Arenediazonium *o*-Benzenedisulfonimides in Heck-Type Arylation of Allylic Alcohols

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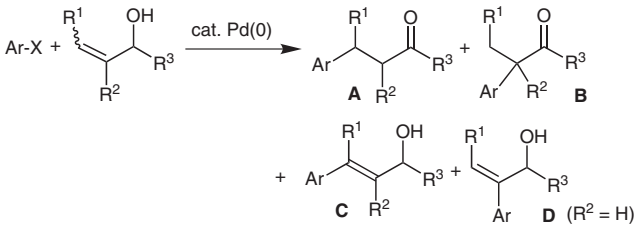
Abstract: Arenediazonium *o*-benzenedisulfonimides were reacted with primary and secondary allylic alcohols. The reactions, carried out in aqueous ethanol in the presence of palladium(II) acetate as precatalyst and sodium hydrogen carbonate as base, gave the arylation products with good overall conversion. In all cases, the major products were the β-arylated carbonyl derivatives. The *o*-benzenedisulfonimide was recovered in high yield from all the reactions, and it was recycled for the preparation of other salts.

Key words: allylic alcohols, arenediazonium salts, cross coupling, Heck reaction, arylations

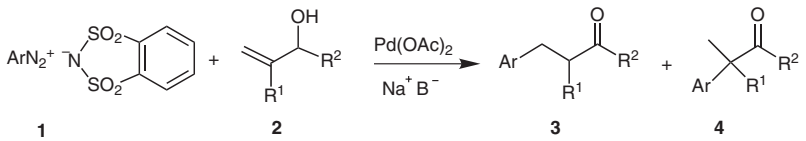
Palladium-catalyzed carbon–carbon bond formation, which was developed in the 1970s (Mizoroki–Heck or Heck reaction), is certainly the most powerful synthetic method involving sp^2 carbons.[1] Arylation of allylic alcohols starting from aryl halides has been widely studied by various authors, from the earlier papers of Heck[2] and Chalk,[3] to the procedures proposed by Jeffery and other groups,[4,5] and the synthetic procedures performed in ionic liquids,[6,7] in the presence of more efficient catalysts, or with substituted alcohols.[8] These reactions were generally poorly regioselective, leading to mixtures of β- and α-arylated carbonyl compounds A and B, respectively, and of the arylated allylic alcohols C and D (Scheme 1). Jeffery's procedures were proposed to selectively afford ketones A and B, or alcohols C and D.[4]



Scheme 1 Palladium-catalyzed arylation products of allylic alcohols.

By contrast, there are only a few reports related to the palladium-catalyzed arylation of allylic alcohols by arenediazonium salts, namely chlorides[9,10] (5 and 1 examples, respectively) or tetrafluoroborates (12 and 16 examples)[11,12] or their precursors (1 example).[13] Amongst them, an article in 2001[11] reported the Heck coupling of four examples of arenediazonium tetrafluoroborates with two examples of primary alcohols and one example of a secondary allylic alcohol, in ethanol in the presence of palladium(II) acetate (2 mol%) as a precatalyst, leading to pure β-arylated carbonyl compounds in modest yields. In research published in 2005,[12] two examples of secondary and two examples of primary allylic alcohols (containing a terminal double bond and 2-substituted, with the exception of prop-2-en-1-ol) were arylated in methanol using bis(dibenzylideneacetone)palladium (5 mol%) as the catalyst, without ligands or base; β-arylated ketones or aldehyde acetals (in a mixture with the α-regioisomer for prop-2-en-1-ol) were obtained in modest to good yields.

In the course of our investigations on the synthetic applications of a new family of dry-state-stable arenediazonium salts, the arenediazonium *o*-benzenedisulfonimides **1**,[14] our attention has been focused on their reactivity in metal-catalyzed cross-coupling reactions.[15] Recently, starting from salts **1**, we found improved general procedures, based on Heck-type arylations, which led to the synthesis of cinnamic acid esters, cinnamic acids, and aldehydes, stilbenes and 1-arylcyclopentenes in high yield.[15a] In the present work, we wish to report the results obtained by reacting the salts **1** with a range of secondary and primary allylic alcohols **2** under Heck-type arylation conditions (Scheme 2, Table 1), the synthetic goal of the reaction being the formation of β-arylated carbonyl compounds **3**, useful intermediates for the synthesis of medicinal or natural compounds with antifungal, antibacterial, anticancer, and antioxidant properties.[16,17]



Scheme 2 Palladium-catalyzed arylation of allylic alcohols with arenediazonium *o*-benzenedisulfonimides.

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Table 1 Substituent Assignments for Compounds **1** and **2**

1	Ar	2	R^1	R^2
1a	4-$O_2NC_6H_4$	**2a**	H	Me
1b	3-$O_2NC_6H_4$	**2b**	H	*n*-C_5H_{11}
1c	2-$O_2NC_6H_4$	**2c**	H	Ph
1d	4-IC_6H_4	**2d**	H	H
1e	4-BrC_6H_4	**2e**	Me	H
1f	2,6-$F_2C_6H_3$			
1g	Ph			
1h	4-MeC_6H_4			
1i	4-$MeOC_6H_4$			
1j	2-$MeOC_6H_4$			

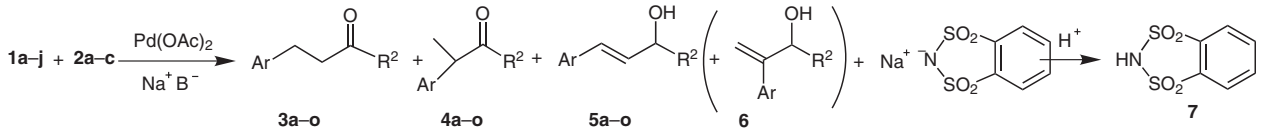
In order to optimize the reaction conditions, 4-nitro- (**1a**) and 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1i**) were reacted with but-3-en-2-ol (**2a**). We considered the influencing factors to be: reactant ratio, solvent, base, precatalyst, and temperature; we examined their effects by isolating the predominant arylation product(s) from the reaction mixture (Table 2). Our conditions used a slight excess of the commercially available allylic alcohol **2a** (1.2 mol with respect to **1**); a greater excess did not give a significant improvement in the yield (Table 2, entries 2, 4, and 12) and a ratio of **1**/**2a** 1.5:1 gave almost the same result (Table 2, entry 3). The reactions were carried out in the presence of an inorganic or an organic base; among the tested bases, sodium hydrogen carbonate and sodium acetate were chosen, in a molar ratio 1:1.2 with **1**.

