.82 Hz), 131.13 (dd, J = 8.82, 30.24 Hz), 130.35 (d, J = 6.30 Hz), 128.80, 128.34 (dd, J = 11.34, 57.96 Hz), 128.28, 128.26, 128.24, 127.33, 114.78 (d, J = 21.42 Hz), 107.65 (d, J = 3.78 Hz), 101.72 (d, J = 2.52 Hz), 44.48 (d, J = 68.04 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.32. ^{19}F NMR (471 MHz, $CDCl_3$) δ -106.19. HRMS (ESI, m/z) calcd for $C_{35}H_{26}FO_2P[M+H]^+$ 529.1727, found 529.1723.

3k', (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.97 – 7.91 (m, 2H), 7.66 – 7.59 (m, 4H), 7.45 – 7.35 (m, 6H), 7.32 – 7.27 (m, 2H), 7.18 – 7.10 (m, 6H), 6.93 – 6.88 (m, 2H), 6.82 (t, J = 8.5 Hz, 2H), 6.65 (d, J = 5.6 Hz, 1H), 5.31 (d, J = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.27 (d, J = 6.30 Hz), 191.23, 165.14 (d, J = 6.30 Hz), 134.96 (dd, J = 5.04, 297.36 Hz), 132.77 (d, J = 20.16 Hz), 131.63 (dd, J = 2.52, 30.24 Hz), 131.34 (d, J = 8.82 Hz), 131.15 (dd, J = 8.82, 21.42 Hz), 130.18 (d, J = 6.30 Hz), 128.80, 128.10 (d, J = 11.34 Hz), 128.56, 128.45, 128.31, 128.22, 128.11, 127.32, 114.85 (d, J = 21.42 Hz), 108.56, 102.03, 44.10 (d, J = 68.04 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.79. ^{19}F NMR (471 MHz, $CDCl_3$) δ -

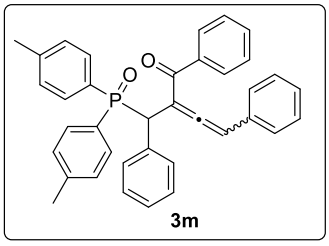
106.22. HRMS (ESI, m/z) calcd for $C_{35}H_{26}FO_2P[M+H]^+$ 529.1727, found 529.1729.



3l

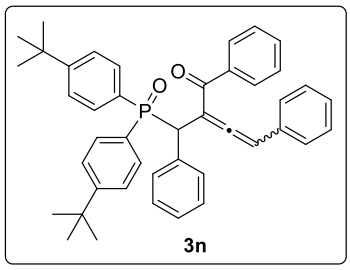
3l, yield: 94% 57/43 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.94 – 7.85 (m, 2H), 7.54 – 7.41 (m, 7H), 7.34 – 7.29 (m, 1H), 7.27 – 7.21 (m, 5H), 7.19 – 7.12 (m, 5H), 6.81 (d, *J* = 5.2 Hz, 1H), 5.20 (d, *J* = 7.9 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.56 (d, *J* = 6.30 Hz), 196.40 (d, *J* = 6.30 Hz), 135.31 (d, *J* = 5.04 Hz), 132.60 (d, *J* = 6.30 Hz), 131.84, 131.56 (dd, *J* = 2.52, 57.96 Hz), 131.25 (dd, *J* = 8.82, 55.44 Hz), 131.23 (d, *J* = 1.26 Hz), 130.24 (d, *J* = 5.04 Hz), 128.76, 128.32 (dd, *J* = 13.86, 59.22 Hz), 128.18, 128.07, 127.22, 109.81 (d, *J* = 3.78 Hz), 101.72 (d, *J* = 2.52 Hz), 42.62 (d, *J* = 68.04 Hz), 26.33. ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.51. HRMS (ESI, m/z) calcd for $C_{30}H_{25}O_2P[M+H]^+$ 449.1656, found 449.1658.

3l', (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.91 – 7.85 (m, 2H), 7.62 – 7.56 (m, 2H), 7.52 – 7.43 (m, 5H), 7.36 – 7.32 (m, 1H), 7.32 – 7.26 (m, 2H), 7.22 – 7.19 (m, 3H), 7.11 – 7.07 (m, 3H), 7.05 – 7.00 (m, 2H), 6.88 (d, *J* = 5.6 Hz, 1H), 5.19 (d, *J* = 8.0 Hz, 1H), 2.05 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.25 (d, *J* = 6.30 Hz), 196.04 (d, *J* = 5.04Hz), 135.78 (d, *J* = 3.78 Hz), 132.66 (d, *J* = 30.24 Hz), 132.00, 131.58 (dd, *J* = 2.52, 37.80 Hz), 132.00, 131.99 (dd, *J* = 8.82, 17.64 Hz), 130.08 (d, *J* = 6.30 Hz), 128.13 (d, *J* = 35.28 Hz), 128.30 (d, *J* = 40.32 Hz), 128.37, 128.35, 128.22 (d, *J* = 3.78 Hz), 127.18, 110.49 (d, *J* = 5.04 Hz), 101.91 (d, *J* = 2.52 Hz), 42.16 (d, *J* = 68.04 Hz), 26.23. ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 30.22. HRMS (ESI, m/z) calcd for $C_{30}H_{25}O_2P[M+H]^+$ 449.1656, found 449.1657.



3m

3m, yield: 84%, 78/22 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.86 – 7.81 (m, 2H), 7.61 – 7.53 (m, 2H), 7.46 – 7.42 (m, 2H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.30 – 7.26 (m, 5H), 7.26 – 7.22 (m, 1H), 7.21 – 7.13 (m, 5H), 7.10 – 7.03 (m, 4H), 6.52 (d, *J* = 5.7 Hz, 1H), 5.32 (d, *J* = 7.9 Hz, 1H), 2.25 (d, *J* = 4.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.59 (d, *J* = 6.30 Hz), 192.83 (d, *J* = 5.04 Hz), 141.91 (dd, *J* = 2.52, 36.54 Hz), 137.38, 136.15 (d, *J* = 3.78 Hz), 132.09, 131.46 (d, *J* = 2.52 Hz), 131.19 (dd, *J* = 10.08, 32.76 Hz), 130.25 (d, *J* = 6.30 Hz), 129.78 (d, *J* = 6.30 Hz), 129.57, 129.11 (dd, *J* = 11.34, 28.98 Hz), 128.69, 128.56, 128.39, 127.92, 127.60 (d, *J* = 6.30 Hz), 127.16, 108.86 (d, *J* = 3.78 Hz), 101.86 (d, *J* = 2.52 Hz), 44.14 (d, *J* = 68.04 Hz), 21.46. ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 30.37. HRMS (ESI, m/z) calcd for $C_{37}H_{31}O_2P[M+H]^+$ 539.2134, found 539.2135.

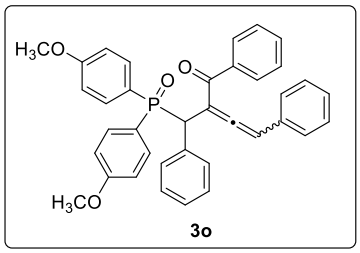


3n

3n, yield: 98%, 56/44 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.92 – 7.86 (m, 2H), 7.67 – 7.59 (m, 2H), 7.59 – 7.51 (m, 2H), 7.45 – 7.40 (m, 2H), 7.38 – 7.32 (m, 4H), 7.32 – 7.24 (m, 6H), 7.22 – 7.16 (m, 3H), 7.02 (t, *J* = 7.7 Hz, 2H), 6.47 (d, *J* = 6.6 Hz, 1H), 5.34 (d, *J* = 8.0 Hz, 1H), 1.23 (s, 9H), 1.14 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.15 (d, *J* = 6.30 Hz), 193.21 (d, *J* = 3.78 Hz), 154.81 (dd, *J* = 2.52, 60.48 Hz), 137.07, 135.81 (d, *J* = 5.04 Hz), 132.12, 132.10, 132.07, 131.24 (dd, *J* = 8.82, 88.20 Hz), 130.49 (d, *J* = 6.30 Hz), 129.47 (d, *J* = 32.76 Hz), 128.72 (d, *J* = 7.56 Hz), 128.46, 128.15, 127.87, 127.47, 127.12, 125.31 (dd, *J* = 11.34, 25.20 Hz), 107.93 (d, *J* = 3.78 Hz), 101.49 (d, *J* = 3.78 Hz), 44.56 (d, *J* = 68.04 Hz), 34.82 (d, *J* = 5.04 Hz), 31.01 (d, *J* = 7.56 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.36. HRMS (ESI, m/z) calcd for $C_{43}H_{43}O_2P[M+H]^+$ 623.3073, found 623.3091.

3n', (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.88 – 7.84 (m, 2H),

7.67 – 7.64 (m, 2H), 7.60 – 7.56 (m, 2H), 7.40 (dd, *J* = 8.4, 2.7 Hz, 2H), 7.33 – 7.25 (m, 5H), 7.17 – 7.06 (m, 8H), 6.86 – 6.82 (m, 2H), 6.67 (d, *J* = 6.1 Hz, 1H), 5.32 (d, *J* = 8.1 Hz, 1H), 1.23 (s, 9H), 1.20 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.42 (d, *J* = 6.30 Hz), 192.79 (d, *J* = 5.04 Hz), 154.93 (dd, *J* = 8.82, 88.20 Hz), 137.30, 136.32 (d, *J* = 5.04 Hz), 132.02, 131.43 (d, *J* = 2.52 Hz), 131.33 (d, *J* = 8.82 Hz), 130.95 (d, *J* = 10.08 Hz), 130.28 (d, *J* = 6.30 Hz), 129.32 (dd, *J* = 3.78, 102.06 Hz), 128.59 (d, *J* = 22.68 Hz), 128.37, 127.86, 127.58, 127.48, 127.12, 125.36 (dd, *J* = 12.60, 17.64 Hz), 109.04 (d, *J* = 3.78 Hz), 101.92 (d, *J* = 2.52 Hz), 44.18 (d, *J* = 68.04 Hz), 34.85, 31.04. ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.92. HRMS (ESI, m/z) calcd for $C_{43}H_{43}O_2P[M+H]^+$ 623.3073, found 623.3085.



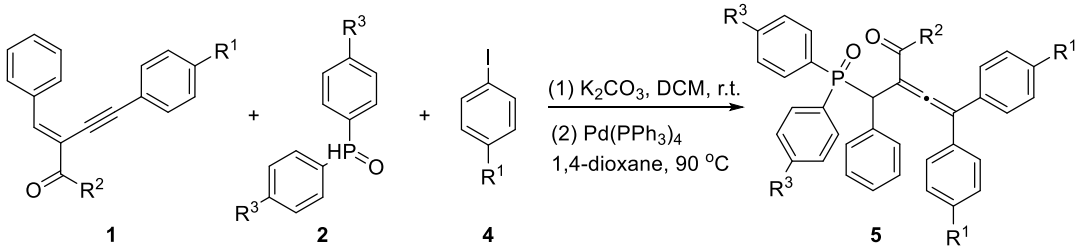
3o

3o, yield: 98%, 56/44 d.r. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.88 – 7.83 (m, 2H), 7.57 – 7.55 (m, 2H), 7.49 – 7.38 (m, 4H), 7.30 – 7.28 (m, 5H), 7.25 – 7.23 (m, 1H), 7.22 – 7.16 (m, 3H), 7.09 (t, *J* = 7.7 Hz, 2H), 6.89 – 6.81 (m, 2H), 6.75 (dd, *J* = 8.8, 2.3 Hz, 2H), 6.52 (d, *J* = 5.6 Hz, 1H), 5.27 (d, *J* = 8.0 Hz, 1H), 3.71 (d, *J* = 9.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.38 (d, *J* = 6.30 Hz), 193.23 (d, *J* = 5.04 Hz), 162.11 (dd, *J* = 2.52, 51.66 Hz), 137.22, 135.63 (d, *J* = 5.04 Hz), 133.03 (dd, *J* = 10.08, 52.92 Hz), 132.20, 131.93 (d, *J* = 1.26 Hz), 130.42 (d, *J* = 6.30 Hz), 128.70 (d, *J* = 17.64 Hz), 128.24 (d, *J* = 12.60 Hz), 127.79, 127.63, 127.18, 124.35, 123.61 (d, *J* = 26.46 Hz), 122.89, 113.91 (dd, *J* = 12.60, 55.44 Hz), 107.91 (d, *J* = 3.78 Hz), 101.49 (d, *J* = 2.52 Hz), 55.19 (d, *J* = 6.30 Hz), 44.94 (d, *J* = 68.04 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.61. HRMS (ESI, m/z) calcd for $C_{37}H_{31}O_4P[M+H]^+$ 517.2033, found 517.2035.

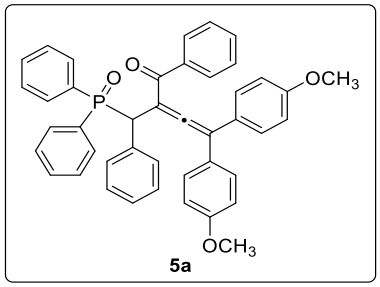
3o', (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.88 – 7.81 (m, 2H), 7.61 – 7.57 (m, 2H), 7.55 – 7.51 (m, 2H), 7.41 – 7.39 (m, 2H), 7.34 – 7.29 (m, 1H),

7.19 – 7.10 (m, 8H), 6.93 – 6.89 (m, 4H), 6.78 (dd, J = 8.8, 2.3 Hz, 2H), 6.66 (d, J = 5.7 Hz, 1H), 5.26 (d, J = 8.2 Hz, 1H), 3.73 (d, J = 9.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 218.56 (d, J = 6.30 Hz), 192.82 (d, J = 5.04 Hz), 162.13 (dd, J = 3.78, 39.06 Hz), 137.37, 136.20 (d, J = 3.78 Hz), 133.02 (dd, J = 10.08, 32.76 Hz), 132.13, 131.47 (d, J = 2.52 Hz), 130.23 (d, J = 6.30 Hz), 128.72, 128.56, 128.39, 127.91, 127.61 (d, J = 13.86 Hz), 127.17, 124.26 (d, J = 22.68 Hz), 123.425 (d, J = 22.60 Hz), 113.93 (dd, J = 12.60, 35.28 Hz), 108.83 (d, J = 3.78 Hz), 101.82 (d, J = 2.52 Hz), 55.23 (d, J =12.60 Hz), 44.47 (d, J = 69.30 Hz). HRMS (ESI, m/z) calcd for $C_{37}H_{31}O_4P[M+H]^+$ 517.2033, found 517.2036.

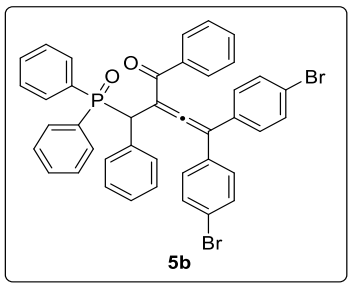
4. Preparation and Characterization of Tetrasubstituted Allenes 5



A mixture of enynones **1** (0.2 mmol), diarylphosphine oxides **2** (0.3 mmol) and K_2CO_3 (0.8 mmol, 4 eq) in DCM (2 mL) was stirred at room temperature for 26 h under the atmosphere of nitrogen. Afterward, the solvent was evaporated in vacuo. The residue were carried out with iodobenzene **4** (1 mmol) and $Pd(PPh_3)_4$ (0.01 mmol) in 1,4-dioxane (2 mL) in a Schlenk tube. The reaction mixture was allowed to stirring under N_2 atmosphere at 90 °C for 24 h. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered and evaporated under reduced pressure and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 5/1 to 3/1) to afford the desired product **5.**

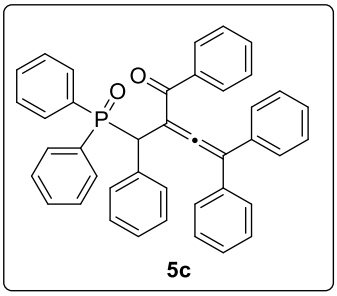


5a, yield: 82%. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.85 – 7.79 (m, 2H), 7.60 – 7.53 (m, 2H), 7.48 – 7.42 (m, 2H), 7.38 – 7.36 (m, 1H), 7.31 – 7.26 (m, 4H), 7.25 – 7.24 (m, 1H), 7.23 – 7.17 (m, 3H), 7.13 – 7.06 (m, 5H), 7.06 – 7.01 (m, 4H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 5.34 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.24 (d, *J* = 6.30 Hz), 194.00 (d, *J* = 6.30 Hz), 159.43 (d, *J* = 6.30 Hz), 137.27, 134.94 (d, *J* = 5.04 Hz), 132.17 (dd, *J* = 100.80, 113.40 Hz), 132.08, 131.28 (dd, *J* = 2.52, 17.64 Hz), 131.05 (d, *J* = 8.82 Hz), 130.39 (d, *J* = 5.04 Hz), 130.00 (d, *J* = 8.82 Hz), 128.23 (d, *J* = 143.64 Hz), 128.25 (dd, *J* = 11.34, 27.72 Hz), 128.12 (d, *J* = 2.52 Hz), 127.29, 127.09 (d, *J* = 2.52 Hz), 126.93, 115.31, 113.82 (d, *J* = 25.20 Hz), 106.37 (d, *J* = 2.52 Hz), 55.30 (d, *J* = 10.08 Hz), 44.94 (d, *J* = 69.30 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.58. HRMS (ESI, m/z) calcd for $C_{43}H_{35}O_4P$ $[M+Na]^+$ 669.2165, found 669.2166.



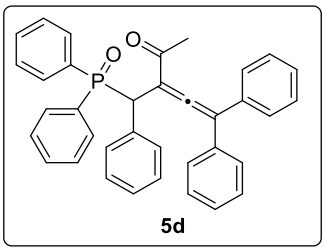
5b

5b, yield: 73%. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.84 – 7.75 (m, 2H), 7.54 – 7.49 (m, 2H), 7.44 – 7.40 (m, 4H), 7.38 – 7.34 (m, 1H), 7.33 – 7.32 (m, 2H), 7.31 – 7.25 (m, 6H), 7.24 – 7.22 (m, 1H), 7.22 – 7.18 (m, 2H), 7.12 – 7.08 (m, 5H), 7.08 – 7.04 (m, 1H), 6.95 – 6.81 (m, 2H), 5.31 – 5.29 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 216.12 (d, *J* = 6.30 Hz), 193.21 (d, *J* = 7.56 Hz), 136.94, 134.43 (d, *J* = 5.04 Hz), 133.33 (d, *J* = 71.82 Hz), 131.81 (dd, *J* = 100.80, 103.32 Hz), 131.68 (d, *J* = 89.46 Hz), 131.90, 131.57, 131.50 (dd, *J* = 3.78, 5.04 Hz), 131.97, 130.90, 130.24 (dd, *J* = 2.52, 8.82 Hz), 128.27 (d, *J* = 102.06 Hz), 128.38 (dd, *J* = 5.04 42.84 Hz), 128.28, 127.39 (d, *J* = 2.52 Hz), 122.40 (d, *J* = 40.32 Hz), 114.18, 107.21 (d, *J* = 2.52 Hz), 44.98 (d, *J* = 69.30 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.69. HRMS (ESI, m/z) calcd for $C_{41}H_{29}Br_2O_2P$ $[M+Na]^+$ 765.0164, found 765.0372.



5c

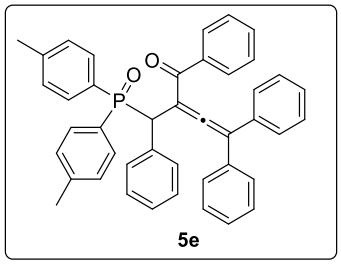
5c, yield: 88%. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.88 – 7.76 (m, 2H), 7.60 – 7.54 (m, 2H), 7.49 – 7.44 (m, 2H), 7.36 – 7.32 (m, 1H), 7.29 – 7.26 (m, 3H), 7.26 -7.24 (m, 6H), 7.23 – 7.22 (m, 1H), 7.21 – 7.16 (m, 5H), 7.15 – 7.13 (m, 1H), 7.13 – 7.09 (m, 2H), 7.09 – 7.05 (m, 3H), 7.01 (t, *J* = 7.7 Hz, 2H), 5.34 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 216.87 (d, *J* = 6.30 Hz), 193.90 (d, *J* = 6.30 Hz), 137.19, 134.96 (d, *J* = 2.52 Hz), 134.82 (d, *J* = 5.04 Hz), 134.45, 132.08 (dd, *J* = 99.54, 115.92 Hz), 132.23, 131.38 (dd, *J* = 2.52, 8.82 Hz), 131.05 (d, *J* = 8.82 Hz), 130.40 (d, *J* = 5.04 Hz), 128.85 (d, *J* = 10.08 Hz), 128.51 (d, *J* = 51.66 Hz), 128.13 (d, *J* = 98.28 Hz), 128.28 (dd, *J* = 11.34, 26.46 Hz), 128.17 (d, *J* = 1.26 Hz), 127.95 (d, *J* = 31.50 Hz), 127.18 (d, *J* = 2.52 Hz), 116.02 (d, *J* = 2.52 Hz), 106.77 (d, *J* = 2.52 Hz), 44.98 (d, *J* = 69.30 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.51. HRMS (ESI, m/z) calcd for $C_{41}H_{31}O_2P$ $[M+Na]^+$ 609.1954, found 609.1951.



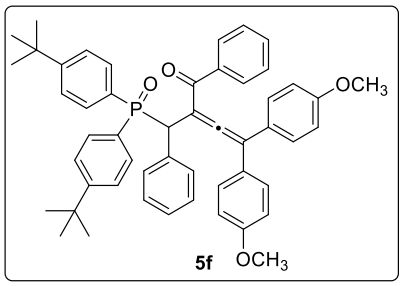
5d

5d, yield: 85%. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.71 – 7.64 (m, 2H), 7.49 – 7.43 (m, 2H), 7.34 – 7.27 (m, 5H), 7.26 – 7.21 (m, 6H), 7.20 – 7.14 (m, 7H), 7.02 – 6.96 (m, 3H), 5.12 (d, *J* = 7.9 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 215.53 (d, *J* = 6.30 Hz), 195.58 (d, *J* = 6.30 Hz), 134.14 (d, *J* = 5.04 Hz), 133.10 (dd, *J* = 2.52, 30.24 Hz), 131.07 (dd, *J* = 55.44, 99.54 Hz), 130.36 (dd, *J* = 3.78, 18.90 Hz), 130.08 (dd, *J* = 8.82, 18.90 Hz), 129.28 (d, *J* = 5.04 Hz), 127.72 (d, *J* = 44.10 Hz), 127.45 (d, *J* = 10.08 Hz), 127.25 (d, *J* = 11.34 Hz), 127.09 (d, *J* = 6.30

Hz), 126.99 (d, *J* = 6.30 Hz), 126.03 (d, *J* = 2.52 Hz), 114.85 (d, *J* = 2.52 Hz), 107.95 (d, *J* = 3.78 Hz), 42.16 (d, *J* = 69.30 Hz), 25.46. ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.56. HRMS (ESI, m/z) calcd for $C_{36}H_{29}O_2P$ $[M+Na]^+$ 547.1797, found 547.1785.



5e, yield: 81%. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.62 – 7.58 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.32 (m, 2H), 7.22 – 7.17 (m, 7H), 7.17 – 7.16 (m, 1H), 7.14 – 7.08 (m, 3H), 7.03 – 6.99 (m, 7H), 6.96 – 6.91 (m, 2H), 6.85 (dd, *J* = 8.1, 2.7 Hz, 2H), 5.21 (d, *J* = 7.6 Hz, 1H), 2.18 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 216.47 (d, *J* = 6.30 Hz), 193.90 (d, *J* = 7.56 Hz), 141.62 (d, *J* = 3.78 Hz), 137.19, 134.83 (d, *J* = 88.20 Hz), 135.01 (d, *J* = 5.04 Hz), 132.22, 130.96 (dd, *J* = 8.82, 12.60 Hz), 130.44 (d, *J* = 5.04 Hz), 129.98, 129.14 (d, *J* = 11.34 Hz), 128.63 (d, *J* = 100.80 Hz), 128.53 (d, *J* = 103.32 Hz), 128.71 (d, *J* = 46.62 Hz), 127.94 (d, *J* = 59.22 Hz), 128.85, 127.85 (d, *J* = 46.62 Hz), 127.06 (d, *J* = 1.26 Hz), 115.83, 106.80 (d, *J* = 2.52 Hz), 45.64 (d, *J* = 69.30 Hz), 21.52 (d, *J* = 3.78 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.75. HRMS (ESI, m/z) calcd for $C_{43}H_{35}O_2P$ $[M+Na]^+$ 637.2267, found 637.2264.

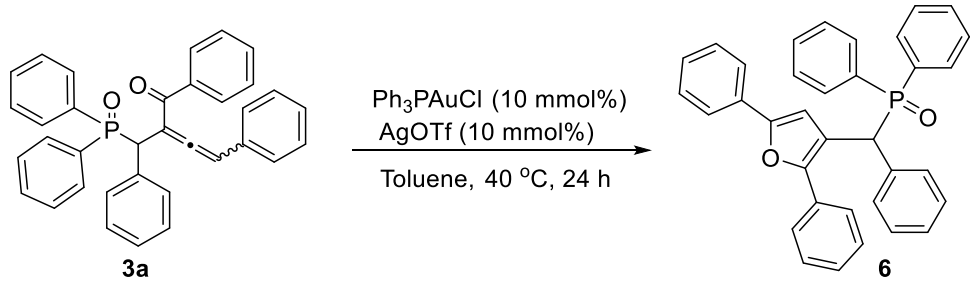


5f, yield: 80%. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.70 – 7.64 (m, 2H), 7.50 – 7.40 (m, 4H), 7.25 – 7.21 (m, 2H), 7.20 – 7.16 (m, 3H), 7.15 – 7.11 (m, 2H), 7.11 – 7.07 (m, 2H), 7.01 – 6.97 (m, 3H), 6.94 – 6.91 (m, 2H), 6.89 – 6.85 (m, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 5.25 (d, *J* = 8.0 Hz, 1H), 3.77

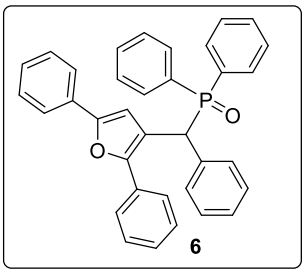
(s, 3H), 3.67 (s, 3H), 1.17 (s, 9H), 1.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 217.11 (d, *J* = 6.30 Hz), 193.99 (d, *J* = 5.04 Hz), 159.31, 154.68 (dd, *J* = 3.78, 7.56 Hz), 137.31, 135.57 (d, *J* = 5.04 Hz), 131.91, 131.07 (dd, *J* = 8.82, 34.02 Hz), 130.42, 130.40, 129.11 (dd, *J* = 78.12, 102.06 Hz), 129.64, 128.15 (d, *J* = 160.02 Hz), 128.02, 127.13 (dd, *J* = 2.52, 7.56 Hz), 126.89, 125.19 (dd, *J* = 3.78, 11.34 Hz), 115.21 (d, *J* = 1.26 Hz), 113.75 (d, *J* = 5.04 Hz), 106.88 (d, *J* = 2.52 Hz), 55.23 (d, *J* = 2.52 Hz), 44.79 (d, *J* = 69.30 Hz), 34.78 (d, *J* = 20.16 Hz), 31.02 (d, *J* = 13.86 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 29.60. HRMS (ESI, m/z) calcd for $C_{51}H_{51}O_4P$ $[M+Na]^+$ 781.3417, found 781.3422.

5. Synthetic Applications

5.1 Synthesis of Trisustituted Furan Derivative 6



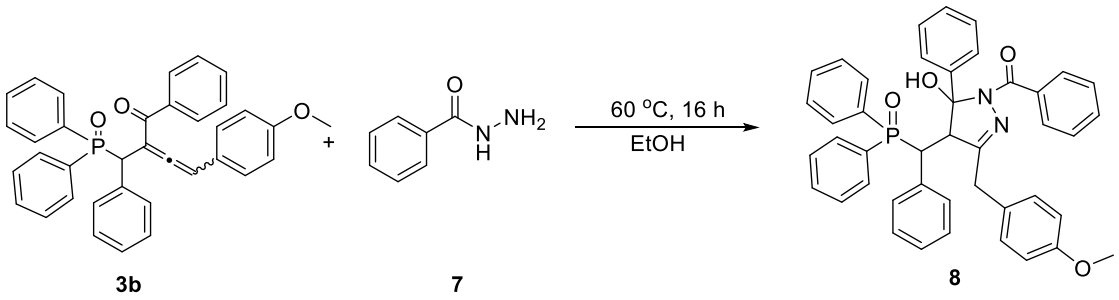
A mixture of **3a** (0.2 mmol), Ph_3PAuCl (10 mmol %) and AgOTf (10 mmol %) in toluene (2 mL) was stirred at 40 °C for 24 h under the atmosphere of nitrogen. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered and evaporated under reduced pressure and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 10/1 to 5/1) to afford the desired product **6**.



6, yield: 84%. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.73 – 7.67 (m, 2H), 7.60 – 7.56 (m, 1H), 7.57 – 7.51 (m, 2H), 7.46 – 7.38 (m, 8H), 7.36 – 7.32 (m,

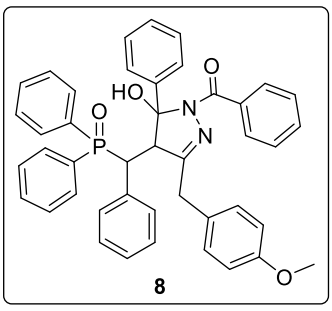
5H), 7.28 – 7.16 (m, 8H), 4.90 (d, J = 9.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 152.83, 150.05 (d, J = 11.34 Hz), 135.66 (d, J = 5.04 Hz), 131.93 (dd, J = 34.02, 98.28 Hz), 131.55 (dd, J = 2.52, 13.86 Hz), 131.23 (dd, J = 8.82, 23.94 Hz), 130.72, 130.51, 129.86 (d, J = 5.04 Hz), 128.76, 128.60, 128.53 (d, J = 1.26 Hz), 128.23 (dd, J = 11.34, 25.20 Hz), 127.92, 127.42, 127.11 (d, J = 2.52 Hz), 126.84, 123.93, 119.08 (d, J = 5.04 Hz), 109.26 (d, J = 3.78 Hz), 44.23 (d, J = 65.52 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 31.76. HRMS (ESI, m/z) calcd for $C_{35}H_{27}O_2P$ $[M+Na]^+$ 533.1641, found 533.1635.

5.2 Synthesis of Tetrasustituted 5-Hydroxypyrazoline 8



3b **7** **8**

A mixture of **3b** (0.2 mmol) and **7** (1.2 eq) in EtOH (2 mL) was stirred at 60 °C for 16 h under the atmosphere of nitrogen. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered and evaporated under reduced pressure and purified by column chromatography (silica gel, Petroleum ether/ EtOAc: 20/1 to 8/1) to afford the desired product **8**.



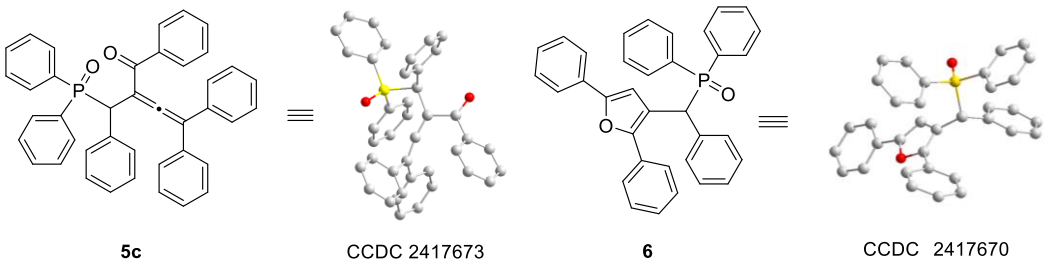
8

8, yield: 78%. (Colorless oil.) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 4H), 7.77 – 7.70 (m, 2H), 7.56 – 7.50 (m, 1H), 7.49 – 7.45 (m, 2H), 7.44 – 7.40 (m, 1H), 7.37 – 7.34 (m, 1H), 7.33 – 7.30 (m, 2H), 7.29 – 7.20 (m, 5H), 7.18 – 7.14 (m, 2H), 7.11 (d, J = 7.4 Hz, 1H), 7.01 (dd, J = 17.1, 8.2 Hz, 4H), 6.71 – 6.64 (m, 2H), 6.52 (d,

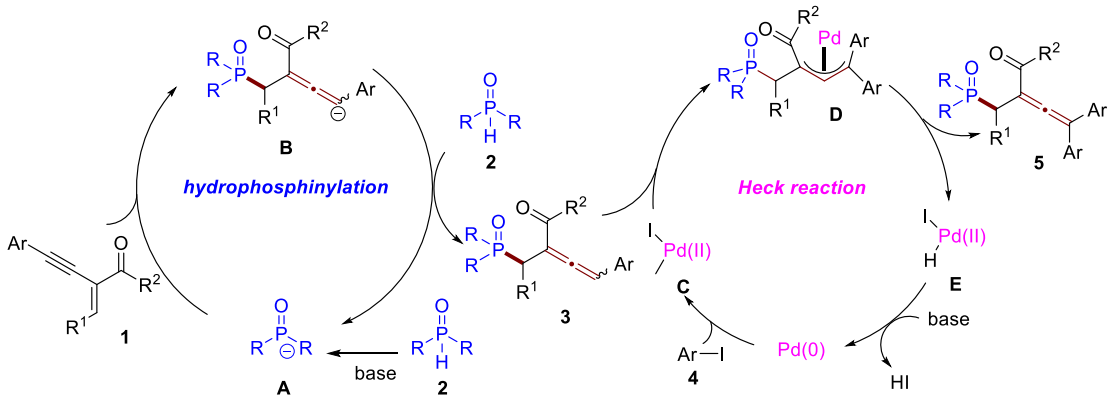
J = 8.6 Hz, 2H), 6.28 (s, 1H), 5.08 (d, J = 10.3 Hz, 1H), 4.51 (d, J = 14.4 Hz, 1H), 3.76 (d, J = 14.4 Hz, 1H), 3.69 (s, 3H), 3.07 (d, J = 13.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 167.76, 161.43, 158.18, 141.29, 133.70 (d, J = 3.78 Hz), 133.02, 132.31 (d, J = 11.34 Hz), 131.78 (d, J = 2.52 Hz), 131.51 (d, J = 2.52 Hz), 131.46, 131.31 (dd, J = 1.26, 7.65 Hz), 131.05 (d, J = 7.56 Hz), 130.10 (d, J = 102.06 Hz), 128.80 (d, J = 11.34 Hz), 128.40 (d, J = 1.26 Hz), 128.37 (d, J = 8.82 Hz), 128.13, 127.53, 127.47 (d, J = 6.30 Hz), 124.26, 113.35, 96.12 (d, J = 11.34 Hz), 57.41, 55.22, 42.63, 42.07, 35.81. ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 33.78. HRMS (ESI, m/z) calcd for $C_{43}H_{37}N_2O_4P$ $[M+Na]^+$ 699.2383, found 699.2384.

6. X-Ray Crystallography

The crystal of **5c** suitable for XRD analysis was prepared by recrystallization from a mixed solvent of DCM and petroleum ether. The crystal of **6** suitable for XRD analysis was prepared by recrystallization from a mixed solvent of DCM and petroleum ether. CCDC 2417673 (**5c**), CCDC 2417670 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



7. Proposed Reaction Mechanism



Scheme S1. Proposed reaction mechanism.

Based on the experimental results outlined above, the proposed mechanism is depicted in Scheme S1. Initially, $R_2P(O)H$ is deprotonated to form the phosphoryl anion **A** in the presence of a base. This anion then undergoes the 1,4-addition reaction with the alkynyl enone, generating the allenyl carbanion intermediate **B**. Intermediate **B** can extract a proton (H^+) from SPOs, leading to the formation of the tri-substituted homoallenyl phosphine oxide **3** and the regeneration of the phosphoryl anion **A**. The two-component product **3** can then undergo the Heck reaction with an aryl iodide in the presence of Pd(0). The resulting aryl palladium(II) intermediate **C**, formed via the oxidative addition of iodobenzene, undergoes the migratory insertion with compound **3**, forming the allyl-Pd complex **D**. Finally, the β-H elimination reaction occurs, yielding the tetra-substituted homologous phosphine oxide **5** and product **E**.

8. NMR and HRMS Spectra of All Compounds

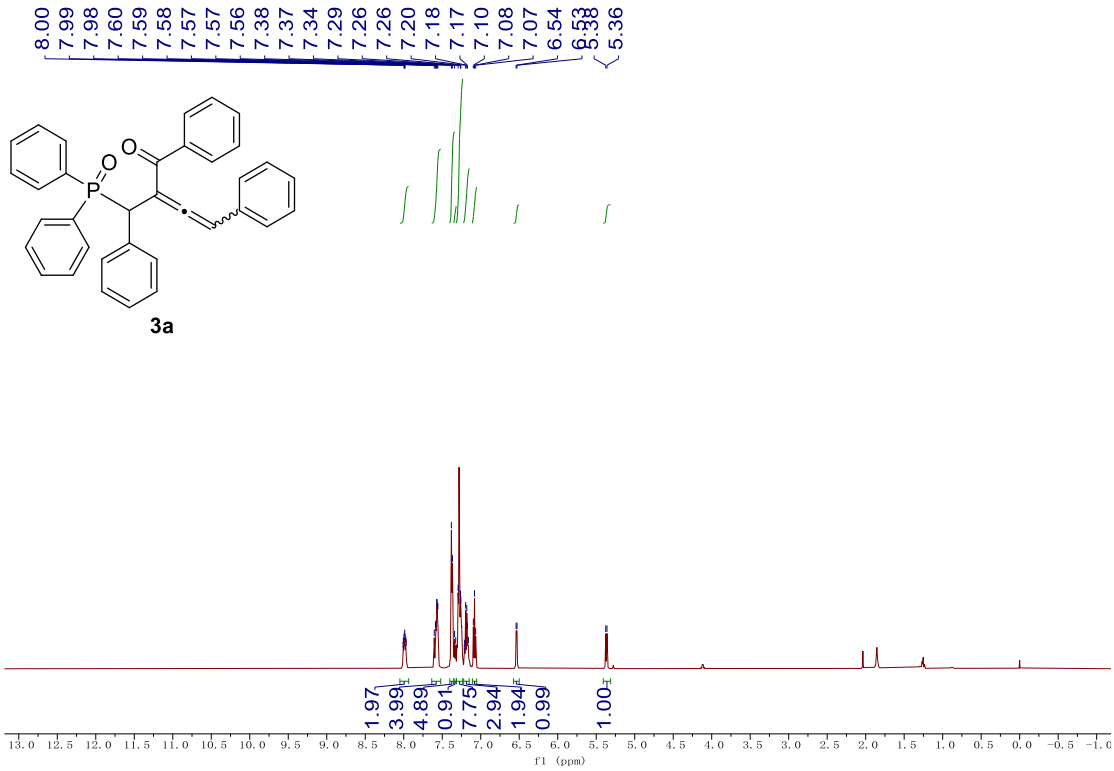


Figure S1. ^{1}H NMR spectrum of compound **3a** (500 MHz, $CDCl_3$).

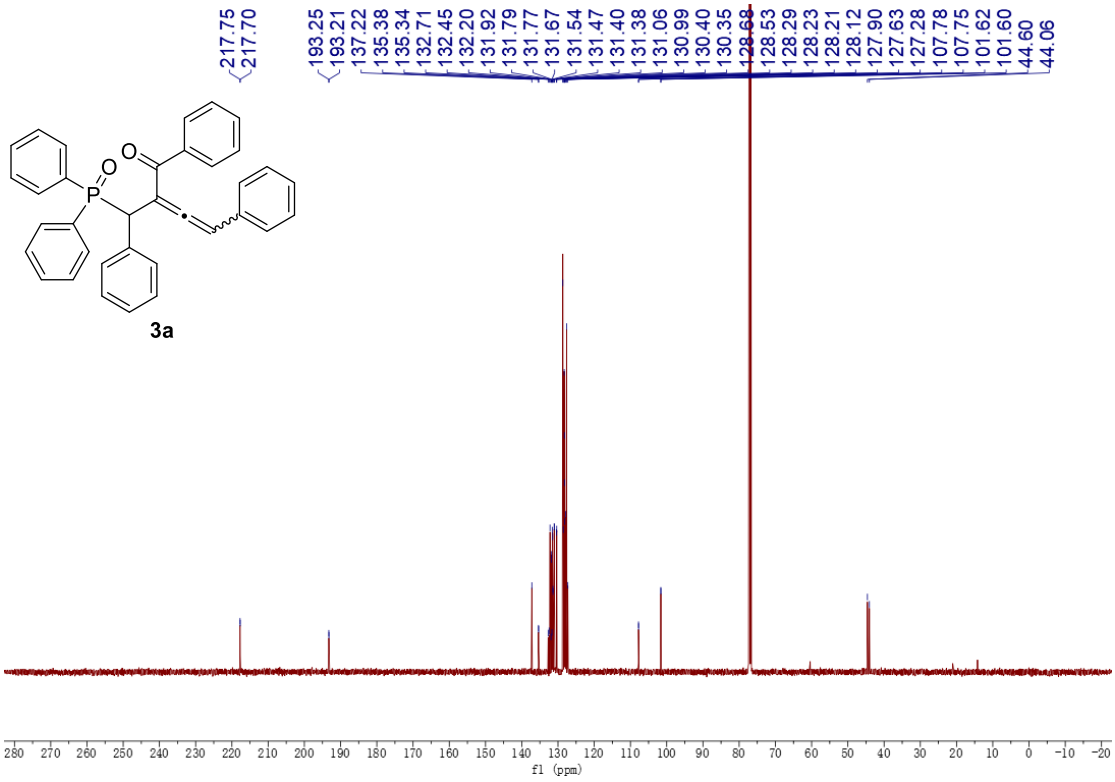


Figure S2. ^{13}C NMR spectrum of compound **3a** (126 MHz, $CDCl_3$).

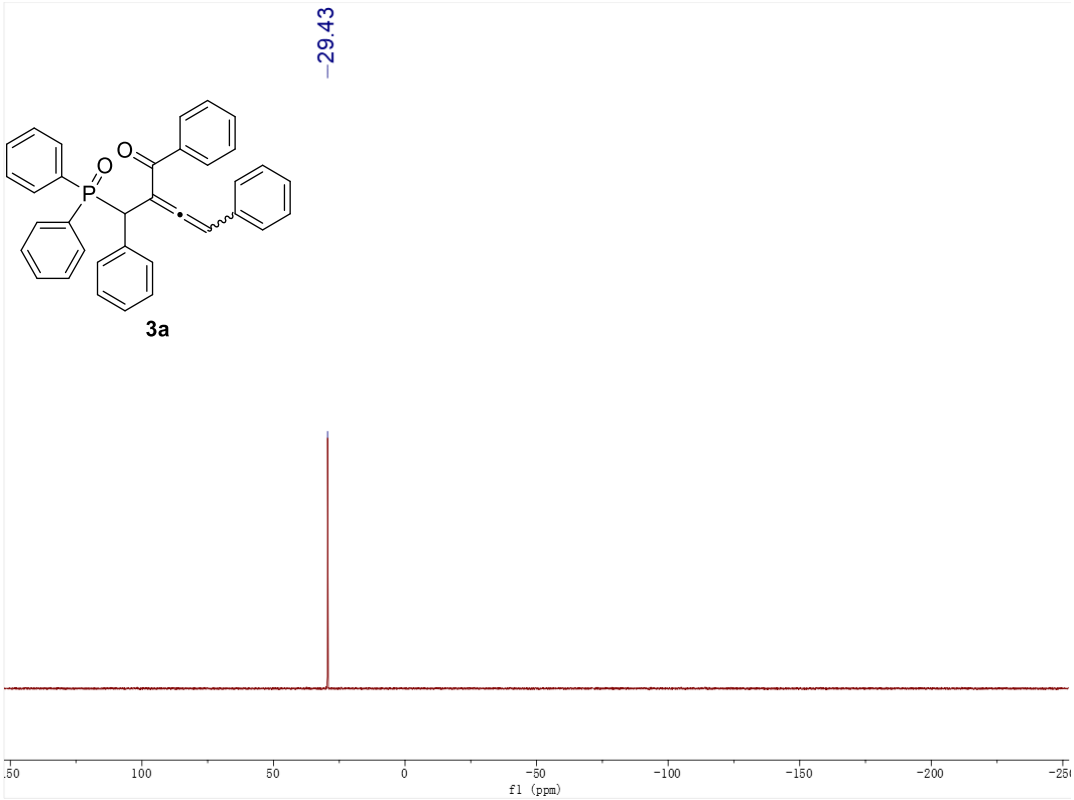


Figure S3. ^{31}P NMR spectrum of compound **3a** (202 MHz, $CDCl_3$).

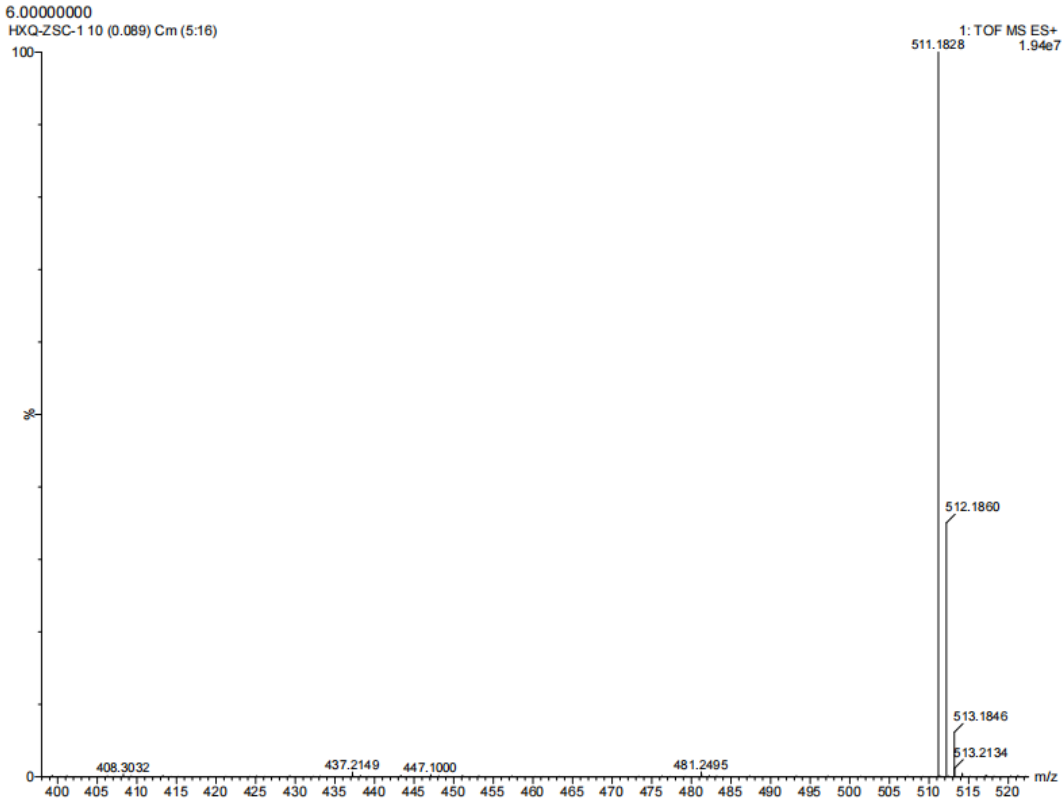
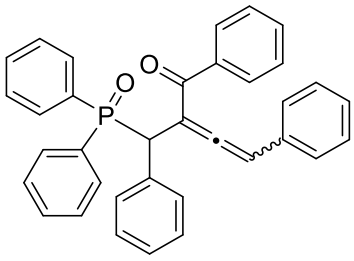


Figure S4. HRMS (ESI) spectrum of compound **3a**.



3a

Chemical Formula: $C_{35}H_{27}O_2P$
Exact Mass: 510.1749
Molecular Weight: 510.5728
m/z: 510.1749 (100.0%), 511.1782 (37.9%), 512.1816 (4.3%), 512.1816 (2.7%)
Elemental Analysis: C, 82.34; H, 5.33; O, 6.27; P, 6.07

HRMS (ESI, m/z) calcd for $C_{35}H_{27}O_2P[M+H]^+$ 511.1821, found 511.1828.

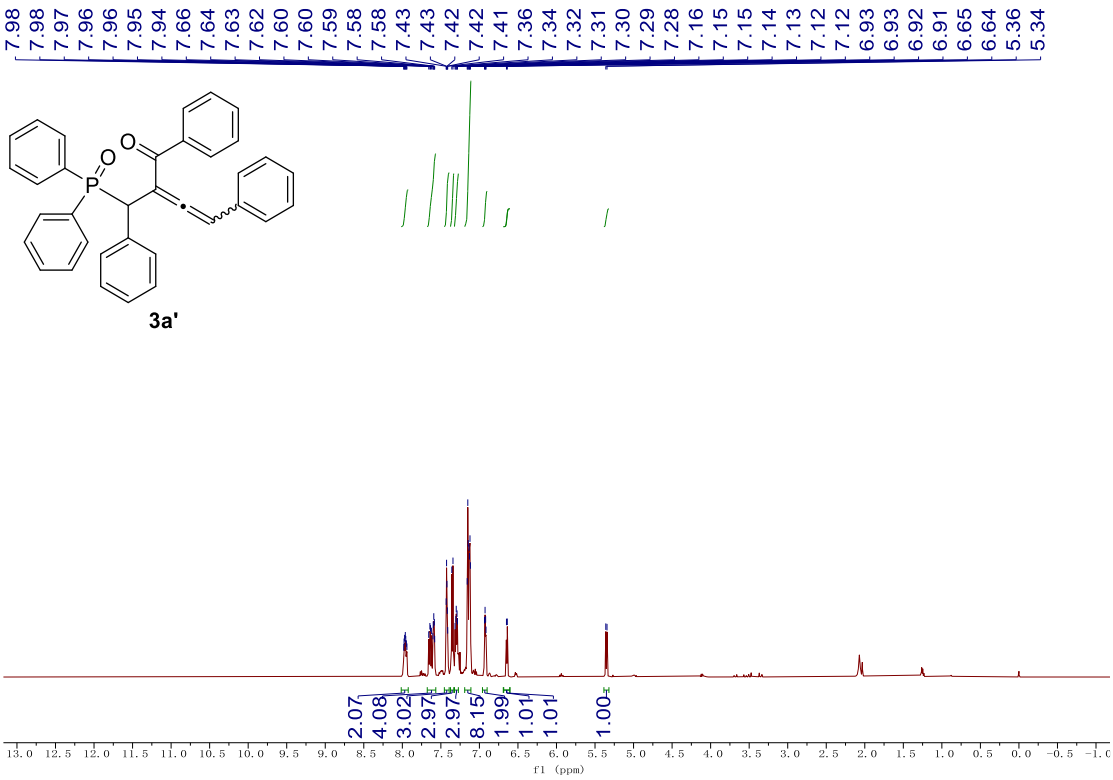


Figure S5. ^{1}H NMR spectrum of compound **3a'** (500 MHz, $CDCl_3$).

