Iron-Catalyzed Alkenylation of Grignard Reagents by Enol Phosphates

Gérard Cahiez,* Olivier Gager, Vanessa Habiak

Laboratoire de Synthèse Organique Sélective et de Chimie Organométallique (SOSCO), UMR 8123 CNRS-UCP-ESCOM, 5 Mail Gay-Lussac, Neuville sur Oise, 95031 Cergy-Pontoise cedex, France
E-mail: gerard.cahiez@u-cergy.fr

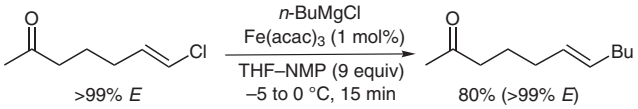
Received 20 March 2008

Abstract: Stereoselective preparation of trisubstituted olefins can be easily performed from an *Z*/*E*-mixture of enol phosphates by reacting only the *E*-isomer with a Grignard reagent in the presence of $Fe(acac)_3$. This procedure combines a kinetic differentiation and a stereoselective reaction. The coupling is very chemoselective in the presence of an alkyl chloride, an ester, a ketone or a nitrile.

Key words: cross-coupling, Grignard reactions, iron, alkenes, stereoselectivity

The first example of iron-catalyzed cross-coupling reactions between a Grignard reagent and a vinylic halide was described by Kharasch in 1945.[1] Kochi, in 1971, studied the mechanism of the coupling between alkylmagnesium reagents and vinyl or propenyl bromide.[2] Unfortunately, from a preparative point of view, the reaction was not very attractive since its scope was limited to reactive vinylic halides such as propenyl bromide or β-bromostyrene.[3] Moreover, as a rule, a large excess of these substrates (3 to 9 equivalents) had to be used in order to obtain satisfactory yields. Twenty years later, the chemistry of iron-catalyzed cross-coupling reactions was still in its infancy since no general preparative procedure had been described. At this time, we were convinced that iron salts such as $FeCl_3$, and $Fe(acac)_3$ were a valuable alternative to the palladium and nickel complexes commonly used as catalysts for many coupling procedures since they were cheaper and much more environmentally sound. Thus, we have reinvestigated the iron-catalyzed coupling of Grignard reagents with alkenyl halides and have finally discovered that, in the presence of *N*-methyl-2-pyrrolidinone (NMP) as an additive, the reaction occurs almost instantaneously to give excellent yields, even from the less reactive alkenyl chlorides.[4,5] In addition, the reaction is highly chemo- and stereoselective (Scheme 1).

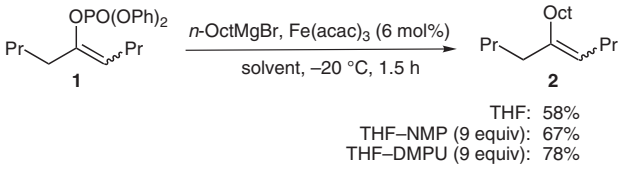
The use of NMP is a major advance in the field of iron-catalyzed cross-coupling reactions. Thus, our conditions have since been used by Fürstner to couple alkylmagnesium reagents with aryl chlorides.[6] In the last few years, iron-catalyzed reactions have received considerable interest as indicated by the increasing number of reports from us[5c,7] and others.[6,8]



Scheme 1

The alkenylation reaction previously described is very efficient and offers many economical and environmental advantages. However, the starting alkenyl halides are not always easy to prepare. To circumvent this problem in the case of the palladium- and nickel-catalyzed reactions, a classical alternative is to replace alkenyl bromides or iodides by the corresponding enol triflates, which often react similarly.[9] However, these substrates are not very convenient for preparative chemistry. Indeed, although triflates are very useful on a laboratory scale, they do not constitute a valuable industrial alternative to alkenyl halides since they are expensive and relatively difficult to handle and purify on a large scale. From this point of view, enol phosphates are much more attractive since they are less expensive. Moreover, they are stable enough to be prepared, stored and isolated without problem. Thus, they can often be purified by distillation or by chromatography on a silica gel column. To extend the scope of the iron-catalyzed alkenylation of Grignard reagents for large-scale applications we have thus developed the iron-catalyzed coupling of organomagnesium reagents with enol phosphates.[10]

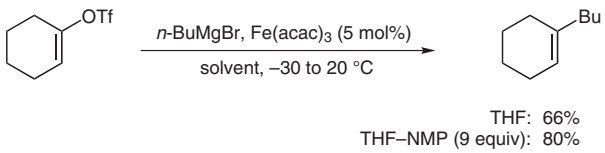
A preliminary experiment (Scheme 2) showed that enol phosphate **1** reacted with octylmagnesium bromide in the presence of 6% $Fe(acac)_3$ and nine equivalents of NMP, in tetrahydrofuran, to give the coupling product **2** in 67% yield (Scheme 2). The yield was improved by replacing NMP by *N*,*N*′-dimethylpropylene urea (DMPU; 78%).



Scheme 2

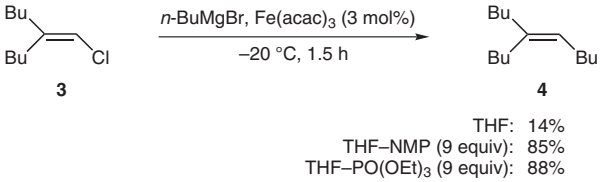
It should be underscored that a 58% yield was obtained in tetrahydrofuran alone, which is surprising since alkenyl halides give very poor yields under these conditions. In fact, it seems that enol phosphates are able to replace, at least partially, NMP. It is interesting to note that enol triflates behave similarly (Scheme 3).

SYNTHESIS 2008, No. 16, pp 2636–2644
Advanced online publication: 24.07.2008
DOI: 10.1055/s-2008-1067194; Art ID: C02408SS



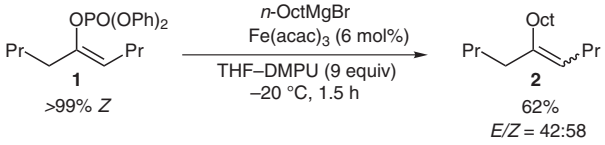
Scheme 3

The above hypothesis was confirmed by the following experiment (Scheme 4). Thus, the coupling between alkenyl chloride **3** and *n*-BuMgBr gave a poor yield in tetrahydrofuran alone, whereas excellent yields of olefin **4** were obtained in the presence of NMP or triethylphosphate as a cosolvent (9 equiv).



Scheme 4

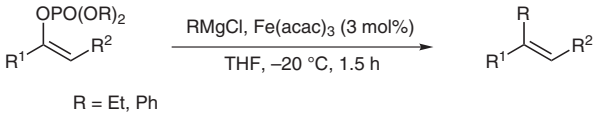
The scope of the reaction is very broad; various enol phosphates derived from aldehydes (Table 1, entries 1 and 2) or ketones (entries 3 to 15) have been used successfully. The reaction conditions depend on the reactivity of the substrate. Thus, enol phosphates derived from aldehydes or acetophenone are reactive enough to give satisfactory yields in tetrahydrofuran alone (entries 1 to 3), whereas the less reactive α,β-disubstituted enol phosphates require the presence of NMP (entries 4 to 9) or even DMPU (entries 10 to 15). Although aromatic and linear aliphatic Grignard reagents lead to good yields of coupling product, secondary and tertiary alkylmagnesium halides either did not couple (entry 12, R = *t*-Bu) or led to poor yields (entry 6, R = *c*-Hex).