Reactions carried out without or with a deficit of base gave less good results (Table 2, entries 5 and 6 and 8–10). Polar protic and aprotic solvents were used: the best solvent was aqueous 95% ethanol, since in anhydrous ethanol the reaction was much slower and less efficient (Table 2, entry 10), at 60 °C (at r.t., the reaction conversion did not reach completion after over 24 h). Other systems explored were ethanol/calcium carbonate, dioxane/sodium hydrogen carbonate, tetrahydrofuran/sodium hydrogen carbonate, anhydrous acetonitrile/sodium acetate, but they did not give better results (Table 2, entries 11–14). Amongst the tested palladium catalysts or precatalysts, palladium(II) acetate and tris(dibenzylideneacetone)dipalladium were almost equally effective in the arylation of but-3-en-2-ol, both in ethanol (Table 2, entries 1 and 4) and in acetonitrile (Table 2, entries 11 and 12), in 1% mol quantity with respect to **1**. The use of a greater amount of precatalyst gave only a slight improve-

Table 2 Initial Screening of Heck-Type Arylation Conditions[a]

Entry	Compd **1**	Ratio **1/2a**	Solvent	Base (equiv)	Catalyst (mol%)	Time	Yield[b] (%)	
							3	**4**
1	**1a**	1: 1.2	aq 95% EtOH[c]	$NaHCO_3$ (1.2)	$Pd(OAc)_2$ (1)	10 min	70	–
2	**1a**	1:1.5	aq 95% EtOH	$NaHCO_3$ (1.5)	$Pd(OAc)_2$ (5)	10 min	72	–
3	**1a**	1.5:1	aq 95% EtOH	$NaHCO_3$ (1.5)	$Pd(OAc)_2$ (1.8)	40 min	72	–
4	**1a**	1:1.5	aq 95% EtOH	$NaHCO_3$ (1.5)	$Pd_2(dba)_3$ (1)	15 min	72	–
5	**1a**	1:1.2	aq 95% EtOH[c]	$NaHCO_3$ (0.6)	$Pd_2(dba)_3$ (1)	45 min	52	–
6	**1a**	1:1.2	aq 95% EtOH[c]	–	$Pd(OAc)_2$ (1)	40 min	45	–
7	**1i**	1:1.2	aq 95% EtOH[c]	$NaHCO_3$ (1.2)	$Pd(OAc)_2$ (1)	13 min	44[d]	10[d]
8	**1i**	1:1.2	aq 95% EtOH	$NaHCO_3$ (0.6)	$Pd(OAc)_2$ (1)	10 min	45	4
9	**1i**	1:1.2	aq 95% EtOH	–	$Pd(OAc)_2$ (1)	3 h	50	11
10	**1i**	1:1.2	anhyd EtOH	$NaHCO_3$ (0.6)	$Pd(OAc)_2$ (1)	4 h	32	6
11	**1i**	1:1.2	anhyd MeCN	NaOAc (1.2)	$Pd(OAc)_2$ (1)	20 min	44	12
12	**1i**	1:1.5	anhyd MeCN	NaOAc (1.5)	$Pd_2(dba)_3$ (1)	25 min	47	13
13	**1i**	1:1.5	anhyd MeCN	NaOAc (1.2)	$PdCl_2(PPh_3)_2$ (1)	1.5 h	–[e]	–[e]
14	**1i**	1:1.5	anhyd MeCN	NaOAc (1.2)	$PdCl_2(dppf)\cdot CH_2Cl_2$ (1)	3.5 h	–[e]	–[e]

[a] All the reactions were carried out at 60 °C; at r.t. the reaction conversions were still incomplete (a test of azo coupling with 2-naphthol was positive) after over 24 h.
[b] Yield of pure product after column chromatography.
[c] In abs EtOH the reaction was still incomplete (a test of azo coupling with 2-naphthol was positive) after several hours.
[d] 1-(4-Methoxyphenyl)-3-ethoxybut-1-ene was isolated in 17% yield.
[e] Anisole was the sole reaction product.



Scheme 3 Palladium-catalyzed arylation of allylic alcohols **2a–c** with arenediazonium *o*-benzenedisulfonimides **1a–j**.

ment in the yield of the arylation product (Table 2, cf. entry 1 with entries 2 and 3). Totally ineffective as precatalysts were dichlorobis(triphenylphosphine)palladium and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium–dichloromethane complex (Table 2, entries 13 and 14).

Next, we applied these reaction conditions to the secondary allylic alcohols **2a–c** with a representative range of arenediazonium *o*-benzenedisulfonimides **1a–j**: from the reaction mixtures we isolated and characterized the products of Scheme 3. The reactions were carried out in aqueous 95% ethanol, under the conditions discussed above, unless otherwise stated; complete results are reported in Table 3. In all the 22 considered examples, the β-aryl ketones **3** were the predominant products with respect to the other expected arylation products (**4**, **5**, and **6**) but, although the overall conversions were generally quite good (52–95%), some information can be gained by consideration of the distribution of the reaction products.

The arylation of **2a** and **2b** with the electron-poor arenediazonium salts **1a–c** was more regioselective than that with electron-rich salts, scince they gave the β-arylated derivatives **3** and **5** as the almost exclusive products. Only traces of α-arylated ketones **4** were separated (Table 3, entries 1–4 and 12, 13). The effect was less important in salt **1b**, where the electron-withdrawing substituent was *meta*; the corresponding α-arylated ketone **4b** was isolated in 11% yield (Table 3, entry 3).

Halo-substituted salts **1d**,**e** showed both high regio- and chemoselectivities (Table 3, entries 5 and 6), as already reported in the literature for Heck-type arylation reactions with arenediazonium tetrafluoroborates or salts **1**.[15]

A steric effect was observed for the salts **1c** and especially **1f** (Table 3, entries 4, 13, and 7).

Reactions of salts **1a** and **1i** with alcohol **2a** carried out in the absence of base confirmed that longer reaction times are required, with lower yields (Table 3, entries 2 and 10).

Table 3 Heck-Type Arylation of Secondary Allylic Alcohols with Arenediazonium *o*-Benzenedisulfonimides **1**[a]

Entry	Substrates		Time (min)	Chromatographic solvent	Products			Yield[b,c] (%)			Conversion[d] (%)
	1	**2**			**3–5**[e]	Ar	R^2	**3**	**4**	**5**	
1	**1a**	**2a**	10	PE–Et_2O (6:4)	**a**	4-$O_2NC_6H_4$	Me	70	3	7	83
2			40		**a**			45[f]	trace	7[f]	80[g]
3	**1b**	**2a**	25	PE–Et_2O (6:4)	**b**	3-$O_2NC_6H_4$	Me	67	11	17	95
4	**1c**	**2a**	15	PE–Et_2O (6:4)	**c**	2-$O_2NC_6H_4$	Me	55[h]	trace	5	60
5	**1d**	**2a**	15	PE–Et_2O (6:4)	**d**	4-IC_6H_4	Me	43	trace	trace	43
6	**1e**	**2a**	10	PE–Et_2O (6:4)	**e**	4-BrC_6H_4	Me	56	trace	6	62
7	**1f**	**2a**	2.25 h	PE–Et_2O (6:4)	**f**	2,6-$F_2C_6H_3$	Me	7	–	–	7
8	**1g**	**2a**	25	PE–Et_2O (7:3)	**g**	Ph	Me	41 (58)[11]	trace	27	73
9	**1i**	**2a**	15	PE–Et_2O (7:3)	**h**	4-$MeOC_6H_4$	Me	42 (62)[11]	10	–	71[i]
10			3 h		**h**			50[f]	11[f]	–	61
11			20		**h**			44	12	–	52
12	**1a**	**2b**	10	PE–Et_2O (7:3)	**i**	4-$O_2NC_6H_4$	*n*-C_5H_{11}	73	trace	7	80
13	**1c**	**2b**	10	PE–Et_2O (8:2)	**j**	2-$O_2NC_6H_4$	*n*-C_5H_{11}	57	trace	–	57
14	**1g**	**2b**	7	PE–Et_2O (8:2)	**k**	Ph	*n*-C_5H_{11}	52	trace	26	84
15	**1h**	**2b**	10	PE–Et_2O (9:1)	**l**	4-MeC_6H_4	*n*-C_5H_{11}	48	trace	–	53[i]
16			25		**l**			45	9[j]	–	54
17	**1i**	**2b**	10	PE–Et_2O (8:2)	**m**	4-$MeOC_6H_4$	*n*-C_5H_{11}	47	7[j]	–	69[i]

