The use of new chiral phosphite and amidophosphite ligands in the Rh-catalyzed hydrogenation of dehydro-β-amino acid derivatives

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New chiral phosphite-type ligands were synthesized. The tests of these ligands in the asymmetric Rh-catalyzed hydrogenation of *N*-acetyl derivatives of dehydro-β-amino acid esters showed their high enantioselectivity (up to 75% *ee*). The reaction of nucleophilic addition of phthalimide to disubstituted alkynes offering access to esters of *N*-phthaloyldehydro-β-amino acids was discovered. Higher conversion and enantioselectivity in the hydrogenation of *N*-acetyl and *N*-phtaloyl derivatives of dehydro-β-amino acids were observed in fluorinated alcohols as compared to common organic solvents.

Key words: hydrogenation, rhodium, enamides, alkynes, nucleophilic addition.

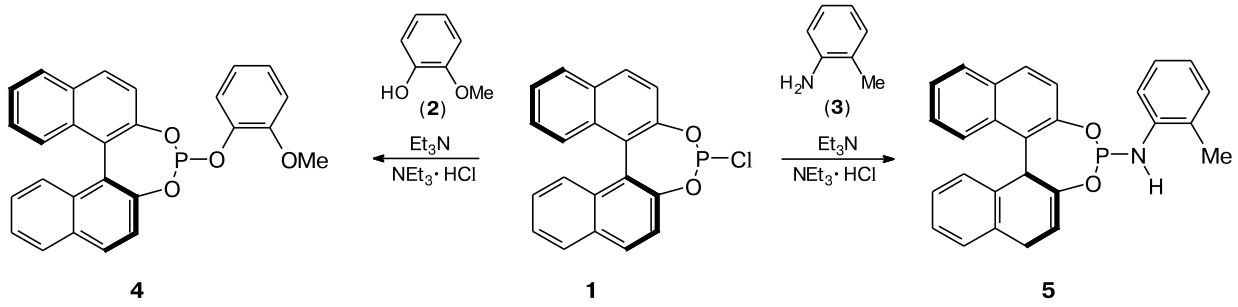
Chiral β-amino acids and their derivatives are valuable objects for the synthesis of β-peptides, β-lactams, antiallergic and antifungal drugs.[1—3] Among reactions leading to the formation of β-amino acids, asymmetric metallocomplex hydrogenation is the most economically reasonable choice due to cheapness of hydrogen and low catalyst loading. The known examples for the metallocomplex hydrogenation of unsaturated precursors of β-amino acids are mainly associated with the use of expensive chiral phosphine ligands.[4] Poor attention is given to the use of synthetically more accessible ligands of the phosphite type in this process.[5] Therefore, search for simple and efficient metallocomplex catalysts containing phosphite or amidophosphite ligands for the asymmetric hydrogenation of unsaturated precursors of β-amino acids is an urgent problem. The predominant number of works on the asymmetric hydrogenation of enamides is related to the involvement of *N*-acetyl-substituted unsaturated substrates in the reaction.[6] Removal of the acetyl protection group after hydrogenation needs fairly drastic conditions,[7,8] which can induce undesirable processes. Unsaturated compounds containing the phthalimide protection group, which are characterized by considerably milder conditions of preparation of target β-amino acids, are more attractive initial components for organic synthesis.[9—11]

In the present work, we report a new reaction of nucleophilic addition of phthalimide to substituted alkynes yielding dehydroamino acid derivatives and the use of new chiral phosphite-type ligands in the Rh-catalyzed hydrogenation of *N*-acetyl- and *N*-phthaloylacrylates.

Results and Discussion

The reactions of phosphorylating agent **1** with methoxyphenyl (**2**) and *o*-toluidine (**3**) in benzene afforded new phosphite **4** and amidophosphite **5** ligands (Scheme 1). Compounds **4** and **5** are easily soluble in the majority of

Scheme 1



4 **1** **5**

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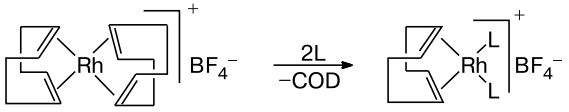
organic solvents and stable under dry atmosphere on prolong storage.

