Cobalt(I)-Catalyzed Stereoselective Olefination of Alkylzinc Reagents with Aldehydes

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Received 17 February 2003; revised 14 April 2003

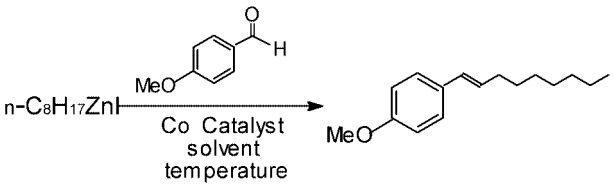
Abstract: The efficient olefination from organozinc reagents with aldehydes is exploited in a new synthesis of aryl and alkyl olefins.

Key words: alkenation, zinc, aldehydes, cobalt, organometallic reagents, alkenes

Olefinations are one of the most useful and fundamental reactions in synthetic organic chemistry, particularly in the synthesis of complex natural products with biological activity. The well know Wittig reaction gives olefins by introducing the double bond regio- and stereoselectively and has found widespread application in synthetic organic chemistry.[1] Numerous reviews have detailed the progress of the Wittig reagent.[1] Many methods have been developed for the olefination such as reductive coupling of carbonyl compounds,[2] self-coupling of α-lithiated benzylic sulfones,[3] and condesation of aldehyde tosylhydrazones with stabilized carbanions.[4] More recently, new procedures for the synthesis of stilbenes have been reported, in which aldehyde tosylhydrazones were treated with benzotriazole stabilized carbanions,[5] trimethyl borate–lithium tertbutoxide, trialkyl boranes, and alkylboron chlorides.[6]

The reaction of alkylzinc reagents and carbonyl compounds represents one of the most reliable methods to prepare optically active secondary alcohols.[7,8] In addition, we have also reported that the substitution reaction of nitro group[9] and dialkylation reaction[10] of alkylzinc reagents using $[Ni(acac)_2]$ as a catalyst in the presence of a tertiary amine and silylating agent. Recently, we have reported the stereoselective synthese of (*E*)-stilbenes[11] by the reaction of organozinc reagent with aryl aldehydes using $[Ni(acac)_2]$ as a catalyst. However, our investigations have shown that (*E*)-alkenes can be formed by the reaction of organozinc halides with aldehydes in the presence of a silylating agent and using $[CoCl(PPh_3)_3]$ as the catalyst.

To our knowledge, the formation of (*E*)-alkenes by the reaction of aldehydes and organozinc reagents, using this catalyst in the presence of chlorotrimethylsilane is yet to be reported. In this article, we wish to report our development of an efficient $[CoCl(PPh_3)_3]$ catalyzed olefination reaction that allows the synthesis of (*E*)-alkenes from aldehydes with organozinc reagents under mild conditions.



Scheme 1 Cobalt catalysed olefination

Table 1 Cobalt-Catalyzed Olefination of *n*-$C_8H_{17}ZnI$ with *p*-Methoxybenzaldehyde[a]

Entry	Catalyst	Catalyst (mol%)	Solvent	Temp (°C)	Yield of **3** (%)
1	$[CoCl(PPh_3)_3]$	3.0	THF	r.t.	43
2	$[CoCl(PPh_3)_3]$	3.0	THF	0	56
3	$[CoCl(PPh_3)_3]$	3.0	THF	–18→0	68
4	$[CoCl(PPh_3)_3]$	6.0	THF	–18→0	68
5	$[CoCl(PPh_3)_3]$	1.5	THF	–18→0	45
6	$[CoCl(PPh_3)_3]$	0	THF	–18→0	0
7	$[CoCl(PPh_3)_3]$	3.0	THF	–18→0	38[b]
8	$[CoCl(PPh_3)_3]$	3.0	THF	–18→0	56[c]
9	$[CoCl(PPh_3)_3]$	3.0	DMF	–18→0	60
10	$[CoCl(PPh_3)_3]$	3.0	MeCN	–18→0	52
11	$[CoCl(PPh_3)_3]$	3.0	Et_2O	–18→0	58
12	$[CoCl(PPh_3)_3]$	3.0	C_6H_6	–18→0	42
13	$[CoCl_2(PPh_3)_2]$	3.0	THF	–18→0	54
14	$CoCl_2$	3.0	THF	–18→0	0

