Synthesis of (*E*)-1-Aryl-1-alkenes via a Novel BF_3·OEt_2-Catalyzed Aldol−Grob Reaction Sequence

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The reactions of aromatic aldehydes with ketones in the presence of various acids were examined. The reactions generate (*E*)-1-aryl-1-alkenes in the presence of boron trifluoride diethyl etherate in nonnucleophilic solvents.

Introduction

The Aldol condensation has proven to be a very useful reaction in organic synthesis.[1] Recently, a variety of boron reagents have been developed for carrying out mixed aldol condensations because of their ability to efficiently control the stereochemistry of the reaction.[2] A β-hydroxy carbonyl compound is the initial product of the aldol reaction but it is often transformed into the corresponding α,β-unsaturated derivative via dehydration.[3] During the course of an investigation involving the stereoselective synthesis of 1,3-diols starting from β-hydroxyketones,[4] we discovered an unprecedented boron trifluoride initiated cleavage when the reactions were carried out in nonetheral solvents. The new reaction resulted in the formation of (*E*)-arylalkenes and carboxylic acids[5] (eq 1). We then found that a boron trifluoride initiated Aldol−Grob reaction sequence could be carried out in a tandem fashion starting from aromatic aldehydes and ketones[6] (eq 2). We now wish to report the results of a detailed study of this Aldol-Grob reaction sequence.

Results and Discussion

The overall sequence is rather remarkable since the reaction conditions appear to be ideal for a straightforward dehydration resulting in the formation of α,β-unsaturated ketones. It would seem that the combination of a powerful Lewis acid and a nonnucleophilic solvent is key to this unexpected behavior and, ultimately, to the success of the reaction.

We examined the effect of various acids on the reaction sequence in order to ascertain which would be most efficient. The results are summarized in Table 1. When a mixture of 5-nonanone, 2-chlorobenzaldehyde, and a small excess of BF_3 gas was refluxed for 2 h in CCl_4, (*E*)-1-(2-chlorophenyl)-1-pentene was obtained in 74% yield (Table 1, entry 1). The reaction also occurred in the presence of other acids, but the yields were substantially lower. For example, the use of either $AlCl_3$ or $TiCl_4$ produced (*E*)-1-(2-chlorophenyl)-1-pentene in 30% (Table 1, entry 4) and 9% (Table 1, entry 5) yields, respectively, under similar reaction conditions. Interestingly, a strong protic acid such as *p*-toluenesulfonic acid monohydrate

Table 1. Reaction of 5-Nonanone with 2-Chlorobenzaldehyde in the Presence of Various Acids

entry[a]	acid[b]	product yields[c] (%)
1	BF_3	74
2[d]	BCl_3	trace
3[d]	BBr_3	trace
4[d]	$AlCl_3$	30
5[d]	$TiCl_4$	9
6[d]	$ZnCl_2$	trace
7[e]	*p*-$CH_3C_6H_4SO_3H$·H_2O	32
8[d]	CF_3CO_2H	<5
9[d]	$C_7F_{15}CO_2H$	trace

[a] Reactions carried out in carbon tetrachloride at reflux for 2 h using 10% excess 2-chlorobenzaldehyde. [b] A small excess of BF_3 was bubbled into the reaction mixture (entry 1); 3 equiv of acid added to the reaction mixture (entries 2−9). [c] Isolated yield of (*E*)-1-(2-chlorophenyl)-1-pentene. [d] GC/MS analysis revealed unreacted starting material. [e] A 60% yield of α,β-unsaturated ketone was isolated in this experiment.

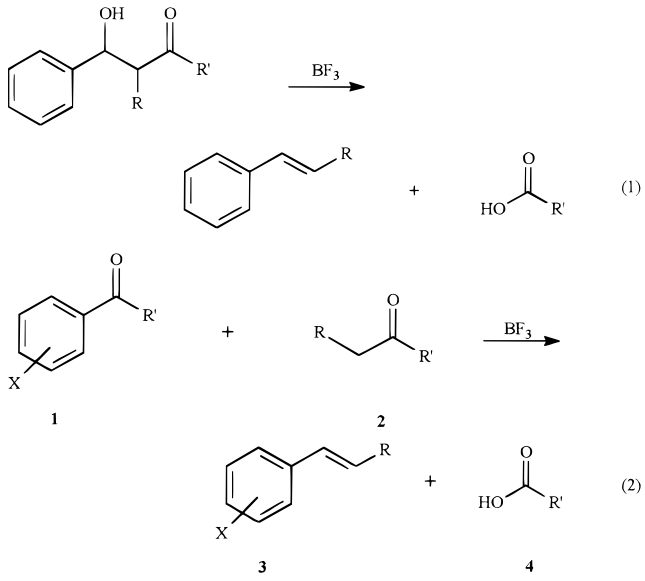

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Table 2. Reaction of 5-Nonanone with 2-Chlorobenzaldehyde in the Presence of Various Boron Trifluoride Complexes

