Supporting Information

Photoinduced Cobaloxime Catalysis for Allylic Mono- and Diphosphinylation of Alkenes with Hydrogen Evolution

Aijun Zhang,[a] Miao-Miao Li,*[a] Lei Guo,[b] Huaixiang Yang,[a] Jiefei Guo,[a] Da Xu,[b] and Wei Ding*[a]

[a] *Division of Molecular Catalysis and Synthesis, Henan Institute of Advanced Technology, Zhengzhou University, Zhengzhou 450001, P. R. China*

[b] *Technology Center, China Tobacco Jiangxi Industrial Co. Ltd., Nanchang 330096, P. R. China.*

Contents

1. General Information 2
2. Preparation of Starting Materials 4
3. Optimization of Reaction Conditions 10
4. Experimental Procedures and Product Characterization 13
5. Product Transformations 72
6. Mechanistic Studies 76
7. X-Ray Diffraction Analysis 87
8. References 93
9. NMR Spectra 95

1. General Information

General. All reactions dealing with air or moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere or in an argon-filled glove box. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed as described by Still et al., using 200-300 mesh silica gel. ^{1}H, ^{13}C, ^{31}P and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCE NEO 400 M NMR spectrometers in Zhengzhou University (North Campus). ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm), $CDCl_3$ (77.0 ppm) and DMSO-d_6 (39.5 ppm), respectively. High-resolution mass spectra (HRMS) were obtained with an Agilent 6210 ESI/TOF mass spectrometer. Melting points were determined using a capillary melting point apparatus.

Materials. Unless otherwise noted, commercial reagents were purchased from Energy Chemical, Bidepharm, J&K Scientific or other commercial suppliers and were used as received. DCM, DCE and MeCN were distilled over CaH_2 and stored under Ar. Toluene and THF were distilled over Na/benzophenone, and stored under Ar. Anhydrous DMF and DMC were purchased from J&K Scientific. Except for some commercially available compounds, cobaloxime catalysts were prepared according to the literature procedures.[1]

Photoreactor. The photoreactors used in this research were bought from GeAo Chem (Figure S1: blue LEDs). Two parallel LED lamps (total 40 W, λ_{max} = 450 nm) are placed perpendicular to the sidewall of the reaction vessels, so that the reaction vessels can be equally exposed to LEDs (about 5 W was distributed to each hole). 10 mL Schlenk tube bought from SYNTHWARE GLASS, was used as photoreaction vessel, which was positioned 2-3 cm from the blue LED lamp. During the reaction, a pinch fan at one end of the equipment keeps working, counteracting the heat generated by the LED lamp and stabilizing the reaction temperature

Figure S1. Photoreaction set-up and reaction vessel.

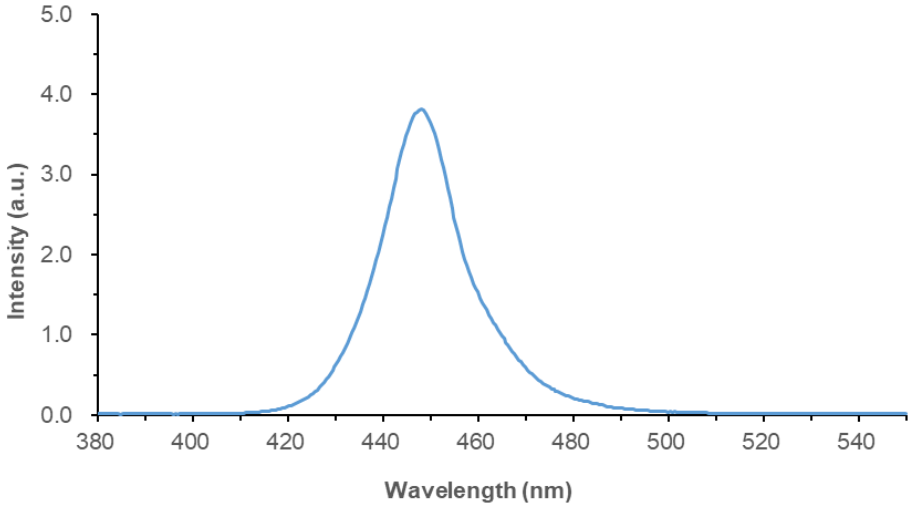
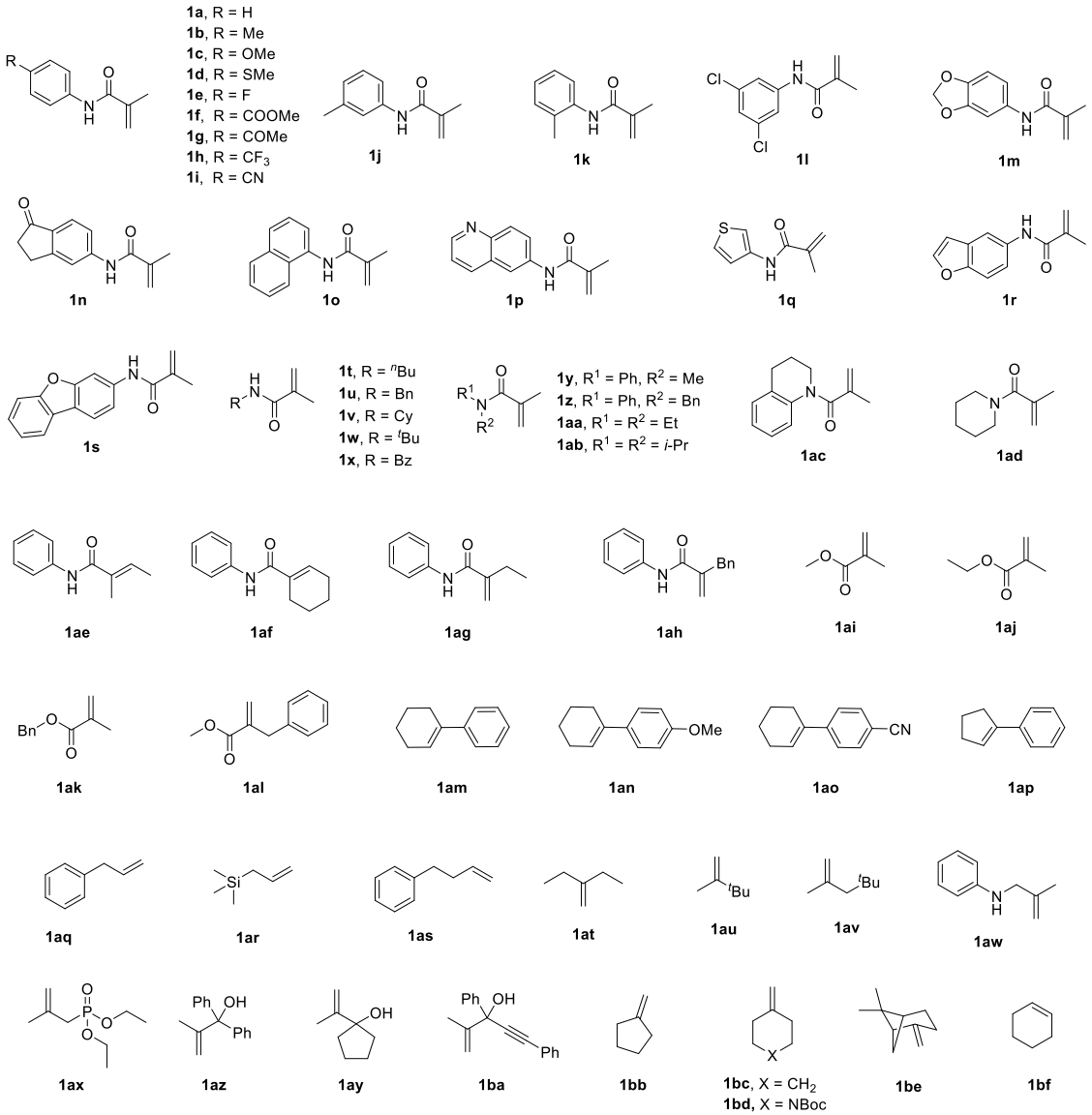


Figure S2. Light spectrum of the photon source: 40 W blue LEDs (λ_{max} = 450 nm).

2. Preparation of Starting Materials

Except for some commercially available compounds, N-phenylmethacrylamide **1a-1c**[2], **1e-1p**[2], **1t-1w**[2], **1x**[3], **1y-1ad**[2],**1ae-1ah**[4], **1am-1ap**[5], **1aw**[6], **1ax**[7], **1az-1ba**[8], **1bg-1bh**[9], **1bo**[10], **1bp-1bq**[2], and phosphine oxides **2c**[11], **2e**[12], **2f-2i**[13], **2m-2n**[12], **2o**[13], **2p**[12] were prepared according to the literature procedures, and purified by flash chromatography on silica gel. Spectral data showed good agreement with the literature data.



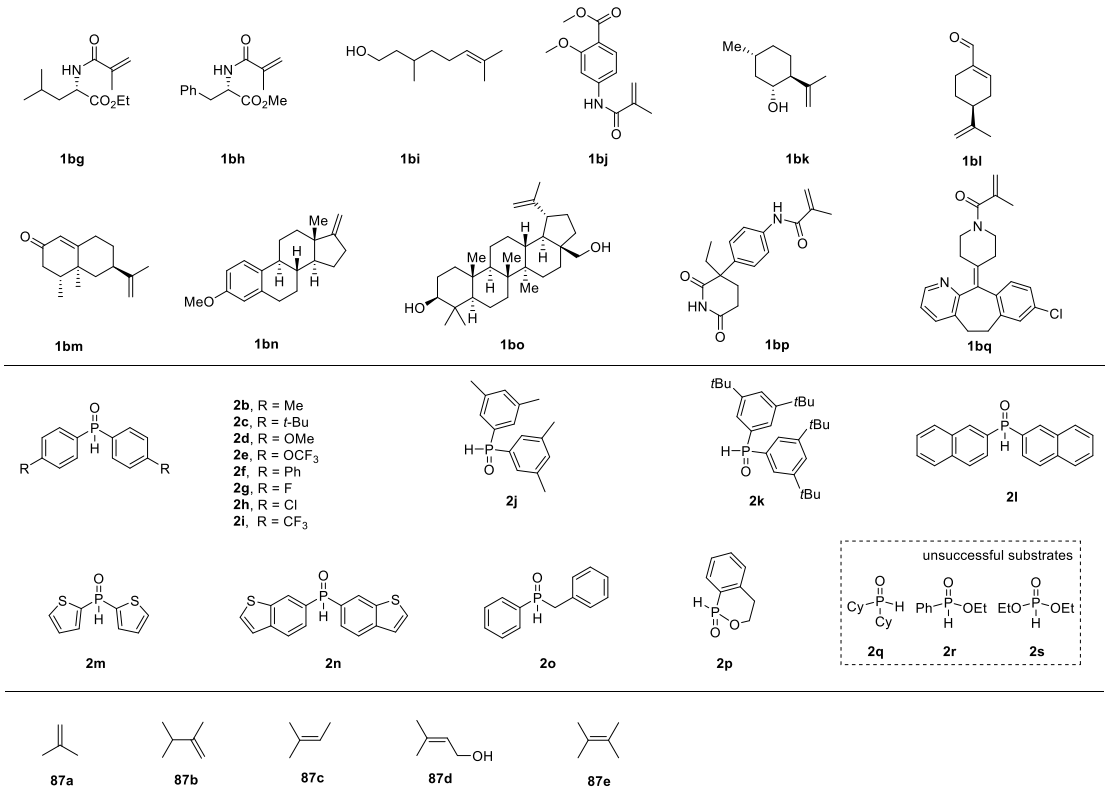
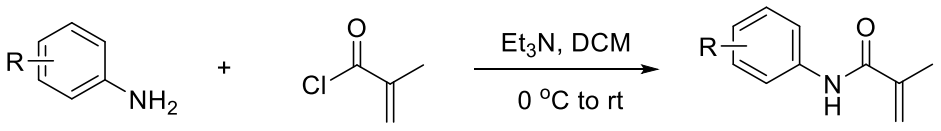
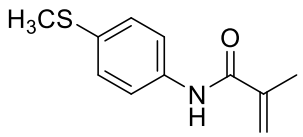


Figure S3. Alkene and secondaryl phosphine oxides in this study.

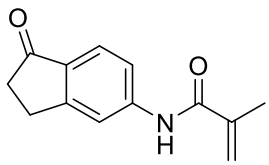


S1 **S2** **1**

General Procedure A: A solution of aniline **S1** (8 mmol) in DCM (25 mL) was cooled to 0 °C in an ice bath, then Et_3N (1.33 mL, 9.6 mmol) and methacryloyl chloride **S2** (0.93 mL, 9.6 mmol) were added. The resulting solution was stirred at room temperature and monitored by TLC. Then, saturated aq. solution of $NaHCO_3$ was added and extracted with DCM. The organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel.

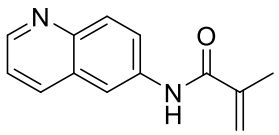


N-(4-(Methylthio)phenyl)methacrylamide (1d): Prepared according to the general procedure A with 4-(methylmercapto)aniline (8 mmol) and methacryloyl chloride, and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to provide the title compound **1d** as a white solid (1.02 g, 62% yield); R_f 0.2 (petroleum ether/ethyl acetate = 5/1); m.p. 116.9-118.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1 H),7.49 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 5.78 (s, 1H), 5.45 (s, 1H), 2.47 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 140.9, 135.4, 133.8, 128.0, 120.6, 119.8, 18.7, 16.7; HRMS (ESI) Calcd for $C_{11}H_{13}NOSNa$ $[M + Na]^+$ 230.0610, found 230.0623.

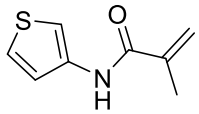


N-(1-Oxo-2,3-dihydro-1*H*-inden-5-yl)methacrylamide (1n): Prepared according to the general procedure A with 5-aminoindan-1-one (8 mmol) and methacryloyl chloride,

and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to provide the title compound **1n** as a white solid (1.12 g, 64% yield); R_f 0.1 (petroleum ether/ethyl acetate = 10/1); m.p. 143.8-145.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 5.83 (s, 1H), 5.53 (s, 1H), 3.13 (t, *J* = 6.0 Hz, 2H), 2.75-2.65 (m, 2H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.6, 166.8, 157.1, 143.8, 140.7, 133.0, 124.6, 120.5, 119.0, 116.7, 36.4, 25.9, 18.6; HRMS (ESI) Calcd for $C_{13}H_{13}NO_2Na$ $[M + Na]^+$ 238.0838, found 238.0843.

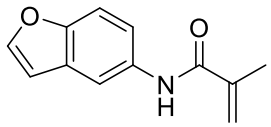


N-(Quinolin-6-yl)methacrylamide (1p): Prepared according to the general procedure A with 6-aminoquinoline (8 mmol) and methacryloyl chloride, and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to provide the title compound **1p** as a white solid (1.21 g, 71% yield); R_f 0.1 (petroleum ether/ethyl acetate = 5/1); m.p. 117.1-118.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.43 (d, *J* = 2.5 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.77 (s, 1H), 7.60 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.86 (s, 1H), 5.53 (s, 1H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 149.5, 145.5, 140.7, 135.9, 135.7, 130.1, 128.8, 123.4, 121.6, 120.2, 116.4, 18.7; HRMS (ESI) Calcd for $C_{13}H_{13}N_2O$ $[M + H]^+$ 213.1022, found 213.1031.

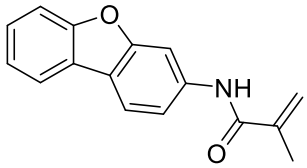


N-(Thiophen-3-yl)methacrylamide (1q): Prepared according to the general procedure A with 3-aminothiophene (6 mmol) and methacryloyl chloride, and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to provide the title compound **1q** as a white solid (0.60 g, 60% yield); R_f 0.1 (petroleum ether/ethyl

acetate = 20/1); m.p. 112.8-114.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.63 (s, 1H), 7.25-7.19 (m, 1H), 7.05-7.03 (m, 1H), 5.78 (s, 1H), 5.44 (s, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 140.3, 135.4, 124.5, 121.1, 119.9, 110.5, 18.7; HRMS (ESI) Calcd for C_8H_9NOSNa $[M + Na]^+$ 190.0297, found 190.0298.

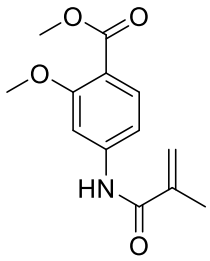


N-(Benzofuran-5-yl)methacrylamide (1r): Prepared according to the general procedure A with 1-benzofuran-5-amine (5 mmol) and methacryloyl chloride, and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to provide the title compound **1r** as a white solid (0.72 g, 70% yield); R_f 0.4 (petroleum ether/ethyl acetate = 5/1); m.p. 102.0-103.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.2 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.59 (s, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.28 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.73 (s, 1H), 5.81 (s, 1H), 5.46 (s, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 152.1, 145.9, 141.0, 133.0, 127.9, 119.6, 117.7, 113.1, 111.5, 106.9, 18.8; HRMS (ESI) Calcd for $C_{12}H_{11}NO_2Na$ $[M + Na]^+$ 224.0682, found 224.0689.



N-(Dibenzo[*b*,*d*]furan-3-yl)methacrylamide (1s): Prepared according to the general procedure A with 3-aminodibenzofuran (8 mmol) and methacryloyl chloride, and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to provide the title compound **1s** as a white solid (1.31 g, 65% yield); R_f 0.3 (petroleum ether/ethyl acetate = 10/1); m.p. 148.8-150.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.9 Hz, 1H), 7.92-7.83 (m, 2H), 7.70 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.46-7.39 (m, 1H), 7.34-7.30 (m, 2H), 5.84 (s, 1H), 5.50 (s, 1H), 2.10 (s, 3H); ^{13}C

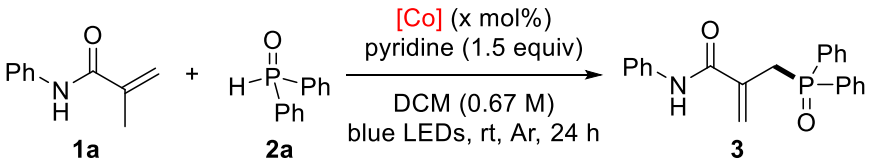
NMR (100 MHz, $CDCl_3$) δ 166.5, 156.7, 141.0, 137.2, 126.6, 124.0, 122.8, 120.6, 120.2, 119.9, 115.1, 111.6, 103.7, 18.8; HRMS (ESI) Calcd for $C_{16}H_{13}NO_2Na$ $[M + Na]^+$ 274.0838, found 274.0847.



Methyl 4-methacrylamido-2-methoxybenzoate (1bj): Prepared according to the general procedure A with methyl 4-amino-2-methoxybenzoate (5 mmol) and methacryloyl chloride, and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **1bj** as a white solid (0.98 g, 78% yield); R_f 0.4 (petroleum ether/ethyl acetate = 1/2); m.p. 85.8-87.6 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 2.0 Hz, 1H), 7.65 (s, 1H), 6.86 (dd, J = 8.5, 2.0 Hz, 1H), 5.82 (s, 1H), 5.53 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.0, 160.6, 142.9, 140.7 132.8, 120.3, 115.1, 110.5, 103.3, 56.0, 51.8, 18.6; HRMS (ESI) Calcd for $C_{13}H_{15}NO_4Na$ $[M + Na]^+$ 272.0893, found 272.0900.

3. Optimization of Reaction Conditions

Table S1. Cobaloxime Catalyst Effect

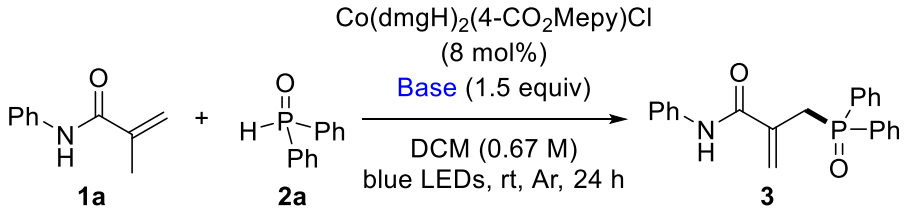


1a **2a** **3**

Entry	[Co]	x (mol%)	yield[a,b] (%)
1	$Co(dmgH)(dmgH_2)Cl_2$	10	79
2	$Co(dmgH)_2pyCl$	10	80
3	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	10	84
4	$Co(dmgH)_2(4\text{-}CNpy)Cl$	10	53
5	$Co(dmgH)_2(4\text{-}DMAPpy)Cl$	10	77
6	$Co(dmgBF_2)_2(H_2O)_2$	10	25
7	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	4	77
8	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	8	84

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), DCM (1.5 mL), irradiation via a 40 W blue LEDs under Ar at room temperature for 24 h. [b] Yields are determined by ^{1}H NMR using dibromomethane as an internal standard.

Table S2. Base Effect

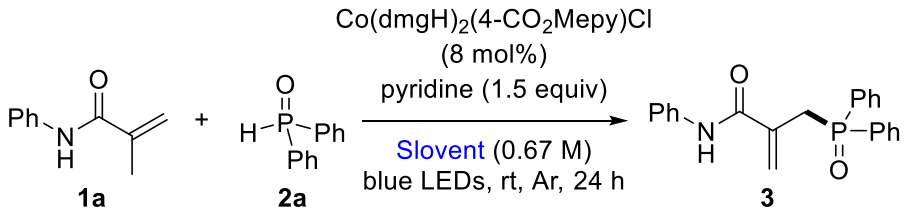


1a **2a** **3**

Entry	Base	Yield[a,b] (%)
1	$4\text{-}CO_2MePy$	69
2	DMAP	67
3	2,6-lutidine	52
4	2,4,6-collidine	45
5	2-PhPy	43(59[c])
6	pyridine	84(78[c])
7	4-CNPy	56
8	K_3PO_4	trace
9	Na_2CO_3	32
10	Me_2NH	25
11	Et_3N	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), DCM (1.5 mL), irradiation via a 40 W blue LEDs under Ar at room temperature for 24 h. [b] Yields are determined by ^{1}H NMR using dibromomethane as an internal standard. [c] Isolated yields are given in parentheses.

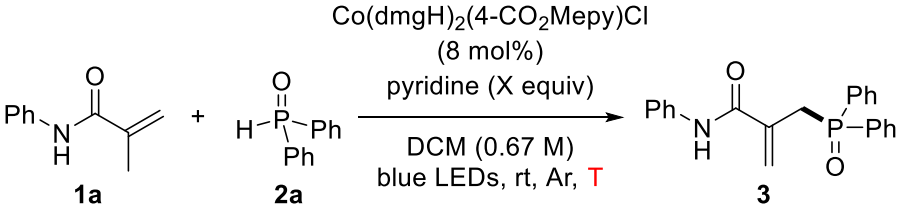
Table S3. Slovent Effect



Entry	Slovent	Yield[a,b] (%)
1	DCM	84
2	DCE	51
3	chlorobenzene	71
4	benzene	61
5	CH_3CN	44
6	toluene	48
7	trifluorotoluene	53
8	DMF	ND
9	THF	ND
10	DMC	35

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), slovent (1.5 mL), irradiation via a 40 W blue LEDs under Ar at room temperature for 24 h. [b] Yields are determined by ^{1}H NMR using dibromomethane as an internal standard.

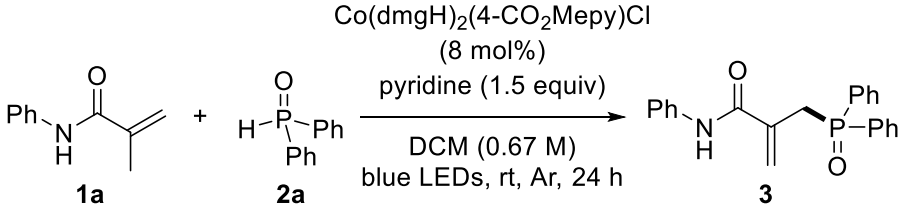
Table S4. The Effect of Amount of Pyridine and Reaction time



Entry	Pyridine (X equiv)	Time	Yield[a,b] (%)
1	0.5	24 h	60
2	1.0	24 h	63
3	1.5	24 h	84
4	2.0	24 h	73
5	2.5	24 h	60
6	1.5	48 h	79
7	1.5	36 h	80
8	1.5	12 h	71

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), DCM (1.5 mL), irradiation via a 40 W blue LEDs under Ar at room temperature for 24 h. [b] Yields are determined by ^{1}H NMR using dibromomethane as an internal standard.

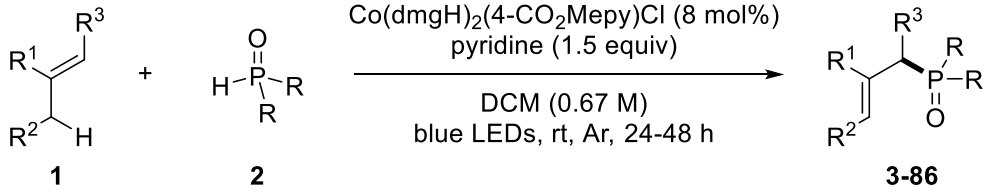
Table S5. The Effect of Amount of **1a** and **2a**, and Control Experiments



Entry	**1a** (eq.)	**2a** (eq.)	[Co]	Light	Base	Yield[a,b] (%)
1	1.0	2.0	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	Blue LEDs	pyridine	21
2	1.0	1.5	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	Blue LEDs	pyridine	39
3	1.0	1.0	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	Blue LEDs	pyridine	48
4	1.3	1.0	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	Blue LEDs	pyridine	62
5	1.5	1.0	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	Blue LEDs	pyridine	70
6	2.0	1.0	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	Blue LEDs	pyridine	84
7	2.5	1.0	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	Blue LEDs	pyridine	83
8	2.0	1.0	-	Blue LEDs	pyridine	0
9	2.0	1.0	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	-	pyridine	0
10	2.0	1.0	$Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$	Blue LEDs	-	0

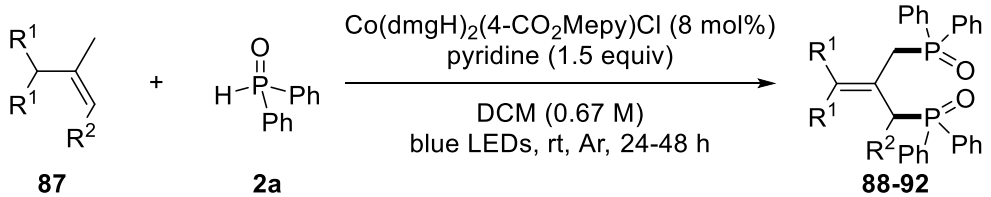
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), DCM (1.5 mL), irradiation via a 40 W blue LEDs under Ar at room temperature for 24 h. [b] Yields are determined by ^1H NMR using dibromomethane as an internal standard.

4. Experimental Procedures and Product Characterization



1 2 3-86

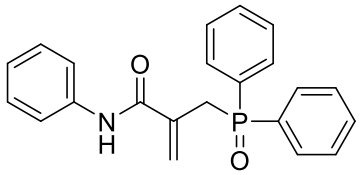
General Procedure B: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$ (7.4 mg, 0.008 mmol, 8 mol%) and alkene **1** (0.4 mmol, 2.0 equiv). Then, the Schlenk tube was introduced into an argon-filled glovebox, and secondary phosphine oxide **2** (0.2 mmol, 1.0 equiv) was added. The tube was taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled with Ar for 3 times. After DCM (3.0 mL) and pyridine (24.4 μL, 0.3 mmol, 1.5 equiv) were added under Ar, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under Ar and was stirred under irradiation of blue LED (40 W) at room temperature for 24-48 h (monitored by TLC analysis). The reaction solution was concentrated under reduced pressure and the crude residue was purified by column chromatography on silica gel to give the desired product.



87 2a 88-92

General Procedure C: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$ (7.4 mg, 0.008 mmol, 8 mol%). Then, the Schlenk tube was introduced into an argon-filled glovebox, and diphenylphosphine oxide **2a** (80.8 mg, 0.4 mmol, 2.0 equiv) was added. The tube was taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled with Ar for 3 times. After DCM (3.0 mL) and pyridine (24.4 μL, 0.3 mmol, 1.5 equiv) were added under Ar, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under Ar. Light alkene **87** (0.2 mmol, 1.0 equiv) was added,

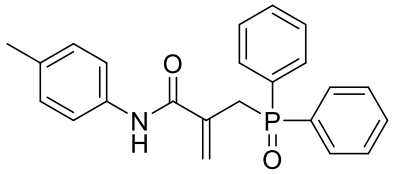
and was stirred under irradiation of blue LED (40 W) at room temperature for 24-48 h (monitored by TLC analysis). The reaction solution was concentrated under reduced pressure and the crude residue was purified by column chromatography on silica gel to give the desired product.



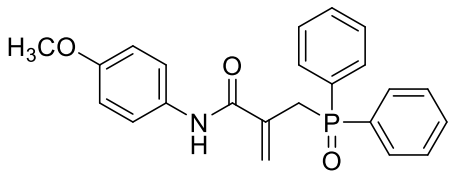
2-((Diphenylphosphoryl)methyl)-N-phenylacrylamide (3): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **3** as a white solid (56.3 mg, 78% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/3); m.p. 122.1-123.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.82-7.77 (m, 4H), 7.73-7.66 (m, 2H), 7.63-7.47 (m, 6H), 7.32 (t, J = 8.0 Hz, 2H), 7.13-7.05 (m, 1H), 6.01 (d, J = 5.2 Hz, 1H), 5.02 (d, J = 5.1 Hz, 1H), 3.47 (d, J = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 138.8, 135.9 (d, $J_{C\text{-}P}$ = 10.6 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 100.3 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.7 Hz), 128.8, 126.6 (d, $J_{C\text{-}P}$ = 8.8 Hz), 123.9, 120.0, 35.2 (d, $J_{C\text{-}P}$ = 64.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.6; HRMS (ESI) Calcd for $C_{22}H_{20}NO_2PNa$ $[M + Na]^+$ 384.1124, found 384.1132.

Procedure for 5.2 mmol-scale reaction: An oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged with $Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$ (192.50 mg, 8 mol%) and alkene **1a** (1.68 g, 10.4 mmol, 2.0 equiv). Then, the Schlenk tube was introduced into an argon-filled glovebox, and diphenylphosphine oxide **2a** (1.05 g, 5.2 mmol, 1.0 equiv) was added. The tube was taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled with Ar for 3 times. After DCM (40 mL) and pyridine (0.63 mL, 1.5 equiv) were added under Ar, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under Ar and was stirred under irradiation of blue LED (40 W) at room temperature for 36 h

(monitored by TLC analysis). The reaction was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel to give the desired product **3** (1.27 g, 68%).

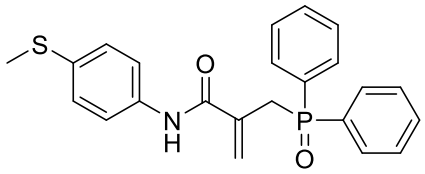


2-((Diphenylphosphoryl)methyl)-N-(p-tolyl)acrylamide (4): Prepared according to the general procedure B from **1b** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **4** as a white solid (55.9 mg, 75% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 154.7-156.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.82-7.63 (m, 4H), 7.59-7.55 (m, 4H), 7.53-7.46 (m, 4H), 7.11 (d, J = 8.1 Hz, 2H), 5.99 (d, J = 5.1 Hz, 1H), 5.03 (d, J = 5.1 Hz, 1H), 3.46 (d, J = 13.7 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (d, $J_{C\text{-}P}$ = 1.7 Hz), 136.1, 135.7 (d, $J_{C\text{-}P}$ = 10.3 Hz), 133.4, 132.4 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 102.4 Hz), 129.2, 128.7 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.1 (d, $J_{C\text{-}P}$ = 9.2 Hz), 120.0, 34.9, 20.8. (d, $J_{C\text{-}P}$ = 63.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.4; HRMS (ESI) Calcd for $C_{23}H_{23}NO_2P$ $[M + H]^+$ 376.1461, found 376.1469.

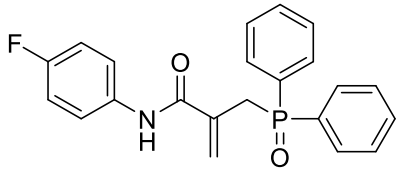


2-((Diphenylphosphoryl)methyl)-N-(p-tolyl)acrylamide (5): Prepared according to the general procedure B from **1c** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **5** as a white solid (54.4 mg, 70% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/3); m.p. 135.7-137.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43

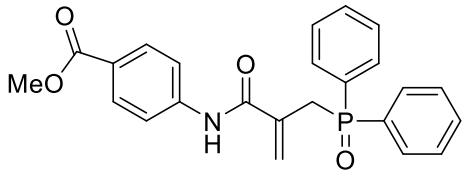
(s, 1H), 7.82-7.76 (m, 4H), 7.64-7.54 (m, 4H), 7.55-7.46 (m, 4H), 6.86 (d, J = 9.0 Hz, 2H), 5.99 (d, J = 5.1 Hz, 1H), 5.03 (d, J = 5.0 Hz, 1H), 3.79 (s, 3H), 3.46 (d, J = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 156.1, 135.8 (d, $J_{C\text{-}P}$ = 10.3 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.1, 131.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.6 (d, $J_{C\text{-}P}$ = 101.0 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.9 Hz), 126.2 (d, $J_{C\text{-}P}$ = 9.1 Hz), 121.5, 114.0, 55.5, 35.5 (d, $J_{C\text{-}P}$ = 64.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.5; HRMS (ESI) Calcd for $C_{23}H_{23}NO_3P$ $[M + H]^+$ 392.1410, found 392.1419.



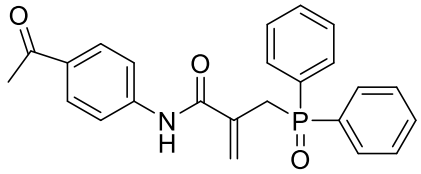
2-((Diphenylphosphoryl)methyl)-N-(4-(methylthio)phenyl)acrylamide (6): Prepared according to the general procedure B from **1d** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **6** as a white solid (57.1 mg, 70% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); m.p. 153.4-155.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 7.85-7.75 (m, 4H), 7.65 (d, J = 8.3 Hz, 2H), 7.62-7.48 (m, 6H), 7.24 (s, 1H), 6.00 (d, J = 5.1 Hz, 1H), 5.00 (d, J = 5.2 Hz, 1H), 3.46 (d, J = 13.6 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 136.7, 135.7 (d, $J_{C\text{-}P}$ = 10.6 Hz), 132.9, 132.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.3 (d, $J_{C\text{-}P}$ = 100.8 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12 Hz), 128.1, 126.7 (d, $J_{C\text{-}P}$ = 9.3 Hz), 120.6, 35.3 (d, $J_{C\text{-}P}$ = 64 Hz), 16.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.7; HRMS (ESI) Calcd for $C_{23}H_{22}NO_2PSNa$ $[M + Na]^+$ 430.1001, found 430.1010.



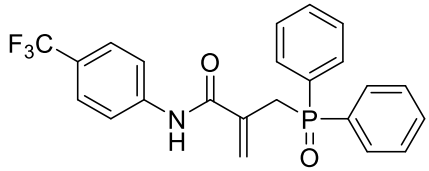
2-((Diphenylphosphoryl)methyl)-N-(4-fluorophenyl)acrylamide (7): Prepared according to the general procedure B from **1e** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **7** as a white solid (55.9 mg, 74% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 141.2-142.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.82-7.76 (m, 4H), 7.72-7.63 (m, 2H), 7.63-7.56 (m, 2H), 7.56-7.46 (m, 4H), 7.05-6.95 (m, 2H), 6.02 (d, J = 5.1 Hz, 1H), 4.99 (d, J = 5.1 Hz, 1H), 3.46 (d, J = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 159.2 (d, $J_{C\text{-}F}$ = 241.1 Hz), 135.6 (d, $J_{C\text{-}P}$ = 10.6 Hz), 134.9 (d, $J_{C\text{-}F}$ = 2.6 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.3 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12 Hz), 126.8 (d, $J_{C\text{-}P}$ = 9.3 Hz), 121.6 (d, $J_{C\text{-}F}$ = 7.9 Hz), 115.3 (d, $J_{C\text{-}F}$ = 22.1 Hz), 35.3 (d, $J_{C\text{-}P}$ = 64.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.8; HRMS (ESI) Calcd for $C_{22}H_{20}FNO_2P$ $[M + H]^+$ 380.1210, found 380.1217.



Methyl 4-(2-((diphenylphosphoryl)methyl)acrylamido)benzoate (8): Prepared according to the general procedure B from **1f** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **8** as a white solid (63.1 mg, 75% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 166.8-168.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.13 (s, 1H), 8.12-7.97 (m, 2H), 7.82-7.77 (m, 6H), 7.67-7.51 (m, 6H), 6.04 (d, J = 5.1 Hz, 1H), 4.99 (d, J = 5.1 Hz, 1H), 3.90 (s, 3H), 3.47 (d, J = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 166.2, 143.2, 135.5 (d, $J_{C\text{-}P}$ = 10.6 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.13 (d, $J_{C\text{-}P}$ = 103.5 Hz), 130.08, 128.9 (d, $J_{C\text{-}P}$ = 11.9 Hz), 127.4 (d, $J_{C\text{-}P}$ = 9.2 Hz), 125.2, 119.3, 51.9, 35.3 (d, $J_{C\text{-}P}$ = 62.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.1; HRMS (ESI) Calcd for $C_{24}H_{22}NO_4PNa$ $[M + Na]^+$ 442.1179, found 442.1182.

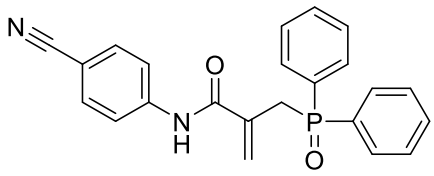


N-(4-acetylphenyl)-2-((diphenylphosphoryl)methyl)acrylamide (9): Prepared according to the general procedure B from **1g** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **9** as a white solid (57.9 mg, 72% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 174.1-176.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.18 (s, 1H), 7.94 (d, J = 8.3 Hz, 2H), 7.91-7.73 (m, 6H), 7.66-7.47 (m, 6H), 6.04 (d, J = 5.1 Hz, 1H), 5.00 (d, J = 5.1 Hz, 1H), 3.47 (d, J = 13.6 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 166.2, 143.4, 135.5 (d, $J_{C\text{-}P}$ = 10.8 Hz), 132.7 (d, $J_{C\text{-}P}$ = 3.3 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.1 (d, $J_{C\text{-}P}$ = 100.8 Hz), 129.5, 128.9 (d, $J_{C\text{-}P}$ = 12.1 Hz), 127.5 (d, $J_{C\text{-}P}$ = 9.4 Hz), 119.3, 35.3 (d, $J_{C\text{-}P}$ = 64.0 Hz), 26.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.2; HRMS (ESI) Calcd for $C_{24}H_{22}NO_3PNa$ $[M + Na]^+$ 426.1230, found 426.1237.

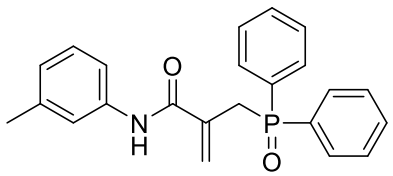


2-((Diphenylphosphoryl)methyl)-N-(4-(trifluoromethyl)phenyl)acrylamide (10): Prepared according to the general procedure B from **1h** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **10** as a white solid (63.1 mg, 74% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/1); m.p. 126.7-127.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.18 (s, 1H), 7.90-7.73 (m, 6H), 7.65-7.48 (m, 8H), 6.04 (d, J = 5.1 Hz, 1H), 5.00 (d, J = 5.1 Hz, 1H), 3.47 (d, J = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 142.0, 135.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.1 (d, $J_{C\text{-}$

$_P$ = 9.4 Hz), 130.1 (d, $J_{C\text{-}P}$ = 101.2 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.5 (d, $J_{C\text{-}P}$ = 8.9 Hz), 126.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.6 (d, $J_{C\text{-}F}$ = 32.6 Hz), 124.3 (q, $J_{C\text{-}F}$ = 269.7 Hz), 119.7, 35.3 (d, $J_{C\text{-}P}$ = 63.7 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -62.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.2; HRMS (ESI) Calcd for $C_{23}H_{20}F_3NO_2P$ $[M + H]^+$ 430.1178, found 430.1187.

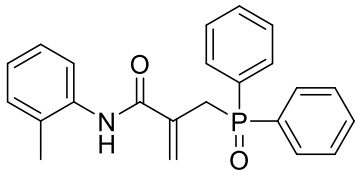


N-(4-cyanophenyl)-2-((diphenylphosphoryl)methyl)acrylamide (11): Prepared according to the general procedure B from **1i** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **11** as a white solid (61.1 mg, 79% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 184.5-186.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.44 (s, 1H), 8.01-7.70 (m, 6H), 7.73-7.47 (m, 8H), 6.05 (d, J = 5.2 Hz, 1H), 5.00 (d, J = 5.1 Hz, 1H), 3.46 (d, J = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.20 (d, $J_{C\text{-}P}$ = 1.6 Hz), 143.1, 135.2 (d, $J_{C\text{-}P}$ = 10.7 Hz), 133.0, 132.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 129.9 (d, $J_{C\text{-}P}$ = 101.1 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.9 (d, $J_{C\text{-}P}$ = 9.4 Hz), 120.0, 119.1, 106.6, 35.3 (d, $J_{C\text{-}P}$ = 63.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.5; HRMS (ESI) Calcd for $C_{23}H_{20}N_2O_2P$ $[M + H]^+$ 387.1257, found 387.1267.

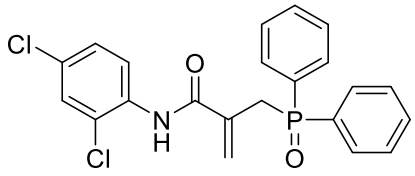


2-((Diphenylphosphoryl)methyl)-N-(m-tolyl)acrylamide (12): Prepared according to the general procedure B from **1j** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate

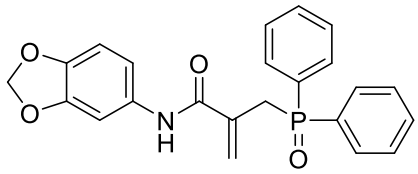
(1:1) to provide the title compound **12** as a white solid (52.2 mg, 70% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 131.1-132.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.85-7.73 (m, 4H), 7.64-7.45 (m, 8H), 7.20 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 5.99 (d, J = 5.2 Hz, 1H), 5.01 (d, J = 5.1 Hz, 1H), 3.46 (d, J = 13.6 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 138.6 (d, $J_{C\text{-}P}$ = 2.1 Hz), 135.8 (d, $J_{C\text{-}P}$ = 10.4 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 131.4 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.6, 126.3 (d, $J_{C\text{-}P}$ = 9.0 Hz), 124.8, 120.6, 117.2, 35.1 (d, $J_{C\text{-}P}$ = 64.1 Hz), 21.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.6; HRMS (ESI) Calcd for $C_{23}H_{23}NO_2P$ $[M + H]^+$ 376.1461, found 376.1469.



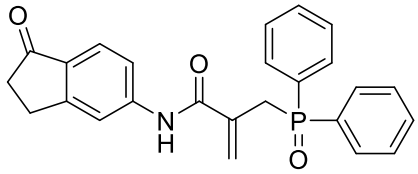
2-((Diphenylphosphoryl)methyl)-N-(o-tolyl)acrylamide (13): Prepared according to the general procedure B from **1k** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **13** as a white solid (52.2 mg, 70% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 140.2-142.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.86-7.76 (m, 4H), 7.64 (d, J = 8.2 Hz, 1H), 7.53 (m, 6H), 7.22-7.14 (m, 2H), 7.06 (t, J = 7.4 Hz, 1H), 5.99 (d, J = 5.3 Hz, 1H), 5.16 (d, J = 5.1 Hz, 1H), 3.50 (d, J = 13.5 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 (d, $J_{C\text{-}P}$ = 2.1 Hz), 136.0, 135.7 (d, $J_{C\text{-}P}$ = 10.2 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.9 (d, $J_{C\text{-}P}$ = 99.9 Hz), 130.7, 130.5, 128.8 (d, $J_{C\text{-}P}$ = 11.9 Hz), 126.2, 125.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 125.2, 123.9, 34.8 (d, $J_{C\text{-}P}$ = 64.8 Hz), 18.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4; HRMS (ESI) Calcd for $C_{23}H_{23}NO_2P$ $[M + H]^+$ 376.1461, found 376.1469.



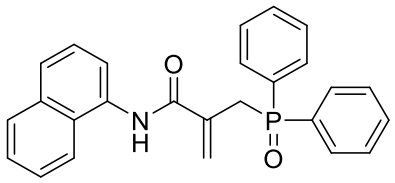
N-(2,4-dichlorophenyl)-2-((diphenylphosphoryl)methyl)acrylamide (14): Prepared according to the general procedure B from **1l** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **14** as a white solid (63.0 mg, 73% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/1); m.p. 184.5-186.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.17 (s, 1H), 7.83-7.74 (m, 4H), 7.71 (d, J = 1.9 Hz, 2H), 7.65-7.57 (m, 2H), 7.56-7.52 (m, 4H), 7.07 (d, J = 2.0 Hz, 1H), 6.02 (d, J = 5.2 Hz, 1H), 4.98 (d, J = 5.1 Hz, 1H), 3.44 (d, J = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 140.8, 135.3 (d, $J_{C\text{-}P}$ = 10.4 Hz), 135.0, 132.7 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.0 (d, $J_{C\text{-}P}$ = 100.7 Hz), 129.0 (d, $J_{C\text{-}P}$ = 12.1 Hz), 127.5 (d, $J_{C\text{-}P}$ = 9.1 Hz), 123.8, 118.3, 35.3 (d, $J_{C\text{-}P}$ = 63.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.4; HRMS (ESI) Calcd for $C_{22}H_{18}Cl_2NO_2PNa$ $[M + Na]^+$ 452.0344, found 452.0354.



N-(benzo[d][1,3]dioxol-5-yl)-2-((diphenylphosphoryl)methyl)acrylamide (15): Prepared according to the general procedure B from **1m** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **15** as a white solid (55.5 mg, 69% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); m.p. 109.9-111.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.91-7.70 (m, 4H), 7.63-7.55 (m, 2H), 7.56-7.50 (m, 4H), 7.42 (d, J = 2.2 Hz, 1H), 7.04 (dd, J = 8.3, 2.2 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 5.99 (d, J = 5.1 Hz, 1H), 5.93 (s, 2H), 5.01 (d, J = 5.1 Hz, 1H), 3.45 (d, J = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 147.6, 143.9, 135.7 (d, $J_{C\text{-}P}$ = 10.5 Hz), 133.2, 132.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.5 (d, $J_{C\text{-}P}$ = 100.4 Hz), 128.8 (d, $J_{C\text{-}P}$ =12 Hz), 126.4 (d, $J_{C\text{-}P}$ = 9.4 Hz), 113.0, 108.0, 102.6, 101.0, 35.3 (d, $J_{C\text{-}P}$ = 64.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.6; HRMS (ESI) Calcd for $C_{23}H_{20}NO_4PNa$ $[M + Na]^+$ 428.1022, found 428.1035.

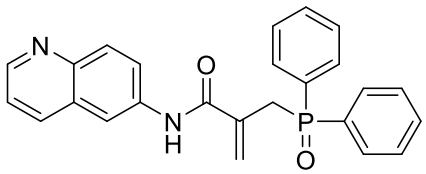


2-((Diphenylphosphoryl)methyl)-N-(1-oxo-2,3-dihydro-1H-inden-5-yl)acrylamide (16): Prepared according to the general procedure B from **1n** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **16** as a white solid (46.7 mg, 56% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); m.p. 208.6-210.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.30 (s, 1H), 8.01 (s, 1H), 7.86-7.75 (m, 4H), 7.72 (d, J = 8.3 Hz, 1H), 7.67-7.58 (m, 3H), 7.57-7.49 (m, 4H), 6.05 (d, J = 5.1 Hz, 1H), 4.99 (d, J = 5.0 Hz, 1H), 3.47 (d, J = 13.6 Hz, 2H), 3.19-3.06 (m, 2H), 2.75-2.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 166.3, 156.9, 144.9,135.5 (d, $J_{C\text{-}P}$ = 10.7 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.0 (d, $J_{C\text{-}P}$ = 101.0 Hz), 129.0 (d, $J_{C\text{-}P}$ = 11.9 Hz), 127.7 (d, $J_{C\text{-}P}$ = 9.5 Hz), 124.6, 119.4, 116.6, 36.5, 35.4 (d, $J_{C\text{-}P}$ = 63.5 Hz), 25.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.4; HRMS (ESI) Calcd for $C_{25}H_{22}NO_3PNa$ $[M + Na]^+$ 438.1230, found 438.1239.

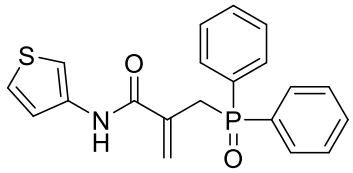


N-(4-acetylphenyl)-2-((diphenylphosphoryl)methyl)acrylamide (17): Prepared according to the general procedure B from **1o** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **17** as a white solid (60.3 mg, 73% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 130.9-132.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 8.24 (d, J = 8.5 Hz, 1H), 7.93-7.79 (m, 6H), 7.68 (d, J = 8.2 Hz, 1H), 7.59-7.42 (m, 9H), 6.08 (d, J = 5.1 Hz, 1H), 5.17 (d, J = 4.9 Hz, 1H), 3.58 (d,

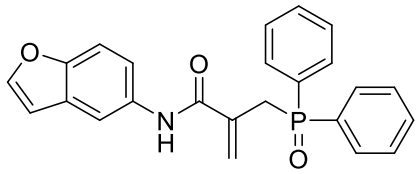
J = 13.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 135.8 (d, $J_{C\text{-}P}$ = 9.7 Hz), 134.2, 133.3, 132.5 (d, $J_{C\text{-}P}$ = 2.4 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.2 Hz), 130.8 (d, $J_{C\text{-}P}$ = 100.2 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.3, 127.7, 126.3, 126.2, 125.8, 125.54, 125.52, 122.2, 120.8, 35.1 (d, $J_{C\text{-}P}$ = 64.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8; HRMS (ESI) Calcd for $C_{26}H_{22}NO_2PNa$ $[M + Na]^+$ 434.1280, found 434.1287.



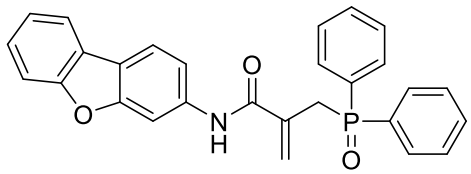
2-((Diphenylphosphoryl)methyl)-N-(quinolin-6-yl)acrylamide (18): Prepared according to the general procedure B from **1p** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **18** as a white solid (73.9 mg, 90% yield); R_f 0.1 (petroleum ether/ethyl acetate = 1/2); m.p. 161.5-163.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.15 (s, 1H), 8.81 (dd, J = 4.2, 1.8 Hz, 1H), 8.42 (d, J = 2.4 Hz, 1H), 8.13 (d, J = 8.3 Hz, 1H), 8.05 (d, J = 8.9 Hz, 1H), 7.91 (dd, J = 9.1, 2.4 Hz, 1H), 7.88-7.75 (m, 4H), 7.62-7.51 (m, 6H), 7.36 (dd, J = 8.3, 4.2 Hz, 1H), 6.07 (d, J = 5.1 Hz, 1H), 5.04 (d, J = 5.1 Hz, 1H), 3.51 (d, J = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 149.1, 145.7, 137.0, 135.8, 135.7 (d, $J_{C\text{-}P}$ = 10.4 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 100.7 Hz), 129.9, 128.9 (d, $J_{C\text{-}P}$ = 12.2 Hz) 127.2 (d, $J_{C\text{-}P}$ = 9.2 Hz), 123.9, 121.3, 116.0, 35.5 (d, $J_{C\text{-}P}$ = 64.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.1; HRMS (ESI) Calcd for $C_{25}H_{22}N_2O_2P$ $[M + H]^+$ 413.1413, found 413.1426.



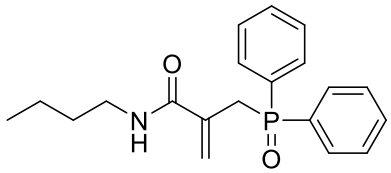
2-((Diphenylphosphoryl)methyl)-N-(thiophen-3-yl)acrylamide (19): Prepared according to the general procedure B from **1q** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **19** as a white solid (55.2 mg, 75% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 156.1-157.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 7.84-7.73 (m, 4H), 7.67 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.62-7.47 (m, 6H), 7.23-7.18 (m, 2H), 6.01 (d, *J* = 5.0 Hz, 1H), 5.01 (d, *J* = 5.0 Hz, 1H), 3.45 (d, *J* = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1(d, J_{C-P} = 1.8 Hz), 136.4, 135.3 (d, J_{C-P} = 10.4 Hz), 132.6 (d, J_{C-P} = 2.7 Hz), 131.1 (d, J_{C-P} = 9.3 Hz), 130.3 (d, J_{C-P} = 100.7 Hz), 128.9 (d, J_{C-P} = 12.0 Hz), 126.8 (d, J_{C-P} = 9.5 Hz), 124.0, 121.7, 110.2, 35.4 (d, J_{C-P} = 64.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.0; HRMS (ESI) Calcd for $C_{20}H_{18}NO_2PSNa$ $[M + Na]^+$ 390.0688, found 390.0699.



N-(benzofuran-5-yl)-2-((diphenylphosphoryl)methyl)acrylamide (20): Prepared according to the general procedure B from **1r** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **20** as a light yellow solid (61.3 mg, 76% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 158.3-161.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 8.07 (d, *J* = 2.1 Hz, 1H), 7.88-7.74 (m, 4H), 7.63-7.48 (m, 8H), 7.42 (d, *J* = 8.8 Hz, 1H), 6.73 (s, 1H), 6.03 (d, *J* = 4.9 Hz, 1H), 5.03 (d, *J* = 4.8 Hz, 1H), 3.49 (d, *J* = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9 (d, J_{C-P} = 1.8 Hz), 151.8, 145.5, 135.7 (d, J_{C-P} = 10.3 Hz), 134.0, 132.5 (d, J_{C-P} = 2.8 Hz), 131.0 (d, J_{C-P} = 9.2 Hz), 130.4 (d, J_{C-P} = 100.6 Hz), 128.8 (d, J_{C-P} = 11.9 Hz), 127.6, 126.3 (d, J_{C-P} = 9.4 Hz), 117.6, 112.5, 111.1, 106.8, 35.1 (d, J_{C-P} = 64.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.6; HRMS (ESI) Calcd for $C_{24}H_{20}NO_3PNa$ $[M + Na]^+$ 424.1073, found 424.1082.

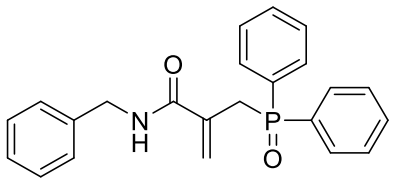


N-(dibenzo[b,d]furan-3-yl)-2-((diphenylphosphoryl)methyl)acrylamide (21): Prepared according to the general procedure B from **1s** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **21** as a white solid (74.1 mg, 82% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 194.6-196.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 8.27 (s, 1H), 7.92-7.76 (m, 6H), 7.61-7.51 (m, 8H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.05 (d, *J* = 5.1 Hz, 1H), 5.03 (d, *J* = 5.1 Hz, 1H), 3.50 (d, *J* = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 156.8, 156.6, 138.5, 135.8 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.4 (d, $J_{C\text{-}P}$ = 100.6 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.9 Hz), 126.8 (d, $J_{C\text{-}P}$ = 9.4 Hz), 126.3, 124.3, 122.6, 120.4, 120.09, 120.08, 115.4, 111.5, 103.5, 35.3 (d, $J_{C\text{-}P}$ = 64.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.9; HRMS (ESI) Calcd for $C_{28}H_{22}NO_3PNa$ $[M + Na]^+$ 474.1230, found 474.1241.

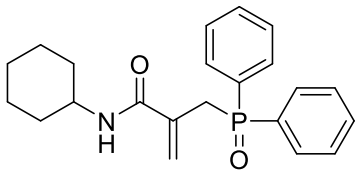


N-butyl-2-((diphenylphosphoryl)methyl)acrylamide (22): Prepared according to the general procedure B from **1t** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **22** as a white solid (50.8 mg, 74% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 154.6-156.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.67 (m, 5H), 7.51 (m, 6H), 5.84 (d, *J* = 5.1 Hz, 1H), 5.11 (d, *J* = 5.0 Hz, 1H), 3.39 (d, *J* = 13.8 Hz, 2H), 3.27-3.17 (m, 2H), 1.56-1.44 (m, 2H), 1.42-1.28 (m, 2H), 0.92 (t, *J* =

7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8 (d, $J_{C\text{-}P}$ = 2.1 Hz), 135.5 (d, $J_{C\text{-}P}$ = 9.9 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.2 (d, $J_{C\text{-}P}$ = 99.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.4 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.9 Hz), 124.6 (d, $J_{C\text{-}P}$ = 9.2 Hz), 39.7, 34.7 (d, $J_{C\text{-}P}$ = 65.4 Hz), 31.3, 20.2, 13.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0; HRMS (ESI) Calcd for $C_{20}H_{24}NO_2PNa$ $[M + Na]^+$ 364.1437, found 364.1446.

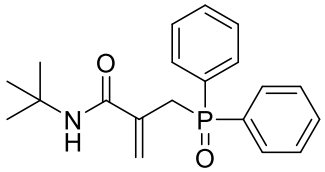


N-benzyl-2-((diphenylphosphoryl)methyl)acrylamide (23): Prepared according to the general procedure B from **1u** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **23** as a white solid (57.4 mg, 77% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/3); m.p. 132.1-134.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.78-7.72 (m, 4H), 7.61-7.42 (m, 6H), 7.32-7.27 (m, 4H), 7.26-7.23 (m, 1H), 5.88 (d, J = 5.0 Hz, 1H), 5.17 (d, *J* = 5.0 Hz, 1H), 4.43 (d, *J* = 5.7 Hz, 2H), 3.43 (d, *J* = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 138.3, 135.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 132.3 (d, $J_{C\text{-}P}$ = 1.9 Hz), 131.2 (d, $J_{C\text{-}P}$ = 100.0 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.6, 127.7, 127.2, 125.0 (d, $J_{C\text{-}P}$ = 8.3 Hz), 43.9, 34.6 (d, $J_{C\text{-}P}$ = 65.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1; HRMS (ESI) Calcd for $C_{23}H_{23}NO_2P$ $[M + H]^+$ 376.1461, found 376.1469.

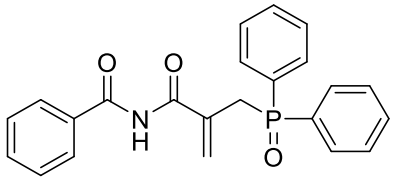


N-cyclohexyl-2-((diphenylphosphoryl)methyl)acrylamide (24): Prepared according to the general procedure B from **1v** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate

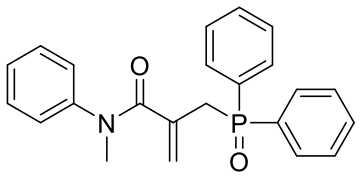
(1:2) to provide the title compound **24** as a white solid (56.1 mg, 76% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/3); m.p. 154.6-156.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 11.6, 7.4 Hz, 4H), 7.69-7.42 (m, 7H), 5.82 (d, *J* = 4.9 Hz, 1H), 5.14 (d, *J* = 4.9 Hz, 1H), 3.73-3.65 (m, 1H), 3.40 (d, *J* = 13.6 Hz, 2H), 1.91-1.78 (m, 2H), 1.70 (m, 2H), 1.64-1.53 (m, 1H), 1.40-1.29 (m, 7.4 Hz, 2H), 1.28-1.10 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9 (d, J_{C-P} = 2.3 Hz), 135.7 (d, J_{C-P} = 9.7 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 131.3 (d, J_{C-P} = 99.7 Hz), 131.0 (d, J_{C-P} = 9.3 Hz), 128.7 (d, J_{C-P} = 11.8 Hz), 124.5 (d, J_{C-P} = 9.0 Hz), 48.6, 34.6 (d, J_{C-P} = 65.3 Hz), 32.7, 25.6, 24.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.7; HRMS (ESI) Calcd for $C_{22}H_{27}NO_2P$ $[M + H]^+$ 368.1774, found 368.1781.



N-(tert-butyl)-2-((diphenylphosphoryl)methyl)acrylamide (25): Prepared according to the general procedure B from **1w** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **25** as a white solid (47.0 mg, 69% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); m.p. 176.9-178.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 11.6, 7.4 Hz, 4H), 7.55-7.45 (m, 6H), 7.14 (s, 1H), 5.76 (d, *J* = 5.1 Hz, 1H), 5.20 (d, *J* = 5.0 Hz, 1H), 3.40 (d, *J* = 13.7 Hz, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 136.5 (d, J_{C-P} = 9.3 Hz), 132.0 (d, J_{C-P} = 2.8 Hz), 131.6 (d, J_{C-P} = 99.5 Hz), 131.0 (d, J_{C-P} = 9.3 Hz), 128.6 (d, J_{C-P} = 11.7 Hz), 123.4 (d, J_{C-P} = 8.8 Hz), 51.1, 34.1 (d, J_{C-P} = 65.7 Hz), 28.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.1; HRMS (ESI) Calcd for $C_{20}H_{24}NO_2PNa$ $[M + Na]^+$ 364.1437, found 364.1442.

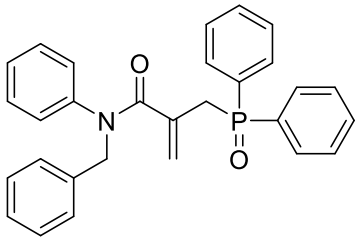


N-(2-((Diphenylphosphoryl)methyl)acryloyl)benzamide (26): Prepared according to the general procedure B from **1x** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **26** as a white solid (55.4 mg, 71% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); m.p. 189.1-191.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 8.31-8.15 (m, 2H), 7.89-7.71 (m, 4H), 7.67-7.44 (m, 9H), 6.10 (d, J = 5.4 Hz, 1H), 4.98 (d, J = 5.1 Hz, 1H), 3.42 (d, J = 13.2 Hz, 2H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.4, 134.5 (d, $J_{C\text{-}P}$ = 10.7 Hz), 133.3, 132.7 (d, $J_{C\text{-}P}$ = 3.1 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.0 (d, $J_{C\text{-}P}$ = 101.6 Hz), 129.1, 128.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.5, 34.4 (d, $J_{C\text{-}P}$ = 63.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.1; HRMS (ESI) Calcd for $C_{23}H_{20}NO_3PNa$ $[M + Na]^+$ 412.1073, found 412.1083.

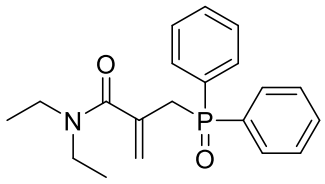


2-((Diphenylphosphoryl)methyl)-N-methyl-N-phenylacrylamide (27): Prepared according to the general procedure B from **1y** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **27** as a white solid (43.6 mg, 58% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/3); m.p. 136.4-137.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 11.4, 8.0 Hz, 4H), 7.54-7.45 (m, 6H), 7.25-7.15 (m, 3H), 7.07-7.00 (m, 2H), 5.44 (d, J = 4.2 Hz, 1H), 5.07 (d, J = 4.1 Hz, 1H), 3.43 (d, J = 13.6 Hz, 2H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3 (d, $J_{C\text{-}P}$ = 4.0 Hz), 144.5, 133.9 (d, $J_{C\text{-}P}$ = 7.9 Hz), 132.9 (d, $J_{C\text{-}P}$ = 99.2 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.2 Hz), 129.2, 128.5 (d, $J_{C\text{-}P}$ = 11.7 Hz), 126.8, 126.6, 125.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 38.8,

34.7 (d, $J_{C\text{-}P}$ = 68.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.6; HRMS (ESI) Calcd for $C_{23}H_{22}NO_2PNa$ $[M + Na]^+$ 398.1280, found 398.1286.

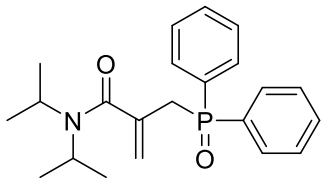


N-benzyl-2-((diphenylphosphoryl)methyl)-N-phenylacrylamide (28): Prepared according to the general procedure B from **1z** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **28** as a white solid (50.4 mg, 56% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/1); m.p. 139.7-142.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 11.5, 7.5 Hz, 4H), 7.53-7.41 (m, 6H), 7.22 (m, *J* = 7.5 Hz, 3H), 7.17-7.12 (m, 5H), 6.87-6.85 (m, 2H), 5.45 (d, *J* = 3.8 Hz, 1H), 5.07 (d, *J* = 3.6 Hz, 1H), 4.90 (s, 2H), 3.45 (d, *J* = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 143.2, 137.2, 133.8 (d, $J_{C\text{-}P}$ = 7.5 Hz), 132.8 (d, $J_{C\text{-}P}$ = 99.3 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.3 Hz), 129.1, 128.6 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.34, 128.31 (d, $J_{C\text{-}P}$ = 6.2 Hz), 127.5, 127.2, 126.9, 126.1, 54.2, 34.4 (d, $J_{C\text{-}P}$ = 68.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.0; HRMS (ESI) Calcd for $C_{29}H_{26}NO_2PNa$ $[M + Na]^+$ 474.1593, found 474.1605.

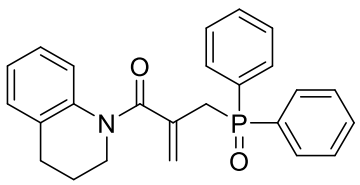


2-((Diphenylphosphoryl)methyl)-N,N-diethylacrylamide (29): Prepared according to the general procedure B from **1aa** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **29** as a colorless oily liquid (30.0 mg, 44% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.76 (m, 4H), 7.63-7.39 (m, 6H), 5.53 (d, *J* = 4.5 Hz, 1H), 5.29 (d, *J* = 4.1 Hz, 1H), 3.53 (d,

J = 13.2 Hz, 2H), 3.11 (app. s, 4H), 0.95 (d, J = 39.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3 (d, $J_{C\text{-}P}$ = 3.1 Hz), 134.3 (d, $J_{C\text{-}P}$ = 8.1 Hz), 132.7 (d, $J_{C\text{-}P}$ = 98.2 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.4 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.7 Hz), 120.0 (d, $J_{C\text{-}P}$ = 8.9 Hz), 43.2, 38.2, 35.6 (d, $J_{C\text{-}P}$ = 67.8 Hz), 13.9, 12.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.7; HRMS (ESI) Calcd for $C_{20}H_{24}NO_2PNa$ $[M + Na]^+$ 364.1437, found 364.1447.

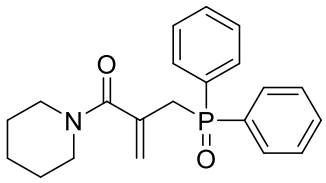


2-((Diphenylphosphoryl)methyl)-N,N-diisopropylacrylamide (30): Prepared according to the general procedure B from **1ab** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **30** as a white solid (33.3 mg, 45% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 134.8-136.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 11.7, 7.3 Hz, 4H), 7.59-7.39 (m, 6H), 5.46 (d, J = 4.3 Hz, 1H), 5.23 (d, J = 4.1 Hz, 1H), 4.13 (app. s, 1H), 3.50 (d, J = 13.2 Hz, 2H), 3.29 (app. s, 1H), 1.10 (app. s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 135.8 (d, $J_{C\text{-}P}$ = 6.8 Hz), 133.1 (d, $J_{C\text{-}P}$ = 97.2 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.7 Hz),119.1 (d, $J_{C\text{-}P}$ = 8.8 Hz), 50.2, 35.2 (d, $J_{C\text{-}P}$ = 68.2 Hz), 20.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1; HRMS (ESI) Calcd for $C_{22}H_{29}NO_2P$ $[M + H]^+$ 370.1930, found 370.1940.

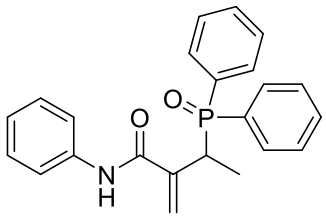


1-(3,4-Dihydroquinolin-1(2H)-yl)-2-((diphenylphosphoryl)methyl)prop-2-en-1-one (31): Prepared according to the general procedure B from **1ac** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with

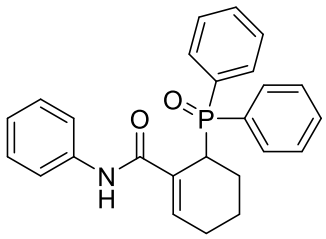
petroleum ether/ethyl acetate (1:1) to provide the title compound **31** as a white solid (39.8 mg, 50% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); m.p. 165.4-167.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 11.5, 7.6 Hz, 4H), 7.57-7.42 (m, 6H), 7.32-7.28 (m, 1H), 7.10-6.98 (m, 3H), 5.58 (d, J = 4.3 Hz, 1H), 5.30 (d, J = 4.3 Hz, 1H), 3.67 (t, J = 6.3 Hz, 2H), 3.48 (d, J = 13.4 Hz, 2H), 2.66 (t, J = 6.7 Hz, 2H), 1.80-1.58 (m, J = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6 (d, J_{C-P} = 3.9 Hz), 138.7, 134.7 (d, J_{C-P} = 7.7 Hz), 132.7 (d, J_{C-P} = 99.2 Hz), 131.9 (d, J_{C-P} = 2.8 Hz), 131.0, 130.9 (d, J_{C-P} = 9.4 Hz), 128.6 (d, J_{C-P} = 11.8 Hz), 128.4, 125.9, 124.8, 124.7, 124.4 (d, J_{C-P} = 8.6 Hz), 45.5, 34.5 (d, J_{C-P} = 68.5 Hz), 26.6, 23.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.6; HRMS (ESI) Calcd for $C_{25}H_{24}NO_2PNa$ $[M + Na]^+$ 424.1437, found 424.1447.



2-((Diphenylphosphoryl)methyl)-1-(piperidin-1-yl)prop-2-en-1-one (32): Prepared according to the general procedure B from **1ad** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **32** as a white solid (32.6 mg, 46% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/3); m.p. 141.8-143.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.69 (m, 4H), 7.53-7.44 (m, 6H), 5.54 (d, J = 4.6 Hz, 1H), 5.23 (d, J = 4.5 Hz, 1H), 3.51 (d, J = 13.3 Hz, 2H), 3.21 (t, J = 13.6 Hz, 4H), 1.48 (t, J = 1.6 Hz, 2H), 1.44-1.17 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2 (d, J_{C-P} = 3.0 Hz), 133.6 (d, J_{C-P} = 8.0 Hz), 132.7 (d, J_{C-P} = 98.2 Hz), 131.8 (d, J_{C-P} = 2.6 Hz), 130.8 (d, J_{C-P} = 9.4 Hz), 128.6 (d, J_{C-P} = 11.6 Hz), 120.7 (d, J_{C-P} = 9.1 Hz), 48.4, 42.7, 35.5 (d, J_{C-P} = 67.7 Hz), 25.6, 25.5, 24.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9; HRMS (ESI) Calcd for $C_{21}H_{25}NO_2P$ $[M + H]^+$ 354.1617, found 354.1626.

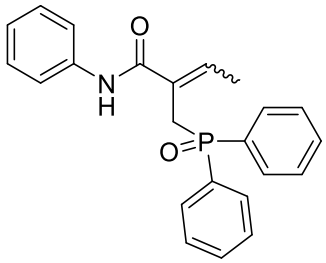


N-benzyl-2-((diphenylphosphoryl)methyl)-N-phenylacrylamide (33): Prepared according to the general procedure B from **1ae** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **33** as a white solid (21.8 mg, 29% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); m.p. 172.1-173.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.90 (dd, *J* = 10.9, 7.5 Hz, 2H), 7.79 (dd, *J* = 11.3, 7.3 Hz, 2H), 7.63-7.52 (m, 5H), 7.42 (d, *J* = 8.3 Hz, 3H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.90 (d, *J* = 4.5 Hz, 1H), 5.24 (d, *J* = 4.6 Hz, 1H), 3.87-3.69 (m, 1H), 1.44 (dd, *J* = 16.1, 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 142.8 (d, $J_{C\text{-}P}$ = 7.1 Hz), 138.4, 132.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.3 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.7 Hz), 130.9 (d, $J_{C\text{-}P}$ = 98.3 Hz), 130.1 (d, $J_{C\text{-}P}$ = 96.0 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.8, 128.6 (d, $J_{C\text{-}P}$ = 11.6 Hz), 124.3 (d, $J_{C\text{-}P}$ = 8.8 Hz), 124.1, 120.1, 37.6 (d, $J_{C\text{-}P}$ = 65.2 Hz), 13.5 (d, $J_{C\text{-}P}$ = 2.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.6; HRMS (ESI) Calcd for $C_{23}H_{22}NO_2PNa$ $[M + Na]^+$ 398.1280, found 398.1289.



6-(Diphenylphosphoryl)-N-phenylcyclohex-1-ene-1-carboxamide (34): Prepared according to the general procedure B from **1af** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **34** as a white solid (64.1 mg, 80% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/1); m.p. 280.1-282.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.92 (m, 2H), 7.77 (dd, *J* = 11.3, 7.3 Hz, 2H), 7.65 (s, 1H), 7.56-7.48

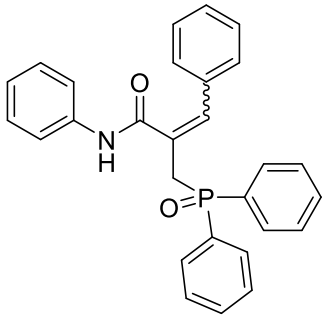
(m, 3H), 7.23-7.13 (m, 6H), 7.02 (t, J = 7.1 Hz, 1H), 6.60 (q, J = 4.0 Hz, 1H), 4.02 (t, J = 8.0 Hz, 1H), 2.34 (m, 2H), 2.28-2.09 (m, 2H), 1.86-1.69 (m, 1H), 1.65 (dd, J = 11.7, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 137.8, 136.0 (d, $J_{C\text{-}P}$ = 8.7 Hz), 132.2 (d, $J_{C\text{-}P}$ = 43.4 Hz), 131.768 (d, $J_{C\text{-}P}$ = 51.3 Hz), 131.766 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.2 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.4 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.3 Hz), 128.5, 128.0 (d, $J_{C\text{-}P}$ = 11.6 Hz), 123.9, 119.8, 34.7 (d, $J_{C\text{-}P}$ = 66.8 Hz), 24.7 (d, $J_{C\text{-}P}$ = 2.5 Hz), 23.1 (d, $J_{C\text{-}P}$ = 2.5 Hz), 18.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.9; HRMS (ESI) Calcd for $C_{25}H_{24}NO_2PNa$ $[M + Na]^+$ 424.1437, found 424.1444.



2-((Diphenylphosphoryl)methyl)-N-phenylbut-2-enamide (35): Prepared according to the general procedure B from **1ag** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **35** as a white solid (41.7 mg, 56% yield, 1.6:1 *Z*/*E*), the configuration was established by the 2D NOESY data;

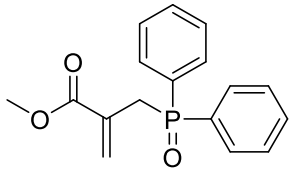
(*Z*)-2-((Diphenylphosphoryl)methyl)-N,3-diphenylacrylamide: R_f 0.5 (petroleum ether/ethyl acetate = 1/1); m.p. 187.1-189.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 7.83-7.77 (m, 4H), 7.70 (d, J = 8.2 Hz, 2H), 7.63-7.56 (m, 2H), 7.56-7.46 (m, 4H), 7.37-7.28 (m, 2H), 7.16-7.02 (m, 1H), 6.81-6.67 (m, 1H), 3.46 (d, J = 13.7 Hz, 2H), 1.15 (dd, J = 7.4, 4.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 139.2, 137.4 (d, J = 9.3 Hz), 132.5 (d, J = 2.9 Hz), 131.2 (d, J = 9.4 Hz), 131.0 (d, J = 99.0 Hz), 128.8 (d, J = 11.8 Hz), 128.7, 127.9 (d, J = 10.5 Hz), 123.7, 120.1, 30.5 (d, J = 65.5 Hz), 13.9 (d, J = 2.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6; HRMS (ESI) Calcd for $C_{23}H_{22}NO_2PNa$ $[M + Na]^+$ 398.1280, found 398.1289.

(*E*)-2-((Diphenylphosphoryl)methyl)-N,3-diphenylacrylamide: R_f 0.4 (petroleum ether/ethyl acetate = 1/1); m.p. 149.2-151.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.87-7.66 (m, 6H), 7.66-7.41 (m, 6H), 7.35-7.28 (m, 2H), 7.10-7.05 (m, 1H), 5.25-5.15 (m, 1H), 3.32 (d, J = 12.3 Hz, 2H), 1.84-1.71 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 138.9, 136.5 (d, $J_{C\text{-}P}$ = 9.3 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.9 (d, $J_{C\text{-}P}$ = 99.0 Hz), 128.8 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.7, 127.0 (d, $J_{C\text{-}P}$ = 11.0 Hz), 123.7, 119.8, 35.9 (d, $J_{C\text{-}P}$ = 65.2 Hz), 15.6 (d, $J_{C\text{-}P}$ = 3.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.1; HRMS (ESI) Calcd for $C_{23}H_{22}NO_2PNa$ $[M + Na]^+$ 398.1280, found 398.1284.

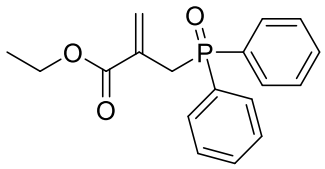


2-((Diphenylphosphoryl)methyl)-N,3-diphenylacrylamide (36): Prepared according to the general procedure B from **1ah** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to provide the title compound **36** as a white solid (52.3 mg, 60% yield, 1:1 *Z*/*E*);
(*Z*)-2-((Diphenylphosphoryl)methyl)-N,3-diphenylacrylamide: R_f 0.5 (petroleum ether/ethyl acetate = 2/1); m.p. 249.1-250.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.86 (s, 1H), 7.78-7.72 (m, 2H), 7.69 (d, J = 4.8 Hz, 1H), 7.63-7.53 (m, 4H), 7.49 (m, 2H), 7.43-7.29 (m, 6H), 7.25-7.24 (m, 3H), 7.10 (t, J = 7.4 Hz, 1H), 7.03-6.90 (m, 2H), 3.78 (d, J = 14.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 140.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 139.1, 135.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 102.6 Hz), 128.8, 128.7, 128.54 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.53, 128.3 (d, $J_{C\text{-}P}$ = 1.7 Hz), 127.8, 123.9, 120.2, 30.6 (d, $J_{C\text{-}P}$ = 64.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.0; HRMS (ESI) Calcd for $C_{28}H_{24}NO_2PNa$ $[M + Na]^+$ 460.1437, found 460.1446.

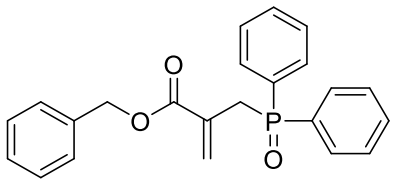
(*E*)-2-((Diphenylphosphoryl)methyl)-N,3-diphenylacrylamide: R_f 0.4 (petroleum ether/ethyl acetate = 2/1); m.p. 153.7-155.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.89-7.75 (m, 4H), 7.60-7.45 (m, 8H), 7.29 (d, J = 7.7 Hz, 2H), 7.25-7.12 (m, 5H), 7.07 (t, J = 7.4 Hz, 1H), 6.12 (d, J = 5.2 Hz, 1H), 3.52 (d, J = 12.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 138.3, 135.8 (d, $J_{C\text{-}P}$ = 9.4 Hz), 134.8 (d, $J_{C\text{-}P}$ = 3.7 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.2 (d, $J_{C\text{-}P}$ = 100.3 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.7, 128.5 (d, $J_{C\text{-}P}$ = 2.1 Hz), 128.3, 128.2, 127.4 (d, $J_{C\text{-}P}$ = 11.2 Hz), 124.0, 119.9, 36.7 (d, $J_{C\text{-}P}$ = 64.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5; HRMS (ESI) Calcd for $C_{28}H_{24}NO_2PNa$ $[M + Na]^+$ 460.1437, found 460.1439.



Methyl 2-((diphenylphosphoryl)methyl)acrylate (37): Prepared according to the general procedure B from **1ai** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **37** as a white solid (28.6 mg, 48% yield) with the hydrogenated product in 16.7:1 ratio; R_f 0.2 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.70 (m, 4H + 0.27H, major + minor), 7.54-7.44 (m, 6H + 0.38H, major + minor), 6.34 (d, J = 4.6 Hz, 1H, major), 5.98 (d, J = 4.4 Hz, 1H, major), 3.56 (s, 3H, major) , 3.48 (s, 0.23H, minor), 3.46 (d, J = 14.0 Hz, 2H, major), 1.29 (d, J = 6.8 Hz, 0.24H, minor); ^{13}C NMR (100 MHz, $CDCl_3$) δ mixture major δ 166.7, 132.3 (d, $J_{C\text{-}P}$ = 99.5 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.4 (d, $J_{C\text{-}P}$ = 8.2 Hz), 130.1 (d, $J_{C\text{-}P}$ = 7.8 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.7 Hz), 52.1, 32.2 (d, $J_{C\text{-}P}$ = 67.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8 (minor), 29.0 (major); HRMS (ESI) Calcd for $C_{17}H_{18}O_3P$ $[M + H]^+$ 301.0988, found 301.0991.

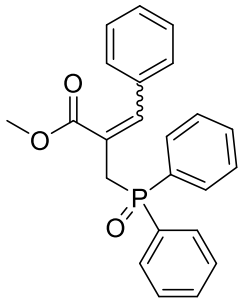


Ethyl 2-((diphenylphosphoryl)methyl)acrylate (38): Prepared according to the general procedure B from **1aj** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **38** as a white solid (31.2 mg, 50% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); m.p. 93.0-95.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.71 (m, 4H), 7.55-7.40 (m, 6H), 6.35 (d, J = 4.7 Hz, 1H), 6.00 (d, J = 4.4 Hz, 1H), 4.01 (q, J = 7.1 Hz, 2H), 3.46 (d, J = 14.1 Hz, 2H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2 (d, $J_{C\text{-}P}$ = 4.7 Hz), 132.4 (d, $J_{C\text{-}P}$ = 99.3 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.6 (d, $J_{C\text{-}P}$ = 8.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 7.9 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.7 Hz), 61.1, 32.0 (d, $J_{C\text{-}P}$ = 67.4 Hz), 14.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.0; HRMS (ESI) Calcd for $C_{18}H_{19}O_3PNa$ $[M + Na]^+$ 337.0964, found 337.0970.



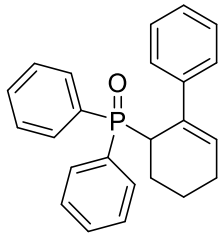
Benzyl 2-((Diphenylphosphoryl)methyl)acrylate (39): Prepared according to the general procedure B from **1ak** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **39** as a white solid (36.6 mg, 49% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/3); m.p. 69.6-71.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.73 (m, 4H), 7.55-7.39 (m, 6H), 7.34-7.31 (m, 3H), 7.25-7.23 (m, 2H), 6.41 (d, J = 4.6 Hz, 1H), 6.04 (d, J = 4.4 Hz, 1H), 5.00 (s, 2H), 3.48 (d, J = 14.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0 (d, $J_{C\text{-}P}$ = 4.7 Hz), 135.7, 132.2 (d, $J_{C\text{-}P}$ = 99.3 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.2 Hz), 130.43 (d, $J_{C\text{-}P}$ = 8.1 Hz), 130.35 (d, $J_{C\text{-}P}$ = 8.4 Hz), 128.6, 128.5 (d, $J_{C\text{-}P}$ = 5.9 Hz), 128.2, 128.0, 66.8, 32.0 (d, $J_{C\text{-}P}$ = 67.4 Hz); ^{31}P NMR

(162 MHz, $CDCl_3$) δ 29.2; HRMS (ESI) Calcd for $C_{23}H_{22}O_3P$ $[M + H]^+$ 377.1301, found 377.1308.

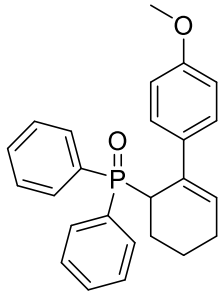


Benzyl 2-((diphenylphosphoryl)methyl)acrylate (40): Prepared according to the general procedure B from **1al** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **40** as a white solid (38.8 mg, 52% yield, 2:1 *Z*/*E*);

(*Z*)-Benzyl 2-((diphenylphosphoryl)methyl)acrylate: R_f 0.4 (petroleum ether/ethyl acetate = 1/1); m.p. 69.6-71.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 4.7 Hz, 1H), 7.79-7.74 (m, 4H), 7.68-7.60 (m, 2H), 7.54-7.48 (m, 2H), 7.48-7.39 (m, 4H), 7.39-7.28 (m, 3H), 3.74 (d, J = 14.3 Hz, 2H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9 (d, $J_{C\text{-}P}$ = 1.9 Hz), 142.7 (d, $J_{C\text{-}P}$ = 8.8 Hz), 134.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.6 (d, $J_{C\text{-}P}$ = 98.5 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.2 Hz), 129.4 (d, $J_{C\text{-}P}$ = 1.6 Hz), 128.9, 128.5, 128.3 (d, $J_{C\text{-}P}$ = 11.8 Hz), 123.6 (d, $J_{C\text{-}P}$ = 9.6 Hz), 51.9, 30.8 (d, $J_{C\text{-}P}$ = 67.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.3; HRMS (ESI) Calcd for $C_{23}H_{21}O_3PNa$ $[M + Na]^+$ 399.1121, found 399.1129.

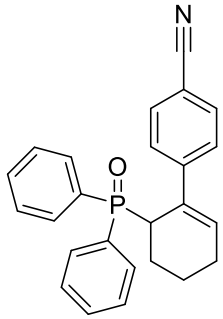


Diphenyl(2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)phosphine oxide (41): Prepared according to the general procedure B from **1am** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to provide the title compound **41** as a white solid (59.9 mg, 84% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/1) ; m.p. 170.2-172.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.73 (m, 2H), 7.52 (dd, *J* = 11.1, 7.7 Hz, 2H), 7.45-7.35 (m, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.13-7.07 (m, 2H), 6.97-6.90 (m, 5H), 6.05-6.02 (m, 1H), 3.76 (dd, *J* = 13.2, 5.5 Hz, 1H), 2.40-2.26 (m, 2H), 2.26-2.08 (m, 2H), 2.01-1.81 (m, 1H), 1.62-1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 133.31 (d, $J_{C\text{-}P}$ = 6.4 Hz), 133.29 (d, $J_{C\text{-}P}$ = 92.4 Hz), 132.7 (d, $J_{C\text{-}P}$ = 93.4 Hz), 132.4 (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.20 (d, $J_{C\text{-}P}$ = 8.8 Hz), 132.16, 130.9 (d, $J_{C\text{-}P}$ = 8.3 Hz), 130.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.0 Hz), 127.7, 127.6 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.7, 126.2, 39.0 (d, $J_{C\text{-}P}$ = 66.7 Hz), 25.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 24.2 (d, $J_{C\text{-}P}$ = 2.5 Hz), 18.7 (d, $J_{C\text{-}P}$ = 2.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.4; HRMS (ESI) Calcd for $C_{24}H_{23}OPNa$ $[M + Na]^+$ 381.1379, found 381.1387.

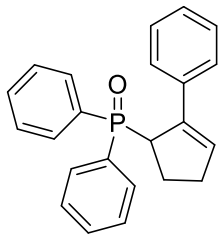


(4'-Methoxy-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)diphenylphosphine oxide (42): Prepared according to the general procedure B from **1an** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **42** as a white solid (70.2 mg, 90% yield); m.p. 174.9-176.8 °C; R_f 0.2 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR

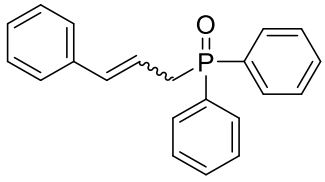
(400 MHz, $CDCl_3$) δ 7.79-7.72 (m, 2H), 7.57-7.49 (m, 2H), 7.46-7.34 (m, 3H), 7.25-7.19 (m, 1H), 7.15-7.10 (m, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.44 (d, J = 8.8 Hz, 2H), 5.98 (q, J = 4.0 Hz, 1H), 3.68 (s, 3H), 2.34-2.20 (m, 3H), 2.14-2.06 (m, 1H), 1.99-1.82 (m, 1H), 1.61-1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 135.1 (d, J_{C-P} = 1.8 Hz), 133.4 (d, J_{C-P} = 92.4 Hz), 132.9 (d, J_{C-P} = 92.4 Hz), 132.8 (d, J_{C-P} = 6.5 Hz), 131.1 (d, J_{C-P} = 8.7 Hz), 131.0, 130.94 (d, J_{C-P} = 8.7 Hz), 130.86 (d, J_{C-P} = 8.3 Hz), 130.4 (d, J_{C-P} = 2.8 Hz), 128.3 (d, J_{C-P} = 11.1 Hz), 127.9, 127.5 (d, J_{C-P} = 11.3 Hz), 113.1, 55.1, 39.4 (d, J_{C-P} = 66.6 Hz), 25.2 (d, J_{C-P} = 2.9 Hz), 24.2 (d, J_{C-P} = 2.6 Hz), 18.7 (d, J_{C-P} = 2.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.4; HRMS (ESI) Calcd for $C_{25}H_{25}O_2PNa$ $[M + Na]^+$ 411.1484, found 411.1494.



2'-(Diphenylphosphoryl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (43): Prepared according to the general procedure B from **1ao** (0.40 mmol) and **2a** (0.20 mmol) for 24 h a and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **43** as a white solid (67.7 mg, 88% yield); m.p. 217.4-219.2 °C; R_f 0.2 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.77 (m, 2H), 7.52-7.42 (m, 5H), 7.26-7.15 (m, 3H), 7.14-6.97 (m, 4H), 6.14 (q, J = 4.0 Hz, 1H), 3.71 (dd, J = 10.5, 4.7 Hz, 1H), 2.36 (d, J = 4.3 Hz, 1H), 2.32-2.15 (m, 3H), 1.99-1.83 (m, 1H), 1.68-1.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 135.1 (d, J_{C-P} = 8.9 Hz), 132.7 (d, J_{C-P} = 94.8 Hz), 132.5 (d, J_{C-P} = 93.9 Hz), 132.2 (d, J_{C-P} = 6.9 Hz), 131.5 (d, J_{C-P} = 6.9 Hz), 131.4, 131.1 (d, J_{C-P} = 9.1 Hz), 131.0 (d, J_{C-P} = 8.7 Hz), 128.6 (d, J_{C-P} = 11.2 Hz), 127.9 (d, J_{C-P} = 11.3 Hz), 127.5, 118.9, 109.6, 38.7 (d, J_{C-P} = 66.8 Hz), 25.5, 24.2, 18.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8; HRMS (ESI) Calcd for $C_{25}H_{22}NOPNa$ $[M + Na]^+$ 406.1331, found 406.1343.

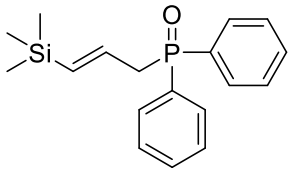


Diphenyl(2-phenylcyclopent-2-en-1-yl)phosphine oxide (44): Prepared according to the general procedure B from **1ap** (0.40 mmol) and **2a** (0.20 mmol) for 24 h a and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **44** as a white solid (49.0 mg, 67% yield); m.p. 163.3-166.1 °C; R_f 0.3 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 11.0, 7.1 Hz, 1H), 7.54 (dd, *J* = 11.1, 7.6 Hz, 1H), 7.50-7.44 (m, 1H), 7.43-7.38 (m, 2H), 7.30-7.26 (m, 1H), 7.19-7.14 (m, 2H), 7.08 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.01-6.90 (m, 3H), 6.19-6.18 (m, 1H), 4.13-4.07 (m, 1H), 2.56-2.48 (m, 1H), 2.48-2.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3 (d, $J_{C\text{-}P}$ = 7.0 Hz), 135.9, 133.2 (d, $J_{C\text{-}P}$ = 93.4 Hz), 132.6 (d, $J_{C\text{-}P}$ = 9.2 Hz), 132.2 (d, $J_{C\text{-}P}$ = 93.7 Hz), 131.4, 131.3 (d, $J_{C\text{-}P}$ = 9.3 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.0 Hz), 127.8(d, $J_{C\text{-}P}$ = 11.3 Hz), 127.7, 126.61, 126.57, 46.8 (d, $J_{C\text{-}P}$ = 68.2 Hz), 32.3, 27.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3; HRMS (ESI) Calcd for $C_{23}H_{21}OPNa$ $[M + Na]^+$ 367.1222, found 367.1233.

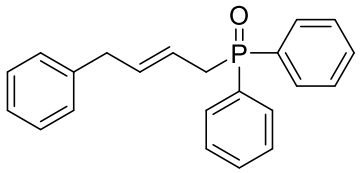


Cinnamyldiphenylphosphine oxide (45): Prepared according to the general procedure B from **1aq** (0.40 mmol) and **2a** (0.20 mmol) for 24 h a and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to provide the title compound **45** as a white solid (31.6 mg, 50% yield, 1:5.9 *Z*/*E*);

(*E*)-Cinnamyldiphenylphosphine oxide: m.p. 170.1-171.6 °C; R_f 0.4 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.72 (m, 4H), 7.57-7.44 (m, 6H), 7.29-7.22 (m, 5H), 7.21-7.18 (m, 1H), 6.42 (dd, *J* = 15.8, 4.4 Hz, 1H), 6.22-6.13 (m, 1H), 3.30 (dd, *J* = 14.9, 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 135.6 (d, $J_{C\text{-}P}$ = 12.1 Hz), 132.5 (d, $J_{C\text{-}P}$ = 98.2 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.4, 127.5, 126.2 (d, $J_{C\text{-}P}$ = 1.5 Hz), 118.5 (d, $J_{C\text{-}P}$ = 9.7 Hz), 35.6 (d, $J_{C\text{-}P}$ = 68.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.9; HRMS (ESI) Calcd for $C_{21}H_{20}OP$ $[M + H]^+$ 319.1246, found 319.1245.

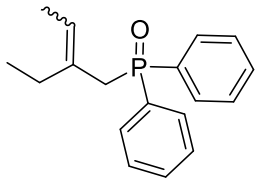


Diphenyl(3-(trimethylsilyl)allyl)phosphine oxide (46): Prepared according to the general procedure B from **1ar** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **46** as a white solid (47.3 mg, 75% yield, 1:2.4 *Z*/*E*); R_f 0.2 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.67 (m, 4H + 1.65H, *E* + *Z*), 7.57-7.41 (m, 6H + 2.47H, *E* + *Z*), 6.40-6.29 (m, 0.43H, *E*), 6.04-5.95 (m, 1H, *Z*), 5.76-5.71 (m, 1H + 0.43H, *E* + *Z*), 3.26-3.18 (m, 2H + 0.82H, *E* + *Z*), 0.03 (s, 3.66H, *Z*), -0.05 (s, 9H, *E*); ^{13}C NMR (100 MHz, $CDCl_3$) δ mixture *Z* δ 135.6 (d, $J_{C\text{-}P}$ = 8.1 Hz), 135.4 (d, $J_{C\text{-}P}$ = 12.1 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.3 Hz), 35.9 (d, $J_{C\text{-}P}$ = 68.4 Hz), -0.1; δ mixture *E* δ 138.4 (d, $J_{C\text{-}P}$ = 10.0 Hz), 134.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 98.5 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.5 (d, $J_{C\text{-}P}$ = 10.9 Hz), 39.4 (d, $J_{C\text{-}P}$ = 66.4 Hz), -1.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.0 (*E*), 29.4 (*Z*); HRMS (ESI) Calcd for $C_{18}H_{24}OPSi$ $[M + H]^+$ 315.1329, found 315.1330.



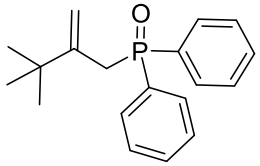
Diphenyl(4-phenylbut-2-en-1-yl)phosphine oxide (47): Prepared according to the general procedure B from **1as** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **47** as a white solid (34.9 mg, 53% yield, 1:17 *Z*/*E*);

(*E*)-Diphenyl(4-phenylbut-2-en-1-yl)phosphine oxide: m.p. 108.7-110.6 °C; R_f 0.3 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.68 (m, 4H), 7.56-7.41 (m, 6H), 7.22-7.13 (m, 3H), 6.94 (d, *J* = 7.2 Hz, 2H), 5.71-5.49 (m, 2H), 3.29 (dd, *J* = 6.3, 3.7 Hz, 2H), 3.12 (dd, *J* = 14.3, 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 135.4 (d, $J_{C\text{-}P}$ = 11.9 Hz), 132.5 (d, $J_{C\text{-}P}$ = 98.0 Hz), 132.0, 131.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.32, 128.26, 125.9, 119.9 (d, $J_{C\text{-}P}$ = 8.9 Hz), 38.9, 34.9 (d, $J_{C\text{-}P}$ = 68.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3; HRMS (ESI) Calcd for $C_{22}H_{21}OPNa$ $[M + Na]^+$ 355.1222, found 355.1232.

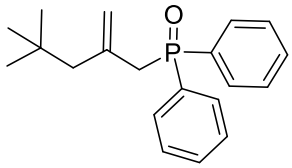


(4,4-Dimethyl-2-methylenepentyl)diphenylphosphine oxide (48): Prepared according to the general procedure B from **1at** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **48** as a white solid (44.9 mg, 79% yield, 1:1.8 *Z*/*E*), the configuration was established by the 2D NOESY data; R_f 0.3 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.72 (m, 4H + 2.1H, *Z* + *E*), 7.56-7.40 (m, 6H +3.2H, *Z* + *E*), 5.42-5.34 (m, 0.54H, *Z*), 5.17 (p, *J* = 6.5 Hz, 1H), 3.15 (d, 1.1H, *Z*), 3.05 (d, *J* = 13.6 Hz, 2H, *E*), 2.15-2.03 (m, 2H + 1.1H, *Z* + *E*), 1.51 (t, *J* = 6.0 Hz, 3H, *Z*), 1.29 (t, *J* = 5.6 Hz, 1.5H, *Z*), 1.00-0.87 (m, 3H + 1.6H, *Z* + *E*);

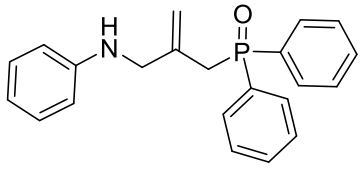
^{13}C NMR (100 MHz, $CDCl_3$) δ mixture *Z* δ 133.4 (d, $J_{C\text{-}P}$ = 96.2 Hz), 132.1 (d, $J_{C\text{-}P}$ = 7.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 122.1 (d, $J_{C\text{-}P}$ = 10.0 Hz), 32.8 (d, $J_{C\text{-}P}$ = 67.9 Hz), 30.8 (d, $J_{C\text{-}P}$ = 0.8 Hz), 13.7 (d, $J_{C\text{-}P}$ = 2.8 Hz), 12.5 (d, $J_{C\text{-}P}$ = 0.6 Hz); δ mixture *E* δ 133.3 (d, $J_{C\text{-}P}$ = 96.9 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.7 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.4 Hz), 124.6 (d, $J_{C\text{-}P}$ = 10.2 Hz), 37.7 (d, $J_{C\text{-}P}$ = 68.1 Hz), 24.0 (d, $J_{C\text{-}P}$ = 2.4 Hz), 13.3 (d, $J_{C\text{-}P}$ = 2.5 Hz), 12.3 (d, $J_{C\text{-}P}$ = 2.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8 (*E*), 29.0 (*Z*); HRMS (ESI) Calcd for $C_{18}H_{21}OPNa$ $[M + Na]^+$ 307.1222, found 307.1232.



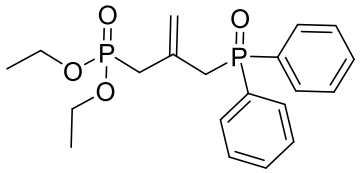
(3,3-Dimethyl-2-methylenebutyl)diphenylphosphine oxide (49): Prepared according to the general procedure B from **1au** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **49** as a white solid (30.8 mg, 52% yield); R_f 0.4 (petroleum ether/ethyl acetate = 1/2); m.p. 100.0-101.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.71 (m, 4H), 7.55-7.41 (m, 6H), 5.19 (d, *J* = 3.1 Hz, 1H), 5.03 (d, *J* = 2.9 Hz, 1H), 3.10 (d, *J* = 13.9 Hz, 2H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0 (d, $J_{C\text{-}P}$ = 7.6 Hz), 133.5 (d, $J_{C\text{-}P}$ = 98.4 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128. 5 (d, $J_{C\text{-}P}$ = 11.4 Hz), 112.9 (d, $J_{C\text{-}P}$ = 7.7 Hz), 36.4 (d, $J_{C\text{-}P}$ = 5.7 Hz), 32.0 (d, $J_{C\text{-}P}$ = 70.1 Hz), 28.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.0; HRMS (ESI) Calcd for $C_{19}H_{23}OPNa$ $[M + Na]^+$ 321.1379, found 321.1385.



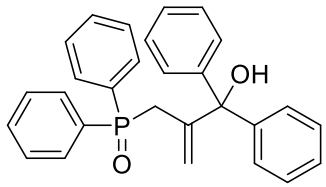
(4,4-Dimethyl-2-methylenepentyl)diphenylphosphine oxide (50): Prepared according to the general procedure B from **1av** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **50** as a white solid (49.5 mg, 79% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/1); m.p. 121.0-122.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.73 (m, 4H), 7.54-7.44 (m, 6H), 4.87 (d, *J* = 4.5 Hz, 1H), 4.82 (d, *J* = 4.9 Hz, 1H), 3.15 (d, *J* = 14.3 Hz, 2H), 1.98 (s, 2H), 0.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3 (d, $J_{C\text{-}P}$ = 9.8 Hz), 133.0 (d, $J_{C\text{-}P}$ = 97.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 118.9 (d, $J_{C\text{-}P}$ = 9.4 Hz), 50.4 (d, $J_{C\text{-}P}$ = 2.4 Hz), 39.6 (d, $J_{C\text{-}P}$ = 66.4 Hz), 31.7 (d, $J_{C\text{-}P}$ = 2.1 Hz), 29.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.5; HRMS (ESI) Calcd for HRMS (ESI) Calcd for $C_{20}H_{25}OPNa$ $[M + Na]^+$ 335.1535, found 335.1543.



Diphenyl(2-((phenylamino)methyl)allyl)phosphine oxide (51): Prepared according to the general procedure B from **1aw** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to provide the title compound **51** as a white solid (25.4 mg, 37% yield); R_f 0.4 (petroleum ether/ethyl acetate = 1/1); m.p. 105.6-107.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.73 (m, 4H), 7.60-7.39 (m, 6H), 7.12 (t, *J* = 7.8 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 5.13 (d, *J* = 4.3 Hz, 1H), 4.79 (d, *J* = 4.6 Hz, 1H), 4.57 (s, 1H), 3.84 (s, 2H), 3.17 (d, *J* = 13.6, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 137.9 (d, $J_{C\text{-}P}$ = 9.4 Hz), 132.5 (d, $J_{C\text{-}P}$ = 98.5 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 129.1, 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 117.0, 116.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 112.8, 49.7 (d, $J_{C\text{-}P}$ = 2.2 Hz), 35.6 (d, $J_{C\text{-}P}$ = 66.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1; HRMS (ESI) Calcd for $C_{22}H_{23}NOP$ $[M + H]^+$ 348.1512, found 348.1521.

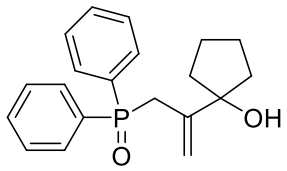


Diethyl (2-((diphenylphosphoryl)methyl)allyl)phosphonate (52): Prepared according to the general procedure B from **1ax** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with ethyl acetate / ethyl alcohol (80:1) to provide the title compound **52** as a colorless oily liquid (58.5 mg, 75% yield); R_f 0.3 (ethyl acetate / ethyl alcohol = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.75 (m, 4H), 7.60-7.37 (m, 6H), 5.06 (t, *J* = 5.2 Hz, 1H), 4.93 (t, *J* = 5.0 Hz, 1H), 4.16-3.99 (m, 4H), 3.41 (dd, *J* = 13.4, 2.4 Hz, 2H), 2.73 (d, *J* = 22.0 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5 (d, J_{C-P} = 98.4 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 130.9 (d, J_{C-P} = 9.3 Hz), 130.7 (d, J_{C-P} = 10.0 Hz), 128.5 (d, J_{C-P} = 11.7 Hz), 120.1 (dd, J_{C-P} = 12.5, 9.8 Hz), 61.9 (d, J_{C-P} = 6.6 Hz), 37.5 (dd, J_{C-P} = 66.7, 2.5 Hz), 34.6 (dd, J_{C-P} = 135.5, 2.3 Hz), 16.3 (d, J_{C-P} = 6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.4, 29.7; HRMS (ESI) Calcd for $C_{20}H_{26}O_4P_2Na$ $[M + Na]^+$ 415.1199, found 415.1208.

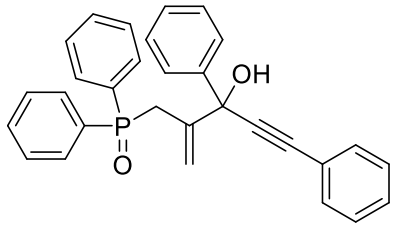


(2-(Hydroxydiphenylmethyl)allyl)diphenylphosphine oxide (53): Prepared according to the general procedure B from **1ay** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to provide the title compound **53** as a white solid (79.8 mg, 90% yield); R_f 0.3 (petroleum ether/ethyl acetate = 2/1); m.p. 210.1-211.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 11.6, 7.7 Hz, 4H), 7.58-7.37 (m, 10H), 7.29 (m, 4H), 7.25-7.18 (m, 2H), 7.03 (s, 1H), 4.63 (d, *J* = 4.6 Hz, 1H), 4.55 (d, *J* = 5.2 Hz, 1H), 3.29 (d, *J* = 12.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 144.2 (d, J_{C-P} = 11.0 Hz), 132.1 (d, J_{C-P} = 2.9 Hz), 131.8 (d, J_{C-P} = 99.5 Hz), 131.2 (d, J_{C-P} = 9.2 Hz), 128.6 (d, J_{C-P} =

11.7 Hz), 127.8, 127.7, 126.9, 120.5 (d, $J_{C\text{-}P}$ = 8.3 Hz), 81.8, 35.0 (d, $J_{C\text{-}P}$ = 64.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.1; HRMS (ESI) Calcd for $C_{28}H_{25}O_2PNa$ $[M + Na]^+$ 447.1484, found 447.1494.

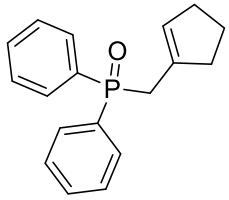


(2-(1-Hydroxycyclopentyl)allyl)diphenylphosphine oxide (54): Prepared according to the general procedure B from **1az** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **54** as a white solid (53.0 mg, 81% yield); R_f 0.2 (petroleum ether/ethyl acetate = 2/1); m.p. 100.0-101.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.67 (m, 4H), 7.67-7.42 (m, 6H), 4.97 (d, *J* = 4.8 Hz, 1H), 4.49 (d, *J* = 5.0 Hz, 1H), 3.35 (d, *J* = 13.5 Hz, 2H), 1.98-1.89 (m, 4H), 1.79-1.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 (d, $J_{C\text{-}P}$ = 10.6 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131. 8 (d, $J_{C\text{-}P}$ = 99.4 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.8 Hz), 114.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 82.5 (d, $J_{C\text{-}P}$ = 1.7 Hz), 40.7, 36.3 (d, $J_{C\text{-}P}$ = 65.6 Hz), 23.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.9; HRMS (ESI) Calcd for $C_{20}H_{23}O_2PNa$ $[M + Na]^+$ 349.1328, found 349.1336.

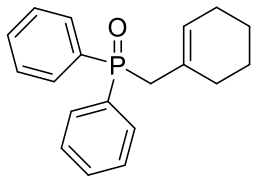


(3-Hydroxy-2-methylene-3,5-diphenylpent-4-yn-1-yl)diphenylphosphine oxide (55): Prepared according to the general procedure B from **1ba** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to provide the title compound **55** as a white solid (68.2 mg, 76% yield,); R_f 0.3 (petroleum ether/ethyl acetate = 2/1); m.p. 183.0-184.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 11.6, 7.5 Hz, 2H), 7.74-7.69 (m, 4H), 7.59-7.41 (m,

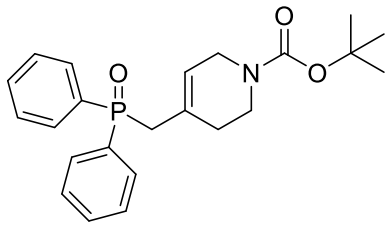
8H), 7.34 (t, J = 7.6 Hz, 2H), 7.31-7.22 (m, 4H), 6.81 (s, 1H), 5.62 (d, J = 5.0 Hz, 1H), 4.62 (d, J = 4.6 Hz, 1H), 3.34-3.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 141.9 (d, $J_{C\text{-}P}$ = 10.2 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.1 (d, $J_{C\text{-}P}$ = 3.0 Hz),132.0 (d, $J_{C\text{-}P}$ = 100.1 Hz), 131.7, 131.5 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.91 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.88 (d, $J_{C\text{-}P}$ = 101.5 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.1 Hz), 128.2, 128.1, 128.0, 127.4, 126.2, 123.0, 118.5 (d, $J_{C\text{-}P}$ = 8.1 Hz), 91.9, 86.1, 74.8, 33.6 (d, $J_{C\text{-}P}$ = 65.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.4; HRMS (ESI) Calcd for $C_{30}H_{25}O_2PNa$ $[M + Na]^+$ 471.1484, found 471.1490.



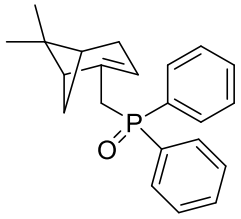
Cyclohex-1-en-1-yldiphenylphosphine oxide (56): Prepared according to the general procedure B from **1bb** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **56** as a white solid (48.6 mg, 86% yield); m.p. 139.6-141.0 °C; R_f 0.3 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.68 (m, 4H), 7.57-7.39 (m, 6H), 5.46 (d, J = 4.6 Hz, 1H), 3.20 (d, J = 14.0 Hz, 2H), 2.33-2.15 (m, 4H), 1.76 (p, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 133.2 (d, $J_{C\text{-}P}$ = 99.3 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.1 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 36.7 (d, $J_{C\text{-}P}$ = 2.5Hz), 33.5 (d, $J_{C\text{-}P}$ = 69.2 Hz), 32.7 (d, $J_{C\text{-}P}$ = 2.3 Hz), 23.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9; HRMS (ESI) Calcd for $C_{18}H_{19}OPNa$ $[M + Na]^+$ 305.1066, found 305.1070.



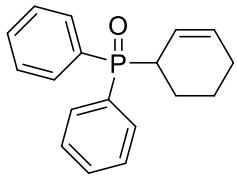
(Cyclohex-1-en-1-ylmethyl)diphenylphosphine oxide (57): Prepared according to the general procedure B from **1bc** (0.40 mmol) and **2a** (0.20 mmol), and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **57** as a white solid (47.7 mg, 81% yield); m.p. 140.1-141.5 °C; R_f 0.3 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (m, 4H), 7.65-7.39 (m, 6H), 5.41 (d, J = 4.5 Hz, 1H), 3.01 (d, J = 13.7 Hz, 2H), 2.06-1.85 (m, 4H), 1.59-1.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1 (d, $J_{C\text{-}P}$ = 97.1 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.2 (d, $J_{C\text{-}P}$ = 9.5 Hz), 127.6 (d, $J_{C\text{-}P}$ = 10.1 Hz), 39.6 (d, $J_{C\text{-}P}$ = 67.7 Hz), 30.3 (d, $J_{C\text{-}P}$ = 2.5 Hz), 25.4 (d, $J_{C\text{-}P}$ = 2.5 Hz), 22.7, 21.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.7;HRMS (ESI) Calcd for $C_{19}H_{22}OP$ $[M + H]^+$ 297.1403, found 297.1409.



Tert-butyl 4-((diphenylphosphoryl)methyl)-3,6-dihydropyridine-1(2H)-carboxylate (58): Prepared according to the general procedure B from **1bd** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **58** as a white solid (58.8 mg, 74% yield); m.p. 169.2-170.8 °C; R_f 0.2 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 11.4, 7.4 Hz, 4H), 7.61-7.40 (m, 6H), 5.37 (app. s, 1H), 3.82-3.69 (m, 2H), 3.35 (t, J = 5.7 Hz, 2H), 3.07 (d, J = 13.5 Hz, 2H), 2.10 (app. s, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 132.7 (d, $J_{C\text{-}P}$ = 97.4 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 127.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 124.0, 79.4, 38.8 (d, $J_{C\text{-}P}$ = 70.3 Hz), 30.08, 30.07, 28.39, 28.36; ^{31}P NMR (162 MHz, DMSO-d_6) δ 27.5; HRMS (ESI) Calcd for $C_{23}H_{28}NO_3PNa$ $[M + Na]^+$ 420.1699, found 420.1710.

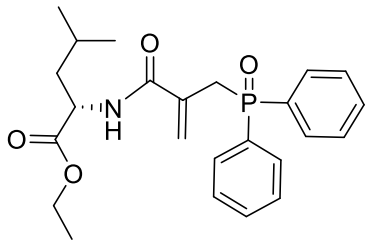


((6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)methyl)diphenylphosphine oxide (59): Prepared according to the general procedure B from **1be** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **59** as a white solid (36.3 mg, 54% yield); m.p. 140.1-141.5 °C; R_f 0.1 (petroleum ether/ethyl acetate = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.68 (m, 4H), 7.51-7.41 (m, 6H), 5.45-5.32 (m, 1H), 3.22-2.99 (m, 2H), 2.25-2.11 (m, 4H), 1.98-1.94 (m, 1H), 1.17 (s, 3H), 0.93 (d, J = 8.6 Hz, 1H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1 (d, $J_{C\text{-}P}$ = 10.4 Hz), 133.6 (d, $J_{C\text{-}P}$ = 96.1 Hz), 133.3 (d, $J_{C\text{-}P}$ = 97.0 Hz), 131.48 (d, $J_{C\text{-}P}$ = 2.2 Hz), 131.45 (d, $J_{C\text{-}P}$ = 2.2 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.9 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 6.8 Hz), 128.3 (d, $J_{C\text{-}P}$ = 6.8 Hz), 122.9 (d, $J_{C\text{-}P}$ = 11.2 Hz), 47.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 40.1, 39.0 (d, $J_{C\text{-}P}$ = 68.3 Hz), 38.0 (d, $J_{C\text{-}P}$ = 1.9 Hz), 31.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 31.5 (d, $J_{C\text{-}P}$ = 2.2 Hz), 26.1, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.3; HRMS (ESI) Calcd for $C_{22}H_{25}OPNa$ $[M + Na]^+$ 359.1535, found 359.1544.

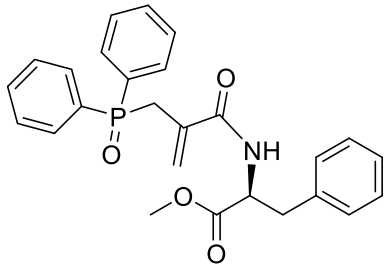


Cyclohex-1-en-1-yldiphenylphosphine oxide (60): Prepared according to the general procedure B from **1bf** (0.40 mmol) and **2a** (0.20 mmol) for 48 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to provide the title compound **60** as a white solid (35.7 mg, 63% yield); m.p. 163.3-166.1 °C; R_f 0.2 (petroleum ether/ethyl acetate = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.81 (m, 2H), 7.81-7.74 (m, 2H), 7.57-7.43 (m, 6H), 5.97-5.92 (m, 1H), 5.55-5.50 (m, 1H), 3.21 (d, J

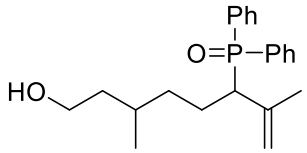
= 22.4 Hz, 1H), 2.04 (app. s, 2H), 1.97-1.83 (m, 3H), 1.80 (app. s, 2H), 1.59-1.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5 (d, $J_{C\text{-}P}$ = 10.3 Hz), 132.4 (d, $J_{C\text{-}P}$ = 94.7 Hz), 131.62 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.55 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.49579 (d, $J_{C\text{-}P}$ = 94.5 Hz),131.49584 (d, $J_{C\text{-}P}$ = 8.3 Hz), 131.1 (d, $J_{C\text{-}P}$ = 8.6 Hz), 128.6 (d, $J_{C\text{-}P}$ = 8.3 Hz), 128.5 (d, $J_{C\text{-}P}$ = 8.2 Hz), 120.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 36.8 (d, $J_{C\text{-}P}$ = 71.5 Hz), 24.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 21.9 (d, $J_{C\text{-}P}$ = 2.6 Hz), 21.1 (d, $J_{C\text{-}P}$ = 8.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.9; HRMS (ESI) Calcd for $C_{18}H_{19}OPNa$ $[M + Na]^+$ 305.1066, found 305.1074.



Ethyl (2-((diphenylphosphoryl)methyl)acryloyl)-L-leucinate (61): Prepared according to the general procedure B from **1bg** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **61** as a colorless oil (45.5 mg, 53% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, 1H), 7.82-7.71 (m, 4H), 7.57-7.45 (m, 6H), 5.89 (d, *J* = 5.0 Hz, 1H), 5.24 (d, *J* = 4.9 Hz, 1H), 4.54-4.43 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.43 (d, *J* = 13.8 Hz, 2H), 1.72-1.58 (m, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.94 (dd, *J* = 11.8, 5.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 167.5 (d, $J_{C\text{-}P}$ = 2.5 Hz), 134.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 132.10 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.08 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 99.8 Hz), 131.10 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.93 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.87 (d, $J_{C\text{-}P}$ = 100.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 4.1 Hz), 128.5 (d, $J_{C\text{-}P}$ = 4.1 Hz), 125.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 61.0, 51.5, 40.9, 34.2 (d, $J_{C\text{-}P}$ = 65.3 Hz), 24.8, 22.7, 21.0, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.8; HRMS (ESI) Calcd for $C_{24}H_{31}NO_4P$ $[M + H]^+$ 428.1985, found 428.1992.

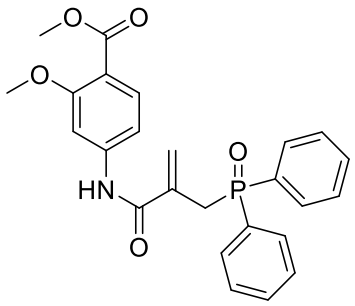


Methyl (2-((diphenylphosphoryl)methyl)acryloyl)-D-phenylalaninate (62): Prepared according to the general procedure B from **1bh** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **62** as a colorless oil (57.2 mg, 64% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.4 Hz, 1H), 7.84-7.65 (m, 4H), 7.62-7.41 (m, 6H), 7.24-7.08 (m, 5H), 5.76 (d, *J* = 5.0 Hz, 1H), 5.19 (d, *J* = 4.9 Hz, 1H), 4.74-4.68 (m, 1H), 3.70 (s, 3H), 3.40-3.20 (m, 2H), 3.20-3.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 167.5 (d, J_{C-P} = 2.4 Hz), 136.4, 134.8 (d, J_{C-P} = 9.7 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 99.2 Hz), 131.13 (d, J_{C-P} = 5.0 Hz), 131.08 (d, J_{C-P} = 99.9 Hz), 131.0 (d, J_{C-P} = 5.0 Hz), 129.3, 128.7 (d, J_{C-P} = 4.2 Hz), 126.6 (d, J_{C-P} = 4.2 Hz), 128.3, 126.8, 125.0 (d, J_{C-P} = 9.1 Hz), 54.0, 52.2, 37.7, 34.1 (d, J_{C-P} = 65.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.7; HRMS (ESI) Calcd for $C_{26}H_{27}NO_4P$ $[M + H]^+$ 448.1672, found 448.1675.

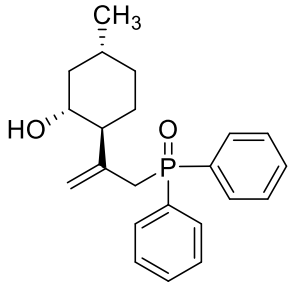


(8-Hydroxy-2,6-dimethyloct-1-en-3-yl)diphenylphosphine oxide (63): Prepared according to the general procedure B from **1bi** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **63** as a light yellow oil (32.8 mg, 46% yield, 1:1 dr.); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.84 (m, 4H), 7.76-7.72 (m, 4H), 7.54-7.48 (m, 6H,), 7.46-7.36 (m, 6H), 4.88 (s, 2H), 4.80 (d, *J* = 4.0 Hz, 2H), 3.69-3.54 (m, 4H), 2.97-2.90 (m, 2H), 1.98-1.87 (m, 4H),

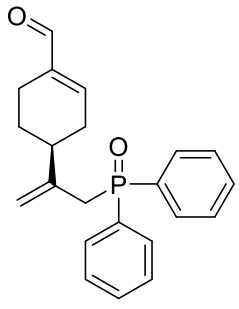
1.74-1.68 (m, 6H), 1.58-1.45 (m, 4H), 1.41-1.31 (m, 2H), 1.29-1.20 (m, 3H), 1.12-1.03 (m, 1H), 0.81 (d, J = 6.4 Hz, 3H), 0.78 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 140.0 (d, $J_{C\text{-}P}$ = 3.3 Hz), 132.5 (d, $J_{C\text{-}P}$ = 95.4 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.2 Hz), 131.04 (d, $J_{C\text{-}P}$ = 4.0 Hz), 130.95 (d, $J_{C\text{-}P}$ = 3.2 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.0 Hz), 128.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 116.7 (d, $J_{C\text{-}P}$ = 4.0 Hz), 116.6 (d, $J_{C\text{-}P}$ = 3.9 Hz), 60.80, 60.75, 48.2 (d, $J_{C\text{-}P}$ = 66.9 Hz), 48.0 (d, $J_{C\text{-}P}$ = 67.1 Hz), 40.1, 39.1, 35.3 (d, $J_{C\text{-}P}$ = 13.1 Hz), 34.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 29.2, 28.8, 23.9, 23.8, 22.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 21.8 (d, $J_{C\text{-}P}$ = 2.4 Hz), 19.8, 19.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2, 32.1; HRMS (ESI) Calcd for $C_{22}H_{30}O_2P$ $[M + H]^+$ 357.1978, found 357.1977.



Methyl 4-(2-((diphenylphosphoryl)methyl)acrylamido)-2-methoxybenzoate (64): Prepared according to the general procedure B from **1bj** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **64** as a white solid (52.8 mg, 59% yield); R_f 0.1 (petroleum ether/ethyl acetate = 1/2); m.p. 174.5-176.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.13 (s, 1H), 7.86-7.72 (m, 6H), 7.64-7.47 (m, 6H), 7.15-7.12 (m, 1H), 6.03 (d, J = 5.1 Hz, 1H), 4.99 (d, J = 5.1 Hz, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 3.46 (d, J = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.1, 160.5, 144.1, 135.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.70, 132.66, 131.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.1 (d, $J_{C\text{-}P}$ = 100.6 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.4 (d, $J_{C\text{-}P}$ = 9.3 Hz), 114.6, 111.2, 103.4, 56.1, 51.7, 35.3 (d, $J_{C\text{-}P}$ = 63.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.2; HRMS (ESI) Calcd for $C_{25}H_{25}NO_5P$ $[M + H]^+$ 450.1465, found 450.1477.

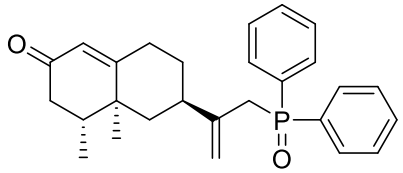


(2-((1*S*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl)allyl)diphenylphosphine oxide (65): Prepared according to the general procedure B from **1bk** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **65** as a white solid (49.7 mg, 70% yield); R_f 0.2 (petroleum ether/ethyl acetate = 2/1); m.p. 138.2-140.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.68 (m, 4H), 7.62-7.40 (m, 6H), 5.00 (d, J = 5.2 Hz, 1H), 4.38 (d, J = 4.7 Hz, 1H), 3.56-3.52 (m, 1H), 3.21-3.05 (m, 2H), 2.12-2.00 (m, 2H), 1.67-1.56 (m, 2H), 1.50-1.41 (m, 1H), 1.32-1.20 (m, 1H), 1.04 (q, J = 11.9 Hz, 1H), 0.92 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1 (d, $J_{C\text{-}P}$ = 10.0 Hz), 133.8 (d, $J_{C\text{-}P}$ = 99.8 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.2 (d, $J_{C\text{-}P}$ = 93.9 Hz), 130.8 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.8 Hz), 116.9 (d, $J_{C\text{-}P}$ = 8.9 Hz), 70.6, 55.1 (d, $J_{C\text{-}P}$ = 2.1 Hz), 43.4, 34.3, 34.2 (d, $J_{C\text{-}P}$ = 66.6 Hz), 31.6, 31.4, 22.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4; HRMS (ESI) Calcd for $C_{22}H_{27}O_2PNa$ $[M + Na]^+$ 377.1641, found 377.1650.



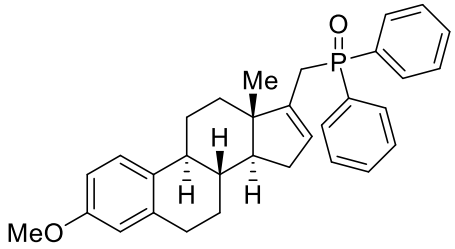
(*S*)-4-(3-(Diphenylphosphoryl)prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (66): Prepared according to the general procedure B from **1bl** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum

ether/ethyl acetate (1:1) to provide the title compound **66** as a colorless oli (30.2 mg, 43% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.88-7.63 (m, 4H), 7.65-7.39 (m, 6H), 6.77-6.74 (m, 1H), 4.89 (d, *J* = 4.2 Hz, 1H), 4.85 (d, *J* = 4.4 Hz, 1H), 3.18 (dd, *J* = 14.0, 3.0 Hz, 2H), 2.58-2.50 (m, 1H), 2.35-2.30 (m, 2H), 2.21-2.11 (m, 1H), 2.08-1.98 (m, 1H), 1.90-1.83 (m, 1H), 1.41-1.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 150.3, 143.0 (d, J_{C-P} = 9.1 Hz), 141.0, 132.7 (d, J_{C-P} = 98.2 Hz), 132.6 (d, J_{C-P} = 98.6 Hz), 131.81 (d, J_{C-P} = 2.8 Hz), 131.78 (d, J_{C-P} = 3.0 Hz), 131.0 (d, J_{C-P} = 9.0 Hz), 130.9 (d, J_{C-P} = 9.0 Hz), 128.6 (d, J_{C-P} = 3.4 Hz), 128.5 (d, J_{C-P} = 3.4 Hz), 114.4 (d, J_{C-P} = 9.2 Hz), 39.6 (d, J_{C-P} = 2.6 Hz), 37.2 (d, J_{C-P} = 66.8 Hz), 31.9, 26.5, 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.5; HRMS (ESI) Calcd for $C_{22}H_{23}O_2PNa$ $[M + Na]^+$ 373.1328, found 373.1337.

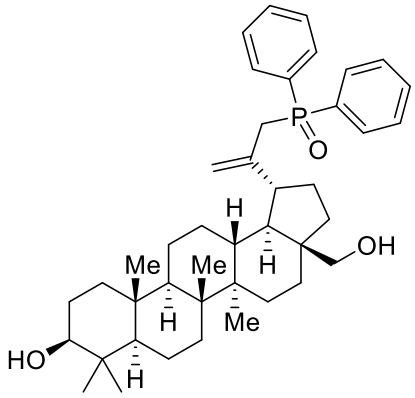


(4*R*,4a*S*,6*R*)-6-(3-(Diphenylphosphoryl)prop-1-en-2-yl)-4,4a-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (67): Prepared according to the general procedure B from **1bm** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **67** as a white solid (53.9 mg, 64% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); m.p. 151.8-153.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 11.3, 7.4 Hz, 4H), 7.56-7.44 (m, 6H), 5.72 (s, 1H), 4.87 (dd, *J* = 8.3, 4.2 Hz, 2H), 3.18 (dd, *J* = 14.0, 5.9 Hz, 2H), 2.42-2.28 (m, 3H), 2.28-2.19 (m, 2H), 1.97-1.88 (m, 3H), 1.22-1.18 (m, 1H), 0.97 (s, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 170.2, 143.5 (d, J_{C-P} = 9.1 Hz), 132.94 (d, J_{C-P} = 97.5 Hz), 132.92 (d, J_{C-P} = 97.9 Hz), 131.8 (d, J_{C-P} = 2.6 Hz), 130.99 (d, J_{C-P} = 9.1 Hz), 130.97 (d, J_{C-P} = 9.0 Hz), 128.5 (d, J_{C-P} = 11.5 Hz), 124.6, 114.2 (d, J_{C-P} = 9.3 Hz), 44.0, 42.0, 40.3, 39.3, 39.0 (d, J_{C-P} = 2.4 Hz), 37.5 (d, J_{C-P} = 66.7 Hz), 32.9, 32.0, 16.6, 14.9; ^{31}P NMR (162

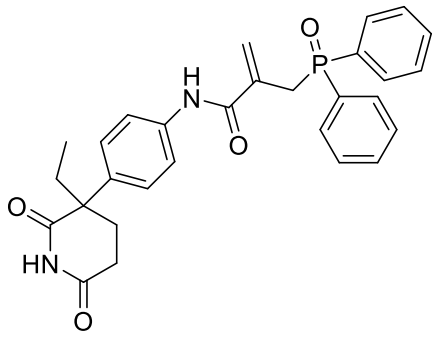
MHz, $CDCl_3$) δ 28.8; HRMS (ESI) Calcd for $C_{27}H_{32}O_2P$ $[M + H]^+$ 419.2134, found 419.2136.



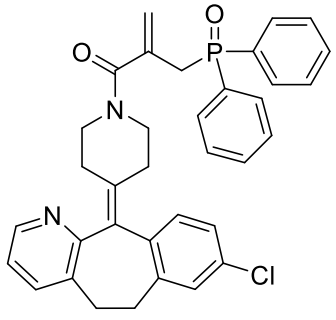
(((13*S*,14*S*)-3-Methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthren-17-yl)methyl)diphenylphosphine oxide (68): Prepared according to the general procedure B from **1bn** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **68** as a light yellow oil (81.9 mg, 85% yield); R_f 0.1 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.74 (m, 4H), 7.54-7.44 (m, 6H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.69 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.62 (d, *J* = 2.8 Hz, 1H), 5.64 (s, 1H), 3.77 (d, *J* = 0.8 Hz, 3H), 3.14-2.98 (m, 2H), 2.91-2.81 (m, 2H), 2.32-2.78 (m, 1H), 2.23-2.18 (m, 1H), 2.15-2.09 (m, 1H), 1.93-1.84 (m, 2H), 1.77-1.72 (m, 1H), 1.55-1.45 (m, 3H), 1.43-1.29 (m, 2H), 0.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 143.8 (d, $J_{C\text{-}P}$ = 8.4 Hz), 137.9, 133.5 (d, $J_{C\text{-}P}$ = 98.7 Hz), 133.3 (d, $J_{C\text{-}P}$ = 99.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.54, 128.50 (d, $J_{C\text{-}P}$ = 1.7 Hz), 128.47, 128.4 (d, $J_{C\text{-}P}$ = 1.6 Hz), 125.9, 113.7, 111.3, 55.3, 55.1, 47.6 (d, $J_{C\text{-}P}$ = 5.9 Hz), 44.1, 37.4, 34.0, 31.4 (d, $J_{C\text{-}P}$ = 1.8 Hz), 29.6, 28.2 (d, $J_{C\text{-}P}$ = 69.9 Hz), 27.6, 26.3, 15.5 (d, $J_{C\text{-}P}$ = 2.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4; HRMS (ESI) Calcd for $C_{32}H_{35}O_2PNa$ $[M + Na]^+$ 505.2267, found 505.2272.



(2-((1*R*,3a*S*,5a*R*,5b*R*,7a*R*,9*S*,11a*R*,11b*R*,13b*R*)-9-Hydroxy-3a-(hydroxymethyl)-5a,5b,8,8,11a-pentamethylicosahydro-1H-cyclopenta[a]chrysen-1-yl)allyl)diphenylphosphine oxide (69): Prepared according to the general procedure B from **1bo** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate/ethyl alcohol (30:30:1) to provide the title compound **71** as a white solid (59.0 mg, 46% yield); R_f 0.4 (petroleum ether/ethyl acetate/ethyl alcohol = 10/10/1); m.p. 91.1-93.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.70 (m, 4H), 7.54-7.41 (m, 6H), 4.88 (d, *J* = 3.6 Hz, 1H), 4.80 (d, *J* = 3.7 Hz, 1H), 3.71 (d, *J* = 10.9 Hz, 1H), 3.26-3.17 (m, 2H), 3.14 (d, *J* = 15.0 Hz, 1H), 3.07 (t, *J* = 14.6 Hz, 1H), 2.33 (dt, *J* = 16.2, 5.5 Hz, 1H), 2.06-1.96 (m, 1H), 1.90 (d, *J* = 13.4 Hz, 1H), 1.79 (dd, *J* = 12.3, 8.2 Hz, 1H), 1.74-1.54 (m, 7H), 1.38 (s, 3H), 1.32-1.26 (m, 3H), 1.21-1.14 (m, 3H), 1.04 (app. s, 2H), 0.98 (d, *J* = 10.5 Hz, 6H), 0.93 (s, 3H), 0.89-0.85 (m, 4H), 0.83 (s, 3H), 0.76 (s, 3H), 0.66 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.4 (d, $J_{C\text{-}P}$ = 97.3 Hz), 133.0 (d, $J_{C\text{-}P}$ = 97.9 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.0(d, $J_{C\text{-}P}$ = 8.9 Hz), 130.8 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.5 (d, $J_{C\text{-}P}$ = 7.2 Hz), 128.4 (d, $J_{C\text{-}P}$ = 7.5 Hz), 112.9, 78.9, 60.4, 55.3, 50.5, 50.3, 47.7, 46.2, 42.6, 40.9, 38.8, 38.7, 37.1, 37.0, 33.9 (d, $J_{C\text{-}P}$ = 69.3 Hz), 31.4, 29.3, 28.0, 27.4, 27.21, 27.18, 27.0, 21.0, 18.3, 16.1, 16.0, 15.4, 14.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9; HRMS (ESI) Calcd for $C_{42}H_{59}O_3PNa$ $[M + Na]^+$ 665.4094, found 665.4102.