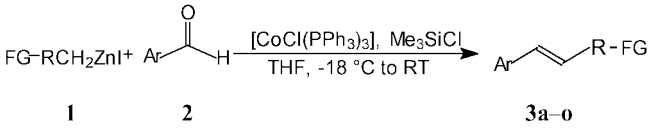
[a] Unless other wise indicated, all reactions were conducted on the following scale: *p*-methoxybenzaldehyde (10 mmol), *n*-C_8H_7ZnI (11 mmol), cobalt catalyst and Me_3SiCl (20 mmol), in solvent (20 mL) for 8 h.
[b] Yield after 3 h.
[c] Yield after 6 h.

Synthesis 2003, No. 10, Print: 21 07 2003.
Art Id.1437-210X,E;2003,0,10,1506,1510,ftx,en;F01403SS.pdf.

To demonstrate this concept, initial experiments examined the reaction of *n*-$C_8H_{17}ZnI$ (1.1 equiv) with *p*-methoxybenzaldehyde in the presence of various cobalt complexes and cobalt salt (Scheme 1). As summarized in Table 1, the (*E*)-1-(*p*-methoxyphenyl)-1-nonene is typical of an effective protocol for the (*E*)-alkene synthesis.

$[CoCl(PPh_3)_3]$ is superior to $[CoCl_2(PPh_3)_2]$ (Table 1, entries 3 and 13). The amount of $[CoCl(PPh_3)_3]$ affected the yield and the use of 3 mol% of the catalyst gave the best results (Table 1, entries 3–5). Further, the solvent influenced the reaction remarkably. When THF, DMF, Et_2O, MeCN and benzene were employed as a solvent, in the reaction of *n*-$C_8H_{17}ZnI$ with *p*-methoxybenzaldehyde in the presence of 3 mol% $[CoCl(PPh_3)_3]$ and Me_3SiCl, the yields of the corresponding (*E*)-alkenes were 68, 60, 58, 52, and 42%, respectively (Table 1, entries 3, and 9–12). THF was found to be the best solvent. We have also investigated the effects of time and temperature on the reaction. It was found the highest yield of (*E*)-1-(*p*-methoxyphenyl)-1-nonylene can be obtained at –18 °C to room temperature for 8 h. When the reactions were conducted with $CoCl_2$ (Table 1, entry 14) and in the absence of $[CoCl(PPh_3)_3]$ and Me_3SiCl (Table 1, entry 6), the reactant aldehyde was recovered in >95%. We have found that this reaction is sensitive to the molecular structure of the aldehydes and ketones. For example, under the same conditions, the use of aliphatic aldehydes, ketones, and aromatic ketones led to several side reactions. The impact of $[CoCl(PPh_3)_3]$ and $[NiCl_2(PPh_3)_2]$[11] as catalysts for the synthesis of compound **3a** has been compared and the results showed that the yield of compound **3a** was 69, and 67%, respectively. The $[CoCl(PPh_3)_3]$ and $[NiCl_2(PPh_3)_2]$ were found to be effective catalysts for the olefination reaction.

In order to define the scope and limitation of this new method for the (*E*)-alkenes synthesis, the reaction of various aldehydes and organozinc reagents in the presence of a silylation agent using $[CoCl(PPh_3)_3]$ as catalyst were examined as shown in Scheme 2 and Table 2. We have also found that the reaction of substituted aromatic aldehydes with alkylzinc iodides in the presence of a catalytic amount of $[CoCl(PPh_3)_3]$ gives the corresponding (*E*)-alkenes in good to excellent yields (56–89%, Table 2, entries 1–15). Various substituents on the phenyl ring, such as methyl, methoxyl, and benzyloxy could be tolerated and had little effect on the yields. Unsaturated aldehydes, such as phenylacrylic aldehyde, reacted similarly and provided the corresponding (1*E*,3*E*)-1-phenyl-1,3-octadiene and (1*E*,3*E*)-1-phenyl-1,3-(6,8,8-trimethyl)nonadiene in excellent isolated yield (Table 2, entries 13 and 14).



