APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 855–868
Published online 22 September 2006 in Wiley InterScience
(www.interscience.wiley.com) DOI:10.1002/aoc.1143

Heck reactions of aryl halides with alk-1-en-3-ol derivatives catalysed by a tetraphosphine–palladium complex

Florian Berthiol, Henri Doucet* and Maurice Santelli*

Laboratoire de Synthèse Organique, UMR 6180 CNRS and Université d'Aix-Marseille III: 'Chirotechnologies: catalyse et biocatalyse', Faculté des Sciences de Saint Jérôme, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France

Received 28 June 2006; Accepted 11 July 2006

***cis,cis,cis*-1,2,3,4-Tetrakis(diphenylphosphinomethyl)cyclopentane–$[PdCl(C_3H_5)]_2$ efficiently catalyses the Heck reaction of alk-1-en-3-ol with a variety of aryl halides. In the presence of hex-1-en-3-ol or oct-1-en-3-ol, the β-arylated carbonyl compounds were selectively obtained. Turnover numbers up to 84 000 can be obtained for this reaction. Linalool and 2-methylbut-3-en-2-ol led regio- and stereoselectively to the corresponding (*E*)-1-arylalk-1-en-3-ol derivatives. A minor electronic effect of the substituents of the aryl bromide was observed. Quite similar reaction rates were generally observed in the presence of activated aryl bromides such as bromoacetophenone and deactivated aryl bromides such as bromoanisole, indicating that, with these alkenols and this catalyst, the oxidative addition of aryl bromides to palladium is not the rate-limiting step. It should be noted that this reaction also proceeds with sterically very congested aryl bromides such as 9-bromoanthracene or 2,4,6-triisopropylbromobenzene or with a vinyl bromide. On the other hand, low yields were obtained with aryl chlorides. Copyright © 2006 John Wiley & Sons, Ltd.**

KEYWORDS: palladium; catalysis; tetraphosphine; aryl halide; alk-1-en-3-ol

INTRODUCTION

The palladium-catalysed Heck vinylation reaction is one of the most powerful methods for the formation of C–C bonds.[1–5] The efficiency of several catalysts for the reaction of aryl halides with acrylates or styrene derivatives has been studied in detail. On the other hand, the reaction in the presence of alk-1-en-3-ols has attracted less attention.[6] Moreover, most of the results described with these alkenes were obtained in the presence of reactive but expensive aryl iodides.[7–23] Relatively few results have been reported in the presence of aryl bromides.[24–37] The reaction of alk-1-en-3-ol and aryl bromides can be performed with a Pd/triphenylphosphine catalyst, but the palladium complexes formed with this ligand are generally not very efficient in terms of substrate–catalyst ratio.[24–27] $Pd(OAc)_2$ (10 mol%) associated with P(*o*tol)$_3$ (20 mol%) also catalyses the arylation of but-1-en-3-ol.[28,29] This reaction also proceeds using $Pd(OAc)_2$ or $PdCl_2$ without added ligand, but 5% catalyst is generally used.[30–32] Among ligand-free reactions the best results were obtained by de Vries *et al*. They described the coupling of bromobenzene or 4-bromoacetophenone with 3-buten-1-ol in high turnover numbers (TON) using $Pd(OAc)_2$ as source of ligand-free palladium.[33] In recent years, an efficient catalyst has been tested with these substrates by Calo *et al*. They reported that 1% of a Pd-benzothiazole carbene complex catalyses the reaction of but-1-en-3-ol, pent-1-en-3-ol or oct-1-en-3-ol with aryl bromides in ionic liquids.[34] The coupling of tertiary allylic alcohol 2-methylbut-3-en-1-ol has been performed using the water-soluble ligand TPPTS (20 mol%) and $Pd(OAc)_2$ (10 mol%) in water.[35] Herrmann's palladacycle (3 mol%) has been successfully employed for the coupling of 3-phenylprop-1-en-3-ol with a variety of aryl bromides.[36] Finally, 6-methoxy-2-bromonaphthalene and but-1-en-3-ol using tris(2,4-di-*t*-butylphenyl)phosphite ligand with $Pd(OAc)_2$ gave the corresponding 1-arylbutan-3-one in high TON.[37] If monophosphine, phosphite, carbene

*Correspondence to: Henri Doucet and Maurice Santelli, UMR 6180 CNRS and Université d'Aix-Marseille III: 'Chirotechnologies: catalyse et biocatalyse', Faculté des Sciences de Saint Jérôme, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France.
E-mail: henri.doucet@univ-cezanne.fr and m.santelli@univ.u-3mrs.fr

ligands, a palladacycle or ligand-free palladium systems have been successfully used for the Heck reaction with these alk-1-en-3-ols, to the best of our knowledge, the efficiency of polydentate ligands such as a tetraphosphines has not been demonstrated.

In order to obtain stable and efficient palladium catalysts, we have prepared the new tetraphosphine ligand, *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane or Tedicyp[38] (Fig. 1) in which four diphenylphosphino groups are stereospecifically bound to the same face of a cyclopentane ring. The central idea of the design of this ligand is that intermediate Pd(0) species have to be protected by internal ligation against possible decomposition pathways through under-ligation and subsequent colloid formation. We have already reported the results obtained in allylic substitution,[38] for Suzuki cross-coupling,[39] Sonogashira alkynylation[40] and Heck vinylation[41–50] using Tedicyp as the ligand. For example, we have described the reaction of a few protected allylic alcohols[49] or homoallylic alcohols[50] with aryl halides. We have also reported preliminary results for Heck vinylation of alk-1-en-3-ol derivatives.[51] In order to further establish the requirements for a successful Heck reaction using alk-1-en-3-ol derivatives with our catalyst, we herein report on the reaction of a variety of aryl and heteroaryl halides or β-bromostyrene with the alk-1-en-3-ol derivatives: hex-1-en-3-ol, oct-1-en-3-ol, linalool and 2-methylbut-3-en-2-ol.

For this study, based on previous results,[41] DMF was chosen as the solvent and K_2CO_3 as the base. The reactions were performed at 130 °C under argon in the presence of a 1:2 ratio of $[Pd(C_3H_5)Cl]_2$–Tedicyp as catalyst. We first examined the reactivity of hex-1-en-3-ol with several aryl halides in the presence of 0.1–0.001 mol% catalyst (Scheme 1, Table 1). It is known that the Heck reaction in the presence of alk-1-en-3-ol generally leads to the formation of β-arylated ketones.[5] However, it should be noted that, with several catalytic systems, mixtures of β-arylated ketones and β-aryl allylic alcohol were obtained.[15,26,33] With our catalyst, the β-arylated ketones were selectively obtained in all cases indicating that the Pd–Tedicyp catalyst is probably a neutral complex favouring β-elimination to form the corresponding enol rather than the β-aryl allylic alcohol.[2] We observed that Tedicyp–Pd catalyst system is tolerant of a wide variety of aryl halides. Surprisingly, iodobenzene led to the coupling adduct in a lower TON: 780 than the reaction performed in the presence of 4-*t*-butylbromobenzene: 8300 (Table 1, entries 1, 11 and 12). A minor influence of the electronic factors of the aryl bromides on the reaction rates was observed. For example, quite similar TONs were obtained using activated 4-bromoacetophenone and deactivated 4-bromoanisole: 6900 and 8400, respectively (Table 1, entries 4, 5, 13 and 14), indicating that the rate-limiting step of the reaction with these alkenols is probably not the oxidative addition of the aryl bromide to the palladium catalyst. The reaction performed with 4-bromoacetophenone, 4-bromobenzaldehyde, 4-trifluoromethylbromobenzene or 4-fluorobromobenzene also proceed in good yield using 0.01% catalyst (Table 1, entries 2, 3 and 6–10). The coupling using the *ortho*-substituted aryl bromides 2-trifluoromethylbromobenzene, 2-fluorobromobenzene or 2-methylbromobenzene gave similar or higher TONs of 33 000, 67 000 and 7500 than the *para*-substituted aryl bromides (Table 1, entries 17–22). The di-*ortho*-substituted 2,6-difluorobromobenzene was also reacted using 0.01% catalyst (Table 1, entry 25).

Palladium chemistry involving heterocycles has its unique characteristics stemming from the heterocycles inherently different structural and electronic properties in comparison to the corresponding carbocyclic aryl compounds. Pyridines or quinolines are π-electron deficient. Thiophenes are π-electron excessive. If the oxidative addition of the aryl halides to the palladium complex is the rate-limiting step of the reaction with this catalyst, the reactions should be slower with thiophenes than with pyridines. We observed that the heteroaromatic substrates 3-bromopyridine, 3-bromoquinoline or 4-bromoisoquinoline in the presence of hex-1-en-3-ol led to the expected 1-arylhexan-3-ones **15**–**17** in 2500–34 000 TONs and in good yields (Table 1, entries

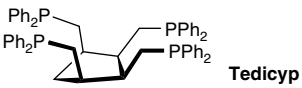
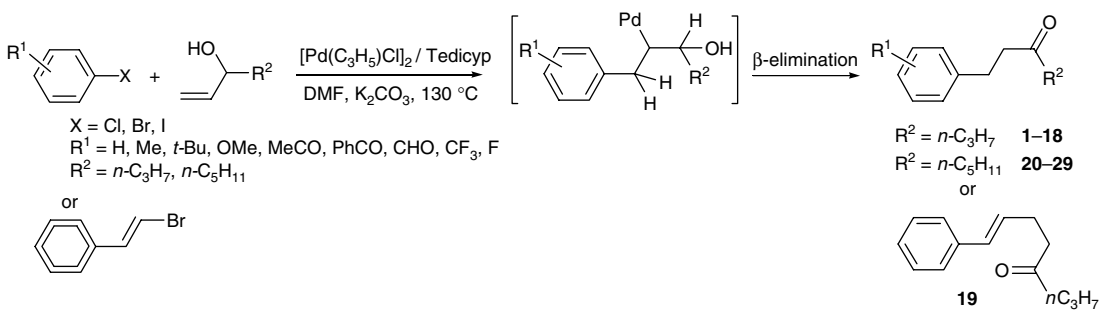


Figure 1.



Scheme 1. Heck reaction with hex-1-en-3-ol or oct-1-en-3-ol.

DOI: 10.1002/aoc

Table 1. Heck reactions with hex-1-en-3-ol catalysed by the Tedicyp–palladium complex (Scheme 1)

Entry	Aryl halide	Ratio substrate–catalyst	Product	Yield (%)[a]
1	Iodobenzene	1 000	**1**	78
2	4-Bromoacetophenone	1 000	**2**	85 (100)
3	4-Bromoacetophenone	10 000	**2**	(69)
4	4-Bromobenzophenone	10 000	**3**	91 (100)
5	4-Bromobenzophenone	100 000	**3**	(69)
6	4-Bromobenzaldehyde	10 000	**4**	94 (100)
7	4-Trifluoromethylbromobenzene	1 000	**5**	92 (100)
8	4-Trifluoromethylbromobenzene	10 000	**5**	(83)
9	4-Fluorobromobenzene	1 000	**6**	(100)
10	4-Fluorobromobenzene	10 000	**6**	84
11	4-*t*-Butylbromobenzene	1 000	**7**	(97)
12	4-*t*-Butylbromobenzene	10 000	**7**	83
13	4-Bromoanisole	1 000	**8**	(100)
14	4-Bromoanisole	10 000	**8**	84
15	6-Methoxy-2-bromonaphthalene	1 000	**9**	92 (100)
16	6-Methoxy-2-bromonaphthalene	10 000	**9**	(46)
17	2-Trifluoromethylbromobenzene	10 000	**10**	90 (100)
18	2-Trifluoromethylbromobenzene	100 000	**10**	(33)
19	2-Fluorobromobenzene	10 000	**11**	94 (100)
20	2-Fluorobromobenzene	100 000	**11**	(67)
21	2-Methylbromobenzene	1 000	**12**	93 (100)
22	2-Methylbromobenzene	10 000	**12**	(75)
23	1-Bromonaphthalene	10 000	**13**	96 (100)
24	1-Bromonaphthalene	100 000	**13**	(41)
25	2,6-Difluorobromobenzene	10 000	**14**	89 (100)
26	3-Bromopyridine	10 000	**15**	91 (100)
27	3-Bromopyridine	100 000	**15**	(31)
28	3-Bromoquinoline	10 000	**16**	92 (100)
29	3-Bromoquinoline	100 000	**16**	(34)
30	4-Bromoisoquinoline	1 000	**17**	95 (100)
31	4-Bromoisoquinoline	10 000	**17**	(25)
32	2-Bromothiophene	1 000	**18**	81 (100)
33	2-Bromothiophene	10 000	**18**	(95)
34	β-Bromostyrene	1 000	**19**	85 (100)
35	β-Bromostyrene	10 000	**19**	(68)

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$ – Tedicyp 1 : 2 see Ref. 38, ArX (1 equiv.), hex-1-en-3-ol (2 equiv.), K_2CO_3 (2 equiv.), DMF, 20 h, 130 °C, under argon, isolated yields, ratio substrate–catalyst based on the aryl halide, in a few cases traces of 1-arylalk-1-en-3-ol derivatives were observed.
[a] Yields in parentheses correspond to GC and NMR yields.

