Heck Reaction of Aryl Bromides with Pent-4-en-2-ol, 2-Phenylpent-4-en-2-ol, or Hept-6-en-3-ol Catalysed by a Palladium–Tetraphosphine Complex

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Received 2 June 2005

Abstract: The tetraphosphine *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane in combination with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ affords a very efficient catalyst for the Heck reaction of aryl bromides with pent-4-en-2-ol, 2-phenylpent-4-en-2-ol, or hept-6-en-3-ol. With pent-4-en-2-ol or hept-6-en-3-ol, the selectivity in favour of the formation of the 5-arylpentan-2-one or 7-arylheptan-3-one derivatives, respectively, depends on the substituents on the aryl bromide and on the base. Sterically congested and electron-rich aryl bromides gave selectively the linear ketones by migration of the double bond. With electron-poor aryl bromides, the formation of large amounts of (*E*)-1-arylalk-1-enol derivatives or side products was observed in some cases. Similar reactions rates were observed with electron-poor and electron-rich aryl bromides. Several reactions can be performed with as little as 0.01% catalyst. A wide variety of substituents, such as methoxy, dimethylamino, fluoro, trifluoromethyl, acetyl, benzoyl, formyl, carboxy, or cyano groups, on the aryl bromides are tolerated. The coupling of very sterically congested aryl bromides, such as 9-bromoanthracene or 2-bromo-1,3,5-triisopropylbenzene, also proceeds in good yields. Heck reaction with 2-phenylpent-4-en-2-ol gave the expected (*E*)-5-aryl-2-phenylpent-4-en-2-ol derivatives in high turnover numbers (TONs) and high selectivities in most cases. However, with some electron-poor aryl bromides the selective formation of 1-arylprop-1-ene derivatives resulting from a C–C bond cleavage was observed.

Key words: Heck reaction, aryl bromides, palladium catalysis, alkenols

The palladium-catalysed so-called Heck reaction is one of the most powerful methods for the formation of C–C bonds.[1–6] In recent years, several thermally stable palladium catalysts have been successfully used in Heck reactions, but most of these catalysts have not been tested for use in the synthesis of enols or ketones by coupling aryl halides with β- or γ-alk-1-enol derivatives. The reaction of aryl halides with β- or γ-alk-1-enol derivatives can afford the corresponding arylalkenols, or β- or γ-aryl-substituted ketones by migration of the double bond, and is a very powerful method for the preparation of such compounds.[7] Most of the results described for this reaction were obtained using palladium(II) acetate $[Pd(OAc)_2]$ in association with ammonium halides and in the absence of ligand in most cases.[8–16] As a catalyst, $Pd(OAc)_2$ was not very efficient in terms of the substrate/catalyst ratio required and 2–45% catalyst had to be used. Moreover, several results were described with very reactive, but expensive aryl iodides.[8–10] We found only one example of the formation of such products using triphenylphosphine (Ph_3P) ligands.[17] In this paper, the reaction of pent-4-en-2-ol with 2-bromothiophene in the presence of 1% $Pd(OAc)_2$ and 3% Ph_3P as catalyst gave the corresponding ketone in 55% yield.[17] However, to our knowledge, low-catalyst loading Heck reactions using β- or γ-alk-1-enol derivatives have not been reported.

In order to obtain a highly stable palladium catalyst, we have prepared the tetraphosphine ligand *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane or Tedicyp[18] (Figure 1). We have already reported the results obtained for allylic substitution,[18] Suzuki cross coupling,[19] and the Sonogashira reaction[20] using Tedicyp as the ligand. We have also reported several results obtained for the Heck reaction.[21–31] In order to further establish the requirements for a successful Heck reaction using our catalyst, we herein report the synthesis of γ- or δ-aryl-substituted ketones by the reaction of aryl bromides with pent-4-en-2-ol or hept-6-en-3-ol, and also the synthesis of 5-aryl-2-phenylpent-4-en-2-ol derivatives by using 2-phenylpent-4-en-2-ol as reactant.

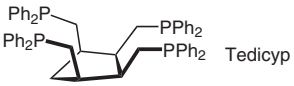


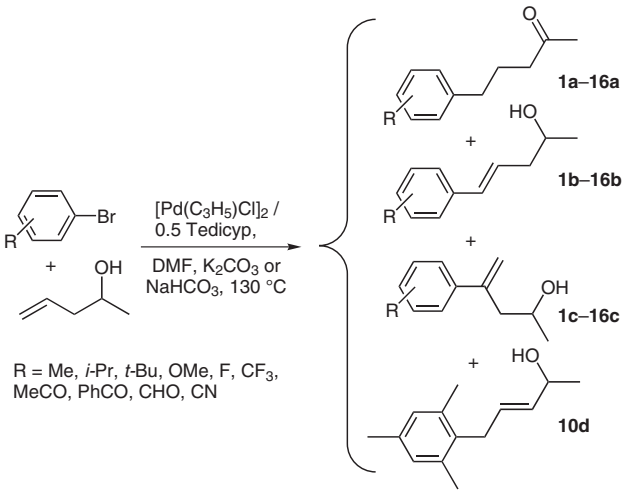
Figure 1

For this study, based on our previous results,[21–31] *N*,*N*-dimethylformamide (DMF) was chosen as the solvent and potassium carbonate (K_2CO_3) as the base. The reactions were performed at 130 °C, under argon, in the presence of a 1:2 ratio of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/Tedicyp as catalyst.

First, we studied the coupling of pent-4-en-2-ol with several aryl bromide derivatives (Scheme 1, Table 1). The *para* substituents on the aryl bromide have a minor influence on the selectivity for this reaction. We observed that in most cases the formation of the linear ketones **1a–7a** in 60–81% selectivity together with the linear and branched nonisomerised alcohols **1b–7b** and **1c–7c** (Scheme 1, Table 1, entries 1, 3, 6, 9, 11, 13 and 15). Similar reactions rates were observed with electron-poor and electron-rich aryl bromides. These results seem to indicate that the ox-

SYNTHESIS 2005, No. 20, pp 3589–3602
Advanced online publication: 25.10.2005
DOI: 10.1055/s-2005-918427; Art ID: Z10705SS

idative addition of aryl bromides to palladium is not the rate-determining step of this reaction. Turnover numbers (TONs) of up to 19000 can be achieved with this catalyst (Table 1, entry 16). In order to improve the selectivity of these reactions we also studied the influence of bases. In the presence of sodium hydrogen carbonate ($NaHCO_3$), higher selectivities in favour of the formation of isomers **1a–7a** were generally observed (Table 1, entries 2, 4, 5, 7, 10, 12, 14 and 17). For example, 4-bromoacetophenone in the presence of K_2CO_3 gave the isomer **1a** in 77% selectivity and with $NaHCO_3$ a selectivity of 89% was obtained (Table 1, entries 1 and 2, respectively). However, with electron-rich aryl bromides slower reactions were observed in the presence of this base.



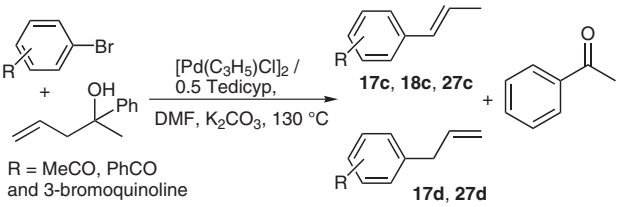
Scheme 1

Then, we studied the influence of the presence of *ortho* substituents on the aryl bromides on the selectivity and on the reaction rate with K_2CO_3 and $NaHCO_3$ as bases. We observed that the coupling of 1-bromo-2-(trifluoromethyl)benzene or 2-bromotoluene with pent-4-en-2-ol proceeds in the presence of 0.01 and 0.1% catalyst with K_2CO_3 (Table 1, entries 18, 20 and 21); the ketones **8a** and **9a** were obtained in 76–78% selectivity. The reactions performed using $NaHCO_3$ with these two substrates were much slower (Table 1, entries 19 and 22).

Next, we tried to evaluate the difference in selectivity for this reaction using mono- and di-*ortho*-substituted aryl bromides with K_2CO_3, and we observed that even highly hindered aryl bromides could be coupled efficiently with pent-4-en-2-ol. For example, in the reaction with 2-bromo-1,3,5-trimethylbenzene and 9-bromoanthracene in the presence of 0.01 and 0.1% catalyst, the corresponding ketones **10a** and **11a** were obtained in 4900 and 1000 TONs, respectively (Table 1, entries 24 and 25). Because of steric reasons, in the reactions with these two di-*ortho*-substituted aryl bromides very high selectivities in favour of the formation of the ketones were observed. This coupling reaction also proceeds using highly sterically hindered 2-bromo-1,3,5-triisopropylbenzene. With this substrate, the ketone **12a** was selectively obtained, but the use of 0.1–0.4% catalyst was necessary (Table 1, entries 26 and 27).

We have also investigated this reaction using four heteroaryl bromides. The expected linear ketones **13a–16a** were obtained in moderate yields in the presence of 0.1–1% catalyst with 2- or 3-bromothiophenes and 0.01–0.4% catalyst with 3-bromopyridine and 3-bromoquinoline (Table 1, entries 28–38). In all cases, significant amounts of the linear alcohols **13b–16b** were also obtained in the reaction when K_2CO_3 was used as base. These results seem to indicate that with these heteroaryl bromides, a possible interaction between the nitrogen or sulfur atom and the palladium complex affects the selectivity of the reaction. With these substrates, better selectivity, but lower TONs were obtained using $NaHCO_3$ as base.

