Catalytic Asymmetric Cross-Dehydrogenative Coupling: Activation of C-H Bonds by a Cooperative Bimetallic Catalyst System**

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Supporting Information

CONTENTS:

(A) General remarks ........................................................................................................................................... 3
(B) Typical procedure for substrates preparation .......................................................................................... 4
(C) Typical procedure for the preparation of the racemic products ............................................................... 5
(D) Typical procedure for catalytic asymmetric CDC reaction ........................................................................ 5
(E) Optimization of the Oxidant ...................................................................................................................... 6
(F) The analytical and spectral characterization data of catalyst L5 and products .......................................... 6
(G) Typical procedure for the reduction of 3a .................................................................................................. 20
(H) The analytical and spectral characterization data of 6 ............................................................................ 21
(I) Typical procedure for the scale-up reaction ............................................................................................... 22
(J) The electrospray ionization mass spectrometry (ESI-MS) analysis ......................................................... 22
(K) The possible catalytic cycle of iron complex .............................................................................................. 23
(L) X-ray structures of 3d ............................................................................................................................... 24
(M) Copy of CD spectras for products ........................................................................................................... 24
(N) Copy of $^1$H NMR and $^{13}$C NMR spectra for catalyst L5 products ....................................................... 26
(A) General remarks

$^1$H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl$_3$, $\delta = 7.26$). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment.

$^{13}$C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl$_3$, $\delta = 77.0$). Melting points (m.p.) were measured on electrothermal digital melting point apparatus and were uncorrected. Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 25 °C. Optical rotations were reported as follows: $[\alpha]_D^T$ (c g/100 mL, in CH$_2$Cl$_2$). HRMS was recorded on a commercial apparatus (ESI Source). All catalytic reactions were run in dried glassware using standard techniques. THF was distilled from sodium benzophenone ketyl. CHCl$_3$CHCl$_2$ was distilled after dried over K$_2$CO$_3$. MeOH was distilled over magnesium rod. 1b, 1c, 1d and 1e were prepared following a literature procedure,$^{[1]}$ xanthene was used after recrystallized, $^1$BuOOH was 5.0-6.0 M in decane. All of racemic samples were prepared by using 10 mol% (DL)-piperolic acid derived L-Fe(BF$_4$)$_2$·6H$_2$O complex as the catalyst.
**B** Typical procedure for substrates preparation.

1) The synthesis of phosphorus ylide

To a solution of triphenylphosphine in toluene, methyl bromoacetate was added. The mixture was stirred at room temperature for 2 h, then filtrated. The residue was washed with toluene. 1M NaOH was used to all the solid dissolved, CH₂Cl₂ extracted for three times, dried by MgSO₄, removing CH₂Cl₂ in vacuum.

2) The synthesis of α,β-unsaturated esters

To a solution of phosphorus ylide in toluene, aldehyde was added. The reaction was stirred at room temperature for 3 h, removing CH₂Cl₂ in vacuum without further purification.

3) The synthesis of esters

The α,β-unsaturated esters was reducing to esters under H₂ atmosphere in MeOH with palladium 10% on carbon as the catalyst. filtrated, removing MeOH in vacuum, the residue was purified by flash chromatography on silica gel, formed pure products.

4) The synthesis of substituted indenone
To ice-cooled TFSA (100 equiv) was slowly added esters, and the solution was stirred at 25 °C for 96 h. To the solution was added CH₂Cl₂ and the mixture was poured into ice-water, which was extracted with CH₂Cl₂. The organic phase was washed with brine and dried over Na₂SO₄, and the solvent was evaporated under reduced pressure to give a residue, which was purified via column chromatography on silica gel and to give pure substituted indenone.

2) The synthesis of β-ketoesters

To a solution of NaH in THF was slowly added indenone under N₂ atmosphere. After 20 min, dimethyl carboxylate was added and warmed to reflux. The reaction was monitored by TLC. The solvent was evaporated under reduced pressure, and 1 M HCl was added making pH to 4, extracted with CH₂Cl₂, the organic phase was washed with brine and dried over Na₂SO₄, and the solvent was evaporated under reduced pressure to give a residue, which was purified via column chromatography on silica gel and to give β-ketoesters.

(C) Typical procedure for the preparation of the racemic products

A mixture of (+)-L (0.01 mmol), Fe(BF₄)₂·6H₂O (0.01 mmol), β-ketoesters (0.1 mmol), xanthene (0.1mmol) and tBuOOH (20 µL) were stirred in CHCl₂CHCl₂ (0.5 mL) at 30 °C for 10 h. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford the pure racemic product.

