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Short communication

Pd(0)/iodide salt-mediated Heck reaction of aryl nonaflates: Application to the synthesis of 2-(1-alkenyl)phenylphosphonates

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ABSTRACT

Iodide salt, such as NaI, KI or *n*-Bu_4NI (TBAI), rather than bromide or chloride salt, was found to play a key role in the Pd(0)-catalyzed Heck reaction of aryl nonaflates and terminal alkenes. In the presence of $PdCl_2(PPh_3)_2$, NaI or TBAI in DMF, a class of 2-(1-alkenyl)phenylphosphonates was first synthesized via the reaction of *o*-phosphonylphenyl nonaflates with alkenes, the yields, regioselectivities and stereoselectivities were much dependent on the nature of the substituents. In case of the aryl nonaflates without bearing the sterically hindered phosphonyl group with the alkenes, the reactions proceeded more smoothly under the same conditions, leading to the linear products regioselectively in good to excellent yields. A rationale for this reaction is discussed.

1. Introduction

In the last decades, aryl/vinyl nonaflates have attracted much attention since in comparison of aryl/vinyl triflates, the nonaflates are not only more stable and not prone to hydrolyze during synthesis and handling, but display similar or slightly superior reactivities in most of the metal-catalyzed cross-coupling reactions and can be prepared easily from nonaflyl fluoride (NfF) which is a commercially accessible, cheap, industrial product [1]. Generally, the addition of stoichiometric LiCl has benefical effects in the coupling reactions of the nonaflates or triflates [2]. Recently, we have demonstrated that 2-(1-alkynyl)phenylphosphonates could be prepared conveniently via the reaction of the aryl nonaflates with alkynes and the addition of excess LiCl indeed improved the reactions [3]. However, during the course of our investigation to synthesize the corresponding 2-(1-alkenyl)phenylphosphonates via the Heck reaction of the same aryl nonaflates, we found that the presence of iodide salt is necessary for the reaction. Although the palladium-catalyzed Heck reaction is one of the most well-established and valuable synthetic methods in organic synthesis and has been investigated extensively [4], such iodide anion effect and using aryl nonaflates with a hindered ortho-phosphonyl group as substrates for the Heck reaction has never been reported so far. Herein, we wish to report this interesting iodide anion effect and its synthetic applications in this paper.

2. Results and discussion

We first examined the reaction of 4-chloro-2-phosphonylphenyl nonaflate **1a** with methyl acrylate **2a**, and the results were summarized in Table 1. Under standard Heck reaction conditions, no desired reaction was detected (Entries 1–5, Table 1). After conducting a series of examinations, we found that the presence of iodide anion was essential for the success of this reaction. When addition of 0.1 equiv. of anhydrous NaI, the starting material **1a** was consumed completely and the desired product **3a** was isolated in 80% yield with high regioselectivity and no other isomers were observed (Entry 6, Table 1). Using NaI as a dihydrate ($NaI{\cdot}2H_2O$) resulted in the same result, suggesting the presence of trace amount of water has no unfavorable effect on the reaction (Entry 7, Table 1). Other iodide salt, such as KI and *n*-Bu_4NI (TBAI) were also effective, while bromide salt or chloride salt, such as NaBr, NaCl, LiCl, *n*-Bu_4NCl (TBAC) could not make the reaction take place at all (Entries 8–13, Table 1), indicating that iodide anion other than chloride or bromide anion plays important role in this reaction. Further reaction optimization demonstrated that DMF was the best solvent and Et_3N was the appropriate base.

To explore the scope and limitations of this reaction, the reactions of **1a–c** with several alkenes **2** (4 equiv.) were carried out in the presence of $PdCl_2(PPh_3)_2$ (0.05 equiv.), Et_3N (4 equiv.), NaI (0.1 equiv.) at 80–90 °C in DMF. As shown in Table 2, the yields, regioselectivities and stereoselectivities were much dependent on the nature of R^1 and R^2. As expected, the electron-deficient nonaflate **1a** (R^1 = Cl) displayed good reactivity. The reaction of **1a** with activated methyl acrylate **2a** proceeded smoothly, leading to the *trans* linear product **3a** absolutely (Entry 1, Table 2), while the