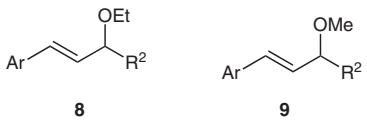
Table 3 Heck-Type Arylation of Secondary Allylic Alcohols with Arenediazonium *o*-Benzenedisulfonimides **1**[a] (continued)

Entry	Substrates		Time (min)	Chromatographic solvent	Products			Yield[b,c] (%)			Conversion[d] (%)
	1	**2**			**3–5**[e]	Ar	R^2	**3**	**4**	**5**	
18			30		**m**			66	5	17	88
19	**1i**	**2c**	5	PE–acetone (9:1)	**n**	4-$MeOC_6H_4$	Ph	19	trace	–	26[k]
20			40		**n**			53	6	–	59
21	**1j**	**2c**	20	PE–acetone (8:2)	**o**	2-$MeOC_6H_4$	Ph	20	trace	–	43[k]
22			2 h		**o**			32	trace	–	32

[a] Reaction conditions: molar ratio **1/2** 1: 1.2, $NaHCO_3$ (1.2 equiv), $Pd(OAc)_2$ (1% mol), aq 95% EtOH, 60 °C; entries 11, 16, 18, 20, and 22 used NaOAc (1.2 equiv), MeCN.
[b] Yields of pure products after purification by column chromatography.
[c] In parentheses are the literature yields reported from arenediazonium salts.
[d] Overall.
[e] R^1 = H.
[f] In entries 2 and 10 the reactions were carried out in the absence of base.
[g] Nitrobenzene was isolated in 28% yield.
[h] A yield of 62% was obtained when the reaction was carried out in the presence of $Pd(OAc)_2$ (3% mol).
[i] In entries 9, 15, and 17 compounds **8a**, **8b**, and **8c** were isolated partially in mixture with products **3** and/or **4** (GC yield 17%, 5% and 15% respectively).
[j] Isolated in mixture with compound **3**; the yield was calculated via GC ratio of the two products.
[k] In entries 19 and 21, compounds **8d/8e** and **8f/8g** were isolated as inseparable mixtures (yield: 7% and 23%, respectively).

It is known in the literature that electron-rich haloarenes disfavor Heck-type reactions,[1b] the arylation of **2a–c** with salts **1h–j** gave β-arylated ketones **3** in inferior yields, accompanied by α-arylated ketones **4** in low yields or in traces (Table 3, entries 9, 15, 17, 19, and 21).

Interestingly, from all of the reactions of salts **1h–j** in ethanol, the corresponding 1-aryl-3-ethoxyalk-1-enes **8a–c** and 1-aryl-3-ethoxy-3-phenylprop-1-enes **8d** and **8f** (isolated as inseparable mixtures with their isomeric derivatives, 3-aryl-3-ethoxy-1-phenylprop-1-enes **8e** and **8g**, respectively) were isolated and identified by GC-MS and ^{1}H NMR spectra (Table 3, entries 9, 15, 17, 19, and 21) (Figure 1, Table 4). These products are probably derived from the nucleophilic attack of ethanol on an intermediate π-allylpalladium complex, formed by oxidative addition of palladium(0) to the allylic compounds **5** (Tsuji–Trost reaction).[18] This was confirmed by carrying out the arylation of **2b** with **1i** in methanol: compound **9a** was isolated from the reaction mixture and confirmed by ^{1}H NMR and GC-MS spectra. To overcome the formation of these derivatives, the arylation of **2a–c** with salts **2h–j** was carried out in aqueous 95% ethanol in the absence of base (Table 3, entry 10) and in acetonitrile/sodium acetate (Table 3, entries 11, 16, 18, 20, and 22; in the latter three entries, an improvement in the overall salt conversion was evident).



8 **9**

Figure 1

Table 4 Substituent Assignments for Compounds **8** and **9a**

Compound	Ar	R^2
8a	4-$MeOC_6H_4$	Me
8b	4-MeC_6H_4	*n*-C_5H_{11}
8c	4-$MeOC_6H_4$	*n*-C_5H_{11}
8d[a]	4-$MeOC_6H_4$	Ph
8e[a]	Ph	4-$MeOC_6H_4$
8f[b]	2-$MeOC_6H_4$	Ph
8g[b]	Ph	2-$MeOC_6H_4$
9a	4-$MeOC_6H_4$	*n*-C_5H_{11}

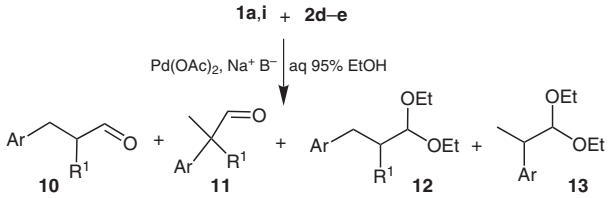
[a] Obtained as a mixture of **8d/8e**.
[b] Obtained as a mixture of **8f/8g**.

Amongst all the considered examples, in literature only ketones **3g** and **3h** have been reported as synthesized from the corresponding tetrafluoroborates.[11]

It should be noted that under the conditions used, α-arylated compounds **6** were never detected.

From all the reactions, after the workup of the reaction mixture, *o*-benzenedisulfonimide (**7**) was recovered in over 90% yield and this was recycled for the preparation of other salts **1**; this has economic and ecological advantages.

To further explore the reactivity of the dry arenediazonium *o*-benzenedisulfonimides **1** in the Heck-type arylation of allylic alcohols, we carried out the reaction of salts **1a**



Scheme 4 Palladium-catalyzed arylation of **2d**,**e** with salts **1a** and **1i**.

Table 5 Substituent Assignments for Compounds **10–13**

10–13	Ar	R^1
a	4-$O_2NC_6H_4$	H
b	4-$MeOC_6H_4$	H
c	4-$O_2NC_6H_4$	Me
d	4-$MeOC_6H_4$	Me

and **1i** with the primary allylic alcohols **2d** and **2e** (Scheme 4, Tables 5 and 6).

The reactions were carried out in aqueous 95% ethanol/sodium hydrogen carbonate (1.2 equiv, except Table 6, entry 2), with a molar ratio **1/2** of 1:1.2, at 60 °C, in the presence of palladium(II) acetate as precatalyst (1% mol, except Table 6, entries 5 and 7, where a 5% mol quantity was used). Our results are reported in Table 6, which shows our examples and gives a direct comparison with the literature data from arenediazonium chlorides[9] and tetrafluoroborates.[11,12]

Under our conditions, with the few tried modifications, we obtained a mixture of the aldehydes **10** and/or **11** with their diethyl acetals **12** and **13**. As for the arylation of **2a–c**, β-aryl carbonyl derivatives **10a–d** and **12a–c** were the predominant (Table 6, entries 1–3) or sole products (Table 6, entries 4–7); the overall conversions were good and comparable with that of literature, except for the reaction of **1i** with **2e** (Table 6, entries 6 and 7).

