Palladium-Tetraphosphine Catalysed Heck Reaction with Simple Alkenes: Influence of Reaction Conditions on the Migration of the Double Bond

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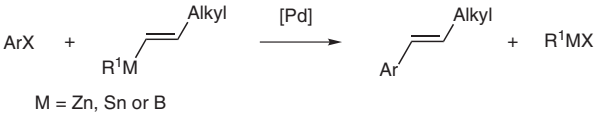
Abstract: The Heck reaction of aryl halides with simple alk-1-enes is a powerful method for the synthesis of (*E*)-1-arylalk-1-ene derivatives. The major problem of this reaction is the palladium-catalysed migration of the carbon–carbon double bond along the alkyl chain. We observed that this migration could be partially controlled using appropriate reaction conditions. The ramification of the alkyl chain and the substituents on the aryl halide has also an important influence on this migration. The *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane/$[Pd(C_3H_5)Cl]_2$ system catalyses efficiently the Heck reaction of a wide variety of aryl halides with the linear alkenes oct-1-ene and dec-1-ene or the branched alkenes 4-methylhex-1-ene, 5-methylhex-1-ene, allylcyclopentane, or allylcyclohexane. In most cases, selectivities of 70–80% were obtained. In some cases, up to 97% in favour of (*E*)-1-arylalk-1-enes can be observed. Moreover several reactions can be performed using very low catalyst loadings.

Key words: Heck reaction, palladium, alkenes, double bond migration

Palladium-catalysed Heck reaction is one of the most powerful methods for the formation of C–C bonds. The arylation of alkenes such as acrylates, styrenes, or, more recently, enol ethers, catalysed by palladium has been extensively developed in the last thirty years.[1–4] On the other hand, the palladium-catalysed Heck alkenylation using simple linear of branched alkenes remains open to study, since migration of the carbon–carbon double bond along the alkyl chain generally leads to mixtures of regio- and stereoisomers. In fact, the classical method to prepare selectively (*E*)-1-arylalk-1-ene is to employ an aryl halide with an organometallic derivative of the alkene [metal = ZnX,[1] SnR_3[2] $B(OR)_2$[3]] using a palladium catalyst (Scheme 1). These reactions are very regio- and stereoselective in favour of the formation of (*E*)-1-arylalk-1-ene derivatives.[5–7] However, these reactions require the preparation of the alkyl organometallic derivative and provide an organometallic (MX) as a by-product.

To our knowledge, only a few examples of Heck reactions in the presence of non-functionalised linear or branched alkenes have been reported so far.[8,9] Moreover, in most cases only one or two examples of such reactions have been described and the selectivity is often not clearly reported. In a few cases the crude mixture of regio- and stereoisomers was hydrogenated to give the corresponding mixture of 1- and 2-arylalkanes.[8] Only a few catalysts have been used for the reaction with this class of alkenes. For example, the system $Pd(OAc)_2$/P(*o*-Tol)$_3$ (10 mol%) catalyses the coupling of pent-1-ene with an aryl bromide in 59% yield and 69:31 selectivity of 1-arylpent-1-ene and 2-arylpent-1-ene.[9a] Fu et al. have reported the regioselective formation of an 1-arylhex-1-ene in 70% yield using 4-chloroacetophenone and hex-1-ene, with $Pd_2(dba)_3$ (1.5 mol%) associated to P(*t*-Bu)$_3$ (6 mol%) as catalyst. However, a mixture of *E*- and *Z*-isomers was obtained in 86:14 ratio.[9c] Milstein et al. have reported the palladium coupling of pentafluorobromobenzene with hex-1-ene in 37% yield as a mixture of isomers.[9d] The reaction of 4-bromotoluene with hex-1-ene using a $Pd(OAc)_2$/diazabutadiene catalyst (3 mol%) was described by Nolan et al. Using this catalyst, the selectivity between terminal and internal isomers was 75:25, and the stereoselectivity of (*E*)- and (*Z*)-1-arylhex-1-enes was 95:5.[9e] A dendridic catalyst also led to a mixture of isomers for the coupling of iodobenzene and oct-1-ene.[9g] Finally, 3 mol% of $PdCl_2(PCy_3)_2$ catalyses the alkenylation of chlorobenzene. Using this catalyst, the (*E*)-1-phenyloct-1-ene was obtained in 60% selectivity.[9h]



Scheme 1

In summary, very few regio- and stereoselective Heck reactions using non-functionalized linear or branched alk-1-enes have been reported so far. To our knowledge, the influence of the reaction conditions and of the substituents on the aryl halide or on the alkyl chain of the alk-1-ene has not been explored in detail. Thus, an effective and selective method using low catalyst loadings for the preparation of (*E*)-1-arylalk-1-enes is still subject to significant improvement.

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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.[10] The idea of the design of this ligand was that intermediate Pd(0) species have to be protected by internal ligation against possible decomposition pathways through under-ligation and subsequent colloid formation. We have already reported the results obtained in allylic substitution,[11] for Suzuki or Negishi cross-coupling,[12] for Sonogashira reaction[13] and for coupling of furans and aryl bromides via CH activation[14] using Tedicyp as the ligand. We have also described several results obtained for Heck reaction.[15,16] For example, we have reported the reaction with *n*-butyl acrylate,[15,16a] styrene,[16b] acrolein ethylene acetal,[16c] alkenols[16d,e,h] enolethers,[16b,g] vinylsilanes[16f] or vinylsulfur[16i] with a variety of aryl bromides. We have also reported preliminary results using simple alkenes such as dec-1-ene, 3,3-dimethylbut-1-ene, or cycloalkenes.[17] Using 3,3-dimethylbut-1-ene or cycloalkenes, regioselective reactions had generally been obtained. On the other hand, using dec-1-ene or oct-1-ene, the (*E*)-1-arylalk-1-ene derivatives were obtained in 34–70% selectivities. Such selectivities are not good enough to give a useful process compared to the coupling reactions using organometallic derivatives of the alkene.[5–7] Therefore, in order to improve this selectivity of the arylation with such alkenes, we decided to study the influence of several parameters on the regio- and stereocontrol of this reaction.

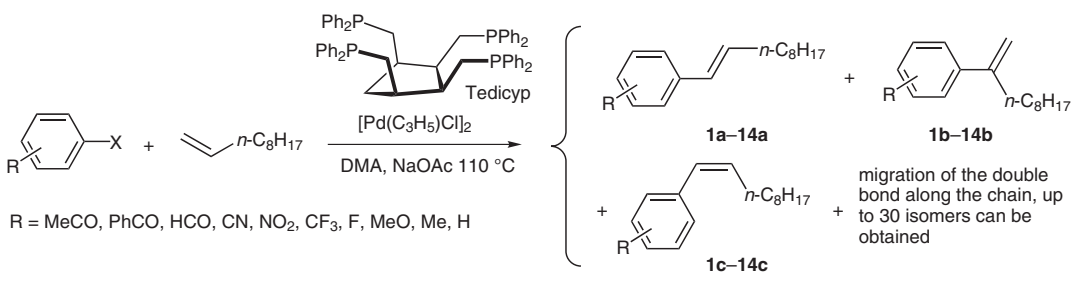
Since there are only a few examples of Heck alkenylation using simple alk-1-enes in the literature, we began by exploring the reaction of dec-1-ene with 4-bromoacetophenone using various reaction conditions (Scheme 2, Table 1). The first reactions were performed at 130 °C, under argon, in the presence of a ratio 1:2 of $[Pd(C_3H_5)Cl]_2$/Tedicyp as catalyst.

After extensive screening of the reaction conditions, we found that the most suitable base appears to be NaOAc. Bases such as $NaHCO_3$, Na_2CO_3 or KF using DMF as solvent led to the (*E*)-1-aryldec-1-ene **1a** only in 29–38% selectivity (Table 1, entries 1–3). The best selectivities using DMF as solvent were obtained using K_2CO_3 or NaOAc as base in 64% and 54% yield, respectively (Table 1, entries 4 and 5). Then, we examined the influence of a few solvents. The nonpolar solvent xylene using K_2CO_3 as base gave extremely low selectivities in **1a** of 9% and 10% (Table 1, entries 6 and 7). On the other hand, the polar solvents NMP or DMA gave **1a** in 51 and 53% selectivities with K_2CO_3 as base and 57% or 67% using NaOAc (Table 1, entries 9–12).

The temperature has also an influence on this selectivity. When using a lower temperature of 110 °C instead of 130 °C, the selectivity increased from 67% to 73%. Using a higher substrate/catalyst ratio of 10000, a selectivity of 76% in **1a** was obtained (Table 1, entry 15). Finally, in the absence of ligand or with PPh_3 the reaction did not proceed (Table 1, entries 16 and 17). It should be noted that a reverse selectivity in favour of regioisomer **1b** was obtained using acetonitrile as solvent (Table 1, entries 18 and 19). However, in this solvent the reaction was much slower than in DMA. Such internal arylations have already been reported in a few cases for example for the reaction with unsaturated alcohols using ionic liquid as solvent.[18]

After this optimisation of the reaction conditions, we performed several arylations using dec-1-ene (Table 2), oct-1-ene (Table 3), 4-methylhex-1-ene, 5-methylhex-1-ene, allylcyclopentane or allylcyclohexane (Table 4) with a set of aryl bromides.

