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Synthesis of diethyl 2-(aryl)vinylphosphonates by the Heck reaction catalysed by well-defined palladium complexes

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ABSTRACT

Pd-catalysed procedures for the direct Heck arylation of diethyl vinylphosphonate with various aryl or heteroaryl halides toward the synthesis of diethyl 2-(aryl)vinylphosphonates are reported. Several homogeneous catalytic systems (i.e. Herrmann palladacycle, Nolan (NHC)-palladium catalyst, $Pd(OAc)_2/PPh_3$) were used and compared within the study. High conversions and selectivities were achieved under optimised conditions (2 mol% [Pd], NMP, K_2CO_3, 140 °C) whatever the homogeneous catalyst used.

1. Introduction

Vinylphosphonates are valuable compounds due to their widespread applications in organic synthesis [1]. Among them, 2-(aryl)vinylphosphonates constitute a particularly interesting group since they are commonly used as starting material for the synthesis of pharmaceutically relevant molecules like metabolites, anticancer, antiviral drugs, immunosuppressives, insecticides, antibacterial and antifungal [2–7]. These building blocks are also involved in the preparation of flame retardant [8,9] or polymer, fuel and lubricant additives [10]. Some of them were also evaluated for their own pharmaceutical activity [11,12].

Owing their relevance, several methodologies to synthesise these compounds have been reported. Organometallic approaches include the *syn*-addition of organocuprates to 1-alkynylphosphonates [13,14], *anti*-hydrotelluration of 1-alkynylphosphonates [15], the formation of titanacycles from 1-alkynylphosphonates [16,17], the reaction of α-stannylated phosphonates with aldehydes to give *E*/*Z* mixtures [18], hydrozirconation of alkynes followed by phosphorylation [19,20], and olefin metathesis [21]. These methods are sometimes difficult to handle and often intolerant towards sensitive functional groups. Furthermore, the reagents are not always readily accessible. As alternatives α-lithiation of β-oxy or β-thio vinylphosphonates [22], NaH catalysed olefination of benzenesulfinylmethylphosphonates [23] and addition of sodium organyl chalcogenolates to 1-alkynylphosphonates were reported [24]. However, in practice these methods led to formation of regio- and stereo-isomers mixture.

To overcome these limitations palladium-catalysed procedures including the Heck reactions using aryl halides [25–28] or aryldiazonium salts [29], the reactions between vinyl bromides and dialkylphosphonates [30] or the coupling of boronic acids with vinylphosphonates were reported [31–33]. Generally good yields and high selectivities were achieved; however, these procedures were limited to few examples or remained linked to the preparation of the reagents.

Therefore, a direct synthesis from commercially available reagents applicable to a wide range of substrates is highly desirable regarding the growing importance of 2-(aryl)vinylphosphonates. We previously reported the Heck coupling of acrolein derivatives with a large range of aromatic and heteroaromatic derivatives in the presence of palladium catalysts [34–37]. Based on this experience, we describe in this contribution a study on the Heck coupling reaction between aryl and heteroaryl halides with diethyl vinylphosphonate comparing various homogeneous catalytic systems.

2. Results and discussion

Initially the reaction was studied with iodo- and bromo-benzene using either the isolated well-defined Herrmann palladacycle pre-catalyst (Fig. 1a) [38] or the *in situ* made $Pd(OAc)_2/PPh_3$

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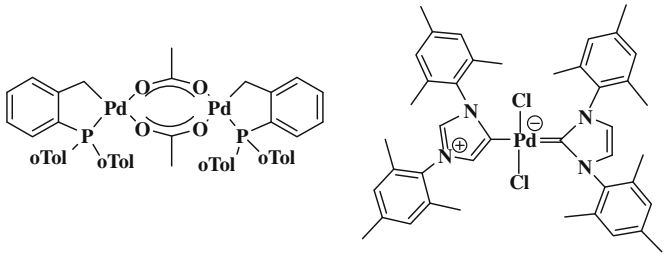
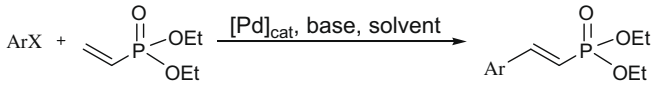


a. Herrmann's palladacycle b. Nolan's catalyst

Fig. 1. Homogeneous catalysts used in this study.



X = I, Br

Ar = simple and condensed aryl and heteroaryl nucleuses.

Scheme 1. Heck arylation of diethyl vinylphosphonate with various aryl and heteroaryl bromides.

catalytic system under standard conditions (90–140 °C, 2 mol% [Pd], 1.1 eq. base, polar solvent) (Scheme 1). The results are reported in Table 1.

Several parameters were evaluated for the coupling reaction of iodo-benzene with the diethyl vinylphosphonate: the base, the solvent, the reaction temperature and the nature of the pre-catalyst. Initially, the reaction parameters were optimised using iodo-benzene. Working at 110 °C with the Herrmann's palladacycle resulted in a poor 30% yield (Table 1 entry 7) while moderate yields (78%) were achieved with the $Pd(OAc)_2$/NaOAc catalytic system in presence or not of phosphine ligand (Table 1 entries 12, 15). In the case of the Herrmann's palladacycle improved yields (90%) were achieved by increasing the reaction temperature to 140 °C (Table 1 entry 8). Insoluble or poorly soluble bases, like $Ca(OH)_2$ or $CaCO_3$ in DMF (Table 1, entries 9, 10) or K_2CO_3 in NMP (Table 1 entry 5), led to low conversions. On the other hand, when the reaction was carried out in DMF in the presence of K_2CO_3 as base, quantitative conversion was achieved (Table 1, entry 1). Interestingly, under these conditions the reaction temperature can be lowered up to 90 °C giving still high conversions (Table 1, entry 3), the optimised conditions being achieved at 110 °C in DMF with K_2CO_3 as base (Table 1, entry 2). Under these conditions weak influence of the palladium source was observed given that K_2CO_3 or Et_3N are used (Table 1, entries 2, 6, 11, 13, 14, 16). Unexpectedly, while commonly used in Heck coupling reaction, NMP as solvent led to low conversions at 110 °C whatever the base used and we had to perform the reaction at 140 °C to get significant yields (Table 1, entries 5 and 8). Moreover, no conversion was achieved while the reaction was carried out in non polar solvent like toluene (not reported). Generally, all evaluated palladium sources gave high conversions under optimised conditions (DMF, K_2CO_3, 110 °C); the best pre-catalyst being the palladacycle that could be attributed to its higher stability. The same tendencies were observed with the less reactive bromo-benzene (Table 1 entries 17–22). However, a stronger influence regarding the nature of the base was observed as Et_3N is almost ineffective (Table 1, entries 19 *versus* 6).

Table 1
Initial study of the Heck coupling reaction of diethyl vinylphosphonate with iodo- and bromo-benzene under homogeneous conditions (Scheme 1)[a].

