A Triple-functiona"ised Metal Centre-Catalyzed Enantioselective Multicomponent Reactions

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1. Materials and Methods

All reactions and manipulations were carried out under an air atmosphere, in a flame-dried or oven-dried flask containing magnetic stir bar. All $^1$H NMR, and $^{13}$C NMR spectra were recorded using a Brucker 400 MHz spectrometer in CDCl$_3$. Tetramethylsilane (TMS) served as an internal standard ($\delta = 0$) for $^1$H NMR, and CDCl$_3$ was used as internal standard ($\delta = 77.0$) for $^{13}$C NMR. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). HRMS (ESI) Mass spectra were recorded on IonSpec FT-ICR mass spectrometer. Chiralpak AD-H, IA, OD-H, IC, chiral columns were purchased from Daicel Chemical Industries, LTD. For the React IR experiments, the reaction spectra were recorded using an IC 15 from Mettler Toledo AutoChem. Data manipulation was carried out using the ICIR software, version 4.3. The racemic standards used in HPLC studies were prepared according to the general procedure by using [Rh(COD)Cl]$_2$ and Cinchonine as catalyst. Dichloromethane (DCM), 1, 2-dichloroethane (DCE) and toluene were distilled over calcium hydride. Solvents for the column chromatography were distilled before use. All reactions were carried out under an air atmosphere in glassware $L_1$ and $L_7$ were purchased from sigma-aldrich. $L_2-L_6$ were prepared according to the literature.$^1$ Nitroacrylates were prepared according to literature.$^2$

2. Experimental Procedures

General Procedure for Racemic Three-Component Reactions:

To a flask charged with 2 mol% [Rh(COD)Cl]$_2$, nitroacrylate (0.2 mmol) Cinchonine was added directly to the flask and stirred for another 30 minutes. Aromatic amine 2 (0.22 mmol) and diazooxindole 1 (0.22 mmol) in toluene (1 mL) were introduced by syringe pump over 1 hour at room temperature and the reaction solution was stirred for another 2 hours. After the completion of the reaction (monitored by TLC), the reaction mixture was filtrated and the filtrate was evaporated in vacuo to give the crude product. And then the crude product was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:20 ~ 1:5) to give the pure product.

General Procedure for Enantioselective Three-Component Reactions:

To a flask charged with 2 mol% [Rh(COD)Cl]$_2$ (1.97 mg, 0.0040 mmol, 2mol%), 4 mol% $L_7$ (7.93 mg, 0.01mmol, 5mol%) in toluene (1 ml) was stirred at 30°C for 1h. Nitroacrylate (0.2mmol) was added directly to the flask and stirred for another 30 minutes. Aromatic amine 2 (0.22mmol) and diazooxindole 1 (0.22mmol) in toluene (2 mL) were introduced by syringe pump over 2 hours at room temperature and the reaction solution was stirred for another 1 hours. After the completion of the reaction (monitored by TLC), the reaction mixture was filtrated and the filtrate was evaporated in vacuo to give the crude product. And then the crude product was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:20 ~ 1:5) to give the pure product.
Table S1 Optimisation of reaction conditions.$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>L</th>
<th>[M]</th>
<th>solvent</th>
<th>yield (%)$^b$</th>
<th>d.r.$^c$</th>
<th>er (%)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L7</td>
<td>[Rh(COD)Cl]$_2$</td>
<td>toluene</td>
<td>57</td>
<td>98:2</td>
<td>95:5</td>
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<td>2</td>
<td>L7</td>
<td>[Rh(COD)Cl]$_2$</td>
<td>xylene</td>
<td>23</td>
<td>92:8</td>
<td>78:22</td>
</tr>
<tr>
<td>3</td>
<td>L7</td>
<td>[Rh(COD)Cl]$_2$</td>
<td>DCE</td>
<td>82</td>
<td>90:10</td>
<td>75:25</td>
</tr>
<tr>
<td>4</td>
<td>L7</td>
<td>[Rh(COD)Cl]$_2$</td>
<td>DCM</td>
<td>23</td>
<td>92:8</td>
<td>78:22</td>
</tr>
<tr>
<td>5</td>
<td>L7</td>
<td>[Rh(COD)Cl]$_2$</td>
<td>CHCl$_3$</td>
<td>76</td>
<td>95:5</td>
<td>88:12</td>
</tr>
<tr>
<td>6</td>
<td>L7</td>
<td>[Rh(COD)Cl]$_2$</td>
<td>THF</td>
<td>55</td>
<td>88:12</td>
<td>71:29</td>
</tr>
</tbody>
</table>

$^a$ Unless otherwise noted, all reactions were carried out on a 0.2 mmol scale with 2a:3a:4a = 1.1:1.1:1.0.
$^b$ Yields of isolated products were determined after purification using column chromatography.
$^c$ Diastereomeric ratio (d.r.) was determined using $^1$H NMR spectroscopy.
$^d$ Determined using high-performance liquid chromatography (HPLC) analysis.
$^e$ N.P.: no product. DCE = 1,2-dichloroethane; THF = tetrahydrofuran.
Figure S1 The single crystal analysis for 6i
Figure S2 In situ analyze the reaction mixture to confirm the active catalyst in the three-component reaction

6.

The [Rh(COD)Cl]₂ was dissolved in CDCl₃, then different ratio of L₇ was added. The integration was detected by ¹H NMR.

Figure S3 The ¹H spectra of L₇ with addition of [Rh(COD)Cl]₂
Figure S3-1 H NMR spectra of [Rh(COD)Cl]$_2$

Figure S3-2 $^1$H NMR spectra of [Rh(COD)Cl]$_2$ and 0.1 eq (DHQ)$_2$PHAL
Figure S3-3 $^1$H NMR spectra of [Rh(COD)Cl)$_2$ and 0.2 eq (DHQ)$_2$PHAL.

Figure S3-4 $^1$H NMR spectra of [Rh(COD)Cl)$_2$ and 0.3 eq (DHQ)$_2$PHAL.
Figure S3-5 \( ^1 \)H NMR spectra of [Rh(COD)Cl]_2 and 0.4eq (DHQ)_2PHAL

Figure S3-6 \( ^1 \)H NMR spectra of [Rh(COD)Cl]_2 and 0.5eq (DHQ)_2PHAL
Figure S3-7 $^1$H spectra of $[\text{Rh(COD)Cl}]_2$ and 0.6 eq (DHQ)$_2$PHAL

Figure S3-8 $^1$H spectra of $[\text{Rh(COD)Cl}]_2$ and 0.7 eq (DHQ)$_2$PHAL
Figure S3-9 $^1$H spectra of [Rh(COD)Cl]$_2$ and 0.7 eq (DHQ)$_2$PHAL

Figure S3-10 The combination of $^1$HNMR spectra of the titration experiments
Figure S3-11 The expansion spectra of titration experiments

7.

Figure S4 The DFT calculation of relative energies and the NPA charges of [Rh(COD)Cl]$_2$
The $^1$HNMR study interaction between [Rh(COD)Cl]$_2$, L7, and 4d

Figure S5 The $^1$H NMR spectra of the mixture solution of L7, 4d and [Rh(COD)Cl]$_2$ in CDCl$_3$
Figure S5-1 $^1$HNMR spectrum of 4d

The $^1$H NMR Spectrum of 4d: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J$ = 13.5 Hz, 1H), 7.32 (s, 5H), 7.05 (d, $J$ = 13.5 Hz, 1H), 5.21 (s, 2H).

Figure S5-2 $^1$HNMR spectrum of L7
Figure S5-3 $^1$HNMR spectrum of $[\text{Rh(COD)Cl}]_2$

Figure S5-4 $^1$HNMR spectrum of $[\text{Rh(COD)Cl}]_2$ and 4d
Figure S5-5 $^1$HNMR spectrum of [Rh(COD)(L7)Cl]

Figure S5-6 $^1$HNMR spectrum of the mixture L7 and 4d
The $^1$H NMR Spectroscopy of 4d in the mixture: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 13.5$ Hz, 1H), 7.29 (s, 5H), 7.02 (d, $J = 13.4$ Hz, 2H), 5.18 (s, 2H).

Figure S5-7 $^1$HNMR spectrum of the mixture [Rh(L$_7$)COD]Cl and 4d

The $^1$H NMR Spectroscopy of 4d in the mixture: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 13.5$ Hz, 1H), 7.29 (s, 5H), 7.02 (d, $J = 13.4$ Hz, 2H), 5.18 (s, 2H).

9.
Figure S6 The $^1$H NMR spectra of the mixture solution of L7, 4a and [Rh(COD)Cl]$_2$ in CDCl$_3$.

The $^1$H NMR Spectroscopy of 4a: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, $J = 13.4$ Hz, 1H), 7.07 (d, $J = 13.4$ Hz, 1H), 5.22 – 5.07 (m, 1H), 1.33 (d, $J = 6.3$ Hz, 6H).
Figure S6-2 $^1$H NMR spectrum of the mixture of L7 and 4a

The $^1$H NMR Spectroscopy of 4a in the mixture: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 (d, $J$ = 13.4 Hz, 1H), 7.07 (d, $J$ = 13.5 Hz, 1H), 5.15 (m, $J$ = 6.3 Hz, 1H), 1.32 (d, $J$ = 6.2 Hz, 6H).

Figure S6-3 $^1$H NMR spectrum of the mixture of [Rh(L7)COD]Cl and 4a
10. Figure S7 The photo of the precipitation from the mixture solution of Rh(COD)(L7)Cl and 4d. A: 4d; B: L7; C: [Rh(COD)Cl]2; D: Rh+L7+4d.

11. Figure S8 The operando IR spectra of solvent toluene in the reaction.

12. Figure S9 The proposed activation models by the multiple Rh1 center.
13. $^1$H NMR, $^{13}$C NMR data and HPLC data of compounds

Synthesis of methyl-2-(((R)-1-benzyl-3-((S)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)b enzoate(6a).

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 57% yield (60mg) as a white solid.

NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.17 (s, 1H), 7.90 (d, $J = 9.8$ Hz, 1H), 7.41 (d, $J = 6.5$ Hz, 2H), 7.33 (ddd, $J = 16.5$, 10.1, 4.8 Hz, 5H), 7.12 (d, $J = 7.4$ Hz, 1H), 7.02 – 6.94 (m, 2H), 6.78 (d, $J = 7.0$ Hz, 1H), 6.57 (t, $J = 7.5$ Hz, 1H), 5.56 (d, $J = 8.4$ Hz, 1H), 5.35 – 5.16 (m, 4H), 3.92 (s, 3H), 3.55 (dd, $J = 10.8$, 3.2 Hz, 1H), 1.21 (d, $J = 6.3$ Hz, 3H), 1.13 (d, $J = 6.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 174.88, 168.80, 168.37, 147.20, 141.38, 135.24, 134.11, 131.87, 130.22, 128.94, 128.31, 128.20, 126.63, 124.56, 123.30, 117.04, 112.95, 112.71, 110.13, 71.54, 70.47, 63.17, 51.98, 49.82, 44.69, 21.43, 21.41.

HRMS(ESI) Calcd for C$_{29}$H$_{31}$N$_3$O$_7$ (M+Na)$^+$ :554.1093; Found: 554.1094.

95:5 e.r. HPLC (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), $t_1$ = 41.59 min (minor), $t_2$ = 66.05 min (major).

Synthesis of tert-butyl(2R)-3-(((S)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-3-((2-(methoxycarbonyl)phenyl)amino)-2-oxoindoline-1-carboxylate (6b)

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 45% yield (48mg) as a colorless solid.
NMR Spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.99 (s, 1H), 7.93 – 7.84 (m, 2H), 7.38 – 7.33 (m, 1H), 7.10 – 7.06 (m, 2H), 6.98 (m, J = 18.7, 1.7 Hz, 1H), 6.57 (td, J = 7.6, 1.1 Hz, 1H), 5.84 – 5.79 (m, 1H), 5.16 – 5.10 (m, 1H), 5.06 – 4.90 (m, 3H), 3.85 (s, 3H), 3.72 (dt, J = 10.8, 2.3 Hz, 1H), 1.58 (s, 9H), 1.10 (d, J = 6.2 Hz, 3H), 0.98 (d, J = 6.3 Hz, 3H).

\(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 171.76, 167.88, 166.81, 147.84, 145.83, 137.70, 133.41, 131.00, 129.61, 124.74, 124.03, 123.11, 116.43, 114.87, 112.02, 84.37, 70.32, 69.58, 51.04, 48.55, 27.07, 20.35, 20.17.


83:17 e.r. HPLC (Chiral AD-H, \(\lambda = 254\) nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), \(t_1\) = 7.32 min (minor), \(t_2\) = 8.12 min (major).

Synthesis of Methyl2-(((R)-3-((S)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-1-methyl-2-oxoindolin-3-yl)amino)benzoate (6c)

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 53% yield (48mg) as a white solid.

NMR Spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.01 (s, 1H), 7.97 – 7.83 (m, 1H), 7.39 (t, J = 7.7 Hz, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.06 (m, 3H), 6.60 (t, J = 7.6 Hz, 1H), 5.69 (dd, J = 12.0, 8.4 Hz, 1H), 5.11 – 4.97 (m, 1H), 4.87 (ddd, J = 27.3, 13.8, 4.7 Hz, 2H), 3.92 (s, 3H), 3.88 (dd, J = 11.3, 3.2 Hz, 1H), 3.30 (s, 3H), 1.18 (d, J = 6.2 Hz, 3H), 0.94 (d, J = 6.3 Hz, 3H).

\(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 174.12, 168.97, 168.46, 147.73, 142.76, 134.37, 131.83, 130.48, 126.26, 124.97, 123.50, 117.23, 112.71, 108.97, 72.28, 70.07, 63.22, 51.92, 51.02, 26.64, 21.34, 20.97.


78:22 e.r. HPLC (Chiral AD-H, \(\lambda = 254\) nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), \(t_1\) = 41.59 min (minor), \(t_2\) = 66.05 min (major).

Synthesis of methyl2-(((R)-3-((S)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-1-(4-methoxybenzyl)-2-oxoindolin-3-yl)amino)benzoate (6d)
Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 45% yield (44.8 mg) as a white solid.

NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.01 (s, 1H), 7.91 – 7.87 (m, 1H), 7.07 – 6.95 (m, 2H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.88 – 6.83 (m, 2H), 6.79 (ddd, $J = 8.7$, 7.2, 1.7 Hz, 1H), 6.58 (t, $J = 7.5$ Hz, 1H), 5.61 (d, $J = 8.4$ Hz, 1H), 5.08 – 4.97 (m, 2H), 4.93 – 4.83 (m, 2H), 4.71 (d, $J = 15.1$ Hz, 1H), 3.92 (s, 3H), 3.86 (dd, $J = 11.2$, 2.9 Hz, 1H), 3.79 (s, 3H), 1.20 (d, $J = 6.4$ Hz, 3H), 0.95 (d, $J = 6.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 174.22, 168.91, 167.94, 159.45, 147.61, 141.94, 134.18, 131.81, 130.22, 129.69, 127.19, 126.33, 125.09, 123.37, 117.23, 114.22, 113.19, 109.99, 72.23, 70.17, 63.25, 55.31, 51.94, 50.89, 44.14, 21.43, 21.00.

HRMS (ESI) Calcd. For C$_{30}$H$_{31}$N$_{3}$O$_{8}$ (M+Na)$^+$: 562.2189; Found: 562.2211.

84:16 e.r. HPLC (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), $t_1 = 32.00$ min (minor), $t_2 = 52.29$ min (major).

Synthesis of Methyl-2-((R)-1-((4-bromobenzyl)-3-((S)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 53% yield (64.5 mg) as a white solid.

NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.96 (s, 1H), 7.84 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.25 (dt, $J = 14.5$, 7.5 Hz, 6H), 7.19 (s, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.81 – 6.70 (m, 2H), 6.55 (t, $J = 7.6$ Hz, 1H), 5.51 (d, $J = 8.4$ Hz, 1H), 5.03 (dd, $J = 15.2$, 12.2 Hz, 2H), 4.91 – 4.74 (m, 2H), 3.86 (s, 3H), 3.79 (dd, $J = 11.3$, 2.9 Hz, 1H), 1.12 (d, $J = 6.3$ Hz, 3H), 0.83 (d, $J = 6.3$ Hz, 3H).
13C NMR (101 MHz, CDCl3) δ 173.32, 167.93, 166.94, 146.52, 140.57, 133.13, 133.02, 132.63, 130.88, 129.30, 128.63, 125.35, 122.61, 116.41, 111.99, 111.82, 108.80, 71.20, 69.16, 62.21, 59.38, 51.02, 49.89, 43.02, 28.68, 20.36, 20.05, 19.94, 13.18.

HRMS (ESI) Calcd. For C29H28BrN3O7 (M+Na)+: 632.1024; Found: 632.1008.

70:30 e.r. HPLC (Chiral AD-H, λ=254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t1 = 7.26 min (minor), t2 = 11.33 min (major).

Synthesis of
Methyl-2-((R)-1-benzyl-5-chloro-3-((S)-1-isoproxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 45% yield (59.8mg) as a white solid.

NMR Spectroscopy: 1H NMR (400 MHz, CDCl3) δ 9.23 (s, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.41 – 7.35 (m, 6H), 7.28 (d, J = 2.1 Hz, 1H), 7.09 (d, J = 2.1 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.89 – 6.75 (m, 2H), 6.62 (d, J = 7.8 Hz, 1H), 5.43 (d, J = 8.4 Hz, 2H), 5.30 – 5.20 (m, 2H), 4.77 (d, J = 15.7 Hz, 1H), 3.96 (s, 3H), 3.91 – 3.85 (m, 1H), 1.19 (d, J = 6.3 Hz, 3H), 0.93 (d, J = 6.3 Hz, 3H).

13C NMR (101 MHz, CDCl3) δ 174.58, 168.81, 168.68, 146.78, 139.62, 134.74, 134.17, 132.02, 130.14, 129.07, 128.97, 128.94, 128.44, 128.32, 125.04, 117.28, 112.82, 112.50, 111.13, 71.34, 52.13, 49.47, 44.87, 21.45.

HRMS (ESI) Calcd. For C29H28ClN3O7 (M+Na)+: 588.1513; Found: 588.1539.

99:1 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t1 = 20.46 min (minor), t2 = 25.71 min (major).

Synthesis of
Methyl-2-((R)-1-benzyl-6-chloro-3-((S)-1-isoproxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate
Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 71% yield (80.2mg) as a white solid.

NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.96 (s, 1H), 7.83 (d, $J$ = 7.9 Hz, 1H), 7.37 – 7.27 (m, 4H), 7.22 – 7.17 (m, 3H), 6.98 (t, $J$ = 7.6 Hz, 1H), 6.84 (d, $J$ = 7.9 Hz, 1H), 6.73 (t, $J$ = 7.8 Hz, 1H), 6.52 (t, $J$ = 7.5 Hz, 1H), 5.55 (d, $J$ = 8.4 Hz, 1H), 5.10 – 4.93 (m, 2H), 4.86 – 4.79 (m, 2H), 3.85 (s, 3H), 3.82 – 3.76 (m, 1H), 1.13 (d, $J$ = 6.3 Hz, 3H), 0.87 (d, $J$ = 6.2 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.28, 167.91, 166.94, 146.55, 140.85, 134.12, 133.20, 130.81, 129.25, 127.85, 127.29, 127.12, 125.28, 124.06, 116.26, 112.13, 111.73, 108.98, 71.20, 69.17, 62.23, 50.97, 49.85, 43.72, 20.38, 19.97.

HRMS(ESI) Calcd. For C$_{29}$H$_{28}$ClN$_3$O$_7$ (M+Na)$^+$: 588.1513; Found: 588.1539.

80:20 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), $t_1 = 17.26$ min (minor), $t_2 = 22.54$ min (major).

Synthesis of Methyl-2-((R)-1-benzyl-7-chloro-3-((S)-1-isoproxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 56% yield (63.2mg) as an white solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.92 (s, 1H), 7.83 (dd, $J$ = 7.9, 1.7 Hz, 1H), 7.34 – 7.27 (m, 6H), 7.15 – 7.02 (m, 3H), 6.97 (d, $J$ = 1.6 Hz, 1H), 6.81 – 6.73 (m, 1H), 6.56 (t, $J$ = 7.5 Hz, 1H), 5.54 (d, $J$ = 8.4 Hz, 1H), 5.06 – 4.99 (m, 1H), 4.86 – 4.79 (m, 2H), 4.65 (d, $J$ = 15.3 Hz, 1H), 3.85 (s, 3H), 3.78 (dd, $J$ = 11.3, 2.9 Hz, 1H), 1.13 (d, $J$ = 6.3 Hz, 3H), 0.88 (d, $J$ = 6.3 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 174.58, 167.77, 167.24, 145.70, 136.44, 135.60, 133.11, 131.89, 130.92, 128.85, 127.70, 126.83, 126.80, 123.05, 122.07, 116.26, 115.41, 111.83, 111.79, 70.33, 69.66, 61.73, 51.04, 48.82, 44.60, 28.68, 20.43.
HRMS(ESI) Calcd. For C_{29}H_{28}ClN_{3}O_{7} (M+Na)^+: 588.1513; Found: 588.1539.
97:3 e.r. HPLC (Chiral AD-H, \( \lambda = 254 \) nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min),
t_1 = 36.35 min (minor), t_2 = 49.04 min (major).

Synthesis of
Methyl-2-((\((R\))\)-1-benzyl-7-chloro-3-((S)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)-5-bromobenzoate

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title
compound was obtained in 64% yield (77.9mg) as a white solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.96 (s, 1H), 7.84 (d, \( J = 7.7 \) Hz, 1H), 7.25 (dt, \( J = 12.1, 7.6 \) Hz, 6H),
7.00 (t, \( J = 7.5 \) Hz, 1H), 6.75 (dd, \( J = 19.0, 7.9 \) Hz, 2H), 6.55 (t, \( J = 7.5 \) Hz, 1H), 5.51 (d, \( J = 8.4 \) Hz,
1H), 5.01 (d, \( J = 14.9 \) Hz, 2H), 4.87 (dd, \( J = 15.1, 2.5 \) Hz, 1H), 4.68 (d, \( J = 15.3 \) Hz, 1H), 4.05 (d, \( J =
7.2 \) Hz, 1H), 3.86 (s, 3H), 3.79 (dd, \( J = 11.2, 2.5 \) Hz, 1H), 1.12 (d, \( J = 6.2 \) Hz, 3H), 0.83 (d, \( J = 6.2 \) Hz,
3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 173.33, 167.95, 166.96, 146.53, 140.58, 133.14, 133.03, 132.64,
130.89, 129.32, 128.65, 128.02, 125.36, 124.17, 122.62, 116.42, 112.00, 111.83, 108.81, 71.21, 69.16,
62.22, 51.02, 49.90, 43.03, 20.36, 19.94.

HRMS(ESI) C_{29}H_{28}BrN_{3}O_{7} Calcd. For (M+Na)^+: 632.1024; Found: 632.1008.
87:13 e.r. HPLC (Chiral AD-H, \( \lambda = 254 \) nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min),
t_1 = 29.45 min (minor), t_2 = 35.24 min (major).

Synthesis of
methyl2-((\((R\))\)-1-benzyl-7-chloro-3-((S)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)
amino)-5-chlorobenzoate

\( (2R, 3S)-6k \)
Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 63% yield (71.2 mg) as a white solid.

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\delta 8.96 (s, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.25 (dt, J = 12.1, 7.6 Hz, 6H), 7.00 (t, J = 7.5 Hz, 1H), 6.75 (dd, J = 19.0, 7.9 Hz, 2H), 6.55 (t, J = 7.5 Hz, 1H), 5.51 (d, J = 8.4 Hz, 1H), 5.01 (d, J = 14.9 Hz, 2H), 4.87 (dd, J = 15.1, 2.5 Hz, 1H), 4.68 (d, J = 15.3 Hz, 1H), 4.05 (d, J = 7.2 Hz, 1H), 3.86 (s, 3H), 3.79 (dd, J = 11.2, 2.5 Hz, 1H), 1.12 (d, J = 6.2 Hz, 3H), 0.83 (d, J = 6.2 Hz, 3H); \]

\[ ^13C\text{ NMR (101 MHz, CDCl}_3\delta 173.33, 167.95, 166.96, 146.53, 140.58, 133.14, 133.03, 132.64, 130.89, 129.32, 128.65, 128.02, 125.36, 124.17, 122.62, 116.42, 112.00, 111.83, 108.81, 71.21, 69.16, 62.22, 51.02, 49.90, 43.03, 20.36, 19.94. \]

HRMS(ESI) C_{29}H_{27}Cl_2N_3O_7 Calcd. For (M+Na)^+: 588.1513; Found: 588.1539.

95:5 e.r. HPLC (Chiral AD-H, \( \lambda = 254 \) nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), \( t_1 = 30.19 \) min (minor), \( t_2 = 36.63 \) min (major).

Synthesis of isopropyl (S)-2-((R)-1-benzyl-3-((2-methoxyphenyl)amino)-2-oxindolin-3-yl)-3-nitropropanoate

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 61% yield (61.3 mg) as a yellow solid.

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\delta 7.24 – 7.17 (m, 6H), 7.12 (d, J = 7.4 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.79 (d, J = 7.8 Hz, 1H), 6.67 (dd, J = 8.0, 1.5 Hz, 1H), 6.59 (dd, J = 7.7, 1.6 Hz, 1H), 6.27 (td, J = 7.7, 1.4 Hz, 1H), 5.89 (s, 1H), 5.63 (dd, J = 7.9, 1.5 Hz, 1H), 5.10 – 4.84 (m, 4H), 4.66 (d, J = 15.3 Hz, 1H), 3.82 (s, 3H), 3.70 (dd, J = 10.5, 3.6 Hz, 1H), 1.17 (s, 4H), 1.10 (d, J = 6.3 Hz, 3H); \]

\[ ^13C\text{ NMR (101 MHz, CDCl}_3\delta 173.97, 167.95, 166.96, 146.34, 140.19, 134.12, 132.87, 129.22, 127.85, 126.99, 126.95, 125.86, 123.40, 122.33, 119.69, 118.54, 115.53, 109.05, 108.95, 70.59, 69.49, 62.82, 54.70, 48.69, 43.50, 20.48, 20.37. \]

HRMS(ESI) C_{28}H_{30}N_3O_6 Calcd. For (M+Na)^+: 526.1954; Found: 526.1930.

86:14 e.r. HPLC (Chiral AD-H, \( \lambda = 254 \) nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), \( t_1 = 14.94 \) min (minor), \( t_2 = 27.17 \) min (major).

Synthesis of
isopropyl (S)-2-((R)-3-((2-benzylophenyl)amino)-1-benzyl-2-oxindolin-3-yl)-3-nitropropanoate

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 54% yield (62.3mg) as a yellow solid.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 9.53 (s, 1H), 7.64 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.45 (dd, J = 16.1, 7.8 Hz, 6H), 7.38 – 7.30 (m, 5H), 7.06 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.84 (t, J = 7.8 Hz, 1H), 6.57 (t, J = 7.5 Hz, 1H), 5.77 (d, J = 8.4 Hz, 1H), 5.20 – 5.06 (m, 2H), 4.89 – 4.71 (m, 2H), 3.91 (dd, J = 11.2, 2.9 Hz, 1H), 1.19 (d, J = 6.3 Hz, 3H), 0.91 (d, J = 6.4 Hz, 3H). \]

\[ ^13C \text{ NMR (101 MHz, CDCl}_3) \delta 199.62, 174.14, 167.91, 147.93, 142.02, 139.67, 135.33, 135.17, 134.36, 131.37, 130.31, 129.50, 129.38, 128.96, 128.89, 128.30, 128.14, 128.10, 128.06, 126.25, 125.18, 123.50, 120.38, 116.78, 113.99, 109.98, 72.22, 70.19, 63.36, 51.00, 44.78, 21.38, 20.98. \]

HRMS(ESI) \[ C_{28}H_{29}N_{3}O_6 \text{Calcd. For (M+Na)}^+: 600.2111; \text{Found: 600.2151}. \]

96:4 e.r. HPLC (Chiral AD-H, \( \lambda = 254 \) nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), \( t_1 = 33.70 \) min (minor), \( t_2 = 67.23 \) min (major).

Synthesis of
Isopropyl-(S)-2-((R)-3-((2-acetylophenyl)amino)-1-benzyl-7-chloro-2-oxindolin-3-yl)-3-nitropropanoate

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 56% yield (61.5mg) as a yellow solid.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 10.18 (s, 1H), 7.68 (dd, J = 8.0, 1.7 Hz, 1H), 7.35 (dd, J = 7.5, 2.0 Hz, 2H), 7.25 (t, J = 8.0 Hz, 4H), 7.19 (d, J = 1.6 Hz, 1H), 6.95 (dd, J = 7.4, 1.5 Hz, 1H), 6.89 (t, J = 7.38) \]
Synthesis of
Methyl 2-(((R)-1-benzyl-3-((S)-1-(tert-butoxy)-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 52% yield (56.68 mg) as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.02 (s, 1H), 7.90 (dd, J = 7.9, 1.8 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.30 (t, J = 7.7 Hz, 5H), 7.14 – 7.07 (m, 1H), 7.03 – 6.95 (m, 1H), 6.86 – 6.80 (m, 1H), 6.60 (t, J = 7.6 Hz, 1H), 5.63 (d, J = 8.4 Hz, 1H), 5.42 (d, J = 9.8 Hz, 2H), 5.22 – 5.06 (m, 2H), 3.92 (s, 3H), 3.51 (dd, J = 10.7, 3.5 Hz, 1H), 1.41 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 175.66, 168.78, 167.12, 146.90, 138.30, 137.57, 136.70, 134.14, 132.84, 131.91, 129.98, 128.66, 127.76, 123.89, 123.54, 117.37, 116.32, 113.20, 112.89, 84.17, 71.60, 62.97, 52.01, 50.58, 45.60, 27.70.

HRMS (ESI) C$_{30}$H$_{30}$ClN$_3$O$_7$ Calcd. For (M+Na)$^+$: 602.1670; Found: 602.1680.

95:5 e.r. HPLC (Chiral AD, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t$_1$ = 27.64 min (minor), t$_2$ = 34.72 min (major).

Synthesis of methyl
2-(((R)-1-benzyl-3-((S)-1-ethoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate
Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 52% yield (56.68 mg) as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.08 (s, 1H), 8.31 (d, $J = 7.3$ Hz, 1H), 7.87 – 7.82 (m, 1H), 7.22 (s, 3H), 7.11 (d, $J = 7.8$ Hz, 1H), 7.01 (d, $J = 7.4$ Hz, 1H), 6.92 – 6.87 (m, 2H), 6.70 (d, $J = 7.7$ Hz, 3H), 6.58 (t, $J = 7.6$ Hz, 1H), 5.48 (d, $J = 8.4$ Hz, 1H), 5.07 – 4.99 (m, 1H), 4.83 (s, 2H), 4.10 – 3.97 (m, 2H), 3.75 (s, 3H), 3.52 (dd, $J = 10.6$, 3.2 Hz, 1H), 1.01 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 175.24, 168.99, 168.54, 149.87, 142.83, 135.67, 134.59, 131.65, 129.33, 128.81, 128.31, 127.64, 126.50, 124.47, 123.12, 116.39, 112.76, 109.42, 72.05, 63.35, 62.22, 55.76, 51.62, 44.11, 29.69.

HRMS(ESI) C$_{28}$H$_{27}$N$_3$O$_7$ Calcd. for (M+Na)$^+$, 540.1747; Found: 540.1779.

95:5 e.r.
HPLC (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), $t_1$ = 10.23 min (minor), $t_2$ = 13.02 min (major).

Synthesis of methyl-2-(((R)-1-benzyl-3-((S)-1-(benzyloxy)-3-nitro-1-oxopropan-2-yl)-2-oxindolin-3-yl)amino)benzoate

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 70% yield (81 mg) as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.18 (s, 1H), 7.90 (dd, $J = 8.0$, 1.7 Hz, 1H), 7.42 – 7.28 (m, 10H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.97 – 6.84 (m, 2H), 6.83 – 6.75 (m, 1H), 6.58 (t, $J = 7.6$ Hz, 1H), 5.54 (d, $J = 8.4$ Hz, 1H), 5.40 – 5.05 (m, 6H), 4.63 (d, $J = 15.2$ Hz, 1H), 3.92 (s, 3H), 3.68 (dd, $J = 10.7$, 3.1 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 174.80, 169.01, 168.86, 147.12, 141.23, 135.14, 134.52, 134.16, 131.90, 130.20, 128.95, 128.91, 128.88, 128.60, 128.54, 128.33, 128.28, 128.22, 126.46, 124.32, 123.45, 117.13, 112.90, 112.72, 110.21, 71.31, 67.97, 63.12, 52.07, 49.58, 44.59.

HRMS(ESI) C$_{33}$H$_{29}$N$_3$O$_7$ Calcd. For (M+Na)$^+$: 602.1903; Found: 602.1860
86:14 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 = 37.44 min (minor), t_2 = 55.37 min (major).

14. \(^1\)H and \(^{13}\)C NMR Spectra
15. HPLC Spectra

![HPLC Spectra Diagram]

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16. IR Data and Spectra

1) The IR Spectra of toluene

[Graph of IR Spectra of toluene]

①The IR Spectra of [Rh(COD)Cl]₂ (dissolved in toluene)

[Graph of IR Spectra of [Rh(COD)Cl]₂]

②The IR Spectra of L7 (dissolved in toluene)

[Graph of IR Spectra of L7]
③ The IR Spectra of 4a (dissolved in toluene)

④ The IR Spectra of 4d (dissolved in toluene)
5. The full Spectra of Figure 4B

6. The full Spectra of Figure 4C
17. Computational Methods

All the calculations were carried out with the Gaussian 09 software program. Geometry optimization and energy calculations were employed with B3LYP functional. The LANL2DZ basis set with ECP was used for Rhodium and the 6-31G(d) basis set was used for all other atoms. And this is referred to as B1. Frequency analysis was handled at the same level to obtain the thermodynamic energy corrections. With the optimized geometries, single point energies were calculated in toluenesolvent using M06-2X/SDD-6-311G(d) level referred as B2 using SMD solvation model. Natural bond orbital (NBO) analysis provided Natural population analysis charges.

Coordinates of the Optimized Structures

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C -3.37018500 -1.38877100 -0.63373100
C -3.24230600  1.42070000  0.77039900
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H -2.63103400  2.22165200  1.18646400
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C -4.16549000  1.76875700  0.63373100
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### 18. Supplementary References