First, we examined the influence of the substituents on the aryl bromides on the yields, selectivities and reaction rates for the arylation of dec-1-ene (Table 2). Higher reactions rates and selectivities in favour of (*E*)-1-aryldec-1-ene had been observed with electron-poor aryl bromides than with electron-rich aryl bromides when the reactions were conducted in DMF using K_2CO_3 as base.[17] Using DMA and NaOAc as base, quite different results were obtained. Using electron-poor aryl bromides, such as 4-bromobenzaldehyde, 4-bromobenzophenone or 3,5-bistrifluoromethylbromobenzene, selectivities of 66%, 64% and 70% have been obtained using the DMF/K_2CO_3 procedure and 81%, 80% and 83% using the DMA/NaOAc procedure (Table 2, entries 2–14). The presence of electron-donating substituents on the aryl bromides generally decreases the selectivity in favour of (*E*)-1-aryldec-1-ene. Using the electron-rich aryl bromides, 4-bromoanisole or 2-bromothiophene lower selectivities of 63% and 60% were obtained using DMA/NaOAc conditions. Again, lower selectivities of 51% and 34% had been obtained using DMF/K_2CO_3 system (Table 2, entries 19–21, 26 and 27). With the *ortho*-substituted aryl bromide, 2-bromotoluene, a good selectivity of 70% in favour of **11a** was also observed (36% in DMF/K_2CO_3) (Table 2, entries 22 and 23).



Scheme 2

Table 1 Influence of the Conditions on the Selectivity of Palladium-Catalysed Coupling of 4-Bromoacetophenone with Dec-1-ene; (Scheme 2)[a]

Entry	Base	Solvent	Temp (°C)	Substrate/catalyst ratio	Selectivity in favour of isomer **1a** (%)	Yield (%)
1	KF	DMF	130	250	29	100
2	$NaHCO_3$	DMF	130	250	32	100
3	Na_2CO_3	DMF	130	250	38	35
4	K_2CO_3	DMF	130	10000	64	80
5	NaOAc	DMF	130	250	54	94
6	NaOAc	DMF	130	250	49	39[b]
7	K_2CO_3	xylene	100	100	10	100
8	K_2CO_3	xylene	110	250	9	93
9	K_2CO_3	NMP	130	250	51	100
10	K_2CO_3	DMA	130	250	53	100
11	NaOAc	NMP	130	250	57	100
12	NaOAc	DMA	130	1000	67	100
13	NaOAc	pentan-1-ol	130	250	46	100
14	NaOAc	DMA	110	1000	73	100
15	NaOAc	DMA	110	10000	76	99 (96)[c]
16	NaOAc	DMA	110	10000	–	0[d]
17	NaOAc	DMA	110	10000	–	0[e]
18	K_2CO_3	MeCN	100	100	82[f]	36
19	NaOAc	MeCN	100	100	84[f]	53

[a] Conditions: $[Pd(C_3H_5)Cl]_2$/Tedicyp = 1:2, 4-bromoacetophenone: 1 mmol, dec-1-ene: 2 mmol, base: 2 mmol, 20 h, argon. GC and NMR yields.
[b] Two mmol of Bu_4NI was added.
[c] Isolated yield.
[d] Reaction performed without ligand.
[e] Reaction performed with $[Pd(C_3H_5)Cl]_2/PPh_3$ = 1:4 as catalyst.
[f] Selectivity in favour of isomer **1b**.

On the other hand, in the presence of di-*ortho*-substituted aryl bromides such as bromomesitylene or 9-bromoanthracene, mixtures of isomers were obtained (Table 2, entries 24 and 25).

The heteroaromatics, 3-bromopyridine and 3-bromoquinoline also led to isomers **13a** and **14a** in similar selectivities of 70% and 75% (Table 2, entries 25–27).

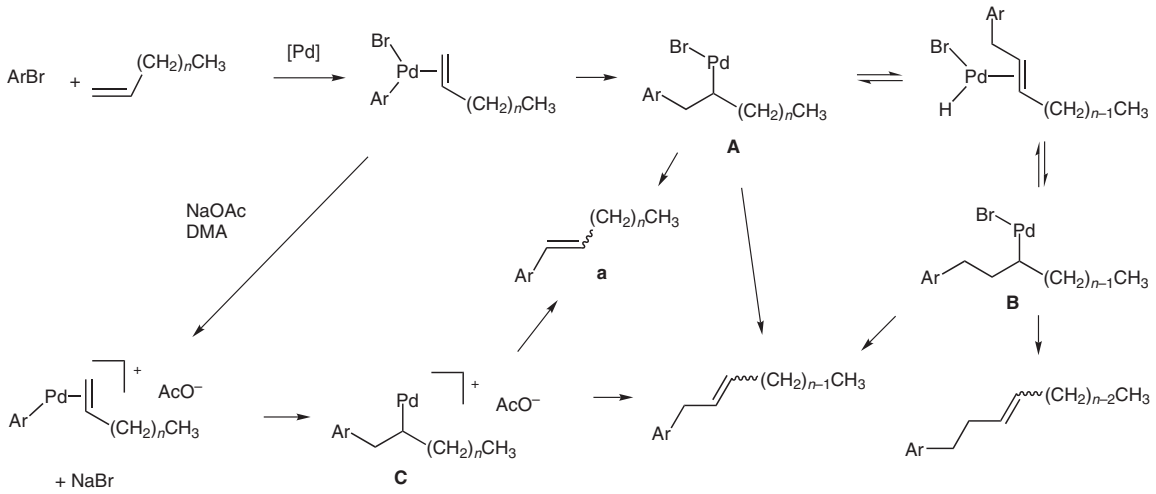
In summary, in all cases the DMA/NaOAc conditions gave higher selectivities than the DMF/K_2CO_3 conditions. The migration of the double bond of the alkene occurs after ordinary Heck arylation on the terminal (or internal) carbon (Scheme 3). Then, an elimination-readdition of HPdBr to give intermediate **B** would occur. We assumed that using the DMA/NaOAc conditions, a sodium acetate mediated abstraction of bromide from the arylpalladium bromide takes place. This intermediate would form a π alkene-palladium complex from which the aryl is transferred to the terminal position to give complex **C**. Then, the 1-arylalk-1-enes would be formed after irreversible elimination of a PdH species.

We have further investigated this reaction in the presence of oct-1-ene (Scheme 4, Table 3). The length of the alkyl chain on the alkene has a minor influence on the selectivity. Similar or slightly higher selectivities in favour of (*E*)-1-arylalk-1-enes were obtained with oct-1-ene than with dec-1-ene. For example selectivities of 84% and 75% in favour of products **16a** and **21a** were obtained for the coupling of oct-1-ene with 4-bromobenzaldehyde or 4-fluorobromobenzene instead of 81% and 70% with dec-1-ene (Table 3, entries 3 and 12). With this alkene we also examined the selectivity of the reaction using a several other aryl bromides. For example, with methyl 4-bromoben-

Table 2 Palladium-Catalysed Coupling of Aryl Halides with Dec-1-ene (Scheme 2)[a]

Entry	Aryl halide	Solvent	Base	Substrate/catalyst ratio	Product number Isomer **a**	Ratio of isomers **a**:**b**:other isomers (%)	Yield (%)
1	4-bromoacetophenone	DMAc	NaOAc	10000	**1a**	76:10:14	99 (96)
2	4-bromobenzaldehyde	DMAc	NaOAc	1000	**2a**	82:9:9	100 (97)
3	4-bromobenzaldehyde	DMA	NaOAc	10000	**2a**	81:10:9	92
4	4-bromobenzaldehyde	DMF	K_2CO_3	10000	**2a**	66:14:20	100[b]
5	4-bromobenzophenone	DMA	NaOAc	1000	**3a**	76:10:14	98 (96)
6	4-bromobenzophenone	DMA	NaOAc	10000	**3a**	80:7:13	33
7	4-bromobenzophenone	DMF	K_2CO_3	10000	**3a**	64:14:22	80[b]
8	4-trifluoromethylbromobenzene	DMA	NaOAc	10000	**4a**	73:9:18	100 (97)
9	4-trifluoromethylbromobenzene	DMF	K_2CO_3	10000	**4a**	59:11:30	95[b]
10	4-bromobenzonitrile	DMA	NaOAc	10000	**5a**	76:10:14	99 (95)
11	4-bromobenzonitrile	DMF	K_2CO_3	10000	**5a**	52:20:28	92[b]
12	4-bromonitrobenzene	DMA	NaOAc	10000	**6a**	80:10:10	95 (93)
13	3,5-bistrifluoromethylbromobenzene	DMA	NaOAc	10000	**7a**	83:8:9	100 (95)
14	3,5-bistrifluoromethylbromobenzene	DMF	K_2CO_3	10000	**7a**	70:15:15	82[b]
15	4-fluorobromobenzene	DMA	NaOAc	1000	**8a**	69:12:19	100 (95)
16	iodobenzene	DMA	NaOAc	10000	**9a**	68:9:23	100 (94)
17	iodobenzene	DMF	K_2CO_3	10000	**9a**	43:25:32	88[b]
18	bromobenzene	DMA	NaOAc	1000	**9a**	64:14:22	93 (82)
19	4-bromoanisole	DMA	NaOAc	1000	**10a**	63:15:22	100 (96)
20	4-bromoanisole	DMA	NaOAc	10000	**10a**	62:15:23	22
21	4-bromoanisole	DMF	K_2CO_3	100	**10a**	51:21:28	58
22	2-bromotoluene	DMA	NaOAc	10000	**11a**	70:3:27	96 (93)
23	2-bromotoluene	DMF	K_2CO_3	1000	**11a**	36:8:56	70[b]
24	bromomesitylene	DMA	NaOAc	1000	–	nd	nd[c]
25	9-bromoanthracene	DMA	NaOAc	1000	–	nd	nd[c]
26	2-bromothiophene	DMA	NaOAc	1000	**12a**	60:28:12	100 (94)
27	2-bromothiophene	DMF	K_2CO_3	1000	**12a**	34:24:42	82[b]
28	3-bromopyridine	DMA	NaOAc	10000	**13a**	70:12:18	100 (94)
29	3-bromopyridine	DMF	K_2CO_3	1000	**13a**	50:18:32	100[b]
30	3-bromoquinoline	DMA	NaOAc	10000	**14a**	75:15:10	92 (90)

[a] Conditions: $[Pd(C_3H_5)Cl]_2$/Tedicyp = 1:2, aryl halide: 1 mmol, dec-1-ene: 2 mmol, base: 2 mmol, 20 h, 110 °C, argon. GC and NMR yields, yields in parenthesis are isolated mixtures of all the isomers.
[b] Reaction performed at 130 °C.
[c] Unidentified mixture of isomers.

