## SUPPORTING INFORMATION

# Chiral N-Heterocyclic-Carbene-Catalyzed Cascade Asymmetric Desymmetrization of Cyclopentenediones with Enals: Access to Optically Active 1,3-Indandione <br> <br> Derivatives 

 <br> <br> Derivatives}
Jia-Ming Hu ${ }^{\text {a }}$, Jun-Qi Zhang ${ }^{\text {a }}$, Bing-Bing Sun ${ }^{\text {a }}$, Jun-Bo Chen ${ }^{\text {a }}$, Jie-Qiang Yu ${ }^{\text {a }}$, Xiao-
Peng Yang ${ }^{\text {a }}$, Hao-Peng Lv ${ }^{\text {a }}$, Zheng Wang ${ }^{\text {b* }}$ and Xing-Wang Wang*a
${ }^{a}$ Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry,Chemical Engineering and Materials Science, Soochow University, Suzhou 215123,China
${ }^{b}$ State Key Laboratory of Organometallic Chemistry, Center for Excellence inMolecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy ofSciences, Shanghai 200032, China
E-mail: wangxw@suda.edu.cn; wzsioc@mail.sioc.ac.cn
Contents
I: General methods .....  1
II: General and Typical experimental procedures .....  2
III: Experimental screening details .....  5
IV: Crystal data and ORTEP diagram for compound 3ad .....  8
V: Characterization of products .....  9
VI: NMR spectra of new compounds. ..... 25
VII: HPLC profile spectrum of compounds ..... 64

## I: General methods

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen in oven-dried Schlenk tube with magnetic stirring, all reagents obtained from commercial suppliers were used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated glass plates $(0.2 \pm 0.03 \mathrm{~mm}$ thickness, GF-254, particle size $0.01-0.04 \mathrm{~mm}$ ) from Yantai Chemical Industry Research Institute. TLC were visualized by UV fluorescence ( 254 nm ). Flash column chromatography was performed with silica gel (particle size $0.04-0.05 \mathrm{~mm}$ ). ${ }^{1} \mathrm{H}$ NMR, ${ }^{13} \mathrm{C}$ NMR and ${ }^{19} \mathrm{~F}$ NMR spectroscopic data were recorded using Bruker AMX-400 instrument and calibrated by using the residual solvent peaks as an internal reference $\left(\mathrm{CDCl}_{3}\left[{ }^{1} H: 7.26,{ }^{13} \mathrm{C}: 77.23\right]\right.$. Coupling constants $(J)$ are given in Hz. High-resolution mass spectra (HRMS) for all the compounds were determined on a Micromass GCTTOF mass spectrometer with ESI or CI resource. High performance liquid chromatography (HPLC) was performed on Agilent 1200 Series chromatographs using a Daicel Chiralpak AD-H, IG-H, IA-H, AS-H ( $0.46 \mathrm{~cm} \times 25 \mathrm{~cm}$ ). X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractomrter. Optical rotations are reported as follows: $[\alpha]_{\mathrm{D}}^{20}$ ( $c$ in g per 100 mL , solvent).

## II: General and Typical experimental procedures

General procedure for the catalytic synthesis of products 3:


To a 25 mL pre-dried round-bottom Schlenk tube with a magnetic stir bar, were added $4 \AA$ MS ( 160 mg ), oxidant 4 ( $164 \mathrm{mg}, 2.0$ equiv), 2,2-disubstituted cyclopentenediones 2 ( $0.2 \mathrm{mmol}, 1.0$ equiv), triazolium salt $\mathbf{C 8}(8.4 \mathrm{mg}, 0.02 \mathrm{mmol}$, 0.1 equiv), DMAP ( $5.2 \mathrm{mg}, 0.04 \mathrm{mmol}, 0.2$ equiv) and $\beta, \beta$-disubstituted enals 1 ( 0.3 mmol, 1.5 equiv), followed by an addition of anhydrous toluene ( 2 mL ). Then the Schlenk tube was closed with septum and the reaction mixture was stirred at room temperature for two days. After completion of the reaction monitored by TLC, the reaction mixture went through fast flash column chromatography to yield the crude products. Next, to the solution of crude products (calculated as 1.0 equiv) in anhydrous acetone ( 2 mL ), was included $\mathrm{K}_{2} \mathrm{CO}_{3}$ ( 2.0 equiv) and $\mathrm{CH}_{3} \mathrm{I}$ (2.0 equiv), and the reaction mixture was stirred at room temperature about 2 hours. After the completion of the reaction monitored by TLC, solvent was removed under vacuum. The crude products were purified by flash column chromatography $(\mathrm{PE} / \mathrm{EA}=6 / 1)$ to provide 3 .

Note: The racemic samples described in this work were synthesized according above procedure, which were catalyzed by mixed C8 and ent-C8 as ligands in a 1:1 ratio.

## Typical procedure for the scale up synthesis of products 3aa:



To a 100 mL pre-dried round-bottom Schlenk tube with a magnetic stir bar, were added $4 \AA$ MS ( 2.0 g ), oxidant $4(4.0 \mathrm{~g}, 2.0$ equiv), 2,2-disubstituted
cyclopentenediones 2a( $1.0 \mathrm{~g}, 5.0 \mathrm{mmol}, 1.0$ equiv), triazolium salt $\mathbf{C 8}(0.21 \mathrm{~g}, 0.5$ mmol, 0.1 equiv), DMAP ( $0.13 \mathrm{~g}, 1.0 \mathrm{mmol}, 0.2$ equiv) and $\beta, \beta$-disubstituted enals 1 a $(1.10 \mathrm{~g}, 7.5 \mathrm{mmol}, 1.5$ equiv), followed by an addition of 50 mL anhydrous toluene. Then the Schlenk tube was closed with septum and the reaction mixture was stirred at room temperature for two days. After completion of the reaction monitored by TLC, the reaction mixture went through fast flash column chromatography to yield the crude products. Next, to the solution of crude products ( 1.06 g ) in anhydrous acetone ( 30 mL ), was added $\mathrm{K}_{2} \mathrm{CO}_{3}\left(0.84 \mathrm{~g}, 2.0\right.$ equiv) and $\mathrm{CH}_{3} \mathrm{I}(0.86 \mathrm{~g}, 0.38 \mathrm{~mL}, 2.0$ equiv) and the reaction mixture was stirred at room temperature. When the reaction was complete monitored by TLC, the solvent was removed under vacuum. The mixtures were purified by flash column chromatography ( $\mathrm{PE} / \mathrm{EA}=6 / 1$ ) to furnished the desired products $\mathbf{3 a}$ in overall $58 \%$ yield ( 1.03 g ) with $87 \%$ ee.

## Transformation of 3aa to 4



To a dry 25 mL Schlenk tube, equipped with a magnetic stir bar, was added 3aa (36 $\mathrm{mg}, 0.1 \mathrm{mmol}, 1.0$ equiv) and $\mathrm{CeCl}_{3} \cdot 7 \mathrm{H}_{2} \mathrm{O}(75 \mathrm{mg}, 0.2 \mathrm{mmol}, 2.0$ equiv), followed by an addition of 1 mL absolute methanol under Argon and the reaction mixture was cooled to $0{ }^{\circ} \mathrm{C}$. Then $\mathrm{NaBH}_{4}$ was added ( $8 \mathrm{mg}, 0.2 \mathrm{mmol}, 2.0$ equiv) at once and the reaction mixture stirred at $0{ }^{\circ} \mathrm{C}$. After 30 min , the reaction mixture solution was quenched with 2 mL saturated $\mathrm{NH}_{4} \mathrm{Cl}$ solution and diluted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. Organic phase was separated from aqueous phase, the aqueous layer was extracted twice with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. Combined organic phase was dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, concentrated under vacuum and purified by flash column chromatography $(\mathrm{PE} / \mathrm{EA}=5 / 1)$ to give a white solid product 4.

## Transformation of 3at to 5



In a 25 mL of Schlenk tube equipped with a magnetic stirring bar, 9 -BBN dimer ( $72.6 \mathrm{mg}, 0.3 \mathrm{mmol}$ ) was dissolved in anhydrous THF ( 2 mL ), and the resulting solution was cooled to $0^{\circ} \mathrm{C}$. After the mixture was stirred for 5 min , a solution of 3at $(61.3 \mathrm{mg}$, $0.20 \mathrm{mmol})$ in THF ( 1 mL ) was added to the reaction flask at $0^{\circ} \mathrm{C}$ and stirred for about 12 h until the substrate was consumed. Then $\mathrm{NaBO}_{3}(400 \mathrm{mg})$ in water ( 6 mL ) was added to the reaction flask, and the resulting mixture was stirred at room temperature for 6 h . The organic layer was separated, and the aqueous layer was extracted with EtOAc $(3 \times 10 \mathrm{~mL})$. The combined organic layers were washed with the saturated aqueous NaCl solution, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and finally evaporated under reduced pressure. Purification of the crude product was performed with flash chromatography $(\mathrm{PE} / \mathrm{EA}=2 / 1)$ to give the pure product 5 as a white solid.

## Transformation of 3ad to 6



In a 25 mL of Schlenk tube, equipped with a magnetic stirring bar, was added 3ad ( $79 \mathrm{mg}, 0.18 \mathrm{mmol}$ ), phenylboronic acid ( $32.9 \mathrm{mg}, 0.27 \mathrm{mmol}, 1.5$ equiv), $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}$ ( $20.8 \mathrm{mg}, 0.018 \mathrm{mmol}, 0.1$ equiv) and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(117.3 \mathrm{mg}, 0.36 \mathrm{mmol}, 2.0$ equiv) in toluene $/ \mathrm{CH}_{3} \mathrm{OH}(3 / 1,4 \mathrm{~mL})$ solution. Then, the mixture was degassed under $\mathrm{N}_{2}$ for 30 $\min$ at $-78^{\circ} \mathrm{C}$. Subsequently, the resulting mixture was stirred and heated to reflux for overnight. After complete consumption of starting material, the mixture was cooled to room temperature, passed through a pad of celite and extracted with ethyl acetate. Combined organic layer was washed with water and brine, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated to give a crude product. Finally, it was purified by column
chromatography on silica gel with $\mathrm{PE} / \mathrm{EA}(4 / 1)$ to give the pure product $\mathbf{6}$ as a white solid.

## Transformation of 3da to 7



In a 25 mL of Schlenk tube, equipped with a magnetic stirring bar, was added 3da ( $79 \mathrm{mg}, 0.18 \mathrm{mmol}$ ), pyridine-4-boronic acid ( $33.2 \mathrm{mg}, 0.27 \mathrm{mmol}, 1.5$ equiv), $\operatorname{Pd}\left(\mathrm{PPh}_{3}\right)_{4}\left(20.8 \mathrm{mg}, 0.018 \mathrm{mmol}, 0.1\right.$ equiv) and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(117.3 \mathrm{mg}, 0.36 \mathrm{mmol}, 2.0$ equiv) in toluene $/ \mathrm{CH}_{3} \mathrm{OH}(3 / 1,4 \mathrm{~mL})$ solution. Then, the mixture was degassed under $\mathrm{N}_{2}$ for 30 min at $-78^{\circ} \mathrm{C}$. Subsequently, the resulting mixture was stirred and heated to reflux for overnight. After complete consumption of starting material, the mixture was cooled to room temperature, passed through a pad of celite and extracted with ethyl acetate. Combined organic layer was washed with water and brine, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated to give a crude product. Finally, it was purified by column chromatography on silica gel with PE/EA (1/1) to give the pure product 7 as a white solid.

