

# Construction of Quaternary Stereocenters by Nickel-Catalysis of Asymmetric Michael Reactions

Jens Christoffers,<sup>\*,[a]</sup> Ulrich Rößler,<sup>[a]</sup> and Thomas Werner<sup>[a]</sup>

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Quaternary stereocenters were constructed with an enantioselectivity of up to 91% *ee* under aerobic conditions and at ambient temperature in the Michael reaction of  $\beta$ -dicarbonyl

compounds and methyl vinyl ketone with  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and optically active *trans*-1,2-diaminocyclohexane as a chiral catalyst.

## Introduction

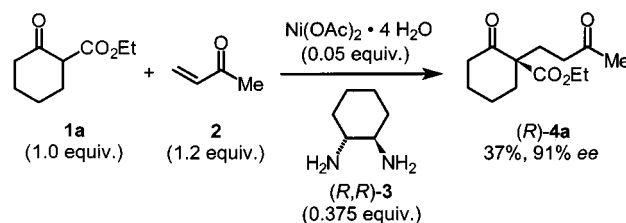
The Michael reaction is one of the most important C–C bond forming reactions and is usually catalyzed by a strong Brønsted base.<sup>[1]</sup> However, under basic reaction conditions the chemoselectivity of this method suffers from a number of drawbacks, namely side reactions and subsequent processes such as aldol-cyclizations and retro-Claisen type decompositions. These disadvantages can be avoided by the use of transition metal catalysts which, moreover, allow an asymmetric catalysis of this reaction by the application of chiral ligands.<sup>[2,3]</sup>

Shibasaki et al. recently introduced the excellent heterobimetallic LSB-catalyst for the Michael reaction of 1,3-dicarbonyl compounds with  $\alpha,\beta$ -unsaturated ketones. However, the reaction conditions are strongly basic and therefore often lead to the above-mentioned disadvantages.<sup>[4]</sup> The use of a neutral transition metal catalyst has been investigated with varying degrees of success by a number of groups in the past few years: Brunner et al. introduced  $\text{Co}(\text{acac})_2$  together with an optically active diamine,<sup>[5]</sup> Desimoni et al. reported on chiral copper catalysts derived from natural  $\alpha$ -amino acids,<sup>[6]</sup> and Pfaltz et al. presented chiral tetradentate oxazolines as ligands for  $\text{Co}^{\text{II}}$ -catalyzed asymmetric Michael reactions.<sup>[7]</sup> All these methods, however, suffer either from the need for anhydrous reaction conditions, low reaction temperatures or low yields.

We are searching for an alternative to Shibasaki's bimetallic catalysis of the Michael reaction,<sup>[4]</sup> which avoids basic reaction conditions, and we have already reported on this subject several times.<sup>[8]</sup> It is our strategy to screen a large number of metal complexes, generated in situ by the combination of many ligands with metal salts, for their activity and selectivity. Herein we wish to report on a new  $\text{Ni}^{\text{II}}$ -catalyzed asymmetric Michael reaction under aerobic reaction conditions as an alternative to, and in completion of, the existing procedures.

## Results and Discussion

In the course of our search for a chiral catalyst we have found a combination of metal salt and chiral ligand which catalyzes the conversion of Michael donor **1a** with methyl vinyl ketone (MVK, **2**) to give the product **4a** with 91% *ee* (Scheme 1). In a typical procedure one equiv. of **1a** and 1.2 equiv. of **2** in  $\text{CHCl}_3$  under aerobic conditions and at ambient temperature give the product **4a** with the above mentioned selectivity and in 37% yield using a catalyst generated in situ from 0.05 equiv.  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and 0.375 equiv. (*R,R*)-*trans*-1,2-diaminocyclohexane (**3**) (Scheme 1). A higher selectivity in the synthesis of **4a** (93% *ee*) has been achieved so far only at  $-50^\circ\text{C}$  by use of the La-Na-BINOL complex (LSB) according to Shibasaki et al.<sup>[9]</sup> Koga and co-workers achieved 90% *ee* at  $-100^\circ\text{C}$  by the use of a chiral auxiliary and a stoichiometric amount of a base.<sup>[10]</sup> Consequently, we report herein on the first enantioselective preparation of **4a** exceeding 90% *ee* at room temperature and without anhydrous conditions.

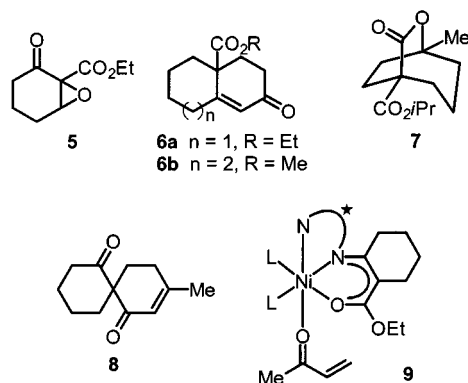


Scheme 1

Our methodology is a case of ligand-accelerated catalysis, since the nickel salt or ligand **3** alone show no catalytic activity (after three days the conversion is less than 10%). Regarding the donor, 0.05 equiv. Ni salt were applied. The selectivity was strongly dependent on the ligand-to-Ni ratio and was found to be optimal at 7.5:1 with 91% *ee*. Different ligand-to-Ni ratios gave lower selectivities (e.g. 82% *ee* at 1:1, and 70% *ee* at 20:1). The use of other solvents ( $\text{CH}_2\text{Cl}_2$ : 88% *ee*,  $\text{MeOtBu}$ : 81% *ee*) or the variation of the temperature ( $0^\circ\text{C}$ : 88% *ee*,  $40^\circ\text{C}$ : 89% *ee*) gave no further improvement. Below  $0^\circ\text{C}$  the turnover rate was very low. The reaction tolerates air and moisture (addition of water does not lower the selectivity); however, an excess of the acceptor had to be added in order to minimize formation of the by-

