Supporting Information:

Palladium-Catalyzed Asymmetric Dearomative Alkenylation of Indoles through Reductive-Heck Reaction

Ren-Xiao Liang, Run-Ze Yang, Ren-Rong Liu and Yi-Xia Jia*

College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China

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1. General information

Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware was heated under oven for two hours prior to use. $^1$H and $^{13}$C spectra were recorded on Bruker AVANCE III 500 MHz using CDCl$_3$ as solvent with TMS as internal standard. Anhydrous MeOH, EtOH and iPrOH were freshly distilled over Mg and I$_2$. Melting points were measured on a Büchi Melting Point B-545 apparatus and uncorrected. Commercial reagents were used without further purification unless otherwise noticed. HRMS were recorded on Agilent 6210 TOF LC/MS mass spectrometer. Optical rotations were determined using a Rudolph Autopol IV polarimeter. HPLC analyses were performed using Agilent 1260 Infinity II. Chiralpak AD columns were purchased from Daicel Chemical Industries, LTD. Cellulose-2/3 columns were purchased from Phenomenex. Column chromatography was carried out using silica gel (200-300 mesh).

2. Substrate synthesis

![Chemical structure](image)

To a stirred solution of the appropriate indole derivative (1 equiv, 0.5 M) in THF in a Schlenk tube was added 60% dispersion of NaH in mineral oil (1.2 equiv) at 0 °C slowly, which was stirred for 5 minutes at that temperature. After stirring for extra 30 mins at room temperature, the sodium indolate solution was then re-cooled to 0 °C, to which a solution of acid chloride derivative (prepared from the corresponding acid with oxalyl chloride) in THF, was added dropwise. After that, the reaction was stirred at room temperature until the substrate completely consumed by the TLC determination. Then the mixture was cooled to 0 °C and quenched with a saturated solution of NH$_4$Cl, which was then extracted with EtOAc for three times. The combined organic phase was washed with brine and water, respectively. After drying with Na$_2$SO$_4$, the solvent was removed by vacuum and the crude mixture obtained was purified by column chromatography using the indicated fluent.

$^{2}$-Bromocyclohex-1-en-1-yl)(2-methyl-1H-indol-1-yl)methanone (1a)$^{[1]}$

Yield 85%, pale red solid, Mp 88-90 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.06-7.98 (m, 1 H), 7.47-7.42 (m, 1 H), 7.25-7.20 (m, 1 H), 6.39 (s, 1H), 2.62 (s, 2H), 2.56 (d, J = 0.8 Hz, 3H), 2.47 (dd, J = 6.7, 3.3 Hz, 2H), 1.84 (s, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 169.0, 136.7, 136.4, 135.1, 129.8, 123.8, 123.6, 123.5, 119.7, 114.8, 110.2, 35.8, 29.1, 23.8, 21.3, 16.2.

(2-Chlorocyclohex-1-en-1-yl)(2-methyl-1H-indol-1-yl)methanone (1a)

Yield 85%, pink solid, Mp 65-68 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); 1H NMR (500 MHz, CDCl3): δ 8.07 (d, J = 7.5 Hz, 1H), 7.48 (dd, J = 6.5, 2.1 Hz, 1H), 7.27 (dddd, J = 6.9, 4.1, 1.5 Hz, 2H), 6.41 (s, 1H), 2.58 (s, 3H), 2.56-2.43 (m, 4H), 1.87 (dd, J = 5.9, 4.5 Hz, 2H), 1.82 (d, J = 2.8 Hz, 2H); 13C NMR (125 MHz, CDCl3) δ 168.4, 136.6, 136.4, 132.7, 131.9, 129.8, 123.7, 123.5, 119.7, 114.7, 110.0, 33.3, 28.1, 22.9, 21.3, 16.0. HRMS m/z (ESI+): Calculated for C16H18BrNO ([M+K]+): 312.0552, Found 312.0563.

(2-Bromocyclohex-1-en-1-yl)(2-ethyl-1H-indol-1-yl)methanone (1b)

Yield 84%, white solid, Mp 63-65 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); 1H NMR (500 MHz, CDCl3): δ 7.87-7.80 (m, 1H), 7.51-7.44 (m, 1H), 7.25-7.20 (m, 2H), 6.46 (s, 1H), 3.01 (s, 2H), 2.64 (s, 2H), 2.57-2.40 (m, 2H), 1.95-1.77 (m, 4H), 1.36 (t, J = 7.3 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 169.0, 143.9, 136.2, 135.2, 130.0, 123.8, 123.6, 123.3, 120.0, 114.0, 107.8, 36.0, 29.00, 23.8, 22.8, 21.4, 12.9. HRMS m/z (ESI+): Calculated for C17H19BrNO ([M+H]+): 332.0644, Found 332.0645, HRMS m/z (ESI+): Calculated for C17H1981BrNO ([M+H]+): 334.0625, Found 334.0625.

(2-Bromocyclohex-1-en-1-yl)(2-cyclopropyl-1H-indol-1-yl)methanone (1c)

Yield 82%, yellow transparent viscous liquid; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); 1H NMR (500 MHz, CDCl3): δ 8.09 (d, J = 8.2 Hz, 1H), 7.44-7.38 (m, 1H), 7.26-7.21 (m, 1H), 7.19 (td, J = 7.4, 1.1 Hz, 1H), 6.29 (s, 1H), 2.56 (d, J = 14.4 Hz, 4H), 2.16-2.06 (m, 1H), 1.79 (s, 4H), 0.94 (dd, J = 8.2, 1.8 Hz, 2H), 0.80 (s, 2H); 13C NMR (125 MHz, CDCl3) δ 169.1, 142.6, 136.6, 135.0, 129.4, 123.9, 123.6, 123.4, 119.8, 114.9, 107.6, 35.9, 29.2, 23.7, 21.2, 10.2, 7.7. HRMS m/z (ESI+): Calculated for C18H1981BrNO ([M+H]+): 344.0645, Found 344.0632, HRMS m/z (ESI+): Calculated for C18H1981BrNO ([M+H]+): 346.0625, Found 346.0621.

(2-Bromocyclohex-1-en-1-yl)(2-phenyl-1H-indol-1-yl)methanone (1d)

Yield 81%, white solid, Mp 113-116 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); 1H NMR (500 MHz, CDCl3): δ 8.35 (d, J = 8.3 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 6.5 Hz, 2H), 7.44-7.35 (m, 4H), 7.31 (dd, J = 11.1, 3.9 Hz, 1H), 6.61 (s, 1H), 2.14 (d, J = 61.9 Hz, 4H), 1.22 (d, J = 33.4 Hz, 4H); 13C NMR (125 MHz, CDCl3) δ 170.0, 139.8, 137.1, 134.5, 133.8, 129.5, 128.4, 128.2, 128.0, 127.0, 125.1, 123.9, 120.3, 115.8, 111.8, 36.2, 29.4, 23.2, 20.6. HRMS m/z (ESI+): Calculated for C21H1981BrNO ([M+H]+):
380.0645, Found 380.0635, HRMS m/z (ESI+): Calculated for C_{21}H_{19}^{81}BrNO ([M+H]^{-}): 382.0625, Found 382.0620.

**2-(Bromocyclohex-1-en-1-yl)(2-(p-tolyl)-1H-indol-1-yl)methanone (1e)**

Yield 82%, red solid, Mp 83-86 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); 

$^1$H NMR (500 MHz, CDCl$_3$): \(\delta \) 8.34 (d, \(J = 8.2\) Hz, 1H), 7.54 (d, \(J = 7.5\) Hz, 1H), 7.36 (ddd, \(J = 9.6, 7.3, 2.0\) Hz, 3H), 7.29 (td, \(J = 7.6, 0.8\) Hz, 1H), 7.21 (d, \(J = 7.9\) Hz, 2H), 6.57 (s, 1H), 2.40 (s, 3H), 2.11 (t, \(J = 36.3\) Hz, 4H), 1.37-1.00 (m, 4H);

$^{13}$C NMR (125 MHz, CDCl$_3$) \(\delta \) 170.1, 139.9, 138.1, 137.1, 134.5, 129.6, 128.6, 128.3, 126.8, 124.9, 123.9, 120.2, 115.7, 111.5, 36.3, 29.4, 23.2, 21.2, 20.6. HRMS m/z (ESI+):

Calculated for C$_{22}$H$_{20}$BrNONa ([M+Na]^{-}): 416.0621, Found 416.0622.

