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Synthesis of α-Cyanocinnamaldehydes from Acrylonitrile and Benzaldehydes Catalyzed by $Pd(OAc)_2/HPMoV/FeCl_3/O_2$ System

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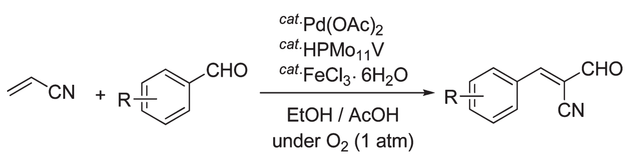


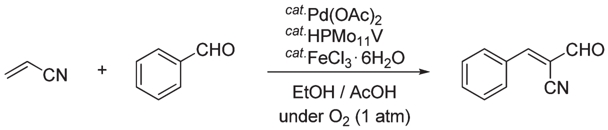
A facile direct synthesis of (*E*)-α-cyanocinnamaldehydes from acrylonitrile and benzaldehydes is successfully achieved in a mixed solvent of EtOH/AcOH by $Pd(OAc)_2$/HPMoV/$FeCl_3$/O_2 catalyst system. The reaction was found to proceed via the cross-aldol condensation of diethyl acetal derived from acrylonitrile with aldehydes.

Compounds including cyanoaldehyde moieties are widely used as precursors of pharmaceuticals, heterocyclic compounds, and biologically active molecules.[1] Especially, (*E*)-α-cyanocinnamic aldehydes are important building blocks for the construction of various *N*-heterocyclic molecules.[2] There have been several reports on the synthesis of (*E*)-α-cyanocinnamic aldehydes.[3] For example, Basavaiah et al. reported the synthesis of (*E*)-α-cyanocinnamaldehydes by the oxidation of the corresponding allylic alcohols derived from the Baylis−Hillman adducts.[3a] Yoshimatsu et al. prepared the same compound, (*E*)-2-cyano-3-phenylprop-2-enal, by α-cyanoformylation of carbonyl compounds using α-lithio-*β*-ethoxyacrylonitrile obtained by lithiation of *β*-ethoxyacrylonitrile.[3b] The reaction of benzaldehyde with 3,3-dimethoxypropionitrile under NaOMe followed by deprotection of the methoxy group with hydrochloric acid is reported to lead to (*E*)-α-cyanocinnamaldehydes.[3c] Direct access to (*E*)-α-cyanocinnamaldehydes from cheap and readily available benzaldehydes and acrylonitrile represents a technically simple and unexplored alternative to the existing approaches.

The reaction of acrylonitrile with benzaldehyde under potassium hydroxide has been examined by Wasserman et al., but desired (*E*)-α-cyanocinnamaldehyde was formed in a low yield as a minor component of products.[4] Therefore, this method is not used for the purpose obtaining this compound.

Quite recently, we reported that the reaction of acrylates with aldehydes in the presence of catalytic amounts of Pd(II), $H_4PMo_{11}VO_{40}$ ($HPMo_{11}V$), and $CeCl_3$ in a mixed solvent of methanol and acetic acid under dioxygen produced substituted furoates in substantial yields.[5] During the course of this study, the reaction of acrylonitrile (**1**) with aldehydes (**2**) like benzaldehyde (**2a**) was found to bring about the exclusive formation of (*E*)-α-cyanocinnamaldehyde **3a** in good yield. In this paper, we report a facile direct synthesis of (*E*)-α-cyanocinnamaldehydes (**3**) from acrylonitrile (**1**) and several benzaldehydes.

The reaction of **1** with **2a** was chosen as a model reaction and was carried out under the influence of catalytic amounts of Pd(II), $H_4PMo_{11}VO_{40}\cdot 13H_2O$ ($HPMo_{11}V$), and Lewis acid under various conditions (eq 1 and Table 1).