Scheme 5

While considering the results presented in Table 1, it seems that the reaction is not stereoselective (entries 10 to 15) and indeed this is true for the *Z*-enol phosphates (Scheme 5). However, by following the evolution of the reaction (GC monitoring, Figure 1) between octylmagnesium bromide and a mixture of *Z*- and *E*-enol phosphates **1** (entry 11), it is clear that the *E*-isomer reacts much faster than the *Z*-isomer. Thus, after 25 minutes, 98.5% of the *E*-isomer was consumed whereas less than 5% of the *Z*-isomer reacted. Moreover, it is interesting to note that at the beginning of the reaction, the *E*-enol phosphate reacts almost exclusively to give the coupling product stereoselectively (≥99% *E*).

Table 1 Iron-Catalyzed Alkenylation of RMgCl by Enol Phosphates



R = Et, Ph

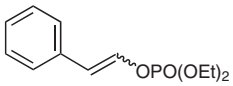
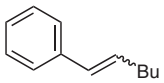
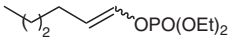
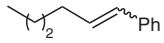
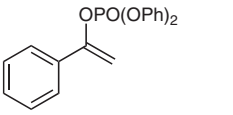
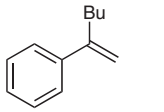
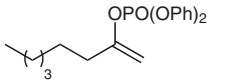
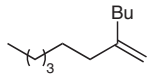
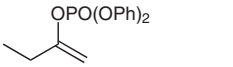
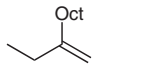
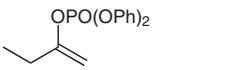
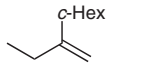
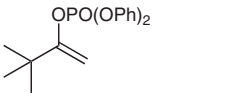
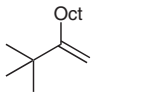
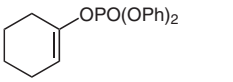
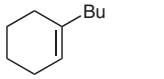
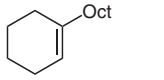
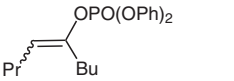
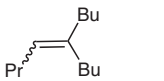
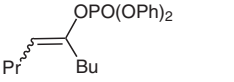
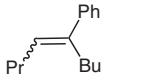
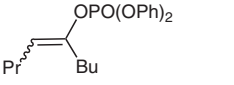
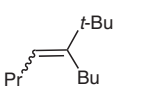
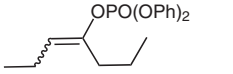
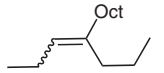
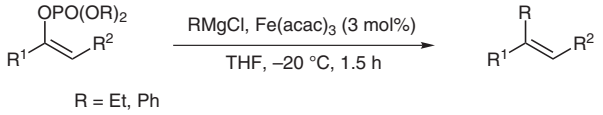
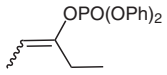
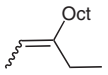
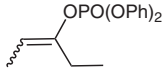
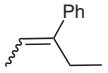
Entry	Enol phosphate (*E*/*Z*)	R	Product (*E*/*Z*)	Yield (%)[a]
1	 (84:16)	Bu	 **5** (90:10)	87
2	 (70:30)	Ph	 **5** (85:15)	81
3		Bu	 **6**	90
4		Bu	 **7**	75[b,c]
5		Oct	 **8**	82[b,c]
6		*c*-Hex	 **9**	20[b]
7		Oct	 **10**	75[b,d]
8		Bu	 **11**	90[b]
9		Oct	 **12**	90[b]
10	 (68:32)	Bu	 **13**	80[c]
11	 (68:32)	Ph	 **14** (94:6)	70[e]
12	 (68:32)	*t*-Bu		0 [c]
13	 (70:30)	Oct	 **15** (88:12)	75[e]

Table 1 Iron-Catalyzed Alkenylation of RMgCl by Enol Phosphates (continued)



Entry	Enol phosphate (*E*/*Z*)	R	Product (*E*/*Z*)	Yield (%)[a]
14	 (71:29)	Oct	 **16** (83:17)	81[e]
15	 (71:29)	Ph	 **17** (93:7)	73[e]

[a] Yield of isolated product.
[b] The reaction was performed in the presence of NMP (9 equiv).
[c] The reaction was performed with RMgBr.
[d] OctMgCl (2 equiv) was used.
[e] The reaction was performed in the presence of DMPU (9 equiv).

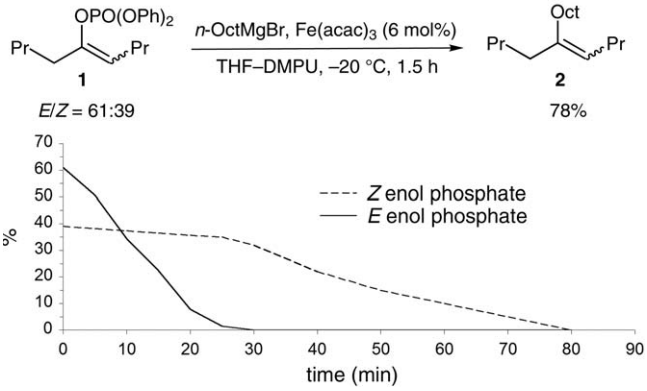
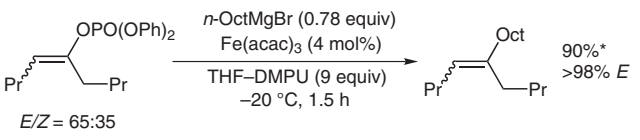


Figure 1

In the light of these observations, we performed the same reaction using only a stoichiometric amount of Grignard reagent based on the *E*-enol phosphate (Scheme 6). Under these conditions, the coupling took place quickly and stereoselectively to give the pure *E*-olefin **2** in excellent yield (90%). Moreover, at the end of the reaction the unreacted *Z*-enol phosphate was recovered in 95% yield (≥95% *Z*).

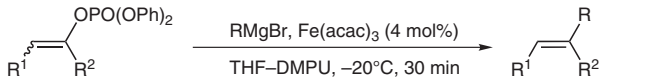


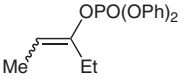
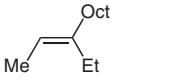
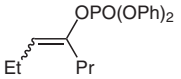
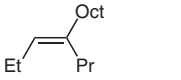
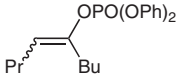
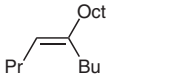
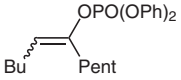
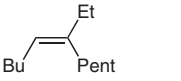
* The unreacted (*Z*) enol phosphate was recovered in 95% yield (>95% *Z*).

Scheme 6

It should be noted that this procedure combines a kinetic differentiation and a stereoselective reaction. From a preparative point of view, this is very interesting since it is possible to avoid the tedious preparation of pure *E*-enol phosphates. Other applications of this procedure are presented in Table 2.