entry[a]	boron trifluoride complex[b]	product yield[c] (%)
1	BF_3 gas	84
2	$BF_3{\cdot}OEt_2$	84
3	$BF_3{\cdot}THF$	84
4	$BF_3{\cdot}2CH_3CO_2H$	78
5	$BF_3{\cdot}2H_2O$	66
6[d]	$BF_3{\cdot}2PhOH$	0
7[e]	$BF_3{\cdot}C_2H_5NH_2$	0

[a] Reaction carried out in hexane at reflux for 1 h using 10% excess 2-chlorobenzaldehyde. [b] A small excess BF_3 gas bubbled into the reaction mixture (entry 1); 2.2 equiv of the BF_3 complex was added to the reaction mixture (entries 2−7). [c] Isolated yield of (*E*)-1-(2-chlorophenyl)-1-pentene. [d] GC/MS analysis revealed acetalization of 2-chlorobenzaldehyde with phenol. [e] GC/MS analysis revealed unreacted starting material.

Table 3. Reaction of 5-Nonanone with 2-Chlorobenzaldehyde in Various Solvents

entry[a]	solvents	product yield[b] (%)
1	CCl_4	64
2	hexane	70
3	CH_2Cl_2	68
4	toluene	37
5[c]	Et_2O	trace
6[c]	THF	0

[a] Reaction carried out in the presence of 2.2 equiv of $BF_3{\cdot}OEt_2$ in various solvents at room temperature for 24 h using 10% excess 2-chlorobenzaldehyde. [b] Isolated yield of (*E*)-1-(2-chlorophenyl)-1-pentene. [c] Both the starting aldehyde and ketone were recovered.

also produced (*E*)-1-(2-chlorophenyl)-1-pentene in 32% yield in addition to the expected α,*β*-unsaturated ketone 60% (Table 1, entry 7). We conclude that boron trifluoride is the most effective acid catalyst for the new tandem condensation−cleavage sequence.

We then examined the reaction of 5-nonanone with 2-chlorobenzaldehyde in the presence of various commercially available complexes of boron trifluoride. The results are summarized in Table 2. As shown, the aldol-cleavage reaction can be initiated by complexes of boron trifluoride with diethyl etherate, tetrahydrofuran, acetic acid, and water. The complexes produced (*E*)-1-(2-chlorophenyl)-1-pentene in good to excellent yields (Table 2, entries 1−5). None of the desired cleavage reaction occurred when the boron trifluoride−phenol complex (Table 2, entry 6) was used; only acetal formation occurred. The boron trifluoride−ethylamine complex was apparently too stable to initiate the reaction. Both ketone and aldehyde were recovered unchanged (Table 2, entry 7). Even though a number of boron trifluoride reagents are effective, boron trifluoride etherate was chosen for further evaluation for economic reasons.

The $BF_3{\cdot}OEt_2$-catalyzed reactions of 5-nonanone with 2-chlorobenzaldehyde in various solvents were investigated, and the results are summarized in Table 3. All the reactions were carried out at room temperature. The most significant observation is that a nonnucleophilic solvent is required. A donor solvent such as THF or diethyl ether inhibits the formation of the product. Apparently, the Lewis acidity of boron trifluoride is moderated sufficiently by complexation to donor solvents to render it ineffective as an aldol catalyst. Although there is an appreciable difference in the reaction rates, all of the nonnucleophilic solvents examined in this study produced (*E*)-1-(2-chlorophenyl)-1-pentene in good yields. For safety and economic reasons, hexane was chosen as the solvent for the remainder of the study and the reactions were carried out in hexane at reflux in order to enhance the reaction rate.

Table 4. Reaction of 5-Nonanone with 2-Chlorobenzaldehyde in the Presence of Various Amounts of $BF_3{\cdot}OEt_2$

entry[a]	$BF_3{\cdot}OEt_2$ (molar equiv)	reaction time (h)	yield[b] (%)
1	2.2	1	84
2	1.4	1	84
3	1.0	1	88
4	0.7	1	88
5[c]	0.7	1	80
6[d]	0.7	2.5	84
7	0.5	1	84
8	0.4	1	71
9	0.4	2.5	78
10	0.4	4	81
11	0.2	4	25
12	0.1	4	4

[a] All reactions carried out in hexane at reflux using 10% excess 2-chlorobenzaldehyde except where noted. [b] Isolated yield of (*E*)-1-(2-chlorophenyl)-1-pentene. [c] In this experiment, 1 molar equiv each of ketone and aldehyde were used. [d] The product was found to slowly dimerize (evidenced by GC/MS) when the reaction time was lengthened.

