The Asymmetric Cu(II)-Indolinylmethanol Complex Catalyzed Diels-Alder Reaction of 2-Vinylindoles with β,γ-Unsaturated α-Ketoesters: An Efficient Route to Functionalized Tetrahydrocarbazoles

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1. General information

All reactions were carried out under an atmosphere of nitrogen in flame dried glassware with magnetic stirring. The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200-300 mesh).

$^1$H NMR spectra were recorded on a Bruker Advance III spectrometer (400 MHz). Chemical shifts were reported as parts per million (ppm) in the $\delta$ scale downfield from TMS. Peaks were labeled as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). $^{13}$C NMR spectra were recorded on Bruker spectrometer with complete proton decoupling, and chemical shifts were reported in ppm from TMS with the solvent as the internal reference (CDCl$_3$, $\delta = 77.0$ ppm). HPLC analyses were conducted on an Agilent 1200 instrument using Daicel columns (0.46 cm diameter $\times$ 25 cm length). Optical rotations were recorded on a Perkin Elmer polarimeter (Model 341). MS spectra were recorded on an ESI-ion trap Mass spectrometer (Shimadzu LCMS-IT-TOF). Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

2. Preparation of ligands

The ligands were prepared following the literature methods.

(S)-Indolin-2-yldiphenylmethanol (L1)

$^{[a]}_{D} = -105.0$ (c = 1.0, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.62 (d, $J = 7.4$ Hz, 2H), 7.53 (d, $J = 7.4$ Hz, 2H), 7.40-7.15 (m, 6H), 6.99 (t, $J = 7.7$ Hz, 2H), 6.71 (t, $J = 7.4$ Hz, 1H), 6.56 (d, $J = 7.7$ Hz, 1H), 5.12 (t, $J = 9.6$ Hz, 1H), 3.81 (s, 1H), 3.56 (s, 1H), 3.07 (dd, $J = 16.1$, 10.5 Hz, 1H), 2.76 (dd, $J = 16.1$, 8.9 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 150.09, 146.95, 144.08, 129.22, 128.67, 128.21, 127.24, 127.04, 126.77, 125.83, 125.50, 124.75, 119.67, 109.79, 77.18, 66.86, 31.18.

(S)-2-(Indolin-2-yl)-1,3-diphenylpropan-2-ol (L2)

$^{[a]}_{D} = -18.4$ (c = 1.0, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.33-7.19 (m, 9H), 7.07 (d, $J = 7.3$ Hz, 1H), 6.98 (dd, $J = 14.0$, 6.4 Hz, 2H), 6.69 (t, $J = 7.4$ Hz, 1H), 6.49 (d, $J = 7.7$ Hz, 1H), 3.94 (t,
$J = 9.5 \text{ Hz, 1H}, 3.57 \text{ (s, 1H)}, 3.21-3.00 \text{ (m, 3H)}, 2.79 \text{ (s, 2H)}, 2.71 \text{ (d, } J = 13.8 \text{ Hz, 1H)}, 2.42 \text{ (s, 1H)}. \ 1^3 \text{C NMR (101 MHz, CDCl}_3\delta:\ 150.58, 137.52, 137.16, 130.82, 130.27, 128.48, 128.41, 128.26, 127.30, 126.67, 126.52, 124.52, 119.00, 109.52, 75.31, 65.83, 44.09, 42.21, 31.52.

(S)-2-(Indolin-2-yl)-1,3-bis(4-methoxyphenyl)propan-2-ol (L3)

\[
\begin{align*}
[a]_D^{10} & = -10.5 \text{ (c = 0.9, CH}_2Cl}_2. \ 1^1 \text{H NMR (400 MHz, CDCl}_3)\delta:\ 7.21 \text{ (d, } J = 8.6 \text{ Hz, 2H)}, 7.12 \text{ (d, } J = 8.6 \text{ Hz, 2H)}, 7.06 \text{ (d, } J = 7.2 \text{ Hz, 1H}), 6.97 \text{ (t, } J = 7.6 \text{ Hz, 1H}), 6.84 \text{ (dd, } J = 10.9, 8.6 \text{ Hz, 4H)}, 6.68 \text{ (t, } J = 7.3 \text{ Hz, 1H}), 6.51 \text{ (d, } J = 7.7 \text{ Hz, 1H}), 3.91 \text{ (t, } J = 9.5 \text{ Hz, 1H}), 3.80 \text{ (s, 3H)}, 3.79 \text{ (s, 3H)}, 3.07 \text{ (ddd, } J = 27.5, 18.4, 11.9 \text{ Hz, 3H)}, 2.72 \text{ (s, 2H)}, 2.63 \text{ (d, } J = 14.0 \text{ Hz, 1H}), 2.34 \text{ (s, 1H)}, 1.61 \text{ (s, 1H)}. \ 1^3 \text{C NMR (101 MHz, CDCl}_3)\delta:\ 158.45, 158.33, 150.64, 131.72, 131.17, 129.39, 129.07, 128.48, 127.27, 124.52, 118.93, 113.91, 113.70, 109.47, 75.25, 65.73, 55.27, 55.24, 43.01, 41.08, 31.47.

(S)-1,3-bis(2-Fluorophenyl)-2-(indolin-2-yl)propan-2-ol (L4)

\[
[a]_D^{10} = +5.6 \text{ (c = 1.0, CH}_2Cl}_2. \ 1^1 \text{H NMR (400 MHz, CDCl}_3)\delta:\ 7.39 \text{ (td, } J = 7.6, 1.5 \text{ Hz, 1H}), 7.24-7.14 \text{ (m, 3H)}, 7.13-6.92 \text{ (m, 6H)}, 6.70 \text{ (t, } J = 7.4 \text{ Hz, 1H}), 6.60 \text{ (d, } J = 7.7 \text{ Hz, 1H}), 3.91 \text{ (t, } J = 9.3 \text{ Hz, 1H)}, 3.13 \text{ (d, } J = 9.3 \text{ Hz, 2H)}, 3.02 \text{ (dd, } J = 17.5, 14.4 \text{ Hz, 2H}), 2.83 \text{ (dd, } J = 14.0, 9.9 \text{ Hz, 2H}), 2.37 \text{ (s, 1H)}, 1.67 \text{ (s, 1H)}. \ 1^3 \text{C NMR (101 MHz, CDCl}_3)\delta:\ 161.70 \text{ (} J_{CF} = 243.5 \text{ Hz)}, 161.60 \text{ (} J_{CF} = 243.5 \text{ Hz)}, 150.67, 133.12 \text{ (} J_{CF} = 20.8 \text{ Hz)}, 133.08 \text{ (} J_{CF} = 20.8 \text{ Hz)}, 128.67, 128.50, 128.42, 128.33, 127.36, 124.61, 124.12, 124.04, 123.98, 119.03, 115.34 \text{ (} J_{CF} = 23.4 \text{ Hz)}, 115.27 \text{ (} J_{CF} = 23.4 \text{ Hz)}, 109.63, 76.15, 64.95, 35.33, 33.92, 31.43.