We then studied the coupling reactions of a variety of aryl bromides with 2-phenylpent-4-en-2-ol (Schemes 2 and 3, Table 2). With this tertiary alcohol, the formation of an aryl ketone by migration of the double bond is not possible; therefore, the selectivity of the reaction should be in favour of the formation of the (*E*)-5-aryl-2-phenylpent-4-en-2-ol derivatives **19a–26a**. However, we observed that in the presence of electron-poor aryl bromides, such as 4-bromoacetophenone, 4-bromobenzophenone, or 3-bromoquinoline, the formation of such compounds was not observed. In the reaction with these substrates, an aryl–allyl elimination occurs and the arylpropene derivatives **17c**, **17d**, **18c**, **27c**, and **27d** were obtained, together with acetophenone (Scheme 2, Table 2, entries 1–4, 21, and 22). Even at a lower temperature (100 °C), or in the presence of $NaHCO_3$ as base, the formation of these arylpropenes was observed, but the reactions were slower. Similar allyl eliminations via the selective cleavage of C–C bonds in homoallylic alcohols at elevated temperature[32] or catalysed by ruthenium or rhodium complexes have already been described.[33]



Scheme 2

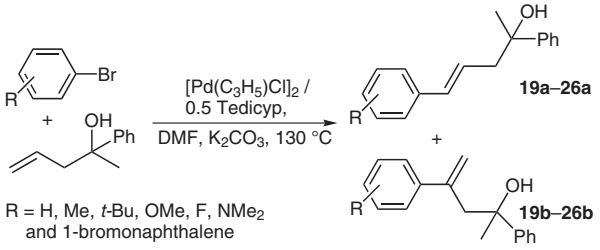
With electron-rich aryl bromides, and even with 1-bromo-4-fluorobenzene, this C–C bond cleavage was not observed, and the (*E*)-5-aryl-2-phenylpent-4-en-2-ol derivatives **19a–26a** were obtained in high selectivities (Scheme 3, Table 2, entries 5–20). Bromobenzene and 1-bromo-4-fluorobenzene gave mainly derivatives **19a** and **20a**, respectively, but 6–9% of the branched alcohols **19b** and **20b** and approximately 10% of unidentified isomers were also observed (Table 2, entries 5–8). 1-Bromo-4-*tert*-butylbenzene, 4-bromoanisole, 2-bromo-6-methoxynaphthalene, and 1-bromo-4-(dimethylamino)benzene also led to linear/branched alcohol mixtures in 91:9 to

Table 1 Palladium-Catalysed Coupling of Aryl Bromides with Pent-4-en-2-ol[a]

Entry	Aryl bromide	Ratio (substrate/catalyst)	Product	Ratio (**a/b/c**)	Yield[b] (%)
1	4-bromoacetophenone	1000	**1a–c**	77:21:2	100
2	4-bromoacetophenone	1000	**1a** and **b**	89:11:0	100 (77)[c]
3	4-bromobenzophenone	1000	**2a–c**	64:32:4	100
4	4-bromobenzophenone	1000	**2a** and **b**	87:13:0	100 (80)[c]
5	4-bromobenzophenone	5000	**2a–c**	84:15:1	49[c]
6	4-bromobenzaldehyde	1000	**3a–c**	62:35:3	100
7	4-bromobenzaldehyde	1000	**3a–c**	74:25:1	100 (70)[c]
8	4-bromobenzaldehyde	10000	**3a–c**	57:41:2	8[c]
9	4-bromobenzonitrile	1000	**4a–c**	60:35:5	100 (55)
10	4-bromobenzonitrile	1000	**4a–c**	84:15:1	72[c]
11	1-bromo-4-fluorobenzene	10000	**5a–c**	69:26:5	100
12	1-bromo-4-fluorobenzene	5000	**5a–c**	86:13:1	100 (81)[c]
13	1-bromo-4-*tert*-butylbenzene	25000	**6a–c**	81:18:1	100 (75)
14	1-bromo-4-*tert*-butylbenzene	1000	**6a–c**	85:14:1	80[c]
15	4-bromoanisole	10000	**7a–c**	69:26:5	100 (63)
16	4-bromoanisole	100000	**7a–c**	65:32:3	19
17	4-bromoanisole	1000	**7a** and **b**	88:12:0	69[c]
18	1-bromo-2-(trifluoromethyl)benzene	10000	**8a** and **b**	78:22:0	100 (73)
19	1-bromo-2-(trifluoromethyl)benzene	1000	**8a–c**	90:7:3	84[c]
20	2-bromotoluene	1000	**9a–c**	76:22:2	100
21	2-bromotoluene	10000	**9a–c**	77:22:1	98 (72)
22	2-bromotoluene	1000	**9a** and **b**	78:22:0	25[c]
23	2-bromo-1,3,5-trimethylbenzene	1000	**10a**, **c**, and **d**	81:0:2[d]	100 (60)
24	2-bromo-1,3,5-trimethylbenzene	10000	**10a**, **c**, and **d**	88:0:1[e]	49
25	9-bromoanthracene	1000	**11a** and **c**	99:0:1[f]	100 (81)
26	2-bromo-1,3,5-triisopropylbenzene	250	**12a**	100:0:0[f]	100 (46)
27	2-bromo-1,3,5-triisopropylbenzene	1000	**12a**	100:0:0[f]	50
28	3-bromopyridine	1000	**13a–c**	61:32:7	100
29	3-bromopyridine	250	**13a** and **b**	89:11:0	100 (80)[c]
30	3-bromopyridine	1000	**13a** and **b**	83:17:0	53[c]
31	3-bromoquinoline	1000	**14a–c**	56:37:7	100
32	3-bromoquinoline	10000	**14a–c**	57:36:7	69
33	3-bromoquinoline	1000	**14a–c**	87:12:1	100 (79)[c]
34	2-bromothiophene	250	**15a–c**	48:43:9	76
35	2-bromothiophene	250	**15a–c**	66:31:3	74 (42)[c]
36	3-bromothiophene	250	**16a–c**	40:53:7	100 (36)
37	3-bromothiophene	1000	**16a–c**	41:51:8	87
38	3-bromothiophene	100	**16a–c**	79:19:2	48[c]

[a] See Scheme 1; conditions: ratio of $[Pd(\eta^3\text{-}C_3H_5)\,Cl]_2$/Tedicyp 1:2, aryl bromide (1 mmol), pent-4-en-2-ol (2 mmol), K_2CO_3 (2 mmol), DMF, argon, 130 °C, 20 h; GC and NMR spectroscopic yields of the product mixtures are given.
[b] Yields in parentheses are isolated yields of the ketone **a**.
[c] $NaHCO_3$ (2 mmol) was used as base.
[d] The formation of alcohol **10d** (17%) was also observed.
[e] The formation of alcohol **10d** (11%) was also observed.
[f] Debromination product was also observed.

96:4 ratios (Table 2, entries 9–16). With these substrates, only traces of unidentified isomers were detected by GC and NMR spectroscopy. The reactivity of the two *ortho*-substituted aryl bromides, 2-bromotoluene and 1-bromonaphthalene was also studied. In both cases, high selectivities in favour of the formation of linear alcohols **25a** and **26a** were observed (Table 2, entries 17–20).



Scheme 3

Finally, we studied the reactivity of hept-6-en-3-ol towards several aryl bromides (Scheme 4, Table 3). Few results have been described with such γ-alk-1-enols.[16,34,35] The corresponding linear aryl-substituted ketone was obtained in 85% selectivity by Larock et al. using iodobenzene in the presence of a mixture of lithium acetate, lithium chloride, and tetrabutylammonium chloride with 3% $Pd(OAc)_2$ as catalyst. The formation of 15% of a branched alcohol, such as **c** (Scheme 4), was also observed. Wolfe et al. recently described the selective direct synthesis of tetrahydrofuran derivatives, such as **d** (Scheme 4), by intramolecular cyclisation in the presence of the strong base sodium *tert*-butoxide in tetrahydrofuran.[34,35] They have also reported that in polar solvents, such as DMF, little or no tetrahydrofuran compound was obtained.

With our catalyst and using standard conditions (DMF, K_2CO_3, 130 °C), we observed the formation of mixtures of isomers in most cases. Potassium carbonate appeared to be strong enough to promote the formation of the tetrahydrofuran products **d** when electron-poor aryl bromides were used, even in DMF (Table 3, entries 1, 3, 6, 8, 11, and 16). On the other hand, in the presence of electron-rich aryl bromides, such as 1-bromo-4-*tert*-butylbenzene, 4-bromoanisole, 2-bromotoluene, 1-bromonaphthalene, 2-bromo-1,3,5-trimethylbenzene, or 2-bromo-1,3,5-triisopropylbenzene, the formation of the corresponding tetrahydrofuran derivatives was not observed, and the aryl-substituted ketones **33a**, **34a**, **36a**–**39a** were obtained in high selectivities (80–100%) and good yields (Table 3, entries 13–15 and 18–23). With 1-bromo-4-*tert*-butylbenzene and 4-bromoanisole, the formation of the aryl alcohols **33b** and **c** and **34b** and **c**, respectively, in low yields was also observed. Because of steric reasons, such aryl alcohols were observed in very low yields or were not de-

Table 2 Palladium-Catalysed Coupling of Aryl Bromides with 2-Phenylpent-4-en-2-ol[a]

Entry	Aryl bromide	Ratio (substrate/catalyst)	Product	Ratio (**a/b/c/d**)	Yield[b] (%)
1	4-bromoacetophenone	250	**17c**	0:0:100:0	100 (81)
2	4-bromoacetophenone	1000	**17c** and **d**	0:0:85:15	44
3	4-bromobenzophenone	250	**18c**	0:0:100:0	100 (78)
4	4-bromobenzophenone	1000	**18c**	0:0:100:0	70
5	1-bromo-4-fluorobenzene	10000	**19a** and **b**	93:7:0:0[c]	100 (71)
6	1-bromo-4-fluorobenzene	25000	**19a** and **b**	93:7:0:0[c]	96
7	bromobenzene	1000	**20a** and **b**	94:6:0:0[c]	100 (70)
8	bromobenzene	10000	**20a** and **b**	91:9:0:0[c]	82
9	1-bromo-4-*tert*-butylbenzene	10000	**21a** and **b**	93:7:0:0[d]	100 (84)
10	1-bromo-4-*tert*-butylbenzene	25000	**21a** and **b**	94:6:0:0[d]	67
11	4-bromoanisole	10000	**22a** and **b**	92:8:0:0[d]	100 (84)
12	4-bromoanisole	25000	**22a** and **b**	92:8:0:0[d]	96
13	2-bromo-6-methoxynaphthalene	1000	**23a** and **b**	95:5:0:0[d]	100 (82)
14	2-bromo-6-methoxynaphthalene	5000	**23a** and **b**	96:4:0:0[d]	44
15	1-bromo-4-(dimethylamino)benzene	100	**24a** and **b**	91:9:0:0[d]	100 (86)
16	1-bromo-4-(dimethylamino)benzene	250	**24a** and **b**	91:9:0:0[d]	70
17	2-bromotoluene	1000	**25a** and **b**	95:5:0:0	100 (73)
18	2-bromotoluene	10000	**25a** and **b**	96:4:0:0	66
19	1-bromonaphthalene	1000	**26a** and **b**	96:4:0:0[c]	100 (70)
20	1-bromonaphthalene	10000	**26a** and **b**	96:4:0:0[c]	27
21	3-bromoquinoline	250	**27c** and **d**	0:0:65:35	100 (56)
22	3-bromoquinoline	1000	**27c** and **d**	0:0:52:48	50

[a] See Schemes 2 and 3; conditions: ratio of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/Tedicyp 1:2, aryl bromide (1 mmol), 2-phenylpent-4-en-2-ol (2 mmol), K_2CO_3 (2 mmol), DMF, argon, 130 °C, 20 h; GC and NMR spectroscopic yields of the product mixtures are given.
[b] Yields in parentheses are isolated yields of products **a** or **c**.
[c] The formation of other isomers was also observed by GC and NMR spectroscopy.
[d] Traces of other isomers were also detected by GC and NMR spectroscopy.

tected at all in the reactions performed with *ortho*-substituted aryl bromides.

