DOI: 10.1002/ejoc.200900432

Selective Cyclodimerization and Cyclotrimerization of Acetals Bearing Electron-Withdrawing Groups Catalyzed by Lewis Acids

Sayuki Maeda,[a] Yasushi Obora,[a] and Yasutaka Ishii*[a]

Keywords: Cyclodimerization / Cyclotrimerization / Acetals / Lewis acids / Annulation

Acetals like 3,3-diethoxypropionate bearing electron-withdrawing groups were found to undergo cyclodimerization and cyclotrimerization in the presence of Lewis acids to give coumalates and 1,3,5-trisubstituted benzenes. The selectivity of these products depended on the Lewis acids employed. For instance, ethyl coumalate was obtained from ethyl 3,3-diethoxypropionate in high selectivity under the influence of d-block Lewis acids like $FeCl_3$, whereas triethyl 1,3,5-benzenetricarboxylate was obtained in preference to ethyl coumalate under the influence of lanthanoid Lewis acids like $GdCl_3$. Various coumalates were synthesized by the $FeCl_3$-catalyzed cross-cyclodimerization of acetals with active methylene compounds. From 4,4-dimethoxy-2-butanone, however, 1,3,5-triacetylbenzene, which is difficult to prepare regioselectively by conventional methods, was formed in quantitative yield under the influence of $AlCl_3$. This reaction would provide a very convenient route to 1,3,5-triacetylbenzene.

Introduction

Coumalic acid derivatives are very important starting compounds for preparing various natural and unnatural complex molecules.[1] In particular, coumalic acids participate in Diels–Alder reactions with various dienophiles with excellent stereochemical control. For instance, the double Diels–Alder reaction of methyl coumalate with 1-methylcycloprop-2-en-1-carbonitrile[2] and the cycloaddition of coumalic acid with vinylene carbonate leading to 2-*epi*-validamine[3] have been performed. Recently, 3-cyano-1-naphthalenecarboxylic acid, which is an important intermediate required for the manufacture of tachykinin receptor antagonists, was synthesized using coumalic acid as a starting material.[4] In spite of the synthetic importance of coumalic acids, however, there have been few methods on the synthesis of coumalic acids so far. The most frequently used method is based on the condensation of malic acid by strong acids like fuming sulfuric acid.[5] Kvita reported an alternative method for preparing ethyl coumalate through Claisen condensation of diethyl 2-pentadioate followed by cyclization under the influence of formic acid.[6] However, the yields of the desired compounds by these methods were moderate. Therefore, the development of a new versatile route to coumalic acids from readily available compounds seems to be interesting.

[a] Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering & High Technology Research Center, Kansai University,
Suita, Osaka 564-8680, Japan
Fax: +81-6-6339-4026
E-mail: ishii@ipcku.kansai-u.ac.jp
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900432.

In a previous paper, we reported the trisannelation of acrylates to 1,3,5-benzenetricarboxylates by using a $Pd(OAc)_2$/HPMoV/$CeCl_3$/O_2 system in a mixed solvent consisting of acetic acid and methanol.[7] The reaction was found to be initiated by the Pd^{II}-catalyzed acetalization[8] of acrylates with alcohols, leading to 3,3-dimethoxypropionates, followed by the $CeCl_3$-catalyzed aldol-type condensation of the resulting acetals with acrylates to give 1,3,5-benzenetricarboxylates.

Therefore, when ethyl 3,3-diethoxypropionate was used as a starting material, the trisannelation was achieved only by using the $CeCl_3$ catalyst to form triethyl 1,3,5-benzenetricarboxylate in good yield.[7] In continuation of this study, we have now found that acetals like ethyl 3,3-diethoxypropionate react under the influence of d-block Lewis acids like $FeCl_3$[9] to form a cyclodimerization product, ethyl coumalate, in good yield, whereas the same reaction using lanthanide Lewis acids led to a cyclotrimerization product, triethyl 1,3,5-benzenetricarboxylate, as a main product. We report here a new synthetic approach to coumalic acid derivatives by self-dimerization of acetals and by cross-dimerization of acetals with activated methylene compounds, as well as a selective route to 1,3,5-triacetylbenzene by cyclotrimerization of acetal catalyzed by Lewis acids.

Results and Discussion

Ethyl 3,3-diethoxypropionate (**1a**) was chosen as a model substrate and was allowed to react under the influence of a catalytic amount of various Lewis acids. The reaction gave rise to ethyl coumalate (**2**) and triethyl 1,3,5-benzenetricarboxylate (**3**) as major products [Equation (1), Table 1].