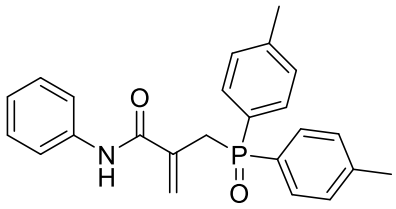


2-((Diphenylphosphoryl)methyl)-N-(4-(3-ethyl-2,6-dioxopiperidin-3-yl)phenyl)acrylamide (70): Prepared according to the general procedure B from **1bp** (0.40 mmol) and **2a** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **69** as a white solid (56.2 mg, 56% yield); R_f 0.1 (petroleum ether/ethyl acetate = 1/2); m.p. 191.7-193.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.84 (s, 1H), 7.89 (s, 1H), 7.84-7.68 (m, 6H), 7.63-7.56 (m, 2H), 7.55-7.50 (m, 4H), 7.25-7.17 (m, 2H), 6.02 (d, J = 5.2 Hz, 1H), 5.00 (d, J = 5.1 Hz, 1H), 3.46 (d, J = 13.6 Hz, 2H), 2.58 (dd, J = 18.2, 4.7 Hz, 1H), 2.46-2.34 (m, 2H), 2.24-2.16 (m, 1H), 2.06-2.00 (m, 1H), 1.96-1.87 (m, 1H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 172.4, 166.1, 138.1, 135.5 (d, J_{C-P} = 10.4 Hz), 134.0, 132.5 (d, J_{C-P} = 2.8 Hz), 131.1 (d, J_{C-P} = 9.4 Hz), 130.2 (d, J_{C-P} = 100.6 Hz), 128.8 (d, J_{C-P} = 12.0 Hz), 126.6 (d, J_{C-P} = 9.2 Hz), 126.5, 120.4, 50.6, 35.1 (d, J_{C-P} = 64.4 Hz), 32.8, 29.2, 27.1, 9.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.9; HRMS (ESI) Calcd for $C_{29}H_{30}N_2O_4P$ $[M + H]^+$ 501.1938, found 501.1937.

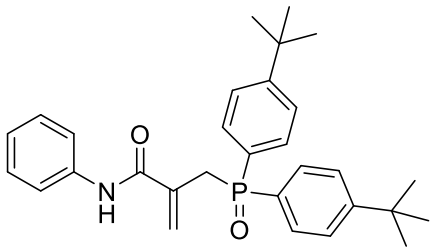


1-(4-(8-Chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidin-1-yl)-2-((diphenylphosphoryl)methyl)prop-2-en-1-one (71): Prepared according to the general procedure B from **1bq** (0.40 mmol) and **2a** (0.20

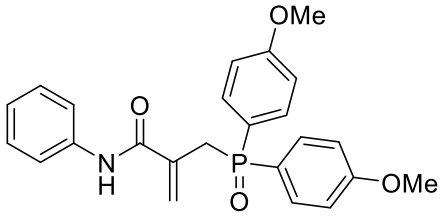
mmol) for 24 h and purified by column chromatography on silica gel with ethyl acetate/ethyl alcohol (30:1) to provide the title compound **70** as a light brown solid (61.4 mg, 53% yield); R_f 0.1 (petroleum ether/ethyl acetate = 1/4); m.p. 180.1-181.5 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 4.7 Hz, 1H), 7.83-7.70 (m, 4H), 7.53-7.38 (m, 7H), 7.17-7.04 (m, 4H), 5.46 (d, J = 4.7 Hz, 1H), 5.24 (d, J = 4.5 Hz, 1H), 3.64 (d, J = 60.2 Hz, 4H), 3.38-3.27 (m, 2H), 3.00 (app. s, 2H), 2.88-2.75 (m, 2H), 2.32 (app. s, 1H), 2.16 (app. s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 156.8, 146.6, 139.4, 137.6, 137.4, 137.1, 133.64 (d, $J_{C\text{-}P}$ = 112.4 Hz), 133.58 (d, $J_{C\text{-}P}$ = 8.4 Hz), 133.3, 133.0, 130.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.5, 129.0, 128.6 (d, $J_{C\text{-}P}$ = 11.7 Hz), 126.2, 122.3, 120.9 (d, $J_{C\text{-}P}$ = 9.2 Hz), 48.2, 42.7, 35.5 (d, $J_{C\text{-}P}$ = 67.3 Hz), 31.6, 31.4, 30.6, 30.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.3; HRMS (ESI) Calcd for $C_{35}H_{33}ClN_2O_2P$ $[M + H]^+$ 579.1963, found 579.1973.



2-((Bis(4-methoxyphenyl)phosphoryl)methyl)-N-phenylacrylamide (72): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2b** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **72** as a white solid (38.2 mg, 49% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/1); m.p. 64.3-66.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.68 (s, 1H), 7.76-7.61 (m, 6H), 7.35-7.26 (m, 6H), 7.12-7.03 (m, 1H), 5.99 (d, J = 5.0 Hz, 1H), 5.01 (d, J = 4.8 Hz, 1H), 3.41 (d, J = 13.7 Hz, 2H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (d, $J_{C\text{-}P}$ = 1.8 Hz), 143.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 138.9, 136.0 (d, $J_{C\text{-}P}$ = 10.4 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.5 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.7, 127.3 (d, $J_{C\text{-}P}$ = 102.9 Hz), 126.3 (d, $J_{C\text{-}P}$ = 9.3 Hz), 123.8, 120.0, 35.5 (d, $J_{C\text{-}P}$ = 64.3 Hz), 21.6 (d, $J_{C\text{-}P}$ = 1.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.0; HRMS (ESI) Calcd for $C_{24}H_{25}NO_2P$ $[M + H]^+$ 390.1617, found 390.1619.

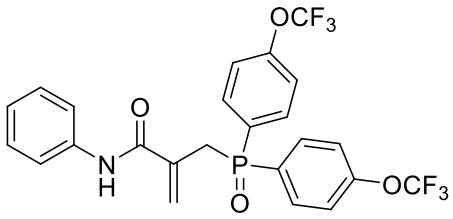


2-((Bis(4-(tert-butyl)phenyl)phosphoryl)methyl)-N-phenylacrylamide (73): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2c** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **73** as a light yellow solid (61.5 mg, 65% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/1); m.p. 178.3-180.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.76-7.67 (m, 6H), 7.52 (dd, *J* = 8.4, 2.7 Hz, 4H), 7.35-7.29 (m, 2H), 7.10-7.05 (m, 1H), 6.01 (d, *J* = 5.1 Hz, 1H), 5.04 (d, *J* = 5.1 Hz, 1H), 3.43 (d, *J* = 13.6 Hz, 2H), 1.32 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 156.0, 138.9, 136.1 (d, $J_{C\text{-}P}$ = 10.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 128.8, 127.3 (d, $J_{C\text{-}P}$ = 102.5 Hz), 126.4 (d, $J_{C\text{-}P}$ = 9.5 Hz), 125.8 (d, $J_{C\text{-}P}$ = 12.1 Hz), 123.8, 120.0, 35.6 (d, $J_{C\text{-}P}$ = 63.7 Hz), 35.1, 31.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.4; HRMS (ESI) Calcd for $C_{30}H_{37}NO_2P$ $[M + H]^+$ 474.2556, found 474.2560.

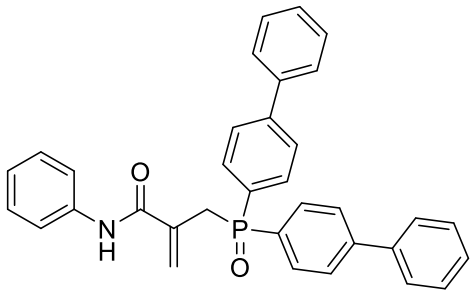


2-((Bis(4-methoxyphenyl)phosphoryl)methyl)-N-phenylacrylamide (74): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2d** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:2) to provide the title compound **74** as a light yellow oil (58.6 mg, 70% yield); R_f 0.1 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 7.71-7.66 (m, 6H), 7.34-7.26 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.99 (dd, *J* = 8.8,

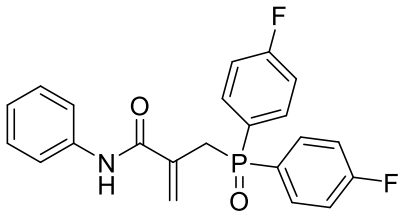
2.4 Hz, 4H), 5.99 (d, J = 5.1 Hz, 1H), 5.02 (d, J = 5.1 Hz, 1H), 3.82 (s, 6H), 3.39 (d, J = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (d, $J_{C\text{-}P}$ = 1.8 Hz), 162.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 138.8, 136.1 (d, $J_{C\text{-}P}$ = 10.4 Hz), 132.9 (d, $J_{C\text{-}P}$ = 10.8 Hz), 128.7, 126.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 123.8, 121.7 (d, $J_{C\text{-}P}$ = 107.4 Hz), 119.9, 114.3 (d, $J_{C\text{-}P}$ = 13.0 Hz), 55.3, 35.7 (d, $J_{C\text{-}P}$ = 64.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.7; HRMS (ESI) Calcd for $C_{24}H_{24}NO_4PNa$ $[M + Na]^+$ 444.1335, found 444.1346.



2-((Bis(4-(trifluoromethoxy)phenyl)phosphoryl)methyl)-N-phenylacrylamide (75): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2e** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **75** as a light yellow solid (68.8 mg, 65% yield); R_f 0.1 (petroleum ether/ethyl acetate = 1/1); m.p. 108.1-110.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.92-7.77 (m, 4H), 7.66-7.55 (m, 2H), 7.42-7.28 (m, 6H), 7.10 (t, J = 7.6 Hz, 1H), 6.04 (d, J = 5.2 Hz, 1H), 5.21 (d, J = 5.1 Hz, 1H), 3.50 (d, J = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 152.5, 138.3, 135.4 (d, $J_{C\text{-}P}$ = 10.0 Hz), 133.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.86, 128.85 (d, $J_{C\text{-}P}$ = 102.2 Hz), 126.2 (d, $J_{C\text{-}P}$ = 8.9 Hz), 124.3, 120.9 (d, $J_{C\text{-}P}$ = 12.7 Hz), 120.2 (q, $J_{C\text{-}F}$ = 257.7 Hz), 120.0, 34.8 (d, $J_{C\text{-}P}$ = 65.8 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -57.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.1; HRMS (ESI) Calcd for $C_{24}H_{19}F_6NO_4P$ $[M + H]^+$ 530.0950, found 530.0954.

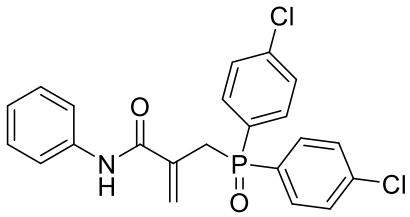


2-((Di([1,1'-biphenyl]-4-yl)phosphoryl)methyl)-N-phenylacrylamide (76): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2f** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **76** as a light yellow solid (76.5 mg, 75% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/1); m.p. 164.2-166.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.89 (dd, J = 11.4, 7.9 Hz, 4H), 7.79-7.67 (m, 6H), 7.59 (d, J = 7.6 Hz, 4H), 7.47 (t, J = 7.5 Hz, 4H), 7.40 (t, J = 7.3 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 6.05 (d, J = 5.1 Hz, 1H), 5.15 (d, J = 5.1 Hz, 1H), 3.54 (d, J = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 145.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 139.5, 138.7, 135.8 (d, $J_{C\text{-}P}$ = 10.4 Hz), 131.6 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.0 (d, $J_{C\text{-}P}$ = 102.1 Hz), 129.0, 128.8, 128.3, 127.5 (d, $J_{C\text{-}P}$ = 12.1 Hz), 127.2, 126.4 (d, $J_{C\text{-}P}$ = 9.2 Hz), 123.9, 120.0, 35.3 (d, $J_{C\text{-}P}$ = 64.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.4; HRMS (ESI) Calcd for $C_{34}H_{29}NO_2P$ $[M + H]^+$ 514.1930, found 514.1935.

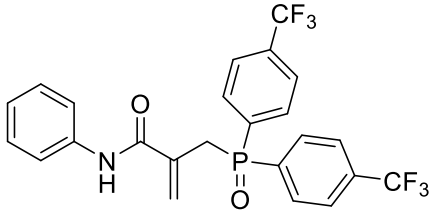


2-((Bis(4-fluorophenyl)phosphoryl)methyl)-N-phenylacrylamide (77): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2g** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **77** as a white solid (48.3 mg, 61% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/1); m.p. 160.1-161.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.82-7.75 (m, 4H), 7.64 (d, J = 8.1 Hz, 2H), 7.32 (t, J = 7.7 Hz,

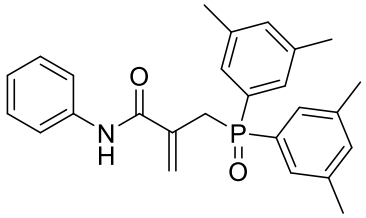
2H), 7.21 (m, 4H), 7.10 (t, J = 7.4 Hz, 1H), 6.02 (d, J = 5.2 Hz, 1H), 5.11 (d, J = 5.1 Hz, 1H), 3.46 (d, J = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, J = 1.8 Hz), 165.4 (dd, $J_{C\text{-}F}$ = 253.8 Hz, $J_{C\text{-}P}$ = 3.3 Hz), 138.5, 135.6 (d, $J_{C\text{-}P}$ = 10.3 Hz), 133.6 (dd, $J_{C\text{-}F}$ = 10.8 Hz, $J_{C\text{-}P}$ = 8.8 Hz), 128.8, 126.4 (dd, $J_{C\text{-}F}$ =3.3 Hz, $J_{C\text{-}P}$ = 103.8 Hz), 126.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 124.1, 120.0, 116.4 (dd, $J_{C\text{-}F}$ = 21.4 Hz, $J_{C\text{-}P}$ = 13.1 Hz), 35.2 (d, $J_{C\text{-}P}$ = 65.6 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -105.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0; HRMS (ESI) Calcd for $C_{22}H_{19}F_2NO_2P$ $[M + H]^+$ 398.1116, found 398.1121.



2-((Bis(4-chlorophenyl)phosphoryl)methyl)-N-phenylacrylamide (78): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2h** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **78** as a white solid (53.0 mg, 62% yield); R_f 0.3 (petroleum ether/ethyl acetate = 1/1.5); m.p. 133.4-135.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.77-7.66 (m, 4H), 7.62 (d, J = 7.7 Hz, 2H), 7.51-7.48 (m, 4H), 7.32 (t, J = 7.9 Hz, 2H), 7.10 (t, J = 7.4 Hz, 1H), 6.07-5.94 (m, 1H), 5.15 (d, J = 5.1 Hz, 1H), 3.46 (d, J = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (d, $J_{C\text{-}P}$ = 2.1 Hz), 139.5 (d, $J_{C\text{-}P}$ = 3.3 Hz), 138.4, 135.4 (d, $J_{C\text{-}P}$ = 10.2 Hz), 132.4 (d, $J_{C\text{-}P}$ = 10.2 Hz), 129.3 (d, $J_{C\text{-}P}$ = 12.7 Hz), 128.9, 128.8 (d, $J_{C\text{-}P}$ = 101.1 Hz), 126.4 (d, $J_{C\text{-}P}$ = 9.0 Hz), 124.2, 120.0, 34.8 (d, $J_{C\text{-}P}$ = 65.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0; HRMS (ESI) Calcd for $C_{22}H_{18}Cl_2NO_2PNa$ $[M + Na]^+$ 452.0344, found 452.0352.

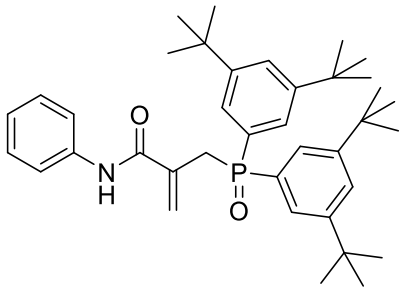


2-((Bis(4-(trifluoromethyl)phenyl)phosphoryl)methyl)-N-phenylacrylamide (79): Prepared according to the general procedure from **1a** (0.40 mmol) and **2i** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **79** as a white solid (56.4 mg, 57% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/1); m.p. 193.8-195.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), δ 7.95 (dd, *J* = 11.3, 8.0 Hz, 2H), 7.78 (dd, *J* = 8.4, 2.5 Hz, 4H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.02 (d, *J* = 5.1 Hz, 1H), 5.32 (d, *J* = 5.1 Hz, 1H), 3.57 (d, *J* = 13.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 138.0, 135.1 (d, J_{C-P} = 9.4 Hz), 134.7 (d, J_{C-P} = 101.1 Hz), 134.6 (dd, J_{C-F} = 33.1 Hz, J_{C-P} = 2.8 Hz), 131.6 (d, J_{C-P} = 9.7 Hz), 128.9, 126.0 (d, J_{C-P} = 10.0 Hz), 125.9 (dq, J_{C-F} = 12.1 Hz, J_{C-P} = 3.7 Hz), 124.4, 123.2 (q, J_{C-F} = 271.4 Hz), 120.0, 34.2 (d, J_{C-P} = 66.0 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -63.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3; HRMS (ESI) Calcd for $C_{24}H_{19}F_6NO_2P$ $[M + H]^+$ 498.1052, found 498.1059.

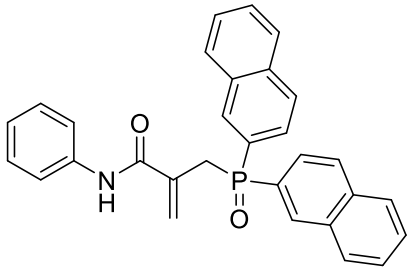


2-((Bis(3,5-dimethylphenyl)phosphoryl)methyl)-N-phenylacrylamide (80): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2j** (0.20 mmol) for 48 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **80** as a light yellow oil (56.1 mg, 67% yield); R_f 0.4 (petroleum ether/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 12.0 Hz, 4H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.17 (s, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 5.99 (d, *J* = 5.1 Hz, 1H), 5.03 (d, *J* = 5.1 Hz, 1H), 3.43 (d, *J* = 13.7 Hz, 2H), 2.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 138.9, 138.5 (d, J_{C-P} = 12.7 Hz), 136.0 (d, J_{C-P} = 10.4 Hz), 134.1 (d, J_{C-P} = 2.9 Hz), 130.4 (d, J_{C-P} = 99.5 Hz), 128.7, 128.5 (d, J_{C-P} = 9.4 Hz), 126.2 (d, J_{C-P} = 9.2 Hz), 123.8,

120.0, 35.0 (d, $J_{C\text{-}P}$ = 63.7 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.0; HRMS (ESI) Calcd for $C_{26}H_{29}NO_2P$ $[M + H]^+$ 418.1930, found 418.1934.

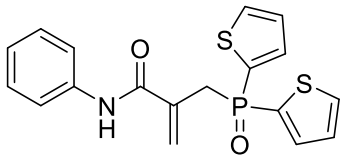


2-((Bis(3,5-di-tert-butylphenyl)phosphoryl)methyl)-N-phenylacrylamide (81): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2k** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to provide the title compound **81** as a white solid (62.8 mg, 54% yield); R_f 0.2 (petroleum ether/ethyl acetate = 3/1); m.p. 208.2-211.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 7.73 (d, J = 8.1 Hz, 2H), 7.62 (m, 6H), 7.33 (m, 2H), 7.08 (t, J = 7.7 Hz, 1H), 6.02 (d, J = 4.3 Hz, 1H), 5.00 (d, J = 4.4 Hz, 1H), 3.42 (d, J = 13.6 Hz, 2H), 1.32 (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 151.4 (d, $J_{C\text{-}P}$ = 11.7 Hz), 139.0, 136.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 129.7 (d, $J_{C\text{-}P}$ = 99.4 Hz), 128.7, 126.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 126.1 (d, $J_{C\text{-}P}$ = 9.1 Hz), 125.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 123.8, 120.1, 36.2 (d, $J_{C\text{-}P}$ = 63.0 Hz), 35.1, 31.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.3; HRMS (ESI) Calcd for $C_{38}H_{52}NO_2PNa$ $[M + Na]^+$ 608.3628, found 608.3636.

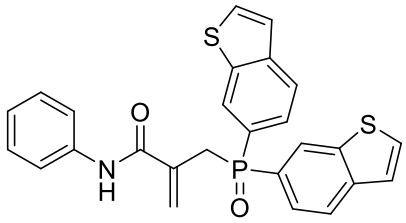


2-((Di(naphthalen-2-yl)phosphoryl)methyl)-N-phenylacrylamide (82): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2l** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **82** as a white solid (66.3 mg, 72% yield); R_f

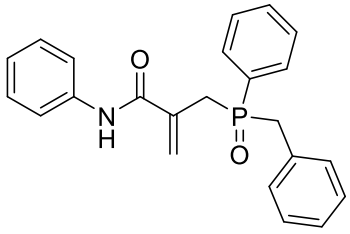
0.2 (petroleum ether/ethyl acetate = 1/1); m.p. 151.2-152.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.47 (d, *J* = 13.6 Hz, 2H), 7.99-7.91 (m, 4H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.75 (t, *J* = 9.1 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.65-7.56 (m, 4H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.98 (d, *J* = 5.2 Hz, 1H), 5.07 (d, *J* = 5.1 Hz, 1H), 3.66 (d, *J* = 13.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 138.7, 135.8 (d, $J_{C\text{-}P}$ = 10.3 Hz), 134.6 (d, $J_{C\text{-}P}$ = 2.3 Hz), 133.5 (d, $J_{C\text{-}P}$ = 8.5 Hz), 132.4 (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.9, 128.77 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.75, 128.6, 127.9, 127. 6 (d, $J_{C\text{-}P}$ = 100.0 Hz), 127.3, 126.4 (d, $J_{C\text{-}P}$ = 9.2 Hz), 125.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 123.9, 34.9 (d, $J_{C\text{-}P}$ = 64.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.9; HRMS (ESI) Calcd for $C_{30}H_{25}NO_2P$ $[M + H]^+$ 462.1617, found 462.1624.



2-((Di(thiophen-2-yl)phosphoryl)methyl)-N-phenylacrylamide (83): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2m** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to provide the title compound **83** as a white oil (33.1 mg, 44% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.81-7.76 (m, 2H), 7.71-7.65 (m, 4H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.26-7.22 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.09 (d, *J* = 5.7 Hz, 1H), 5.22 (d, *J* = 5.7 Hz, 1H), 3.49 (d, *J* = 14.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (d, $J_{C\text{-}P}$ = 2.2 Hz), 138.6, 136.5 (d, $J_{C\text{-}P}$ = 9.9 Hz), 135.3 (d, $J_{C\text{-}P}$ = 11.0 Hz), 134.3 (d, $J_{C\text{-}P}$ = 5.3 Hz), 131.2 (d, $J_{C\text{-}P}$ = 116.1 Hz), 128.8, 128.6 (d, $J_{C\text{-}P}$ = 14.4 Hz), 126.7 (d, $J_{C\text{-}P}$ = 10.2 Hz), 124.0, 120.0, 39.0 (d, $J_{C\text{-}P}$ = 72.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.7; HRMS (ESI) Calcd for $C_{18}H_{17}NO_2PS_2$ $[M + H]^+$ 374.0433, found 374.0439.

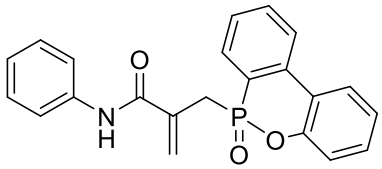


2-((Bis(benzo[b]thiophen-6-yl)phosphoryl)methyl)-N-phenylacrylamide (84): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2n** (0.20 mmol) for 48 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **84** as a colorless oil (68.7 mg, 73% yield); R_f 0.1 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.35 (d, *J* = 12.7 Hz, 2H), 8.02 (dd, *J* = 8.3, 2.6 Hz, 2H), 7.71-7.66 (m, 5H), 7.57 (d, *J* = 5.4 Hz, 2H), 7.42 (d, *J* = 5.5 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 5.98 (d, *J* = 5.2 Hz, 1H), 5.05 (d, *J* = 5.1 Hz, 1H), 3.60 (d, *J* = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 143.8 (d, J_{C-P} = 2.8 Hz), 139.4 (d, J_{C-P} = 13.6 Hz), 138.8, 135.9 (d, J_{C-P} = 10.3 Hz), 128.8, 128.3, 127.5 (d, J_{C-P} = 9.7 Hz), 126.4 (d, J_{C-P} = 9.4 Hz), 126.3 (d, J_{C-P} = 102.1 Hz), 125.2 (d, J_{C-P} = 11.5 Hz), 124.1, 123.9, 123.1 (d, J_{C-P} = 13.3 Hz), 120.0, 35.5 (d, J_{C-P} = 64.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.0; HRMS (ESI) Calcd for $C_{26}H_{21}NO_2PS_2$ $[M + H]^+$ 474.0746, found 474.0749.

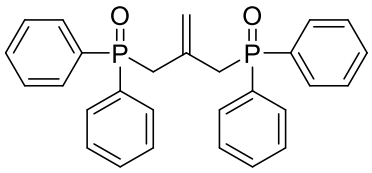


2-((Benzyl(phenyl)phosphoryl)methyl)-N-phenylacrylamide (85): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2o** (0.20 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to provide the title compound **85** as a white solid (43.9 mg, 59% yield); R_f 0.2 (petroleum ether/ethyl acetate = 1/1.5); m.p. 152.2-154.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.67-7.62 (m, 4H), 7.57-7.43 (m, 4H), 7.32-7.27 (m, 2H), 7.27-7.21 (m, 4H), 7.18-7.13 (m, *J* = 7.3, 2.2 Hz, 2H), 7.10-7.05 (m, 1H), 6.03 (dd, *J* = 5.0,

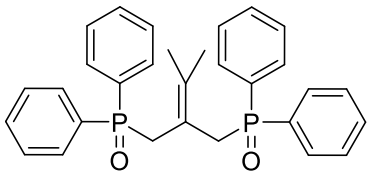
1.9 Hz, 1H), 5.16 (d, J = 4.9 Hz, 1H), 3.54-3.41 (m, 2H), 3.22-3.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 138.7, 136.0 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.4 (d, $J_{C\text{-}P}$ = 7.6 Hz), 129.9 (d, $J_{C\text{-}P}$ = 5.1 Hz), 129.1 (d, $J_{C\text{-}P}$ = 94.7 Hz), 128.79, 128.75, 128.6, 127.3 (d, $J_{C\text{-}P}$ = 3.1 Hz), 126.2 (d, $J_{C\text{-}P}$ = 8.6 Hz), 123.9, 120.0, 37.7 (d, $J_{C\text{-}P}$ = 63.2 Hz), 34.4 (d, $J_{C\text{-}P}$ = 61.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.7; HRMS (ESI) Calcd for $C_{23}H_{23}NO_2P$ $[M + H]^+$ 376.1461, found 376.1463.



2-((1-Oxido-3,4-dihydrobenzo[*c*][1,2]oxaphosphinin-1-yl)methyl)-N-phenylacrylamide (86): Prepared according to the general procedure B from **1a** (0.40 mmol) and **2p** (0.20 mmol) for 48 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to provide the title compound **86** as a white solid (42.9 mg, 57% yield); R_f 0.2 (petroleum ether/ethyl acetate = 2/1); m.p. 150.6-152.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.01-7.91 (m, 3H), 7.75 (t, J = 7.7 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.55-7.50 (m, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.36-7.30 (m, 3H), 7.25-7.22 (m, 1H), 7.12 (t, J = 7.4 Hz, 1H), 6.12 (d, J = 5.8 Hz, 1H), 5.21 (d, J = 5.7 Hz, 1H), 3.22-3.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 149.0 (d, $J_{C\text{-}P}$ = 8.0 Hz), 138.4, 136.0 (d, $J_{C\text{-}P}$ = 6.9 Hz), 134.8 (d, $J_{C\text{-}P}$ = 11.0 Hz), 134.1 (d, $J_{C\text{-}P}$ = 2.4 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.9, 128.5 (d, $J_{C\text{-}P}$ = 13.0 Hz), 126.4 (d, $J_{C\text{-}P}$ = 10.6 Hz), 125.3, 125.1, 124.2, 124.0 (d, $J_{C\text{-}P}$ = 9.9 Hz), 122.6 (d, $J_{C\text{-}P}$ = 121.8 Hz), 122.1 (d, $J_{C\text{-}P}$ = 11.0 Hz), 120.5 (d, $J_{C\text{-}P}$ = 6.5 Hz), 120.0, 33.6 (d, $J_{C\text{-}P}$ = 88.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.1; HRMS (ESI) Calcd for $C_{22}H_{19}NO_3P$ $[M + H]^+$ 376.1097, found 376.1105.

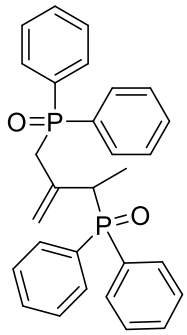


(2-Methylenepropane-1,3-diyl)bis(diphenylphosphine oxide) (88): Prepared according to the general procedure C from **87a** (0.20 mmol) and **2a** (0.40 mmol) for 24 h and purified by column chromatography on silica gel with dichloromethane/methyl alcohol (80:1) to provide the title compound **88** as a white solid (56.8 mg, 62% yield); R_f 0.2 (dichloromethane/methyl alcohol = 50/1); m.p. 138.6-139.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.64 (m, 8H), 7.52-7.41 (m, 12H), 4.82 (t, J = 4.5 Hz, 2H), 3.32 (d, J = 14.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6 (d, $J_{C\text{-}P}$ = 98.6 Hz), 131.7, 131.006 (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.005 (dd, $J_{C\text{-}P}$ = 8.4 Hz), 130.6 (t, $J_{C\text{-}P}$ = 9.8 Hz), 128.505 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.504 (dd, $J_{C\text{-}P}$ = 9.1 Hz), 120.8 (t, $J_{C\text{-}P}$ = 9.4 Hz), 38.3 (d, $J_{C\text{-}P}$ = 67.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.7; HRMS (ESI) Calcd for $C_{28}H_{26}O_2P_2Na$ $[M + Na]^+$ 479.1300, found 479.1312.

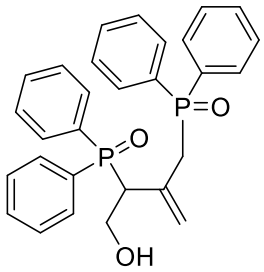


(2-(Propan-2-ylidene)propane-1,3-diyl)bis(diphenylphosphine oxide) (89): Prepared according to the general procedure C from **87b** (0.20 mmol) and **2a** (0.40 mmol) for 48 h and purified by column chromatography on silica gel with dichloromethane/methyl alcohol (80:1) to provide the title compound **89** as a white solid (39.7 mg, 41% yield); R_f 0.3 (dichloromethane/methyl alcohol = 50/1); m.p. 182.5-184.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.64 (m, 8H), 7.52-7.39 (m, 12H), 3.37 (d, J = 12.8 Hz, 4H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1 (t, J = 9.9 Hz), 133.0 (d, J = 96.5 Hz), 131.4, 130.8 (dd, J = 8.9 Hz), 128.2 (dd, J = 11.5 Hz), 113.0 (t, J = 10.6 Hz), 34.5 (d, J = 68.2 Hz), 20.9 (t, J = 2.9 Hz); ^{31}P NMR (162 MHz,

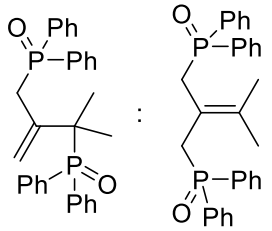
$CDCl_3$) δ 29.4; HRMS (ESI) Calcd for $C_{30}H_{30}O_2P_2Na$ $[M + Na]^+$ 507.1618, found 507.1624.



(2-Methylenebutane-1,3-diyl)bis(diphenylphosphine oxide) (90): Prepared according to the general procedure C from **87c** (0.20 mmol) and **2a** (0.40 mmol) for 24 h and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1:3) to provide the title compound **90** as a white solid (57.2 mg, 61% yield); R_f 0.1 (petroleum ether/ethyl acetate = 1/2); m.p. 198.3-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.77 (m, 4H), 7.72-7.61 (m, 4H), 7.52-7.39 (m, 12H), 5.13 (t, J = 4.0 Hz, 1H), 5.00 (t, J = 4.3 Hz, 1H), 3.67 (dd, J = 9.2, 7.1 Hz, 1H), 3.11-2.85 (m, 2H), 1.20 (dd, J = 16.2, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7 (t, $J_{C\text{-}P}$ = 7.8 Hz), 133.3 (d, $J_{C\text{-}P}$ = 122.3 Hz), 132.7 (d, $J_{C\text{-}P}$ = 95.1 Hz), 132.4 (d, $J_{C\text{-}P}$ = 102.2 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.50 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.45 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.40 (d, $J_{C\text{-}P}$ = 94.5 Hz), 131.37 (d, $J_{C\text{-}P}$ = 3.3 Hz), 131.1 (d, $J_{C\text{-}P}$ = 8.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.1 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.6 (d, $J_{C\text{-}P}$ = 7.0 Hz), 128.5, 128.4 (d, $J_{C\text{-}P}$ = 1.9 Hz), 128.4 (d, $J_{C\text{-}P}$ = 7.9 Hz), 120.1 (t, $J_{C\text{-}P}$ = 9.0 Hz), 39.5 (dd, $J_{C\text{-}P}$ = 66.0, 2.1 Hz), 38.7 (dd, $J_{C\text{-}P}$ = 67.2, 2.6 Hz), 14.3 (d, $J_{C\text{-}P}$ = 2.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8 (d, J = 6.3 Hz), 29.7 (d, J = 6.3 Hz); HRMS (ESI) Calcd for $C_{29}H_{29}O_2P_2$ $[M + H]^+$ 471.1637, found 471.1643.



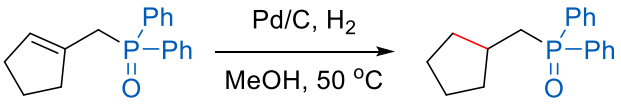
(4-Hydroxy-2-methylenebutane-1,3-diyl)bis(diphenylphosphine oxide) (91): Prepared according to the general procedure C from **1a** (0.20 mmol) and **87d** (0.40 mmol) for 24 h and purified by column chromatography on silica gel with dichloromethane/methyl alcohol (70:1) to provide the title compound **91** as a white solid (48.3 mg, 50% yield); R_f 0.1 (dichloromethane/methyl alcohol = 50/1); m.p. 169.2-171.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 11.0, 7.2 Hz, 2H), 7.80-7.64 (m, 6H), 7.57-7.37 (m, 12H), 4.99 (s, 1H), 4.46 (s, 1H), 4.23 (t, *J* = 11.3 Hz, 1H), 3.83 (d, *J* = 12.1 Hz, 1H), 3.70 (t, *J* = 14.4 Hz, 1H), 3.58 (t, *J* = 10.3 Hz, 1H), 3.05 (t, *J* = 13.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.174 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.167 (d, $J_{C\text{-}P}$ = 100.2 Hz), 132.15 (d, $J_{C\text{-}P}$ = 100.3 Hz), 132.03 (d, $J_{C\text{-}P}$ = 95.5 Hz),132.02 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.2 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.4 (d, $J_{C\text{-}P}$ = 9.2 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.8 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.83 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.78 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.7 Hz), 123.0 (t, $J_{C\text{-}P}$ = 9.2 Hz), 59.2, 52.1 (d, $J_{C\text{-}P}$ = 62.8 Hz), 34.9 (d, $J_{C\text{-}P}$ = 64.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.4 (d, *J* = 7.0 Hz), 30.5 (d, *J* = 4.4 Hz); HRMS (ESI) Calcd for $C_{29}H_{28}O_3P_2Na$ $[M + Na]^+$ 509.1406, found 509.1411.



(3-Methyl-2-methylenebutane-1,3-diyl)bis(diphenylphosphine oxide) (92): Prepared according to the general procedure C from **1a** (0.20 mmol) and **87e** (0.40 mmol) for 24 h and purified by column chromatography on silica gel with petroleum

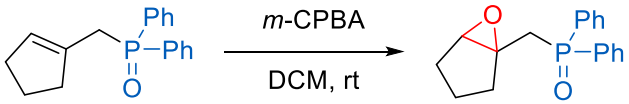
ether/ethyl acetate (1:2) to provide an inseparated mixture of compounds **92** and **89** as a white solid (38.4 mg, 40% yield) in 6.6:1 ratio; R_f 0.1 (petroleum ether/ethyl acetate = 1/2); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 10.2, 7.8 Hz, 4H, major), 7.77 (dd, *J* = 11.5, 7.5 Hz, 4H, major), 7.71 (dd, *J* = 10.7, 7.5 Hz, 1.39H, minor), 7.49 (q, *J* = 7.2 Hz, 4H, major), 7.41 (m, 8H + 1.88H, major + minor), 5.59 (t, *J* = 3.4 Hz, 1H, major), 5.00 (t, *J* = 3.3 Hz, 1H, major), 3.52 (d, *J* = 13.1 Hz, 2H, major), 3.37 (d, *J* = 12.8 Hz, 0.61H, minor), 1.32 (s, 3H, major), 1.28 (s, 3H + 0.93H, major + minor); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9 (dd, $J_{C\text{-}P}$ = 6.6, 4.9 Hz), 133.5 (d, $J_{C\text{-}P}$ = 98.1 Hz), 132.4 (d, $J_{C\text{-}P}$ = 8.0 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.124 (d, $J_{C\text{-}P}$ = 90.7 Hz), 131.121 (d, $J_{C\text{-}P}$ = 9.2 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.1 (d, $J_{C\text{-}P}$ = 10.9 Hz), 119.2 (t, $J_{C\text{-}P}$ = 8.1 Hz), 43.9 (dd, $J_{C\text{-}P}$ = 64.4, 6.1 Hz), 34.0 (d, $J_{C\text{-}P}$ = 69.2 Hz), 23.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.2 (d, *J* = 4.2 Hz), 29.5 (d, *J* = 4.1 Hz); HRMS (ESI) Calcd for $C_{30}H_{31}O_2P_2$ $[M + H]^+$ 485.1794, found 485.1803.

5. Product Transformations



56 **93**, 99%

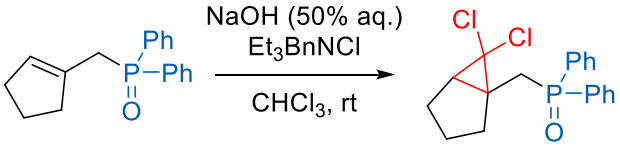
(Cyclopentylmethyl)diphenylphosphine oxide (93): Under a hydrogen gas atmosphere (1.0 atm), **56** (56.4 mg, 0.2 mmol) was dissolved in MeOH (4 mL), and then 10% Pd/C (21.0 mg, 10 mol%) was added. The reaction mixture was stirred at 50 °C in oil bath for 6 hours. Then the resulting mixture was filtrated through celite and was concentrated to give the pure product **93** in quantitative yield; m.p. 89.3-90.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-73 (m, 4H), 7.56-7.40 (m, 6H), 2.37 (dd, J = 10.9, 6.8 Hz, 2H), 2.23-2.17 (m, 1H), 1.83-1.75 (m, 2H), 1.57 (app. s, 2H), 1.49-1.42 (m, 2H), 1.21-1.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9 (d, $J_{C\text{-}P}$ = 96.5 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.3 Hz), 35.7 (d, $J_{C\text{-}P}$ = 71.1 Hz), 34.4 (d, $J_{C\text{-}P}$ = 8.3 Hz), 34.1 (d, $J_{C\text{-}P}$ = 4.2 Hz), 24.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8; HRMS (ESI) Calcd for $C_{18}H_{22}OP$ $[M + H]^+$ 285.1403, found 285.1412.



56 **94**, 99%

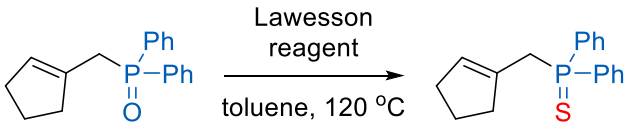
((6-Oxabicyclo[3.1.0]hexan-1-yl)methyl)diphenylphosphine oxide (94): To a solution of **56** (28.2 mg, 0.1 mmol, 1.0 eq.) in DCM (5.0 mL) was added m-CPBA (81.2 mg, 0.4 mmol, 4.0 eq.) at room temperature under argon atmosphere. After being stirred at room temperature for 48 hours, the reaction mixture was washed by Na_2CO_3 saturated solution (10 mL x 3). The organic phase was dried by anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1 to 1/1) to obtain **94** as a white solid (quantitative); R_f 0.3 (petroleum ether/ethyl acetate = 1/2); m.p. 102.3-104.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.72 (m, 4H), 7.55-7.45 (m, 6H), 3.19 (s, 1H), 2.99 (dd, J = 15.2, 12.4 Hz, 1H), 2.67 (dd, J = 15.3, 11.6 Hz, 1H), 1.96 (dd, J =

14.0, 8.2 Hz, 1H), 1.84 (dd, J = 13.8, 8.4 Hz, 2H), 1.52-1.40 (m, 2H), 1.36-1.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2 (d, $J_{C\text{-}P}$ = 99.3 Hz), 133.0 (d, $J_{C\text{-}P}$ = 99.5 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.8 (d, $J_{C\text{-}P}$ = 8.3 Hz), 130.7 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.8 Hz), 63.2 (d, $J_{C\text{-}P}$ = 2.0 Hz), 63.0 (d, $J_{C\text{-}P}$ = 4.0 Hz), 33.7 (d, $J_{C\text{-}P}$ = 68.6 Hz), 31.3, 27.4, 19.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1; HRMS (ESI) Calcd for $C_{18}H_{20}O_2P_2$ $[M + H]^+$ 299.1195, found 299.1194.



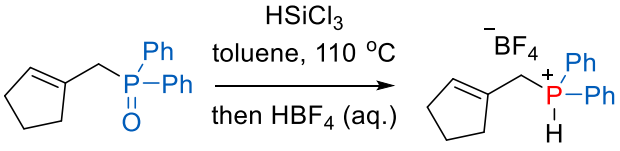
56 **95**, 80%

((6,6-Dichlorobicyclo[3.1.0]hexan-1-yl)methyl)diphenylphosphine oxide (95): To a solution of the **56** (28.2 mg, 0.1 mmol) in $CHCl_3$ (1 mL) was added benzyltriethylammonium chloride (6.8 mg, 0.03 mmol) and 50% aq. NaOH (1.0 mL). The resulting mixture was vigorously stirred at room temperature for 6 h. H_2O (5 mL) was added, and then the mixture was extracted with CH_2Cl_2 (5 mL x 3). The combined organic layer was washed with H_2O (5 mL) and brine (5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/ ethyl acetate = 2/1) to afford the title compound as a white solid (29.1 mg, 80% yield); m.p. 105.2-106.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.71 (m, 4H), 7.62-7.41 (m, 6H), 2.98-2.77 (m, 2H), 2.68-2.60 (m, 1H), 2.09-2.02 (m, 1H), 1.91-1.84 (m, 2H), 1.77-1.66 (m, 1H), 1.60-1.52 (m, 1H), 1.49-1.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7 (d, $J_{C\text{-}P}$ = 98.4 Hz), 132.9 (d, $J_{C\text{-}P}$ = 97.6 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.8 (d, $J_{C\text{-}P}$ = 3.1 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.1 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.6 Hz), 72.6 (d, $J_{C\text{-}P}$ = 14.9 Hz), 41.5 (d, $J_{C\text{-}P}$ = 6.2 Hz), 40.0 (d, $J_{C\text{-}P}$ = 3.6 Hz), 33.9, 31.7 (d, $J_{C\text{-}P}$ = 70.3 Hz), 28.5, 24.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.5; HRMS (ESI) Calcd for $C_{19}H_{20}Cl_2OP$ $[M + H]^+$ 365.0623, found 365.0629.



56 **96**, 69%

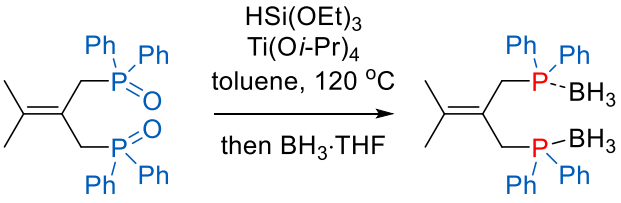
(Cyclopent-1-en-1-ylmethyl)diphenylphosphine sulfide (96): A 10 mL oven-dried sealed tube equipped with a magnetic stir bar was charged with **56** (0.1 mmol, 1.0 equiv), Lawesson reagent (0.2 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon (three times) and then toluene (0.5 mL) was added via a syringe. The resulting mixture was stirred for 4 h at 120 °C. After that, the reaction was cooled to room temperature and volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the desired product **96** (20.7 mg, 69% yield); m.p. 72.3-73.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.82 (m, 4H), 7.52-7.42 (m, 6H), 5.50-5.39 (m, 1H), 3.43 (d, J = 14.2 Hz, 2H), 2.27-2.19 (m, 2H), 2.16-2.10 (m, 2H), 1.74 (p, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.5 (d, $J_{C\text{-}P}$ = 9.2 Hz), 133.0 (d, $J_{C\text{-}P}$ = 78.8 Hz), 131.4 (d, $J_{C\text{-}P}$ = 3.1 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.9 Hz), 36.6 (d, $J_{C\text{-}P}$ = 53.3 Hz), 36.6 (d, $J_{C\text{-}P}$ = 2.5 Hz), 32.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 23.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.4; HRMS (ESI) Calcd for $C_{18}H_{19}PSNa$ $[M + Na]^+$ 321.0837, found 321.0847.



56 **97**, 72%

An oven-dried Schlenk tube with a stirred bar was charged with **56** (28.2 mg, 0.1 mmol) and toluene (2 mL) under Ar atmosphere. $HSiCl_3$ (107.6 mg, 0.4 mmol) was added dropwise. The reaction system was stirred 120 °C for half an hour. Then the reaction mixture was allowed to cool to rt and HBF_4 (2 mL, 40% in H_2O) was added and stirred at rt for 1 h. Then the resulting mixture was filtrated to desired a white solid **97** (51.1 mg, 72% yield); m.p. 130.8-132.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 0.5H), 7.85 (m, 4H), 7.82-7.72 (m, 2H), 7.68-7.61 (m, 4H), 7.48 (s, 0.5H), 5.78-5.68 (m, 1H),

3.79 (d, J = 16.4 Hz, 2H), 2.26 (d, J = 8.3 Hz, 2H), 2.17 (d, J = 5.6 Hz, 2H), 1.83-1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.21 (d, $J_{C\text{-}P}$ = 11.7 Hz), 135.16 (d, $J_{C\text{-}P}$ = 3.0 Hz), 133.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 13.0 Hz), 129.4 (d, $J_{C\text{-}P}$ = 10.6 Hz), 115.8 (d, $J_{C\text{-}P}$ = 83.2 Hz), 35.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 32.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 23.4 (d, $J_{C\text{-}P}$ = 46.9 Hz), 23.3; ^{19}F NMR (376 MHz, CDCl3) δ -150.27 ($^{10}BF_4^-$), -150.33 ($^{11}BF_4^-$); ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.0; HRMS (ESI) Calcd for $C_{18}H_{20}P^+$ $[M - BF_4^-]^+$ 267.1297, found 267.1283.



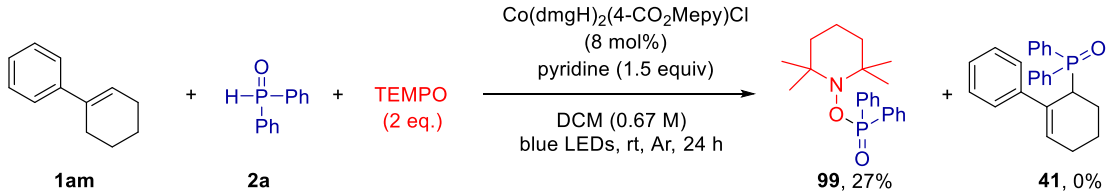
89 **98**, 83%

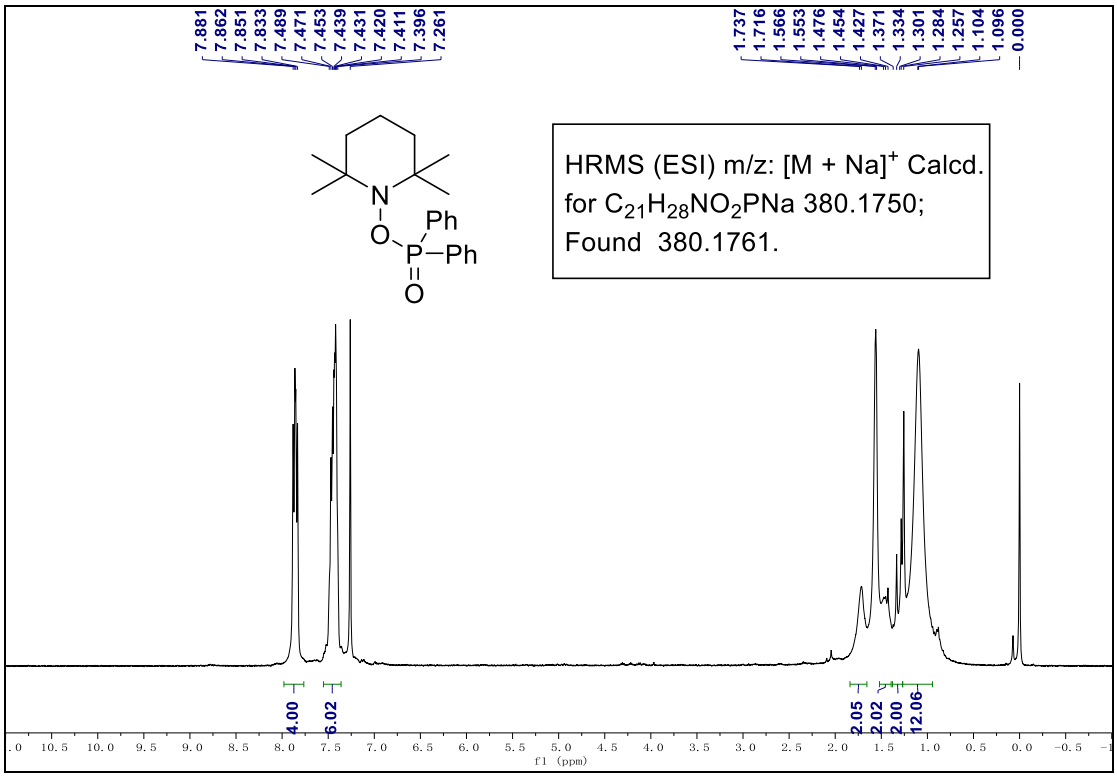
An oven-dried Schlenk tube with a stirred bar was charged with **89** (78.2 mg, 0.16 mmol) and toluene (4 mL) under Ar atmosphere. $HSi(OEt)_3$ (156.7 mg , 0.96 mmol) and $Ti(O\text{-}iPr)_4$ (25.6 mg, 0.56 mmol) were added sequentially. The reaction system was stirred 120 ℃ for half an hour. Then the reaction mixture was allowed to cool to rt and BH_3·THF (0.96 mL, 1 M in THF, 0.96 mmol) was added and stirred at rt for 1 h. After removal of the volatiles under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/dichloromethane = 5/1) to afford **98** (63.8 mg, 83% yield); m.p. 151.7-153.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 10.1, 7.5 Hz, 8H), 7.49-7.45 (m, 4H), 7.43-7.37 (m, 8H), 3.15 (d, J = 12.8 Hz, 4H), 1.12 (t, J = 4.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1 (t, $J_{C\text{-}P}$ = 9.8 Hz), 132.6 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.0 Hz), 129.7 (d, $J_{C\text{-}P}$ = 52.9 Hz), 128.7 (d, $J_{C\text{-}P}$ = 9.5 Hz), 114.4, 30.8 (d, $J_{C\text{-}P}$ = 32.3 Hz), 21.2 (t, $J_{C\text{-}P}$ = 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.5 (d, J = 44.7 Hz); HRMS (ESI) Calcd for $C_{30}H_{36}B_2P_2Na$ $[M + Na]^+$ 503.2371, found 503.2381.

6. Mechanistic Studies

(a) Radical trapping experiment:

Following the standard procedure of the model reaction, when 2 equiv of radical inhibitor 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) was added to the reaction mixture, the formation of the desired product **41** was completely inhibited, and the radical trapping product **99** between phosphinoyl radical and TEMPO was obtained in 27% yield.





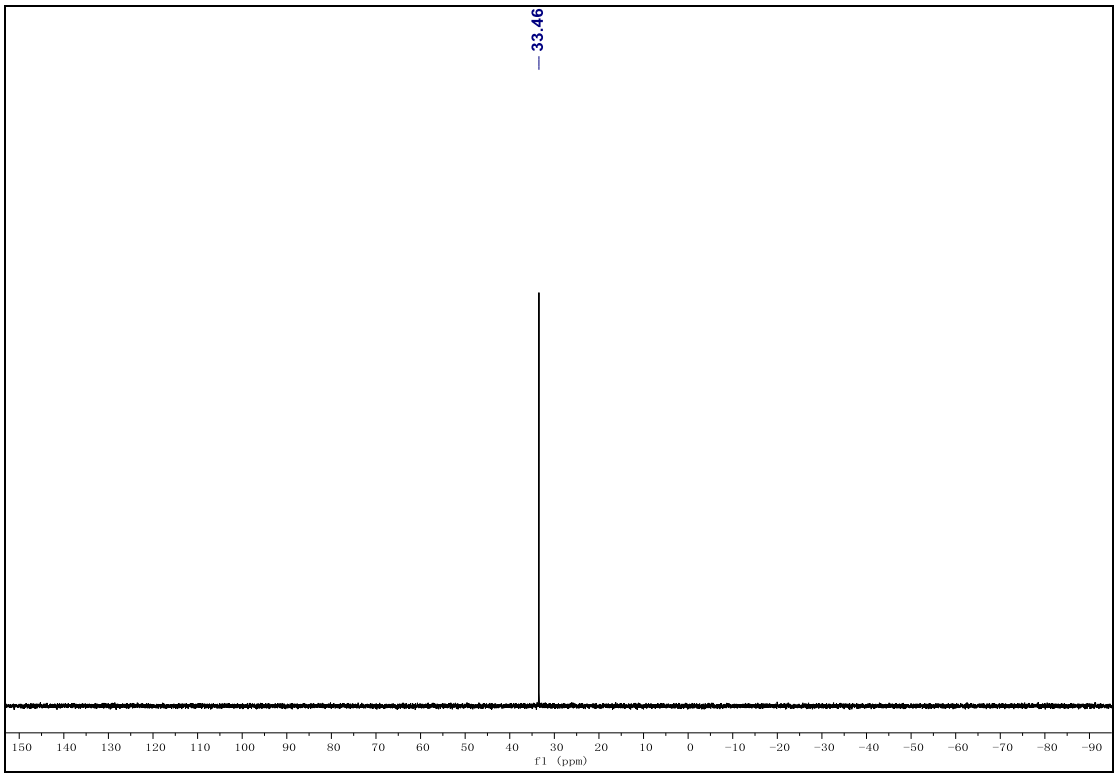
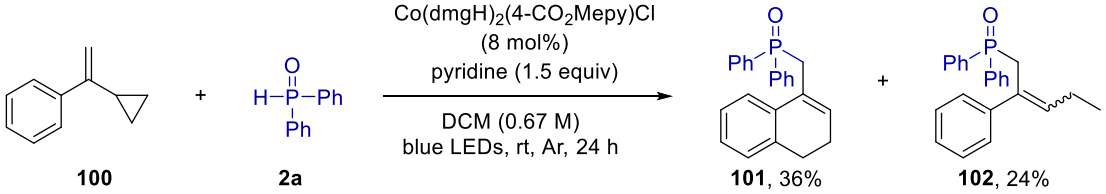
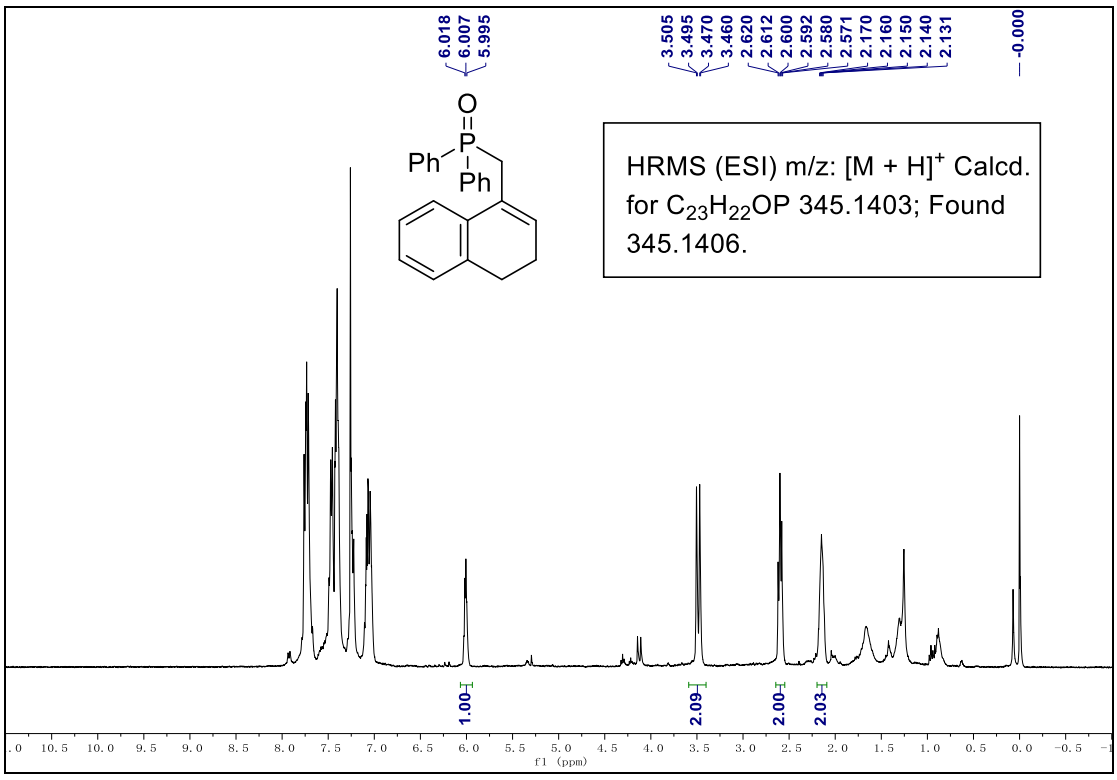


Figure S4. The ^{1}H NMR spectrum, ^{31}P NMR spectrum and HRMs petruim of the radical trapping product **99**.

(b) Radical clock experiment:



An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$ (3.7 mg, 0.008 mmol, 8 mol%) and **100** (57.7 mg, 0.2 mmol, 2.0 eq.). Then, the Schlenk tube was introduced into a glovebox, and secondaryl phosphine oxide **2a** (20.2 mg, 0.1 mmol, 1.0 equiv) was added. The tube was taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled with Ar for 3 times. After DCM (1.5 mL) and pyridine (0.15 mmol, 1.5 equiv) were added under Ar, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere and was stirred under blue LEDs (40 W) at rt for 24 h monitored by TLC analysis. Two kinds of products with cyclopropane-opening were detected by ^1H NMR (characteristic signals) and MS. Unfortunately, these two by-products is hard for further purification.



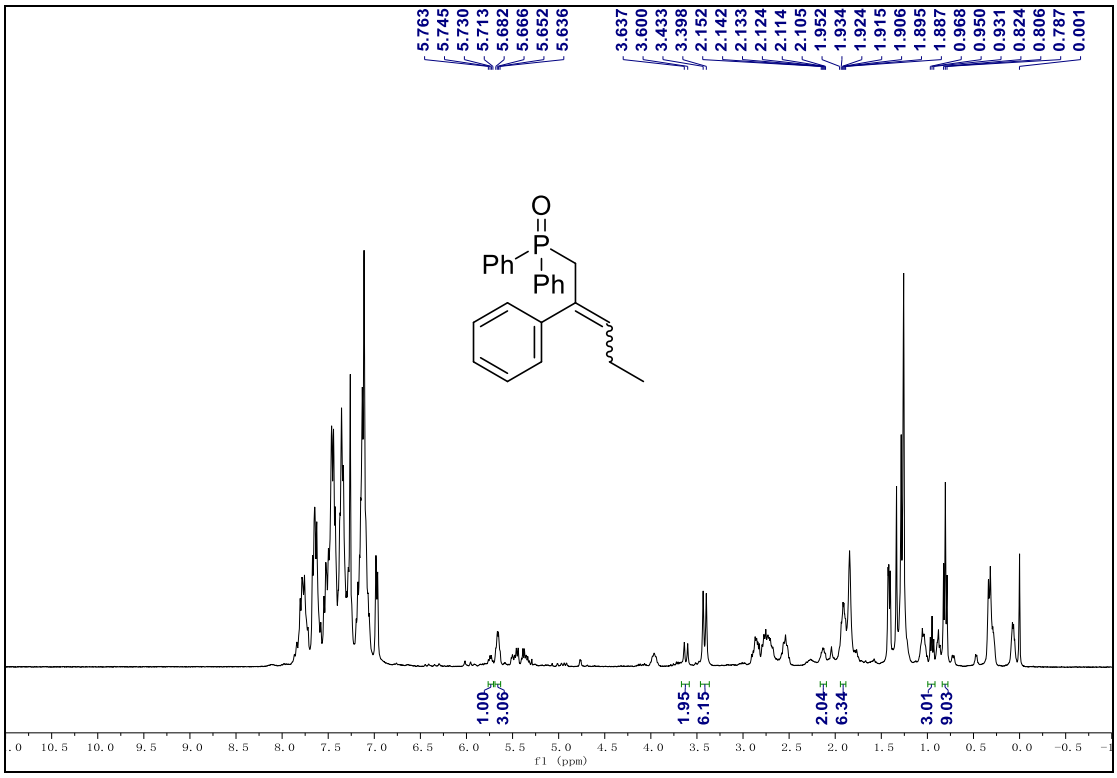
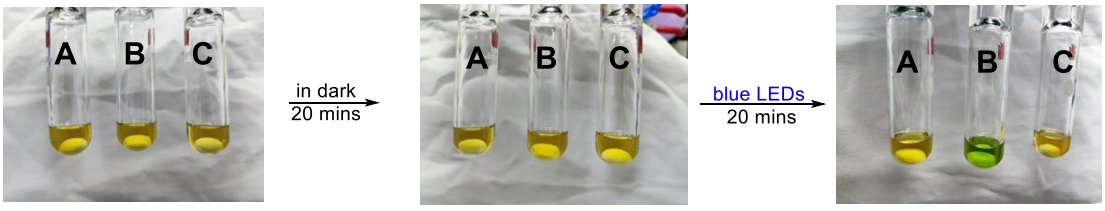


Figure S5. The ^{1}H NMR spectrum, ^{31}P NMR spectrum and HRMs petruim of the radical ring-opening product.

(c) Control experiments for reaction mixture color change.

We noted that the yellow color of the reaction mixture quickly turned light green during the reaction process. The control experiments were performed with the solutions A, B, and C to examine the color change. As shown in Figure S6, after stirred in dark for 20 mins, no color change was detected for all solutions. However, upon irradiation by blue LEDs for 20 minutes, the color alteration from yellow to light green was observed for the solution B, while the colors of other solutions were no changed.

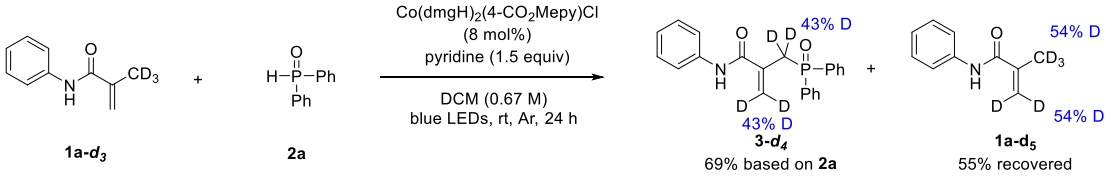


A: Co(dmgH)$_2$(4-CO$_2$Mepy)Cl; **B**: Co(dmgH)$_2$(4-CO$_2$Mepy)Cl + **2a** + pyridine;

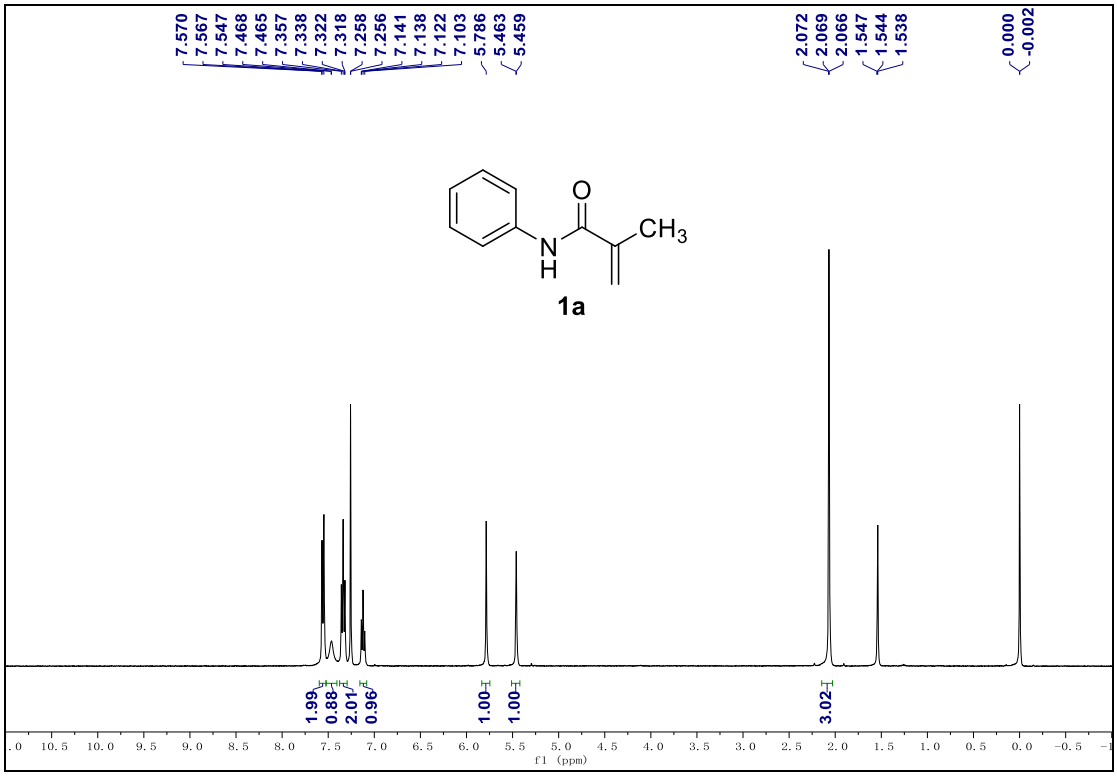
C: Co(dmgH)$_2$(4-CO$_2$Mepy)Cl + **2a**.

Figure S6. The color change of different solutions.

(d) Deuterium-labelling experiments:



The solution of 2-(methyl-d_3)-N-phenylacrylamide **1a-*d*$_3$** (0.4 mmol), **2a** (0.2 mmol), Co(dmgH)$_2$(4-CO_2Mepy) Cl (8 mol %) and pyridine (0.3 mmol) in DCM (3 mL) was irradiated with blue LEDs for 24 hours under argon atmosphere at ambient temperature. After reaction, upon removal of solvent under vacuum, the residue was purified by chromatography on silica gel to get unreacted olefin and product, which subsequently detected by ^{1}H NMR analysis. The results were listed as follow:



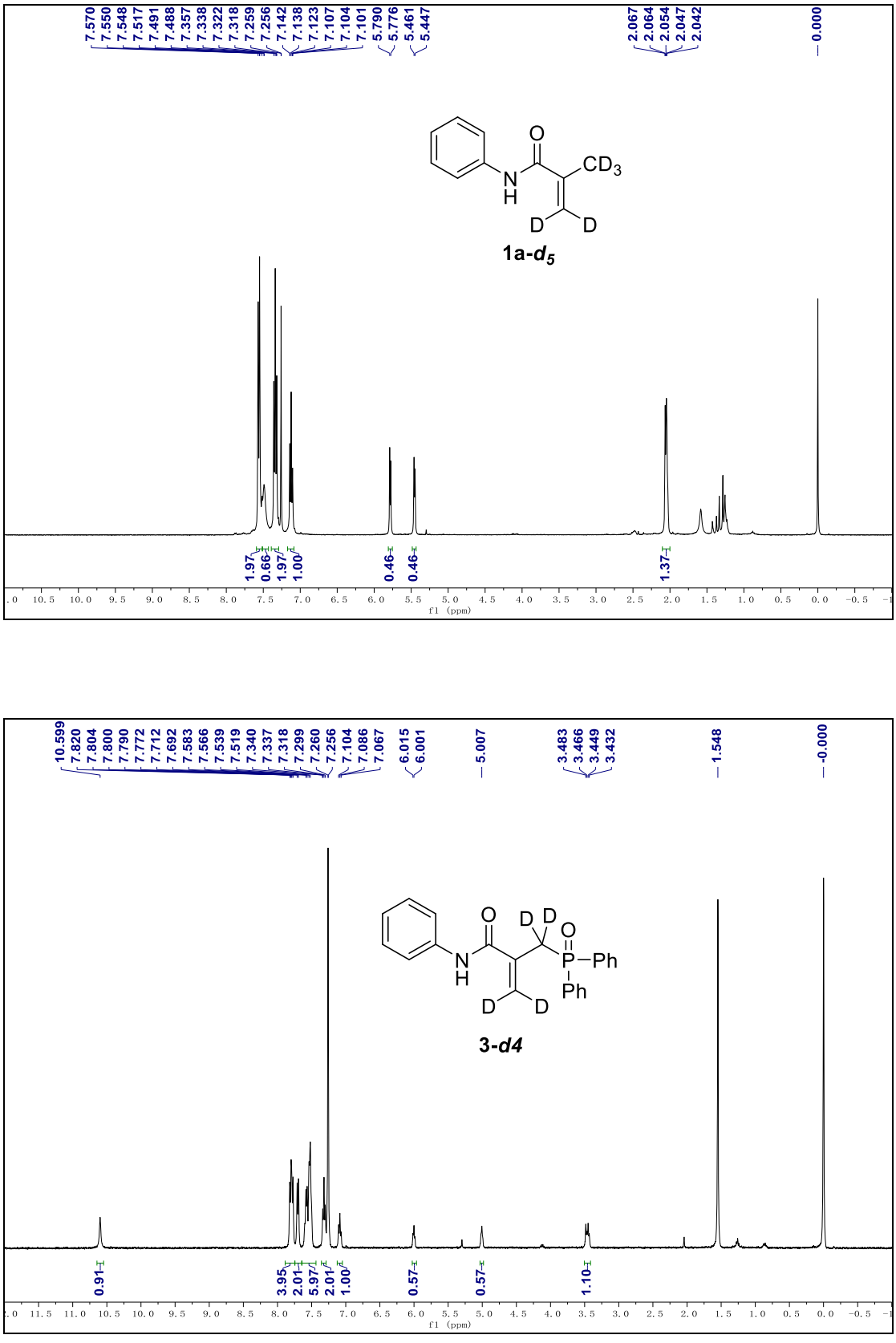
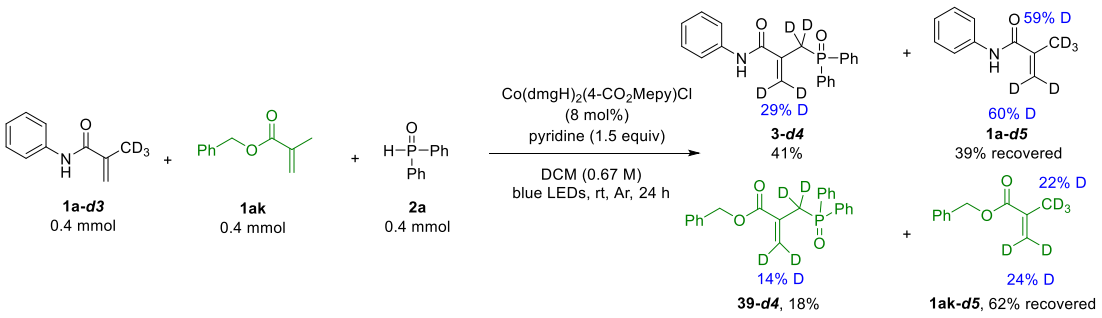
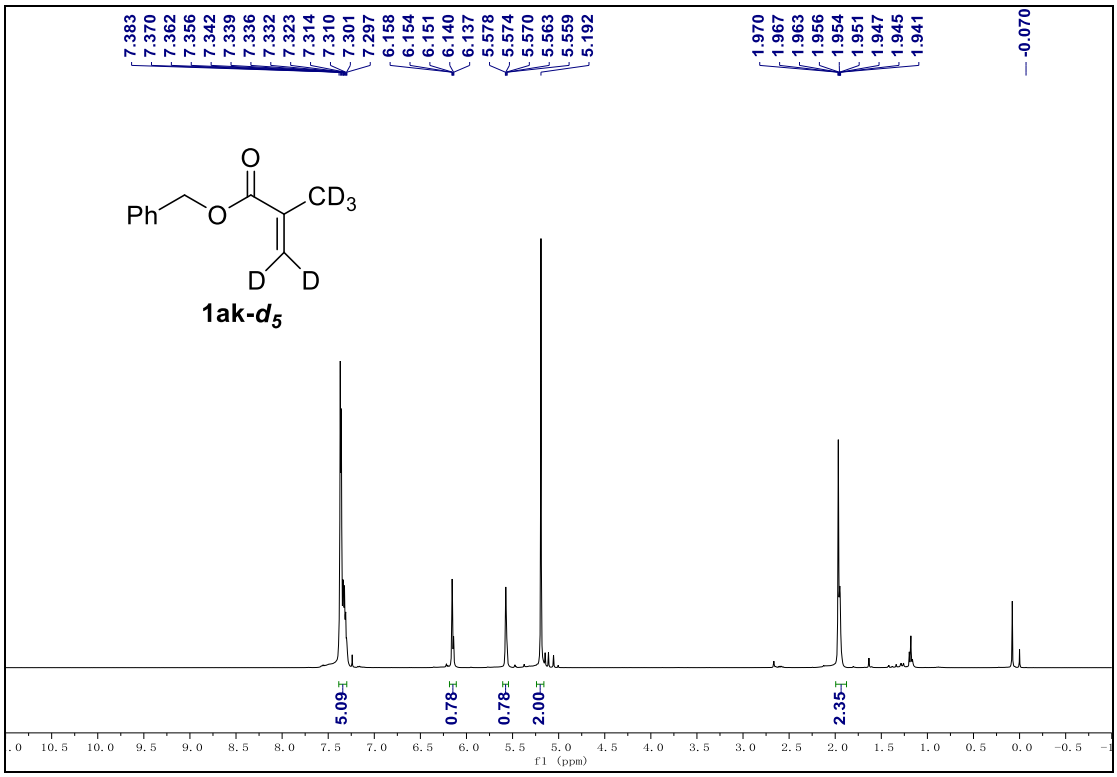
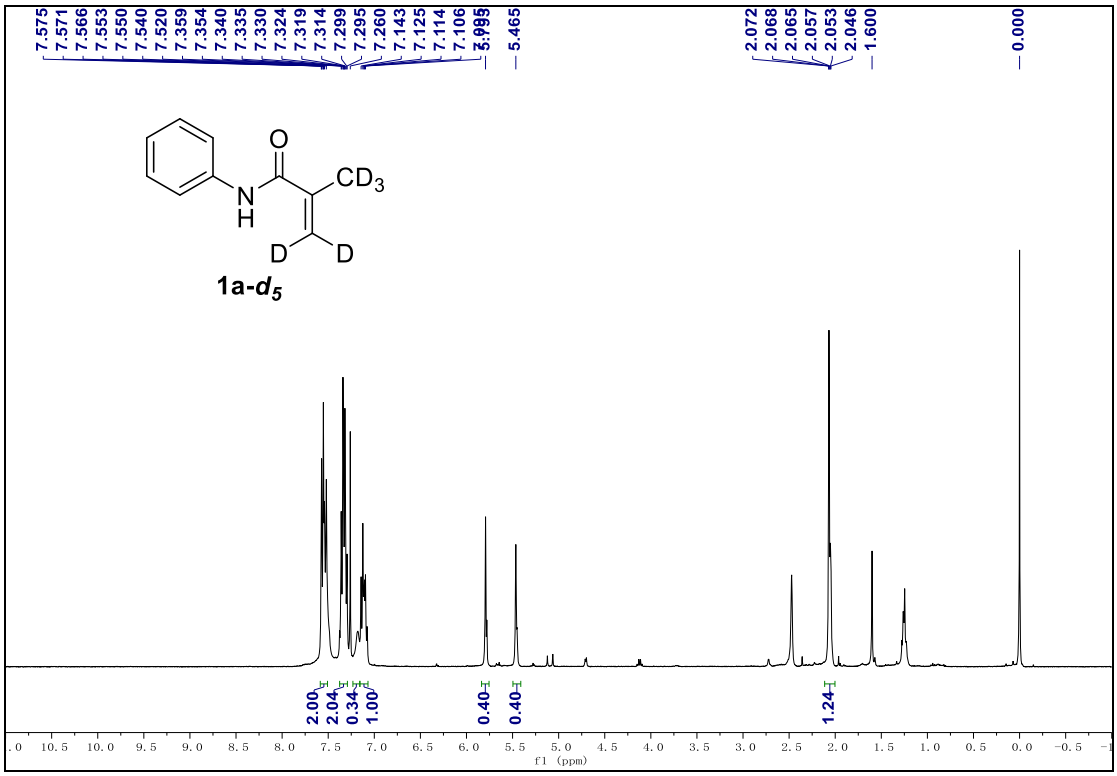


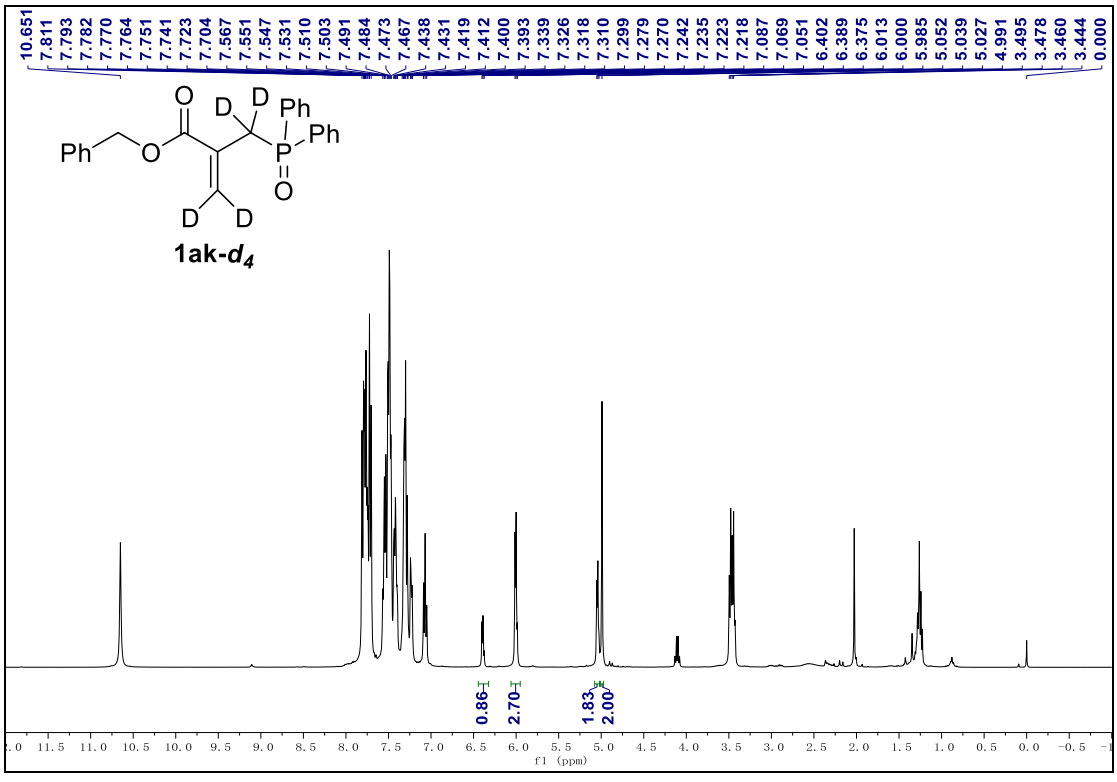
Figure S7. the ^{1}H NMR spectrum of the deuterated d_5-N-phenylacrylamide and the deuterated product.



Subjection of 2-(methyl-d3)-N-phenylacrylamide **1a-*d*$_3$** (0.4 mmol, 65.6 mg) and benzyl methacrylate **1ak** (0.4 mmol, 70.5 mg) to the standard conditions furnished product with H/D exchange between β–carbon and β′–carbon position. Analysis of the recovered **1a-*d*$_5$** and **1ak-*d*$_5$** showed the H/D exchange between β–carbon and β′–carbon position as well. The results suggested the Co-catalyzed isomerization of alkene occurred.




7.575
7.571
7.566
7.553
7.550
7.540
7.520
7.359
7.354
7.340
7.335
7.330
7.324
7.319
7.314
7.299
7.295
7.260
7.143
7.125
7.114
7.106
5.465
2.072
2.068
2.065
2.057
2.053
2.046
1.600
0.000
O
N
H
CD3
D
D
1a-d5
2.00
2.04
0.34
1.00
0.40
0.40
1.24
f1 (ppm)


10.651
7.811
7.793
7.782
7.770
7.764
7.751
7.741
7.723
7.704
7.567
7.551
7.547
7.531
7.510
7.503
7.491
7.484
7.473
7.467
7.438
7.431
7.419
7.412
7.400
7.393
7.339
7.326
7.318
7.310
7.299
7.279
7.270
7.242
7.235
7.223
7.218
7.087
7.069
7.051
6.402
6.389
6.375
6.013
6.000
5.985
5.052
5.039
5.027
4.991
3.495
3.478
3.460
3.444
0.000
O
D
D
Ph
Ph
Ph
O
P
O
D
D
1ak-d4
0.86
2.70
1.83
2.00
f1 (ppm)

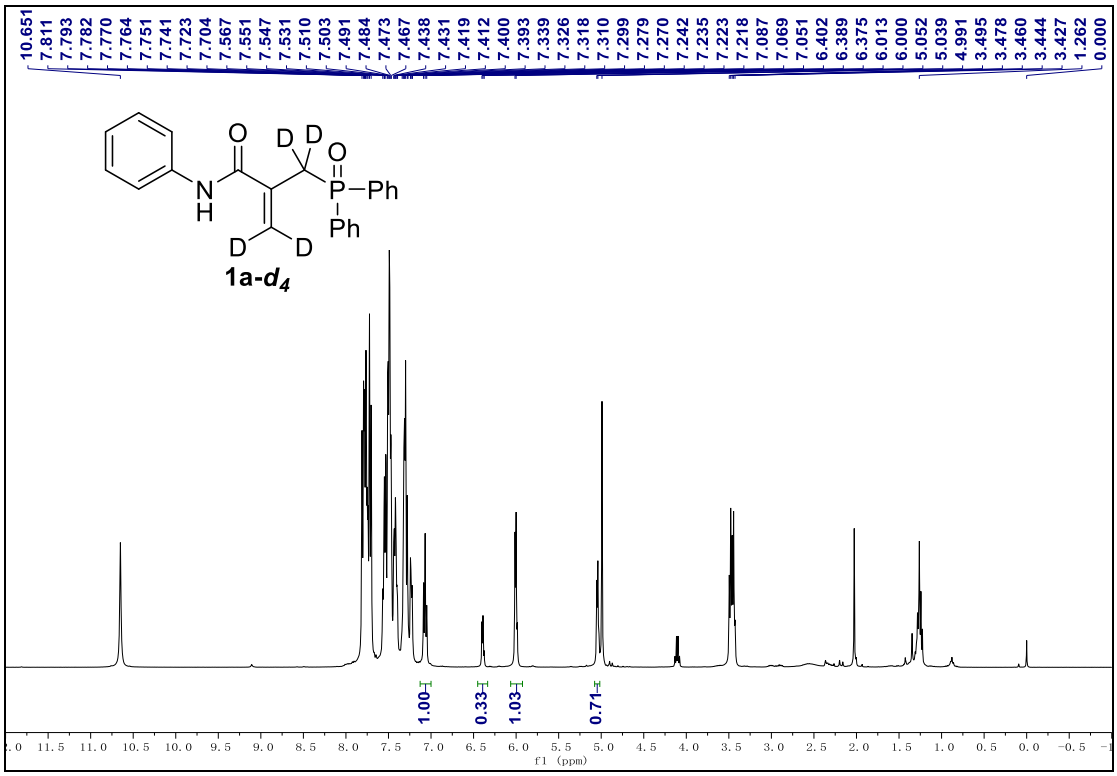
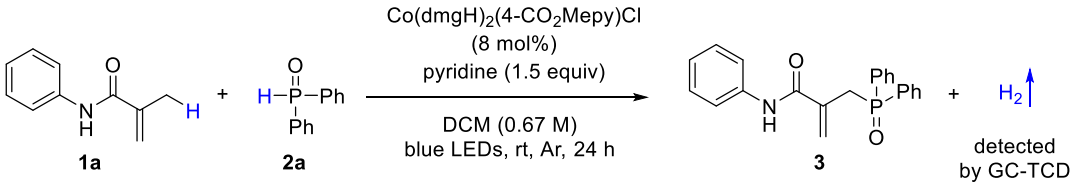


Figure S8. the ^{1}H NMR spectrum of the cross deuteration alkene and cross deuterated product.

(e) Detection of hydrogen gas H_2



An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$ (3.7 mg, 0.008 mmol, 8 mol%) and **1a** (32.3mg, 0.2 mmol, 2.0 eq.). Then, the Schlenk tube was introduced into a glovebox, and secondaryl phosphine oxide **2** (20.2 mg, 0.1 mmol, 1.0 equiv) was added. The tube was taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled with Ar for 3 times. After DCM (1.5 mL) and pyridine (0.15 mmol, 1.5 equiv) were added under Ar, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere and was stirred under blue LEDs (40 W) at rt for 24 h. After completion of the reaction, the extracted 1000 μL gas from the reaction system was analyzed by GC-TCD. According to the spectra (Figure S8), the only peak stands for the generation of hydrogen gas.

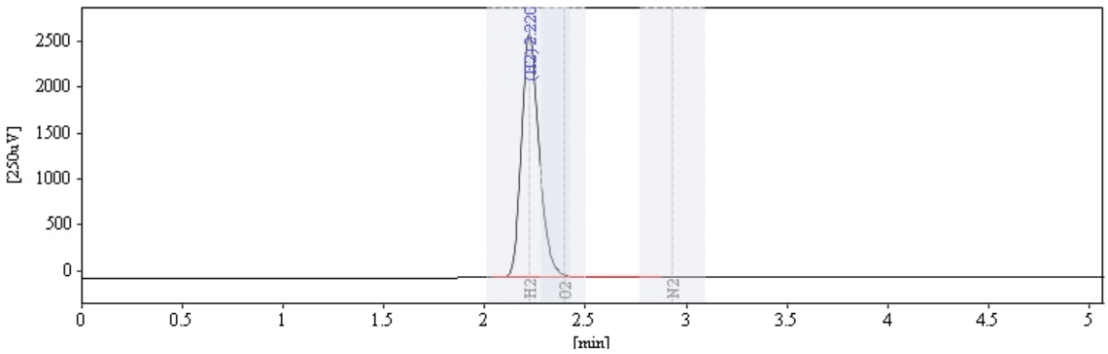


Figure S9. Hydrogen detected by GC-TCD.

(f) The On-Off-Light Experiment:

To study the necessity of continuous irradiation with visible light for the progress of the reaction, we started a reaction with successive irradiation and black periods. An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with triphenylphosphine oxide (111.4 mg, 0.4 mmol, 1.0 equiv, internal standard), $Co(dmgH)_2(4\text{-}CO_2Mepy)Cl$ (14.8 mg, 0.008 mmol, 8 mol%) and **1a** (128.8 mg, 0.4 mmol, 2.0 eq.). Then, the Schlenk tube was introduced into a glovebox, and secondaryl phosphine oxide **2a** (80.8 mg, 0.4 mmol, 1.0 equiv) and was added. The tube was taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled with Ar for 3 times. After DCM (6 mL) and pyridine (48.6 μL, 1.5 equiv) were added under Ar. The mixture was degassed for 3 times. The resulting solution was stirred under irradiation of 40 W blue LEDs at room temperature or in the dark at room temperature for the corresponding time (Figure S9). The yield was determined by ^{31}P NMR spectroscopy using triphenylphosphine oxide as the internal standard.

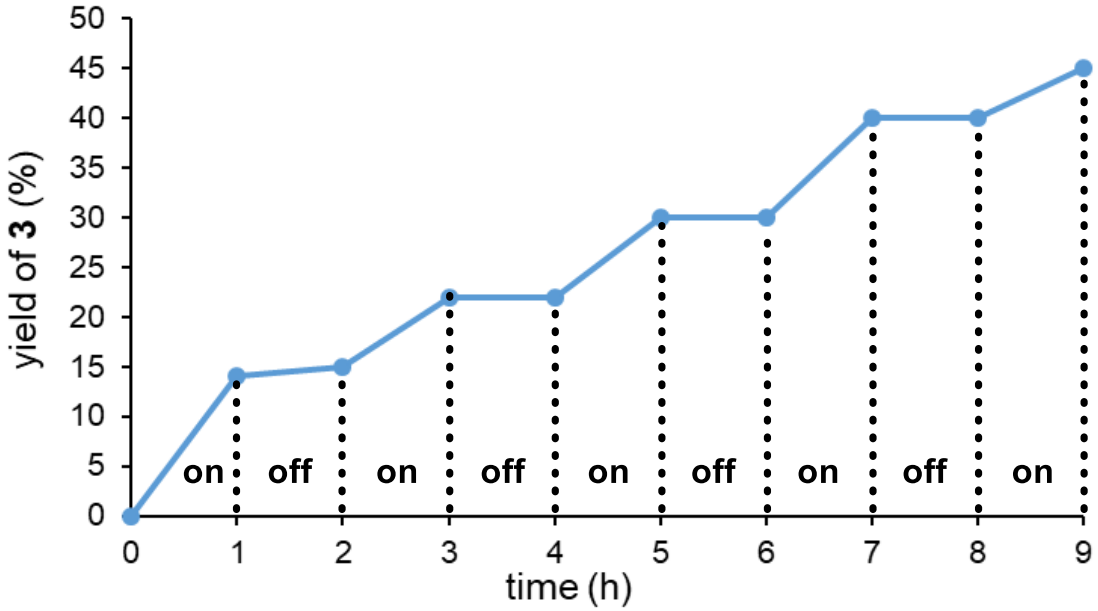


Figure S10. Light on-off Experiment

7. X-Ray Diffraction Analysis

Recrystallization from PE/EA afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of **10** (Figure S10). A suitable crystal was selected andon a XtaLAB AFC12 (RINC): Kappa single diffractometer. The crystal was kept at 119.99(15) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

Figure S10. X-ray structure of **10** (CCDC: 2372952) (The thermal ellipsoid was drawn at the 50% probability level).

Table S6. Crystal data and structure refinement for **10.**

Identification code	**10**
Empirical formula	$C_{23}H_{19}F_3NO_2P$
Formula weight	429.36
Temperature/K	119.99(15)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.2823(3)
b/Å	10.2123(2)
c/Å	17.0172(3)
α/°	90
β/°	112.613(2)
γ/°	90
Volume/Å^3	2130.81(8)
Z	4
ρ_{calc}g/cm^3	1.338

μ/mm^{-1}	1.546
F(000)	888.0
Crystal size/mm^3	0.14 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.242 to 140.04
Index ranges	$-15 \leq h \leq 16$, $-12 \leq k \leq 11$, $-20 \leq l \leq 14$
Reflections collected	10037
Independent reflections	3979 [R_{int} = 0.0261, R_{sigma} = 0.0327]
Data/restraints/parameters	3979/60/311
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0392, wR_2 = 0.1003
Final R indexes [all data]	R_1 = 0.0478, wR_2 = 0.1048
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.36

Recrystallization from PE/EA afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of **39** (Figure S11).A suitable crystal was selected and measured on a SuperNova, Dual, Cu at zero, Atlas S2 diffractometer. The crystal was kept at 293.0(3) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

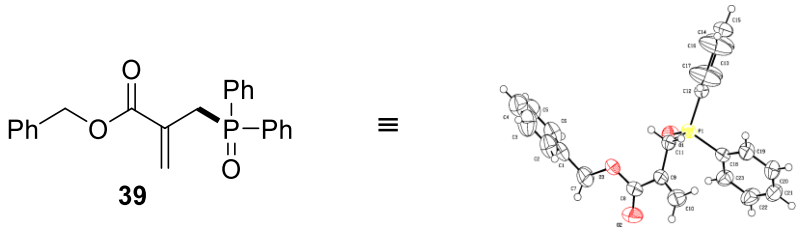


Figure S11. X-ray structure of **39** (CCDC: 2372953) (The thermal ellipsoid was drawn at the 50% probability level).

Table S7. Crystal data and structure refinement for **39.**

Identification code	**39**
Empirical formula	$C_{23}H_{21}O_3P$
Formula weight	376.37
Temperature/K	293.0(3)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.7326(12)
b/Å	5.7350(7)
c/Å	29.594(3)
α/°	90
β/°	90.789(10)
γ/°	90
Volume/Å^3	1991.1(4)
Z	4
ρ_{calc}g/cm^3	1.256

μ/mm^{-1}	0.158
F(000)	792.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.36 to 49.984
Index ranges	$-13 \leq h \leq 12$, $-6 \leq k \leq 6$, $-24 \leq l \leq 35$
Reflections collected	9099
Independent reflections	3501 [R_{int} = 0.0281, R_{sigma} = 0.0341]
Data/restraints/parameters	3501/196/260
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0539, wR_2 = 0.1231
Final R indexes [all data]	R_1 = 0.0696, wR_2 = 0.1330
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.34

Recrystallization from PE/EA afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of **89** (Figure S12).A suitable crystal was selected and measured on a SuperNova, Dual, Cu at zero, Atlas S2 diffractometer. The crystal was kept at 169.99(10) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Figure S12. X-ray structure of **89** (CCDC: 2372954) (The thermal ellipsoid was drawn at the 50% probability level).

Table S8. Crystal data and structure refinement for **89.**

Identification code	**89**
Empirical formula	$C_{30}H_{30}O_2P_2$
Formula weight	484.48
Temperature/K	169.99(10)
Crystal system	orthorhombic
Space group	Pbcn
a/Å	12.6884(2)
b/Å	11.3043(2)
c/Å	35.0872(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5032.68(17)
Z	8
ρ_{calc}g/cm^3	1.279

μ/mm^{-1}	1.762
F(000)	2048.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.038 to 147.166
Index ranges	$-15 \leq h \leq 15$, $-13 \leq k \leq 13$, $-43 \leq l \leq 42$
Reflections collected	12078
Independent reflections	4969 [R_{int} = 0.0315, R_{sigma} = 0.0350]
Data/restraints/parameters	4969/0/310
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0469, wR_2 = 0.1225
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.1264
Largest diff. peak/hole / e $Å^{-3}$	0.42/-0.43

8. References

[1] Davies, A. M.; D. Hernandez, R.; Tunge, J. A. Direct Aroylation of Olefins through a Cobalt/Photoredox-Catalyzed Decarboxylative and Dehydrogenative Coupling with α-Oxo Acids. *Chem. Eur. J.* **2022**, *28*, e202202781.

[2] Yu, W.; Luo, Y.; Yan, L.; Liu, D.; Wang, Z.; Xu, P. Dehydrogenative Silylation of Alkenes for the Synthesis of Substituted Allylsilanes by Photoredox, Hydrogen-Atom Transfer, and Cobalt Catalysis. *Angew. Chem. Int. Ed.* **2019**, *131*, 11057–11061.

[3] Shi, Y.; Yu, T.; Chi, L.; Shen, W.; Xu, J.; Zhang, M.; You, S.; Deng, C. Computational Chemistry-Assisted Highly Selective Radical Cascade Cyclization of 1,6-Enynes with Thiols: Access to Sulfur-Substituted 4-Enyl-2-Pyrrolidones. *J. Org. Chem.* **2022**, *87*, 9479–9487.

[4] Lahdenperä, A. S. K.; Bacoş, P. D.; Phipps, R. J. Enantioselective Giese Additions of Prochiral α-Amino Radicals. *J. Am. Chem. Soc.* **2022**, *144*, 22451−22457

[5] Fan, H.; Pan, P.; Zhang, Y.; Wang, W. Synthesis of 2-Quinolinones via a Hypervalent Iodine(III)-Mediated Intramolecular Decarboxylative Heck-Type Reaction at Room Temperature. *Org. Lett.* **2018**, *20*, 7929–7932.

[6] Renata K. Everett and John P. Wolf. Aza-Wittig Rearrangements of N-Benzyl and N-Allyl Glycine Methyl Esters. Discovery of a Surprising Cascade Aza-Wittig Rearrangement/Hydroboration Reaction. *J. Org. Chem.* 2015, *80*, 9041-9056.

[7] Movahhed, S.; Westphal, J.; Kempa, A.; Schumacher, C. E.; Sperlich, J.; Neudörfl, J.; Teusch, N.; Hochgürtel, M.; Schmalz, H. Total Synthesis of (+) -Erogorgiaene and the Pseudopterosin A−F Aglycone via Enantioselective Cobalt-Catalyzed Hydrovinylation. *Chem. Eur. J.* **2021**, *27*, 11574–11579.

[8] Zhang, H.; Zhang, G.-M.; He, S.; Shi, Z.-C.; Zhang, X.-M.; Wang, J.-Y. A Construction of α-Alkenyl Lactones via Reduction Radical Cascade Reaction of Allyl Alcohols and Acetylenic Acids. *Org. Lett.* **2020**, *22*, 8337–8344.

[9] Feng, W.; Qiao, J.; Li, D.; Qi, L. Chiral Ligand Exchange Capillary Electrochromatography with Dual Ligands for Enantioseparation of D, L-Amino Acids. *Talanta* **2019**, *194*, 430–436.

[10] Green, S. A.; Huffman, T. R.; McCourt, R. O.; Van Der Puyl, V.; Shenvi, R. A. Hydroalkylation of Olefins to Form Quaternary Carbons. *J. Am. Chem. Soc.* **2019**, *141*, 7709–7714.

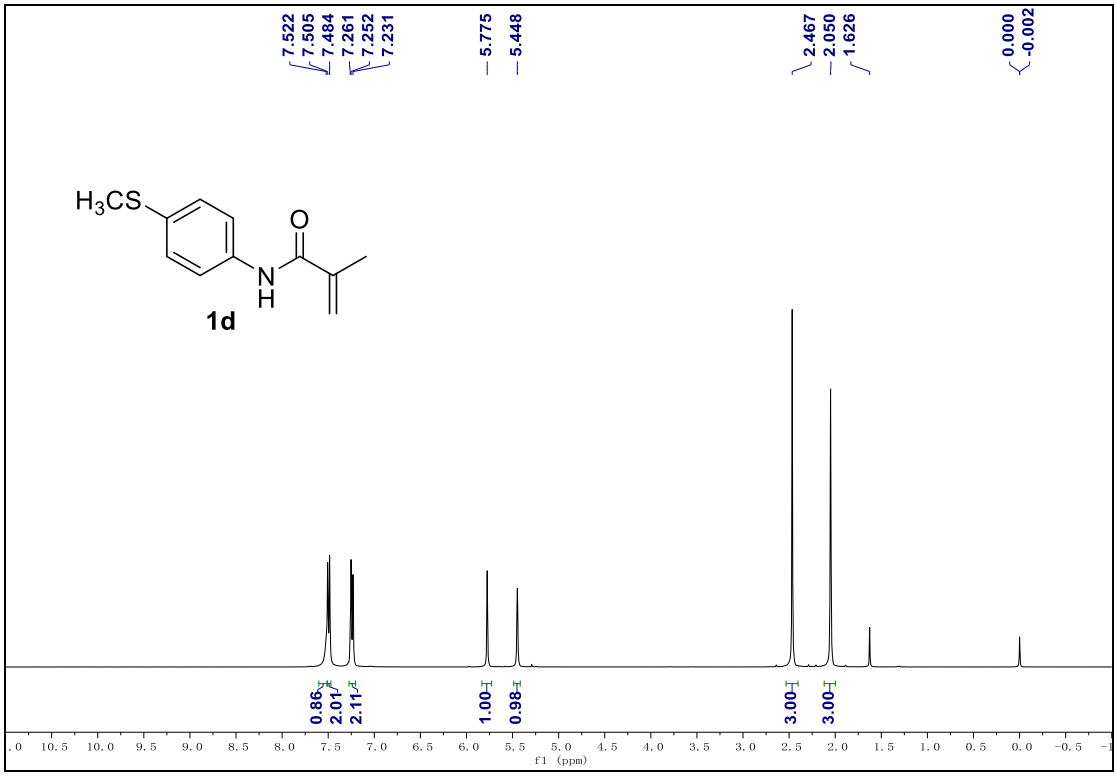
[11] Y. Sato, S. Kawaguchi and A. Ogawa, Photoinduced reductive perfluoroalkylation of phosphine oxides: synthesis of P-perfluoroalkylated phosphines using TMDPO and perfluoroalkyl iodides, *Chem. Commun*. **2015**, *51*, 10385-10388.

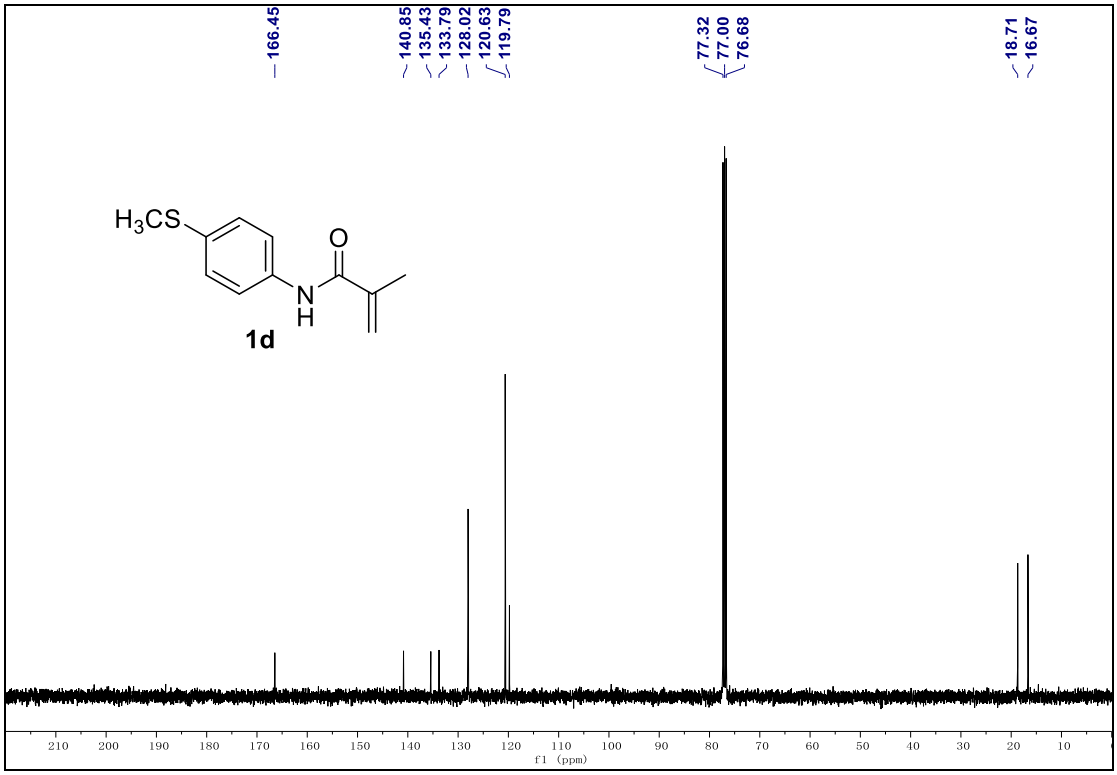
[12] Y. Zhang, X. Zhang, J. Zhao and J. Jiang, $B(C_6F_5)_3$-catalyzed O-H insertion reactions of diazoalkanes with phosphinic acids, *Org. Biomol. Chem.* **2021**, *19*, 5772-5776.

[13] H. Hou, B. Zhou, J. Wang, D. Zhao, D. Sun, X. Chen, Y. Han, C. Yan, Y. Shi and S. Zhu, Stereo- and Regioselective cis-Hydrophosphorylation of 1,3-Enynes Enabled by the Visible-Light Irradiation of $NiCl_2(PPh_3)_2$, *Org. Lett.* **2021**, *23*, 2981-2987.

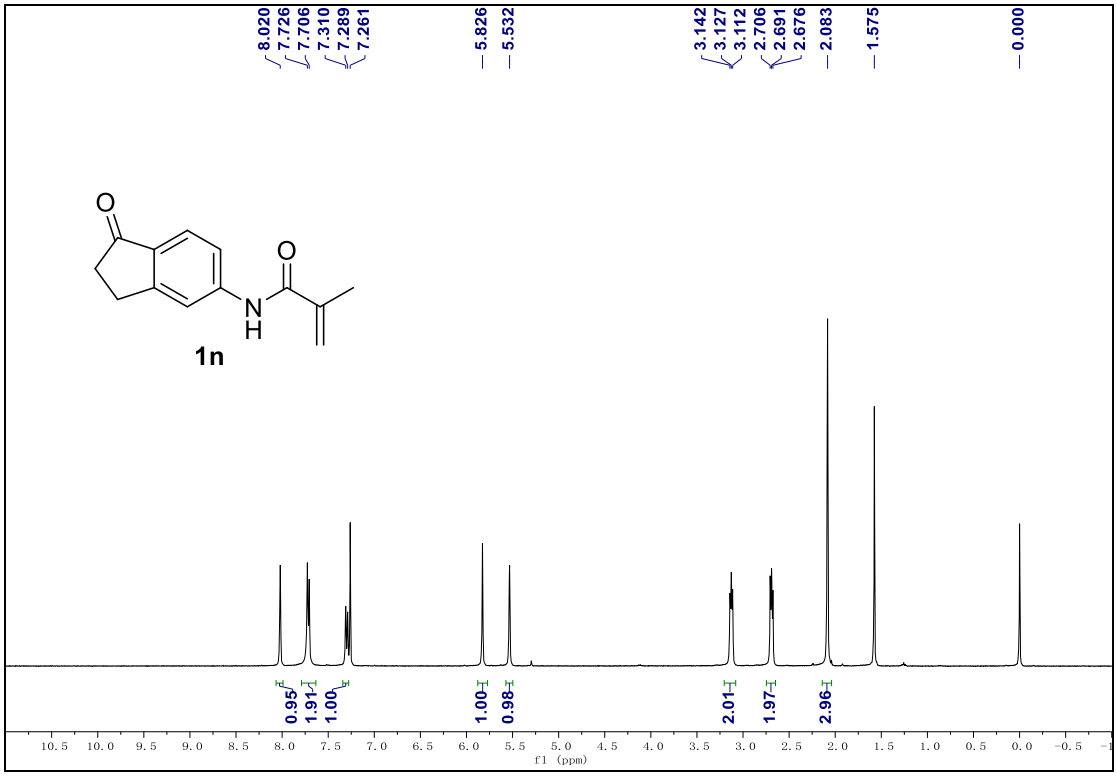
9. NMR Spectra

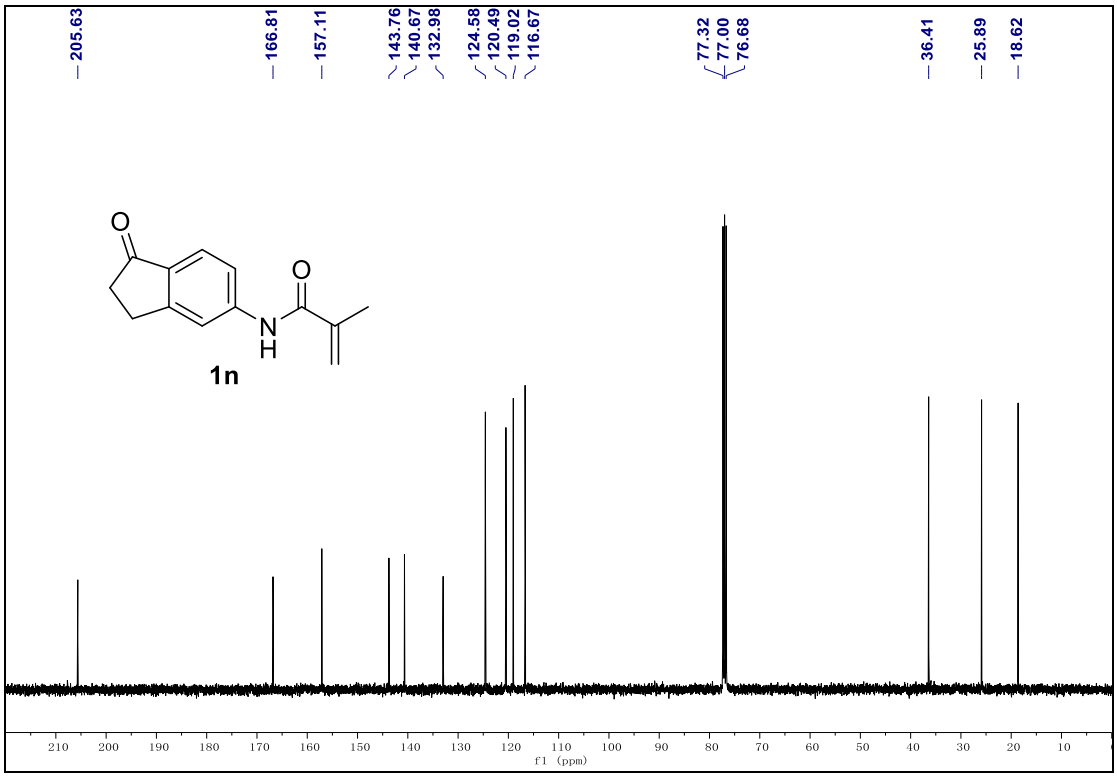
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1d.



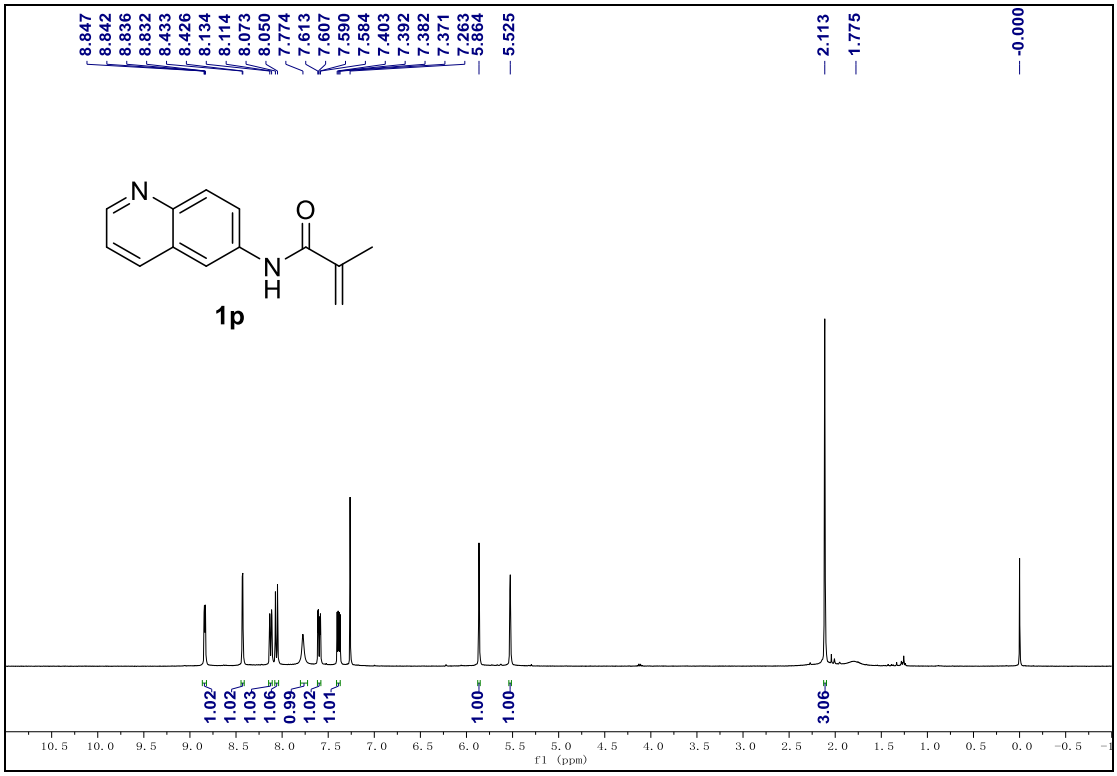


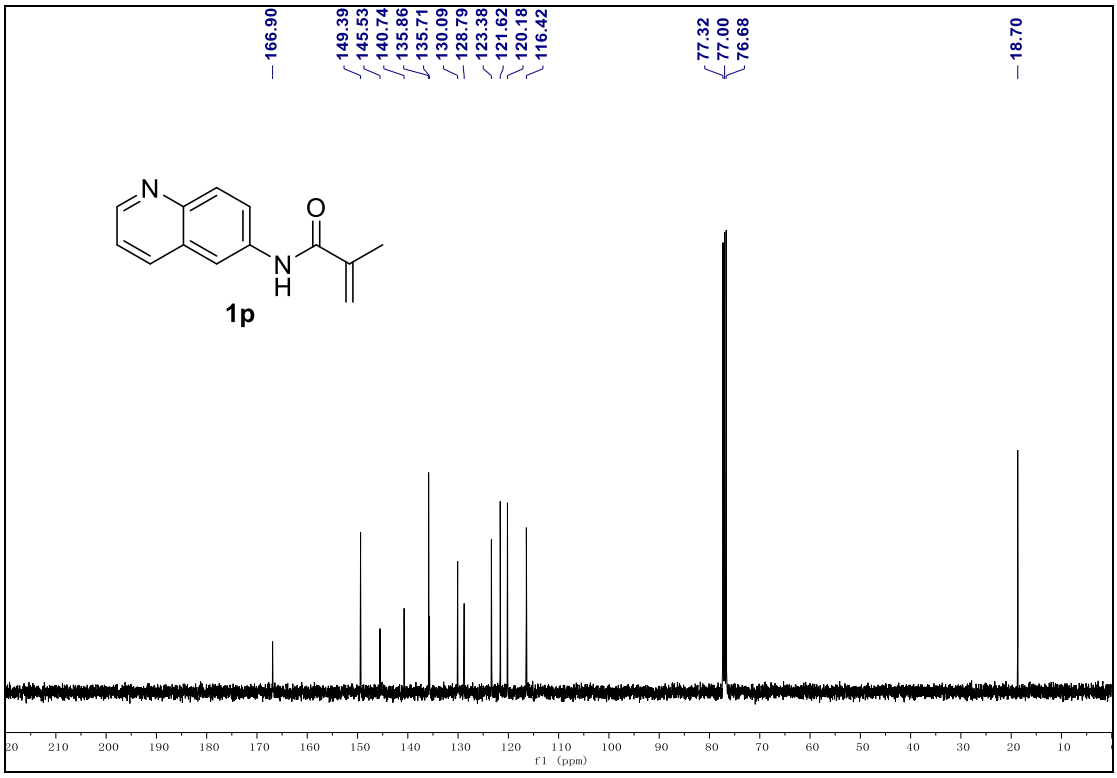
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1n.



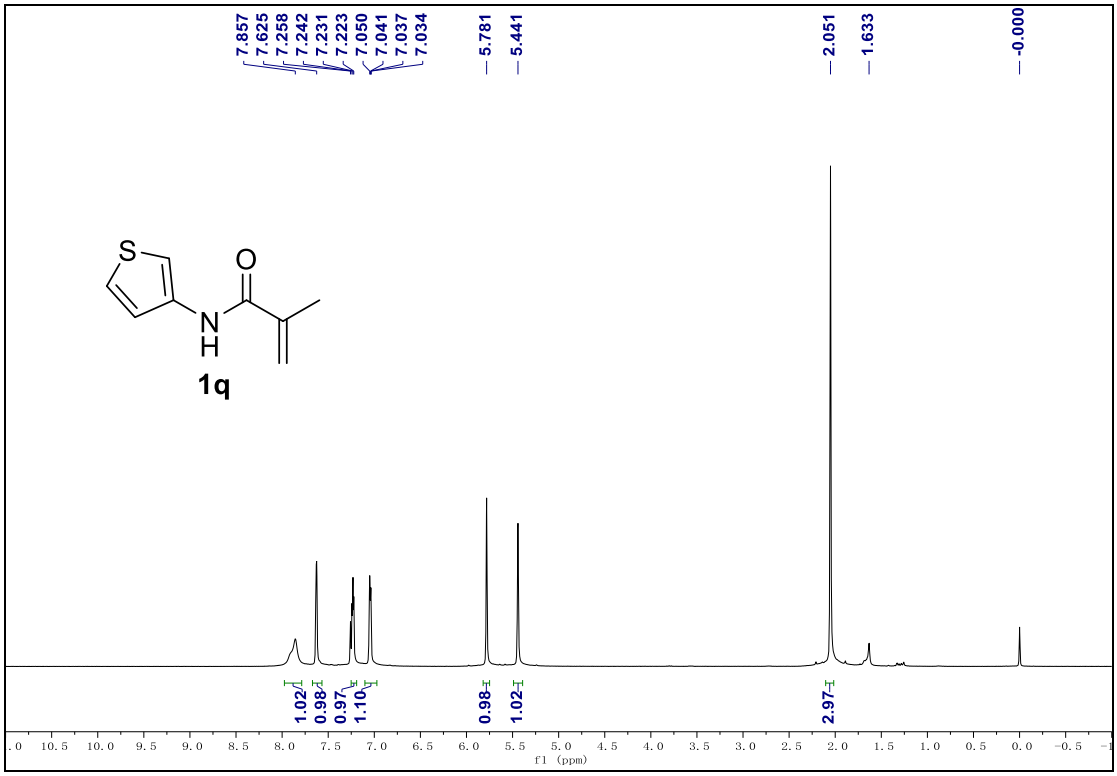


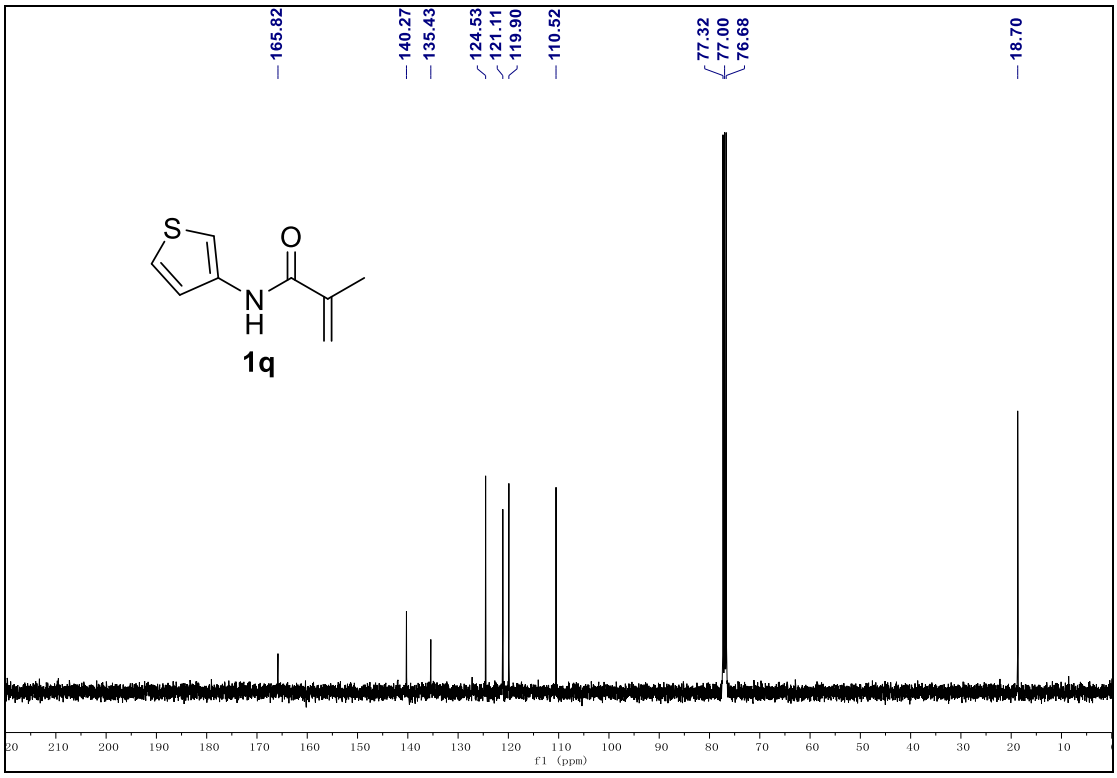
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1p.



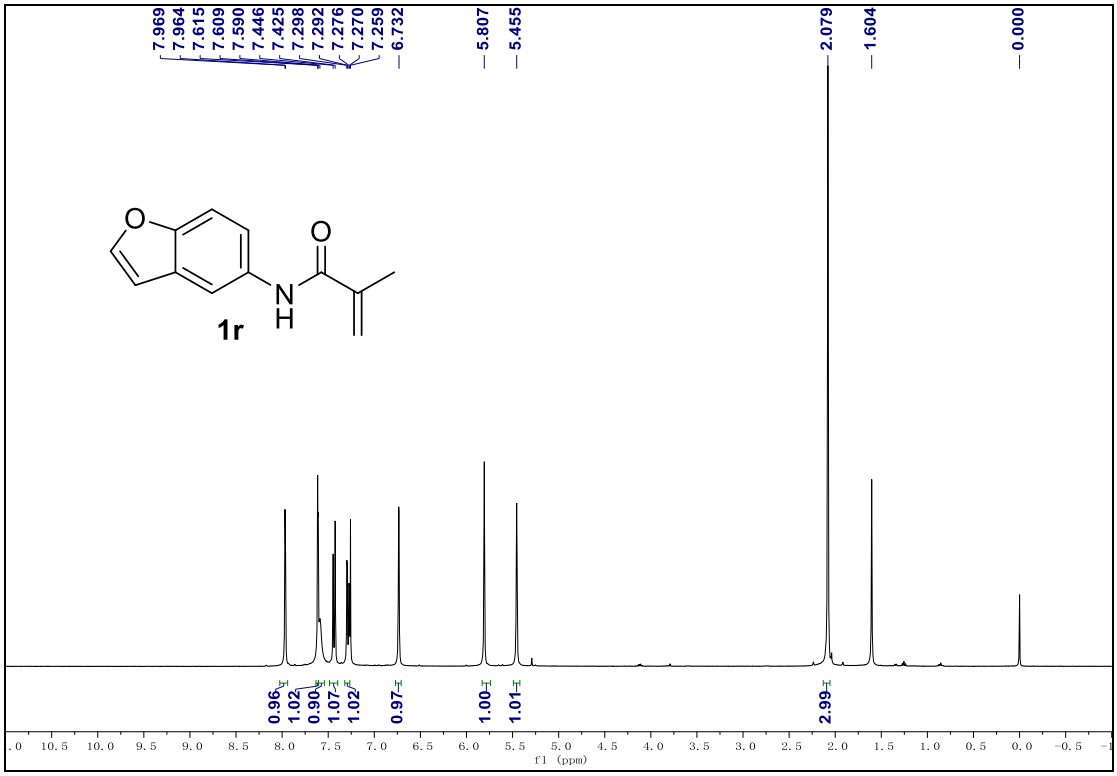


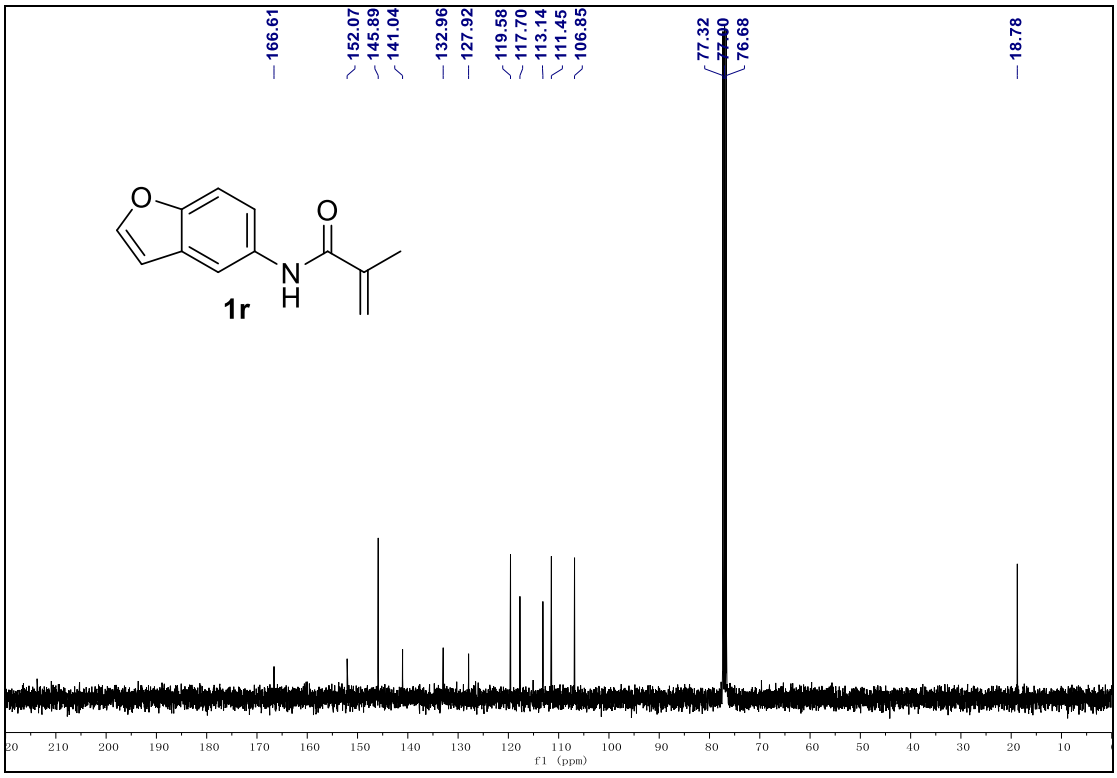
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1q.



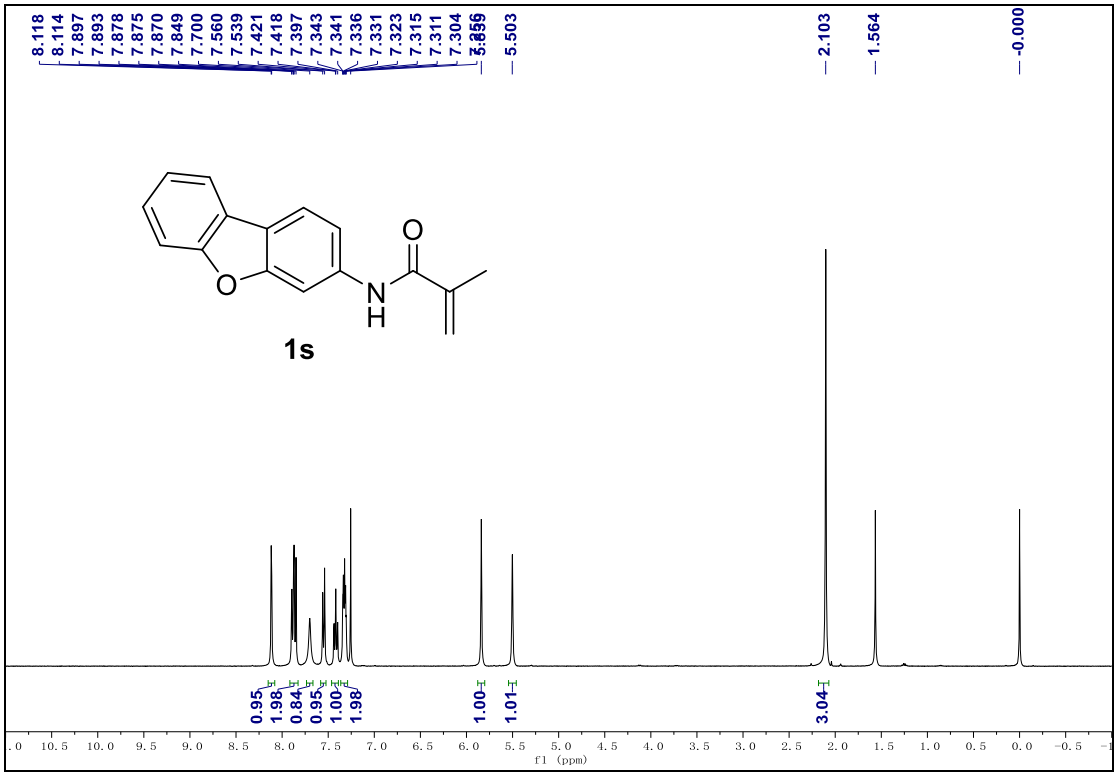


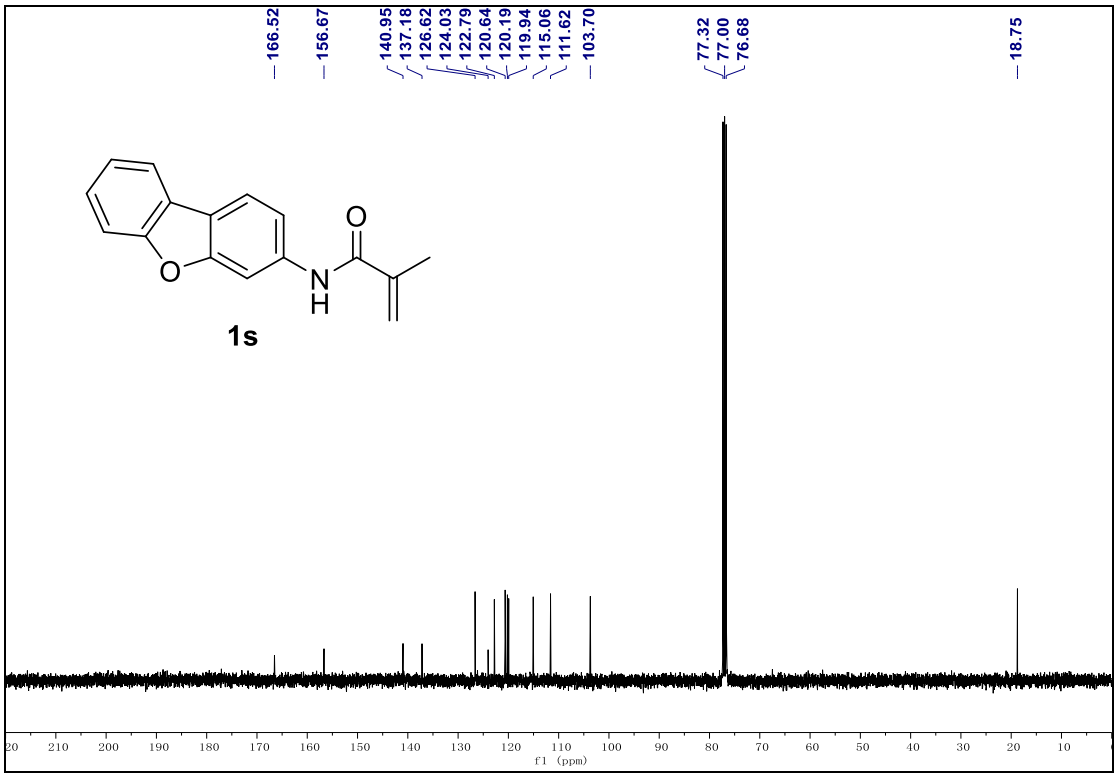
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1r.



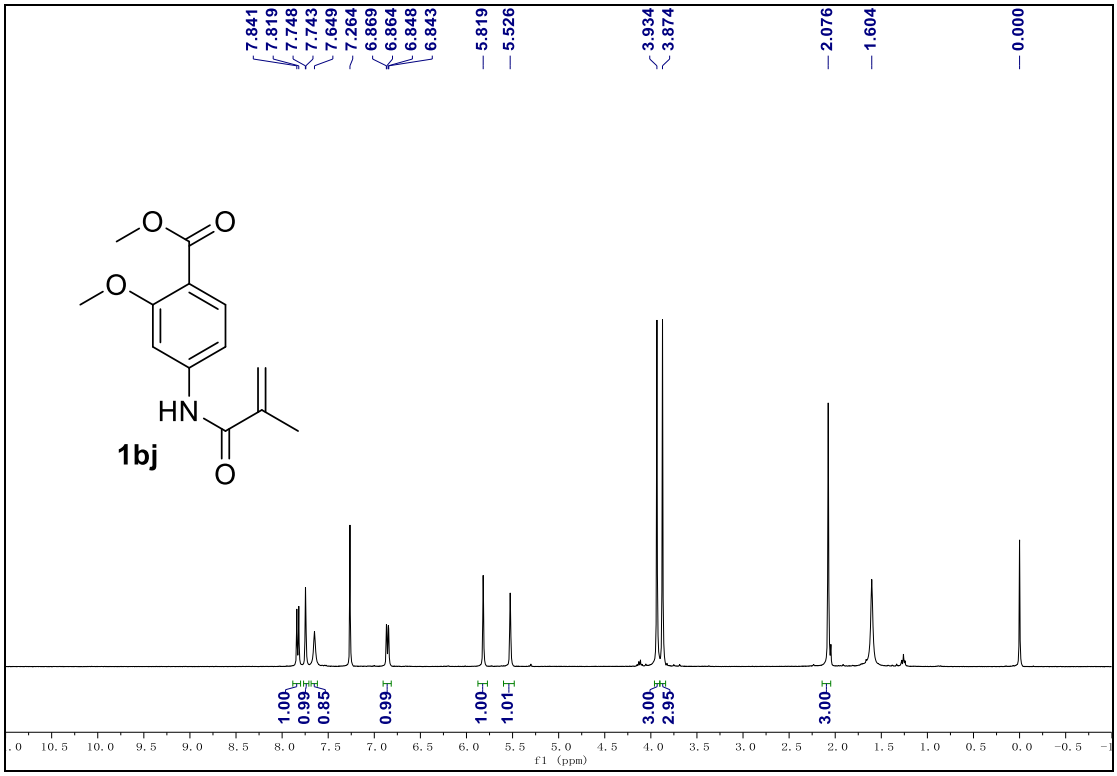


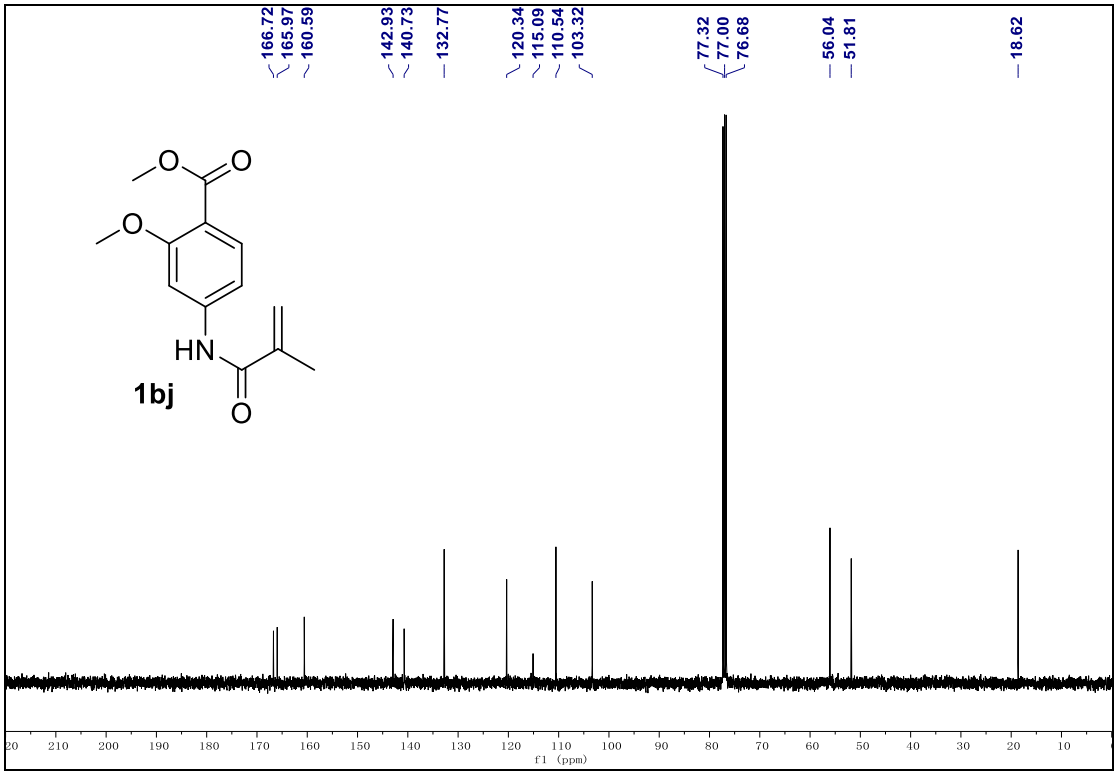
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1s.