We then examined the affect of varying the quantity of $BF_3{\cdot}OEt_2$ on the reaction. The results are summarized in Table 4. All experiments were carried out in refluxing hexane using a 10% excess 2-chlorobenzaldehyde, except for entry 5 where 1 molar equiv each of ketone and aldehyde were utilized. An excess of the aldehyde produced (*E*)-1-(2-chlorophenyl)-1-pentene in slightly higher yield (Table 4, entries 4 and 5). Using a 10% excess of aldehyde, the reactions generally gave (*E*)-1-(2-chlorophenyl)-1-pentene in 80−88% yield when 0.5−2.2 molar equiv of $BF_3{\cdot}OEt_2$ was added. The use of 0.4 molar equiv of $BF_3{\cdot}OEt_2$ gave the alkene in 71% yield after 1 h (Table 4, entry 8) but the yields of the product could be increased slightly by lengthening the reaction time (Table 4, entries 9 and 10). The alkene product was found to slowly dimerize (evidenced by GC−MS) when the reaction time was increased significantly (Table 4, entries 4 and 6). In addition, the reactions were very slow if less than 0.4 molar equiv of $BF_3{\cdot}OEt_2$ was used. For example, the use of 0.2 or 0.1 molar equiv of $BF_3{\cdot}OEt_2$ gave (*E*)-1-(2-chlorophenyl)-1-pentene in only 25% and 4% yields, respectively, even after refluxing for 4 h. We conclude that 0.5−1.0 molar equiv of $BF_3{\cdot}OEt_2$ is optimum for the tandem Aldol-cleavage reaction.

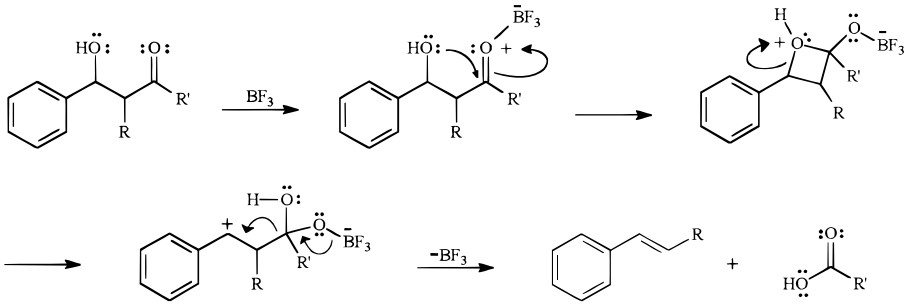
The reaction was found to be general for aromatic aldehydes (Table 5, entries 1−12). The yields were dependent on the electronic nature of the substituent, being generally higher in instances where electron-withdrawing groups were present, a fact attributed to the stability of the styrenyl products under the reaction conditions. Chloro-, bromo-, methoxycarbonyl-, carboxyl-, and trifluoromethyl-substituted benzaldehydes gave the corresponding alkenes in good to excellent yields (Table 5, entries 3−5, 8, and 10−12). However, the presence of strong electron-withdrawing groups such as nitro and cyano led to lower yields of the corresponding alkenes. These groups presumably destabilize the formation of the carbocation intermediate and subsequent cleavage reaction, allowing side reactions to compete more effectively. Indeed, α,*β*-unsaturated ketone products were isolated in these cases (Table 5, entries 6, and 7, and 9). The reactions of benzaldehyde and 4-methylbenzaldehyde

Table 5. Reactions of Aromatic Aldehydes with Ketones in the presence of BF_3·OEt_2

