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TETRAHEDRON

A Tandem Aldol-Grob Reaction of Ketones with Aromatic Aldehydes

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ABSTRACT: Aromatic aldehydes react with ketones to produce (*E*)-1-aryl-1-alkenes via a tandem Aldol-Grob cleavage reaction sequence. The reaction, initiated by boron trifluoride, also produces a carboxylic acid fragment.

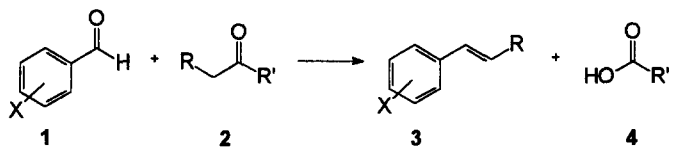
Keywords: Aldol, Grob Fragmentation, Boron Trifluoride, Alkene

INTRODUCTION

The Aldol condensation is one of the most useful reactions in organic chemistry.[1] Aldol chemistry has been extensively investigated since the self condensation of acetone was first reported by Kane in 1838.[2] Interestingly, aldol (3-hydroxybutanal, which gives its name to this reaction) was synthesized years later via the self condensation of acetaldehyde.[3] Although aqueous acidic conditions were used in these early reactions, the aldol condensation is also known to be induced by bases. The initial product of the aldol condensation is a β-hydroxy carbonyl compound but the corresponding α,β-unsaturated carbonyl derivative is often formed via dehydration.[1,4]

In recent years, boron reagents of the type R_2BX (X = OTf, Cl, Br, I) have been developed for use in mixed aldol condensations because of their ability to efficiently control the stereochemistry of the resulting β-hydroxy ketones.[5] During the course of an investigation involving the synthesis of stereochemically defined β-hydroxy ketones,[6] we discovered an unprecedented boron trifluoride initiated cleavage reaction which resulted in the formation of (*E*)-1-aryl-1-alkenes and carboxylic acids.[7] Since β-hydroxy ketones are often prepared via acid catalyzed aldol reactions, we reasoned that the reaction sequence would be more synthetically useful if it could be carried out in a tandem fashion starting from aromatic aldehydes and appropriate ketones.

We wish to report the details of a study in which the aldol condensation of ketones with aromatic aldehydes, in the presence of boron trifluoride, in non-nucleophilic solvents, affords the corresponding (*E*)-1-arylalkene in a single reaction vessel. The overall sequence is rather remarkable since the reaction conditions appear to be ideal for the formation of the corresponding α,β-unsaturated ketones. It would seem that the combination of a powerful Lewis acid and a non-nucleophilic solvent are key to this unexpected behavior and, ultimately, to the success of the reaction.



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RESULTS AND DISCUSSION

When a mixture of 5-nonanone, BF_3 and 2-chlorobenzaldehyde in CCl_4 was refluxed for 2 hours, (*E*)-1-(2-chlorophenyl)-1-pentene was obtained in 74% yield. Although the reaction could also be achieved in the presence of other acids, the yields were substantially lower.[8] For example, the use of either $AlCl_3$ or $TiCl_4$ produced (*E*)-1-(2-chlorophenyl)-1-pentene in 30% and 9% yields, respectively, under similar reaction conditions. Interestingly, a strong protic acid such as *p*-toluenesulfonic acid monohydrate also produced (*E*)-1-(2-chlorophenyl)-1-pentene in 32% yield in addition to the expected α,β-unsaturated ketone (60%), which formed via dehydration of the aldol condensation intermediate.

We examined the new BF_3 induced reaction of 5-nonanone and 3-chlorobenzaldehyde in various solvents.[8] A donor solvent such as diethyl ether completely inhibited the condensation reaction. Apparently, the Lewis acidity of BF_3 is sufficiently moderated by complexation to diethyl ether that it is ineffective as an aldol catalyst. In fact, in the presence of BF_3 in diethyl ether, 5-nonanone and 3-chlorobenzaldehyde were recovered unchanged after 12 hours. The results obtained when the reaction was carried out in various solvents are summarized in Table 1. Although there is an appreciable difference in the reaction rates, the non-nucleophilic solvents examined in this study produced (*E*)-1-(3-chlorophenyl)-1-pentene in good yields. For safety and economic reasons, we conclude that hexane is the ideal solvent for the reaction.