## III: Experimental screening details

Table S1. Screening of NHC precatalysts.


| entry $^{a}$ | cat. | yield $^{b}$ <br> $(\%)$ | $\mathrm{ee}^{c}$ <br> $(\%)$ |
| :---: | :---: | :---: | :---: |
| 1 | $\mathbf{C 1}$ | nr | -- |
| 2 | $\mathbf{C 2}$ | nr | -- |
| 3 | $\mathbf{C 3}$ | nr | -- |
| 4 | $\mathbf{C 4}$ | nr | -- |
| 5 | $\mathbf{C 5}$ | nr | -- |
| 6 | $\mathbf{C 6}$ | 52 | 74 |
| 7 | C7 | 48 | 74 |
| 8 | C8 | 54 | 80 |

${ }^{a}$ Reaction conditions: $\mathbf{1 a}$ ( $0.075 \mathrm{mmol}, 1.5$ equiv), $\mathbf{2 a}\left(0.05 \mathrm{mmol}, 1.0\right.$ equiv), $\mathrm{NHC}(10 \mathrm{~mol} \%), \mathrm{Cs}_{2} \mathrm{CO}_{3}(20 \mathrm{~mol} \%)$, 4 ( $0.1 \mathrm{mmol}, 2.0$ equiv), toluene ( 1 mL ), rt, 24 hours. ${ }^{b}$ Isolated yield. ${ }^{c}$ Determined by HPLC.

Table S2. Screening of bases.


[^0]Table S3. Screening of solvents, reaction temperature and additives.


| entry $^{a}$ | solvent | additive | X <br> $(\mathrm{mol} \%)$ | T <br> $\left({ }^{\circ} \mathrm{C}\right)$ | yield $^{b}$ <br> $(\%)$ | $\mathrm{ee}^{c}$ <br> $(\%)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $p$-xylene | -- | -- | rt | 49 | 85 |
| 2 | $m$-xylene | -- | -- | rt | 51 | 85 |
| 3 | mesitylene | -- | -- | rt | 54 | 83 |
| 4 | ethylbenzene | -- | -- | rt | 46 | 86 |
| 5 | fluorobenzene | -- | -- | rt | 23 | 81 |
| 6 | pentafluorobenzene | -- | -- | rt | 22 | 76 |
| 7 | DCM | -- | -- | rt | 46 | 40 |
| 8 | DCE | -- | -- | rt | 45 | 45 |
| 9 | 1,4 -dioxane | -- | -- | rt | 52 | 82 |
| 10 | Et2O | -- | -- | rt | 45 | 87 |
| 11 | MTBE | -- | -- | rt | 38 | 89 |
| 12 | toluene | -- | -- | 0 | $<5 \%$ | - |
| 13 | toluene | -- | -- | 40 | 56 | 84 |
| 14 | toluene | $\mathrm{Sc}(\mathrm{OTf})_{3}$ | 20 | rt | nr | -- |
| 15 | toluene | $\mathrm{Mg}(\mathrm{OTf})_{2}$ | 20 | rt | nr | -- |
| 16 | toluene | LiCl | 20 | rt | trace | $\mathrm{n} . \mathrm{d}$. |
| 17 | toluene | I | 20 | rt | 33 | 82 |
| 18 | toluene | II | 20 | rt | 31 | 84 |
| 19 | toluene | $\mathrm{Na} \mathrm{SO}_{4}$ | 20 mg | rt | 46 | 88 |
| 20 | toluene | MgSO | 20 mg | rt | 43 | 86 |
| 21 | toluene | $3 \AA \mathrm{MS}$ | 20 mg | rt | 55 | 85 |
| 22 | toluene | $4 \AA \mathrm{MS}$ | 20 mg | rt | 54 | 90 |
| 23 | toluene | $5 \AA \mathrm{MS}$ | 20 mg | rt | 35 | 88 |
| 24 | toluene | $4 \AA \mathrm{MS}$ | 40 mg | rt | 55 | 90 |
| 25 | toluene | $4 \AA \mathrm{MS}$ | 60 mg | rt | 50 | 90 |
| $26^{d}$ | toluene | $4 \AA \mathrm{MS}$ | 40 mg | rt | 60 | 90 |

[^1]
## IV: Crystal data and ORTEP diagram for compound 3ad

X-ray data of 3ad

| Identification code | mo_20190418f_0ma_a |
| :---: | :---: |
| Empirical formula | $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{BrO}_{3}$ |
| Formula weight | 435.30 |
| Temperature | 149.99 K |
| Wavelength | 0.71073 £ |
| Crystal system | orthorhombic |
| Space group | P 212121 |
| Unit cell dimensions | $a=6.9776(2) \AA \quad \alpha=90^{\circ}$ |
|  | $b=14.8155(5) \AA \beta=90^{\circ}$ |
|  | $c=19.0346(7) \AA \gamma=90^{\circ}$ |
| Volume | 1967.73 (11) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.469 \mathrm{mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $2.111 \mathrm{~mm}^{-1}$ |
| F(000) | 888.0 |
| Crystal size | $0.35 \times 0.3 \times 0.2 \mathrm{~mm}^{3}$ |
| Theta range for data collection | $2.544^{\circ}$ to $27.502{ }^{\circ}$ |
| Index ranges | $-9 \leqslant h \leqslant 9,-19 \leqslant k \leqslant 19,-24 \leqslant 1 \leqslant 24$ |
| Reflections collected | 50231 |
| Independent reflections | $4510\left[\mathrm{R}_{\text {int }}=0.0562\right]$ |
| Completeness to theta $=25.00^{\circ}$ | 99.5\% |
| Absorption correction | Semi-empirical from equivalents |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{\wedge} 2$ |
| Data / restraints / parameters | 4510 / 0 / 256 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.035 |
| Final R indices [ $1>2 \operatorname{sigma}(\mathrm{I})$ ] | $R_{1}=0.0237, w R_{2}=0.0551$ |

R indices (all data)
Absolute structure parameter
Largest diff. peak and hole
$R_{1}=0.0277, w R_{2}=0.0567$
0.015(8)
0.265 and -0.413 e. $\AA^{-3}$


Figure S1. ORTEP drawing of 3ad
The crystal was prepared from the solution of $\mathbf{3 a d}$ in petroleum n hexane/dichloromethane. CCDC 1911223 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

## V: Characterization of products

## (S)-2-Benzyl-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione (3aa).

39.8 mg , overall $60 \%$ yield, white solid, m. p. $90-91^{\circ} \mathrm{C} ; 90 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=10.82, \mathrm{t}$
$($ minor $)=14.64 ;[\alpha]_{\mathrm{D}}^{20}=-10.0\left(\right.$ c 1, $\left.\mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.65-7.51$ $(\mathrm{m}, 3 \mathrm{H}), 7.49-7.36(\mathrm{~m}, 3 \mathrm{H}), 7.29(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.15-6.90(\mathrm{~m}, 5 \mathrm{H}), 4.01(\mathrm{~s}$, $3 \mathrm{H}), 3.30-2.98(\mathrm{~m}, 2 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 204.4, 201.2, $157.5,150.9,143.9,139.1,136.2,129.9,129.2,129.1,128.1,127.4,127.3,126.6,116.3$, 113.2, 56.5, 56.4, 41.2, 20.8. IR (neat, $\mathrm{cm}^{-1}$ ): 1733, 1699, 1600, 1494, 1173, 1103, 1054, 996, 872, 801, 760, 701, 635. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{O}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+}$ 379.1305; found: 379.1305 .
(S)-2-(4-Fluorobenzyl)-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione
(3ab). 38.2 mg , overall $51 \%$ yield, white solid, m. p. $73-74^{\circ} \mathrm{C} ; 90 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}$ (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=11.93, \mathrm{t}$ $($ minor $)=13.71 ;[\alpha]_{\mathrm{D}}^{20}=-12.9\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.58(\mathrm{td}, J$ $=4.0,1.6 \mathrm{~Hz}, 3 \mathrm{H}), 7.52-7.38(\mathrm{~m}, 3 \mathrm{H}), 7.32(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.11-6.89(\mathrm{~m}, 2 \mathrm{H})$, $6.74(\mathrm{t}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 4.03(\mathrm{~s}, 3 \mathrm{H}), 3.25-2.97(\mathrm{~m}, 2 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 204.3,201.1,162.9,160.4,157.5,151.1,143.8,139.0,131.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=\right.$ $8.0 \mathrm{~Hz}) 129.2,129.1,127.5,127.3,116.4,114.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=21.0 \mathrm{~Hz}\right), 113.3,56.5,56.4$, 40.1, 20.9. ${ }^{19}$ F NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-116.2$ ( $\mathrm{Ar}-\mathrm{F}$ ). IR (neat, $\mathrm{cm}^{-1}$ ): 1737, 1700, 1601, 1570, 1509, 1333, 1220, 997, 872, 820, 764, 751, 696. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{FO}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+}$397.1210; found: 397.1208.
(S)-2-(4-Chlorobenzyl)-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione
(3ac). 43.0 mg , overall $55 \%$ yield, white solid, m. p. $145-146{ }^{\circ} \mathrm{C} ; 89 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=13.23$, $\mathrm{t}($ minor $)=15.42 ;[\alpha]_{\mathrm{D}}^{20}=-28.7\left(c \mathrm{1}, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.68-$ $7.53(\mathrm{~m}, 3 \mathrm{H}), 7.54-7.40(\mathrm{~m}, 3 \mathrm{H}), 7.35(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.12-6.93(\mathrm{~m}, 4 \mathrm{H}), 4.06$ $(\mathrm{s}, 3 \mathrm{H}), 3.23-3.03(\mathrm{~m}, 2 \mathrm{H}), 1.39(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.1,201.0$, $157.6,151.2,143.7,139.0,134.7,132.5,131.3,129.2,129.2,128.3,127.5,127.2,116.5$, 113.3, 56.4, 56.3, 40.1, 21.1. IR (neat, $\mathrm{cm}^{-1}$ ): 1735, 1700, 1604, 1568, 1449, 1407, 1368,

1337, 1255, 1236, 1171, 1100, 995, 871, 816, 772, 762, 698. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{ClO}_{3}{ }^{+}[\mathrm{M}+\mathrm{H}]^{+}$391.1095; found: 391.1095.

