

Supporting Information

Efficient synthesis of α -amino-vinylphosphine oxides between alkyl nitriles *via* manganese-catalyzed phosphinoenamination

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1.Experimental Procedures

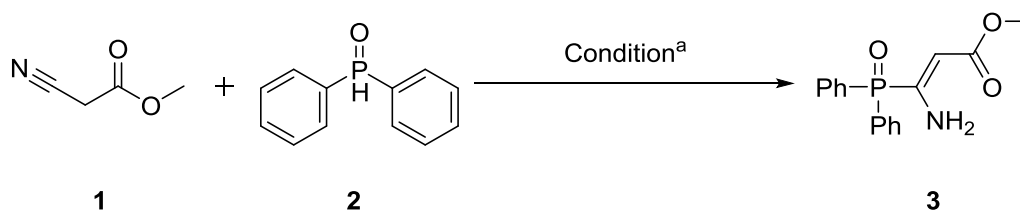
Preparation of free guanidine: On an analytical balance, GuHCl (57 mg, 0.6 mmol, 2.0 equiv.) and ^tBuONa (57.6 mg, 0.6 mmol, 1.0 equiv.) were weighed and added to a dry Schlenk tube (15 mL) with a magnetic stirrer, and was evacuated using a vacuum pump to remove air and then flushed with nitrogen gas. 2 mL of C₂H₅OH was added to the Schlenk tube under a nitrogen atmosphere. The tube was sealed and the mixture was stirred for 15 minutes. Then, the mixture was allowed settle into layers, and the upper layer of the clear solution containing guanidine (28.5 mg, 0.3 mmol, 1.0 equiv.) in C₂H₅OH (1 mL) was collected.

2 General procedure for the synthesis of α -amino-vinylphosphine oxides: diphenylphosphine

oxide (60.6 mg, 0.3 mmol, 1.0 equiv.), Mn(OAc)₂ (5.2 mg, 0.03 mmol, 15 mol%) were added to a dry Schlenk tube (15 mL) containing a magnetic stirrer and dissociative guanidine (28.5 mg, 0.3 mmol, 1.0 equiv.). The Schlenk tube was evacuated using a vacuum pump and then flushed with nitrogen gas. Under a nitrogen atmosphere, **1** Methyl 2-cyanoacetate (74.5 mg, 0.75 mmol, 2.5 equiv.) and 1,4-dioxane (2 mL) were added to the Schlenk tube. The reaction mixture was then stirred at 60°C for 12 hours. The progress was monitored by thin-layer chromatography (TLC). The product was concentrated by distillation under reduced pressure and further purified by column chromatography using silica gel with a petroleum ether/ethyl acetate eluent.

2. Optimization of the Reaction Conditions

Table S1. Catalyst Screening^a

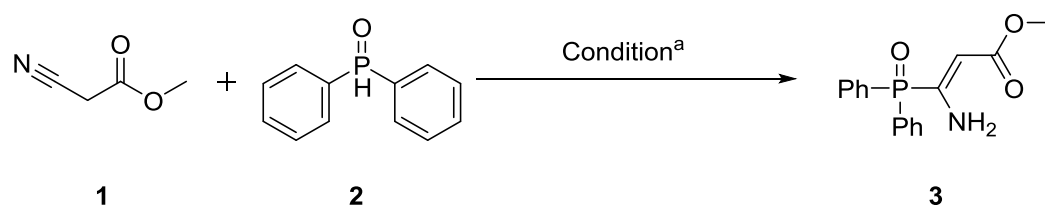


Entry	Catalyst	mol%	Yield(%)
1	Mn(OAc) ₂	15%	95%
2	Mn(OAc) ₂	10%	82%
3	Mn(OAc) ₂	5%	59%
4	Mn(OAc) ₂	1%	23%
5	Mn(ClO ₄) ₂	10%	32%
6	MnCl ₂	10%	41%
7	Mn(C ₂ O ₄) ₂	10%	50%
8	Mn(acac) ₃	10%	34%
9	Mn(CO) ₁₂	10%	20%
10	Mn(OAc) ₃	10%	47%
11	Ni(OAc) ₂	10%	20%
12	NiBr ₂	10%	17%
13	Ni(PPh ₂) ₂ Cl ₂	10%	35%
14	NiF ₂	10%	21%
15	Ni(OTf) ₂	10%	70%
16	Cu(OTf) ₂	10%	11%

17	CoCl ₂	10%	17%
18	Pd(OAc) ₂	10%	59%

^a Reaction conditions: **1** (74.5 mg, 0.75 mmol), **2** (60.6mg, 0.3 mmol, 1.0 equiv.), Catalyst (15 mol%), base (0.3 mmol, 1.0 equiv.), 1,4-dioxane (3 mL) were mixed at 60°C under N₂ for 12 h.

Table S2. Base Screening ^a



Entry	base	n	Yield(%)
1 ^b	guanidine	1.0 equiv.	95%
2	DABCO	1.0 equiv.	30%
3	tBuOK	1.0 equiv.	43%
4	Na ₂ CO ₃	1.0 equiv.	20%
5	DIPEA	1.0 equiv.	27%
6	NaOH	1.0 equiv.	33%
7	KOH	1.0 equiv.	35%

^a Reaction conditions : **1** (74.5 mg, 0.75 mmol, 2.5 equiv.), **2** (60.6mg, 0.3 mmol, 1.0 equiv.), Mn(OAc)₂ (15 mol%), base (0.3 mmol), 1,4-dioxane (3 mL) were mixed at 60°C under N₂ for 12 h. ^b Dissociative guanidine.

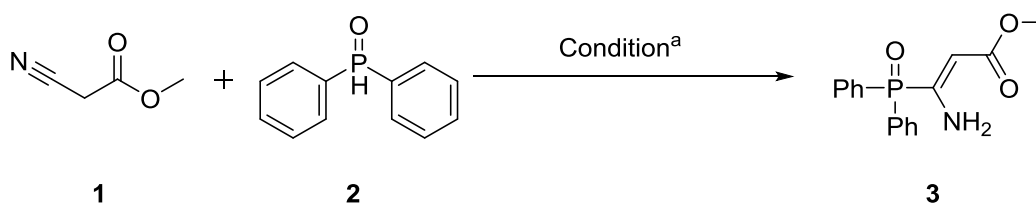
Table S3. Time and Temperatures Screening ^a

Entry	Time	Temperatures	yield(%)
1	12 h	60°C	95%
2	9 h	60°C	72%
3	18 h	60°C	90%

4	12 h	120°C	86%
5	12 h	80°C	88%
6	12h	40°C	70%

^a Reaction conditions: **1** (74.5 mg, 0.75 mmol, 2.5 equiv.), **2** (60.6mg, 0.3 mmol, 1.0 equiv.), Mn(OAc)₂ (15 mol%), guanidine (0.3 mmol), 1,4-dioxane (3 mL) were mixed under N₂.

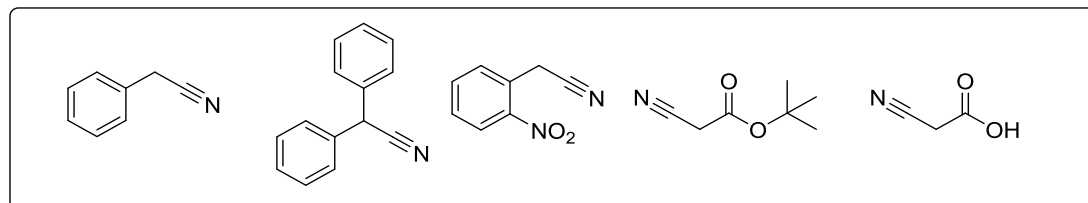
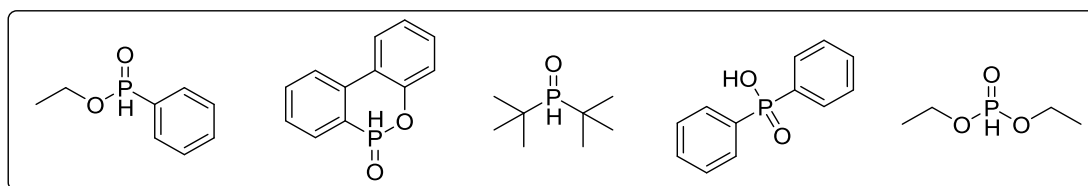
Table S4. Solvent Screening ^a



Entry	Catalyst	Solvent	Yield(%)
1	Mn(OAc) ₂	1,4-dioxane	95%
2	Mn(OAc) ₂	DCM	20%
3	Mn(OAc) ₂	DCE	17%
4	Mn(OAc) ₂	CH ₃ OH	33%
5	Mn(OAc) ₂	CH ₃ CN	30%
6	Mn(OAc) ₂	DMF	26%
7	Mn(OAc) ₂	DMAc	10%
8	Mn(OAc) ₂	THF	Nr.
9	Mn(OAc) ₂	DMSO	Nr.
10	Mn(OAc) ₂	Tol.	Nr.

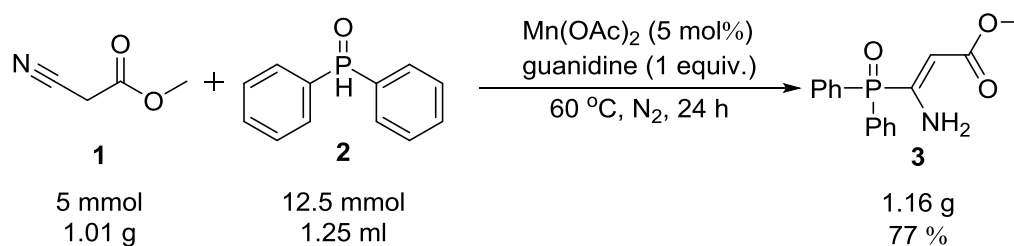
^a Reaction conditions : **1** (74.5 mg, 0.75 mmol, 2.5 equiv.), **2** (60.6mg, 0.3 mmol, 1.0 equiv.), Mn(OAc)₂ (15 mol%), guanidine (0.3 mmol, 1.0 equiv.), Solvent (3 mL) were mixed at 60°C under N₂ for 12 h;

3. The examination of other H-P(O)R₂ and nitriles



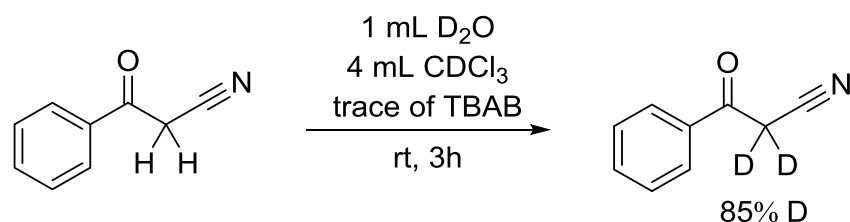
No Reaction

4. Gram-scale reaction

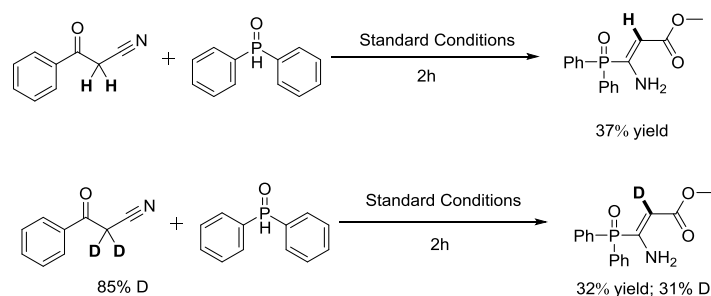


Diphenylphosphine oxide **1** (1.01 g, 5 mmol, 1.0 equiv.), Mn(OAc)₂ (61 mg, 0.25 mmol, 5 mol%) and guanidine (300 mg, 5 mmol, 1.0 equiv.) in C₂H₅OH (1 mL) were added to a dry Schlenk tube (100 mL) with a magnetic stirrer. The C₂H₅OH in the Schlenk tube was evacuated using a vacuum pump to remove any remaining air, then flushed with nitrogen gas. Under a nitrogen atmosphere, Methyl 2-cyanoacetate **2** (12.5 ml, 1.25 mmol, 2.5 equiv.) and 1,4-dioxane (20 mL) were added to the Schlenk tube and sealed. The reaction mixture was then stirred at 60 °C for 12 hours, after which the heating was turned off. The reaction was allowed to cool to room temperature. The product was concentrated by distillation under reduced pressure and further purified by column chromatography using silica gel. The product was purified using silica gel column chromatography with a petroleum ether/ethyl acetate eluent, 1.16 g of product **3** was obtained, with a yield of 77%.

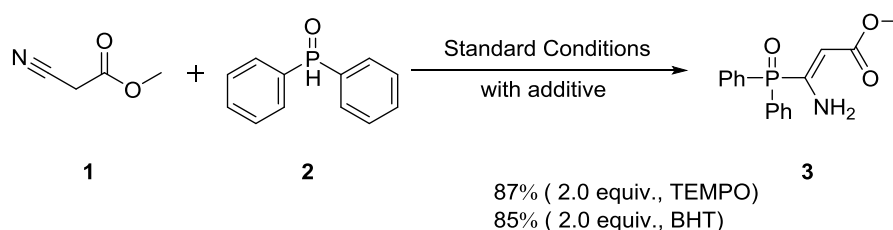
5. Parallel KIE experiment



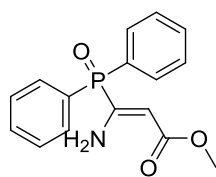
3-Oxo-3-phenylpropanenitrile (145 mg, 1 mmol, 1 equiv.) and TBAB (32.2 mg, 0.1 mmol, 0.1 equiv.) were added to a dry Schlenk tube (15 mL) with a magnetic stirrer under N₂. D₂O (1 ml) and CDCl₃ (4 ml) was added to the Schlenk tube under a nitrogen atmosphere. The reaction was performed at room temperature for 3 hours and distill under reduced pressure to obtain 85% D products.



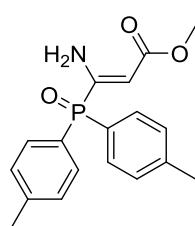
6. Single electron transfer (SET) process detection experiment



Methyl 3-amino-3-(diphenylphosphoryl)acrylate (3). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (87.1 mg), 95% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.73 (m, J = 12.4, 8.3, 1.4 Hz, 4H), 7.62 – 7.55 (m, 2H), 7.49 (td, J = 7.6, 3.2 Hz, 4H), 6.87 (s, 2H), 4.73 (d, J = 13.6 Hz, 1H), 3.64 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 169.03 (d, J = 21.1 Hz), 154.48, 153.51, 132.85 (d, J = 2.8 Hz), 132.11, 132.01, 128.84, 128.71, 92.08 (d, J = 16.5 Hz), 50.74; ³¹P NMR (162 MHz, CDCl₃) δ (ppm) 28.08.; HRMS (ESI) (m/z): calcd for C₁₆H₁₆NO₃P [M+H]⁺: 302.0946, found: 302.0944.

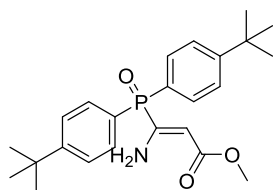


(Methyl 3-amino-3-(di-*p*-tolylphosphoryl)acrylate) (4). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (86.8 mg), 88% yield (*Z*:*E* = 1:1) (petroleum ether/ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.62 (dd, *J* = 12.3, 8.1 Hz, 4 H), 7.29 (dd, *J* = 7.9, 2.4 Hz, 4H), 6.81 (s, 1H), 4.72



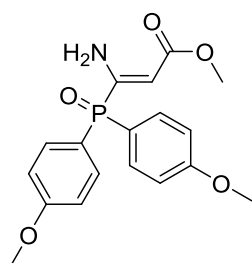
(d, *J* = 13.6 Hz, 1H), 3.65 (s, 3H), 2.41 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 169.09 (d, *J* = 20.8 Hz), 155.15, 154.18, 143.44 (d, *J* = 3.0 Hz), 132.11, 132.00, 129.53, 129.40, 126.71, 125.63, 91.68 (d, *J* = 16.4 Hz), 50.65, 21.63; ³¹P NMR (162 MHz, CDCl₃) δ (ppm) 28.36.; HRMS (ESI) (*m/z*): calcd for C₁₈H₂₀NO₃P [M+H]⁺: 330.1259, found: 330.1261.

Methyl 3-amino-3-(bis(4-(*tert*-butyl)phenyl)phosphoryl) acrylate) (5). The title compound was prepared according to the general procedure and purified by column chromatography to give white



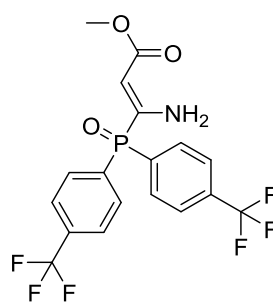
solid (85.4 mg), 69% yield (*Z*:*E* = 1:1) (petroleum ether/ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.65 (dd, *J* = 12.1, 8.4 Hz, 5H), 7.51 – 7.42 (m, 6H), 6.92 (s, 1H), 4.77 (d, *J* = 13.5 Hz, 1H), 3.64 (s, 3H), 1.31 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 169.10 (d, *J* = 20.8 Hz), 156.32 (d, *J* = 2.8 Hz), 131.93 (dd, *J* = 10.4, 4.6 Hz), 125.74 (d, *J* = 12.9 Hz), 125.34 (d, *J* = 12.3 Hz), 91.49 (d, *J* = 16.4 Hz), 50.64, 31.08, 31.02; ³¹P NMR (162 MHz, CDCl₃) δ (ppm) 27.86.; HRMS (ESI) (*m/z*): calcd for C₂₄H₃₂NO₃P [M+H]⁺: 414.2198, found: 414.2201.

Methyl 3-amino-3-(bis(4-methoxyphenyl)phosphoryl) Acrylate (6). The title compound was prepared according to the general procedure and purified by column chromatography to give white



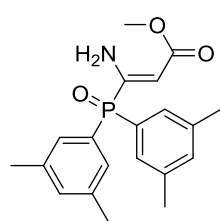
solid (81.2mg), 75% yield (*Z*:*E* = 1:1) (petroleum ether/ethyl acetate = 1:2). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.63 (dd, *J* = 11.9, 8.7 Hz, 4H), 6.97 (dd, *J* = 8.8, 2.3 Hz, 4H), 6.70 (s, 2H), 4.68 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 6H), 3.63 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 169.14 (d, *J* = 20.6 Hz), 163.11 (d, *J* = 2.7 Hz), 155.56, 154.58, 133.99 (d, *J* = 11.8 Hz), 121.17, 120.04, 114.32 (d, *J* = 13.7 Hz), 91.52 (d, *J* = 16.6 Hz), 55.39, 50.66; ³¹P NMR (162 MHz, CDCl₃) δ (ppm) 27.89.; HRMS (ESI) (*m/z*): calcd for C₁₈H₂₀NO₅P [M+H]⁺: 362.1157, found: 362.1154.

Methyl-3-amino-3-(bis(4-(trifluoromethyl)phenyl) phosphoryl)acrylate) (7). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (90.9 mg), 90% yield (*Z*:*E* = 1:1.1) (petroleum ether/ethyl



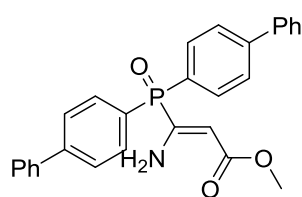
acetate = 1:2). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.84 (dd, *J* = 12.1, 8.0 Hz, 4H), 7.75 (d, *J* = 6.1 Hz, 4H), 6.89 (d, *J* = 34.8 Hz, 2H), 4.65 (d, *J* = 14.2 Hz, 1H), 3.63 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 168.71, 152.51, 151.51, 134.93 (dd, *J* = 33.1, 3.1 Hz), 132.58, 132.47, 126.03 – 125.57 (m), 123.21 (d, *J* = 272.4 Hz), 92.83 (d, *J* = 17.1 Hz), 50.90; ³¹P NMR (162 MHz, CDCl₃) δ (ppm) 28.90 (d, *J* = 6.1 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) -63.46; HRMS (ESI) (*m/z*): calcd for C₁₆H₁₄F₂NO₃P [M+H]⁺: 438.0694, found: 438.0691.

Methyl 3-amino-3-(bis(3,5-dimethylphenyl)phosphoryl) acrylate (8). The title compound was prepared according to the general procedure and purified by column chromatography to give white



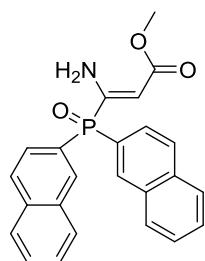
solid (82.4 mg), 77% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.35 (s, 2H), 7.31 (s, 2H), 7.21 (s, 2H), 6.57 (s, 2H), 4.77 (d, *J* = 13.4 Hz, 1H), 3.67 (s, 3H), 2.35 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 169.16 (d, *J* = 20.7 Hz), 154.98, 154.01, 138.56, 138.43, 134.60, 134.57, 134.22, 134.19, 129.53, 129.43, 128.18, 128.07, 91.86 (d, *J* = 16.4 Hz), 50.66, 21.27, 21.19. ³¹P NMR (162 MHz, CDCl₃) δ (ppm) 28.87.; HRMS (ESI) (*m/z*): calcd for C₂₀H₂₄NO₃P [M+H]⁺: 358.1572, found: 358.1576.

(Methyl 3-amino-3-(di([1,1'-biphenyl]-4-yl)phosphoryl) acrylate (9). The title compound was prepared according to the general procedure and purified by column chromatography to give white



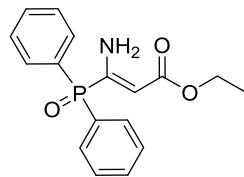
solid (103.2 mg), 76% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 2:1). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.85 (dd, *J* = 12.1, 8.1 Hz, 4H), 7.72 (dd, *J* = 8.3, 2.8 Hz, 4H), 7.61 (d, *J* = 7.6 Hz, 4H), 7.47 (t, *J* = 7.5 Hz, 4H), 7.40 (t, *J* = 7.1 Hz, 2H), 7.18 (s, 1H), 4.84 (d, *J* = 13.6 Hz, 1H), 3.67 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 169.09 (d, *J* = 21.2 Hz), 154.76, 153.78, 145.67 (d, *J* = 2.9 Hz), 139.60, 132.69, 132.58, 129.04, 128.41, 127.53, 127.40, 127.30, 91.98 (d, *J* = 16.7 Hz), 50.77; ³¹P NMR (162 MHz, CDCl₃) δ (ppm) 28.03.; HRMS (ESI) (*m/z*): calcd for C₂₈H₂₄NO₃P [M+H]⁺: 454.1572, found: 454.1568.

(Methyl 3-amino-3-(di(naphthalen-2-yl)phosphoryl)acrylate (10). The title compound was prepared according to the general procedure and purified by column chromatography to give white



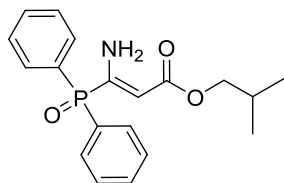
solid (107.1 mg), 89% yield (Z:E = 1:1.1) (petroleum ether/ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.36 (d, *J* = 14.1 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 7.9 Hz, 4H), 7.74 (t, *J* = 9.3 Hz, 2H), 7.56 (dt, *J* = 24.4, 7.1 Hz, 4H), 7.07 (s, 2H), 4.86 (d, *J* = 12.9 Hz, 1H), 3.63 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 169.10 (d, *J* = 21.0 Hz), 154.62, 153.64, 135.13 (d, *J* = 1.9 Hz), 134.44 (d, *J* = 9.8 Hz), 132.38 (d, *J* = 13.9 Hz), 129.05, 128.89 – 128.64 (m), 127.92, 127.22, 126.96, 126.41 (d, *J* = 10.8 Hz), 125.90, 92.33 (d, *J* = 16.4 Hz), 50.75. ³¹P NMR (162 MHz, CDCl₃) δ (ppm) 28.66.; HRMS (ESI) (*m/z*): calcd for C₂₄H₂₀NO₃P [M+H]⁺: 402.1259, found: 402.1260.

(Ethyl 3-amino-3-(diphenylphosphoryl)acrylate (12). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid



(87.9 mg), 93% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 1:1). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.73 (t, *J* = 9.0 Hz, 4H), 7.59 (t, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 5.3 Hz, 4H), 7.09 – 6.53 (m, 1H), 4.72 (d, *J* = 16.4 Hz, 1H), 4.11 (d, *J* = 4.3 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 168.75 (d, *J* = 21.0 Hz), 154.27, 153.30, 132.83 (d, *J* = 2.8 Hz), 132.12, 132.02, 129.88, 128.83, 128.71, 92.53 (d, *J* = 16.4 Hz), 59.50, 14.32; ³¹P NMR (162 MHz, CDCl₃) δ (ppm) 28.17.; HRMS (ESI) (*m/z*): calcd for C₁₇H₁₈NO₃P₃ [M+H]⁺: 316.1103, found: 316.1105.

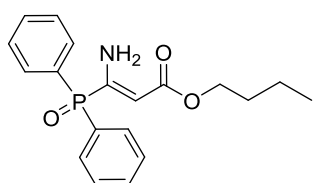
(Ethyl 3-amino-3-(diphenylphosphoryl)acrylate) (13). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (87.5mg), 85% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 2:1).



^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.74 (dd, $J = 12.1, 7.6$ Hz, 4H), 7.59 (t, $J = 7.4$ Hz, 2H), 7.49 (t, $J = 7.3$ Hz, 4H), 7.25 (s, 2H), 4.78 (d, $J = 13.3$ Hz, 1H), 3.84 (d, $J = 6.7$ Hz, 2H), 1.92 – 1.84 (m, 1H), 0.89 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm)

168.89 (d, $J = 20.6$ Hz), 154.25, 153.27, 132.82 (d, $J = 2.1$ Hz), 132.08 (d, $J = 10.1$ Hz), 129.97, 128.84, 128.71, 92.61 (d, $J = 16.1$ Hz), 69.78, 27.75, 19.16. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 28.04.; HRMS (ESI) (m/z): calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 343.1337, found: 343.1340.

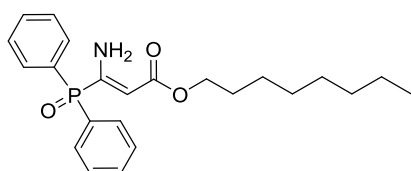
(Butyl 3-amino-3-(diphenylphosphoryl)acrylate) (14). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (84.3mg), 82% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 1:1).



^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.73 (t, $J = 9.0$ Hz, 4H), 7.58 (t, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 7.4$ Hz, 4H), 6.72 (d, $J = 62.3$ Hz, 2H), 4.74 (d, $J = 15.0$ Hz, 1H), 4.04 (td, $J = 6.8, 2.1$ Hz, 2H), 1.65 – 1.49 (m, 2H), 1.33 (h, $J = 7.3$ Hz, 2H), 0.89 (td, $J = 7.4, 2.2$

Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 168.87 (d, $J = 20.9$ Hz), 154.26, 153.28, 132.79 (d, $J = 2.3$ Hz), 132.12, 132.02, 128.81, 128.69, 92.53 (d, $J = 16.3$ Hz), 63.44, 30.79, 19.12, 13.70. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 28.02.; HRMS (ESI) (m/z): calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 344.1416, found: 344.1413.

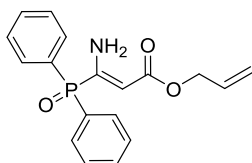
(Octyl 3-amino-3-(diphenylphosphoryl)acrylate) (15). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (83.7mg), 70% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 1:1).



^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.74 (dd, $J = 12.7, 7.5$ Hz, 4H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 4H), 6.76 (s, 1H), 4.74 (d, $J = 13.9$ Hz, 1H), 4.04 (t, $J = 6.9$ Hz, 2H), 1.58 (t, $J = 7.0$ Hz, 2H), 1.24 (s, 12H), 0.90 – 0.81 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 168.87 (d, $J = 21.0$ Hz), 154.23,

153.25, 132.80 (d, $J = 3.0$ Hz), 132.13, 132.03, 129.96, 128.90, 128.82, 128.69, 92.57 (d, $J = 16.3$ Hz), 63.79, 31.73, 29.20, 29.12, 28.73, 25.92, 22.59, 14.05. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 28.03 (d, $J = 14.8$ Hz).; HRMS (ESI) (m/z): calcd for $\text{C}_{23}\text{H}_{30}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 400.2042, found: 400.2040.

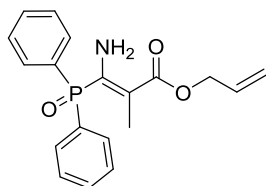
(Allyl 3-amino-3-(diphenylphosphoryl)acrylate) (16). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (81.4mg), 83% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 1:1).



^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.77 – 7.70 (m, 4H), 7.61 – 7.56 (m, 2H), 7.49 (td, $J = 7.6, 3.2$ Hz, 4H), 6.94 (s, 1H), 5.96 – 5.81 (m, 1H), 5.31 – 5.15 (m, 2H), 4.75 (d, $J = 13.5$ Hz, 1H), 4.56 (d, $J = 5.8$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 168.31 (d, $J = 20.9$

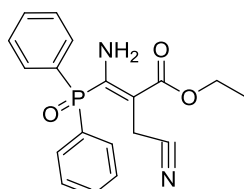
(Hz), 154.78, 153.81, 132.86 (d, $J = 2.6$ Hz), 132.58, 132.07 (d, $J = 10.2$ Hz), 129.82, 128.78 (d, $J = 12.5$ Hz), 118.17, 91.94 (d, $J = 16.4$ Hz), 64.34. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 28.08.; HRMS (ESI) (m/z): calcd for $\text{C}_{18}\text{H}_{18}\text{NO}_3\text{P}$ [$\text{M}+\text{H}$] $^+$: 328.1103, found: 328.1107.

(Ethyl 3-amino-3-(diphenylphosphoryl)-2-methylacrylate) (17). The title compound was prepared according to the general procedure and purified by column chromatography to give white



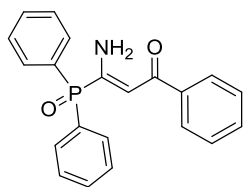
solid (49.3 mg), 52% yield ($Z:E = 1:1.1$) (petroleum ether/ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.76 (dd, $J = 12.3, 7.0$ Hz, 4H), 7.62 – 7.55 (m, 2H), 7.53 – 7.46 (m, 4H), 6.91 – 6.60 (m, 2H), 4.16 (q, $J = 7.1$ Hz, 2H), 1.67 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 170.34 (d, $J = 19.2$ Hz), 149.12, 148.14, 132.62 (d, $J = 2.9$ Hz), 131.91, 131.81, 130.55, 129.51, 128.98, 128.85, 99.19 (d, $J = 13.5$ Hz), 59.83, 14.64 (d, $J = 5.6$ Hz), 14.35. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 29.37.; HRMS (ESI) (m/z): calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_3\text{P}$ [$\text{M}+\text{H}$] $^+$: 330.1259, found: 330.1260.

(Ethyl 3-amino-2-(cyanomethyl)-3-(diphenylphosphoryl) acrylate) (18). The title compound was prepared according to the general procedure and purified by column chromatography to give



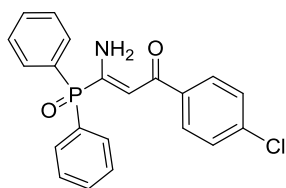
white solid (74.3 mg), 70% yield ($Z:E = 1:1$) (petroleum ether/ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.77 (dd, $J = 12.5, 7.1$ Hz, 4H), 7.69 – 7.62 (m, 2H), 7.56 (td, $J = 7.5, 3.0$ Hz, 4H), 6.70 (s, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 3.61 (s, 2H), 1.30 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 168.46 (d, $J = 16.8$ Hz), 153.41, 152.49, 133.53 (d, $J = 2.9$ Hz), 131.93, 131.83, 129.45, 129.33, 128.87, 127.83, 118.00 (d, $J = 1.6$ Hz), 94.14 (d, $J = 10.9$ Hz), 60.68, 16.71 (d, $J = 5.2$ Hz), 14.22. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 29.92.; HRMS (ESI) (m/z): calcd for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_3\text{P}$ [$\text{M}+\text{H}$] $^+$: 355.1212, found: 355.1215.

(Amino-3-(diphenylphosphoryl)-1-phenylprop-2-en-1-one) (19). The title compound was prepared according to the general procedure and purified by column chromatography to give white



solid (72.8 mg), 70% yield ($Z:E = 1:1$) (petroleum ether/ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 9.91 (s, 1H), 7.91 – 7.65 (m, 6H), 7.59 (d, $J = 6.8$ Hz, 2H), 7.50 (s, 4H), 7.41 (d, $J = 7.2$ Hz, 1H), 7.35 (d, $J = 7.7$ Hz, 2H), 6.39 (s, 1H), 5.95 (d, $J = 12.8$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 190.50 (d, $J = 14.6$ Hz), 156.28, 155.34, 139.15 (d, $J = 3.3$ Hz), 133.00 (d, $J = 2.9$ Hz), 132.11 (d, $J = 10.3$ Hz), 131.76, 129.92, 128.91 (d, $J = 12.5$ Hz), 128.41, 127.36, 97.48 (d, $J = 13.1$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 27.25; HRMS (ESI) (m/z): calcd for $\text{C}_{21}\text{H}_{18}\text{NO}_2\text{P}$ [$\text{M}+\text{H}$] $^+$: 348.1152, found: 348.1155.

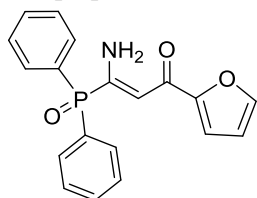
(3-Amino-1-(4-chlorophenyl)-3-(diphenylphosphoryl) prop-2-en-1-one) (20). The title



compound was prepared according to the general procedure and purified by column chromatography to give white solid (57.1mg), 50% yield ($Z:E = 1:1$) (petroleum ether/ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.79 (dd, $J = 12.8, 8.0$ Hz, 4H), 7.73 (d, $J = 7.1$ Hz, 2H), 7.66 – 7.58 (m, 2H), 7.54 – 7.50 (m, 3H), 7.44 (t, $J = 7.3$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H), 5.97 (d, $J = 12.9$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 190.48 (d, $J = 14.6$ Hz), 156.29, 155.35, 139.14 (d, $J = 3.3$ Hz), 133.02 (d,

$J = 2.9$ Hz), 132.10 (d, $J = 10.3$ Hz), 131.76, 129.86, 128.91 (d, $J = 12.6$ Hz), 128.41, 127.35, 97.48 (d, $J = 13.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 28.42.; HRMS (ESI) (m/z): calcd for $\text{C}_{21}\text{H}_{17}\text{ClNO}_2\text{P}$ $[\text{M}+\text{H}]^+$: 382.0764, found: 382.0762.

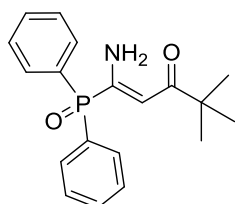
(3-Amino-3-(diphenylphosphoryl)-1-(furan-2-yl)prop-2-en-1-one) (21). The title compound was prepared according to the general procedure and purified by column chromatography to give



white solid (76.8 mg), 76% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 1:1). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm) 9.56 (s, 1H), 7.81 (s, 1H), 7.78 – 7.73 (m, 3H), 7.68 (d, $J = 5.7$ Hz, 3H), 7.60 (td, $J = 7.2$, 6.7, 2.2 Hz, 4H), 7.53 (td, $J = 7.2$, 2.2 Hz, 1H), 7.07 (d, $J = 3.5$ Hz, 1H), 6.60 (dd, $J = 3.5$, 1.7 Hz, 1H), 5.92 (d, $J = 12.2$ Hz, 1H). ^{13}C NMR (101

MHz, $\text{DMSO}-d_6$) δ (ppm) 178.61 (d, $J = 15.2$ Hz), 158.09, 157.17, 153.55 (d, $J = 4.0$ Hz), 146.65, 133.38 (d, $J = 2.7$ Hz), 132.89 (d, $J = 2.9$ Hz), 132.15 (d, $J = 10.1$ Hz), 130.76, 130.63 (d, $J = 3.1$ Hz), 129.46 (dd, $J = 12.3$, 3.9 Hz), 115.15, 112.92, 95.96 (d, $J = 13.4$ Hz). ^{31}P NMR (162 MHz, $\text{DMSO}-d_6$) δ (ppm) 27.98.; HRMS (ESI) (m/z): calcd for $\text{C}_{19}\text{H}_{16}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 338.0946, found: 338.0948.

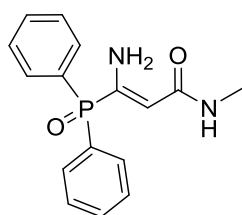
(1-Amino-1-(diphenylphosphoryl)-4,4-dimethylpent-1-en-3-one) (22). The title compound was prepared according to the general procedure and purified by column chromatography to give white



solid (80.4 mg), 82% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 9.32 (s, 1H), 7.75 – 7.67 (m, 4H), 7.58 (td, $J = 7.3$, 1.5 Hz, 2H), 7.47 (td, $J = 7.6$, 3.2 Hz, 4H), 6.02 (s, 1H), 5.44 (d, $J = 13.5$ Hz, 1H), 1.02 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 206.54 (d, $J = 13.1$ Hz), 154.12 (d, $J = 95.6$ Hz), 132.81 (d, $J = 2.9$ Hz), 132.05, 131.95, 130.11, 129.06, 128.80, 128.68, 97.20 (d, $J = 12.7$

Hz), 42.63, 27.05. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 27.36.; HRMS (ESI) (m/z): calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_2\text{P}$ $[\text{M}+\text{H}]^+$: 328.1466, found: 328.1461.

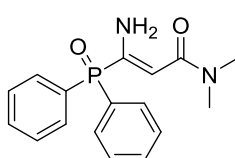
(3-Amino-3-(diphenylphosphoryl)-N-methylacrylamide) (23). The title compound was prepared according to the general procedure and purified by column chromatography to give white



solid (67.5 mg), 75% yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 1:20). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.23 (s, 2H), 7.94 (d, $J = 8.0$ Hz, 4H), 7.82 (t, $J = 8.0$ Hz, 4H), 7.48 (t, $J = 8.0$ Hz, 2H), 7.30-7.35 (m, 6H), 7.31 (d, $J = 8.0$ Hz, 6H), 2.39 (t, $J = 12.0$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 148.9, 144.0, 133.2 (t, $J = 4.0$ Hz), 132.7 (t, $J = 4.0$ Hz), 132.1, 132.0, 131.0, 130.0, 129.5, 128.5, 128.2 (t, $J = 6.1$ Hz), 127.9

(t, $J = 4.0$ Hz), 66.2 (t, $J = 60.1$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 34.09; HRMS (ESI) (m/z): calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 301.1106, found: 301.1108.

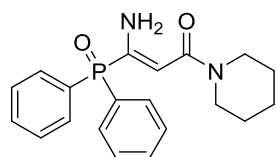
(3-Amino-3-(diphenylphosphoryl)-N,N-dimethylacrylamide) (24). The title compound was prepared according to the general procedure and purified by column chromatography to give white



solid (74.2 mg), 79 % yield (Z:E = 1:1) (petroleum ether/ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.70 (t, $J = 11.1$ Hz, 4H), 7.53 (t, $J = 7.7$ Hz, 2H), 7.43 (t, $J = 7.7$ Hz, 4H), 6.57 (s, 2H), 5.18 (d, $J = 14.6$ Hz, 1H), 2.83 (d, $J = 31.8$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm)

168.94, 151.06 (d, $J = 101.0$ Hz), 132.61, 132.06, 131.97, 130.42, 129.38, 128.75, 128.63, 92.86 (d, $J = 15.9$ Hz), 37.25, 34.92. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 27.94. HRMS (ESI) (m/z): calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 315.1262, found: 315.1267.

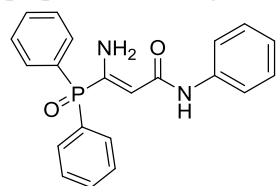
(3-Amino-3-(diphenylphosphoryl)-1-(piperidin-1-yl)prop-2-en-1-one) (25). The title compound was prepared according to the general procedure and purified by column



chromatography to give white solid (80.7 mg), 76% yield ($\text{Z}:\text{E} = 1:1$) (petroleum ether/ethyl acetate = 1:1). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.70 (t, $J = 9.9$ Hz, 4H), 7.51 (d, $J = 7.5$ Hz, 2H), 7.45 – 7.41 (m, 4H), 6.90 (s, 2H), 5.30 (d, $J = 14.2$ Hz, 1H), 3.49 (d, $J = 5.7$ Hz, 2H), 3.44 (s, 3H), 3.30 (t, $J = 5.2$ Hz, 2H), 1.43 (s, 3H) ^{13}C NMR (101 MHz,

CDCl_3) δ (ppm) 159.81, 151.06 (d, $J = 101.8$ Hz), 132.62, 131.97 (d, $J = 9.7$ Hz), 130.60 (d, $J = 11.4$ Hz), 128.91, 128.63, 114.23, 93.00, 47.45, 25.59 (d, $J = 84.4$ Hz), 24.90, 24.26 (d, $J = 47.7$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 29.72. HRMS (ESI) (m/z): calcd for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 355.1575, found: 355.1577.

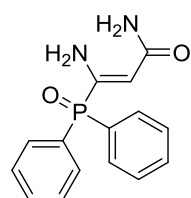
(3-Amino-3-(diphenylphosphoryl)-N-phenylacrylamide) (26). The title compound was prepared according to the general procedure and purified by column chromatography to give white



solid (73.8 mg), 68% yield ($\text{Z}:\text{E} = 1:1$) (petroleum ether/ethyl acetate = 1:1). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm) 9.81 (s, 1H), 7.78 – 7.67 (m, 6H), 7.61 (td, $J = 7.3, 3.0$ Hz, 6H), 7.26 (t, $J = 7.9$ Hz, 2H), 6.97 (d, $J = 7.3$ Hz, 1H), 5.32 (d, $J = 13.7$ Hz, 1H). ^{13}C NMR (101 MHz,

$\text{DMSO}-d_6$) δ (ppm) 167.67 (d, $J = 18.5$ Hz), 152.77, 151.78, 140.13, 133.10 (d, $J = 2.9$ Hz), 132.92 (d, $J = 2.8$ Hz), 132.14 (d, $J = 9.9$ Hz), 131.30, 130.78, 130.67, 130.28, 129.43, 129.31, 129.11, 122.96, 119.19, 95.87 (d, $J = 14.3$ Hz). ^{31}P NMR (162 MHz, $\text{DMSO}-d_6$) δ (ppm) 23.79.; HRMS (ESI) (m/z): calcd for $\text{C}_{19}\text{H}_{12}\text{N}_2\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 363.1262, found: 363.1264.

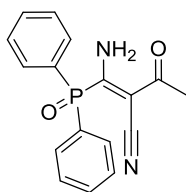
(3-Amino-3-(diphenylphosphoryl)acrylamide) (27). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (60.0 mg),



70% yield ($\text{Z}:\text{E} = 1:1$) (petroleum ether/ethyl acetate = 1:1). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm) 7.72 (dd, $J = 12.4, 7.3$ Hz, 4H), 7.57 (d, $J = 7.7$ Hz, 2H), 7.48 (td, $J = 7.7, 2.9$ Hz, 4H), 6.76 (d, $J = 17.6$ Hz, 2H), 5.29 (s, 2H), 4.88 (d, $J = 13.8$ Hz, 1H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ (ppm) 171.11 (d, $J = 18.1$ Hz), 151.47, 150.47, 133.06 (d, $J = 2.7$ Hz), 132.05, 131.95, 131.15, 130.13, 129.30 (d, $J = 11.9$ Hz), 95.78 (d, $J = 14.3$ Hz). ^{31}P NMR (162 MHz,

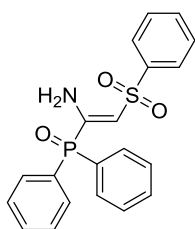
$\text{DMSO}-d_6$) δ (ppm) 30.64.; HRMS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 287.0949, found: 287.0951.

