Supporting Information

Copper-Catalyzed Asymmetric 1,4-Conjugate Addition of Grignard Reagents to Linear $\alpha,\beta,\gamma,\delta$-unsaturated ketones

Zhenni Ma, Fang Xie*, Han Yu, Yiren Zhang, Xiaoting Wu and Wanbin Zhang*

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

Table of Contents

1. General Experimental Conditions .................................................................................. 2
2. General Procedure for Preparation of the Substrates1 ............................................... 2
3. General Procedure for Copper-Catalyzed Enantioselective Conjugate Addition ...... 2
   Solvent Screen for Preliminary Reaction Conditions Optimizing ................................. 3
4. Characterization of the New Substrates and Products ................................................ 3
5. Conversion of 2a to 5a ......................................................................................... 11
   Proposed stereochemical transition states ................................................................... 12
   References .................................................................................................................. 12
6. NMR Charts of New Compounds ............................................................................. 13
7. Chiarl HPLC Charts ................................................................................................. 27
8. X-ray structure of 2a ................................................................................................. 47
1. General Experimental Conditions

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen. Dichloromethane were dried according to published procedures. Commercially available reagents were used without further purification. All reactions were performed under a nitrogen atmosphere, and the workup was carried out in air unless otherwise stated.

NMR spectra were recorded on a Varian MERCURY plus-400 spectrometer. The chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Coupling constants are reported in Hz and refer to apparent peak multiplicities. Optical rotations were measured with a SPSI SGW-1 polarimeter. All ee values were determined by HPLC using a Daicel Chiralcel OD-H or AD-H column.

2. General Procedure for Preparation of the Substrates 1

To a solution of 2.2 g of NaOH in 20 mL of H₂O and 43 mmol of aromatic ketone in 12 mL ethanol at 0 °C was gradually added 1 equiv of aromatic aldehyde (43 mmol). The mixture was then allowed to warm to room temperature and stirred for 4 h, after which a precipitate of the product formed. The product was collected by suction filtration on a Buchner funnel and washed repeatedly with cold water in order to remove all traces of sodium hydroxide. Recrystallization of the product from ethanol afforded enones 1a-r. Dienones 1a (CAS: 29179-25-7), 1c (CAS: 1301638-20-9), 1d (CAS: 133505-13-2), 1e (CAS: 40414-49-1), 1g (CAS: 40414-46-8), 1h (CAS: 884489-91-2), 1i (CAS: 873873-33-7), 1j (CAS: 127099-89-2), 1k (CAS: 296759-66-5), 1l (CAS: 1222540-12-6), 1m (CAS: 141368-95-8), 1n (CAS: 1108204-11-0), 1o (CAS: 175477-55-1), 1p (CAS: 137444-54-3), 1q (CAS: 135950-66-2), and 1r (CAS: 29179-13-3) are in good agreement with reported literature data. New compounds 1b and 1f were prepared according to the procedures used for 1a.

3. General Procedure for Copper-Catalyzed Enantioselective Conjugate Addition

A flame dried Schlenk tube was charged with Cu(I)(MeCN)₄ClO₄ 2.9 mg (0.009 mmol) and 1.1 equivalents of ligand (0.010 mmol) under nitrogen, and the mixture was dissolved in dry dichloromethane (1.5 mL), resulting an orange solution. The solution was stirred at 25 °C for 2 h and then cooled to −70 °C. The substrate 1 (0.30 mmol dissolved in 1.0 mL dry toluene) was then added dropwise over 3 min. The solution was stirred for 5 min at −70 °C and gradually turned to light yellow. Grignard reagent (0.45 mmol, 0.15 mL of 3 M sol. in hexane) was added dropwise over 3 min.
The reaction mixture was stirred at \(-70^\circ C\) for 24 h and monitored by TLC until full conversion of product was observed. The reaction mixture was quenched with aqueous saturated NH\(_4\)Cl and extracted with ethyl acetate (5 mL \(\times\) 3). The organic extracts were combined, concentrated and the residue was purified by silica gel column chromatography to afford the product \(2\text{-}4\). Enantiomeric excess was determined by chiral HPLC. Melting points of racemic product \(2\text{-}4\) was measured with SGW X-4 micro melting point apparatus.

### Solvent Screen for Preliminary Reaction Conditions Optimizing

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)(^a)</th>
<th>Ee (%)(^b)</th>
</tr>
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<tr>
<td>1</td>
<td>DCM</td>
<td>77</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>83</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
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<td>38</td>
</tr>
<tr>
<td>4</td>
<td>Et(_2)O</td>
<td>80</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^a\) Yield of the isolated product. \(^b\) Determined by HPLC, Chiralcel AD-H column.