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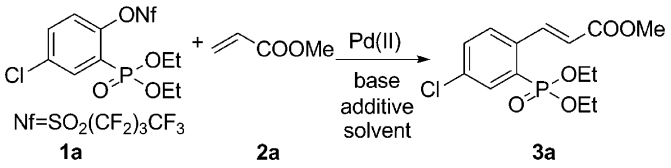
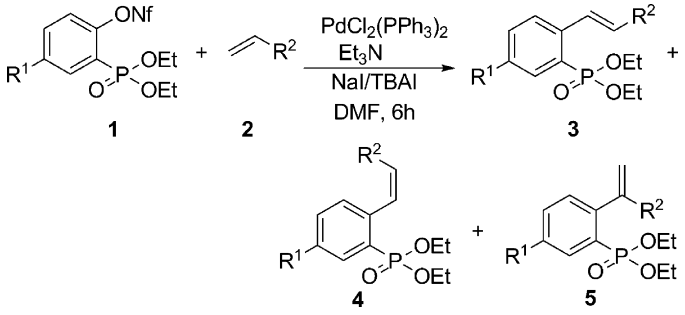
Table 1
Optimization of the Heck reaction conditions of **1a** and **2a**.[a]



Entry	Solvent	Base (equiv.)	Additive (equiv.)	Temp. (time)	Yield **3a** (%)
1	Dioxane	Cs_2CO_3 (1)	–	90 °C (8 h)	NR[d]
2	DMF	Et_3N (4)	LiCl (3)	80 °C (8 h)	NR
3	DMF	Et_3N (4)	CuI (0.1)	80 °C (8 h)	NR
4[b]	DMF	Et_3N (4)	LiCl (3)	80 °C (8 h)	NR
5[c]	EtOH	K_2CO_3 (2)	DABCO (0.2)	80 °C (8 h)	NR
6	DMF	Et_3N (4)	NaI (0.1)	80 °C (6 h)	80[e]
7	DMF	Et_3N (4)	NaI·$2H_2O$ (0.1)	80 °C (6 h)	83[f]
8	DMF	Et_3N (4)	KI (0.1)	80 °C (6 h)	83[f]
9	DMF	Et_3N (4)	TBAI (0.1)	80 °C (6 h)	83[f]
10	DMF	Et_3N (4)	NaBr (0.1)	80 °C (6 h)	NR
11	DMF	Et_3N (4)	NaCl (0.1)	80 °C (6 h)	NR
12	DMF	Et_3N (4)	TBAC (0.1)	80 °C (6 h)	NR
13	DMF	Et_3N (4)	LiCl (0.1)	80 °C (6 h)	NR

[a] All reactions were catalyzed by 0.05 equiv. of $PdCl_2(PPh_3)_2$ unless otherwise specified.
[b] 0.05 equiv. of $Pd(OAc)_2$ and 0.1 equiv. of PPh_3 were used as catalysts.
[c] 0.2 equiv. of CuI was used as catalyst.
[d] NR means no reaction was detected by TLC and most starting material was recovered.
[e] Isolated yield.
[f] The yield was determined by ^{31}P NMR spectral analysis of the crude reaction mixture.

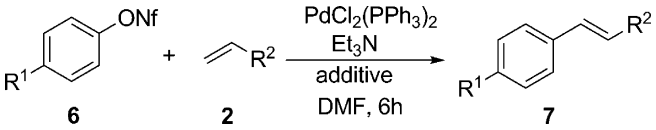
Table 2
Iodide anion-mediated Heck reaction of **1** and **2**.[a]



Entry	**1** (R^1)	**2** (R^2)	Additive (equiv.)	Yield (%)[b]
1	**1a** (Cl)	**2a** (COOMe)	NaI (0.1)	**3a** (80)
2	**1a** (Cl)	**2b** (CN)	NaI (0.1)	**3b** (30)[c]
3	**1a** (Cl)	**2c** (Ph)	NaI (0.1)	**3c** (65)[d]
4	**1b** (H)	**2a** (COOMe)	NaI (0.1)	**3d** (50)
5	**1b** (H)	**2b** (CN)	NaI (0.1)	Trace
6	**1b** (H)	**2b** (CN)	TBAI (1)	**3e** + **4e** (11)[e]
7	**1b** (H)	**2c** (Ph)	NaI (0.1)	Trace
8	**1b** (H)	**2c** (Ph)	TBAI (1)	**3f** (60)[d]
9	**1c** (MeO)	**2a** (COOMe)	NaI (0.1)	Trace
10	**1c** (MeO)	**2a** (COOMe)	TBAI (1)	**3g** + **4g** (17)[f]
11	**1c** (MeO)	**2b** (CN)	NaI (0.1)	Trace
12	**1c** (MeO)	**2c** (Ph)	NaI (0.1)	Trace
13	**1c** (MeO)	**2c** (Ph)	TBAI (1)	**3h** + **5h** (47)[g]