(2-(Amino(diphenylphosphoryl)methylene)-3-oxobutanenitrile) (28). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (49.2 mg), 53% yield ($\text{Z}:\text{E} = 1:1$) (petroleum ether/ethyl acetate = 1:10). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 11.32 (d, $J = 29.4$ Hz, 1H), 7.91 (dd, $J = 12.4, 7.8$ Hz, 4H), 7.70 (t, $J = 7.5$



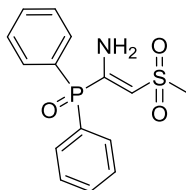
Hz, 2H), 7.59 (td, $J = 7.8, 7.1, 2.9$ Hz, 4H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 164.43, 133.89 (d, $J = 2.8$ Hz), 132.81, 132.70, 129.18, 129.04, 127.06, 125.98, 29.68, 28.77 (d, $J = 2.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 24.60.; HRMS (ESI) (m/z): calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 311.0949, found: 311.0947.

(1-Amino-2-(phenylsulfonyl)vinyl)diphenylphosphine oxide (29). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (73.5 mg), 64% yield ($Z:E = 1:1$) (petroleum ether/ethyl acetate = 2:1).



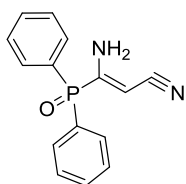
^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.82 (d, $J = 8.1$ Hz, 2H), 7.61 (d, $J = 8.1$ Hz, 3H), 7.58 – 7.54 (m, 4H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.42 (td, $J = 8.0, 3.2$ Hz, 4H), 6.50 (s, 2H), 4.95 (d, $J = 13.8$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 150.14 (d, $J = 91.2$ Hz), 143.16, 133.18 (d, $J = 2.8$ Hz), 132.96, 132.02, 131.92, 129.11, 128.98, 128.85, 127.91, 126.03, 100.03, 99.88. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 28.71.; HRMS (ESI) (m/z): calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_3\text{PS}$ $[\text{M}+\text{H}]^+$: 384.0823, found: 384.0825.

(1-Amino-2-(methylsulfonyl)vinyl)diphenylphosphine oxide (30). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (74.1 mg), 77% yield ($Z:E = 1:1$) (petroleum ether/ethyl acetate = 2:1).



^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.71 (dd, $J = 12.3, 7.7$ Hz, 4H), 7.60 (d, $J = 7.7$ Hz, 2H), 7.50 (td, $J = 7.7, 3.0$ Hz, 4H), 6.49 – 6.27 (m, 2H), 4.94 (d, $J = 13.8$ Hz, 1H), 2.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 151.31, 150.40, 133.31, 133.28, 132.05, 131.94, 129.08, 128.96, 99.00, 98.84, 44.25, 44.24. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 28.63; HRMS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_3\text{PS}$ $[\text{M}+\text{H}]^+$: 322.0667, found: 322.0664.

(3-Amino-3-(diphenylphosphoryl)acrylonitrile (31). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (48.2 mg), 60% yield ($Z:E = 1:1$) (petroleum ether/ethyl acetate = 2:1).



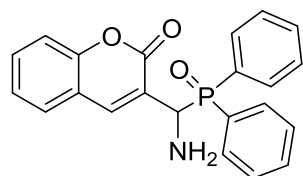
^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.71 (t, $J = 10.0$ Hz, 4H), 7.63 (d, $J = 7.4$ Hz, 2H), 7.53 (d, $J = 7.7$ Hz, 4H), 5.49 (d, $J = 13.0$ Hz, 2H), 4.13 (d, $J = 11.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 133.30 (d, $J = 3.0$ Hz), 132.02, 131.91, 129.08, 128.95, 73.43, 73.21. ^{31}P NMR (162 MHz, CDCl_3) δ (ppm) 27.93.; HRMS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{OP}$ $[\text{M}+\text{H}]^+$: 269.0844, found: 269.0848.

(Diethyl (2-amino-2-(diphenylphosphoryl)vinyl)phosphonate (32). The title compound was prepared according to the general procedure and purified by column chromatography to give white solid (77.3 mg), 68% yield ($Z:E = 1:1$) (petroleum ether/ethyl acetate = 2:1).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.71 (dd, $J = 12.3, 7.6$ Hz, 4H), 7.55 (t, $J = 7.5$ Hz, 2H), 7.46 (d, $J = 7.6$ Hz, 4H), 6.16 (d, $J = 17.6$ Hz, 2H), 4.20 (dd, $J = 17.6, 12.5$ Hz, 1H), 3.95 (h, $J = 9.4$ Hz, 4H), 1.21 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 155.82 (d, $J = 95.9$ Hz), 132.77 (d, $J = 2.8$ Hz), 131.95 (d, $J = 10.1$ Hz), 129.83, 128.72 (d, $J = 12.5$ Hz), 86.03 (d, $J = 13.4$ Hz), 84.22 (d, $J = 13.5$ Hz), 61.44 (d, $J = 5.0$ Hz), 29.59, 16.22 (d, $J = 6.4$ Hz); ^{31}P NMR (162 MHz) δ

(ppm) 28.74 (d, $J = 85.0$ Hz), 21.65 (d, $J = 69.5$ Hz). HRMS (ESI) (m/z): calcd for $C_{18}H_{23}NO_4P_2$ $[M+H]^+$: 380.1181, found: 380.1185.

(3-(Amino(diphenylphosphoryl)methylene)isochroman-1-one) (33). The title compound was prepared according to the general procedure and purified by column chromatography to give white



solid (54.0 mg), 48% yield ($Z:E = 1:1$) (petroleum ether/ethyl acetate = 2:1). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.91 (s, 1H), 7.79 (dd, $J = 12.4, 7.7$ Hz, 4H), 7.72 (d, $J = 7.6$ Hz, 2H), 7.64 (s, 2H), 7.56–7.49 (m, 4H), 7.44 (d, $J = 14.6$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 2H), 5.97 (d, $J = 12.9$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 190.52 (d, $J = 14.4$ Hz), 156.19, 155.26, 139.13 (d, $J = 3.5$ Hz),

133.02 (d, $J = 2.9$ Hz), 132.12 (d, $J = 10.3$ Hz), 131.77, 129.84, 128.98, 128.85, 128.40, 127.36, 97.52 (d, $J = 13.1$ Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) 27.48.; HRMS (ESI) (m/z): calcd for $C_{22}H_{18}NO_3P$ $[M+H]^+$: 376.3638, found: 376.3635.

7. X-Ray diffraction analysis of 3a

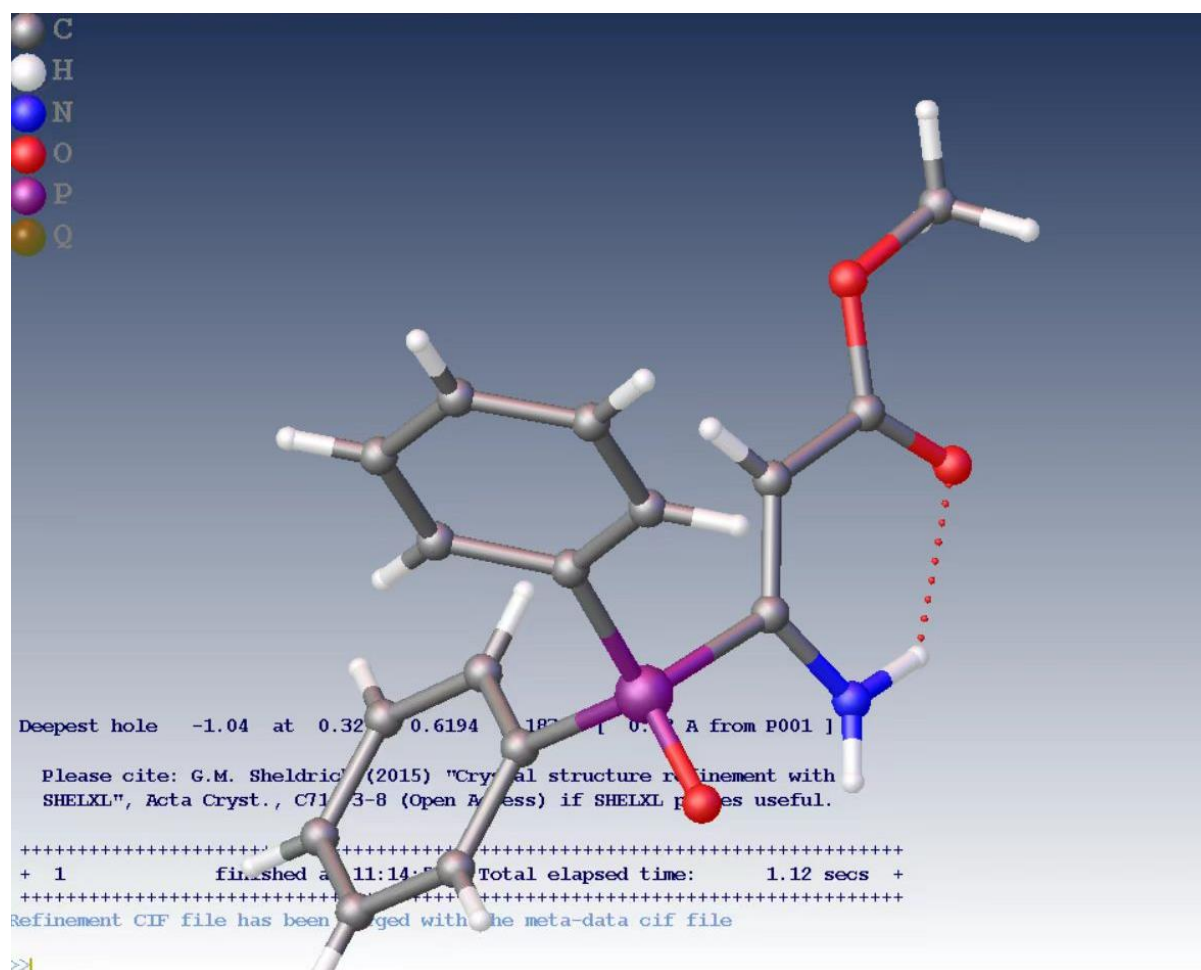


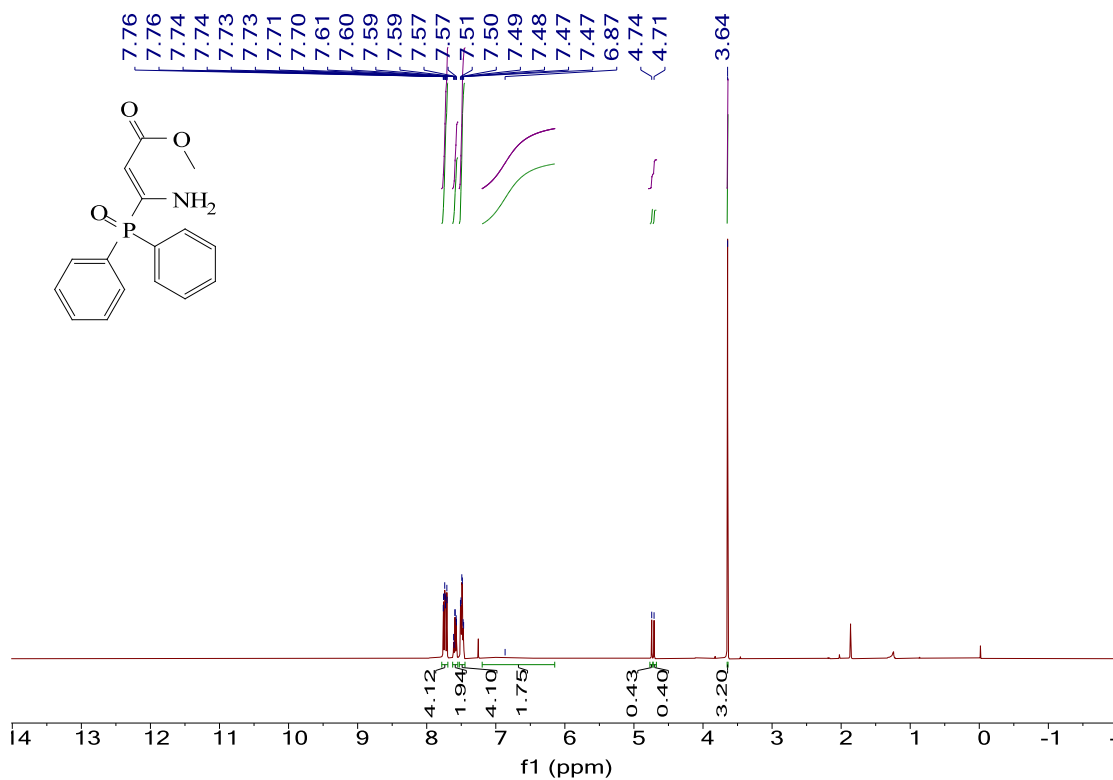
Figure S1. Structure of 3a

Formula	C ₁₆ H ₁₆ O ₃ NP
CCDC numbers	2286021
Formula Mass	301.09
Crystal system	monoclinic
Space group	C 2/c
a (Å)	22.033(2)
b (Å)	13.718(2)
c (Å)	10.1323(12)
α (°)	90
β (°)	97.804(3)
γ (°)	90
V (Å) ³	3034.0(7)
Z	40
Pcalc(g/cm ³)	1.620
F (000)	1480.0
Index ranges	-28 ≤ h ≤ 25, -11 ≤ k ≤ 17, -13 ≤ l ≤ 11
μ (Mo Kα, mm ⁻¹)	0.625
Reflections collected	9104
Independent reflections	3494 [R _{int} = 0.0255, R _{sigma} = 0.0330]
Data/restraints/parameters	3494/0/94
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0881, wR ₂ = 0.2345
Final R indexes [all data]	R ₁ = 0.1135, wR ₂ = 0.2628
Goodness-of-fit on F ²	1.037
Largest diff. peak/hole / e Å ⁻³	0.70/-1.04

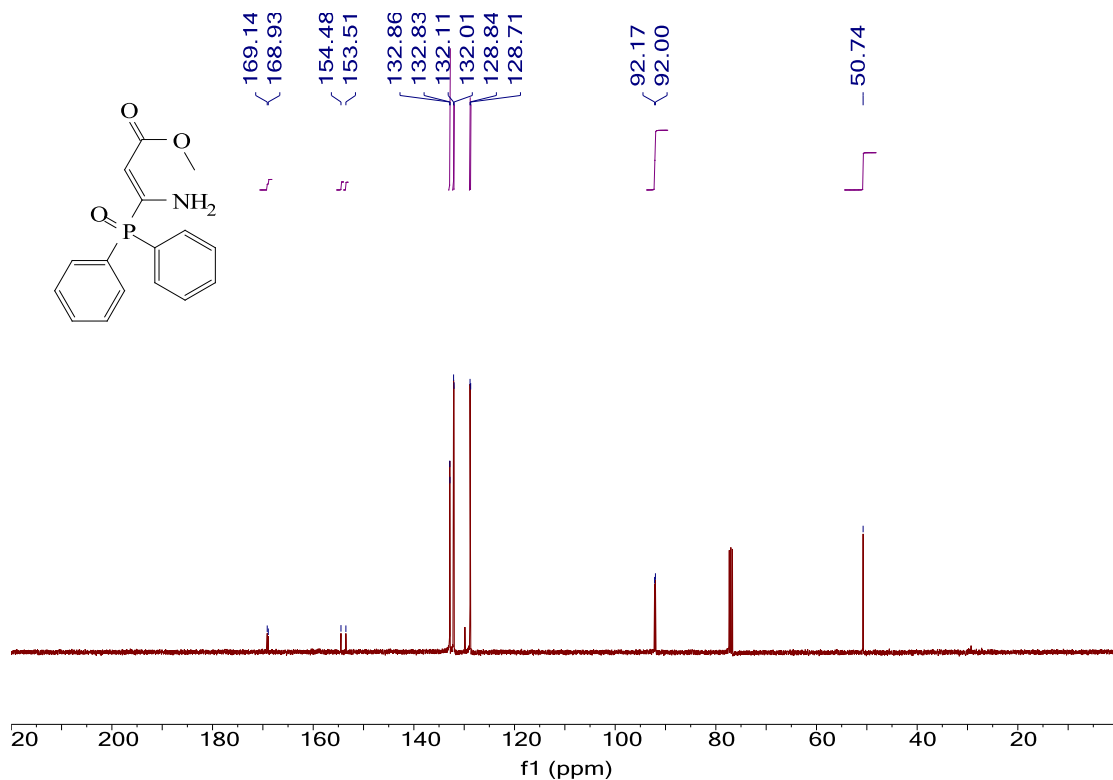
8. Copies of product ^1H NMR, ^{13}C NMR, ^{31}P NMR

Methyl -3-amino-3-(diphenylphosphoryl)acrylate (3)

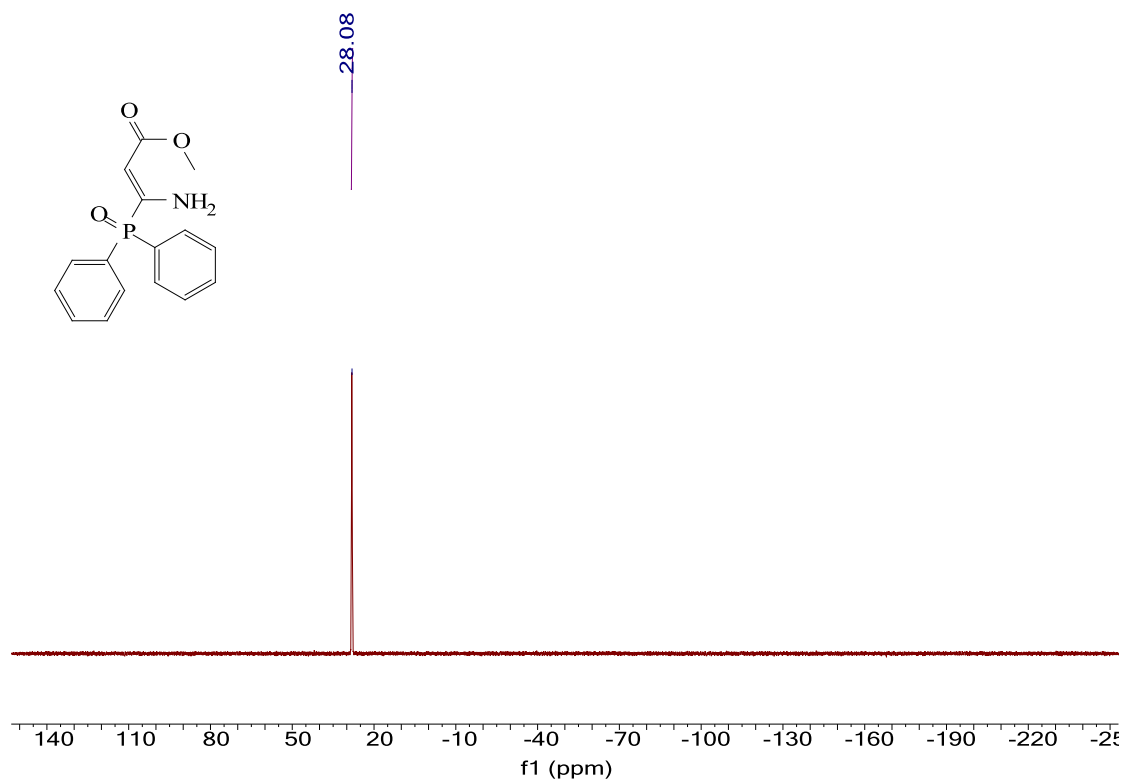
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (101 MHz, CDCl_3)

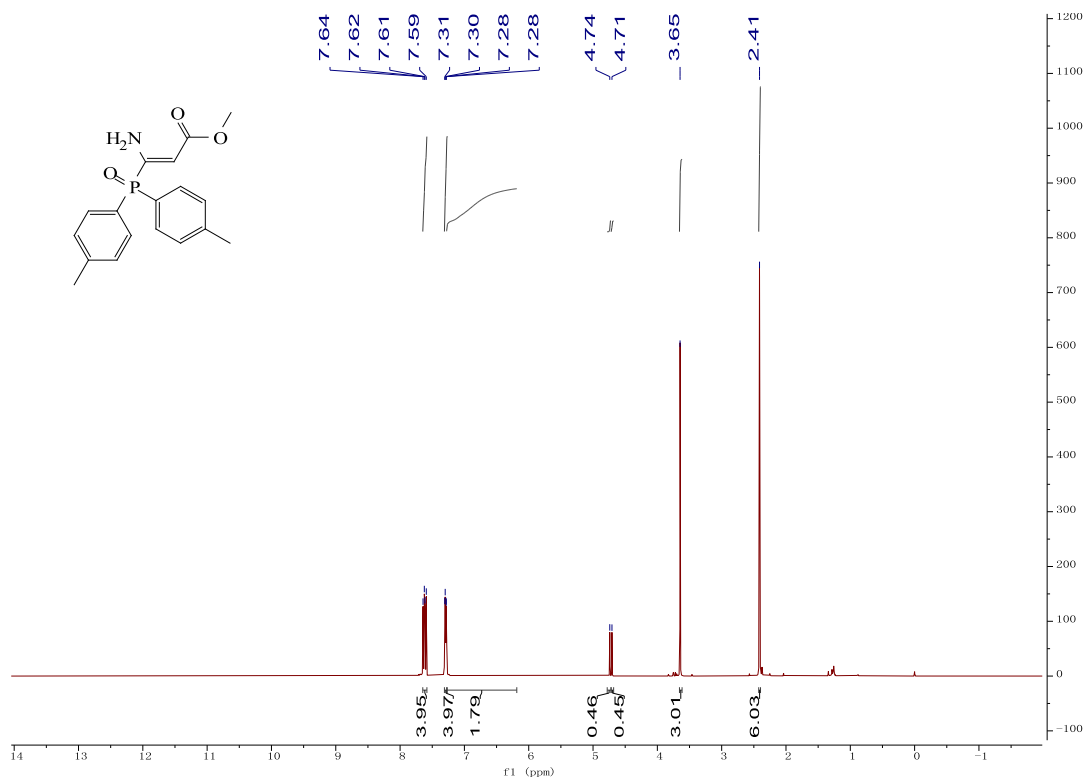


^{31}P NMR (162 MHz, CDCl_3)

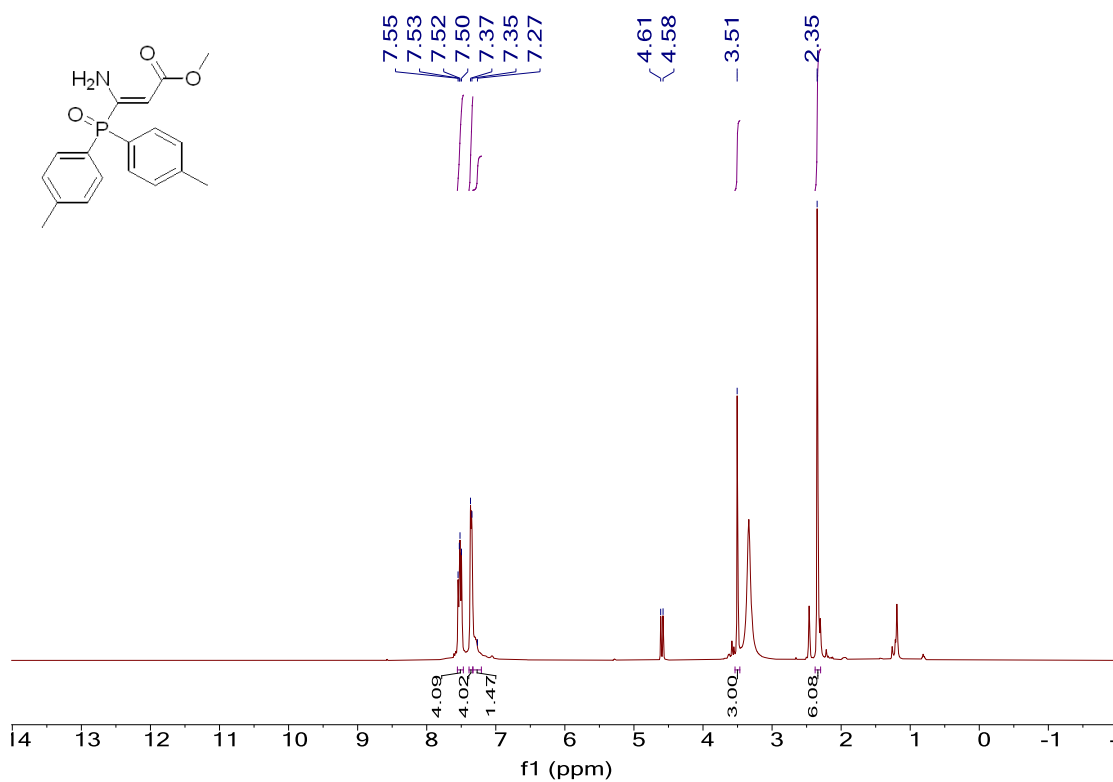


Methyl 3-amino-3-(di-p-tolylphosphoryl)acrylate (4)

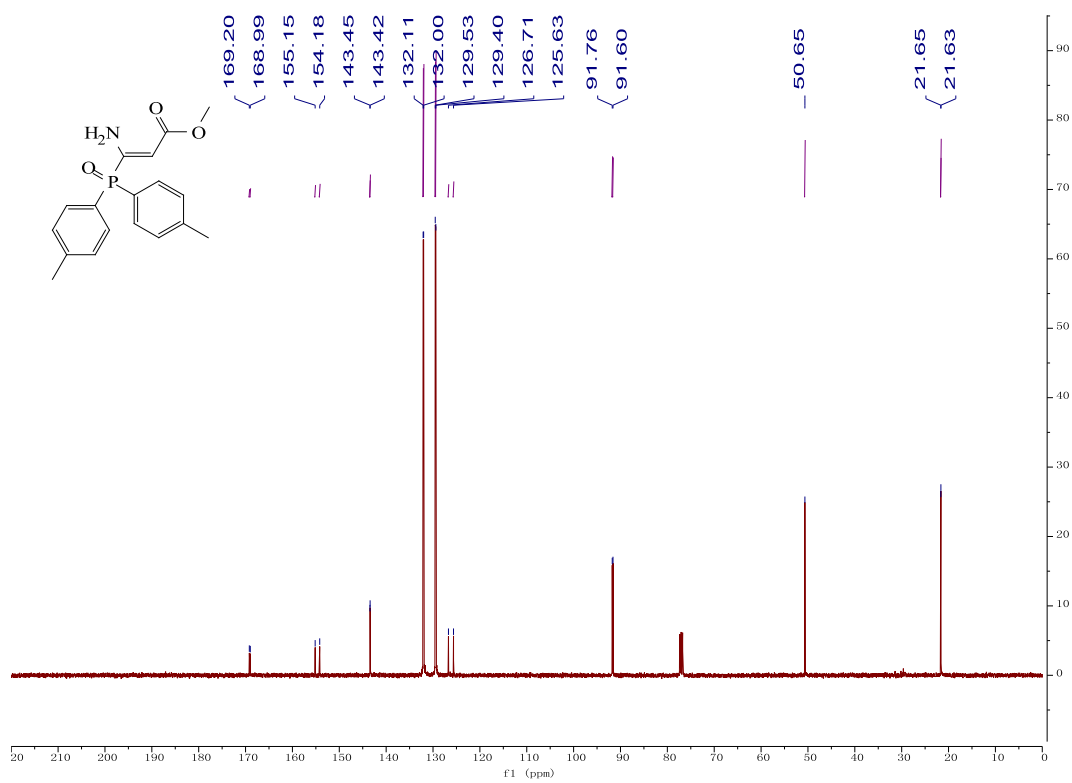
^1H NMR (400 MHz, CDCl_3)



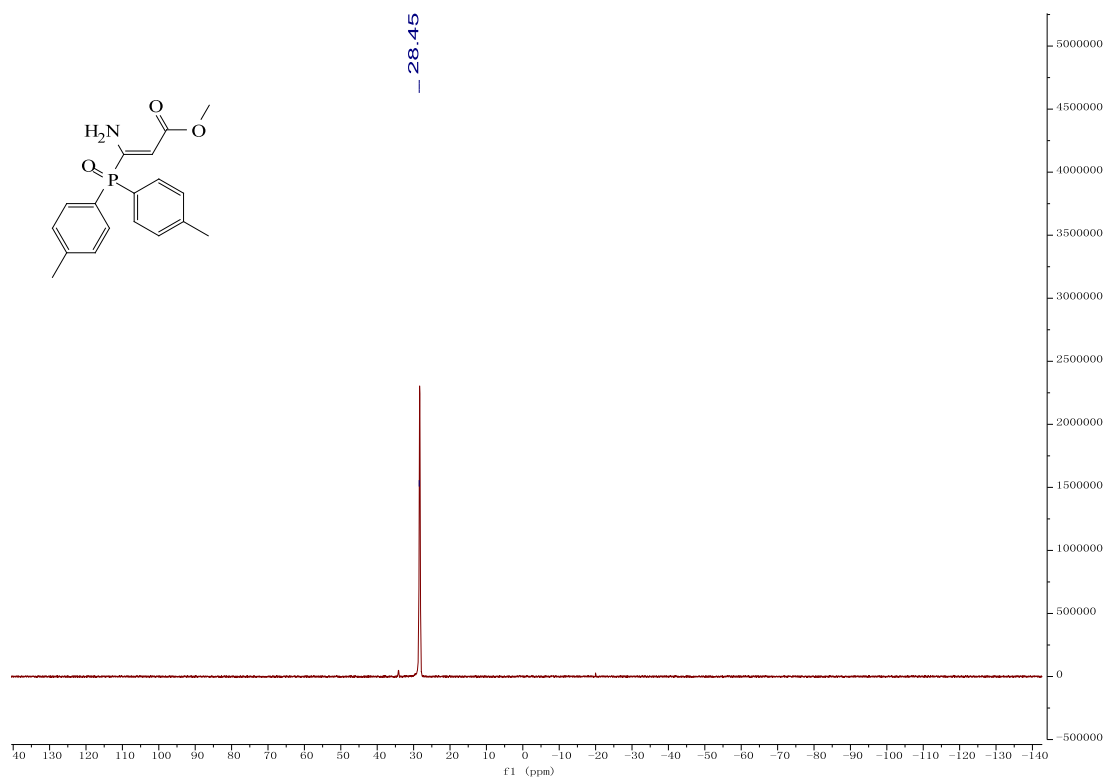
^1H NMR (400 MHz, $\text{DMSO-}d_6$)



^{13}C NMR (101 MHz, CDCl_3)

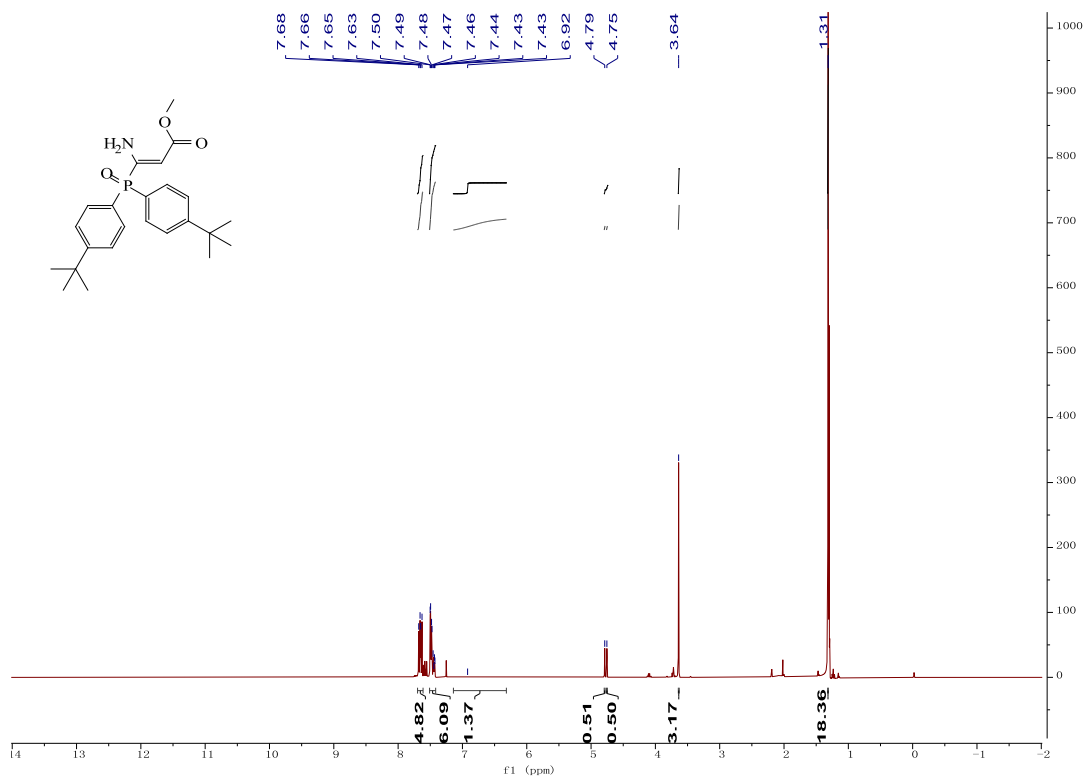


^{31}P NMR (162 MHz, CDCl_3)

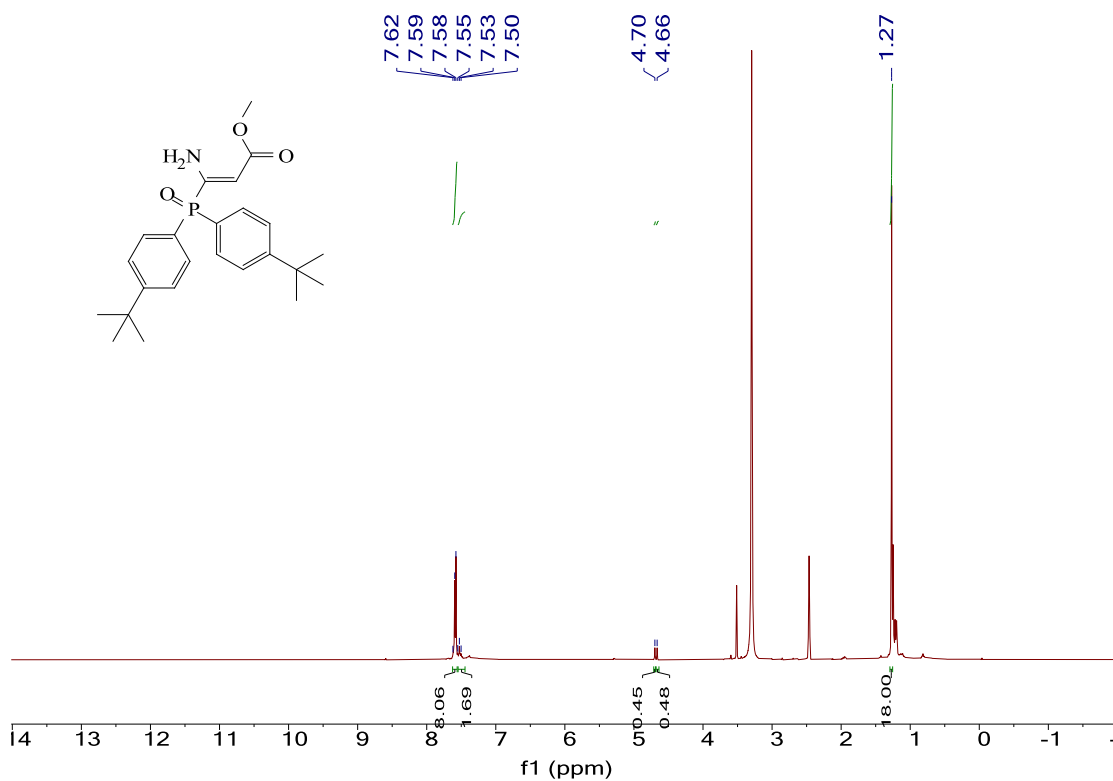


Methyl 3-amino-3-(bis(4-(tert-butyl)phenyl)phosphoryl)acrylate (5)

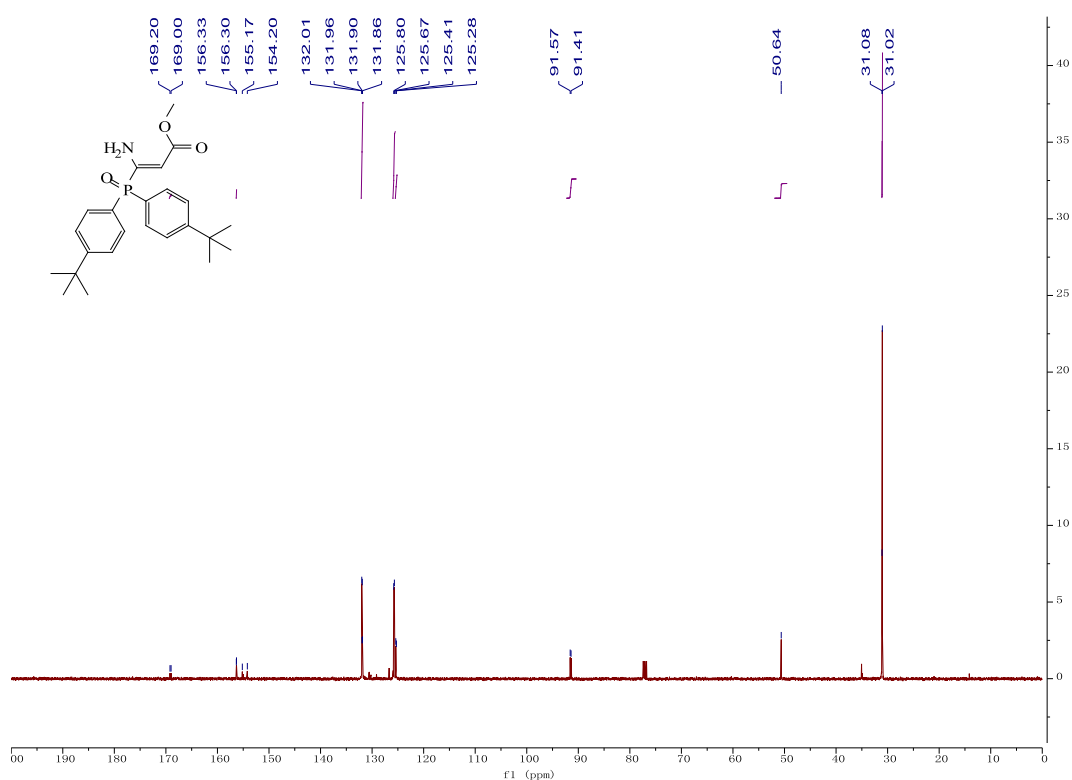
^1H NMR (400 MHz, CDCl_3)



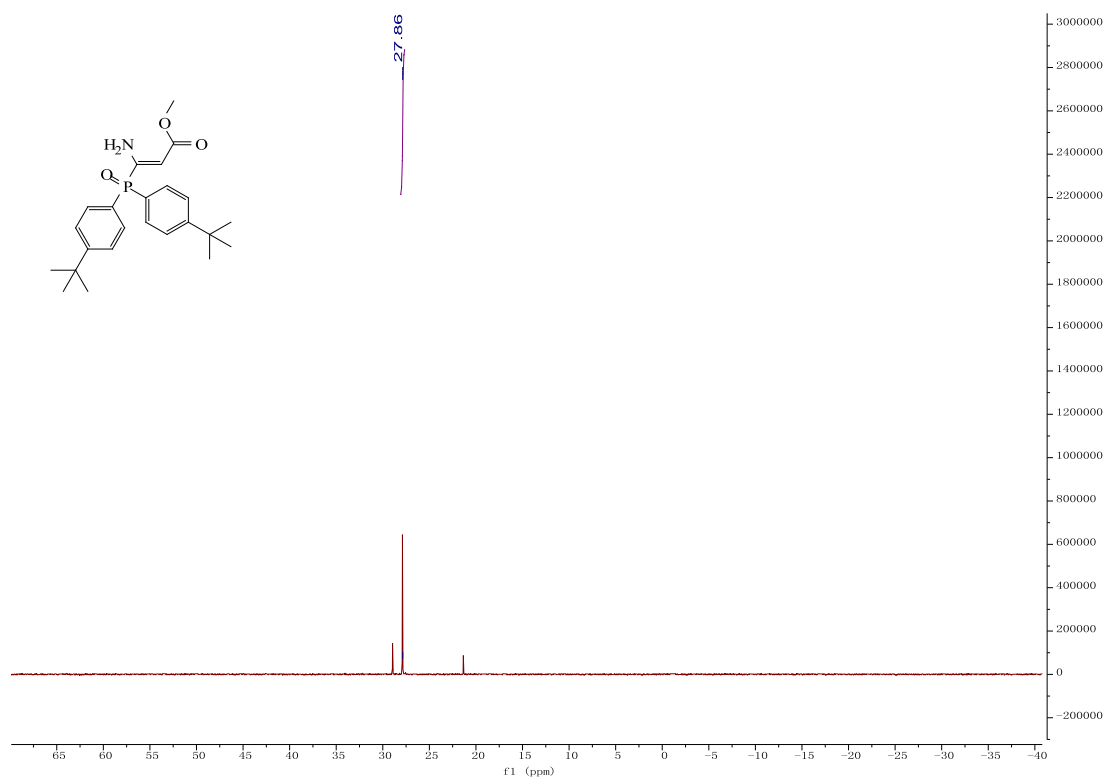
¹H NMR (400 MHz, DMSO-*d*₆)



¹³C NMR (101 MHz, CDCl₃)

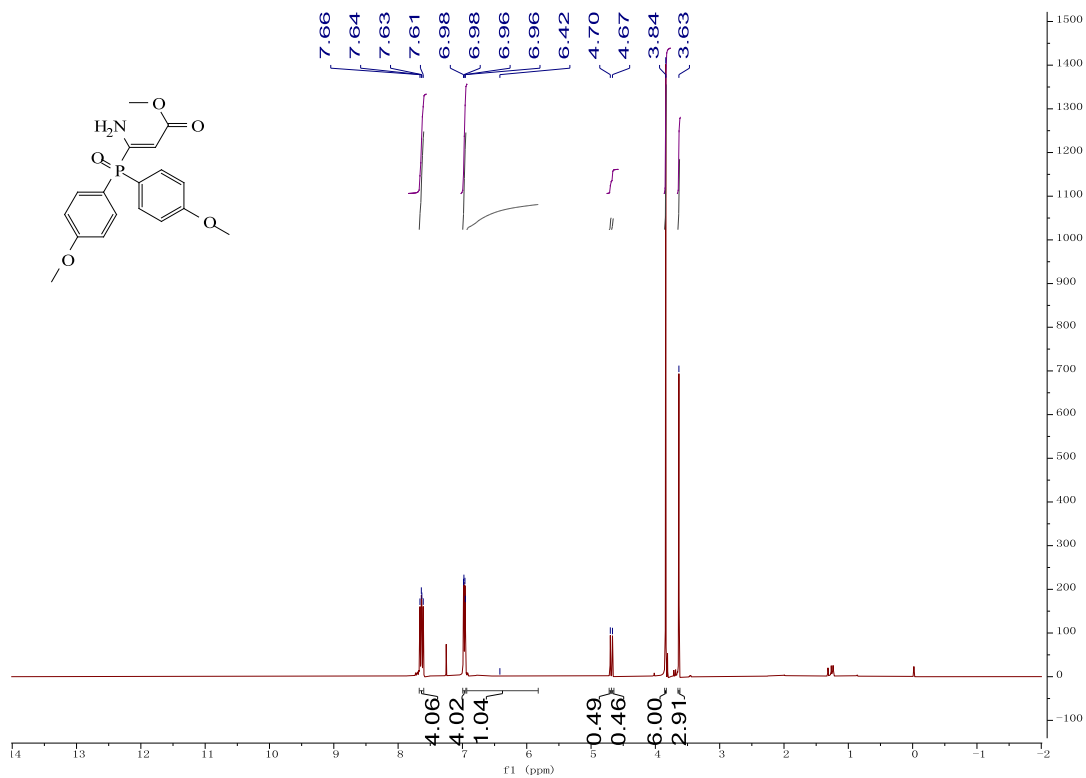


^{31}P NMR (162 MHz, CDCl_3)