<sup>[a]</sup> Technische Universität Berlin, Institut für Organische Chemie, Sekretariat C 3, Straße des 17. Juni 135, D-10623 Berlin, Germany, Fax: (internat.) + 49-30/723-1233, E-mail: jchr@wap0105.chem.tu-berlin.de

product **5**<sup>[11]</sup> (Scheme 2). Both enantiomers of the diamine **3** can be obtained in large quantities by simple resolution of the racemate with tartaric acid.<sup>[12]</sup> Ligand **3** (0.375 equiv. based on **1a**) does not, however, act catalytically, but as an auxiliary. Initial results show that **3** can be partly recovered after workup.



Scheme 2

We tried to transfer the result obtained for **1a** to other Michael donor molecules. The selectivities obtained in the conversion of cyclic  $\beta$ -keto esters and  $\beta$ -diketones **1b** to **1i** are lower (Table 1), but in case of the *iso*-butyl ester **4e** (74% *ee*) still significant. However, it is remarkable that the use of a different alcohol residue at the cyclic keto esters may invert the selectivity: compound **4e** was obtained as the (*S*)-enantiomer, while all other five-membered ring products yielded the (*R*)-compound as the major isomer.

Table 1. Asymmetric Ni<sup>II</sup>-catalyzed Michael reaction with *trans*-1,2-diaminocyclohexane as auxiliary

| Starting material | Product <sup>[a]</sup>    | <i>ee</i> / %     |
|-------------------|---------------------------|-------------------|
|                   | <b>1a</b>                 |                   |
|                   | ( <i>R</i> )- <b>4a</b>   | 91 <sup>[b]</sup> |
|                   | <b>1b</b> R = Me          |                   |
|                   | ( <i>R</i> )- <b>4b</b>   | 31                |
|                   | <b>1c</b> R = Et          |                   |
|                   | ( <i>R</i> )- <b>4c</b>   | 40                |
|                   | <b>1d</b> R = <i>i</i> Pr |                   |
|                   | ( <i>R</i> )- <b>4d</b>   | 6                 |
|                   | <b>1e</b> R = <i>i</i> Bu |                   |
|                   | ( <i>S</i> )- <b>4e</b>   | 74                |
|                   | <b>1f</b> R = Bn          |                   |
|                   | ( <i>R</i> )- <b>4f</b>   | 21                |
|                   | <b>1g</b>                 |                   |
|                   | <b>4g</b>                 | 2                 |
|                   | <b>1h</b> n = 1           |                   |
|                   | <b>4h</b>                 | 7                 |
|                   | <b>1i</b> n = 2           |                   |
|                   | <b>4i</b>                 | 41                |

<sup>[a]</sup> Use of (*R,R*)-**3**. – <sup>[b]</sup> Use of (*S,S*)-**3** yields (*S*)-(*S*)-**4a** with 91% *ee*.

Details of the preparation of **4b** to **4i** are contained in the Experimental Section. Selectivities have been analyzed by chiral GC and configurations have been assigned by comparison with literature values.<sup>[13]</sup> In the case of **4a** the exact enantiomeric ratio was double checked after conver-

sion into compound **6a**.<sup>[14]</sup> In case of **4e** and **4f**, selectivities were determined after transesterification with DMAP (**4c** from **4e**, **4b** from **4f**); the configurations of compounds **4b**–**4f** were correlated by pairs. The selectivities of compounds **4d**, **4g** and **4i** were determined after derivatization to the corresponding bicyclic aldol products with *conc.* H<sub>2</sub>SO<sub>4</sub>: **7**<sup>[15]</sup> from **4d**, **6b**<sup>[16]</sup> from **4g**, and **8** from **4i**<sup>[17]</sup> (Scheme 2).

With regard to the mechanism of the overall conversion, we can only speculate at the moment. We were, however, able to show that the primary diamine **3** reacts rapidly with donor **1a** in the presence of a catalytic amount of nickel acetate to form an enamine,<sup>[18]</sup> which could coordinate to a nickel center as a tridentate ligand as shown in structure **9** (Scheme 2). By this coordination of the derived donor to the nickel atom the planar dienone system is subject to diastereofacial differentiation. Moreover, the acceptor **2** is activated by coordination to the Lewis acidic metal center. A detailed experimental study of a model intermediate **9** is the subject of present work in our laboratory. Moreover, we are making great efforts to improve the so far moderate yields, to minimize the amount of optically active diamine and to improve the enantioselectivities of the donors **1b** to **1i**.

## Conclusion

Quaternary stereocenters can be constructed enantioselectively by Michael reactions of cyclic  $\beta$ -dicarbonyl compounds with methyl vinyl ketone. The chiral catalyst is generated in situ by combination of Ni(OAc)<sub>2</sub> · 4H<sub>2</sub>O with optically active *trans*-1,2-diaminocyclohexane. In at least one case the selectivity exceeds 90% *ee*. Importantly, this result was obtained at ambient temperature under neutral reaction conditions and without exclusion of air and moisture, which is a significant improvement on current procedures. However, the isolated yield of the product did not exceed the amount of applied chiral diamine.

