Mild, Efficient, and Robust Method for Stereocomplementary Iron-Catalyzed Cross-Coupling Using (*E*)- and (*Z*)-Enol Tosylates

Hiroshi Nishikado, Hidefumi Nakatsuji, Kanako Ueno, Ryohei Nagase, Yoo Tanabe*

Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan
Fax +81(79)5659077; E-mail: tanabe@kwansei.ac.jp

Received 3 May 2010

Abstract: Iron-catalyzed cross-coupling of Grignard reagents (RMgX) with (*E*)- and (*Z*)-enol tosylates proceeded smoothly to give a variety of the corresponding (*E*)- and (*Z*)-trisubstituted α,β-unsaturated methyl esters (total 30 examples; 55–98% yield). The simple, mild, stereoretentive method utilized iron(III) chloride ($FeCl_3$), iron(III) acetylacetonate [$Fe(acac)_3$], and iron(III) tris(dibenzylmethane) [$Fe(dbm)_3$]. The (*E*)- and (*Z*)-enol tosylates were readily prepared by the reported stereocomplementary tosylation method from methyl β-keto esters or α-formyl esters. Methyl α-formyl esters were obtained via a practical and robust $TiCl_4$–Et_3N-mediated α-formylation of methyl esters with methyl formate.

Key words: cross-coupling, iron, stereoselective synthesis, enol tosylate, α,β-unsaturated ester

Various stereoretentive cross-coupling reactions using (*E*)- and (*Z*)-vinyl halides and their derivatives have been developed over the past decades for the synthesis of natural products and pharmaceuticals due to their advantageous features, such as the wide range of possible substrates and catalysts, mild reaction conditions, functional compatibility, etc. Among a number of investigations, iron-catalyzed cross-couplings have recently attracted considerable attention due to their low cost and toxicity, and environmentally benign catalysis.[1]

Stereocontrolled preparation of (*E*)- and (*Z*)-α,β-unsaturated esters is a major topic in organic synthesis, because these compounds serve as useful structural scaffolds for various (*E*)- and (*Z*)-stereodefined olefins. The stereoselective Horner–Wadsworth–Emmons reaction,[2] dehydration of β-hydroxy esters,[3] Michael reaction[4] or hydroxylation–alkylation using α-alkynyl esters[5] are representative methods.

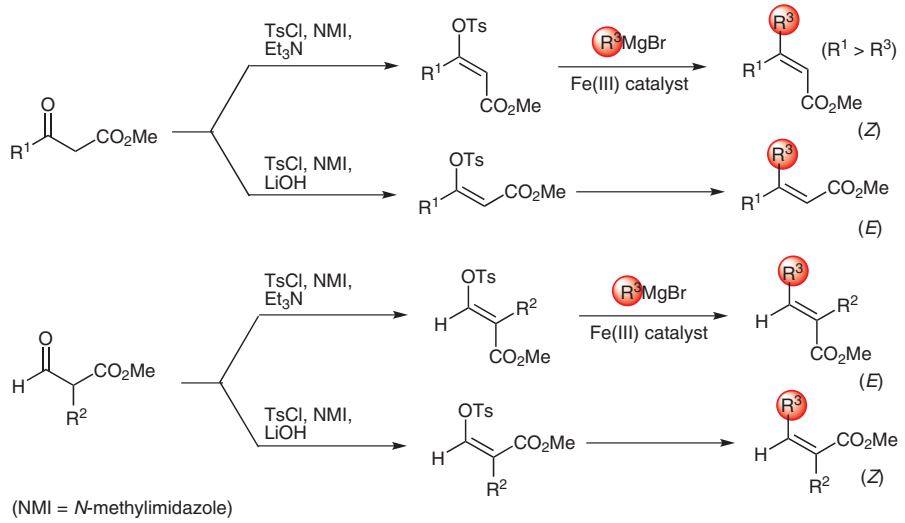
Accordingly, there is a high demand for development of efficient methods to improve stereo-, regio-, and chemoselectivity and substrate generality. The (*E*)- and (*Z*)-stereodefined enol sulfonates derived from β-keto and α-formyl esters are promising stereoretentive cross-coupling partners. Enol triflate analogues are popularly used for this purpose,[6] but they have two drawbacks, particularly for process chemistry, instability, and high cost. We recently reported a couple of practical stereocomplementary preparations of various β-oxo ester enol *p*-toluenesulfonates (tosylates), followed by stereoretentive Negishi, Sonogashira, and Suzuki–Miyaura cross-couplings to give a number of β,β- or α,β-disubstituted (*E*)- and (*Z*)-α,β-unsaturated esters with high substrate generality (total 54 examples).[7]