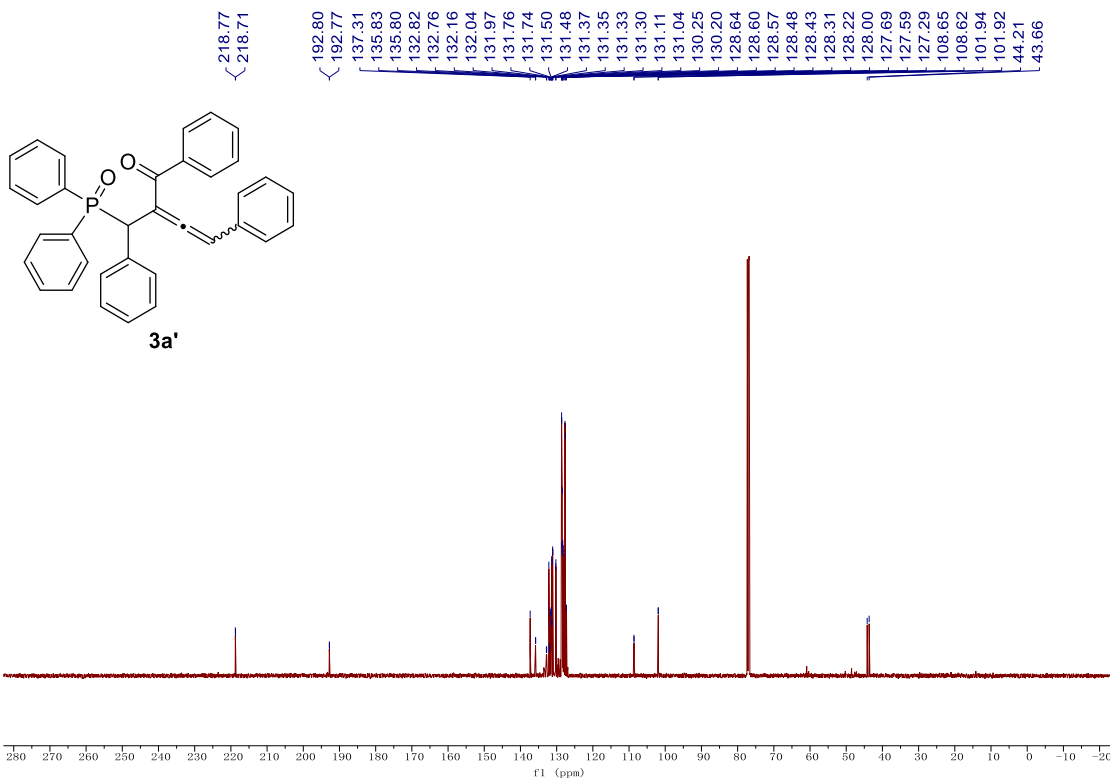


Figure S6. ^{13}C NMR spectrum of compound **3a'** (126 MHz, $CDCl_3$).

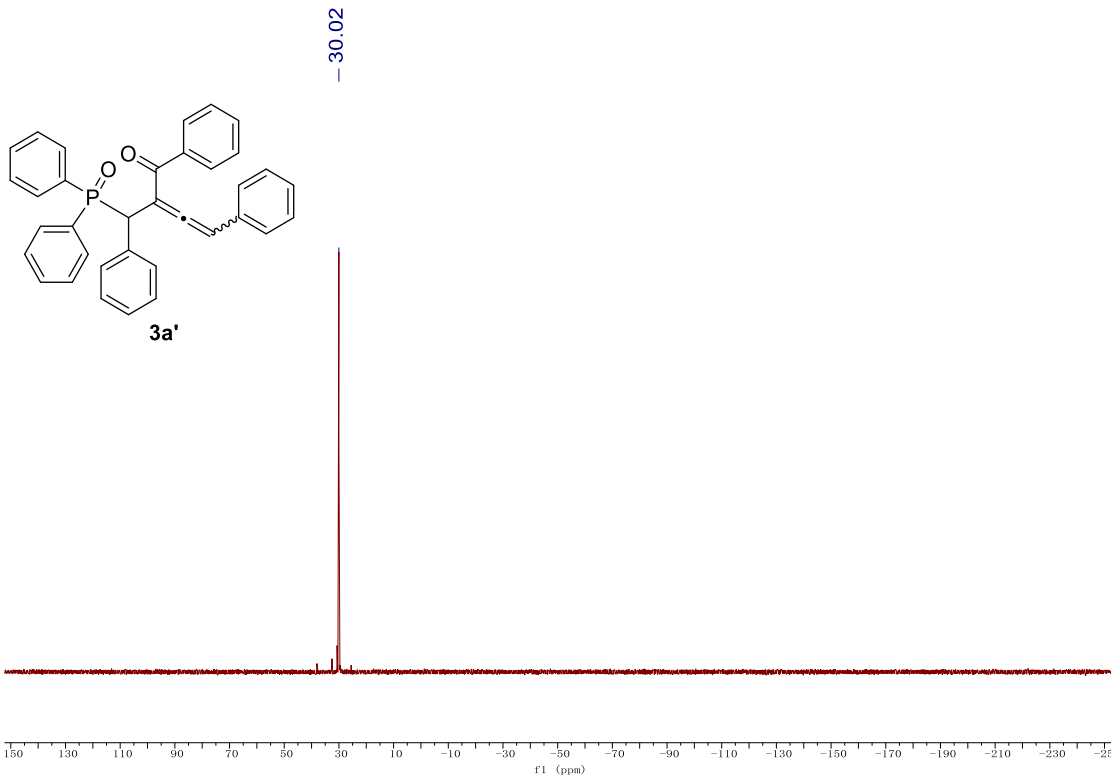


Figure S7. ^{31}P NMR spectrum of compound **3a'** (202 MHz, $CDCl_3$).

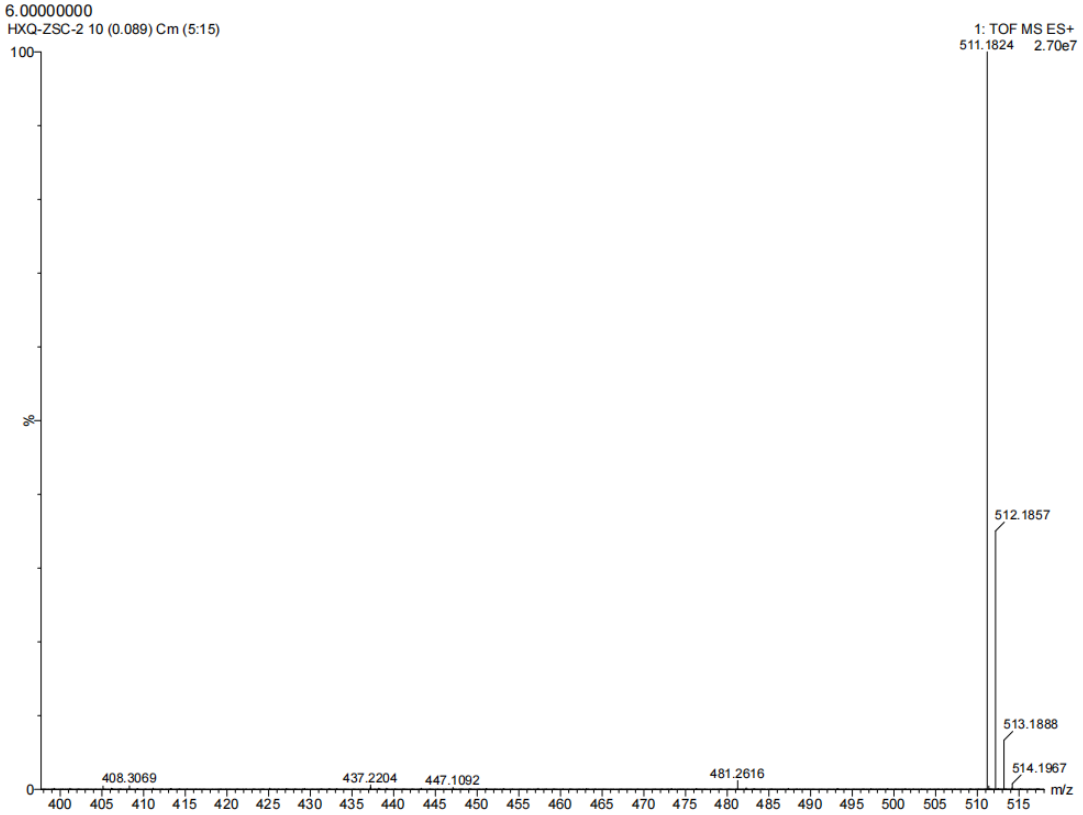
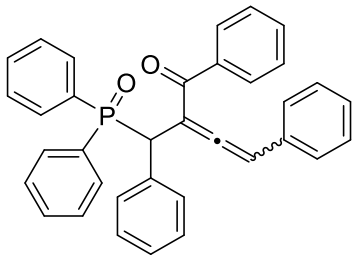


Figure S8. HRMS (ESI) spectrum of compound **3a'**.



3a'

Chemical Formula: $C_{35}H_{27}O_2P$
Exact Mass: 510.1749
Molecular Weight: 510.5728
m/z: 510.1749 (100.0%), 511.1782 (37.9%), 512.1816 (4.3%), 512.1816 (2.7%)
Elemental Analysis: C, 82.34; H, 5.33; O, 6.27; P, 6.07

HRMS (ESI, m/z) calcd for $C_{35}H_{27}O_2P[M+H]^+$ 511.1821, found 511.1824.

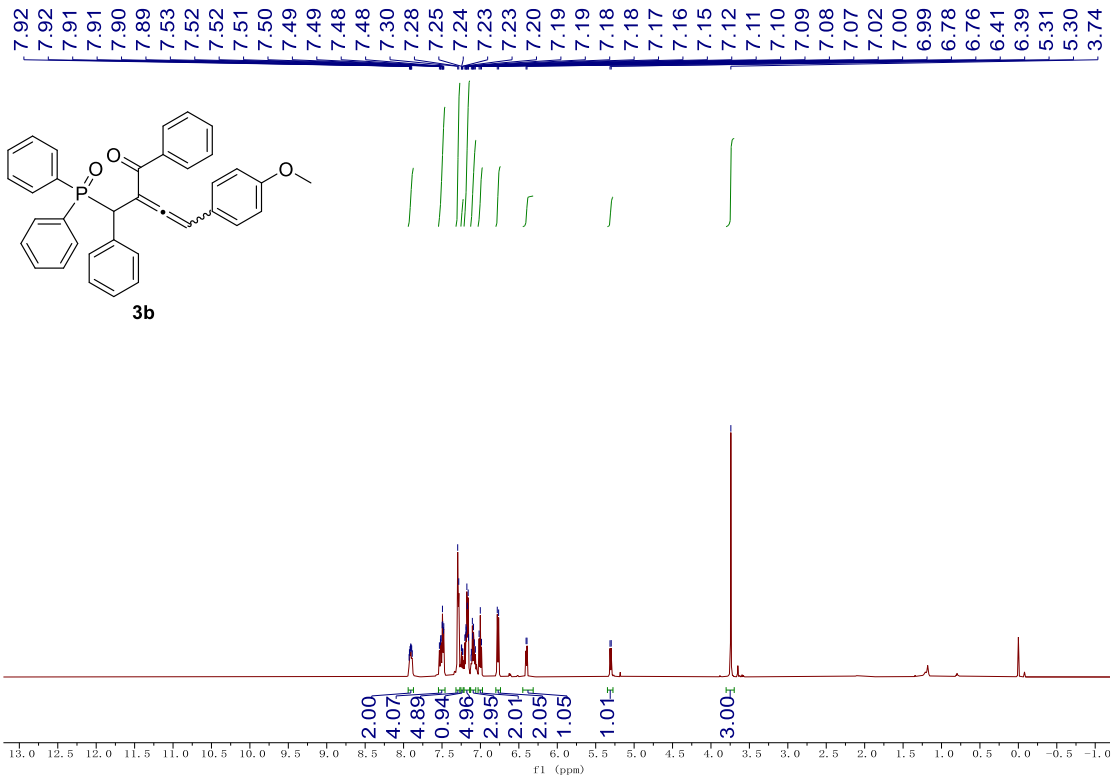


Figure S9. ^{1}H NMR spectrum of compound **3b** (500 MHz, $CDCl_3$).

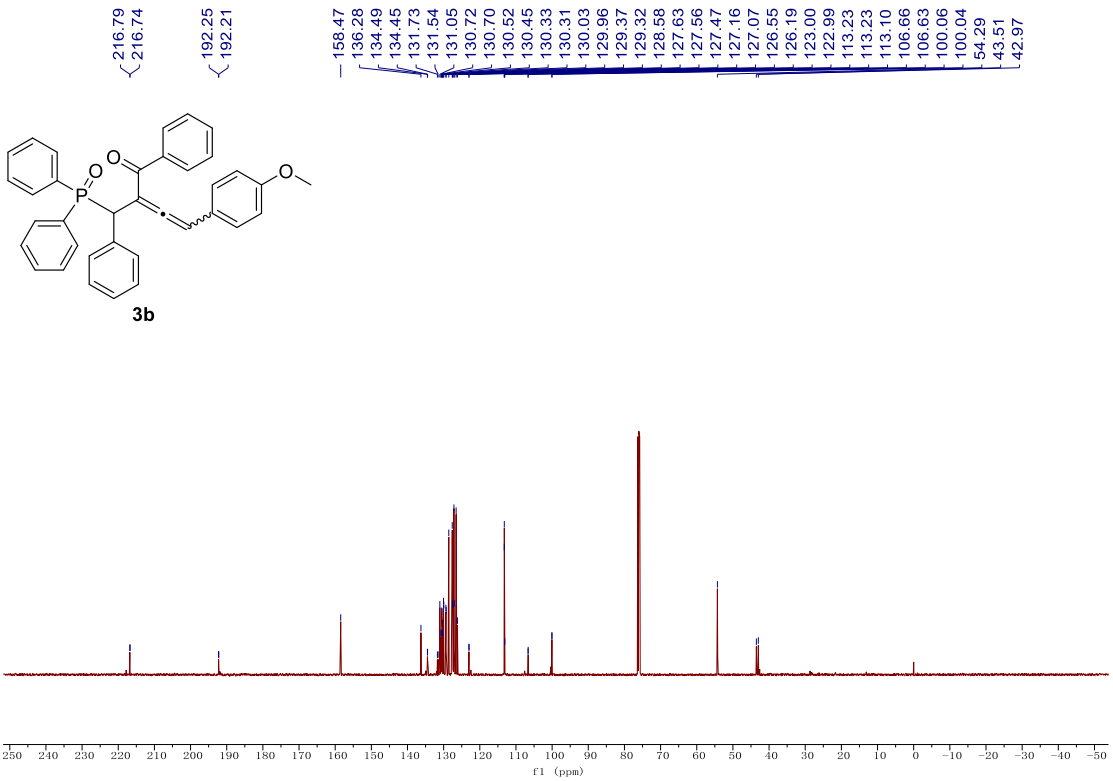


Figure S10. ^{13}C NMR spectrum of compound **3b** (126 MHz, $CDCl_3$).

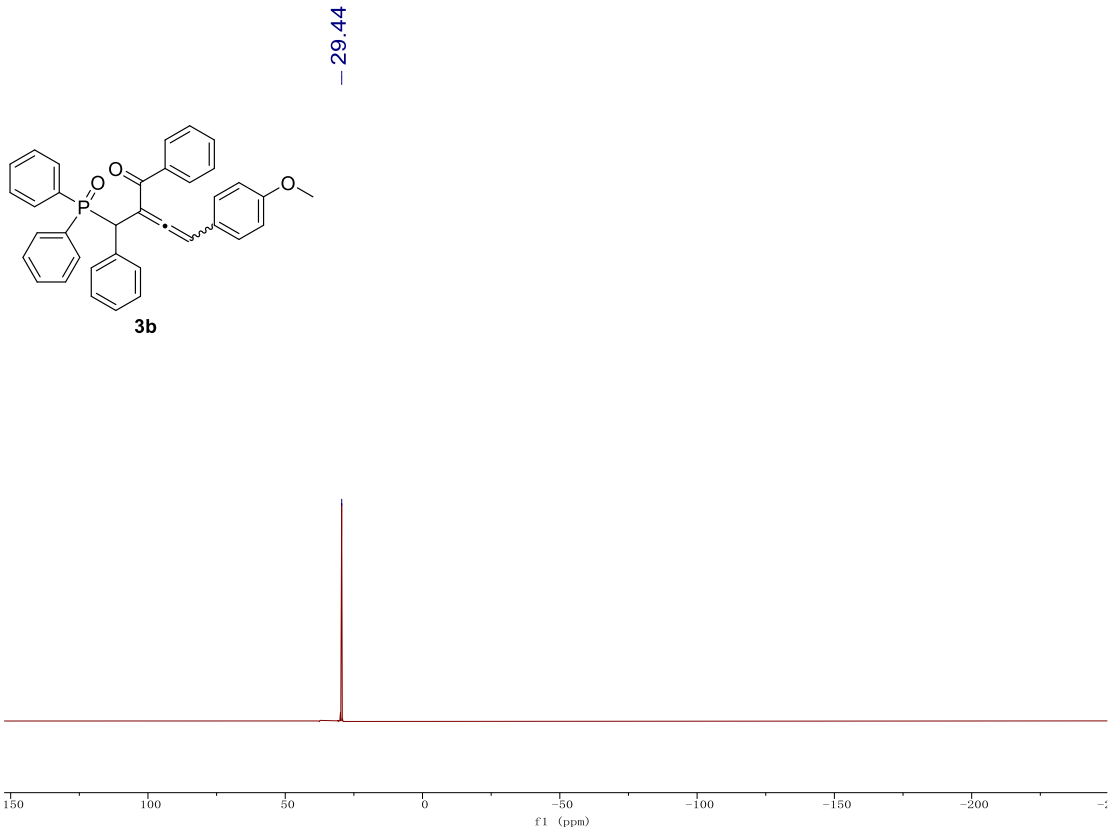


Figure S11. ^{31}P NMR spectrum of compound **3b** (202 MHz, $CDCl_3$).

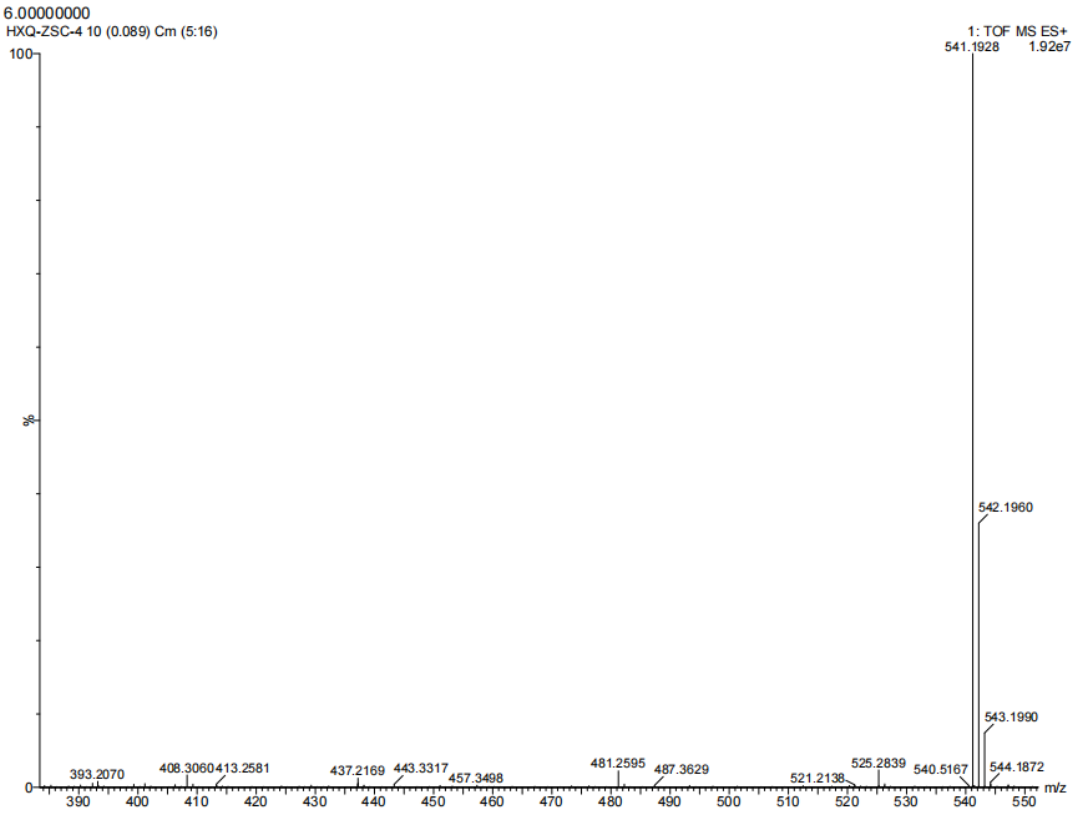
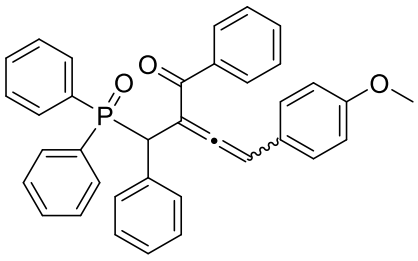


Figure S12. HRMS (ESI) spectrum of compound **3b**.



3b

Chemical Formula: $C_{36}H_{29}O_3P$
Exact Mass: 540.1854
Molecular Weight: 540.5988
m/z: 540.1854 (100.0%), 541.1888 (38.9%), 542.1921 (7.4%)
Elemental Analysis: C, 79.98; H, 5.41; O, 8.88; P, 5.73

HRMS (ESI, m/z) calcd for $C_{36}H_{29}O_3P[M+H]^+$ 541.1927, found 541.1928.

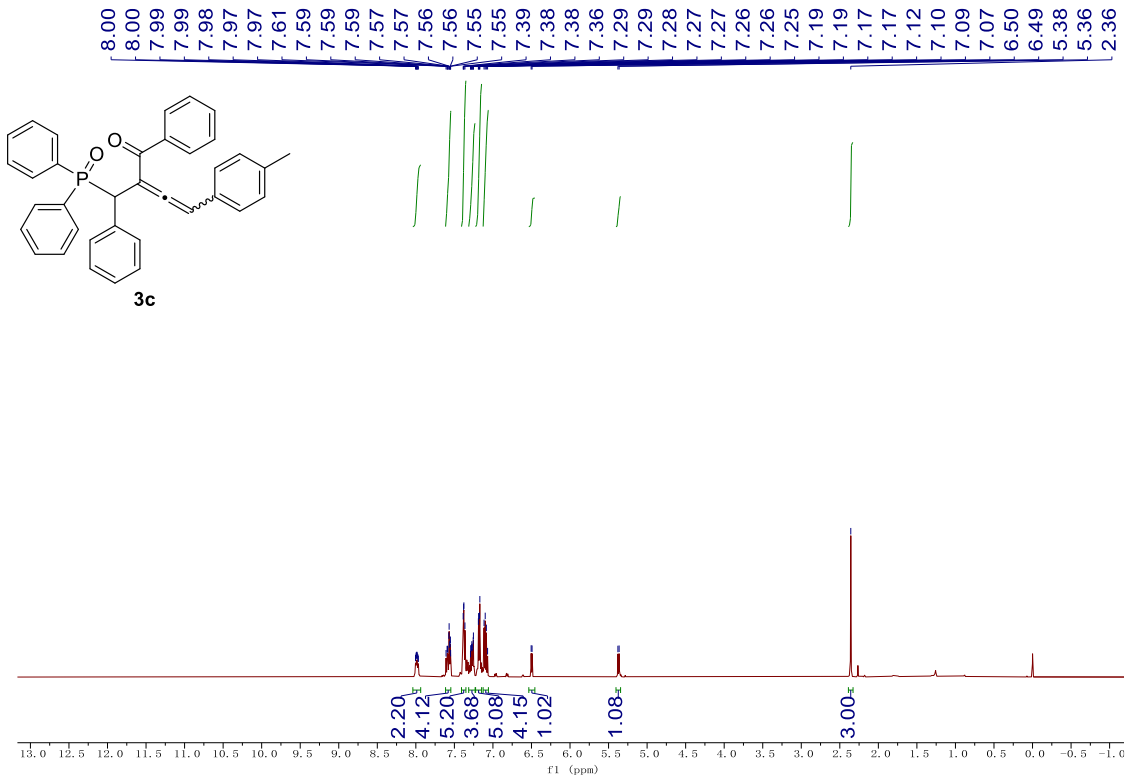


Figure S13. ^{1}H NMR spectrum of compound **3c** (500 MHz, $CDCl_3$).

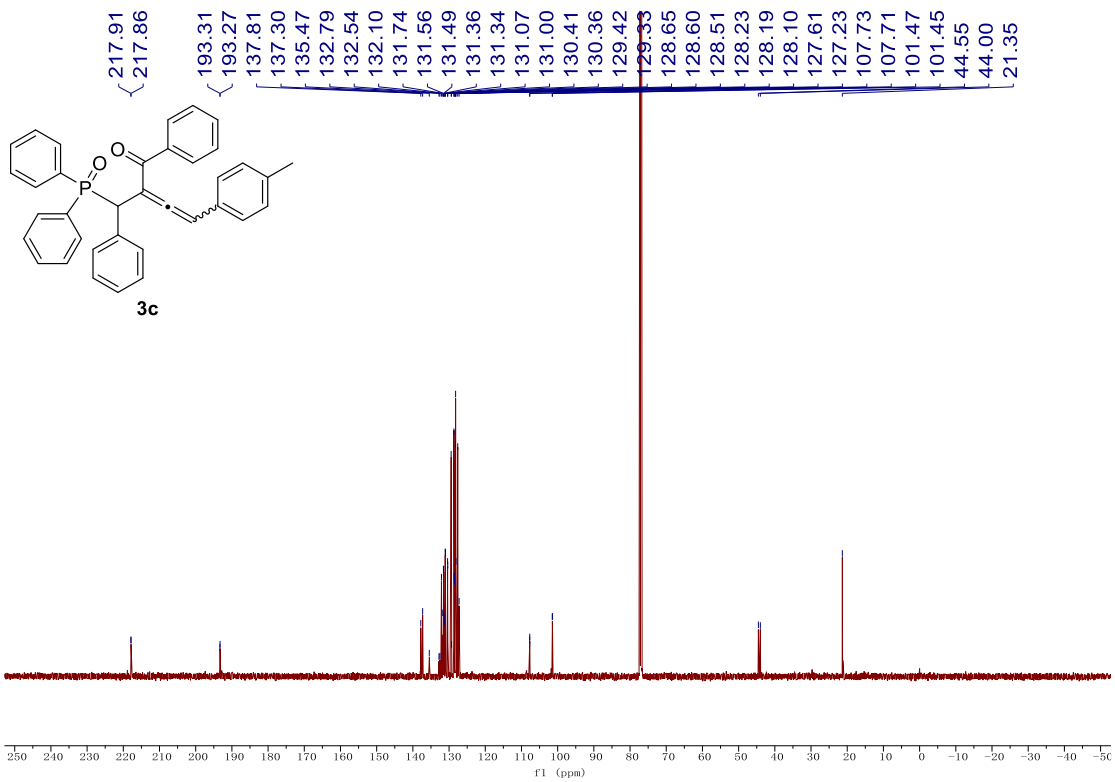


Figure S14. ^{13}C NMR spectrum of compound **3c** (126 MHz, $CDCl_3$).

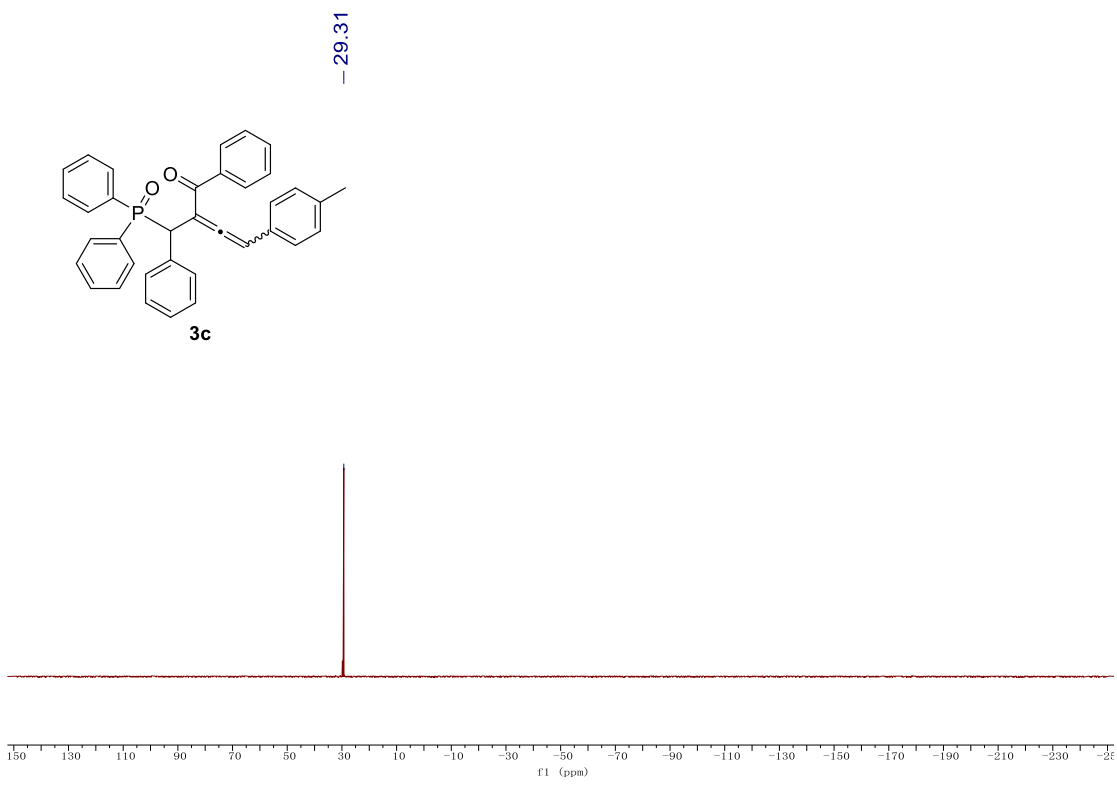


Figure S15. ^{31}P NMR spectrum of compound **3c** (202 MHz, $CDCl_3$).

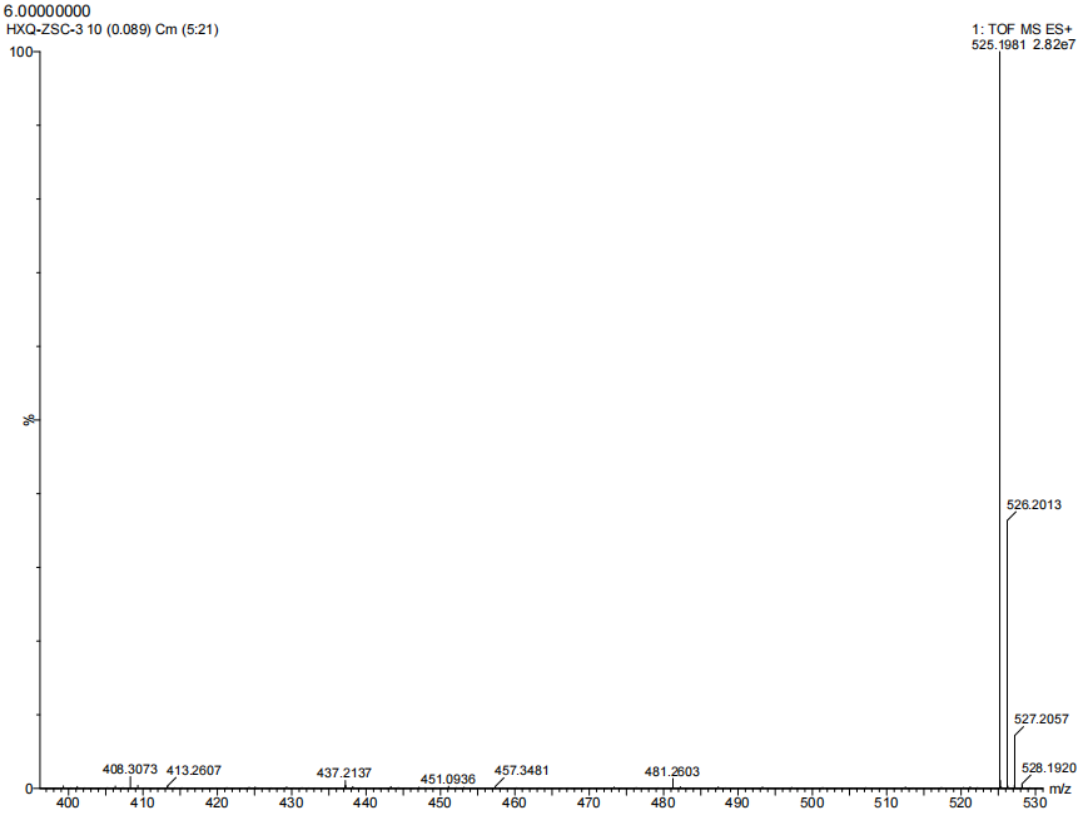
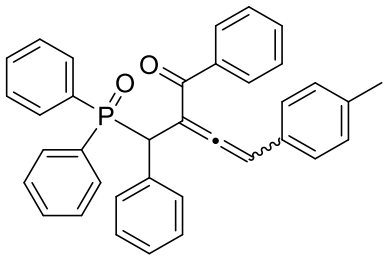


Figure S16. HRMS (ESI) spectrum of compound **3c**.



3c

Chemical Formula: $C_{36}H_{29}O_2P$
Exact Mass: 524.1905
Molecular Weight: 524.5998
m/z: 524.1905 (100.0%), 525.1939 (38.9%), 526.1972 (4.7%), 526.1972 (2.7%)
Elemental Analysis: C, 82.42; H, 5.57; O, 6.10; P, 5.90

HRMS (ESI, m/z) calcd for $C_{36}H_{29}O_2P[M+H]^+$ 525.1978, found 525.1981.

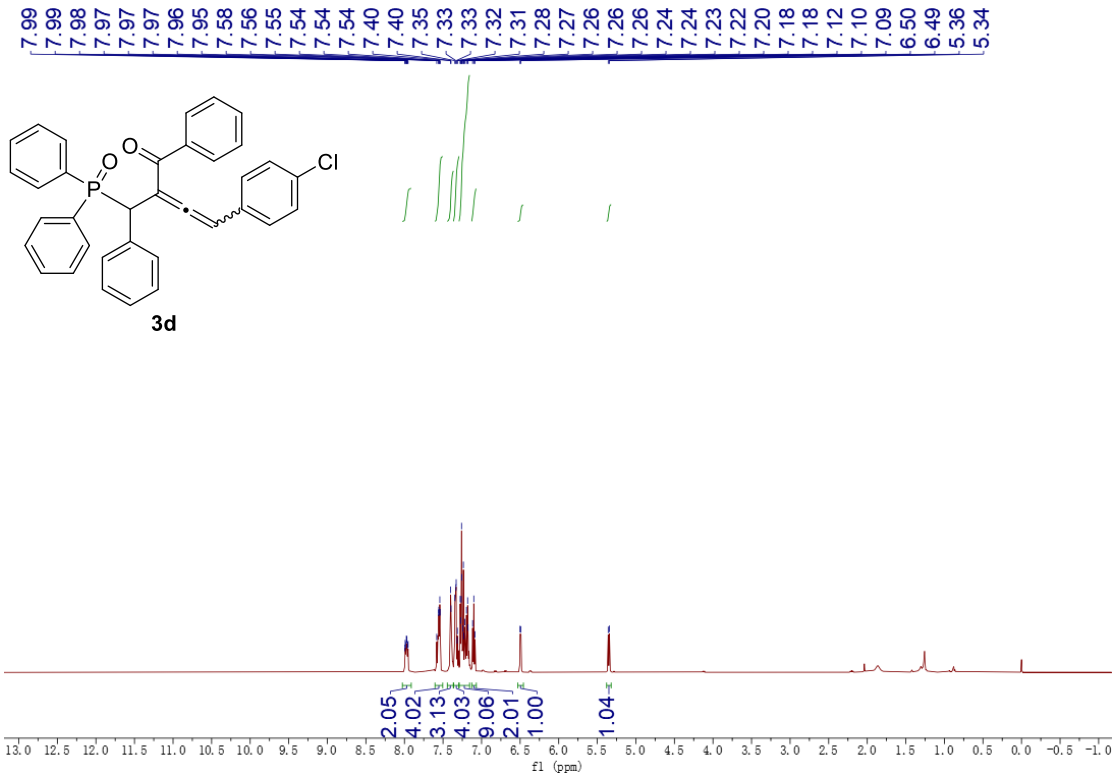


Figure S17. ^{1}H NMR spectrum of compound **3d** (500 MHz, $CDCl_3$).

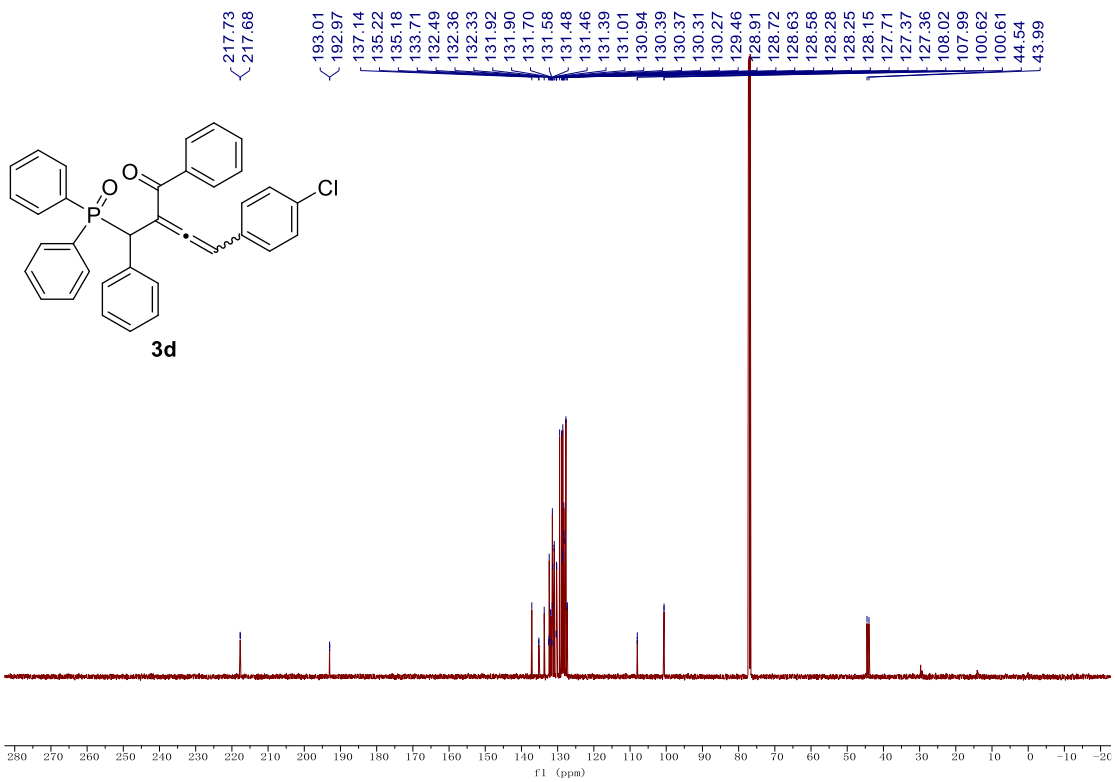


Figure S18. ^{13}C NMR spectrum of compound **3d** (126 MHz, $CDCl_3$).

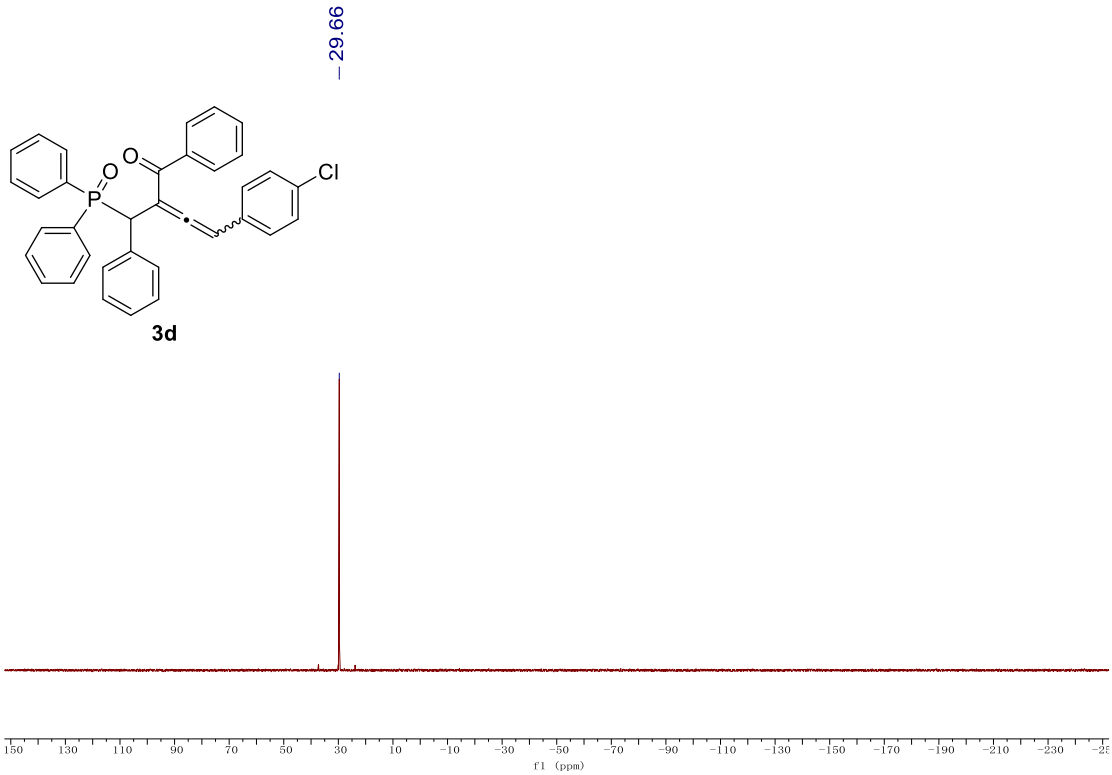


Figure S19. ^{31}P NMR spectrum of compound **3d** (202 MHz, $CDCl_3$).

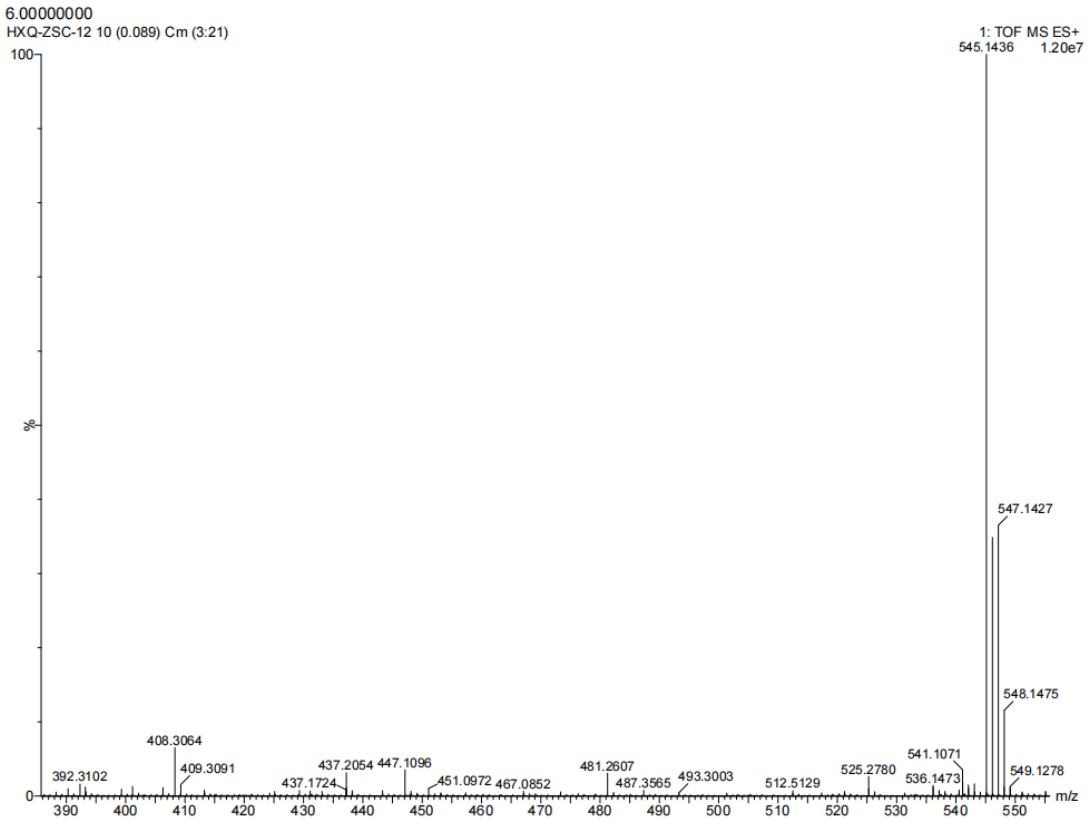
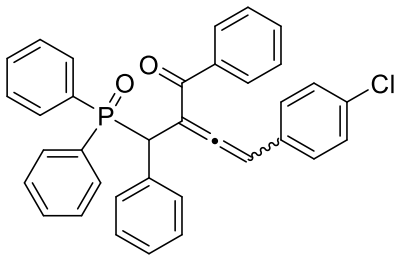


Figure S20. HRMS (ESI) spectrum of compound **3d**.



3d

Chemical Formula: $C_{35}H_{26}ClO_2P$
Exact Mass: 544.1359
Molecular Weight: 545.0148
m/z: 544.1359 (100.0%), 545.1392 (37.9%), 546.1329 (32.0%), 547.1363 (12.1%), 546.1426 (7.0%), 548.1397 (2.2%)
Elemental Analysis: C, 77.13; H, 4.81; Cl, 6.50; O, 5.87; P, 5.68

HRMS (ESI, m/z) calcd for $C_{35}H_{26}ClO_2P[M+H]^+$ 545.1432, found 545.1436.

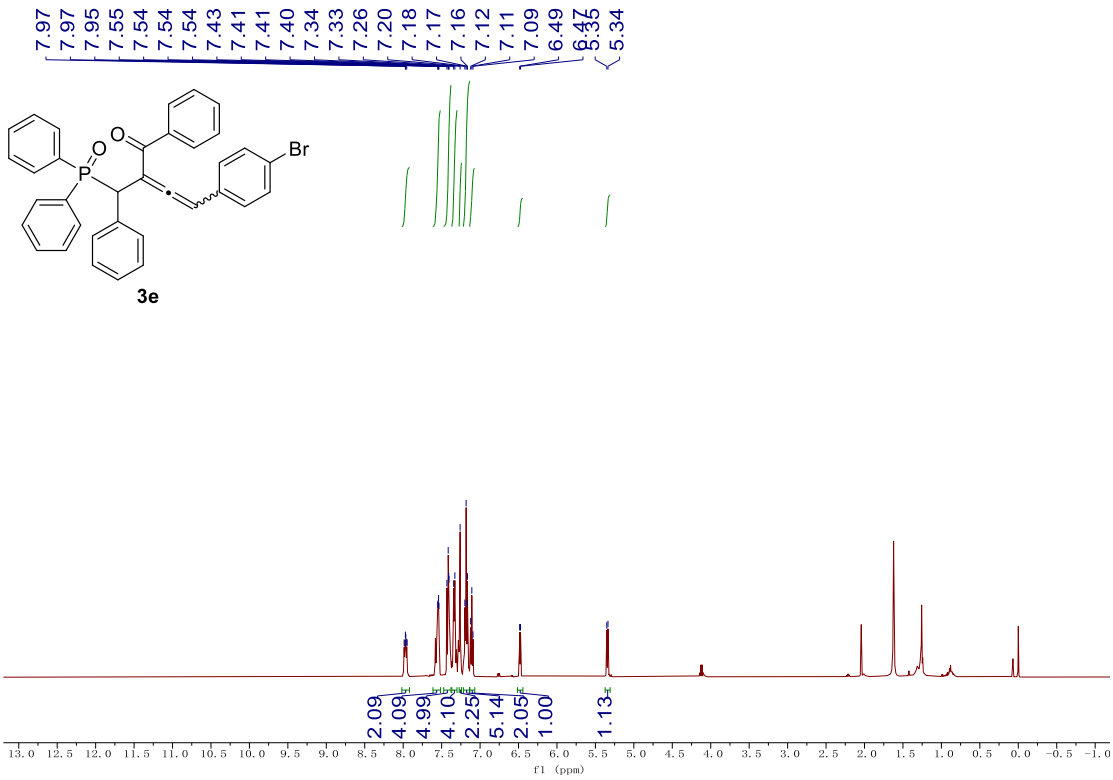


Figure S21. ^{1}H NMR spectrum of compound **3e** (500 MHz, $CDCl_3$).

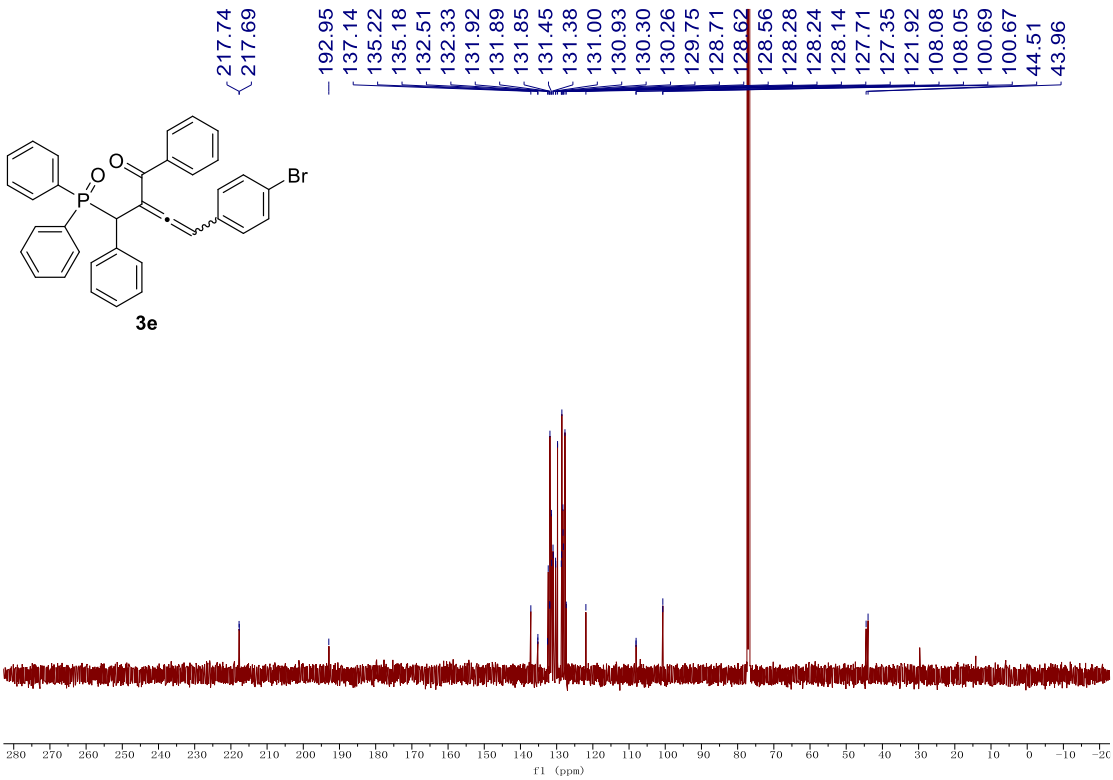


Figure S22. ^{13}C NMR spectrum of compound **3e** (126 MHz, $CDCl_3$).

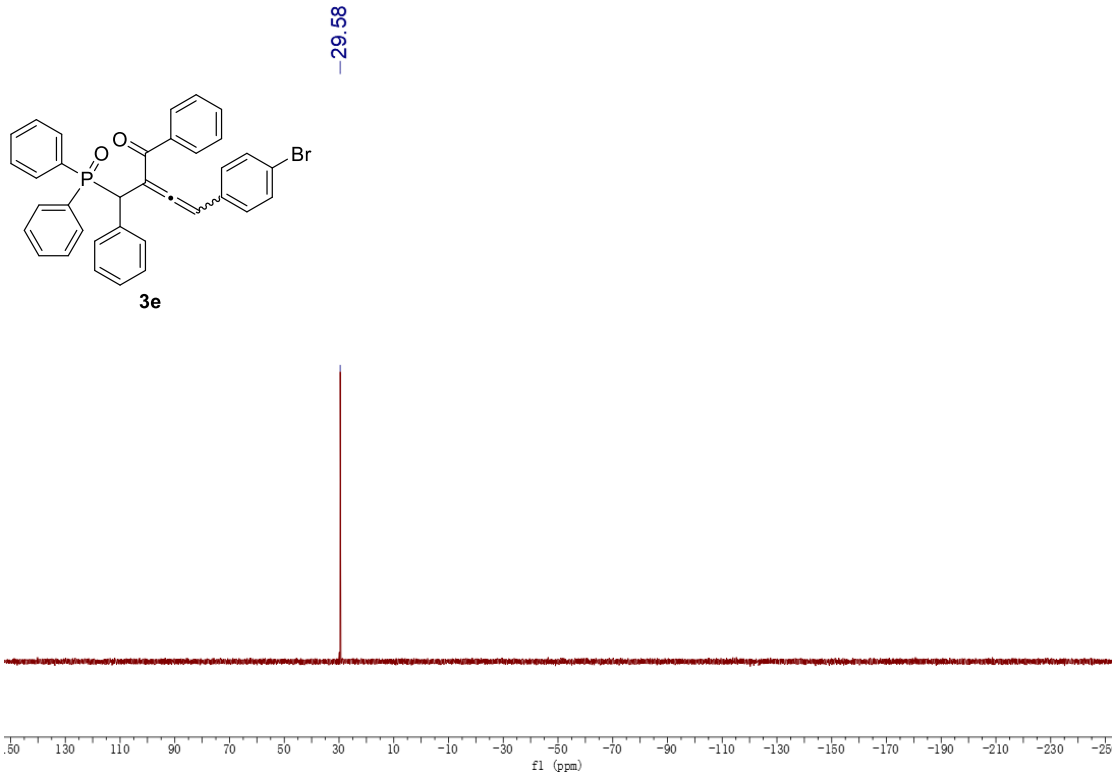


Figure S23. ^{31}P NMR spectrum of compound **3e** (202 MHz, $CDCl_3$).