[a] General reaction conditions: **1** (1 equiv.), **2** (4 equiv.), $PdCl_2(PPh_3)_2$ (0.05 equiv.), Et_3N (4 equiv.), NaI or TBAI in DMF at 80–90 °C for 6 h.
[b] Isolated yield.
[c] **4b** was isolated in about 28% yield but it was not very pure for full characterization (**3b**:**4b** is about 1:1 of the crude products from ^{31}P NMR and ^1H NMR).
[d] Small amount of branched isomer **5** was detected by ^{31}P NMR and ^1H NMR.
[e] **3e**:**4e** = 2:3 of the products from the ^{31}P NMR and ^1H NMR.
[f] **3g**:**4g** = 4:1 of the products from the ^{31}P NMR and ^1H NMR.
[g] **3h**:**5h** = 2.36:1 of the crude products from the ^{31}P NMR and ^1H NMR, accompany with an unidentified compound.

Table 3
Iodide anion-mediated Heck reaction of **6** and **2**.[a]



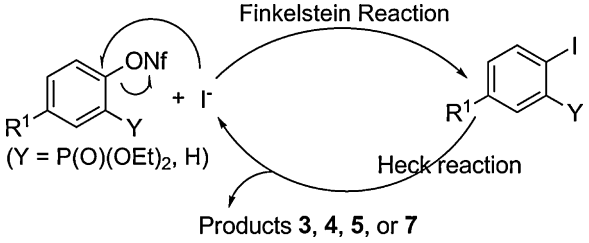
Entry	**6** (R^1)	**2** (R^2)	Additive (equiv.)	Yield (%)[b]
1	**6a** (Cl)	**2a** (COOMe)	LiCl (1)	**7a** (20)
2	**6a** (Cl)	**2a** (COOMe)	–	**7a** (50)
3	**6a** (Cl)	**2a** (COOMe)	NaI (0.1)	**7a** (97)
4	**6a** (Cl)	**2b** (Ph)	NaI (0.1)	**7b** (70)
5	**6b** (H)	**2a** (COOMe)	NaI (0.1)	**7c** (78)
6	**6b** (H)	**2b** (Ph)	NaI (0.1)	**7d** (46)
7	**6c** (MeO)	**2a** (COOMe)	NaI (0.1)	Trace
8	**6c** (MeO)	**2a** (COOMe)	TBAI (1)	**7e** (51)

[a] General reaction conditions: **6** (1 equiv.), **2** (4 equiv.), $PdCl_2(PPh_3)_2$ (0.05 equiv.), Et_3N (4 equiv.), additive (0.1 equiv. or 1 equiv.) in DMF at 80–90 °C for 6 h.
[b] Isolated yield.

reaction of **1a** with acrylonitrile **2b** gave a mixture of *trans*/*cis* isomers (**3b**:**4b** is about 1:1, Entry 2, Table 2). In the case of **1a** with styrene **2c**, the reaction afforded the *trans* linear product **3c** in 65% yield with observation of branched isomer **5c** formation (Entry 3, Table 2). Further studies showed that the reactivity of **1b** (R^1 = H) and **1c** (R^1 = OMe) decreased apparently. When using NaI as additive, except that the reaction of **1b** with **2a** gave **3d** in 50% yield, other reactions of **1b** and **1c** with alkenes only led to recovered starting materials and trace amount of the desired products (Entries 5, 7, 9, 11, and 12, Table 2). To our delight, by adding 1 equiv. of TBAI instead of 0.1 equiv. of NaI, all above reactions took place at the end. For example, with the addition of 1 equiv. of TBAI, the reaction of **1b** with **2b** gave the product **3f** in 60% isolated yield (Entry 8, Table 2). For this reaction, stoichiometric TBAI was necessary since most of the starting material was recovered when the amount of TBAI was decreased to 0.5 equiv. In this case, increasing the amount of NaI to 1 equiv. had no such favourable effect. Unfortunately, even in the presence of 1 equiv. of TBAI, the reactions of **1b** with **2b** and **1c** with **2a** or **2c** only resulted in mixtures of isomers in low yields, which were difficult to isolate (Entries 6, 10, and 13, Table 2).

