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Tetrahedron 62 (2006) 4372–4383
Tetrahedron

Synthesis of β-aryl ketones by tetraphosphine/palladium catalysed Heck reactions of 2- or 3-substituted allylic alcohols with aryl bromides

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Received 30 January 2006; revised 21 February 2006; accepted 21 February 2006

Available online 13 March 2006

Abstract—Through the use of $[PdCl(C_3H_5)]_2$/*cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane as a catalyst, a range of aryl bromides undergoes Heck reaction using 2- or 3-subtituted allylic alcohols. With these sterically congested alkenes, the selective formation of β-aryl ketones was observed when appropriate reaction conditions were used. The influence of the functional group on the aryl bromide and of the base on the selectivity is remarkable. With several substrates, much higher selectivities were obtained using $NaHCO_3$ instead of K_2CO_3 as base. Furthermore, this catalyst can be used at low loading with several substrates.

1. Introduction

Aryl ketones are important building blocks in organic synthesis. The palladium-catalysed Heck reaction using alkenol derivatives and aryl halides is a powerful method for the preparation of such compounds.[1,2] The reaction of alkenols with terminal double bonds such as alk-1-en-3-ol derivatives generally gave regioselectively the corresponding 1-arylalkan-3-one derivatives by migration of the double bond. The reaction using allyl alcohols with disubstituted double bonds has attracted less attention. The reaction with such substrates is slower than with alk-1-enols for steric reasons, and most of the results were described using aryl iodides.[3–8] Only a few results were obtained with aryl bromides.[9–11] Caló et al. described the efficiency of a Pd–benzothiazole–carbene complex for the Heck reaction of 2-methylprop-1-en-3-ol, but-2-en-1-ol[11a] or Baylis–Hillman adducts[11b] with aryl bromides. They performed the reactions using tetrabutylammonium bromide as solvent with 1–2% catalyst. The best result had been obtained by Littke and Fu.[12] They described the reaction of 4-chlorobenzonitrile with 2-methylprop-1-en-3-ol using 1.5% $Pd_2(dba)_3$ and 3% of P(*t*-Bu)$_3$ as catalyst. The Heck reaction of arenediazonium salts with substituted allylic alcohols using $Pd(dba)_2$ as catalyst has also been described recently.[13] If monophosphine or carbene ligands have been successfully used for the Heck reaction of allyl alcohols with disubstituted double bonds, to the best of our knowledge, the efficiency of polydentate phosphine ligands has not been demonstrated. Moreover, an effective and selective method using high substrate/catalyst ratios for the reaction of these allyl alcohols with aryl bromides is still subject to significant improvement.

In order to find more efficient palladium catalysts, we have prepared the tetrapodal phosphine ligand, tedicyp[14] (Fig. 1). We have reported several results obtained in allylic substitution,[14] Suzuki cross-coupling,[15] Sonogashira[16] and Heck reaction[17–20] using tedicyp as ligand. Here, in order to further establish the requirements for a successful Heck reaction, we wish to report on the coupling of aryl bromides with 2- or 3-substituted allyl alcohols such as 2-methylpent-1-en-3-ol or pent-3-en-2-ol using tedicyp as the ligand.

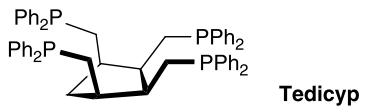

Figure 1.

2. Results and discussion

The regioselectivity of the insertion of Heck reaction is mainly controlled by steric factors, and with 1,1-disubstituted alkenes we should observed selectively the addition on the unsubstituted carbon of the alkene.[17g] On the other hand, with 1,2-disubstituted alkenes, the selectivity of the insertion

Keywords: Heck reaction; Baylis–Hillman adduct; Tedicyp; β-aryl.
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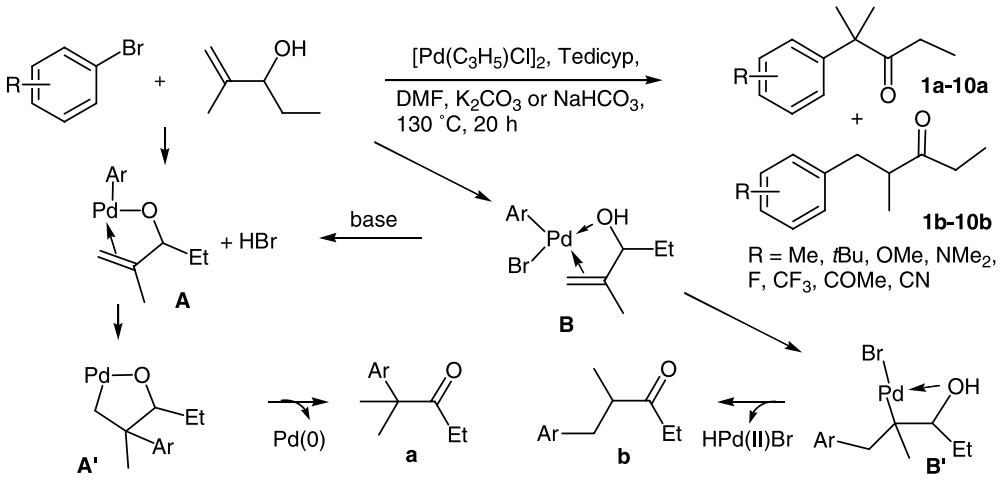
0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.02.061



Scheme 1.

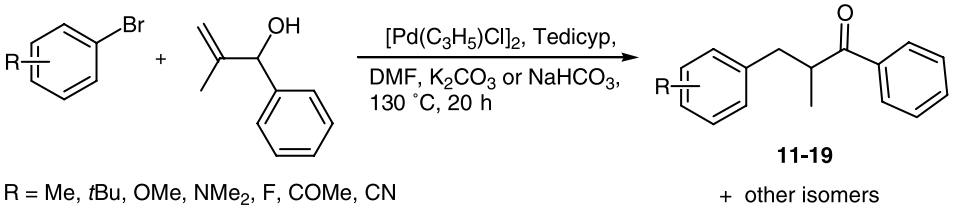
depends on the electronic and steric effects and also of the functions of the alkene substituents. The regioselectivity of the insertion can be partially controlled by the presence of functions capable of coordinating the palladium catalyst. Alcohol function of alkenols is capable of such coordination and imposes conformational changes in the structures of the (aryl)Pd(alkenol) intermediates. Therefore, the electronic or steric control of the regioselectivity of the addition appears to be modified by an adjacent alcohol function on the alkene. The reaction with alkenols is part of the Heck substrate-directed reactions. For these reasons, the regioselectivity of the reactions with the disubstituted alkenes: 2-methylpent-1-en-3-ol or pent-3-en-2-ol is quite unpredictable and should depend on the reaction conditions.

First, we studied the reactivity of 2-methylpent-1-en-3-ol (Scheme 1, Table 1). With this alkenol, for steric reasons, the formation of isomer **b** should be favoured. For this study, based on previous results,[17–20] DMF was chosen as the solvent for polarity reasons and potassium carbonate as the base. The reactions were generally performed at 130 °C under argon in the presence of a ratio 1:2 of $[Pd(C_3H_5)Cl]_2$/tedicyp as

Table 1. Palladium–tedicyp catalysed Heck reactions with 2-methylpent-1-en-3-ol (Scheme 1)

Entry	Aryl bromide	Ratio substrate/catalyst	Base	Product number	Ratio **a/b**	Yield (%)[a]
1	4-*t*-Butylbromobenzene	1000	K_2CO_3	**1a**,**b**	18/82	71 (100)
2	4-*t*-Butylbromobenzene	10,000	K_2CO_3	**1a**,**b**	12/88	(81)
3	4-*t*-Butylbromobenzene	100	$NaHCO_3$	**1a**,**b**	4/96	(61)
4	4-Bromoanisole	10,000	K_2CO_3	**2a**,**b**	5/95	92 (100)
5	4-Bromoanisole	25,000	K_2CO_3	**2a**,**b**	8/92	(63)
6	4-*N*,*N*-Dimethylaminobromobenzene	1000	K_2CO_3	**3a**,**b**	10/90	85 (100)
7	4-*N*,*N*-Dimethylaminobromobenzene	10,000	K_2CO_3	**3a**,**b**	8/92	(54)
8	4-Fluorobromobenzene	1000	K_2CO_3	**4a**,**b**	8/92	87 (100)
9	4-Fluorobromobenzene	10,000	K_2CO_3	**4a**,**b**	14/86	(69)
10	4-Trifluoromethylbromobenzene	1000	K_2CO_3	**5a**,**b**	24/76	65 (100)
11	4-Trifluoromethylbromobenzene	2500	K_2CO_3	**5a**,**b**	23/77	(76)
12	4-Trifluoromethylbromobenzene	100	$NaHCO_3$	**5a**,**b**	5/95	89 (100)
13	4-Trifluoromethylbromobenzene	1000	$NaHCO_3$	**5a**,**b**	2/98	(67)
14	4-Bromoacetophenone	1000	K_2CO_3	**6a**,**b**	19/81	76 (100)
15	4-Bromoacetophenone	10,000	K_2CO_3	**6a**,**b**	27/73	(51)
16	4-Bromoacetophenone	100	$NaHCO_3$	**6a**,**b**	8/92	88 (100)
17	4-Bromoacetophenone	1000	$NaHCO_3$	**6a**,**b**	5/95	(86)
18	4-Bromobenzonitrile	250	K_2CO_3	**7a**,**b**	47/53	(60)
19	4-Bromobenzonitrile	100	$NaHCO_3$	**7a**,**b**	9/91	90 (100)
20	4-Bromobenzonitrile	1000	$NaHCO_3$	**7b**	0/100	(39)
21	2-Bromotoluene	10,000	K_2CO_3	**8a**,**b**	16/84	78 (100)
22	2-Bromotoluene	25,000	K_2CO_3	**8b**	0/100	(10)
23	2-Bromotoluene	100	$NaHCO_3$	**8a**,**b**	4/96	93 (100)
24	2-Bromotoluene	1000	$NaHCO_3$	**8b**	0/100	(48)
25	3-Bromopyridine	250	K_2CO_3	**9a**,**b**	40/60	51 (100)
26	3-Bromopyridine	1000	K_2CO_3	**9a**,**b**	31/69	(19)
27	3-Bromopyridine	100	$NaHCO_3$	**9a**,**b**	9/91	80 (100)
28	3-Bromopyridine	1000	$NaHCO_3$	**9b**	0/100	(63)
29	3-Bromoquinoline	250	K_2CO_3	**10a**,**b**	31/69	66 (100)
30	3-Bromoquinoline	1000	K_2CO_3	**10a**,**b**	30/70	(50)
31	3-Bromoquinoline	100	$NaHCO_3$	**10a**,**b**	2/98	97 (100)
32	3-Bromoquinoline	1000	$NaHCO_3$	**10a**,**b**	1/99	(71)

[a] Conditions: catalyst: $[ClPd(C_3H_5)]_2$/tedicyp=1:2, aryl bromide (1 equiv), 2-methylpent-1-en-3-ol (1.2 equiv), K_2CO_3 or $NaHCO_3$ (2 equiv), DMF, 130 °C, 20 h, isolated yields of products **1b–10b**. Yields in parenthesis are GC and NMR conversions.