The key issue of these two methods lies in the *E*- and *Z*-stereocomplementary enol tosylations utilizing an efficient TsCl-*N*-methylimidazole (NMI) scaffold[8] and a stereoretentive cross-coupling protocol using Pd catalysis. As a novel extension, we present herein an efficient $FeCl_3$-, $Fe(acac)_3$ [iron(III) acetylacetonate]-, or $Fe(dbm)_3$ [(iron(III) tris(dibenzylmethane)]-catalyzed cross-coupling using (*E*)- and (*Z*)-enol tosylates as outlined in Scheme 1. The upper and lower figures depict the reaction sequences starting from methyl β-keto esters and α-formyl esters, respectively. Despite the usefulness of iron-catalyzed cross-coupling, to our knowledge, there are no methods with substrate generality for β-oxo enol sulfonate partners.

The initial trial was guided by the methylation of a pair of (*E*)- and (*Z*)-enol tosylates [(*E*)-**1a** and (*Z*)-**1a**][7a] derived from methyl 3-oxononadecanate using MeMgBr to give respective (*Z*)-**2a** and (*E*)-**2a** α,β-unsaturated esters (Table 1, entries 1, 2; notice: due to the sequence rule, a reverse configuration of *E* and *Z* of **2a**–**g** is indicated for this stereoretentive reaction). Among several commercially available Fe(III) salts screened, $FeCl_3$ and $Fe(dbm)_3$ afforded the best results under mild conditions (THF solvent, 0–5 °C, 2 h).[9] This simple and accessible, but successful result prompted us to investigate the substrate generality for the present cross-coupling reaction using various (*E*)- and (*Z*)-enol tosylates [(*E*)-**1** and (*Z*)-**1**] derived from β-keto esters.

Table 1 lists the successful results for preparing stereodefined β,β-disubstituted α,β-unsaturated esters [(*Z*)-**2** and (*E*)-**2**] and the salient features are as follows. (i) All examples examined produced good to excellent yield (18 examples; 55–98% yield) under identical conditions (THF solvent, 0–5 °C, 2 h). (ii) Nearly complete stereoretention was obtained for both *E*- and *Z*-substrates. (iii) With regard to the yield, the $FeCl_3$ catalyst worked best with (*E*)-enol tosylates (*E*)-**1**, whereas the $Fe(dbm)_3$ catalyst worked best with (*Z*)-enol tosylates (*Z*)-**1**. (iv) $Fe(acac)_3$ (acac = acetylacetonyl) with the NMP co-solvent method by Cahiez's group[10] was effective for EtMgBr and BuMgBr nucleophiles (entries 3, 5). (v) A terminal double bond, chloro and ester functional groups were compatible (entries 7–12). (vi) Slight *E* → *Z* isomerization occurred

SYNLETT 2010, No. 14, pp 2087–2092
Advanced online publication: 09.07.2010
DOI: 10.1055/s-0030-1258131; Art ID: U03410ST



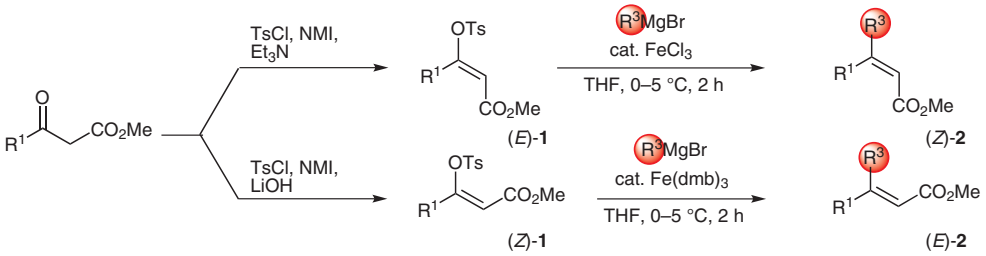
Scheme 1 Stereocomplementary preparation of (*E*)- and (*Z*)-α,β-unsaturated methyl esters utilizing iron-catalyzed cross-couplings of R^3MgBr with (*E*)- and (*Z*)-enol tosylates

