# 27
# Bidentate Ligands Containing a Heteroatom–Phosphorus Bond

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## 27.1
## Introduction

Bidentate phosphorus ligands containing one or more heteroatom-phosphorus bonds are of high interest because they are relatively easy to prepare, and because a huge multitude of inexpensive, commercially available chiral diols, diamines, amino alcohols and amino acids can serve as the scaffold. Although the heteroatoms in these scaffolds are usually electronegative in nature, the reactivity and enantioselectivity of the metal complexes based on some of these ligands are quite remarkable, and sometimes even surpass those of the complexes based on electron-rich phosphines. This chapter compiles the comprehensive data concerning the asymmetric hydrogenation of various prochiral olefins mediated by the rhodium(I) complexes of this class of chiral ligands.

## 27.2
## Aminophosphine-Phosphinites (AMPPs)

The ease of synthesis from chiral amino alcohols with a wide array of derivatives in one step established its good potential in the field of asymmetric catalysis. The general preparation of "semi-symmetrical" AMPPs involves the nucleophilic attack of two equivalents of chlorophosphine in the presence of a base (Fig. 27.1). A "mixed" AMPP can also be prepared by virtue of the fact that phosphorus-based electrophiles have a strong preference for hydroxy over secondary amine or amide. Clearly, this synthetic method allows the preparation of a large variety of AMPP ligands with adjustable electronic and steric properties. Agbossou recently reviewed the state of the art of AMPPs [1]. In consideration to the modern high-throughput methods, this approach allowed a rapid combinatorial screening of various catalysts and reactions.

In general, applications of AMPP have concentrated on the asymmetric hydrogenation of functionalized olefins, especially dehydroamino acids. Among

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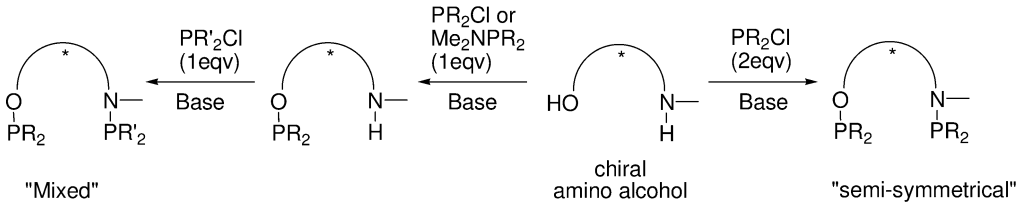
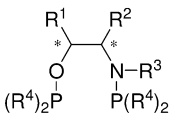
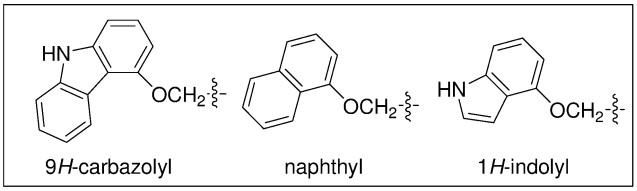



**Fig. 27.1** The preparation of AMPPs.

these substrates, (*Z*)-methyl *α*-acetamidocinnamate was the most frequently used benchmark substrate. A strong influence of the solvent on catalytic activity and enantioselectivity was a common phenomenon, and protic solvents were found to be the most effective. However, to avoid the problem of solvolysis of the ligands, polar aprotic solvents were commonly used to obtain the best results. Although the *in-situ* preparation of cationic rhodium complexes was frequently used, no significant dependence of their catalytic performance on the manner of their preparation could be observed. Most Rh complexes allowed the use of atmospheric pressure for hydrogenation with high reaction rate at room temperature. In all cases, the ligands formed a chelation ring with the metal.