**2-(Bromocyclohex-1-en-1-yl)(2-(4-methoxyphenyl)-1H-indol-1-yl)methanone (1f)**

Yield 85%, green solid, Mp 76-80 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v);

$^1$H NMR (500 MHz, CDCl$_3$): \(\delta \) 8.34 (d, \(J = 8.3\) Hz,1H), 7.55 (d, \(J = 7.7\) Hz, 1H), 7.40 (d, \(J = 8.6\) Hz, 2H), 7.38-7.33 (m, 1H), 6.94 (d, \(J = 8.7\) Hz, 2H), 6.55 (s, 1H), 3.86 (s, 3H), 2.16 (d, \(J = 32.8\) Hz, 4H), 1.37-1.15 (m, 4H);

$^{13}$C NMR (125 MHz, CDCl$_3$) \(\delta \) 170.0, 159.8, 139.6, 137.0, 134.6, 129.7, 129.6, 126.6, 126.3, 124.8, 123.9, 120.1, 115.7, 113.5, 111.3, 55.5, 36.3, 29.4, 23.3, 20.7. HRMS m/z (ESI+):

Calculated for C$_{22}$H$_{21}$BrNO$_2$ ([M+H]^{-}): 432.0570, Found 432.0739, HRMS m/z (ESI+):

Calculated for C$_{22}$H$_{21}$BrNO$_2$ ([M+Na]^{-}): 434.0550, Found 434.0736.

**2-(Bromocyclohex-1-en-1-yl)(2-(4-fluorophenyl)-1H-indol-1-yl)methanone (1g)**

Yield 75%, white solid, Mp 102-105 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v);

$^1$H NMR (500 MHz, CDCl$_3$): \(\delta \) 8.33 (d, \(J = 8.3\) Hz,1H), 7.55 (d, \(J = 7.7\) Hz, 1H), 7.49-7.42 (m, 2H), 7.41-7.34 (m, 1H), 7.31 (dd, \(J = 11.0, 4.0\) Hz, 1H), 7.12 (t, \(J = 8.6\) Hz, 2H), 6.59 (s, 1H), 2.19 (dd, \(J = 26.2, 18.9\) Hz, 4H), 1.39-1.15 (m, 4H);

$^{13}$C NMR (125 MHz, CDCl$_3$) \(\delta \) 169.7, 162.7 (d, \(J = 246.3\) Hz), 138.3, 137.2, 134.5, 130.1 (d, \(J = 8.8\) Hz), 129.9 (d, \(J = 3.8\) Hz), 129.4, 127.0, 125.2, 124.0, 120.3, 115.7, 115.1 (d, \(J = 21.3\) Hz), 112.1, 36.3, 29.4, 23.3, 20.7. HRMS m/z (ESI+):

Calculated for C$_{21}$H$_{17}$BrFNONa ([M+Na]^{-}): 420.0370, Found 420.0363, HRMS m/z (ESI+):

Calculated for C$_{21}$H$_{17}$BrFNONa ([M+Na]^{-}): 422.0350, Found 422.0349.
(2-Bromocyclohex-1-en-1-yl)(2-(4-(trifluoromethyl)phenyl)-1H-indol-1-yl)methanone (1h)

Yield 65%, yellow solid, Mp 104-107 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); 1H NMR (500 MHz, CDCl3): δ 8.32 (d, J = 8.3 Hz, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.64-7.56 (m, 3H), 7.44-7.37 (m, 1H), 7.36-7.30 (m, 1H), 6.68 (s, 1H), 2.36-1.90 (m, 4H), 1.40-1.03 (m, 4H); 13C NMR (125 MHz, CDCl3) δ 169.5, 138.1, 137.3 (d, J = 23.8 Hz), 134.4, 130.5 (q, J = 32.5 Hz), 129.3, 128.5, 127.6, 125.6, 124.9 (dd, J = 7.5, 3.8 Hz), 124.2, 122.9, 120.6, 115.7, 112.9, 36.3, 29.5, 23.1, 20.6. HRMS m/z (ESI+): Calculated for C22H17BrF3NONa ([M+Na]+): 470.0338, Found 470.0008. HRMS m/z (ESI+): Calculated for C22H1781BrF3NONa ([M+Na]+): 472.0381, Found 471.9992.

(2-Bromocyclohex-1-en-1-yl)(2-(3-chlorophenyl)-1H-indol-1-yl)methanone (1i)

Yield 73%, pale red solid, Mp 96-99 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); 1H NMR (500 MHz, CDCl3): δ 8.34 (d, J = 8.3 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.45 (s, 1H), 7.43-7.35 (m, 4H), 7.34-7.28 (m, 1H), 6.64 (s, 1H), 2.15 (dd, J = 63.6, 23.1 Hz, 4H), 1.47-1.01 (m, 4H); 13C NMR (125 MHz, CDCl3) δ 169.7, 138.1, 137.2, 135.6, 134.0, 129.4, 129.3, 128.3, 128.3, 127.3, 126.5, 125.5, 124.1, 120.5, 115.8, 112.4, 36.3, 29.5, 23.3, 20.7. HRMS m/z (ESI+): Calculated for C21H1779BrClNONa ([M+Na]+): 436.0075, Found 436.0070, HRMS m/z (ESI+): Calculated for C21H1781BrClNONa ([M+Na]+): 438.0055, Found 438.0008, HRMS m/z (ESI+): Calculated for C21H1779BrCl3NONa ([M+Na]+): 438.0045, Found 438.0055, HRMS m/z (ESI+): Calculated for C21H1781BrCl3NONa ([M+Na]+): 440.0025, Found 440.0042.

(2-Bromocyclohex-1-en-1-yl)(2-(2-chlorophenyl)-1H-indol-1-yl)methanone (1j)

Yield 70%, yellow solid, Mp 135-140 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); 1H NMR (500 MHz, CDCl3): δ 8.36 (d, J = 7.7 Hz, 1H), 7.73-7.52 (m, 2H), 7.45 (d, J = 7.2 Hz, 1H), 7.42-7.26 (m, 4H), 6.63 (s, 1H), 2.58-1.91 (m, 4H), 1.54-1.06 (m, 4H); 13C NMR (125 MHz, CDCl3) δ 169.5, 136.8, 136.0, 134.6, 134.0, 133.2, 130.8, 129.9, 129.5, 129.2, 126.9, 126.6, 125.4, 123.8, 120.5, 115.8, 113.0, 36.4, 29.2, 23.5, 20.9. HRMS m/z (ESI+): Calculated for C21H1879BrCl3CINO ([M+H]+): 414.0255, Found 414.0246, HRMS m/z (ESI+): Calculated for C21H1881BrCl3CINO ([M+H]+): 416.0235, Found 416.0235, HRMS m/z (ESI+): Calculated for C21H1879BrCl3CINO ([M+H]+): 416.0225, Found 416.0235, HRMS m/z (ESI+): Calculated for C21H1881BrCl3CINO ([M+H]+): 418.0205, Found 418.0219.
(2-Bromocyclohex-1-en-1-yl)(2-(naphthalen-2-yl)-1H-indol-1-yl)methanone (1k)

Yield 75%, yellow solid, Mp 144-148 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); "H NMR (500 MHz, CDCl₃): δ 8.39 (d, J = 8.3 Hz, 1H), 7.95 (s, 1H), 7.87 (dd, J = 8.5 Hz, 3H), 7.64-7.56 (m, 2H), 7.56-7.46 (m, 2H), 7.43-7.36 (m, 1H), 7.32 (t, J = 7.5 Hz, 1H), 6.71 (s, 1H), 2.34-2.08 (m, 2H), 1.92 (dd, J = 11.5, 7.1 Hz, 2H), 1.10-0.65 (m, 4H); "C NMR (125 MHz, CDCl₃) δ 170.0, 139.8, 137.3, 134.6, 132.9, 132.8, 131.1, 129.6, 127.9, 127.7, 127.6, 127.1, 126.8, 126.5, 126.4, 125.1, 124.0, 120.3, 115.8, 112.1, 36.2, 29.5, 23.0, 20.4. HRMS m/z (ESI+): Calculated for C₂₅H₂₀BrNONa ([M+Na]⁺): 454.0601, Found 454.0592.