in two cases (entries 14 and 17) and one considerable $Z \rightarrow E$ isomerization unfortunately took place (entry 18).

Next, we turned our attention on the reaction using (*E*)- and (*Z*)-enol tosylates [(*E*)-**3** and (*Z*)-**3**] derived from methyl α-formyl esters. As described in our earlier report,[7b] α-formylation of various esters using $TiCl_4$–HCO_2Me reagent (a kind of Ti-Claisen condensation) is efficient due to its higher yield, accessibility, and reproducibility, compared with the traditional method using base reagents (NaOR, NaH, etc.).[11] Utilizing this Ti-Claisen condensation and subsequent stereocomplementary enol tosylation, various stereodefined enol tosylates [(*E*)-**3** and (*Z*)-**3**] were prepared.[7b]

With these substrates [(*E*)-**3** and (*Z*)-**3**] in our hands, the present iron-catalyzed cross-coupling protocol was applied. Table 2 lists the successful results for preparing stereodefined α,β-disubstituted α,β-unsaturated esters [(*E*)-**4** and (*Z*)-**4**] and the salient features are as follows. (i) A little contrary to the case using (*E*)-**1** and (*Z*)-**1**, $Fe(dbm)_3$ instead of $FeCl_3$ produced better result for both substrates [(*E*)-**3** and (*Z*)-**3**]. (ii) All reactions examined produced moderate to excellent yield (12 examples; 58–98%) under identical conditions (THF solvent, 0–5 °C, 2 h). (iii) The reaction also proceeded with both nearly complete *E*- and *Z*-stereoretention. (iv) It is noteworthy that the reaction velocity was consistently higher than that using (*E*)-**1** and (*Z*)-**1**, whose tendency is apparently contrary to the reported methods for Negishi, Sonogashira, and Suzuki–Miyaura couplings.[7] (v) In three cases, slight $Z \rightarrow E$ isomerization occurred (entries 2, 6, and 12).

Table 1 Stereocomplementary Iron-Catalyzed Cross-Coupling of (*E*)-and (*Z*)-Enol Tosylates **1** Derived from Methyl β-Keto Esters



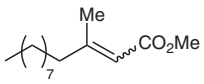
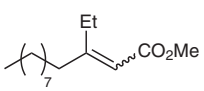
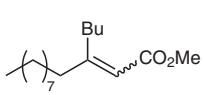
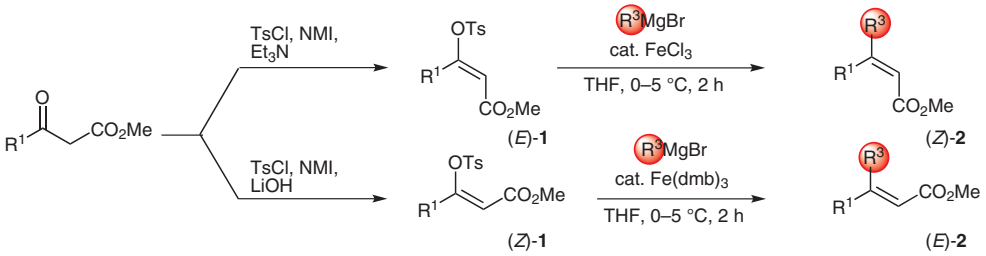
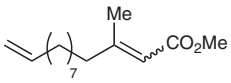
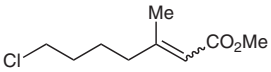
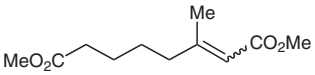
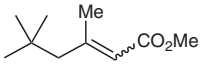
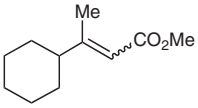
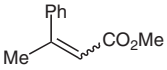
Entry	Enol tosylate	R^3	Product		Yield (%)[a]
1	(*E*)-**1a**	Me		(*Z*)-**2a**	94
2	(*Z*)-**1a**			(*E*)-**2a**	98
3	(*E*)-**1a**	Et		(*Z*)-**2b**	78[b]
4	(*Z*)-**1a**			(*E*)-**2b**	76
5	(*E*)-**1a**	Bu		(*Z*)-**2c**	67, 81[b]
6	(*Z*)-**1a**			(*E*)-**2c**	71