entry[a]	product[b]	X	R	R′	BF_3·OEt_2 (molar equiv)	time[c] (h)	yield[d] (%)
1	**3a**	H	Pr	Bu	0.4	0.5	50
2	**3b**	4-CH_3	Pr	Bu	0.4	0.5	51
3	**3c**	2-Cl	Pr	Bu	0.7	1.0	88
4	**3d**	3-Cl	Pr	Bu	0.7	1.0	78
5[c]	**3e**	4-Cl	Pr	Bu	0.7	1.5	91
6	**3f**[e]	3-NO_2	Pr	Bu	0.7	2.0	41
7	**3g**[f]	4-NO_2	Pr	Bu	0.7	4.5	23
8	**3h**	4-Br	Pr	Bu	0.7	1.5	89
9	**3i**[g]	4-CN	Pr	Bu	0.7	5.0	13
10	**3j**	4-COOME	Pr	Bu	0.7	3.5	69
11	**3k**	4-COOH	Pr	Bu	0.7	3.5	61
12	**3l**	4-CF_3	Pr	Bu	0.7	2.0	78
13	**3m**	2-Cl	Me	Et	0.7	1.0	61
14	**3n**	2-Cl	Et	Pr	0.7	1.0	83
15	**3o**	2-Cl	Bu	Pentyl	0.7	1.3	87
16	**3p**	2-Cl	*i*-Pr	*i*-$PrCH_2$	0.7	4.5	83
17	**3q**	2-Cl	Ph	$PhCH_2$	0.8	4.5	41
18	**3c**	2-Cl	Pr	Ph	0.7	2.0	62
19	**3r**	2-Cl	Pentyl	t-Bu	0.7	21.0	66
20	**3o**	2-Cl	Bu	Me	0.7	1.0	30

[a] Reactions carried out in hexane at reflux using 10% excess aldehyde. [b] The structure of product was confirmed by spectral and elemental analysis. [c] Reaction time required to obtain optimum yield. [d] Isolated yields of **3**; refer to eq 2. [e] 34% of the dehydration product isolated. [f] Dehydration product isolated in 49% yield. [g] Dehydration product isolated in 41% yield.

Scheme 1



with 5-nonane were very fast but gave the corresponding alkenes (**3a** and **3b**) in only 50% yield along with some dimer product (Table 5, entries 1 and 2). The reaction conditions were optimized by reducing the reaction time and the quantity of catalyst, which minimized loss of the styrenyl products due to polymerization. None of the desired reaction occurred between 5-nonanone with *p*-anisaldehyde or 4-*N*,*N*-dimethylaminobenzaldehyde even in the presence of excess BF_3·OEt_2. Presumably, the methoxy and dimethylamino groups complexed to the BF_3·OEt_2 as evidenced by the formation of a white solid in these reactions.

The other product in the reactions leading to **3a**−**l** was pentanoic acid. A 67% isolated yield of pentanoic acid was obtained from the reaction of 2-chlorobenzaldehyde with 5-nonanone leading to (*E*)-1-(2-chlorophenyl)-1-pentene (Table 5, entry 3). A small amount of ethyl pentanoate was also generated in the BF_3·OEt_2-catalyzed reactions. Nonaromatic aldehydes failed to produce alkene products, suggesting that a benzylic carbocation intermediate is involved in the reaction mechanism.

We then examined the reactions of various ketones with 2-chlorobenzaldehyde in the presence of BF_3·OEt_2 (Table 5, entries 13−20). The results reveal that symmetrical ketones produced the styrenyl products in high yields (Table 5, entries 3 and 14−16). The result using small symmetrical ketones revealed that sterically less hindered styrenyl products were prone to polymerization (Table 5, entry 13). The reaction of 1,3-diphenylacetone produced alkene (**3q**) in moderate yield (Table 5, entry 17). The reaction of 2-chlorobenzaldehyde with 1-phenyl-1-pentanone produced alkene (**3c**) in 62% yield (entry 18) along with some α,β-unsaturated ketone. The reaction of 2,2-dimethyl-3-nonanone with 2-chlorobenzaldehyde slowly generated (*E*)-1-(2-chlorophenyl)-1-heptene in 66% yield after refluxing for 21 h (Table 5, entry 19). Methyl alkyl ketones (entry 20) produced lower yields of β-alkylstyrenes since the initial aldol condensation does not occur exclusively at the methylene group as evidenced by the formation of hexanoic acid in the reaction of 2-heptanone with 2-chloro-benzaldehyde.

Although a detailed study of the reaction mechanism has not yet been completed, the consistent formation of (*E*)-alkene products, [7,8] as well as the fact that aromatic aldehydes appear to be required, would point toward the intermediacy of a carbocation derivative. A reasonable mechanism would involve the formation of the mixed aldol followed by the formation and subsequent nonsynchronous ring opening of a lactol as shown in Scheme 1. The proposed fragmentation is reminiscent of two step Grob[9] fragmentations that have been reported for *N*-halo-α-amino acids.[10] and cyclobutane hemiacetals[11] as well

(7) Control experiments revealed that (Z)-1-phenyl-1-alkenes do not isomerize to the corresponding *E* isomers under the reaction conditions.