## (S)-2-(4-Bromobenzyl)-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione

(3ad). 51.2 mg , overall $59 \%$ yield, white solid, m. p. $156-157{ }^{\circ} \mathrm{C}$; $87 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer $\mathrm{t}($ major $)=13.93$, t (minor) $=15.98 ;[\alpha]_{\mathrm{D}}^{20}=-38.6\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.67-$ $7.53(\mathrm{~m}, 3 \mathrm{H}), 7.52-7.39(\mathrm{~m}, 3 \mathrm{H}), 7.34(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.23-7.12(\mathrm{~m}, 2 \mathrm{H}), 7.00$ $-6.87(\mathrm{~m}, 2 \mathrm{H}), 4.04(\mathrm{~s}, 3 \mathrm{H}), 3.18-2.99(\mathrm{~m}, 2 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 204.1,200.9,157.6,151.2,143.6,139.0,135.3,131.7,131.2,129.2,129.1$, $127.5,127.1,120.7,116.5,113.4,56.4,56.3,40.1,21.2$. IR (neat, $\mathrm{cm}^{-1}$ ): 1734, 1698 , 1602, 1407, 1233, 1180, 1154, 1099, 1072, 1040, 922, 871, 803, 768, 712, 632. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{BrO}_{3}{ }^{+}[\mathrm{M}+\mathrm{H}]^{+} 435.0590$; found: 435.0590 .
(S)-4-Methoxy-2-methyl-2-(4-methylbenzyl)-6-phenyl-1H-indene-1,3(2H)-dione (3ae). 41.5 mg , overall $56 \%$ yield, white solid, m. p. $101-102{ }^{\circ} \mathrm{C} ; 91 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=10.63$, t (minor) $=16.29 ;[\alpha]_{\mathrm{D}}^{20}=-6.0\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.57(\mathrm{dd}, J$ $=8.4,1.6 \mathrm{~Hz}, 3 \mathrm{H}), 7.50-7.38(\mathrm{~m}, 3 \mathrm{H}), 7.31(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.94(\mathrm{~d}, J=8.0 \mathrm{~Hz}$, $2 \mathrm{H}), 6.87(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 4.03(\mathrm{~s}, 3 \mathrm{H}), 3.20-3.02(\mathrm{~m}, 2 \mathrm{H}), 2.14(\mathrm{~s}, 3 \mathrm{H}), 1.36(\mathrm{~s}$, $3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 204.4, 201.4, 157.5, 150.8, 143.9, 139.1, 136.0, 133.1, 129.8, 129.2, 129.1, 128.8, 127.4, 127.3, 116.3, 113.3, 56.5, 56.4, 40.7, 21.0, 20.9. IR (neat, $\mathrm{cm}^{-1}$ ): 1736, 1702, 1600, 1568, 1368, 1337, 1254, 1233, 1171, 1101, 1056, 996, 943, 869, 765, 699. HRMS (ESI): calcd. For $\mathrm{C}_{25} \mathrm{H}_{23} \mathrm{O}_{3}{ }^{+}[\mathrm{M}+\mathrm{H}]^{+} 371.1642$; found: 371.1628.
(S)-4-Methoxy-2-methyl-6-phenyl-2-(4-(trifluoromethyl)benzyl)-1H-indene-1,3(2H)-dione (3af). 48.4 mg , overall $57 \%$ yield, white solid, m. p. $140-141^{\circ} \mathrm{C} ; 86 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i$\operatorname{PrOH}(90: 10)$ as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t
$($ major $)=10.41, \mathrm{t}($ minor $)=12.95 ;[\alpha]_{\mathrm{D}}^{20}=-7.9\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 7.63-7.53(\mathrm{~m}, 3 \mathrm{H}), 7.51-7.38(\mathrm{~m}, 3 \mathrm{H}), 7.37-7.29(\mathrm{~m}, 3 \mathrm{H}), 7.19(\mathrm{~d}, J=$ $8.0 \mathrm{~Hz}, 2 \mathrm{H}), 4.03(\mathrm{~s}, 3 \mathrm{H}), 3.26-3.12(\mathrm{~m}, 2 \mathrm{H}), 1.40(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 203.8,200.6,157.6,151.3,143.5,140.4,139.0,130.3,129.3,129.2,128.7,127.5$, $127.0,125.1\left(\mathrm{q}, J_{\mathrm{C}-\mathrm{F}}=3.8 \mathrm{~Hz}\right), 116.5,113.4,56.4,56.3,40.3,21.3$. ${ }^{19} \mathrm{~F}$ NMR ( 376 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta-62.5(\mathrm{Ar}-\mathrm{F})$. IR (neat, $\left.\mathrm{cm}^{-1}\right): 1738,1703,1602,1570,1325,1254,1235$, 1159, 1121, 1099, 1066, 997, 703, 633. HRMS (ESI): calcd. For $\mathrm{C}_{25} \mathrm{H}_{19} \mathrm{~F}_{3} \mathrm{O}_{3} \mathrm{Na}^{+}[\mathrm{M}+$ $\mathrm{Na}]^{+}$447.1179; found: 447.1183.
(S)-4-Methoxy-2-methyl-2-(4-nitrobenzyl)-6-phenyl-1H-indene-1,3(2H)-dione (3ag). 69.8 mg , overall $87 \%$ yield, white solid, m. p. $175-176{ }^{\circ} \mathrm{C}$; $89 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}$ ]: major diastereoisomer t ( major ) $=28.11$, t (minor) $=31.53 ;[\alpha]_{\mathrm{D}}^{20}=-30.9\left(\right.$ c $\left.1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.01-$ $7.84(\mathrm{~m}, 2 \mathrm{H}), 7.65-7.50(\mathrm{~m}, 3 \mathrm{H}), 7.50-7.38(\mathrm{~m}, 3 \mathrm{H}), 7.34(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.27$ $-7.18(\mathrm{~m}, 2 \mathrm{H}), 4.04(\mathrm{~s}, 3 \mathrm{H}), 3.30-3.14(\mathrm{~m}, 2 \mathrm{H}), 1.41(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 203.5,200.3,157.7,151.5,146.8,144.0,143.3,138.8,130.9,129.4,129.2$, $127.5,126.8,123.4,116.7,113.4,56.4,56.3,40.0,21.4$. IR (neat, $\mathrm{cm}^{-1}$ ): 1735, 1699 , 1600, 1568, 1517, 1452, 1099, 998, 830, 775, 766, 720, 698. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{NO}_{5} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 424.1155$; found: 424.1154.
(S)-2-(3-Chlorobenzyl)-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione
(3ah). 31.2 mg , overall $40 \%$ yield, white solid, m. p. $46-47^{\circ} \mathrm{C} ; 87 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}$ (90:10) as the eluent, flow: $1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}$ ]: major diastereoisomer t (major) $=10.89, \mathrm{t}$ $($ minor $)=13.79 ;[\alpha]_{\mathrm{D}}^{20}=+4.3\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.63-7.54$ $(\mathrm{m}, 3 \mathrm{H}), 7.51-7.40(\mathrm{~m}, 3 \mathrm{H}), 7.33(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.06(\mathrm{~s}, 1 \mathrm{H}), 7.03-6.98(\mathrm{~m}$, $2 \mathrm{H}), 6.98-6.90(\mathrm{~m}, 1 \mathrm{H}), 4.04(\mathrm{~s}, 3 \mathrm{H}), 3.17-3.03(\mathrm{~m}, 2 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 203.9,200.7,157.6,151.1,143.7,139.0,138.2,133.8,129.9$, 129.4, 129.2, 129.2, 128.2, 127.5, 127.2, 126.9, 116.5, 113.4, 56.4, 56.3, 40.5, 20.9. IR (neat, $\mathrm{cm}^{-1}$ ): 1737, 1699, 1600, 1449, 1371, 1332, 1207, 1079, 997, 924, 869, 787, 758,

697, 564, 469. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{ClO}_{3}{ }^{+}[\mathrm{M}+\mathrm{H}]+$ 391.1095; found: 391.1096.

## (S)-2-(3-Bromobenzyl)-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione

(3ai). 36.6 mg , overall $42 \%$ yield, white solid, m. p. $49-50^{\circ} \mathrm{C}$; 86\% ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=11.17, \mathrm{t}$ $($ minor $)=14.06 ;[\alpha]_{D}^{20}=+12.0\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.64-7.54$ (m, 3H), $7.52-7.39(\mathrm{~m}, 3 \mathrm{H}), 7.33(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.24-7.18(\mathrm{~m}, 1 \mathrm{H}), 7.15(\mathrm{dt}, J$ $=8.0,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.03-6.88(\mathrm{~m}, 2 \mathrm{H}), 4.04(\mathrm{~s}, 3 \mathrm{H}), 3.17-3.02(\mathrm{~m}, 2 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 203.9,200.7,157.6,151.1,143.7,139.1,138.5,132.8$, 129.9, 129.7, 129.3, 129.2, 128.7, 127.5, 127.2, 122.1, 116.5, 113.4, 56.4, 56.3, 40.5, 20.9. IR (neat, $\mathrm{cm}^{-1}$ ): 1737, 1670, 1602, 1567, 1127, 1333, 1234, 1208, 1073, 997, 869, 758, 695, 668. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{BrO}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 457.0410$; found: 457.0413.
(S)-4-Methoxy-2-(3-methoxybenzyl)-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione (3aj). 33.2 mg , overall $43 \%$ yield, colorless oily liquid; $87 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}$ ]: major diastereoisomer t (major) $=12.65, \mathrm{t}$ $($ minor $)=17.05 ;[\alpha]_{D}^{20}=+12.0\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.63-7.53$ (m, 3H), $7.52-7.39(\mathrm{~m}, 3 \mathrm{H}), 7.30(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.95(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.64$ (dt, $J=7.6,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.59(\mathrm{t}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.55(\mathrm{ddd}, J=3.6,2.8,1.2 \mathrm{~Hz}, 1 \mathrm{H})$, $4.03(\mathrm{~s}, 3 \mathrm{H}), 3.67(\mathrm{~s}, 3 \mathrm{H}), 3.19-3.07(\mathrm{~m}, 2 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 204.4,201.2,159.1,157.5,150.8,143.9,139.1,137.7,129.2,129.2,129.1$, $127.4,122.4,116.3,114.9,113.2,112.8,56.4,56.3,55.1,41.4,20.8$. IR (neat, $\mathrm{cm}^{-1}$ ): 2921, 1737, 1699, 1600, 1449, 1332, 1231, 1048, 995, 868, 760, 695, 476. HRMS (ESI): calcd. for $\mathrm{C}_{25} \mathrm{H}_{22} \mathrm{O}_{4} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 409.1410$; found: 409.1400.
(S)-4-Methoxy-2-methyl-2-(3-methylbenzyl)-6-phenyl-1H-indene-1,3(2H)-dione (3ak). 25.9 mg , overall $35 \%$ yield, colorless oily liquid; $88 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the
eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=8.90, \mathrm{t}$ $($ minor $)=12.12 ;[\alpha]_{\mathrm{D}}^{20}=+6.4\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.67-7.52$ (m, 3H), $7.51-7.38(\mathrm{~m}, 3 \mathrm{H}), 7.30(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.95(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.90-$ $6.73(\mathrm{~m}, 3 \mathrm{H}), 4.02(\mathrm{~s}, 3 \mathrm{H}), 3.20-3.00(\mathrm{~m}, 2 \mathrm{H}), 2.16(\mathrm{~s}, 3 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.4,201.3,157.5,150.8,143.9,139.1,137.6,136.1,130.7$, $129.2,129.1,128.0,127.4,127.3,127.0,116.3,113.2,56.5,56.4,41.2,21.3,20.8$. IR (neat, $\mathrm{cm}^{-1}$ ): 2919, 1737, 1700, 1601, 1448, 1332, 1230, 995, 866, 790, 759, 696, 564, 468. HRMS (ESI): calcd. for $\mathrm{C}_{25} \mathrm{H}_{23} \mathrm{O}_{3}{ }^{+}[\mathrm{M}+\mathrm{H}]^{+}$371.1642; found: 371.1642.
(S)-2-(2-Fluorobenzyl)-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione
(3al). 35.2 mg , overall $47 \%$ yield, white solid, m. p. $101-102{ }^{\circ} \mathrm{C} ; 66 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=13.53, \mathrm{t}$ $($ minor $)=18.84 ;[\alpha]_{\mathrm{D}}^{20}=+26.0\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.64(\mathrm{~d}, J$ $=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.64-7.56(\mathrm{~m}, 2 \mathrm{H}), 7.52-7.39(\mathrm{~m}, 3 \mathrm{H}), 7.36(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.13$ $-7.02(\mathrm{~m}, 2 \mathrm{H}), 6.95-6.82(\mathrm{~m}, 2 \mathrm{H}), 4.05(\mathrm{~s}, 3 \mathrm{H}), 3.15(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 203.5,200.6,162.1,159.7,157.7,151.0,143.5,139.1$, 132.3, 132.2, 129.2, 129.1, $128.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=8.0 \mathrm{~Hz}\right), 127.5,127.0,123.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=4.0\right.$ $\mathrm{Hz}), 116.4,115.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=22.0 \mathrm{~Hz}\right), 113.4,56.4,55.2,33.9,33.9,19.6 .{ }^{19} \mathrm{~F}$ NMR ( 376 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-114.8(\mathrm{Ar}-\mathrm{F})$. IR (neat, $\mathrm{cm}^{-1}$ ): 1740, 1703, 1601, 1585, 1493, 1450, 1334, 1210, 1182, 1077, 1028, 997, 869, 756, 699. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{FO}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+}$397.1210; found: 397.1208.