Table 1. Reaction of 5-Nonanone with 3-Chlorobenzaldehyde in Various Solvents.[a]

Entry	Solvent	Time[b]	Temperature	Yield (%)[c]
1	Hexane	2.5 hr	68 - 70 °C	89
2	CCl_4[d]	6 hr	76 - 77 °C	91
3	CH_2Cl_2	3 hr	40 °C	75
4	Toluene	4 hr	110 °C	84

[a]Reactions were carried out using a 30% molar excess of aldehyde. [b]Reaction time required to obtain optimum yield. [c]Isolated yields of (*E*)-1-(3-chlorophenyl)-1-pentene. [d]NMR analysis indicated that pentenoic acid formed prior to hydrolysis of the reaction mixture

Benzaldehyde and a large number of substituted benzaldehydes **1a-1m** were found to produce the corresponding (*E*)-1-aryl-1-alkenes upon reaction with 5-nonanone in the presence of BF_3 (Table 2). The yields were dependent on the 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- and bromo-substituted benzaldehydes **1b-1g** gave excellent yields of the corresponding alkenes **3b-3g**. The yields were not sensitive to the position of the aryl substituent and the alkene products were found to be fairly stable to the reaction conditions although the alkene products were found to slowly dimerize (evidenced by GC/MS and ^{1}H-NMR data) when the reaction times were lengthened. The formation of alkene products using nitro-substituted benzaldehydes **1h-1j** was found to be very dependent on the substitution site. While 3-nitrobenzaldehyde produced an 83% yield of the corresponding alkene **3i**, the yields were lower for both 4-nitro- and 2-nitrobenzaldehyde. The nitro groups might retard the formation/cleavage of the intermediate lactol which would allow dehydration to

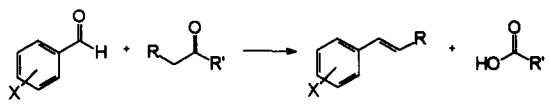

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Table 2. Reaction of Substituted Aldehydes with Ketones in the Presence of BF_3.[a]

Entry	X	R	R'	Time[b]	Yield[c] of 3	(E/Z)[d]
a	H	Pr	Bu	1 hr	78	97:3
b	2-Cl	Pr	Bu	4 hr	91	98:2
c	3-Cl	Pr	Bu	2.5 hr	89	95:5
d	4-Cl	Pr	Bu	4 hr	91	94:6
e	2-Br	Pr	Bu	4 hr	88	98:2
f	3-Br	Pr	Bu	2.5 hr	92	95:5
g	4-Br	Pr	Bu	4 hr	86	96:4
h	2-NO_2	Pr	Bu	4 hr	8	98:2
i	3-NO_2	Pr	Bu	2 hr	83	92:8
j	4-NO_2	Pr	Bu	1.5 hr	49	94:6
k	4-CH_3	Pr	Bu	2.5 hr	66	98:2
l	4-CF_3	Pr	Bu	4 hr	82	96:4
m	3-OCH_3	Pr	Bu	1.5 hr	20	96:4
n	3-OH	Pr	Bu	1 hr	0	---
o	4-CO_2H	Pr	Bu	1 hr	0	---
p	3-Cl	H	Me	1 hr	0	---
q	3-Cl	Me	Et	2.5 hr	50	96:4
r	3-Cl	Et	Pr	2.5 hr	81	98:2
s	2-Cl	Bu	Pent	4 hr	84	98:2
t	3-Cl	Bu	Pent	2.5 hr	86	95:5
u	3-Cl	i-Pr	i-$PrCH_2$	5 hr	71	97:3
v	H	Ph	Bz	3 hr	48	>99:1
w	3-Cl	Ph	Bz	5 hr	43	>99:1
x	4-Cl	Ph	Bz	4 hr	43	>99:1
y	3-Cl	Pr	Me	2.5 hr	52	98:2
z	3-Cl	Bu	Me	2.5 hr	58	96:4
aa	2-Cl	Pr	Ph	1.5 hr	50	96:4
ab	3-Cl	Pr	Ph	2.5 hr	48	96:4