(S)-3-(Indolin-2-yl)-1,5-diphenylpentan-3-ol (L5)

\[
[a]_D^{10} = -44.8 \text{ (c = 0.65, CH}_2Cl}_2. \ 1^1 \text{H NMR (400 MHz, CDCl}_3)\delta:\ 7.39-7.29 \text{ (m, 4H)}, 7.29-7.19 \text{ (m, 6H)}, 7.11 \text{ (d, } J = 7.3 \text{ Hz, 1H}), 7.04 \text{ (t, } J = 7.6 \text{ Hz, 1H}), 6.77 \text{ (td, } J = 7.4, 0.9 \text{ Hz, 1H)}, 6.67 \text{ (d, } J = 7.7 \text{ Hz, 1H}), 4.08 \text{ (dd, } J = 10.6, 9.2 \text{ Hz, 1H}), 3.84 \text{ (s, 1H)}, 3.19 \text{ (dd, } J = 15.5, 10.7 \text{ Hz, 1H}), 2.99 \text{ (dd, } J = 15.6, 9.1 \text{ Hz, 1H}), 2.93-2.61 \text{ (m, 4H)}, 2.46 \text{ (s, 1H)}, 2.11-1.74 \text{ (m, 4H)}. \ 1^3 \text{C NMR (101 MHz, CDCl}_3)\delta:\ 150.33, 142.25, 142.09, 129.25, 128.59, 128.54, 128.31, 128.29, 127.28, 126.05, 126.03, 124.76, 119.70, 110.09, 73.64, 66.17, 39.73, 36.18, 30.27, 30.14, 30.00.
(S)-5-(Indolin-2-yl)nonan-5-ol (L6)

\[
\begin{align*}
[a]_D^{20} &= -52.9 \text{ (c = 1.0, CH}_2\text{Cl}_2). \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)} &\delta: 7.08 (d, J = 7.3 \text{ Hz, 1H}), 7.01 (t, J = 7.6 \text{ Hz, 1H}), 6.73 (td, J = 7.4, 0.7 \text{ Hz, 1H}), 6.66 (d, J = 7.7 \text{ Hz, 1H}), 3.95 (dd, J = 10.8, 9.0 \text{ Hz, 1H}), 3.10 (dd, J = 15.6, 10.9 \text{ Hz, 1H}), 2.90 (dd, J = 15.6, 9.0 \text{ Hz, 1H}), 2.24 (s, 1H), 1.62-1.14 (m, 12H), 0.94 (td, J = 7.1, 4.6 \text{ Hz, 7H}). \\
^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} &\delta: 150.53, 129.51, 127.13, 124.70, 119.42, 109.88, 73.62, 66.43, 37.46, 34.04, 30.12, 25.82, 25.55, 23.43, 14.11, 14.03.
\end{align*}
\]

(S)-2-(1-Methylindolin-2-yl)-1,3-diphenylpropan-2-ol (L7)

\[
\begin{align*}
[a]_D^{20} &= -2.6 \text{ (c = 1.0, CH}_2\text{Cl}_2). \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)} &\delta: 7.33-7.14 (m, 9H), 7.06 (dd, J = 16.2, 7.7 \text{ Hz, 2H}), 6.95 (dd, J = 18.3, 6.6 \text{ Hz, 1H}), 6.64 (t, J = 7.3 \text{ Hz, 1H}), 6.47 (d, J = 7.8 \text{ Hz, 1H}), 3.41 (dd, J = 10.2, 8.3 \text{ Hz, 1H}), 3.29 (dd, J = 16.1, 10.3 \text{ Hz, 1H}), 3.16 (d, J = 13.7 \text{ Hz, 1H}), 2.96 (dd, J = 16.1, 8.1 \text{ Hz, 1H}), 2.90 (s, 3H), 2.82 (d, J = 14.2 \text{ Hz, 1H}), 2.73 (dd, J = 14.0, 7.5 \text{ Hz, 2H}), 1.66 (s, 1H). \\
^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} &\delta: 154.32, 136.99, 136.72, 131.09, 130.43, 128.25, 128.23, 127.88, 127.60, 126.56, 126.48, 123.92, 117.59, 107.83, 77.76, 71.67, 43.63, 40.53, 38.64, 32.19.
\end{align*}
\]

2-((2S)-octahydro-1H-indol-2-yl)-1,3-diphenylpropan-2-ol (L8)

\[
\begin{align*}
[a]_D^{20} &= -1.3 \text{ (c = 0.62, CH}_2\text{Cl}_2). \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)} &\delta: 7.40-7.09 (m, 10H), 3.82-3.54 (m, 2H), 3.24 (t, J = 8.3 \text{ Hz, 1H}), 3.05-2.91 (m, 2H), 2.64 (t, J = 10.7 \text{ Hz, 3H}), 2.03-1.88 (m, 2H), 1.78-1.10 (m, 10H). \\
^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} &\delta: 138.69, 138.30, 130.75, 130.28, 128.55, 128.11, 128.02, 126.11, 73.99, 63.61, 55.95, 45.33, 43.10, 37.61, 31.06, 31.00, 27.91, 22.92, 22.82.
\end{align*}
\]

4-Nitro-N-(((2S)-octahydro-1H-indol-2-yl)methyl)benzenesulfonamide (L9)

\[
\begin{align*}
[a]_D^{20} &= +7.0 \text{ (c = 1.3, CH}_2\text{Cl}_2). \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)} &\delta: 8.36 (d, J = 8.8 \text{ Hz, 2H}), 8.06 (d, J = 8.8 \text{ Hz, 2H}), 3.60-3.32 (m, 3H), 3.18-3.07 (m, 2H), 2.92 (dd, J = 12.4, 7.4 \text{ Hz, 1H}), 2.04 (dt, J = 13.0, 6.5 \text{ Hz, 1H}), 1.99-1.87 (m, 1H), 1.66-1.36 (m, 6H), 1.35-1.16 (m, 3H). \\
^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} &\delta: ...
\end{align*}
\]
CDCl₃ δ: 149.91, 146.42, 128.22, 124.30, 57.41, 56.57, 48.43, 38.17, 33.57, 29.65, 27.98, 23.10, 22.24.

(S)-diPhenyl(pyrrolidin-2-yl)methanol (L10)

\[
\begin{align*}
\text{[S]}-	ext{Alphenyl(pyrrolidin-2-yl)methanol (L10)} & \nonumber \\
\end{align*}
\]

\[
[a]_D^{20} = -68.6 \text{ (c = 1.0, CHCl₃)}. \quad \begin{aligned}
\text{H NMR (400 MHz, CDCl₃)} & \delta: 7.66-7.35 \text{ (m, 4H)}, 7.32-6.92 \text{ (m, 6H)}, 4.56 \text{ (s, 1H)}, 4.25 \text{ (t, J = 7.6 Hz, 1H)}, 3.09-2.68 \text{ (m, 2H)}, 1.80-1.41 \text{ (m, 4H)}. \\
\end{aligned}
\]

\[
[\alpha]_D^{13}C \text{ NMR (101 MHz, CDCl₃)} \delta: 148.17, 145.41, 128.22, 127.96, 126.45, 126.34, 125.86, 125.53, 77.11, 64.49, 46.76, 26.28, 25.51.
\]

(4S,4'S)-2,2'-(Propane-2,2-diyl)bis(4-isopropyl-4,5-dihydrooxazole) (L11)

\[
\begin{align*}
\text{[S]}-	ext{2,2'-(Propane-2,2-diyl)bis(4-isopropyl-4,5-dihydrooxazole) (L11)} & \nonumber \\
\end{align*}
\]

\[
[a]_D^{20} = -82.3 \text{ (c = 0.8, CH₂Cl₂)}. \quad \begin{aligned}
\text{H NMR (400 MHz, CDCl₃)} & \delta: 4.24-4.16 \text{ (m, 2H)}, 4.03-3.94 \text{ (m, 4H)}, 1.84-1.75 \text{ (m, 2H)}, 1.52 \text{ (s, 6H)}, 0.92 \text{ (d, J = 6.8 Hz, 6H)}, 0.86 \text{ (d, J = 6.8 Hz, 6H)}. \\
\end{aligned}
\]

\[
[\alpha]_D^{13}C \text{ NMR (101 MHz, CDCl₃)} \delta: 168.81, 71.52, 69.94, 38.59, 32.20, 24.45, 18.52, 17.36.
\]

3. Synthesis of β,γ-unsaturated α-ketoesters 1a-f, 1h, 1j-k, 1m-1n and 1p.

The β,γ-unsaturated α-ketoesters 1a-1f, 1h, 1j-k, 1m-n and 1p were prepared following the literature methods.5