The study of the coordination behavior of ligands **4** and **5** with $[Rh(COD)_2]BF_4$ (COD is cycloocta-1,5-diene) indicates the monodentate coordination of the ligands and formation of complexes $[Rh(COD)L_2]BF_4$ (Scheme 2), which was confirmed by the data of ^{31}P NMR spectroscopy and elemental analysis.

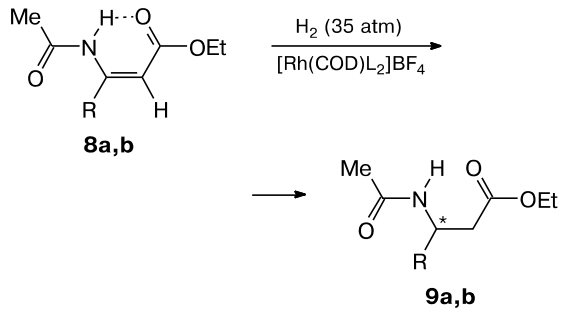
Scheme 2



6 (L = **4**),
7 (L = **5**)

The efficiency of complexes **6** and **7** was primarily tested in the Rh-catalyzed hydrogenation of (*Z*)-ethyl 3-acetamido-2-butenoate (**8a**) (Scheme 3) in isopropanol (Table 1, entries *1* and *2*).

Scheme 3



8a,b

9a,b

R = Me (**a**), Ph (**b**)

When the reaction was carried out at 40 °C and an H_2 pressure of 35 atm, the complete conversion was achieved within 4 h; however, enantioselectivity was low. In order to increase the enantiomeric excess of product **9a** in this reaction, we used the fluorinated analog of isopropanol, namely, 1,1,1,3,3,3-hexafluoropropan-2-ol (hexafluoroisopropanol). We succeeded in obtaining already up to 63% *ee* at the complete conversion of the initial substrate **8a** in hexafluoroisopropanol under other equal reaction conditions (see Table 1, entries *3* and *4*). The use of fluorinated alcohols in combination with the metallocomplex catalysts containing the chiral phosphine ligands can favor an increase in enantioselectivity in the hydrogenation of enamides and dimethyl itaconate compared to traditional organic solvents.[12–15] Similar increase in enantioselectivity has earlier been observed in the Rh-catalyzed hydrogenation of enamides[16] with the amidophosphite ligand containing the carborane substituent. In order to optimize enantioselectivity, we decreased the hydrogenation temperature from 40 to 20 °C. In the case of Rh complex **6** containing the phosphite ligand, the enantiomeric excess of the reaction product decreases (see Table 1, entries *3* and *5*), whereas complex **7** with the amidophosphite ligand at a lower temperature provides a higher enantioselectivity (see Table 1, entries *4* and *6*). Interestingly, using considerably more accessible fluorinated alcohol (2,2,2-trifluoroethanol) as a solvent a further increase in the enantiomeric excess of the reaction product in the case of complex **7** can be recorded (see Table 1, entries *6* and *8*). However, when using trifluoroethanol in the case of complex **6**, a little lower enantioselectivity compared to that for hexafluoroisopropanol is observed (see Table 1, entries *5* and *7*). The use of catalyst **7** at higher temperature (40 °C) considerably accelerates hydrogenation, although a small decrease in the enantiomeric excess of the reaction product is observed in this case (see Table 1, entries *8* and *9*).