(2-Bromocyclohex-1-en-1-yl)(2-(thiophen-2-yl)-1H-indol-1-yl)methanone (1l)

Yield 77%, white solid, Mp 105-108 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); "H NMR (500 MHz, CDCl₃): δ 8.32 (d, J = 8.2 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.38 (ddd, J = 13.4, 6.8, 1.2 Hz, 2H), 7.34-7.27 (m, 1H), 7.13 (dd, J = 3.5, 1.2 Hz, 1H), 7.08 (dd, J = 5.1, 3.6 Hz, 1H), 6.72 (s, 1H), 2.27 (d, J = 33.0 Hz, 4H), 1.35 (d, J = 10.5 Hz, 4H); "C NMR (125 MHz, CDCl₃) δ 170.0, 137.1, 134.3, 134.3, 131.7, 129.1, 127.6, 126.9, 126.8, 126.4, 125.4, 124.0, 120.4, 115.6, 113.6, 36.3, 29.6, 23.5, 20.8. HRMS m/z (ESI+): Calculated for C₁₉H₁₆BrNO₂ ([M+Na]⁺): 408.0029, Found 408.0021, HRMS m/z (ESI+): Calculated for C₁₉H₁₆BrNO₂ ([M+Na]⁺): 410.0009, Found 409.9995.

Methyl 1-(2-bromocyclohex-1-ene-1-carbonyl)-1H-indole-2-carboxylate (1m)

Yield 82%, light yellow solid, Mp 76-80 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); "H NMR (500 MHz, CDCl₃): δ 8.21 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.50-7.44 (m, 1H), 7.34-7.29 (m, 1H), 7.27 (s, 1H), 3.90 (s, 3H), 2.74-2.64 (m, 2H), 2.56-2.44 (m, 2H), 1.75 (dt, J = 9.9, 3.7 Hz, 4H); "C NMR (125 MHz, CDCl₃) δ 169.6, 161.9, 137.9, 136.3, 130.3, 127.8, 127.6, 125.3, 124.1, 122.2, 117.4, 115.4, 52.4, 36.9, 29.8, 23.9, 21.2. HRMS m/z (ESI+): Calculated for C₁₇H₁₆BrNO₂ ([M+Na]⁺): 384.0206, Found 384.0200, HRMS m/z (ESI+): Calculated for C₁₇H₁₆BrNO₂ ([M+Na]⁺): 386.0186, Found 386.0181.

(2-Bromocyclohex-1-en-1-yl)(5-chloro-2-methyl-1H-indol-1-yl)methanone (1n)

Yield 78%, pink solid, Mp 64-67 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v):
$^1$HNMR (500 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J$ = 8.8 Hz, 1H), 7.40 (d, $J$ = 1.2 Hz, 1H), 7.19 (dd, $J$ = 8.7, 1.4 Hz, 1H), 6.32 (s, 1H), 2.60 (s, 2H), 2.54 (s, 3H), 2.47 (s, 2H), 1.83 (s, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 168.9, 138.0, 134.9, 134.8, 131.1, 129.1, 124.1, 123.8, 119.3, 115.9, 109.4, 35.8, 29.1, 21.3, 16.1. HRMS m/z (ESI+): Calculated for C$_{16}$H$_{15}$Br$_2$ClINaO ($[\text{M+Na}]^+$): 373.9918, Found 373.9915. HRMS m/z (ESI+): Calculated for C$_{16}$H$_{15}$Br$_3$ClINaO ($[\text{M+Na}]^+$): 375.9898, Found 375.9907, HRMS m/z (ESI+): Calculated for C$_{16}$H$_{15}$Br$_3$ClINaO ($[\text{M+Na}]^+$): 375.9888, Found 375.9907.

(2-Bromocyclohex-1-en-1-yl)(5-fluoro-2-methyl-1H-indol-1-yl)methanone (1o)

Yield 75%, white solid, Mp 81-84 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.03 (dd, $J$ = 9.0, 4.6 Hz, 1H), 7.09 (dd, $J$ = 8.6, 2.5 Hz, 1H), 6.95 (td, $J$ = 9.1, 2.6 Hz, 1H), 6.34 (s, 1H), 2.60 (s, 2H), 2.54 (s, 3H), 2.47 (s, 2H), 1.83 (s, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 168.9, 159.7 (d, $J$ = 238.8 Hz), 138.2, 135.0, 132.9, 131.0 (d, $J$ = 10.0 Hz), 123.9, 116.1 (d, $J$ = 8.8 Hz), 111.3 (d, $J$ = 25.0 Hz), 109.9 (d, $J$ = 3.8 Hz), 105.4 (d, $J$ = 23.8 Hz), 35.8, 29.2, 23.8, 21.3, 16.2. HRMS m/z (ESI+): Calculated for C$_{16}$H$_{16}$Br$_2$FNO ($[\text{M+H}]^+$): 336.0394, Found 336.0379, HRMS m/z (ESI+): Calculated for C$_{16}$H$_{16}$Br$_2$FNO ($[\text{M+H}]^+$): 338.0359, Found 338.0363.

(2-Bromocyclohex-1-en-1-yl)(2,5-dimethyl-1H-indol-1-yl)methanone (1p)

Yield 80%, red oily liquid; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.90 (d, $J$ = 8.4 Hz, 1H), 7.19 (s, 1H), 7.08-6.98 (m, 1H), 6.28 (s, 1H), 2.56 (s, 2H), 2.51 (s, 3H), 2.43 (s, 2H), 2.39 (s, 3H), 1.78 (s, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 168.6, 136.4, 135.0, 134.4, 132.7, 129.9, 124.8, 123.0, 119.6, 114.3, 109.9, 35.5, 28.8, 23.5, 21.0, 16.0. HRMS m/z (ESI+): Calculated for C$_{17}$H$_{18}$BrNONa ($[\text{M+Na}]^+$): 354.0464, Found 354.0467, HRMS m/z (ESI+): Calculated for C$_{17}$H$_{18}$BrNONa ($[\text{M+Na}]^+$): 356.0444, Found 356.0442.

(2-Bromocyclohex-1-en-1-yl)(5-methoxy-2-methyl-1H-indol-1-yl)methanone (1q)

Yield 80%, white solid, Mp 81-84 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J$ = 9.0 Hz, 1H), 6.93 (d, $J$ = 2.5 Hz, 1H), 6.85 (dd, $J$ = 9.1, 2.6 Hz, 1H), 6.33 (s, 1H), 3.85 (s, 3H), 2.61 (s, 2H), 2.55 (d, $J$ = 0.8 Hz, 3H), 2.51 (d, $J$ = 26.7 Hz, 2H), 1.85 (s, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 168.7, 156.4, 137.3, 135.2, 131.1, 130.9, 123.3, 115.8, 111.7, 110.2, 102.9, 55.6, 35.7, 29.1, 23.8, 21.3, 16.2. HRMS m/z (ESI+): Calculated for C$_{17}$H$_{18}$BrNO$_2$Na ($[\text{M+Na}]^+$): 370.0414, Found 370.0407, HRMS m/z (ESI+): Calculated for
\[ \text{C}_{17}\text{H}_{18}^{81}\text{BrNO}_{2}\text{Na} ([M+Na]) \]: 372.0394, Found 372.0396.

**2-bromocyclohex-1-en-1-yl)(6-chloro-2-methyl-1H-indol-1-yl)methanone (1r)**

Yield 71%, colorless liquid; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); \(^1\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3): \delta 8.13 (s, 1H), 7.35 (d, \text{J} = 8.2 \text{ Hz, 1H}), 7.21 (\text{dd}, \text{J} = 8.2, 1.7 \text{ Hz, 1H}), 6.36 (s, 1H), 2.62 (s, 2H), 2.54 (s, 3H), 2.49 (\text{dd}, \text{J} = 18.6, 14.7 \text{ Hz, 2H}), 1.85 (s, 4H); \(^{13}\text{C} \text{NMR} (125 \text{ MHz, CDCl}_3): \delta 168.9, 137.2, 136.9, 134.8, 129.6, 128.3, 124.1, 124.0, 120.3, 115.5, 109.7, 35.8, 29.1, 23.7, 21.2, 16.1. \text{HRMS} \text{m/z } (\text{ESI}+): \text{Calculated for C}_{18}\text{H}_{16}^{79}\text{BrNO}\text{(M+H)}^+: 389.9657, \text{Found 389.9641.} \]