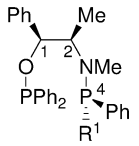
Many structurally diverse ephedrine-derived AMPP ligands (Fig. 27.2) have been prepared, and most of these were applied to the asymmetric hydrogenation of olefins. Cesarotti was one of the earliest pioneers in the development of aminophosphine-phosphinite **1** based on (*S*)-2-(ethylamino)butan-1-ol as a starting material. However, the results were only moderate to good [2]. Almost simultaneously with Cesarotti in 1982, Pracejus reported a similar approach [3]. Ephedrine-based Propraphos and its derivatives occupied the major area of this research field. The chiral Rh–Propraphos systems were widely applied in the enantiomeric hydrogenation of *α*-dehydroamino acids, with 31 to 95% e.e. The products included (*S*) and (*R*)-aromatic [4–6] and heteroaromatic alanine derivatives [7–16], and usually have a configuration which is opposite to that of the ligand. 2-Acetamido-cinnamic acid derivatives carrying an electron-withdrawing group at the *para*-position of the phenyl ring could be hydrogenated with relatively high enantioselectivities. In most cases, turnover frequencies (TOFs) could be obtained of up to 3000 $h^{-1}$, and up to 11 515 $h^{-1}$ for a special case (Table 27.1, entry 392). The use of Rh-**15** in the hydrogenation of dimethyl itaconate gave the product with 80% ee (Table 27.1, entry 432). Structural analogues of Propraphos, Pindophos and Caraphos [7, 17] led to similar ee-values; however, a longer reaction time was required with the Caraphos–Rh complex. Use of (*R*)-Pindophos–Rh in the diastereoselective hydrogenation of dehydrodipetides produced good selectivity (up to 91% ee in the case of *para*-trifluoromethyl-phenylalanyl-phenylalanine [7] (Table 27.2, entry 10). A series of novel ephedrine-based ligands have been shown to be highly effective in the Rh-catalyzed hydrogenation of dehydroamino acids, giving the products with 95–99% ee [18, 19]. The hydrogenation of (*Z*)-acetamidocinnamate with a substrate:catalyst ratio (SCR) of



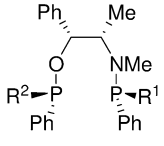



(*S*)-**1** (Butaphos) $R^1$ = H; $R^2$ = Et; $R^3$ = Et; $R^4$ = Ph
(*S*)-**2** (NEtAlaNOP) $R^1$ = H; $R^2$ = Me; $R^3$ = Et; $R^4$ = Ph
(1*R*,2*S*)-**3** $R^1$ = Ph; $R^2$ = Me; $R^3$ = Me; $R^4$ = Ph
(1*R*)-**4** $R^1$ = Ph; $R^2$ = H; $R^3$ = Me; $R^4$ = Ph
(1*R*,2*R*)-**5** $R^1$ = Ph; $R^2$ = Me; $R^3$ = Me; $R^4$ = Ph
(2*R*)-**6** $R^1$ = H; $R^2$ = Ph; $R^3$ = Me; $R^4$ = Ph
(1*R*,2*S*)-**7** (DPAMPP) $R^1$ = $R^2$ = Ph; $R^3$ = Me; $R^4$ = Ph
(1*S*,2*S*)-**7** (DPAMPP) $R^1$ = $R^2$ = Ph; $R^3$ = Me; $R^4$ = Ph
(1*S*,2*R*)-**7** (DPAMPP) $R^1$ = $R^2$ = Ph; $R^3$ = Me; $R^4$ = Ph
(*R*)-**8** $R^1$ = naphthyl; $R^2$ = H; $R^3$ = *i*Pr; $R^4$ = Cy

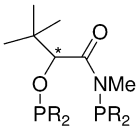
(*S*)-**9** (Propraphos) $R^1$ = naphthyl; $R^2$ = H; $R^3$ = *i*Pr, $R^4$ = Ph
(*R*)-**9** (Propraphos) $R^1$ = naphthyl; $R^2$ = H; $R^3$ = *i*Pr, $R^4$ = Ph
(*S*)-**10** (Pindophos) $R^1$ = 1*H*-indolyl; $R^2$ = H; $R^3$ = *i*Pr, $R^4$ = Ph
(*R*)-**10** (Pindophos) $R^1$ = 1*H*-indolyl; $R^2$ = H; $R^3$ = *i*Pr, $R^4$ = Ph
(*R*)-**11** (Caraphos) $R^1$ = 9*H*-carbazolyl; $R^2$ = H; $R^3$ = *i*Pr, $R^4$ = Ph
(*S*)-**12** $R^1$ = naphthyl; $R^2$ = H; $R^3$ = H, $R^4$ = Ph
(*S*)-**13** $R^1$ = naphthyl; $R^2$ = H; $R^3$ = Me, $R^4$ = Ph
(*S*)-**14** $R^1$ = naphthyl; $R^2$ = H; $R^3$ = $CHEt_2$, $R^4$ = Ph
(*S*)-**15** $R^1$ = naphthyl; $R^2$ = H; $R^3$ = Cyclopentyl, $R^4$ = Ph
(*S*)-**16** $R^1$ = naphthyl; $R^2$ = H; $R^3$ = Cyclohexyl, $R^4$ = Ph