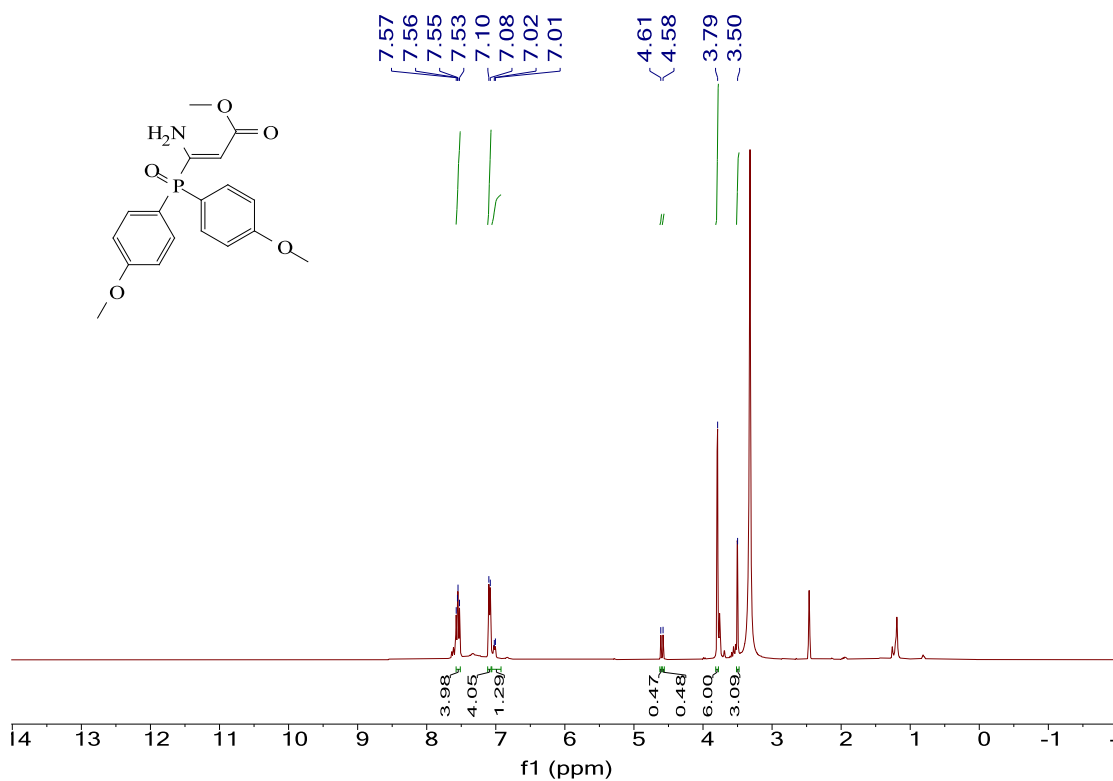


Methyl 3-amino-3-(bis(4-methoxyphenyl)phosphoryl)acrylate (6)

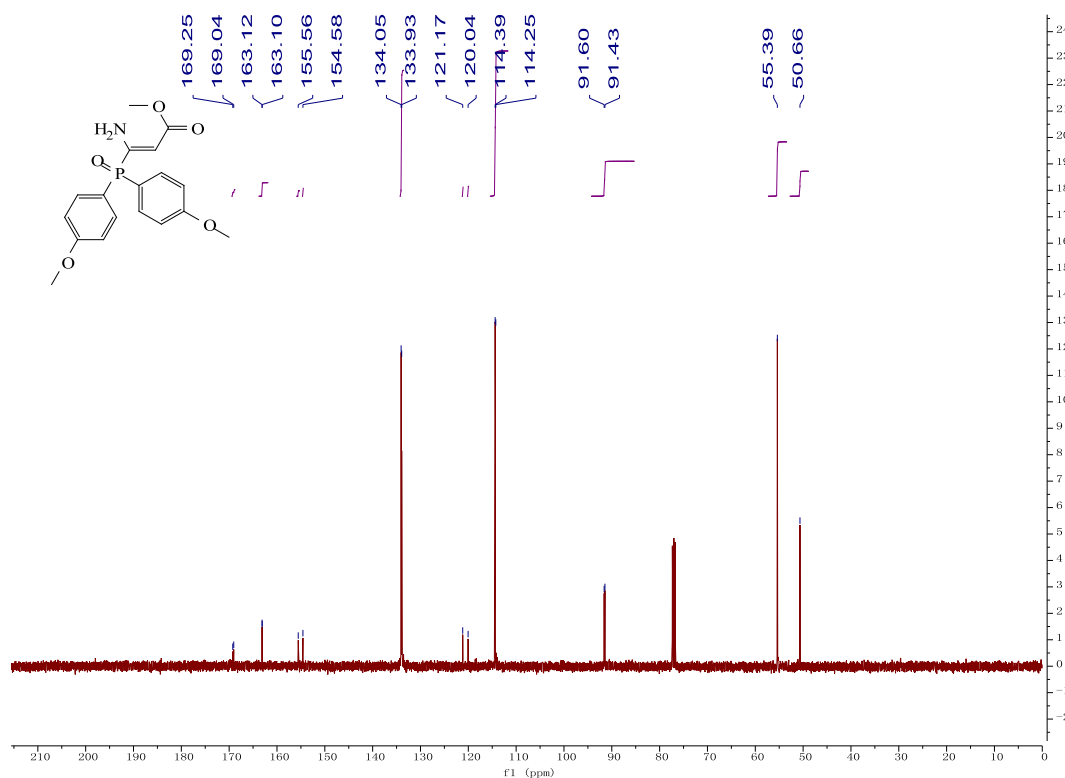
^1H NMR (400 MHz, CDCl_3)



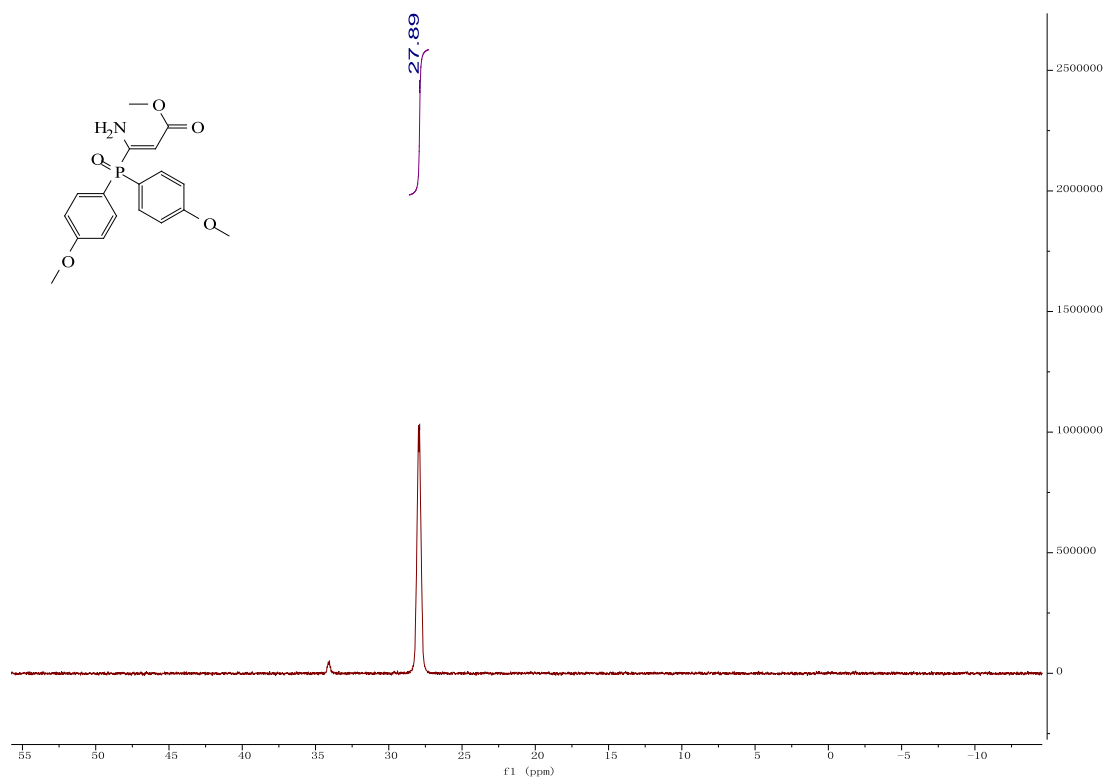
¹H NMR (400 MHz, DMSO-d₆)



¹³C NMR (101 MHz, CDCl₃)

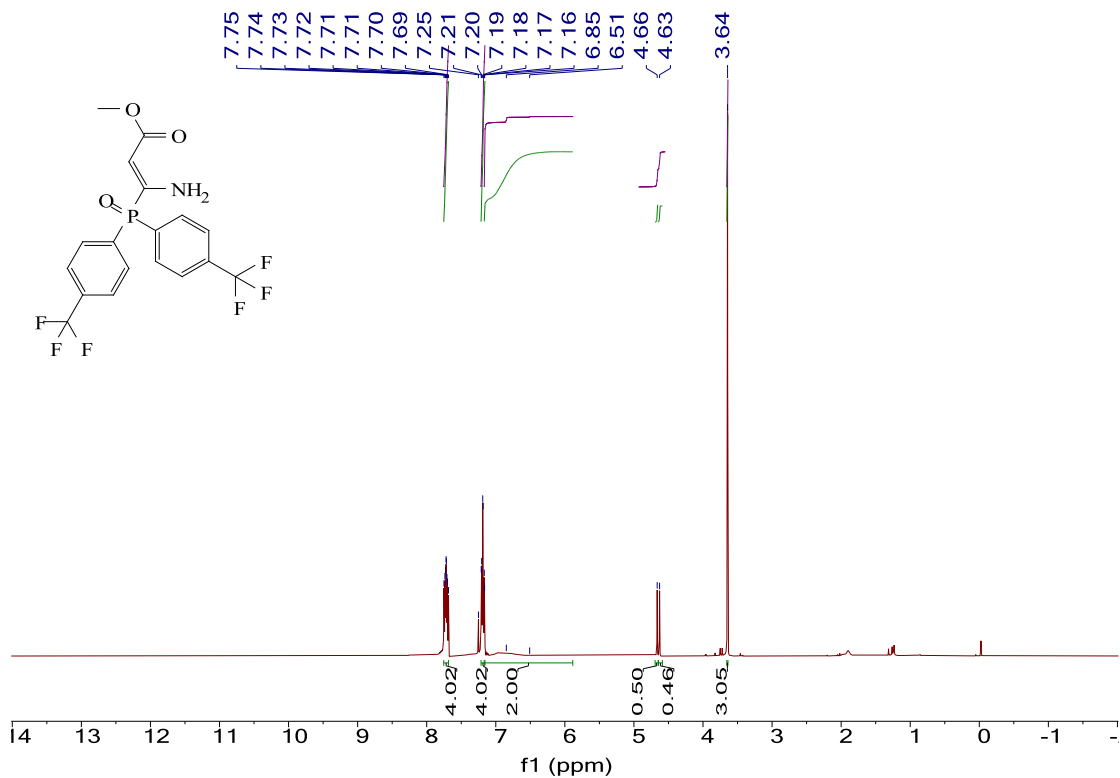


³¹P NMR (162 MHz, CDCl₃)

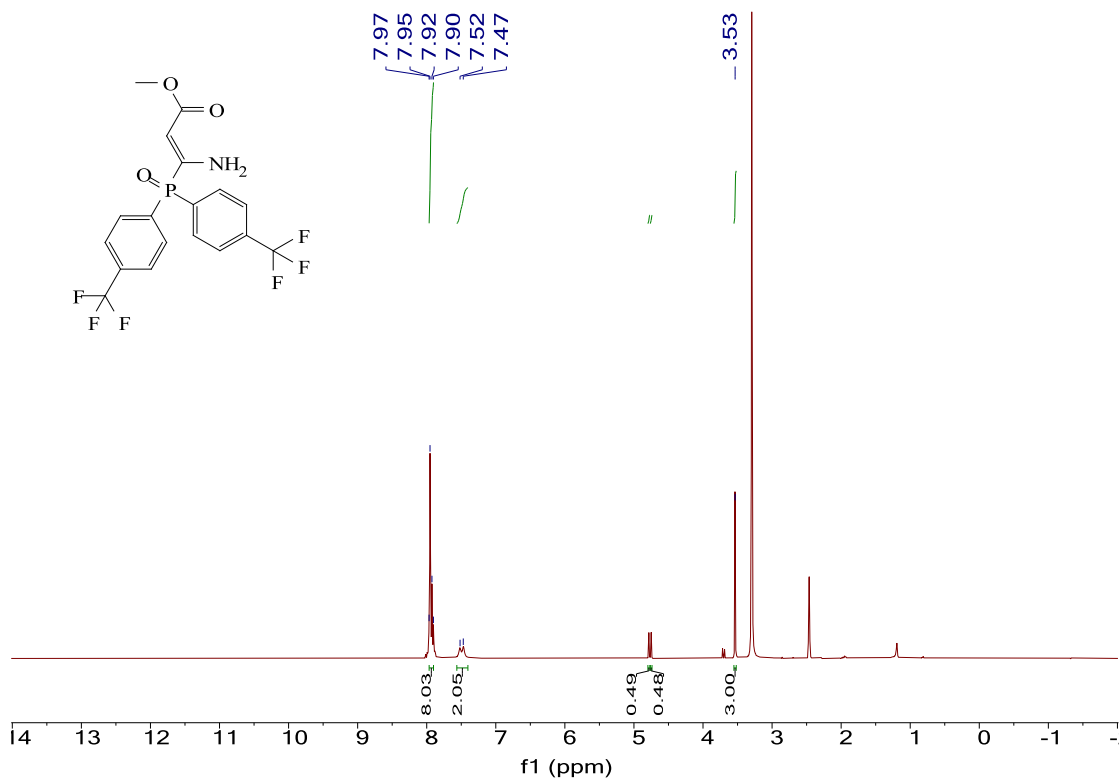


Methyl-3-amino-3-(bis(4-(trifluoromethyl)phenyl)phosphoryl)acrylate (7)

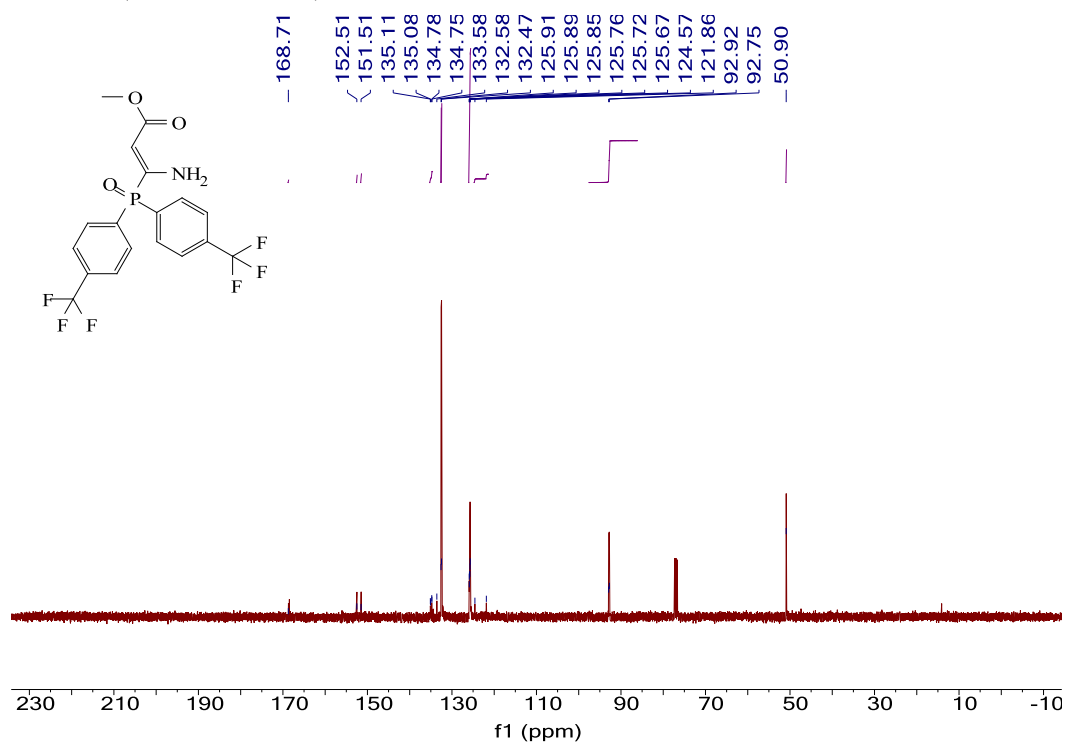
¹H NMR (400 MHz, CDCl₃)



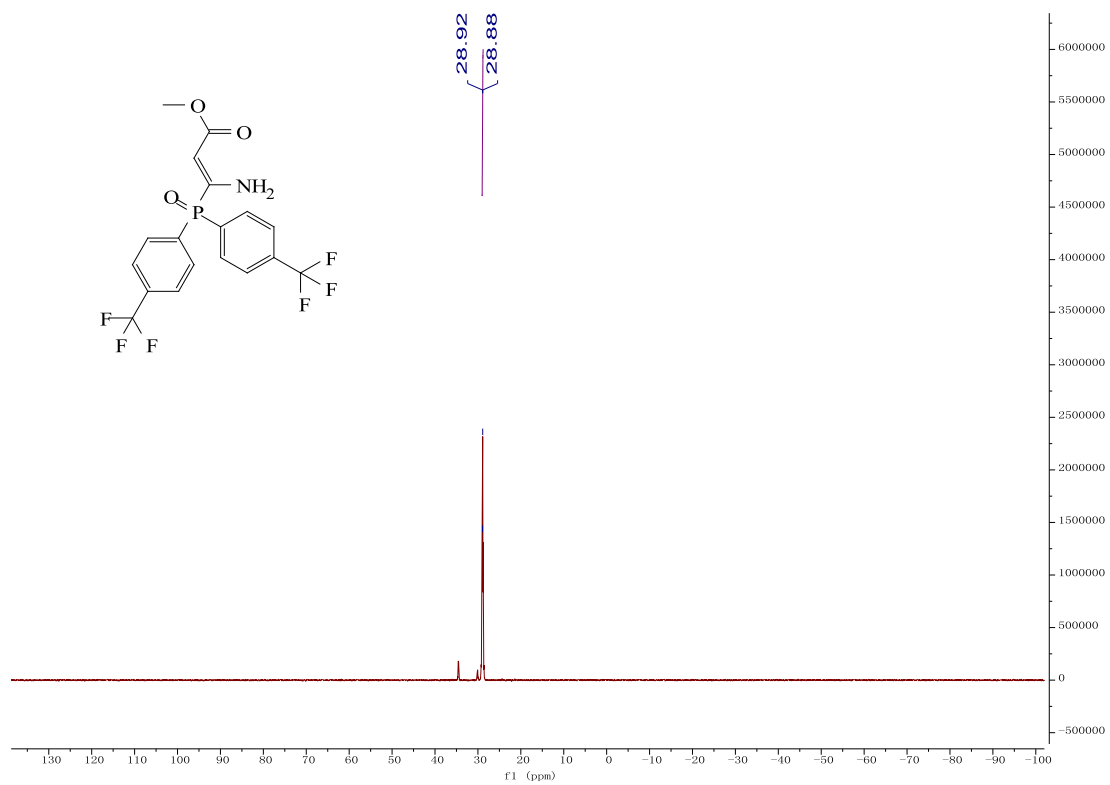
^1H NMR (400 MHz, $\text{DMSO-}d_6$)



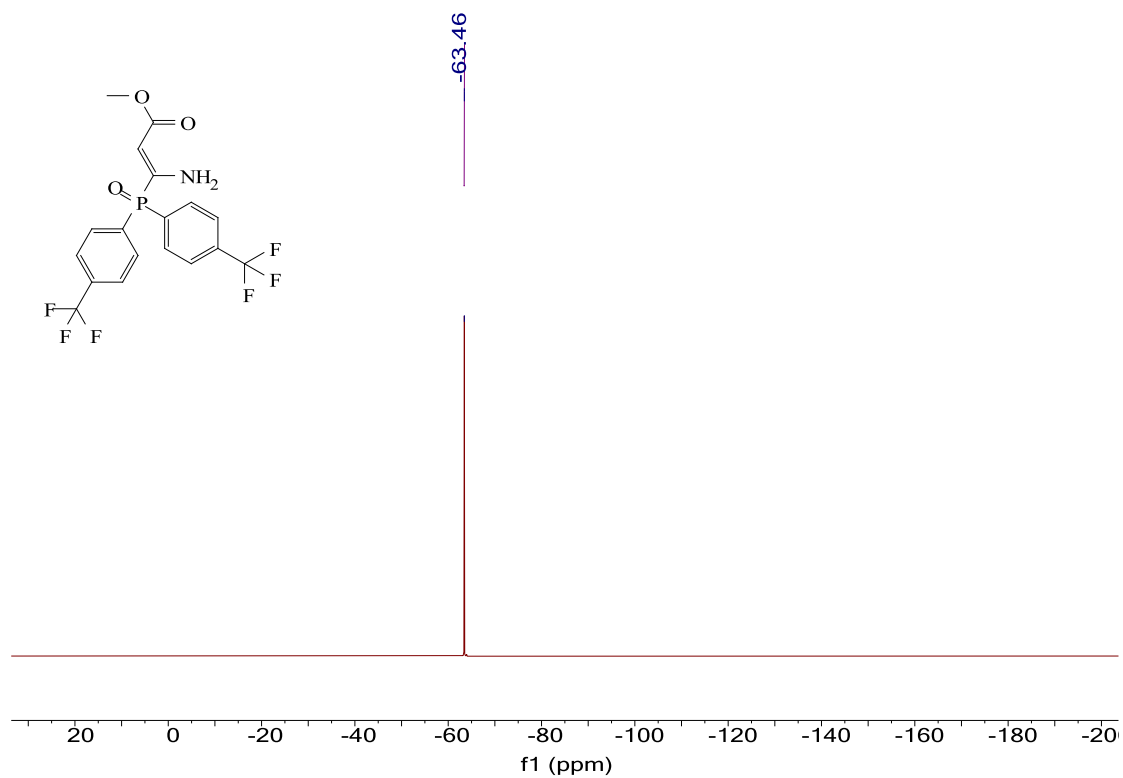
^{13}C NMR (101 MHz, CDCl_3)



^{31}P NMR (162 MHz, CDCl_3)

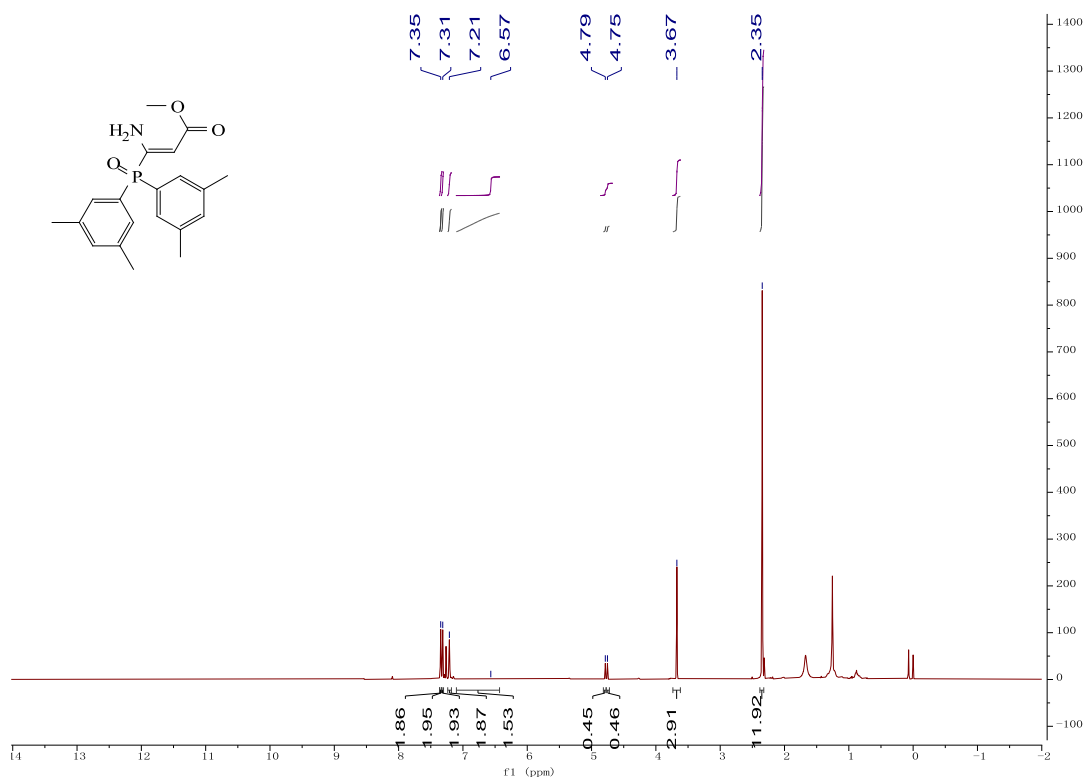


^{19}F NMR (376 MHz, CDCl_3)

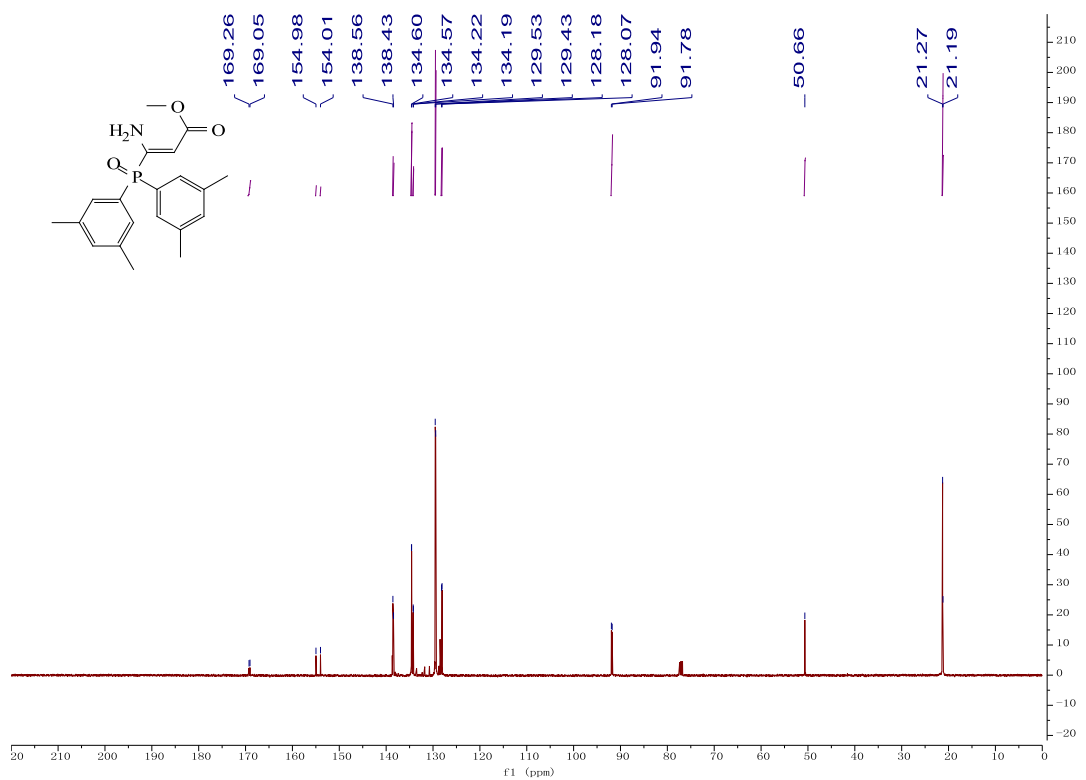


Methyl 3-amino-3-(bis(3,5-dimethylphenyl)phosphoryl) acrylate (8)

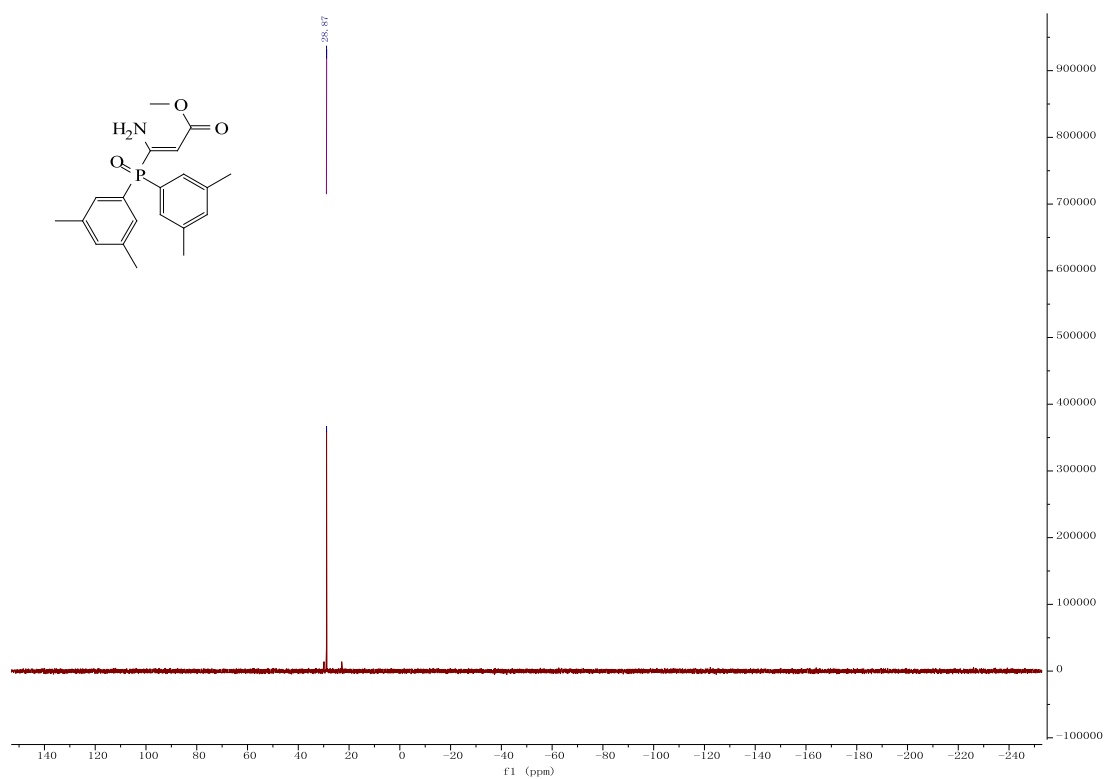
$^1\text{H NMR}$ (400 MHz, CDCl_3)



$^{13}\text{C NMR}$ (101 MHz, CDCl_3)

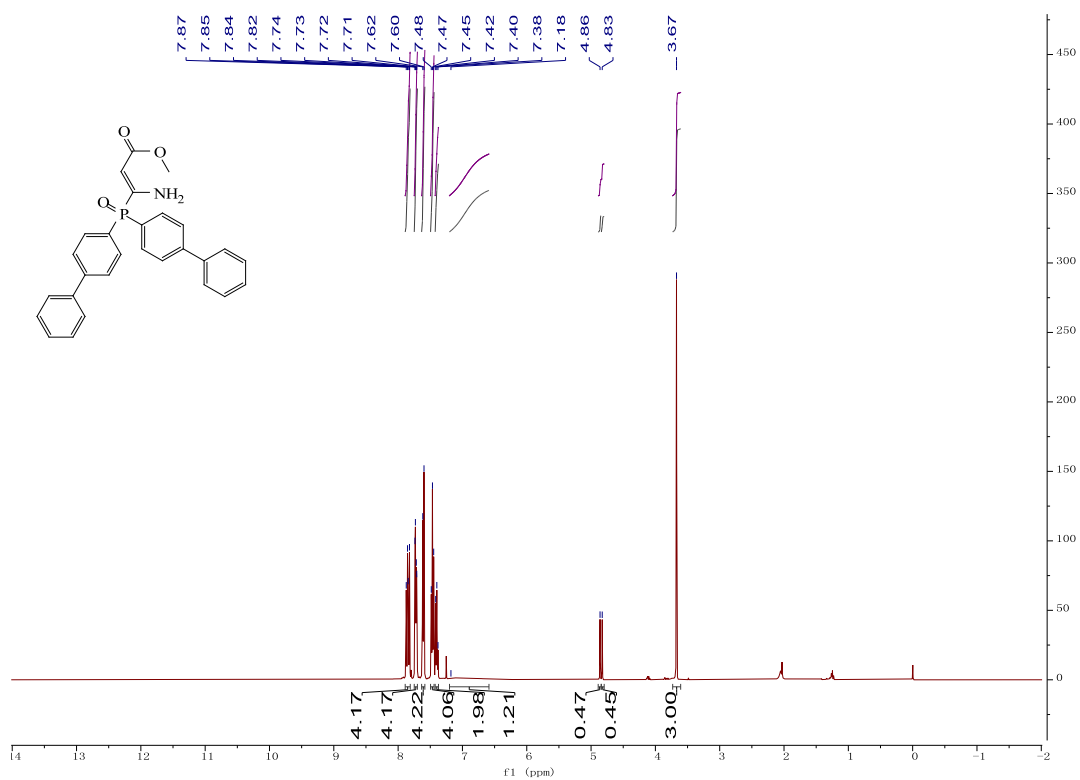


^{31}P NMR (162 MHz, CDCl_3)

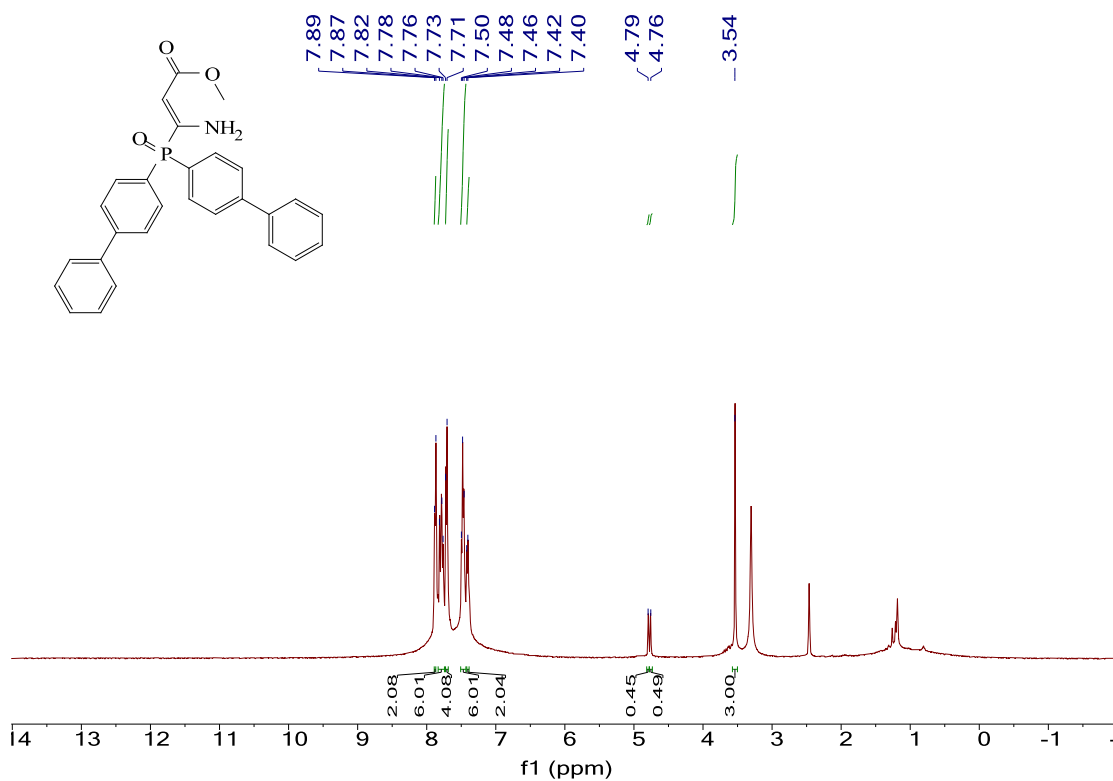


Methyl 3-amino-3-(di([1,1'-biphenyl]-4-yl)phosphoryl)acrylate (9)

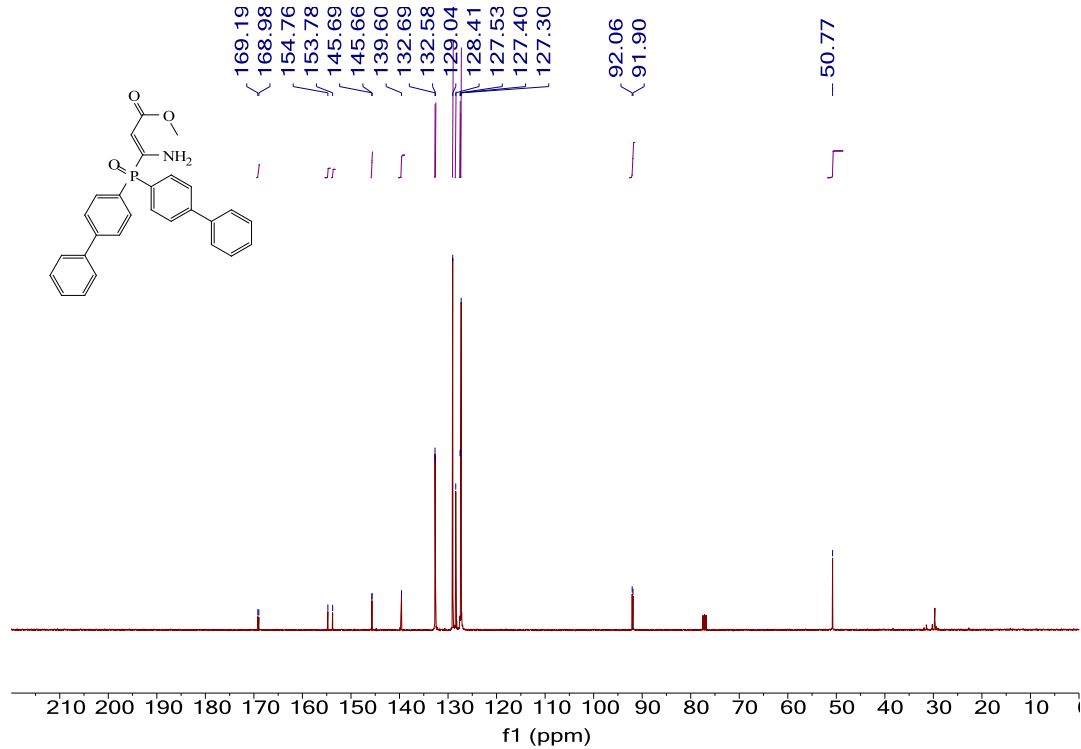
^1H NMR (400 MHz, CDCl_3)



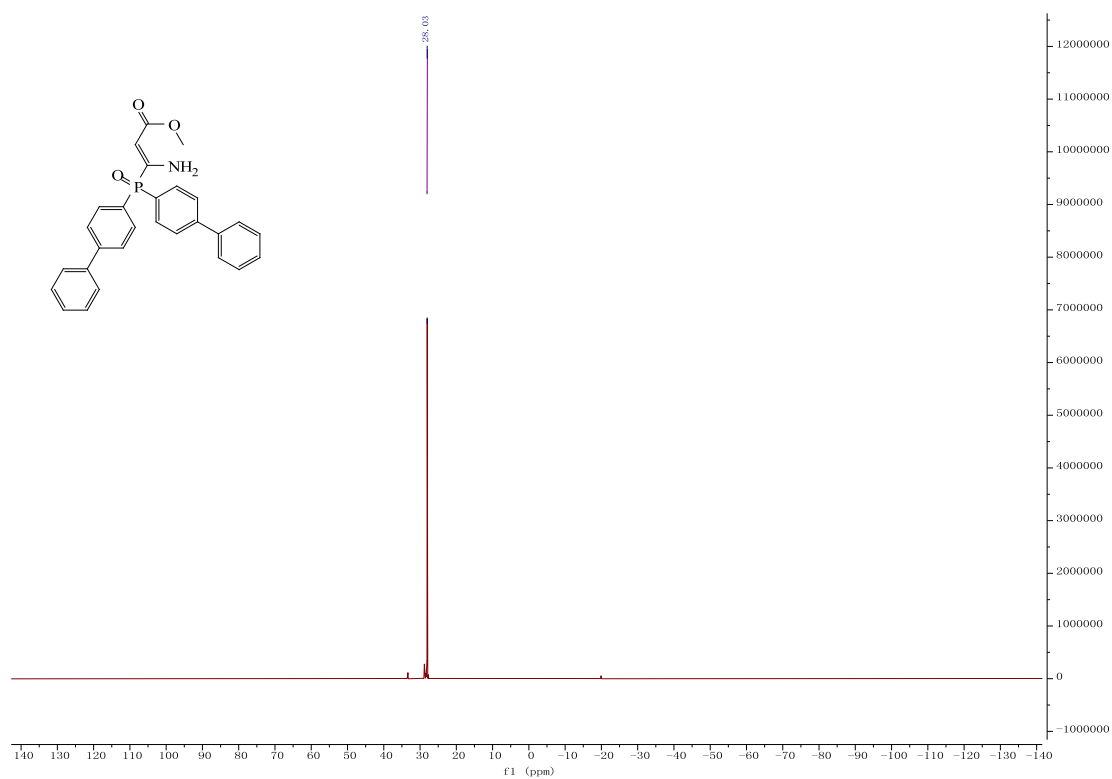
¹H NMR (400 MHz, DMSO-d₆)



¹³C NMR (101 MHz, CDCl₃)

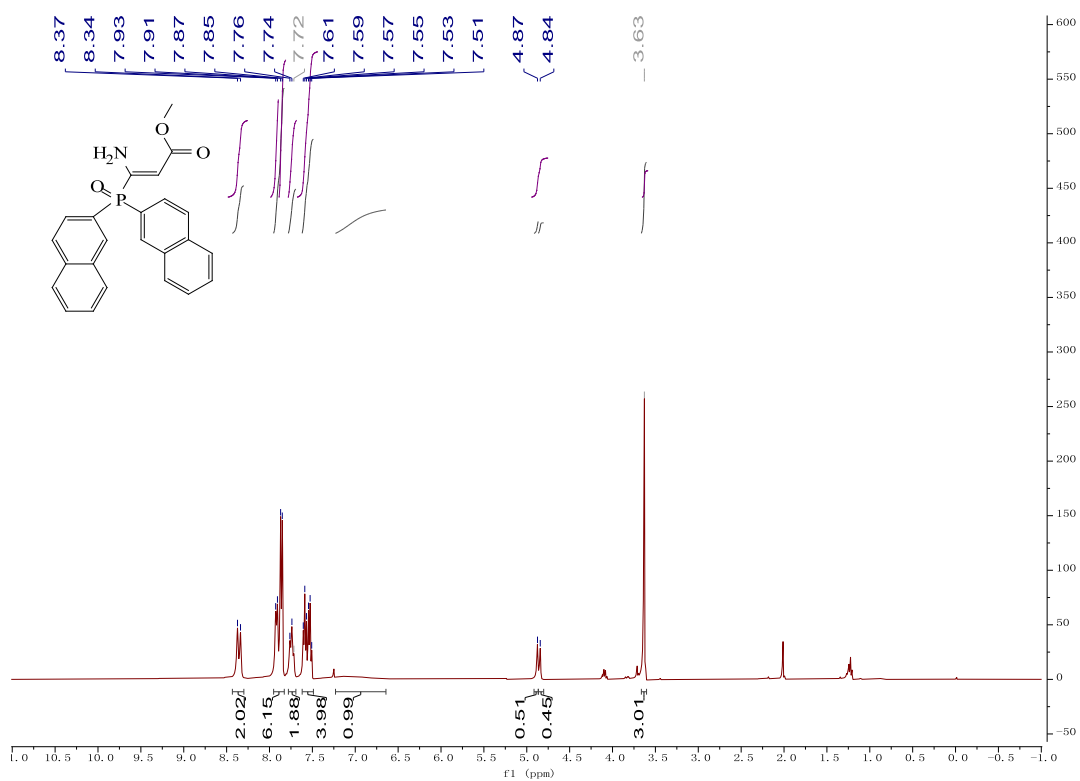


^{31}P NMR (162 MHz, CDCl_3)

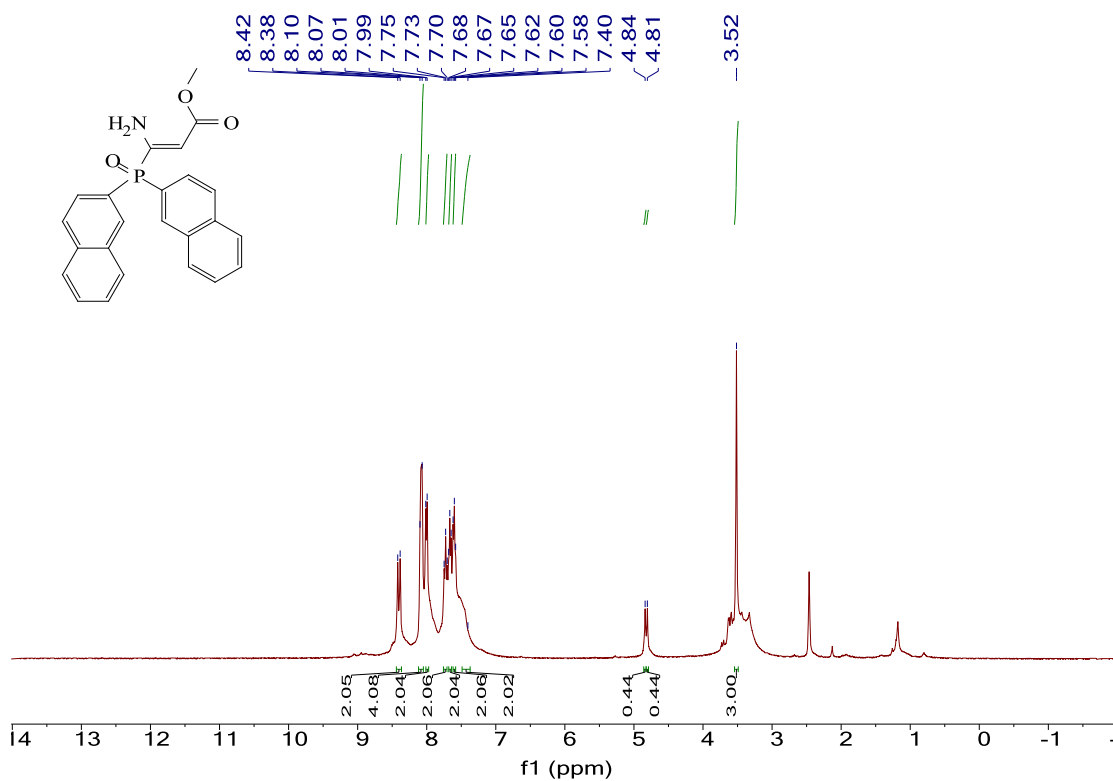


Methyl -3-amino-3-(di(naphthalen-2-yl)phosphoryl)acrylate (10).