## Experimental Section

**General:** Column chromatography was accomplished with Merck silica gel (Type 60, 0.063–0.200 mm) using *tert*-butyl methyl ether (MTB) and hexanes (PE) as solvents. – <sup>1</sup>H NMR spectra were recorded with Bruker AM 400 (400 MHz) and Bruker AC 200 (200 MHz). – <sup>13</sup>C NMR spectra were recorded with a Bruker AC 200 (50 MHz), assignments were made using DEPT experiments. – MS spectra were obtained with a Varian MAT 711 and MAT 955Q (high resolution). – IR spectra were recorded with a Nicolet Magna IR 750. – Elemental analyses were obtained with an Analytik Jena Vario EL. – Optical rotations were measured with a Perkin–Elmer polarimeter 341. – Chiral GC analysis was performed with a Packard 437A with FI detection, a Shimadzu C-R6A integrator and a Macherey–Nagel column FS-LIPODEX E (25 m, 0.25 mm) with nitrogen carrier gas.

Starting materials **1a**, **1b**, **1c**, **1g** and **2a** were commercially available and used as purchased. Compounds **1e**<sup>[19]</sup> and **3** (both enantiomers)<sup>[12]</sup> were prepared according to literature protocols. The synthesis of racemates of **4a**, **4c**, **4e**, **4g**, and **4h**<sup>[20]</sup> and of by-product

**5**<sup>[11]</sup> as well as their analytical and spectroscopic data have been reported previously.

**Isopropyl 2-Oxocyclopentanecarboxylate (1d):** Oxo ester **1c** (10.9 g, 69.8 mmol) and DMAP (426 mg, 3.49 mmol) were dissolved in *i*PrOH (39.6 g, 659 mmol) and heated to reflux for 12 h. All volatile materials were removed in vacuo and the residue redissolved in *i*PrOH (42.1 g, 701 mmol). The mixture was heated to reflux again for 15 h, then all volatile materials were removed in vacuo and the residue fractionated in high vacuum through a 10 cm Vigreux column to yield the title compound **1d** as a colorless liquid (9.71 g, 57.0 mmol, 81%), bp. 53 °C/0.1 mm. – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 1.22 (d, *J* = 6.3 Hz, 3 H), 1.24 (d, *J* = 6.3 Hz, 3 H), 1.71–1.94 (m, 1 H), 2.01–2.17 (m, 1 H), 2.19–2.36 (m, 4 H), 3.08 (t, *J* = 8.9 Hz, 1 H), 5.02 (heptet, *J* = 6.3 Hz, 1 H). – <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, CDCl<sub>3</sub>): δ = 20.6 (CH<sub>2</sub>), 21.3 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 27.0 (CH<sub>2</sub>), 37.7 (CH<sub>2</sub>), 54.6 (CH), 68.4 (CH), 168.7 (C), 212.1 (C). – MS (EI, 70 eV); *m/z* (%): 170 (21) [M<sup>+</sup>], 142 (20), 111 (100), 100 (74), 73 (44), 55 (46). – IR (ATR):  $\tilde{\nu}$  = 2980 (s), 1754 (vs), 1721 (vs), 1374 (s), 1297 (s), 1256 (s), 1193 (s), 1146 (s), 1105 (vs) cm<sup>−1</sup>. – C<sub>9</sub>H<sub>14</sub>O<sub>3</sub> (170.2): calcd. C 63.51, H 8.29; found C 62.78, H 8.06. – HRMS: calcd. 170.0943; found 170.0945.

**Benzyl 2-Oxocyclopentanecarboxylate (1f):** Oxo ester **1b** (9.93 g, 69.8 mmol), benzyl alcohol (8.31 g, 76.8 mmol), DMAP (427 mg, 3.50 mmol), and cyclohexane (50 mL) were heated to reflux in a Dean–Stark trap for 20 h. The solvent was removed by rotary evaporation and the residue vacuum distilled through a 10 cm Vigreux column (bp. 150 °C/0.1 mm) to yield the title compound **1f** (13.5 g, 61.9 mmol, 89%) as a colorless oil. – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 1.71–1.88 (m, 1 H), 2.03–2.22 (m, 1 H), 2.25–2.57 (m, 4 H), 3.21 (t, *J* = 9.1 Hz, 1 H), 5.18 (s, 2 H), 7.33–7.38 (m, 5 H). – <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, CDCl<sub>3</sub>): δ = 20.7 (CH<sub>2</sub>), 27.2 (CH<sub>2</sub>), 37.9 (CH<sub>2</sub>), 54.6 (CH), 66.8 (CH<sub>2</sub>), 127.9 (CH), 128.1 (CH), 128.4 (CH), 135.5 (C), 169.1 (C), 211.9 (C). – MS (EI, 70 eV); *m/z* (%): 218 (23) [M<sup>+</sup>], 190 (59), 91 (100), 84 (88), 65 (44). – IR (ATR):  $\tilde{\nu}$  = 1753 (vs), 1723 (vs), 1295 (s), 1253 (s), 1182 (s), 1157 (s), 1109 (s), 749 (s), 698 (s) cm<sup>−1</sup>. – C<sub>13</sub>H<sub>14</sub>O<sub>3</sub> (218.3): calcd. C 71.50, H 6.47; found C 71.51, H 6.46. – HRMS: calcd. 218.0943; found 218.0945.

