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Graphical Abstract

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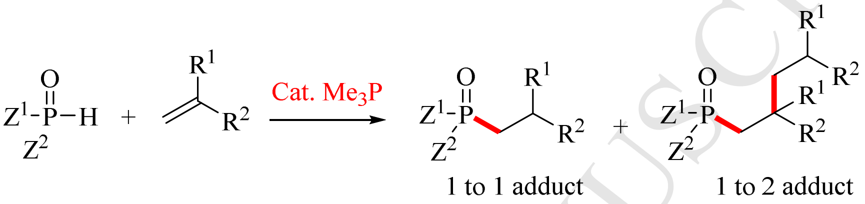

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ABSTRACT

Trimethyl phosphine was used as an efficient catalyst for the addition of P(O)-H compounds to electron-deficient alkenes. The addition reactions were generally conducted using a catalytic amount of Me_3P under mild reaction conditions. Both 1 to 1 and 1 to 2 adducts were obtained.

1. Introduction

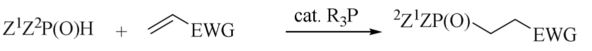
It is well-known that, as insecticides and herbicides, organophosphoryl compounds bearing a phosphoryl group P(O) play an important role in agrochemistry.[1] Phosphorus compounds are also very useful starting materials in organic synthesis (the Horner-Wadsworth-Emmons reaction, for example) and ligands for transition metal catalysts.[2] Therefore, the development of new methods for their preparation is of current concern.

The nucleophilic addition of a hydrogen phosphonate to an electron-deficient alkene is a simple method for the preparation of phosphonates (eq 1). This reaction has been carried out in the presence of bases,[3] Lewis acids,[4] transition metals,[5] microwaves,[6] and radical initiators such as AIBN.[7]

(1)

EWG = an electron-withdrawing group;
cat. = a base, Lewis acid, transition metal, radical initiator etc.

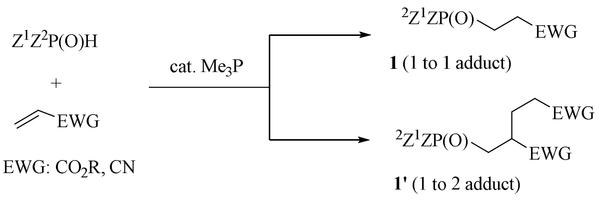
Recently, we and others reported that phosphine can efficiently catalyze the addition of a variety of hydrogen phosphoryl compounds to electron-deficient alkenes to produce the corresponding phosphoryl compounds in high yields (eq 2).[8,9] Enantiomerically pure P(O)-H starting chemicals also could be used in this reaction to give the corresponding phosphoryl compounds with retention of configuration at the phosphorus center. In addition to its high efficiency, the primary advantage using Me_3P as a catalyst, compared with other catalysts such as the metal-catalysts,[5] is the easy purification of the resulted products because the Me_3P catalyst (and the corresponding phosphine oxide $Me_3P(O)$) can be easily removed under *vacuum* from the products.



(2)

EWG = $P(O)Z^3Z^4$, COZ^5, CN

A further study on the synthetic potential of this Me_3P-catalyzed addition by changing the vinylphosphoryl compounds to other CH_2=CHEWG (*α*, *β*-unsaturated esters and nitriles etc.), interestingly revealed that, in addition to the expected 1 to 1 (one molecule P(O)H with one molecule olefin) adduct **1**, a novel 1 to 2 (one molecule P(O)H with two molecules olefin) adduct **1'** was also generated (eq 3). Noteworthy is that such an adduct **1'** has only been recognized as a trace amount of by-products of such addition reactions of P(O)H to an electron-deficient alkene.[9a, 9d] Here below we report the details.



(3)

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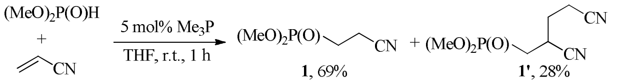
2. Results and discussion

To a mixture of $(MeO)_2P(O)H$ (1.0 mmol) and acrylonitrile (2.0 mmol) in THF (1.0 mL) was added Me_3P (0.05 mmol, 1.0 mol/L in THF) at 0 °C. The cooling ice bath was then removed and the solution was stirred at room temperature for 1 h. GC analysis showed that 97% $(MeO)_2P(O)H$ was consumed and the adduct **1** (1 to 1 adduct) by the addition of one molecule $(MeO)_2P(O)H$ to one molecule acrylonitrile and **1'** (1 to 2 adduct) by the addition of one molecule $(MeO)_2P(O)H$ to two molecules acrylonitrile were generated in 69% and 28% yields, respectively (eq 4).[10]



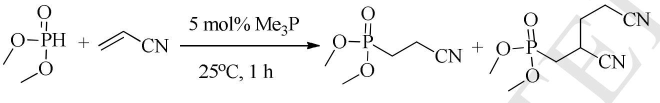
1, 69% **1'**, 28% (4)

Although the formation of the 1 to 1 adduct **1** is somewhat a result within prediction, as mentioned above, the formation of the 1 to 2 adduct **1'** was rather unexpected, i.e. it seems this is the first time to reveal its formation in such addition reactions of P(O)H compounds.[3-7] In order to selectively obtain the two adducts, the reaction conditions were subsequently optimized.

*2.1. Selective generation of **1**.*

As a model reaction, we started our optimization by conducting the addition of dimethyl phosphite to acrylonitrile in the presence of Me_3P catalyst (Table 1). The addition reaction at room temperature in MeCN took place rapidly to produce 98% total yield of **1**/**1'** with a ratio of **1**/**1'** = 70/30 (Table 1, entry 1) in an hour. Stirring the reaction mixture for a longer time (8 h) did not give difference in yields and ratios of the products, which indicates that both **1** and **1'**, once formed, are stable under current conditions (entry 2). The reaction could also be carried out using less Me_3P (1 mol%), albeit the yield of the adducts slightly decreased (entry 3). Similarly, when 1.0 mmol acrylonitrile was used, a moderate yield of the adduct 54% (entry 4) was obtained. Interestingly, however, compared to entry 1, the use of more acrylonitrile only has a tiny effect on the reaction (entries 5 and 6). On the other hand, the reaction temperature can affect the ratio of the two products **1**/**1'**. Thus, the selectivity to **1'** constantly increased as the reaction temperature decreased (entries 7-10). The reaction also progressed rapidly in toluene, CH_2Cl_2 and EtOAc (entries 11-13). However, only low yields of the products were obtained in DMF, DMSO and acetone (entries 14-16). On the other hand, no addition products were observed when the reaction was conducted in EtOH. Surprisingly, however, **1** was selectively generated in a high yield when *t*-BuOH was used as the solvent (entry 18).