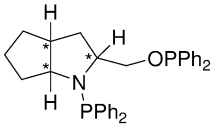
(1*S*,2*R*)-**17** (EPHOS) $R^1$ = Ph
(1*S*,3*R*,4S)-**18** $R^1$ = Me
(1*S*,2*R*,4*R*)-**19** $R^1$ = *o*-An
(1*S*,2*R*,4*R*)-**20** $R^1$ = 1-Np
(1*S*,2*R*,4*R*)-**21** $R^1$ = 2-Np
(1*S*,2*R*,4*S*)-**22** $R^1$ = *t*Bu



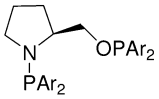
(1*S*,2*R*,4*R*)-**23** $R^1$ = Ph; $R^2$ = *o*-An
(1*S*,3*S*,4*R*,6*R*)-**24** $R^1$ = $R^2$ = *o*-An



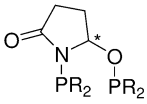
(*R*)-**25** (Ph-tLANOP) R = Ph
(*S*)-**26** (Cy-tLANO) R = Cy
(*S*)-**27** (2-Furyl-tLANOP) R = 2-furyl



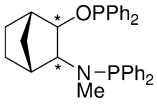
(1*R*,3*R*,5*R*)-**28**
(1*S*,3*S*,5*S*)-**28**



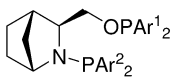
**29** (ProNOP/prolophos) Ar = Ph
**30** (Cy-ProNOP) Ar = Cy
**31** (Bu-ProNOP) Ar = Bu



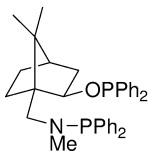
(*S*)-**32** (Ph-oxoProNOP) R = Ph
(*S*)-**33** (Cy-oxoProNOP) R = Cy
(*S*)-**34** ((2-Furyl)-oxoProNOP) R = 2-furyl



(+)-(2*S*,3S)-**35**
(–)-(2*R*,3*R*)-**35**



(1*R*,3*S*,4*S*)-**36** $Ar^1$ = $Ar^2$ = Ph
(1*R*,3*S*,4*S*)-**37** $Ar^1$ = $Ar^2$ = *p*-Tol
(1*R*,3*S*,4*S*)-**38** $Ar^1$ = Ph; $Ar^2$ = *p*-Tol
(1*R*,3*S*,4*S*)-**39** $Ar^1$ = *p*-Tol; $Ar^2$ = Ph