(E)-Methyl 2-oxo-4-phenylbut-3-enoate (1a)

\[
\begin{align*}
\text{[E]-Methyl 2-oxo-4-phenylbut-3-enoate (1a)} & \nonumber \\
\end{align*}
\]

\[
\begin{aligned}
\text{H NMR (400 MHz, CDCl₃)} & \delta: 7.89 \text{ (d, J = 16.1 Hz, 1H)}, 7.64 \text{ (dd, J = 7.4, 1.1 Hz, 2H)}, 7.49-7.33 \text{ (m, 4H)}, 3.94 \text{ (s, 3H)}. \\
\end{aligned}
\]

\[
[\alpha]_D^{13}C \text{ NMR (101 MHz, CDCl₃)} \delta: 182.43, 162.56, 148.66, 133.99, 131.70, 129.10, 129.07, 120.48, 53.03.
\]

(E)-Ethyl 2-oxo-4-phenylbut-3-enoate (1b)

\[
\begin{align*}
\text{[E]-Ethyl 2-oxo-4-phenylbut-3-enoate (1b)} & \nonumber \\
\end{align*}
\]

\[
\begin{aligned}
\text{H NMR (400 MHz, CDCl₃)} & \delta: 7.85 \text{ (d, J = 16.1 Hz, 1H)}, 7.68-7.57 \text{ (m, 2H)}, 7.45-7.31 \text{ (m, 4H)},
\end{aligned}
\]
4.38 (q, \( J = 7.1 \) Hz, 2H), 1.40 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta: 182.92, 162.22, 148.47, 134.01, 131.63, 129.08, 129.03, 120.58, 62.50, 14.05. \)

\( (E)-iso \)Propyl 2-oxo-4-phenylbut-3-enoate (1c)

\( ^{1}H \) NMR (400 MHz, CDCl\(_3\)) \( \delta: 7.84 \) (d, \( J = 16.1 \) Hz, 1H), 7.62 (d, \( J = 5.9 \) Hz, 2H), 7.49-7.37 (m, 3H), 7.33 (d, \( J = 16.1 \) Hz, 1H), 5.23 (dt, \( J = 16.3, 6.2 \) Hz, 1H), 1.39 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta: 183.32, 161.92, 148.21, 134.11, 131.53, 129.06, 128.97, 120.79, 70.65, 21.64. \)

\( (E)-Methyl \) 4-(2-fluorophenyl)-2-oxobut-3-enoate (1d)

\( ^{1}H \) NMR (400 MHz, CDCl\(_3\)) \( \delta: 8.01 \) (d, \( J = 16.3 \) Hz, 1H), 7.65 (td, \( J = 7.7, 1.6 \) Hz, 1H), 7.24-7.17 (m, 1H), 7.14 (m, \( J = 10.5, 8.3, 1.0 \) Hz, 1H), 3.95 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta: 182.48, 162.40, 161.97 \) (d, \( J = 256.2 \) Hz), 140.91 (d, \( J = 3.1 \) Hz), 133.15 (d, \( J = 8.9 \) Hz), 129.55 (d, \( J = 2.4 \) Hz), 124.65 (d, \( J = 3.7 \) Hz), 122.64 (d, \( J = 6.6 \) Hz), 122.21 (d, \( J = 11.3 \) Hz), 116.42 (d, \( J = 21.8 \) Hz), 53.04.

\( (E)-Methyl \) 4-(3-fluorophenyl)-2-oxobut-3-enoate (1e)

\( ^{1}H \) NMR (400 MHz, CDCl\(_3\)) \( \delta: 7.83 \) (d, \( J = 16.1 \) Hz, 1H), 7.43-7.30 (m, 4H), 7.19-7.12 (m, 1H), 3.95 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta: 182.14, 163.01 \) (d, \( J = 247.7 \) Hz), 162.27, 146.92 (d, \( J = 2.7 \) Hz), 136.18 (d, \( J = 7.6 \) Hz), 130.67 (d, \( J = 8.2 \) Hz), 125.09 (d, \( J = 2.8 \) Hz), 121.61, 118.50 (d, \( J = 21.5 \) Hz), 115.04 (d, \( J = 22.0 \) Hz), 53.09.

\( (E)-Methyl \) 4-(4-fluorophenyl)-2-oxobut-3-enoate (1f)

\( ^{1}H \) NMR (400 MHz, CDCl\(_3\)) \( \delta: 7.84 \) (d, \( J = 16.1 \) Hz, 1H), 7.64 (dd, \( J = 8.6, 5.5 \) Hz, 2H), 7.31 (d, \( J = 16.1 \) Hz, 1H), 7.12 (t, \( J = 8.6 \) Hz, 2H), 3.94 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta: 182.15, 164.74 \) (d, \( J = 253.9 \) Hz), 162.47, 147.18, 131.11 (d, \( J = 8.8 \) Hz), 130.31 (d, \( J = 3.4 \) Hz), 120.17, 116.38 (d, \( J = 22.1 \) Hz), 53.04.

\( (E)-Methyl \) 4-(4-chlorophenyl)-2-oxobut-3-enoate (1h)
$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.83 (d, $J = 16.1$ Hz, 1H), 7.57 (d, $J = 8.6$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 16.1$ Hz, 1H), 3.94 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 182.13, 162.39, 146.96, 137.75, 132.49, 130.15, 129.44, 120.87, 53.06.

(E)-Methyl 2-oxo-4-(p-tolyl)but-3-enoate (1j)

$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.86 (d, $J = 16.1$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 16.1$ Hz, 1H), 7.23 (d, $J = 7.9$ Hz, 2H), 3.93 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 182.45, 162.70, 148.76, 142.56, 131.33, 129.86, 129.14, 119.51, 52.95, 21.63.

(E)-Methyl 4-((1,1′-biphenyl)-4-yl)-2-oxobut-3-enoate (1k)

$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.92 (d, $J = 16.1$ Hz, 1H), 7.73-7.59 (m, 6H), 7.42 (m, $J = 13.5$, 10.5, 5.7 Hz, 4H), 3.95 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 182.32, 162.62, 148.17, 144.48, 139.84, 132.94, 129.63, 128.97, 128.16, 127.71, 127.09, 120.26, 53.02.

(E)-Methyl 4-(3-methoxyphenyl)-2-oxobut-3-enoate (1m)

$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.84 (d, $J = 16.1$ Hz, 1H), 7.33 (dd, $J = 12.0$, 4.0 Hz, 2H), 7.23 (d, $J = 7.6$ Hz, 1H), 7.14 (s, 1H), 7.07-6.94 (m, 1H), 3.94 (s, 3H), 3.85 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 182.41, 162.56, 160.04, 148.54, 135.34, 130.06, 121.85, 120.77, 117.77, 113.57, 55.36, 52.96.

(E)-Methyl 4-(4-methoxyphenyl)-2-oxobut-3-enoate (1n)

$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.86 (d, $J = 16.0$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 2H), 7.26 (d, $J = 16.0$ Hz, 1H), 6.95 (d, $J = 8.8$ Hz, 2H), 3.94 (s, 3H), 3.87 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 182.26, 162.88, 162.69, 148.52, 131.09, 126.83, 118.16, 114.63, 55.47, 52.91.
(E)-Methyl 4-(furan-2-yl)-2-oxobut-3-enoate (1p)

\[
\begin{align*}
\text{O} & \quad \text{COOMe} \\
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.63 (d, J = 15.8 \text{ Hz}, 1 \text{H}), 7.60-7.56 (m, 1 \text{H}), 7.26-7.19 (m, 1 \text{H}), 6.83 (d, J = 3.5 \text{ Hz}, 1 \text{H}), 6.55 (dd, J = 3.4, 1.7 \text{ Hz}, 1 \text{H}), 3.92 (d, J = 0.4 \text{ Hz}, 3 \text{H}). \)

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta: 181.96, 162.41, 151.06, 146.37, 133.67, 118.60, 118.04, 113.17, 52.94. \)

4. Synthesis of \(\beta,\gamma\)-unsaturated \(\alpha\)-ketoesters 1g, 1i, 1l and 1o.

a) Preparation of aryl acetal derivatives\(^5a\)

A solution of aldehyde (50 mmol), \(p\)-toluenesulfonic acid monohydrate (2.5 mmol) and trimethyl orthoformate (0.5 mol) in dry methanol (100 mL) was heated to reflux for 24 h. Part of the solvent was evaporated \(\text{in vacuo}\), then Et\(_2\)O (125 mL) was added to the residue (ca. 25 mL), and the mixture was washed with saturated NaHCO\(_3\) solution (125 mL). The organic layer was separated, dried over Na\(_2\)SO\(_4\) and concentrated \(\text{in vacuo}\). The residue was purified by flash chromatography.