26–31). Reaction of 2-bromothiophene led to adduct **18** in 9500 TON (Table 1, entries 32 and 33). With these heteroaromatic bromides, the oxidative addition to palladium does not appears to be the rate-limiting step of the reactions. Finally, we examined the coupling of the vinyl bromide β-bromostyrene with hex-1-en-3-ol. The corresponding (*E*)-1-phenyloct-1-en-5-one, **19**, was selectively obtained (Scheme 1, Table 1, entries 34 and 35).

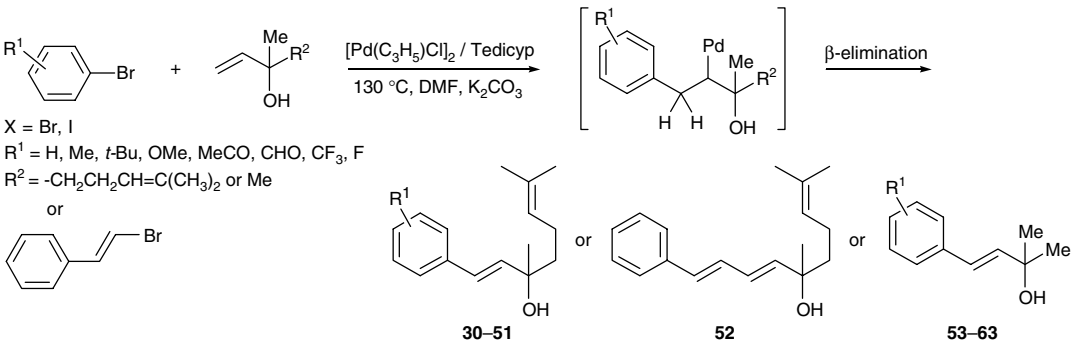
As expected, quite similar reaction rates to those of hex-1-en-3-ol were obtained for the coupling of aryl bromides with oct-1-en-3-ol (Table 2). 4-Bromoanisole and 4-bromobenzophenone gave the 1-aryloctan-3-ones **20** and **24** in 40 000 and 87 000 TONs (Table 2, entries 1, 2, 8 and 9). The *ortho*-substituted aryl bromides 2-trifluoromethylbromobenzene or 2-methylbromobenzene gave **25** and **26** in 84 000 and 9400 TONs (Table 2, entries 10–12). On the other hand, the aryl chloride 4-chlorobenzaldehyde was found to be less reactive. With this substrate a low conversion was observed using 0.4% catalyst (Table 2, entry 4). The heteroaromatic substrates 3-bromopyridine or 2-bromothiophene and oct-1-en-3-ol were reacted using 0.01–0.001% catalyst (Table 2, entries 13, 14, 16 and 17). Coupling of 3-chloropyridine or 3-bromothiophene with oct-1-en-3-ol under conditions similar to those employed

DOI: 10.1002/aoc

Table 2. Heck reactions with oct-1-en-3-ol catalysed by the Tedicyp–palladium complex (Scheme 1)

Entry	Aryl halide	Ratio substrate–catalyst	Product	Yield (%)[a]
1	4-Bromobenzophenone	10 000	**20**	(100)
2	4-Bromobenzophenone	50 000	**20**	80
3	4-Bromobenzaldehyde	10 000	**21**	81 (100)
4	4-Chlorobenzaldehyde	250	**21**	(20)
5	4-Fluorobromobenzene	10 000	**22**	89 (100)
6	4-*t*-Butylbromobenzene	1 000	**23**	84 (100)
7	4-*t*-Butylbromobenzene	10 000	**23**	(62)
8	4-Bromoanisole	10 000	**24**	100
9	4-Bromoanisole	100 000	**24**	87 (91)
10	2-Trifluoromethylbromobenzene	10 000	**25**	82 (100)
11	2-Trifluoromethylbromobenzene	100 000	**25**	(84)
12	2-Methylbromobenzene	10 000	**26**	91 (94)
13	3-Bromopyridine	10 000	**27**	92 (100)
14	3-Bromopyridine	100 000	**27**	(15)
15	3-Chloropyridine	250	**27**	16 (20)
16	2-Bromothiophene	10 000	**28**	92 (100)
17	2-Bromothiophene	100 000	**28**	(40)
18	3-Bromothiophene	250	**29**	73 (80)

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$ – Tedicyp 1 : 2 see Ref 38, ArX (1 equiv.), oct-1-en-3-ol (2 equiv.), K_2CO_3 (2 equiv.), DMF, 20 h, 130 °C, under argon, isolated yields, ratio substrate/catalyst based on the aryl halide, in a few cases traces of 1-arylalk-1-en-3-ol derivatives were observed.
[a] Yields in parentheses correspond to GC and NMR yields.



Scheme 2. Heck reaction with linalool or 2-methylbuten-3-ol.

for 3-bromopyridine led to lower TONs of 50 and 200, respectively (Table 2, entries 15 and 18). With these substrates, the oxidative addition to palladium appears to be the rate-limiting step of the reactions with this catalyst.

Having demonstrated that linear alk-1-en-3-ol derivatives can be reacted efficiently with aryl bromides, we investigated the scope of this coupling reaction using substituted alk-1-en-3-ol derivatives. We studied the reactivity of two 3-substituted alk-1-en-3-ols: linalool and 2-methylbut-3-en-2-ol (Scheme 2, Tables 3 and 4). With linalool the expected (*E*)-1-arylalk-1-en-3-ols **30**–**52** were obtained regio- and stereoselectively, but slower reactions were observed than with the unsubstituted alkenols. Linalool led to the expected the coupling adducts in TONs of 740–10 000. The results presented in Table 3 unfold again a minor substituent effect of the aryl bromide on the reaction rate (Table 3, entries 2–13). For example, TONs of 8400 can be achieved with this catalyst for the reaction of linalool with the activated substrate 4-bromoacetophenone and with the deactivated substrate 4-bromoanisole (Table 2, entries 2, 3, 12 and 13).

We also studied the influence of *ortho*-substituents on the aryl bromide for this reaction. 2-Trifluoromethylbromobenzene, 2-fluorobromobenzene and 2-methylbromobenzene led to adducts **39**–**41** in similar TONs to the *para*-substituted aryl bromides (Table 2, entries 12–17). It should be noted that, even the sterically very congested aryl bromides, 2-bromomesitylene, 9-bromoanthracene or 2,4,6-triisopropylbromobenzene, have been reacted successfully with linalool using 0.1–1% catalyst (Table 3, entries 23–28). The coupling of linalool with a variety of heteroaryl bromides

DOI: 10.1002/aoc

Table 3. Heck reactions with linalool catalysed by the Tedicyp–palladium complex (Scheme 2)

Entry	Aryl halide	Product	Ratio substrate–catalyst	Yield (%)[a]
1	Iodobenzene	**30**	1 000	69 (74)
2	4-Bromoacetophenone	**31**	1 000	(100)
3	4-Bromoacetophenone	**31**	10 000	84
4	4-Bromobenzophenone	**32**	10 000	92 (100)
5	4-Bromobenzaldehyde	**33**	1 000	78 (83)
6	4-Trifluoromethylbromobenzene	**34**	1 000	93 (100)
7	4-Fluorobromobenzene	**35**	10 000	81 (87)
8	4-*t*-Butylbromobenzene	**36**	1 000	(100)
9	4-*t*-Butylbromobenzene	**36**	10 000	90
10	6-Methoxy-2-bromonaphthalene	**37**	1 000	86 (100)
11	6-Methoxy-2-bromonaphthalene	**37**	10 000	28
12	4-Bromoanisole	**38**	1 000	(100)
13	4-Bromoanisole	**38**	10 000	84
14	2-Trifluoromethylbromobenzene	**39**	1 000	91 (100)
15	2-Trifluoromethylbromobenzene	**39**	10 000	(54)
16	2-Fluorobromobenzene	**40**	10 000	88 (93)
17	2-Methylbromobenzene	**41**	1 000	87 (100)
18	2-Methylbromobenzene	**41**	10 000	(69)
19	1-Bromonaphthalene	**42**	1 000	93 (100)
20	1-Bromonaphthalene	**42**	10 000	(76)
21	2,6-Difluorobromobenzene	**43**	1 000	98 (100)
22	2,6-Difluorobromobenzene	**43**	10 000	(80)
23	2-Bromomesitylene	**44**	100	89 (100)
24	2-Bromomesitylene	**44**	250	(89)
25	9-Bromoanthracene	**45**	250	87 (100)
26	9-Bromoanthracene	**45**	1000	(52)
27	2,4,6-Triisopropylbromobenzene	**46**	100	81 (100)
28	2,4,6-Triisopropylbromobenzene	**46**	250	(59)
29	3-Bromopyridine	**47**	1 000	86 (100)
30	3-Bromopyridine	**47**	10 000	(75)
31	3-Bromoquinoline	**48**	1 000	90 (100)
32	3-Bromoquinoline	**48**	10 000	(82)
33	4-Bromoisoquinoline	**49**	250	93 (100)
34	4-Bromoisoquinoline	**49**	1 000	(73)
35	2-Bromothiophene	**50**	1 000	82 (92)
36	3-Bromothiophene	**51**	1 000	83 (90)
37	β-Bromostyrene	**52**	1 000	83 (100)
38	β-Bromostyrene	**52**	10 000	(51)

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$ – Tedicyp 1 : 2 see Ref 38, ArX (1 equiv.), linalool (2 equiv.), K_2CO_3 (2 equiv.), DMF, 20 h, 130 °C, under argon, isolated yields, ratio substrate/catalyst based on the aryl halide.
[a] Yields in parentheses correspond to GC and NMR yields.

such as 3-bromopyridine or 3-bromothiophene also gave satisfactory results in all cases using 0.1–0.01% catalyst (Table 3, entries 29–36). Finally, β-bromostyrene and linalool gave selectively the triene **52** in 5100 TON (Scheme 2, Table 3, entries 37 and 38).

Then, this procedure was extended to 2-methylbut-3-en-2-ol (Table 4). The reactivity of this alkenol is very similar to linalool and the expected (*E*)-1-aryl-3-methylbut-1-en-3-ols **53–63** were regio- and stereoselectively prepared in good yields. The highest TONs were obtained using 4-bromobenzophenone, 4-bromobenzaldehyde and 4-bromoanisole: 10 000, 25 000 and 6800 respectively (Table 4, entries 1, 3 and 9). With the other aryl or heteroaryl bromides, high yields were obtained using 0.4–0.1% catalyst.

In summary, in the presence of the Tedicyp–palladium complex, the Heck vinylation of several aryl bromides with alk-1-en-3-ol derivatives can be performed with as little as 0.1–0.001 mol% catalyst with most substrates. The products of the reactions depends on the substituents of the alkenes. Addition to linalool or 2-methylbut-3-en-2-ol led

DOI: 10.1002/aoc

Table 4. Heck reactions with 2-methylbut-3-en-2-ol catalysed by the Tedicyp–palladium complex (Scheme 2)

Entry	Aryl halide	Product	Ratio substrate–catalyst	Yield (%)[a]
1	4-Bromobenzophenone	**53**	10 000	93 (100)
2	4-Bromobenzaldehyde	**54**	10 000	87 (100)
3	4-Bromobenzaldehyde	**54**	50 000	(50)
4	4-Trifluoromethylbromobenzene	**55**	1000	90 (98)
5	4-Fluorobromobenzene	**56**	1000	78
6	4-*t*-Butylbromobenzene	**57**	250	(97)
7	4-*t*-Butylbromobenzene	**57**	1000	77 (81)
8	4-Bromoanisole	**58**	1000	90 (100)
9	4-Bromoanisole	**58**	10 000	(68)
10	2-Trifluoromethylbromobenzene	**59**	500	96 (100)
11	2-Fluorobromobenzene	**60**	1000	84 (90)
12	2-Methylbromobenzene	**61**	1000	78 (86)
13	3-Bromopyridine	**62**	250	91 (100)
14	3-Bromopyridine	**62**	1000	(30)
15	2-Bromothiophene	**63**	250	76 (100)
16	2-Bromothiophene	**63**	1000	(45)

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$ $^-$ Tedicyp 1 : 2 see Ref 38, ArX (1 equiv.), 2-methylbut-3-en-2-ol (2 equiv.), K_2CO_3 (2 equiv.), DMF, 20 h, 130 °C, under argon, isolated yields, ratio substrate/catalyst based on the aryl halide, reactions performed in an autoclave.
[a] Yields in parentheses correspond to GC and NMR yields.

to the corresponding 1-aryl-alk-1-en-3-ol**s**. In the presence of hex-1-en-3-ol or oct-1-en-3-ol, the β-arylated carbonyl compounds were selectively obtained. Higher reactions rates were observed with the unsubstituted alk-1-en-3-ols. In general, the rate-limiting step of these reactions does not seem to be the oxidative addition of the aryl bromides. With these alk-1-en-3-ol derivatives similar reaction rates were observed in the presence of 4-bromoacetophenone or 4-bromoanisole. For this reason, this method is applicable to the coupling of both electron-deficient and electron-rich aryl bromides. On the other hand, low yields were obtained with aryl chlorides. The rate-limiting step with aryl bromides could be the β-elimination of the ArCH_2CH(Pd)C*H*(OH)(R) (Scheme 1) and ArCH_2CH(Pd)CMe(OH)(R) (Scheme 2) complexes. The β-elimination of the proton on the carbon bearing the alcohol function to form the β-arylated carbonyl compounds is easier, using DMF–K_2CO_3 and Pd–Tedicyp systems. Such β-elimination in not possible with 3-substituted alk-1-en-3-ols. This would explain the slower reactions observed with these substituted alkenols. With the substituted alkenols linalool or 2-methylbut-3-en-2-ol, the (*E*)-1-arylalk-1-en-3-ol derivatives were regio- and stereoselectively obtained using 0.1–0.01% catalyst with most substrates. Moreover, the reactions with linalool also proceeds with sterically very congested aryl bromides such as 9-bromoanthracene or 2,4,6-triisopropylbromobenzene. In terms of substrate–catalyst ratio, selectivity and reaction scope, this catalyst is effective for Heck reactions of alk-1-en-3-ol derivatives. The 'pressure to coordinate' resulting from the presence of these four phosphines in a half space might accelerate the β-elimination steps in the catalytic cycles. Owing to the high price of palladium, the advantage of such low catalyst loading reactions could become increasingly important for industrial processes.