Table 1. Asymmetric hydrogenation of substrates **8a**,**b**

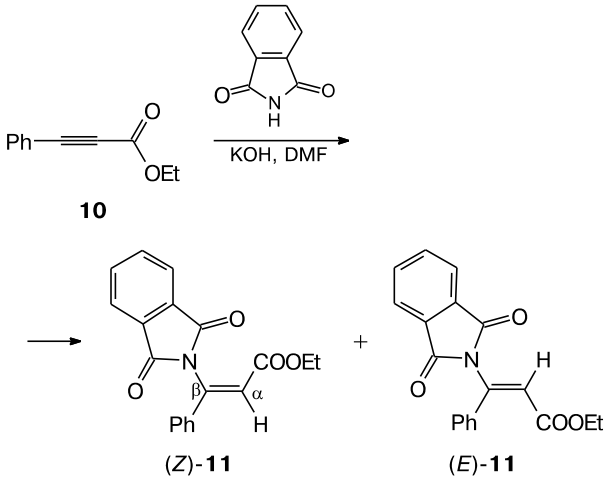
Entry	Substrate	Catalyst	Solvent	*T*/°C	*t*/h	Conversion of compound **8** (%)	*ee* (%)*
1	**8a**	**6**	$HOCHMe_2$	40	4	100	5 (*R*)
2	**8a**	**7**	$HOCHMe_2$	40	4	100	7 (*R*)
3	**8a**	**6**	$HOCH(CF_3)_2$	40	4	100	61 (*R*)
4	**8a**	**7**	$HOCH(CF_3)_2$	40	4	100	63 (*R*)
5	**8a**	**6**	$HOCH(CF_3)_2$	20	16	100	50 (*R*)
6	**8a**	**7**	$HOCH(CF_3)_2$	20	16	100	65 (*R*)
7	**8a**	**6**	$HOCH_2CF_3$	20	16	100	46 (*R*)
8	**8a**	**7**	$HOCH_2CF_3$	20	16	100	75 (*R*)
9	**8a**	**6**	$HOCH_2CF_3$	40	4	100	71 (*R*)
10	**8b**	**6**	$HOCH(CF_3)_2$	20	16	60	5 (*S*)
11	**8b**	**7**	$HOCH(CF_3)_2$	20	16	73	38 (*S*)
12	**8b**	**6**	$HOCH_2CF_3$	20	16	100	31 (*S*)
13	**8b**	**7**	$HOCH_2CF_3$	20	16	100	33 (*S*)

* The configuration of the corresponding product **9** is indicated in parentheses.

Rhodium complexes **6** and **7** were also studied in the hydrogenation of sterically more bulky substrate (*Z*)-ethyl 3-acetamido-3-phenylacrylate (**8b**) (see Scheme 3). When complex **6** containing the phosphite ligand is used, the conversion and enantioselectivity in hexafluoroisopropanol were lower than those in trifluoroethanol (see Table 1, entries *10* and *12*). In the case of complex **7**, a higher conversion is achieved in trifluoroethanol and somewhat higher enantioselectivity is attained in hexafluoroisopropanol (see Table 1, entries *11* and *13*).

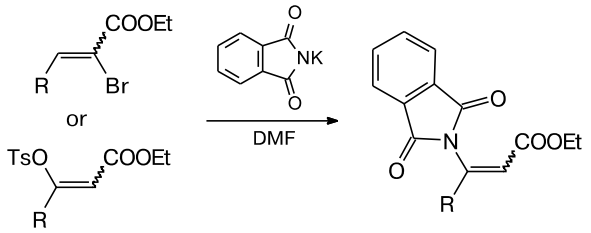
We also developed an approach to the synthesis of esters of *N*-phthaloyldehydro-β-amino acids by refluxing phthalimide with ethyl 3-phenylpropiolate (**10**) in DMF in the presence of a catalytic amount of KOH (Scheme 4).

Scheme 4



The only method known for the synthesis of substrates of this type is the reaction of poorly accessible substituted vinyl bromides and vinyl tosylates with potassium phthalimide (Scheme 5). Regardless of the position of the leaving group (Br or OTs) at the double bond, the product containing the phthalimide group at the β-C carbon atom is formed.[11] In our case (see Scheme 4), phthalimide is also added to the β-position of ethyl 3-phenylpropiolate to give a similar yield of product (*Z*)-**11** under compatible reaction conditions. Therefore, it can be assumed that the reaction follows Scheme 5 through the initial dehydrohalogenation (dehydrotosylation) by treatment with highly basic potassium phthalimide followed by the nucleophilic addition of phthalimide to alkynes formed rather than according to the earlier proposed[11] mechanism of the tandem Michael addition—elimination. However, there is a distinction between two proposed synthetic approaches. We found that reaction product **11** was a mixture of (*Z*)- and (*E*)-isomers in the ratio 4 : 1. The (*Z*)-isomer can be separated from the (*E*)-isomer by single crystallization from the mixture, whereas the (*E*)-isomer can be obtained in the pure form neither by multiple crystallization nor column chromatography. Higher regiospecificity of formation of the (*Z*)-isomer (*Z* : *E* = 50 : 1) is observed when using vinyl bromides (see Scheme 5).