In order to reduce the amount of tetrahydrofuran derivative obtained in the reactions of the electron-poor aryl bromides, we performed a few reactions using other bases. We observed that in the presence of $NaHCO_3$, much higher selectivities (up to 100%) in favour of the formation of ketones **a** were observed (Table 3, entries 2, 4, 5, 7, 9, 10, 12, and 17). For example, with methyl 4-bromobenzoate and K_2CO_3 or $NaHCO_3$ as bases, selectivities of 30 and 90% towards the formation of ketone **30a** were obtained, respectively (Table 3, entries 6 and 7).

Finally, we studied the reaction with heteroaryl bromides. 3-Bromopyridine and 3-bromoquinoline gave the ketones **40a** and **41a**, respectively, in high selectivities using $NaHCO_3$ as base (Table 3, entries 25 and 27); however, 2- and 3-bromothiophene gave mixtures of isomers (Table 3, entries 28–32).

Table 3 Palladium-Catalysed Coupling of Aryl Bromides with Hept-6-en-3-ol[a]

Entry	Aryl bromide	Ratio (substrate/catalyst)	Product	Ratio (**a/b/c/d**)	Yield[b] (%)
1	4-bromoacetophenone	1000	**28a–d**	67:14:3:16	100
2	4-bromoacetophenone	1000	**28a** and **b**	93:7:0:0	100 (83)[c]
3	4-bromobenzophenone	1000	**29a–d**	52:12:4:32	100
4	4-bromobenzophenone	1000	**29a–c**	89:10:1:0	100 (81)[c]
5	4-bromobenzophenone	10000	**29a–d**	78:18:1:3	34[c]
6	methyl 4-bromobenzoate	25000	**30a–d**	30:25:7:38	100
7	methyl 4-bromobenzoate	1000	**30a–c**	90:9:1:0	100 (80)[c]
8	1-bromo-4-(trifluoromethyl)benzene	1000	**31a–d**	69:14:3:14	100
9	1-bromo-4-(trifluoromethyl)benzene	1000	**31a** and **b**	94:6:0:0	100 (82)[c]
10	1-bromo-4-(trifluoromethyl)benzene	10000	**31a** and **b**	94:6:0:0	21[c]
11	1-bromo-4-fluorobenzene	10000	**32a–d**	77:12:7:4	100
12	1-bromo-4-fluorobenzene	1000	**32a–c**	91:8:1:0	80 (71)[c]
13	1-bromo-4-*tert*-butylbenzene	10000	**33a–c**	83:14:3:0	100 (75)
14	4-bromoanisole	100	**34a–c**	80:15:5:0	100
15	4-bromoanisole	25000	**34a–c**	80:15:5:0	100 (74)
16	1-bromo-2-(trifluoromethyl)benzene	5000	**35a, b,** and **d**	72:7:0:21	100
17	1-bromo-2-(trifluoromethyl)benzene	1000	**35a**	100:0:0:0	81 (74)[c]
18	2-bromotoluene	10000	**36a** and **b**	91:9:0:0	100 (80)
19	1-bromonaphthalene	1000	**37a** and **b**	97:3:0:0	100 (83)
20	1-bromonaphthalene	10000	**37a** and **b**	97:3:0:0	97
21	2-bromo-1,3,5-trimethylbenzene	1000	**38a** and **e**	86:0:0:0[d]	100 (77)
22	2-bromo-1,3,5-trimethylbenzene	10000	**38a** and **e**	86:0:0:0[d]	68
23	2-bromo-1,3,5-triisopropylbenzene	100	**39a**	100:0:0:0[e]	100 (69)
24	3-bromopyridine	1000	**40a–d**	56:18:4:22	100
25	3-bromopyridine	1000	**40a–c**	91:8:1:0	100 (83)[c]
26	3-bromoquinoline	1000	**41a–d**	50:21:6:23	100
27	3-bromoquinoline	1000	**41a–d**	89:8:2:1	100 (80)[c]
28	2-bromothiophene	250	**42a–d**	46:29:8:17	100 (41)
29	2-bromothiophene	1000	**42a–d**	49:17:2:32	92
30	2-bromothiophene	250	**42a–c**	44:52:4:0	100[c]
31	3-bromothiophene	500	**43a–c**	65:28:7:0	100 (56)
32	3-bromothiophene	1000	**43a–c**	55:33:12:0	75

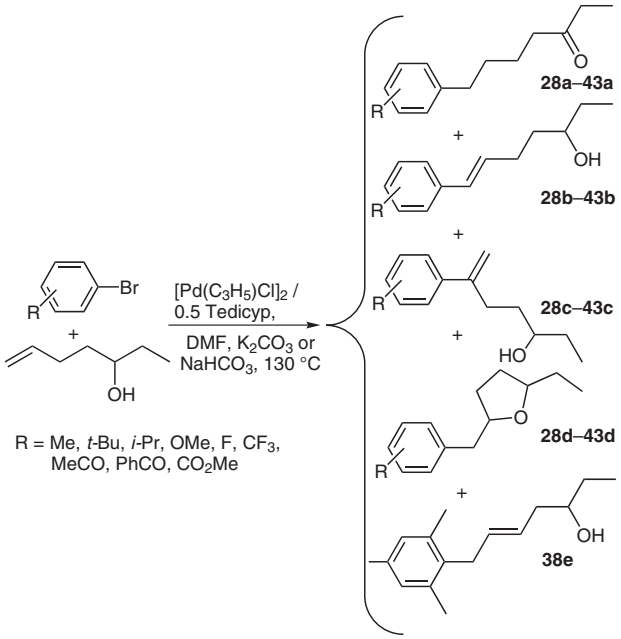
[a] See Scheme 4; conditions: ratio of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/Tedicyp 1:2, aryl halide (1 mmol), hept-6-en-3-ol (2 mmol), K_2CO_3 (2 mmol), DMF, argon, 130 °C, 20 h; GC and NMR spectroscopic yields of the product mixtures are given; tetrahydrofuran derivatives **d** are mixtures of diastereomers.

[b] Yields in parentheses are isolated yields.

[c] $NaHCO_3$ (2 mmol) was used as base.

[d] The formation of alcohol **38e** (14%) was also observed.

[e] Debromination product was also observed.



Scheme 4

The use of the tetradentate ligand Tedicyp associated to a palladium complex provides a convenient catalyst for the reaction of pent-4-en-2-ol, 2-phenylpent-4-en-2-ol, or hept-6-en-3-ol with substituted aryl bromides. In general, the formation of mixtures of isomers was observed. The reactions of pent-4-en-2-ol and hept-6-en-3-ol with aryl bromides allowed for the synthesis of a variety of 5-arylpentan-2-one and 7-arylhept-3-one derivatives by migration of the double bond, but the (*E*)-4-aryl- and 5-arylpent-4-en-2-ol and (*E*)-6-aryl- and 7-arylhept-6-en-3-ol derivatives, respectively, were also observed. The selectivities of the reactions depend on the substituents of the aryl bromide and on the base. Higher selectivities in favour of the formation of the ketones were observed in several cases in the presence of $NaHCO_3$ as base instead of K_2CO_3; however, with this base, slower reactions were observed in some cases. With sterically congested or electron-rich aryl bromides, high selectivities in favour of the formation of the ketones were obtained. With hept-6-en-3-ol, the formation of furan derivatives as side products by intramolecular cyclisation was also observed in the presence of K_2CO_3 with electron-poor aryl bromides, but the use of $NaHCO_3$ as base suppressed this side reaction. Electron-poor and electron-rich aryl bromides can be reacted using similar substrate/catalyst ratios indicating that the oxidative addition of the aryl bromide is not the rate-determining step for the reaction with this catalyst. 2-Phenylpent-4-en-2-ol gave 5-aryl-2-phenylpent-4-en-2-ol derivatives in high selectivities. However, with electron-poor aryl bromides, C–C bond cleavage led to (*E*)-1-aryl- and 3-arylprop-1-ene derivatives. The complex seems to possess a fine balance of steric and electronic properties that generally allow fast catalytic processes. For many substrates, the reactions can be performed with as little as 0.01% catalyst without further optimisation of the reaction conditions. As expected, both the steric hindrance and the electronic properties of the aryl bromides have an effect on the reaction rate. The presence of *ortho* substituents generally led to lower TONs than those reactions performed with *para*-substituted aryl bromides. Di-*ortho*-substituted aryl bromides also gave the coupling products, but lower TONs were observed with the very sterically congested 1-bromo-1,3,5-triisopropylbenzene. We believe that this catalytic system compares favourably with the other catalysts that have been reported for this process. Due to the high price of palladium, the practical advantage of such low catalyst loading reactions could become increasingly important for industrial processes.

Analytical grade DMF (99.8%) was not distilled before use. 99% Potassium carbonate and 99% $NaHCO_3$ were used. All reactions were run under argon using vacuum lines in Schlenk tubes and in oven-dried glassware. The reactions were followed by GC and NMR spectroscopy for high boiling point substrates and by GC for low boiling point substrates. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in $CDCl_3$ solution with a Bruker spectrometer. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$. GC/MS were recorded with a Varian Saturn 2100T spectrometer. Flash chromatography was performed on silica gel (230–400 mesh).

Preparation of the Palladium–Tedicyp Catalyst[18]

An oven-dried, 40-mL Schlenk tube equipped with a magnetic stirring bar and under an argon atmosphere was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (4.2 mg, 11.6 μmol) and Tedicyp (20 mg, 23.2 μmol). Then, anhyd DMF (2.5 mL) was added, and the solution was stirred at r.t. for 10 min. The catalyst solution was used without purification.