*exo*-**40**

**Fig. 27.2** AMPP chiral ligands.

**Table 27.1** Enantiomeric hydrogenation using aminophosphine–phosphinites (AMPP).

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 1 | H | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**1**]$ClO_4$ | 1 | EtOH | 20 | – | 200 | – | 100 | 55 (*S*) [a)] | 2a,b |
| 2 | H | $CO_2H$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 95.2 (*R*) | 18 |
| 3 | H | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**29**]$ClO_4$ | 1 | EtOH | 20 | – | 200 | – | 100 | 80 (*S*) [a)] | 2a,b |
| 4 | H | $CO_2H$ | NHAc | RhCl(COD)(1*S*,2*S*)-**35** | 1 | MeOH | 25 | – | 100 | – | 100 | 89 (*R*) | 37 |
| 5 | H | $CO_2H$ | NHAc | [Rh(COD) (1*S*,2*S*)-**35**]$BF_4$ | 1 | MeOH | 25 | – | 100 | – | 100 | 86 (*R*) | 37 |
| 6 | H | $CO_2H$ | NHAc | RhCl(COD)(1*R*,2*R*)-**35** | 1 | MeOH | 25 | – | 100 | – | 100 | 89 (*S*) | 37 |
| 7 | H | $CO_2H$ | NHBz | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 94.8 (*R*) | 18 |
| 8 | H | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**2**]$ClO_4$ | 1 | EtOH/ PhH | 20 | – | 200 | – | 100 | 66 (*R*) | 32 |
| 9 | H | $CO_2Me$ | NHAc | [Rh(COD)(*S*)- **29**]$ClO_4$ | 1 | EtOH/ PhH | 20 | – | 200 | – | 100 | 67 (*S*) | 32 |
| 10 | H | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**29**]$BF_4$ | 1 | MeOH | r.t. | – | 2500 | – | – | 79 (*S*) | 41 |
| 11 | H | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**29**]$BF_4$ | 1 | DCM | r.t. | – | 1500 | – | – | 69 (*S*) | 41 |
| 12 | H | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**36**]$BF_4$ | 1 | MeOH | r.t. | – | 3500 | – | – | 85 (*S*) | 41 |
| 13 | H | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**36**]$BF_4$ | 1 | DCM | r.t. | – | 1500 | – | – | 70 (*S*) | 41 |
| 14 | H | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**37**]$BF_4$ | 1 | MeOH | r.t. | – | 4000 | – | – | 80 (*S*) | 41 |
| 15 | H | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**37**]$BF_4$ | 1 | DCM | r.t. | – | 2000 | – | – | 61 (*S*) | 41 |
| 16 | H | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**38**]$BF_4$ | 1 | MeOH | r.t. | – | 3600 | – | – | 80 (*S*) | 41 |
| 17 | H | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**38**]$BF_4$ | 1 | DCM | r.t. | – | 1200 | – | – | 63 (*S*) | 41 |
| 18 | H | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**39**]$BF_4$ | 1 | MeOH | r.t. | – | 4500 | – | – | 77 (*S*) | 41 |
| 19 | H | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**39**]$BF_4$ | 1 | DCM | r.t. | – | 2500 | – | – | 59 (*S*) | 41 |
| 20 | H | OAc | Ph | [Rh(COD)(1*R*,2*S*)-**3**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 24 (*R*) | 36 |
| 21 | H | OAc | Ph | [Rh(COD) (1*R*,2*R*)-**5**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 13 (*R*) | 36 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 22 | $(CH_3)_2CH$ | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**29**]$BF_4$ | 1 | EtOH | 20 | – | 200 | – | 100 | 96 (*S*) | 2 b |
| 23 | $(CH_3)_2CH$ | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**1**]$BF_4$ | 1 | EtOH | 20 | – | 200 | – | 100 | 64 (*S*) | 2 b |
| 24 | $(CH_3)_2CH$ | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**1**]$ClO_4$ | 1 | EtOH | 20 | – | 200 | – | 100 | 57 (*S*) | 2 b |