	ArX	Catalysts	Base	T °C	Solvent	Yields (%)[b]
1		Palladacycle	K_2CO_3	140	DMF	100[c]
2			K_2CO_3	110	DMF	100
3			K_2CO_3	90	DMF	80[d]
4			K_2CO_3	105	Dioxane	90
5			K_2CO_3	140	NMP	90
6			Et_3N	110	DMF	95
7			NaOAc	110	DMF	30
8			NaOAc	140	NMP	90
9			$Ca(OH)_2$	110	DMF	5
10			$CaCO_3$	110	DMF	10
11		$Pd(OAc)_2$	K_2CO_3	110	DMF	80
12			NaOAc	110	DMF	78
13			Et_3N	110	DMF	90
14		$Pd(OAc)_2/PPh_3$	K_2CO_3	110	DMF	100
15			NaOAc	110	DMF	78
16			Et_3N	110	DMF	95[e]
17		Palladacycle	K_2CO_3	110	DMF	92
18			NaOAc	110	DMF	37
19			Et_3N	110	DMF	11
20		$Pd(OAc)_2$	K_2CO_3	110	DMF	42
21			NaOAc	110	DMF	5
22			Et_3N	110	DMF	15

[a] Reaction conditions: 0.6 mmol aryl halide, 0.6 mmol diethyl vinylphosphonate, 2 mol% [Pd], 1 eq. base, polar solvent, 90–140 °C, 24 h.
[b] Yields were determined by GC with an internal standard (diethylene glycol di-*n*-butyl ether) (Δ_{rel} = ±5%). In some case dehalogenation was observed.
[c] Reaction time: 1 h.
[d] Reaction time: 48 h.
[e] 85% GC-yield was achieved in 3 h.

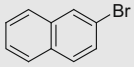
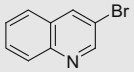
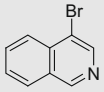
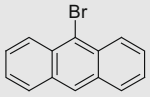
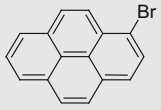
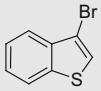
Having the optimised conditions in hands (2 mol% [Pd] as Herrmann's palladacycle, DMF, K_2CO_3, 110 °C) we next applied them to a large range of aryl and heteroaryl halides (Scheme 1). In order to achieve the highest product yields we explored the reactions at two temperatures: 110 °C and 140 °C. The results reported in Table 2 show that the conditions issued from the study with iodo- and bromo-benzene can be indifferently applied to a variety of substrates leading to high yields at both temperatures. In almost all cases, working at 140 °C allows to reduce noticeably the reaction time to few hours (3–6 h). Interestingly heteroaryl halides (Table 2, entries 10–15), including 3-bromobenzothiophene (Table 2, entries 22–24), gave high yields showing the general applicability of the conditions.

In parallel, heterogeneous catalysts were evaluated for this reaction. 2-bromonaphtalene was used as aryl halide model. Under optimised conditions (2 mol% [Pd], DMF, K_2CO_3, 140 °C), 85% conversion was achieved after 24 h in the presence of Pd/C catalyst (Aldrich 5 wt% Pd on dry basis) (Table 2, entry 7). Dehalogenation product was formed (*ca.* 20%) together with the expected product. As expected, better reactivity was observed using the $[Pd(NH_3)_4]$/NaY (3.7 wt% Pd) catalyst [39] as full conversion was achieved after 6 h yielding exclusively the Heck compound (Table 2, entry 8).[40] With this latter, the reaction temperature could be decreased to 110 °C leading to 80% conversion after 24 h (Table 2, entry 9). Unfortunately, none of these heterogeneous catalysts could be recycled and attempts to reuse the material led only to production of naphthalene due to dehalogenation. This is more probably due to the formation of large inactive palladium aggregates as previously reported under similar reaction conditions [41,42].

In order to demonstrate broader applicability of the method we applied next the optimised catalytic system to the coupling of aryl bromides substituted by either electron donating or electron withdrawing groups with the diethyl vinylphosphonate (Scheme 1).

All reactions were performed at 110 °C using the Herrmann's palladacycle (2 mol%) as catalyst. Good to high conversions were achieved for activated aryl bromides (Table 3, entries 3–6; 13–14); however, some limitations were observed particularly when reacting non-activated or deactivated derivatives (Table 3, entries 15–19). In these cases for any reasons, the reaction stops after few hours giving moderate yields. Accounting the lower reactivity

Table 2
Heck coupling reaction of diethyl vinylphosphonate with various aryl- and heteroaryl bromides under homogeneous conditions using the Herrmann palladacycle as catalyst[a].

	ArX	T °C	Time (h)	Conversion (%)[b]	Yields (%)[b] [isolated yields (%)]
1		110	24	100	100
2		140	1	100	100 [65]
3		110	24	92	92
4		140	3	64	64
5		110	3	75	72
6		140	1	100	98 [62]
7		140	24	85	66[c,d]
8		140	6	100	100[e]
9		110	24	83	80[e]
10		110	1	54	54
11		110	3	100	97 [60]
12		140	1	96	96
13		140	2	100	96
14		110	24	100	81
15		140	2	100	100 [65]
16		110	3	57	55
17		110	20	100	98[c]
18		140	3	100	96 [74][c,f]
19		110	2.5	76	76
20		110	6	100	100 [70]
21		140	2	100	100
22		110	3	57	55
23		110	20	100	98[c] [60]
24		140	3	100	96[c]

[a] Reaction conditions: 0.6 mmol aryl halide, 0.6 mmol diethyl vinylphosphonate, 2 mol% [Pd], 1 eq. K_2CO_3, DMF, 110–140 °C.
[b] Conversions and yields were determined by GC ($\Delta_{rel} = \pm 5\%$). Diethylene glycol di-*n*-butyl ether or biphenyl was used as internal standard.
[c] Dehalogenation (*ca.* 20%) was observed in this reaction.
[d] Pd/C catalyst (Aldrich 5 wt% Pd on dry basis) was used.
[e] $[Pd(NH_3)_4]$/NaY (3.7 wt% Pd) catalyst was used.
[f] Due to isomerisation over silica gel or alumina, this product was isolated through crystallisation from a mixture CH_2Cl_2/pentane at reaction completion with a purity ⩾95%.

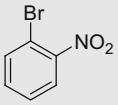
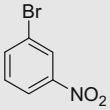
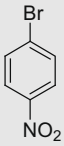
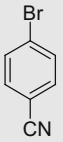
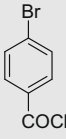
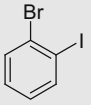
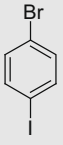
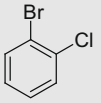
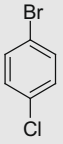
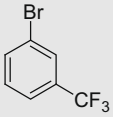
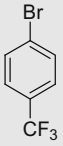
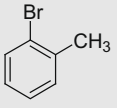
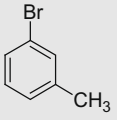
of aryl bromides *versus* iodides, the Heck coupling reaction of 2- and 4-iodobromobenzene with diethyl vinylphosphonate gave a full selectivity towards the bromo compounds (Table 3, entries 7–10). The Heck coupling at the bromo position was never observed preventing the double olefination. Similarly, 2- and 4-bromochlorobenzene gave the chloro vinylderivatives; however, lower yields were achieved due to the lower reactivity of the aryl bromides under our reaction conditions (Table 3, entries 11–12). Another interesting feature of this methodology concerns the possibility to couple HO-free phenols with the diethyl vinylphosphonate under classical reaction conditions with good to high conversions (Table 3, entries 20–21).

In addition, different reactivities were observed when engaging *ortho*, *meta*, or *para* isomers, the *ortho* derivatives giving generally poor conversions (Table 3, entries 1–4; 7–12; 13–19). These results are in agreement with general observations related to lower reactivity of *ortho*-substituted aryl halides compared to *meta*- or *para*-derivatives in such cross-coupling reactions [43,44]. These results indicate also that the reaction rate is more probably controlled by the limiting oxidative addition step than by the steric hindrance comparing the results achieved with various donating/withdrawing substituents.

