Iron-Catalyzed Highly Regio- and Stereoselective Conjugate Addition of 2,3-Allenoates with Grignard Reagents

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Supporting Information

Table S1. Effects of the Amount of MeMgCl on Iron-Catalyzed Conjugate Addition of 2,3-Allenoate 1a

<table>
<thead>
<tr>
<th>entry</th>
<th>X (equiv)</th>
<th>Yield of Z-2a (%) a</th>
<th>Z/E a</th>
<th>Yield of 3a (%) a</th>
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<tr>
<td>1</td>
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<td>81</td>
<td>&gt;99/1</td>
<td>0.9</td>
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<tr>
<td>2</td>
<td>1.5</td>
<td>80</td>
<td>98/2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

a Determined by NMR

Materials. Toluene and THF were distilled from Na/benzophenone. 2,3-Allenoates were prepared according to the known procedure.1 Methyl magnesium chloride (3.0 M solution
in THF) used in this study were purchased from Aldrich. Phenyl magnesium chloride (1.9 M solution in THF) and vinyl magnesium chloride (1.7 M solution in THF) used in this study were purchased from Acros Organics. $\alpha$-Hexyl magnesium chloride (1.5 M solution in THF), $n$-butyl magnesium chloride (1.5 M solution in THF), and $s$-butyl magnesium bromide (1.5 M solution in THF) used in this study were prepared from the reaction of magnesium turnings (17 mmol) with $\alpha$-hexyl chloride, $n$-butyl chloride or $s$-butyl bromide (15 mmol) in THF (10 mL) according to the known procedure. The other commercially available chemicals were purchased and used without additional purification unless noted otherwise.

**General Procedure for Fe(acac)$_3$-Catalyzed Conjugate Addition of 2,3-Allenoates with Grignard Reagents:**

To a dry Schlenk tube, Fe(acac)$_3$ (0.5~5 mol%, 0.002~0.02 mmol), 1 (0.4 mmol), and toluene (5 mL) were added sequentially under a nitrogen atmosphere at room temperature. A solution of requisite Grignard reagent in THF (3 equiv, 1.2 mmol) was then added by a syringe to the reaction mixture within 3~5 min at -78 °C. The reaction was monitored by TLC. After 1~5 h, the reaction mixture was quenched slowly with saturated NH$_4$Cl (1 mL) at -78 °C, followed by warming up to rt naturally and the addition of water (5 mL) at this temperature. After extraction with diethyl ether (3 x 30 mL), the organic layer was washed subsequently with diluted HCl (1%, aq.), a saturated aqueous solution of NaHCO$_3$, brine, and dried over anhydrous Na$_2$SO$_4$. Evaporation and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1 or petroleum ether/dichloromethane = 10/1) afforded the desired product.
(1) Ethyl 4-phenyl-3-methyl-2-propyl-3(Z)-butenoate (Iz-9-144)

\[
\begin{align*}
\text{Ph} & \quad \text{C}_3\text{H}_7-n \\
\text{CO}_2\text{Et} & \quad \text{CH}_3\text{MgCl} \quad \text{Fe(acac)}_3 \quad (5 \text{ mol\%}) \\
\text{in toluene (5 mL)} & \quad 0.4 \text{ mL} \\
0.4 \text{ mmol} & \quad 3 \text{ equiv}
\end{align*}
\]

The reaction of Fe(acac)$_3$ (0.0071 g, 5 mol\%, 0.02 mmol), 1a (0.0929 g, 0.4 mmol), toluene (5 mL), and a solution of CH$_3$MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) afforded Z-2a (0.0767 g, 77\%): Liquid; $^1$H NMR (400 MHz, CDCl$_3$) 7.36-7.27 (m, 4 H), 7.22 (t, $J = 7.0$ Hz, 1 H), 6.49 (s, 1 H), 4.21-4.14 (m, 2 H), 3.69 (dd, $J_1 = 8.0$ Hz, $J_1 = 6.8$ Hz, 1 H), 1.84 (d, $J = 1.6$ Hz, 3 H), 1.81-1.72 (m, 1 H), 1.60-1.48 (m, 1 H), 1.29 (t, $J = 7.2$ Hz, 3 H), 1.25-1.15 (m, 1 H), 1.15-1.02 (m, 1 H), 0.76 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) 173.9, 137.7, 135.4, 129.2, 128.8, 128.1, 126.4, 60.5, 46.4, 31.6, 20.2, 19.6, 14.2, 13.8; MS (m/z) 246 (M$^+$, 30.48), 131 (100); IR (neat, cm$^{-1}$) 2960, 2871, 1731, 1651, 1443, 1179, 1031; HRMS calcd for C$_{16}$H$_{22}$O$_2$ (M$^+$) 246.1620, found 246.1620.