Scheme 2.

catalyst. The results presented in the Table 1, using these conditions, disclose a medium to high selectivity of the insertion of the allylic alcohol. With electron-rich aryl bromides such as 4-*t*-butylbromobenzene, 4-bromoanisole or 4-*N*,*N*-dimethylaminobromobenzene, selectivities of 88–95% in favour of the formation of isomer **1b–3b** were obtained (Table 1, entries 2–7). Moreover, these reactions were performed using as little as 0.1–0.004% catalyst. On the other hand, using electron-poor aryl bromides, lower selectivities were obtained. For example, with 4-trifluoromethylbromobenzene or 4-bromobenzonitrile, 24 and 47% of isomers **5a** and **7a** were obtained, respectively (Table 1, entries 10 and 18). The formation of this isomer **a** probably comes from the palladium intermediates **A** and **A′** in Scheme 1, which arise from the formation of the alcoholate of 2-methylpent-1-en-3-ol.[12]

The selectivity of this reaction seems to depend on the structures of the palladium intermediates. In order to improve the selectivity of the reaction with electron-poor aryl bromides, we performed the coupling using the weaker base: $NaHCO_3$. With this base, the formation of the alcoholate of 2-methylpent-1-en-3-ol is probably not favoured therefore **B** is obtained as the major intermediate. Then, the formation of intermediate **B′** is favoured for steric reasons, and isomers **1b–10b** were obtained in 91–100% selectivities. For example, the electron-poor aryl bromides 4-trifluoromethylbromobenzene or 4-bromoacetophenone gave isomers **5b** and **6b** in high selectivities (98 and 95%) and in high TONs (Table 1, entries 13 and 17). However, with $NaHCO_3$ as base, much slower reactions were observed with electron-rich aryl bromides and 1% catalyst had to be used (Table 1, entries 3 and 23). The influence of the base on the reaction rates might come from a slower coordination of the alkenols to palladium to form intermediate **B**, or to a slower reductive elimination of HBr on HPdBr intermediate at the end of the catalytic cycle.

Pyridines or quinolines are π-electron deficient. As expected, with 3-bromopyridine or 3-bromoquinoline using K_2CO_3 as base, low selectivities of 60–70% in favour of isomers **9b** and **10b** were obtained (Table 1, entries 25, 26, 29 and 30). Again, more selective reactions were obtained using $NaHCO_3$. Selectivities of 99 and 100% were obtained with this base (Table 1, entries 28 and 32).

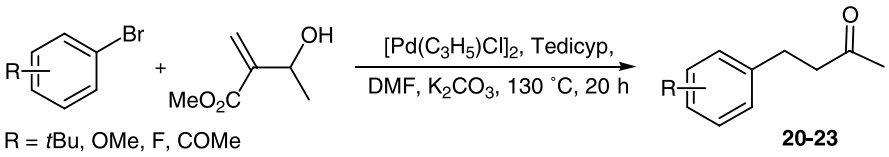
In summary, with 2-methylpent-1-en-3-ol, the best results in terms of selectivities and ratio substrate/catalyst were obtained using K_2CO_3 as base for electron-rich aryl bromide; $NaHCO_3$ should be preferred with electron-poor aryl bromides.

Heck reaction using 2-methyl-3-phenylprop-1-en-3-ol gave quite different results than the reaction with 2-methylpent-1-en-3-ol (Scheme 2, Table 2). With this allyl alcohol, low

Table 2. Palladium–tedicyp catalysed Heck reactions with 2-methyl-3-phenylprop-1-en-3-ol (Scheme 2)

Entry	Aryl bromide	Ratio substrate/catalyst	Base	Product number	Ratio ketone **11–19**/other isomers	Yield (%)[a]
1	4-*t*-Butylbromobenzene	1000	K_2CO_3	**11**	43/57	38 (100)
2	4-*t*-Butylbromobenzene	2500	K_2CO_3	**11**	43/57	(60)
3	4-*t*-Butylbromobenzene	100	$NaHCO_3$	**11**	90/10	(24)
4	4-Bromoanisole	1000	K_2CO_3	**12**	45/55	40 (100)
5	4-Bromoanisole	100	$NaHCO_3$	**12**	71/29	(26)
6	4-*N*,*N*-Dimethylaminobromobenzene	1000	K_2CO_3	**13**	37/63	23 (100)
7	4-*N*,*N*-Dimethylaminobromobenzene	2500	K_2CO_3	**13**	39/61	(25)
8	4-*N*,*N*-Dimethylaminobromobenzene	100	$NaHCO_3$	**13**	93/7	(15)
9	4-Fluorobromobenzene	1000	K_2CO_3	**14**	47/53	(100)
10	4-Fluorobromobenzene	2500	K_2CO_3	**14**	50/50	(93)
11	4-Fluorobromobenzene	1000	$NaHCO_3$	**14**	90/10	88 (100)
12	4-Bromoacetophenone	1000	K_2CO_3	**15**	40/60	(100)
13	4-Bromoacetophenone	2500	K_2CO_3	**15**	41/59	(48)
14	4-Bromoacetophenone	100	$NaHCO_3$	**15**	94/6	86 (96)
15	4-Bromoacetophenone	1000	$NaHCO_3$	**15**	94/6	(14)
16	4-Bromobenzonitrile	250	K_2CO_3	**16**	39/61	(100)
17	4-Bromobenzonitrile	100	$NaHCO_3$	**16**	94/6	87 (100)
18	4-Bromobenzonitrile	1000	$NaHCO_3$	**16**	94/6	(69)
19	2-Fluorobromobenzene	2500	K_2CO_3	**17**	45/55	(100)
20	2-Fluorobromobenzene	10,000	K_2CO_3	**17**	49/51	(13)
21	2-Fluorobromobenzene	100	$NaHCO_3$	**17**	93/7	66 (79)
22	3-Bromopyridine	1000	K_2CO_3	**18**	30/70	(100)
23	3-Bromopyridine	100	$NaHCO_3$	**18**	95/5	36 (42)
24	2-Bromothiophene	1000	K_2CO_3	**19**	30/70	19 (100)
25	2-Bromothiophene	100	$NaHCO_3$	**19**	30/70	(90)

[a] Conditions: catalyst: $[ClPd(C_3H_5)]_2$/tedicyp=1:2, aryl bromide (1 equiv), 2-methyl-3-phenylprop-1-en-3-ol (1.2 equiv), K_2CO_3 or $NaHCO_3$ (2 equiv), DMF, 130 °C, 20 h, isolated yields of products **11–19**. Yields in parenthesis are GC and NMR conversions.



Scheme 3.

selectivities of 30–50% in favour of isomers **11**–**19** were obtained when K_2CO_3 was used. With this alkenol, the formation of unidentified products was also observed. Here again, much better selectivities of 71–95% in compounds **11**–**19**, but slow reactions were observed using $NaHCO_3$. The best result in terms of selectivity and ratio substrate/catalyst was obtained with 4-bromobenzonitrile (Table 2, entries 17 and 18) with a selectivity of 94% in isomer **16** and a TON of 690.

Methyl-3-hydroxy-2-methylenebutenoate as coupling partner gave disappointing results (Scheme 3, Table 3). With this substrate, a decarbomethoxylation of the Baylis–Hillman adduct was observed to give selectively the β-arylated ketones **20**–**23**. The formation of the expected arylketoesters was not observed. Such decarbomethoxylation of the Baylis–Hillman adducts had already been described by Caló et al. with a Pd–benzothiazole–carbene complex[11b] and by Bhat et al. using $Pd(OAc)_2/PPh_3$ as catalyst.[9] Caló et al. explained the exclusive formation of the β-arylated ketones by a fast decarbomethoxylation of the expected arylketoester in tetrabutylammonium bromide as solvent. Our attempts to avoid this decarbomethoxylation using lower reaction temperatures or weaker bases were unsuccessful. The synthesis of 1-arylbutan-3-ones **20**–**23** using a Baylis–Hillman adduct is not attractive, since they can be prepared more easily by Heck reaction of simple alk-1-en-3-ols.[19]

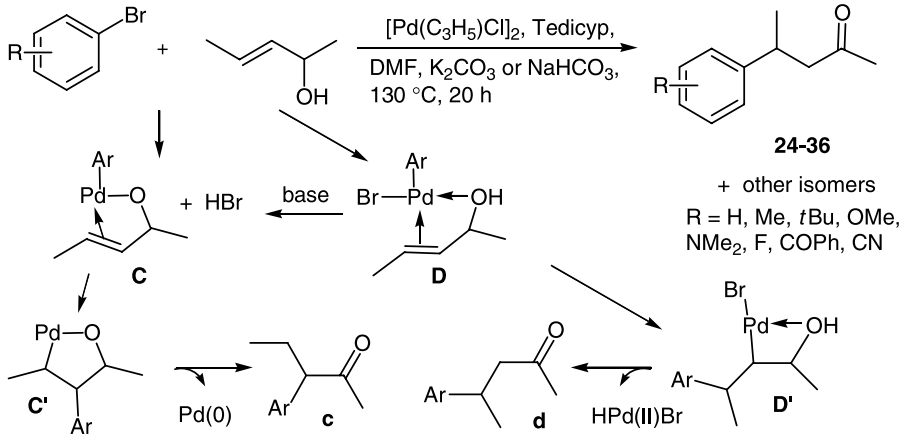
Table 3. Palladium–tedicyp catalysed Heck reactions with methyl-3-hydroxy-2-methylenebutenoate (Scheme 3)