Regioselectivities and stereoselectivities were determined by ^{1}H NMR spectral analysis of the crude reaction mixture. Generally, the *trans* linear products **3** are the main products (Entries 1, 3, 4, 8, 10, and 13, Table 2). When using acryonitril as alkene substrate, the reactions led to 1:1 or 2:3 mixtures of *cis*/*trans*-isomerized products because of the small size of the nitril group (Entries 2 and 6, Table 2). In cases where styrene was used as alkene substrate, branched products **5** were also observed other than the main *trans* linear products (Entries 3, 8, and 13, Table 2).

To further examine the generality of such iodide anion effect on the Heck reaction of aryl nonaflates, other aryl nonaflates without bearing phosphonyl group were then studied. As shown in Table 3, the addition of 0.1 equiv. of NaI accelerated the reaction of 4-chlorophenyl nonaflate **6a** with methyl acrylate **2a** significantly, giving the desired product **7a** in 97% yield entries (Entry 3, Table 3). However, the addition of 1 equiv. of LiCl did not promote but retard this reaction (Entries 1 and 2, Table 3). This finding is interesting since LiCl as additive has often shown stronger promotion ability than the corresponding iodide salts in the cross coupling reactions [2]. Similarly, under the same conditions, compounds **6a** and **6b** reacted with the alkenes smoothly and afforded the desired products **7b** and **7d** in good yields. The reaction of the electron-rich 4-methoxyphenyl nonaflate **6c** with **2a** was also found to need the addition of 1 equiv. of TBAI, no reaction was observed when using catalytic amount of NaI as additive (Entries 7 and 8, Table 3).



Scheme 1. Plausible mechanism of iodide anion-mediated Heck reaction of aryl nonaflates.

The exact contribution of iodide anion in this reaction is still not clear now. It is generally accepted that the halide additives promote the cross-coupling reactions by accelerating the transmetallation step or by coordinating the halide to palladium prior to oxidative addition [2,5]. One or more equiv. of chlorides or bromides are usually used in the literature procedures. However, in our present reaction, only catalytic amount of iodide additive is needed in most cases and chloride or bromide salts are ineffective. We reasoned that a Finkelstein replacement reaction [6] may occur prior to the oxidative addition, in which aryl nonaflates transformed to the more reactive aryl iodides (Scheme 1). That is to say, the iodide anion would promote the reaction by facilitating the exchange of nonaflate for iodide, which then can enter the catalytic cycle of the Heck reaction. For the substrates with electron-donating group (e.g. **1c** and **6c**), it is difficult to proceed the Finkelstein replacement process, herein the iodide additive seems not so effective.

3. Conclusions

The existence of a bulky phosphonyl group at the ortho position of aryl nonaflates makes the nonaflates difficult to proceed the Heck reaction under classical conditions. We found that $PdCl_2(PPh_3)_2$/iodide salt can facilitate the reaction, which is efficient especially for electron-deficient aryl nonaflates. Iodide salt additive was essential for the success of this Heck reaction, while the corresponding chloride and bromide salts were completely ineffective. We synthesized a series of 2-(1-alkenyl)-phenylphosphonates for the first time using the present strategy, these compounds have considerable potential as useful inter-

mediates for the following cyclization reactions. Further investigations on the scope of the reaction and the cyclization of 2-(1-alkenyl)phenylphosphonates are underway.

4. Experimental

4.1. General

The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Mercury-Plus 300 or Varian INOVA 400 NMR instrument. All melting points are uncorrected. EI-mass spectra were recorded on a Thermo DSQ EI-mass spectrometer. ESI-mass spectra were recorded on a LCMS-2010A liquid chromatography mass spectrometer. HRMS were determined by a Thermo MAT95XP high resolution mass spectrometer. IR spectra were recorded as KBr pellets on a Bruker Equinox 55 FT/IR spectrometer. All commercially available reagents were used as received. Column chromatography was performed on 200–300 mesh silica gel. Thin-layer chromatography was conducted on Kieselgel 60 F254. The starting materials **1** and **6** were prepared according to our previous procedures [3b].