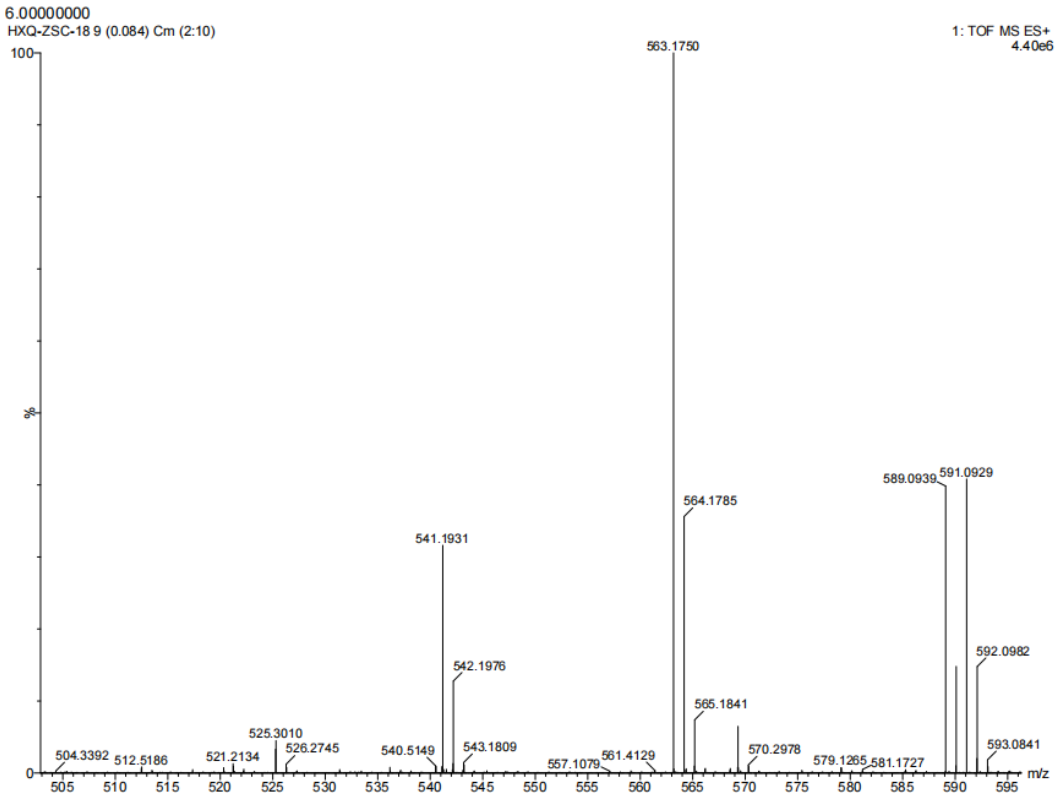
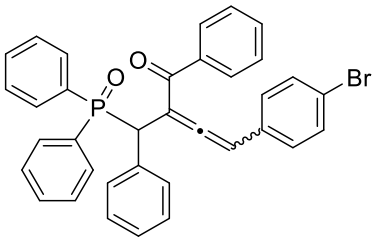


Figure S24. HRMS (ESI) spectrum of compound **3e**.



3e

Chemical Formula: $C_{35}H_{26}BrO_2P$
Exact Mass: 588.0854
Molecular Weight: 589.4688
m/z: 588.0854 (100.0%), 590.0833 (97.3%), 589.0887 (37.9%), 591.0867 (36.8%), 592.0900 (6.8%), 590.0921 (4.7%), 590.0921 (2.2%)
Elemental Analysis: C, 71.32; H, 4.45; Br, 13.56; O, 5.43; P, 5.25

HRMS (ESI, m/z) calcd for $C_{35}H_{26}BrO_2P[M+H]^+$ 589.0927, found 589.0939.

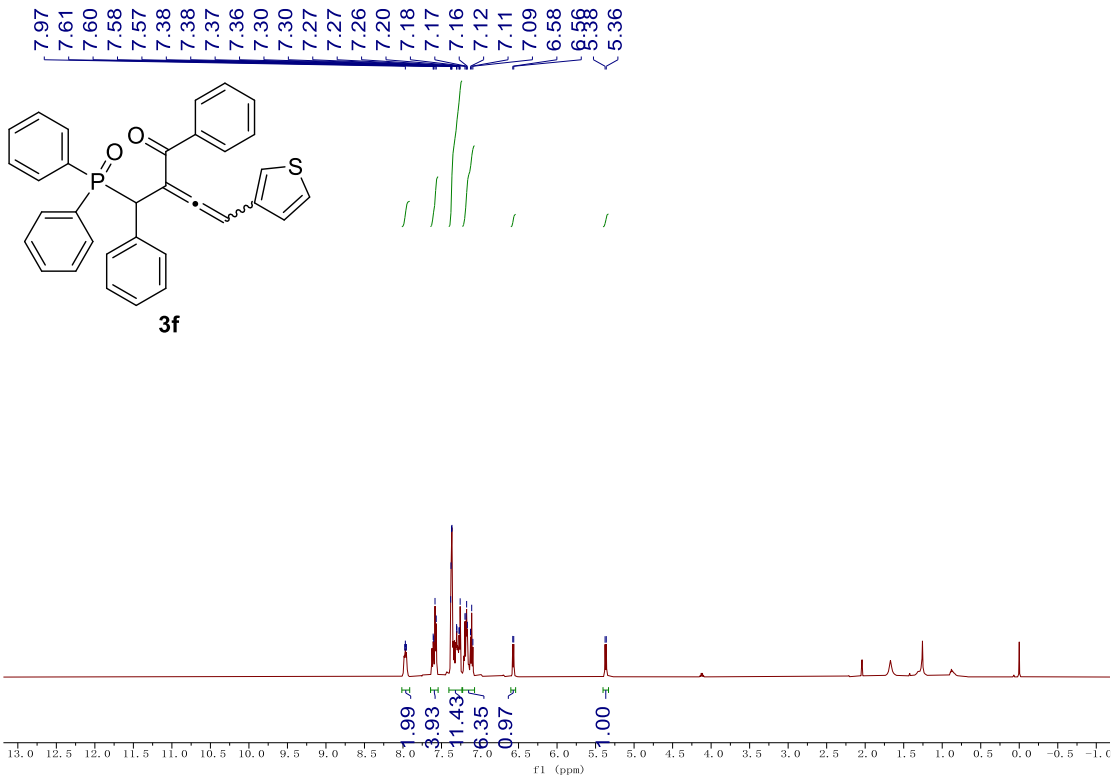


Figure S25. ^{1}H NMR spectrum of compound **3f** (500 MHz, $CDCl_3$).

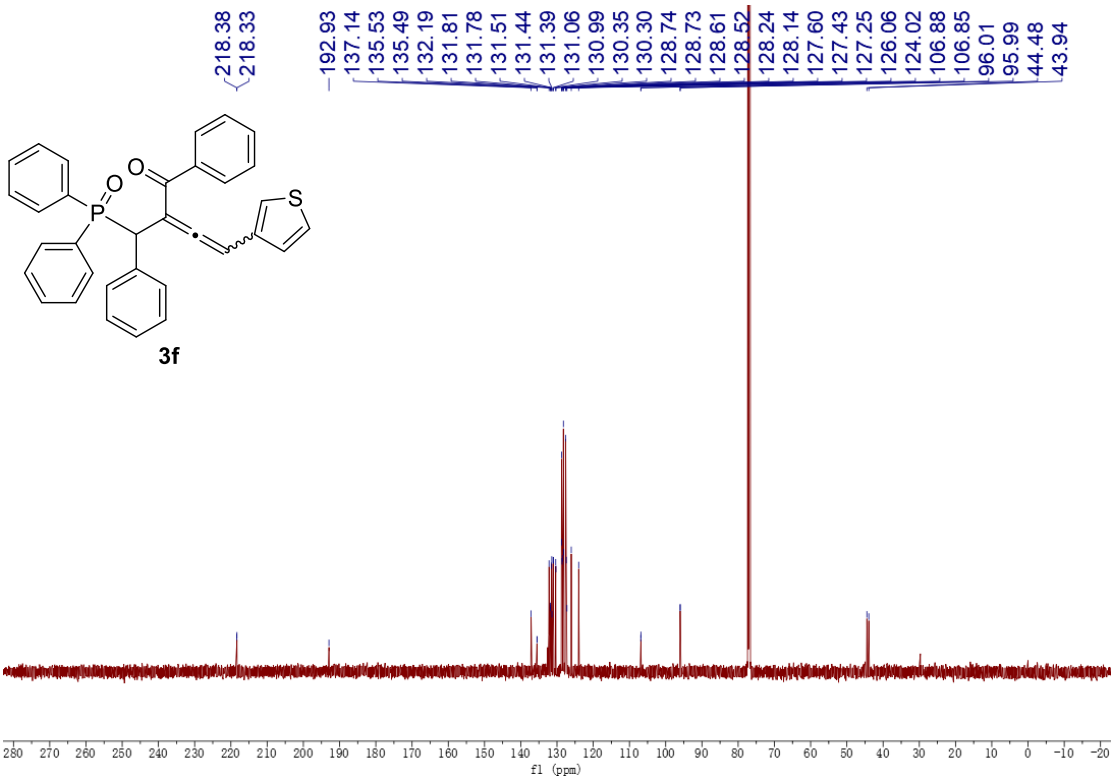


Figure S26. ^{13}C NMR spectrum of compound **3f** (126 MHz, $CDCl_3$).

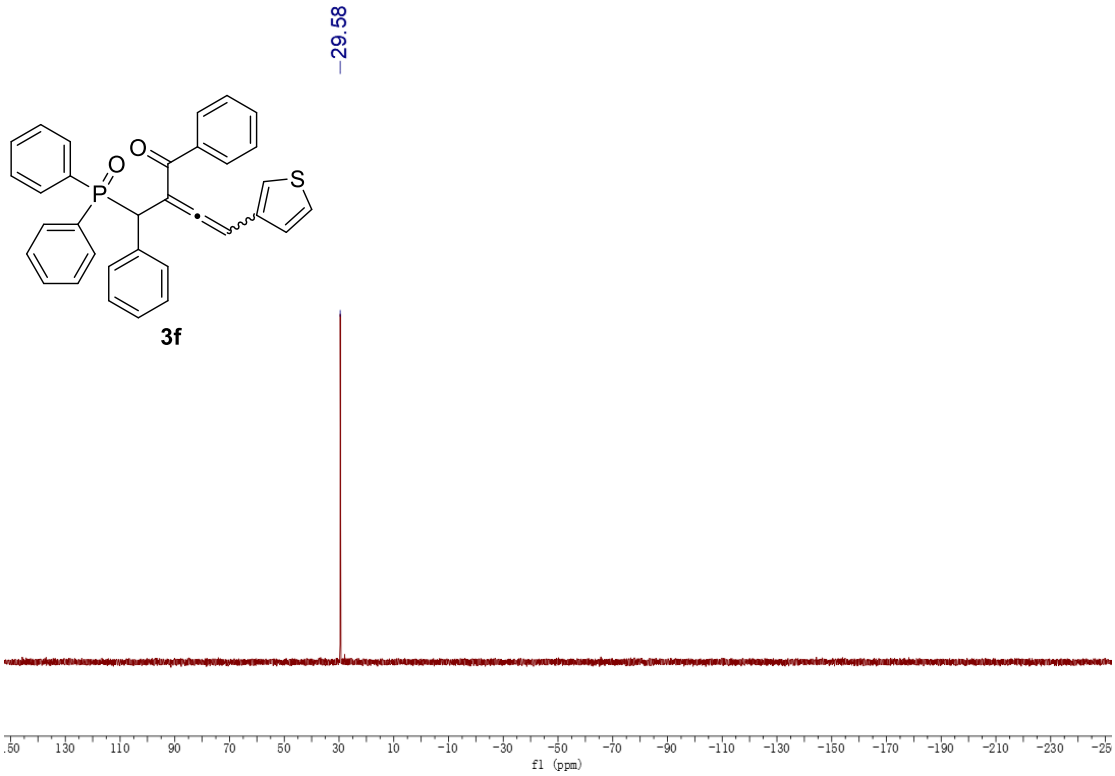


Figure S27. ^{31}P NMR spectrum of compound **3f** (202 MHz, $CDCl_3$).

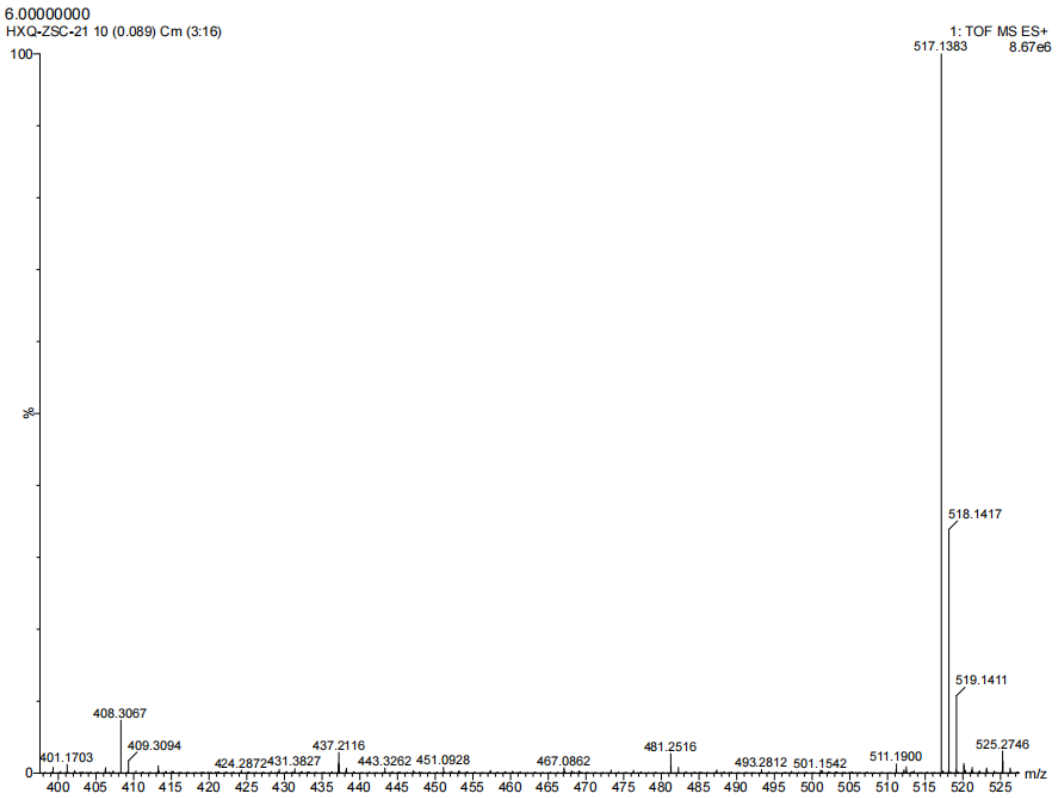
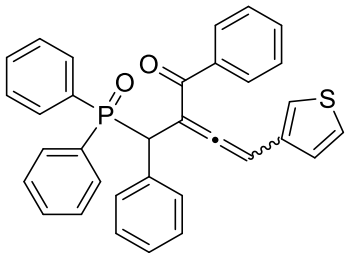


Figure S28. HRMS (ESI) spectrum of compound **3f**.



3f

Chemical Formula: $C_{33}H_{25}O_2PS$
Exact Mass: 516.1313
Molecular Weight: 516.5948
m/z: 516.1313 (100.0%), 517.1346 (35.7%), 518.1380 (6.2%),
518.1271 (4.5%), 519.1304 (1.6%)
Elemental Analysis: C, 76.73; H, 4.88; O, 6.19; P, 6.00; S, 6.21

HRMS (ESI, m/z) calcd for $C_{33}H_{25}O_2PS$ $[M+H]^+$ 517.1386, found 517.1383.

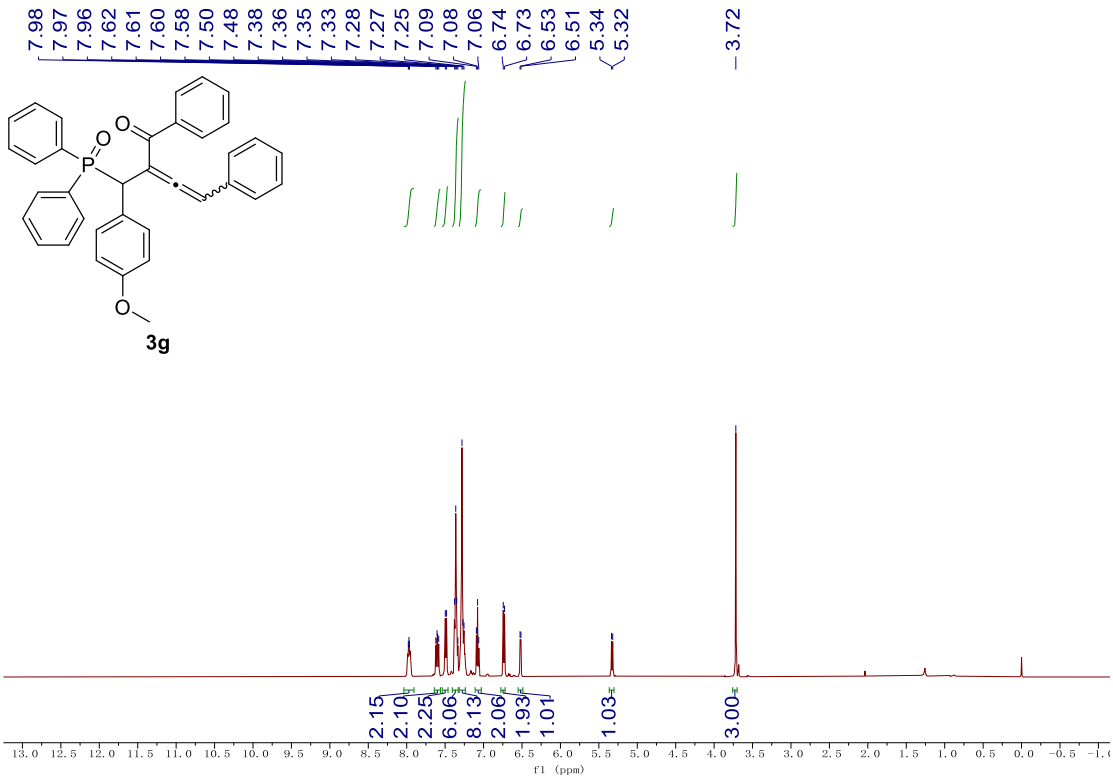


Figure S29. ^{1}H NMR spectrum of compound **3g** (500 MHz, $CDCl_3$).

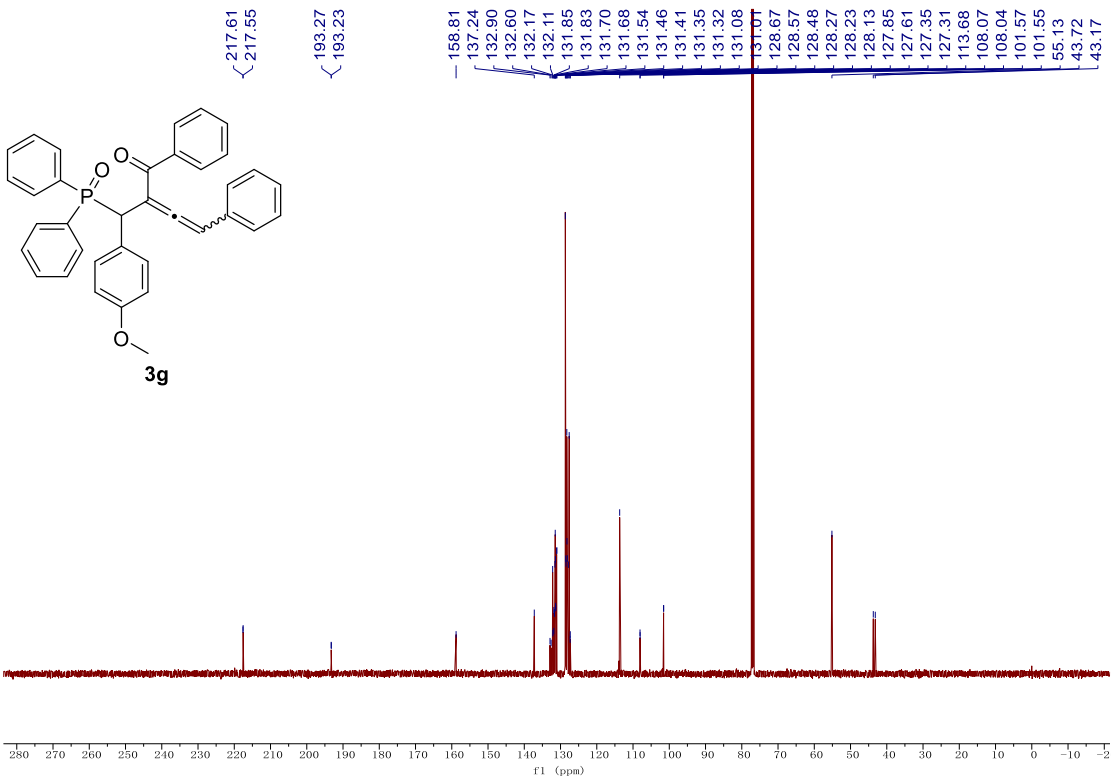


Figure S30. ^{13}C NMR spectrum of compound **3g** (126 MHz, $CDCl_3$).

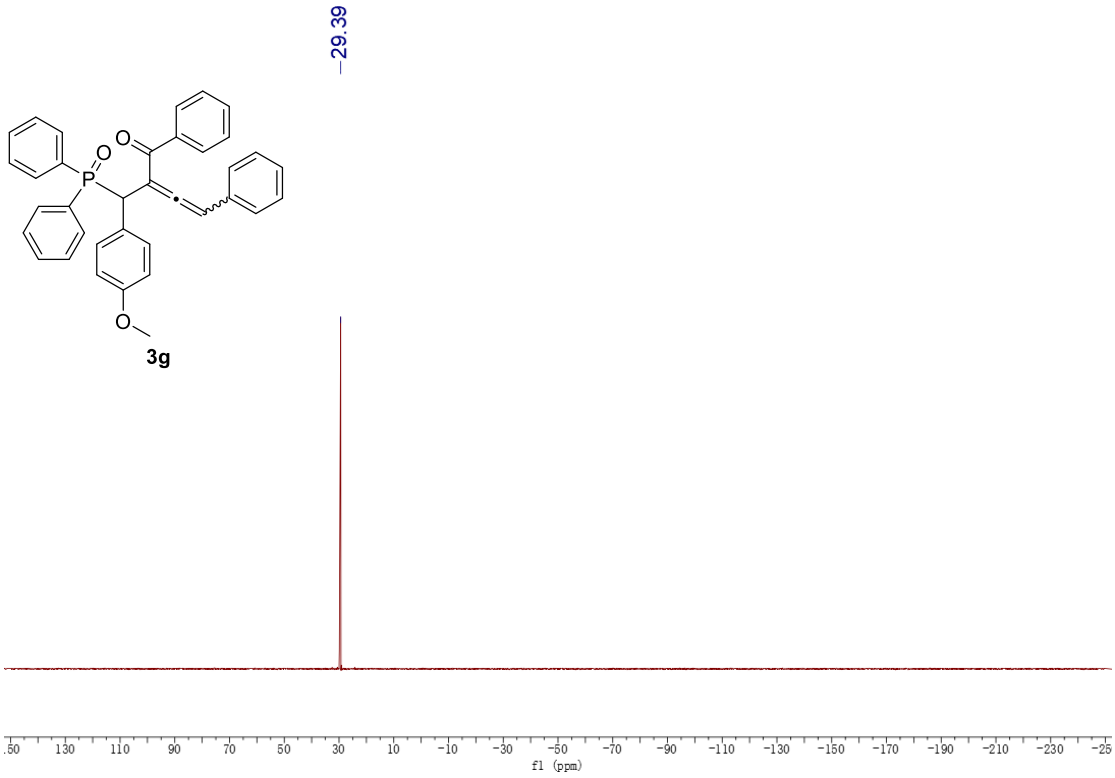


Figure S31. ^{31}P NMR spectrum of compound **3g** (202 MHz, $CDCl_3$).

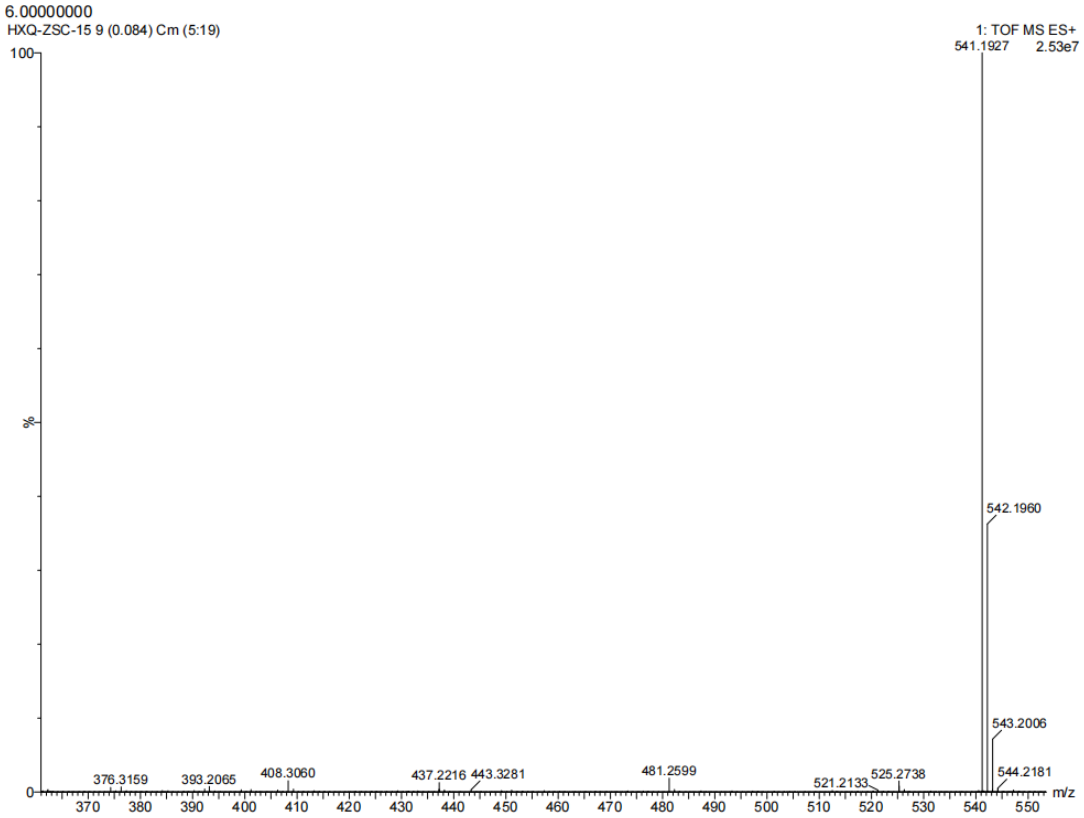
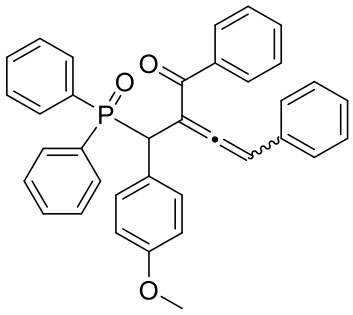


Figure S32. HRMS (ESI) spectrum of compound **3g**.



3g

Chemical Formula: $C_{36}H_{29}O_3P$
Exact Mass: 540.1854
Molecular Weight: 540.5988
m/z: 540.1854 (100.0%), 541.1888 (38.9%), 542.1921 (7.4%)
Elemental Analysis: C, 79.98; H, 5.41; O, 8.88; P, 5.73

HRMS (ESI, m/z) calcd for $C_{36}H_{29}O_3P[M+H]^+$ 541.1927, found 541.1927.

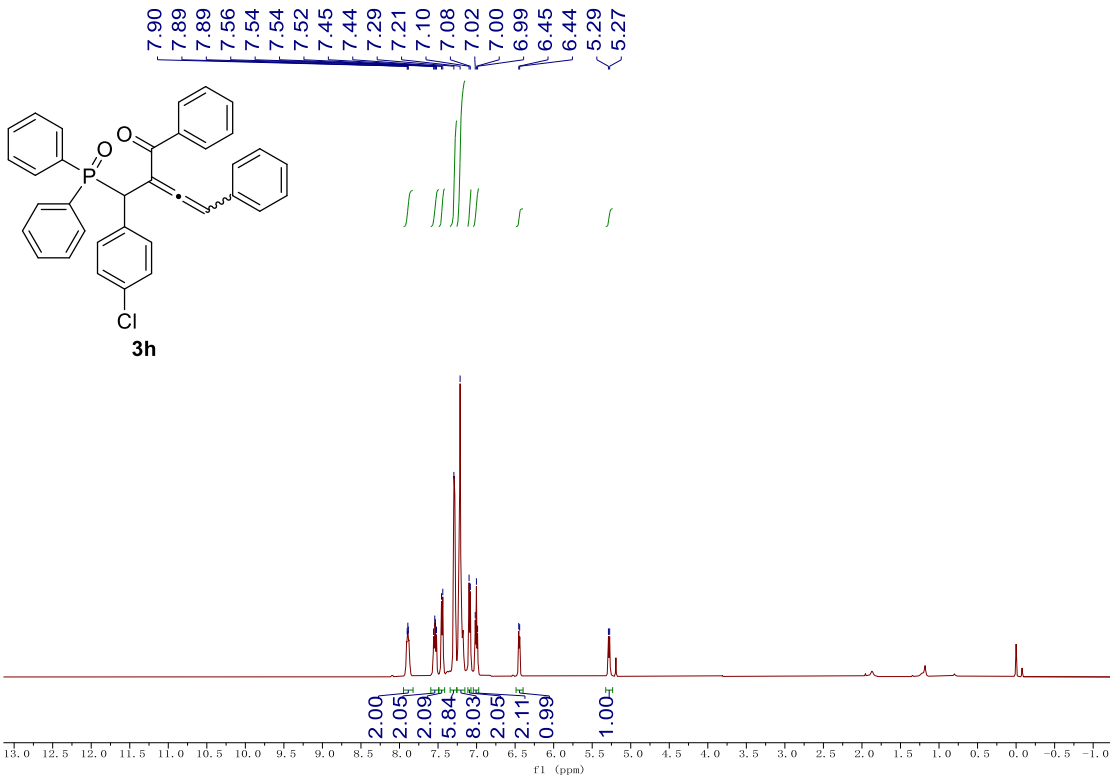


Figure S33. ^{1}H NMR spectrum of compound **3h** (500 MHz, $CDCl_3$).

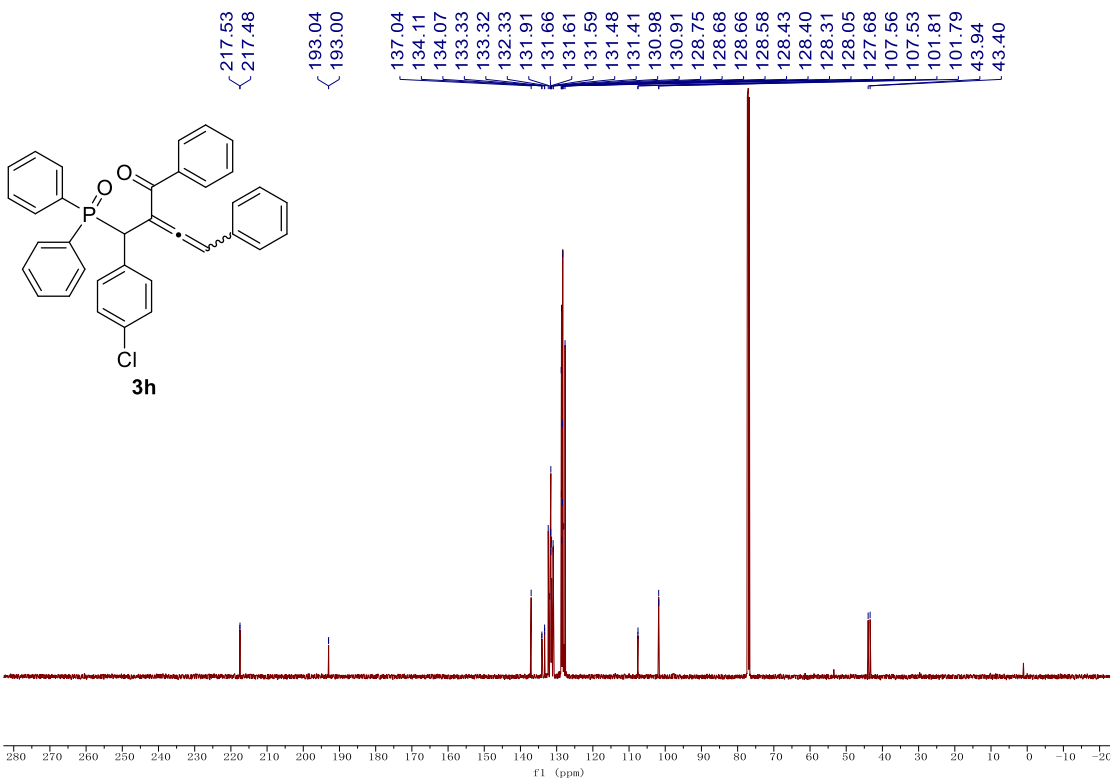


Figure S34. ^{13}C NMR spectrum of compound **3h** (126 MHz, $CDCl_3$).

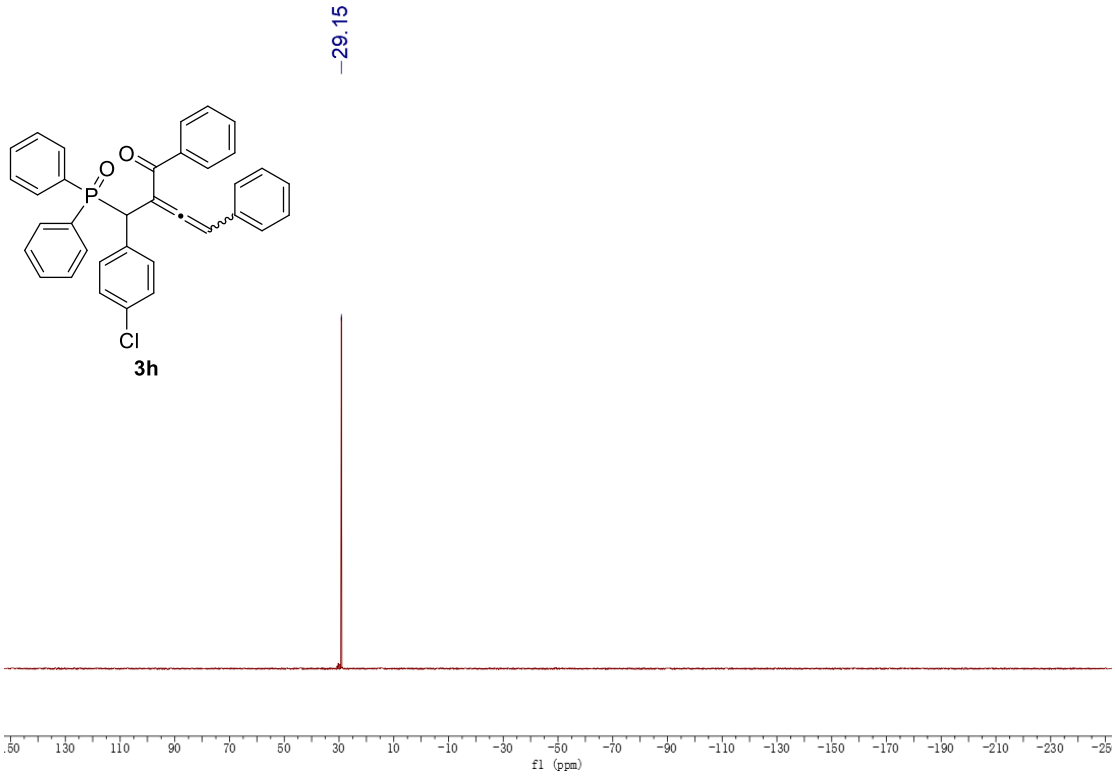


Figure S35. ^{31}P NMR spectrum of compound **3h** (202 MHz, $CDCl_3$).

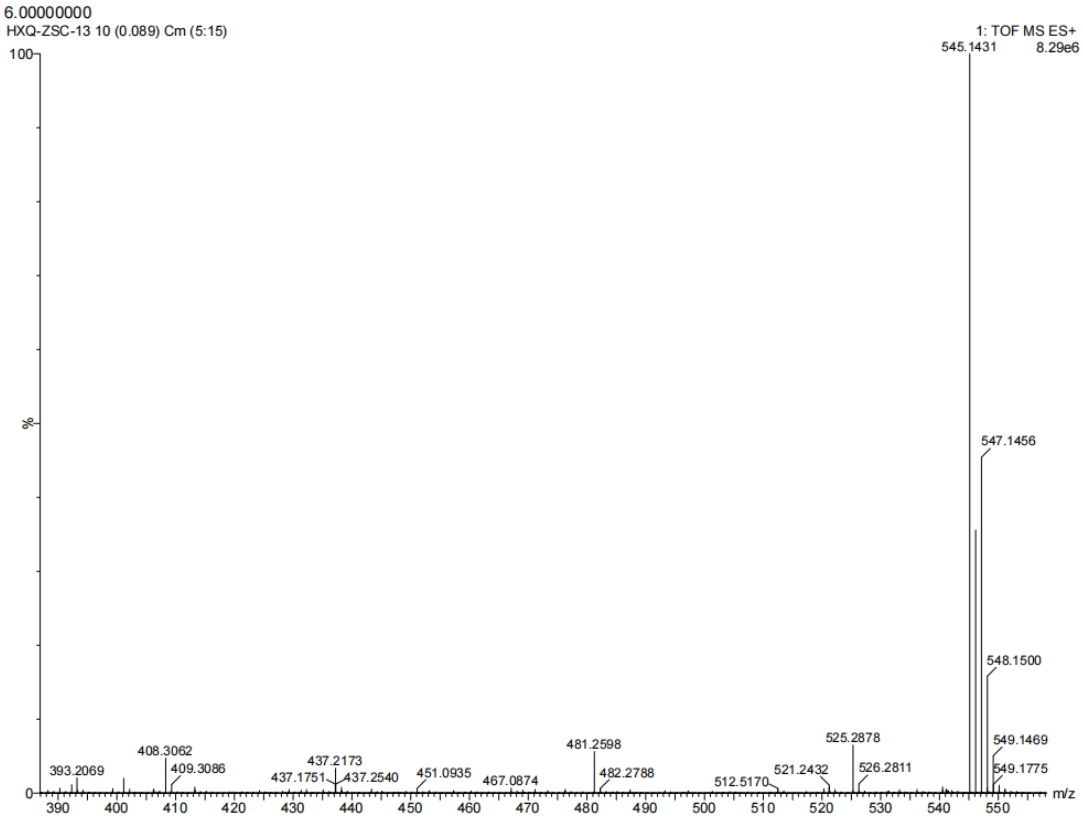
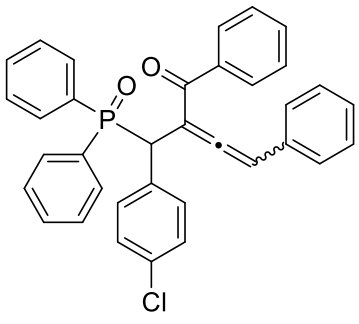


Figure S36. HRMS (ESI) spectrum of compound **3h**.



3h

Chemical Formula: $C_{35}H_{26}ClO_2P$
Exact Mass: 544.1359
Molecular Weight: 545.0148
m/z: 544.1359 (100.0%), 545.1392 (37.9%), 546.1329 (32.0%), 547.1363 (12.1%), 546.1426 (7.0%), 548.1397 (2.2%)
Elemental Analysis: C, 77.13; H, 4.81; Cl, 6.50; O, 5.87; P, 5.68

HRMS (ESI, m/z) calcd for $C_{35}H_{26}ClO_2P[M+H]^+$ 545.1432, found 545.1431.

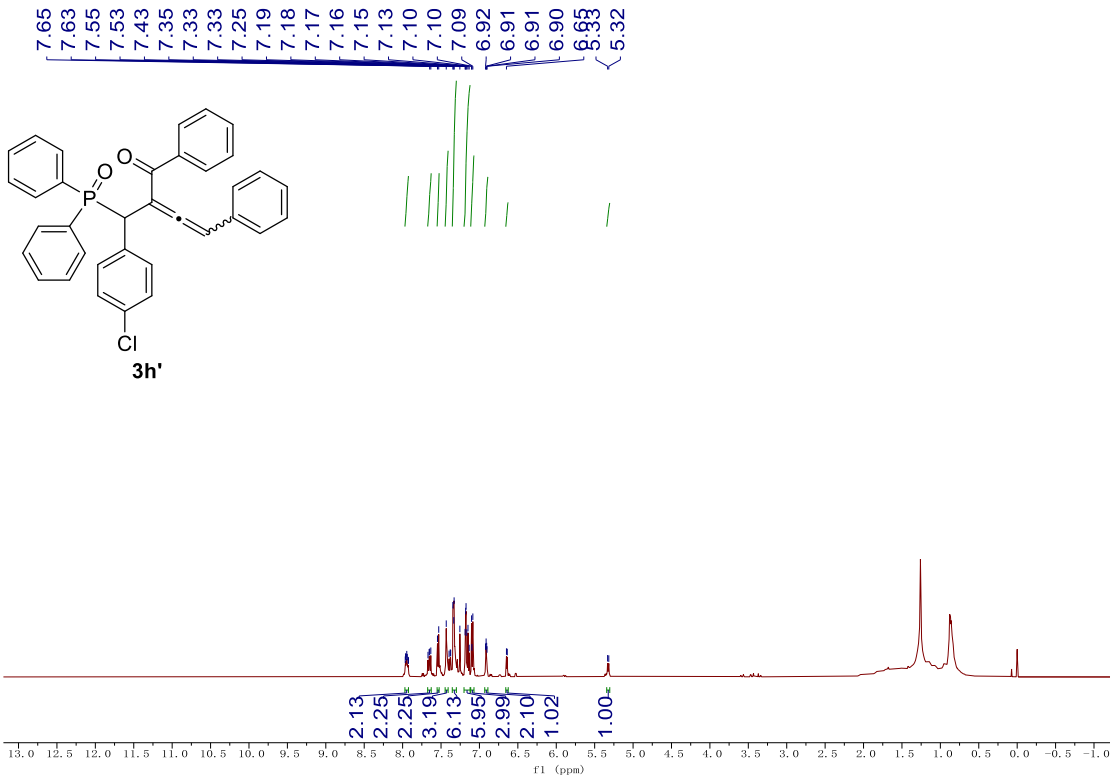


Figure S37. ^{1}H NMR spectrum of compound **3h'** (500 MHz, $CDCl_3$).

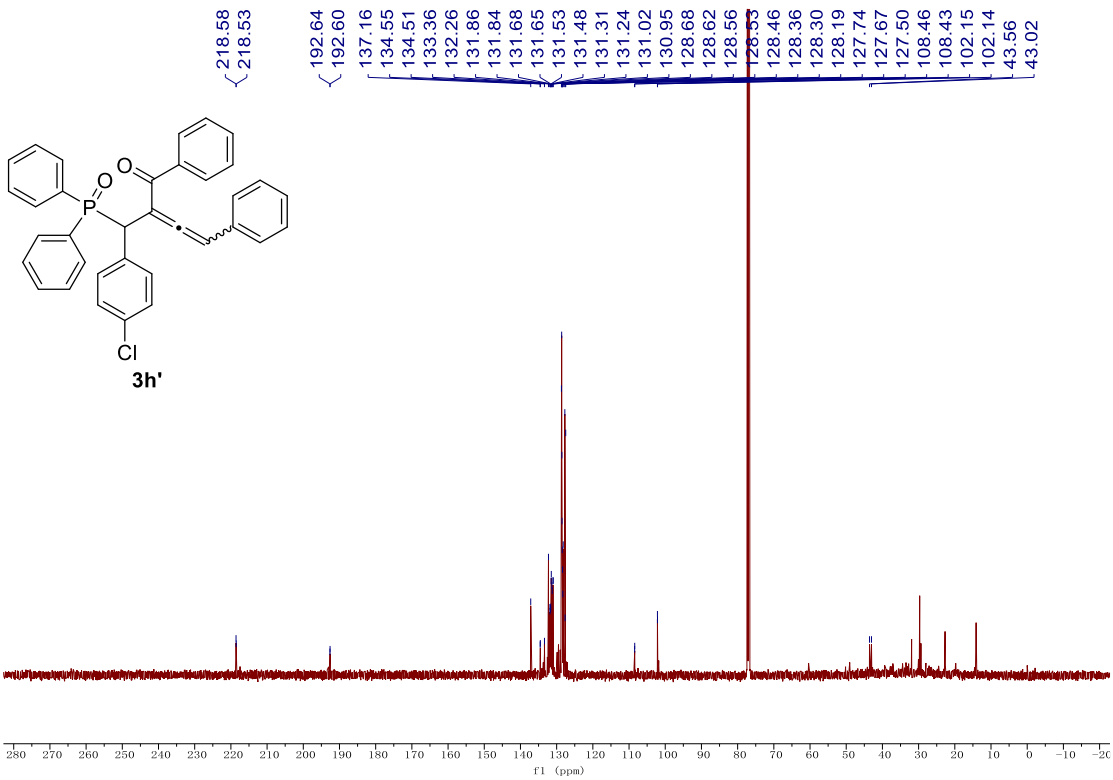


Figure S38. ^{13}C NMR spectrum of compound **3h'** (126 MHz, $CDCl_3$).

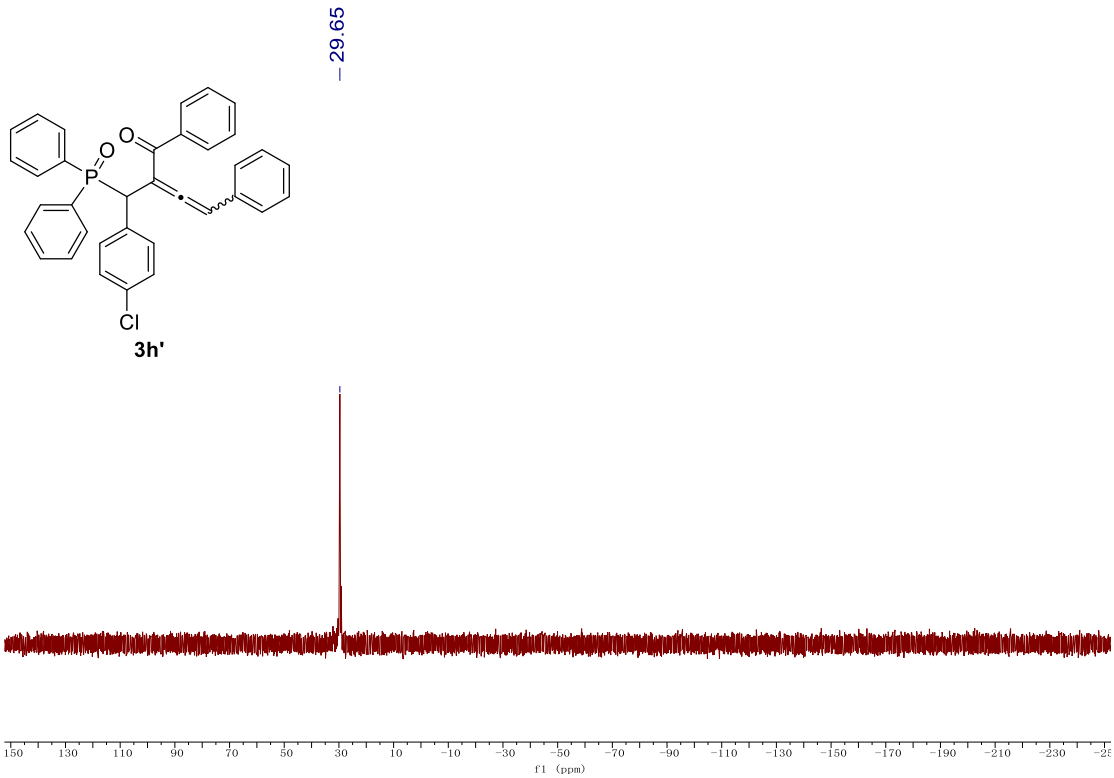


Figure S39. ^{31}P NMR spectrum of compound **3h'** (202 MHz, $CDCl_3$).

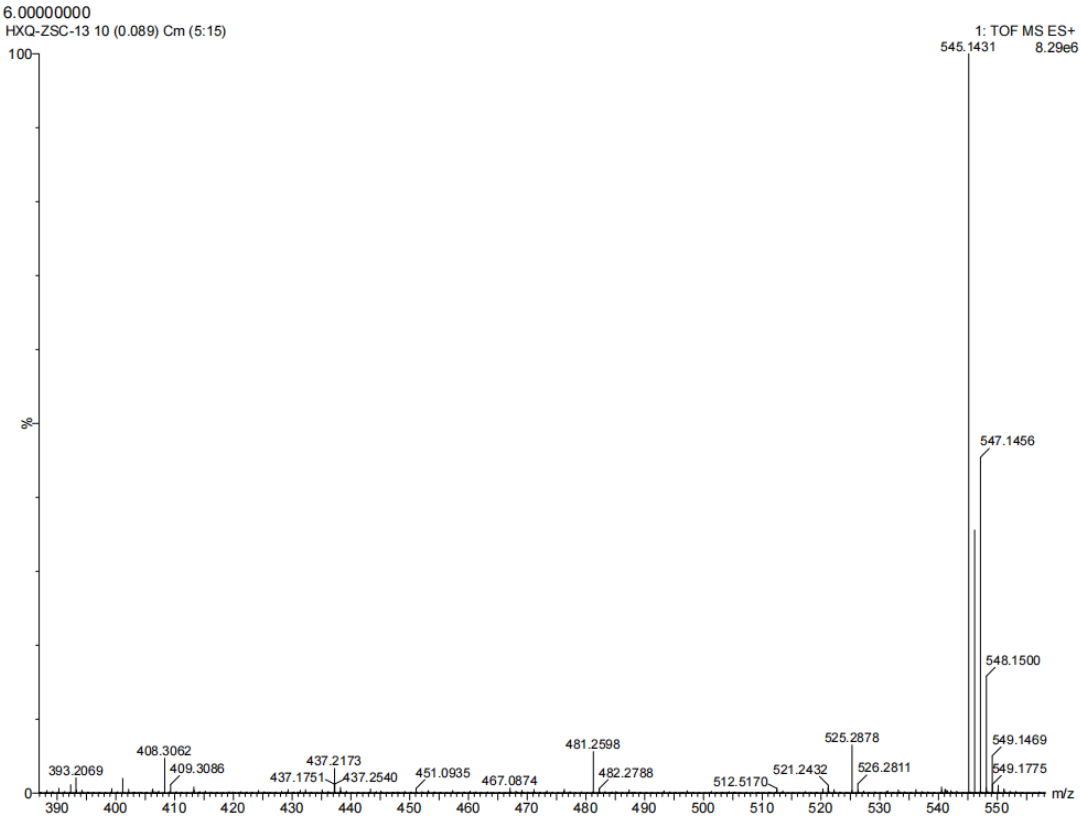
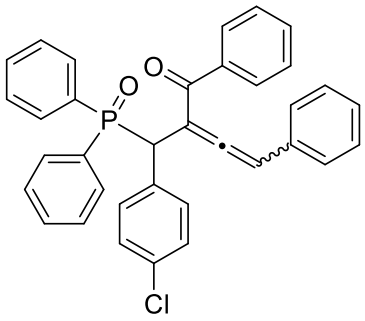


Figure S40. HRMS (ESI) spectrum of compound **3h'**.