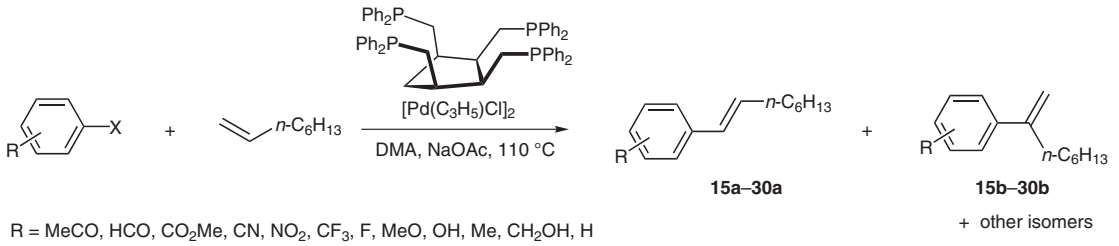


Scheme 3

zoate, bromobenzene or 3-bromonitrobenzene, products **20a**, **22a** and **27a** were obtained in 74%, 79%, and 73% selectivity, respectively (Table 3, entries 11,13 and 18).

Finally, we have investigated this reaction in the presence of four branched alk-1-enes, 4-methylhex-1-ene, 5-methylhex-1-ene, allylcyclopentane, and allylcyclohexane (Scheme 5, Table 4). The best results were obtained using 4-methylhex-1-ene (Table 4, entries 1–13). With this alkene, the migration of the double bond was generally not observed and only 3–9% of the isomers **31b**–**37b** was detected. Therefore, with this alkene, very high selectivities of 91–97% in favour of **31a**–**37a** were obtained. Again, this selectivity does not seem to be largely influenced by electronic factors on the aryl bromide. For example, 4-bromoanisole or 4-bromobenzaldehyde led to similar regio- and stereoselectivities (Table 4, entries 2, 3, 12 and 13). With the other branched alkenes, 5-methylhex-1-ene, allylcyclopentane and allylcyclohexane, selectivities of 74–78% in isomers **38a**–**47a** which are very similar to those obtained using the linear alkenes have been measured (Table 4, entries 14–33). This difference of selectivity between 4-methylhex-1-ene and the other linear of branched alkene probably comes from steric factors. These steric factors seem to have an influence on the elimination–readdition process of HPdBr to give intermediate **B** in Scheme 3.

In summary, in the presence of the Tedicyp/palladium complex, the Heck alkenylation of several aryl halides with linear and branched alk-1-enes can be performed in good yields. With these alkenes, mixtures of isomers are generally obtained due to the partial migration of the alkene carbon–carbon double bond. The selectivity of the reaction depends on the substituents of the aryl halide, on the steric hindrance of the alkene and also on the reaction conditions such as the base, solvent and temperature. In all cases, the major isomer is the (*E*)-1-arylalk-1-ene, and up to 97% of this isomer have been obtained using a branched alkene. However, in most cases selectivities of 70–80% were obtained. Both the *para*-substituted electron-excessive and the electron-deficient aryl bromides were reacted successfully using 0.1–0.01 mol% catalyst. These results indicate that the oxidative addition of the aryl bromide to palladium is probably not the rate-limiting step of the catalytic cycle with such alkenes using this catalyst. For this reason, this method is applicable to both electron-deficient and electron-rich aryl bromides. Even *ortho*-substituted aryl bromides have been used successfully and led to satisfactory regio- and stereoselectivities in favour of isomers **a**. On the other hand, the di-*ortho*-substituted aryl bromides gave mixtures of isomers. We believe that this system compares favourably with other catalyst systems that have been reported for the reactions using simple alk-1-enes. These results represent economically attractive and environmentally friendly procedures. Moreover, several alk-1-enes are commercially available. This is a practical advantage of this reaction compared to the Suzuki, Negishi or Stille coupling procedures using organometallic derivatives of these alkenes.

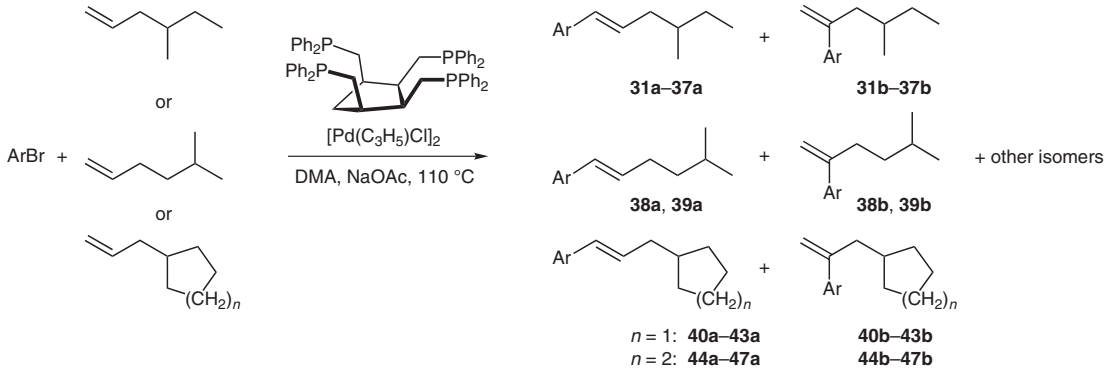


Scheme 4

Table 3 Palladium-Catalysed Coupling of Aryl Halides with Oct-1-ene (Scheme 4)[a]

Entry	Aryl bromide	Substrate/catalyst ratio	Product number Isomer **a**	Ratio of isomers **a**:**b**:other isomers (%)	Yield (%)
1	4-bromoacetophenone	250	**15a**	78:10:12	86 (84)
2	4-bromoacetophenone	1000	**15a**	79:9:12	52
3	4-bromobenzaldehyde	1000	**16a**	84:4:12	98 (94)
4	4-bromobenzaldehyde	10000	**16a**	76:10:14	12
5	4-trifluoromethylbromobenzene	1000	**17a**	75:10:15	100 (92)
6	4-trifluoromethylbromobenzene	10000	**17a**	78:6:26	77
7	4-bromobenzonitrile	250	**18a**	76:9:15	95 (90)
8	4-bromobenzonitrile	1000	**18a**	76:9:15	61
9	4-bromonitrobenzene	1000	**19a**	80:9:11	100 (93)
10	4-bromonitrobenzene	10000	**19a**	74:9:17	60
11	methyl 4-bromobenzoate	1000	**20a**	74:10:16	95 (90)
12	4-fuorobromobenzene	1000	**21a**	75:8:17	94 (89)
13	bromobenzene	1000	**22a**	79:6:15	85 (82)
14	4-bromotoluene	1000	**23a**	77:9:14	100 (94)
15	4-bromoanisole	250	**24a**	62:13:25	93 (90)
16	4-bromophenol	1000	**25a**	70:10:20	40 (36)
17	3-bromobenzaldehyde	1000	**26a**	70:15:15	95 (91)
18	3-bromonitrobenzene	250	**27a**	73:13:14	85 (80)
19	2-bromoacetophenone	250	**28a**	57:nd:43[b]	28 (25)
20	2-bromobenzyl alcohol	250	**29a**	70:nd:30[b]	100 (90)
21	2-bromobenzyl alcohol	1000	**29a**	48:nd:52[b]	20
22	2-bromotoluene	1000	**30a**	74:nd:26[b]	100 (93)

[a] Conditions: $[Pd(C_3H_5)Cl]_2$/Tedicyp = 1:2, aryl bromide: 1 mmol, oct-1-ene: 2 mmol, NaOAc: 2 mmol, DMA, 20 h, 110 °C, argon. GC and NMR yields, yields in parenthesis are isolated mixtures of all the isomers.
[b] nd = not determined.