1 **2** **3a–o**

Scheme 2 Synthesis of (*E*)-alkenes via alkylzinc reagents with aldehydes

One advantage of this reaction, which makes it a particularly attractive synthetic procedure, is its regiospecificity. The double bond is formed between the carbonyl carbon atom of the aldehyde and the carbon atom of alkylzinc reagent. The reaction is also stereoselective, in all cases only the (*E*)-alkenes were isolated after chromatography.

In the well-studied Wittig reaction, alkenes are usually formed in moderate-to-high yield as a mixture of *E* and *Z* isomers, together with triphenylphosphine oxide as a by-product.[1a] Our experimental results showed that this reaction is highly stereoselective and gives only (*E*)-alkenes selectively.

In summary, a new cobalt catalyzed olefination of alkylzinc reagents with aromatic aldehydes has been developed that allows the synthesis of (*E*)-alkenes. The main advantages of this new method are high stereoselectivity, tolerance to unsaturated bonds and substituents, simple operation, and excellent product yields, all under relatively mild reaction conditions.

^1H NMR spectra were recorded on Bruker AM 400 MHz and Bruker AC-E 200 MHz spectrometers in $CDCl_3$ with TMS as an internal standard. ^{13}C NMR spectra were obtained on a Bruker AM-400 operating at 100 MHz or a Bruker AC-E 200 operating at 50 MHz. IR spectra were recorded on an Alpha Centauri FI-IR spectrometer. Mass spectra were recorded on a HP 5988A instrument. Elemental analyses were carried out on a Carlo Erba-1106 instrument. Purification of products was performed via flash chromatography with 200–400 mesh silica gel [petroleum ether (bp 60–90 ºC)–Et_2O, 10:1]. All substrates and reagents were obtained commercially except RZnI and $[COCl(PPh_3)_3]$ which were prepared by standard procedures. THF was distilled from sodium–benzophenone. The stereochemistry of the product olefins were determined by comparison of the ^1H NMR spectrum with that reported in the literature and GC/MS analyses on a VG 7070E instrument.

Olefins 3; Typical Procedure

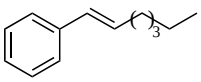
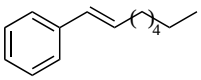
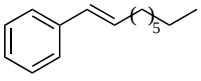
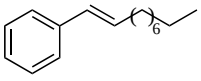
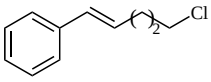
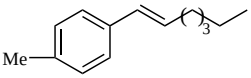
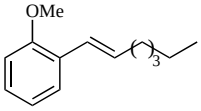
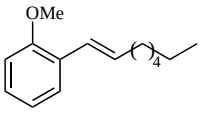
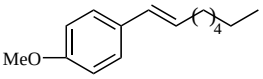
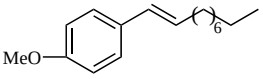
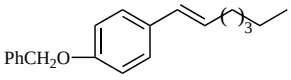
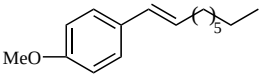
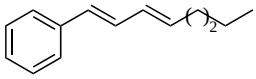
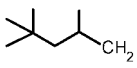
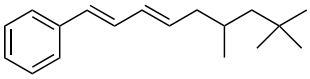
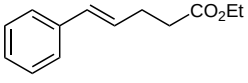
Under an argon atmosphere, a mixture of zinc dust (0.85 g, 13 mmol), 1,2-dibromoethane (0.19 g, 1.0 mmol) and THF (2 mL) in a three-necked flask was heated to 60–70 °C for 2–3 min and then cooled to r.t. Chlortrimethylsilane (0.1 mL) was added, and the mixture was stirred at r.t. for 15 min. A solution of RI (12 mmol) in THF (10 mL) was then added, and the mixture was stirred for 12 h at 35 °C. The resulting solution of RZnI in THF was ready to use. In another three-neck flask, $[COCl(PPh_3)_3]$ (0.27 g, 0.3 mmol) and THF (2 mL) were added and heated at 60 °C for 2 min. The solution of RZnI in THF obtained above was added at r.t., and the resulting mixture was cooled to –18 °C. A solution of aldehyde (10 mmol), TMSCl (20 mmol) and THF (10 mL) was added in a few minutes and the temperature was allowed to rise to r.t. After stirring for 12 h, sat. aq NH_4Cl (10 mL), and Et_2O (10 mL) were added and the mixture was stirred for 10 min. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated. The produce was isolated from the crude reaction mixture by chromatography (silica gel; petroleum ether–EtOAc).