In all cases, the products are obtained as the (*E*)-isomers. The (*E*)-geometry across the double bond was characterized by the value of the $^3J_{(H-H)}$ coupling constants between the two vinylic protons that average 17–18 Hz in all compounds. The exclusive formation of the (*E*)-isomers was expected according to the generally accepted Heck reaction mechanism that implies an *anti*-β-hydride eliminations step to afford the styrene derivative with the (*E*)-geometry.

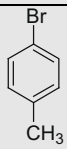
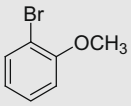
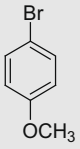
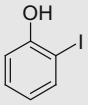
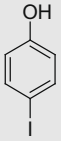
Intrigued by the lack of reactivity of some non-activated aryl bromides in this reaction, we studied further the coupling reaction bromotoluenes and bromoanisoles, comparing the Herrmann palladacycle to a unsymmetrical N-heterocyclic carbene palladium complex (Fig. 1b) recently described by Nolan for Suzuki coupling reactions [45] (Table 4). Initially, these pre-catalysts were evaluated for the coupling reaction of 4-bromotoluene. Using a larger amount of the Herrmann palladacycle (i.e. 10 mol%, entry 2) led to complete conversion of the aryl halide within 3 h affording a good yield (88%; Table 4, entry 2). Interestingly, using the Nolan catalyst (2 mol%) full conversion was achieved within 24 h at both 140 °C and 110 °C (Table 4, entries 4–5) [46]. With this N-heterocyclic carbene palladium complex, we were able to decrease the palladium loading down to 1 mol% giving 83% conversion (Table 4, entry 6). The same trends are observed for the other evaluated aryl bromides (Table 4, entries 7–14). As before, the *ortho* derivatives resulted in lower yields as the corresponding *meta* or *para* compounds. This suggests that for any reasons the Herrmann's palladacycle is somewhat unsuitable with these substrates leading to irreversible deactivation while the (NHC) palladium complex exhibit much higher activity. Further information was gain from kinetic experiments comparing the Herrmann palladacycle and (NHC) palladium complex for the coupling reaction of 2-bromonaphtalene with diethyl vinylphosphonate under strictly the same reaction conditions (2 mol% [Pd], DMF, K_2CO_3) at 140 °C and 110 °C. Fig. 2 shows that while the Herrmann palladacycle presents for that

Table 3
Heck coupling reaction of diethyl vinylphosphonate with substituted aryl bromides and iodides under homogeneous conditions using the Herrmann palladacycle as catalyst[a].

Entry	ArX	Time (h)	Conversion (%)[b]	Yields (%)[b] [isolated yields (%)]
1		8	66	47[g]
2		24	90	59 [45][g]
3		8	100	93 [72][g]
4		8	96	90 [55][g]
5		6	100	95 [62][g]
6		24	100	100 [78]
7		24	51	45
8[c]		4	94	81
9[d]		24	75	75
10		4	100	89[g] [75]
11		24	56	55
12		24	70	70 [43]
13		24	81	77[g]
14		24	100	100 [65]
15[e]		24	24	22
16[e]		24	45	40

(*continued on next page*)

Table 3 (*continued*)

Entry	ArX	Time (h)	Conversion (%)[b]	Yields (%)[b] [isolated yields (%)]
17[e]		24	43	37[g]
18[e]		24	39	31[g]
19[e]		24	64	56[g]
20		7	89	41[f,g]
21		7	100	100 [40][f]

[a] Reaction conditions: 3 mmol aryl halide, 3 mmol diethyl vinylphosphonate, 2 mol% [Pd], 1 eq. K_2CO_3, DMF, 110 °C, unless specified.
[b] Conversions and yields were determined by GC with an internal standard (biphenyl) (Δ_{rel} = ±5%).
[c] 2 eq. of diethyl vinylphosphonate were used. In some cases dehalogenation was observed.
[d] Reaction temperature: 80 °C.
[e] Reaction temperature: 140 °C.
[f] In these reactions, due to side reactions the observed product corresponds to ethyl phenylether derivative (see experimental).
[g] Dehalogenation was observed in these reactions (5–22% yield).

reaction higher initial activity at both reaction temperatures, it tends to deactivate when used at 110 °C leading to a limited 83% conversion while the (NHC) palladium complex exhibits higher stability giving quantitative conversion after 24 h. These kinetic studies confirm that under these conditions the Herrmann palladacycle deactivates more easily than the (NHC) palladium catalyst giving finally lower yields when used with somewhat lower reactive aryl halides (i.e.: deactivated electron rich aryl bromides). To date the origin of this deactivation is not explained as no influence of water [47] or palladium black formation was observed.

Both catalysts evidenced higher reaction rate at 140 °C that could be related to the Heck reaction mechanism. According to several recent reports [42,48], all palladium-catalysed reactions that imply an oxidative addition as the first step of the catalytic cycle proceed through a Pd(0)/Pd(II) mechanism. It is therefore reasonable to conclude that both catalysts are converted to Pd(0)-species in these reactions, generally as palladium nanoparticles when working at relatively high temperature (i.e. 140 °C), the original palladium complexes acting as reservoir of the active species. It is therefore expected that such *conversion* is increased by increasing the reaction temperature. However, we cannot exclude that at lower temperature (i.e. 110 °C) the nature of the so-called active species differs.

3. Conclusions

In this contribution an alternative route using homogeneous palladium catalysts for the synthesis of diethyl 2-(aryl)vinylphosphonate by direct Heck coupling reaction of diethyl vinylphosphonate with various aryl or heteroaryl halides was reported. Several reaction parameters were evaluated in order to optimise the conditions (i.e. 2 mol% [Pd], NMP, K_2CO_3, 140 °C). Generally high conversions and selectivities leading to good isolated yields were achieved whatever the homogeneous catalyst used.

For some aryl halides, like the 4-bromotoluene, limitations were observed. For any reasons, when using the Herrmann palladacycle the reaction stops after few hours giving low conversions (<40%). In some extent, the same observations were made when using the heterogeneous catalysts. For these substrates, it was found that the use of more active palladium pre-catalysts like the N-heterocyclic carbene palladium complex (Fig. 1b) allowed full conversions within 24 h at 110 °C. Further optimisation with this particularly active catalyst allowed reducing the palladium loading to 1 mol%.

In summary, when reacting activated or non-activated (but reactive) aryl halides the Herrmann palladacycle is the best catalyst regarding its easy preparation or its commercial availability as it gives high product yields in short reaction times. Otherwise, for deactivated or low reactive substrates, the Nolan (NHC) complex should be used to achieve high product yields despite longer reaction times.

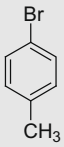
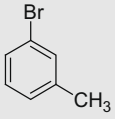
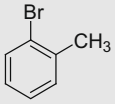
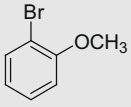
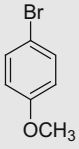
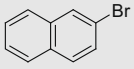
The efficiency of the procedure reported here render the method very practicable and competitive compared to other existing ones.

4. Experimental

4.1. General remarks

All manipulations were conducted under a strict inert atmosphere or vacuum conditions using Schlenk techniques including

Table 4
Heck coupling reaction of diethyl vinylphosphonate with various arylbromides using either the Herrmann palladacycle or the Nolan N-heterocyclic carbene palladium complex as catalyst[a].