(2) Methyl 4-phenyl-3-methyl-2-propyl-3(Z)-butenoate  (Iz-9-197, Iz-10-114, Iz-10-115)

\[
\begin{align*}
\text{Ph} & \quad \text{C}_3\text{H}_7-n \\
\text{CO}_2\text{Me} & \quad \text{CH}_3\text{MgCl} \quad \text{Fe(acac)}_3 \quad (0.5 \text{ mol\%}) \\
\text{in toluene (5 mL)} & \quad 0.4 \text{ mL} \\
0.4 \text{ mmol} & \quad 3 \text{ equiv}
\end{align*}
\]

The reaction of Fe(acac)$_3$ (0.0006 g, 0.5 mol\%, 0.002 mmol), 1b (0.0864 g, 0.4 mmol), toluene (5 mL), and a solution of CH$_3$MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) afforded Z-2b (0.0795 g, 86\%): Liquid; $^1$H NMR (400 MHz, CDCl$_3$) 7.37-7.31 (m, 2 H), 7.30-7.26 (m, 2 H), 7.25-7.20 (m, 1 H), 6.50 (s, 1 H), 3.76-3.71 (m, 4 H), 1.84 (d, $J = 1.6$ Hz, 3 H), 1.84-1.73 (m, 1 H), 1.60-1.48 (m, 1 H), 1.28-1.16 (m, 1 H), 1.16-1.03 (m,
1 H), 0.77 (t, J = 7.2 Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) 174.4, 137.6, 135.2, 129.2, 128.7, 128.2, 126.4, 51.8, 46.3, 31.7, 20.2, 19.6, 13.8; MS (m/z) 232 (M$^+$, 34.90), 131 (100); IR (neat, cm$^{-1}$) 2957, 2873, 1733, 1652, 1600, 1434, 1168; HRMS calcd for C$_{15}$H$_{20}$O$_2$ (M$^+$) 232.1463, found 232.1465.

(3) Benzyl 4-phenyl-3-methyl-2-propyl-3(Z)-butenoate (Iz-9-200)

The reaction of Fe(acac)$_3$ (0.0074 g, 5 mol%, 0.02 mmol), 1c (0.1162 g, 0.4 mmol), toluene (5 mL), and a solution of CH$_3$MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) afforded Z-2c (0.1028 g, 84%): Liquid; $^1$H NMR (400 MHz, CDCl$_3$) 7.40-7.32 (m, 5 H), 7.32-7.27 (m, 4 H), 7.25-7.20 (m, 1 H), 6.53 (s, 1 H), 5.22 (d, J = 12.4 Hz, 1 H), 5.17 (d, J = 12.4 Hz, 1 H), 5.17 (d, J = 12.4 Hz, 1 H), 3.79 (t, J = 7.8 Hz, 1 H), 1.84 (d, J = 0.4 Hz, 3 H), 1.83-1.77 (m, 1 H), 1.65-1.55 (m, 1 H), 1.30-1.17 (m, 1 H), 1.17-1.05 (m, 1 H), 0.79 (t, J = 7.2 Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) 173.6, 137.6, 136.2, 135.1, 129.4, 128.8, 128.5, 128.1, 128.0, 127.8, 126.4, 66.2, 46.4, 31.6, 20.2, 19.6, 13.8; MS (m/z) 308 (M$^+$, 7.09), 91 (100); IR (neat, cm$^{-1}$) 2958, 2872, 1733, 1650, 1599, 1456, 1163; HRMS calcd for C$_{21}$H$_{24}$O$_2$ (M$^+$) 308.1776, found 308.1767.

(4) Ethyl 2,3-dimethyl-4-phenyl-3(Z)-butenoate (Iz-9-171, Iz-10-58, cgb-1-75, cgb-1-76)

The reaction of Fe(acac)$_3$ (0.0028 g, 2 mol%, 0.008 mmol), 1d (0.0853 g, 0.4 mmol),
toluene (5 mL), and a solution of CH₃MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) afforded Z-2d (0.0814 g, 88%): Liquid; ¹H NMR (300 MHz, CDCl₃) 7.38-7.22 (m, 5 H), 6.44 (s, 1 H), 4.24-4.16 (m, 2 H), 3.84 (q, J = 7.2 Hz, 1 H), 1.86 (d, J = 1.5 Hz, 3 H), 1.28 (t, J = 7.2 Hz, 3 H), 1.25 (t, J = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 100 MHz) 174.2, 137.7, 136.8, 128.6, 128.2, 127.9, 126.4, 60.6, 40.9, 19.5, 15.3, 14.2; MS (m/z) 218 (M⁺, 22.71), 145 (100); IR (neat, cm⁻¹) 2979, 2940, 1733, 1652, 1599, 1443, 1187; HRMS calcd for C₁₄H₁₈O₂ (M⁺) 218.1307, found 218.1316.

(5) Ethyl 4-(4’-bromophenyl)-3-methyl-2-propyl-3(Z)-butenoate (lz-10-3, lz-10-112, lz-10-113)

\[
\begin{align*}
\text{Br} & \quad \text{C}_3\text{H}_7-\text{n} \\
\text{CO}_2\text{Et} & \quad \text{CO}_2\text{Et}
\end{align*}
\]