## (S)-2-(2-Chlorobenzyl)-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione

(3am). 39.0 mg , overall $50 \%$ yield, white solid, m. p. $91-92{ }^{\circ} \mathrm{C}$; $52 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=13.66, \mathrm{t}$ $($ minor $)=16.34 ;[\alpha]_{D}^{20}=+38.2 ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.67-7.58(\mathrm{~m}, 1 \mathrm{H})$, $7.52-7.41(\mathrm{~m}, 2 \mathrm{H}), 7.38(\mathrm{~d}, \mathrm{~J}=1.2 \mathrm{~Hz}, 3 \mathrm{H}), 7.25-7.19(\mathrm{~m}, 1 \mathrm{H}), 7.18-7.12(\mathrm{~m}, 1 \mathrm{H})$, $7.09-7.01(\mathrm{~m}, 1 \mathrm{H}), 4.06(\mathrm{~s}, 3 \mathrm{H}), 3.28(\mathrm{~s}, 2 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 203.3,200.5,157.7,151.0,143.6,139.1,134.8,133.9,132.0,129.7,129.2$,
$129.1,128.2,127.5,127.0,126.4,116.4,113.5,56.4,55.2,37.9,19.3$. IR (neat, $\mathrm{cm}^{-1}$ ): $1740,1704,1603,1572,1450,1332,1209,1079,1052,1036,996,864,767,751,719$, 701, 690. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{ClO}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]{ }^{+} 413.0915$; found: 413.0930.
(S)-2-(2-Bromobenzyl)-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione (3an). 45.1 mg , overall $52 \%$ yield, white solid, m. p. $130-131{ }^{\circ} \mathrm{C} ; 46 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}$ ]: major diastereoisomer t (major) $=15.04$, t (minor) $=17.46 ;[\alpha]_{\mathrm{D}}^{20}=+44.4\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.66(\mathrm{~d}, J$ $=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.65-7.56(\mathrm{~m}, 2 \mathrm{H}), 7.54-7.40(\mathrm{~m}, 4 \mathrm{H}), 7.38(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.16$ (dd, $J=7.6,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.09(\mathrm{td}, J=7.6,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.96(\mathrm{td}, J=8.0,2.0 \mathrm{~Hz}, 1 \mathrm{H})$, $4.07(\mathrm{~s}, 3 \mathrm{H}), 3.31(\mathrm{~s}, 2 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 203.2,200.5$, $157.8,151.1,143.6,139.1,135.8,133.1,131.7,129.3,129.2,128.4,127.5,127.0,126.9$, 125.6, 116.4, 113.5, 56.4, 55.2, 40.3, 19.3. IR (neat, $\mathrm{cm}^{-1}$ ): 1738, 1701, 1603, 1567, 1469, 1451, 1335, 1232, 1024, 995, 874, 765, 755, 703, 658. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{BrO}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 457.0410$; found: 457.0416 .
(S)-4-Methoxy-2-methyl-2-(2-methylbenzyl)-6-phenyl-1H-indene-1,3(2H)-dione
(3ao). 31.1 mg , overall $42 \%$ yield, white solid, m. p. $79-80^{\circ} \mathrm{C}$; $85 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=9.12, \mathrm{t}$ $($ minor $)=11.83 ;[\alpha]_{D}^{20}=+52.0\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.64-7.54$ $(\mathrm{m}, 3 \mathrm{H}), 7.52-7.39(\mathrm{~m}, 3 \mathrm{H}), 7.32(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.03-6.94(\mathrm{~m}, 2 \mathrm{H}), 6.92(\mathrm{td}, J$ $=7.2,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.87(\mathrm{td}, J=7.2,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.03(\mathrm{~s}, 3 \mathrm{H}), 3.20(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 2 \mathrm{H})$, $2.32(\mathrm{~s}, 3 \mathrm{H}), 1.40(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.5,201.4,157.5,150.8$, $143.9,139.1,136.8,134.7,130.6,130.2,129.2,129.1,127.5,126.7,125.5,116.3,113.2$, $56.4,56.3,37.7,20.7,19.9$. IR (neat, $\mathrm{cm}^{-1}$ ): 1739, 1704, 1601, 1449, 1323, 1206, 1074, 1050, 993, 865, 766, 746, 689, 565, 456. HRMS (ESI): calcd. for $\mathrm{C}_{25} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{Na}^{+}[\mathrm{M}+$ $\mathrm{Na}]^{+} 393.1461$; found: 393.1457.
(S)-4-Methoxy-2-methyl-2-(naphthalen-2-ylmethyl)-6-phenyl-1H-indene-1,3(2H)dione (3ap). 56.0 mg , overall $69 \%$ yield, white solid, m. p. $120-121^{\circ} \mathrm{C} ; 91 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t ( major ) $=15.44$, t (minor) $=18.27 ;[\alpha]_{\mathrm{D}}^{20}=-54.8\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.74-$ $7.67(\mathrm{~m}, 1 \mathrm{H}), 7.66-7.60(\mathrm{~m}, 1 \mathrm{H}), 7.59-7.53(\mathrm{~m}, 3 \mathrm{H}), 7.53-7.46(\mathrm{~m}, 2 \mathrm{H}), 7.46-$ $7.38(\mathrm{~m}, 3 \mathrm{H}), 7.38-7.29(\mathrm{~m}, 2 \mathrm{H}), 7.25-7.16(\mathrm{~m}, 2 \mathrm{H}), 3.96(\mathrm{~s}, 3 \mathrm{H}), 3.51-3.16(\mathrm{~m}$, 2 H ), $1.45(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.4,201.2,157.5,150.9,143.8$, 139.1, 134.0, 133.2, 132.2, 129.1, 129.1, 128.8, 128.4, 127.9, 127.7, 127.5, 127.4, 127.3, $125.7,125.5,116.4,113.3,56.7,56.3,41.1,21.3$. IR (neat, $\mathrm{cm}^{-1}$ ): 1736, 1699, 1602, 1568, 1449, 1335, 1233, 1173, 997, 854, 815, 762, 744, 703. HRMS (ESI): calcd. for $\mathrm{C}_{28} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 429.1461$; found: 429.1461.
(S)-4-Methoxy-2-methyl-2-(naphthalen-1-ylmethyl)-6-phenyl-1H-indene-1,3(2H)dione (3aq). 43.9 mg , overall $54 \%$ yield, white solid, m. p. $56-57^{\circ} \mathrm{C} ; 85 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=12.14$, t (minor) $=14.95 ;[\alpha]_{\mathrm{D}}^{20}=+95.5\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.15(\mathrm{~d}, J$ $=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.62(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.56-7.29(\mathrm{~m}, 9 \mathrm{H}), 7.26(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H})$, $7.23-7.11$ (m, 2H), $3.90(\mathrm{~s}, 3 \mathrm{H}), 3.64(\mathrm{~s}, 2 \mathrm{H}), 1.48$ ( $\mathrm{s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 204.4,201.2,157.3,150.6,143.7,139.1,133.7,132.6,132.0,129.1,128.7$, $128.3,127.5,127.4,125.8,125.4,125.0,124.9,116.2,113.1,56.6,56.3,37.7,20.4$. IR (neat, $\mathrm{cm}^{-1}$ ): 1737, 1700, 1601, 1570, 1450, 1333, 1231, 1213, 994, 868, 781, 759, 696. HRMS (ESI): calcd. for $\mathrm{C}_{28} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 429.1461$; found: 429.1459 .
(S)-2-Benzyl-2-ethyl-4-methoxy-6-phenyl-1H-indene-1,3(2H)-dione (3ar). 34.8 mg , overall $47 \%$ yield, white solid, m. p. $107-108{ }^{\circ} \mathrm{C} ; 46 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=9.97, \mathrm{t}$ $($ minor $)=12.46 ;[\alpha]_{D}^{20}=+14.4\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.67-7.53$ $(\mathrm{m}, 3 \mathrm{H}), 7.52-7.35(\mathrm{~m}, 3 \mathrm{H}), 7.28(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.13-6.88(\mathrm{~m}, 5 \mathrm{H}), 4.02(\mathrm{~s}$,
$3 \mathrm{H}), 3.22-3.00(\mathrm{~m}, 2 \mathrm{H}), 2.06-1.88(\mathrm{~m}, 2 \mathrm{H}), 0.78(\mathrm{t}, J=7.6 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.8,201.5,157.1,150.7,145.1,139.1,136.0,130.0,129.2,129.1$, $128.7,128.1,127.5,126.5,116.2,112.8,61.4,56.4,40.8,29.1,9.3 . \operatorname{IR}\left(n e a t, \mathrm{~cm}^{-1}\right)$ : 1738, 1701, 1602, 1584, 1452, 1330, 1230, 1206, 870, 763, 741, 699. HRMS (ESI): calcd. for $\mathrm{C}_{25} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 393.1461$; found: 393.1458.
(S)-2-(4-Bromobenzyl)-2-ethyl-4-methoxy-6-phenyl-1H-indene-1,3(2H)-dione
(3as). 45.7 mg , overall $51 \%$ yield, white solid, m. p. $129-130{ }^{\circ} \mathrm{C} ; 44 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak IA-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer $\mathrm{t}($ major $)=10.28$, $\mathrm{t}($ minor $)=8.81 ;[\alpha]_{\mathrm{D}}^{20}=+5.2\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.66-7.55$ $(\mathrm{m}, 3 \mathrm{H}), 7.53-7.39(\mathrm{~m}, 3 \mathrm{H}), 7.33(\mathrm{~s}, 1 \mathrm{H}), 7.24-7.07(\mathrm{~m}, 2 \mathrm{H}), 6.92(\mathrm{~d}, J=8.4 \mathrm{~Hz}$, $2 \mathrm{H}), 4.04(\mathrm{~s}, 3 \mathrm{H}), 3.16-2.99(\mathrm{~m}, 2 \mathrm{H}), 1.95(\mathrm{qd}, J=7.6,2.8 \mathrm{~Hz}, 2 \mathrm{H}), 0.78(\mathrm{t}, J=7.6$ $\mathrm{Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 204.5$, 201.1, 157.2, 151.0, 144.9, 139.0, 135.1, $131.8,131.2,129.2,129.1,128.5,127.5,120.7,116.4,112.9,61.2,56.4,39.6,29.4,9.3$. IR (neat, $\mathrm{cm}^{-1}$ ): 1734, 1698, 1602, 1583, 1407, 1333, 1233, 872, 803, 768, 696, 632. HRMS (ESI): calcd. for $\mathrm{C}_{25} \mathrm{H}_{21} \mathrm{BrO}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]+471.0566$; found: 471.0565.
(S)-2-Allyl-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione (3at). 33.1 mg , overall $54 \%$ yield, white solid, m. p. $159-160{ }^{\circ} \mathrm{C} ; 60 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=10.49, \mathrm{t}$ $($ minor $)=12.06 ;[\alpha]_{D}^{20}=-15.0\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.71(\mathrm{~d}, \mathrm{~J}=$ $1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.68-7.61(\mathrm{~m}, 2 \mathrm{H}), 7.56-7.39(\mathrm{~m}, 4 \mathrm{H}), 5.57(\mathrm{~m}, 1 \mathrm{H}), 5.13-4.86(\mathrm{~m}$, $2 \mathrm{H}), 4.09(\mathrm{~s}, 3 \mathrm{H}), 2.54(\mathrm{~m}, 2 \mathrm{H}), 1.28(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.3$, $201.3,157.8,151.2,143.7,139.2,132.0,129.2,129.1,127.5,127.1,119.3,116.5,113.5$, 56.4, 54.5, 39.6, 19.5. IR (neat, $\mathrm{cm}^{-1}$ ): 2358, 2151, 1948, 1740, 1702, 1601, 1333, 1233, 1004, 775, 702, 588. HRMS (ESI): calcd. for $\mathrm{C}_{20} \mathrm{H}_{19} \mathrm{O}_{3}{ }^{+}[\mathrm{M}+\mathrm{H}]{ }^{+} 307.1329$; found: 307.1328 .