As reported above, from all the reactions, *o*-benzenedisulfonimide (**7**) was recovered in over 90% yield, and could be recycled for the preparation of other salts **1**.

In conclusion, this report describes our findings on the synthetic applications of the dry state stable arenediazonium *o*-benzenedisulfonimides in Heck-type arylations of allylic alcohols. The synthetic methods described may have value in organic synthesis because of the high stability of the starting materials and of the recovery of the parent acid of the stabilizing anion.

Further research is in progress for biologically active naturally occurring compounds.

All reactions were performed in oven-dried glassware when anhydrous solvent was used; no particular device was, however, adopted to exclude moisture or oxygen. The reactions were monitored by GC and GC-MS spectrometry. GC-MS data were recorded with an HP 5989B mass selective detector connected to an HP 5890 GC cross-linked methyl silicone capillary column. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance 200 spectrometer at 200 MHz and 50 MHz, respectively, in $CDCl_3$; chemical shifts are given in ppm relative to $CDCl_3$. IR spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrometer in CCl_4 soln. Column chromatography and TLC were performed on Merck silica

Table 6 Heck-Type Arylation of Primary Allylic Alcohols with Arenediazonium *o*-Benzenedisulfonimides **1**[a]

Entry	Compd **1**	Compd **2**	Time (min)	Products	Yield[b] (%)				Lit.[c] yield (%)				Conversion[d] (%)
				10–13	**10**	**11**	**12**	**13**	**10**	**11**	**12**	**13**	
1	**1a**	**2d**	10[e]	**a**	34	3	37	–	trace[9]		73–76[12]	12–13[12]	74
2			10[f]	**a**	26	–	26	–					52
3	**1i**	**2d**	15[f]	**b**	27	10[g]	46[h] (**12b/13b** 75:21)		50,[11] 20[9] (**10b/11b** 7:3)		34–40[12] (**12b/13b** 62:38)[h,12]		83
4	**1a**	**2e**	20[f]	**c**	42	–	trace	–			79–83[12]		42[i]
5			20[f]	**c**	60	–	7	–					74[i]
6	**1i**	**2e**	30[f]	**d**	19	–	–	–	54[11]		53–60[12]		19
7			30[f]	**d**	34	–	–	–					34

[a] Conditions: ratio **1/2** 1:1.2, $Pd(OAc)_2$ (1% mol; except entries 5 and 7: 5% mol) $NaHCO_3$ (1.2 equiv; except for entry 2, carried out in the absence of base), aq 95% EtOH, 60 °C.
[b] Yields of pure products after purification by column chromatography.
[c] Literature data from arenediazonium salts.
[d] Overall.
[e] PE–Et_2O (6:4).
[f] PE–Et_2O (7:3).
[g] Isolated partially in mixture with **10b**; the yield was calculated via ^{1}H NMR integration.
[h] The products were isolated as an inseparable mixture; the ratio of the two compounds was calculated via ^{1}H NMR integration.
[i] Nitrobenzene was isolated in 28% yield in entry 4 and in 7% yield in entry 5.

gel 60 (70–230 mesh ASTM) and GF 254, respectively. Petroleum ether refers to the fraction boiling in the range 40–60 °C and is abbreviated as PE. Details for the reactions and yields for the pure (GC, GC-MS, TLC, ^{1}H NMR) isolated products are listed in Tables 3 and 6. Structure and purity of all the products were confirmed by comparison of their physical (mp or bp) and spectral data (MS and ^{1}H NMR) with those reported in the literature. Commercially available reagents, solvents and palladium compounds were purchased from Aldrich and used without purification or distillation before use; Dowex 50X8 ion-exchange resin was purchased from Fluka.

Dry arenediazonium *o*-benzenedisulfonimides **1a–c**,**e**,**g–j**,[1b] **1d**,[19a] and **1f**[19b] were prepared as described previously by us and used without further crystallization. **CAUTION**: In our laboratory there was no case of sudden decomposition during the preparation, purification, and handling of salts **1**; nevertheless it must be borne in mind that diazonium salts in the dry state are potentially explosive and they must be carefully stored and handled.

Palladium-Catalyzed Arylation of Allylic Alcohols 2a–e with Arenediazonium *o*-Benzenedisulfonimides 1a–j; General Procedure

The salt **1** (1.5 mmol) was added in one portion with stirring to a soln of the allylic alcohol **2** (1.8 mmol), base (1.8 mmol), and $Pd(OAc)_2$ (0.004 g, 0.015 mmol, 1 mol%) in the solvent (15 mL); then the mixture was placed in an oil bath at 60 °C. The salt dissolved at once, the resultant soln turned quickly to dark brown and evolution of N_2 was observed. When the reaction was complete (negative test of azo coupling with 2-naphthol), the mixture was evaporated under reduced pressure and the residue was poured into Et_2O–H_2O (1:1, 40 mL). The aqueous layer was separated and extracted with Et_2O (2 × 20 mL). The combined organic extracts were washed with H_2O (20 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The crude residue was chromatographed on a short column of silica gel to provide the arylation products, which are listed below in order of elution (reactions carried out in 95% EtOH); the appropriate eluents are reported in Tables 3 and 6. ^{1}H and ^{13}C NMR, IR, and MS spectra confirmed the proposed structures and, when reported, were identical to that in the literature. The aqueous layer and aqueous washing were collected and evaporated under reduced pressure; the residue was passed through a column of Dowex 50X8 ion-exchange resin (1.6 g for 1 g of product), eluting with H_2O (ca. 30 mL).[15] After removal of H_2O under reduced pressure, virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**7**) was recovered; yield: 0.31 g (93%); mp 192–194 °C (toluene) (Lit.[14a] mp 192–194 °C). Alternatively, at completion of the reactions in aq 95% EtOH, Et_2O (35 mL) was added to the mixture: the sodium salt of **7** was precipitated, collected by filtration under vacuum, dissolved in H_2O and passed through the column of ion-exchange resin, as described above, to afford pure **7**.

Arylation of 2a with 1a

3-(4-Nitrophenyl)butan-2-one (4a)[20]

Colorless oil; yield: 0.01 g (3%).

^{1}H NMR: δ = 1.46 (d, *J* = 7.2 Hz, 3 H), 2.12 (s, 3 H), 3.91 (q, *J* = 6.8 Hz, 1 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 8.22 (d, *J* = 8.2 Hz, 2 H).

MS (EI): *m*/*z* (%) = 151 (100) $[M - COCH_2]^+$.

4-(4-Nitrophenyl)butan-2-one (3a)[21]

Pale yellow crystals; yield: 0.20 g (70%); mp 39.9–40.3 °C (CH_2Cl_2/PE) (Lit.[21] mp 37–40 °C).

IR: 1723 (C=O) cm^{-1}.