### 4. Characterization of the New Substrates and Products

![Chemical Structure](image)

\((2E,4E)\)-1-phenyl-5-\(\alpha\)-tolylpenta-2,4-dien-1-one (1b)

Yellow solid, 68% yield; mp: 57-58 \(^\circ\)C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.01-7.97 (m, 2H), 7.69-7.55 (m, 3H), 7.52-7.47 (m, 2H), 7.32-7.18 (m, 4H), 7.10 (d, \(J = 15.6\) Hz, 1H), 6.96 (dd, \(J = 11.6, 15.6\) Hz, 1H), 2.41 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 190.7, 145.4, 139.8, 138.5, 137.0, 135.2, 133.0, 131.0, 129.3, 128.9, 128.6, 128.1, 126.6, 125.8, 125.5, 20.0; HRMS (ESI-TOF) Calcd. for C\(_{18}\)H\(_{17}\)O (M+H\(^+\)) 249.1279, found 249.1265; IR (\(\nu/cm^{-1}\)): 3086, 3054, 3011, 2924, 2740, 2601, 1957, 1652, 1575, 1384.
(2E,4E)-5-(2-chlorophenyl)-1-phenylpenta-2,4-dien-1-one (1f)

Yellow solid, 76% yield; mp: 58-59 °C; 1H NMR (CDCl₃, 400 MHz) δ 7.97 (dd, J = 1.6, 8.0 Hz, 2H), 7.69-7.38 (m, 8H), 7.31-7.22 (m, 1H), 7.11 (d, J = 15.6 Hz, 1H), 7.02 (dd, J = 11.2, 15.6 Hz, 1H); 13C NMR (CDCl₃, 100 MHz) δ 190.8, 144.7, 138.3, 137.5, 134.3, 133.0, 130.4, 129.4, 128.8, 128.7, 128.4, 127.2, 127.0, 126.7; HRMS (EI) m/z HRMS (ESI-TOF) Calcd. for C₁₇H₁₄ClO (M+H)+ 265.1592, found 265.1592; IR (v/cm⁻¹): 2961, 2924, 2857, 1659, 1597, 1576, 1032, 1017, 803, 770, 749.

(E)-3-methyl-1,5-diphenylpent-4-en-1-one (2a)

Pale yellow solid, mp: 42-43 °C; 86% yield and 94% ee (R); 1H NMR (CDCl₃, 400 MHz) δ 7.99-7.95 (m, 2H), 7.59-7.54 (m, 1H), 7.50-7.42 (m, 2H), 7.32-7.27 (m, 2H), 7.23-7.17 (m, 1H), 6.43 (d, J = 15.6 Hz, 1H), 6.23 (dd, J = 7.2, 15.6 Hz, 1H), 3.17-2.96 (m, 3H), 1.21 (d, J = 6.4 Hz, 3H); 13C NMR (CDCl₃, 100 MHz) δ 199.4, 137.7, 137.5, 135.1, 133.2, 128.9, 128.8, 128.7, 128.3, 127.3, 126.3, 45.8, 33.4, 20.5; HRMS (ESI-TOF) Calcd. for C₁₈H₁₉O (M+H)+ 251.1436, found 251.1442; [α]D²⁵ = 58.383 (c = 0.13 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: i-PrOH 98:2, UV 254 nm, 0.5 mL/min, t_R= 15.14 min (major) and t_R= 16.67 min (minor).

(E)-3-methyl-1-phenyl-5-o-tolylpent-4-en-1-one (2b)

Yellow oil, 84% yield and 94% ee (R); 1H NMR (CDCl₃, 400 MHz) δ 8.01-7.94 (m, 2H), 7.59-7.54 (m, 1H), 7.51-7.44 (m, 2H), 7.38-7.35 (m, 1H), 7.14-7.09 (m, 3H), 6.60 (d, J = 15.6 Hz, 1H), 6.07 (dd, J = 6.8, 15.6 Hz, 1H), 3.16-2.96 (m, 3H), 2.29 (s, 3H), 1.21 (d, J = 6.4 Hz, 3H); 13C NMR (CDCl₃, 100 MHz) δ 199.5, 137.6, 136.9, 136.5, 135.3, 133.2, 130.3, 128.8, 128.3, 127.2, 126.8, 126.2, 125.7, 45.9, 33.9, 20.7, 20.0; HRMS (ESI-TOF) Calcd. for C₁₀H₁₂O (M+H)+ 265.1592, found 265.1575; [α]D²⁵ = -6.914 (c = 0.26 MeOH); HPLC conditions: HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: i-PrOH 98:2, UV 254 nm, 0.5 mL/min, t_R= 12.70 min (major) and t_R= 13.57 min (minor).
(E)-3-methyl-1-phenyl-5-m-tolylpent-4-en-1-one (2c)

