## Electronic Supplementary Information for:

Endo-5-norbornene-2,3-dimethanol promoted asymmetric Heck/Suzuki cascade reaction of $\boldsymbol{N}$-(2-bromophenyl)acrylamides<br>Ming Chen, Xing-Xing Xu, Xucai Wang, Zhi-Hui Ren, Zheng-Hui Guan*<br>Key Laboratory of Synthetic and Natural Functional Molecule of the Ministry of Education, Department of Chemistry \& Materials Science, Northwest University, Xi'an 710127, P.R. China.<br>E-mail: guanzhh@nwu.edu.cn

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## 1. General information.

## Chemicals

Chemicals were commercially purchased from Adamas-beta, Energy Chemical, Aladdin, Daicel Chiral Technologies (China) Co., etc, and directly used without further purification unless otherwise stated. $\operatorname{Pd}(\mathrm{TFA})_{2}$ was purchased from Adamas-beta. Toluene and mesitylene were purified by freshly distilled prior to use. Phosphoramidite ligand $\mathbf{L} 1$ was prepared according to our previous report (M. Chen, X. Wang, P. Yang, X. Kou, Z.-H. Ren and Z.-H. Guan, Angew. Chem. Int. Ed., 2020, 59, 12199-12205; M. Chen, X. Wang, Z.-H. Ren and Z.-H. Guan, CCS Chem., 2021, 3, 69-77.)
L1: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.09(\mathrm{~s}, 4 \mathrm{H}), 7.87(\mathrm{~s}, 1 \mathrm{H}), 7.73(\mathrm{~s}, 1 \mathrm{H}), 7.27(\mathrm{~s}$, $1 \mathrm{H}), 7.21(\mathrm{~s}, 1 \mathrm{H}), 7.06(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.95(\mathrm{t}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.68(\mathrm{~s}, 1 \mathrm{H}), 6.48$ (d, $J=4.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.37(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.34(\mathrm{~s}, 2 \mathrm{H}), 4.14(\mathrm{~d}, J=16.0 \mathrm{~Hz}, 1 \mathrm{H})$, $3.43(\mathrm{dd}, J=16.0,4.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.93(\mathrm{~s}, 4 \mathrm{H}), 2.72(\mathrm{~s}, 2 \mathrm{H}), 2.42(\mathrm{~s}, 2 \mathrm{H}), 2.02(\mathrm{~s}, 6 \mathrm{H})$, 1.94-1.79 (m, 6H), 1.77-1.57 (m, 2H); ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 144.6,144.2$, 143.3, 143.1, 140.0, 139.7, 139.6, 139.5, 137.8, 136.8, 135.5, 135.0, 132.0, 131.8, $131.6,131.4,131.3$, 131.1, 130.7, 130.1, 129.9, 129.8, 129.4, 129.1, 128.9, 128.7, $128.2,125.6,125.5,125.1,124.9,124.7,124.6,122.2,122.0,121.9,120.9,120.7$, 120.2, 49.3 29.2, 29.2, 27.9, 27.9, 22.6, 22.6, 22.5, 22.4, 20.9. HRMS calcd (ESI) m/z for $\mathrm{C}_{52} \mathrm{H}_{39} \mathrm{~F}_{15} \mathrm{NNaO}_{2} \mathrm{P}:[\mathrm{M}+\mathrm{Na}]^{+}$1048.2371, found 1048.2356.
The norbornenes N10 was prepared according to literature procedures. (J. M. Goll and E. Fillion, Organometallics, 2008, 27, 3622-3625; P. Liu, M. Yasir and A. F. M. Kilbinger, Angew. Chem. Int. Ed., 2019, 58, 15278-15282.)

## Chromatography

Analytical thin-layer chromatography (TLC) was carried out with silica gel pre-coated glass plates (TLC-Silica gel GF254, coating thickness: $0.20-0.25 \mathrm{~mm}$, particle size: $10-40 \mu \mathrm{~m}$ ) purchased from Xinnuo Chemical (Yantai, China). The TLC was visualized with a UV lamp ( 254 or 365 nm ).
Flash Column chromatography was carried out on silica gel ( $60 \AA, 200-300$ mesh) purchased from Xinnuo Chemicals (Yantai, China) with technical grade solvents as the eluent. All the yields referred to spectroscopically and chromatographically pure compounds.

## Nuclear magnetic resonance (NMR) spectroscopy

${ }^{1} \mathrm{H}$ NMR spectra were recorded on Bruker AVANCE III instrument ( 400 MHz
spectrometer). The analytical sample was dissolved in an appropriate deuterated solvent. The employed deuterated solvent and the measuring frequency are indicated in each ${ }^{1} \mathrm{H}$ NMR data. Chemical shifts are reported in parts per million (ppm) with the solvent resonance as the internal reference $\left(\mathrm{CDCl}_{3} \delta\right.$ 7.26). The following abbreviations (or combinations thereof) were used to explain multiplicities: $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{q}=$ quartet, $\mathrm{m}=$ multiplet, $\mathrm{b}=$ broad. Coupling constants, J were reported in Hertz unit (Hz).
${ }^{13} \mathrm{C}$ NMR spectra were recorded on Bruker AVANCE III instrument (101 MHz spectrometer). The employed deuterated solvent and the measuring frequency are both indicated in each ${ }^{13} \mathrm{C}$ NMR data. Chemical shifts are reported in ppm with the solvent resonance as the internal reference $\left(\mathrm{CDCl}_{3} \delta 77.0\right)$.

## High resolution mass spectrometry (HRMS)

HRMS were recorded on a liquid chromatography/quadrupole time-of-flight mass spectrometer (MicroTof-Q II mass spectrometer, Bruker Daltonics) using electrospray ionization-time of flight (ESI-TOF) at the Instrumental Analysis Center of Northwest University. The calculated values are based on the most abundant isotope.

## Optical rotations

Optical rotations were measured with a WZZ-2S automatic polarimeter purchased from Shanghai INESA Physico-Optical instrument company using a sodium lamp (sodium D line, $\lambda=589 \mathrm{~nm}$ ) in the indicated solvent at the indicated temperature. The measurements were carried out in a 1.5 mL cell ( 50 mm length) with concentrations $(\mathrm{g} / 100 \mathrm{~mL})$ reported in the corresponding solvent. The optical rotation values ([ $\alpha] \mathrm{D}$ ) were reported at a given temperature $\left({ }^{\circ} \mathrm{C}\right)$ in deg. $\mathrm{mL} \mathrm{g}-1 \mathrm{dm}-1$.

## High performance liquid chromatography (HPLC)

HPLC analysis was performed on an Agilent Technologies 1260 Series using Chiralpak columns IA, IC, or IG (Daicel Chiral Reagent Company). The solvents (n-hexane and iso-propanol, HPLC-grade) used as the eluent were purchased from Oceanpak. The column type and the eluent (a mixture of $n$-hexane and iso-propanol) are indicated for each experiment.

## X-ray crystallography

X-ray crystallography was performed on a BRUKERSMA RTAPEXIICCD diffractometer at Instrumental Analysis Center of Northwest University.

## 2. Typical procedure for the asymmetric Heck/Suzuki reaction.



The 10 mL round-bottom flask was charged with acrylamides $\mathbf{1}(0.1 \mathrm{mmol}, 1.0$ equiv), $\mathrm{RB}(\mathrm{OH})_{2}\left(2.0\right.$ equiv), $\operatorname{Pd}(\mathrm{TFA})_{2}(8 \mathrm{~mol} \%)$, $\mathbf{L 1}(16 \mathrm{~mol} \%)$, $\mathbf{N 1 0}$ ( $60 \mathrm{~mol} \%$ ), $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (3.0 equiv) and $\mathrm{H}_{2} \mathrm{O}(0.1 \mathrm{~mL})$ in mesitylene ( 0.5 mL ) under $\mathrm{N}_{2}$ atmosphere. The reaction was then heated in $50^{\circ} \mathrm{C}$ and stirred for 12 h . Upon completion of the reaction, the reaction mixture was cooled down to room temperature. The reaction was purified by column chromatography on silica gel with hexanes: ethyl acetate (10:1) as the eluent to afford the corresponding product $\mathbf{3}$ or $\mathbf{4}$.

## 3. Typical procedure for synthesis of the racemic Heck/Suzuki products.



The 10 mL round-bottom flask was charged with acrylamides $\mathbf{1}(0.1 \mathrm{mmol}, 1.0$ equiv), $\mathrm{RB}(\mathrm{OH})_{2}$ ( 2.0 equiv), $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(5 \mathrm{~mol} \%), \mathrm{KHCO}_{3}$ (3.0 equiv) and $\mathrm{H}_{2} \mathrm{O}(50$ equiv) in toluene ( 0.8 mL ) under $\mathrm{N}_{2}$ atmosphere. The reaction was then heated in 80 ${ }^{\circ} \mathrm{C}$ and stirred for 12 h . Upon completion of the reaction, the reaction mixture was cooled down to room temperature. The reaction was purified by column chromatography on silica gel with hexanes: ethyl acetate (10:1) as the eluent to afford the corresponding product $( \pm) \mathbf{3}$ or $\mathbf{4}$.

## 4. Table S1. Screening of catalyst and solvent. ${ }^{a}$

|  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| entry | [Pd] | solvent | yield (\%) | ee (\%) |
| 1 | $\mathrm{Pd}(\mathrm{OAc})_{2}$ | Toluene | 34 | 49 |
| 2 | $\mathrm{Pd}(\mathrm{TFA})_{2}$ | Toluene | 58 | 68 |
| 3 | Pd (acac) 2 | Toluene | 8 | 56 |
| 4 | $\mathrm{Pd}(\mathrm{dba})_{2}$ | Toluene | 51 | 65 |
| 5 | $\mathrm{Pd}(\mathrm{TFA})_{2}$ | Dioxane | 10 | 61 |
| 6 | $\mathrm{Pd}(\mathrm{TFA})_{2}$ | $\mathrm{CH}_{3} \mathrm{CN}$ | 0 | -- |
| 7 | $\mathrm{Pd}(\mathrm{TFA})_{2}$ | DMF | 0 | -- |
| 8 | $\mathrm{Pd}(\mathrm{TFA})_{2}$ | Mesitylene | 64 | 72 |
| $9^{\text {b }}$ | Pd (TFA) 2 | Mesitylene | 75 | 70 |

${ }^{a}$ Conditions: 1a ( 0.1 mmol ), 2a( 0.2 mmol ), $[\mathrm{Pd}](8 \mathrm{~mol} \%), \mathbf{L 1}(16 \mathrm{~mol} \%), \mathrm{Cs}_{2} \mathrm{CO}_{3}$ $(0.3 \mathrm{mmol})$, solvent $(0.5 \mathrm{~mL}), \mathrm{N}_{2}, 50^{\circ} \mathrm{C}, 12 \mathrm{~h}$. Isolated yield, and enantiomeric excess (ee) were determined by chiral HPLC analysis. ${ }^{b} \mathrm{H}_{2} \mathrm{O}(0.1 \mathrm{~mL})$ was added.

Table S2. Screening of phosphoramidite ligands. ${ }^{a}$




L6

$\mathrm{Ar}=3,5-\left(\mathrm{CF}_{3}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{3}$
L7

$\mathrm{Ar}=3,5-\left(\mathrm{CF}_{3}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{3}$
L8

$\mathrm{Ar}=3,5-\left(\mathrm{CF}_{3}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{3}$
L9


$\mathrm{Ar}=3,5-\left(\mathrm{CF}_{3}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{3}$
L10

$\mathrm{Ar}=3,5-\left(\mathrm{CF}_{3}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{3}$
L11

$\mathrm{Ar}=3,5-\left(\mathrm{CF}_{3}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{3}$
L12
${ }^{a}$ Conditions: 1a ( 0.1 mmol ), 2a ( 0.2 mmol ), $\mathrm{Pd}(\mathrm{TFA})_{2}(8 \mathrm{~mol} \%)$, $\mathbf{L n}(16 \mathrm{~mol} \%), \mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( 0.3 mmol ), mesitylene ( 0.5 mL ), $\mathrm{H}_{2} \mathrm{O}(0.1 \mathrm{~mL}), \mathrm{N}_{2}, 50^{\circ} \mathrm{C}, 12 \mathrm{~h}$. Isolated yield, and enantiomeric excess (ee) were determined by chiral HPLC analysis.