The reaction of Fe(acac)₃ (0.0029 g, 2 mol%, 0.008 mmol), 1e (0.1235 g, 0.4 mmol), toluene (5 mL), and a solution of CH₃MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) afforded Z-2e (0.1145 g, 88%): Liquid; ¹H NMR (400 MHz, CDCl₃) 7.44 (d, J = 7.6 Hz, 2 H), 7.17 (d, J = 7.6 Hz, 2 H), 6.39 (s, 1 H), 4.17 (q, J = 7.2 Hz, 2 H), 3.60 (dd, J₁ = 8.0 Hz, J₂ = 7.2 Hz, 1 H), 1.82 (d, J = 1.2 Hz, 3 H), 1.80-1.70 (m, 1 H), 1.58-1.47 (m, 1 H), 1.28 (t, J = 7.2 Hz, 3 H), 1.24-1.13 (m, 1 H), 1.13-1.01 (m, 1 H), 0.77 (t, J = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 100 MHz) 173.5, 136.5, 136.3, 131.3, 130.5, 128.0, 120.3, 60.6, 46.5, 31.6, 20.2, 19.6, 14.2, 13.8; MS (m/z) 326 (M⁺ (⁷⁹Br), 15.06), 324 (M⁺ (⁷⁹Br), 17.46), 172 (100); IR (neat, cm⁻¹) 2959, 2872, 1732, 1650, 1587, 1487, 1178; HRMS calcd for C₁₆H₁₇O₂ ³⁷⁹Br (M⁺ (⁷⁹Br)) 324.0725, found 324.0734.
(6) Ethyl 2,3-dimethyl-4-(4'-bromophenyl)-3(Z)-butenoate (Iz-10-15, cgb-1-66, 67)

![Chemical structure](attachment:image.png)

The reaction of Fe(acac)_3 (0.0007 g, 0.5 mol%, 0.002 mmol), 1f (0.1119 g, 0.4 mmol), toluene (5 mL), and a solution of CH_3MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) afforded Z-2f (0.1044 g, 88%): Liquid; ^1H NMR (400 MHz, CDCl_3) 7.44 (d, J = 8.6 Hz, 2 H), 7.14 (d, J = 8.6 Hz, 2 H), 6.34 (s, 1 H), 4.22-4.10 (m, 2 H), 3.73 (q, J = 6.8 Hz, 1 H), 1.82 (d, J = 1.2 Hz, 3 H), 1.26 (d, J = 7.2 Hz, 3 H), 1.22 (d, J = 6.8 Hz, 3 H); ^13C NMR (CDCl_3, 100 MHz) 173.9, 137.7, 136.5, 131.3, 130.3, 126.7, 120.4, 60.7, 40.9, 19.5, 15.2, 14.2; MS (m/z) 298 (M⁺ (81Br), 12.02), 296 (M⁺ (79Br), 12.66), 144 (100); IR (neat, cm⁻¹) 2979, 2939, 1733, 1648, 1587, 1487, 1185; HRMS calcd for C_{14}H_{17}O_{279Br} (M⁺ (79Br)) 296.0412, found 296.0413.

(7) Ethyl 3-methyl-2-propyl-3(Z)-undecenoate (Iz-9-156)

![Chemical structure](attachment:image.png)

The reaction of Fe(acac)_3 (0.0073 g, 5 mol%, 0.02 mmol), 1g (0.1005 g, 0.4 mmol), toluene (5 mL), and a solution of CH_3MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) afforded Z-2g (0.0909 g, 85%): Liquid; ^1H NMR (400 MHz, CDCl_3) 5.30 (t, J = 7.4 Hz, 1 H), 4.10 (q, J = 6.9 Hz, 2 H), 3.46 (t, J = 7.4 Hz, 1 H), 2.10-1.97 (m, 2 H), 1.84-1.74 (m, 1 H), 1.63 (d, J = 0.9 Hz, 3 H), 1.52-1.42 (m, 1 H), 1.38-1.19 (m, 15 H), 0.92-0.82 (m, 6
H); $^{13}$C NMR (CDCl$_3$, 100 MHz) 174.0, 131.7, 129.4, 60.2, 46.1, 31.8, 31.5, 29.8, 29.3, 29.2, 27.8, 22.7, 20.5, 19.5, 14.2, 14.1, 14.0; MS (m/z) 268 (M$^+$, 4.83), 55 (100); IR (neat, cm$^{-1}$) 2958, 2927, 2856, 1735, 1465, 1176; HRMS calcd for C$_{17}$H$_{32}$O$_2$ (M$^+$) 268.2402, found 268.2399.

(8) Methyl 3-methyl-2-benzyl-3(Z)-octenoate (Iz-10-4, cgb-1-73)

$$\text{n-C}_4\text{H}_9 \text{Bn} \text{CO}_2\text{Me} + \text{CH}_3\text{MgCl in THF (3 M)} \xrightarrow{\text{Fe(acac)}_3 (2 \text{ mol\%})} \text{n-C}_4\text{H}_9 \text{BnCO}_2\text{Me}$$

The reaction of Fe(acac)$_3$ (0.0027 g, 5 mol%, 0.008 mmol), 1h (0.0983 g, 0.4 mmol), toluene (5 mL), and a solution of CH$_3$MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) afforded Z-2h (0.0895 g, 85%): Liquid; $^1$H NMR (300 MHz, CDCl$_3$) 7.29-7.22 (m, 2 H), 7.21-7.14 (m, 3 H), 5.27 (t, $J = 7.2$ Hz, 1 H), 3.78 (t, $J = 7.8$ Hz, 1 H), 3.64 (s, 3 H), 3.21 (dd, $J_1 = 13.8$ Hz, $J_2 = 7.8$ Hz, 1 H), 2.75 (dd, $J_1 = 13.8$ Hz, $J_2 = 7.8$ Hz, 1 H), 2.00-1.86 (m, 1 H), 1.83-1.77 (m, 1 H), 1.71 (s, 3 H), 1.26-1.16 (m, 3 H), 1.16-1.00 (m, 1 H), 0.84 (t, $J = 6.9$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) 173.8, 139.5, 130.6, 130.1, 128.9, 128.2, 126.1, 51.7, 48.4, 35.6, 31.6, 27.4, 22.3, 19.8, 13.9; MS (m/z) 260 (M$^+$, 0.16), 201 ((M-CO$_2$Me)$^+$, 6.55), 169 (100); IR (neat, cm$^{-1}$) 2955, 2858, 1738, 1605, 1497, 1161; Elemental analysis: Calcd for C$_{17}$H$_{24}$O$_2$: C, 78.42; H, 9.29; Found: C, 78.39; H, 9.29.