Table 1. Reaction condition optimization for the selective generation of **1**.[a]



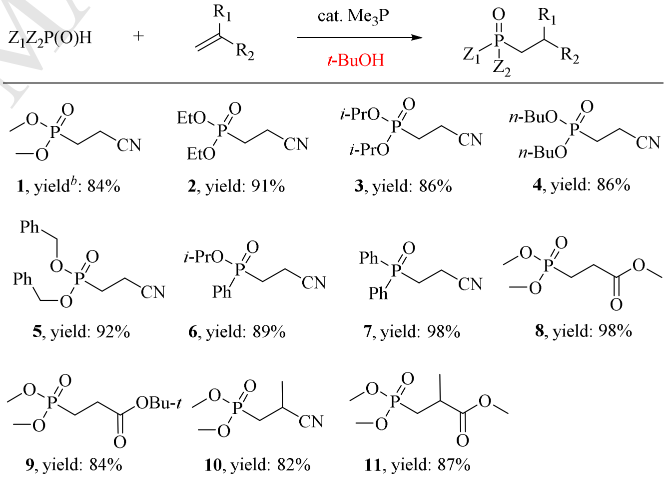
1 **1'**

Entry	Solvent	Total yield of **1** and **1'** (%)	Ratio of **1**/**1'**
1	MeCN	98	70/30
2[b]	MeCN	97	70/30
3[c]	MeCN	65	68/32
4[d]	MeCN	54	76/24
5[e]	MeCN	96	69/31
6[f]	MeCN	97	70/30
7	THF	97	71/29
8[g]	THF	93	67/33
9[h]	THF	84	60/40
10[i]	THF	81	57/43
11	Toluene	95	81/19
12	CH_2Cl_2	83	89/11
13	EtOAc	83	73/27
14	DMF	34	56/44
15	DMSO	32	50/50
16	Acetone	38	81/19
17	EtOH	0	0/0
18	*t*-BuOH	97	96/4

[a] Reaction conditions: to a solution of dimethyl phosphite (1.0 mmol) and acrylonitrile (2.0 mmol) in solvent (1.0 mL) was added Me_3P (0.05 mmol, 1.0 mol/L in THF) at 0 °C. The reaction mixture was stirred at 25 °C for 1 h. Yield was determined by GC. [b] 8 h. [c] Me_3P (0.01 mmol). [d] 1.0 mmol acrylonitrile was used. [e] 3.0 mmol acrylonitrile was used. [f] 4.0 mmol acrylonitrile was used. [g] at 0 °C. [h] at -40 °C. [i] at -60 °C.

Next, in order to clarify the scope and limitations of this reaction, the additions of a variety of P(O)H compounds to electron-deficient alkenes under this optimized reaction condition (entry 18) were carried out. As shown in Table 2, all the dialkyl phosphites tested could produce the corresponding products in good yields with excellent selectivity to the 1 to 1 adduct **1** (Table 2, products **1**-**5**). H-phosphinate isopropyl phenylphosphinate and secondary phosphine oxide diphenylphosphine oxide were also applicable to this reaction, generating the corresponding 1 to 1 adducts in high yield with high selectivity (products **6**, **7**). The electron-deficient methyl acrylate and *tert*-butyl acrylate were found as reactive as acrylonitrile to react with dimethyl phosphite, furnishing the expected products **1** in high yields (products **8**, **9**). The steric bulky methacrylonitrile and methyl methacrylate also worked well under the present reaction conditions and the desired products were given in high yields (products **10**, **11**).

Table 2. Selective 1 to 1 addition of a P(O)H compound to an electron-deficient alkene.[a]



1, yield[b]: 84% **2**, yield: 91% **3**, yield: 86% **4**, yield: 86%

5, yield: 92% **6**, yield: 89% **7**, yield: 98% **8**, yield: 98%

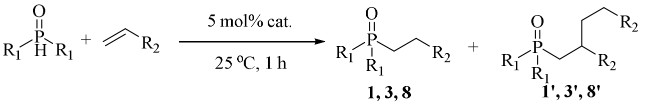
9, yield: 84% **10**, yield: 82% **11**, yield: 87%

[a] Reaction conditions: phosphite (1.0 mmol), alkene (2.0 mmol), Me_3P (0.05 mmol), *t*-BuOH (1.0 mL), 25 °C, 1 h. [b] Isolated yield.

*2.2. Attempted selective generation of **1'***

Since the 1 to 1 addition product **1** was successfully generated selectively, we turned our attention to the selective generation of **1'**. As described in Table 1, the selective generation of **1'** was not achieved under the conditions of Table 1. Therefore, we decided to further optimize the conditions in order to selectively obtain **1'** (Table 3). The addition also took place readily with methyl acrylate (entries 1 and 2). Similar to acrylnitrile, when 1.0 equivalence was used, 52% yield of the adducts with a ratio of **1**/**1'** = 60/40 was obtained (entry 1). With 2.0 equivalents of methyl acrylate, 96% yield of the adducts was obtained, albeit the ratio of the adducts changed little (**1**/**1'** = 58/42) (entry 2). The addition also took place smoothly with the bulky diisopropyl phosphosite to give 88% yield of the adducts with 65/35 selectivity (entry 3). In addition to Me_3P, the reaction could also be catalyzed efficiently by other trialkyl phosphines Et_3P, n-Bu_3P and even the very bulky t-Bu_3P and Cy_3P (entries 4-7). Dimethylphenylphosphine also well catalyzed the addition (entry 8). However, the bulky dicyclohexylphenylphoshine only gave a low yield of the products under similar conditions (entry 9). The catalytic activity of diphenylmethylphosphine was also low (entry 10), while triarylphosphines like Ph_3P, (p-MeC_6H_4)$_3$P, (p-MeO-C_6H_4)$_3$P all could not catalyze the addition reaction (entries 11-13). When we used triethylamine (pK_b = 3.2), which is a stronger base than triethylphosphine (pK_b = 5.4),[11] as catalyst under similar conditions, the addition failed (entry 14), showing that basicity is important but is not the only factor for a catalyst. Very interestingly, however, with a combination of these inactive phosphine and Et_3N, the addition could also take place (entries 15 and 16). Thus, the combination of (p-$MeOC_6H_4$)$_3$P gave 16% yield of the adducts (entry 15), and the combination of Cy_2PhP with Et_3N gave 42% yield of the adducts (entry 16). As expected, the triarylphsophine having an amino group (p-$Me_2NC_6H_4$)$_3$P could also catalyze the reaction (entry 17). However, despite such an extensive study on the reaction, the selective formation of **1'** has not been found yet.

Table 3. Reaction condition optimization for the selective generation of **1'**.[a]