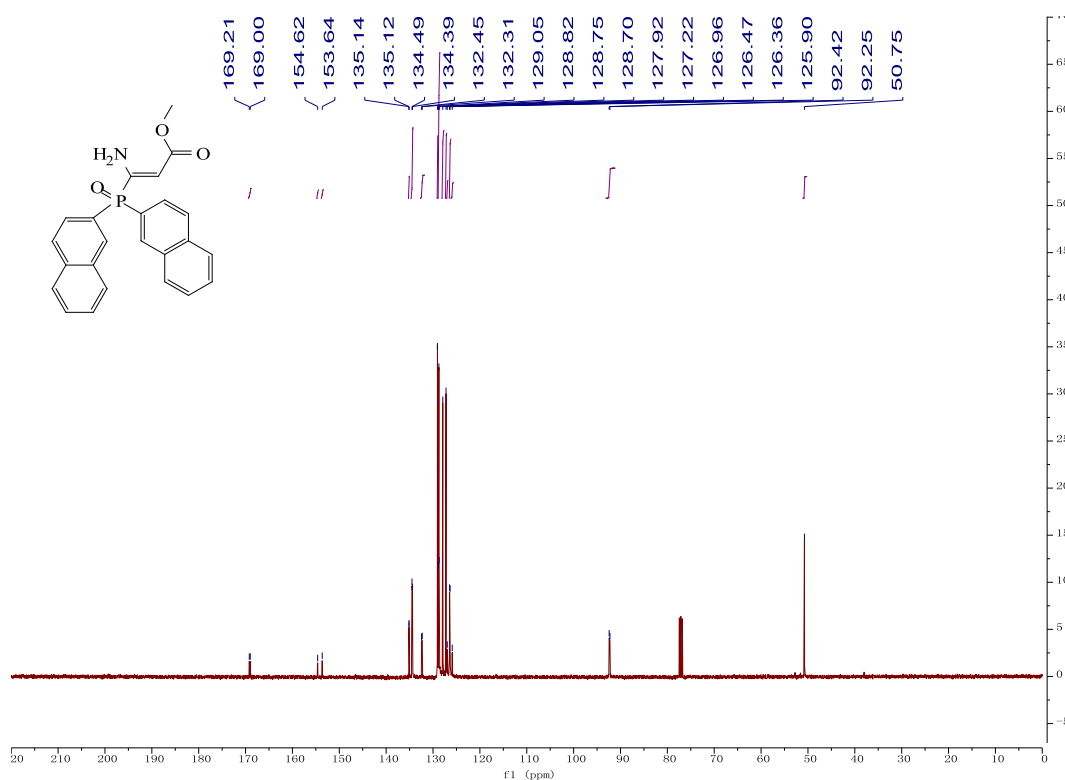
^1H NMR (400 MHz, CDCl_3)



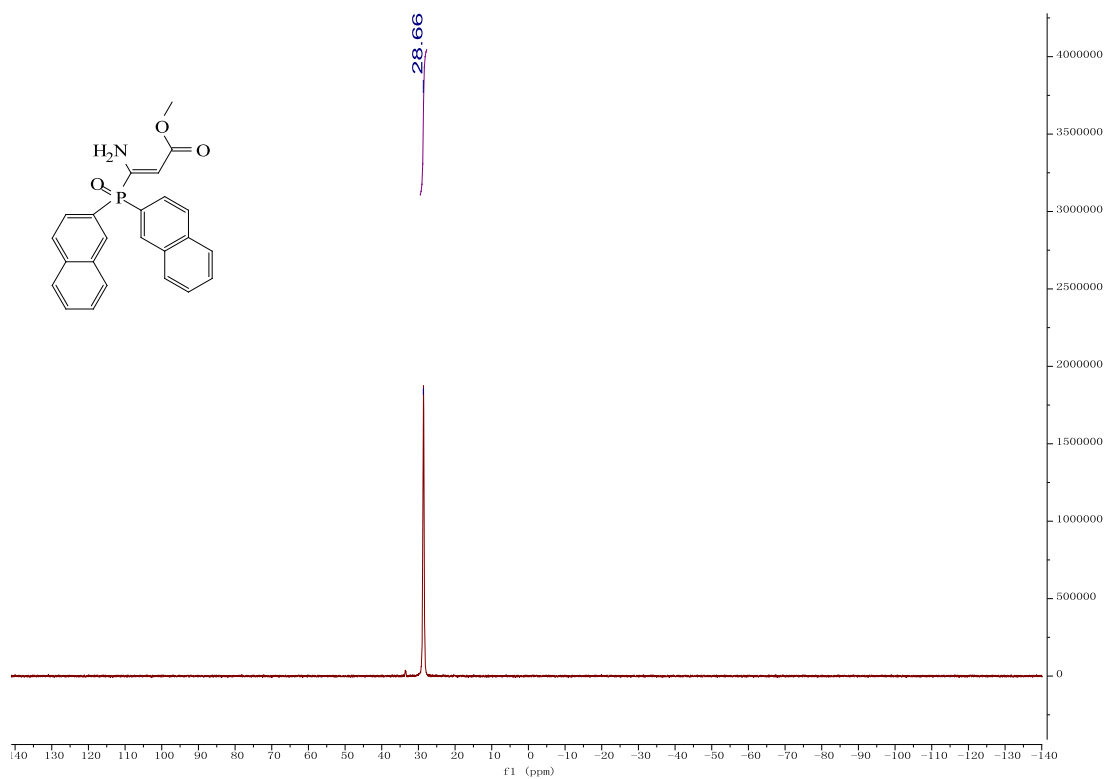
¹H NMR (400 MHz, DMSO-d₆)



¹³C NMR (101 MHz, CDCl₃)

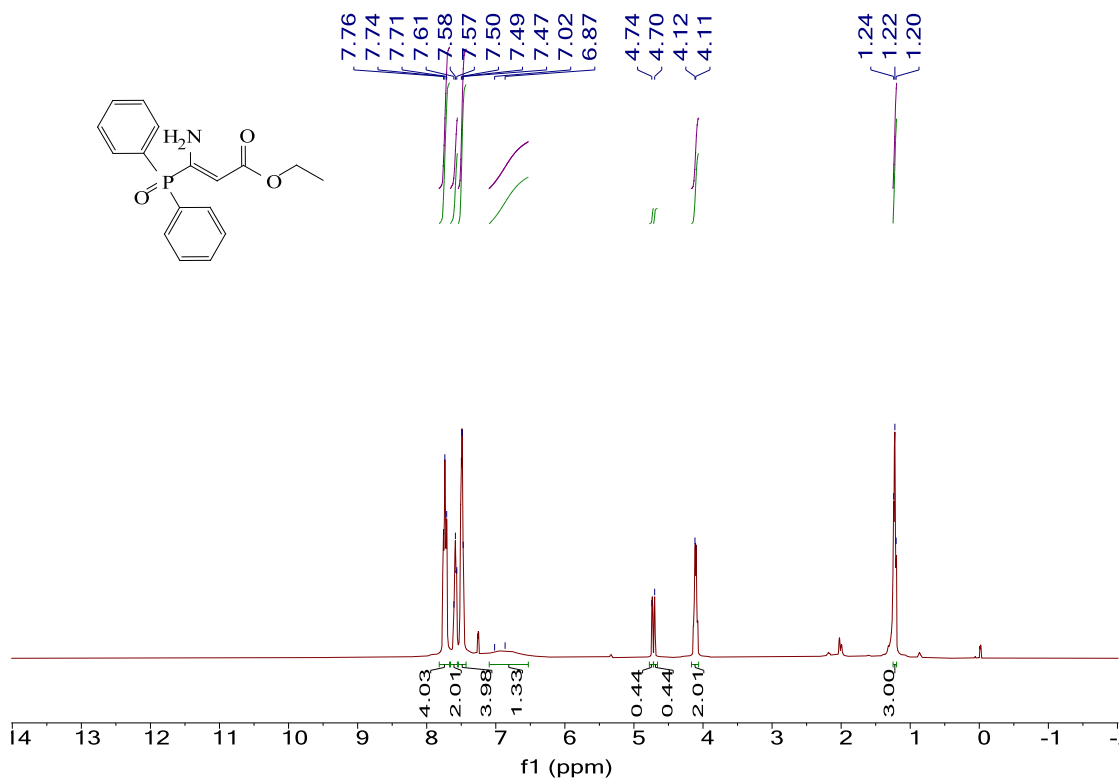


^{31}P NMR (162 MHz, CDCl_3)

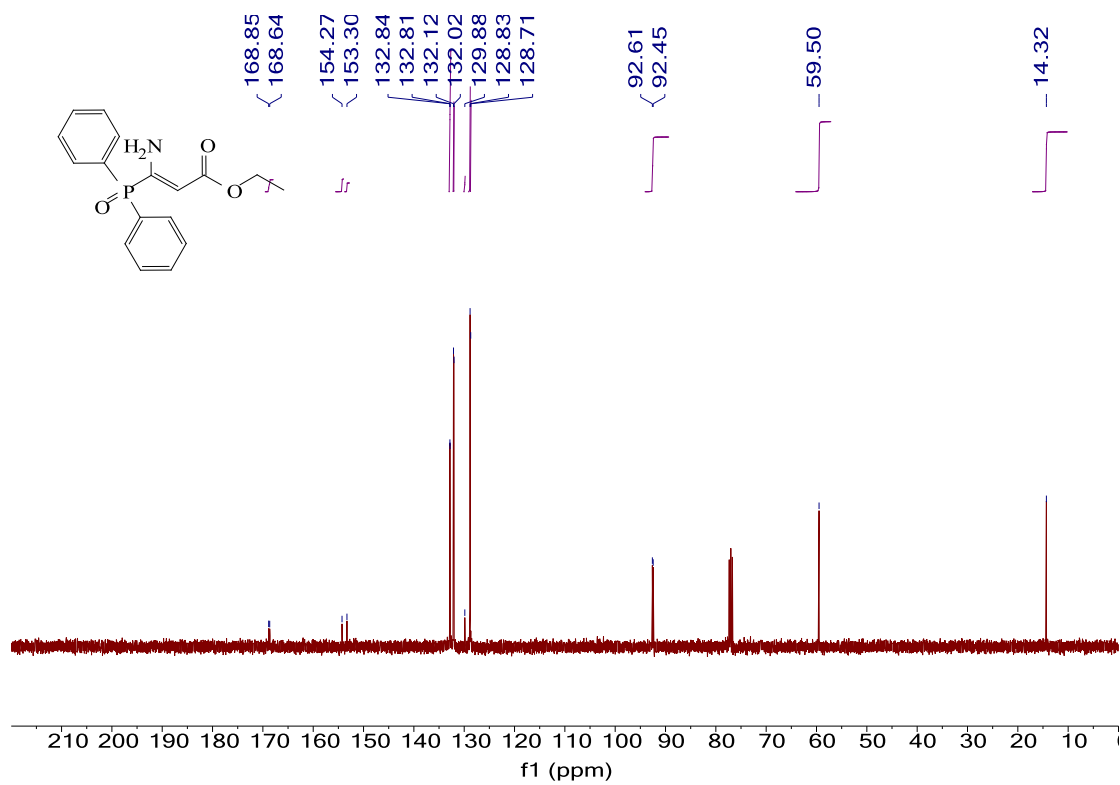


Ethyl 3-amino-3-(diphenylphosphoryl)acrylate (12).

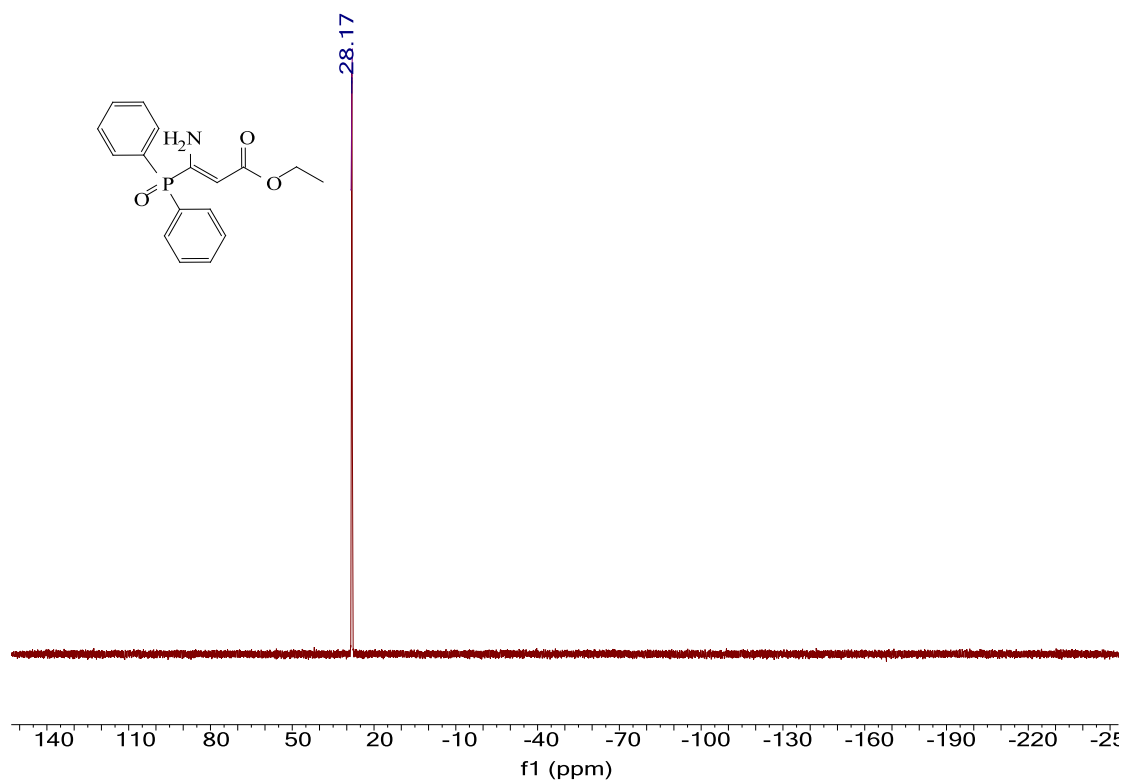
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (101 MHz, CDCl_3)

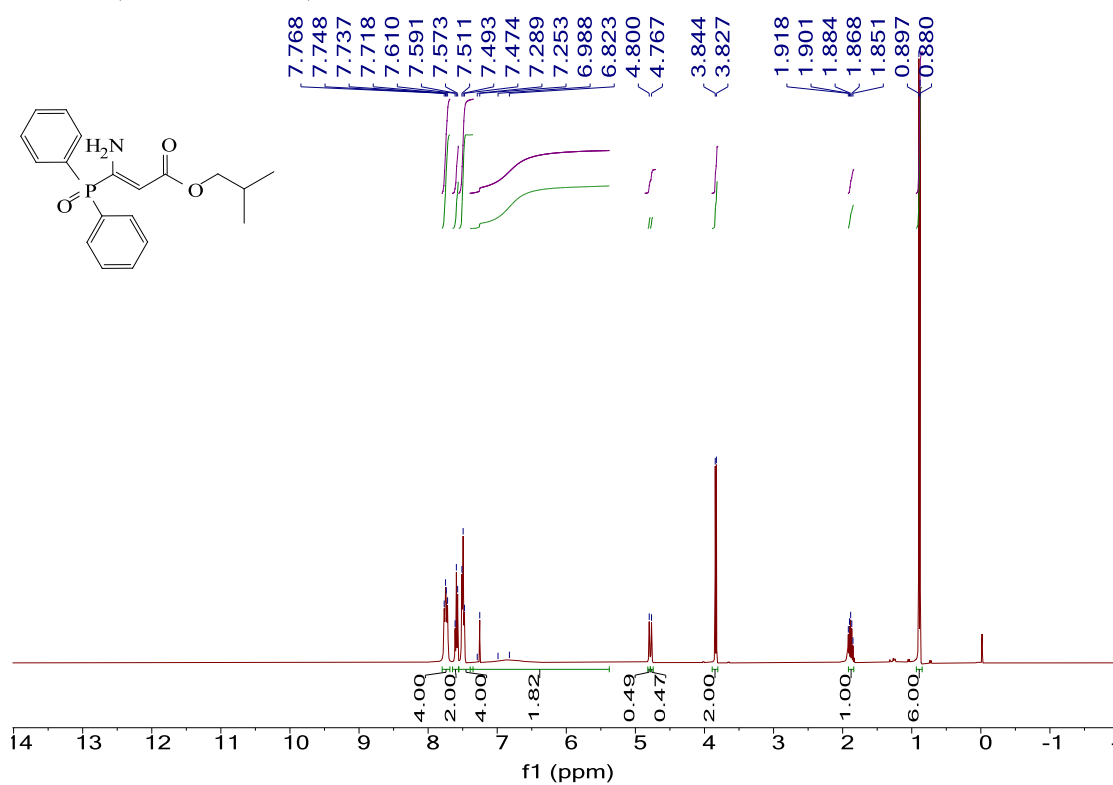


^{31}P NMR (162 MHz, CDCl_3)

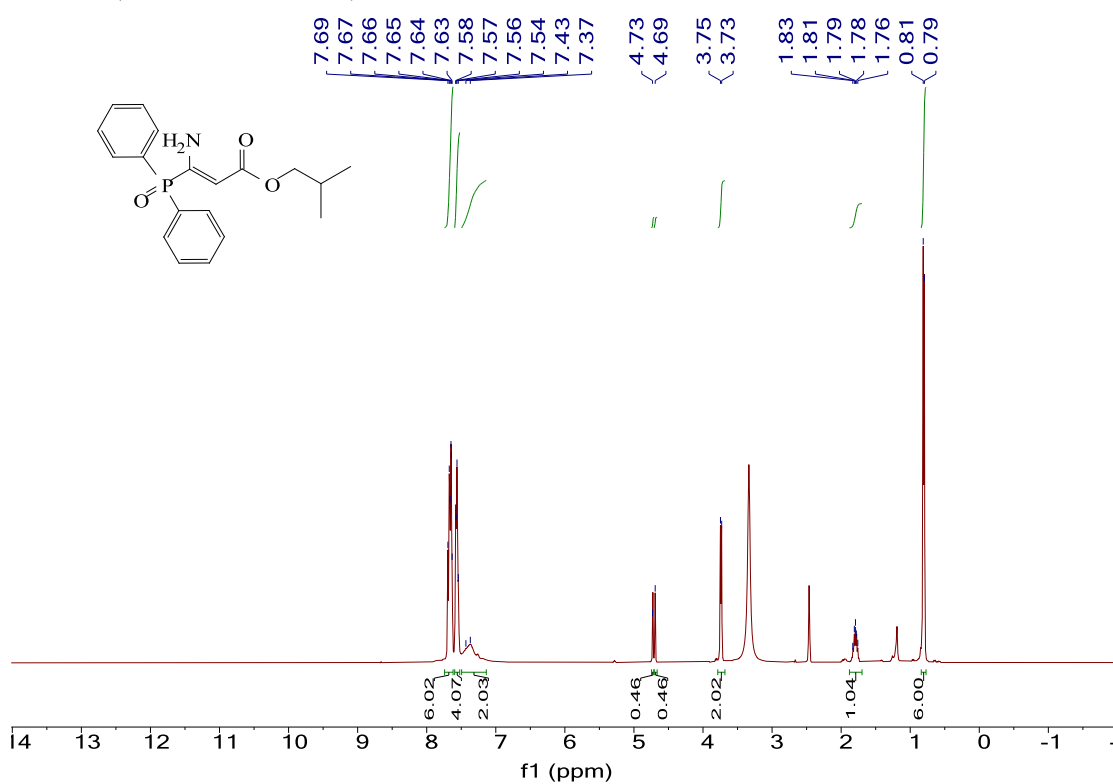


Ethyl 3-amino-3-(diphenylphosphoryl)acrylate (13).

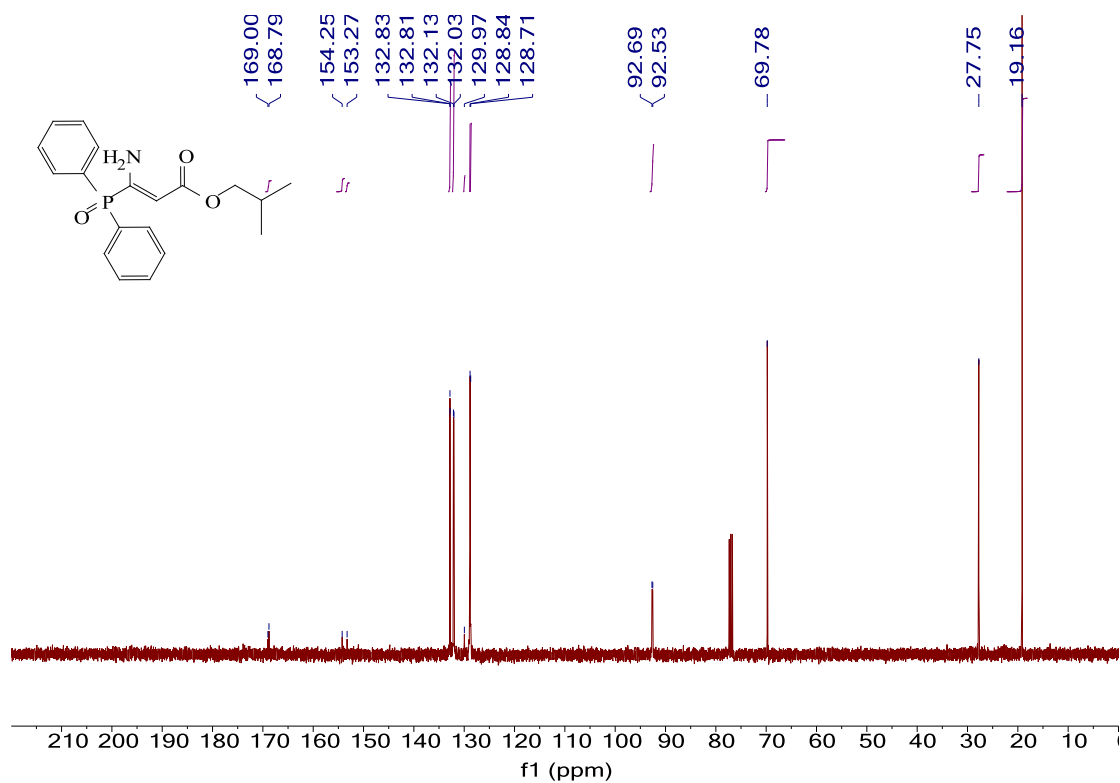
¹H NMR (400 MHz, CDCl₃)



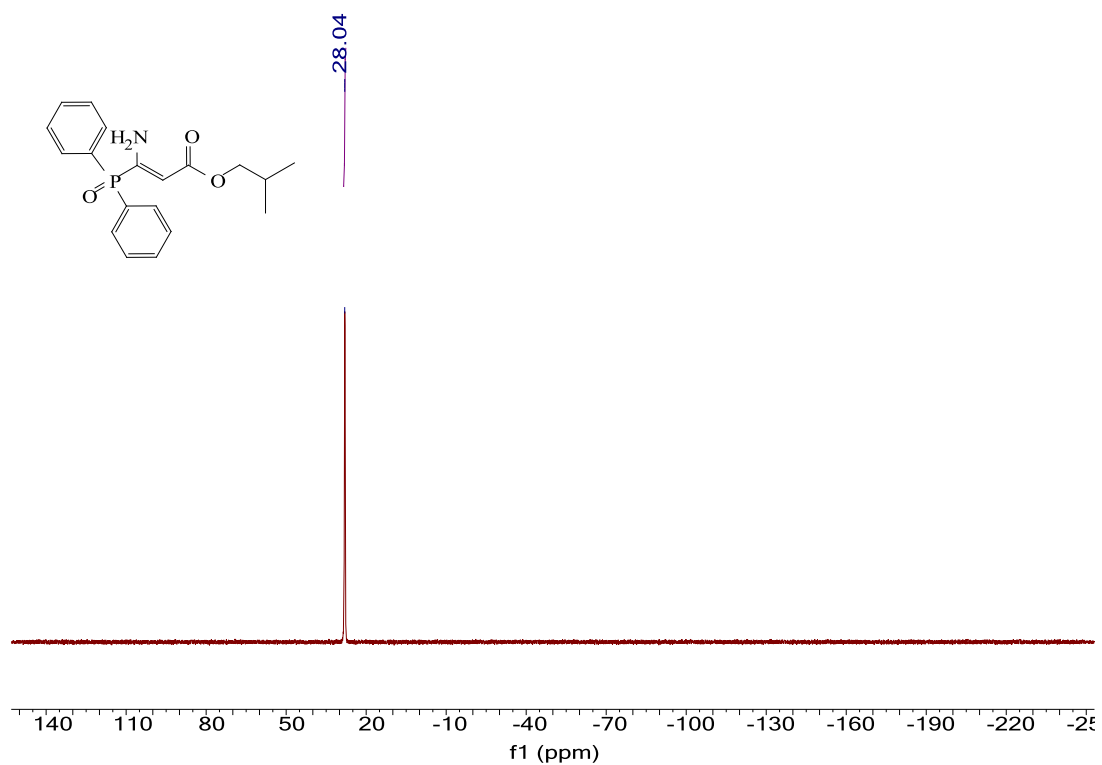
¹H NMR (400 MHz, DMSO-*d*₆)



^{13}C NMR (101 MHz, CDCl_3)

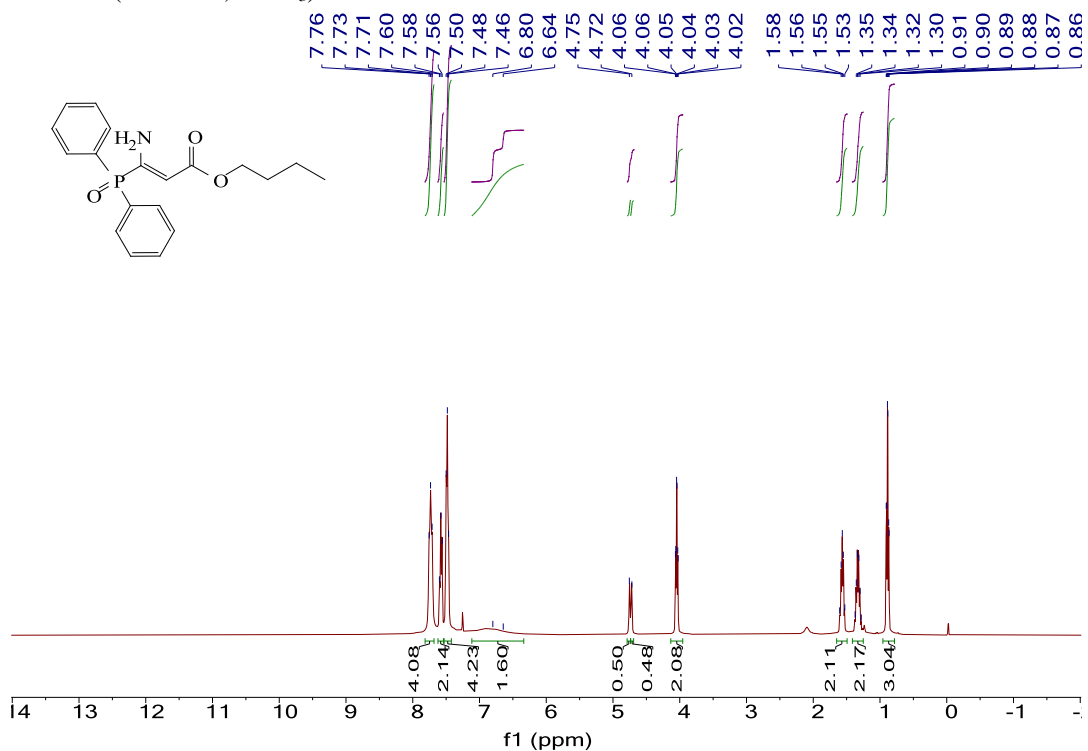


^{31}P NMR (162 MHz, CDCl_3)

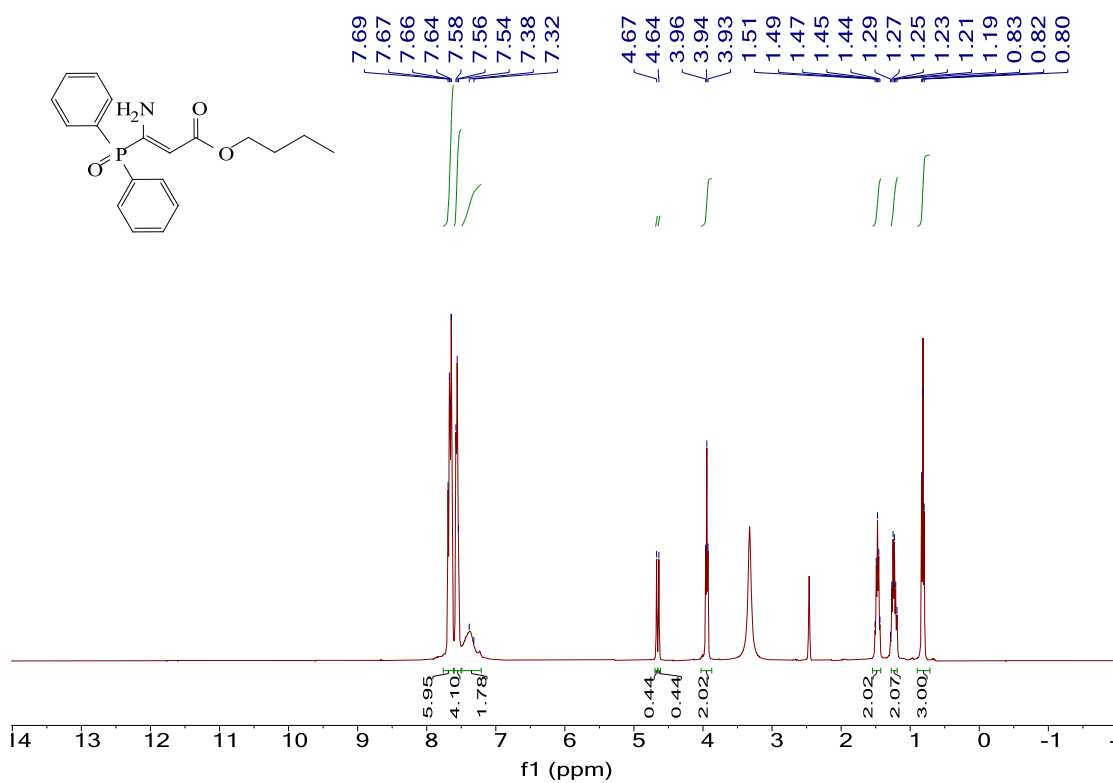


Butyl 3-amino-3-(diphenylphosphoryl)acrylate (14).

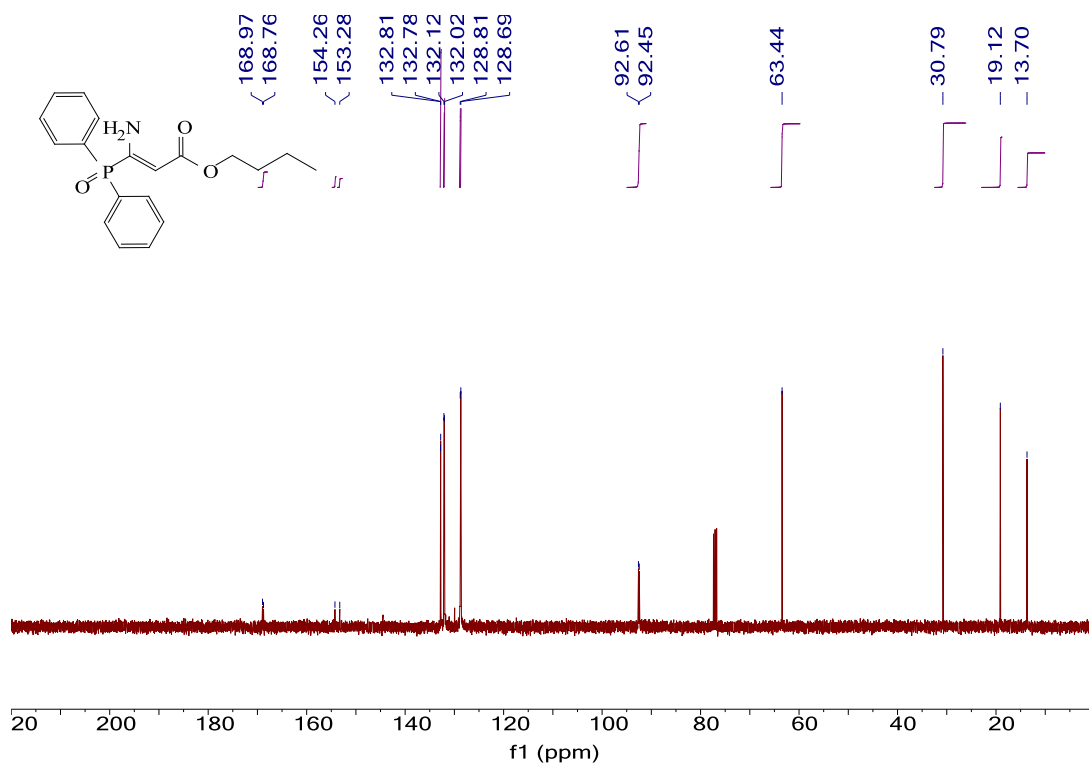
$^1\text{H NMR}$ (400 MHz, CDCl_3)



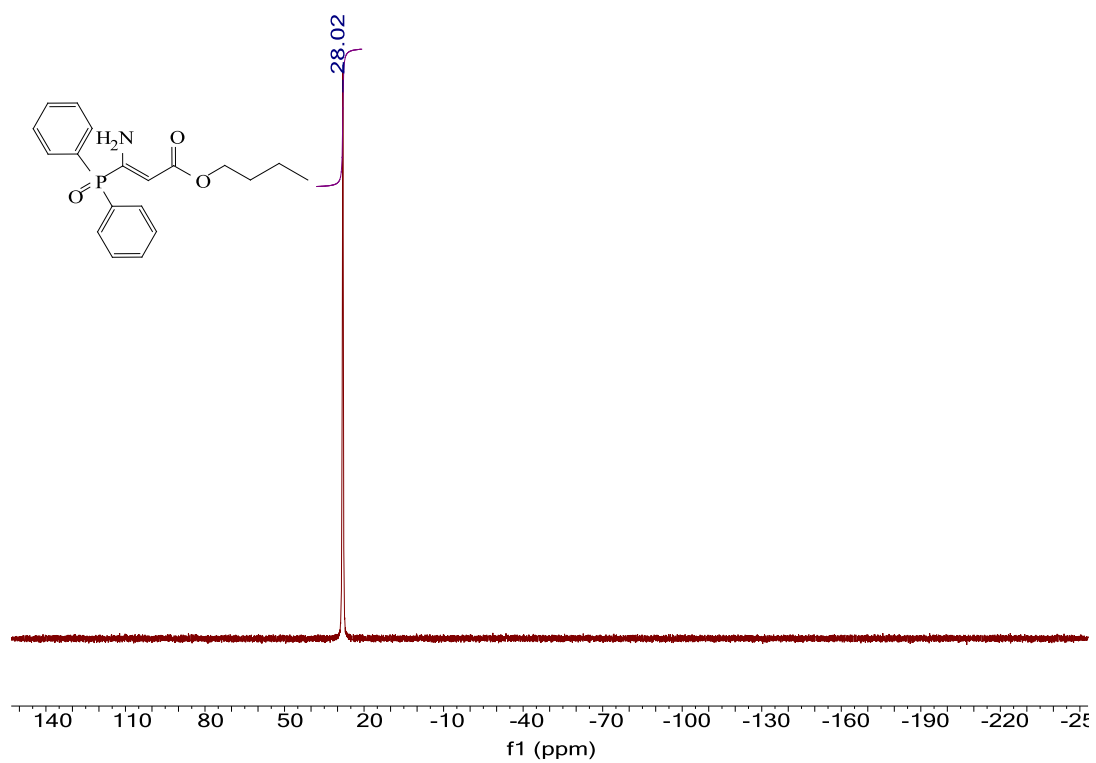
$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$)



^{13}C NMR (101 MHz, CDCl_3)

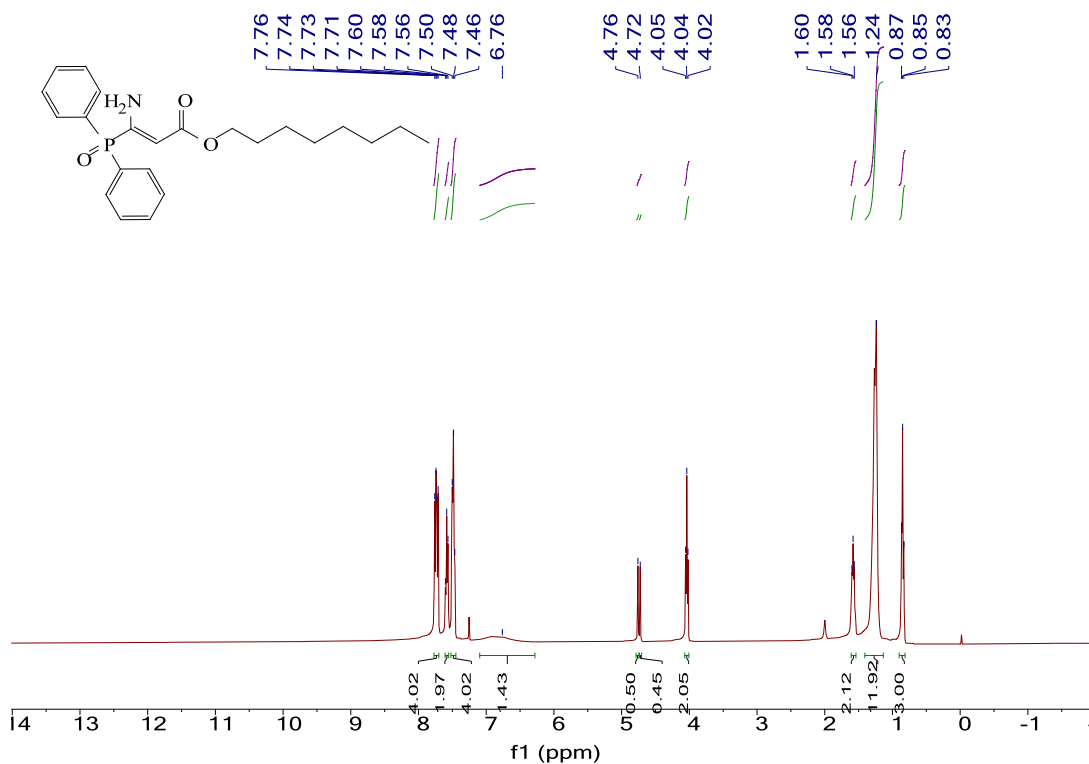


^{31}P NMR (162 MHz, CDCl_3)