**2-bromocyclohex-1-en-1-yl)(6-fluoro-2-methyl-1H-indol-1-yl)methanone (1s)**

Yield 75%, yellow liquid; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); \(^1\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3): \delta 7.89 (\text{dd}, \text{J} = 10.6, 1.7 \text{ Hz, 1H}), 7.34 (\text{dd}, \text{J} = 8.4, 5.6 \text{ Hz, 1H}), 6.98 (\text{td}, \text{J} = 8.9, 2.3 \text{ Hz, 1H}), 6.35 (s, 1H), 2.60 (s, 2H), 2.52 (s, 3H), 2.51-2.39 (m, 2H), 1.83 (s, 4H); \(^{13}\text{C} \text{NMR} (125 \text{ MHz, CDCl}_3): \delta 168.9, 160.5 (\text{d, J} = 237.5 \text{ Hz}), 136.6 (\text{d, J} = 3.8 \text{ Hz}), 136.5, 134.7, 126.0, 123.9, 120.0 (\text{d, J} = 10.0 \text{ Hz}), 111.4 (\text{d, J} = 23.8 \text{ Hz}), 109.7, 102.9 (\text{d, J} = 28.8 \text{ Hz}), 35.7, 29.1, 23.6, 21.1, 16.0. \text{HRMS} \text{m/z } (\text{ESI}+): \text{Calculated for C}_{18}\text{H}_{16}^{79}\text{BrNO}\text{(M+H)}^+: 336.0394, \text{Found 336.0396, HRMS} \text{m/z } (\text{ESI}+): \text{Calculated for C}_{18}\text{H}_{16}^{81}\text{BrNO}\text{(M+H)}^+: 338.0374, \text{Found 338.0382.} \]

**2-Bromocyclopent-1-en-1-yl)(2-methyl-1H-indol-1-yl)methanone (1t)**

Yield 82%, pink solid, \text{Mp 51-55 °C}; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); \(^1\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3): \delta 7.86-7.80 (\text{m, 1H}), 7.48-7.42 (\text{m, 1H}), 7.24-7.17 (\text{m, 2H}), 6.39 (\text{s, 1H}), 2.84 (\text{ddd}, \text{J} = 7.6, 5.6, 4.0, 1.8 \text{ Hz, 4H}), 2.52 (\text{d, J} = 1.0 \text{ Hz, 3H}), 2.20-2.11 (\text{m, 2H}); \(^{13}\text{C} \text{NMR} (125 \text{ MHz, CDCl}_3): \delta 166.2, 137.3, 136.3, 136.1, 129.6, 126.1, 123.4, 123.1, 119.6, 114.0, 109.5, 41.3, 34.2, 22.2, 15.6. \text{HRMS} \text{m/z } (\text{ESI}+): \text{Calculated for C}_{18}\text{H}_{16}^{79}\text{BrNO}\text{(M+H)}^+: 304.0332, \text{Found 304.0335, HRMS} \text{m/z } (\text{ESI}+): \text{Calculated for C}_{18}\text{H}_{16}^{81}\text{BrNO}\text{(M+H)}^+: 306.0312, \text{Found 306.0322.} \]

**2-Bromocyclohept-1-en-1-yl)(2-methyl-1H-indol-1-yl)methanone (1u)**

Yield 84%, light red oil; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); \(^1\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3): \delta 8.03 (\text{d, J} = 7.6 \text{ Hz, 1H}), 7.45-7.39 (\text{m, 1H}), 7.26-7.16 (\text{m, 2H}), 6.36 (\text{s, 1H}), 2.88-2.83 (\text{m, 2H}), 2.54 (\text{d, J} = 0.8 \text{ Hz, 3H}), 2.51 (\text{d, J} = 4.1 \text{ Hz, 2H}), 1.80 (\text{m, 4H}), 1.73 (\text{d, J} = 4.7 \text{ Hz, 2H}); \(^{13}\text{C} \text{NMR} (125 \text{ MHz, CDCl}_3): \delta \text{...} \]
Yield 80%, yellowish oil; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.04 (d, $J$ = 6.2 Hz, 1H), 7.43–7.38 (m, 1H), 7.23–7.16 (m, 2H), 6.34 (s, 1H), 2.72 (s, 2H), 2.51 (s, 3H), 2.44 (t, $J$ = 6.1 Hz, 2H), 1.77 (d, $J$ = 40.4 Hz, 4H), 1.62 (s, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 168.8, 136.8, 136.6, 136.4, 129.7, 126.0, 123.5, 123.3, 119.5, 114.9, 109.9, 36.7, 31.3, 29.7, 28.1, 26.1, 25.4, 16.3. HRMS m/z (ESI+): Calculated for C$_{18}$H$_{21}$NO ($[M+H]^+$): 346.0802, Found 346.0796, HRMS m/z (ESI+): Calculated for C$_{18}$H$_{21}$NO ($[M+H]^+$): 348.0782, Found 348.0780.

3. Procedure for the Vinylative Dearomatization of Indoles

In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added Pd(OAc)$_2$ (5 mol %), L3 (6 mol %), indole 1 (0.2 mmol) and 2.0 mL of anhydrous MeOH, after that, TMEDA and formic acid were injected into the reaction system by syringe. The mixture was then conducted in oil-bath at 100 °C for 12 h. When the reaction was complete, the solvent was removed by rotatory evaporation and the crude obtained was purified by column chromatography with silica gel to give the desired tetracyclic products 2.

(S)-10b-methyl-7,8,9,10,10b,11-hexahydro-6H-isooindolo[2,1-a]indol-6-one (2a)

Yield 91%, white solid, Mp 88-90 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [a]$^D_{20}$ = +156.0 (c 1.0, CH$_2$Cl$_2$), 99% ee [Lux 5u Cellulose-3 column (25 cm × 0.46 cm ID), $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.50 (d, $J$ = 7.8 Hz, 1H), 7.25 (d, $J$ = 9.7 Hz, 1H), 7.16 (d, $J$ = 7.5 Hz, 1H), 7.04 (d, $J$ = 7.4 Hz, 1H), 3.01 (d, $J$ = 15.1 Hz, 1H), 2.78 (d, $J$ = 15.1 Hz, 1H), 2.40-2.28 (m, 1H), 2.27-2.13 (m, 3H), 1.81 (dd, $J$ = 11.2, 5.7 Hz, 1H), 1.72 (tt, $J$ = 11.0, 5.7 Hz, 3H), 1.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 172.8, 161.9, 139.9, 134.7, 131.0, 127.8, 125.4, 123.9, 116.9, 73.1, 38.4, 24.7, 22.6, 21.9, 21.7, 20.1. HRMS m/z (ESI+): Calculated for C$_{16}$H$_{18}$N0
(S)-10b-methyl-7,8,9,10,10b,11-hexahydro-6H-isooindolo[2,1-a]indol-6-one (2a)

Derived from chloro-substituted substrate. Yield 79%; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D20 = +196.0 (c 1.0, CH2Cl2), 98% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), 5% hexane/PrOH = 95/05, 1.0 mL/min, 254 nm; 1H NMR (500 MHz, CDCl3): δ 7.51 (d, J = 7.8 Hz, 1H), 7.25 (dd, J = 15.3, 7.7 Hz, 1H), 7.16 (d, J = 7.4 Hz, 1H), 7.03 (td, J = 7.5, 0.7 Hz, 1H), 3.02 (d, J = 15.1 Hz, 1H), 2.79 (d, J = 15.1 Hz, 1H), 2.39-2.29 (m, 1H), 2.29-2.13 (m, 3H), 1.88-1.78 (m, 1H), 1.78-1.65 (m, 3H), 1.43 (s, 3H).

(R)-10b-cyclopropyl-7,8,9,10,10b,11-hexahydro-6H-isooindolo[2,1-a]indol-6-one (2c)

Yield 53%, pink solid, Mp 108-112 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D20 = +144.0 (c 1.0, CH2Cl2), 99% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), 5% hexane/PrOH = 95/05, 1.0 mL/min, 254 nm; 1H NMR (500 MHz, CDCl3): δ 7.42 (d, J = 7.8 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.4 Hz, 1H), 7.00 (td, J = 7.6, 0.7 Hz, 1H), 3.13 (d, J = 15.4 Hz, 1H), 2.94 (d, J = 15.4 Hz, 1H), 2.46 (ddd, J = 10.0, 6.4, 3.1 Hz, 1H), 2.31-2.08 (m, 3H), 1.82 (dd, J = 6.0, 2.2 Hz, 1H), 1.77-1.66 (m, 3H), 1.08 (ddd, J = 13.4, 6.7, 4.1 Hz, 1H), 0.41 (ddd, J = 8.6, 6.1, 4.2 Hz, 1H), 0.33-0.17 (m, 2H), 0.13 (ddd, J = 9.0, 7.4, 4.5 Hz, 1H); 13C NMR (125 MHz, CDCl3): δ 174.4, 162.9, 141.4, 135.2, 130.3, 127.7, 125.0, 123.9, 116.4, 74.6, 36.9, 23.0, 22.0, 21.8, 20.1, 18.1, 2.3, -0.8. HRMS m/z (ESI+): Calculated for C13H27NO ([M+H]+): 266.1539, Found 266.1539.
(R)-10b-phenyl-7,8,9,10,10b,11-hexahydro-6H-isoidolo[2,1-a]indol-6-one (2d)