Yellow oil, 82% yield and 87% ee (R); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.98-7.94 (m, 2H), 7.59-7.53 (m, 1H), 7.49-7.43 (m, 2H), 7.20-7.10 (m, 3H), 7.01 (d, J = 7.2 Hz, 1H), 6.38 (d, J = 15.6 Hz, 1H), 6.21 (dd, J = 6.8, 15.6 Hz, 1H), 3.15-2.95 (m, 3H), 2.32 (s, 3H), 1.19 (d, J = 6.4 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 199.5, 138.2, 137.7, 137.5, 134.9, 133.2, 128.9, 128.8, 128.6, 128.3, 128.1, 127.0, 123.5, 45.8, 33.4, 21.6, 20.5; HRMS (ESI-TOF) Calcd. for C$_{19}$H$_{21}$O (M+H)$^+$ 265.1592, found 265.1578; $\left[\alpha\right]_D^{25} = 36.202$ (c = 0.16 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: i-PrOH 98:2, UV 254 nm, 0.5 mL/min, $t_R$ = 14.19 min (major) and $t_R$ = 15.41 min (minor).

(E)-3-methyl-1-phenyl-5-p-tolylpent-4-en-1-one (2d)

Yellow oil, 90% yield and 76% ee (R); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.98-7.94 (m, 2H), 7.58-7.53 (m, 1H), 7.49-7.43 (m, 2H), 7.24-7.20 (m, 2H), 7.11-7.06 (m, 2H), 6.38 (d, J = 15.6 Hz, 1H), 6.17 (dd, J = 6.8, 15.6 Hz, 1H), 3.15-2.95 (m, 3H), 2.31 (s, 3H), 1.18 (d, J = 6.4 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 199.5, 137.5, 137.0, 134.9, 134.1, 133.2, 129.4, 128.8, 128.7, 128.4, 126.2, 45.9, 33.4, 21.4, 20.5; HRMS (ESI-TOF) Calcd. for C$_{19}$H$_{21}$O (M+H)$^+$ 265.1592, found 265.1582; $\left[\alpha\right]_D^{25} = -3.329$ (c = 0.10 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: i-PrOH 98:2, UV 254 nm, 0.5 mL/min, $t_R$ = 13.96 min (major) and $t_R$ = 16.84 min (minor).

(E)-5-(4-methoxyphenyl)-3-methyl-1-phenylpent-4-en-1-one (2e)$^{22}$

Yellow oil, 85% yield and 83% ee (R); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.98-7.94 (m, 2H), 7.58-7.53 (m, 1H), 7.49-7.43 (m, 2H), 7.27-7.24 (m, 2H), 6.84-6.80 (m, 2H), 6.35 (d, J = 15.6 Hz, 1H), 6.08 (dd, J = 6.8, 15.6 Hz, 1H), 3.79 (s, 3H), 3.14-2.95 (m, 3H), 1.18 (d, J = 6.8 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 199.6, 159.0, 137.5, 133.2, 133.0, 130.5, 128.8, 128.3, 128.1, 127.4, 114.1, 55.5, 45.9, 33.4, 20.6; HRMS (ESI-TOF) Calcd. for C$_{19}$H$_{23}$O$_2$ (M+H)$^+$ 281.1542, found 281.1541; $\left[\alpha\right]_D^{25} = 56.766$ (c = 0.38 MeOH); HPLC conditions: The enantiomeric excess was
determined by HPLC (Chiralcel AD-H), Hex: \(i\)-PrOH 98:2, UV 254 nm, 0.5 mL/min, \(t_R=30.81\) min (major) and \(t_R=33.00\) min (minor).

**(E)-5-(2-chlorophenyl)-3-methyl-1-phenylpent-4-en-1-one (2f)**

Yellow oil, 83% yield and 96% ee (\(R\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.99-7.94 (m, 2H), 7.59-7.54 (m, 1H), 7.50-7.44 (m, 3H), 7.34-7.29 (m, 1H), 7.21-7.10 (m, 2H), 6.78 (d, \(J = 15.6\) Hz, 1H), 6.23 (dd, \(J = 6.8, 15.6\) Hz, 1H), 3.18-2.99 (m, 3H), 1.22 (d, \(J = 6.4\) Hz, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 199.3, 138.0, 137.5, 136.8, 133.3, 133.0, 129.8, 128.8, 128.4, 128.3, 127.0, 126.9, 125.1, 45.7, 33.6, 20.3; HRMS (ESI-TOF) Calcd. for C\(_{18}\)H\(_{18}\)ClO (M+H)\(^+\) 285.1046, found 285.1035; \([\alpha]_D^{25} = 49.933\) (c = 0.18 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: \(i\)-PrOH 98:2, UV 254 nm, 0.5 mL/min, \(t_R=15.25\) min (major) and \(t_R=16.19\) min (minor).