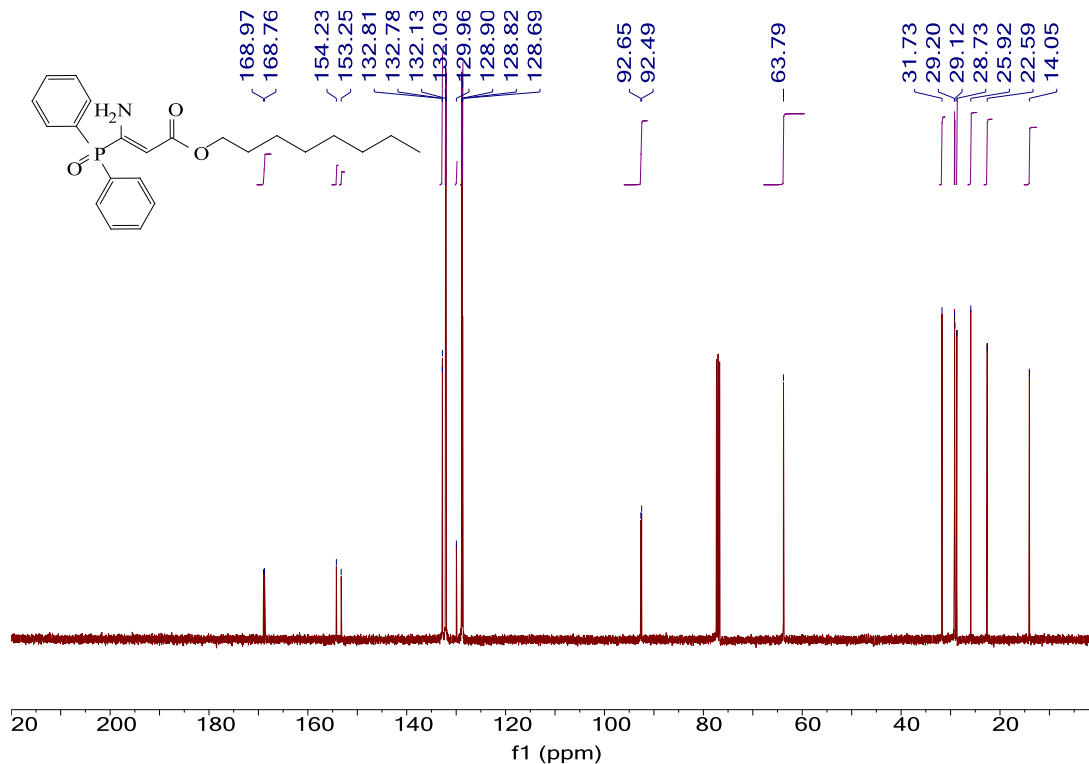


Octyl 3-amino-3-(diphenylphosphoryl)acrylate (15)

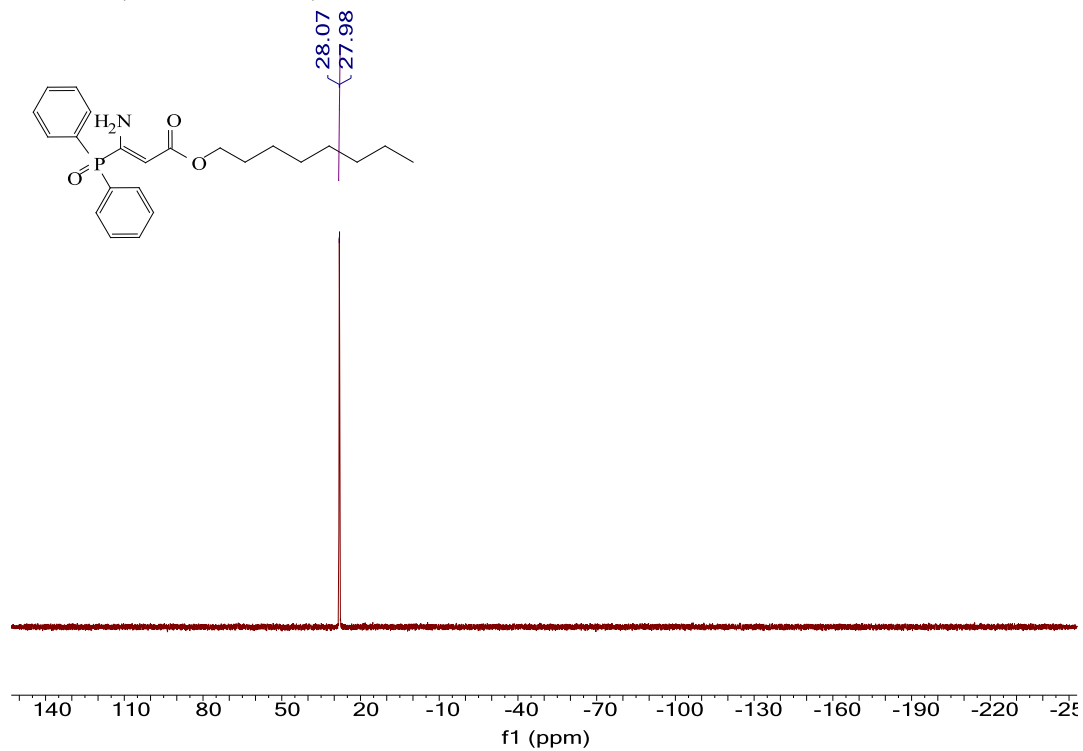
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

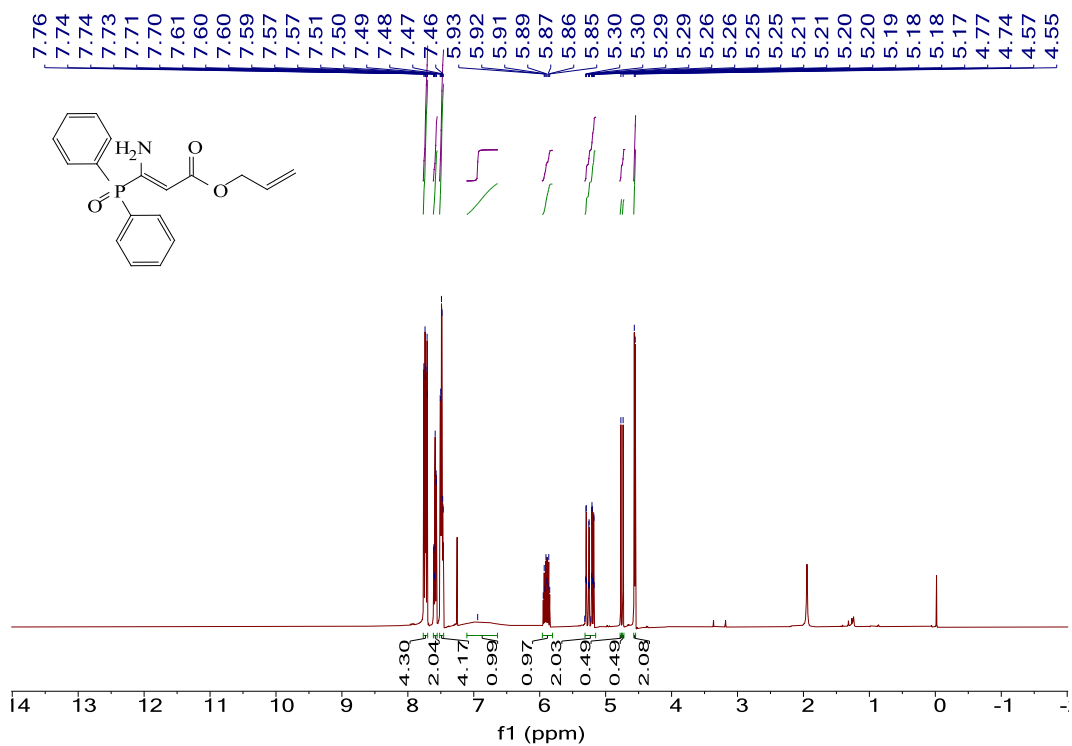


³¹P NMR (162 MHz, CDCl₃)

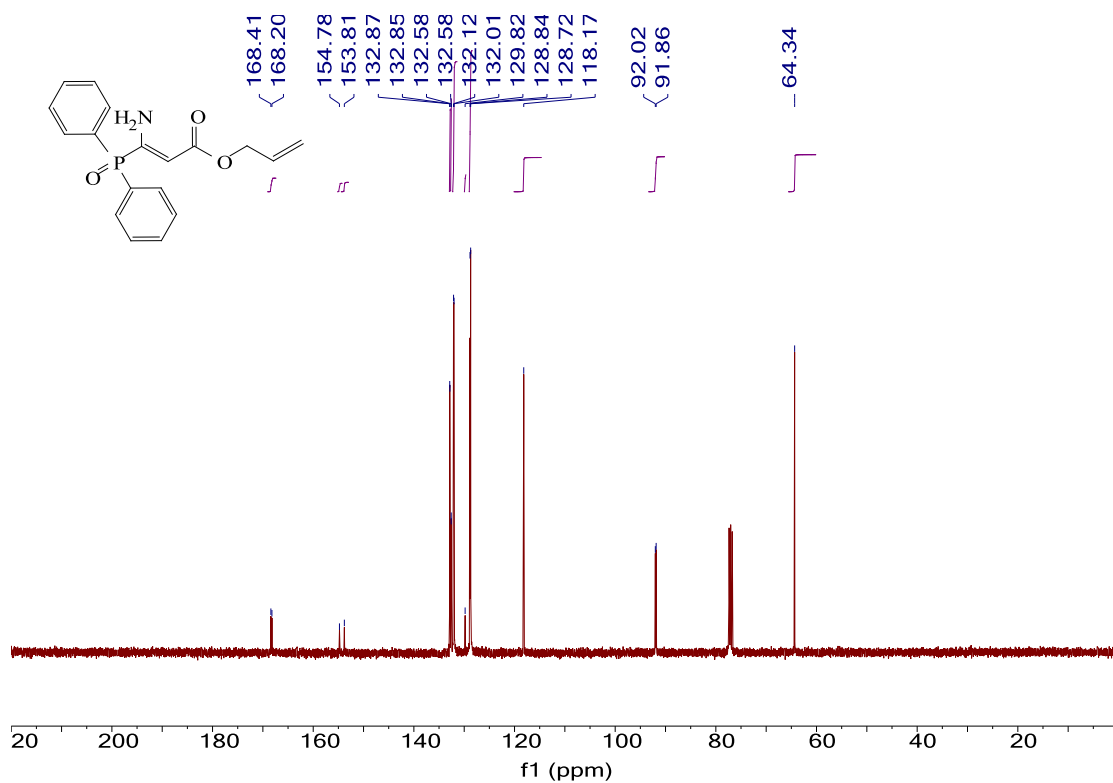


Allyl 3-amino-3-(diphenylphosphoryl)acrylate (16).

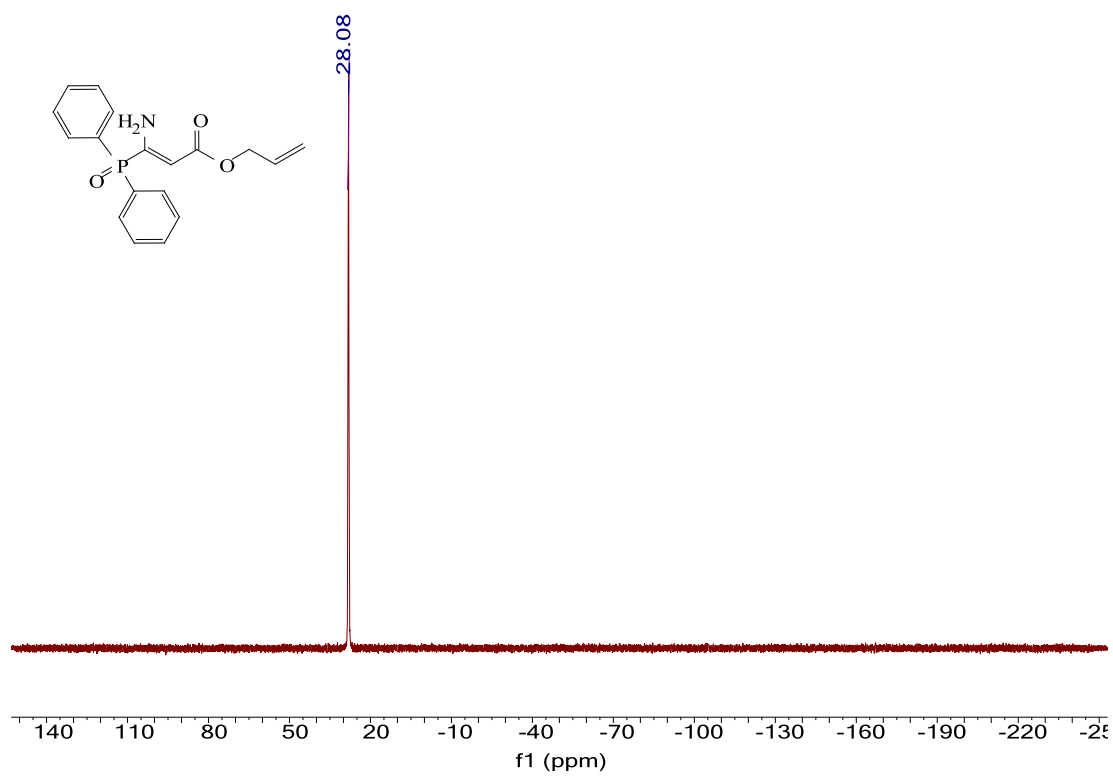
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

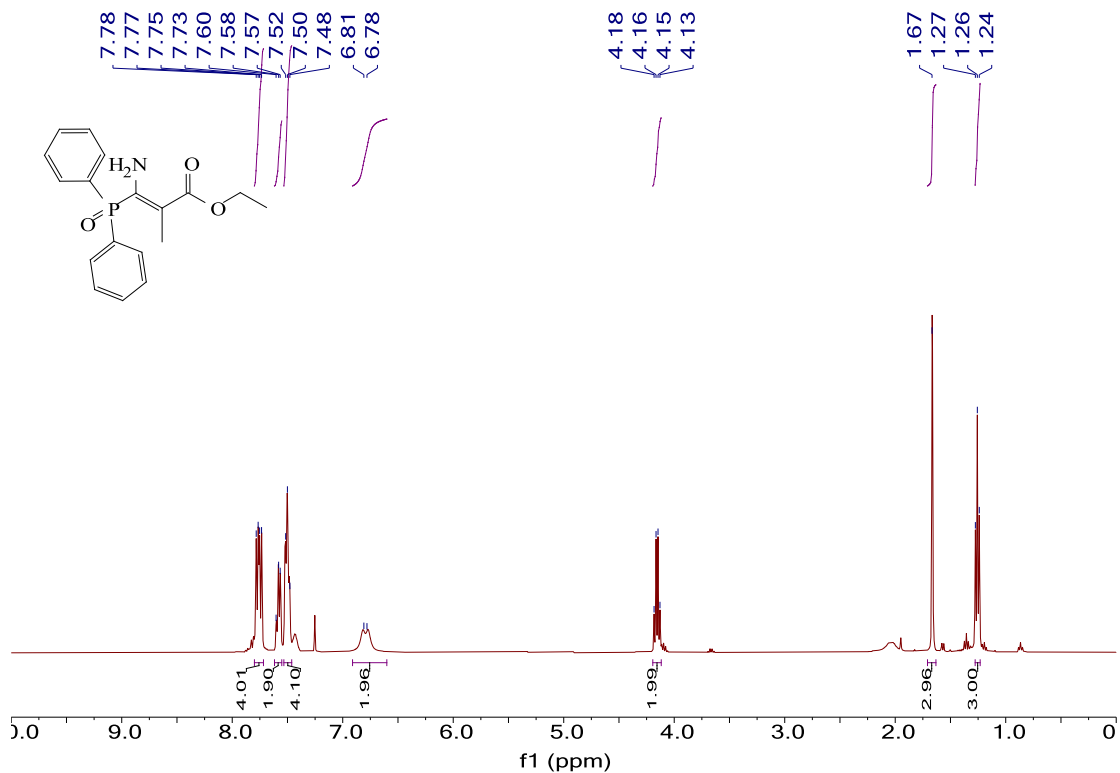


³¹P NMR (162 MHz, CDCl₃)

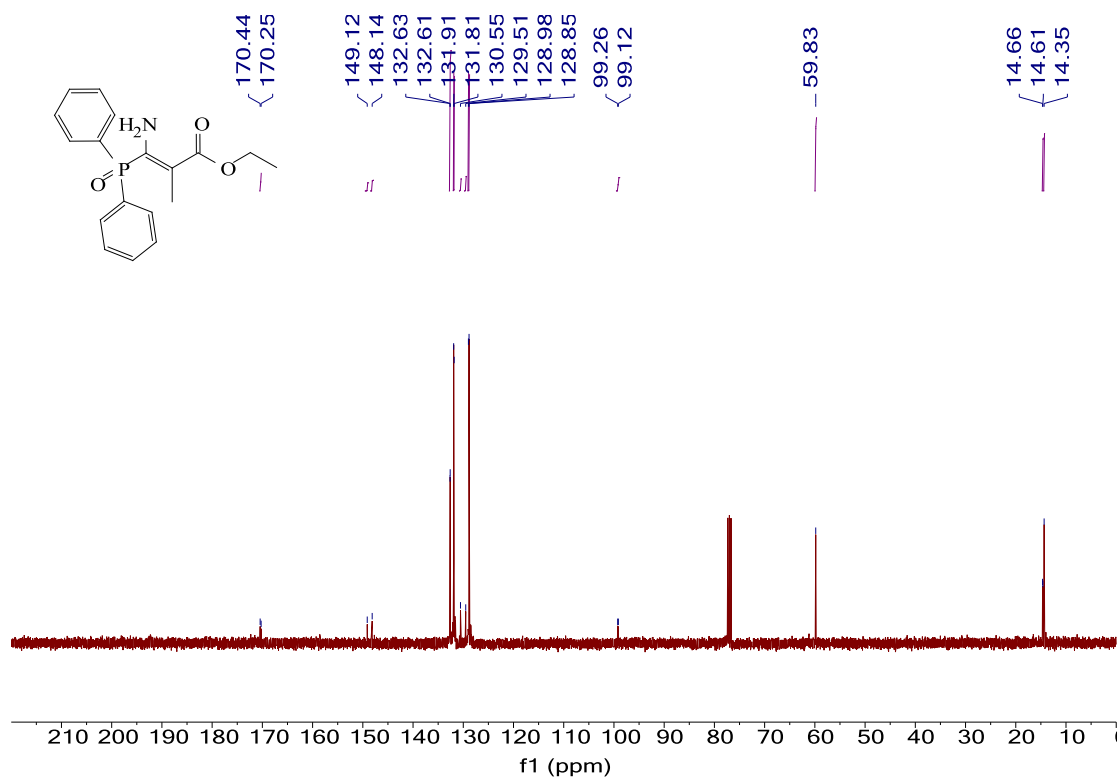


Ethyl 3-amino-3-(diphenylphosphoryl)-2-methylacrylate (17)

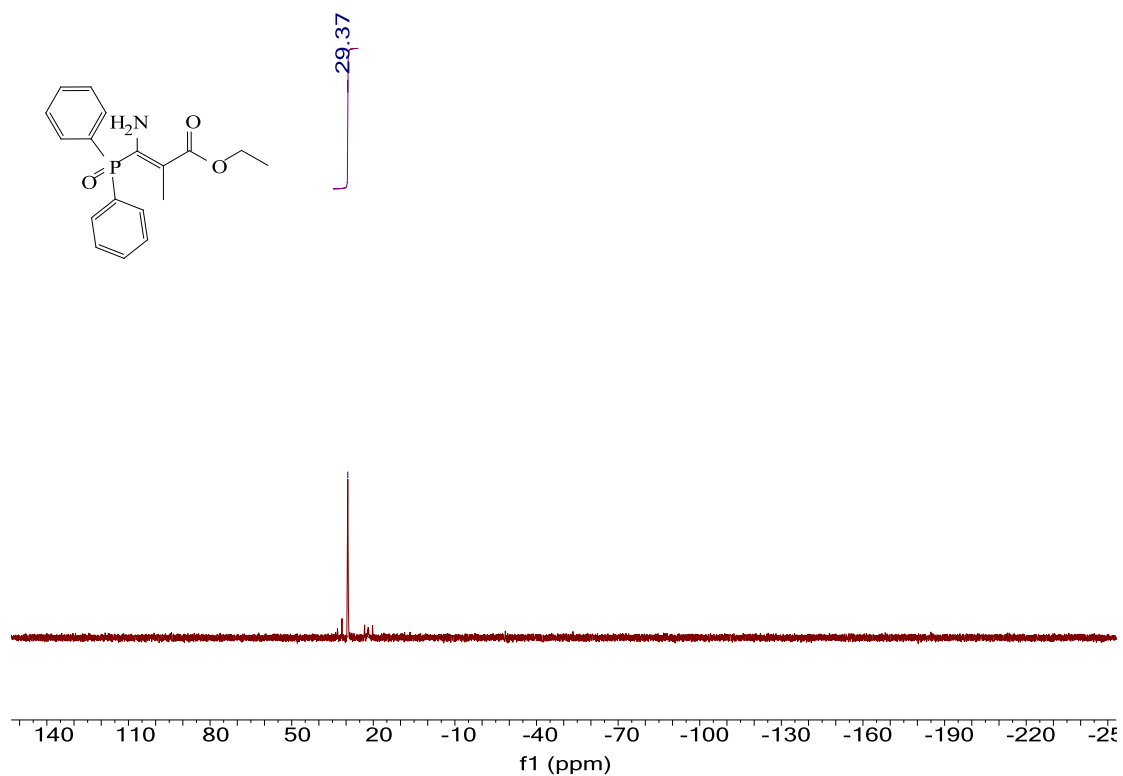
$^1\text{H NMR}$ (400 MHz, CDCl_3)



$^{13}\text{C NMR}$ (101 MHz, CDCl_3)

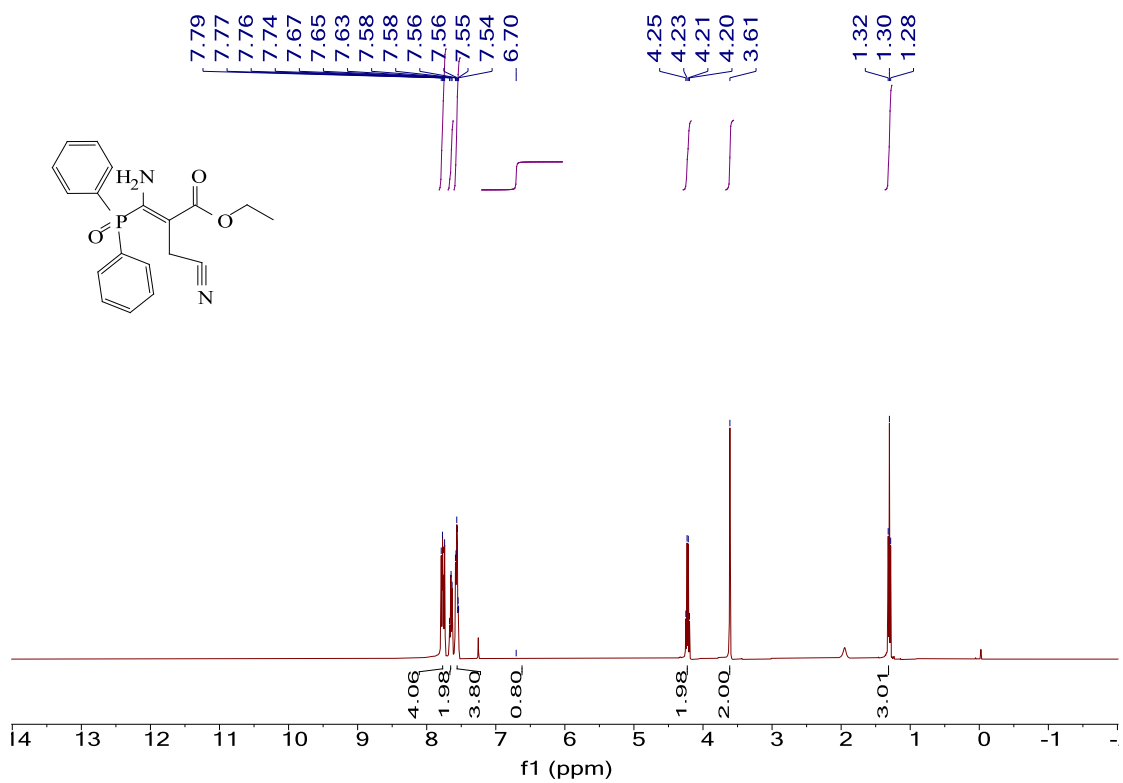


^{31}P NMR (162 MHz, CDCl_3)

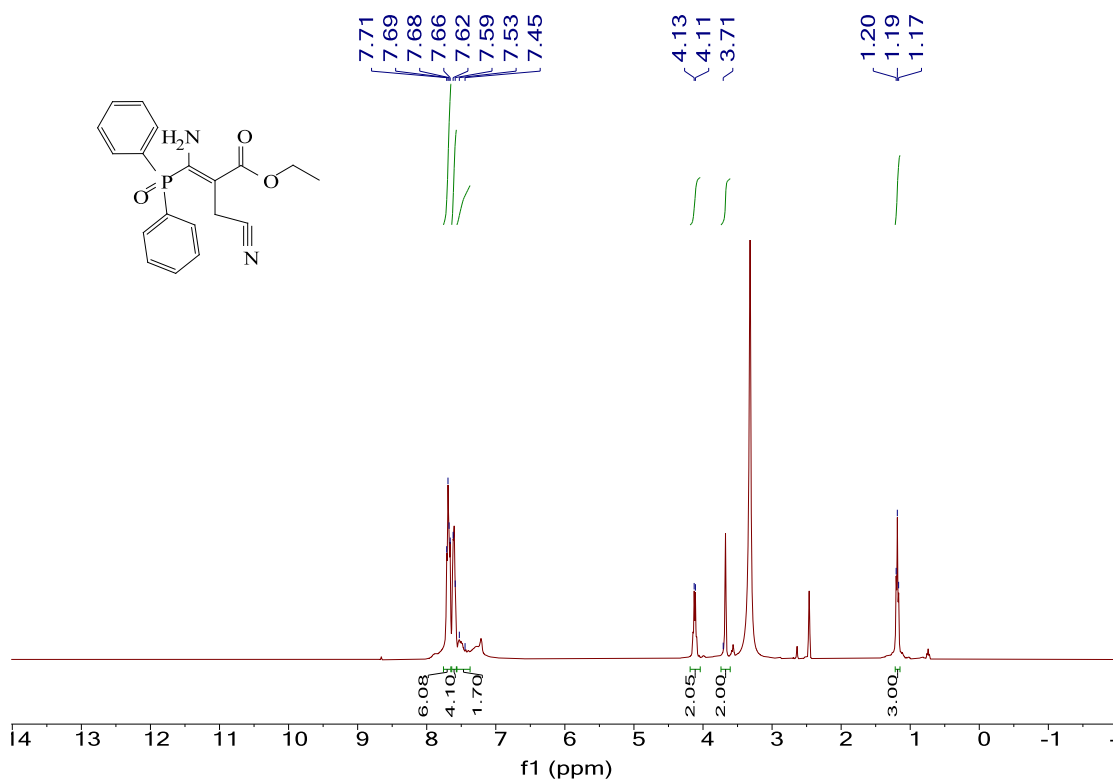


Ethyl 3-amino-2-(cyanomethyl)-3-(diphenylphosphoryl) acrylate (18)

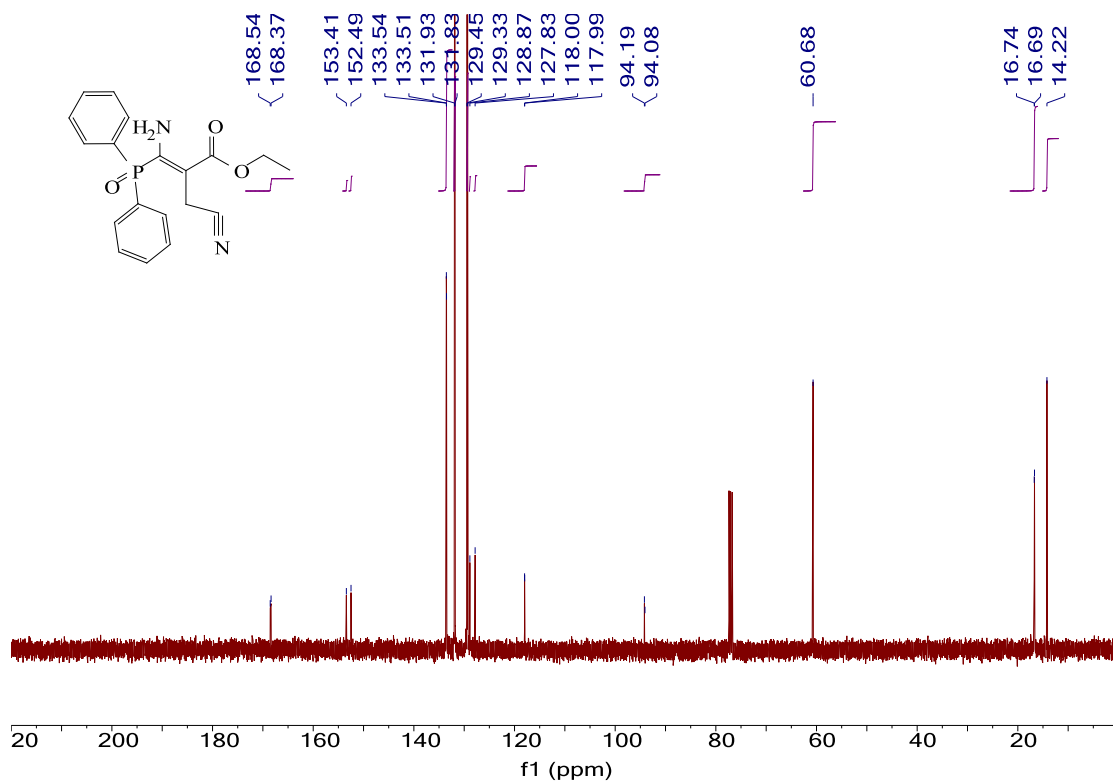
^1H NMR (400 MHz, CDCl_3)



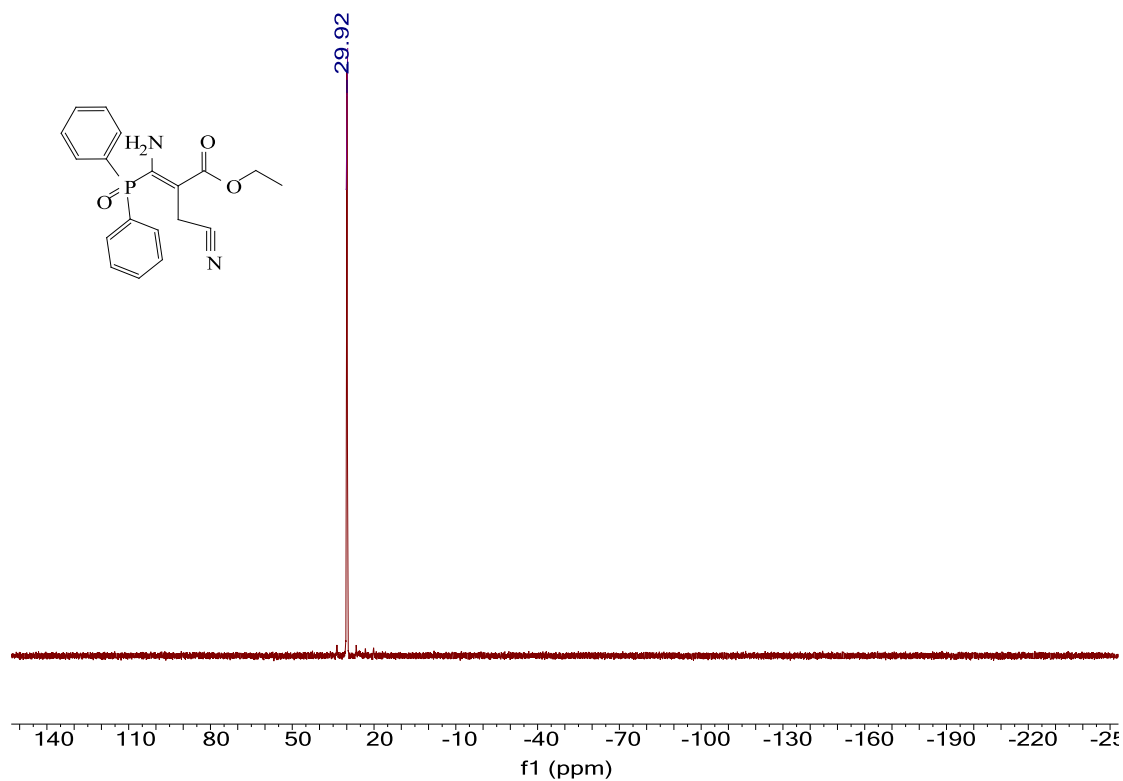
¹H NMR (400 MHz, DMSO-d₆)



¹³C NMR (101 MHz, CDCl₃)

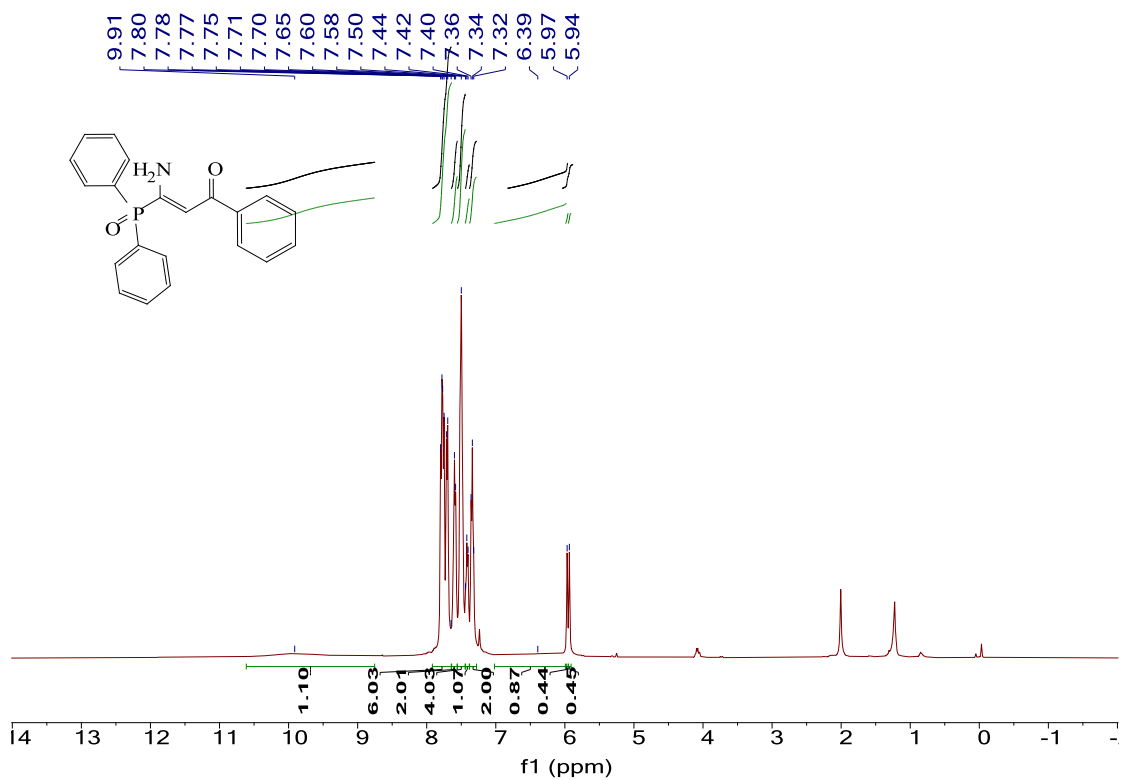


^{31}P NMR (162 MHz, CDCl_3)

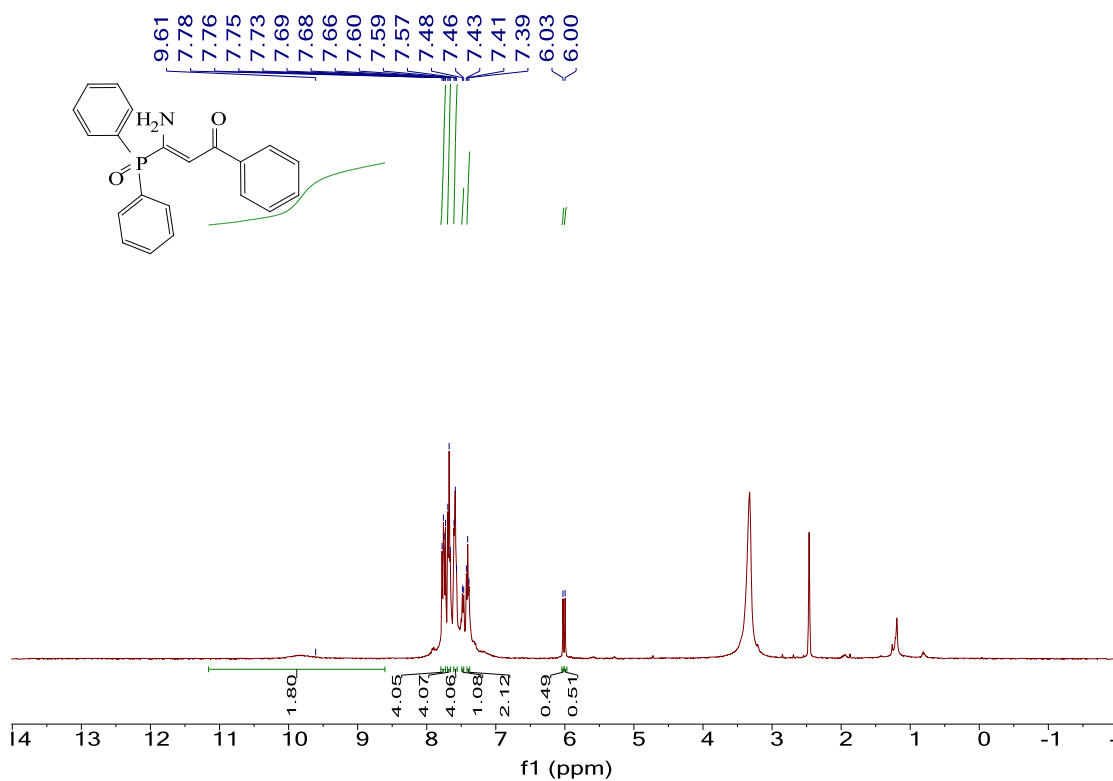


Amino-3-(diphenylphosphoryl)-1-phenylprop-2-en-1-one (19)

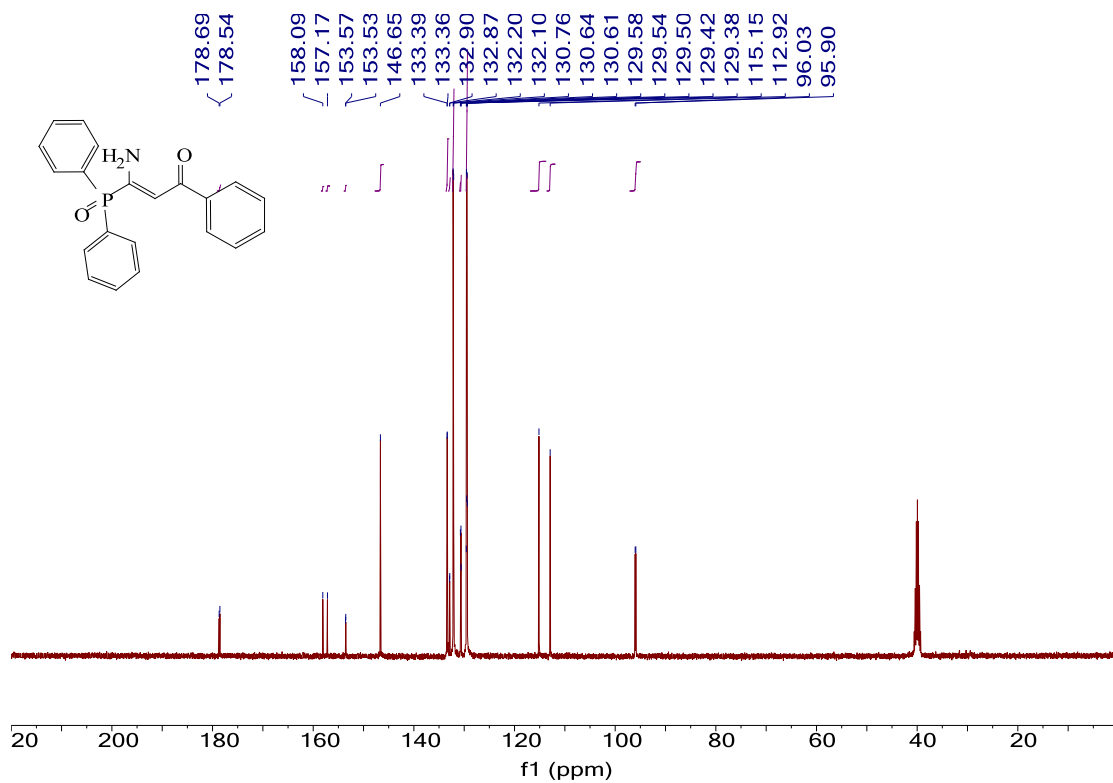
^1H NMR (400 MHz, CDCl_3)



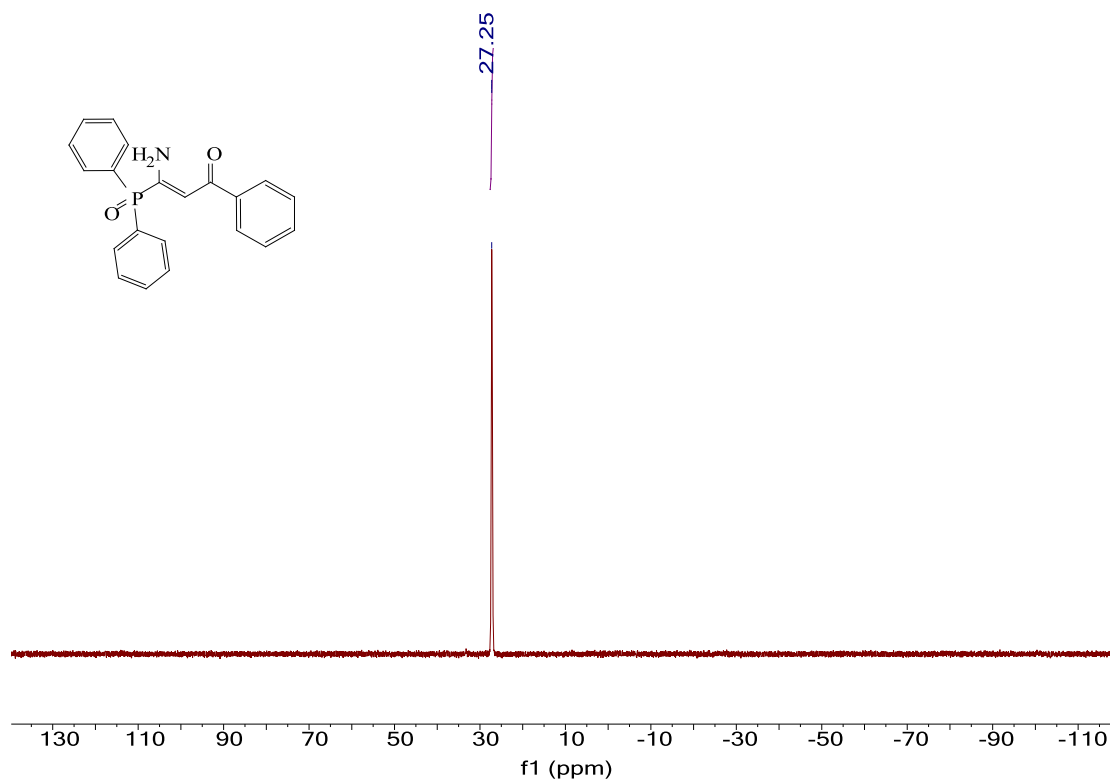
¹H NMR (400 MHz, DMSO-d₆)