Methyl (S)-2-(4-methoxy-2-methyl-1,3-dioxo-6-phenyl-2,3-dihydro-1H-inden-2-yl) acetate (3au). 40.6 mg , overall $60 \%$ yield, white solid, m. p. $151-152{ }^{\circ} \mathrm{C} ; 57 \%$ ee.

The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\mathrm{PrOH}$ ( $90: 10$ ) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \min ^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=19.26, \mathrm{t}($ minor $)=23.32 ;[\alpha]_{\mathrm{D}}^{20}=-18.0\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.75 (d, J = $1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.69-7.60(\mathrm{~m}, 2 \mathrm{H}), 7.56-7.39(\mathrm{~m}, 4 \mathrm{H}), 4.08(\mathrm{~s}, 3 \mathrm{H}), 3.52$ (s, 3H), $3.18-2.92(\mathrm{~m}, 2 \mathrm{H}), 1.27(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 203.0, 200.2, $171.3,157.9,151.0,143.4,139.4,129.2,129.1,127.5,126.7,116.4,113.8,56.3,52.0$, 51.8, 38.4, 21.1. IR (neat, $\mathrm{cm}^{-1}$ ): 2920, 2357, 2217, 2194, 2162, 2015, 1947, 1731, 1702, 1603, 1334, 1208, 796, 623. HRMS (ESI): calcd. for $\mathrm{C}_{20} \mathrm{H}_{19} \mathrm{O}_{5}{ }^{+}[\mathrm{M}+\mathrm{H}]^{+}$339.1227; found: 339.1222.
(S)-4-Methoxy-2-methyl-6-phenyl-2-(thiophen-2-ylmethyl)-1H-indene-1,3(2H)dione (3av). 41.3 mg , overall $57 \%$ yield, colorless oily liquid; $84 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}$ ]: major diastereoisomer t (major) $=14.03, \mathrm{t}$ $($ minor $)=18.26 ;[\alpha]_{D}^{20}=-6.5\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.68-7.55$ $(\mathrm{m}, 3 \mathrm{H}), 7.52-7.40(\mathrm{~m}, 3 \mathrm{H}), 7.35(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.91(\mathrm{dd}, J=4.8,2.0 \mathrm{~Hz}, 1 \mathrm{H})$, $6.70(\mathrm{~m}, 2 \mathrm{H}), 4.05(\mathrm{~s}, 3 \mathrm{H}), 3.48-3.30(\mathrm{~m}, 2 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 204.1,200.8,157.7,151.0,144.0,139.1,137.6,129.2,129.1,127.5,127.4$, 126.6, 124.3, 116.4, 113.4, 56.4, 56.3, 34.8, 20.7. IR (neat, $\mathrm{cm}^{-1}$ ): 2924, 1737, 1699, $1600,1449,1332,1209,1078,996,758,693,552$. HRMS (ESI): calcd. for $\mathrm{C}_{22} \mathrm{H}_{19} \mathrm{O}_{3} \mathrm{~S}^{+}$ $[\mathrm{M}+\mathrm{H}]^{+} 363.1049$ found: 363.1043.
(S)-2-Benzyl-6-(4-fluorophenyl)-4-methoxy-2-methyl-1H-indene-1,3(2H)-dione (3ba). 33.7 mg , overall $45 \%$ yield, white solid, m. p. $108-109{ }^{\circ} \mathrm{C} ; 90 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=13.96$, t (minor) $=18.04 ;[\alpha]_{\mathrm{D}}^{20}=+14.4\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.62-$ 7.43 (m, 3H), 7.23 (d, $J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.20-7.10(\mathrm{~m}, 2 \mathrm{H}), 7.11-6.92(\mathrm{~m}, 5 \mathrm{H}), 4.01$ (s, 3H), 3.22-3.06(m, 2H), $1.38(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, CDCl3) $\delta 204.3,201.2$, $163.5\left(\mathrm{~d}, J_{\mathrm{CF}}=248.0 \mathrm{~Hz}\right), 157.5,149.7,143.9,136.1,135.3,135.2,129.9,129.2\left(\mathrm{~d}, J_{\mathrm{CF}}\right.$ $=8.0 \mathrm{~Hz}), 128.1,127.4,126.6,116.3,116.1,113.0,56.5,56.4,41.2,20.8 .{ }^{19}$ F NMR
( $564 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-112.2$ ( $\mathrm{Ar}-\mathrm{F}$ ). IR (neat, $\mathrm{cm}^{-1}$ ): 1732, 1700, 1599, 1573, 1516, 1332, 1242, 1210, 1161, 998, 832, 771, 748, 703. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{FO}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+}$397.1210; found: 397.1211.

## (S)-2-Benzyl-6-(4-chlorophenyl)-4-methoxy-2-methyl-1H-indene-1,3(2H)-dione

 (3ca). 46.8 mg , overall $60 \%$ yield, white solid, m. p. $91-92^{\circ} \mathrm{C} ; 89 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}$ ]: major diastereoisomer t (major) $=15.77, \mathrm{t}$ $($ minor $)=19.26 ;[\alpha]_{\mathrm{D}}^{20}=-11.4\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.52(\mathrm{~d}, J$ $=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.51-7.47(\mathrm{~m}, 2 \mathrm{H}), 7.45-7.39(\mathrm{~m}, 2 \mathrm{H}), 7.24(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.10$ $-6.96(\mathrm{~m}, 5 \mathrm{H}), 4.01(\mathrm{~s}, 3 \mathrm{H}), 3.20-3.07(\mathrm{~m}, 2 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 204.2,201.1,157.6,149.5,143.9,137.5,136.1,135.5,129.9,129.4,128.7$, 128.1, 127.6, 126.6, 116.0, 113.0, 56.5, 56.4, 41.2, 20.8. IR (neat, $\mathrm{cm}^{-1}$ ): 1734, 1702, $1600,1497,1452,1395,1333,1237,1093,998,924,825,769,749,702,556,512,489$. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{ClO}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 413.0915$; found: 413.0915.(S)-2-Benzyl-6-(4-bromophenyl)-4-methoxy-2-methyl-1H-indene-1,3(2H)-dione (3da). 42.5 mg , overall $49 \%$ yield, white solid, m. p. $57-58{ }^{\circ} \mathrm{C} ; 89 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\mathrm{PrOH}$ (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=16.80, \mathrm{t}$ $($ minor $)=19.97 ;[\alpha]_{D}^{20}=-16.2\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.62-7.54$ $(\mathrm{m}, 2 \mathrm{H}), 7.52(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.46-7.37(\mathrm{~m}, 2 \mathrm{H}), 7.23(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.11-$ $6.93(\mathrm{~m}, 5 \mathrm{H}), 4.01(\mathrm{~s}, 3 \mathrm{H}), 3.21-3.07(\mathrm{~m}, 2 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 204.2,201.1,157.6,149.5,144.0,138.0,136.1,132.3,129.9,129.0,128.1$, 127.6, 126.6, 123.7, 116.0, 113.0, 56.5, 56.4, 41.2, 20.8. IR (neat, $\mathrm{cm}^{-1}$ ): 1737, 1699, 1494, 1451, 1391, 1331, 1234, 1073, 998, 922, 821, 745, 699, 556, 510. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{BrO}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 457.0410$; found: 457.0417.

## (S)-2-Benzyl-6-(4-iodophenyl)-4-methoxy-2-methyl-1H-indene-1,3(2H)-dione

(3ea). 48.2 mg , overall $50 \%$ yield, white solid, m. p. $170-171^{\circ} \mathrm{C} ; 90 \%$ ee. The ee value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \min ^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t ( major ) $=16.93$,
$\mathrm{t}($ minor $)=19.87 ;[\alpha]_{\mathrm{D}}^{20}=-22.5\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.84-$ $7.72(\mathrm{~m}, 2 \mathrm{H}), 7.52(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.32-7.24(\mathrm{~m}, 2 \mathrm{H}), 7.23(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H})$, $7.11-6.93(\mathrm{~m}, 5 \mathrm{H}), 4.00(\mathrm{~s}, 3 \mathrm{H}), 3.20-3.05(\mathrm{~m}, 2 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.2,201.1,157.6,149.6,144.0,138.5,138.3,136.1,129.9,129.1$, 128.1, 127.7, 126.7, 116.0, 113.0, 95.5, 56.5, 56.4, 41.2, 20.8. IR (neat, $\mathrm{cm}^{-1}$ ): 1699, 1601, 1333, 1244, 1003, 818, 701, 508, 422. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{IO}_{3}{ }^{+}[\mathrm{M}+$ H] ${ }^{+}$483.0452; found: 483.0440 .
(S)-2-Benzyl-4-methoxy-2-methyl-6-(p-tolyl)-1H-indene-1,3(2H)-dione (3fa). 36.3 mg , overall $49 \%$ yield, white solid, m. p. $121-122{ }^{\circ} \mathrm{C} ; 89 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}$ ]: major diastereoisomer t (major) $=10.55, \mathrm{t}$ $($ minor $)=14.51 ;[\alpha]_{D}^{20}=-2.7\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.56(\mathrm{~d}, J=$ $1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.53-7.40(\mathrm{~m}, 2 \mathrm{H}), 7.34-7.25(\mathrm{~m}, 2 \mathrm{H}), 7.25(\mathrm{~d}, J=3.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.16-$ $6.84(\mathrm{~m}, 5 \mathrm{H}), 4.01(\mathrm{~s}, 3 \mathrm{H}), 3.32-2.96(\mathrm{~m}, 2 \mathrm{H}), 2.40(\mathrm{~s}, 3 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 204.5,201.2,157.5,150.8,143.8,139.4,136.2,136.1,129.9$, $129.9,128.1,127.3,127.1,126.6,116.0,113.0,56.5,56.3,41.1,21.2,20.9$. IR (neat, $\left.\mathrm{cm}^{-1}\right): 2365,1733,1699,1598,1451,1332,1241,1205,999,817,746,700,553,491$. HRMS (ESI): calcd. for $\mathrm{C}_{25} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+}$393.1461; found: 393.1456.
(S)-2-Benzyl-4-methoxy-2-methyl-6-(3-nitrophenyl)-1H-indene-1,3(2H)-dione
(3ga). 40.9 mg , overall $51 \%$ yield, white solid, m. p. $58-59^{\circ} \mathrm{C}$; $92 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak IG-H with hexane $/ i-\mathrm{PrOH}$ (90:10) as the eluent, flow: $1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}$ ]: major diastereoisomer t (major) $=40.59, \mathrm{t}$ (minor) $=64.39 ;[\alpha]_{\mathrm{D}}^{20}=+35.0\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.43(\mathrm{t}, J=$ $2.0 \mathrm{~Hz}, 1 \mathrm{H}), 8.29(\mathrm{dd}, J=8.0,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.91(\mathrm{dd}, J=8.0,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.67(\mathrm{t}, J=$ $8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.31(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.17-6.87(\mathrm{~m}, 5 \mathrm{H})$, $4.07(\mathrm{~s}, 3 \mathrm{H}), 3.25-3.08(\mathrm{~m}, 2 \mathrm{H}), 1.40(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.0$, $201.1,157.8,148.8,147.9,144.1,140.8,136.0,133.3,130.3,129.9,128.3,128.2,126.7$, 123.7, 122.3, 116.3, 113.3, 56.6, 56.6, 41.3, 20.7. IR (neat, $\mathrm{cm}^{-1}$ ): 2359, 1738, 1702,