**(E)-5-(4-chlorophenyl)-3-methyl-1-phenylpent-4-en-1-one (2g)**

Yellow oil, 86% yield and 97% ee (\(R\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.97-7.93 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.44 (m, 2H), 7.25-7.20 (m, 4H), 6.36 (d, \(J = 16.0\) Hz, 1H), 6.20 (dd, \(J = 7.2, 16.0\) Hz,1H), 3.14-2.97 (m, 3H), 1.19 (d, \(J = 6.8\) Hz, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 199.3, 137.5, 136.2, 135.8, 133.2, 132.8, 128.8, 128.7, 128.3, 127.7, 127.6, 45.7, 33.3, 20.4; HRMS (ESI-TOF) Calcd. for C\(_{19}\)H\(_{18}\)ClO (M+H)\(^+\) 285.1046, found 285.1050; \([\alpha]_D^{25} = 20.597\) (c = 0.32 MeOH); HPLC conditions: HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: \(i\)-PrOH 98:2, UV 254 nm, 0.5 mL/min, \(t_R=22.13\) min (major) and \(t_R=24.36\) min (minor).

**(E)-3-methyl-5-phenyl-1-\(o\)-tolylpent-4-en-1-one (2h)**

Yellow oil, 73% yield and 36% ee (\(R\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.61 (d, \(J = 7.6\) Hz, 1H), 7.39-7.16 (m, 8H), 6.38 (d, \(J = 16.0\) Hz, 1H), 6.18 (dd, \(J = 7.2, 16.0\) Hz, 1H), 3.08-2.90 (m, 3H), 2.46 (s, 3H), 1.19 (d, \(J = 6.4\) Hz, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 203.9, 138.7, 138.2, 137.7, 135.0, 132.2, 131.4, 128.9, 128.8, 128.6, 127.3, 126.4, 125.9, 48.9, 33.8, 21.4, 20.7; HRMS (ESI-TOF) Calcd. for C\(_{19}\)H\(_{21}\)O (M+H)\(^+\)
265.1592, found 265.1585; [α]D\(^{25}\) = 5.447 (c = 0.11 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: i-PrOH 98:2, UV 254 nm, 0.5 mL/min, t\(_R\) = 13.80 min (major) and t\(_R\) = 14.50 min (minor).

\[(E)-3\text{-methyl-5-phenyl-1-\text{-}m\text{-}tolylpent-4-en-1-one (2i)}\]

Yellow oil, 84% yield and 92% ee (R); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.78-7.73 (m, 2H), 7.38-7.27 (m, 6H), 7.22-7.16 (m, 1H), 6.41 (d, \(J\) = 15.6 Hz, 1H), 6.23 (dd, \(J\) = 6.8, 15.6 Hz, 1H), 3.14-2.95 (m, 3H), 2.41 (s, 3H), 1.19 (d, \(J\) = 6.4 Hz, 3H); \(^1\)3C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 199.7, 138.6, 137.7, 137.6, 135.2, 134.0, 128.9, 128.7, 128.6, 127.2, 127.1, 126.3, 125.6, 45.9, 33.4, 21.6, 20.4; HRMS (ESI-TOF) Calcd. for C\(_{19}\)H\(_{21}\)O (M+H)\(^+\) 265.1592, found 265.1584; [α]D\(^{25}\) = 21.971 (c = 0.10 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: i-PrOH 98:2, UV 254 nm, 0.5 mL/min, t\(_R\) = 14.59 min (major) and t\(_R\) = 16.51 min (minor).

\[(E)-3\text{-methyl-5-phenyl-1-\text{-}p\text{-}tolylpent-4-en-1-one (2j)}\]

Yellow oil, 87% yield and 82% ee (R); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.86 (d, \(J\) = 8.0 Hz, 2H), 7.35-7.23 (m, 6H), 7.21-7.16 (m, 1H), 6.41 (d, \(J\) = 16.0 Hz, 1H), 6.22 (dd, \(J\) = 7.2, 16.0 Hz, 1H), 3.12-2.92 (m, 3H), 2.41 (s, 3H), 1.18 (d, \(J\) = 6.0 Hz, 3H); \(^1\)3C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 199.1, 144.0, 137.7, 135.3, 135.0, 129.5, 128.7, 128.5, 127.2, 127.1, 126.3, 45.7, 33.4, 21.8, 20.5; HRMS (ESI-TOF) Calcd. for C\(_{19}\)H\(_{23}\)O (M+H)\(^+\) 265.1592, found 265.1592; [α]D\(^{25}\) = 25.421 (c = 0.22 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: i-PrOH 98:2, UV 254 nm, 0.5 mL/min, t\(_R\) = 16.56 min (major) and t\(_R\) = 19.20 min (minor).

\[(E)-1\text{-}(3\text{-chlorophenyl)-3\text{-methyl-5-phenylpent-4-en-1-one (2k)}\]