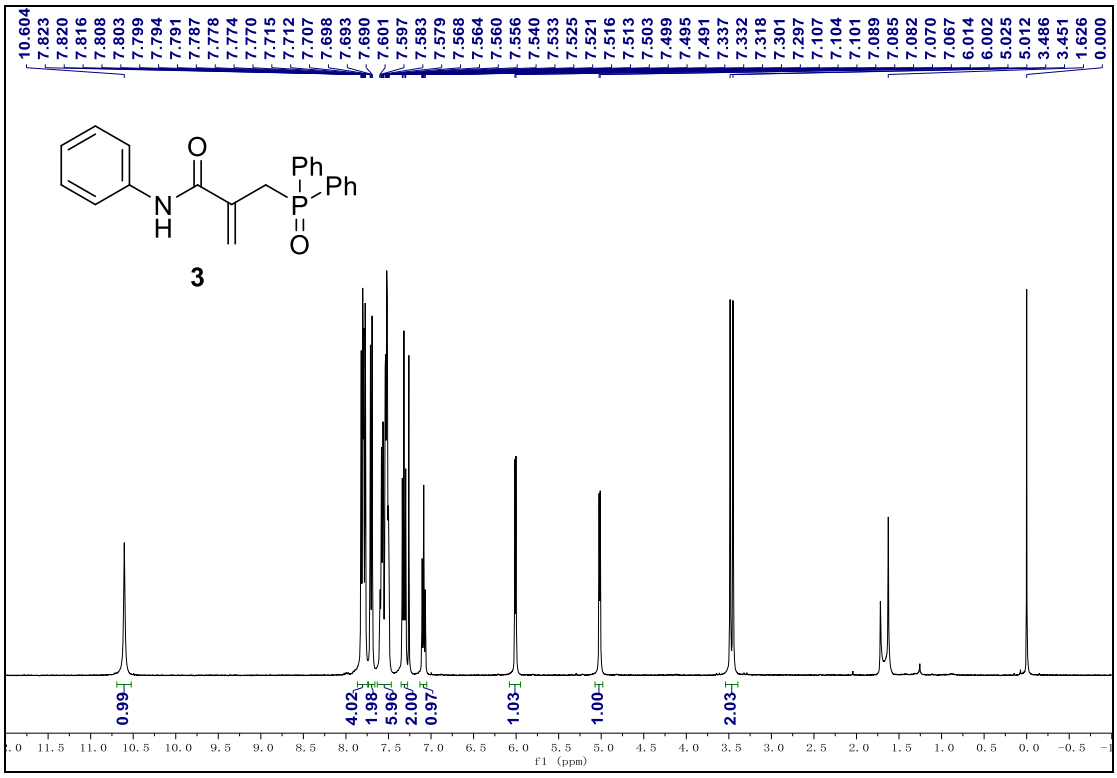


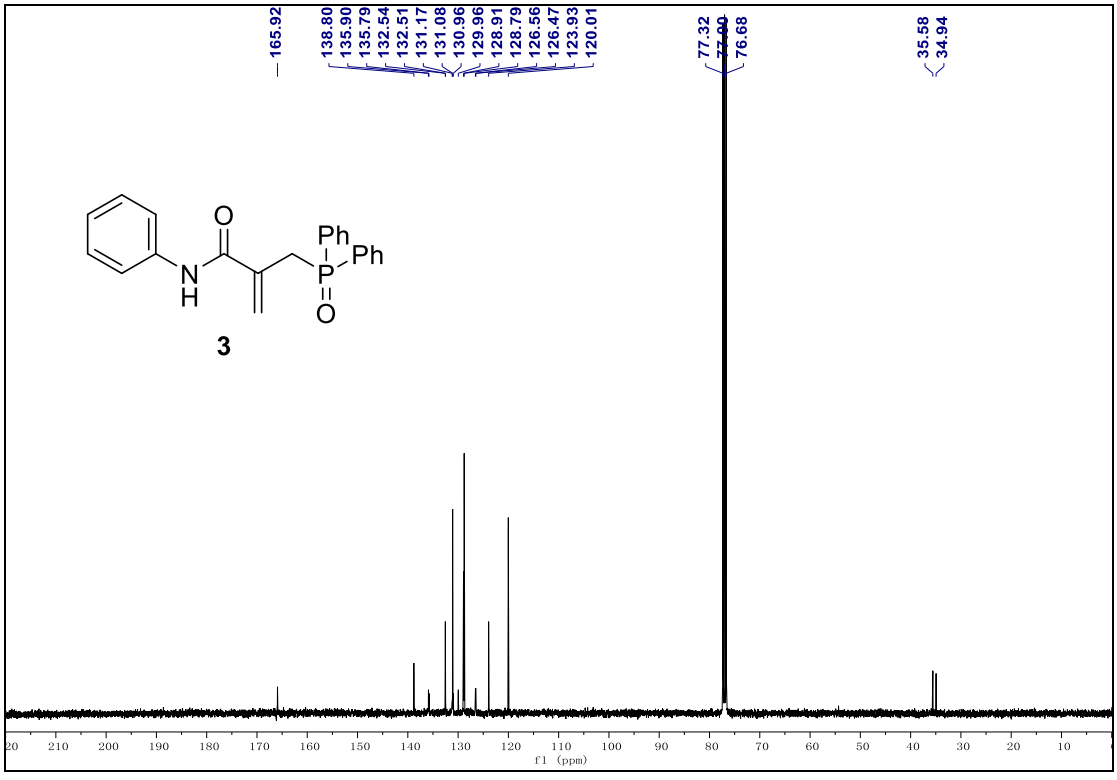
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1bj.

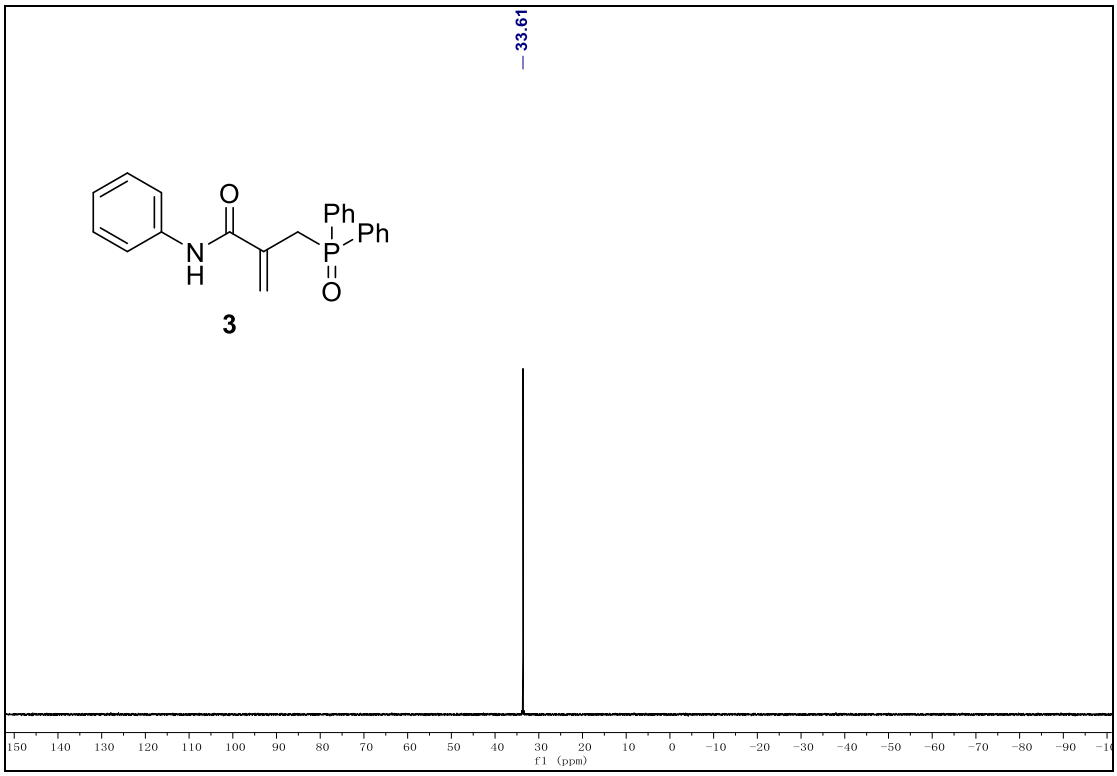




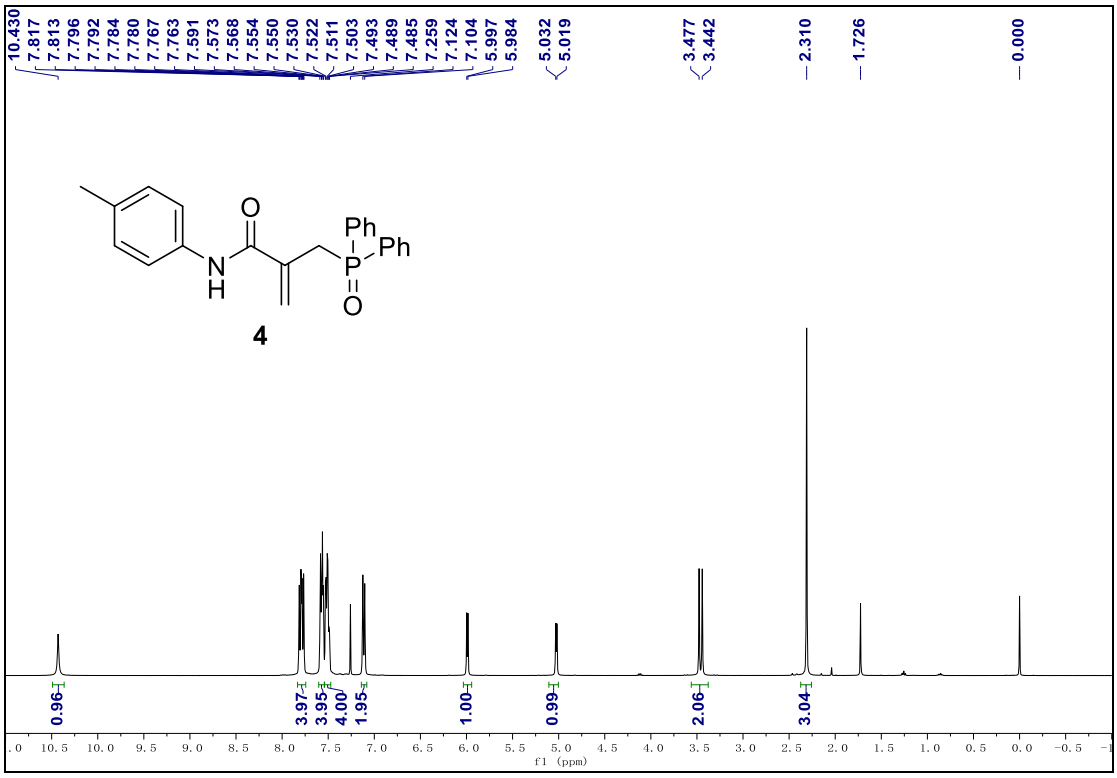
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 3.

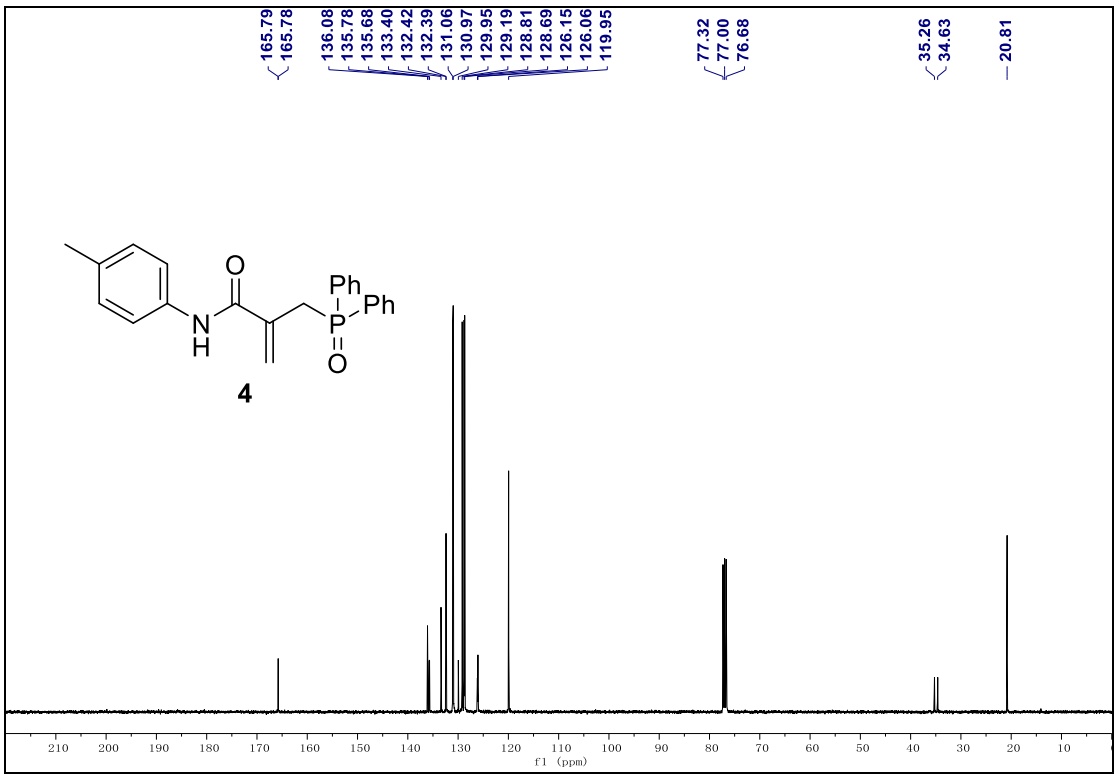


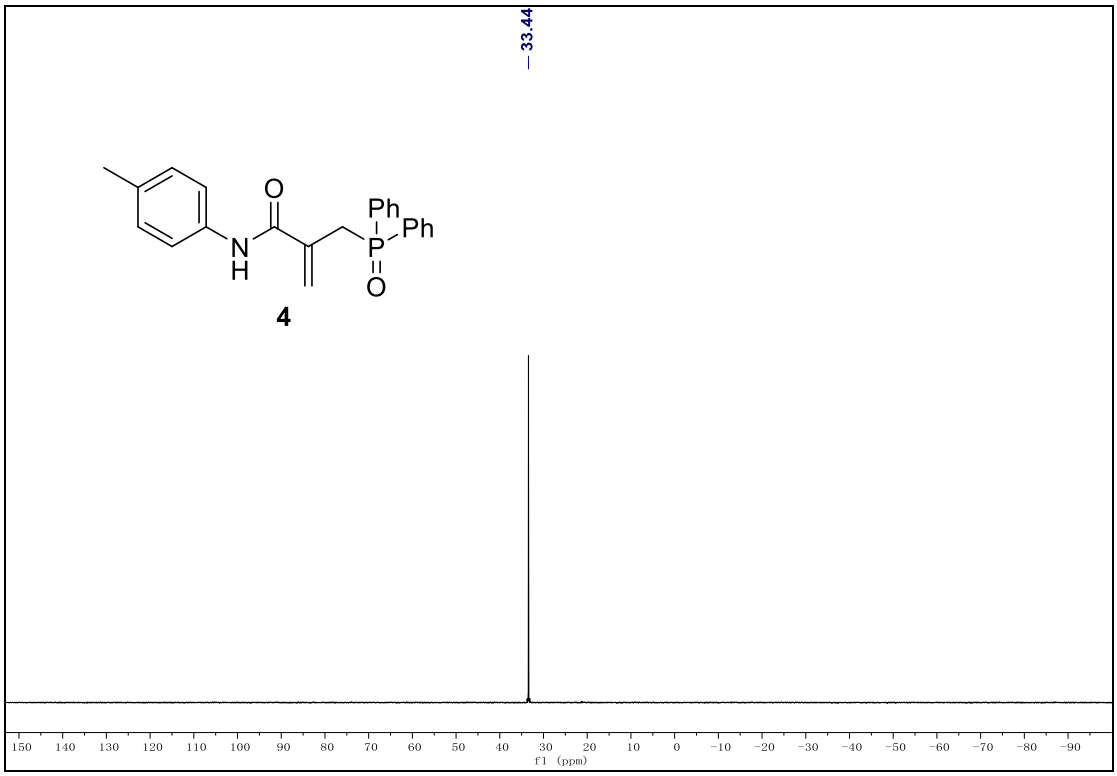



33.61
O
N
H
Ph
Ph
P
O
3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

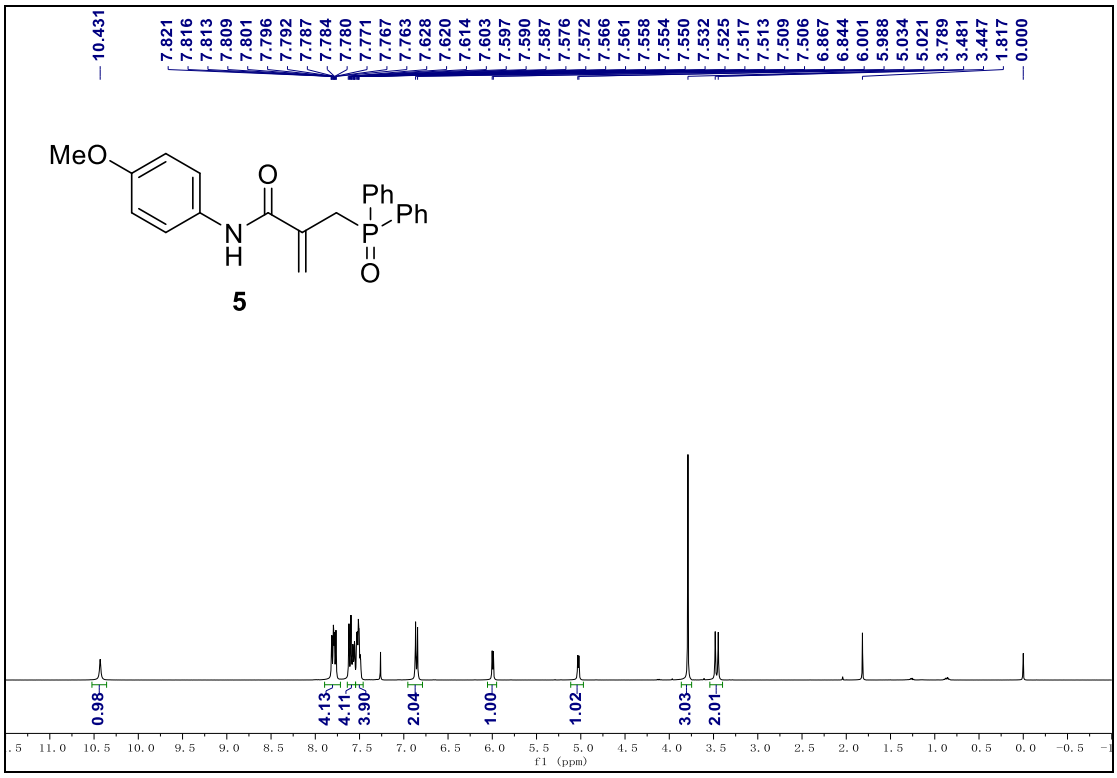
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 4.

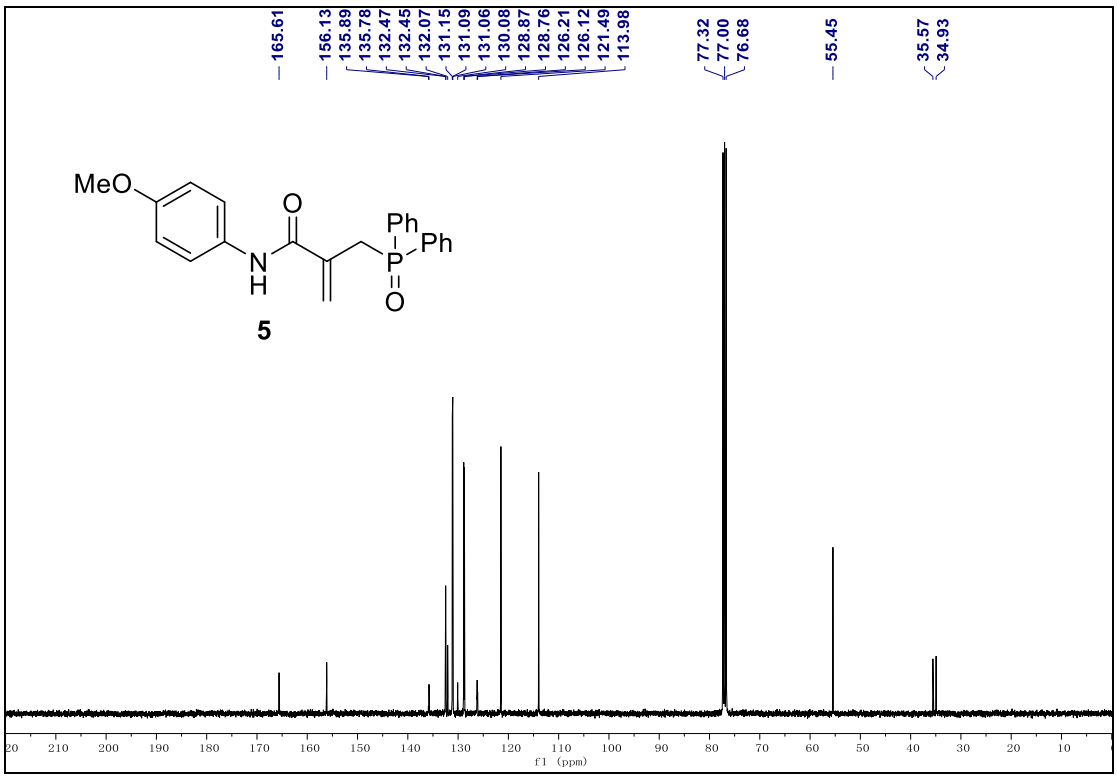


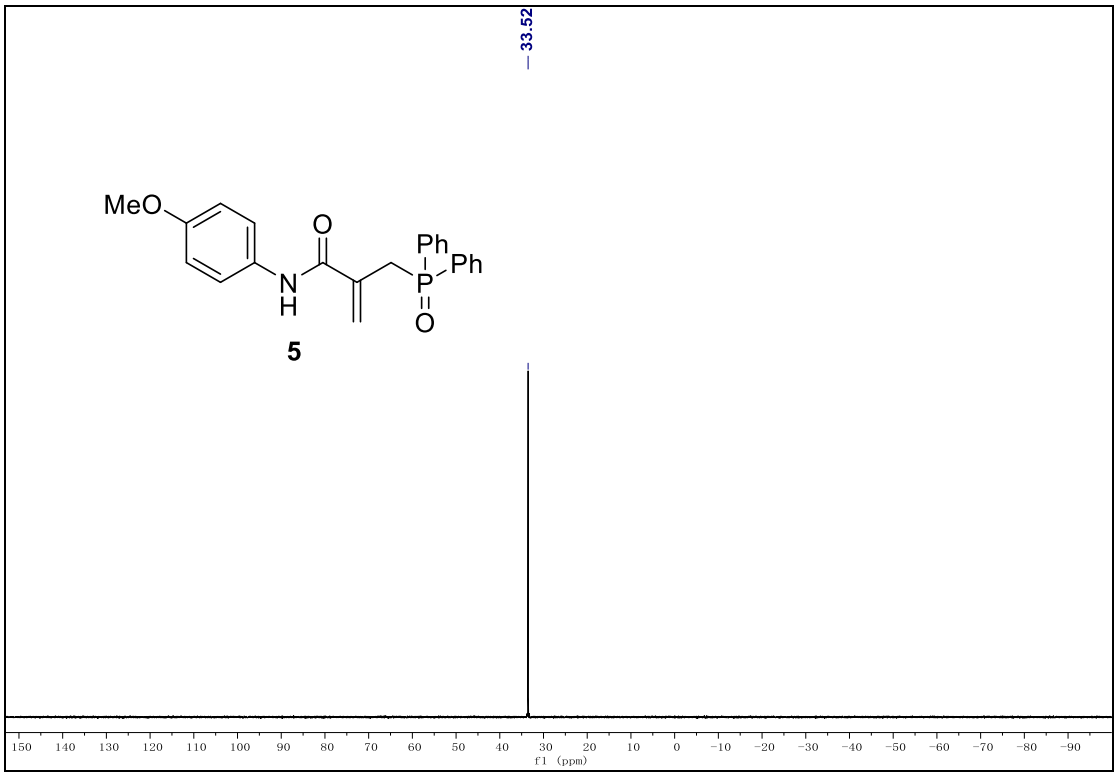



33.44
O
Ph
Ph
N
H
P
O
4
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

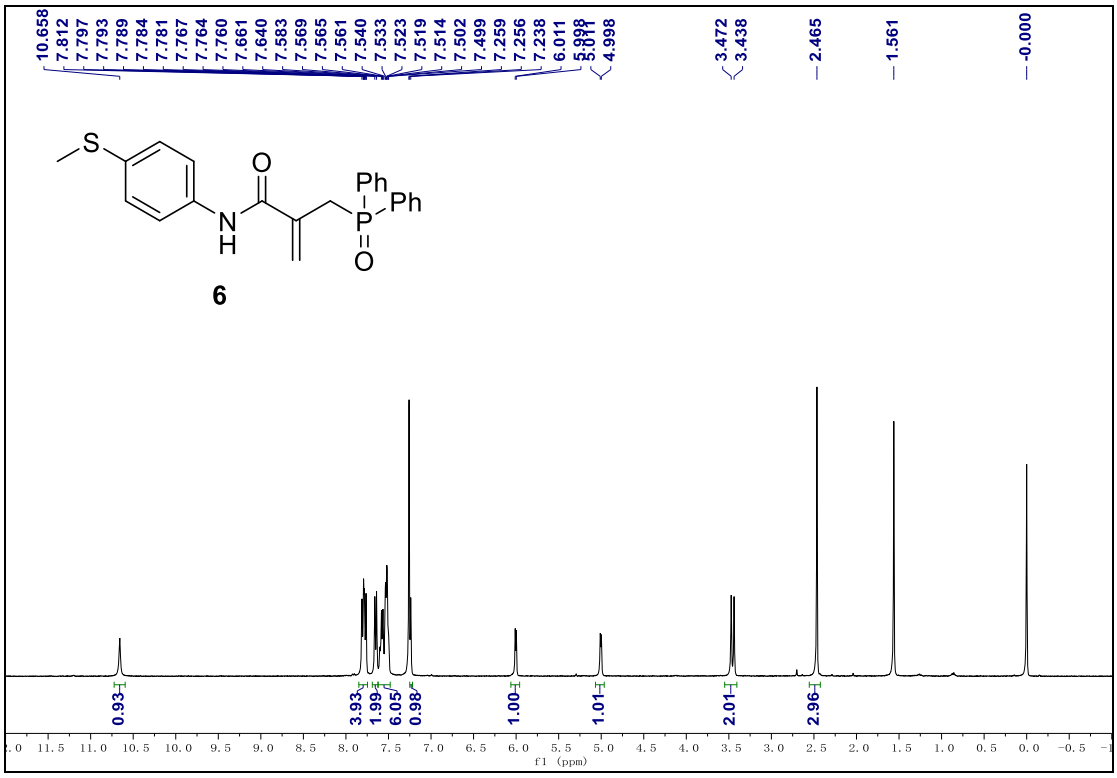
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 5.

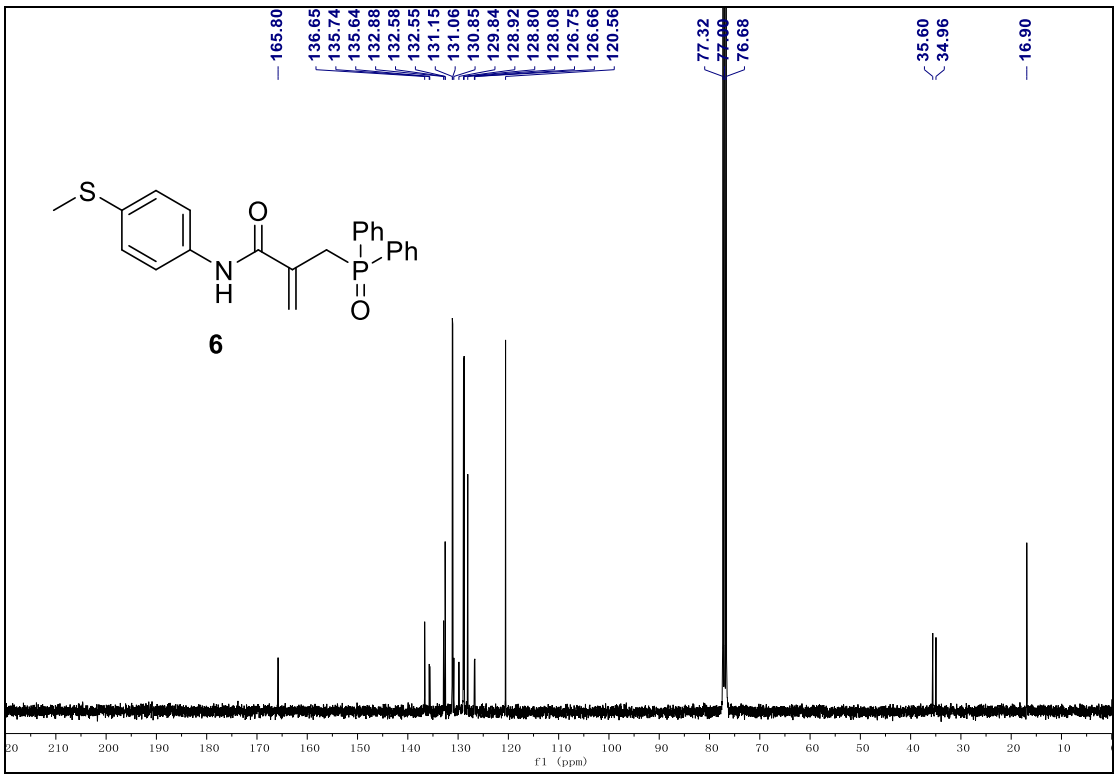


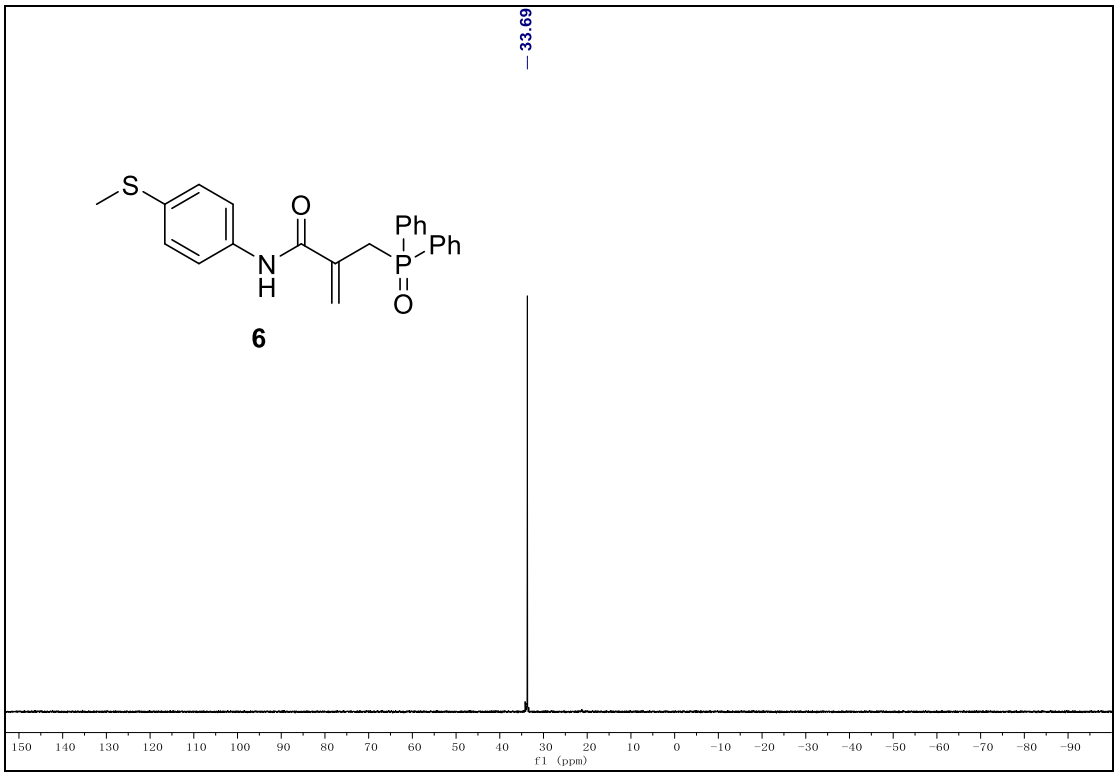



33.52
MeO
O
N
H
Ph
Ph
P
O
5
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

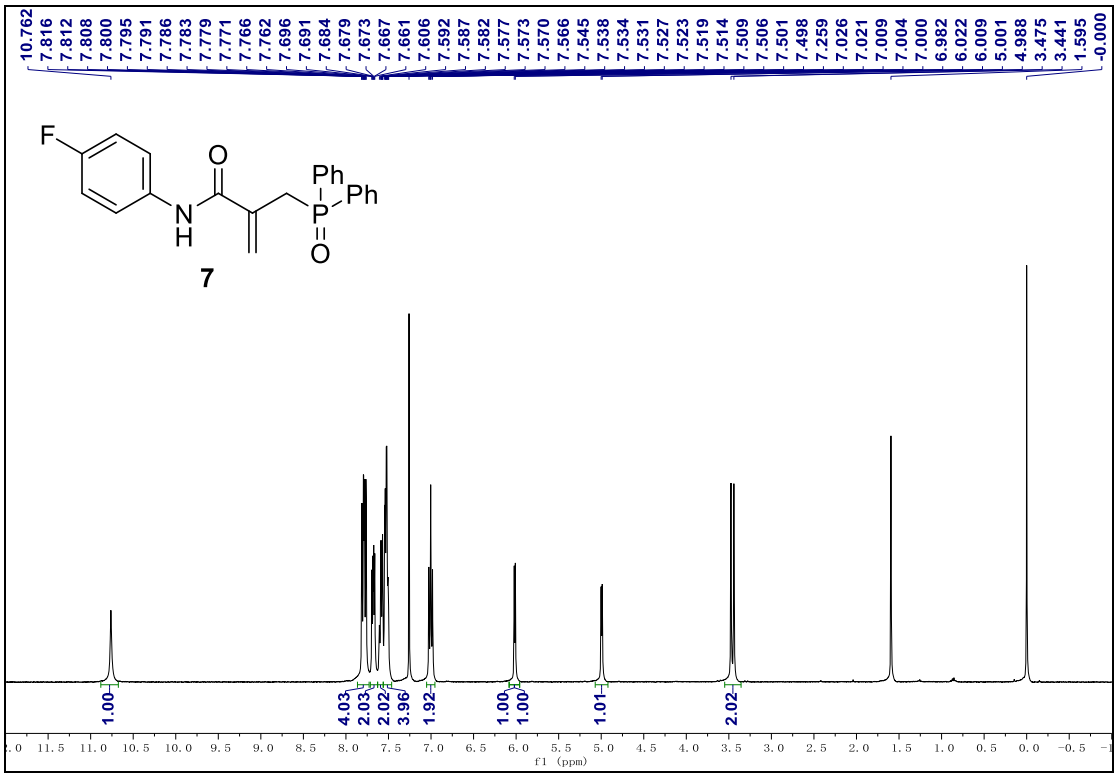
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 6.

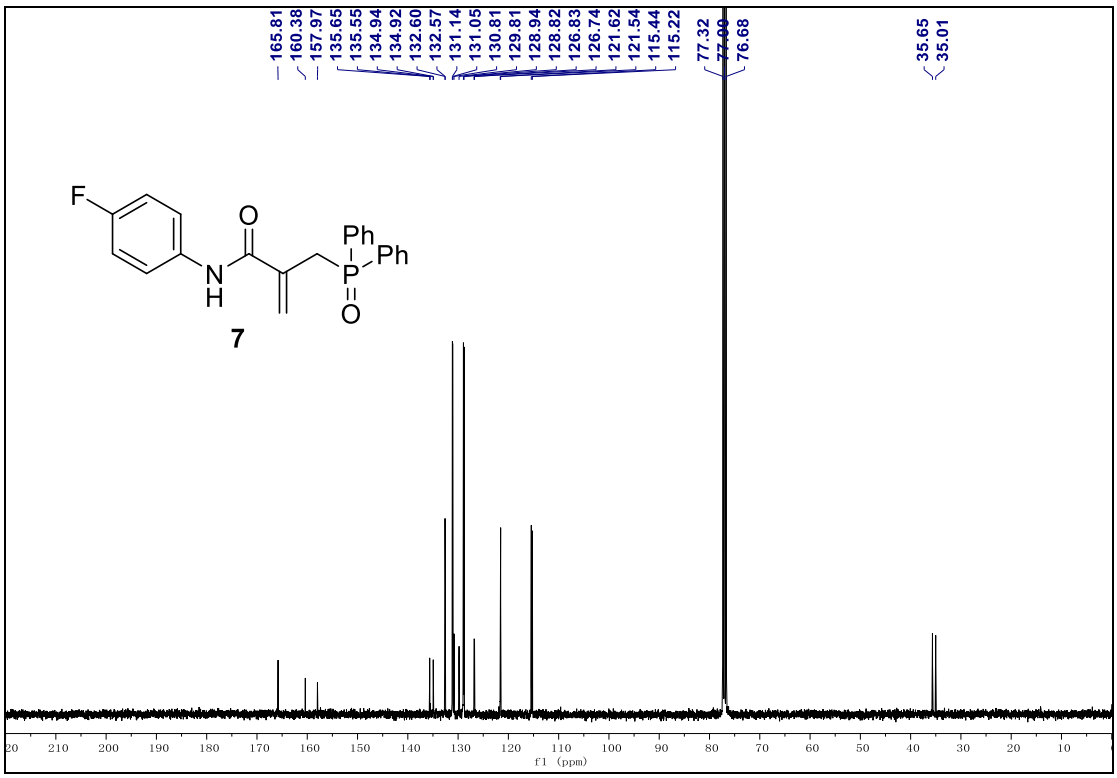


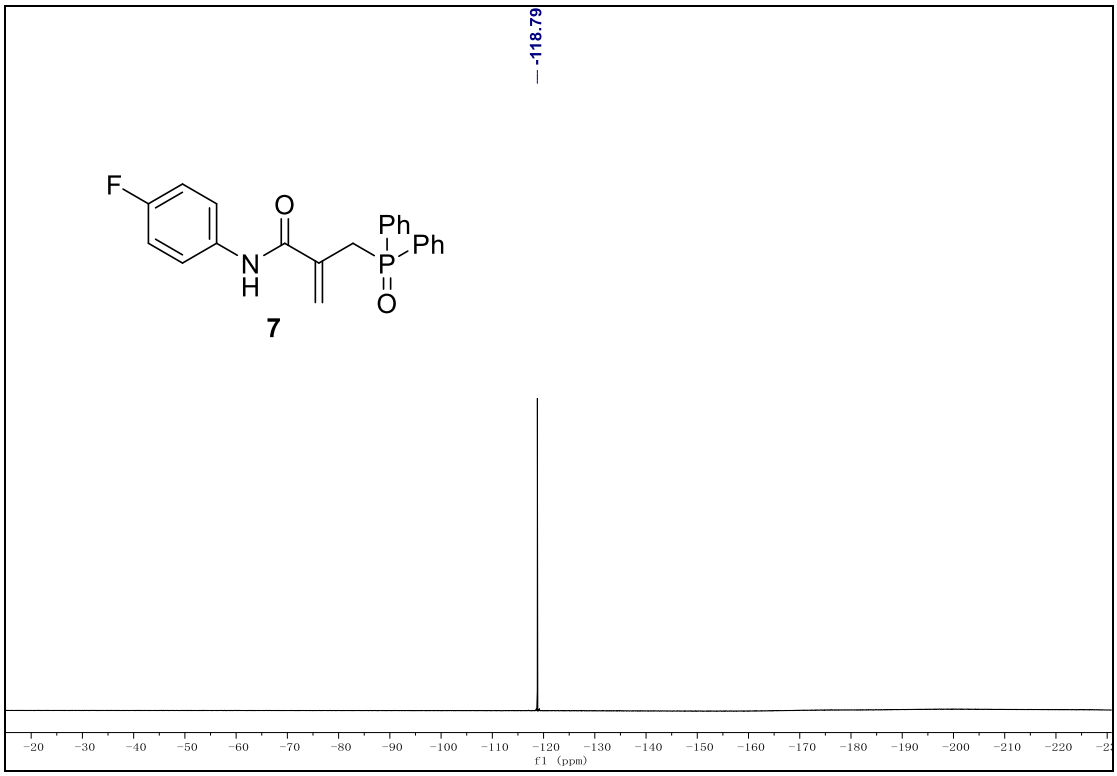


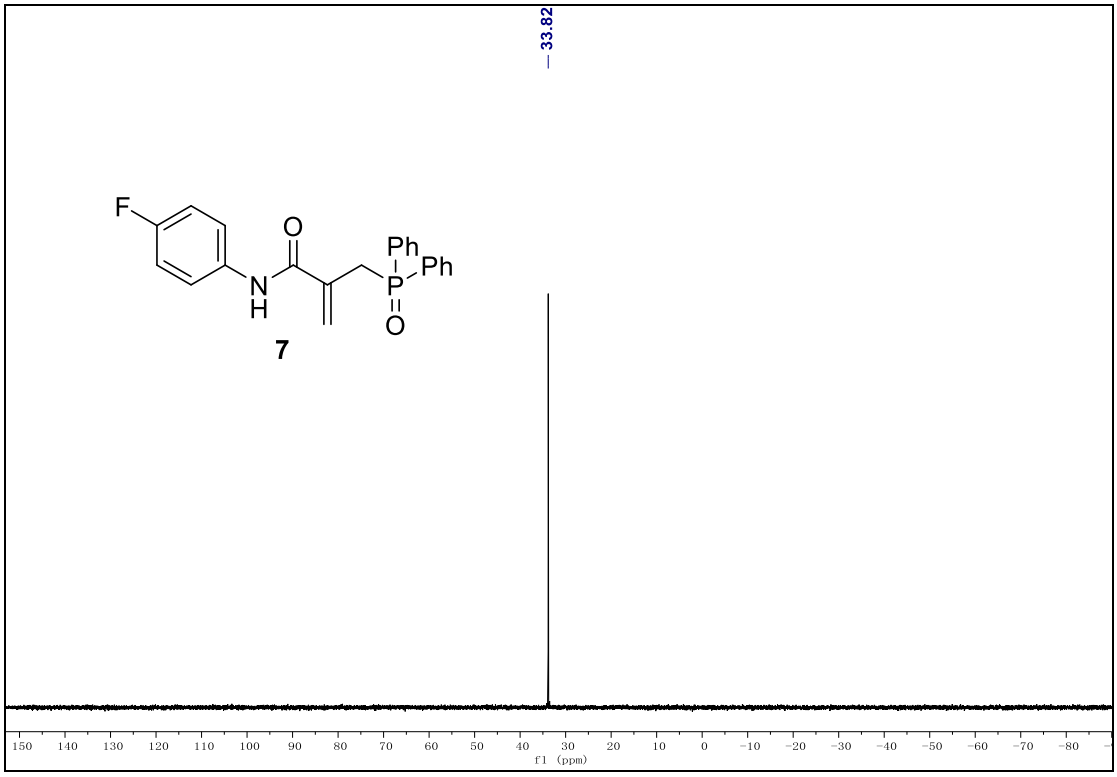

33.69
S
O
Ph
Ph
N
H
P
O
6
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, CDCl3) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 7.

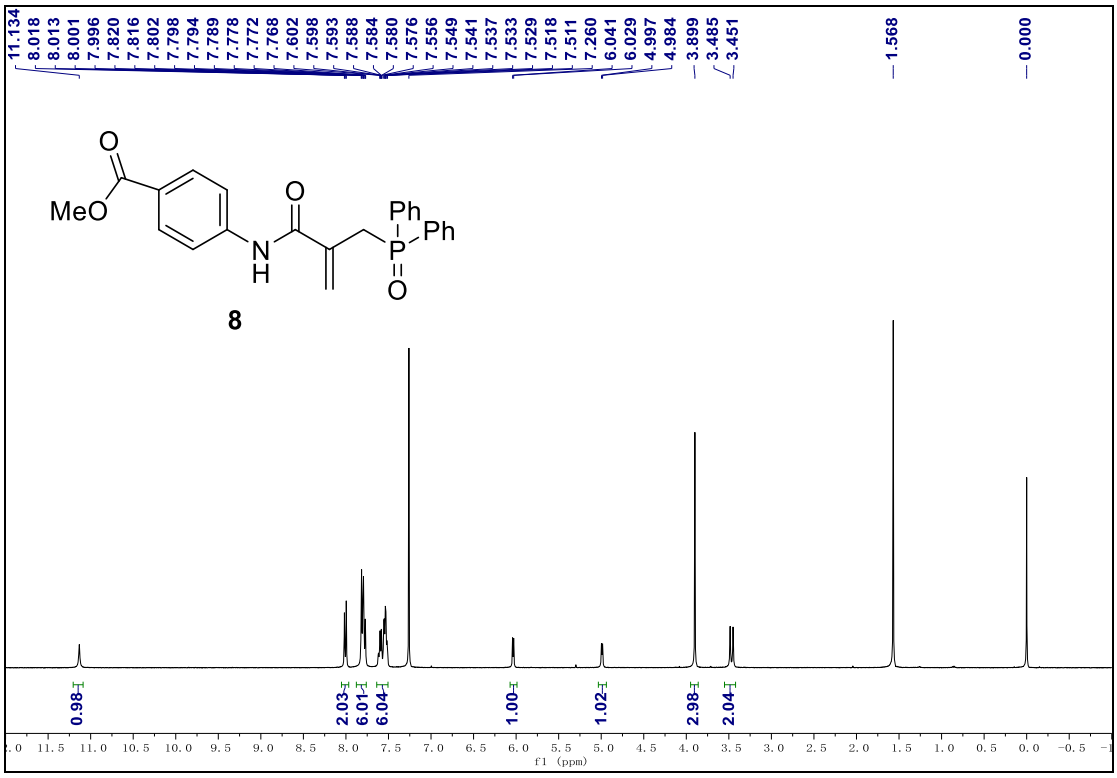


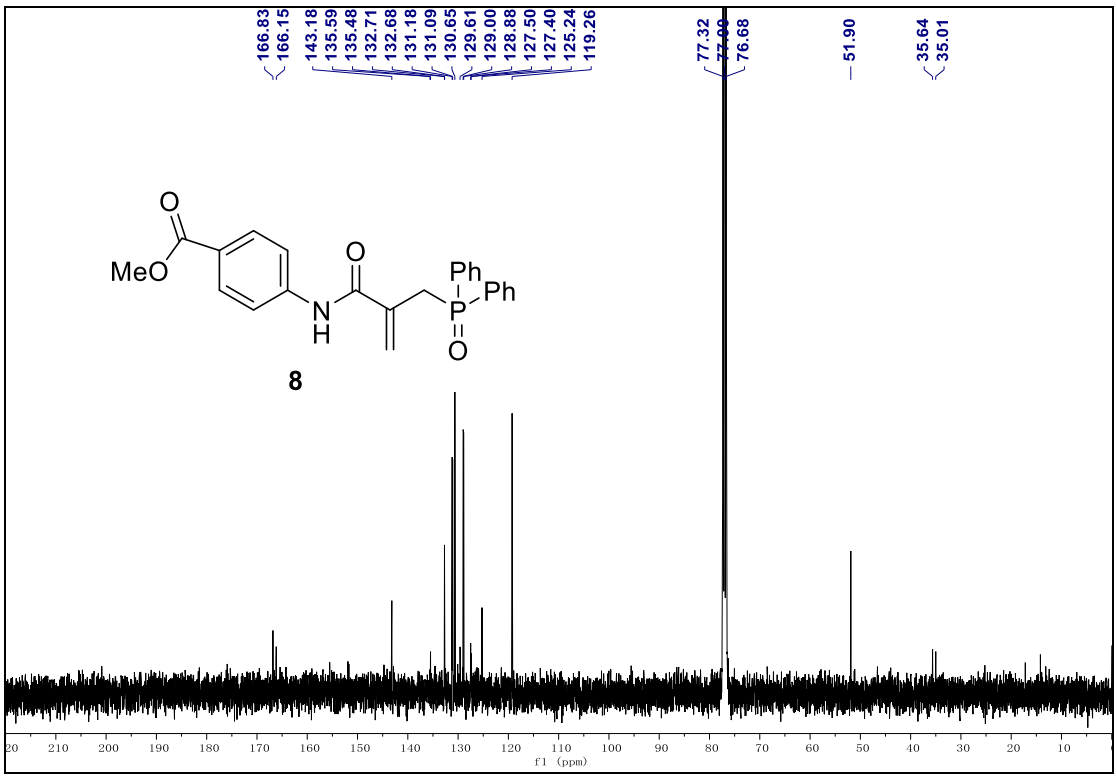


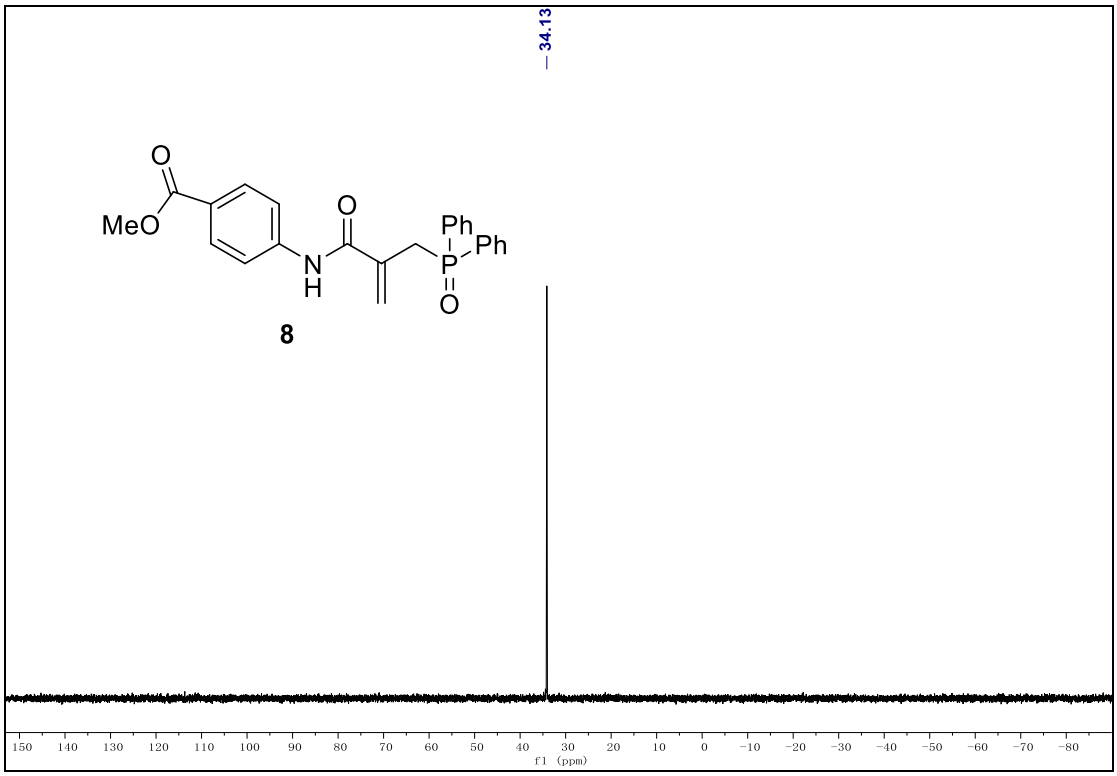

-118.79
F
O
Ph
Ph
N
H
P
O
7
f1 (ppm)


33.82
F
O
Ph
Ph
N
H
P
O
7
f1 (ppm)

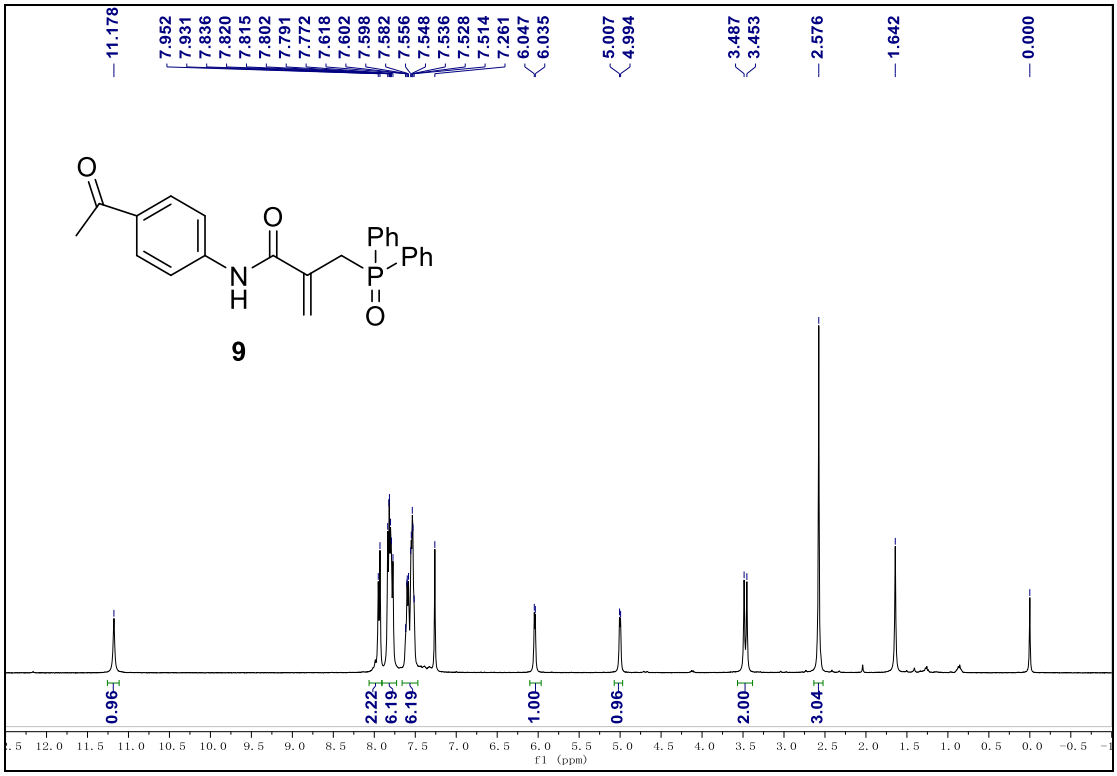
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 8.

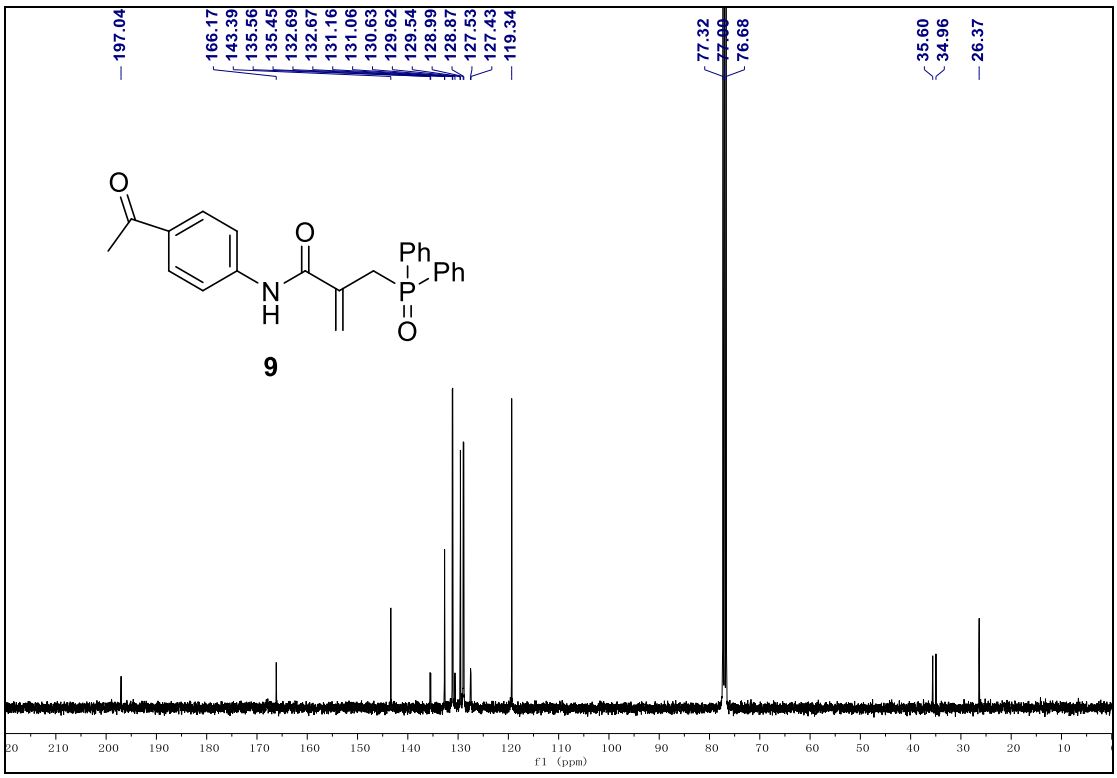


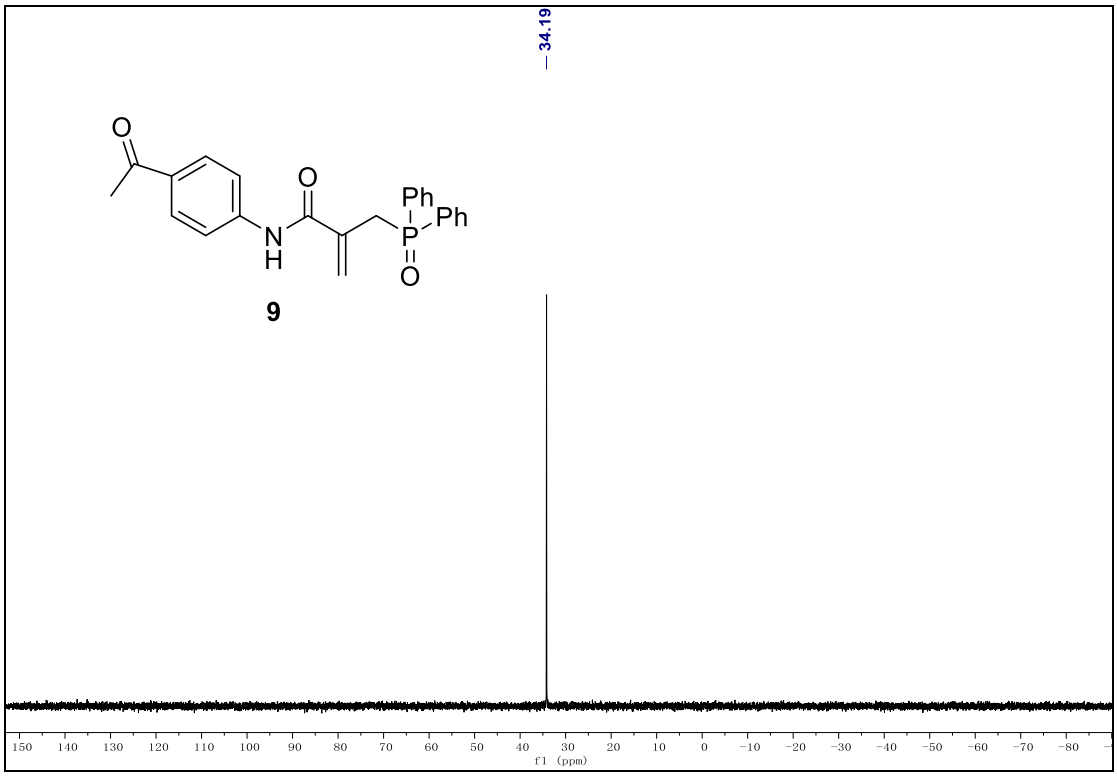



34.13
O
MeO
O
N
H
Ph
Ph
P
O
8
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

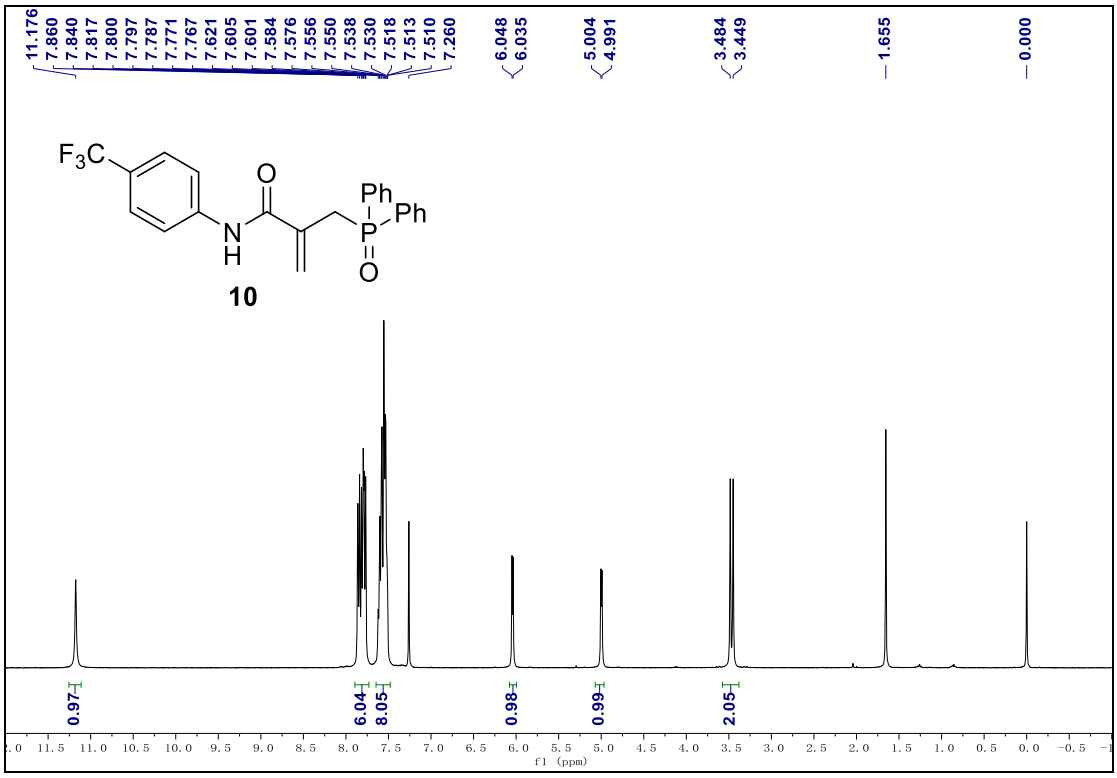
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 9.

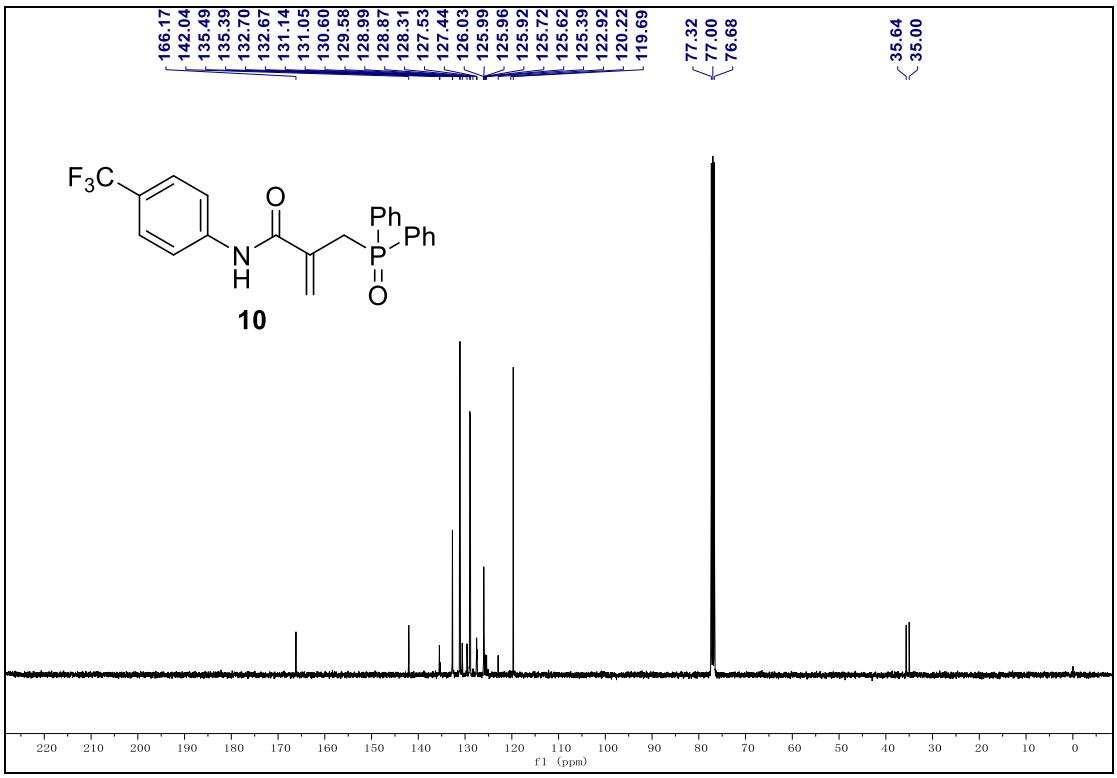


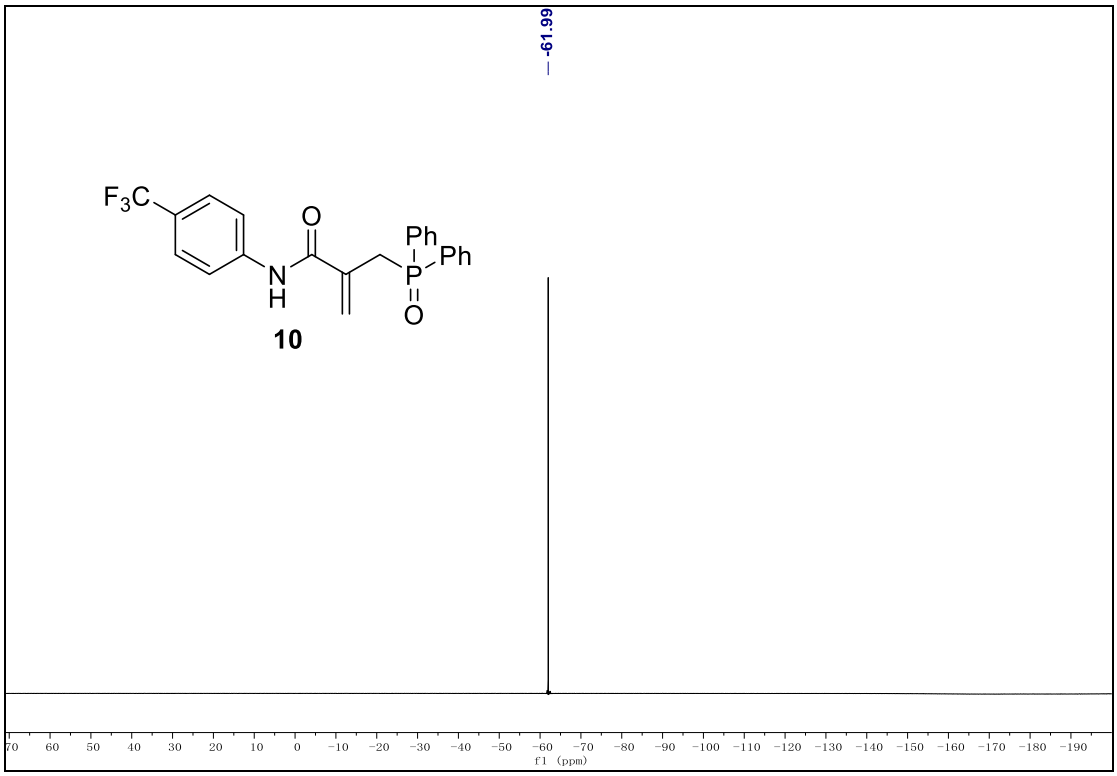


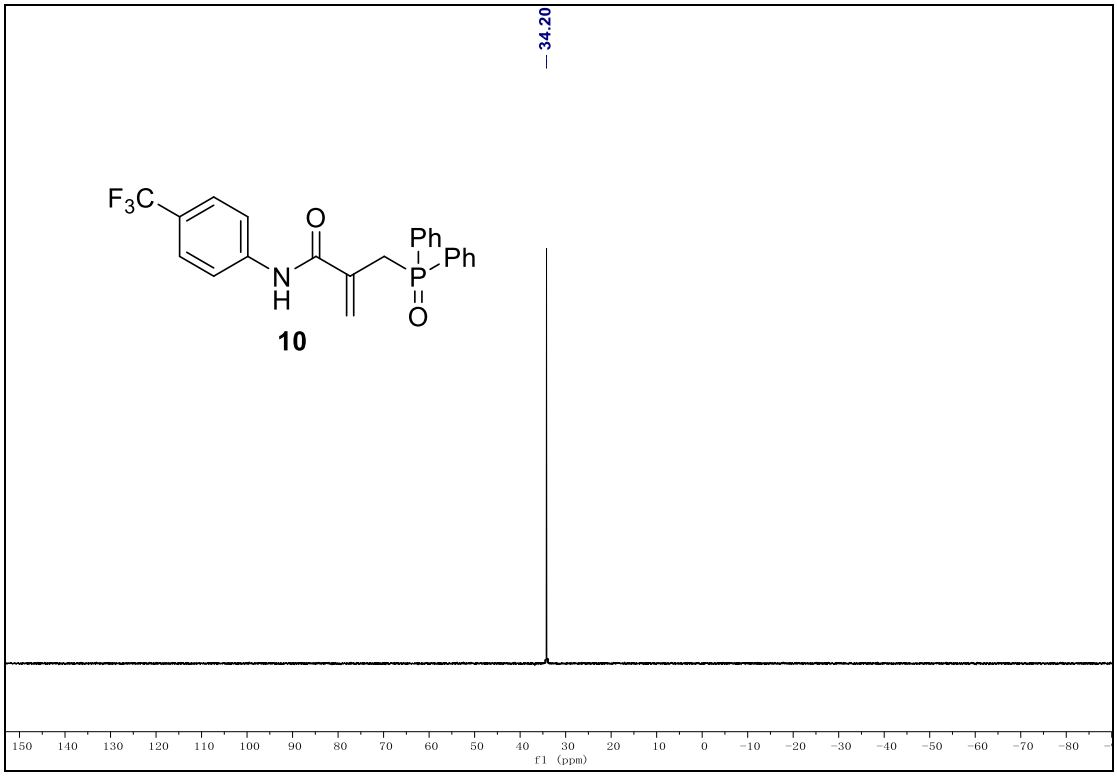

34.19
O
O
N
H
Ph
Ph
P
O
9
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, CDCl3) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 10.

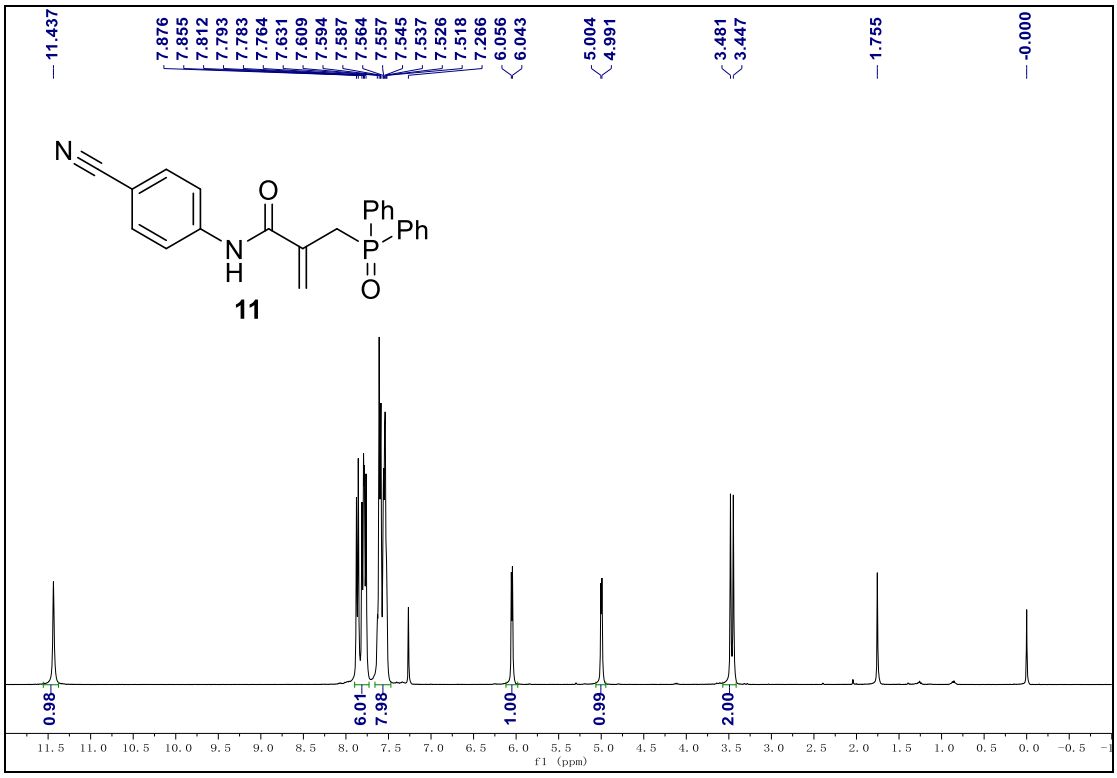


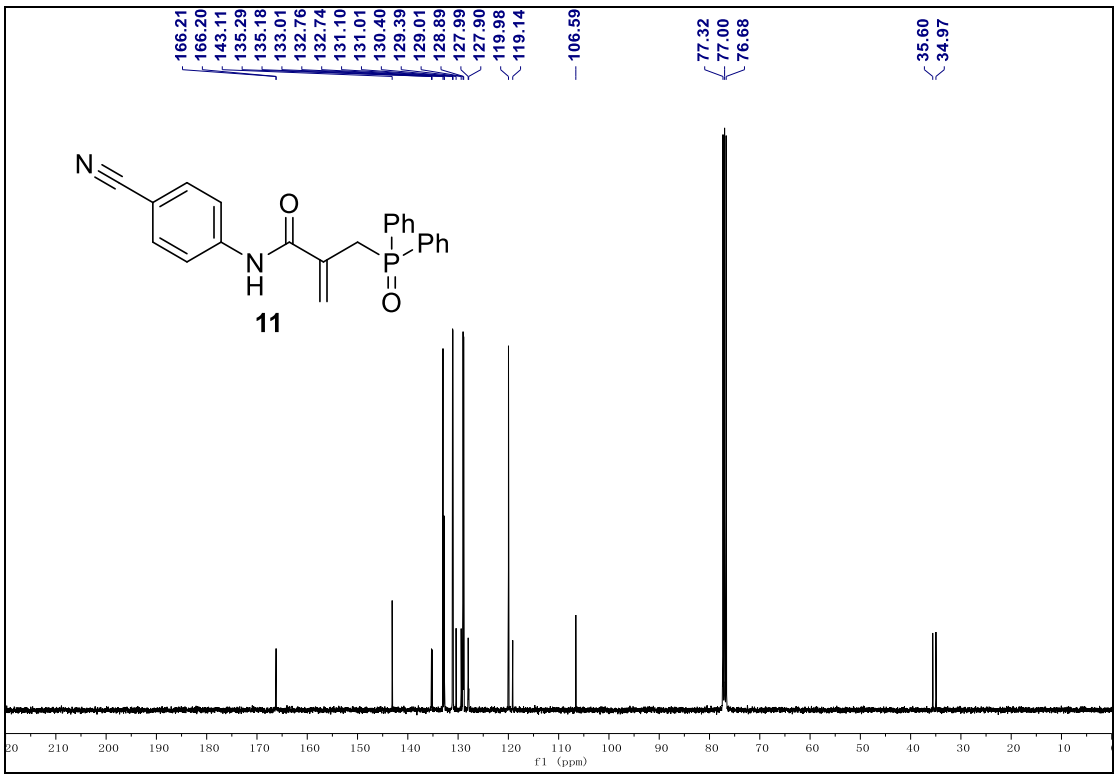


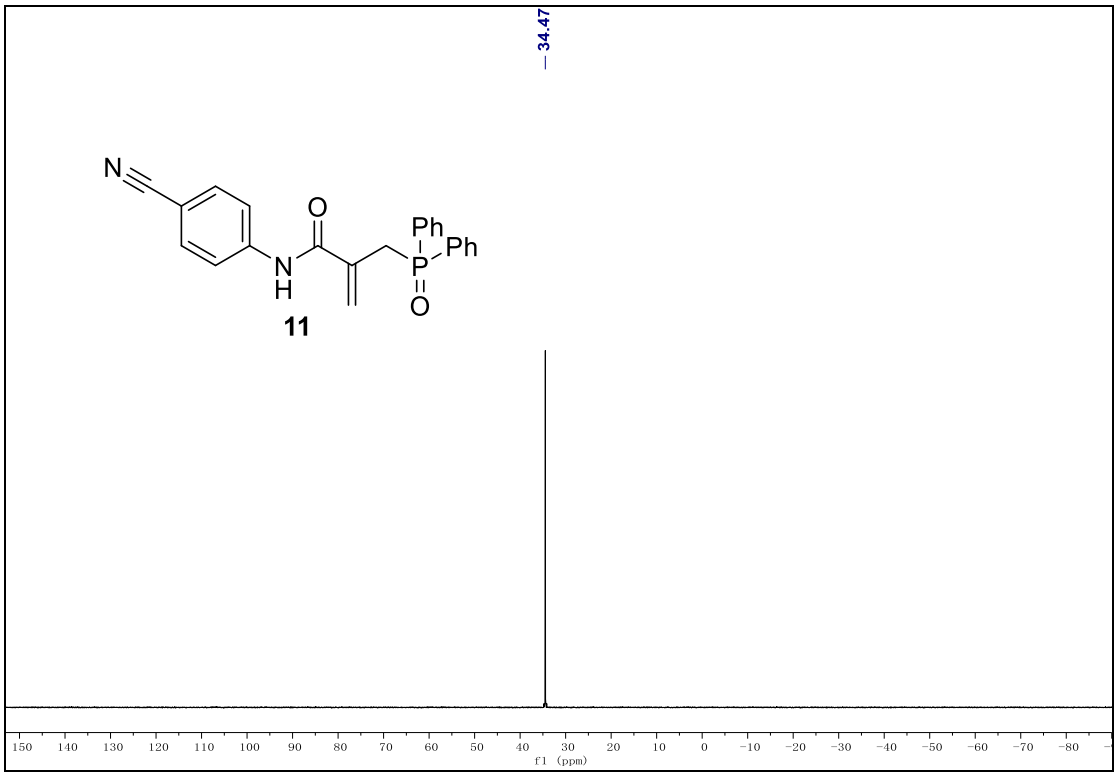

-61.99
F3C
O
Ph
Ph
N
H
P
O
10
70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)


34.20
F3C
O
Ph
Ph
N
H
P
O
10
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

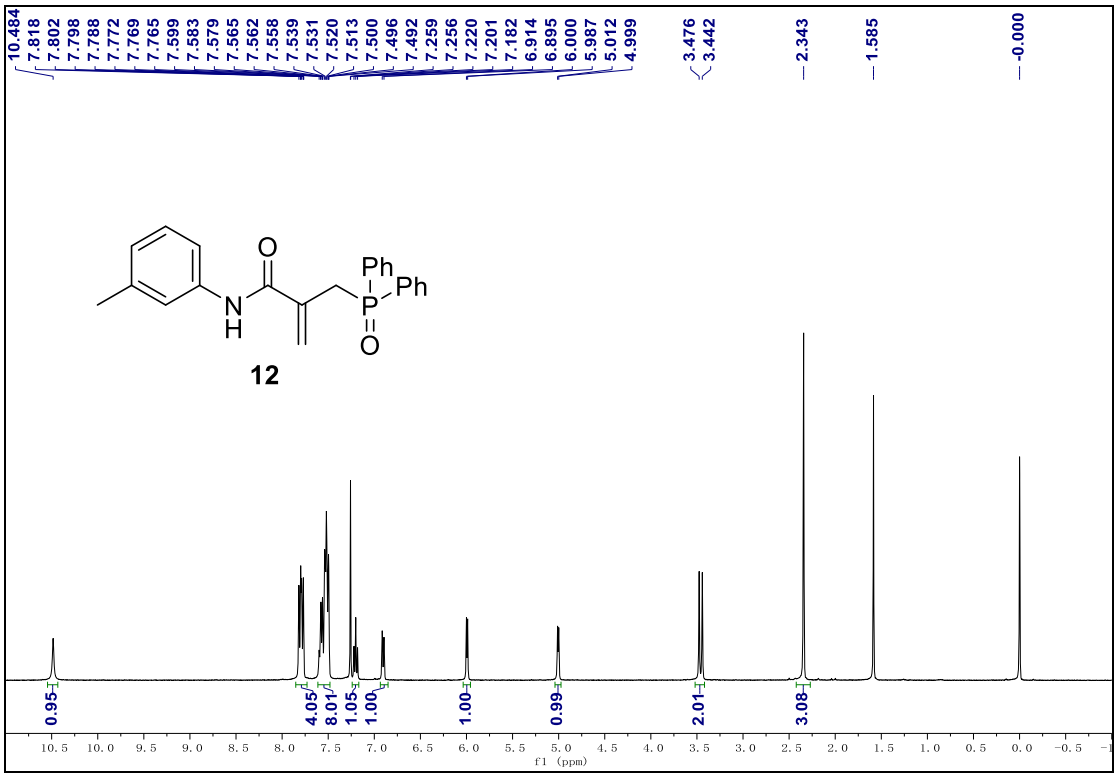
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 11.

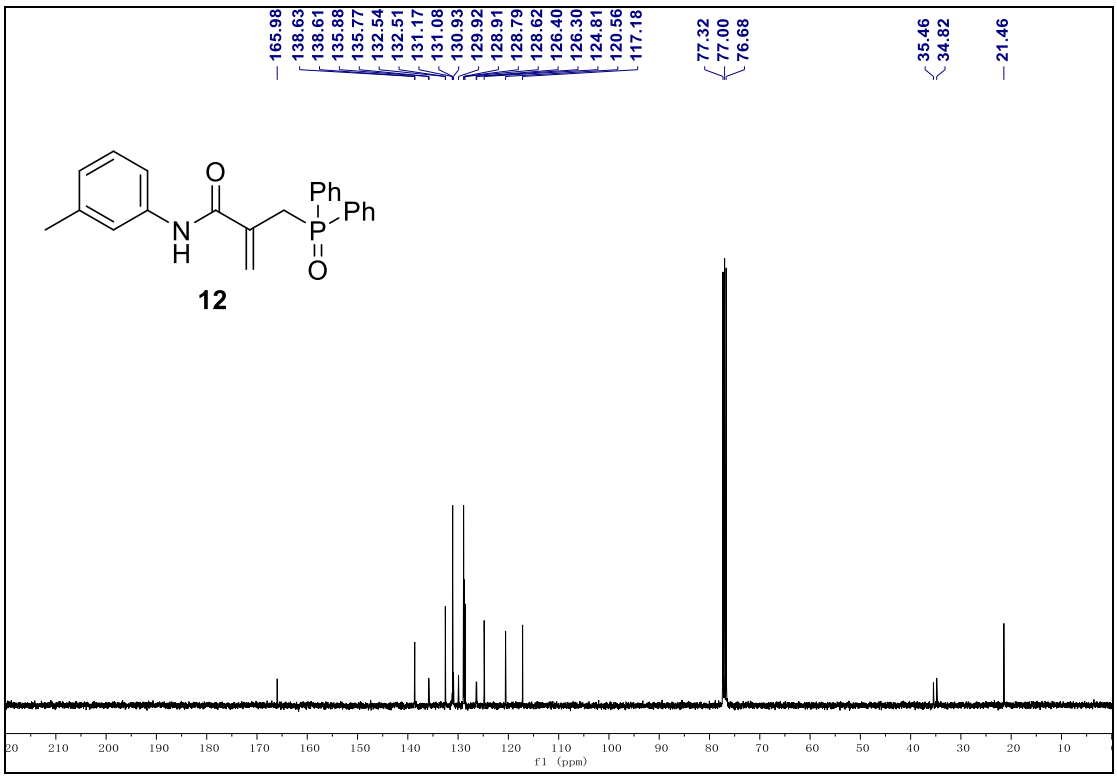


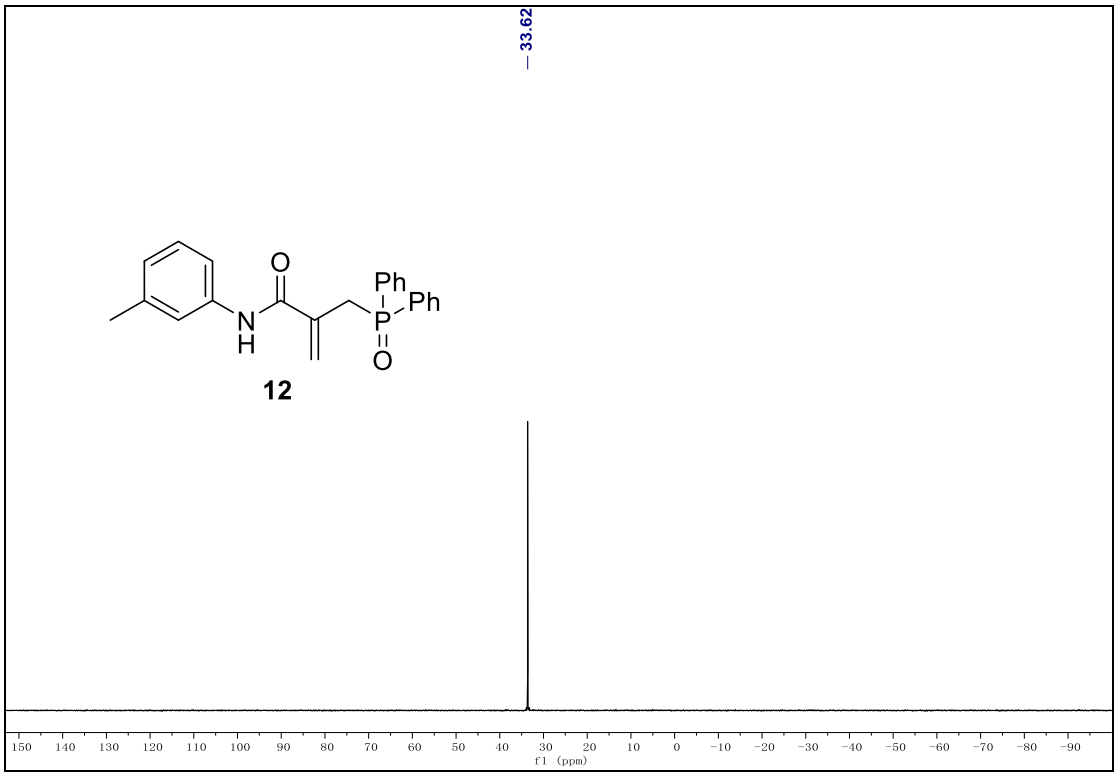



34.47
N
O
Ph
Ph
N
H
P
O
11
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

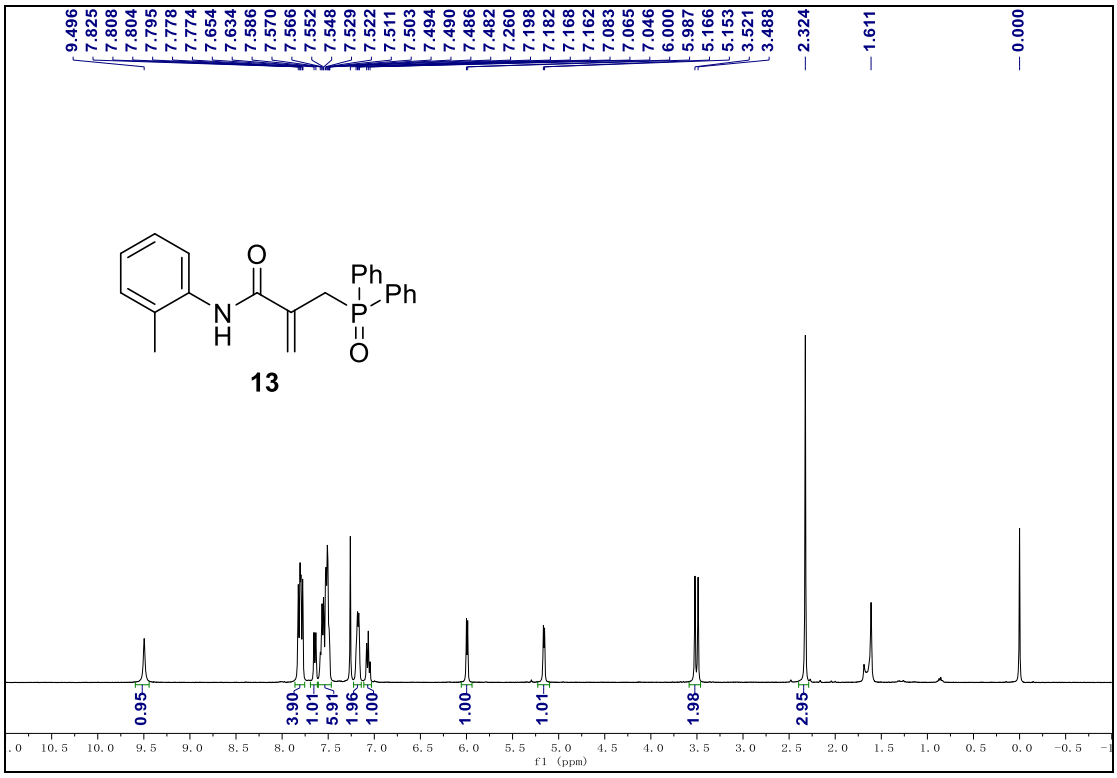
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 12.

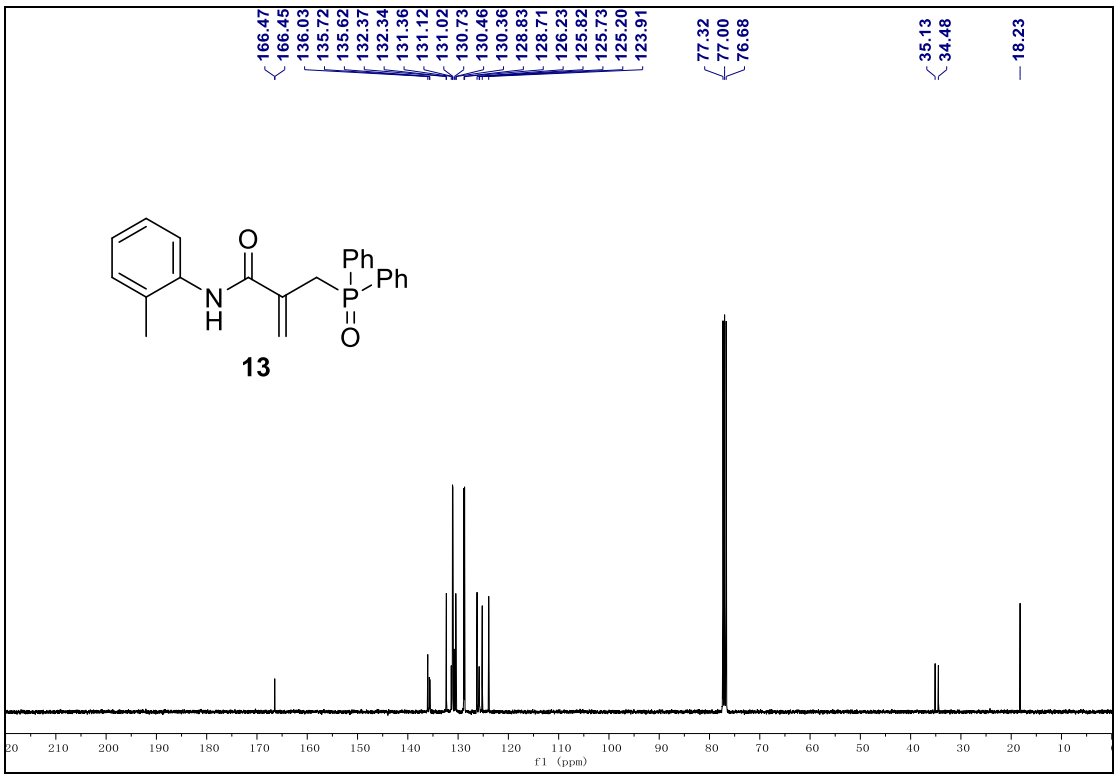


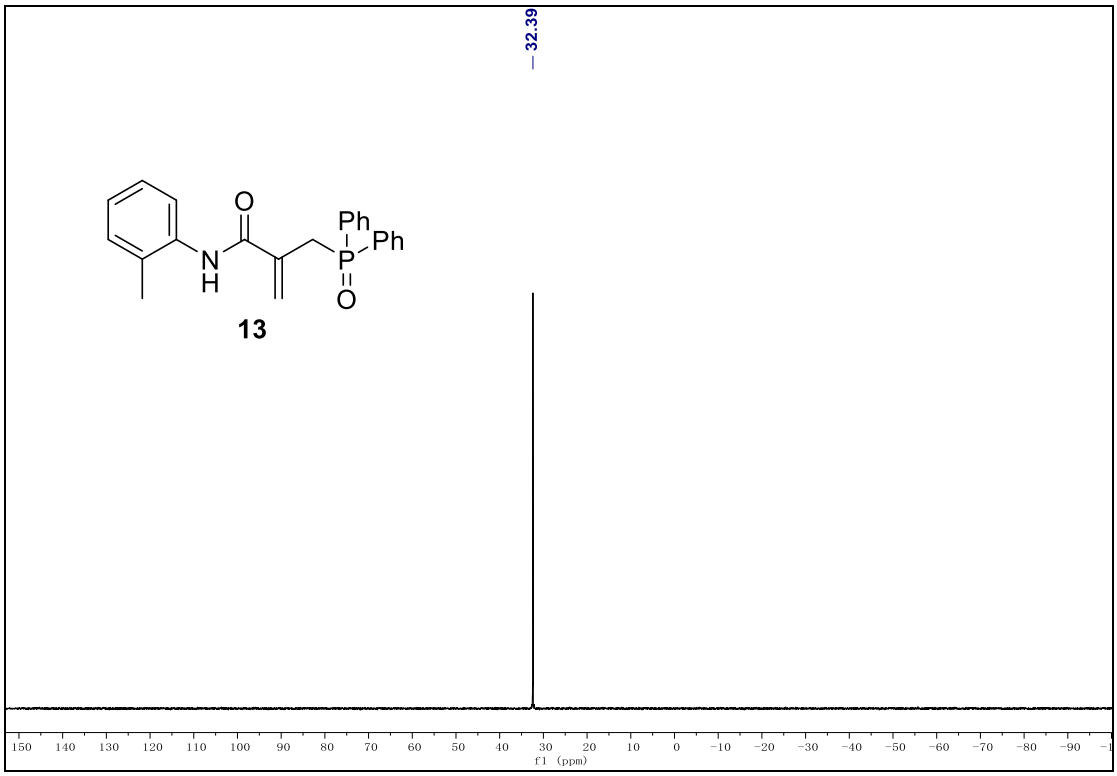



33.62
O
Ph
Ph
N
H
P
O
12
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

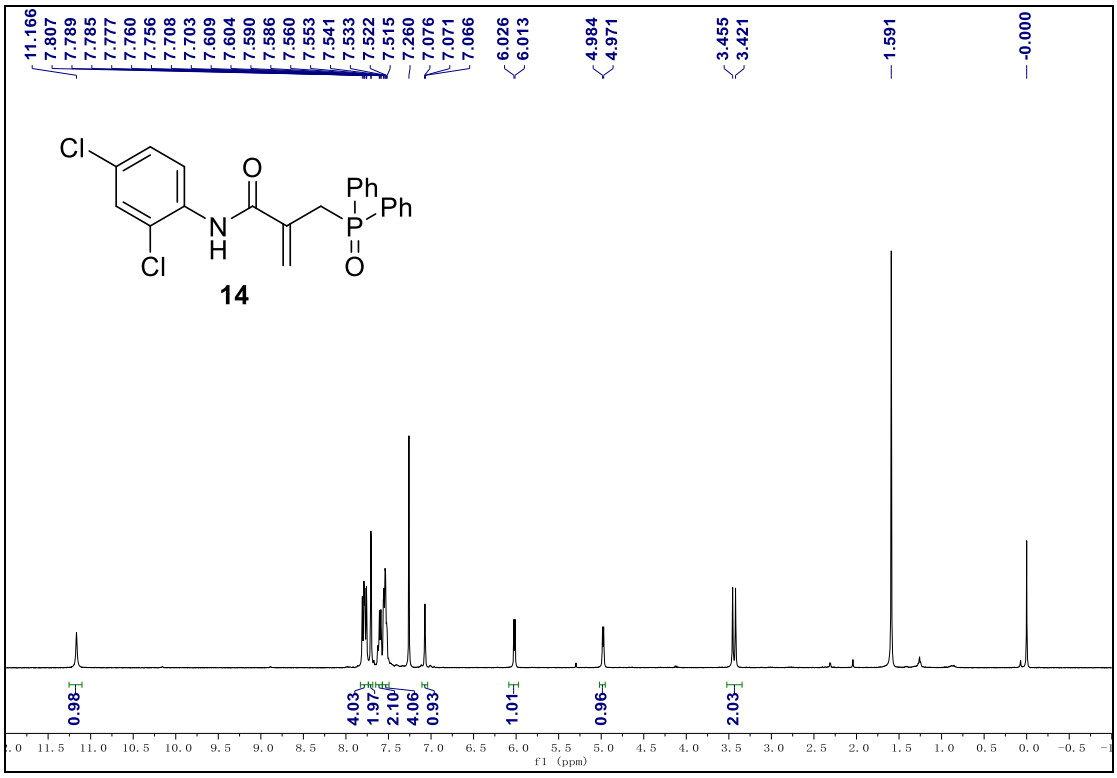
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 13.

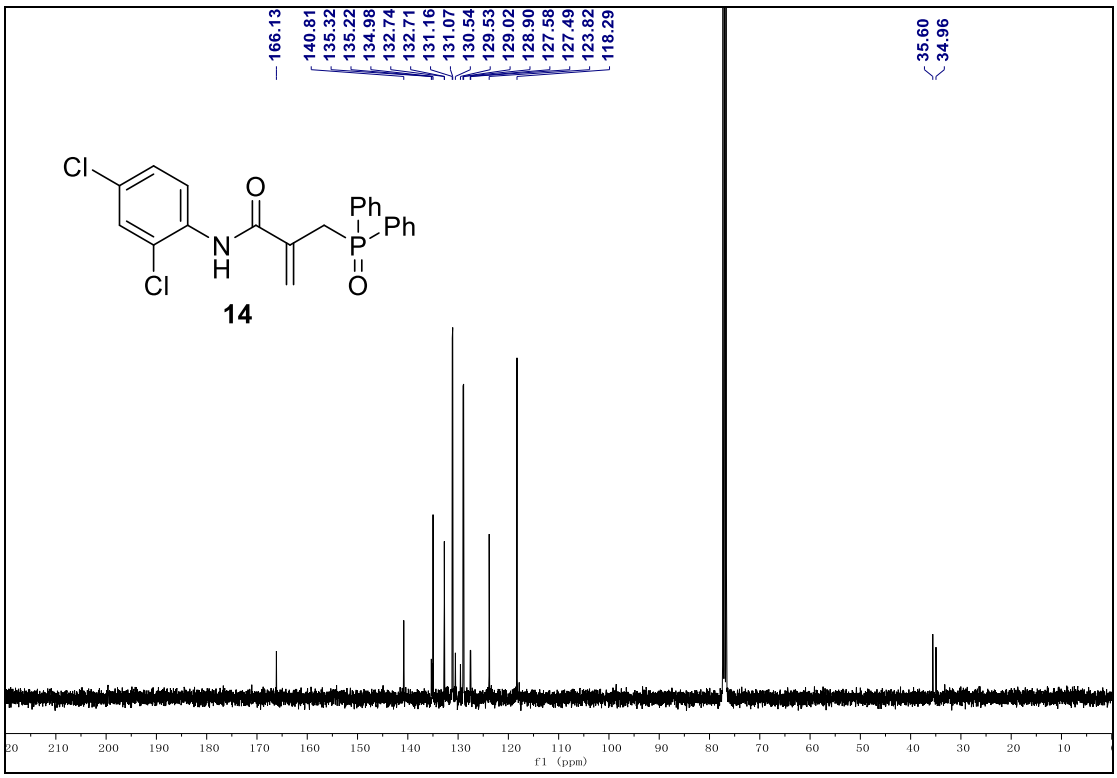


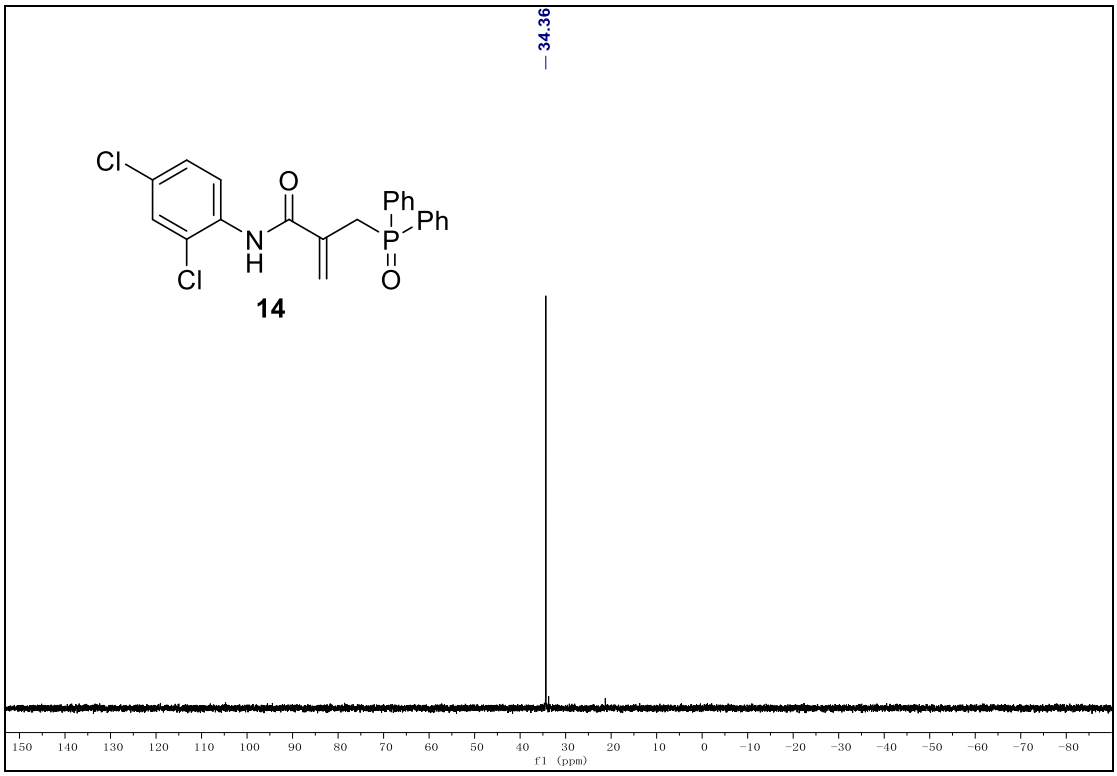



32.39
O
N
H
Ph
Ph
P
O
13
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

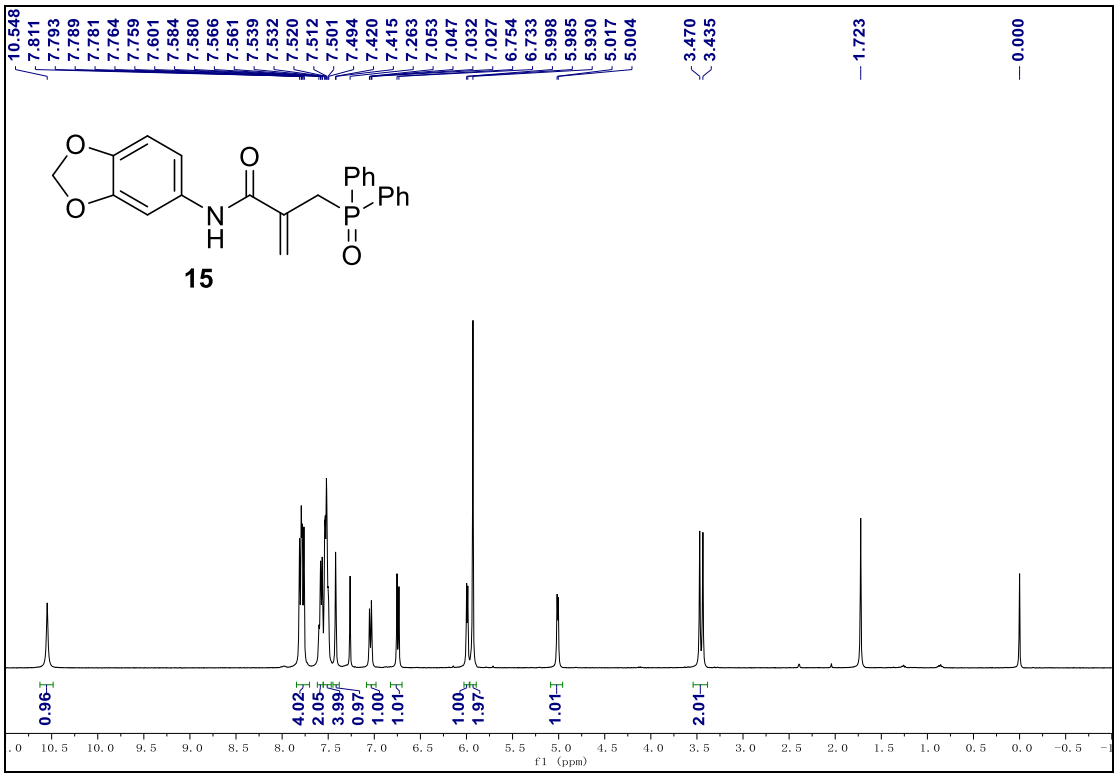
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 14.

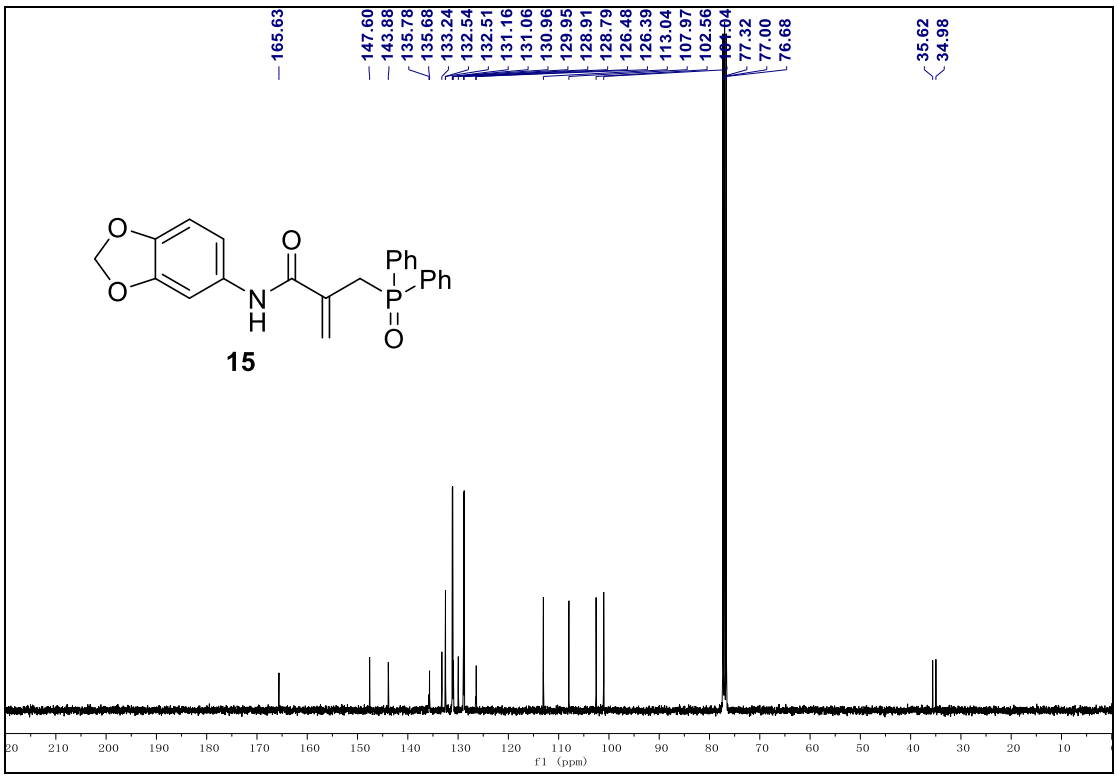


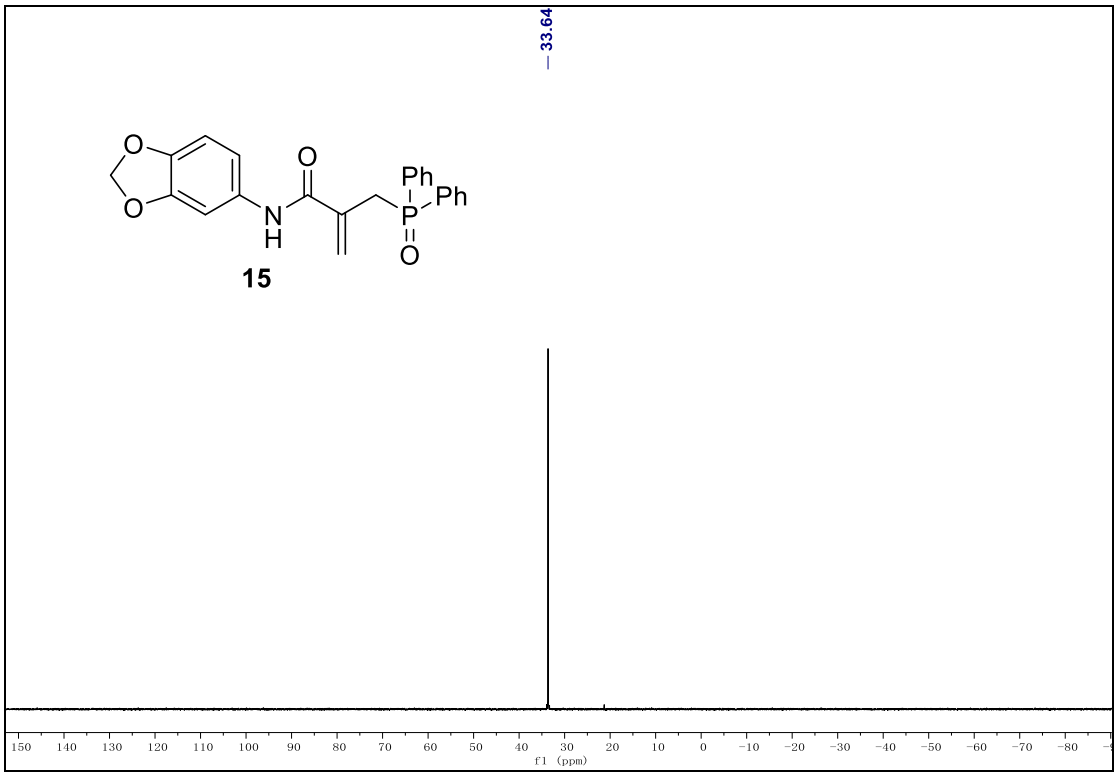



34.36
Cl
O
Ph
Ph
N
H
P
O
Cl
14
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

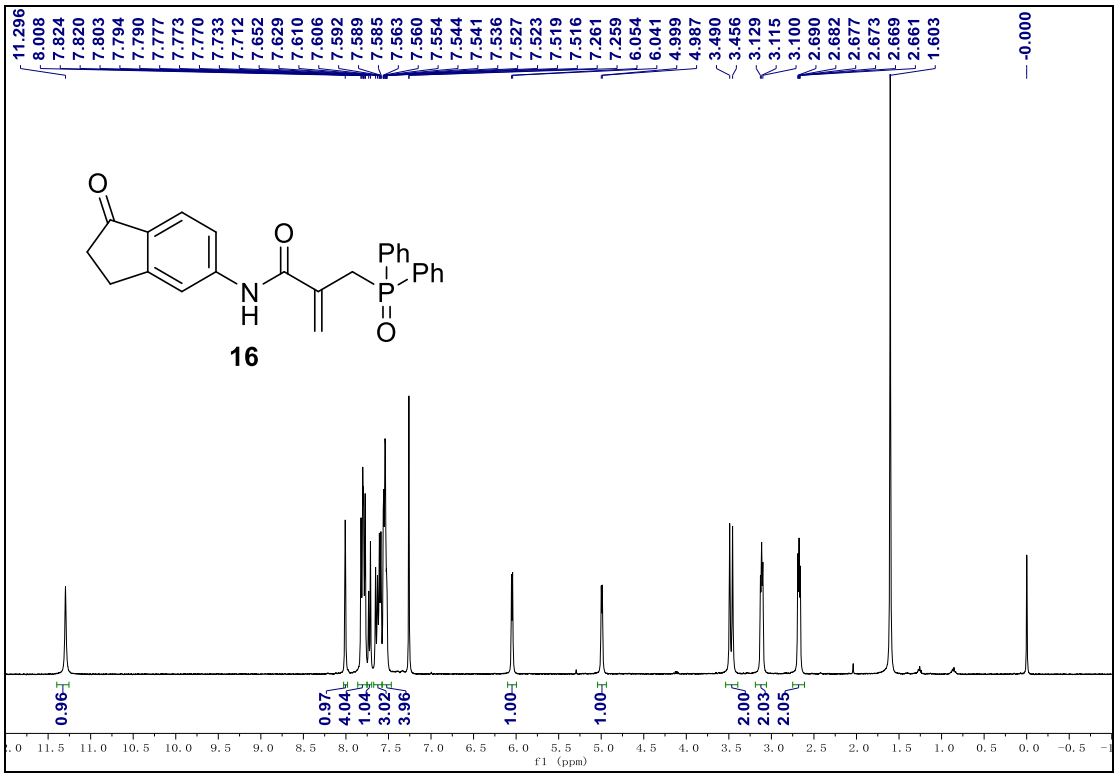
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 15.

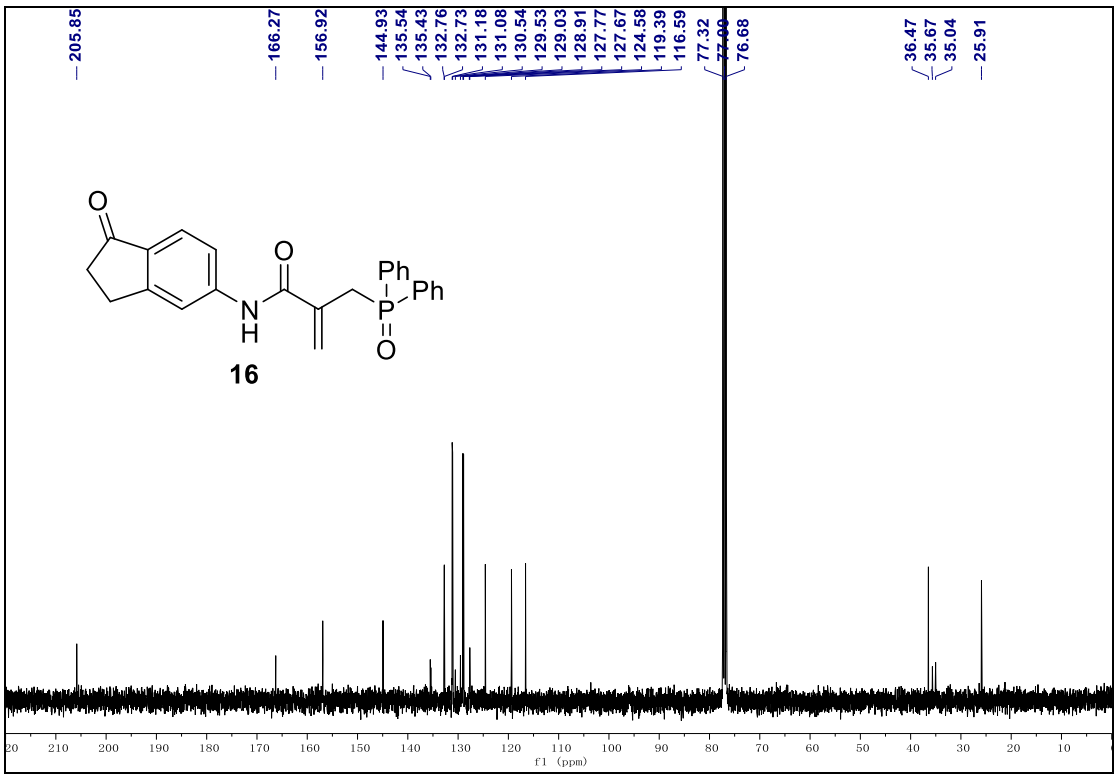


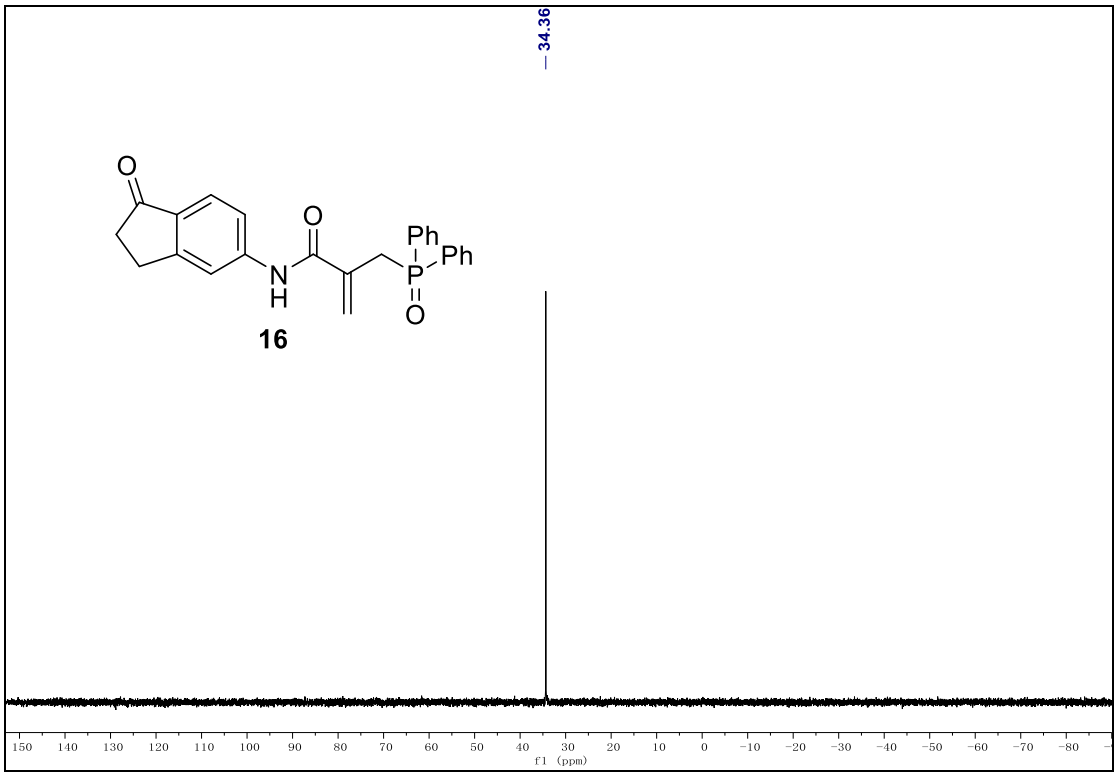



33.64
O
O
N
H
O
Ph
Ph
P
O
15
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

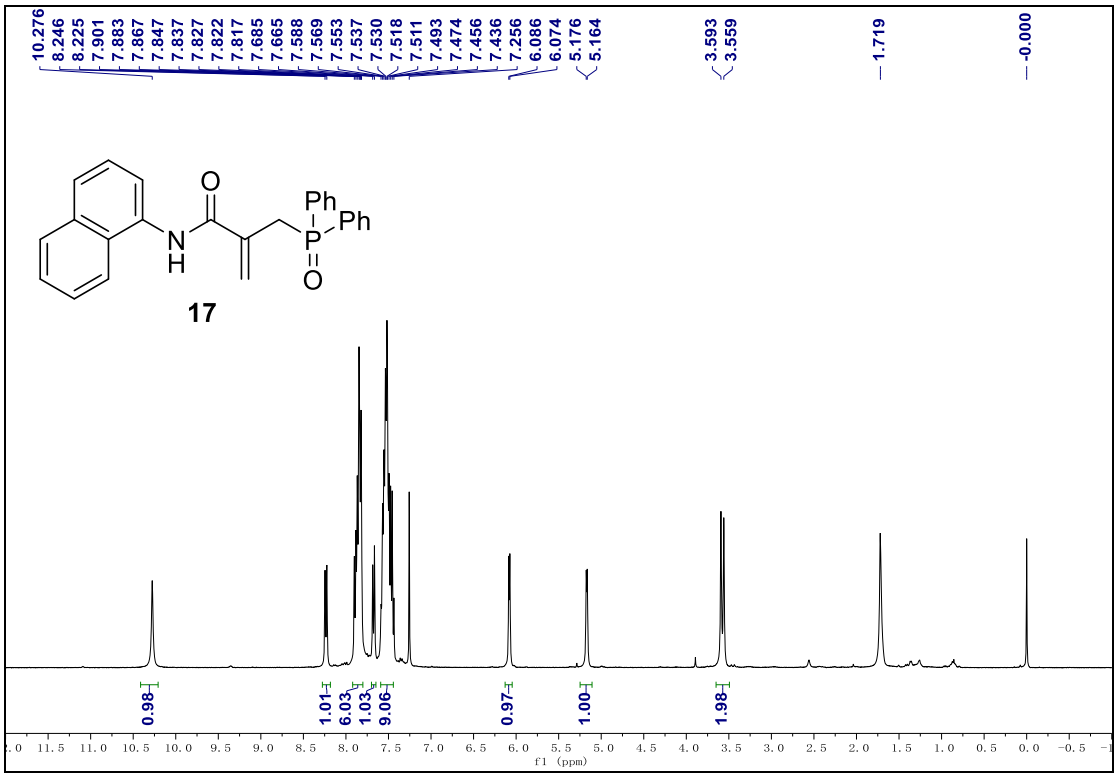
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 16.

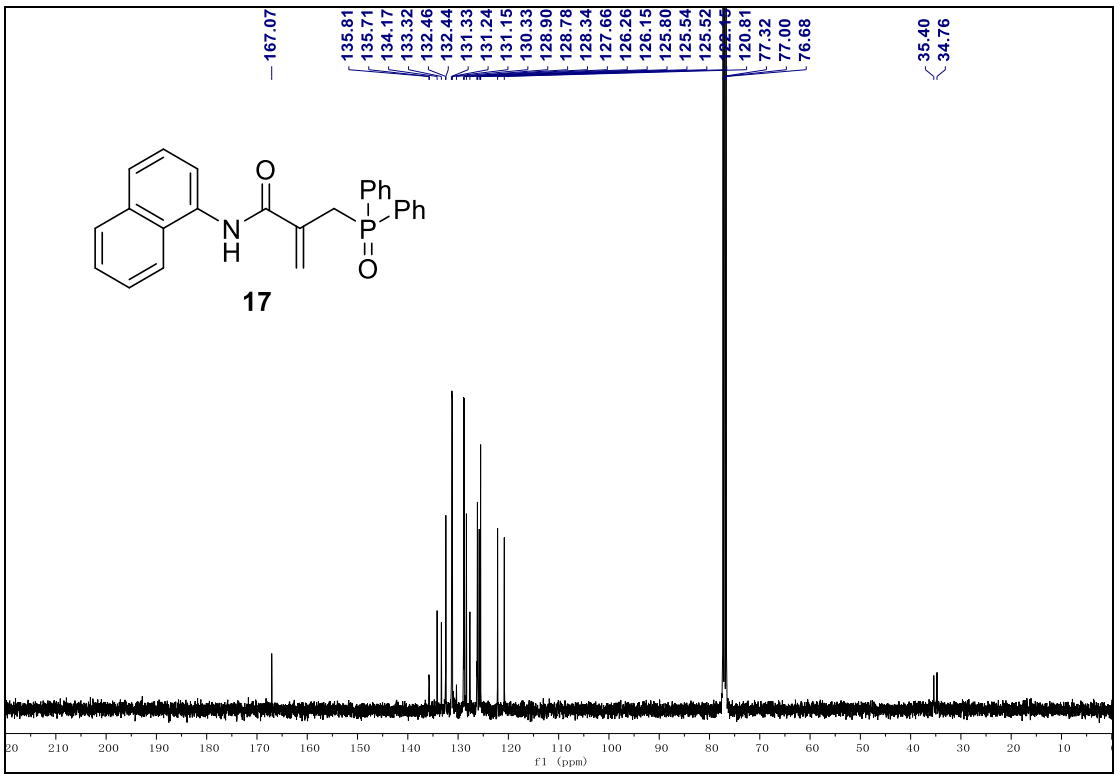


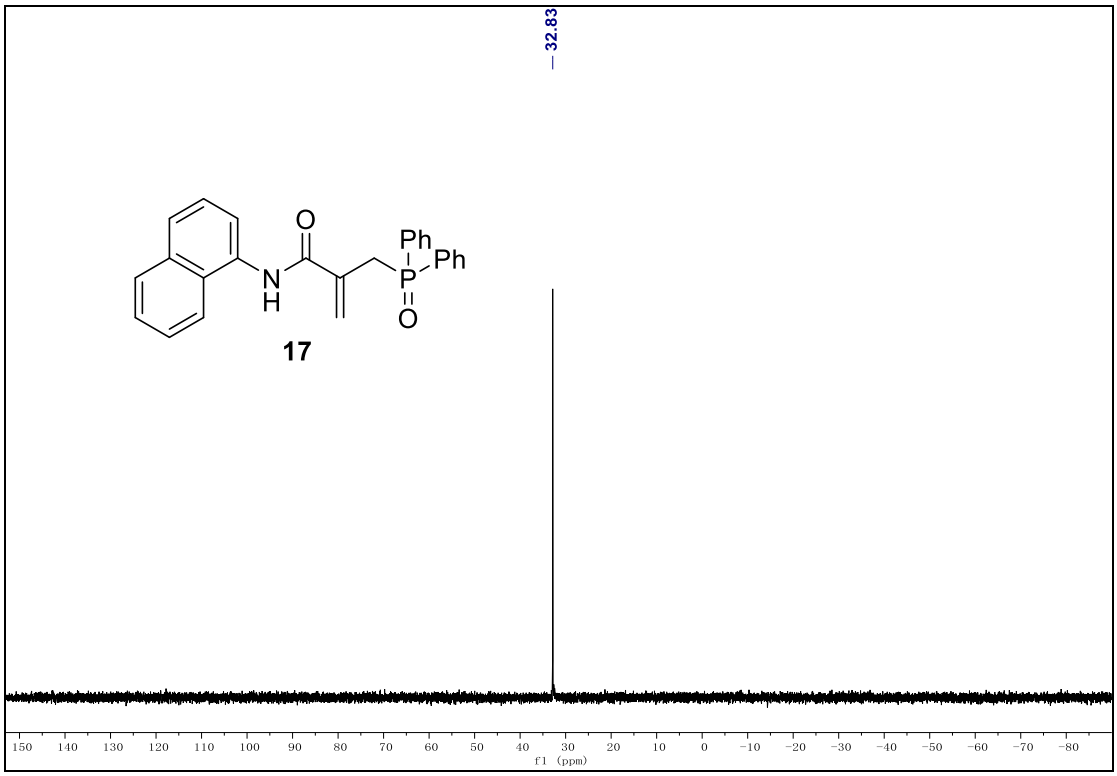



34.36
O
O
N
H
Ph
Ph
P
O
16
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

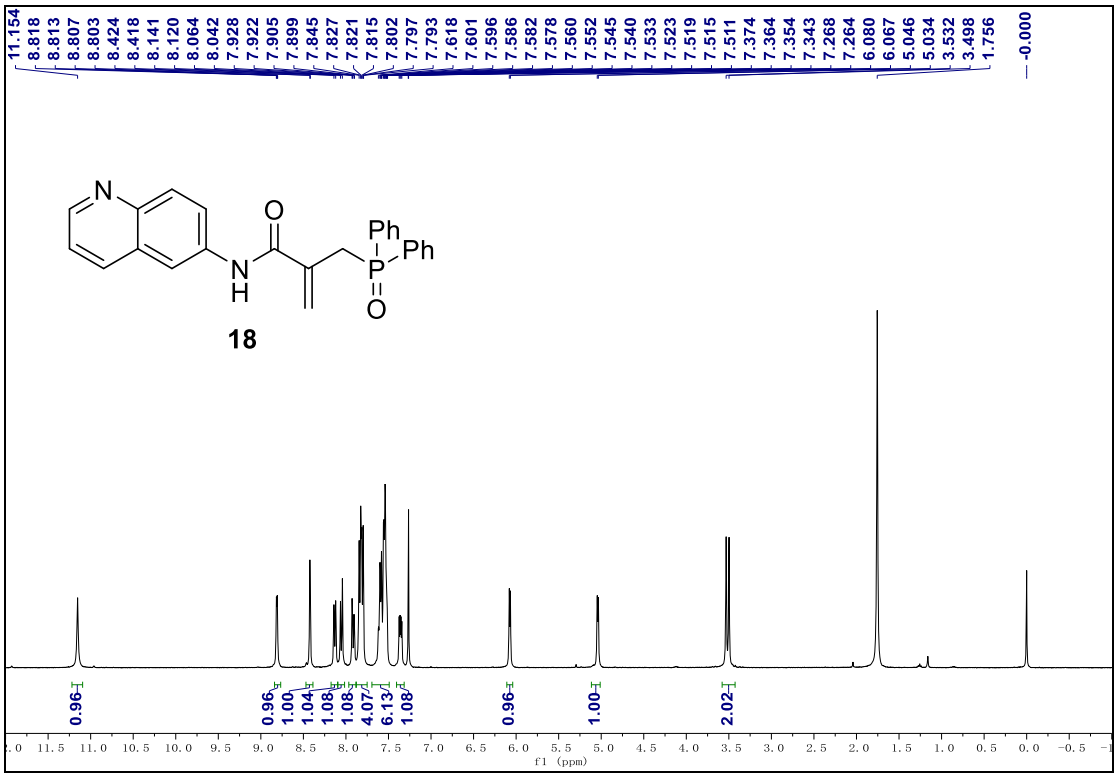
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 17.

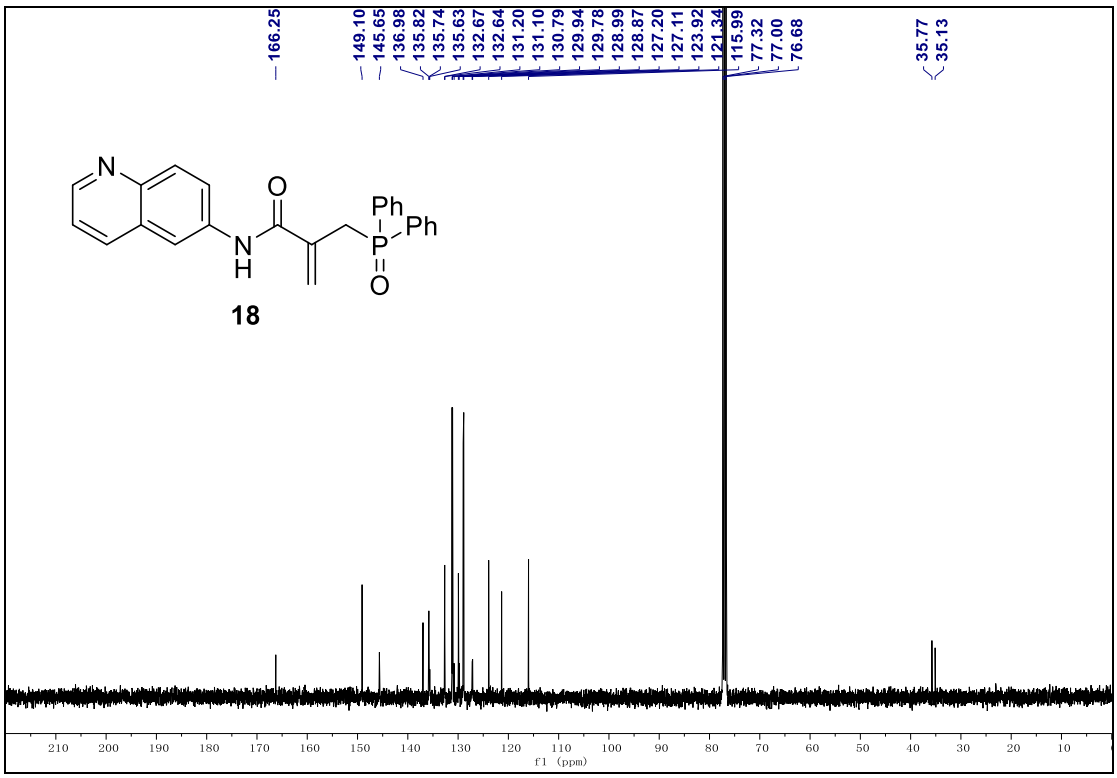


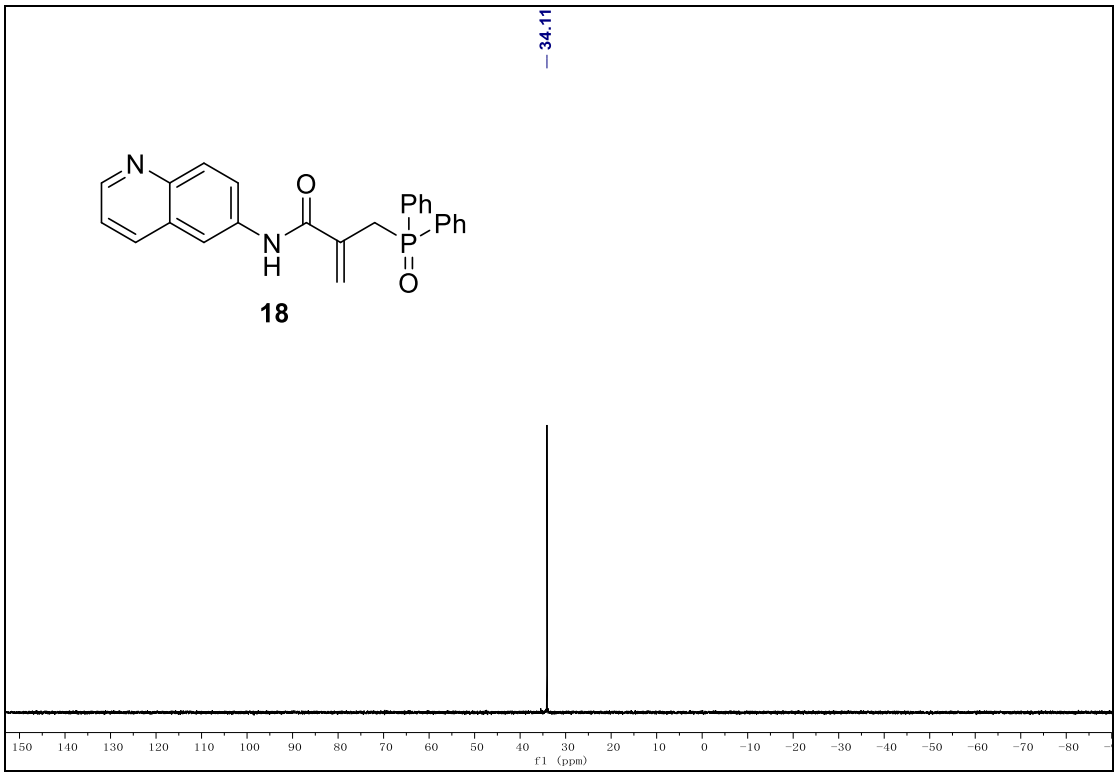



32.83
O
N
H
Ph
Ph
P
O
17
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

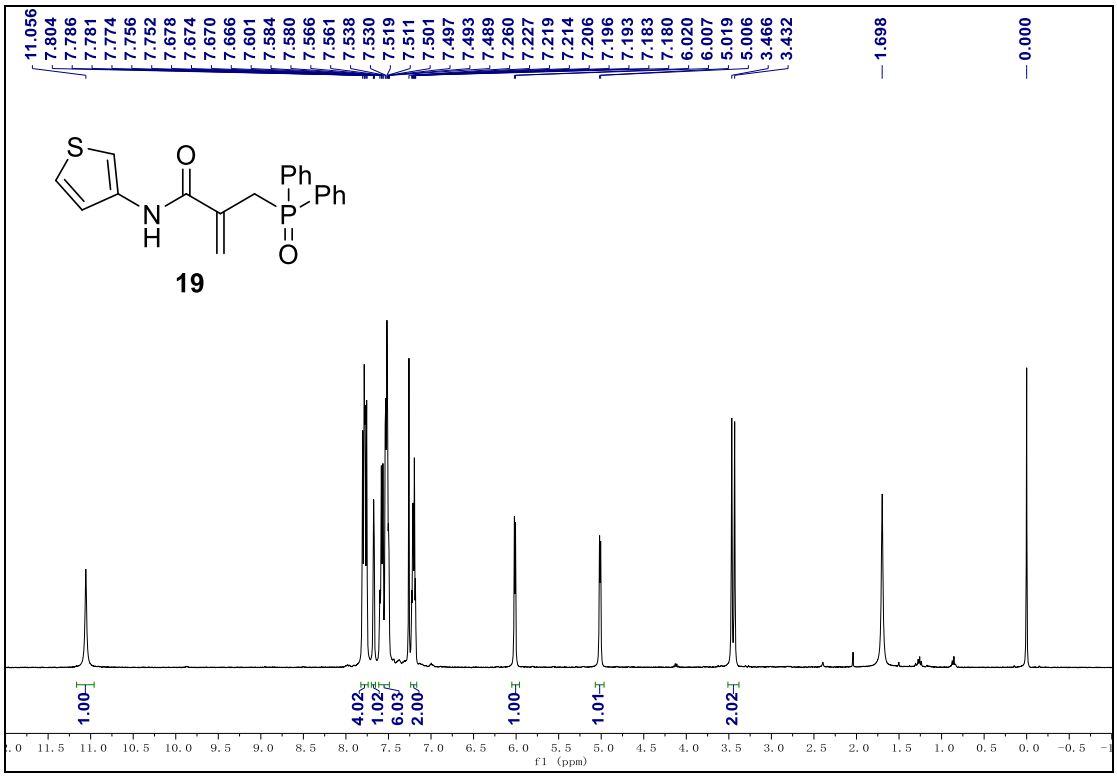
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 18.