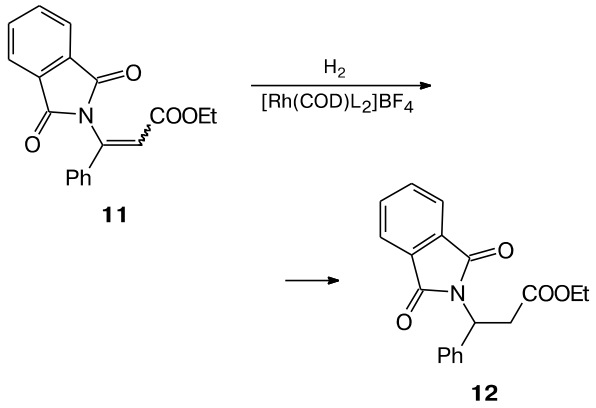
Scheme 5



R = Ar, Alk

The study of the efficiency of hydrogenation of (*Z*)-**11** and (*E*)-**11** (Scheme 6) was started from an experiment with an equimolar mixture of isomers **11** using Pd/C (3 mol.%) as a catalyst in a $MeOH—CH_2Cl_2$ mixture in order to increase solubility of the substrate (35 atm H_2, 30 °C). When the reaction time was 1 h, we found that the (*Z*)-isomer was hydrogenated quantitatively, whereas only the 30% conversion was observed for the (*E*)-isomer. When the duration of the experiment was extended to 5 h, the complete conversion of both the isomers was achieved. These results indicate a considerably lower reactivity of the (*E*)-isomer.

Scheme 6



Rhodium complexes **6** and **7** were also studied in the asymmetric hydrogenation of (*Z*)-**11** (see Scheme 6 and Table 2). It was shown that complex **7** in methylene chloride and methanol does not react, whereas the use of ethyl acetate gave racemic product **12** (see Table 2, entries *1—3*). The use of hexafluoroisopropanol as a solvent gives 51% *ee* at the 54% conversion within 24 h. Catalysis by complex **6** containing the phosphite ligand proceeds

with lower enantioselectivity and conversion (see Table 2, entries *4* and *5*). In the presence of frifluoroethanol, the results close to those with hexafluoroisopropanol were obtained under the same reaction conditions (see Table 2, *cf.* pairs of entries *4* and *5*, *6* and *7*). Increasing the hydrogen pressure slightly increases the conversion, and different enantiodiscriminating behavior of catalysts **6** and **7** are observed. A lower enantioselectivity resulted from the use of an enhanced hydrogen pressure in the presence of complex **7** (see Table 2, *cf.* entries *6* and *8*). Catalyst **6** makes it possible to increase the values of enantiomeric excess of the reaction product (see Table 2, *cf.* entries *7* and *9*). Elevated temperature (50 °C) and hydrogen pressure (50 atm) produced the same enantioselectivity on both the catalysts and close values of conversion (see Table 2, entries *10* and *11*).