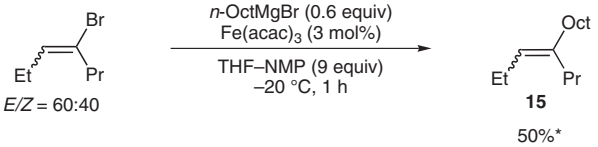
Table 2 Stereoselective and Stereodifferentiating Iron-Catalyzed Cross-Coupling Reactions



Entry	Enol phosphate (*E*/*Z*)	Product	Yield (%)[a]
1	 (68:32)	 **16**	81 (≥99% *E*)
2		 **15**	86 (≥98% *E*)[b]
3	 (65:35)	 **2**	90 (≥98% *E*)
4	 (69:31)	 **18**	91 (93% *Z*)

[a] Yield of isolated product based on the *E*-enol phosphate using RMgBr (1.2 equiv based on the *E*-enol phosphate).
[b] OctMgBr (1.4 equiv) was used.

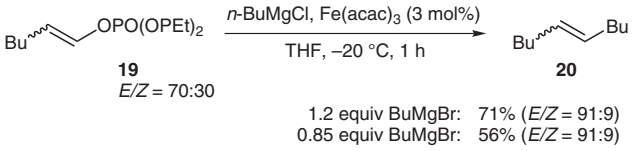
Interestingly, the stereoselectivity can be improved by adjusting the amount of Grignard reagent. Thus in the last example (entry 4), the use of 1.05 instead of 1.2 equivalents of EtMgBr led to only 68% yield but the stereochemical purity jumped from 93% to 98%. It should be noted that when the reaction was performed on a mixture of the corresponding *Z*- and *E*-alkenyl bromides, which are much more reactive, the selectivity was clearly lower (Scheme 7).



* GC yield based on OctMgBr.

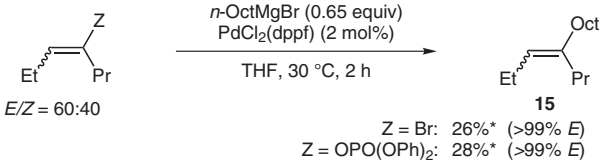
Scheme 7

From β-monosubstituted alkenyl phosphates such as **19**, which are more reactive than the α,β-disubstituted analogues, the formation of the *E*-coupling product was also favored. However, the kinetic differentiation was less clear cut and the *E*-selectivity could not be improved by lowering the amount of Grignard reagent used (Scheme 8).



Scheme 8

It is interesting to note that the iron- and palladium-catalyzed reactions are complementary. Indeed, Rossi has shown that, under palladium catalysis, it is possible to obtain the *E*-olefin with excellent selectivity (≥98% *E*) from a mixture of (*E*)- and (*Z*)-1-bromo-1-alkenes.[11] Unfortunately, this procedure is not applicable to either the α,β-disubstituted alkenyl halides or phosphates, which are clearly less reactive and give unsatisfactory yields (Scheme 9).



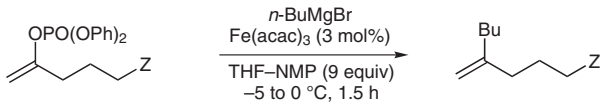
* GC yield based on OctMgBr.

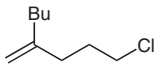
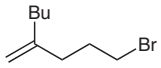
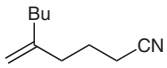
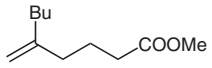
Scheme 9

In fact, the iron-catalyzed procedure is currently the only way to prepare a stereodefined trisubstituted olefin selectively from an *E*/*Z* mixture of α,β-disubstituted alkenyl phosphates.

The alkenylation reaction described above can be performed chemoselectively in the presence of aliphatic chlorides, nitrile or ester groups (Table 3, entries 1, 3 and 4). However, in the presence of aliphatic bromides (entry 2) the reaction gave a mixture of β-elimination products characteristic of the reaction of alkyl Grignard reagents with alkyl bromides in the presence of iron salts.[12]

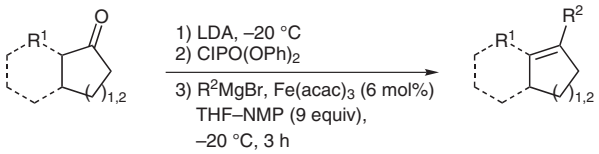
Table 3 Chemoselectivity of the Cross-Coupling Reaction

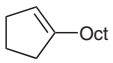
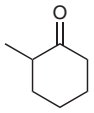
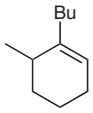
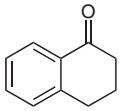
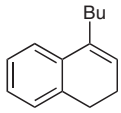


Entry	Product	Yield (%)
1	 **22a**	90
2		0
3	 **22b**	96
4	 **22c**	84

Interestingly, both the preparation of the enol phosphates and the iron-catalyzed cross-coupling reaction can be performed in good yields according to a one-pot procedure (Table 4).[13]

Table 4 Preparation and Coupling of the Enol Phosphate in a One-Pot Procedure



Entry	Starting ketone	Product	Yield (%)[a]
1		 **23**	82
2		 **24**	88
3		 **25**	94

[a] Yield of isolated product.

In summary, we have shown that the cross-coupling reaction between Grignard reagents and enol phosphates is efficiently catalyzed by $Fe(acac)_3$. These results extend the scope of the iron-catalyzed alkenylation of Grignard reagents by alkenyl halides described previously.[3] The use of enol phosphates is especially interesting when the corresponding alkenyl halide is difficult to prepare. It should be noted that olefins of defined configuration are easily prepared via this procedure from a mixture of *Z*- and *E*-enol phosphates since the *E*-isomer reacts exclusively and stereoselectively. This is important since the tedious preparation of pure *E*-enol phosphates can thus be avoided. The procedure represents the first examples of transition-metal-catalyzed alkenylation of organometallics involving a stereoselective kinetic differentiation to give trisubstituted alkenes. From an economical and environmental point of view, this procedure is an interesting alternative to the nickel- and palladium-catalyzed reactions.

THF was purchased from Merck and freshly distilled from sodium/benzophenone under a nitrogen atmosphere before use. Iron(III) acetylacetonate (99+%) was purchased from Acros. Products were purified by distillation or by chromatography on a silica gel column (40–63μm). All reactions were performed under a nitrogen atmosphere. Enol phosphates were prepared from the corresponding ketones according to the procedures described in the literature.[14]

GC analyzes were performed on a Hewlett–Packard HP 6890 chromatograph equipped with a capillary column HP-5MS (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. Mass spectra (MS) were obtained on a Hewlett–Packard HP 5973 mass spectrometer via a GC/MS coupling with a Hewlett–Packard HP 6890 chromatograph equipped with a capillary column HP-5MS. Ionization was performed by electron impact (EI) or chemical ionization with methane (IC, CH_4). Mass spectra are reported as *m*/*z* (% relative intensity). ^1H and ^{13}C NMR spectra (δ, ^1H ±0.01 ppm, ^{13}C ±0.05 ppm, TMS as internal standard, *J* values in Hz ±0.3 Hz) were recorded ei-

ther on a JEOL JNM-EX 270 (270 MHz for ^{1}H) spectrometer or a JEOL ECX 400 (400 MHz for ^{1}H) spectrometer. FT-IR spectra were recorded on a Nicolet Impact 400 instrument (OMNIC software).