Scheme 5

Table 4 Palladium-Catalysed Coupling of Aryl Halides with 4-Methylhex-1-ene, 5-Methylhex-1-ene, Allylcyclopentane, or Allylcyclohexane (Scheme 5)[a]

Entry	Aryl bromide	Alkene	Substrate/catalyst ratio	Product number Isomer **a**	Ratio of isomers **a**:**b**:other isomers (%)	Yield (%)
1	4-bromoacetophenone	4-methylhex-1-ene	1000	**31a**	92:8:0	100 (95)
2	4-bromoacetophenone	4-methylhex-1-ene	10000	**31a**	92:8:0	60
3	4-bromobenzaldehyde	4-methylhex-1-ene	1000	**32a**	92:8:0	100 (94)
4	4-bromobenzophenone	4-methylhex-1-ene	250	**33a**	91:9:0	100 (95)
5	4-bromobenzophenone	4-methylhex-1-ene	10000	**33a**	91:9:0	15
6	4-trifluoromethylbromobenzene	4-methylhex-1-ene	250	**34a**	97:3:0	100 (94)
7	4-trifluoromethylbromobenzene	4-methylhex-1-ene	1000	**34a**	97:3:0	90
8	4-bromobenzonitrile	4-methylhex-1-ene	250	**35a**	95:5:0	100 (95)
9	4-bromobenzonitrile	4-methylhex-1-ene	1000	**35a**	97:3:0	35
10	4-bromonitrobenzene	4-methylhex-1-ene	250	**36a**	96:4:0	92 (87)
11	4-bromonitrobenzene	4-methylhex-1-ene	1000	**36a**	96:4:0	38
12	4-bromoanisole	4-methylhex-1-ene	250	**37a**	92:8:0	98 (94)
13	4-bromoanisole	4-methylhex-1-ene	1000	**37a**	90:8:2	79
14	4-bromoacetophenone	5-methylhex-1-ene	1000	**38a**	76:10:14	100 (96)
15	4-bromoacetophenone	5-methylhex-1-ene	10000	**38a**	78:8:14	18
16	4-bromobenzophenone	5-methylhex-1-ene	250	**39a**	74:12:14	100 (94)
17	4-bromobenzophenone	5-methylhex-1-ene	1000	**39a**	75:11:14	45
18	4-bromoacetophenone	allylcyclopentane	250	**40a**	76:11:13	92 (87)
19	4-bromoacetophenone	allylcyclopentane	1000	**40a**	75:11:14	83
20	4-bromobenzophenone	allylcyclopentane	250	**41a**	77:12:11	83 (80)
21	4-bromobenzophenone	allylcyclopentane	1000	**41a**	77:11:12	38
22	4-bromonitrobenzene	allylcyclopentane	250	**42a**	75:11:14	100 (93)
23	4-bromonitrobenzene	allylcyclopentane	1000	**42a**	74:12:14	52
24	3-bromopyridine	allylcyclopentane	250	**43a**	78:8:14	100 (91)
25	3-bromopyridine	allylcyclopentane	1000	**43a**	78:8:14	50
26	4-bromoacetophenone	allylcyclohexane	1000	**44a**	76:9:15	97 (94)
27	4-bromoacetophenone	allylcyclohexane	10000	**44a**	78:8:14	37
28	4-bromonitrobenzene	allylcyclohexane	250	**45a**	76:7:17	100 (92)
29	4-bromonitrobenzene	allylcyclohexane	1000	**45a**	78:7:15	52
30	3-bromotoluene	allylcyclohexane	250	**46a**	77:13:10	100 (91)
31	3-bromotoluene	allylcyclohexane	1000	**46a**	77:12:11	70
32	3-bromopyridine	allylcyclohexane	1000	**47a**	77:13:10	100 (94)
33	3-bromopyridine	allylcyclohexane	10000	**47a**	78:13:9	13

[a] Conditions: $[Pd(C_3H_5)Cl]_2$/Tedicyp = 1:2, aryl bromide: 1 mmol, alk-1-ene: 2 mmol, NaOAc: 2 mmol, DMA, 20 h, 110 °C, argon. GC and NMR yields, yields in parenthesis are isolated mixtures of all the isomers.

DMA (*N*,*N*-dimethylacetamide) analytical grade (99%) was not distilled before use. NaOAc 99% was used. Aryl halides and alkenes were used without purification. All reactions were run under argon using vacuum lines in Schlenk tubes in oven-dried glassware. The reactions were followed by GC and NMR. Conversions were determined using ^{1}H NMR and the GC analysis of the crude mixture without internal standard. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$. Flash chromatography was performed on silica gel (230–400 mesh). The isolated yields given are for mixtures of all the isomers. The NMR analyses were performed on the cleanest purified fraction.

Pd-Tedicyp Catalyst[10]

An oven-dried 40-mL Schlenk tube equipped with a magnetic stirring bar under argon, 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). Anhyd DMF (2.5 mL) was added, and the solution was stirred at r.t. for 10 min.

Heck Reaction of Alk-1-enes with Aryl Halides; General Procedure

A mixture of aryl halide (1 mmol), alk-1-ene (2 mmol) and NaOAc (0.164 g, 2 mmol) in DMA (3 mL) was heated at 110 °C for 20 h in the presence of *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane/$[Pd(C_3H_5)Cl]_2$ complex (1:2, prepared as above) under argon. The corresponding products or mixture of 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 on silica gel (pentane–Et_2O).

(*E*)-1-Acetyl-4-(dec-1-enyl)benzene (1a) (Table 2, Entry 1)[5b]

The reaction of 4-bromoacetophenone (0.199 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **1a** in 76% selectivity and in 96% (0.248 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.7 Hz, 2 H), 7.39 (d, *J* = 8.7 Hz, 2 H), 6.41 (d, *J* = 15.9 Hz, 1 H), 6.34 (m, 1 H), 2.57 (s, 3 H), 2.25–2.10 (m, 2 H), 1.50–1.35 (m, 2 H), 1.35–1.15 (m, 10 H), 0.87 (m, 3 H).

(*E*)-1-Acetyl-4-(dec-1-en-2-yl)benzene (1b)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.7 Hz, 2 H), 7.48 (d, *J* = 8.7 Hz, 2 H), 5.35 (s, 1 H), 5.15 (s, 1 H), 2.59 (s, 3 H), 2.50–2.40 (m, 2 H), 1.50–1.10 (m, 12 H), 0.86 (t, *J* = 7.7 Hz, 3 H).

(*E*)-4-(Dec-1-enyl)benzaldehyde (2a) (Table 2, Entry 2)

The reaction of 4-bromobenzaldehyde (0.185 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **2a** in 82% selectivity and in 97% (0.237 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.94 (s, 1 H), 7.78 (d, *J* = 8.3 Hz, 2 H), 7.46 (d, *J* = 8.3 Hz, 2 H), 6.41 (m, 2 H), 2.30–2.20 (m, 2 H), 1.50–1.23 (m, 12 H), 0.93–0.53 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.7, 144.1, 135.5, 134.8, 130.1, 128.9, 126.3, 33.2, 31.8, 30.9, 29.4, 29.2, 29.0, 22.6, 14.0.

Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.29; H, 9.91.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.37 (s, 1 H), 5.18 (s, 1 H).

(*E*)-1-Benzoyl-4-(dec-1-enyl)benzene (3a) (Table 2, Entry 5)

The reaction of 4-bromobenzophenone (0.261 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **3a** in 76% selectivity and in 96% (0.307 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.3 Hz, 2 H), 7.73 (d, *J* = 8.3 Hz, 2 H), 7.56 (t, *J* = 7.6 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.42 (d, *J* = 8.3 Hz, 2 H), 6.45 (d, *J* = 15.7 Hz, 1 H), 6.39 (dt, *J* = 15.7, 7.0 Hz, 1 H), 2.27–2.18 (m, 2 H), 1.53–1.40 (m, 2 H), 1.40–1.18 (m, 10 H), 0.87 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.3, 142.6, 137.0, 134.9, 132.5, 131.9, 131.0, 130.3, 129.3, 128.6, 126.0, 33.6, 32.2, 31.3, 29.8, 29.6, 29.5, 23.0, 14.5.

Anal. Calcd for $C_{23}H_{28}O$: C, 86.20; H, 8.81. Found: C, 86.14; H, 8.97.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.36 (s, 1 H), 5.17 (s, 1 H).

(*E*)-1-(Dec-1-enyl)-4-trifluoromethylbenzene (4a) (Table 2, Entry 8)[5b]

The reaction of 4-trifluoromethylbromobenzene (0.225 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **4a** in 73% selectivity and in 97% (0.276 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 6.40 (d, *J* = 15.7 Hz, 1 H), 6.32 (dt, *J* = 15.7, 7.0 Hz, 1 H), 2.27–2.18 (m, 2 H), 1.53–1.40 (m, 2 H), 1.40–1.18 (m, 10 H), 0.88 (t, *J* = 7.0 Hz, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.31 (s, 1 H), 5.12 (s, 1 H).

(*E*)-4-(Dec-1-enyl)benzonitrile (5a) (Table 2, Entry 10)[5b]

The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **5a** in 76% selectivity and in 95% (0.229 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 6.37 (m, 2 H), 2.27–2.18 (m, 2 H), 1.53–1.40 (m, 2 H), 1.40–1.18 (m, 10 H), 0.87 (t, *J* = 7.0 Hz, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.31 (s, 1 H), 5.16 (s, 1 H).

(*E*)-1-(Dec-1-enyl)-4-nitrobenzene (6a) (Table 2, Entry 12)[5b]

The reaction of 4-bromonitrobenzene (0.202 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **6a** in 80% selectivity and in 93% (0.243 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.9 Hz, 2 H), 7.43 (d, *J* = 7.9 Hz, 2 H), 6.46–6.34 (m, 2 H), 2.30–2.15 (m, 2 H), 1.50–1.40 (m, 2 H), 1.40–1.10 (m, 10 H), 0.90–0.75 (m, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.37 (s, 1 H), 5.21 (s, 1 H).

(*E*)-1-(Dec-1-enyl)-3,5-bis(trifluoromethyl)benzene (7a) (Table 2, Entry 13)

The reaction of 3,5-bis(trifluoromethyl)bromobenzene (0.293 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **7a** in 83% selectivity and in 95% (0.335 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (s, 2 H), 7.65 (s, 1 H), 6.43 (d, *J* = 15.9 Hz, 1 H), 6.35 (m, 1 H), 2.30–2.17 (m, 2 H), 1.52–1.15 (m, 12 H), 0.90–0.80 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5, 135.2, 131.3 (q, *J* = 32.3 Hz), 126.8, 125.2 (m), 123.1 (q, *J* = 273.1 Hz), 119.7 (m), 33.0, 31.8, 30.9, 29.4, 29.2, 29.0, 22.6, 14.1.