(D) Typical procedure for catalytic asymmetric CDC reaction

To a dry volumetric flask (1.0 mL), L2 or L5 (0.02 mmol), Fe(BF₄)₂·6H₂O (0.02 mmol, 6.8 mg) and
THF (1.0 mL) were added and stirred at 30 °C for 0.5 h. Then the catalyst solution (100 μL) was added to a dry reaction tube. After removing THF in vacuum, additional L2 or L5 (0.01 mmol), NiBr2 (0.01 mmol, 2.2 mg), β-ketoesters (0.1 mmol) were added under N2 atmosphere, and stirred at 30 °C for 0.5 h. Next, xanthene (0.11-0.2 mmol) and tBuOOH (20 μL) were added, and the mixture continued stirring at 30 °C for the indicated time. The residue was purified by flash chromatography on silica gel (0-5 °C) to afford the corresponding products.

(E) Optimization of the Oxidant

Table 1: Optimization of the Oxidant.

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<th>Entry</th>
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<th>Yield of 3a (%)</th>
<th>ee of 3a (%)</th>
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<tbody>
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<td>H2O2</td>
<td>NR</td>
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</tr>
<tr>
<td>2e</td>
<td>DDQ</td>
<td>85</td>
<td>0</td>
</tr>
<tr>
<td>3f</td>
<td>m-CPBA</td>
<td>trace</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>TBHP</td>
<td>51</td>
<td>99</td>
</tr>
</tbody>
</table>

a Unless otherwise noted, all reactions were performed with NiBr2/L5 (10 mol%, 1:1), 1a (0.10 mmol), 2 (0.11 mmol), oxidant (0.10 mmol) at 30 °C for 24 h. b Isolated yield. c Determined by chiral HPLC analysis of ID column. d NR = no reaction. e DDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. f m-CPBA = 3-Chloroperoxybenzoic acid.

(F) The analytical and spectral characterization data of catalyst the L5 and products

White solid, ¹H NMR (400 MHz, CDCl₃) δ 12.44 (S, 2H), 7.01 (S, 4H), 3.88 – 3.59 (m, 6H), 3.54 – 3.32 (m, 4H), 3.12 – 2.96 (m, 4H), 2.95 – 2.78 (m, 4H), 2.76 – 2.44 (m, 6H), 2.22 – 1.88 (m, 4H), 1.24 (d, J = 6.8 Hz, 22H), 1.18 (d, J = 6.8 Hz, 12H). ¹³C
NMR (101 MHz, CDCl$_3$) $\delta$ = 166.40, 148.06, 144.53, 128.67, 121.37, 68.21, 64.05, 34.29, 29.06, 27.57, 24.09, 23.28, 20.33, 19.80; HRMS (ESI-TOF) calcd for C$_{43}$H$_{68}$N$_4$O$_4$ ([M+H$^+$]) = 705.5319, Found 705.5320.

(R)-tert-butyl 1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

White solid, m.p. 98 –100 °C, 90% yield, 99% ee; $[\alpha]_D^{25}$ = $-188.57$ (c = 0.70 in CH$_2$Cl$_2$); the ee was determined by HPLC analysis using a chiral ID column (hexane/PrOH = 95/5, 1.0 mL/min, 254 nm) $t_r$ (major) = 8.33 min, $t_r$ (minor) = 9.67 min; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 – 7.28 (m, 5H), 7.25 – 7.23 (m, 1H), 7.21 – 7.13 (m, 2H), 7.12 – 7.05 (m, 1H), 7.04 – 6.97 (m, 1H), 6.96 – 6.91 (m, 1H), 6.87 – 6.76 (m, 1H), 5.36 (s, 1H), 3.48 (d, $J$ = 17.6 Hz, 1H), 3.10 (d, $J$ = 17.6 Hz, 1H), 1.42 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 200.40, 167.34, 154.35, 153.58, 153.46, 134.98, 134.91, 130.83, 129.79, 128.46, 128.20, 127.06, 125.77, 124.32, 123.44, 123.30, 122.32, 120.77, 116.73, 116.44, 82.69, 71.39, 42.97, 31.61, 27.86; HRMS (ESI-TOF) calcd for C$_{27}$H$_{24}$O$_4$ ([M+Na$^+$]) = 435.1572, Found 435.1576.
tert-butyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate

\[ \delta \text{H NMR (400 MHz, CDCl}_3\text{): } 7.79 (d, J = 7.7 \text{ Hz, 1H}), 7.64 (t, J = 7.2 \text{ Hz, 1H}), 7.48 (d, J = 7.7 \text{ Hz, 1H}), 7.41 (t, J = 7.5 \text{ Hz, 1H}), 4.02 (s, 1H), 3.65 (d, J = 17.1 \text{ Hz, 1H}), 3.22 (d, J = 17.1 \text{ Hz, 1H}), 1.36 (s, 9H). \]

\[ \delta \text{C NMR (101 MHz, CDCl}_3\text{): 200.37, 169.53, 151.31, 134.85, 132.89, 126.92, 125.26, 124.05, 82.93, 79.51, 38.42, 26.66.} \]