Cross-Coupling of Enol Phosphates with Grignard Reagents; Typical Procedure A

Preparation of 2-(3-Chloropropyl)hex-1-ene (22a)

A dried four-necked flask equipped with a mechanical stirrer, a thermometer and a septum was charged with a solution of $Fe(acac)_3$ (60 mg, 0.17 mmol, 3%) in THF (5 mL), *N*-methylpyrrolidinone (4.9 mL, 51.1 mmol, 9 equiv) and 5-chloro-2-diphenoxyphosphoryloxypent-1-ene (2 g, 5.67 mmol, 1 equiv). After stirring for 1 min, butylmagnesium bromide (5 mL, 6.8 mmol, 1.2 equiv) was added dropwise at –20 °C. The resulting mixture was then stirred at 20 °C for 2 h then hydrolyzed with aq HCl (1 M, 20 mL). After extraction with Et_2O (3 × 30 mL), the combined organic layers were washed successively with aq HCl (1 M, 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (cyclohexane) to give the pure product **22a**.

Yield: 0.83 g (90%); yellow oil.

IR (neat): 2940, 1660, 750 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.81 (1 H, s), 4.74 (1 H, s), 3.54 (2 H, t, *J* = 7.3 Hz), 2.16 (2 H, t, *J* = 7.3 Hz), 2.00 (2 H, t, *J* = 7.3 Hz), 1.91 (2 H, quint, *J* = 7.3 Hz), 1.41 (2 H, quint, *J* = 7.3 Hz), 1.32 (2 H, sext, *J* = 7.3 Hz), 0.91 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 148.2 (C), 109.6 (CH_2), 44.6 (CH_2), 35.7 (CH_2), 33.0 (CH_2), 30.6 (CH_2), 29.9 (CH_2), 22.4 (CH_2), 14.0 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 160 (64) $[M + H]^+$, 118 (66), 95 (26), 81 (43), 69 (92), 56 (100).

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_9H_{17}Cl$: 160.1019; found: 160.1022.

Preparation of 3-Ethylundec-2-ene (16); Typical Procedure B

A dried four-necked flask equipped with a mechanical stirrer, a thermometer and a septum was charged with a solution of $Fe(acac)_3$ (212 mg, 0.6 mmol, 3%) in THF (20 mL), DMPU (21.8 mL, 180 mmol, 9 equiv) and 3-diphenoxyphosphoryloxypent-2-ene (6.36 g, 20 mmol, 1 equiv). After stirring for 1 min, octylmagnesium bromide (20 mL, 24 mmol, 1.2 equiv) was added dropwise at –20 °C. The resulting mixture was then stirred at 20 °C for 2 h then hydrolyzed with aq HCl (1 M, 50 mL). After extraction with Et_2O (3 × 30 mL), the combined organic layers were washed successively with aq HCl (1 M, 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel column (cyclohexane) to give **16** as a mixture of stereoisomers (*E*/*Z* = 83:17).

Yield: 2.96 g (81%); colorless oil.

IR (neat): 2945, 1640 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 5.14 (1 H, q, *J* = 6.9 Hz), 1.94 (2 H, q, *J* = 7.3 Hz), 1.90 (2 H, t, *J* = 7.3 Hz), 1.67 (3 H, d, *J* = 6.9 Hz), 1.33 (2 H, quint, *J* = 7.3 Hz), 1.19 (10 H, m), 0.88 (3 H, t, *J* = 7.3 Hz), 0.81 (3 H, t, *J* = 7.1 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 142.1 (C), 117.5 (CH), 116.9 (CH), 36.7 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 28.3 (CH_2), 22.7 (2 × C, CH_2), 14.1 (CH_3), 12.8 (2 × C, CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 182 (16) $[M + H]^+$, 153 (4), 111 (4), 97 (18), 84 (100), 69 (78), 55 (65).

Anal. Calcd for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.25; H, 14.49.

Preparation of 6-Ethylundec-5-ene (18);[15] Typical Procedure C

A dried four-necked flask equipped with a mechanical stirrer, a thermometer and a septum was charged with a solution of $Fe(acac)_3$ (433 mg, 1.2 mmol, 4%) in THF (30 mL), DMPU (30 mL, 248 mmol, 8.3 equiv) and 6-diphenoxyphosphoryloxyundec-5-ene (12.07 g, 30 mmol, 1 equiv). After stirring for 1 min, ethylmagnesium bromide (24.8 mL, 24.8 mmol, 0.83 equiv) was added dropwise in 2 h at –20 °C. The resulting mixture was then stirred at 20 °C for 2 h and hydrolyzed with aq HCl (1 M, 100 mL). After extraction with Et_2O (3 × 30 mL), the combined organic layers were washed successively with aq HCl (1 M, 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (cyclohexane) to give the product as a mixture of stereoisomers (*E*/*Z* = 3:97).

Yield: 3.2 g (71%); colorless oil.

IR (neat): 2940, 1650, 1440 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.10 (1 H, t, *J* = 7.3 Hz), 2.02–1.96 (6 H, m, 2), 1.38–1.23 (10 H, m), 0.98 (3 H, t, *J* = 7.3 Hz), 0.89 (6 H, t, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1 (C), 123.5 (CH), 36.7 (CH_2), 32.5 (CH_2), 32.0 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 28.2 (CH_2), 27.4 (CH_2), 23.9 (CH_2), 22.6 (CH_2), 22.4 (CH_2), 14.0 (2 × C, CH_3), 13.0 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 182 (39) $[M + H]^+$, 126 (6), 111 (26), 97 (74), 83 (61), 69 (100), 55 (73).

Preparation of 1-Octylcyclopent-1-ene (23);[16] Typical Procedure D

A dried four-necked flask equipped with a mechanical stirrer and a thermometer was charged with a solution of diisopropylamine (4.2 mL, 30 mmol, 1.2 equiv) in THF (40 mL). A solution of *n*-BuLi (1.6 M in hexanes, 17.2 mL, 27.5 mmol, 1.1 equiv) was added dropwise at –40 °C. After stirring at 0 °C for 30 min, cyclopentanone (2.1 g, 41.5 mmol, 1 equiv) and, 30 min later, diphenylchlorophosphate (5.8 mL, 27.5 mmol, 1.1 equiv) was added dropwise. The reaction mixture was stirred at 20 °C for 2 h then $Fe(acac)_3$ (441 mg, 1.25 mmol, 5%) and NMP (22 mL, 225 mmol, 9 equiv) were added. Finally, a solution of octylmagnesium bromide (0.8 M in THF, 40.6 mL, 32.5 mmol, 1.3 equiv) was added dropwise at –15 °C and stirring was continued for 30 min at –5 °C and for 1.5 h at 20 °C. The reaction mixture was then hydrolyzed with aq HCl (1 M, 50 mL), extracted with Et_2O (3 × 40 mL) and the combined organic layers were washed successively with aq HCl (1 M, 80 mL) and brine (80 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (pentane) to give **23**.

Yield: 3.68 g (82%); colorless oil.

IR (neat): 2940, 1660, 1452 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.30 (1 H, m), 2.28 (2 H, m), 2.21 (2 H, t, *J* = 7.3 Hz), 2.04 (2 H, t, *J* = 7.3 Hz), 1.84 (2 H, quint, *J* = 7.3 Hz), 1.43 (2 H, quint, *J* = 7.3 Hz), 1.30–1.20 (10 H, m), 0.88 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1 (C), 122.9 (CH), 35.1 (CH_2), 32.4 (CH_2), 31.9 (CH_2), 31.2 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 23.5 (CH_2), 22.7 (CH_2), 14.1 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 180 (32) $[M + H]^+$, 123 (8), 95 (32), 82 (80), 67 (100), 55 (12).