(9) Ethyl 4-phenyl-3-butyl-2-propyl-3(Z)-butenoate (cgb-2-26)

$$\text{Ph} \text{CO}_2\text{Et} + \text{n-BuMgCl in THF (1.5 M)} \xrightarrow{\text{Fe(acac)}_3 (5 \text{ mol\%})} \text{Ph}\text{Bu} \text{CO}_2\text{Et}$$

The reaction of Fe(acac)$_3$ (0.0074 g, 5 mol%, 0.02 mmol), 1a (0.0925 g, 0.4 mmol),
toluene (5 mL), and a solution of \( n \)-BuMgCl in THF (0.8 mL, 1.5 M, 3 equiv, 1.2 mmol, prepared from the reaction of magnesium turnings (17 mmol) with \( n \)-butyl chloride (15 mmol) in THF(10 mL)) afforded Z-2i (0.0812 g, 70%): Liquid; \(^1\)H NMR (300 MHz, CDCl\(_3\)) 7.36-7.27 (m, 4 H), 7.25-7.18 (m, 1 H), 6.49 (s, 1 H), 4.16 (q, \( J = 7.1 \) Hz, 2 H), 3.71 (dd, \( J_1 = 8.1 \) Hz, \( J_2 = 6.9 \) Hz, 1 H), 2.15-2.08 (m, 2 H), 1.85-1.71 (m, 1 H), 1.59-1.43 (m, 3 H), 1.43-1.33 (m, 2 H), 1.28 (t, \( J = 7.2 \) Hz, 3 H), 1.23-1.00 (m, 2 H), 0.94 (t, \( J = 7.2 \) Hz, 3 H), 0.75 (t, \( J = 7.4 \) Hz, 3 H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) 174.2, 139.6, 138.1, 128.8, 128.1, 127.7, 126.3, 60.4, 46.5, 31.8, 31.5, 30.7, 22.7, 20.3, 14.2, 14.1, 13.8; MS (m/z) 311.0 ((M+Na\(^+\)), 100); IR (neat, cm\(^{-1}\)) 2958, 2932, 2872, 1732, 1643, 1599, 1465, 1178; HRMS calcd for C\(_{19}\)H\(_{28}\)O\(_2\)Na (M+Na\(^+\)) 311.1982, found 311.1981.

(10) Ethyl 4-phenyl-3-(\( c \)-hexyl)-2-propyl-3(Z)-butenoate  (cgb-1-20)

![Chemical structure diagram]

The reaction of Fe(acac\(_3\)) (0.0069 g, 5 mol%, 0.02 mmol), 1a (0.0923 g, 0.4 mmol), toluene (5 mL), and a solution of \( c \)-hexMgCl in THF (0.8 mL, 3 equiv, 1.2 mmol, prepared from the reaction of magnesium turnings (17 mmol) with \( c \)-hexyl chloride (15 mmol) in THF(10 mL)) afforded Z-2j (0.1074 g, 86%): Liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) 7.36-7.27 (m, 4 H), 7.22-7.18 (m, 1 H), 6.54 (s, 1 H), 4.15 (q, \( J = 7.2 \) Hz, 2 H), 3.71 (t, \( J = 7.4 \) Hz, 1 H), 2.11-2.02 (m, 1 H), 1.82-1.65 (m, 6 H), 1.55-1.40 (m, 1 H), 1.40-1.00 (m, 10 H), 0.73 (t, \( J = 7.2 \) Hz, 3 H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 174.2, 145.6, 138.2, 128.9, 128.1, 127.2, 126.2, 60.4, 46.8, 39.8, 35.3, 35.0, 31.9, 27.1, 27.0, 26.2, 20.4, 14.2, 13.8; MS (m/z) 314 (M\(^+\), 9.93), 117 (100); IR (neat, cm\(^{-1}\)) 2928, 2852, 1732, 1643,
(11) Ethyl 3-(c-hexyl)-2-propyl-3(Z)-undecenoate (lz-10-76)

\[
\begin{align*}
1g & \quad \text{n-C}_7\text{H}_{15} \quad \text{C}_3\text{H}_7 - n \\
\text{CO}_2\text{Et} & \quad \text{+ c-hexMgCl in THF (1.5 M)} \\
\text{Fe(acac)}_3 (5 \text{ mol\%}) & \quad \text{Fe(acac)}_3 (5 \text{ mol\%}) \\
\text{-78 °C, 1 h} & \quad -78 ^\circ \text{C, 1 h} \\
\text{Z-2k} & \quad \text{n-C}_7\text{H}_{15} \quad \text{CO}_2\text{Et}
\end{align*}
\]