3h'

Chemical Formula: $C_{35}H_{26}ClO_2P$
Exact Mass: 544.1359
Molecular Weight: 545.0148
m/z: 544.1359 (100.0%), 545.1392 (37.9%), 546.1329 (32.0%), 547.1363 (12.1%), 546.1426 (7.0%), 548.1397 (2.2%)
Elemental Analysis: C, 77.13; H, 4.81; Cl, 6.50; O, 5.87; P, 5.68

HRMS (ESI, m/z) calcd for $C_{35}H_{26}ClO_2P[M+H]+$ 545.1432, found 545.1431.

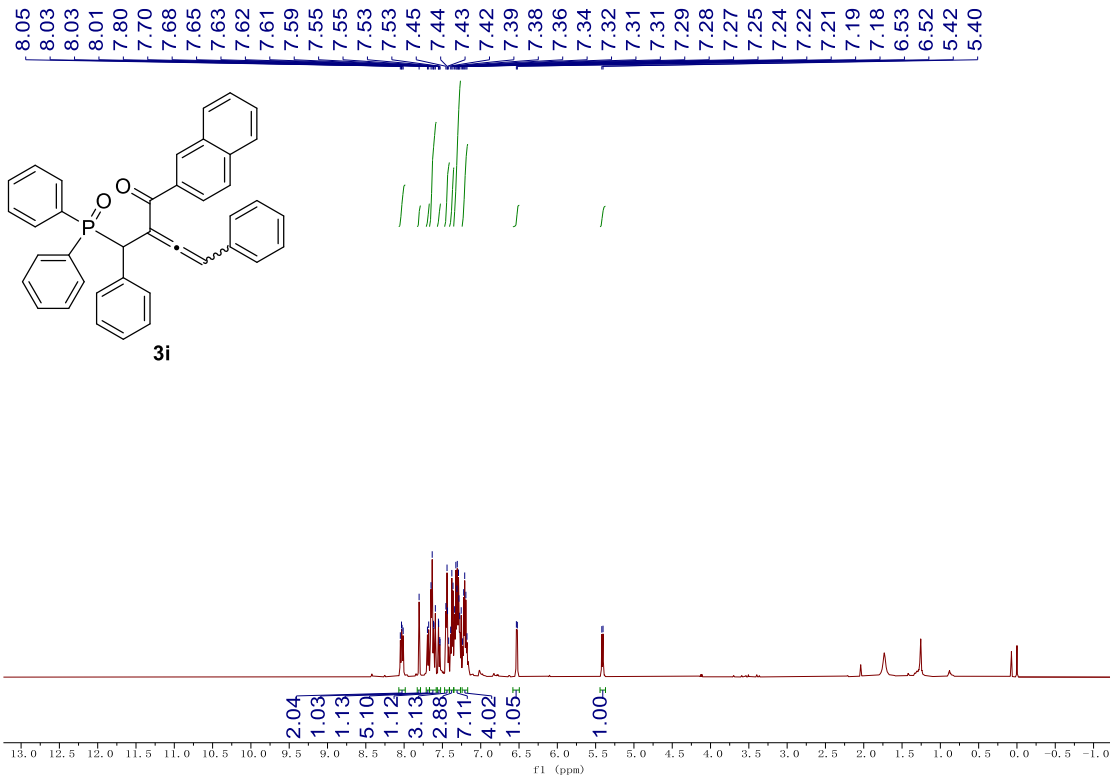


Figure S41. ^{1}H NMR spectrum of compound **3i** (500 MHz, $CDCl_3$).

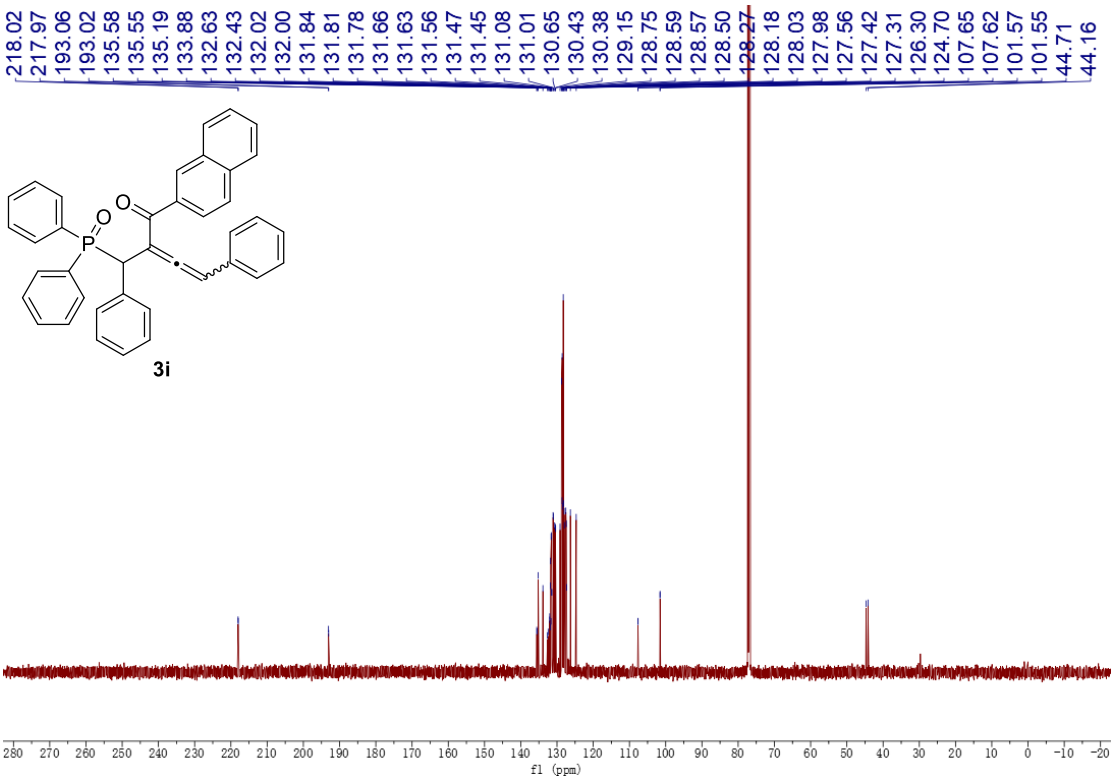


Figure S42. ^{13}C NMR spectrum of compound **3i** (126 MHz, $CDCl_3$).

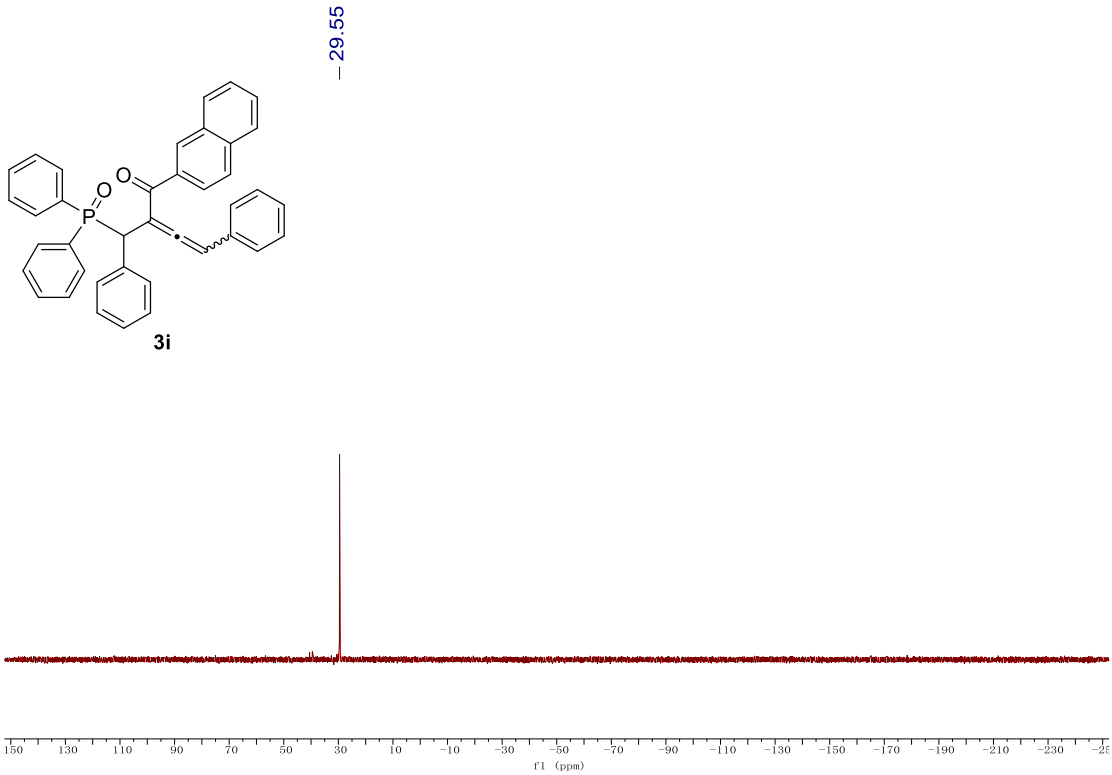


Figure S43. ^{31}P NMR spectrum of compound **3i** (202 MHz, $CDCl_3$).

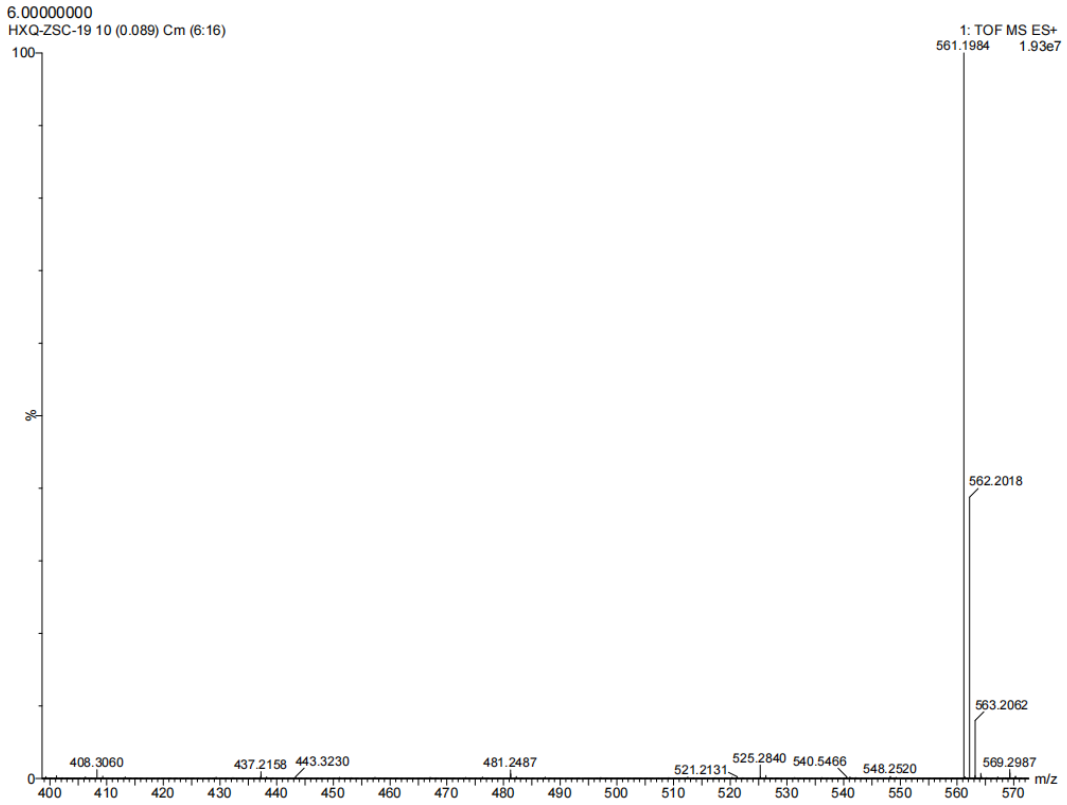
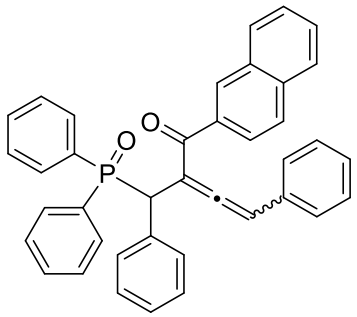


Figure S44. HRMS (ESI) spectrum of compound **3i**.



3i

Chemical Formula: $C_{39}H_{29}O_2P$
Exact Mass: 560.1905
Molecular Weight: 560.6328
m/z: 560.1905 (100.0%), 561.1939 (42.2%), 562.1972 (6.0%), 562.1972 (2.7%)
Elemental Analysis: C, 83.55; H, 5.21; O, 5.71; P, 5.52

HRMS (ESI, m/z) calcd for $C_{39}H_{29}O_2P[M+H]^+$ 561.1978, found 561.1984.

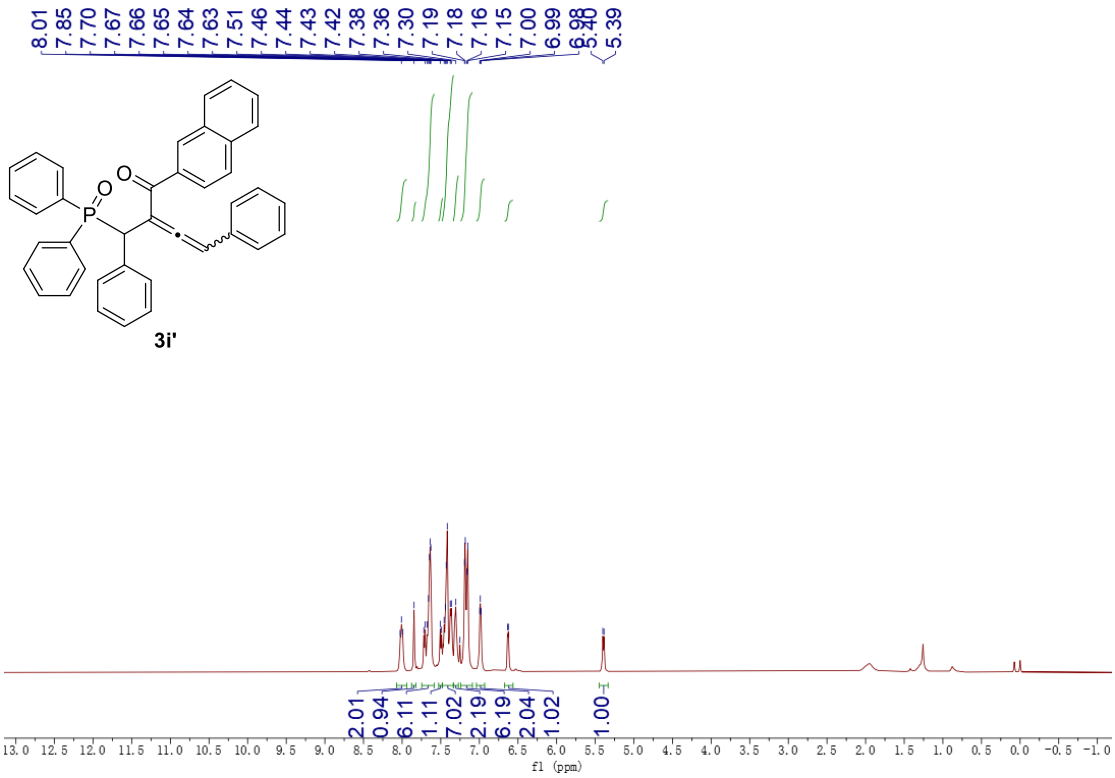


Figure S45. ^{1}H NMR spectrum of compound **3i'** (500 MHz, $CDCl_3$).

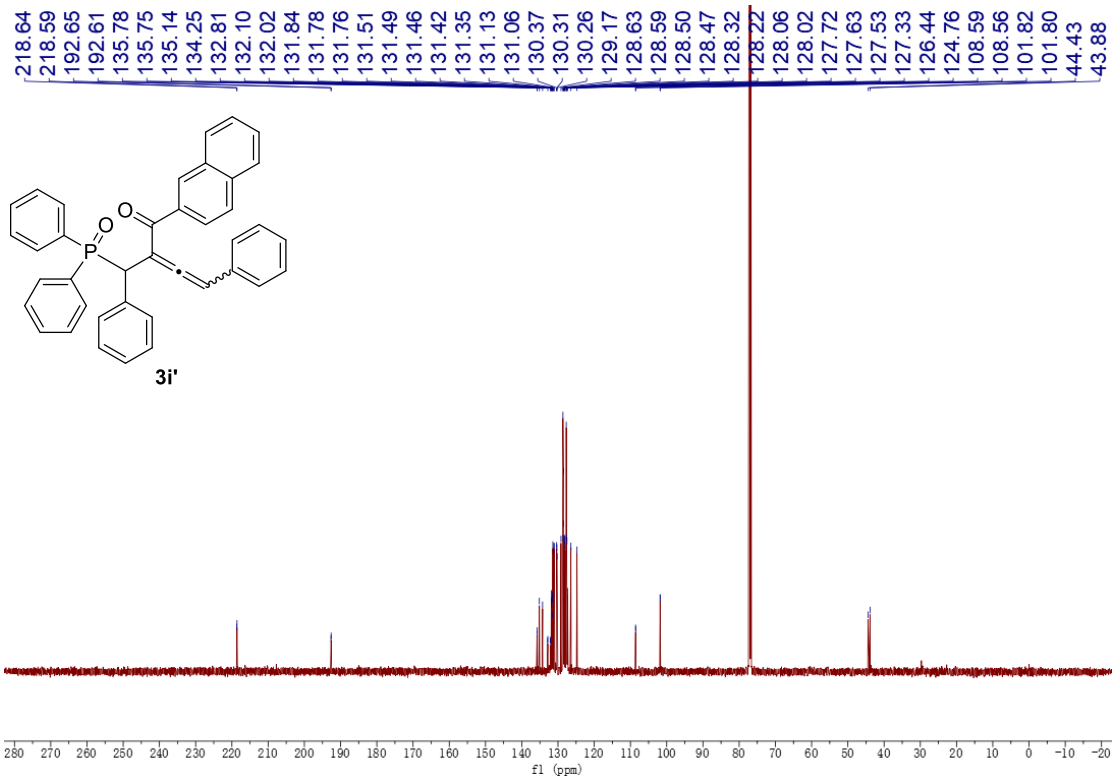


Figure S46. ^{13}C NMR spectrum of compound **3i'** (126 MHz, $CDCl_3$).

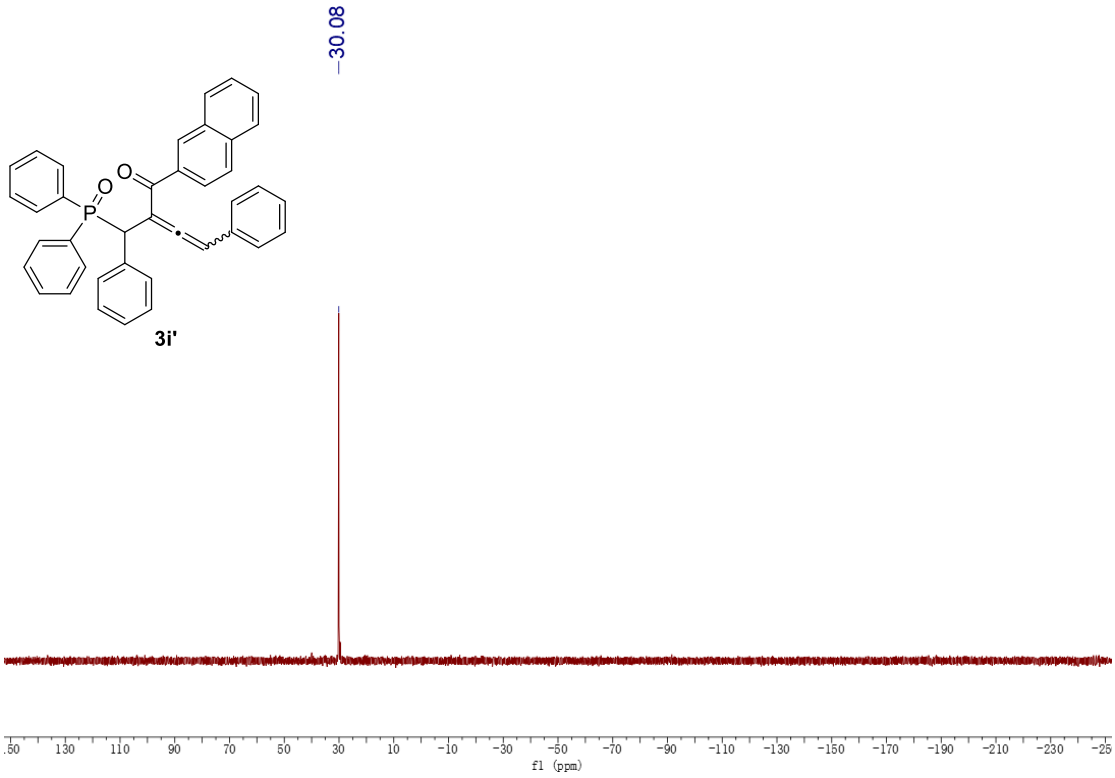


Figure S47. ^{31}P NMR spectrum of compound **3i'** (202 MHz, $CDCl_3$).

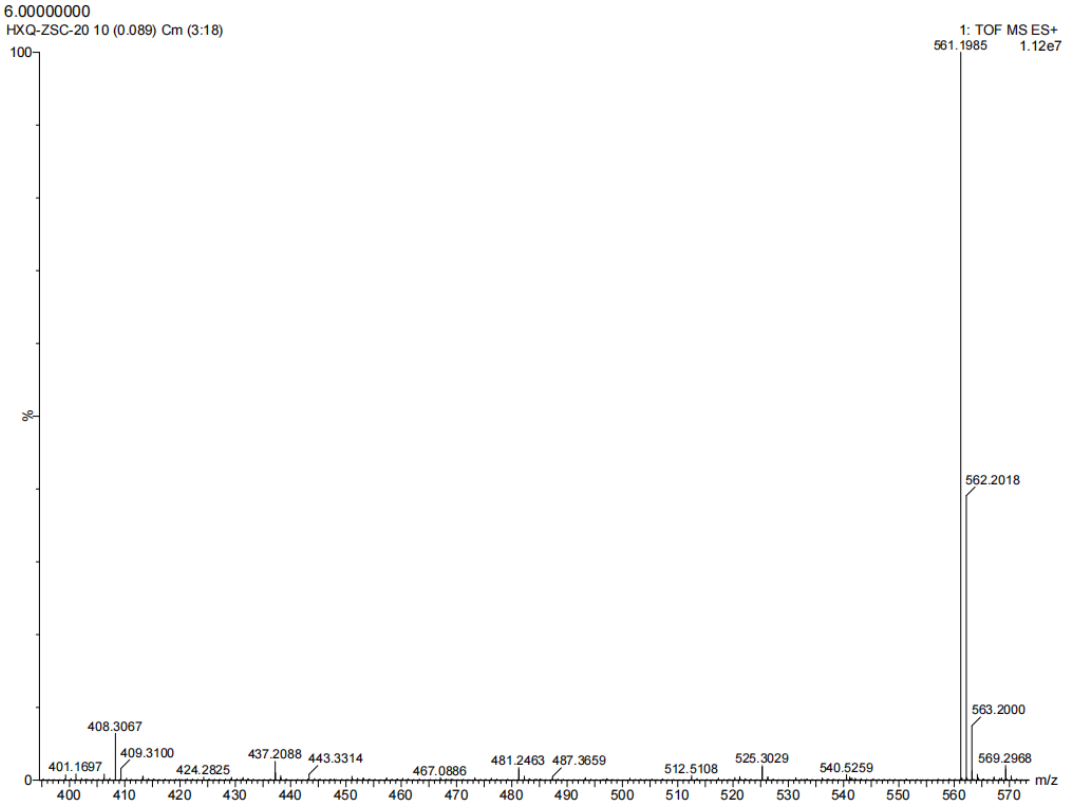
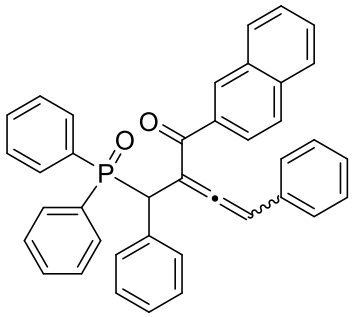


Figure S48. HRMS (ESI) spectrum of compound **3i'**.



3i'

Chemical Formula: $C_{39}H_{29}O_2P$
Exact Mass: 560.1905
Molecular Weight: 560.6328
m/z: 560.1905 (100.0%), 561.1939 (42.2%), 562.1972 (6.0%), 562.1972 (2.7%)
Elemental Analysis: C, 83.55; H, 5.21; O, 5.71; P, 5.52

HRMS (ESI, m/z) calcd for $C_{39}H_{29}O_2P[M+H]^+$ 561.1978, found 561.1985.

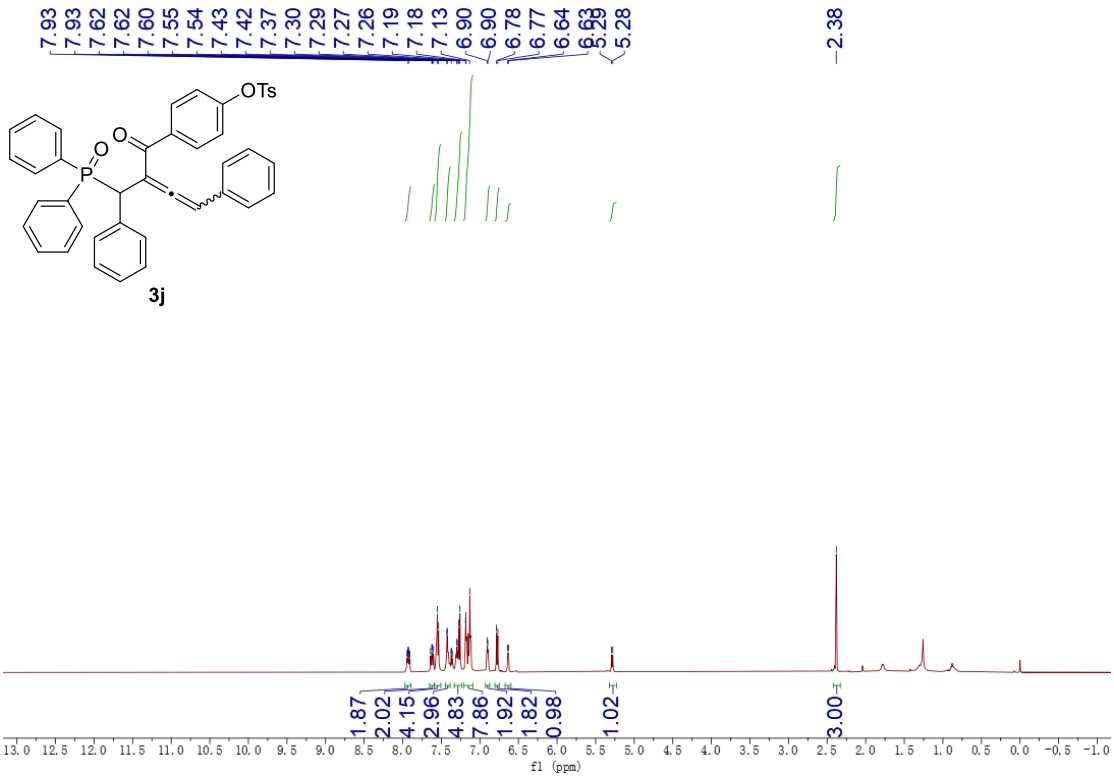


Figure S49. ^{1}H NMR spectrum of compound **3j** (500 MHz, $CDCl_3$).

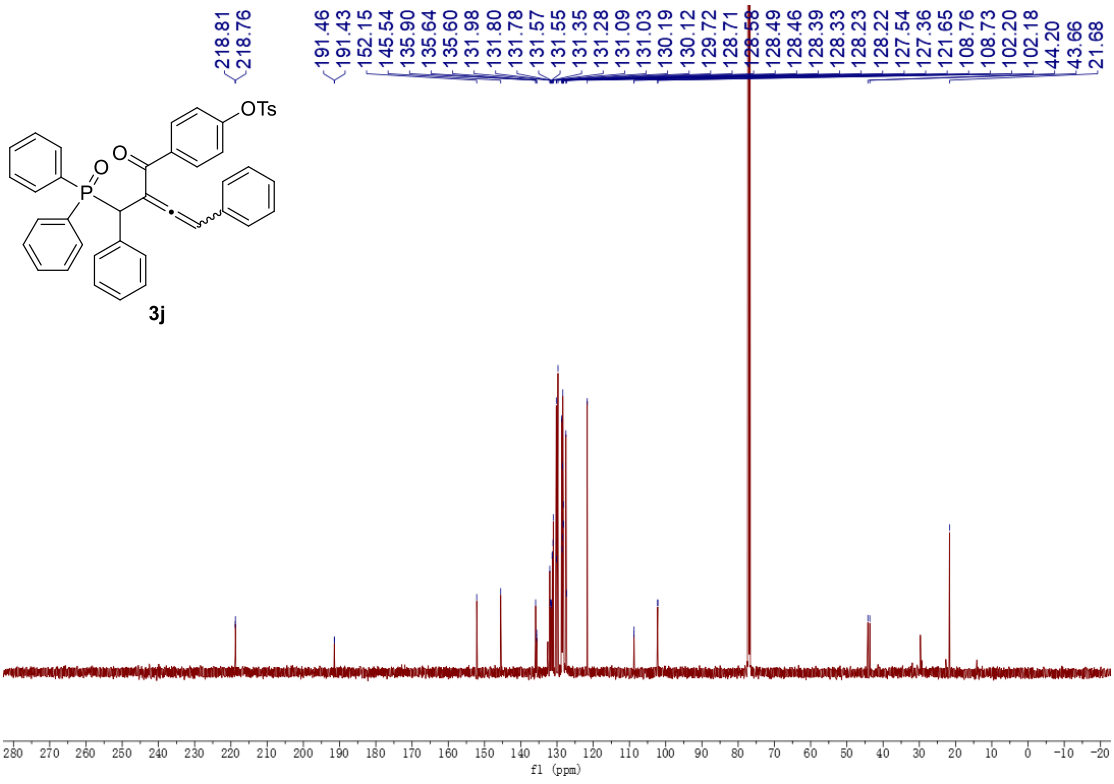


Figure S50. ^{13}C NMR spectrum of compound **3j** (126 MHz, $CDCl_3$).

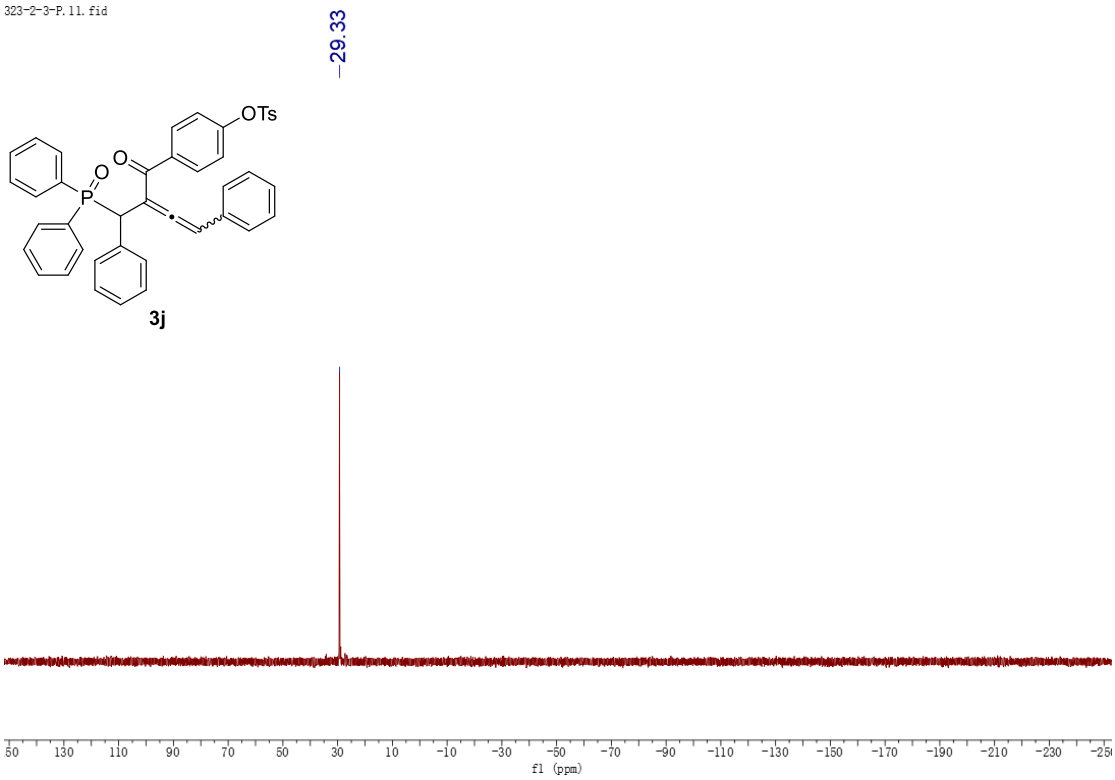


Figure S51. ^{31}P NMR spectrum of compound **3j** (202 MHz, $CDCl_3$).

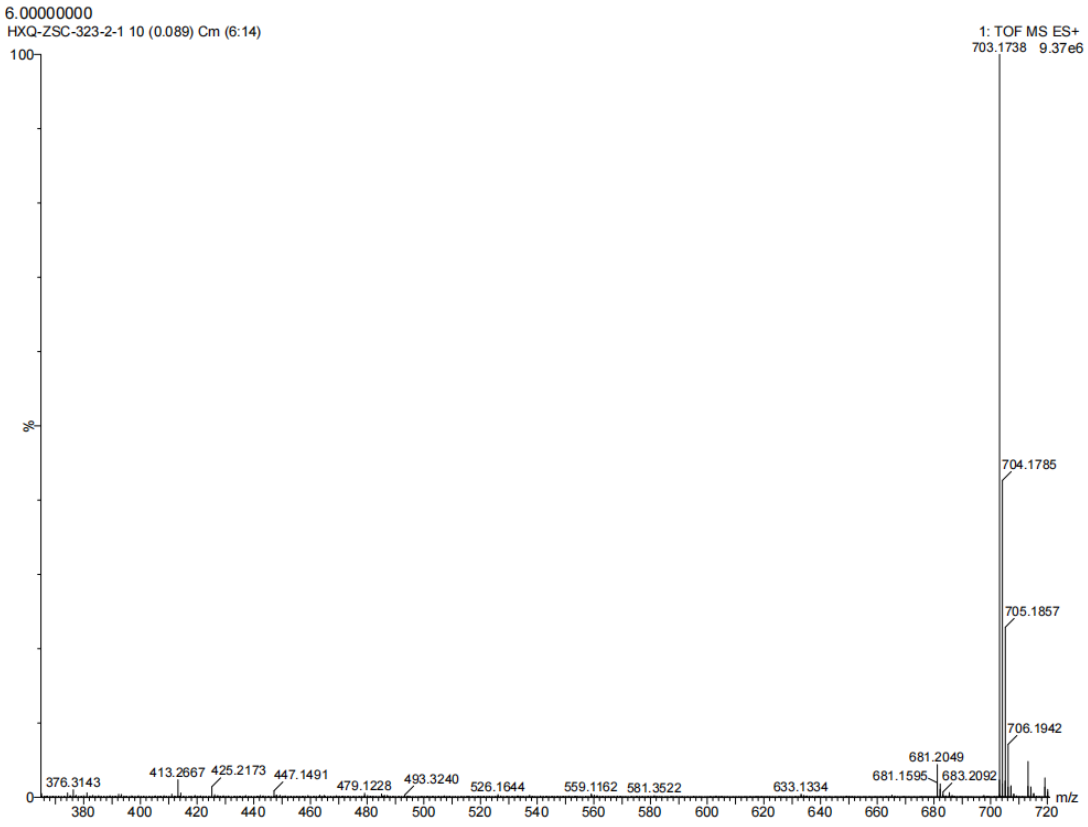
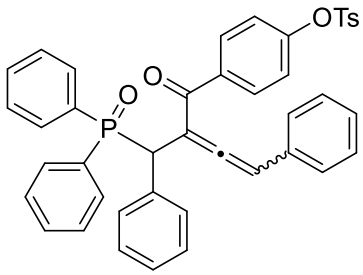


Figure S52. HRMS (ESI) spectrum of compound **3j**.



3j

Chemical Formula: $C_{42}H_{33}O_5PS$
Exact Mass: 680.1786
Molecular Weight: 680.7548
m/z: 680.1786 (100.0%), 681.1820 (45.4%), 682.1853 (10.1%), 682.1744 (4.5%), 683.1778 (2.1%), 683.1887 (1.5%), 682.1829 (1.0%)
Elemental Analysis: C, 74.10; H, 4.89; O, 11.75; P, 4.55; S, 4.71

HRMS (ESI, m/z) calcd for $C_{42}H_{33}O_5PS[M+Na]^+$ 703.1679, found 703.1738.

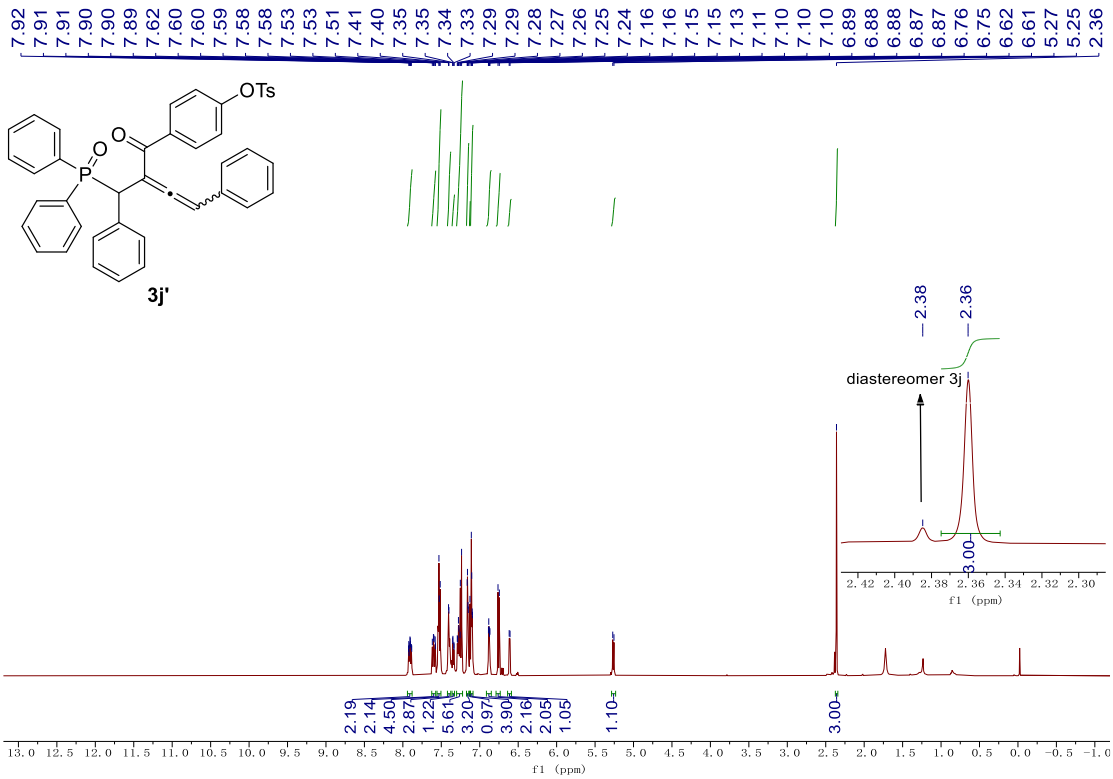


Figure S53. ^{1}H NMR spectrum of compound **3j'** (500 MHz, $CDCl_3$).

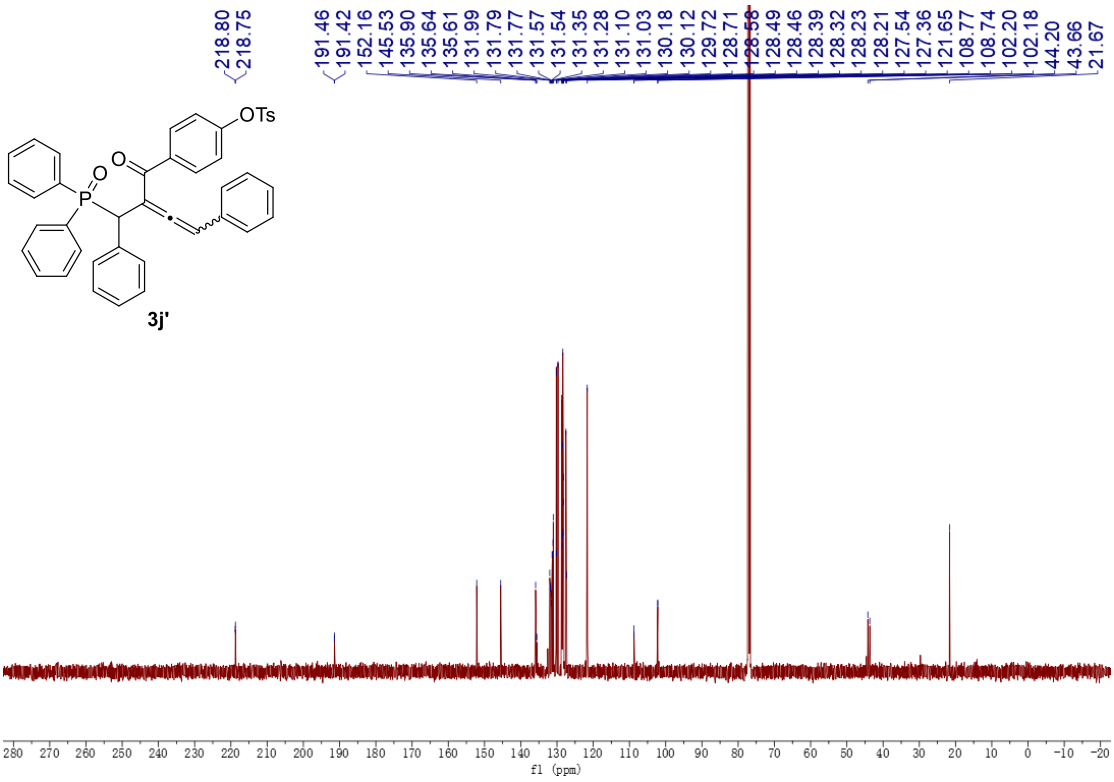


Figure S54. ^{13}C NMR spectrum of compound **3j'** (126 MHz, $CDCl_3$).

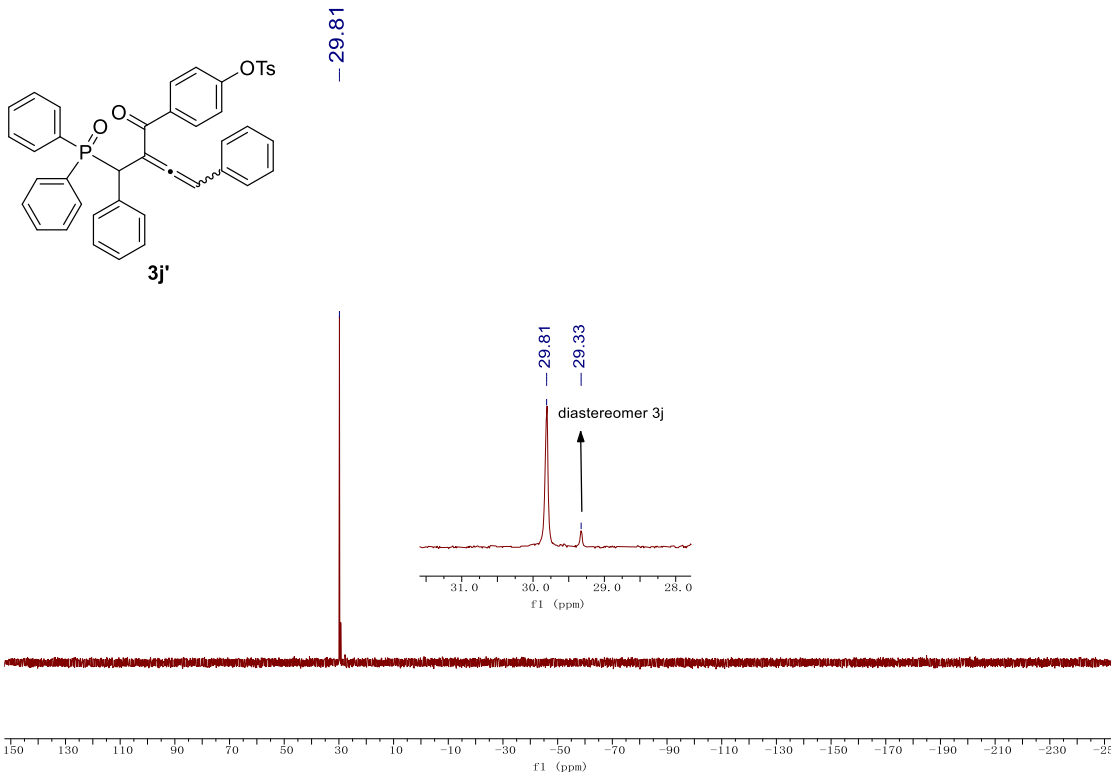


Figure S55. ^{31}P NMR spectrum of compound **3j'** (202 MHz, $CDCl_3$).

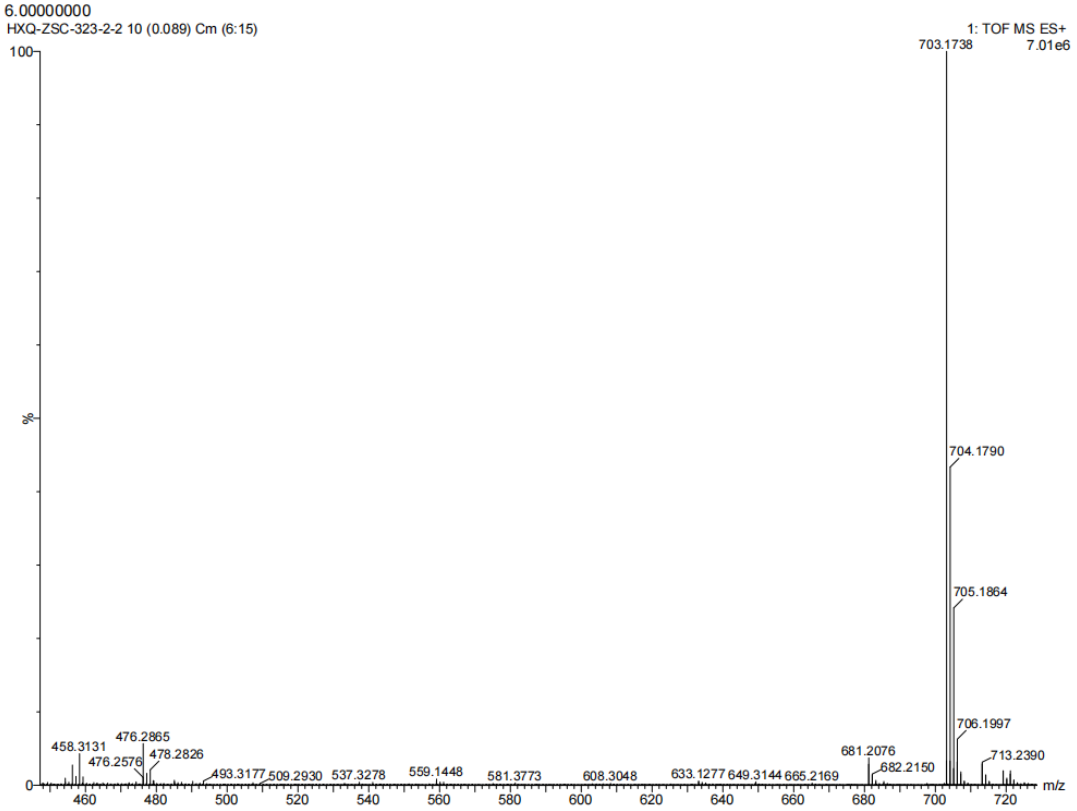
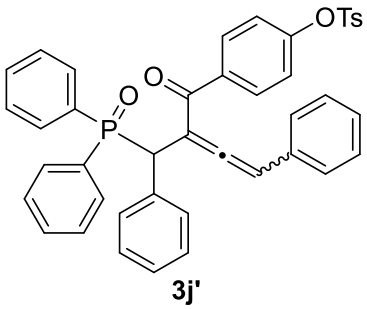


Figure S56. HRMS (ESI) spectrum of compound **3j'**.



3j'

Chemical Formula: $C_{42}H_{33}O_5PS$
Exact Mass: 680.1786
Molecular Weight: 680.7548
m/z: 680.1786 (100.0%), 681.1820 (45.4%), 682.1853 (10.1%), 682.1744 (4.5%), 683.1778 (2.1%), 683.1887 (1.5%), 682.1829 (1.0%)
Elemental Analysis: C, 74.10; H, 4.89; O, 11.75; P, 4.55; S, 4.71

HRMS (ESI, m/z) calcd for $C_{42}H_{33}O_5PS[M+Na]^+$ 703.1679, found 703.1738.

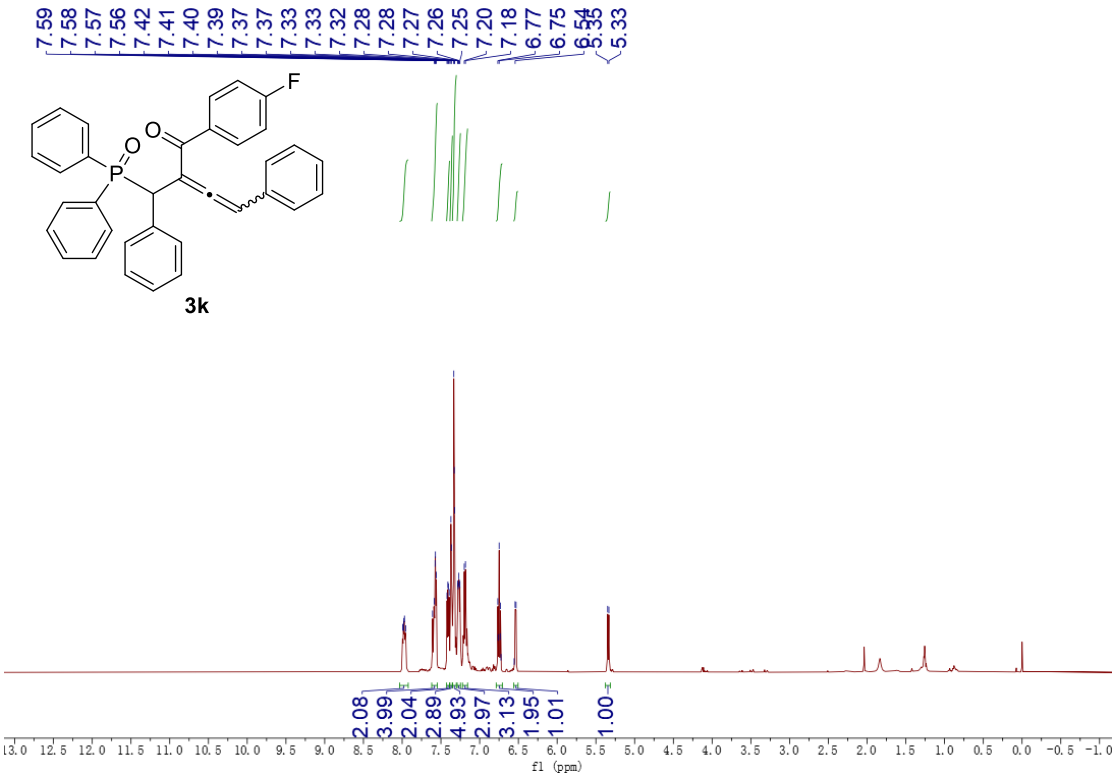


Figure S57. ^{1}H NMR spectrum of compound **3k** (500 MHz, $CDCl_3$).