EXPERIMENTAL

General

Allylic alcohols, aryl halides and DMF analytical grade (99.8%) were not purified before use. Potassium carbonate 99 + % was used. All reactions were run under argon using vacuum lines in Schlenk tubes in oven-dried glassware. The reactions were followed by GC and NMR for high boiling point substrates and by GC for low boiling point substrates. ^{1}H (300 MHz) and ^{13}C (75 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shift (δ) are reported in ppm relative to $CDCl_3$. Flash chromatographies were performed on silica gel (230–400 mesh).

Preparation of the Pd–Tedicyp catalyst[38]

An oven-dried 40 ml Schlenk tube equipped with a magnetic stirring bar, under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (4.2 mg, 11.6 μmol) and Tedicyp (20 mg, 23.2 μmol). A 2.5 ml aliquot of anhydrous DMF was added, then the solution was stirred at room temperature for 10 min.

General procedure

As a typical experiment, the reaction of aryl halide (10 mmol), alkenol (20 mmol) and K_2CO_3 (2.76 g, 20 mmol) at 130 °C during 20 h in dry DMF (10 ml) in the presence of *cis*,*cis*,*cis*-1,2,3,4-*tetrakis*(diphenylphosphinomethyl)cyclopentane–1/2 $[PdCl(C_3H_5)]_2$ complex under argon affords the corresponding products after addition of water (50 ml), extraction with

DOI: 10.1002/aoc

dichloromethane (50 ml), separation, drying ($MgSO_4$), evaporation and purification by chromatography on silica gel.

*1-Phenylhexan-3-one (**1**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), iodobenzene (1.12 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **1** was obtained in 78% (1.37 g) yield. ^{1}H RMN: $\delta = 0.89$ (t, $J = 7.4$ Hz, 3H), 1.59 (sext., $J = 7.4$ Hz, 2H), 2.36 (t, $J = 7.4$ Hz, 2H), 2.71 (t, $J = 7.4$ Hz, 2H), 2.90 (t, $J = 7.4$ Hz, 2H), 7.20–7.40 (m, 5H).

*1-(4-Acetylphenyl)-hexan-3-one (**2**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 4-bromoacetophenone (1.99 g, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **2** was obtained in 85% (1.85 g) yield. ^{1}H RMN: $\delta = 0.88$ (t, $J = 7.4$ Hz, 3H), 1.58 (sext., $J = 7.4$ Hz, 2H), 2.36 (t, $J = 7.4$ Hz, 2H), 2.57 (s, 3H), 2.73 (t, $J = 7.4$ Hz, 2H), 2.94 (t, $J = 7.4$ Hz, 2H), 7.26 (d, $J = 8.2$ Hz, 2H), 7.85 (d, $J = 8.2$ Hz, 2H). ^{13}C RMN: $\delta = 13.6$, 17.1, 26.4, 29.5, 43.4, 44.8, 128.5 (2C), 135.1, 146.9, 197.6, 209.4. $C_{14}H_{18}O_2$ (218.1): calcd C 77.03, H 8.31; found C 77.00, H 8.28. MS (EI, 70 eV); m/z (%): 218 (70) [M^+].

*1-(4-Benzoylphenyl)-hexan-3-one (**3**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 4-bromobenzophenone (2.61 g, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **3** was obtained in 91% (2.55 g) yield. ^{1}H RMN: $\delta = 0.88$ (t, $J = 7.4$ Hz, 3H), 1.58 (sext., $J = 7.4$ Hz, 2H), 2.38 (t, $J = 7.4$ Hz, 2H), 2.77 (t, $J = 7.4$ Hz, 2H), 2.97 (t, $J = 7.4$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.47 (d, $J = 8.1$ Hz, 2H), 7.55 (m, 1H), 7.69–7.83 (m, 4H). ^{13}C RMN: $\delta = 13.6$, 17.1, 29.5, 43.4, 44.7, 126.0, 128.2, 129.8, 130.3, 132.1, 135.3, 137.6, 146.2, 196.2, 209.5 $C_{19}H_{20}O_2$ (280.1): calcd C 81.40, H 7.19; found C 81.56, H 7.16. MS (EI, 70 eV); m/z (%): 280 (48) [M^+].

*1-(3-Oxohexyl)benzaldehyde (**4**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 4-bromobenzaldehyde (1.85 g, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **4** was obtained in 94% (1.92 g) yield. ^{1}H RMN: $\delta = 0.87$ (t, $J = 7.4$ Hz, 3H), 1.57 (sext., $J = 7.4$ Hz, 2H), 2.36 (t, $J = 7.4$ Hz, 2H), 2.74 (t, $J = 7.4$ Hz, 2H), 2.96 (t, $J = 7.4$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.78 (d, $J = 8.0$ Hz, 2H), 9.95 (s, 1H). ^{13}C RMN: $\delta = 13.6$, 17.2, 29.7, 43.4, 44.9, 129.0, 130.0, 134.6, 148.6, 191.9, 209.4. $C_{13}H_{16}O_2$ (204.1): calcd C 76.44, H 7.90; found C 76.27, H 7.88. MS (EI, 70 eV); m/z (%): 204 (100) [M^+].

*1-(4-Trifluoromethylphenyl)-hexan-3-one (**5**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 4-trifluoromethylbromobenzene (1.39 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **5** was obtained in 92% (2.24 g) yield. ^{1}H RMN: $\delta = 0.88$ (t, $J = 7.4$ Hz, 3H), 1.58 (sext., $J = 7.4$ Hz, 2H), 2.36 (t, $J = 7.4$ Hz, 2H), 2.73 (t, $J = 7.4$ Hz, 2H), 2.94 (t, $J = 7.4$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 2H), 7.52 (d, $J = 8.1$ Hz, 2H). ^{13}C RMN: $\delta = 15.2$, 17.2, 29.4, 43.7, 44.9, 124.3 (q, $J_{C-F} = 271.9$ Hz), 125.4 (q, $^3J_{C-F} = 4.0$ Hz), 128. 5 (d, $^2J_{C-F} = 32.3$ Hz), 128.7, 145.4, 209.5. $C_{13}H_{15}F_3O$ (244.1): calcd C 63.93, H 6.19; found C 64.01, H 6.25. MS (EI, 70 eV); m/z (%): 244 (93) [M^+].

*1-(4-Fluorophenyl)-hexan-3-one (**6**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 4-fluorobromobenzene (1.10 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **6** was obtained in 84% (1.63 g) yield. ^{1}H RMN: $\delta = 0.87$ (t, $J = 7.4$ Hz, 3H), 1.56 (sext., $J = 7.4$ Hz, 2H), 2.33 (t, $J = 7.4$ Hz, 2H), 2.70 (t, $J = 7.4$ Hz, 2H), 2.84 (t, $J = 7.4$ Hz, 2H), 6.93 (t, $J = 8.5$ Hz, 2H), 7.11 (dd, $J = 8.0$, 5.9 Hz, 2H).

*1-(4-tert-Butylphenyl)-hexan-3-one (**7**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 4-*tert*-butylbromobenzene (1.75 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **7** was obtained in 83% (1.93 g) yield. ^{1}H RMN: $\delta = 0.91$ (t, $J = 7.4$ Hz, 3H), 1.33 (s, 9H), 1.62 (sext., $J = 7.4$ Hz, 2H), 2.38 (t, $J = 7.4$ Hz, 2H), 2.73 (t, $J = 7.4$ Hz, 2H), 2.89 (t, $J = 7.4$ Hz, 2H), 7.13 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.3$ Hz, 2H). ^{13}C RMN: $\delta = 13.7$, 17.2, 29.2, 31.3, 34.3, 44.2, 44.9, 125.3, 127.9, 138.0, 148.8, 210.3. $C_{16}H_{24}O$ (232.2): calcd C 82.70, H 10.41; found C 82.62, H 10.19. MS (EI, 70 eV); m/z (%): 232 (1) [M^+].

*1-(4-Methoxyphenyl)-hexan-3-one (**8**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 4-bromoanisole (1.25 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **8** was obtained in 84% (1.73 g) yield. ^{1}H RMN: $\delta = 0.88$ (t, $J = 7.4$ Hz, 3H), 1.57 (sext., $J = 7.4$ Hz, 2H), 2.34 (t, $J = 7.4$ Hz, 2H), 2.67 (t, $J = 7.4$ Hz, 2H), 2.83 (t, $J = 7.4$ Hz, 2H), 3.76 (s, 3H), 6.80 (d, $J = 8.7$ Hz, 2H), 7.08 (d, $J = 8.7$ Hz, 2H).

*1-(6-Methoxynaphthalen-2-yl)-hexan-3-one (**9**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 6-methoxy-2-bromonaphthalene (2.37 g, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **9** was obtained in 92% (2.36 g) yield. ^{1}H RMN: $\delta = 0.88$ (t, $J = 7.4$ Hz, 3H), 1.59 (sext., $J = 7.4$ Hz, 2H), 2.37 (t, $J = 7.4$ Hz, 2H), 2.78 (t, $J = 7.4$ Hz, 2H), 3.02 (t, $J = 7.4$ Hz, 2H), 3.90 (s, 3H), 7.05–7.17 (m, 2H), 7.24–7.32 (m, 2H), 7.53 (bs, 1H), 7.66 (d, $J = 8.9$ Hz, 1H). ^{13}C RMN: $\delta = 13.7$, 17.2, 29.7, 44.3, 45.0, 55.3, 105.6, 118.75, 126.2, 126.9, 127.5, 128.9, 129.1, 133.1, 136.3, 157.3, 210.2. $C_{17}H_{20}O_2$ (256.1): calcd C 79.65, H 7.86; found C 79.43, H 7.75. MS (EI, 70 eV); m/z (%): 256 (100) [M^+].

*1-(2-Trifluoromethylphenyl)hexan-3-one (**10**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 2-trifluoromethylbromobenzene (1.36 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **10** was obtained in 90% (2.20 g) yield. ^{1}H RMN: $\delta = 0.90$ (t, $J = 7.4$ Hz, 3H), 1.62 (sext., $J = 7.4$ Hz, 2H), 2.37 (t, $J = 7.4$ Hz, 2H), 2.69 (t, $J = 7.4$ Hz, 2H), 3.05 (t, $J = 7.4$ Hz, 2H), 7.27–7.34 (m, 2H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 7.8$ Hz, 1H). ^{13}C RMN: $\delta = 13.7$, 17.3, 26.6,

DOI: 10.1002/aoc

44.4, 44.7, 125.5 (q, $J_{C-F} = 273.6$ Hz), 126.1 (q, $^3J_{C-F} = 5.8$ Hz), 126.2, 128.5 (d, $^2J_{C-F} = 29.8$ Hz), 131.2, 131.9, 140.1, 209.6. $C_{13}H_{15}F_3O$ (244.1): calcd C 63.93, H 6.19; found C 63.67, H 6.18. MS (EI, 70 eV); *m/z* (%): 244 (8) [M^+].

*1-(2-Fluorophenyl)hexan-3-one (**11**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 2-fluorobromobenzene (1.09 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **11** was obtained in 94% (1.82 g) yield. ^{1}H RMN: $\delta = 0.88$ (t, $J = 7.4$ Hz, 3H), 1.57 (sext., $J = 7.4$ Hz, 2H), 2.35 (t, $J = 7.4$ Hz, 2H), 2.70 (t, $J = 7.4$ Hz, 2H), 2.87 (t, $J = 7.4$ Hz, 2H), 6.96–7.06 (m, 2H), 7.10–7.21 (m, 2H). ^{13}C RMN: $\delta = 13.7, 17.2, 23.4, 42.6, 44.8, 115.2$ (d, $^2J_{C-F} = 22.4$ Hz), 124.0 (d, $^4J_{C-F} = 3.4$ Hz), 127.8 (d, $^3J_{C-F} = 8.0$ Hz), 127.9 (d, $^2J_{C-F} = 15.4$ Hz), 130.7 (d, $^3J_{C-F} = 5.2$ Hz), 161.1 (d, $J_{C-F} = 244.4$ Hz), 209.9. $C_{12}H_{15}FO$ (194.1): calcd C 74.20, H 7.78; found C 74.09, H 7.79. MS (EI, 70 eV); *m/z* (%): 194 (79) [M^+].