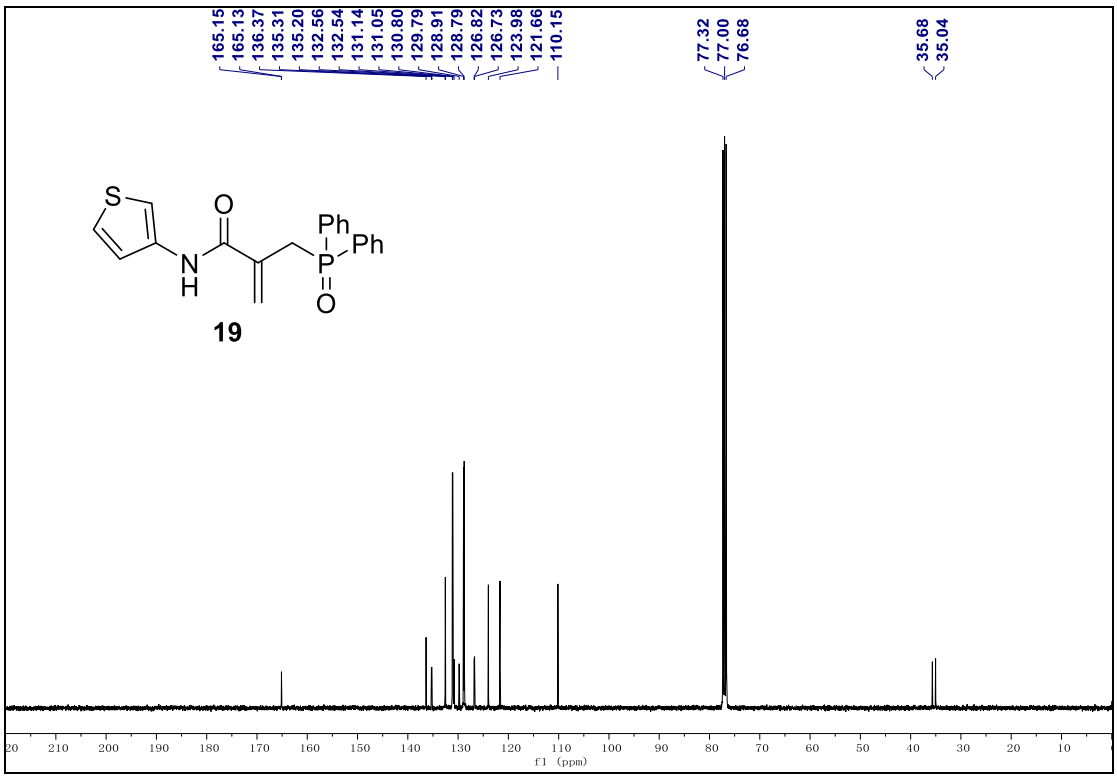


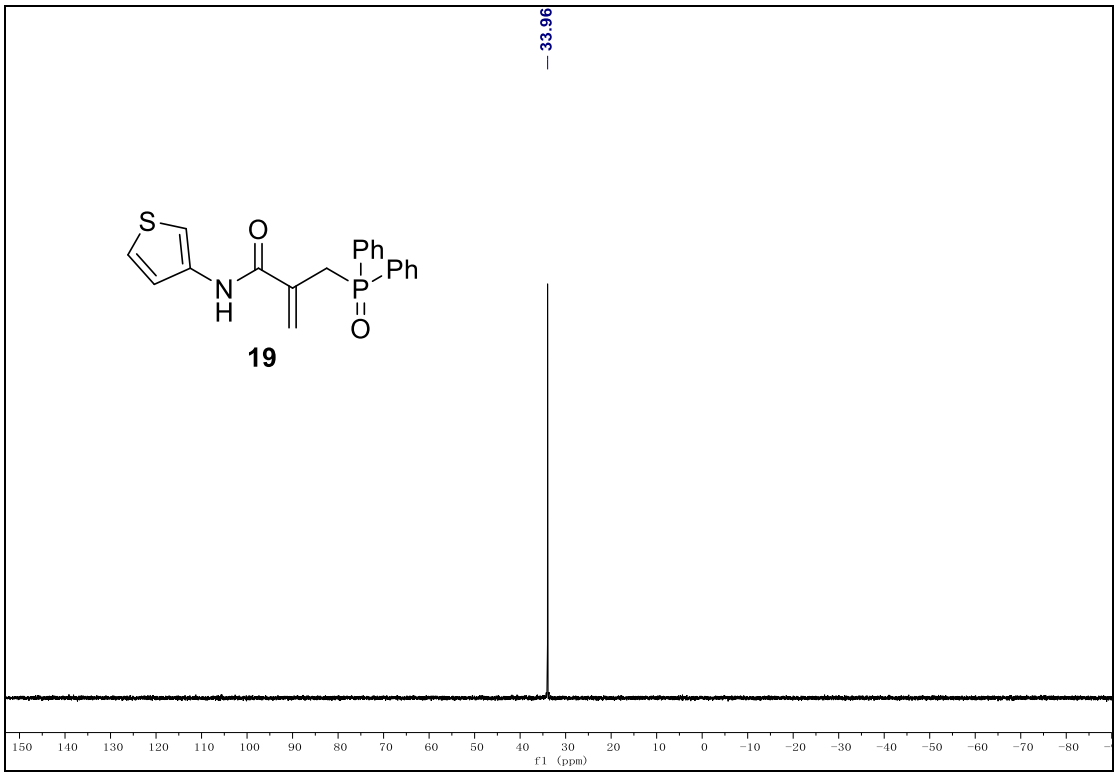



34.11
N
O
Ph
Ph
N
H
P
O
18
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

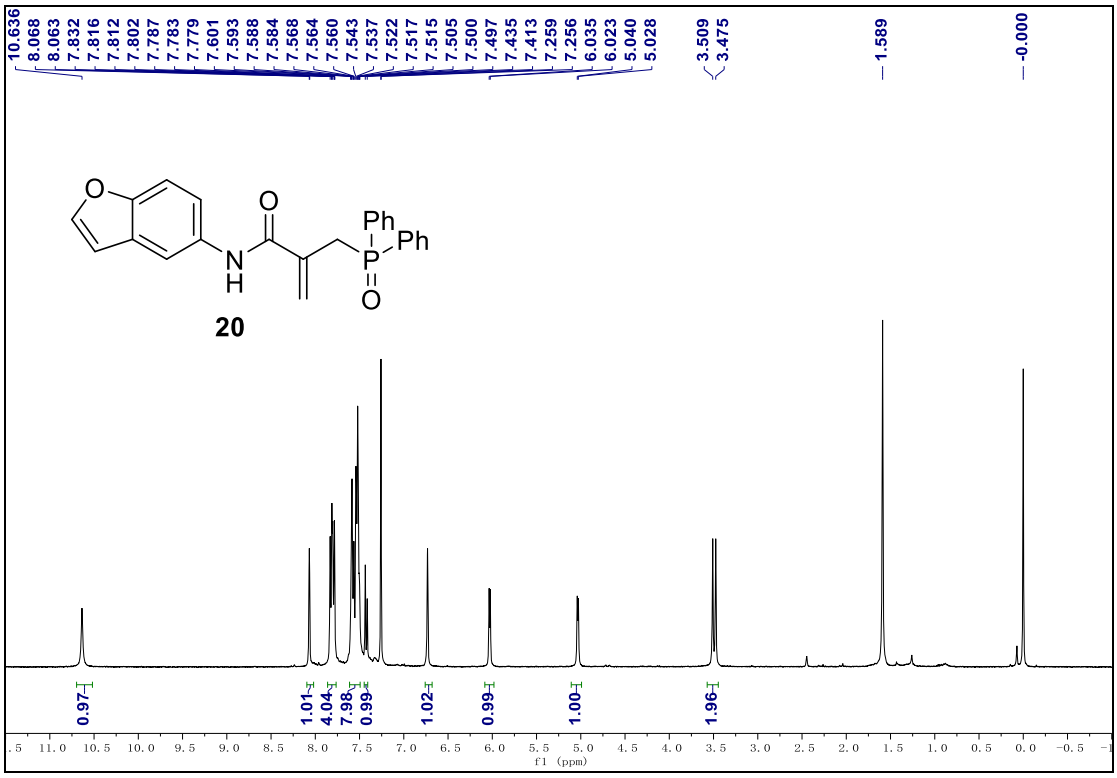
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 19.

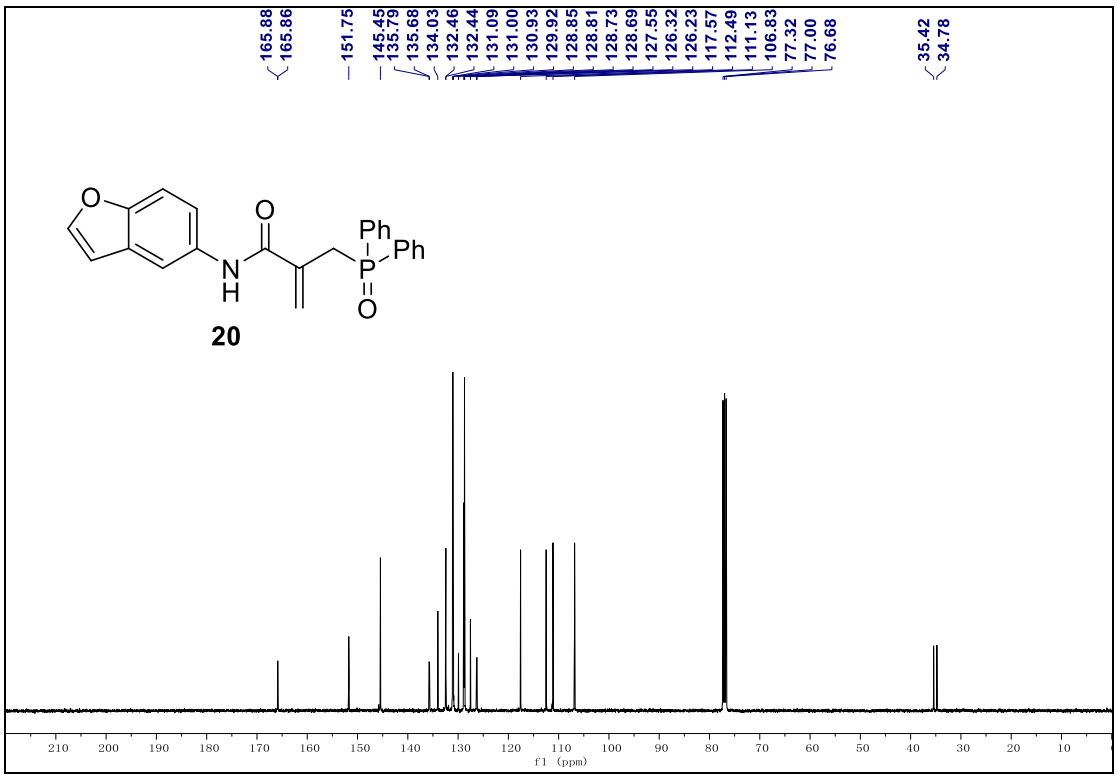


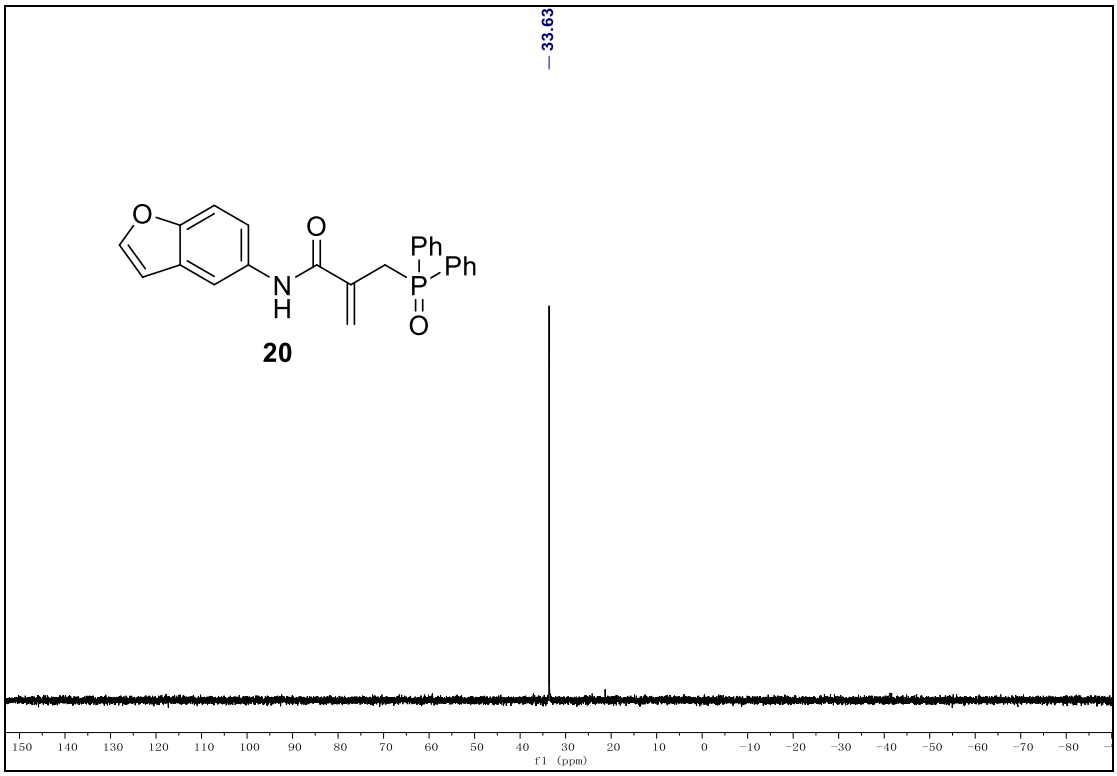



33.96
S
O
Ph
Ph
N
H
P
O
19
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

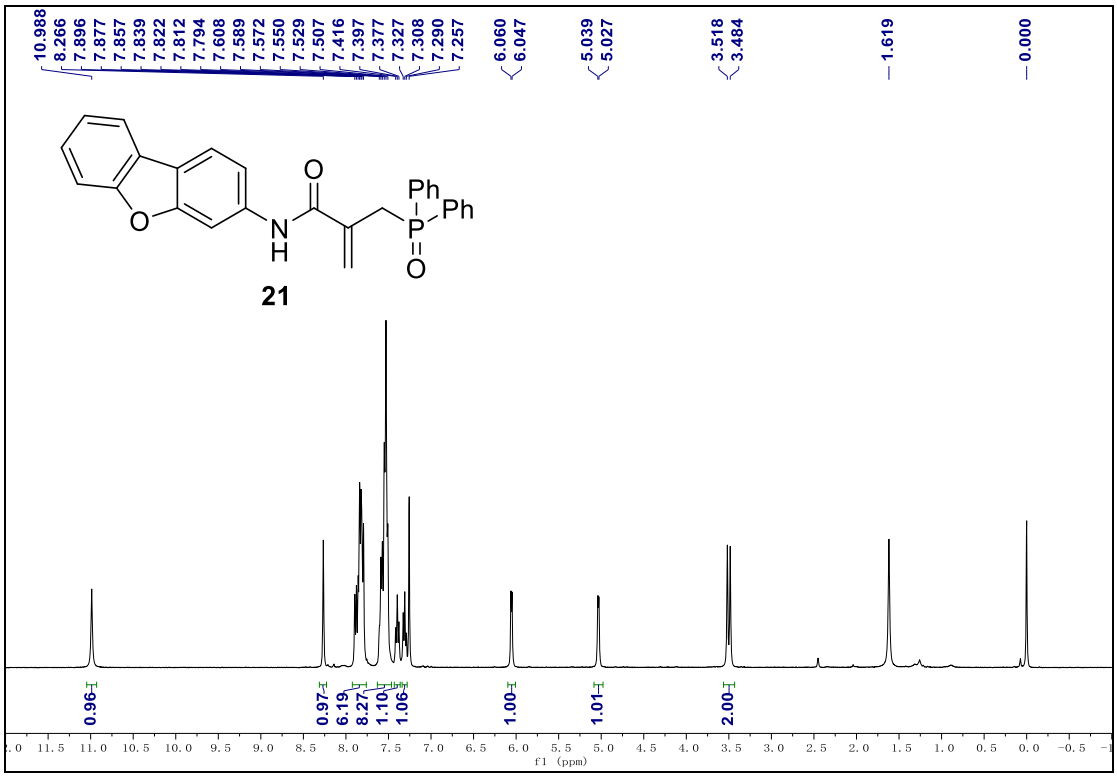
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 20.

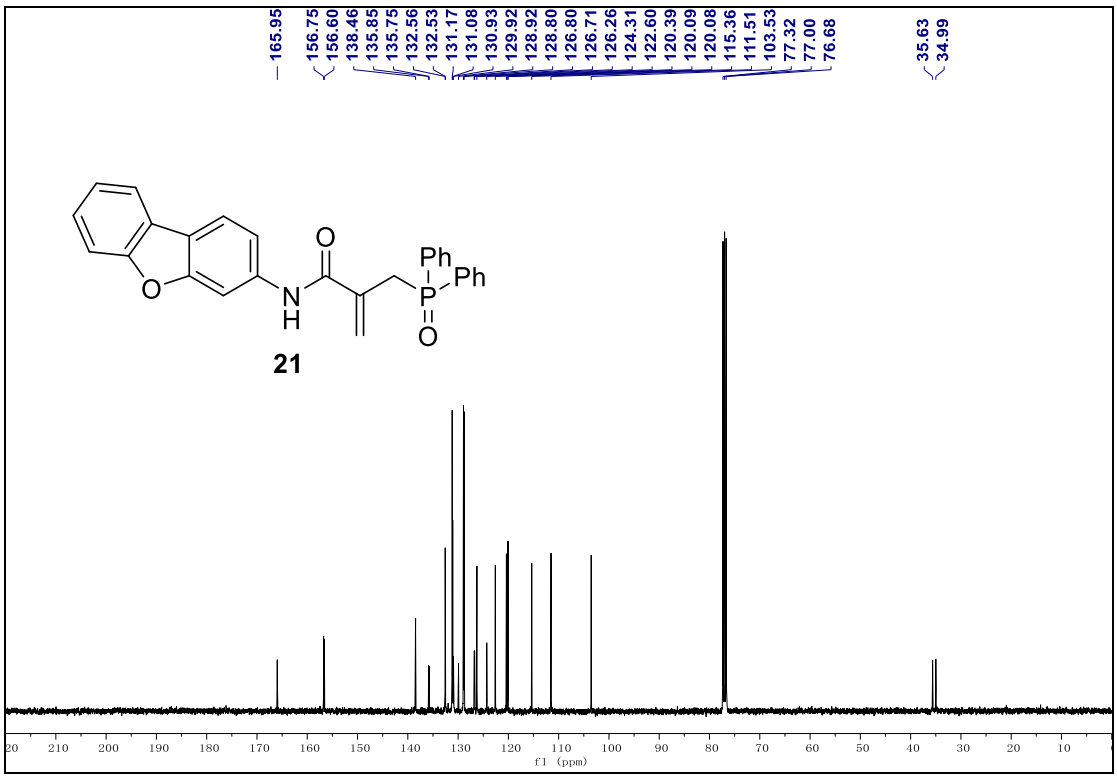


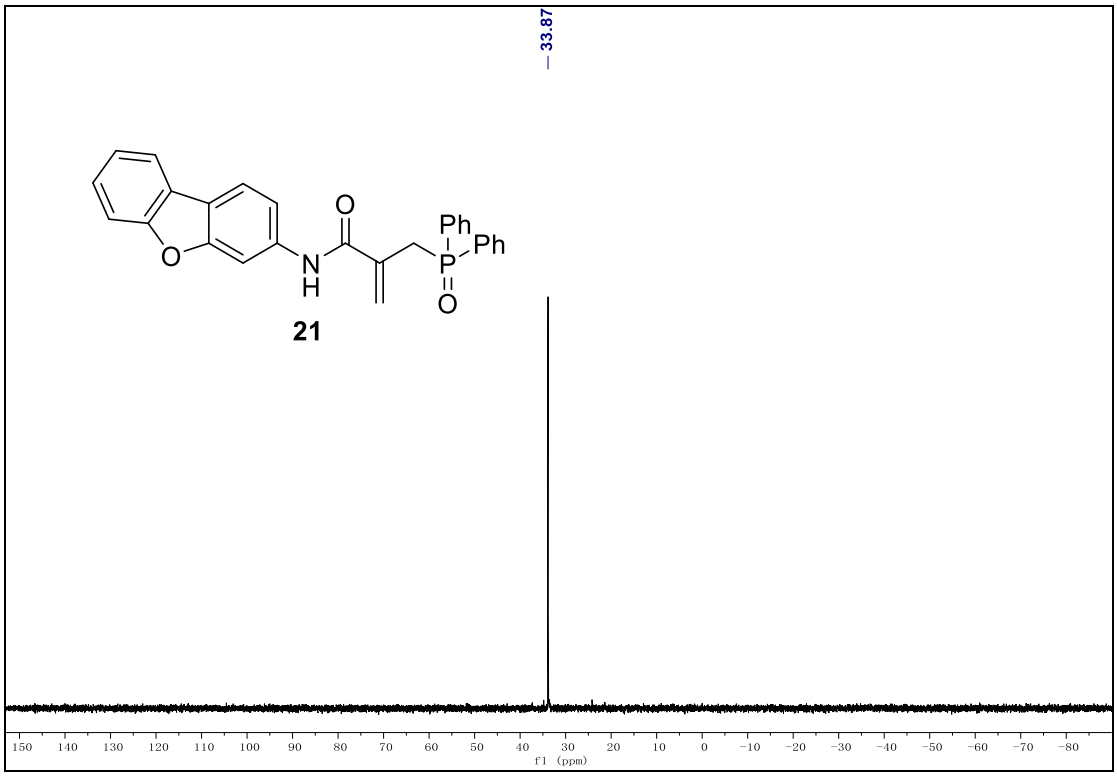



33.63
O
O
N
H
Ph
Ph
P
O
20
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

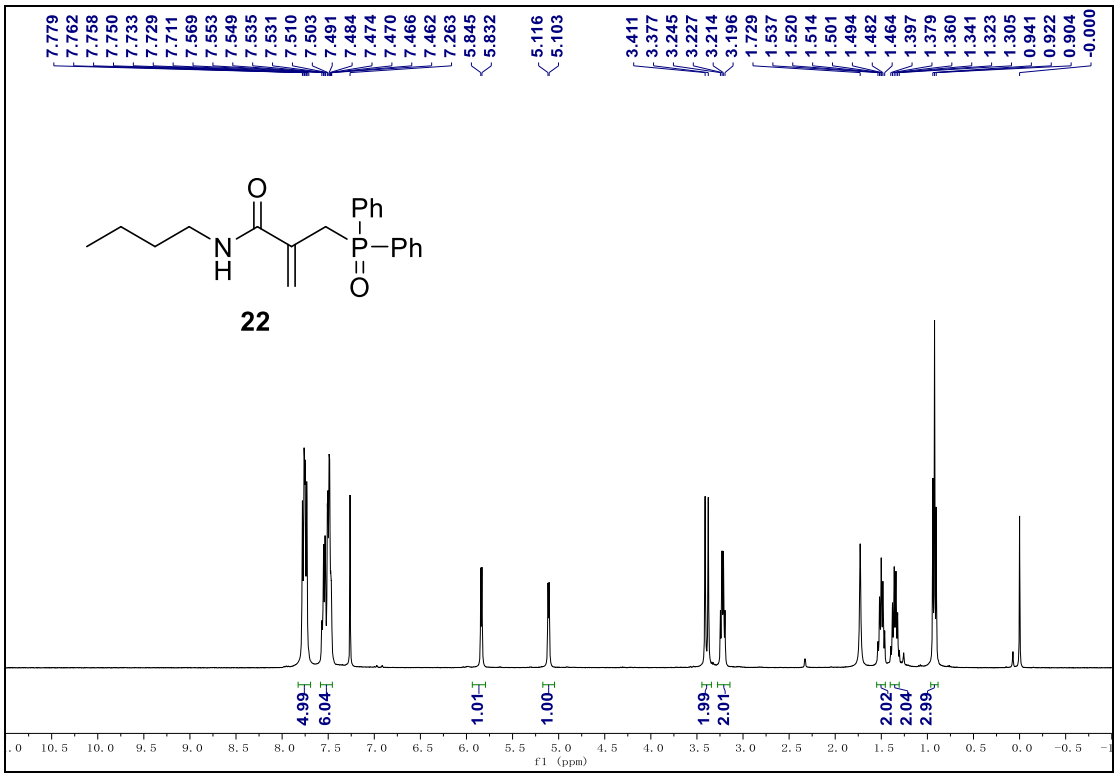
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 21.

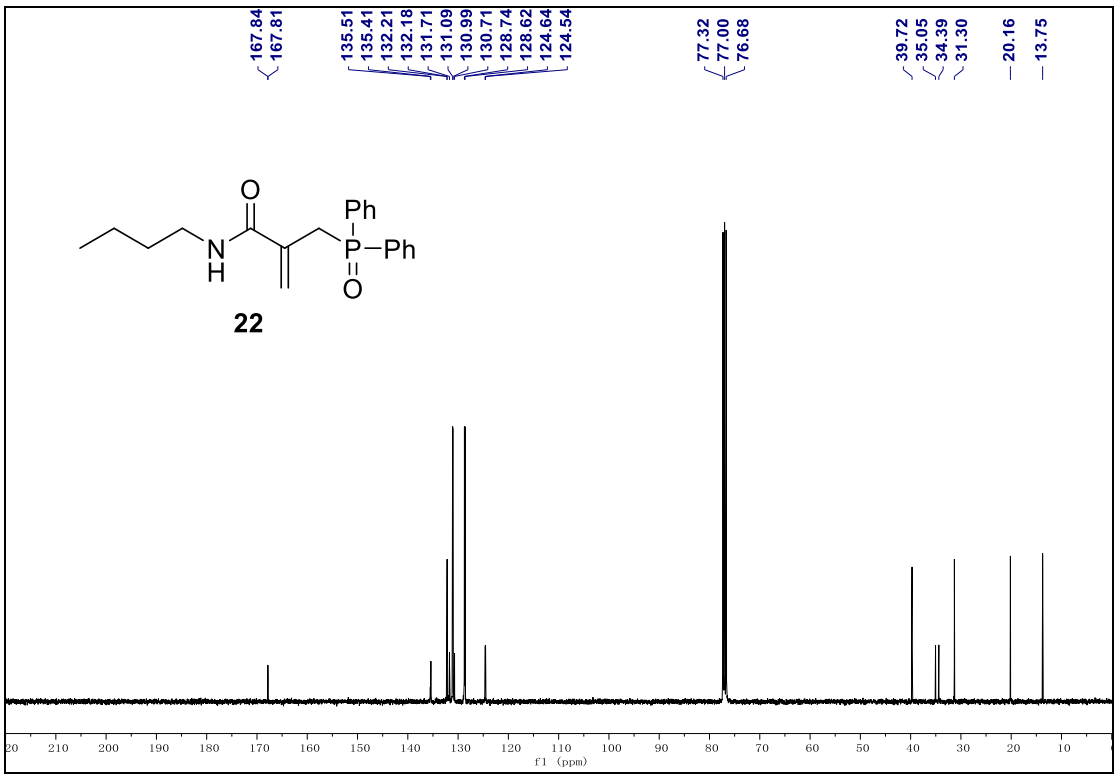


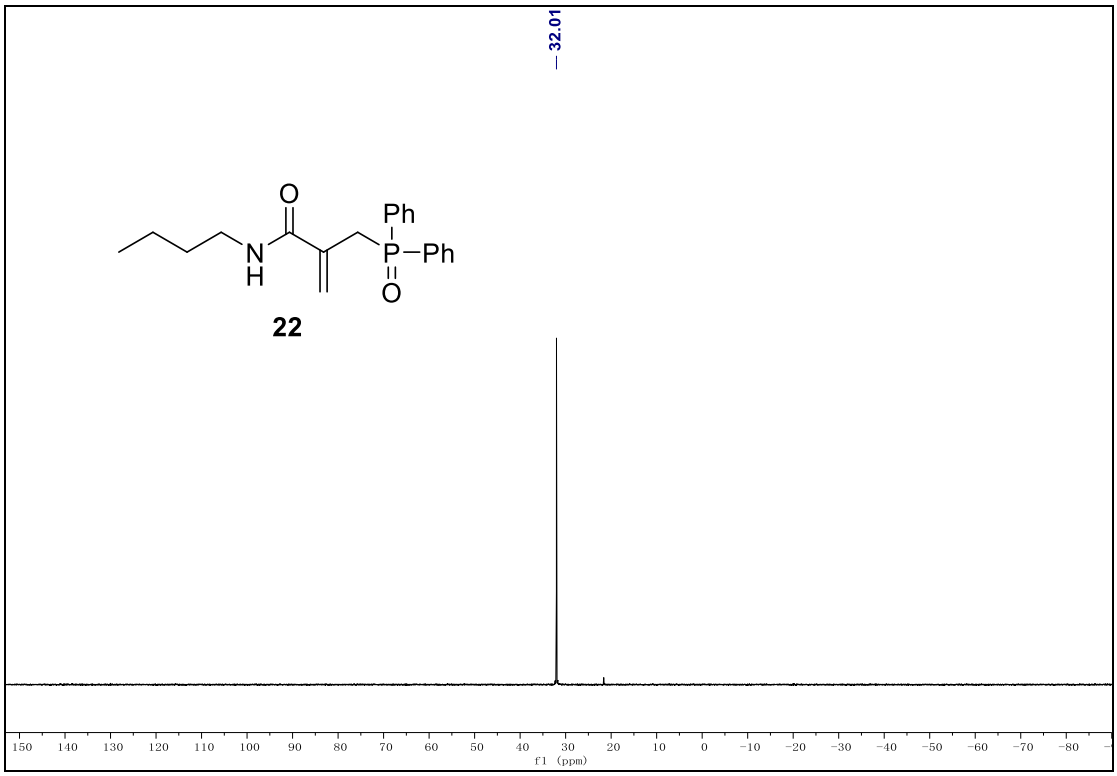



33.87
O
N
H
O
Ph
Ph
P
O
21
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

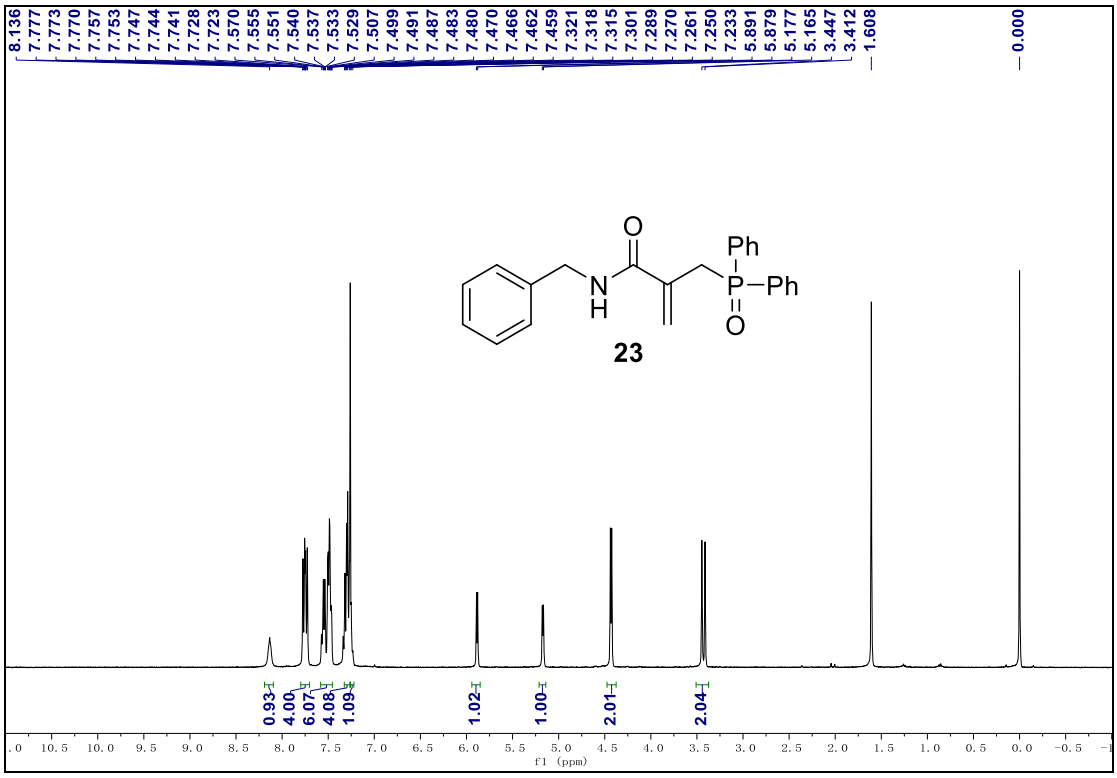
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 22.

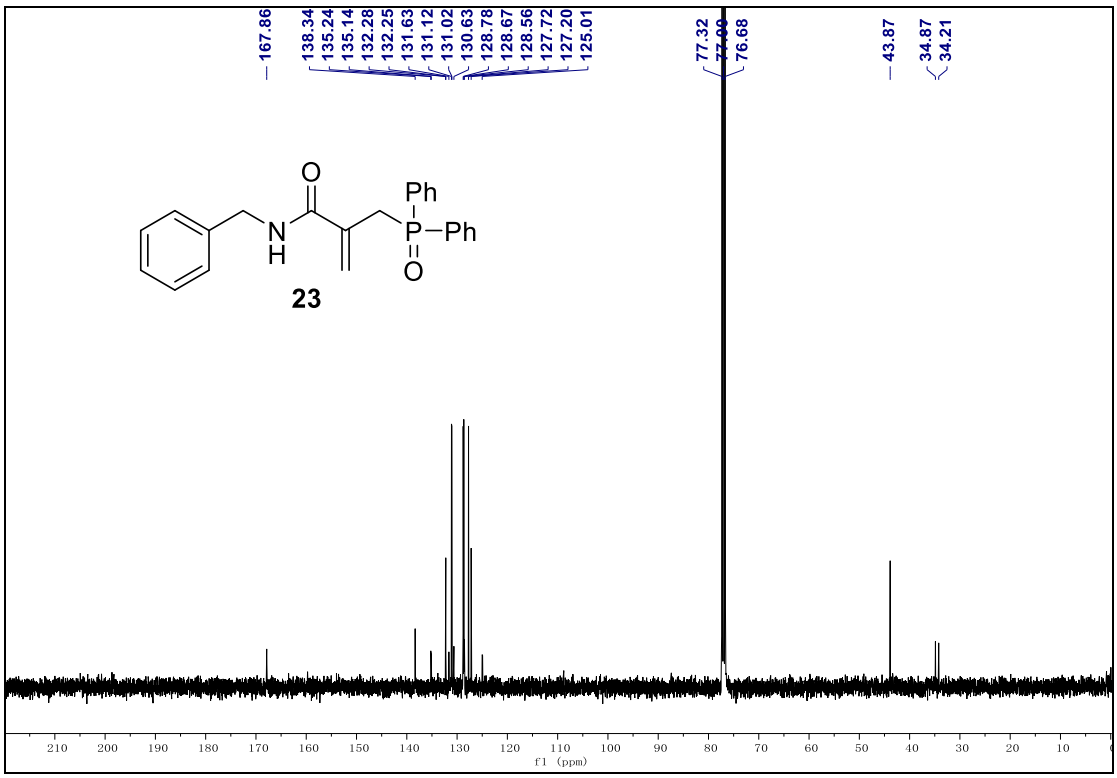


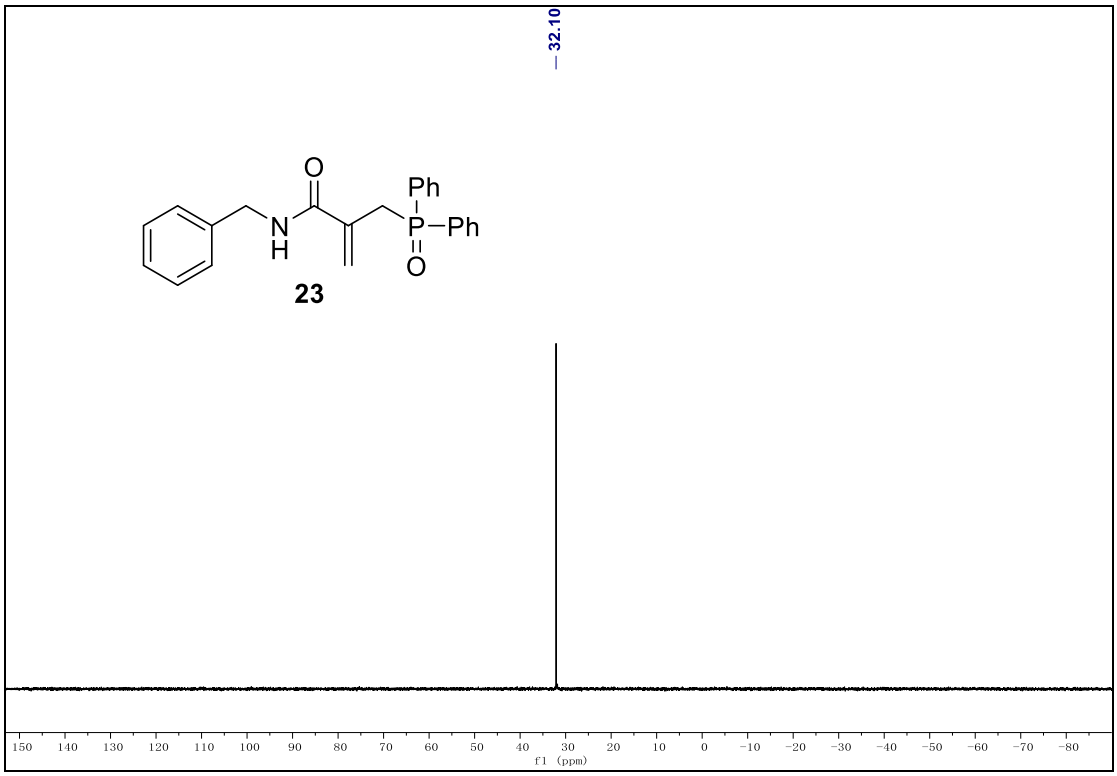



32.01
O
Ph
N
H
P
Ph
O
22
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

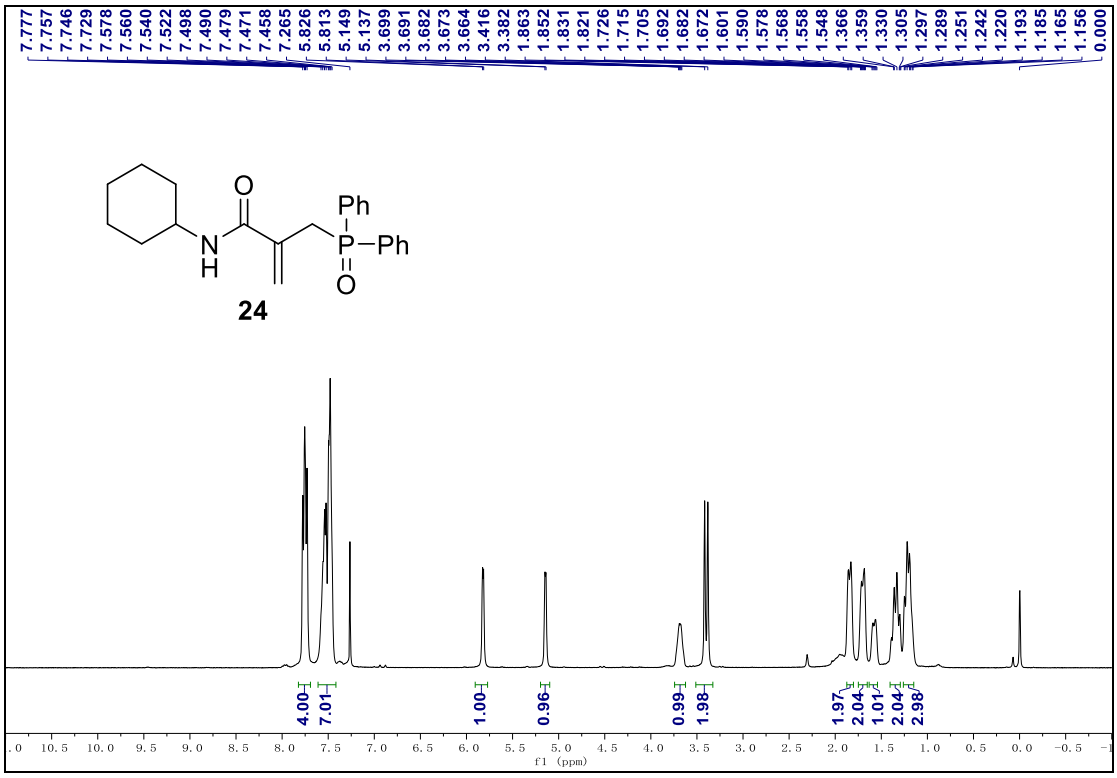
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 23.

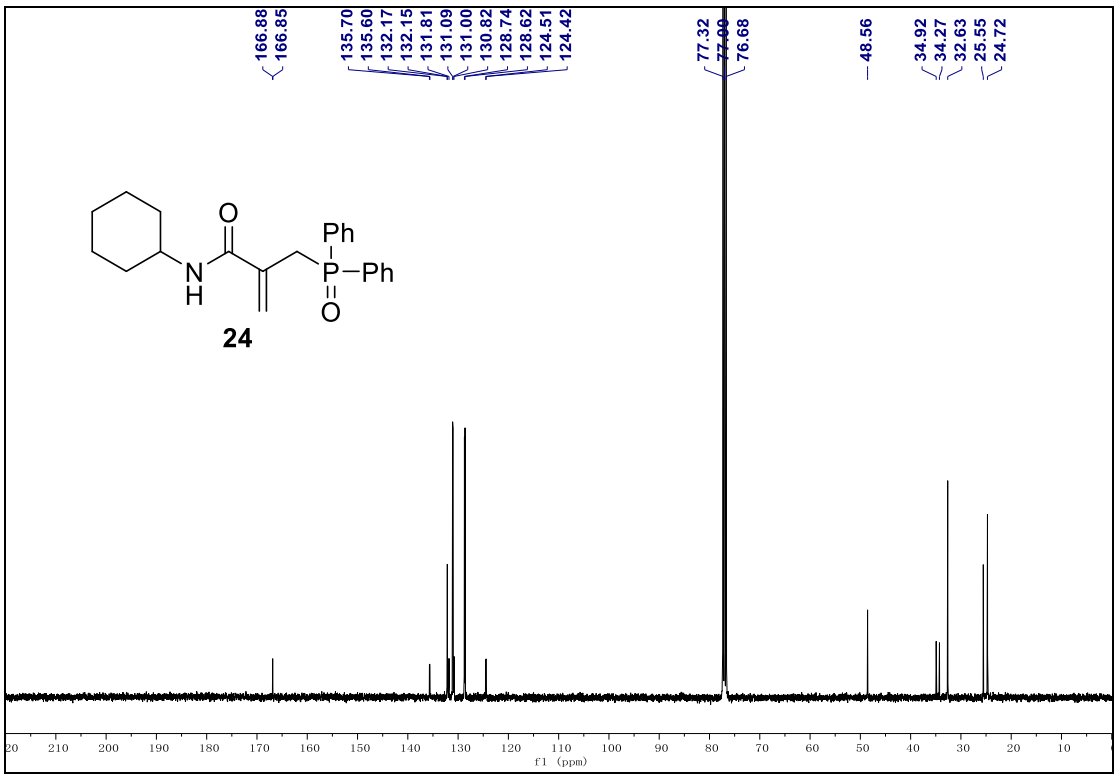


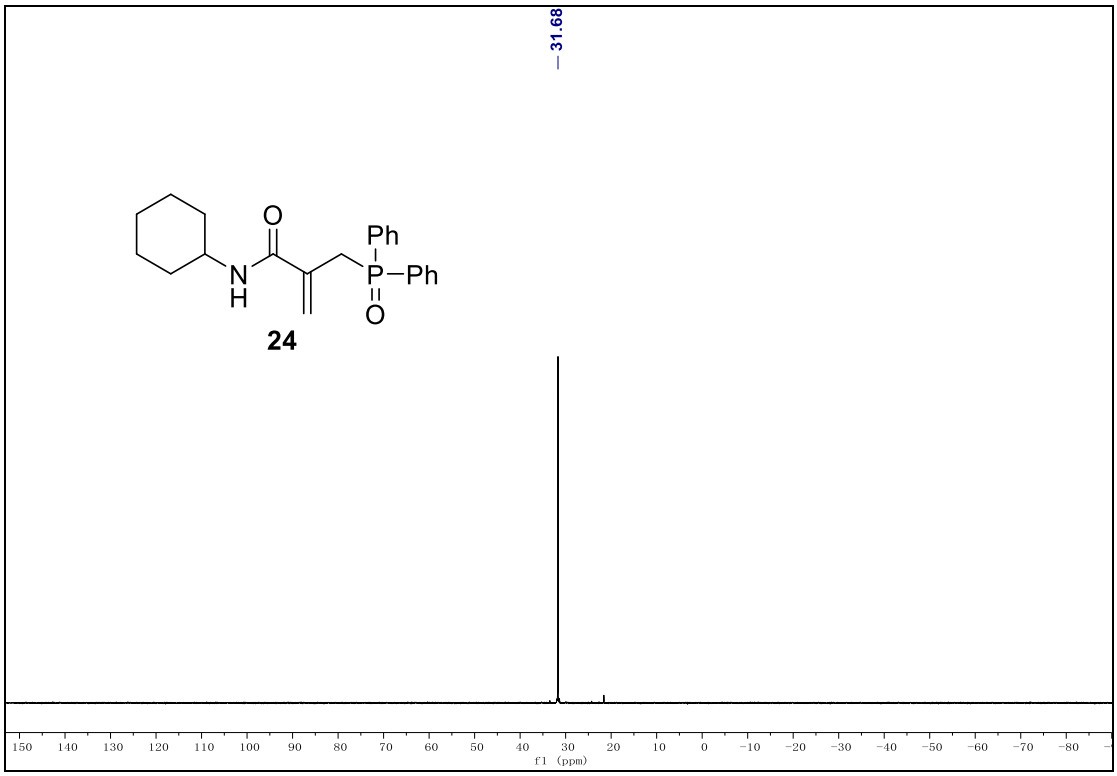



32.10
O
Ph
N
H
P
Ph
O
23
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

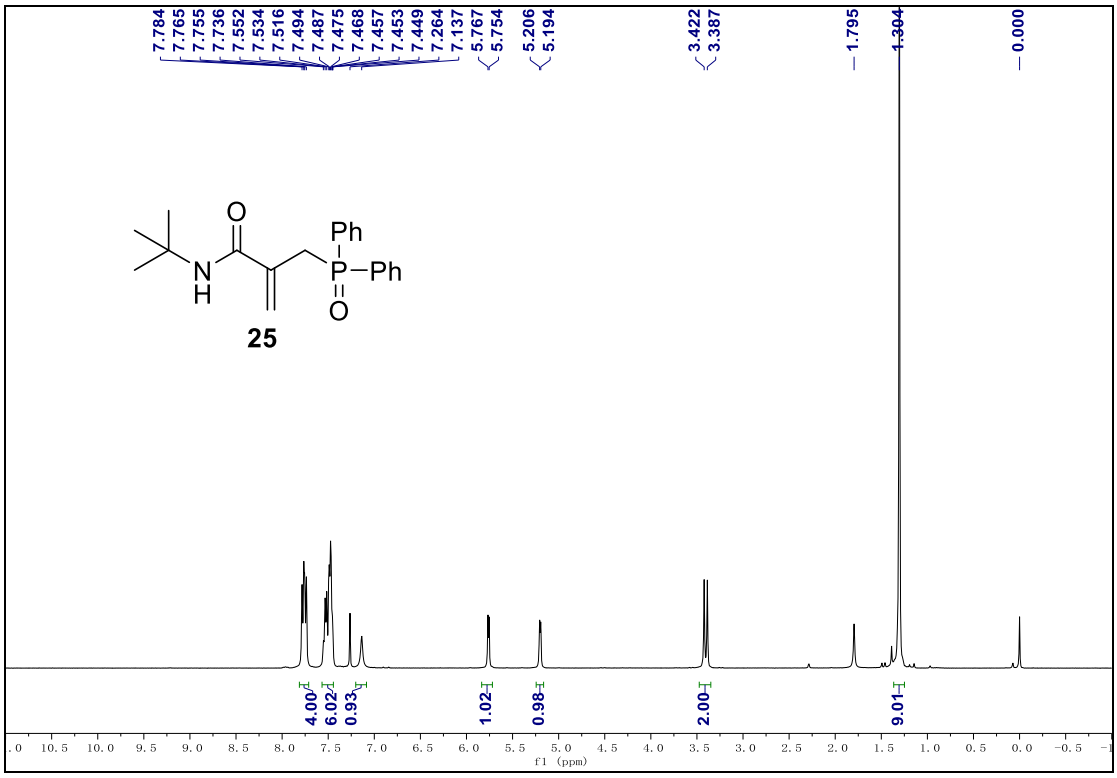
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 24.

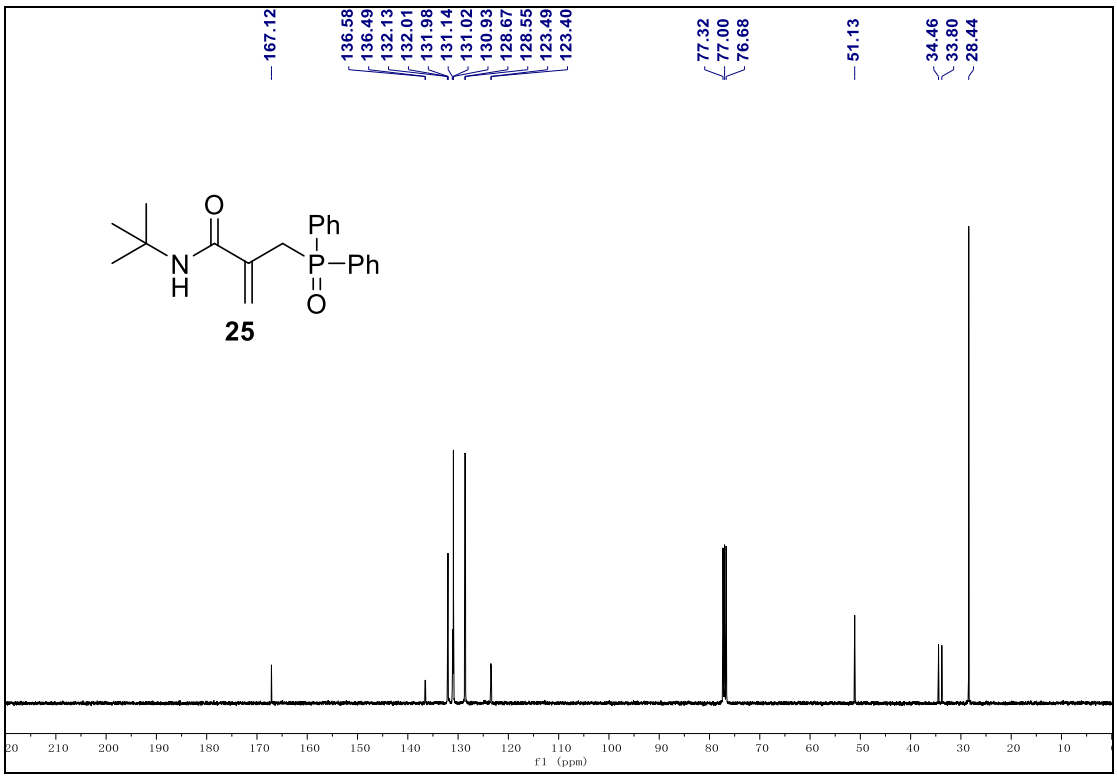


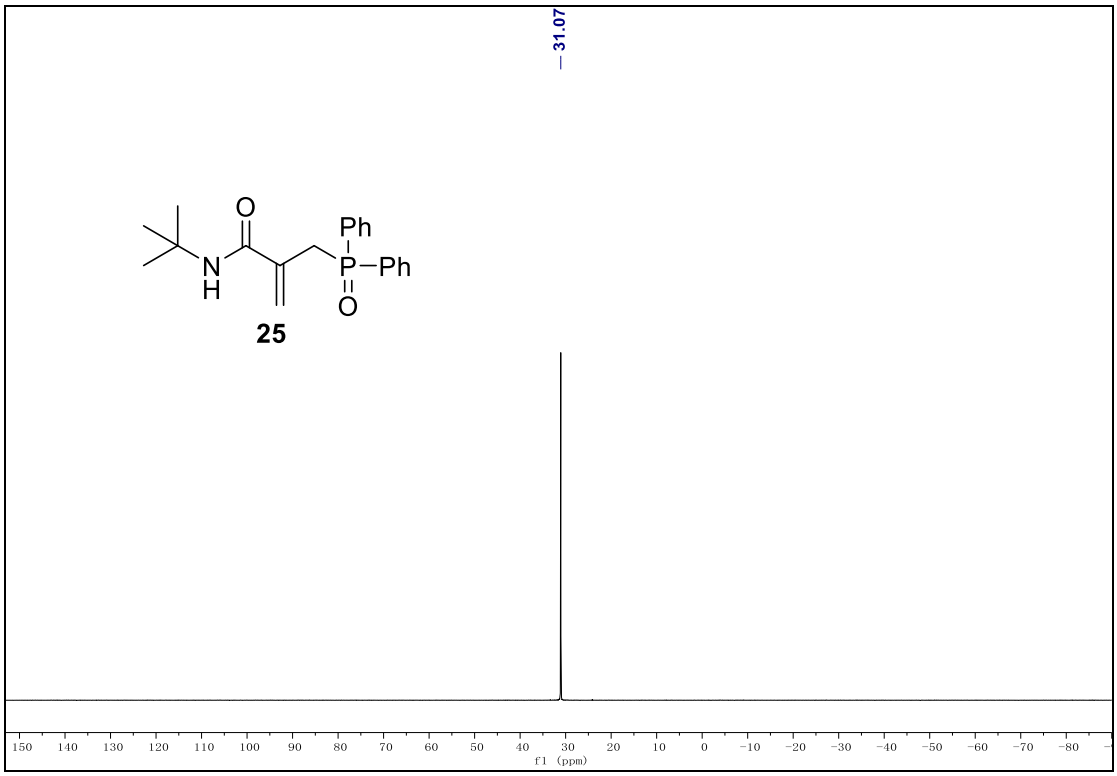



31.68
O
Ph
N
H
P
Ph
O
24
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

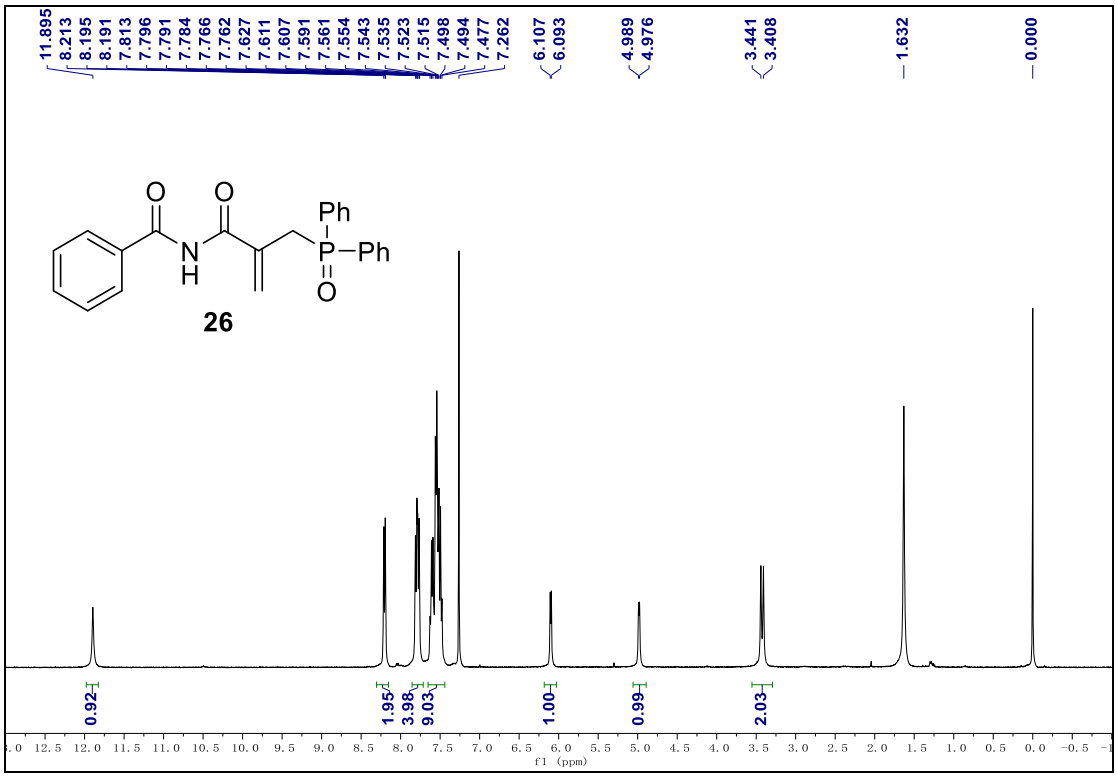
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 25.

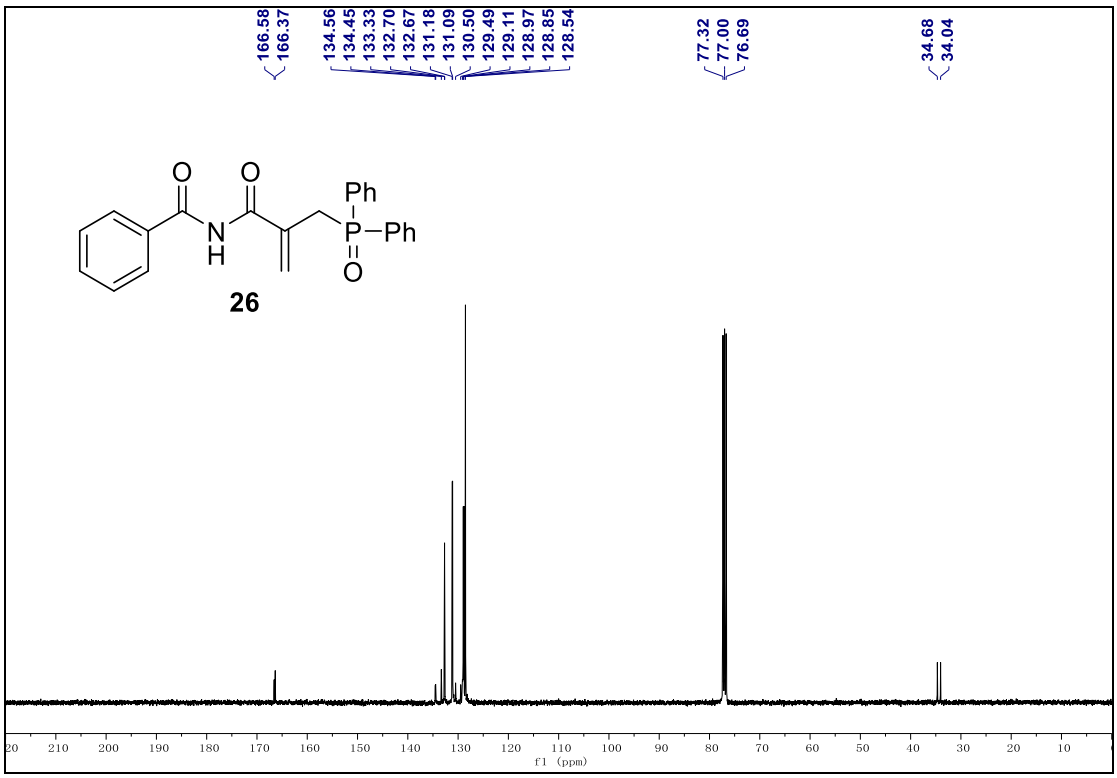


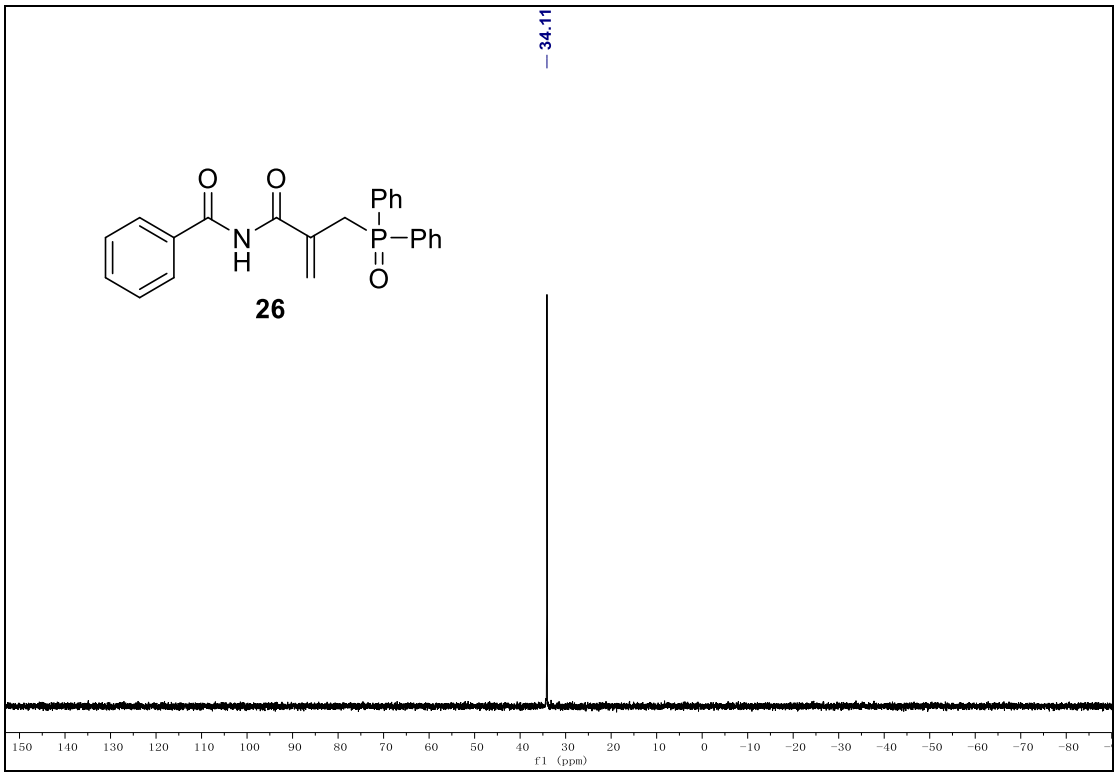



31.07
O
N
H
Ph
P
Ph
O
25
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

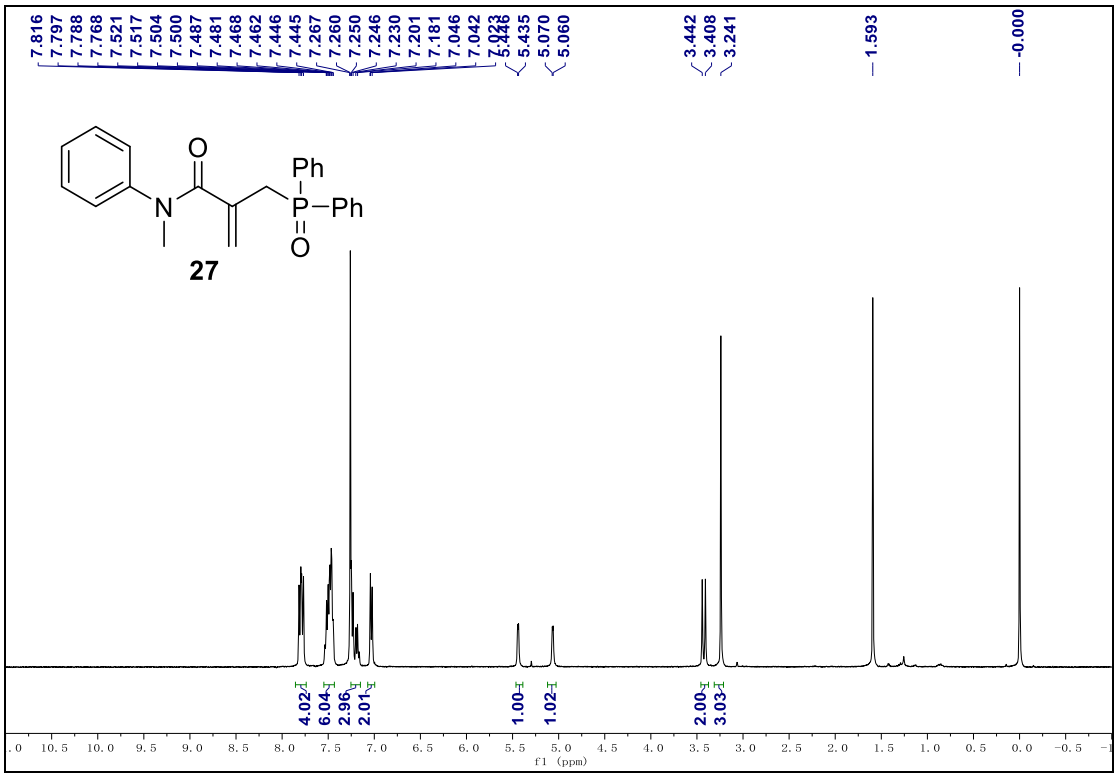
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 26.

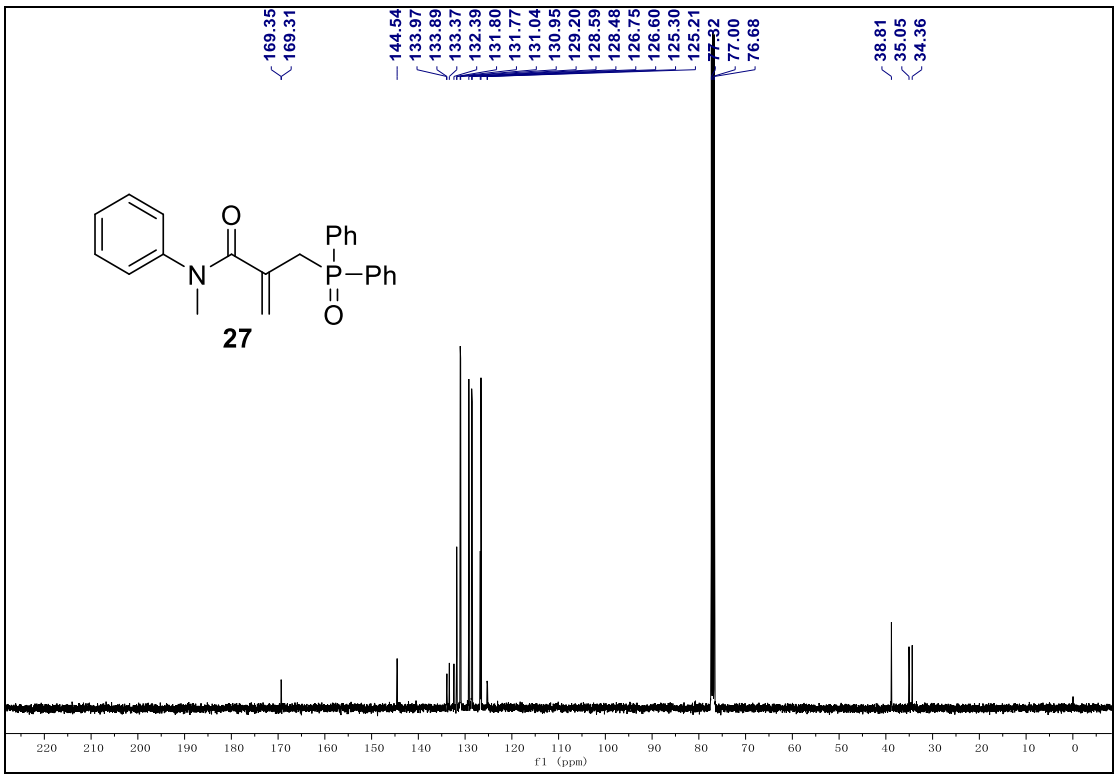


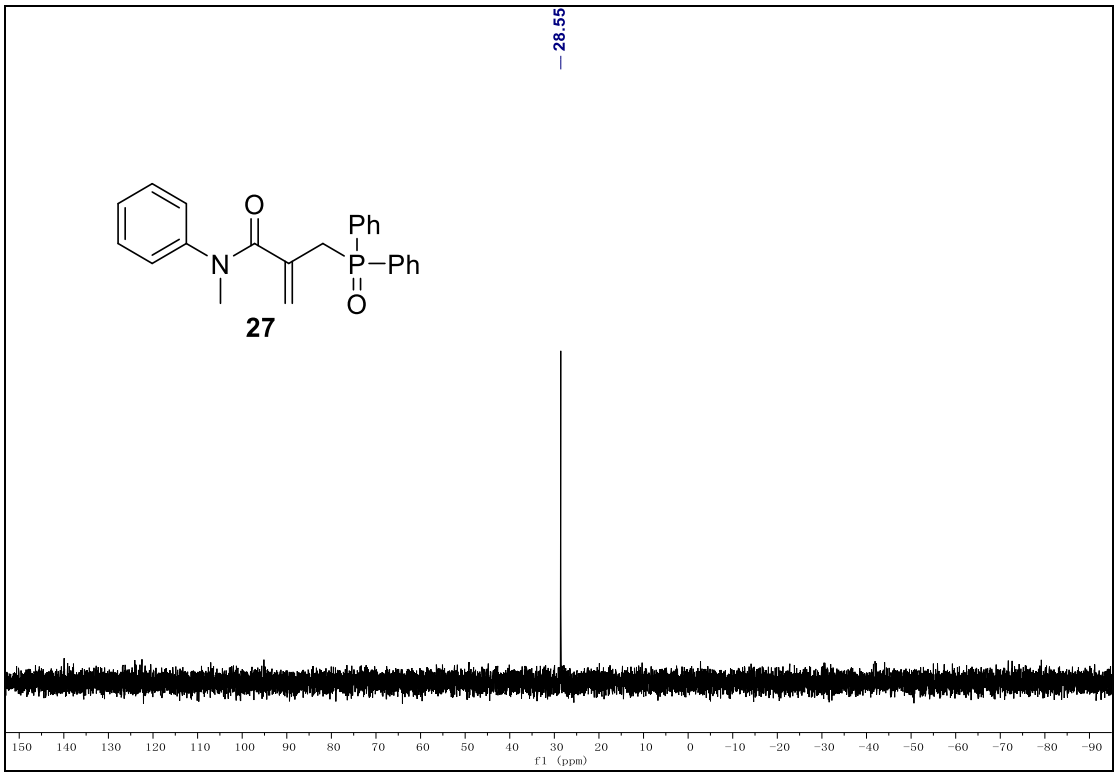



34.11
O
O
N
H
Ph
P
Ph
O
26
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

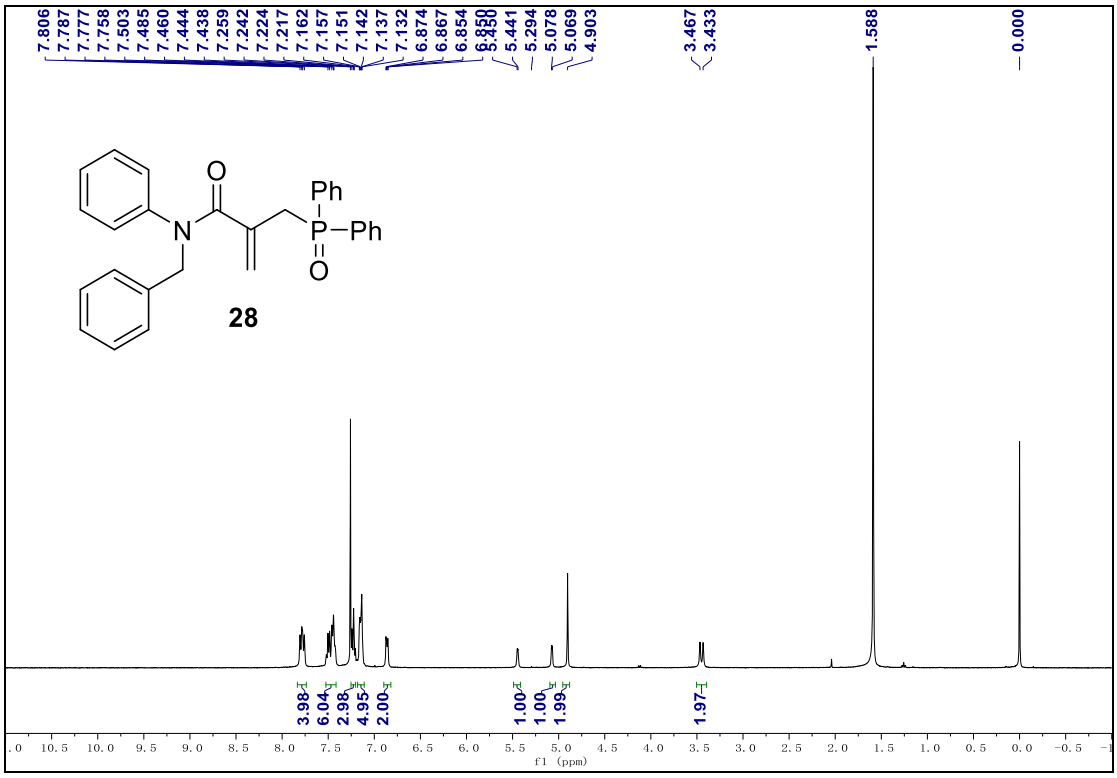
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 27.

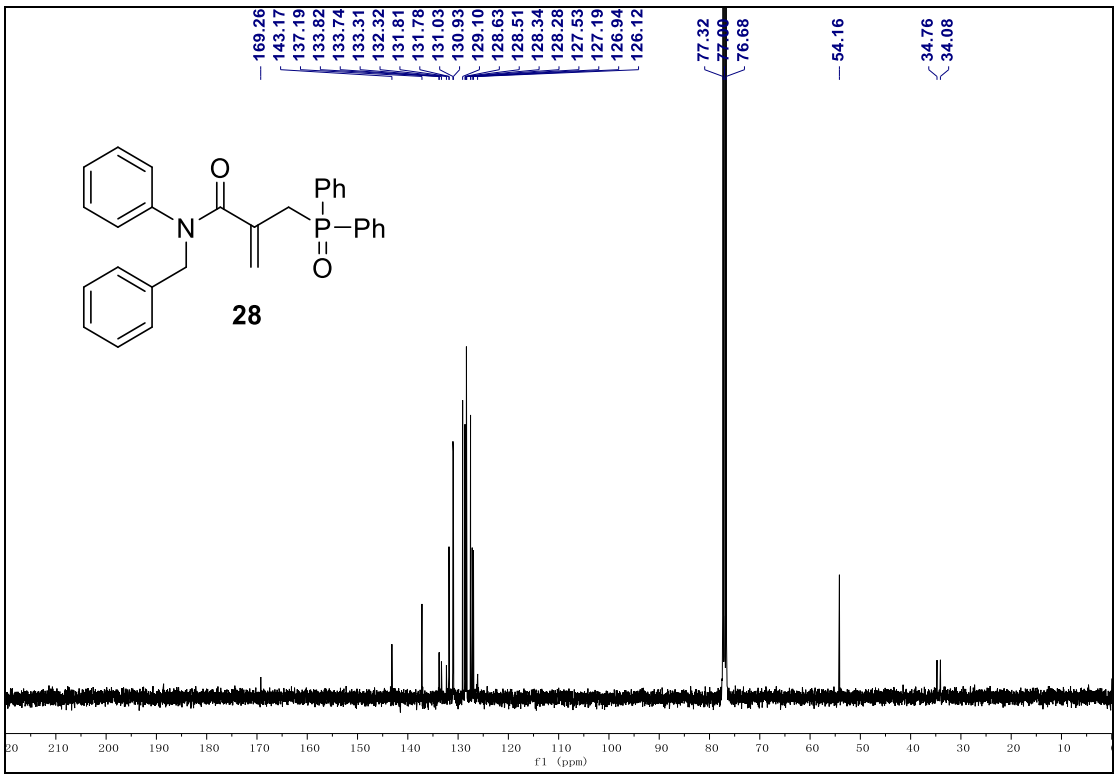


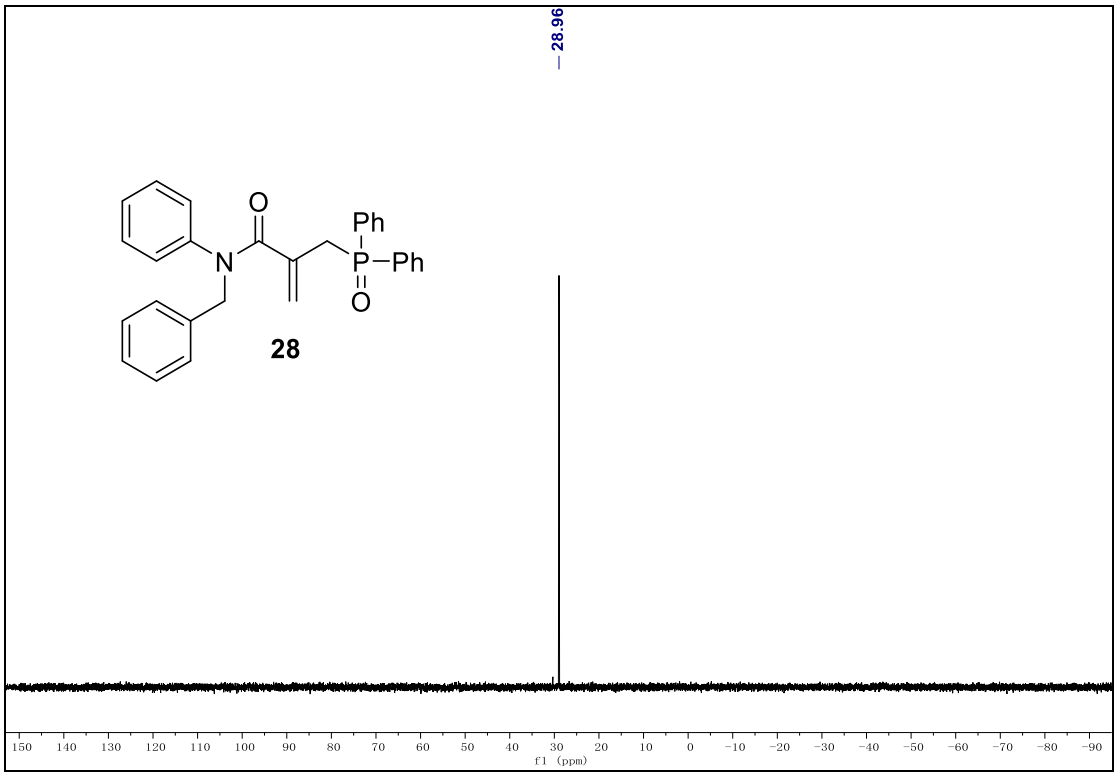



28.55
O
N
Ph
P
Ph
O
27
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

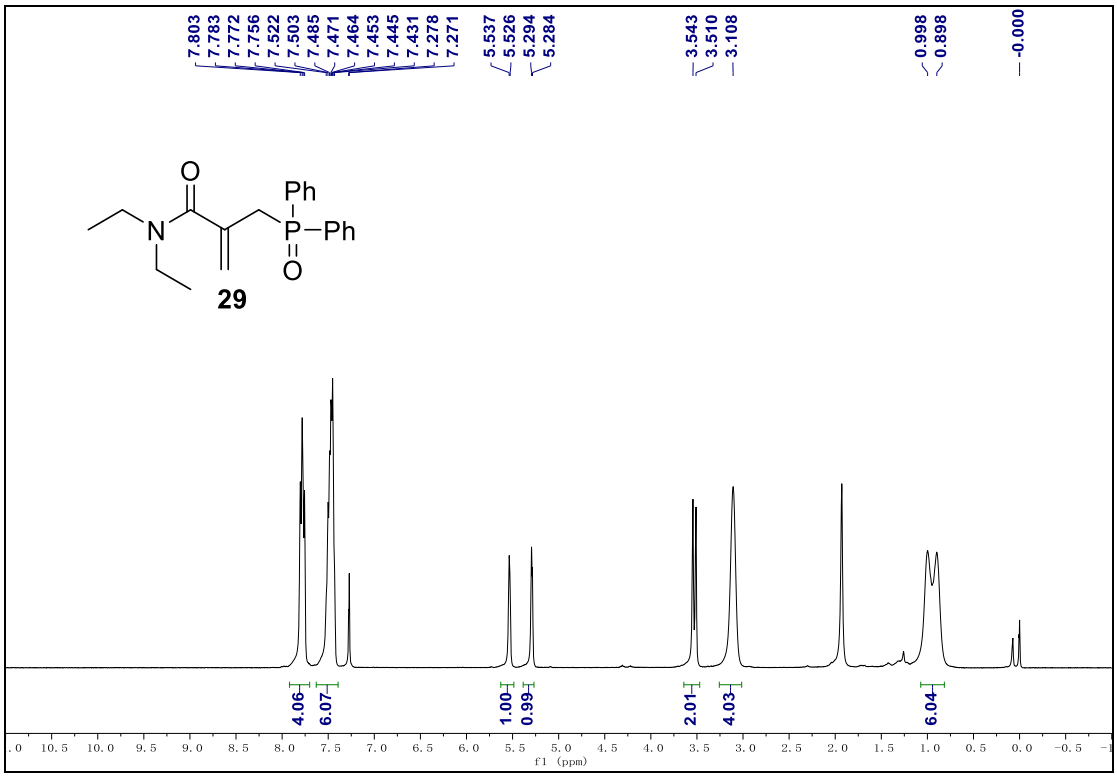
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 28.

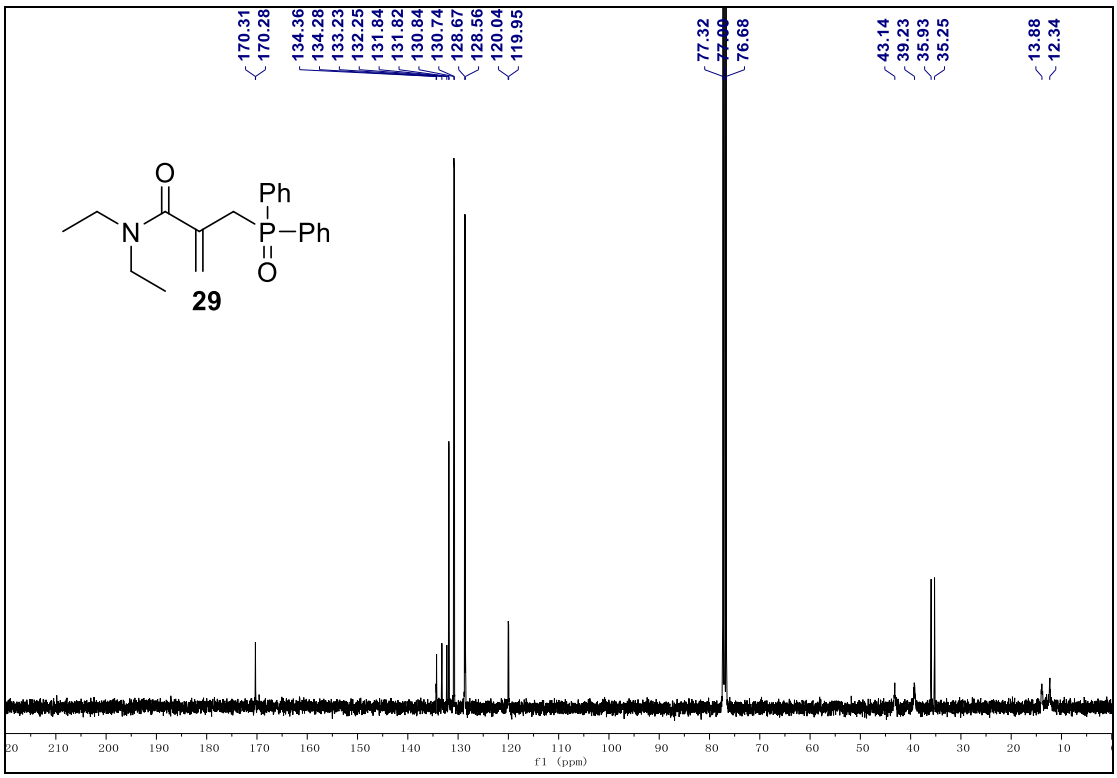


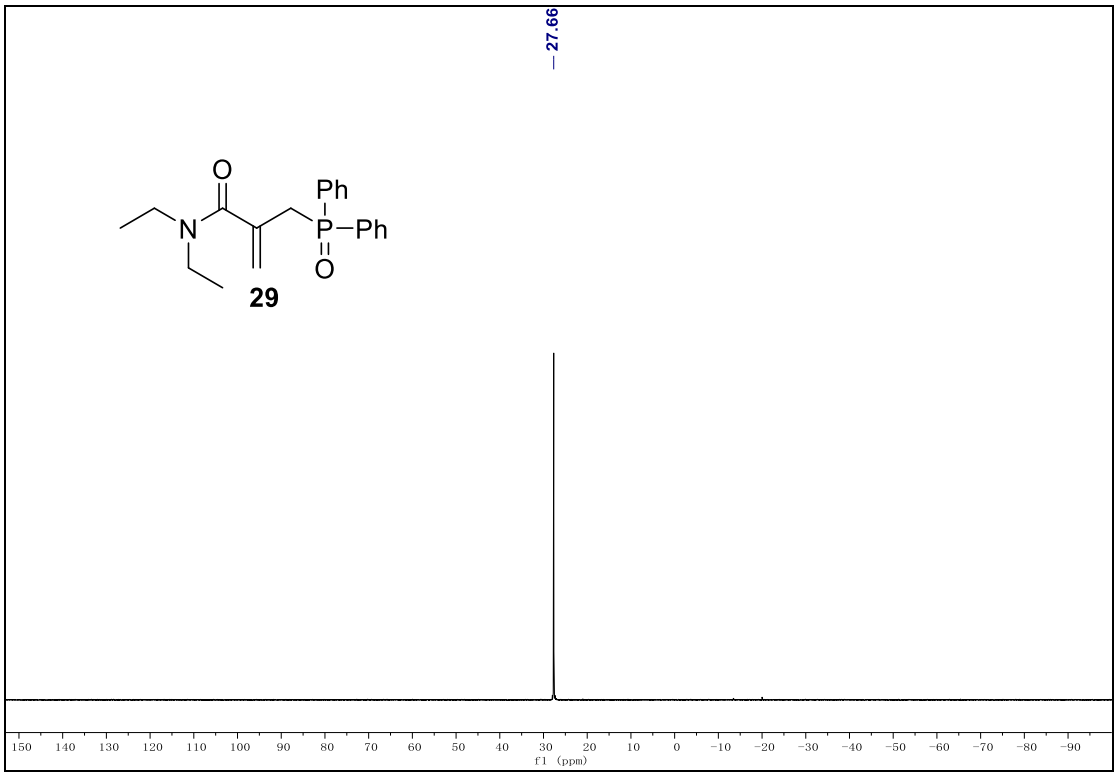



28.96
O
N
Ph
P
Ph
O
28
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

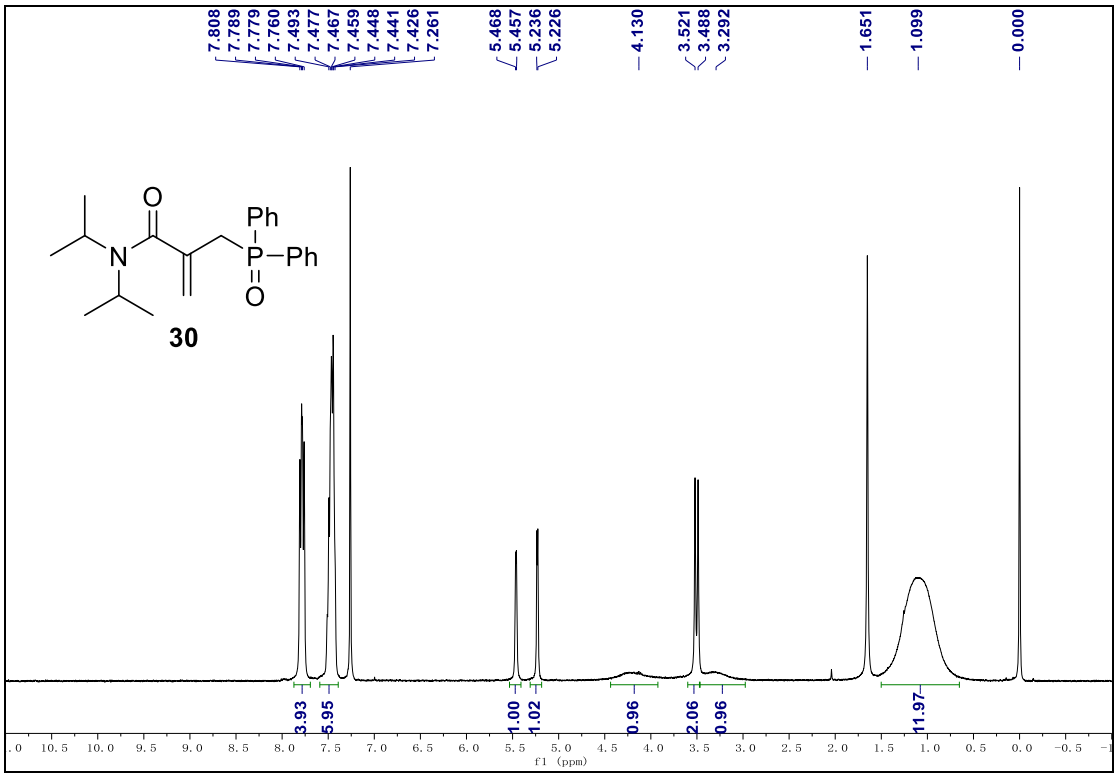
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 29.

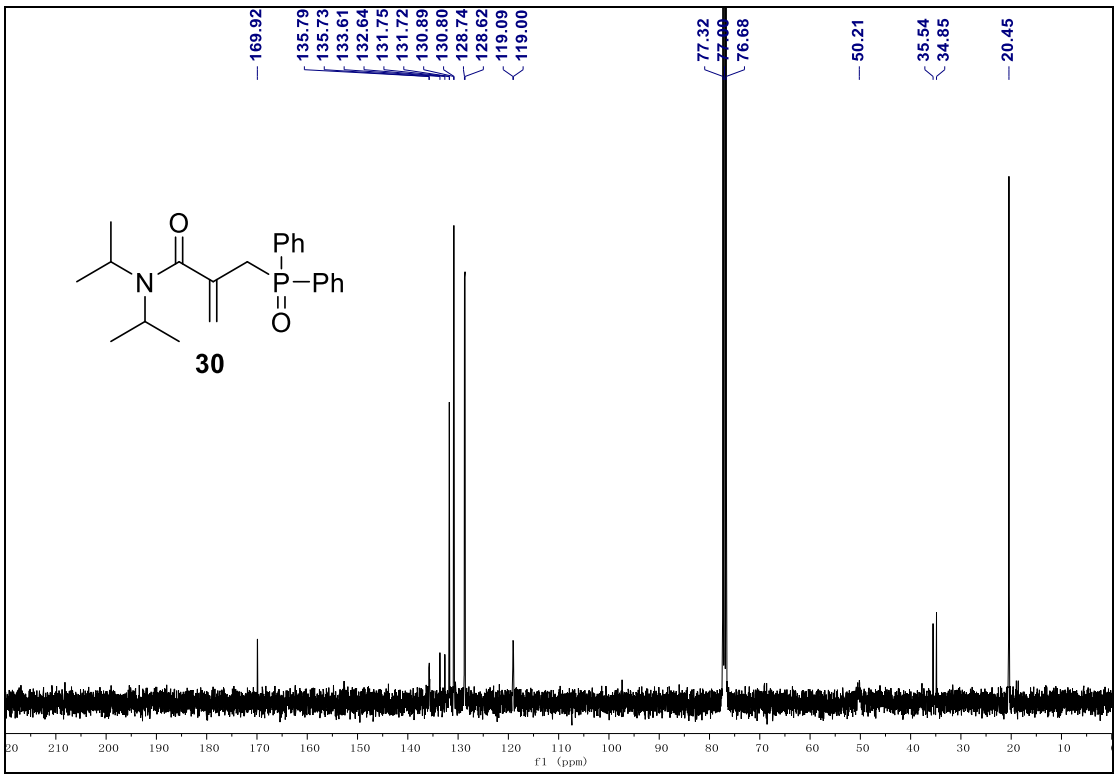


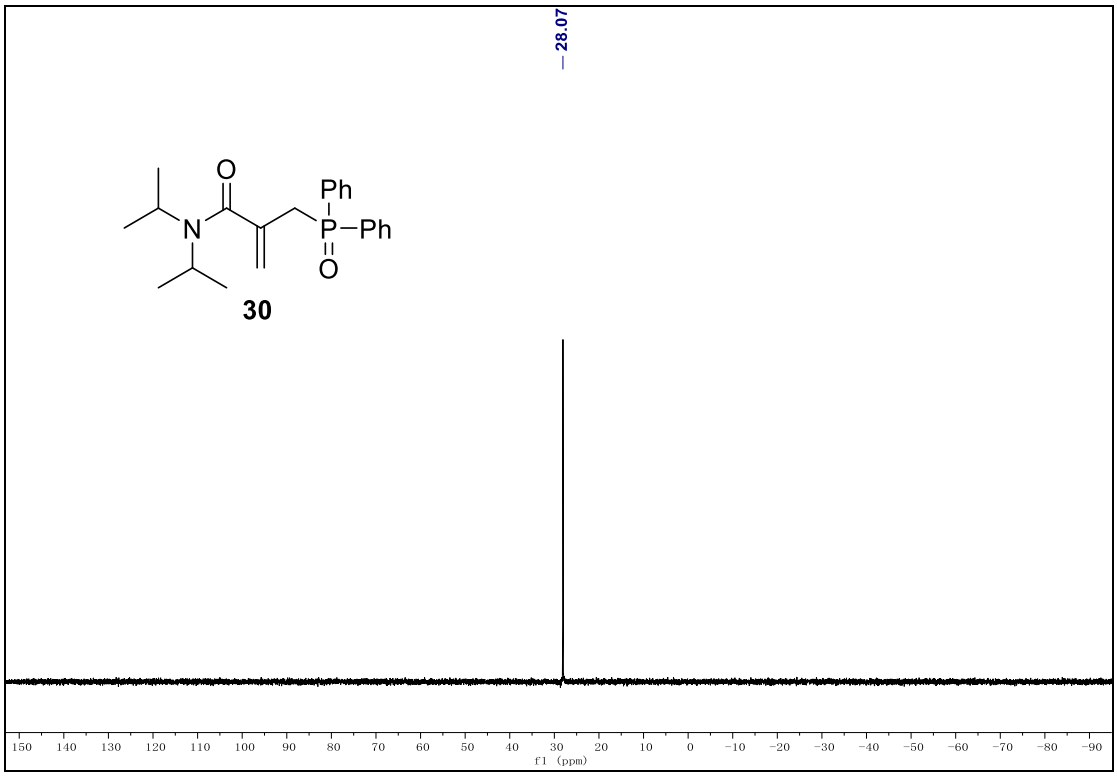



27.66
O
Ph
N
P
Ph
O
29
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

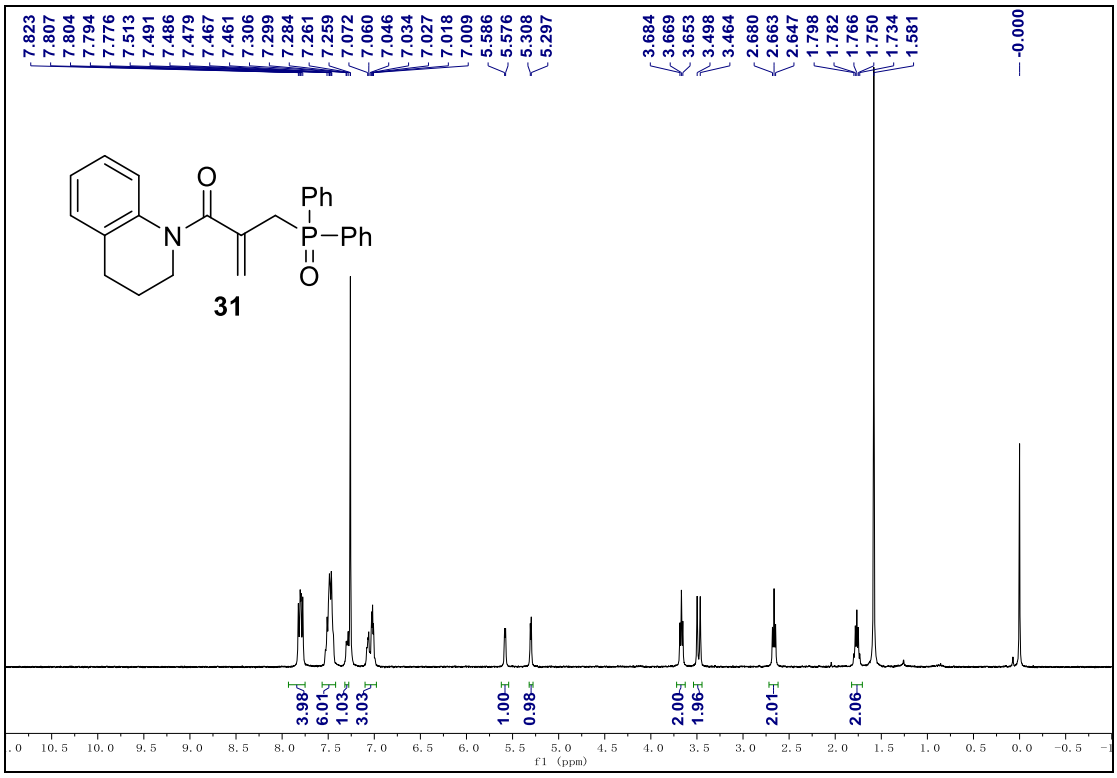
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 30.

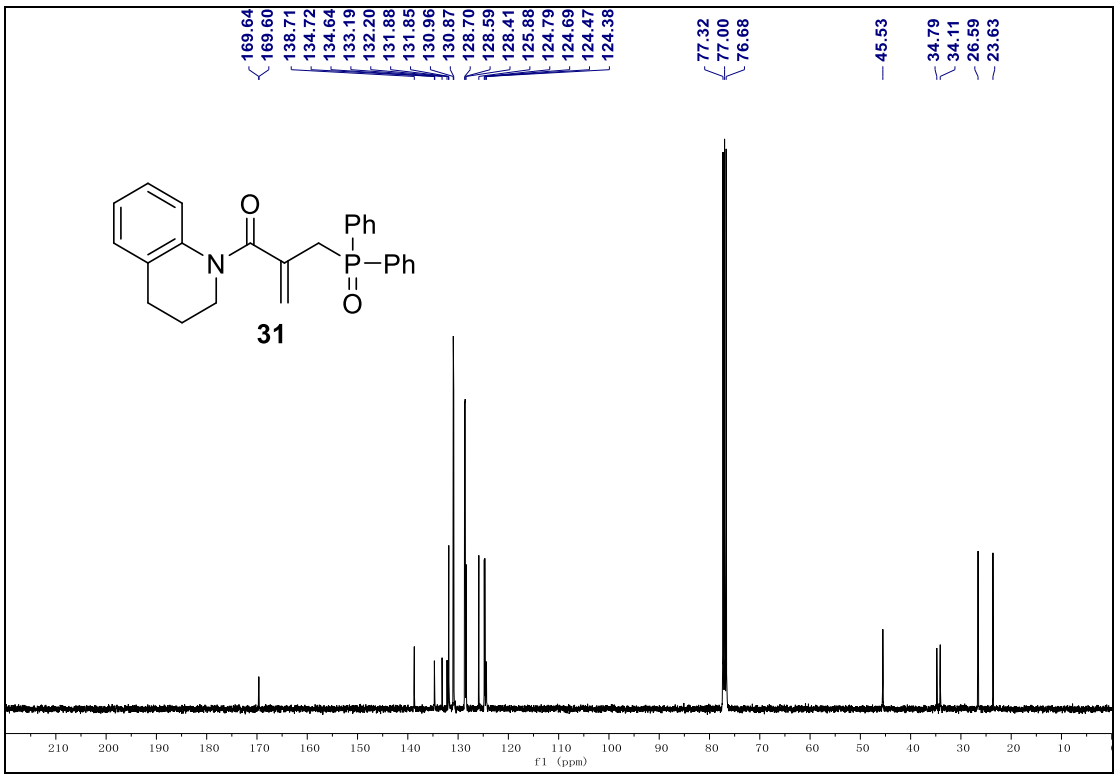


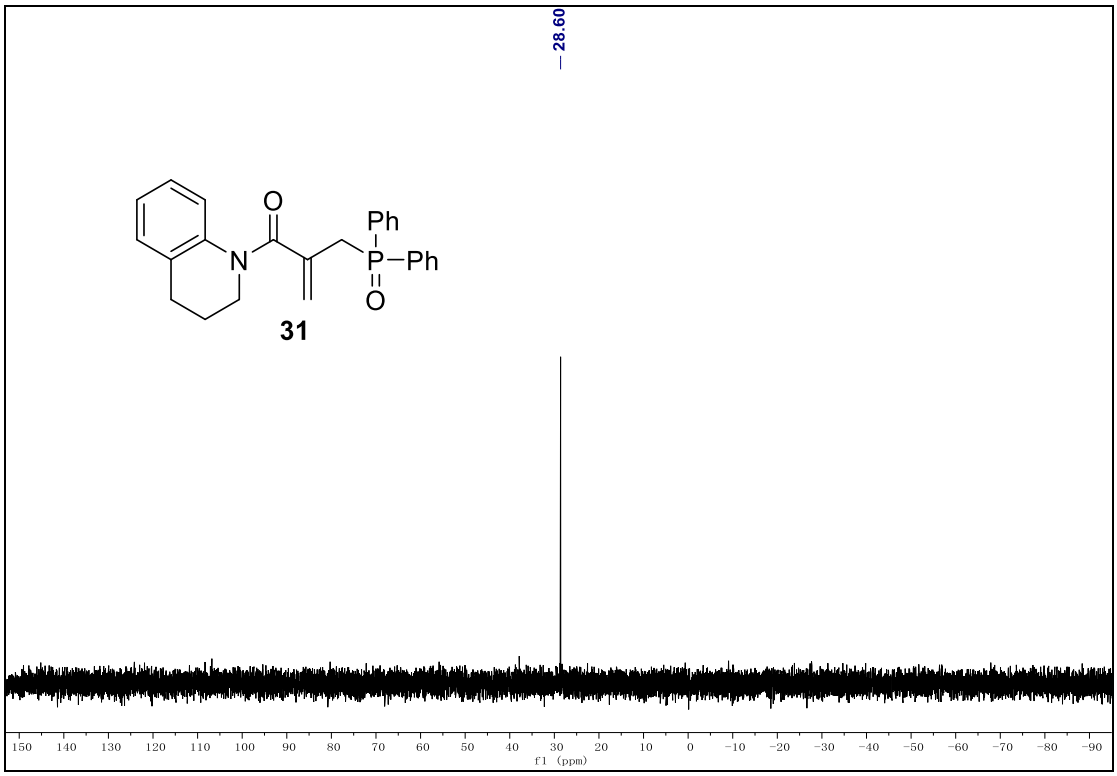



28.07
O
Ph
N
P–Ph
O
30
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

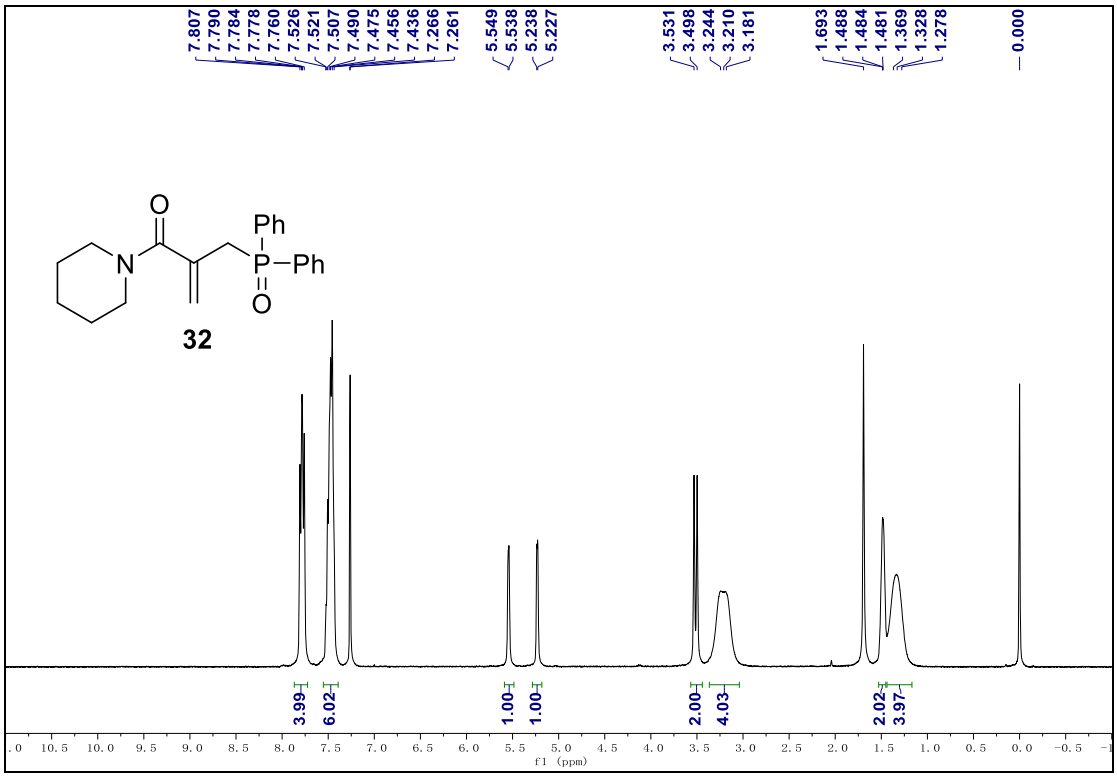
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 31.

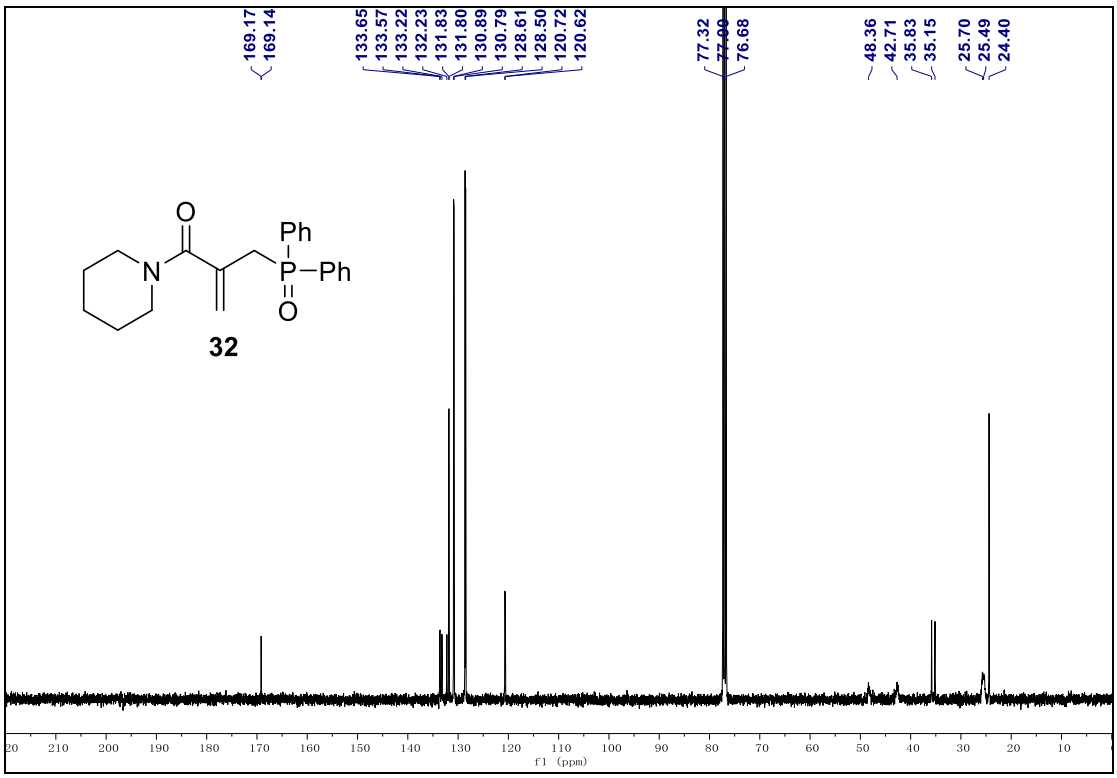


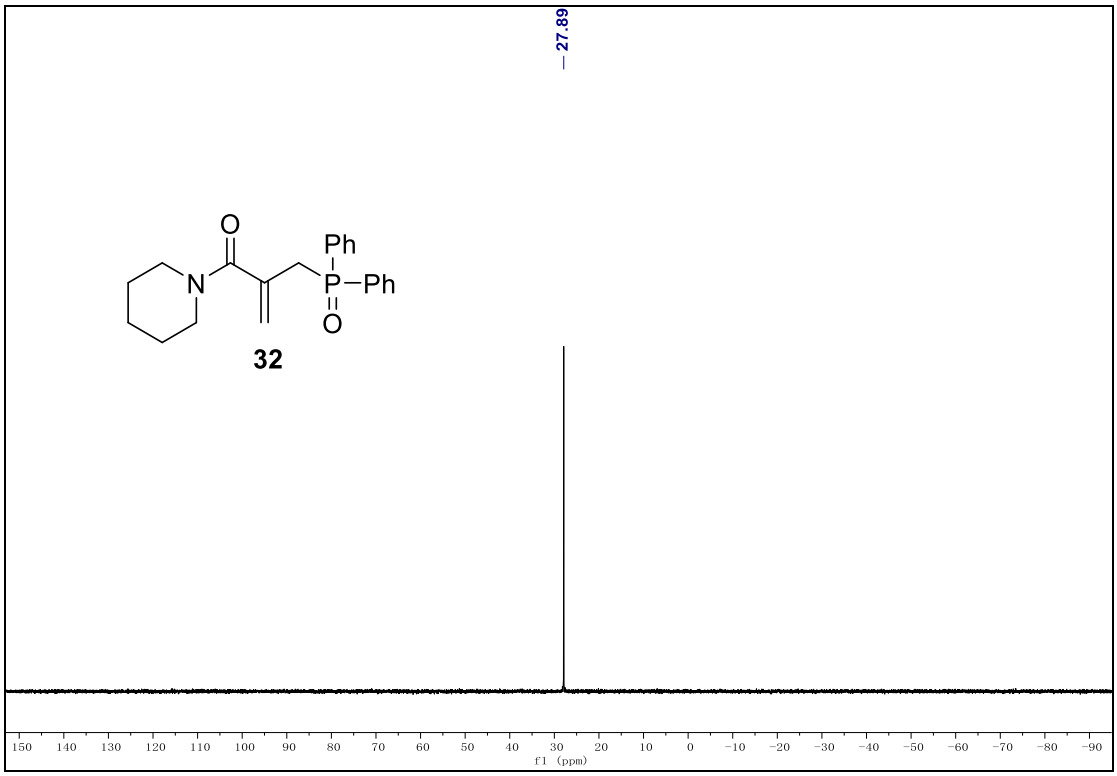



28.60
O
Ph
N
P
Ph
O
31
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

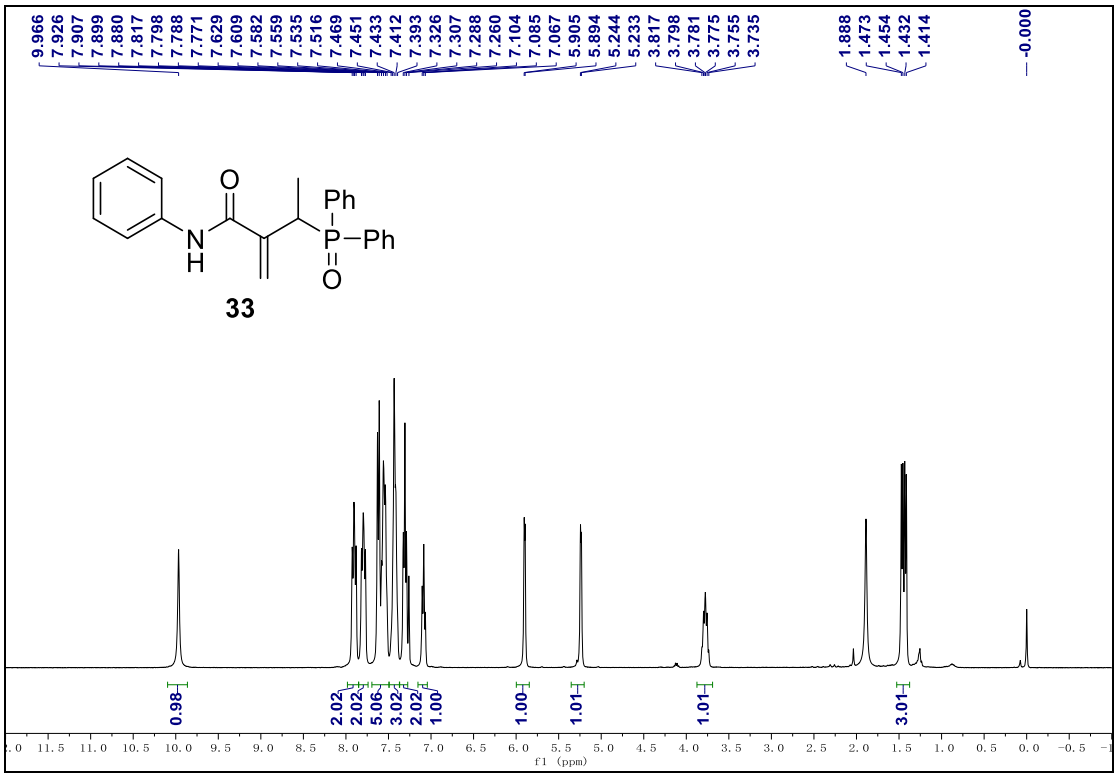
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 32.

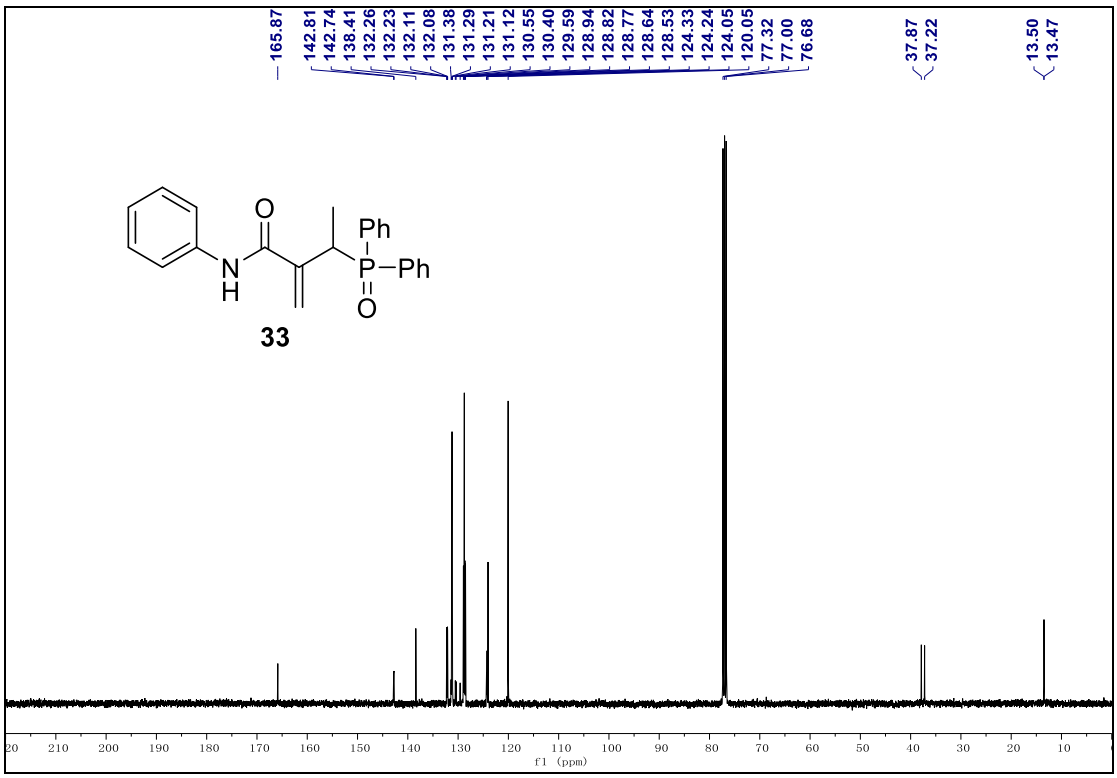


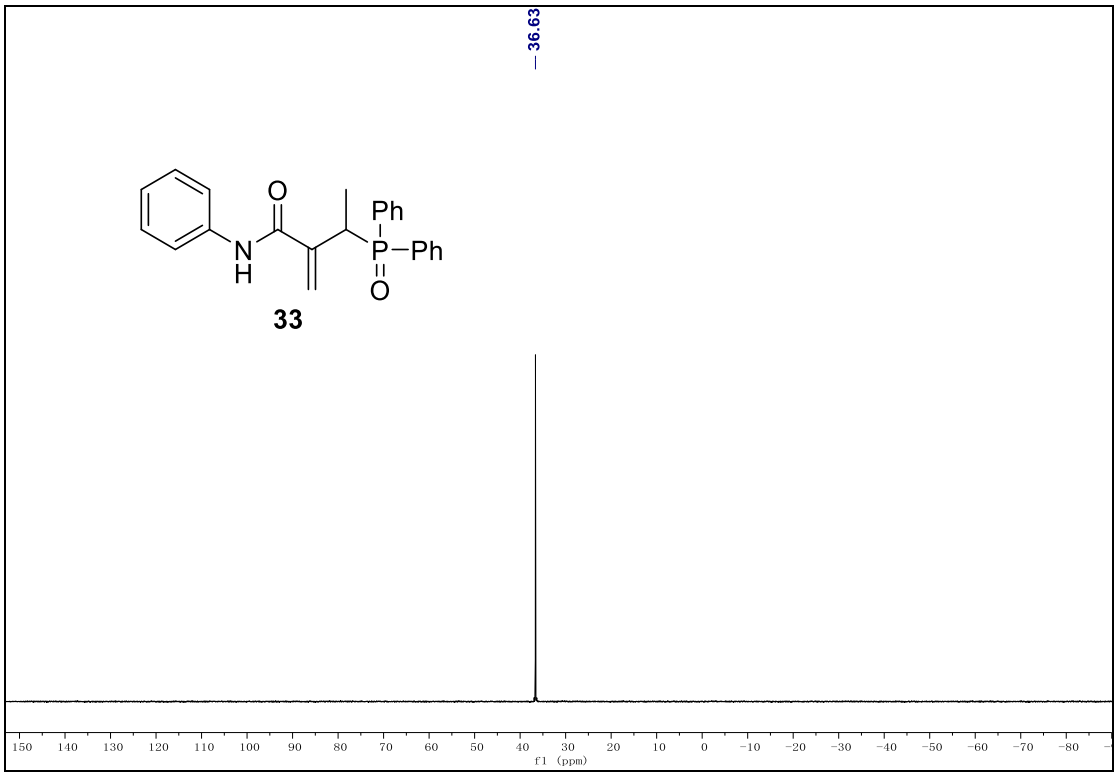



27.89
O
Ph
N
P
Ph
O
32
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

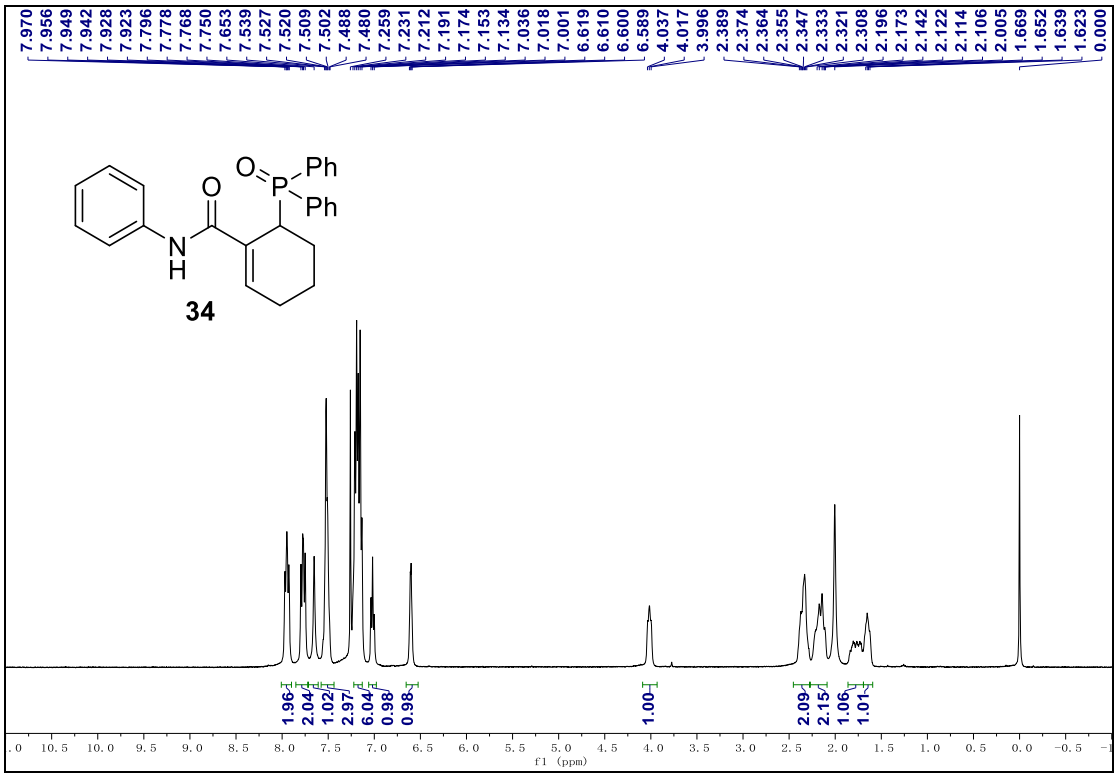
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 33.

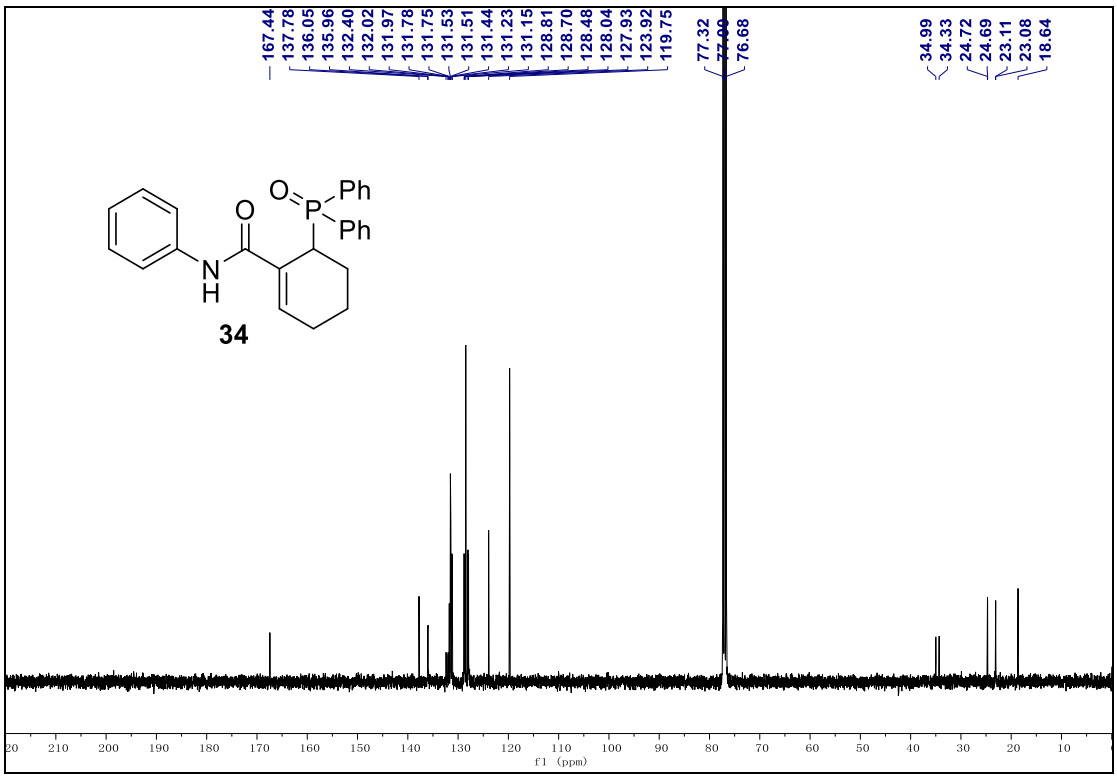


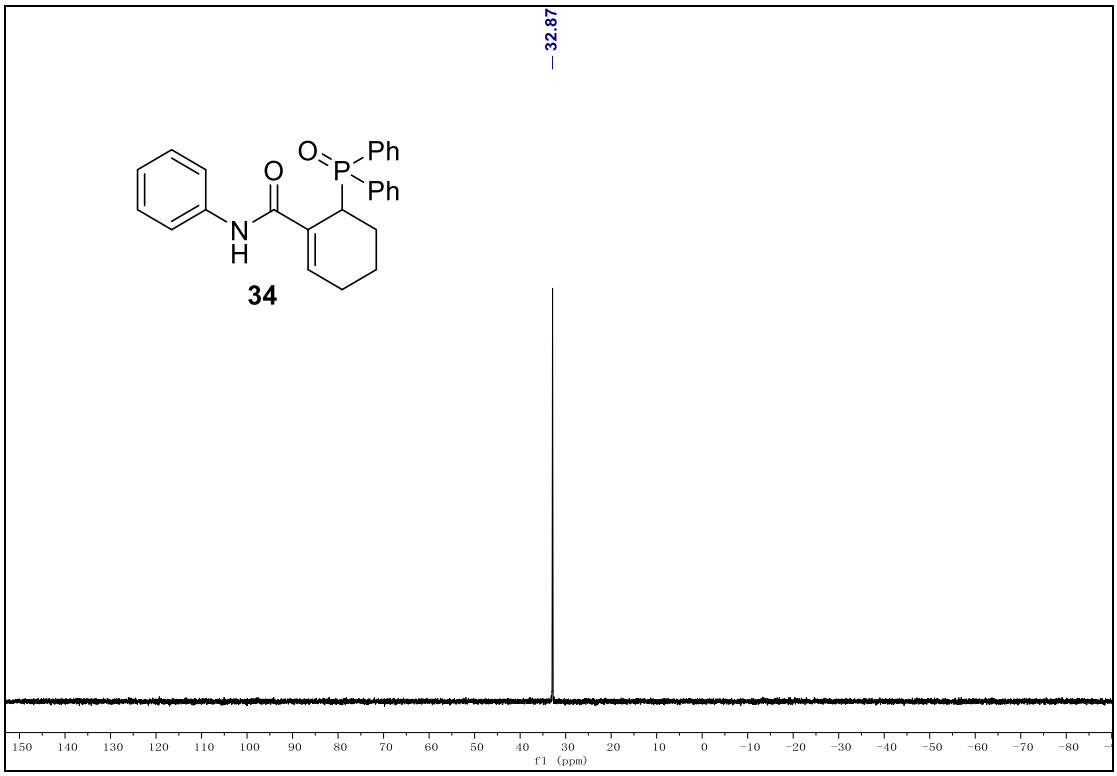



36.63
O
N
H
Ph
P
Ph
O
33
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

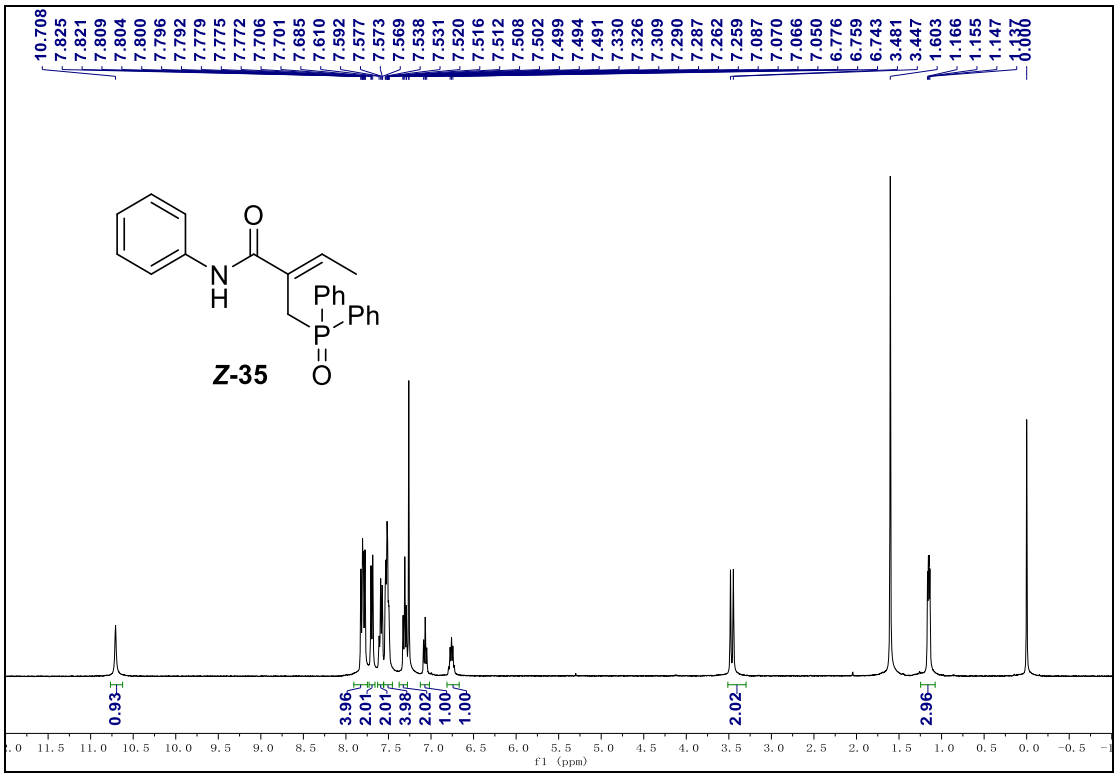
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 34.