(8) 8.Isomeric mixtures of *syn*- and *anti*-β-aryl-β-hydroxy ketones consistently yield (*E*)-alkenes.

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as the acid-catalyzed fragmentation of β-hydroxyacetals.[12,13] Grob fragmentations have been reported in numerous syntheses including the preparation of medium-sized carbocycles,[14] hormones,[15] pharmaceuticals,[16] and carbohydrates.[17]

Conclusion

The reaction of ketones with aromatic aldehydes in the presence of boron trifluoride diethyl etherate in non-nucleophilic solvent produces (*E*)-1-arylalkenes. Several features of this reaction make it synthetically useful: (1) The starting materials are readily available and inexpensive. (2) The reaction is stereoselective, and the yields of (*E*)-alkenes are moderate to excellent. (3) The reaction conditions tolerate a variety of functional groups. (4) The reaction provides a useful alternative to Wittig, Heck, Peterson, and related reactions.[18]

Experimental Section

All reactions were carried out under an argon atmosphere. All glassware and syringes were oven-dried. Hexane, dichloromethane, and toluene were distilled over calcium hydride. THF and diethyl ether were distilled from sodium benzophenone ketyl. All other materials were obtained from commercial suppliers and used as received. ^{1}H NMR and ^{13}C NMR data were recorded on a 250 MHz spectrometer. *J* values are given in Hz. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

Reactions of 5-Nonanone with 2-Chlorobenzaldehyde in the Presence of Various Acids. To a mixture of 5-nonanone (2.5 mmol) and 2-chlorobenzaldehyde (2.75 mmol) in carbon tetrachloride (5 mL) was introduced a small excess of BF_3 gas or a 3-fold excess of acid (~7.5 mmol). After the reaction was stirred at reflux for 2 h, the mixture was quenched with water (5 mL). The product (*E*)-1-(2-chlorophenyl)-1-pentene was extracted into ether (3 × 10 mL), analyzed by GC/MS, and isolated by flash chromatography (silica gel using hexane as eluent). The results are summarized in Table 1.

Reactions of 5-Nonanone with 2-Chlorobenzaldehyde in the Presence of Various Boron Trifluoride Complexes. To a dry 25 mL round-bottom flask were added 5-nonanone (2.5 mmol), 2-chlorobenzaldehyde (2.75 mmol), hexane (5 mL), and a small excess of BF_3 gas or BF_3·complex (5.5 mmol). The reaction mixture was stirred at reflux for 1 h and then quenched with water (5 mL). The product (*E*)-1-(2-chlorophenyl)-1-pentene was extracted into ether (3 × 10 mL), analyzed by GC/MS, and purified by silica gel chromatography (hexane as eluent). The results are presented in Table 2.

Reactions of 5-Nonanone with 2-Chlorobenzaldehyde in the Presence of BF_3·OEt_2 in Various Solvents. To a dry 25 mL round-bottom flask were added 5-nonanone (2.5 mL), 2-chlorobenzaldehyde (2.75 mmol), hexane (5 mL), and BF_3·OEt_2 (5.5 mmol). The reaction mixture was stirred at room temperature for 24 h and then quenched with water (5 mL). The product (*E*)-1-(2-chlorophenyl)-1-pentene was extracted with into ether (3 × 10 mL), analyzed by GC/MS, and purified by silica gel chromatography (hexane as eluent). The reaction was repeated using CCl_4, CH_2Cl_2, toluene, Et_2O, and THF. The results are summarized in Table 3.

Reactions of 5-Nonanone with 2-Chlorobenzaldehyde in the Presence of Various Quantities of BF_3·OEt_2. To the mixture of 5-nonanone (2.5 mmol) and 2-chlorobenzaldehyde (2.75 mmol) in hexane (5 mL) were added various quantities of BF_3·OEt_2 (0.1−2.2 molar equiv). The reaction mixture was stirred at reflux for 1−4 h and then cooled to room temperature and quenched with water (5 mL). The product (*E*)-1-(2-chlorophenyl)-1-pentene was extracted into ether (3 × 10 mL), analyzed by GC/MS, and purified by flash silica gel chromatography using hexane as eluent. The results are presented in Table 4.