In order to increase conversion, we also used supercritical carbon dioxide ($scCO_2$) as a medium for hydrogenation with trifluoroethanol as a co-solvent. The $scCO_2$ medium in combination with metal complexes containing the phosphite-type ligands can significantly accelerate hydrogenation; this property is due to high values of diffusion coefficient and easy miscibility with reaction gases, which result in intense mass exchange in the reaction system.[17–20] Indeed, in $scCO_2$ we achieved high conversion within 10 h and somewhat higher enantioselectivity compared to that obtained with trifluoroethanol as a solvent under all other reaction conditions being equal (see Table 2, *cf.* entries *12*, *13* and *10*, *11*). The reaction does not occur in $scCO_2$ without a cosolvent (see Table 2, entries *14* and *15*). This is related most likely to the low solubility of rhodium catalysts **6** and **7** in $scCO_2$, whose dielectric constant is similar to that of hexane,[21] and to easy precipitation of the catalyst in nonpolar media (see Experimental). The use of lower temperature (35 °C) for the hydrogenation of (*Z*)-**11** in $scCO_2$ containing trifluoroethanol decreases the rate of the process and reduces an enantiomeric excess of the reaction product (see Table 2, entries *12* and *16*).

Thus, in this work we were able to synthesize new chiral phosphite-type ligands, study their coordination behavior towards $[Rh(COD)_2]BF_4$, and examine their activity in the reactions of the Rh-catalyzed hydrogenation of *N*-acetyl- and *N*-phthaloyl-β-dehydroamino acid derivatives. The new approach to the synthesis of esters of *N*-phthaloyl-β-dehydroamino acids was developed that includes the nucleophilic addition of phthalimide to disubstituted alkynes. It was shown that higher enantioselectivities were observed in fluorinated alcohols compared to common organic solvents and, in several cases, higher conversions were observed for the hydrogenation of unsaturated derivatives of dehydro-β-amino acids.

Experimental

^1H and ^{31}P NMR spectra were recorded on a Bruker Avance 400 instrument (400.13 and 161.98 MHz, respectively) relative to Me_4Si and 85% H_3PO_4 in D_2O, respectively. Mass spectra (EI, 70 eV) were measured on a Finnigan Polaris Q instrument. Elemental analysis was carried out at the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences. All reactions were carried out under dry argon in anhydrous solvents. The phosphorylating agent (S_b)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]-dioxaphosphepine (**1**), (*Z*)-ethyl 3-acetamido-2-butenoate (**8a**), (*Z*)-ethyl 3-acetamido-3-phenylacrylate (**8b**), and initial complex $[Rh(COD)_2]BF_4$ were synthesized according to published

Table 2. Rh-Catalyzed hydrogenation of compound (*Z*)-**11**

Entry	Catalyst	Solvent	Cosolvent	*T*/°C	P_{H_2}/atm	*t*/h	Conversion (%)	*ee* (%)[a]
1	**7**	CH_2Cl_2	—	40	35	24	0	—
2	**7**	MeOH	—	40	35	24	0	—
3	**7**	EtOAc	—	40	35	5	31	0
4	**7**	$HOCH(CF_3)_2$	—	30	35	24	54	51 (+)
5	**6**	$HOCH(CF_3)_2$	—	30	35	24	48	37 (+)
6	**7**	$HOCH_2CF_3$	—	30	35	24	50	50 (+)
7	**6**	$HOCH_2CF_3$	—	30	35	24	45	37 (+)
8	**7**	$HOCH_2CF_3$	—	30	50	24	60	37 (+)
9	**6**	$HOCH_2CF_3$	—	30	50	24	52	40 (+)
10	**7**	$HOCH_2CF_3$	—	50	50	24	71	30 (+)
11	**6**	$HOCH_2CF_3$	—	50	50	24	67	30 (+)
12	**7**	$scCO_2$[b]	$HOCH_2CF_3$	50	50	10	89	37 (+)
13	**6**	$scCO_2$[b]	$HOCH_2CF_3$	50	50	10	92	34 (+)
14	**7**	$scCO_2$[b]	—	50	50	10	0	—
15	**6**	$scCO_2$[b]	—	50	50	10	0	—
16	**7**	$scCO_2$[b]	$HOCH_2CF_3$	35	50	24	50	33 (+)

[a] The sign of the specific rotation angle of product **12** is indicated in parentheses.
[b] The total pressure is 100 atm.

procedures.[22—24] Ethyl 3-phenylpropiolate (**10**) is a commercially available compound (Aldrich).