Preparation of 1-Phenylhex-1-ene (5);[17] Typical Procedure E

A dried four-necked flask equipped with a mechanical stirrer and a thermometer was charged with a solution of $Fe(acac)_3$ (35 mg, 0.10 mmol, 1%) in THF (20 mL) and 1-diethoxyphosphoryloxy-2-phe-

nylethene (2.562 g, 10 mmol). After stirring for 1 min, butylmagnesium bromide (10 mL, 12 mmol, 1.2 equiv) was added dropwise over 20 min. After stirring for 15 min, the reaction mixture was quenched with aq HCl (1 M, 50 mL) and the aqueous phase was extracted with cyclohexane (3 × 30 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (cyclohexane) to give **5** as a mixture of stereoisomers (*E*/*Z* = 90:10).

Yield: 694 mg (87%); colorless oil.

IR (neat): 2957, 1598, 1494, 1448, 964 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.15 (5 H, m), 6.39 (0.1 H, d, *J* = 11.9 Hz), 6.37 (0.9 H, d, *J* = 16.1 Hz), 6.22 (0.9 H, dt, *J* = 16.1, 6.9 Hz), 5.66 (0.1 H, dt, *J* = 11.9, 6.9 Hz), 2.32 (0.2 H, dt, *J* = 7.3, 6.9 Hz), 2.18 (1.8 H, dt, *J* = 7.3, 6.9 Hz), 1.47 (2 H, quint, *J* = 7.3 Hz), 1.39 (2 H, sext, *J* = 7.3 Hz), 0.94 (2.7 H, t, *J* = 7.3 Hz), 0.91 (0.3 H, t, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9 (C), 137.8 (C), 133.2 (CH), 131.2 (CH), 129.6 (CH), 128.7 (2 × C, CH), 128.6 (CH), 128.4 (2 × C, CH), 128.1 (2 × C, CH), 126.7 (CH), 126.4 (CH), 125.9 (2 × C, CH), 32.7 (CH_2), 32.2 (CH_2), 31.5 (CH_2), 28.3 (CH_2), 22.4 (CH_2), 22.3 (CH_2), 14.0 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 160 (30) $[M + H]^+$, 131 (5), 117 (100), 104 (58), 91 (28), 77 (5), 65 (4), 51 (3).

5-Butyltridec-4-ene (2)[18]
Prepared according to typical procedure B.

The residue was purified by flash chromatography on a silica gel column (cyclohexane) to give the product as a mixture of stereoisomers (*E*/*Z* = 74:26).

Yield: 5.57 g (78%); colorless oil.

IR (neat): 2940, 1650 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 5.10 (1 H, t, *J* = 7.3 Hz), 1.97 (6 H, m), 1.41–1.26 (18 H, m), 0.93–0.85 (9 H, m).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 140.3 (C), 126.7 (CH), 37.5 (CH_2), 37.2 (CH_2), 32.5 (CH_2), 31.3 (CH_2), 31.2 (CH_2), 30.4, 30.3, 30.2, 30.1, 29.9 (5 × C, CH_2), 29.1 (CH_2), 28.9 (CH_2), 23.8 (CH_2), 23.4 (CH_2), 23.2 (CH_2), 23.1 (CH_2), 14.6 (3 × C, CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 238 (33) $[M + H]^+$, 196 (4), 154 (8), 140 (24), 125 (11), 111 (25), 98 (59), 83 (74), 70 (100), 55 (90).

Anal. Calcd for $C_{17}H_{34}$: C, 85.63; H, 14.37. Found: C, 85.45; H, 14.58.

5-Butyldec-5-ene (4)[19]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 1.67 g (85%); colorless oil.

IR (neat): 2940, 1650, 1452 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.10 (1 H, t, *J* = 6.9 Hz), 2.01–1.93 (6 H, m), 1.40–1.22 (12 H, m), 0.90–0.80 (9 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5 (C), 124.6 (CH), 36.7 (CH_2), 32.5 (CH_2), 30.6 (CH_2), 30.2 (CH_2), 29.8 (CH_2), 27.4 (CH_2), 22.9 (2 × C, CH_2), 22.5 (CH_2), 14.1 (3 × C, CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 196 (34) $[M + H]^+$, 154 (6), 139 (6), 112 (24), 97 (75), 83 (84), 69 (80), 55 (100).

2-Phenylhex-1-ene (6)[20]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 4.311 g (90%); colorless oil.

IR (neat): 2940, 1627, 1580, 1494 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.12 (5 H, m), 5.25 (1 H, s), 5.05 (1 H, s), 2.48 (2 H, t, *J* = 7.3 Hz), 1.42 (2 H, quint, *J* = 7.3 Hz), 1.33 (2 H, sext, *J* = 7.3 Hz), 0.79 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7 (C), 141.4 (C), 128.2 (CH), 127.2 (CH), 126.1 (CH), 112.0 (CH_2), 35.0 (CH_2), 30.4 (CH_2), 22.4 (CH_2), 13.9 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 160 (9) $[M + H]^+$, 131 (5), 118 (100), 103 (14), 91 (14), 77 (8), 65 (2), 51 (3).

2-Butyloct-1-ene (7)[21]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 1.26 g (75%); colorless oil.

IR (neat): 2960, 2932, 1652, 1468, 1376 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 4.68 (2 H, s), 1.99 (4 H, t, *J* = 6.9 Hz), 1.50–1.26 (12 H, m), 0.87 (6 H, t, *J* = 6.9 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 150.2 (C), 108.4 (CH_2), 36.1 (CH_2), 35.8 (CH_2), 31.9 (CH_2), 30.1 (CH_2), 29.2 (CH_2), 27.8 (CH_2), 22.6 (2 × CH_2), 14.0 (2 × CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 168 (20) $[M + H]^+$, 126 (5), 111 (32), 98 (17), 83 (20), 69 (51), 56 (100).

2-Ethyldec-1-ene (8)[22]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 0.86 g (82%); colorless oil.

IR (neat): 2960, 1646, 1460 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 4.61 (2 H, s), 1.93 (4 H, m), 1.38–1.18 (12 H, m), 0.95 (3 H, t, *J* = 6.3 Hz), 0.81 (3 H, t, *J* = 6.9 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 151.6 (C), 107.3 (CH_2), 36.4 (CH_2), 32.0 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 28.8 (CH_2), 27.9 (CH_2), 22.8 (CH_2), 14.1 (CH_3), 12.3 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 168 (4) $[M + H]^+$, 139 (7), 97 (7), 83 (22), 70 (100), 55 (45).

2-Cyclohexylbut-1-ene (9)[23]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 0.18 g (20%); colorless oil.

IR (neat): 2940, 1640, 1462 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 4.63 (1 H, s), 4.60 (1 H, s), 1.96 (2 H, q, *J* = 7.3 Hz), 1.76 (1 H, quint, *J* = 7.3 Hz), 1.48 (10 H, m), 0.95 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 157.0 (C), 105.5 (CH_2), 44.5 (CH), 43.5 (CH_2), 32.6 (2 × C, CH_2), 30.2 (CH_2), 26.9 (2 × C, CH_2), 12.6 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 138 (34) $[M + H]^+$, 123 (2), 109 (92), 96 (34), 91 (4), 81 (69), 67 (100), 55 (34).

2-(1,1-Dimethylethyl)dec-1-ene (10)[24]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 0.69 g (75%); colorless oil.