Yield 86%, white solid, Mp 151-155 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); $[\alpha]_D^{20} = +353.0$ (c 1.0, CH$_2$Cl$_2$), 97% ee [Lux 5u Cellulose-2 column (25 cm x 0.46 cm ID), $\delta$hexane/PrOH = 80/20, 0.7 mL/min, 254 nm; $t_{\text{major}} = 11.0$ min, $t_{\text{minor}} = 12.9$ min]; $^1$H NMR (500 MHz, CDCl$_3$): $7.57$ (d, $J = 7.8$ Hz, 1H), 7.53-7.43 (m, 2H), 7.35-7.27 (m, 2H), 7.27-7.17 (m, 2H), 7.09 (d, $J = 7.5$ Hz, 1H), 6.98 (td, $J = 7.5$, 0.8 Hz, 1H), 3.51 (d, $J = 15.3$ Hz, 1H), 3.36 (d, $J = 15.2$ Hz, 1H), 2.40-2.05 (m, 4H), 1.80-1.47 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.4, 161.5, 141.0, 140.1, 134.8, 130.9, 128.6, 127.9, 127.7, 125.5, 125.0, 124.3, 117.0, 78.9, 39.5, 23.3, 22.0, 21.4, 20.4. HRMS m/z (ESI+): Calculated for C$_{21}$H$_{20}$NO ([M+H]$^+$): 302.1539, Found 302.1537.

(R)-10b-(p-tolyl)-7,8,9,10,10b,11-hexahydro-6H-isoidolo[2,1-a]indol-6-one (2e)

Yield 89%, pink solid, Mp 171-175 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); $[\alpha]_D^{20} = +324.1$ (c 1.0, CH$_2$Cl$_2$), 97% ee [Daicel Chiralpak AD-H column (25 cm x 0.46 cm ID), $\delta$hexane/PrOH = 90/10, 0.7 mL/min, 254 nm; $t_{\text{major}} = 17.0$ min, $t_{\text{minor}} = 22.9$ min]; $^1$H NMR (500 MHz, CDCl$_3$): $7.55$ (d, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.19 (t, $J = 7.7$ Hz, 1H), 7.10 (d, $J = 8.1$ Hz, 2H), 7.07 (d, $J = 7.4$ Hz, 1H), 6.96 (td, $J = 7.6$, 0.7 Hz, 1H), 3.48 (d, $J = 15.2$ Hz, 1H), 3.33 (d, $J = 15.2$ Hz, 1H), 2.35-2.18 (m, 6H), 2.19-2.06 (m, 1H), 1.77-1.60 (m, 3H), 1.60-1.49 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.3, 161.6, 140.0, 137.9, 137.4, 134.9, 130.7, 129.2, 127.8, 125.4, 124.9, 124.2, 117.0, 78.7, 39.3, 23.2, 21.9, 21.4, 20.9, 20.3. HRMS m/z (ESI+): Calculated for C$_{22}$H$_{22}$NO ([M+H]$^+$): 316.1696, Found 316.1693.

(R)-10b-(4-methoxyphenyl)-7,8,9,10,10b,11-hexahydro-6H-isoidolo[2,1-a]indol-6-one (2f)

Yield 61%, light red solid, Mp 185-188 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); $[\alpha]_D^{20} = +333.0$ (c 1.0, CH$_2$Cl$_2$), 95% ee [Daicel Chiralpak AD-H column (25 cm x 0.46 cm ID), $\delta$hexane/PrOH = 90/10, 1.0 mL/min, 254 nm; $t_{\text{major}} = 20.2$ min, $t_{\text{minor}} = 24.6$ min]; $^1$H NMR (500 MHz, CDCl$_3$): $7.56$ (d, $J = 7.8$ Hz, 1H), 7.42-7.36 (m, 2H), 7.23 (dd, $J = 18.3$, 10.7 Hz, 1H), 7.10 (d, $J = 7.4$ Hz, 1H), 6.99 (t, $J = 7.4$ Hz, 1H), 6.87-6.81 (m, 2H), 3.75 (s, 3H), 3.48 (d, $J = 15.2$ Hz, 1H), 3.33 (d, $J = 15.2$ Hz, 1H), 2.35-2.21 (m, 3H), 2.20-2.09 (m, 1H), 1.68 (m, 3H), 1.63-1.52 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.3, 161.8, 159.1, 140.0, 134.9, 132.7, 130.5, 127.8, 126.6, 125.0, 124.2, 117.0, 113.9, 78.5, 55.1, 39.3, 23.2,
(R)-10b-(4-fluorophenyl)-7,8,9,10,10b,11-hexahydro-6H-isooindolo[2,1-a]indol-6-one (2g)

Yield 75%, white solid, Mp 186-189 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D20 = +339.0 (c 1.0, CH2Cl2), 95% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), δ hexane/PrOH = 90/10, 1.0 mL/min, 254 nm; t_major = 11.3 min, t_minor = 16.3 min]. 1H NMR (500 MHz, CDCl3): δ 7.57 (d, J = 7.8 Hz, 1H), 7.50-7.41 (m, 2H), 7.24 (dd, J = 14.2, 6.6 Hz, 1H), 7.11 (d, J = 7.4 Hz, 1H), 7.05-6.94 (m, 3H), 3.47 (d, J = 15.3 Hz, 1H), 3.37 (d, J = 15.3 Hz, 1H), 2.26 (ddd, J = 13.2, 11.1, 8.2 Hz, 3H), 2.13 (dd, J = 6.2, 3.1 Hz, 1H), 1.75-1.63 (m, 3H), 1.62-1.51 (m, 1H); 13C NMR (125 MHz, CDCl3) δ 173.3, 163.2, 161.3 (d, J = 8.8 Hz), 139.9, 136.7 (d, J = 2.5 Hz), 134.5, 131.0, 128.0, 127.2 (d, J = 8.8 Hz), 125.0, 124.4, 117.2, 115.4 (d, J = 21.2 Hz), 78.4, 39.5, 23.2, 21.9, 21.4, 20.3. HRMS m/z (ESI+): Calculated for C22H22FNO ([M+H]+): 332.1645, Found 332.1644.

(R)-10b-(4-(trifluoromethyl)phenyl)-7,8,9,10,10b,11-hexahydro-6H-isooindolo[2,1-a]indol-6-one (2h)

Yield 87%, yellowish green solid, Mp 46-49 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D20 = +235.1 (c 1.0, CH2Cl2), 96% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), δ hexane/PrOH = 90/10, 1.0 mL/min, 254 nm; t_major = 7.1 min, t_minor = 9.6 min]. 1H NMR (500 MHz, CDCl3): δ 7.61 (d, J = 18.2 Hz, 5H), 7.37-6.86 (m, 3H), 3.47 (dd, J = 37.4, 14.0 Hz, 2H), 2.36-2.14 (m, 4H), 1.71-1.58 (m, 4H); 13C NMR (125 MHz, CDCl3) δ 173.2, 160.6, 145.2, 139.8, 134.2, 131.6, 130.1 (q, J = 32.5 Hz), 128.1, 126.0, 125.6 (d, J = 3.8 Hz), 125.0, 124.6, 117.1, 78.7, 39.6, 23.3, 21.9, 21.3, 20.4. HRMS m/z (ESI+): Calculated for C22H19F3NO ([M+H]+): 370.1413, Found 370.1413.

(R)-10b-(3-chlorophenyl)-7,8,9,10,10b,11-hexahydro-6H-isooindolo[2,1-a]indol-6-one (2i)

Yield 73%, white solid, Mp 138-142 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D20 = +325.0 (c 1.0, CH2Cl2), 86% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), δ hexane/PrOH = 90/10, 1.0 mL/min, 254 nm; t_major = 12.8 min, t_minor = 11.2 min]. 1H NMR (500 MHz, CDCl3): δ 7.60 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 1.8 Hz, 1H), 7.40 (dt, J = 7.4, 1.5 Hz, 1H), 7.30-7.21 (m, 3H), 7.12 (d, J = 7.4 Hz, 1H), 7.02 (td, J = 7.5, 0.8 Hz, 1H), 3.49 (d, J = 15.3 Hz, 1H), 3.40 (d, J = 15.3 Hz, 1H), 2.40-2.21 (m, 3H), 2.20-2.07 (m, 1H), 1.79-1.64 (m, 3H), 1.64-1.51 (m, 1H); 13C NMR (125 MHz, CDCl3) δ 173.2, 160.8, 143.3, 139.9, 134.6, 134.3, 131.3, 129.8, 128.0, 128.0, 125.8, 125.0, 124.5.