Anal. Calcd for $C_{18}H_{22}F_6$: C, 61.36; H, 6.29. Found: C, 61.49; H, 6.40.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.36 (s, 1 H), 5.22 (s, 1 H).

(*E*)-1-Fluoro-4-(dec-1-enyl)benzene (8a) (Table 2, Entry 15)[5b]
The reaction of 4-fluorobromobenzene (0.175 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **8a** in 69% selectivity and in 95% (0.223 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (dd, *J* = 8.6, 5.5 Hz, 2 H), 6.96 (t, *J* = 8.6 Hz, 2 H), 6.32 (d, *J* = 15.7 Hz, 1 H), 6.12 (dt, *J* = 15.7, 7.0 Hz, 1 H), 2.25–2.10 (m, 2 H), 1.50–1.40 (m, 2 H), 1.40–1.10 (m, 10 H), 0.87 (t, *J* = 7.0 Hz, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.19 (s, 1 H), 5.02 (s, 1 H).

(*E*)-1-Phenyldec-1-ene (9a) (Table 2, Entry 16)[19]
The reaction of iodobenzene (0.204 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **9a** in 68% selectivity and in 94% (0.203 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.10 (m, 5 H), 6.37 (d, *J* = 15.8 Hz, 1 H), 6.22 (dt, *J* = 15.8, 6.8 Hz, 1 H), 2.25–2.10 (m, 2 H), 1.55–1.10 (m, 12 H), 0.87 (t, *J* = 7.0 Hz, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.24 (s, 1 H), 5.01 (s, 1 H).

(*E*)-1-(Dec-1-enyl)-4-methoxybenzene (10a) (Table 2, Entry 19)[5b]
The reaction of 4-bromoanisole (0.187 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **10a** in 63% selectivity and in 96% (0.236 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.7 Hz, 2 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 6.30 (d, *J* = 15.8 Hz, 1 H), 6.05 (dt, *J* = 15.8, 7.1 Hz, 1 H), 3.80 (s, 3 H), 2.20–2.10 (m, 2 H), 1.50–1.40 (m, 2 H), 1.40–1.10 (m, 10 H), 0.88 (t, *J* = 7.0 Hz, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.18 (s, 1 H), 4.96 (s, 1 H).

(*E*)-1-(Dec-1-enyl)-2-methylbenzene (11a) (Table 2, Entry 22)
The reaction of 2-bromotoluene (0.171 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **11a** in 70% selectivity and in 93% (0.214 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.2 Hz, 1 H), 7.15–7.05 (m, 3 H), 6.55 (d, *J* = 15.7 Hz, 1 H), 6.07 (dt, *J* = 15.7, 7.0 Hz, 1 H), 2.31 (s, 3 H), 2.27–2.07 (m, 2 H), 1.50–1.40 (m, 2 H), 1.40–1.15 (m, 10 H), 0.87 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.8, 135.6, 133.3, 130.8, 128.3, 127.4, 126.7, 126.2, 34.1, 32.6, 30.3, 30.2, 30.0, 29.9, 23.4, 20.5, 14.8.

Anal. Calcd for $C_{17}H_{26}$: C, 88.63; H, 11.37. Found: C, 88.50; H, 11.17.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.15 (s, 1 H), 4.81 (s, 1 H).

(*E*)-2-(Dec-1-enyl)thiophene (12a) (Table 2, Entry 26)[20]
The reaction of 2-bromothiophene (0.163 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **12a** in 60% selectivity and in 94% (0.209 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05 (m, 1 H), 6.92 (m, 1 H), 6.85 (m, 1 H), 6.48 (d, *J* = 15.8 Hz, 1 H), 6.06 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.20–2.10 (m, 2 H), 1.50–1.40 (m, 2 H), 1.40–1.10 (m, 10 H), 0.88 (t, *J* = 7.0 Hz, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.37 (s, 1 H), 4.93 (s, 1 H).

(*E*)-3-(Dec-1-enyl)pyridine (13a) (Table 2, Entry 28)[5b]
The reaction of 3-bromopyridine (0.158 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **13a** in 70% selectivity and in 94% (0.204 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (s, 1 H), 8.40 (d, *J* = 4.7 Hz, 1 H), 7.65 (d, *J* = 7.5 Hz, 1 H), 7.21 (dd, *J* = 7.5, 4.7 Hz, 1 H), 6.35 (d, *J* = 15.8 Hz, 1 H), 6.29 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.25–2.15 (m, 2 H), 1.50–1.40 (m, 2 H), 1.40–1.10 (m, 10 H), 0.88 (t, *J* = 7.0 Hz, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.30 (s, 1 H), 5.14 (s, 1 H).

(*E*)-3-(Dec-1-enyl)quinoline (14a) (Table 2, Entry 30)
The reaction of 3-bromoquinoline (0.208 g, 1 mmol) and dec-1-ene (0.280 g, 2 mmol) afforded **14a** in 75% selectivity and in 90% (0.240 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.95 (d, *J* = 2.2 Hz, 1 H), 8.04 (d, *J* = 8.1 Hz, 1 H), 7.94 (d, *J* = 2.2 Hz, 1 H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 1 H), 6.51 (d, *J* = 15.8 Hz, 1 H), 6.43 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.30–2.20 (m, 2 H), 1.55–1.45 (m, 2 H), 1.40–1.10 (m, 10 H), 0.87 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.3, 147.1, 134.0, 131.4, 130.8, 129.1, 128.7, 128.1, 127.6, 126.7, 126.5, 33.3, 31.8, 29.4, 29.3, 29.2, 29.1, 22.6, 14.1.

Anal. Calcd for $C_{19}H_{25}N$: C, 85.34; H, 9.42. Found: C, 85.30; H, 9.27.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.45 (s, 1 H), 5.24 (s, 1 H).

(*E*)-1-Acetyl-4-(oct-1-enyl)benzene (15a) (Table 3, Entry 1)[21]
The reaction of 4-bromoacetophenone (0.199 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **15a** in 78% selectivity and in 84% (0.193 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.5 Hz, 2 H), 7.39 (d, *J* = 8.5 Hz, 2 H), 6.41 (d, *J* = 15.9 Hz, 1 H), 6.33 (m, 1 H), 2.56 (s, 3 H), 2.30–2.15 (m, 2 H), 1.65–1.10 (m, 8 H), 0.90–0.65 (m, 3 H).

Traces of branched isomer were also observed.

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

(*E*)-4-(Oct-1-enyl)benzaldehyde (16a) (Table 3, Entry 3)[5a]
The reaction of 4-bromobenzaldehyde (0.185 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **16a** in 84% selectivity and in 94% (0.203 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.95 (s, 1 H), 7.80 (d, *J* = 8.1 Hz, 2 H), 7.47 (d, *J* = 8.1 Hz, 2 H), 6.44 (d, *J* = 15.9 Hz, 1 H), 6.40–6.30 (m, 1 H), 2.30–2.10 (m, 2 H), 1.60–1.10 (m, 8 H), 0.88 (t, *J* = 7.0 Hz, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.35 (s, 1 H), 5.14 (s, 1 H).

(*E*)-1-(Oct-1-enyl)-4-(trifluoromethyl)benzene (17a) (Table 3, Entry 5)[22]
The reaction of 4-trifluoromethylbromobenzene (0.225 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **17a** in 75% selectivity and in 92% (0.236 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.3 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 2 H), 6.39 (d, *J* = 15.9 Hz, 1 H), 6.30 (m, 1 H), 2.25–2.15 (m, 2 H), 1.60–1.10 (m, 8 H), 0.95–0.65 (m, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.29 (s, 1 H), 5.13 (s, 1 H).

(*E*)-4-(Oct-1-enyl)benzonitrile (18a) (Table 3, Entry 7)[23]
The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **18a** in 76% selectivity and in 90% (0.192 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.5 Hz, 2 H), 7.39 (d, *J* = 8.5 Hz, 2 H), 6.40 (d, *J* = 15.9 Hz, 1 H), 6.35 (m, 1 H), 2.30–2.10 (m, 2 H), 1.65–1.10 (m, 8 H), 0.95–0.65 (m, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.33 (s, 1 H), 5.19 (s, 1 H).

(*E*)-1-Nitro-4-(oct-1-enyl)benzene (19a) (Table 3, Entry 9)[23]
The reaction of 4-bromonitrobenzene (0.202 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **19a** in 80% selectivity and in 93% (0.217 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.8 Hz, 2 H), 7.42 (d, *J* = 8.8 Hz, 2 H), 6.41 (d, *J* = 15.9 Hz, 1 H), 6.37 (m, 1 H), 2.30–2.15 (m, 2 H), 1.55–1.10 (m, 8 H), 0.88 (t, *J* = 7.0 Hz, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.36 (s, 1 H), 5.21 (s, 1 H).

(*E*)-Methyl 4-(oct-1-enyl)benzoate (20a) (Table 3, Entry 11)[24]
The reaction of methyl 4-bromobenzoate (0.215 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **20a** in 74% selectivity and in 90% (0.222 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.5 Hz, 2 H), 7.37 (d, *J* = 8.5 Hz, 2 H), 6.40 (d, *J* = 15.9 Hz, 1 H), 6.31 (m, 1 H), 3.86 (m, 3 H), 2.30–2.10 (m, 2 H), 1.60–1.10 (m, 8 H), 0.90–0.70 (m, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.28 (s, 1 H), 5.11 (s, 1 H).