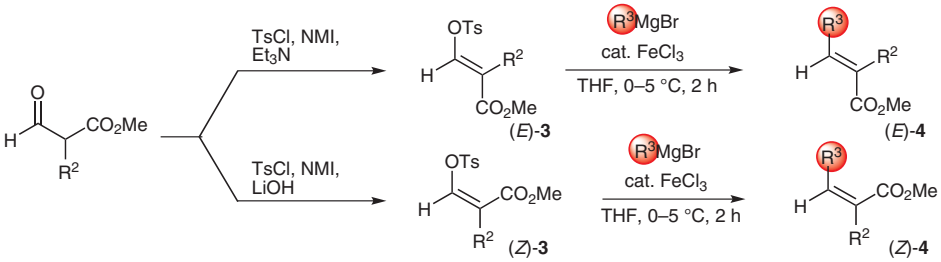
Table 1 Stereocomplementary Iron-Catalyzed Cross-Coupling of (*E*)-and (*Z*)-Enol Tosylates **1** Derived from Methyl β-Keto Esters (continued)



Entry	Enol tosylate	R^3	Product		Yield (%)[a]
7	(*E*)-**1b**	Me		(*Z*)-**2d**	94
8	(*Z*)-**1b**			(*E*)-**2d**	82
9	(*E*)-**1c**	Me		(*Z*)-**2e**	71
10	(*Z*)-**1c**			(*E*)-**2e**	88
11	(*E*)-**1d**	Me		(*Z*)-**2f**	90
12	(*Z*)-**1d**			(*E*)-**2f**	88
13	(*E*)-**1e**	Me		(*Z*)-**2g**	72
14	(*Z*)-**1e**			(*E*)-**2g**	94[c]
15	(*E*)-**1f**	Me		(*Z*)-**2h**	53, 94[d]
16	(*Z*)-**1f**			(*E*)-**2h**	95
17	(*E*)-**1g**	Ph		(*E*)-**2i**	55[e]
18	(*Z*)-**1g**			(*Z*)-**2i**	68[f]

[a] Isolated.
[b] $Fe(acac)_3$ was used instead of $FeCl_3$ with 1.0 equiv of *N*-methylpyrrolidone (NMP) as co-solvent.
[c] *E*/*Z* = 89:11.
[d] $Fe(dbm)_3$ was used instead of $FeCl_3$.
[e] *E*/*Z* = 87:13.
[f] *E*/*Z* = 77:23.

Table 2 Stereocomplementary Iron-Catalyzed Cross-Coupling of (*E*)-and (*Z*)-Enol Tosylates **3** Derived from Methyl α-Formyl Esters