Entry	Aryl bromide	Ratio substrate/catalyst	Product number	Yield (%)[a]
1	4-*t*-Butylbromobenzene	100	**20**	75 (100)
2	4-*t*-Butylbromobenzene	250	**20**	(88)
3	4-Bromoanisole	100	**21**	87 (100)
4	4-Bromoanisole	250	**21**	(62)
5	4-Fluorobromobenzene	100	**22**	85 (100)
6	4-Fluorobromobenzene	250	**22**	(73)
7	4-Bromoacetophenone	2500	**23**	91 (100)
8	4-Bromoacetophenone	10,000	**23**	(50)

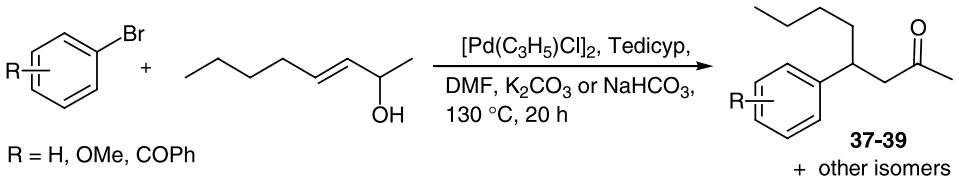
[a] Conditions: catalyst: $[ClPd(C_3H_5)]_2$/tedicyp = 1:2, aryl bromide (1 equiv), methyl-3-hydroxy-2-methylenebutenoate (1.2 equiv), K_2CO_3 or $NaHCO_3$ (2 equiv), DMF, 130 °C, 20 h, isolated yields of products **20**–**23**. Yields in parenthesis are GC and NMR conversions.

Then, we studied the selectivity of the reaction using three 3-substituted allylic alcohols: pent-3-en-2-ol, oct-3-en-2-ol and hept-2-en-4-ol (Schemes 4–6, Tables 4–6). The coupling of pent-3-en-2-ol with electron-rich aryl bromides such as 4-*t*-butylbromobenzene or 4-*N*,*N*-dimethylaminobromobenzene using K_2CO_3 as base gave β-aryl ketones **25**–**28** in 45–68% selectivities (Table 4, entries 4, 5, 7, 9, 10, 12 and 13). Reactions of pent-3-en-2-ol with the electron-poor aryl bromides 4-bromobenzophenone or 4-bromobenzonitrile were less selective, and the β-aryl ketones **31** and **32** were obtained in 28 and 39% selectivities (Table 4, entries 21, 22, 25 and 26). Presumably, with K_2CO_3, the formation of the alcoholate of pent-3-en-2-ol led to the intermediates **C** and **C′** of Scheme 4, then, intermediate **C′** gave the α-aryl ketone **c** with a mixture of isomers due to the partial migration of the double bond.

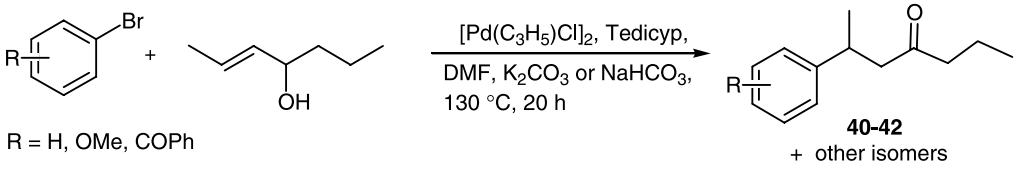
Again, using $NaHCO_3$ as base, higher selectivities and slower reactions were observed in all cases. With this base, the formation of the alcoholate of pent-3-en-2-ol is probably not favoured, therefore **D** and **D′** in Scheme 4 are formed as the major intermediates and β-aryl ketones **d** were obtained in 80–100% selectivities. An interaction of the alcohol function with the palladium centre probably imposes a conformation in the structures of the (aryl)-Pd(alkenol) intermediate leading to an higher regiocontrol of the insertion. This interaction might also control the migration of the double bond. With electron-rich aryl bromides, selectivities of 80–93% in β-aryl ketones **25**–**27**



Scheme 4.



Scheme 5.



Scheme 6.

were obtained (Table 4, entries 6, 8 and 11). Electron-poor aryl bromides gave products **30**–**32** in 81–85% selectivities (Table 4, entries 20, 23, 24, 27 and 28). As expected, the reactions with the heteroaromatic substrates 3-bromopyridine and 3-bromoquinoline also led to higher selectivities with $NaHCO_3$ as base (Table 4, entries 36–42).

Oct-3-en-2-ol gave quite similar selectivities than pent-3-en-2-ol (Scheme 5, Table 5). Very low selectivities were

Table 4. Palladium–tedicyp catalysed Heck reactions with pent-3-en-2-ol (Scheme 4)

Entry	Aryl bromide	Ratio substrate/catalyst	Base	Product number	Ratio ketone **24**–**36**/other isomers	Yield (%)[a]
1	Bromobenzene	2500	K_2CO_3	**24**	54/46	(97)
2	Bromobenzene	250	$NaHCO_3$	**24**	81/19	77 (100)
3	Bromobenzene	1000	$NaHCO_3$	**24**	82/18	(79)
4	4-Bromotoluene	1000	K_2CO_3	**25**	68/32	60 (100)
5	4-Bromotoluene	2500	K_2CO_3	**25**	45/55	(97)
6	4-Bromotoluene	100	$NaHCO_3$	**25**	93/7	(25)
7	4-*t*-Butylbromobenzene	2500	K_2CO_3	**26**	54/46	39 (97)
8	4-*t*-Butylbromobenzene	1000	$NaHCO_3$	**26**	80/20	(38)
9	4-Bromoanisole	1000	K_2CO_3	**27**	47/53	(100)
10	4-Bromoanisole	2500	K_2CO_3	**27**	49/51	41 (97)
11	4-Bromoanisole	250	$NaHCO_3$	**27**	80/20	31 (43)
12	4-*N*,*N*-Dimethylaminobromobenzene	2500	K_2CO_3	**28**	56/44	46 (100)
13	4-*N*,*N*-Dimethylaminobromobenzene	10,000	K_2CO_3	**28**	46/54	(49)
14	6-Methoxy-2-bromonaphthalene	1000	K_2CO_3	**29**	57/43	45 (94)
15	6-Methoxy-2-bromonaphthalene	2500	K_2CO_3	**29**	50/50	(31)
16	6-Methoxy-2-bromonaphthalene	250	$NaHCO_3$	**29**	81/19	77 (100)
17	6-Methoxy-2-bromonaphthalene	1000	$NaHCO_3$	**29**	83/17	(18)
18	4-Fluorobromobenzene	1000	K_2CO_3	**30**	64/36	58 (100)
19	4-Fluorobromobenzene	2500	K_2CO_3	**30**	50/50	(40)
20	4-Fluorobromobenzene	100	$NaHCO_3$	**30**	82/18	66 (89)
21	4-Bromobenzophenone	1000	K_2CO_3	**31**	39/61	(100)
22	4-Bromobenzophenone	2500	K_2CO_3	**31**	28/72	(47)
23	4-Bromobenzophenone	100	$NaHCO_3$	**31**	82/18	76 (100)
24	4-Bromobenzophenone	1000	$NaHCO_3$	**31**	81/19	(31)
25	4-Bromobenzonitrile	250	K_2CO_3	**32**	28/72	(100)
26	4-Bromobenzonitrile	1000	K_2CO_3	**32**	39/61	(40)
27	4-Bromobenzonitrile	100	$NaHCO_3$	**32**	85/15	82 (100)
28	4-Bromobenzonitrile	1000	$NaHCO_3$	**32**	84/16	(26)
29	2-Bromotoluene	1000	K_2CO_3	**33**	58/42	51 (100)
30	2-Bromotoluene	2500	K_2CO_3	**33**	70/30	(18)
31	2-Bromotoluene	50	$NaHCO_3$	**33**	—	(0)
32	1-Bromonaphthalene	1000	K_2CO_3	**34**	63/37	55 (100)
33	1-Bromonaphthalene	2500	K_2CO_3	**34**	57/43	(52)
34	1-Bromonaphthalene	100	$NaHCO_3$	**34**	100/0	97 (100)
35	1-Bromonaphthalene	1000	$NaHCO_3$	**34**	100/0	(68)
36	3-Bromopyridine	250	K_2CO_3	**35**	62/38	53 (100)
37	3-Bromopyridine	100	$NaHCO_3$	**35**	84/16	72 (100)
38	3-Bromopyridine	1000	$NaHCO_3$	**35**	83/17	(34)
39	3-Bromoquinoline	250	K_2CO_3	**36**	69/31	61 (100)
40	3-Bromoquinoline	1000	K_2CO_3	**36**	63/37	(72)
41	3-Bromoquinoline	100	$NaHCO_3$	**36**	81/19	78 (100)
42	3-Bromoquinoline	1000	$NaHCO_3$	**36**	83/17	(46)

[a] Conditions: catalyst: $[ClPd(C_3H_5)]_2$/tedicyp = 1:2, aryl bromide (1 equiv), pent-3-en-2-ol (1.2 equiv), K_2CO_3 or $NaHCO_3$ (2 equiv), DMF, 130 °C, 20 h, isolated yields of products **24**–**36**. Yields in parenthesis are GC and NMR conversions.