(*E*)-1-Fluoro-4-(oct-1-enyl)benzene (21a) (Table 3, Entry 12)
The reaction of 4-fluorobromobenzene (0.175 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **21a** in 75% selectivity and in 89% (0.183 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (dd, *J* = 8.6, 5.5 Hz, 2 H), 6.97 (t, *J* = 8.6 Hz, 2 H), 6.33 (d, *J* = 15.7 Hz, 1 H), 6.12 (dt, *J* = 15.7, 7.0 Hz, 1 H), 2.25–2.15 (m, 2 H), 1.55–1.10 (m, 8 H), 0.88 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.4 (d, *J* = 245.4 Hz), 133.7 (m), 130.5, 128.1, 126.8 (d, *J* = 7.7 Hz), 114.8 (d, *J* = 21.4 Hz), 32.5, 31.3, 28.9, 28.5, 22.2, 13.7.

Anal. Calcd for $C_{14}H_{19}F$: C, 81.51; H, 9.28. Found: C, 81.67; H, 9.20.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.19 (s, 1 H), 5.03 (s, 1 H).

(*E*)-1-Phenyloct-1-ene (22a) (Table 3, Entry 13)[25]
The reaction of bromobenzene (0.157 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **22a** in 79% selectivity and in 82% (0.154 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.10 (m, 5 H), 6.35 (d, *J* = 15.9 Hz, 1 H), 6.20 (dt, *J* = 15.9, 6.6 Hz, 1 H), 2.25–2.05 (s, 2 H), 1.60–1.10 (m, 12 H), 0.95–0.70 (m, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.22 (s, 1 H), 5.01 (s, 1 H).

(*E*)-1-Methyl-4-(oct-1-enyl)benzene (23a) (Table 3, Entry 14)[9e]
The reaction of 4-bromotoluene (0.171 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **23a** in 77% selectivity and in 94% (0.190 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.3 Hz, 2 H), 7.12 (d, *J* = 8.3 Hz, 2 H), 6.38 (d, *J* = 15.8 Hz, 1 H), 6.20 (dt, *J* = 15.8, 6.8 Hz, 1 H), 2.35 (s, 3 H), 2.25–2.10 (m, 2 H), 1.55–1.10 (m, 8 H), 1.00–0.75 (m, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.25 (s, 1 H), 5.02 (s, 1 H).

(*E*)-1-Methoxy-4-(oct-1-enyl)benzene (24a) (Table 3, Entry 15)[22]
The reaction of 4-bromoanisole (0.187 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **24a** in 62% selectivity and in 90% (0.196 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.5 Hz, 2 H), 6.82 (d, *J* = 8.5 Hz, 2 H), 6.30 (d, *J* = 15.8 Hz, 1 H), 6.07 (dt, *J* = 15.8, 7.0 Hz, 1 H), 3.80 (s, 3 H), 2.20–2.08 (m, 2 H), 1.55–1.10 (m, 8 H), 0.90–0.75 (m, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.17 (s, 1 H), 4.95 (s, 1 H).

(*E*)-4-(Oct-1-enyl)phenol (25a) (Table 3, Entry 16)[26]
The reaction of 4-bromophenol (0.173 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **25a** in 70% selectivity and in 36% (0.074 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.5 Hz, 2 H), 6.76 (d, *J* = 8.5 Hz, 2 H), 6.28 (d, *J* = 15.8 Hz, 1 H), 6.03 (dt, *J* = 15.8, 7.0 Hz, 1 H), 2.20–2.05 (m, 2 H), 1.55–1.10 (m, 8 H), 0.90–0.75 (m, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.15 (s, 1 H), 4.92 (s, 1 H).

(*E*)-3-(Oct-1-enyl)benzaldehyde (26a) (Table 3, Entry 17)[27]
The reaction of 3-bromobenzaldehyde (0.185 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **26a** in 70% selectivity and in 91% (0.197 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.99 (s, 1 H), 7.83 (s, 1 H), 7.69 (d, *J* = 6.4 Hz, 1 H), 7.57 (d, *J* = 7.7 Hz, 1 H), 7.43 (t, *J* = 7.4 Hz, 1 H), 6.42 (d, *J* = 15.7 Hz, 1 H), 6.34 (dt, *J* = 15.7, 7.0 Hz, 1 H), 2.25–2.10 (m, 2 H), 1.55–1.10 (m, 8 H), 0.90–0.75 (m, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.30 (s, 1 H), 5.14 (s, 1 H).

(*E*)-1-Nitro-3-(oct-1-enyl)benzene (27a) (Table 3, Entry 18)[28]
The reaction of 3-nitrobromobenzene (0.202 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **27a** in 73% selectivity and in 80% (0.186 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (s, 1 H), 8.01 (d, *J* = 7.9 Hz, 1 H), 7.60 (d, *J* = 7.6 Hz, 1 H), 7.42 (t, *J* = 8.2 Hz, 1 H), 6.43 (d, *J* = 15.7 Hz, 1 H), 6.35 (dt, *J* = 15.7, 7.0 Hz, 1 H), 2.30–2.15 (m, 2 H), 1.55–1.10 (m, 8 H), 0.90–0.70 (m, 3 H).

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.36 (s, 1 H), 5.19 (s, 1 H).

(*E*)-1-Acetyl-2-(oct-1-enyl)benzene (28a) (Table 3, Entry 19)[29]
The reaction of 2-bromoacetophenone (0.199 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **28a** in 57% selectivity and in 25% (0.061 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.47 (m, 2 H), 7.38–7.22 (m, 2 H), 6.82 (d, *J* = 16.1 Hz, 1 H), 6.09 (dt, *J* = 16.1, 6.8 Hz, 1 H), 2.57 (s, 3 H), 2.25–2.15 (m, 2 H), 1.50–1.15 (m, 8 H), 0.90 (t, *J* = 7.0 Hz, 3 H).

(*E*)-[(2-Oct-1-enyl)phenyl]methanol (29a) (Table 3, Entry 20)[30]
The reaction of 2-bromobenzyl alcohol (0.187 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **29a** in 70% selectivity and in 90% (0.196 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.2 Hz, 1 H), 7.35–7.15 (m, 3 H), 6.70 (d, *J* = 15.7 Hz, 1 H), 6.17 (dt, *J* = 15.7, 6.8 Hz, 1 H), 4.72 (s, 2 H), 2.29–2.20 (m, 2 H), 1.60–1.15 (m, 8 H), 0.90 (t, *J* = 7.0 Hz, 3 H).

(*E*)-1-Methyl-2-(oct-1-enyl)benzene (30a) (Table 3, Entry 22)[23]
The reaction of 2-bromotoluene (0.171 g, 1 mmol) and oct-1-ene (0.224 g, 2 mmol) afforded **30a** in 74% selectivity and in 93% (0.188 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 6.4 Hz, 1 H), 7.19–7.06 (m, 3 H), 6.55 (d, *J* = 15.7 Hz, 1 H), 6.07 (dt, *J* = 15.7, 7.0 Hz, 1 H), 2.29 (s, 3 H), 2.28–2.10 (m, 2 H), 1.70–1.05 (m, 8 H), 0.95–0.60 (m, 3 H).

(*E*)-1-Acetyl-4-(4-methylhex-1-enyl)benzene (31a) (Table 4, Entry 1)
The reaction of 4-bromoacetophenone (0.199 g, 1 mmol) and 4-methylhex-1-ene (0.196 g, 2 mmol) afforded **31a** in 92% selectivity and in 95% (0.205 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.5 Hz, 2 H), 7.40 (d, *J* = 8.5 Hz, 2 H), 6.41 (d, *J* = 15.8 Hz, 1 H), 6.36 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.57 (s, 3 H), 2.30–2.00 (m, 2 H), 1.60–1.10 (m, 3 H), 0.90–0.65 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.1, 142.2, 134.9, 132.8, 129.6, 128.3, 125.5, 39.8, 34.4, 28.8, 26.1, 18.7, 11.0.

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.40; H, 9.17.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.34 (s, 1 H), 5.12 (s, 1 H).

(*E*)-4-(4-Methylhex-1-enyl)benzaldehyde (32a) (Table 4, Entry 3)
The reaction of 4-bromobenzaldehyde (0.185 g, 1 mmol) and 4-methylhex-1-ene (0.196 g, 2 mmol) afforded **32a** in 92% selectivity and in 94% (0.190 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.95 (s, 1 H), 7.79 (d, *J* = 8.5 Hz, 2 H), 7.47 (d, *J* = 8.3 Hz, 2 H), 6.43 (d, *J* = 15.9 Hz, 1 H), 6.38 (m, 1 H), 2.30–2.00 (m, 2 H), 1.50–1.10 (m, 3 H), 0.90–0.65 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.1, 144.4, 135.0, 134.6, 130.6, 130.5, 126.8, 40.8, 35.3, 29.6, 19.6, 11.9.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.00; H, 9.07.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.36 (s, 1 H), 5.15 (s, 1 H).

(*E*)-1-Benzoyl-4-(4-methylhex-1-enyl)benzene (33a) (Table 4, Entry 4)
The reaction of 4-bromobenzophenone (0.261 g, 1 mmol) and 4-methylhex-1-ene (0.196 g, 2 mmol) afforded **33a** in 91% selectivity and in 95% (0.264 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.4 Hz, 2 H), 7.75 (d, *J* = 8.4 Hz, 2 H), 7.58 (t, *J* = 7.5 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 6.44 (d, *J* = 15.8 Hz, 1 H), 6.37 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.30–2.00 (m, 2 H), 1.60–1.10 (m, 3 H), 0.90–0.80 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.6, 142.5, 138.3, 136.0, 133.5, 132.5, 131.0, 130.5, 130.3, 128.6, 126.1, 40.7, 35.3, 29.6, 19.6, 11.9.

Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.54; H, 8.14.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.37 (s, 1 H), 5.14 (s, 1 H).

(*E*)-1-(4-Methylhex-1-enyl)-4-(trifluoromethyl)benzene (34a) (Table 4, Entry 6)
The reaction of 4-trifluoromethylbromobenzene (0.225 g, 1 mmol) and 4-methylhex-1-ene (0.196 g, 2 mmol) afforded **34a** in 97% selectivity and in 94% (0.228 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.3 Hz, 2 H), 7.41 (d, *J* = 8.3 Hz, 2 H), 6.39 (d, *J* = 15.8 Hz, 1 H), 6.33 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.30–1.95 (m, 2 H), 1.55–1.10 (m, 3 H), 0.95–0.80 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.8, 129.6 (m), 127.5, 126.0, 125.4 (q, *J* = 3.8 Hz), 40.2, 34.8, 29.2, 19.1, 11.4.

Anal. Calcd for $C_{14}H_{17}F_3$: C, 69.40; H, 7.07. Found: C, 69.51; H, 6.91.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.31 (s, 1 H), 5.11 (s, 1 H).

(*E*)-4-(4-Methylhex-1-enyl)benzonitrile (35a) (Table 4, Entry 8)
The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol) and 4-methylhex-1-ene (0.196 g, 2 mmol) afforded **35a** in 95% selectivity and in 95% (0.189 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 7.4 Hz, 2 H), 7.40 (d, *J* = 7.4 Hz, 2 H), 6.39 (d, *J* = 15.9 Hz, 1 H), 6.32 (dt, *J* = 15.9, 7.4 Hz, 1 H), 2.30–1.95 (m, 2 H), 1.55–1.10 (m, 3 H), 0.95–0.80 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4, 134.3, 132.3, 129.5, 126.3, 119.1, 109.9, 40.2, 34.8, 29.2, 19.1, 11.4.

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60. Found: C, 84.02; H, 8.89.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.33 (s, 1 H), 5.14 (s, 1 H).

(*E*)-1-(4-Methylhex-1-enyl)-4-nitrobenzene (36a) (Table 4, Entry 10)
The reaction of 4-bromonitrobenzene (0.202 g, 1 mmol) and 4-methylhex-1-ene (0.196 g, 2 mmol) afforded **36a** in 96% selectivity and in 87% (0.191 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.9 Hz, 2 H), 7.45 (d, *J* = 8.9 Hz, 2 H), 6.51 (d, *J* = 15.9 Hz, 1 H), 6.47 (dt, *J* = 15.9, 7.4 Hz, 1 H), 2.35–2.10 (m, 2 H), 1.65–1.10 (m, 3 H), 0.90–0.75 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8, 144.8, 135.8, 129.6, 126.7, 124.3, 40.7, 35.2, 29.6, 19.6, 11.8.

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81. Found: C, 71.29; H, 7.68.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.36 (s, 1 H), 5.20 (s, 1 H).

(*E*)-1-Methoxy-4-(4-methylhex-1-enyl)benzene (37a) (Table 4, Entry 12)
The reaction of 4-bromoanisole (0.187 g, 1 mmol) and 4-methylhex-1-ene (0.196 g, 2 mmol) afforded **37a** in 92% selectivity and in 94% (0.192 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.3 Hz, 2 H), 6.82 (d, *J* = 8.3 Hz, 2 H), 6.30 (d, *J* = 15.9 Hz, 1 H), 6.05 (dt, *J* = 15.9, 7.4

Hz, 1 H), 3.80 (s, 3 H), 2.25–1.95 (m, 2 H), 1.60–1.10 (m, 3 H), 0.90–0.70 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.6, 130.8, 130.1, 127.7, 126.9, 113.9, 55.3, 40.1, 35.0, 29.1, 19.1, 11.5.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.37; H, 10.08.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.17 (s, 1 H), 4.92 (s, 1 H).

1-Acetyl-4-(5-methylhex-1-enyl)benzene (38a) (Table 4, Entry 14)

The reaction of 4-bromoacetophenone (0.199 g, 1 mmol) and 5-methylhex-1-ene (0.196 g, 2 mmol) afforded **38a** in 76% selectivity and in 96% (0.207 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.5 Hz, 2 H), 7.39 (d, *J* = 8.5 Hz, 2 H), 6.42 (d, *J* = 15.8 Hz, 1 H), 6.34 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.57 (s, 3 H), 2.26 (m, 2 H), 1.65 (m, 1 H), 1.39 (m, 2 H), 0.92 (d, *J* = 7.8 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.0, 143.1, 135.8, 135.1, 129.2, 129.1, 126.3, 38.6, 31.4, 27.9, 26.9, 22.8.

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.48; H, 9.12.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.34 (s, 1 H), 5.16 (s, 1 H).

1-Benzoyl-4-(5-methylhex-1-enyl)benzene (39a) (Table 4, Entry 16)

The reaction of 4-bromobenzophenone (0.261 g, 1 mmol) and 5-methylhex-1-ene (0.196 g, 2 mmol) afforded **39a** in 74% selectivity and in 94% (0.261 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.5 Hz, 2 H), 7.75 (d, *J* = 8.5 Hz, 2 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 2 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 6.45 (d, *J* = 15.8 Hz, 1 H), 6.38 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.26 (m, 2 H), 1.65 (m, 1 H), 1.39 (m, 2 H), 0.92 (d, *J* = 7.8 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.6, 142.6, 138.4, 136.0, 135.0, 132.7, 131.0, 130.3, 129.2, 128.6, 126.0, 38.7, 31.4, 28.0, 22.9.

Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.07; H, 8.04.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.34 (s, 1 H), 5.15 (s, 1 H).

1-Acetyl-4-(3-cyclopentylpropenyl)benzene (40a) (Table 4, Entry 18)

The reaction of 4-bromoacetophenone (0.199 g, 1 mmol) and allylcyclopentane (0.220 g, 2 mmol) afforded **40a** in 76% selectivity and in 87% (0.198 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.5 Hz, 2 H), 7.39 (d, *J* = 8.5 Hz, 2 H), 6.43 (d, *J* = 15.8 Hz, 1 H), 6.34 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.58 (s, 3 H), 2.23 (m, 2 H), 1.95–1.10 (m, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.5, 142.7, 135.4, 133.9, 129.3, 128.7, 125.9, 39.8, 39.5, 32.2, 26.5, 25.1.

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.40; H, 8.73.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.31 (s, 1 H), 5.14 (s, 1 H).

1-Benzoyl-4-(3-cyclopentylpropenyl)benzene (41a) (Table 4, Entry 20)

The reaction of 4-bromobenzophenone (0.261 g, 1 mmol) and allylcyclopentane (0.220 g, 2 mmol) afforded **41a** in 77% selectivity and in 80% (0.232 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.5 Hz, 2 H), 7.75 (d, *J* = 8.5 Hz, 2 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 2 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 6.45 (d, *J* = 15.8 Hz, 1 H), 6.35 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.24 (m, 2 H), 1.95–1.10 (m, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.6, 142.5, 138.3, 136.0, 132.5, 132.0, 131.9, 131.0, 130.3, 128.6, 126.0, 40.2, 39.9, 32.7, 25.5.

Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.99; H, 7.82.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.34 (s, 1 H), 5.16 (s, 1 H).

1-(3-Cyclopentylpropenyl)-4-nitrobenzene (42a) (Table 4, Entry 22)

The reaction of 4-bromonitrobenzene (0.202 g, 1 mmol) and allylcyclopentane (0.220 g, 2 mmol) afforded **42a** in 75% selectivity and in 93% (0.215 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.5 Hz, 2 H), 7.43 (d, *J* = 8.5 Hz, 2 H), 6.45 (d, *J* = 15.8 Hz, 1 H), 6.41 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.25 (m, 2 H), 1.95–1.10 (m, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.9, 136.4, 128.9, 126.7, 124.4, 124.0, 40.1, 39.9, 32.8, 25.5.

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41. Found: C, 72.89; H, 7.50.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.34 (s, 1 H), 5.22 (s, 1 H).

3-(3-Cyclohexylpropenyl)pyridine (43a) (Table 4, Entry 24)

The reaction of 3-bromopyridine (0.158 g, 1 mmol) and allylcyclopentane (0.220 g, 2 mmol) afforded **43a** in 78% selectivity and in 91% (0.170 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (s, 1 H), 8.39 (d, *J* = 4.7 Hz, 1 H), 7.64 (d, *J* = 7.5 Hz, 1 H), 7.20 (dd, *J* = 7.5, 4.7 Hz, 1 H), 6.32 (d, *J* = 15.8 Hz, 1 H), 6.26 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.25 (m, 2 H), 1.95–1.10 (m, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.8, 147.7, 133.5, 133.1, 132.4, 126.6, 123.3, 39.8, 39.5, 32.3, 25.1.

Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15. Found: C, 83.37; H, 9.21.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.26 (s, 1 H), 5.12 (s, 1 H).

1-Acetyl-4-(3-Cyclohexylpropenyl)benzene (44a) (Table 4, Entry 26)

The reaction of 4-bromoacetophenone (0.199 g, 1 mmol) and allylcyclohexane (0.248 g, 2 mmol) afforded **44a** in 76% selectivity and in 94% (0.228 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.5 Hz, 2 H), 7.38 (d, *J* = 8.5 Hz, 2 H), 6.39 (d, *J* = 15.9 Hz, 1 H), 6.35 (m 1 H), 2.55 (s, 3 H), 2.20 (m, 2 H), 1.95–0.85 (m, 11 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.2, 143.2, 135.9, 133.7, 130.5, 129.3, 126.5, 41.7, 38.6, 33.8, 27.1, 26.9, 26.8.