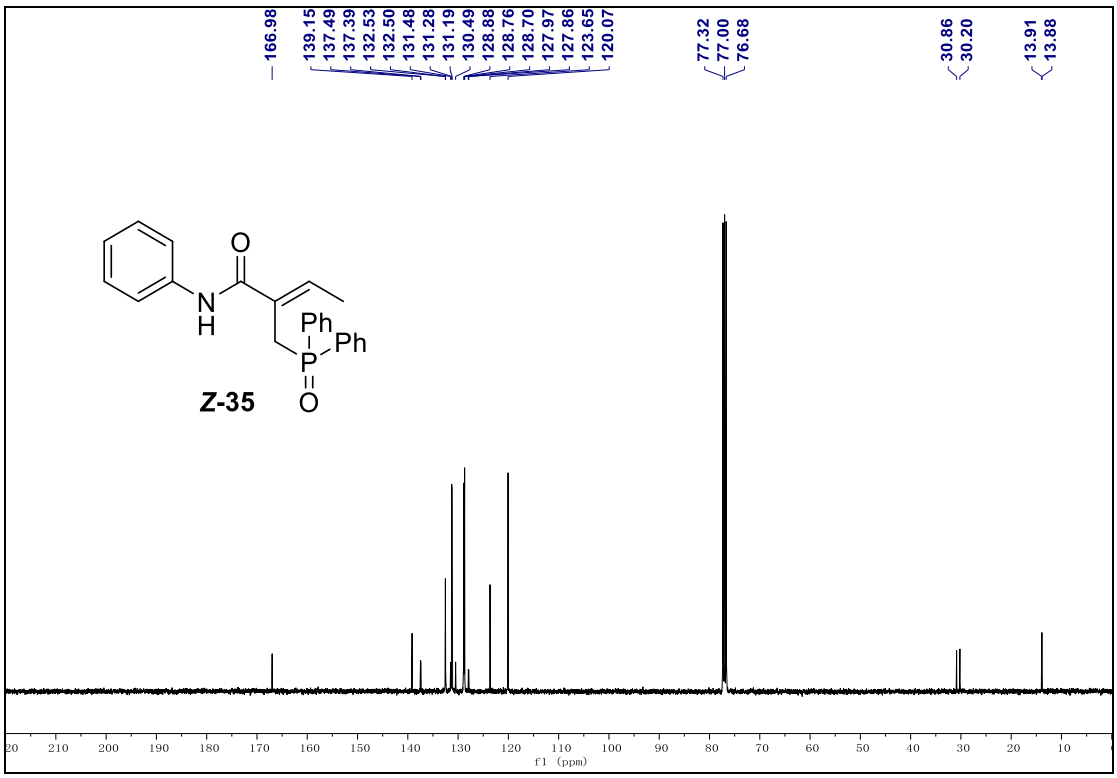


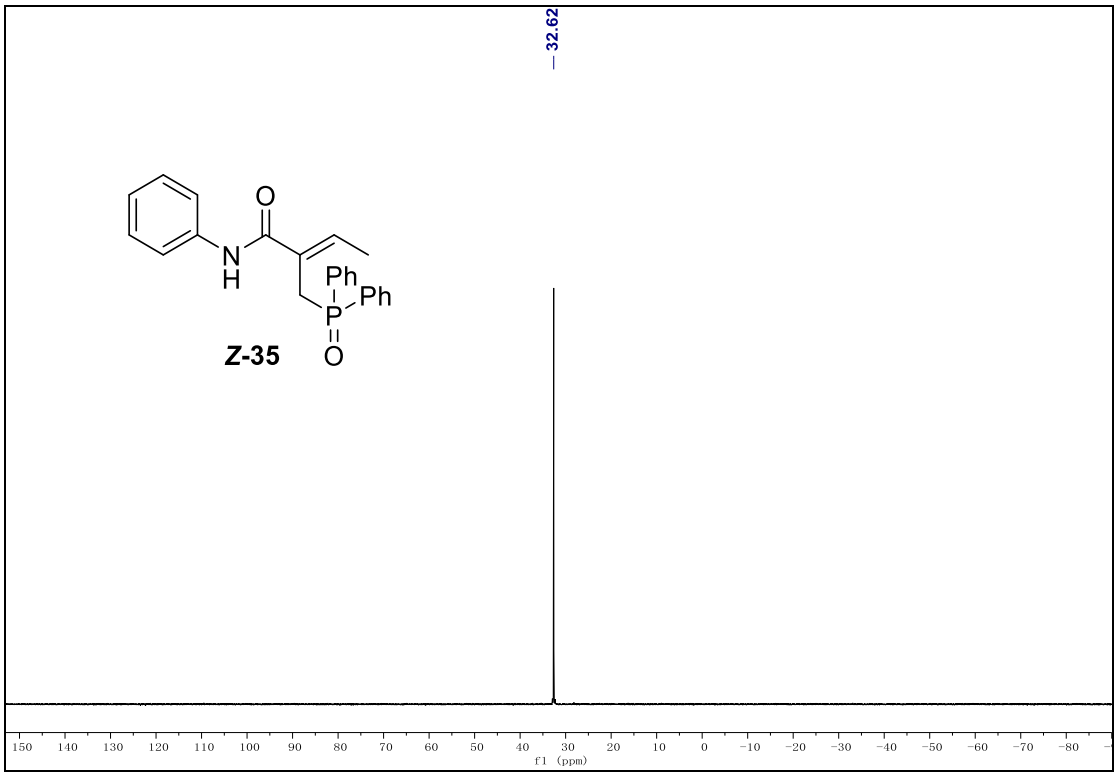



32.87
O
P
Ph
Ph
N
H
34
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

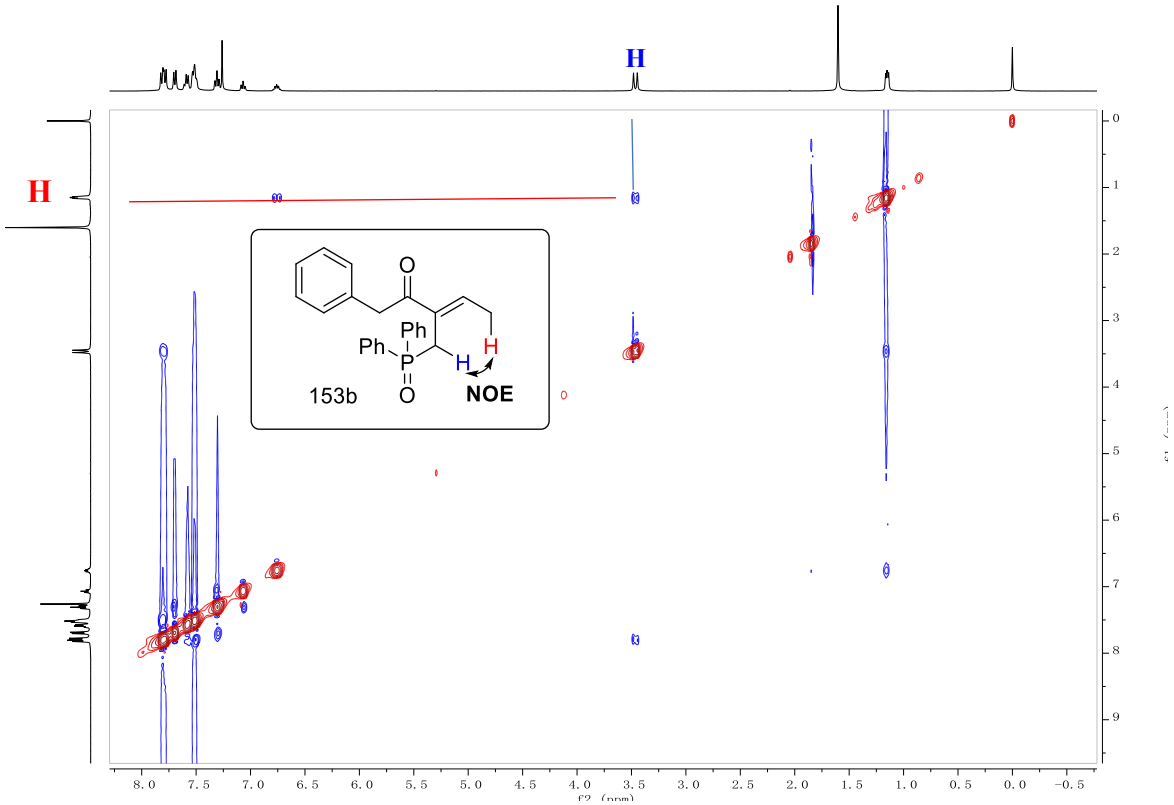
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of *Z*-35.



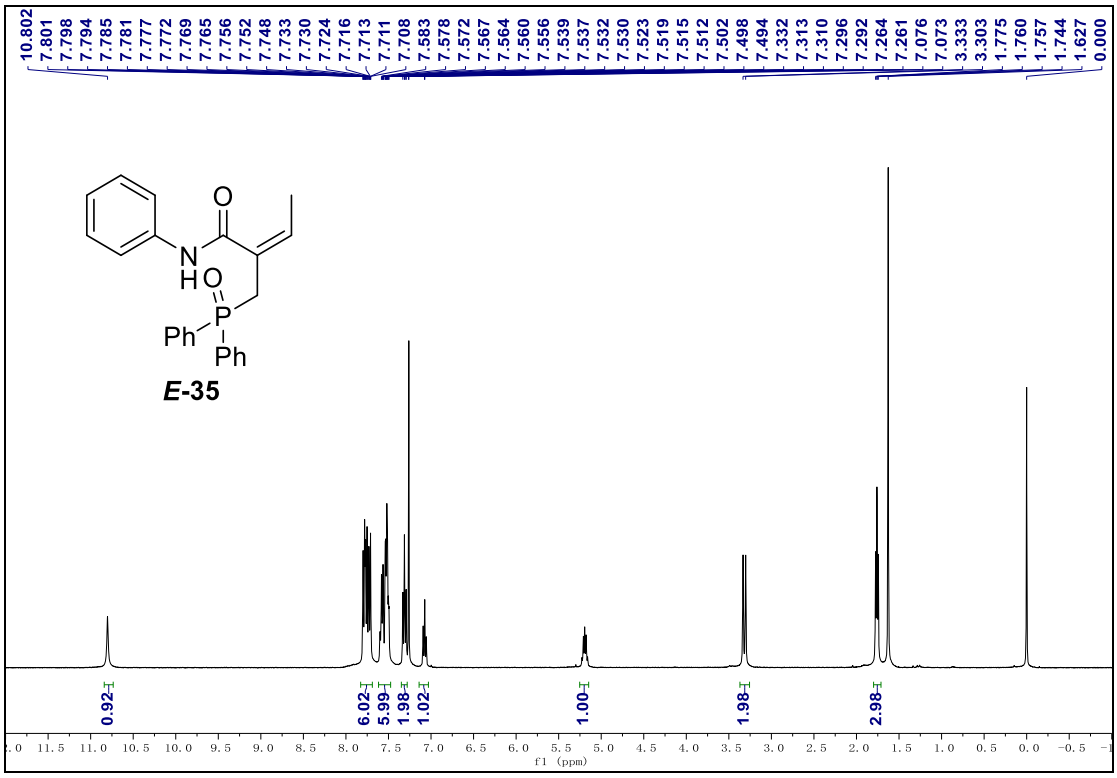


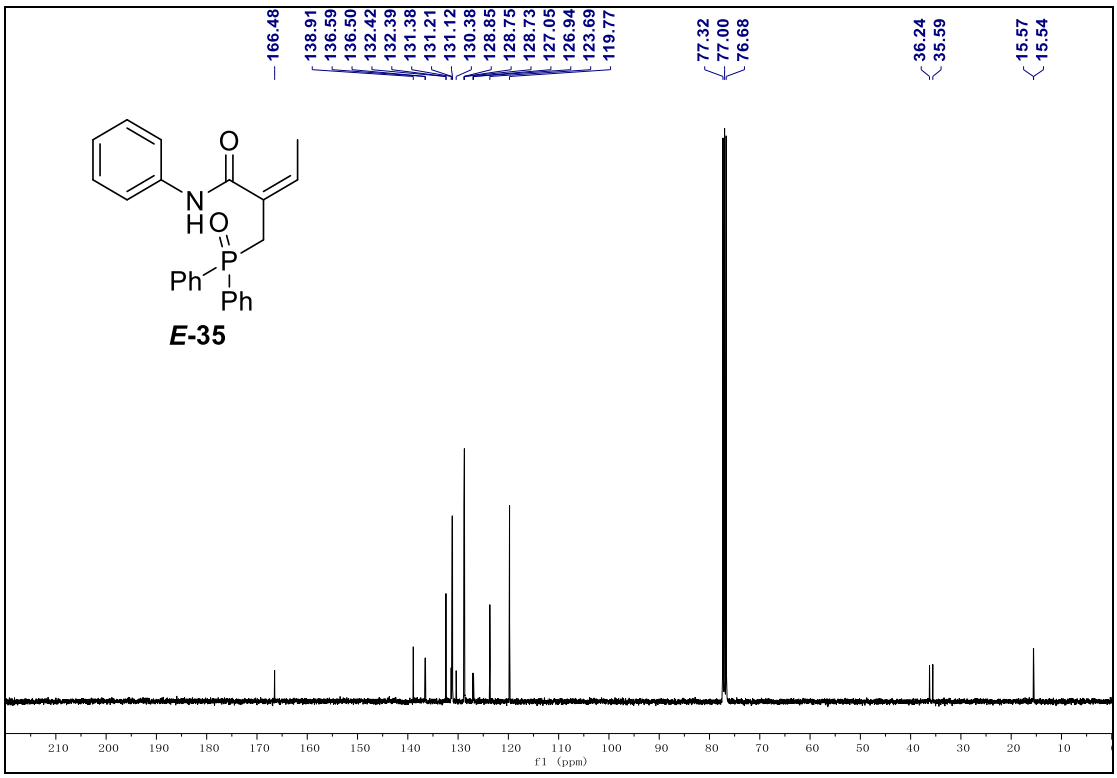


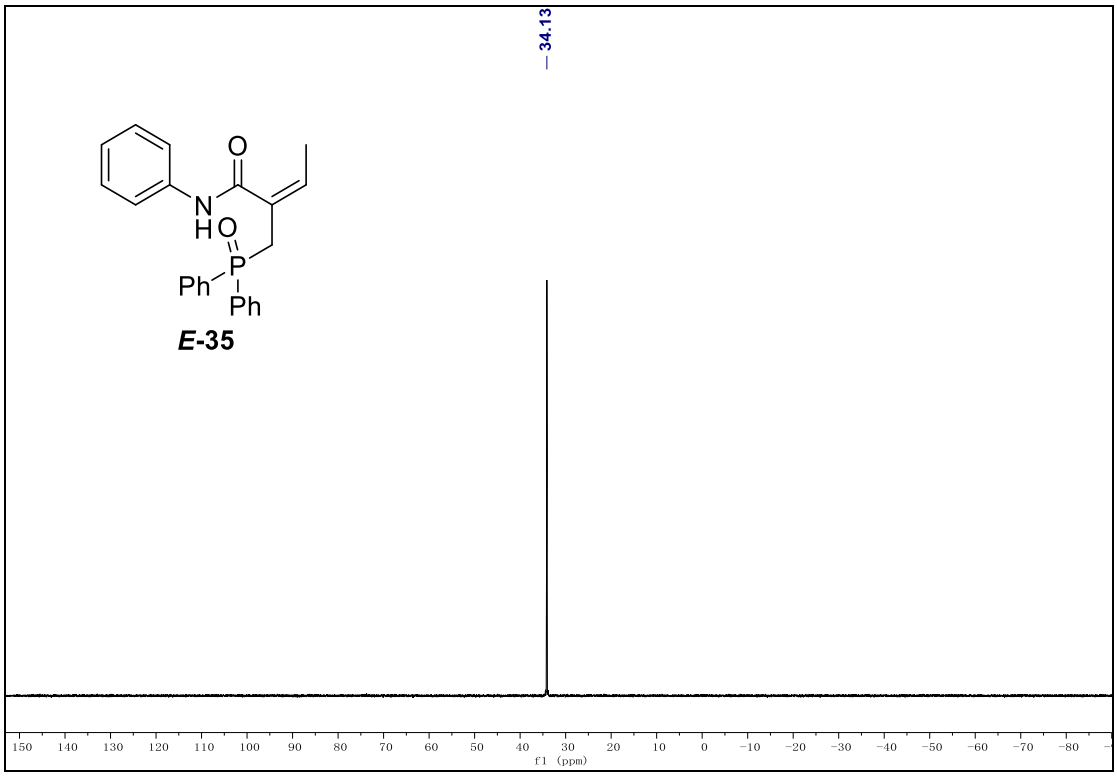
NOESY spectrum of *Z*-35



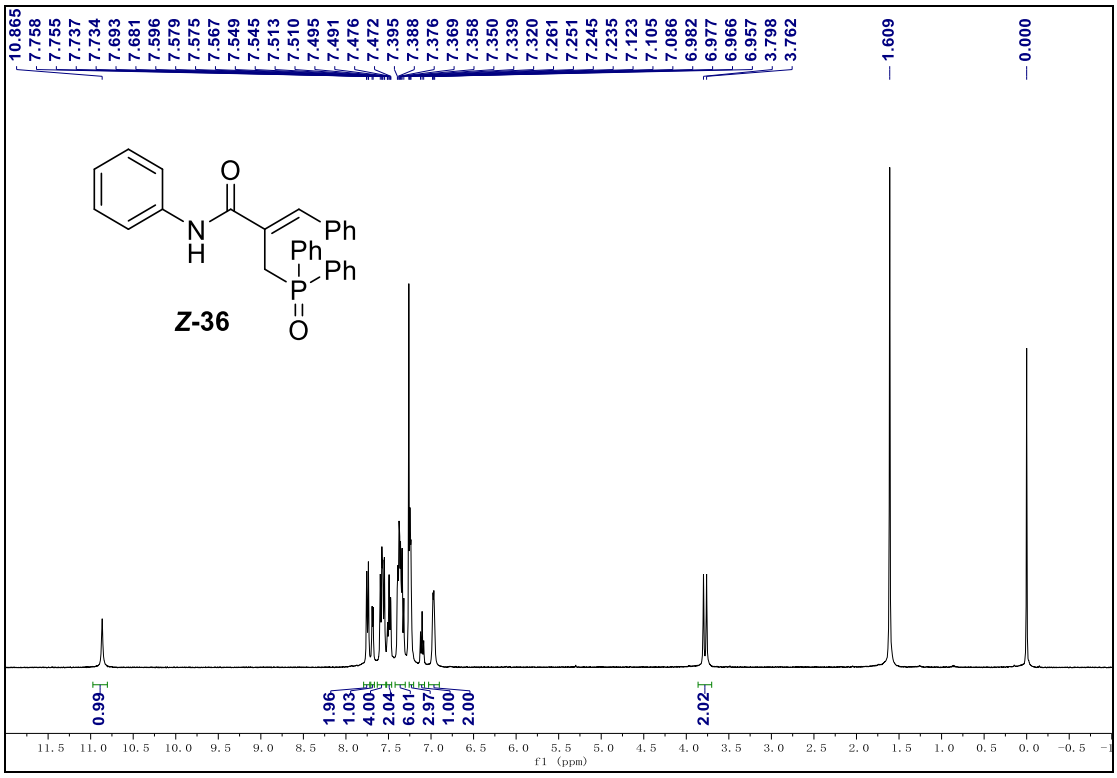
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of *E*-35.

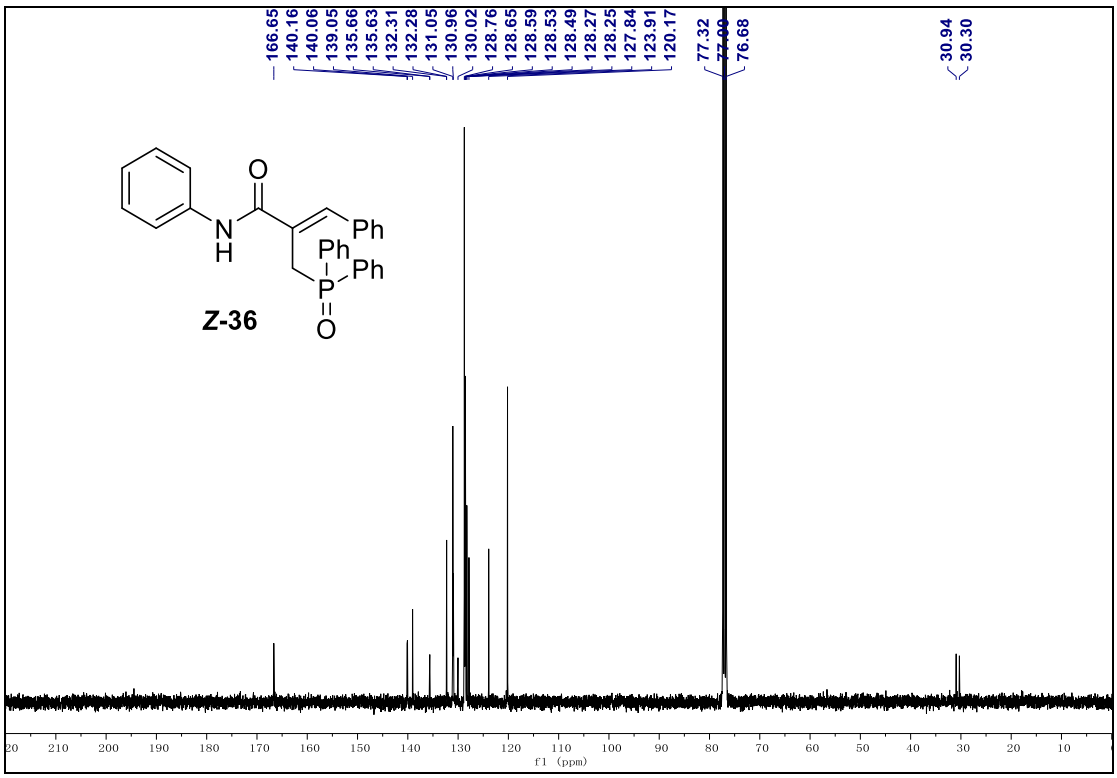


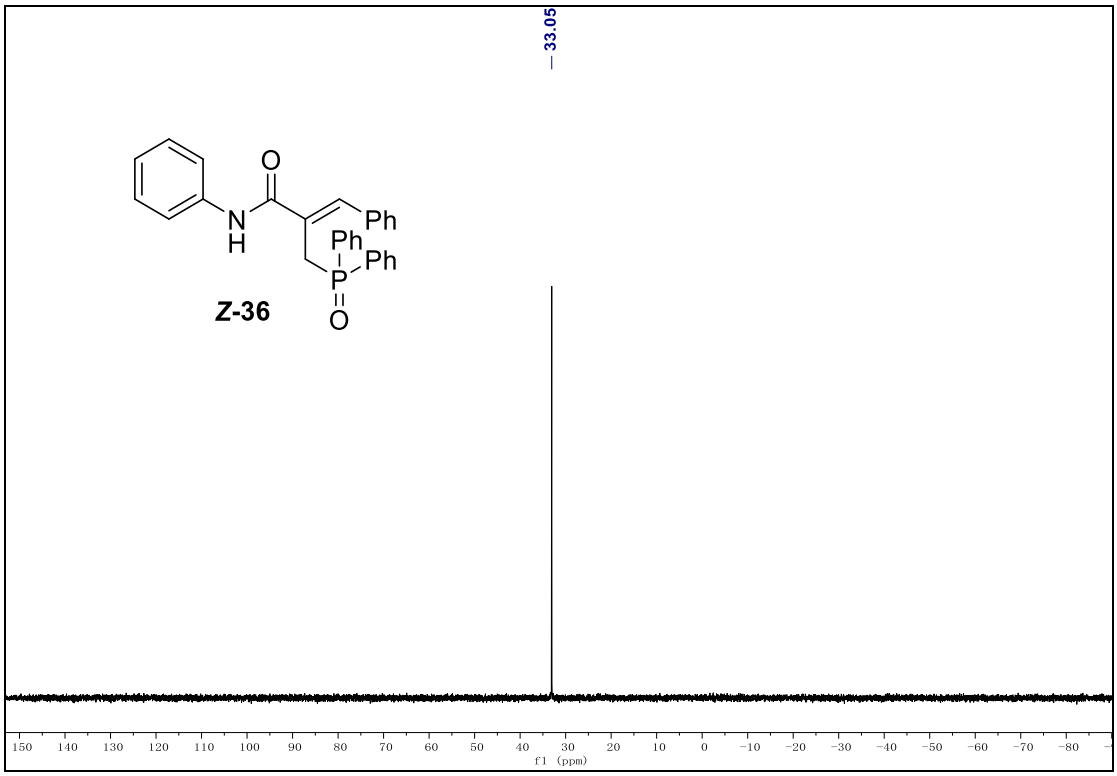



34.13
O
N
H
O
P
Ph
Ph
E-35
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

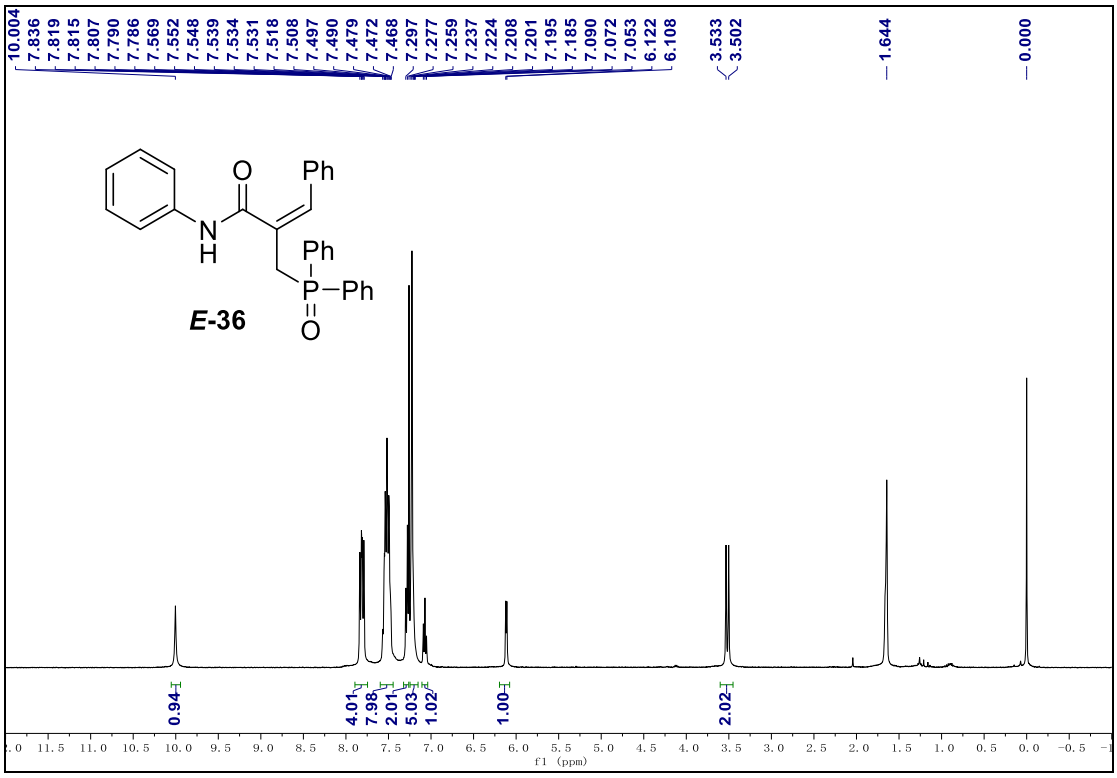
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of *Z*-36.

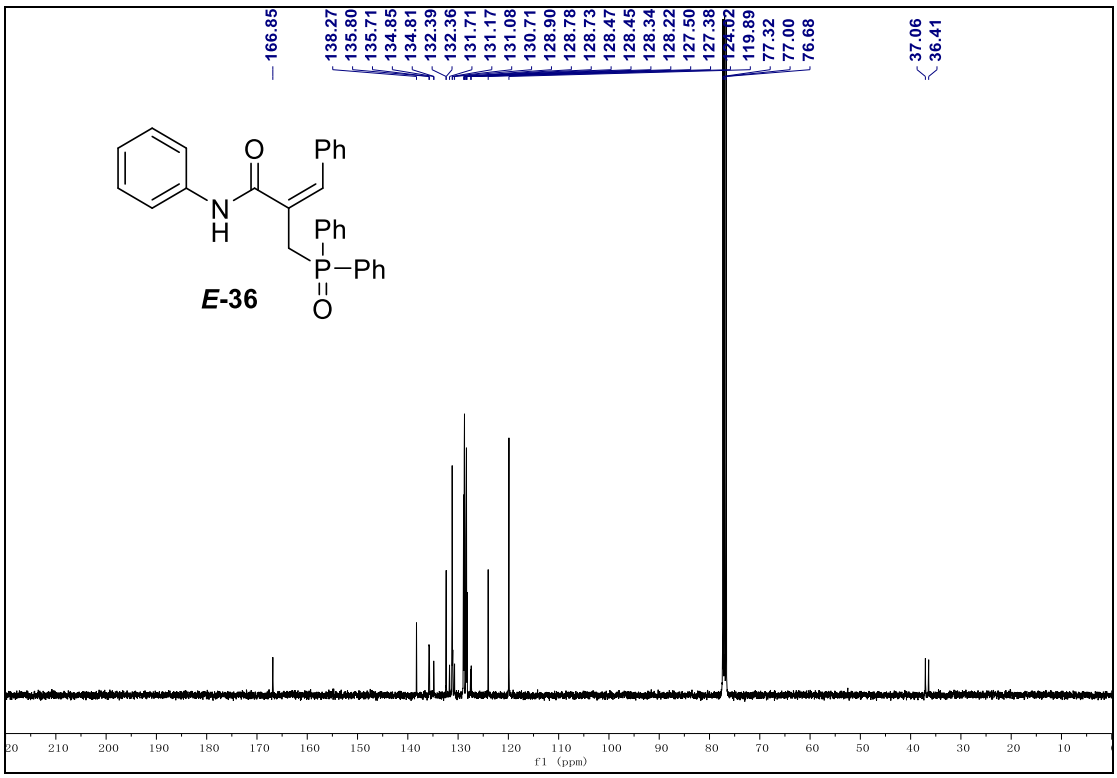


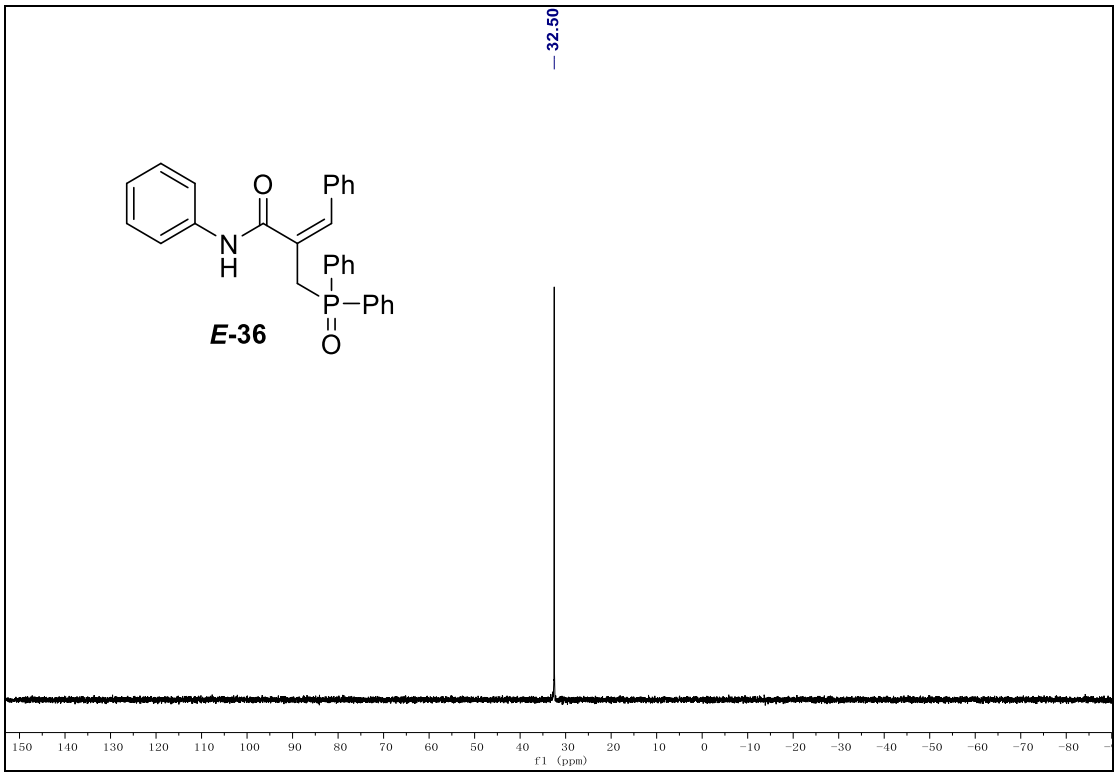



33.05
O
N
H
Ph
Ph
Ph
P
O
Z-36
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

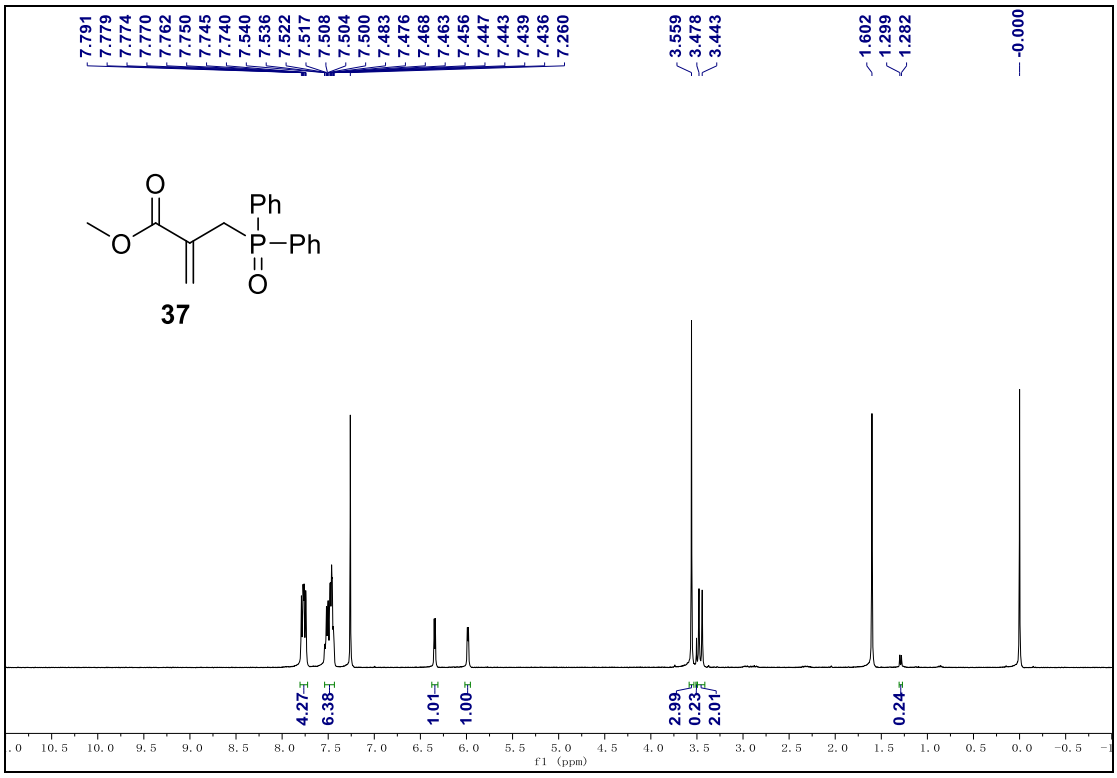
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of *E*-36.

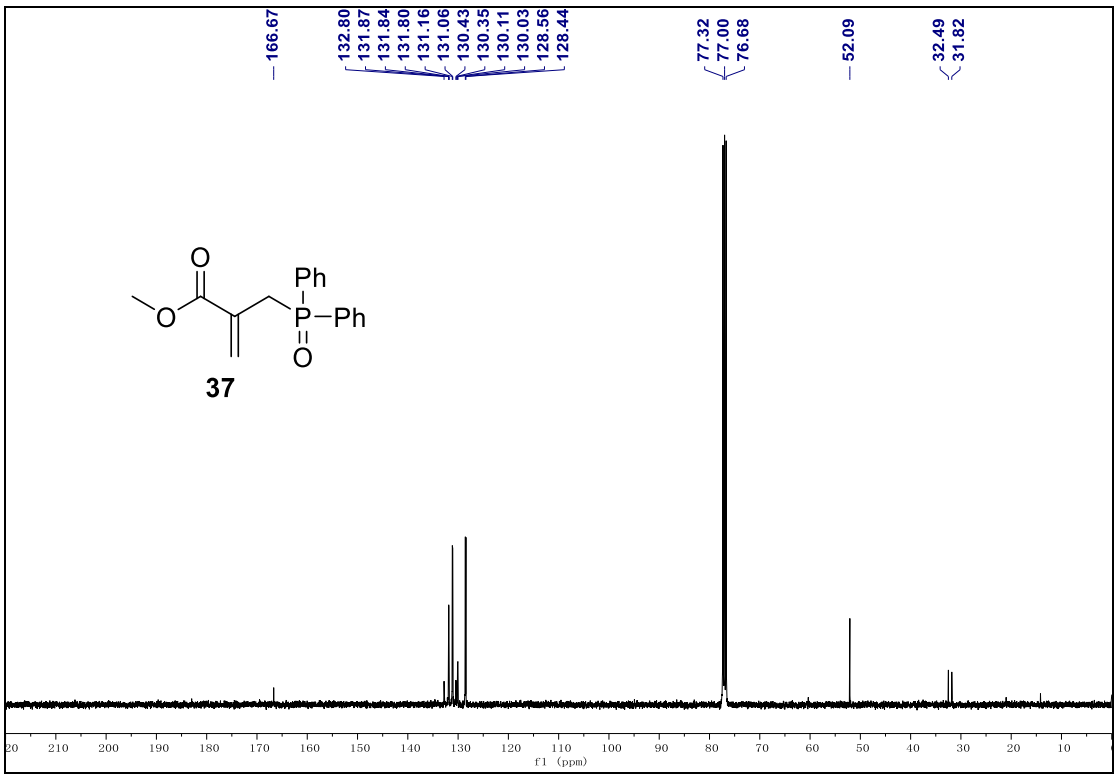


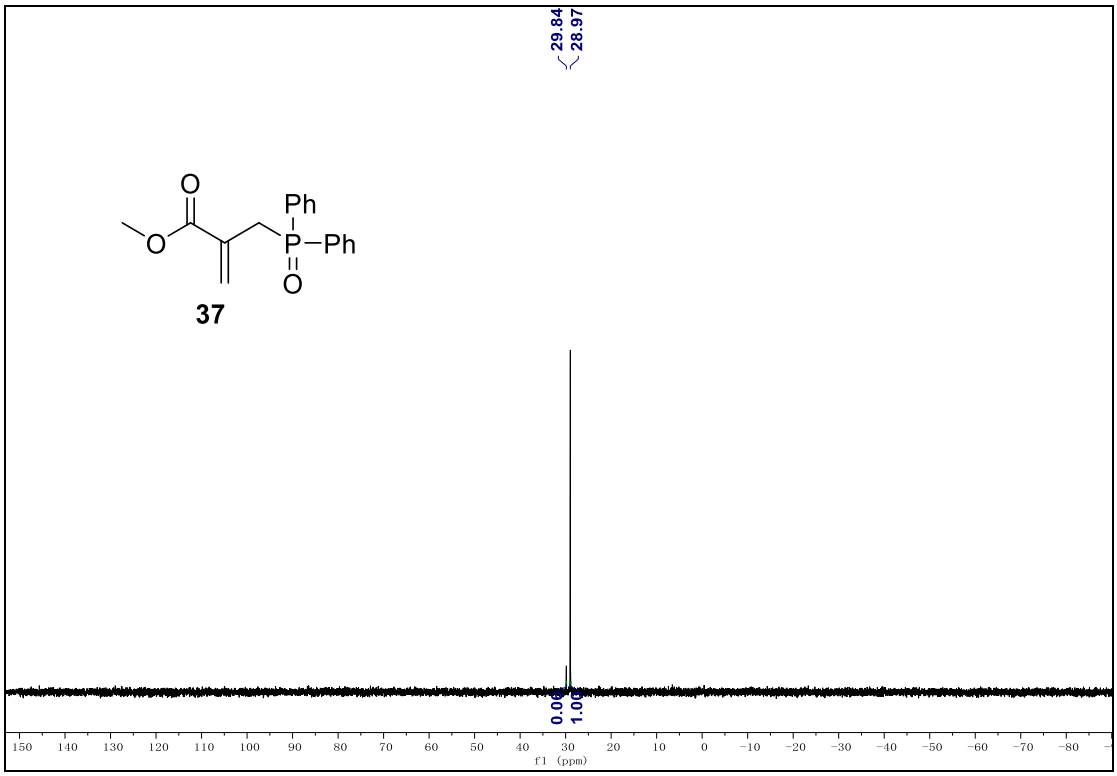



32.50
O
Ph
N
H
Ph
P
Ph
O
E-36
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

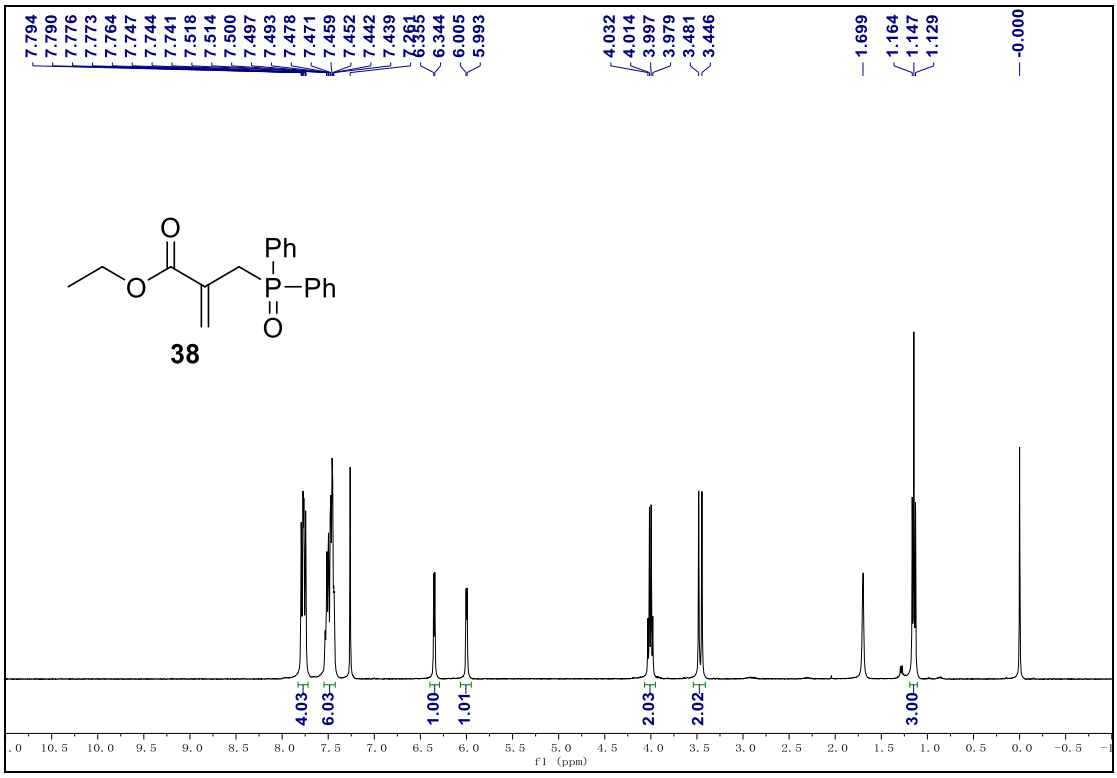
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 37.

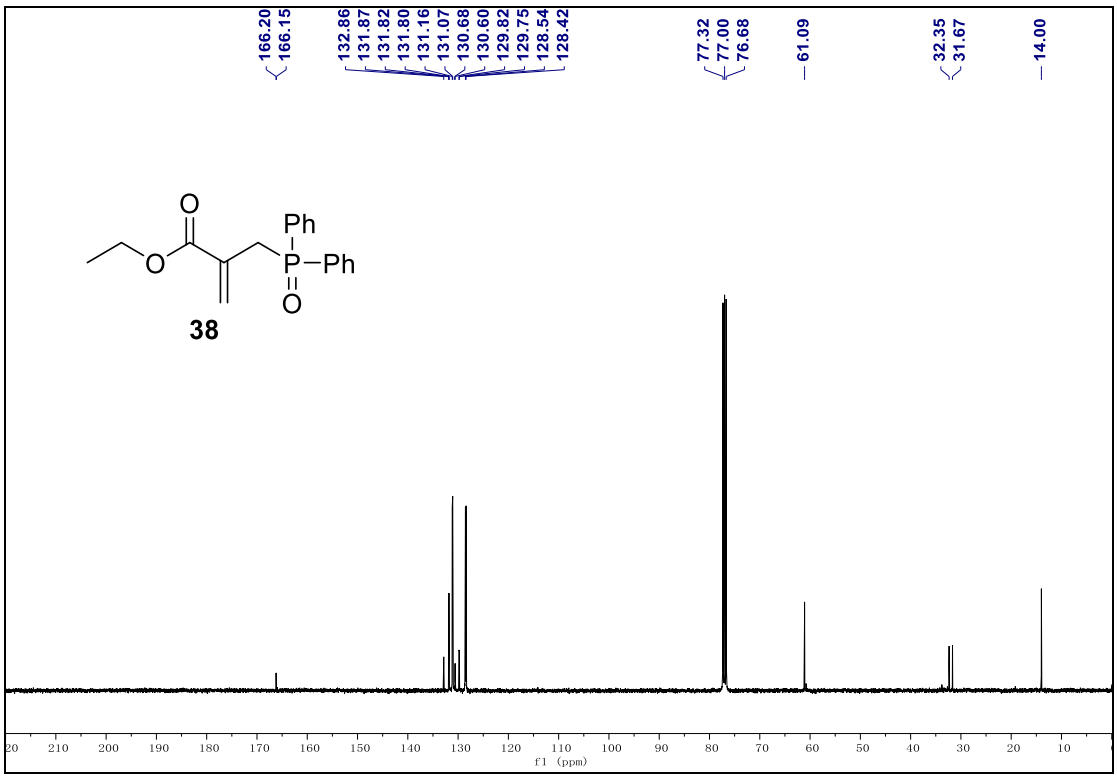


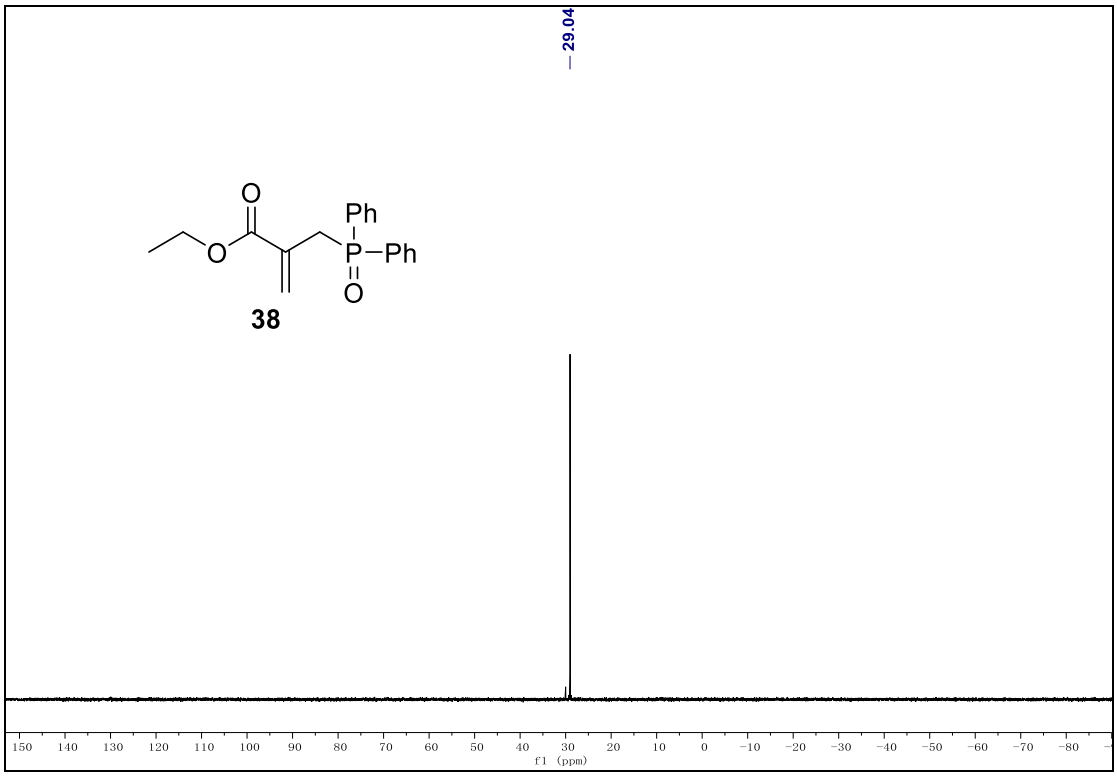



29.84
28.97
O
O
Ph
P
Ph
O
37
0.00
1.05
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

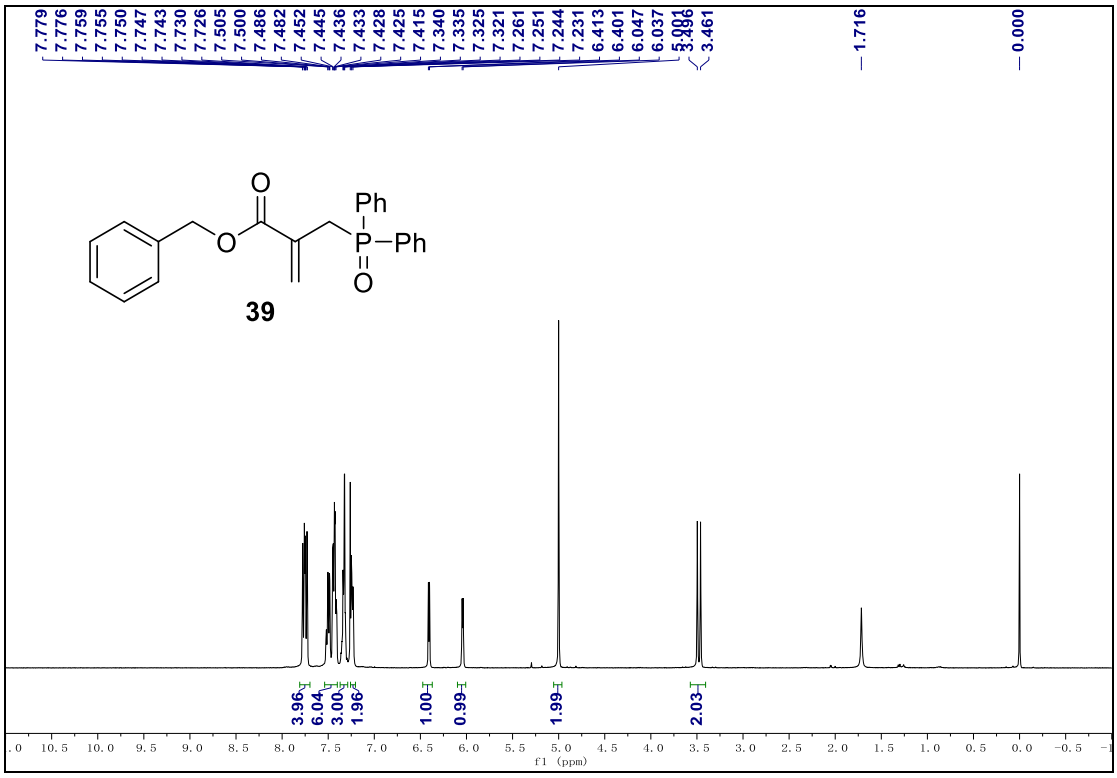
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 38.

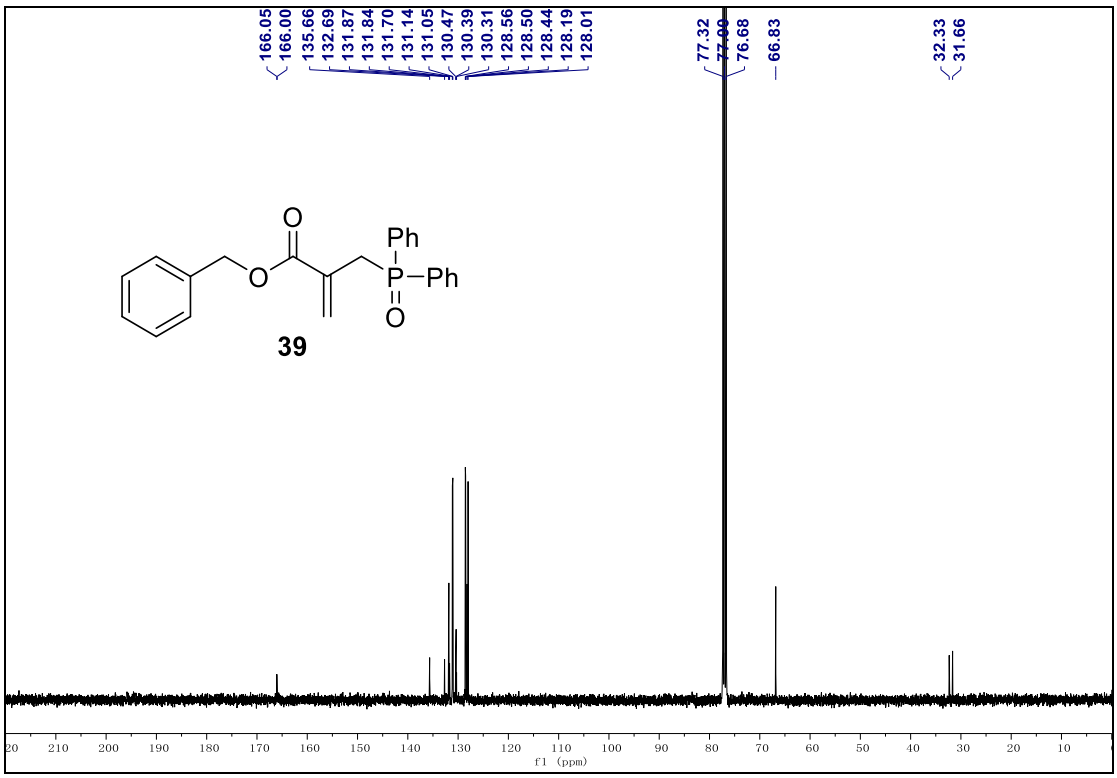


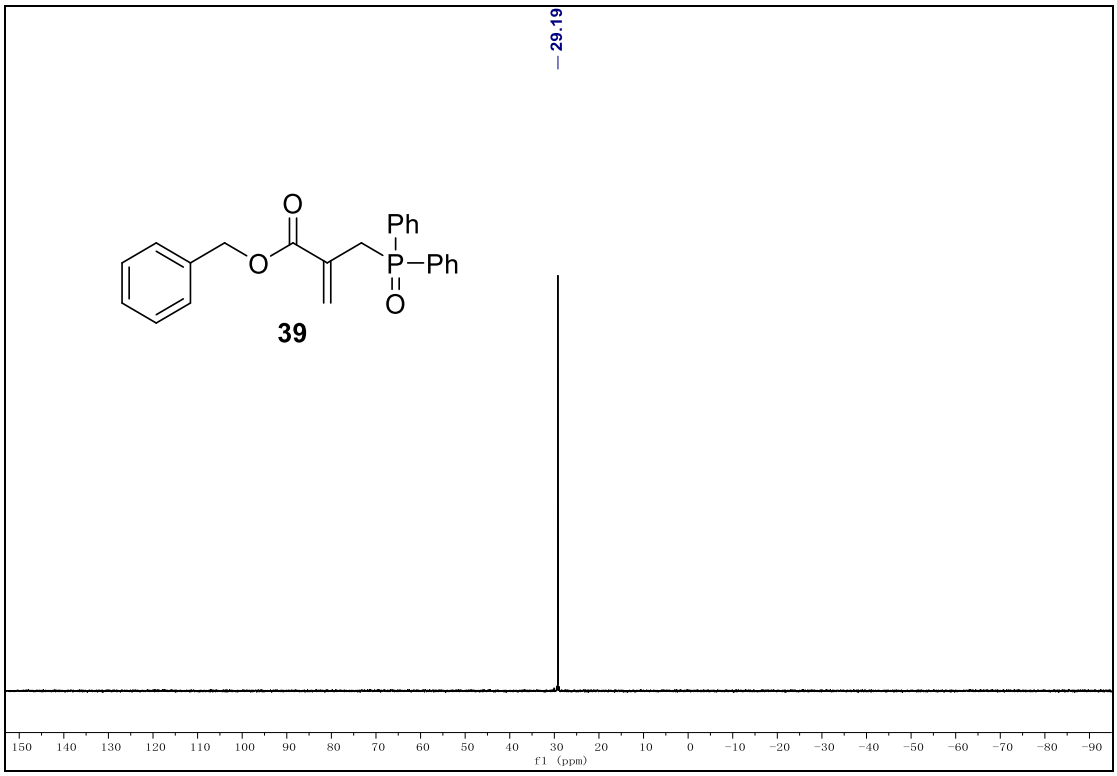



29.04
O
Ph
O
P
Ph
O
38
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

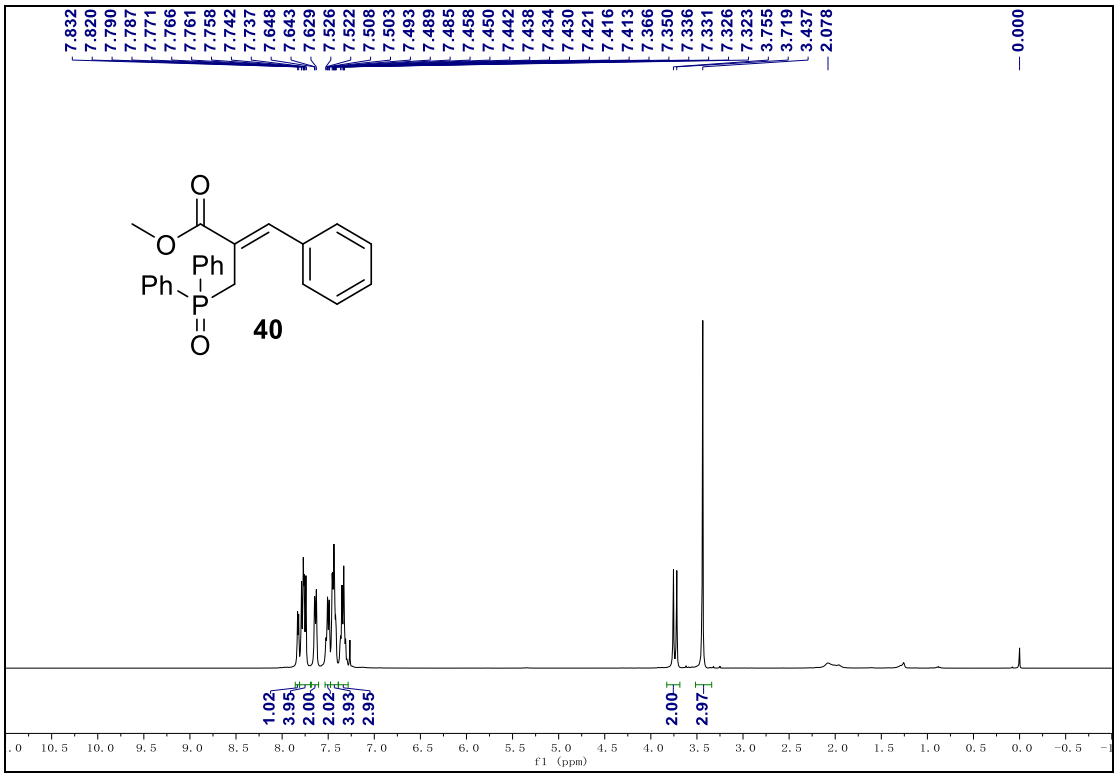
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 39.

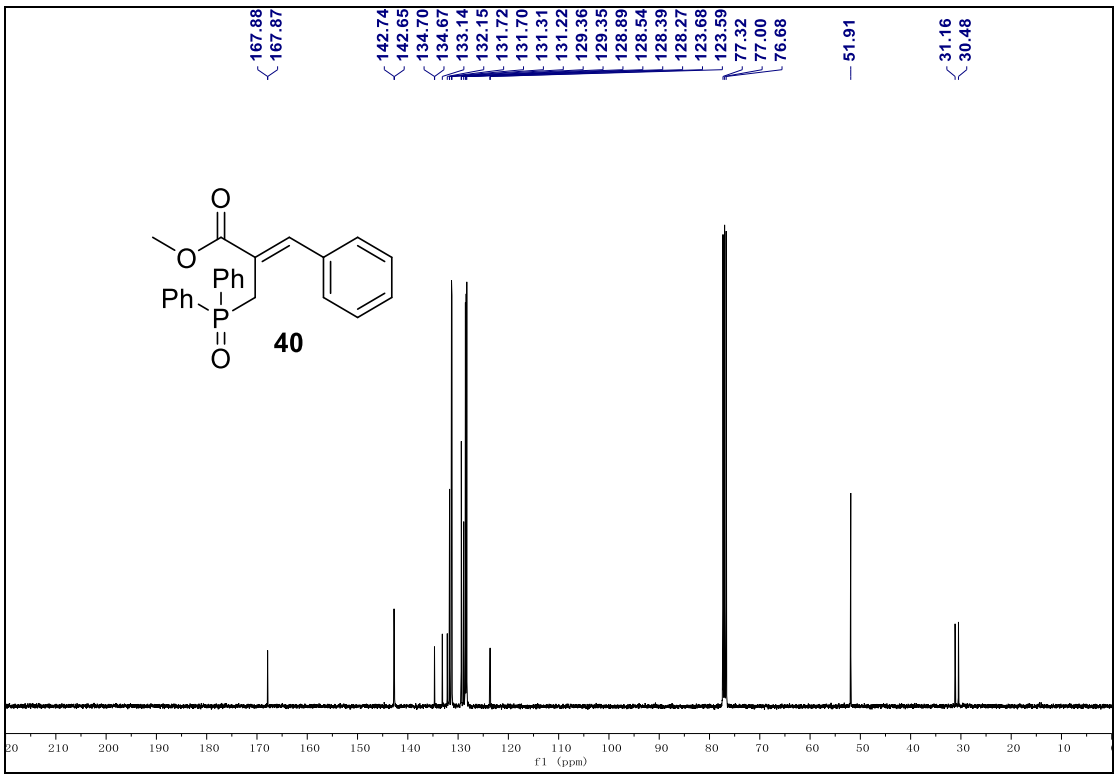


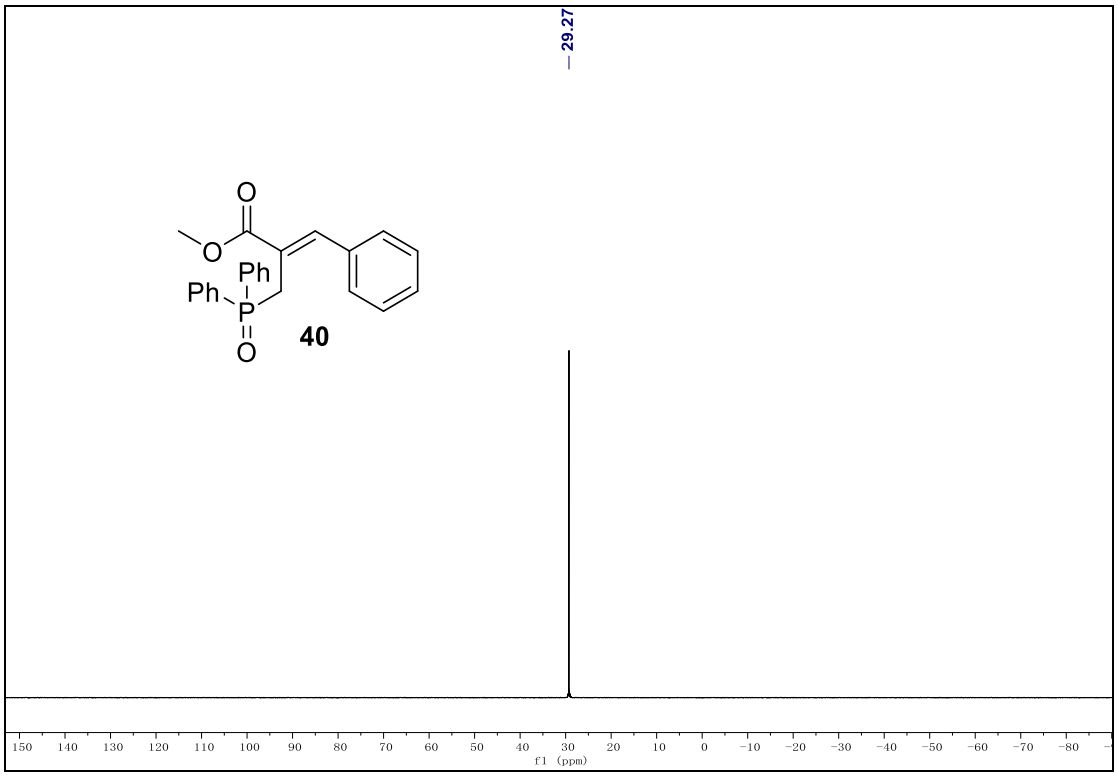



29.19
O
O
Ph
P
Ph
O
39
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

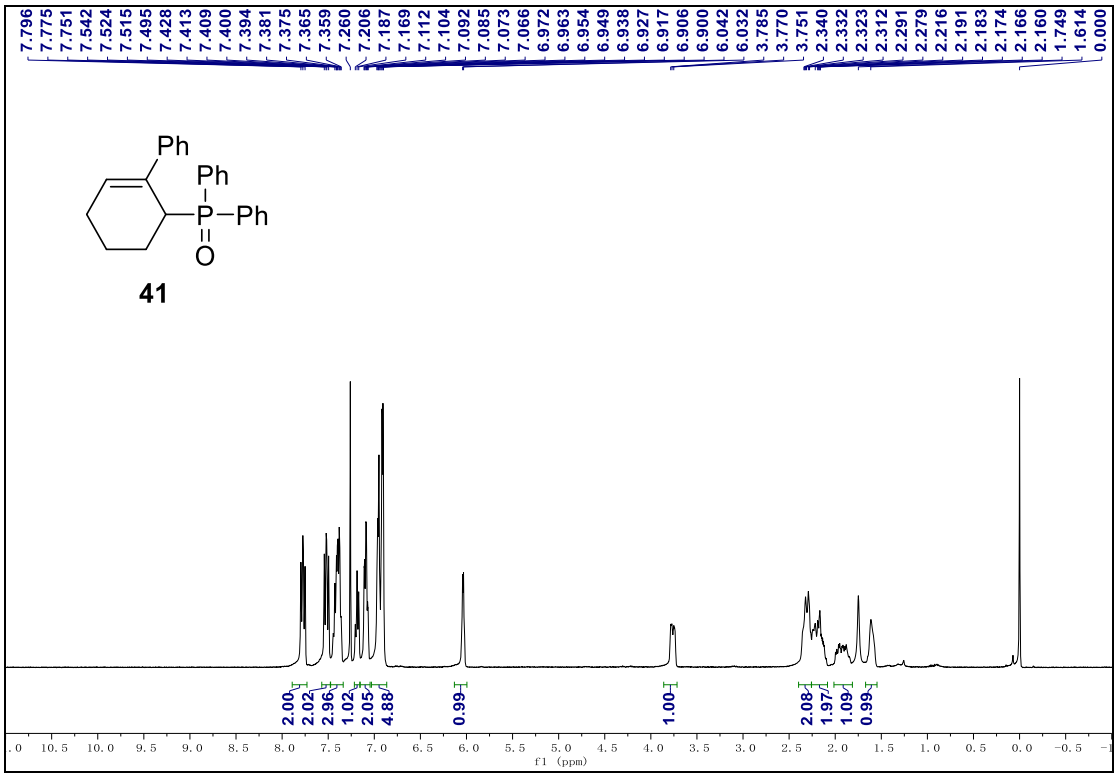
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 40.

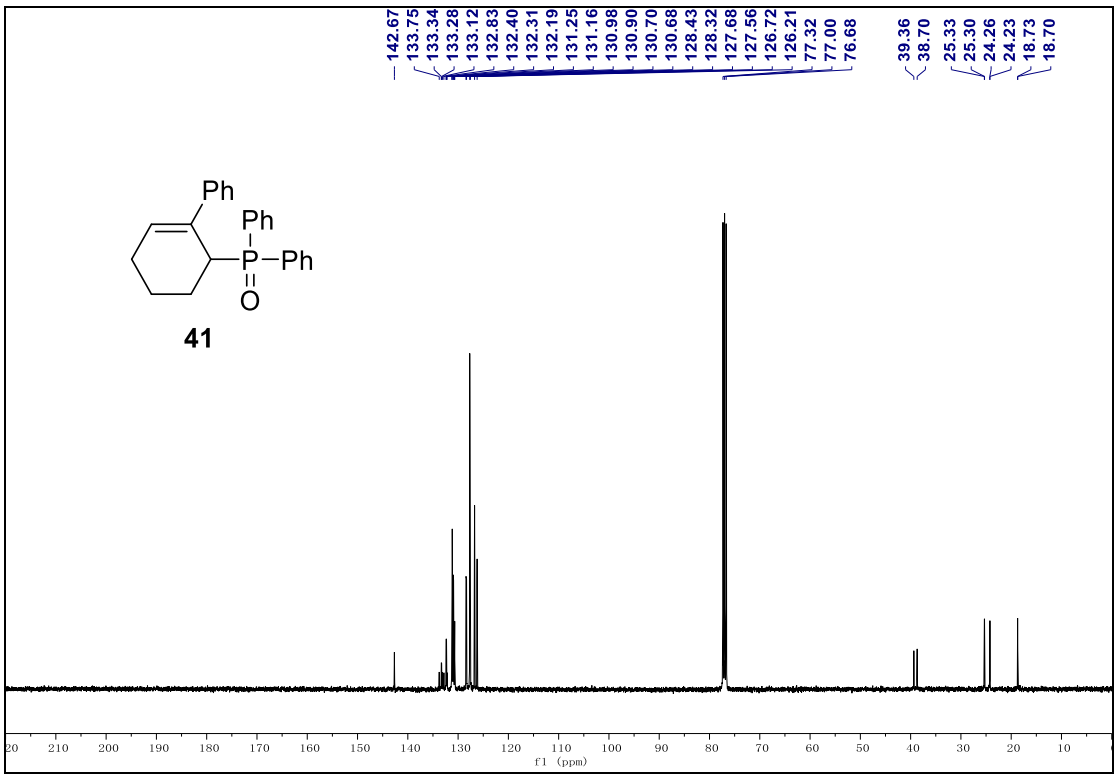


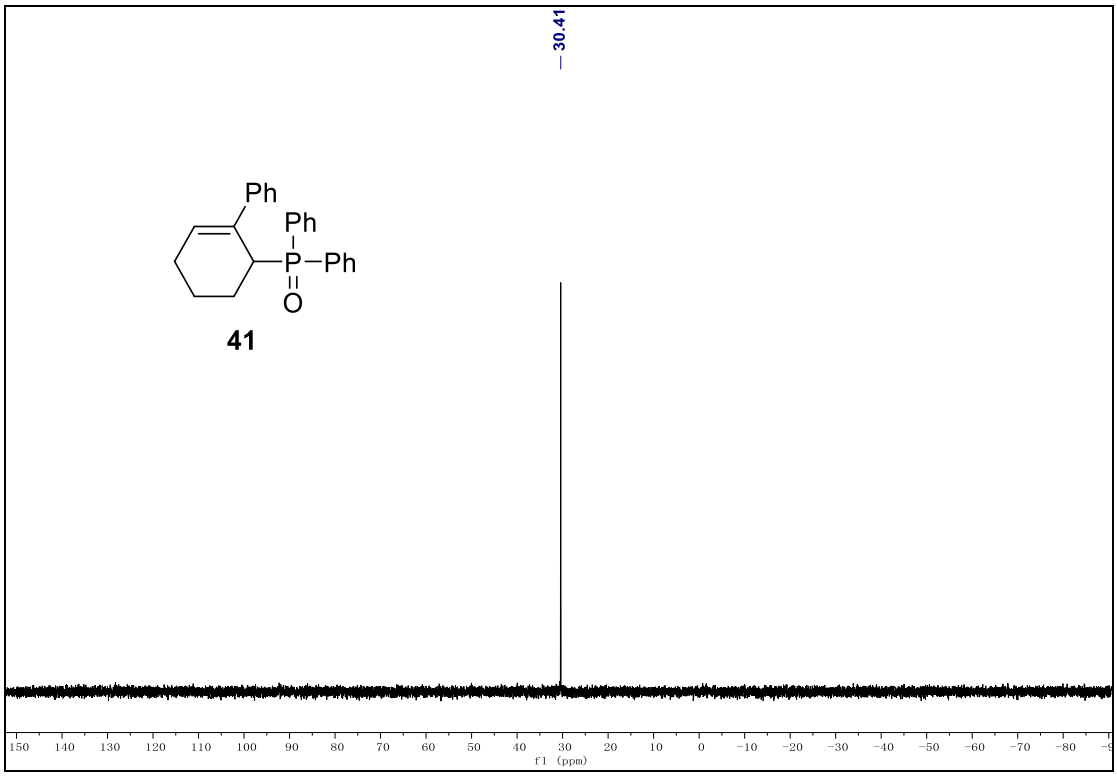



29.27
O
O
Ph
Ph
P
O
40
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

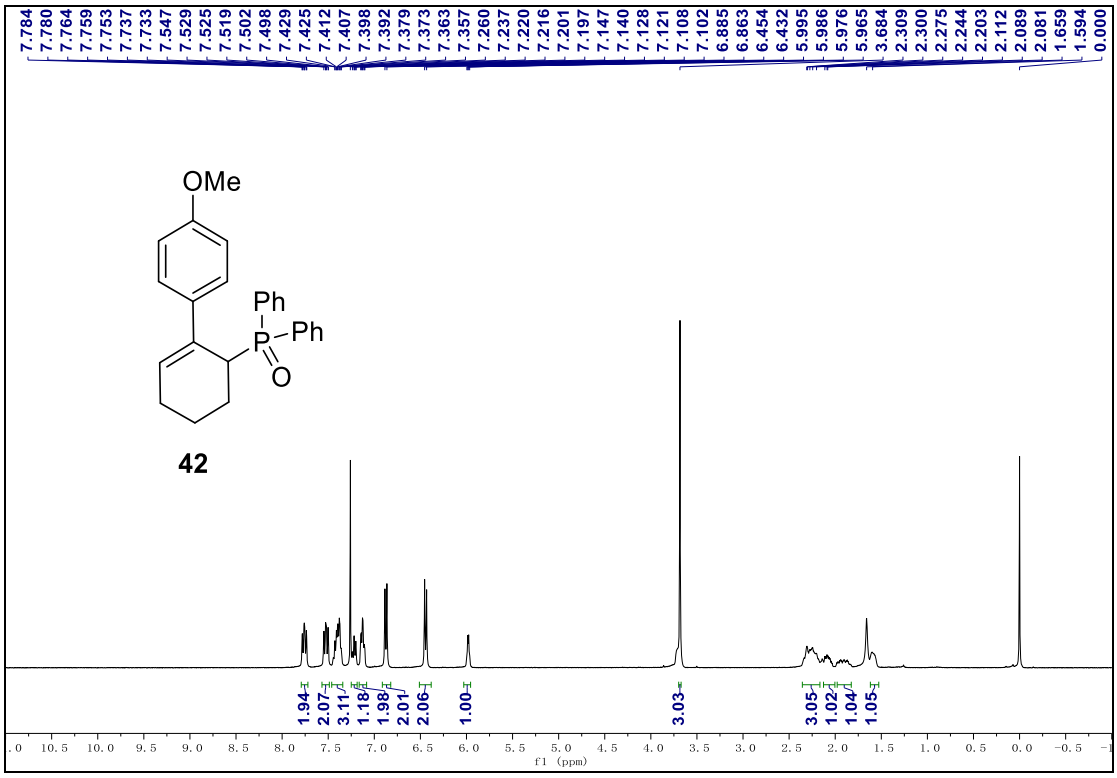
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 41.

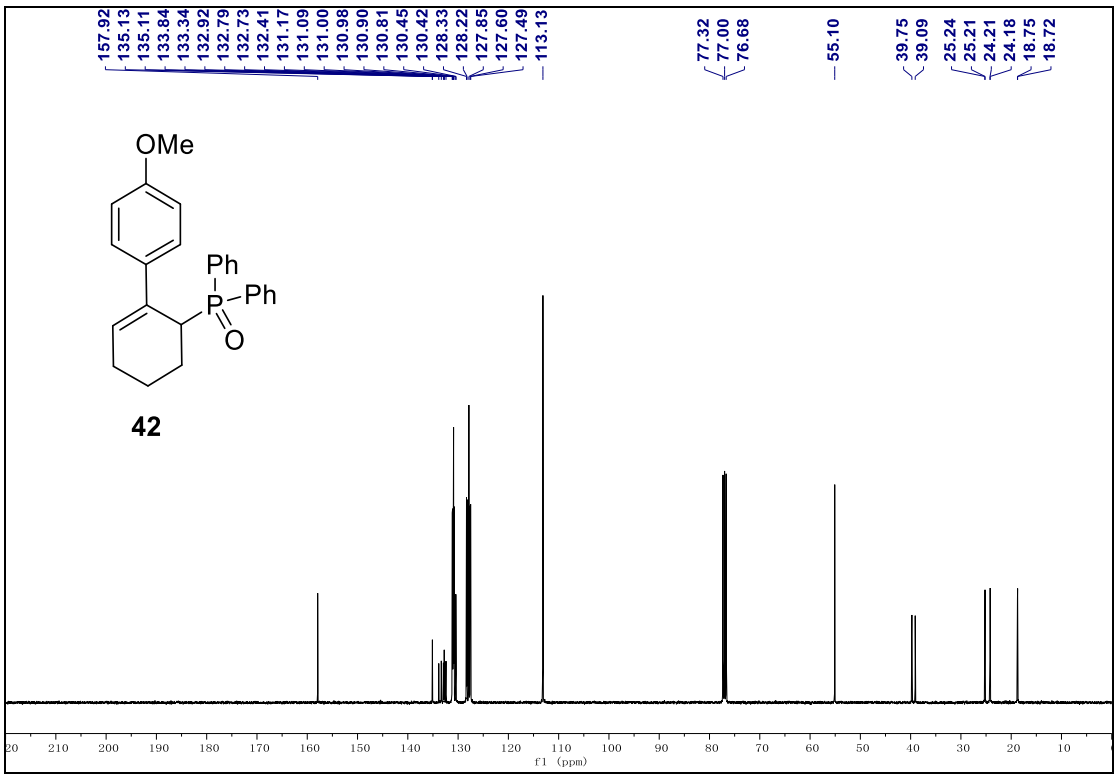


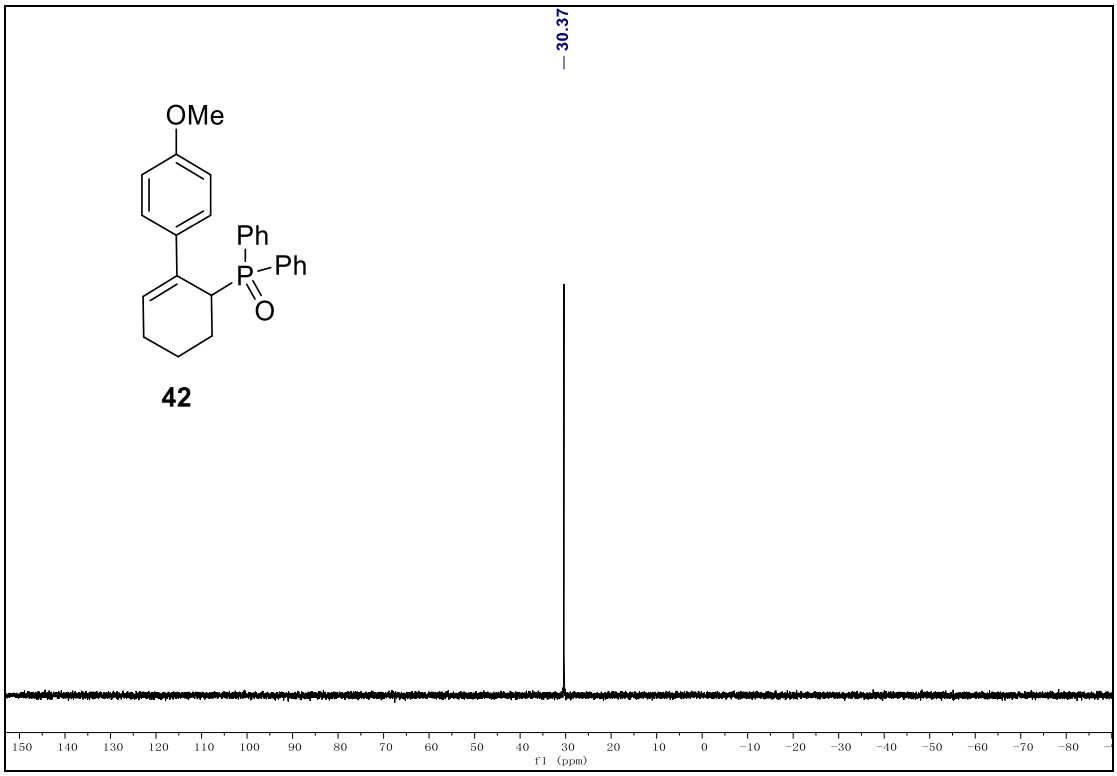



30.41
Ph
Ph
P
Ph
O
41
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

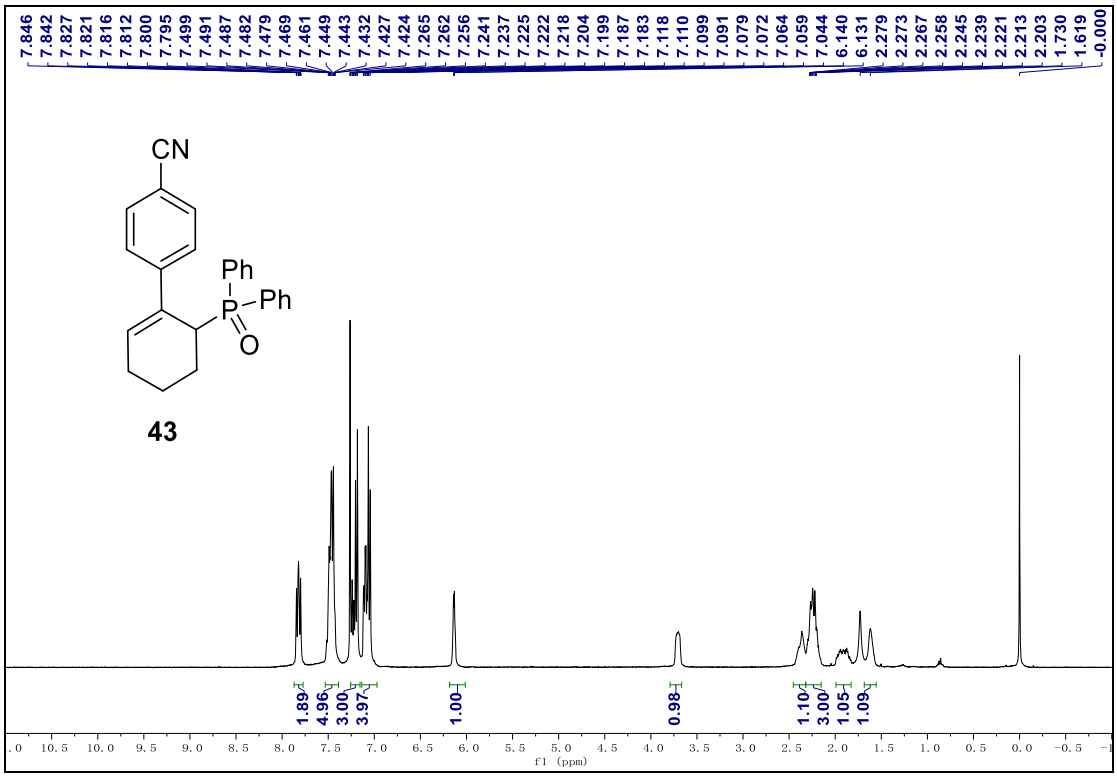
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 42.

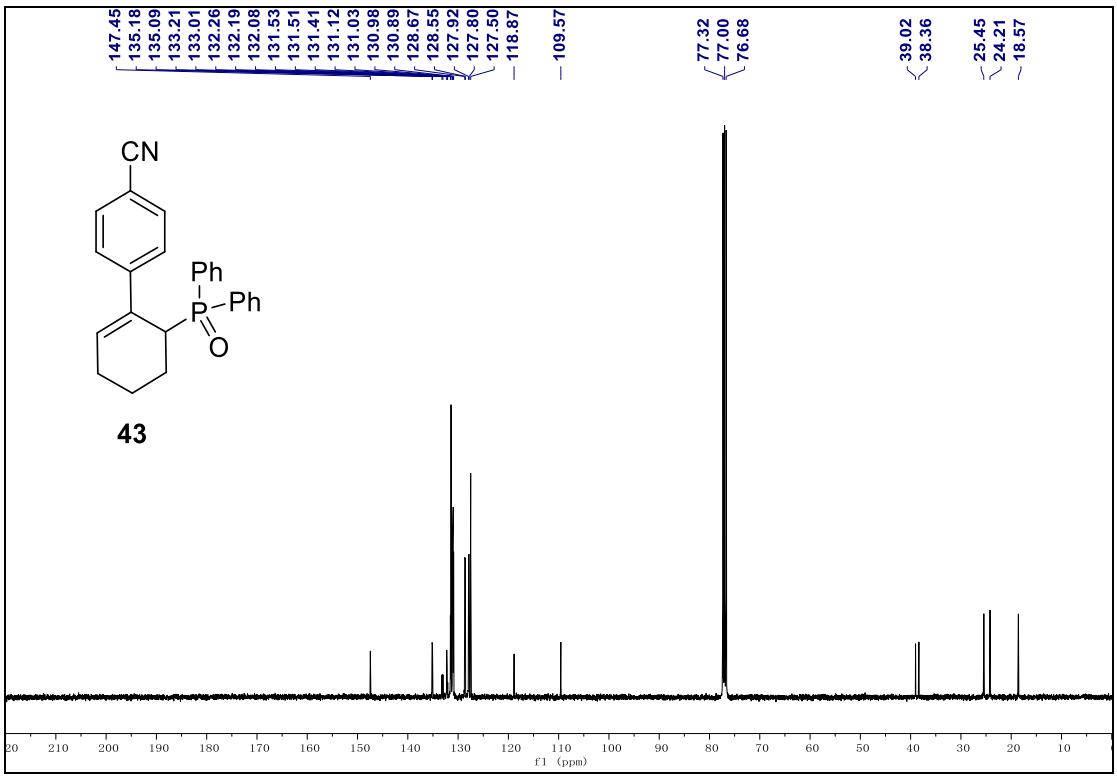


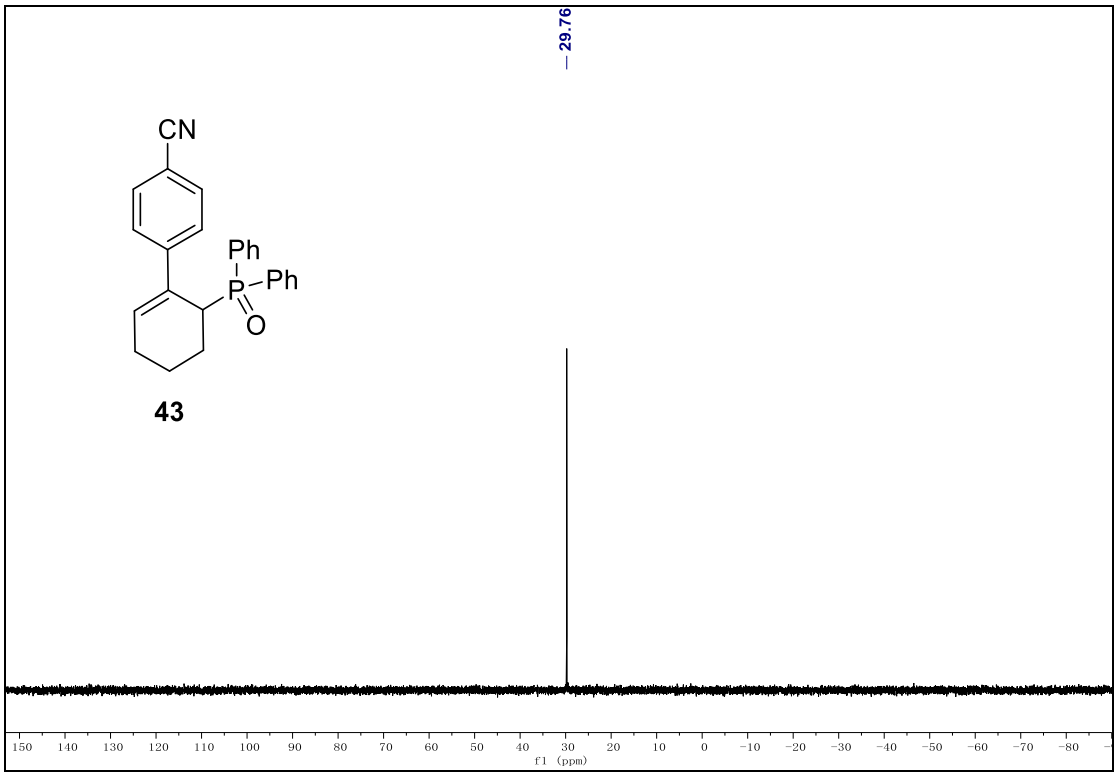



30.37
OMe
Ph
P
Ph
O
42
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

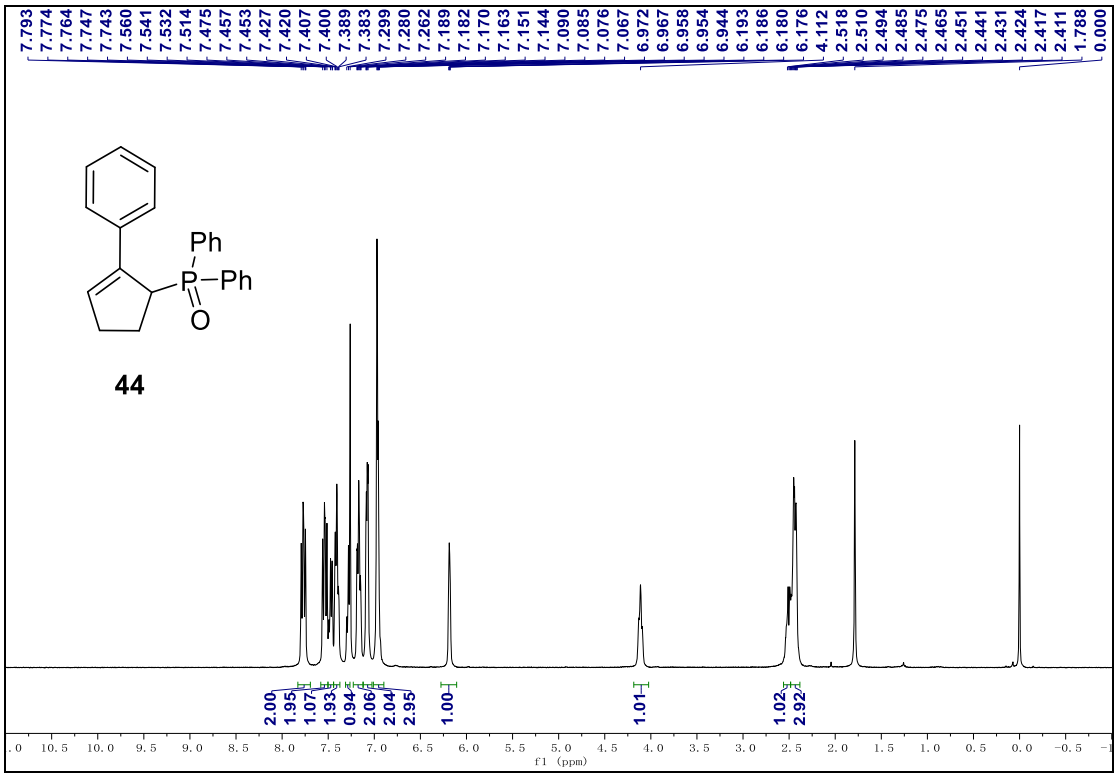
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 43.

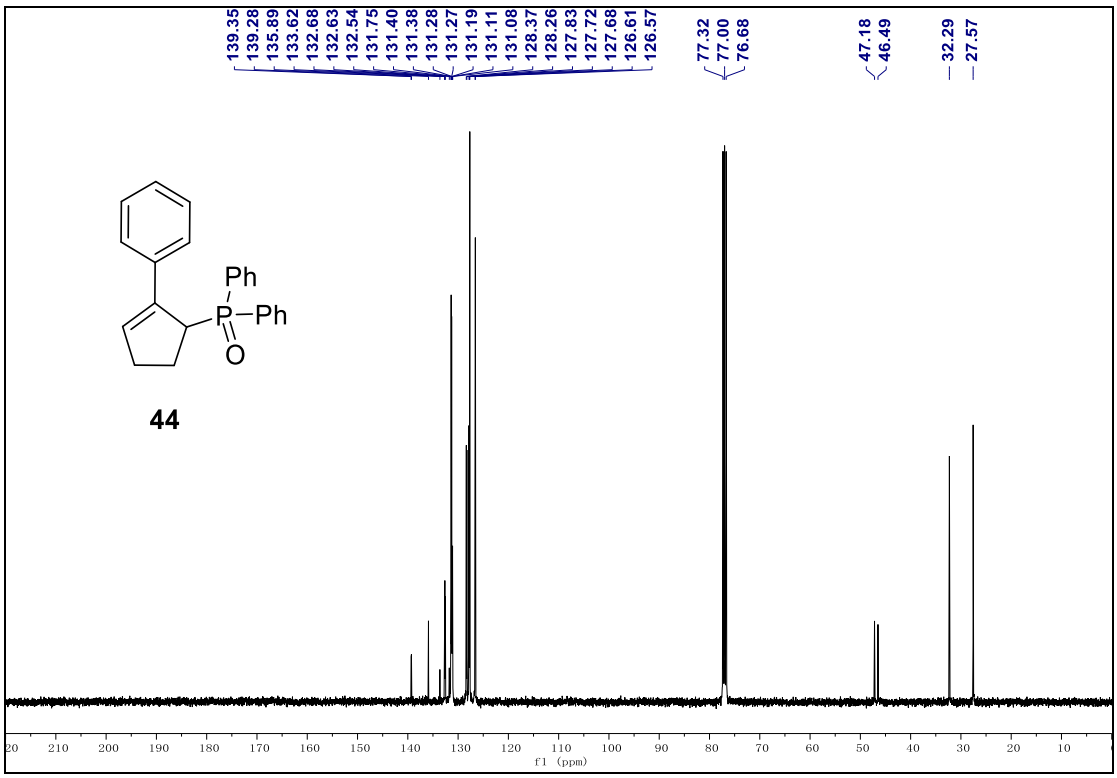


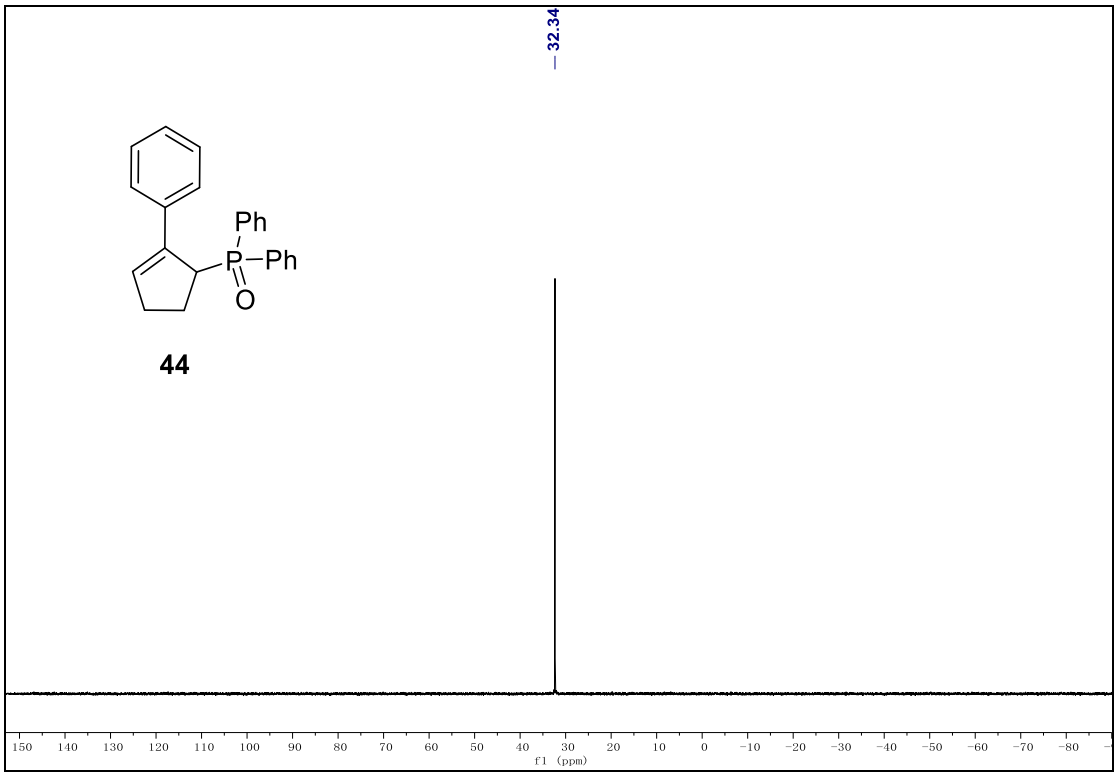



29.76
CN
Ph
P
Ph
O
43
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

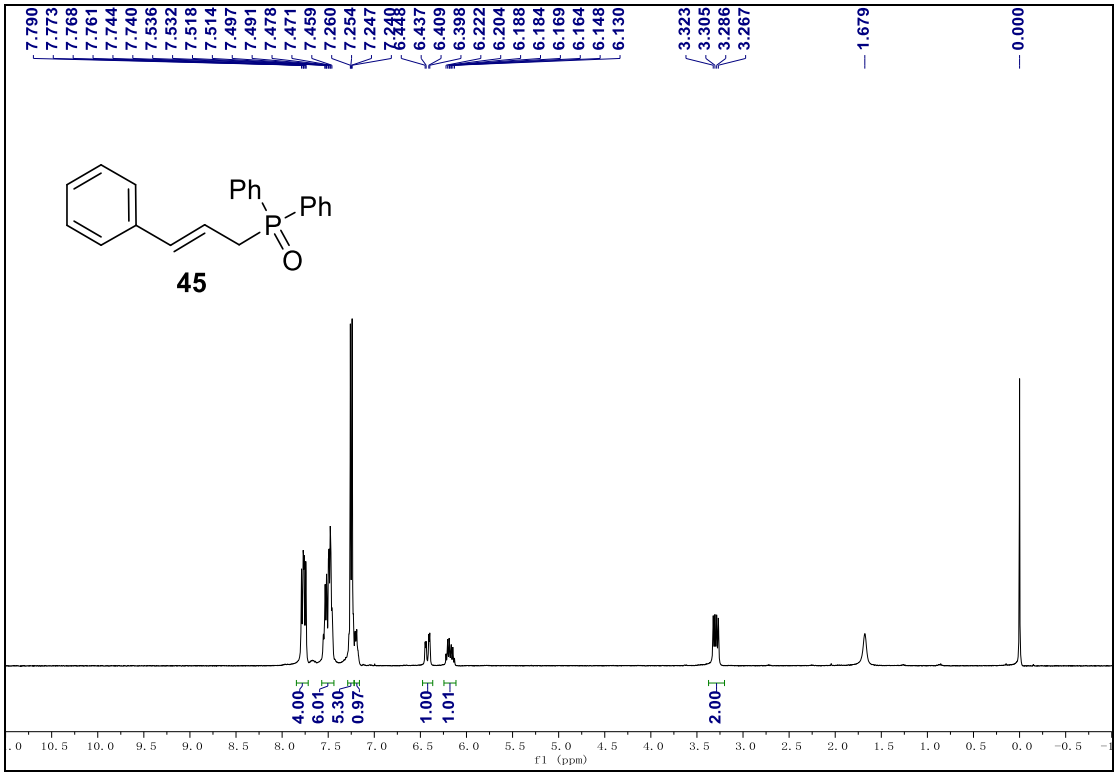
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 44.

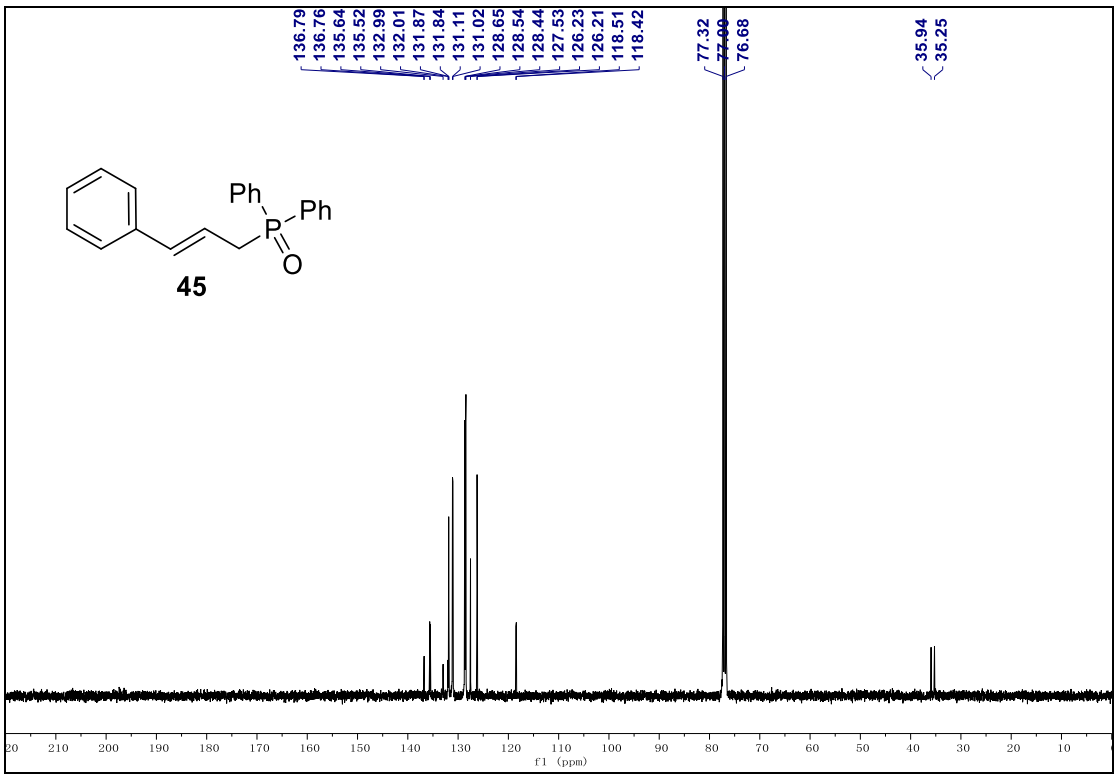


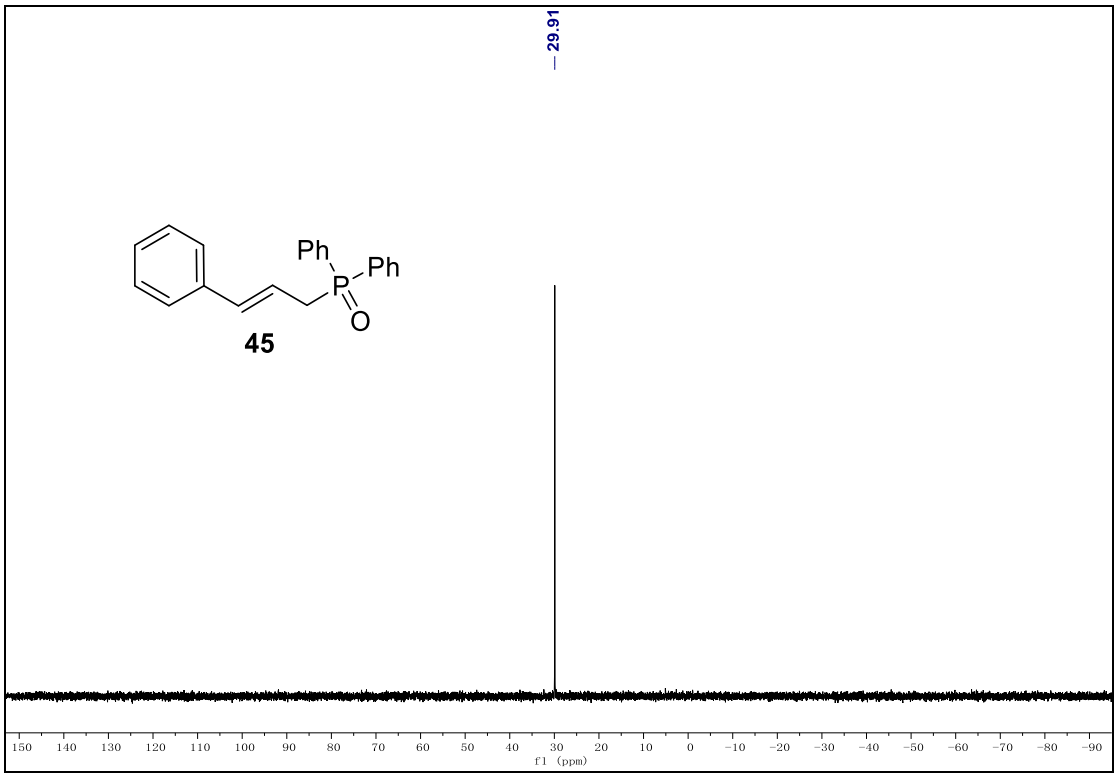



32.34
Ph
P
Ph
O
44
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

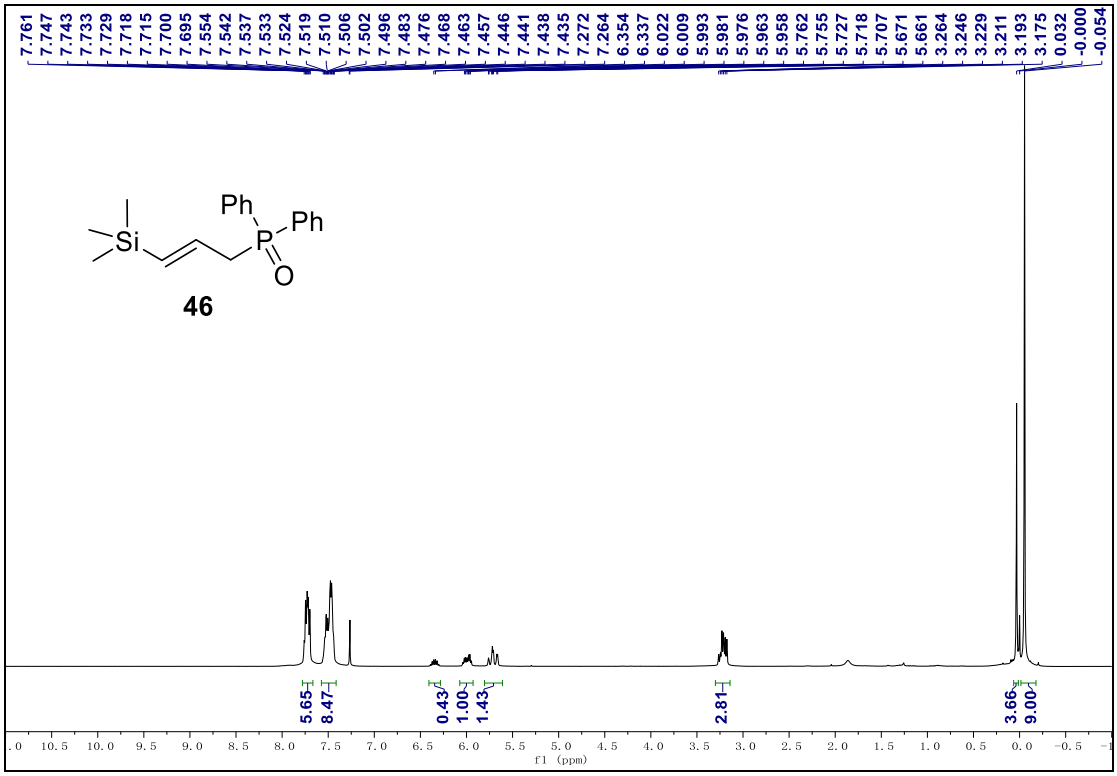
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 45.

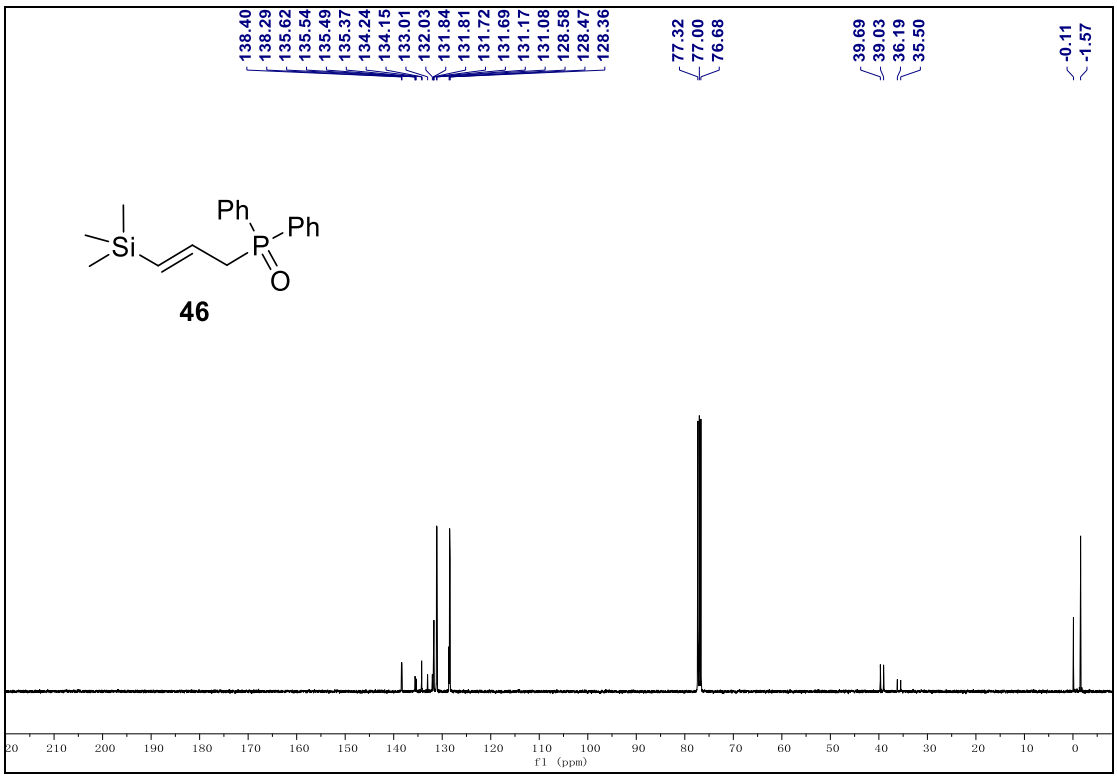


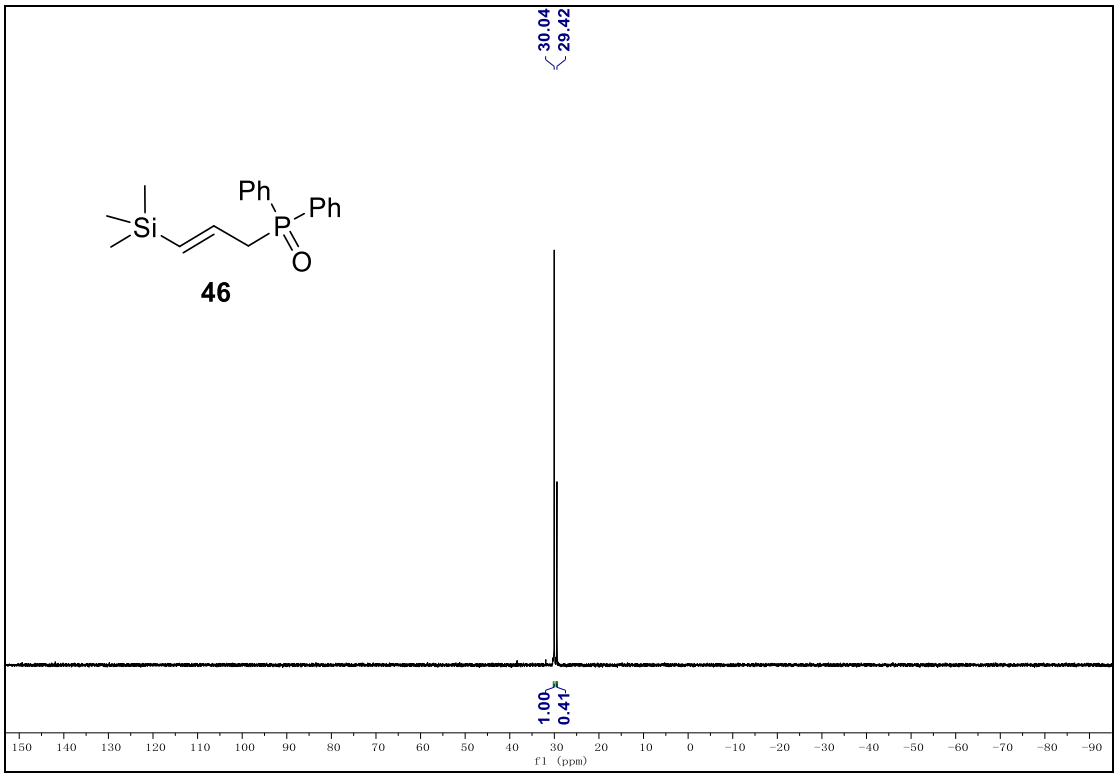



29.91
Ph
Ph
P
O
45
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

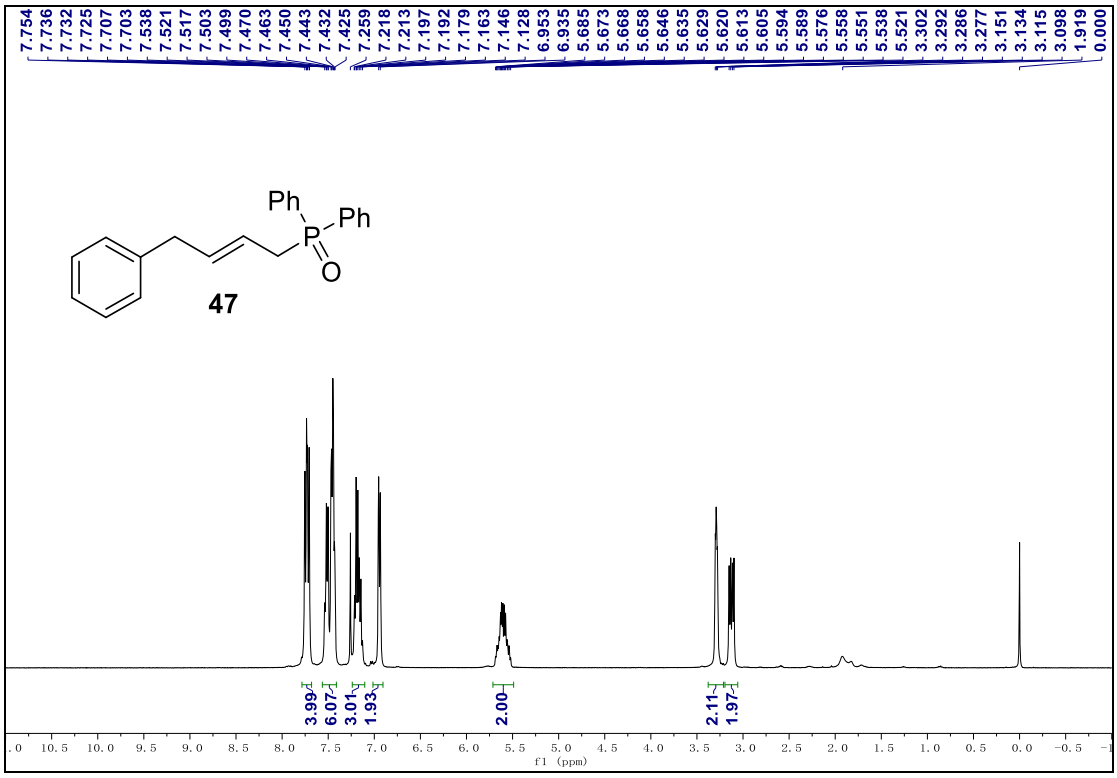
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 46.

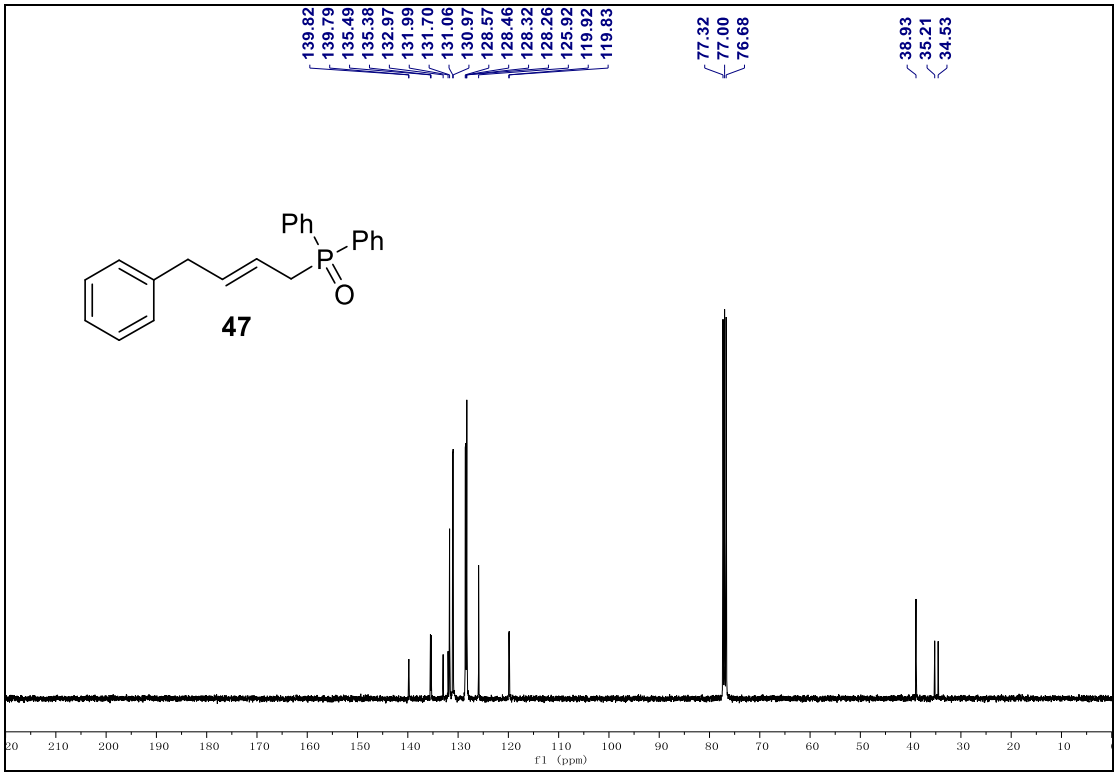


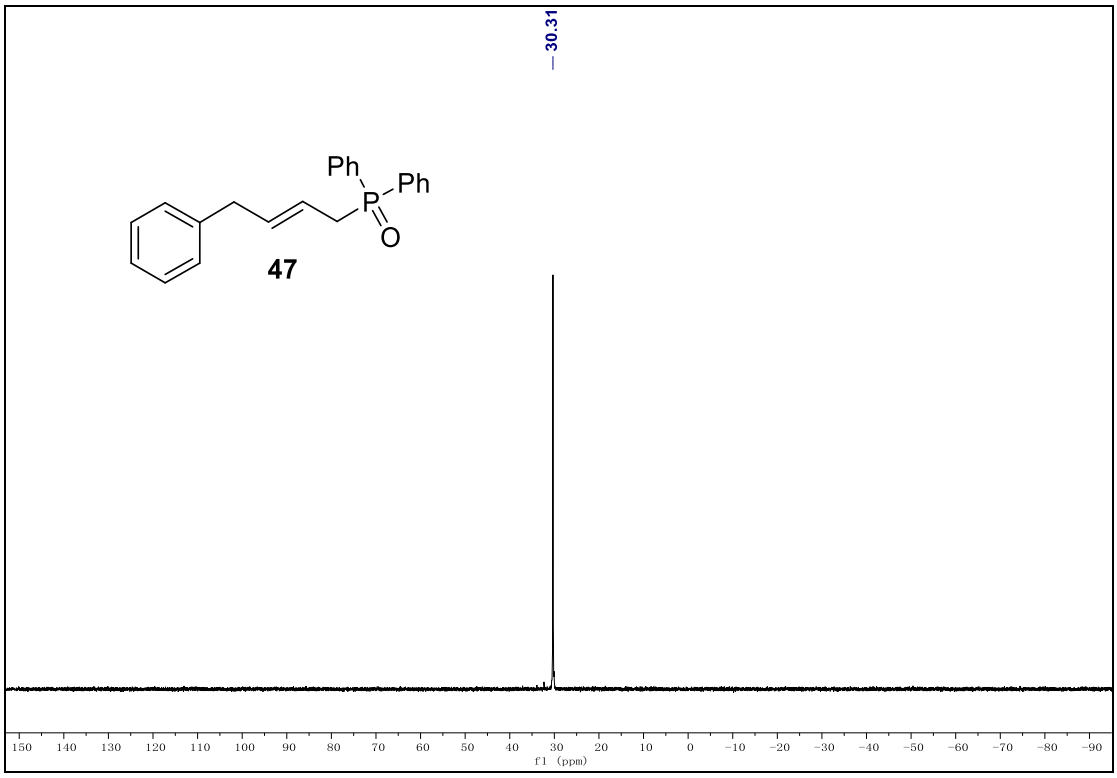



30.04
29.42
Ph
Ph
Si
P
O
46
1.00
0.41
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

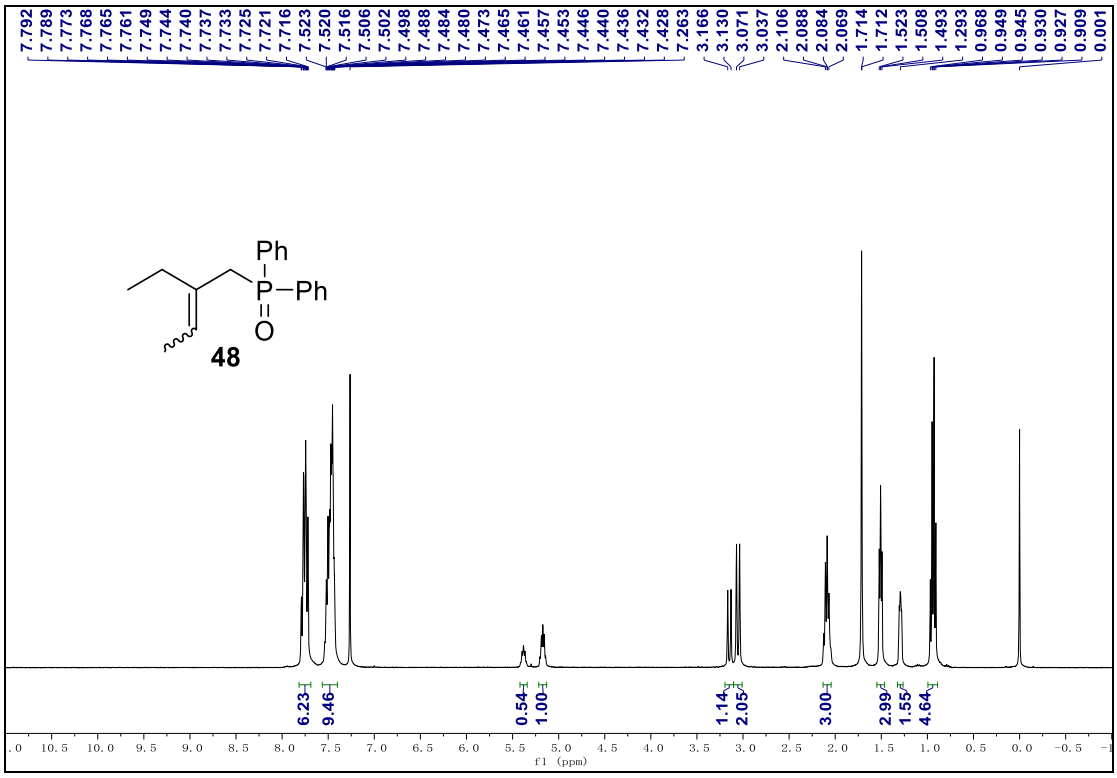
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 47.

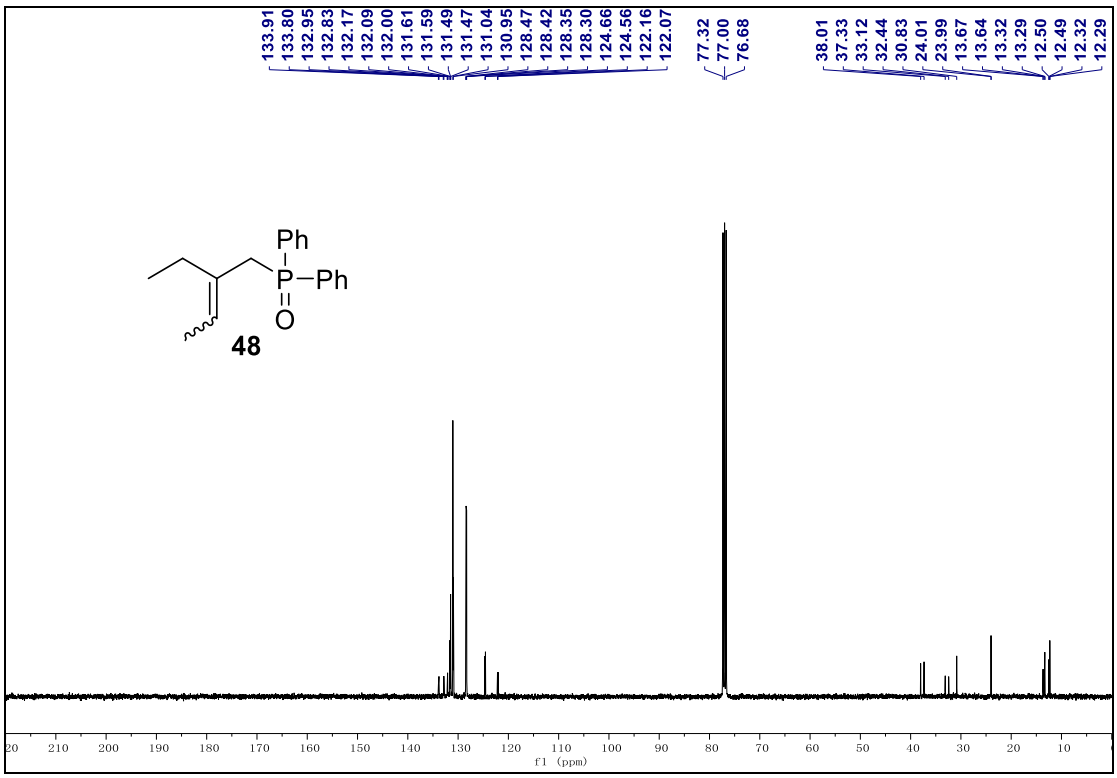


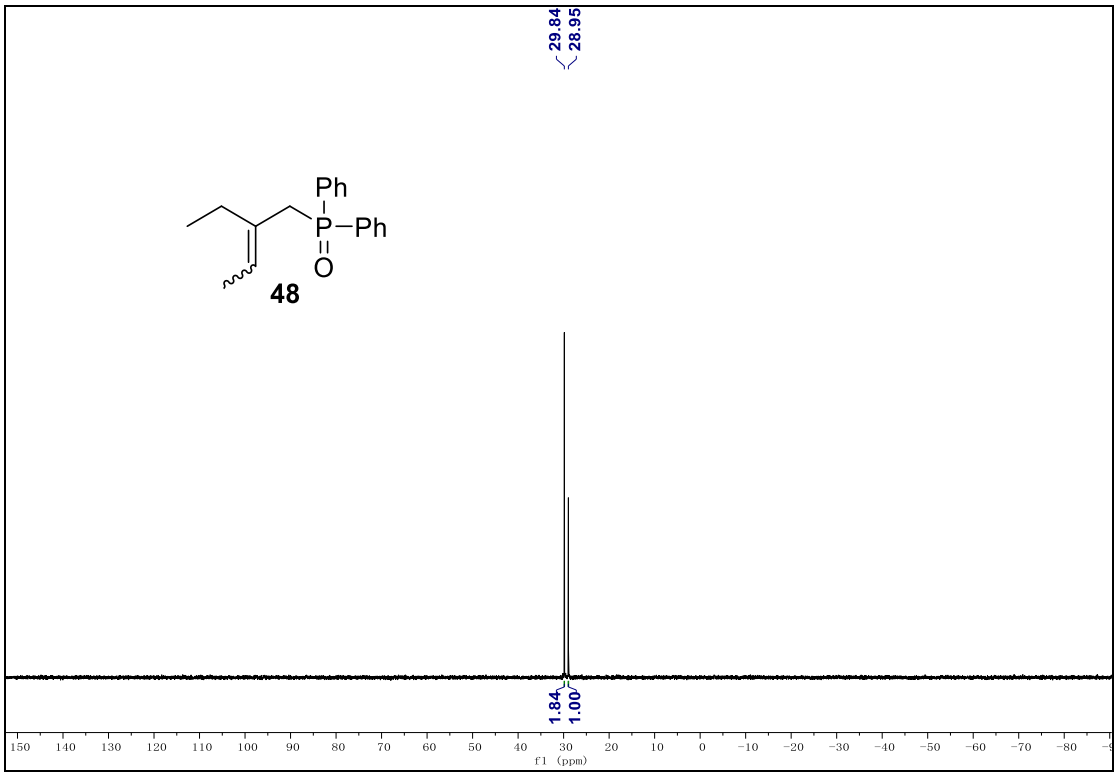



30.31
Ph
Ph
P
O
47
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

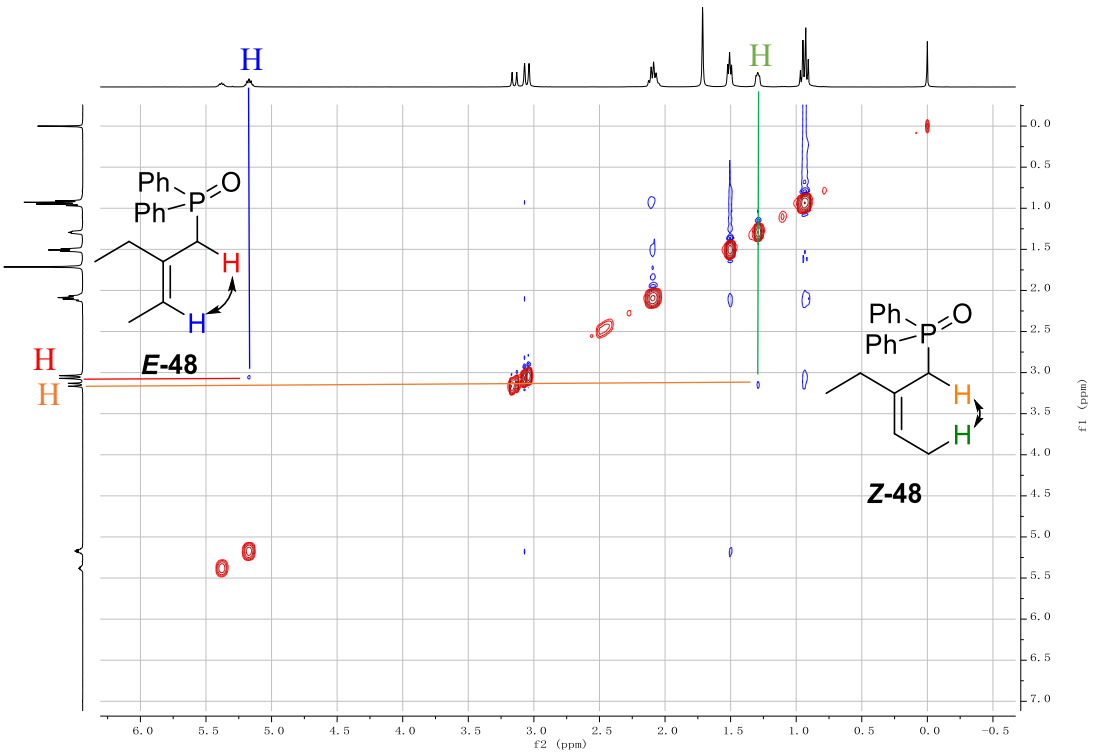
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 48.