^{1}H NMR: δ = 2.17 (s, 3 H), 2.82 (t, *J* = 7.0 Hz, 2 H), 2.97 (t, *J* = 7.2 Hz, 2 H), 7.35 (d, *J* = 8.6 Hz, 2 H), 8.15 (d, *J* = 8.6 Hz, 2 H).

MS (EI): *m*/*z* (%) = 193 (100) $[M^+]$.

4-(4-Nitrophenyl)but-3-en-2-ol (5a)[22]

Colorless oil; yield: 0.02 g (7%).

^{1}H NMR: δ = 1.34 (d, *J* = 6.4 Hz, 3 H), 1.62–1.72 (m, 1 H), 4.42–4.51 (m, 1 H), 6.38 (dd, *J* = 16.0 Hz, 5.6 Hz, 1 H), 6.60 (d, *J* = 16.2 Hz, 1 H), 7.44 (d, *J* = 8.8 Hz, 2 H), 8.11 (d, *J* = 8.8 Hz, 2 H).

MS (EI): *m*/*z* (%) = 175 (25) $[M - H_2O]^+$.

Arylation of 2a with 1b

3-(3-Nitrophenyl)butan-2-one (4b)

Colorless oil; yield: 0.03 g (11%).

^{1}H NMR: δ = 1.40 (d, *J* = 7.0 Hz, 3 H), 2.06 (s, 3 H), 3.83 (q, *J* = 7.0 Hz, 1 H), 7.45–7.50 (m, 2 H), 8.05–8.10 (m, 2 H).

^{13}C NMR: δ = 205.8, 147.0, 140.8, 132.4, 128.3, 121.4, 120.8, 51.5, 27.1, 15.9.

MS (EI): *m*/*z* (%) = 151 (62) $[M - COCH_2]^+$.

4-(3-Nitrophenyl)butan-2-one (3b)[23]

Pale yellow crystals; yield: 0.19 g (67%); mp 44.0–44.8 °C (CH_2Cl_2/PE) (Lit.[23] mp 44 °C).

IR: 1723 (C=O) cm^{-1}.

^{1}H NMR: δ = 2.10 (s, 3 H), 2.76 (t, *J* = 7.0 Hz, 2 H), 2.93 (t, *J* = 7.2 Hz, 2 H), 7.33–7.50 (m, 2 H), 7.95–8.01 (m, 2 H).

MS (EI): *m*/*z* (%) = 150 (11) $[M - COCH_3]^+$, 133 (100).

4-(3-Nitrophenyl)but-3-en-2-ol (5b)

Colorless oil; yield: 0.05 g (17%).

^{1}H NMR: δ = 1.34 (d, *J* = 6.6 Hz, 3 H), 1.62–1.70 (m, 1 H), 4.42–4.52 (m, 1 H), 6.35 (dd, *J* = 16.2 Hz, 5.9 Hz, 1 H), 6.59 (d, *J* = 16.0 Hz, 1 H), 7.45–7.38 (m, 1 H), 7.60 (d, *J* = 7.4 Hz, 1 H), 8.04–7.99 (m, 1 H), 8.00 (s, 1 H).

^{13}C NMR: δ = 147.0, 137.1, 135.3, 130.8, 127.9, 125.3, 120.6, 119.4, 66.8, 21.9.

MS (EI): *m*/*z* (%) = 193 (28) $[M^+]$, 176 (100) $[M - OH]^+$.

Arylation of 2a with 1c

3-(2-Nitrophenyl)butan-2-one (4c)[20]

Trace.

MS (EI): *m*/*z* (%) = 151 (67) $[M - COCH_2]^+$, 134 (100).

4-(2-Nitrophenyl)butan-2-one (3c)[24]

Colorless oil; yield: 0.16 g (55%); bp 162 °C/0.266 mbar (Lit.[25] bp 183–185 °C/17.3 mbar).

IR: 1718 (C=O) cm^{-1}.

^{1}H NMR: δ = 2.09 (s, 3 H), 2.78 (t, *J* = 7.2 Hz, 2 H), 3.08 (t, *J* = 7.2 Hz, 2 H), 7.19–7.50 (m, 3 H), 7.87 (d, *J* = 8.0 Hz, 1 H).

MS (EI): *m*/*z* (%) = 147 (100) $[M - NO_2]^+$.

4-(2-Nitrophenyl)but-3-en-2-ol (5c)

Colorless oil; yield: 0.02 g (5%).

^{1}H NMR: δ = 1.41 (d, *J* = 6.4 Hz, 3 H), 1.78–1.86 (m, 1 H), 4.52–4.59 (m, 1 H), 6.25 (dd, *J* = 15.6 Hz, 6.0 Hz, 1 H), 7.05 (d, *J* = 15.8 Hz, 1 H), 7.35–7.44 (m, 1 H), 7.65–7.50 (m, 2 H), 7.93 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR: δ = 148.1, 139.2, 137.0, 133.9, 128.9, 128.3, 124.7 (2 C), 68.7, 23.3.

MS (EI): *m*/*z* (%) = 176 (10) $[M - OH]^+$, 130 (100).

Arylation of 2a with 1d

3-(4-Iodophenyl)butan-2-one (4d)

Trace.

MS (EI): *m*/*z* (%) = 274 (36) [M$^+$], 231 (100) [M – $COCH_3$]$^+$.

4-(4-Iodophenyl)butan-2-one (3d)
Yield: 0.17 g (43%); mp 76.6–77.9 °C (PE).

IR: 1722 (C=O) cm^{-1}.

^{1}H NMR: δ = 2.07 (s, 3 H), 2.71 (m, 4 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 7.52 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR: δ = 205.9, 139.1, 136.0 (2 C), 128.9 (2 C), 89.6, 43.3, 28.6, 27.6.

MS (EI): *m*/*z* (%) = 274 (100) [M$^+$], 217 (45) [M – CH_2COCH_3]$^+$.

4-(4-Iodophenyl)but-3-en-2-ol (5d)
Trace.

^{1}H NMR: δ = 1.38 (d, *J* = 6.4 Hz, 3 H), 1.60–1.70 (m, 1 H), 4.40–4.52 (m, 1 H), 6.27 (dd, *J* = 15.9 Hz, 6.0 Hz, 1 H), 6.51 (d, *J* = 15.9 Hz, 1 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 8.3 Hz, 2 H).

MS (EI): *m*/*z* (%) = 274 (10) [M$^+$], 257 (30) [M – OH]$^+$, 130 (100).

Arylation of 2a with 1e
3-(4-Bromophenyl)butan-2-one (4e)[26]
Trace.

MS (EI): *m*/*z* (%) = 226 (18) [M$^+$], 183 (84) [M – $COCH_3$]$^+$.

4-(4-Bromophenyl)butan-2-one (3e)[27]
Yield: 0.19 g (56%); bp 142 °C/0.13 mbar.

IR: 1719 (C=O) cm^{-1}.

^{1}H NMR: δ = 2.06 (s, 3 H), 2.66–2.77 (2 m, 4 H), 6.98 (d, *J* = 8.6 Hz, 2 H), 7.31 (d, *J* = 8.5 Hz, 2 H).

MS (EI): *m*/*z* (%) = 226 (100) [M$^+$], 169 (70) [M – CH_2COCH_3]$^+$.