Synthesis of ligands 4 and 5 (general procedure). A solution of 2-methoxyphenol or 2-methylaniline (1.4 mmol) and NEt_3 (0.3 mL, 2.1 mmol) in C_6H_6 (10 mL) were added to a solution of dioxaphosphepane (**1**) (0.5 g, 1.4 mmol) in C_6H_6 (15 mL). The reaction mixture was heated to boiling and then cooled to room temperature, and a precipitate of $NEt_3 \cdot HCl$ was filtered off. The obtained solution was subjected to flash chromatography on silica gel (benzene as eluent). The solvent was removed *in vacuo*.

(S_b)-4-(2-Methoxyphenoxy)dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine (4). The yield was 0.534 g (87%), white powder, m.p. 95—97 °C. Found (%): C, 74.08; H, 4.40; P, 6.98. $C_{27}H_{19}O_4P$. Calculated (%): C, 73.97; H, 4.37; P, 7.07. $^{31}P\{H\}$ NMR ($CDCl_3$), δ: 146.68. ^1H NMR ($CDCl_3$), δ: 3.93 (s, 3 H, OMe); 6.82—7.61 (m, 12 H, Ar); 7.85—8.03 (m, 4 H, Ar). MS, *m/z* (I_{rel} (%)): 252 (40), 268 (100), 315 (70), 333 (41), 437 (60) $[M]^+$.

(S_b)-4-(*N*-*o*-Tolylamino)dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine (5). The yield was 0.478 r (81%), white powder, m.p. 110—111 °C. Found (%): C, 76.89; H, 4.84; N, 3.39. $C_{27}H_{20}NO_2P$. Calculated (%): C, 76.95; H, 4.78; N, 3.32. $^{31}P\{H\}$ NMR ($CDCl_3$), δ: 146.92. ^1H NMR ($CDCl_3$), δ: 2.08 (s, 3 H, Me); 5.01 (br.s, 1 H, NH); 6.91—7.60 (m, 12 H, Ar); 7.86—8.04 (m, 4 H, Ar). MS, *m/z* (I_{rel} (%)): 239 (40), 268 (100), 286 (90), 313 (62), 357 (20), 421 (50) $[M]^+$.

Synthesis of rhodium complexes 6 and 7 (general procedure). A solution of ligand **4** or **5** (0.2 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise for 2 min to a solution of $[Rh(COD)_2]BF_4$ (0.04 g, 0.1 mmol) in CH_2Cl_2 (0.5 mL). Hexane (10 mL) was added to the obtained mixture, and precipitated complexes **6** or **7** were separated by centrifuging and dried *in vacuo* (1 Torr).

{Bis[(S_b)-4-(2-methoxyphenoxy)dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine]}(η-cycloocta-1,5-diene)rhodium(I) tetrafluoroborate (6). The yield was 108 mg (94%), yellow powder, m.p. 121—123 °C (with decomp.). Found (%): C, 63.47; H, 4.23; P, 5.34. $C_{62}H_{50}BF_4O_8P_2Rh$. Calculated (%): C, 63.39; H, 4.29; P, 5.27. ^{31}P NMR ($CDCl_3$), δ: 123.9 (d, $J_{P,Rh}$ = 260.0 Hz).

{Bis[(S_b)-4-(*N*-*o*-tolylamino)dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine]}(η-cycloocta-1,5-diene)rhodium(I) tetrafluoroborate (7). The yield was 103 mg (92%), yellow powder, m.p. 144—146 °C (with decomp.). Found (%): C, 65.33; H, 4.66; N, 2.39. $C_{62}H_{52}BF_4N_2O_4P_2Rh$. Calculated (%): C, 65.28; H, 4.59; N, 2.46. ^{31}P NMR ($CDCl_3$), δ: 131.6 (d, $J_{P,Rh}$ = 238.5 Hz).