Synthesis of (*E*)-1-(2-Chlorophenyl)-1-pentene (3c). Typical Procedure. BF_3·OEt_2 (1.8 mmol) was added via syringe to a mixture of 5-nonanone (2.5 mmol), 2-chlorobenzaldehyde (2.75 mmol), and hexane (5 mL). The reaction mixture was stirred at reflux for 1 h and then quenched with water (5 mL), extracted with ether (3 × 10 mL), analyzed via GC/MS, and purified by flash chromatography (silica gel using hexane as eluent) to yield 0.40 g (88%) of (*E*)-1-(2-chlorophenyl)-1-pentene:[19] ^{1}H NMR ($CDCl_3$/TMS) δ 7.50 (dd, 1H, *J* = 7.6, 1.9), 7.32 (dd, 1H, *J* = 7.6, 1.6), 7.24−7.08 (m, 2H), 6.75 (d, 1H, *J* = 15.8), 6.20 (dt, 1H, *J* = 15.8, 7.0), 2.28−2.19 (m, 2H), 1.59−1.44 (m, 2H), 0.97 (t, 3H, *J* = 7.4); ^{13}C NMR ($CDCl_3$) δ 136.0, 132.5, 129.6, 127.8, 126.7, 126.6, 126.2, 35.2, 22.4, 13.7; GC/MS (EI) *m*/*z* 180 (M^+).

All other (*E*)-1-aryl-1-alkenes were prepared via the procedure outlined for **3c**. Yields of these reactions and the reaction conditions are summarized in Table 3. The physical and spectral characteristics of the products are as follows:

(*E*)-1-Phenyl-1-pentene (3a):[20] ^{1}H NMR ($CDCl_3$/TMS) δ 7.33 B 7.14 (m, 5H), 6.29 (d, 1H, *J* = 15.9), 6.18 (dt, 1H, *J* = 15.9, 6.7), 2.20 B 2.11 (m, 2H), 1.55 B 1.40 (m, 2H), 0.94 (t, 3H, *J* = 7.4); ^{13} C NMR ($CDCl_3$) δ 138.0, 130.9, 120.0, 128.4, 126.7, 125.9, 35.1, 22.6, 13.7; GC/MS (EI) *m*/*z* 146 (M^+).

(*E*)-1-(4-Methylphenyl)-1-pentene (3b):[21] ^{1}H NMR ($CDCl_3$/TMS) δ 7.22 (d, 2H, *J* = 8.1), 7.07 (d, 2H, *J* = 8.1), 6.34 (d, 1H, *J* = 15.8), 6.14 (dt, 1H, *J* = 15.8, 6.8), 2.30 (s, 3H), 2.20 B 2.11 (m, 2H), 1.54 B 1.40 (m, 2H), 0.94 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$) δ 136.3, 135.2, 129.8, 129.7, 129.1, 125.3, 35.1, 22.6, 21.1, 13.7; GC/MS (EI) *m*/*z* 160 (M^+).

(*E*)-1-(3-Chlorophenyl)-1-pentene (3d):[22] ^{1}H NMR ($CDCl_3$/TMS) δ 7.31 (s, 1H), 7.19−7.11 (m, 3h), 6.34 (d, 1H, *J* = 15.9), 6.24 (dt, 1H, *J* = 15.9, 6.2), 2.21−2.13 (m, 2H), 1.52−1.41 (m, 2H), 0.93 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$) δ 139.8, 134.4, 132.6, 129.6, 128.7, 126.6, 125.8, 124.1, 35.0, 22.4, 13.7; GC/MS (EI) *m*/*z* 180 (M^+).

(*E*)-1-(4-Chlorophenyl)-1-pentene (3e)[21,23] ^{1}H NMR ($CDCl_3$/TMS) δ 7.23 (s, 4H), 6.32 (d, 1H, *J* = 16.0), 6.18 (dt, 1H, *J* = 16.0, 6.6), 2.21−2.12 (m, 2H), 1.55−1.41 (m, 2H), 0.94 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$) δ 136.4, 131.7, 130.0, 128.7, 128.5, 127.1, 35.0, 22.4, 13.7; GC/Ms (EI) *m*/*z* 180 (M^+).

(*E*)-1-(3-Nitrophenyl)-1-pentene (3f): ^{1}H NMR ($CDCl_3$/TMS) δ 8.17 (t, 1H, *J* = 1.9), 8.03−7.99 (m, 1H), 7.64−7.60 (m, 1H), 7.43 (t, 1H, *J* = 8.0), 6.44 (d, 1H, *J* = 15.3), 6.40−6.30 (m, 1H), 2.27−2.19 (m, 2H), 1.60−1.45 (m, 2H), 0.97 (t, 3H, *J* = 7.4); ^{13}C NMR ($CDCl_3$) δ 148.5, 139.7, 134.4, 131.7, 129.2, 127.8, 121.3, 120.4, 35.0, 22.2, 13.6; GC/MS (EI) *m*/*z* 191 (M^+). Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.84; H, 6.84; N, 7.11.