4.2. Typical procedure for iodide anion-mediated Heck reaction of 1 and 2 or 6 and 2

To a mixture of **1** (0.5 mmol), $PdCl_2(PPh_3)_2$ (0.025 mmol), Et_3N (2.0 mmol), NaI (0.050 mmol) or *n*-Bu_4NI (0.5 mmol), and DMF (3.0 mL) was added dropwise the terminal alkene **2** (2.0 mmol) at room temperature. After stirring at 80–90 °C for 6 h under nitrogen, the reaction mixture was diluted with EtOAc and washed with aqueous NH_4Cl until neutral and brine, dried (Na_2SO_4), and evaporated in vacuo. The residue was chromatographed on silica gel using hexane/EtOAc (6:1–4:1) as eluent to give the corresponding products. Among these products, compounds **3**, **4** and **5** are new compounds; compounds **7a**–**e** are known compounds which were confirmed by the results of NMR spectra and MS (ESI) data compared to the literature values.

4.2.1. (E)-3-[4-chloro-2-(diethoxy-phosphoryl)-phenyl]-acrylic acid methyl ester (3a)

White solid. Mp: 62–64 °C. IR (KBr): 2986, 1725, 1637, 1248, 1164, 1023 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, J = 15.8 Hz, 1H), 8.01 (dd, J = 15.0, 2.3 Hz, 1H), 7.60–7.65 (m, 1H), 7.49–7.54 (m, 1H), 6.35 (d, J = 15.8 Hz, 1H), 4.05–4.29 (m, 4H), 3.83 (s, 3H), 1.35 (t, J = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.79, 142.06 (d, J_{C-P} = 4.2 Hz), 136.18 (d, J_{C-P} = 7.9 Hz), 135.75, 134.43 (d, J_{C-P} = 10.4 Hz), 132.86 (d, J_{C-P} = 2.3 Hz), 130.28 (d, J_{C-P} = 181.9 Hz), 128.68 (d, J_{C-P} = 14.6 Hz), 121.27, 62.87 (d, J_{C-P} = 5.7 Hz), 52.03, 16.41 (d, J_{C-P} = 6.1 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 16.32 ppm. MS (ESI): m/z: 333 $[M+H]^+$. Anal. Calcd. for $C_{14}H_{18}ClO_5P$ (332.72): C, 50.54; H, 5.45. Found: C, 50.71; H, 5.59.

4.2.2. [5-Chloro-2-((E)-2-cyano-vinyl)-phenyl]-phosphonic acid diethyl ester (3b)

White solid. Mp: 83–85 °C. IR (KBr): 2922, 2217, 1622, 1246, 1155, 1028 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (d, J = 16.5 Hz, 1H), 7.90 (dd, J = 15.0, 2.0 Hz, 1H), 7.44–7.54 (m, 2H), 5.82 (d, J = 16.5 Hz, 1H), 3.97–4.20 (m, 4H), 1.28 (t, J = 7.1 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.87 (d, J_{C-P} = 3.4 Hz), 136.77 (d, J_{C-P} = 19.8 Hz), 134.84 (d, J_{C-P} = 8.2 Hz), 134.36 (d, J_{C-P} = 9.8 Hz), 132.87, 130.09 (d, J_{C-P} = 181.4 Hz), 127.84 (d, J_{C-P} = 14.6 Hz), 117.45, 99.68, 63.10 (d, J_{C-P} = 5.7 Hz), 16.53 (d, J_{C-P} = 5.9 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 15.66 ppm. MS (ESI): m/z: 300 $[M+H]^+$, 322 $[M+Na]^+$. Anal. Calcd. for $C_{13}H_{15}ClNO_3P$ (299.69): C, 52.10; H, 5.04; N, 4.67. Found: C, 51.94; H, 5.24; N, 4.43.

4.2.3. [5-Chloro-2-((E)-styryl)-phenyl]-phosphonic acid diethyl ester (3c)

Slightly yellow oil. IR (film): 2982, 1633, 1388, 1248, 1154, 1023 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (dd, J = 14.8, 2.7 Hz, 1H), 7.82 (d, J = 16.2 Hz, 1H), 7.68–7.74 (m, 1H), 7.47–7.56 (m, 3H), 7.28–7.39 (m, 3H), 7.03 (d, J = 16.2 Hz, 1H), 4.03–4.26 (m, 4H), 1.33 (t, J = 7.0 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.30 (d, J_{C-P} = 9.2 Hz), 136.89, 133.98 (d, J_{C-P} = 10.1 Hz), 133.00 (d, J_{C-P} = 19.5 Hz), 132.64, 131.97, 129.14, 128.81, 128.26 (d, J_{C-P} = 131.33 Hz), 128.25, 127.60, 126.89, 125.91 (d, J_{C-P} = 4.2 Hz), 62.57 (d, J_{C-P} = 4.4 Hz), 16.54 (d, J_{C-P} = 6.2 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 17.84 ppm. MS (ESI): m/z: 351 $[M+H]^+$. Anal. Calcd. for $C_{18}H_{20}ClO_3P$ (350.78): C, 61.63; H, 5.75. Found: C, 61.65; H, 6.00.