¹³C NMR (101 MHz, CDCl₃)

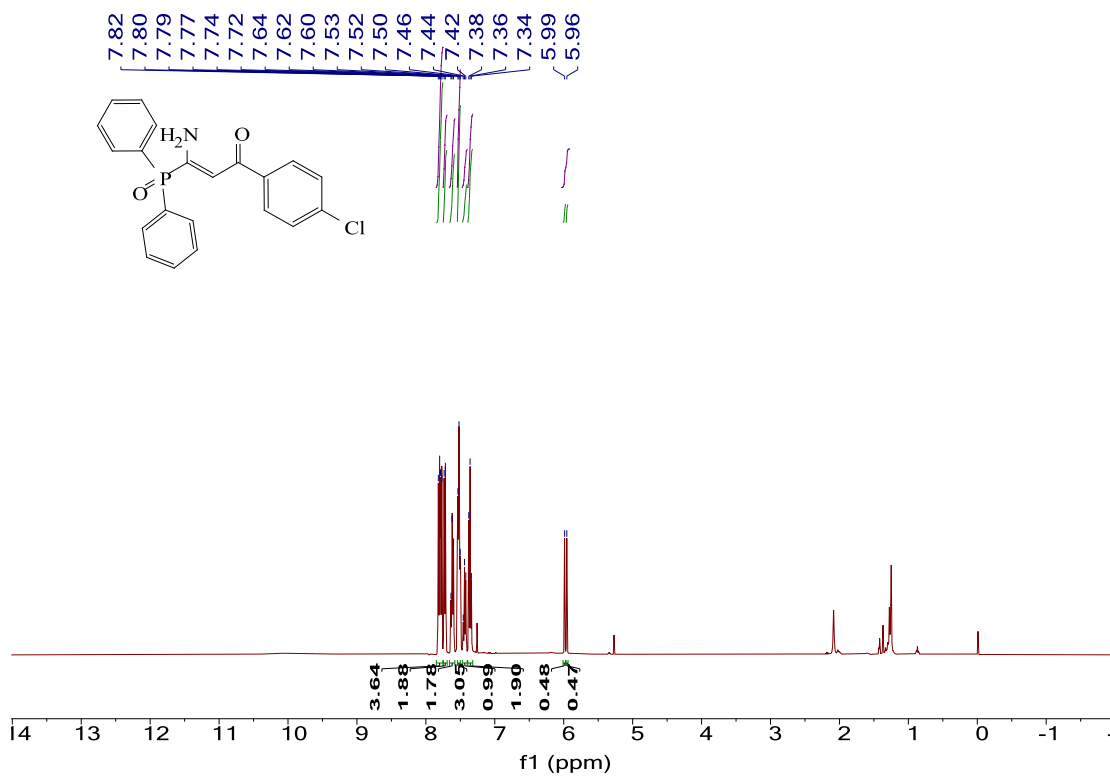


³¹P NMR (162 MHz, CDCl₃)

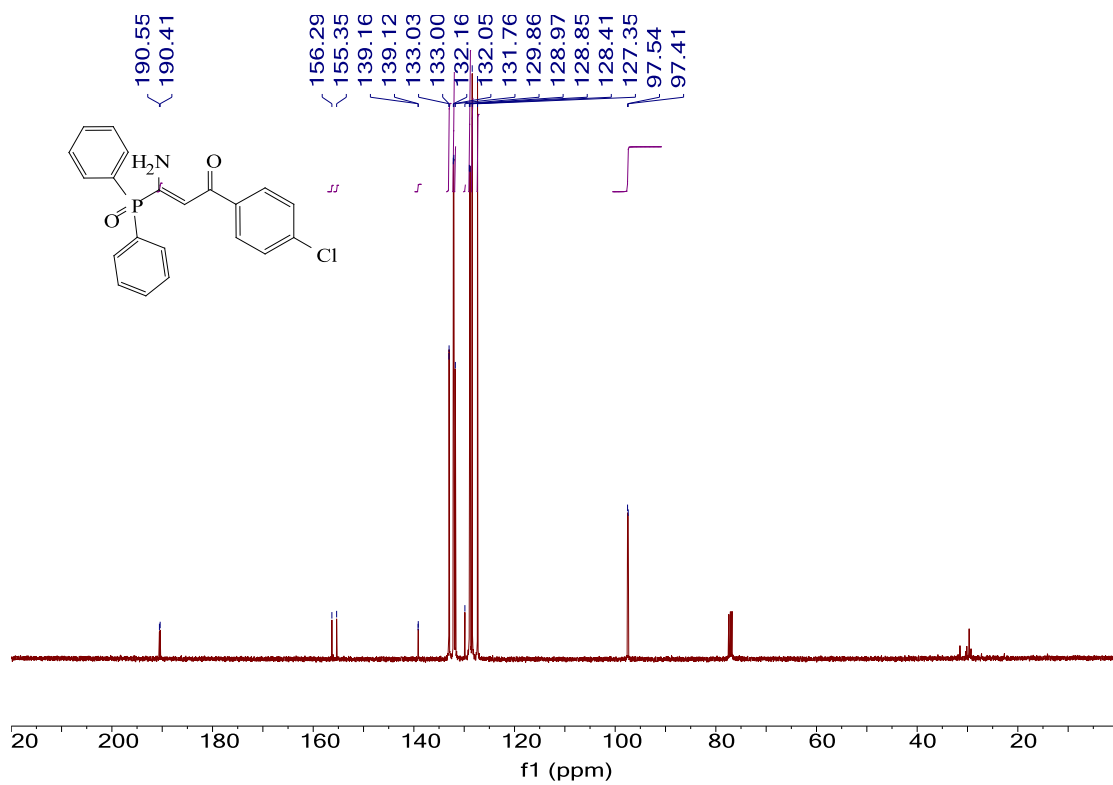


3-Amino-1-(4-chlorophenyl)-3-(diphenylphosphoryl) prop-2-en-1-one (20)

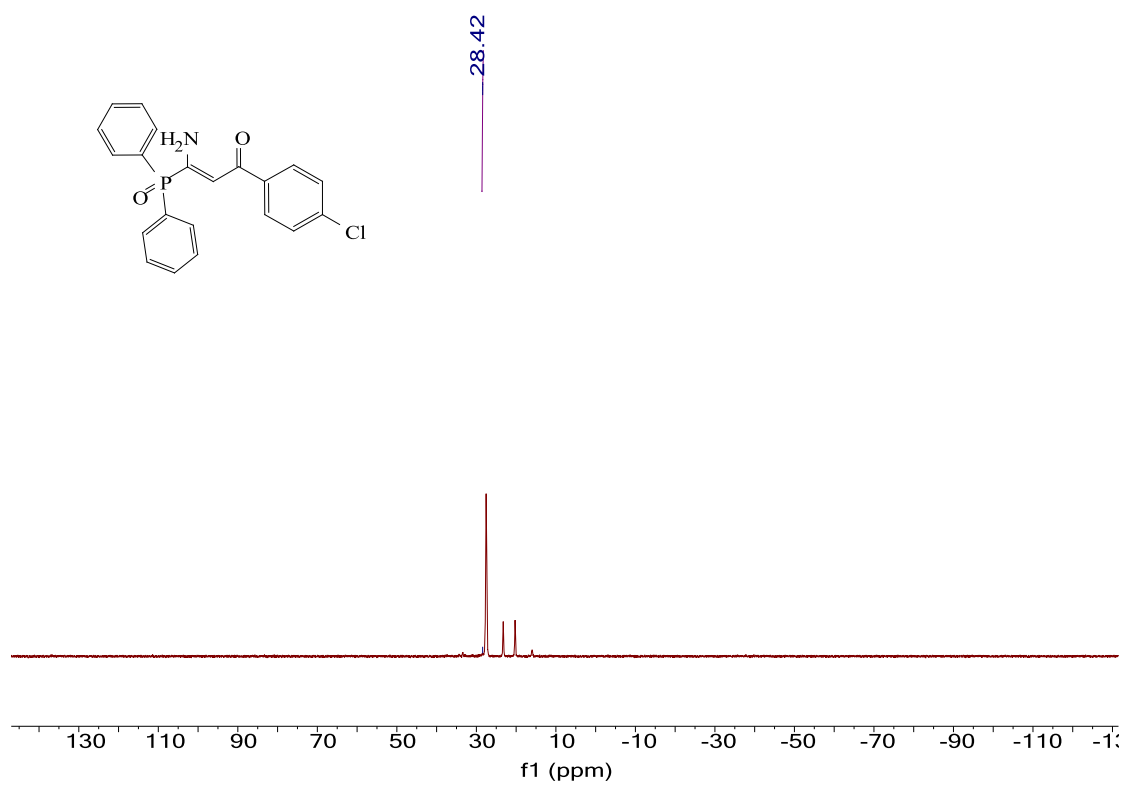
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

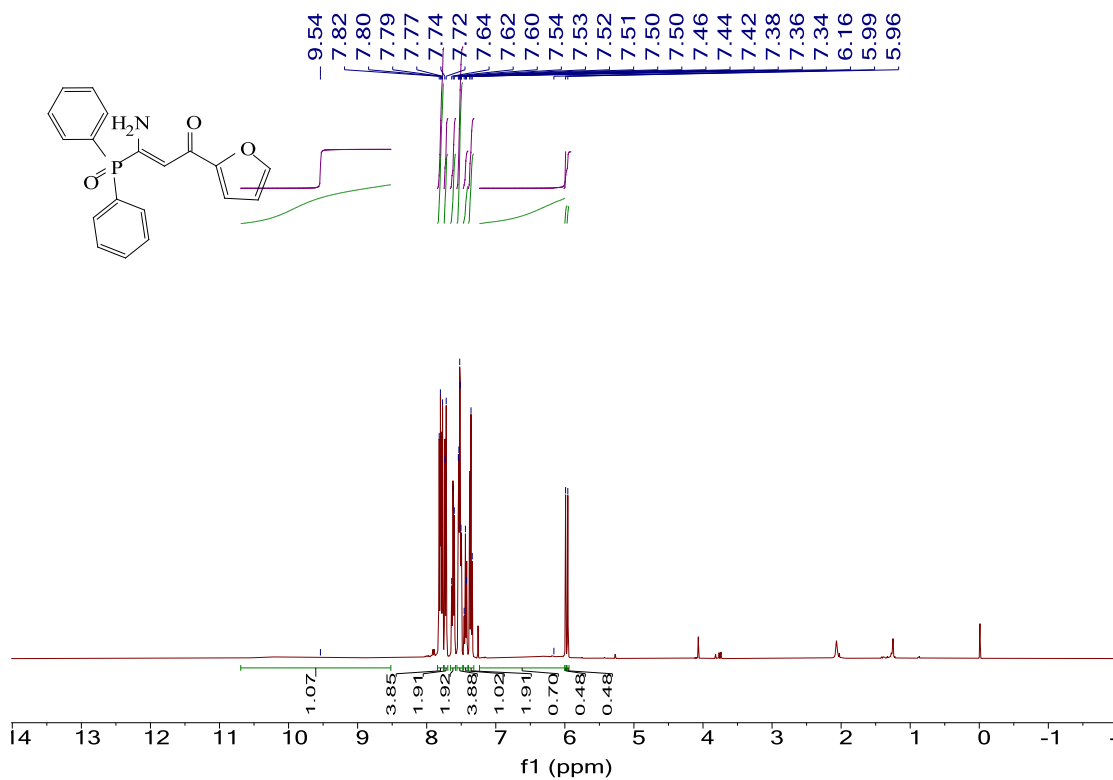


³¹P NMR (162 MHz, CDCl₃)

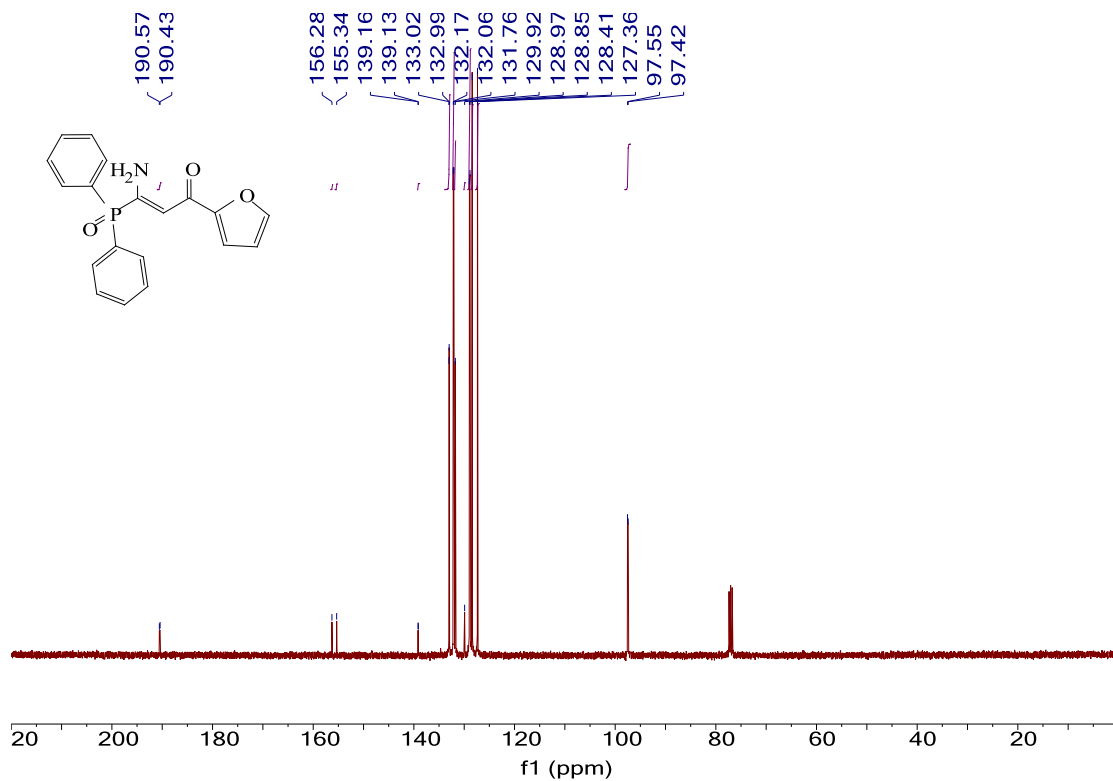


3-Amino-3-(diphenylphosphoryl)-1-(furan-2-yl)prop-2-en-1-one (21)

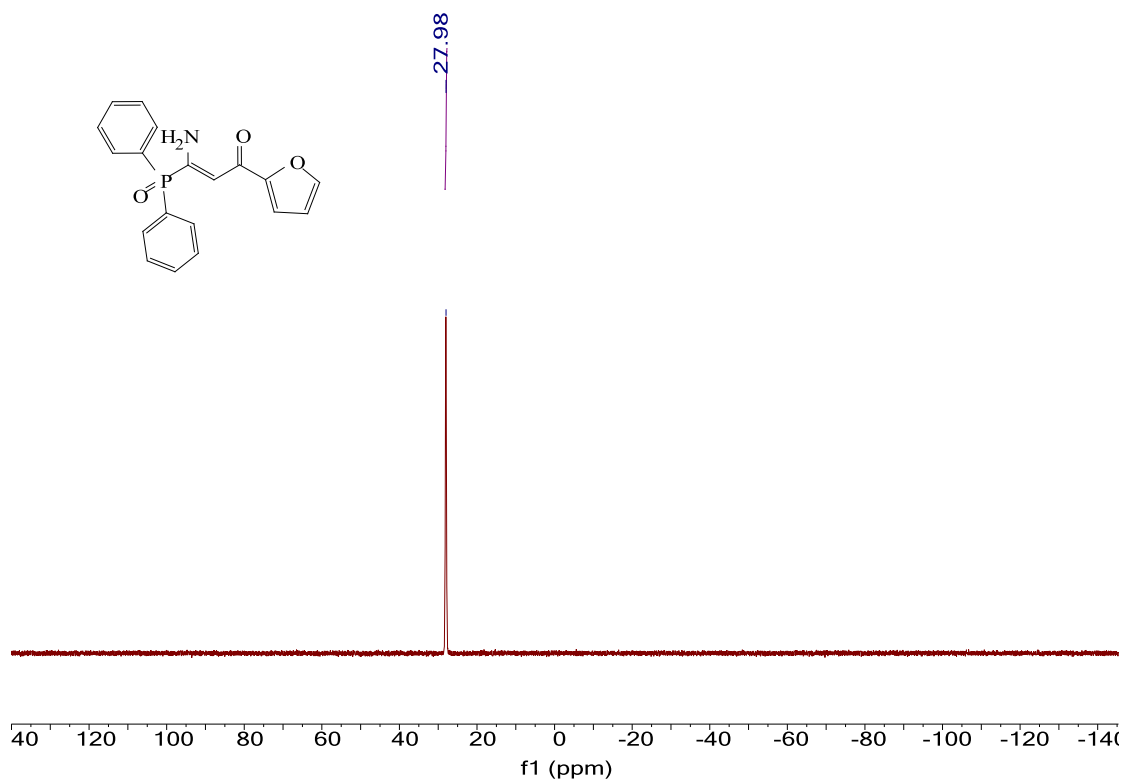
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (101 MHz, CDCl_3)

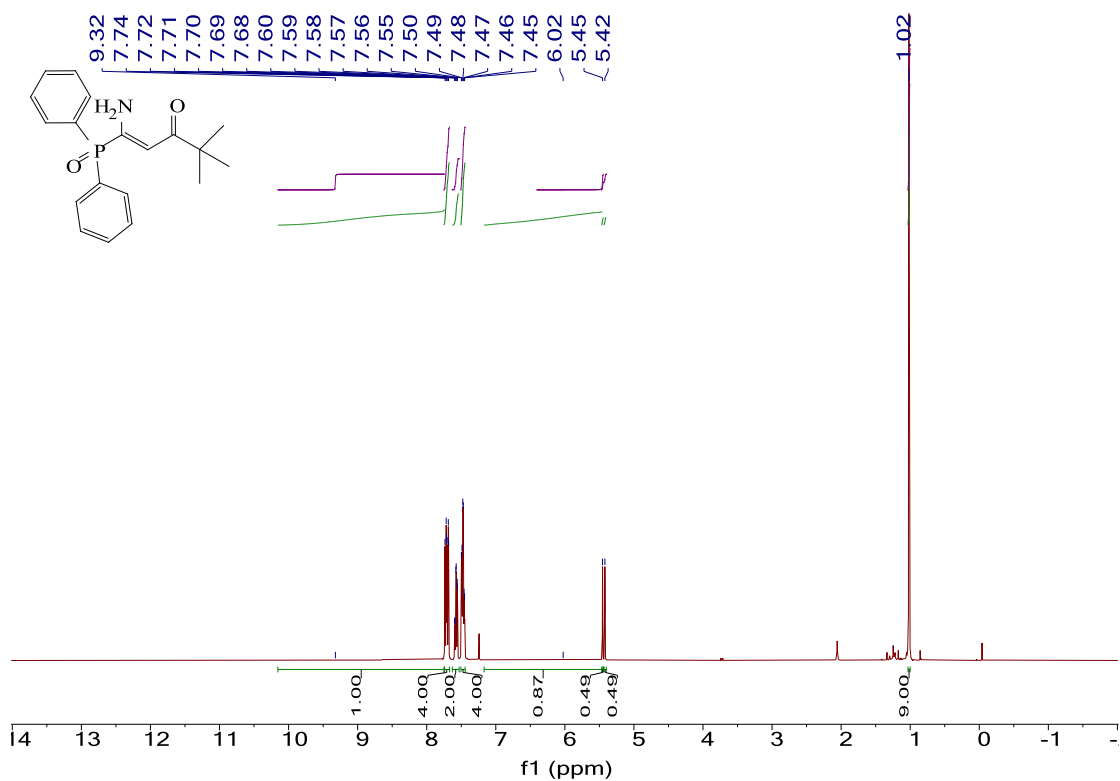


^{31}P NMR (162 MHz, CDCl_3)

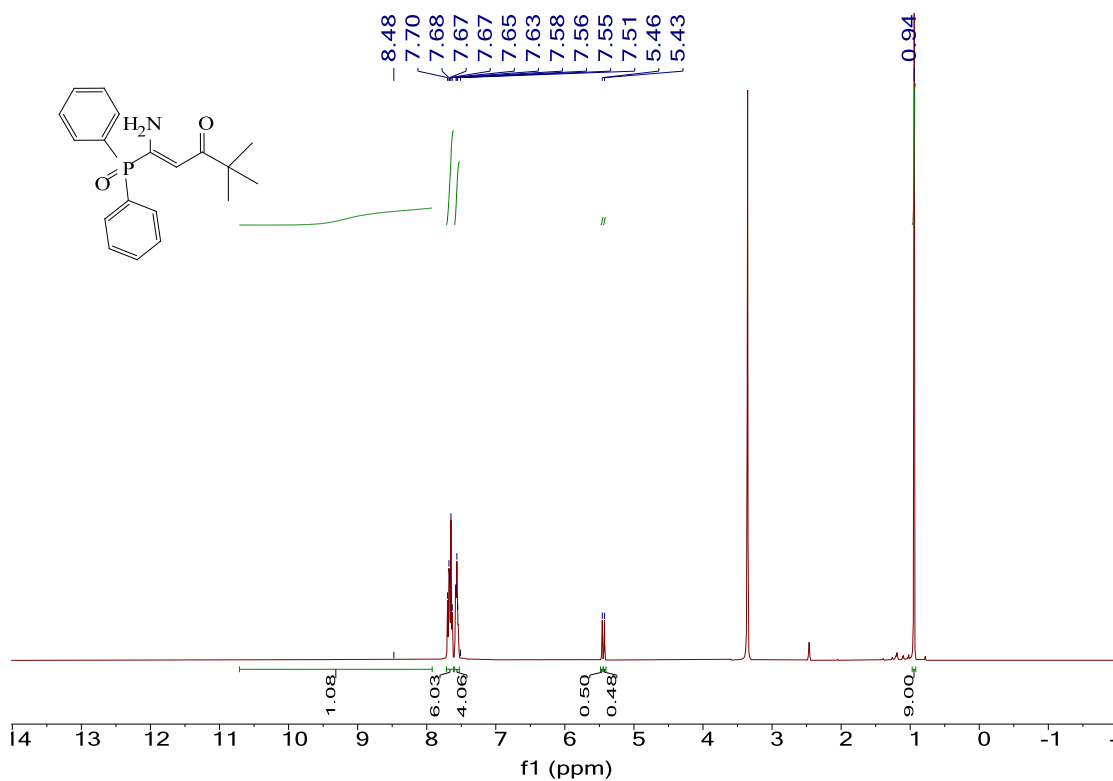


1-Amino-1-(diphenylphosphoryl)-4,4-dimethylpent-1-en-3-one (22)

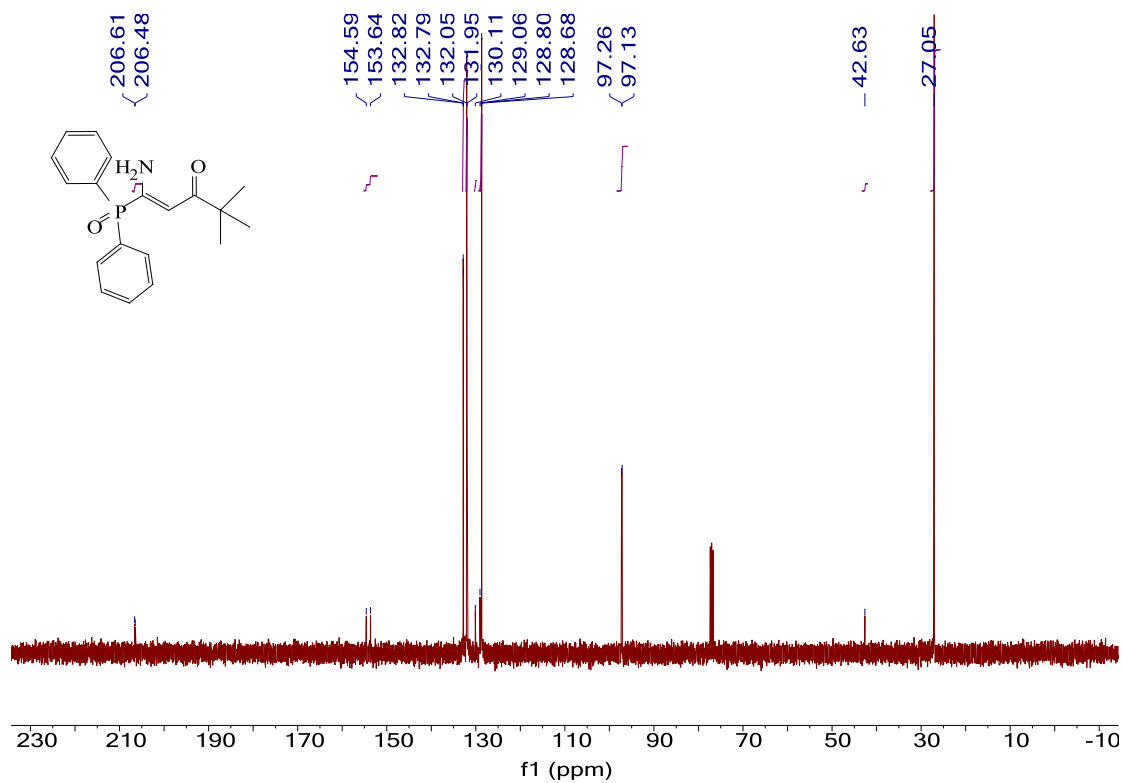
^1H NMR (400 MHz, CDCl_3)



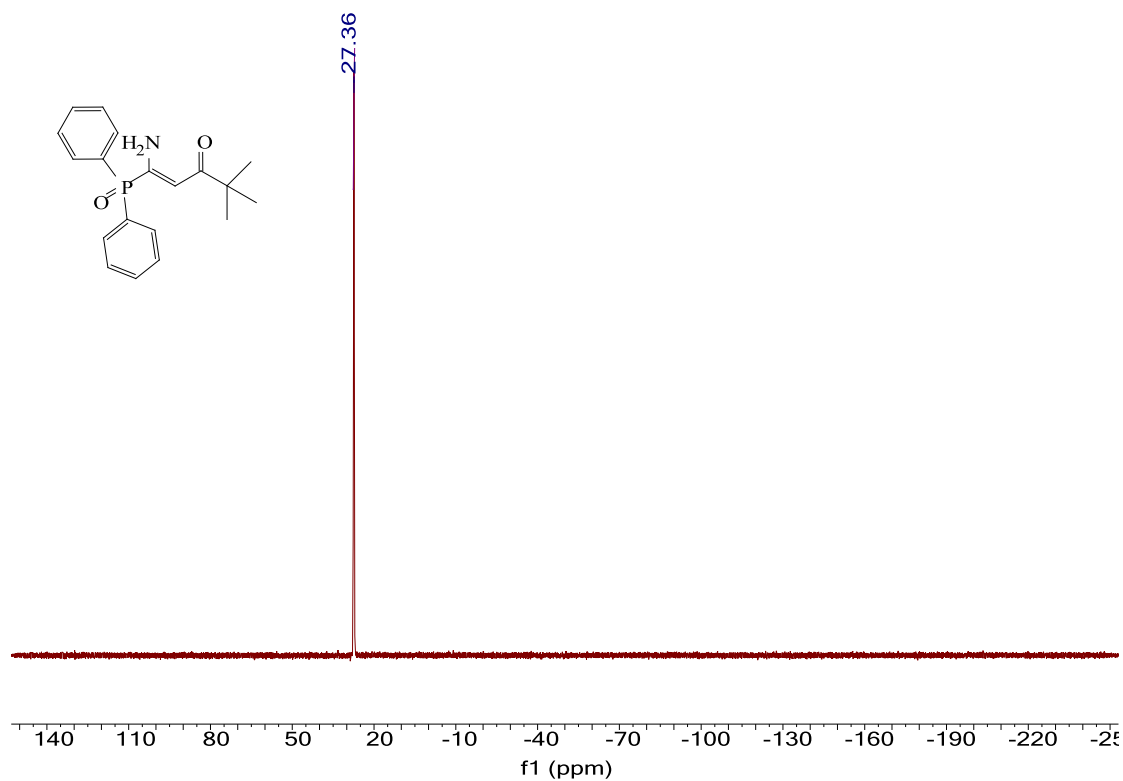
^1H NMR (400 MHz, $\text{DMSO-}d_6$)



^{13}C NMR (101 MHz, CDCl_3)

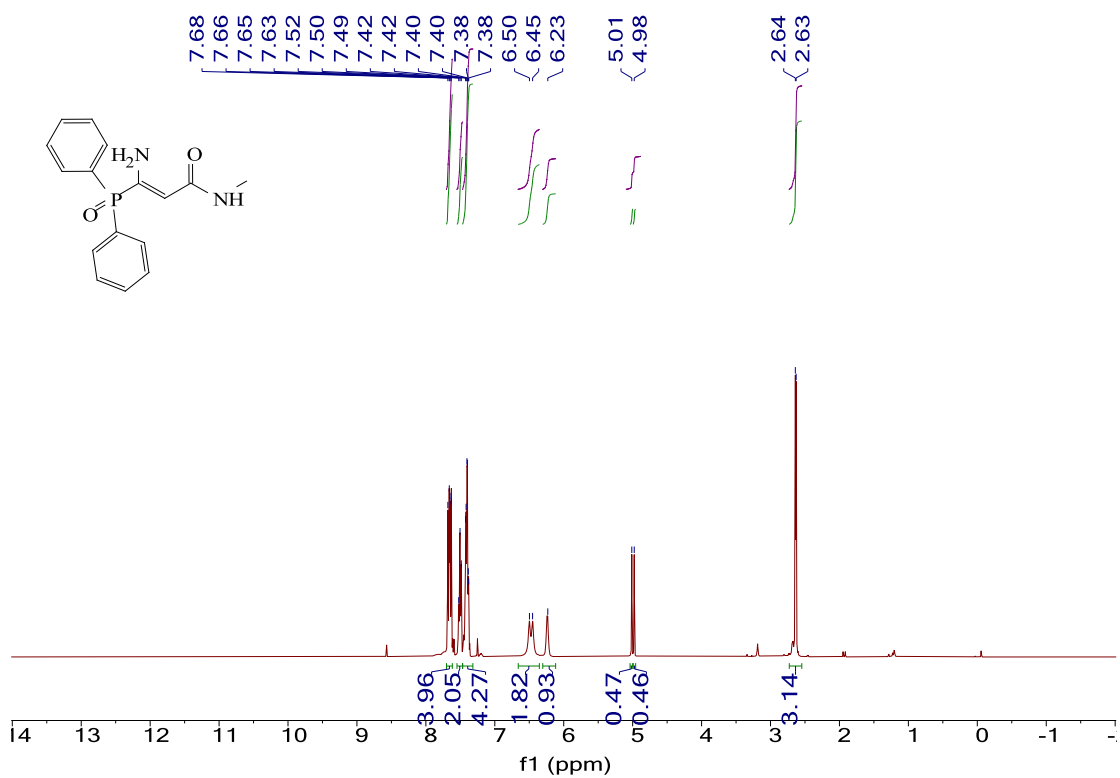


^{31}P NMR (162 MHz, CDCl_3)

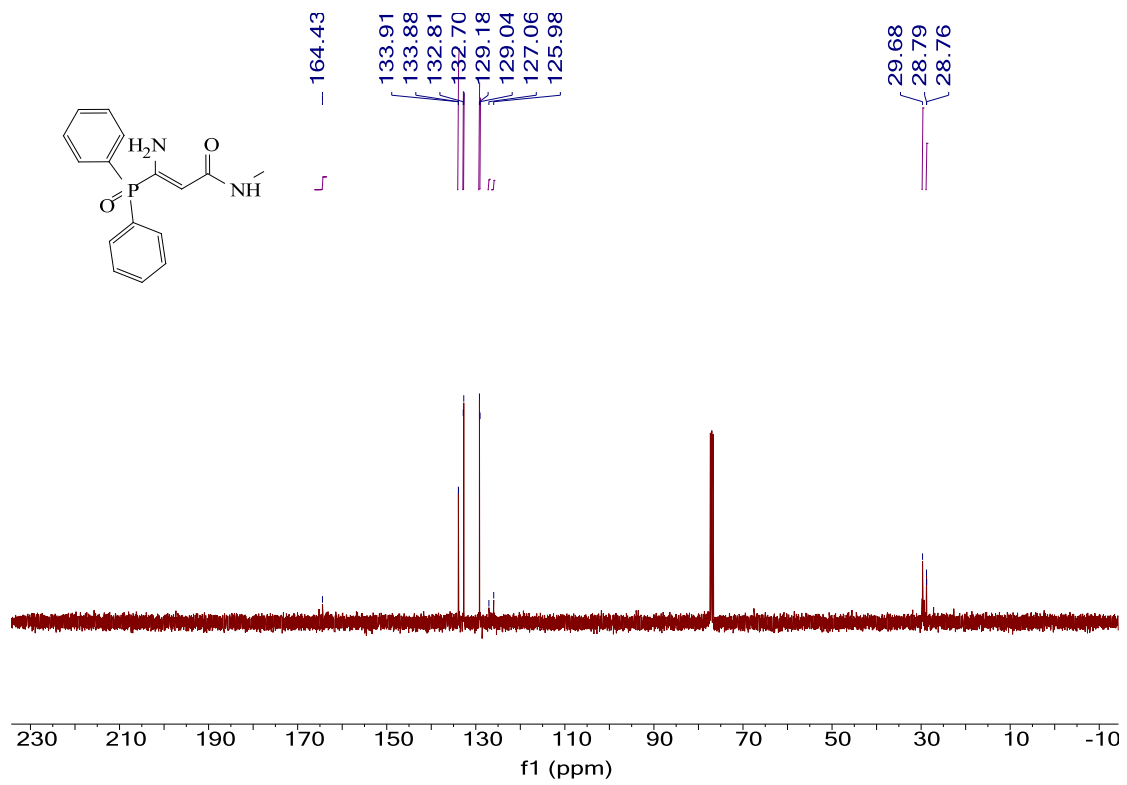


3-Amino-3-(diphenylphosphoryl)-N-methylacrylamide (23).

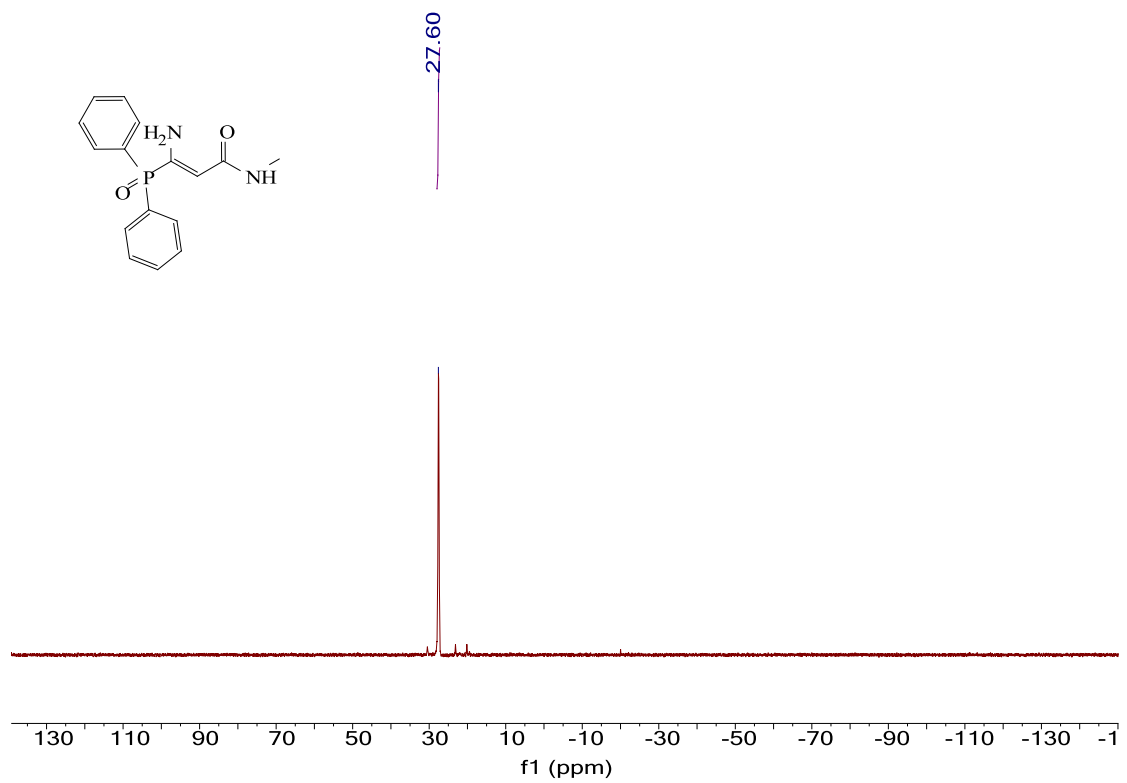
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (101 MHz, CDCl_3)

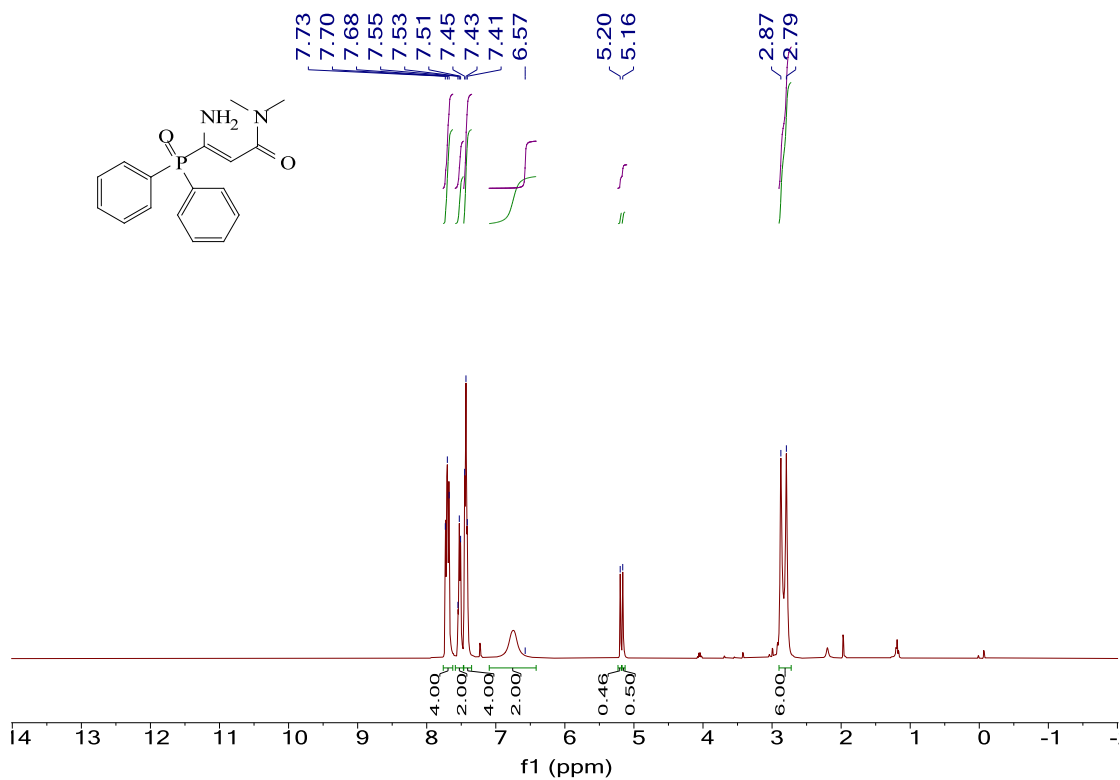


^{31}P NMR (162 MHz, CDCl_3)

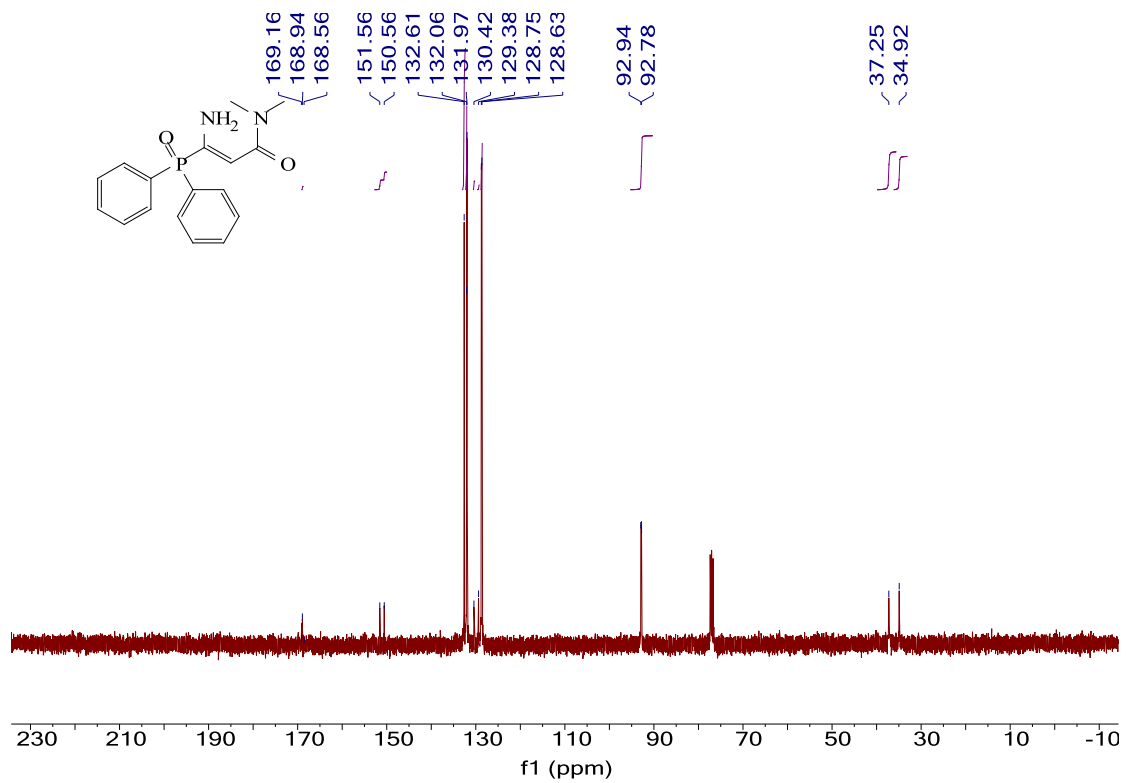


3-Amino-3-(diphenylphosphoryl)-N,N-dimethylacrylamide (24)