The reaction of Fe(acac)_3 (0.0073 g, 5 mol%, 0.02 mmol), 1a (0.1002 g, 0.4 mmol),
toluene (5 mL), and a solution of c-hexMgCl in THF (0.8 mL, 3 equiv, 1.2 mmol,
prepared from the reaction of magnesium turnings (17 mmol) with c-hexyl chloride (15
mmol) in THF(10 mL)) afforded Z-2k (0.1196 g, 90%): Liquid; ^1H NMR (400 MHz,
CDCl_3) 5.30 (t, J = 7.2 Hz, 1 H), 4.08 (q, J = 7.2 Hz, 2 H), 3.36 (t, J = 7.2 Hz, 1 H),
2.14-1.96 (m, 2 H), 1.82-1.82 (m, 2 H), 1.75-1.50 (m, 5 H), 1.46-1.05 (m, 21 H),
0.93-0.82 (m, 6 H); ^13C NMR (CDCl_3, 100 MHz) 174.4, 142.3, 127.1, 60.1, 46.7, 40.9,
34.7, 34.6, 32.2, 31.8, 29.9, 29.2, 27.7, 27.1, 27.0, 26.3, 22.6, 20.9, 14.2, 14.08, 14.06;
MS (m/z) 336 (M^+, 16.81), 293 (100); IR (neat, cm\(^{-1}\)) 2926, 2853, 1733, 1448, 1177;
HRMS calcd for C_{22}H_{40}O_{2} (M^+) 336.3023, found 336.3037.

(12) Ethyl 4-phenyl-3-(c-hexyl)-2-methyl-3(Z)-butenoate (lz-10-75)

\[
\begin{align*}
1d & \quad \text{Ph} \quad \text{CH}_3 \\
\text{CO}_2\text{Et} & \quad \text{+ c-hexMgCl in THF (1.5 M)} \\
\text{Fe(acac)}_3 (5 \text{ mol\%}) & \quad \text{Fe(acac)}_3 (5 \text{ mol\%}) \\
\text{-78 °C, 1 h} & \quad -78 ^\circ \text{C, 1 h} \\
\text{Z-2l} & \quad \text{Ph} \quad \text{CO}_2\text{Et}
\end{align*}
\]

The reaction of Fe(acac)_3 (0.0071 g, 5 mol%, 0.02 mmol), 1d (0.0829 g, 0.4 mmol),
toluene (5 mL), and a solution of c-hexMgCl in THF (0.8 mL, 3 equiv, 1.2 mmol,
prepared from the reaction of magnesium turnings (17 mmol) with c-hexyl chloride (15
mmol) in THF(10 mL)) afforded Z-2l (0.0911 g, 78%): Liquid; ^1H NMR (400 MHz,
CDCl\textsubscript{3}) 7.35-7.32 (m, 2 H), 7.31-7.25 (m, 2 H), 7.22 (t, J = 7.0 Hz, 1 H), 6.47 (s, 1 H), 4.18-4.08 (m, 2 H), 3.84 (q, J = 7.1 Hz, 1 H), 2.04-1.96 (m, 1 H), 1.82-1.65 (m, 5 H), 1.40-1.18 (m, 11 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) 174.5, 147.0, 138.1, 128.7, 128.1, 126.3, 126.1, 60.5, 41.4, 40.5, 35.6, 34.7, 27.1, 26.9, 26.2, 15.7, 14.2; MS (m/z) 286 (M\textsuperscript{+}, 35.25), 184 (100); IR (neat, cm\textsuperscript{-1}) 2927, 2852, 1732, 1646, 1599, 1447, 1187; HRMS calcd for C\textsubscript{19}H\textsubscript{26}O\textsubscript{2} (M\textsuperscript{+}) 286.1927, found 286.1932.

(13) Ethyl 3-(s-butyl)-2-propyl-3(Z)-undecenoate (lz-11-82)

\[
\begin{array}{c}
\text{n-C\textsubscript{7}H\textsubscript{15}} \\
+ \text{s-BuMgBr in THF (1.5 M)}
\end{array} \xrightarrow{\text{Fe(acac)}_3 (5 \text{ mol\%})-78 \degree C, 1 \text{ h}} \text{Z-2m}
\]

The reaction of Fe(acac)\textsubscript{3} (0.0072 g, 5 mol\%, 0.02 mmol), 1\text{g} (0.0990 g, 0.4 mmol), toluene (5 mL), and a solution of s-BuMgBr in THF (0.8 mL, 3 equiv, 1.2 mmol, prepared from the reaction of magnesium turnings (17 mmol) with s-butyl bromide (15 mmol) in THF(10 mL)) afforded Z-2m (0.1143 g, 94%): Liquid; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) 5.30-5.23 (m, 1 H), 4.14-4.00 (m, 2 H), 3.38-3.31 (m, 1H), 2.16-1.96 (m, 3 H), 1.96-1.80 (m, 1 H), 1.50-1.18 (m, 18 H), 0.99-0.73 (m, 12 H); MS (m/z) 310 (M\textsuperscript{+}, 5.86), 267 ((M-C\textsubscript{3}H\textsubscript{7})\textsuperscript{+}, 100); IR (neat, cm\textsuperscript{-1}) 2959, 2927, 2873, 2857, 1734, 1647, 1463, 1178; Elemental analysis: Cald for C\textsubscript{20}H\textsubscript{38}O\textsubscript{2}: C, 77.36; H, 12.33; Found: C, 77.37; H, 12.37.