[a]Reaction carried out in hexane at reflux. [b]Reaction time required to obtain optimum yield. [c] Yield of the corresponding 1-aryl-1-alkene; spectral data are in agreement with the proposed structures. [d]Isomer ratios determined by integration of non-overlapping signals in the ^{1}H-NMR spectrum.

compete more effectively. Indeed, the α,β-unsaturated ketone products were isolated in both cases.[5] As observed for the chloro- and bromo-substituted alkene products **3b-3g**, the nitro-substituted alkene products **3h-3j** were found to be fairly stable to the reaction conditions.

Generally, substituted benzaldehydes bearing electron donating groups produce lower yields of alkenes because the styrenyl products are more prone to polymerization under the reaction conditions. For example, *p*-methylbenzaldehyde gave the corresponding alkene **3k** in 66% yield. (*E*)-1-(3-Methoxyphenyl)-1-pentene, **3m**, was isolated in only 20% yield, while the 3-hydroxystyrenyl product was completely lost to polymerization. The other product of the reactions leading to **3a-3n** was pentanoic acid. As an example, an isolated yield of 84% of pentanoic acid was obtained from the reaction of benzaldehyde leading to (*E*)-1-phenyl-1-pentene **3a**. Non-aromatic aldehydes, such as heptanal, pivalaldehyde and formaldehyde failed to produce alkene products, suggesting that a benzylic carbocation intermediate is involved in the reaction mechanism.

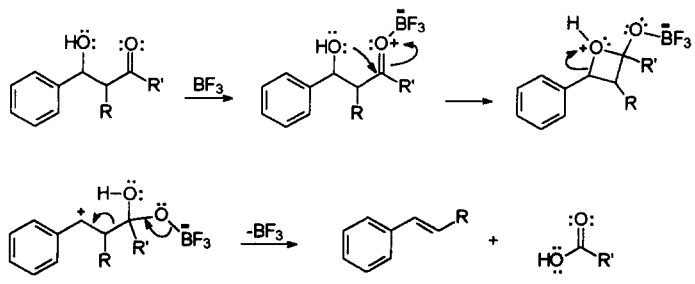
We then examined the reactions of various enolizable ketones with chloro-substituted benzaldehydes in the presence of BF_3 (Table 2). The results reveal that symmetrical ketones produce the styrenyl products in higher yields than the corresponding phenyl and methyl ketones. While (*E*)-1-(3-chlorophenyl)-1-pentene, (entry **c**), was synthesized from 5-nonanone in 89% yield, the same product, (entry **y**) was obtained from 2-hexanone in 52% yield and from valerophenone in 48% yield. The results using small symmetrical ketones **2p** and **2q** revealed that sterically unhindered styrenyl products were prone to polymerization. In fact, 3-chlorostyrene, **3p**, could not be isolated but (*E*)-1-(3-chlorophenyl)-1-propene, **3q**, was isolated in only 50% yield.

Methyl alkyl ketones (entries **y** and **z** vs **c**) gave lower yields of β-alkylstyrenes than the corresponding symmetrical dialkyl ketones since the initial aldol condensation does not occur exclusively at the methylene group (thermodynamic product). As evidenced by the presence of pentanoic acid in the reaction of 2-hexanone with 3-chlorobenzaldehyde, the kinetic aldol intermediate also formed in the reaction.