## 5. Synthesis of intermediate INT-1 and mechanistic study.



In a 10 mL round-bottom flask, acrylamides $\mathbf{1 a}(0.1 \mathrm{mmol}, 1.0$ equiv) was added to the solution of $\mathrm{Pd}_{2}(\mathrm{dba})_{3}(0.05 \mathrm{mmol}, 0.5$ eqiuv) and $\mathbf{L 1}(0.1 \mathrm{mmol}, 1.0$ equiv) in mesitylene ( 2 mL ). Then, the flask was evacuated and back-filled with argon ( 3 times) and then stirred at $50{ }^{\circ} \mathrm{C}$ for 12 h . The residue was purified by column chromatography on silica gel (hexanes: ethyl acetate $=15: 1$ ) to give the $\sigma$-alkyl palladium INT-1 ( $45 \%$ yield). ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 8.53$ (s, 2H), 8.15 (s, $2 \mathrm{H}), 7.81(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}), 7.56-7.54(\mathrm{~m}, 2 \mathrm{H}), 7.36(\mathrm{~s}, 1 \mathrm{H}), 7.31(\mathrm{~d}, J=7.6 \mathrm{~Hz}$, $4 \mathrm{H}), 7.18-7.15(\mathrm{~m}, 3 \mathrm{H}), 6.82(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.59(\mathrm{~s}$, $1 \mathrm{H}), 6.38(\mathrm{~s}, 1 \mathrm{H}), 5.76(\mathrm{~s}, 1 \mathrm{H}), 3.95(\mathrm{~d}, J=18.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.25(\mathrm{~d}, J=16.8 \mathrm{~Hz}, 1 \mathrm{H})$, $2.95(\mathrm{~s}, 3 \mathrm{H}), 2.80(\mathrm{~s}, 3 \mathrm{H}), 2.21-2.16(\mathrm{~m}, 2 \mathrm{H}), 2.05-2.01(\mathrm{~m}, 1 \mathrm{H}), 1.90-1.83(\mathrm{~m}$, $14 \mathrm{H}), 1.68(\mathrm{t}, J=10.4 \mathrm{~Hz}, 1 \mathrm{H}), 0.88(\mathrm{~s}, 3 \mathrm{H})$. HRMS calcd (ESI) $\mathrm{m} / \mathrm{z}$ for $\mathrm{C}_{68} \mathrm{H}_{53} \mathrm{~F}_{15} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{PPd}:[\mathrm{M}-\mathrm{Br}]^{+}$1367.2606, found: 1367.2642.

In a 10 mL round-bottom flask, the $\sigma$-alkyl palladium INT-1 $(0.045 \mathrm{mmol}, 1.0$ equiv), $\mathrm{PhB}(\mathrm{OH})_{2}$ ( $0.09 \mathrm{mmol}, 2.0$ equiv), $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( $0.09 \mathrm{mmol}, 2.0$ equiv) in mesitylene ( 0.5 mL ) was heated at $50^{\circ} \mathrm{C}$ under stirring for 12 h . After the completion of the reaction, the residue was purified by column chromatography on silica gel (hexanes: ethyl acetate = 10: 1) to give the product 3a ( $30 \%$ yield, $93 \%$ ee).

## 6. Characterization data of the products.


(S)-3-benzyl-1-methyl-3-phenylindolin-2-one (3a)

Yield: $72 \%(22.5 \mathrm{mg})$, ee $=94 \%,[\alpha] \mathrm{D}^{21}=-79.5\left(\mathrm{c}=1.1, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.51-7.48(\mathrm{~m}, 2 \mathrm{H}), 7.34-7.30(\mathrm{~m}, 2 \mathrm{H}), 7.27-7.24(\mathrm{~m}, 1 \mathrm{H}), 7.21-$ 7.16 (m, 2H), $7.07-6.97$ (m, 4H), 6.83 (dd, $J=8.0,2.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.58(\mathrm{~d}, J=8.0 \mathrm{~Hz}$, $1 \mathrm{H}), 3.70(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.44(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.91(\mathrm{~s}, 3 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR (101 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.7,143.6,139.6,135.6,131.1,129.9,128.5,128.1,127.3,127.2$, $126.4,125.4,122.1,107.9,58.2,43.9,25.9$. HRMS (ESI) calcd. for $\mathrm{C}_{2} \mathrm{H}_{20} \mathrm{NO}$ $[\mathrm{M}+\mathrm{H}]^{+}: 314.1539$, found: 314.1547.

The ee of compound $\mathbf{3 a}$ was determined by HPLC using an IA $A_{\text {Daicel }}$ column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=10.24 \mathrm{~min}$, $\left.t_{\text {minor }}=12.26 \mathrm{~min}\right)$.


## (S)-3-benzyl-1,5-dimethyl-3-phenylindolin-2-one (3b)

Yield: $65 \%(21.4 \mathrm{mg})$, ee $=97 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-32.7\left(\mathrm{c}=1.2, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.49(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.05-6.99(\mathrm{~m}, 5 \mathrm{H}), 6.82$ (dd, $J=7.6,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.49(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.68$ (d, $J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.44(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.91(\mathrm{~s}, 3 \mathrm{H}), 2.34(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 177.7,141.4,139.9,135.7,131.6,131.4,130.0,128.5,128.4$, 127.3, 127.2, 126.4, 126.1, 107.7, 58.3, 43.8, 26.0, 21.2. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}: 328.1696$, found: 328.1696 .

The ee of compound 3b was determined by HPLC using an IA Daicel column ( n -hexane/i-PrOH $=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.67 \mathrm{~min}, \mathrm{t}_{\text {minor }}$ $=12.60 \mathrm{~min}$ ).



(S)-3-benzyl-1,6-dimethyl-3-phenylindolin-2-one (3c)

Yield: $77 \%(25.2 \mathrm{mg})$, ee $=96 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-70.9\left(\mathrm{c}=1.1, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.31(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.24(\mathrm{t}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.06-7.00(\mathrm{~m}, 4 \mathrm{H}), 6.88-6.83(\mathrm{~m}, 3 \mathrm{H}), 6.43(\mathrm{~s}, 1 \mathrm{H}), 3.65(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H})$, $3.43(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.91(\mathrm{~s}, 3 \mathrm{H}), 2.31(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 178.0, 143.7, 139.9, 138.1, 135.8, 130.0, 128.4, 128.0, 127.3, 127.2, 127.2, 126.4, 125.2, 122.6, 108.9, 57.9, 43.9, 25.9, 21.7. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}$: 328.1696, found: 328.1697.

The ee of compound $\mathbf{3 c}$ was determined by HPLC using an IC Daicel column (n-hexane/i-PrOH $=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=6.74 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=11.60 \mathrm{~min}$ ).


| \# | $\begin{aligned} & \text { Meas. RT } \\ & \text { [min] } \end{aligned}$ | Peak | Type | Peak Height [mAU] | $\begin{gathered} \text { Peak Width } \\ {[\text { min }]} \end{gathered}$ | Peak Area [mAU*s] | Peak Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 6. 742 \| |  | BB | 596.690\| | O. 155 | 6074.348 \| | 97.760 |
| 21 | 11.6021 |  | MM | 6.411 | O. 362 \| | 139.177\| | 2. 240 |



(S)-3-benzyl-1,5,6-trimethyl-3-phenylindolin-2-one (3d)

Yield: $53 \%(18.0 \mathrm{mg})$, ee $=93 \%,[\alpha] \mathrm{D}^{32}=-38.8\left(\mathrm{c}=1.2, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.49(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.35-7.31(\mathrm{~m}, 2 \mathrm{H}), 7.28-7.24(\mathrm{~m}, 1 \mathrm{H})$, $7.05-6.99(\mathrm{~m}, 3 \mathrm{H}), 6.93(\mathrm{~s}, 1 \mathrm{H}), 6.83(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.42(\mathrm{~s}, 1 \mathrm{H}), 3.64(\mathrm{~d}, J=$ $13.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.45(\mathrm{~d}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.91(\mathrm{~s}, 3 \mathrm{H}), 2.24(\mathrm{t}, J=2.0 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.9,141.6,140.1,136.2,135.9,130.0,129.9,128.5$, 128.4, 127.3, 127.2, 126.6, 126.4, 109.4, 58.1, 43.8, 26.0, 20.2, 19.6. HRMS (ESI) calcd. for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}: 342.1852$, found: 342.1859.

The ee of compound 3d was determined by HPLC using an IC Daicel column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=80 / 20$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=8.83 \mathrm{~min}$, $\left.\mathrm{t}_{\text {minor }}=15.46 \mathrm{~min}\right)$.

|  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| \# | $\begin{gathered} \text { Meas. RT } \\ \text { [min] } \end{gathered}$ | Peak | Type | Peak Height [mAU] | $\begin{aligned} & \text { Peak Width } \\ & {[\text { min }]} \end{aligned}$ | Peak Area [mAU*s] | Peak $\%$ | Area |
| 1 \| | 8. 8321 |  | MM | 602. 2841 | O. 207 | 7479.896 |  | 9. 320 |
| 21 | 15.457 |  | MM | 15.659 \| | O. 304 | 285.814 |  | 3. 680 |




## (S)-3-benzyl-5-ethyl-1-methyl-3-phenylindolin-2-one (3e)

Yield: $72 \%(24.6 \mathrm{mg})$, ee $=97 \%,[\alpha]_{\mathrm{D}}{ }^{19}=-56.6\left(\mathrm{c}=1.0, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.05-6.98(\mathrm{~m}, 5 \mathrm{H}), 6.82(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.52(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.67(\mathrm{~d}, J$ $=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.45(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.93(\mathrm{~s}, 3 \mathrm{H}), 2.68-2.60(\mathrm{~m}, 2 \mathrm{H}), 1.22(\mathrm{t}, J$ $=7.6 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.8,141.5,139.8,138.3,135.8$, $131.2,130.0,128.5,127.3,127.3,127.3,126.4,125.2,107.7,58.3,44.0,28.7,26.1$, 16.2. HRMS (ESI) calcd. for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}: 342.1852$, found: 342.1860.

The ee of compound $\mathbf{3 e}$ was determined by HPLC using an IADaicel column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=12.60 \mathrm{~min}$, $t_{\text {minor }}=16.21 \mathrm{~min}$ ).


(S)-3-benzyl-5-isopropyl-1-methyl-3-phenylindolin-2-one (3f)

Yield: $70 \%(24.9 \mathrm{mg})$, ee $=97 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-79.6\left(\mathrm{c}=0.7, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.51(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.06-6.98(\mathrm{~m}, 5 \mathrm{H}), 6.81(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.52(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.66(\mathrm{~d}, J$ $=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.46(\mathrm{~d}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.95(\mathrm{~s}, 3 \mathrm{H}), 2.93-2.86(\mathrm{~m}, 1 \mathrm{H}), 1.24(\mathrm{t}, J$ $=6.4 \mathrm{~Hz}, 6 \mathrm{H}$ ) ; ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.8,142.9,141.6,139.7,135.8$, $130.9,130.0,128.5,127.4,127.3,126.4,125.8,123.9,107.6,58.3,44.1,33.9,26.1$, 24.6, 24.0. HRMS (ESI) calcd. for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}: 356.2009$, found: 356.2011 .

The ee of compound $\mathbf{3 f}$ was determined by HPLC using an IA $A_{\text {Daicel }}$ column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.51 \mathrm{~min}, \mathrm{t}_{\text {minor }}$ $=10.34 \mathrm{~min}$ ).


(S)-3-benzyl-5-butyl-1-methyl-3-phenylindolin-2-one (3g)

Yield: $56 \%(20.7 \mathrm{mg})$, ee $=98 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-146.8\left(\mathrm{c}=0.4, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.05-6.98(\mathrm{~m}, 5 \mathrm{H}), 6.83(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.51(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.69(\mathrm{~d}, J$ $=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.44(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.94(\mathrm{~s}, 3 \mathrm{H}), 2.60(\mathrm{dd}, J=15.2,7.6 \mathrm{~Hz}$, $2 \mathrm{H}), 1.61-1.56(\mathrm{~m}, 2 \mathrm{H}), 1.34(\mathrm{dd}, J=14.8,7.2 \mathrm{~Hz}, 2 \mathrm{H}), 0.95(\mathrm{t}, J=7.2 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 177.8,141.5,139.9,136.8,135.8,131.1,130.0,128.5$, $127.9,127.3,127.3,126.4,125.7,107.6,58.3,43.9,35.3,34.0,26.1,22.1,14.0$. HRMS (ESI) calcd. for $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}: 370.2165$, found: 370.2162 .

The ee of compound $\mathbf{3 g}$ was determined by HPLC using an IADaicel column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.18 \mathrm{~min}, \mathrm{t}_{\text {minor }}=$ $9.12 \mathrm{~min})$.



(S)-3-benzyl-5-(tert-butyl)-1-methyl-3-phenylindolin-2-one (3h)

Yield: $74 \%(27.3 \mathrm{mg})$, ee $=98 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-88.4\left(\mathrm{c}=0.5, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.52(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=6.8 \mathrm{~Hz}$, $1 \mathrm{H}), 7.21(\mathrm{dd}, J=8.4,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.17(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.04-6.98(\mathrm{~m}, 3 \mathrm{H}), 6.80$ (d, $J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.54(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.65(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.47(\mathrm{~d}, J=$ $13.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), $2.96(\mathrm{~s}, 3 \mathrm{H}), 1.31(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.9,145.1$, 141.3, 139.7, 135.9, 130.4, 130.1, 128.5, 127.4, 127.3, 126.4, 124.4, 123.3, 107.3, 58.3, 44.2, 34.5, 31.5, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}: 370.2165$, found: 370.2168 .

The ee of compound $\mathbf{3 h}$ was determined by HPLC using an IADaicel column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=6.86 \mathrm{~min}, \mathrm{t}_{\text {minor }}$ $=9.06 \mathrm{~min}$ ).