(R)-tert-butyl 6-methyl-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

White solid, m.p. 168 – 170 °C, 71% yield, 98% ee; \([\alpha]_D^{25} = -173.93 \text{ (c = 0.56 in CH}_2\text{Cl}_2\text{); the ee was determined by HPLC analysis using a chiral IC column (hexane/iPrOH = 90/10, 1.0 mL/min, 254 nm) t_r (major) = 4.57 min, t_r (minor) = 6.26 min; } \]

\[ \delta \text{H NMR (400 MHz, CDCl}_3\text{): 7.58 (dd, J = 7.7, 1.4 Hz, 1H), 7.38 (s, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.10 (m, 4H), 7.09 – 7.00 (m, 2H), 6.97 – 6.92 (m, 1H), 6.87 – 6.80 (m, 1H), 5.36 (s, 1H), 3.41 (d, J = 17.4 Hz, 1H), 3.04 (d, J = 17.4 Hz, 1H), 2.28 (s, 3H), 1.42 (s, 9H). \]

\[ \delta \text{C NMR (101 MHz, CDCl}_3\text{): 200.36, 167.42, 153.59, 153.49, 151.81, 136.93, 136.27, 135.13, 130.91, 129.78, 128.40, 128.16, 125.44, 124.22, 123.40, 123.32, 122.40, 120.94, 116.71, 116.40, 82.60, 71.79, 42.86, 31.21, 27.86, 20.95; } \]

HRMS (ESI-TOF) calcd for C_{28}H_{26}O_4 ([M+Na^+]) = 449.1729, Found 449.1728.
(R)-tert-butyl 6-fluoro-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

White solid, m.p. 90 –92 °C, 71% yield, 99% ee; [α]D25 = −111.21 (c = 0.66 in CH₂Cl₂); the ee was determined by HPLC analysis using a chiral ID column (hexane/iPrOH = 78/2, 0.8 mL/min, 254 nm) tr (major) = 10.08 min, tr (minor) = 11.42 min; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, J = 7.7, 1.4 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.23 – 7.19 (m, 2H), 7.19 – 7.13 (m, 2H), 7.13 – 7.06 (m, 2H), 7.05 – 7.00 (m, 1H), 6.97 – 6.93 (m, 1H), 6.85 (dd, J = 7.5, 1.2 Hz, 1H), 5.34 (s, 1H), 3.43 (d, J = 17.4 Hz, 1H), 3.06 (d, J = 17.4 Hz, 1H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ = 198.59, 165.98, 152.51, 152.42, 148.75, 129.69, 128.72, 127.54, 127.31, 126.15, 126.07, 122.47, 122.36, 121.76, 121.53, 121.06, 119.54, 115.76, 115.48, 109.02, 108.80, 81.92, 71.23, 42.08, 30.08, 26.83; HRMS (ESI-TOF) calcd for C₂₇H₂₃FO₄ ([M+Na⁺]) = 453.1478, Found 453.1475.
(R)-tert-butyl 6-chloro-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

White solid, m.p. 120 – 122 °C, 75% yield, 98% ee; $[\alpha]_D^{25} = -164.58$ (c = 0.24 in CH$_2$Cl$_2$); the ee was determined by HPLC analysis using a chiral IC column (hexane/$^6$PrOH = 95/5, 0.8 mL/min, 254 nm) $t_r$ (major) = 5.59 min, $t_r$ (minor) = 6.36 min; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 – 7.50 (m, 2H), 7.35 (dd, $J$ = 8.1, 2.1 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.21 (dd, $J$ = 7.8, 1.5 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.11 – 7.02 (m, 2H), 6.98 – 6.92 (m, 1H), 6.88 – 6.82 (m, 1H), 5.34 (s, 1H), 3.43 (d, $J$ = 17.8 Hz, 1H), 3.06 (d, $J$ = 17.8 Hz, 1H), 1.43 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.23, 165.88, 152.51, 152.42, 151.40, 135.40, 133.91, 132.39, 129.71, 128.71, 127.56, 127.37, 125.98, 122.96, 122.49, 122.43, 121.02, 119.52, 115.77, 115.51, 82.00, 70.95, 42.02, 30.25, 26.83; HRMS (ESI-TOF) calcd for C$_{27}$H$_{23}$O$_{3}$ClO$_4$ ([M+Na$^+$]) = 469.1183, Found 469.1185.