Asymmetric hydrogenation of enamides 8a,b (general procedure). A solution of rhodium complex **6** or **7** (0.006 mmol) and a substrate (0.6 mmol) in 1.5 mL of the corresponding alcohol were placed in an autoclave. The solution in the closed autoclave was purged with argon, and the autoclave was filled with hydrogen (35 atm) and heated to a required temperature. Experiments were carried out with magnetic stirring (see Table 1). After discharging hydrogen, the reaction mixture was diluted with CH_2Cl_2 (2 mL) and purified from the catalyst by filtration through a thin layer of silica gel. The solvents were removed *in vacuo*. The conversion of enamides **8a**,**b** was determined by ^1H NMR spectroscopy. Enantiomeric excesses of reaction products **9a**,**b** (see Ref. 23) were measured by HPLC on an Agilent HP-1100 chromatograph using the Chiralcel OJ-H and Chiralcel OD-H columns according to the literature data.[16] The absolute configuration of the reaction products was established by a comparison of the signs of optical rotation with the known values.[25,26]

Ethyl 3-(1,3-dioxoisoindolin-2-yl)-3-phenylacrylate (11). Phthalimide (5.15 g, 0.035 mol) and KOH (50 mg) were added to a solution of ethyl 3-phenylpropiolate (**10**) (5.53 g, 0.032 mol) in DMF (40 mL). The mixture was refluxed for 20 h with stirring. After cooling to room temperature, water (60 mL) was added to the solution and the product was extracted with ethyl acetate (3×30 mL). The organic layer was washed with water (3×30 mL), dried with Na_2SO_4, and the solvent was removed *in vacuo*. The obtained light yellow solid product was washed with diethyl ether (2×5 mL) on the Schott filter to remove DMF residues, dissolved in 70 mL of $CHCl_3$, and subjected to flash chromatography on silica gel ($CHCl_3$ as eluent). The product obtained in a yield of 5.111 g (0.016 mol, 50%) contains, according to the ^1H NMR spectrum, 80% of known (*Z*)-ethyl 3-(1,3-dioxoisoindolin-2-yl)-3-phenylacrylate[11] and 20% of its (*E*)-isomer. ^1H NMR for (*E*)-isomer ($CDCl_3$), δ: 1.13 (t, 3 H, Me, *J* = 7.1 Hz); 4.10 (q, 2 H, CH_2, *J* = 7.1 Hz); 6.19 (s, 1 H, CH), 7.30—7.97 (m, 9 H, Ar). Crystallization from ethyl acetate on cooling the solution to −10 °C gave 3.1 g of the (*Z*)-isomer of product **11**. If the recrystallized product contains small amounts (5—7%) of phthalimide, the product should be dissolved in $CHCl_3$ and subjected to consequent flash chromatography. The evaporation of the mother liquor results in the product with approximately equal content of the (*Z*)- and (*E*)-isomers. The crystallization of the (*E*)-isomer from ethyl acetate is not reasonable because of the low subsequent enrichment (5—7%); however, additional 200—300 mg of the pure (*Z*)-isomer can be obtained in this case.

Asymmetric hydrogenation of (*Z*)-ethyl 3-(1,3-dioxoisoindolin-2-yl)-3-phenylacrylate ((*Z*)-11). Substrate (*Z*)-**11** (96 mg, 0.3 mmol), rhodium complex **6** or **7** (0.003 mmol), and the corresponding solvent (1.5 mL) were placed in an autoclave (see Table 2). The solution in the closed autoclave was purged with argon, and the autoclave was filled with hydrogen to a required pressure (in some cases, with carbon dioxide) using a manually operated pump (High Pressure Equipment). Experiments were carried out with stirring and heating to a required temperature. After discharging hydrogen and CO_2, the reaction mixture was diluted with CH_2Cl_2 (3 mL) and purified from the catalyst by filtration through a thin layer of silica gel and the solvents were removed *in vacuo*. The conversion of (*Z*)-**11** was determined by ^1H NMR spectroscopy. Enantiomeric excess of reaction product **12** (see Ref. 11) was determined by HPLC on an Agilent HP-1100 chromatograph using the Whelk-O1 column (UV, λ = 219 nm, hexane—isopropanol (7 : 3), flow rate 0.8 mL min^{-1}). The retention times for enantiomers **12** were 15.2 min for the (+)-isomer, 17.1 min for the (−)-isomer, and 20.2 min for enamide (*Z*)-**11**.

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