**General Procedure 1 (GP1).** – **Iron(III)-Catalyzed Synthesis of Racemates:** A mixture of donor **1** (1.00 equiv.), MVK (**2**) (1.20 equiv.) and FeCl<sub>3</sub> · 6H<sub>2</sub>O (0.0500 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (0.1 mL/mmol donor **1**) or without solvent was stirred at ambient temperature for ca. 18 h. The mixture was directly chromatographed on SiO<sub>2</sub> (PE/MTB 1:1) to yield the Michael reaction product **4** in 75–95% yield.

**rac-Methyl 2-Oxo-1-(3-oxobutyl)cyclopentanecarboxylate (4b):** Following GP1, oxo ester **1b** (485 mg, 3.41 mmol), MVK (**2**) (359 mg, 5.12 mmol) and FeCl<sub>3</sub> · 6H<sub>2</sub>O (46.1 mg, 0.17 mmol) were reacted without additional solvent to yield the title compound **4b** after chromatography (SiO<sub>2</sub>, PE/MTB 1:1, *R*<sub>f</sub> = 0.26) as a colorless oil (651 mg, 3.07 mmol, 90%). – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 1.75–2.12 (m, 5 H), 2.07 (s, 3 H), 2.23–2.48 (m, 4 H), 2.61 (ddd, *J* = 17.9 Hz, *J* = 9.4 Hz, *J* = 6.0 Hz, 1 H), 3.64 (s, 3 H). – <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, CDCl<sub>3</sub>): δ = 19.4 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 29.8 (CH<sub>3</sub>), 34.1 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 38.7 (CH<sub>2</sub>), 52.4 (CH<sub>3</sub>), 58.8 (C), 171.7 (C), 207.6 (C), 214.6 (C). – MS (EI, 70 eV); *m/z* (%): 212 (6) [M<sup>+</sup>], 184 (100), 142 (39), 137 (43), 125 (76), 111 (47), 110 (56), 97 (49). – IR (ATR):  $\tilde{\nu}$  = 1748 (s), 1715 (vs), 1165 (s), 1117 (m) cm<sup>−1</sup>. – C<sub>11</sub>H<sub>16</sub>O<sub>4</sub> (212.3): calcd. C 62.25, H 7.60; found C 62.19, H 7.78. – HRMS: calcd. 212.1049; found 212.1044.

**rac-Isopropyl 2-Oxo-1-(3-oxobutyl)cyclopentanecarboxylate (4d):** Following GP1, oxo ester **1d** (560 mg, 3.29 mmol), MVK (**2**) (349 mg, 4.94 mmol) and FeCl<sub>3</sub> · 6H<sub>2</sub>O (44 mg, 0.17 mmol) were

reacted without additional solvent to yield the title compound **4d** (563 mg, 2.34 mmol, 71%) after removal of all volatile materials in vacuo and Kugelrohr distillation of the residue (oven temp. 150 °C, *p* = 0.1 mm) as a colorless oil. – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 1.19 (d, *J* = 6.3 Hz, 3 H), 1.21 (d, *J* = 6.2 Hz, 3 H), 1.77–2.16 (m, 4 H), 2.10 (s, 3 H), 2.19–2.51 (m, 5 H), 2.70 (ddd, *J* = 17.7 Hz, *J* = 9.6 Hz, *J* = 5.8 Hz, 1 H), 4.98 (heptet, *J* = 6.3 Hz, 1 H). – <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, CDCl<sub>3</sub>): δ = 19.5 (CH<sub>2</sub>), 21.5 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 26.9 (CH<sub>2</sub>), 29.9 (CH<sub>3</sub>), 34.4 (CH<sub>2</sub>), 37.9 (CH<sub>2</sub>), 38.8 (CH<sub>2</sub>), 58.9 (C), 68.9 (CH), 170.9 (C), 207.9 (C), 214.9 (C). – MS (EI, 70 eV); *m/z* (%): 240 (8) [M<sup>+</sup>], 212 (42), 170 (74), 152 (38), 137 (77), 128 (72), 125 (100). – IR (ATR):  $\tilde{\nu}$  = 1748 (s), 1717 (vs), 1168 (s), 1105 (s) cm<sup>−1</sup>. – C<sub>13</sub>H<sub>20</sub>O<sub>4</sub> (240.3): calcd. C 64.98, H 8.39; found C 64.84, H 8.58. – HRMS: calcd. 240.1362; found 240.1362.