(*E*)-1-Phenyl-1-heptene (3a)

Oil.[12]

IR: 3057, 3026, 2959, 2928, 2856, 1655, 1599, 1493, 1462, 964, 740, 692 cm^{-1}.

Table 2 Cobalt(I) Complex Catalyzed Synthesis of (*E*)-Alkenes

Entry	Ar	R-FG	Product[a]		Yield[b] (%)
1	Ph	*n*-C_5H_{11}		**3a**	69
2	Ph	*n*-C_6H_{13}		**3b**	68
3	Ph	*n*-C_7H_{15}		**3c**	67
4	Ph	*n*-C_8H_{17}		**3d**	64
5	Ph	$Cl(CH_2)_3$		**3e**	67
6	4-Me (C_6H_4)	*n*-C_5H_{11}		**3f**	74
7	2-MeO(C_6H_4)	*n*-C_5H_{11}		**3g**	58
8	2-MeO(C_6H_4)	*n*-C_6H_{13}		**3h**	56
9	4-MeO(C_6H_4)	*n*-C_6H_{13}		**3i**	74
10	4-MeO(C_6H_4)	*n*-C_8H_{17}		**3j**	68
11	4-$PhCH_2O$(C_6H_4)	*n*-C_5H_{11}		**3k**	89
12	4-MeO(C_6H_4)	*n*-C_7H_{15}		**3l**	68
13	$PhCH=CH_2$	*n*-C_4H_9		**3m**	65
14	$PhCH=CH_2$			**3n**	56
15	Ph	EtO_2CCH_2		**3o**	65

[a] *E*/*Z* ratios of isolated all products are 100:0.
[b] Isolated yield.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.18–7.39 (m, 5 H), 6.44 (d, 1 H, *J* = 16.0 Hz), 6.30 (dt, 1 H, *J* = 16.0 Hz), 2.05–2.41 (m, 2 H), 1.24–1.45 (m, 6 H), 0.91 (t, 3 H, *J* = 7.4 Hz).

EI-MS: *m*/*z* = 174 (M^+, 4.2), 117 (100), 104 (61).

(*E*)-1-Phenyl-1-octene (3b)
Oil.[13]

IR: 3059, 3025, 2956, 2925, 2854, 1650, 1598, 1494, 1462, 1377, 1297, 1256, 1209, 1172, 1069, 963, 844, 741, 692 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.17–7.37 (m, 5 H), 6.43 (d, 1 H, *J* = 15.8 Hz), 6.27 (dt, 1 H, *J* = 15.8 Hz), 2.15 (q, 2 H, *J* = 5.8 Hz), 1.27–1.44 (m, 8 H), 0.89 (t, 3 H, *J* = 6.6 Hz).

EI-MS: *m*/*z* = 188 (M^+, 20.8), 129 (6.0), 117 (100), 104 (86.2), 91 (52.1), 77 (11.1).

(*E*)-1-Phenyl-1-nonene (3c)
Oil.[14]

IR: 3058, 3021, 2955, 2925, 2855, 1644, 1597, 1492, 1457, 1374, 986, 745, 692 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.10–7.38 (m, 5 H), 6.28 (d, 1 H, *J* = 15.8 Hz), 6.10 (dt, 1 H, *J* = 15.8 Hz), 2.19 (q, 2 H, *J* = 7.0 Hz), 1.05–1.60 (m, 10 H), 0.88 (t, 3 H, *J* = 6.6 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, TMS): δ = 137.9, 131.1, 129.7, 128.4, 126.6, 125.8, 33.0, 31.8, 29.4, 29.3, 29.2 22.6, 14.0.

EI-MS: *m*/*z* = 202 (M^+, 10.4), 131 (3.7), 117 (9.9), 104 (100), 91 (45.4), 77 (9.7).