*1-(o-Tolyl)hexan-3-one (**12**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 2-methylbromobenzene (1.20 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **12** was obtained in 93% (1.77 g) yield. ^{1}H RMN: $\delta = 0.94$ (t, $J = 7.4$ Hz, 3H), 1.62 (sext., $J = 7.4$ Hz, 2H), 2.31 (s, 3H), 2.39 (t, $J = 7.4$ Hz, 2H), 2.67 (t, $J = 7.4$ Hz, 2H), 2.89 (t, $J = 7.4$ Hz, 2H), 7.12 (s, 4H). ^{13}C RMN: $\delta = 13.7, 17.2, 19.2, 27.0, 42.9, 44.8, 126.0, 126.2, 128.5, 130.2, 135.8, 139.2, 210.2$. $C_{13}H_{18}O$ (190.1): calcd C 82.06, H 9.53; found C 82.29, H 9.32. MS (EI, 70 eV); *m/z* (%): 190 (5) [M^+].

*1-(Naphthalen-1-yl)hexan-3-one (**13**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 1-bromonaphthalene (1.39 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **13** was obtained in 96% (2.17 g) yield. ^{1}H RMN: $\delta = 0.92$ (t, $J = 7.4$ Hz, 3H), 1.63 (sext., $J = 7.4$ Hz, 2H), 2.37 (t, $J = 7.4$ Hz, 2H), 2.84 (t, $J = 7.4$ Hz, 2H), 3.38 (t, $J = 7.4$ Hz, 2H), 7.27–7.47 (m, 2H), 7.47–7.56 (m, 2H), 7.74 (d, $J = 8.6$ Hz, 1H), 7.84–7.92 (m, 1H), 7.97–8.06 (m, 1H). ^{13}C RMN: $\delta = 13.7, 17.2, 26.7, 43.4, 44.8, 123.4, 125.5$ (2C), 125.9 (2C), 126.8, 128.8, 131.5, 133.8, 137.1, 210.1. $C_{16}H_{18}O$ (226.1): calcd C 84.91, H 8.02; found C 84.70, H 8.15. MS (EI, 70 eV); *m/z* (%): 226 (100) [M^+].

*1-(2,6-Difluorophenyl)hexan-3-one (**14**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 2,6-difluorobromobenzene (1.93 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **14** was obtained in 89% (1.89 g) yield. ^{1}H RMN: $\delta = 0.87$ (t, $J = 7.4$ Hz, 3H), 1.54 (sext., $J = 7.4$ Hz, 2H), 2.36 (t, $J = 7.4$ Hz, 2H), 2.64 (t, $J = 7.4$ Hz, 2H), 2.90 (t, $J = 7.4$ Hz, 2H), 6.80 (t, $J = 7.7$ Hz, 2H), 7.11 (quint., $J = 7.7$ Hz, 1H). ^{13}C RMN: $\delta = 13.7$, 16.6 (t, $^3J_{C-F} = 3.2$ Hz), 17.2, 41.8, 44.6, 111.0 (dd, $^2J_{C-F} = 17.8, 8.0$ Hz), 116.5 (t, $^2J_{C-F} = 20.0$ Hz), 127.5 (t, $^3J_{C-F} = 10.4$ Hz), 161.5 (dd, $J_{C-F} = 246.7$, 8.6 Hz), 209.5. $C_{12}H_{14}F_2O$ (212.1): calcd C 67.91, H 6.65; found C 67.67, H 6.46. MS (EI, 70 eV); *m/z* (%): 212 (72) [M^+].

*1-(3-Pyridinyl)hexan-3-one (**15**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 3-bromopyridine (0.96 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **15** was obtained in 91% (1.61 g) yield. ^{1}H RMN: $\delta = 0.81$ (t, $J = 7.4$ Hz, 3H), 1.50 (sext., $J = 7.4$ Hz, 2H), 2.29 (t, $J = 7.4$ Hz, 2H), 2.65 (t, $J = 7.4$ Hz, 2H), 2.81 (t, $J = 7.4$ Hz, 2H), 7.12 (ddd, $J = 7.9, 4.9, 0.8$ Hz, 1H), 7.42 (dt, $J = 7.9, 2.0$ Hz, 1H), 8.40–8.50 (m, 2H). ^{13}C RMN: $\delta = 13.5, 17.0, 26.5, 43.4, 44.7, 123.2, 135.8, 136.4, 147.3, 149.6, 209.2$. $C_{11}H_{15}NO$ (177.1): calcd C 74.54, H 8.53; found C 74.67, H 8.45. MS (EI, 70 eV); *m/z* (%): 177 (2) [M^+].

*1-(3-Quinolinyl)hexan-3-one (**16**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 3-bromoquinoline (1.36 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **16** was obtained in 92% (2.09 g) yield. ^{1}H RMN: $\delta = 0.82$ (t, $J = 7.4$ Hz, 3H), 1.53 (sext., $J = 7.4$ Hz, 2H), 2.31 (t, $J = 7.4$ Hz, 2H), 2.75 (t, $J = 7.4$ Hz, 2H), 3.00 (t, $J = 7.4$ Hz, 2H), 7.45 (td, $J = 7.5, 1.0$ Hz, 1H), 7.59 (td, $J = 7.0, 1.5$ Hz, 1H), 7.69 (dd, $J = 8.1, 1.0$ Hz, 1H), 7.85 (d, $J = 1.5$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 8.72 (d, $J = 2.3$ Hz, 1H). ^{13}C RMN: $\delta = 13.5, 17.0, 26.7, 43.3, 44.7, 126.5, 127.2, 127.9, 128.6, 128.9, 133.7, 134.3, 146.7, 151.6, 209.1$. $C_{15}H_{17}NO$ (227.1): calcd C 79.26, H 7.54; found C 79.05, H 7.48. MS (EI, 70 eV); *m/z* (%): 227 (100) [M^+].

*1-(4-Isoquinolinyl)hexan-3-one (**17**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 4-bromoisoquinoline (2.08 g, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **17** was obtained in 95% (2.16 g) yield. ^{1}H RMN: $\delta = 0.86$ (t, $J = 7.4$ Hz, 3H), 1.58 (sext., $J = 7.4$ Hz, 2H), 2.35 (t, $J = 7.4$ Hz, 2H), 2.80 (t, $J = 7.4$ Hz, 2H), 3.27 (t, $J = 7.4$ Hz, 2H), 7.54 (td, $J = 8.1, 1.3$ Hz, 1H), 7.70 (td, $J = 8.1, 1.3$ Hz, 1H), 7.93 (d, $J = 8.1$ Hz, 2H), 8.34 (bs, 1H), 9.08 (bs, 1H). ^{13}C RMN: $\delta = 13.1, 16.6, 23.0, 42.2, 44.1, 121.9, 126.3, 127.7, 129.7, 129.8, 133.7, 141.83, 150.8, 161.8, 208.7$. $C_{15}H_{17}NO$ (227.1): calcd C 79.26, H 7.54; found C 79.30, H 7.77. MS (EI, 70 eV); *m/z* (%): 227 (100) [M^+].

*1-(2-Thienyl)hexan-3-one (**18**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), 2-bromothiophene (0.97 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **18** was obtained in 81% (1.47 g) yield. ^{1}H RMN: $\delta = 0.88$ (t, $J = 7.4$ Hz, 3H), 1.59 (sext., $J = 7.4$ Hz, 2H), 2.36 (t, $J = 7.4$ Hz, 2H), 2.76 (t, $J = 7.4$ Hz, 2H), 3.09 (t, $J = 7.4$ Hz, 2H), 6.77 (d, $J = 3.4$ Hz, 1H), 6.88 (dd, $J = 5.1, 3.4$ Hz, 1H), 7.08 (d, $J = 5.1$ Hz, 1H). ^{13}C RMN: $\delta = 13.7, 17.2, 23.8, 44.3, 44.9, 123.2, 124.5, 126.8, 143.8, 209.5$. $C_{10}H_{14}OS$ (182.1): calcd C 65.89, H 7.74; found C 65.56, H 7.81. MS (EI, 70 eV); *m/z* (%): 182 (100) [M^+].

*(E)-8-Phenyloct-7-en-4-one (**19**)*

From hex-1-en-3-ol (2.41 ml, 20 mmol), β-bromostyrene (1.28 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **19** was obtained in 85% (1.72 g) yield. ^{1}H RMN: $\delta = 0.89$ (t, $J = 7.4$ Hz, 3H), 1.62 (sext., $J = 7.4$ Hz,

DOI: 10.1002/aoc

2H), 2.30–2.76 (m, 6H), 6.18 (dt, $J = 15.9$, 6.4 Hz, 1H), 6.39 (d, $J = 15.9$ Hz, 1H), 7.10–7.45 (m, 5H). ^{13}C RMN: $\delta = 13.7$, 17.2, 27.0, 42.1, 44.8, 125.9, 127.0, 128.4, 128.9, 130.6, 137.4, 210.3. $C_{14}H_{18}O$ (202.1): calcd C 83.12, H 8.97; found C 83.29, H 9.01. MS (EI, 70 eV); m/z (%): 202 (100) [M^+].

*1-(4-Benzoylphenyl)octan-3-one (**20**)*

From oct-1-en-3-ol (3.09 ml, 20 mmol), 4-bromobenzophenone (2.61 g, 10 mmol), Pd complex (2×10^{-4} mmol) and K_2CO_3 (2.76 g, 20 mmol), **20** was obtained in 80% (2.46 g) yield. ^{1}H RMN: $\delta = 0.87$ (t, $J = 7.4$ Hz, 3H), 1.14–1.37 (m, 4H), 1.54 (quint., $J = 7.4$ Hz, 2H), 2.37 (t, $J = 7.4$ Hz, 2H), 2.74 (t, $J = 7.4$ Hz, 2H), 2.95 (t, $J = 7.4$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.53 (m, 1H), 7.66–7.79 (m, 4H). ^{13}C RMN: $\delta = 13.8$, 22.3, 23.3, 29.5, 31.2, 42.9, 43.5, 126.1, 128.1, 129.8, 130.3, 132.1, 135.4, 137.6, 146.3, 196.2, 209.6. $C_{21}H_{24}O_2$ (308.2): calcd C 81.78, H 7.84; found C 81.87, H 7.72. MS (EI, 70 eV); m/z (%): 308 (4) [M^+].

*4-(3-Oxooctyl)benzaldehyde (**21**)*

From oct-1-en-3-ol (3.09 ml, 20 mmol), 4-bromobenzaldehyde (1.85 g, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **21** was obtained in 81% (1.88 g) yield. ^{1}H RMN: $\delta = 0.83$ (t, $J = 7.4$ Hz, 3H), 1.10–1.37 (m, 4H), 1.52 (quint., $J = 7.4$ Hz, 2H), 2.35 (t, $J = 7.4$ Hz, 2H), 2.73 (t, $J = 7.4$ Hz, 2H), 2.94 (t, $J = 7.4$ Hz, 2H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 2H), 9.93 (s, 1H). ^{13}C RMN: $\delta = 13.8$, 22.3, 23.4, 29.7, 31.3, 42.9, 43.4, 129.0, 129.9, 134.6, 148.6, 191.8, 209.5. $C_{15}H_{20}O_2$ (232.1): calcd C 77.55, H 8.68; found C 77.42, H 8.49. MS (EI, 70 eV); m/z (%): 232 (1) [M^+].

*1-(4-Fluorophenyl)octan-3-one (**22**)*

From oct-1-en-3-ol (3.09 ml, 20 mmol), 4-fluorobromobenzene (1.10 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **22** was obtained in 89% (1.98 g) yield. ^{1}H RMN: $\delta = 0.86$ (t, $J = 7.4$ Hz, 3H,), 1.05–1.35 (m, 4H), 1.52 (quint., $J = 7.4$ Hz, 2H), 2.34 (t, $J = 7.4$ Hz, 2H), 2.70 (t, $J = 7.4$ Hz, 2H), 2.80 (t, $J = 7.4$ Hz, 2H), 6.92 (t, $J = 8.9$ Hz, 2H), 7.10 (dd, $J = 7.6$, 4.5 Hz, 2H). ^{13}C RMN: $\delta = 13.8$, 22.3, 23.4, 28.8, 31.3, 43.0, 44.1, 115.2 (d, $^2J_{C-F} = 20.2$ Hz), 129.7 (d, $^3J_{C-F} = 8.0$ Hz), 136.8, 161.0 (d, $J_{C-F} = 267.9$ Hz), 210.1. $C_{14}H_{19}FO$ (222.1): calcd C 75.64, H 8.61; found C 75.48, H 8.59. MS (EI, 70 eV); m/z (%): 222 (6) [M^+].

*1-(4-tert-Butylphenyl)octan-3-one (**23**)*

From oct-1-en-3-ol (3.09 ml, 20 mmol), 4-*tert*-butylbromobenzene (1.75 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **23** was obtained in 84% (2.18 g) yield. ^{1}H RMN: $\delta = 0.90$ (t, $J = 7.4$ Hz, 3H), 1.33 (m, 13H), 1.57 (quint., $J = 7.4$ Hz, 2H), 2.38 (t, $J = 7.4$ Hz, 2H), 2.72 (t, $J = 7.4$ Hz, 2H), 2.87 (t, $J = 7.4$ Hz, 2H), 7.12 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H). ^{13}C RMN: $\delta = 13.8$, 22.3, 23.4, 29.1, 31.2, 31.3, 34.2, 42.9, 44.1, 125.2, 127.9, 138.0, 148.7, 210.4. $C_{18}H_{28}O$ (260.2): calcd C 83.02, H 10.84; found C 83.17, H 11.01. MS (EI, 70 eV); m/z (%): 260 (86) [M^+].