Heck Reaction of Aryl Bromides with Alkenols Using the Palladium–Tedicyp Catalyst; General Procedure

A mixture of the aryl halide (1 mmol), alkenol (2 mmol), and K_2CO_3 (0.276 g, 2 mmol) or $NaHCO_3$ (0.168 g, 2 mmol) in dry DMF (3 mL) and in the presence of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/Tedicyp (1:2) was reacted for a period of 20 h under argon at 130 °C (see Tables 1– 3 for the base and amounts of catalyst used). The corresponding products were obtained after addition of H_2O (20 mL), extraction with CH_2Cl_2 (20 mL), separation, drying ($MgSO_4$), evaporation, and purification by chromatography (silica gel, pentane–Et_2O).

5-(4-Acetylphenyl)pentan-2-one (1a) (Table 1, Entry 2)

The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **1a**.

Yield: 0.157 g (77%).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.1 Hz, 2 H), 7.20 (d, *J* = 8.1 Hz, 2 H), 2.61 (t, *J* = 7.6 Hz, 2 H), 2.51 (s, 3 H), 2.38 (t, *J* = 7.2 Hz, 2 H), 2.05 (s, 3 H), 1.85 (quin, *J* = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.3, 197.7, 147.4, 135.1, 128.6, 128.5, 42.5, 34.9, 29.9, 26.1, 24.7.

MS (EI, 70 eV): *m*/*z* (%) = 204 (64) [M^+].

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.18; H, 8.00.

Before purification **1b** was also observed.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.49 (d, *J* = 15.8 Hz, 1 H), 6.36 (dt, *J* = 15.8, 6.8 Hz, 1 H).

Alcohol **1c** was also observed in the reaction described in Table 1, entry 1.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.47 (s, 1 H), 5.25 (s, 1 H).

5-(4-Benzoylphenyl)pentan-2-one (2a) (Table 1, Entry 4)
The reaction of 4-bromobenzophenone (0.261 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **2a**.

Yield: 0.213 g (80%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 6.8 Hz, 2 H), 7.72 (d, *J* = 8.2 Hz, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.44 (dt, *J* = 6.8, 7.4 Hz, 2 H), 7.26 (d, *J* = 8.2 Hz, 2 H), 2.68 (t, *J* = 7.5 Hz, 2 H), 2.44 (t, *J* = 7.3 Hz, 2 H), 2.10 (s, 3 H), 1.92 (quin, *J* = 7.4 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.3, 196.4, 146.9, 137.9, 135.5, 132.3, 130.4, 130.0, 128.4, 128.3, 42.7, 35.1, 30.0, 24.9.

MS (EI, 70 eV): *m*/*z* (%) = 266 (99) [M$^+$].

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.41; H, 6.71.

Before purification **2b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.53 (d, *J* = 16.1 Hz, 1 H), 6.38 (dt, *J* = 16.1, 6.7 Hz, 1 H).

Alcohol **2c** was also observed in the reactions described in Table 1, entries 3 and 5.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.48 (d, *J* = 1.1 Hz, 1 H), 5.27 (d, *J* = 1.1 Hz, 1 H).

4-(4-Oxopentyl)benzaldehyde (3a) (Table 1, Entry 7)
The reaction of 4-bromobenzaldehyde (0.185 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **3a**.

Yield: 0.133 g (70%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.96 (s, 1 H), 7.79 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 2.69 (t, *J* = 7.3 Hz, 2 H), 2.44 (t, *J* = 7.3 Hz, 2 H), 2.11 (s, 3 H), 1.91 (quin, *J* = 7.3 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.2, 191.9, 149.1, 134.6, 130.0, 129.1, 42.6, 35.2, 30.0, 24.7.

MS (EI, 70 eV): *m*/*z* (%) = 190 (73) [M$^+$].

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.54; H, 7.57.

Before purification **3b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.54 (d, *J* = 15.9 Hz, 1 H), 6.41 (dt, *J* = 16.0, 6.4 Hz, 1 H).

Alcohol **3c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.51 (s, 1 H), 5.31 (s, 1 H).

4-(4-Oxopentyl)benzonitrile (4a)[15] (Table 1, Entry 9)
The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **4a**.

Yield: 0.103 g (55%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 2.65 (t, *J* = 7.7 Hz, 2 H), 2.43 (t, *J* = 7.2 Hz, 2 H), 2.10 (s, 3 H), 1.90 (quin, *J* = 7.5 Hz, 2 H).

MS (EI, 70 eV): *m*/*z* (%) = 187 (21) [M$^+$].

Before purification **4b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.49 (d, *J* = 15.9 Hz, 1 H), 6.37 (dt, *J* = 15.9, 6.4 Hz, 1 H).

Alcohol **4c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.47 (s, 1 H), 5.30 (s, 1 H).

5-(4-Fluorophenyl)pentan-2-one (5a)[36] (Table 1, Entry 12)
The reaction of 1-bromo-4-fluorobenzene (0.175 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **5a**.

Yield: 0.146 g (81%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (dd, *J* = 8.7, 5.5 Hz, 2 H), 6.94 (t, *J* = 8.7 Hz, 2 H), 2.57 (t, *J* = 7.5 Hz, 2 H), 2.41 (t, *J* = 7.4 Hz, 2 H), 2.10 (s, 3 H), 1.88 (quin, *J* = 7.2 Hz, 2 H).

MS (EI, 70 eV): *m*/*z* (%) = 180 (16) [M$^+$].

Before purification **5b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.43 (d, *J* = 15.8 Hz, 1 H), 6.13 (dt, *J* = 15.8, 7.3 Hz, 1 H).

Alcohol **5c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.34 (s, 1 H), 5.14 (s, 1 H).

5-(4-*tert*-Butylphenyl)pentan-2-one (6a) (Table 1, Entry 13)
The reaction of 1-bromo-4-*tert*-butylbenzene (0.213 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **6a**.

Yield: 0.164 g (75%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.3 Hz, 2 H), 7.11 (d, *J* = 8.3 Hz, 2 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.45 (t, *J* = 7.4 Hz, 2 H), 2.12 (s, 3 H), 1.91 (quin, *J* = 7.4 Hz, 2 H), 1.32 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.7, 148.7, 138.4, 128.1, 125.2, 42.9, 34.5, 34.3, 31.4, 29.8, 25.2.

MS (EI, 70 eV): *m*/*z* (%) = 218 (6) [M$^+$].

Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.34; H, 9.99.

Before purification **6b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.47 (d, *J* = 15.9 Hz, 1 H), 6.16 (dt, *J* = 15.9 and 7.2 Hz, 1 H).

Alcohol **6c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.41 (d, *J* = 1.2 Hz, 1 H), 5.13 (d, *J* = 1.2 Hz, 1 H).

5-(4-Methoxyphenyl)pentan-2-one (7a)[37] (Table 1, Entry 15)
The reaction of 4-bromoanisole (0.187 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **7a**.

Yield: 0.121 g (63%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 8.7 Hz, 2 H), 6.81 (d, *J* = 8.7 Hz, 2 H), 3.76 (s, 3 H), 2.54 (t, *J* = 7.5 Hz, 2 H), 2.40 (t, *J* = 7.5 Hz, 2 H), 2.08 (s, 3 H), 1.85 (quin, *J* = 7.2 Hz, 2 H).

MS (EI, 70 eV): *m*/*z* (%) = 192 (8) [M$^+$].

Before purification **7b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.43 (d, *J* = 16.0 Hz, 1 H).

Alcohol **7c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.33 (s, 1 H), 5.07 (s, 1 H).

5-[2-(Trifluoromethyl)phenyl]pentan-2-one (8a) (Table 1, Entry 18)
The reaction of 1-bromo-2-(trifluoromethyl)benzene (0.225 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **8a**.

Yield: 0.168 g (73%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.1 Hz, 1 H), 7.47 (t, *J* = 7.2 Hz, 1 H), 7.38–7.25 (m, 2 H), 2.77 (t, *J* = 7.5 Hz, 2 H), 2.49 (t, *J* = 7.5 Hz, 2 H), 2.13 (s, 3 H), 1.88 (quin, *J* = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.3, 140.5, 131.7, 130.9, 128.4 (q, $^2J_{C–F}$ = 29.8 Hz), 126.0, 125.8 (q, $^3J_{C–F}$ = 5.7 Hz), 124.6 (q, $J_{C–F}$ = 273.8 Hz), 43.0, 31.6, 29.8, 25.3.

MS (EI, 70 eV): *m*/*z* (%) = 230 (1) [M$^+$].

Anal. Calcd for $C_{12}H_{13}F_3O$: C, 62.60; H, 5.69. Found: C, 62.47; H, 5.84.

Before purification **8b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.84 (d, *J* = 16.1 Hz, 1 H), 6.22 (dt, *J* = 16.1, 7.6 Hz, 1 H).

5-(2-Tolyl)pentan-2-one (9a)[38] (Table 1, Entry 21)
The reaction of 2-bromotoluene (0.171 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **9a**.

Yield: 0.127 g (72%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.05 (m, 4 H), 2.61 (t, *J* = 7.6 Hz, 2 H), 2.48 (t, *J* = 7.2 Hz, 2 H), 2.31 (s, 3 H), 2.13 (s, 3 H), 1.90 (quin, *J* = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.6, 139.8, 135.9, 130.2, 128.9, 126.1, 125.9, 43.1, 32.4, 29.9, 24.0, 19.2.

MS (EI, 70 eV): *m*/*z* (%) = 176 (1) [M$^+$].

Before purification **9b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.68 (d, *J* = 15.6 Hz, 1 H), 6.09 (dt, *J* = 15.6, 7.6 Hz, 1 H).

Alcohol **9c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.29 (d, *J* = 2.1 Hz, 1 H), 5.00 (d, *J* = 2.1 Hz, 1 H).

5-Mesitylpentan-2-one (10a)[39] (Table 1, Entry 23)
The reaction of 2-bromo-1,3,5-trimethylbenzene (0.199 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **10a**.

Yield: 0.123 g (60%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.83 (s, 2 H), 2.57 (t, *J* = 8.3 Hz, 2 H), 2.53 (t, *J* = 7.3 Hz, 2 H), 2.29 (s, 6 H), 2.24 (s, 3 H), 2.15 (s, 3 H), 1.73 (quin, *J* = 7.3 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.8, 136.1, 135.6, 135.2, 129.0, 43.8, 30.1, 28.9, 23.4, 20.9, 19.8.

MS (EI, 70 eV): *m*/*z* (%) = 204 (6) [M$^+$].

Before purification **10c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.37 (d, *J* = 1.8 Hz, 1 H), 4.96 (d, *J* = 1.8 Hz, 1 H).

(*E*)-5-Mesitylpent-3-en-2-ol **(10d)** has also been isolated in pure form.