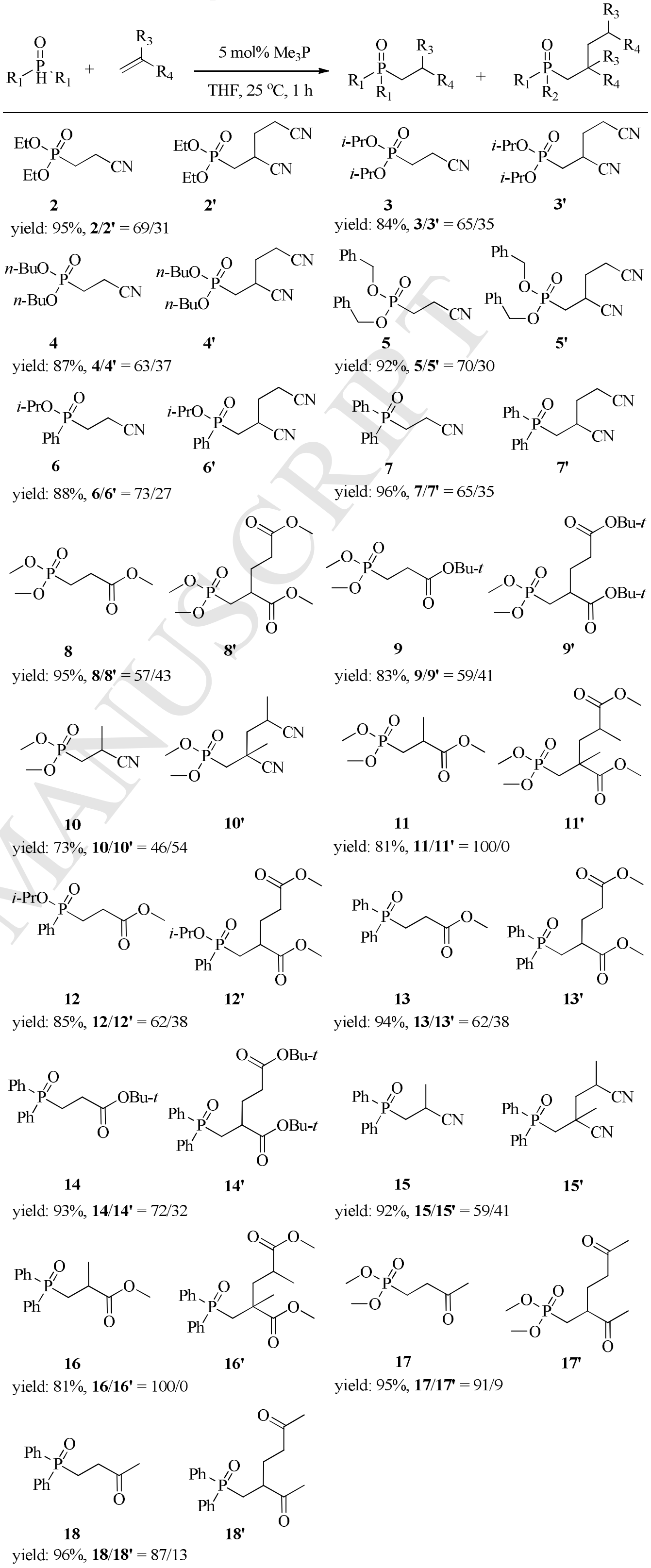


Entry	R_1	R_2	Cat.	Yield (%)[b]	Ratio (1/1')[c]
1[d,e]	MeO	COOMe	Me_3P	52	60/40
2[e]	MeO	COOMe	Me_3P	96	58/42
3[e]	i-PrO	CN	Me_3P	88	65/35
4[f]	MeO	CN	Et_3P	92	70/30
5[f]	MeO	CN	n-Bu_3P	86	70/30
6[f]	MeO	CN	t-Bu_3P	84	70/30
7[f]	MeO	CN	Cy_3P	72	66/34
8[f]	MeO	CN	Me_2PhP	85	70/30
9[f]	MeO	CN	Cy_2PhP	12	60/40
10[f]	MeO	CN	$MePh_2P$	8	50/50
11[f]	MeO	CN	Ph_3P	0	-
12[f]	MeO	CN	(p-MePh)$_3$P	0	-
13[f]	MeO	CN	(p-MeOPh)$_3$P	0	-
14[f]	MeO	CN	Et_3N	0	-
15[f]	MeO	CN	(p-MeOPh)$_3$P, Et_3N	16	46/54
16[f]	MeO	CN	Cy_2PhP, Et_3N	42	52/48
17[f]	MeO	CN	(p-Me_2NPh)$_3$P	58	58/42

[a]Reaction conditions: phosphine (1.0 mmol), alkene (2 mmol), catalyst (0.05 mmol), solvent (1.0 mL), 25 °C, 1 h. [b]Total GC yield of **1** and **1'**. [c]Ratio of **1/1'** GC yield. [d]1 mmol alkene was used. [e]THF as solvent. [f]MeCN as solvent.

As summarized in Table 4, in addition to $(MeO)_2P(O)H$, other dialkylphosphites $(RO)_2P(O)H$ (R = Et, n-Bu, i-Pr, $PhCH_2$) also reacted readily to give the products in high yields (Table 4, products **2-5** and **2'-5'**). Not limited to dialkyl phosphite, isopropyl phenylphosphinate (products **6** and **6'**), and diphenylphosphine oxide (products **7** and **7'**) could also be used as the substrates to give the corresponding adducts in high yields.

Table 4. Scope and limitations of the Me_3P-catalyzed reaction between P(O)H compounds with an electron-deficient alkenes.[a]



2, **2'**: yield: 95%, **2/2'** = 69/31

3, **3'**: yield: 84%, **3/3'** = 65/35

4, **4'**: yield: 87%, **4/4'** = 63/37

5, **5'**: yield: 92%, **5/5'** = 70/30

6, **6'**: yield: 88%, **6/6'** = 73/27

7, **7'**: yield: 96%, **7/7'** = 65/35

8, **8'**: yield: 95%, **8/8'** = 57/43

9, **9'**: yield: 83%, **9/9'** = 59/41

10, **10'**: yield: 73%, **10/10'** = 46/54

11, **11'**: yield: 81%, **11/11'** = 100/0

12, **12'**: yield: 85%, **12/12'** = 62/38

13, **13'**: yield: 94%, **13/13'** = 62/38

14, **14'**: yield: 93%, **14/14'** = 72/32

15, **15'**: yield: 92%, **15/15'** = 59/41

16, **16'**: yield: 81%, **16/16'** = 100/0

17, **17'**: yield: 95%, **17/17'** = 91/9

18, **18'**: yield: 96%, **18/18'** = 87/13

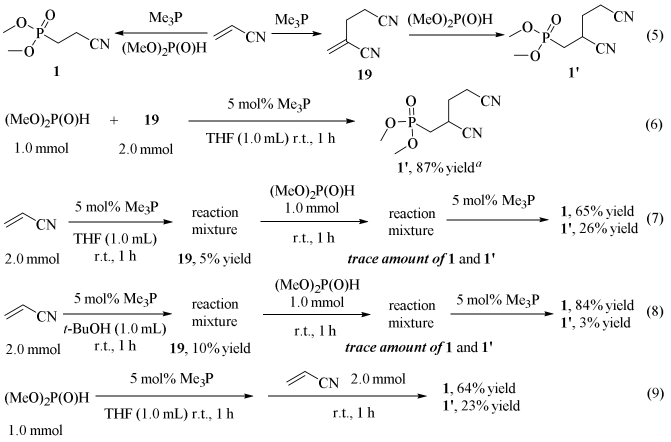
[a]Reaction conditions: P(O)-H compounds (1.0 mmol), alkene (2.0 mmol) Me_3P (0.05 mmol), THF (1.0 mL), 25 °C, 1 h. The yields in the table were isolated yields.

In addition to acrylonitrile, satisfactory results were also obtained in the reaction of $(MeO)_2P(O)H$ with several acrylates such as methyl acrylate (products **8** and **8'**), *tert*-butyl acrylate (products **9** and **9'**), methyl acrylonitrile (products **10** and **10'**), and methyl methacrylate (products **11** and **11'**), in 73% to 95% yields. Good results were also obtained with isopropyl phenylphosphinate and methyl acrylate (products **12** and **12'**). Diphenyl phosphine oxide also served well to react with acrylates, producing the products in high yields (products **13-16** and **13'-16'**). It is worth noting that under the reaction conditions, the 1 to 1 adduct **11** and **16** were obtained selectively (products **11** and **16**). Methyl vinylketone also could be used as the substrate to give the 1 to 1 adduct **17** and **18** predominantly. The two adducts could be separated and isolated in pure form by conventional techniques. All these compounds we obtained have been fully characterized spectroscopically as shown in the experimental section.

2.3. Mechanistic study.

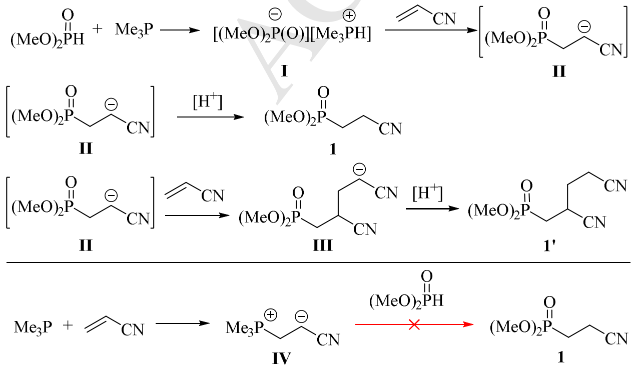
To gain some insights into the reaction mechanism, a series of control experiments were carried out (Scheme 1). It was known that acrylonitrile could dimerize to produce 2-methyleneglutaronitrile **19**.[12] Therefore, it was first thought that the addition of P(O)-H compounds to acrylonitrile should give the 1 to 1 adduct **1**, while the addition to **19** should give the 1 to 2 adduct **1'** (eq. 5). Indeed, a separate experiment using **19** confirmed that the addition did occur to produce **1'** (eq. 6). However, as described below, this reaction path, although could not be completely excluded out, should not be the major path for the formation of **1'** under the reaction conditions.