(S)-3-benzyl-5-methoxy-1-methyl-3-phenylindolin-2-one (3i)

Yield: $74 \%(25.4 \mathrm{mg})$, ee $=97 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-40.0\left(\mathrm{c}=1.4, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.49(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.36-7.32(\mathrm{~m}, 2 \mathrm{H}), 7.30-7.26(\mathrm{~m}, 1 \mathrm{H})$, $7.06-7.00(\mathrm{~m}, 3 \mathrm{H}), 6.86(\mathrm{dd}, J=7.2,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.79(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{dd}$, $J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.51(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.69(\mathrm{~d}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H})$, 3.45 (d, $J=12.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), $2.92(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.4,155.6$, $139.6,137.3,135.6,132.5,130.0,128.6,127.4,127.2,126.5,112.8,112.5,108.2$, 58.6, 55.8, 43.8, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 344.1645$, found: 344.1644.

The ee of compound $\mathbf{3 i}$ was determined by HPLC using an ICDaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=60 / 40$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.93 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=14.32 \mathrm{~min}$ ).

|  |  | 7.928 |  | $\underset{\underset{\sim}{\underset{~}{2}}}{\substack{2}}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 5 |  | 7.5 | 10 | 12.5 | 15 |  | min |
|  | $\begin{gathered} \text { Meas. RT } \\ {[m i n]} \end{gathered}$ | Peak | Type | Peak Height [mAU] | $\begin{gathered} \text { Peak Width } \\ {[\text { min }]} \end{gathered}$ | Peak Area [mAU*s] | Peak \% | Area |
| 1 \| | 7.928\| |  | MF | 1169.367\| | O. 210 \| | 14745.798 | 98 | . 562 |
| 21 | 14.322 |  | MF | 8. 200 | O. 437 | 215.148 |  | . 438 |



| \# | $\begin{gathered} \text { Meas. RT } \\ \text { [min] } \end{gathered}$ | Peak Type | Peak Height [mAU] | Peak Width [min] | Peak Area [mAU*s] | Peak Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 \| | 7. 946 | MM | 106. 129 | O. 198 \| | 1259. 153 \| | 50. 440 |
| $2 \mid$ | 14.338 | MF | 49. 402 | O. 417 \| | 1237. 180 | 49.560 |


(S)-3-benzyl-6-methoxy-1-methyl-3-phenylindolin-2-one (3j)

Yield: $74 \%(25.4 \mathrm{mg})$, ee $=96 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-69.7\left(\mathrm{c}=1.0, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.08-7.00(\mathrm{~m}, 4 \mathrm{H}), 6.84(\mathrm{dd}, J=7.6,1.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.58(\mathrm{dd}, J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H})$, $6.20(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 3.65(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.43(\mathrm{~d}, J=12.8 \mathrm{~Hz}$, $1 \mathrm{H}), 2.92(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 178.3,160.1,144.9,140.0,135.9$, $130.0,128.5,127.4,127.3,127.2,126.4,126.1,123.0,106.1,95.8,57.7,55.4,44.1$, 26.0. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 344.1645$, found: 344.1643 .

The ee of compound $\mathbf{3 j}$ was determined by HPLC using an IC Daicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=80 / 20$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.44 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=11.85 \mathrm{~min}$ ) .



| \# | $\begin{gathered} \text { Meas. RT } \\ {[\text { min] }} \end{gathered}$ | Peak | Type | Peak Height [mAU] | Peak Width [min] | Peak Area [mAU*s] | Peak Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 7. 512 |  | MF | 39.594 | O. 196 | 465. 5.52 | 49.788 |
| 21 | 12.000 |  | BB | 22. 888 | O. 315 \| | 469.520 | 50.212 |


(S)-3-benzyl-5,6-dimethoxy-1-methyl-3-phenylindolin-2-one (3k)

Yield: $58 \%(21.6 \mathrm{mg})$, ee $=97 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-63.5\left(\mathrm{c}=1.6, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.48(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=6.8 \mathrm{~Hz}$, $1 \mathrm{H}), 7.07-7.02(\mathrm{~m}, 3 \mathrm{H}), 6.84(\mathrm{dd}, J=7.6,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.70(\mathrm{~s}, 1 \mathrm{H}), 6.27(\mathrm{~s}, 1 \mathrm{H})$, $3.87(\mathrm{~s}, 3 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H}), 3.62(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.47(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.96(\mathrm{~s}$, 3 H ) ${ }^{13}{ }^{3} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 178.1, 149.4, 144.6, 139.8, 137.6, 135.9, 130.0, $128.5,127.5,127.4,127.3,126.5,121.5,110.5,93.8,58.3,56.8,56.2,43.8,26.2$. HRMS (ESI) calcd. for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{H}]^{+}: 374.1750$, found: 374.1758.

The ee of compound $\mathbf{3 k}$ was determined by HPLC using an IC $_{\text {Daicel }}$ column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=60 / 40$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.19 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=13.89 \mathrm{~min}$ ).

|  |  | " |  |  | oimm |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 6 |  | 8 | 10 | 12 | 14 |  | min |
| \# | $\begin{gathered} \text { Meas. RT } \\ {[\text { min] }} \end{gathered}$ | Peak | Type | Peak Height [mAU] | Peak Width [min] | Peak Area $[\mathrm{mAU} * \mathrm{~s}]$ | Peak \% | Area |
| 11 | 9. 187 |  | BB | 37.614 | O. 283 | 704.698 \| | 98 | . 615 |
| 21 | 13.889 |  | MM | O. 352 | O. 469 | 9. 900 |  | . 385 |



(S)-3-benzyl-5-ethoxy-1-methyl-3-phenylindolin-2-one (3I)

Yield: $63 \%(22.5 \mathrm{mg})$, ee $=97 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-35.8\left(\mathrm{c}=1.2, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.49(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.03(\mathrm{dd}, J=13.2,6.0 \mathrm{~Hz}, 3 \mathrm{H}), 6.86(\mathrm{dd}, J=7.6,1.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.81(\mathrm{~d}, J=2.4$ $\mathrm{Hz}, 1 \mathrm{H}), 6.74(\mathrm{dd}, J=8.8,2.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.50(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.02-3.93(\mathrm{~m}, 2 \mathrm{H})$, $3.69(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.43(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.91(\mathrm{~s}, 3 \mathrm{H}), 1.40(\mathrm{t}, J=7.2 \mathrm{~Hz}$, 3 H ); ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.5,154.9,139.7,137.3,135.7,132.5,130.0$, $128.6,127.4,127.4,127.2,126.5,113.5,113.4,108.3,64.2,58.7,43.8,26.1,14.9$. HRMS (ESI) calcd. for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 358.1802$, found: 358.1814.

The ee of compound 31 was determined by HPLC using an IADaicel column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=12.60 \mathrm{~min}$, $t_{\text {minor }}=16.21 \mathrm{~min}$ ).



(S)-3-benzyl-5-fluoro-1-methyl-3-phenylindolin-2-one (3m)

Yield: $67 \%(22.2 \mathrm{mg})$, ee $=93 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-69.1\left(\mathrm{c}=1.3, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.47(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.36(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.30(\mathrm{t}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.07-7.01(\mathrm{~m}, 3 \mathrm{H}), 6.97-6.88(\mathrm{~m}, 2 \mathrm{H}), 6.86(\mathrm{dd}, J=7.2,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.52(\mathrm{q}$, $J=4.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.72(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.43(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.94(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.5,158.9\left(\mathrm{~d}, J_{C F}=238.9 \mathrm{~Hz}\right), 139.7,139.1,135.2$, $133.0\left(\mathrm{~d}, J_{C F}=7.9 \mathrm{~Hz}\right), 129.9,128.7,127.7,127.5,127.1,126.7,114.4\left(\mathrm{~d}, J_{C F}=23.4\right.$ $\mathrm{Hz}), 113.4\left(\mathrm{~d}, J_{C F}=24.6 \mathrm{~Hz}\right), 108.4\left(\mathrm{~d}, J_{C F}=8.1 \mathrm{~Hz}\right), 58.7,43.8,26.2$. HRMS (ESI) calcd. for $\mathrm{C}_{22} \mathrm{H}_{19} \mathrm{FNO}[\mathrm{M}+\mathrm{H}]^{+}: 332.1445$, found: 332.1445.

The ee of compound $\mathbf{3 m}$ was determined by HPLC using an IADaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=90 / 10$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.54 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=10.79 \mathrm{~min}$ ).


(S)-3-benzyl-6-fluoro-1-methyl-3-phenylindolin-2-one (3n)

Yield: $65 \%(21.5 \mathrm{mg})$, ee $=94 \%,[\alpha]{ }_{\mathrm{D}}{ }^{18}=-85.9\left(\mathrm{c}=1.1, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.47(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.31-7.27(\mathrm{~m}, 1 \mathrm{H})$, $7.13(\mathrm{dd}, J=8.4,5.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.09-7.01(\mathrm{~m}, 3 \mathrm{H}), 6.4(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.78-6.73$ (m, 1H), $6.35(\mathrm{dd}, J=8.8,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.69(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.42(\mathrm{~d}, J=12.8 \mathrm{~Hz}$, $1 \mathrm{H}), 2.92(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 178.1,163.0\left(\mathrm{~d}, J_{C F}=243.6 \mathrm{~Hz}\right.$ ), $145.2\left(\mathrm{~d}, J_{C F}=11.5 \mathrm{~Hz}\right), 139.4,135.4,129.9,128.6,127.5,127.2,127.1\left(\mathrm{~d}, J_{C F}=\right.$ $92.2 \mathrm{~Hz}), 126.5,126.4,108.2\left(\mathrm{~d}, J_{C F}=22.2 \mathrm{~Hz}\right), 96.7\left(\mathrm{~d}, J_{C F}=27.3 \mathrm{~Hz}\right), 57.9,44.0$, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{22} \mathrm{H}_{19} \mathrm{FNO}[\mathrm{M}+\mathrm{H}]^{+}: 332.1445$, found: 332.1443.

The ee of compound $\mathbf{3 n}$ was determined by HPLC using an IADaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=10.63 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=13.53 \mathrm{~min}$ ).

|  |  |  |  |  | ल̆ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 10 |  |  | 12 | 14 |  | min |
| \# | $\begin{gathered} \text { Meas. RT } \\ \text { [min] } \end{gathered}$ | Peak | Type | Peak Height [mAU] | ```Peak Width [min]``` | Peak Area [mAU*s] | Peak \% | Area |
| 11 | $\begin{aligned} & 10.634 \\ & 13.526 \end{aligned}$ |  | MF | 759. 276 | O. 222 | 10123.767 | 97 | . 040 |
| 21 |  |  | MF | 16. 73 | O. 308 | 308. 802 |  | . 960 |



(S)-3-benzyl-5-chloro-1-methyl-3-phenylindolin-2-one (3o)

Yield: $55 \%(19.1 \mathrm{mg})$, ee $=95 \%,[\alpha]_{\mathrm{D}}{ }^{19}=-17.0\left(\mathrm{c}=1.0, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.45(\mathrm{~d}, J=6.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.36-7.30(\mathrm{~m}, 3 \mathrm{H}), 7.18(\mathrm{~s}, 2 \mathrm{H}), 7.05(\mathrm{~s}$, $3 \mathrm{H}), 6.85(\mathrm{~s}, 2 \mathrm{H}), 6.51(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.71(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.43(\mathrm{~d}, J=12.4$ $\mathrm{Hz}, 1 \mathrm{H}$ ), $2.92(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.3,142.3,139.0,135.1$, 133.2, 129. 9, 128.7, 128.1, 127.7, 127.5, 127.1, 126.7, 125.6, 108.9, 58.5, 43.8, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{22} \mathrm{H}_{19} \mathrm{ClNO}[\mathrm{M}+\mathrm{H}]^{+}: 348.1150$, found: 348.1149.

The ee of compound 30 was determined by HPLC using an IA Daicel column ( n -hexane/i-PrOH $=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=10.92 \mathrm{~min}$, $\left.t_{\text {minor }}=17.15 \mathrm{~min}\right)$.

|  | mAU 200 200 200 400 200 200 100 |  | I్ |  |  |  | $\stackrel{\text { 总 }}{\stackrel{1}{*}}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 10 |  | 12 | 14 | 16 |  | min |
| \# | $\begin{gathered} \text { Meas. RT } \\ \text { [min] } \end{gathered}$ | Peak | Type | Peak Height [mAU] | Peak Width [min] | Peak Area [mAU*s] | Peak \% | Area |
| 1 \| | 10. 923 \| |  | MF | 754. 395 | 0. 235 | 10641. 728 |  | 7. 254 |
| $2 \mid$ | 17. 154 \| |  | MF | 14. 392 \| | O. 348 | 300. 525 |  | 2. 746 |



(S)-3-benzyl-5-bromo-1-methyl-3-phenylindolin-2-one (3p)

Yield: $50 \%(19.6 \mathrm{mg})$, ee $=95 \%,[\alpha] \mathrm{D}^{27}=-18.5\left(\mathrm{c}=2.8, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ MHz, ) $\delta 7.46-7.44(\mathrm{~m}, 2 \mathrm{H}), 7.39-7.31(\mathrm{~m}, 5 \mathrm{H}), 7.08-7.03(\mathrm{~m}, 3 \mathrm{H}), 6.84(\mathrm{dd}, J=$ $6.8,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.48(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.70(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.43(\mathrm{~d}, J=12.8$ $\mathrm{Hz}, 1 \mathrm{H}$ ), 2.92 ( $\mathrm{s}, 3 \mathrm{H}$ ) ${ }^{13} \mathrm{C}^{\mathrm{C}} \mathrm{NMR}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ), $\delta 177.2,142.7,138.9,135.1$, $133.5,131.0,129.9,128.7,128.4,127.7,127.5,127.1,126.7,114.8,109.4,58.5,43.7$, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{BrNNaO}[\mathrm{M}+\mathrm{Na}]^{+}: 414.0464$, found: 414.0466 .