(*E*)-1-(4-Nitrophenyl)-1-pentene (3g): ^{1}H NMR ($CDCl_3$/TMS) δ 8.12 (d, 2H, *J* = 8.9), 7.45 (d, 2H, *J* = 8.9), 6.45−6.42

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(m, 2H), 2.28−2.20 (m, 2H), 1.60−1.43 (m, 2H), 0.97 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$) *δ* 146.3, 144.3, 136.3, 128.1, 126.2, 123.8, 35.1, 22.0, 13.6; GC/MS (EI) *m*/*z* 191 (M^+). Anal. Calcd. for $C_{11}H_{13}NO_2$; C, 69.09; H, 6.85; N, 7.32. Found: C, 68.99; H, 6.87; N, 7.32.

(*E*)-1-(4-Bromophenyl)-1-pentene (3h):[24,25] ^{1}H NMR ($CDCl_3$/TMS) *δ* 7.35 (d, 2H, *J* = 8.5), 7.13 (d, 2H, *J* = 8.5), 6.26 (d, 1H, *J* = 16.0), 6.15 (dt, 1H, *J* = 16.0, 6.4), 2.17−2.09 (m, 2H), 1.53−1.38 (m, 2H), 0.93 (t, 3H, *J* = 7.4); ^{13}C NMR ($CDCl_3$) *δ* 136.8, 131.7, 131.4, 128.7, 127.4, 120.3, 35.0, 22.4, 13.7; GC/MS (EI) *m*/*z* 224 (M^+).

(*E*)-1-(4-Cyanophenyl)-1-pentene (3i):[25] ^{1}H NMR ($CDCl_3$/TMS) *δ* 7.56 (d, 2H, *J* = 8.5), 7.40 (d, 2H, *J* = 8.25), 6.42−6.33 (m, 2H), 2.31−2.16 (m, 2H), 1.60−1.40 (m, 2H), 0.96 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$) *δ* 142.3, 135.3, 132.2, 128.5, 126.3, 119.1, 109.8, 35.1, 22.1, 13.8; (GC/MS (EI) *m*/*z* 171 (M^+).

(*E*)-1-(4-Carbomethoxyphenyl)-1-pentene (3j): ^{1}H NMR ($CDCl_3$/TMS) *δ* 7.94 (d, 2H, *J* − 8.4); 7.34 (d, 2H, *J* − 8.4), 6.43−6.23 (m, 2H), 3.86 (s, 3H), 2.23−2.10 (m, 2H), 1.57−1.38 (m, 2H), 0.94 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$/TMS) *δ* 166.6, 142.2, 133.6, 129.6, 129.0, 128.0, 125.5, 51.6, 35.0, 22.1, 13.5; GC/MS (EI) *m*/*z* 204 (M^+). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.42; H, 7.92.

(*E*)-1-(4-Carboxylphenyl)-1-pentene (3k): ^{1}H NMR ($CDCl_3$/TMS) *δ* 12.30 (brs, 1H), 8.04 (d, 2H, *J* = 8.3), 7.42 (d, 2H, *J* = 8.3), 6.50−6.30 (m, 2H), 2.30−2.10 (m, 2H), 1.60−1.40 (m, 2H), 0.97 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$/TMS) *δ* 172.1, 143.4, 134.5, 130.5, 129.1, 127.3, 125.8, 35.2, 22.3, 13.7; GC/MS (EI) *m*/*z* 190 (M^+). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.51; H, 7.51.

(*E*)-1-(4-Trifluoromethylphenyl)-1-pentene (3l): ^{1}H NMR ($CDCl_3$/TMS) *δ* 7.51 (d, 2H, *J* = 8.3), 7.39 (d, 2H, *J* = 8.3), 6.40 (d, 1H, *J* = 16.0), 6.20 (dt, 1H, *J* = 16.0, 6.2), 2.24−2.16 (m, 2H), 1.57−1.43 (m, 2H), 0.95 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$) *δ* 141.5, 133.8, 128.8, 126.0, 125.4, 125.4, 35.1, 22.4, 13.7; GC/MS (EI) *m*/*z* 214 (M^+). Anal. Calcd for $C_{12}H_{13}F_3$: C, 67.28; H, 6.12. Found: C, 67.39; H, 6.05.