Valerophenone derivatives produced lower yields (entries **aa** and **ab**)of the corresponding alkylstyrenes because the products polymerized readily under the reaction conditions. The boron trifluoride-benzoic acid complex formed in these reactions may polymerize the styrenyl products more rapidly than the boron trifluoride-pentanoic acid complex formed when 5-nonanone was used (entries **b** and **c**).[9]

Although a detailed study of the reaction mechanism has not yet been completed, the consistent formation of (*E*)-alkene products, as well as the fact that aromatic aldehydes appear to be required would point toward a benzylic carbocation intermediate. A reasonable mechanism would involve the formation of the mixed aldol product followed by the formation and subsequent non-synchronous ring opening of a lactol as shown in Scheme 1. The proposed fragmentation is reminiscent of two step Grob[10] framentations that have been reported for N-halo-α-aminoacids[11] and cyclobutane hemiacetals[12] as well as the acid catalyzed fragmentation of β-hydroxyacetals.[13,14]

Scheme 1



CONCLUSION

The reaction of ketones with aromatic aldehydes in the presence of boron trifluoride produces (*E*)-1-arylalkenes as well as carboxylic acids. 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) Moderate reaction temperatures and non-nucleophilic solvents are effective. (4) The reactions are relatively rapid. (5) The reaction provides a useful alternative to the Wittig, Heck, Peterson and related syntheses.[15] (6) The reaction may provide a possible alternative to the Baeyer-Villiger oxidation reaction.

EXPERIMENTAL

All reactions were performed in oven-dried glassware under a nitrogen atmosphere and with continuous magnetic stirring. Air and moisture sensitive compounds were introduced via syringe or cannula through a rubber septum. All solvents were dried and distilled prior to use. Products were purified by flash chromatography using 230-400 mesh ASTM 60 Å silica gel. All ^{1}H and ^{13}C-NMR spectra were recorded on a 250 MHz Bruker AC250 spectrometer. All ^{1}H and ^{13}C-NMR data were obtained in $CDCl_3$ solution, chemical shifts are given in ppm (δ) relative to TMS, and coupling constants (*J*) are given in Hz. All elemental analyses were performed by Atlantic Microlabs, Norcross, Georgia. All GC/MS data were obtained using a Hewlett Packard 6890 Series GC System equipped with a 5973 Mass Selective Detector or a Hewlett Packard 5890 Series GC System equipped with a 5970 Mass Selective Detector.

(*E*)-1-Phenyl-1-pentene (3a).[16] The synthesis of (*E*)-1-phenyl-1-pentene is representative: a small excess of BF_3 is bubbled into a solution of 5-nonanone (4.26 mmol) in hexane (10 mL). The reaction flask is flushed with nitrogen to remove excess BF_3. Benzaldehyde (5.54 mmol) is then added to the reaction mixture and the solution heated to reflux for one hour. The reaction is quenched with distilled water (10 mL), the product extracted into ether (3 x 10 mL), and the combined ether layers dried over anhydrous $MgSO_4$. The solvent is removed under reduced pressure and the mixture purified by flash chromatography (silica gel using hexanes as the eluent) to yield 0.49 g (78%) of (*E*)-Phenyl–1-pentene. ^{1}H-NMR ($CDCl_3$/TMS) δ 7.33 – 7.14 (m, 5H), 6.29 (d, 1H, *J* = 15.9), 6.18 (dt, 1H, *J* = 15.9, 6.7), 2.20 – 2.11 (m, 2H), 1.55 – 1.40 (m, 2H), 0.94 (t, 3H, *J* = 7.4); ^{13} C-NMR ($CDCl_3$) δ 138.0, 130.9, 130.0, 128.4, 126.7, 125.9 , 35.1, 22.6, 13.7; GC/MS (EI) m/z (relative intensity) 146 (M^+, 29), 117 (100), 115 (44), 104 (34), 91 (31).