Scheme 1. Control experiments



Firstly, under the reaction conditions in the absence of $(MeO)_2P(O)H$, the dimerization product **19** from acrylonitrile in THF and *t*-BuOH, was obtained in only 5% and 10% yield, respectively (eq.s 7 and 8). Very surprisingly, the addition almost did not take place when $(MeO)_2P(O)H$ was subsequently added to the mixtures. On the other hand, by the addition of another 5 mol% Me_3P, the addition took place rapidly to give the adducts in high yields (eq. 8). Therefore, it can be safely concluded that the combination of $CH_2{=}CHCN$ with Me_3P can significantly deactivate the catalytic activity of Me_3P in the addition of $(MeO)_2P(O)H$ to $CH_2{=}CHCN$. However, interestingly, such a deactivation of the catalyst Me_3P was not observed with the combination of $(MeO)_2P(O)H$ with Me_3P, because the addition still took place readily when $CH_2{=}CHCN$ was subsequently added to the mixture of $(MeO)_2P(O)H$ with Me_3P (eq 9).

Scheme 2. A plausible mechanism for the Me_3P-catalyzed addition of $(MeO)_2P(O)H$ to acrylonitrile.



Although a detailed mechanism is not clear, on the basis of the above results, a simplified mechanism for the Me_3P-catalyzed addition of $(MeO)_2P(O)H$ to $CH_2{=}CHCN$ is proposed (Scheme 2). Dimethylphosphite and trimethylphosphine may generate an intermediate **I**. This intermediate **I** adds to acrylonitrile, perhaps *via* an intermediate **II**, to give the 1 to 1 adduct **1**. On the other hand, intermediate **II** may add to another molecule acrylonitrile to generated **III** which, *via* a subsequent protonation, will give the 1 to 2 adduct **1'**. 1 to 1 adduct **1** was major product when *t*-BuOH as solvent since *t*-BuOH provides the proton which can quickly quench the intermediate **II.** Although the addition of Me_3P to acrylonitrile generating a zwitterionic species **IV** is also a long-proposed reasonable reaction, however, apparently, this is a dead path for the catalytic addition of $(MeO)_2P(O)H$ to acrylonitrile as shown in eq.s 7-9.

3. Conclusion

In conclusion, we have disclosed a simple Me_3P-catalyzed addition of hydrogen phosphoryl compounds P(O)H to electron-deficient alkenes to give the very useful functional phosphoryl compounds. The reaction produced not only the 1 to 1 adduct **1** but also 1 to 2 adduct **1'**. The generation of the 1 to 1 adduct **1** was selective. Although a selective generation of **1'** was not achieved, this adduct could be isolated *via* conventional techniques. The workup of the reaction mixture is very simple compared with other methods since the catalyst can be easily removed from the product under *vacuum*.

4. Experimental section

General information: All materials were purchased and used without further purification. ^1H NMR spectra were recorded on JEOL JNM-ECS400 (400 MHz) FT NMR in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were taken on JEOL JNM-ECS400 (100 MHz) FT NMR system in $CDCl_3$. ^{31}P NMR spectra were taken on JEOL JNM-ECX400 (162 MHz) FT NMR system in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. HPLC (recycle GPC) method for isolation was performed on JAPAN ANALYTICAL INDUSTRY LC-908 with JAIGEL-1H (polystyrene-based column). High resolution mass spectra were obtained on JEOL JMS700 at Kyoto-Nara Advanced Nanotechnology Network. *Caution: trimethylphosphine has toxicity and high volatility. When trimethylphosphine is manipulated, ventilate the bench carefully.*

General procedure for Me_3P catalyzed addition of P(O)-H compounds to electron-deficient alkenes: A glass schlenk tube was charged with P(O)-H compounds (1.0 mmol), electron-deficient alkenes (1.0 mmol) and 1.0 mL solvent. After the tube was cooled in an ice-water bath, Me_3P (1.0 mol/L in THF, 0.05 mL) was injected with a syringe. After stirring for 5 minutes, the ice bath was removed. The reaction mixture was warmed up to room temperature and stirred for 1 h. The solvent and PMe_3 was removed under reduce pressure. The crude product was purified by GPC to get the analytically pure samples.

*4.1. Dimethyl (2-cyanoethyl)phosphonate (**1**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 3.54 (6H, d, *J* 11.2 Hz), 2.40 (2H, td, *J* 8.0 Hz, *J* 15.2 Hz), 1.87 (2H, td, *J* 8.0 Hz, *J* 18.0 Hz); δ_C (100 MHz, $CDCl_3$) 117.96 (d, *J* 16.2 Hz), 52.23 (d, *J* 6.7 Hz), 21.03 (d, *J* 144.8 Hz), 10.84 (d, *J* 3.8 Hz); δ_P (162 MHz, $CDCl_3$) 29.48. This compound is known.[13]

*4.2. Dimethyl (2,4-dicyanobutyl)phosphonate (**1'**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 3.74 (6H, d, *J* 11.2 Hz, d, *J* 10.8 Hz), 3.06~3.03 (1H, m), 2.76~2.46 (2H, m), 2.20~1.94 (2H, m); δ_C (100 MHz, $CDCl_3$) 119.04 (d, *J* 11.4 Hz), 117.70, 52.89 (d, *J* 6.6 Hz), 52.82 (d, *J* 8.6 Hz), 28.58 (d, *J* 10.5 Hz), 27.79 (d, *J* 143.9 Hz), 25.40 (d, *J* 3.8 Hz), 14.99; δ_P (162 MHz, $CDCl_3$) 27.54.

HRMS (ESI) Calcd for $[M+H]^+$ $C_8H_{14}N_2O_3P$: 217.0742, Found: 217.0729.

*4.3. Diethyl (2-cyanoethyl)phosphonate (**2**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 4.13~4.05 (4H, m), 2.63~2.55 (2H, m), 2.08~1.99 (2H, m), 1.30 (6H, td, *J* 1.6 Hz, *J* 7.6 Hz,); δ_C (100 MHz, $CDCl_3$) 118.37 (d, *J* 18.1 Hz), 62.34 (d, *J* 6.7 Hz), 22.844 (d, *J* 144.8 Hz), 16.41 (d, *J* 5.7 Hz), 11.59 (d, *J* 3.8 Hz); δ_P (162 MHz, $CDCl_3$) 26.62. This compound is known.[13]

*4.4. Diethyl (2,4-dicyanobutyl)phosphonate (**2'**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 4.17~4.09 (4H, m), 3.13~3.03 (1H, m), 2.67~2.50 (2H, m), 2.22~2.12 (2H, m), 2.08~1.94 (2H, m), 1.33 (6H, t, *J* 7.2 Hz); δ_C (100 MHz, $CDCl_3$) 119.17 (d, *J* 11.5 Hz), 117.63, 62.59 (d, *J* 6.7 Hz), 62.56 (d, *J* 6.7 Hz), 28.91 (d, *J* 11.5 Hz), 28.70 (d, *J* 123.0 Hz), 25.67 (d, *J* 3.8 Hz), 16.37 (d, *J* 4.8 Hz), 15.15; δ_P (162 MHz, $CDCl_3$): δ (ppm) 24.63. HRMS (ESI) Calcd for $[M+H]^+$ $C_{10}H_{18}N_2O_3P$: 245.1055, Found: 245.1079.

*4.5. Diisopropyl (2-cyanoethyl)phosphonate (**3**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 4.71~4.63 (2H, m), 2.60~2.52 (2H, m), 2.03~1.94 (2H, m), 1.29 (12 H, dd, *J* 3.2 Hz, *J* 6.4 Hz); δ_C (100 MHz, $CDCl_3$) 118.49 (d, *J* 19.1 Hz), 71.09 (m, *J* 6.7 Hz), 23.95 (d, *J* 3.8 Hz), 23.89 (d, *J* 136.3 Hz), 11.68 (d, *J* 3.9 Hz); δ_P (162 MHz, $CDCl_3$) 24.33. HRMS (ESI) Calcd for $[M+H]^+$ $C_9H_{19}NO_3P$: 220.1102, Found: 220.111.