(*E*)-1-Phenyl-1-decene (3d)
Oil.[15]

IR: 3061, 3026, 2956, 2924, 2853, 1601, 1493, 1461, 1377, 1303, 1161, 1028, 963, 742, 697 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.08–7.24 (m, 5 H), 6.38 (d, 1 H, *J* = 16.0 Hz), 6.10 (dt, 1 H, *J* = 16.0, 7.0 Hz), 2.19 (q, 2 H, *J* = 7.0 Hz), 1.10–1.60 (m, 12 H), 0.90 (t, 3 H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, TMS): δ = 137.9, 131.2, 129.7, 128.3, 126.7, 125.9, 33.0, 31.9, 29.4, 29.3, 29.1, 29.2, 22.6, 14.0.

EI-MS: *m*/*z* = 216 (M^+, 8.2), 117 (65.3), 115 (24.5), 104 (100), 91 (30.8), 77 (4.7).

(*E*)-1-Phenyl-5-chloro-1-pentene (3e)
Oil.[16]

IR: 3060, 3035, 2938, 2860, 2841, 1648, 1591, 1556, 1469, 1441, 966, 750, 694, 651 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.17–7.37 (m, 5 H), 6.44 (d, 1 H, *J* = 16 Hz), 6.16 (dt, 1 H *J* = 16.0, 6.8 Hz), 3.57 (t, 2 H, *J* = 6.4 Hz), 2.37 (q, 2 H, *J* = 7.4 Hz), 1.62–1.92 (m, 2 H).

^{13}C NMR ($CDCl_3$, 50 MHz, TMS): δ = 137.4, 131.2, 128.6, 128.5, 128.3, 127.1, 126.1, 126.0, 44.3, 32.5, 29.7.

EI-MS: *m*/*z* = 182 (M^+ + 2, 1), 180 (M^+, 2), 117 (100).

(*E*)-1-(4-Methylphenyl)-1-heptene (3f)
Oil.[17]

IR: 3021, 2956, 2925, 2855, 1652, 1612, 1512, 1464, 1378, 1305, 1209, 1175, 1106, 1039, 965, 824, 791, 726, 516 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.22 (d, 2 H, *J* = 8.2 Hz), 7.08 (d, 2 H, *J* = 8.1 Hz), 6.34 (d, 1 H, *J* = 15.8 Hz), 6.14 (dt, 1 H, *J* = 15.8, 6.8 Hz), 2.30 (s, 3 H), 2.11–2.20 (m, 2H), 1.28–1.54 (m, 6 H), 0.94 (t, 3 H, *J* = 7.4 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, TMS): δ = 136.3, 135.2, 129.8, 129.7, 129.2, 129.1, 125.3, 35.1, 31.5, 22.6, 21.2, 13.9.

EI-MS: *m*/*z* = 188 (M^+, 16), 143 (4), 131 (100), 118 (46), 115 (24), 105 (16), 91 (32), 77 (9).

(*E*)-1-(2-Methoxyphenyl)-1-heptene (3g)
Oil.[18]

IR: 2925, 2854, 1597, 1489, 1461, 1438, 1291, 1243, 1178, 1104, 1031, 970, 844 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.43 (dd, 1 H, *J* = 7.8, 1.8 Hz), 7.17 (qd, 1 H, *J* = 8.6, 1.8 Hz), 6.88 (qd, 2 H, *J* = 7.4, 1.1 Hz), 6.71 (d, 1 H, *J* = 15.8 Hz), 6.31 (dt, 1 H, *J* = 16.0, 6.8 Hz), 3.87 (s, 3 H), 2.22 (q, 2 H, *J* = 6.8 Hz), 1.45–1.53 (m, 2 H), 1.30 (br s, 4 H), 0.92 (t, 3 H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, TMS): δ = 156.2, 131.9, 127.7, 127.0, 126.3, 124.1, 120.6, 110.7, 55.4, 33.5, 31.8, 29.5, 22.6, 14.1.

EI-MS: *m*/*z* = 204 (M^+, 99), 147 (100), 134 (66), 121, (65), 91 (95), 77 (11).

(*E*)-1-(2-Methoxyphenyl)-1-octene (3h)
Oil.