The ee of compound $\mathbf{3 p}$ was determined by HPLC using an IADaicel column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=90 / 10$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.84 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=11.67 \mathrm{~min}$ ).


(S)-3-benzyl-1-methyl-3-phenyl-5-(trifluoromethyl)indolin-2-one (3q)

Yield: $71 \%(27.1 \mathrm{mg})$, ee $=92 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-24.2\left(\mathrm{c}=1.0, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50-7.42(\mathrm{~m}, 4 \mathrm{H}), 7.39-7.35(\mathrm{~m}, 2 \mathrm{H}), 7.34-7.30(\mathrm{~m}, 1 \mathrm{H}), 7.08-$ $7.00(\mathrm{~m}, 3 \mathrm{H}), 6.79(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.66(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.73(\mathrm{~d}, J=12.8 \mathrm{~Hz}$, $1 \mathrm{H}), 3.47(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.98(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.8$, $146.7,138.6,135.0,131.9,129.8,128.8,127.8,127.6,127.1,126.8,125.9\left(q, J_{C F}=\right.$ $4.0 \mathrm{~Hz}), 124.2,122.5\left(\mathrm{q}, J_{C F}=3.7 \mathrm{~Hz}\right), 107.7,58.3,44.0,26.2$. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{19} \mathrm{~F}_{3} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}: 382.1413$, found: 382.1413.

The ee of compound $\mathbf{3 q}$ was determined by HPLC using an IADaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.87 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=11.28 \mathrm{~min}$ ).



(S)-3-benzyl-1-methyl-3-(p-tolyl)indolin-2-one (3r)

Yield: $70 \%(22.9 \mathrm{mg})$, ee $=93 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-99.7\left(\mathrm{c}=0.9, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.37(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.21-7.18(\mathrm{~m}, 2 \mathrm{H}), 7.14(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H})$, $7.08-6.98(\mathrm{~m}, 4 \mathrm{H}), 6.83(\mathrm{dd}, J=7.6,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.60(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.70(\mathrm{~d}, J$ $=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.42(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.93(\mathrm{~s}, 3 \mathrm{H}), 2.32(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.9,143.7,137.1,136.7,135.7,131.4,130.0,129.2,128.0,127.4$, 127.1, 126.4, 125.4, 122.1, 107.9, 58.0, 43.9, 26.0, 21.0. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{21} \mathrm{NNaO}[\mathrm{M}+\mathrm{Na}]^{+}: 350.1515$, found: 350.1520 .

The ee of compound $\mathbf{3 r}$ was determined by HPLC using an IADaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=10.46 \mathrm{~min}$, $\left.t_{\text {minor }}=16.30 \mathrm{~min}\right)$.


(S)-3-benzyl-1-methyl-3-(m-tolyl)indolin-2-one (3s)

Yield: $69 \%(22.6 \mathrm{mg})$, ee $=92 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-71.9\left(\mathrm{c}=0.8, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.30(\mathrm{~s}, 1 \mathrm{H}), 7.27-2.25(\mathrm{~m}, 1 \mathrm{H}), 7.24-7.18(\mathrm{~m}, 3 \mathrm{H}), 7.09(\mathrm{t}, J=6.4$ $\mathrm{Hz}, 2 \mathrm{H}), 7.05-6.98(\mathrm{~m}, 3 \mathrm{H}), 6.83(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.59(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.71$ $(\mathrm{d}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.44(\mathrm{~d}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.93(\mathrm{~s}, 3 \mathrm{H}), 2.34(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 177.8,143.7,139.7,138.2,135.7,131.5,130.0,128.4,128.2$, $128.2,127.8,127.3,126.4,125.3,124.2,122.1,107.9,58.2,43.8,26.0,21.6$ HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}: 328.1696$, found: 328.1707.

The ee of compound $3 \mathbf{s}$ was determined by HPLC using an IA $A_{\text {Daicel }}$ column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=8.72 \mathrm{~min}$, $\left.\mathrm{t}_{\text {minor }}=9.99 \mathrm{~min}\right)$.



(S)-3-benzyl-3-(4-methoxyphenyl)-1-methylindolin-2-one (3t)

Yield: $67 \%(23.0 \mathrm{mg})$, ee $=89 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-21.5\left(\mathrm{c}=1.0, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.42(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.23-7.18(\mathrm{~m}, 2 \mathrm{H}), 7.08-6.98(\mathrm{~m}, 4 \mathrm{H})$, $6.87(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.83(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.61(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.79(\mathrm{~s}$, $3 \mathrm{H}), 3.67(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.41(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.94(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 178.0,158.8,143.7,135.7,131.7,131.3,130.0,128.4,128.1,127.4$, 126.4, 125.4, 122.1, 113.9, 108.0, 57.5, 55.3, 44.1, 26.0. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 344.1645$, found: 344.1651.

The ee of compound $\mathbf{3 t}$ was determined by HPLC using an IADaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=80 / 20$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=6.95 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=11.62 \mathrm{~min}$ ).



(S)-3-benzyl-3-(4-fluorophenyl)-1-methylindolin-2-one (3u)

Yield: $70 \%(23.3 \mathrm{mg})$, ee $=90 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-104.2\left(\mathrm{c}=0.6, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50-7.47(\mathrm{~m}, 2 \mathrm{H}), 7.25-7.18(\mathrm{~m}, 2 \mathrm{H}), 7.10-6.99(\mathrm{~m}, 6 \mathrm{H}), 6.81(\mathrm{~d}$, $J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.62(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.65(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.41(\mathrm{~d}, J=12.8$ $\mathrm{Hz}, 1 \mathrm{H}), 2.95(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 177.6,162.1\left(\mathrm{~d}, J_{C F}=245.0 \mathrm{~Hz}\right)$, $143.7,135.4,130.8,129.9,129.0\left(\mathrm{~d}, J_{C F}=8.0 \mathrm{~Hz}\right), 128.3,127.4,126.6,125,5,122.2$, $115.3\left(\mathrm{~d}, J_{C F}=21.2 \mathrm{~Hz}\right), 108.1,57.6,44.3,26.1$. HRMS (ESI) calcd. for $\mathrm{C}_{22} \mathrm{H}_{19} \mathrm{FNO}$ $[\mathrm{M}+\mathrm{H}]^{+}: 332.1445$, found: 332.1458 .

The ee of compound $\mathbf{3 u}$ was determined by HPLC using an $\mathrm{IC}_{\text {Daicel }}$ column (n-hexane/i-PrOH $=80 / 20$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=6.21 \mathrm{~min}$, $\left.t_{\text {minor }}=8.81 \mathrm{~min}\right)$.


(S)-3-benzyl-3-(3-chlorophenyl)-1-methylindolin-2-one (3v)

Yield: $63 \%(21.8 \mathrm{mg})$, ee $=84 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-69.5\left(\mathrm{c}=0.8, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.47(\mathrm{~s}, 1 \mathrm{H}), 7.42-7.40(\mathrm{~m}, 1 \mathrm{H}), 7.28-7.27(\mathrm{~m}, 2 \mathrm{H}), 7.25-7.19(\mathrm{~m}$, 2H), 7.11-7.00 (m, 4H), 6.81 (d, $J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.62(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.66(\mathrm{~d}, J$ $=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.41(\mathrm{~d}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.95(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.1,143.6,141.7,135.2,134.4,130.5,129.9,129.8,128.4,127.6,127.5,127.4$, 126.6, 125.6, 125.4, 122.4, 108.2, 58.0, 44.0, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{22} \mathrm{H}_{19} \mathrm{ClNO}[\mathrm{M}+\mathrm{H}]^{+}: 348.1150$, found: 348.1161 .

The ee of compound $\mathbf{3 v}$ was determined by HPLC using an IA Daicel column ( n -hexane/i-PrOH $=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.64 \mathrm{~min}$, $t_{\text {minor }}=11.74 \mathrm{~min}$ ).



(S)-3-benzyl-1-methyl-3-(naphthalen-2-yl)indolin-2-one (3w)

Yield: $65 \%(23.6 \mathrm{mg})$, ee $=90 \%,[\alpha]{ }_{\mathrm{D}}{ }^{18}=-99.6\left(\mathrm{c}=0.7, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.91(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.83-7.79(\mathrm{~m}, 3 \mathrm{H}), 7.60(\mathrm{dd}, J=8.4,2.0 \mathrm{~Hz}$, $1 \mathrm{H}), 7.48-7.44(\mathrm{~m}, 2 \mathrm{H}), 7.26-7.22(\mathrm{~m}, 2 \mathrm{H}), 7.11-7.00(\mathrm{~m}, 4 \mathrm{H}), 6.86(\mathrm{dd}, J=8.0$, $1.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.64(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.82(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.57(\mathrm{~d}, J=12.4 \mathrm{~Hz}$, $1 \mathrm{H}), 2.97(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.8,143.8,137.1,135.6,133.2$, $132.6,131.3,130.0,128.3,128.2,128.2,127.4,126.5,126.1,126.0,125.5,125.4$, 122.3, 108.1, 99.9, 58.4, 43.7, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{26} \mathrm{H}_{22} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}$: 364.1696, found: 364.1693.

The ee of compound $\mathbf{3 w}$ was determined by HPLC using an IA $_{\text {Daicel }}$ column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=80 / 20$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=8.13 \mathrm{~min}$, $t_{\text {minor }}=9.50 \mathrm{~min}$ ).



## (S)-3-benzyl-1,3-dimethylindolin-2-one (3x)

Yield: $42 \%(10.5 \mathrm{mg})$, ee $=12 \%,[\alpha] \mathrm{D}^{33}=-11.3(\mathrm{c}=0.53, \mathrm{MeOH})$, or $[\alpha] \mathrm{D}^{33}=$ $-14.2\left(\mathrm{c}=0.53,{ }^{i} \mathrm{PrOH}\right),{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.18(\mathrm{td}, J=7.6,1.2 \mathrm{~Hz}, 1 \mathrm{H})$, $7.13(\mathrm{dd}, J=7.6,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.08-7.01(\mathrm{~m}, 4 \mathrm{H}), 6.86-6.83(\mathrm{~m}, 2 \mathrm{H}), 6.61(\mathrm{~d}, J=$ $7.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.12(\mathrm{~d}, J=12.8,1 \mathrm{H}), 3.01(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.99(\mathrm{~s}, 3 \mathrm{H}), 1.47(\mathrm{~s}$, $3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 180.0, 143.1, 136.1, 133.0, 129.8, 127.7, 127.5, 126.4, 123.3, 122.0, 107.7, 49.9, 44.5, 25.9, 22.7.

The ee of compound $\mathbf{3 x}$ was determined by HPLC using an IGDaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=98 / 2$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$, tmajor $=10.77 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=11.48 \mathrm{~min}$ ).


(S)-5-methoxy-1-methyl-3-(4-methylbenzyl)-3-phenylindolin-2-one (4a)

Yield: $70 \%(25.0 \mathrm{mg})$, ee $=96 \%,[\alpha]_{\mathrm{D}}{ }^{19}=-22.3\left(\mathrm{c}=1.1, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.48(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 6.83(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.79(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.76-6.73(\mathrm{~m}, 3 \mathrm{H}), 6.54(\mathrm{~d}, J$ $=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.64(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.41(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.94$ (s, 3H), 2.19 ( $\mathrm{s}, 3 \mathrm{H}$ ); ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.5,155.5,139.7,137.4,135.9$, 132.6, 132.5, 129.8, 128.5, 128.2, 127.3, 127.2, 112.8, 112.5, 108.3, 58.6, 55.8, 43.4, 26.1, 21.0. HRMS (ESI) calcd. for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 358.1802$, found: 358.1819 .

The ee of compound $\mathbf{4 a}$ was determined by HPLC using an IC Daicel column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=8.48 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=14.00 \mathrm{~min}$ ).



| \# | $\begin{gathered} \text { Meas. RT } \\ \text { [min] } \end{gathered}$ | Peak Type |  | Peak Height [mAU] | Peak Width [min] | Peak Area [mAU*s] | $\begin{gathered} \text { Peak Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 \| | 8. 403 |  |  | 52. 118 | O. 207 | 711.713 | 49. 979 |
| 21 | 13. 674 \| | BB |  | 29. 043 | O. 378 | 712.302 | 50. 021 |


(S)-3-(4-ethylbenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4b)

Yield $72 \%(26.7 \mathrm{mg})$, ee $=95 \%,[\alpha]_{\mathrm{D}}{ }^{21}=-22.4\left(\mathrm{c}=1.4, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.49(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 6.86(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.77-6.74(\mathrm{~m}, 4 \mathrm{H}), 6.53(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.77(\mathrm{~s}$, $3 \mathrm{H}), 3.62(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.44(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.93(\mathrm{~s}, 3 \mathrm{H}), 2.49(\mathrm{q}, J=7.6$ $\mathrm{Hz}, 2 \mathrm{H}), 1.12(\mathrm{t}, J=7.6 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.5,155.5,142.4$, 139.7, 137.4, 132.8, 132.6, 129.9, 128.5, 127.4, 127.3, 126.9, 112.7, 112.6, 108.3, 58.6, 55.8, 43.4, 28.3, 26.1, 15.6. HRMS (ESI) calcd. for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}$: 372.1958, found: 372.1971.