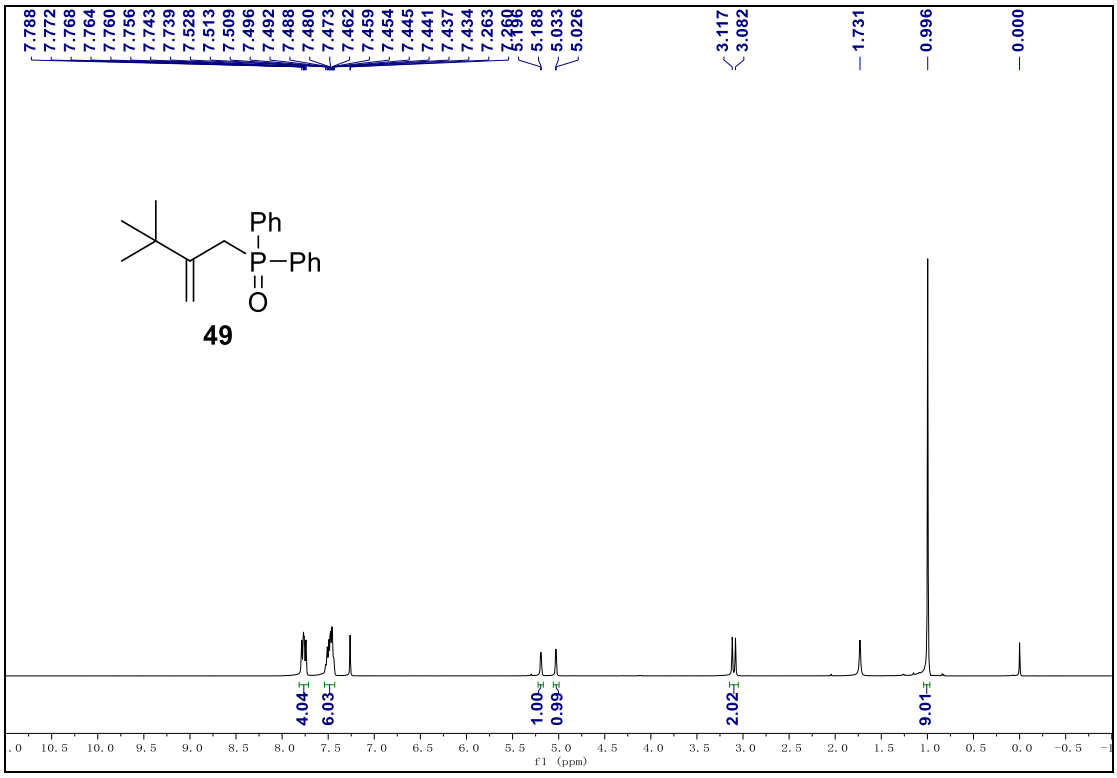


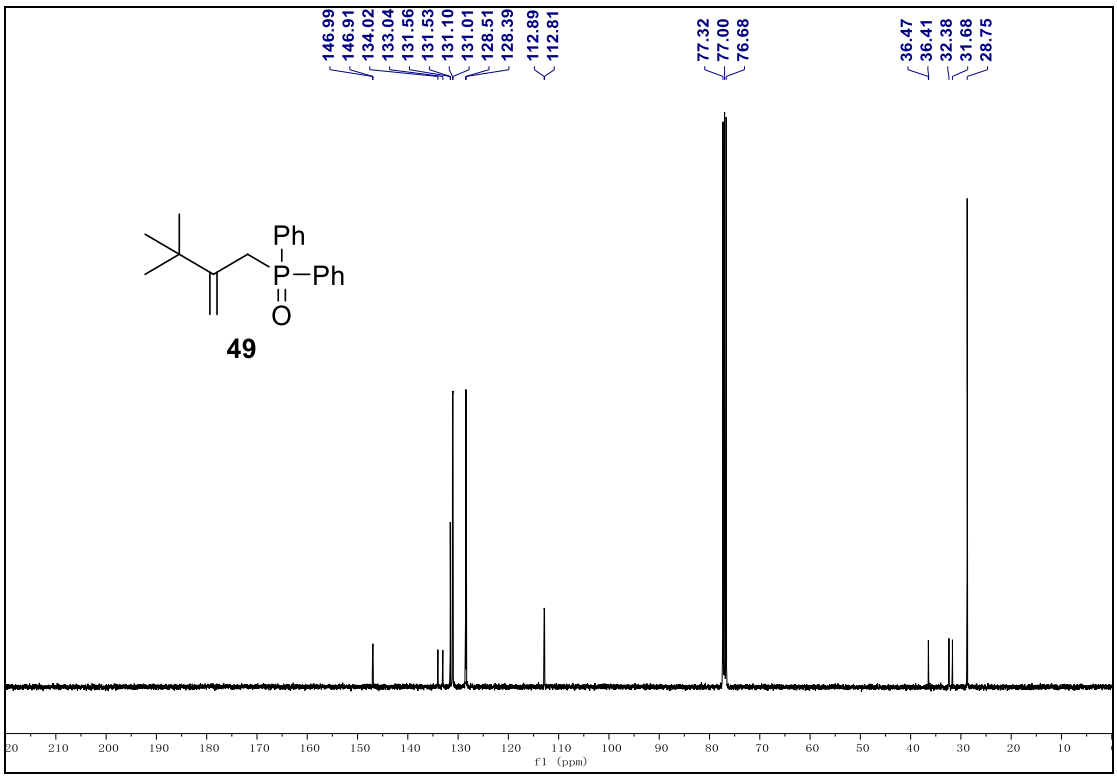


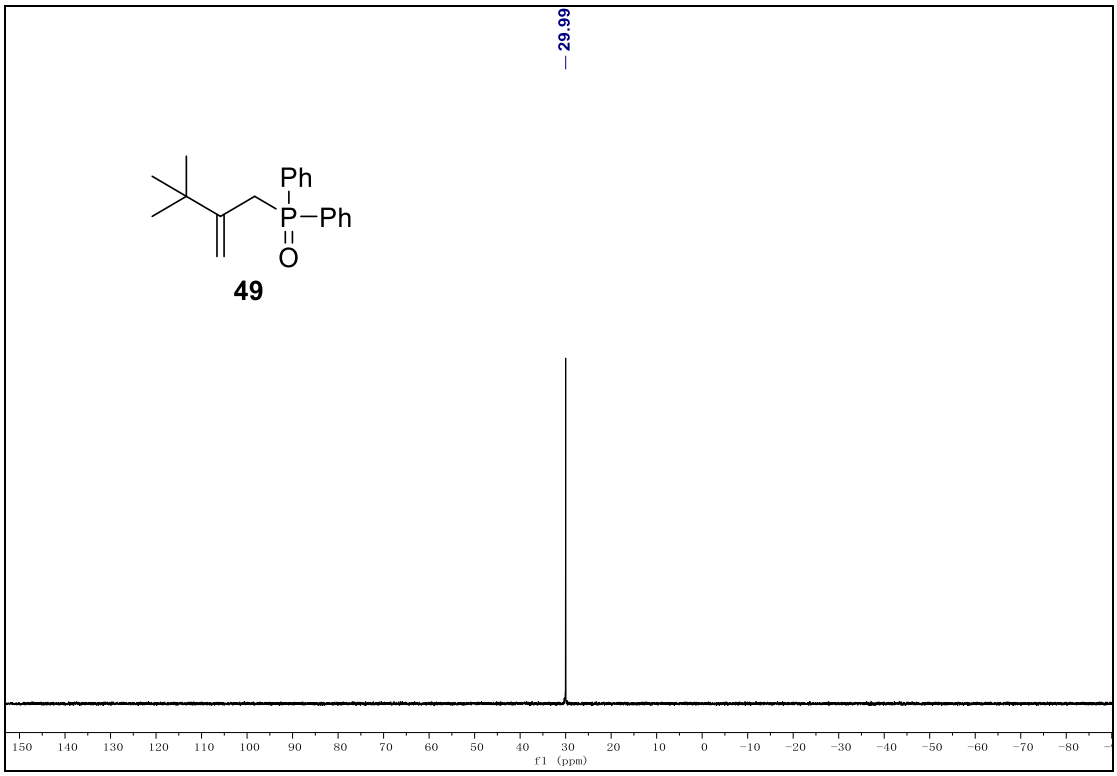
NOESY spectrum of 48



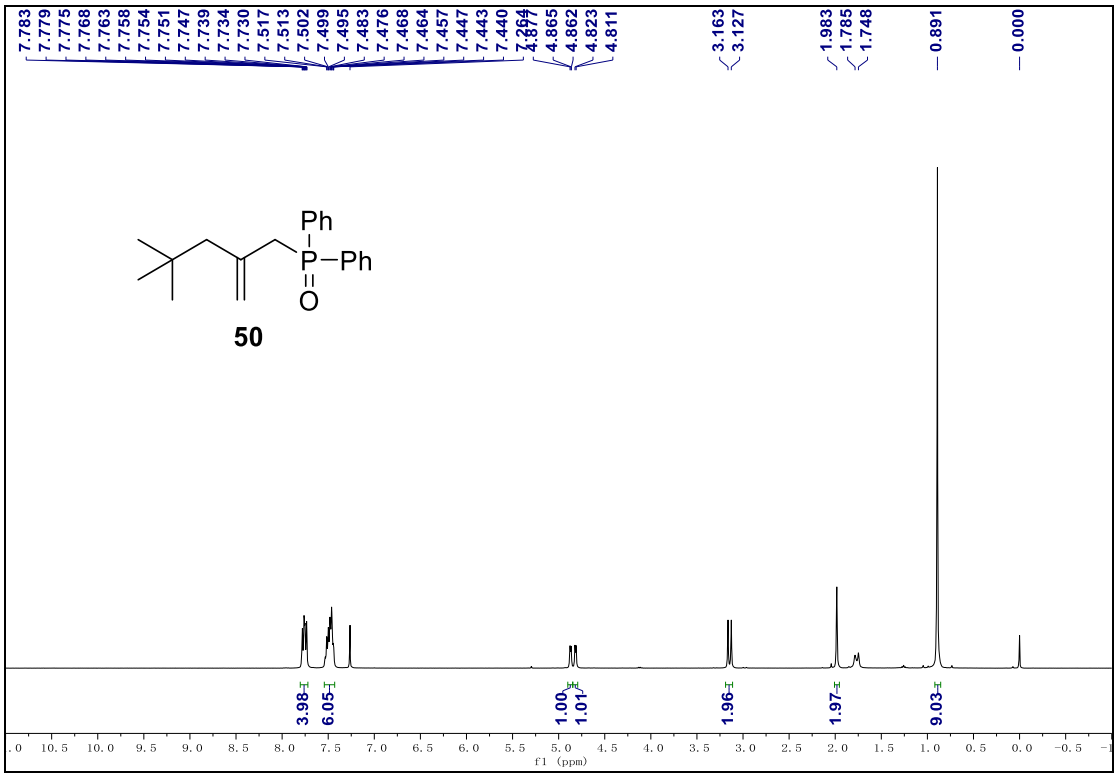
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 49.

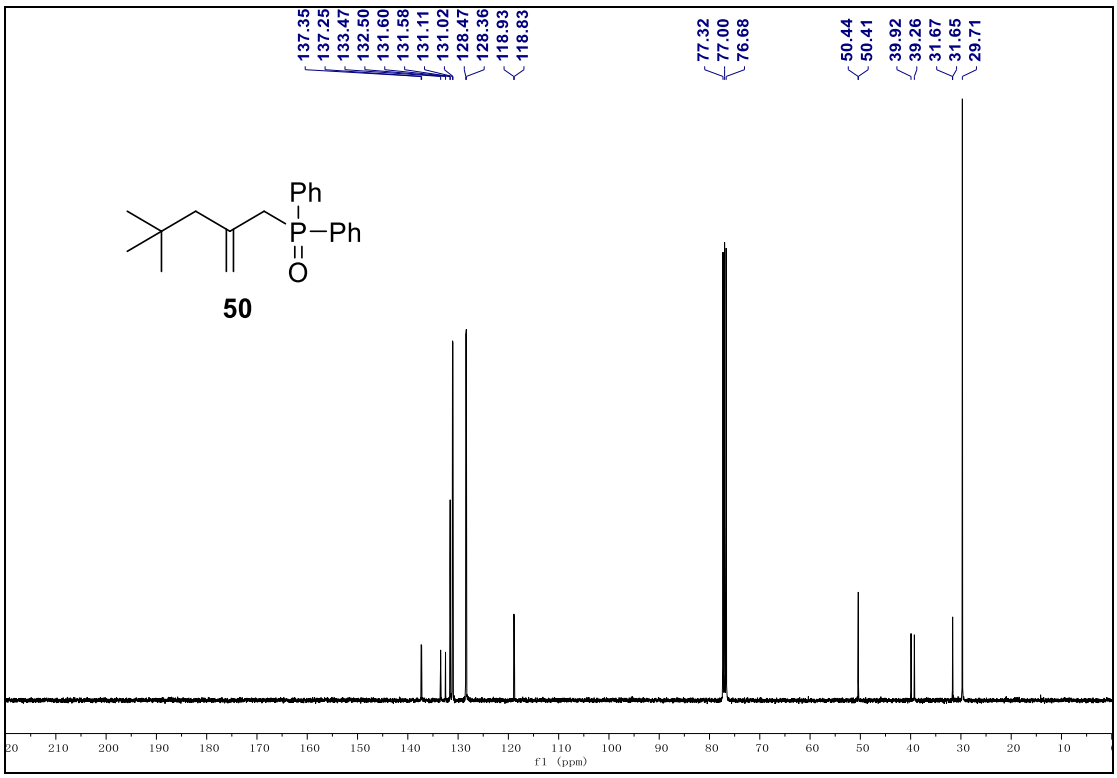


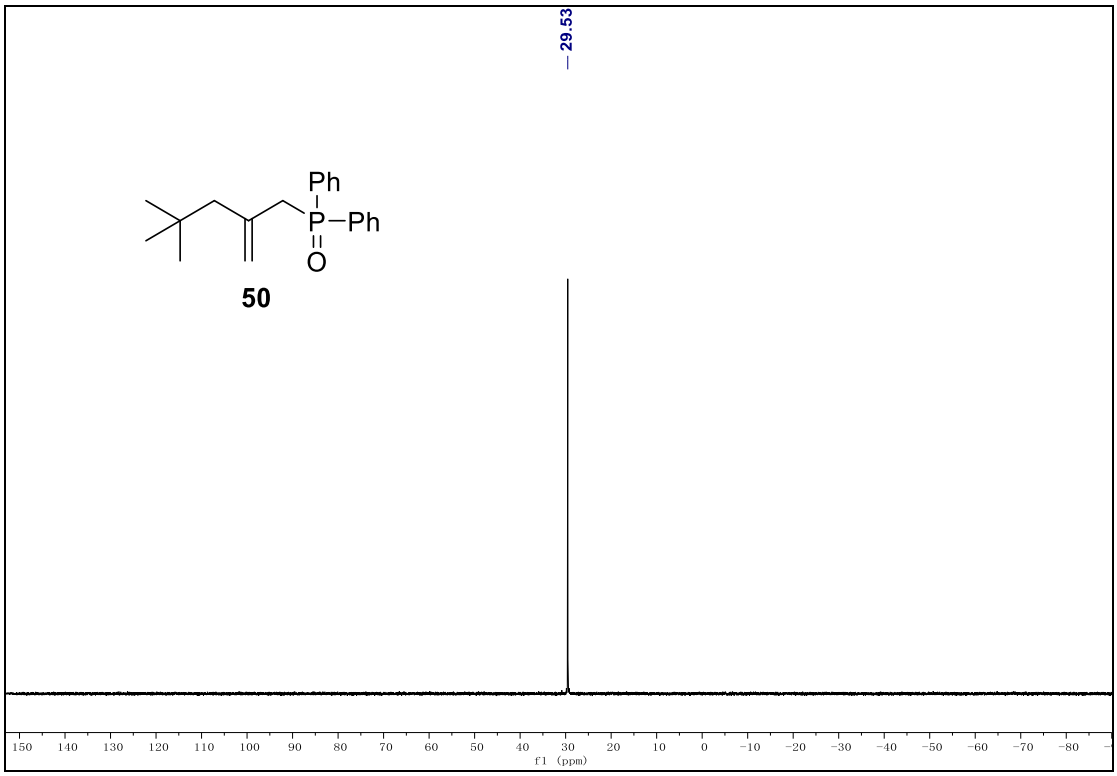



29.99
Ph
P
Ph
O
49
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

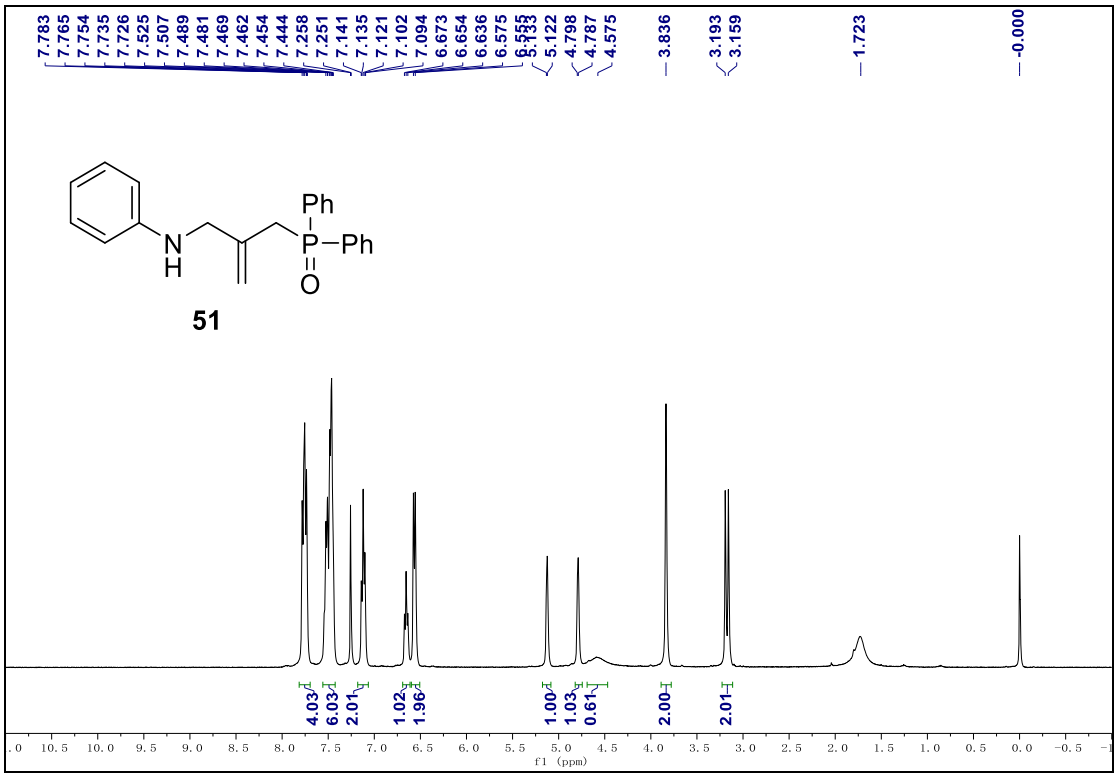
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 50.

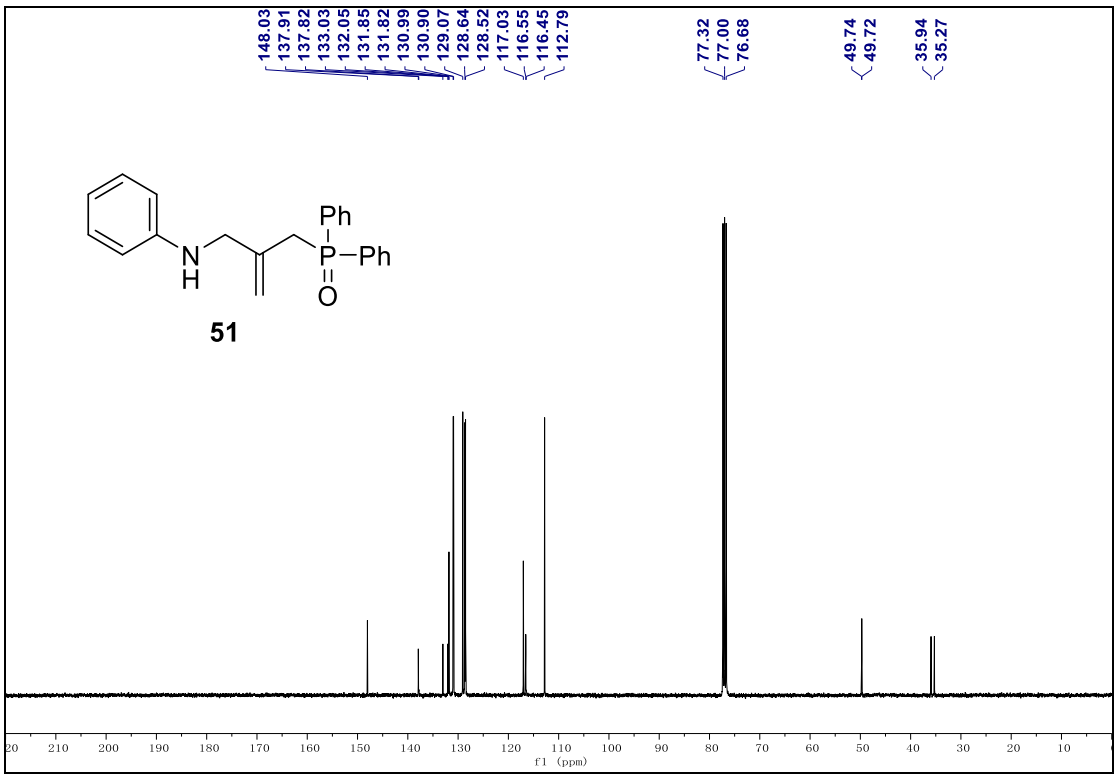


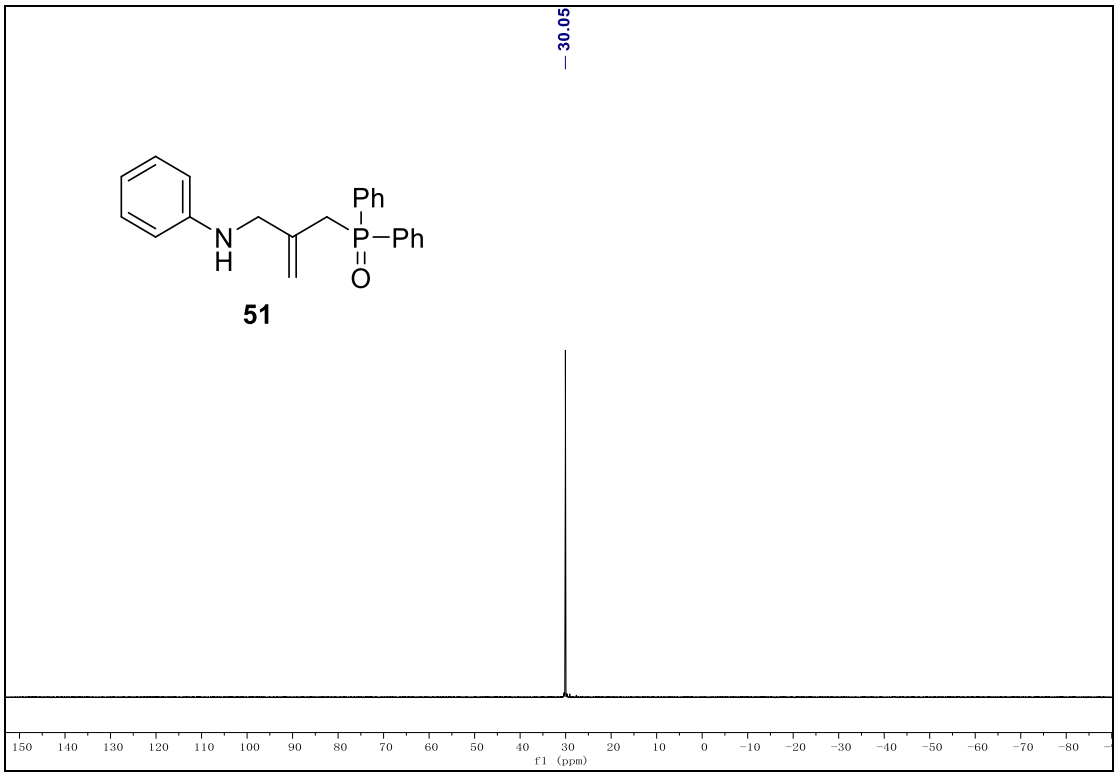



29.53
Ph
P
Ph
O
50
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

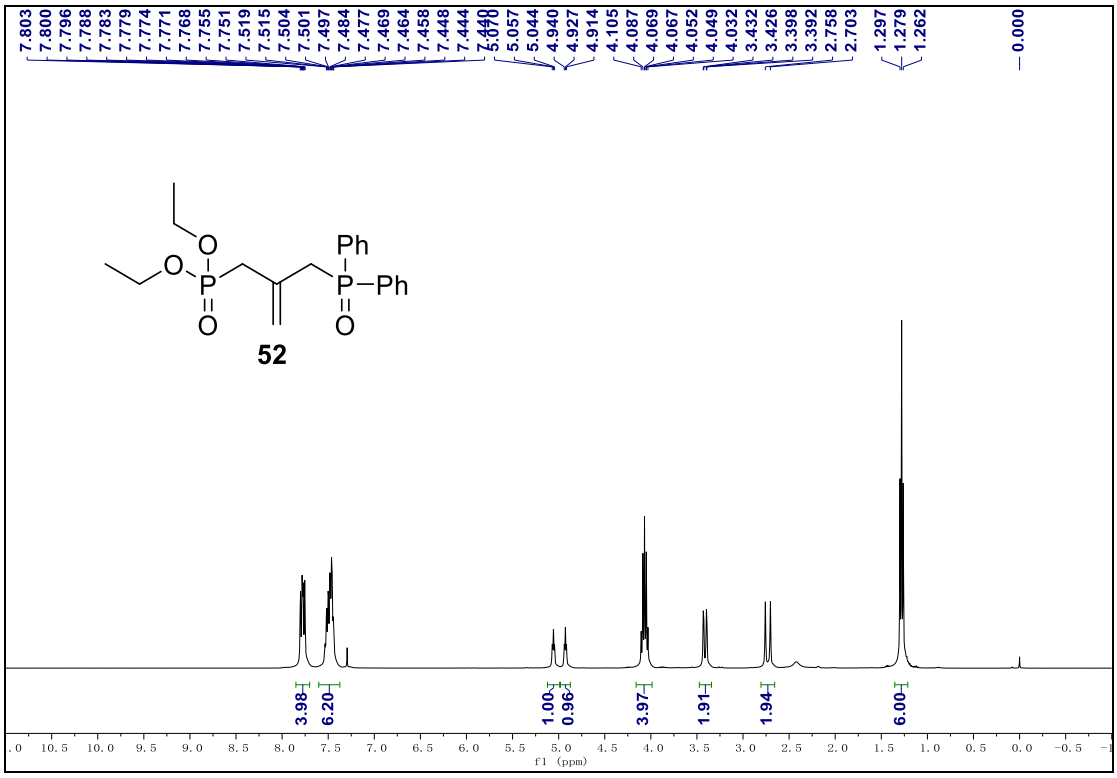
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 51.

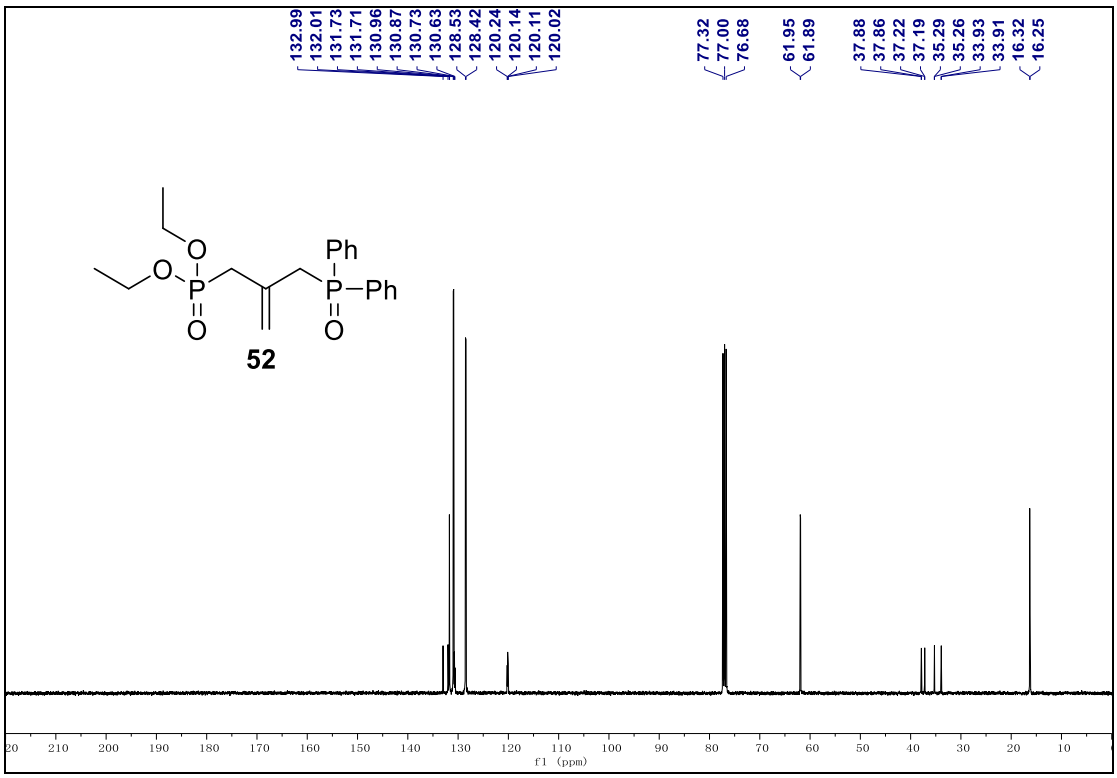


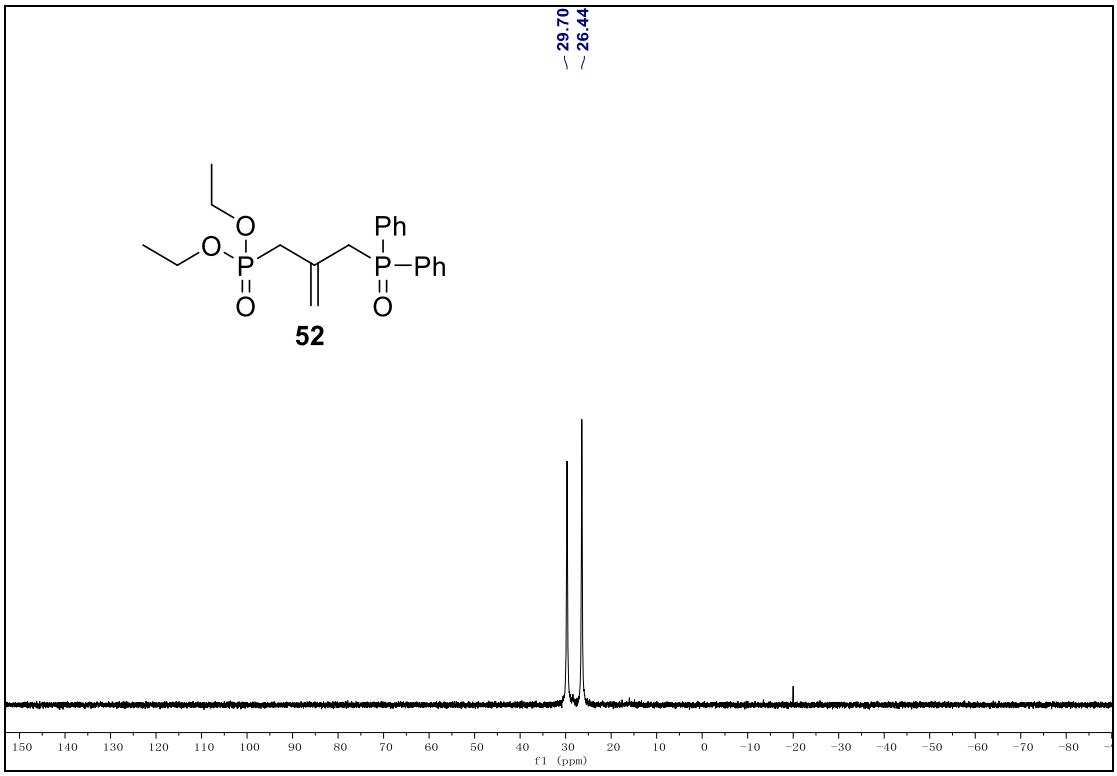



30.05
Ph
N
H
P
Ph
O
51
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

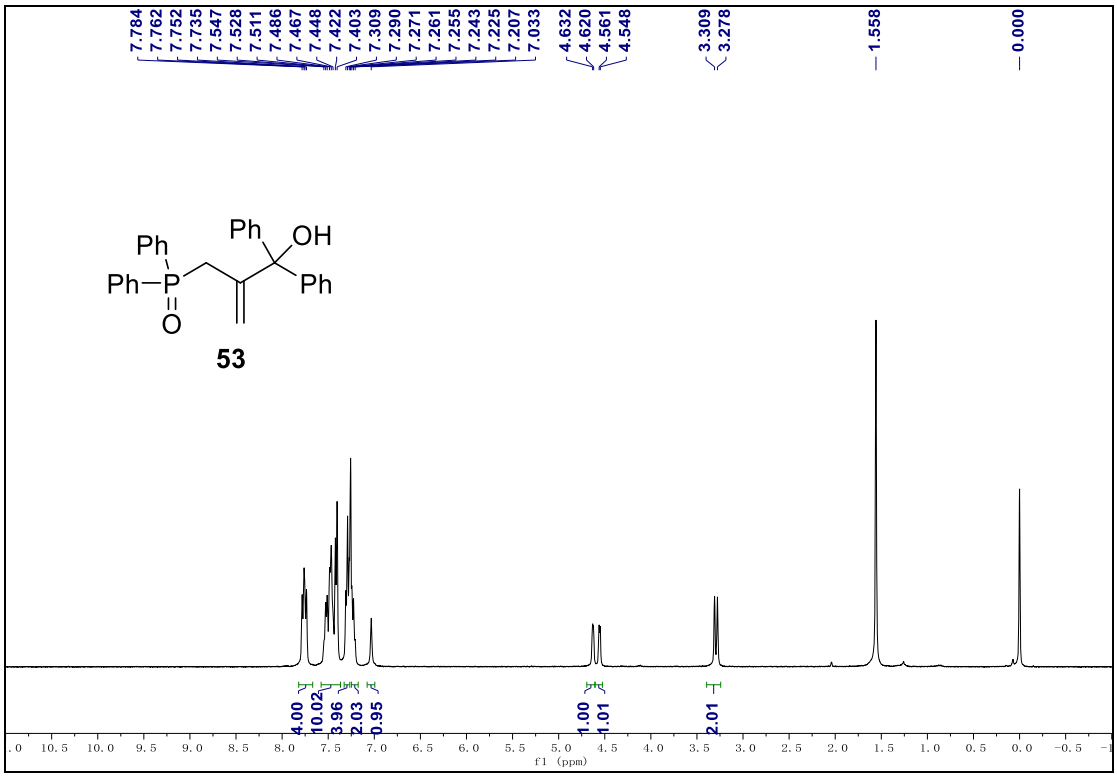
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 52.

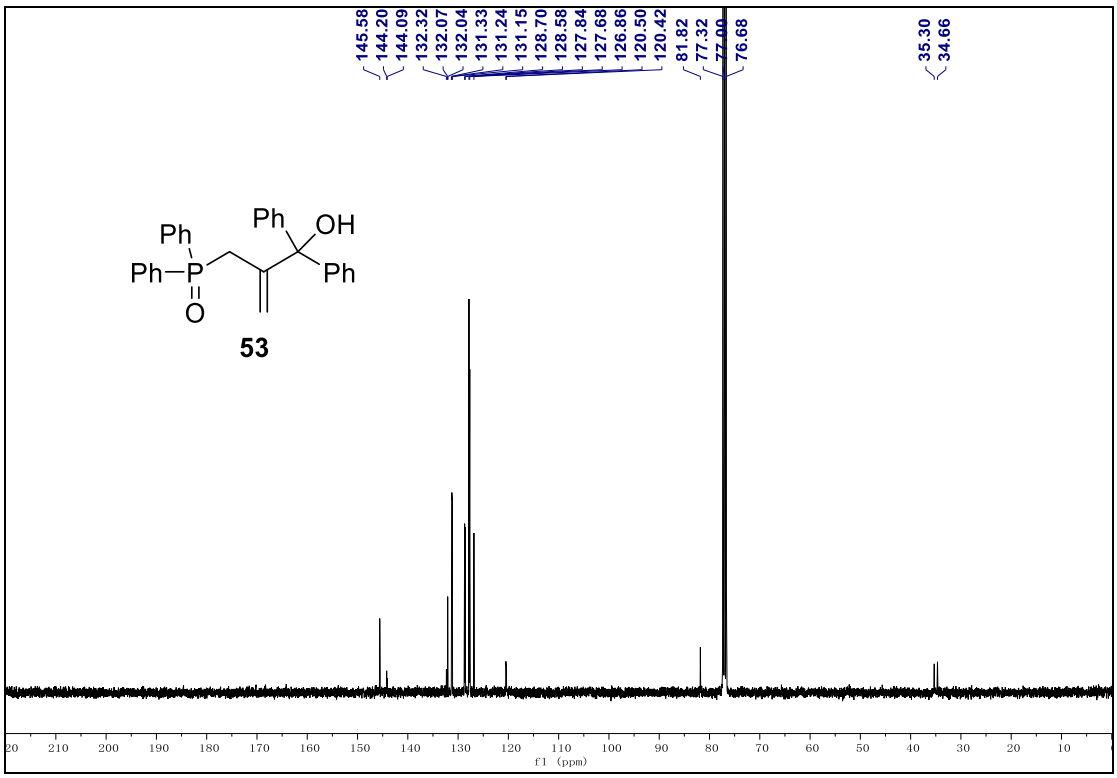


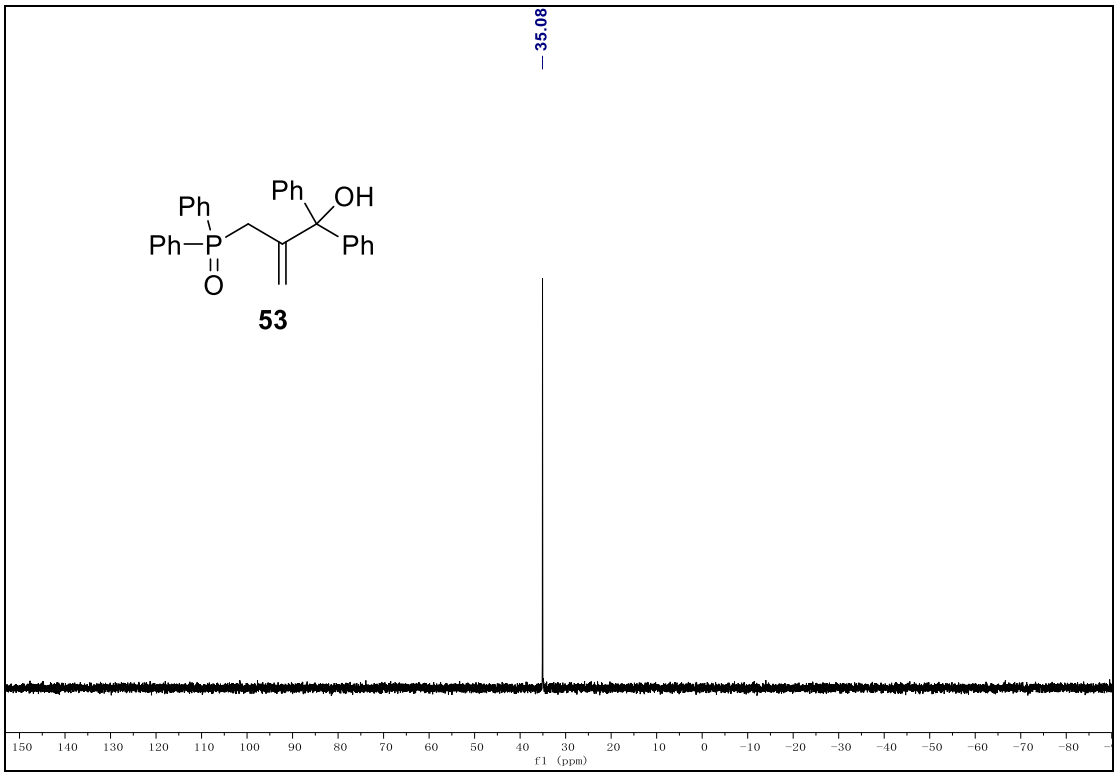



29.70
26.44
O
O
P
O
Ph
P
Ph
O
52
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

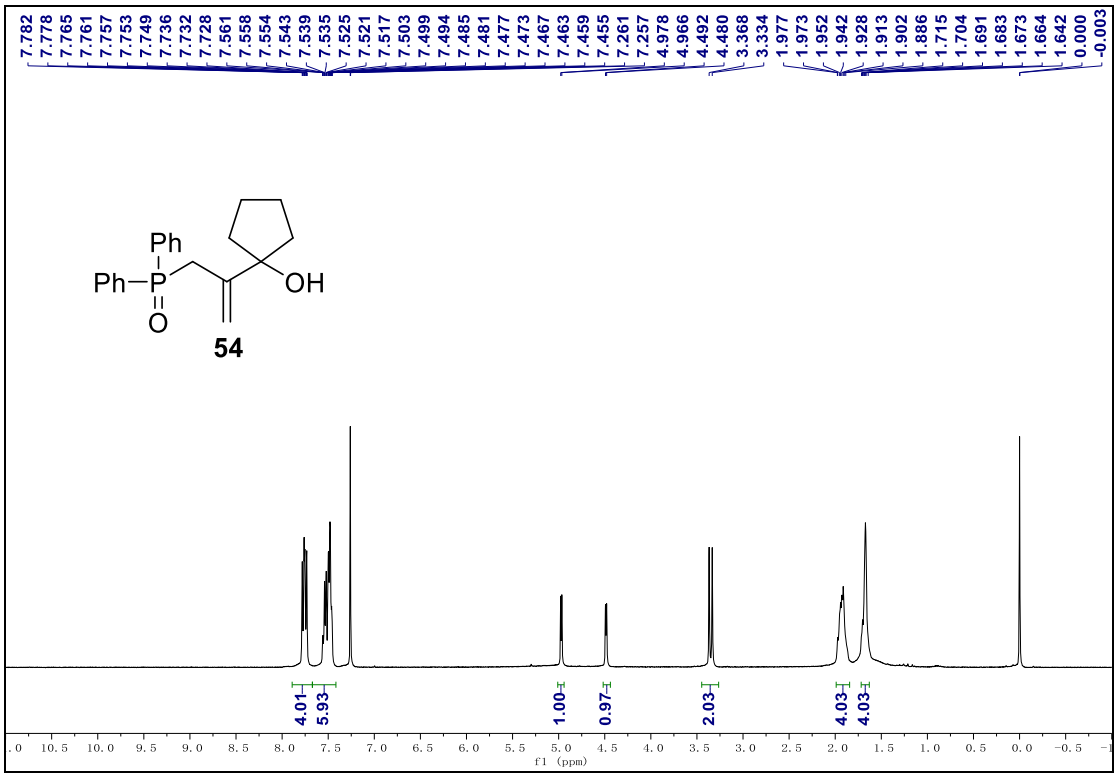
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 53.

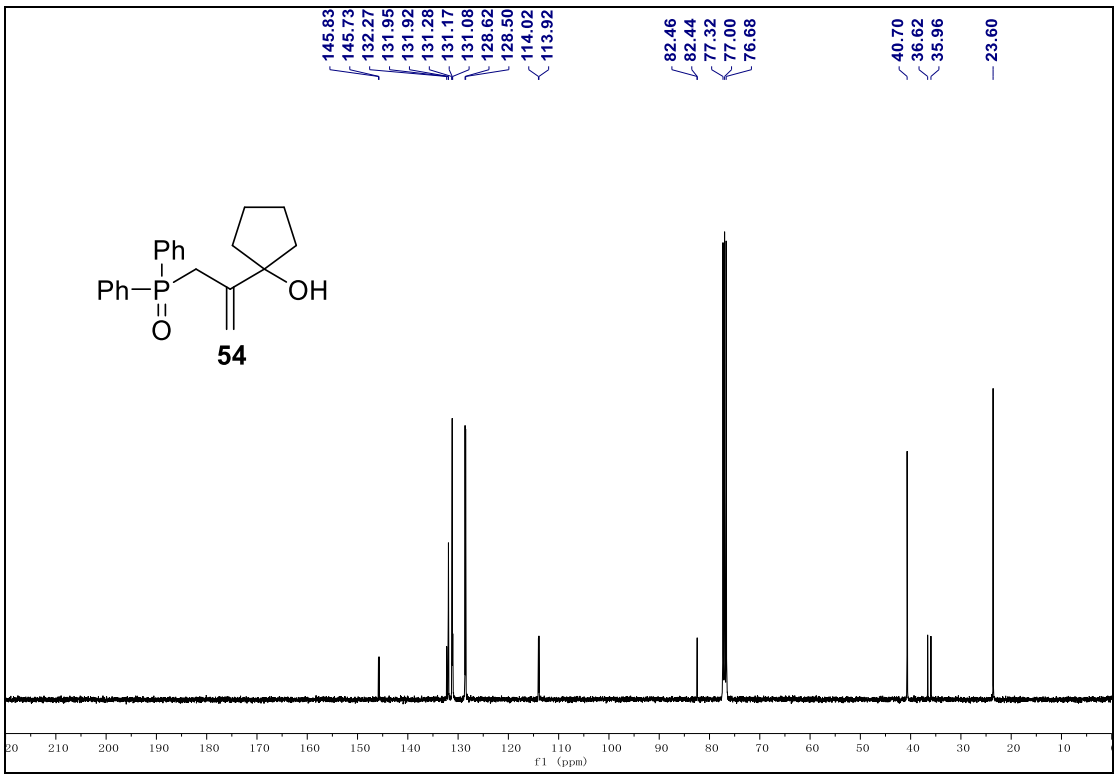


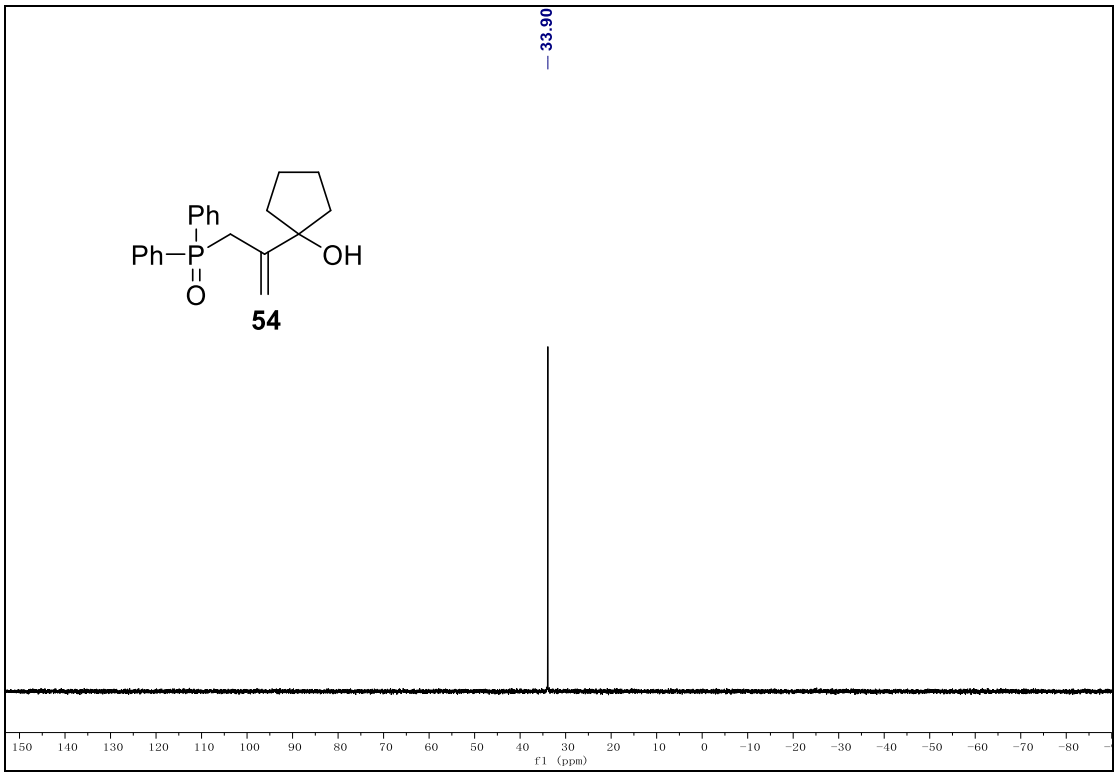



35.08
Ph
Ph
OH
Ph
Ph
P
O
53
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

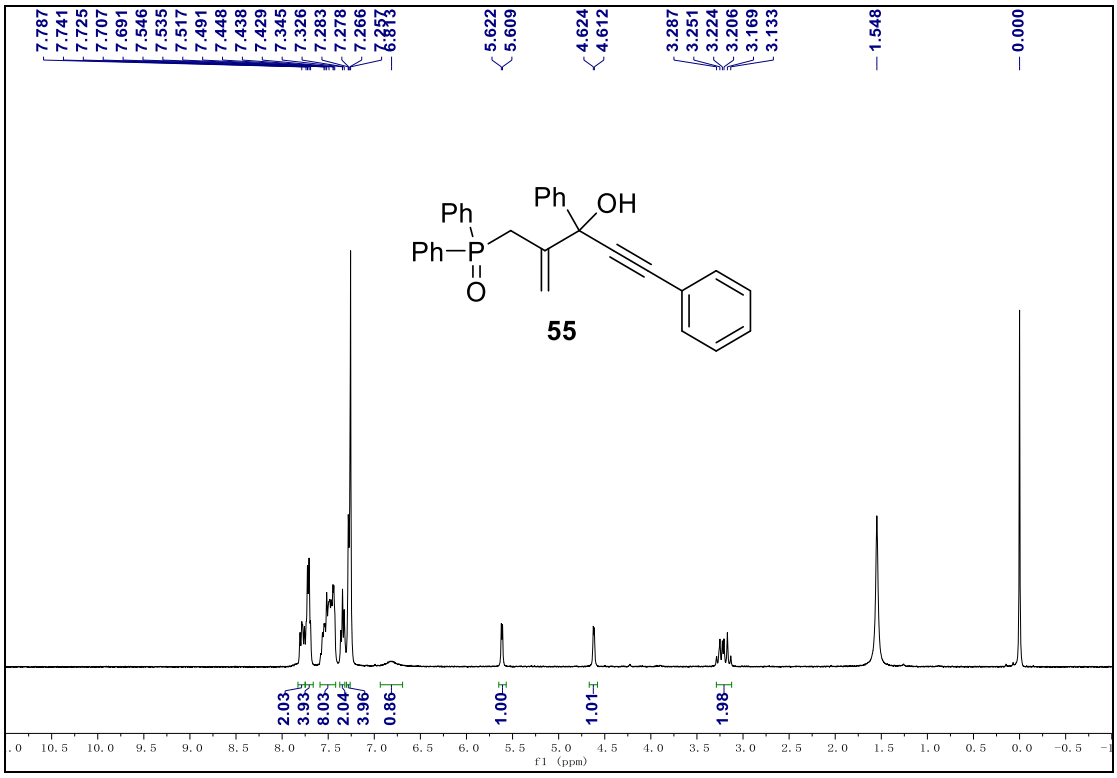
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 54.

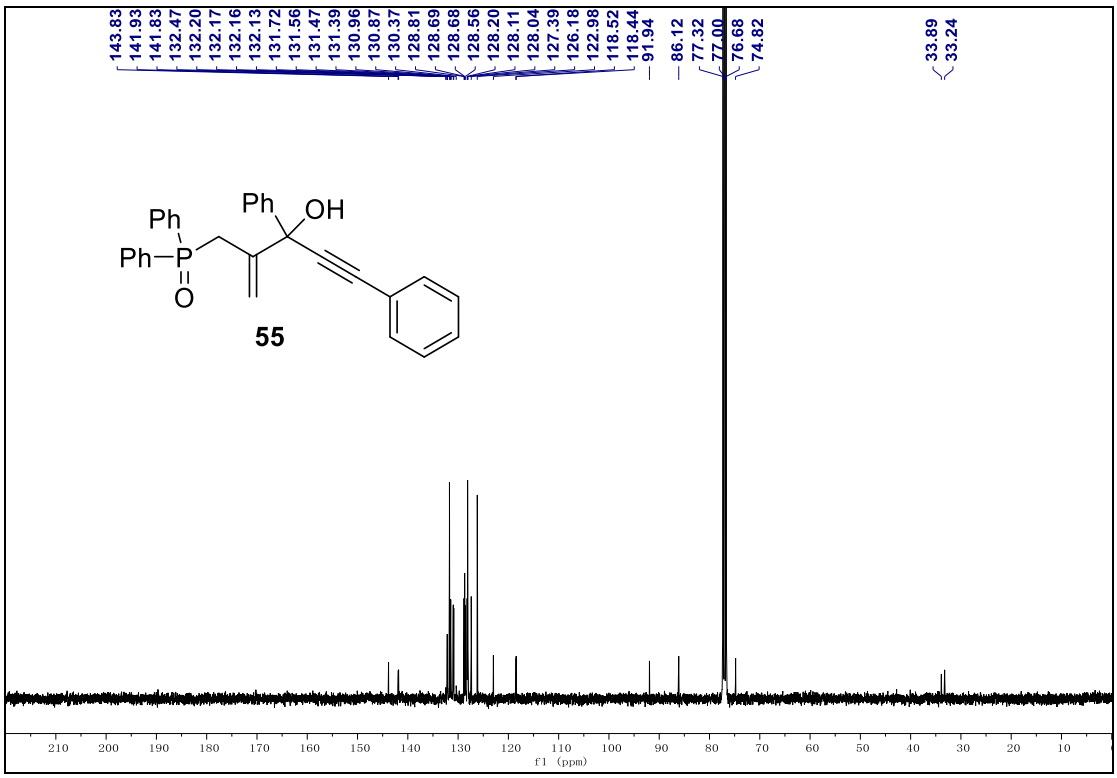


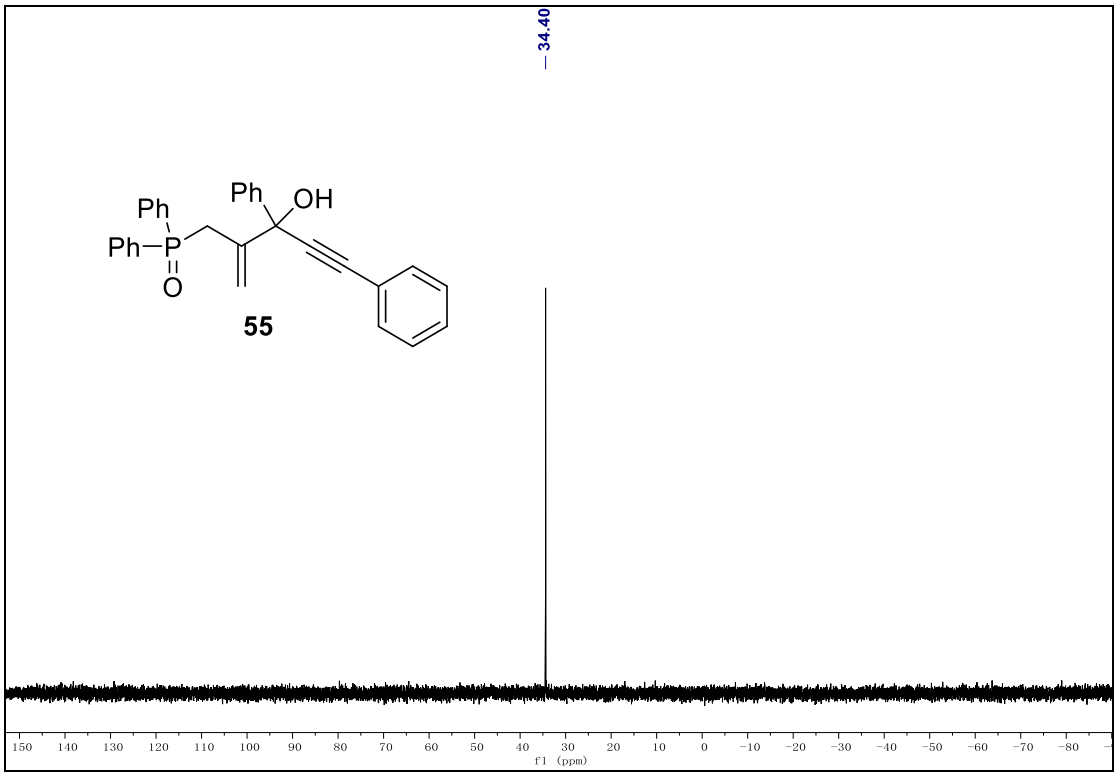



33.90
Ph
Ph—P
O
OH
54
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

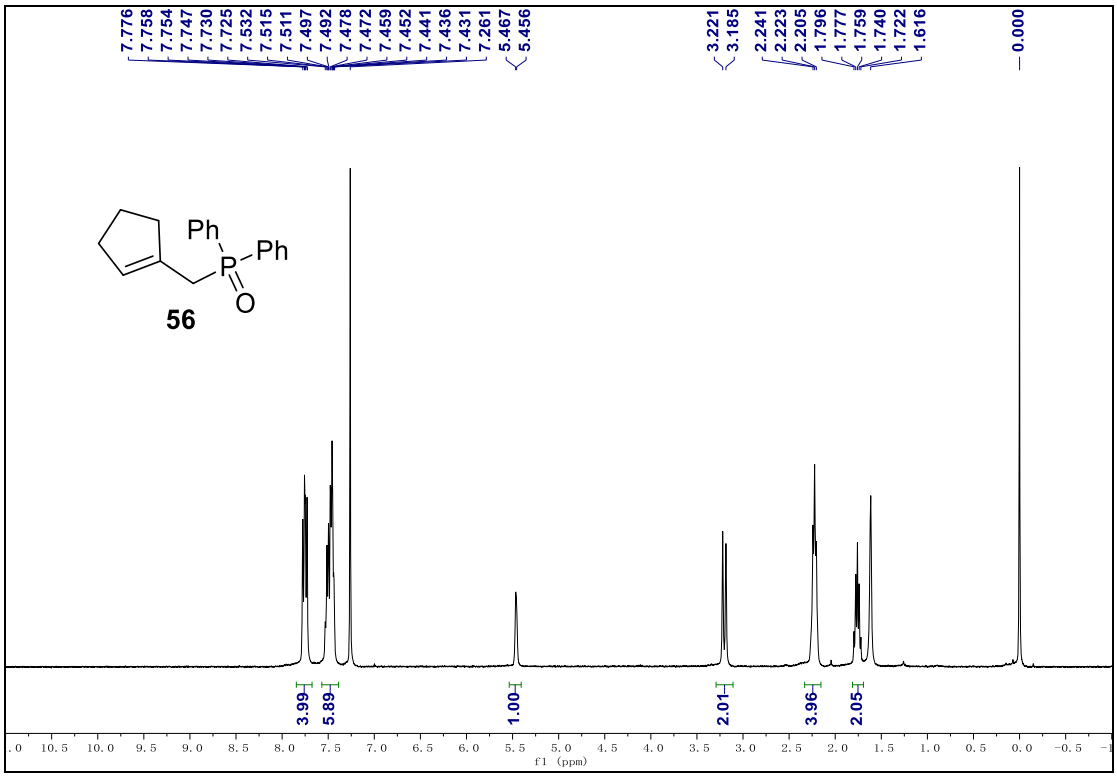
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 55.

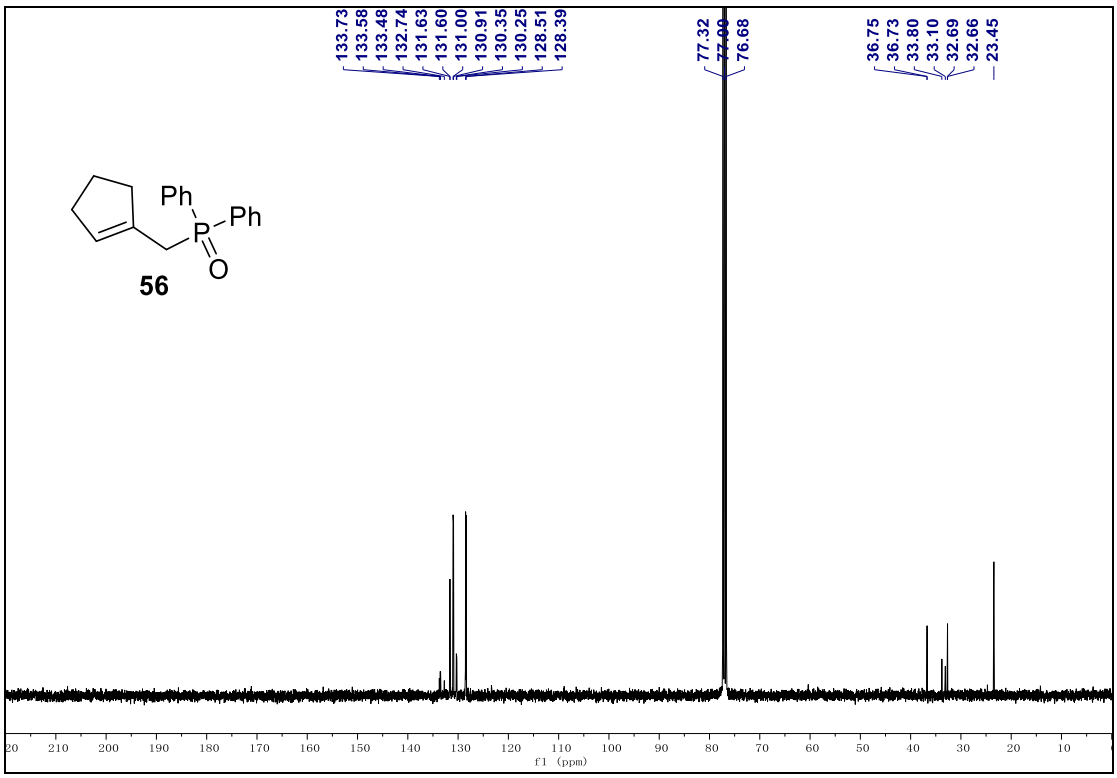


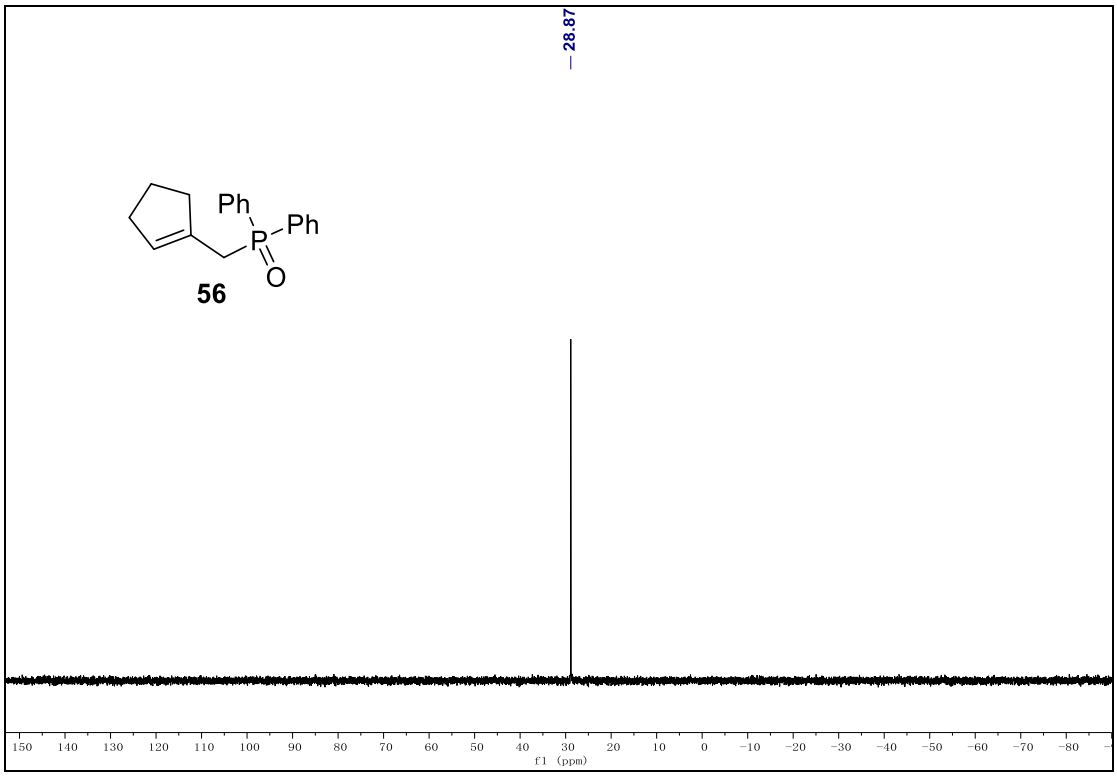



34.40
Ph
Ph
OH
Ph
P
O
55
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

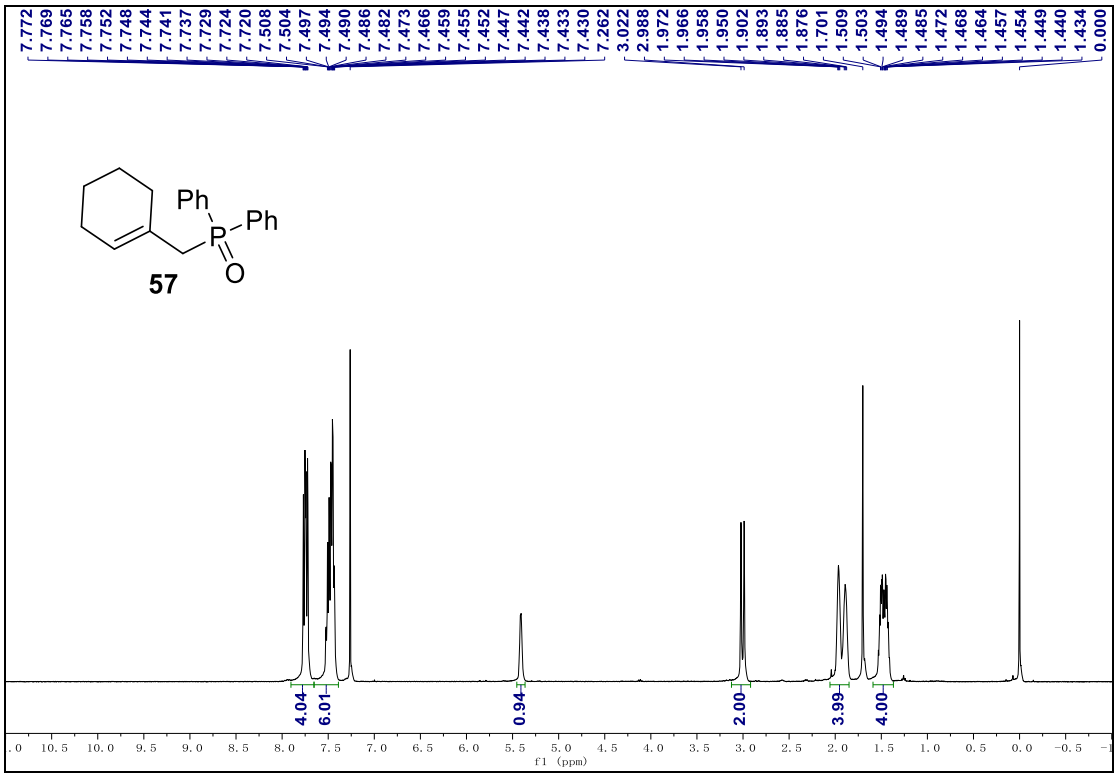
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 56.

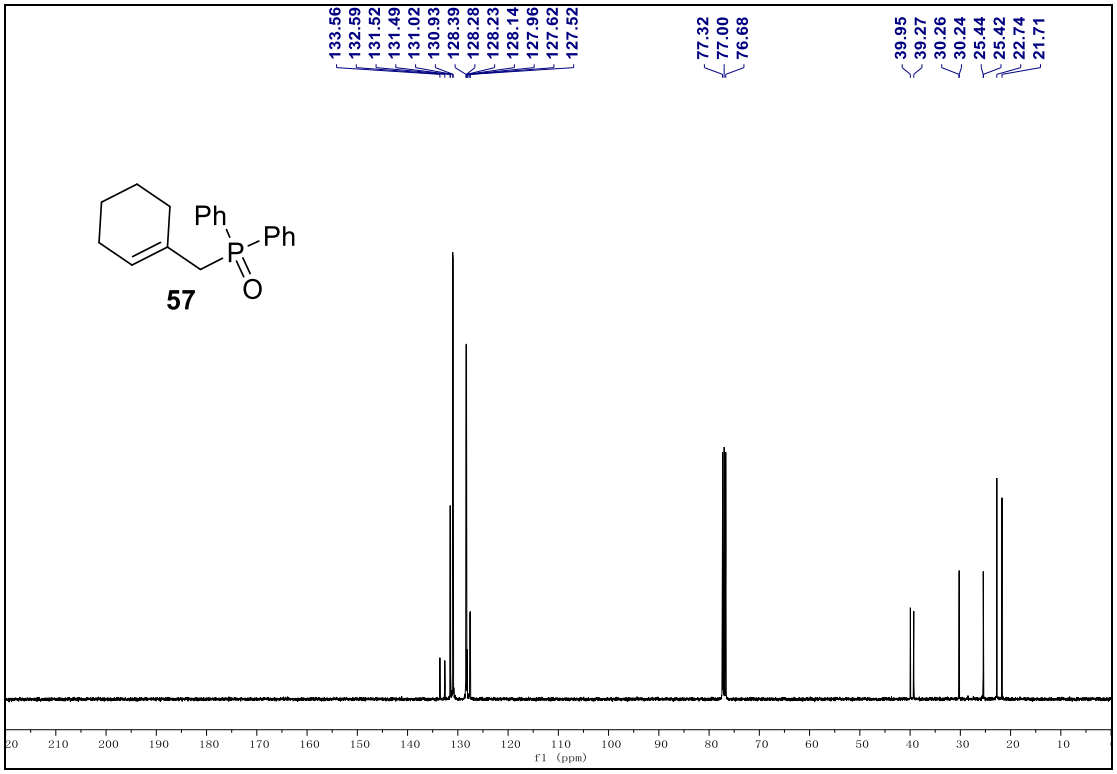


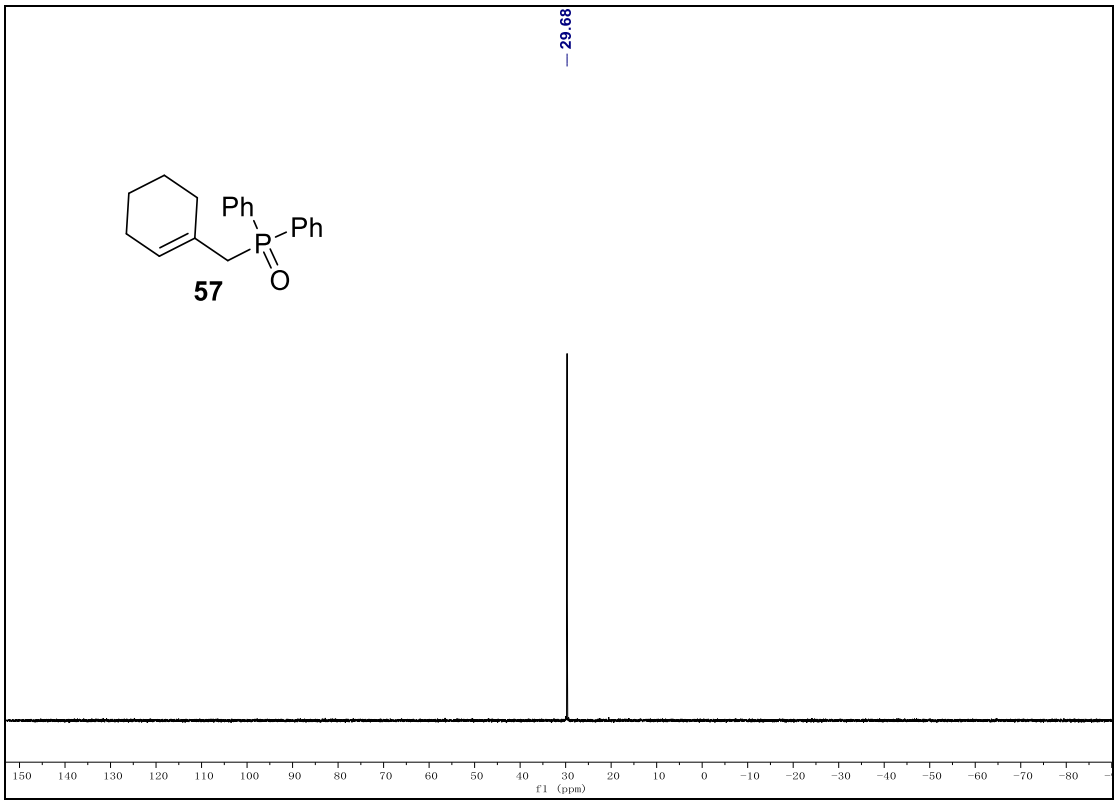



28.87
Ph
Ph
P
O
56
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

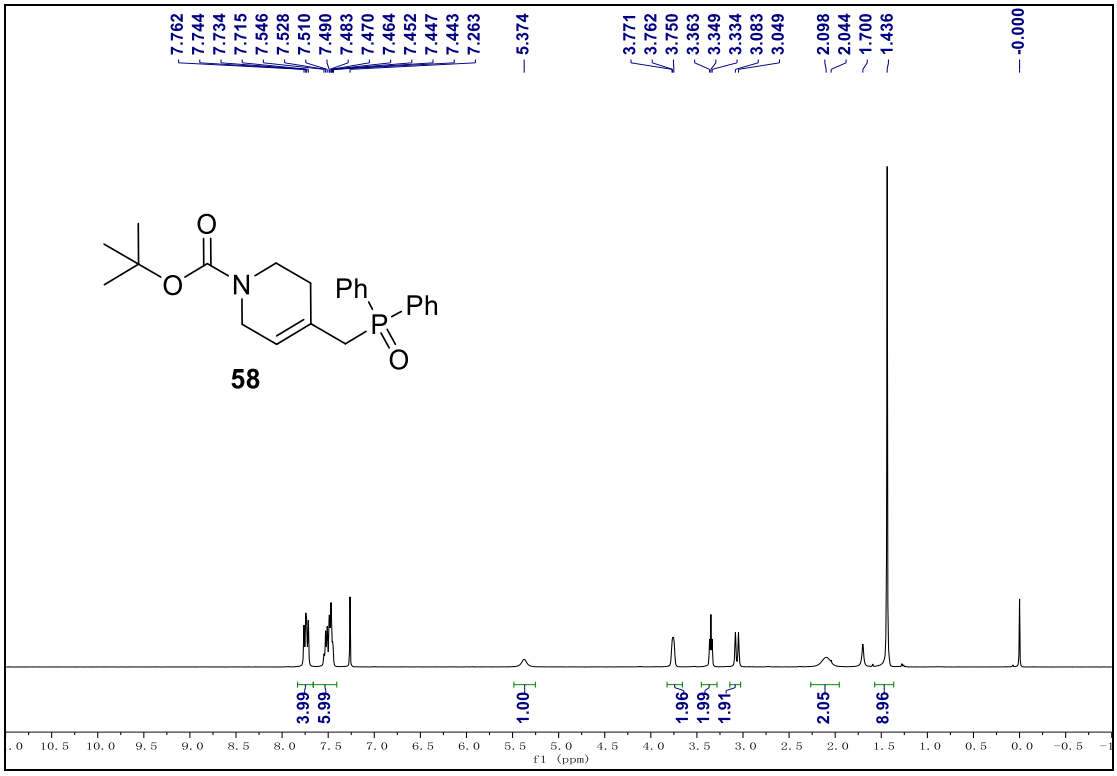
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 57.

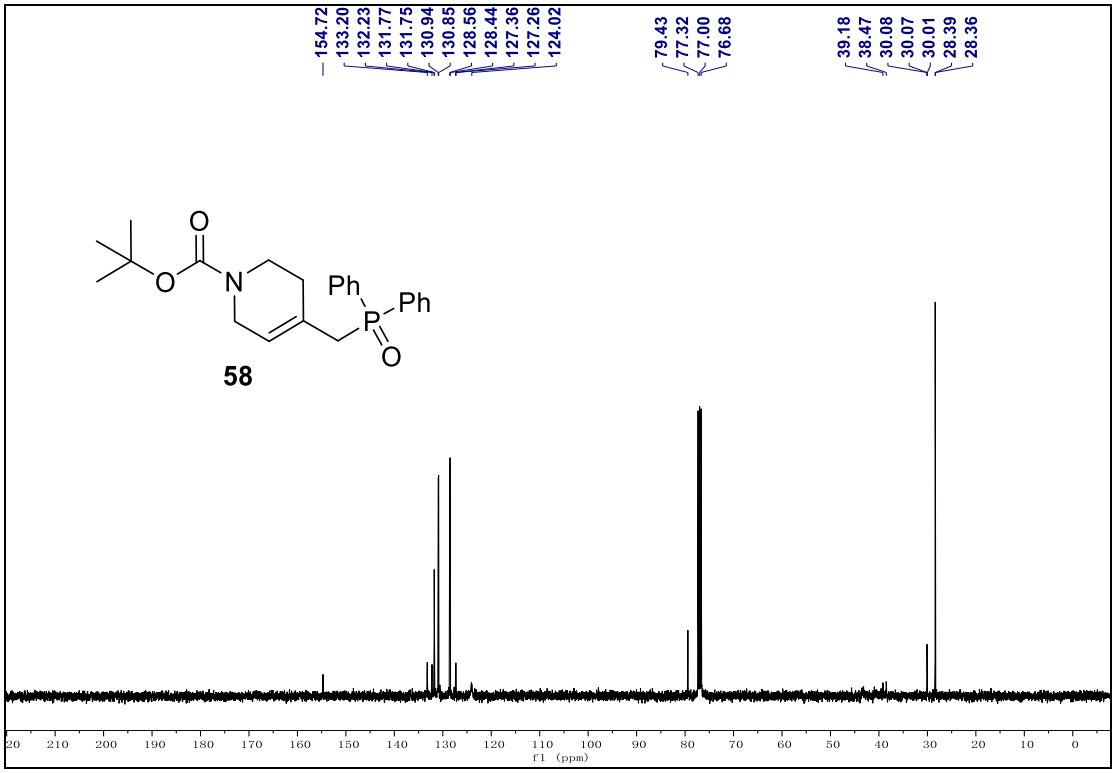


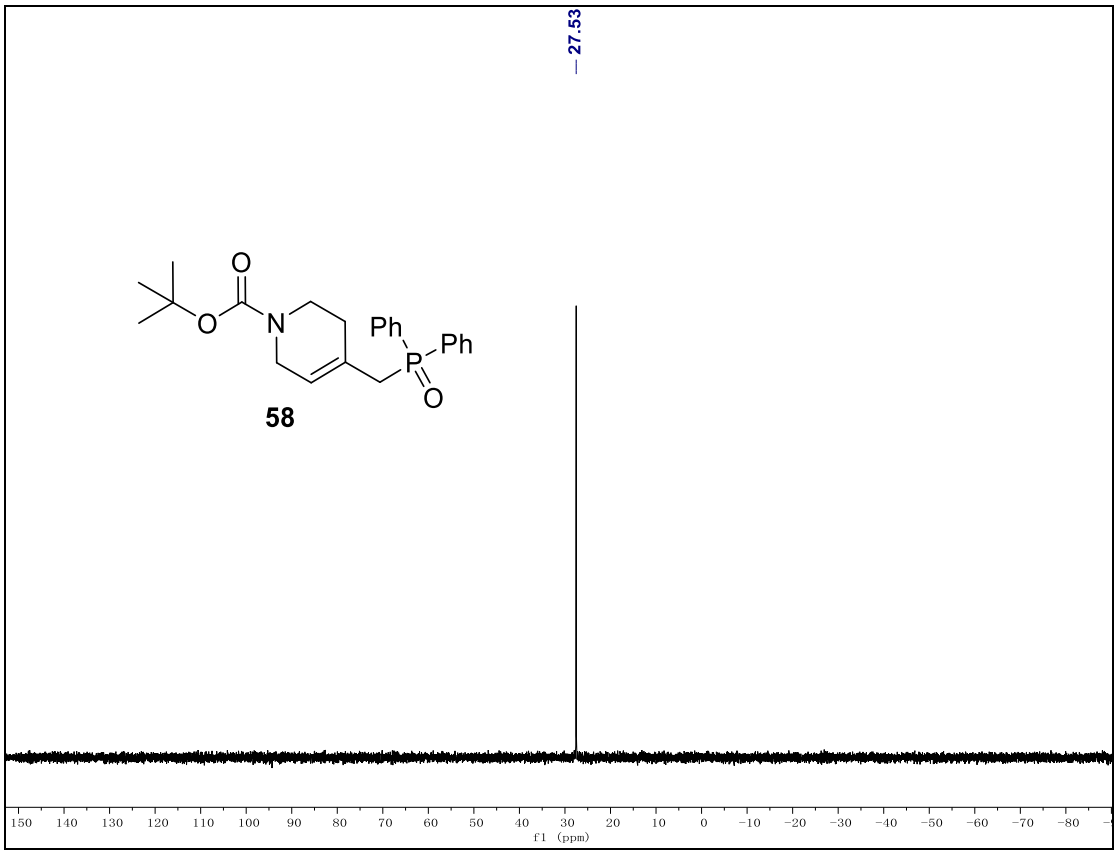



29.68
Ph
Ph
P
O
57
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

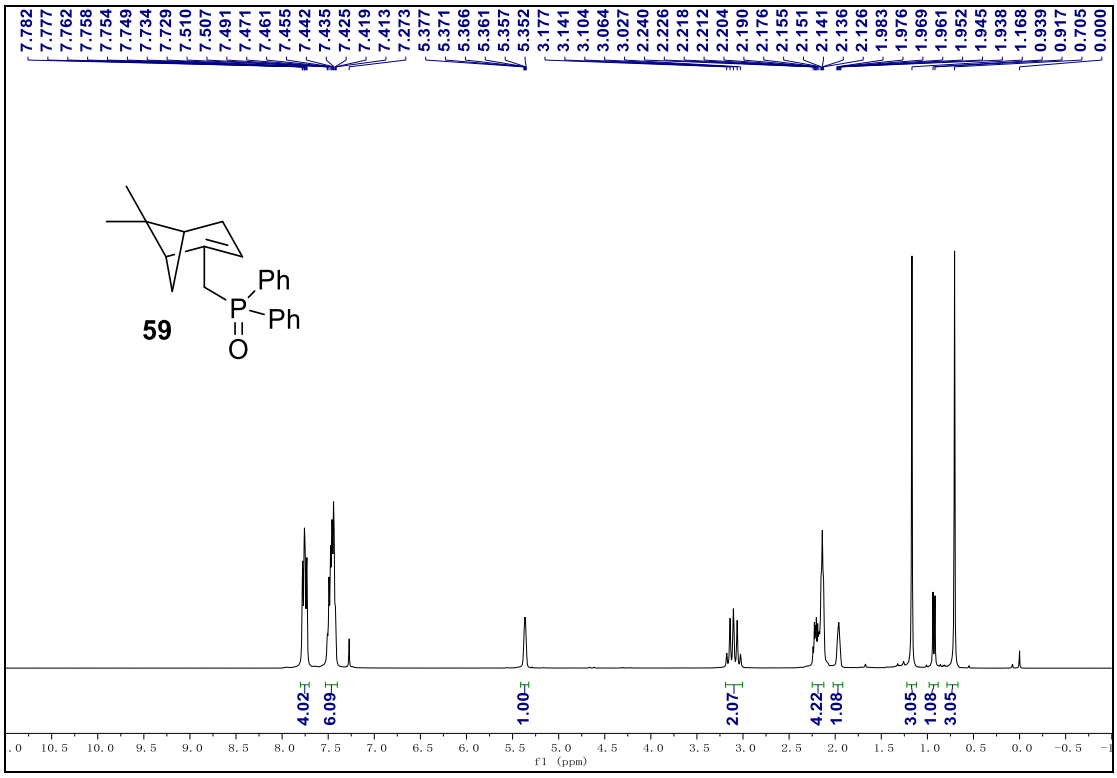
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 58.

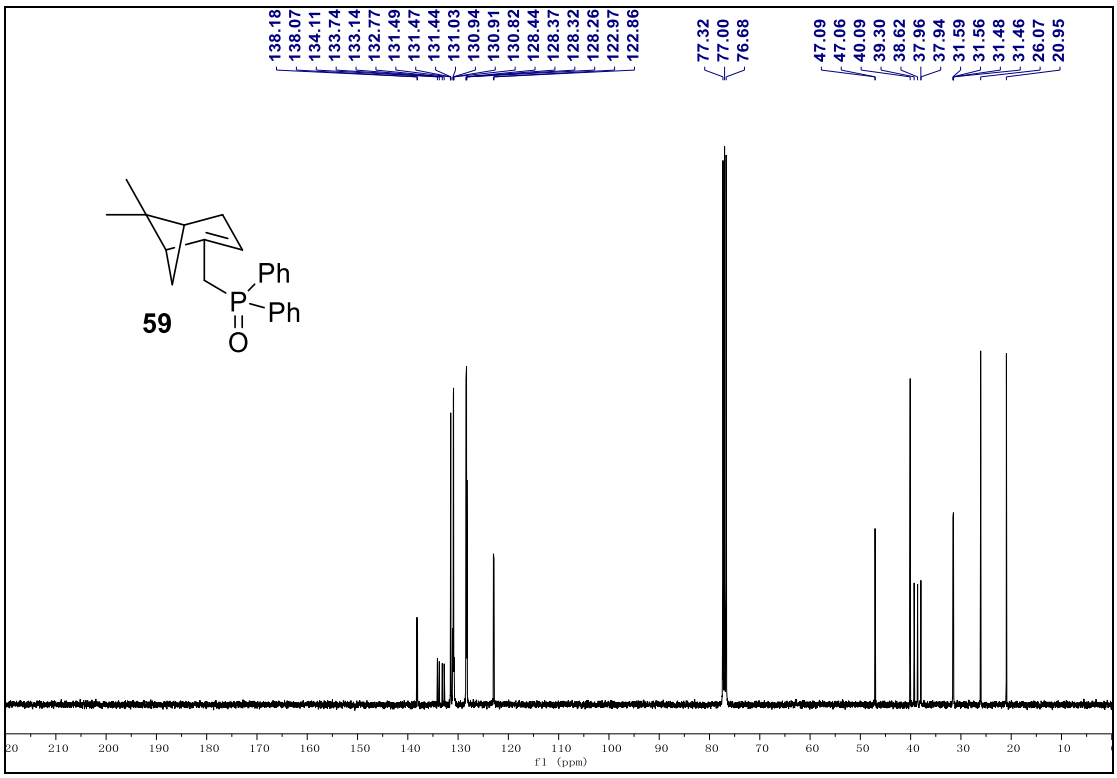


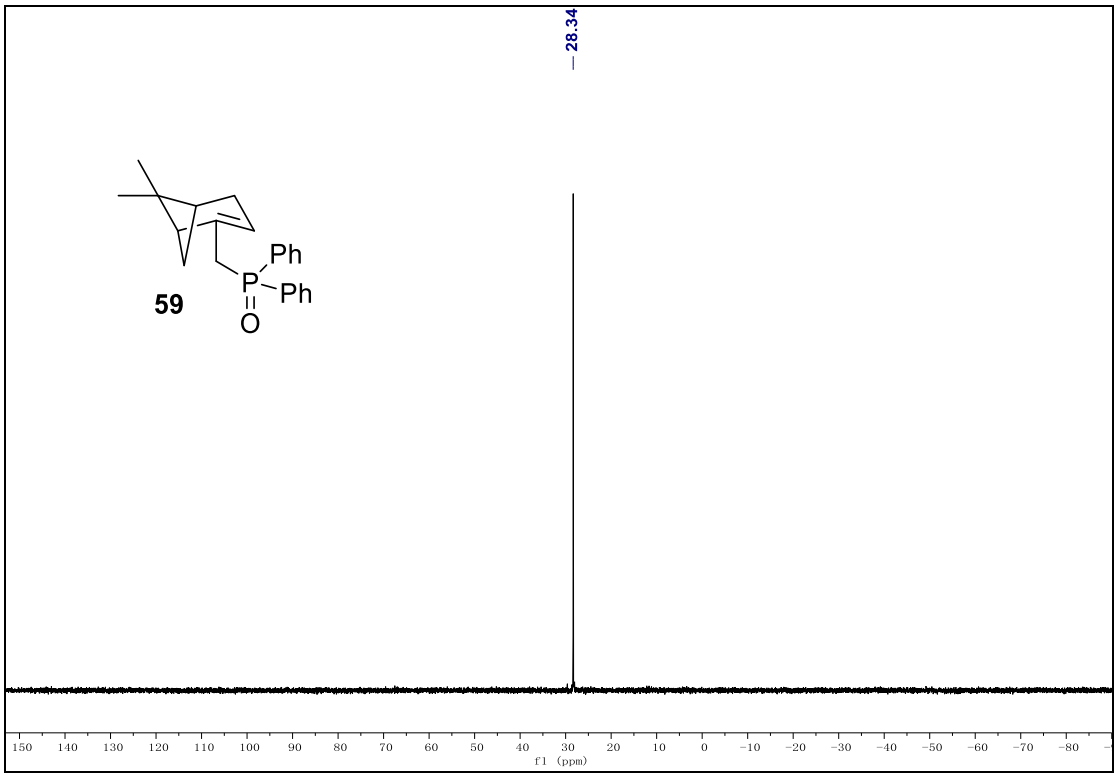



27.53
O
O
N
Ph
Ph
P
O
58
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

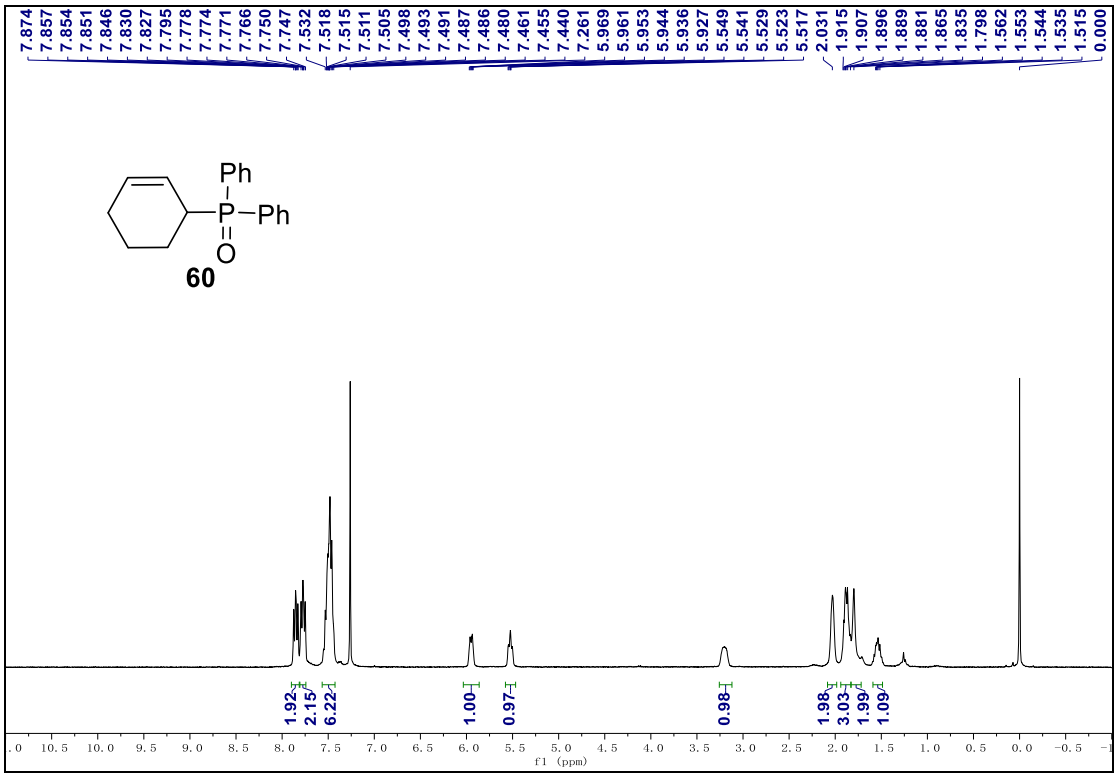
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 59.

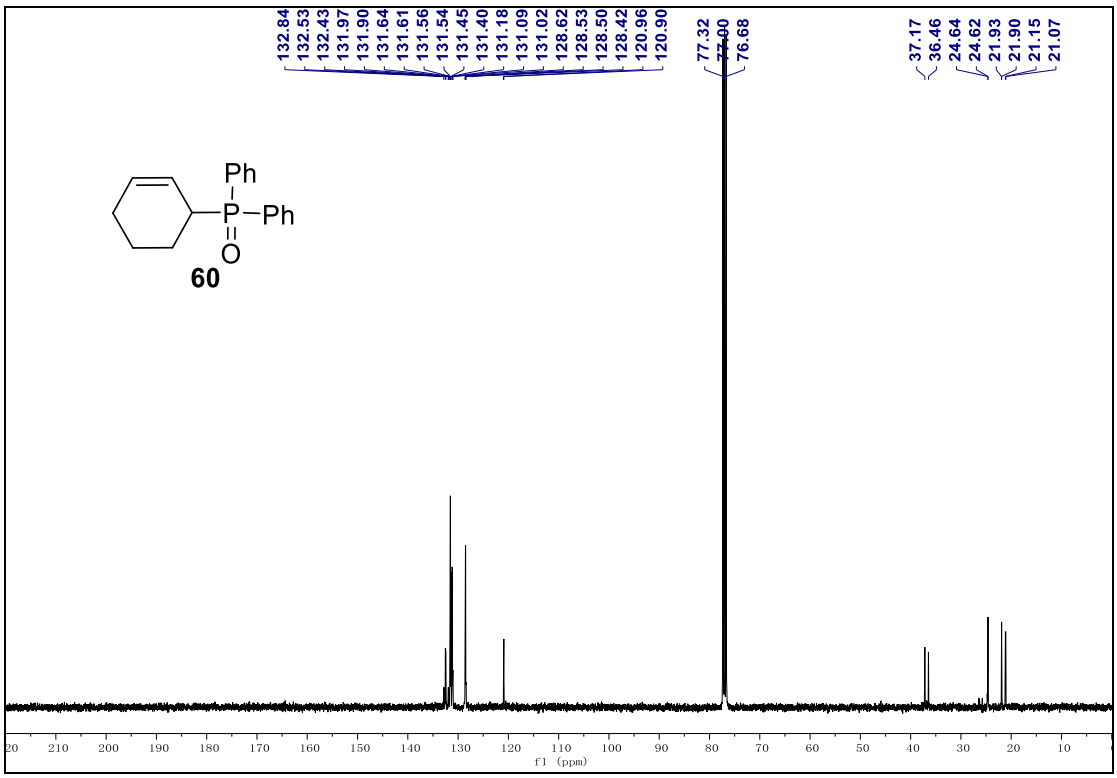


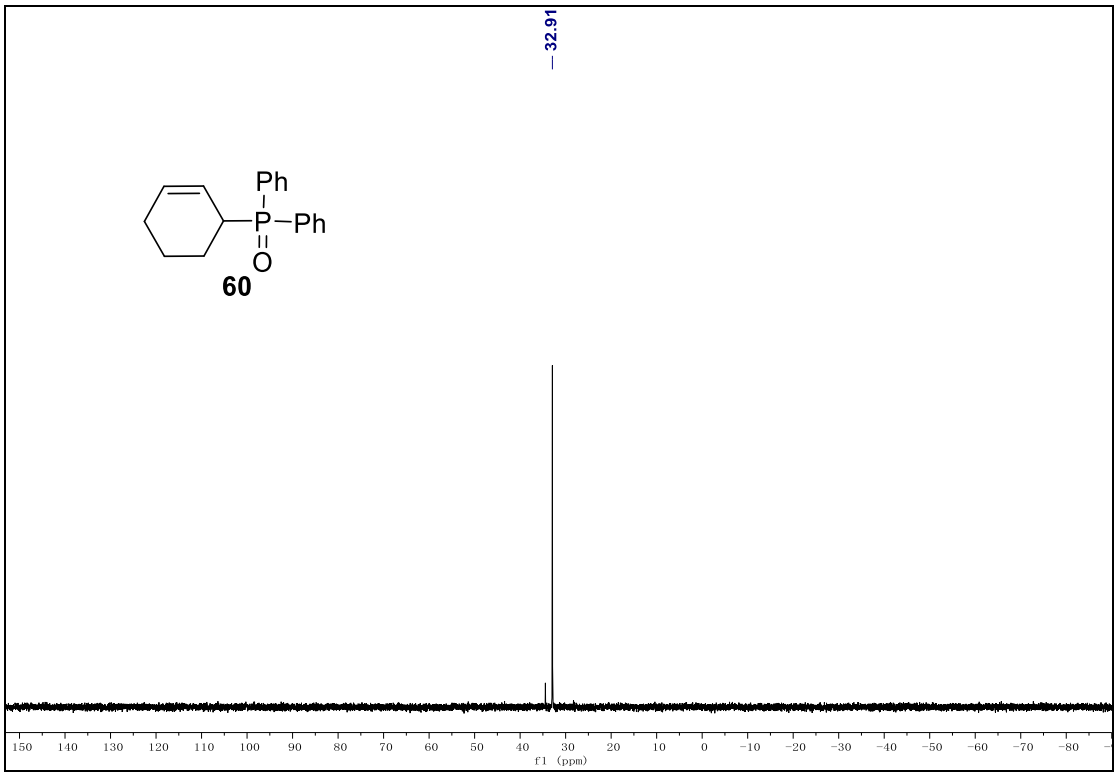



28.34
Ph
P
Ph
O
59
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

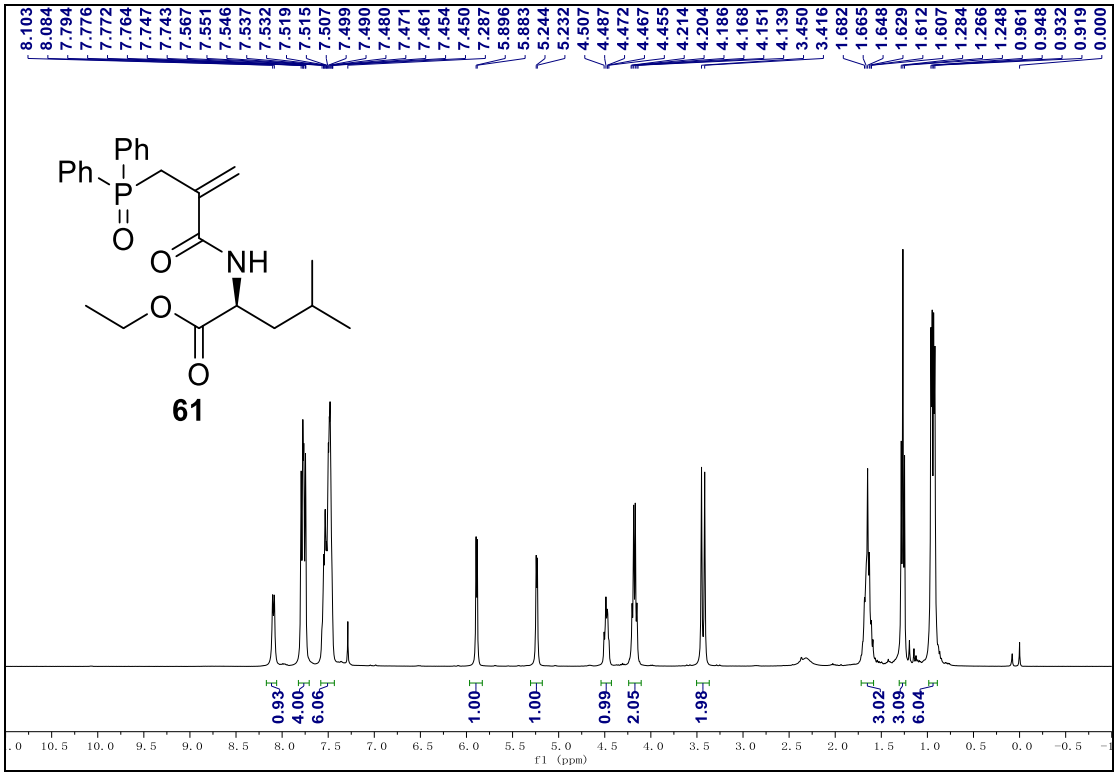
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 60.

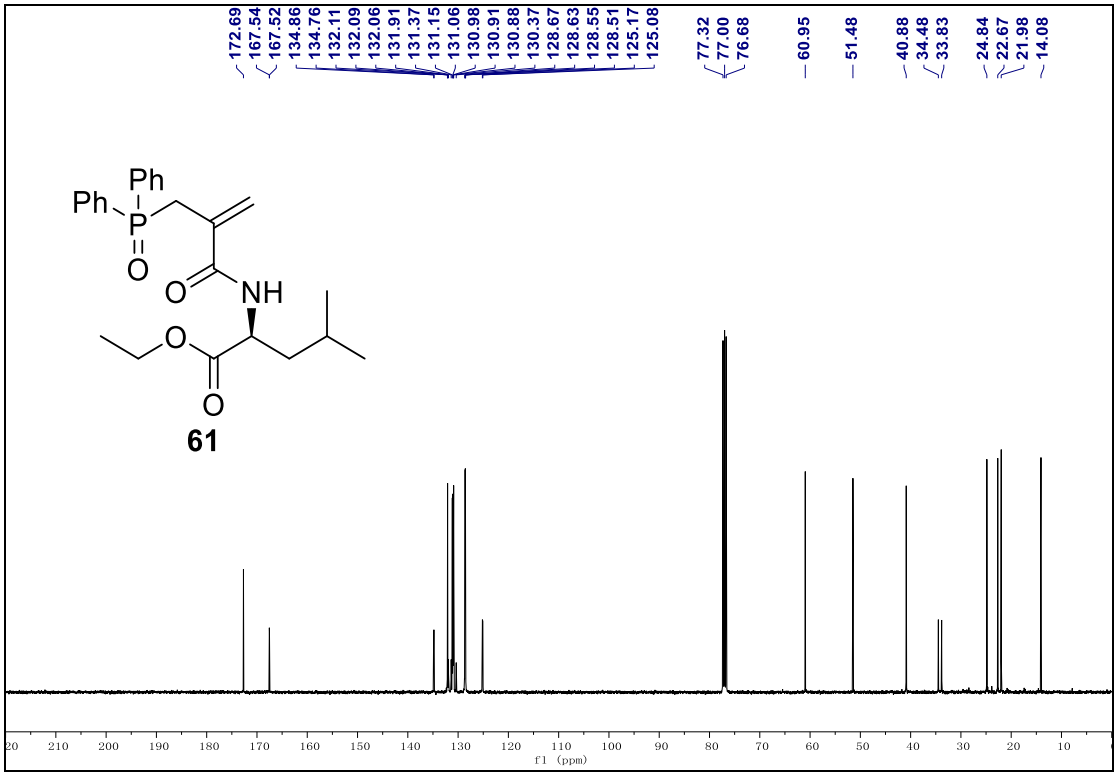


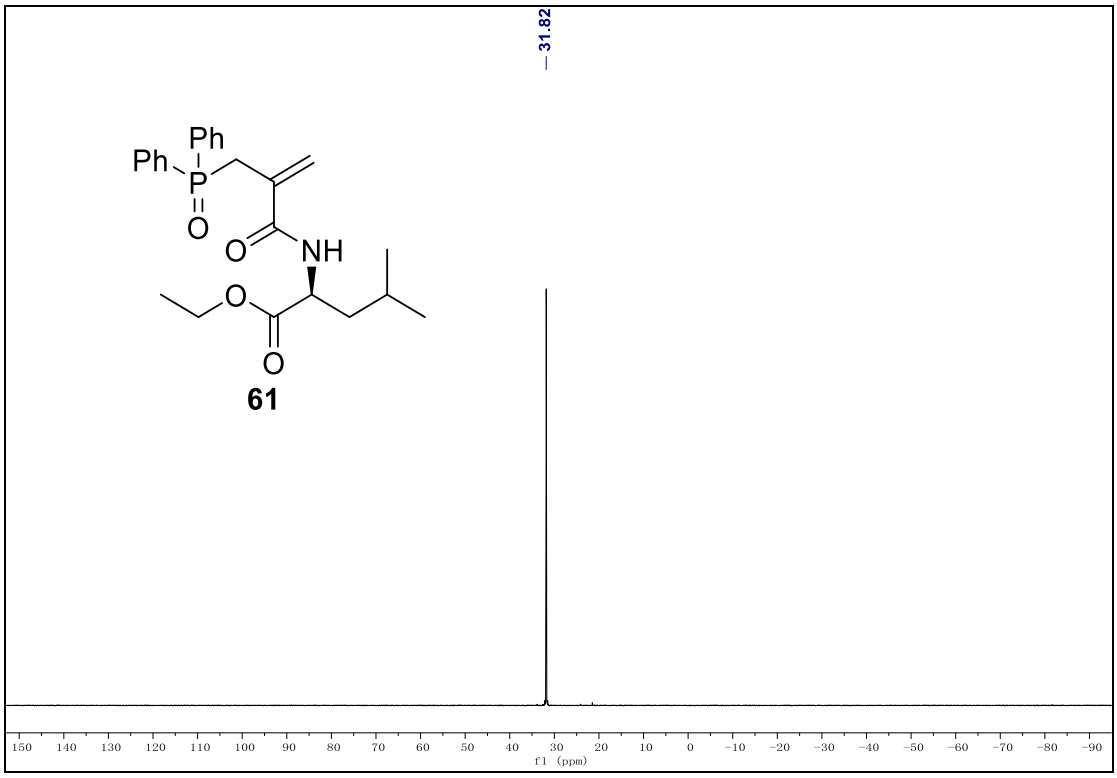



32.91
Ph
P
Ph
O
60
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

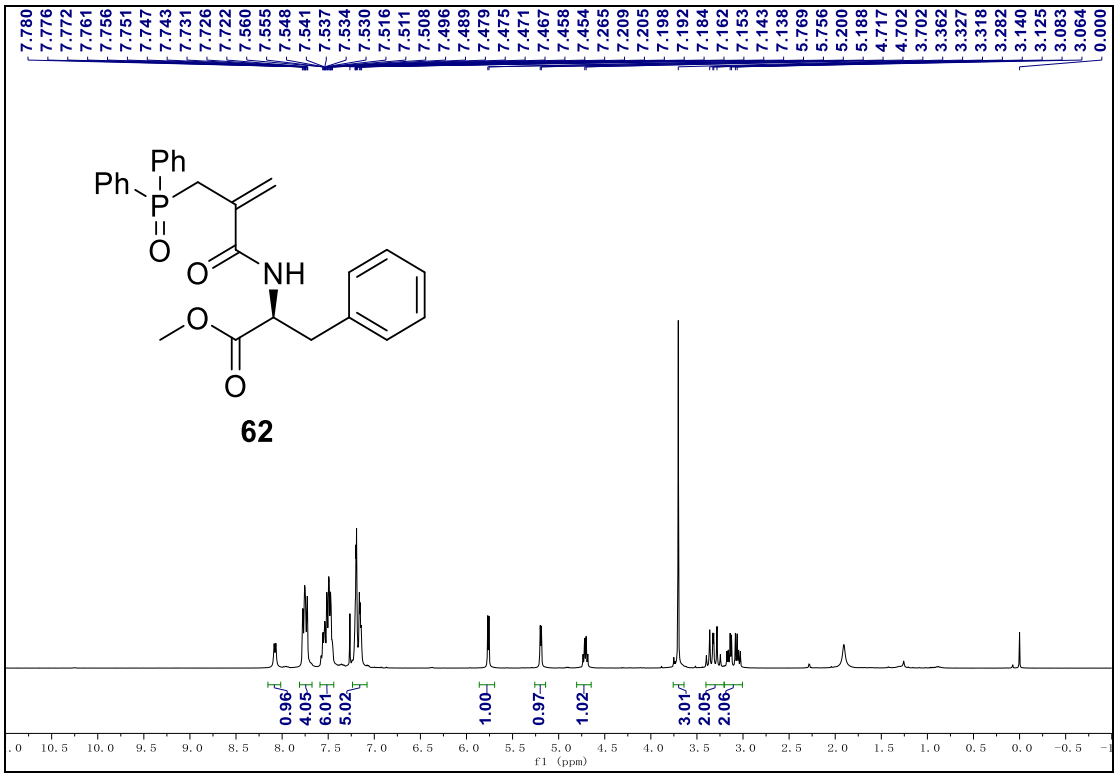
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 61.

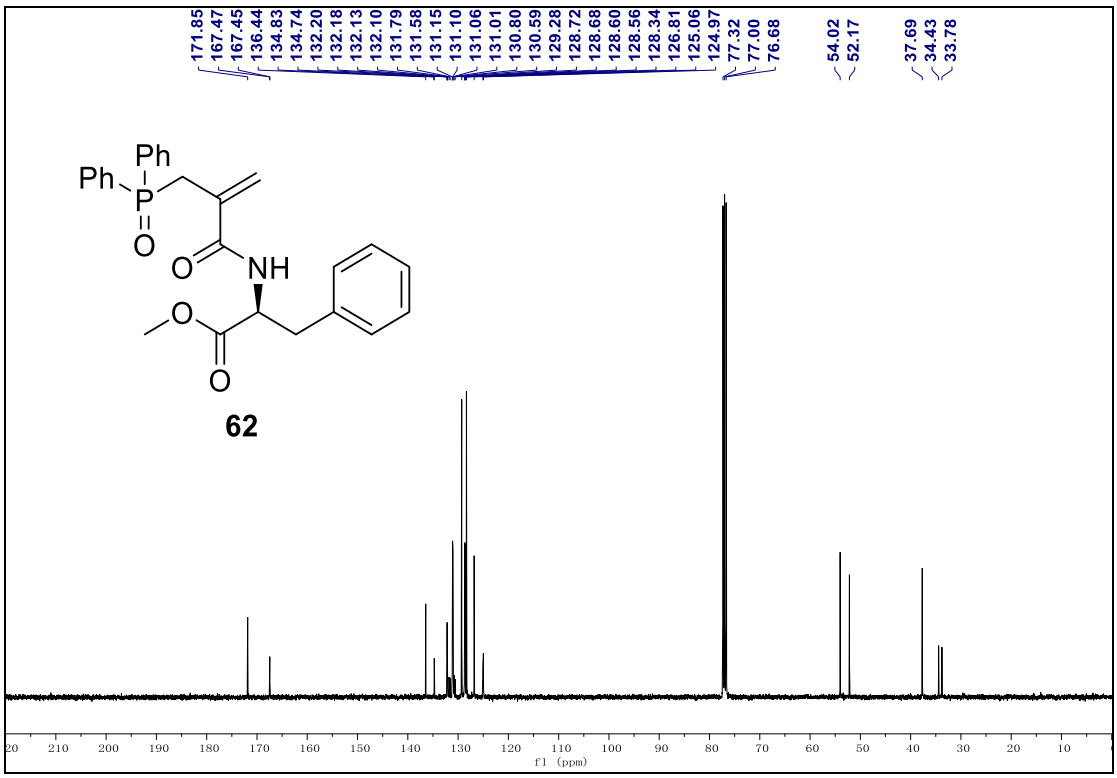


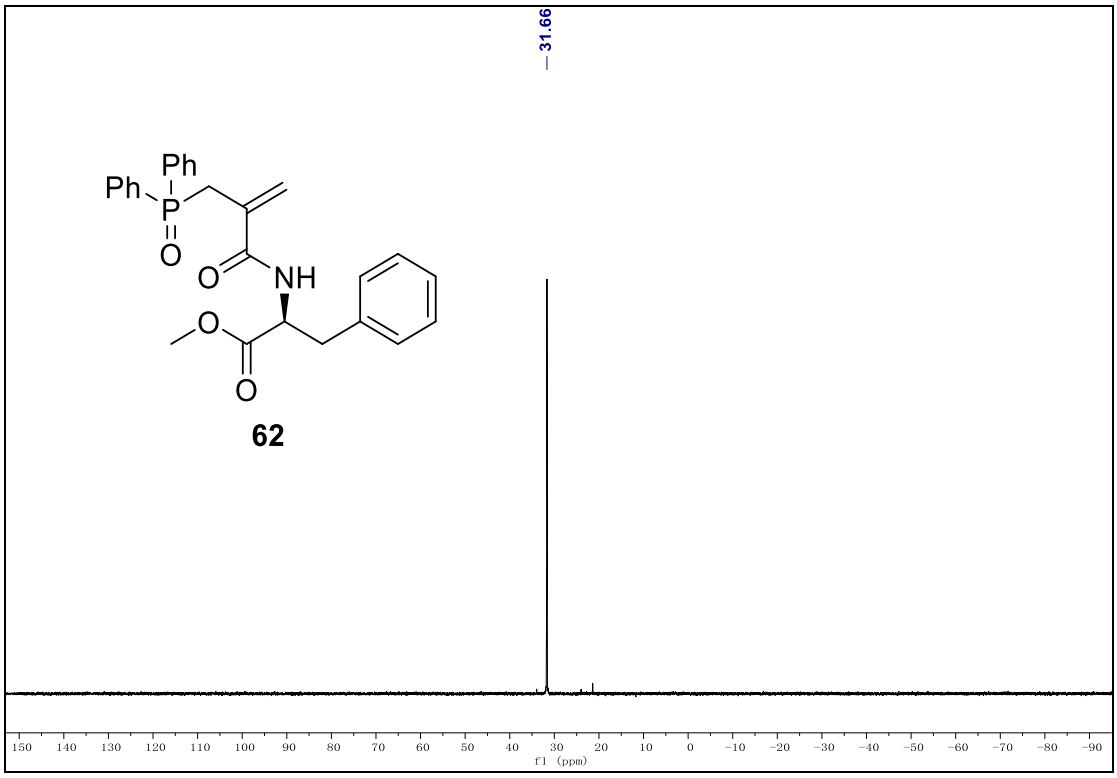



31.82
Ph
Ph
P
O
O
NH
O
O
61
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

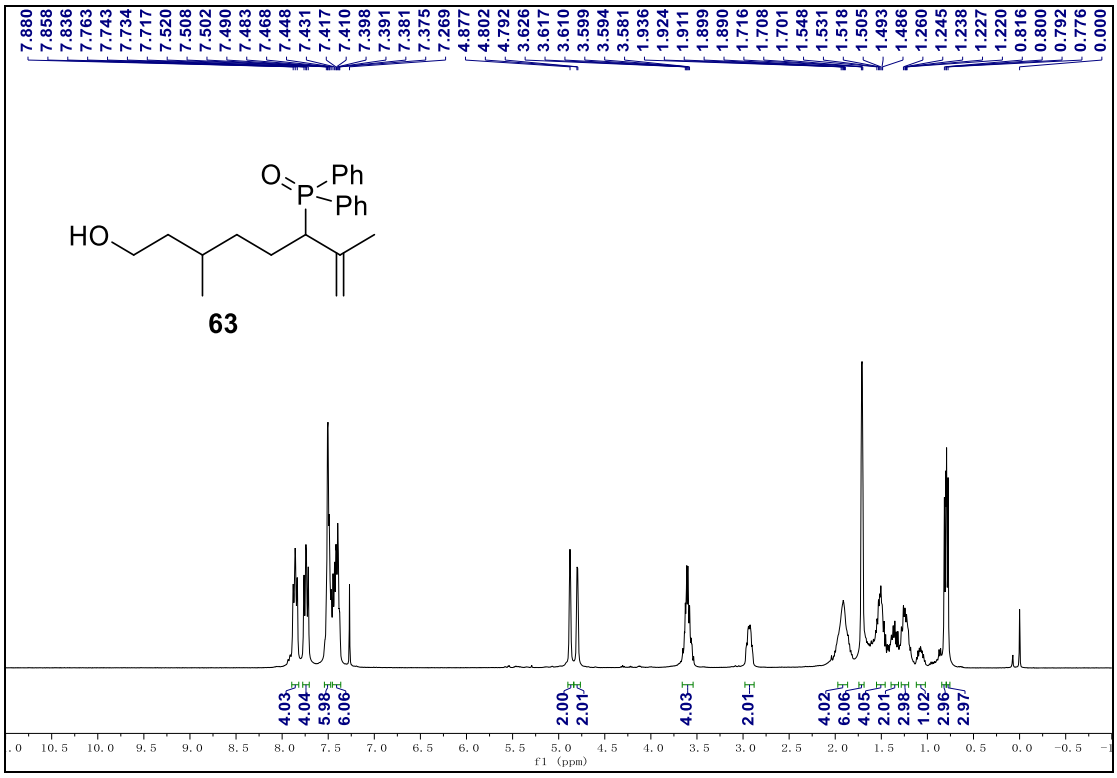
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 62.

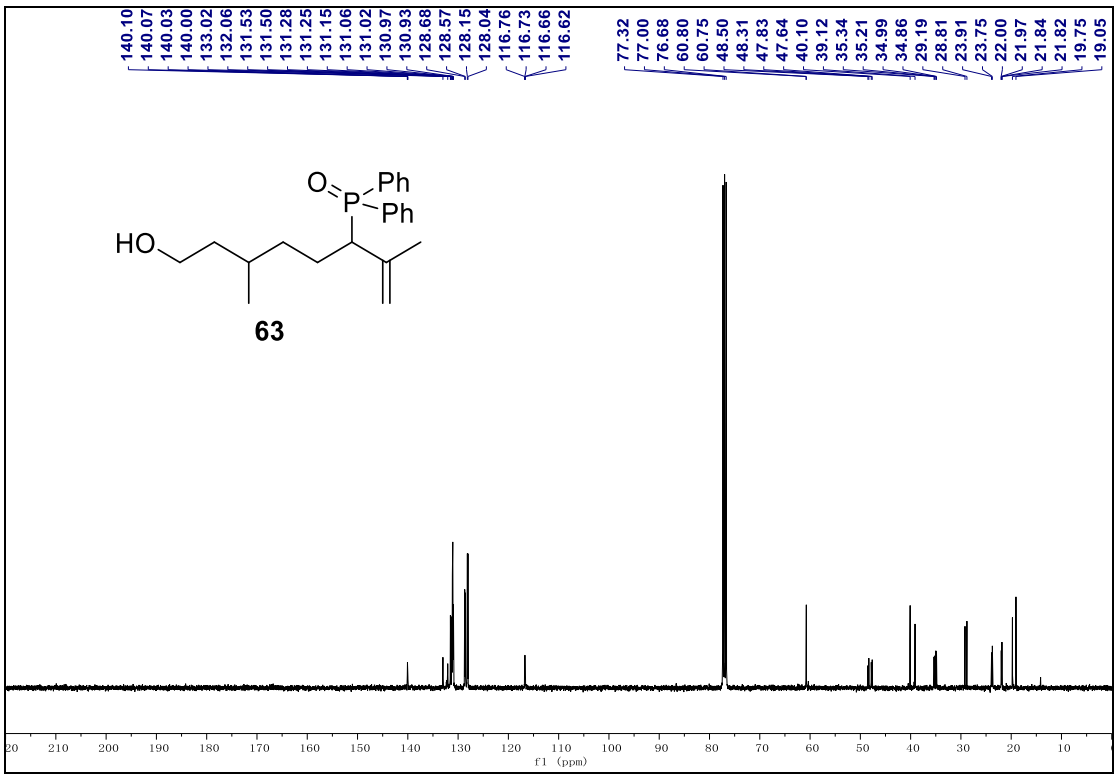


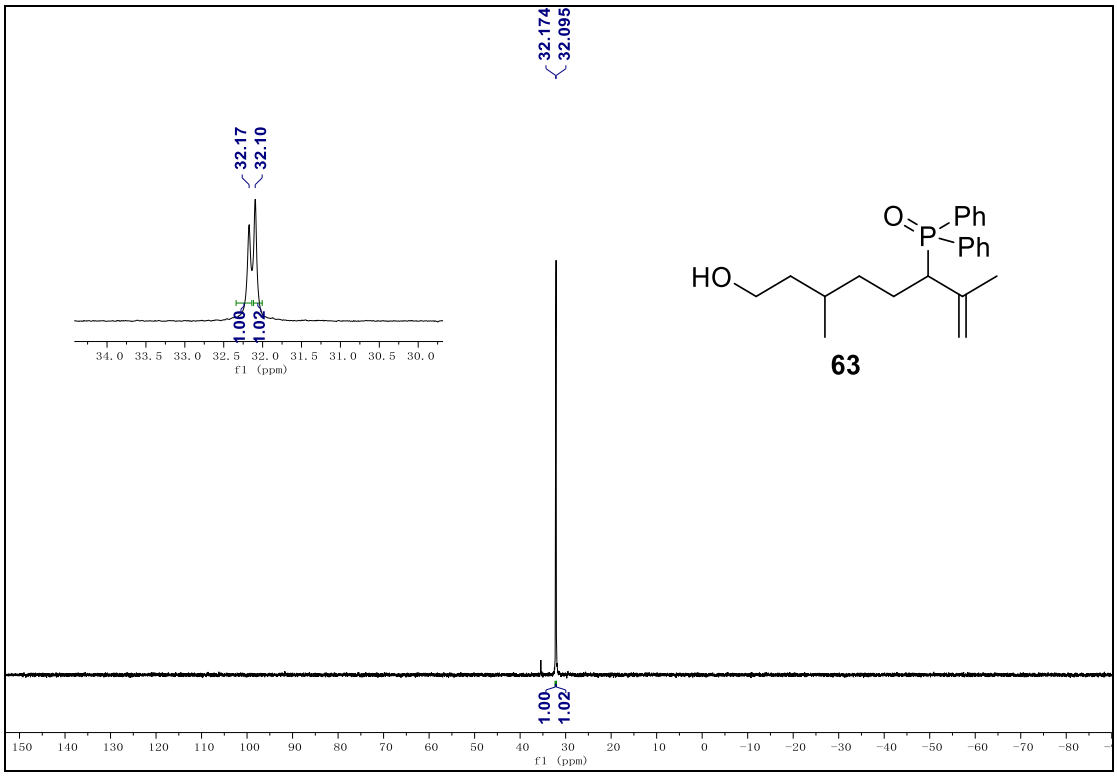



31.66
Ph
Ph
P
O
O
NH
O
O
62
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

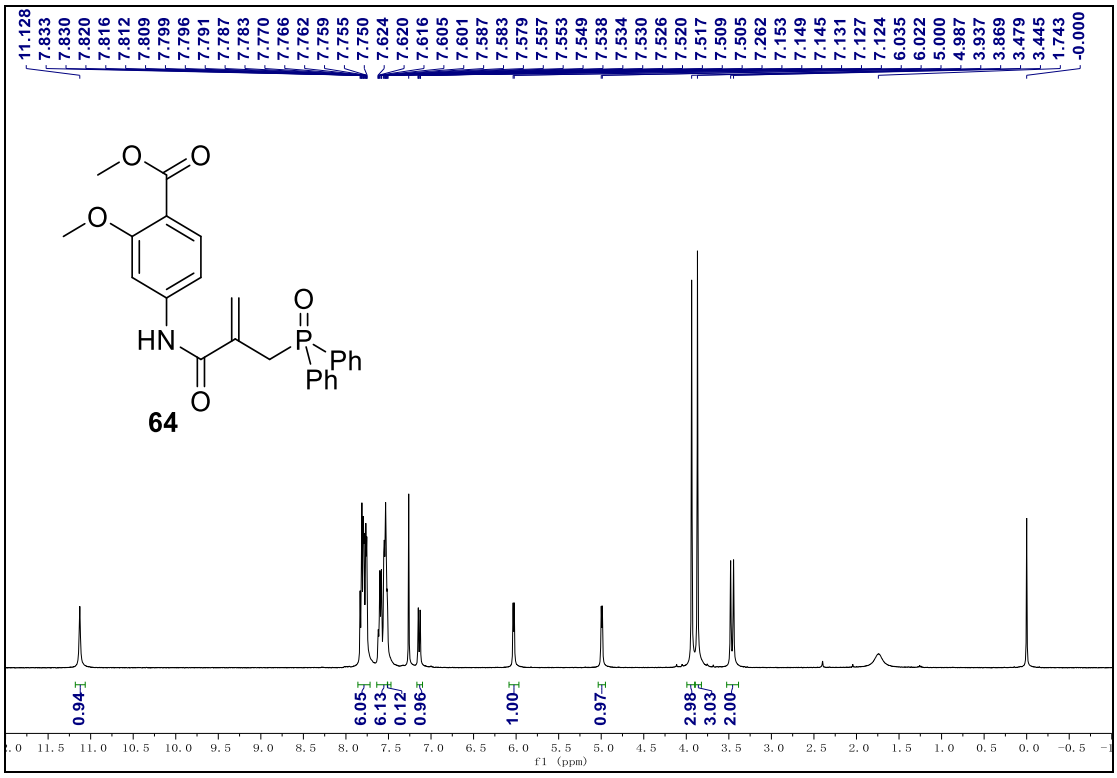
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 63.

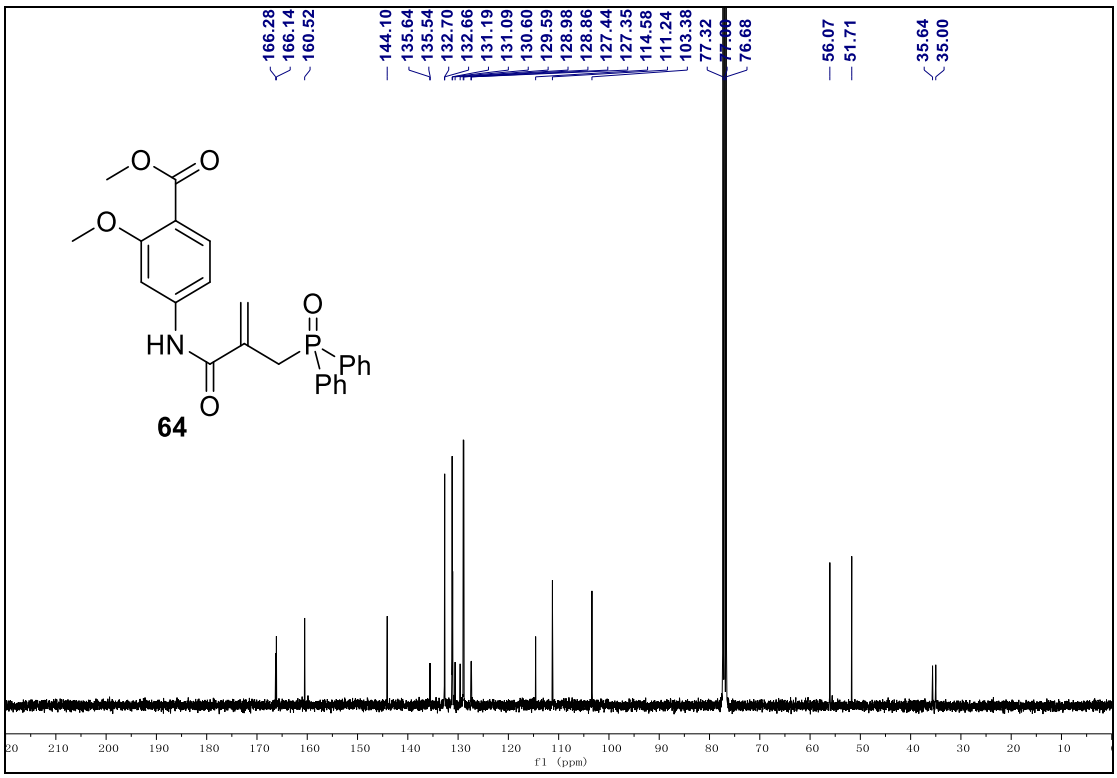


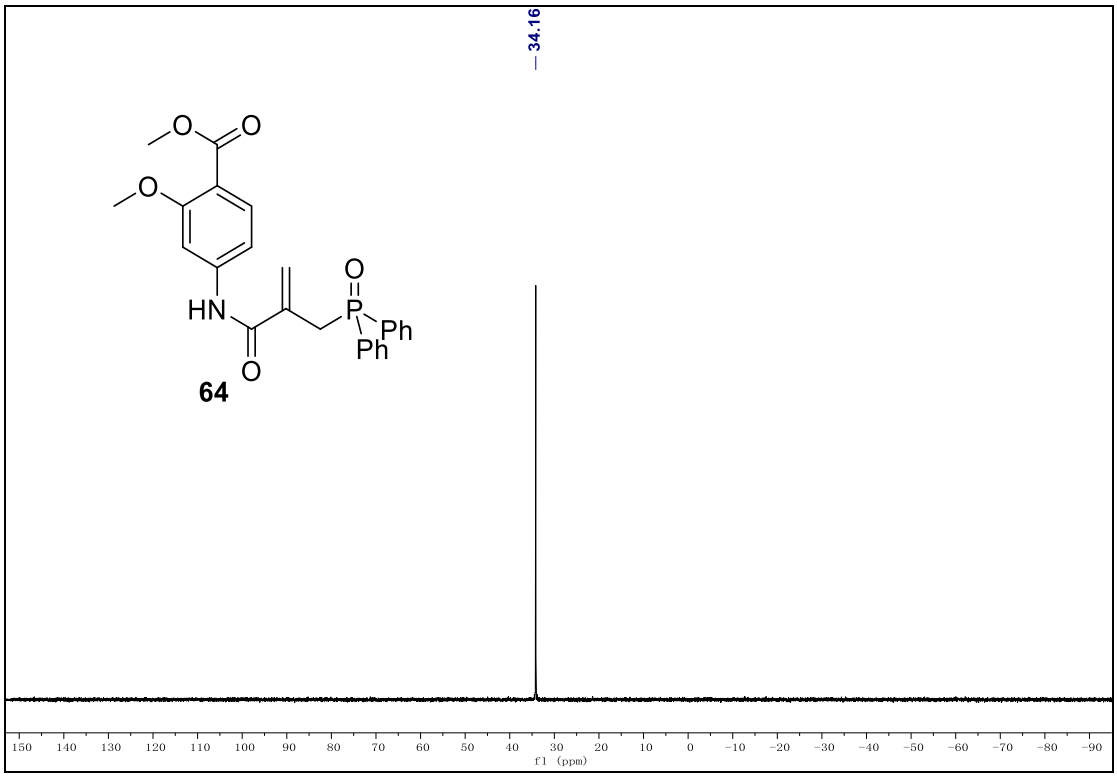



32.174
32.095
32.17
32.10
1.00
1.02
34.0 33.5 33.0 32.5 32.0 31.5 31.0 30.5 30.0
f1 (ppm)
O
P
Ph
Ph
HO
63
1.00
1.02
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

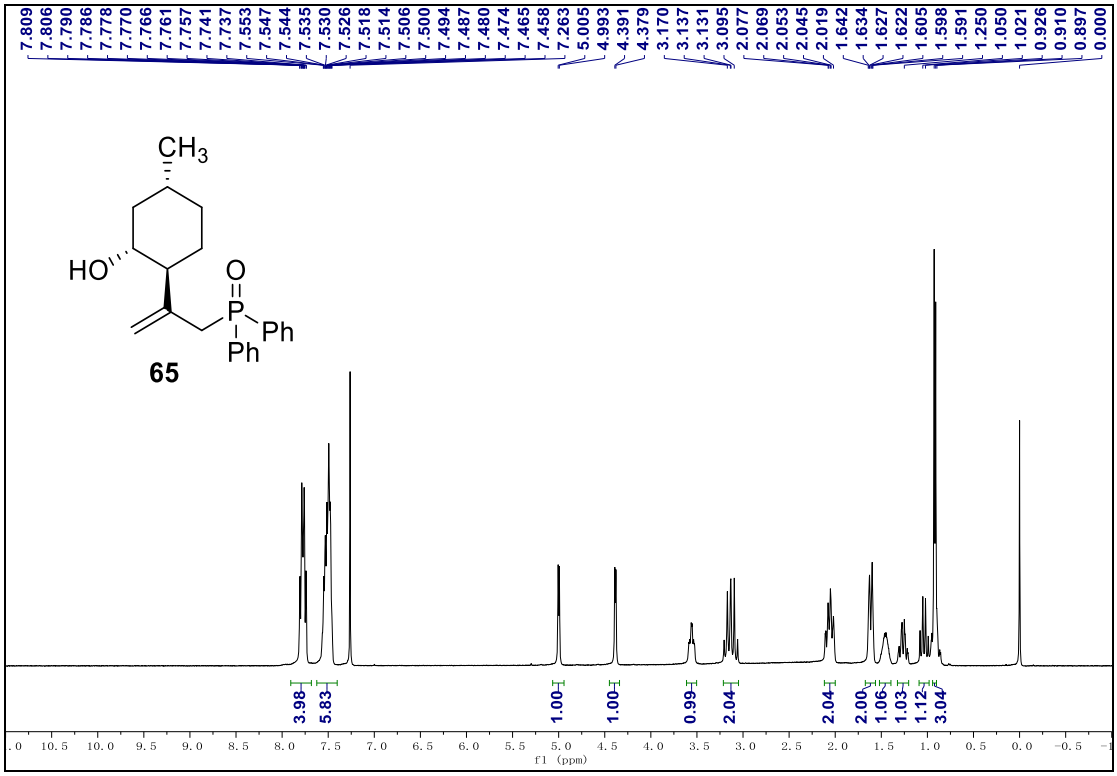
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 64.

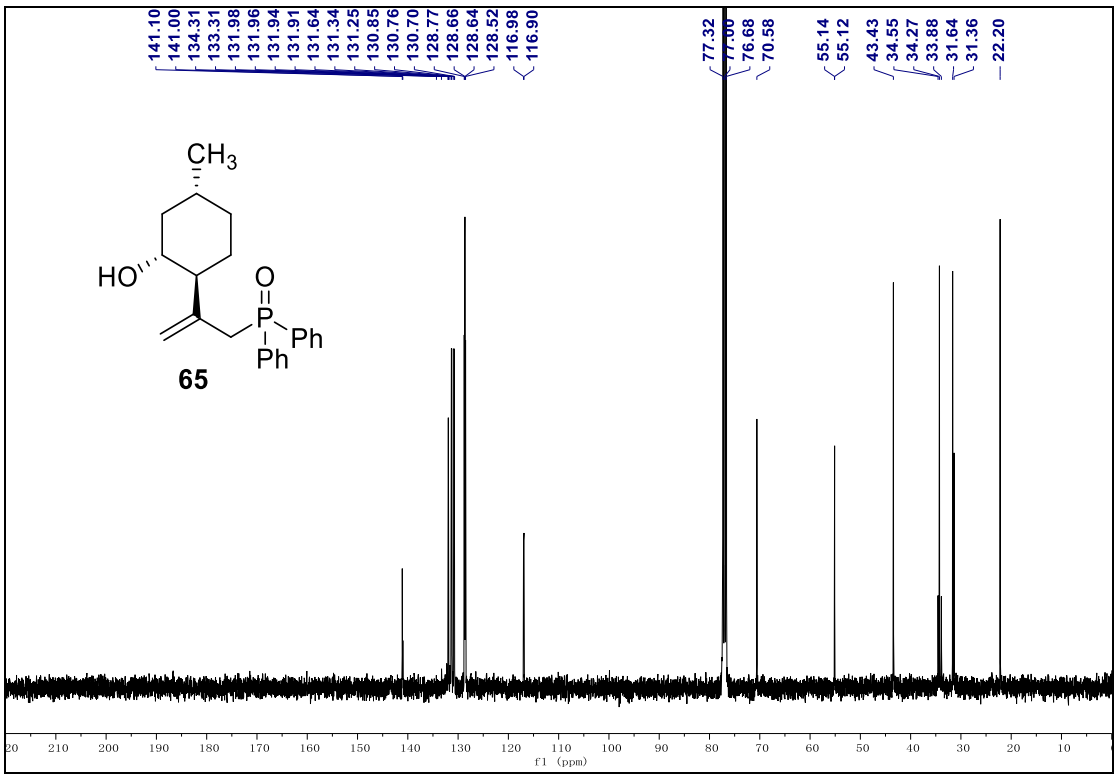


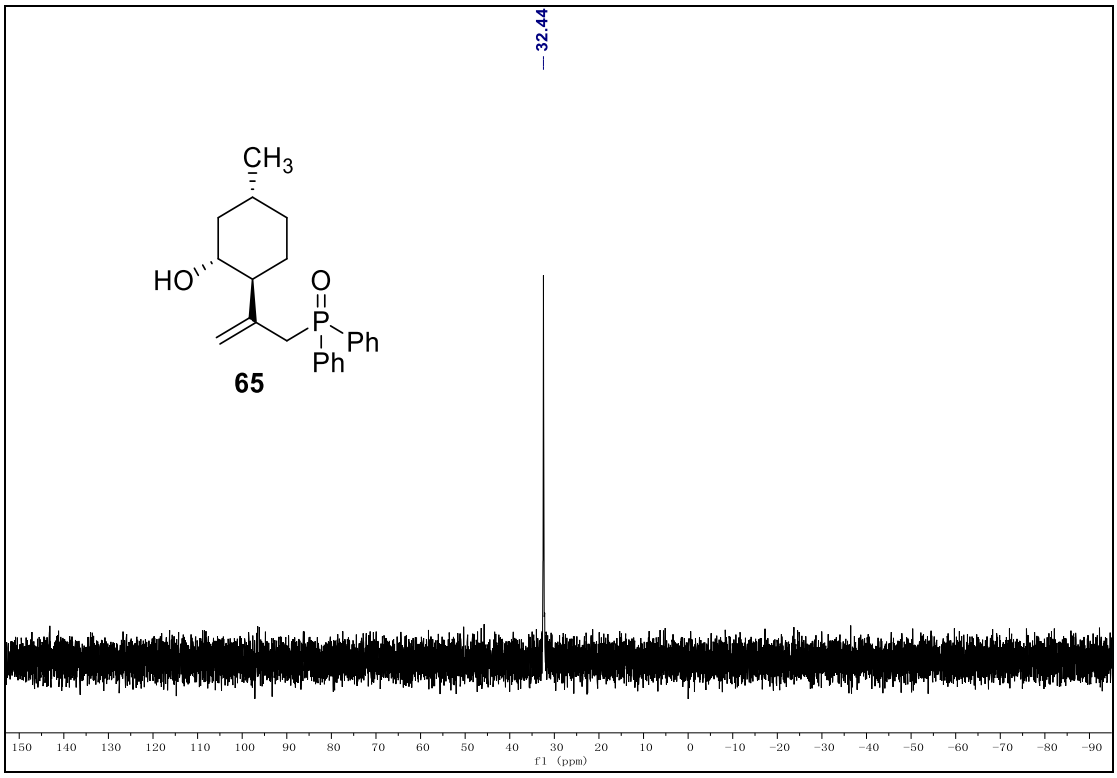



34.16
O
O
O
HN
O
O
P
Ph
Ph
64
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

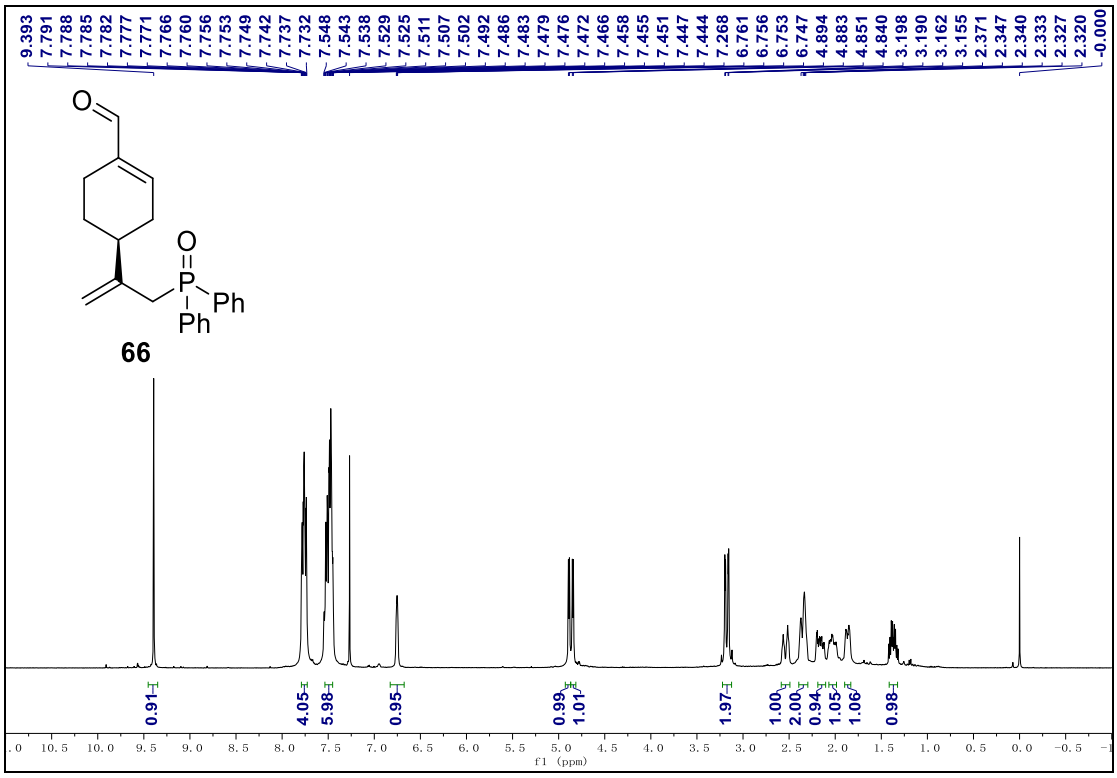
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 65.