(R)-tert-butyl 6-bromo-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

White solid, m.p. 80 – 82 °C, 80% yield, 97% ee; $[\alpha]_D^{25} = -216.30$ (c =
0.46 in CH₂Cl₂); the ee was determined by HPLC analysis using a chiral ID column (hexane/iPrOH = 98/2, 1.0 mL/min, 254 nm) tᵣ (major) = 10.06 min, tᵣ (minor) = 12.83 min; ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.53 (m, 2H), 7.38 (dd, J = 7.4, 1.0 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 7.22 – 7.18 (m, 1H), 7.16 – 7.14 (m, 1H), 7.09 (dd, J = 7.5, 1.2 Hz, 1H), 6.99 (dd, J = 7.1, 1.5 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.83 (dd, J = 7.5, 1.2 Hz, 1H), 5.36 (s, 1H), 3.47 (d, J = 17.6 Hz, 1H), 3.10 (d, J = 17.6 Hz, 1H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ = 199.34, 166.32, 153.32, 152.56, 152.44, 133.97, 133.87, 129.81, 128.77, 127.43, 127.17, 126.03, 124.74, 123.30, 122.41, 122.28, 121.30, 119.75, 115.71, 115.40, 81.66, 70.37, 41.95, 30.60, 26.84; HRMS (ESI-TOF) calcd for C₂₇H₂₃₇₈BrO₄ ([M+Na⁺]) = 513.0677, Found 513.0684.

(R)-tert-butyl 5-fluoro-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

White solid, m.p. 126 –128 °C, 81% yield, 97% ee; [α]D²⁵ = −189.16 (c = 0.48 in CH₂Cl₂); the ee was determined by HPLC analysis using a chiral ID column (hexane/iPrOH = 98/2, 1.0 mL/min, 254 nm) tᵣ (major) = 8.31 min, tᵣ (minor) = 10.02 min; ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.51 (m, 1H), 7.38 – 7.33 (m, 2H), 7.18 – 7.14 (m, 1H), 7.05 – 7.01 (m, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.89 – 6.85 (m, 2H), 5.23 (s, 1H), 3.31 (d, J = 17.6 Hz, 1H), 3.09 (d, J = 17.6 Hz, 1H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ = 199.50, 166.27, 153.35, 152.60, 152.48, 133.98, 133.88, 129.84, 128.80, 127.44, 127.19, 126.05, 124.75, 123.31, 122.42, 122.29, 121.31, 119.77, 115.72, 115.41, 81.66, 70.37, 41.95, 30.60, 26.84; HRMS (ESI-TOF) calcd for C₂₇H₂₃₇₈BrO₄ ([M+Na⁺]) = 513.0677, Found 513.0684.
2H), 7.33 – 7.26 (m, 1H), 7.23 (dd, J = 7.7, 1.3 Hz, 1H), 7.18 – 7.12 (m, 1H), 7.11 – 7.06 (m, 1H), 7.04 – 6.93 (m, 2H), 6.92 – 6.79 (m, 3H), 5.34 (s, 1H), 3.47 (d, J = 17.9 Hz, 1H), 3.09 (d, J = 17.9 Hz, 1H), 1.44 (s, 9H). 13C NMR (101 MHz, CDCl3) δ = 198.53, 167.11, 153.54, 153.44, 130.75, 129.76, 128.56, 128.34, 126.70, 126.59, 123.52, 123.34, 122.13, 120.56, 116.79, 116.53, 115.66, 115.42, 112.60, 112.38, 82.91, 71.60, 42.99, 31.58, 27.87; HRMS (ESI-TOF) calcd for C27H23FO4 ([M+Na+]) = 453.1478, Found 453.1479.

(R)-tert-butyl 5-chloro-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

White solid, m.p. 172 – 174 °C, 68% yield, 99% ee; [α]D25 = −187.04 (c = 0.54 in CH2Cl2); the ee was determined by HPLC analysis using a chiral ID column (hexane/iPrOH = 95/5, 1.0 mL/min, 254 nm) tR (major) = 5.97 min, tR (minor) = 6.82 min; 1H NMR (400 MHz, CDCl3) δ = 7.57 (dd, J = 7.7, 1.3 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 2H), 7.11 – 7.01 (m, 2H), 6.99 – 6.94 (m, 2H), 6.87 – 6.79 (m, 1H), 5.34 (s, 1H), 3.45 (d, J = 17.8 Hz, 1H), 3.08 (d, J = 17.8 Hz, 1H), 1.43 (s, 9H). 13C NMR (101 MHz, CDCl3) δ = 199.02, 166.98,
155.71, 153.54, 153.44, 141.52, 133.43, 130.73, 128.58, 128.39, 128.00, 126.01, 125.38, 
123.52, 123.37, 122.07, 120.55, 116.81, 116.58, 82.99, 71.51, 43.01, 31.42, 27.86; HRMS (ESI-TOF) 
calcd for C_{27}H_{23}\textsuperscript{34.9689}ClO_{4} ([M+Na\textsuperscript{+}]) = 469.1183, Found 469.1183.