**rac-Benzyl 2-Oxo-1-(3-oxobutyl)cyclopentanecarboxylate (4f):** Following GP1, oxo ester **1f** (546 mg, 2.50 mmol), MVK (**2**) (210 mg, 3.00 mmol) and FeCl<sub>3</sub> · 6H<sub>2</sub>O (33.8 mg, 0.13 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) were reacted to yield the title compound **4f** after chromatography (SiO<sub>2</sub>, PE/MTB 1:1, *R*<sub>f</sub> = 0.23) as a colorless oil (643 mg, 2.23 mmol, 89%). – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.84–2.04 (m, 4 H), 2.07 (s, 3 H), 2.09–2.18 (m, 1 H), 2.22–2.50 (m, 4 H), 2.64 (ddd, *J* = 17.9 Hz, *J* = 9.7 Hz, *J* = 5.7 Hz, 1 H), 5.12 (d, *J* = 12.4 Hz, 1 H), 5.16 (d, *J* = 12.4 Hz, 1 H), 7.26–7.38 (m, 5 H). – <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, CDCl<sub>3</sub>): δ = 19.1 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 29.3 (CH<sub>3</sub>), 33.6 (CH<sub>2</sub>), 37.4 (CH<sub>2</sub>), 38.2 (CH<sub>2</sub>), 58.4 (C), 66.4 (CH<sub>2</sub>), 127.4 (2 CH), 127.8 (CH), 128.1 (2 CH), 135.1 (C), 170.6 (C), 207.0 (C), 213.9 (C). – MS (EI, 70 eV); *m/z* (%): 288 (1) [M<sup>+</sup>], 179 (28), 169 (77), 154 (28), 91 (100), 65 (29). – IR (ATR):  $\tilde{\nu}$  = 1748 (s), 1716 (vs), 1162 (s) cm<sup>−1</sup>. – C<sub>17</sub>H<sub>20</sub>O<sub>4</sub> (288.3): calcd. C 70.81, H 6.99; found C 70.73, H 7.01. – HRMS: calcd. 288.1362; found 288.1365.

**rac-2-Acetyl-2-(3-oxobutyl)cyclohexanone (4i):** Following GP1, diketone **1i** (350 mg, 2.50 mmol), MVK (**2**) (210 mg, 3.00 mmol) and FeCl<sub>3</sub> · 6H<sub>2</sub>O (33.8 mg, 0.13 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) were reacted to yield the title compound **4i** after chromatography (SiO<sub>2</sub>, PE/MTB 1:1, *R*<sub>f</sub> = 0.17) as a colorless oil (413 mg, 1.96 mmol, 79%). – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.46–2.08 (m, 7 H), 2.10 (s, 3 H), 2.12 (s, 3 H), 2.26–2.50 (m, 5 H). – <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, CDCl<sub>3</sub>): δ = 21.9 (CH<sub>2</sub>), 26.0 (CH<sub>3</sub>), 26.9 (CH<sub>2</sub>), 27.0 (CH<sub>2</sub>), 29.8 (CH<sub>3</sub>), 34.7 (CH<sub>2</sub>), 38.1 (CH<sub>2</sub>), 41.1 (CH<sub>2</sub>), 66.4 (C), 207.5 (C), 207.6 (C), 209.9 (C). – MS (EI, 70 eV); *m/z* (%): 210 (2) [M<sup>+</sup>], 168 (53), 150 (32), 111 (100), 98 (41). – IR (ATR):  $\tilde{\nu}$  = 1713 (vs), 1694 (vs), 1358 (s), 1165 (s) cm<sup>−1</sup>. – C<sub>12</sub>H<sub>18</sub>O<sub>3</sub> (210.3): calcd. C 68.55, H 8.63; found C 68.02, H 8.63. – HRMS: calcd. 210.1255; found 210.1255.

**General Procedure 2 (GP2).** – **Asymmetric Nickel(II) Catalysis:** Ni(OAc)<sub>2</sub> · 4H<sub>2</sub>O (0.05 equiv.) was added to a solution of (*R,R*)-**3** (0.375 equiv.) in CHCl<sub>3</sub> (1.0 mL/mmol donor **1**) and the mixture was stirred for 1 h at 23 °C. Donor **1** (1.00 equiv.), and after further stirring for 2 h at 23 °C, MVK **2** (1.20 equiv.) were added. After stirring for 16 h at 23 °C all volatile materials were removed in vacuo and the residue was chromatographed on SiO<sub>2</sub> (PE/MTB 1:1).

**(R)-(+)-Ethyl 2-Oxo-1-(3-oxobutyl)cyclohexanecarboxylate (R-4a):** According to GP2, donor **1a** (1.97 g, 11.6 mmol), acceptor **2** (974 mg, 13.9 mmol), diamine (*R,R*)-**3** (496 mg, 4.34 mmol) and Ni(OAc)<sub>2</sub> · 4H<sub>2</sub>O (144 mg, 0.58 mmol) were reacted. After chromatography on SiO<sub>2</sub> (PE/MTB 1:1), donor **1a** was partly recovered in a first fraction (528 mg, 3.10 mmol, 27%, *R*<sub>f</sub> = 0.55). Fraction 2 contained product (*R*)-**4a** (colorless oil, 1.04 g, 4.33 mmol, 37% reg. **1a**, 100% based on **3**, *R*<sub>f</sub> = 0.27). Finally, a third fraction was eluted



containing compound **5** (colorless oil, 201 mg, 1.09 mmol, 9% reg. **1a**,  $R_f = 0.21$ ).

Compound **4a** was analyzed by chiral GC: isotherm elution at 115 °C,  $t(S) = 114.2$  min,  $t(R) = 120.8$  min. Enantiomeric excess was checked after conversion into compound **6a** according to GP3. Optical rotation of a 91% *ee* material:  $[\alpha]_D^{23} = +88.5$  ( $c = 3.3$ ,  $\text{CHCl}_3$ ),  $[\alpha]_D^{378} = +93.3$  ( $c = 6.9$ ,  $\text{CCl}_4$ ).