Table 5. Palladium–tedicyp catalysed Heck reactions with oct-3-en-2-ol (Scheme 5)

Entry	Aryl bromide	Ratio substrate/catalyst	Base	Product number	Ratio ketone **37–39**/other isomers	Yield (%)[a]
1	Bromobenzene	250	K_2CO_3	**37**	65/35	55 (100)
2	Bromobenzene	1000	K_2CO_3	**37**	68/32	(95)
3	Bromobenzene	100	$NaHCO_3$	**37**	83/17	53 (71)
4	4-Bromoanisole	100	K_2CO_3	**38**	68/32	47 (100)
5	4-Bromoanisole	250	K_2CO_3	**38**	80/20	(80)
6	4-Bromoanisole	50	$NaHCO_3$	**38**	—	(0)
7	4-Bromobenzophenone	1000	K_2CO_3	**39**	26/74	(100)
8	4-Bromobenzophenone	2500	K_2CO_3	**39**	14/86	(51)
9	4-Bromobenzophenone	100	$NaHCO_3$	**39**	81/19	75 (100)
10	4-Bromobenzophenone	1000	$NaHCO_3$	**39**	85/15	(11)

[a] Conditions: catalyst: $[ClPd(C_3H_5)]_2$/tedicyp=1:2, aryl bromide (1 equiv), oct-3-en-2-ol (1.2 equiv), K_2CO_3 or $NaHCO_3$ (2 equiv), DMF, 130 °C, 20 h, isolated yields of products **37–39**. Yields in parenthesis are GC and NMR conversions.

Table 6. Palladium–tedicyp catalysed Heck reactions with hept-2-en-4-ol (Scheme 6)

Entry	Aryl bromide	Ratio substrate/catalyst	Base	Product number	Ratio ketone **40–42**/other isomers	Yield (%)[a]
1	Bromobenzene	1000	K_2CO_3	**40**	24/76	(100)
2	Bromobenzene	2500	K_2CO_3	**40**	42/58	(88)
3	Bromobenzene	1000	$NaHCO_3$	**40**	73/27	69 (100)
4	4-Bromoanisole	1000	K_2CO_3	**41**	34/66	22 (100)
5	4-Bromoanisole	2500	K_2CO_3	**41**	51/49	(57)
6	4-Bromoanisole	100	$NaHCO_3$	**41**	78/22	71 (100)
7	4-Bromoanisole	1000	$NaHCO_3$	**41**	71/29	(18)
8	4-Bromobenzophenone	1000	K_2CO_3	**42**	34/66	(100)
9	4-Bromobenzophenone	1000	$NaHCO_3$	**42**	71/29	64 (100)

[a] Conditions: catalyst: $[ClPd(C_3H_5)]_2$/tedicyp=1:2, aryl bromide (1 equiv), hept-2-en-4-ol (1.2 equiv), K_2CO_3 or $NaHCO_3$ (2 equiv), DMF, 130 °C, 20 h, isolated yields of products **40–42**. Yields in parenthesis are GC and NMR conversions.

observed for the coupling with 4-bromobenzophenone using K_2CO_3 as base: 14 and 26%, but with $NaHCO_3$, β-aryl ketone **39** was obtained in 81–85% selectivities (Table 5, entries 7–10). Bromobenzene or 4-bromoanisole using K_2CO_3 gave **37** and **38** in 65–80% selectivities (Table 5, entries 1, 2, 4 and 5). On the other hand, hept-2-en-4-ol gave ketones **40–42** with low selectivities (24–51%) in all cases using K_2CO_3 as base (Scheme 6, Table 6). Again, higher selectivities in β-aryl ketones **40–42** were obtained with $NaHCO_3$: 71–78% (Table 6, entries 3, 6, 7 and 9).

In summary, we have established that the tedicyp–palladium system provides an efficient catalyst for the selective synthesis of β-aryl ketones from allylic alcohols with disubstituted double bonds and aryl bromides. The electronic properties and steric hindrance of the aryl bromide has an important effect on the selectivities of the reactions. In general, medium to high selectivities in β-aryl ketones were obtained using electron-rich aryl bromides and K_2CO_3 as base. More selective reactions were generally obtained using $NaHCO_3$ as base, especially with electron-poor aryl bromides, however, with this base slower reactions were observed in most cases. With sterically hindered aryl bromides higher selectivities in favour of the formation of the β-aryl ketones were obtained. A wide range of functions such as methoxy, fluoro, acetyl, formyl, benzoyl, dimethylamino or nitrile on the aryl bromide are tolerated. A few heteroaromatic substrates have also been used successfully. Electron-poor and electron-rich aryl bromides can be reacted at similar substrate/catalyst ratios when K_2CO_3 was used as base indicating that the oxidative addition of the aryl bromide is not the rate-limiting step for the reaction with this catalyst. It should de noted that the formation of non-arylated ketones deriving from allylic rearrangement was not observed. With this Pd–tetraphosphine catalyst, these reactions can be performed with as little as 0.01% catalyst with some substrates without further optimisation of the reaction conditions. Due to the high price of palladium, the practical advantage of such low catalyst loadings can become increasingly important for industrial processes. Moreover, these allylic alcohols are commercially available and this is a practical advantage of this reaction.

3. Experimental

3.1. General remarks

All reactions were run under argon in Schlenk tubes using vacuum lines. DMF analytical grade was not distilled before use. Potassium carbonate (99+) or sodium hydrogen carbonate (99+) were used. Commercial aryl bromides and allylic alcohols were used without purification. The reactions were followed by GC and NMR for high boiling point substrates and by GC for low boiling point substrates. ^1H and ^{13}C spectrum were recorded with a Bruker 300 MHz spectrometer in $CDCl_3$ solutions. Chemical shift are reported in parts per million relative to $CDCl_3$ (7.25 for ^1H NMR and 77.0 for ^{13}C NMR). Flash chromatography were performed on silica gel (230–400 mesh). GC and NMR yields in the tables are conversions of the aryl halides into the product calculated with GC and ^1H NMR spectrum of the crude mixtures.

3.1.1. Preparation of the Pd–tedicyp catalyst. An oven-dried 40-mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (30 mg, 81 μmol) and tedicyp (140 mg, 162 μmol). Anhydrous DMF (10 mL) were added, then the solution was stirred at room temperature for 10 min. The appropriate catalyst concentration was obtained by successive dilutions. ^{31}P NMR (162 MHz, $CDCl_3$) δ 25 ($w=80$ Hz), 19.4 ($w=110$ Hz).

3.2. General procedure

In a typical experiment, the aryl halide (1 mmol), allylic alcohols (1.2 mmol) and K_2CO_3 (0.276 g, 2 mmol) or $NaHCO_3$ (0.168 g, 2 mmol) were dissolved in DMF (3 mL) under an argon atmosphere. The prepared Pd–tedicyp catalyst complex (see Tables) was then transferred to the reaction flask via cannula. The reaction mixture was stirred at 130 °C for 20 h. The solution was diluted with H_2O (5 mL), then the product was extracted three times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography.

3.2.1. 1-(4-*tert*-Butylphenyl)-2-methylpentan-3-one (1b) (Table 1, entry 1). From 4-*tert*-butylbromobenzene (0.213 g, 1 mmol), 2-methylpent-1-en-3-ol (0.120 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (1 μmol), product **1b** was obtained in 71% (0.165 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, $J=8.3$ Hz, 2H), 7.06 (d, $J=8.3$ Hz, 2H), 2.92 (dd, $J=13.2$, 6.8 Hz, 1H), 2.82 (sext., $J=7.0$ Hz, 1H), 2.52 (dd, $J=13.2$, 7.3 Hz, 1H), 2.44 (dq, $J=17.8$, 7.3 Hz, 1H), 2.29 (dq, $J=17.8$, 7.3 Hz, 1H), 1.29 (s, 9H), 1.07 (d, $J=6.8$ Hz, 3H), 0.97 (t, $J=7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.9, 149.0, 136.7, 128.6, 125.2, 47.9, 38.7, 35.0, 34.3, 31.4, 16.6, 7.6; MS (70 eV); *m/z* (%) 232 ($M^{+\cdot}$, 40); $C_{16}H_{24}O$: calcd C 82.70, H 10.41; Found C 82.76, H 10.24. Before purification **1a** was also observed ^1H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, $J=7.4$ Hz, 3H).

3.2.2. 1-(4-Methoxyphenyl)-2-methylpentan-3-one (2b) (Table 1, entry 4). From 4-bromoanisole (0.187 g, 1 mmol), 2-methylpent-1-en-3-ol (0.120 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (0.1 μmol), product **2b** was obtained in 92% (0.190 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, $J=8.7$ Hz, 2H), 6.80 (d, $J=8.7$ Hz, 2H), 3.77 (s, 3H), 2.89 (dd, $J=13.1$, 7.3 Hz, 1H), 2.79 (sext., $J=6.9$ Hz, 1H), 2.50 (dd, $J=13.1$, 6.8 Hz, 1H), 2.42 (dq, $J=17.8$, 7.3 Hz, 1H), 2.24 (dq, $J=17.8$, 7.3 Hz, 1H), 1.06 (d, $J=6.8$ Hz, 3H), 0.96 (t, $J=7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 158.0, 131.9, 129.8, 113.8, 55.2, 48.1, 38.5, 35.2, 16.5, 7.6; MS (70 eV); *m/z* (%) 206 ($M^{+\cdot}$, 37); $C_{13}H_{18}O_2$: calcd C 75.69, H 8.80; Found C 75.43, H 8.73. Before purification **2a** was also observed ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, $J=7.3$ Hz, 3H).