The ee of compound $\mathbf{4 b}$ was determined by HPLC using an ICDaicel column (n-hexane/i-PrOH $=60 / 40$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.08 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=11.37 \mathrm{~min}$ ).



(S)-3-(4-isopropylbenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4c)

Yield: $74 \%(28.5 \mathrm{mg}), 95 \% \mathrm{ee},[\alpha]_{\mathrm{D}}{ }^{21}=-25.6\left(\mathrm{c}=1.6, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.49(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 6.89(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.75(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 4 \mathrm{H}), 6.53(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.76$ (s, 3H), $3.59(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.46(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.91(\mathrm{~s}, 3 \mathrm{H}), 2.79-2.72$ $(\mathrm{m}, 1 \mathrm{H}), 1.13(\mathrm{dd}, J=6.8,1.6 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.5,155.5$, $147.1,139.6,137.4,132.9,132.6,129.9,128.5,127.4,127.3,125.4,112.7,112.6$, 108.2, 58.6, 55.8, 43.5, 33.5, 26.1, 24.0, 23.8. HRMS (ESI) calcd. for $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{NO}_{2}$ $[\mathrm{M}+\mathrm{H}]^{+}: 386.2115$, found: 386.2128 .

The ee of compound $\mathbf{4 c}$ was determined by HPLC using an ICDaicel column (n-hexane/i-PrOH $=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.95 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=13.73 \mathrm{~min}$ ).

|  | $\begin{array}{r} m A U \\ 300 \\ 250 \\ 200 \\ 20 \\ 150 \\ 100 \\ 10 \end{array}$ |  | $\stackrel{\sim}{\sim}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | 10 | 12 | 14 |  | min |
|  | Meas. RT [min] | Peak Type | Peak Height [mAU] | $\begin{gathered} \text { Peak Width } \\ {[\text { min }]} \end{gathered}$ | Peak Area $[\mathrm{mAU} * \mathrm{~s}]$ | Peak \% | Area |
| 1 \| | 7.949 \| | FM | 324. 456 | O. 2261 | 4407.672 | 97 | . 344 |
| $2 \mid$ | 13. 732 \| | MF | 4. 658 | O. 430 | 120. 261 |  | . 656 |



(S)-3-(4-(tert-butyl)benzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4d)

Yield: $70 \%(27.9 \mathrm{mg})$, ee $=93 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-26.1\left(\mathrm{c}=1.7, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.05(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.76-6.72(\mathrm{~m}, 4 \mathrm{H}), 6.53(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.75(\mathrm{~s}$, $3 \mathrm{H}), 3.57(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.48(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.91(\mathrm{~s}, 3 \mathrm{H}), 1.20(\mathrm{~s}, 9 \mathrm{H})$; ${ }^{13}{ }^{13}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.5,155.5,149.3,139.6,137.4,132.6,132.6,129.6$, $128.5,127.3,124.2,112.8,112.6,108.2,58.6,55.8,43.4,34.2,31.2,26.1$. HRMS (ESI) calcd. for $\mathrm{C}_{27} \mathrm{H}_{30} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 400.2271$, found: 400.2287.

The ee of compound $\mathbf{4 d}$ was determined by HPLC using an IC $_{\text {Daicel }}$ column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.51 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=12.72 \mathrm{~min}$ ).



(S)-3-([1,1'-biphenyl]-4-ylmethyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4e)

Yield: $79 \%(33.1 \mathrm{mg})$, ee $=97 \%,[\alpha] \mathrm{D}^{19}=+33.5\left(\mathrm{c}=1.7, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50(\mathrm{t}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.36(\mathrm{q}, J=7.6 \mathrm{~Hz}, 4 \mathrm{H}), 7.30-7.27(\mathrm{~m}, 4 \mathrm{H})$, 6.93 (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.83(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{dd}, J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.52$ $(\mathrm{d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.72(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.49(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H})$, $2.94(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 177.4, 155.6, 140.6, 139.6, 139.1, 137.4, $134.8,132.5,130.4,128.7,128.6,127.4,127.2,127.1,126.8,126.0,112.8,112.6$, 108.4, 58.6, 55.8, 43.5, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{29} \mathrm{H}_{26} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 420.1958$, found: 420.1954 .

The ee of compound $\mathbf{4 e}$ was determined by HPLC using an IC Daicel column (n-hexane/i-PrOH $=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.58 \mathrm{~min}$, $\left.\mathrm{t}_{\text {minor }}=17.28 \mathrm{~min}\right)$.


(S)-5-methoxy-3-(4-methoxybenzyl)-1-methyl-3-phenylindolin-2-one (4f)

Yield: $74 \%(27.6 \mathrm{mg})$, ee $=97 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-6.8\left(\mathrm{c}=1.1, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.48(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 6.81-6.73(\mathrm{~m}, 4 \mathrm{H}), 6.55(\mathrm{dd}, J=13.2,8.4 \mathrm{~Hz}, 3 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.69(\mathrm{~s}, 3 \mathrm{H})$, $3.63(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.39(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.94(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 177.5,158.2,155.6,139.7,137.4,132.7,131.0,128.5,127.7,127.3,127.2$, $112.8,112.7,112.5,108.3,58.7,55.8,55.0,43.0,26.1$. HRMS (ESI) calcd. for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{H}]^{+}: 374.1751$, found:374.1769.

The ee of compound $\mathbf{4 f}$ was determined by HPLC using an IC $_{\text {Daicel }}$ column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=10.28 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=17.87 \mathrm{~min}$ ).



(S)-3-(4-ethoxybenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4g)

Yield: $76 \%(29.4 \mathrm{mg})$, ee $=97 \%,[\alpha]{ }^{20}=-10.7\left(\mathrm{c}=0.9, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.48(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=8.4 \mathrm{~Hz}$, $1 \mathrm{H}), 6.81-6.74(\mathrm{~m}, 4 \mathrm{H}), 6.57-6.52(\mathrm{~m}, 3 \mathrm{H}), 3.90(\mathrm{q}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H})$, $3.63(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.38(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.94(\mathrm{~s}, 3 \mathrm{H}), 1.34(\mathrm{t}, J=6.8 \mathrm{~Hz}$, $3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.6,157.5,155.6,139.7,137.4,132.7,131.0$, $128.5,127.6,127.4,127.2,113.4,112.7,112.4,108.3,63.2,58.8,55.8,43.0,26.1$, 14.8. HRMS (ESI) calcd. for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{H}]^{+}: 388.1907$, found: 388.1924.

The ee of compound $\mathbf{4 g}$ was determined by HPLC using an IC $_{\text {Daicel }}$ column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.30 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=16.45 \mathrm{~min}$ ).



(S)-3-(4-(benzyloxy)benzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4h)

Yield: $71 \%(31.9 \mathrm{mg})$, ee $=98 \%,[\alpha]_{\mathrm{D}}{ }^{20}=-2.1\left(\mathrm{c}=2.1, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.48(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.36-7.25(\mathrm{~m}, 8 \mathrm{H}), 6.80-6.74(\mathrm{~m}, 4 \mathrm{H})$, $6.64(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.52(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.94(\mathrm{~s}, 2 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.63(\mathrm{~d}, J$ $=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.39(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.91(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.5,157.3,155.6,139.6,137.4,137.0,132.7,131.0,128.5,128.4,128.0,127.8$, 127.4, 127.2, 113.8, 112.7, 112.4, 108.3, 69.7, 58.7, 55.8, 43.0, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{30} \mathrm{H}_{28} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{H}]^{+}: 450.2064$, found: 450.2061.

The ee of compound $\mathbf{4 h}$ was determined by HPLC using an IADaicel column $\left(\mathrm{n}\right.$-hexane $/ \mathrm{i}-\mathrm{PrOH}=80 / 20$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {minor }}=8.78 \mathrm{~min}$, $\mathrm{t}_{\text {major }}=9.96 \mathrm{~min}$ ).

|  |  | $\underset{\infty}{\infty}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\begin{gathered} \text { Meas. RT } \\ \text { [min] } \end{gathered}$ |  |  | Peak Height [mAU] | $\begin{aligned} & \text { Peak Width } \\ & \text { [min] } \end{aligned}$ | Peak Area [mAU*s] | $\begin{gathered} \text { Peak Area } \\ \% \end{gathered}$ |
|  | 8. 782 <br> 9. 964 |  | $\begin{aligned} & \text { VB } \\ & \text { MF } \end{aligned}$ | $14.087 \mid$ 1127.314 | $\begin{aligned} & \text { o. } 200 \\ & 0.237 \end{aligned}$ | $\begin{array}{r} 178.114 \mid \\ 16011.175 \end{array}$ | $\begin{array}{r} 1.100 \\ 98.900 \end{array}$ |
|  | $m A U$ 100 80 60 60 | $8$ |  | $\stackrel{\text { Co }}{\infty}$ |  |  |  |
| \# | $\begin{aligned} & \text { Meas. RT } \\ & \text { [min] } \end{aligned}$ | Peak | Type | Peak Height [mAU] | $\begin{aligned} & \text { Peak Width } \\ & \text { [min] } \end{aligned}$ | Peak Area [mAU*s] | $\begin{gathered} \text { Peak Area } \\ \% \end{gathered}$ |
| 1\| | $\begin{array}{r} 8.845 \\ 10.065 \end{array}$ |  | $\begin{aligned} & \text { FM } \\ & \text { MF } \end{aligned}$ | $\begin{array}{r} 109.458 \\ 98.750 \end{array}$ | $\begin{aligned} & \text { o. } 260 \\ & \text { o. } 290 \end{aligned}$ | 1706.348 1720.251 | $\begin{aligned} & 49.797 \\ & 50.203 \end{aligned}$ |


(S)-3-(4-fluorobenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4i)

Yield: $82 \%(29.6 \mathrm{mg}), 96 \%$ ee, $[\alpha]_{\mathrm{D}}{ }^{18}=-32.7\left(\mathrm{c}=1.9, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.47(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=6.8 \mathrm{~Hz}$, $1 \mathrm{H}), 6.84-6.81(\mathrm{~m}, 3 \mathrm{H}), 6.77-6.69(\mathrm{~m}, 3 \mathrm{H}), 6.54(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H})$, $3.68(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.39(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.93(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 177.3,161.6\left(\mathrm{~d}, J_{C F}=243.4 \mathrm{~Hz}\right), 155.7,139.4,137.3,132.4,131.4\left(\mathrm{~d}, J_{C F}=\right.$ $7.8 \mathrm{~Hz}), 131.3\left(\mathrm{~d}, J_{C F}=3.2 \mathrm{~Hz}\right), 128.6,127.5,127.1,114.2\left(\mathrm{~d}, J_{C F}=20.9 \mathrm{~Hz}\right), 112.6$ $\left(\mathrm{d}, J_{C F}=29.2 \mathrm{~Hz}\right), 108.4,58.6,55.8,42.9,26.1$. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{21} \mathrm{FNO}_{2}$ $[\mathrm{M}+\mathrm{H}]^{+}: 362.1551$, found: 362.1550 .

The ee of compound $\mathbf{4 i}$ was determined by HPLC using an ICDaicel column (n-hexane/i-PrOH $=80 / 20$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=8.62 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=17.72 \mathrm{~min}$ ).



(S)-3-(4-chlorobenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4j)

Yield: $78 \%(29.4 \mathrm{mg})$, ee $=95 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-20.0\left(\mathrm{c}=1.6, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.46(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2, \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.00(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.82-6.79(\mathrm{~m}, 3 \mathrm{H}), 6.76(\mathrm{dd}, J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.55$ (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.68(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.39(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H})$, $2.94(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 177.2, 155.7, 139.4, 137.3, 134.2, 132.4, $132.3,131.3,128.6,127.6,127.5,127.1,112.8,112.5,108.5,58.5,55.8,43.0,26.2$. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{21} \mathrm{ClNO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 378.1255$, found: 378.1265.

The ee of compound $\mathbf{4 j}$ was determined by HPLC using an IC Daicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.15 \mathrm{~min}$, $\left.\mathrm{t}_{\text {minor }}=12.87 \mathrm{~min}\right)$.



| \# | $\begin{gathered} \text { Meas. RT } \\ \text { [min] } \end{gathered}$ | Peak Type | Peak Height [mAU] | $\begin{aligned} & \text { Peak Width } \\ & {[\text { min] }} \end{aligned}$ | Peak Area [mAU*s] | Peak Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 \| | 7. 137 | FM | 1177.625 \| | O. 186 | 13118.810\| | 50. 021 |
| $2 \mid$ | 12. 806 | FM | 590. 722 \| | O. 370 \| | 13107. 754 \| | 49. 979 |


methyl (S)-4-((5-methoxy-1-methyl-2-oxo-3-phenylindolin-3-yl)methyl)benzoate (4k)

Yield: $62 \%(24.9 \mathrm{mg})$, ee $=96 \%,[\alpha]_{\mathrm{D}}{ }^{27}=-12.5\left(\mathrm{c}=1.92, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.71(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.47(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{t}, J=7.2 \mathrm{~Hz}$, 2H), 7.30 (d, $J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.95$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.83$ (d, $J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.74$ (dd, $J=8.4,2.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.51(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.84(\mathrm{~s}, 3 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.78(\mathrm{~d}$, $J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.46(\mathrm{~d}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.92(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.1,167.0,155.7,141.2,139.4,137.2,132.1,130.0,128.7,128.6,128.3,127.5$, 127.1, 112.8, 112.5, 108.4, 58.4, 55.8, 51.9, 43.6, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{25} \mathrm{H}_{23} \mathrm{NNaO}_{4}[\mathrm{M}+\mathrm{Na}]^{+}: 424.1519$, found: 424.1534 .