1 **2a** **3a** (1)

In a previous reaction of acrylates with aldehydes,[5] we showed that furoates are obtained in good yields by using a combined catalytic system consisting of $Pd(OAc)_2$, $HPMo_{11}V$, and $CeCl_3$. Thus, we first tried the reaction using the same catalytic system. Namely, the reaction of **1** (2 mmol) with **2a** (10 mmol) under O_2 (1 atm) in the presence of $Pd(OAc)_2$ (0.1 mmol), $HPMo_{11}V$ (35 mg, ca. 17 μmol), and $CeCl_3\cdot 7H_2O$ (0.5 mmol) at 90 °C for 8 h was run, but **3a** was formed in poor yield (7%) (entry 1). To improve the yield of **3a**, the effect of several Lewis acids such as $AlCl_3$, $ZrCl_4$, $GdCl_3$, and $Gd(OTf)_3$ was investigated under these reaction conditions (entries 2−5). By the use of these Lewis acids, however, **3a** was not formed, and a complex mixture of polymeric products derived from **1** was observed. A protic acid (*p*-TsOH) was also ineffective (entry 6). Among the Lewis acids examined, $FeCl_3\cdot 6H_2O$ was found to be the best additive. The reaction using $FeCl_3$ under several conditions is shown in entries 7−9. The yield of **3a** was found to be markedly improved by excess use of **2a** to **1**. When 5 or 10 equiv of **2a** was used with respect to **1**, the desired product **3a** was obtained in 88 or >99%, respectively (entries 8 and 9). When the amount of $FeCl_3$ was reduced to 0.2 mmol, the

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TABLE 1. Reaction of Acrylonitrile (1) with Benzaldehyde (2a) by Pd(II)/HPMo$_{11}$V/FeCl$_3$/O$_2$ System under Various Conditions[a]

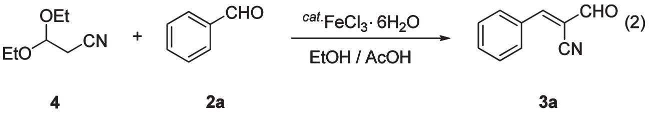
entry	Pd(II)	**2a** (equiv)	Lewis acid	conv/%[b]	yield of **3a**/%[b]
1	Pd(OAc)$_2$	5	CeCl$_3$·7H$_2$O	37	7
2	Pd(OAc)$_2$	5	AlCl$_3$	>99	[c]
3	Pd(OAc)$_2$	5	GdCl$_3$·6H$_2$O	>99	[c]
4	Pd(OAc)$_2$	5	ZrCl$_4$	>99	[c]
5	Pd(OAc)$_2$	5	Gd(OTf)$_3$	>99	[c]
6	Pd(OAc)$_2$	5	*p*-TsOH	>99	[c]
7	Pd(OAc)$_2$	2	FeCl$_3$·6H$_2$O	98	36
8	Pd(OAc)$_2$	5	FeCl$_3$·6H$_2$O	>99	83
9	Pd(OAc)$_2$	10	FeCl$_3$·6H$_2$O	>99	>99 (85)
10[d]	Pd(OAc)$_2$	10	FeCl$_3$·6H$_2$O	92	78
11	Pd(acac)$_2$	5	FeCl$_3$·6H$_2$O	98	83
12	Pd(dba)$_2$	5	FeCl$_3$·6H$_2$O	97	53
13	PdCl$_2$	5	FeCl$_3$·6H$_2$O	95	77
14[e]	$^{5wt\%}$Pd/C	5	FeCl$_3$·6H$_2$O	43	22
15[f]	Pd(OAc)$_2$	5	FeCl$_3$·6H$_2$O	76	57
16[g]	Pd(OAc)$_2$	5	FeCl$_3$·6H$_2$O	98	83
17	Pd(OAc)$_2$	5	none	>99	[c]

[a] **1** (2 mmol) was reacted with **2a** in the presence of Pd(II) (0.1 mmol), HPMo$_{11}$V (35 mg, ca. 17 μmol), FeCl$_3$·6H$_2$O (0.5 mmol), in EtOH (1 mL)/AcOH (5 mL) at 90 °C for 8 h. [b] Based on **1** used. Number in parentheses shows isolated yield. [c] Not detected by GC. [d] FeCl$_3$·6H$_2$O (0.2 mmol) was used. [e] Pd/C (5 wt %, 213 mg) was used. [f] Reaction was performed at 70 °C. [g] Reaction time was 6 h.

yield of **3a** was still high (78%) (entry 10). To examine the catalytic performance of palladium species, several palladium catalysts were examined. The reaction using Pd(acac)$_2$ produced **3a** in almost the same yield as Pd(OAc)$_2$ (entry 11), while Pd(dba)$_2$ (dba: dibenzylideneacetone), PdCl$_2$, and Pd/C afforded **3a** in 53, 77, and 22% yields, respectively (entries 12−14). From these results, the Pd(OAc)$_2$ combined with FeCl$_3$ was found to induce the selective coupling of **1** with **2a** leading to **3a** in high yield.