Yield: 0.026 g (13%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.84 (s, 2 H), 5.68 (dtd, *J* = 15.4, 5.8, 0.9 Hz, 1 H), 5.40 (ddt, *J* = 15.4, 6.3, 1.5 Hz, 1 H), 4.24 (quin, *J* = 6.5 Hz, 1 H), 3.33 (d, *J* = 5.7 Hz, 2 H), 2.35 (s, 9 H), 1.21 (d, *J* = 6.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.4, 135.5, 134.6, 133.2, 128.9, 127.6, 68.8, 31.8, 23.3, 20.8, 19.8.

MS (EI, 70 eV): *m*/*z* (%) = 204 (30) [M$^+$].

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.14; H, 9.97.

5-Anthracen-9-ylpentan-2-one (11a) (Table 1, Entry 25)
The reaction of 9-bromoanthracene (0.257 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **11a**.

Yield: 0.212 g (81%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1 H), 8.32 (d, *J* = 9.3 Hz, 2 H), 8.00 (d, *J* = 8.3 Hz, 2 H), 7.57–7.42 (m, 4 H), 3.62 (t, *J* = 6.8 Hz, 2 H), 2.59 (t, *J* = 6.8 Hz, 2 H), 2.13 (s, 3 H), 2.13 (quin, *J* = 6.8 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.6, 134.1, 131.5, 129.7, 129.1, 125.8, 125.5, 124.8, 124.3, 43.1, 30.0, 26.9, 24.8.

MS (EI, 70 eV): *m*/*z* (%) = 262 (100) [M$^+$].

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 87.12; H, 6.78.

Before purification **11c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.88 (s, 1 H), 5.33 (s, 1 H).

5-(2,4,6-Triisopropylphenyl)pentan-2-one (12a) (Table 1, Entry 26)
The reaction of 2-bromo-1,3,5-triisopropylbenzene (0.283 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **12a**.

Yield: 0.133 g (46%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.99 (s, 2 H), 3.20 (sept, *J* = 7.0 Hz, 2 H), 2.87 (sept, *J* = 7.0 Hz, 1 H), 2.70–2.52 (m, 4 H), 2.15 (s, 3 H), 1.86–1.65 (m, 2 H), 1.25 (d, *J* = 7.0 Hz, 18 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.5, 146.5, 146.3, 132.8, 120.9, 43.8, 34.1, 29.8, 29.1, 27.2, 25.9, 24.5, 24.0.

MS (EI, 70 eV): *m*/*z* (%) = 288 (30) [M$^+$].

Anal. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.41; H, 11.29.

5-Pyridin-3-ylpentan-2-one (13a)[40] (Table 1, Entry 29)
The reaction of 3-bromopyridine (0.158 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **13a**.

Yield: 0.131 g (80%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35–8.45 (m, 2 H), 7.45 (d, *J* = 7.8 Hz, 1 H), 7.16 (dd, *J* = 7.8, 4.9 Hz, 1 H), 2.56 (t, *J* = 7.7 Hz, 2 H), 2.40 (t, *J* = 7.3 Hz, 2 H), 2.07 (s, 3 H), 1.84 (quin, *J* = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.1, 149.8, 147.4, 136.7, 135.7, 123.3, 42.4, 32.0, 29.9, 24.7.

MS (EI, 70 eV): *m*/*z* (%) = 163 (8) [M$^+$].

(*E*)-5-Pyridin-3-ylpent-4-en-2-ol (**13b**) has also been isolated in pure form. Yield: 0.011 g (7%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 1.9 Hz, 1 H), 8.40 (dd, *J* = 4.8, 1.2 Hz, 1 H), 7.67 (dt, *J* = 7.9, 1.9 Hz, 1 H), 7.23 (dd, *J* = 7.9, 4.8 Hz, 1 H), 6.43 (d, *J* = 16.0 Hz, 1 H), 6.31 (dt, *J* = 16.0, 6.8 Hz, 1 H), 3.94 (sept, *J* = 6.2 Hz, 1 H), 2.50–2.30 (m, 2 H), 1.24 (d, *J* = 6.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.4, 147.3, 133.2, 133.1, 129.5, 128.9, 123.6, 67.2, 42.8, 23.0.

MS (EI, 70 eV): *m*/*z* (%) = 163 (7) [M$^+$].

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03. Found: C, 73.41; H, 7.87.

Compound **13c** was also observed in the reaction described in Table 1, entry 28.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.41 (s, 1 H), 5.24 (s, 1 H).

5-Quinolin-3-ylpentan-2-one (14a) (Table 1, Entry 33)
The reaction of 3-bromoquinoline (0.208 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **14a**.

Yield: 0.169 g (79%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.73 (s, 1 H), 8.04 (d, *J* = 8.5 Hz, 1 H), 7.88 (s, 1 H), 7.73 (d, *J* = 8.2 Hz, 1 H), 7.64 (td, *J* = 7.7, 1.4 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 1 H), 2.76 (t, *J* = 7.8 Hz, 2 H), 2.45 (t, *J* = 7.2 Hz, 2 H), 2.09 (s, 3 H), 1.96 (quin, *J* = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.0, 151.8, 146.8, 134.2, 134.1, 129.0, 128.6, 128.0, 127.2, 126.5, 42.4, 32.1, 29.9, 24.7.

MS (EI, 70 eV): *m*/*z* (%) = 213 (35) [M$^+$].

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09. Found: C, 78.69; H, 7.21.

(*E*)-5-(Quinolin-3-yl)pent-4-en-2-ol **(14b)** has also been isolated in pure form. Yield: 0.019 g (9%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.86 (s, 1 H), 8.01 (d, *J* = 8.5 Hz, 1 H), 7.84 (s, 1 H), 7.67 (d, *J* = 8.1 Hz, 1 H), 7.60 (td, *J* = 7.7, 1.5 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 6.50 (d, *J* = 16.1 Hz, 1 H), 6.47 (ddt, *J* = 16.1, 6.2, 1.8 Hz, 1 H), 3.99 (sept, *J* = 6.2 Hz, 1 H), 2.50–2.30 (m, 2 H), 1.26 (d, *J* = 6.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.8, 146.8, 131.8, 130.2, 129.7, 129.0, 128.9, 128.7, 127.9, 127.6, 126.8, 67.1, 43.0, 23.1.

MS (EI, 70 eV): *m*/*z* (%) = 213 (30) [M$^+$].

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09. Found: C, 78.62; H, 7.14.

Before purification **14c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.52 (s, 1 H), 5.31 (s, 1 H).

5-Thiophen-2-ylpentan-2-one (15a)[11] (Table 1, Entry 35)
The reaction of 2-bromothiophene (0.163 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **15a**.

Yield: 0.071 g (42%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (dd, *J* = 5.1, 0.9 Hz, 1 H), 6.91 (dd, *J* = 5.1, 3.4 Hz, 1 H), 6.78 (dd, *J* = 3.4, 0.9 Hz, 1 H), 2.84 (t, *J* = 7.4 Hz, 2 H), 2.47 (t, *J* = 7.3 Hz, 2 H), 2.12 (s, 3 H), 1.95 (quin, *J* = 7.3 Hz, 2 H).

(*E*)-5-Thiophen-2-ylpent-4-en-2-ol **(15b)**[11] has also been isolated in pure form. Yield: 0.042 g (25%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11 (d, *J* = 4.7 Hz, 1 H), 6.94 (dd, *J* = 4.7, 1.9 Hz, 1 H), 6.90 (d, *J* = 1.9 Hz, 1 H), 6.60 (d, *J* = 15.7 Hz, 1 H), 6.04 (dt, *J* = 15.7, 7.6 Hz, 1 H), 3.90 (sept, *J* = 6.3 Hz, 1 H), 2.43–2.17 (m, 2 H), 1.26 (d, *J* = 6.3 Hz, 3 H).

Before purification **15c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.50 (s, 1 H), 5.09 (s, 1 H).

5-Thiophen-3-ylpentan-2-one (16a) (Table 1, Entry 36)
The reaction of 3-bromothiophene (0.163 g, 1 mmol), pent-4-en-2-ol (0.172 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **16a**.

Yield: 0.061 g (36%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.12 (m, 1 H), 6.92–6.82 (m, 2 H), 2.58 (t, *J* = 7.5 Hz, 2 H), 2.37 (t, *J* = 7.3 Hz, 2 H), 2.05 (s, 3 H), 1.84 (quin, *J* = 7.4 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.7, 141.9, 128.1, 125.4, 120.4, 42.8, 29.9, 29.4, 24.4.

MS (EI, 70 eV): *m*/*z* (%) = 168 (64) [M$^+$].

Anal. Calcd for $C_9H_{12}OS$: C, 64.24; H, 7.19. Found: C, 64.12; H, 7.01.

(*E*)-5-Thiophen-3-ylpent-4-en-2-ol **(16b)** has also been isolated in pure form. Yield: 0.079 g (47%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.15 (m, 2 H), 7.09 (s, 1 H), 6.49 (d, *J* = 15.9 Hz, 1 H), 6.06 (dt, *J* = 15.9, 7.6 Hz, 1 H), 3.90 (sept, *J* = 5.8 Hz, 1 H), 2.25–2.20 (m, 2 H), 1.24 (d, *J* = 5.8 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.9, 127.4, 126.1, 125.9, 124.9, 121.2, 67.3, 42.8, 22.9.

MS (EI, 70 eV): *m*/*z* (%) = 168 (63) [M$^+$].

Anal. Calcd for $C_9H_{12}OS$: C, 64.24; H, 7.19. Found: C, 64.41; H, 7.41.

Before purification **16c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.47 (s, 1 H), 5.10 (s, 1 H).

(*E*)-1-(4-Propenylphenyl)ethanone (17c)[41] (Table 2, Entry 1)
The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **17c**.

Yield: 0.130 g (81%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.3 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 2 H), 6.44 (d, *J* = 15.8 Hz, 1 H), 6.42–6.30 (m, 1 H), 2.57 (s, 3 H), 1.91 (d, *J* = 5.1 Hz, 3 H).

Compound **17d**[42] was also observed in the reaction described in Table 2, entry 2.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00–5.85 (m, 1 H), 5.15–5.05 (m, 2 H).

(*E*)-Phenyl(4-propenylphenyl)methanone (18c)[43] (Table 2, Entry 3)
The reaction of 4-bromobenzophenone (0.261 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **18c**.