	ArX	Catalyst	T °C	Time (h)	Conversion (%)[b]	Yields (%)[b]
1		Herrmann	140	24	43	37[d]
2		Herrmann[c]	140	3	100	88[d]
3		Herrmann	110	24	<5	–
4		Nolan	140	24	100	85[d]
5		Nolan	110	24	100	85[d]
6		Nolan	110	24	83	80[e]
7		Herrmann	140	24	45	40[d]
8		Nolan	140	24	66	66
9		Herrmann	140	24	24	22
10		Nolan	140	24	32	32
11		Herrmann	140	24	39	31[d]
12		Nolan	110	24	58	55
13		Herrmann	140	24	64	56[d]
14		Nolan	110	24	75	75
15		Herrmann	110	3	75	72
16		Herrmann	140	1	100	98
17		Nolan	140	2	100	98
18		Nolan	110	8	100	99

[a] Reaction conditions: 0.6 mmol aryl halide, 0.6 mmol diethyl vinylphosphonate, 2 mol% [Pd], 1 eq. K_2CO_3, DMF, unless specified.
[b] Conversions and yields were determined by GC with an internal standard (biphenyl) (Δ_{rel} = ±5%).
[c] 10 mol% Herrmann's palladacycle was used in this experiment.
[d] Dehalogenation was observed in these reactions (5–12% yield).
[e] 1 mol% (NHC) complex was used in this reaction.

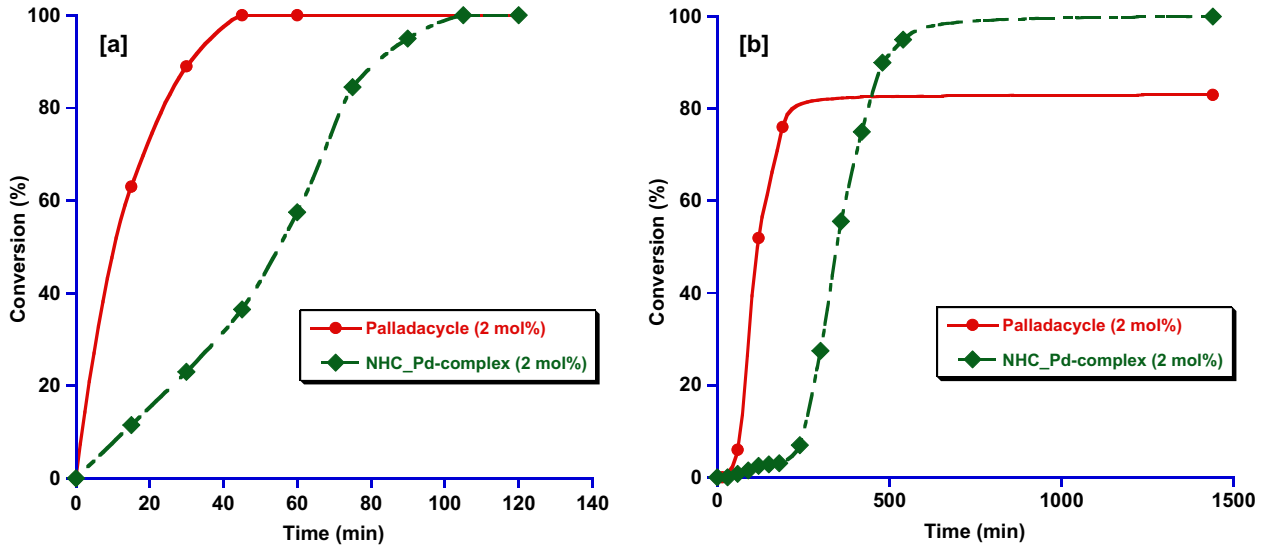


Fig. 2. Conversions *versus* the time for the coupling reaction of 2-bromonaphtalene with the diethyl vinylphosphonate using the Herrmann palladacycle (●) or the (NHC) palladium complex (♦) at 140 °C ([a]) or 110 °C ([b]). Reaction conditions: 3 mmol 2-bromonaphtalene, 3 mmol diethyl vinylphosphoate, 2 mol% [Pd], 3 mmol K_2CO_3, 30 mL DMF.

the transfer of the catalysts to the reaction vessel. All glassware was base- and acid-washed and oven dried.

The solvents used for the synthesis of the molecular palladium precursors and catalysts were dried using standard methods. The solvents used for the catalytic experiments are used as received from Aldrich (Chromasolv-plus, water content <0.03% or 0.05% depending on the solvent). All other chemicals (organic reagents and solvents) were deaerated by an argon flow before they were

used. The Herrmann's palladacycle was prepared according a procedure reported in the literature [38] and the N-heterocyclic carbene palladium complex was prepared following the procedure reported by Noland and co-workers [45]. Both complexes were stored under inert atmosphere until use.

The catalytic reactions were carried out in a three-necked flask, or alternatively in pressure sealed tubes, under argon. The qualitative and quantitative analysis of the reactants and the products was made by Gas chromatography. Conversions and yields were determined by GC based on the relative area of GC-signals referred to an internal standard (biphenyl or diethylene glycol di-*n*-butyl ether) calibrated to the corresponding pure compound.

The palladium content determinations of the heterogeneous catalyst {[$Pd(NH_3)_4$]/NaY} was performed by ICP-AES spectroscopy from a solution obtained by treatment of the catalysts with a mixture of HBF_4, HNO_3 and HCl in a Teflon reactor at 180 °C.

NMR spectra in solution were recorded on a BRUKER AC-250 spectrometer. All chemical shifts were measured relative to residual ^1H or ^{13}C NMR resonances in the deuterated solvents: $CDCl_3$, δ: 7.25 ppm for ^1H, 77.0 ppm for ^{13}C; C_7D_8, δ: 2.11 ppm for ^1H, 20.4 ppm for ^{13}C; CD_2Cl_2, δ: 5.32 ppm for ^1H, 53.7 ppm for ^{13}C. Flash chromatography was performed at a pressure slightly greater than atmospheric pressure using silica (Merck Silica Gel 60, 230–400 mesh). Thin layer chromatography was performed on Fluka Silica Gel 60 F_{254}.

GC analyses were performed on a HP 5890 chromatograph equipped with a FID detector, a HP 6890 autosampler and a HP-5 column (cross-linked 5% phenyl-methylsiloxane, 30 m × 0.25 mm i.d. × 0.25 μm film thickness). Nitrogen is used as carrier gas. The mass spectra were obtained on a Shimadzu GCMS-QP2010S (EI) equipped with a Sulpelco SLB-5MS column (95% methylpolysiloxane + 5% phenylpolysiloxane, 30 m × 0.25 mm × 0.25 μm) using He as carrier gas was used. The experimental error was estimated to be $\Delta_{rel} = \pm 5\%$.

4.2. General procedure for the catalytic tests under Heck conditions

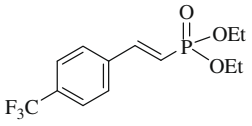
0.6 mmol of aryl halide, 0.6 mmol of diethyl vinylphosphonate, 0.6 mmol of K_2CO_3 and 2 mol% of Pd-catalyst were introduced in a pressure tube under argon. DMF previously deaerated (6 mL) were added and the mixture was deaerated by an argon flow for 5 min. The reactor was then placed in a pre-heated oil bath at 110–140 °C for 4–24 h under vigorous stirring and then cooled to room temperature before the reaction mixture was analyzed by GC. At completion of the reaction, the mixture was diluted with 100 mL of water and the resulting mixture was extracted with 4 × 20 mL CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and evaporated. The residue was then purified by flash chromatography on silica gel eluting with petroleum–ether/ethylacetate (9:1) [49] except for the anthracyl derivative that was obtained by crystallization from a mixture CH_2Cl_2/pentane (1:2).