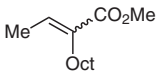
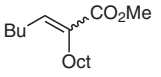
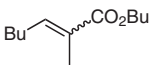
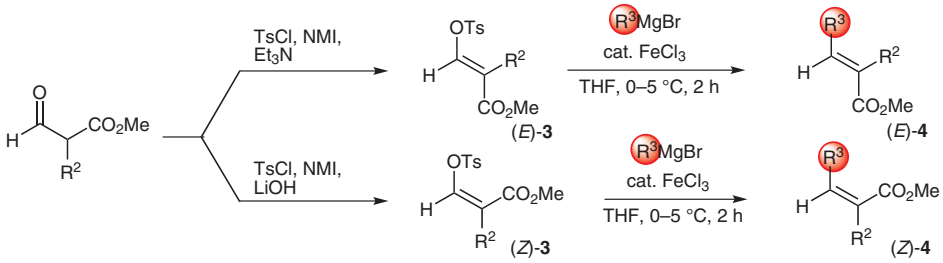
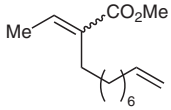
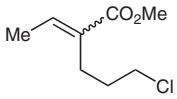
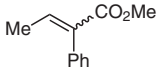
Entry	Enol tosylate	R^3	Product		Yield (%)[a]
1	(*E*)-**3a**	Me		(*E*)-**4a**	94
2	(*Z*)-**3a**			(*Z*)-**4a**	93[b]
3	(*E*)-**3a**	Bu		(*E*)-**4b**	83[c]
4	(*Z*)-**3b**			(*Z*)-**4b**	83[c]
5	(*E*)-**3c**	Bu		(*E*)-**4c**	82[c]
6	(*Z*)-**3c**			(*Z*)-**4c**	58[c,d]

Table 2 Stereocomplementary Iron-Catalyzed Cross-Coupling of (*E*)-and (*Z*)-Enol Tosylates **3** Derived from Methyl α-Formyl Esters (continued)



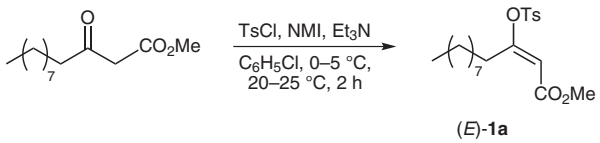
Entry	Enol tosylate	R^3	Product		Yield (%)[a]
7	(*E*)-**3d**	Me		(*E*)-**4d**	88
8	(*Z*)-**3d**			(*Z*)-**4d**	81
9	(*E*)-**3e**	Me		(*E*)-**4e**	68
10	(*Z*)-**3e**			(*Z*)-**4e**	69
11	(*E*)-**3f**	Me		(*E*)-**4f**	98
12	(*Z*)-**3f**			(*Z*)-**4f**	80[e]

[a] Isolated.
[b] *E*/*Z* = 5:95.
[c] BuMgBr used: 2 equiv.
[d] *E*/*Z* = 8:92.
[e] *E*/*Z* = 9:91.

In conclusion, we developed a stereocomplementary method for iron-catalyzed cross-coupling using (*E*)- and (*Z*)-stereodefined enol tosylates. The present simple, mild, robust, and totally efficient method will open a new avenue for the synthesis of a wide range of stereodefined (*E*)- and (*Z*)-α,β-unsaturated esters.

NMR spectra were recorded on a JEOL DELTA 300 spectrometer, operating at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. Chemical shifts (δ, ppm) in $CDCl_3$ were reported downfield from TMS (δ = 0) or $CHCl_3$ (δ = 7.26 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to $CDCl_3$ (δ = 77.00 ppm) as an internal reference. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer.

(*E*)-Methyl 3-(*p*-Toluenesulfonyloxy)-2-dodecenoate [(*E*)-1a] (Scheme 2)

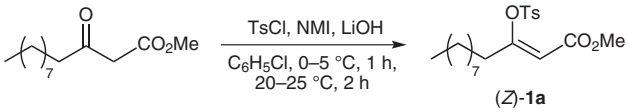


Scheme 2

TsCl (4.28 g, 22.5 mmol) in chlorobenzene (15 mL) was added dropwise to a stirred solution of methyl 3-oxododecanoate (3.42 g, 15 mmol), NMI (1.85 g, 22.5 mmol), and Et_3N (2.28 g, 22.5 mmol) in chlorobenzene (15 mL) at 0–5 °C under an Ar atmosphere, and the mixture was stirred at 20–25 °C for 2 h. H_2O was added to the mixture, which was extracted twice with EtOAc. The combined organic phase was washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on SiO_2 (hexane–EtOAc = 5:1) to give the desired ester (4.59 g, 81%).

Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 7.6 Hz), 1.13–1.36 (12 H, m), 1.37–1.47 (2 H, m), 2.47 (3 H, s), 2.68 (2 H, t, *J* = 7.6 Hz), 3.69 (3 H, s), 5.80 (1 H, s), 7.33–7.40 (2 H, m), 7.79–7.85 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 21.6, 22.6, 26.3, 28.9, 29.2 (2 C), 29.3, 31.3, 31.8, 51.4, 109.1, 128.1, 129.9, 132.9, 145.7, 165.7, 166.3. IR (neat): 2928, 2857, 1727, 1599, 1437, 1364, 1194, 1181cm^{-1}. ESI-HRMS: *m*/*z* calcd for $C_{20}H_{30}O_5S$ [M + Na$^+$]: 405.1712; found: 405.1713.

(*Z*)-Methyl 3-(*p*-Toluenesulfonyloxy)-2-dodecenate [(*Z*)-1a] (Scheme 3)



Scheme 3

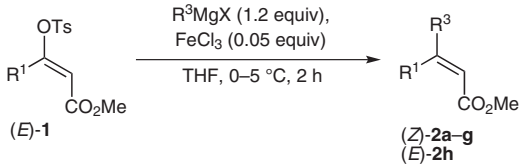
TsCl (4.28 g, 22.5 mmol) in chlorobenzene (15 mL) was added dropwise to a stirred suspension of 3-oxododecanoate (3.42 g, 15 mmol), NMI (1.85 g, 22.5 mmol), and LiOH powder (commercially available, anhyd; 539 mg, 22.5 mmol) in chlorobenzene (20 mL) at 0–5 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 1 h, followed by being stirred at 20–25 °C for 1 h. A similar workup for preparing (*E*)-**1a**, the residue was purified by column chromatography on SiO_2 (hexane–EtOAc = 25:1 to 5:1) to give the desired ester (4.11 g, 72%).

Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 7.2 Hz), 1.15–1.35 (12 H, m), 1.41–1.55 (2 H, m), 2.37 (2 H, t,

J = 7.2 Hz), 2.46 (3 H, s), 3.59 (3 H, s), 5.53 (1 H, s), 7.32–7.40 (2 H, m), 7.87–7.93 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 21.6, 22.6, 26.1, 28.6, 29.1, 29.1, 29.3, 31.7, 35.1, 51.3, 109.9, 128.3, 129.6, 133.5, 145.2, 160.2, 163.4.

(*E*)- and (*Z*)-**1b–g**[7a] and (*E*)- and (*Z*)-**3a–f** are known compounds.[7b]

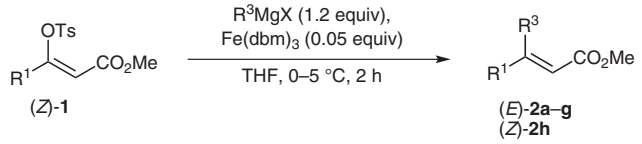
General Procedure for Preparing (*Z*)- or (*E*)-β-Substituted α,β-Unsaturated Esters [(*Z*)-2a–g (R^3 = Me, Et, Bu) or (*E*)-2h (R^3 = Ph)] (Scheme 4)



Scheme 4

1 M R^{3}MgX (1.20 mmol in THF) was added to a stirred solution of an (*E*)-enol tosylate (**1**; 1.00 mmol) and $FeCl_3$ (8 mg, 0.05 mmol) in THF (1.0 mL) at 0–5 °C under an Ar atmosphere, and the mixture was stirred for 2 h. H_2O was added to the mixture, which was filtered using Celite®. The resultant mixture was extracted twice with EtOAc, and the organic phase was washed with brine, dried (Na_2SO_4), and concentrated to give the residue, which was purified by column chromatography on SiO_2 (hexane–EtOAc = 100:1 to 25:1) to give the desired product.