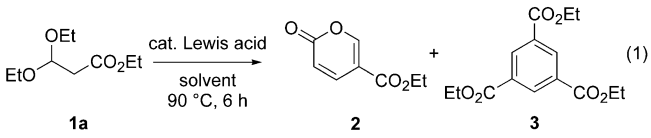


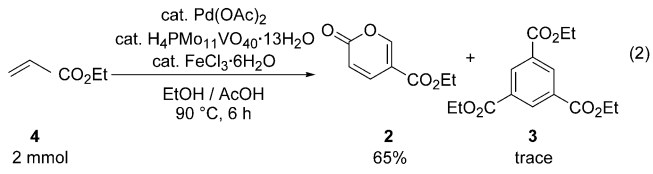
Table 1. Reaction of ethyl 3,3-diethoxypropionate (**1**) by various Lewis acids under several conditions.[a]

Entry	Lewis acid	Solvent (mL)	Conv. [%]	Yield [%][b]	
				2	**3**
1	$FeCl_3·6H_2O$	EtOH (1) / AcOH (8)	>99	89 (88)	n.d.[c]
2	$FeCl_3$	EtOH (1) / AcOH (8)	>99	63	8
3	$AlCl_3·6H_2O$	EtOH (1) / AcOH (8)	>99	63	4
4	$AlCl_3$	EtOH (1) / AcOH (8)	>99	68	7
5	$ZrCl_4$	EtOH (1) / AcOH (8)	>99	54	2
6	$SmCl_3·6H_2O$	EtOH (1) / AcOH (8)	>99	18	43
7	$CeCl_3·7H_2O$	EtOH (1) / AcOH (8)	>99	17	43
8	$GdCl_3·6H_2O$	EtOH (1) / AcOH (8)	>99	26 (25)	69 (68)
9	$Gd(OTf)_2$	EtOH (1) / AcOH (8)	>99	24	34
10	*p*-TsOH	EtOH (1) / AcOH (8)	>99	6	n.d.[c]
11	$FeCl_3·6H_2O$	AcOH (8)	>99	74	n.d.[c]
12	$FeCl_3·6H_2O$	EtOH (8)	86	n.d.[c]	n.d.[c]
13	$FeCl_3·6H_2O$	H_2O (8)	>99	n.d.[c]	14

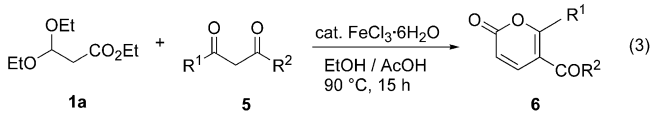
[a] **1a** (2 mmol) was allowed to react in the presence of Lewis acid (0.3 mmol) in EtOH/AcOH at 90 °C for 6 h. [b] Yields were determined by GC. The numbers in the parentheses show isolated yields. [c] Not detected.

For example, the reaction of **1a** (2 mmol) in the presence of $FeCl_3·6H_2O$ (0.3 mmol) in a mixed solvent of acetic acid (8 mL) and ethanol (1 mL) at 90 °C for 6 h produced **2** in 89% yield without formation of **3** (Table 1, Entry 1). It is important to note that **2** was obtained through a catalytic process from **1a**, which is easily available from commercial sources. So far, compound **2** was prepared from malic acid by several methods,[4,5] but most reactions require the use of very strong acids such as fuming sulfuric acid, and the yield of **2** was moderate (65–75%). Therefore, this method provides a very simple route to **2**. The reaction using anhydrous $FeCl_3$ was less efficient than that by $FeCl_3·6H_2O$ in this transformation (Table 1, Entry 2). Typical Lewis acids such as $AlCl_3$ and $ZrCl_4$ gave **2** in 68 and 54% yield and small amounts of **3** in 7 and 2% yield, respectively (Table 1, Entries 4 and 5). In the $ZrCl_4$-catalyzed reaction, polymeric products were increased (Table 1, Entry 5). The reaction using lanthanide chlorides such as $SmCl_3·6H_2O$, $CeCl_3·7H_2O$, and $GdCl_3·6H_2O$ gave trimer **3** as a principal product, and $GdCl_3·6H_2O$ was found to be an efficient catalyst for the cyclotrimerization to **3** (Table 1, Entries 6–8). It is interesting to note that lanthanide chlorides resulted in cyclotrimerization product **3** in contrast to the reaction using d-block Lewis acids such as $FeCl_3·6H_2O$ and $AlCl_3$, which gave dimeric product **2** rather than trimeric product **3**. This is believed to be due to the difference in ionic radii between the d-block metal ions and lanthanide metal ions as discussed below. Protic acids such as *p*-TsOH resulted in unidentified polymeric products of **1a** (Table 1, Entry 10). To obtain information on the solvent effect, several solvents were examined with the use of $FeCl_3·6H_2O$ as a catalyst (Table 1, Entries 11–13). The reaction of **1a** in acetic acid afforded **2** in slightly lower yield (74%) than that in a mixed solvent (Table 1, Entry 11 vs. 1), but the reaction in ethanol in the absence of acetic acid brought about a complex mixture without formation of **2** and **3** (Table 1, Entry 12). However, a small amount of **3** (14%) was obtained in the reaction in water (Table 1, Entry 13).