4.3. GLC analysis

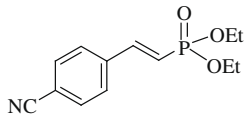
A homogeneous 3 mL sample of the reaction mixture was sampled and quenched with 3 mL of water in a test tube. The mixture was extracted with 2 mL of CH_2Cl_2 and the organic layer was filtered through a $MgSO_4$ pad. The resulting dry organic layer was then analysed by GLC. GLC-rate program: 2 min at 100 °C, heating 15 K/min up to 170 °C, 2 min at 170 °C, heating 35 K/min up to 240 °C, 10 min at 240 °C, heating 50 K/min up to 270 °C and 2 min at 270 °C.

4.4. Characterizations of organic compounds

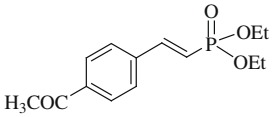
All compounds were characterized trough MS spectra obtained from GC–MS. Additionally isolated compounds were fully characterized through ^1H, ^{13}C and ^{31}P NMR. Data are given for new isolated compounds; all other products gave satisfactory data compared to reported literature {Ar–C=C–$PO(OEt)_2$ with Ar=C_6H_5 [50], $C_{10}H_7$ [50], *o*-C_6H_4Br [29], *o*-C_6H_4Cl [51], *o*-$CH_3C_6H_4$ [28], *m*-$CH_3C_6H_4$ [52], *o*-$CH_3OC_6H_4$ [53], *p*-$CH_3OC_6H_4$ [29]}.



65% as a slightly beige oil. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm}: 7.56 (d, 2H; ^3J = 8.7 Hz, *o*-CF_3–C_6H_4–); 7.55 (d, 2H, ^3J = 8.7 Hz, *m*-CF_3–C_6H_4–); 7.45 (dd, 1H, ^3J = 17.5 Hz, $^3J_{H-P}$ = 22.3 Hz, P–CH=C*H*–); 6.29 (dd, 1H, ^3J = 17.5 Hz, $^2J_{H-P}$ = 17.2 Hz, P–C*H*=CH–); 4.08 (*pseudo*-q, 4H, ^3J = 7.2 Hz, CH_3CH_2O); 1.29 (t, 6H, ^3J = 7.2 Hz, CH_3CH_2O). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_{ppm}: 146.7 (d, $^2J_{C-P}$ = 6.7 Hz, P–CH=*C*H–); 138.1 (d, $^3J_{C-P}$ = 24.6 Hz, Cq(vinyl)–C_6H_4); 131.7 (q, $^2J_{C-F}$ = 32.8 Hz, Cq(CF_3)–C_6H_4); 127.8 (*m*-F_3–C_6H_4–); 125.8 (q, $^3J_{C-F}$ = 3.8 Hz, *o*-F_3–C_6H_4); 123.7 (q, J_{C-F} = 270.2 Hz, *C*F_3); 117.1 (d, $^1J_{C-P}$ = 190.8 Hz, P–*C*H=CH–); 62.3 (d, $^2J_{C-P}$=5.6 Hz, CH_3CH_2O); 16.3 (d, $^3J_{C-P}$ = 6.4 Hz, CH_3CH_2O). ^{31}P NMR (101.2 MHz, $CDCl_3$): 18.27. $C_{13}H_{16}F_3O_3P$: 308.08 g/mol; MS *m/z* (%) = 308 [M^+] (20).

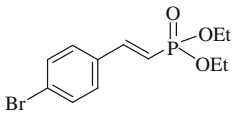


62% as an orange oil. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm}: 7.62 (d, 2H; ^3J = 8.6 Hz, *o*-CN–C_6H_4–); 7.52 (d, 2H, ^3J = 8.7 Hz, *m*-CN–C_6H_4–); 7.42 (dd, 1H, ^3J = 17.5 Hz, $^3J_{H-P}$ = 22.2 Hz, –P–CH=C*H*–); 6.32 (dd, 1H, ^3J = 17.5 Hz, $^2J_{H-P}$ = 16.5 Hz, P–C*H*=CH–); 4.08 (*pseudo*-q, 4H, ^3J = 7.2 Hz, CH_3–CH_2–O–P); 1.29 (t, 6H, ^3J = 7.0 Hz,CH_3–CH_2–O–P). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_{ppm}: 146.1 (d, $^2J_{C-P}$ = 6.8 Hz, –P–CH=*C*H–); 139.0 (d, $^3J_{C-P}$ = 23.6 Hz, Cq(vinyl)–C_6H_4), 132.6 (*m*-CN–C_6H_4); 128.1 (*o*-CN–C_6H_4); 118.5 (d, $^1J_{C-P}$ = 190.5 Hz, P–*C*H=CH); 118.3 (*C*N); 113.3 (Cq(CN)–C_6H_4); 62.2 (d, $^2J_{C-P}$ = 5.6 Hz, CH_3CH_2O); 16.4 (d, $^3J_{C-P}$ = 6.3 Hz, *C*H_3CH_2O). ^{31}P NMR (101.2 MHz, $CDCl_3$): 17.66. $C_{13}H_{16}NO_3P$: 265.08 g/mol; MS *m/z* (%) = 265 [M^+] (15).

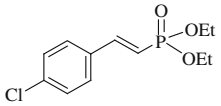


78% as a red liquid. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm}: 7.90 (d, 2H; ^3J = 8.4 Hz, *o*-$COCH_3$–C_6H_4); 7.52 (d, 2H, ^3J = 8.5 Hz, *m*-$COCH_3$–C_6H_4); 7.46 (dd, 1H, ^3J = 17.5 Hz, $^3J_{H-P}$ = 22.4 Hz, –P–CH=C*H*–); 6.31 (dd, 1H, ^3J = 17.5 Hz, $^2J_{H-P}$ = 17.2 Hz, P–C*H*=CH); 4.08 (*pseudo*-q, 4H, ^3J = 7.0 Hz, CH_3CH_2O); 2.5 (s, 3H, $COCH_3$); 1.30 (t, 6H, ^3J = 7.0 Hz, CH_3CH_2O). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_{ppm}: 197.3 ($COCH_3$); 147.1 (d, $^2J_{C-P}$ = 6.6 Hz, P–CH=CH–); 139.0 (d, $^3J_{C-P}$ = 23.2 Hz, Cq(vinyl)–C_6H_4), 138.0 (Cq(CH_3CO)–C_6H_4); 128.8 (*o*-CH_3CO–C_6H_4); 127.1 (*p*-CH_3CO–C_6H_4); 116.5 (d, $^1J_{C-P}$ = 190.7 Hz, –P–CH=CH–); 113.3 62.0 (d, $^2J_{C-P}$ = 5.6 Hz, CH_3CH_2O); 26.6

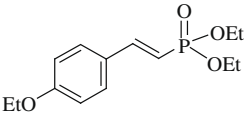
(COCH$_3$); 16.4 (d, $^3J_{C-P}$ = 6.3 Hz, *C*H$_3$CH$_2$O). ^{31}P NMR (101.2 MHz, CDCl$_3$): 18.44. $C_{13}H_{16}F_3O_3P$: 282.28 g/mol; MS *m/z* (%) = 82 [M$^+$] (10).