Yellow oil, 80% yield and 96% ee (R); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.94-7.92 (m, 1H), 7.85-7.81 (m, 1H), 7.55-7.51 (m, 1H), 7.43-7.39 (m, 1H), 7.35-7.24 (m, 4H), 7.22-7.19 (m, 1H), 6.42 (d, \(J\) = 15.6 Hz, 1H), 6.21 (dd, \(J\) = 6.8, 15.6 Hz, 1H),
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0. Excess was determined by HPLC (Chiralcel A)

3.13-2.95 (m, 3H), 1.20 (d, J = 6.8 Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.1, 139.0, 137.6, 137.3, 134.8, 133.1, 130.2, 129.0, 128.7, 128.5, 127.4, 126.4, 126.3, 45.9, 33.3, 20.5; HRMS (ESI-TOF) Calcd. for C\(_{18}\)H\(_{18}\)OCl (M+H)\(^+\) 285.1046, found 285.1043; \([\alpha]_D^{25}\) = -3.745 (c = 0.32 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: \(i\)-PrOH 98:2, UV 254 nm, 0.5 mL/min, \(t_R\) = 13.49 min (major) and \(t_R\) = 14.48 min (minor).

\[
\begin{align*}
\text{(E)} & \quad \text{-1-(4-chlorophenyl)-3-methyl-5-phenylpent-4-en-1-one (2l)} \\
\text{Yellow oil, 88% yield and 97% ee (R); } & \quad ^1\text{H NMR (CDCl}_3\text{, 400 MHz)} \quad \delta \ 7.92-7.88 \\
& \text{(m, 2H), 7.45-7.41 (m, 2H), 7.34-7.25 (m, 4H), 7.22-7.17 (m, 1H), 6.40 (d, J = 15.6} \\
& \text{Hz, 1H), 6.20 (dd, J = 6.8, 15.6 Hz, 1H), 3.11-2.93 (m, 3H), 1.19 (d, J = 6.8 Hz, 3H);} \\
& \quad \text{\(^{13}\)C NMR (CDCl}_3\text{, 100 MHz)} \quad \delta \ 198.1, 139.7, 137.6, 135.8, 134.9, 129.8, 129.1, 129.0, \\
& \text{128.7, 127.4, 126.3, 45.8, 33.4, 20.5; HRMS (ESI-TOF) Calcd. for C\(_{18}\)H\(_{18}\)OCl} \\
& \text{(M+H)}^+ \quad \text{285.1046, found 285.1066; } \quad \text{\([\alpha]_D^{25}\) = 16.852 (c = 0.32 MeOH); HPLC} \\
& \text{conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: } \\
& \text{\(i\)-PrOH 98:2, UV 254 nm, 0.5 mL/min, } \text{\(t_R\) = 20.65 min (major) and } \text{\(t_R\) = 23.48 min (minor).} \\
\end{align*}
\]

\[
\begin{align*}
\text{(E)-3-methyl-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (2m)} \\
\text{Yellow oil, 92% yield and 95% ee (R); } & \quad ^1\text{H NMR (CDCl}_3\text{, 400 MHz)} \quad \delta \ 8.05 (d, J = 8.4} \\
& \text{Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.35-7.27 (m, 4H), 7.23-7.17 (m, 1H), 6.42 (d,} \\
& \text{J = 15.6 Hz, 1H), 6.23 (dd, J = 6.8, 15.6 Hz, 1H), 3.18-2.99 (m, 3H), 1.21 (d, J = 6.4} \\
& \text{Hz, 3H); \quad \text{\(^{13}\)C NMR (CDCl}_3\text{, 100 MHz)} \quad \delta \ 198.4, 140.2, 137.6, 135.8, 134.6, \\
& \text{134.5 (q, J = 35.3} \\
& \text{Hz), 129.1, 128.7, 128.6, 127.4, 126.3, 125.9 (q, J = 3.7 Hz), 123.8 (q, J = 271.0 Hz),} \\
& \quad 46.1, 33.3, 20.5; HRMS (ESI-TOF) Calcd. for C\(_{19}\)H\(_{18}\)OF\(_3\) (M+H)\(^+\) \text{317.1153, found} \\
& \text{317.1163; } \quad \text{\([\alpha]_D^{25}\) = 29.960 (c = 0.20 MeOH); HPLC conditions: The enantiomeric} \\
& \text{excess was determined by HPLC (Chiralcel AD-H), Hex: } \quad \text{\(i\)-PrOH 98:2, UV 254 nm,} \\
& \text{0.5 mL/min, } \text{\(t_R\) = 11.99 min (major) and } \text{\(t_R\) = 14.08 min (minor).} \\
\end{align*}
\]