The ee of compound $\mathbf{4 k}$ was determined by HPLC using an IA $A_{\text {Daicel }}$ column ( n -hexane/i-PrOH $=90 / 10$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {minor }}=12.41 \mathrm{~min}$, $\mathrm{t}_{\text {major }}=14.02 \mathrm{~min}$ ).



(S)-5-methoxy-1-methyl-3-phenyl-3-(4-(trifluoromethyl)benzyl)indolin-2-one (41)

Yield: $79 \%(32.5 \mathrm{mg})$, ee $=91 \%,[\alpha]_{\mathrm{D}}{ }^{21}=-25.3\left(\mathrm{c}=1.8, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.48(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.31-7.28(\mathrm{~m}, 3 \mathrm{H})$, $6.99(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.82(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.77(\mathrm{dd}, J=8.4,2.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.55$ $(\mathrm{d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.76(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.48(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H})$, 2.93 (s, 3H); ${ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 177.1,155.8,139.9,138.2\left(\mathrm{~d}, J_{C F}=\right.$ 206.0 Hz ), 132.1, 130.3, $128.8\left(\mathrm{~d}, J_{C F}=32.1 \mathrm{~Hz}\right), 128.7,127.6,127.1,124.1\left(\mathrm{~d}, J_{C F}=\right.$ $270.3 \mathrm{~Hz}), 124.3\left(\mathrm{q}, J_{C F}=3.8 \mathrm{~Hz}\right), 112.7\left(\mathrm{~d}, J_{C F}=11.9 \mathrm{~Hz}\right), 108.6,58.4,55.8,43.4$, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{24} \mathrm{H}_{21} \mathrm{~F}_{3} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 412.1519$, found: 412.1534 .

The ee of compound $\mathbf{4 1}$ was determined by HPLC using an ICDaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=5.83 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=10.02 \mathrm{~min}$ ).

|  |  |  |  |  | $\stackrel{\stackrel{\rightharpoonup}{\circ}}{-}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | 6 |  | 8 |  |  | 12 | min |
| \# | $\begin{gathered} \text { Meas. RT } \\ {[m i n]} \end{gathered}$ | Peak | Type |  | Peak Height [mAU] |  | $\begin{aligned} & \text { Peak Width } \\ & {[m i n]} \end{aligned}$ | Peak Area $[\mathrm{mAU} * \mathrm{ks}]$ | $\begin{array}{r} \text { Peak } \\ \% \end{array}$ | Area |
| 11 | 5.8291 |  | MF |  | 779.785 |  | O. 149 | 6994. 180 |  | . 376 |
| 21 | 10.017 |  | MF |  | 19.286 |  | O. 293 | 339. 084 |  | . 624 |




## (S)-5-methoxy-1-methyl-3-(4-nitrobenzyl)-3-phenylindolin-2-one (4m)

Yield: $76 \%(29.5 \mathrm{mg})$, ee $=93 \%,[\alpha]{ }_{\mathrm{D}}{ }^{20}=-13.7\left(\mathrm{c}=1.9, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.90(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.48-7.46(\mathrm{~m}, 2 \mathrm{H}), 7.36(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H})$, $7.32-7.31(\mathrm{~m}, 1 \mathrm{H}), 7.06(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.87(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.77(\mathrm{dd}, J=$ $8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.56(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.84(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H})$, $3.50(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.95(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 176.8,155.8$, 146.7 143.6, 139.0, 137.0, 131.7, 130.8, 128.7, 127.7, 127.0, 122.6, 112.8, 112.5, 108.7, 58.3, 55.8, 43.3, 26.2. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}_{4}[\mathrm{M}+\mathrm{H}]^{+}: 389.1496$, found: 389.1507.

The ee of compound $\mathbf{4 m}$ was determined by HPLC using an IADaicel column (n-hexane/i-PrOH $=80 / 20$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {minor }}=9.51 \mathrm{~min}$, $\mathrm{t}_{\text {major }}=13.66 \mathrm{~min}$ ).

|  | $m A \cup$ <br> 250 <br> 200 <br> 20 <br> 150 <br> $=$ <br> 100 <br> $=$ <br> 50 | $\frac{m}{i}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 8 | 10 | 12 | 14 | min |
| \# | $\begin{gathered} \text { Meas. RT } \\ \text { [min] } \end{gathered}$ | Peak Type | Peak Height [mAU] | $\begin{aligned} & \text { Peak Width } \\ & {[\text { min }]} \end{aligned}$ | Peak Area [mAU*s] | Peak Area \% |
| 1 \| | 9. 5131 | MM | 14. 516 | O. 230 | 200. 671 | 3. 518 |
| 21 | 13. 664 \| | MF | 278. 325 | O. 330 | 5503. 377 | 96. 482 |



(S)-5-methoxy-1-methyl-3-(2-methylbenzyl)-3-phenylindolin-2-one (4n)

Yield: $84 \%(30.0 \mathrm{mg})$, ee $=95 \%,[\alpha]_{\mathrm{D}}{ }^{21}=-62.9\left(\mathrm{c}=1.5, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.54(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.30-7.27(\mathrm{~m}, 1 \mathrm{H})$, 6.99-6.97 (m, 2H), $6.84(\mathrm{td}, J=8.0,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.78(\mathrm{dd}, J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.69$ $(\mathrm{d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.63(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.54(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.69(\mathrm{~s}, 3 \mathrm{H})$, 3.63 (d, $J=13.6 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.58 (d, $J=13.6 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.04 (s, 3H), 2.05 (s, 3 H ); ${ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 177.9,155.3,139.5,137.3,137.2,134.5,131.9,130.1$, $129.5,128.5,127.5,127.4,126.6,125.1,113.1,113.0,108.3,57.9,55.7,39.8,26.3$, 20.1. HRMS (ESI) calcd. for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 358.1802$, found: 358.1820 .

The ee of compound $\mathbf{4} \mathbf{n}$ was determined by HPLC using an IC Daicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=7.15 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=9.64 \mathrm{~min}$ ).



(S)-5-methoxy-1-methyl-3-(3-methylbenzyl)-3-phenylindolin-2-one (4o)

Yield: $60 \%(21.4 \mathrm{mg})$, ee $=99 \%,[\alpha]_{\mathrm{D}}{ }^{19}=-43.7\left(\mathrm{c}=1.2, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.49(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 6.93-6.85(\mathrm{~m}, 2 \mathrm{H}), 6.79(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{dd}, J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.67$ $-6.64(\mathrm{~m}, 2 \mathrm{H}), 6.52(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.64(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.41$ $(\mathrm{d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.93(\mathrm{~s}, 3 \mathrm{H}), 2.14(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.5$, 155.6, 139.6, 137.4, 136.9, 135.6, 132.6, 130.8, 128.5, 127.4, 127.3, 127.1, 127.0, $112.9,112.6,108.2,58.6,55.9,43.8,26.1,21.1$. HRMS (ESI) calcd. For $\mathrm{C}_{24} \mathrm{H}_{2} \mathrm{NO}_{2}$ $[\mathrm{M}+\mathrm{H}]^{+}: 358.1802$, found: 358.1815 .

The ee of compound 40 was determined by HPLC using an ICDaicel column (n-hexane/i-PrOH $=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=8.03 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=12.21 \mathrm{~min}$ ).


(S)-3-(2,6-dimethylbenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4p)

Yield: $68 \%(25.2 \mathrm{mg})$, ee $=90 \%,[\alpha] \mathrm{D}^{21}=-119.9\left(\mathrm{c}=1.3, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.67(\mathrm{dd}, J=8.4,1.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.32-7.27(\mathrm{~m}, 3 \mathrm{H}), 6.98(\mathrm{t}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 6.86(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.84-6.81(\mathrm{~m}, 1 \mathrm{H}), 6.74(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.90(\mathrm{~d}, J$ $=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{~d}, J=14.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.51(\mathrm{~s}, 3 \mathrm{H}), 3.45(\mathrm{~d}, J=14.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.17$ ( $\mathrm{s}, 3 \mathrm{H}$ ), $1.60(\mathrm{~s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 178.8,154.7,140.0,138.4,137.2$, $134.7,129.7,128.3,128.1,127.8,127.3,126.5,114.0,108.3,55.9,55.7,39.2,26.5$, 20.6. HRMS (ESI) calcd. for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 372.1958$, found: 372.1969 .

The ee of compound $\mathbf{4 p}$ was determined by HPLC using an IADaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=8.90 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=10.92 \mathrm{~min}$ )


(S)-3-(3,5-dimethylbenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4q)

Yield: $90 \%$ ( 33.4 mg ), ee $=93 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-47.1\left(\mathrm{c}=1.8, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.49(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=6.8 \mathrm{~Hz}$, $1 \mathrm{H}), 6.78$ (d, $J=2.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.74$ (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.68(\mathrm{~s}, 1 \mathrm{H}), 6.53$ (d, $J=8.4$ $\mathrm{Hz}, 1 \mathrm{H}), 6.46$ (s, 2H), 3.76 (s, 3H), 3.59 (d, $J=12.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.37 (d, $J=12.8 \mathrm{~Hz}$, $1 \mathrm{H}), 2.94(\mathrm{~s}, 3 \mathrm{H}), 2.09(\mathrm{~s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.6,155.5,139.7$, $137.5,136.7,135.5,132.6,128.5,127.9,127.8,127.3,113.1,112.7,108.1,58.5,56.0$, 43.8, 26.1, 21.0. HRMS (ESI) calcd. for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 372.1958$, found: 372.1971 .

The ee of compound $\mathbf{4 q}$ was determined by HPLC using an IC Daicel column ( n -hexane/i-PrOH $=80 / 20$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.75 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=13.67 \mathrm{~min}$ ).

|  |  | $\stackrel{8}{0}$ |  |  | $\begin{aligned} & \tilde{\omega} \\ & \stackrel{\rightharpoonup}{e} \end{aligned}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 6 |  | 8 | 10 | 12 | 14 |  | min |
| \# | $\begin{gathered} \text { Meas. RT } \\ {[m i n]} \end{gathered}$ | Peak | Type | Peak Height [mAU] | ```Peak Width [min]``` | Peak Area <br> [mAU*s] | Peak \% | Area |
| 1 \| | 9. 750 |  | MF | 927. 359 | O. 261 | 14549.935 | 96 | . 435 |
| 21 | 13.672 |  | MF | 23. 631 | O. 379 | 537.8131 |  | . 565 |



(S)-5-methoxy-1-methyl-3-phenyl-3-(2,4,6-trimethylbenzyl)indolin-2-one (4r)

Yield: $88 \%(33.9 \mathrm{mg})$, ee $=93 \%,[\alpha]_{\mathrm{D}}{ }^{21}=-113.0\left(\mathrm{c}=1.4, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H} \operatorname{NMR}(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.68(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.29-7.25(\mathrm{~m}, 3 \mathrm{H}), 6.82(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, 6.74 (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.69(\mathrm{~s}, 2 \mathrm{H}), 5.93(\mathrm{~s}, 1 \mathrm{H}), 3.82(\mathrm{~d}, J=14.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.51$ (s, $3 \mathrm{H}), 3.39(\mathrm{~d}, J=14.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.17(\mathrm{~s}, 3 \mathrm{H}), 2.19(\mathrm{~s}, 3 \mathrm{H}), 1.54(\mathrm{~s}, 6 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR (101 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 178.8,154.6,139.9,138.3,137.2,135.8,131.5,129.9,128.8,128.2$, 127.8, 127.2, 114.1, 114.0, 108.2, 56.0, 55.5, 38.9, 26.5, 20.7, 20.4. HRMS (ESI) calcd. for $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 386.2115$, found: 386.2128 .

The ee of compound $\mathbf{4 r}$ was determined by HPLC using an IA Daicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=98 / 2$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=10.46 \mathrm{~min}$, $t_{\text {minor }}=11.37 \mathrm{~min}$ ).


| \# | $\begin{aligned} & \text { Meas. RT } \\ & {[\mathrm{min}]} \end{aligned}$ | Peak Type | Peak Height [mAU] | Peak Width [min] | Peak Area [mAU*s] | $\begin{gathered} \text { Peak Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10. 476 | BV | 103. 417 | O. 220 \| | 1471.273 \| | 49. 913 |
| 21 | 11.370 | MF | 96. 060 | O. 256 \| | 1476. 398 \| | 50. 087 |



## (S)-5-methoxy-3-(2-methoxybenzyl)-1-methyl-3-phenylindolin-2-one (4s)

Yield: $88 \%(32.8 \mathrm{mg})$, ee $=94 \%,[\alpha] \mathrm{D}^{21}=-105.9\left(\mathrm{c}=1.8, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.48(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.32(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.27(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, 1H), $7.03-6.99(\mathrm{~m}, 2 \mathrm{H}), 6.83(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.70-6.66(\mathrm{~m}, 2 \mathrm{H}), 6.54(\mathrm{~d}, J=$ $8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.48(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.85(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.72(\mathrm{~s}, 3 \mathrm{H}), 3.57$ (d, $J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.54(\mathrm{~s}, 3 \mathrm{H}), 3.03(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 178.2$, $157.1,155.1,140.3,137.2,132.4,130.5,128.4,127.8,127.2,124.7,119.6,113.6$, 112.2, 109.7, 107.4, 58.4, 55.7, 54.6, 35.8, 26.2. HRMS (ESI) calcd. for $\mathrm{C}_{24} \mathrm{H}_{2} \mathrm{NO}_{3}$ $[\mathrm{M}+\mathrm{H}]^{+}: 374.1751$, found: 374.1765 .