3.2.3. 1-(4-(Dimethylamino)phenyl)-2-methylpentan-3-one (3b) (Table 1, entry 6). From 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), 2-methylpent-1-en-3-ol (0.120 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (1 μmol), product **3b** was obtained in 85% (0.186 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.00 (d, $J=8.7$ Hz, 2H), 6.67 (d, $J=8.7$ Hz, 2H), 2.90 (s, 6H), 2.86 (dd, $J=12.9$, 6.8 Hz, 1H), 2.78 (sext., $J=6.9$ Hz, 1H), 2.49 (dd, $J=12.9$, 6.9 Hz, 1H), 2.41 (dq, $J=17.9$, 7.2 Hz, 1H), 2.27 (dq, $J=17.9$, 7.2 Hz, 1H), 1.05 (d, $J=6.8$ Hz, 3H), 0.97 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.3, 149.1, 129.5, 127.9, 112.9, 48.2, 40.8, 38.4, 35.1, 16.4, 7.6; MS (70 eV); *m/z* (%) 219 ($M^{+\cdot}$, 67); $C_{14}H_{21}NO$: calcd C 76.67, H 9.65; Found C 76.77, H 9.57. Before purification **3a** was also observed ^1H NMR (300 MHz, $CDCl_3$) δ 1.00 (t, $J=7.5$ Hz, 3H).

3.2.4. 1-(4-Fluorophenyl)-2-methylpentan-3-one (4b) (Table 1, entry 8). From 4-fluorobromobenzene (0.175 g, 1 mmol), 2-methylpent-1-en-3-ol (0.120 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (1 μmol), product **4b** was obtained in 87% (0.169 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.08 (dd, $J=8.7$, 5.5 Hz, 2H), 6.94 (t, $J=8.7$ Hz, 2H), 2.93 (dd, $J=13.3$, 7.5 Hz, 1H), 2.79 (sext., $J=7.1$ Hz, 1H), 2.51 (dd, $J=13.3$, 6.9 Hz, 1H), 2.43 (dq, $J=17.8$, 7.3 Hz, 1H), 2.23 (dq, $J=17.8$, 7.3 Hz, 1H), 1.07 (d, $J=6.9$ Hz, 3H), 0.95 (t, $J=7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.6, 161.9 (d, $J_{C-F}=243.8$ Hz), 135.5 (d, $^4J_{C-F}=3.4$ Hz), 130.2 (d, $^3J_{C-F}=8.0$ Hz), 115.1 (d, $^2J_{C-F}=21.3$ Hz), 47.9, 38.3, 35.2, 16.6, 7.6; MS (70 eV); *m/z* (%) 194 ($M^{+\cdot}$, 25); $C_{12}H_{15}FO$: calcd C 74.20, H 7.78; Found C 74.36, H 7.81. Before purification **4a** was also observed ^1H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, $J=7.3$ Hz, 3H).

3.2.5. 1-(4-(Trifluoromethyl)phenyl)-2-methylpentan-3-one (5b) (Table 1, entry 12). From 4-trifluoromethylbromobenzene (0.225 g, 1 mmol), 2-methylpent-1-en-3-ol (0.120 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **5b** was obtained in 89% (0.217 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, $J=8.1$ Hz, 2H), 7.24 (d, $J=8.1$ Hz, 2H), 3.04 (dd, $J=13.4$, 7.4 Hz, 1H), 2.84 (sext., $J=7.0$ Hz, 1H), 2.61 (dd, $J=13.4$, 7.2 Hz, 1H), 2.47 (dq, $J=17.8$, 7.3 Hz, 1H), 2.25 (dq, $J=17.8$, 7.3 Hz, 1H), 1.09 (d, $J=7.1$ Hz, 3H), 0.97 (t, $J=7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.0, 144.1, 129.3, 128.6 (q, $^2J_{C-F}=32.4$ Hz), 125.3 (q, $^3J_{C-F}=4.0$ Hz), 124.2 (q, $J_{C-F}=271.9$ Hz), 47.6, 38.7, 35.1, 16.8, 7.6; MS (70 eV); *m/z* (%) 244 ($M^{+\cdot}$, 62); $C_{13}H_{15}F_3O$: calcd C 63.93, H 6.19; Found C 64.04, H 6.16. Before purification **5a** was also observed ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, $J=7.3$ Hz, 3H).

3.2.6. 1-(4-Acetylphenyl)-2-methylpentan-3-one (6b) (Table 1, entry 16). From 4-bromoacetophenone (0.199 g, 1 mmol), 2-methylpent-1-en-3-ol (0.120 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **6b** was obtained in 88% (0.192 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, $J=8.4$ Hz, 2H), 7.22 (d, $J=8.4$ Hz, 2H), 3.03 (dd, $J=13.0$, 7.3 Hz, 1H), 2.85 (sext., $J=6.9$ Hz, 1H), 2.62 (dd, $J=13.0$, 6.8 Hz, 1H), 2.56 (s, 3H), 2.45 (dq, $J=17.9$, 7.2 Hz, 1H), 2.21 (dq, $J=17.9$, 7.2 Hz, 1H), 1.09 (d, $J=6.8$ Hz, 3H), 0.96 (t, $J=7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.0, 197.7, 145.7, 135.4, 129.2, 128.5, 47.5, 39.0, 35.1, 26.5, 16.8, 7.8; MS (70 eV); *m/z* (%) 218 ($M^{+\cdot}$, 80); $C_{14}H_{18}O_2$: calcd C 77.03, H 8.31; Found C 77.12, H 8.38. Before purification **6a** was also observed ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, $J=7.3$ Hz, 3H).

3.2.7. 1-(4-Cyanophenyl)-2-methylpentan-3-one (7b) (Table 1, entry 19). From 4-bromobenzonitrile (0.182 g, 1 mmol), 2-methylpent-1-en-3-ol (0.120 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **7b** was obtained in 90% (0.181 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J=8.1 Hz, 2H), 7.24 (d, J=8.1 Hz, 2H), 3.04 (dd, J=13.4, 7.5 Hz, 1H), 2.81 (sext., J=7.1 Hz, 1H), 2.61 (dd, J=13.4, 6.8 Hz, 1H), 2.47 (dq, J=17.8, 7.3 Hz, 1H), 2.23 (dq, J=17.8, 7.3 Hz, 1H), 1.09 (d, J=6.9 Hz, 3H), 0.96 (t, J=7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.5, 145.5, 132.0, 129.6, 118.7, 109.9, 47.2, 38.7, 34.8, 16.7, 7.4; $C_{13}H_{15}NO$: calcd C 77.58, H 7.51; Found C 77.32, H 7.72. Before purification **7a** was also observed ^1H NMR (300 MHz, $CDCl_3$) δ 1.10 (t, J=7.3 Hz, 3H).

3.2.8. 2-Methyl-1-(*o*-tolyl)pentan-3-one (8b) (Table 1, entry 23). From 2-methylbromobenzene (0.171 g, 10 mmol), 2-methylpent-1-en-3-ol (0.120 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **8b** was obtained in 93% (0.177 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.13–7.05 (m, 4H), 2.96 (dd, J=13.4, 7.0 Hz, 1H), 2.83 (sext., J=7.0 Hz, 1H), 2.56 (dd, J=13.5, 7.3 Hz, 1H), 2.42 (dq, J=17.9, 7.3 Hz, 1H), 2.31 (s, 3H), 2.23 (dq, J=17.9, 7.3 Hz, 1H), 1.09 (d, J=6.7 Hz, 3H), 0.96 (t, J=7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.9, 138.0, 136.0, 130.4, 129.7, 126.3, 125.9, 46.4, 36.5, 35.3, 19.4, 16.6, 7.6; MS (70 eV); m/z (%) 190 ($M^{+\cdot}$, 15); $C_{13}H_{18}O$: calcd C 82.06, H 9.53; Found C 82.01, H 9.72. Before purification **8a** was also observed ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, J=7.3 Hz, 3H).

3.2.9. 2-Methyl-1-(3-pyridinyl)pentan-3-one (9b) (Table 1, entry 27). From 3-bromopyridine (0.158 g, 1 mmol), 2-methylpent-1-en-3-ol (0.120 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **9b** was obtained in 80% (0.142 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 8.39 (dd, J=4.8, 1.6 Hz, 1H), 8.37 (d, J=2.0 Hz, 1H), 7.41 (dt, J=7.8, 2.0 Hz, 1H), 7.14 (ddd, J=7.8, 4.8, 0.7 Hz, 1H), 2.96 (dd, J=13.5, 7.3 Hz, 1H), 2.78 (sext., J=7.0 Hz, 1H), 2.56 (dd, J=13.5, 7.0 Hz, 1H), 2.43 (dq, J=17.9, 7.3 Hz, 1H), 2.22 (dq, J=17.9, 7.3 Hz, 1H), 1.06 (d, J=6.9 Hz, 3H), 0.93 (t, J=7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.8, 150.2, 147.6, 136.4, 135.2, 123.2, 47.4, 35.9, 35.0, 16.7, 7.5; $C_{11}H_{15}NO$: calcd C 74.54, H 8.53; Found C 74.72, H 8.38. Before purification **9a** was also observed ^1H NMR (300 MHz, $CDCl_3$) δ 1.14 (t, J=7.3 Hz, 3H).

3.2.10. 2-Methyl-1-(3-quinolyl)pentan-3-one (10b) (Table 1, entry 31). From 3-bromoquinoline (0.136 mL, 1 mmol), 2-methylpent-1-en-3-ol (0.120 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **10b** was obtained in 97% (0.220 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 8.74 (d, J=1.8 Hz, 1H), 8.07 (d, J=8.6 Hz, 1H), 7.90 (d, J=1.8 Hz, 1H), 7.75 (dd, J=8.2, 1.0 Hz, 1H), 7.65 (td, J=8.2, 1.4 Hz, 1H), 7.51 (td, J=8.1, 1.1 Hz, 1H), 3.18 (dd, J=13.7, 7.4 Hz, 1H), 2.93 (sext., J=7.1 Hz, 1H), 2.74 (dd, J=13.7, 6.9 Hz, 1H), 2.50 (dq, J=17.8, 7.3 Hz, 1H), 2.26 (dq, J=17.8, 7.3 Hz, 1H), 1.15 (d, J=6.9 Hz, 3H), 0.96 (t, J=7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.8, 151.8, 146.7, 135.4, 132.6, 129.0, 128.9, 128.0, 127.4, 126.8, 47.5, 36.1, 35.1, 16.9, 7.6; MS (70 eV); m/z (%) 227 ($M^{+\cdot}$, 100); $C_{15}H_{17}NO$: calcd C 79.26, H 7.54; Found C 79.35, H 7.46. Before purification **10a** was also observed ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, J=7.3 Hz, 3H).