\[
\begin{align*}
\text{(E)-3-methyl-1-(naphthalen-2-yl)-5-phenylpent-4-en-1-one (2n)} \\
\text{Yellow oil, 70% yield and 83% ee (R); } & \quad ^1\text{H NMR (CDCl}_3\text{, 400 MHz)} \quad \delta \ 8.48 (s,}
\end{align*}
\]
1H), 8.06-8.02 (m, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.91-7.87 (m, 2H), 7.62-7.53 (m, 2H), 7.35-7.25 (m, 4H), 7.22-7.17 (m, 1H), 6.45 (d, J = 16.0 Hz, 1H), 6.27 (dd, J = 6.8, 16.0 Hz, 1H), 3.27-3.10 (m, 3H), 1.24 (d, J = 6.4 Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 199.4, 137.7, 135.8, 135.2, 134.8, 132.8, 130.0, 129.8, 128.8, 128.7, 128.6, 128.0, 127.3, 127.0, 126.3, 124.2, 45.9, 33.5, 20.5; HRMS (ESI-TOF) Calcd. for \(\text{C}_{22}\text{H}_{20}\text{ONa}+\) 323.14/12, found 323.13/6; \([\alpha]_D^{25}\) = -2.497 (c = 0.10 MeOH);

**HPLC conditions:** The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: \(i\)-PrOH 98:2, UV 254 nm, 0.5 mL/min, \(t_R= 18.00\) min (major) and \(t_R= 23.08\) min (minor).

(E)-1,5-bis(4-chlorophenyl)-3-methylpent-4-en-1-one (2o)

Pale yellow solid, 92% yield and 98% ee (R); mp: 68-69 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.91-7.87 (m, 2H), 7.45-7.41 (m, 2H), 7.24 (s, 4H), 6.36 (d, J = 16.4 Hz, 1H), 6.18 (dd, J = 7.2, 16.4 Hz, 1H), 3.11-2.93 (m, 3H), 1.19 (d, J = 6.4 Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.0, 139.7, 136.1, 135.7, 135.5, 132.9, 129.7, 129.2, 128.8, 127.8, 127.5, 45.6, 33.3, 20.4; HRMS (ESI-TOF) Calcd. for \(\text{C}_{18}\text{H}_{17}\text{OCl}_2\) (M+H\(^+\)) 319.0618, found 319.0636; \([\alpha]_D^{25}\) = 50.984 (c = 0.38 MeOH);

**HPLC conditions:** The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: \(i\)-PrOH 98:2, UV 254 nm, 0.5 mL/min, \(t_R= 22.64\) min (major) and \(t_R= 25.64\) min (minor).

(E) -3-methyl-5-phenyl-1-(thiophen-2-yl)pent-4-en-1-one (2p)

Yellow oil, 69% yield and 62% ee (R); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.73-7.71 (m, 1H), 7.64-7.62 (m, 1H), 7.34-7.26 (m, 4H), 7.22-7.19 (m, 1H), 7.14-7.11 (m, 1H), 6.43 (d, J = 15.6 Hz, 1H), 6.21 (dd, J = 6.8, 15.6 Hz, 1H), 3.13-2.88 (m, 3H), 1.20 (d, J = 6.8 Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 192.3, 145.0, 137.6, 134.8, 133.9, 132.1, 128.9, 128.7, 128.3, 127.3, 126.3, 46.6, 33.8, 20.4; HRMS (ESI-TOF) Calcd. for \(\text{C}_{16}\text{H}_{15}\text{OS}\) (M+H\(^+\)) 257.1000, found 257.0999; \([\alpha]_D^{25}\) = -7.490 (c = 0.10 MeOH);

**HPLC conditions:** The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: \(i\)-PrOH 98:2, UV 254 nm, 0.5 mL/min, \(t_R= 40.06\) min (major) and \(t_R= 45.96\) min (minor).
\( (E) \)-1-(furan-2-yl)-3-methyl-5-phenylpent-4-en-1-one (2q)

Yellow oil, 86% yield and 89% ee (\( R \)); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) 7.59-7.57 (m, 1H), 7.35-7.26 (m, 4H), 7.21-7.16 (m, 2H), 6.54-6.51 (m, 1H), 6.40 (d, \( J = 16.0 \) Hz, 1H), 6.19 (dd, \( J = 7.2, 16.0 \) Hz, 1H), 3.10-2.80 (m, 3H), 1.18 (d, \( J = 6.8 \) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta \) 188.6, 153.2, 146.6, 137.6, 134.8, 128.9, 128.7, 127.3, 126.3, 117.4, 112.5, 45.6, 33.6, 20.5; HRMS (ESI-TOF) Calcd. for C\(_{16}\)H\(_{17}\)O\(_2\) (M+H)\(^+\) 241.1229, found 241.1217; \([\alpha]_D^{25} = 14.596 \) (c = 0.26 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: \( i\)-PrOH 98:2, UV 254 nm, 0.5 mL/min, \( t_R = 21.68 \) min (major) and \( t_R = 25.00 \) min (minor).