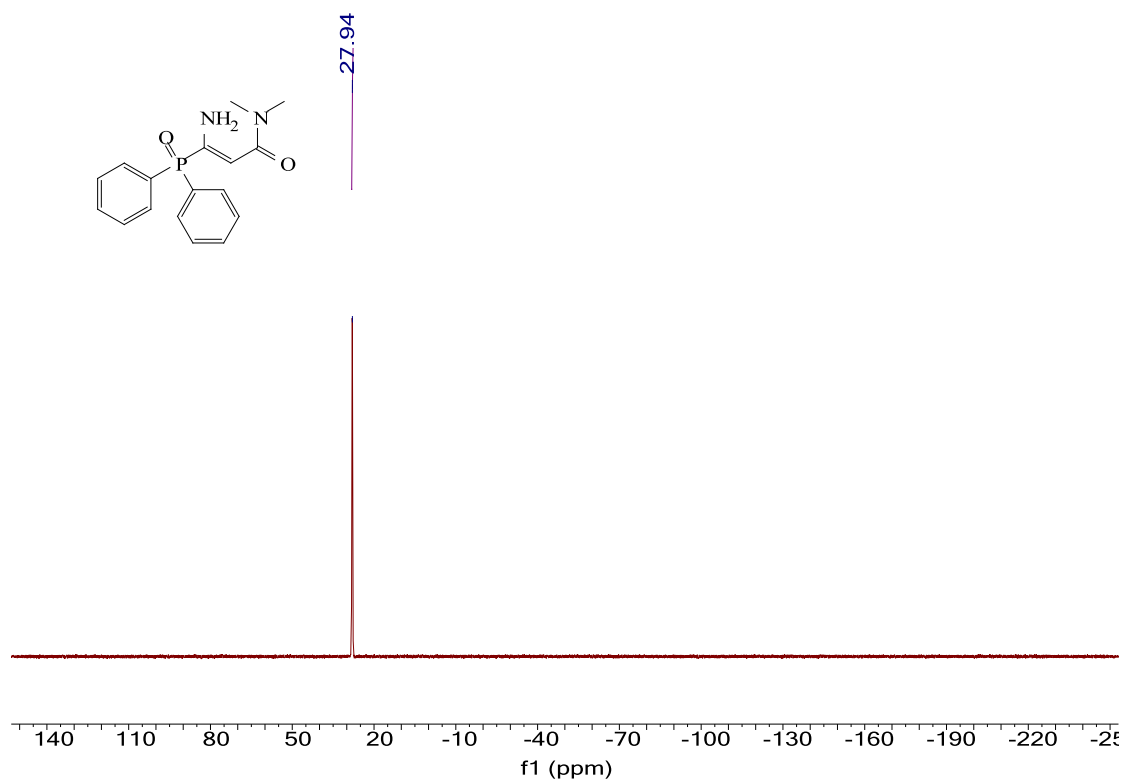
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

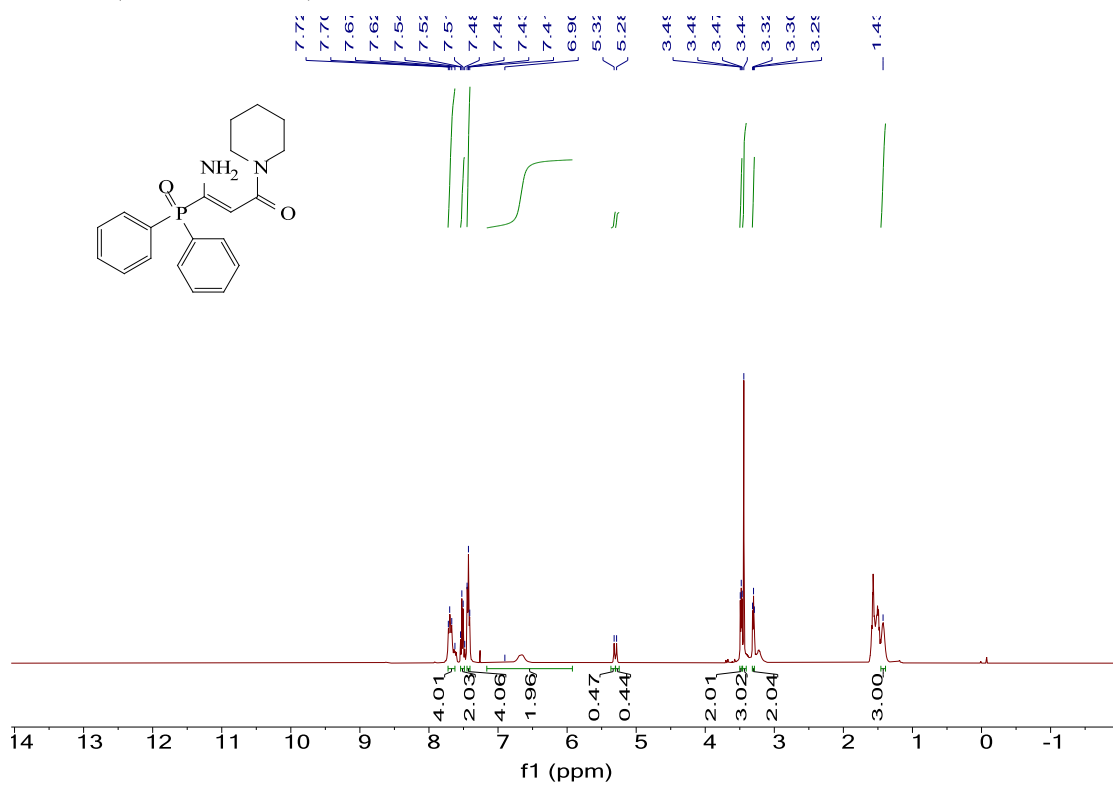


^{31}P NMR (162 MHz, CDCl_3)

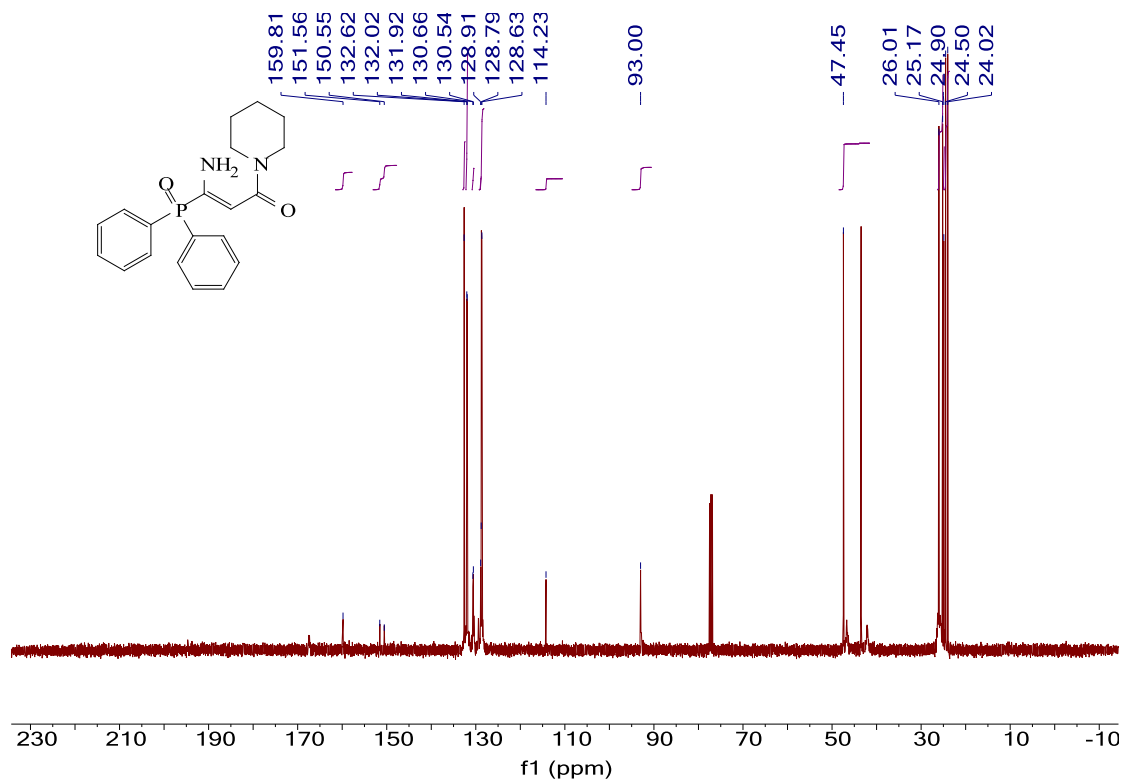


3-Amino-3-(diphenylphosphoryl)-1-(piperidin-1-yl)prop-2-en-1-one (25)

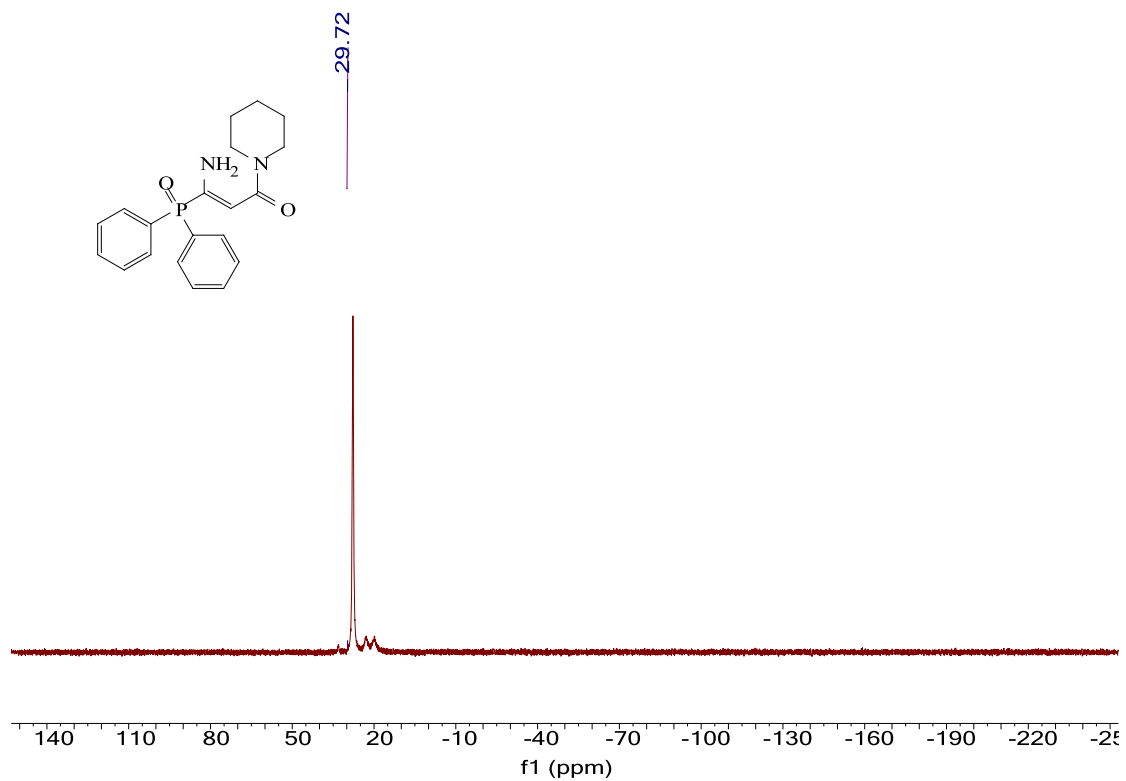
^1H NMR (400 MHz, CDCl_3)



¹³C NMR (101 MHz, CDCl₃)

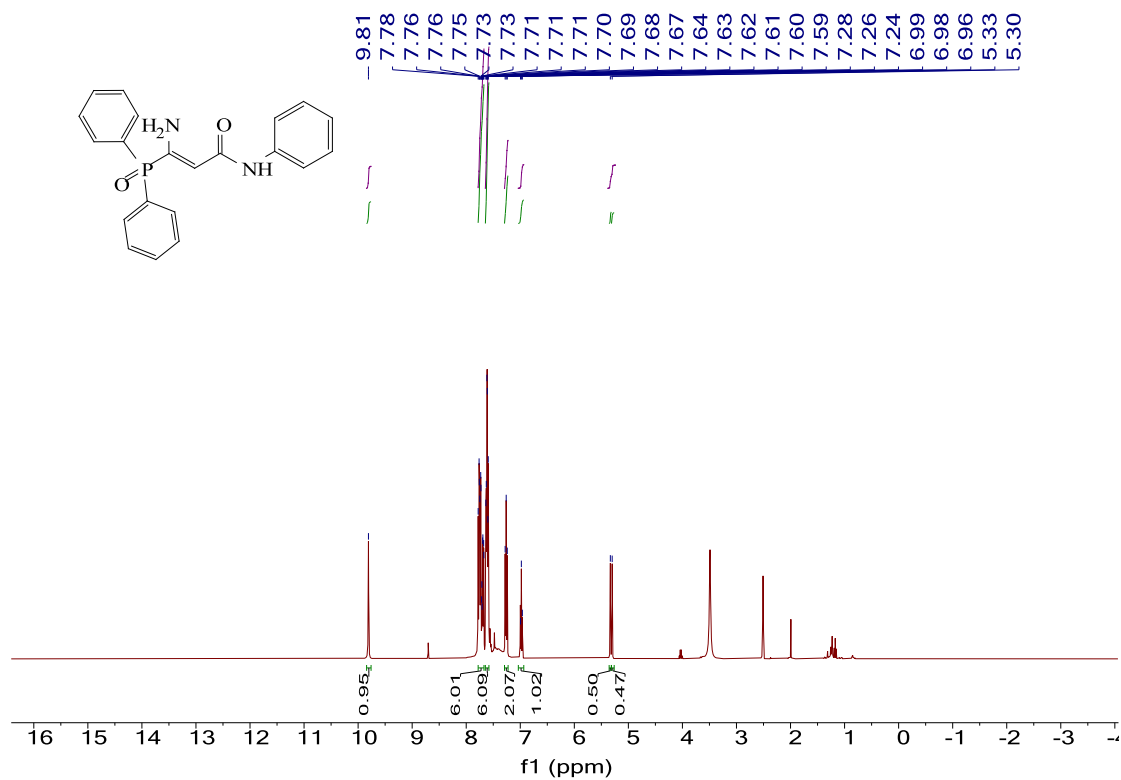


³¹P NMR (162 MHz, CDCl₃)

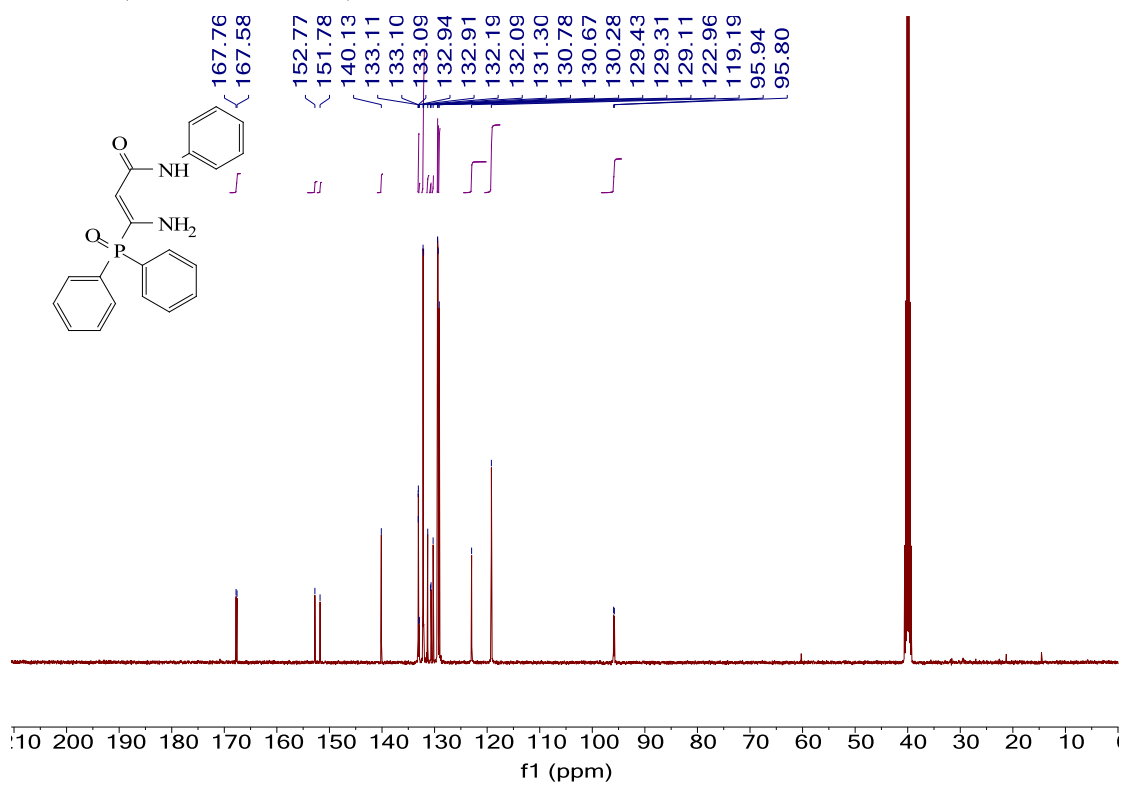


3-Amino-3-(diphenylphosphoryl)-N-phenylacrylamide (26).

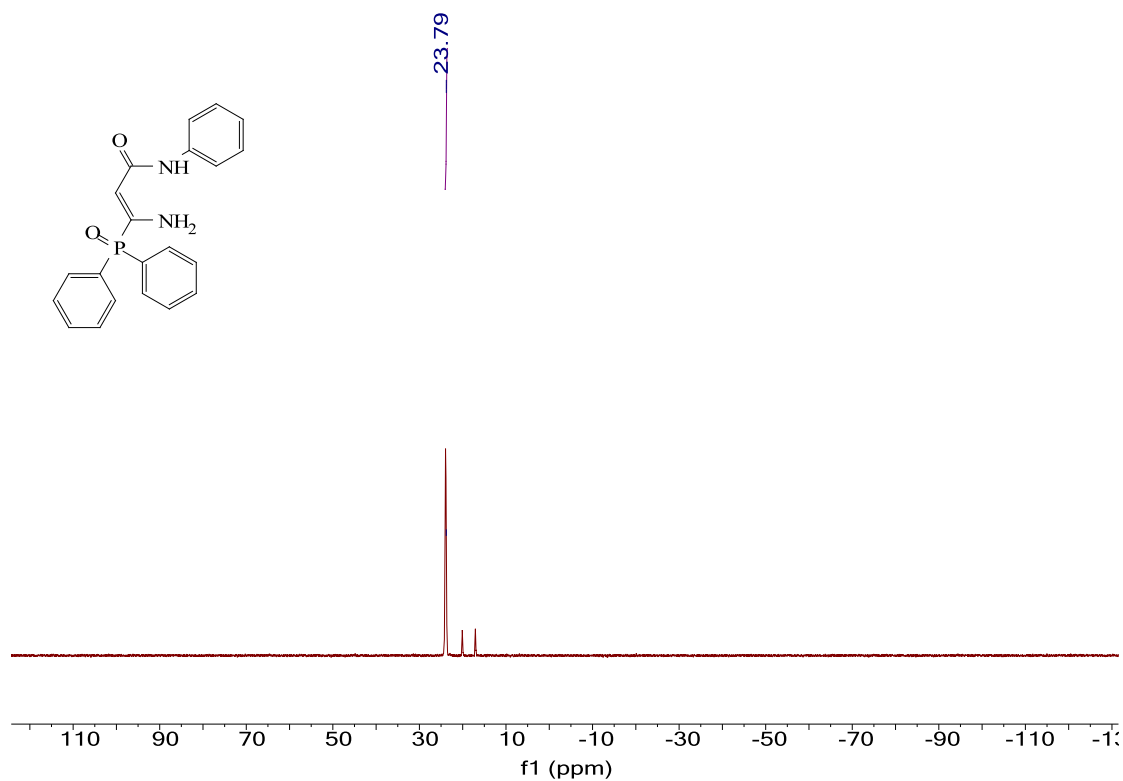
^1H NMR (400 MHz, $\text{DMSO-}d_6$)



^{13}C NMR (101 MHz, $\text{DMSO-}d_6$)

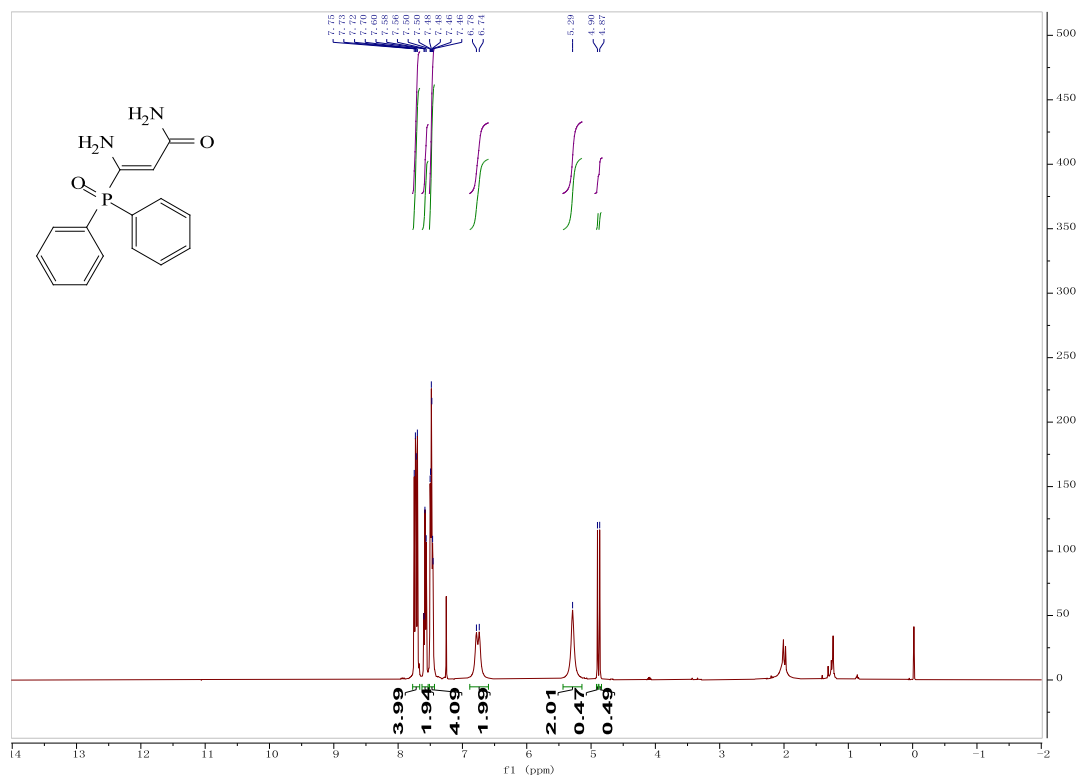


^{31}P NMR (162 MHz, $\text{DMSO-}d_6$)

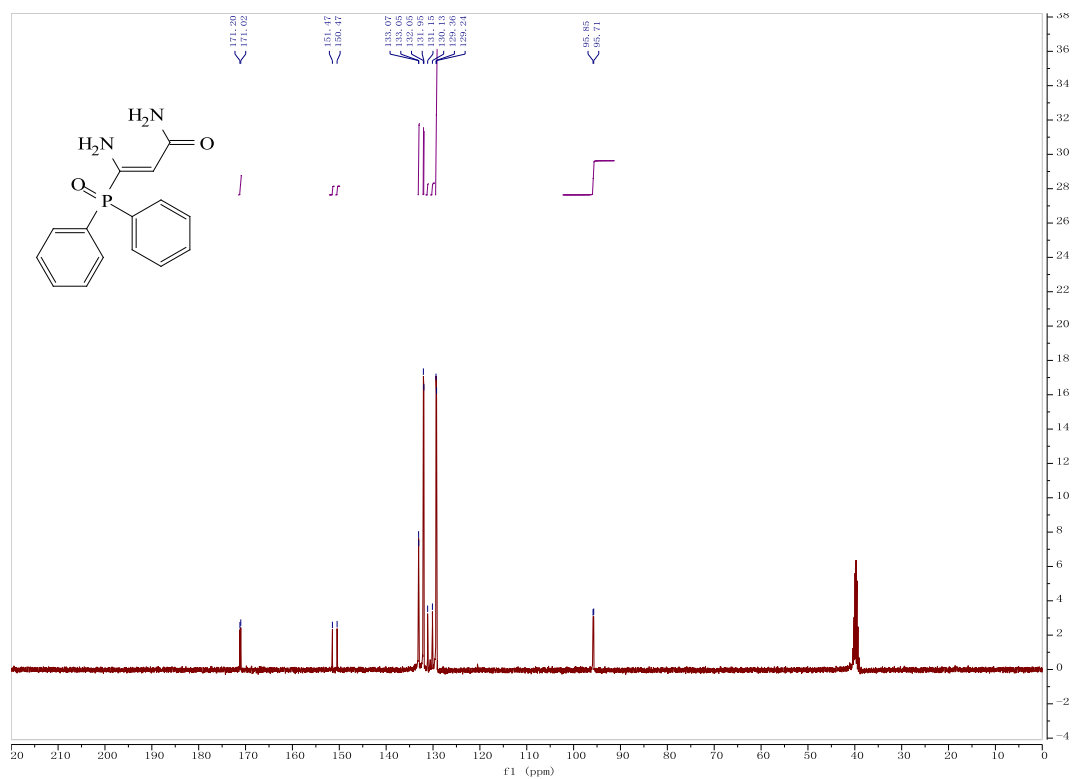


3-Amino-3-(diphenylphosphoryl)acrylamide (27)

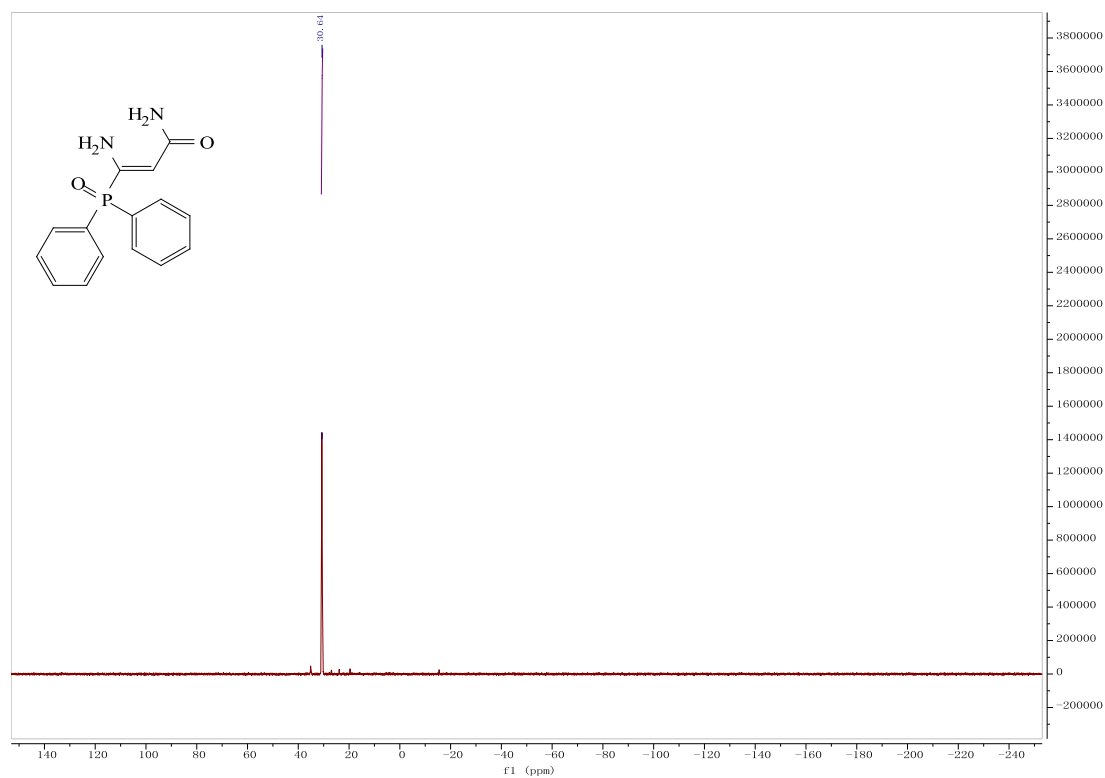
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (101 MHz, $\text{DMSO-}d_6$)

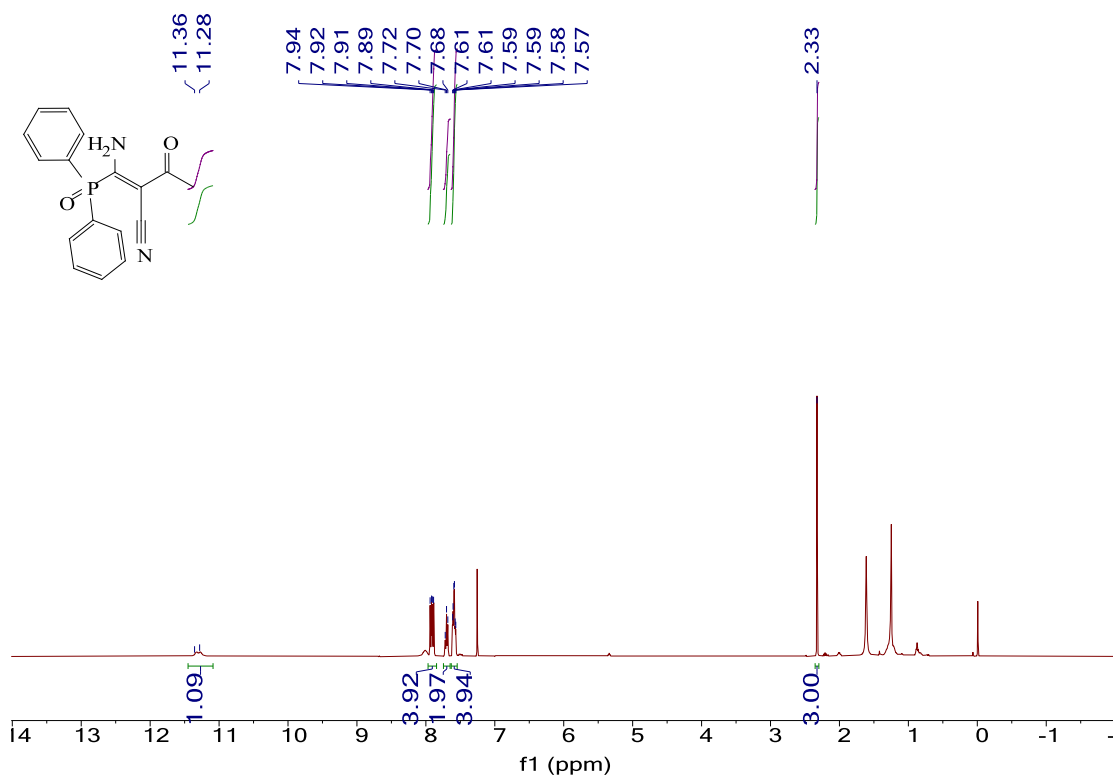


^{31}P NMR (162 MHz, $\text{DMSO-}d_6$)

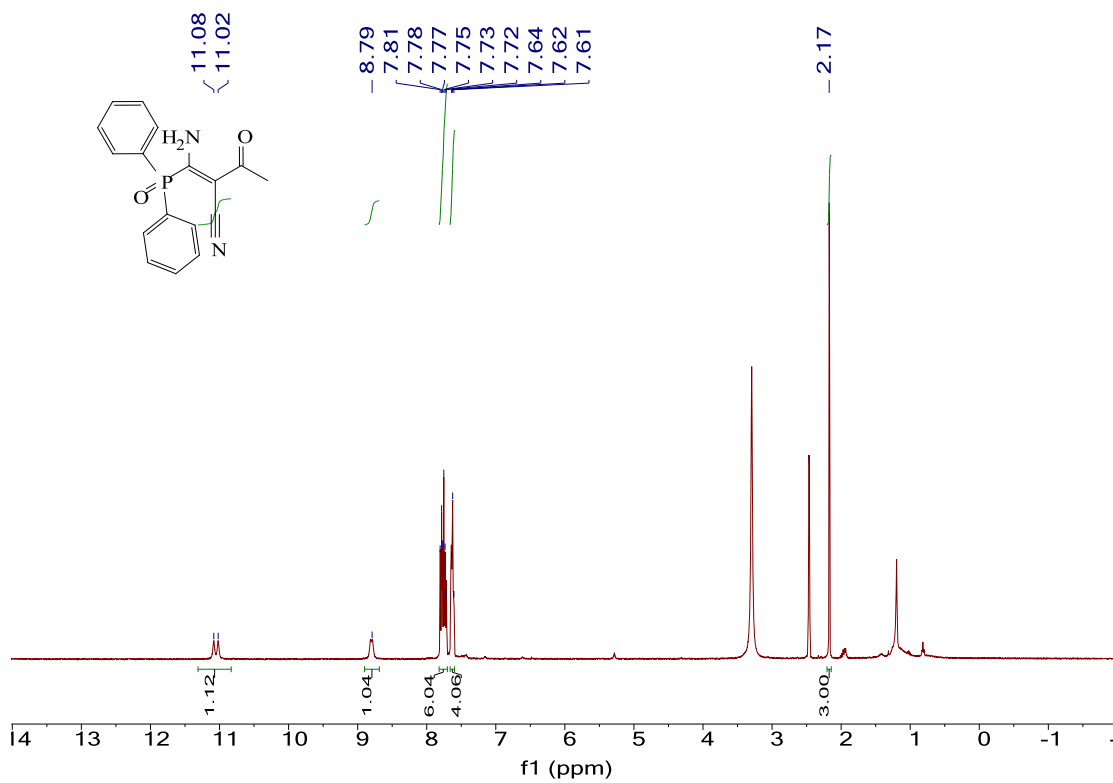


2-(Amino(diphenylphosphoryl)methylene)-3-oxobutanenitrile (28)

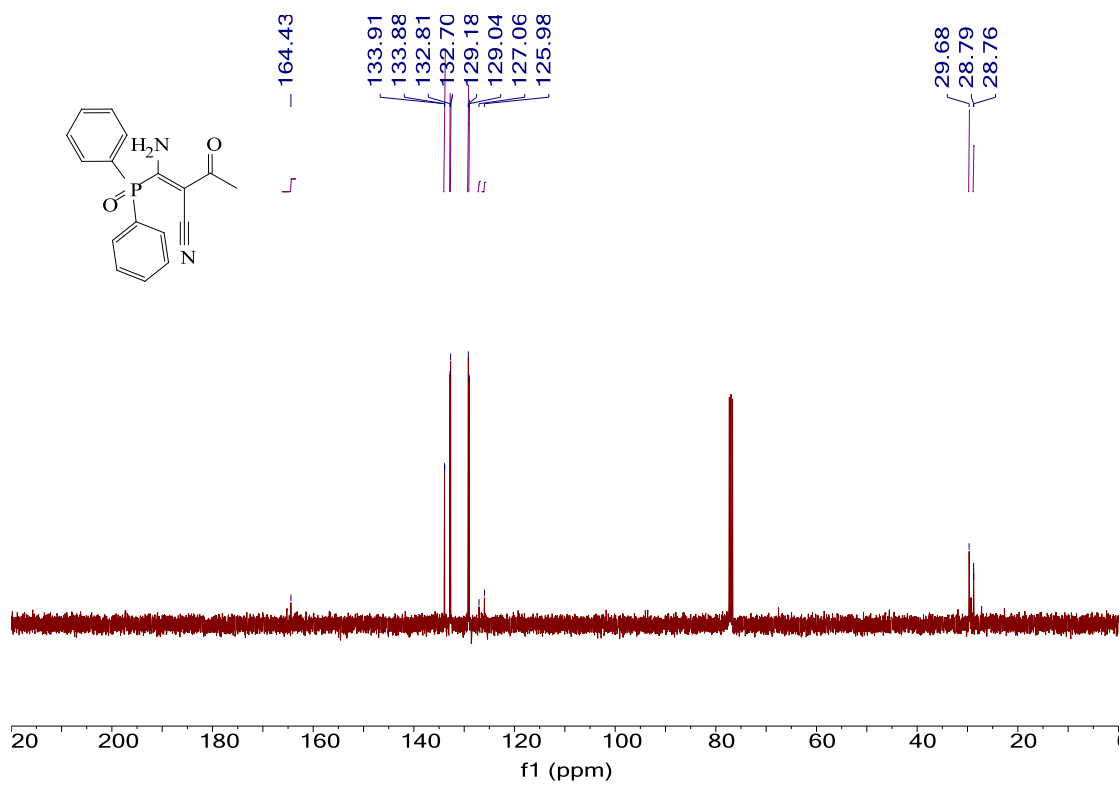
^1H NMR (400 MHz, CDCl_3)



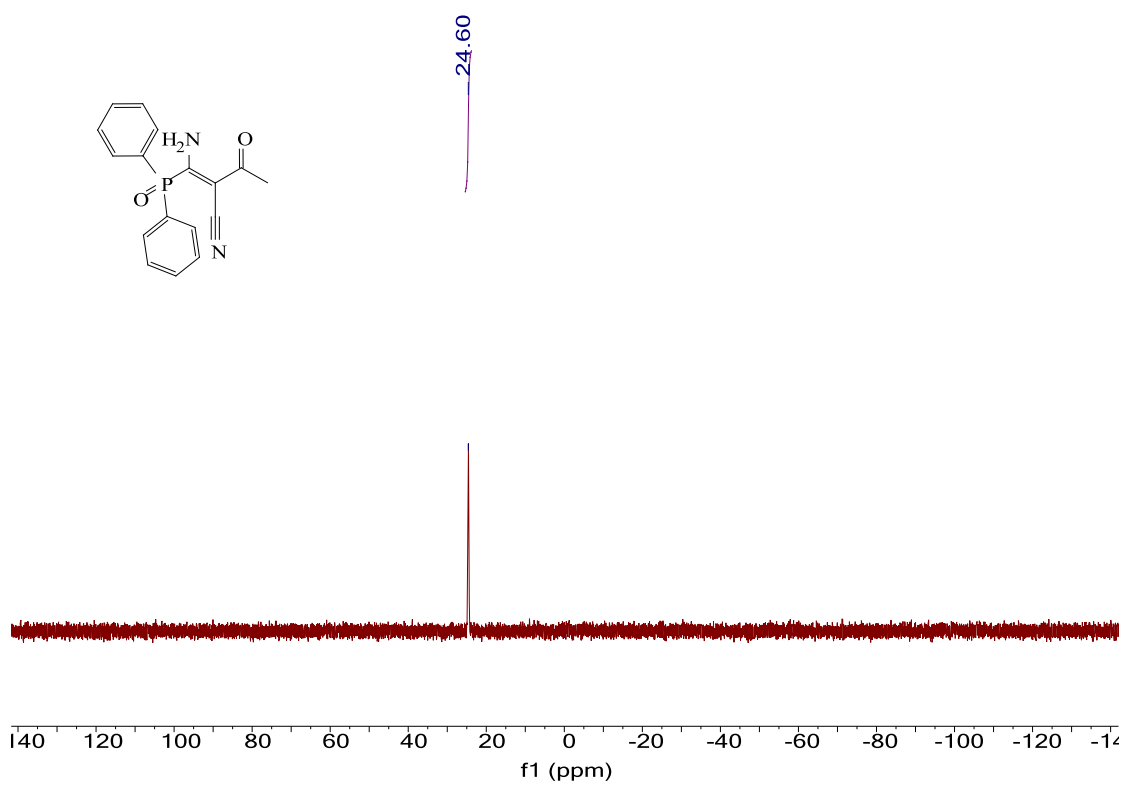
^1H NMR (400 MHz, $\text{DMSO}-d_6$)



^{13}C NMR (101 MHz, CDCl_3)

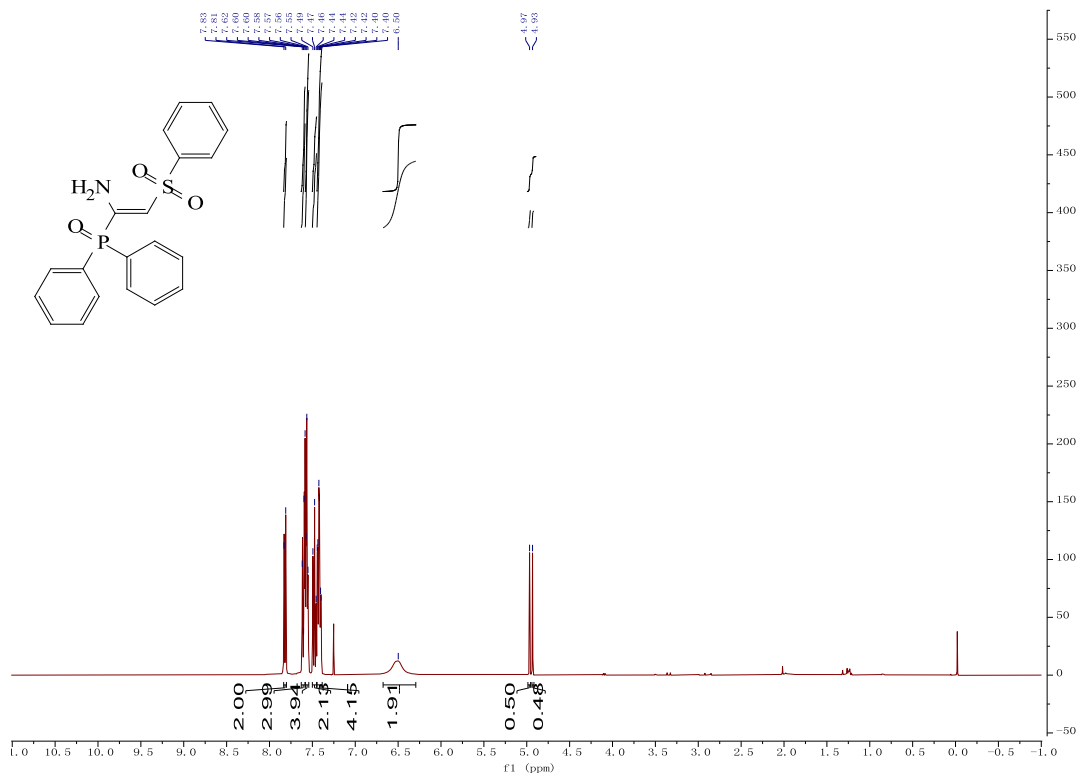


^{31}P NMR (162 MHz, CDCl_3)

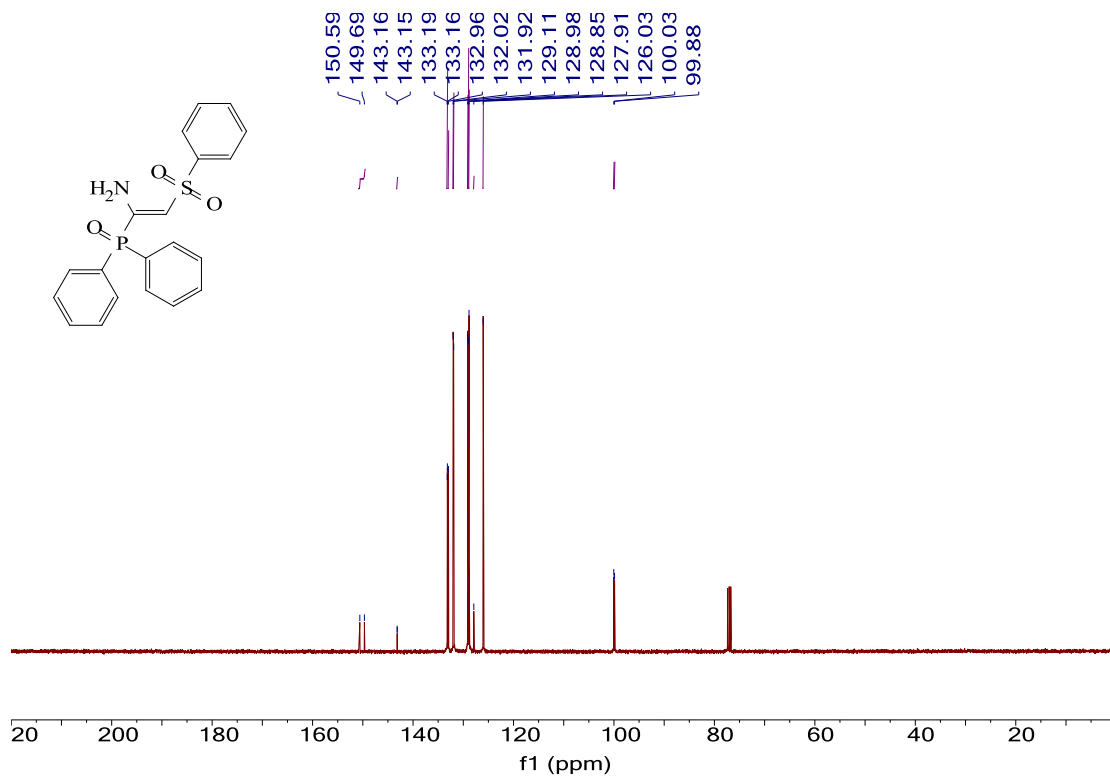


Amino-2-(phenylsulfonyl)vinyl)diphenylphosphine oxide (29)