IR (neat): 2960, 1638, 1468 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 4.84 (1 H, s), 4.68 (1 H, s), 2.01 (2 H, t, *J* = 7.6 Hz), 1.43 (2 H, quint, *J* = 7.6 Hz), 1.36–1.28 (10 H, m), 1.05 (9 H, s), 0.88 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 157.8 (C), 105.5 (CH_2), 36.1 (C), 31.9 (CH_2), 31.3 (CH_2), 29.9, 29.7, 29.5, 29.4, 29.3 (7 × C, CH_2 or CH_3), 22.7 (CH_2), 14.1 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 196 (5) $[M + H]^+$, 138 (7), 111 (5), 98 (28), 83 (100), 69 (21), 55 (28).

1-Butylcyclohex-1-ene (11)[25]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 0.85 g (90%); yellow oil.

IR (neat): 2940, 1660 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 5.38–5.32 (1 H, m), 1.97–1.91 (6 H, m), 1.65–1.50 (4 H, m), 1.37 (2 H, quint, *J* = 7.3 Hz), 1.28 (2 H, sext, *J* = 7.3 Hz), 0.90 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 137.9 (C), 120.5 (CH), 37.7 (CH_2), 30.0 (CH_2), 28.3 (CH_2), 25.5 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 22.7 (CH_2), 14.0 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 138 (50) $[M + H]^+$, 109 (10), 96 (55), 81 (100), 67 (55), 55 (17).

1-Octylcyclohex-1-ene (12)[16]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 0.87 g (90%); yellow oil.

IR (neat): 2960, 2930, 1670, 1460 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 5.40–5.34 (1 H, m), 1.97–1.89 (6 H, m), 1.65–1.52 (4 H, m), 1.45–1.30 (12 H, m), 0.91 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 138.0 (C), 120.5 (CH), 38.1 (CH_2), 32.0 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 28.3 (CH_2), 27.8 (CH_2), 25.2 (CH_2), 22.7 (3 × C, CH_2), 14.1 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 194 (40) $[M + H]^+$, 109 (13), 96 (90), 81 (100), 67 (40), 55 (18).

5-Butylnon-4-ene (13)[26]
Prepared according to typical procedure B.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 2.92 g (80%); colorless oil.

IR (neat): 2940, 1660 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 5.10 (1 H, t, *J* = 7.3 Hz), 1.97–1.92 (6 H, m), 1.43–1.25 (10 H, m), 0.93–0.85 (9 H, m).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 139.7 (C), 124.5 (CH), 36.7 (CH_2), 30.6 (2 × C, CH_2), 29.8 (2 × C, CH_2), 23.3 (CH_2), 22.9 (CH_2), 22.5 (CH_2), 14.0 (2 × C, CH_3), 13.9 (CH_2).

MS (EI, 70 eV): *m*/*z* (%) = 182 (47) $[M + H]^+$, 140 (18), 125 (7), 111 (11), 98 (39), 83 (69), 69 (100), 55 (92).

5-Phenylnon-4-ene (14)[27]
Prepared according to typical procedure B.

The residue was purified by flash chromatography on a silica gel column (cyclohexane) to give the product as a mixture of stereoisomers (*E*/*Z* = 94:6).

Yield: 3.27 g (70%); colorless oil.

IR (neat): 2940, 1660, 1594, 1450 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 7.36–7.17 (5 H, m), 5.60 (1 H, t, *J* = 7.1 Hz), 2.50 (2 H, t, *J* = 6.9 Hz), 2.16 (2 H, q, *J* = 7.1 Hz), 1.50 (2 H, sext, *J* = 7.1 Hz), 1.31–1.29 (4 H, m), 0.96 (3 H, t, *J* = 7.3 Hz), 0.86 (3 H, t, *J* = 7.1 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 143.5 (C), 140.3 (C), 128.9 (CH), 128.1 (2 × C, CH), 126.3 (2 × C, CH_2), 30.9 (CH_2), 30.6 (CH_2), 29.5 (CH_2), 23.1 (CH_2), 22.7 (CH_2), 13.9 (2 × C, CH_2).

MS (EI, 70 eV): *m*/*z* (%) = 202 (13) $[M + H]^+$, 160 (9), 145 (57), 131 (17), 118 (100), 103 (8), 91 (46), 77 (9).

4-Propyldodec-3-ene (15)
Prepared according to typical procedure B.

The residue was purified by flash chromatography on a silica gel column (cyclohexane) to give the product as a mixture of stereoisomers (*E*/*Z* = 88:12).

Yield: 0.92 g (75%); colorless oil.

IR (neat): 2952, 1644 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 5.01 (1 H, t, *J* = 7.3 Hz), 1.90 (6 H, m), 1.28 (4 H, m), 1.19 (10 H, m), 0.86 (3 H, t, *J* = 7.6 Hz), 0.81 (6 H, t, *J* = 7.1 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 138.7 (C), 126.7 (CH), 39.2 (CH_2), 37.0 (CH_2), 32.1 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 28.7 (CH_2), 28.5 (CH_2), 22.8 (CH_2), 21.7 (CH_2), 21.4 (CH_2), 21.1 (CH_2), 14.16 (CH_3), 14.12 (2 × C, CH_3).

Anal. Calcd for $C_{15}H_{30}$: C, 85.63; H, 14.37. Found: C, 85.24; H, 14.72.

3-Phenylpent-2-ene (17)[28]
Prepared according to typical procedure B.

The residue was purified by flash chromatography on a silica gel column (cyclohexane) to give the product as a mixture of stereoisomers (*E*/*Z* = 93:7).

Yield: 2.13 g (73%); colorless oil.

IR (neat): 2948, 1642, 1599 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 7.47–7.18 (5 H, m), 5.70 (1 H, q, *J* = 6.9 Hz), 2.50 (2 H, q, *J* = 7.6 Hz), 1.80 (3 H, d, *J* = 6.9 Hz), 0.98 (3 H, t, *J* = 7.6 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 143.3 (C), 142.3 (C), 128.2 (2 × C, CH), 127.1 (CH), 126.2 (2 × C, CH), 122.0 (CH), 22.6 (CH_2), 13.9 (CH_3), 13.2 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 146 (62) $[M + H]^+$, 131 (20), 117 (100), 103 (4), 91 (29), 77 (7).

Dec-5-ene (20)[29]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on a silica gel column (cyclohexane) to give the product as a mixture of stereoisomers (*E*/*Z* = 91:9).

Yield: 496 mg (71%); colorless oil.

IR (neat): 2940, 1671, 1468, 1378, 967 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.38 (1.8 H, m), 5.34 (0.2 H, m), 1.97 (4 H, m), 1.30 (8 H, m), 0.88 (6 H, t, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.3 (CH), 129.8 (CH), 32.3 (CH_2), 31.8 (CH_2), 26.9 (CH_2), 22.2 (CH_2), 14.0 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 140 (37) $[M + H]^+$, 111 (4), 97 (17), 83 (15), 69 (51), 55 (100).

2-(3-Cyanopropyl)hex-1-ene (22b)[30]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 0.85 g (96%); yellow oil.