\( (E) \)-3-ethyl-1,5-diphenylpent-4-en-1-one (3a)

Pale yellow solid, 77% yield and 66% ee (\( R \)); mp: 75-76 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) 7.95 (m, 2H), 7.57-7.53 (m, 1H), 7.48-7.43 (m, 2H), 7.34-7.26 (m, 4H), 7.21-7.16 (m, 1H), 6.40 (d, \( J = 16.0 \) Hz, 1H), 6.07 (dd, \( J = 7.2, 16.0 \) Hz, 1H), 3.12-3.04 (m, 2H), 2.90-2.80 (m, 1H), 1.69-1.40 (m, 2H), 0.94 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta \) 199.7, 137.7, 137.6, 133.5, 133.2, 130.6, 128.8, 128.7, 128.4, 127.3, 126.3, 44.2, 41.0, 28.2, 12.1; HRMS (ESI-TOF) Calcd. for C\(_{19}\)H\(_{22}\)O (M+H)\(^+\) 265.1592, found 265.1596; \([\alpha]_D^{25} = -2.497 \) (c = 0.16 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: \( i\)-PrOH 98:2, UV 254 nm, 0.5 mL/min, \( t_R = 17.46 \) min (major) and \( t_R = 20.57 \) min (minor).

\( (E) \)-3-benzyl-1,5-diphenylpent-4-en-1-one (4a)

Pale yellow solid, 40% yield and 4% ee (\( R \)); mp: 103-104 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) 7.90-7.87 (m, 2H), 7.57-7.52 (m, 1H), 7.46-7.41 (m, 2H), 7.31-7.17 (m, 1H), 6.33 (d, \( J = 16.0 \) Hz, 1H), 6.18 (dd, \( J = 7.2, 16.0 \) Hz, 1H), 3.31-3.24 (m, 1H), 3.10-3.07 (m, 2H), 2.86 (d, \( J = 6.4 \) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta \) 199.4, 139.8, 137.6, 133.2, 132.9, 130.4, 129.7, 128.8, 128.5, 128.3, 127.3, 126.4, 126.3, 43.1, 41.6, 40.5; HRMS (ESI-TOF) Calcd. for C\(_{24}\)H\(_{23}\)O (M+H)\(^+\) 327.1749,
found 327.1751; [α]_D^{25} = -14.980 (c = 0.10 MeOH); HPLC conditions: The enantiomeric excess was determined by HPLC (Chiralcel AD-H), Hex: i-PrOH 98:2, UV 254 nm, 0.5 mL/min, t_R = 36.34 min (major) and t_R = 42.28 min (minor).

(3E,5E)-2-methyl-6-phenylhexa-3,5-dien-2-ol (1,2-addition product)

Pale yellow oil, 81% yield; ^1^H NMR (CDCl_3, 400 MHz) δ 7.41-7.19 (m, 5H), 6.80-6.72 (m, 1H), 6.55 (d, J = 16.0 Hz, 1H), 6.44-6.36 (m, 1H), 5.96 (d, J = 16.0 Hz, 1H), 1.38 (s, 6H); ^13^C NMR (CDCl_3, 100 MHz) δ 142.0, 137.5, 132.5, 128.9, 127.7, 127.5, 127.2, 126.5, 71.1, 30.0.

5. Conversion of 2a to 5a

To a solution of (R)-2a (30 mg, 0.12 mmol, 97% ee) and potassium carbonate (5.8 mg, 0.04 mmol) in t-butyl alcohol (10 mL) and water (2 mL), an aqueous solution (8 mL) of sodium metaperiodate (128.2 mg, 0.60 mmol), potassium permanganate (9.5 mg, 0.06 mmol), and potassium carbonate (5.8 mg, 0.04 mmol) was added dropwise at 0 °C. The resulting mixture was stirred at the same temperature for 30 min, then warmed to room temperature (12 °C) and further stirred for 10 h. The reaction mixture was acidified with 1 M of hydrochloric acid at 0 °C to pH ca. 2, and solid sodium pyrosulfite was added until reddish color disappeared. Then, the mixture was evaporated to remove t-butyl alcohol. The resulting aqueous solution was extracted with dichloromethane (20 mL × 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous sodium sulfate, and concentrated to give a residue, which was purified by flash column chromatography (ethyl acetate: petroleum ether = 1:5) to (E)-4-methyl-2-oxo-6-phenylhex-5-enoic acid (5a) (20.4 mg, 89%) as a white solid.

5a: white solid, 89% yield and 94% ee (R); mp: 138-139 °C; ^1^H NMR (CDCl_3, 400 MHz) δ 7.99-7.95 (m, 2H), 7.60-7.53 (m, 1H), 7.50-7.44 (m, 2H), 3.48 (dd, J = 6.8, 16.0 Hz, 1H), 3.23-3.13 (m, 1H), 3.07 (d, J = 16.0 Hz, 1H), 1.33 (d, J = 6.8 Hz, 3H); LC-MS (ESI-Negtive) 191.15; ^13^C NMR (CDCl_3, 100 MHz) δ 198.1, 182.4, 136.6, 133.5, 128.8, 128.3, 42.0, 35.0, 17.3; [α]_D^{25} = 18.329 (c = 0.10 MeOH); HPLC
conditions: The enantiomeric excess was determined by HPLC (Chiralcel OD-H), Hex: i-PrOH: TFA= 94:6:0.1, UV 254 nm, 0.5 mL/min, t_R= 21.98 min (major) and t_R= 25.78 min (minor).