b) Preparation of methyl 2-((trimethylsilyl)oxy)acrylate\(^6\)

TEA (18.8 mL, 13.66 g, 135 mmol) was added dropwise to a mixture of methyl pyruvate (10.21 g, 100 mmol) and TMSCl (14.2 mL, 12.17 g, 112 mmol) in THF (100 mL) under N\(_2\). After 3.5 h, pentane (150 mL) was added, and the reaction mixture was filtered. The filtrate was washed with water (50 mL) and brine (50 mL) in turn, dried over Na\(_2\)SO\(_4\) and evaporated to give methyl 2-((trimethylsilyl)oxy)acrylate as a clear liquid (14.8 g, 85% yield), which was used without further purification.

c) Preparation of methyl 2-oxo-4-arylbut-3-enoate\(^5a,7\)

To a mixture of acetal (20 mmol) and methyl 2-((trimethylsilyl)oxy)acrylate (24 mmol) in dry dichloromethane (100 mL) was added boron trifluoridediethyl ether (22 mmol) dropwise under N\(_2\).
at -78 °C. The reaction mixture was warmed to 0 °C and stirred at the same temperature for 2 h. Saturated NaHCO₃ was added, the mixture was extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to afford crude γ-alkoxy-α-oxo ester, which was dissolved in toluene (100 mL). Then silica gel (30 g) was added and the mixture was heated at 110 °C with vigorous stirring for 12 h. After being cooled to room temperature, the mixture was filtered and the residue was washed with DCM for several times. The filtrate was combined, concentrated to give the crude β,γ-unsaturated α-ketoester. The purification was carried out by flash column chromatography with petroleum ether/ethyl acetate to afford yellow oil or solid.

**(E)-Methyl 4-(2-chlorophenyl)-2-oxobut-3-enoate (1g)**

![Chemical structure of (E)-Methyl 4-(2-chlorophenyl)-2-oxobut-3-enoate](image)

**¹H NMR (400 MHz, CDCl₃) δ:** 8.31 (d, J = 16.2 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.50-7.28 (m, 4H), 3.95 (s, 3H). **¹³C NMR (101 MHz, CDCl₃) δ:** 182.25, 162.37, 144.05, 136.19, 132.26, 130.44, 127.97, 127.21, 122.73, 99.99, 53.05.

**(E)-Methyl 4-(2-bromophenyl)-2-oxobut-3-enoate (1i)**

![Chemical structure of (E)-Methyl 4-(2-bromophenyl)-2-oxobut-3-enoate](image)

**¹H NMR (400 MHz, CDCl₃) δ:** 8.28 (d, J = 16.1 Hz, 1H), 7.75 (dd, J = 7.8, 1.5 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.34-7.31 (m, 1H), 7.31-7.28 (m, 1H), 3.96 (s, 3H). **¹³C NMR (101 MHz, CDCl₃) δ:** 182.19, 162.36, 146.70, 133.74, 132.38, 129.39, 128.10, 126.65, 122.96, 53.08.

**(E)-Methyl 4-(2-methoxyphenyl)-2-oxobut-3-enoate (1l)**

![Chemical structure of (E)-Methyl 4-(2-methoxyphenyl)-2-oxobut-3-enoate](image)

**¹H NMR (400 MHz, CDCl₃) δ:** 8.21 (d, J = 16.2 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.49-7.35 (m, 2H), 7.05-6.90 (m, 2H), 3.93 (s, 3H), 3.91 (s, 3H). **¹³C NMR (101 MHz, CDCl₃) δ:** 183.05, 162.95, 159.29, 144.15, 133.11, 129.53, 123.02, 120.92, 120.84, 111.35, 55.57, 52.87.

**(E)-Methyl 4-(2,5-dimethoxyphenyl)-2-oxobut-3-enoate (1o)**

![Chemical structure of (E)-Methyl 4-(2,5-dimethoxyphenyl)-2-oxobut-3-enoate](image)

**¹H NMR (400 MHz, CDCl₃) δ:** 8.21 (d, J = 16.2 Hz, 1H), 7.40 (d, J = 16.2 Hz, 1H), 7.15 (d, J =
3.0 Hz, 1H), 7.01 (dd, J = 9.0, 3.0 Hz, 1H), 6.89 (d, J = 9.0 Hz, 1H), 3.95 (s, 3H), 3.88 (s, 3H), 3.82 (s, 3H). 13C NMR (101 MHz, CDCl3) δ: 182.89, 162.90, 153.89, 153.53, 143.84, 123.42, 120.96, 119.30, 113.22, 112.62, 56.09, 55.84, 52.89.

5. Preparation of 2-vinylindoles 2

The 2-vinylindoles were prepared following the literature methods. 

(E)-1-Methyl-2-styryl-1H-indole (2a)

\[
\text{\includegraphics[width=2cm]{structure.png}}
\]

1H NMR (400 MHz, CDCl3) δ: 7.59 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 8.1 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.33-7.27 (m, 2H), 7.21 (d, J = 7.0 Hz, 1H), 7.18 (s, 2H), 7.10 (t, J = 7.4 Hz, 1H), 6.81 (s, 1H), 3.82 (s, 3H). 13C NMR (101 MHz, CDCl3) δ: 138.42, 138.18, 137.18, 130.93, 128.78, 128.00, 127.85, 126.45, 121.78, 120.43, 119.91, 117.09, 109.14, 99.08, 29.92.

(E)-2-(4-Bromostyryl)-1-methyl-1H-indole (2b)

\[
\text{\includegraphics[width=2cm]{structure.png}}
\]

1H NMR (400 MHz, CDCl3) δ: 7.59 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.2 Hz, 1H), 7.20 (dd, J = 15.0, 7.1 Hz, 1H), 7.15-7.05 (m, 3H), 6.80 (s, 1H), 3.81 (s, 3H). 13C NMR (101 MHz, CDCl3) δ: 138.25, 137.98, 136.13, 131.87, 129.44, 127.93, 127.86, 121.99, 121.51, 120.51, 120.00, 117.75, 109.17, 99.44, 29.92.

(E)-1-Methyl-2-(4-methylstyryl)-1H-indole (2c)

\[
\text{\includegraphics[width=2cm]{structure.png}}
\]

1H NMR (400 MHz, CDCl3) δ: 7.57 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.26-7.04 (m, 7H), 6.76 (s, 1H), 3.76 (s, 3H), 2.36 (s, 3H). 13C NMR (101 MHz, CDCl3) δ: 138.67, 138.14, 137.85, 134.44, 130.97, 129.52, 128.08, 126.40, 121.65, 120.37, 119.87, 116.10, 109.12, 98.78, 29.90, 21.32.

6. General procedure for the asymmetric Diels–Alder reaction

To a 10 mL tube was added chiral ligand L2 (3.3 mg, 0.01 mmol), enone 1 (0.12 mmol), Cu(OTf)2 (3.6 mg, 0.01 mmol) and 1.5 mL DCM (containing 0.1mmol H2O) under N2. The solution was
stirred at 30 °C for 30 min, then 2-vinylindole 2 (0.8 mmol) was added. After completion of the reaction (about 10 min), the mixture was quenched with saturated NaHCO₃ solution (1 mL) and extracted with DCM (3 × 3 mL). The DCM layer was combined, dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure to give the crude product, which was purified by column chromatography on silica gel to provide pure 3.