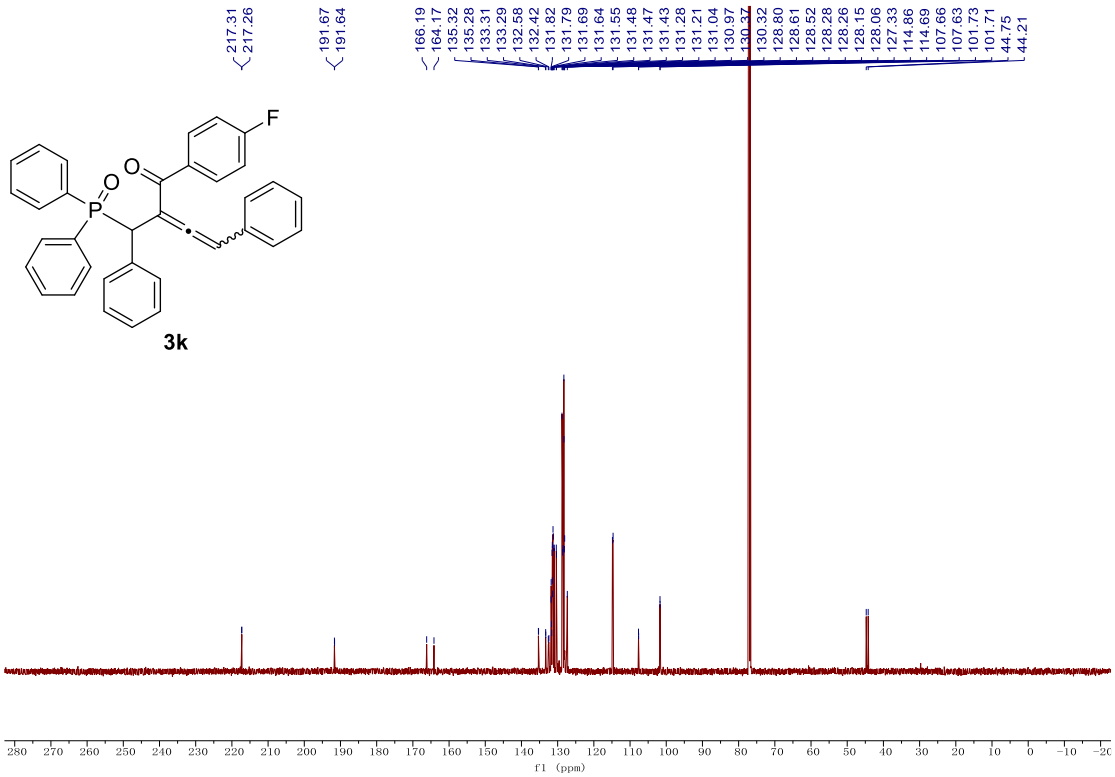


Figure S58. ^{13}C NMR spectrum of compound **3k** (126 MHz, $CDCl_3$).

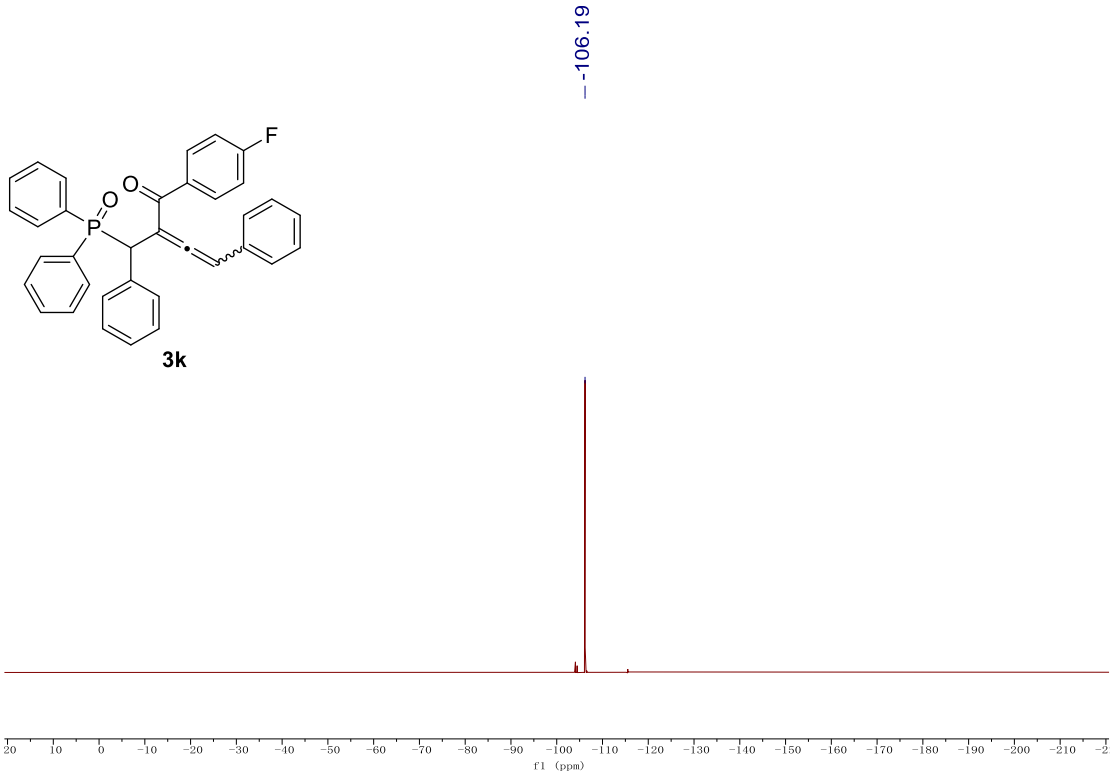


Figure S59. ^{31}P NMR spectrum of compound **3k** (202 MHz, $CDCl_3$).

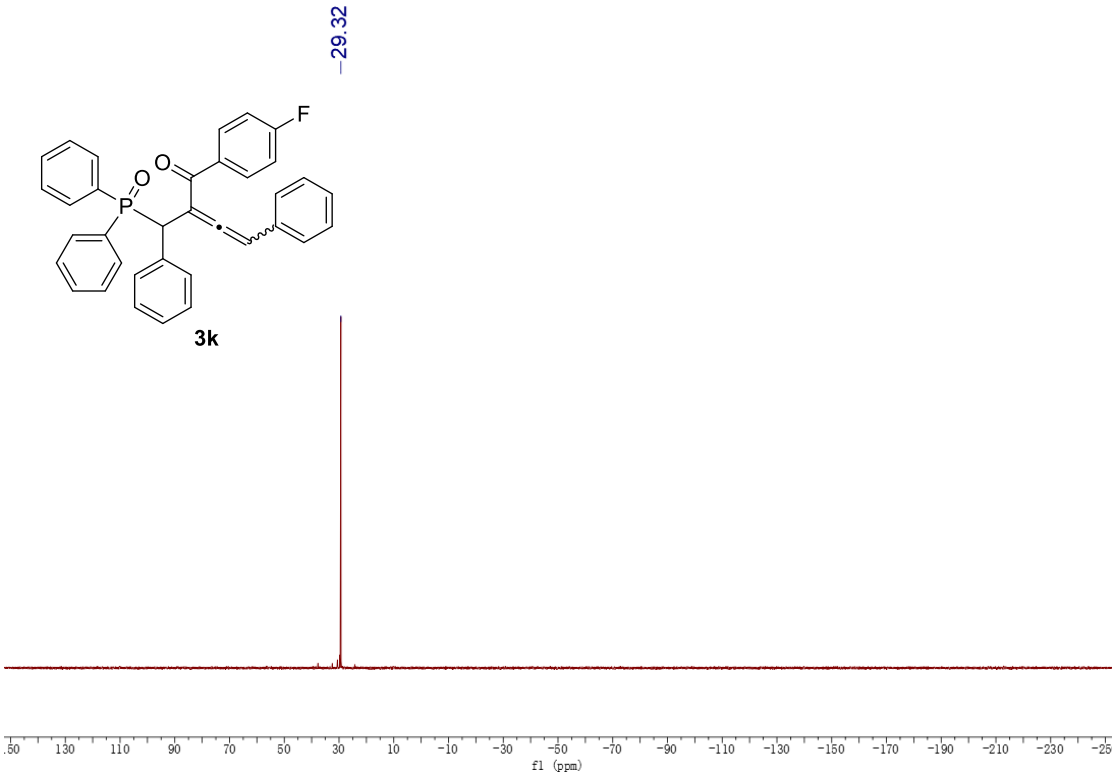


Figure S60. ^{19}F NMR spectrum of compound **3k** (470 MHz, $CDCl_3$).

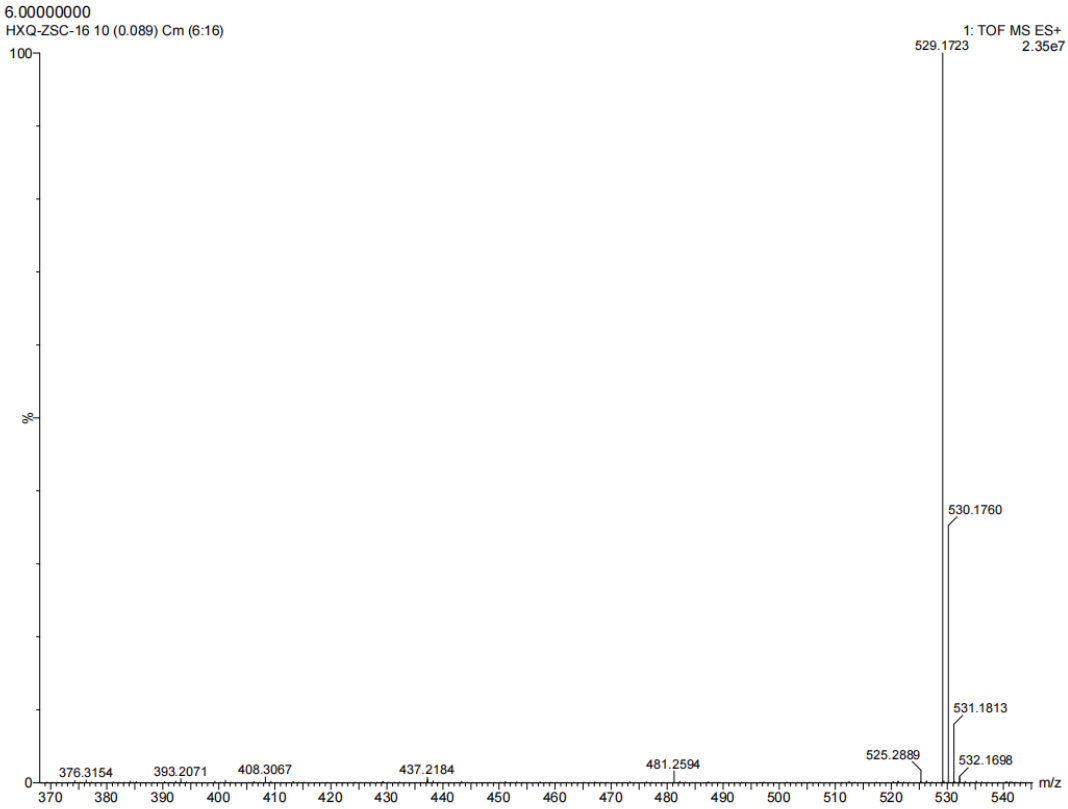
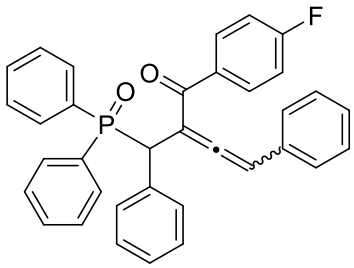


Figure S61. HRMS (ESI) spectrum of compound **3k**.



3k

Chemical Formula: $C_{35}H_{26}FO_2P$
Exact Mass: 528.1654
Molecular Weight: 528.5632
m/z: 528.1654 (100.0%), 529.1688 (37.9%), 530.1722 (7.0%)
Elemental Analysis: C, 79.53; H, 4.96; F, 3.59; O, 6.05; P, 5.86

HRMS (ESI, m/z) calcd for $C_{35}H_{26}FO_2P[M+H]^+$ 529.1727, found 529.1723.

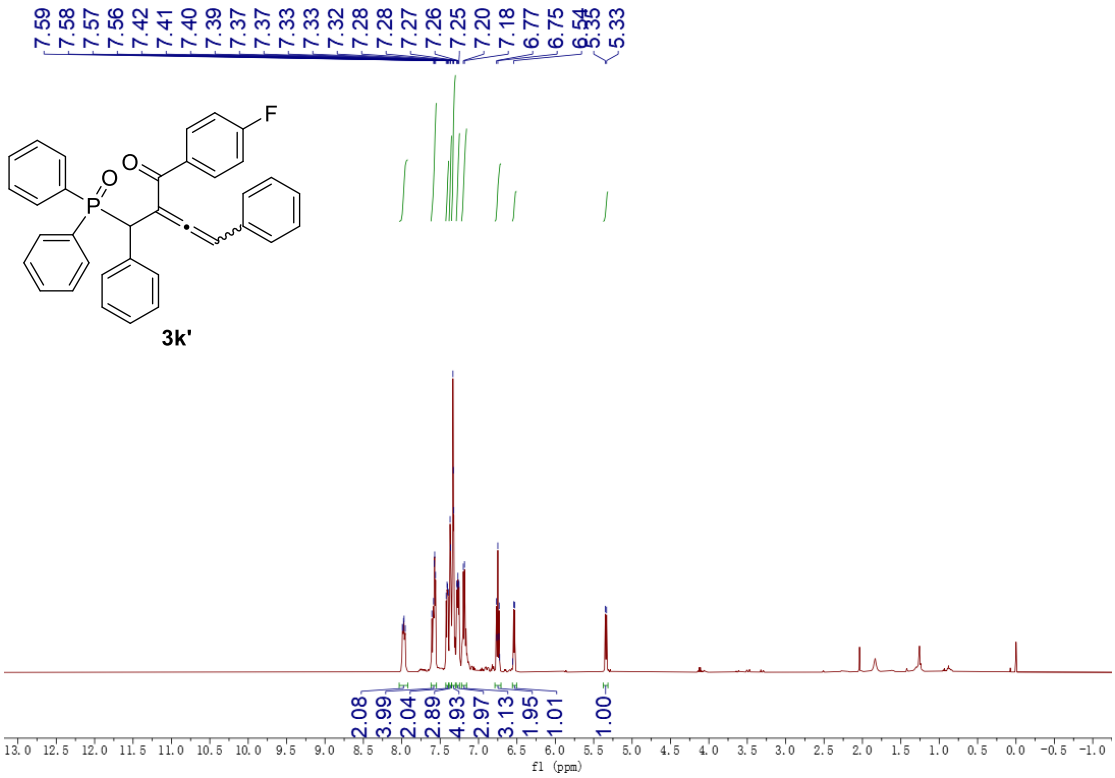


Figure S62. ^{1}H NMR spectrum of compound **3k'** (500 MHz, $CDCl_3$).

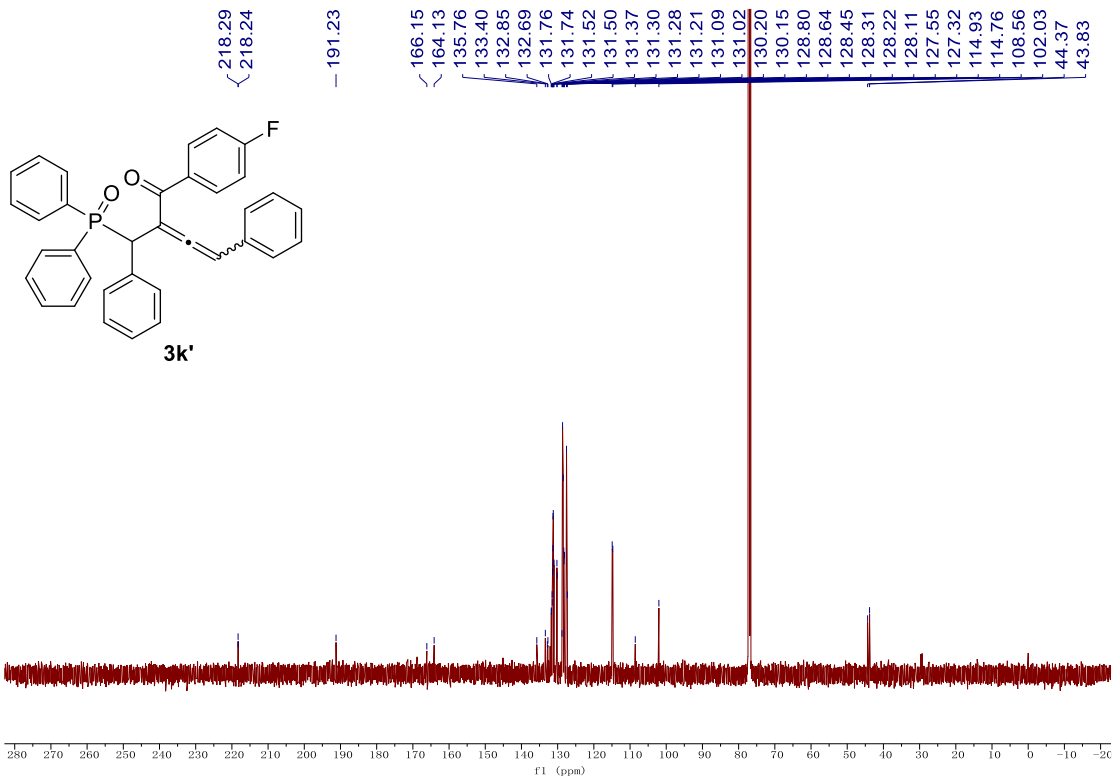


Figure S63. ^{13}C NMR spectrum of compound **3k'** (126 MHz, $CDCl_3$).

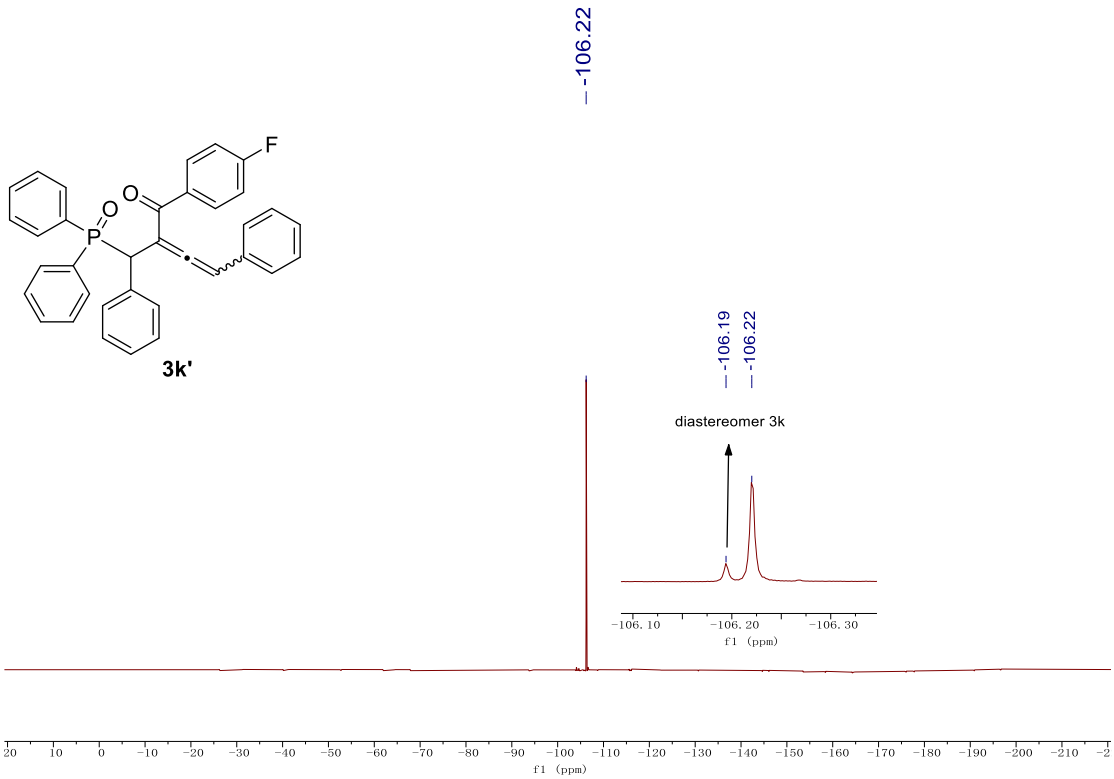


Figure S64. ^{31}P NMR spectrum of compound **3k'** (202 MHz, $CDCl_3$).

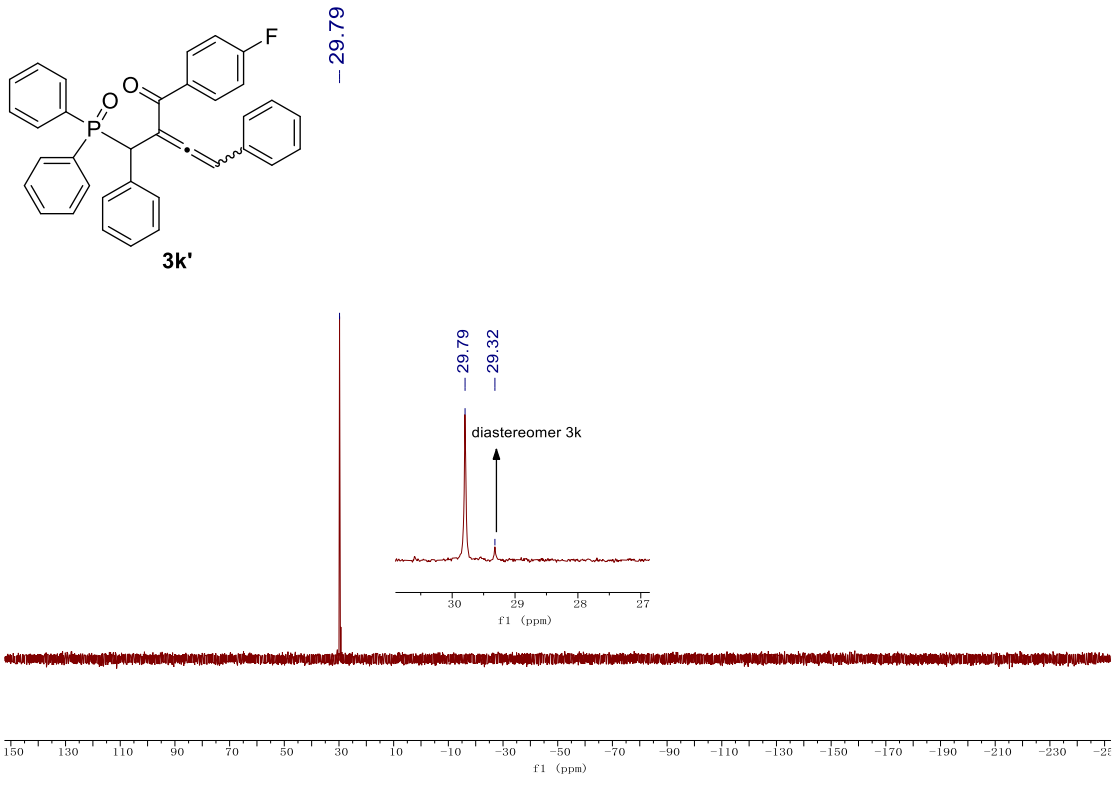


Figure S65. ^{19}F NMR spectrum of compound **3k'** (470 MHz, $CDCl_3$).

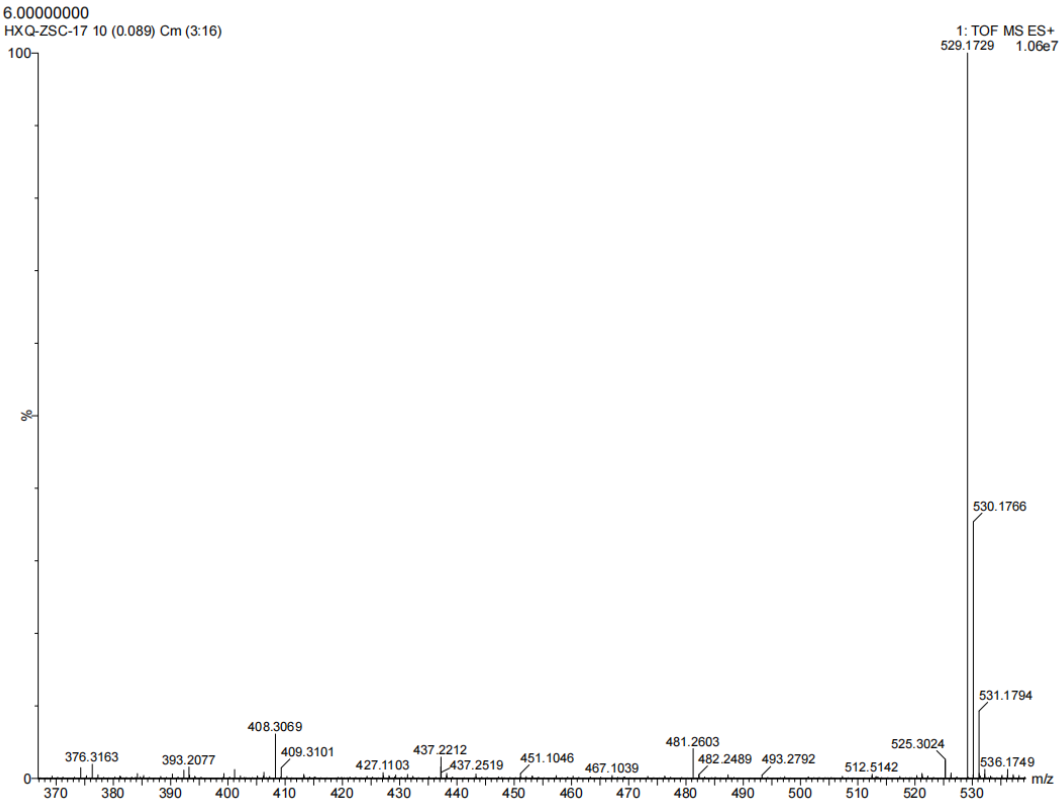
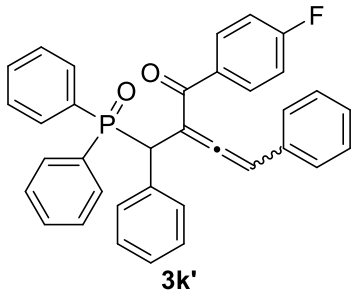


Figure S66. HRMS (ESI) spectrum of compound **3k'**.



3k'

Chemical Formula: $C_{35}H_{26}FO_2P$
Exact Mass: 528.1654
Molecular Weight: 528.5632
m/z: 528.1654 (100.0%), 529.1688 (37.9%), 530.1722 (7.0%)
Elemental Analysis: C, 79.53; H, 4.96; F, 3.59; O, 6.05; P, 5.86

HRMS (ESI, m/z) calcd for $C_{35}H_{26}FO_2P[M+H]^+$ 529.1727, found 529.1729.

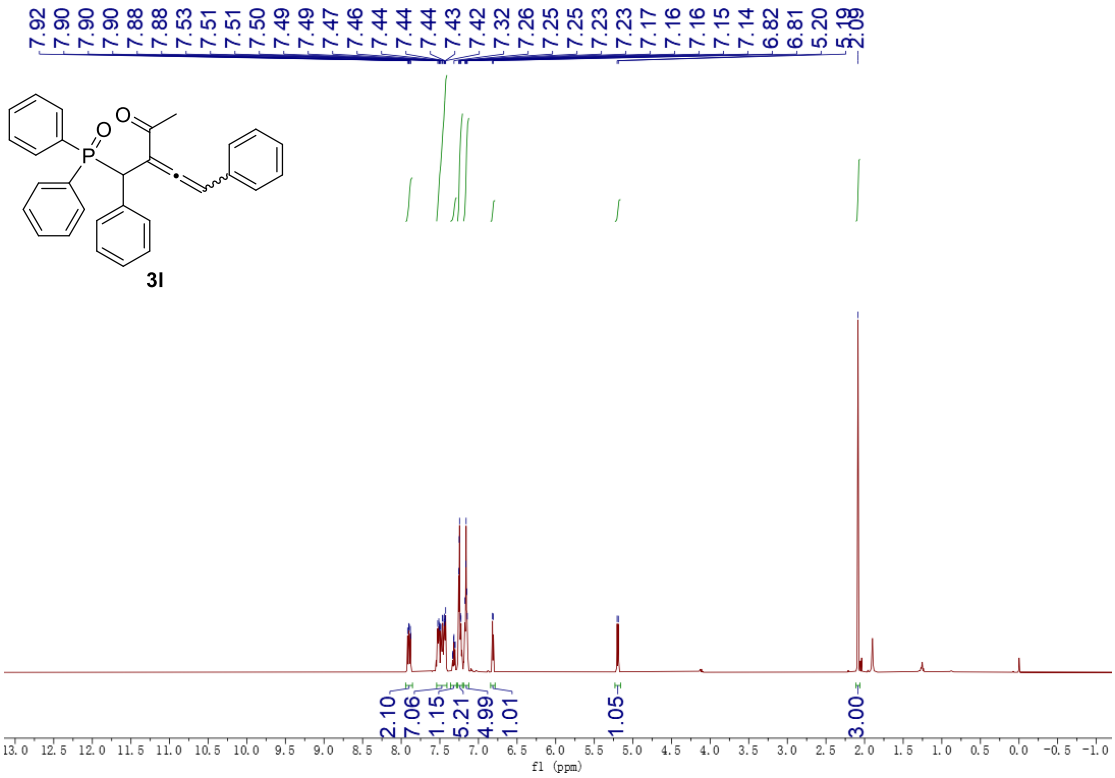


Figure S67. ^{1}H NMR spectrum of compound **3a** (500 MHz, $CDCl_3$).

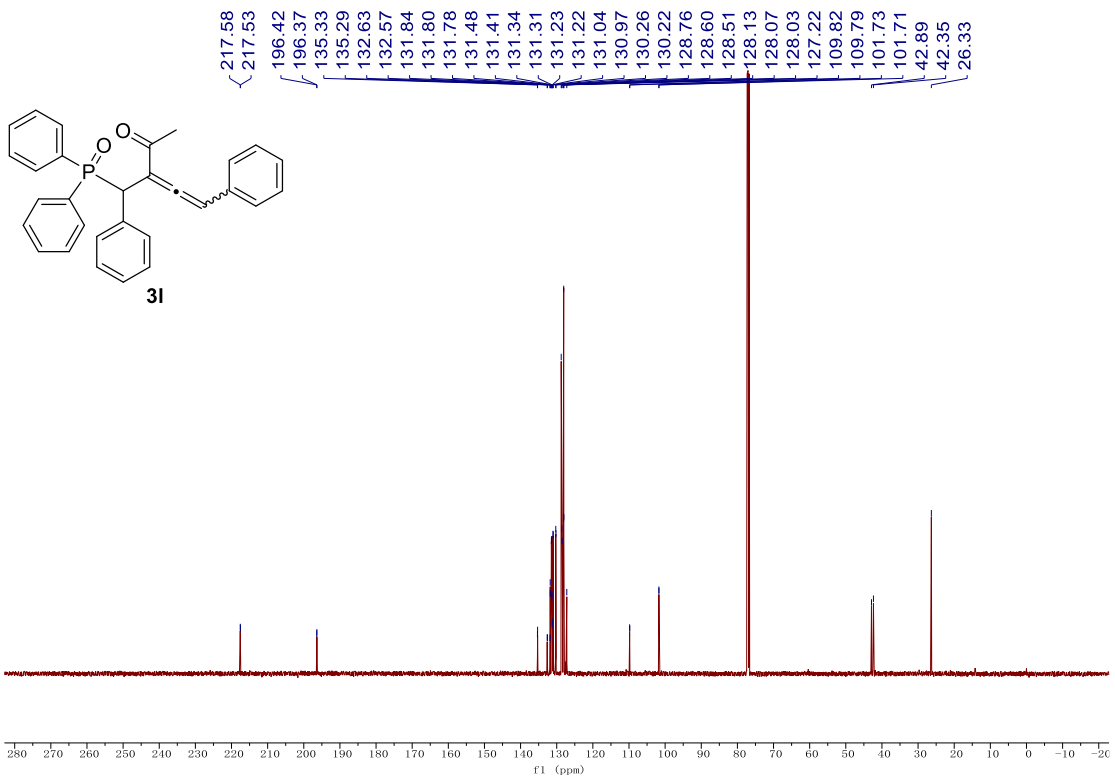


Figure S68. ^{13}C NMR spectrum of compound **3l** (126 MHz, $CDCl_3$).

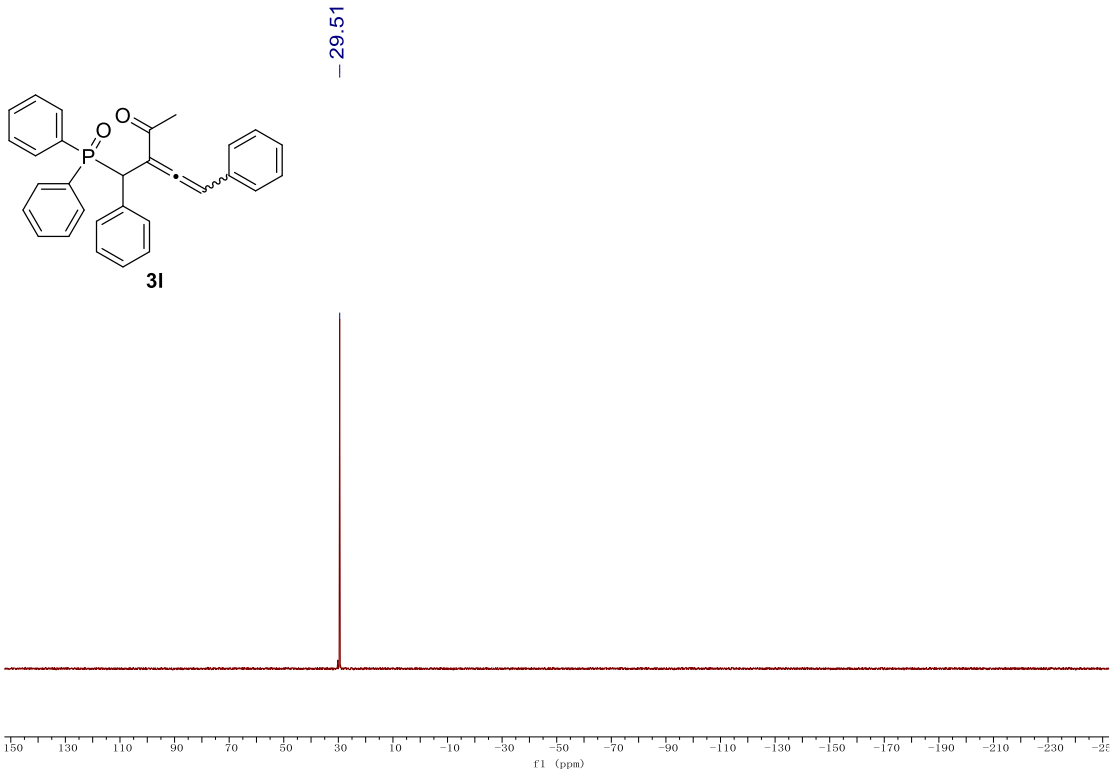


Figure S69. ^{31}P NMR spectrum of compound **3l** (202 MHz, $CDCl_3$).

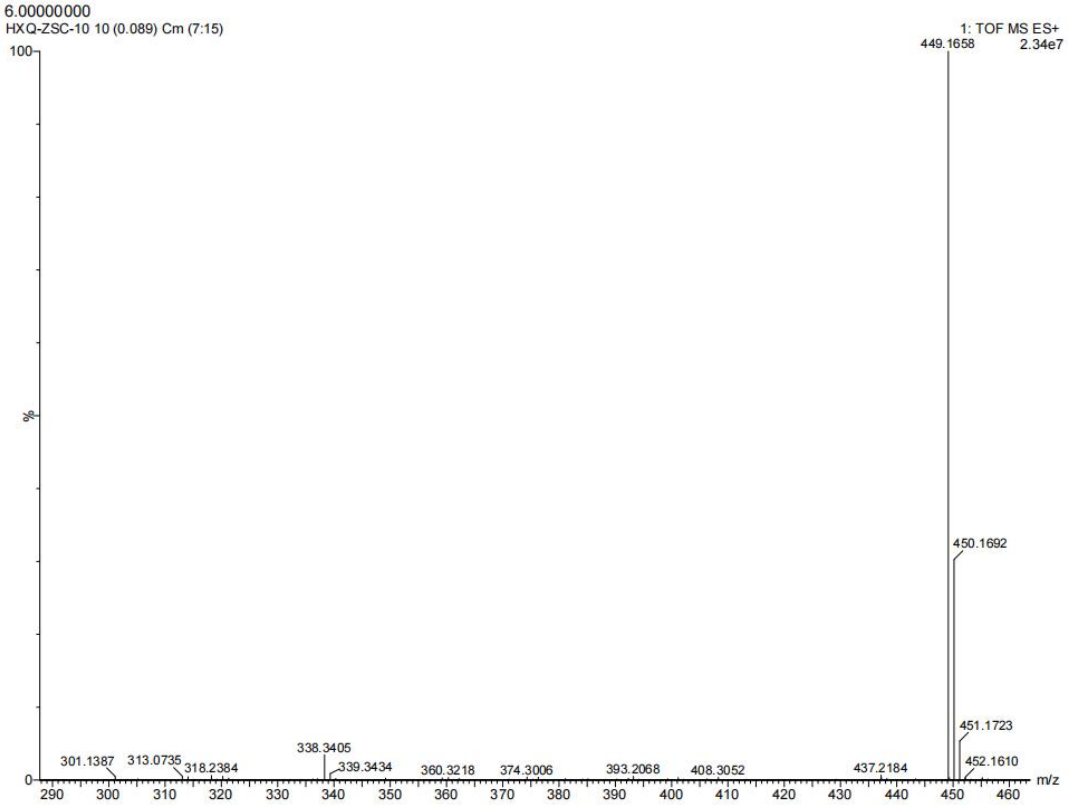
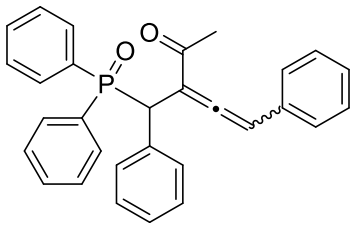


Figure S70. HRMS (ESI) spectrum of compound **3l**.



3l

Chemical Formula: $C_{30}H_{25}O_2P$
Exact Mass: 448.1592
Molecular Weight: 448.5018
m/z: 448.1592 (100.0%), 449.1626 (32.4%), 450.1659 (2.7%), 450.1659 (2.4%)
Elemental Analysis: C, 80.34; H, 5.62; O, 7.13; P, 6.91

HRMS (ESI, m/z) calcd for $C_{30}H_{25}O_2P[M+H]^+$ 449.1656, found 449.1658.

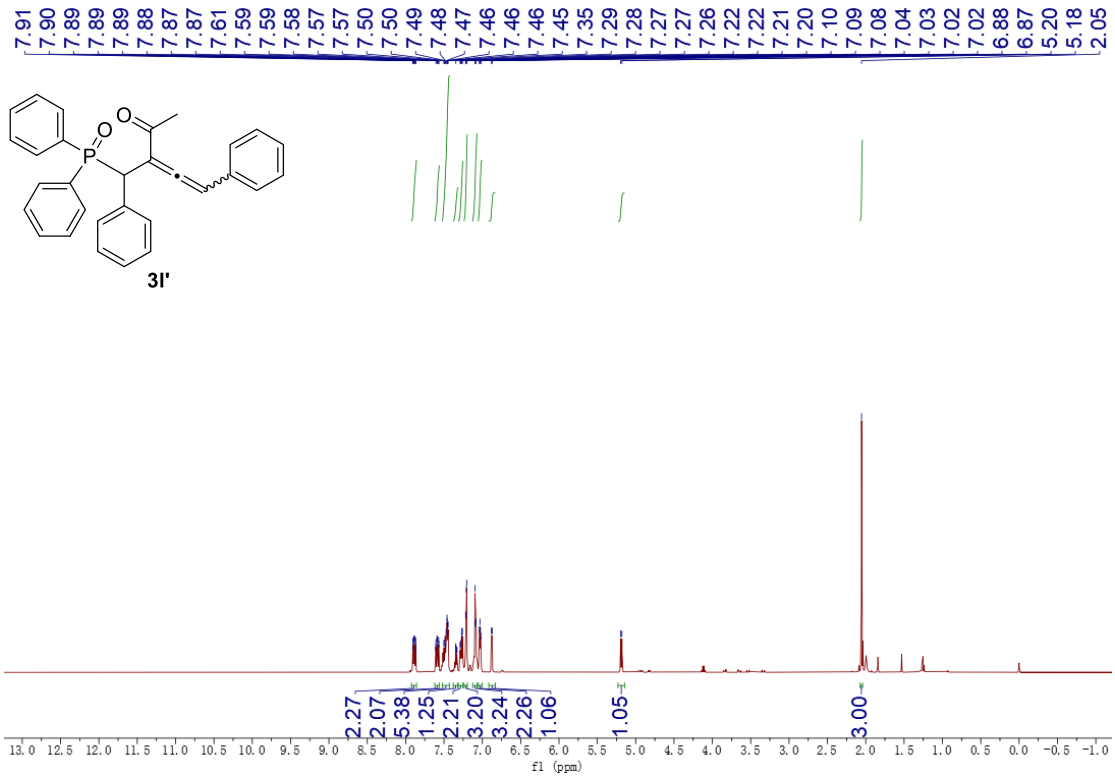


Figure S71. ^{1}H NMR spectrum of compound **3l'** (500 MHz, $CDCl_3$).

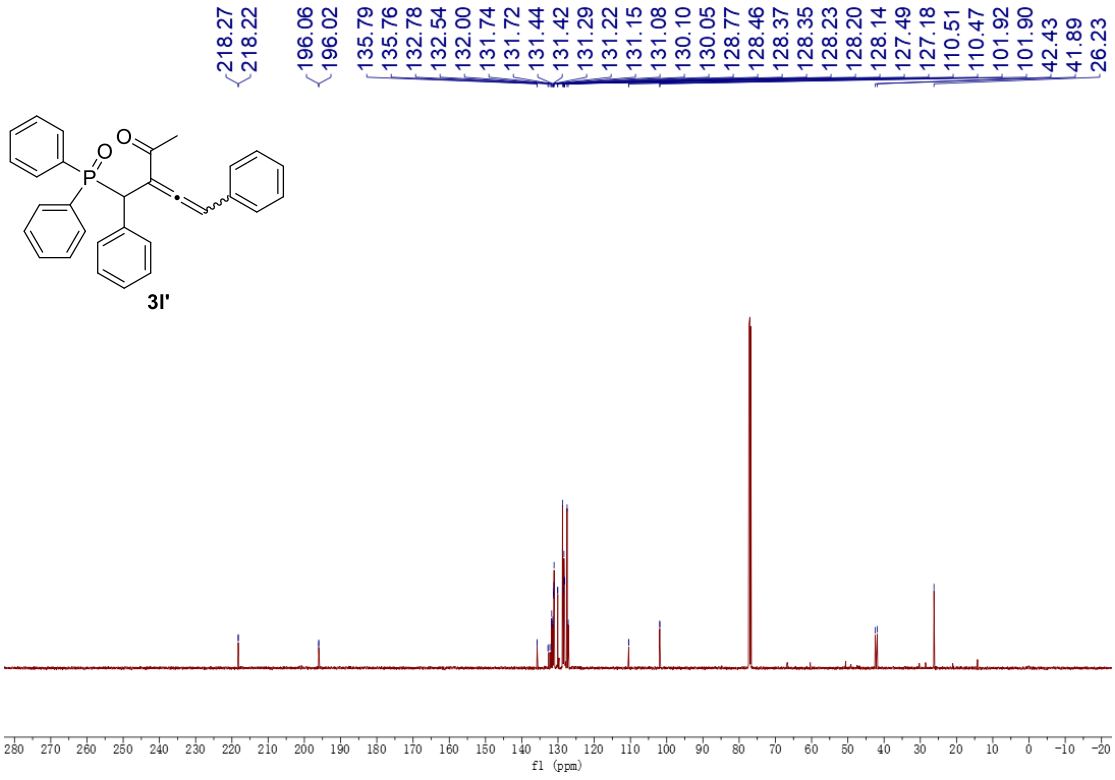


Figure S72. ^{13}C NMR spectrum of compound **3l'** (126 MHz, $CDCl_3$).

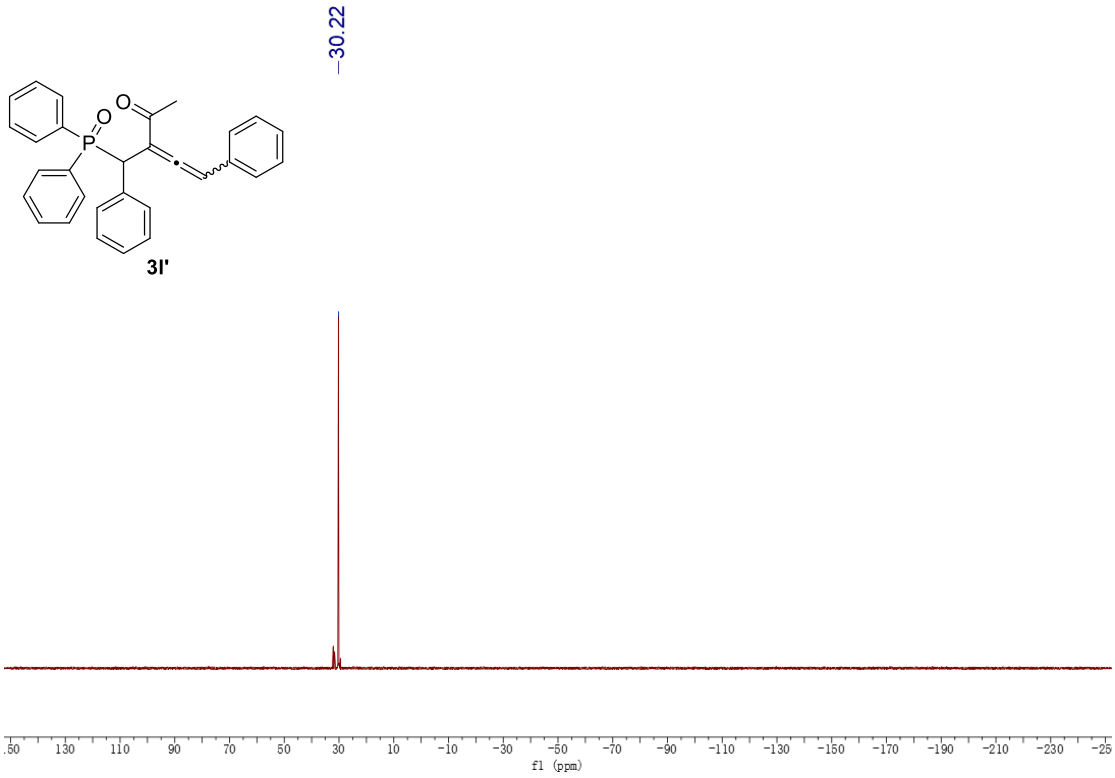


Figure S73. ^{31}P NMR spectrum of compound **3l'** (202 MHz, $CDCl_3$).

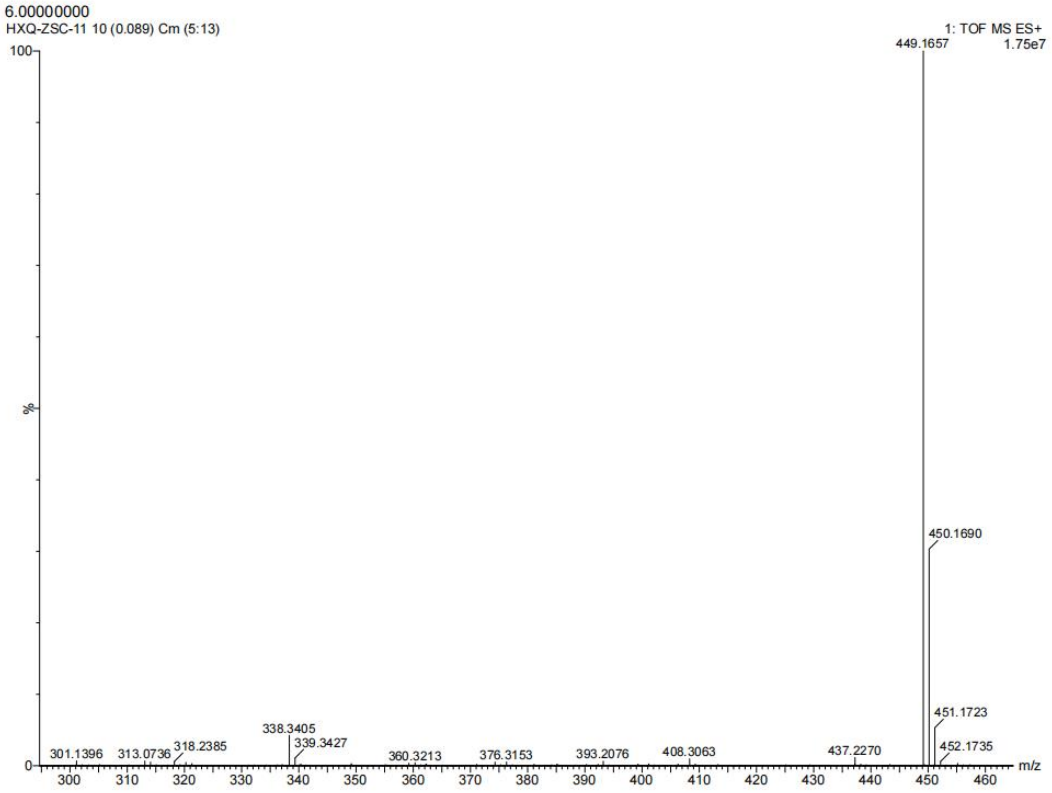
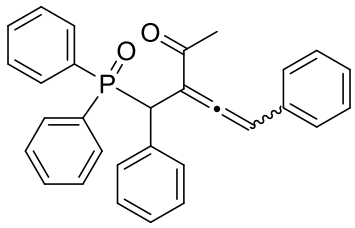


Figure S74. HRMS (ESI) spectrum of compound **3l'**.



3l'

Chemical Formula: $C_{30}H_{25}O_2P$
Exact Mass: 448.1592
Molecular Weight: 448.5018
m/z: 448.1592 (100.0%), 449.1626 (32.4%), 450.1659 (2.7%), 450.1659 (2.4%)
Elemental Analysis: C, 80.34; H, 5.62; O, 7.13; P, 6.91

HRMS (ESI, m/z) calcd for $C_{30}H_{25}O_2P[M+H]^+$ 449.1656, found 449.1657.

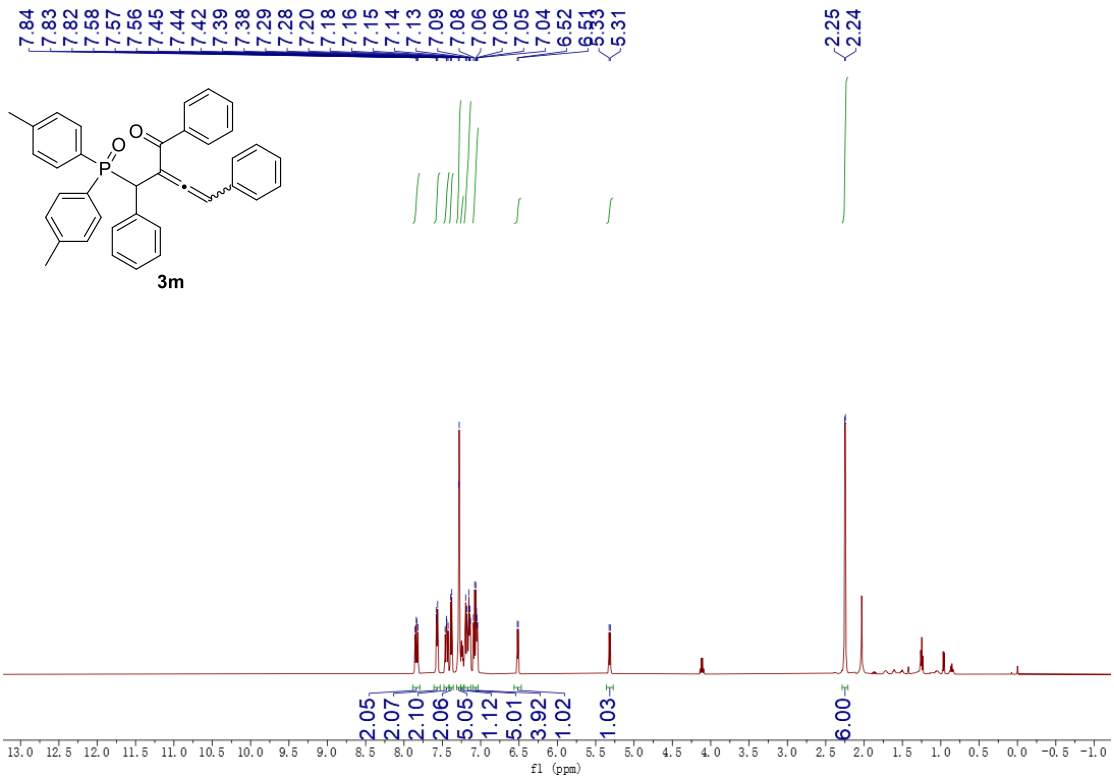


Figure S75. ^{1}H NMR spectrum of compound **3m** (500 MHz, $CDCl_3$).

