Asymmetric Synthesis of Tetrahydrobenzofurans and Annulated Dihydropyrans via Cooperative One-Pot Organo- and Silver-Catalysis

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Abstract
A low catalyst loading of a squaramide (0.5 mol%) and a silver(I) salt (1 mol%) efficiently catalyzes a one-pot asymmetric Michael addition/hydroalkoxylation reaction between 1,3-diketones and alkyne-tethered nitroalkenes. Depending on the 1,3-dicarbonyl substrate this cooperative catalytic approach opens access to tetrahydrobenzofurans or annulated dihydropyrans in moderate to excellent yields and very good to excellent enantioselectivities.

Key words asymmetric synthesis, organocatalysis, one-pot synthesis, silver catalysis, annulation

Benzofuran and its partially hydrogenated analogues are important heterocyclic building blocks and very common structures in natural products with interesting biological and pharmaceutical properties. This is also true for structurally isomeric annulated dihydropyrans. Natural products such as the furanomonoterpene evodone (I), which has been isolated from Evodia hortensis, exhibits significant inhibitory activity on the seed germination of certain species. Curzerenone (II) and bisabolangelone (III) are other natural products with antibacterial and anti-inflammatory activities, respectively, whereas the diterpenoid maoeocrystal V (IV) is a potent selective HeLa cell inhibitor. The dihydropyran-type natural product crolibulin (V) and the pharmaceutical HA14-1 (VI) show anticancer properties (Figure 1).

Recently, much effort has been invested in the synthesis of tetrahydrobenzofuran and dihydropyran core structures. Singh and co-workers developed a silver-catalyzed interrupted Feist–Bénary reaction between ynones and β-diketones to provide dihydrofurans in moderate to good yields and good to excellent enantioselectivities (Scheme 1). Feng and co-workers reported an asymmetric domino Michael addition/O-alkylation reaction between cyclohexane-1,3-dione derivatives and bromonitrostyrenes catalyzed by a bifunctional N,N′-dioxide organocatalyst to afford polysubstituted bicyclic dihydrofurans. Calter’s group published another interesting synthesis of highly substituted furanoids via an organocatalytic asymmetric aldol/oxa-Michael addition sequence between 2-ene-1,4-diketones and dimeredone in the presence of a bis(cinchona alkaloid)-pyrimidine catalyst. The Schneider group developed an interesting enantioselective phosphoric acid-catalyzed syn-
thesis of 4-aryl-4H-chromenes via a conjugate addition of 1,3-diketones to in situ generated ortho-quinone methides followed by a cyclodehydration reaction.\textsuperscript{11}

In search of new methods for acquiring valuable bioactive heterocyclic compounds and our interest in the combination of organocatalysts and silver(I) salts,\textsuperscript{16} we investigated an asymmetric Michael addition/hydroalkoxylation sequence between 1,3-diketones and alkyne-tethered nitroalkenes catalyzed by a bifunctional squaramide\textsuperscript{17} and a silver(I) salt to provide the desired tetrahydrobenzofuran.

We began our investigation by choosing dimedone (1) and nitroalkene 2a as model substrates. To our delight, the one-pot reaction of 1 and 2a in CH\textsubscript{2}Cl\textsubscript{2} at room temperature catalyzed by squaramide A and Ag\textsubscript{2}O afforded the desired 5-exo–dig cyclization product 3a in 98% yield and 94% enantiomeric excess (Scheme 2). Inspired by these excellent results, the reaction was carried out with different squaramide and thiourea catalysts A–I along with Ag\textsubscript{2}O as silver(I) salt. All squaramide catalysts as well as thiourea catalysts provided the tetrahydrobenzofuran in high yields and moderate to very good enantioselectivities. The best result was obtained with squaramide A, which gave 98% yield and 94% ee.