Proposed stereochemical transition states

The steric repulsion between the phenyl group of the ligand and the aryl groups of the substrate may determine the absolute configuration of the products in the 1,4-addition according to the mechanism of the 1,4-ACA of Grignard reagents reported by Feringa group\(^5\) (Figure 3). For the transition states, steric repulsion between the phenyl group of the ligand and the aryl group of the substrate in TS2 is larger than that in TS1. This leads to Cu(III) intermediate (C), in which the absolute configuration is fixed.

References


6. NMR Charts of New Compounds

$^1$H NMR of 1b

![NMR Chart of 1b](image)
**$^{13}$C NMR of 2b**

**$^1$H NMR of 2c**

**$^{13}$C NMR of 2c**
$^1$H NMR of 2d

$^{13}$C NMR of 2d

$^1$H NMR of 2f
$^{13}$C NMR of 2f

$^1$H NMR of 2g

$^{13}$C NMR of 2g
$^1$H NMR of 2h

$^{13}$C NMR of 2h

$^1$H NMR of 2i
$^{13}$C NMR of 2i

$^1$H NMR of 2j

$^{13}$C NMR of 2j
$^1$H NMR of 2k

$^{13}$C NMR of 2k

$^1$H NMR of 2l
$^{13}$C NMR of 2l

$^1$H NMR of 2m

$^{13}$C NMR of 2m
\(^1\)H NMR of 2n

\(^{13}\)C NMR of 2n

\(^1\)H NMR of 2o
$^{13}$C NMR of 2o

$^1$H NMR of 2p

$^{13}$C NMR of 2p
$^{1}\text{H NMR of } 2q$

![$^{13}\text{C NMR of } 2q$](image)

$^{1}\text{H NMR of } 3a$
$^{13}$C NMR of 3a

$^1$H NMR of 4a

$^{13}$C NMR of 4a
$^1$H NMR of (3$E$,5$E$)-2-methyl-6-phenylhexa-3,5-dien-2-ol

(1,2-addition product)

$^{13}$C NMR of (3$E$,5$E$)-2-methyl-6-phenylhexa-3,5-dien-2-ol

(1,2-addition product)
7. Chiral HPLC Charts

HPLC data of 2a, racemic sample

HPLC data of 2a, catalytic sample
HPLC data of 2b, racemic sample

HPLC data of 2b, catalytic sample
HPLC data of 2c, racemic sample

HPLC data of 2c, catalytic sample
HPLC data of 2d, racemic sample

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HPLC data of 2d, catalytic sample

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HPLC data of 2e, racemic sample

HPLC data of 2e, catalytic sample
**HPLC data of 2f, racemic sample**

![HPLC Data of 2f, Racemic Sample](image1)

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**HPLC data of 2f, catalytic sample**

![HPLC Data of 2f, Catalytic Sample](image2)

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**HPLC data of 2g, racemic sample**

![HPLC graph for racemic sample](image)

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**HPLC data of 2g, catalytic sample**

![HPLC graph for catalytic sample](image)

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HPLC data of 2h, racemic sample

![HPLC graph of racemic sample](image1)

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HPLC data of 2h, catalytic sample

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HPLC data of 2i, racemic sample

HPLC data of 2i, catalytic sample
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HPLC data of 2l, catalytic sample
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HPLC data of 2m, catalytic sample
HPLC data of 2n, racemic sample

HPLC data of 2n, catalytic sample
HPLC data of 2o, racemic sample

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HPLC data of 2p, racemic sample

HPLC data of 2p, catalytic sample
HPLC data of 2q, racemic sample

HPLC data of 2q, catalytic sample
HPLC data of 3a, racemic sample

HPLC data of 3a, catalytic sample

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**HPLC data of 4a, racemic sample**

![HPLC data of 4a, racemic sample](image)

**HPLC data of 4a, catalytic sample**

![HPLC data of 4a, catalytic sample](image)
HPLC data of 5a, racemic sample

HPLC data of 5a, catalytic sample
8. X-ray structure of 2a

Bond precision:
- C-C = 0.0041 Å
- Wavelength = 0.71073 Å

Cell:
- a = 11.3820(9) Å
- b = 5.6425(6) Å
- c = 11.8926(10) Å
- α = 90°
- β = 106.817(8)°
- γ = 90°

Temperature: 293 K

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Correction method = MULTI-SCAN
CCDC-930399 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.