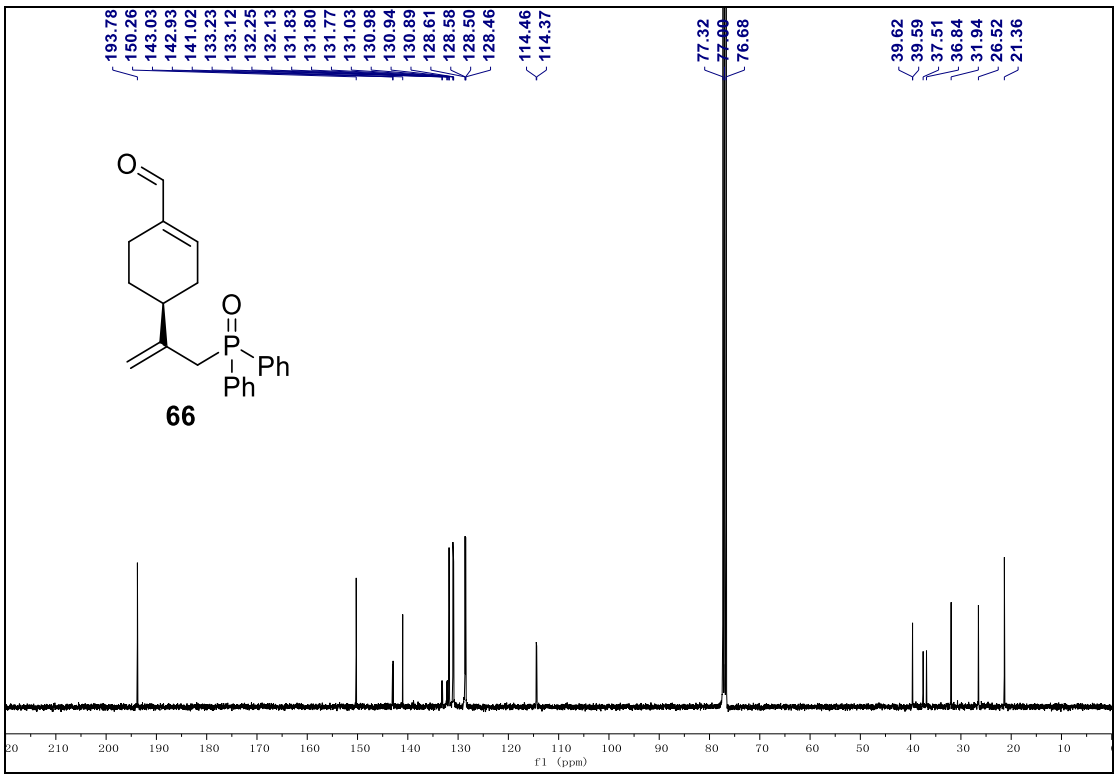


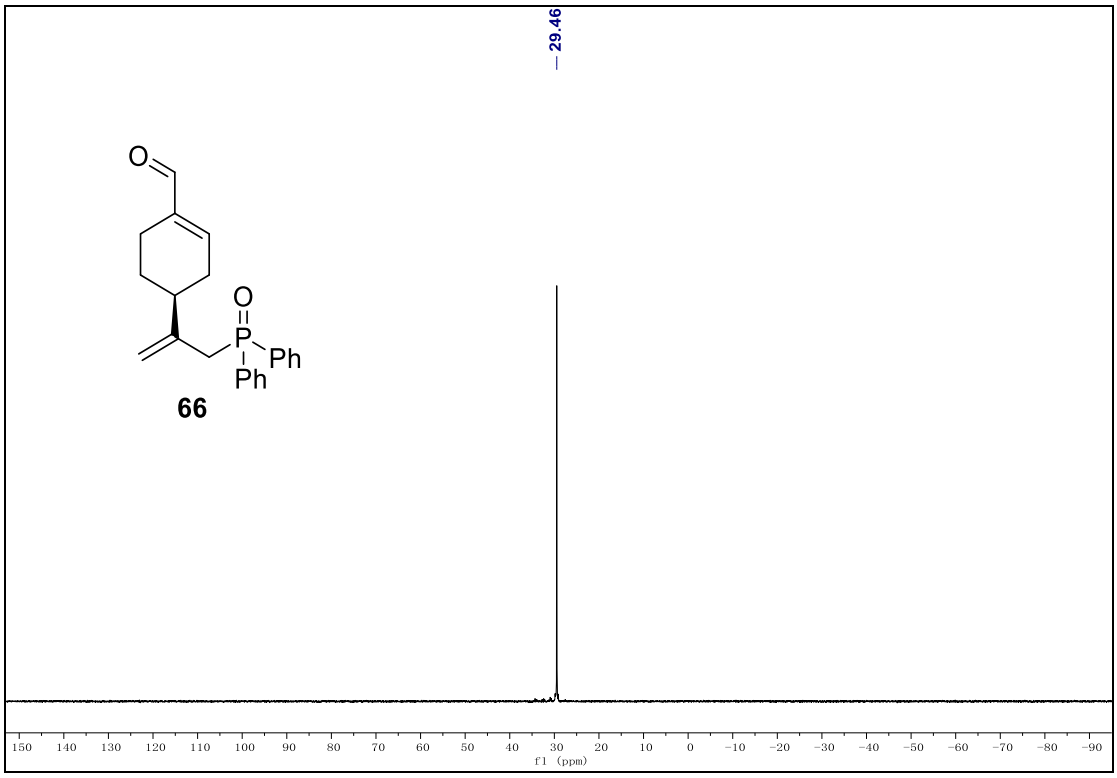



32.44
CH3
HO
O
P
Ph
Ph
65
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

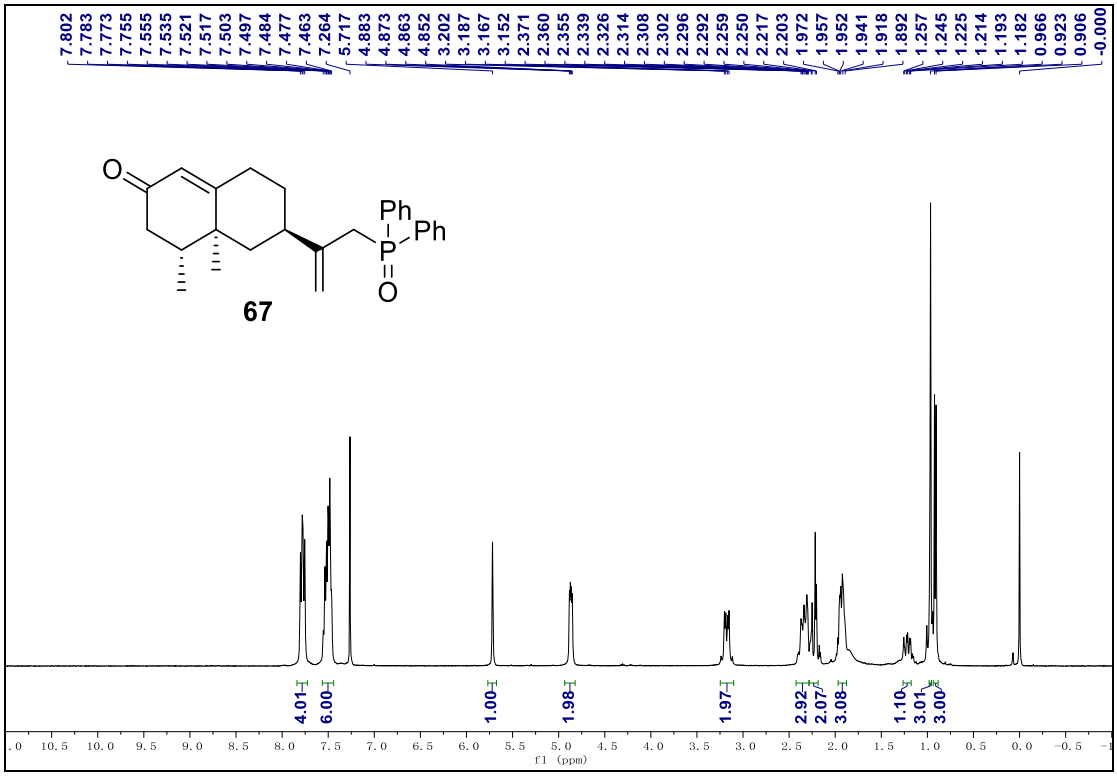
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 66.

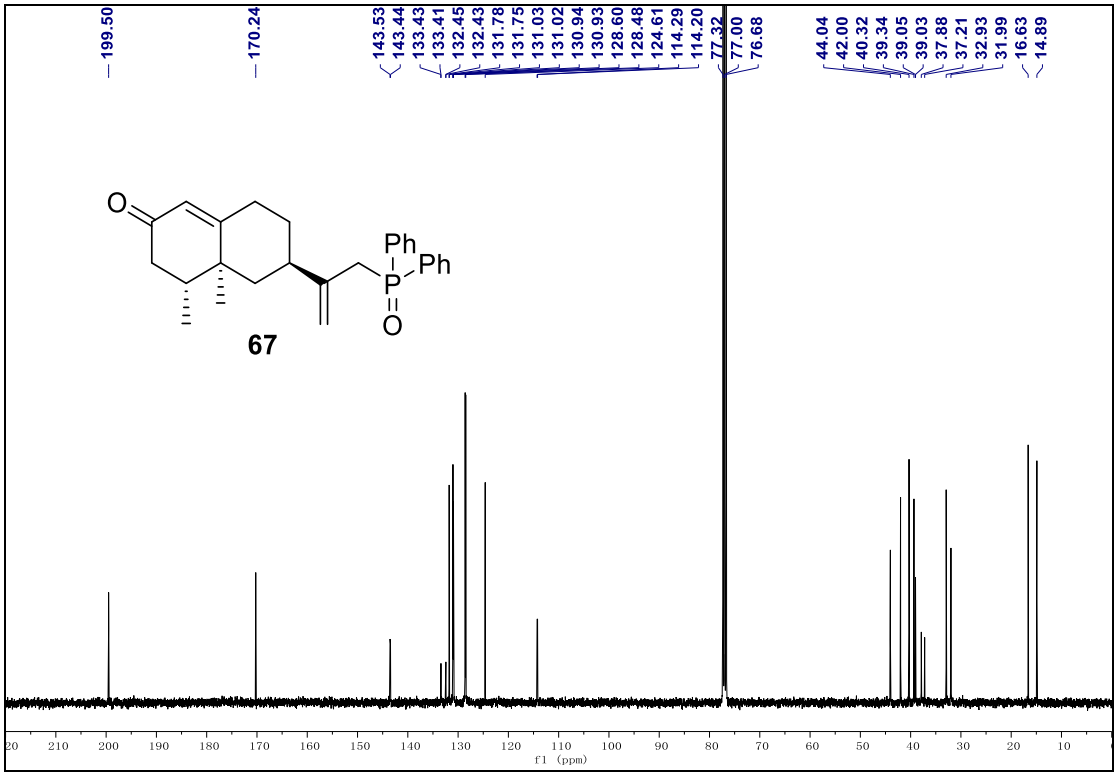


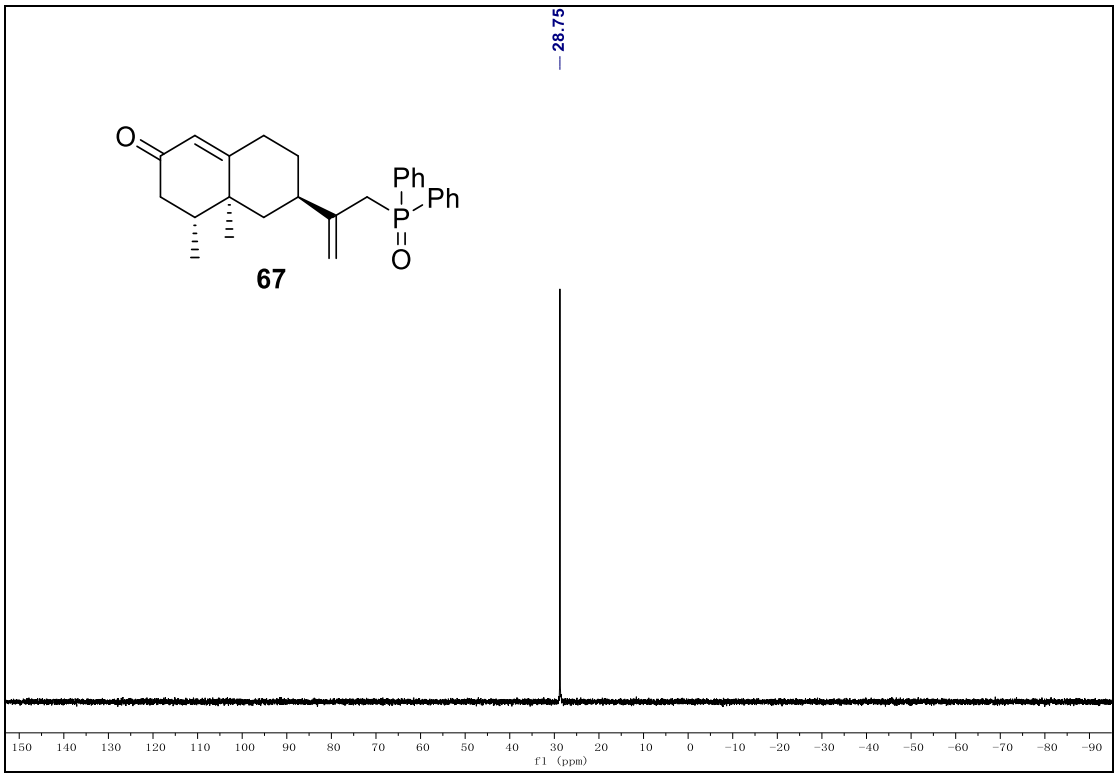



29.46
O
O
P
Ph
Ph
66
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

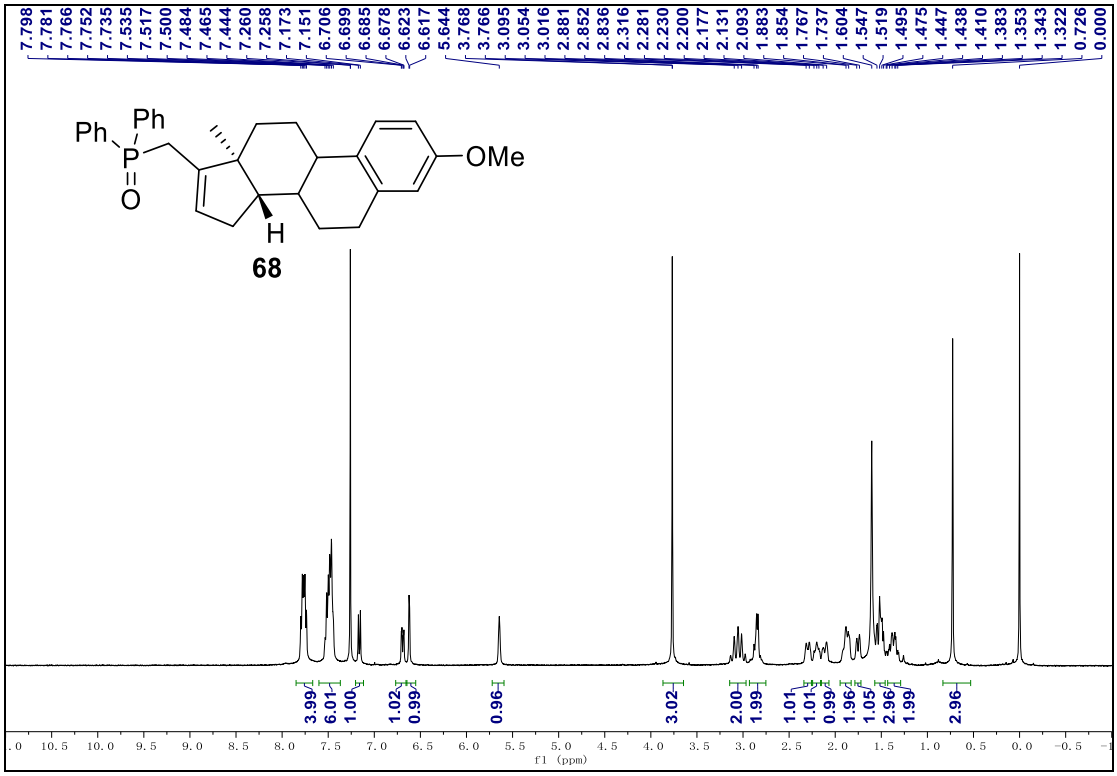
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 67.

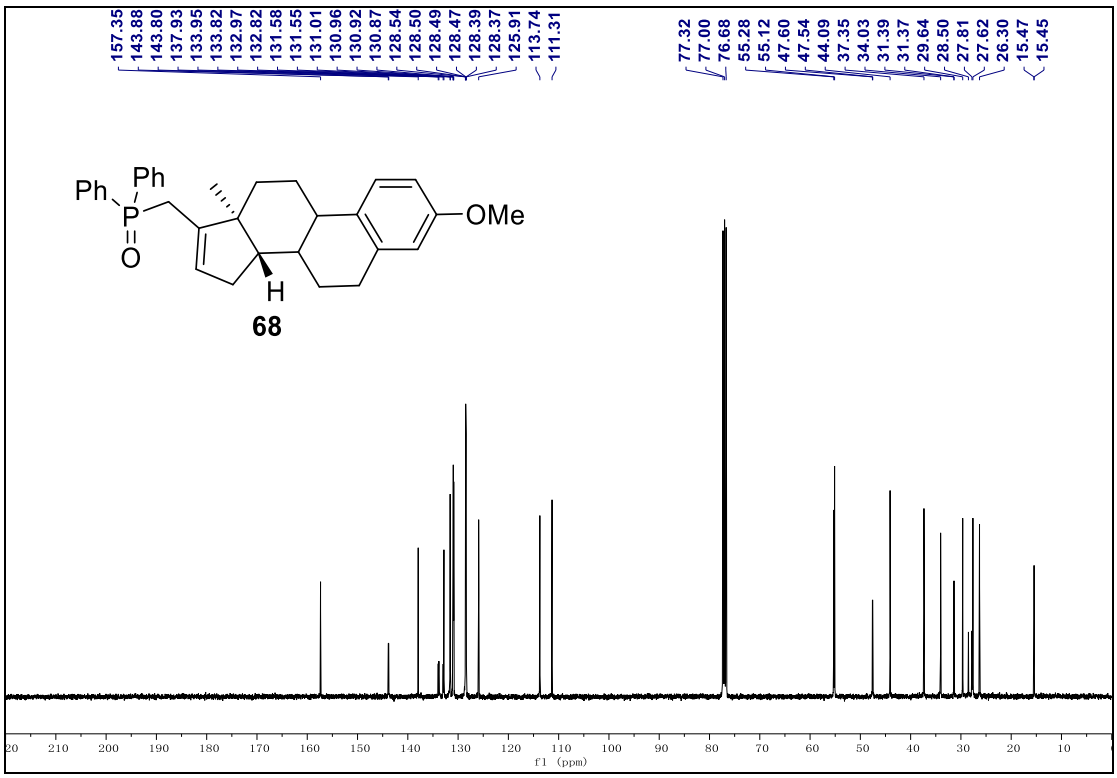


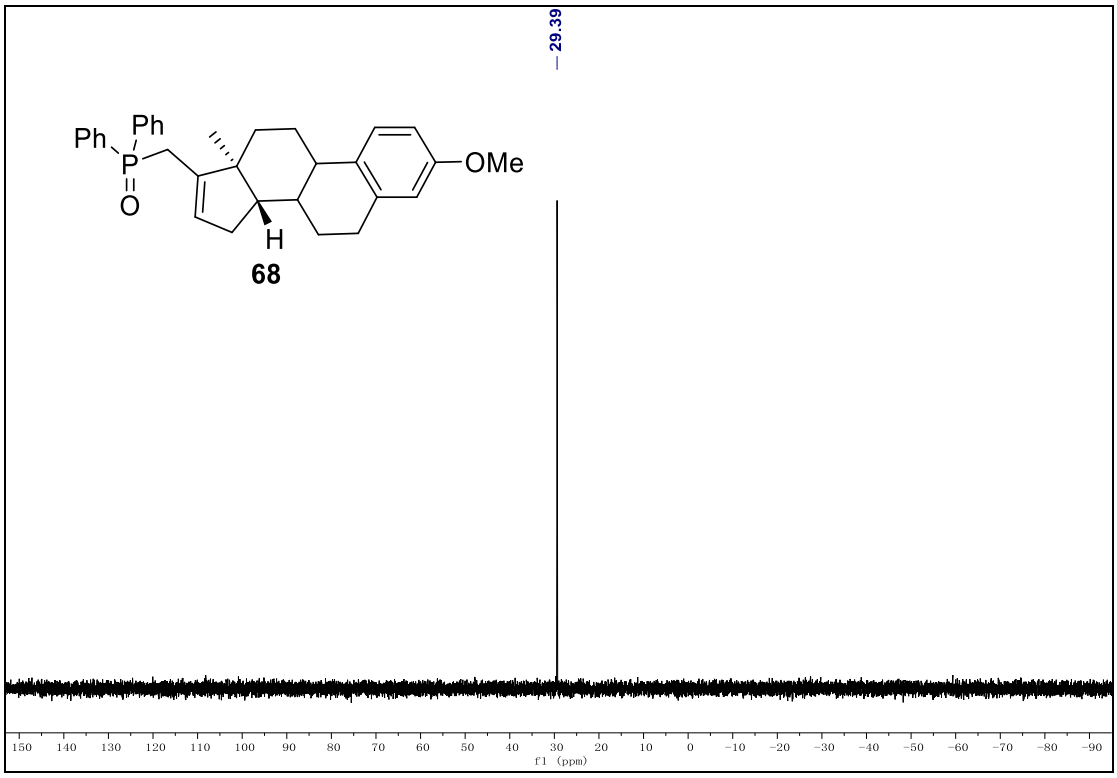



28.75
O
Ph
Ph
P
O
67
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

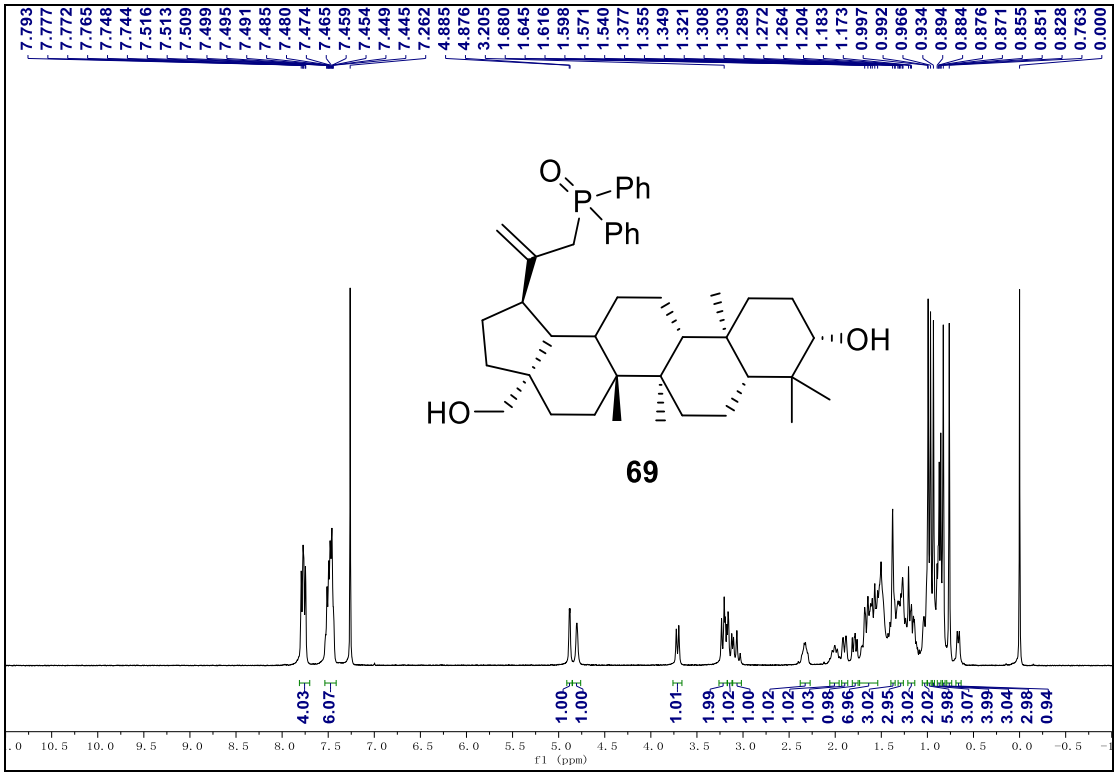
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 68.

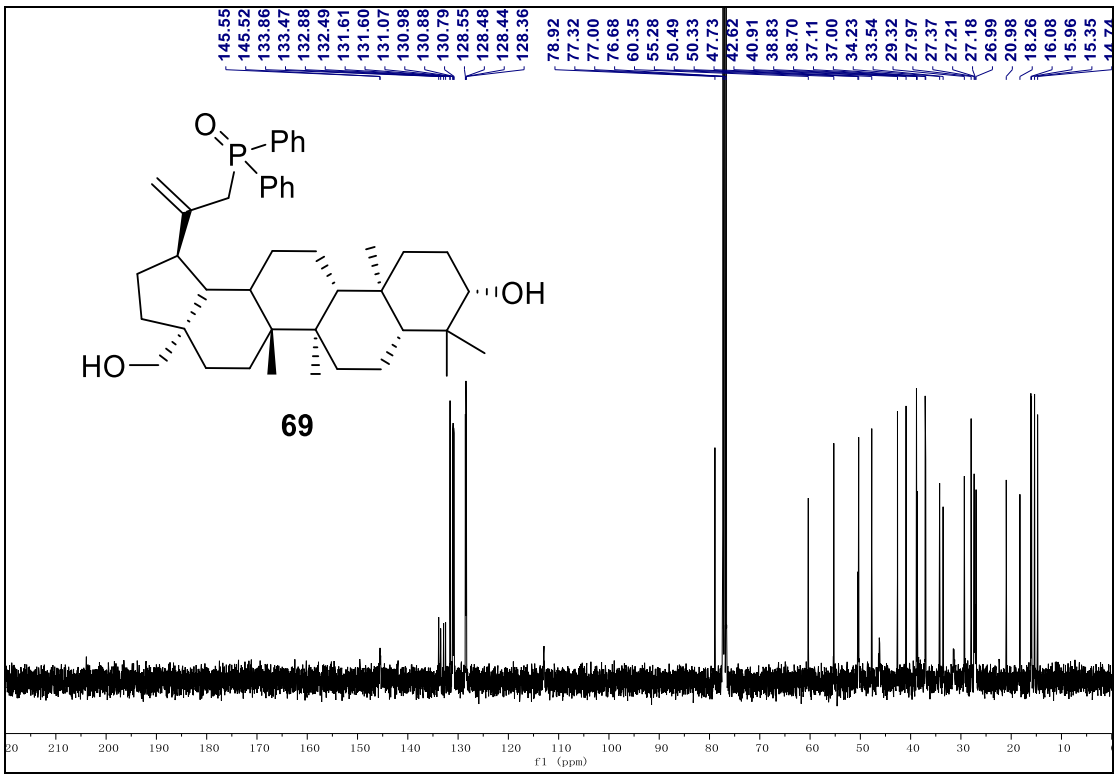


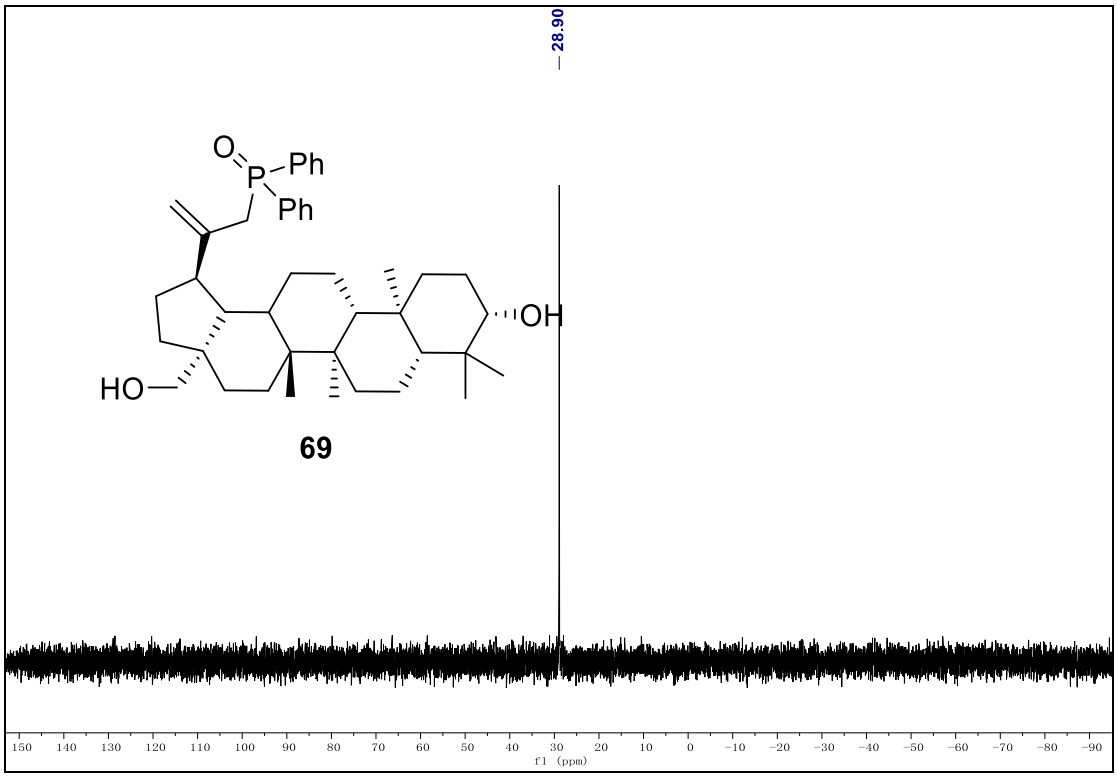



29.39
Ph
Ph
P
O
OMe
H
68
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

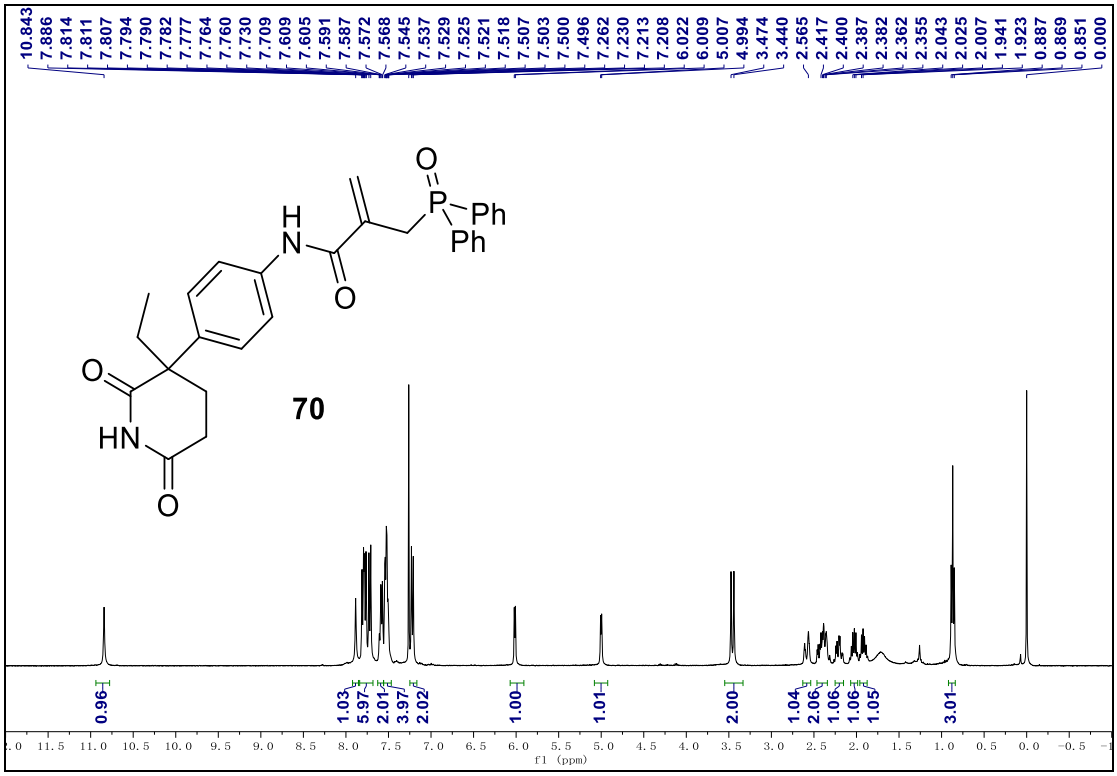
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 69.

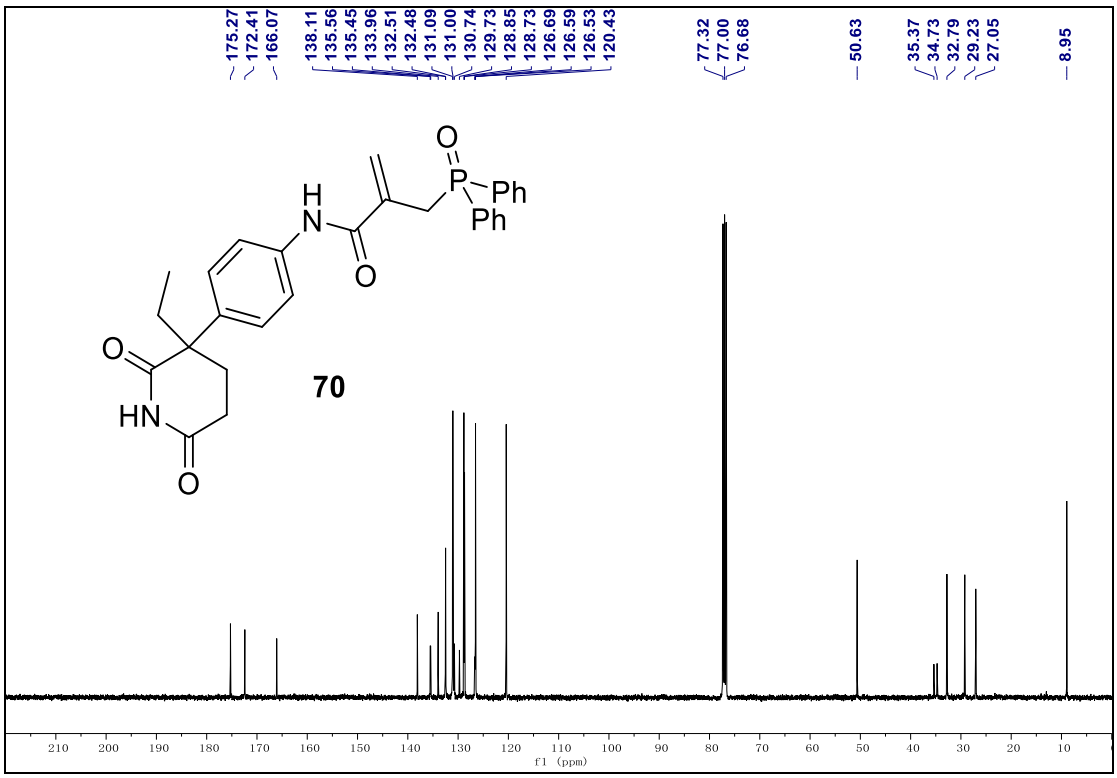


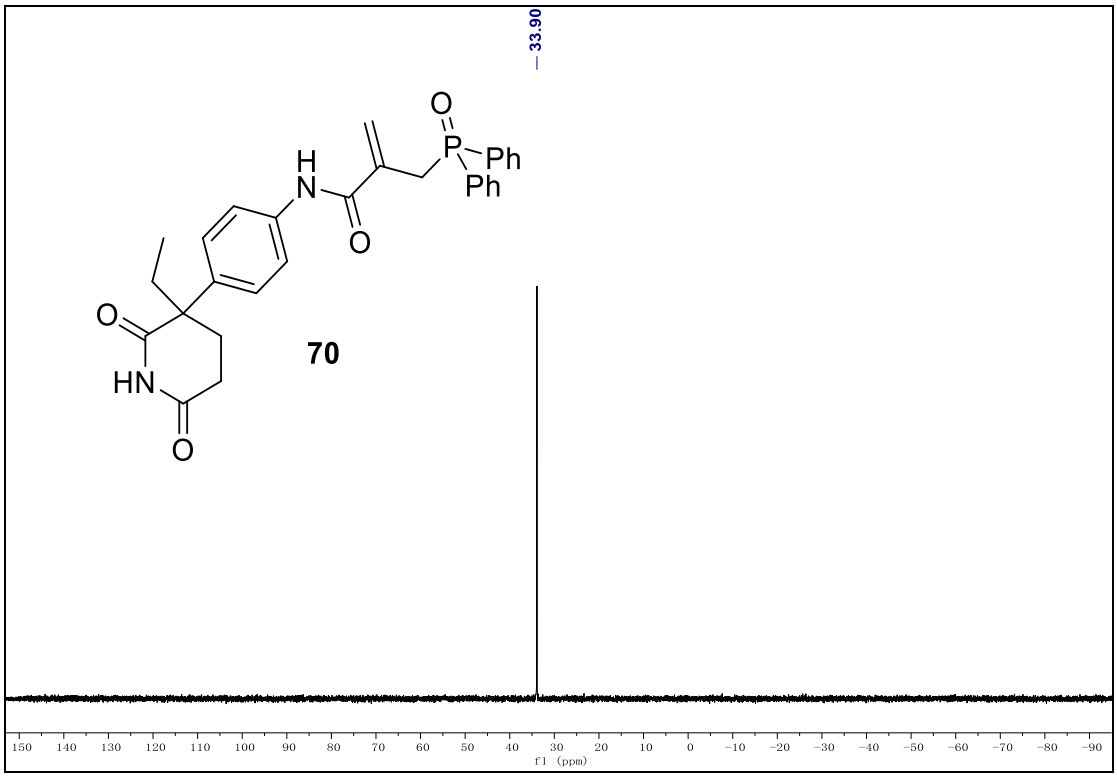



28.90
O
P
Ph
Ph
OH
HO
69
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

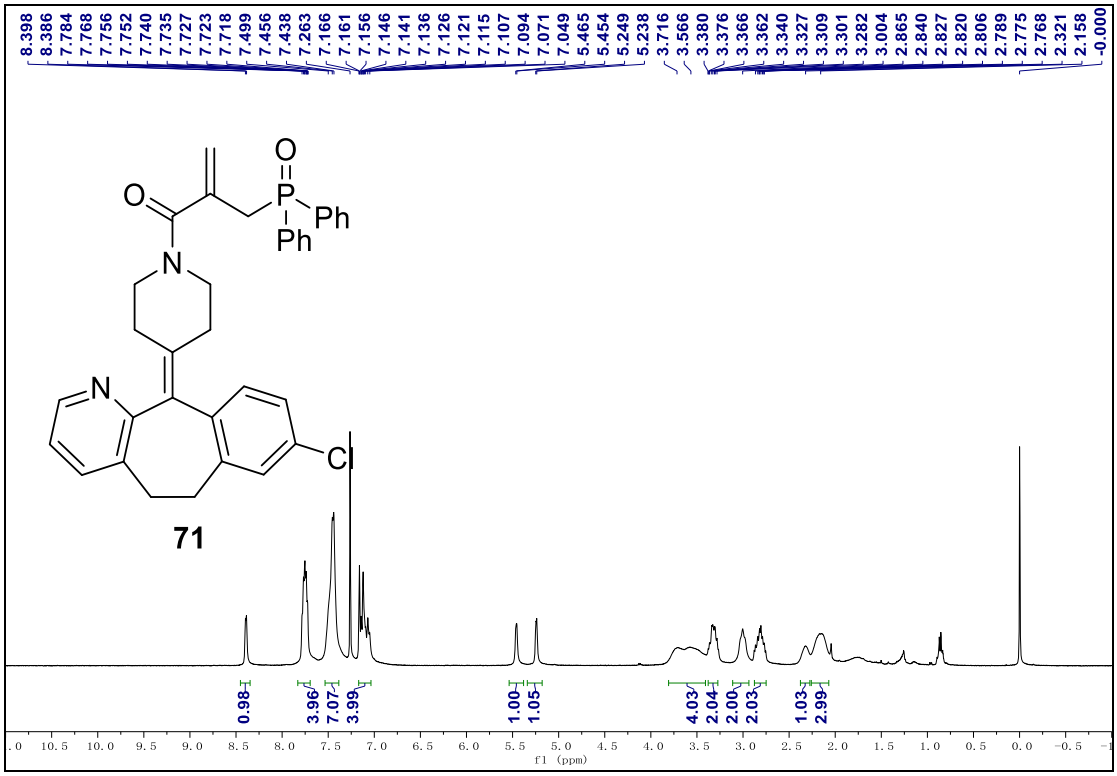
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 70.

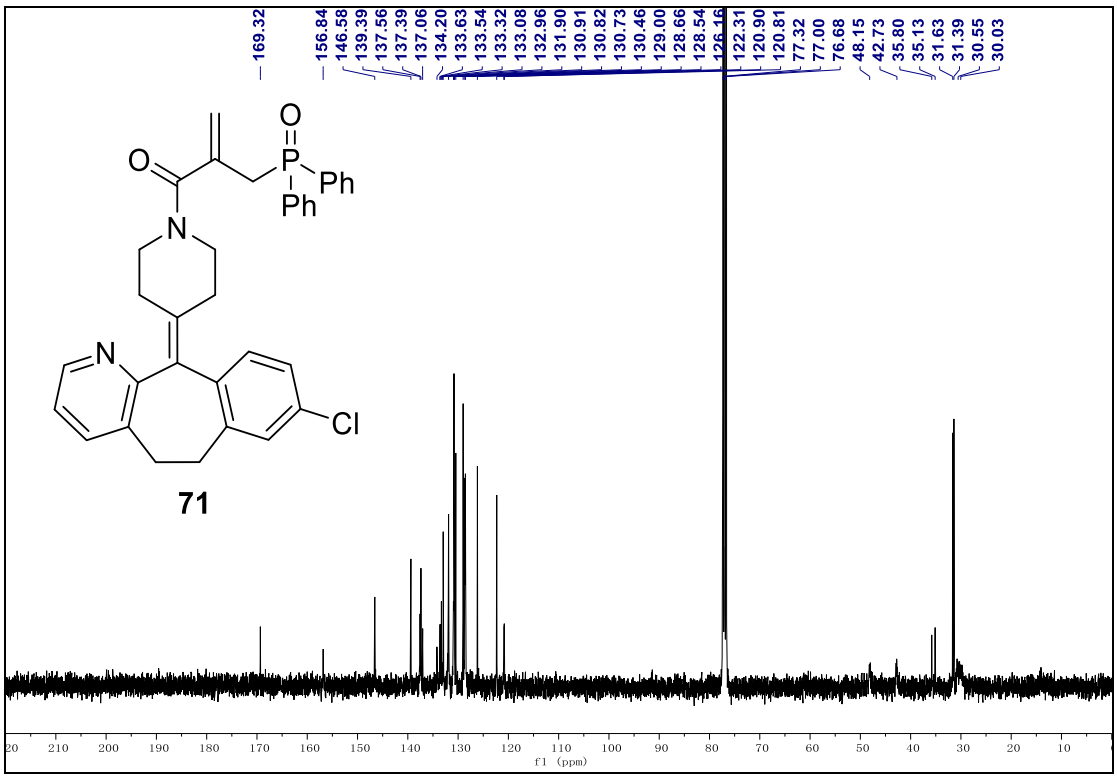


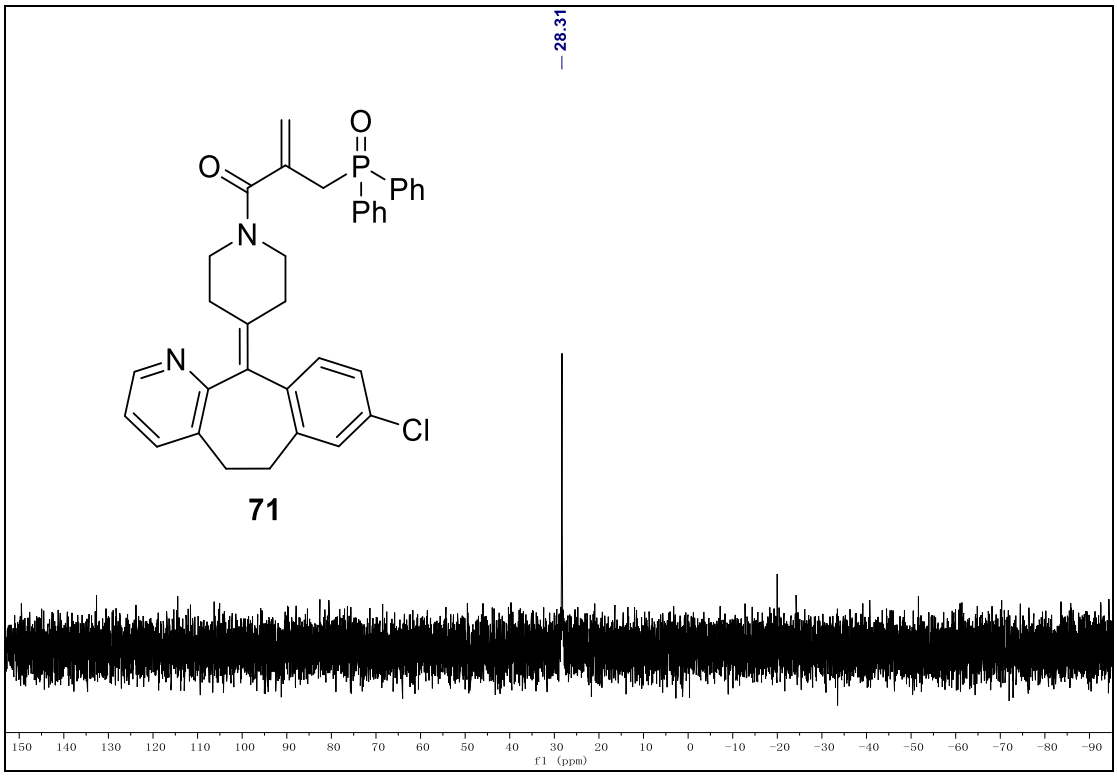



33.90
O
P
Ph
Ph
H
N
O
O
HN
O
70
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

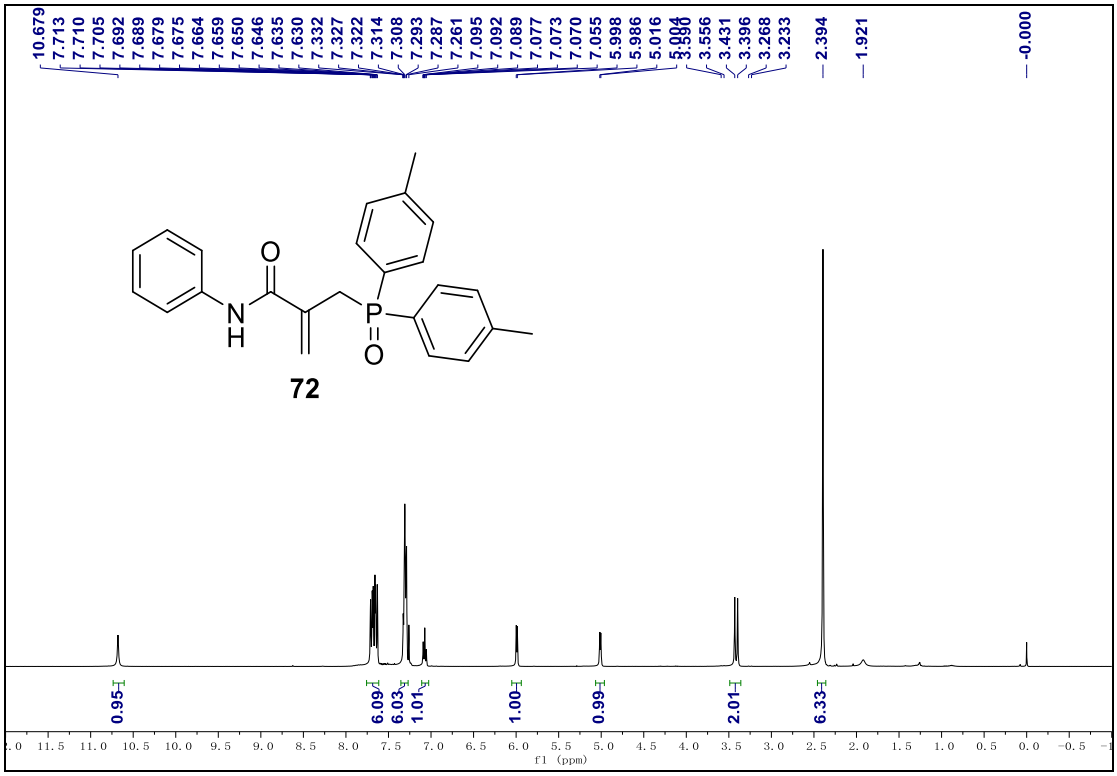
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 71.

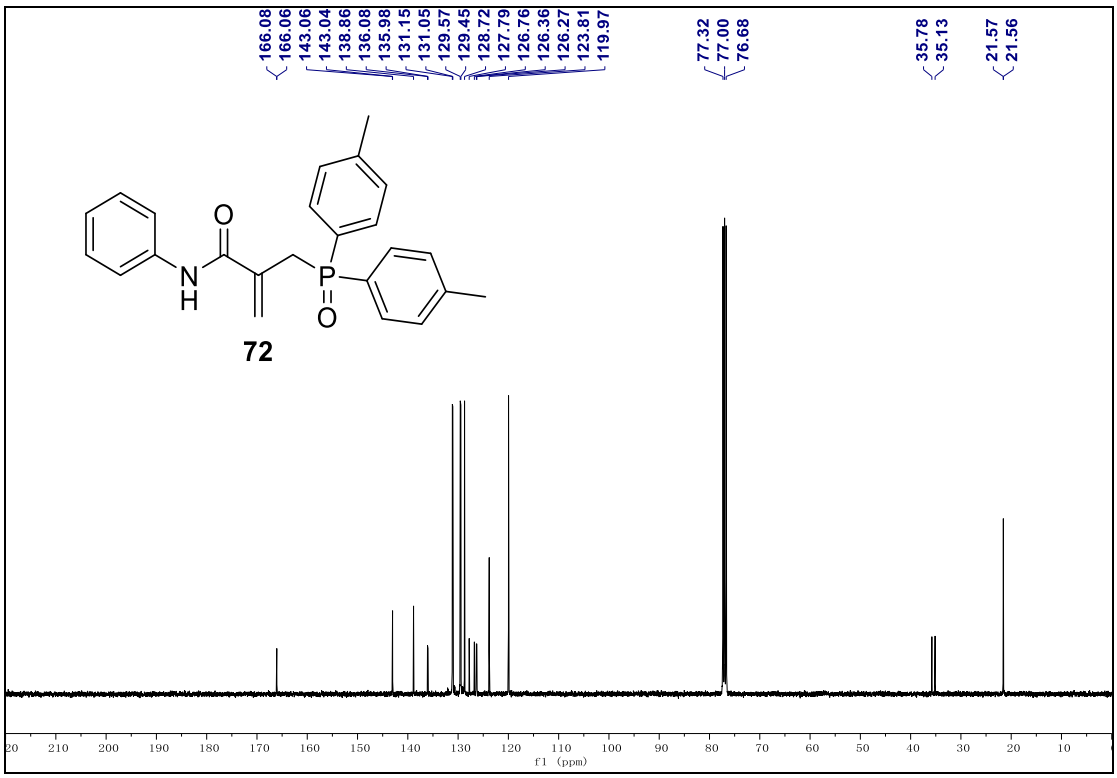


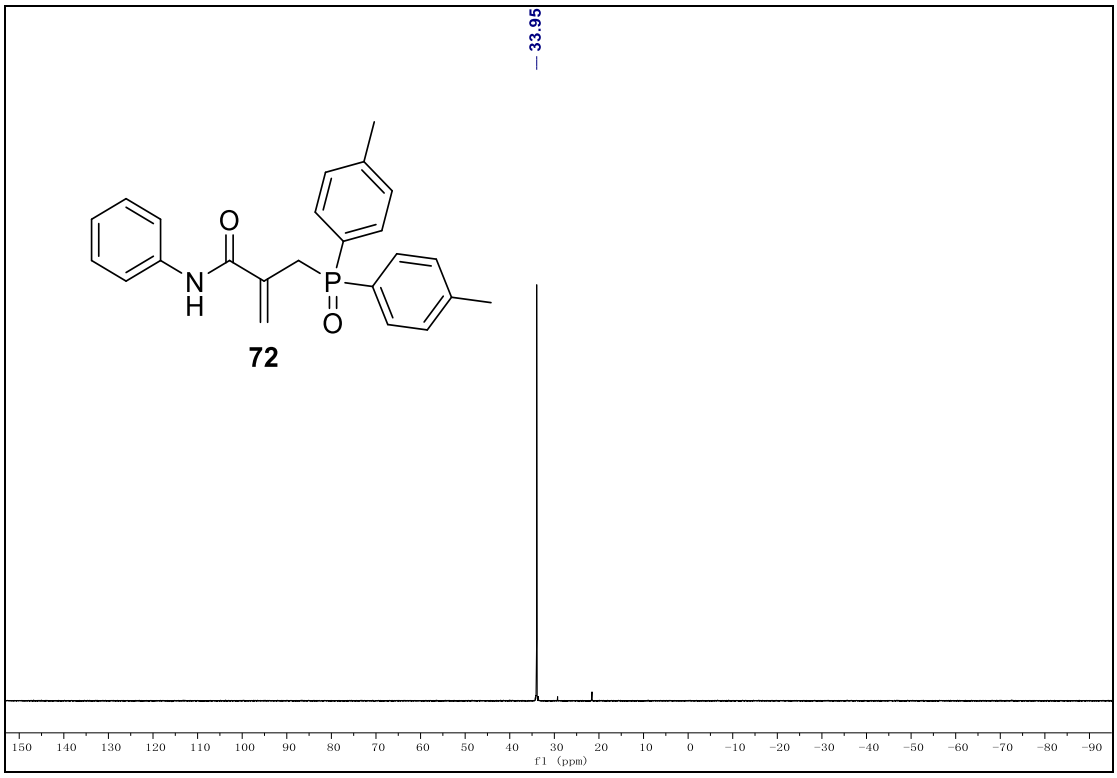



28.31
O
O
P
Ph
Ph
N
N
Cl
71
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

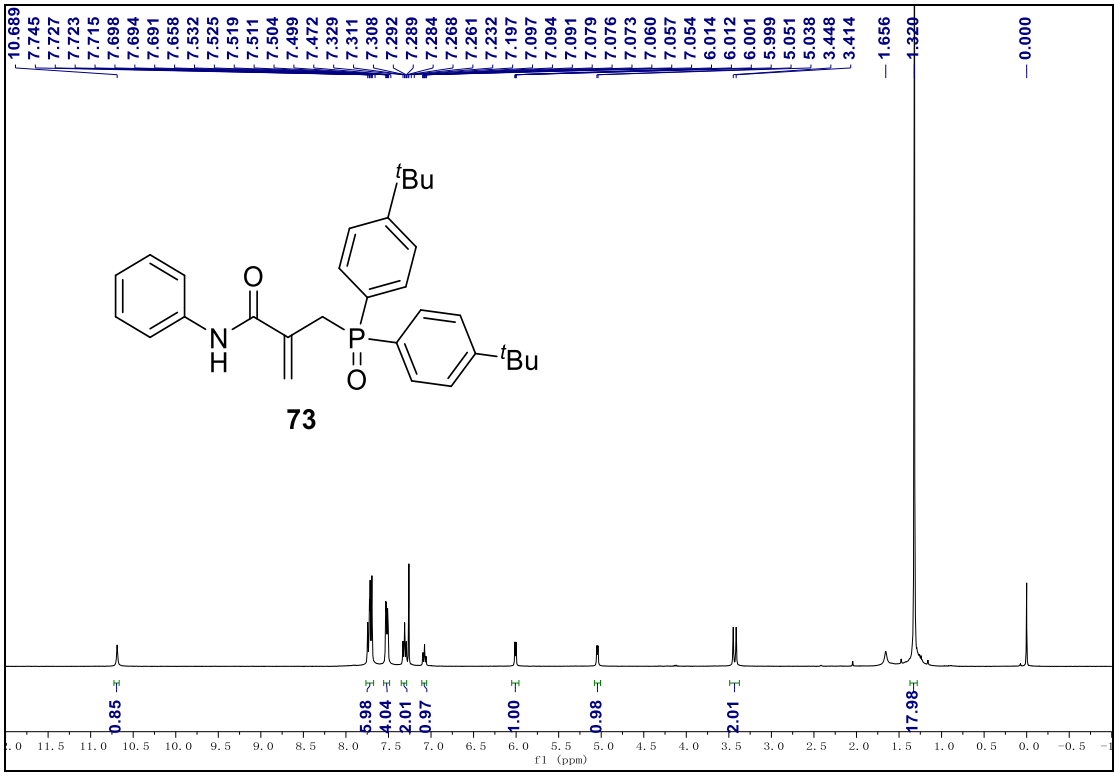
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 72.

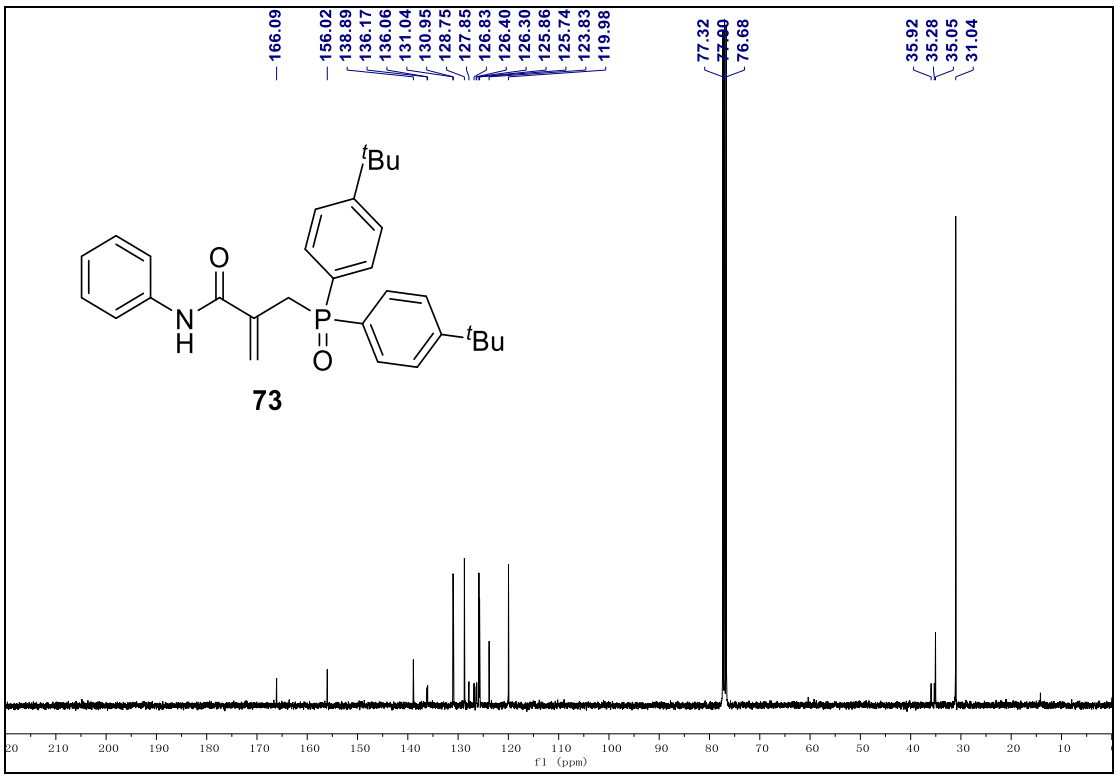


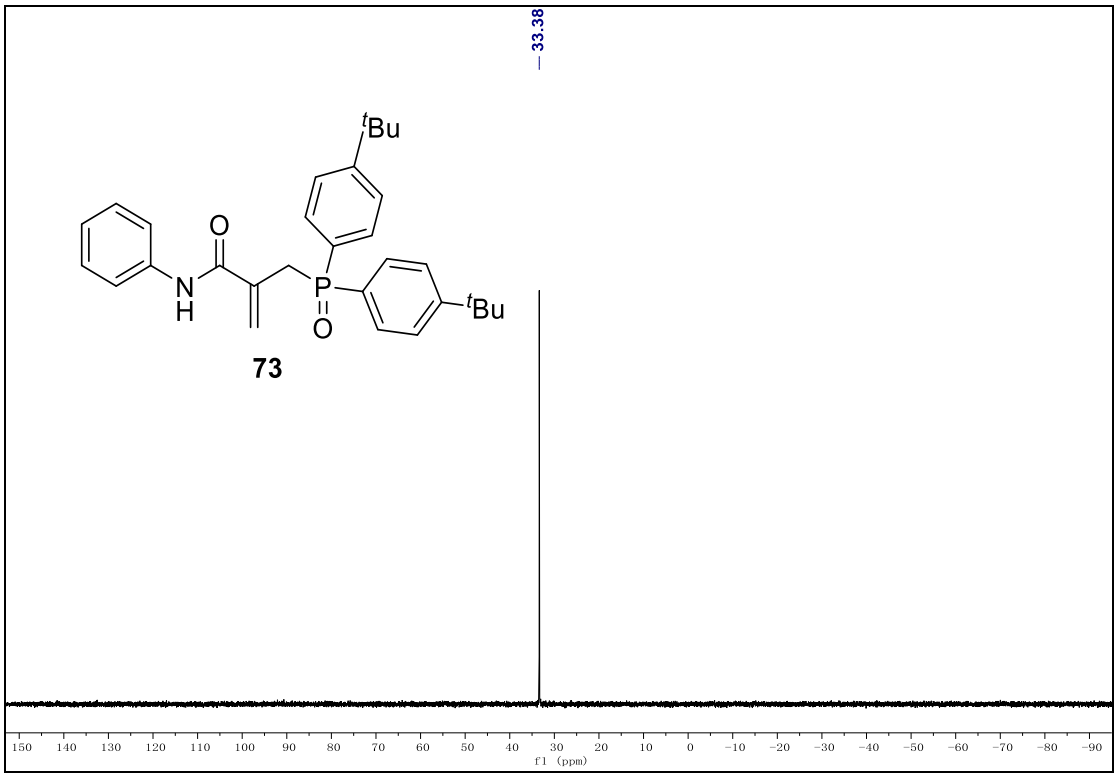



33.95
O
N
H
P
O
72
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

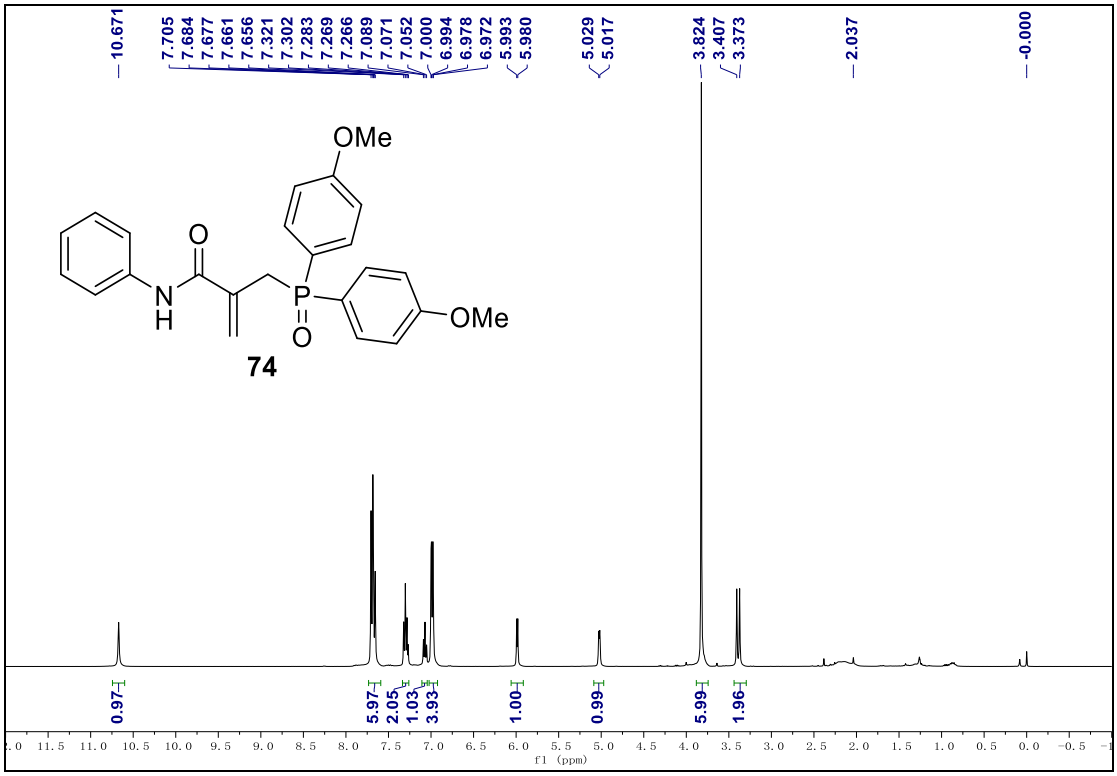
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 73.

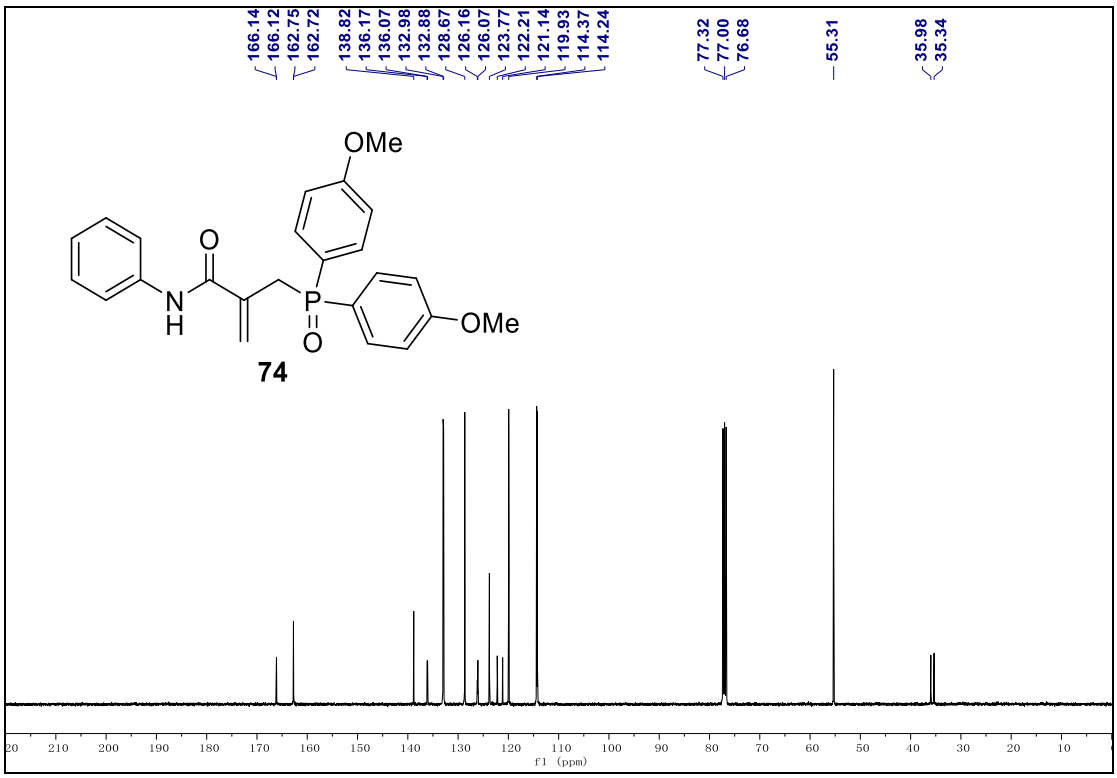


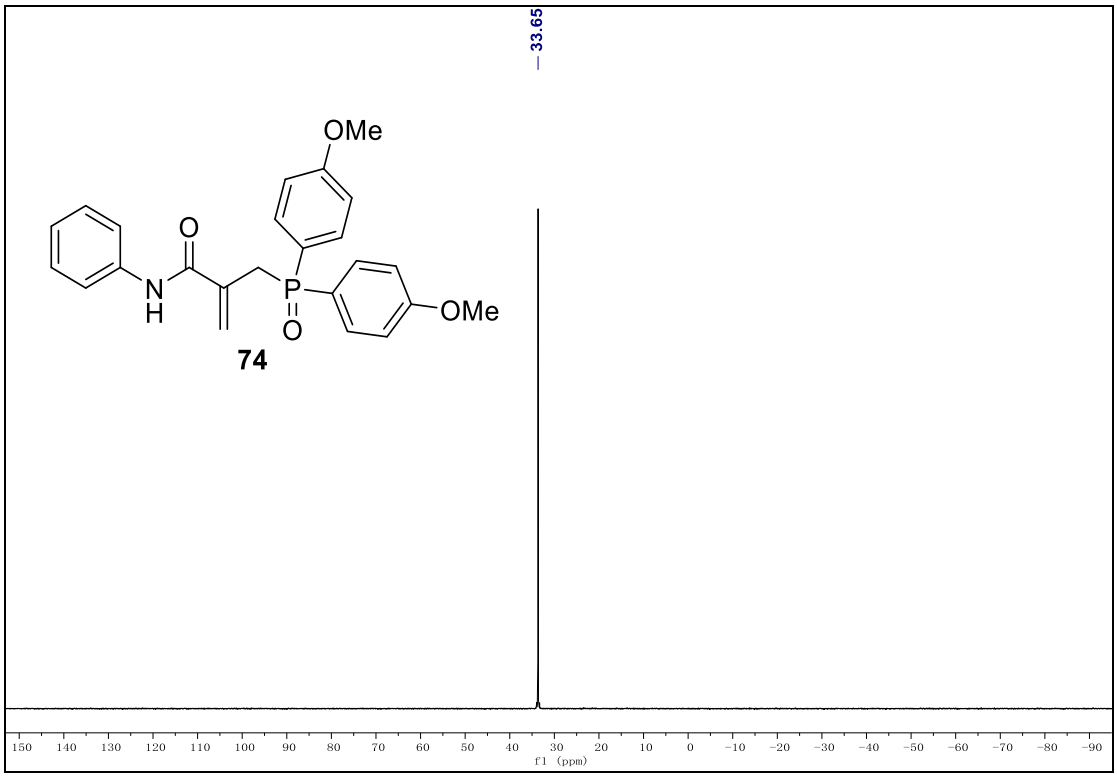



33.38
tBu
O
N
H
P
O
tBu
73
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

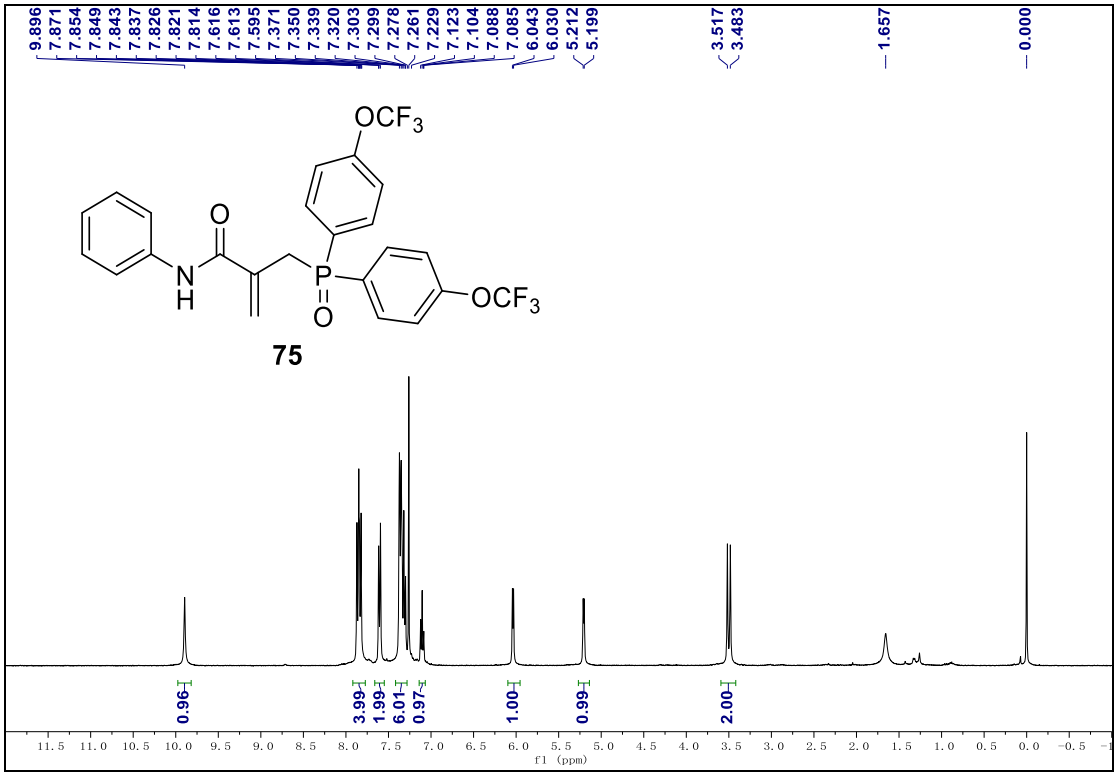
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 74.

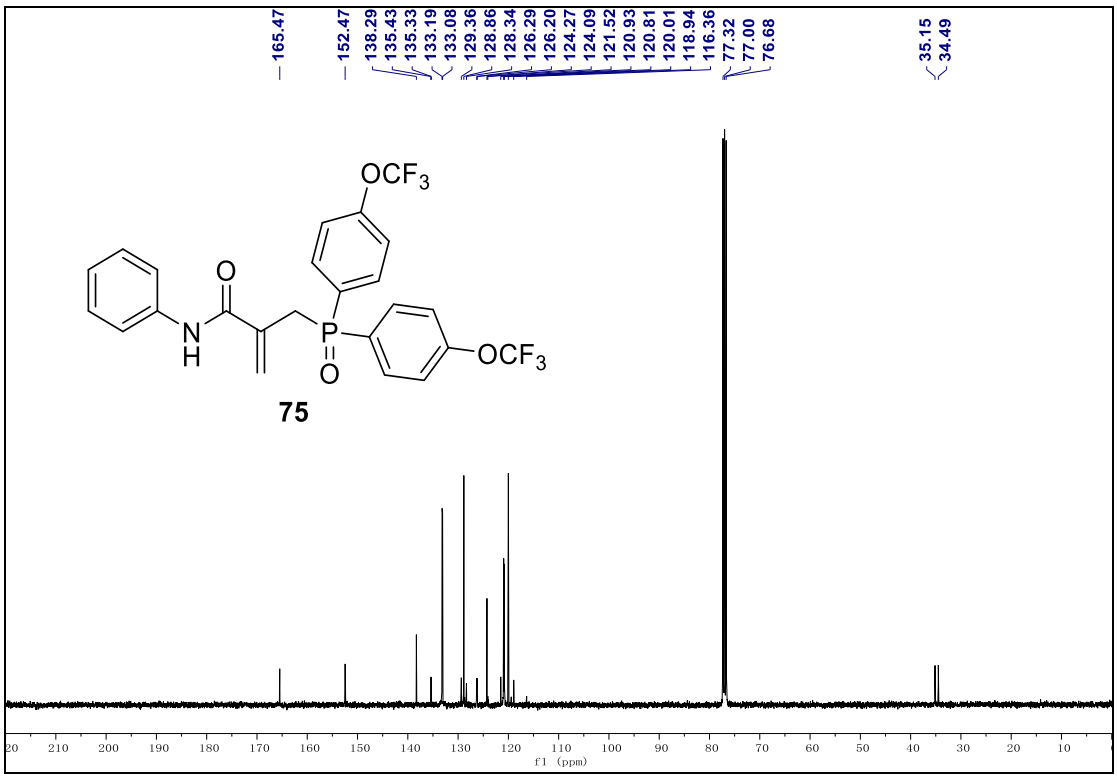


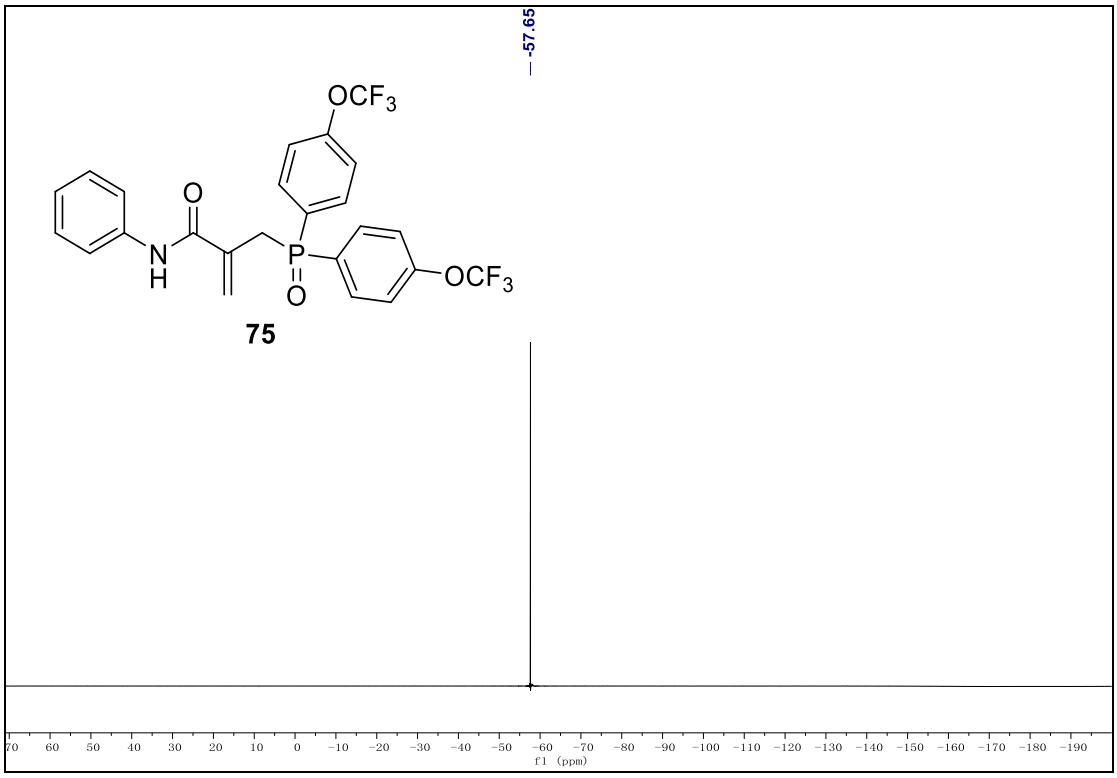


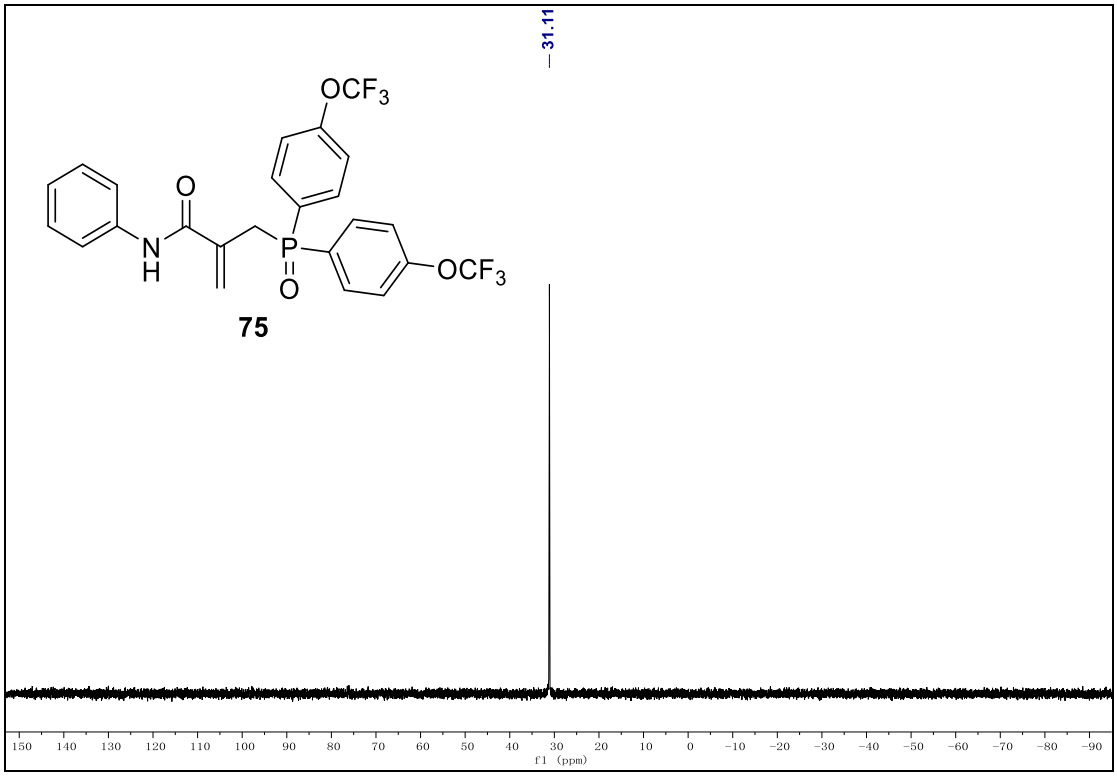

33.65
OMe
O
N
H
P
O
OMe
74
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 75.

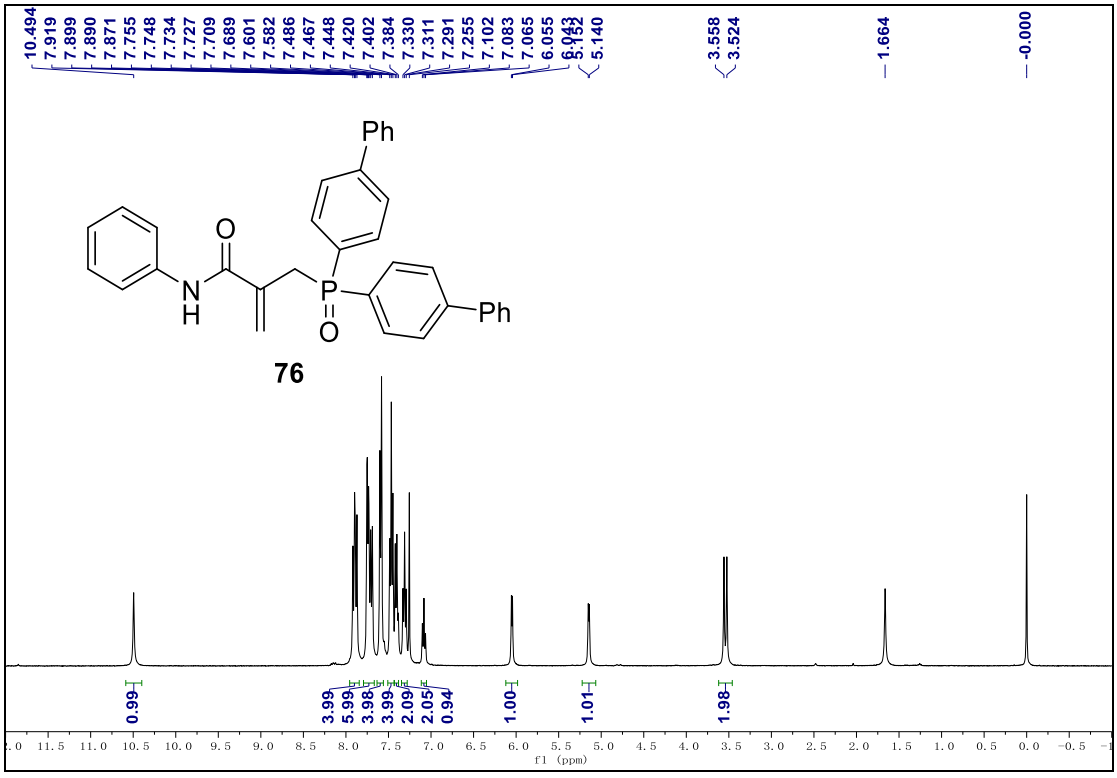


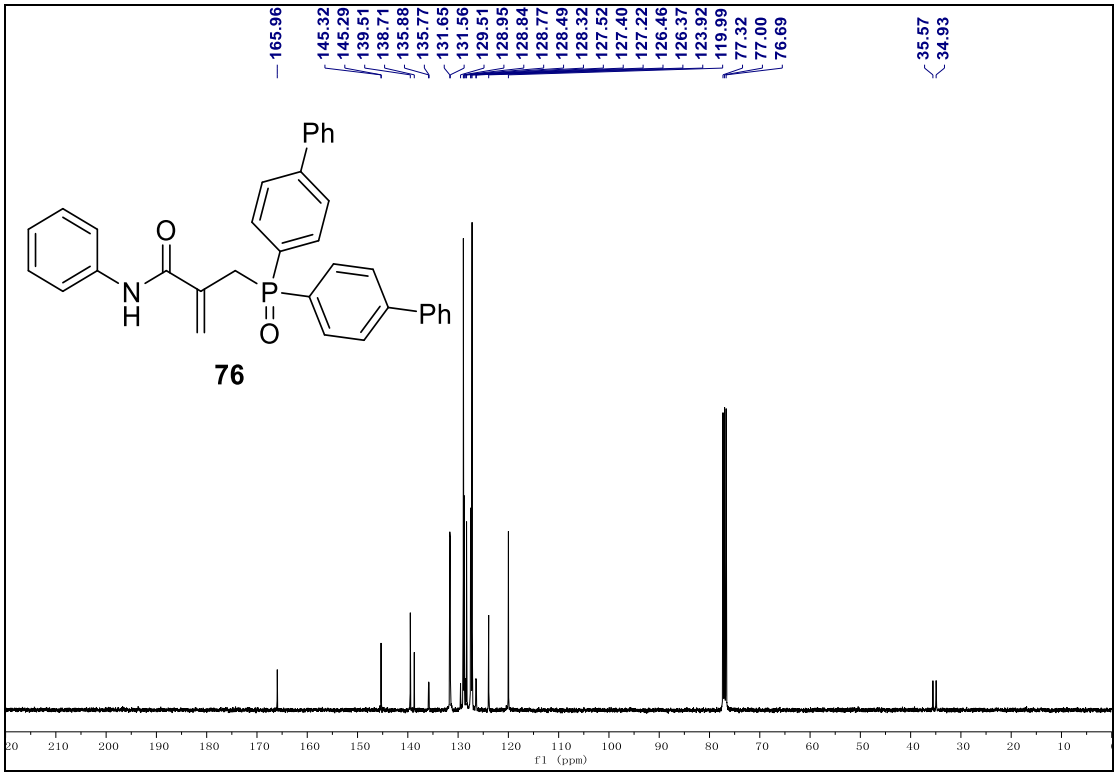


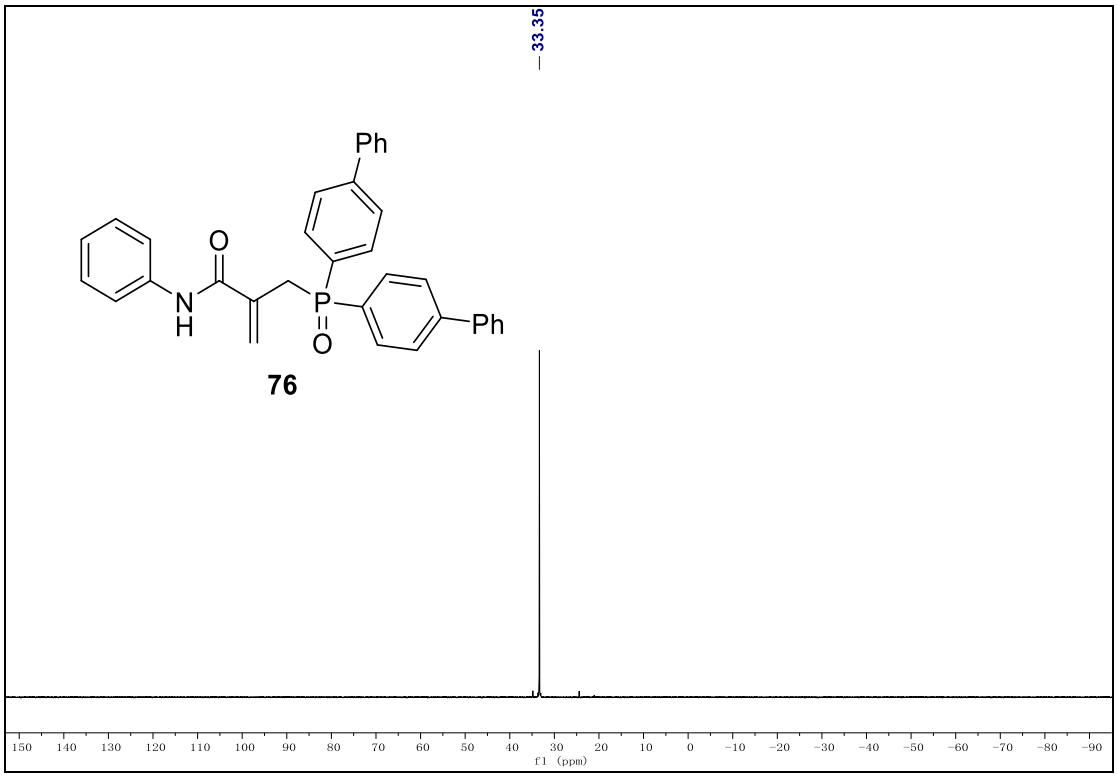

-57.65
OCF3
O
N
H
P
O
OCF3
75
70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)


31.11
OCF3
O
N
H
P
O
OCF3
75
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

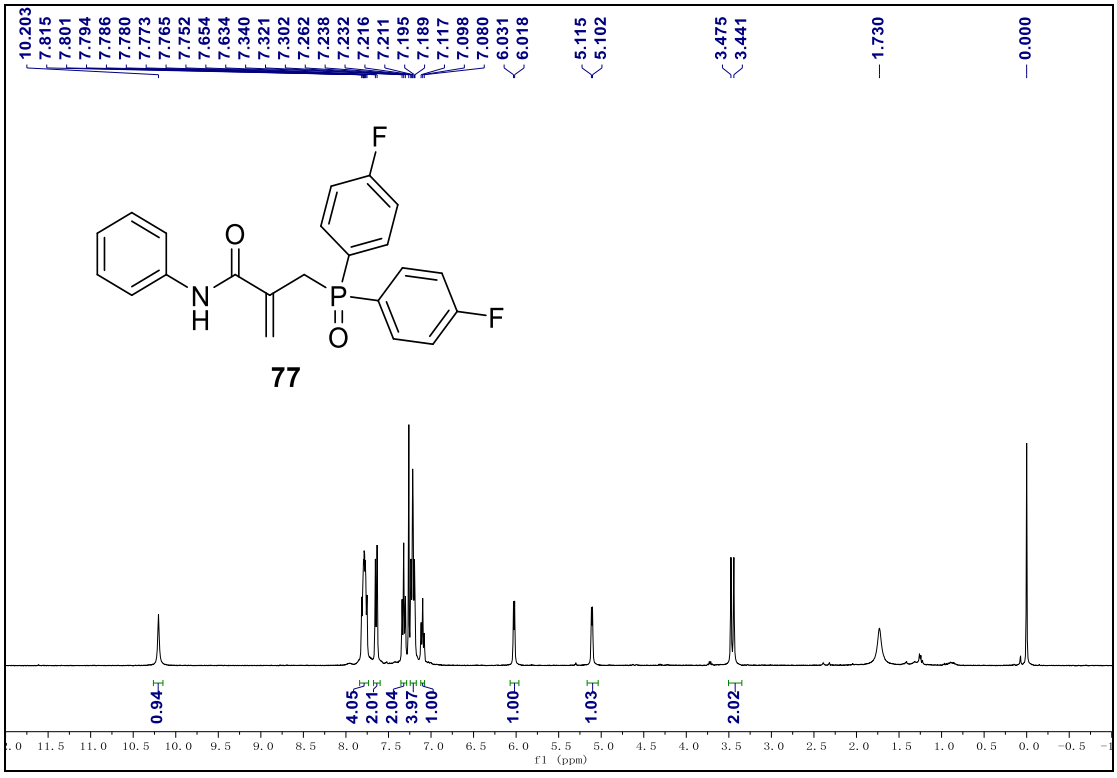
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 76.

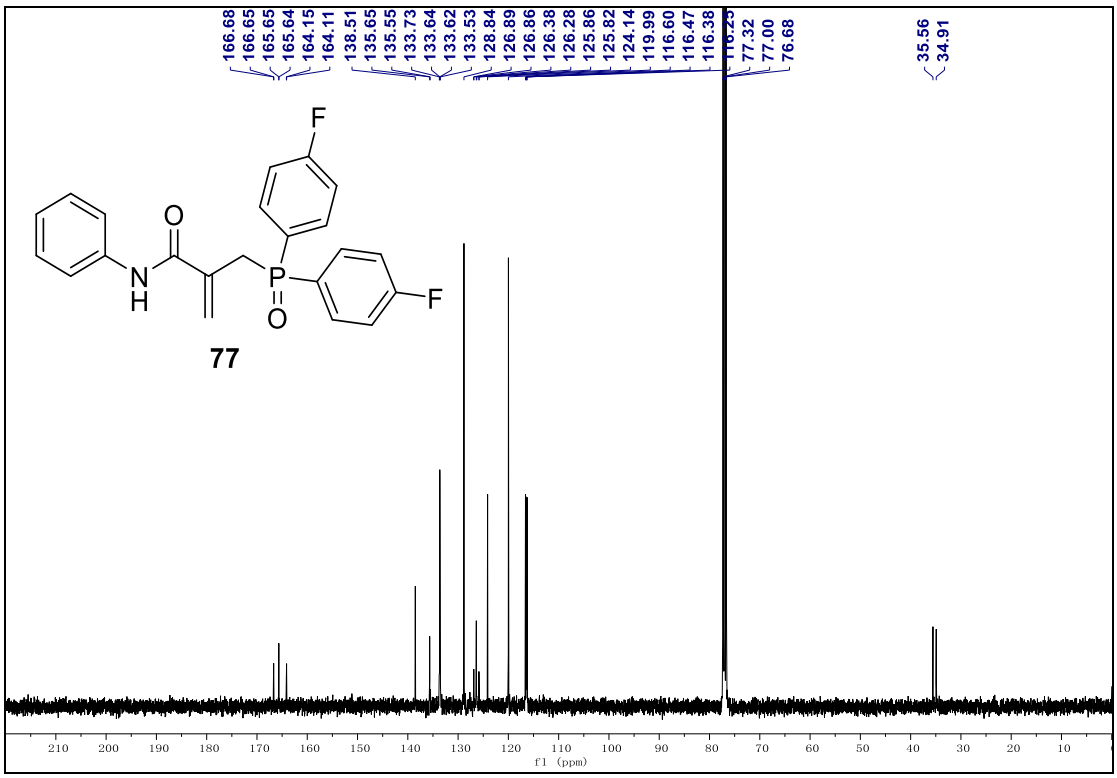


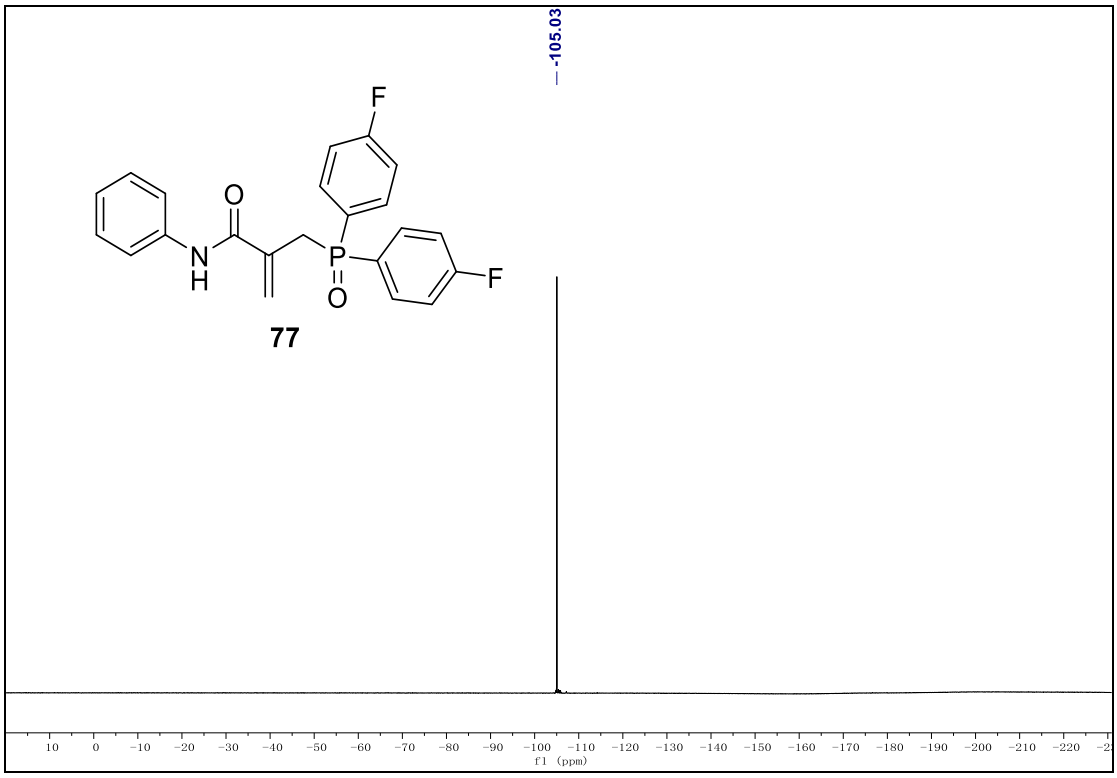


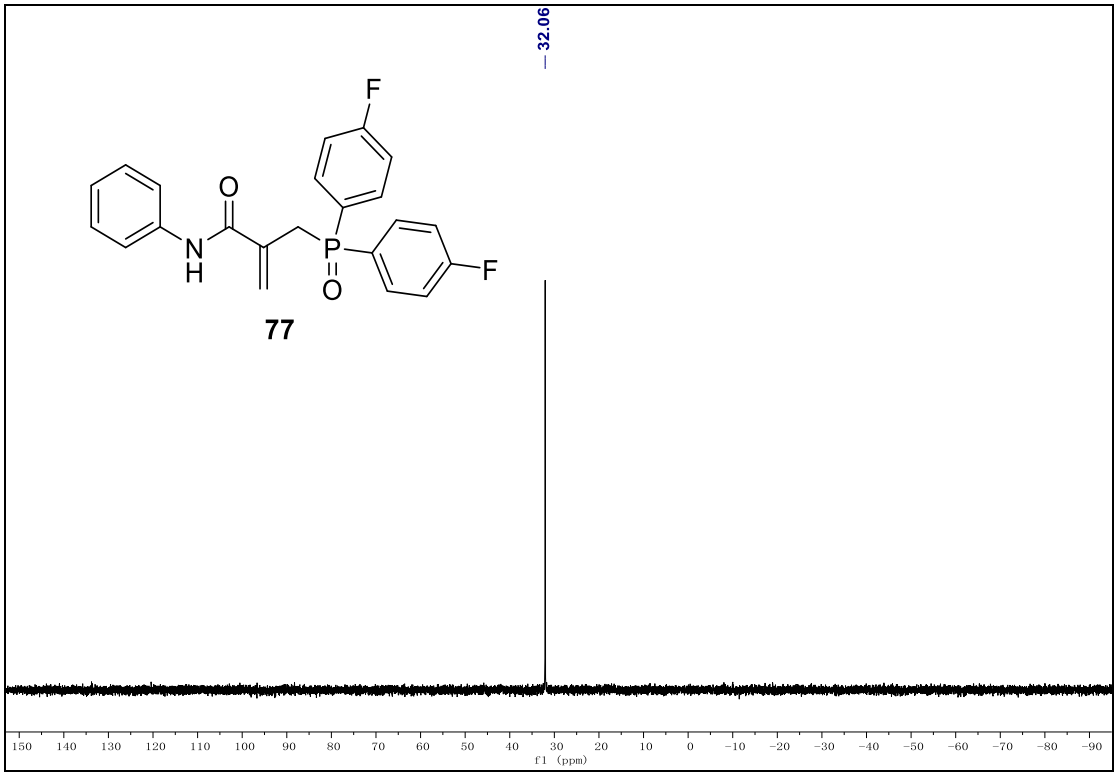

33.35
Ph
O
N
H
P
O
Ph
76
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz) spectrum of 77.

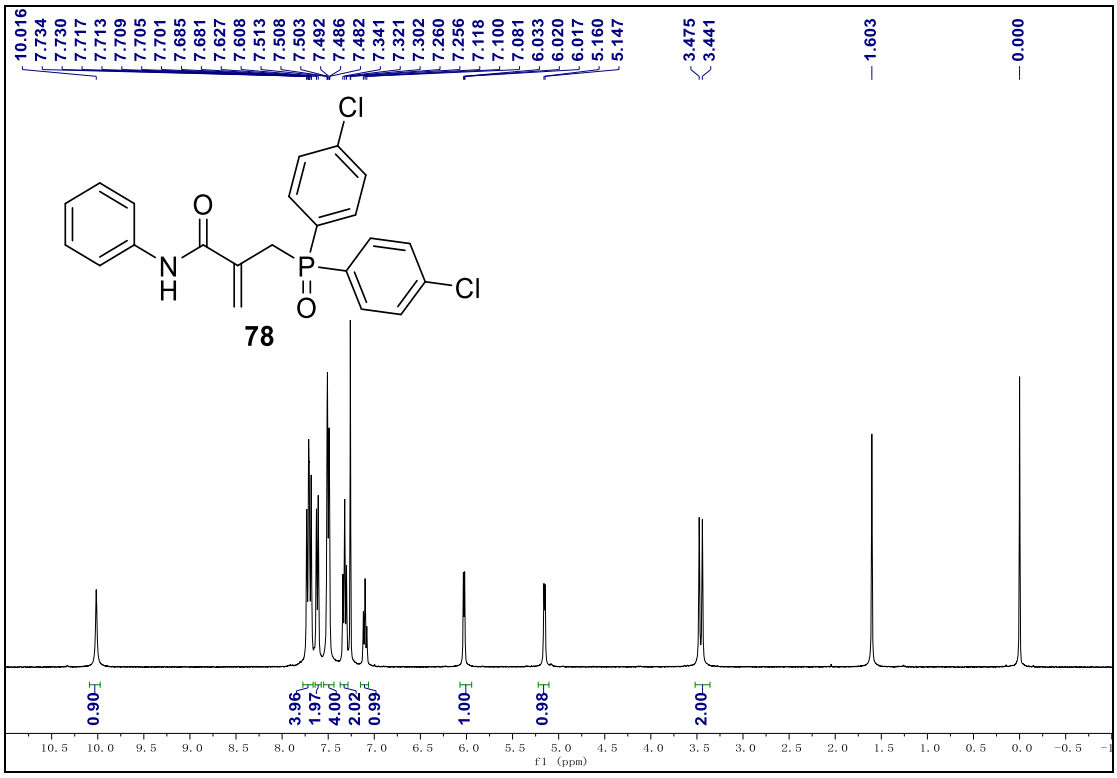


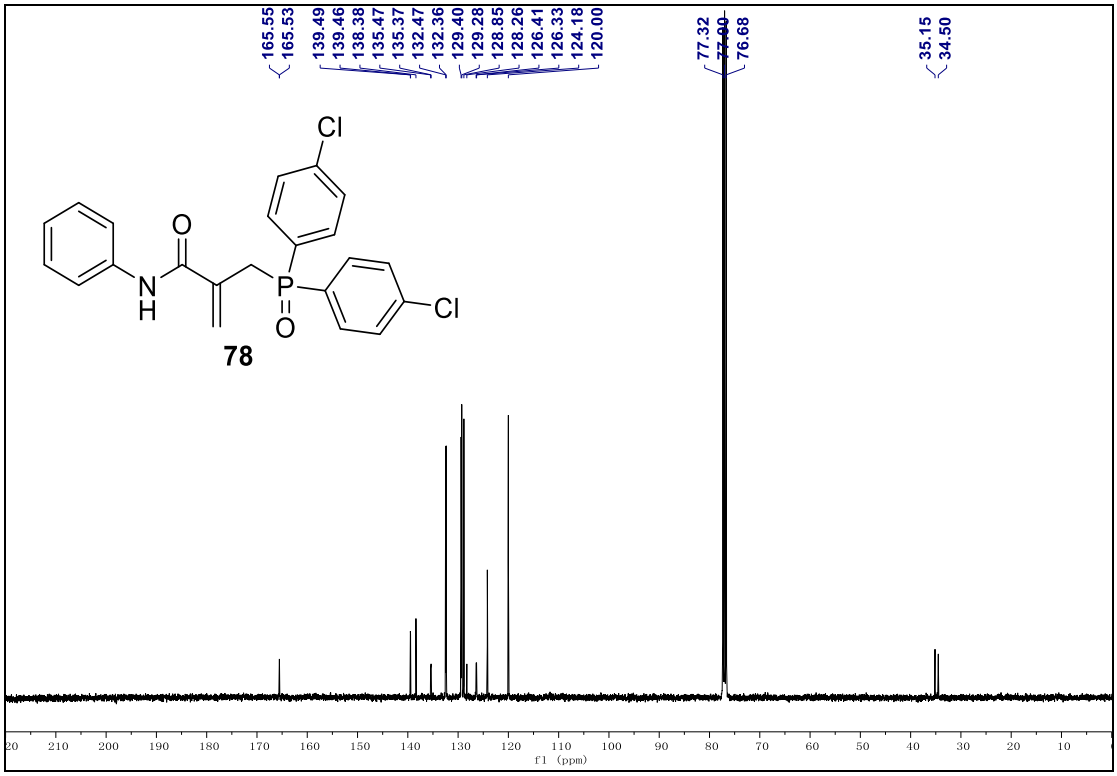


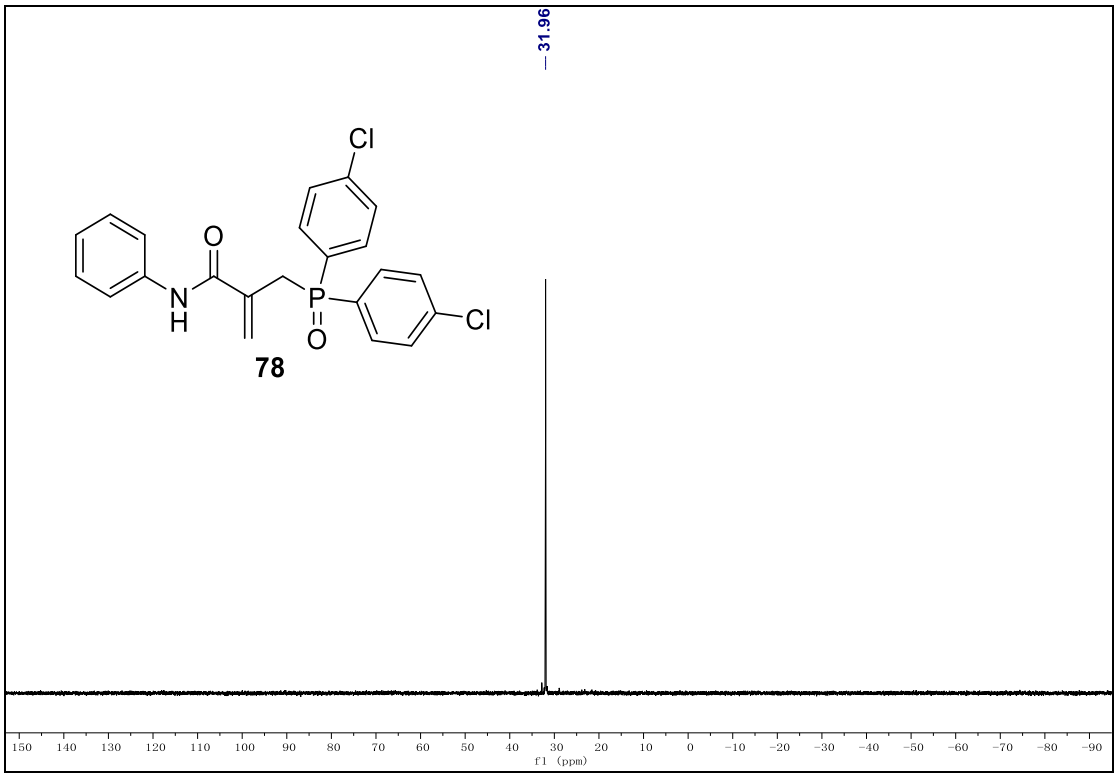

-105.03
F
O
N
H
P
O
F
77
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)


32.06
F
O
N
H
P
O
F
77
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

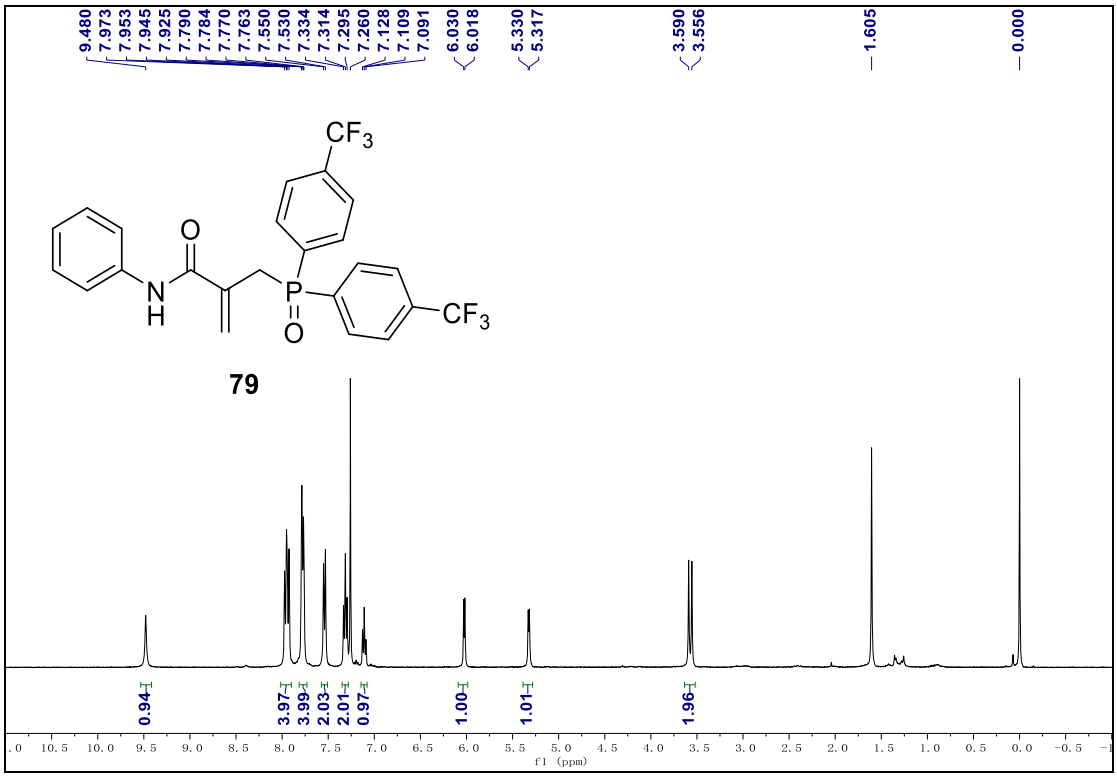
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 78.

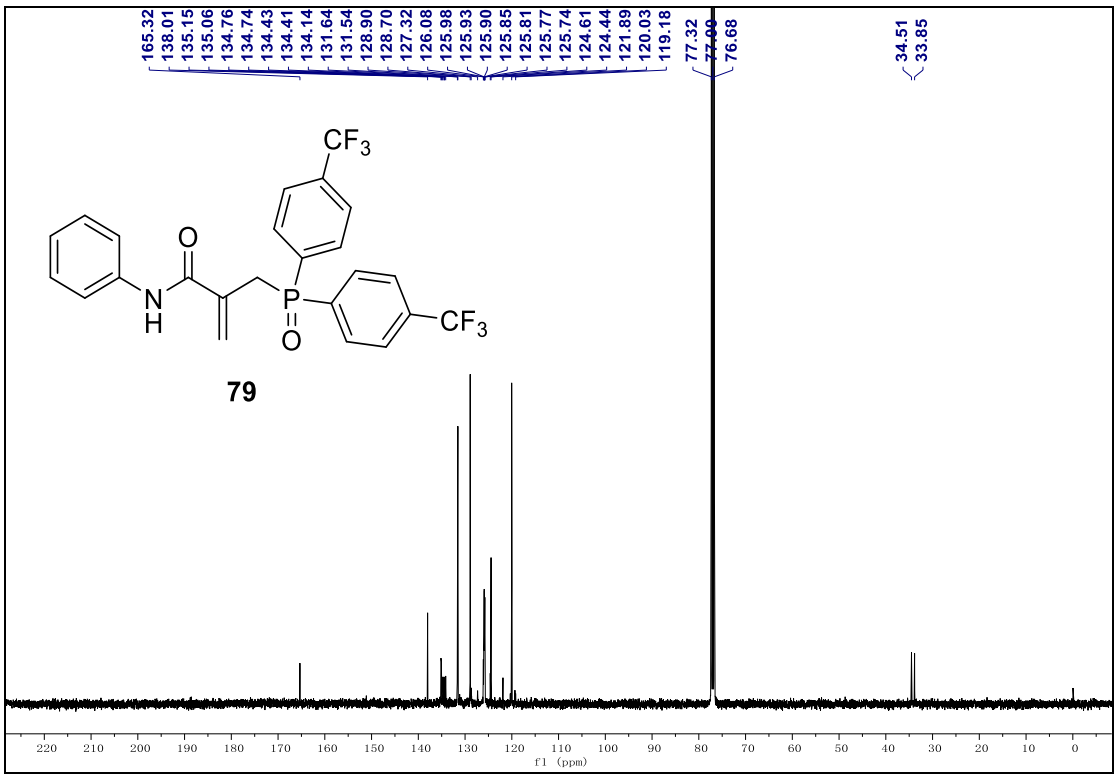


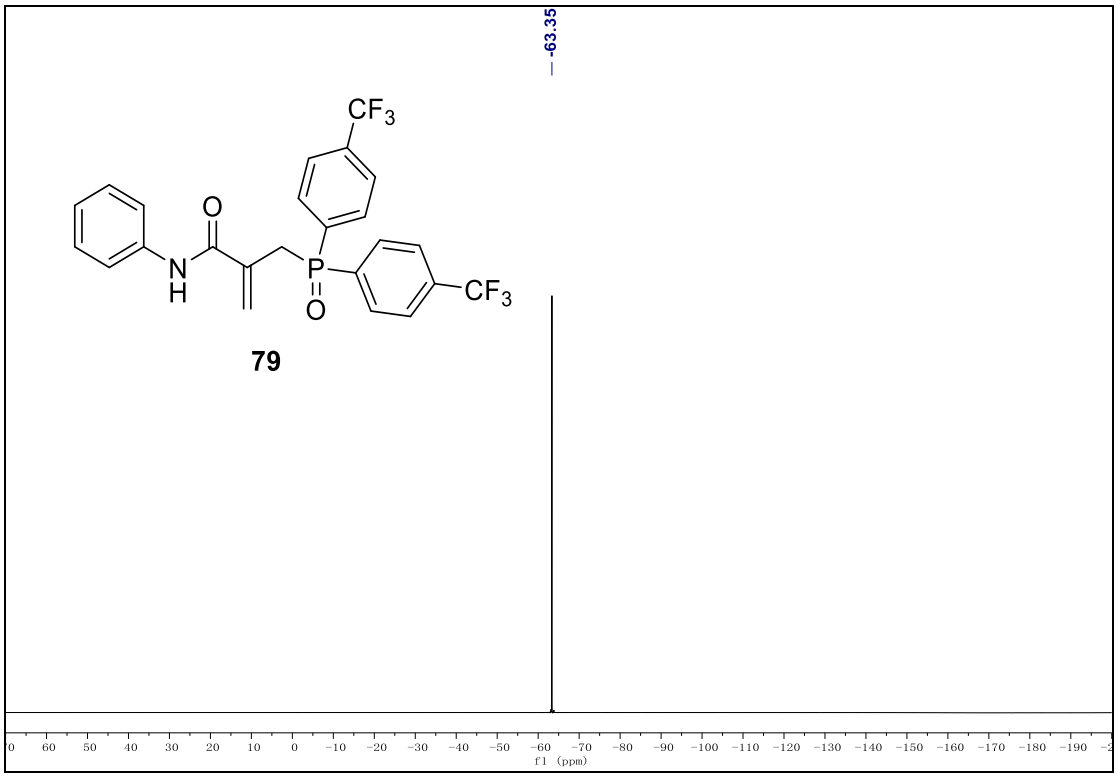


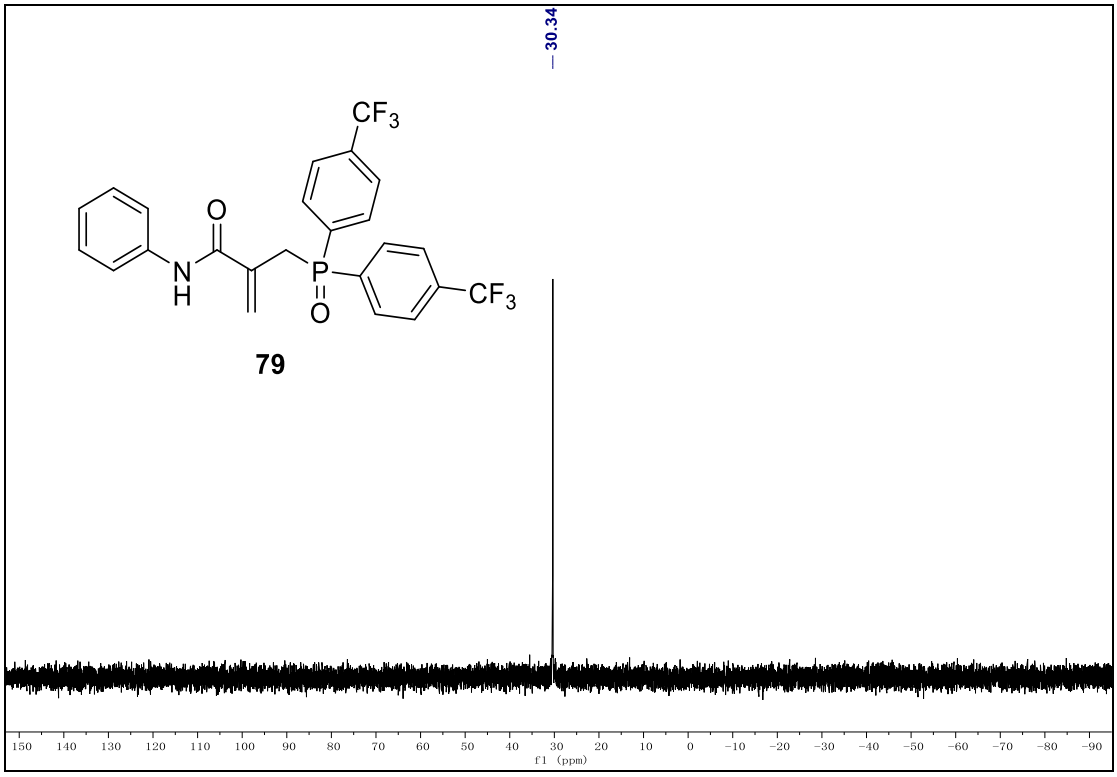

31.96
Cl
O
N
H
P
O
Cl
78
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 79.

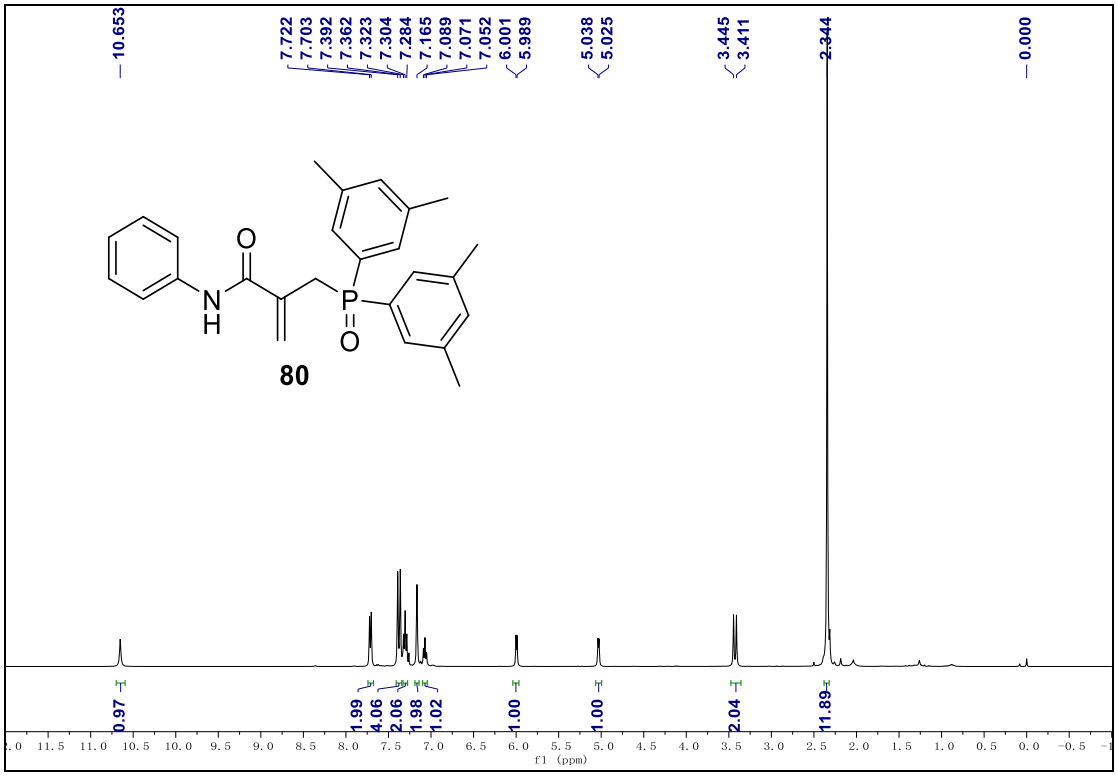


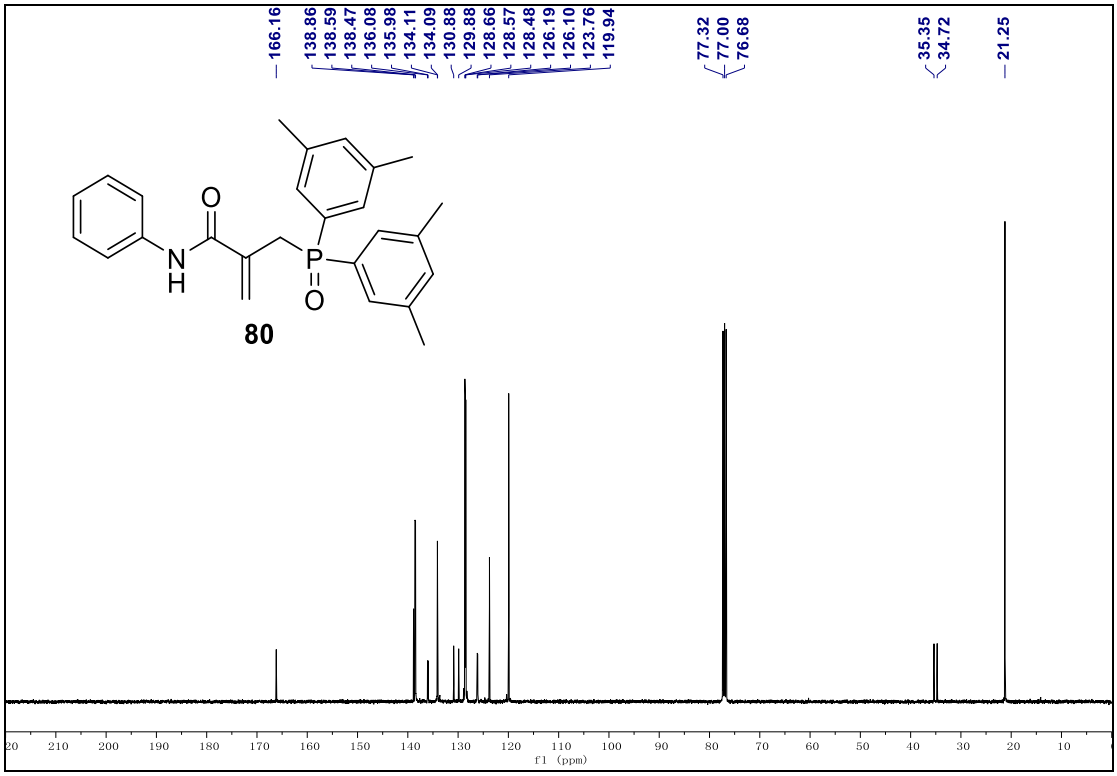


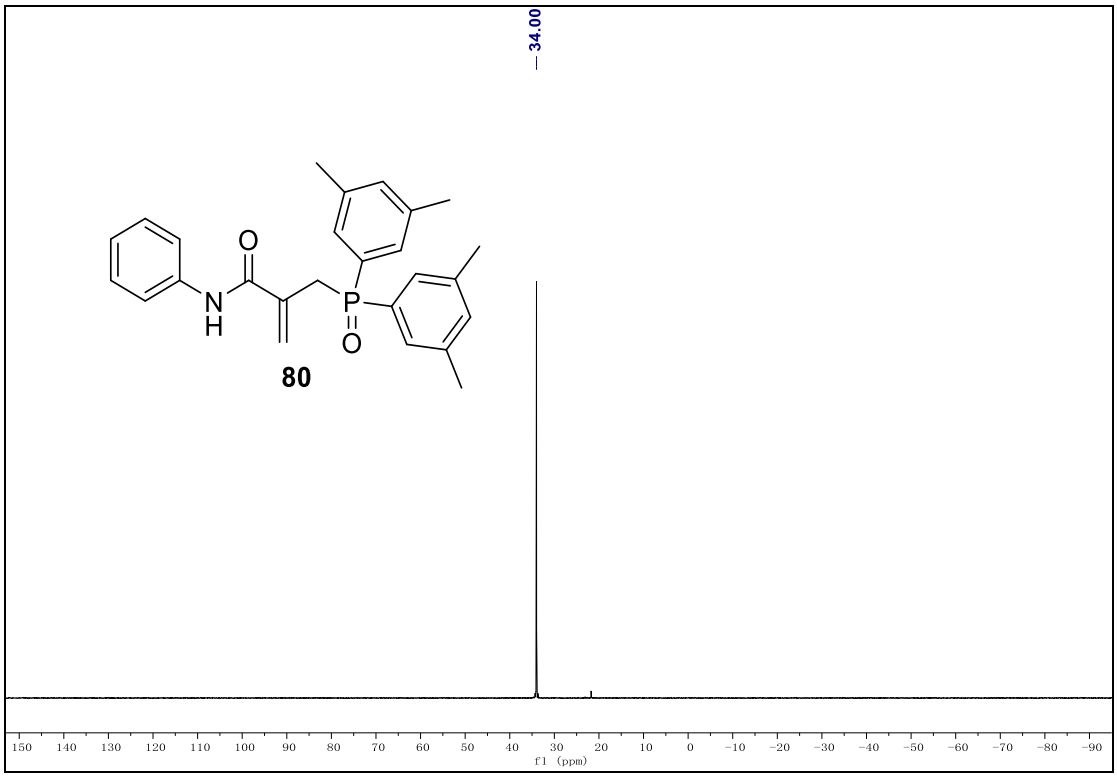

-63.35
CF3
O
N
H
P
O
CF3
79
f1 (ppm)


30.34
CF3
O
N
H
P
O
CF3
79
f1 (ppm)

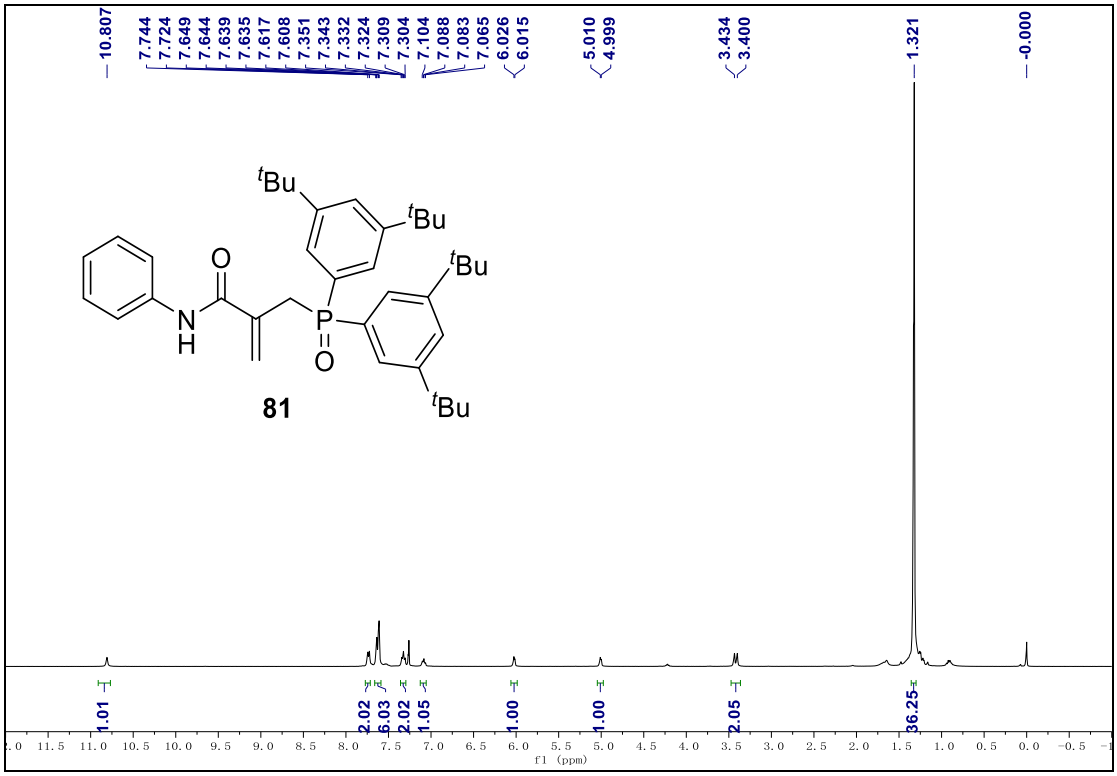
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 80.