4-(4-Bromophenyl)but-3-en-2-ol (5e)[28]
Colorless oil; yield: 0.02 g (6%).

^{1}H NMR: δ = 1.30 (d, *J* = 6.4 Hz, 3 H), 1.55–1.60 (m, 1 H), 4.39–4.45 (m, 1 H), 6.18 (dd, *J* = 15.9 Hz, 6.1 Hz, 1 H), 6.45 (d, *J* = 16.0 Hz, 1 H), 7.18 (d, *J* = 8.8 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H).

MS (EI): *m*/*z* (%) = 208 (20) [M – H_2O]$^+$, 129 (100).

Arylation of 2a with 1f
4-(2,6-Difluorophenyl)butan-2-one (3f)
Colorless oil; yield: 0.02 g (7%).

IR: 1718 (C=O) cm^{-1}

^{1}H NMR: δ = 2.18 (s, 3 H), 2.70–2.78 (m, 2 H), 2.89– 2.99 (m, 2 H), 6.82–6.89 (m, 2 H), 7.09–7.10 (m, 1 H).

^{13}C NMR: δ = 207.4, 161.6 (dd, *J* = 250, 8.5 Hz), 127.9 (t, *J* = 10.5 Hz), 116.5 (t, *J* = 19.5 Hz), 111.3 (d, *J* = 16.0 Hz), 43.0, 29.9, 16.6.

MS (EI): *m*/*z* (%) = 184 (100) [M$^+$], 127 (85) [M – CH_2COCH_3]$^+$.

Arylation of 2a with 1g
3-Phenylbutan-2-one (4g)[29]
Trace.

MS (EI): *m*/*z* (%) = 148 (15) [M$^+$], 105 (100) [M – $COCH_3$]$^+$.

4-Phenylbutan-2-one (3g)[11,30]
Yield: 0.09 g (41%); bp 92 °C/0.266 mbar (Lit.[31] bp 90–92/0.399 mbar).

IR: 1718 (C=O) cm^{-1}.

^{1}H NMR: δ = 2.08 (s, 3 H), 2.66–2.70 (m, 2 H), 2.81–2.87 (m, 2 H), 7.10–7.22 (m, 5 H).

MS (EI): *m*/*z* (%) = 148 (100) [M$^+$], 91 (70) [M – CH_2COCH_3]$^+$.

4-Phenylbut-3-en-2-ol (5g)[28]
Colorless oil; yield: 0.06 g (27%).

^{1}H NMR: δ = 1.30 (d, *J* = 7.4 Hz, 3 H), 1.51–1.61 (m, 1 H), 4.38–4.47 (m, 1 H), 6.20 (dd, *J* = 15.8 Hz, 6.0 Hz, 1 H), 6.51 (d, *J* = 15.6 Hz, 1 H), 7.17–7.22 (m, 5 H).

MS (EI): *m*/*z* (%) = 148 (10) [M$^+$], 131 (100) [M – OH]$^+$.

Arylation of 2a with 1i
3-Ethoxy-1-(4-methoxyphenyl)but-1-ene (8a)[32]
Isolated partially in mixture; 17% GC yield; oil.

^{1}H NMR: δ = 1.22 (t, *J* = 7.0 Hz, 3 H), 3.34 (d, *J* = 6.2 Hz, 3 H), 3.37–3.62 (2 m, 2 H), 3.82 (s, 3 H), 3.82–4.02 (m, 1 H), 5.99 (dd, *J* = 15.8, 7.6 Hz, 1 H), 6.47 (d, *J* = 16.0 Hz, 1 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 7.34 (d, *J* = 8.6 Hz, 2 H).

MS (EI): *m*/*z* (%) = 206 (96) [M$^+$].

3-(4-Methoxyphenyl)butan-2-one (4h)[33]
Colorless oil; yield: 0.03 g (10%).

IR: 1716 (C=O) cm^{-1}.

^{1}H NMR: δ = 1.38 (d, *J* = 7.0 Hz, 3 H), 2.05 (s, 3 H), 3.74 (q, *J* = 7.0 Hz, 1 H), 3.81 (s, 3 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 7.15 (d, *J* = 8.8 Hz, 2 H).

MS (EI): *m*/*z* (%) = 178 (10) [M$^+$], 135 (100) [M – $COCH_3$]$^+$.

4-(4-Methoxyphenyl)butan-2-one (3h)[11]
Yield: 0.11 g (42%); bp 138 °C/0.266 mbar (Lit.[34] bp 100–103/0.266 mbar).

IR: 1719 (C=O) cm^{-1}.

^{1}H NMR: δ = 2.02 (s, 3 H), 2.66 (t, *J* = 7.5 Hz, 2 H), 2.77 (t, *J* = 7.5 Hz, 2 H), 3.71 (s, 3 H), 6.75 (d, *J* = 8.3 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H).

MS (EI): *m*/*z* (%) = 178 (40) [M$^+$], 121 (100) [M – CH_2COCH_3]$^+$.

Arylation of 2b with 1a
2-(4-Nitrophenyl)octan-3-one (4i)
Trace.

^{1}H NMR: δ = 0.84 (d, *J* = 6.8 Hz, 3 H), 1.21–1.36 (m, 4 H), 1.43–1.61 (d, *J* = 7.0 Hz, 5 H), 2.39 (t, *J* = 7.4 Hz, 2 H), 3.91 (q, *J* = 7.1 Hz, 1 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 8.20 (d, *J* = 8.6 Hz, 2 H).

MS (EI): *m*/*z* (%) = 249 (5) [M$^+$], 151 (100).

1-(4-Nitrophenyl)octan-3-one (3i)
Oil; yield: 0.27 g (73%).

IR: 1718 (C=O) cm^{-1}.

^{1}H NMR: δ = 0.88 (t, *J* = 6.70, 3 H), 1.20–1.35 (m, 4 H), 1.49–1.63 (m, 2 H), 2.40 (t, *J* = 7.50 Hz, 2 H), 2.78 (t, *J* = 7.2 Hz, 2 H), 3.01 (t, *J* = 7.2 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 8.14 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR: δ = 207.7, 147.7, 144.9, 127.7 (2 C), 122.1 (2 C), 41.6, 41.4, 28.7, 27.8, 21.9, 20.8, 12.3.

MS (EI): *m*/*z* (%) = 249 (15) [M$^+$], 136 (10) [M – $CH_2COC_5H_{11}$]$^+$, 99 (100).

1-(4-Nitrophenyl)oct-1-en-3-ol (5i)
Oil; yield: 0.02 g (7%).

^{1}H NMR: δ = 0.82–0.94 (m, 3 H), 1.33–1.43 (m, 6 H), 1.60–1.76 (m, 2 H), 4.30–4.40 (m, 1 H), 6.43 (dd, *J* = 15.9, 5.9 Hz, 1 H), 6.67 (d, *J* = 15.9 Hz, 1 H), 7.51 (d, *J* = 8.7 Hz, 2 H), 8.18 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR: δ = 147.0, 143.6, 137.8, 127.9, 127.1 (2 C), 124.2 (2 C), 72.7, 37.5, 31.9, 25.3, 22.8, 14.2.

MS (EI): *m*/*z* (%) = 231 (60) [M – H_2O]$^+$.