The ee of compound $4 \mathbf{s}$ was determined by HPLC using an IC $C_{\text {Daicel }}$ column (n-hexane/i-PrOH $=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.09 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=13.82 \mathrm{~min}$ ).


(S)-5-methoxy-3-(3-methoxybenzyl)-1-methyl-3-phenylindolin-2-one (4t)

Yield: $78 \%(27.8 \mathrm{mg})$, ee $=96 \%,[\alpha]_{\mathrm{D}}{ }^{18}=-49.4\left(\mathrm{c}=1.6, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 6.95(\mathrm{t}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.79-6.74(\mathrm{~m}, 2 \mathrm{H}), 6.62(\mathrm{dd}, J=8.0,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.55$ $(\mathrm{d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.50(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.36(\mathrm{~s}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H}), 3.64(\mathrm{~d}, J=$ $12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.57(\mathrm{~s}, 3 \mathrm{H}), 3.44(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.95(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.4,158.7,155.6,139.6,137.4,137.2,132.5,128.6,128.4,127.4$, $127.2,122.6,114.5,113.1,112.9,112.6,108.3,58.5,55.8,54.9,43.9,26.1$. HRMS (ESI) calcd. for $\mathrm{C}_{24} \mathrm{H}_{23} \mathrm{NNaO}_{2}[\mathrm{M}+\mathrm{Na}]^{+}: 380.1621$, found: 380.1609.

The ee of compound $4 \mathbf{t}$ was determined by HPLC using an ICDaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.75 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=14.51 \mathrm{~min}$ ).




## (S)-3-(2-fluorobenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4u)

Yield: $88 \%(31.8 \mathrm{mg})$, ee $=92 \%,[\alpha] \mathrm{D}^{21}=-64.0\left(\mathrm{c}=1.9, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.48(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.06-7.01(\mathrm{~m}, 2 \mathrm{H}), 6.88-6.84(\mathrm{~m}, 2 \mathrm{H}), 6.77-6.72(\mathrm{~m}, 2 \mathrm{H}), 6.52(\mathrm{~d}, J=8.4 \mathrm{~Hz}$, 1 H ), 3.76 (s, 3H), $3.68\left(\mathrm{q}, ~ J=13.2 \mathrm{~Hz}, 2 \mathrm{H}\right.$ ), $3.03(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.6,160.7\left(\mathrm{~d}, J_{C F}=244.4 \mathrm{~Hz}\right), 155.6,139.7,137.0,131.8,131.0\left(\mathrm{~d}, J_{C F}=3.6 \mathrm{~Hz}\right)$, $128.6,128.4\left(\mathrm{~d}, J_{\text {CF }}=8.2 \mathrm{~Hz}\right), 127.5,127.1,123.4,123.3\left(\mathrm{~d}, J_{C F}=3.5 \mathrm{~Hz}\right), 114.8(\mathrm{~d}$, $\left.J_{C F}=23.1 \mathrm{~Hz}\right), 113.3,112.7,108.0,58.1,55.8,35.3,26.3$. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{21} \mathrm{FNO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 362.1551$, found: 362.1565 .

The ee of compound $\mathbf{4 u}$ was determined by HPLC using an IC Daicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=6.94 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=11.39 \mathrm{~min}$ ).


(S)-3-(2,4-difluorobenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4v)

Yield: $81 \%(30.7 \mathrm{mg})$, ee $=92 \%,[\alpha] \mathrm{D}^{20}=-62.9\left(\mathrm{c}=1.0, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.46(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=6.8 \mathrm{~Hz}$, $1 \mathrm{H}), 7.03(\mathrm{q}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.89(\mathrm{~s}, 1 \mathrm{H}), 6.75(\mathrm{dd}, J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.83-6.49$ (m, 3H), 3.77 ( $\mathrm{s}, 3 \mathrm{H}$ ), $3.64(\mathrm{~s}, 2 \mathrm{H}), 3.04(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.5$, $160.7\left(\mathrm{~d}, J_{C F}=258.8 \mathrm{~Hz}\right), 155.7,139.5,137.0,131.8\left(\mathrm{q}, J_{C F}=5.4 \mathrm{~Hz}\right), 131.6,128.6$, $127.5,127.0,119.2\left(\mathrm{~d}, J_{C F}=15.9 \mathrm{~Hz}\right), 113.3,112.7,110.5\left(\mathrm{dd}, J_{C F}=20.6,3.4 \mathrm{~Hz}\right)$, 108.2, 103.2 ( $\mathrm{t}, J_{C F}=25.9 \mathrm{~Hz}$ ), 58.1, 55.8, 34.9, 26.3. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{20} \mathrm{~F}_{2} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 380.1457$, found: 380.1463.

The ee of compound $\mathbf{4} \mathbf{v}$ was determined by HPLC using an IC Daicel column (n-hexane/i-PrOH $=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=6.24 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=10.67 \mathrm{~min}$ ).




## (S)-3-(3,5-difluorobenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4w)

Yield: $90 \%(34.1 \mathrm{mg})$, ee $=92 \%,[\alpha]_{\mathrm{D}}{ }^{21}=-45.7\left(\mathrm{c}=1.9, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.46(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.31-7.27(\mathrm{~m}, 1 \mathrm{H})$, $6.81-6.77(\mathrm{~m}, 2 \mathrm{H}), 6.61(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.54-6.50(\mathrm{~m}, 1 \mathrm{H}), 6.43(\mathrm{dd}, J=8.4$, $2.0 \mathrm{~Hz}, 2 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.68(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.39(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.00(\mathrm{~s}$, $3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 177.0,162.1\left(\mathrm{dd}, J_{C F}=246.1,12.7 \mathrm{~Hz}\right), 155.8$, $139.7\left(\mathrm{t}, J_{C F}=9.2 \mathrm{~Hz}\right), 139.1,137.2,131.8,128.7,127.7,127.0,112.8\left(\mathrm{~d}, J_{C F}=24.8\right.$ $\mathrm{Hz}), 112.8\left(\mathrm{~d}, J_{C F}=11.9 \mathrm{~Hz}\right), 112.8\left(\mathrm{~d}, J_{C F}=1.0 \mathrm{~Hz}\right), 108.6,102.1\left(\mathrm{t}, J_{C F}=25.1 \mathrm{~Hz}\right)$, 58.1, 55.9, 43.2, 26.2. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{19} \mathrm{~F}_{2} \mathrm{NNaO}_{2}[\mathrm{M}+\mathrm{Na}]^{+}: 402.1276$, found: 402.1289.

The ee of compound $\mathbf{4 w}$ was determined by HPLC using an ICDaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=5.97 \mathrm{~min}$, $\left.\mathrm{t}_{\text {minor }}=7.98 \mathrm{~min}\right)$.


(S)-3-(2-chlorobenzyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4x)

Yield: $91 \%(34.3 \mathrm{mg})$, ee $=92 \%[\alpha]_{\mathrm{D}}{ }^{21}=-118.6\left(\mathrm{c}=2.1, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.50-7.48(\mathrm{~m}, 2 \mathrm{H}), 7.34(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.30-7.28(\mathrm{~m}, 1 \mathrm{H})$, $7.14-7.12$ (m, 1H), 7.06 (dd, $J=6.4,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.99-6.96$ (m, 2H), 6.87 (d, $J=$ $2.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.73(\mathrm{dd}, J=8.4,2.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.56(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.91(\mathrm{~d}, J=13.2$ $\mathrm{Hz}, 1 \mathrm{H}), 3.80(\mathrm{~d}, J=13.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.73(\mathrm{~s}, 3 \mathrm{H}), 3.09(\mathrm{~s}, 3 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 177.8,155.3,139.7,136.9,134.7,134.3,131.2,130.4,129.3,128.6,127.9$, $127.5,127.2,126.1,113.5,113.1,108.1,58.1,55.8,39.1,26.4$. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{21} \mathrm{ClNO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 378.1255$, found: 378.1270.

The ee of compound $\mathbf{4 x}$ was determined by HPLC using an IC Daicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=6.69 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=9.98 \mathrm{~min}$ ).


(S)-5-methoxy-1-methyl-3-(naphthalen-1-ylmethyl)-3-phenylindolin-2-one (4y)

Yield: $84 \%(33.0 \mathrm{mg})$, ee $=94 \%,[\alpha]_{\mathrm{D}}{ }^{21}=-72.4\left(\mathrm{c}=1.8, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.94-7.91(\mathrm{~m}, 1 \mathrm{H}), 7.69-7.67(\mathrm{~m}, 1 \mathrm{H}), 7.58-7.56(\mathrm{~m}, 3 \mathrm{H}), 7.38-$ $7.30(\mathrm{~m}, 5 \mathrm{H}), 7.15(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.06(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.58-6.56(\mathrm{~m}, 2 \mathrm{H})$, 6.42 (d, $J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.17(\mathrm{~d}, J=14.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.03(\mathrm{~d}, J=14.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.47$ (s, 3 H ), 2.92 ( $\mathrm{s}, 3 \mathrm{H}$ ); ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.9,155.1,139.8,137.1,133.4$, 132.4, 132.4, 131.6, 128.5, 128.2, 127.7, 127.4, 127.4, 127.3, 125.1, 125.1, 124.6, 124.4, 113.3, 113.3, 108.1, 58.3, 55.6, 39.0, 26.2. HRMS (ESI) calcd. for $\mathrm{C}_{27} \mathrm{H}_{2} \mathrm{NO}_{2}$ $[\mathrm{M}+\mathrm{H}]^{+}: 394.1802$, found: 394.1819.

The ee of compound $\mathbf{4 y}$ was determined by HPLC using an ICDaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.23 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=12.45 \mathrm{~min}$ ).

| mAU700600500400300200 |  | $9.232$ <br> 1 |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 10 | 12 | 14 |  | min |
|  | $\begin{gathered} \text { Meas. RT } \\ {[\mathrm{min}]} \end{gathered}$ |  |  |  | Peak | Type |  | Peak Height [mAU] | $\begin{aligned} & \text { Peak Width } \\ & {[\text { min] }} \end{aligned}$ | Peak Area [mAU*s] | Peak $\%$ | Area |
| 1 \| | 9. 2321 |  | MF | I | 729.340 \| | O. 2671 | 11670.873 |  | 6. 884 |
| 2 \| | 12.454\| |  |  |  | 16. 614 | O. 377 \| | 375.385 |  |  |




(S)-5-methoxy-1-methyl-3-(naphthalen-2-ylmethyl)-3-phenylindolin-2-one ( $\mathbf{4 z}$ )

Yield: $60 \%(23.6 \mathrm{mg})$, ee $=94 \%,[\alpha]_{\mathrm{D}}{ }^{21}=-25.9\left(\mathrm{c}=1.7, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.68(\mathrm{dd}, J=6.0,3.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.61(\mathrm{dd}, J=6.0,3.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.54-$ 7.49 (m, 3H), $7.38-7.34$ (m, 5H), $7.32-7.30(\mathrm{~m}, 1 \mathrm{H}), 6.98$ (dd, $J=8.8,2.0 \mathrm{~Hz}, 1 \mathrm{H})$, $6.85(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.69(\mathrm{dd}, J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.43(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.86$ $(\mathrm{d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.74(\mathrm{~s}, 3 \mathrm{H}), 3.60(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.87(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 177.5,155.6,139.7,137.3,133.3,132.9,132.4,132.1,128.8$, $128.6,128.3,127.6,127.5,127.3,127.2,126.8,125.6,125.4,112.9,112.6,108.4$, 58.6, 55.9, 43.9, 26.1. HRMS (ESI) calcd. for $\mathrm{C}_{27} \mathrm{H}_{24} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 394.1802$, found: 394.1811 .