3.2.11. 3-(4-*tert*-Butylphenyl)-2-methyl-1-phenylpropan-1-one (11) (Table 2, entry 1). From 4-*tert*-butylbromobenzene (0.213 g, 1 mmol), 2-methyl-3-phenylprop-1-en-3-ol (0.178 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (1 μmol), product **11** was obtained in 38% (0.107 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J=7.4 Hz, 2H), 7.52 (t, J=7.4 Hz, 1H), 7.42 (t, J=7.4 Hz, 2H), 7.29 (d, J=8.4 Hz, 2H), 7.11 (d, J=8.4 Hz, 2H), 3.73 (sext., J=7.0 Hz, 1H), 3.13 (dd, J=13.8, 6.1 Hz, 1H), 2.65 (dd, J=13.8, 7.9 Hz, 1H), 1.28 (s, 9H), 1.20 (d, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9, 149.0, 136.8, 136.5, 132.8, 128.7, 128.6, 128.3, 125.2, 42.7, 38.8, 34.3, 31.4, 17.4; MS (70 eV); m/z (%) 280 ($M^{+\cdot}$, 58); $C_{20}H_{24}O$: calcd C 85.67, H 8.63; Found C 85.59, H 8.66.

3.2.12. 3-(4-Methoxyphenyl)-2-methyl-1-phenylpropan-1-one (12) (Table 2, entry 4). From 4-bromoanisole (0.187 g, 1 mmol), 2-methyl-3-phenylprop-1-en-3-ol (0.178 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (1 μmol), product **12** was obtained in 40% (0.102 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J=7.4 Hz, 2H), 7.54 (t, J=7.4 Hz, 1H), 7.44 (t, J=7.4 Hz, 2H), 7.10 (d, J=8.6 Hz, 2H), 6.80 (d, J=8.6 Hz, 2H), 3.76 (s, 3H), 3.70 (sext., J=7.1 Hz, 1H), 3.13 (dd, J=13.8, 6.6 Hz, 1H), 2.63 (dd, J=13.8, 7.7 Hz, 1H), 1.19 (d, J=7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9, 158.0, 136.5, 132.9, 132.0, 130.0, 128.6, 128.3, 113.8, 55.2, 43.0, 38.5, 17.3; MS (70 eV); m/z (%) 254 ($M^{+\cdot}$, 40).

3.2.13. 3-[4-(Dimethylamino)phenyl]-2-methyl-1-phenylpropan-1-one (13) (Table 2, entry 6). From 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), 2-methyl-3-phenylprop-1-en-3-ol (0.178 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (1 μmol), product **13** was obtained in 23% (0.062 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J=7.4 Hz, 2H), 7.54 (t, J=7.4 Hz, 1H), 7.44 (t, J=7.4 Hz, 2H), 7.08 (d, J=8.7 Hz, 2H), 6.68 (d, J=8.7 Hz, 2H), 3.70 (sext., J=7.0 Hz, 1H), 3.07 (dd, J=13.9, 5.9 Hz, 1H), 2.90 (s, 6H), 2.59 (dd, J=13.8, 8.0 Hz, 1H), 1.19 (d, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.1, 158.0, 136.6, 129.7, 128.6, 128.3, 127.6, 126.4, 112.9, 43.0, 40.8, 38.4, 17.1; MS (70 eV); m/z (%) 267 ($M^{+\cdot}$, 40); $C_{18}H_{21}NO$: calcd C 80.86, H 7.92; Found C 80.78, H 8.05.

3.2.14. 3-(4-Fluorophenyl)-2-methyl-1-phenylpropan-1-one (14) (Table 2, entry 11). From 4-fluorobromobenzene (0.175 g, 1 mmol), 2-methyl-3-phenylprop-1-en-3-ol (0.178 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (1 μmol), product **14** was obtained in 88% (0.213 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J=7.4 Hz, 2H), 7.54 (t, J=7.4 Hz, 1H), 7.43 (t, J=7.4 Hz, 2H), 7.14 (dd, J=8.7, 5.3 Hz, 2H), 6.93 (d, J=8.8 Hz, 2H), 3.71 (sext., J=6.9 Hz, 1H), 3.13 (dd, J=13.8, 6.8 Hz, 1H), 2.67 (dd, J=13.8, 7.9 Hz, 1H), 1.19 (d, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.5, 161.4 (d, J_{C-F}=243.8 Hz), 136.4, 135.5 (d, $^4J_{C-F}$=2.9 Hz), 133.0, 130.5 (d, $^3J_{C-F}$=8.0 Hz), 128.6, 128.2, 115.1 (d, $^2J_{C-F}$=21.3 Hz), 42.8, 38.5,

17.5; MS (70 eV); *m/z* (%) 242 ($M^{+\cdot}$, 41); $C_{16}H_{15}FO$: calcd C 79.32, H 6.24; Found C 79.50, H 6.36.

3.2.15. 3-(4-Acetylphenyl)-2-methyl-1-phenylpropan-1-one (15) (Table 2, entry 14). From 4-bromoacetophenone (0.199 g, 1 mmol), 2-methyl-3-phenylprop-1-en-3-ol (0.178 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **15** was obtained in 86% (0.229 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, $J=7.3$ Hz, 2H), 7.84 (d, $J=8.3$ Hz, 2H), 7.54 (t, $J=7.3$ Hz, 1H), 7.44 (t, $J=7.4$ Hz, 2H), 7.28 (d, $J=8.3$ Hz, 2H), 3.77 (sext., $J=7.0$ Hz, 1H), 3.22 (dd, $J=13.7$, 6.9 Hz, 1H), 2.76 (dd, $J=13.7$, 7.3 Hz, 1H), 2.55 (s, 3H), 1.21 (d, $J=7.1$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.1, 197.8, 145.8, 136.2, 135.4, 133.1, 129.3, 128.7, 128.5, 128.2, 42.4, 39.2, 26.5, 17.7; MS (70 eV); *m/z* (%) 266 ($M^{+\cdot}$, 51); $C_{18}H_{18}O_2$: calcd C 81.17, H 6.81; Found C 81.12, H 6.96.

3.2.16. 3-(4-Cyanophenyl)-2-methyl-1-phenylpropan-1-one (16) (Table 2, entry 17). From 4-bromobenzonitrile (0.182 g, 1 mmol), 2-methyl-3-phenylprop-1-en-3-ol (0.178 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **16** was obtained in 87% (0.217 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, $J=7.3$ Hz, 2H), 7.53 (d, $J=8.2$ Hz, 2H), 7.52 (t, $J=7.3$ Hz, 1H), 7.45 (t, $J=7.4$ Hz, 2H), 7.29 (d, $J=8.2$ Hz, 2H), 3.75 (sext., $J=7.0$ Hz, 1H), 3.22 (dd, $J=13.7$, 7.3 Hz, 1H), 2.77 (dd, $J=13.7$, 6.9 Hz, 1H), 1.22 (d, $J=6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.7, 145.7, 136.0, 133.2, 132.2, 129.9, 129.5, 128.7, 128.2, 110.1, 42.3, 39.2, 18.0; MS (70 eV); *m/z* (%) 249 ($M^{+\cdot}$, 31); $C_{17}H_{15}NO$: calcd C 81.90, H 6.06; Found C 81.82, H 6.06.

3.2.17. 3-(2-Fluorophenyl)-2-methyl-1-phenylpropan-1-one (17) (Table 2, entry 21). From 2-fluorobromobenzene (0.175 g, 1 mmol), 2-methyl-3-phenylprop-1-en-3-ol (0.178 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **17** was obtained in 66% (0.160 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, $J=7.4$ Hz, 2H), 7.54 (t, $J=7.4$ Hz, 1H), 7.46 (t, $J=7.4$ Hz, 2H), 7.21–7.10 (m, 2H), 6.94–7.02 (m, 2H), 3.82 (sext., $J=7.0$ Hz, 1H), 3.16 (dd, $J=13.6$, 6.3 Hz, 1H), 2.72 (dd, $J=13.6$, 7.2 Hz, 1H), 1.19 (d, $J=7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.5, 161.3 (d, $J_{C-F}=245.0$ Hz), 136.3, 133.0, 131.8 (d, $^3J_{C-F}=5.2$ Hz), 129.4, 128.6, 128.3, 128.1 (d, $^2J_{C-F}=9.2$ Hz), 123.9 (d, $^3J_{C-F}=3.5$ Hz), 115.2 (d, $^2J_{C-F}=21.8$ Hz), 41.0, 33.1, 17.2; MS (70 eV); *m/z* (%) 242 ($M^{+\cdot}$, 52); $C_{16}H_{15}FO$: calcd C 79.32, H 6.24; Found C 79.41, H 6.36.

3.2.18. 2-Methyl-1-phenyl-3-(3-pyridinyl)propan-1-one (18) (Table 2, entry 23). From 3-bromopyridine (0.158 g, 1 mmol), 2-methyl-3-phenylprop-1-en-3-ol (0.178 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **18** was obtained in 36% (0.081 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.42 (d, $J=4.8$ Hz, 1H), 7.89 (d, $J=7.5$ Hz, 2H), 7.54 (m, 2H), 7.46 (d, $J=7.5$ Hz, 2H), 7.19 (dd, $J=7.8$, 4.9 Hz, 1H), 3.74 (sext., $J=7.0$ Hz, 1H), 3.17 (dd, $J=13.9$, 7.1 Hz, 1H), 2.72 (dd, $J=13.9$, 7.0 Hz, 1H), 1.22 (d, $J=7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9, 150.0, 147.3, 137.0, 136.1, 135.6, 133.2, 128.7, 128.3, 123.4, 42.5, 36.3, 17.8; MS (70 eV); *m/z* (%) 225 ($M^{+\cdot}$, 45); $C_{15}H_{15}NO$: calcd C 79.97, H 6.71; Found C 79.71, H 6.85.