Arylation of 2b with 1c
1-(2-Nitrophenyl)octan-3-one (3j)
Oil; yield: 0.21 g (57%).

IR: 1718 (C=O) cm^{-1}.

^{1}H NMR: δ = 0.88 (t, *J* = 7.2 Hz, 3 H), 1.33–1.25 (m, 4 H), 1.65–1.50 (m, 2 H), 2.40 (t, *J* = 7.3 Hz, 2 H), 2.82 (t, *J* = 7.29 Hz, 2 H), 3.16 (t, *J* = 7.40 Hz, 2 H), 7.37–7.52 (m, 3 H), 7.86 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR: δ = 208.0, 147.6, 134.9, 131.6, 130.9, 125.8, 123.3, 41.5, 41.1, 29.8, 25.7, 21.9, 20.9, 12.3.

MS (EI): *m*/*z* (%) = 150 (60) [M – COC_5H_{11}]$^+$.

Arylation of 2b with 1g
2-Phenyloctan-3-one (4k)[6b]
Trace.

^{1}H NMR: δ = 0.75–0.85 (m, 3 H), 1.10–1.60 (m, 9 H), 2.35 (t, *J* = 7.47 Hz, 2 H), 3.76 (q, *J* = 6.9 Hz, 1 H), 7.23–7.31 (m, 5 H).

MS (EI): *m*/*z* (%) = 204 (5) [M$^+$], 105 (50) [M – COC_5H_{11}]$^+$.

1-Phenyloctan-3-one (3k)[30,35]
Yield: 0.16 g (52%); bp 136 °C/0.266 mbar (Lit.[35] bp 108–111/0.399 mbar).

IR: 1712 (C=O) cm^{-1}.

^{1}H NMR: δ = 0.93–0.85 (m, 3 H), 1.18–1.28 (m, 4 H), 1.51–1.60 (m, 2 H), 2.39 (t, *J* = 7.51 Hz, 2 H), 2.74 (t, *J* = 7.29 Hz, 2 H), 2.91 (t, *J* = 7.21 Hz, 2 H), 7.17–7.29 (m, 5 H).

MS (EI): *m*/*z* (%) = 204 (32) [M$^+$], 91 (100) [M – $CH_2COC_5H_{11}$]$^+$.

1-Phenyloct-1-en-3-ol (5k)
Colorless oil; yield: 0.08 g (26%).

^{1}H NMR: δ = 0.90 (t, *J* = 6.1 Hz, 3 H), 1.18–1.68 (m, 8 H), 4.26 (m, 1 H), 6.23 (dd, *J* = 15.8 Hz, 6.6 Hz, 1 H), 6.58 (d, *J* = 15.8 Hz, 1 H), 7.21–7.43 (m, 5 H).

^{13}C NMR: δ = 137.0, 132.8, 130.4, 128.8 (2 C), 127.8, 126.7 (2 C), 73.3, 37.5, 32.0, 25.4, 22.8, 14.3.

MS (EI): *m*/*z* (%) = 204 (5) [M$^+$], 133 (100) [M – C_5H_{11}]$^+$.

Arylation of 2b with 1h
3-Ethoxy-1-(4-methylphenyl)oct-1-ene (8b)
Isolated in mixture with **4l**; GC yield: 5%.

^{1}H NMR: δ = 0.70 (t, *J* = 6.8 Hz, 3 H), 1.14 (t, *J* = 7.0 Hz, 3 H), 1.20–1.59 (m, 8 H), 2.27 (s, 3 H), 3.49–3.72 (2 m, 3 H), 5.95 (dd, *J* = 16.2, 8.2 Hz, 1 H), 6.40 (d, *J* = 16.2 Hz, 1 H), 7.04 (d, *J* = 7.8 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR: δ = 137.6, 134.2, 131.6, 130.4, 129.4, 126.5, 81.1, 63.9, 36.1, 32.0, 25.4, 22.8, 21.2, 15.6, 14.3.

MS (EI): *m*/*z* (%) = 246 (10) [M$^+$], 175 (100) [M – C_5H_{11}]$^+$.

2-(4-Methylphenyl)octan-3-one (4l)
Trace.

IR: 1716 (C=O) cm^{-1}

MS (EI): *m*/*z* (%) = 218 (10) [M$^+$], 119 (100) [M – COC_5H_{11}]$^+$.

1-(4-Methylphenyl)octan-3-one (3l)[36]
Yield: 0.16 g (48%); bp 150 °C/0.266 mbar.

IR: 1717 (C=O) cm^{-1}.

^{1}H NMR: δ = 0.81 (t, *J* = 6.7 Hz, 3 H), 1.15–1.22 (m, 4 H), 1.47–1.54 (m, 2 H), 2.25 (s, 3 H), 2.31 (t, *J* = 7.3 Hz, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 2.73 (t, *J* = 7.8 Hz, 2 H), 7.02 (br s, 4 H).

MS (EI): *m*/*z* (%) = 218 (30) [M$^+$], 105 (100) [M – $CH_2COC_5H_{11}$]$^+$.

Arylation of 2b with 1i
3-Ethoxy-1-(4-methoxyphenyl)oct-1-ene (8c)
Isolated in mixture with **4m**; GC yield: 15%.

^{1}H NMR: δ = 0.70–0.85 (m, 3 H), 1.14 (t, *J* = 7.0 Hz, 3 H), 1.20–1.55 (m, 8 H), 3.49–3.68 (2 m, 3 H), 3.74 (s, 3 H), 5.86 (dd, *J* = 16.0, 8.0 Hz, 1 H), 6.38 (d, *J* = 15.8 Hz, 1 H), 6.80 (d, *J* = 8.6 Hz, 2 H), 7.27 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR: δ = 159.4, 131.2, 129.8, 129.6, 127.8 (2 C), 114.2 (2 C), 81.2, 63.8, 55.5, 36.1, 32.7, 25.4, 22.8, 15.6, 14.3.

MS (EI): *m*/*z* (%) = 262 (10) [M$^+$], 191 (100) [M – C_5H_{11}]$^+$.

2-(4-Methoxyphenyl)octan-3-one (4m)
Colorless oil; yield: 0.02 g (7%).

IR: 1716 (C=O) cm^{-1}.

^{1}H NMR: δ = 0.84 (t, *J* = 6.4 Hz, 3 H), 1.14–1.19 (m, 4 H), 1.36 (d, *J* = 7.0 Hz, 3 H), 1.44–1.49 (m, 2 H), 2.34 (t, *J* = 6.4 Hz, 2 H), 3.79 (m, 1 H), 3.80 (s, 3 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 7.14 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR: δ = 211.6, 158.8, 133.0, 129.0 (2 C), 114.4 (2 C), 55.4, 52.2, 41.0, 31.4, 23.8, 22.6, 17.7, 14.1.

MS (EI): *m*/*z* (%) = 234 (10) [M$^+$], 135 (100) [M – COC_5H_{11}]$^+$.

1-(4-Methoxyphenyl)octan-3-one (3m)[36]
Yield: 0.16 g (47%); bp 165–166 °C/0.266 mbar.

IR: 1716 (C=O) cm^{-1}.