Previously, we reported that the trisannelation of isobutyl acrylate by the $Pd(OAc)_2$/HPMoV/$CeCl_3$ catalytic system under O_2 produced triisobutyl 1,3,5-benzenetricarboxylate in moderate yield (55%).[7] Thus, ethyl acrylate was allowed to react in the presence of $Pd(OAc)_2$, $H_4PMo_{11}VO_{40}·13H_2O$, and $FeCl_3·6H_2O$ under O_2 (1 atm) in EtOH (1 mL)/AcOH (8 mL) at 90 °C for 6 h, giving **2** in 65% isolated yield and a trace amount of **3** [Equation (2)]. This is the first successful direct synthesis of **2** from acrylate **4**.

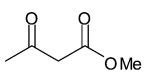
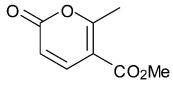
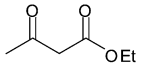
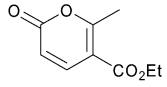
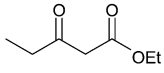
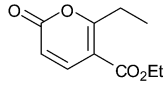
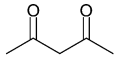
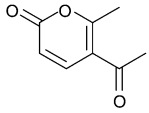
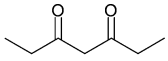
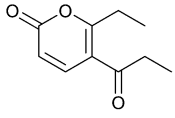


We next tried the cross-cyclocondensation of **1a** with several active methylene compounds **5** under similar reaction conditions as Entry 1 in Table 1 [Equation (3), Table 2]. In order to depress the self-condensation of **1a** to **2**, **1a** was allowed to react with an excess amount (5 equiv.) of acetate **5a** in the presence of $FeCl_3·6H_2O$ in EtOH/AcOH at 90 °C for 15 h, giving cross-cyclodimer methyl 4-methylcoumalate (**6a**) in almost quantitative yields (Table 2, Entries 1 and 2).



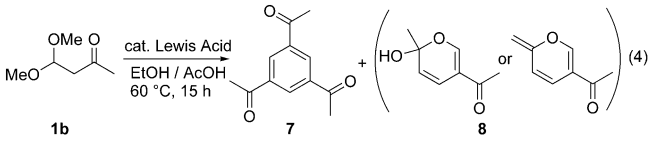
The reaction of **1a** with **5a** (2 equiv.) afforded **6a** (51%) along with the dimer of **1a**, ethyl coumalate **2** (23%; Table 2, Entry 3). Similarly, the reaction of **1a** with ethyl acetoacetate (**5b**) gave corresponding coumalate **6b** in good yields (Table 2, Entries 4–6). When **1a** was allowed to react with ethyl propionylacetate (**5c**), ethyl 4-ethylcoumalate (**6c**) was obtained in quantitative yield (Table 2, Entry 7). As expected, the reaction of **1a** with 1,3-diketones like acetylacetone (**4d**) and 3,5-heptadione (**4e**) afforded the corresponding pyrone derivatives, **6d** and **6e**, as principal products (Table 2, Entries 8 and 9).