*1-(4-Methoxyphenyl)octan-3-one (**24**)*

From oct-1-en-3-ol (3.09 ml, 20 mmol), 4-bromoanisole (1.25 ml, 10 mmol), Pd complex (10^{-4} mmol) and K_2CO_3 (2.76 g, 20 mmol), **24** was obtained in 87% (2.04 g) yield. ^{1}H RMN: $\delta = 0.87$ (t, $J = 7.4$ Hz, 3H), 1.10–1.45 (m, 4H), 1.54 (quint., 2H), 2.34 (t, $J = 7.4$ Hz, 2H), 2.67 (t, $J = 7.4$ Hz, 2H), 2.82 (t, $J = 7.4$ Hz, 2H), 3.75 (s, 3H), 6.80 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H). ^{13}C RMN: $\delta = 13.8$, 22.3, 23.3, 28.8, 31.3, 42.9, 44.4, 55.1, 113.7, 129.1, 133.1, 157.8, 210.4. $C_{15}H_{22}O_2$ (234.2): calcd C 76.88, H 9.46; found C 76.61, H 9.43. MS (EI, 70 eV); m/z (%): 234 (61) [M^+].

*1-(2-Trifluoromethylphenyl)octan-3-one (**25**)*

From oct-1-en-3-ol (3.09 ml, 20 mmol), 2-trifluoromethylbromobenzene (1.36 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **25** was obtained in 82% (2.23 g) yield. ^{1}H RMN: $\delta = 0.87$ (t, $J = 7.4$ Hz, 3H), 1.15–1.40 (m, 4H), 1.56 (quint., $J = 7.4$ Hz, 2H), 2.38 (t, $J = 7.4$ Hz, 2H), 2.70 (t, $J = 7.4$ Hz, 2H), 3.06 (t, $J = 7.4$ Hz, 2H), 7.30 (m, 2H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 8.1$ Hz, 1H). ^{13}C RMN: $\delta = 13.8$, 22.4, 23.4, 29.4, 31.3, 43.0, 43.6, 124.6 (q, $J_{C-F} = 273.6$ Hz), 126.1 (q, $^3J_{C-F} = 5.7$ Hz), 126.3, 128.5 (d, $^2J_{C-F} = 29.8$ Hz), 131.2, 131.8, 140.1, 209.7. $C_{15}H_{19}F_3O$ (272.1): calcd C 66.16, H 7.03; found C 66.04, H 7.19. MS (EI, 70 eV); m/z (%): 272 (2) [M^+].

*1-(o-Tolyl)octan-3-one (**26**)*

From oct-1-en-3-ol (3.09 ml, 20 mmol), 2-methylbromobenzene (1.20 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **26** was obtained in 91% (1.98 g) yield. ^{1}H RMN: $\delta = 0.89$ (t, $J = 7.4$ Hz, 3H), 1.31–1.43 (m, 4H), 1.58 (quint., $J = 7.4$ Hz, 2H), 2.31 (s, 3H), 2.39 (t, $J = 7.4$ Hz, 2H), 2.67 (t, $J = 7.4$ Hz, 2H), 2.88 (t, $J = 7.4$ Hz, 2H), 7.09–7.14 (m, 3H), 7.14–7.17 (m, 1H). ^{13}C RMN: $\delta = 13.9$, 19.2, 22.4, 23.5, 27.0, 31.3, 42.8, 42.9, 126.0, 126.2, 128.5, 130.2, 135.8, 139.2, 210.4. $C_{15}H_{22}O$ (218.2): calcd C 82.52, H 10.16; found C 82.52, H 10.41. MS (EI, 70 eV); m/z (%): 218 (1) [M^+].

*1-(3-Pyridinyl)octan-3-one (**27**)*

From oct-1-en-3-ol (3.09 ml, 20 mmol), 3-bromopyridine (0.96 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **27** was obtained in 92% (1.89 g) yield. ^{1}H RMN: $\delta = 0.80$ (t, $J = 7.4$ Hz, 3H), 1.20–1.30 (m, 4H), 1.48 (quint., $J = 7.4$ Hz, 2H), 2.31 (t, $J = 7.4$ Hz, 2H), 2.67 (t, $J = 7.4$ Hz, 2H), 2.82 (t, $J = 7.4$ Hz, 2H), 7.13 (dd, $J = 7.9$, 4.9 Hz, 1H), 7.45 (dt, $J = 7.9$, 2.0 Hz, 1H), 8.32–8.42 (m, 2H). ^{13}C RMN: $\delta = 13.7$, 22.3, 23.3, 26.6, 31.2, 42.8, 43.4, 123.2, 135.9, 136.5, 147.3, 149.6, 209.4. $C_{13}H_{19}NO$ (205.1): calcd C 76.06, H 9.33; found C 76.13, H 9.40. MS (EI, 70 eV); m/z (%): 205 (5) [M^+].

*1-(2-Thienyl)octan-3-one (**28**)*

From oct-1-en-3-ol (3.09 ml, 20 mmol), 2-bromothiophene (0.97 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **28** was obtained in 92% (1.93 g) yield. ^{1}H RMN: $\delta = 0.80$ (t, $J = 7.4$ Hz, 3H), 1.10–1.40 (m, 4H),

DOI: 10.1002/aoc

1.48 (quint., $J = 7.4$ Hz, 2H), 2.31 (t, $J = 7.4$ Hz, 2H), 2.67 (t, $J = 7.4$ Hz, 2H), 2.85 (t, $J = 7.4$ Hz, 2H), 6.78 (dd, $J = 3.4$, 1.0 Hz, 1H), 6.89 (dd, $J = 5.1$, 3.4 Hz, 1H), 7.10 (dd, $J = 5.1$, 1.2 Hz, 1H). ^{13}C RMN: $\delta = 13.9$, 22.4, 23.4, 23.9, 31.3, 43.0, 44.3, 123.2, 124.5, 126.7, 143.8, 209.7 $C_{12}H_{18}OS$ (210.1): calcd C 68.52, H 8.63; found C 68.27, H 8.75. MS (EI, 70 eV); m/z (%): 210 (60) [M^+].

*1-(3-Thienyl)octan-3-one (**29**)*

From oct-1-en-3-ol (3.09 ml, 20 mmol), 3-bromothiophene (0.94 ml, 10 mmol), Pd complex (4×10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **29** was obtained in 73% (1.53 g) yield. ^{1}H RMN: $\delta = 0.87$ (t, $J = 7.4$ Hz, 3H), 1.15–1.40 (m, 4H), 1.55 (quint., $J = 7.4$ Hz, 2H), 2.37 (t, $J = 7.4$ Hz, 2H), 2.71 (t, $J = 7.4$ Hz, 2H), 2.91 (t, $J = 7.4$ Hz, 2H), 6.89–6.95 (m, 2H), 7.23 (dd, $J = 4.9$, 3.0 Hz, 1H). ^{13}C RMN: $\delta = 13.9$, 22.4, 23.5, 24.2, 31.4, 43.0, 43.3, 120.4, 125.5, 128.1, 141.4, 210.3. $C_{12}H_{18}OS$ (210.1): calcd C 68.52, H 8.63; found C 68.85, H 8.72. MS (EI, 70 eV); m/z (%): 210 (24) [M^+].

*(E)-3,7-Dimethyl-1-phenylocta-1,6-dien-3-ol (**30**)*

From linalol (3.55 ml, 20 mmol), iodobenzene (1.12 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **30** was obtained in 69% (1.59 g) yield. ^{1}H RMN: $\delta = 1.26$ (s, 3H), 1.58 (s, 3H), 1.66 (s, 3H), 1.55–1.70 (m, 2H), 1.73 (s, 1H), 1.92–2.12 (m, 2H), 5.10 (t, $J = 7.2$ Hz, 1H), 6.26 (d, $J = 16.0$ Hz, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 7.20 (t, $J = 7.3$ Hz, 1H), 7.29 (t, $J = 7.3$ Hz, 2H), 7.37 (d, $J = 7.3$ Hz, 2H). ^{13}C RMN: $\delta = 15.6$, 22.7, 25.6, 27.8, 42.0, 73.37, 111.6, 124.3, 126.3, 127.2, 128.5, 131.8, 136.6, 145.0. $C_{16}H_{22}O$ (230.2): calcd C 83.43, H 9.63; found C 83.19, H 9.54. MS (EI, 70 eV); m/z (%): 212 (19) [$M^+ - 18$].

*(E)-3,7-Dimethyl-1-(4-acetylphenyl)octa-1,6-dien-3-ol (**31**)*

From linalol (3.55 ml, 20 mmol), 4-bromoacetophenone (1.99 g, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **31** was obtained in 84% (2.28 g) yield. ^{1}H RMN: $\delta = 1.38$ (s, 3H), 1.58 (s, 3H), 1.67 (s, 3H), 1.64–1.73 (m, 2H), 1.83 (s, 1H), 2.00–2.20 (m, 2H), 2.58 (s, 3H), 5.13 (t, $J = 7.1$ Hz, 1H), 6.39 (d, $J = 16.0$ Hz, 1H), 6.64 (d, $J = 16.0$ Hz, 1H), 7.44 (d, $J = 8.3$ Hz, 2H), 7.90 (d, $J = 8.3$ Hz, 2H). ^{13}C RMN: $\delta = 17.7$, 22.9, 25.7, 26.5, 28.4, 42.4, 73.6, 124.1, 126.2, 126.4, 128.7, 132.3, 135.8, 139.6, 141.8, 197.6. $C_{18}H_{24}O_2$ (272.2): calcd C 79.37, H 8.88; found C 77.28, H 8.74. MS (EI, 70 eV); m/z (%): 254 (7) [$M^+ - 18$].

*(E)-3,7-Dimethyl-1-(4-benzoylphenyl)octa-1,6-dien-3-ol (**32**)*

From linalol (3.55 ml, 20 mmol), 4-bromobenzophenone (2.61 g, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **32** was obtained in 92% (3.07 g) yield. ^{1}H RMN: $\delta = 1.39$ (s, 3H), 1.54 (s, 3H), 1.67 (s, 3H), 1.65–1.75 (m, 2H), 1.89 (s, 1H), 2.00–2.20 (m, 2H), 5.14 (t, $J = 6.9$ Hz, 1H), 6.41 (d, $J = 16.0$ Hz, 1H), 6.67 (d, $J = 16.0$ Hz, 1H), 7.40–7.52 (m, 4H), 7.52–7.63 (m, 1H), 7.70–7.83 (m, 4H). ^{13}C RMN: $\delta = 17.5$, 22.7, 25.5, 28.1, 42.3, 73.2, 124.1, 125.9, 126.0, 128.0, 129.7, 130.4, 131.7, 132.1, 135.8, 137.5, 139.6, 141.3, 196.0. $C_{23}H_{26}O_2$ (334.2): calcd C 82.60, H 7.84; found C 82.47, H 8.02. MS (EI, 70 eV); m/z (%): 334 (5) [M^+].

*(E)-4-(3-Hydroxy-3,7-dimethylocta-1,6-dienyl) benzaldehyde (**33**)*

From linalol (3.55 ml, 20 mmol), 4-bromobenzaldehyde (1.85 g, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **33** was obtained in 78% (2.01 g) yield. ^{1}H RMN: $\delta = 1.38$ (s, 3H), 1.58 (s, 3H), 1.67 (s, 3H), 1.60–1.74 (m, 2H), 1.80 (s, 1H), 2.00–2.20 (m, 2H), 5.13 (t, $J = 7.1$ Hz, 1H), 6.43 (d, $J = 16.0$ Hz, 1H), 6.67 (d, $J = 16.0$ Hz, 1H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.82 (d, $J = 8.1$ Hz, 2H), 9.96 (s, 1H). ^{13}C RMN: $\delta = 17.7$, 22.9, 25.7, 28.4, 42.4, 73.6, 124.1, 126.2, 126.8, 130.1, 132.4, 138.6, 140.5, 143.3, 191.7. $C_{17}H_{22}O_2$ (258.2): calcd C 79.03, H 8.58; found C 79.21, H 8.56. MS (EI, 70 eV); m/z (%): 258 (3) [M^+].

*(E)-3,7-Dimethyl-1-(4-trifluoromethylphenyl) octa-1,6-dien-3-ol (**34**)*

From linalol (3.55 ml, 20 mmol), 4-trifluoromethylbromobenzene (1.39 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **34** was obtained in 93% (2.77 g) yield. ^{1}H RMN: $\delta = 1.24$ (s, 1H),1.38 (s, 3H), 1.58 (s, 3H), 1.67 (s, 3H), 1.63–1.77 (m, 2H), 2.00–2.20 (m, 2H), 5.13 (t, $J = 7.0$ Hz, 1H), 6.36 (d, $J = 16.0$ Hz, 1H), 6.63 (d, $J = 16.0$ Hz, 1H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.55 (d, $J = 8.2$ Hz, 2H). ^{13}C RMN: $\delta = 17.6$, 22.9, 25.6, 28.2, 42.4, 73.4, 124.1, 124.2 (q, $J = 272.0$ Hz), 125.4 (q, $^3J = 4.0$ Hz), 125.9, 126.4, 129.0 (q, $^2J = 32.7$ Hz), 132.1, 139.4, 145.0. $C_{17}H_{21}F_3O$ (298.2): calcd C 68.44, H 7.09; found C 68.62, H 6.98. MS (EI, 70 eV); m/z (%): 280 (10) [$M^+ - 18$].