(S)-10b-(2-chlorophenyl)-7,8,9,10,10b,11-hexahydro-6H-isooindolo[2,1-a]indol-6-one (2j)

Yield 68%, white solid, Mp 185-190 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D 20 = +283.0 (c 1.0, CH₂Cl₂), 98% ee [Lux 5u Cellulose-3 column (25 cm × 0.46 cm ID), ⁶DClNO H NMR (500 MHz, CDCl₃): δ 7.82-7.72 (m, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.46-7.35 (m, 1H), 7.32-7.15 (m, 3H), 7.12 (d, J = 7.5 Hz, 1H), 7.01 (td, J = 7.5, 0.7 Hz, 1H), 4.24 (d, J = 16.1 Hz, 1H), 3.43 (d, J = 16.1 Hz, 1H), 2.75-2.59 (m, 1H), 2.45-2.30 (m, 1H), 2.25 (ddd, J = 8.2, 5.6, 2.4 Hz, 2H), 1.81-1.49 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 172.9, 162.2, 139.5, 138.1, 135.3, 132.1, 131.9, 131.3, 129.3, 128.2, 127.7, 127.6, 124.8, 124.4, 116.8, 79.6, 38.1, 25.4, 22.3, 21.1, 20.6. HRMS m/z (ESI+): Calculated for C_{21}H_{19}^{35}ClNO ([M+H]^+): 336.1150, Found 336.1146, HRMS m/z (ESI+): Calculated for C_{21}H_{19}^{37}ClNO ([M+H]^+): 338.1120, Found 338.1122.

(R)-10b-(naphthalen-2-yl)-7,8,9,10,10b,11-hexahydro-6H-isooindolo[2,1-a]indol-6-one (2k)

Yield 87%, white solid, Mp 142-146 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D 20 = +370.0 (c 1.0, CH₂Cl₂), 96% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), ⁶DClNO H NMR (500 MHz, CDCl₃): δ 7.97 (d, J = 1.4 Hz, 1H), 7.83-7.72 (m, 3H), 7.63 (d, J = 7.8 Hz, 1H), 7.55 (dd, J = 8.6, 1.9 Hz, 1H), 7.48-7.37 (m, 2H), 7.22 (dd, J = 10.4, 5.0 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 7.02-6.91 (m, 1H), 3.64 (d, J = 15.3 Hz, 1H), 3.42 (d, J = 15.3 Hz, 1H), 2.43-2.06 (m, 4H), 1.74-1.46 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 173.4, 161.6, 140.0, 138.1, 134.7, 133.1, 132.8, 130.9, 128.3, 128.0, 127.9, 127.4, 126.3, 126.2, 125.0, 124.3, 123.6, 117.0, 79.0, 39.1, 23.4, 21.9, 21.4, 20.3. HRMS m/z (ESI+): Calculated for C_{23}H_{23}NO ([M+H]^+): 352.1696, Found 352.1698.

(S)-10b-(thiophen-2-yl)-7,8,9,10,10b,11-hexahydro-6H-isooindolo[2,1-a]indol-6-one (2l)

Yield 88%, pink solid, Mp 173-177 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D 20 = +307.0 (c 1.0, CH₂Cl₂), 99% ee [Lux 5u Cellulose-3 column (25 cm × 0.46 cm ID), ⁶DClNO H NMR (500 MHz, CDCl₃): δ 7.53 (d, J = 7.8 Hz, 1H), 7.23 (dd, J = 13.6, 6.0 Hz, 1H), 7.14 (d, J = 6.0 Hz, 2H), 7.08-7.05 (m, 1H), 7.02 (t, J = 7.4 Hz, 1H).
1H), 6.91 (dd, J = 4.8, 3.8 Hz, 1H), 3.50 (d, J = 15.3 Hz, 1H), 3.36 (d, J = 15.3 Hz, 1H), 2.25 (m, 4H), 1.78-1.60 (m, 4H); 13C NMR (125 MHz, CDCl3) δ 173.0, 161.0, 145.9, 139.9, 134.5, 131.1, 128.1, 127.0, 125.1, 124.7, 124.5, 124.2, 117.3, 40.2, 23.0, 21.9, 21.5, 20.3, 1.0. HRMS m/z (ESI+): Calculated for C13H18NOS: [M+H]+: 308.1104, Found 308.1100.

Methyl(S)-6-oxo-7,8,9,10-tetrahydro-6H-isindolo[2,1-alindole-10b(11H)-carboxylate (2m)

Yield 93%, white solid, Mp 141-145 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D20 = +291.3 (c 1.0, CH2Cl2), 99% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), hexane/PrOH = 90/10, 0.7 mL/min, 254 nm; t_major = 18.2 min, t_minor = 14.9 min]; 1H NMR (500 MHz, CDCl3): δ 7.50 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 9.7 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H), 3.01 (d, J = 15.1 Hz, 1H), 2.78 (d, J = 15.1 Hz, 1H), 2.40-2.28 (m, 1H), 2.27-2.13 (m, 3H), 1.81 (dd, J = 11.2, 5.7 Hz, 1H), 1.72 (tt, J = 11.0, 5.7 Hz, 3H), 1.43 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 173.3, 171.2, 156.0, 140.2, 134.2, 133.5, 128.0, 125.0, 124.3, 116.5, 73.1, 38.4, 24.7, 22.6, 21.9, 21.7, 20.1. HRMS m/z (ESI+): Calculated for C13H18NO3: [M+H]+: 284.1281, Found 284.1284.

(S)-2-chloro-10b-methyl-7,8,9,10b,11-hexahydro-6H-isindolo[2,1-alindol-6-one (2n)

Yield 95%, white solid, Mp 169-173 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D20 = +104.0 (c 1.0, CH2Cl2), 99% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), hexane/PrOH = 90/10, 0.7 mL/min, 254 nm; t_major = 9.9 min, t_minor = 11.0 min]; 1H NMR (500 MHz, CDCl3): δ 7.39 (d, J = 8.3 Hz, 1H), 7.21-7.15 (m, 1H), 7.10 (s, 1H), 2.97 (d, J = 15.4 Hz, 1H), 2.74 (d, J = 15.4 Hz, 1H), 2.38-2.25 (m, 1H), 2.25-2.08 (m, 3H), 1.85-1.60 (m, 4H), 1.39 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 172.6, 161.9, 138.6, 136.5, 131.0, 129.1, 127.8, 125.7, 117.6, 73.4, 38.4, 24.7, 22.6, 21.8, 21.6, 20.1. HRMS m/z (ESI+): Calculated for C14H17ClNO ((M+H)+): 274.0993, Found 274.0992, HRMS m/z (ESI+): Calculated for C14H17ClNO ((M+H)+): 276.0963, Found 276.0962.

(S)-2-fluoro-10b-methyl-7,8,9,10b,11-hexahydro-6H-isindolo[2,1-alindol-6-one (2o)

Yield 90%, white solid, Mp 115-118 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]D20 = +151.0 (c 1.0, CH2Cl2), 99% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), hexane/PrOH = 90/10, 1.0 mL/min, 254 nm; t_major = 8.5 min, t_minor = 9.0 min]; 1H NMR (500 MHz, CDCl3): δ 7.42 (dd, J = 8.5, 4.8 Hz, 1H), 6.93 (td, J = 8.9, 2.3 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 3.01 (d, J = 15.4 Hz, 1H), 2.77 (d, J = 15.4 Hz, 1H), 2.42-2.27 (m, 1H), 2.27-2.12 (m, 3H), 1.87-1.77 (m, 1H), 1.78-1.65 (m, 3H), 1.43 (s, 3H); 13C
NMR (125 MHz, CDCl3) δ 172.9, 161.3 (d, J = 122.5 Hz), 158.9, 136.6 (d, J = 7.5 Hz), 136.1, 131.0, 117.5 (d, J = 8.8 Hz), 114.1 (d, J = 22.5 Hz), 112.9 (d, J = 23.8 Hz), 73.6, 38.6, 24.6, 22.6, 21.9, 21.6, 20.1. HRMS m/z (ESI+): Calculated for C_{16}H_{17}FNO ([M+H]^+): 258.1289, Found 258.1286.