4.2.4. (E)-3-[2-(diethoxy-phosphoryl)-phenyl]-acrylic acid methyl ester (3d)

Slightly yellow oil. IR (film): 2985, 1719, 1637, 1392, 1247, 1024 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, J = 15.9 Hz, 1H), 7.97–8.05 (m, 1H), 7.65–7.70 (m, 1H), 7.52–7.58 (m, 1H), 7.41–7.48 (m, 1H), 6.36 (d, J = 15.9 Hz, 1H), 4.03–4.26 (m, 4H), 3.81 (s, 3H), 1.33 (t, J = 7.0 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.81, 143.19 (d, J_{C-P} = 4.4 Hz), 137.79 (d, J_{C-P} = 6.5 Hz), 134.44 (d, J_{C-P} = 9.8 Hz), 132.71, 129.35, 128.00 (d, J_{C-P} = 172.3 Hz), 127.19 (d, J_{C-P} = 13.5 Hz), 120.81, 62.54 (d, J_{C-P} = 5.2 Hz), 51.95, 16.49 (d, J_{C-P} = 6.5 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 18.40 ppm. MS (ESI): m/z: 299 $[M+H]^+$. Anal. Calcd. for $C_{16}H_{24}ClO_3P$ (330.79): C, 56.37; H, 6.42. Found: C, 56.52; H, 6.63.

4.2.5. Mixture of [2-((E)-2-cyano-vinyl)-phenyl]-phosphonic acid diethyl ester (3e) and [2-((Z)-2-cyano-vinyl)-phenyl]-phosphonic acid diethyl ester (4e)

Slightly yellow oil. IR (film): 2922, 2219, 1627, 1246, 1147, 1023 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, J = 16.2 Hz, 0.4H), 7.96–8.07 (m, 2H), 7.49–7.65 (m, 2.6H), 5.86 (d, J = 16.2 Hz, 0.4H), 5.61 (d, J = 12.0 Hz, 0.6H), 4.01–4.27 (m, 4H), 1.31–1.38 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.19, 148.47, 136.63 (d, J_{C-P} = 9.2 Hz), 134.63, 134.21, 132.91, 130.30, 130.10, 129.95, 129.76, 128.95, 126.80, 126.57, 126.41, 117.16, 116.79, 99.26, 98.48, 62.65 (d, J_{C-P} = 4.6 Hz), 16.53 (br s) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 17.79, 17.77 ppm. MS (EI): m/z (%) = 265 (26) $[M^+]$, 237 (23), 220 (35), 208 (34), 182 (100), 156 (44), 128 (14). HRMS (EI) calcd. for $C_{13}H_{15}ClNO_3P$ (M^+): 265.0862. Found: 265.0861.

4.2.6. [2-((E)-styryl)-phenyl]-phosphonic acid diethyl ester (3f)

Colorless oil. IR (film): 2982, 1634, 1392, 1245, 1138, 1025 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93–8.01 (m, 1H), 7.88 (d, J = 16.2 Hz, 1H), 7.74–7.87 (m, 1H), 7.48–7.55 (m, 3H), 7.23–7.38 (m, 4H), 7.04 (d, J = 16.2 Hz, 1H), 4.00–4.26 (m, 4H), 1.30 (td, J = 7.0, 0.3 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.88 (d, J_{C-P} = 9.4 Hz), 137.14, 134.28 (d, J_{C-P} = 9.2 Hz), 132.60, 131.40, 130.86, 128.70, 127.95, 127.05 (d, J_{C-P} = 5.8 Hz), 126.80, 126.04 (d, J_{C-P} = 13.8 Hz), 124.69, 62.18 (d, J_{C-P} = 4.1 Hz), 16.50 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 20.06 ppm. MS (ESI): m/z: 317 $[M+H]^+$, 339 $[M+Na]^+$. Anal. Calcd. for $C_{18}H_{21}O_3P$ (316.33): C, 68.34; H, 6.69. Found: C, 68.19. H, 6.61.