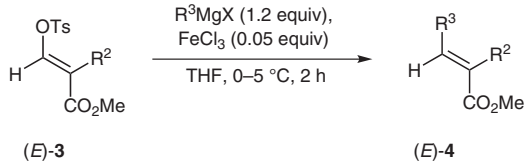
General Procedure for Preparing (*E*)- or (*Z*)-β-Substituted α,β-Unsaturated Esters [(*E*)-2a–g (R^3 = Me, Et, Bu) or (*Z*)-2h (R^3 = Ph)] (Scheme 5)



Scheme 5

1 M R^{3}MgX (1.20 mmol in THF) was added to a stirred solution of a (*Z*)-enol tosylate (**1**; 1.00 mmol) and $Fe(dbm)_3$ (18 mg, 0.05 mmol) in THF (1.0 mL) at 0–5 °C under an Ar atmosphere, and the mixture was stirred for 2 h. A workup similar to that for the preparation of (*Z*)-**2a–g** gave the desired product.

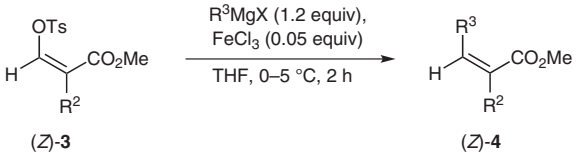
General Procedure for Preparing (*E*)-α-Substituted α,β-Unsaturated Esters (*E*)-4a–f (Scheme 6)



Scheme 6

1 M R^{3}MgX (1.20 mmol in THF) was added to a stirred solution of an (*E*)-enol tosylate (1.00 mmol) and $FeCl_3$ (8 mg, 0.05 mmol) in THF (1.0 mL) at 0–5 °C under an Ar atmosphere, and the mixture was stirred for 2 h. A workup similar to that for the preparation of (*Z*)-**2a–g** gave the desired product.

General Procedure for Preparing *Z*-α-Substituted α,β-Unsaturated Esters (*Z*)-4a–f (Scheme 7)



Scheme 7

1 M R^{3}MgX (1.20 mmol in THF) was added to a stirred solution of a (*Z*)-enol tosylate (1.00 mmol) and $FeCl_3$ (8 mg, 0.05 mmol) in THF (1.0 mL) at 0–5 °C under an Ar atmosphere, and the mixture was stirred for 2 h. A workup similar to that for the preparation of (*Z*)-**2a–g** using (*E*)-**2** gave the desired products.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

Acknowledgment

This research was partially supported by Grant-in-Aids for Scientific Research on Basic Areas (B) '18350056', Priority Areas (A) '17035087' and 'Exploratory Research '17655045' from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

References and Notes

(1) Recent books: (a) *Iron Catalysis in Organic Chemistry*; Plietker, B., Ed.; Wiley-VCH: Weinheim, **2008**. (b) Nakamura, M.; Ito, S. In *Modern Arylation Methods*; Ackermann, L., Ed.; Wiley-VCH: Weinheim, **2009**, 155. Recent reviews: (c) Fürstner, A.; Leitner, A. *Angew. Chem. Int. Ed.* **2002**, *41*, 609. (d) Bolm, C.; Legros, J.; Paih, J. L.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217. (e) Shinokubo, H.; Oshima, K. *Eur. J. Org. Chem.* **2004**, 2081. (f) Fürstner, A.; Martin, R. *Chem. Lett.* **2005**, *34*, 624. (g) Bauer, E. B. *Curr. Org. Chem.* **2008**, *12*, 1341 . A recent iron-catalyzed cross-coupling of zinc reagents with alkyl tosylates: (h) Ito, S.; Fujiwara, Y.; Nakamura, E.; Nakamura, M. *Org. Lett.* **2009**, *11*, 4306; and relevant references cited therein.

(2) (a) Wothers, P.; Greeves, N.; Warren, S.; Clayden, J. *Organic Chemistry*; Oxford: New York, **2001**, 817. (b) Smith, M. B.; March, J. *Advanced Organic Chemistry*, 6th ed.; Wiley: New York, **2007**, 1375.

(3) For examples: (a) Zimmerman, H. E.; Ahramjian, L. *J. Am. Chem. Soc.* **1959**, *81*, 2086. (b) Sai, H.; Ohmizu, H. *Tetrahedron Lett.* **1999**, *40*, 5019. (c) Feuillet, F. J. P.; Robinson, D. E. J.; Bull, S. D. *Chem. Commun.* **2003**, 2184. (d) Mani, N. S.; Mapes, C. M.; Wu, J.; Deng, X.; Jones, T. K. *J. Org. Chem.* **2006**, *71*, 5039.