(S)-2,10b-dimethyl-7,8,9,10,10b,11-hexahydro-6H-isindolo[2,1-a]indol-6-one (2p)

Yield 98%, white solid, Mp 120-124 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v);

[α]D^20 = +117.0 (c 1.0, CH2Cl2). 98% ee [Daiceel Chiralpak AD-H column (25 cm × 0.46 cm ID), hexane/PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 12.1 min, t_{minor} = 13.7 min]; ¹H NMR (500 MHz, CDCl3): δ 7.38 (d, J = 7.9 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.97 (s, 1H), 2.97 (d, J = 5.4 Hz, 1H), 1.76-1.63 (m, 3H), 1.41 (s, 3H); ¹³C NMR (125 MHz, CDCl3) δ 172.8, 161.6, 133.5, 130.9, 128.2, 126.1, 116.5, 73.2, 38.4, 24.6, 22.6, 21.9, 21.7, 21.0, 20.1. HRMS m/z (ESI+): Calculated for C_{17}H_{20}NO ([M+H]^+): 254.1539, Found 254.1540.

(S)-2-methoxy-10b-methyl-7,8,9,10,10b,11-hexahydro-6H-isindolo[2,1-a]indol-6-one (2q)

Yield 91%, white solid, Mp 127-130 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v);

[α]D^20 = +107.0 (c 1.0, CH2Cl2). 97% ee [Lux 5u Cellulose-3 column (25 cm × 0.46 cm ID), hexane/PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 8.6 min, t_{minor} = 7.9 min]; ¹H NMR (500 MHz, CDCl3): δ 7.40 (d, J = 8.5 Hz, 1H), 6.82-6.70 (m, 2H), 3.76 (s, 3H), 2.99 (d, J = 15.2 Hz, 1H), 2.74 (d, J = 15.3 Hz, 1H), 2.39-2.27 (m, 1H), 2.27-2.11 (m, 3H), 1.80 (d, J = 5.3 Hz, 1H), 1.72 (ddd, J = 16.4, 11.2, 5.6 Hz, 3H), 1.41 (s, 3H); ¹³C NMR (125 MHz, CDCl3) δ 173.0, 161.5, 156.8, 136.3, 133.5, 131.0, 117.2, 112.2, 112.1, 73.5, 55.6, 38.7, 24.5, 22.6, 21.9, 21.7, 20.1. HRMS m/z (ESI+): Calculated for C_{17}H_{20}NO ([M+H]^+): 270.1489, Found 270.1486.

(S)-3-chloro-10b-methyl-7,8,9,10,10b,11-hexahydro-6H-isindolo[2,1-a]indol-6-one (2r)

Yield 72%, light yellow solid, Mp 151-154 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v);

[α]D^20 = +190.0 (c 1.0, CH2Cl2). 99% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), hexane/PrOH = 97/03, 1.0 mL/min, 254 nm; t_{major} = 21.9 min, t_{minor} = 24.2 min]; ¹H NMR (500 MHz, CDCl3): δ 7.50 (d, J = 1.8 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 7.01 (d, J = 1.9 Hz, 1H), 2.97 (d, J = 15.2 Hz, 1H), 2.76 (d, J = 15.2 Hz, 1H), 2.38-2.30 (m, 1H), 2.29-2.16 (m, 3H), 1.81 (dt, J = 14.1, 7.2 Hz, 1H), 1.73 (ddd, J = 16.7, 11.4, 5.8 Hz, 3H), 1.43 (s, 3H); ¹³C NMR (125 MHz, CDCl3) δ 172.6, 162.2, 141.0,
133.4, 133.2, 131.0, 126.2, 124.0, 117.3, 73.7, 38.0, 24.8, 22.7, 21.9, 21.7, 20.2. HRMS m/z (ESI+): Calculated for C_{16}H_{17}ClNO ([M+H]+): 274.0993, Found 274.0995.

**(S)-3-fluoro-10b-methyl-7,8,9,10b,11-hexahydro-6H-isinoindolo[2,1-a]indol-6-one (2s)**

Yield 59%, white solid, Mp 106-109 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]_{D}^{20} = -146.4 (c 1.0, CHCl₂), 99% ee [Daicel Chiralpak OD-H column (25 cm × 0.46 cm ID), hexane/PrOH = 95/05, 1.0 mL/min, 254 nm; t_{major} = 6.5 min, t_{minor} = 5.8 min]; ¹H NMR (500 MHz, CDCl₃): δ 7.22 (dd, J = 8.9, 1.9 Hz, 1H), 7.12-7.01 (m, 1H), 6.78-6.65 (m, 1H), 2.97 (d, J = 14.9 Hz, 1H), 2.75 (d, J = 15.0 Hz, 1H), 2.41-2.29 (m, 1H), 2.22 (d, J = 3.6 Hz, 3H), 1.82 (dd, J = 11.1, 5.5 Hz, 1H), 1.73 (dt, J = 27.2, 5.5 Hz, 3H), 1.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.6, 162.7 (d, J = 242.5 Hz), 162.3, 141.2 (d, J = 11.3 Hz), 131.0, 129.9, 125.9 (d, J = 10.0 Hz), 110.4 (d, J = 22.5 Hz), 105.0 (d, J = 26.3 Hz), 74.0, 37.8, 24.8, 22.7, 21.9, 21.7, 20.2. HRMS m/z (ESI+): Calculated for C_{16}H_{17}FNO ([M+H]+)^+: 258.1289, Found 258.1294.

**(S)-10a-methyl-2,3,10,10a-tetrahydrocyclopenta[3,4]pyrrolo[1,2-a]indol-4(1H)-one (2t)**

Yield 80%, white solid, Mp 116-120 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]_{D}^{20} = +168.0 (c 1.0, CHCl₂), 98% ee [Lux 5u Cellulose-3 column (25 cm × 0.46 cm ID), hexane/PrOH = 95/05, 0.7 mL/min, 254 nm; t_{major} = 12.5 min, t_{minor} = 13.4 min]; ¹H NMR (500 MHz, CDCl₃): δ 7.48 (d, J = 7.8 Hz, 1H), 7.25 (dd, J = 13.8, 6.2 Hz, 1H), 7.16 (d, J = 7.4 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 3.08 (d, J = 15.1 Hz, 1H), 2.79 (d, J = 15.1 Hz, 1H), 2.67-2.48 (m, 4H), 2.40 (ddd, J = 22.6, 11.7, 6.6 Hz, 2H), 1.46 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.4, 169.2, 141.4, 140.1, 134.7, 127.8, 125.5, 123.9, 116.6, 70.3, 38.1, 27.8, 27.5, 25.6, 24.6. HRMS m/z (ESI+): Calculated for C_{16}H_{16}NO ([M+H]+)^+: 226.1226, Found 226.1227.

**(S)-11b-methyl-8,9,10,11,11b,12-hexahydrocyclohepta[3,4]pyrrolo[1,2-a]indol-6(7H)-one (2u)**

Yield 78%, pink solid, Mp 96-99 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); [α]_{D}^{20} = +96.0 (c 1.0, CHCl₂), 99% ee [Lux 5u Cellulose-3 column (25 cm × 0.46 cm ID), hexane/PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 5.1 min, t_{minor} = 6.3 min]; ¹H NMR (500 MHz, CDCl₃): δ 7.49 (d, J = 7.8 Hz, 1H), 7.24 (dd, J = 15.1, 7.4 Hz, 1H), 7.15 (d, J = 7.4 Hz, 1H), 7.02 (td, J = 7.4, 0.8 Hz, 1H), 3.03 (d, J = 15.1 Hz, 1H), 2.78 (d, J = 15.1 Hz, 1H), 2.51-2.42 (m, 2H), 2.42-2.30 (m, 2H), 1.92-1.81 (m, 1H), 1.76 (ddd, J = 9.8, 7.2, 4.8, 2.3 Hz, 2H), 1.72-1.55 (m, 2H), 1.52 (ddd, J = 9.0, 6.9, 4.5 Hz, 1H), 1.44 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.9, 164.3, 140.2, 134.8, 134.2, 127.8, 125.5, 124.0, 116.8, 73.1,
38.3, 30.9, 28.3, 27.0, 26.8, 24.6, 24.5. HRMS m/z (ESI+): Calculated for C\textsubscript{17}H\textsubscript{19}BrNO ([M+H])\textsuperscript{+}: 254.1539, Found 254.1538.