3.2.19. 1-Phenyl-2-[(2-thienyl)methyl]propan-1-one (19) (Table 2, entry 24). From 2-bromothiophene (0.163 g, 1 mmol), 2-methyl-3-phenylprop-1-en-3-ol (0.178 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (1 μmol), product **19** was obtained in 19% (0.044 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, $J=7.3$ Hz, 2H), 7.54 (t, $J=7.3$ Hz, 1H), 7.46 (d, $J=7.3$ Hz, 2H), 7.09 (dd, $J=5.1$, 1.3 Hz, 1H), 6.88 (dd, $J=5.1$, 3.4 Hz, 1H), 6.80 (dd, $J=3.4$, 1.0 Hz, 1H), 3.77 (sext., $J=7.0$ Hz, 1H), 3.38 (ddd, $J=14.8$, 6.7, 0.8 Hz, 1H), 2.94 (dd, $J=13.8$, 7.3 Hz, 1H), 1.24 (d, $J=7.1$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.2, 142.4, 136.3, 133.0, 128.7, 128.3, 126.8, 125.6, 123.6, 43.2, 33.2, 17.8; MS (70 eV); *m/z* (%) 230 ($M^{+\cdot}$, 70); $C_{14}H_{14}OS$: calcd C 73.01, H 6.13; Found C 72.88, H 6.01.

3.2.20. 4-(4-*tert*-Butylphenyl)butan-2-one (20) (Table 3, entry 1). From 4-*tert*-butylbromobenzene (0.213 g, 1 mmol), methyl-3-hydroxy-2-methylenebutyrate (0.175 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (10 μmol), product **20** was obtained in 75% (0.153 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, $J=8.4$ Hz, 2H), 7.11 (d, $J=8.4$ Hz, 2H), 2.86 (t, $J=7.7$ Hz, 2H), 2.75 (t, $J=7.7$ Hz, 2H), 2.14 (s, 3H), 1.30 (s, 9H).

3.2.21. 4-(4-Methoxyphenyl)butan-2-one (21) (Table 3, entry 3). From 4-bromoanisole (0.187 g, 1 mmol), methyl-3-hydroxy-2-methylenebutyrate (0.175 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (10 μmol), product **21** was obtained in 87% (0.155 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, $J=8.7$ Hz, 2H), 6.82 (d, $J=8.7$ Hz, 2H), 3.77 (s, 3H), 2.83 (t, $J=7.3$ Hz, 2H), 2.71 (t, $J=7.3$ Hz, 2H), 2.12 (s, 3H).

3.2.22. 4-(4-Fluorophenyl)butan-2-one (22) (Table 3, entry 5). From 4-fluorobromobenzene (0.175 g, 1 mmol), methyl-3-hydroxy-2-methylenebutyrate (0.175 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (10 μmol), product **22** was obtained in 85% (0.141 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (dd, $J=8.5$, 5.5 Hz, 2H), 6.95 (t, $J=8.7$ Hz, 2H), 2.86 (t, $J=7.0$ Hz, 2H), 2.72 (t, $J=7.0$ Hz, 2H), 2.12 (s, 3H).

3.2.23. 4-(4-Acetylphenyl)butan-2-one (23) (Table 3, entry 7). From 4-bromoacetophenone (0.199 g, 1 mmol), methyl-3-hydroxy-2-methylenebutyrate (0.175 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (0.4 μmol), product **23** was obtained in 91% (0.173 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, $J=8.2$ Hz, 2H), 7.26 (d, $J=8.2$ Hz, 2H), 2.93 (t, $J=7.4$ Hz, 2H), 2.76 (t, $J=7.4$ Hz, 2H), 2.55 (s, 3H), 2.13 (s, 3H).

3.2.24. 4-Phenylpentan-2-one (24) (Table 4, entry 2). From bromobenzene (0.157 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (4 μmol), product **24** was obtained in 77% (0.125 g) yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.14 (m, 5H), 3.30 (sext., $J=7.0$ Hz, 1H), 2.75 (dd, $J=16.1$, 6.5 Hz, 1H), 2.64 (dd, $J=16.3$, 7.8 Hz, 1H), 2.05 (s, 3H), 1.26 (d, $J=6.9$ Hz, 3H).

3.2.25. 4-(*p*-Tolyl)pentan-2-one (25) (Table 4, entry 4). From 4-bromotoluene (0.171 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (1 μmol), product **25** was obtained in 60% (0.106 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (m, 4H), 3.26 (sext., J=6.9 Hz, 1H), 2.73 (dd, J=16.1, 6.1 Hz, 1H), 2.63 (dd, J=16.2, 7.9 Hz, 1H), 2.30 (s, 3H), 2.05 (s, 3H), 1.24 (d, J=7.0 Hz, 3H).

3.2.26. 4-(4-*tert*-Butylphenyl)pentan-2-one (26) (Table 4, entry 7). From 4-*tert*-butylbromobenzene (0.213 g, 10 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (0.4 μmol), product **26** was obtained in 39% (0.085 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J=8.3 Hz, 2H), 7.12 (d, J=8.3 Hz, 2H), 3.26 (sext., J=6.9 Hz, 1H), 2.74 (dd, J=16.2, 6.2 Hz, 1H), 2.63 (dd, J=16.3, 8.1 Hz, 1H), 2.06 (s, 3H), 1.29 (s, 9H), 1.26 (d, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.1, 149.0, 143.0, 126.3, 125.4, 52.1, 34.8, 34.3, 31.4, 30.5, 21.9; MS (70 eV); *m/z* (%) 218 ($M^{+\cdot}$, 11); $C_{15}H_{22}O$: calcd C 82.52, H 10.16; Found C 82.45, H 10.12.

3.2.27. 4-(4-Methoxyphenyl)pentan-2-one (27) (Table 4, entry 10). From 4-bromoanisole (0.187 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (0.4 μmol), product **27** was obtained in 41% (0.079 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, J=8.7 Hz, 2H), 6.83 (d, J=8.7 Hz, 2H), 3.77 (s, 3H), 3.25 (sext., J=6.9 Hz, 1H), 2.71 (dd, J=16.1, 6.1 Hz, 1H), 2.61 (dd, J=16.2, 7.7 Hz, 1H), 2.04 (s, 3H), 1.24 (d, J=6.9 Hz, 3H).

3.2.28. 4-[4-(Dimethylamino)phenyl]pentan-2-one (28) (Table 4, entry 12). From 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (0.4 μmol), product **28** was obtained in 46% (0.095 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, J=8.7 Hz, 2H), 6.70 (d, J=8.7 Hz, 2H), 3.21 (sext., J=7.0 Hz, 1H), 2.91 (s, 6H), 2.71 (dd, J=15.9, 6.7 Hz, 1H), 2.60 (dd, J=15.9, 8.0 Hz, 1H), 2.04 (s, 3H), 1.23 (d, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.5, 149.2, 134.3, 127.3, 113.0, 52.4, 40.8, 34.7, 30.5, 22.2; MS (70 eV); *m/z* (%) 205 ($M^{+\cdot}$, 83); $C_{13}H_{19}NO$: calcd C 76.06, H 9.33; Found C 76.13, H 9.25.

3.2.29. 4-(6-Methoxynaphthalen-2-yl)-pentan-2-one (29) (Table 4, entry 16). From 6-methoxy-2-bromonaphthalene (0.237 g, 10 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (4 μmol), product **29** was obtained in 77% (0.187 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J=8.5 Hz, 2H), 7.54 (s, 1H), 7.31 (d, J=8.5 Hz, 1H), 7.15–7.07 (m, 2H), 3.90 (s, 3H), 3.43 (sext., J=7.0 Hz, 1H), 2.83 (dd, J=16.2, 6.6 Hz, 1H), 2.71 (dd, J=16.3, 7.8 Hz, 1H), 2.05 (s, 3H), 1.32 (d, J=6.9 Hz, 3H).

3.2.30. 4-(4-Fluorophenyl)pentan-2-one (30) (Table 4, entry 20). From 4-fluorobromobenzene (0.175 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **30** was obtained in 66% (0.119 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (dd, J=8.4, 5.4 Hz, 2H), 6.96 (t, J=8.7 Hz, 2H), 3.29 (sext., J=7.0 Hz, 1H), 2.72 (dd, J=16.4, 6.7 Hz, 1H), 2.63 (dd, J=16.3, 7.5 Hz, 1H), 2.05 (s, 3H), 1.24 (d, J=7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.6, 161.3 (d, J_{C-F}=243.8 Hz), 141.7, 128.1 (d, $^3J_{C-F}$=8.0 Hz), 115.2 (d, $^2J_{C-F}$=20.6 Hz), 52.0, 34.7, 30.6, 22.1; MS (70 eV); *m/z* (%) 180 ($M^{+\cdot}$, 100); $C_{11}H_{13}FO$: calcd C 73.31, H 7.27; Found C 73.29, H 7.40.

3.2.31. 4-(4-Benzoylphenyl)pentan-2-one (31) (Table 4, entry 23). From 4-bromobenzophenone (0.261 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **31** was obtained in 76% (0.202 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J=7.3 Hz, 2H), 7.75 (d, J=8.2 Hz, 2H), 7.57 (t, J=7.3 Hz, 1H), 7.47 (t, J=7.3 Hz, 2H), 7.32 (d, J=8.2 Hz, 2H), 3.40 (sext., J=7.0 Hz, 1H), 2.80 (dd, J=16.7, 6.7 Hz, 1H), 2.71 (dd, J=16.3, 7.5 Hz, 1H), 2.09 (s, 3H), 1.29 (d, J=7.0 Hz, 3H).