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.04; H, 9.27.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.31 (s, 1 H), 5.14 (s, 1 H).

1-(3-Cyclohexylpropenyl)-4-nitrobenzene (45a) (Table 4, Entry 28)

The reaction of 4-bromonitrobenzene (0.202 g, 1 mmol) and allylcyclohexane (0.248 g, 2 mmol) afforded **45a** in 76% selectivity and in 92% (0.225g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.5 Hz, 2 H), 7.43 (d, *J* = 8.5 Hz, 2 H), 6.48 (d, *J* = 15.8 Hz, 1 H), 6.38 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.20 (m, 2 H), 1.95–0.85 (m, 11 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.8, 135.7, 129.4, 126.7, 125.4, 124.4, 41.2, 37.9, 33.2, 26.4, 26.3.

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81. Found: C, 73.28; H, 7.89.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.39 (s, 1 H), 5.18 (s, 1 H).

1-(3-Cyclohexylpropenyl)-3-methylbenzene (46a) (Table 4, Entry 30)

The reaction of 3-bromotoluene (0.171 g, 1 mmol) and allylcyclohexane (0.248 g, 2 mmol) afforded **46a** in 77% selectivity and in 91% (0.195 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–6.94 (m, 4 H), 6.33 (d, *J* = 15.8 Hz, 1 H), 6.20 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.32 (s, 3 H), 2.20 (m, 2 H), 1.85–0.85 (m, 11 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.3, 137.2, 130.0, 128.9, 127.7, 126.9, 125.9, 122.4, 40.4, 37.6, 32.5, 25.9, 25.7.

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.90; H, 10.41.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.23 (s, 1 H), 4.98 (s, 1 H).

3-(3-Cyclohexylpropenyl)pyridine (47a) (Table 4, Entry 32)

The reaction of 3-bromopyridine (0.158 g, 1 mmol) and allylcyclohexane (0.248 g, 2 mmol) afforded **47a** in 77% selectivity and in 94% (0.189 g) yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (s, 1 H), 8.39 (d, *J* = 4.7 Hz, 1 H), 7.65 (d, *J* = 7.5 Hz, 1 H), 7.20 (dd, *J* = 7.5, 4.7 Hz, 1 H), 6.32 (d, *J* = 15.8 Hz, 1 H), 6.27 (dt, *J* = 15.8, 7.1 Hz, 1 H), 2.08 (m, 2 H), 1.85–0.85 (m, 11 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.7, 147.6, 133.5, 132.5, 132.4, 127.1, 123.3, 41.1, 38.0, 33.1, 26.4, 26.3.

Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51. Found: C, 83.40; H, 9.47.

Traces of branched isomer were also observed.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.28 (s, 1 H), 5.08 (s, 1 H).

References

(1) Beletskaya, I.; Cheprakov, A. *Chem. Rev.* **2000**, *100*, 3009.
(2) Withcombe, N.; Hii (Mimi), K. K.; Gibson, S. *Tetrahedron* **2001**, *57*, 7449.
(3) Littke, A.; Fu, G. *Angew. Chem. Int. Ed.* **2002**, *41*, 4176.
(4) Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553.
(5) For couplings of alk-1-enylboronic acids with aryl halides via Suzuki reaction, see: (a) Wright, S. W.; Hageman, D. L.; McClure, L. D. *J. Org. Chem.* **1994**, *59*, 6095. (b) Molander, G. A.; Bernardi, C. R. *J. Org. Chem.* **2002**, *67*, 8424. (c) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *J. Org. Chem.* **2003**, *38*, 7733. (d) Peyroux, E.; Berthiol, F.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2004**, 1075.
(6) For couplings of alk-1-enyl stannanes with aryl bromides via Stille reaction, see: (a) Falcou, A.; Marsacq, D.; Hourquebie, P.; Duchêne, A. *Tetrahedron* **2000**, *56*, 225. (b) Wang, X.; Parlow, J. J.; Porco, J. A. Jr. *Org. Lett.* **2000**, *2*, 3509.
(7) For couplings of alk-1-enyl zinc with aryl halides via Negishi reaction, see: Betzemeier, B.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2623.
(8) (a) Mabic, S.; Vaysse, L.; Benezra, C.; Lepoittevin, J.-P. *Synthesis* **1999**, 1127. (b) Kline, T.; Bowman, J.; Iglewski, B. H.; de Kievit, T.; Kakai, Y.; Passador, L. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 3447. (c) Cho, S. Y.; Ahn, J. H.; Ha, J. D.; Kang, S. K.; Baek, J. Y.; Han, S. S.; Shin, E. Y.; Kim, S. S.; Kim, K. R.; Cheong, H. G.; Choi, J.-K. *Bull. Korean Chem. Soc.* **2003**, *24*, 1455.
(9) For examples of Heck reaction using aryl halides and alk-1-enes: (a) Mabic, S.; Lepoittevin, J.-P. *Tetrahedron Lett.* **1995**, *36*, 1705. (b) Bräse, S.; Rümper, J.; Voigt, K.; Albecq, S.; Thurau, G.; Villard, R.; Waegell, B.; de Meijere, A. *Eur. J. Org. Chem.* **1998**, 671. (c) Littke, A.; Fu, G. *J. Am. Chem. Soc.* **2001**, *123*, 6989. (d) Albéniz, A. C.; Espinet, P.; Martin-Ruiz, B.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 11504. (e) Grasa, G. A.; Singh, R.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2003**, *687*, 269. (f) Xu, L.; Mo, J.; Baillie, C.; Xiao, J. *J. Organomet. Chem.* **2003**, *687*, 301. (g) Smith, G. S.; Mapolie, S. F. *J. Mol. Catal. A: Chem.* **2004**, *213*, 187. (h) Yi, C.; Hua, R. *Tetrahedron Lett.* **2006**, *47*, 2573.
(10) Laurenti, D.; Feuerstein, M.; Pèpe, G.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 1633.
(11) Doucet, H.; Santelli, M. *Synlett* **2006**, 2001.
(12) (a) Feuerstein, M.; Laurenti, D.; Bougeant, C.; Doucet, H.; Santelli, M. *Chem. Commun.* **2001**, 325. (b) Kondolff, I.; Doucet, H.; Santelli, M. *Organometallics* **2006**, *25*, 5219.
(13) Feuerstein, M.; Berthiol, F.; Doucet, H.; Santelli, M. *Org. Biomol. Chem.* **2003**, *1*, 2235.
(14) Kondolff, I.; Doucet, H.; Santelli, M. *Organometallics* **2007**, *26*, 472.
(15) Feuerstein, M.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 5923.
(16) (a) Feuerstein, M.; Doucet, H.; Santelli, M. *Synlett* **2001**, 1980. (b) Feuerstein, M.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2002**, *43*, 2191. (c) Lemhadri, M.; Doucet, H.; Santelli, M. *Tetrahedron* **2004**, *50*, 11533. (d) Berthiol, F.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2004**, *45*, 5633. (e) Berthiol, F.; Doucet, H.; Santelli, M. *Synthesis* **2005**, 3589. (f) Battace, A.; Zair, T.; Doucet, H.; Santelli, M. *J. Organomet. Chem.* **2005**, *690*, 3790. (g) Kondolff, I.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2006**, 765. (h) Berthiol, F.; Doucet, H.; Santelli, M. *Appl. Organomet. Chem.* **2006**, *20*, 855. (i) Battace, A.; Zair, T.; Doucet, H.; Santelli, M. *Synthesis* **2006**, 3495.
(17) Berthiol, F.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2003**, *44*, 1221.
(18) Mo, J.; Xu, L.; Ruan, J.; Liu, S.; Xiao, J. *Chem. Commun.* **2006**, 3591.
(19) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Sato, M.; Suzuki, A. *J. Am. Chem.Soc.* **1989**, *111*, 314.
(20) Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Heterocycles* **1990**, *30*, 303.
(21) Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Tetrahedron* **1992**, *48*, 2113.
(22) Hosoi, K.; Nozaki, K.; Hiyama, T. *Chem. Lett.* **2002**, *2*, 138.
(23) Nakao, Y.; Imanaka, H.; Chen, J.; Yada, A.; Hiyama, T. *J. Organomet. Chem.* **2007**, *692*, 585.
(24) Fürstner, A.; Leitner, A. *Synlett* **2001**, 290.

(25) Huang, Z.; Qian, M.; Babinski, D. J.; Negishi, E. *Organometallics* **2005**, *24*, 475.
(26) Korenev, K. D.; Zavorotnyi, V. A. *Khimiya i Tekhnologiya Topliv Masel* **2000**, *36*, 274; *Chem. Abstr.* **2001**, *134*, 164781.
(27) Fujita, T.; Sasaki, S.; Yoneta, M.; Mishina, T.; Adachi, K.; Chiba, K. WO Patent WO 9408943, **1994**; *Chem. Abstr.* **1995**, *122*, 239193.
(28) Crowe, W. E.; Zhang, Z. J. *J. Am. Chem. Soc.* **1993**, *115*, 10998.
(29) Lim, S.-G.; Lee, J. H.; Moon, C. W.; Hong, J.-B.; Jun, C.-H. *Org. Lett.* **2003**, *5*, 2759.
(30) Brase, S.; Schroen, M. *Angew. Chem. Int. Ed.* **1999**, *38*, 1071.