*(E)-1-(4-Fluorophenyl)-3,7-dimethylocta-1,6-dien-3-ol (**35**)*

From linalol (3.55 ml, 20 mmol), 4-fluorobromobenzene (1.10 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **35** was obtained in 81% (2.01 g) yield. ^{1}H RMN: $\delta = 1.36$ (s, 3H), 1.58 (s, 3H), 1.67 (s, 3H), 1.52–1.70 (m, 2H), 1.72 (s, 1H), 1.95–2.15 (m, 2H, CH_2), 5.15 (t, $J = 6.8$ Hz, 1H, C*H*=), 6.17 (d, $J = 16.1$ Hz, 1H, C*H*=), 6.55 (d, $J = 16.1$ Hz, 1H), 6.98 (t, $J = 8.7$ Hz, 2H), 7.33 (dd, $J = 8.5$, 5.5 Hz, 2H). ^{13}C RMN: $\delta = 17.7$, 22.9, 25.7, 28.4, 42.5, 73.4, 115.4 (d, $^2J_{C-F} = 21.2$ Hz), 124.3, 126.0, 127.9 (d, $^3J_{C-F} = 8.0$ Hz), 132.2, 133.2, 136.4, 162.3 (d, $J_{C-F} = 246.1$ Hz). $C_{16}H_{21}FO$ (248.2): calcd C 77.38, H 8.52; found C 77.58, H 8.64. MS (EI, 70 eV); m/z (%): 230 (29) [$M^+ - 18$].

*(E)-1-(4-tert-Butylphenyl)-3,7-dimethylocta-1,6-dien-3-ol (**36**)*

From linalol (3.55 ml, 20 mmol), 4-*tert*-butylbromobenzene (1.75 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **36** was obtained in 90% (2.57 g) yield. ^{1}H RMN: $\delta = 1.34$ (s, 9H), 1.39 (s, 3H), 1.63 (s, 3H), 1.71 (s, 3H), 1.67–1.75 (m, 2H), 1.91 (s, 1H), 2.00–2.20 (m, 2H), 5.16 (t, $J = 6.8$ Hz, 1H), 6.27 (d, $J = 16.0$ Hz, 1H), 6.60 (d, $J = 16.0$ Hz,

DOI: 10.1002/aoc

1H), 7.35 (s, 4H). ^{13}C RMN: $\delta = 17.7$, 22.9, 25.6, 28.3, 31.2, 34.4, 42.5, 73.3, 124.3, 125.4, 126.0, 126.7, 131.8, 134.2, 135.9, 150.3. $C_{20}H_{30}O$ (286.2): calcd C 83.86, H 10.56; found C 83.69, H 10.72. MS (EI, 70 eV); m/z (%): 268 (18) [$M^+ - 18$].

*(E)-1-(6-Methoxynaphthalen-2-yl)-3,7-dimethylocta-1,6-dien-3-ol (**37**)*

From linalol (3.55 ml, 20 mmol), 6-methoxy-2-bromonaphthalene (2.37 g, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **37** was obtained in 86% (2.67 g) yield. ^{1}H RMN: $\delta = 1.45$ (s, 3H), 1.65 (s, 3H), 1.73 (s, 3H), 1.60–1.90 (m, 2H), 2.08 (bs, 1H), 2.05–2.30 (m, 2H), 3.90 (s, 3H), 5.20 (t, $J = 7.1$ Hz, 1H), 6.37 (d, $J = 16.1$ Hz, 1H), 6.76 (d, $J = 16.1$ Hz, 1H), 7.05–7.26 (m, 2H), 7.50–7.80 (m, 4H). ^{13}C RMN: $\delta = 17.6$, 22.9, 25.6, 28.2, 42.6, 55.1, 73.3, 105.8, 118.8, 124.1, 124.4, 125.9, 126.9, 127.1, 129.0, 129.3, 131.8, 132.4, 133.9, 136.0, 157.5. $C_{21}H_{26}O_2$ (310.2): calcd C 81.25, H 8.44; found C 81.41, H 8.60. MS (EI, 70 eV); m/z (%): 310 (1) [M^+].

*(E)-1-(4-Methoxyphenyl)-3,7-dimethylocta-1,6-dien-3-ol (**38**)*

From linalol (3.55 ml, 20 mmol), 4-bromoanisole (1.25 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **38** was obtained in 84% (2.18 g) yield. ^{1}H RMN: $\delta = 1.27$ (s, 3H), 1.59 (s, 3H), 1.68 (s, 3H), 1.58–1.70 (m, 2H), 1.91 (s, 1H), 2.00–2.15 (m, 2H), 3.79 (s, 3H), 5.14 (t, $J = 7.2$ Hz, 1H), 6.14 (d, $J = 16.4$ Hz, 1H), 6.55 (d, $J = 16.4$ Hz, 1H), 6.85 (d, $J = 8.7$ Hz, 2H), 7.31 (d, $J = 8.7$ Hz, 2H).

*(E)-3,7-Dimethyl-1-(2-trifluoromethylphenyl) octa-1,6-dien-3-ol (**39**)*

From linalol (3.55 ml, 20 mmol), 2-trifluoromethylbromobenzene (1.36 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **39** was obtained in 91% (2.71 g) yield. ^{1}H RMN: $\delta = 1.27$ (s, 1H), 1.39 (s, 3H), 1.59 (s, 3H), 1.68 (s, 3H), 1.62–1.75 (m, 2H), 2.00–2.20 (m, 2H), 5.13 (t, $J = 7.0$ Hz, 1H), 6.21 (d, $J = 15.9$ Hz, 1H), 6.96 (dq, $J = 15.9$, 2.3 Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.58 (d, $J = 8.1$ Hz, 1H), 7.62 (d, $J = 8.1$ Hz, 1H). ^{13}C RMN: $\delta = 17.6$, 22.8, 25.7, 28.2, 42.4, 73.5, 111.7, 123.6 (q, $^4J_{C-F} = 1.8$ Hz), 124.2, 124.3 (q, $J_{C-F} = 273.6$ Hz), 125.7 (q, $^3J_{C-F} = 5.7$ Hz), 127.0, 127.4 (q, $^2J_{C-F} = 29.8$ Hz), 127.5, 131.7, 132.2. $C_{17}H_{21}F_3O$ (298.2): calcd C 68.44, H 7.09; found C 68.67, H 7.23. MS (EI, 70 eV); m/z (%): 298 (1) [M^+].

*(E)-1-(2-Fluorophenyl)-3,7-dimethylocta-1,6-dien-3-ol (**40**)*

From linalol (3.55 ml, 20 mmol), 2-fluorobromobenzene (1.09 ml, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **40** was obtained in 90% (2.23 g) yield. ^{1}H RMN: $\delta = 1.38$ (s, 3H), 1.60 (s, 3H), 1.68 (s, 3H), 1.64–1.72 (m, 2H), 2.01 (bs, 1H), 1.98–2.17 (m, 2H), 5.15 (tt, $J = 7.2$, 1.3 Hz, 1H), 6.37 (d, $J = 16.3$ Hz, 1H), 6.75 (d, $J = 16.3$ Hz, 1H), 6.97–7.10 (m, 2H), 7.12–7.22 (m, 1H), 7.43 (td, $J = 7.7$, 1.7 Hz, 1H). ^{13}C RMN: $\delta = 17.6$, 22.9, 25.6, 28.2, 42.4, 73.5, 115.6 (d, $^2J_{C-F} = 22.5$ Hz), 119.6 (d, $^3J_{C-F} = 3.8$ Hz), 123.9 (d, $^3J_{C-F} = 3.8$ Hz), 124.2, 124.8 (d, $^2J_{C-F} = 12.1$ Hz), 127.4 (d, $^3J_{C-F} = 3.8$ Hz), 128.4 (d, $^4J_{C-F} = 8.2$ Hz), 132.0, 139.3 (d, $^4J_{C-F} = 5$ Hz), 160.2 (d, $J_{C-F} = 249.2$ Hz). $C_{16}H_{21}FO$ (248.2): calcd C 77.38, H 8.52; found C 77.21, H 8.63. MS (EI, 70 eV); m/z (%): 248 (1) [M^+].

*(E)-3,7-Dimethyl-1-(o-tolyl)octa-1,6-dien-3-ol (**41**)*

From linalol (3.55 ml, 20 mmol), 2-methylbromobenzene (1.20 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **41** was obtained in 87% (2.12 g) yield. ^{1}H RMN: $\delta = 1.40$ (s, 3H), 1.62 (s, 3H), 1.70 (s, 3H), 1.59–1.74 (m, 2H), 1.86 (s, 1H), 2.00–2.20 (m, 2H), 2.37 (s, 3H), 5.16 (t, $J = 8.1$ Hz, 1H), 6.15 (d, $J = 15.9$ Hz, 1H), 6.82 (d, $J = 15.9$ Hz, 1H), 7.15 (m, 3H), 7.44 (m, 1H). ^{13}C RMN: $\delta = 17.7$, 19.8, 23.0, 25.7, 28.5, 42.5, 73.6, 124.3, 125.0, 125.6, 126.0, 127.2, 130.2, 132.0, 135.4, 136.3, 138.2. $C_{17}H_{24}O$ (244.2): calcd C 83.55, H 9.90; found C 83.61, H 9.77. MS (EI, 70 eV); m/z (%): 226 (25) [$M^+ - 18$].

*(E)-3,7-Dimethyl-1-(naphthalen-1-yl)octa-1,6-dien-3-ol (**42**)*

From linalol (3.55 ml, 20 mmol), 1-bromonaphthalene (1.39 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **42** was obtained in 93% (2.60 g) yield. ^{1}H RMN: $\delta = 1.49$ (s, 3H), 1.65 (s, 3H), 1.73 (s, 3H), 1.60–1.90 (m, 2H), 2.04 (bs, 1H), 2.10–2.35 (m, 2H), 5.18 (tt, $J = 7.1$, 1.3 Hz, 1H), 6.32 (d, $J = 15.6$ Hz, 1H), 7.33–7.64 (m, 5H), 7.74–7.92 (m, 2H), 8.13–8.24 (m, 1H). ^{13}C RMN: $\delta = 17.7$, 23.0, 25.7, 28.5, 42.6, 73.7, 123.6, 123.9, 124.3, 124.4, 125.5, 125.7, 125.8, 127.6, 128.4, 131.2, 132.0, 133.6, 135.0, 140.0. $C_{20}H_{24}O$ (280.2): calcd C 85.67, H 8.63; found C 85.49, H 8.64. MS (EI, 70 eV); m/z (%): 280 (8) [M^+].

*(E)-1-(2,6-Difluorophenyl)-3,7-dimethylocta-1,6-dien-3-ol (**43**)*

From linalol (3.55 ml, 20 mmol), 2,6-difluorobromobenzene (1.93 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **43** was obtained in 98% (2.61 g) yield. ^{1}H RMN: $\delta = 1.37$ (s, 3H), 1.59 (s, 3H), 1.67 (s, 3H), 1.64–1.72 (m, 2H), 1.76 (bs, 1H), 2.00–2.17 (m, 2H), 5.14 (tt, $J = 7.2$, 1.3 Hz, 1H), 6.57 (d, $J = 16.4$ Hz, 1H), 6.64 (d, $J = 16.4$ Hz, 1H), 6.84 (t, $J = 8.3$ Hz, 2H), 7.11 (tt, $J = 8.3$, 6.3 Hz, 1H). ^{13}C RMN: $\delta = 17.6$, 22.9, 25.6, 28.3, 42.3, 73.8, 111.4 (dd, $^2J_{C-F} = 17.8$, 8.0 Hz), 113.5 (t, $^4J_{C-F} = 2.0$ Hz), 114.4 (t, $^2J_{C-F} = 15.5$ Hz), 124.2, 127.6 (t, $^3J_{C-F} = 10.6$ Hz), 132.1, 143.7 (t, $^3J_{C-F} = 7.2$ Hz), 160.8 (dd, $J_{C-F} = 250.7$, 8.1 Hz). $C_{16}H_{20}F_2O$ (266.1): calcd C 72.16, H 7.57; found C 72.44, H 7.42. MS (EI, 70 eV); m/z (%): 266 (1) [M^+].

*(E)-3,7-Dimethyl-1-(2,4,6-trimethylphenyl)octa-1,6-dien-3-ol (**44**)*

From linalol (3.55 ml, 20 mmol), 2-bromomesitylene (1.53 ml, 10 mmol), Pd complex (0.1 mmol) and K_2CO_3 (2.76 g, 20 mmol), **44** was obtained in 89% (2.42 g) yield. ^{1}H RMN: $\delta = 1.42$ (s, 3H), 1.64 (s, 3H), 1.72 (s, 3H), 1.59–1.74 (m, 3H), 2.05–2.28 (m, 2H), 2.29 (s, 9H), 5.18 (t, $J = 7.1$ Hz, 1H), 5.75

DOI: 10.1002/aoc

(d, $J = 16.4$ Hz, 1H), 6.54 (d, $J = 16.4$ Hz, 1H), 6.89 (s, 2H). ^{13}C RMN: $\delta = 17.6, 20.7, 20.8, 23.0, 25.7, 28.5, 42.5, 73.5, 124.3, 124.6, 128.4, 131.9, 134.0, 135.7, 135.9, 141.4$. $C_{19}H_{28}O$ (272.2): calcd C 83.77, H 10.36; found C 83.98, H 10.25. MS (EI, 70 eV); m/z (%): 272 (3) [M^+].