3.2.32. 4-(4-Cyanophenyl)pentan-2-one (32) (Table 4, entry 27). From 4-bromobenzonitrile (0.182 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **32** was obtained in 82% (0.154 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J=8.4 Hz, 2H), 7.31 (d, J=8.4 Hz, 2H), 3.42 (sext., J=7.0 Hz, 1H), 2.76 (dd, J=17.0, 6.8 Hz, 1H), 2.71 (dd, J=17.1, 7.3 Hz, 1H), 2.10 (s, 3H), 1.26 (d, J=7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.6, 151.8, 132.4, 127.7, 118.9, 110.2, 51.2, 35.2, 30.5, 21.6.

3.2.33. 4-(*o*-Tolyl)pentan-2-one (33) (Table 4, entry 29). From 2-bromotoluene (0.171 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (1 μmol), product **33** was obtained in 51% (0.090 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.03 (m, 4H), 3.55 (sext., J=6.9 Hz, 1H), 2.75 (dd, J=16.5, 6.0 Hz, 1H), 2.64 (dd, J=16.5, 8.3 Hz, 1H), 2.36 (s, 3H), 2.07 (s, 3H), 1.21 (d, J=6.8 Hz, 3H).

3.2.34. 4-Naphthalen-1-yl-pentan-2-one (34) (Table 4, entry 34). From 1-bromonaphthalene (0.207 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **34** was obtained in 97% (0.206 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J=8.2 Hz, 1H), 7.86 (d, J=8.4 Hz, 1H), 7.72 (d, J=8.0 Hz, 1H), 7.57–7.33 (m, 4H), 4.21 (sext., J=6.8 Hz, 1H), 2.91 (dd, J=16.9, 4.8 Hz, 1H), 2.77 (dd, J=16.9, 9.0 Hz, 1H), 2.13 (s, 3H), 1.40 (d, J=6.8 Hz, 3H).

3.2.35. 4-(3-Pyridinyl)pentan-2-one (35) (Table 4, entry 37). From 3-bromopyridine (0.158 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **35** was obtained in 72% (0.118 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, J=1.5 Hz, 1H), 8.44 (dd, J=4.7, 1.5 Hz, 1H), 7.55 (dt, J=7.9, 2.0 Hz, 1H), 7.24 (dd, J=7.9, 4.7 Hz, 1H), 3.35 (sext., J=7.1 Hz, 1H), 2.77 (dd, J=15.6, 4.4 Hz, 1H), 2.72 (dd, J=15.7, 7.1 Hz, 1H), 2.08 (s, 3H), 1.28 (d, J=7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.8, 148.4, 147.4, 141.6, 134.8, 123.6, 51.3, 32.8, 30.5, 21.7; MS (70 eV); *m/z* (%) 163 ($M^{+\cdot}$, 28); $C_{10}H_{13}NO$: calcd C 73.59, H 8.03; Found C 73.38, H 8.00.

3.2.36. 4-(3-Quinolyl)pentan-2-one (36) (Table 4, entry 41). From 3-bromoquinoline (0.208 g, 1 mmol), pent-3-en-2-ol (0.103 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **36** was obtained in 78% (0.167 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.83 (d, J=2.3 Hz, 1H), 8.08 (d, J=8.4 Hz, 1H), 7.95 (d, J=2.3 Hz, 1H), 7.77 (d, J=7.8 Hz, 1H), 7.66 (t, J=7.0 Hz, 1H), 7.52 (t, J=7.0 Hz, 1H), 3.55 (sext., J=7.0 Hz, 1H), 2.89 (dd, J=17.0, 6.8 Hz, 1H), 2.80 (dd, J=17.0, 7.5 Hz, 1H), 2.10 (s, 3H), 1.38 (d, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.8, 150.6, 146.8, 138.7, 133.1, 129.0, 128.9, 128.1, 127.5, 126.8, 51.4, 32.8, 30.6, 21.7; MS (70 eV); *m/z* (%) 213 ($M^{+\cdot}$, 92); $C_{14}H_{15}NO$: calcd C 78.84, H 7.09; Found C 78.97, H 6.98.

3.2.37. 4-Phenyloctan-2-one (37) (Table 5, entry 1). From bromobenzene (0.157 g, 1 mmol), oct-3-en-2-ol (0.154 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (4 μmol), product **37** was obtained in 55% (0.112 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.26 (m, 2H), 7.22–7.13 (m, 3H), 3.15–3.03 (m, 1H), 2.70 (d, J=7.2 Hz, 2H), 2.00 (s, 3H), 1.65–1.40 (m, 2H), 1.30–1.00 (m, 4H), 0.81 (t, J=7.0 Hz, 3H).

3.2.38. 4-(4-Methoxyphenyl)octan-2-one (38) (Table 5, entry 4). From 4-bromoanisole (0.187 g, 1 mmol), oct-3-en-2-ol (0.154 g, 1.2 mmol), K_2CO_3 (0.276 g, 2 mmol) and Pd complex (10 μmol), product **38** was obtained in 47% (0.110 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, J=8.7 Hz, 2H), 6.82 (d, J=8.7 Hz, 2H), 3.77 (s, 3H), 3.10–2.98 (m, 1H), 2.66 (d, J=7.3 Hz, 2H), 1.99 (s, 3H), 1.65–1.40 (m, 2H), 1.30–1.00 (m, 4H), 0.81 (t, J=7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.3, 158.0, 128.3, 127.0, 113.8, 55.2, 51.2, 40.6, 36.3, 30.7, 29.7, 22.6, 14.0; MS (70 eV); *m/z* (%) 234 ($M^{+\cdot}$, 60); $C_{15}H_{22}O_2$: calcd C 76.88, H 9.46; Found C 76.71, H 9.38.

3.2.39. 4-(4-Benzoylphenyl)octan-2-one (39) (Table 5, entry 9). From 4-bromobenzophenone (0.261 g, 1 mmol), oct-3-en-2-ol (0.154 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **39** was obtained in 75% (0.231 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.70 (m, 4H), 7.55 (t, J=7.5 Hz, 1H), 7.46 (t, J=7.5 Hz, 2H), 7.28 (d, J=8.2 Hz, 2H), 3.26–3.15 (m, 1H), 2.75 (d, J=7.1 Hz, 2H), 2.04 (s, 3H), 1.70–1.45 (m, 2H), 1.40–1.05 (m, 4H), 0.81 (t, J=7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.3, 196.4, 149.9, 137.7, 135.6, 132.2, 130.4, 129.9, 128.2, 127.4, 50.4, 41.0, 35.9, 30.6, 29.5, 22.5, 13.8; MS (70 eV); *m/z* (%) 308 ($M^{+\cdot}$, 92); $C_{21}H_{24}O_2$: calcd C 81.78, H 7.84; Found C 81.65, H 8.03.

3.2.40. 2-Phenylheptan-4-one (40) (Table 6, entry 3). From bromobenzene (0.157 g, 1 mmol), hept-2-en-4-ol (0.137 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (1 μmol), product **40** was obtained in 69% (0.132 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J=7.4 Hz, 2H), 7.40–7.10 (m, 3H), 3.31 (sext., J=7.0 Hz, 1H), 2.72 (dd, J=16.1, 6.5 Hz, 1H), 2.61 (dd, J=16.2, 7.9 Hz, 1H), 2.35–2.20 (m, 2H), 1.53 (sext., J=7.4 Hz, 2H), 1.25 (d, J=7.0 Hz, 3H), 0.84 (t, J=7.5 Hz, 3H).

3.2.41. 2-(4-Methoxyphenyl)heptan-4-one (41) (Table 6, entry 6). From 4-bromoanisole (0.187 g, 1 mmol), hept-2-en-4-ol (0.137 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (10 μmol), product **41** was obtained in 71% (0.156 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, J=8.6 Hz, 2H), 6.82 (d, J=8.6 Hz, 2H), 3.76 (s, 3H), 3.42 (sext., J=7.0 Hz, 1H), 2.67 (dd, J=16.0, 6.7 Hz, 1H), 2.57 (dd, J=16.0, 7.7 Hz, 1H), 2.32–2.18 (m, 2H), 1.52 (sext., J=7.4 Hz, 2H), 1.22 (d, J=6.9 Hz, 3H), 0.83 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.1, 157.9, 138.3, 127.6, 113.8, 55.1, 51.3, 45.3, 34.6, 22.1, 17.0, 13.6; $C_{14}H_{20}O_2$: calcd C 76.33, H 9.15; Found C 76.04, H 8.94.

3.2.42. 2-(4-Benzoylphenyl)heptan-4-one (42) (Table 6, entry 9). From 4-bromobenzophenone (0.261 g, 1 mmol), hept-2-en-4-ol (0.137 g, 1.2 mmol), $NaHCO_3$ (0.168 g, 2 mmol) and Pd complex (1 μmol), product **42** was obtained in 64% (0.189 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80–7.71 (m, 4H), 7.56 (t, J=7.4 Hz, 1H), 7.46 (d, J=7.4 Hz, 2H), 7.31 (d, J=8.2 Hz, 2H), 3.42 (sext., J=7.0 Hz, 1H), 2.76 (dd, J=16.5, 6.7 Hz, 1H), 2.66 (dd, J=16.5, 7.5 Hz, 1H), 2.38–2.23 (m, 2H), 1.55 (sext., J=7.4 Hz, 2H), 1.28 (d, J=7.0 Hz, 3H), 0.85 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.4, 196.4, 151.4, 137.8, 135.6, 132.2, 130.5, 129.9, 128.2, 126.8, 50.6, 45.4, 35.2, 21.8, 17.1, 13.6; MS (70 eV); *m/z* (%) 294 ($M^{+\cdot}$, 100); $C_{20}H_{22}O_2$: calcd C 81.60, H 7.53; Found C 81.73, H 7.38.

Registry no. Beilstein: **12**, 9393189; CAS: **20**, 65170-86-7; **21**, 104-20-1; **22**, 63416-61-5; **23**, 57918-94-2; **24**, 17013-10-9; **25**, 451-25-2; **27**, 18344-26-8; **29**, 56600-70-5; **31**, 65170-91-4; **32**, 189119-45-7; **33**, 652994-34-8; **34**, 182482-36-6; **37**, 35583-33-6; 40, 59540-81-7.

Acknowledgements

We thank CNRS for financial support.

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