Use of diamine (*S,S*)-**3** yielded product (*S*)-**4a** (89.1 mg, 0.37 mmol, 37%) from **1a** (170 mg, 1.00 mmol) with 91% *ee*. –  $[\alpha]_D^{23} = -87.9$  ( $c = 3.4$ ,  $\text{CHCl}_3$ ),  $[\alpha]_D^{378} = -91.3$  ( $c = 6.9$ ,  $\text{CCl}_4$ ).

**(R)-(-)-Methyl 2-Oxo-1-(3-oxobutyl)cyclopentanecarboxylate (R-4b):** According to GP2, donor **1b** (574 mg, 4.04 mmol), acceptor **2** (340 mg, 4.85 mmol), diamine (*R,R*)-**3** (214 mg, 1.87 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (50.3 mg, 0.202 mmol) were reacted to yield compound (*R*)-**4b** (305 mg, 1.44 mmol, 36%) after chromatography on  $\text{SiO}_2$  (PE/MTB 1:1,  $R_f = 0.16$ ). Chiral GC: isotherm elution at 115 °C:  $t(S) = 78.1$  min,  $t(R) = 81.2$  min. Optical rotation of a 31% *ee* material:  $[\alpha]_D^{23} = -5.6$  ( $c = 9.9$ ,  $\text{CHCl}_3$ ).

**(R)-(-)-Ethyl 2-Oxo-1-(3-oxobutyl)cyclopentanecarboxylate (R-4c):** According to GP2, donor **1c** (125 mg, 0.80 mmol), acceptor **2** (67.9 mg, 1.00 mmol), diamine (*R,R*)-**3** (35.1 mg, 0.31 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (10.0 mg, 0.040 mmol) were reacted to yield compound (*R*)-**4c** (73.0 mg, 0.32 mmol, 40%) after chromatography on  $\text{SiO}_2$  (PE/MTB 1:1,  $R_f = 0.25$ ). Chiral GC: isotherm elution at 130 °C:  $t(S) = 32.9$  min,  $t(R) = 34.7$  min. Optical rotation of a 40% *ee* material:  $[\alpha]_D^{23} = -6.9$  ( $c = 5.3$ ,  $\text{CHCl}_3$ ).

**(R)-(+)-Isopropyl 2-Oxo-1-(3-oxobutyl)cyclopentanecarboxylate (R-4d):** According to GP2, donor **1d** (137 mg, 0.81 mmol), acceptor **2** (67.8 mg, 0.967 mmol), diamine (*R,R*)-**3** (34.6 mg, 0.30 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (10.1 mg, 0.041 mmol) were reacted to yield compound (*R*)-**4d** (102 mg, 0.42 mmol, 53%) after chromatography on  $\text{SiO}_2$  (PE/MTB 1:1,  $R_f = 0.24$ ). Enantiomeric excess of (*R*)-**4d** was determined after conversion into compound **7** according to GP3. Optical rotation of a 6% *ee* material:  $[\alpha]_D^{23} = +0.2$  ( $c = 11.4$ ,  $\text{CHCl}_3$ ).

**(S)-(-)-Isobutyl 2-Oxo-1-(3-oxobutyl)cyclopentanecarboxylate (S-4e):** According to GP2, donor **1e** (297 mg, 1.61 mmol), acceptor **2** (136 mg, 1.94 mmol), diamine (*R,R*)-**3** (85.6 mg, 0.749 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (20.1 mg, 0.081 mmol) were reacted to yield compound (*S*)-**4e** (126 mg, 0.50 mmol, 31%) after chromatography on  $\text{SiO}_2$  (PE/MTB 1:1,  $R_f = 0.24$ ). The enantiomeric excess of (*S*)-**4e** was determined after transesterification to (*S*)-**4c** according to GP4. Optical rotation of a 74% *ee* material:  $[\alpha]_D^{23} = -2.1$  ( $c = 6.1$ ,  $\text{CHCl}_3$ ).

**(R)-(-)-Benzyl 2-Oxo-1-(3-oxobutyl)cyclopentanecarboxylate (R-4f):** According to GP2, donor **1f** (218 mg, 1.00 mmol), acceptor **2** (84.1 mg, 1.20 mmol), diamine (*R,R*)-**3** (42.8 mg, 0.375 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (12.4 mg, 0.050 mmol) were reacted to yield compound (*R*)-**4f** (225 mg, 0.78 mmol, 78%) after chromatography on  $\text{SiO}_2$  (PE/MTB 1:1,  $R_f = 0.23$ ). The enantiomeric excess of (*R*)-**4f** was determined after transesterification to (*R*)-**4b** according to GP4. Optical rotation of a 21% *ee* material:  $[\alpha]_D^{23} = -0.5$  ( $c = 44.1$ ,  $\text{CHCl}_3$ ).

**(-)-Methyl 2-Oxo-1-(3-oxobutyl)cycloheptanecarboxylate (4g):** According to GP2, donor **1g** (137 mg, 0.81 mmol), acceptor **2** (67.8 mg, 0.97 mmol), diamine (*R,R*)-**3** (34.7 mg, 0.304 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (10.1 mg, 0.041 mmol) were reacted to yield compound **4g** (27.0 mg, 0.11 mmol, 14%) after chromatography on  $\text{SiO}_2$  (PE/MTB 1:1,  $R_f = 0.18$ ). Enantiomeric excess of **4g** was de-

termined after conversion into compound **6b** according to GP3. Optical rotation of a 2% *ee* material:  $[\alpha]_D^{23} = -2.3$  ( $c = 7.1$ ,  $\text{CHCl}_3$ ).