Yield: 0.173 g (78%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85–7.70 (m, 4 H), 7.63–7.50 (m, 1 H), 7.50–7.35 (m, 4 H), 6.47 (d, *J* = 16.4 Hz, 1 H), 6.44–6.30 (m, 1 H), 1.92 (d, *J* = 5.3 Hz, 3 H).

5-(4-Fluorophenyl)-2-phenylpent-4-en-2-ol (19a) (Table 2, Entry 5)
The reaction of 1-bromo-4-fluorobenzene (0.175 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **19a**.

Yield: 0.182 g (71%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.2 Hz, 2 H), 7.36 (t, *J* = 7.2 Hz, 2 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 7.24 (dd, *J* = 8.8, 5.6 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 6.42 (d, *J* = 15.8 Hz, 1 H), 5.93 (ddd, *J* = 15.8, 8.4, 6.6 Hz, 1 H), 2.81 (ddd, *J* = 13.8, 6.6, 1.3 Hz, 1 H), 2.64 (ddd, *J* = 13.8, 8.4, 0.9 Hz, 1 H), 2.05 (br s, 1 H), 1.59 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.1 (d, J_{C-F} = 246.5 Hz), 147.6, 133.3 (d, $^4J_{C-F}$ = 3.3 Hz), 133.1, 128.3, 127.6 (d, $^3J_{C-F}$ = 8.3 Hz), 126.7, 124.8 (d, $^5J_{C-F}$ = 2.2 Hz), 124.7, 115.3 (d, $^2J_{C-F}$ = 21.4 Hz), 74.2, 47.7, 29.9.

MS (EI, 70 eV): *m*/*z* (%) = 256 (1) [M$^+$].

Anal. Calcd for $C_{17}H_{17}FO$: C, 79.66; H, 6.69. Found: C, 79.34; H, 6.59.

Before purification **19b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.24 (d, *J* = 1.5 Hz, 1 H), 4.99 (d, *J* = 1.5 Hz, 1 H).

2,5-Diphenylpent-4-en-2-ol (20a)[44] (Table 2, Entry 7)
The reaction of bromobenzene (0.157 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **20a**.

Yield: 0.167 g (70%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.6 Hz, 2 H), 7.37 (t, *J* = 7.6 Hz, 2 H), 7.31–7.16 (m, 6 H), 6.48 (d, *J* = 15.9 Hz, 1 H), 6.03

(ddd, *J* = 15.9, 8.4, 6.7 Hz, 1 H), 2.83 (ddd, *J* = 13.7, 6.7, 1.0 Hz, 1 H), 2.66 (dd, *J* = 13.7, 8.4 Hz, 1 H), 2.10 (br s, 1 H), 1.60 (s, 3 H).

Before purification **20b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.30 (d, *J* = 1.5 Hz, 1 H), 5.02 (d, *J* = 1.5 Hz, 1 H).

5-(4-*tert*-Butylphenyl)-2-phenylpent-4-en-2-ol (21a) (Table 2, Entry 9)

The reaction of 1-bromo-4-*tert*-butylbenzene (0.213 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **21a**.

Yield: 0.247 g (84%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.2 Hz, 2 H), 7.38 (t, *J* = 7.2 Hz, 2 H), 7.32 (d, *J* = 8.5 Hz, 2 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 7.24 (d, *J* = 8.5 Hz, 2 H), 6.48 (d, *J* = 15.9 Hz, 1 H), 5.98 (ddd, *J* = 15.9, 8.4, 6.6 Hz, 1 H), 2.83 (ddd, *J* = 13.7, 6.6, 1.4 Hz, 1 H), 2.65 (ddd, *J* = 13.7, 8.4, 1.1 Hz, 1 H), 2.16 (br s, 1 H), 1.60 (s, 3 H), 1.31 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.5, 147.7, 134.2, 128.2, 128.1, 126.6, 125.9, 125.4, 124.8, 124.2, 74.1, 47.7, 34.5, 31.2, 29.8.

MS (EI, 70 eV): *m*/*z* (%) = 276 (7) [M^+ – 18].

Anal. Calcd for $C_{21}H_{26}O$: C, 85.67; H, 8.90. Found: C, 85.38; H, 9.11.

Before purification **21b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.31 (d, *J* = 1.3 Hz, 1 H), 4.99 (d, *J* = 1.3 Hz, 1 H).

5-(4-Methoxyphenyl)-2-phenylpent-4-en-2-ol (22a) (Table 2, Entry 11)

The reaction of 4-bromoanisole (0.187 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **22a**.

Yield: 0.225 g (84%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.2 Hz, 2 H), 7.36 (t, *J* = 7.2 Hz, 2 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 7.23 (d, *J* = 8.8 Hz, 2 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 6.43 (d, *J* = 15.9 Hz, 1 H), 5.88 (ddd, *J* = 15.9, 8.5, 6.6 Hz, 1 H), 3.78 (s, 3 H), 2.82 (ddd, *J* = 13.7, 6.6, 1.4 Hz, 1 H), 2.64 (ddd, *J* = 13.7, 8.5, 1.0 Hz, 1 H), 2.17 (br s, 1 H), 1.59 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 147.7, 133.8, 129.9, 128.2, 127.3, 126.6, 124.8, 122.6, 113.8, 74.1, 55.2, 47.7, 29.8.

MS (EI, 70 eV): *m*/*z* (%) = 268 (1) [M^+].

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.30; H, 7.49.

Before purification **22b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.26 (d, *J* = 1.3 Hz, 1 H), 4.93 (d, *J* = 1.3 Hz, 1 H).

5-(6-Methoxynaphthalen-2-yl)-2-phenylpent-4-en-2-ol (23a) (Table 2, Entry 13)

The reaction of 2-bromo-6-methoxynaphthalene (0.237 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **23a**.

Yield: 0.261 g (82%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.23 (m, 9 H), 7.19–7.06 (m, 2 H), 6.62 (d, *J* = 15.9 Hz, 1 H), 6.12 (ddd, *J* = 15.9, 8.3, 6.6 Hz, 1 H), 3.90 (s, 3 H), 2.89 (ddd, *J* = 13.8, 6.6, 1.2 Hz, 1 H), 2.70 (ddd, *J* = 13.8, 8.3, 0.9 Hz, 1 H), 2.23 (br s, 1 H), 1.64 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 147.7, 134.5, 134.0, 132.5, 129.4, 128.9, 128.2, 126.9, 126.6, 125.7, 124.8, 124.3, 124.1, 118.9, 105.8, 74.1, 55.2, 47.8, 29.8.

MS (EI, 70 eV): *m*/*z* (%) = 198 (100) [M^+ – 120].

Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: C, 82.79; H, 7.10.

Before purification **23b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.42 (d, *J* = 1.3 Hz, 1 H), 5.07 (d, *J* = 1.3 Hz, 1 H).

5-[4-(Dimethylamino)phenyl]-2-phenylpent-4-en-2-ol (24a) (Table 2, Entry 15)

The reaction of 1-bromo-4-(dimethylamino)benzene (0.200 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **24a**.

Yield: 0.242 g (86%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.2 Hz, 2 H), 7.37 (t, *J* = 7.2 Hz, 2 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 7.20 (d, *J* = 8.8 Hz, 2 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 6.43 (d, *J* = 15.9 Hz, 1 H), 5.80 (ddd, *J* = 15.9, 8.4, 6.6 Hz, 1 H), 3.94 (s, 6 H), 2.82 (ddd, *J* = 13.6, 6.6, 1.3 Hz, 1 H), 2.62 (ddd, *J* = 13.6, 8.4, 0.7 Hz, 1 H), 2.24 (br s, 1 H), 1.59 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.0, 147.9, 134.5, 128.1, 127.1, 126.5, 125.7, 124.8, 120.3, 112.4, 74.0, 47.8, 40.5, 29.8.

MS (EI, 70 eV): *m*/*z* (%) = 281 (14) [M^+].

Anal. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24. Found: C, 80.92; H, 8.43.

Before purification **24b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.24 (d, *J* = 1.6 Hz, 1 H), 4.86 (d, *J* = 1.6 Hz, 1 H).

2-Phenyl-5-(2-tolyl)pent-4-en-2-ol (25a) (Table 2, Entry 17)

The reaction of 2-bromotoluene (0.171 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **25a**.

Yield: 0.184 g (73%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.2 Hz, 2 H), 7.37 (t, *J* = 7.2 Hz, 2 H), 7.33–7.24 (m, 2 H), 7.18–7.08 (m, 3 H), 6.66 (d, *J* = 15.7 Hz, 1 H), 5.91 (ddd, *J* = 15.7, 8.3, 6.7 Hz, 1 H), 2.85 (ddd, *J* = 13.7, 6.7, 1.4 Hz, 1 H), 2.69 (ddd, *J* = 13.7, 8.3, 0.9 Hz, 1 H), 2.29 (s, 3 H), 2.11 (br s, 1 H), 1.62 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.6, 136.3, 135.1, 132.4, 130.2, 128.2, 127.3, 126.7, 126.4, 126.0, 125.6, 124.8, 74.1, 48.0, 29.9, 19.8.

MS (EI, 70 eV): *m*/*z* (%) = 234 (76) [M^+ – 18].

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.47; H, 7.87.

Before purification **25b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.17 (d, *J* = 2.0 Hz, 1 H), 4.99 (d, *J* = 2.0 Hz, 1 H).

5-Naphthalen-1-yl-2-phenylpent-4-en-2-ol (26a) (Table 2, Entry 19)

The reaction of 1-bromonaphthalene (0.207 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **26a**.

Yield: 0.202 g (70%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04–7.97 (m, 1 H), 7.87–7.81 (m, 1 H), 7.75 (d, *J* = 8.1 Hz, 1 H), 7.55–7.35 (m, 8 H), 7.28 (t, *J* = 7.2 Hz, 1 H), 7.22 (d, *J* = 15.6 Hz, 1 H), 6.07 (ddd, *J* = 15.6, 8.2, 6.8 Hz,

1 H), 2.95 (ddd, *J* = 13.7, 6.8, 1.4 Hz, 1 H), 2.81 (ddd, *J* = 13.7, 8.2, 1.1 Hz, 1 H), 2.19 (br s, 1 H), 1.68 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.6, 135.0, 133.5, 131.7, 131.0, 128.4, 128.2, 128.1, 127.7, 126.7, 125.9, 125.7, 125.5, 124.8, 123.8, 123.7, 74.3, 48.1, 29.9.

MS (EI, 70 eV): *m*/*z* (%) = 288 (1) [M$^+$].

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.21; H, 7.12.

Before purification **26b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.39 (d, *J* = 1.2 Hz, 1 H), 5.22 (d, *J* = 1.2 Hz, 1 H).