The reaction conditions were optimized further by varying the solvent (Table 1). The solvent screening indicated that the chlorinated solvents and Et\textsubscript{2}O gave very good results. The best yields were obtained with CH\textsubscript{2}Cl\textsubscript{2} and CHCl\textsubscript{3}. We chose CH\textsubscript{2}Cl\textsubscript{2} over CHCl\textsubscript{3} on the basis of its lower toxic-
Further optimization studies were carried out by screening transition metal catalysts for the hydroalkoxylation reaction. Ag₂CO₃ provided the annulated product with 99% yield and 95% ee. The cost aspect led to our decision to use Ag₂O instead of Ag₂CO₃. After carrying out the reaction at different temperatures and catalyst loadings of the squaramide and the silver(I) salt, we determined the optimal reaction conditions, these being 0.5 mol% of the squaramide and 1 mol% of Ag₂O, and CH₂Cl₂ as solvent at room temperature.

The developed one-pot asymmetric transformation was also conducted with various 5-substituted 1,3-cyclohexanediones to introduce another stereocenter via desymmetrization. The desired tetrahydrobenzofuran could be obtained in very good yields and excellent enantiomeric excesses (Table 2). Furthermore, the one-pot Michael addition/hydroalkoxylation sequence with heteroaryl-substituted nitroalkenes provided the desired annulated product 3i in excellent yields and enantioselectivity.

An extended substrate scope was investigated using different cyclic 1,3-diketones based on five- and six-membered rings. The reaction with 1,3-cyclopentanedione led to the tetrahydrobenzofuran product in good yield and excellent enantioselectivity (Scheme 3, 5a). Interestingly, a dihydropyran derivative 5b could be obtained in moderate yield and good enantiomeric excess using 1,3-cyclopentanediol. The substrate scope of the cooperative catalytic reaction was extended further to 1,3-diketones bearing heteroatoms, which also provided dihydropyran derivatives in moderate to very good yields and high enantioselectivities (Scheme 3, 5c, d).

The developed one-pot asymmetric transformation was also conducted with various 5-substituted 1,3-cyclohexanediones to introduce another stereocenter via desymmetrization. The desired tetrahydrobenzofuran could be obtained in very good yields and enantioselectivities, but the diastereomeric ratio was virtually 1:1 in all attempts (Scheme 4, 7a–d).

To evaluate the efficiency and synthetic utility of the current Michael addition/hydroalkoxylation strategy, tetrahydrobenzofuran 3a was prepared on a gram-scale maintaining the excellent yield and ee value (Scheme 5).

### Table 1 Further Optimization Studies

<table>
<thead>
<tr>
<th>Entry</th>
<th>M-catalyst</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>ee (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>Ag₂O</td>
<td>toluene</td>
<td>90</td>
<td>92</td>
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<tr>
<td>2</td>
<td>Ag₂O</td>
<td>Et₂O</td>
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<td>92</td>
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<td>5</td>
<td>Ag₂O</td>
<td>CH₂Cl₂</td>
<td>99</td>
<td>95</td>
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<tr>
<td>6</td>
<td>PtCl₂</td>
<td>CH₂Cl₂</td>
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<tr>
<td>7</td>
<td>CuCl</td>
<td>CH₂Cl₂</td>
<td>37</td>
<td>94</td>
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<td>8</td>
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<td>CH₂Cl₂</td>
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<tr>
<td>9</td>
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<td>CH₂Cl₂</td>
<td>20</td>
<td>47</td>
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<tr>
<td>10</td>
<td>Ag₂CO₃</td>
<td>CH₂Cl₂</td>
<td>99</td>
<td>95</td>
</tr>
<tr>
<td>11</td>
<td>AuCl₃PPh₃</td>
<td>CH₂Cl₂</td>
<td>n.d.</td>
<td>–</td>
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<tr>
<td>12</td>
<td>Ag₂O</td>
<td>CH₂Cl₂</td>
<td>99</td>
<td>96</td>
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<tr>
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<td>Ag₂O</td>
<td>CH₂Cl₂</td>
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<tr>
<td>15</td>
<td>Ag₂O</td>
<td>CH₂Cl₂</td>
<td>99</td>
<td>97</td>
</tr>
</tbody>
</table>

* Reaction conditions: Dimedone (1; 0.25 mmol), nitroalkene 2a (1.1 equiv), cat. A (1 mol%), Ag₂O (10 mol%), solvent (2.5 mL, 0.1 M).
* Yield of 3a after flash chromatography.
* The enantiomeric excess was determined by HPLC on a chiral stationary phase.
* The reaction was carried out with Ag₂O (1 mol%) and A (0.5 mol%).
* The reaction was carried out with Ag₂O (0.5 mol%) at 0 °C.