*4.6. Diisopropyl (2,4-dicyanobutyl)phosphonate (**3'**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 4.77~4.67 (2H, m), 3.12~3.02 (1H, m), 2.67~2.50 (2H, m), 2.25~1.88 (4H, m), 1.33 (12H, dd, *J* 2.0 Hz, *J* 6.0 Hz); δ_C (100 MHz, $CDCl_3$) 119.32 (d, *J* 12.4 Hz), 117.64, 71.59 (d, *J* 6.7 Hz), 71.52 (d, *J* 6.6 Hz), 30.08 (d, *J* 129.6 Hz), 28.70 (d, *J* 6.7 Hz), 25.83 (d, *J* 3.8 Hz), 23.98 (d, *J* 3.8 Hz), 15.17; δ_P (162 MHz, $CDCl_3$): δ (ppm) 22.39. HRMS (ESI) Calcd for $[M+H]^+$ $C_{12}H_{22}N_2O_3P$: 273.1368, Found: 273.1389.

*4.7. Dibutyl (2-cyanoethyl)phosphonate (**4**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 4.07~3.95 (4H, m), 2.61~2.54 (2H, m), 2.08~1.99(2H, m), 1.65~1.58 (4H, m), 1.40~1.31 (4H, m), 0.89 (6H, t, *J* 7.2 Hz); δ_C (100 MHz, $CDCl_3$) 118.33 (d, *J* 18.1 Hz), 65.99 (d, *J* 6.7 Hz), 32.42 (d, *J* 5.7Hz), 22.66 (d, *J* 144.8 Hz), 18.63, 13.48, 11.56 (d, *J* 3.8 Hz); δ_P (162 MHz, $CDCl_3$) 26.62. HRMS (ESI) Calcd for $[M+H]^+$ $C_{11}H_{23}NO_3P$: 248.1415, Found: 248.1435.

*4.8. Dibutyl (2,4-dicyanobutyl)phosphonate (**4'**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 4.12~4.00 (4H, m), 3.13~3.02(1H, m), 2.67~2.50 (2H, m), 2.23~2.13 (2H, m), 2.08~1.94 (2H, m), 1.69~1.62 (4H, m), 1.43~1.34 (4H, m), 0.92 (6H, t, *J* 7.2 Hz); δ_C (100 MHz, $CDCl_3$) 119.20 (d, *J* 12.4 Hz), 117.58, 66.36 (d, *J* 6.7 Hz), 66.34 (d, *J* 6.7 Hz), 32.49 (d, *J* 5.8 Hz), 32.47 (d, *J* 5.8 Hz), 28.89 (d, *J* 143.9 Hz), 28.86 (d, *J* 9.5 Hz), 25.75 (d, *J* 3.8 Hz), 18.71, 15.22, 13.57; δ_P (162 MHz, $CDCl_3$) 24.65. HRMS (ESI) Calcd for $[M+H]^+$ $C_{14}H_{26}N_2O_3P$: 301.1681, Found: 301.1663.

*4.9. Dibenzyl (2-cyanoethyl)phosphonate (**5**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.38~7.24 (10H, m), 5.08~4.92 (4H, m), 2.52~2.45 (2H, m), 2.05~1.94 (2H, m); δ_C (100 MHz, $CDCl_3$) 135.70 (d, *J* 5.7 Hz), 128.81 (d, *J* 6.7 Hz), 128.21, 118.25 (d, *J* 19.1 Hz), 67.95 (d, *J* 6.6 Hz), 23.38 (d, *J* 144.0 Hz), 11.42 (d, *J* 2.8 Hz); δ_P (162 MHz, $CDCl_3$): δ (ppm) 27.82. HRMS (ESI) Calcd for $[M+H]^+$ $C_{17}H_{19}NO_3P$: 316.1102, Found: 316.1136.

*4.10. Dibenzyl (2,4-dicyanobutyl)phosphonate (**5'**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.35 (10H, b), 5.10~4.92 (4H, m), 3.00~2.89 (1H, m), 2.55~2.36 (2H, m), 2.17~2.00 (2H, m), 1.96~1.85 (2H, m); δ_C (100 MHz, $CDCl_3$) 135.57 (d, *J* 5.7 Hz), 135.51 (d, *J* 4.7 Hz), 128.96, 128.92, 128.84, 128.80, 128.45, 128.37, 119.08 (d, *J* 12.4 Hz), 117.52, 68.31 (d, *J* 6.6 Hz), 68.20 (d, *J* 6.7 Hz), 29.53 (d, *J* 143.9 Hz), 28.68 (d, *J* 8.6 Hz), 25.59 (d, *J* 2.9 Hz), 15.12; δ_P (162 MHz, $CDCl_3$) 25.88. HRMS (ESI) Calcd for $[M+H]^+$ $C_{20}H_{22}N_2O_3P$: 369.1368, Found: 369.1387.

*4.11. Isopropyl (2-cyanoethyl)(phenyl)phosphinate (**6**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.66~7.61 (2H, m), 7.45~7.41 (1H, m), 7.37~7.33 (2H, m), 4.46~4.34 (1H, m), 2.56~2.33 (2H, m), 2.17~1.92 (2H, m), 1.24 (3H, d, *J* 6.0 Hz), 1.03 (3H, d, *J* 6.4 Hz); δ_C (100 MHz, $CDCl_3$) 132.52 (d, *J* 1.9 Hz), 131.30 (d, *J* 10.4 Hz), 130.29 (d, *J* 126.8 Hz), 128.55 (d, *J* 12.4 Hz), 118.21 (d, *J* 18.1 Hz), 70.28 (d, *J* 6.6 Hz), 26.41 (d, *J* 101.0 Hz), 24.14 (d, *J* 2.8 Hz), 23.55 (d, *J* 4.8 Hz), 10.31, δ_P (162 MHz, $CDCl_3$) 38.70. HRMS (ESI) Calcd for $[M+H]^+$ $C_{12}H_{17}NO_2P$: 238.0996, Found: 238.0994.

*4.12. Isopropyl (2,4-dicyanobutyl)(phenyl)phosphinate (**6'**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.76~7.71 (2H, m), 7.57~7.52 (1H, m), 7.49~7.44 (2H, m), 4.55~4.45 (1H, m), 3.29~3.16 (0.6H, m), 3.03~2.92 (0.4H, m), 2.62~2.45 (2H, m), 2.38~1.91 (4H, m,), 1.36 (3H, d, *J* 6.4 Hz, d, *J* 6.4 Hz), 1.13 (3H, d, *J* 6.0 Hz, d, *J* 6.4 Hz); δ_C (100 MHz, $CDCl_3$) 133.01 (d, *J* 2.8 Hz), 132.91 (d, *J* 1.9 Hz), 131.63 (d, *J* 9.5 Hz), 131.51 (d, *J* 10.5 Hz), 131.04 (d, *J* 127.8 Hz), 130.31 (d, *J* 127.7 Hz), 128.92 (d, *J* 12.4 Hz), 128.86 (d, *J* 12.4 Hz), 119.33 (d, *J* 11.6 Hz), 119.14 (d, *J* 12.4 Hz), 117.65, 70.98 (d, *J* 5.7 Hz), 70.95 (d, *J* 5.8 Hz), 32.76 (d, *J* 100.1 Hz), 32.39 (d, *J* 100.0 Hz), 28.85 (d, *J* 7.6 Hz), 28.56 (d, *J* 6.7 Hz), 24.96 (d, *J* 6.7 Hz), 24.89 (d, *J* 3.8 Hz), 24.43 (d, *J* 2.9 Hz), 24.35 (d, *J* 2.8 Hz), 23.77 (d, *J* 2.8 Hz), 23.73 (d, *J* 2.9 Hz), 15.07, 14.97; δ_P (162 MHz, $CDCl_3$) 37.68 (s), 37.01. HRMS (ESI) Calcd for $[M+H]^+$ $C_{15}H_{20}N_2O_2P$: 291.1262, Found: 291.1226.