The reaction at lower temperature (70 °C) resulted in a considerable decrease of **3a** (57%) (entry 15). In absence of Lewis acid, no coupling product **3a** was obtained, although the formation of a small amount of 3,3-diethoxypropionitrile (**4**) was observed (entry 17). In a previous paper, we reported that acrylonitrile **1** undergoes efficient acetalization with ethanol by Pd(OAc)$_2$ in the presence of molybdovanadophosphate to form 3,3-diethoxypropionitrile (**4**) in good yield.[6] In the present reaction, it is reasonable to assume that the acetalization of **1** with ethanol is initiated by Pd(OAc)$_2$ and HPMo$_{11}$V and then the resulting acetal **4** reacts with **2a** under the influence of FeCl$_3$ to give **3a**.

Thus, an independent reaction of **4** with **2a** in the presence of several Lewis acids was examined in a mixed solvent of acetic acid and ethanol under conditions (eq 2) (Table 2).



(2)

4 2a 3a

TABLE 2. Reaction of 3,3-Diethoxypropionitrile (4) with Benzaldehyde (2a) by FeCl$_3$ under Various Conditions[a]

entry	Lewis acid	**2a** (equiv)	yield of **3a**/%[b]
1[c]	FeCl$_3$	1	47
2	FeCl$_3$	1	36
3	FeCl$_3$	2	59
4	FeCl$_3$	5	>99
5	CeCl$_3$	1	14
6	CeCl$_3$	2	27
7	GdCl$_3$	1	16
8	GdCl$_3$	2	29
9	Gd(OTf)$_3$	1	10
10	Gd(OTf)$_3$	2	19
11	AlCl$_3$	1	38
12	AlCl$_3$	2	79

[a] **4** (2 mmol) was reacted with **2a** under the influence of FeCl$_3$·6H$_2$O (0.5 mmol, 25 mol %), in EtOH (1 mL)/AcOH(5 mL) at 90 °C for 8 h. [b] Based on **4** used. [c] AcOH (5 mL) was employed.

A stoichiometric reaction of **2a** with **4** in the presence of FeCl$_3$ in acetic acid or in a mixed solvent of ethanol and acetic acid gave **3a** in 47 and 36% yields, respectively (entries 1 and 2). When 2 equiv of **2a** toward **4** was employed, the yield of **3a** increased to 59% (entry 3). As expected, **3a** was obtained in quantitative yield by the use of 5 equiv of **2a** (entry 4). The reaction of **2a** with **4** was prompted to some extent by lanthanoid Lewis acids such as CeCl$_3$, GdCl$_3$, and Gd(OTf)$_3$ to give **3a** in low yields (entries 5−10). It is interesting to note that the reaction using AlCl$_3$ led to **3a** in relatively good yields (entries 11 and 12), although the direct reaction of **1** with **2a** by Pd(OAc)$_2$/HPMo$_{11}$V/AlCl$_3$ system produced only polymeric products, as shown in entry 2 in Table 1. This indicates that AlCl$_3$ may inhibit the acetalization of **1** with ethanol by Pd(OAc)$_2$/HPMo$_{11}$V.

The rate of reaction of **2a** with **1** was compared with that of **2a** with **4** to obtain insight on the present reaction. Figure 1 shows the time dependence curves of the reaction of **2a** with **1** or **4**. At an early stage of the reaction, it was found that **3a** is formed faster from **2a** and **4** (Figure 1, curve A) than from **2a** and **1** (Figure 1, curve B). After an induction period of about 0.5 h, the reaction of **2a** with **1** was found to progress in almost the same rate as that of **2a** with **4**. Therefore, the induction time observed here may correspond to the time needed for the generation of an active Pd species which promotes the acetalization of **1** with ethanol in the reaction system. This observation also indicates that the acetalization of **1** with ethanol takes place faster or at a comparable rate to that of the coupling of **2a** with **4** under the reaction conditions. Therefore, it may be concluded that excess aldehyde must be used to prevent the polymerization as well as the degradation of acetal **4** by the catalysts employed.