### Table 2 Substrate Scope

<table>
<thead>
<tr>
<th>R</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Ph</td>
<td>99</td>
<td>96</td>
</tr>
<tr>
<td>b 3-MeOC₆H₄</td>
<td>98</td>
<td>96</td>
</tr>
<tr>
<td>c 2-ClC₆H₄</td>
<td>97</td>
<td>95</td>
</tr>
<tr>
<td>d 4-F₆C₆H₄</td>
<td>93</td>
<td>94</td>
</tr>
<tr>
<td>e 3-MeC₆H₄</td>
<td>97</td>
<td>95</td>
</tr>
<tr>
<td>f 3,4-(OCH₂O)C₆H₃</td>
<td>97</td>
<td>95</td>
</tr>
<tr>
<td>g 2-naphthyl</td>
<td>94</td>
<td>97</td>
</tr>
<tr>
<td>h 1-naphthyl</td>
<td>90</td>
<td>95</td>
</tr>
<tr>
<td>i 2-furanyl</td>
<td>96</td>
<td>96</td>
</tr>
</tbody>
</table>

* Reaction conditions: Dimedone (1; 0.25 mmol), nitroalkene 2 (1.1 equiv), cat. A (0.5 mol%), Ag₂O (1 mol%), solvent (2.5 mL, 0.1 M).
* Yield of 3a after flash chromatography.
* The enantiomeric excess was determined by HPLC on a chiral stationary phase.
The absolute configuration of the tetrahydrobenzofuran was determined by X-ray crystal structure analysis of compound \(5a\) (Figure 2)\(^{18}\) in combination with a CD measurement and calculation (Figure 3).

The absolute configuration of the dihydropyran derivatives is based on an X-ray crystallographic analysis of compound \(5d\) (Figure 4).\(^{18}\)

This one-pot Michael addition/hydroalkoxylation protocol is proposed to proceed via two catalytic cycles (Scheme 6). The first organocatalytic cycle involves the synergistic activation of the 1,3-diketone \(1\) and the nitroalkene \(2\) by the bifunctional squaramide \(A\), where the squaramide moiety activates the nitroalkene \(2\) through the formation of hydrogen bonds to the nitro group and simultaneously the 1,3-diketone undergoes activation by the tertiary amine to promote the Michael addition from the \(\text{Re}\)-face. In the second catalytic cycle the silver forms a \(\pi\)-complex for the electrophilic activation of the internal alkyne to facilitate a 5-\(\text{exo}\)-dig or a 6-\(\text{endo}\)-dig annulation reaction leading to the vinylsilver intermediate. The latter undergoes a fast proto-deargentation to provide the desired product \(3, 5\) and \(7\).

In conclusion, we have developed a one-pot asymmetric Michael addition/hydroalkoxylation protocol by merging a bifunctional squaramide and a silver(1) salt at a very low...
Tetrahydrobenzofurans and Annulated Dihydropyrans; General Procedure

A mixture of 1,3-diketones 1, 4, or 6 (0.25 mmol), nitroalkene 2 (0.275 mmol, 1.1 equiv), catalyst A (0.5 mol%), and Ag₂O (1 mol%) in CH₂Cl₂ (2.5 mL, 0.1 M) was stirred at r.t. until the intermediate Michael adduct was completely converted as indicated by TLC. The crude product was directly subjected to flash chromatography on silica (n-pentane/Et₂O or n-pentane(CH₂Cl₂) to afford the corresponding product 3, 5, or 7.

(R)-(Z)-2-Benzylidene-6,6-dimethyl-3-(nitromethyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3a)

Compound 3a was isolated after flash chromatography (n-pentane/Et₂O, 1:1); yield: 75 mg (96%); colorless solid; mp 136–138 °C; [α]D (c = 0.2, CH₂Cl₂) = 90.1 (38, [CH₂C₆H₅]+), 77.1 (27, [C₆H₅]+).

HPLC: Daicel Chiralpak IC, n-heptane/i-ProOH (7:3), 1.0 mL/min, λ = 254 nm, tₘ (major) = 7.6 min, tₘ (minor) = 6.4 min; 96% ee.