**Methyl 2-((2R,2R,4R)-9-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3a)**

![Image of the compound](image_url)

Yield: 90%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_major = 21.34 min, t_minor = 26.97 min, 95% ee. [α]D2 = -42.6 (c = 0.76, CH₂Cl₂). mp 150-153 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.34-7.18 (m, 9H), 7.18-7.12 (m, 1H), 7.10 (dd, J = 7.8, 1.4 Hz, 2H), 6.95-6.86 (m, 2H), 4.63 (d, J = 4.1 Hz, 1H), 4.17 (dd, J = 4.1, 3.0 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.67-3.56 (m, 2H), 3.25 (q, J = 9.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ: 193.35, 161.47, 143.56, 141.37, 137.68, 136.17, 136.17, 128.67, 128.52, 128.43, 128.02, 127.04, 126.68, 126.58, 121.02, 118.96, 118.83, 108.67, 107.78, 56.22, 52.92, 39.11, 38.07, 29.33, 25.60. HRMS (ESI) m/z calcd. for C₂₈H₂₆NO₃ [M+H]+: 424.1907, found: 424.1905.

**Ethyl 2-((2R,3R,4R)-9-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3b)**

![Image of the compound](image_url)

Yield: 89%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 98/2, flow rate 0.6 mL/min, λ = 220 nm), t_major = 25.88 min, t_minor = 37.77 min, 53% ee. [α]D2 = -32.5 (c = 0.67, CH₂Cl₂). mp 172-176 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.36-7.06 (m, 12H), 6.92 (dt, J = 14.5, 7.3 Hz, 2H), 4.64 (d, J = 3.6 Hz, 1H), 4.31-4.07 (m, 3H), 3.73 (s, 3H), 3.68-3.57 (m, 2H), 3.32-3.07 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ: 193.35, 161.17, 143.56, 141.37, 137.68, 136.17, 128.67, 128.52, 128.43, 128.02, 127.04, 126.68, 126.58, 121.02, 118.96, 118.83, 108.67, 107.78, 56.22, 52.92, 39.11, 38.07, 29.33, 25.60. HRMS (ESI) m/z calcd. for C₂₉H₂₈NO₃ [M+H]+: 438.2064, found: 438.2066.

**isoPropyl 2-((2R,3R,4R)-9-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3c)**
Yield: 95%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 12.86 min, t_{minor} = 18.88 min, 34% ee. [α]_D^25 = -21.5 (c = 0.86, CH₂Cl₂), mp 115-118 °C. \(^1\)H NMR (400 MHz, CDCl₃) δ: 7.39-7.20 (m, 9H), 7.20-7.14 (m, 3H), 7.03-6.92 (m, 2H), 5.15-5.04 (m, 1H), 4.69 (d, J = 3.6 Hz, 1H), 4.21 (t, J = 3.0 Hz, 1H), 3.77 (s, 3H), 3.71 (t, J = 8.0 Hz, 1H), 3.68-3.64 (m, 1H), 3.26 (dd, J = 14.8, 4.5 Hz, 1H), 1.31 (dd, J = 10.6, 6.3 Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl₃) δ: 194.13, 160.85, 143.73, 141.62, 137.70, 136.39, 128.65, 128.52, 128.43, 128.05, 126.98, 126.66, 121.01, 118.97, 118.76, 108.69, 107.70, 70.77, 56.01, 39.26, 37.97, 29.33, 25.53, 21.56. HRMS (ESI) m/z calcd. for C₃₀H₃₀NO₃ [M+H]^+: 452.2220, found: 452.2224.

Methyl 2-((2R,3R,4S)-4-(2-fluorophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3d)

Yield: 96%, pale yellow solid. HPLC: Chiralcel OD-H (hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 22.68 min, t_{minor} = 26.33 min, 93% ee. [α]_D^25 = -23.9 (c = 0.82, CH₂Cl₂), mp 198-201 °C. \(^1\)H NMR (400 MHz, CDCl₃) δ: 7.30 (d, J = 8.2 Hz, 1H), 7.28-7.05 (m, 8H), 7.02-6.86 (m, 4H), 4.88 (d, J = 3.6 Hz, 1H), 4.23 (dd, J = 20.4, 16.7 Hz, 1H), 3.74 (d, J = 13.2 Hz, 3H), 3.68 (s, 3H), 3.67-3.61 (m, 1H), 3.52 (dd, J = 16.0, 9.1 Hz, 1H), 3.23 (dd, J = 22.1, 11.1 Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl₃) δ: 194.27, 161.84, 160.72 (J_{CF} = 247.2 Hz), 140.97, 137.69, 136.28, 130.97, 130.13 (d, J_{CF} = 13.7 Hz), 128.58, 128.53, 127.87, 127.17, 126.26, 123.99, 121.12, 119.06, 118.44, 115.6 (d, J_{CF} = 21.9 Hz), 108.76, 106.82, 53.83, 52.77, 38.45, 33.03, 29.34, 25.33. HRMS (ESI) m/z calcd. for C₂₈H₂₅FNO₃ [M+H]^+: 442.1813, found: 442.1814.

Methyl 2-((2R,3R,4R)-4-(3-fluorophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3e)
Yield: 94%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 96/4, flow rate 0.5 mL/min, λ = 220 nm), t\textsubscript{major} = 23.38 min, t\textsubscript{minor} = 27.66 min, 50% ee. [\alpha]\textsuperscript{D} = -36.3 (c = 0.81, CH\textsubscript{2}Cl\textsubscript{2}). mp 140-145 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.31 (d, J = 7.8 Hz, 1H), 6.96-6.88 (m, 3H), 4.62 (d, J = 4.1 Hz, 1H), 4.18-4.10 (m, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.65-3.56 (m, 2H), 3.26 (q, J = 10.3 Hz, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ: 193.04, 163.01 (J\textsubscript{CF} = 245.6 Hz), 161.36, 146.44 (J = 6.6 Hz), 141.10, 137.72, 136.23, 129.89 (J = 8.3 Hz), 128.60, 128.01, 127.18, 126.40, 124.41, 121.18, 119.14, 118.70, 115.65 (J = 21.7 Hz), 113.73 (d, J = 21.2 Hz), 108.81, 107.29, 106.10, 53.01, 38.89, 38.20, 29.36, 25.62. HRMS (ESI) m/z calcd. for C\textsubscript{28}H\textsubscript{25}FNO\textsubscript{3} [M+H]\textsuperscript{+}: 442.1813, found: 442.1818.

Methyl 2-((2\textsubscript{R},3\textsubscript{R},4\textsubscript{R})-4-(4-fluorophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3f)

Yield: 86%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 94/6, flow rate 0.5 mL/min, λ = 220 nm), t\textsubscript{major} = 18.88 min, t\textsubscript{minor} = 22.82 min, 52% ee. [\alpha]\textsuperscript{D} = -38.1 (c = 0.70, CH\textsubscript{2}Cl\textsubscript{2}). mp 179-183 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.34 (d, J = 8.2 Hz, 1H), 7.02-6.87 (m, 4H), 4.62 (d, J = 4.6 Hz, 1H), 4.14 (dd, J = 4.6, 3.1 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.69-3.56 (m, 2H), 3.29 (dd, J = 15.1, 4.6 Hz, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ: 193.15, 161.71 (J\textsubscript{CF} = 246.5 Hz), 161.40, 141.13, 137.69, 136.06, 130.24, 128.56, 127.99, 127.14, 126.38, 121.12, 119.05, 118.77, 108.75, 107.83, 56.38, 52.98, 38.31, 38.21, 29.33, 25.74. HRMS (ESI) m/z calcd. for C\textsubscript{28}H\textsubscript{25}FNO\textsubscript{3} [M+H]\textsuperscript{+}: 442.1813, found: 442.1818.