On the basis of these results, the reaction of **1** with several aldehydes was examined and the result is shown in Table 3.

The reaction of **1** with 4-chlolobenzaldehyde (**2b**) and 4-methoxybenzaldehyde (**2c**) gave rise to the corresponding cyanoaldehydes, **3b** and **3c**, in quantitative yields (entries 1 and 2). In the reaction with 4-cyanobenzaldehyde (**2d**) bearing an electron-withdrawing group, however, the yield of 2-formyl-3-(4-cyanophenyl)-2-propenenitrile (**3d**) decreased considerably (entry 3). The reaction with 2-furaldehyde led to (*E*)-2-formyl-3-(2-furyl)acrylonitrile (**3e**) in moderate yield (59%) (entry 4). For the reaction of **1** with cinnamaldehyde (**2f**), (2*E*,4*E*)-2-formyl-5-phenylpenta-2,4-dienenitrile (**3f**) was obtained in high yield (95%) (entry 5). The reaction with 2-naphthaldehyde (**2g**) gave the corresponding cyanoaldehyde (**3g**) in fair yield (entry 6). A striking features of the present condensation is that the reaction takes place stereoselectively to afford (*E*)-cinnamaldehyde, exclusively.

Unfortunately, the reaction of **1** with aliphatic aldehydes like butyraldehyde afforded a complex mixture due to the self-condensation of aldehyde itself.

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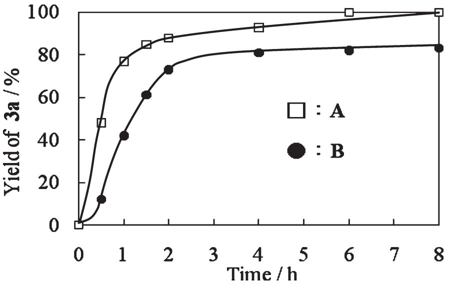
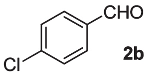
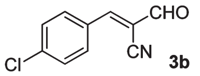
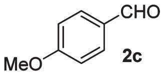
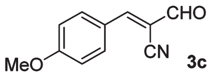
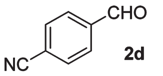
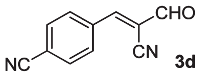
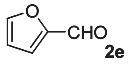
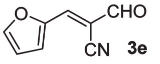
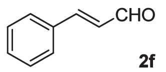
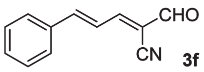
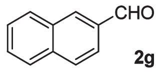
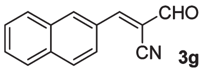


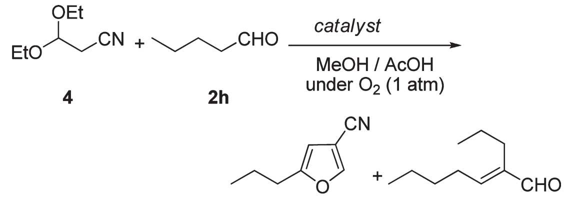
FIGURE 1. Time dependence curve for the formation of **3a**. (A) Reaction of **2a** with **4** under the conditions shown in entry 4, Table 2. (B) Reaction of **1** with **2a** under the conditions shown in entry 8, Table 1.

TABLE 3. Reaction of 1 with Aldehydes (2) by Pd(II)/HPMo$_{11}$V/FeCl$_3$/O$_2$ System[a]

Entry	Aldehyde (**2**)	Conv. (%)[b]	Product (**3**)	Yield (%)[c]
1	 **2b**	>99	 **3b**	>99 (86)
2	 **2c**	>99	 **3c**	>99 (90)
3	 **2d**	97	 **3d**	36 (30)
4	 **2e**	97	 **3e**	59 (55)
5[d]	 **2f**	97	 **3f**	(95)
6	 **2g**	94	 **3g**	63 (55)