IR: 3032, 2955, 2925, 2854, 1647, 1597, 1579, 1489, 1462, 1437, 1377, 1290, 1243, 1177, 1104, 1053, 1031, 971, 844, 749, 579.0 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.44 (dd, 1 H, *J* = 7.6, 1.8 Hz), 7.18 (qdd, 1 H, *J* = 8.0, 1.8, 0.4 Hz), 6.86 (qdd, 2 H, *J* = 7.6, 1.0, 0.4 Hz), 6.72 (d, 1 H, *J* = 16.0 Hz), 6.31 (dt, 1 H, *J* = 16.0, 6.8 Hz), 3.83 (s, 3 H), 2.24 (qd, 2 H, *J* = 6.8, 1.2 Hz), 1.16–1.63 (m, 8 H), 0.89 (t, 3 H, *J* = 7.4 Hz).

EI-MS: *m*/*z* = 218 (M^+, 68), 147 (100), 134 (34), 121, (35), 91 (41), 77 (14).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.43; H, 10.37.

(*E*)-1-(4-Methoxyphenyl)-1-octene (3i)
Oil.[19]

IR: 2926, 2854, 1610, 1584, 1511, 1463, 1382, 1345, 1247, 1175, 1098, 1039, 964, 831, 723 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.17–7.32 (m, 4 H), 6.35 (d, 1 H, *J* = 15.8 Hz), 6.12 (dt, 1 H, *J* = 15.8, 6.6 Hz), 3.81 (s, 3 H), 2.20 (q, 2 H, *J* = 6.6 Hz), 1.10–1.41 (m, 8 H), 0.92 (t, 3 H, *J* = 6.4 Hz).

EI-MS: *m*/*z* = 218 (M^+, 6.9), 147 (100), 134 (34), 121, (35), 91 (41), 77 (14).

(*E*)-1-(4-Methoxyphenyl)-1-decene (3j)
Oil.[20]

IR: 2927, 2855, 1610, 1511, 1465, 1370, 1301, 1240, 1174, 1090, 1040, 964, 831, 723, 574 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.24 (dd, 2 H, *J* = 13.4, 6.8 Hz), 6.86 (t, 2 H, *J* = 8.2 Hz,), 6.35 (d, 1 H, *J* = 15.8 Hz), 6.12 (dt, 1 H, *J* = 15.8, 6.6 Hz), 3.81 (s, 3 H), 3.17–3.35 (m, 2 H), 1.45–1.88 (m, 2 H), 1.27 (br s 10 H), 0.92 (t, 3 H, *J* = 6.4 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, TMS): δ = 158.7, 135.4, 128.9, 128.1, 127.7, 113.5, 55.1, 33.0, 31.8, 29.5, 29.4, 29.3, 29.2, 22.6, 14.0.

EI-MS: *m*/*z* = 247 (M^+ + 1, 3), 246 (M^+, 11), 159 (2), 147 (100), 134 (22), 121, (51), 91 (24), 77 (9).

(*E*)-1-(4-Benzyloxyphenyl)-1-heptene (3k)
Oil.

IR: 3035, 2828, 2742, 1689, 1601, 1573, 1505, 1455, 1424, 1391, 1304, 1257, 1219, 1161, 1110, 1021, 942, 906, 862, 826, 734, 694, 651, 513 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.32–7.45 (m, 4 H), 7.26 (dt, 3 H, *J* = 8.8, 2.8 Hz,), 6.89 (dt, 2 H, *J* = 8.8, 2.8), 6.31 (d, 1 H, *J* = 15.8 Hz), 6.06 (dt, 1 H, *J* = 15.8, 6.8 Hz), 5.04 (s, 2 H), 2.17 (q, 2 H, *J* = 6.6 Hz,), 1.40–1.51 (m, 2 H), 1.29 (br s, 4 H), 0.89 (t, 3 H, *J* = 6.2 Hz).

EI-MS: *m*/*z* = 280 (M^+, 7), 225 (2), 198, (2), 121 (5), 91 (100), 77, (5), 65 (8), 57 (3), 43 (4).

Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.78; H, 8.82.