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White solid, m.p. 177 –179 ºC, 76% yield, 99% ee; [\alpha]_D\textsuperscript{25} = –193.93 (c = 
0.56 in CH\textsubscript{2}Cl\textsubscript{2}); the ee was determined by HPLC analysis using a chiral 
ID column (hexane/iPrOH = 95/5, 1.0 mL/min, 254 nm) t\textsubscript{r} (major) = 6.08 
min, t\textsubscript{r} (minor) = 6.75 min; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.60 – 7.54 (m, 
1H), 7.48 – 7.30 (m, 2H), 7.36 – 7.26 (m, 1H), 7.21 (d, J = 7.7 Hz, 1H), 7.15 (d, J = 7.7 Hz, 1H), 
7.11 – 7.02 (m, 2H), 7.00 – 6.90 (m, 1H), 6.88 – 6.78 (m, 1H), 5.34 (s, 1H), 3.46 (d, J = 17.9 Hz, 1H), 
3.08 (d, J = 17.9 Hz, 1H), 1.43 (s, 9H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \delta = 199.26, 166.92, 155.81, 
153.53, 153.44, 133.80, 130.82, 130.72, 130.48, 129.72, 129.09, 128.58, 128.40, 125.44, 123.51, 
123.38, 122.05, 120.54, 116.81, 116.59, 83.00, 71.43, 42.99, 31.36, 27.86; HRMS (ESI-TOF) calcd 
for C_{27}H_{23}\textsuperscript{78.9185}BrO_{4} ([M+Na\textsuperscript{+}]) = 513.0677, Found 513.0684.
**Retention Time** | **Area** | **% Area**
---|---|---
1 | 6.081 | 8178647 | 99.88%
2 | 6.750 | 9557 | 0.12%

### White solid, m.p. 176 – 178 °C, 72% yield, 99% ee; $[\alpha]_D^{25} = -105.12$ (c = 0.52 in CH$_2$Cl$_2$); the ee was determined by HPLC analysis using a chiral ID column (hexane/iPrOH = 90/10, 1.0 mL/min, 254 nm) $t_r$ (major) = 7.59 min, $t_r$ (minor) = 10.47 min; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 – 7.54 (m, 2H), 7.42 – 7.36 (m, 1H), 7.32 – 7.26 (m, 1H), 7.26 – 7.12 (m, 4H), 7.17 – 7.12 (m, 1H), 7.05 – 6.98 (m, 1H), 6.97 – 6.92 (m, 1H), 6.86 – 6.78 (m, 1H), 5.36 (s, 1H), 3.47 (d, $J = 17.6$ Hz, 1H), 3.08 (d, $J = 17.6$ Hz, 1H), 2.20 – 2.10 (m, 4H), 2.19 – 2.14 (m, 5H), 1.64 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 200.44, 166.98, 154.35, 153.56, 153.47, 135.03, 134.89, 130.89, 129.83, 128.43, 128.18, 127.04, 125.78, 124.32, 123.47, 123.30, 122.33, 120.83, 116.69, 116.42, 82.83, 71.56, 42.88, 41.05, 36.09, 31.63, 30.88; HRMS (ESI-TOF) calcd for C$_{33}$H$_{30}$O$_4$ ([M+Na$^+$]) = 513.2042, Found 513.2036.
tert-butyl 1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

Viscous oil, 70% yield, 99% ee; \([\alpha]_D^{25} = -53.88\) (c = 0.18 in CH\(_2\)Cl\(_2\)); the ee was determined by HPLC analysis using a chiral ID column (hexane/iPrOH = 80/20, 1.0 mL/min, 254 nm) \(t_r\) (minor) = 6.36 min, \(t_r\) (major) = 9.97 min;