| 25 | $(CH_3)_2CH$ | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**29**]$ClO_4$ | 1 | EtOH | 20 | – | 200 | – | 100 | 45 (*S*) | 2 b |
| 26 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**1**] $ClO_4$ | 1 | EtOH | 20 | – | – | – | – | 23 (*S*)[a)] | 2 a, b |
| 27 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,2*S*)-**3**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 80 (*R*) | 36 |
| 28 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,2*S*)-**3**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 12 (*R*) | 36 |
| 29 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*R*)-**4**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 56 (*R*) | 36 |
| 30 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*R*)-**4**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 5 (*R*) | 36 |
| 31 | Ph | $CO_2H$ | NHAc | [Rh(COD) (1*R*,2*R*)-**5**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 3 (*S*) | 36 |
| 32 | Ph | $CO_2H$ | NHAc | [Rh(COD) (1*R*,2*R*)-**5**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 9 (*R*) | 36 |
| 33 | Ph | $CO_2H$ | NHAc | [Rh(COD)(2*R*)-**6**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 24 (*R*) | 36 |
| 34 | Ph | $CO_2H$ | NHAc | [Rh(COD)(2*R*)-**6**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 0.5 (*S*) | 36 |
| 35 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 96.5 (*R*) | 18 |
| 36 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.03[b)] | 50 | 1667 | 50 | 87 (*R*) | 8 |
| 37 | Ph | $CO_2H$ | NHAc | RhCl(COD)(*S*)-**9** | 1 | MeOH | 25 | 0.12[b)] | 50 | 417 | 50 | 88 (*R*) | 8 |
| 38 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.092[b)] | 1000 | 10870 | 50 | 86 (*S*) | 9 |
| 39 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.343[b)] | 1500 | 4373 | 50 | 85 (*S*) | 9 |
| 40 | Ph | $CO_2H$ | NHAc | Rh(COD)(*S*)-**9** | 1 | MeOH | 25 | 0.12[b)] | 50 | 417 | 50 | 88 (*R*) | 15 |
| 41 | Ph | $CO_2H$ | NHAc | Rh(COD)(*S*)-**9** | 1 | MeOH | 25 | 0.58[b)] | 500 | 862 | 50 | 85 (*R*)[l)] | 15 |
| 42 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.02[b)] | 50 | 2500 | 50 | 87 (*R*)[m)] | 15 |
| 43 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.15[b)] | 500 | 3333 | 50 | 84 (*R*)[m)] | 15 |
| 44 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.22[b)] | 500 | 2273 | 50 | 89 (*R*) | 15 |
| 45 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.03[b)] | 50 | 1667 | 50 | 85 (*R*)[m,n)] | 15 |
| 46 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.58[b)] | 50 | 86 | 50 | 82 (*R*)[m,o)] | 15 |
| 47 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | PhH | 25 | 1.33[b)] | 50 | 38 | 50 | 69 (*S*) | 15 |
| 48 | Ph | $CO_2H$ | NHAc | [(*R*)-**9**+CuCl]/$[Ru(COD)Cl]_2$ | 1 | MeOH | 25 | 0.02[b)] | 50 | 2500 | 50 | 88 (*S*) | 15 |
| 49 | Ph | $CO_2H$ | NHAc | [(*R*)-**9**+CuCl]/$[Ru(COD)Cl]_2$ | 1 | MeOH | 25 | 0.12[b)] | 500 | 4167 | 50 | 88 (*S*) | 15 |
| 50 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*R*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.058[b)] | 500 | 8621 | 50 | 91 (*S*) | 9 |
| 51 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*R*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.117[b)] | 1000 | 8547 | 50 | 90 (*S*) | 9 |