*4.13. 3-(diphenylphosphoryl)propanenitrile (**7**)*. White solid; δ_H (400 MHz, $CDCl_3$) 7.74~7.69 (4H, m), 7.58~7.47 (6H, m), 2.67~2.56 (4H, m); δ_C (100 MHz, $CDCl_3$) 132.57 (d, *J* 2.8 Hz), 131.48 (d, *J* 101.1 Hz), 130.80 (d, *J* 9.5 Hz), 129.11 (d, *J* 11.4 Hz), 118.64 (d, *J* 18.1 Hz), 26.63 (d, *J* 69.6 Hz), 10.47; δ_P (162 MHz, $CDCl_3$) 30.04. This compound is known.[14]

*4.14. 2-((diphenylphosphoryl)methyl)pentanedinitrile (**7'**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.79~7.70 (4H, m), 7.61~7.47 (6H, m), 3.20~3.11 (1H, m), 2.78~2.70 (1H, m), 2.63~2.44 (3H, m), 2.37~2.29 (1H, m), 2.08~1.98 (1H, m); δ_C (100 MHz, $CDCl_3$) 132.79 (d, *J* 2.8 Hz), 132.66 (d, *J* 2.9 Hz), 132.48 (d, *J* 101.9 Hz), 131.03 (d, *J* 9.5 Hz), 130.83 (d, *J* 100.0 Hz), 130.53 (d, *J* 9.5 Hz), 129.23 (d, *J* 12.4 Hz), 129.17 (d, *J* 12.4 Hz), 119.28 (d, *J* 11.4 Hz), 117.61, 32.48 (d, *J* 67.7 Hz), 28.97 (d, *J* 4.8 Hz), 25.16 (d, *J* 1.9 Hz), 15.24; δ_P (162 MHz, $CDCl_3$) 28.72. HRMS (ESI) Calcd for $[M+H]^+$ $C_{18}H_{17}N_2OP$: 308.1078, Found: 308.1080.

*4.15. Methyl 3-(dimethoxyphosphoryl)propanoate (**8**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 3.67 (9H, d, *J* 10.4 Hz, s), 2.57~2.50 (2H, m), 2.07~1.99 (2H, m); δ_C (100 MHz, $CDCl_3$) 172.41 (d, *J* 18.1 Hz), 52.48 (d, *J* 6.7 Hz), 51.99, 27.17 (d, *J* 3.8 Hz), 20.69 (d, *J* 143.9 Hz); δ_P (162 MHz, $CDCl_3$) 33.39. HRMS (ESI) Calcd for $[M+H]^+$ $C_6H_{14}O_5P$: 197.0578, Found: 197.0554. This compound is known.[13]

*4.16. Dimethyl 2-((dimethoxyphosphoryl)methyl)pentanedioate (**8'**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 3.69~3.62 (12 H, m), 2.80~2.70 (1H, m), 2.31~2.15 (3H, m), 1.96~1.77 (3H, m); δ_C (100 MHz, $CDCl_3$) 174.33 (d, *J* 8.6 Hz), 172.79, 52.55 (d, *J* 6.6 Hz), 52.46 (d, *J* 6.7 Hz), 52.05, 51.69, 39.05 (d, *J* 3.8 Hz), 31.19, 28.42 (d, *J* 12.4 Hz), 27.65 (d, *J* 142.0 Hz); δ_P (162 MHz, $CDCl_3$) 31.77. HRMS (ESI) Calcd for $[M+H]^+$ $C_{10}H_{20}O_7P$: 283.0946, Found: 283.0927.

*4.17. tert-butyl 3-(dimethoxyphosphoryl)propanoate (**9**)*. Colorless oil; δ_H (400 MHz, $CDCl_3$) 3.69 (6H, d, *J* 10.8 Hz), 2.48~2.41 (2H, m,), 2.03~1.94 (2H, m), 1.39 (9H, s); δ_C (100

MHz, CDCl$_3$) 171.08 (d, *J* 18.1 Hz), 80.90, 52.38 (d, *J* 6.7 Hz), 28.41 (d, *J* 3.8 Hz), 27.94, 20.68 (d, *J* 143.0 Hz); δ_P (162 MHz, CDCl$_3$) 33.99. HRMS (ESI) Calcd for $[M+H]^+$ $C_9H_{20}O_5P$: 239.1048, Found: 239.1076.

*4.18. Di-tert-butyl 2-((dimethoxyphosphoryl)methyl)pentanedioate (**9’**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 3.69 (6 H, d, *J* 2.4 Hz, d, *J* 3.2 Hz), 2.67~2.57 (1H, m), 2.25~2.13 (3H, m), 1.86~1.69 (3H, m), 1.42 (18H, s, s); δ_C (100 MHz, CDCl$_3$) 169.14 (d, *J* 7.6 Hz), 167.75, 77.05, 76.41, 48.38 (d, *J* 6.7 Hz), 48.28 (d, *J* 6.7 Hz), 35.80 (d, *J* 2.9 Hz), 28.60, 25.01 (d, *J* 13.3 Hz), 24.00, 23.93, 23.44 (d, *J* 142.0 Hz); δ_P (162 MHz, CDCl$_3$) 32.55. HRMS (ESI) Calcd for $[M+H]^+$ $C_{16}H_{32}O_7P$: 367.1885, Found: 367.1886.

*4.19. Dimethyl (2-cyanopropyl)phosphonate (**10**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 3.72~3.68(6H, d, *J* 10.8 Hz, d, *J* 11.2 Hz), 2.99~2.87 (1H, m), 2.16~2.05 (1H, m), 1.93~1.83 (1H, m), 1.39~1.37 (3H, d, *J* 7.2 Hz, d, *J* 6.0 Hz); δ_C (100 MHz, CDCl$_3$) 121.56 (d, *J* 12.4 Hz), 52.72 (d, *J* 6.7 Hz), 52.59 (d, *J* 6.6 Hz), 29.97 (d, *J* 142.9 Hz), 20.39 (d, *J* 3.8 Hz), 19.28 (d, *J* 9.5 Hz); δ_P (162 MHz, CDCl$_3$) 28.65. HRMS (ESI) Calcd for $[M+H]^+$ $C_6H_{13}NO_3P$: 178.0633, Found: 178.0646.

*4. 20. Dimethyl (2,4-dicyano-2-methylpentyl)phosphonate (**10’**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 3.76 ~3.72 (6H, m), 2.88~2.80 (1H, m), 2.31~1.98 (4H, m), 1.63~1.59 (3H, s, s,), 1.41~1.39 (3H, d, *J* 7.2 Hz, d, *J* 6.8 Hz,); δ_C (100 MHz, CDCl$_3$) 122.24, 122.13, 121.98 (d, *J* 11.4 Hz), 121.80 (d, *J* 11.4 Hz), 52.91 (d, *J* 6.6 Hz), 52.84 (d, *J* 7.7 Hz), 52.71 (d, *J* 5.7 Hz), 43.11 (d, *J* 7.7 Hz), 42.93 (d, *J* 7.7 Hz), 36.09 (d, *J* 142.9 Hz), 33.78 (d, *J* 142.0 Hz), 33.37 (d, *J* 2.9 Hz), 33.07 (d, *J* 2.9 Hz), 26.28 (d, *J* 5.7 Hz), 25.20 (d, *J* 7.6 Hz), 22.09 (d, *J* 26.6 Hz), 19.59 (d, *J* 16.2 Hz); δ_P (162 MHz, CDCl$_3$) 26.48. HRMS (ESI) Calcd for $[M+H]^+$ $C_{10}H_{18}N_2O_3P$: 245.1055, Found: 245.1067.