Table 2. Cross-cyclocondensation of **1a** with active methylene compounds **5** by $FeCl_3 \cdot 6H_2O$.[a]

Entry	Substrate	Equiv.[b]		Product	Product Yield [%][c] 6	2	3
1[d]		**5a**	5		**6a**	99	n.d.[e]	trace
2[f]		**5a**	5		**6a**	quant. (95)	n.d.[e]	n.d.[e]
3[f]		**5a**	2		**6a**	51	23	n.d.[e]
4		**5b**	10		**6b**	quant. (87)	n.d.[e]	n.d.[e]
5[f]		**5b**	5		**6b**	86	n.d.[e]	n.d.[e]
6[f]		**5b**	2		**6b**	71	19	n.d.[e]
7[f]		**5c**	5		**6c**	quant. (85)	n.d.[e]	n.d.[e]
8[f]		**5d**	10		**6d**	61 (57)	5	trace
9[f]		**5e**	10		**6e**	72 (65)	7	3

[a] **1a** (2 mmol) was allowed to react with active methylene compounds **5** (2–10 equiv.) in the presence of $FeCl_3 \cdot 6H_2O$ (0.3 mmol) at 90 °C for 15 h in EtOH (1 mL)/AcOH (8 mL). [b] Based on **1a** used. [c] Yields were determined by GC. The numbers in the parentheses show isolated yields. [d] Reaction time was 6 h. [e] Not detected. [f] **1a** (2 mmol) in EtOH (0.5 mL) was added using a syringe pump (5 μL min^{-1}) to a mixture of **5** and $FeCl_3 \cdot 6H_2O$ in EtOH (0.5 mL)/AcOH (8 mL).

In contrast, it was found that 4,4-dimethoxy-2-butanone (**1b**) reacted in the presence of Lewis acids to give 1,3,5-triacetylbenzene (**7**) without formation of cyclodimer **8** [Equation (4), Table 3]. For example, **1b** was selectively cyclotrimerized by $AlCl_3$ to afford **7** in almost quantitative yield (89% isolated yield; Table 3, Entry 1).

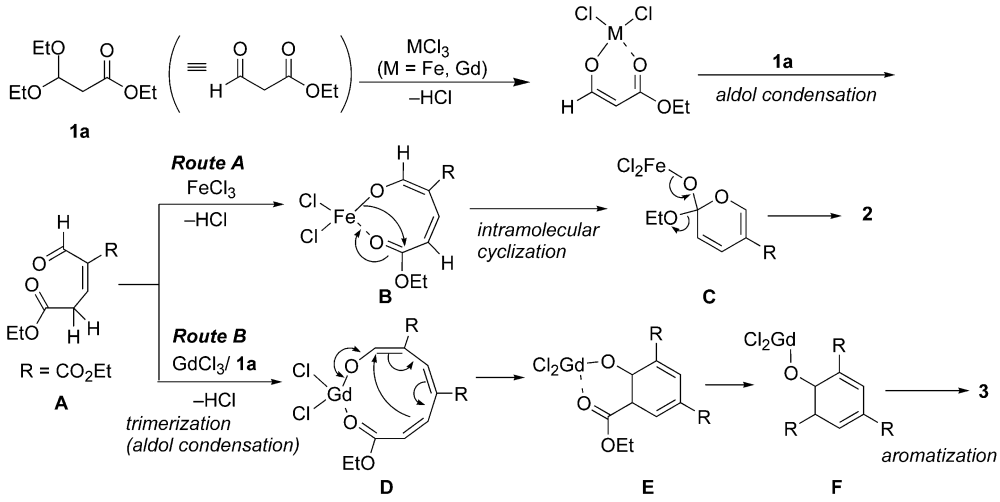


There have been several reports on the synthesis of **7** by cyclotrimerization of 3-butyn-2-one,[10] but this method is difficult to avoid the formation of regioisomers of **7** and 1,2,4-triacetoxybenzene. Jiang et al. reported the Pd-catalyzed cyclotrimerization of methyl vinyl ketone to **7** in a moderate yield (58%).[11] Therefore, the present reaction is thought to provide a novel selective synthetic route to **7** from **1b**, which is easily available from commercial sources. Among the Lewis acids examined, $AlCl_3$ was the best catalyst for the cyclotrimerization of **1b** (Table 3, Entry 1). $AlCl_3 \cdot 6H_2O$ was found to be less efficient than $AlCl_3$ (Table 3, Entry 7), but the catalytic activity of other Lewis acids having crystal water were roughly the same as that of their anhydrous salts. In this reaction, lanthanide chlorides were less efficient than d-block Lewis acids (Table 3, Entries 10–15). It is difficult to explain the selective formation of trimer **7** from **1b** by $AlCl_3$ rather than lanthanide chlorides, but it seems to be due to the difficulty of the forma-

Table 3. Cyclotrimerization of **1b** by Lewis acids.[a]