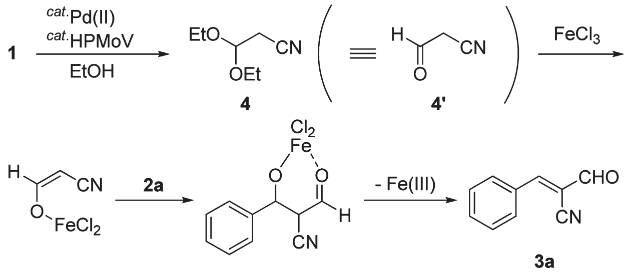
[a] **1** (2 mmol) was reacted with **2** (10 equiv), Pd(OAc)$_2$ (0.1 mmol, 5 mol %), HPMoV (35 mg, ca. 17 μmol), FeCl$_3$·6H$_2$O (0.5 mmol, 40 mol %), in EtOH (1 mL)/AcOH (5 mL) at 90 °C for 8 h. [b] Based on **1** used. [c] Based on **1** used. Numbers in parentheses show isolated yields. [d] *trans*-Cinnamaldehyde (5 equiv) was used.

SCHEME 1. Reaction of 4 with 2h



catalyst	3h	3h'
$^{cat.}$FeCl$_3$·6H$_2$O	24%	14%
$^{cat.}$Pd(OAc)$_2$/HPMo$_{11}$V/FeCl$_3$·6H$_2$O	50%	10%

SCHEME 2. Plausible Reaction Path for the Reaction of Acrylonitrile with Aldehyde by Pd(OAc)$_2$/HPMoV/FeCl$_3$ under O$_2$



In contrast, the reaction of acetal **4** with aliphatic aldehydes like valeraldehyde (**2h**) in the presence of FeCl$_3$·6H$_2$O was found to give 5-propyl-3-cyanofuran (**3h**) in low yield (24%) along with self-condensation product (*E*)-2-propylhept-2-enal (**3h′**) (14%) (Scheme 1). The yield of the product **3h** was increased to 50% by using Pd(OAc)$_2$/HPMo$_{11}$V/FeCl$_3$·6H$_2$O catalyst system. It is difficult to explain clearly the reaction pathway for the formation of **3h**, but the Pd species is an important component for the formation of **3h**, as we previously reported the formation of furoates from acrylates with aldehydes by Pd(OAc)$_2$/HPMoV/CeCl$_3$ system.[5]

A plausible reaction path for the formation of **3a** from **1** and **2a** is shown in Scheme 2. First, **1** undergoes the acetalization with ethanol by palladium catalyst to give acetal **4** on which subsequent aldol-type condensation with **2a** by FeCl$_3$ affords an α,β-unsaturated carbonyl condensate **3a**. Finally, the reduced Pd(0) was reoxidized to Pd(II) by the action of HPMo$_{11}$V/O$_2$ reoxidation system as reported previously.[7]

In conclusion, we have developed a direct route to cyanocinnamic aldehydes (**3**) from acryronitrile (**1**) and aldehydes (**2**) in the presence of catalytic amounts of Pd(II), HPMo$_{11}$V, and FeCl$_3$ under O$_2$. The reaction was found to proceed via the cross-aldol condensation of aldehydes with diethyl acetal **4** derived from acryronitrile. This method provides the direct route to various aromatic cyanoaldehydes which are difficult to obtain by conventional reactions.

Experimental Section

Compounds **3a**,[3,8] **3b**,[3a,d,8] **3c**,[8] **3d**,[9] **3e**,[3c] **3g**,[3c] and **3h′**[10] were reported previously. Heteropolyacid H$_4$PMo$_{11}$VO$_{40}$·13H$_2$O (HPMo$_{11}$V) was prepared according to a literature procedure.[11] The conversions and yields of products were estimated by GC from the peak areas, based on an internal standard technique using dimethyl adipate as standard.

Typical Procedure for Reaction of 1 with 2a (Table 1, entry 3): To a solution of Pd(OAc)$_2$ (22 mg, 0.1 mmol, 5 mol %), H$_4$PMo$_{11}$VO$_{40}$·13H$_2$O (HPMo$_{11}$V) (35 mg, 17 μmol, 0.85 mol %), and FeCl$_3$·6H$_2$O (135 mg, 0.5 mmol, 25 mol %) in EtOH (1.0 mL) were added **1** (106 mg, 2 mmol), **2a** (2.12 g, 20 mmol),

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and AcOH (5 mL), and the mixture was stirred at 90 °C for 8 h under O_2 (1 atm, balloon). After the reaction, GC and GC−MS analyses were performed. Solvents were removed under reduced pressure. The residue was then neutralized with sodium bicarbonate and extracted with ethyl acetate (50 mL). After concentration, the crude product was purified by column chromatography (silica gel, hexane/ethyl acetate = 5/1), and (*E*)-α-cyanocinnamaldehyde (**3a**) was isolated as a yellow solid.