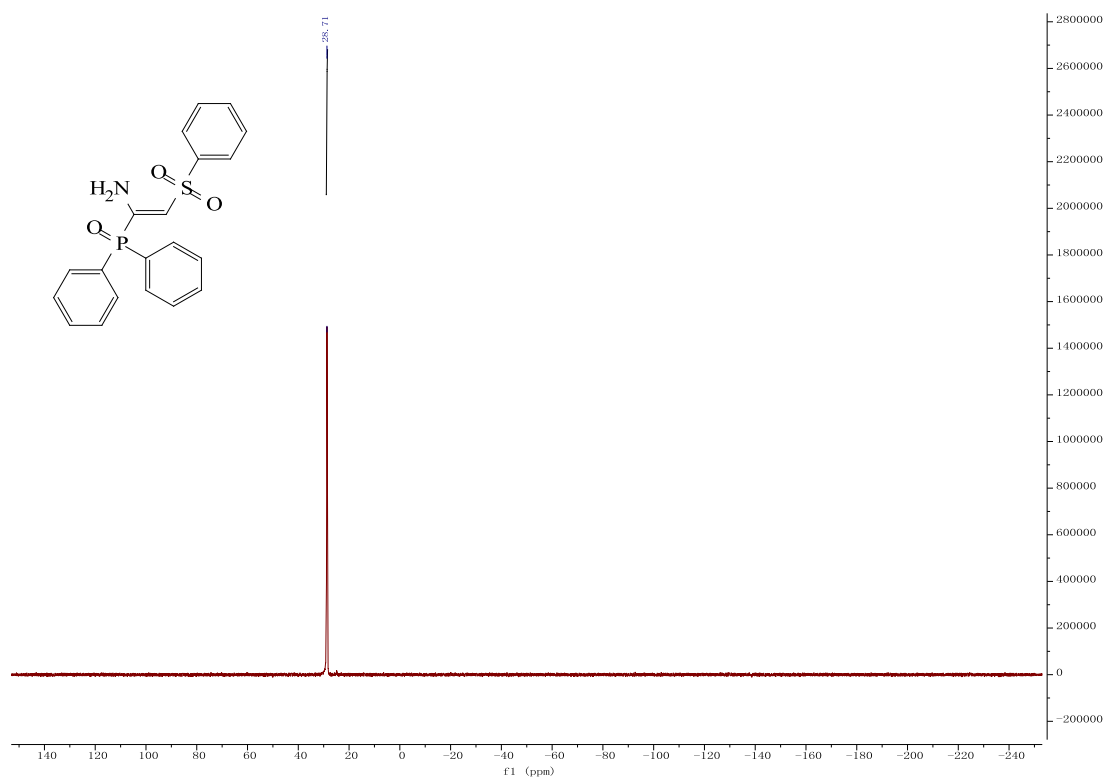
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (101 MHz, CDCl_3)

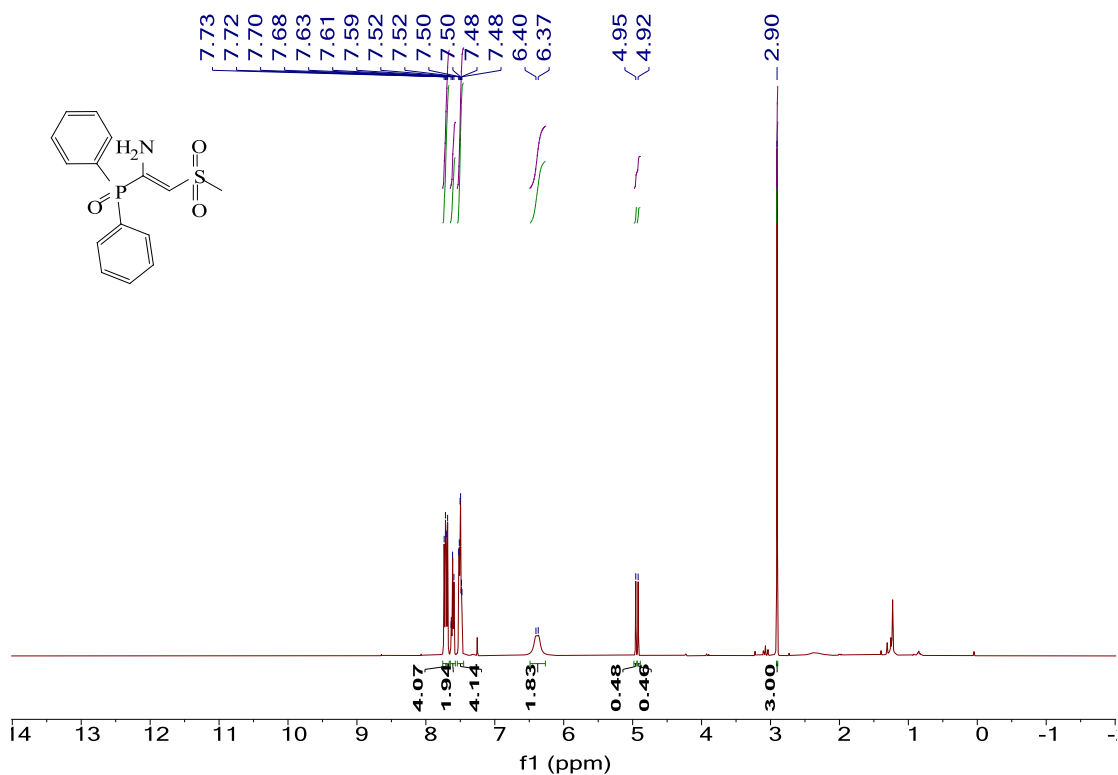


^{31}P NMR (162 MHz, CDCl_3)

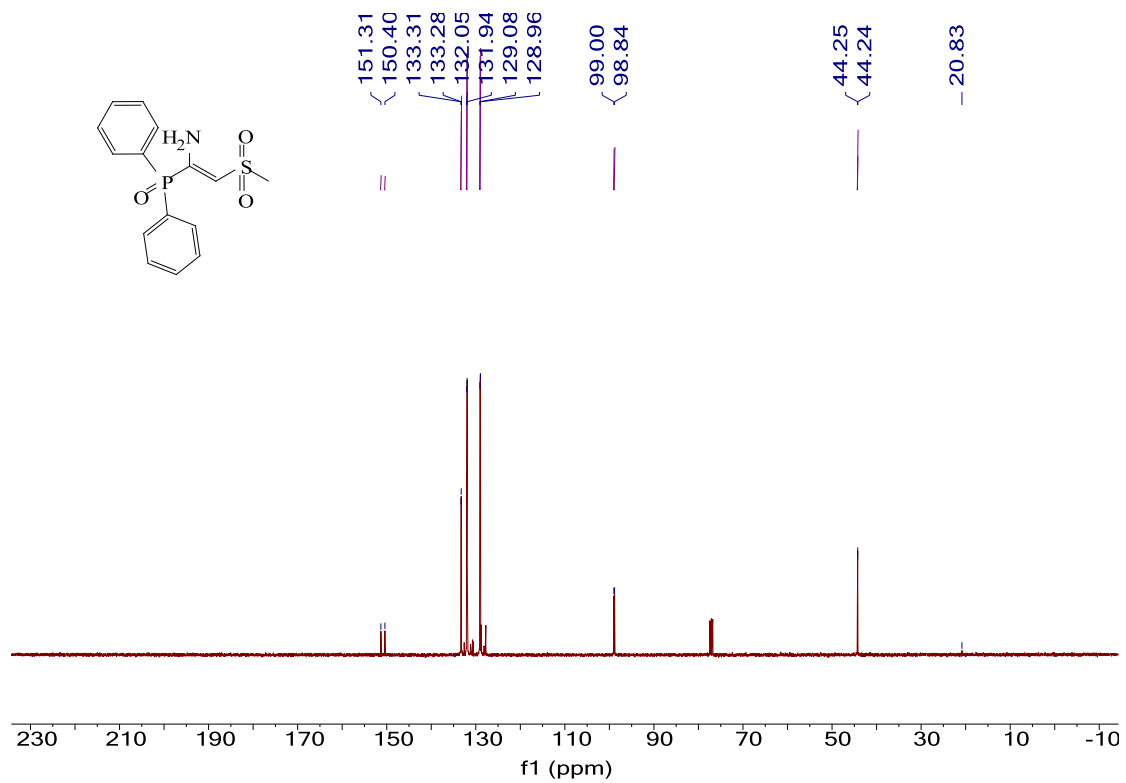


Amino-2-(methylsulfonyl)vinyl)diphenylphosphine oxide) (30)

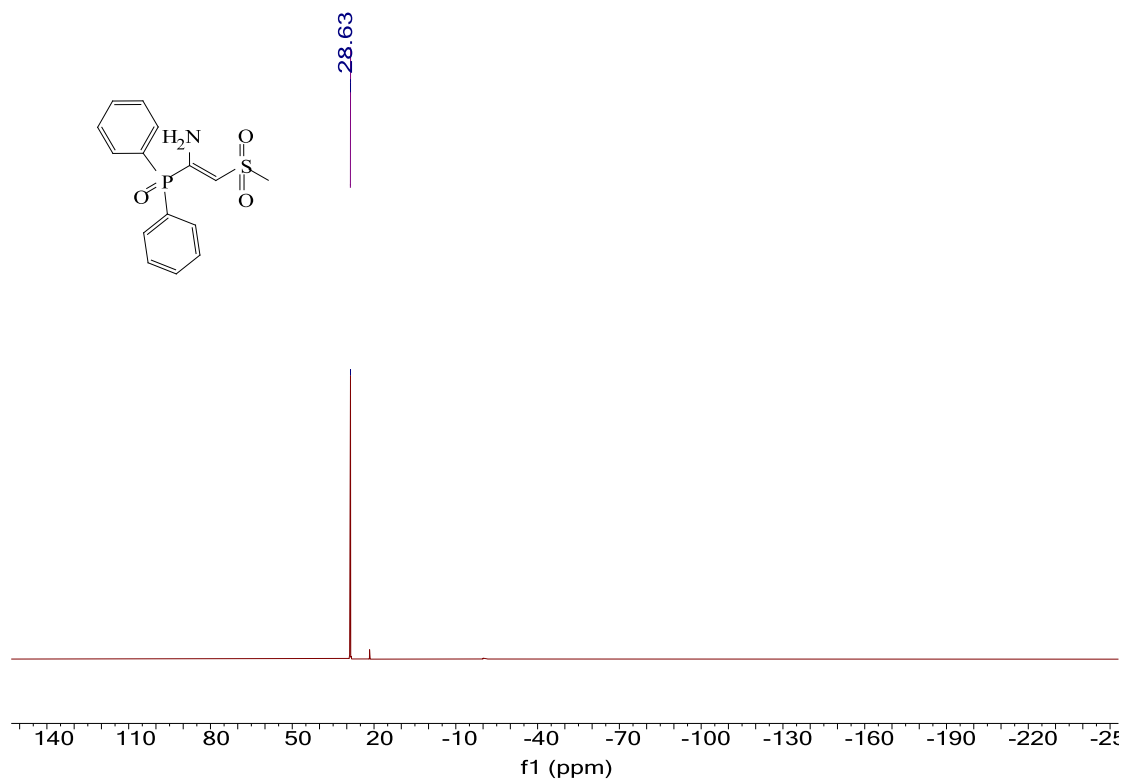
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (101 MHz, CDCl_3)

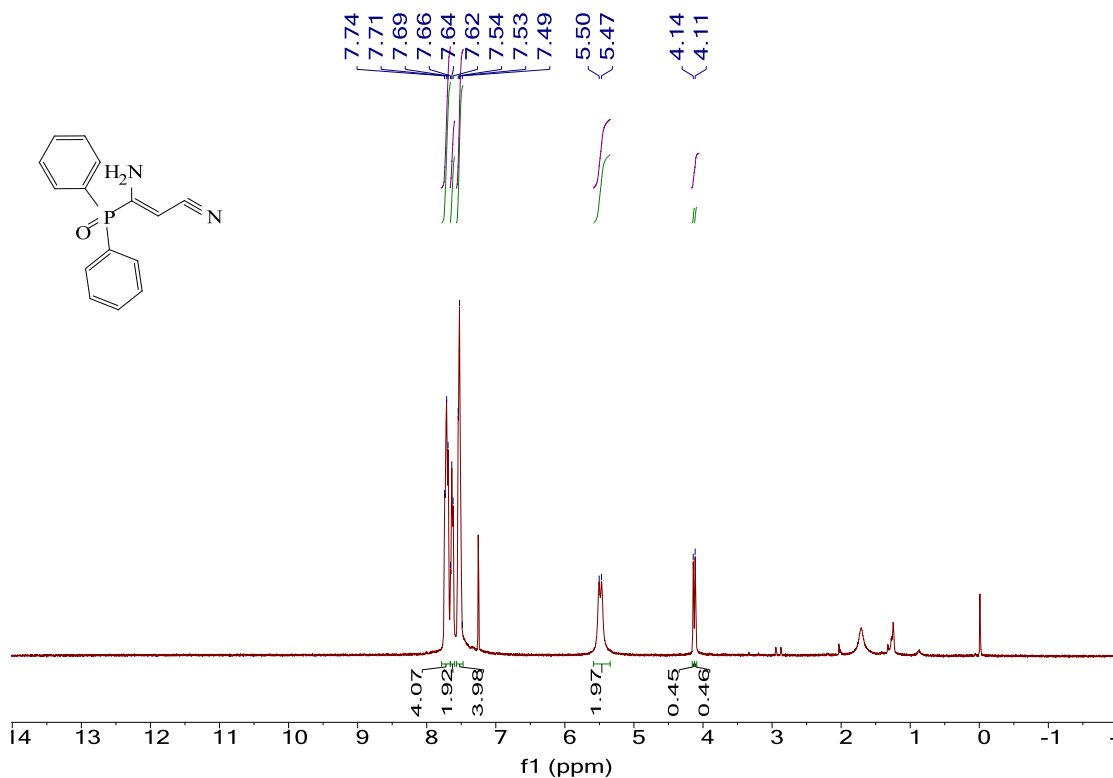


^{31}P NMR (162 MHz, CDCl_3)

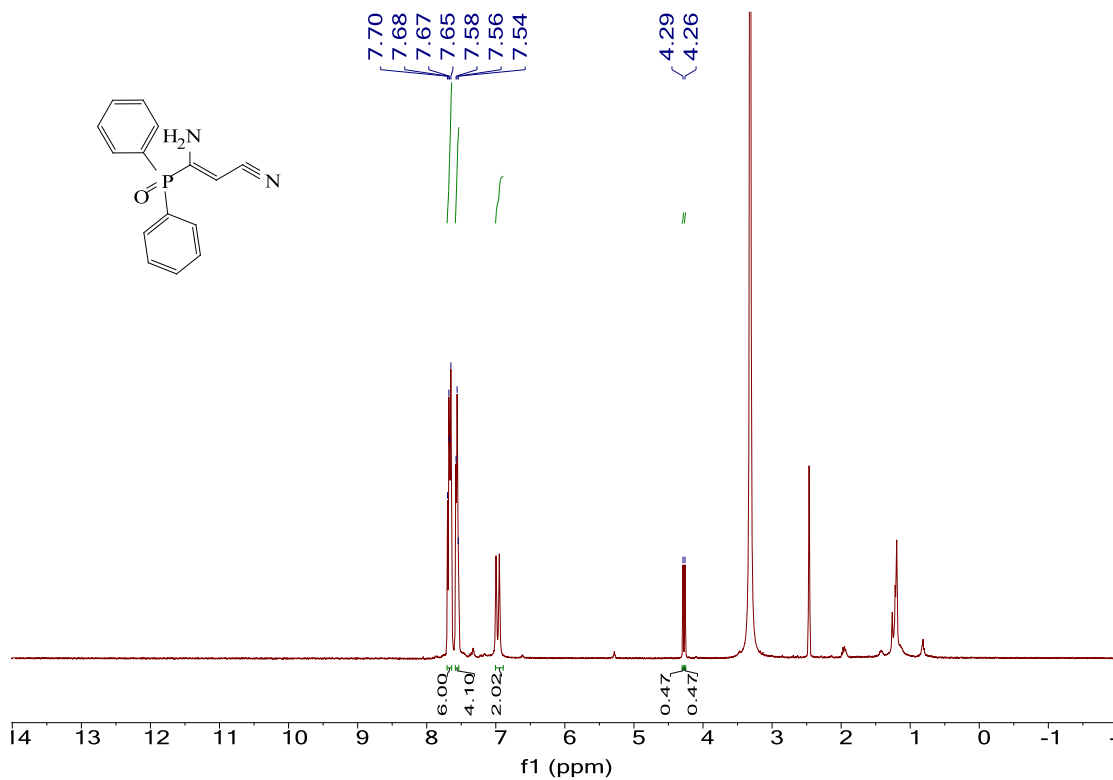


3-Amino-3-(diphenylphosphoryl)acrylonitrile (31)

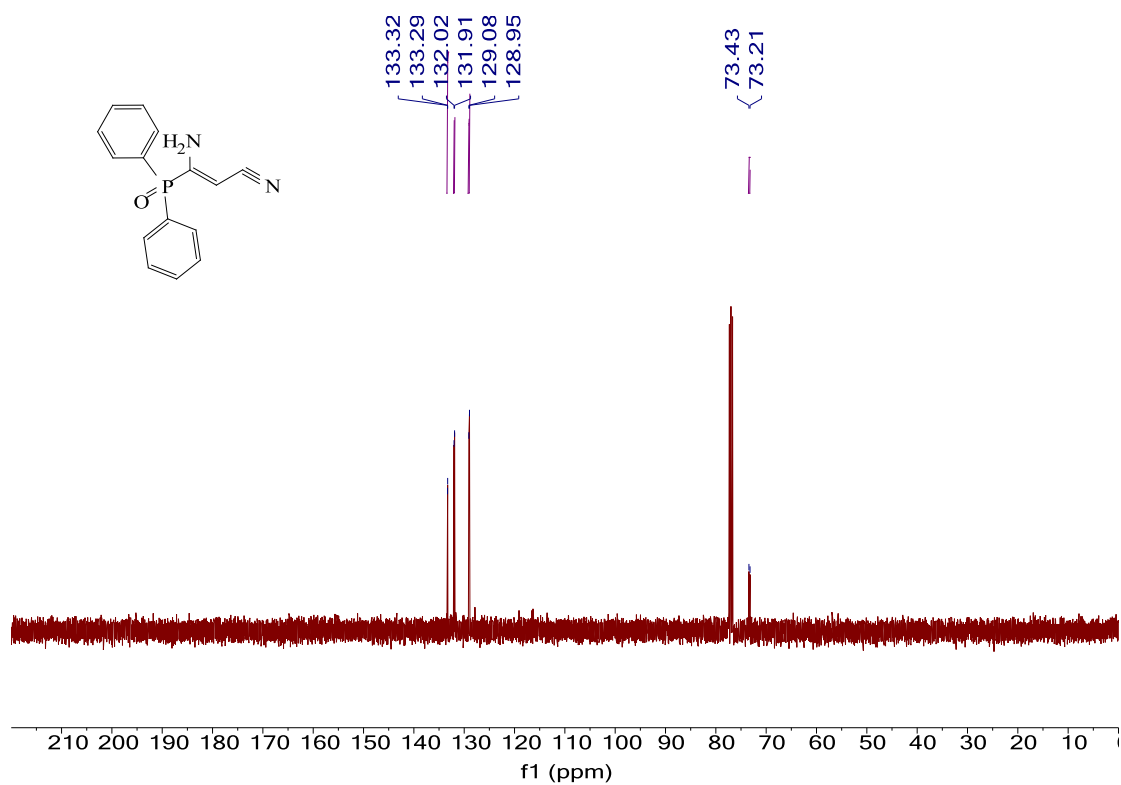
$^1\text{H NMR}$ (400 MHz, CDCl_3)



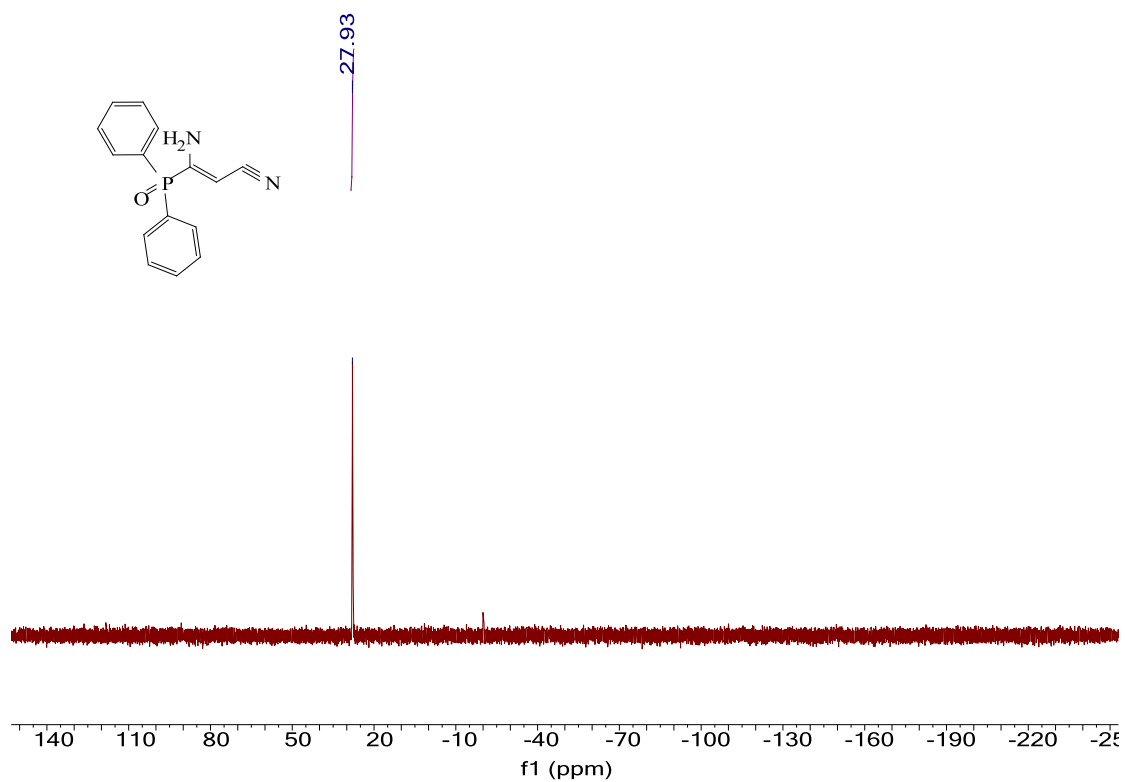
$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$)



^{13}C NMR (101 MHz, CDCl_3)

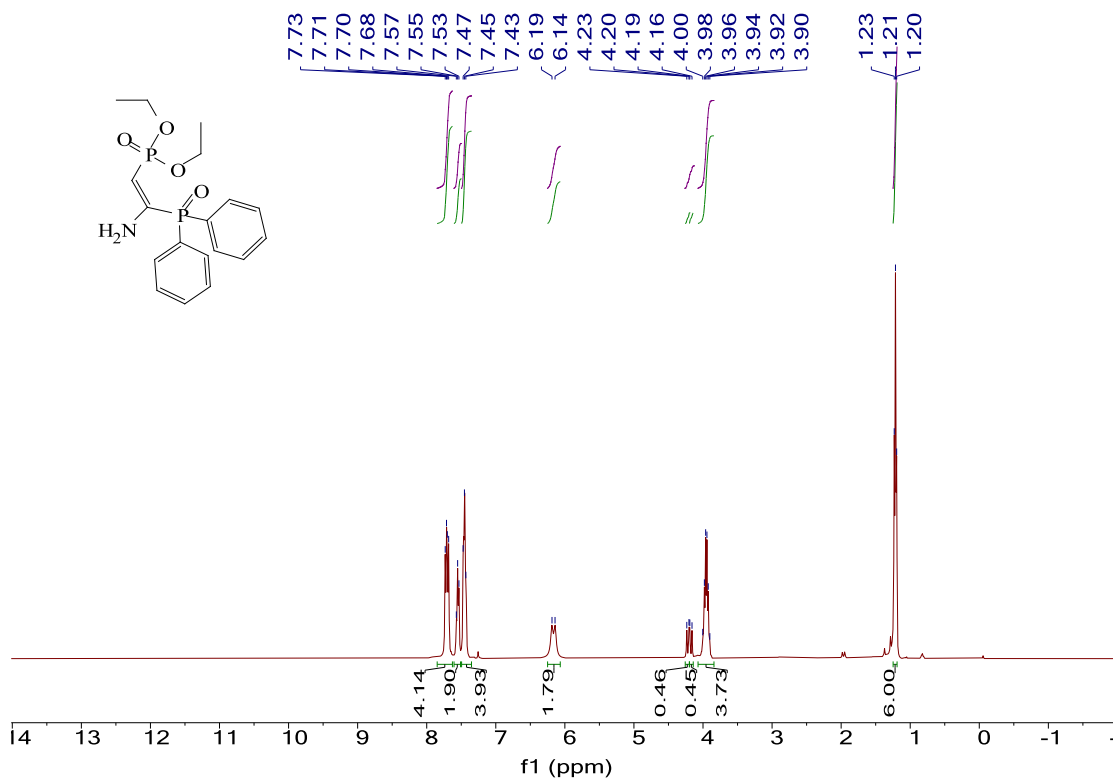


^{31}P NMR (162 MHz, CDCl_3)

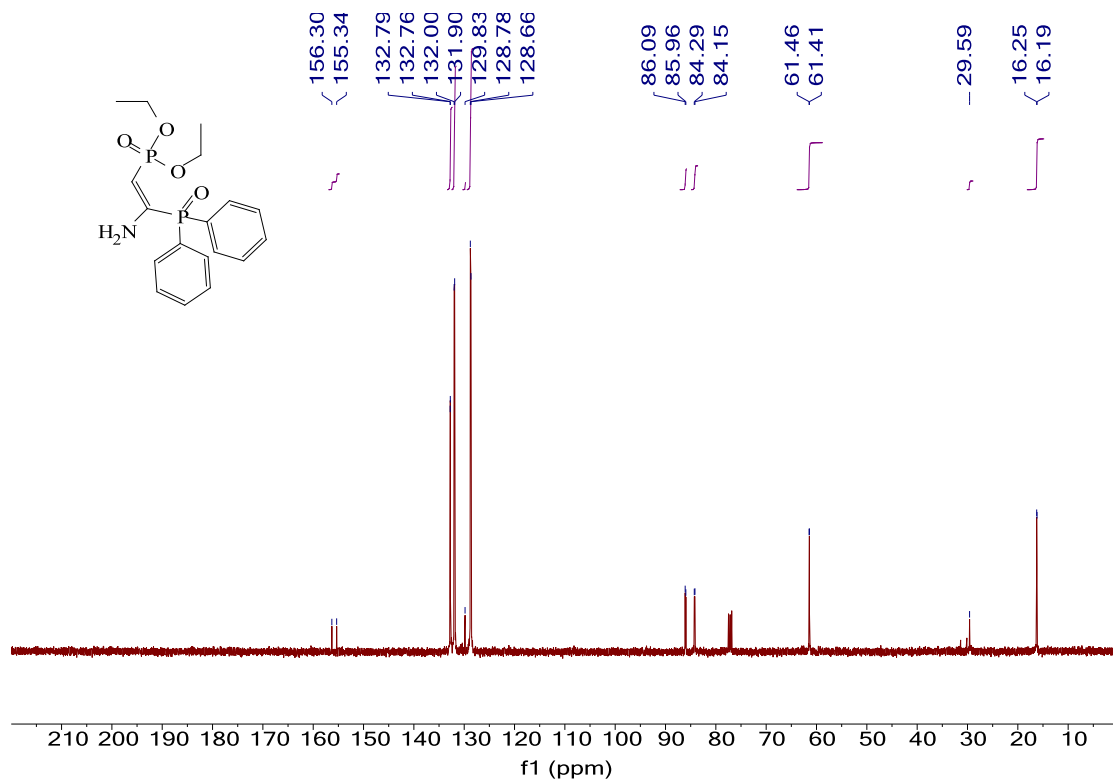


Diethyl (2-amino-2-(diphenylphosphoryl)vinyl)phosphonate (32)

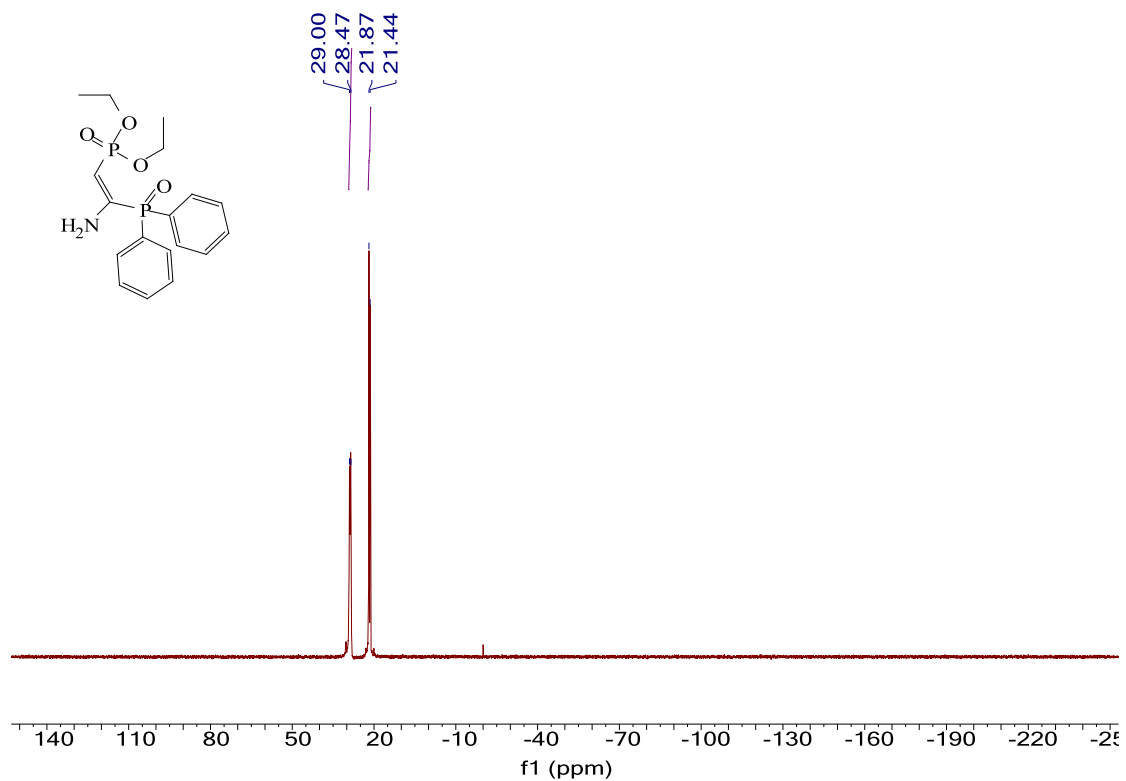
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (101 MHz, CDCl_3)

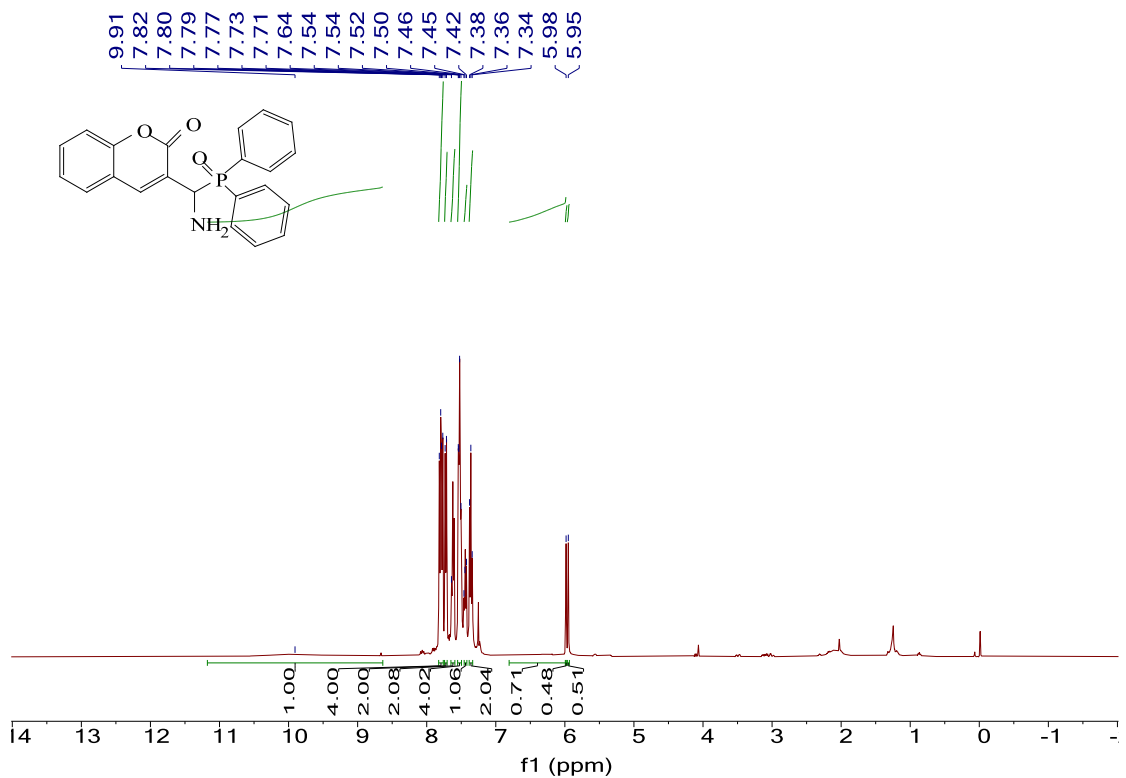


³¹P NMR (162 MHz, CDCl₃)

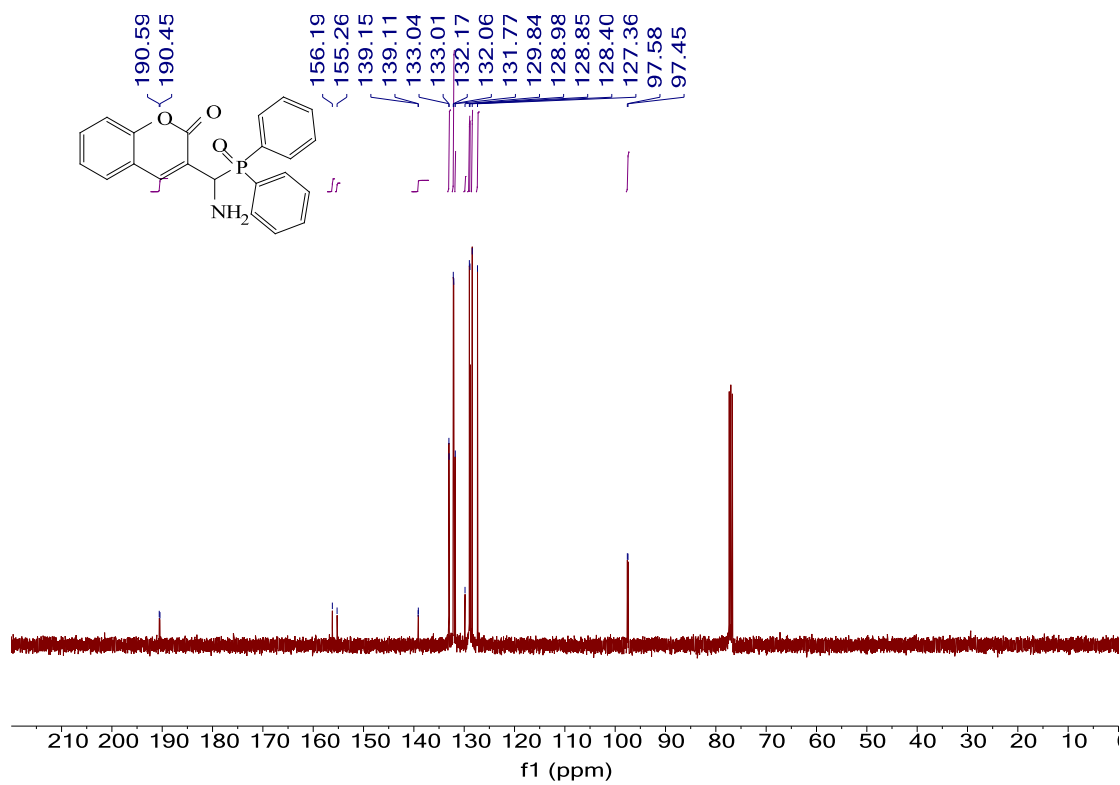


3-(Amino(diphenylphosphoryl)methylene)isochroman-1-one (33).

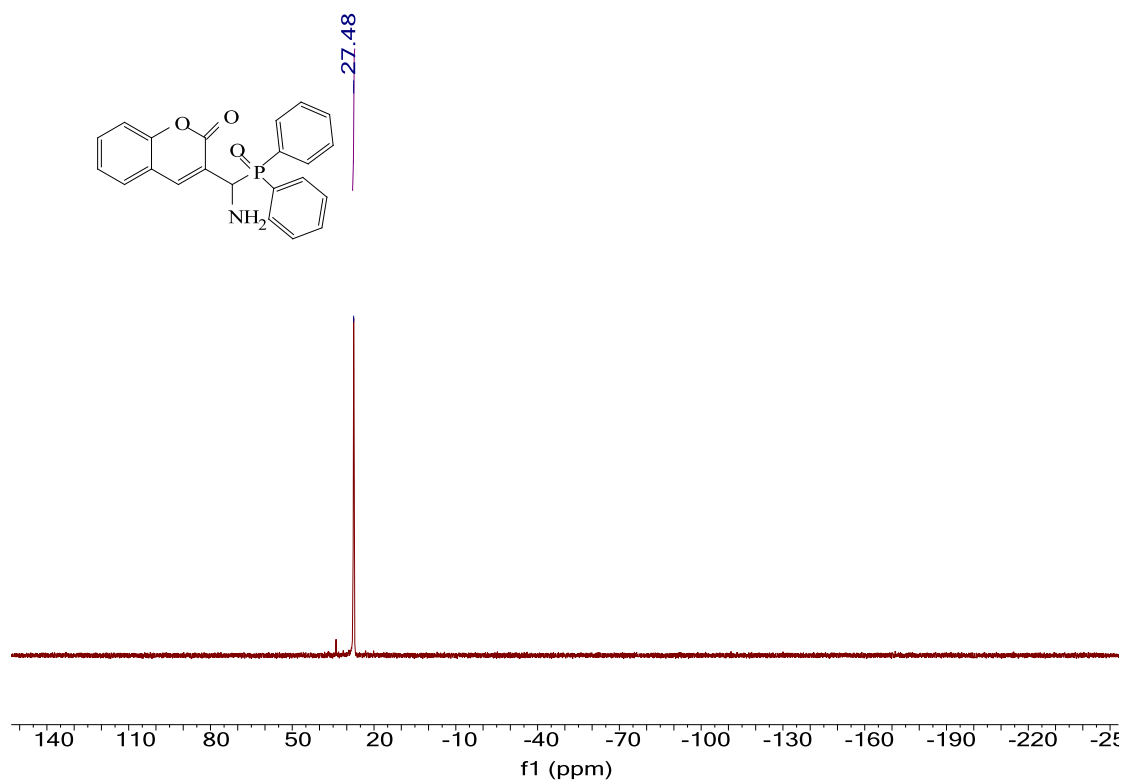
¹H NMR (400 MHz, CDCl₃)



^{13}C NMR (101 MHz, CDCl_3)

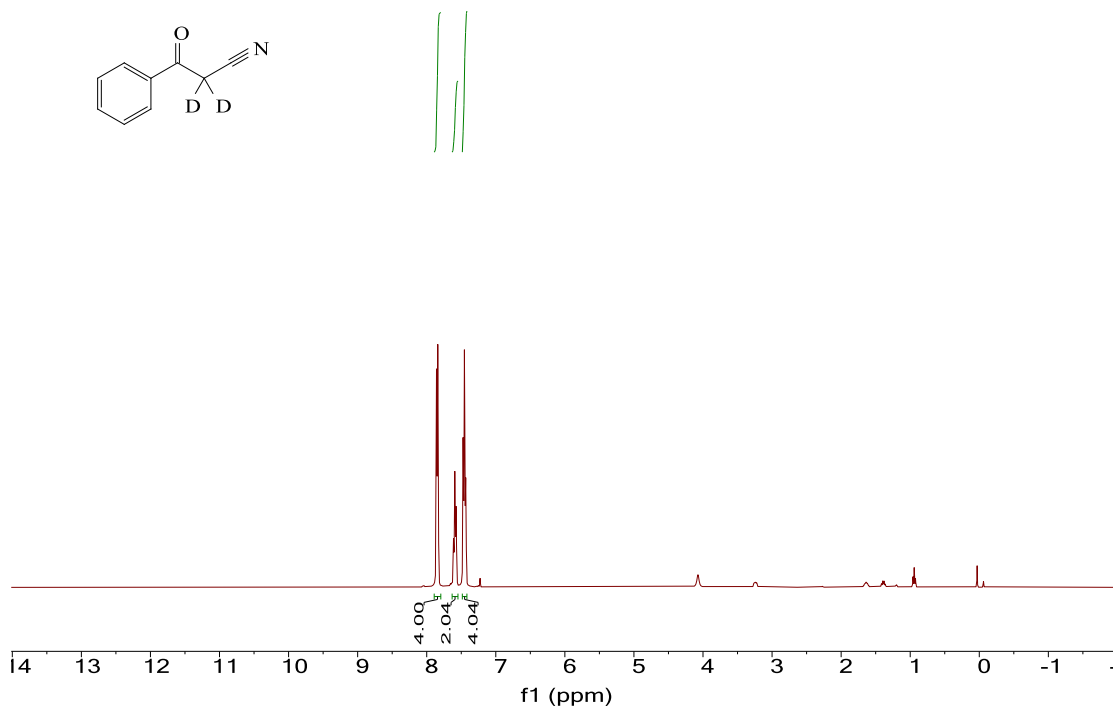


^{31}P NMR (162 MHz, CDCl_3)



3-oxo-3-phenylpropanenitrile-2,2-d2 (34)

$^1\text{H NMR}$ (400 MHz, CDCl_3)



3-amino-3-(diphenylphosphoryl)-1-phenylprop-2-en-1-one-2-d (35)

$^1\text{H NMR}$ (400 MHz, CDCl_3)