Entry	Lewis acid	Solvent (mL)	Yield [%][b] 7
1	$AlCl_3$	EtOH (1) / AcOH (8)	>99(89)
2[c]	$AlCl_3$	EtOH (1) / AcOH (8)	82
3[d]	$AlCl_3$	EtOH (1) / AcOH (8)	46
4	$AlCl_3$	EtOH (1) / AcOH (1)	38
5	$AlCl_3$	EtOH (5)	n.d.[e]
6	$AlCl_3$	AcOH (5)	71
7	$AlCl_3 \cdot 6H_2O$	EtOH (1) / AcOH (8)	52
8	$FeCl_3$	EtOH (1) / AcOH (8)	21
9	$FeCl_3 \cdot 6H_2O$	EtOH (1) / AcOH (8)	31
10	$CeCl_3$	EtOH (1) / AcOH (8)	30
11	$CeCl_3 \cdot 7H_2O$	EtOH (1) / AcOH (8)	33
12	$GdCl_3$	EtOH (1) / AcOH (8)	33
13	$GdCl_3 \cdot 6H_2O$	EtOH (1) / AcOH (8)	30
14	$SmCl_3$	EtOH (1) / AcOH (8)	32
15	$SmCl_3 \cdot 6H_2O$	EtOH (1) / AcOH (8)	27

[a] **1b** (2 mmol) was allowed to react in the presence of Lewis acid (0.3 mmol) in EtOH (1 mL)/AcOH (8 mL) at 60 °C for 15 h. [b] Yields were determined by GC. The number in the parenthesis shows isolated yield. [c] Reaction time was for 6 h. [d] Reaction was performed at 90 °C. [e] Not detected.



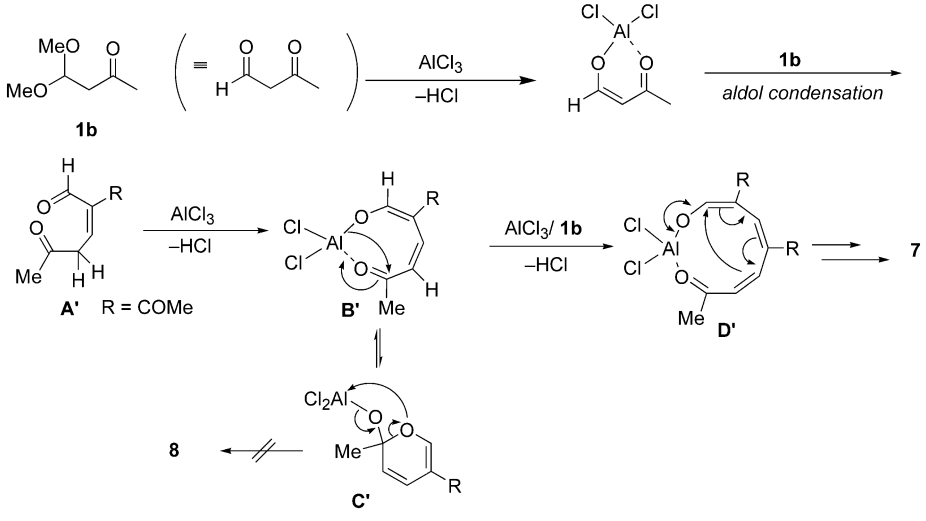
Scheme 1. A plausible reaction path for the formation of **2** and **3** from **1a** catalyzed by $FeCl_3$ (route A) or $GdCl_3$ (route B).

tion of an imaginary dimeric condensation product **8**, which is thought to be provided from **1b** through a similar reaction path as **1a** (Scheme 1 vs. Scheme 2). In fact, compound **8** has not been prepared so far.

Scheme 1 shows a plausible reaction path for the formation of **2** and **3** from **1a** by $FeCl_3$ and $GdCl_3$.

The reaction is thought to initiate the self-aldol (Knoevenagel) condensation of **1a** by $FeCl_3$ to form condensate **A** as an intermediate followed by intramolecular cyclization via **B** and **C** to lead to **2**. When lanthanide chlorides are used as catalysts, condensate **A** reacts further with **1a** to form intermediate **D**, which easily cyclized to form **3** via intermediates **E** and **F**. Cross-condensates **6** from **1a** and activated methylene compounds **5** can be explained by a similar reaction pathway shown in Scheme 1. It is well known that the ionic radii of the lanthanide ions are larger than those of the d-block metal ions.[12] In the reaction of **1a** using lanthanide chlorides, therefore, it is thought that the reaction is preferable to progress through ten-membered ring transition state **D** rather than eight-membered ring transition state **B**, which is thought to be desirable for d-block Lewis acids.