**Table 27.1** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 52 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*R*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.267 [b] | 1500 | 5618 | 50 | 90 (*S*) | 9 |
| 53 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**12**]$BF_4$ | 1 | MeOH | 25 | 0.2 [b] | 50 | 250 | 50 | 2 (*S*) | 8 |
| 54 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**13**]$BF_4$ | 1 | MeOH | 25 | 0.032 [b] | 50 | 1563 | 50 | 45 (*R*) | 8 |
| 55 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**13**]$BF_4$ | 1 | MeOH | 25 | 0.67 [b] | 500 | 746 | 50 | 9 (*R*) | 8 |
| 56 | Ph | $CO_2H$ | NHAc | RhCl(COD)(*S*)-**13** | 1 | MeOH | 25 | 0.25 [b] | 50 | 200 | 50 | 20 (*R*) | 8 |
| 57 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**14**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 87 (*R*) | 8 |
| 58 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**15**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 91 (*R*) | 8 |
| 59 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**16**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 89 (*R*) | 8 |
| 60 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*S*,3*S*,5*S*)-**28**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 57 (*S*) [m] | 40 |
| 61 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,3*R*,5*R*)-**28**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 54 (*R*) [m] | 40 |
| 62 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**29**] $ClO_4$ | 1 | EtOH | 20 | – | – | – | – | 78 (*S*) [a] | 2b |
| 63 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**29**]$BF_4$ | 1 | MeOH | r.t. | – | – | 250 | – | 80 (*S*) [c] | 41 |
| 64 | Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**29**]$BF_4$ | 1 | DCM | r.t. | – | – | 2000 | – | 65 (*S*) [c] | 41 |
| 65 | Ph | $CO_2H$ | NHAc | RhCl(COD)(1*S*,2*S*)-**35** | 1 | MeOH | 25 | – | 100 | – | 100 | 85 (*R*) | 37 |
| 66 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*S*,2*S*)-**35**]$BF_4$ | 1 | MeOH | 25 | – | 100 | – | 100 | 83 (*R*) | 37 |
| 67 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,2*R*)-**35**]Cl | 1 | MeOH | 25 | – | 100 | – | 100 | 85 (*S*) | 37 |
| 68 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**36**]$BF_4$ | 1 | MeOH | r.t. | – | – | 3100 | – | 90 (*S*) [c] | 41 |
| 69 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**36**]$BF_4$ | 1 | DCM | r.t. | – | – | 600 | – | 83 (*S*) [c] | 41 |
| 70 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**37**]$BF_4$ | 1 | MeOH | r.t. | – | – | 2400 | – | 86 (*S*) [c] | 41 |
| 71 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**37**]$BF_4$ | 1 | DCM | r.t. | – | – | 300 | – | 66 (*S*) [c] | 41 |
| 72 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**38**]$BF_4$ | 1 | MeOH | r.t. | – | – | 2000 | – | 82 (*S*) [c] | 41 |
| 73 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**38**]$BF_4$ | 1 | DCM | r.t. | – | – | 300 | – | 67 (*S*) [c] | 41 |
| 74 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**39**]$BF_4$ | 1 | MeOH | r.t. | – | – | 2400 | – | 80 (*S*) [c] | 41 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 75 | Ph | $CO_2H$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**39**]$BF_4$ | 1 | DCM | r.t. | – | – | 300 | – | 65 (*S*) [c] | 41 |
| 76 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**1**]$ClO_4$ | 1 | EtOH | 20 | – | 200 | – | 100 | 49 (*S*) | 2 b |
| 77 | Ph | $CO_2H$ | NHBz | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 96.4 (*R*) | 18, 19 |
| 78 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 89 (*R*) | 8 |
| 79 | Ph | $CO_2H$ | NHBz | Rh$Cl$(*S*)-**9** | 1 | MeOH | 25 | 0.25 [b] | 500 | 2000 | 50 | 89 (*R*) | 8 |
| 80 | Ph | $CO_2H$ | NHBz | [(*R*)-**9**+CuCl]/$[Ru(COD)Cl]_2$ | 1 | MeOH | 25 | 0.5 [b] | 1500 | 3000 | 50 | 89 (*S*) | 15 |
| 81 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.72 [b] | 500 | 694 | 50 | 79 (*S*) | 15 |
| 82 | Ph | $CO_2H$ | NHBz | Rh$Cl$(*R*)-**9** | 1 | MeOH | 25 | 0.25 [b] | 500 | 200 | 50 | 89 (*S*) | 15 |
| 83 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.72 [b] | 500 | 694 | 50 | 79 (*S*) | 42 |
| 84 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**12**]$BF_4$ | 1 | MeOH | 25 | 0.27 [b] | 50 | 185 | 50 | 8 (*S*) | 8 |
| 85 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**13**]$BF_4$ | 1 | MeOH | 25 | 0.04 [b] | 50 | 1250 | 50 | 41 (*R*) | 8 |
| 86 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**13**]$BF_4$ | 1 | MeOH | 25 | 0.67 [b] | 500 | 746 | 50 | 3 (*R*) | 8 |
| 87 | Ph | $CO_2H$ | NHBz | Rh$Cl$(*S*)-**13** | 1 | MeOH | 25 | 0.2 [b] | 50 | 250 | 50 | 24 (*R*) | 8 |
| 88 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**14**]$BF_4$ | 1 | MeOH | 25 | 0.07 [b] | 50 | 714 | 50 | 88 (*R*) | 8 |
| 89 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**15**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 94 (*R*) | 8 |
| 90 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**16**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 92 (*R*) | 8 |
| 91 | Ph | $CO_2H$ | NHBz | [Rh(COD)(1*S*,3*S*,5*S*)-**28**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 62 (*S*) | 40 |
| 92 | Ph | $CO_2H$ | NHBz | [Rh(COD)(1*R*,3*R*,5*R*)-**28**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 58 (*R*) | 40 |
| 93 | Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**29**]$ClO_4$ | 1 | EtOH | 20 | – | 200 | – | 100 | 62 (*S*) | 2b |
| 94 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**3**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 75 (*R*) | 36 |
| 95 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**3**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 12 (*R*) | 36 |
| 96 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*)-**4**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 55 (*R*) | 36 |
| 97 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*)-**4**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 5 (*R*) | 36 |
| 98 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*R*)-**5**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 10 (*R*) | 36 |
| 99 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*R*)-**5**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 2 (S) | 36 |
| 100 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(2*R*)-**6**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 14 (R) | 36 |
| 101 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(2*R*)-**6**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 6 (*R*) | 36 |
| 102 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$Cl$ | 50 | MeOH | r.t. | 17 | 31.3 | 1.84 | 31.3 | 27 (*S*) | 18 |
| 103 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 50 | MeOH | r.t. | 1 | 100 | 100 | 100 | 96.9 (*S*) | 18 |
| 104 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | r.t. | 1 | 100 | 100 | 100 | 98.3 (*R*) | 18 |