**(-)-2-Acetyl-2-(3-oxobutyl)cyclopentanone (4h):** According to GP2, donor **1h** (407 mg, 3.23 mmol), acceptor **2** (271 mg, 3.87 mmol), diamine (*R,R*)-**3** (138 mg, 1.21 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (40.1 mg, 0.16 mmol) were reacted to yield compound **4h** (263 mg, 1.34 mmol, 41%) after chromatography on  $\text{SiO}_2$  (PE/MTB 1:1,  $R_f = 0.12$ ). Chiral GC: isotherm elution at 115 °C:  $t_1 = 90.5$  min,  $t_2 = 100.2$  min. Optical rotation of a 7% *ee* material:  $[\alpha]_D^{23} = -10.6$  ( $c = 4.1$ ,  $\text{CHCl}_3$ ).

**(+)-2-Acetyl-2-(3-oxobutyl)cyclohexanone (4i):** According to GP2, donor **1i** (140 mg, 1.00 mmol), acceptor **2** (84.1 mg, 1.20 mmol), diamine (*R,R*)-**3** (42.8 mg, 0.375 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (12.4 mg, 0.050 mmol) were reacted to yield compound **4i** (120 mg, 0.57 mmol, 57%) after chromatography on  $\text{SiO}_2$  (PE/MTB 1:1,  $R_f = 0.17$ ). Enantiomeric excess was determined after conversion into compound **8** according to GP3. Optical rotation of a 41% *ee* material:  $[\alpha]_D^{23} = +66.4$  ( $c = 12.2$ ,  $\text{CHCl}_3$ ),  $[\alpha]_D^{378} = +63.8$  ( $c = 15.6$ ,  $\text{C}_6\text{H}_6$ ).

**General Procedure 3 (GP3). – Derivatization of Compounds 4 with conc.  $\text{H}_2\text{SO}_4$ :** Compound **4** was dissolved in a threefold volume of conc.  $\text{H}_2\text{SO}_4$  and stirred for ca. 18 h at ambient temperature (at 50 °C for compound **4a**). Ice was added to the mixture, and the resulting aqueous solution was extracted with MTB. After washing with  $\text{NaHCO}_3$  (saturated aqueous solution) and drying ( $\text{Na}_2\text{SO}_4$ ) the organic extract was evaporated and the residue chromatographed on  $\text{SiO}_2$  (PE/MTB 1:1).

**Ethyl Bicyclo[4.4.0]dec-1-en-3-one-6-carboxylate (6a):** According to GP3, compound **4a** (250 mg, 1.04 mmol) was converted into **6a** (colorless oil, 103 mg, 0.46 mmol, 45%,  $R_f = 0.31$ ). Chiral GC: gradient elution from 115 °C to 160 °C with  $0.5 \text{ K min}^{-1}$ ,  $t(S) = 58.9$  min,  $t(R) = 62.7$  min. –  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.25$  (t,  $J = 7.2$  Hz, 3 H), 1.30–1.47 (m, 2 H), 1.68–1.98 (m, 3 H), 1.24–2.46 (m, 7 H), 4.20 (q,  $J = 7.1$  Hz, 2 H), 5.91 (s, 1 H). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.2$  ( $\text{CH}_3$ ), 23.2 ( $\text{CH}_2$ ), 26.5 ( $\text{CH}_2$ ), 34.2 ( $\text{CH}_2$ ), 34.7 ( $\text{CH}_2$ ), 34.8 ( $\text{CH}_2$ ), 38.4 ( $\text{CH}_2$ ), 48.9 (C), 61.4 ( $\text{CH}_2$ ), 126.5 (CH), 163.1 (C), 173.4 (C), 198.9 (C). – MS (EI, 70 eV);  $m/z$  (%): 222 (54) [ $\text{M}^+$ ], 149 (100), 138 (24), 122 (52), 107 (50), 91 (46), 79 (44). – IR (ATR):  $\tilde{\nu} = 2936$  (s), 1724 (vs), 1679 (vs), 1258 (s), 1233 (s), 1231 (s), 1185 (s)  $\text{cm}^{-1}$ . –  $\text{C}_{13}\text{H}_{18}\text{O}_3$  (222.3): calcd. C 65.53, H 7.61; found C 65.91, H 7.79. – HRMS: calcd. 222.1256; found 222.1255.

**Methyl Bicyclo[5.4.0]undec-7-en-9-one-1-carboxylate (6b):** According to GP3, compound **4g** (985 mg, 4.10 mmol) was converted into **6b** (colorless oil, 351 mg, 1.58 mmol, 39%,  $R_f = 0.29$ ). Chiral GC: gradient elution from 115 °C to 160 °C with  $0.33 \text{ K min}^{-1}$ ,  $t_1 = 94.5$  min,  $t_2 = 98.0$  min. –  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.19$ –1.38 (m, 2 H), 1.43–1.55 (m, 1 H), 1.61–1.83 (m, 3 H), 1.86–1.95 (m, 1 H), 1.97–2.11 (m, 2 H), 2.25 (dt,  $J = 13.4$  Hz,  $J = 3.9$  Hz, 1 H), 2.30–2.44 (m, 2 H), 2.45–2.52 (m, 2 H), 3.69 (s, 3 H), 5.96 (s, 1 H). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 23.8$  ( $\text{CH}_2$ ), 30.2 ( $\text{CH}_2$ ), 30.7 ( $\text{CH}_2$ ), 33.2 ( $\text{CH}_2$ ), 34.8 ( $\text{CH}_2$ ), 35.7 ( $\text{CH}_2$ ), 37.1 ( $\text{CH}_2$ ), 51.0 (C), 52.4 ( $\text{CH}_3$ ), 129.5 (CH), 167.0 (C), 174.5 (C), 198.8 (C). – MS (EI, 70 eV);  $m/z$  (%): 222 (60) [ $\text{M}^+$ ], 166 (46), 163 (100), 121 (38). – IR (ATR):  $\tilde{\nu} = 2928$  (s), 1726 (vs), 1680 (vs), 1447 (s), 1248 (s), 1210 (s), 1163 (s)  $\text{cm}^{-1}$ . – HRMS: calcd. 222.1256; found 222.1252.