Methyl 2-((2\textsubscript{R},3\textsubscript{R},4\textsubscript{S})-4-(2-chlorophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3g)

Yield: 91%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 90/10, flow rate 0.8 mL/min, λ = 220 nm), t\textsubscript{major} = 13.05 min, t\textsubscript{minor} = 33.68 min, 67% ee. [\alpha]\textsuperscript{D} = -12.8 (c = 0.74, CH\textsubscript{2}Cl\textsubscript{2}). mp 180-184 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.46 (d, J = 7.6 Hz, 1H), 7.07 (t, J = 7.3 Hz, 1H), 7.02-6.89 (m, 3H), 4.15 (s, 1H), 3.75 (s, 3H), 3.55 (s, 4H), 3.42 (dd, J = 16.0, 10.6 Hz, 1H), 3.19 (d, J = 12.9 Hz, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ:
Methyl 2-((2R,3R,4R)-4-(4-chlorophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3h)

Yield: 84%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_major = 28.32 min, t_minor = 31.49 min, 56% ee. [α]_D^23 = -41.7 (c = 0.70, CHCl₃). mp 170-176 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.31 (d, J = 8.2 Hz, 1H), 7.26-7.21 (m, 6H), 7.17 (ddd, J = 9.5, 8.5, 3.8 Hz, 2H), 7.08 (dd, J = 7.7, 1.6 Hz, 2H), 6.91 (ddd, J = 16.3, 11.7, 4.2 Hz, 2H), 4.58 (d, J = 4.6 Hz, 1H), 4.11 (dd, J = 4.6, 3.1 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.60 (dd, J = 20.7, 7.2 Hz, 2H), 3.27 (dd, J = 14.3, 3.7 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ: 193.05, 161.36, 142.11, 141.04, 137.70, 136.13, 132.46, 130.13, 128.59, 128.00, 127.19, 126.34, 121.18, 119.12, 118.76, 108.79, 107.51, 56.24, 53.02, 38.48, 38.26, 29.36, 25.73. HRMS (ESI) m/z calcd. for C₂₈H₂₅ClNO₃ [M+H]^+: 458.1517, found: 458.1518.

Methyl 2-((2R,3R,4S)-4-(2-bromophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3i)

Yield: 80%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 90/10, flow rate 0.8 mL/min, λ = 220 nm), t_major = 15.00 min, t_minor = 32.64 min, 71% ee. [α]_D^25 = -8.2 (c = 0.80, CH₂Cl₂). mp 143-147 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.71-7.62 (m, 1H), 7.35-7.19 (m, 4H), 7.14 (ddd, J = 16.7, 7.2, 2.6 Hz, 5H), 6.95 (dt, J = 14.5, 7.3 Hz, 3H), 4.97 (s, 1H), 4.13 (s, 1H), 3.74 (s, 3H), 3.63-3.54 (m, 1H), 3.49 (s, 3H), 3.36 (dd, J = 15.8, 11.4 Hz, 1H), 3.17 (dd, J = 16.0, 5.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ: 195.64, 162.18, 142.31, 140.66, 137.77, 136.43, 133.23, 130.72, 128.58, 128.53, 127.77, 127.42, 126.22, 124.53, 121.21, 119.11, 118.69, 108.77, 107.48, 53.64, 52.57, 39.27, 38.47, 29.36, 24.25. HRMS (ESI) m/z calcd. for C₂₈H₂₅BrNO₃ [M+H]^+: 502.1012, found: 502.1013.

Methyl 2-((2R,3R,4R)-9-methyl-2-phenyl-4-(p-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3j)
Yield: 77%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 220$ nm), $t_{major} = 21.14$ min, $t_{minor} = 30.94$ min, 59% ee. $\left[a\right]_D^{25} = -48.3$ (c = 0.77, CH$_2$Cl$_2$). mp 140-147 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.30 (d, $J = 8.2$ Hz, 1H), 7.25-7.05 (m, 10H), 6.92 (dt, $J = 14.1$, 7.2 Hz, 2H), 4.60 (d, $J = 3.8$ Hz, 1H), 4.18-4.10 (m, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.66-3.57 (m, 2H), 3.28-3.15 (m, 1H), 2.31 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 193.48, 161.51, 141.50, 140.54, 137.68, 136.15, 129.15, 128.84, 128.51, 128.05, 127.01, 126.65, 120.99, 118.95, 118.88, 108.66, 107.92, 56.31, 52.91, 38.76, 38.03, 29.33, 25.56, 21.10. HRMS (ESI) m/z calcd. for C$_{29}$H$_{28}$NO$_3$ [M+H]$^+$: 438.2064, found: 438.2063.

**Methyl 2-((2R,3R,4R)-4-((1,1'-biphenyl)-4-yl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3k)**

Yield: 68%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 93/7, flow rate 0.5 mL/min, $\lambda = 210$ nm), $t_{major} = 41.16$ min, $t_{minor} = 23.45$ min, 57% ee. $\left[a\right]_D^{25} = -65.0$ (c = 0.65, CH$_2$Cl$_2$). mp 167-174 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.64-7.58 (m, 2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.48-7.31 (m, 7H), 7.29-7.20 (m, 2H), 7.16 (dd, $J = 9.1$, 7.4 Hz, 3H), 7.01 (d, $J = 7.6$ Hz, 1H), 6.95 (t, $J = 7.3$ Hz, 1H), 4.70 (d, $J = 4.1$ Hz, 1H), 4.28-4.20 (m, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.67 (dd, $J = 21.0$, 7.3 Hz, 2H), 3.30 (dd, $J = 14.0$, 3.6 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 193.32, 161.45, 142.67, 141.35, 140.88, 139.42, 137.69, 136.18, 129.07, 128.72, 128.53, 128.02, 127.11, 127.06, 126.99, 126.58, 121.06, 119.00, 118.87, 108.70, 107.72, 56.18, 52.94, 38.82, 38.13, 29.34, 25.61. HRMS (ESI) m/z calcd. for C$_{34}$H$_{30}$NO$_3$ [M+H]$^+$: 500.2220, found: 500.2220.

**Methyl 2-((2R,3R,4S)-4-(2-methoxyphenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3l)**

Yield: 80%, yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.6 mL/min,
λ = 220 nm), $t_{\text{major}} = 18.46$ min, $t_{\text{minor}} = 21.14$ min, 87% ee. $[\alpha]_D^{25} = +6.7$ (c = 0.72, CH$_2$Cl$_2$). mp 167-171 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$: 7.31 (d, $J = 8.2$ Hz, 1H), 7.28-7.23 (m, 1H), 7.23-7.11 (m, 6H), 7.04 (d, $J = 7.7$ Hz, 1H), 6.98-6.90 (m, 2H), 6.82 (dd, $J = 7.5$, 1.7 Hz, 1H), 6.74 (td, $J = 7.4$, 0.9 Hz, 1H), 4.92 (s, 1H), 4.12 (dd, $J = 3.3$, 1.8 Hz, 1H), 3.91 (s, 3H), 3.74 (s, 3H), 3.63 (s, 3H), 3.57-3.43 (m, 2H), 3.11 (dd, $J = 15.2$, 4.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$: 196.05, 162.80, 156.68, 141.75, 137.74, 137.00, 131.37, 129.93, 128.46, 127.92, 126.89, 126.66, 120.91, 120.25, 118.82, 118.69, 110.30, 108.63, 106.93, 55.31, 52.86, 52.44, 38.30, 33.72, 29.30, 24.80. HRMS (ESI) $m/z$ calcd. for C$_{29}$H$_{28}$NO$_4$ [M+H]$: 454.2013, found: 454.2010.

**Methyl 2-((2R,3R,4R)-4-(3-methoxyphenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3m)**

Yield: 84%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 98/2, flow rate 0.8 mL/min, λ = 220 nm), $t_{\text{major}} = 36.73$ min, $t_{\text{minor}} = 27.95$ min, 58% ee. $[\alpha]_D^{25} = -38.3$ (c = 0.78, CH$_2$Cl$_2$), mp 80-82 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$: 7.30 (d, $J = 8.2$ Hz, 1H), 7.20 (dd, $J = 13.2$, 7.9, 4.3 Hz, 4H), 7.12 (dd, $J = 8.0$, 6.6 Hz, 3H), 7.00-6.86 (m, 4H), 6.77 (dd, $J = 7.9$, 2.1 Hz, 1H), 4.61 (d, $J = 3.9$ Hz, 1H), 4.17 (dd, $J = 4.8$, 2.2 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.64-3.56 (m, 2H), 3.24 (q, $J = 10.4$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$: 193.35, 161.46, 159.68, 145.37, 141.41, 137.70, 136.14, 129.35, 128.50, 128.03, 127.01, 126.63, 121.11, 121.00, 118.97, 118.80, 114.90, 111.68, 108.64, 107.64, 56.09, 55.17, 52.88, 39.20, 38.09, 29.30, 25.52. HRMS (ESI) $m/z$ calcd. for C$_{29}$H$_{28}$NO$_4$ [M+H]$: 454.2013, found: 454.2014.