Reaction of 3,3-Diethoxypropionitrile (4) with Benzaldehyde (2a) in the Presence of $FeCl_3$ (eq 2): To a solution of $FeCl_3\cdot 6H_2O$ (135 mg, 0.5 mmol, 25 mol %) in a solvent of ethanol (1.0 mL) were added **4** (286 mg, 2 mmol), **2a** (1.06 g, 10 mmol), and acetic acid (5 mL), and the mixture was stirred at 90 °C for 8 h. GC and GC−MS analyses of the reaction mixture showed that **3a** was formed in quantitative yield.

Reaction of 3,3-Diethoxypropionitrile (4) with Valeraldehyde (2h) in the Presence of $Pd(OAc)_2$, HPMoV, and $FeCl_3$ (Scheme 1): To a solution of $Pd(OAc)_2$ (11 mg, 0.05 mmol, 5 mol %), $H_4PMo_{11}VO_{40}\cdot 13H_2O$ ($HPMo_{11}V$) (17.5 mg, 8.5 μmol, 0.85 mol %), and $FeCl_3\cdot 6H_2O$ (67.5 mg, 0.25 mmol, 25 mol %) in methanol (1.0 mL) were added **4** (143 mg, 1 mmol), **2h** (861 mg, 10 mmol), and acetic acid (2.5 mL), and the mixture was stirred at 70 °C for 15 h under O_2 (1 atm, balloon). After the reaction, GC and GC−MS analyses were performed. The solvent was removed under reduced pressure. The residue was then neutralized with sodium bicarbonate and extracted with ethyl acetate (50 mL). After concentration, the crude product was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 25/1). The products 5-propyl-3-cyanofuran (**3h**) and (*E*)-2-propylhept-2-enal (**3h′**) were isolated as colorless oils.

3d:[9] yellow solid; ^{1}H NMR (400 MHz, CD_3OD) δ 8.06−8.29 (m, 5H), 8.52 (s, 1H), 9.73 (s, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 114.2 (C), 116.5 (CN), 116.9 (CN), 118.5 (C), 129.0 (CN), 130.1 (CH), 132.0 (CH), 133.9 (CH), 136.6 (C), 158.6 (CH), 188.7 (CO); GC-MS (EI) *m*/*z* (relative intensity) 182 (72) $[M]^+$, 154 (63), 127 (100), 103 (53).

3f: orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.50 (m, 5H), 7.60−7.67 (m, 2H), 7.73−7.80 (m, 1H), 9.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.3 (C), 113.9 (C), 123.1 (CH), 128.9 (CH), 129.3 (CH), 131.9 (CH), 134.4 (C), 150.7 (CH), 158.3 (CH), 185.9 (CO); GC−MS (EI) *m*/*z* (relative intensity) 183 (100) $[M]^+$, 154 (79), 127 (50), 115 (27). Anal. Calcd for $C_{12}H_9ON$: C, 78.67; H, 4.95; N, 7.65%. Found: C, 78.30; H, 4.99; N, 7.60%.

3h: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 6.20 (s, 1H), 2.61 (t, 2H), 1.67 (sext, 2H), 0.96 (t, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ13.5 (CH_3), 20.9 (CH_2), 29.5 (CH_2), 97.9 (C), 105.9 (CH), 113.5 (C), 148.1 (CH), 158.5 (C); GC−MS (EI) *m*/*z* (relative intensity) 135 (25) $[M]^+$, 106(100), 78 (14), 51 (11); HRMS (EI) *m*/*z* calcd for C_8H_9ON $[M]^+$ 135.0684, found 135.0688.

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Supporting Information Available: Spectra data and copies of ^{1}H and ^{13}C NMR of the products. This material is available free of charge via the Internet at http://pubs.acs.org.