IR (ATR): 2955, 2330, 2086, 1900, 1645, 1546, 1492, 1397, 1335, 1286, 1187, 1130, 1108, 1035, 979, 960, 915 cm⁻¹.


(R)-(Z)-2-(3-Methoxybenzylidene)-6,6-dimethyl-3-(nitromethyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3b)

Compound 3b was isolated after flash chromatography (n-pentane/Et₂O, 1:1); yield: 84 mg (98%); colorless solid; mp 127–129 °C; [α]D (c = 0.4, benzene) = 313.1 (1, [M]+), 267.1 (17, [M – NO₂]+), 253.0 (7, [M – CH₃NO₂]+), 90.1 (38, [CH₃C₆H₅]+), 77.1 (27, [C₆H₅]+).


Unless otherwise noted, all commercially available chemicals were used without purification. All solvents were distilled and purified according to standard procedures. Analytical TLC was performed using SIL G–25 UV254 from Macherey & Nagel (particle size 0.040–0.063 mm; 230–240 mesh, flash) and visualized with ultraviolet radiation at 254 nm. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded at ambient temperature on a Varian Innova 400 or Innova 600 spectrometer. Chemical shifts for ¹H NMR and ¹³C NMR spectra are reported in parts per million (ppm) and coupling constants in hertz (Hz). Standard abbreviations are used for the spin multiplicity (q = quintet). Optical rotations were measured on a PerkinElmer 241 polarimeter. Melting points were measured on a LLG MPM-H2 melting point instrument. Mass spectra were acquired on a Finnigan SSQ7000 (EI, 70 eV) spectrometer and on a ThermoFinnigan LCQ Deca XP plus (ESI) spectrometer and high-resolution ESI spectra on a ThermoFisher Scientific LTQ Orbitrap XL. Analytical HPLC was performed on an Allient 1100, Allient 1260, or Hewlett-Packard 1100 Series instrument using chiral stationary phases (Daicel Chiralpak IC, Daicel Chiralpak IA, Daicel Chiralpak AD, Daicel Chiralpak AS, Daicel Chiralpak IB columns). Analytical SFC was performed on a THAR-SFC MethodStation II with a WATERS 2998 Photodiode Array Detector using chiral stationary phases (Daicel Chiralcel OJ-H). Catalyst A and B, D–F and the nitroalkenes 2 were prepared according to known procedures.
\[ \text{Zylidene-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3f)} \]

**Compound 3f** was isolated after flash chromatography (n-pentane/EtOH, 1:2); yield: 106 mg (93%); colorless solid; mp 158–160 °C; 95% ee.

**HPLC:** Daicel Chiralpak LC, octadeclsilane (ODS-2, 5 μm), 10 μL/min, λ = 254 nm, tα (major) = 16.5 min, tβ (minor) = 17.4 min; 95% ee.

**HRMS:** m/z [M + Na]+ calcld for C₁₉H₁₈F₃NO₄Na: 430.1136; found: 430.1135.

**(R)-Z-2-(Benzoyl[d][1,3]dioxol-5-ylmethylene)-6,6-dimethyl-3-(nitrilmethyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3f)**

Compound 3f was isolated after flash chromatography (n-pentane/EtO, 1:2); yield: 106 mg (93%); colorless solid; mp 158–160 °C; 95% ee.

**HPLC:** Daicel Chiralpak LC, octadeclsilane (ODS-2, 5 μm), 10 μL/min, λ = 254 nm, tα (major) = 16.5 min, tβ (minor) = 17.4 min; 95% ee.