IR (neat): 2940, 1660, 1200 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 4.73 (1 H, s), 4.69 (1 H, s), 2.27 (2 H, t, *J* = 7.3 Hz), 2.10 (2 H, t, *J* = 7.3 Hz), 1.93 (2 H, t, *J* = 7.3 Hz), 1.73 (2 H, quint, *J* = 7.3 Hz), 1.33 (2 H, quint, *J* = 7.3 Hz), 1.28 (2 H, sext, *J* = 7.3 Hz), 0.84 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 147.1 (C), 119.5 (C), 110.2 (CH_2), 35.2 (CH_2), 34.4 (CH_2), 29.7 (CH_2), 23.1 (CH_2), 22.2 (CH_2), 16.3 (CH_2), 13.8 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 151 (2) $[M + H]^+$, 136 (13), 122 (22), 109 (63), 94 (34), 81 (39), 69 (67), 56 (100).

Methyl 4-Methenyloctanoate (22c)[31]
Prepared according to typical procedure A.

The residue was purified by flash chromatography on silica gel (cyclohexane–EtOAc, 90:10).

Yield: 0.91 g (84%); yellow oil.

IR (neat): 2940, 1730, 1650, 1200, 1180 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 4.67 (1 H, s), 4.63 (1 H, s), 3.61 (3 H, s), 2.37 (2 H, dt, *J* = 6.9, <1 Hz), 2.26 (2 H, t, *J* = 6.9 Hz), 1.95 (2 H, t, *J* = 6.9 Hz), 1.34–1.30 (4 H, m), 1.23 (2 H, t, *J* = 6.9 Hz), 0.83 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 173.5 (C), 149.9 (C), 108.9 (CH_2), 51.3 (CH_3), 35.8 (CH_2), 32.3 (CH_2), 30.6 (CH_2), 29.5 (CH_2), 22.2 (CH_2), 13.7 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 170 (4) $[M + H]^+$, 141 (2), 128 (56), 113 (2), 101 (100), 84 (11), 71 (34), 55 (8).

1-Butyl-6-methylcyclohex-1-ene (24)[32]
Prepared according to typical procedure D.

The residue was purified by flash chromatography on a silica gel column (cyclohexane).

Yield: 3.38 g (88%); colorless oil.

IR (neat): 2950, 1660 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.35 (1 H, m), 2.11 (1 H, m), 2.08–1.85 (4 H, m), 1.73–1.22 (8 H, m), 0.98 (3 H, d, *J* = 7.0 Hz), 0.89 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 142.2 (C), 120.6 (CH), 34.9 (CH_2), 31.6 (CH_2), 31.3 (CH), 30.2 (CH_2), 25.7 (CH_2), 22.6 (CH_2), 19.9 (CH_2), 19.6 (CH_3), 14.1 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 152 (38) $[M + H]^+$, 109 (39), 95 (100), 81 (49), 67 (39), 55 (14).

1-Butyl-3,4-dihydronaphthalene (25)[33]
Prepared according to typical procedure D.

The residue was purified by flash chromatography on a silica gel column (pentane).

Yield: 4.4 g (94%); colorless oil.

IR (neat): 2950, 1640, 1490, 1450, 740 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.10 (4 H, m), 5.83 (1 H, t, *J* = 1.5, 1.4 Hz), 2.72 (2 H, t, *J* = 7.8 Hz), 2.42 (2 H, dt, *J* = 7.3, 1.4 Hz), 2.22 (2 H, dt, *J* = 7.8, 1.5 Hz), 1.51 (2 H, quint, *J* = 7.3 Hz), 1.37 (2 H, sext, *J* = 7.3 Hz), 0.92 (3 H, t, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.9 (C), 136.7 (C), 135.2 (C), 127.6 (CH), 126.5 (CH), 126.3 (CH), 124.7 (CH), 122.8 (CH), 32.6 (CH_2), 30.8 (CH_2), 28.6 (CH_2), 23.2 (CH_2), 22.8 (CH_2), 14.1 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 186 (25) $[M + H]^+$, 144 (100), 129 (93), 115 (18), 102 (2), 91 (4), 77 (3).

Acknowledgment

The authors thank the CNRS and the Ecole Supérieure de Chimie Organique et Minérale (ESCOM) for their financial support and the Fondation de France for a grant to O.G and V.H.

References

(1) Kharasch, M. S.; Fuchs, C. F. *J. Org. Chem.* **1945**, *10*, 292.
(2) (a) Tamura, M.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1487. (b) Tamura, M.; Kochi, J. K. *Synthesis* **1971**, 303. (c) Tamura, M.; Kochi, J. K. *J. Organomet. Chem.* **1971**, *31*, 289. (d) Tamura, M.; Kochi, J. K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3063. (e) Kochi, J. K. *Acc. Chem. Res.* **1974**, *7*, 351. (f) Neumann, S.; Kochi, J. K. *J. Org. Chem.* **1975**, *40*, 599. (g) Smith, R. S.; Kochi, J. K. *J. Org. Chem.* **1976**, *41*, 502.
(3) For coupling of aromatic Grignard reagents with 2-bromostyrene, see: Molander, G. A.; Rahn, B. J.; Shubert, D. C.; Bonde, S. E. *Tetrahedron Lett.* **1983**, *24*, 5449.
(4) (a) Cahiez, G.; Avedissian, H. *Synthesis* **1998**, 1199. (b) The iron-catalyzed alkenylation of RMnX has also been reported, see: Cahiez, G.; Marquais, S. *Pure Appl. Chem.* **1996**, *68*, 53.
(5) We have shown that the use of NMP or DMPU as a co-solvent also has a remarkable beneficial influence on the Cu-catalyzed alkylation of RMnX or RMgX, see: (a) Cahiez, G.; Marquais, S. *Synlett* **1994**, 45. (b) Cahiez, G.; Chaboche, C.; Jézéquel, M. *Tetrahedron* **2000**, *56*, 2733. For Co-catalyzed alkenylation of RMgX, see: (c) Cahiez, G.; Marquais, S. *Tetrahedron Lett.* **1996**, *37*, 1773.
(6) Fürstner, A.; Leitner, A. *Angew. Chem. Int. Ed.* **2002**, *41*, 609.
(7) (a) Cahiez, G.; Chavant, P. Y.; Metais, E. *Tetrahedron Lett.* **1992**, *33*, 5245. (b) Dohle, W.; Kopp, F.; Cahiez, G.; Knochel, P. *Synlett* **2001**, 1901. (c) Duplais, C.; Bures, F.; Korn, T.; Sapountzis, I.; Cahiez, G.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 2968. (d) Cahiez, G.; Chaboche, C.; Mahuteau-Betzer, F.; Ahr, M. *Org. Lett.* **2005**, *7*, 1943. (e) Cahiez, G.; Habiak, V.; Duplais, C.; Moyeux, A. *Angew. Chem. Int. Ed.* **2007**, *46*, 4364. (f) Cahiez, G.; Duplais, C.; Moyeux, A. *Org. Lett.* **2007**, *9*, 3253. (g) Cahiez, G.; Moyeux, A.; Buendia, J.; Duplais, C. *J. Am. Chem. Soc.* **2007**, *129*, 13788.
(8) (a) Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856. (b) Quintin, J.; Frank, X.; Hocquemiller, R.; Figadère, B. *Tetrahedron Lett.* **2002**, *43*, 3547. (c) Martin, R.; Fürstner, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 3955. (d) Scheiper, B.; Bonnekessel, M.; Krause, H.; Fürstner, A. *J. Org. Chem.* **2004**, *69*, 3943. (e) Nakamura, M.; Matsuo, K.; Ito, S.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 3686. (f) Dos Santos, M.; Franck, X.; Hocquemiller, R.; Figadère, B.; Peyrat, J.-F.; Provot, O.; Brion, J.-D.; Alami, M. *Synlett* **2004**, 2697. (g) Nagano, T.; Hayashi, T. *Org. Lett.* **2004**, *6*, 1297. (h) Bedford, R. B.; Bruce, D. W.; Frost, R. M.; Goodby, J. W.; Hird, M. *Chem. Commun.* **2004**, 2822. (i) Nagano, T.; Hayashi, T. *Org. Lett.* **2005**, *7*, 491. (j) Bedford, R. B.; Bruce, D. W.; Frost, R. M.;