**Methyl 2-((2R,3R,4R)-4-(4-methoxyphenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3n)**

Yield: 86%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 90/10, flow rate 0.4 mL/min, λ = 220 nm), $t_{\text{major}} = 32.85$ min, $t_{\text{minor}} = 26.14$ min, 78% ee. $[\alpha]_D^{25} = -56.7$ (c = 0.78, CH$_2$Cl$_2$), mp 188-191 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$: 7.31 (d, $J = 8.2$ Hz, 1H), 7.24-7.08 (m, 8H), 6.97-6.88 (m, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 4.58 (d, $J = 4.1$ Hz, 1H), 4.17-4.08 (m, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.64-3.56 (m, 2H), 3.24 (q, $J = 9.8$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$: 193.47, 161.49, 158.33, 141.46, 137.68, 136.05, 135.62, 129.65, 128.51, 128.04,
127.02, 126.61, 121.00, 118.95, 118.91, 113.81, 108.66, 108.14, 56.46, 55.21, 52.90, 38.32, 38.10, 29.32, 25.64. HRMS (ESI) m/z calcd. for C_{29}H_{28}NO_{4} [M+H]^+: 454.2013, found: 454.2015.

Methyl 2-((2R,3R,4S)-4-(2,5-dimethoxyphenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3o)

Yield: 84%, yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 20.40 min, t_{minor} = 15.60 min, 91% ee. [α]_D^{5} = +1.2 (c = 0.82, CH_2Cl_2). mp 197-203 °C. 1H NMR (400 MHz, CDCl_3): δ: 7.32-7.23 (m, 2H), 7.23-7.10 (m, 5H), 7.06 (d, J = 7.8 Hz, 1H), 6.96-6.89 (m, 1H), 6.87 (d, J = 8.8 Hz, 1H), 6.73 (dd, J = 8.8, 3.1 Hz, 1H), 6.44 (d, J = 3.1 Hz, 1H), 4.89 (s, 1H), 4.17-4.05 (m, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 3.62 (s, 3H), 3.59 (s, 3H), 3.53 (d, J = 11.1 Hz, 2H), 3.10 (q, J = 11.2 Hz, 1H). 13C NMR (101 MHz, CDCl_3): δ: 195.88, 162.75, 153.27, 151.09, 141.69, 137.77, 136.87, 133.02, 128.45, 127.81, 126.87, 126.62, 120.86, 118.81, 118.61, 117.63, 110.90, 110.77, 108.59, 106.70, 55.80, 55.55, 52.78, 52.43, 38.17, 33.81, 29.27, 24.80. HRMS (ESI) m/z calcd. for C_{30}H_{30}NO_{5} [M+H]^+: 484.2118, found: 484.2115.

Methyl 2-((2R,3R,4S)-4-(furan-2-yl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3p)

Yield: 86%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 90/10, flow rate 0.6 mL/min, λ = 220 nm), t_{major} = 15.03 min, t_{minor} = 13.58 min, 42% ee. [α]_D^{5} = -0.4 (c = 0.71, CH_2Cl_2). mp 140-146 °C. 1H NMR (400 MHz, CDCl_3): δ: 7.39 (dd, J = 1.8, 0.8 Hz, 1H), 7.34-7.10 (m, 8H), 7.06-6.96 (m, 1H), 6.27 (dd, J = 3.1, 1.9 Hz, 1H), 6.07-5.96 (m, 1H), 4.69 (d, J = 4.0 Hz, 1H), 4.45-4.35 (m, 1H), 3.78-3.72 (m, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.57-3.47 (m, 1H), 3.20 (dd, J = 16.3, 5.9 Hz, 1H). 13C NMR (101 MHz, CDCl_3): δ: 193.62, 161.46, 155.63, 141.84, 141.08, 137.47, 135.62, 128.58, 127.97, 127.18, 126.46, 121.11, 119.18, 118.46, 110.24, 108.79, 108.14, 106.27, 52.89, 52.35, 38.83, 33.48, 29.29, 25.29. HRMS (ESI) m/z calcd. for C_{26}H_{24}NO_{4} [M+H]^+: 414.1700, found: 414.1704.

Methyl 2-((2R,3R,4R)-2-(4-bromophenyl)-9-methyl-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3q)
Yield: 82%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_major = 18.48 min, t_minor = 34.28 min, 59% ee. [α]D 25 = -56.7 (c = 0.82, CH₂Cl₂), mp 171-177 °C. 1H NMR (400 MHz, CDCl₃) δ: 7.41-7.36 (m, 2H), 7.36-7.22 (m, 6H), 7.18 (ddd, J = 8.2, 4.6, 3.6 Hz, 1H), 7.01 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 4.2 Hz, 2H), 4.65 (d, J = 4.2 Hz, 1H), 4.16 (dd, J = 4.2, 3.0 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.67-3.57 (m, 2H), 3.26 (dd, J = 19.3, 9.4 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ: 193.11, 161.36, 143.32, 140.42, 137.70, 135.72, 131.59, 129.83, 128.62, 128.49, 126.79, 126.47, 121.16, 120.94, 119.06, 118.85, 108.72, 107.71, 56.15, 53.02, 39.03, 37.60, 29.36, 25.40. HRMS (ESI) m/z calcd. for C₂₈H₂₅BrNO₃ [M+H]+: 502.1012, found: 502.1015.

**Methyl 2-((2R,3R,4S)-2-(4-bromophenyl)-4-(2-fluorophenyl)-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3r)**

Yield: 79%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.6 mL/min, λ = 220 nm), t_major = 20.00 min, t_minor = 24.34 min, 56% ee. [α]D 25 = -28.8 (c = 0.82, CH₂Cl₂), mp 203-208 °C. 1H NMR (400 MHz, CDCl₃) δ: 7.36 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.2 Hz, 1H), 7.26-7.19 (m, 1H), 7.15 (ddd, J = 8.2, 5.7, 2.5 Hz, 1H), 7.13-7.06 (m, 1H), 7.02-6.89 (m, 6H), 4.86 (d, J = 4.0 Hz, 1H), 4.16 (td, J = 3.7 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.61 (dd, J = 9.0, 5.7, 3.4 Hz, 1H), 3.56-3.44 (m, 1H), 3.24 (dd, J = 16.2, 5.8 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ: 193.90, 161.75, 160.69 (JC,F = 247.4 Hz), 140.04, 137.69, 135.80, 131.64, 130.97, 130.93, 129.83 (d, JC,F = 13.3 Hz), 129.67, 128.72, 128.64, 126.14, 124.04, 124.01, 121.24, 121.04, 119.15, 118.43, 115.63 (d, JC,F = 20.47 Hz), 108.79, 106.79, 53.67, 52.88, 37.97, 32.96, 29.35, 25.40. HRMS (ESI) m/z calcd. for C₂₈H₂₃BrNO₃ [M+H]+: 520.0918, found: 520.0920.

**Methyl 2-((2R,3R,4S)-2-(4-bromophenyl)-4-(2,5-dimethoxyphenyl)-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3s)**

Yield: 82%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_major = 18.48 min, t_minor = 34.28 min, 59% ee. [α]D 25 = -56.7 (c = 0.82, CH₂Cl₂), mp 171-177 °C. 1H NMR (400 MHz, CDCl₃) δ: 7.41-7.36 (m, 2H), 7.36-7.22 (m, 6H), 7.18 (ddd, J = 8.2, 4.6, 3.6 Hz, 1H), 7.01 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 4.2 Hz, 2H), 4.65 (d, J = 4.2 Hz, 1H), 4.16 (dd, J = 4.2, 3.0 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.67-3.57 (m, 2H), 3.26 (dd, J = 19.3, 9.4 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ: 193.11, 161.36, 143.32, 140.42, 137.70, 135.72, 131.59, 129.83, 128.62, 128.49, 126.79, 126.47, 121.16, 120.94, 119.06, 118.85, 108.72, 107.71, 56.15, 53.02, 39.03, 37.60, 29.36, 25.40. HRMS (ESI) m/z calcd. for C₂₈H₂₅BrNO₃ [M+H]+: 502.1012, found: 502.1015.