**Isopropyl 5-Methyl-6-oxabicyclo[3.2.2]nonan-7-one-1-carboxylate (7):** According to GP3, compound **4d** (132 mg, 0.55 mmol) was converted into **7** (colorless oil, 29 mg, 0.12 mmol, 22%,  $R_f = 0.30$ ).

Chiral GC: isotherm elution at 115 °C,  $t_1$  = 233 min,  $t_2$  = 241 min. –  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.27 (d,  $J$  = 6.2 Hz, 6 H), 1.40 (s, 3 H), 1.76–1.89 (m, 4 H), 1.94–2.00 (m, 2 H), 2.20 (dd,  $J$  = 10.9 Hz,  $J$  = 5.8 Hz, 1 H), 2.08–2.13 (m, 1 H), 2.55–2.62 (m, 1 H), 5.08 (heptet,  $J$  = 6.3 Hz, 1 H). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.7 ( $\text{CH}_2$ ), 21.5 ( $\text{CH}_3$ ), 21.7 ( $\text{CH}_3$ ), 24.6 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 30.1 ( $\text{CH}_3$ ), 30.9 ( $\text{CH}_2$ ), 38.1 ( $\text{CH}_2$ ), 51.8 (C), 69.2 (CH), 82.8 (C), 170.9 (C), 173.0 (C). – MS (EI, 70 eV);  $m/z$  (%): 240 (4) [ $\text{M}^+$ ], 212 (36), 170 (65), 137 (82), 125 (100), 111 (69), 97 (78). – IR (ATR):  $\tilde{\nu}$  = 2979 (s), 1739 (vs), 1722 (vs), 1374 (s), 1263 (s), 1232 (s), 1192 (s), 1158 (s), 1106 (s), 1047 (s)  $\text{cm}^{-1}$ . –  $\text{C}_{13}\text{H}_{20}\text{O}_4$  (240.3): calcd. C 64.98, H 8.39; found C 64.32, H 8.32. – HRMS: calcd. 240.1361; found 240.1364.

**4-Methylspiro[5.5]undec-3-en-2,7-dione (8):** According to GP3, compound **4i** (187 mg, 0.89 mmol) was converted into **8** (colorless solid, 22.0 mg, 0.11 mmol, 13%,  $R_f$  = 0.18). Chiral GC: gradient elution from 100 °C to 140 °C with 0.25 K  $\text{min}^{-1}$ ,  $t_1$  = 97.5 min,  $t_2$  = 115.1 min. –  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.52 (ddd,  $J$  = 13.8 Hz,  $J$  = 10.2 Hz,  $J$  = 3.6 Hz, 1 H), 1.66–1.80 (m, 3 H), 1.80–1.90 (m, 1 H), 1.93 (s, 3 H), 1.96–2.04 (m, 1 H), 2.22–2.44 (m, 3 H), 2.44–2.58 (m, 2 H), 2.75 (ddd,  $J$  = 14.2 Hz,  $J$  = 10.2 Hz,  $J$  = 5.8 Hz, 1 H), 5.80 (s, 1 H). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 21.0 ( $\text{CH}_2$ ), 23.9 ( $\text{CH}_3$ ), 27.0 ( $\text{CH}_2$ ), 28.1 ( $\text{CH}_2$ ), 30.9 ( $\text{CH}_2$ ), 35.1 ( $\text{CH}_2$ ), 41.1 ( $\text{CH}_2$ ), 58.6 (C), 125.4 (CH), 161.0 (C), 198.3 (C), 210.9 (C). – MS (EI, 70 eV);  $m/z$  (%): 193 (40) [ $\text{M} + \text{H}^+$ ], 192 (2) [ $\text{M}^+$ ], 174 (43), 164 (19), 136 (31), 121 (30), 82 (100). – IR (ATR):  $\tilde{\nu}$  = 2937 (s), 1704 (vs), 1661 (vs), 1209 (s)  $\text{cm}^{-1}$ . –  $\text{C}_{12}\text{H}_{16}\text{O}_3$  (192.3): calcd. C 74.97, H 8.39; found C 74.72, H 8.37. – HRMS: calcd. 193.1229; found 193.1230 [ $\text{M} + \text{H}^+$ ].

**General Procedure 4 (GP4). – Transesterification:** A mixture of compound **4** (1 equiv.) and DMAP (3 equiv.) in absolute MeOH or EtOH (50 equiv.) was heated in a sealed reaction flask to 50 °C for 30 h. The mixture was diluted with MTB and filtered through  $\text{SiO}_2$  (3 cm) to yield a mixture of starting material **4** and transesterified product **4'**, which was analyzed by chiral GC.

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