Hird, M. *Chem. Commun.* **2005**, 4161. (k) Bedford, R. B.; Betham, M.; Bruce, D. W.; Danopoulos, A. A.; Frost, R. M.; Hird, M. *J. Org. Chem.* **2006**, *71*, 1104. (l) Zhang, D.; Ready, J. *J. Am. Chem. Soc.* **2006**, *128*, 15050. (m) Xu, X.; Cheng, D.; Pei, W. *J. Org. Chem.* **2006**, *71*, 6637. (n) Durandetti, M.; Perichon, J. *Tetrahedron Lett.* **2006**, *47*, 6255. (o) Durandetti, M.; Perichon, J. *Synthesis* **2006**, 1542. (p) Ottesen, L. K.; Ek, F.; Olsson, R. *Org. Lett.* **2006**, *8*, 1771. (q) Plietker, B. *Angew. Chem. Int. Ed.* **2006**, *45*, 1469. (r) Dunet, G.; Knochel, P. *Synlett* **2006**, 407. (s) Aakermark, B.; Sjoegren, M. P. T. *Adv. Synth. Catal.* **2007**, *349*, 2641. (t) Correa, A.; Bolm, C. *Angew. Chem. Int. Ed.* **2007**, *46*, 8862. (u) Lu, Z.; Chai, G.; Ma, S. *J. Am. Chem. Soc.* **2007**, *129*, 14546. (v) Song, R.-J.; Deng, C.-L.; Xie, Y.-X.; Li, J.-H. *Tetrahedron Lett.* **2007**, *48*, 7845. (w) Guerinot, A.; Reymond, S.; Cossy, J. *Angew. Chem. Int. Ed.* **2007**, *46*, 6521. (x) Taillefer, M.; Xia, N.; Ouali, A. *Angew. Chem. Int. Ed.* **2007**, *46*, 934. (y) Hatakeyama, T.; Nakamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 9844. (z) Kofink, C. C.; Blank, B.; Pagano, S.; Goetz, N.; Knochel, P. *Chem. Commun.* **2007**, 1954. (aa) Dongol, K. G.; Koh, H.; Sau, M.; Chai, C. L. L. *Adv. Synth. Catal.* **2007**, *349*, 1015. (bb) Yamagami, T.; Shintani, R.; Shirakawa, E.; Hayashi, T. *Org. Lett.* **2007**, *9*, 1045. (cc) Furstner, A.; De Souza, D.; Turet, L.; Fenster, M. D. B.; Parra-Rapado, L.; Wirtz, C.; Mynott, R.; Lehmann, C. W. *Chem. Eur. J.* **2007**, *13*, 115.

(9) (a) Ritter, K. *Synthesis* **1993**, 735. (b) It is also possible to use enol triflates under our reaction conditions, see ref. 8e.

(10) (a) We have previously reported one preliminary example of such a reaction (see ref. 4). Another atypical example was reported. In this case, it is necessary to add TMEDA to have a complete reaction whereas, as a rule, the addition of TMEDA has a detrimental influence, see: Larsen, U. S.; Martiny, L.; Begtrup, M. *Tetrahedron Lett.* **2005**, *46*, 4261. For some examples of Pd- or Ni-catalyzed cross-coupling reactions from enol phosphates, see: (b) Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915. (c) Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1980**, *21*, 2531. (d) Takai, K.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 108. (e) Sum, F.-W.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1431. (f) Nicolaou, K. C.; Shi, G. Q.; Gunzer, J. L.; Gärtner, P.; Yang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 5467. (g) Sato, M.; Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1609. (h) Blaszczak, L.; Winkler, J.; Kuhn, S. O. *Tetrahedron Lett.* **1976**, *17*, 4405. (i) Lepifre, F.; Buon, C.; Rabot, R.; Bouyssou, P.; Coudert, G. *Tetrahedron Lett.* **1999**, *40*, 6373.

(11) Rossi, R.; Carpita, A. *Tetrahedron Lett.* **1986**, *27*, 2529.

(12) Kharash, M. S.; Fields, E. K. *J. Am. Chem. Soc.* **1941**, *63*, 2316.

(13) A similar one-pot procedure using a Pd-catalyzed cross-coupling reaction has been reported, see: Miller, J. A. *Tetrahedron Lett.* **2002**, *43*, 7111.

(14) See, for instance, ref. 10f

(15) Whitmore, F. C.; Williams, F. E. *J. Am. Chem. Soc.* **1933**, *55*, 406.

(16) Millon, J.; Lorne, R.; Linstrumelle, G. *Synthesis* **1975**, *7*, 434.

(17) Alonso, D. A.; Fuensanta, M.; Najera, C.; Varea, M. *J. Org. Chem.* **2005**, *70*, 6404.

(18) Uijttewaal, A. P.; Jonkers, F. L.; Van der Gen, A. *J. Org. Chem.* **1979**, *44*, 3157.

(19) Gerard, J.; Hevesi, L. *Tetrahedron* **2001**, *57*, 9109.

(20) Abramovitch, A.; Varghese, J.-P.; Marek, I. *Org. Lett.* **2004**, *6*, 621.

(21) Broene, R. D.; Brookhart, M.; Lamanna, W. M.; Volpe, A. F. Jr. *J. Am. Chem. Soc.* **2005**, *127*, 17194.

(22) Gagneur, S.; Montchamp, J.-L.; Negishi, E. *Organometallics* **2000**, *19*, 2417.

(23) Barluenga, J.; Yus, M.; Concellon, J. M.; Bernad, P. *J. Org. Chem.* **1983**, *48*, 3116.

(24) Matsubara, S.; Mizuno, T.; Otake, T.; Kobata, M.; Utimoto, K.; Takai, K. *Synlett* **1998**, 1369.

(25) Shibuya, M.; Ito, S.; Takahashi, M.; Iwabuchi, Y. *Org. Lett.* **2004**, *6*, 4303.

(26) Fristad, W. E.; Brandvold, T. A.; Peterson, J. R.; Thompson, S. R. *J. Org. Chem.* **1985**, *50*, 3647.

(27) Maslak, P.; Chapman, W. H. Jr.; Vallombroso, T. M.; Watson, B. A. *J. Am. Chem. Soc.* **1995**, *117*, 12380.

(28) Xu, G .-C.; Liu, L.-P.; Lu, J.-M.; Shi, M. *J. Am. Chem. Soc.* **2005**, *127*, 14552.

(29) Kenneth, A. M.; Helquist, P.; Kerber, R.-C. *J. Am. Chem. Soc.* **1981**, *103*, 1862.

(30) Sidduri, A.; Rozema, M. J.; Knochel, P. *J. Org. Chem.* **1993**, *58*, 2694.

(31) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Tetrahedron Lett.* **1986**, *27*, 955.

(32) Baba, T.; Avasthi, K.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1571.

(33) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H.; Karimi, B. *Synth. Commun.* **2003**, *33*, 3653.