(14) Ethyl 3-phenyl-3(E)-octenoate (lz-10-38, lz-10-117)

\[
\begin{array}{c}
\text{n-C\textsubscript{4}H\textsubscript{9}} \\
+ \text{PhMgCl in THF (1.9 M)}
\end{array} \xrightarrow{\text{Fe(acac)}_3 (2 \text{ mol\%})-78 \degree C, 1.3 \text{ h}} \text{E-2n}
\]

The reaction of Fe(acac)\textsubscript{3} (0.0027 g, 2 mol\%, 0.008 mmol), 1\text{i} (0.0681 g, 0.4 mmol),
toluene (5 mL), and a solution of PhMgCl in THF (0.6 mL, 1.9 M, 3 equiv, 1.1 mmol) afforded $E$-2n (0.0628 g, 63%): Liquid; $^1$H NMR (400 MHz, CDCl$_3$) 7.38 (d, $J = 7.6$ Hz, 2 H), 7.31 (t, $J = 7.4$ Hz, 2 H), 7.22 (t, $J = 7.4$ Hz, 1 H), 5.95 (t, $J = 7.2$ Hz, 1 H), 4.11 (q, $J = 7.1$ Hz, 2 H), 3.52 (s, 2 H), 2.24 (q, $J = 7.2$ Hz, 2 H), 1.52-1.37 (m, 4 H), 1.19 (t, $J = 7.1$ Hz, 3 H), 0.95 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) 171.4, 142.4, 132.7, 132.3, 128.2, 126.7, 125.9, 60.6, 36.0, 31.5, 28.7, 22.4, 14.0, 13.9; MS (m/z) 246 (M$^+$, 33.08), 129 (100); IR (neat, cm$^{-1}$) 2958, 2930, 2872, 1736, 1599, 1446, 1154; HRMS calcd for C$_{16}$H$_{22}$O$_2$ (M$^+$) 246.1614, found 246.1619.

(15) Ethyl 3-phenyl-3($E$)-undecenoate  (Iz-10-95)

The reaction of Fe(acac)$_3$ (0.0074 g, 5 mol%, 0.02 mmol), 1j (0.0829 g, 0.4 mmol), toluene (5 mL), and a solution of PhMgCl in THF (0.6 mL, 1.9 M, 3 equiv, 1.1 mmol) afforded $E$-2o (0.0720 g, 63%): Liquid; $^1$H NMR (400 MHz, CDCl$_3$) 7.39 (d, $J = 7.6$ Hz, 2 H), 7.31 (t, $J = 7.6$ Hz, 2 H), 7.23 (t, $J = 7.6$ Hz, 1 H), 5.96 (t, $J = 7.2$ Hz, 1 H), 4.11 (q, $J = 7.2$ Hz, 2 H), 3.52 (s, 2 H), 2.23 (q, $J = 7.5$ Hz, 2 H), 1.52-1.43 (m, 2 H), 1.41-1.23 (m, 8 H), 1.19 (t, $J = 7.2$ Hz, 3 H), 0.91 (t, $J = 6.8$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) 171.4, 142.4, 132.8, 132.3, 128.2, 126.7, 125.9, 60.6, 36.0, 31.8, 29.4, 29.3, 29.2, 29.0, 22.6, 14.1; MS (m/z) 288 (M$^+$, 33.17), 129 (100); IR (neat, cm$^{-1}$) 2926, 2855, 1736, 1599, 1446, 1154; HRMS calcd for C$_{19}$H$_{28}$O$_2$ (M$^+$) 288.2084, found 288.2082.

(16) Ethyl 4-phenyl-3-vinyl-2-propyl-3($Z$)-butenoate  (Iz-11-78)
The reaction of Fe(acac)$_3$ (0.0067 g, 5 mol%, 0.02 mmol), 1a (0.0923 g, 0.4 mmol), toluene (5 mL), and a solution of vinyl magnesium chloride in THF (0.71 mL, 1.7 M, 3 equiv, 1.2 mmol) afforded Z-2p (0.0850 g, 82%): Liquid; $^1$H NMR (300 MHz, CDCl$_3$) 7.39-7.30 (m, 4 H), 7.28-7.21 (m, 1 H), 6.79 (s, 1 H), 6.37 (dd, $J_1 = 17.6$ Hz, $J_2 = 11.1$ Hz, 1 H), 5.40 (dd, $J_1 = 17.6$ Hz, $J_2 = 1.1$ Hz, 1 H), 5.11 (d, $J = 11.1$ Hz, 1 H), 4.18 (q, $J = 7.1$ Hz, 2 H), 3.81 (dd, $J_1 = 8.4$ Hz, $J_2 = 6.3$ Hz, 1 H), 1.96-1.83 (m, 1 H), 1.74-1.60 (m, 1 H), 1.27 (t, $J = 7.2$ Hz, 3 H), 1.40-1.12 (m, 2 H), 0.73 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) 174.1, 137.8, 137.2, 137.1, 131.9, 128.8, 128.3, 127.0, 114.9, 60.7, 44.5, 31.9, 20.4, 14.2, 13.8; MS (m/z) 280.9 ((M+Na$^+$), 100); IR (neat, cm$^{-1}$) 2960, 2934, 2872, 1732, 1607, 1492, 1446, 1185; HRMS calcd for C$_{17}$H$_{22}$O$_2$Na (M+Na$^+$) 281.1512, found 281.1511.