(*E*)-1-(2-Chlorophenyl)-1-propene (3m):[25] ^{1}H NMR ($CDCl_3$/TMS) *δ* 7.46 (dd, 1H, *J* = 7.6, 1.7), 7.31 (dd, 1H, *J* = 7.6, 1.4), 7.22−7.03 (m, 2H), 6.77 (d, 1H, *J* = 15.7) 6.20 (dt, 1H, *J* = 15.7, 6.7), 1.91 (dd, 3H, *J* = 6.7, 1.6); ^{13}C NMR ($CDCl_3$/TMS) *δ* 135.9, 132.3, 129.5, 128.6, 127.7, 127.3, 126.7, 126.5, 18.7; GC/MS (EI) *m*/*z* 152 (M^+).

(*E*)-1-(2-Chlorophenyl)-1-butene (3n): ^{1}H NMR ($CDCl_3$/TMS)*δ* 7.46 (d, 1H, *J* = 7.6), 7.29 (d, 1H, *J* = 7.6), 7.20−7.00 (m, 2H), 6.75 (d, 1H, *J* = 15.7), 6.21 (dt, 1H, *J* = 15.7, 6.5), 2.33−2.14 (m, 2H), 1.09 (dt, 3H, *J* = 7.4, 2.1); ^{13}C NMR ($CDCl_3$) *δ* 135.9, 135.4, 132.5, 129.5, 127.7, 126.6, 126.5, 125.1, 26.2, 13.4; GC/MS (E1) *m*/*z* 166 (M^+). Anal. Calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.65. Found: C, 72.35; H, 6.71.

(*E*)-1-(2-Chlorophenyl)-1-hexene (3o): ^{1}H NMR ($CDCl_3$-TMS) *δ* 7.47 (d, 1H, *J* = 7.67), 7.30 (d, 1H, *J* = 7.8), 7.18−7.07 (m, 2H), 6.75 (d, 1H, *J* = 15.9), 6.18 (dt, 1H, *J* = 15.9,7.0), 2.27−2.18 (m, 2H), 1.49−1.31 (m, 4H), 0.92 (t, 3H, *J* = 6.8); ^{13}C NMR ($CDCl_3$) *δ* 136.0, 134.1, 132.5, 129.5, 126.7, 126.6, 126.0, 32.9, 31.4, 22.3, 13.9; GC/MS (EI) *m*/*z* 194 (M^+). Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.03; H, 7.75. Found: C, 74.13; H, 7.77.

(*E*)-1-(2-Chlorophenyl)-3-methyl-1-butene (3p): ^{1}H NMR ($CDCl_3$/TMS) *δ* 7.43 (d, 1H, *J* = 7.7), 7.26 (d, 1H, *J* = 7.6), 7.10−7.01 (m, 2H), 6.72 (d, 1H, *J* = 15.9), 6.12 (dt, 1H, *J* = 15.9, 6.9), 2.48−2.44 (m, 1H), 1.07 (d, 6H, *J* = 6.7); ^{13}C NMR ($CDCl_3$) *δ* 140.6, 136.0, 132.7, 129.5, 127.7, 126.6, 126.5, 123.3, 31.8, 22.3; GC/MS (E1) *m*/*z* 180 (M^+). Anal. Calcd for $C_{11}H_{13}$-Cl: C, 73.13; H, 7.25. Found: C, 73.36; H, 7.18.

(*E*)-1-Phenyl-2-(2-chlorophenyl)ethene (3q):[26] ^{1}H NMR ($CDCl_3$/TMS) *δ* 7.65 (d, 1H, *J* = 7.6), 7.58−7.45 (m, 3H), 7.39−7.11 (m, 6H), 7.05 (d, 1H, *J* = 16.3); ^{13}C NMR ($CDCl_3$) *δ* 137.0, 135.4, 133.4, 131.2, 129.8, 128.7, 128.5, 128.0, 126.8, 126.4, 124.7; GC/MS (E1) *m*/*z* 214 (M^+).

(*E*)-1-(2-Chlorophenyl)-1-heptene (3r): ^{1}H NMR ($CDCl_3$/TMS) *δ* 7.50 (dd, 1H, *J* = 7.5, 1.6), 7.32 (dd, 1H, *J* = 7.7, 1.5), 7.28−7.00 (m, 2H), 6.75 (d, 1H, *J* = 15.8), 6.21 (dt, 1H, *J* = 15.8, 6.9), 2.32−2.11 (m, 2H), 1.59−1.16 (m, 6H), 0.91 (t, 3H, *J* = 6.8); ^{13}C NMR ($CDCl_3$) *δ* 136.0, 134.2, 132.5, 129.6, 127.7, 126.7, 126.6, 126.0, 33.2, 31.4, 28.9, 14.0; GC/MS (El) *m*/*z* 208 (M^+). Anal. Calcd for $C_{13}H_{17}Cl$: C, 74.81; H, 8.21. Found: C, 74.53; H, 8.19.

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