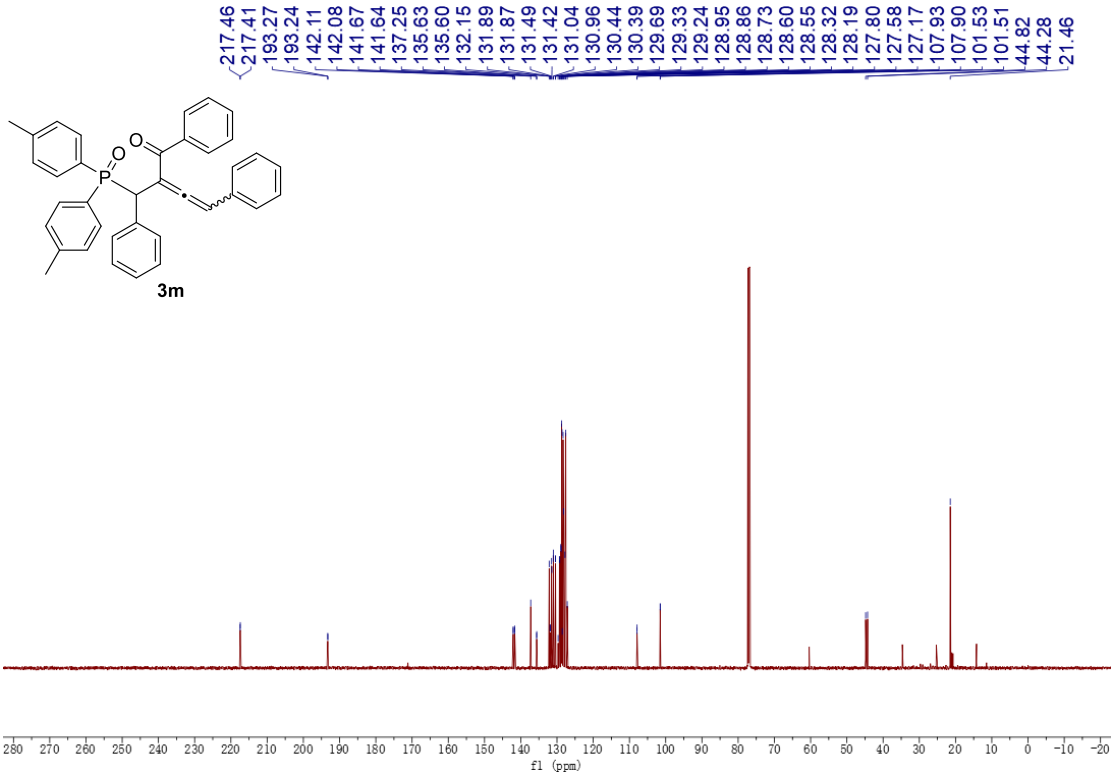


Figure S76. ^{13}C NMR spectrum of compound **3m** (126 MHz, $CDCl_3$).

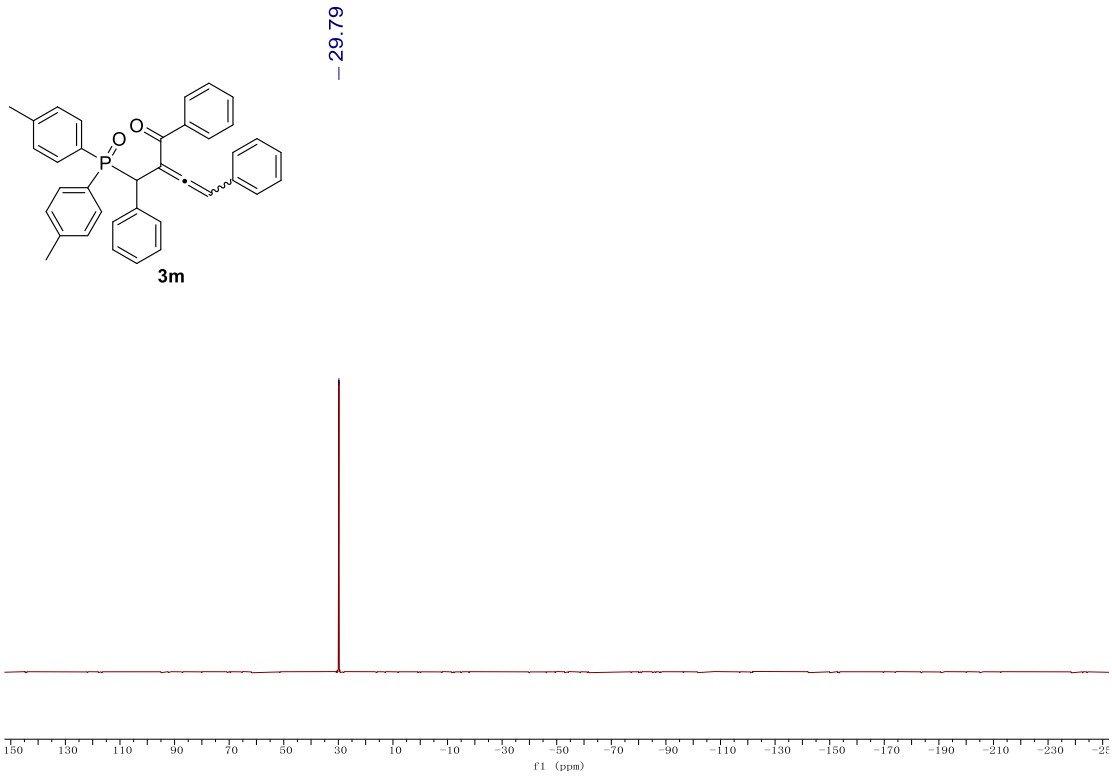


Figure S77. ^{31}P NMR spectrum of compound **3m** (202 MHz, $CDCl_3$).

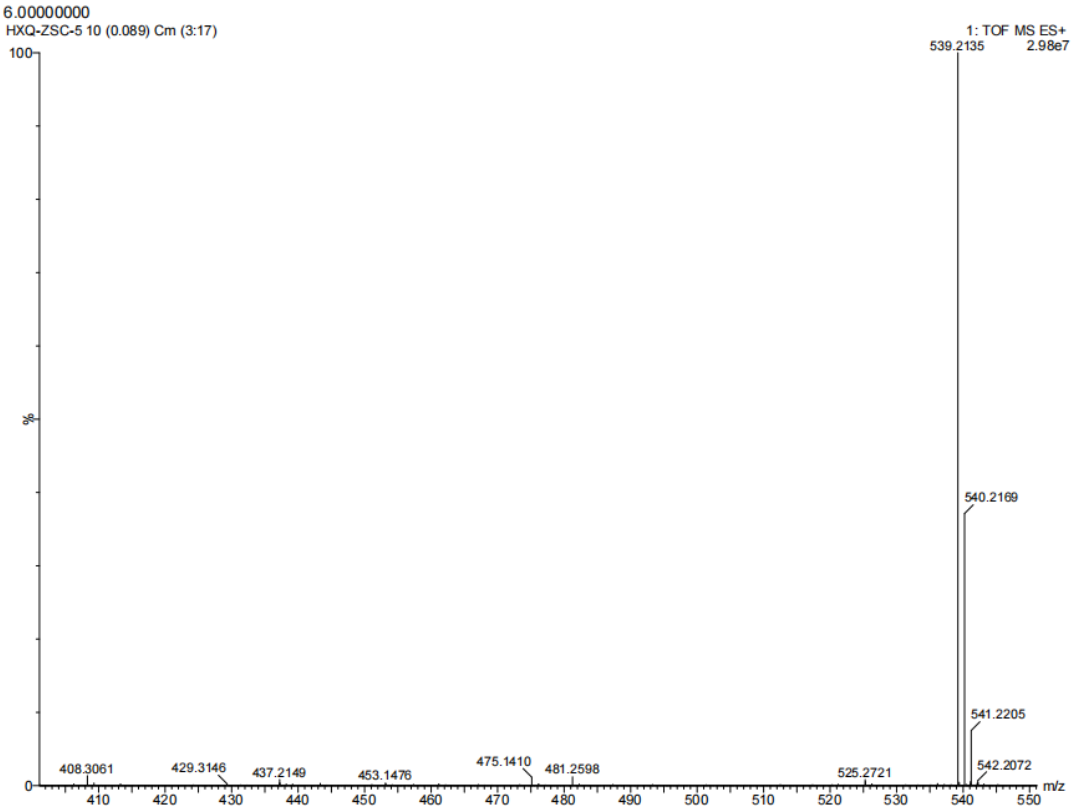
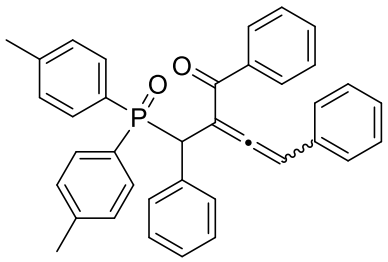


Figure S78. HRMS (ESI) spectrum of compound **3m**.



3m

Chemical Formula: $C_{37}H_{31}O_2P$
Exact Mass: 538.2062
Molecular Weight: 538.6268
m/z: 538.2062 (100.0%), 539.2095 (40.0%), 540.2129 (5.1%), 540.2129 (2.7%)
Elemental Analysis: C, 82.51; H, 5.80; O, 5.94; P, 5.75

HRMS (ESI, m/z) calcd for $C_{37}H_{31}O_2P[M+H]^+$ 539.2134, found 539.2135.

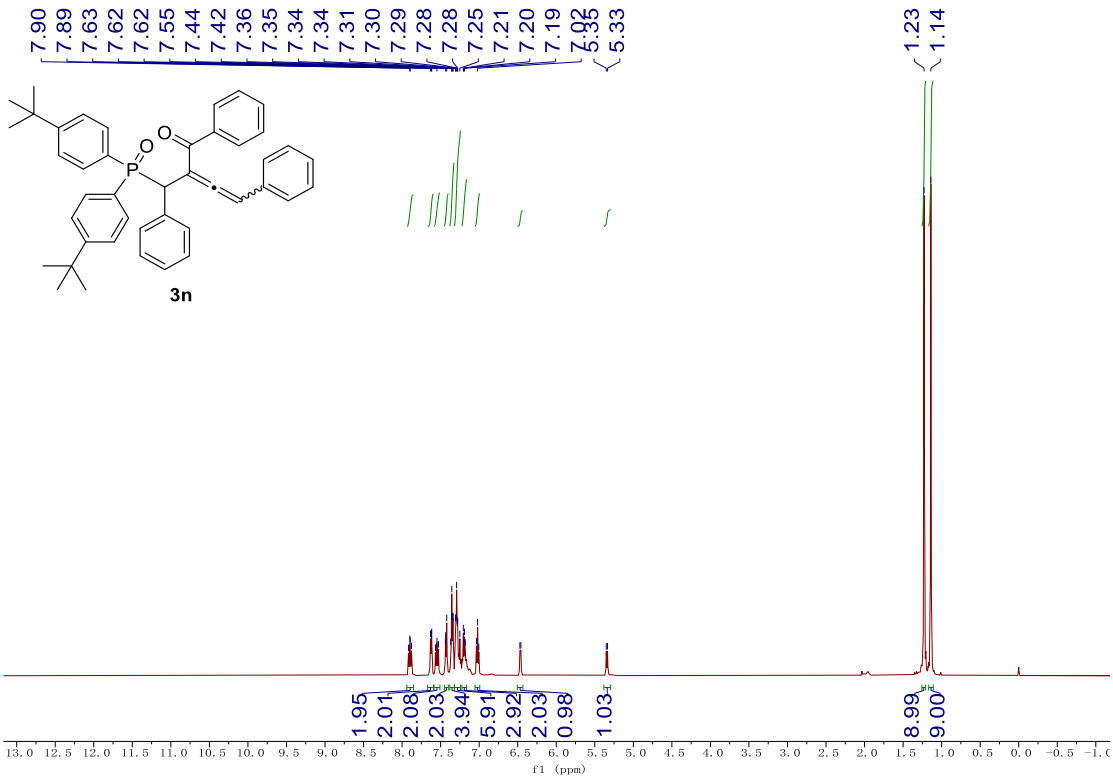


Figure S79. ^{1}H NMR spectrum of compound **3n** (500 MHz, $CDCl_3$).

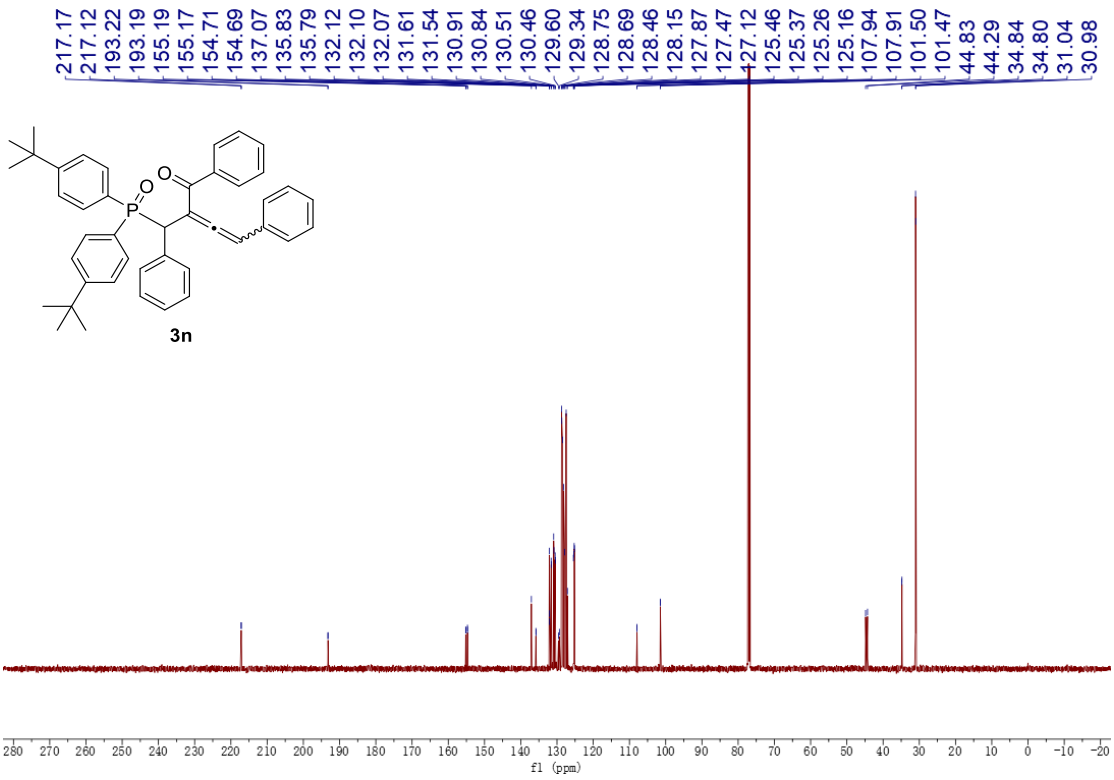


Figure S80. ^{13}C NMR spectrum of compound **3n** (126 MHz, $CDCl_3$).

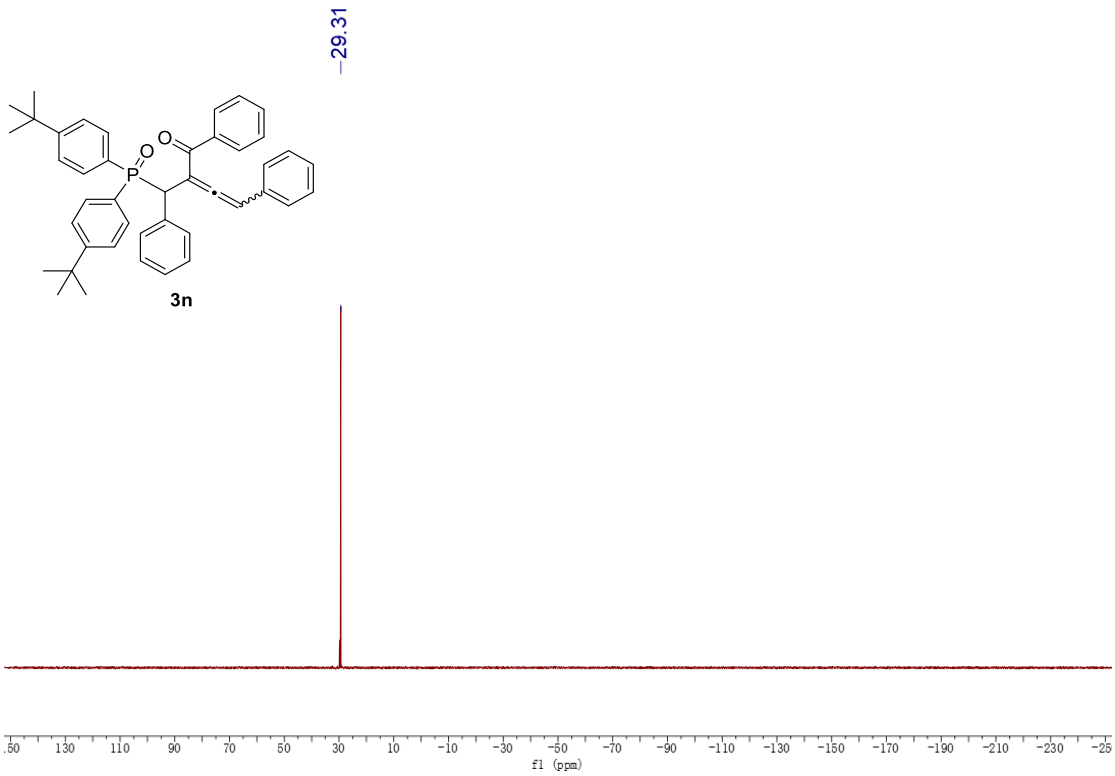


Figure S81. ^{31}P NMR spectrum of compound **3n** (202 MHz, $CDCl_3$).

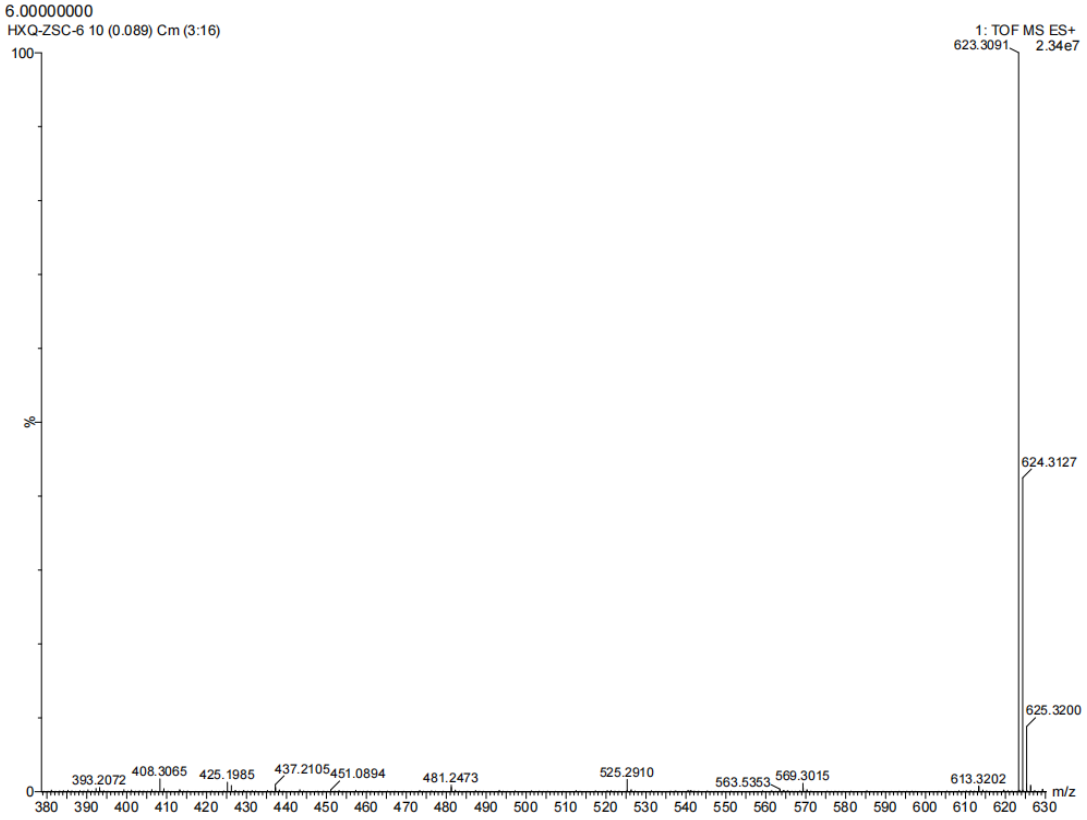
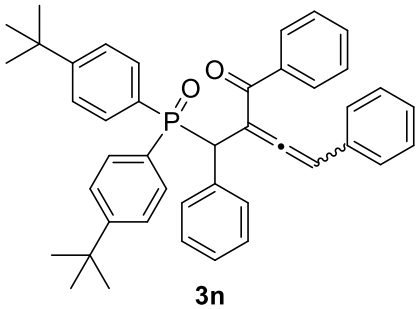


Figure S82. HRMS (ESI) spectrum of compound **3n**.



3n

Chemical Formula: $C_{43}H_{43}O_2P$
Exact Mass: 622.3001
Molecular Weight: 622.7888
m/z: 622.3001 (100.0%), 623.3034 (46.5%), 624.3068 (10.6%)
Elemental Analysis: C, 82.93; H, 6.96; O, 5.14; P, 4.97

HRMS (ESI, m/z) calcd for $C_{43}H_{43}O_2P[M+H]^+$ 623.3073, found 623.3091.

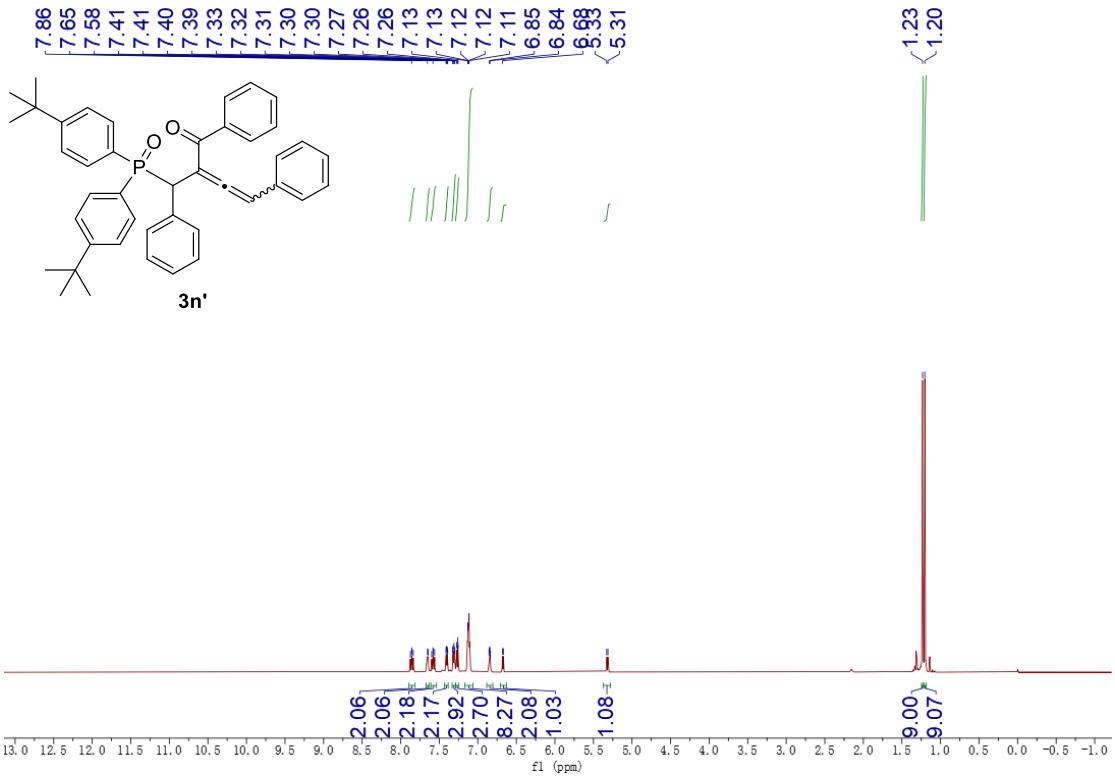


Figure S83. ^{1}H NMR spectrum of compound **3n'** (500 MHz, $CDCl_3$).

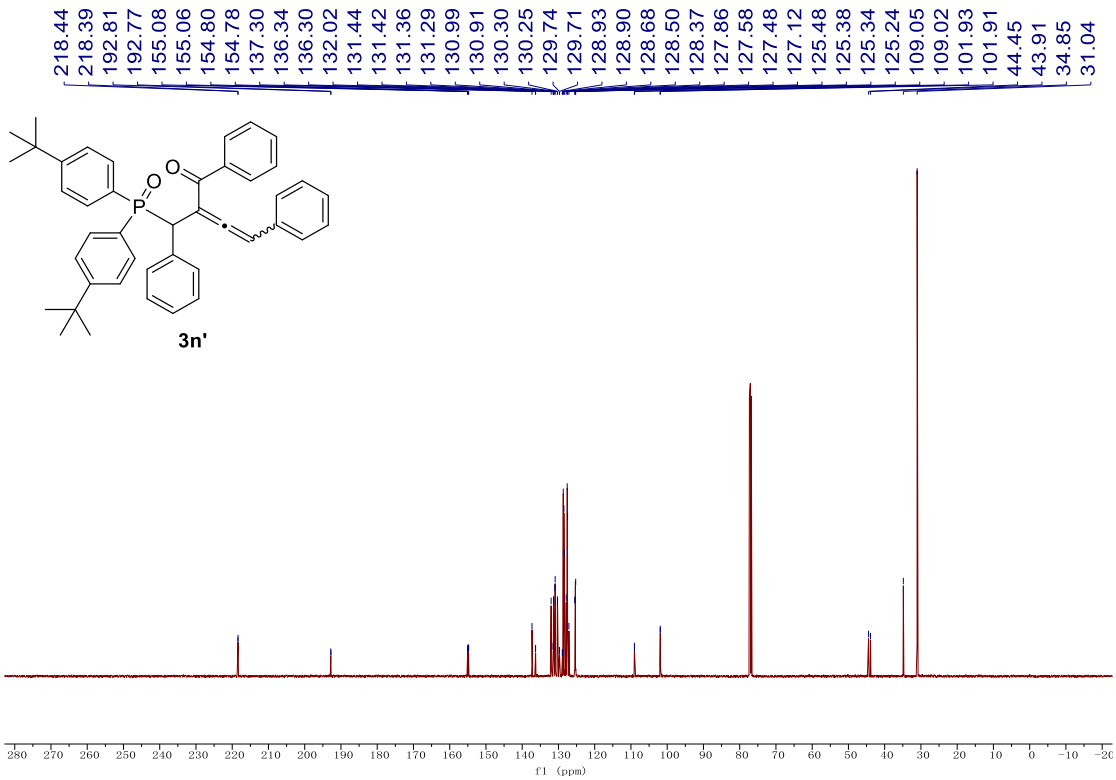


Figure S84. ^{13}C NMR spectrum of compound **3n'** (126 MHz, $CDCl_3$).

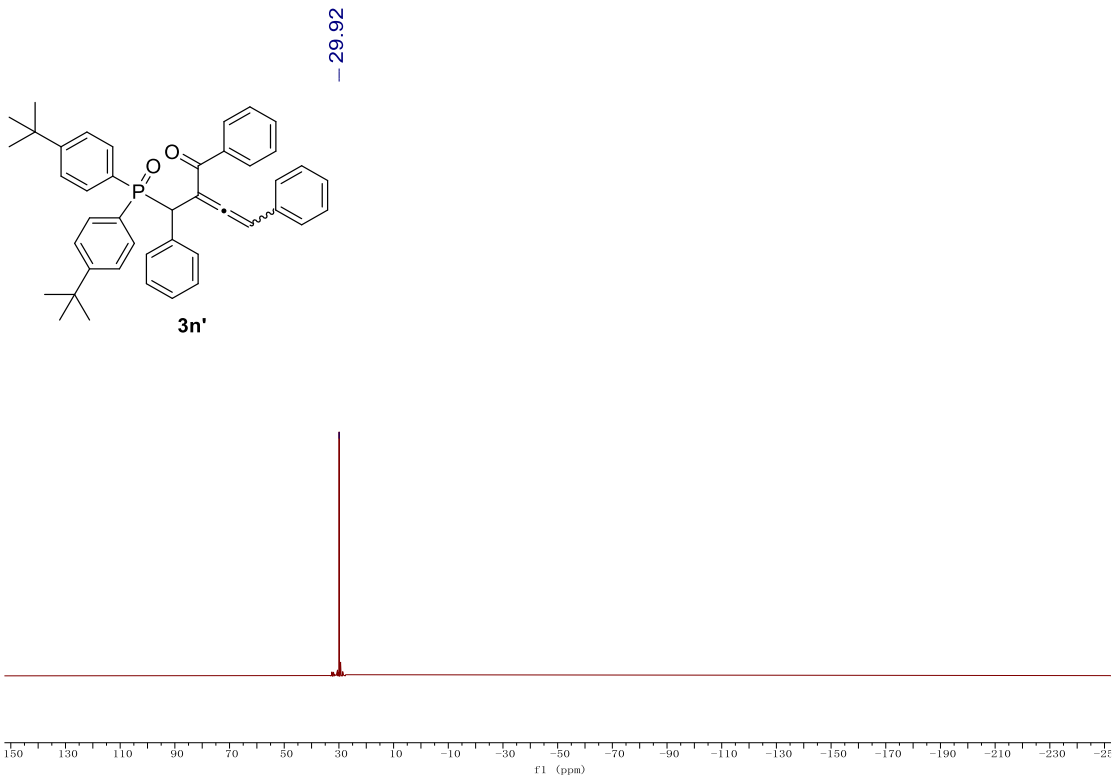


Figure S85. ^{31}P NMR spectrum of compound **3n'** (202 MHz, $CDCl_3$).

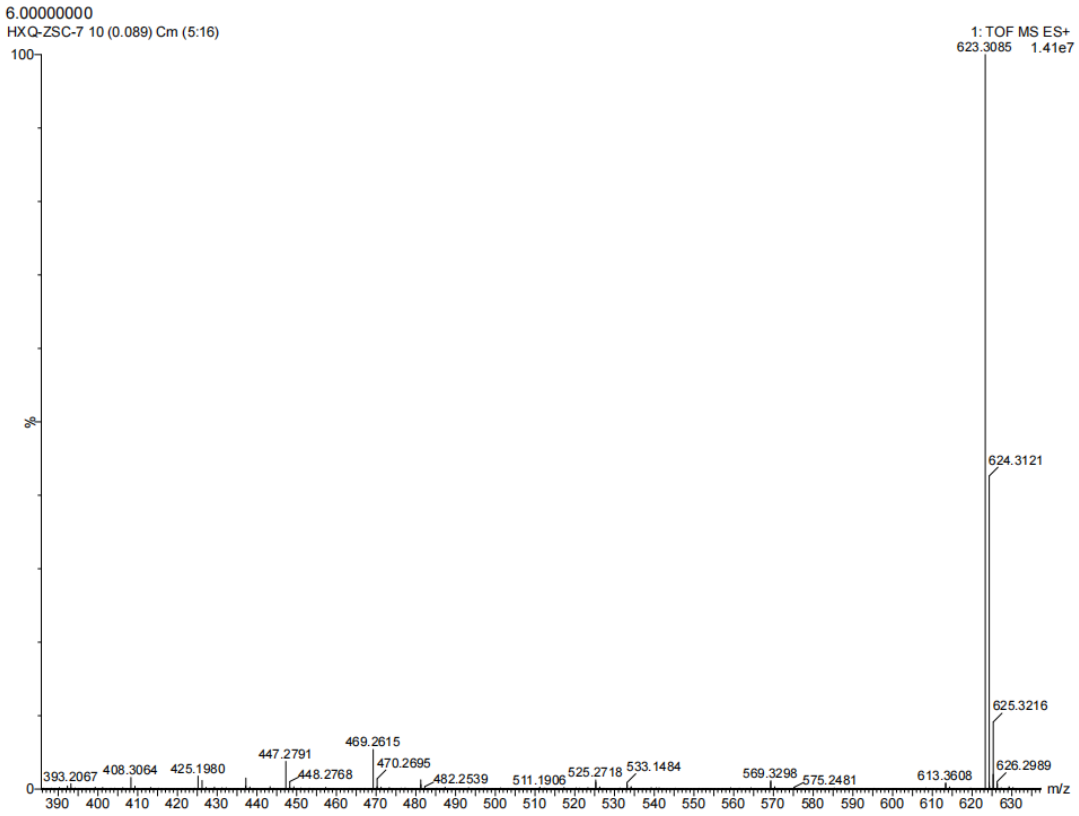
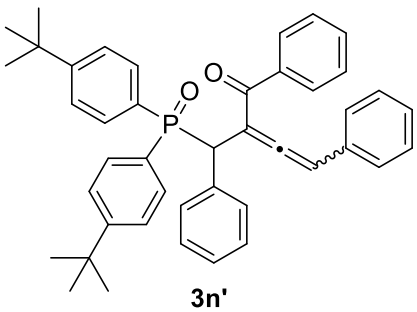


Figure S86. HRMS (ESI) spectrum of compound **3n'**.



3n'

Chemical Formula: $C_{43}H_{43}O_2P$
Exact Mass: 622.3001
Molecular Weight: 622.7888
m/z: 622.3001 (100.0%), 623.3034 (46.5%), 624.3068 (10.6%)
Elemental Analysis: C, 82.93; H, 6.96; O, 5.14; P, 4.97

HRMS (ESI, m/z) calcd for $C_{43}H_{43}O_2P[M+H]^+$ 623.3073, found 623.3085.

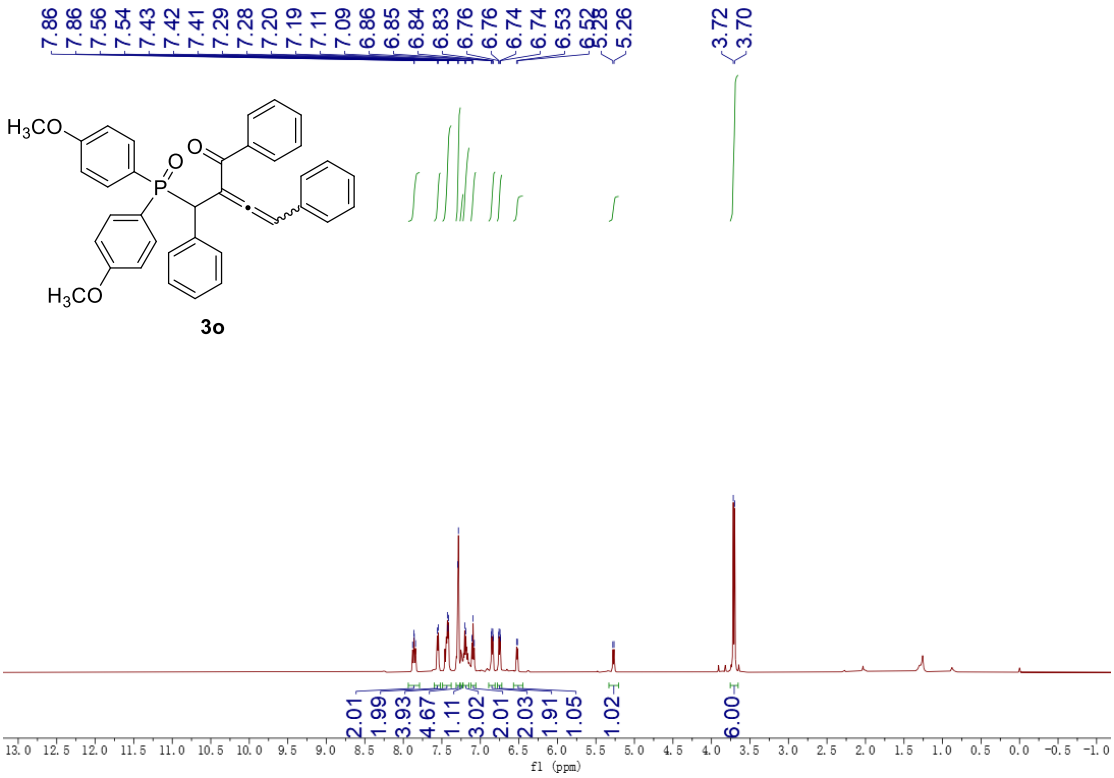


Figure S87. ^{1}H NMR spectrum of compound **3o** (500 MHz, $CDCl_3$).

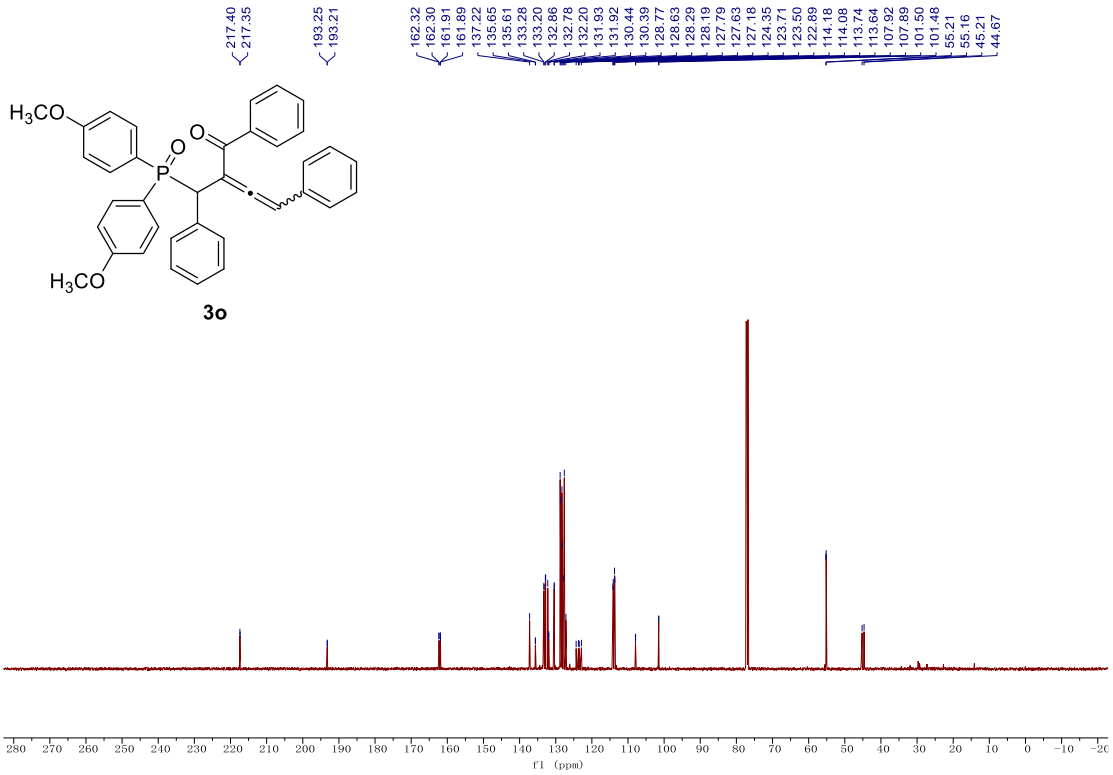


Figure S88. ^{13}C NMR spectrum of compound **3o** (126 MHz, $CDCl_3$).

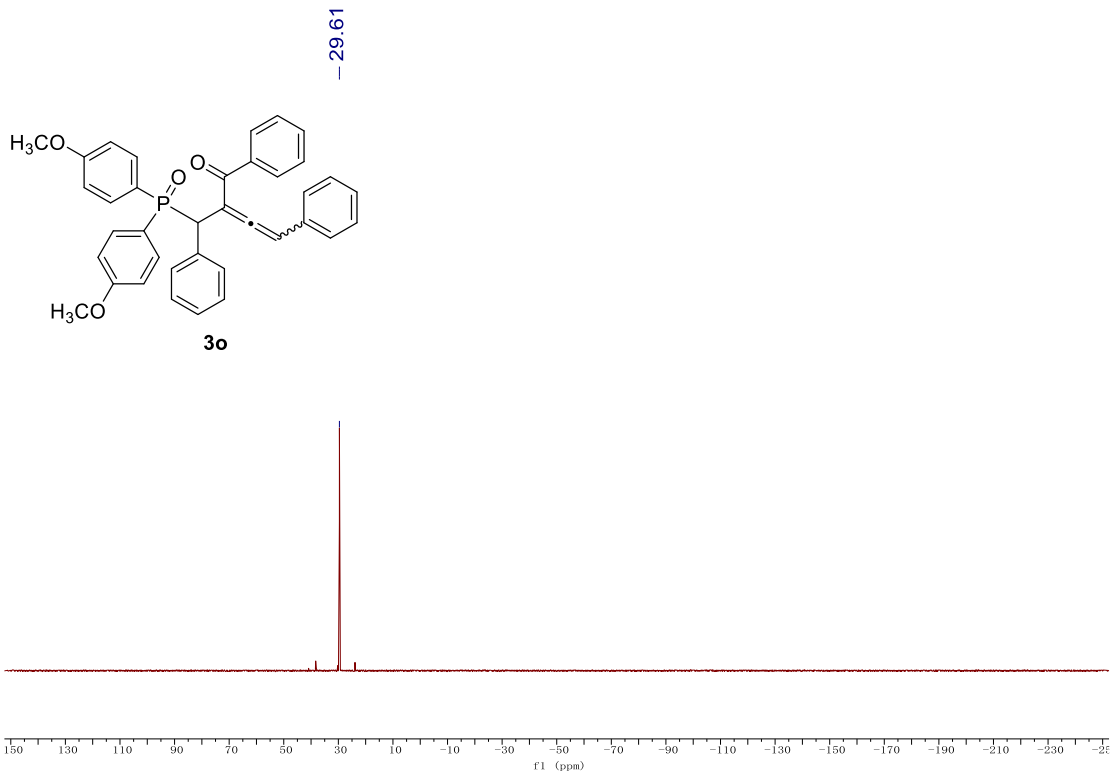


Figure S89. ^{31}P NMR spectrum of compound **3o** (202 MHz, $CDCl_3$).

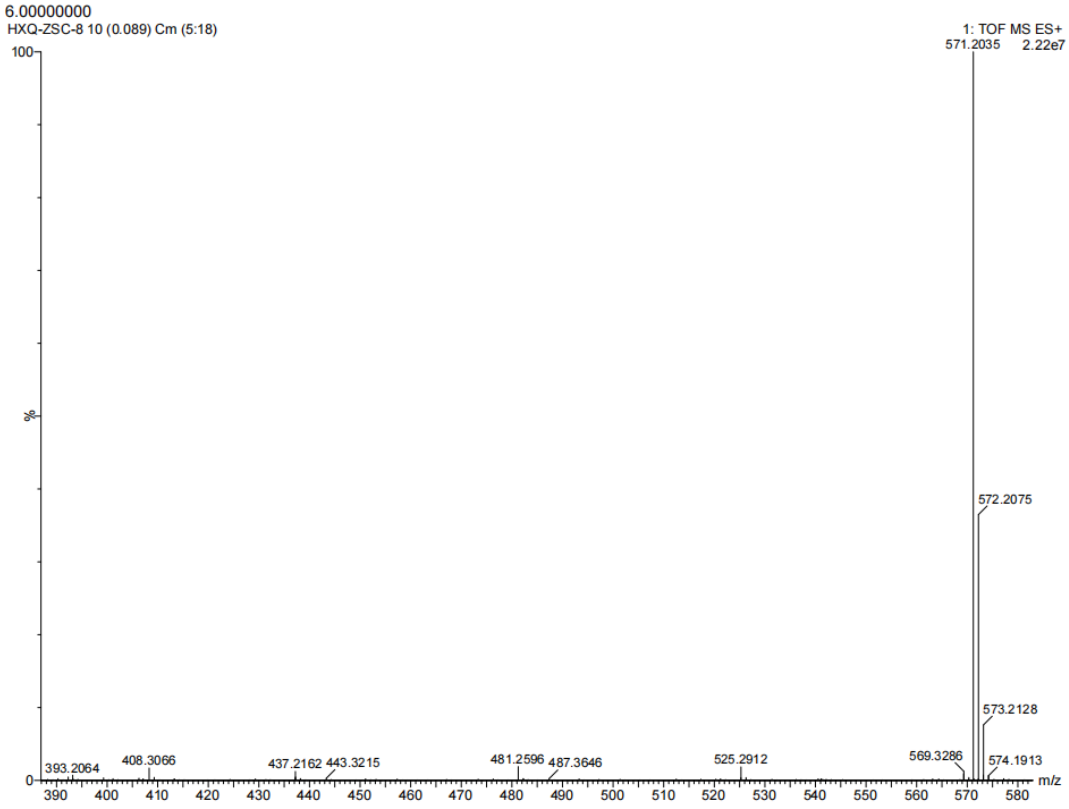
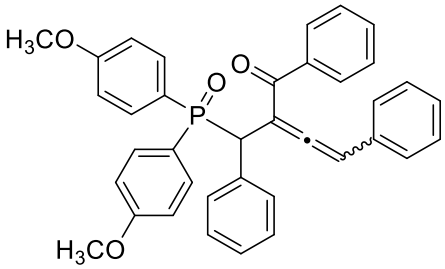


Figure S90. HRMS (ESI) spectrum of compound **3o**.



3o

Chemical Formula: $C_{37}H_{31}O_4P$
Exact Mass: 570.1960
Molecular Weight: 570.6248
m/z: 570.1960 (100.0%), 571.1994 (40.0%), 572.2027 (5.1%), 572.2027 (2.7%)
Elemental Analysis: C, 77.88; H, 5.48; O, 11.22; P, 5.43

HRMS (ESI, m/z) calcd for $C_{37}H_{31}O_4P[M+H]^+$ 517.2033, found 517.2035.

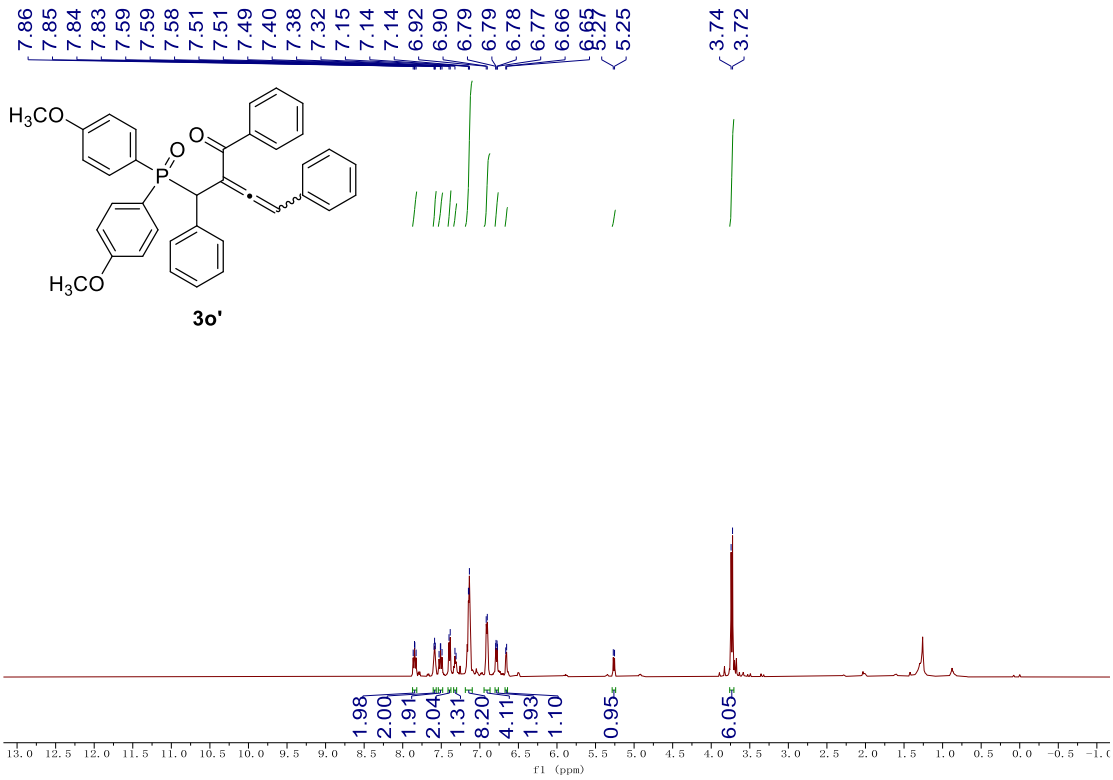


Figure S91. ^{1}H NMR spectrum of compound **3o'** (500 MHz, $CDCl_3$).

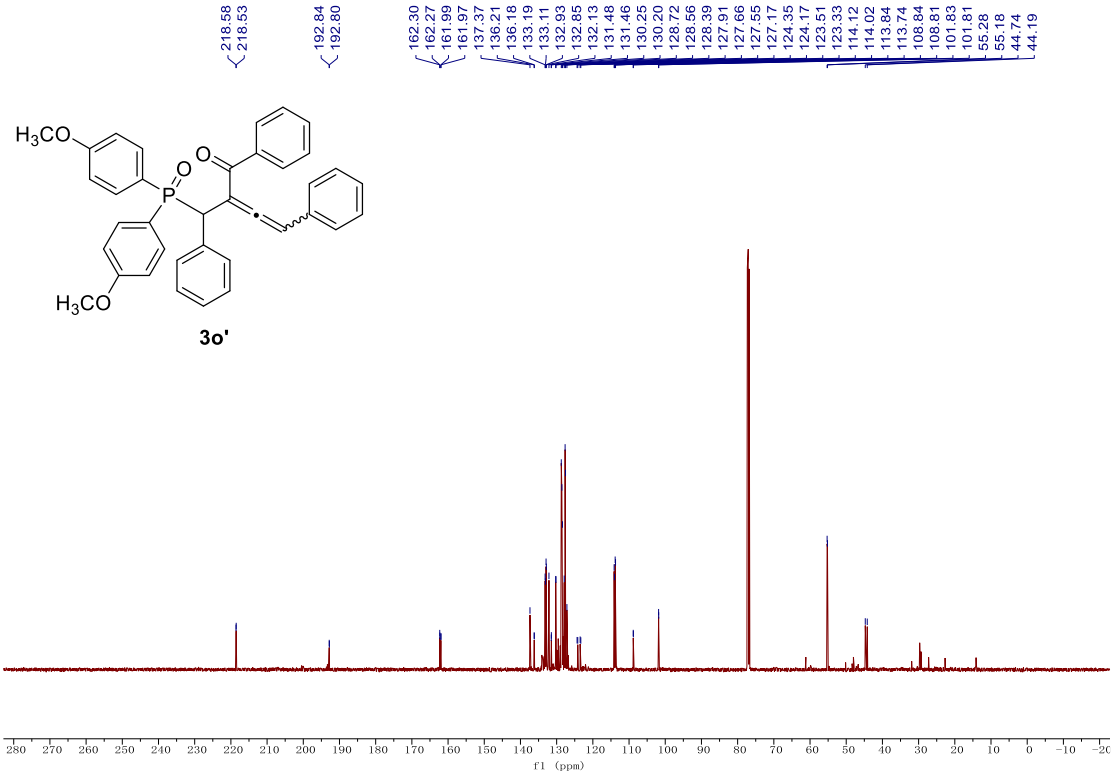


Figure S92. ^{13}C NMR spectrum of compound **3o'** (126 MHz, $CDCl_3$).