(17) Ethyl 3-vinyl-2-propyl-3(Z)-undecenoate (lz-11-79)

The reaction of Fe(acac)$_3$ (0.0069 g, 5 mol%, 0.02 mmol), 1g (0.0977 g, 0.4 mmol), toluene (5 mL), and a solution of vinyl magnesium chloride in THF (0.71 mL, 1.7 M, 3 equiv, 1.2 mmol) afforded Z-2q (0.0938 g, 86%): Liquid; $^1$H NMR (300 MHz, CDCl$_3$) 6.21 (dd, $J_1 = 17.7$ Hz, $J_2 = 11.1$ Hz, 1 H), 5.65 (t, $J = 7.4$ Hz, 1 H), 5.15 (d, $J = 17.7$ Hz, 1 H), 4.91 (d, $J = 11.1$ Hz, 1 H), 4.11 (q, $J = 7.2$ Hz, 2 H), 3.48 (dd, $J_1 = 8.3$ Hz, $J_2 = 6.5$ Hz, 1 H).
Fe(acac)₃-Catalyzed Conjugate Addition of 1a with Grignard Reagents followed by quenching with D₂O affording Ethyl 4-phenyl-3-methyl-3-deuterium-2-propyl-3(Z)-butenoate Z-9 (lz-10-1)

![Diagram of the reaction]

The reaction of Fe(acac)₃ (0.0072 g, 5 mol%, 0.02 mmol), 1a (0.0940 g, 0.4 mmol), and toluene (5 mL) with a solution of CH₃MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) formed the solution at -78 °C after 2 h. The reaction mixture was quenched slowly with D₂O (0.5 mL) at -78 °C. After warming up to rt naturally, water (5 mL) was added. After extraction with diethyl ether (3 x 30 mL), the organic layer was washed subsequently with diluted HCl (1%, aq.), a saturated aqueous solution of NaHCO₃, brine, and dried over anhydrous Na₂SO₄. Evaporation and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded Z-9 (0.0909 g, 89%) (D: 97%): Liquid; 

**¹H NMR (400 MHz, CDCl₃)** 7.36-7.27 (m, 4 H), 7.22 (t, J = 7.0 Hz, 1 H), 6.49 (s, 1 H), 4.21-4.14 (m, 2 H), 3.70 (t, J = 7.6 Hz, 0.03 H), 1.84 (s, 3 H), 1.81-1.72 (m, 1 H), 1.60-1.48 (m, 1 H), 1.29 (t, J = 7.2 Hz, 3 H), 1.25-1.15 (m, 1 H), 1.15-1.02 (m, 1 H), 0.77
1,2-Addition Reaction of Acrylaldehyde with the Organometallic Intermediate 8
Formed via Fe(acac)₃-Catalyzed Conjugate Addition of 1d with CH₃MgCl. Synthesis of Ethyl 4-phenyl-3-methyl-2-(1′-hydroxyl-2-propenyl)-2-methyl-3(Z)-butenoate Z-10:

The reaction of Fe(acac)₃ (0.0074 g, 5 mol%, 0.02 mmol), 1d (0.0803 g, 0.4 mmol), and toluene (5 mL) with a solution of CH₃MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) formed the solution at -78 °C after 1 h. To the reaction mixture was added acrylaldehyde (0.0734 g, 1.3 mmol) at -78 °C. After 1.5 h, the reaction mixture was quenched slowly with saturated NH₄Cl (1 mL) at -78 °C, followed by warming up to rt naturally and the addition of water (5 mL) at this temperature. After extraction with diethyl ether (3 x 30 mL), the organic layer was washed subsequently with diluted HCl (1%, aq.), a saturated aqueous solution of NaHCO₃, brine, and dried over anhydrous Na₂SO₄. Evaporation and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) afforded Z-10 (major isomer: 0.0531 g, 51%, minor isomer: 0.0218 g, 18%, dr = 71/29). Major isomer (more polar): Liquid; ¹H NMR (400 MHz, CDCl₃) 7.25 (t, J = 7.2 Hz, 2 H), 7.20-7.14 (m, 3 H), 6.60 (s, 1 H), 6.15-6.05 (m, 1 H), 5.32 (d, J = 17.2 Hz, 1 H), 5.23 (d,
$J = 10.8 \text{ Hz, 1 H), 4.39 (t, } J = 5.6 \text{ Hz, 1 H), 3.79-3.70 (m, 1 H), 3.58-3.48 (m, 1 H), 2.71$
(d, $J = 6.4 \text{ Hz, 1 H), 1.97 (d, } J = 1.2 \text{ Hz, 3 H), 1.27 (s, 3 H), 1.09 (t, } J = 7.2 \text{ Hz, 3 H); } ^{13}\text{C}$
NMR (CDCl$_3$, 100 MHz) 175.0, 138.2, 137.2, 136.1, 129.9, 128.7, 127.5, 126.4, 116.6,
76.5, 60.5, 55.3, 23.8, 21.1, 13.7; MS (ESI, m/z) 297.1 ((M+Na$^+$), 100); IR (neat, cm$^{-1}$)
3509, 2982, 2939, 1729, 1645, 1598, 1442, 1241; Elemental analysis: Cald for C$_{17}$H$_{22}$O$_3$:
C, 74.42; H, 8.08; Found: C, 74.46; H, 8.05. The following $^1$H NMR data were recorded
for the minor isomer (less polar): Liquid, $^1$H NMR (400 MHz, CDCl$_3$) 7.25 (t, $J = 7.4 \text{ Hz,}$
2 H), 7.18 (t, $J = 7.0 \text{ Hz, 1 H), 7.08 (d, } J = 8.0 \text{ Hz, 2 H), 6.56 (s, 1 H), 5.83-5.74 (m, 1 H),}$
5.34 (d, $J = 17.2 \text{ Hz, 1 H), 5.21 (d, } J = 10.8 \text{ Hz, 1 H), 4.41 (t, } J = 6.4 \text{ Hz, 1 H), 3.67 (d, } J$
$= 7.6 \text{ Hz, 1 H), 3.55-3.43 (m, 1 H), 3.43-3.37 (m, 1 H), 2.04 (d, } J = 1.2 \text{ Hz, 3 H), 1.33 (s,}$
3 H), 1.06 (t, $J = 7.0 \text{ Hz, 3 H).}$