**Table 27.1** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 105 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*S*)-**7**]$BF_4$ | 50 | MeOH | r.t. | 1 | 100 | 100 | 100 | 40.6 (*R*) | 18 |
| 106 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 10 | MeOH | r.t. | 1 | 100 | 100 | 100 | 97.0 (*S*) | 18 |
| 107 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 10 | Acetone | r.t. | 1 | – | 100 | 100 | 95.1 (*S*) | 18 |
| 108 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 10 | THF | r.t. | 1 | – | 100 | 100 | 94.8 (*S*) | 18 |
| 109 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 10 | IPA | r.t. | 1 | – | 100 | 100 | 92.7 (*S*) | 18 |
| 110 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 80 | MeOH | 25 | 0.5 | 100 | 200 | 100 | 96.8 (*S*) | 18 |
| 111 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 96.9 (*S*) | 18 |
| 112 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 20 | MeOH | 25 | 1 | 100 | 100 | 100 | 96.4 (*S*) | 18 |
| 113 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 1 | MeOH | 25 | 4 | 100 | 25 | 100 | 97.2 (*S*) | 18 |
| 114 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 10 | Acetone | 25 | – | 100 | – | 100 | 96.2 (*S*) | 18 |
| 115 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 10 | Acetone | 25 | – | 100 | – | 100 | 95.8 (*S*) | 18 |
| 116 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 10 | Acetone | 25 | – | 100 | – | 100 | 94.5 (*S*) | 18 |
| 117 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 10 | Acetone | 25 | – | 100 | – | 100 | 93.8 (*S*) | 18 |
| 118 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 98.3 (*R*) | 18 |
| 119 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 4 | 1 000 | 250 | 100 | 97.5 (*R*) | 18 |
| 120 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 16 | 10 000 | 625 | 100 | 97.0 (*R*) | 18 |
| 121 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 64 | 41 350 | 646 | 82.7 | 97.0 (*R*) | 18 |
| 122 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 64 | 41 700 | 652 | 41.7 | 93.0 (*R*) | 18 |
| 123 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*R*)-**8**]$BF_4$ | 1 | MeOH | 25 | 1.5 [b] | 50 | 33 | 50 | 13 (*R*) | 15 |
| 124 | Ph | $CO_2Me$ | NHAc | Rh(COD)(*R*)-**9** | 1 | MeOH | 25 | 0.23 [b] | 50 | 217 | 50 | 86 (*S*) [m] | 15 |
| 125 | Ph | $CO_2Me$ | NHAc | Rh(COD)(*R*)-**9** | 1 | MeOH | 25 | 0.33 [b] | 50 | 152 | 50 | 85 (*S*) [k] | 15 |
| 126 | Ph | $CO_2Me$ | NHAc | Rh(COD)(*S*)-**9** | 1 | MeOH | 25 | 0.58 [b] | 500 | 862 | 50 | 82 (*R*) [l] | 15 |
| 127 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 87 (*S*) | 15 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 128 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.6 [b] | 500 | 833 | 50 | 85 (*R*) | 15 |
| 129 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 88 (*S*) | 15 |
| 130 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 88 (*S*)[q] | 15 |
| 131 | Ph | $CO_2Me$ | NHAc | [(*R*)-**9**+CuCl]/[Ru(COD)Cl]$_2$ | 1 | MeOH | 25 | 0.2 [b] | 500 | 2500 | 50 | 85 (*S*) | 15 |
| 132 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*R*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.067 [b] | 500 | 7463 | 50 | 90 (*S*) | 9 |
| 133 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*R*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.062 [b] | 1000 | 16129 | 50 | 89 (*S*) | 9 |
| 134 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*R*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 78 (*S*) | 17 |
| 135 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 76 (*R*) | 17 |
| 136 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**12**]$BF_4$ | 1 | MeOH | 25 | 0.18 [b] | 50 | 278 | 50 | 35 (*R*) | 8 |
| 137 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**13**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 47 (*R*) | 8 |
| 138 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**13**]$BF_4$ | 1 | MeOH | 25 | 0.12 [b] | 50 | 417 | 50 | 40 (*R*) | 8 |
| 139 | Ph | $CO_2Me$ | NHAc | RhCl(*S*)-**13** | 1 | MeOH | 25 | 0.33 [b] | 50 | 152 | 50 | 47 (*R*) | 8 |
| 140 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**14**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 85 (*R*) | 8 |
| 141 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**15**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 89 (*R*) | 8 |
| 142 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**16**]$BF_4$ | 1 | MeOH | 25 | 0.03 [b] | 50 | 1667 | 50 | 86 (*R*) | 8 |
| 143 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**17**]$BF_4$ | 15 | DCM | r.t. | 18 | 30 | 1.7 | 98 | 11 (*S*) | 31 |
| 144 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**17**]$BF_4$ | 15 | PhH | r.t. | 22 | 30 | 1.4 | 95 | 46 (*S*) | 31 |
| 145 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,3*R*,4*S*)-**18**]$BF_4$ | 15 | DCM | r.t. | 3 | 30 | 10 | 95 | 22 (*R*) | 31 |
| 146 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*R*,4*S*)-**19**]$BF_4$ | 15 | DCM | r.t. | 10.5 | 30 | 2.9 | 99 | 89 (*S*) | 31 |
| 147 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*R*,4*S*)-**19**]$BF_4$ | 15 | PhH | r.t. | 20 | 30 | 1.5 | 98 | 99 (*S*) | 31 |
| 148 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*R*,4*S*)-**20**]$BF_4$ | 15 | DCM | r.t. | 4 | 30 | 7.5 | 99 | 88 (*S*) | 31 |
| 149 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*R*,4*S*)-**20**]$BF_4$ | 15 | PhH | r.t. | 17 | 30 | 1.8 | 98 | 95 (*S*) | 31 |
| 150 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*R*,4*S*)-**21**]$BF_4$ | 15 | DCM | r.t. | 4.5 | 30 | 6.7 | 96 | 16 (*S*) | 31 |
| 151 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,3*R*,4*S*)-**22**]$BF_4$ | 15 | DCM | r.t. | 4 | 30 | 7.5 | 95 | 2 (*S*) | 31 |
| 152 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*,4*R*)-**23**]$BF_4$ | 15 | DCM | r.t. | 13 | 30 | 2.3 | 98 | 80 (*S*) | 31 |
| 153 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,3*S*,4*R*,6*R*)-**24**]$BF_4$ | 15 | DCM | r.t. | 12 | 30 | 2.5 | 94 | 1 (*S*) | 31 |
| 154 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,3*S*,5*S*)-**28**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 70 (*S*) | 40 |
| 155 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*R*,5*R*)-**28**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 69 (*R*) | 40 |
| 156 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**29**]$BF_4$ | 1 | MeOH | r.t. | – | – | 1100 | – | 80 (*S*) | 41 |
| 157 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**29**]$BF_4$ | 1 | DCM | r.t. | – | – | 2000 | – | 79 (*S*) | 41 |