(4) Ref. 2b, p. 1501.

(5) Hayashi, T.; Inoue, K.; Taniguchi, N.; Ogasawara, M. *J. Am. Chem. Soc.* **2001**, *123*, 9918.

(6) For examples: (a) Scheiper, B.; Bonnekessel, M.; Krause, H.; Fürstner, A. *J. Org. Chem.* **2004**, *69*, 3943. (b) Babinski, D.; Soltani, O.; Frantz, D. E. *Org. Lett.* **2008**, *10*, 2901. (c) Specklin, S.; Bertus, P.; Weibel, J. M.; Pale, P. *J. Org. Chem.* **2008**, *73*, 7845. (d) Maity, P.; Lepore, S. D. *J. Org. Chem.* **2009**, *74*, 158 . Alkenyl and dienyl phospahates: (e) Cahiez, G.; Gager, O.; Habiak, V. *Synthesis* **2008**, 2636. (f) Cahiez, G.; Habiak, V.; Gager, O. *Org. Lett.* **2008**, *10*, 2389. Recent alkenyl pivalates: (g) Li, B.-J.; Xu, L.; Wu, Z.-H.; Guan, B.-T.; Sun, C.-L.; Wang, B.-Q.; Shi, Z.-J. *J. Am. Chem. Soc.* **2009**, *131*, 14656.

(7) (a) Nakatsuji, H.; Ueno, K.; Misaki, T.; Tanabe, Y. *Org. Lett.* **2008**, *10*, 2131. (b) Nakatsuji, H.; Nishikado, H.; Ueno, K.; Tanabe, Y. *Org. Lett.* **2009**, *11*, 4258.

(8) (a) Wakasugi, K.; Iida, A.; Misaki, T.; Nishii, Y.; Tanabe, Y. *Adv. Synth. Catal.* **2003**, *345*, 1209. (b) Yasukochi, H.; Atago, T.; Tanaka, A.; Yoshida, E.; Kakehi, A.; Nishii, Y.; Tanabe, Y. *Org. Biomol. Chem.* **2008**, *6*, 540. Utilization of relevant reactive ammonium intermediates between RCOCl and NMI: (c) Misaki, T.; Nagase, R.; Matsumoto, K.; Tanabe, Y. *J. Am. Chem. Soc.* **2005**, *127*, 2854. (d) Iida, A.; Nakazawa, S.; Okabayashi, T.; Horii, A.; Misaki, T.; Tanabe, Y. *Org. Lett.* **2006**, *8*, 5215. (e) Nakatsuji, H.; Morita, J.; Misaki, T.; Tanabe, Y. *Adv. Synth. Catal.* **2006**, *348*, 2057. (f) Nakatsuji, H.; Morimoto, M.; Misaki, T.; Tanabe, Y. *Tetrahedron* **2007**, *50*, 12071.

(9) In the absence of Fe(III) catalysts, the major side reaction was an addition to the ester moiety and the desired coupling products were not obtained. The basic reactivity order of the Fe(III) catalysts is as follows: $Fe(dbm)_3 > Fe(acac)_3$ with NMP > $Fe(acac)_3 > FeCl_3$. Due to the accessibility and cheapness, the choice order was $FeCl_3$, $Fe(acac)_3$, and $Fe(dbm)_3$; For (*E*)-**1**, (*E*)-**3**, and (*Z*)-**3**, $FeCl_3$ sufficiently worked well, whereas reactive $Fe(dbm)_3$ was required for (*Z*)-**1**.

(10) (a) Cahiez, G.; Avedissaian, H. *Synthesis* **1998**, 1199. (b) Cahiez, G.; Marquais, S. *Pure Appl. Chem.* **1996**, *68*, 53.

(11) Yields of the traditional basic method range from 0 to 50%. Reexamination of NaH-promoted α-formylation using an aliphatic simple esters, $Me(CH_2)_4CO_2Me$, in our hands, however, was not reproducible under identical conditions. These strongly basic and heterogeneous conditions might be troublesome.