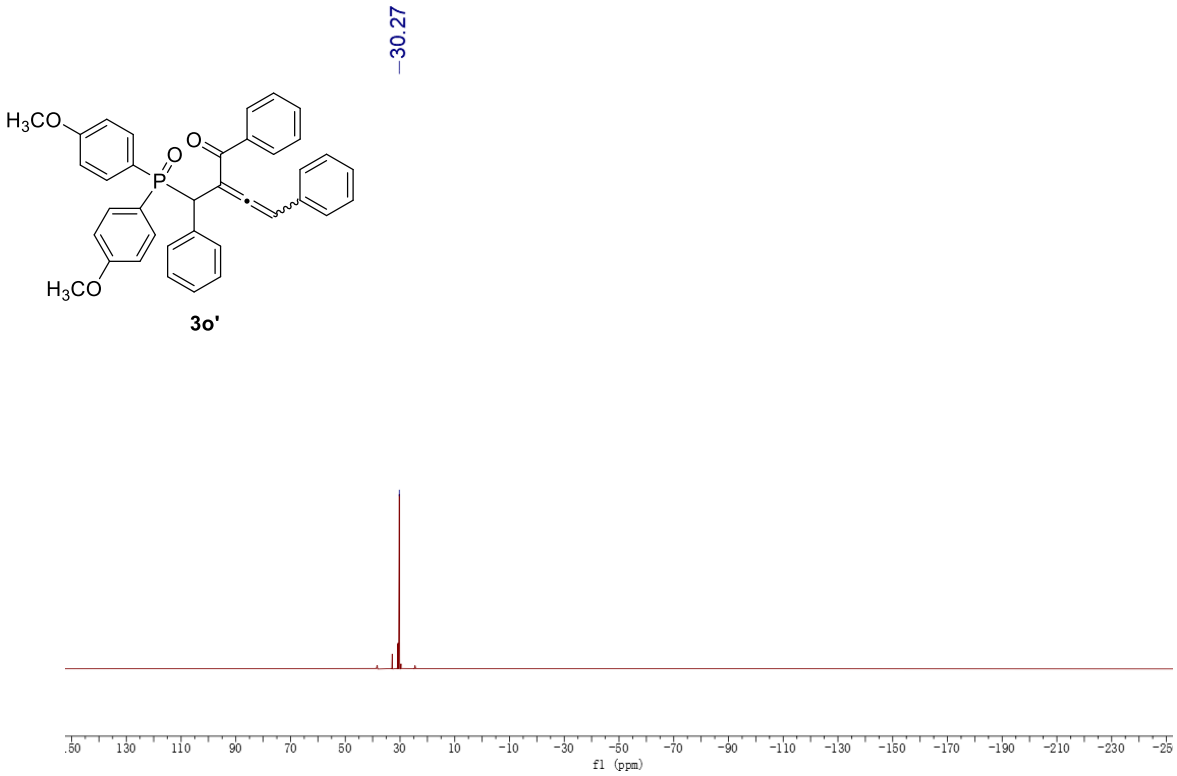


Figure S93. ^{31}P NMR spectrum of compound **3o'** (202 MHz, $CDCl_3$).

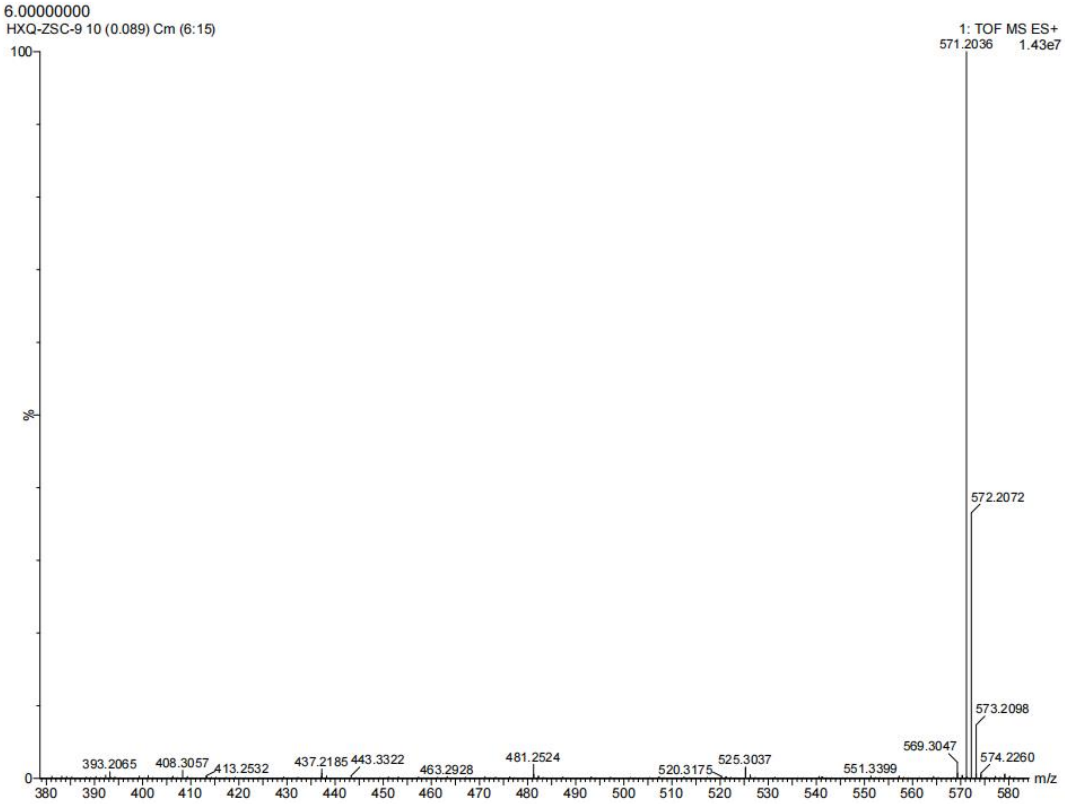
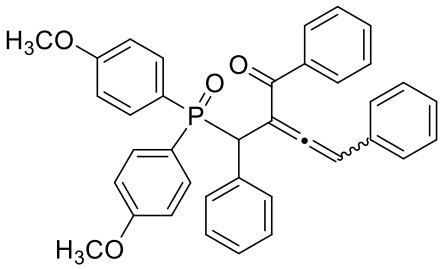


Figure S94. HRMS (ESI) spectrum of compound **3o'**.



3o'

Chemical Formula: $C_{37}H_{31}O_4P$
Exact Mass: 570.1960
Molecular Weight: 570.6248
m/z: 570.1960 (100.0%), 571.1994 (40.0%), 572.2027 (5.1%), 572.2027 (2.7%)
Elemental Analysis: C, 77.88; H, 5.48; O, 11.22; P, 5.43

HRMS (ESI, m/z) calcd for $C_{37}H_{31}O_4P[M+H]^+$ 571.2033, found 571.2036.

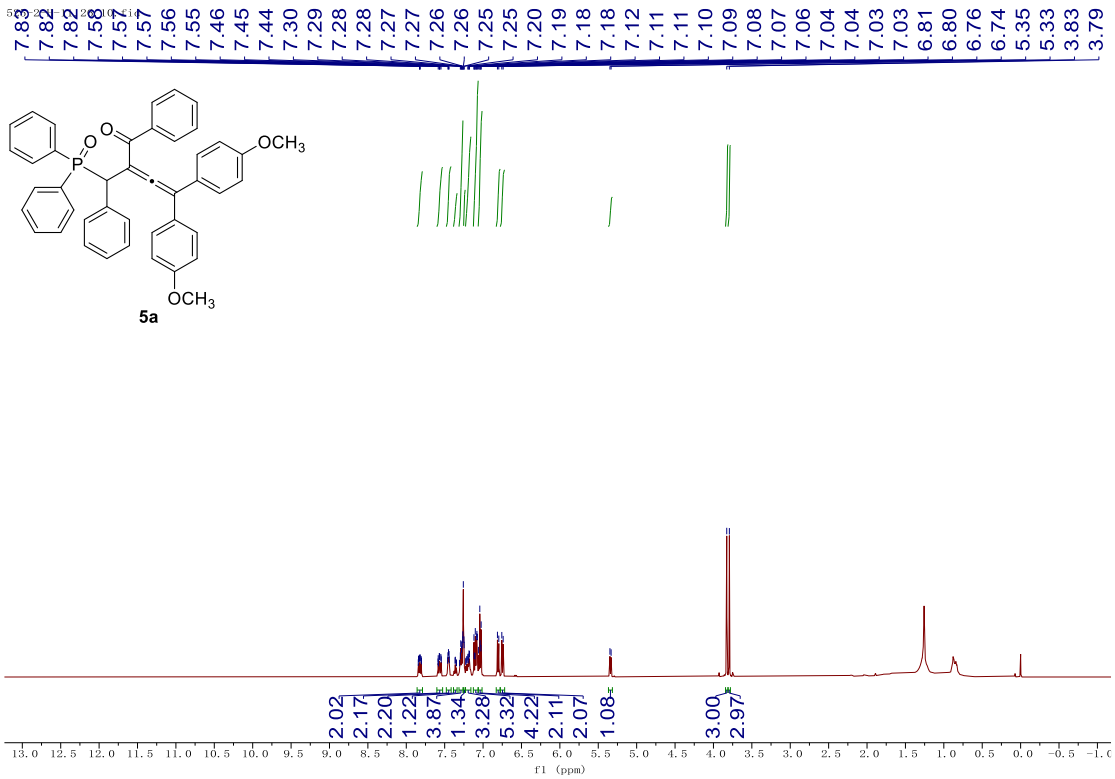


Figure S95. ^{1}H NMR spectrum of compound **5a** (500 MHz, $CDCl_3$).

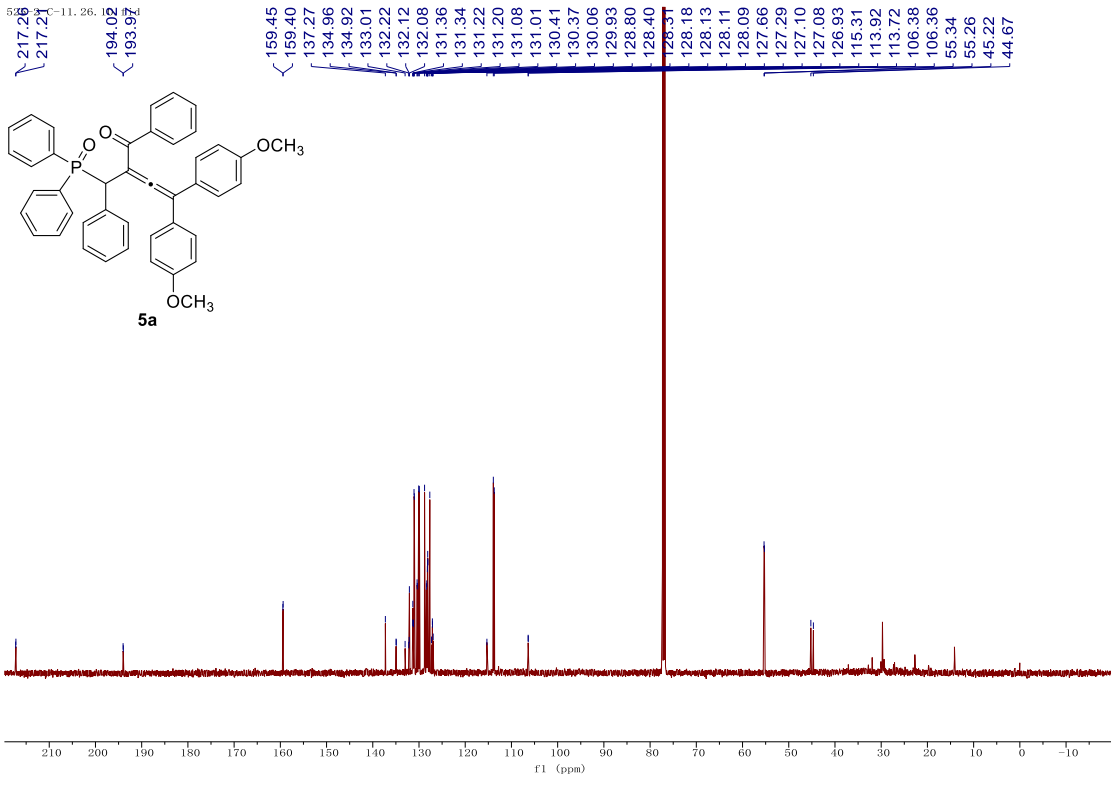


Figure S96. ^{13}C NMR spectrum of compound **5a** (126 MHz, $CDCl_3$).

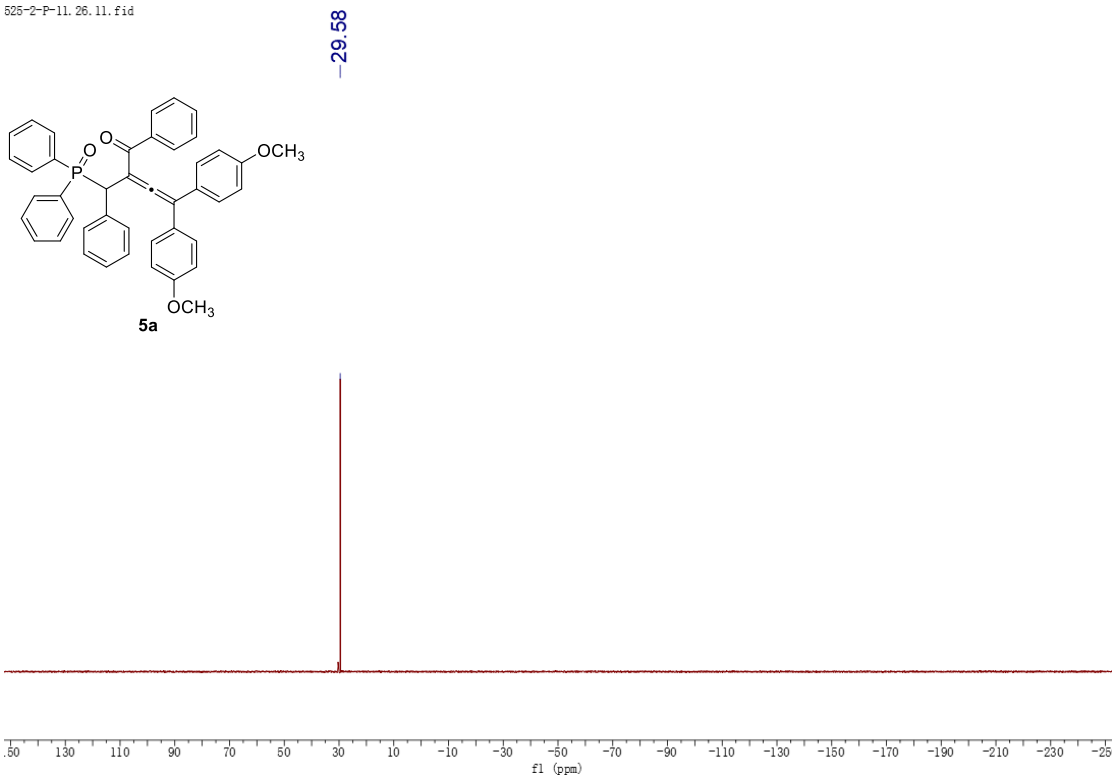


Figure S97. ^{31}P NMR spectrum of compound **5a** (202 MHz, $CDCl_3$).

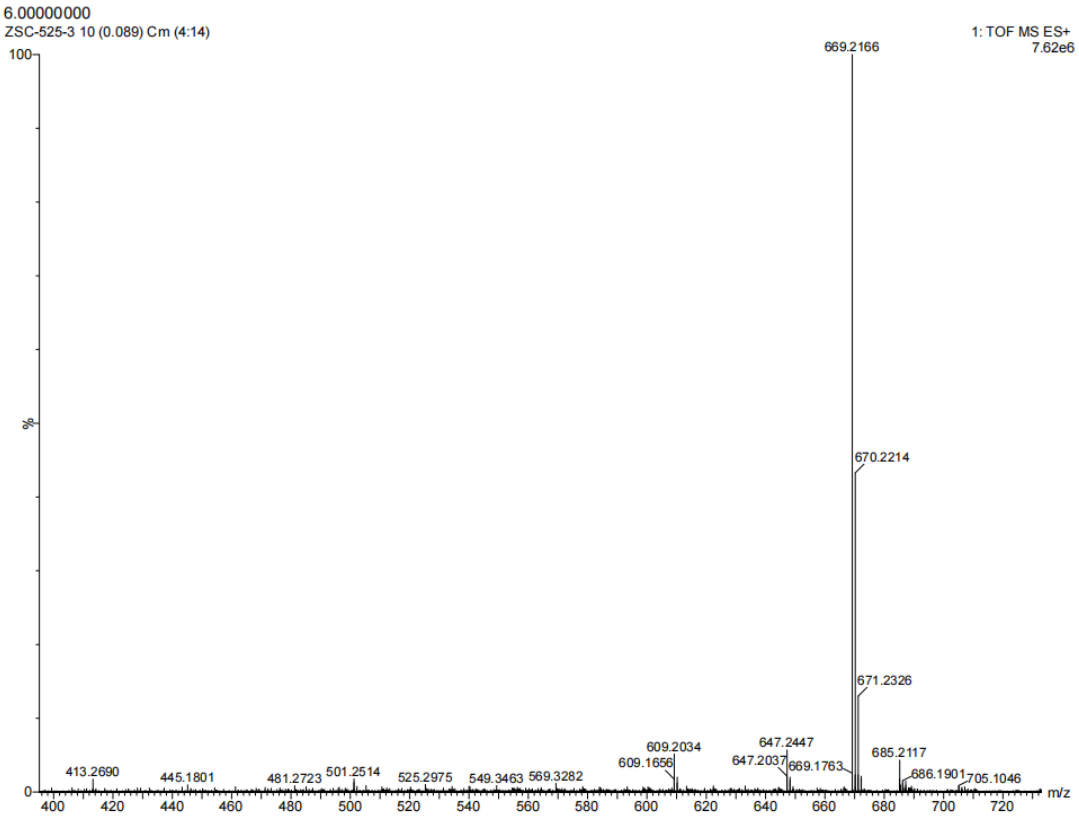
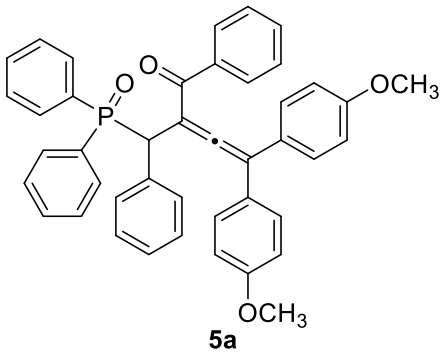


Figure S98. HRMS (ESI) spectrum of compound **5a**.



5a

Chemical Formula: $C_{43}H_{35}O_4P$
Exact Mass: 646.2273
Molecular Weight: 646.7228
m/z: 646.2273 (100.0%), 647.2307 (46.5%), 648.2340 (10.6%)
Elemental Analysis: C, 79.86; H, 5.46; O, 9.90; P, 4.79

HRMS (ESI, m/z) calcd for $C_{43}H_{35}O_4P$ $[M+Na]^+$ 669.2165, found 669.2166.

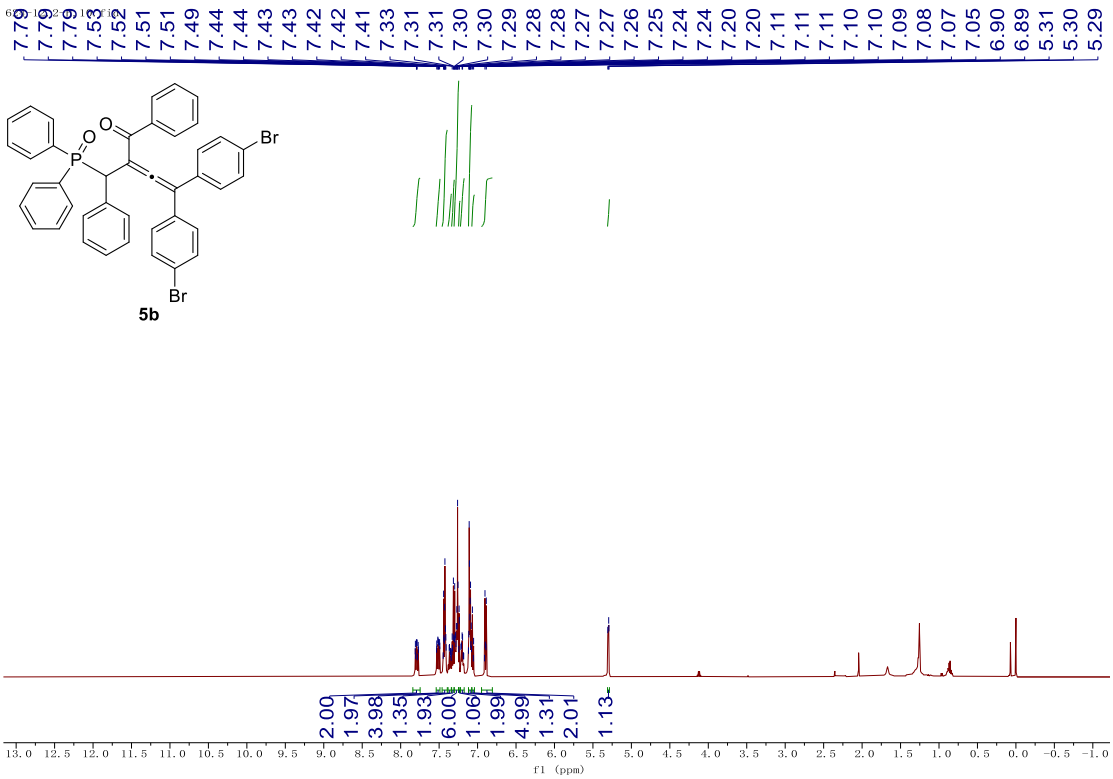


Figure S99. ^{1}H NMR spectrum of compound **5b** (500 MHz, $CDCl_3$).

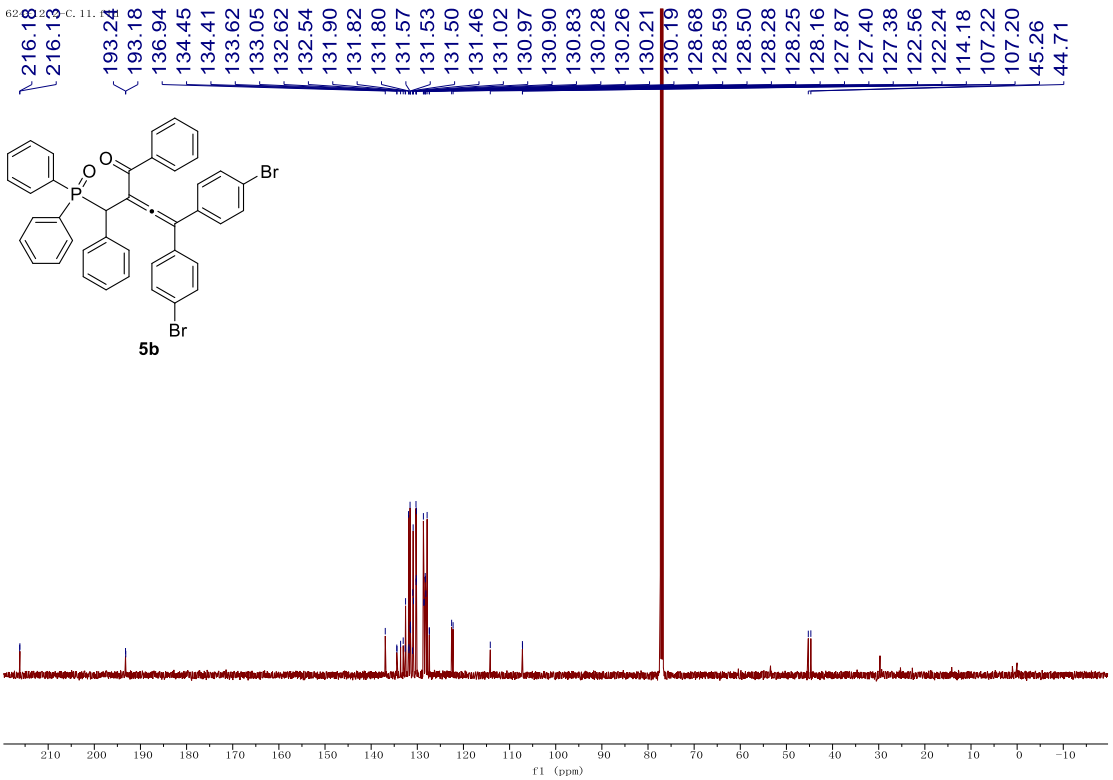


Figure S100. ^{13}C NMR spectrum of compound **5b** (126 MHz, $CDCl_3$).

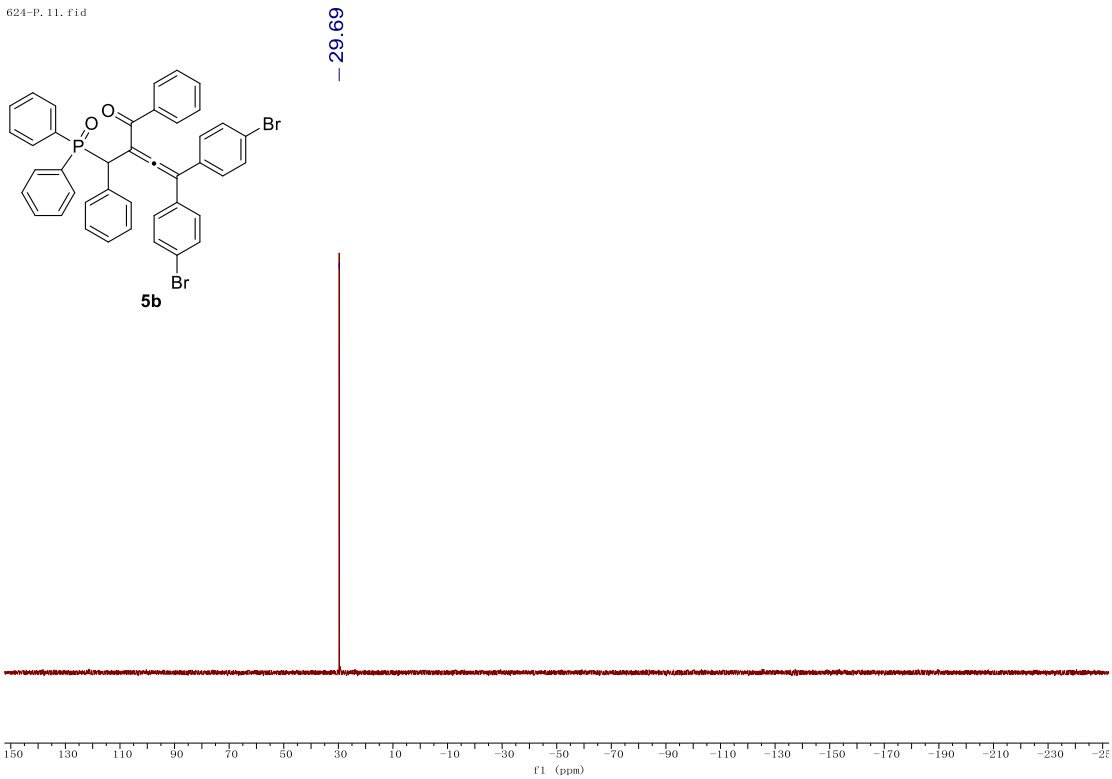


Figure S101. ^{31}P NMR spectrum of compound **5b** (202 MHz, $CDCl_3$).

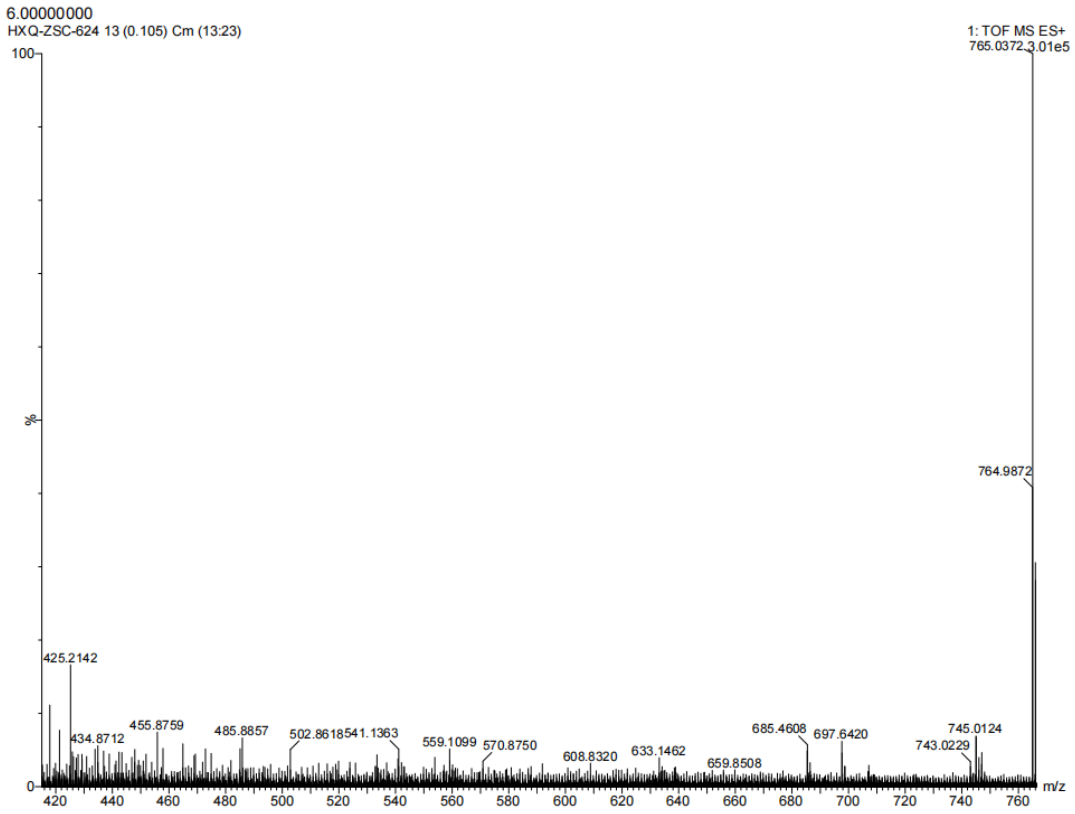
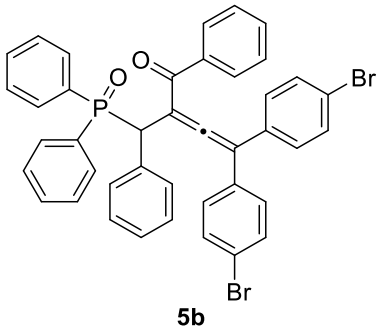


Figure S102. HRMS (ESI) spectrum of compound **5b**.



5b

Chemical Formula: $C_{41}H_{29}Br_2O_2P$
Exact Mass: 742.0272
Molecular Weight: 744.4628
m/z: 744.0251 (100.0%), 742.0272 (51.4%), 746.0231 (48.6%), 745.0285 (44.3%), 747.0265 (21.6%), 743.0305 (16.7%), 746.0319 (7.0%), 743.0305 (6.1%), 748.0298 (4.7%), 744.0339 (3.3%), 746.0319 (2.6%), 744.0339 (1.6%)
Elemental Analysis: C, 66.15; H, 3.93; Br, 21.47; O, 4.30; P, 4.16

HRMS (ESI, m/z) calcd for $C_{41}H_{29}Br_2O_2P$ $[M+Na]^+$ 765.0164, found 765.0372.

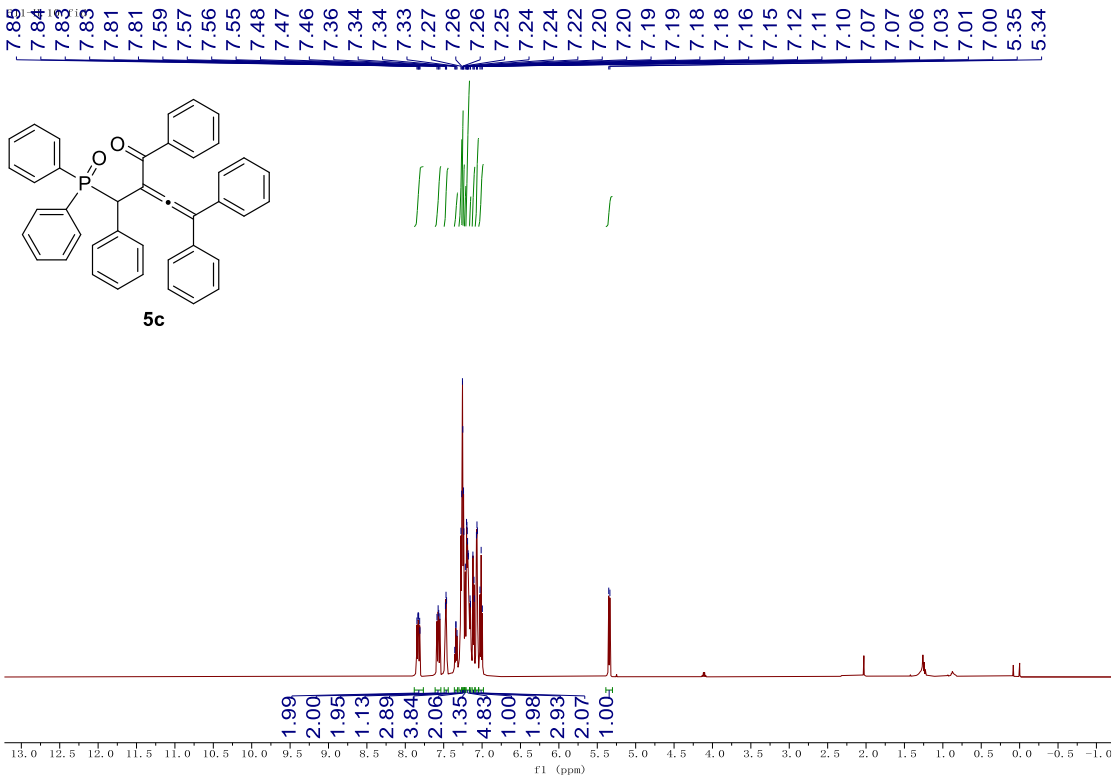


Figure S103. ^{1}H NMR spectrum of compound **5c** (500 MHz, $CDCl_3$).

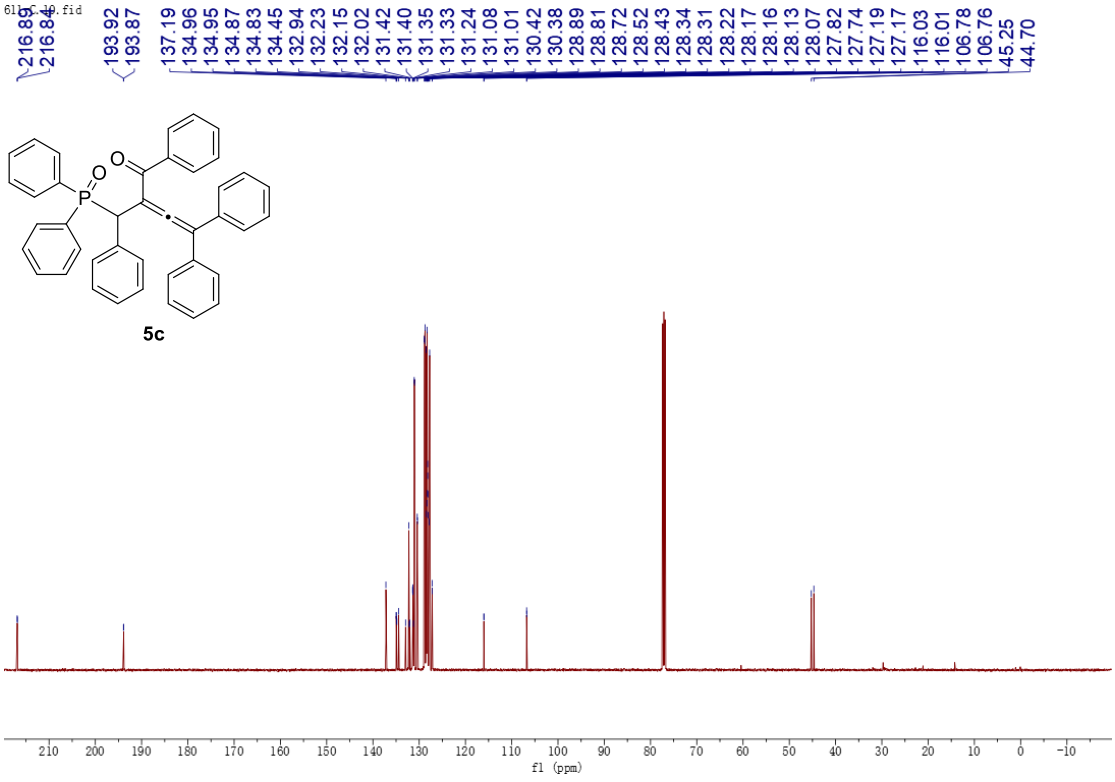


Figure S104. ^{13}C NMR spectrum of compound **5c** (126 MHz, $CDCl_3$).

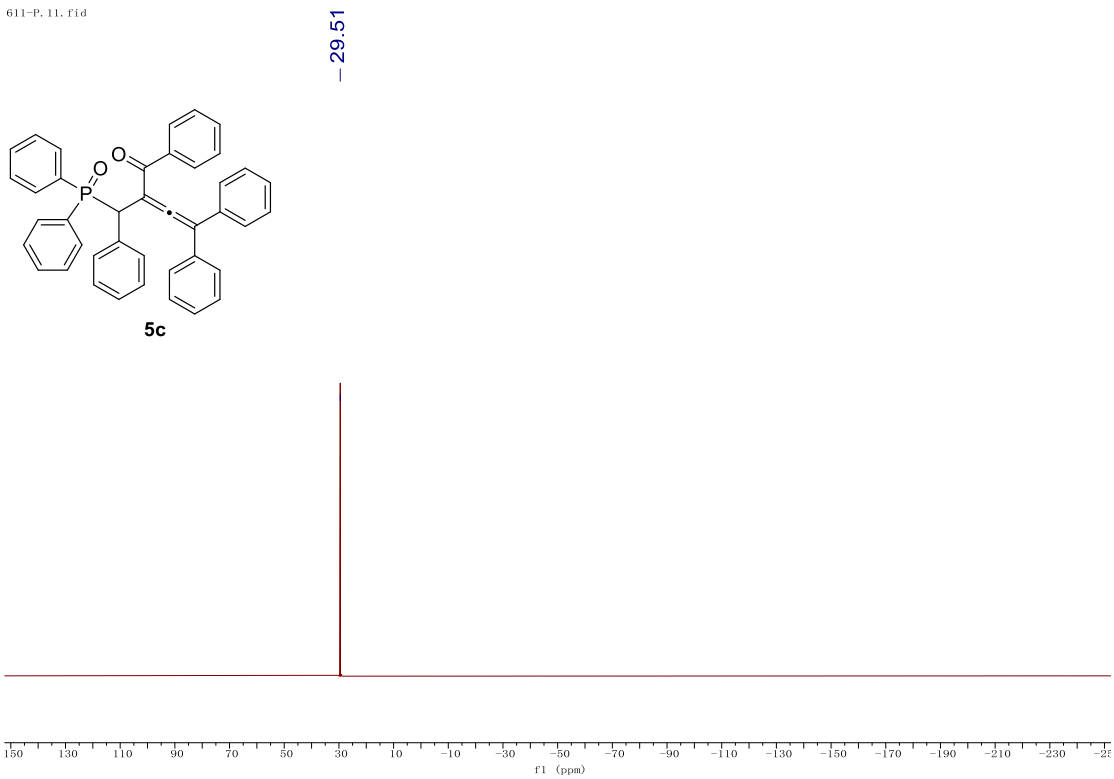


Figure S105. ^{31}P NMR spectrum of compound **5c** (202 MHz, $CDCl_3$).

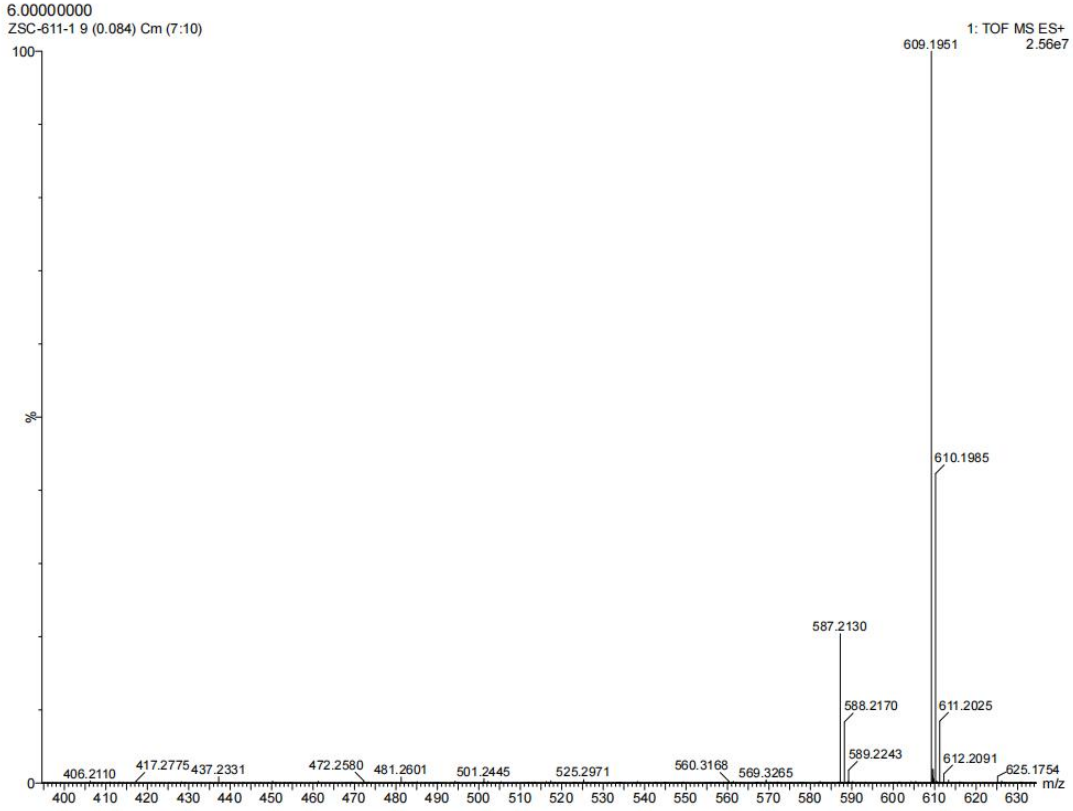
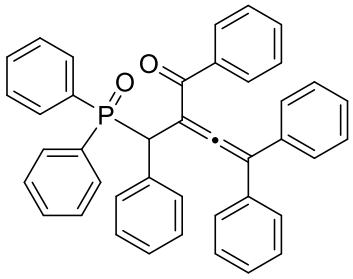


Figure S106. HRMS (ESI) spectrum of compound **5c**.



5c

Chemical Formula: $C_{41}H_{31}O_2P$
Exact Mass: 586.2062
Molecular Weight: 586.6708
m/z: 586.2062 (100.0%), 587.2095 (44.3%), 588.2129 (9.6%)
Elemental Analysis: C, 83.94; H, 5.33; O, 5.45; P, 5.28

HRMS (ESI, m/z) calcd for $C_{41}H_{31}O_2P$ $[M+Na]^+$ 609.1954, found 609.1951.

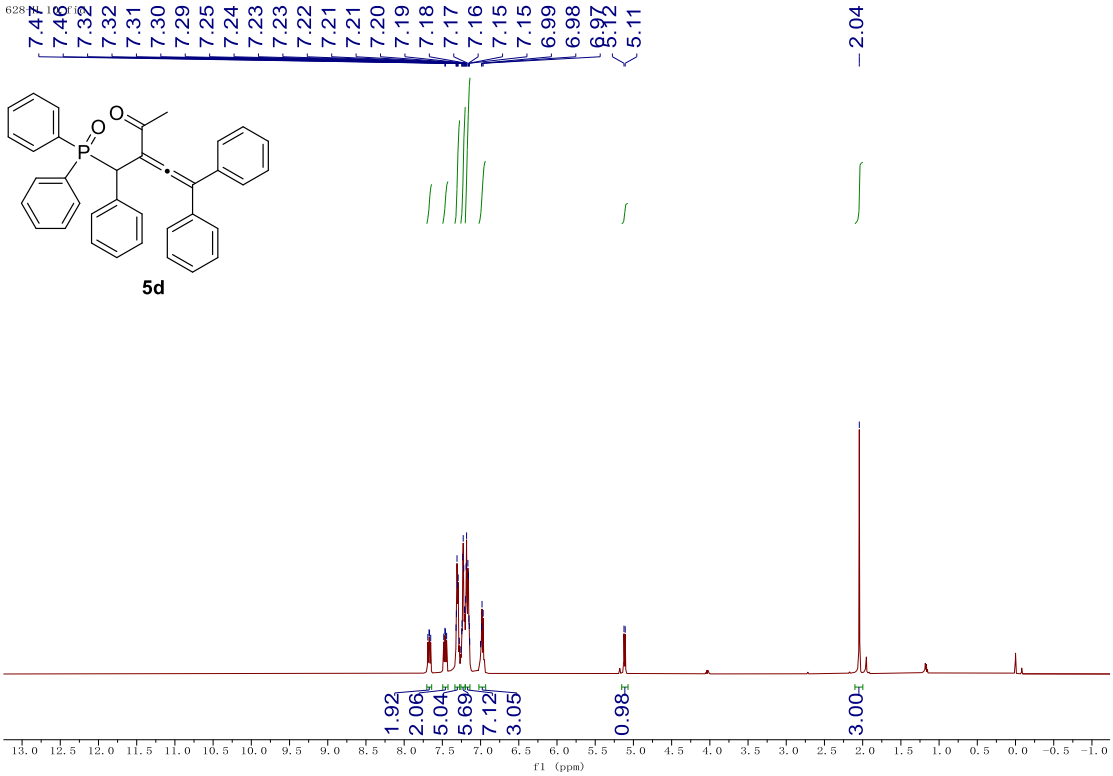


Figure S107. ^{1}H NMR spectrum of compound **5d** (500 MHz, $CDCl_3$).

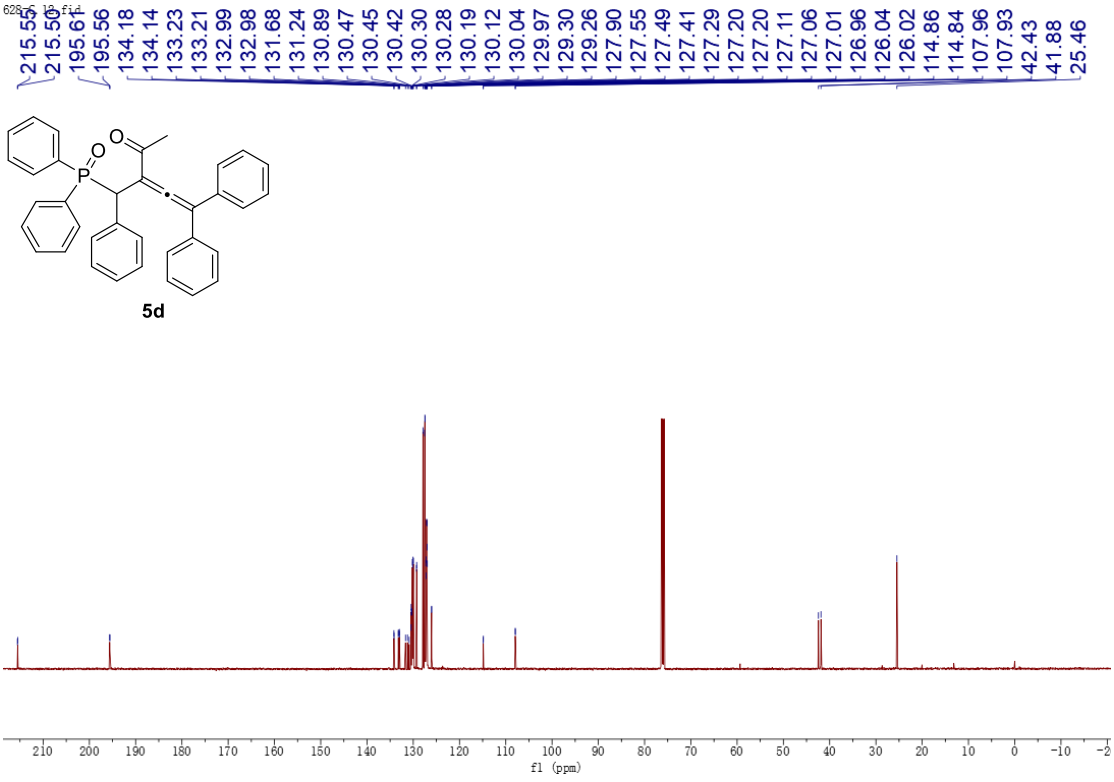


Figure S108. ^{13}C NMR spectrum of compound **5d** (126 MHz, $CDCl_3$).

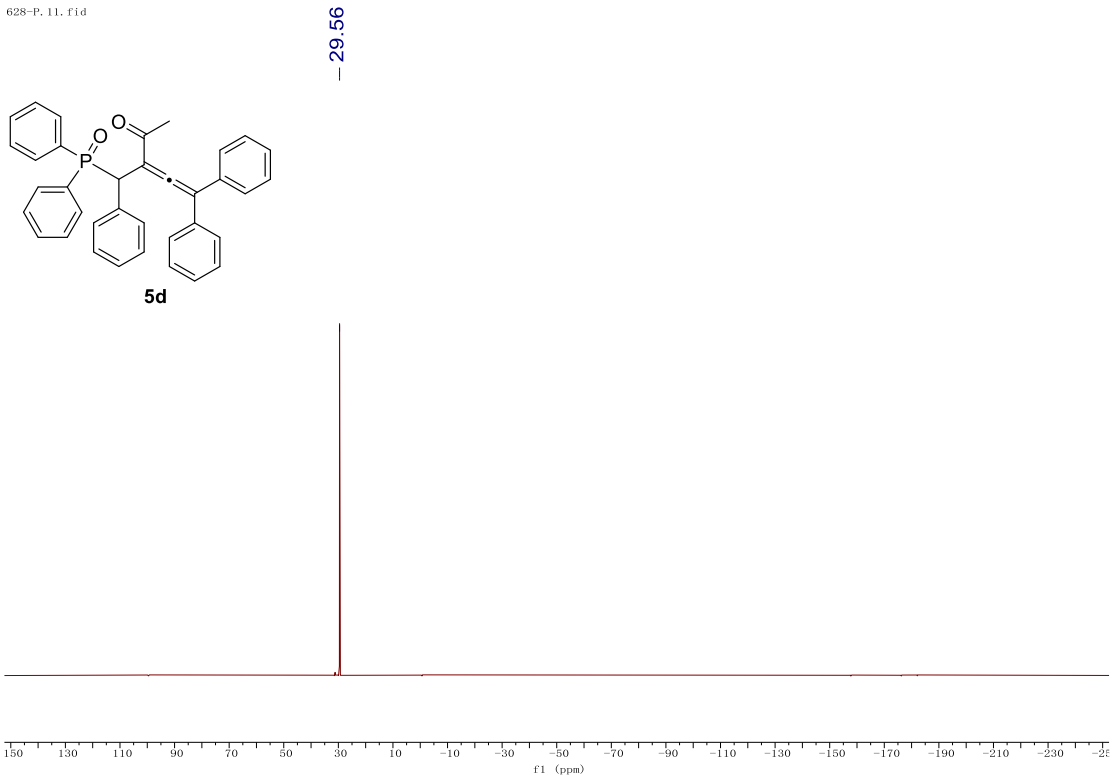


Figure S109. ^{31}P NMR spectrum of compound **5d** (202 MHz, $CDCl_3$).