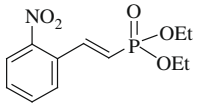
75% as a pale brown solid. mp: 82 °C. ^{1}H NMR (250 MHz, CDCl$_3$): δ_{ppm}: 7.46 (d, 2H, ^3J = 8.5 Hz, *o*-Br–C$_6$*H*$_4$); 7.37 (dd, 1H, ^3J = 17.5 Hz, $^3J_{H-P}$ = 18.2 Hz, P–CH=C*H*–); 7.30 (d, 2H, ^3J = 8.5 Hz, *m*-Br–C$_6$*H*$_4$); 6.18 (dd, 1H, ^3J = 17.5 Hz, $^2J_{H-P}$ = 17.0 Hz, P–C*H*=CH–); 4.07 (*pseudo*-q, 4H, ^3J = 7.5 Hz, CH$_3$–C*H*$_2$O); 1.29 (t, 6H, ^3J = 7.0 Hz,*C*H$_3$CH$_2$O). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ_{ppm}: 147.3 (d, $^2J_{C-P}$ = 6.9 Hz, –P–CH=*C*H–); 133.7 (d, $^3J_{C-P}$ = 24.0 Hz, Cq(vinyl)–C$_6$H$_4$), 132.6 (*m*-Br–C$_6$H$_4$); 128.5 (*o*-Br–C$_6$H$_4$); 124.4 (Cq(Br)–C$_6$H$_4$); 114.8 (d, $^1J_{C-P}$ = 192.0 Hz, P–*C*H=CH); 61.9 (d, $^2J_{C-P}$ = 5.6 Hz, CH$_3$CH$_2$O); 16.4 (d, $^3J_{C-P}$ = 7.0 Hz, *C*H$_3$CH$_2$O). ^{31}P NMR (101.2 MHz, CDCl$_3$): 19.06. $C_{12}H_{16}BrO_3P$: 318 g/mol; MS, *m/z* (%) = 318 [M$^+$] (8).



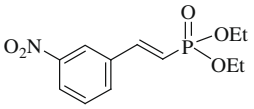
43% as an orange liquid. ^{1}H NMR (250 MHz, CDCl$_3$): δ_{ppm}: 7.38 (dd, 1H, ^3J = 17.3 Hz, $^3J_{H-P}$ = 22.2 Hz, P–CH=C*H*–); 7.37 (d, 2H, ^3J = 8.7 Hz, *o*-Cl–C$_6$*H*$_4$); 7.29 (d, 2H, ^3J = 8.6 Hz, *m*-Cl–C$_6$*H*$_4$); 6.16 (dd, 1H, ^3J = 17.3 Hz, $^2J_{H-P}$ = 17.3 Hz, P–C*H*=CH–); 4.07 (*pseudo*-q, 4H, ^3J = 7.0 Hz, CH$_3$C*H*$_2$O); 1.29 (t, 6H, ^3J = 7.0 Hz, C*H*$_3$CH$_2$O). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ_{ppm}: 147.2 (d, $^2J_{C-P}$ = 6.8 Hz, P–CH=*C*H–); 136.1 (Cq(Cl)–C$_6$H$_4$); 133.3 (d, $^3J_{C-P}$ = 23.7 Hz, Cq(vinyl)–C$_6$H$_4$), 129.1 (*m*-Cl–C$_6$H$_4$); 128.8 (*o*-Cl–C$_6$H$_4$); 114.7 (d, $^1J_{C-P}$ = 191.6 Hz, P–*C*H=CH); 61.9 (d, $^2J_{C-P}$ = 5.5 Hz, CH$_3$–*C*H$_2$O); 16.4 (d, $^3J_{C-P}$ = 6.4 Hz, *C*H$_3$CH$_2$O). ^{31}P NMR (101.2 MHz, CDCl$_3$): 19.1. $C_{12}H_{16}ClO_3P$: 274.05 g/mol; MS *m/z* (%) = 274 [M$^+$] (10).



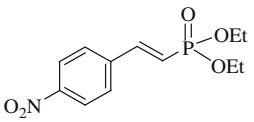
40% as a dark red oil. ^{1}H NMR (250 MHz, CDCl$_3$): δ_{ppm}: 7.38 (dd, 1H, ^3J = 17.6 Hz, $^3J_{H-P}$ = 22.5 Hz, P–CH=C*H*); 7.36 (d, 2H, ^3J = 8.9 Hz, *o*-OEt–C$_6$H$_4$); 6.82 (d, 2H, ^3J = 8.8 Hz, *m*-OEt–C$_6$H$_4$); 6.01 (dd, 1H, ^3J = 17.6 Hz, $^2J_{H-P}$ = 17.7 Hz, P–C*H*=CH); 4.05 (*pseudo*-q, 4H, ^3J = 7.0 Hz, CH$_3$C*H*$_2$OP); 3.99 (q, 2H, ^3J = 7.5 Hz, O–C*H*$_2$CH$_3$); 1.36 (t, 3H, ^3J = 7.0 Hz, O–CH$_2$C*H*$_3$); 1.28 (t, 6H, ^3J = 7.2 Hz,C*H*$_3$CH$_2$OP). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ_{ppm}: 160.7 (Cq(OEt)–C$_6$H$_4$), 148.7 (d, $^2J_{C-P}$ = 6.8 Hz, P–CH=*C*H); 129.3 (*m*-C$_6$H$_4$–OEt); 127.3 (d, Cq, $^3J_{C-P}$ = 23.6 Hz, Cq(vinyl)–C$_6$H$_4$), 114.7 (*o*-OEt–C$_6$H$_4$); 110.5 (d, C, $^1J_{C-P}$ = 193.6 Hz, P–*C*H=CH); 63.6(O*C*H$_2$CH$_3$); 61.8 (d, $^2J_{C-P}$ = 5.4 Hz, CH$_3$*C*H$_2$OP); 16.3 (d, C, $^3J_{C-P}$ = 6.5 Hz, *C*H$_3$–CH$_2$OP); 14.7 (OCH$_2$*C*H$_3$). ^{31}P NMR (101.2 MHz, CDCl$_3$): 20.71. $C_{12}H_{17}O_4P$: 284.12 g/mol; MS *m/z* (%) = 284 [M$^+$] (40).



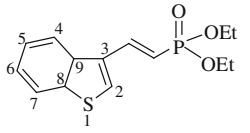
45% as a slightly brown oil. ^{1}H NMR (250 MHz, CDCl$_3$): δ_{ppm}: 7.99 (dd, 1H; ^3J = 8.2 Hz; ^4J = 1.25 Hz, *o*-NO$_2$–C$_6$H$_4$); 7.80 (dd, 1H, ^3J = 17.5 Hz, $^3J_{H-P}$ = 22.0 Hz, –P–CH=C*H*–); 7.63–7.44 (m, 3H, C$_6$H$_4$); 6.16 (dd, 1H, ^3J = 17.5 Hz, $^2J_{H-P}$ = 17.5 Hz, –P–C*H*=CH–); 4.12 (*pseudo*-q, 4H, ^3J = 7.1 Hz, CH$_3$–C*H*$_2$O); 1.31 (t, 6H, ^3J = 7.1 Hz,C*H*$_3$–CH$_2$O). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ_{ppm}: 147.7 (Cq(NO$_2$)C$_6$H$_4$); 143.7(d, $^2J_{C-P}$ = 7.9 Hz, P–CH=*C*H–); 133.6 (*p*-NO$_2$–C$_6$H$_4$); 131.4 (d, $^3J_{C-P}$ = 24.5 Hz, Cq(vinyl)C$_6$H$_4$), 130.2 (*m*-NO$_2$–C$_6$H$_4$); 129.1 (d, $^4J_{C-P}$ = 1.76 Hz, *m*-NO$_2$–C$_6$H$_4$); 124.79 (*o*-NO$_2$–C$_6$H$_4$); 119.5 (d, $^1J_{C-P}$ = 189.0 Hz, P–*C*H=CH–); 62.3 (d, $^2J_{C-P}$ = 5.6 Hz, CH$_3$–CH$_2$O); 16.4 (d, $^3J_{C-P}$ = 6.4 Hz, *C*H$_3$–CH$_2$O). ^{31}P NMR (101.2 MHz, CDCl$_3$): 16.64. $C_{12}H_{16}NO_5P$: 285.07 g/mol; MS *m/z* (%) = 239 [M$^+$–NO$_2$] (15); 148 [M$^+$–(PO(OEt)$_2$)] (50); 120 [M$^+$–(PO(OEt)$_2$–CH=CH)] (90).