In contrast, a plausible reaction path for the cyclotrimerization of **1b** is shown in Scheme 2. The self-aldol condensation of **1b** by Lewis acids such as $AlCl_3$ occurs in a similar manner as shown in Table 1 to form intermediate **A′**. Formed **A′** reacts with **1b** to form intermediate **B′**, which may lead to the formation of intermediate **C′** through the similar reaction pathway as shown in Scheme 1, route A. However, **C′** did not undergo further intramolecular cyclization to form **8** as a product, because the methyl substituent on the acetyl group functions as a poor leaving group. Alternatively, trimerization reaction proceeds preferentially to form **7** as a sole product.



Scheme 2. A plausible reaction path for the formation of **7** from **1b** catalyzed by $AlCl_3$.

Conclusions

We have developed a novel selective route to coumalate derivatives and 1,3,5-triacetylbenzene from easily available acetals by choosing either d-block Lewis acids or lanthanide chlorides.

Experimental Section

General: All starting materials were commercially available and used without any purification. Heteropolyacid ($H_4PMo_{11}VO_{40}\cdot 13H_2O$) was prepared according to a literature procedure.[13] Compounds **2**,[6] **3**,[7] **6a**,[14] and **7**[10a] were reported previously.

Typical Reaction Procedure for the Formation of Ethyl Coumalate: $FeCl_3\cdot 6H_2O$ (81 mg, 0.30 mmol, 15 mol-%) was added to **1a** (380 mg, 2 mmol) in a mixed solvent of ethanol (1 mL) and acetic acid (8 mL) in open air. The reaction mixture was stirred at 90 °C for 6 h. After the reaction was complete, GC and GC–MS analyses were performed. The conversions and yields of products were estimated from the peak areas, based on the GC internal standard technique. The solvent was removed under reduced pressure, the residue was neutralized with sodium hydrogen carbonate and then extracted with ethyl acetate (50 mL). Product **2** was isolated by column chromatography (SiO_2; hexane/ethyl acetate, 5:1) in 88% yield (148 mg; Table 1, Entry 1).

One-Pot Synthesis of Ethyl Coumalate (2) from Ethyl Acrylate (4) in the Presence of $Pd(OAc)_2$/HPMoV/$FeCl_3$: A mixture of $Pd(OAc)_2$ (22 mg, 0.1 mmol, 5 mol-%), $H_4PMo_{11}VO_{40}\cdot 13H_2O$ ($HPMo_{11}V$; 35 mg, 17 μmol, 0.85 mol-%) and $FeCl_3\cdot 6H_2O$ (81 mg, 0.30 mmol, 15 mol-%) was added to ethyl acrylate (200 mg, 2 mmol) in a mixed solvent of ethanol (1 mL) and acetic acid (8 mL) under an atmosphere of O_2 (1 atm). The reaction mixture was stirred at 90 °C for 6 h. The conversions and yields of products were estimated from the peak areas, based on the GC internal standard technique. The solvent was removed under reduced pressure, and the residue was neutralized with sodium hydrogen carbonate and then extracted with ethyl acetate (50 mL). Product **2** was isolated by column chromatography (SiO_2; hexane/ethyl acetate, 5:1) in 65% yield [109 mg; Equation (2)].

Reaction of Ethyl 3,3-Diethoxypropionate (1a) with Methyl Acetoacetic Acid (5a) in the Presence $FeCl_3$: To a solution of $FeCl_3\cdot 6H_2O$ (81 mg, 0.30 mmol, 15 mol-%) and **5a** (1160 mg, 10 mmol) in a mixed solvent of ethanol (0.5 mL) and acetic acid (8 mL) was added a solution of **1a** (380 mg, 2 mmol) in ethanol (0.5 mL) over a period of 3 h by using a syringe pump in open air, and the mixture was stirred at 90 °C for an additional 12 h. After the reaction was complete, GC and GC–MS analyses were performed. The conversions and yields of products were estimated from the peak areas, based on the GC internal standard technique. The solvent was removed under reduced pressure, and the residue was neutralized with sodium hydrogen carbonate and then extracted with ethyl acetate (50 mL). Product **6a** was isolated by Kugelrohr distillation and column chromatography (SiO_2; hexane/ethyl acetate, 5:1) in 95% yield (319 mg; Table 2, Entry 2).