(*E*)-1-(4-Methoxyphenyl)-1-nonene (3l)
Oil.[21]

IR: 2927, 2855, 1618, 1511, 1465, 1370, 1301, 1240, 1174, 1098, 1040, 964, 831, 723, 574 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.23 (dt, 2 H, *J* = 8.2, 2.0 Hz), 6.86 (t, 2 H *J* = 8.4 Hz), 6.28 (d, 1 H, *J* = 15.8 Hz), 6.02 (dt, 1 H, *J* = 15.8, 7.2 Hz), 3.81 (s, 3 H), 2.17 (q, 2 H, *J* = 6.6 Hz), 1.08–1.41 (m, 10 H), 0.89 (t, 3 H, *J* = 6.4 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, TMS): δ = 158.7, 135.4, 128.9, 128.1, 127.7, 113.5, 55.1, 33.0, 31.8, 29.5, 29.4, 29.2, 22.6, 14.0.

EI-MS: *m*/*z* = 232 (M^+, 17.5), 147 (100), 134 (22.5), 121, (46.8), 91 (24), 77 (7.0).

(1*E*,3*E*)-1-Phenyl-1,3-octadiene (3m)
Oil.[22]

IR: 3058, 3021, 2956, 2925, 2861, 1681, 1640, 1597, 1547, 1491, 1454, 1371, 1298, 1117, 1073, 1024, 986, 744, 691, 666, 617, 506 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.22–7.48 (m, 5 H), 6.83 (dd, 1 H, *J* = 15.6, 10.2 Hz), 6.55 (t, 1 H, *J* = 15.6 Hz), 6.28 (dd, 1 H, *J* = 15.1, 10.2 Hz), 5.90 (dt, 1 H, *J* = 15.2, 7.0 Hz), 2.22 (q, 2 H, *J* = 6.4 Hz), 1.41–1.50 (m, 4 H), 0.89 (t, 3 H, *J* = 6.6 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz, TMS): δ = 137.7, 135.9, 130.5, 129.9, 129.4, 128.5, 127.0, 126.1, 32.6, 31.4, 22.2, 13.9.

EI-MS: *m*/*z* = 187 (M^+ + 1, 3), 186 (M^+, 19), 157 (2), 143 (43), 131 (13), 129 (100), 115 (31), 104 (11), 91 (26), 77 (11).

(1*E*,3*E*)-1-Phenyl-1,3-(6,8,8-trimethyl)nonadiene (3n)
Oil.

IR: 3059, 3022, 2954, 2867, 1681, 1596, 1493, 1465, 1363, 1245, 1199, 1124, 1070, 986, 902, 744, 691, 621, 566, 504 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.19–7.45 (m, 5 H), 6.82 (dd, 1 H, *J* = 16.8, 10.2 Hz), 6.53 (t, 1 H, *J* = 16.8 Hz), 6.25 (dd, 1 H, *J* = 15.2, 10.2 Hz), 5.83 (dt, 1 H, *J* = 15.0, 7.0 Hz), 1.95–2.30 (m, 2 H), 1.62–1.78 (m, 1 H), 1.06–1.40 (m, 2 H), 0.91–1.04 (m, 12 H).

^{13}C NMR ($CDCl_3$, 50 MHz, TMS): δ = 137.6, 134.7, 131.7, 129.9, 129.4, 128.5, 127.0, 126.1, 50.5, 43.1, 31.1, 30.0, 22.5, 21.7.

EI-MS: *m*/*z* = 242 (M^+, 5), 197 (2), 183 (1), 169 (1), 157 (1), 143 (47), 128 (28), 117 (7), 104 (2), 91 (13), 77 (5), 57 (100), 41 (57).

Anal. Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 89.07; H, 10.75.

(*E*)-4-Phenyl-3-ethylcrotonate (3o)
Oil.[23]

IR: 3449, 2981, 2939, 2874, 1736, 1606, 1451, 1421, 1374, 1350, 1251, 1180, 1032, 919, 861, 750, 704 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz, TMS): δ = 7.17–7.39 (m, 5 H), 6.45 (d, 1 H, *J* = 15.8 Hz), 6.10 (dt, 1 H, *J* = 10.0, 7.0 Hz), 4.14 (q, 2 H, *J* = 7.2 Hz), 3.17–3.32 (m, 2 H), 1.22 (t, 3 H, *J* = 7.0 Hz).

EI-MS: *m*/*z* = 190 (M^+, 19), 177 (2), 117 (100), 105 (21), 91 (23), 77 (16).

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No.20272047) and the Northwest Normal University Science and Technology Development Foundation of China (KJCXGC-04).

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