*4.21. Methyl 3-(dimethoxyphosphoryl)-2-methylpropanoate (**11**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 3.68~3.64 (9H, m), 2.84~2.72 (1H, m), 2.28~2.18 (1H, m), 1.81~1.70 (1H, m), 1.25 (3H, d, *J* 8.0 Hz); δ_C (100 MHz, CDCl$_3$) 175.58 (d, *J* 12.4 Hz), 52.36 (d, *J* 4.8 Hz), 52.00, 34.30 (d, *J* 2.9 Hz), 28.95 (d, *J* 141.1 Hz), 18.67 (d, *J* 9.6 Hz); δ_P (162 MHz, CDCl$_3$) 32.55. HRMS (ESI) Calcd for $[M+H]^+$ $C_7H_{16}O_5P$: 211.0735, Found: 211.0764.

*4.22. Methyl 3-(isopropoxy(phenyl)phosphoryl)propanoate (**12**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 7.67~7.62 (2H, m), 7.42~7.31 (3H, m), 4.59~4.34 (1H, m), 3.47 (3H, s), 2.53~2.31 (2H, m), 2.17~1.95 (2H, m), 1.24 (3H, d, *J* 6.4 Hz), 1.02 (3H, d, *J* 6.4 Hz); δ_C (100 MHz, CDCl$_3$) 172.36 (d, *J* 17.2 Hz), 132.08 (d, *J* 1.9 Hz), 131.45 (d, *J* 123.9 Hz), 131.41 (d, *J* 9.5 Hz), 128.38 (d, *J* 12.3 Hz), 69.59 (d, *J* 5.8 Hz), 51.62, 26.38, 25.79 (d, *J* 102.0 Hz), 24.31 (d, *J* 2.9 Hz), 23.71 (d, *J* 4.8 Hz); δ_P (162 MHz, CDCl$_3$) 41.79. HRMS (ESI) Calcd for $[M+H]^+$ $C_{13}H_{20}O_4P$: 271.1099, Found: 271.1080.

*4.23. Dimethyl 2-((isopropoxy(phenyl)phosphoryl)methyl)pentanedioate (**12’**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 7.74~7.67 (2H, m), 7.49~7.38 (3H, m), 4.48~4.37 (1H, m), 3.56 (6H, d, *J* 12.4 Hz, d, *J* 65.2 Hz), 2.84~2.67 (1H, m), 2.42~2.18 (3H, m), 2.00~1.77 (3H, m), 1.28 (3H, d, *J* 6.0 Hz, d, *J* 5.6 Hz), 1.05 (3H, d, *J* 5.2 Hz, d, *J* 6.0 Hz); δ_C (100 MHz, CDCl$_3$) 174.42 (d, *J* 6.6 Hz), 174.21 (d, *J* 7.6 Hz), 172.77, 172.70, 132.20, 132.08 (d, *J* 124.9 Hz), 131.75 (d, *J* 10.4 Hz), 131.72 (d, *J* 123.9 Hz), 131.63 (d, *J* 10.5 Hz), 128.50 (d, *J* 12.4 Hz), 128.43 (d, *J* 12.4 Hz), 69.88 (d, *J* 6.7 Hz), 69.82 (d, *J* 6.6 Hz), 51.80, 51.68, 51.54, 38.48, 38.44, 32.86 (d, *J* 101.0 Hz), 32.65 (d, *J* 101.1 Hz), 31.16, 28.71 (d, *J* 12.4 Hz), 28.51 (d, *J* 11.4 Hz), 24.46 (d, *J* 2.9 Hz), 24.38 (d, *J* 2.8 Hz), 23.82 (d, *J* 4.8 Hz); δ_P (162 MHz, CDCl$_3$) 40.71, 40.29. HRMS (ESI) Calcd for $[M+H]^+$ $C_{17}H_{26}O_6P$: 357.1467, Found: 357.1477.

*4.24. Methyl 3-(diphenylphosphoryl)propanoate (**13**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 7.86~7.63 (4H, m), 7.45~7.36 (6H, m), 3.53 (3H, s), 2.59~2.47 (4H, m); δ_C (100 MHz, CDCl$_3$) 172.63 (d, *J* 16.2 Hz), 132.51 (d, *J* 99.1 Hz)， 131.82 (d, *J* 2.8 Hz), 130.63 (d, *J* 9.6 Hz), 128.63 (d, *J* 11.5 Hz), 51.84, 26.11 (d, *J* 1.9 Hz), 25.24 (d, *J* 72.9 Hz); δ_P (162 MHz, CDCl$_3$) 32.02. This compound is known.[15]

*4.25. Dimethyl 2-((diphenylphosphoryl)methyl)pentanedioate (**13’**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 7.69~7.64 (4H, m), 7.46~7.36 (6H, m), 3.53 (3H, s), 3.35 (3H, s), 2.91~2.72 (2H, m), 2.32~2.21 (3H, m), 1.97~1.92 (2H, m); δ_C (100 MHz, CDCl$_3$) 174.32 (d, *J* 6.7 Hz), 172.63, 133.51 (d, *J* 99.2 Hz), 132.34 (d, *J* 98.1 Hz), 131.77 (d, *J* 3.8 Hz), 131.73 (d, *J* 2.8 Hz), 130.94 (d, *J* 9.5 Hz), 130.48 (d, *J* 8.6 Hz), 128.63 (d, *J* 11.5 Hz), 128.48 (d, *J* 12.4 Hz), 51.73, 51.51, 38.16 (d, *J* 2.9 Hz), 32.11 (d, *J* 70.5 Hz), 31.18, 29.90 (d, *J* 9.5 Hz); δ_P (162 MHz, CDCl$_3$) 30.11. This compound is known.[16]

*4.26. tert-butyl 3-(diphenylphosphoryl)propanoate (**14**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 7.74~7.69 (4H, m), 7.51~7.42 (6H, m), 2.57~2.47 (4H, m), 1.36 (9H, s); δ_C (100 MHz, CDCl$_3$) 171.61 (d, *J* 17.2 Hz), 132.85 (d, *J* 101.9 Hz), 131.85, 130.79 (d, *J* 8.6 Hz), 128.73 (d, *J* 11.4 Hz), 81.02, 27.97, 27.43 (d, *J* 1.9 Hz), 25.36 (d, *J* 72.5 Hz); δ_P (162 MHz, CDCl$_3$) 32.35. This compound is known.[17]

*4.27. 5-((diphenylphosphoryl)methyl)-2,2,10,10-tetramethylundecane-4,8-dione (**14’**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 7.72~7.64 (4 H, m), 7.45~7.36 (6H, m), 3.55 (3H, d), 3.43 (3H, d). 2.83~2.76 (1H, m), 2.51~2.41 (2H, m), 2.30~2.24 (1H, m), 2.16~2.05 (1H, m), 1.24 (3H, d), 1.02 (3H, d); δ_C (100 MHz, CDCl$_3$) 169.33 (d, *J* 6.7 Hz), 167.74, 129.91 (d, *J* 101.1 Hz), 128.90 (d， *J*= 98.2 H)， 127.67， 127.02 (d, *J* 9.5 Hz), 126.60 (d, *J* 8.6 Hz), 124.63 (d, *J* 8.6 Hz), 124.51 (d, *J* 8.6 Hz), 77.05, 76.26, 34.90, 28.74, 27.81 (d, *J* 70.5 Hz), 25.48 (d, *J* 8.6 Hz), 23.97, 23.83; δ_P (162 MHz, CDCl$_3$) 30.62. HRMS (ESI) Calcd for $[M]^+$ $C_{26}H_{35}O_5P$: 458.2222, Found:458.2246.