**Coupling Reaction of Methyl Chloroformate with the Organometallic Intermediate**
8 Formed via Fe(acac)$_3$-Catalyzed Conjugate Addition of 1d with CH$_3$MgCl.

**Synthesis of Ethyl 4-phenyl-3-methyl-2-methoxycarbonyl-2-methyl-3(Z)-butenoate**
Z-11:

![Reaction Diagram]

The reaction of Fe(acac)$_3$ (0.0074 g, 5 mol%, 0.02 mmol), 1d (0.0800 g, 0.4 mmol),
and toluene (5 mL) with a solution of CH$_3$MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol)
formed the solution at -78 °C after 1 h. To the reaction mixture was added methyl
chloroformate (0.1907 g, 2 mmol) at -78 °C followed by warming up to rt naturally. After
7 h, the reaction mixture was sequentially quenched with saturated NH$_4$Cl (1 mL) at 0 °C.
and water (5 mL) at rt. After extraction with diethyl ether (3 x 30 mL), the organic layer was washed subsequently with diluted HCl (1%, aq.), a saturated aqueous solution of NaHCO₃, brine, and dried over anhydrous Na₂SO₄. Evaporation and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded Z-11 (Z/E = 34/1) (0.0650 g, 59%): Liquid; ¹H NMR (300 MHz, CDCl₃) 7.27-7.15 (m, 5 H), 6.61 (s, 1 H), 3.95-3.82 (m, 2 H), 3.39 (s, 3 H), 1.92 (s, 3 H), 1.56 (s, 3 H), 1.18 (t, J = 7.1 Hz, 3 H); ¹³C NMR (CDCl₃, 100 MHz) 171.6, 170.9, 137.4, 134.0, 129.6, 128.5, 127.7, 126.6, 61.4, 58.8, 52.2, 23.3, 22.1, 13.7; MS (ESI, m/z) 277.4 ((M+H⁺), 100), 299.3 ((M+Na⁺), 37.50); IR (neat, cm⁻¹) 2981, 2951, 1744, 1732, 1647, 1599, 1442, 1258, 1109; Elemental analysis: Cald for C₁₆H₂₀O₄: C, 69.54; H, 7.30; Found: C, 69.56; H, 7.30.

**Coupling Reaction of Acetyl Chloride with the Organometallic Intermediate 8 Formed via Fe(acac)₃-Catalyzed Conjugate Addition of 1d with CH₃MgCl. Synthesis of Ethyl 4-phenyl-3-methyl-2-methylcarbonyl-2-methyl-3(Z)-butenoate Z-12:**

The reaction of Fe(acac)₃ (0.0074 g, 5 mol%, 0.02 mmol), 1d (0.0809 g, 0.4 mmol), and toluene (5 mL) with a solution of CH₃MgCl in THF (0.4 mL, 3 M, 3 equiv, 1.2 mmol) formed the solution at -78 °C after 1 h. To the reaction mixture was slowly added acetyl chloride (0.14 mL, 2 mmol) at -78 °C. After 1 h, the reaction mixture was quenched sequentially with saturated NH₄Cl (1 mL) at -78 °C and water (5 mL) at rt. After extraction with diethyl ether (3 x 30 mL), the organic layer was washed subsequently with diluted HCl (1%, aq.), a saturated aqueous solution of NaHCO₃, brine, and dried.
over anhydrous Na$_2$SO$_4$. Evaporation and column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 60/1) afforded Z-12 (0.0630 g, 61%): Liquid; $^1$H NMR (300 MHz, CDCl$_3$) 7.27 - 7.18 (m, 3 H), 7.14 (d, $J$ = 6.9 Hz, 2 H), 6.65 (s, 1 H), 3.90 - 3.70 (m, 2 H), 2.04 (s, 3 H), 1.91 (d, $J$ = 1.5 Hz, 3 H), 1.51 (s, 3 H), 1.16 (t, $J$ = 7.1 Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) 205.5, 171.3, 137.1, 135.0, 129.9, 128.8, 127.8, 126.9, 65.0, 61.3, 27.3, 23.6, 20.9, 13.7; MS (ESI, m/z) 283.2 ((M+Na$^+$), 100), 315.2 ((M+MeOH+Na$^+$), 15.00); IR (neat, cm$^{-1}$) 2982, 1736, 1715, 1637, 1599, 1443, 1244, 1095; Elemental analysis: Cald for C$_{16}$H$_{20}$O$_3$: C, 73.82; H, 7.74; Found: C, 73.76; H, 7.77.

References:
