Supporting Information

For

Aromatic C-H Bond Functionalized via Zwitterion Intermediates to Construct Bioxindole Containing Continuous Quaternary Carbons

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1. Screen of Other Substrates

Scheme S1. Screen of other substrates

Screen of diazo:

Screen of aniline:

Screen of isatin ketimine:

2. Exploration on Enantioselectivities.

Table S1. Screen of chiral phosphoric acid (CPA)\textsuperscript{a}
 Unless otherwise noted, all reactions were carried out on a 0.3 mmol scale and \(1a/2a/3a=1:1:1:1.0\). Subsequently 4 Å MS (100 mg), 1 mol% [M] and 5 mol% CPA* were added. b isolated yield of 4a based on 3a were obtained after purification by column chromatography. c Determined by \(^1\)H NMR analysis. d Determined by chiral HPLC analysis.

### 3. Gram-scale Synthesis of 4f.

A mixture of \(N,N\)-dibenzylaniline 1a (3.3 mmol, 0.9217 g), isatin ketimine 3a (3.0 mmol, 1.0092 g), \(\text{Rh}_2(\text{OAc})_4\) (0.03 mmol, 13.2 mg) and 4 Å MS (1.0 g) in DCM (10 mL) were stirred at room temperature. 3-diazooxindoles 2d (3.3 mmol, 0.9022 g) in DCM (10 mL) were then added over 2 h via a syringe pump at room temperature. After completion of the addition, the reaction mixture was stirred for another 2 h under 25 °C. After the completion of the reaction (monitored by TLC, until the full conversion of 3-diazooxindoles 2d), the reaction mixture was filtrated and evaporated in vacuo to give the crude reaction mixture. Diastereoselectivity was determined as > 20:1 by \(^1\)H NMR spectroscopy of the crude reaction mixture. The crude mixture was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:20–1:5) to give the pure products 4f (2.4560 g, 95% yield, >20:1 dr) as a white solid.
4. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of 4a-4p

$^1$H NMR spectrum of syn-4a (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4a (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4b (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4b (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4c (400 MHz, CDCl$_3$)

13C NMR spectrum of syn-4c (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4d (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4d (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4e (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4e (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4f (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4f (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4g (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4g (100 MHz, CDCl$_3$)
\( ^1 \text{H NMR spectrum of syn-4h (400 MHz, CDCl}_3 \) 

\( ^{13} \text{C NMR spectrum of syn-4h (100 MHz, CDCl}_3 \)
$^1$H NMR spectrum of syn-4i (400 MHz, CDCl₃)

$^{13}$C NMR spectrum of syn-4i (100 MHz, CDCl₃)
$^1$H NMR spectrum of syn-4j (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4j (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4k (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4k (100 MHz, CDCl$_3$)
$^{19}$F NMR spectrum of syn-4k (376 MHz, CDCl$_3$)
$^1$H NMR spectrum of $\text{syn-4l}$ (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of $\text{syn-4l}$ (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4m (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4m (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4n (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4n (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4o (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4o (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of syn-4p (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of syn-4p (100 MHz, CDCl$_3$)
5. X-ray Diffraction Parameters and Data of 4d (CDCC No.:1910044)

Bond precision: C-C = 0.0034 Å

Wavelength=1.54184

Cell:
- a=13.7602(1) Å
- b=13.8078(2) Å
- c=16.1032(2) Å
- alpha=65.362(1)°
- beta=78.621(1)°
- gamma=61.072(1)°

Temperature: 293 K

Volume: Calculated 2434.00(6) Å³, Reported 2434.00(6) Å³

Space group: Calculated P -1, Reported P -1

Hall group: Calculated -P 1, Reported -P 1

Moiety formula: C55 H49 Cl N4 O4 [+ solvent], C55 H49 Cl N4 O4

Sum formula: C55 H49 Cl N4 O4 [+ solvent], C55 H49 Cl N4 O4

Mr: Calculated 865.43, Reported 865.43

Dx,g cm⁻³: Calculated 1.181, Reported 1.181

Z: Calculated 2, Reported 2

Mu (mm⁻¹): Calculated 1.078, Reported 1.078

F000: Calculated 912.0, Reported 912.0

F000': Calculated 915.23, Reported 915.23

h,k,lmax: Calculated 17,17,20, Reported 17,16,20

Nref: Calculated 9988, Reported 9714

Tmin,Tmax: Calculated 0.659,0.708, Reported 0.711,1.000

Correction method= # Reported T Limits: Tmin=0.711 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.973, Theta(max)= 74.654

R(reflections)= 0.0488( 8641), wR2(reflections)= 0.1504( 9714)

S = 1.073, Npar= 581

In a 20 mL test tube, a solution of compound 4d (20 mg) in EA (1mL) was added in one portion. Then PE (20 mL) was added slowly along the wall of the test tube in order to keep the PE and EA solution separated into two layers. Then left the test tube standing still in the room temperature until the single crystal was formed. Crystals grew as colorless bricks.