1602, 1527, 1450, 1331, 1235, 998, 808, 737, 698, 555, 507. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{NO}_{5} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 424.1155$; found: 424.1155.
(S)-2-Benzyl-6-(2-fluorophenyl)-4-methoxy-2-methyl-1H-indene-1,3(2H)-dione
(3ha). 33.7 mg , overall $45 \%$ yield, colorless oily liquid; $89 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=10.18, \mathrm{t}$ $($ minor $)=13.43 ;[\alpha]_{D}^{20}=+10.0\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.53(\mathrm{~s}$, $1 \mathrm{H}), 7.47-7.35(\mathrm{~m}, 2 \mathrm{H}), 7.31(\mathrm{~s}, 1 \mathrm{H}), 7.26-7.13(\mathrm{~m}, 2 \mathrm{H}), 7.13-6.91(\mathrm{~m}, 5 \mathrm{H}), 4.00$ (s, 3H), 3.26-3.01 (m, 2H), 1.39 ( $\mathrm{s}, 3 \mathrm{H}$ ). ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.1,201.2$, $157.1,145.3,143.5,136.1,130.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=8.0 \mathrm{~Hz}\right), 130.6,130.5,130.0,128.1,127.6$, $126.6,124.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=4.0 \mathrm{~Hz}\right), 118.4,118.3,116.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=22.0 \mathrm{~Hz}\right), 115.2,56.4$, 56.3, 41.2, 20.8. ${ }^{19}$ F NMR ( $564 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-116.9(\mathrm{Ar}-\mathrm{F})$. IR (neat, $\mathrm{cm}^{-1}$ ): 2921, 1738, 1701, 1602, 1496, 1450, 1334, 1232, 1078, 998, 874, 801, 757, 699, 556, 505. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{FO}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+}$397.1210; found: 397.1202.0
(S)-2-Benzyl-4-methoxy-2-methyl-6-(o-tolyl)-1H-indene-1,3(2H)-dione (3ia). 27.4 mg , overall $37 \%$ yield, colorless oily liquid; $89 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: 1.0 $\left.\mathrm{mL} \cdot \mathrm{min}^{-1}, \lambda=254 \mathrm{~nm}\right]:$ major diastereoisomer $\mathrm{t}($ major $)=7.78, \mathrm{t}($ minor $)=10.01 ;[\alpha]$ ${ }_{\mathrm{D}}^{20}=+60.0\left(c \quad 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.35-7.24(\mathrm{~m}, 3 \mathrm{H}), 7.24(\mathrm{dd}$, $J=7.2,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.15(\mathrm{dd}, J=7.6,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.11-6.95(\mathrm{~m}, 6 \mathrm{H}), 3.95(\mathrm{~s}, 3 \mathrm{H})$, $3.28-3.03(\mathrm{~m}, 2 \mathrm{H}), 2.19(\mathrm{~s}, 3 \mathrm{H}), 1.39(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.4$, $201.3,156.9,151.9,143.3,139.9,136.1,135.0,130.7,129.9,129.2,128.6,128.1,127.3$, $126.6,126.1,118.6,115.4,56.4,56.3,41.6,20.4,20.3$. IR (neat, $\mathrm{cm}^{-1}$ ): 2925, 1738 , 1701, 1600, 1452, 1331, 1229, 1081, 998, 872, 759, 699, 557, 504. HRMS (ESI): calcd. for $\mathrm{C}_{25} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+}$393.1461; found: 393.1459.
(S)-2-Benzyl-4-methoxy-2-methyl-6-(naphthalen-2-yl)-1H-indene-1,3(2H)-dione (3ja). 49.6 mg , overall $61 \%$ yield, white solid, m. p. $132-133{ }^{\circ} \mathrm{C}$; $89 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=15.02, \mathrm{t}$
$($ minor $)=19.65 ;[\alpha]_{D}^{20}=+28.7\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.03(\mathrm{~d}, J$ $=2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.95-7.82(\mathrm{~m}, 3 \mathrm{H}), 7.70(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.66(\mathrm{dd}, J=8.4,2.0 \mathrm{~Hz}$, $1 \mathrm{H}), 7.58-7.48$ (m, 2H), 7.41 (d, $J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.16-6.96(\mathrm{~m}, 5 \mathrm{H}), 4.05(\mathrm{~s}, 3 \mathrm{H})$, $3.27-3.05(\mathrm{~m}, 2 \mathrm{H}), 1.41(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.5,201.3,157.6$, $150.8,143.9,136.3,136.2,133.4,130.0,129.0,128.5,128.2,127.8,127.4,127.1,127.0$, $126.9,126.7,124.9,116.4,113.5,56.6,56.4,41.2,20.9$. IR (neat, $\mathrm{cm}^{-1}$ ): 1735, 1698 , $1602,1571,1448,1332,1315,1247,1176,1003,879,857,820,745,698,563,553$, $505,476,447$, 408. HRMS (ESI): calcd. for $\mathrm{C}_{28} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 429.1461$; found: 429.1441 .
(S)-2-Benzyl-6-(furan-2-yl)-4-methoxy-2-methyl-1H-indene-1,3(2H)-dione (3ka). 34.6 mg , overall $50 \%$ yield, white solid, m. p. $82-83{ }^{\circ} \mathrm{C} ; 84 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, flow: $1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}$ ]: major diastereoisomer t (major) $=12.20, \mathrm{t}$ $($ minor $)=13.54 ;[\alpha]_{\mathrm{D}}^{20}=+20.0\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.59(\mathrm{~d}, J$ $=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.52(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.40(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.09-6.94(\mathrm{~m}, 5 \mathrm{H})$, $6.86(\mathrm{dd}, J=3.6,0.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.52(\mathrm{dd}, J=3.6,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.01(\mathrm{~s}, 3 \mathrm{H}), 3.20-3.05$ $(\mathrm{m}, 2 \mathrm{H}), 1.36(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.4,200.9,157.8,151.8,144.1$, $143.9,139.2,136.1,129.8,128.1,127.0,126.6,112.5,111.9,109.6,109.5,56.4,56.3$, 41.3, 20.7. IR (neat, $\mathrm{cm}^{-1}$ ): 1735, 1697, 1603, 1450, 1328, 1240, 1179, 1056, 1023, 1004, 864, 810, 747, 704, 593, 561, 511. HRMS (ESI): calcd. for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{O}_{4} \mathrm{Na}^{+}[\mathrm{M}+$ $\mathrm{Na}]^{+}$369.1097; found: 369.1097.
(S)-2-Benzyl-4-methoxy-2-methyl-6-(thiophen-2-yl)-1H-indene-1,3(2H)-dione
(31a). 37.7 mg , overall $52 \%$ yield, white solid, m. p. $113-114{ }^{\circ} \mathrm{C}$; $86 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]$ : major diastereoisomer t (major) $=12.16, \mathrm{t}$ (minor) $=14.59 ;[\alpha]_{D}^{20}=-14.0\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.58(\mathrm{~d}, J$ $=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.44(\mathrm{dd}, J=3.6,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.40(\mathrm{dd}, J=5.2,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.27(\mathrm{~d}, J$ $=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.15-6.95(\mathrm{~m}, 6 \mathrm{H}), 4.01(\mathrm{~s}, 3 \mathrm{H}), 3.22-3.04(\mathrm{~m}, 2 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.3,200.8,157.7,144.0,143.4,141.9,136.1,129.9,128.6$,
128.1, 127.8, 127.3, 126.7, 126.0, 114.3, 111.5, 56.5, 56.4, 41.2, 20.8. IR (neat, $\mathrm{cm}^{-1}$ ): 1734, 1697, 1601, 1570, 1451, 1412, 1374, 1311, 1240, 1179, 1076, 1031, 993, 856, 834, 749, 701, 558, 507. HRMS (ESI): calcd. for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{O}_{3} \mathrm{SNa}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 385.0869$; found: 385.0868.
(2S)-2-Benzyl-4-methoxy-2-methyl-6-phenyl-2,3-dihydro-1H-indene-1,3-diol (4). $24.0 \mathrm{mg}, 67 \%$ yield, white solid, m. p. $87-88^{\circ} \mathrm{C} ;>20: 1 \mathrm{dr}, 91 \%$ ee. The $d r$ and $e e$ value were determined by HPLC [Daicel Chiralpak IA-H with hexane/i-PrOH (75:25) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]: \mathrm{t}($ major $)=19.27, \mathrm{t}($ minor $)=+8.21 ;[\alpha]$ ${ }_{\mathrm{D}}^{20}=51.4\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.64-7.54(\mathrm{~m}, 2 \mathrm{H}), 7.53-7.46$ $(\mathrm{m}, 2 \mathrm{H}), 7.49-7.40(\mathrm{~m}, 2 \mathrm{H}), 7.41-7.27(\mathrm{~m}, 4 \mathrm{H}), 7.28-7.20(\mathrm{~m}, 1 \mathrm{H}), 7.03(\mathrm{~d}, J=1.2$ $\mathrm{Hz}, 1 \mathrm{H}), 4.74(\mathrm{~s}, 1 \mathrm{H}), 4.47(\mathrm{~s}, 1 \mathrm{H}), 3.93(\mathrm{~s}, 3 \mathrm{H}), 3.25-3.06(\mathrm{~m}, 2 \mathrm{H}), 2.40(\mathrm{~s}, 2 \mathrm{H}), 0.70$ $(\mathrm{s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 156.8,147.9,144.7,141.2,139.2,131.5,130.7$, 128.8, 128.1, 127.6, 127.3, 125.9, 117.1, 110.0, 82.3, 78.2, 55.4, 50.7, 36.6, 22.7. IR (neat, $\mathrm{cm}^{-1}$ ): 3551, 1592, 1574, 1461, 1399, 1329, 1195, 1164, 1036, 1023, 853, 806, $762,749,705,693$. HRMS (ESI): calcd. for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{O}_{3} \mathrm{Na}^{+}[\mathrm{M}+\mathrm{Na}]^{+} 383.1618$; found: 383.1598.
(S)-2-(3-hydroxypropyl)-4-methoxy-2-methyl-6-phenyl-1H-indene-1,3(2H)-dione (5). $53.8 \mathrm{mg}, 83 \%$ yield, colorless oily liquid; $60 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AS-H with hexane $/ i-\operatorname{PrOH}$ (85:15) as the eluent, flow: 1.0 $\left.\mathrm{mL} \cdot \mathrm{min}^{-1}, \lambda=254 \mathrm{~nm}\right]: \mathrm{t}($ major $)=20.02, \mathrm{t}($ minor $)=16.95 ;[\alpha]_{\mathrm{D}}^{20}=-6.0\left(c 1, \mathrm{CHCl}_{3}\right) ;$ ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.74-7.68(\mathrm{~m}, 1 \mathrm{H}), 7.68-7.60(\mathrm{~m}, 2 \mathrm{H}), 7.48(\mathrm{~m}, 3 \mathrm{H})$, $7.43(\mathrm{~m}, 1 \mathrm{H}), 4.08(\mathrm{~m}, 3 \mathrm{H}), 3.50(\mathrm{~m}, 2 \mathrm{H}), 1.88(\mathrm{~m}, 2 \mathrm{H}), 1.40(\mathrm{~m}, 2 \mathrm{H}), 1.27(\mathrm{~m}, 3 \mathrm{H})$, $1.24(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 205.0,202.0,157.8,151.4,143.6,139.1$, $129.3,129.2,127.5,127.0,116.6,113.5,62.6,56.4,54.2,31.6,28.2,20.1$. IR (neat, $\mathrm{cm}^{-}$ ${ }^{1}$ ): 2923, 1737, 1695, 1602, 1449, 1332, 1214, 1057, 989, 868, 757, 693, 561. HRMS (ESI): calcd. for $\mathrm{C}_{20} \mathrm{H}_{21} \mathrm{O}_{4}{ }^{+}[\mathrm{M}+\mathrm{H}]^{+}$325.1434; found: 325.1430.
(S)-2-([1,1'-biphenyl]-4-ylmethyl)-4-methoxy-2-methyl-6-phenyl-1H-indene-
$\mathbf{1 , 3 ( 2 H})$-dione (6). $71.6 \mathrm{mg}, 92 \%$ yield, colorless oily liquid; $87 \%$ ee. The $e e$ value were determined by HPLC [Daicel Chiralpak IA-H with hexane $/ i-\operatorname{PrOH}(90: 10)$ as the
eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]: \mathrm{t}$ (major) $=12.41, \mathrm{t}($ minor $)=13.75 ;[\alpha]_{\mathrm{D}}^{20}=$ $-60.0\left(c 1, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.61(\mathrm{~d}, \mathrm{~J}=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.59-7.54$ (m, 2H), $7.50-7.39$ (m, 5H), $7.38-7.28$ (m, 5H), 7.26 (m, 1H), 7.14 (d, J = 8.0 Hz , $2 \mathrm{H}), 4.02(\mathrm{~s}, 3 \mathrm{H}), 3.31-3.09(\mathrm{~m}, 2 \mathrm{H}), 1.42(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 204.4, 201.3, 157.6, 151.0, 143.8, 140.6, 139.2, 139.1, 135.4, 130.4, 129.2, 129.1, 128.7, $127.5,127.3,127.1,126.8,126.7,116.4,113.3,56.6,56.4,40.7,21.0$. IR (neat, $\mathrm{cm}^{-1}$ ): 2359, 2182, 2149, 1702, 1601, 1332, 999, 760, 513, 466. HRMS (ESI): calcd. for $\mathrm{C}_{30} \mathrm{H}_{25} \mathrm{O}_{3}{ }^{+}[\mathrm{M}+\mathrm{H}]^{+} 433.1798$; found: 433.1798.
(S)-2-benzyl-4-methoxy-2-methyl-6-(4-(pyridin-4-yl)phenyl)-1H-indene-1,3(2H)dione (7). $74.1 \mathrm{mg}, 95 \%$ yield, white solid, m. p. $59-60^{\circ} \mathrm{C} ; 87 \%$ ee. The $e e$ value was determined by HPLC [Daicel Chiralpak AD-H with hexane/i-PrOH (80:20) as the eluent, flow: $\left.1.0 \mathrm{~mL} \cdot \mathrm{~min}^{-1}, \lambda=254 \mathrm{~nm}\right]: \mathrm{t}($ major $)=22.52, \mathrm{t}($ minor $)=34.77 ;[\alpha]_{\mathrm{D}}^{20}=$ -3.8 (c 1, $\left.\mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.75-8.60(\mathrm{~m}, 2 \mathrm{H}), 7.70(\mathrm{~m}, 4 \mathrm{H})$, $7.60(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.55-7.46(\mathrm{~m}, 2 \mathrm{H}), 7.32(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.11-6.93(\mathrm{~m}$, $5 \mathrm{H}), 4.02(\mathrm{~s}, 3 \mathrm{H}), 3.27-2.99(\mathrm{~m}, 2 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 204.3, 201.1, 157.6, 150.4, 149.7, 147.2, 143.9, 139.7, 138.9, 136.1, 129.9, 128.2, 128.1, 127.7, 127.6, 126.6, 121.5, 116.2, 113.2, 56.5, 56.4, 41.2, 20.8. IR (neat, $\mathrm{cm}^{-1}$ ): 2225, 2149, 2093, 1983, 1700, 1598, 1333, 1233, 1002, 812, 700. HRMS (ESI): calcd. for $\mathrm{C}_{29} \mathrm{H}_{24} \mathrm{NO}_{3}{ }^{+}[\mathrm{M}+\mathrm{H}]^{+} 434.1751$; found: 434.1766.