Reaction of 4,4-Dimethoxy-2-butanone (1b) in the Presence of $AlCl_3$: $AlCl_3$ (45 mg, 0.3 mmol, 15 mol-%) was added to **1b** (264 mg, 2 mmol) in a mixed solvent of ethanol (1 mL) and acetic acid (8 mL) in open air. The reaction mixture was stirred at 60 °C for 15 h. After the reaction was complete, GC and GC–MS analyses were performed. The conversions and yields of products were estimated from the peak areas, based on the GC internal standard technique. The solvent was removed under reduced pressure, and the residue was neutralized with sodium hydrogen carbonate and then extracted with ethyl acetate (50 mL). Product **7** was isolated by column chromatography (SiO_2; hexane/ethyl acetate, 5:1) in 89% yield [121 mg; Equation (4)].

Compound 6b: Yield: 87% (317 mg). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.70 (d, J = 10 Hz, 1 H, 5-H), 6.04 (d, J = 10 Hz, 1 H, 6-H), 4.18 (q, J = 7 Hz, 2 H, -CO_2-CH_2-CH_3), 2.52 (s, 3 H, -CH_3), 1.23 (t, J = 7 Hz, 3 H, -CO_2-CH_2-CH_3) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 13.86 (CH_3), 20.05 (CH_3), 61.03 (CH_2), 108.83 (C), 111.75 (CH), 143.60 (CH), 160.09 (C), 163.48 (C), 170.65 (C) ppm. IR (neat): $\tilde{\nu}$ = 778, 852, 1017, 1084, 1175, 1317, 1553, 1628, 1735, 2979 cm^{-1}. GC–MS (EI): m/z (%) = 182 (89) $[M]^+$, 137 (74), 126 (81), 43 (100). $C_9H_{10}O_4$ (182.18): calcd. C 59.34, H 5.53; found C 59.07, H 5.81.

Compound 6c: Yield: 85% (334 mg). M.p. 49–50 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.81 (d, J = 10 Hz, 1 H, 5-H), 6.17 (d, J = 10 Hz, 1 H, 6-H), 4.30 (q, J = 7 Hz, 2 H, -CO_2-CH_2-CH_3), 3.03 (q, J = 7 Hz, 2 H, -CH_2-CH_3), 1.35 (t, J = 7 Hz, 3 H, -CH_3), 1.27 (t, J = 7 Hz, 3 H, -CH_3) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 11.63 (CH_3), 14.03 (CH_3), 26.69 (CH_2), 61.37 (CH_2), 108.37 (C), 112.02 (CH), 144.06 (CH), 160.72 (C), 163.71 (C), 175.35 (C) ppm. IR (neat): $\tilde{\nu}$ = 774, 1050, 1095, 1186, 1272, 1618, 1712, 1774, 2976, 3107 cm^{-1}. GC–MS (EI): m/z (%) = 196 (38) $[M]^+$, 168 (20), 150 (59), 139 (100). HRMS (EI): calcd. for $C_{10}H_{12}O_4$ 196.0736; found 196.0732.

Compound 6d: Yield: 57% (173 mg). M.p. 62–64 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.66 (d, J = 10 Hz, 1 H, 5-H), 6.16 (d, J = 10 Hz, 1 H, 6-H), 2.55 (s, 3 H, -CH_3), 2.40 (s, 3 H, -CO_2-CH_3) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 20.85 (CH_3), 29.21 (CH_3), 112.12 (CH), 116.16 (C), 143.22 (CH), 160.10 (C), 170.42 (C), 194.83 (C) ppm. IR (neat): $\tilde{\nu}$ = 581, 951, 1202, 1297, 1363, 1605, 1684, 1737, 3078, 2918 cm^{-1}. GC–MS (EI): m/z (%) = 152 (78) $[M]^+$, 137 (48), 109 (100), 95 (83). HRMS (EI): calcd. for $C_8H_8O_3$ 152.0473; found 152.0478.

Compound 6e: Yield: 65% (234 mg). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.67 (d, J = 10 Hz, 1 H, 5-H), 6.14 (d, J = 10 Hz, 1 H, 6-H), 2.86 (q, J = 7 Hz, 2 H, -CO-CH_2-CH_3), 2.71 (q, J = 7 Hz, 2 H, -CH_2-CH_3), 1.21 (t, J = 7 Hz, 3 H, -CO-CH_2-CH_3), 1.09 (t, J = 7 Hz, 3 H, -CH_2-CH_3) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 7.68 (CH_3), 11.41 (CH_3), 26.57 (CH_2), 34.06 (CH_2), 111.91 (CH), 115.22 (C), 142.79 (CH), 160.13 (C), 173.91 (C), 197.75 (C) ppm. IR (neat): $\tilde{\nu}$ = 807, 938, 1058, 1215, 1455, 1542, 1612, 1746, 2937, 2980 cm^{-1}. GC–MS (EI): m/z (%) = 180 (42) $[M]^+$, 151 (100), 95 (66), 57 (36). HRMS (EI): calcd. for $C_{10}H_{12}O_3$180.0786; found 180.0789.