72% as a dark orange oil. ^{1}H NMR (250 MHz, CDCl$_3$): δ_{ppm}: 8.30 (s, 1H, *o*-NO$_2$–C$_6$H$_4$); 8.17 (d, 1H, ^3J = 8.2 Hz, *o*-NO$_2$–C$_6$H$_4$); 7.73 (d, 1H, ^3J = 7.7 Hz, *p*-NO$_2$–C$_6$H$_4$); 7.52 (brt, 1H, ^3J = 8.0 Hz, *m*-NO$_2$–C$_6$H$_4$); 7.48 (dd, 1H, ^3J = 17.5 Hz, $^3J_{H-P}$ = 22.2 Hz, –P–CH=C*H*–); 6.36 (dd, 1H, ^3J = 17.5 Hz, $^2J_{H-P}$ = 16.0 Hz, –P–C*H*=CH–); 4.09 (*pseudo*-q, 4H, ^3J = 7.1 Hz, CH$_3$–C*H*$_2$–O–P); 1.30 (t, 6H, ^3J = 7.1 Hz,C*H*$_3$–CH$_2$–O–P). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ_{ppm}: 148.6 (Cq(NO$_2$)C$_6$H$_4$); 145.5 (d, $^2J_{C-P}$ = 6.3 Hz, P–CH=*C*H); 136.5 (d, $^3J_{C-P}$ = 24.2 Hz, Cq(vinyl)C$_6$H$_4$); 133.5 (*p*-NO$_2$–C$_6$H$_4$); 129.9 (*m*-NO$_2$–C$_6$H$_4$); 124.5 (*o*-NO$_2$–C$_6$H$_4$); 121.9 (*o*-NO$_2$–C$_6$H$_4$); 117.9 (d, $^1J_{C-P}$ = 190.8 Hz, P–*C*H=CH); 62.1 (d, $^2J_{C-P}$ = 5.6 Hz, CH$_3$–CH$_2$O); 16.4 (d, $^3J_{C-P}$ = 6.3 Hz, *C*H$_3$–CH$_2$O). ^{31}P NMR (101.2 MHz, CDCl$_3$): 17.63. $C_{12}H_{16}NO_5P$: 285.07 g/mol; MS *m/z* (%) = 285 [M$^+$] (15); 239 [M$^+$–NO$_2$] (15); 130 [M$^+$–(PO(OEt)$_2$)–H$_2$O] (100).

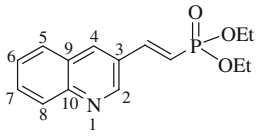


55% as a yellow solid. mp: 107–108 °C. ^{1}H NMR (250 MHz, CDCl$_3$): δ_{ppm}: 8.19 (d, 2H; ^3J = 8.7 Hz, *o*-NO$_2$–C$_6$H$_4$–); 7.58 (d, 2H, ^3J = 8.8 Hz, *m*-NO$_2$–C$_6$H$_4$–); 7.47 (dd, 1H, ^3J = 17.5 Hz, $^3J_{H-P}$ = 22.3 Hz, –P–CH=C*H*–); 6.37 (dd, 1H, ^3J = 17.5 Hz, $^2J_{H-P}$ = 16.2 Hz, –P–C*H*=CH–); 4.10 (*pseudo*-q, 4H, ^3J = 7.2 Hz, CH$_3$C*H*$_2$O); 1.30 (t, 6H, ^3J = 7.0 Hz, C*H*$_3$CH$_2$O). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ_{ppm}: 148.5 (Cq(NO$_2$)–C$_6$H$_4$); 145.5 (d, $^2J_{C-P}$ = 7.0 Hz, P–CH=*C*H–); 140.7 (d, $^3J_{C-P}$ = 23.2 Hz; Cq(vinyl)–C$_6$H$_4$); 128.3 (*m*-NO$_2$–C$_6$H$_4$); 124.1 (*o*-NO$_2$–C$_6$H$_4$); 119.5 (d, $^1J_{C-P}$ = 190.8 Hz, P–*C*H=CH–); 62.3 (d, $^2J_{C-P}$ = 5.6 Hz, CH$_3$*C*H$_2$O); 16.4 (d, $^3J_{C-P}$ = 6.3 Hz, *C*H$_3$CH$_2$O). ^{31}P NMR (101.2 MHz, CDCl$_3$): 17.36. $C_{12}H_{16}NO_5P$: 285.08 g/mol; MS *m/z* (%) = 285 [M$^+$] (10).

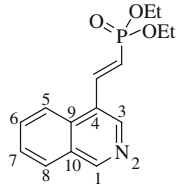


60% as a red liquid. ^{1}H NMR (250 MHz, CDCl$_3$): δ_{ppm}: 7.94 (m, 1H, *H*^{7}); 7.80 (m, 1H, *H*^{4}); 7.70 (dd, 1H, ^3J = 17.6 Hz, $^3J_{H-P}$ = 22.9 Hz, ^3J = 0.6 Hz, P–CH=C*H*–); 7.66 (s, 1H, *H*^{2}); 7.36 (td, ^3J = 7.2 Hz, ^4J = 1.5 Hz, 1H, *H*$^{5\ ou\ 6}$); 7.33 (td, ^3J = 7.2 Hz, ^4J = 1.5 Hz, 1H, *H*$^{5\ ou6}$); 6.27 (dd, 1H, ^3J = 17.6 Hz, $^2J_{H-P}$ = 17.8 Hz, P–C*H*=CH); 4.09 (*pseudo*-q, 4H, ^3J = 7.2 Hz, CH$_3$C*H*$_2$O); 1.30 (t, 6H, ^3J = 7.2 Hz,C*H*$_3$CH$_2$O).

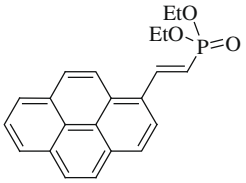
^{13}C NMR (62.9 MHz, $CDCl_3$): δ_{ppm}: 140.5 (d, $^2J_{C-P}$ = 7.0 Hz, P–CH=*C*H); 140.5 (Cq–C_8H_5S); 136.9 (Cq–C_8H_5S); 132.2 (d, $^3J_{C-P}$ = 24.8 Hz, P–CH=CH), 127.5 (d, $^4J_{C-P}$ = 2.2 Hz, CH–C_8H_5S); 125.0, 124.9, 123.0 and 121.9 (CH–C_8H_5S); 114.6 (d, $^1J_{C-P}$ = 191.2 Hz, P–*C*H=C); 61.9 (d, $^2J_{C-P}$ = 5.6 Hz, $CHCH_2O$); 16.4 (d, $^3J_{C-P}$ = 6.3 Hz, CH_3CH_2O). ^{31}P NMR (101.2 MHz, $CDCl_3$): 19.53. $C_{14}H_{17}O_3PS$: 296.06 g/mol; MS *m/z* (%) = 296 [M^+] (50).