**Methyl 2-((2R,3R,4S)-2-(4-bromophenyl)-4-(2-fluorophenyl)-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3r)**

Yield: 79%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.6 mL/min, λ = 220 nm), t_major = 20.00 min, t_minor = 24.34 min, 56% ee. [α]D 25 = -28.8 (c = 0.82, CH₂Cl₂), mp 203-208 °C. 1H NMR (400 MHz, CDCl₃) δ: 7.36 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.2 Hz, 1H), 7.26-7.19 (m, 1H), 7.15 (ddd, J = 8.2, 5.7, 2.5 Hz, 1H), 7.13-7.06 (m, 1H), 7.02-6.89 (m, 6H), 4.86 (d, J = 4.0 Hz, 1H), 4.16 (td, J = 3.7 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.61 (dd, J = 9.0, 5.7, 3.4 Hz, 1H), 3.56-3.44 (m, 1H), 3.24 (dd, J = 16.2, 5.8 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ: 193.90, 161.75, 160.69 (JC,F = 247.4 Hz), 140.04, 137.69, 135.80, 131.64, 130.97, 130.93, 129.83 (d, JC,F = 13.3 Hz), 129.67, 128.72, 128.64, 126.14, 124.04, 124.01, 121.24, 121.04, 119.15, 118.43, 115.63 (d, JC,F = 20.47 Hz), 108.79, 106.79, 53.67, 52.88, 37.97, 32.96, 29.35, 25.40. HRMS (ESI) m/z calcd. for C₂₈H₂₃BrNO₃ [M+H]+: 520.0918, found: 520.0920.
Yield: 82%, yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 90/10, flow rate 0.6 mL/min, λ = 220 nm), t_major = 18.82 min, t_minor = 15.42 min, 68% ee. [α]D23° = +11.0 (c = 0.92, CH2Cl2), mp 185-187 °C. 1H NMR (400 MHz, CDCl3) δ: 7.41-7.33 (m, 2H), 7.29 (d, J = 8.2 Hz, 1H), 7.18-7.10 (m, 1H), 7.05 (d, J = 8.4 Hz, 3H), 6.97-6.90 (m, 1H), 6.87 (d, J = 8.8 Hz, 1H), 6.73 (dd, J = 8.8, 3.1 Hz, 1H), 6.41 (d, J = 3.1 Hz, 1H), 4.88 (s, 1H), 4.06 (dd, J = 3.1, 2.2 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 3.59 (s, 3H), 3.56-3.38 (m, 2H), 3.08 (dd, J = 15.3, 4.9 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ: 195.53, 162.77, 153.27, 151.04, 140.82, 137.76, 136.49, 132.73, 131.51, 129.66, 126.51, 121.00, 120.72, 118.90, 118.58, 117.64, 110.95, 110.81, 108.64, 106.59, 55.80, 55.53, 52.70, 52.57, 37.64, 33.75, 29.29, 24.83. HRMS (ESI) m/z calcd. for C30H29BrNO5 [M+H]+: 562.1224, found: 562.1225.

Methyl 2-((2R,3R,4S)-2-(4-bromophenyl)-4-(2-methoxyphenyl)-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3t)

Yield: 69%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.6 mL/min, λ = 220 nm), t_major = 16.46 min, t_minor = 30.33 min, 90% ee. [α]D23° = -5.2 (c = 0.73, CH2Cl2), mp 171-178 °C. 1H NMR (400 MHz, CDCl3) δ: 7.39 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.2 Hz, 1H), 7.24 (dd, J = 7.7, 1.4 Hz, 1H), 7.21-7.14 (m, 1H), 7.07 (dd, J = 7.6, 5.5 Hz, 3H), 7.00-6.91 (m, 2H), 6.82 (dd, J = 7.5, 1.7 Hz, 1H), 6.76 (td, J = 7.4, 0.8 Hz, 1H), 4.94 (s, 1H), 4.08 (dt, J = 22.1, 11.1 Hz, 1H), 3.93 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 3.62-3.51 (m, 1H), 3.49-3.38 (m, 1H), 3.12 (dd, J = 15.8, 5.4 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ: 195.67, 162.79, 156.62, 140.88, 137.72, 136.61, 131.51, 131.07, 129.90, 129.66, 128.03, 126.54, 121.03, 120.72, 120.28, 118.90, 118.65, 110.32, 108.65, 106.79, 55.30, 52.70, 52.57, 37.75, 33.65, 29.32, 24.83. HRMS (ESI) m/z calcd. for C29H27BrNO4 [M+H]+: 532.1118, found: 532.1118.

Methyl 2-((2R,3R,4S)-9-methyl-4-phenyl-2-(p-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3u)

Yield: 73%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_major = 18.82 min, t_minor = 28.65 min, 56% ee. [α]D23° = -59.1 (c = 0.64, CH2Cl2), mp 176-180 °C. 1H NMR (400 MHz, CDCl3) δ: 7.33-7.18 (m, 6H), 7.14 (dt, J = 8.2, 4.1
Hz, 1H), 7.03 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 3.9 Hz, 2H), 4.61 (d, J = 4.4 Hz, 1H), 4.15 (dd, J = 4.4, 3.1 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.66-3.51 (m, 2H), 3.24 (dd, J = 15.2, 4.9 Hz, 1H), 2.28 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 193.39, 161.46, 143.59, 138.31, 137.66, 136.63, 136.18, 129.19, 128.72, 128.40, 127.88, 126.63, 126.59, 120.96, 118.93, 118.86, 108.64, 107.92, 56.29, 52.89, 39.03, 37.81, 29.31, 25.87, 20.98. HRMS (ESI) $m/z$ calcd. for C$_{29}$H$_{28}$NO$_3$ [M+H$^+$]: 438.2064, found: 438.2063.

Methyl 2-((2R,3R,4S)-4-(2-methoxyphenyl)-9-methyl-2-(p-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3v)

Yield: 91%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/i-PrOH = 95/5, flow rate 0.6 mL/min, $\lambda = 220$ nm), $t_{\text{major}}$ = 15.60 min, $t_{\text{minor}}$ = 25.67 min, 50% ee. $[\alpha]_D^{25} = -2.2$ (c = 0.85, CH$_2$Cl$_2$), mp 174-178 ºC. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.30 (d, J = 8.2 Hz, 1H), 7.22-7.18 (m, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.09-7.00 (m, 5H), 6.97-6.88 (m, 2H), 6.82 (dd, J = 7.5, 1.6 Hz, 1H), 6.74 (t, J = 7.3 Hz, 1H), 4.91 (s, 1H), 4.10 (dt, J = 15.0, 7.5 Hz, 1H), 3.89 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H), 3.58-3.36 (m, 2H), 3.09 (dd, J = 15.3, 4.6 Hz, 1H), 2.28 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 196.11, 162.78, 156.68, 138.70, 137.70, 137.09, 136.42, 131.40, 129.94, 129.11, 127.86, 127.68, 126.67, 120.85, 120.23, 118.78, 118.68, 110.26, 108.59, 106.92, 55.28, 52.88, 52.42, 37.94, 33.69, 29.28, 24.98, 20.97. HRMS (ESI) $m/z$ calcd. for C$_{30}$H$_{30}$NO$_4$ [M+H$^+$]: 468.2169, found: 468.2167.

7. References


5 a) L. Gremaud, A. Alexakis, Angew. Chem., Int. Ed. 2012, 51, 794; b) D. Belmessieri, L. C. Morrill,


8. HPLC spectra

![HPLC spectra](image)

**Racemic product**

![HPLC spectra](image)

**Optically enriched product**
Racemic product

Optically enriched product
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Optically enriched product

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Optically enriched product

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Racemic product

Optically enriched product
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9. $^1$H and $^{13}$C NMR spectra