(*E*)-3-Propenylquinoline (27c)[45] (Table 2, Entry 21)
The reaction of 3-bromoquinoline (0.208 g, 1 mmol), 2-phenylpent-4-en-2-ol (0.324 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **27c**.

Yield: 0.095 g (56%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.95 (d, *J* = 1.9 Hz, 1 H), 8.05 (d, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 1.9 Hz, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.63 (td, *J* = 8.4, 1.4 Hz, 1 H), 7.50 (td, *J* = 8.3, 1.1 Hz, 1 H), 6.55 (d, *J* = 16.0 Hz, 1 H), 6.51–6.40 (m, 1 H), 1.96 (d, *J* = 5.1 Hz, 3 H).

3-Prop-2-enylquinoline **(27d)**[46] has also been isolated in pure form.
Yield: 0.051 g (30%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 1.4 Hz, 1 H), 8.09 (d, *J* = 8.4 Hz, 1 H), 7.92 (d, *J* = 1.4 Hz, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.66 (td, *J* = 8.4, 1.5 Hz, 1 H), 7.53 (td, *J* = 8.4, 1.5 Hz, 1 H), 6.10–5.90 (m, 1 H), 5.19–5.06 (m, 2 H), 3.57 (d, *J* = 6.5 Hz, 2 H).

7-(4-Acetylphenyl)heptan-3-one (28a) (Table 3, Entry 2)
The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **28a**.

Yield: 0.193 g (83%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 2.70–2.60 (m, 2 H), 2.56 (s, 3 H), 2.45–2.30 (m, 4 H), 1.65–1.55 (m, 4 H), 1.02 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.3, 197.8, 148.0, 135.0, 128.6, 128.5, 42.0, 35.9, 35.7, 30.6, 26.5, 23.4, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 232 (90) [M$^+$].

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.71; H, 8.80.

Before purification **28b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.46 (d, *J* = 16.0 Hz, 1 H), 6.38 (dt, *J* = 16.0, 6.0 Hz, 1 H).

Alcohol **28c** was also observed in the reaction described in Table 3, entry 1.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.38 (d, *J* = 1.3 Hz, 1 H), 5.20 (d, *J* = 1.3 Hz, 1 H).

Tetrahydrofuran **28d** was also observed in the reaction described in Table 3, entry 1.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.07 (quin, *J* = 6.4 Hz, 1 H), 3.76 (quin, *J* = 6.6 Hz, 1 H) and 4.20 (quin, *J* = 6.2 Hz, 1 H), 3.88 (quin, *J* = 6.4 Hz, 1 H).

7-(4-Benzoylphenyl)heptan-3-one (29a) (Table 3, Entry 4)
The reaction of 4-bromobenzophenone (0.261 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **29a**.

Yield: 0.238 g (81%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.6 Hz, 2 H), 7.73 (d, *J* = 8.3 Hz, 2 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 7.44 (td, *J* = 7.6, 6.0 Hz, 2 H), 7.26 (d, *J* = 8.3 Hz, 2 H), 2.75–2.60 (m, 2 H), 2.50–2.30 (m, 4 H), 1.75–1.55 (m, 4 H), 1.03 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.3, 206.2, 147.4, 137.9, 135.3, 132.1, 130.3, 129.9, 128.3, 128.2, 42.0, 35.9, 35.8, 30.6, 23.4, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 294 (100) [M$^+$].

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.49; H, 7.37.

Before purification **29b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.49 (d, *J* = 16.1 Hz, 1 H), 6.38 (dt, *J* = 16.1, 6.4 Hz, 1 H).

Alcohol **29c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.39 (s, 1 H), 5.20 (s, 1 H).

Tetrahydrofuran **29d** was also observed in the reactions described in Table 3, entries 3 and 5.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.10 (quin, *J* = 6.5 Hz, 1 H), 3.79 (quin, *J* = 6.5 Hz, 1 H) and 4.22 (quin, *J* = 6.1 Hz, 1 H), 3.90 (quin, *J* = 6.1 Hz, 1 H).

Methyl 4-(5-Oxoheptyl)benzoate (30a) (Table 3, Entry 7)
The reaction of methyl 4-bromobenzoate (0.215 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **30a**.

Yield: 0.199 g (80%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.2 Hz, 2 H), 7.23 (d, *J* = 8.2 Hz, 2 H), 3.89 (s, 3 H), 2.74–2.57 (m, 2 H), 2.50–2.30 (m, 4 H), 1.75–1.50 (m, 4 H), 1.03 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.4, 167.1, 147.8, 129.7, 128.4 (2 C), 52.0, 42.0, 35.9, 35.8, 30.6, 23.4, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 248 (5) [M$^+$].

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.56; H, 8.30.

Before purification **30b** was also observed in the reaction described in Table 3, entry 6.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.46 (d, *J* = 15.9 Hz, 1 H), 6.35 (dt, *J* = 15.9, 5.9 Hz, 1 H).

Alcohol **30c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.36 (s, 1 H), 5.18 (s, 1 H).

Tetrahydrofuran **30d** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.02 (quin, *J* = 6.4 Hz, 1 H) and 4.15 (quin, *J* = 6.5 Hz, 1 H).

7-[4-(Trifluoromethyl)phenyl]heptan-3-one (31a) (Table 3, Entry 9)
The reaction of 1-bromo-4-(trifluoromethyl)benzene (0.225 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **31a**.

Yield: 0.212 g (82%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.2 Hz, 2 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 2.71–2.61 (m, 2 H), 2.47–2.33 (m, 4 H), 1.65–1.56 (m, 4 H), 1.03 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.4, 146.3, 128.6, 128.1 (q, $^2J_{C–F}$ = 32.1 Hz), 125.2 (q, $^3J_{C–F}$ = 4.0 Hz), 124.3 (q, $J_{C–F}$ = 271.7 Hz), 42.0, 35.9, 35.6, 30.7, 23.3, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 258 (8) [M$^+$].

Anal. Calcd for $C_{14}H_{17}F_3O$: C, 65.10; H, 6.63. Found: C, 64.95; H, 6.69.

Before purification **31b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.45 (d, *J* = 16.0 Hz, 1 H), 6.34 (dt, *J* = 16.0, 6.4 Hz, 1 H).

Alcohol **31c** was also observed in the reaction described in Table 3, entry 8.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.34 (d, *J* = 1.2 Hz, 1 H), 5.19 (d, *J* = 1.2 Hz, 1 H).

Tetrahydrofuran **31d** was also observed in the reaction described in Table 3, entry 8.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.06 (quin, *J* = 6.4 Hz, 1 H), 3.77 (quin, *J* = 6.4 Hz, 1 H) and 4.19 (quin, *J* = 6.2 Hz, 1 H), 3.88 (quin, *J* = 6.2 Hz, 1 H).

7-(4-Fluorophenyl)heptan-3-one (32a) (Table 3, Entry 12)
The reaction of 1-bromo-4-fluorobenzene (0.175 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **32a**.

Yield: 0.148 g (71%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (dd, *J* = 8.7, 5.5 Hz, 2 H), 6.93 (t, *J* = 8.7 Hz, 2 H), 2.62–2.53 (m, 2 H), 2.45–2.29 (m, 4 H), 1.65–1.50 (m, 4 H), 1.03 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.5, 161.2 (d, J_{C-F} = 243.2 Hz), 137.8 (d, $^4J_{C-F}$ = 2.8 Hz), 129.6 (d, $^3J_{C-F}$ = 7.5 Hz), 115.0 (d, $^2J_{C-F}$ = 21.3 Hz), 42.1, 35.9, 34.9, 31.1, 23.4, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 208 (46) [M$^+$].

Anal. Calcd for $C_{13}H_{17}FO$: C, 74.97; H, 8.23. Found: C, 74.81; H, 8.07.

Before purification **32b** was also observed in the reaction described in Table 3, entry 11.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.37 (d, *J* = 15.9 Hz, 1 H), 6.14 (dt, *J* = 15.9, 6.9 Hz, 1 H).

Alcohol **32c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.21 (d, *J* = 1.1 Hz, 1 H), 5.07 (d, *J* = 1.1 Hz, 1 H).

Tetrahydrofuran **32d** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.01 (quin, *J* = 6.5 Hz, 1 H), 3.75 (quin, *J* = 6.5 Hz, 1 H) and 4.13 (quin, *J* = 6.2 Hz, 1 H), 3.87 (quin, *J* = 6.2 Hz, 1 H).

7-(4-*tert*-Butylphenyl)heptan-3-one (33a) (Table 3, Entry 13)
The reaction of 1-bromo-4-*tert*-butylbenzene (0.213 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **33a**.

Yield: 0.185 g (75%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.3 Hz, 2 H), 7.10 (d, *J* = 8.3 Hz, 2 H), 2.62–2.53 (m, 2 H), 2.46–2.33 (m, 4 H), 1.70–1.52 (m, 4 H), 1.30 (s, 9 H), 1.03 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.7, 148.5, 139.1, 128.0, 125.2, 42.2, 35.9, 35.2, 34.3, 31.4, 31.0, 23.6, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 246 (24) [M$^+$].

Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.97; H, 10.78.

Before purification **33b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.38 (d, *J* = 15.9 Hz, 1 H), 6.16 (dt, *J* = 15.9, 6.9 Hz, 1 H).

Alcohol **33c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.26 (d, *J* = 1.1 Hz, 1 H), 5.03 (d, *J* = 1.1 Hz, 1 H).

7-(4-Methoxyphenyl)heptan-3-one (34a) (Table 3, Entry 15)
The reaction of 4-bromoanisole (0.187 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **34a**.

Yield: 0.163 g (74%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 8.7 Hz, 2 H), 6.81 (d, *J* = 8.7 Hz, 2 H), 3.77 (s, 3 H), 2.60–2.50 (m, 2 H), 2.45–2.29 (m, 4 H), 1.65–1.50 (m, 4 H), 1.03 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.6, 157.7, 134.3, 129.2, 113.8, 55.2, 42.2, 35.8, 34.8, 31.2, 23.5, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 220 (57) [M$^+$].

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.17; H, 9.00.

Before purification **34b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.36 (d, *J* = 15.7 Hz, 1 H), 6.08 (dt, *J* = 15.7, 7.0 Hz, 1 H).

Alcohol **34c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.21 (d, *J* = 1.0 Hz, 1 H), 5.00 (d, *J* = 1.0 Hz, 1 H).