(S)-12b-methyl-7,8,9,10,11,12,12b,13-octahydro-6H-cycloocta[3,4]pyrrolo[1,2-a]indol-6-one (2v)

Yield 82%, light yellow solid, Mp 88-90 °C; Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); \([\alpha]_D^{20} = +104.0\) (c 1.0, CH\textsubscript{2}Cl\textsubscript{2}), 93% ee [Lux 5u Cellulose-3 column (25 cm × 0.46 cm ID), \textsuperscript{6}hexane/PrOH = 90/10, 1.0 mL/min, 254 nm; \(t_{\text{major}} = 4.8\) min, \(t_{\text{minor}} = 6.2\) min]. \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.51 (d, \(J = 7.8\) Hz, 1H), 7.25 (dd, \(J = 13.1, 5.5\) Hz, 1H), 7.16 (d, \(J = 7.4\) Hz, 1H), 7.04 (dt, \(J = 7.9, 3.9\) Hz, 1H), 3.03 (d, \(J = 15.1\) Hz, 1H), 2.81 (d, \(J = 15.1\) Hz, 1H), 2.60-2.48 (m, 2H), 2.48-2.37 (m, 2H), 1.83 (dd, \(J = 12.4, 6.2\) Hz, 2H), 1.75-1.57 (m, 3H), 1.52 (dd, \(J = 11.7, 6.3\) Hz, 3H), 1.47 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 172.8, 162.2, 140.0, 135.0, 132.3, 127.8, 125.4, 124.0, 116.9, 73.4, 38.8, 27.4, 27.1, 26.1, 25.7, 25.4, 24.7, 21.7. HRMS m/z (ESI+): Calculated for C\textsubscript{18}H\textsubscript{22}NO ([M+H])\textsuperscript{+}: 268.1696, Found 268.1692.

4. The gram-scale reaction

To a dried Schlenk tube were added Pd(OAc)\textsubscript{2} (5 mol%, 38.8 mg, 0.17 mmol), ligand L\textsubscript{3} (6 mol%, 152.7 mg, 0.21 mmol), \textit{1} (1.1 g, 3.46 mmol), and then TMEDA (1.0 mL, 6.92 mmol), HCOOH (0.26 mL, 6.92 mmol) was introduced via syringe. After that, the mixture was stirred at 100 °C for 10 h. When the reaction was complete, the solvent was removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl/petroleum ether 1:10 (v/v) to afford the products 2\textit{a} in yield 94% (0.78 g) and 99% ee, [Lux 5u Cellulose-3 column (25 cm × 0.46 cm ID), \textsuperscript{6}hexane/PrOH = 95/5, 1.0 mL/min, 254 nm; \(t_{\text{major}} = 7.5\) min, \(t_{\text{minor}} = 10.0\) min].
5. Synthetic transformations of product 2a

1) Hydrogenation of 2a with Pd/C

![Chemical structure of 2a and 3](image)

The mixture of Pd/C (10 mol%) and compound 2a (0.2 mmol, 1.0 eq) in EtOAc (5.0 mL) was stirred with hydrogen (a balloon with 1 atm) at room temperature for 3 days. The resulting mixture was then filtered and washed with EtOAc. After that, the solvent EtOAc was removed under vacuum, and the residue was purified by flash column chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to give compound 3 (29.4 mg, 61%) as a white solid, Mp 157-160 °C; [α]D20 = +36.1 (c 1.0, CH2Cl2), 99% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), hexane/PrOH = 90/10, 0.7 mL/min, tmajor = 12.7 min, tminor = 10.9 min]. 1H NMR (500 MHz, CDCl3): δ 7.59 (d, J = 7.8 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.3 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 2.97 (d, J = 15.3 Hz, 1H), 2.82 (d, J = 15.2 Hz, 1H), 2.72-2.61 (m, 1H), 2.58 (t, J = 7.7 Hz, 1H), 2.26-2.12 (m, 1H), 1.98-1.83 (m, 2H), 1.80-1.61 (m, 2H), 1.62-1.49 (m, 2H), 1.49-1.36 (m, 4H); 13C NMR (125 MHz, CDCl3) δ 174.9, 138.8, 133.7, 127.6, 125.6, 124.2, 115.9, 72.4, 47.0, 45.2, 42.4, 25.8, 24.8, 23.7, 23.2, 22.0. HRMS m/z (ESI+): Calculated for C16H20NO ([M+H]+): 242.1539, Found 242.1536.

2) Epoxidation of 2a

![Chemical structure of 2a and 4](image)

The mixture of m-CPBA (3.0 equiv) and 2a (0.2 mmol, 1.0 eq) in DCM (2.0 mL) was stirred at room temperature for 10 h under N2 atmosphere. The resulting mixture was then quenched with saturated Na2SO3 (aq.) and extracted with Et2O, the combined organic phases were concentrated under vacuum, and the crude was purified by flash column chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:30 (v/v) to give compound 4 (26.0 mg, 51%) as a white solid, Mp 83-86 °C; [α]D20 = +10.0 (c 1.0, CH2Cl2), 93% ee [Daicel Chiralpak AD-H column (25 cm × 0.46 cm ID), hexane/PrOH = 90/10, 0.7 mL/min, 254 nm; tmajor = 14.6 min, tminor = 15.5 min]. 1H NMR (500 MHz, CDCl3): δ 7.51 (d, J = 7.8 Hz, 1H), 7.21 (dt, J = 14.9, 7.5 Hz, 2H), 7.05 (dd, J = 13.9, 6.6 Hz, 1H), 3.33 (d, J = 15.0 Hz, 1H), 2.68 (d, J = 15.0 Hz, 1H), 2.28 (ddd, J = 15.5, 6.1, 4.9 Hz, 1H), 2.10-1.99 (m, 3H), 1.68-1.59 (m, 2H), 1.57-1.44 (m, 2H), 1.40 (s, 3H); 13C NMR
(125 MHz, CDCl₃) δ 170.8, 139.5, 132.9, 127.6, 125.6, 124.5, 116.2, 71.0, 65.3, 63.9, 36.2, 24.4, 21.7, 19.9, 19.5, 19.4. HRMS m/z (ESI+): Calculated for C₁₆H₁₈NO₂ ([M+H]⁺): 256.1332, Found 256.1328

6. Crystal structure of 2a with thermal ellipsoids shown at 30% probability

![Crystal structure of 2a with thermal ellipsoids shown at 30% probability](image)

Identification code exp_chem_y-6-23
Empirical formula C₃₂H₃₁N₂O₂
Formula weight 475.59
Temperature 293(2) K
Wavelength 0.71073 Å
Crystal system, space group Orthorhombic, P 2₁ 2₁ 2₁
Unit cell dimensions
  - a = 7.2924(4) Å  alpha = 90 deg
  - b = 14.2140(8) Å  beta = 90 deg
  - c = 25.7900(15) Å  gamma = 90 deg
Volume 2673.2(3) Å³
Z, Calculated density 4, 1.182 Mg/m³
Absorption coefficient 0.074 mm⁻¹
F(000) 1012
Crystal size 0.1 x 0.2 x 0.3 mm
Theta range for data collection 3.21 to 24.99 deg
Limiting indices -7 ≤ h ≤ 8, -16 ≤ k ≤ 16, -30 ≤ l ≤ 30
Reflections collected / unique 12519 / 4687 [R(int) = 0.0273]
Completeness to theta = 24.99 99.6 %
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4687 / 1 / 327
Goodness-of-fit on F² 1.029
Final R indices [I>2sigma(I)] R1 = 0.0523, wR2 = 0.1398
R indices (all data) R1 = 0.0708, wR2 = 0.1527
Absolute structure parameter 2.0(19)
Largest diff. peak and hole 0.271 and -0.177 e.Å⁻³
7. Copies of NMR and HPLC of the Compounds

1a

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
\textbf{1a'}

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
1b

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
1c

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
1d

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
1e

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
If

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^{1}H$ NMR ($CDCl_3$, 500 MHz)

$^{13}C$ NMR ($CDCl_3$, 125 MHz)
1h

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
\textbf{1i}

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz)

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz)
**1j**

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
1k

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^{1}$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
1m

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
In

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
1o

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
1p

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)

S36
Ir

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
Is

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
1t

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
1u

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
iv

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2a

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2b

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2c

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2d

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2e

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2f

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2g

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2h

$^{1}$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2i

\(^1\)H NMR (CDCl\(_3\), 500 MHz)

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz)
$^{1}H$ NMR (CDCl$_3$, 500 MHz)

$^{13}C$ NMR (CDCl$_3$, 125 MHz)
2k

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^{1}H$ NMR (CDCl$_3$, 500 MHz)

$^{13}C$ NMR (CDCl$_3$, 125 MHz)
2m

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2n

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$^{13}C$ NMR (CDCl$_3$, 125 MHz)
2r

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
**2s**

**$^1$H NMR (CDCl$_3$, 500 MHz)**

- [NMR spectrum image]

**$^{13}$C NMR (CDCl$_3$, 125 MHz)**

- [NMR spectrum image]
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2u

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2v

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
HPLC chromatograms

2a

信号 1: DAD1 A, Sig=254.4 Ref=360,100

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信号 1: DADI A, Sig=254,4 Ref=360,100

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