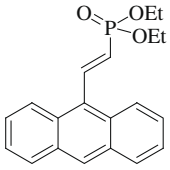
60% as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ_{ppm}: 9.01 (d, 1H, ^4J = 2.2 Hz, H^2); 8.16 (d, 1H, ^4J = 1.7 Hz, H^4); 7.91 (dd, 1H, ^3J = 17.5 Hz, $^3J_{H-P}$ = 23.4 Hz, P–CH=C*H*); 7.70 (td, 1H, ^3J = 6.5 Hz, ^4J = 1.5 Hz, H^6); 7.60 (d, 1H, ^3J = 6.5 Hz, H^8); 7.53 (d, 1H, ^3J = 6.5 Hz, H^5); 7.6 (td, 1H, ^3J = 6.5 Hz, ^4J = 1.0 Hz, H^7); 6.45 (dd, 1H, ^3J = 17.5 Hz, $^2J_{H-P}$ = 16.7 Hz, P–C*H*=CH); 4.11 (*pseudo*-q, 4H, ^3J = 7.2 Hz, CH_3CH_2O); 1.32 (t, 6H, ^3J = 7.5 Hz,CH_3CH_2O). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_{ppm}: 148.6 (C^2–C_9H_7N); 148.0 (C^{10}–C_9H_7N); 145.0 (d, $^2J_{C-P}$ = 6.8 Hz, P–CH=*C*H); 135.6 (C^4–C_9H_7N); 130.7(C^6–C_9H_7N); 129.1 (C^5–C_9H_7N); 128.3 (C^8–C_9H_7N); 127.9(C^9–C_9H_7N); 127.6 (C^7–C_9H_7N); 127.5 (d, C^3–C_9H_7N, $^3J_{C-P}$ = 2.5 Hz); 116.7 (d, $^1J_{C-P}$ = 191.3 Hz, P–*C*H=CH); 62.1 (d, $^2J_{C-P}$ = 5.6 Hz, CH_3CH_2O); 16.4 (d, $^3J_{C-P}$ = 6.4 Hz, CH_3CH_2O). ^{31}P NMR (101.2 MHz, $CDCl_3$): 18.18. $C_{15}H_{18}NO_3P$: 291.10 g/mol; MS *m/z* (%) = 291[M^+] (30).



65% as a red liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ_{ppm}: 9.20 (s, 1H, H^1); 8.66 (s, 1H, H^3); 8.2 (d, 1H, ^3J = 17.5 Hz, H^5); 8.13 (dd, 1H, ^3J = 17.4 Hz, $^3J_{H-P}$ = 21.9 Hz, P–CH=C*H*); 8.05 (d, 1H, ^3J = 18.0 Hz, H^8); 7.76 (td, 1H, ^3J = 7.0 Hz, ^4J = 1.5 Hz, –H^6); 7.63 (td, 1H, ^3J = 7.0 Hz, ^4J = 1.0 Hz, H^7); 6.41 (dd, 1H, ^3J = 17.4 Hz, $^2J_{H-P}$ = 17.9 Hz, P–C*H*=CH); 4.14 (*pseudo*-q, 4H, ^3J = 7.2 Hz, CH_3CH_2O); 1.33 (t, 6H, ^3J = 7.2 Hz,CH_3CH_2O). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_{ppm}: 153.7 (C^1–C_9H_7N); 142.8 (d, $^2J_{C-P}$ = 7.0 Hz, P–CH=*C*H); 140.8 (C^3–C_9H_7N); 133.4 (C^9–C_9H_7N); 131.4 (C^6–C_9H_7N); 128.4 (C^4–C_9H_7N); 128.3 (C^8–C_9H_7N); 128.0 (C^{10}–C_9H_7N); 127.8 (C^7–C_9H_7N); 122.5 (C^5–C_9H_7N); 119.4 (d, 1C, $^1J_{C-P}$ = 188.8 Hz, P–*C*H=CH); 62.1 (d, $^2J_{C-P}$ = 5.6 Hz, CH_3CH_2O); 16.4 (d, $^3J_{C-P}$ = 6.3 Hz, CH_3CH_2O). ^{31}P NMR (101.2 MHz, $CDCl_3$): 18.98. $C_{15}H_{18}NO_3P$: 291.10 g/mol; MS *m/z* (%) = 291 [M^+] (20).



70% as a dark orange oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ_{ppm}: 8.57 (dd, 1H, ^3J = 17.2 Hz, $^3J_{H-P}$ = 22.5 Hz, P–CH=C*H*); 8.4–7.9 (m, 9H, $C_{16}H_9$); 6.47 (dd, 1H, ^3J = 17.2 Hz, $^2J_{H-P}$ = 18.3 Hz, P–*C*H=CH); 4.17 (*pseudo*-q, 4H, ^3J = 7.0 Hz, CH_3CH_2O); 1.36 (t, 6H, ^3J = 7.0 Hz, CH_3CH_2O). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_{ppm}: 145.3 (d, $^2J_{C-P}$ = 7.3 Hz, P–CH=*C*H); 132.3, 131.0, 130.3, 129.0, 128.6, 124.6 (d, $^3J_{C-P}$ = 10.0 Hz) and 124.3 (Cq–$C_{16}H_9$); 128.3, 128.2, 127.0, 126.0, 125.6, 125.5, 124.7, 123.6 and 122.1 (CH–$C_{16}H_9$); 128.3 (d, $^3J_{C-P}$ = 3.7 Hz, P–CH=CH); 115.5 (d, $^1J_{C-P}$ = 190.7 Hz, P–*C*H=CH); 62.0 (d, $^2J_{C-P}$ = 5.0 Hz, CH_3CH_2O); 16.5 (d, $^3J_{C-P}$ = 6.3 Hz, CH_3CH_2O). ^{31}P NMR (101.2 MHz, $CDCl_3$): 19.61. $C_{22}H_{21}O_3P$: 364.12 g/mol; MS *m/z* (%) = 364 [M^+] (30).



74% as a red oil. ^{1}H NMR (250 MHz, C_7D_8): δ_{ppm}: 8.51 (dd, 1H, ^3J = 17.7 Hz, $^3J_{H-P}$ = 22.7 Hz, –P–CH=C*H*–); 8.25–8.2 (m, 2H, $C_{14}H_9$); 8.08 (s, 1H, $C_{14}H_9$); 7.76–7.70 (m, 2H, $C_{14}H_9$); 7.23–7.19 (m, 4H $C_{14}H_9$); 6.18 (dd, 1H, ^3J = 17.7 Hz, $^2J_{H-P}$ = 19.7 Hz, –P–C*H*=CH–); 4.08 (*pseudo*-q, 4H, ^3J = 7.2 Hz, CH_3–CH_2O); 1.17 (t, 6H, ^3J = 7.2 Hz, CH_3–CH_2O). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ_{ppm}: 146.7 (d, $^2J_{C-P}$ = 5.7 Hz, –P–CH=*C*H–); 132.3 (Cq–$C_{14}H_9$); 131.6 (d, $^3J_{C-P}$ = 22.5 Hz, Cq(vinyl)–$C_{14}H_9$); 129.9 (Cq–$C_{14}H_9$); 129.8 ($C_{14}H_9$); 129.8 ($C_{14}H_9$); 127.4 ($C_{14}H_9$); 126.5 ($C_{14}H_9$); 126.2 ($C_{14}H_9$); 126.1(d, $^1J_{C-P}$ = 185.6 Hz, –P–*C*H=CH–); 62.4 (d, $^2J_{C-P}$ = 5.6 Hz, CH_3–CH_2O); 16.7 (d, $^3J_{C-P}$ = 6.2 Hz, CH_3–CH_2O). ^{31}P NMR (101.2 MHz, C_7D_8): 17.08. $C_{20}H_{21}O_3P$: 340.00 g/mol; MS *m/z* (%) = 340 [M^+] (15); 202 [M^+–(PO(OEt)$_2$)] (100).

Acknowledgments

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