4.2.7. Mixture of (E)-3-[2-(diethoxy-phosphoryl)-4-methoxy-phenyl]-acrylic acid methyl ester (3g) and (Z)-3-[2-(diethoxy-phosphoryl)-4-methoxy-phenyl]-acrylic acid methyl ester (4g)

Slightly yellow oil. IR (film): 2983, 1718, 1636, 1245, 1175, 1025 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, J = 15.8 Hz, 0.8H), 7.40–7.64 (m, 2.2H), 6.93–7.03 (m, 1H), 6.23 (d, J = 15.8 Hz, 0.8H), 5.94 (d, J = 12.9 Hz, 0.2H), 3.92–4.24 (m, 4H), 3.81 (s, 2.4H), 3.80 (s, 0.6H), 3.74 (s, 2.4H), 3.58 (s, 0.6H), 1.21–1.32 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.97, 166.16, 160.07 (d, J_{C-P} = 18.2 Hz),

159.01 (d, J_{C-P} = 18.1 Hz), 142.92, 142.47, 132.17, 131.95, 130.75, 129.63 (d, J_{C-P} = 8.1 Hz), 128.74 (d, J_{C-P} = 5.7 Hz), 128.46 (d, J_{C-P} = 16.5 Hz), 119.62, 119.01 (d, J_{C-P} = 10.6 Hz), 118.70, 118.47 (d, J_{C-P} = 13.5 Hz), 118.25 (d, J_{C-P} = 6.6 Hz), 117.36 (d, J_{C-P} = 8.4 Hz), 62.45 (d, J_{C-P} = 4.1 Hz), 62.21 (d, J_{C-P} = 4.0 Hz), 55.64, 55.49, 51.67, 51.22, 16.36 (br s) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 18.51, 18.26 ppm. MS (EI): m/z (%) = 328 (21) [M^+], 269 (84), 241 (35), 213 (100), 191 (56), 149 (53). HRMS (EI) calcd. for $C_{15}H_{21}O_6P$ (M^+): 328.1070. Found: 328.1069.

*4.2.8. (E)-3-(4-chloro-phenyl)-acrylic acid methyl ester (**7a**) [7]*

White solid. Mp: 73–76 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, J = 15.9 Hz, 1H), 7.31–7.39 (m, 4H), 6.36 (d, J = 15.9 Hz, 1H), 3.77 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.01, 143.30, 136.13, 1332.80, 129.17, 129.11, 118.34, 51.86 ppm. MS (ESI): m/z: 197 [M+H]$^+$.

*4.2.9. 1-Chloro-4-((E)-styryl)-benzene (**7b**) [8]*

White solid. Mp: 124–125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25–7.53 (m, 9H), 7.07 (d, J = 1.6 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.00, 135.87, 133.19, 129.35, 128.87, 128.77, 127.90, 127.69, 127.40, 126.58 ppm. MS (ESI): m/z: 215 [M+H]$^+$.

*4.2.10. (E)-3-phenyl-acrylic acid methyl ester (**7c**) [7]*

Slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, J = 16.0 Hz, 1H), 7.51–7.54 (m, 2H), 7.36–7.39 (m, 3H), 6.45 (d, J = 16.0 Hz, 1H), 3.82 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.36, 144.85, 134.36, 130.29, 128.89, 128.07, 117.80, 51.83 ppm. MS (ESI): m/z: 163 [M+H]$^+$, 185 [M+Na]$^+$, 201 [M+K]$^+$.

*4.2.11. (E)-Stilbene (**7d**) [6,9]*

White solid. Mp: 130–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52–7.56 (m, 4H), 7.35–7.41 (m, 4H), 7.27–7.31 (m, 2H), 7.13 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.35, 128.72, 127.65, 126.55 ppm. MS (ESI): m/z: 181 [M+H]$^+$.

*4.2.12. (E)-3-(4-methoxy-phenyl)-acrylic acid methyl ester (**7e**) [7]*

White solid. Mp: 89–93 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, J = 16.0 Hz, 1H), 7.45–7.49 (m, 2H), 6.88–6.92 (m, 2H), 6.31 (d, J = 15.9 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.71, 161.35, 144.52, 129.74, 127.15, 115.30, 114.35, 55.53, 51.74 ppm. MS (ESI): m/z: 193 [M+H]$^+$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.06.029.

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