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (d, \(J = 7.9\) Hz, 1H), 7.46 – 7.33 (m, 3H), 7.32 – 7.26 (m, 1H), 7.25 – 7.22 (m, 1H), 7.21 – 7.13 (m, 2H), 7.12 – 7.01 (m, 3H), 6.98 (t, \(J = 7.5\) Hz, 1H), 5.47 (s, 1H), 3.13 – 3.00 (m, 1H), 2.74 – 2.63 (m, 1H), 2.23 – 2.35 (m, 1H), 1.81 – 1.67 (m, 1H), 1.21 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 193.22, 167.63, 154.58, 154.27, 142.92, 133.25, 132.64, 130.83, 130.29, 128.57, 128.28, 128.10, 128.09, 126.40, 123.37, 123.02, 122.38, 122.14, 116.49, 116.33, 82.68, 65.91, 42.46, 27.66, 25.90, 25.76; HRMS (ESI-TOF) calcd for C\(_{28}\)H\(_{26}\)O\(_4\) ([M+Na\(^+\)]) = 449.1729, Found 449.1725.
<table>
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**tert-butyl 5,7-dimethyl-1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate**

Viscous oil, 36% yield, 99% ee; \([\alpha]_D^{25} = -46.00\) (c = 0.10 in CH₂Cl₂); the ee was determined by HPLC analysis using a chiral IC column (hexane/iPrOH = 90/10, 1.0 mL/min, 254 nm) \(t_r\) (major) = 4.72 min, \(t_r\) (minor) = 5.81 min; \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.73 (s, 1H), 7.47 (d, \(J = 6.6\) Hz, 1H), 7.34 (d, \(J = 7.5\) Hz, 1H), 7.28 (s, 1H), 7.25 – 7.15 (m, 2H), 7.14 – 7.07 (m, 1H), 7.08 (s, 1H), 7.07 – 7.02 (m, 1H), 6.99 (t, \(J = 7.4\) Hz, 1H), 5.46 (s, 1H), 2.83 – 2.71 (m, 1H), 2.64 – 2.54 (m, 1H), 2.38 – 2.31 (m, 1H), 2.30 (s, 3H), 2.11 (s, 3H), 1.72 – 1.64 (m, 1H), 1.26 – 1.10 (m, 9H). \(^13\)C NMR (101 MHz, CDCl₃) \(\delta\) = 193.74, 167.72, 154.62, 154.29, 138.28, 136.11, 135.66, 135.56, 132.71, 130.91, 130.29, 128.21, 128.05, 125.98, 123.34, 123.01, 122.49, 122.32, 116.47, 116.27, 82.46, 65.28, 42.14, 27.63, 25.19, 23.21, 20.81, 18.97; HRMS (ESI-TOF) calcd for C₃₀H₃₀O₄ ([M+Na⁺]) = 477.2042, Found 477.2040.
tert-butyl 7-bromo-1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

Viscous oil, 60% yield, 99% ee; $[\alpha]_D^{25} = -56.89$ (c = 0.58 in CH$_2$Cl$_2$); the ee was determined by HPLC analysis using a chiral IC column (hexane/iPrOH = 90/10, 1.0 mL/min, 254 nm) $t_r$ (major) = 4.15 min, $t_r$ (minor) = 5.07 min; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J$ = 2.1 Hz, 1H), 7.48 (dd, $J$ = 8.2, 2.2 Hz, 1H), 7.38 (dd, $J$ = 7.7, 1.3 Hz, 1H), 7.33 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.22 – 7.13 (m, 2H), 7.12 – 7.03 (m, 2H), 7.02 – 6.93 (m, 2H), 5.44 (s, 1H), 3.06 – 2.85 (m, 1H), 2.72 – 2.55 (m, 1H), 2.37 – 2.23 (m, 1H), 1.78 – 1.66 (m, 1H), 1.25 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 191.99, 167.29, 154.57, 154.25, 141.68, 136.06, 134.03, 130.76, 130.70, 130.41, 130.26, 128.40, 128.24, 123.46, 123.07, 122.14, 121.85, 120.45, 116.55, 116.40, 83.00, 65.80, 42.53, 27.70, 25.65, 25.50; HRMS (ESI-TOF) calcd for C$_{28}$H$_{25}$BrO$_4$ ([M+Na$^+$]) = 527.0834, Found 527.0830.