*4.28. 3-(diphenylphosphoryl)-2-methylpropanenitrile (**15**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 7.74~7.66 (4H, m), 7.50~7.38 (6H, m), 3.10~3.05 (1H, m), 2.73~2.65 (1H, m), 2.46~2.37 (1H, m), 1.36 (3H, d, *J* 7.6 Hz); δ_C (100 MHz, CDCl$_3$) 132.86 (d, *J* 100.0 Hz), 132.23 (d, *J* 2.9 Hz), 132.10 (d, *J* 2.9 Hz), 131.46 (d, *J* 100.0 Hz), 130.76 (d, *J* 9.5 Hz), 130.34 (d, *J* 9.6 Hz), 128.79 (d, *J* 11.4 Hz), 121.76 (d, *J* 12.4 Hz), 34.09 (d, *J* 68.6 Hz), 19.63 (d, *J* 1.9 Hz), 19.51 (d, *J* 5.7 Hz); δ_P (162 MHz, CDCl$_3$) 28.79. HRMS (ESI) Calcd for $[M]^+$ $C_{11}H_{16}NOP$: 269.0969, Found: 269.0947.

*4.29. 2-((diphenylphosphoryl)methyl)-2,4-dimethylpentanedinitrile (**15’**)*. Colorless oil; δ_H (400 MHz, CDCl$_3$) 7.83~7.71 (4H, m), 7.51~7.44 (6H, m), 2.93~2.67 (3H, m), 2.31~1.96 (2H, m), 1.57 (3H, d, *J* 2.4 Hz), 1.35 (3H, t, *J* 7.2 Hz); δ_C (100 MHz, CDCl$_3$) 133.34 (d, *J* 101.0 Hz), 133.17, 132.71 (d, *J* 100.1 Hz), 132.19, 130.77 (8.6 Hz), 130.57 (d, *J* 8.6 Hz), 130.52 (d, *J* 3.8 Hz), 130.43 (d, *J* 2.9 Hz), 128.90 (d, *J* 11.5 Hz), 128.86 (d, *J* 11.5 Hz), 122.40 (d, *J* 11.5 Hz), 121.72 (d, *J* 11.5 Hz), 121.61 (d, *J* 8.5 Hz), 43.34 (d, *J* 4.7 Hz), 43.02 (d, *J* 3.8 Hz), 39.05 (d, *J* 67.6 Hz), 37.04 (d, *J* 67.6 Hz), 34.79 (d, *J* 3.8 Hz), 34.34 (d, *J* 3.8 Hz), 26.75 (d, *J* 4.8 Hz), 25.86 (d, *J* 5.8 Hz), 22.14 (d, *J* 18.2 Hz), 19.51 (d, *J* 17.2 Hz); δ_P (162 MHz, CDCl$_3$) 26.78, 26.34. HRMS (ESI) Calcd for $[M]^+$ $C_{20}H_{21}N_2OP$: 336.1391, Found: 336.1416.

*4.30. Methyl 3-(diphenylphosphoryl)-2-methylpropanoate (**16**).* Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.75~7.71 (4H, m), 7.50~7.42 (6H, m), 3.47 (3H, s), 3.01~2.82 (2H, m), 2.33~2.25 (1H, m), 1.27 (3H, d, *J* 6.8 Hz); δ_C (100 MHz, $CDCl_3$) 175.85 (d, *J* 10.5 Hz), 134.00 (d, *J* 99.1Hz), 132.73 (d, *J* 98.2 Hz), 131.75, 131.00 (d, *J* 9.6 Hz), 130.61 (d, *J* 9.6 Hz), 128.70 (d, *J* 12.4 Hz), 128.62 (d, *J* 11.4), 51.91, 33.69 (d, *J* 92.5 Hz), 33.67 (d, *J* 20.0 Hz), 19.24 (d, *J* 7.7 Hz); δ_P (162 MHz, $CDCl_3$) 30.66. This compound is known.[6]

*4.31. Dimethyl (3-oxobutyl)phosphonate (**17**).* Colorless oil; δ_H (400 MHz, $CDCl_3$) 3.69 (6H, d, *J* 11.2 Hz), 2.72~2.65 (2H, m), 2.13 (3H, s), 2.01~1.92 (2H, m). δ_C (100 MHz, $CDCl_3$) 205.65 (d, *J* 14.3 Hz), 52.43 (d, *J* 6.7 Hz), 36.11 (d, *J* 3.8 Hz), 29.60, 18.93 (d, *J* 14.4 Hz). δ_P (162 MHz, $CDCl_3$) 34.98. This compound is known.[18]

*4.32. Dimethyl (2-acetyl-5-oxohexyl)phosphonate (**17’**).* Colorless oil; δ_H (400 MHz, $CDCl_3$) 3.66~3.62 (6H, m), 2.93~2.83 (1H, m), 2.45~2.29 (2H, m), 2.25~2.14 (4H, m), 2.08 (3H, d), 1.94~1.85 (1H, m), 1.78~1.60 (2H, m). δ_C (100 MHz, $CDCl_3$) 209.43 (d, *J* 5.8 Hz), 207.20, 52.51 (d, *J* 7.6 Hz), 52.43 (d, *J* 6.7 Hz), 45.20 (d, *J* 2.9 Hz), 39.69, 30.05, 29.32, 26.05 (d, *J* 3.8 Hz), 25.92 (d, *J* 132.5 Hz). δ_P (162 MHz, $CDCl_3$) 32.95. HRMS (ESI) Calcd for $[M+H]^+$ $C_{10}H_{20}O_5P$: 251.1048, Found: 251.1030.

*4.33. 4-(diphenylphosphoryl)butan-2-one (**18**).* White solid; δ_H (400 MHz, $CDCl_3$) 7.69~7.64 (4H, m), 7.48~7.38 (6H, m), 2.73~2.67 (2H, m), 2.51~2.44 (2H, m), 2.05 (3H, s); δ_C (100 MHz, $CDCl_3$) 206.20 (d, *J* 13.4 Hz), 132.88, 131.93 (d, *J* 2.0 Hz), 130.75 (d, *J* 9.6 Hz), 128.80 (d, *J* 11.5 Hz), 35.24 (d, *J* 1.9 Hz), 29.75, 23.68 (d, *J* 73.4 Hz); δ_P (162 MHz, $CDCl_3$) 33.11. This compound is known.[19]

*4.34. 3-((diphenylphosphoryl)methyl)heptane-2,6-dione (**18’**).* Colorless oil; δ_H (400 MHz, $CDCl_3$) 7.69~7.58 (4H, m), 7.45, 7.33 (6H, m), 2.97~2.79 (2H, m), 2.43~2.24 (2H, m), 2.12~2.04 (1H, m), 1.99 (3H, s), 1.93~1.84 (4H, m), 1.73~1.64 (1H, m); δ_C (100 MHz, $CDCl_3$) 209.41 (d, *J* 4.8 Hz), 207.20, 133.56 (d, *J* 87.7 Hz), 132.36 (d, *J* 86.7 Hz), 131.79 (d, *J* 2.0 Hz), 130.81 (d, *J* 9.5 Hz), 130.44 (d, *J* 8.6 Hz), 128.65 (d, *J* 11.5 Hz), 128.54 (d, *J* 12.3 Hz), 44.22 (d, *J* 1.9 Hz), 39.58, 30.25 (d, *J* 71.4 Hz), 29.81, 28.99, 26.33 (d, *J* 8.6 Hz); δ_P (162 MHz, $CDCl_3$) 31.51. HRMS (ESI) Calcd for $[M+H]^+$ $C_{20}H_{24}O_3P$: 343.1463, Found: 343.1440.

*4.35. 2-methylenepentanedinitrile (**19**).* Colorless oil; δ_H (400 MHz, $CDCl_3$) 6.02 (1H, s), 5.91 (1H, s), 2.64~2.56 (4H, m); δ_C (100 MHz, $CDCl_3$) 133.38, 119.00, 117.46, 117.09, 30.35, 16.03. This compound is known.[12]

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