*(E)-1-Anthracen-9-yl-3,7-dimethylocta-1,6-dien-3-ol (**45**)*

From linalol (3.55 ml, 20 mmol), 9-bromoanthracene (2.57 g, 10 mmol), Pd complex (4×10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **45** was obtained in 87% (2.87 g) yield. ^{1}H RMN: $\delta = 1.44$ (s, 3H), 1.54 (s, 3H), 1.58 (s, 3H), 1.50–1.75 (m, 2H), 1.85 (bs, 1H), 2.05–2.25 (m, 2H), 5.09 (tt, $J = 7.0$, 1.3 Hz, 1H), 5.97 (d, $J = 16.0$ Hz, 1H), 7.14 (d, $J = 16.0$ Hz, 1H), 7.25–7.39 (m, 4H), 7.78–7.91 (m, 2H), 8.08–8.24 (m, 2H), 8.22 (s, 1H). ^{13}C RMN: $\delta = 17.7, 23.2, 25.7, 28.7, 42.6, 73.9, 123.0, 124.2, 125.0, 125.2, 125.9, 126.0, 128.6, 129.5, 131.4, 132.2, 132.8, 145.1$. $C_{24}H_{26}O$ (330.2): calcd C 87.23, H 7.93; found C 87.33, H 7.82. MS (EI, 70 eV); m/z (%): 330 (70) [M^+].

*(E)-3,7-Dimethyl-1-(2,4,6-triisopropylphenyl) octa-1,6-dien-3-ol (**46**)*

From linalol (3.55 ml, 20 mmol), 2,4,6-triisopropylbromobenzene (2.53 ml, 10 mmol), Pd complex (0.1 mmol) and K_2CO_3 (2.76 g, 20 mmol), **46** was obtained in 81% (2.88 g) yield. ^{1}H RMN: $\delta = 1.20$ (d, $J = 6.8$ Hz, 12H), 1.27 (d, $J = 6.8$ Hz, 6H), 1.40 (s, 3H), 1.63 (s, 3H), 1.71 (s, 3H), 1.60–1.75 (m, 3H), 2.02–2.24 (m, 2H), 2.89 (sept., $J = 6.8$ Hz, 1H), 3.22 (sept., $J = 6.8$ Hz, 2H), 5.16 (tt, $J = 7.1$, 1.3 Hz, 1H), 5.66 (d, $J = 16.4$ Hz, 1H), 6.64 (d, $J = 16.4$ Hz, 1H), 7.00 (s, 2H). ^{13}C RMN: $\delta = 17.6, 23.0, 23.8, 24.1, 25.7, 28.6, 30.0, 34.2, 42.6, 73.6, 120.4, 124.3, 124.4, 132.0, 132.9, 141.3, 146.3, 147.3$. $C_{25}H_{40}O$ (356.3): calcd C 84.21, H 11.31; found C 84.42, H 11.37. MS (EI, 70 eV); m/z (%): 356 (1) [M^+].

*(E)-3,7-Dimethyl-1-(3-pyridinyl)octa-1,6-dien-3-ol (**47**)*

From linalol (3.55 ml, 20 mmol), 3-bromopyridine (0.96 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **47** was obtained in 86% (1.99 g) yield. ^{1}H RMN: $\delta = 1.37$ (s, 3H), 1.56 (s, 3H), 1.65 (s, 3H), 1.61–1.71 (m, 2H), 2.06 (m, 2H), 2.33 (s, 1H), 5.11 (t, $J = 7.0$ Hz, 1H), 6.32 (d, $J = 16.0$ Hz, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 7.20 (dd, $J = 7.5$, 4.7 Hz, 1H), 7.65 (dt, $J = 8.0$, 1.7 Hz, 1H), 8.42 (dd, $J = 4.7$, 1.7 Hz, 1H), 8.57 (d, $J = 2.1$ Hz, 1H). ^{13}C RMN: $\delta = 17.7, 22.9, 25.7, 28.3, 42.4, 73.3, 123.4, 123.6, 124.2, 132.2, 132.8, 132.9, 139.2, 148.2$. $C_{15}H_{21}NO$ (231.2): calcd C 77.88, H 9.15; found C 77.77, H 9.04. MS (EI, 70 eV); m/z (%): 231 (4) [M^+].

*(E)-3,7-Dimethyl-1-(3-quinolinyl)octa-1,6-dien-3-ol (**48**)*

From linalol (3.55 ml, 20 mmol), 3-bromoquinoline (1.36 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **48** was obtained in 90% (2.53 g) yield. ^{1}H RMN: $\delta = 1.37$ (s, 3H), 1.52 (s, 3H), 1.60 (s, 3H), 1.56–1.71 (m, 2H), 2.07 (m, 2H), 3.49 (s, 1H), 5.07 (t, $J = 7.0$ Hz, 1H), 6.46 (d, $J = 16.2$ Hz, 1H), 6.72 (d, $J = 16.2$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 1.5$ Hz, 1H), 8.03 (d, $J = 8.5$ Hz, 1H), 8.90 (d, $J = 2.1$ Hz, 1H). ^{13}C RMN: $\delta = 17.5, 22.8, 25.5, 28.0, 42.4, 73.0, 123.6, 124.2, 126.7, 127.5, 127.9, 128.7, 128.8, 130.0, 131.6, 132.1, 139.5, 146.8, 149.0$. $C_{19}H_{23}NO$ (281.2): calcd C 81.10, H 10.24; found C 81.38, H 10.37. MS (EI, 70 eV); m/z (%): 281 (4) [M^+].

*(E)-1-Isoquinolin-4-yl-3,7-dimethylocta-1,6-dien-3-ol (**49**)*

From linalol (3.55 ml, 20 mmol), 4-bromoisoquinoline (2.08 g, 10 mmol), Pd complex (4×10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **49** was obtained in 93% (2.61 g) yield. ^{1}H RMN: $\delta = 1.46$ (s, 3H), 1.61 (s, 3H), 1.69 (s, 3H), 1.58–1.90 (m, 2H), 2.03 (s, 1H), 2.06–2.55 (m, 2H), 5.17 (tt, $J = 7.1$, 1.3 Hz, 1H), 6.36 (d, $J = 15.9$ Hz, 1H), 7.22 (d, $J = 15.9$ Hz, 1H), 7.52 (td, $J = 8.1$, 1.3 Hz, 1H), 7.55 (td, $J = 8.1$, 1.3 Hz, 1H), 8.00 (d, $J = 8.1$ Hz, 1H), 8.10 (d, $J = 8.6$ Hz, 1H), 8.57 (bs, 1H), 9.14 (bs, 1H). ^{13}C RMN: $\delta = 17.4, 22.7, 25.4, 28.1, 42.5, 72.8, 120.5, 122.8, 124.2, 126.8, 127.6, 127.7, 128.8, 130.0, 131.3, 133.5, 139.4, 142.2, 150.7$. $C_{19}H_{23}NO$ (281.2): calcd C 81.10, H 10.24; found C 81.18, H 10.06. MS (EI, 70 eV); m/z (%): 281 (80) [M^+].

*(E)-3,7-Dimethyl-1-(2-thienyl)octa-1,6-dien-3-ol (**50**)*

From linalol (3.55 ml, 20 mmol), 2-bromothiophene (0.97 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **50** was obtained in 82% (1.94 g) yield. ^{1}H RMN: $\delta = 1.35$ (s, 3H), 1.55 (s, 3H), 1.67 (s, 3H), 1.55–1.70 (m, 2H), 1.72 (s, 1H), 2.05 (m, 2H), 5.12 (t, $J = 7.0$ Hz, 1H), 6.11 (d, $J = 15.9$ Hz, 1H), 6.72 (d, $J = 15.9$ Hz, 1H), 6.90–6.98 (m, 2H), 7.12 (d, $J = 5.1$ Hz, 1H). ^{13}C RMN: $\delta = 17.7, 22.9, 25.7, 28.3, 42.4, 73.3, 120.6, 123.8, 124.2, 125.4, 127.3, 132.2, 136.3, 142.3$. $C_{14}H_{20}OS$ (236.1): calcd C 71.14, H 8.53; found C 71.38, H 8.66. MS (EI, 70 eV); m/z (%): 236 (4) [M^+].

*(E)-3,7-Dimethyl-1-(3-thienyl)octa-1,6-dien-3-ol (**51**)*

From linalol (3.55 ml, 20 mmol), 3-bromothiophene (0.94 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **51** was obtained in 83% (1.96 g) yield. ^{1}H RMN: $\delta = 1.36$ (s, 3H), 1.60 (s, 3H), 1.68 (s, 3H), 1.61–1.71 (m, 2H), 1.89 (s, 1H), 2.07 (m, 2H), 5.13 (t, $J = 7.0$ Hz, 1H), 6.13 (d, $J = 16.1$ Hz, 1H), 6.60 (d, $J = 16.1$ Hz, 1H), 7.12 (d, $J = 2.8$ Hz, 1H), 7.19 (dd, $J = 5.1$, 1.1 Hz, 1H), 8.42 (t, $J = 4.2$ Hz, 1H). ^{13}C RMN: $\delta = 17.7, 22.9, 25.6, 28.2, 42.5, 73.2, 121.4, 121.6, 124.3, 124.9, 125.9, 131.9, 136.5, 139.6$. $C_{14}H_{20}OS$ (236.1): calcd C 71.14, H 8.53; found C 71.26, H 8.39. MS (EI, 70 eV); m/z (%): 236 (12) [M^+].

*(E,E)-5,9-Dimethyl-1-phenyldeca-1,3,8-trien-5-ol (**52**)*

From linalol (3.55 ml, 20 mmol), β-bromostyrene (1.28 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **52** was obtained in 83% (2.12 g) yield. ^{1}H RMN: $\delta = 1.27$ (s, 3H), 1.33 (bs, 1H), 1.60 (s, 3H), 1.67 (s, 3H), 1.55–1.70 (m, 2H), 1.91–2.12 (m, 2H), 5.12 (t, $J = 7.0$ Hz, 1H), 5.89 (d, $J = 16.3$ Hz, 1H), 6.40 (dd, $J = 16.3$, 10.4 Hz, 1H) 6.54 (d, $J = 15.7$ Hz, 1H), 6.67 (dd, $J = 15.7$, 10.4 Hz, 1H),

DOI: 10.1002/aoc

7.20–7.50 (m, 5H). ^{13}C RMN: $\delta = 15.2, 17.6, 25.6, 27.8, 42.0, 73.2, 124.3, 126.2, 127.3, 127.8, 128.5, 128.6, 131.9, 137.3, 140.9, 145.0$. $C_{18}H_{24}O$ (256.2): calcd C 84.32, H 9.44; found C 84.46, H 9.24. MS (EI, 70 eV); m/z (%): 258 (3) [M^+].

*(E)-4-(4-Benzoylphenyl)-2-methylbut-3-en-2-ol (**53**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 4-bromobenzophenone (2.61 g, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **53** was obtained in 93% (2.47 g) yield. ^{1}H RMN: $\delta = 1.40$ (s, 6H), 2.67 (s, 1H), 6.46 (d, $J = 16.2$ Hz, 1H), 6.62 (d, $J = 16.2$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 2H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 7.0$ Hz, 2H), 7.75 (d, $J = 7.0$ Hz, 2H). ^{13}C RMN: $\delta = 29.6, 70.7, 125.2, 126.0, 128.1, 129.7, 130.4, 132.1, 135.8, 137.5, 140.5, 141.2, 196.0$. $C_{18}H_{18}O_2$ (266.1): calcd C 81.17, H 6.81; found C 81.45, H 7.03. MS (EI, 70 eV); m/z (%): 266 (6) [M^+].

*(E)-4-(3-Hydroxy-3-methylbut-1-enyl)benzaldehyde (**54**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 4-bromobenzaldehyde (1.85 g, 10 mmol), Pd complex (10^{-3} mmol) and K_2CO_3 (2.76 g, 20 mmol), **53** was obtained in 87% (1.65 g) yield. ^{1}H RMN: $\delta = 1.43$ (s, 6H), 1.80 (s, 1H), 6.49 (d, $J = 16.1$ Hz, 1H), 6.65 (d, $J = 16.1$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 8.4$ Hz, 2H), 9.95 (s, 1H). ^{13}C RMN: $\delta = 29.6, 70.8, 125.2, 126.7, 123.0, 135.0, 141.3, 143.2, 191.7$. $C_{12}H_{14}O_2$ (190.1): calcd C 75.76, H 7.42; found C 75.61, H 7.45. MS (EI, 70 eV); m/z (%): 190 (8) [M^+].

*(E)-2-Methyl-4-(4-trifluoromethylphenyl)-but-3-en -2-ol (**55**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 4-trifluoromethylbromobenzene (1.39 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **54** was obtained in 90% (2.07 g) yield. ^{1}H RMN: $\delta = 1.40$ (s, 6H), 2.02 (s, 1H), 6.42 (d, $J = 16.1$ Hz, 1H), 6.62 (d, $J = 16.1$ Hz, 1H), 7.43 (d, $J = 8.2$ Hz, 2H), 7.53 (d, $J = 8.2$ Hz, 2H).

*(E)-4-(4-Fluorophenyl)-2-methyl-but-3-en-2-ol (**56**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 4-fluorobromobenzene (1.10 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **55** was obtained in 78% (1.40 g) yield. ^{1}H RMN: $\delta = 1.41$ (s, 6H), 1.87 (s, 1H), 6.25 (d, $J = 16.0$ Hz, 1H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.98 (t, $J = 8.5$ Hz, 2H), 7.31 (dd, $J = 7.4$, 5.3 Hz, 2H). ^{13}C RMN: $\delta = 29.8, 70.9, 115.3$ (d, $^2J_{C-F} = 21.4$ Hz), 125.1, 127.7, 133.0 (d, $^3J_{C-F} = 8.2$ Hz), 137.2, 161.7 (d, $J_{C-F} = 246.5$ Hz). $C_{11}H_{13}FO$ (180.1): calcd C 73.31, H 7.27; found C 73.56, H 7.22. MS (EI, 70 eV); m/z (%): 180 (13) [M^+].