(*E*)-1-(2-Chlorophenyl)-1-pentene (3b,3aa).[17] ^{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, 133.9, 132.5, 129.6, 127.8, 126.7, 126.6, 126.2, 35.2, 22.4, 13.7; GC/MS (EI) m/z (relative intensity) 180 (M^+, 37), 151 (65), 138 (78), 125 (30), 115 (100), 103 (24), 89 (22).

(*E*)-1-(3-Chlorophenyl)-1-pentene (3c,3y,3ab).[18] ^{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 (relative intensity) 180 (M^+, 46), 151 (84), 138 (85), 115 (100), 103 (18), 89 (17).

(*E*)-1-(4-Chlorophenyl)-1-pentene (3d).[17,19] ^{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 (relative intensity) 180 (M^+, 32), 151 (90), 138 (38), 125 (15), 115 (100).

(*E*)-1-(2-Bromophenyl)-1-pentene (3e). ^{1}H-NMR ($CDCl_3$/TMS) δ 7.49 (td, 2H, *J* = 7.8, 1.4), 7.22 (t, 1H, *J* = 7.3), 7.03 (td, 1H, *J* = 7.7, 1.6), 6.71 (d, 1H, *J* = 15.7), 6.16 (dt, 1H, *J* = 15.7, 7.0), 2.27 – 2.18 (m, 2H), 1.59 – 1.44 (m, 2H), 0.96 (t, 3H, *J* = 7.4); ^{13}C-NMR ($CDCl_3$) δ 137.7, 134.0, 132.8, 128.8, 128.0, 127.3, 126.8, 123.1, 35.1, 22.4, 13.7; GC/MS (EI) m/z (relative intensity) 224 (M^+, 12), 182 (22), 1445 (10), 116 (100), 103 (15), 89 (14); Anal. calcd. for $C_{11}H_{13}Br$: C, 55.69; H, 5.82. Found: C, 58.54; H, 5.81.

(*E*)-1-(3-Bromophenyl)-1-pentene (3f).[20] ^{1}H-NMR ($CDCl_3$/TMS) δ 7.46 (t, 1H, *J* = 1.8), 7.31 – 7.06 (m, 3H), 6.27 (d, 1H, *J* = 15.9), 6.18 (dt, 1H, *J* = 15.9, 6.1), 2.20 – 2.12 (m, 2H), 1.55 – 1.40 (m, 2H), 0.94 (t, 3H, *J* = 7.3); ^{13}C-NMR ($CDCl_3$) δ 140.1, 132.6, 129.8, 129.6, 128.7, 128.6, 124.6, 122.7, 35.0, 22.4, 13.7; GC/MS (EI) m/z (relative intensity) 224 (M^+, 12), 182 (20), 145 (12), 116 (100), 103 (10), 89 (11), 77 (10); b.p. = 251 °C/730 mm Hg; Anal. calcd. for $C_{11}H_{13}Br$: C, 55.69; H, 5.82. Found: C, 58.54; H, 5.81.

(*E*)-1-(4-Bromophenyl)-1-pentene (3g).[19,21] ^{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 (relative intensity) 224 (M^+, 10), 195 (12), 182 (11), 116 (100), 89 (9).

(*E*)-1-(2-Nitrophenyl)-1-pentene (3h).[22] ^{1}H-NMR ($CDCl_3$/TMS) δ 7.87 (dd, 1H, *J* = 8.1, 1.1), 7.61 – 7.52 (m, 2H), 7.33 (td, 1H, *J* = 7.3, 1.1), 6.84 (d, 1H, *J* = 15.6), 6.23 (dt, 1H, *J* = 15.6, 6.9), 2.29 – 2.20 (m, 2H), 1.57 – 1.48 (m, 2H), 0.97 (t, 3H, *J* = 7.3); ^{13}C-NMR ($CDCl_3$) δ 136.7, 133.4, 132.7, 128.4, 127.3, 125.0, 124.3, 35.2, 22.2, 13.6; GC/MS (EI) m/z (relative intensity) 191 (M^+, 5), 146 (27), 132 (33), 120 (60), 115 (71), 92 (100), 77 (72).