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tert-butyl 7-methoxy-1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

White solid, m.p. 113 –115 °C, 71% yield, 99% ee; $[\alpha]_D^{25} = -31.36$ (c = 0.66 in CH$_2$Cl$_2$); the ee was determined by HPLC analysis using a
chiral IC column (hexane/iPrOH = 90/10, 1.0 mL/min, 254 nm) \( t_r \) (major) = 5.46 min, \( t_r \) (minor) = 7.86 min; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.65 (d, \( J = 7.8 \) Hz, 1H), 7.45 (dd, \( J = 7.7, 1.2 \) Hz, 1H), 7.34 (dd, \( J = 7.6, 1.2 \) Hz, 1H), 7.29 – 7.23 (m, 1H), 7.23 – 7.19 (m, 1H), 7.19 – 7.13 (m, 2H), 7.12 – 7.07 (m, 1H), 7.07 – 7.02 (m, 1H), 7.01 – 6.96 (m, 1H), 6.91 (d, \( J = 8.0 \) Hz, 1H), 5.45 (s, 1H), 3.77 (s, 3H), 2.86 – 2.76 (m, 1H), 2.75 – 2.64 (m, 1H), 2.36 – 2.27 (m, 1H), 1.71 – 1.61 (m, 1H), 1.18 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) = 193.47, 167.62, 156.59, 154.61, 154.27, 133.70, 132.03, 130.82, 130.32, 128.23, 128.06, 126.67, 123.31, 122.99, 122.44, 122.26, 119.63, 116.49, 116.31, 113.85, 82.52, 65.46, 55.57, 42.16, 27.62, 25.20, 19.99; HRMS (ESI-TOF) calcd for C\(_{29}\)H\(_{28}\)O\(_5\) ([M+Na\(^+\)]) = 479.1834, Found 479.1837.

**tert-butyl 5-methoxy-1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate**

Viscous oil, 34% yield, 99% ee; \([\alpha]_D^{25} = -7.92 \) (c = 0.24 in CH\(_2\)Cl\(_2\)); the ee was determined by HPLC analysis using a chiral ID column (hexane/iPrOH = 80/20, 1.0 mL/min, 254 nm) \( t_r \) (minor) = 8.93 min, \( t_r \) (major) = 13.95 min; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.44 (s, 1H), 7.35 (d, \( J = 7.7 \) Hz, 1H), 7.26 d, \( J = 7.7 \) Hz, 1H), 7.21 – 7.16 (m, 1H), 7.15 – 7.05 (m, 2H), 7.04 – 6.95 (m, 2H), 6.95 – 6.84 (m, 3H), 6.84 – 6.74 (m, 3H), 6.64 (s, 1H), 3.87 (s, 3H), 2.86 – 2.65 (m, 1H), 2.64 – 2.45 (m, 1H), 2.44 – 2.24 (m, 1H), 1.71 – 1.61 (m, 1H), 1.18 (s, 9H).
5.38 (s, 1H), 3.76 (s, 3H), 2.97 – 2.82 (m, 1H), 2.61 – 2.50 (m, 1H), 2.28 – 2.11 (m, 1H), 1.75 – 1.58 (m, 1H), 1.15 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 193.11, 167.17, 158.15, 154.59, 154.28, 135.48, 133.37, 130.77, 130.33, 129.79, 128.27, 128.11, 123.35, 123.01, 122.41, 122.13, 121.89, 116.50, 116.34, 109.82, 82.68, 65.77, 55.49, 42.51, 27.69, 26.07, 25.13; HRMS (ESI-TOF) calcd for C$_{29}$H$_{28}$O$_5$ ([M+Na$^+$]) = 479.1834, Found 479.1835.

**adamantan-1-yl 1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate**

White solid, m.p. 165 –167 °C, 72% yield, 99% ee; $[\alpha]_D^{25} = -17.14$ (c = 0.14 in CH$_2$Cl$_2$); the ee was determined by HPLC analysis using a chiral ID column (hexane/iPrOH = 90/10, 1.0 mL/min, 254 nm) $t_r$ (minor) = 9.28 min, $t_r$ (major) = 10.63 min; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J$ = 7.8 Hz, 1H), 7.44 (d, $J$ = 7.7 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.21 (m, 1H), 7.20 – 7.12 (m, 2H), 7.12 – 7.02 (m, 3H), 6.98 (t, $J$ = 7.4 Hz, 1H), 5.47 (s, 1H), 3.13 – 3.01 (m, 1H), 2.76 – 2.61 (m, 1H), 2.35 – 2.24 (m, 1H), 2.05 (s, 3H), 1.85 (dd, $J$ = 30.4, 11.3 Hz, 6H), 1.77 – 1.62 (m, 2H), 1.55 (s, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 192.09, 166.16, 153.56, 153.23, 141.98, 132.21,
131.56, 129.82, 129.30, 127.55, 127.23, 127.10, 127.05, 125.35, 122.35, 122.00, 121.37, 121.11,
115.39, 115.27, 81.72, 65.08, 41.48, 39.91, 34.95, 29.73, 24.91, 24.64; HRMS (ESI-TOF) calcd for
C₃₄H₃₂O₄ ([M+Na⁺]) = 527.2189, Found 527.2200.