7-[2-(Trifluoromethyl)phenyl]heptan-3-one (35a) (Table 3, Entry 17)
The reaction of 1-bromo-2-(trifluoromethyl)benzene (0.225 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **35a**.

Yield: 0.191 g (74%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.8 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 7.35–7.20 (m, 2 H), 2.76 (t, *J* = 7.4 Hz, 2 H), 2.50–2.34 (m, 4 H), 1.77–1.62 (m, 4 H), 1.04 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.4, 141.1, 131.7, 130.9, 128.3 (q, $^2J_{C-F}$ = 30.0 Hz), 125.9 (q, $^3J_{C-F}$ = 5.7 Hz), 125.8, 124.6 (q, J_{C-F} = 273.8 Hz), 42.0, 35.9, 32.4, 31.2, 23.8, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 258 (1) [M$^+$].

Anal. Calcd for $C_{14}H_{17}F_3O$: C, 65.10; H, 6.63. Found: C, 65.31; H, 6.50.

Compound **35b** was also observed in the reaction described in Table 3, entry 16.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.77 (d, *J* = 16.0 Hz, 1 H), 6.32 (dt, *J* = 16.0, 6.4 Hz, 1 H).

Tetrahydrofuran **35d** was also observed in the reaction described in Table 3, entry 16.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.10 (quin, *J* = 6.4 Hz, 1 H), 3.79 (quin, *J* = 6.5 Hz, 1 H) and 4.25 (quin, *J* = 6.2 Hz, 1 H), 3.93 (quin, *J* = 6.2 Hz, 1 H).

7-(2-Tolyl)heptan-3-one (36a) (Table 3, Entry 18)
The reaction of 2-bromotoluene (0.171 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **36a**.

Yield: 0.164 g (80%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.05 (m, 4 H), 2.61 (t, *J* = 6.6 Hz, 2 H), 2.49–2.36 (m, 4 H), 2.31 (s, 3 H), 1.74–1.51 (m, 4 H), 1.06 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.5, 140.3, 135.7, 130.1, 128.7, 125.8 (2 C), 42.1, 35.8, 33.0, 29.8, 23.8, 19.2, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 204 (20) [M$^+$].

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.49; H, 10.10.

Before purification **36b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.61 (d, *J* = 15.6 Hz, 1 H), 6.10 (dt, *J* = 15.6, 7.0 Hz, 1 H).

7-Naphthalen-1-ylheptan-3-one (37a) (Table 3, Entry 19)
The reaction of 1-bromonaphthalene (0.207 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **37a**.

Yield: 0.200 g (83%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (dd, *J* = 7.0, 2.1 Hz, 1 H), 7.86 (dd, *J* = 6.0, 3.1 Hz, 1 H), 7.72 (d, *J* = 7.8 Hz, 1 H), 7.56–7.27 (m, 4 H), 3.20–3.02 (m, 2 H), 2.53–2.30 (m, 4 H), 1.85–1.64 (m, 4 H), 1.05 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.5, 138.2, 133.8, 131.8, 128.7, 126.5, 125.9, 125.7, 125.5, 125.3, 123.7, 42.1, 35.8, 32.9, 30.3, 23.9, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 240 (100) [M$^+$].

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.17; H, 8.21.

Before purification **37b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 15.7 Hz, 1 H), 6.26 (dt, *J* = 15.7, 7.0 Hz, 1 H).

7-Mesitylheptan-3-one (38a) (Table 3, Entry 21)
The reaction of 2-bromo-1,3,5-trimethylbenzene (0.199 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **38a**.

Yield: 0.179 g (77%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82 (s, 2 H), 2.62–2.53 (m, 2 H), 2.49–2.36 (m, 4 H), 2.26 (s, 6 H), 2.23 (s, 3 H), 1.77–1.62 (m, 2 H), 1.50–1.36 (m, 2 H), 1.05 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.6, 136.0, 135.8, 134.9, 128.8, 42.2, 35.9, 29.2, 29.0, 24.4, 20.7, 19.7, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 232 (45) [M$^+$].

Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.89; H, 10.18.

Before purification **38e** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.68–5.52 (m, 1 H), 5.39–5.25 (m, 1 H).

7-(2,4,6-Triisopropylphenyl)heptan-3-one (39a) (Table 3, Entry 23)
The reaction of 2-bromo-1,3,5-triisopropylbenzene (0.283 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **39a**.

Yield: 0.219 g (69%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.95 (s, 2 H), 3.11 (sept, *J* = 6.8 Hz, 2 H), 2.84 (sept, *J* = 6.8 Hz, 1 H), 2.66–2.56 (m, 2 H), 2.49–2.36 (m, 4 H), 1.72 (quin, *J* = 7.6 Hz, 2 H), 1.50–1.36 (m, 2 H), 1.22 (d, *J* = 6.9 Hz, 18 H), 1.05 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.6, 146.3, 146.1, 133.4, 120.9, 42.3, 35.9, 34.1, 31.7, 29.2, 27.7, 24.6, 24.5, 24.0, 7.9.

MS (EI, 70 eV): *m*/*z* (%) = 316 (25) [M$^+$].

Anal. Calcd for $C_{22}H_{36}O$: C, 83.48; H, 11.46. Found: C, 83.74; H, 11.60.

7-Pyridin-3-ylheptan-3-one (40a) (Table 3, Entry 25)
The reaction of 3-bromopyridine (0.158 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **40a**.

Yield: 0.159 g (83%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.42 (s, 2 H), 7.48 (dt, *J* = 7.7, 2.0 Hz, 1 H), 7.20 (dd, *J* = 7.9, 4.7 Hz, 1 H), 2.64–2.56 (m, 2 H), 2.45–2.31 (m, 4 H), 1.65–1.56 (m, 4 H), 1.03 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.3, 149.7, 147.2, 137.4, 135.9, 123.3, 41.9, 35.9, 32.8, 30.6, 23.3, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 191 (8) [M$^+$].

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96. Found: C, 75.21; H, 9.14.

Before purification **40b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.38 (d, *J* = 15.9 Hz, 1 H), 6.26 (dt, *J* = 15.9, 6.2 Hz, 1 H).

Alcohol **40c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.32 (d, *J* = 1.3 Hz, 1 H), 5.15 (d, *J* = 1.3 Hz, 1 H).

Tetrahydrofuran **40d** was also observed in the reaction described in Table 3, entry 24.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.05 (quin, *J* = 6.4 Hz, 1 H), 3.76 (quin, *J* = 6.4 Hz, 1 H) and 4.17 (quin, *J* = 6.2 Hz, 1 H), 3.86 (quin, *J* = 6.4 Hz, 1 H).

7-Quinolin-3-ylheptan-3-one (41a) (Table 3, Entry 27)
The reaction of 3-bromoquinoline (0.208 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and $NaHCO_3$ (0.168 g, 2 mmol) afforded **41a**.

Yield: 0.193 g (80%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 2.0 Hz, 1 H), 8.09 (d, *J* = 8.6 Hz, 1 H), 7.93 (d, *J* = 2.0 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.66 (td, *J* = 6.9, 5.3 Hz, 1 H), 7.52 (td, *J* = 8.0, 6.9 Hz, 1 H), 2.88–2.72 (m, 2 H), 2.50–2.32 (m, 4 H), 1.80–1.54 (m, 4 H), 1.03 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.3, 151.7, 146.5, 134.8, 134.5, 128.9, 128.8, 128.2, 127.3, 126.7, 42.0, 36.0, 33.1, 30.6, 23.4, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 241 (50) [M$^+$].

Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94. Found: C, 79.78; H, 7.77.

Before purification **41b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.43 (d, *J* = 15.9 Hz, 1 H), 6.30 (dt, *J* = 15.9, 6.4 Hz, 1 H).

Alcohol **41c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.34 (d, *J* = 1.3 Hz, 1 H), 5.19 (d, *J* = 1.3 Hz, 1 H).

Tetrahydrofuran **41d** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.06 (quin, *J* = 6.4 Hz, 1 H), 3.77 (quin, *J* = 6.4 Hz, 1 H) and 4.19 (quin, *J* = 6.2 Hz, 1 H), 3.88 (quin, *J* = 6.2 Hz, 1 H).

7-Thiophen-2-ylheptan-3-one (42a) (Table 3, Entry 28)
The reaction of 2-bromothiophene (0.163 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **42a**.

Yield: 0.081 g (41%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 (dd, *J* = 5.1, 1.1 Hz, 1 H), 6.90 (dd, *J* = 5.1, 3.3 Hz, 1 H), 6.77 (dd, *J* = 3.3, 1.1 Hz, 1 H), 2.89–2.75 (m, 2 H), 2.48–2.32 (m, 4 H), 1.71–1.59 (m, 4 H), 1.04 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.5, 145.1, 126.7, 124.1, 122.9, 42.0, 35.9, 31.3, 29.7, 23.3, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 196 (38) [M$^+$].

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22. Found: C, 67.48; H, 8.22.

Before purification **42b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.54 (d, *J* = 15.5 Hz, 1 H), 6.06 (dt, *J* = 15.5, 7.0 Hz, 1 H).

Alcohol **42c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.39 (s, 1 H), 4.98 (s, 1 H).

Tetrahydrofuran **42d** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.08 (quin, *J* = 6.6 Hz, 1 H), 3.79 (quin, *J* = 6.6 Hz, 1 H) and 4.20 (quin, *J* = 6.6 Hz, 1 H), 3.91 (quin, *J* = 6.6 Hz, 1 H).

7-Thiophen-3-ylheptan-3-one (43a) (Table 3, Entry 31)
The reaction of 3-bromothiophene (0.163 g, 1 mmol), hept-6-en-3-ol (0.228 g, 2 mmol), and K_2CO_3 (0.276 g, 2 mmol) afforded **43a**.

Yield: 0.110 g (56%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 (t, *J* = 4.2 Hz, 1 H), 6.92 (m, 2 H), 2.70–2.59 (m, 2 H), 2.48–2.32 (m, 4 H), 1.70–1.55 (m, 4 H), 1.04 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.6, 142.5, 128.2, 125.2, 120.0, 42.1, 35.9, 30.1, 30.0, 23.5, 7.8.

MS (EI, 70 eV): *m*/*z* (%) = 196 (47) [M^+].

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22. Found: C, 67.49; H, 8.10.

Before purification **43b** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.43 (d, *J* = 15.7 Hz, 1 H), 6.08 (dt, *J* = 15.7, 7.0 Hz, 1 H).

Alcohol **43c** was also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.35 (d, *J* = 1.2 Hz, 1 H), 5.04 (d, *J* = 1.2 Hz, 1 H).

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