The ee of compound $\mathbf{4 z}$ was determined by HPLC using an ICDaicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=70 / 30$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.35 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=13.12 \mathrm{~min}$ ).


| \# | $\begin{gathered} \text { Meas. RT } \\ \text { [min] } \end{gathered}$ | Peak | Type | Peak Height [mAU] | $\begin{gathered} \text { Peak Width } \\ {[\text { min }]} \end{gathered}$ | Peak Area [mAU*s] | Peak Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 \| | 9. 347 \| |  | FM | 395. 0121 | O. 2721 | 6452. 6051 | 97. 136 |
| 21 | 13. 115 |  | MM | 7. 486 | O. 424 \| | 190. $240 \mid$ | 2. 864 |



(S)-3-(cyclohex-1-en-1-ylmethyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (5a)

Yield: $85 \%(29.5 \mathrm{mg})$, ee $=94 \%,[\alpha] \mathrm{D}^{27}=-18.67\left(\mathrm{c}=1.9, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.41-7.39(\mathrm{~m}, 2 \mathrm{H}), 7.31-7.27(\mathrm{~m}, 2 \mathrm{H}), 7.26-7.21(\mathrm{~m}, 1 \mathrm{H}), 6.86-$ $6.83(\mathrm{~m}, 2 \mathrm{H}), 6.76(\mathrm{dd}, J=7.2,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.29(\mathrm{~s}, 1 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.16(\mathrm{~s}, 3 \mathrm{H})$, $3.10(\mathrm{~d}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.82(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.80(\mathrm{~s}, 2 \mathrm{H}), 1.55(\mathrm{~d}, J=16.4 \mathrm{~Hz}$, $1 \mathrm{H}), 1.39-1.35(\mathrm{~m}, 1 \mathrm{H}), 1.34-1.28(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 178.2$, $155.6,140.4,137.6,133.2,132.8,128.4,127.2,127.0,126.3,113.2,112.5,108.2$, 57.4, 55.9, 46.1, 29.7, 26.4, 25.4, 23.0, 22.0. HRMS (ESI) calcd. for $\mathrm{C}_{23} \mathrm{H}_{25} \mathrm{NNaO}_{2}$ $[\mathrm{M}+\mathrm{Na}]^{+}: 370.1778$, found: 370.1789 .

The ee of compound $\mathbf{5 a}$ was determined by HPLC using an IA Daicel column ( n -hexane $/ \mathrm{i}-\mathrm{PrOH}=90 / 10$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=8.23 \mathrm{~min}$, $\mathrm{t}_{\text {minor }}=13.85 \mathrm{~min}$ ) .




(S)-6-chloro-3-(3-chlorobenzyl)-3-(3-methoxyphenyl)-1-methylindolin-2-one (6)

Yield: $90 \%(37.1 \mathrm{mg})$, ee $=36 \%,[\alpha]_{\mathrm{D}}^{32}=-23.2\left(\mathrm{c}=2.6, \mathrm{CHCl}_{3}\right),{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.26(\mathrm{t}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.09(\mathrm{t}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.05-7.01(\mathrm{~m}, 2 \mathrm{H})$, $6.97(\mathrm{t}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.85-6.82(\mathrm{~m}, 2 \mathrm{H}), 6.72(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.65(\mathrm{~d}, J=1.6$ $\mathrm{Hz}, 1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.65(\mathrm{~d}, J=12.8,1 \mathrm{H}), 3.37(\mathrm{~d}, J=12.8,1 \mathrm{H}), 2.96(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 177.3,159.7,144.8,140.3,137.3,134.1,133.3,129.8$, $129.7,129.0,128.8,128.1,126.9,126.2,122.1,119.4,113.6,112.5,108.9,57.6,55.2$, 43.2, 26.2.

The ee of compound 6 was determined by HPLC using an ICDaicel column (n-hexane $/ \mathrm{i}-\mathrm{PrOH}=80 / 20$, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}, \mathrm{t}_{\text {major }}=9.65 \mathrm{~min}$, $\left.t_{\text {minor }}=11.49 \mathrm{~min}\right)$.



## 7. X-ray structure of $\mathbf{3 o}$ and parameters.



| Bond precision | $\mathrm{C}-\mathrm{C}=0.0161 \mathrm{~A}$ |
| :---: | :---: |
|  | Wavelength $=0.71073$ |
| Cell | $\mathrm{a}=9.050$ (4) $\quad \alpha=96.353$ (8) |
|  | $\mathrm{b}=9.105$ (4) $\quad \beta=93.200$ (7) |
|  | $\mathrm{c}=11.832$ (5) $\quad \gamma=111.089(7)$ |
| Temperature | 296 K |
| Volume | 899.3 (6) |
| Space group | P 1 |
| Sum formula | C 22 H 18 ClNO |
| Mr | 347.82 |
| Dx, $\mathrm{g} \mathrm{cm}^{-3}$ | 1.284 |
| Z | 1 |
| $\mathrm{Mu}(\mathrm{mm}-1)$ | 0.221 |
| F000 | 364.0 |
| h,k, $\operatorname{lmax}$ | 11, 11, 14 |
| Nref | 3950 |
| Tmin,Tmax | 0.528, 0.745 |
| Correction method= \# Reported T Limits | Tmin $=0.528 \quad$ Tmax $=0.745$ |
| AbsCorr = MULTT-SCAN |  |
| Data completeness | 1.12/0.56 |
| Theta(max) | 25.981 |
| R (reflections) | 0.0690 (2104) |
| wR2(reflections) | 0.1990 (3950) |
| S | 1.029 |
| Npar | 454 |

8. Copies of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound 3a




${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound 3a


## 

$\stackrel{\text { No }}{\stackrel{\circ}{\infty}}$





| 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

## ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ) of compound $\mathbf{3 b}$


${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 b}$


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${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 c}$

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${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 c}$


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${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 d}$






${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 d}$





${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ of compound $\mathbf{3 e}$

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${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 e}$
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${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 f}$


$\xrightarrow[\sim]{\infty}$


${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 f}$
$\underset{\text { O }}{\infty}$


## ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ of compound $\mathbf{3 g}$





${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 g}$



${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ of compound $\mathbf{3 h}$

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${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 h}$


${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 i}$



${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 i}$

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## ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 j}$

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${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 j}$
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${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ of compound $\mathbf{3 k}$




${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 k}$

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${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound 31





${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 m}$




${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of compound $\mathbf{3 m}$




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\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 n}\)}





\({ }^{13} \mathrm{C}\) NMR（ \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ）of compound \(\mathbf{3 n}\)
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|}
\hline \[
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& \stackrel{\infty}{\infty} \\
& \stackrel{\circ}{1}
\end{aligned}
\] &  &  &  &  &  &  &  & \[
\begin{aligned}
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& \substack{\infty \\
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\end{aligned}
\] & \[
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\end{tabular}




\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 o}\)}





\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 o}\)

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\section*{\({ }^{1} \mathrm{H}^{2}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 p}\)}

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\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 p}\)



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\section*{\({ }^{1} \mathrm{H}\) NMR \(\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)\) of compound \(\mathbf{3 q}\)}


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\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 q}\)



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\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 r}\)}


\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 r}\)
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\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 , & 1 & 1 & 1 & 1 & 1 & 1 & & 1 & 1 & 1 \\
\hline 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & \[
\begin{aligned}
& 100 \\
& \text { f1 (ppm) }
\end{aligned}
\] & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0 \\
\hline
\end{tabular}
\({ }^{1} \mathrm{H}\) NMR \(\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)\) of compound \(\mathbf{3 s}\)

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\hline N¢\% & ल \\
\hline लがm & \(\cdots\) \\
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\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound 3 s


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\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 t}\)



\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 t}\)



\(\stackrel{\dddot{\%}}{\stackrel{(1)}{\circ}}\)




\section*{\({ }^{1} \mathrm{H}\) NMR \(\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.\) ) of compound \(\mathbf{3 u}\)}




\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 u}\)


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\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 v}\)}

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\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 v}\)

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\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 w}\)}




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\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 w}\)
\(\stackrel{\stackrel{5}{8}}{\underset{\sim}{~}}\)



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\({ }^{1} \mathrm{H}\) NMR（ \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ）of compound \(\mathbf{3 x}\)

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\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{3 x}\)



\(\stackrel{\text { ®ion }}{\stackrel{o}{\circ}}\)



\({ }^{1} \mathrm{H}\) NMR \(\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.\) ) of compound \(\mathbf{4 a}\)



\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 a}\)






\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 b}\)}
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\begin{tabular}{|c|c|c|}
\hline  &  & \% \\
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\end{tabular}

\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 b}\)

\(\begin{array}{ll}\square & \overline{8} \\ \infty & 0 \\ \infty & 10 \\ 0 & 10\end{array}\)
\(\underset{\stackrel{\rightharpoonup}{\top}}{\stackrel{\rightharpoonup}{\top}}\)




\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 c}\)



\(\underset{\sim}{\mathcal{F}} \stackrel{\infty}{\sim} \stackrel{i}{c} \stackrel{-}{c}\)


\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 c}\)




\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 d}\)

\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 d}\)





\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 e}\)

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~MNNNNNNNON
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\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4} \mathbf{e}\)

\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 f}\)





\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 f}\)


\(\underset{\substack{\text { F } \\ \underset{\sim}{*} \\ \hline}}{ }\) \(\underset{\substack{\text { in }}}{\stackrel{\text { In }}{1}}\)




\section*{\({ }^{1} \mathrm{H}\) NMR \(\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.\) ) of compound \(\mathbf{4 g}\)}




\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 g}\)



등
\(\stackrel{\text { j}}{j}\)
\(-14.771\)



\({ }^{1} \mathrm{H}\) NMR \(\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)\) of compound \(\mathbf{4 h}\)





\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 h}\)

\begin{tabular}{|c|c|c|c|c|}
\hline ल-mo & N & হু.0.0 & \(\stackrel{\square}{8}\) & , \\
\hline 송 & \(\stackrel{8}{6}\) & ¢ & ¢ & Y \\
\hline
\end{tabular}



\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 i}\)




\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 i}\)

\begin{tabular}{|c|c|c|}
\hline \(\stackrel{\infty}{\sim} 0_{0}^{\text {O}}\) & 등 & ¢ \\
\hline 今心8 & \(\bigcirc\) & \(\underset{\text { \% }}{ }\) \\
\hline
\end{tabular}




\section*{\({ }^{1} \mathrm{H}\) NMR \(\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)\) of compound \(\mathbf{4 j}\)}

Nore



\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound of \(\mathbf{4 j}\)

No


\(\stackrel{\text { R }}{\stackrel{\circ}{\circ}}\)



\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 k}\)




\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 k}\)



\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound 41


\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 I}\)
\(\stackrel{\circ}{\circ}\)



No

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\({ }^{1} \mathrm{H}\) NMR \(\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)\) of compound \(\mathbf{4 m}\)




S133
\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 m}\)


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\(\stackrel{\circ}{0}\) \\
\(\stackrel{y}{\%}\) \\
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\end{tabular}
8
\(\stackrel{y}{3}\)
\(\stackrel{1}{4}\)




\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 n}\)}



\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 n}\)

\(\stackrel{\leftrightarrow}{\circ}\)


\({ }^{1} \mathrm{H}\) NMR（ \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ）of compound \(\mathbf{4 o}\)

\section*{ \\ }
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\hline  & \(\stackrel{\square}{3}\) \\
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\hline
\end{tabular}

\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound 40

\begin{tabular}{|c|c|c|c|}
\hline  &  & \[
\begin{aligned}
& \stackrel{\Gamma}{\infty} \\
& \underset{y}{j}
\end{aligned}
\] &  \\
\hline
\end{tabular}




\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 p}\)}



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мल ハmm
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\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4} \mathbf{p}\)





\({ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)\) of compound \(\mathbf{4 q}\)

\section*{ \\ }


\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4} \mathbf{q}\)


\(\stackrel{ん}{\infty}\)




\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 r}\)




\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4} \mathbf{r}\)


 \(\widetilde{\sim}\)
\(\underset{\sim}{\infty}\)
\(\underset{\sim}{\infty}\)




\({ }^{1} \mathrm{H}\) NMR (400 MHz, \(\mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 s}\)

NrN~N ©
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\hline ぶ & ल \\
\hline \(\xrightarrow{\text { - }}\) & \\
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\end{tabular}

\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 s}\)


\(\stackrel{\infty}{\stackrel{\infty}{c} \overbrace{i}^{\circ}}\)




\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 t}\)



\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 t}\)

\(\stackrel{\bar{\circ}}{\stackrel{\circ}{\mp}}\)
\(\underset{\substack{0 \\ \hline \multirow{2}{*}{\hline}\\ \hline}}{ }\)




\section*{\({ }^{1} \mathrm{H}\) NMR \(\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.\) ）of compound \(\mathbf{4 u}\)}

送运
ल๓लゅ 픙


\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 u}\)


M 80
ल 80
\(\sim N\)





\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 v}\)

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N~
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\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 v}\)


M
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\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound 4 w






\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound 4 x}



\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 x}\)


읃




\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 y}\)



\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 y}\)


\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 z}\)}




\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{4 z}\)








\section*{\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound 5a}
\begin{tabular}{|c|c|c|c|}
\hline ~ & ® & 8 &  \\
\hline  & 1 & 1 &  \\
\hline
\end{tabular}


\({ }^{13} \mathrm{C}\) NMR ( \(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{5 a}\)



\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & & , & 1 & 1 & 1 & & 1 & & 1 & 1 & & \\
\hline 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0 \\
\hline
\end{tabular}
\({ }^{1} \mathrm{H}\) NMR ( \(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\) ) of compound \(\mathbf{6}\)



\(\underset{\sim}{\text { Nom Mom }}\)


\({ }^{13} \mathrm{C}\) NMR (101 MHz, \(\mathrm{CDCl}_{3}\) ) of compound \(\mathbf{6}\)

\begin{tabular}{|c|c|c|}
\hline  & 융ㄲ & \(\stackrel{7}{\sim}\) \\
\hline 今心io & - & \(\stackrel{\text { ¢ }}{\text { ¢ }}\) \\
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\end{tabular}


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