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The results of other β-ketoesters substrates

(G) Typical procedure for the reduction of 3a

To a solution of 3a (0.02 mmol) in 1 mL MeOH, NaBH₄ (1.5 eq) was added at 0 °C, the reaction was
stirred at this temperature for 30 min. 1 M HCl was added making pH to 5, CH₂Cl₂ extracted for three times, dried by MgSO₄, removing CH₂Cl₂ in vacuum. The residue was purified by flash chromatography on silica gel (0-5 °C) to afford the product 6.

(H) The analytical and spectral characterization data of 6

(1R,2R)-tert-butyl 1-hydroxy-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

White solid, 95% yield, 99/1 dr, 99% ee; [α]D²⁵ = 11.38 (c = 0.36 in CH₂Cl₂); the dr determined was by ¹H NMR; the ee was determined by HPLC analysis using a chiral IC column (hexane/iPrOH = 90/10, 1.0 mL/min, 254 nm) tᵣ (major) = 3.94 min, tᵣ (minor) = 4.94 min; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 7.6 Hz, 1H), 7.26 – 7.16 (m, 4H), 7.10 (t, J = 7.7 Hz, 1H), 7.07 – 6.98 (m, 4H), 6.97 – 6.94 (m, 2H), 6.89 (t, J = 7.4 Hz, 1H), 5.19 (s, 1H), 4.78 (s, 1H), 3.17 (d, J = 15.5 Hz, 1H), 2.95 (d, J = 15.5 Hz, 1H), 0.97 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ = 171.94, 153.99, 153.64, 143.28, 141.80, 130.06, 129.95, 128.64, 127.98, 127.85, 126.76, 124.62, 123.85, 123.13, 123.09, 122.53, 122.48, 116.47, 116.25, 81.00, 77.87, 67.22, 40.71, 37.59, 27.22; HRMS (ESI-TOF) calcd for C₂₇H₂₆O₄ ([M+Na⁺]) = 437.1729, Found 437.1724.

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(I) Typical procedure for the scale-up reaction

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To a dried round flash, L5 (0.1 mmol, 71.0 mg), Fe(BF₄)₂·6H₂O (0.1 mmol, 34 mg) and THF (5 mL) were added and stirred at 30 °C for 2.5 h. After removing THF in vacuum, L5 (0.5 mmol, 355.0 mg), NiBr₂ (0.5 mmol, 108.5 mg), and β-ketoester (5.0 mmol) were added under N₂ atmosphere, and continued stirring at 30 °C for 2.5 h. Next, xanthene (5.5 mmol) and tBuOOH (1.0 mL) were added, the reaction was stirred at 30 °C for 15 h. The residue was purified by flash chromatography on silica gel (0-5 °C) to afford the product 3a.

(J) The electrospray ionization mass spectrometry (ESI-MS) analysis
[(L5-O) + H⁺] Calcd for C_{43}H_{69}N_{4}O_{3} \text{+} 689.5370, found: 689.5372; [Fe^{III} + L5 - 2H⁺] Calcd for: 758.4433 found: 758.4474; [Fe^{III} + (L5-O) + 2OH⁻] Calcd for: 778.4696 found: 778.4512; [O=Fe^{V} + L5 + 2OH⁻] Calcd for: 810.4696 found: 810.4778.

NiBr₂ + L5 + 1a
[ Ni^{II} + (L5 - H⁺) + 1a] Calcd for: 993.5615 found: 993.5626.

(K) The possible catalytic cycle of iron complex

Firstly, L5–Fe^{II} combined to 'BuOOH to generate L5–Fe^{III}–OO'Bu. In the presence of H₂O, the intermediate C undergoes heterolytic O–O bond and O–H cleavage, giving active high-valent L5–Fe^{V} (O)(OH) D. At the same time, a molecular of 'BuOH left up. High-valent iron(V)–oxo specie D activated sp³ benzylic C-H bond of xanthene, and then H-atom abstraction would afford carbocation E.
(L) X-ray structures of 3d

CCDC 910798 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

(M) Copy of CD spectras for products
(N) Copy of $^1$H NMR and $^{13}$C NMR spectra for products

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Electronic Supplementary Material (ESI) for Chemical Communications
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Electronic Supplementary Material (ESI) for Chemical Communications
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S = 1.047  Npar= 292

The following ALERTS were generated. Each ALERT has the format `test-name_ALERT_alert-type_alert-level`.
Click on the hyperlinks for more details of the test.

**Alert level C**

**CELLV02_ALERT_1_C**  The supplied cell volume s.u. differs from that calculated from the cell parameter s.u.’s by > 2
Calculated cell volume su = 10.39
Cell volume su given = 8.00
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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