^{1}H NMR: δ = 0.81 (t, *J* = 6.6 Hz, 3 H), 1.10–1.30 (m, 4 H), 1.40–1.55 (m, 2 H), 2.30 (t, *J* = 7.2 Hz, 2 H), 2.62 (t, *J* = 6.8 Hz, 2 H), 2.77 (t, *J* = 2.6 Hz, 2 H), 3.71 (s, 3 H), 6.75 (d, *J* = 7.8 Hz, 2 H), 7.04 (d, *J* = 7.8 Hz, 2 H).

MS (EI): *m*/*z* (%) = 234 (30) [M$^+$], 121 (100) [M – $CH_2COC_5H_{11}$]$^+$.

Isolated from the reaction carried out in MeCN:

1-(4-Methoxyphenyl)oct-1-en-3-ol (5m)[37]
Oil; yield: 0.06 g (17%).

^{1}H NMR: δ = 0.86–0.95 (m, 3 H), 1.26–1.34 (m, 8 H), 1.64 (s, 1 H), 3.81 (s, 3 H), 4.20–4.35 (m, 1 H), 6.08 (dd, *J* = 15.8, 6.8 Hz, 1 H), 6.51 (d, *J* = 15.5 Hz, 1 H), 6.85 (d, *J* = 8.9 Hz, 2 H), 7.32 (d, *J* = 8.9 Hz, 2 H).

MS (EI): *m*/*z* (%) = 234 (5) [M$^+$], 216 (100) [M – H_2O]$^+$.

Arylation of 2c with 1i
3-Ethoxy-1-(4-methoxyphenyl)-3-phenylprop-1-ene (8d) and 3-Ethoxy-3-(4-methoxyphenyl)-1-phenylprop-1-ene (8e)
Inseparable mixture; oil; yield: 0.03 g (7%).

^{1}H NMR: δ = 1.21 (t, *J* = 7.0 Hz, 6 H), 3.38–3.54 (m, 4 H), 3.74 (s, 3 H), 3.75 (s, 3 H), 4.83 (d, *J* = 6.6 Hz, 1 H), 4.85 (d, *J* = 7.2 Hz, 1 H), 6.12 (dd, *J* = 15.8, 7.2 Hz, 1 H), 6.26 (dd, *J* = 16.0, 6.8 Hz, 1 H), 6.49 (d, *J* = 15.6 Hz, 1 H), 6.53 (d, *J* = 15.8 Hz, 1 H), 6.74–6.87 (m, 4 H), 7.16–7.31 (m, 14 H).

^{13}C NMR: δ = 157.7, 157.6, 140.2, 135.2, 132.1, 129.5, 129.3, 127.0, 126.6, 126.3, 126.1, 126.0, 125.3, 125.0, 112.4, 81.2, 80.5, 62.4, 53.7, 14.0.

MS (EI): *m*/*z* (%) = 268 (90) [M$^+$], 135 (100).

MS (EI): *m*/*z* (%) = 268 (50) [M$^+$], 105 (100).

2-(4-Methoxyphenyl)-1-phenylpropan-1-one (4n)[38]
Trace.

MS (EI): *m*/*z* (%) = 240 (5) [M^+], 135 (100) [$M - COC_6H_5]^+$.

3-(4-Methoxyphenyl)-1-phenylpropan-1-one (3n)[36,38,39]
Oil; yield: 0.07 g (19%).

IR: 1690 (C=O) cm^{-1}.

^1H NMR: δ = 3.03 (t, *J* = 7.3 Hz, 2 H), 3.29 (t, *J* = 7.6 Hz, 2 H), 3.80 (s, 3 H), 6.86 (d, *J* = 8.2 Hz, 2 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 7.42–7.58 (m, 3 H), 7.97 (d, *J* = 6.7 Hz, 2 H).

MS (EI): *m*/*z* (%) = 240 (50) [M^+], 121 (100) [$M - CH_2COC_6H_5]^+$.

Arylation of 2c with 1j
3-Ethoxy-1-(2-methoxyphenyl)-3-phenylprop-1-ene (8f) and 3-Ethoxy-3-(2-methoxyphenyl)-1-phenylprop-1-ene (8g)
Inseparable mixture; oil; yield: 0.10 g (23%).

^1H NMR: δ = 1.22 (t, *J* = 7.0 Hz, 6 H), 3.42–3.58 (m, 4 H), 3.78 (s, 3 H), 3.79 (s, 3 H), 4.90 (d, *J* = 7.6 Hz, 1 H), 5.35 (d, *J* = 6.6 Hz, 1 H), 6.26 (dd, *J* = 16.0, 6.6 Hz, 1 H), 6.27 (dd, *J* = 16.0, 7.6 Hz, 1 H), 6.58 (d, *J* = 15.8 Hz, 1 H), 6.79–6.99 (m, 5 H), 7.12–7.47 (2 m, 14 H).

^{13}C NMR: δ = 157.0, 142.1, 137.3, 133.1, 131.2, 130.4, 130.0, 129.0, 128.6, 127.6, 127.3, 127.1, 127.0, 126.3, 125.7, 121.1, 120.8, 111.1, 110.8, 83.3, 75.8, 64.3, 64.1, 55.7, 15.6.

MS (EI): *m*/*z* (%) = 268 (30) [M^+], 135 (100).

MS (EI): *m*/*z* (%) = 268 (20) [M^+], 105 (100).

2-(2-Methoxyphenyl)-1-phenylpropan-1-one (4o)
Trace.

MS (EI): *m*/*z* (%) = 240 (10) [M^+], 135 (100) [$M - COC_6H_5]^+$.

3-(2-Methoxyphenyl)-1-phenylpropan-1-one (3o)[38]
Oil; yield: 0.07 g (20%).

IR: 1691 (C=O) cm^{-1}.

^1H NMR: δ = 3.03 (t, *J* = 7.2 Hz, 2 H), 3.29 (t, *J* = 7.1 Hz, 2 H), 3.85 (s, 3 H), 6.86–6.94 (m, 2 H), 7.19–7.24 (m, 2 H), 7.43–7.57 (m, 3 H), 8.00 (d, *J* = 6.7 Hz, 2 H).

MS (EI): *m*/*z* (%) = 240 (60) [M^+], 121 (100) [$M - CH_2COC_6H_5]^+$.

Arylation of 2b with 1i
Reaction carried out in MeOH. Isolated from the mixture was **9a**.

3-Methoxy-1-(4-methoxyphenyl)oct-1-ene (9a)
^1H NMR: δ = 0.72–0.85 (m, 3 H), 1.10–1.55 (m, 8 H), 3.24 (s, 3 H), 3.75 (s, 3 H), 5.83 (dd, *J* = 8.0, *J* = 15.8 Hz, 1 H), 6.40 (d, *J* = 16 Hz, 1 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 7.28 (d, *J* = 8.8 Hz, 2 H).

MS (EI): *m*/*z* (%) = 248 (20) [M^+], 177 (100) [$M - C_5H_{11}]^+$.

Arylation of 2d and 2e with 1a and 1i
Structure and purity of the isolated products **10a–d**, **11a**,**b**, **12a–c**, and **13b** (isolated as an inseparable mixture with **12b**), reported in Table 6, were confirmed by comparison of their spectral data (MS and ^1H NMR) with those reported in literature from arenediazonium tetrafluoroborates.[11,12]

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