## VI: NMR spectra of new compounds



3aa


| セ్లిల్రి |  | \% | $\bar{\square}$ |
| :---: | :---: | :---: | :---: |
| ¢ |  | ¢i | F |



3aa






3ab



3ab







$3 a c$


| Hos |  |  | 융 | \% |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 5 |  | $\bigcirc$ | $\bigcirc$ |  |
|  |  |  |  |  |  |




















3ag






3ai


| \%్న్న్ |  | N゙\% | $\bar{\sim}$ |
| :---: | :---: | :---: | :---: |
| ¢ัֹī | ¢ \% | ¢0 | - |
| 17 | 个 Tis\% | 4 |  |



3ai



3aj



3aj





3ak


3al




##  








$\begin{array}{lllllllllllllllllllllll}210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0\end{array}$
 NNNNNNNNNNNNNNNNNNNNNNNNNNNNNONOOOGO



| \%ow |  |  | ® |
| :---: | :---: | :---: | :---: |
| ¢్రిర్స |  | \% | \% |



3an

$\begin{array}{llllllllllllllllllllllllllllll}210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0\end{array}$





|  |  |
| :---: | :---: |
| ずす |  |
| 1 |  |


$3 a 0$


 $\stackrel{\text { on }}{\substack{\text { g } \\ i}}$






3aq





$\circ$
$\stackrel{\circ}{\circ}$

3ar




| 等哭 |  |
| :---: | :---: |
|  |  |
| TT |  |


| 主 | \％ | $\frac{\infty}{7}$ |
| :---: | :---: | :---: |
| ¢ $\square_{0}^{\circ}$ | ¢ | ¢ิ่ |








| ＋${ }_{\text {¢ }}^{\text {M }}$ |  <br>  |  |
| :---: | :---: | :---: |
| \％゙す |  |  |
| 1 |  |  |


| స్ల్ర్ర్ర | \％ |
| :---: | :---: |
| ゼす | $\bigcirc$ |




















| - | - ¢ibingind | $\stackrel{\sim}{0}$ | ® |
| :---: | :---: | :---: | :---: |
|  |  <br>  | ¢0\% | F |








 $\stackrel{\otimes}{\%}$

3fa



3fa



3 ga


| \% ${ }^{\circ}$ |  | \% | $\stackrel{\text { \% }}{ }$ |
| :---: | :---: | :---: | :---: |
| ัั่ร์ |  | ¢ | $\stackrel{\text { \% }}{\square}$ |



3ga


3ha

3ha



3ha






3ja




##  



3ka




3ka


| $\qquad$ |  |
| :---: | :---: |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |



31a









##  





5



6


6

毋్రీ్రnin





## VII: HPLC profile spectrum of compounds

## $3 a \mathbf{a}$





3ab


[^2]
## $3 a c$




## 3ad



| Peak \# | RetTime Type [min] | Width [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~S}\right]} \end{gathered}$ | Height <br> [mAU] | Area $\%$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 14.005 BB | 0.3231 | 787.09344 | 37.46355 | 50.5514 |
| 2 | 16.049 BB | 0.3684 | 769.92291 | 32.26977 | 49.4486 |



## $3 a e$



| Peak \# | ```RetTime Type [min]``` | Width [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~S}]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.648 BB | 0.2428 | 2077.24268 | 131.12067 | 49.8936 |
| 2 | 16.271 BB | 0.3758 | 2086.10425 | 85.76928 | 50.1064 |



## 3af





| $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | ```RetTime [min]``` | Type | $\begin{gathered} \text { Width } \\ \text { [min] } \end{gathered}$ | $\begin{gathered} \text { Area } \\ {\left[m A U^{*} \mathrm{~S}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.410 |  | 0.2430 | 1.17190 e 4 | 739.07532 | 93.0110 |
| 2 | 12.951 | BB | 0.2995 | 880.58612 | 45.56285 | 6.9890 |

## $3 a g$



| $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | $\begin{gathered} \text { RetTime } \\ {[\mathrm{min}]} \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 28.247 | BB | 0.6350 | 1709.41589 | 40.61483 | 50.1819 |
| 2 | 31.666 | BB | 0.7188 | 1697.02380 | 35.17855 | 49.8181 |

DAD1 A, Sig=254,4 Ref=360,100 (E:IWXWIDATAIHJM120190415ILNK004231.D)

| $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | $\begin{gathered} \text { RetTime } \\ {[\mathrm{min}]} \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU} * \mathrm{~s}]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 28.112 |  | 0.6457 | 7792.57324 | 185.65417 | 94.5338 |
| 2 | 31.530 | MM R | 0.7622 | 450.58704 | 9.85304 | 5.4662 |

## 3ah




| $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | $\begin{gathered} \text { RetTime } \\ {[\mathrm{min}]} \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.891 |  | 0.2508 | 1.37193 e 4 | 847.78931 | 93.5002 |
| 2 | 13.794 | MM R | 0.326 | 953.7089 | 48.662 | . 4998 |

## 3ai



| Peak \# | ```RetTime Type [min]``` | Width [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 11.184 BB | 0.2539 | 899.09448 | 54.65664 | 49.9382 |
| 2 | 14.071 BB | 0.3200 | 901.32080 | 43.44766 | 50.0618 |



3aj


| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | $\begin{gathered} \text { Width } \\ {[m i n]} \end{gathered}$ | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{\mathrm{s}}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 12.717 |  | 0.2891 | 603.00537 | 32.10683 | 50.0340 |
| 2 | 17.102 |  | 0.3863 | 602.18518 | 23.87220 | 49.9660 |



| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 12.646 | BB | 0.2925 | 1.05453 e 4 | 553.03259 | 93.5448 |
| 2 | 17.047 | MM R | 0.4086 | 727.68872 | 29.68270 | 6.4552 |

## 3ak




## 3al



| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | $\begin{gathered} \text { Width } \\ \text { [min] } \end{gathered}$ | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 13.568 |  | 0.3019 | 1136.10645 | 57.66617 | 49.9666 |
| 2 | 18.913 | BB | 0.4239 | 1137.62329 | 40.98212 | 50.0334 |



## 3am



| Peak \# | $\begin{gathered} \text { RetTime } \\ {[\mathrm{min}]} \end{gathered}$ | Type | $\begin{gathered} \text { Width } \\ {[\mathrm{min}]} \end{gathered}$ | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~S}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 13.810 | BB | 0.3138 | 965.65308 | 47.77753 | 50.1804 |
| 2 | 16.563 | BB | 0.3748 | 958.70898 | 39.27549 | 49.8196 |



| Peak <br> \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 13.656 | BB | 0.3146 | 1.66103 e 4 | 818.96100 | 76.0361 |
| 2 | 16.337 | MM R | 0.3959 | 5235.00781 | 220.37730 | 23.9639 |