(*E*)-1-(3-Nitrophenyl)-1-pentene (3i). ^{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 (relative intensity) 191 (M^+, 23), 149 (100), 115 (61), 103 (25), 89 (11), 77 (15); 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 (3j). ^{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 (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 (relative intensity) 191 (M^+, 12), 149 (64), 119 (14), 116 (100), 115 (73), 91 (14), 77 (15); 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-Methyphenyl)-1-pentene (3k).[23] ^{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 – 2.11 (m, 2H), 1.54 – 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 (relative intensity) 160 (M^+, 30), 145 (6), 131 (100), 115 (23), 91 (33).

(*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), 6.30 (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, 13.6; GC/MS (EI) m/z (relative intensity) 214 (M^+, 30), 185 (58), 177 (100), 165 (45), 145 (18), 115 (34); Anal. calcd. for $C_{12}H_{13}F_3$: C, 67.28; H, 6.12. Found: C, 67.39; H, 6.05.

(*E*)-1-(3-Methoxyphenyl)-1-pentene (3m).[24] ^{1}H-NMR ($CDCl_3$/TMS) δ 7.20 (t, 1H, *J* = 7.8), 6.94 (d, 1H, *J* = 7.6), 6.89 (d, 1H, *J* = 2.0), 6.74 (dd, 1H, *J* = 8.2, 2.3), 6.36 (d, 1H, *J* = 15.9), 6.21 (dt, 1H, *J* = 15.9, 6.4), 3.80 (s, 3H), 2.23 – 2.14 (m, 2H), 1.61 – 1.43 (2H), 0.95 (t, 3H, *J* = 7.3); ^{13}C-NMR ($CDCl_3$) δ 159.2, 139.4, 131.2, 129.7, 129.3, 118.5, 112.3, 111.2, 55.1, 35.0, 22.3, 13.7; GC/MS (EI) m/z (relative intensity) 176 (M^+, 30), 147

(87), 134 (32), 115 (55), 91 (100), 77(37).

(*E*)-1-(3-Chlorophenyl)-1-propene (3q).[25] ^{1}H-NMR ($CDCl_3$/TMS) δ 7.29 (s, 1H), 7.20 – 7.11 (m, 3H), 6.33 (d, 1H, *J* = 16.1), 6.21 (dq, 1H, *J* = 16.1, 6.2), 1.87 (d, 3H, *J* = 5.4); ^{13}C-NMR ($CDCl_3$) δ 139.8, 134.4, 129.8, 129.6, 127.3, 126.7, 125.8, 124.0, 14.4; GC/MS (EI) m/z (relative intensity) 152 (M^+, 43), 125 (12), 117 (100), 115 (67), 91 (18).

(*E*)-1-(3-Chlorophenyl)-1-butene (3r).[26] ^{1}H-NMR ($CDCl_3$/TMS) δ 7.29 (s, 1H), 7.13 (broad s, 3H), 6.30 – 6.12 (m, 2H), 2.31 (m, 2H), 1.05 (t, 3H, *J* = 7.4); ^{13}C-NMR ($CDCl_3$) δ 139.8, 134.3, 134.0, 129.6, 127.5, 126.6, 125.8, 124.1, 26.0, 13.4; GC/MS (EI) m/z (relative intensity) 166 (M^+, 45), 151 (34), 131 (100), 116 (55), 115 (67), 91 (24).

(*E*)-1-(2-Chlorophenyl)-1-hexene (3s) ^{1}H-NMR ($CDCl_3$/TMS) δ 7.47 (*d*, 1H, *J* - 7.6), 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, 127.7, 126.7, 126.6, 126.0, 32.9, 31.4, 22.3, 13.9; GC/MS (EI) m/z (relative intensity) 194 (m^+, 27) 151 (53) 138 (100) 115 (82) Anal. Calcd. For $C_{12}H_{15}Cl$; C, 7403; H, 7.75 Found: C, 74.13; H, 7.77.