**HRMS:** m/z [M + Na]+ calcld for C₁₉H₁₈F₃NO₄Na: 430.1136; found: 430.1135.

**1H NMR (600 MHz, CDCl₃):** δ = 7.82 (m, 1 H, ArH), 6.72 (m, 1 H, ArH), 6.64 (m, 1 H, ArH), 5.36 (d, J = 2.1 Hz, 1 H, OC=CH), 5.27 (m, 2 H, OCH₂O), 4.31 (dd, J = 12.9, 6.4 Hz, 1 H, CHNO₂), 4.18 (dd, J = 13.0, 8.0 Hz, 1 H, CHNO₂), 3.94 (s, 1 H, CHCH₂), 1.92 (d, J = 16.0 Hz, 1 H, CH₂), 1.84 (d, J = 16.0 Hz, 1 H, CH₂), 1.56 (d, J = 17.9 Hz, 1 H, CH₂), 1.48 (d, J = 17.9 Hz, 1 H, CH₂), 0.63 (s, 3 H, CH₃), 0.57 (s, 3 H, CH₃).
Compound 3g was isolated after flash chromatography (n-pentane/Et2O, 1:2); yield: 85 mg (94%); colorless solid; mp 133–135 °C; Rf = 0.41 (n-pentane/Et2O, 1:1); [α]D20 +49.3 (c = 0.4, benzene).

HPLC: Daicel Chiralpak IA, n-heptane/i-PrOH (7:3), 0.7 mL/min, λ = 254 nm, tα (minor) = 11.1 min, tβ (major) = 9.7 min; 98% ee.

IR (ATR): 2960, 2876, 2081, 1988, 1649, 1554, 1466, 1374, 1292, 1228, 1167, 1089, 1049, 1016, 989, 920, 884, 816, 747, 700, 671 cm⁻¹.

1H NMR (600 MHz, CDCl3): δ = 7.05 (d, J = 1.6 Hz, 1 H, OCH), 6.59 (d, J = 3.3 Hz, 1 H, CH), 6.19 (dd, J = 3.3, 1.8 Hz, 1 H, CH), 5.61 (d, J = 2.3 Hz, 1 H, OC=CH), 4.29 (dd, J = 13.2, 6.1 Hz, 1 H, CH2NO2), 4.04 (dd, J = 13.2, 3.7 Hz, 1 H, CH2NO2), 3.79 (s, 1 H, CH3CH2), 1.90 (d, J = 16.0 Hz, 1 H, CH2), 1.82 (d, J = 16.0 Hz, 1 H, CH2), 1.71 (d, J = 17.8 Hz, 1 H, CH3), 1.63 (d, J = 17.8 Hz, 1 H, CH3), 0.62 (s, 3 H, CH3), 0.57 (s, 3 H, CH3).

13C NMR (151 MHz, CDCl3): δ = 191.6 (CO), 173.2 (Cq), 152.1 (Cq), 149.1 (Cq), 141.2 (OCH), 111.6 (CH), 111.3 (Cq), 109.5 (Cq), 96.2 (OC=CH), 74.8 (CH2NO2), 50.5 (CH2), 41.4 (CH2CH2), 36.2 (CH2), 33.2 (CH2CH3), 28.3 (CH3), 27.2 (CH3).

HPLC: Daicel Chiralpak IB, n-heptane/EtOH (7:3), 0.7 mL/min, λ = 254 nm, tα (minor) = 11.4 min, tβ (major) = 9.7 min; 98% ee.

IR (ATR): 2960, 2876, 2081, 1988, 1649, 1554, 1466, 1374, 1292, 1228, 1167, 1089, 1049, 1016, 989, 920, 884, 816, 747, 700, 671 cm⁻¹.

1H NMR (600 MHz, CDCl3): δ = 7.10 (d, J = 1.5 Hz, 1 H, OCH), 6.54 (d, J = 3.3 Hz, 1 H, CH), 6.19 (dd, J = 3.3, 1.8 Hz, 1 H, CH), 5.61 (d, J = 2.3 Hz, 1 H, OC=CH), 4.26 (dd, J = 13.2, 6.1 Hz, 1 H, CH2NO2), 4.03 (dd, J = 13.2, 3.7 Hz, 1 H, CH2NO2), 3.80 (s, 1 H, CH3CH2), 1.90 (d, J = 16.0 Hz, 1 H, CH2), 1.82 (d, J = 16.0 Hz, 1 H, CH2), 1.71 (d, J = 17.8 Hz, 1 H, CH3), 1.62 (d, J = 17.8 Hz, 1 H, CH3), 0.61 (s, 3 H, CH3), 0.58 (s, 3 H, CH3).