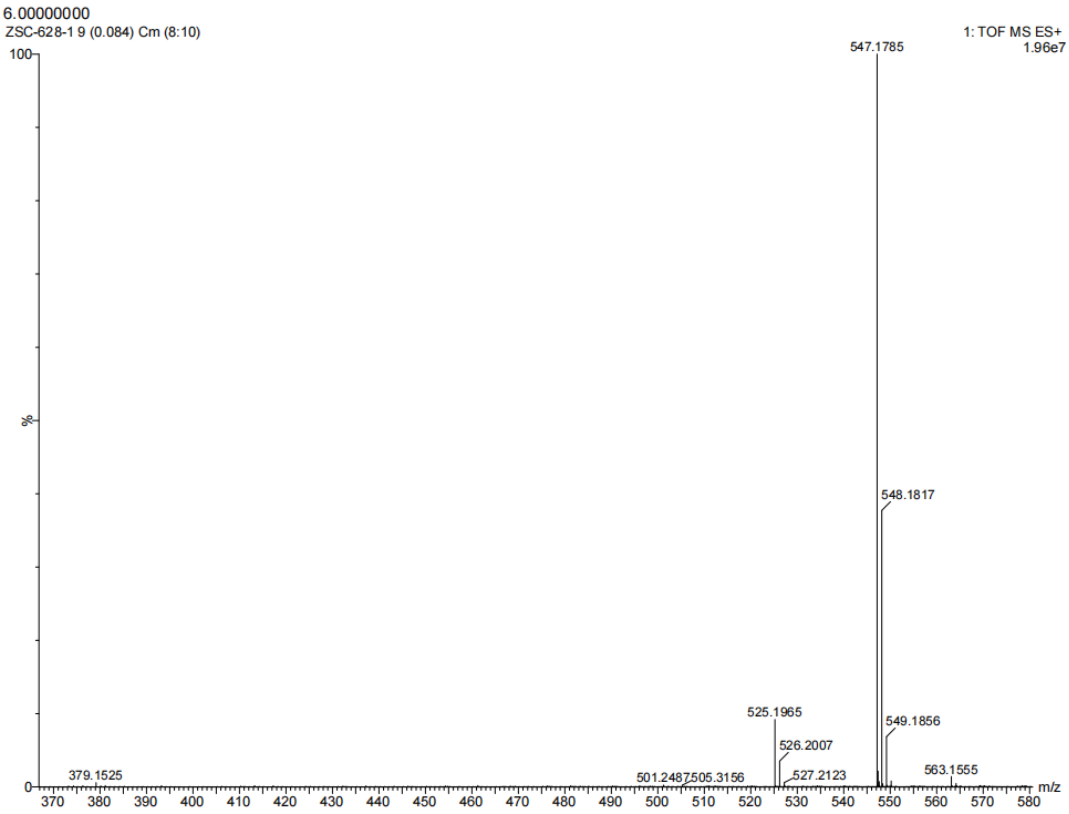
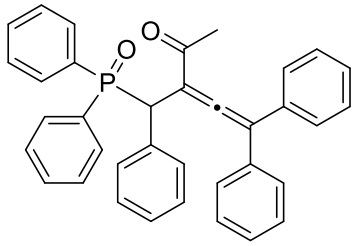


Figure S110. HRMS (ESI) spectrum of compound **5d**.



5d

Chemical Formula: $C_{36}H_{29}O_2P$
Exact Mass: 524.1905
Molecular Weight: 524.5998
m/z: 524.1905 (100.0%), 525.1939 (38.9%), 526.1972 (4.7%), 526.1972 (2.7%)
Elemental Analysis: C, 82.42; H, 5.57; O, 6.10; P, 5.90

HRMS (ESI, m/z) calcd for $C_{36}H_{29}O_2P$ $[M+Na]^+$ 547.1797, found 547.1785.

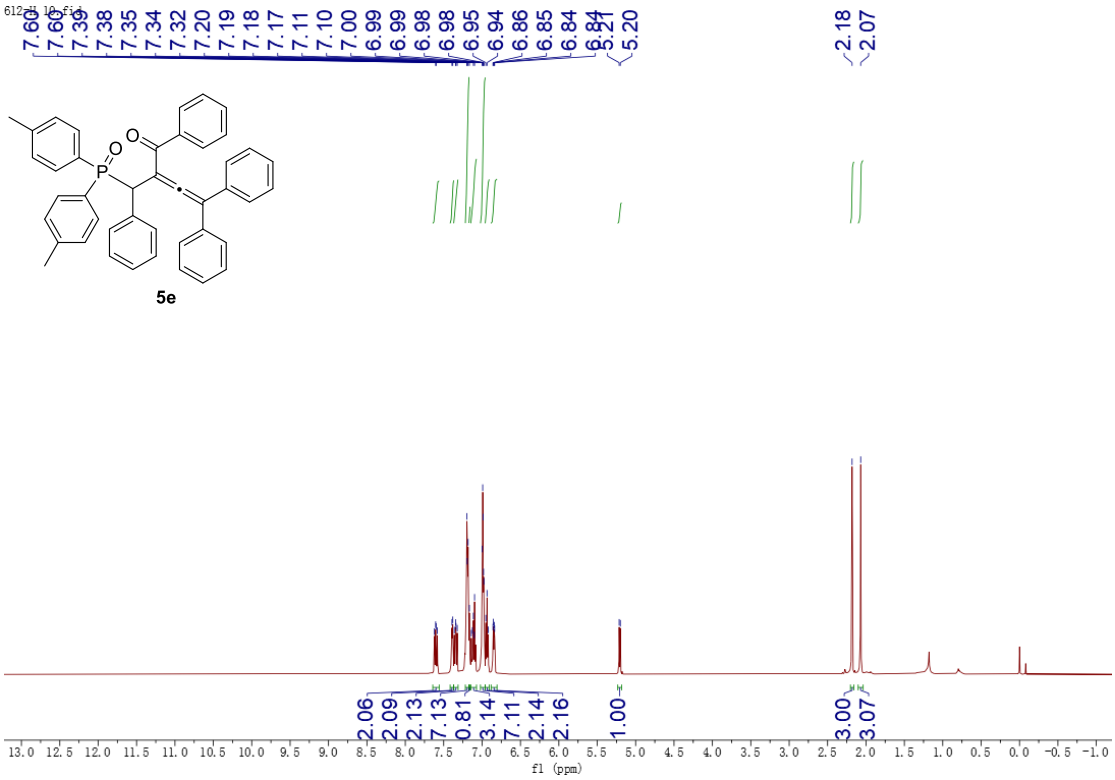


Figure S111. ^{1}H NMR spectrum of compound **5e** (500 MHz, $CDCl_3$).

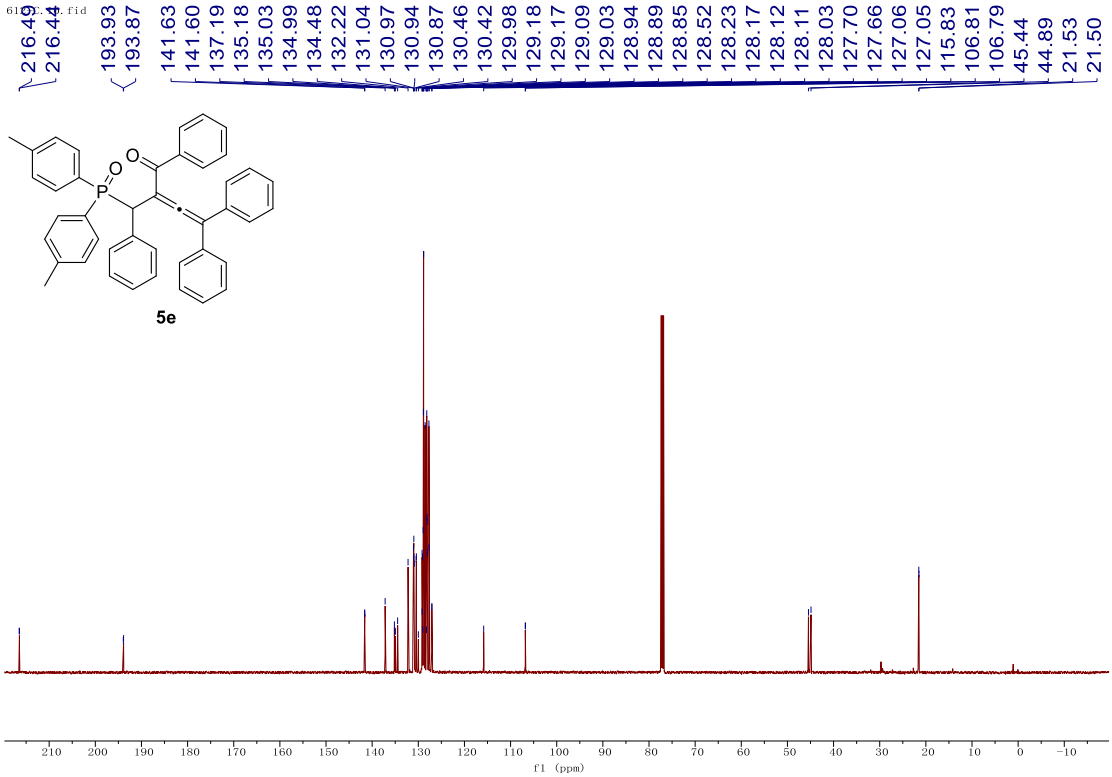


Figure S112. ^{13}C NMR spectrum of compound **5e** (126 MHz, $CDCl_3$).

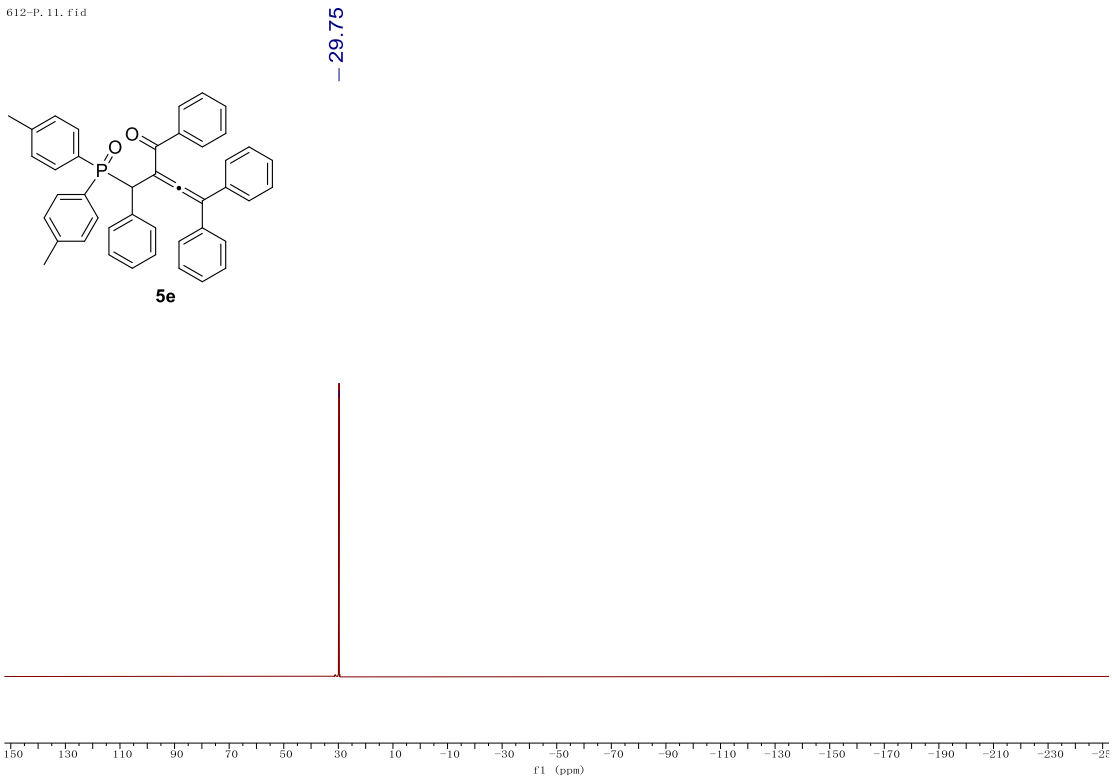


Figure S113. ^{31}P NMR spectrum of compound **5e** (202 MHz, $CDCl_3$).

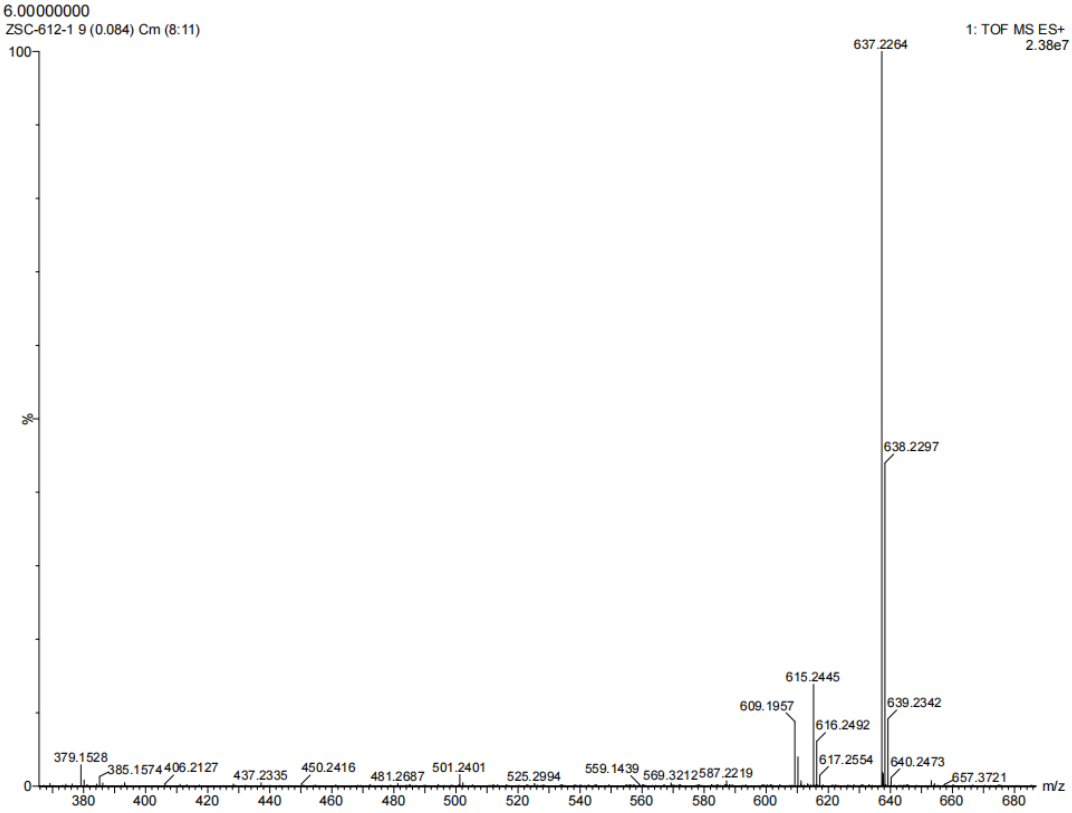
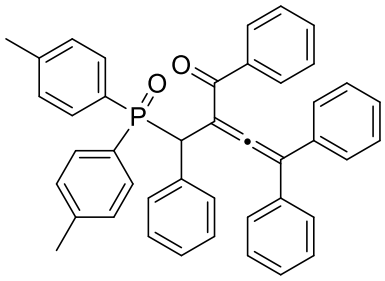


Figure S114. HRMS (ESI) spectrum of compound **5e**.



5e

Chemical Formula: $C_{43}H_{35}O_2P$
Exact Mass: 614.2375
Molecular Weight: 614.7248
m/z: 614.2375 (100.0%), 615.2408 (46.5%), 616.2442 (10.6%), 617.2475 (1.6%)
Elemental Analysis: C, 84.02; H, 5.74; O, 5.21; P, 5.04

HRMS (ESI, m/z) calcd for $C_{43}H_{35}O_2P$ $[M+Na]^+$ 637.2267, found 637.2264.

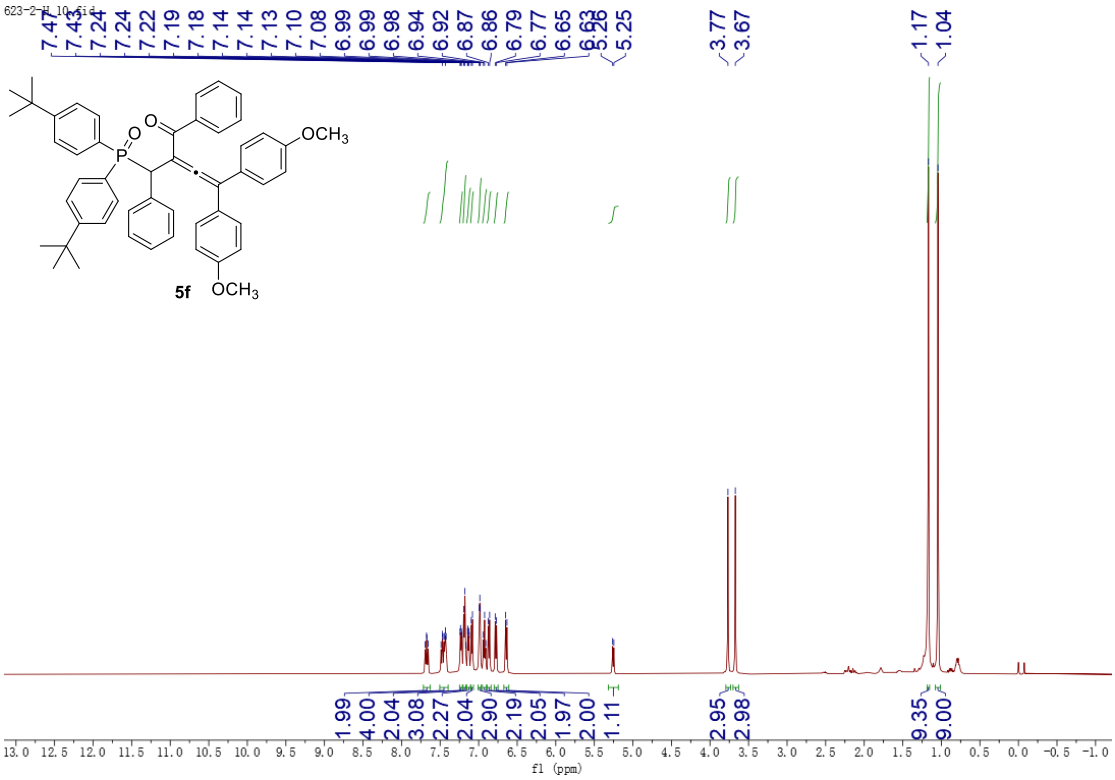


Figure S115. ^{1}H NMR spectrum of compound **5f** (500 MHz, $CDCl_3$).

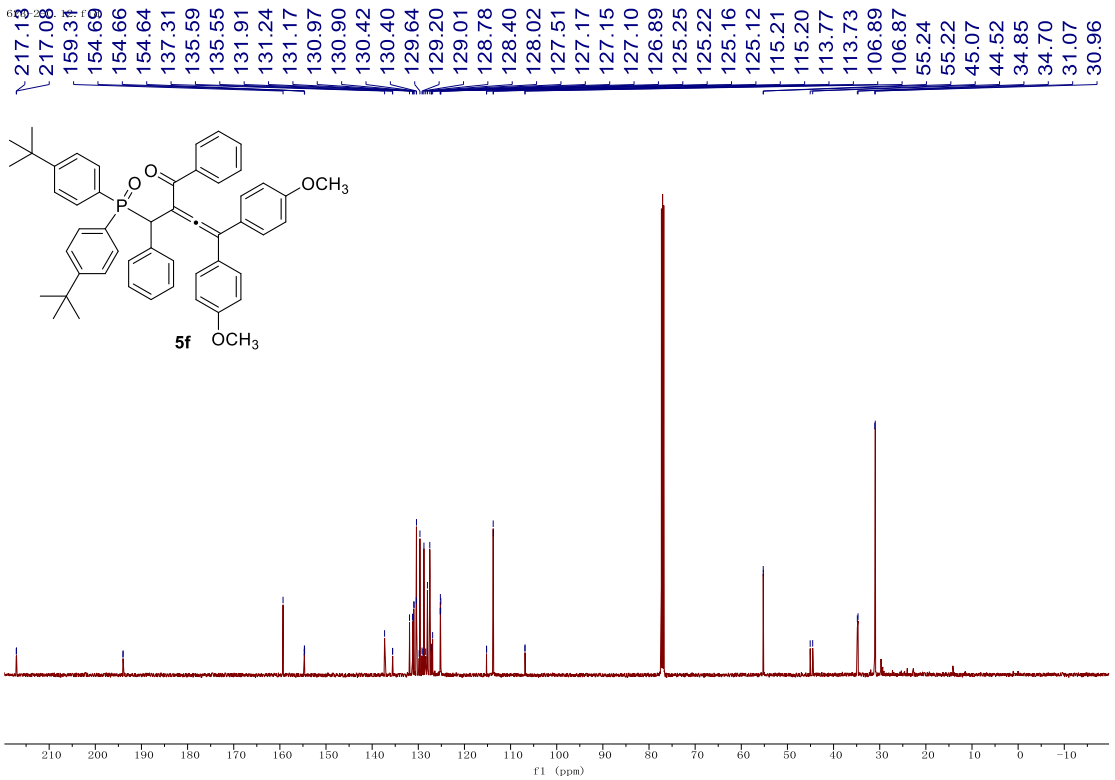


Figure S116. ^{13}C NMR spectrum of compound **5f** (126 MHz, $CDCl_3$).

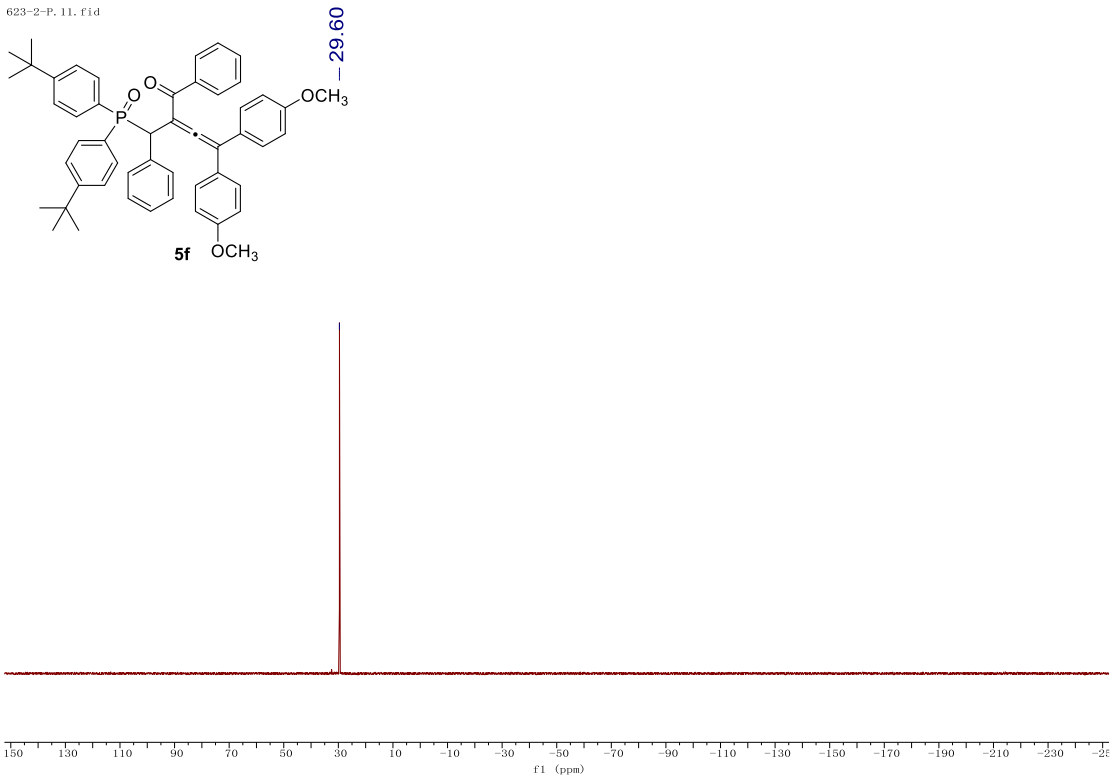


Figure S117. ^{31}P NMR spectrum of compound **5f** (202 MHz, $CDCl_3$).

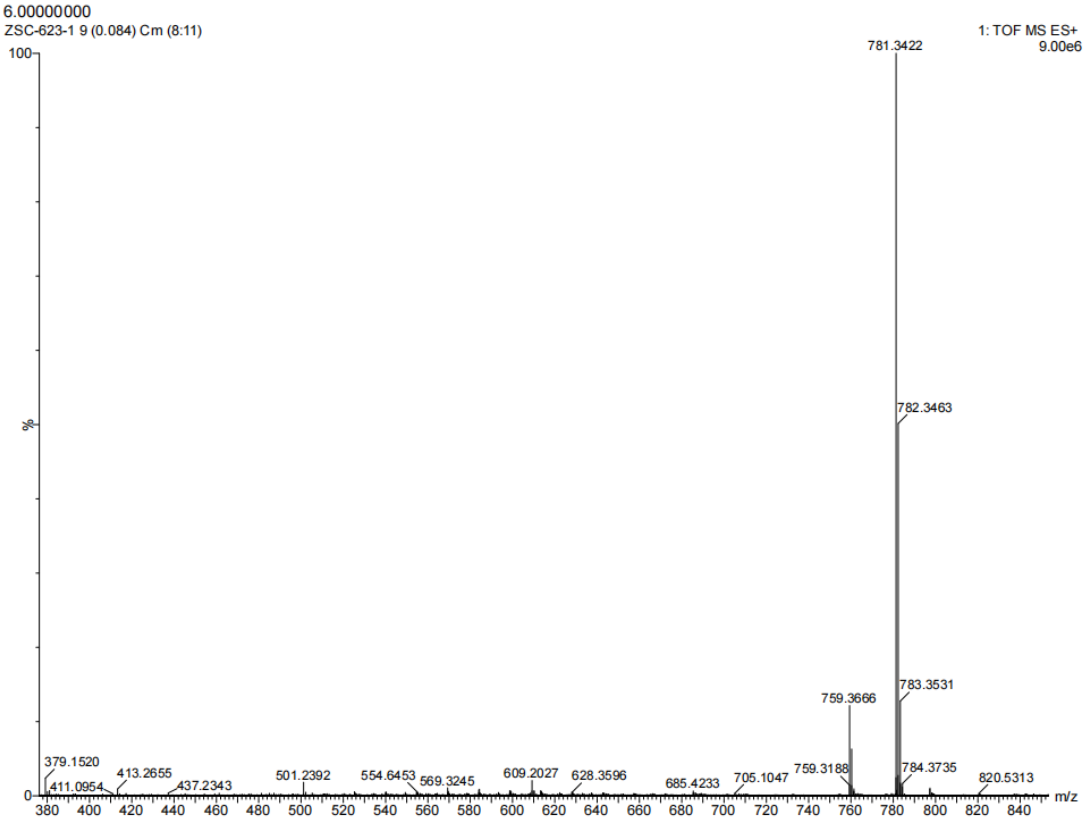
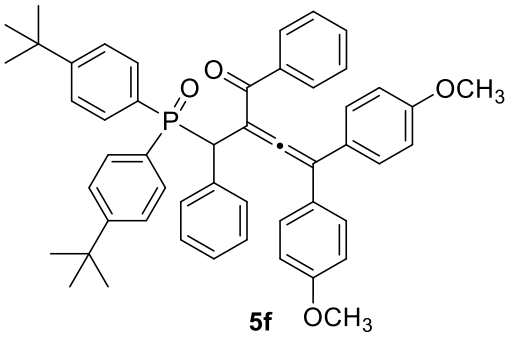


Figure S118. HRMS (ESI) spectrum of compound **5f**.



5f

Chemical Formula: $C_{51}H_{51}O_4P$
Exact Mass: 758.3525
Molecular Weight: 758.9388
m/z: 758.3525 (100.0%), 759.3559 (55.2%), 760.3592 (14.9%), 761.3626 (1.8%)
Elemental Analysis: C, 80.71; H, 6.77; O, 8.43; P, 4.08

HRMS (ESI, m/z) calcd for $C_{51}H_{51}O_4P$ $[M+Na]^+$ 781.3417, found 781.3422.

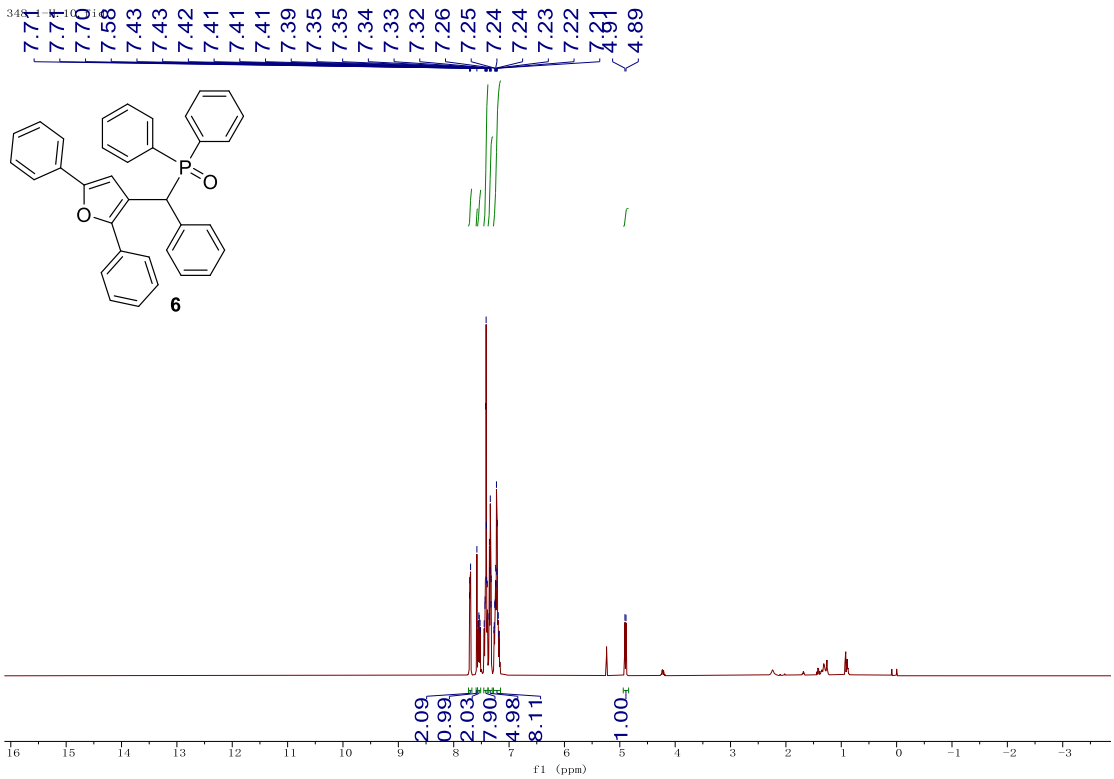


Figure S119. ^{1}H NMR spectrum of compound **6** (500 MHz, $CDCl_3$).

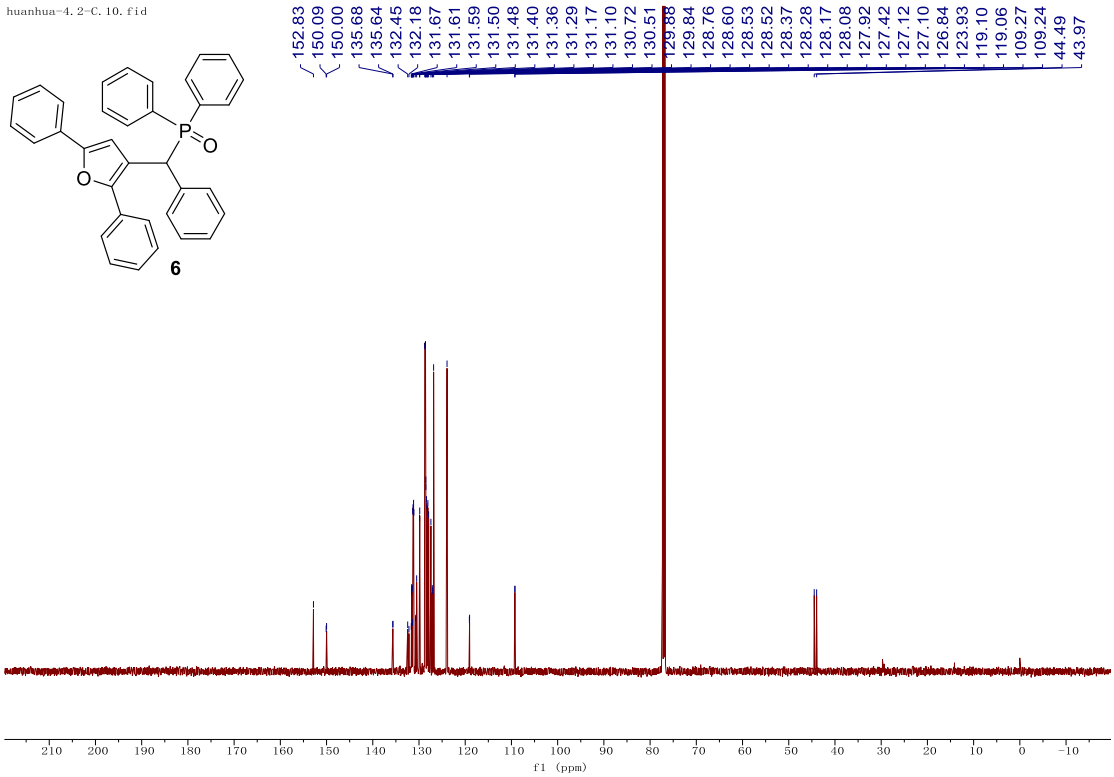


Figure S120. ^{13}C NMR spectrum of compound **6** (126 MHz, $CDCl_3$).

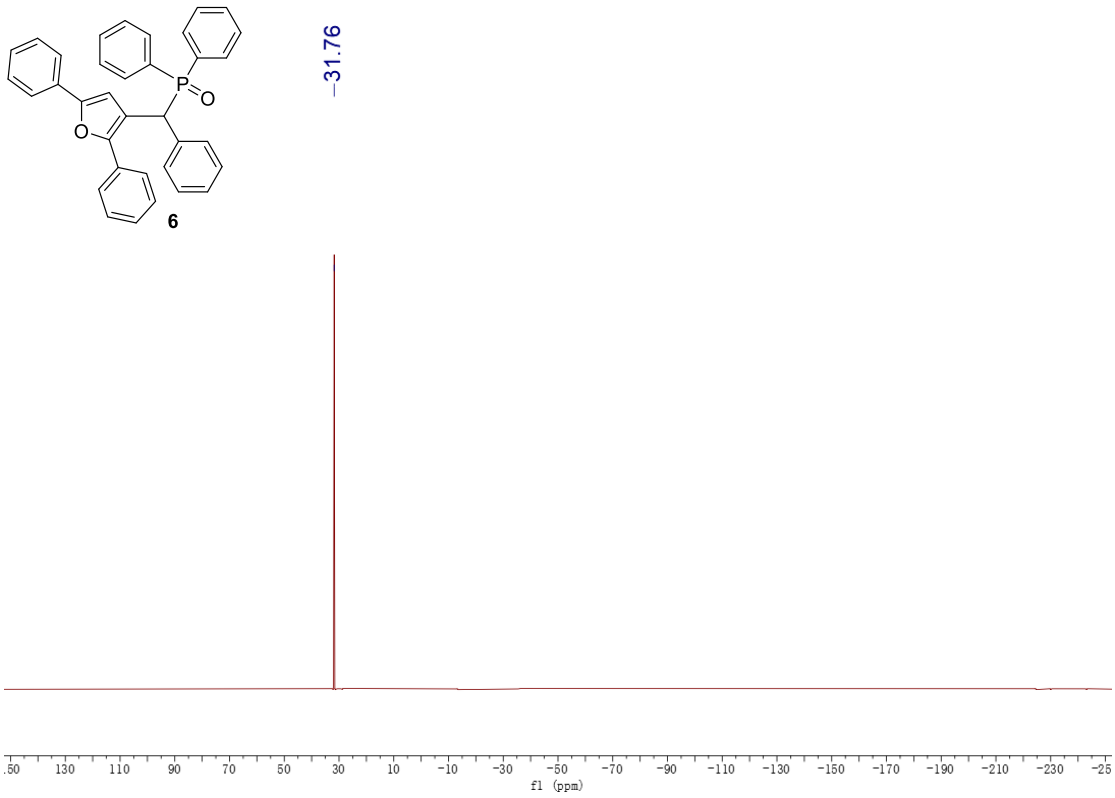


Figure S121. ^{31}P NMR spectrum of compound **6** (202 MHz, $CDCl_3$).

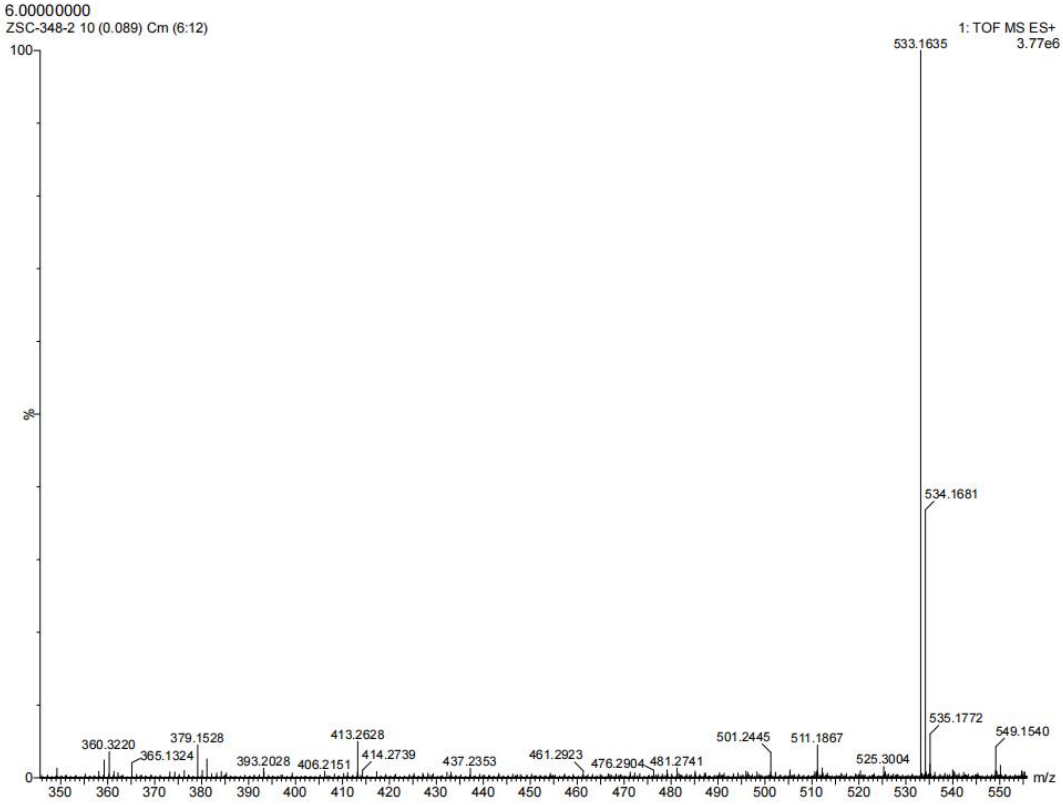
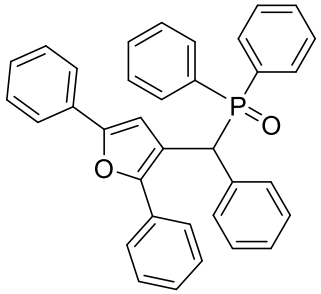


Figure S122. HRMS (ESI) spectrum of compound **6**.



6

Chemical Formula: $C_{35}H_{27}O_2P$
Exact Mass: 510.1749
Molecular Weight: 510.5728
m/z: 510.1749 (100.0%), 511.1782 (37.9%), 512.1816 (4.3%), 512.1816 (2.7%)
Elemental Analysis: C, 82.34; H, 5.33; O, 6.27; P, 6.07

HRMS (ESI, m/z) calcd for $C_{35}H_{27}O_2P$ $[M+Na]^+$ 533.1641, found 533.1635.

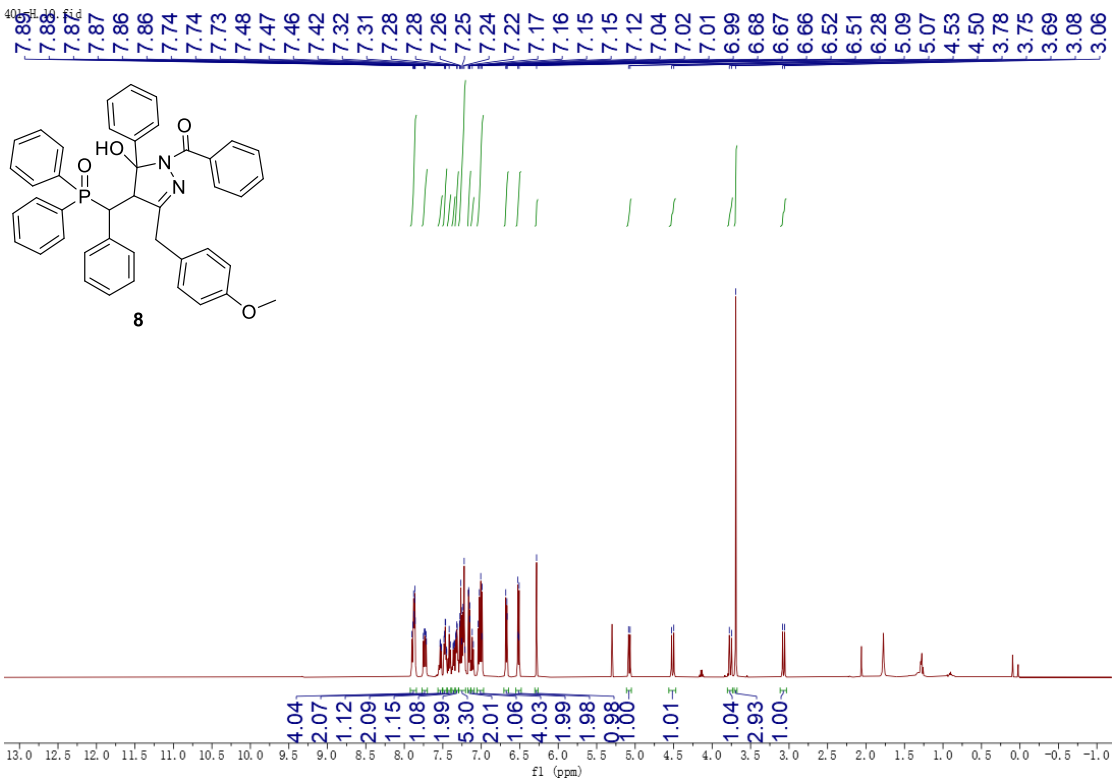


Figure S123. ^{1}H NMR spectrum of compound **8** (500 MHz, $CDCl_3$).

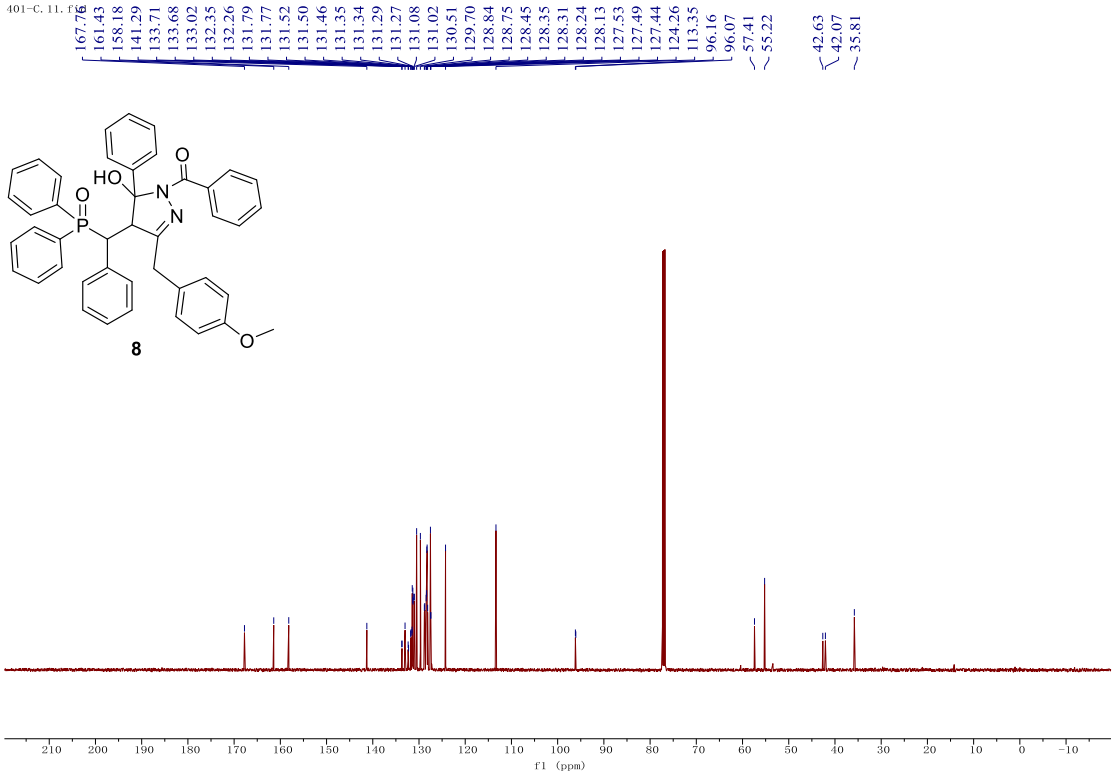


Figure S124. ^{13}C NMR spectrum of compound **8** (126 MHz, $CDCl_3$).

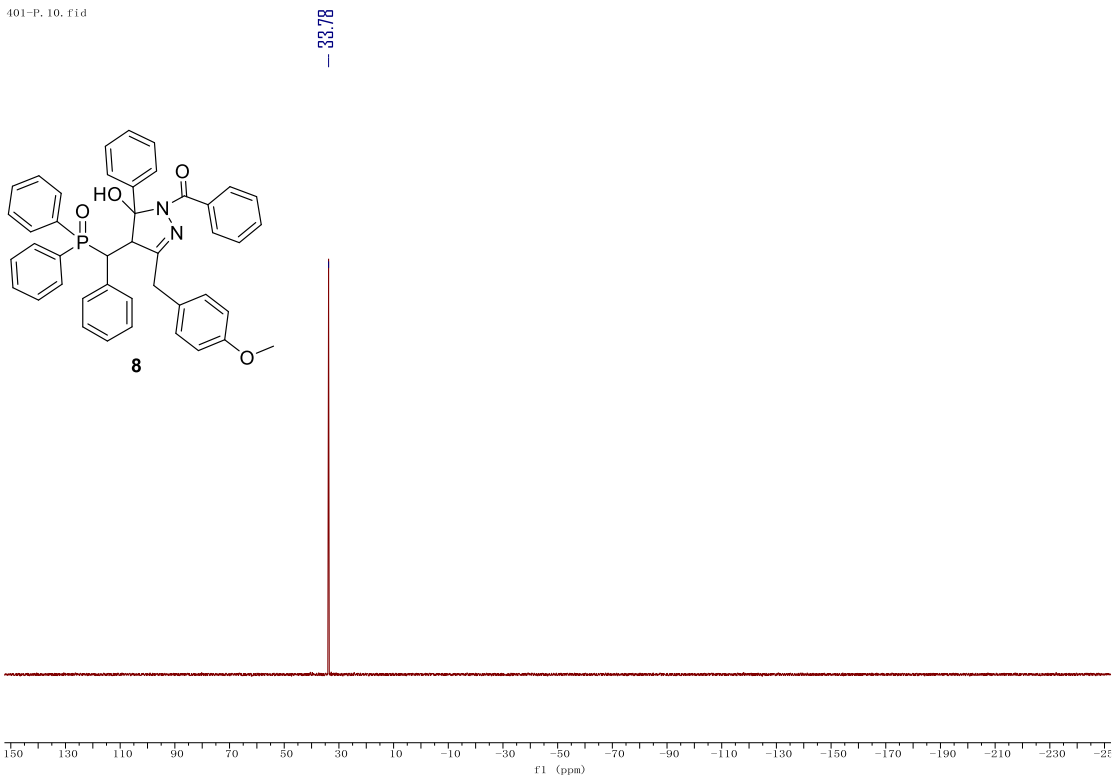


Figure S125. ^{31}P NMR spectrum of compound **8** (202 MHz, $CDCl_3$).

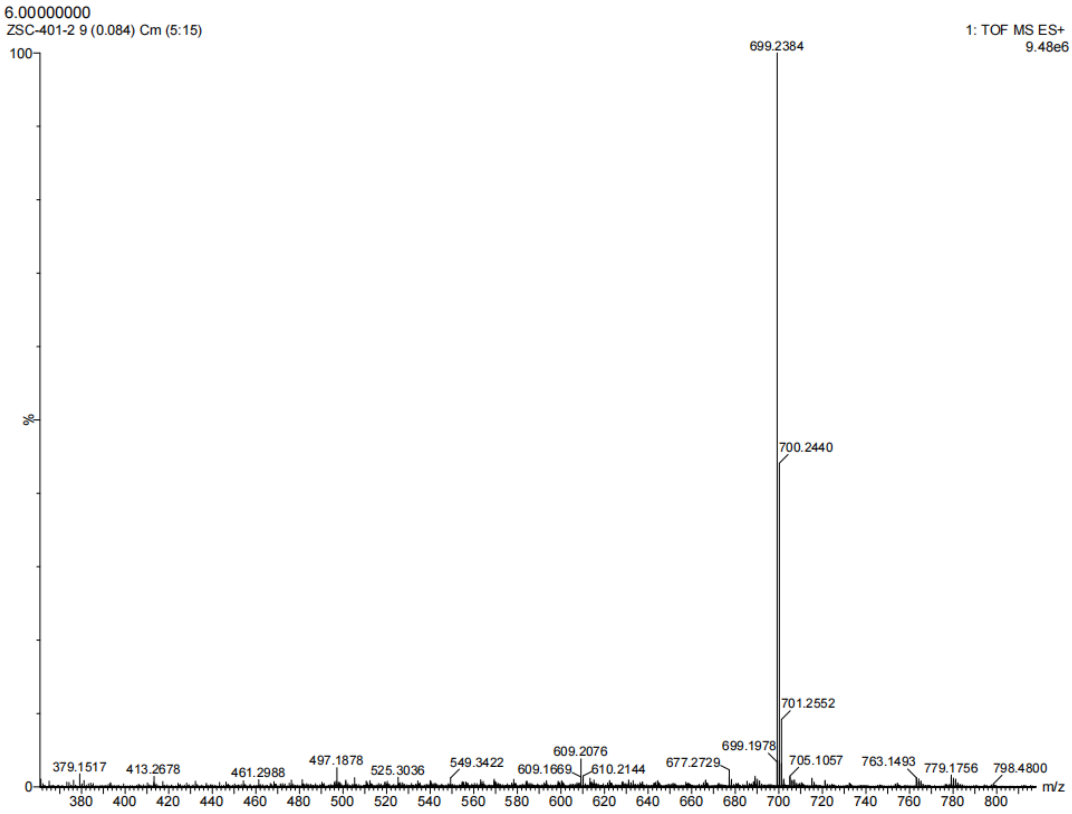
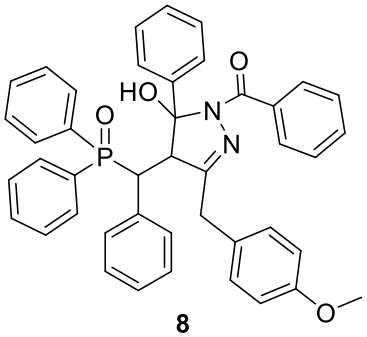


Figure S126. HRMS (ESI) spectrum of compound **8**.



8

Chemical Formula: $C_{43}H_{37}N_2O_4P$
Exact Mass: 676.2491
Molecular Weight: 676.7528
m/z: 676.2491 (100.0%), 677.2524 (46.5%), 678.2558 (10.6%)
Elemental Analysis: C, 76.32; H, 5.51; N, 4.14; O, 9.46; P, 4.58

HRMS (ESI, m/z) calcd for $C_{43}H_{37}N_2O_4P$ $[M+Na]^+$ 699.2383, found 699.2384.