(*E*)-1-(3-Chlorophenyl)-1-hexene (3t, 3z). ^{1}H-NMR ($CDCl_3$/TMS) δ 7.30 (s, 1H), 7.17 – 7.11 (m, 3H), 6.28 (d, 1H, *J* = 15.9), 6.18 (dt, 1H, *J* = 15.9, 6.1), 2.21 – 2.13 (m, 2H), 1.45 – 1.25 (m, 4H), 0.91 (t, 3H, *J* = 6.9); ^{13}C-NMR ($CDCl_3$) δ 139.7 , 134.3 , 132.6 , 129.5, 128.4, 126.5, 125.7, 124.0, 32.6, 31.3, 22.2, 13.8; GC/MS (EI) m/z (relative intensity) 194 (M^+, 26), 151 (59), 140 (33), 138 (100), 117 (21), 116(54) 115 (76); Anal. calcd. for $C_{12}H_{15}Cl$; C, 74.03; H, 7.77. Found: C, 73.97; H, 7.75.

(*E*)-1-(3-Chlorophenyl)-3-methyl-1-butene (3u). ^{1}H-NMR ($CDCl_3$/TMS) δ 7.43 (dd, 1H, *J* = 7.7, 1.7), 7.26 (dd, 1H, *J* = 7.6, 1.3), 7.10 -7.01 (m, 2H), 6.72 (d, 1H, *J* = 15.9), 6.11 (dd, 1H, *J* = 15.9, 6.9), 2.48 – 2.44 (m, 2H), 1.07 (d, 3H, *J* = 6.7); ^{13}C-NMR ($CDCl_3$) δ 140.6, 135.9, 132.7, 129.5, 127.7, 126.6, 126.5, 123.3, 31.8, 22.3; GC/MS (EI) m/z (relative intensity) 180 (M^+, 48), 167 (34), 165 (100), 145 (69), 130 (51), 129 (39), 128 (30), 125 (30). Anal. calcd. for $C_{11}H_{13}Cl$; C, 71.13; H, 7.25. Found: C, 73.18; H, 7.38.

(*E*)-Stilbene (3v).[27] ^{1}H-NMR ($CDCl_3$/TMS) δ 7.49 (d, 4H, *J* = 7.4), 7.33 (d, 4H, *J* = 7.33), 7.30 – 7.20 (m, 2H), 7.09 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ 137.3, 128.6, 127.6, 126.5; GC/MS (EI) m/z (relative intensity) 180 (M^+, 100), 179 (98), 178 (65), 165 (56), 152 (18) 89 (32), 76 (22); m.p. = 122–123 °C; lit. m.p. = 122–124 °C.

(*E*)-3-Chlorostilbene (3w).[28] ^{1}H-NMR ($CDCl_3$/TMS) δ 7.49 – 6.94 (m, 11H); ^{13}C-NMR ($CDCl_3$) δ 139.2, 136.7, 134.6, 130.0, 129.8, 128.7, 128.0, 127.4, 127.1, 126.6, 126.2, 124.7; GC/MS (EI) m/z (relative intensity) 214 (M^+, 59), 179 (94), 178 (100), 177 (15), 89 (14), 76 (13); m.p. = 71-72 °C; lit. m.p. = 73-74 °C.

(*E*)-4-Chlorostilbene (3x).[29] ^{1}H-NMR ($CDCl_3$/TMS) δ 7.51 – 7.26 (m, 9H), 7.05 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ 137.0, 135.8, 133.2, 129.3, 128.8, 128.7, 127.9, 127.6, 127.4, 126.5; GC/MS (EI) m/z (relative intensity) 214 (M^+, 60), 179 (100), 89 (39), 76 (43); m.p. = 126-127 °C; lit. m.p. = 126 -128 °C.

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