## 3an



$$
\begin{aligned}
& \text { Peak RetTime Type Width Area Height Area } \\
& \text { \# [min] [min] [mAU*s] [mAU] \% }
\end{aligned}
$$

$$
\begin{aligned}
& 1 \quad 14.729 \mathrm{BB} \quad 0.3299 \quad 3354.78174 \quad 156.64880 \quad 49.8942 \\
& \begin{array}{lllllll}
2 & 16.990 & \mathrm{BB} & 0.3828 & 3369.01099 & 135.18442 & 50.1058
\end{array}
\end{aligned}
$$



| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | $\begin{gathered} \text { Width } \\ \text { [min] } \end{gathered}$ | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~s}]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area <br> \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 15.039 | BB | 0.3507 | 9177.19824 | 404.49304 | 73.1494 |
| 2 | 17.457 | MM R | 0.4313 | 3368.62256 | 130.16016 | 26.8506 |

## $3 a 0$


DAD1 A, Sig=254,4 Ref=360,100 (E:IWXWIDATAIHJM120190427LLNK004344.D)

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | $\begin{gathered} \text { Width } \\ \text { [min] } \end{gathered}$ | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~S}\right]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 9.123 | BB | 0.2133 | 1.46528 e 4 | 1072.81726 | 92.5232 |
| 2 | 11.833 | MM R | 0.2809 | 1184.08887 | 70.26357 | 7.4768 |

## 3ap



| Peak \# | ```RetTime Type [min]``` | $\begin{aligned} & \text { Width } \\ & \text { [min] } \end{aligned}$ | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~s}]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area 응 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 15.175 BB | 0.3519 | 4232.92383 | 185.73996 | 50.1312 |
| 2 | 17.903 BB | 0.4124 | 4210.76611 | 157.26924 | 49.8688 |


| mAU- |  |  |  | $\underset{\substack{\mathrm{w}}}{\stackrel{\rightharpoonup}{2}}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1 | 10 | 15 | 20 | 25 |  |
| Peak \# | ```RetTime Type [min]``` | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |  |
| 1 | 15.443 BB | 0.3718 | $2.30425 e 4$ | 960.89014 | 95.55 |  |
| 2 | 18.270 MM R | 0.4437 | 1071.60303 | 40.24857 | 4.44 |  |

$3 a q$



## 3ar



| $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | ```RetTime Type [min]``` | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~s}]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & {[m A U]} \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 9.850 BB | 0.2231 | 370.37769 | 94.54195 | 49.9964 |
| 2 | 12.256 BB | 0.2786 | 370.57312 | 75.91089 | 50 |



| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | $\begin{gathered} \text { Width } \\ {[\mathrm{min}]} \end{gathered}$ | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~s}]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 9.973 |  | 0.2283 | 6397.44092 | 433.05740 | 73.0578 |
| 2 | 12.459 | MM R | 0.3091 | 2359.23926 | 127.21201 | 26.9422 |

## 3as



| Peak \# | RetTime <br> [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~s}]} \end{gathered}$ | $\begin{gathered} \text { Height } \\ \text { [mAU] } \end{gathered}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 8.843 |  | 0.1979 | 1293.26160 | 100.65012 | 49.9885 |
| 2 | 10.346 |  | 0.2338 | 1293.85864 | 85.87302 | 50.0115 |



| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | $\begin{gathered} \text { Width } \\ {[\mathrm{min}]} \end{gathered}$ | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~S}]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area $\%$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 8.807 |  | 0.2018 | 6174.36475 | 474.67734 | 27.9379 |
| 2 | 10.277 |  | 0.2412 | 1.59260 e 4 | 1025.17078 | 72.0621 |

## 3at




| Peak \# | RetTime [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{\mathrm{s}}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.492 |  | 0.2236 | 1.68380 e 4 | 1158.36096 | 79.9961 |
| 2 | 12.060 |  | 0.2568 | 4210.53662 | 252.23546 | 20.0039 |

## 3au



| Peak <br> \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~S}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 19.156 |  | 0.4236 | 2004.57068 | 72.71276 | 50.3054 |
| 2 | 23.159 | BB | 0.5143 | 1980.22974 | 59.18496 | 49.6946 |



## 3av



| $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | ```RetTime [min]``` | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[m A U^{*} s\right]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 14.087 | BB | 0.3038 | 465.16116 | 23.61509 | 48.0966 |
| 2 | 18.319 | BB | 0.4149 | 501.97745 | 18.25272 | 51.9034 |



| $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | $\begin{gathered} \text { RetTime } \\ {[\mathrm{min}]} \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[m A U * s]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 14.027 |  | 0.3061 | 1.28820 e 4 | 647.44153 | 92.0418 |
| 2 | 18.26 |  | 0.42 | 113.811 | 39 | . 9582 |

## 3ba



| mAU | DAD1 A Sig=254, Ref=360,100 (E-WWXWIDATAIHJMM20190402 LNK004155 D) |  | 402LLNK004155.D) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |
|  | 15 |  |  | ${ }_{20}$ | 25 |
| Peak RetTime Type \# [min] |  | $\begin{gathered} \text { Width } \\ \text { [min] } \end{gathered}$ | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}^{*} \mathrm{~s}\right]} \end{gathered}$ | $\begin{gathered} \text { Height } \\ \text { [mAU] } \end{gathered}$ | Area \% |
| 1 | 13.957 BB | 0.3334 | . 48810 e4 | 1163.86755 | 94.931 |
| 2 | 18.037 MM R | 0.4258 | 1328.45215 | 52.00061 | 5.068 |

## 3ca




| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | $\begin{aligned} & \text { Width } \\ & {[m i n]} \end{aligned}$ | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~s}]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 15.770 | BB | 0.4218 | 3.93744 e 4 | 1473.06665 | 94.5213 |
| 2 | 19.262 | MM R | 0.4669 | 2282.25146 | 81.46192 | 5.4787 |

3da


| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | $\begin{gathered} \text { Width } \\ \text { [min] } \end{gathered}$ | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 16.610 |  | 0.3788 | 1612.69763 | 66.07236 | 49.9195 |
| 2 | 19.743 |  | 0.4497 | 1617.89771 | 55.55811 | 50.0805 |



3ea


| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | $\begin{gathered} \text { Width } \\ {[m i n]} \end{gathered}$ | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & {[\mathrm{mAU}]} \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 16.793 |  | 0.3841 | 1225.02576 | 48.93368 | 50.0777 |
| 2 | 19.718 | BB | 0.4499 | 1221.22412 | 41.66651 | 49.9223 |



| Peak \# | RetTime <br> [min] | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~S}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 16.934 |  | 0.3966 | 9599.82422 | 375.02945 | 95.0424 |
| 2 | 19.865 | MM R | 0.4639 | 500.74640 | 17.99135 | 4.9576 |

## 3fa



| Peak \# | RetTime [min] | Type | $\begin{aligned} & \text { Width } \\ & \text { [min] } \end{aligned}$ | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU} \mathrm{~m}_{\mathrm{s}}\right]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & {[m A U]} \end{aligned}$ | Area 응 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.518 |  | 0.2341 | 1098.27478 | 72.74692 | 50.1511 |
| 2 | 14.443 | BB | 0.3251 | 1091.65613 | 51.95306 | 49.8489 |




## 3ga




## 3ha


DAD1 A, Sig=254,4 Ref=360,100 (E:IWXWIDATAIHJM120190501L[NK004391.D)

| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~s}]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.180 | BB | 0.2275 | 9590.61035 | 652.34155 | 94.5557 |
| 2 | 13.429 | BB | 0.2925 | 552.20898 | 28.94934 | 5.4443 |

## 3ia




3ja



| $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | $\begin{gathered} \text { RetTime } \\ {[\mathrm{min}]} \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[m A U * s]} \end{gathered}$ | Height [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 15.025 |  | 0.3627 | 1.98147 e 4 | 854.06714 | 94.5417 |
| 2 | 19.646 | MM R | 0.4688 | 1143.99573 | 40.67279 | 5.4583 |

## 3ka




31a



| $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | RetTime Type [min] | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU} \mathrm{~s}_{\mathrm{s}}\right]} \end{gathered}$ | Height [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 12.161 VB | 0.2682 | 8540.95508 | 487.87503 | 92.9257 |
|  |  | 0.3147 |  |  |  |

4


| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~s}]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 8.278 | VV | 0.2261 | 1462.57483 | 100.33953 | 39.5069 |
| 2 | 8.925 | VB | 0.2418 | 389.77615 | 25.01888 | 10.5286 |
| 3 | 14.114 | BB | 0.3802 | 370.96924 | 15.23041 | 10.0206 |
| 4 | 19.477 | BB | 0.5536 | 1478.75818 | 42.11973 | 39.9440 |



## 5



| Peak \# | $\begin{gathered} \text { RetTime } \\ \text { [min] } \end{gathered}$ | Type | $\begin{aligned} & \text { Width } \\ & \text { [min] } \end{aligned}$ | $\begin{gathered} \text { Area } \\ {[\mathrm{mAU*} \mathrm{~s}]} \end{gathered}$ | $\begin{aligned} & \text { Height } \\ & \text { [mAU] } \end{aligned}$ | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 16.984 |  | 0.6828 | 1586.88794 | 35.14643 | 51.1262 |
| 2 | 20.181 | MM R | 0.9870 | 1516.97412 | 25.61695 | 48.8738 |



6


Peak RetTime Type Width Area Height Area \# [min] [min] [mAU*s] [mAU] \%

$\begin{array}{lllllll}1 & 12.407 & \mathrm{BB} & 0.2965 & 5466.01904 & 284.03055 & 52.1984\end{array}$
$2 \quad 13.683 \mathrm{BB} \quad 0.34085005 .60547 \quad 229.1953147 .8016$






[^0]:    ${ }^{a}$ Reaction conditions: 1a ( $0.075 \mathrm{mmol}, 1.5$ equiv), 2a ( $0.05 \mathrm{mmol}, 1.0$ equiv), $\mathbf{C 8}(10 \mathrm{~mol} \%)$, base ( $20 \mathrm{~mol} \%$ ), 4 ( $0.1 \mathrm{mmol}, 2.0$ equiv), toluene $(1 \mathrm{~mL}), \mathrm{rt}, 24$ hours. ${ }^{b}$ Isolated yield. ${ }^{c}$ Determined by HPLC.

[^1]:    ${ }^{a}$ Reaction conditions: 1a ( $0.075 \mathrm{mmol}, 1.5$ equiv), 2a ( $0.05 \mathrm{mmol}, 1.0$ equiv), C8 ( $10 \mathrm{~mol} \%$ ), DMAP ( $20 \mathrm{~mol} \%$ ), 4 ( $0.1 \mathrm{mmol}, 2.0$ equiv), solvent $(1 \mathrm{~mL})$, rt., 24 hours. ${ }^{b}$ Isolated yield. ${ }^{c}$ Determined by HPLC. ${ }^{d}$ reaction time 2 days.

[^2]:    DAD1 A, Sig=254,4 Ref=360,100 (E:IWXWIDATAIHJM120190308LLNK004026.D)

    | $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | RetTime Type [min] | Width <br> [min] | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~S}\right]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
    | :---: | :---: | :---: | :---: | :---: | :---: |

    $1 \quad 11.933 \mathrm{BB} \quad 0.27711 .93844 \mathrm{e} 4 \quad 1092.22046 \quad 95.0033$
    $\begin{array}{llllllll}2 & 13.707 & \text { MM R } 0.3255 & 1019.52667 & 52.19908 & 4.9967\end{array}$