*(E)-4-(4-tert-Butylphenyl)-2-methyl-but-3-en-2-ol (**57**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 4-*tert*-butylbromobenzene (1.75 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **56** was obtained in 77% (1.68 g) yield. ^{1}H RMN: $\delta = 1.28$ (s, 9H), 1.43 (s, 6H), 2.15 (s, 1H), 6.31 (d, $J = 16.1$ Hz, 1H), 6.57 (d, $J = 16.1$ Hz, 1H), 7.33 (s, 4H). ^{13}C RMN: $\delta = 29.8, 31.2, 34.5, 71.0, 125.4, 126.1, 126.0, 134.1, 136.8, 150.4$. $C_{15}H_{22}O$ (218.2): calcd C 82.52, H 10.16; found C 82.64, H 10.04. MS (EI, 70 eV); m/z (%): 218 (9) [M^+].

*(E)-4-(4-Methoxyphenyl)-2-methyl-but-3-en-2-ol (**58**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 4-bromoanisole (1.25 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **57** was obtained in 90% (1.73 g) yield. ^{1}H RMN: $\delta = 1.37$ (s, 6H), 1.78 (s, 1H), 3.77 (s, 3H), 6.20 (d, $J = 16.2$ Hz, 1H), 6.50 (d, $J = 16.2$ Hz, 1H), 6.83 (d, $J = 8.7$ Hz, 2H), 7.29 (d, $J = 8.7$ Hz, 2H).

*(E)-2-Methyl-4-(2-trifluoromethylphenyl)but-3-en-2-ol (**59**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 2-trifluoromethylbromobenzene (1.36 ml, 10 mmol), Pd complex (2×10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **58** was obtained in 96% (2.21 g) yield. ^{1}H RMN: $\delta = 1.43$ (s, 6H), 1.75 (m, 1H), 6.30 (d, $J = 15.9$ Hz, 1H), 6.96 (d, $J = 15.9$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.4$ Hz, 1H), 7.59 (m, 2H). ^{13}C RMN: $\delta = 29.6, 71.1, 122.7, 124.3$ (q, $J_{C,F} = 273.5$ Hz), 125.7 (d, $^3J_{C,F} = 5.5$ Hz), 127.0, 127.3 (q, $^2J_{C,F} = 32.2$ Hz), 127.4, 131.8, 136.3, 141.9. $C_{12}H_{13}F_3O$ (230.1): calcd C 62.60, H 5.69; found C 62.86, H 5.59. MS (EI, 70 eV); m/z (%): 230 (4) [M^+].

*(E)-4-(2-Fluorophenyl)-2-methyl-but-3-en-2-ol (**60**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 2-fluorobromobenzene (1.09 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **59** was obtained in 84% (1.51 g) yield. ^{1}H RMN: $\delta = 1.42$ (s, 6H), 1.78 (s, 1H), 6.43 (d, $J = 16.3$ Hz, 1H), 6.74 (d, $J = 16.3$ Hz, 1H), 6.96–7.11 (m, 2H), 7.13–7.22 (m, 1H), 7.44 (td, $J = 7.5$, 1.7 Hz, 1H). ^{13}C RMN: $\delta = 29.8, 71.1, 115.6$ (d, $^2J_{C-F} = 22.0$ Hz), 118.9 (d, $^4J_{C-F} = 3.3$ Hz), 123.9 (d, $^4J_{C-F} = 3.4$ Hz), 124.7 (d, $^2J_{C-F} = 12.7$ Hz), 127.3 (d, $^3J_{C-F} = 3.9$ Hz), 128.6 (d, $^3J_{C-F} = 8.3$ Hz), 140.0 (d, $^3J_{C-F} = 4.4$ Hz), 159.8 (d, $^1J_{C-F} = 248.7$ Hz). $C_{11}H_{13}FO$ (180.1): calcd C 73.31, H 7.27; found C 73.18, H 7.33. MS (EI, 70 eV); m/z (%): 180 (47) [M^+].

*(E)-2-Methyl-4-(O-tolyl)but-3-en-2-ol (**61**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 2-methylbromobenzene (1.20 ml, 10 mmol), Pd complex (10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **60** was obtained in 78% (1.37 g) yield. ^{1}H RMN: $\delta = 1.44$ (s, 6H), 1.83 (s, 1H), 2.36 (s, 3H), 6.23 (d, $J = 16.1$ Hz, 1H), 6.81 (d, $J = 16.1$ Hz, 1H), 7.15 (m, 3H), 7.43 (m, 1H).

*(E)-2-Methyl-4-(3-pyridinyl)but-3-en-2-ol (**62**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 3-bromopyridine (0.96 ml, 10 mmol), Pd complex (4×10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **61** was obtained in 91% (1.48 g) yield. ^{1}H RMN: $\delta = 1.30$ (s, 6H), 4.03 (s, 1H), 6.34 (d, $J = 16.2$ Hz, 1H), 6.49 (d, $J = 16.2$ Hz, 1H), 7.12 (dd, $J = 8.0$, 4.8 Hz, 1H), 7.58 (dt, $J = 8.0$, 2.0 Hz, 1H), 8.29 (dd, $J = 4.8$, 1.6 Hz, 1H), 8.44 (d, $J = 2.0$ Hz, 1H). ^{13}C RMN: $\delta = 29.6, 70.2,$

DOI: 10.1002/aoc

122.2, 123.3, 132.8, 132.9, 140.6, 147.6, 147.7. $C_{10}H_{13}NO$ (163.1): calcd C 73.59, H 8.03; found C 73.64, H 8.26. MS (EI, 70 eV); m/z (%): 163 (10) [M^+].

*(E)-2-Methyl-4-(2-thienyl)but-3-en-2-ol (**63**)*

From 2-methylbut-3-en-2-ol (2.09 ml, 20 mmol), 2-bromothiophene (0.97 ml, 10 mmol), Pd complex (4×10^{-2} mmol) and K_2CO_3 (2.76 g, 20 mmol), **62** was obtained in 76% (1.28 g) yield. ^{1}H RMN: $\delta = 1.39$ (s, 6H), 1.69 (s, 1H), 6.20 (d, $J = 16.0$ Hz, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 7.11 (dd, $J = 2.9$, 1.2 Hz, 1H), 7.18 (dd, $J = 5.0$, 2.2 Hz, 1H), 7.25 (m, 1H). ^{13}C RMN: $\delta = 29.8$, 70.8, 120.7, 121.8, 125.0, 126.0, 137.5, 139.5. $C_9H_{12}OS$ (168.1): calcd C 64.24, H 7.19; found C 64.33, H 7.25. MS (EI, 70 eV); m/z (%): 168 (10) [M^+].

Registry numbers

CAS: **1,** 29898-25-7; **8**, 90831-80-4; **38**, 127757-22-6; **55**, 96307-82-3; **58**, 57918-91-9; Beilstein: **6**, 8052380; **61**, 8830777.

REFERENCES

1. Beletskaya I, Cheprakov A. *Chem. Rev.* 2000; **100**: 3009.
2. de Meijere A, Meyer F. *Angew. Chem., Int. Edn Engng* 1994; **33**: 2379.
3. Withcombe N, Hii KK, Gibson S. *Tetrahedron* 2001; **57**: 7449.
4. Littke A, Fu G. *Angew. Chem. Int. Edn* 2002; **41**: 4176.
5. Farina V. *Adv. Synth. Catal.* 2004; **346**: 1553.
6. Muzart J. *Tetrahedron* 2005; **61**: 4179.
7. von Werner K. *J. Organomet. Chem.* 1977; **136**: 385.
8. Jeffery T. *J. Chem. Soc., Chem. Commun.* 1984; 1287.
9. Schroeder DR, Stermitz FR. *Tetrahedron* 1985; **41**: 4309.
10. Benhaddou R, Czernecki S, Ville G. *J. Chem. Soc., Chem. Commun.* 1988; 247.
11. Tao W, Nesbitt S, Heck RF. *J. Org. Chem.* 1990; **55**: 63.
12. Jeffery T. *Tetrahedron Lett.* 1991; **32**: 2121.
13. King AO, Corley EG, Anderson RK, Larsen RD, Verhoeven TR, Reider PJ, Xiang YB, Belley M, Leblanc Y, Labelle M, Prasit P, Zamboni RJ. *J. Org. Chem.* 1993; **58**: 3731.
14. Thompson MD, Torabi H. *Synthesis* 1994; 965.
15. Kang SK, Jung KY, Park CH, Namkoong EY, Kim TH. *Tetrahedron Lett.* 1995; **36**: 6287.
16. Björnestedt R, Zhong G, Lerner RA, Barbas III CF. *J. Am. Chem. Soc.* 1996; **118**: 11720.
17. Tonks L, Anson MS, Hellgardt K, Mirza AR, Thompson DF, Williams JMJ. *Tetrahedron Lett.* 1997; **38**: 4319.
18. Sidler DR, Sager JW, Bergan JJ, Wells KM, Bhupathy M, Volante RP. *Tetrahedron: Asymmetry* 1997; **8**: 161.
19. Romesberg FE, Flanagan ME, Uno T, Schultz PG. *J. Am. Chem. Soc.* 1998; **120**: 5160.
20. Tietze LF, Görlitzer J, Schuffenhauer A, Hübner M. *Eur. J. Org. Chem.* 1999; 1075.
21. Leese MP, Williams JMJ. *Synlett* 1999; 1645.
22. Dyker G, Kadzimirsz D, Henkel G. *Tetrahedron Lett.* 2003; **44**: 7905.
23. Dyker G, Kadzimirsz D. *Eur. J. Org. Chem.* 2003; 3167.
24. Fumio Y, Toshifumi H, Masayuki W, Mitsuro S, Masanori S. *Heterocycles* 1986; **24**: 1223.
25. Kirby AJ, Walwyn DR. *Gazz. Chim. Ital.* 1987; **117**: 667.
26. Aslam M, Elango V, Davenport KG. *Synthesis* 1989; 869.
27. Zhao H, Cai MZ, Hu RH, Song CS. *Synth. Commun.* 2001; **31**: 3665.
28. Ohno H, Okumura M, Maeda SI, Iwasaki H, Wakayama R, Tanaka T. *J. Org. Chem.* 2003; **68**: 7722.
29. Palucki M, Yasuda N. *Tetrahedron Lett.* 2005; **46**: 987.
30. Bargar TM, Wilson T, Daniel JK. *J. Heterocycl. Chem.* 1985; **22**: 1583.
31. Goujon JY, Zammattio F, Kirschleger B. *Tetrahedron: Asymmetry* 2000; **11**: 2409.
32. Bouquillon S, Ganchegui B, Estrine B, Hénin F, Muzart J. *J. Organomet. Chem.* 2001; **634**: 153.
33. de Vries AHM, Mulders JMCA, Mommers JHM, Henderickx HJW, de Vries JG. *Org. Lett.* 2003; **5**: 3285.
34. Calo V, Nacci A, Monopoli A, Spinelli M. *Eur. J. Org. Chem.* 2003; 1382.
35. Yokoyama Y, Hikawa H, Mitsuhashi M, Uyama A, Hiroki Y, Murakami Y. *Eur. J. Org. Chem.* 2004; 1244.
36. Briot A, Baehr C, Brouillard R, Wagner A, Mioskowski C. *J. Org. Chem.* 2004; **69**: 1374.
37. Beller M, Zapf A. *Synlett* 1998; 792.
38. Laurenti D, Feuerstein M, Pèpe G, Doucet H, Santelli M. *J. Org. Chem.* 2001; **66**: 1633.
39. Feuerstein M, Laurenti D, Bougeant C, Doucet H, Santelli M. *Chem. Commun.* 2001; 325.
40. Feuerstein M, Berthiol F, Doucet H, Santelli M. *Org. Biomol. Chem.* 2003; 2235.
41. Feuerstein M, Doucet H, Santelli M. *J. Org. Chem.* 2001; **66**: 5923.
42. Feuerstein M, Doucet H, Santelli M. *Synlett* 2001; 1980.
43. Feuerstein M, Doucet H, Santelli M. *Tetrahedron Lett.* 2002; **43**: 2191.
44. Berthiol F, Feuerstein M, Doucet H, Santelli M. *Tetrahedron Lett.* 2002; **43**: 5625.
45. Berthiol F, Doucet H, Santelli M. *Tetrahedron Lett.* 2003; **44**: 1221.
46. Berthiol F, Doucet H, Santelli M. *Synlett* 2003; 841.
47. Kondolff I, Doucet H, Santelli M. *Tetrahedron Lett.* 2003; **44**: 8487.
48. Kondolff I, Doucet H, Santelli M. *Eur. J. Org. Chem.* 2006; 765.
49. Berthiol F, Doucet H, Santelli M. *Eur. J. Org. Chem.* 2005; 1367.
50. Berthiol F, Doucet H, Santelli M. *Synthesis* 2005; 3589.
51. Berthiol F, Doucet H, Santelli M. *Tetrahedron Lett.* 2004; **45**: 5633.

DOI: 10.1002/aoc