13C NMR (151 MHz, CDCl3): δ = 191.5 (CO), 173.2 (Cq), 152.1 (Cq), 149.1 (Cq), 141.2 (OCH), 111.6 (CH), 111.3 (Cq), 109.5 (Cq), 96.2 (OC=CH), 74.8 (CH2NO2), 50.5 (CH2), 41.4 (CH2CH2), 36.2 (CH2), 33.2 (CH2CH3), 28.3 (CH3), 27.2 (CH3).

HPLC: Daicel Chiralpak AS, n-heptane/EtOH (7:3), 0.7 mL/min, λ = 254 nm, tα (minor) = 10.7 min, tβ (major) = 11.7 min; 96% ee.

IR (ATR): 2960, 2876, 2081, 1988, 1649, 1547, 1384, 1217, 1176, 1051, 974, 841, 696 cm⁻¹.

**R**-4-(Nitromethyl)-2-phenyl-4,8-dihydro-2H-pyrano[3,4-b]pyran-5(6H)-one (5d)

Compound 5d was isolated after flash chromatography (n-pentane/EtO, 1:1 to 1:2); yield: 73 mg (98%); colorless solid; mp 175–177 °C; δ = 7.58–7.52 (m, 2 H, ArH), 7.48–7.45 (m, 2 H, ArH), 7.39–7.37 (m, 2 H, ArH), 7.05–7.03 (m, 3 H, H, ArCH(CH₃)₂), 4.25 (dt, J = 6.1 Hz, 1 H, CH₂), 3.67–3.63 (m, 1 H, H, CH₂CH), 3.43 (s, 2 H, CH₂), 3.39 (s, 3 H, CH₃).

IR (ATR): 3352, 2956, 2325, 2096, 1649, 1546, 1381, 1100, 958, 842, 752, 694 cm⁻¹.


**R**-1,3-Dimethyl-5-(nitromethyl)-7-phenyl-1,5-dihydro-2H-pyrano[2,3-d]pyrimidin-4,4(4H)-dione (5d)

Compound 5d was isolated after flash chromatography (n-pentane/CH₂Cl₂, 1:4) to pure CH₂Cl₂; yield: 227 mg (94%); bright yellow solid; mp 224–226 °C; δ = 2.62 (CH₂Cl₂/CH₂/20.1); δ [α]D₂⁴ +144.5 (c = 0.4, CHCl₃).

HPLC: Daicel Chiralpak IA, n-heptane/i-ProH (7:3), 0.7 mL/min, λ = 254 nm, t₁ (minor) = 14.2 min, t₂ (major) = 11.9 min; 90% ee.

IR (ATR): 2954, 2324, 2107, 1645, 1476, 1375, 1203, 1003, 753, 690 cm⁻¹.

**R**-3,5-Dimethyl-6-isopropyl-3-(nitromethyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (7b)

Compound 7b was isolated after flash chromatography (n-pentane/EtO, 1:1 to 1:2); yield: 67 mg (82%); colorless solid; mp 141–143 °C; δ = 2.31 (CH₂Cl₂/CH₂/20.1); δ [α]D²⁴ +52.7 (c = 0.5, benzene).

HPLC: Daicel Chiralpak IC, n-heptane/i-ProH (7:3), 0.5 mL/min, λ = 254 nm, t₁ (minor) = 27.5 min, t₂ (major) = 29.9 min; t₃ (major) = 18.2 min; 94% ee; dr = 1:1.
(R)-(Z)-2-Benzylidene-3-(nitromethyl)-6-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (7c)

Compound 7c was isolated after flash chromatography (n-pentane/EtO, 1:1); yield: 86 mg (98%); colorless solid; mp 143–145 °C; [α]D 24 +64.8 (c = 0.5, benzene).

HPLC: Daicel Chiralpak AD, n-heptane/EtOH (1:1), 1.0 mL/min, λ = 254 nm, tR (minor) = 9.2 min, tR (major) = 17.1 min; tR (minor) = 11.0 min, tR (major) = 13.9 min; 94% ee, dr = 1:1.

IR (ATR): 3027, 2305, 2102, 1910, 1735, 1647, 1546, 1397, 1204, 1002, 1170 cm–1.


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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561468.

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(18) CCDC 1474771 (5a) and CCDC 1474975 (5d) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.  