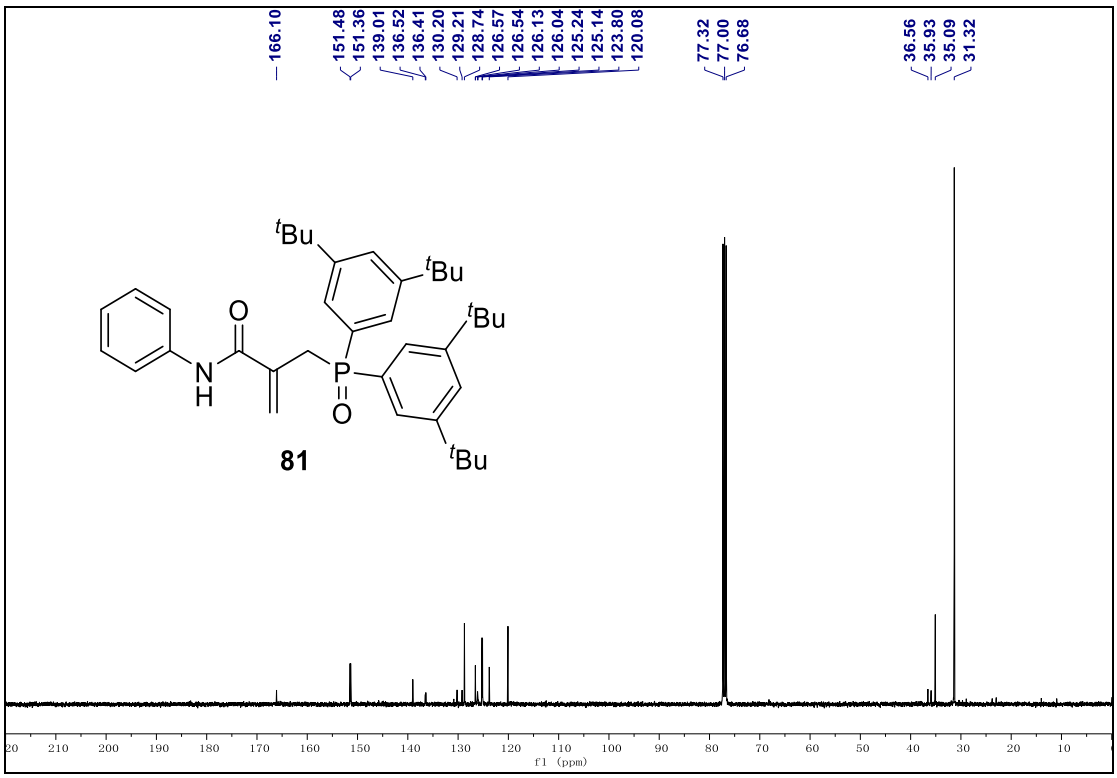


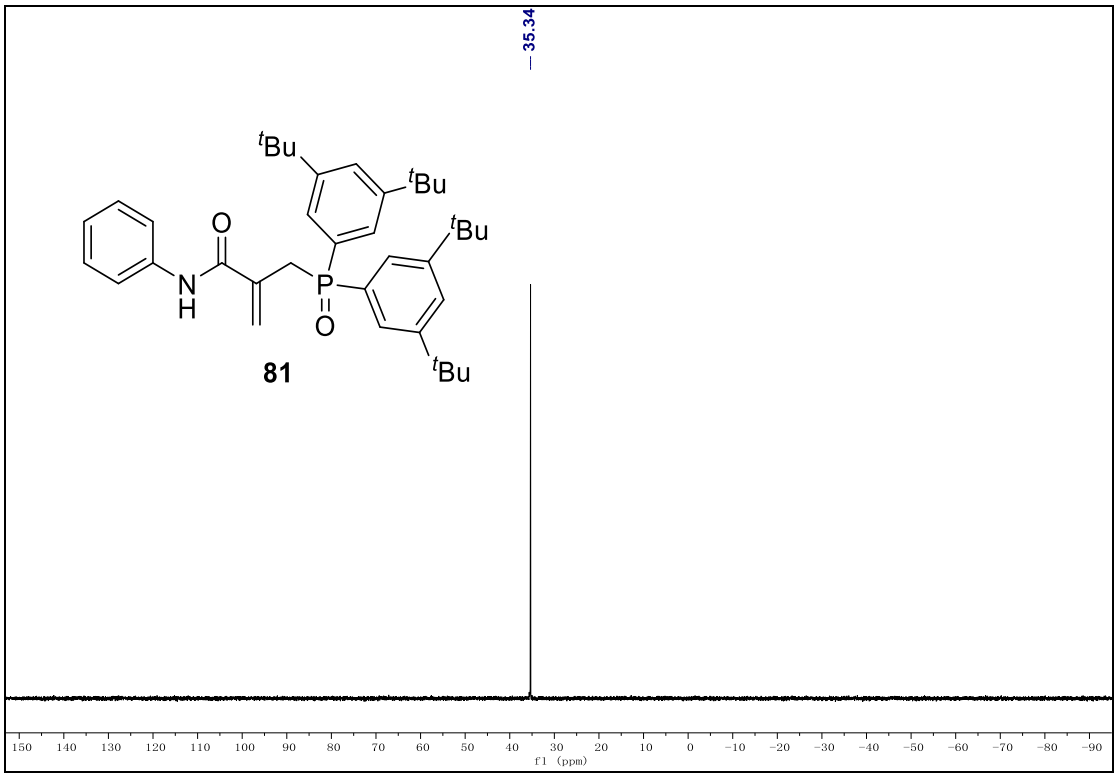



34.00
O
N
H
P
O
80
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

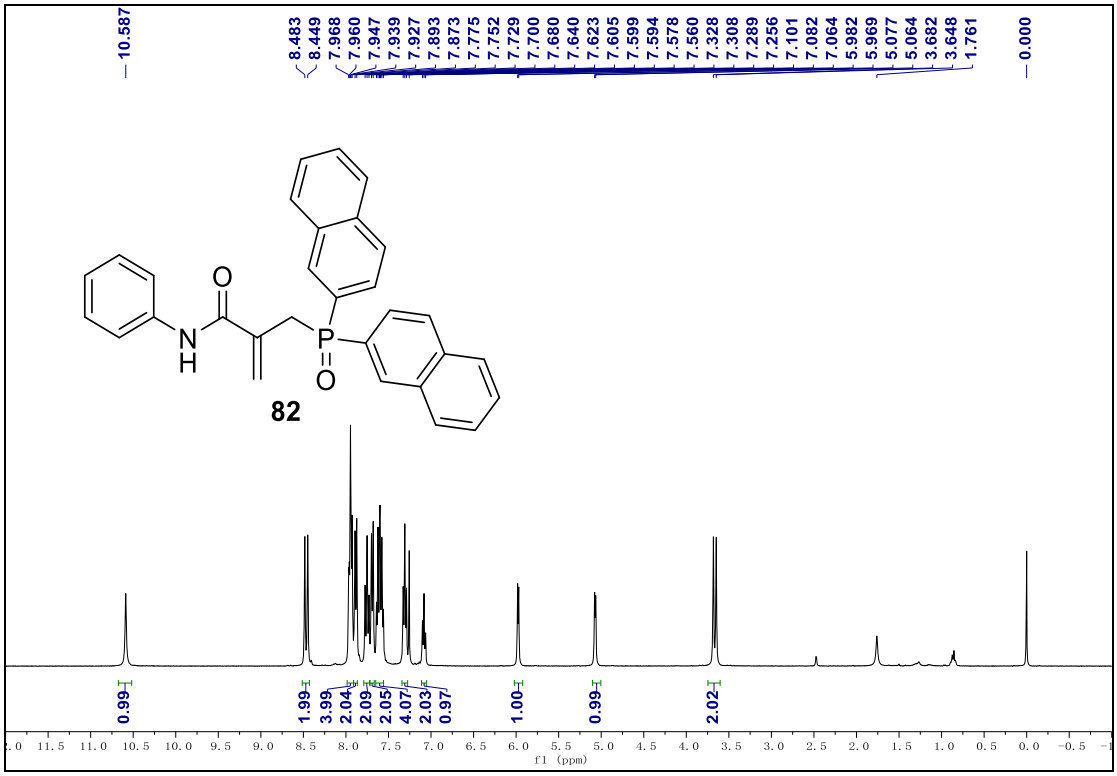
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 81.

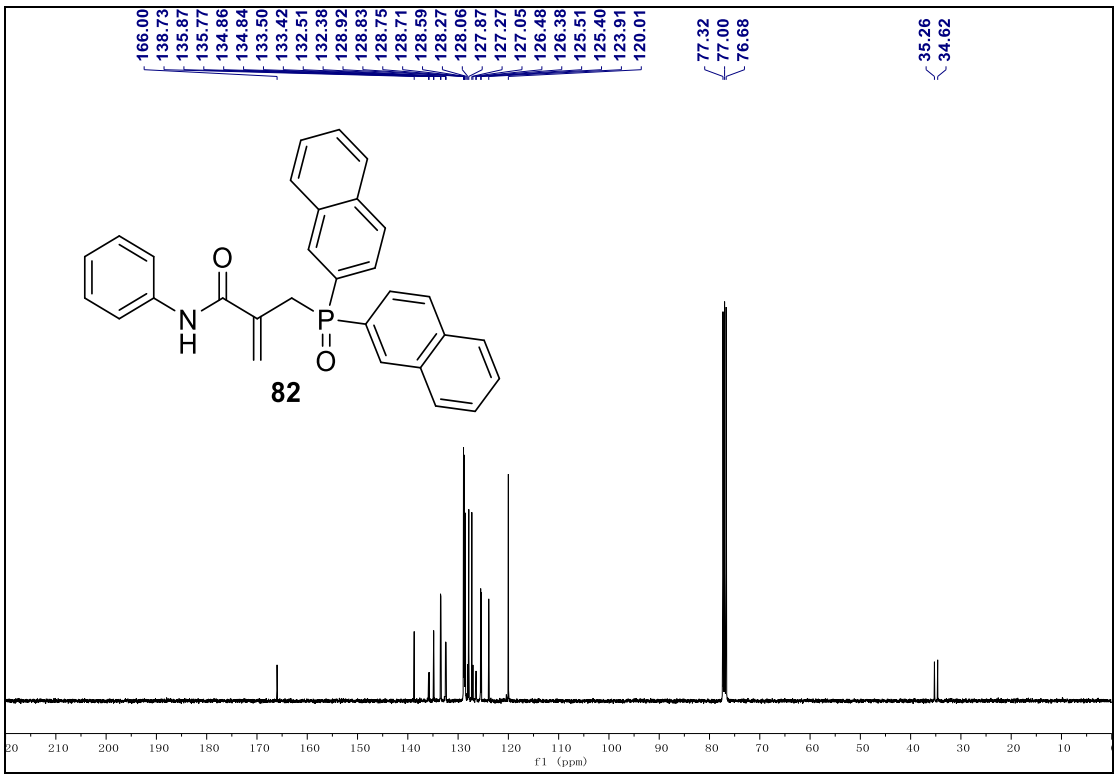


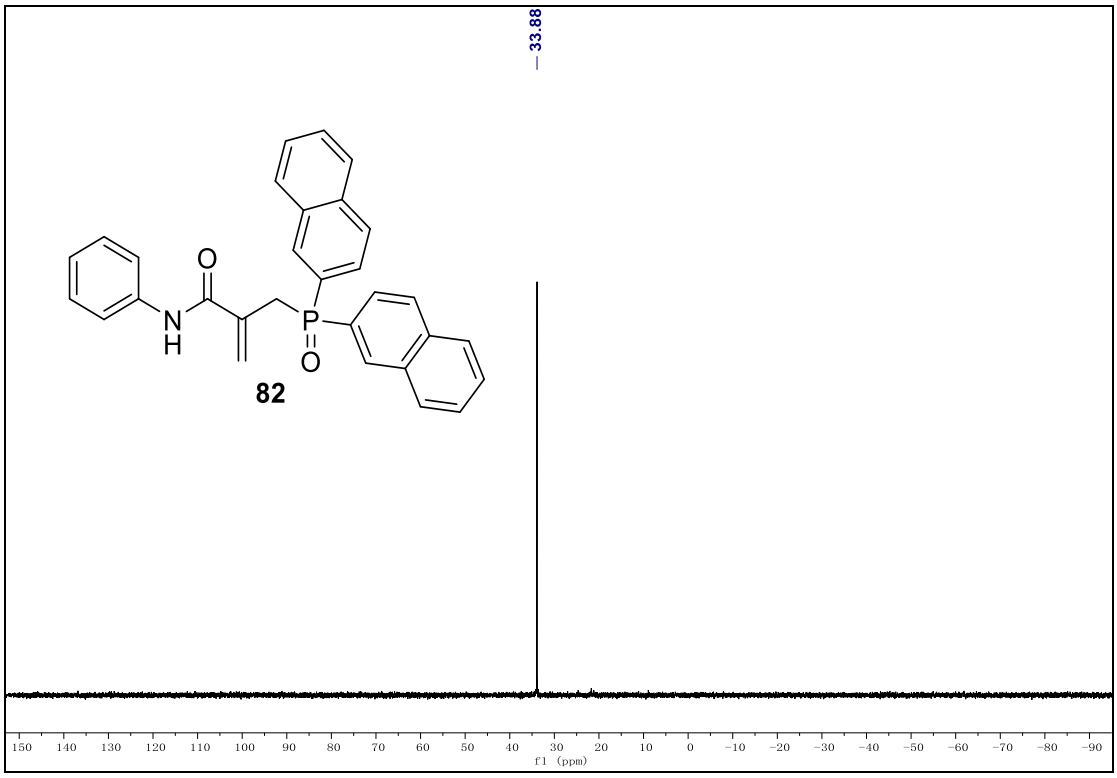



35.34
tBu
tBu
tBu
tBu
O
N
H
P
O
81
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

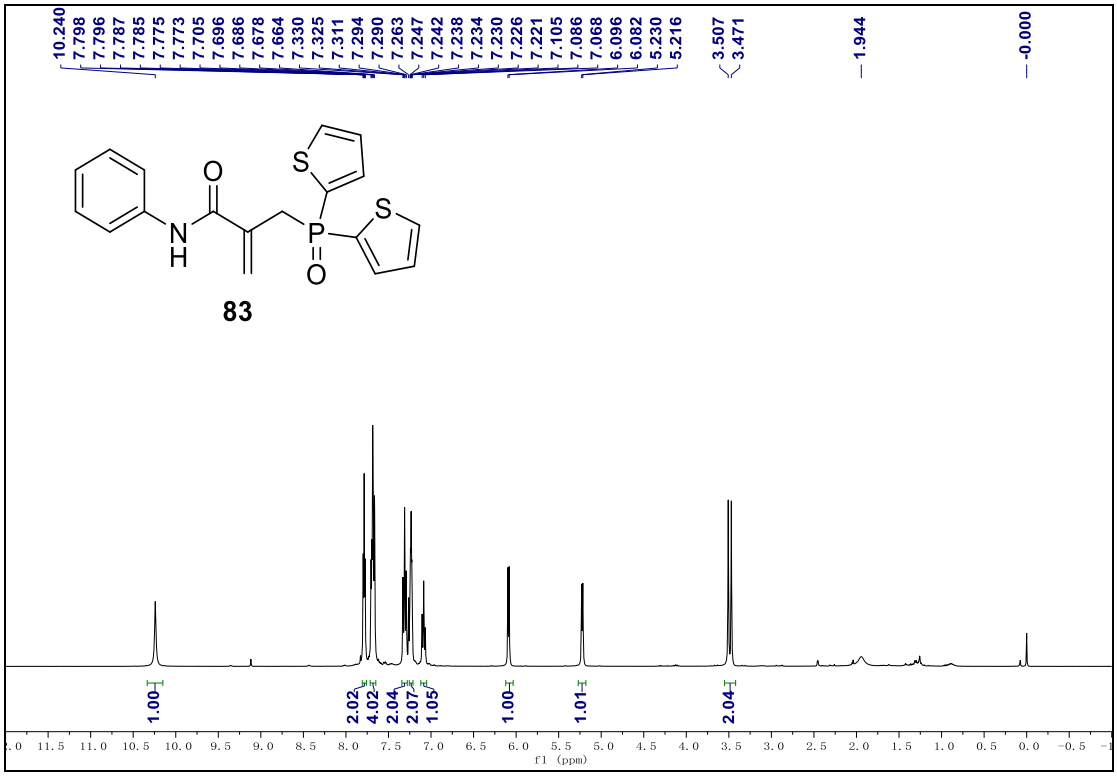
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 82.

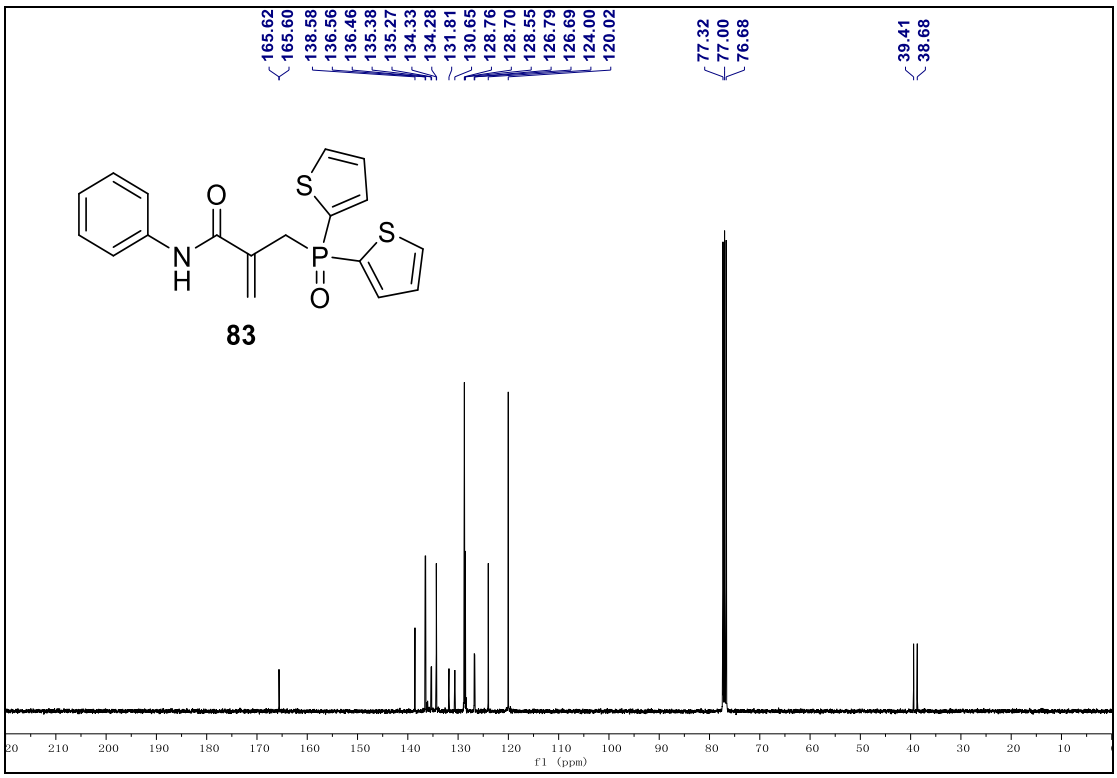


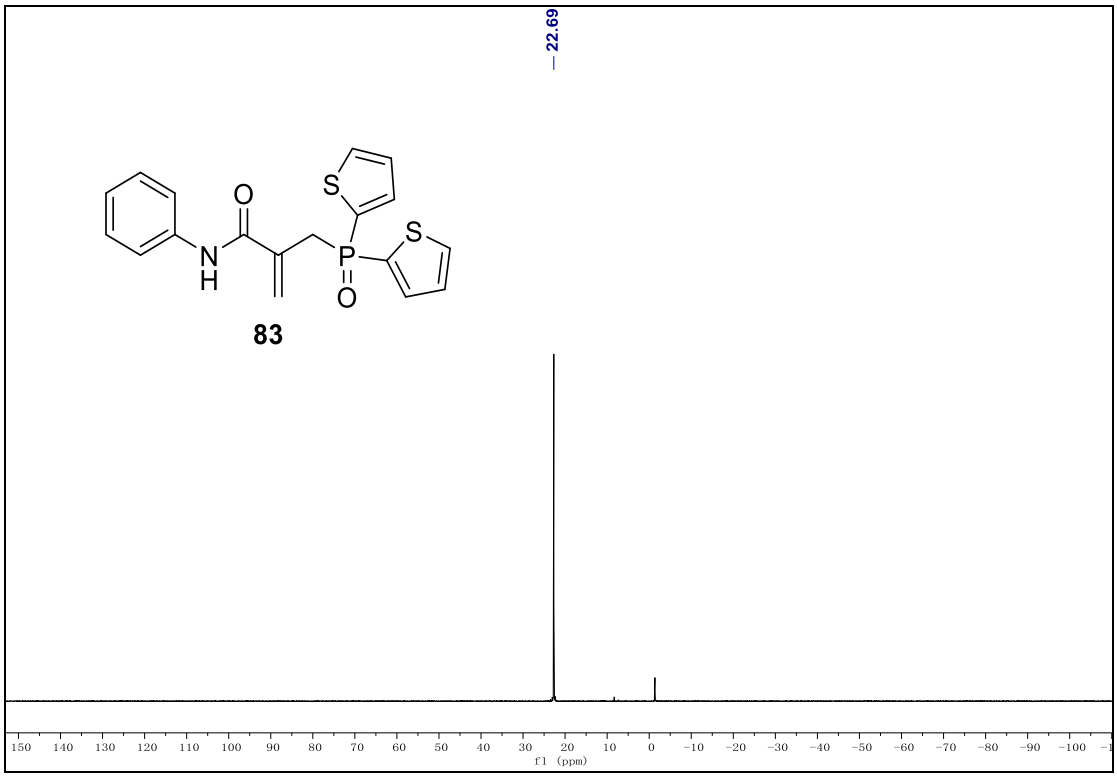



33.88
O
N
H
P
O
82
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 83.

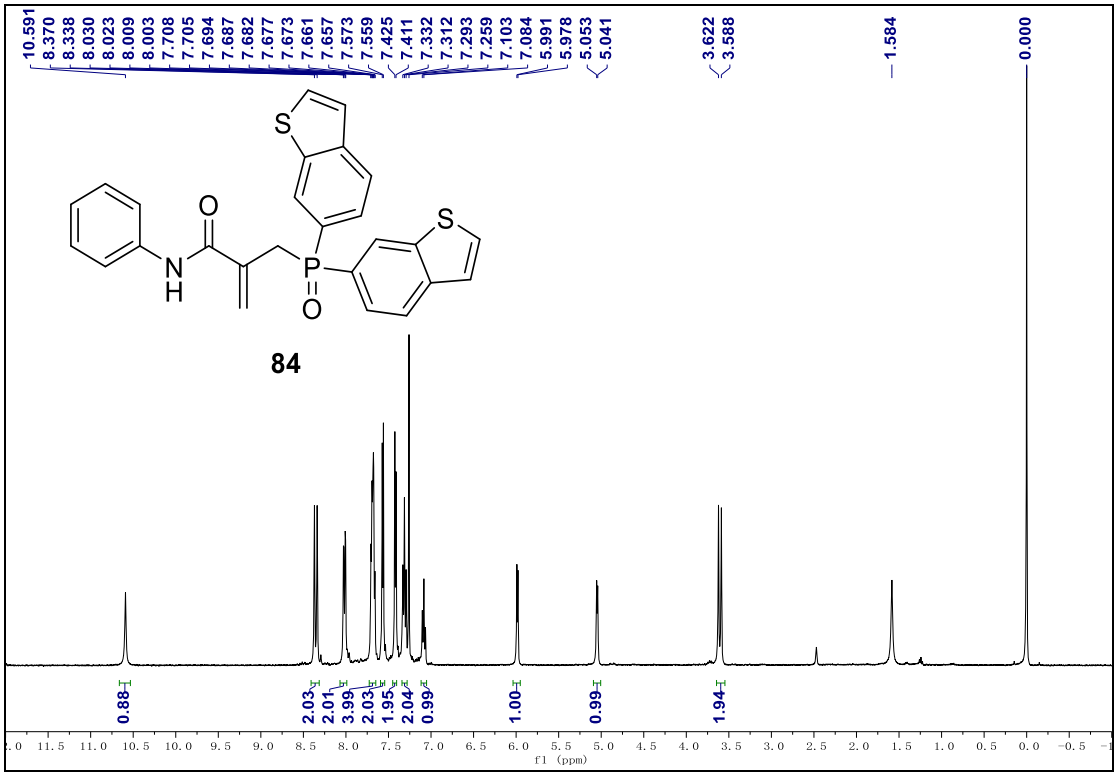


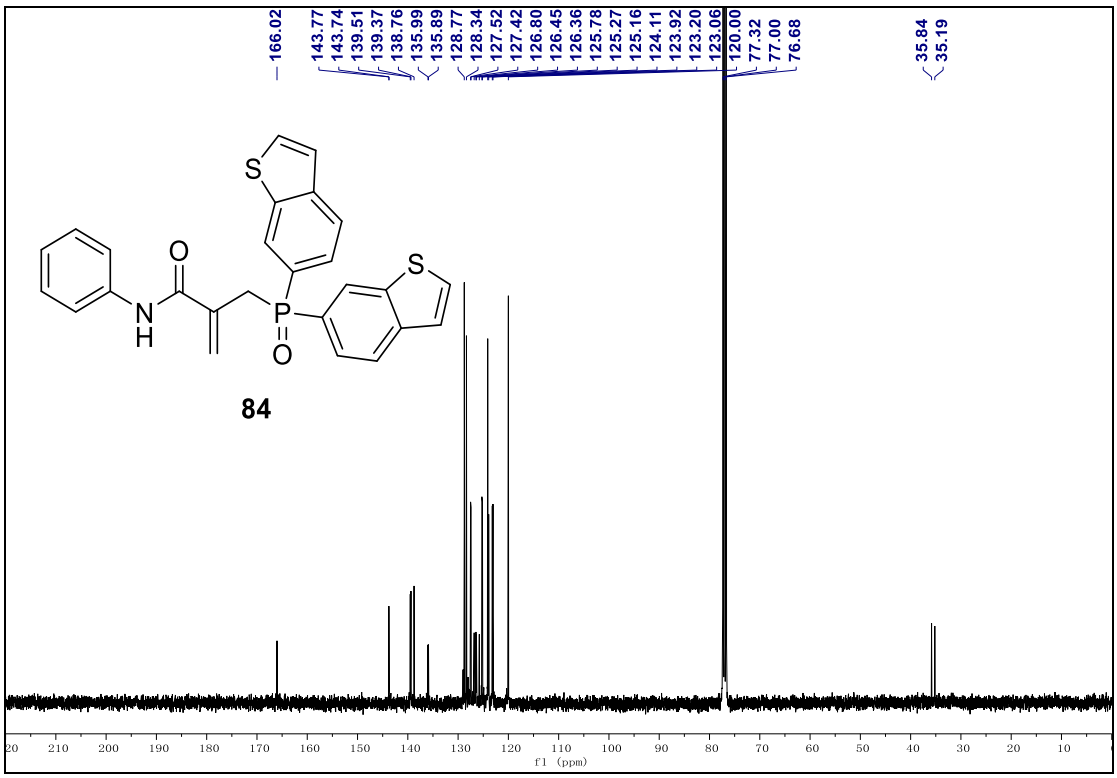


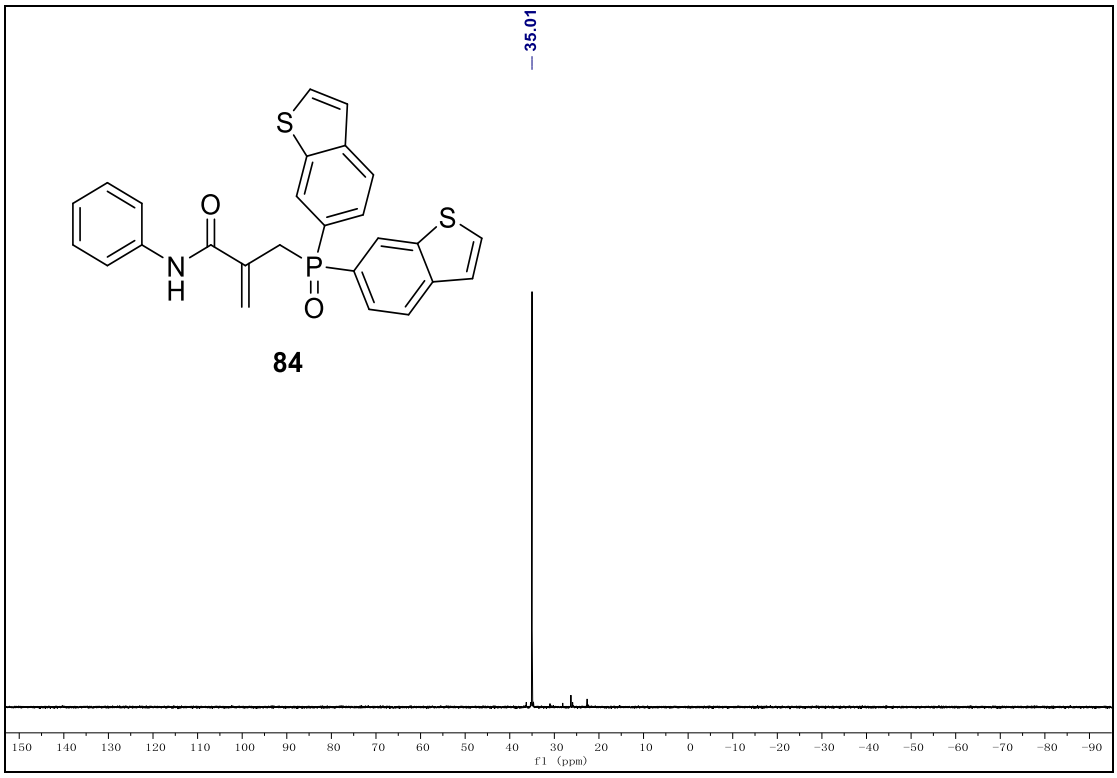

22.69
O
S
S
N
H
P
O
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100
f1 (ppm)

83

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$)) spectrum of 84.

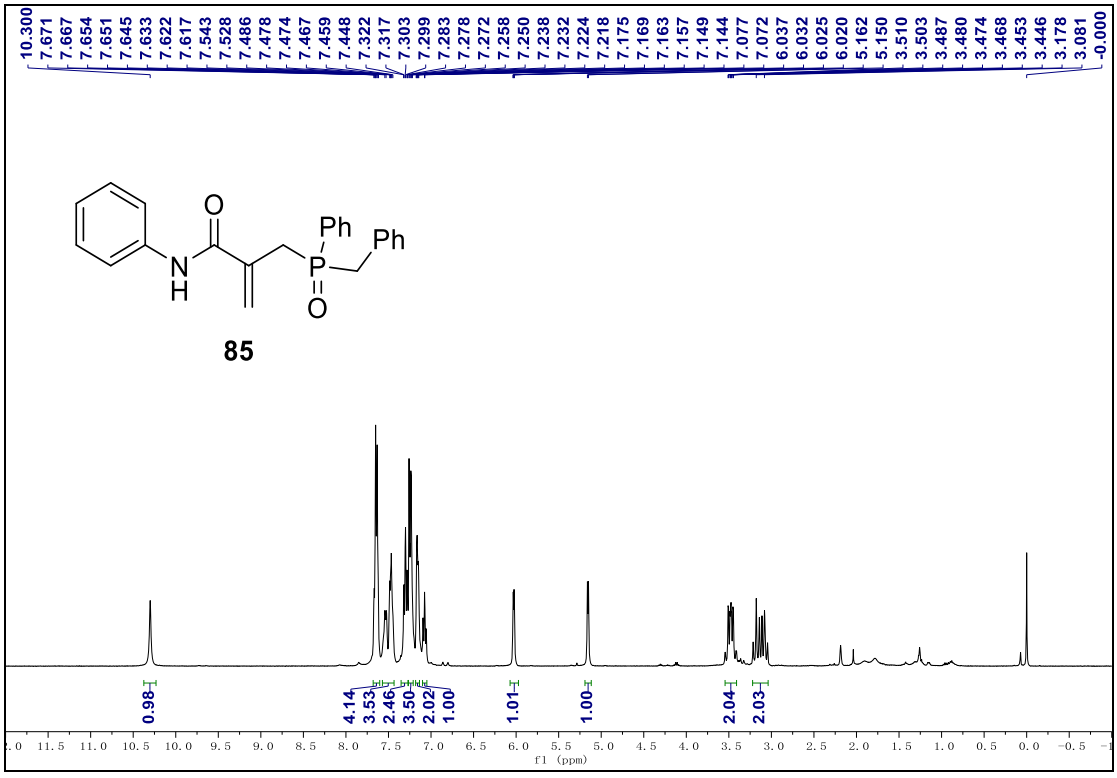


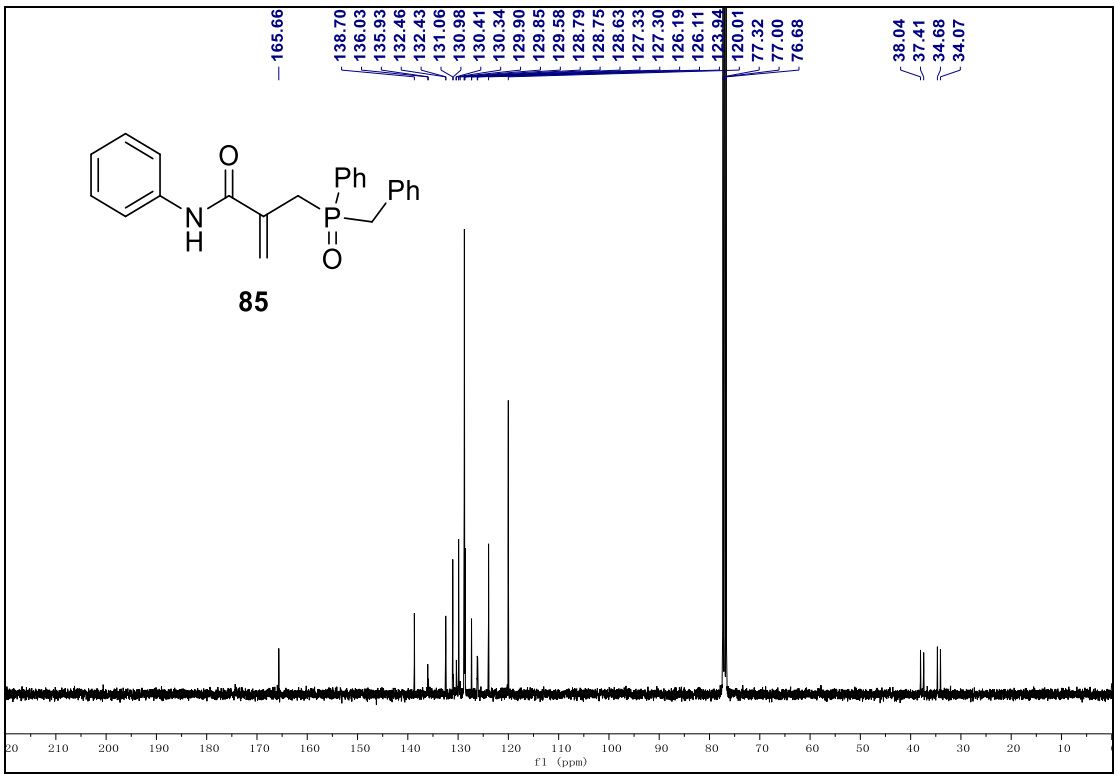


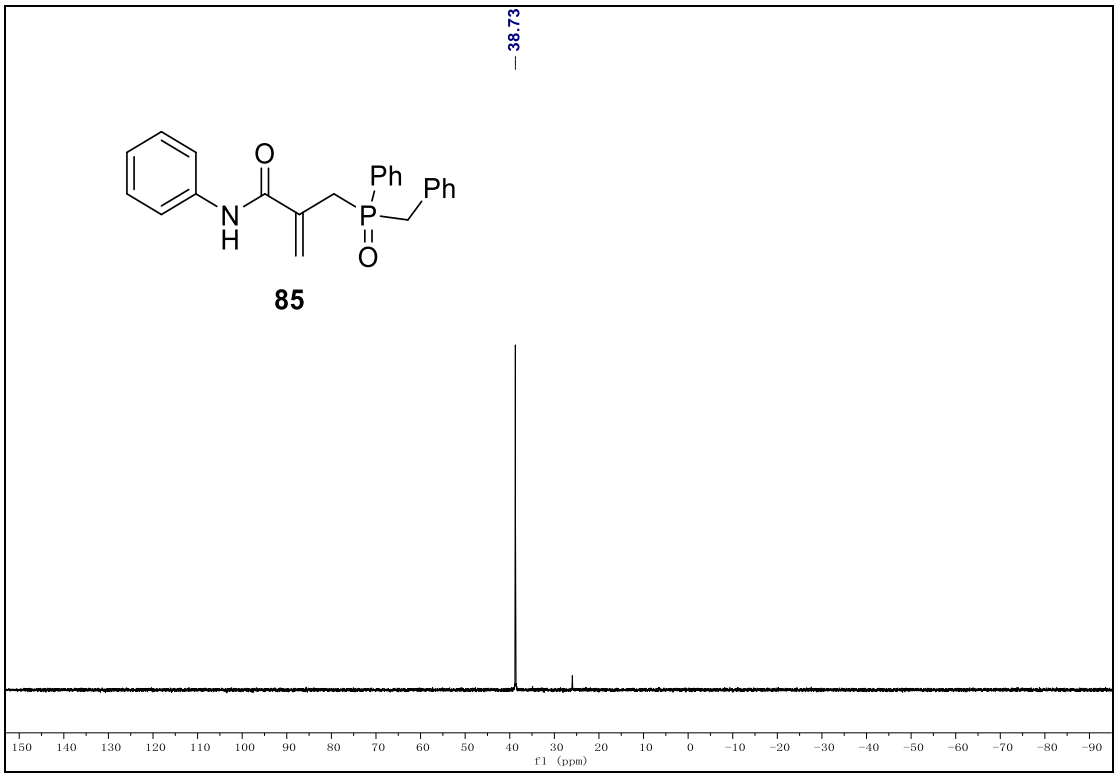

35.01
S
S
O
N
H
P
O
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

84

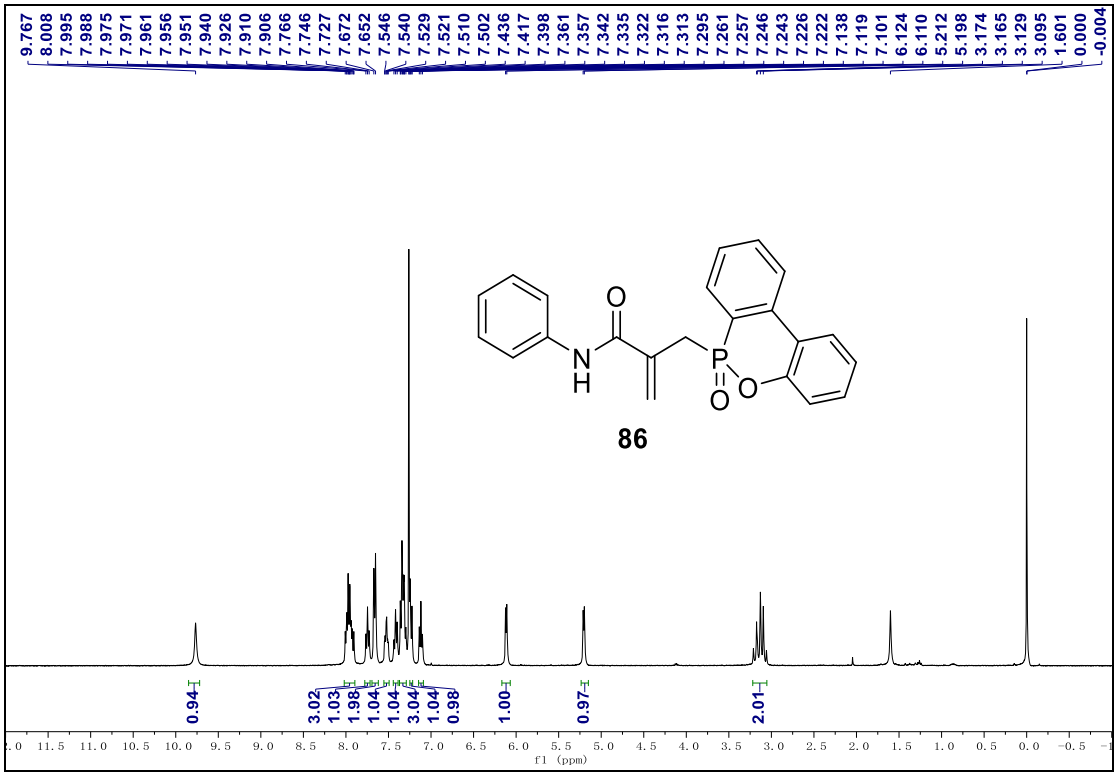
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 85.

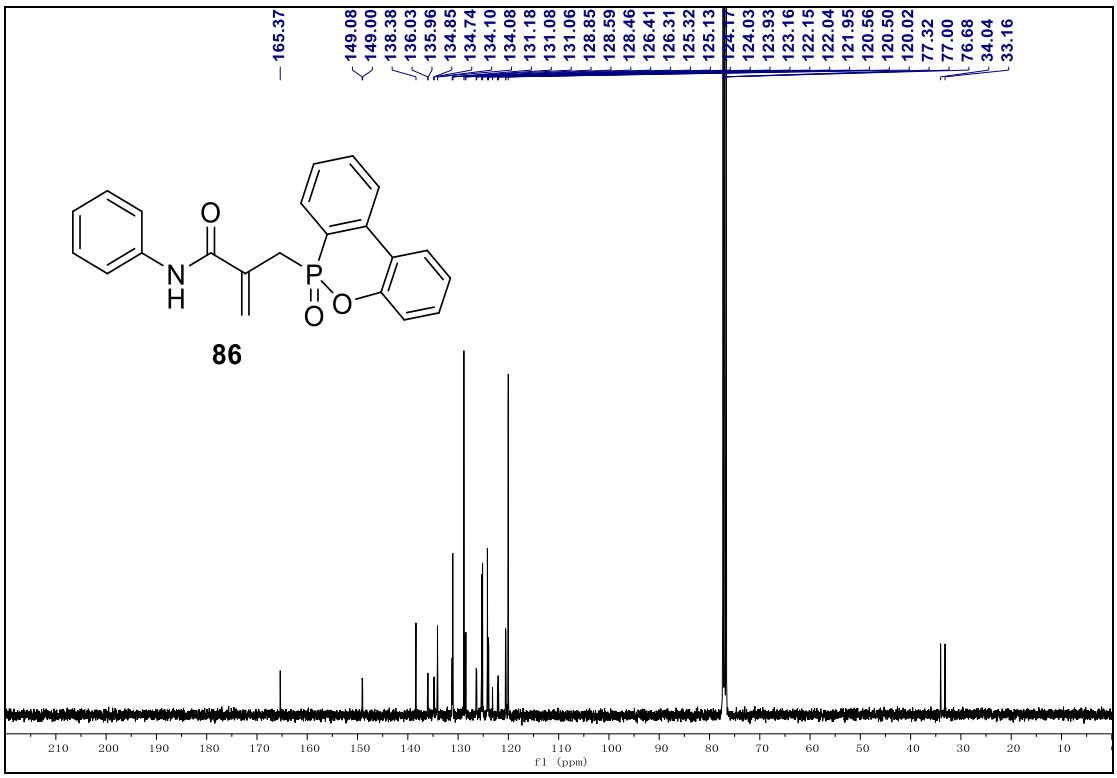


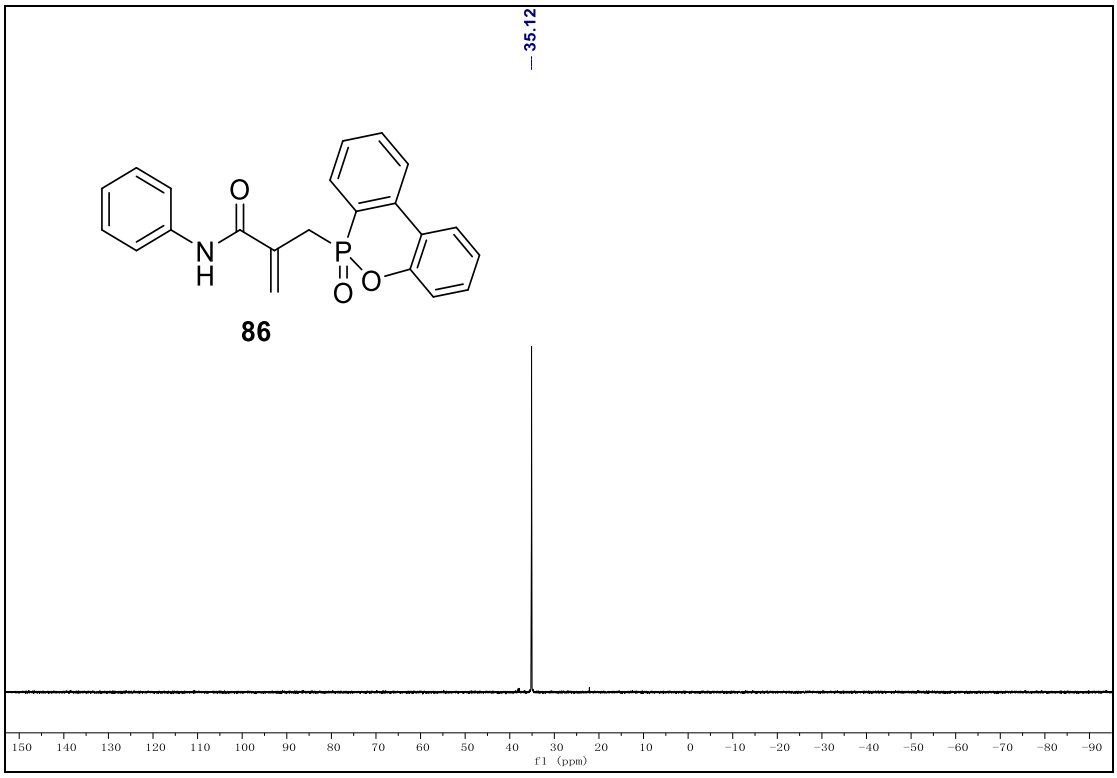



38.73
O
N
H
Ph
Ph
P
O
85
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 86.

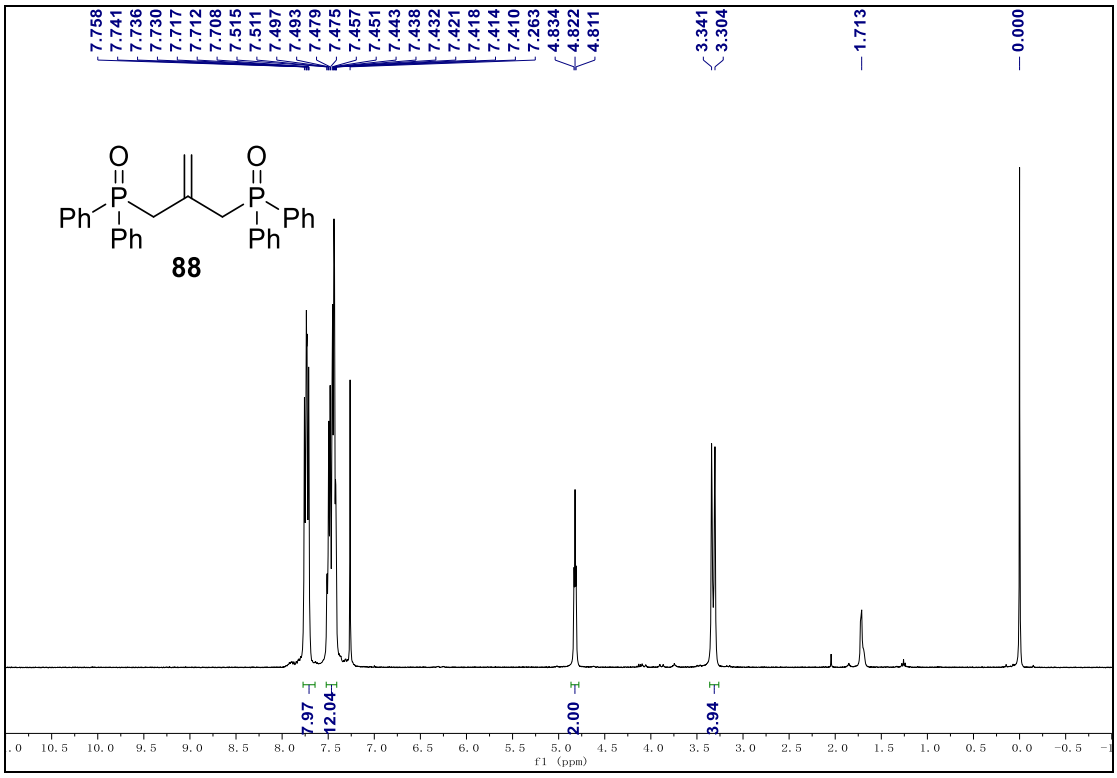


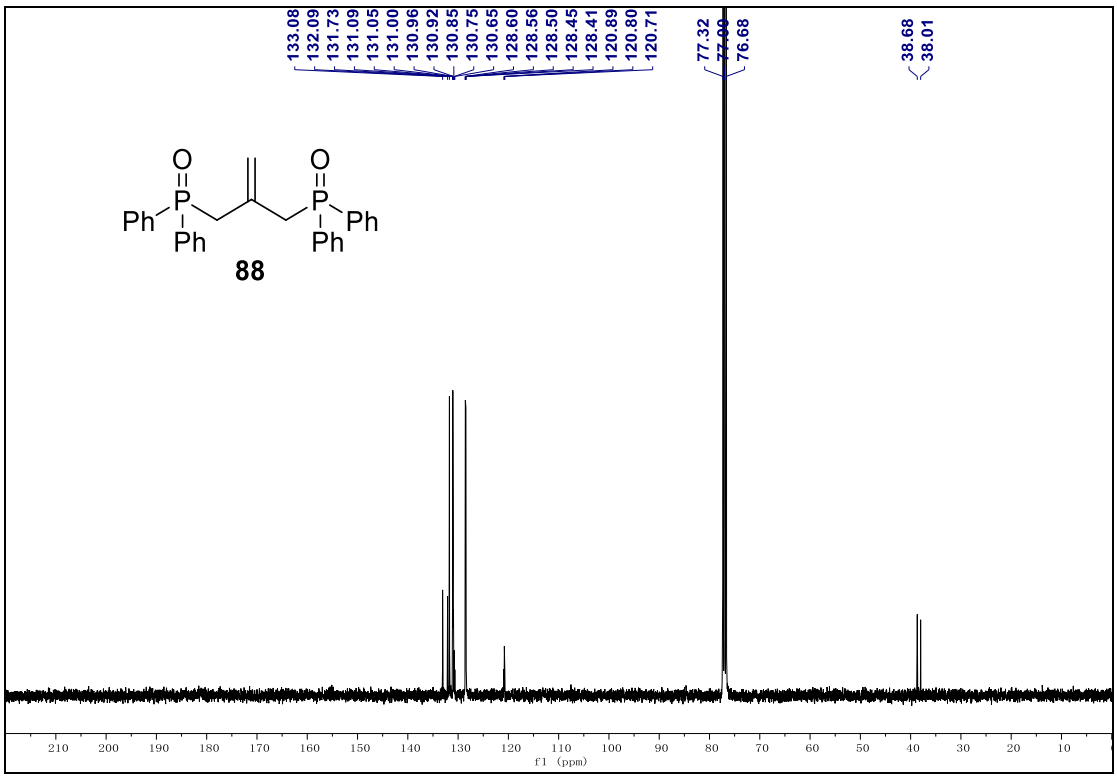


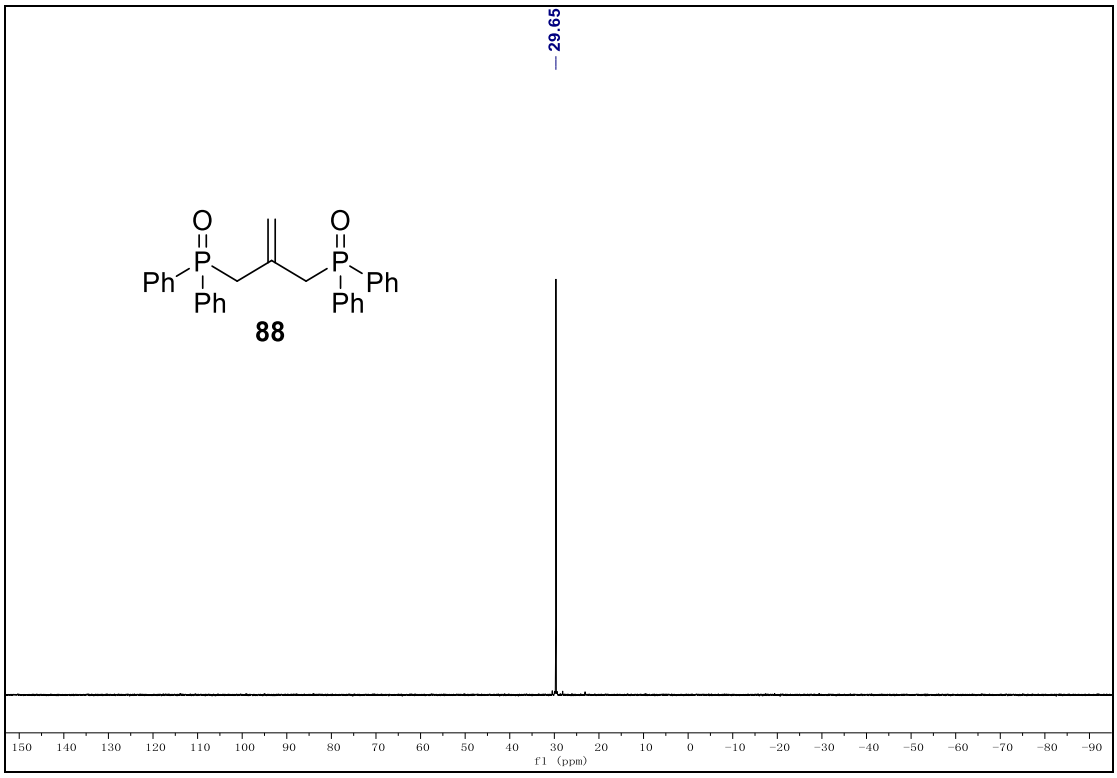

35.12
O
N
H
P
O
O
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

86

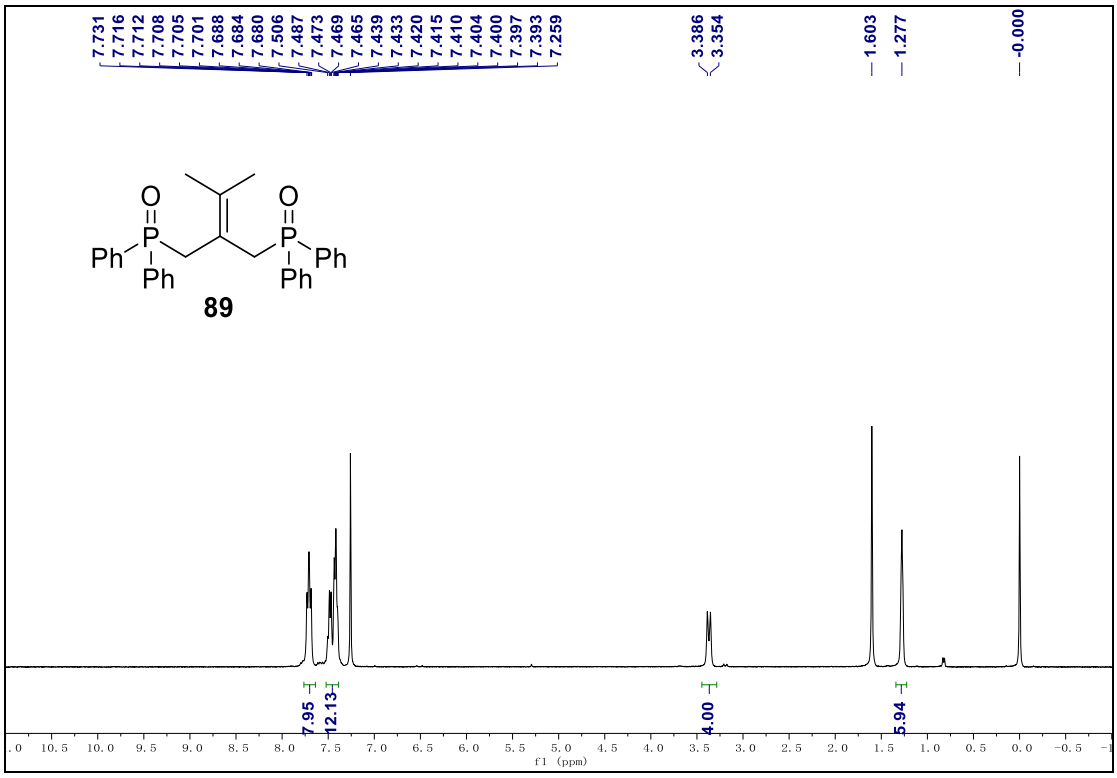
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 88.

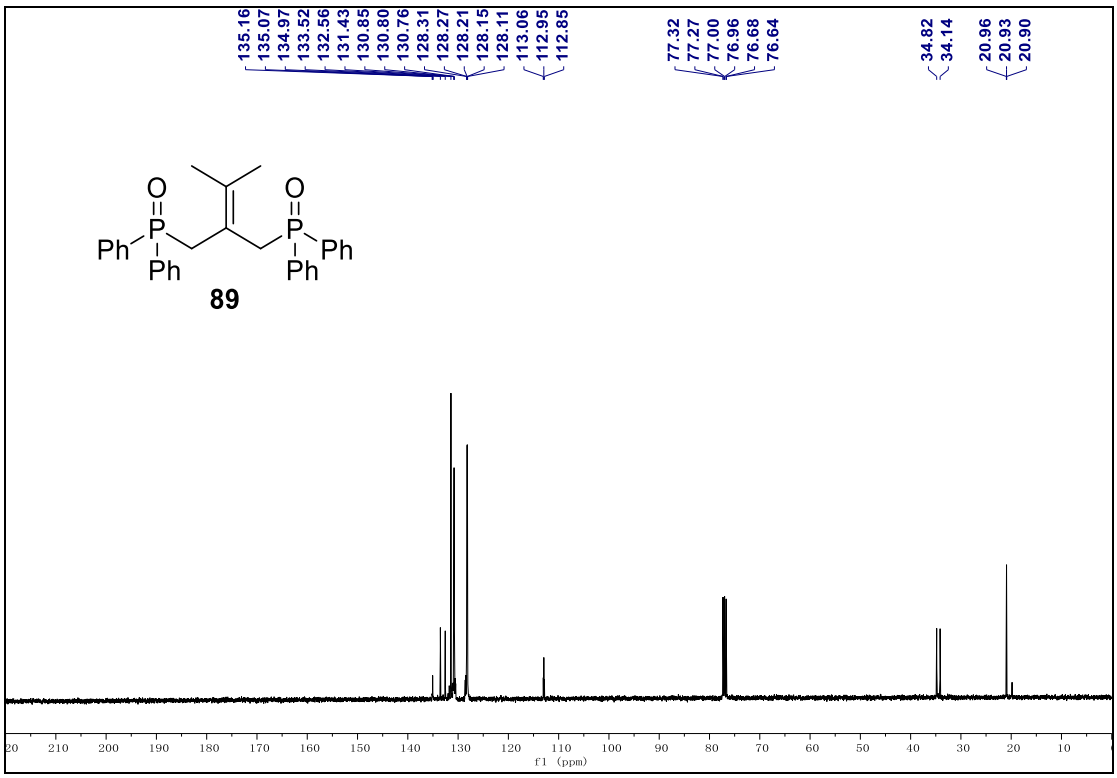


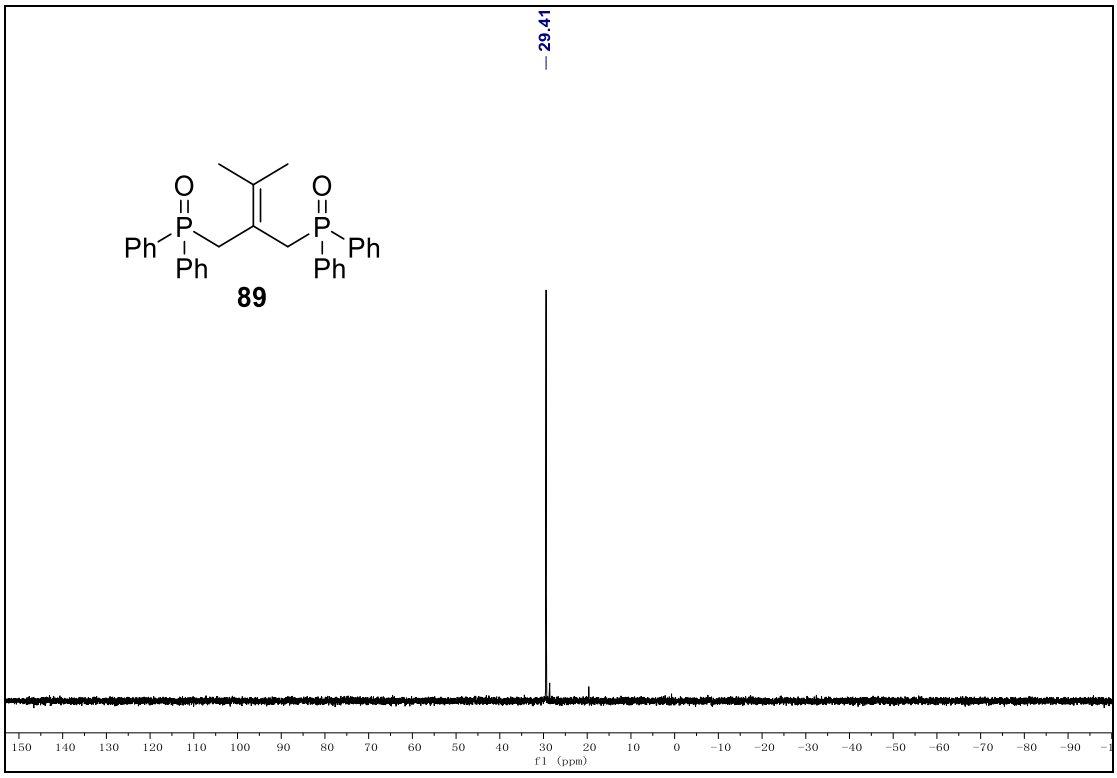



29.65
O
P
Ph
Ph
O
P
Ph
Ph
88
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

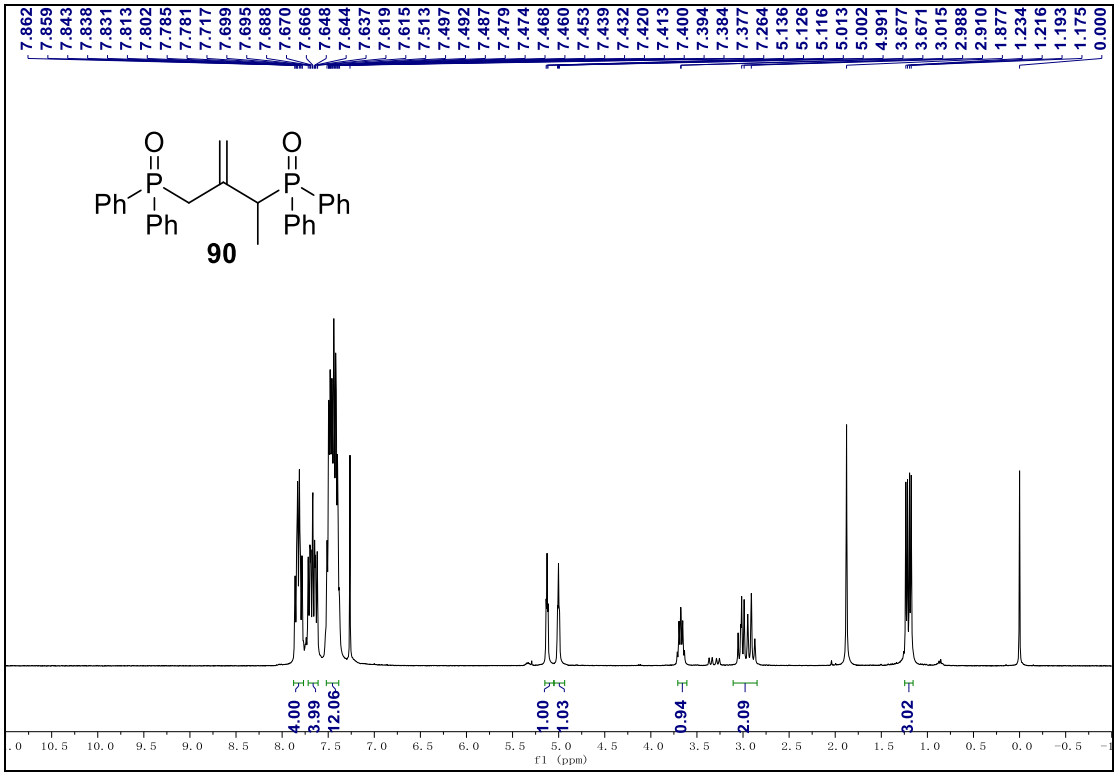
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 89.

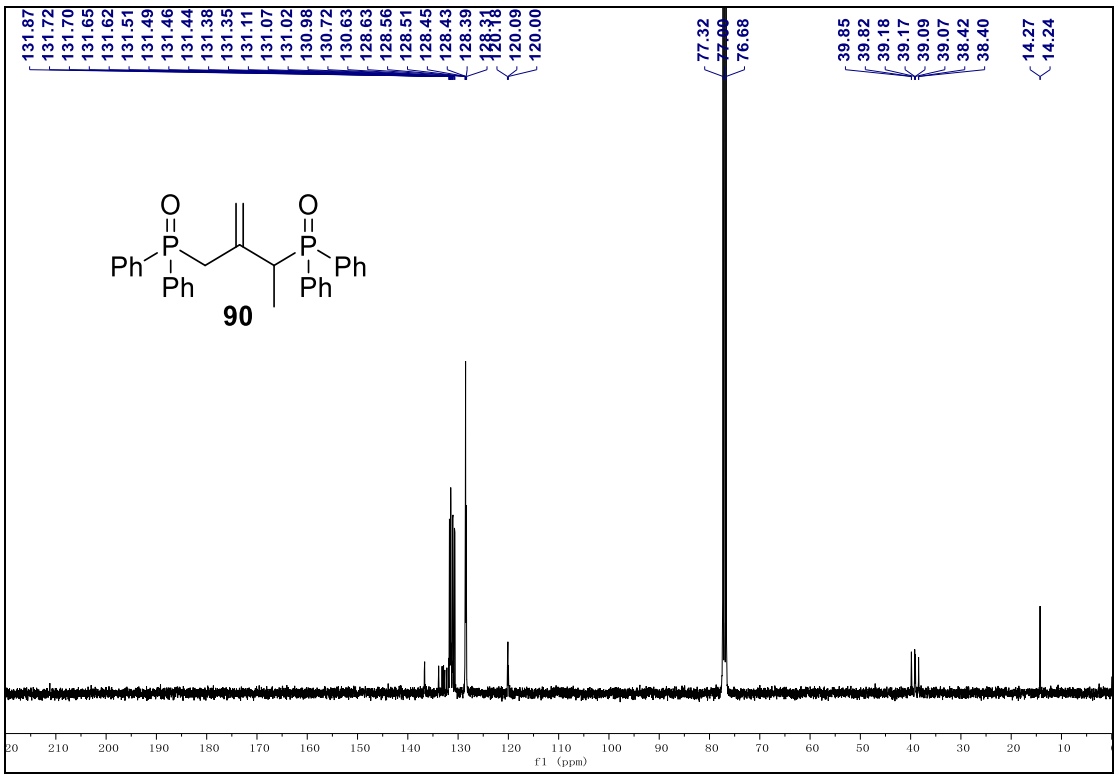


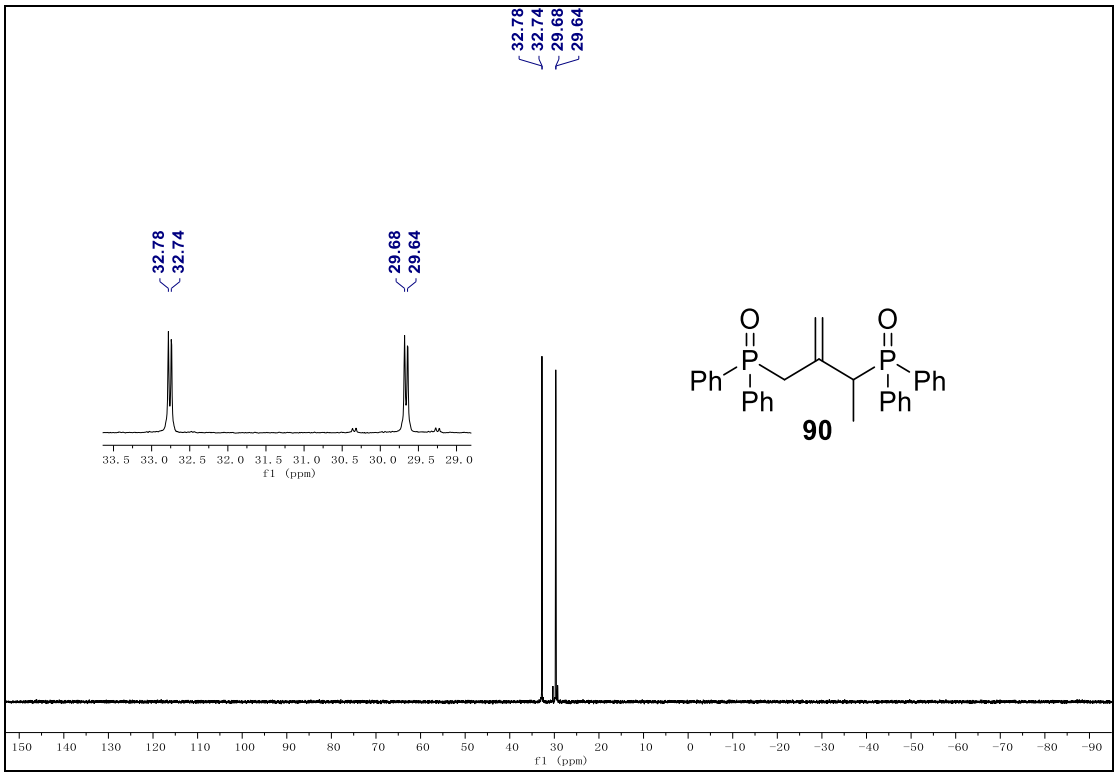



29.41
O
P
Ph
Ph
O
P
Ph
Ph
89
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

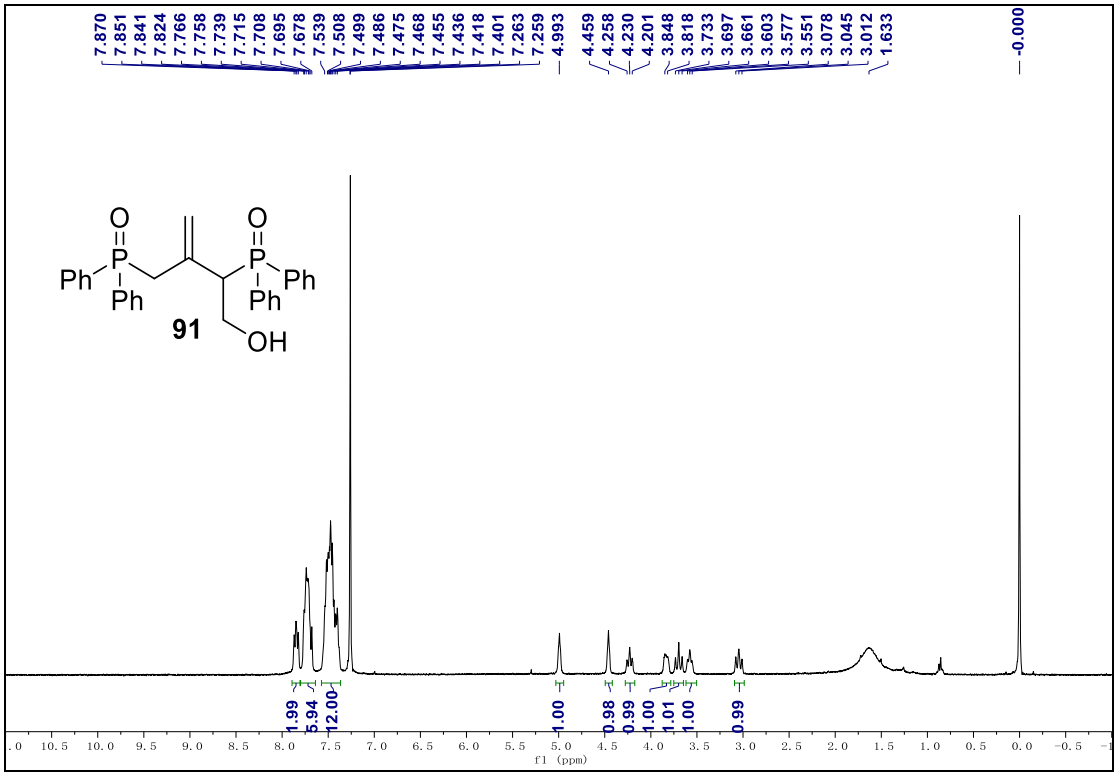
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 90.

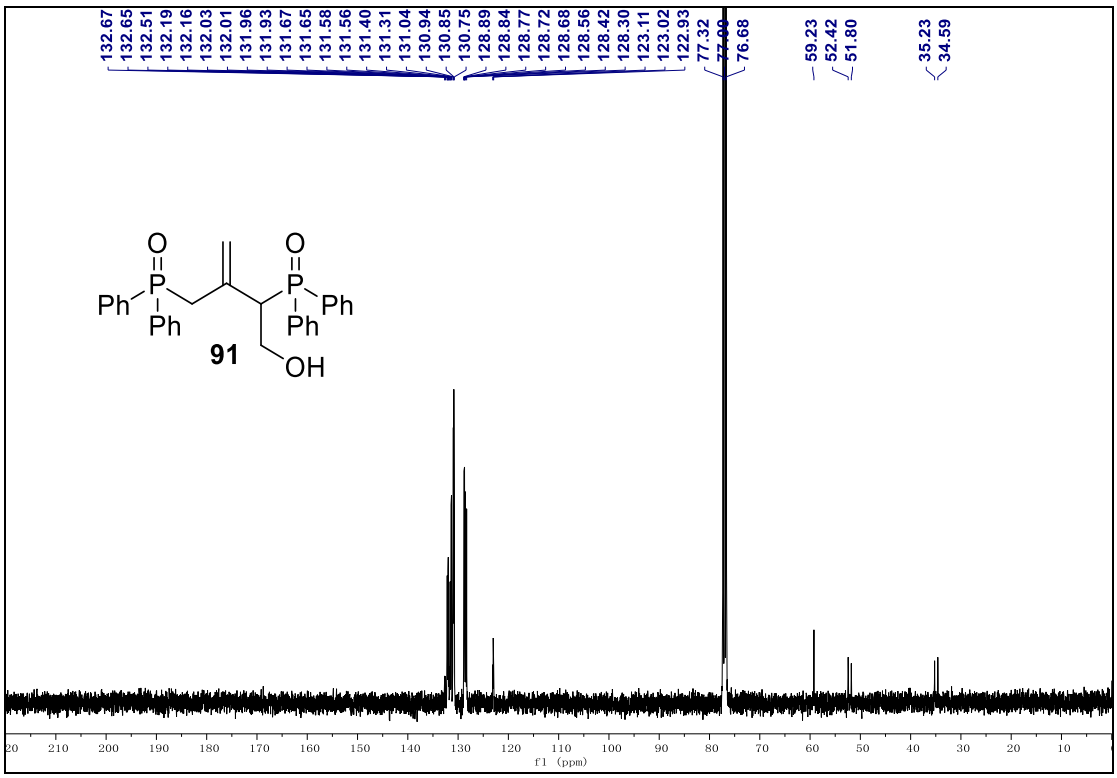


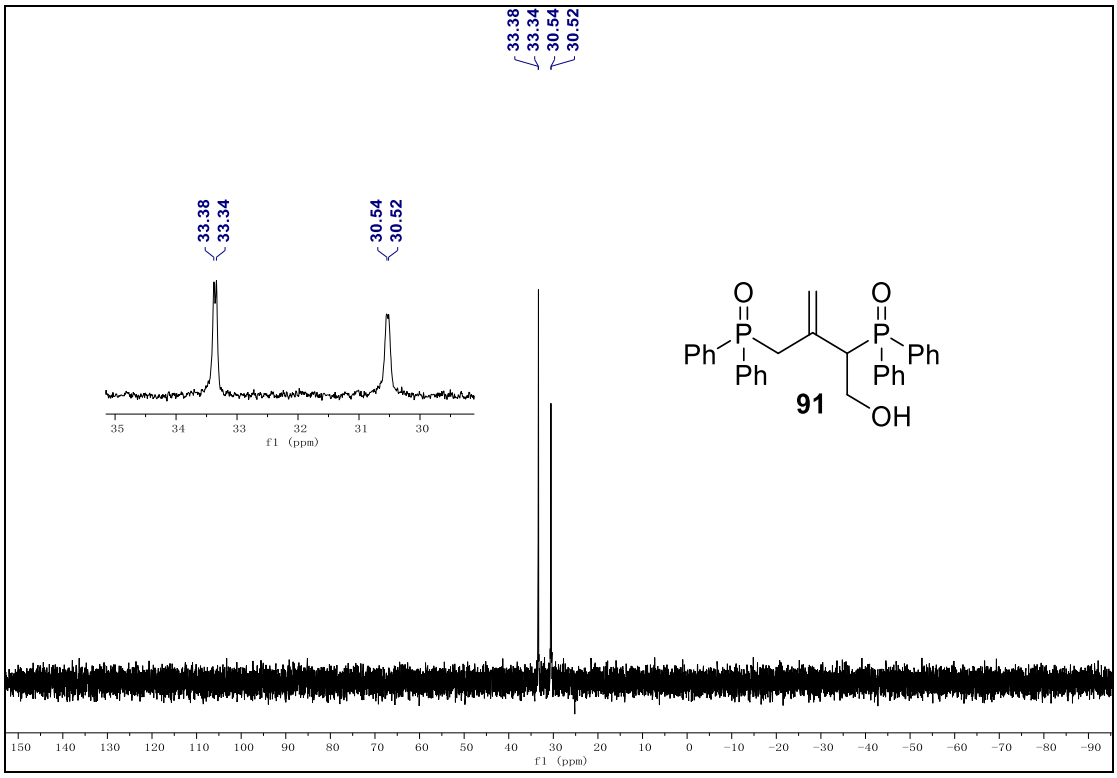



32.78
32.74
29.68
29.64
f1 (ppm)
90

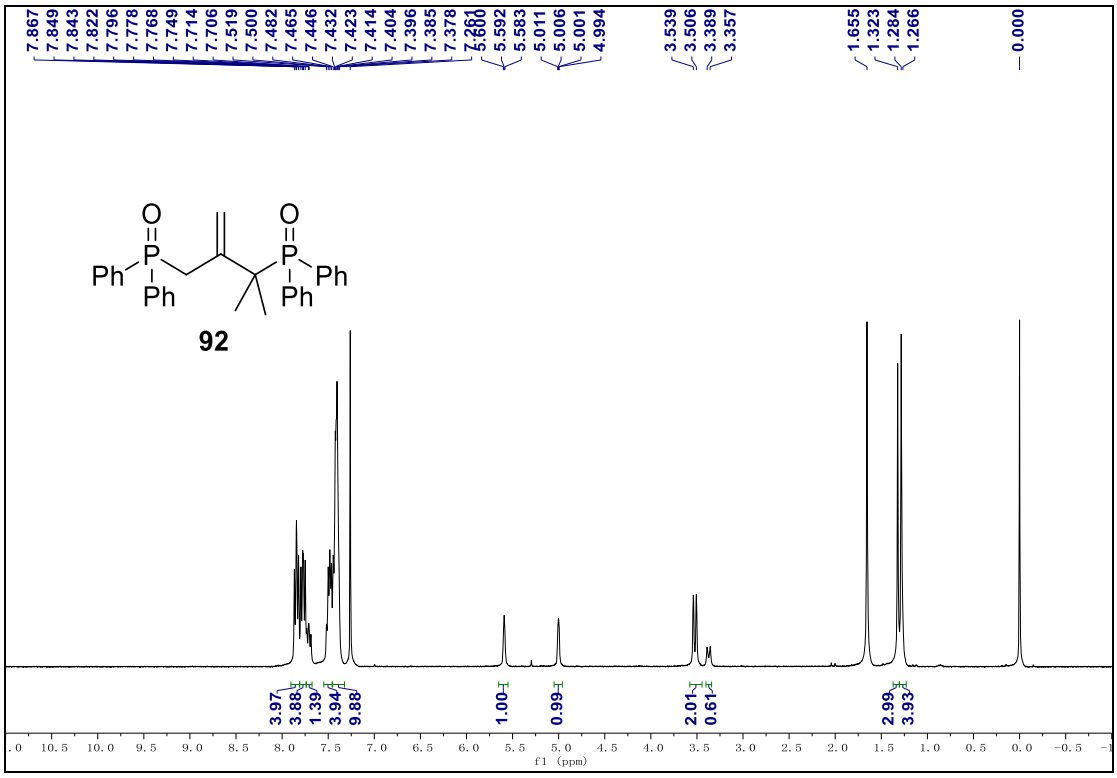
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 91.

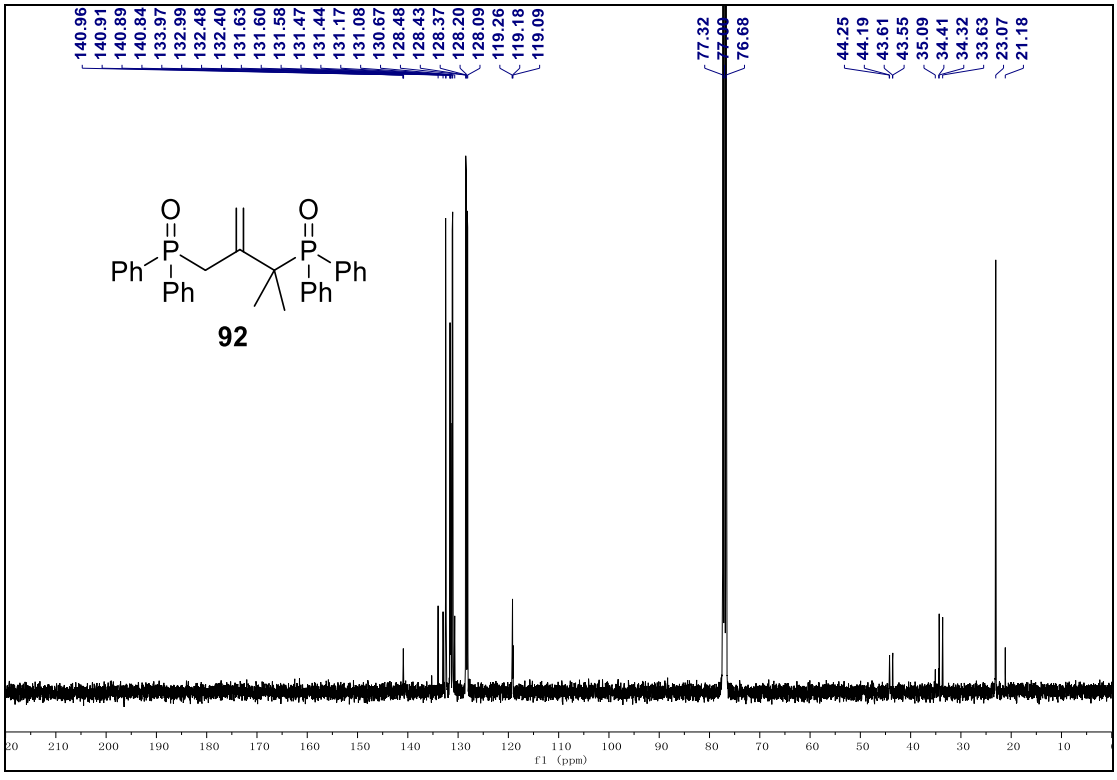


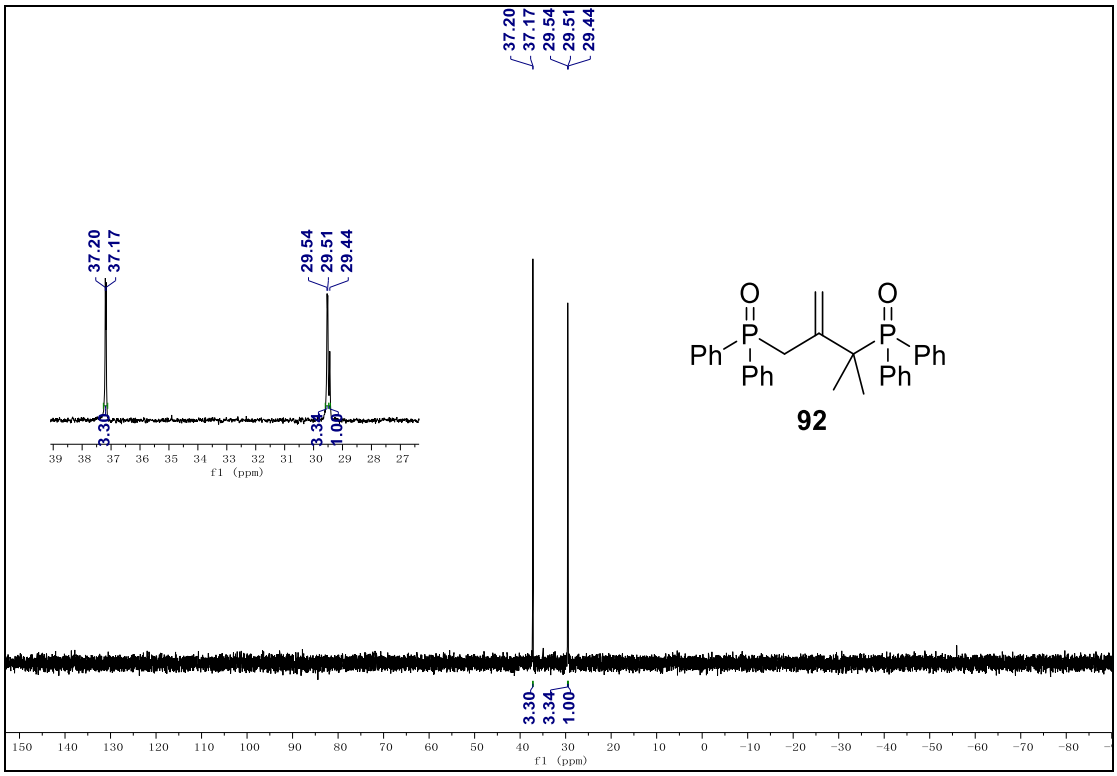



33.38
33.34
30.54
30.52
O
P
Ph
Ph
O
P
Ph
Ph
91
OH
f1 (ppm)

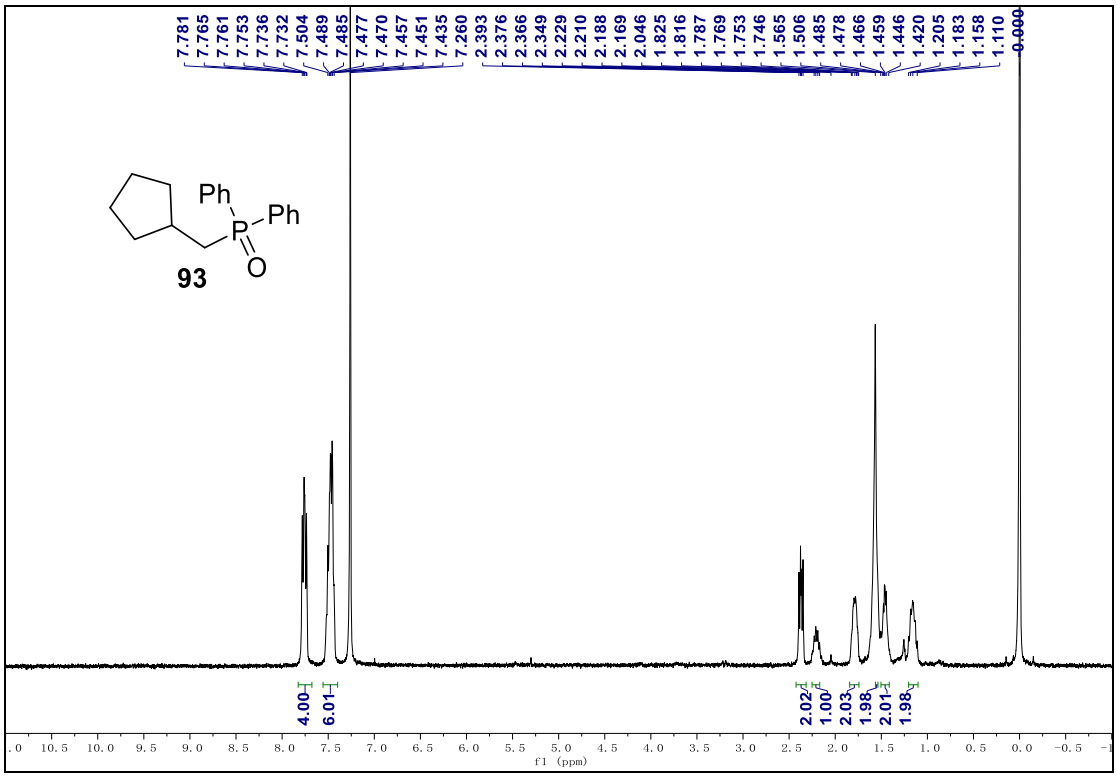
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) of 92.

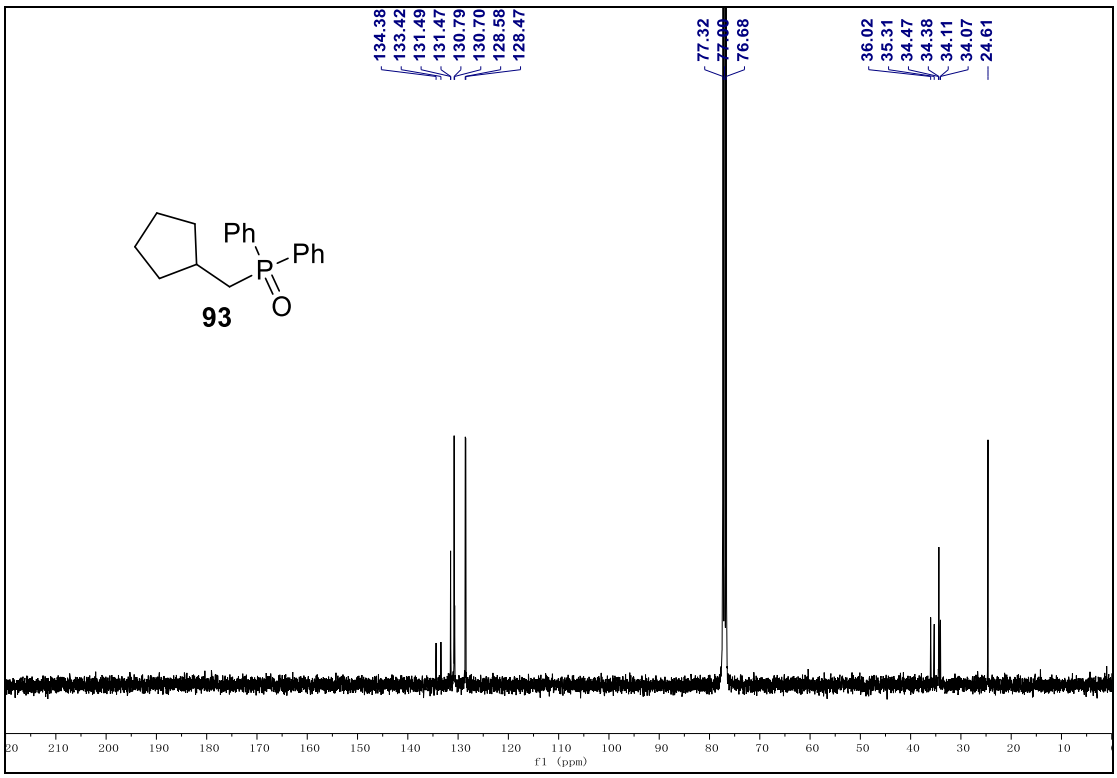


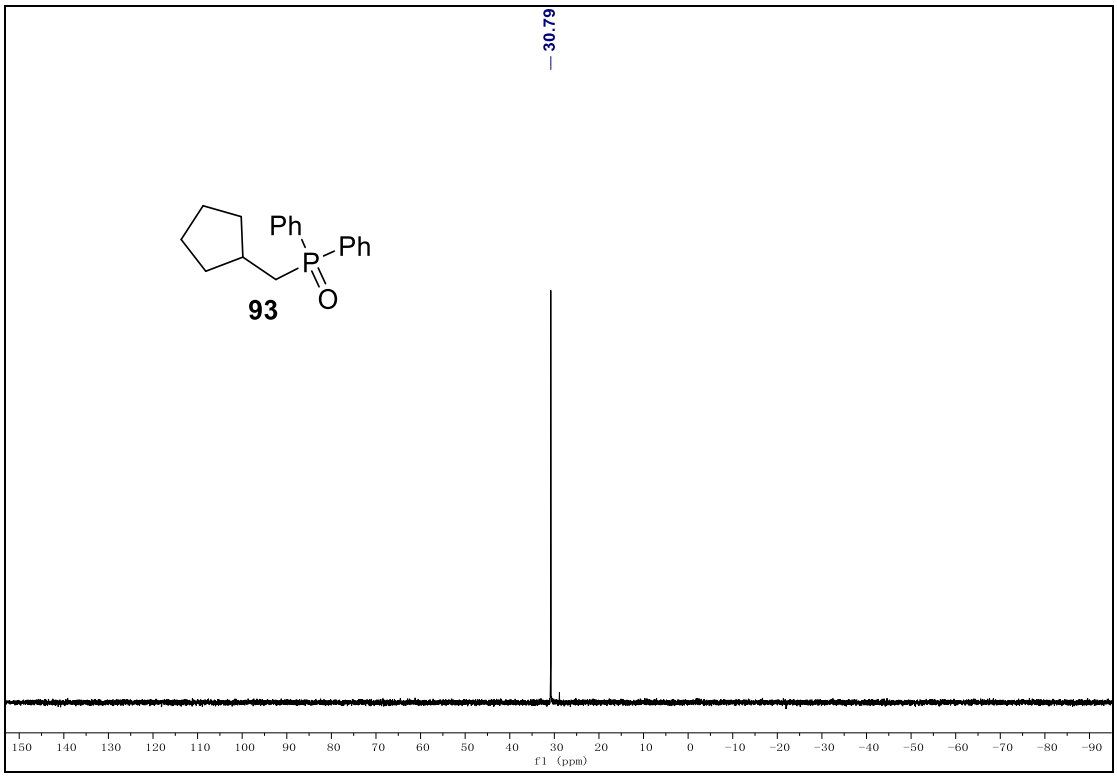



37.20
37.17
29.54
29.51
29.44
3.30
3.34
1.00
f1 (ppm)
O
P
Ph
Ph
O
P
Ph
Ph
92

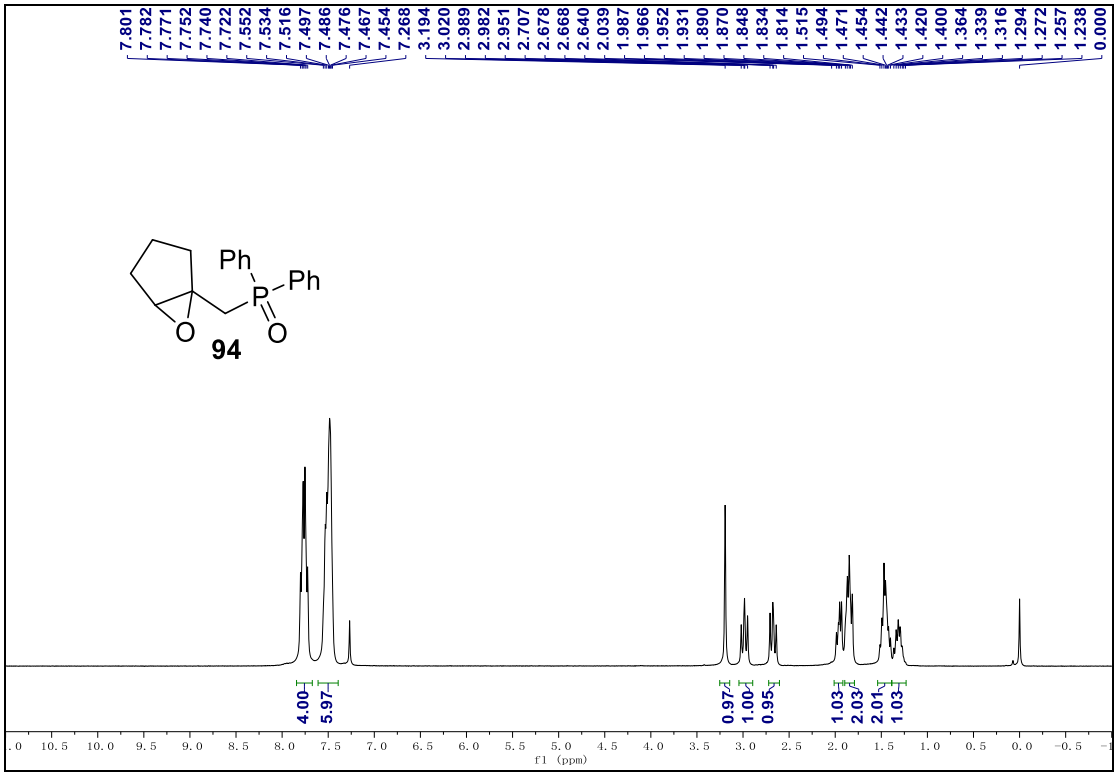
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 93.

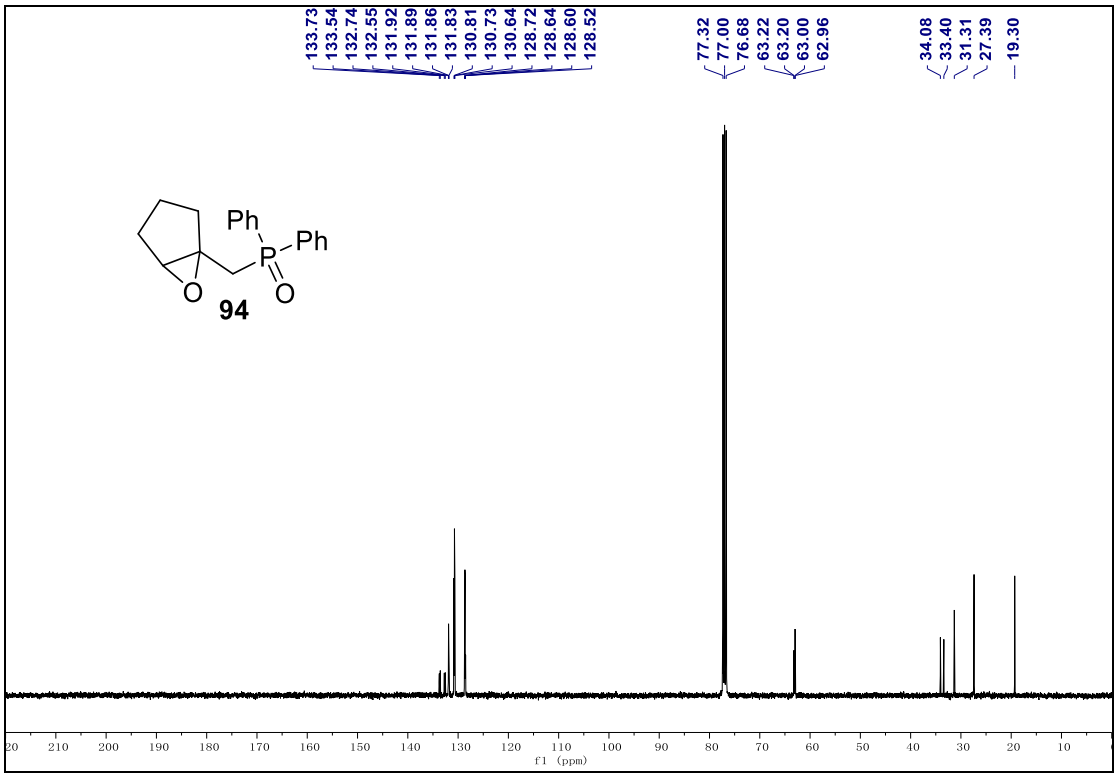


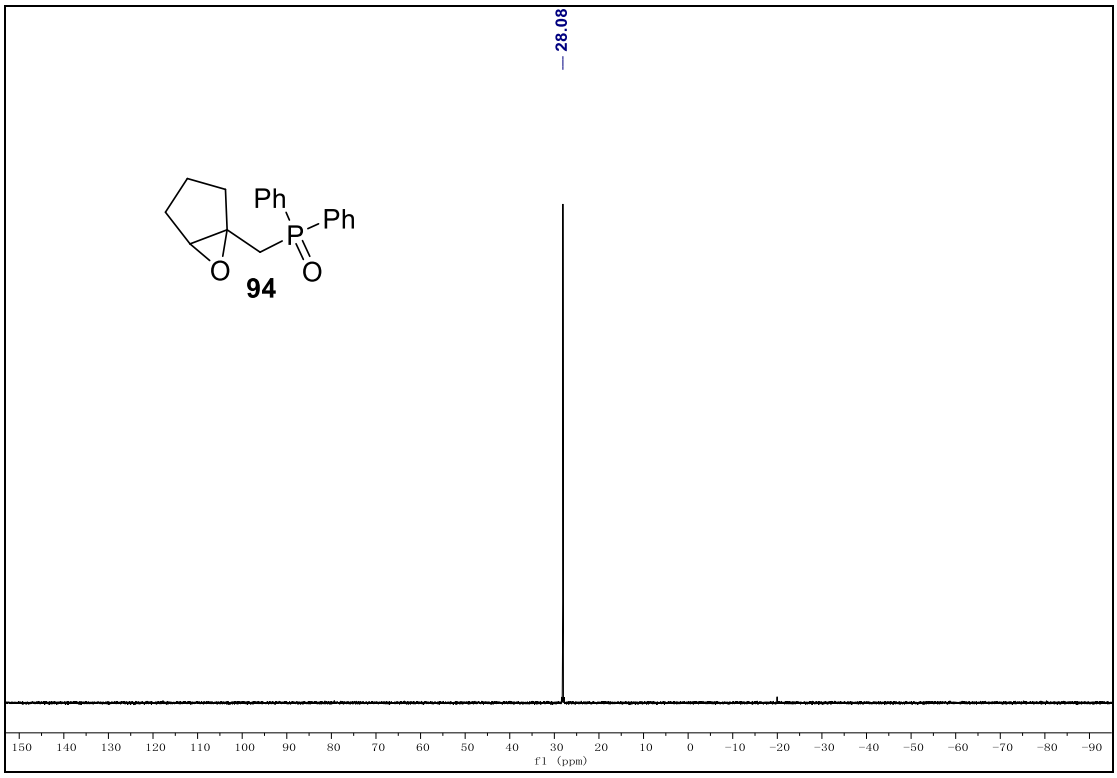



30.79
Ph
Ph
P
O
93
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

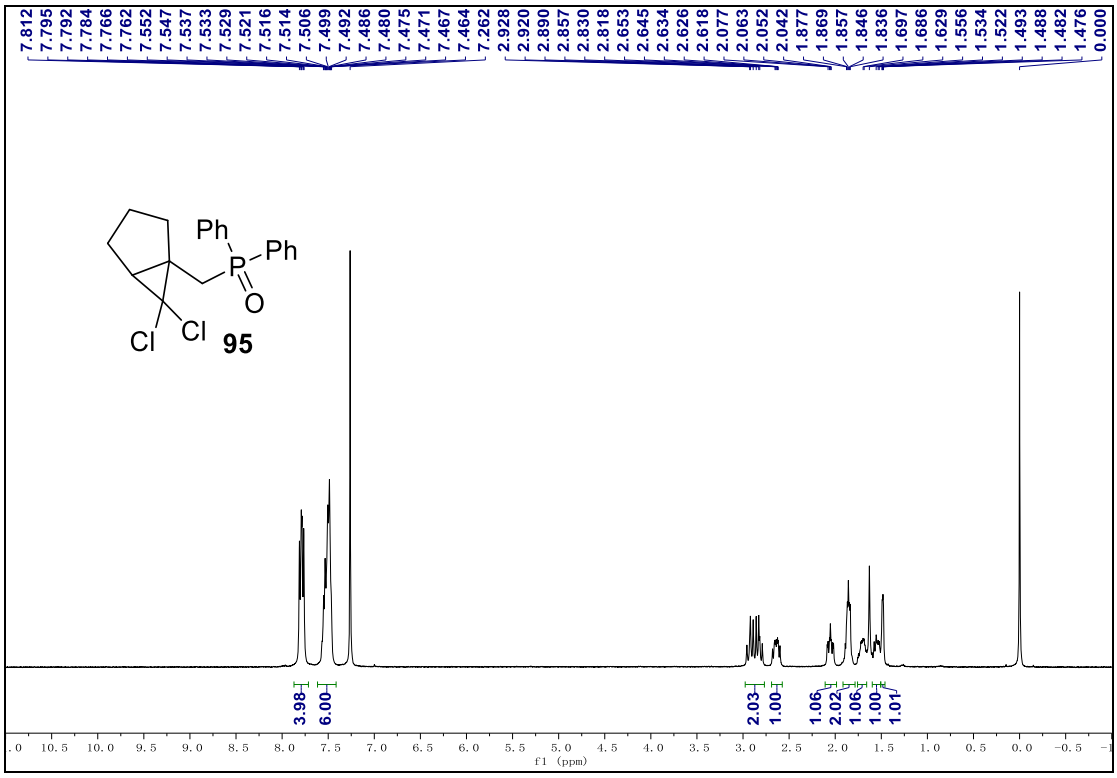
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 94.

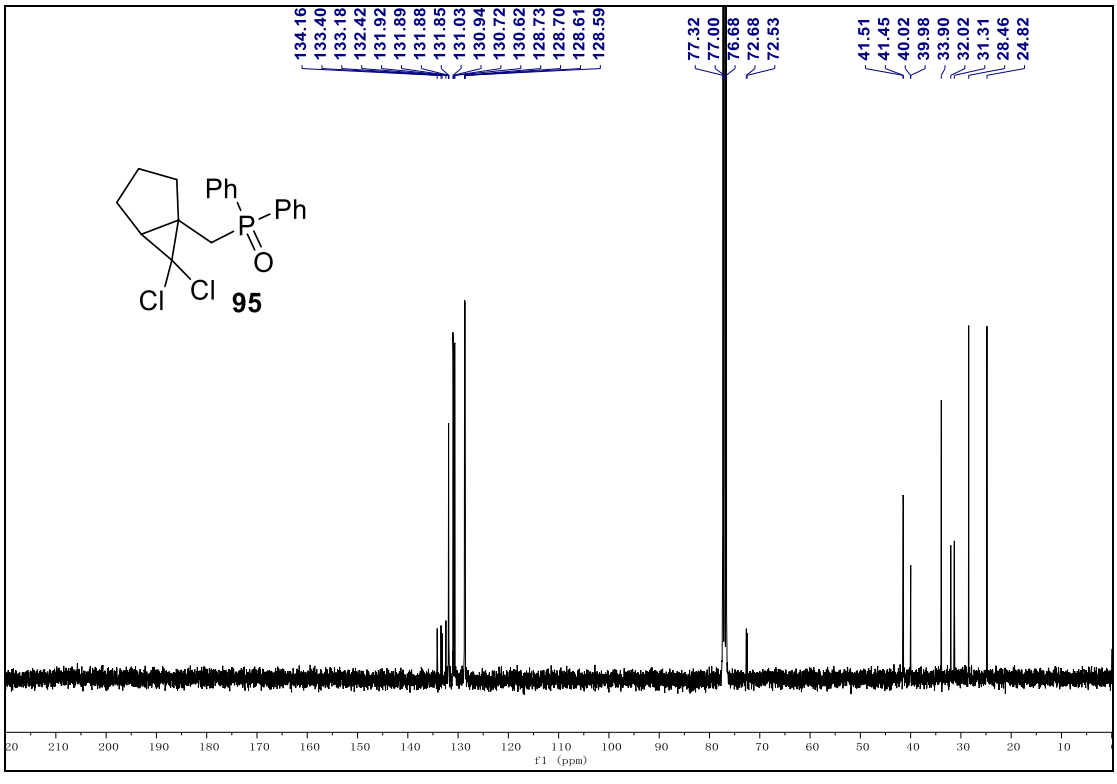


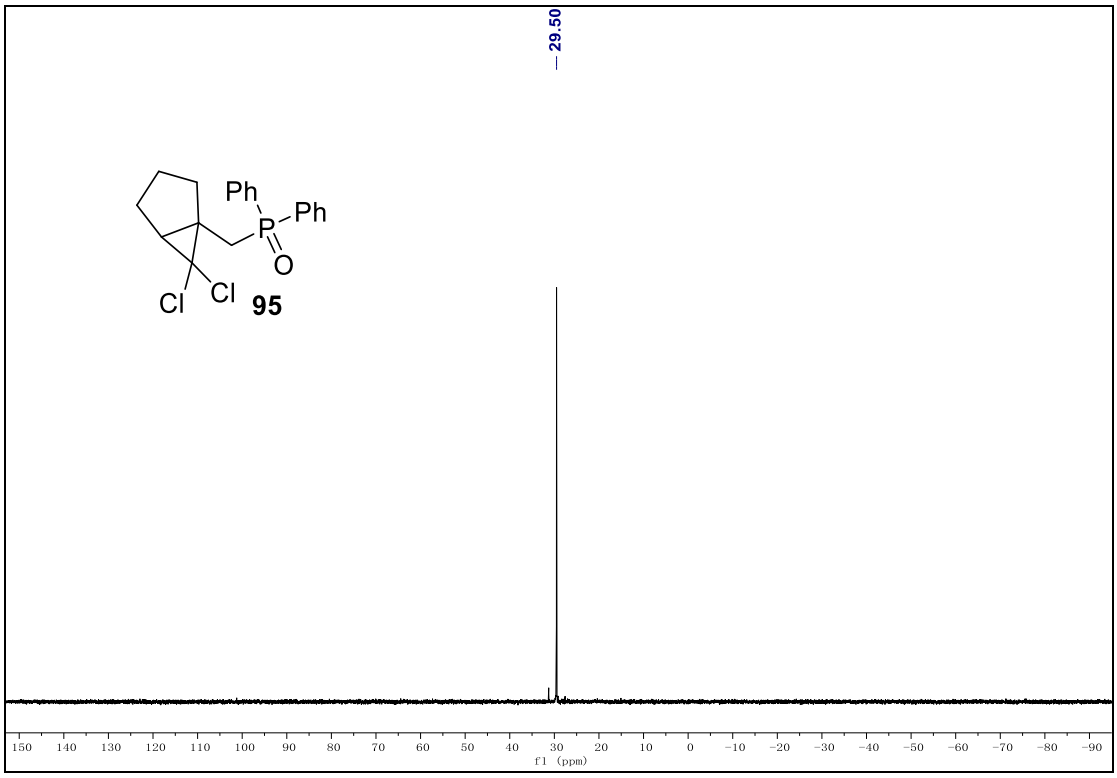



28.08
Ph
Ph
P
O
O
94
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

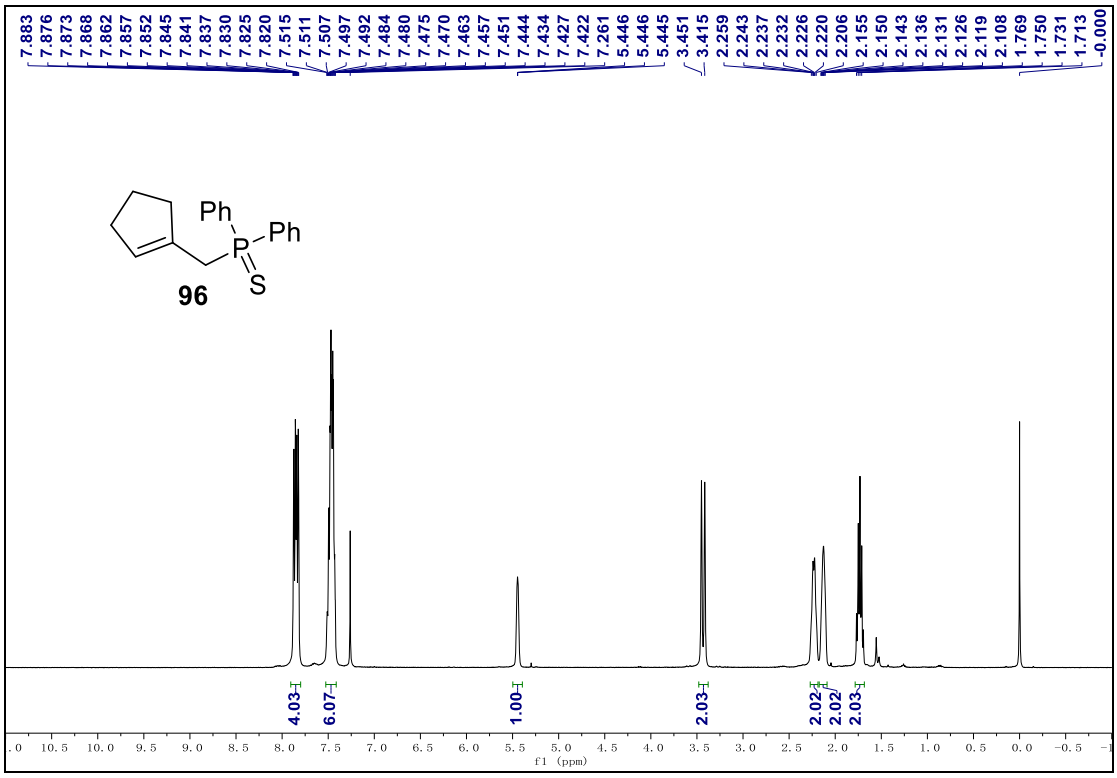
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 95.

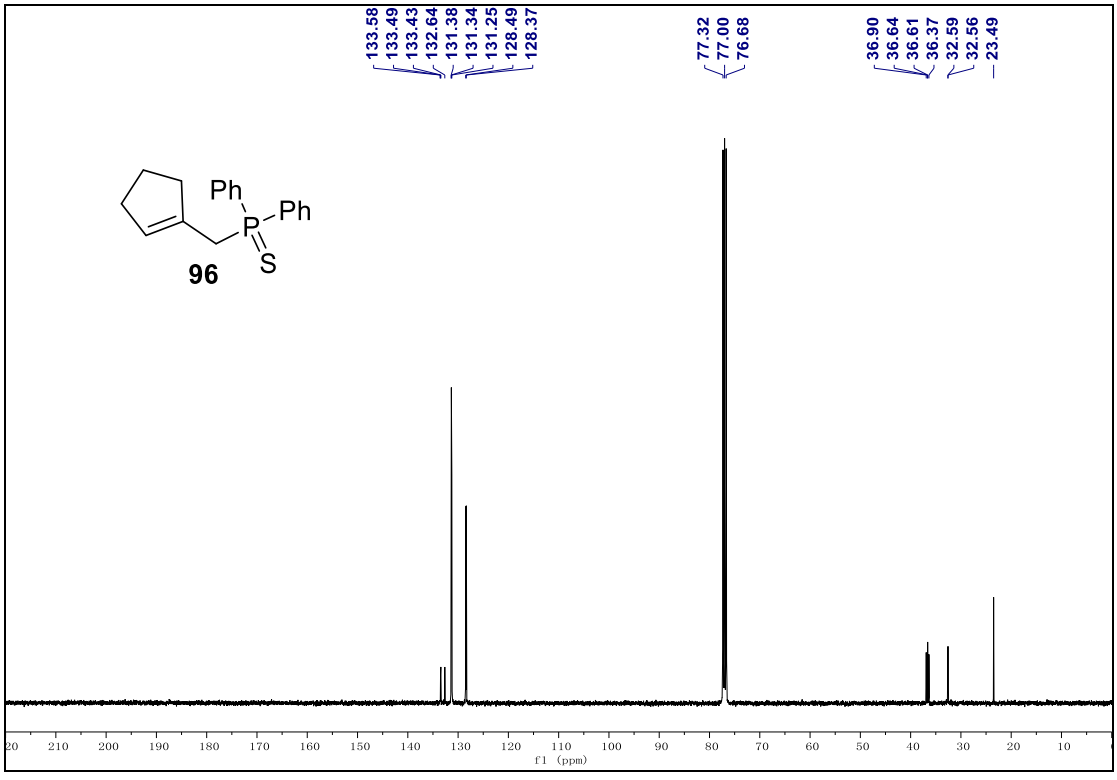


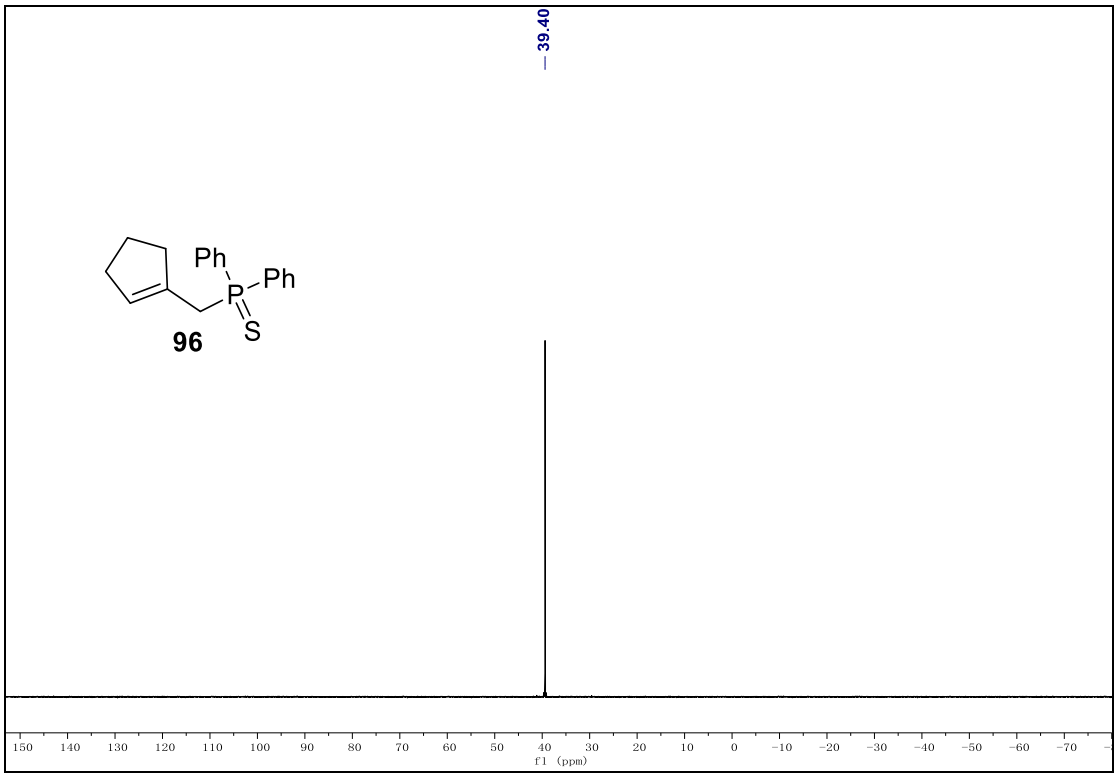



29.50
Ph
Ph
P
O
Cl
Cl
95
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

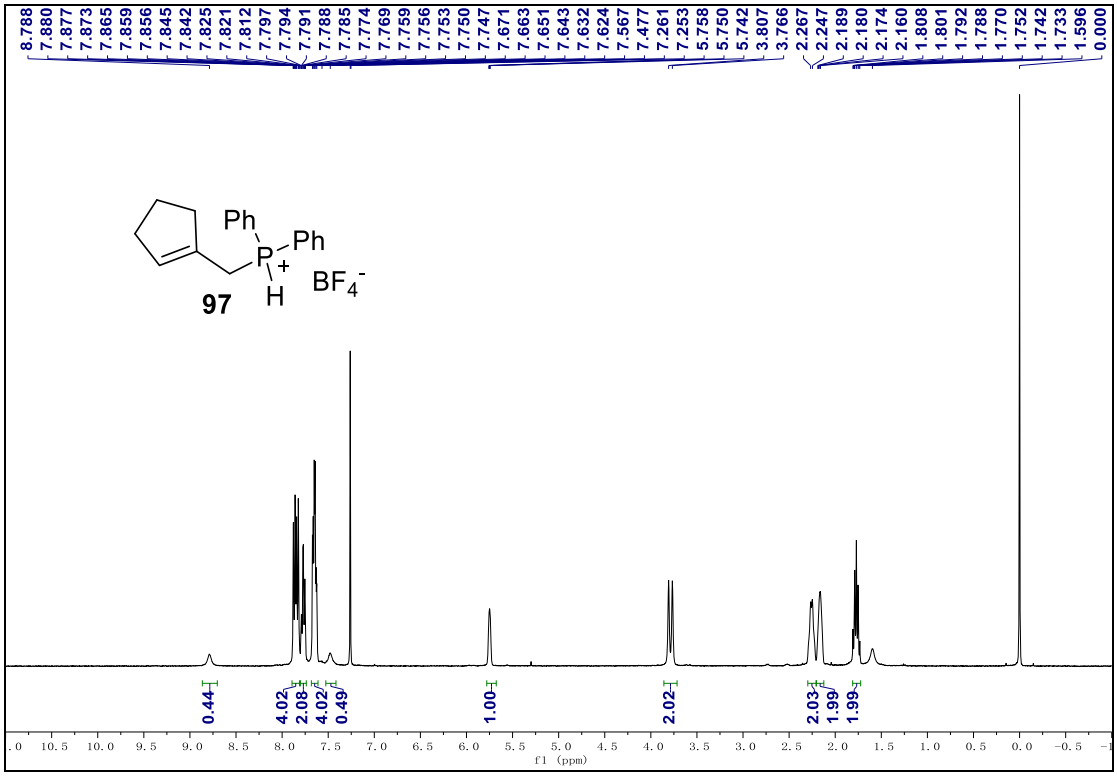
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 96.

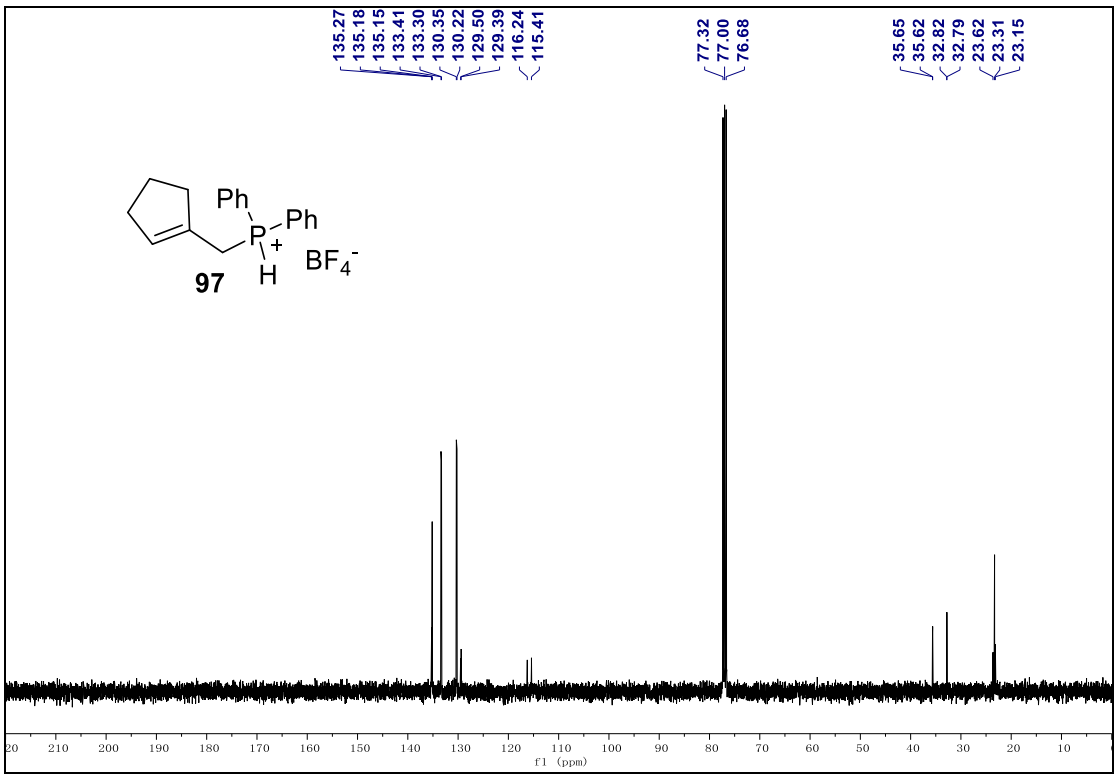


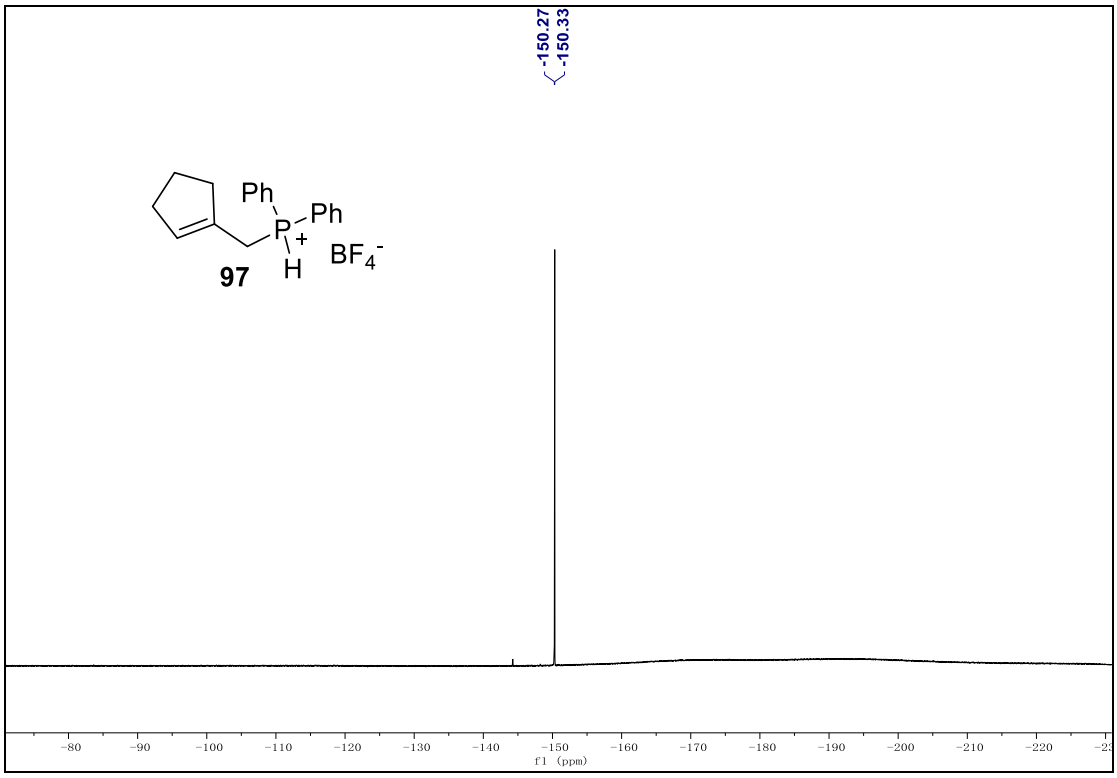


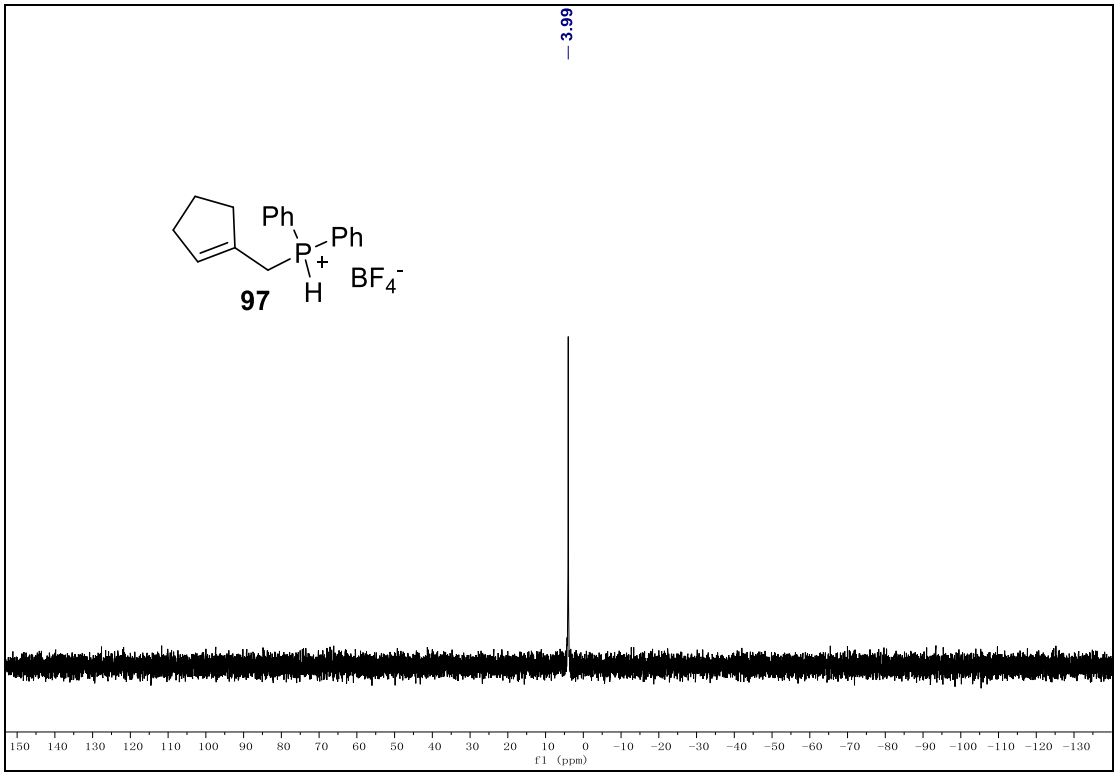

39.40
Ph
Ph
P
S
96
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, CDCl3) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 97.

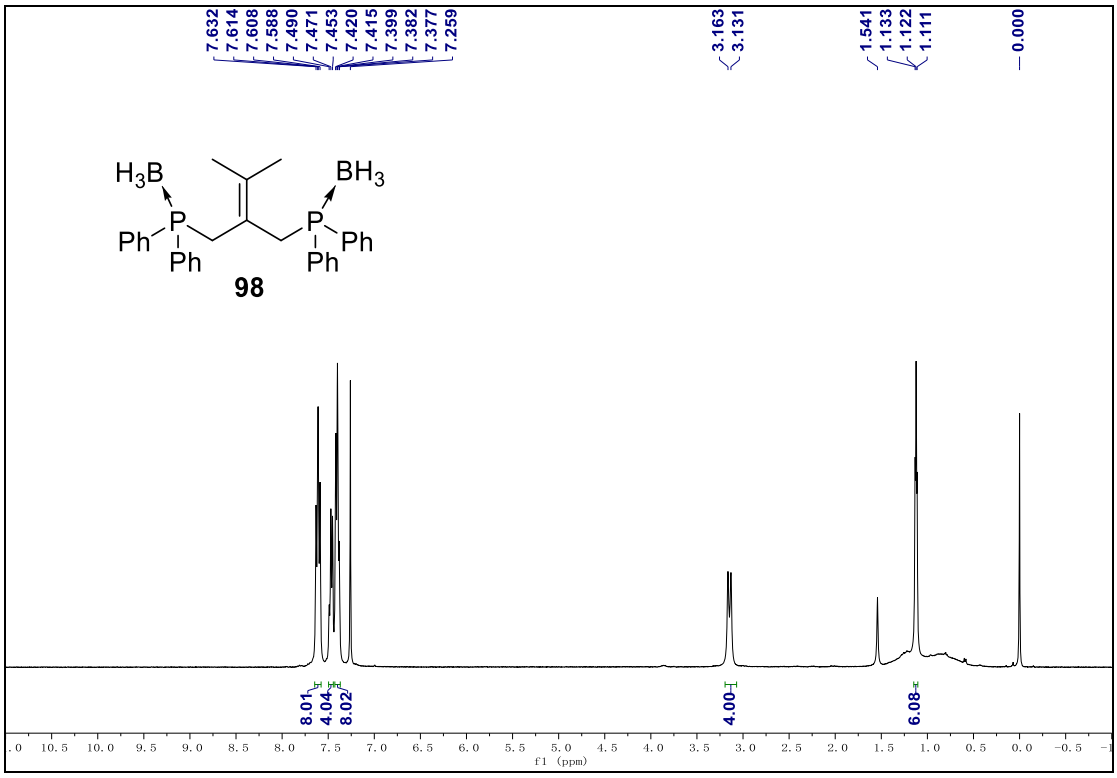


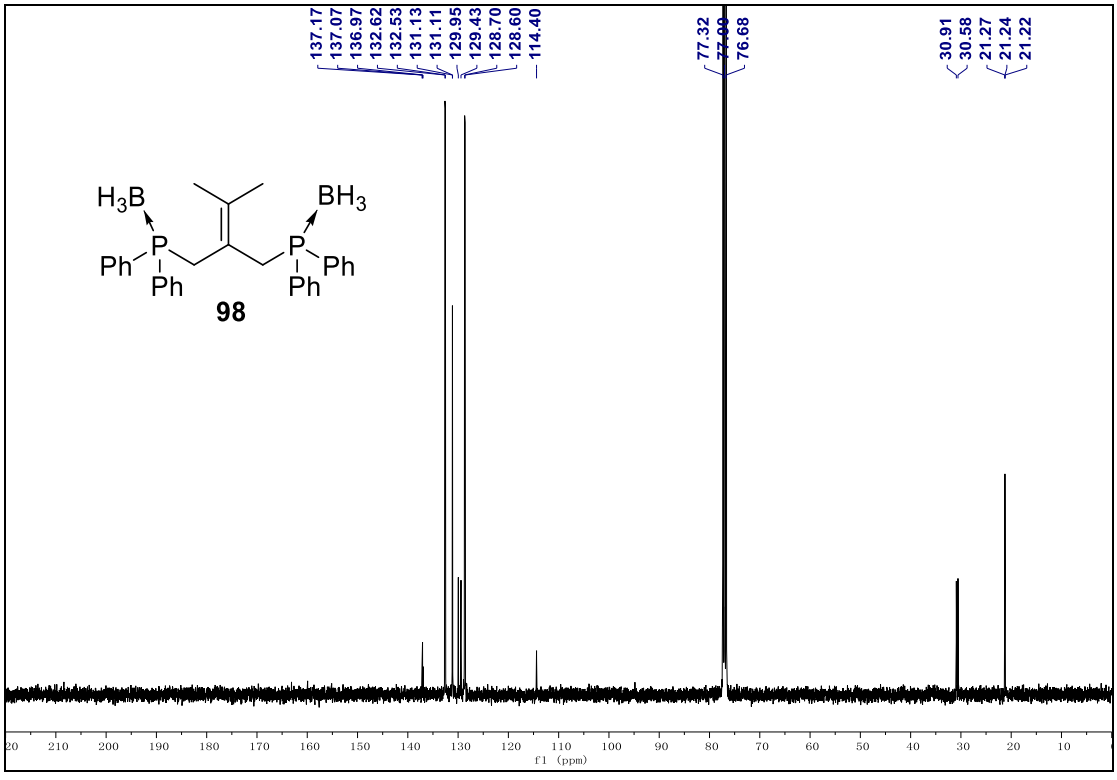


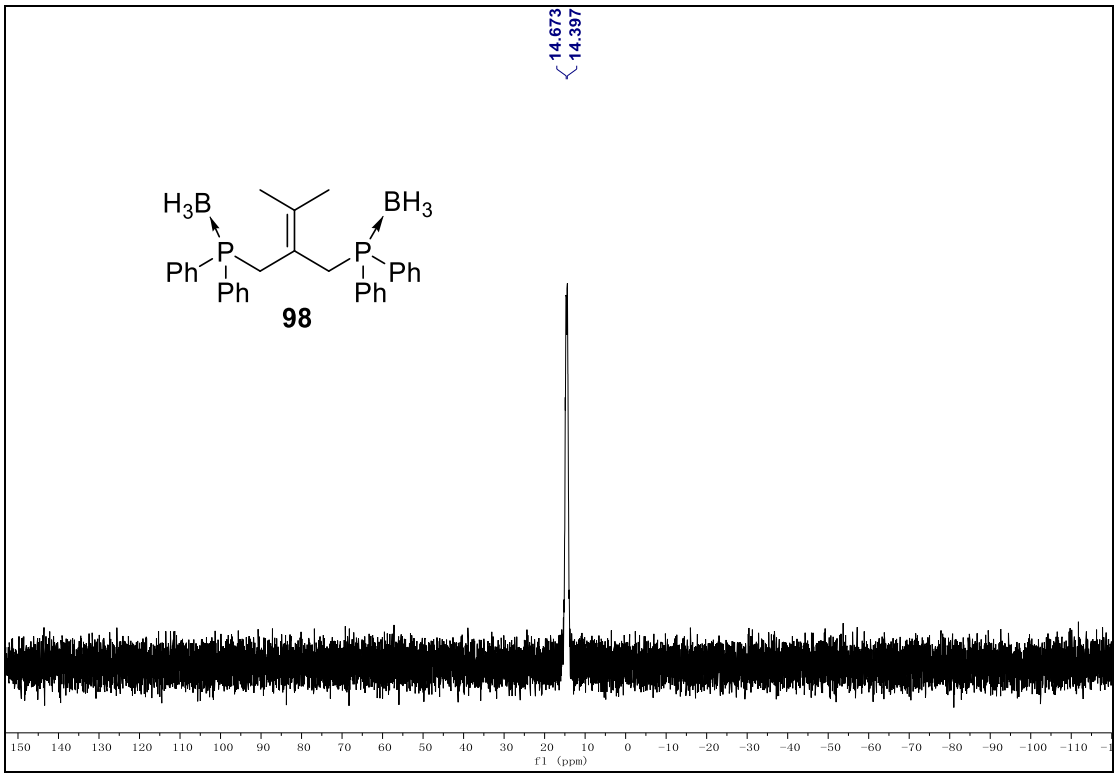

-150.27
-150.33
Ph
Ph
P+
H
BF4-
97
f1 (ppm)


3.99
Ph
Ph
P+
H
BF4-
97
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of 98.






14.673
14.397
H3B
BH3
P
Ph
Ph
Ph
P
Ph
Ph
98
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110
f1 (ppm)