Supporting Information (see footnote on the first page of this article): Experimental procedures and ^{1}H and ^{13}C NMR spectroscopic data for **2**, **3**, **5**, **6**, and **7**.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Advanced Molecular Transformation of Carbon Resources" from the Ministry of Education, Culture, Sports, Science and Technology, Japan, "High-Tech Research Center" Project for Private Universities: matching fund subsidy from the Ministry of Education, Culture, Sports, Science and Technology, 2005–2009.

[1] a) C.-H. Chen, C.-C. Liao, *Org. Lett.* **2000**, *2*, 2049; b) D. Sil, R. Kumar, A. Sharon, P. R. Maulik, V. J. Ram, *Tetrahedron Lett.* **2005**, *46*, 3807 and references cited therein.
[2] V. V. Plemenkov, R. V. Ashirov, O. A. Lodochnikova, I. A. Litvinov, R. N. Zagidullin, *Russ. J. Org. Chem.* **2006**, *42*, 969.
[3] K. Afarinkia, F. Mahmood, *Tetrahedron* **1999**, *55*, 3129.
[4] I. W. Ashworth, M. C. Bowden, B. Dembofsky, D. Levin, W. Moss, E. Robinson, N. Szczur, J. Virica, *Org. Process Res. Dev.* **2003**, *7*, 74.
[5] R. H. Wiley, N. R. Smith, *Organic Syntheses*, Wiley, New York, **1963**, Collect. Vol. IV, p. 201.
[6] V. Kvita, *Helv. Chim. Acta* **1990**, *73*, 411.
[7] K. Tamaso, Y. Hatamoto, S. Sakaguchi, Y. Obora, Y. Ishii, *J. Org. Chem.* **2007**, *72*, 3603.
[8] T. Tokota, S. Fujibayashi, Y. Nishiyama, S. Sakaguchi, Y. Ishii, *J. Mol. Catal. A* **1996**, *114*, 113.
[9] B. Plietker in *Iron Catalysis in Organic Chemistry* (Ed.: B. Plietker), Wiley-VCH, Weinheim, **2008**, p. 197.
[10] a) V. Cadierno, S. E. Garcia-Garrido, J. Gimeno, *J. Am. Chem. Soc.* **2006**, *128*, 15094; b) P. Xue, H. S. Y. Sung, I. D. Williams, G. Jia, *J. Organomet. Chem.* **2006**, *691*, 1945; c) E. Becker, K. Mereiter, M. Puchberger, R. Schmid, K. Kirchner, A. Doppiu, A. Salzer, *Organometallics* **2003**, *22*, 3164; d) H. Yan, A. M. Beatty, T. P. Fehlner, *Organometallics* **2002**, *21*, 5029; e) M. S. Sigman, A. W. Fatland, B. E. Eaton, *J. Am. Chem. Soc.* **1998**, *120*, 5130.
[11] H.-F. Jiang, Y.-X. Shen, Z.-Y. Wang, *Tetrahedron Lett.* **2007**, *48*, 7542.
[12] a) R. Anwander, F. T. Edelman, W. A. Herrmann in *Topics in Current Chemistry* (Ed.: W. A. Herrmann), Springer, Berlin, **1996**, vol. 179; b) F. T. Edelman in *Comprehensive Organometallic Chemistry III* (Eds.: D. M. P. Mingos, R. H. Crabtree, M. Bochmann), Elsevier, Oxford, **2007**, ch. 4.0.1; c) T. Imamoto in *Lanthanides in Organic Synthesis* (Eds.: A. R. Katritzky, O. Meth-Cohn, C. W. Rees), Academic Press, London, **1994**; d) H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865.
[13] L. Pettersson, I. Andersson, J. H. Grate, A. Selling, *Inorg. Chem.* **1994**, *33*, 982.
[14] L. Crombie, M. Eskins, D. E. Games, C. Loader, *J. Chem. Soc. Perkin Trans. 1* **1979**, 478.

Received: April 18, 2009
Published Online: July 14, 2009