**Table 27.1** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 158 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**29**]$BF_4$ | 1 | EtOAc | r.t. | – | – | 500 | – | 74 (*S*) | 41 |
| 159 | Ph | $CO_2Me$ | NHAc | RhCl(COD)(1*S*,2*S*)-**35** | 1 | MeOH | 25 | – | 100 | – | 100 | 87 (*R*) | 37 |
| 160 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*S*)-**35**]$BF_4$ | 1 | MeOH | 25 | – | 100 | – | 100 | 87 (*R*) | 37 |
| 161 | Ph | $CO_2Me$ | NHAc | RhCl(COD)(1*R*,2*R*)-**35** | 1 | MeOH | 25 | – | 100 | – | 100 | 87 (*S*) | 37 |
| 162 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**36**]$BF_4$ | 1 | MeOH | r.t. | – | – | 3500 | – | 91 (*S*) | 41 |
| 163 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**36**]$BF_4$ | 1 | DCM | r.t. | – | – | 1600 | – | 88 (*S*) | 41 |
| 164 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**36**]$BF_4$ | 1 | EtOAc | r.t. | – | – | 2000 | – | 83 (*S*) | 41 |
| 165 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**36**]$BF_4$ | 1 | THF | r.t. | – | – | 1700 | – | 84 (*S*) | 41 |
| 166 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**37**]$BF_4$ | 1 | MeOH | r.t. | – | – | 2700 | – | 85 (*S*) | 41 |
| 167 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**37**]$BF_4$ | 1 | DCM | r.t. | – | – | 1300 | – | 82 (*S*) | 41 |
| 168 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**37**]$BF_4$ | 1 | EtOAc | r.t. | – | – | 2400 | – | 78 (*S*) | 41 |
| 169 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**37**]$BF_4$ | 1 | THF | r.t. | – | – | 1500 | – | 78 (*S*) | 41 |
| 170 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**38**]$BF_4$ | 1 | MeOH | r.t. | – | – | 2700 | – | 71 (*S*) | 41 |
| 171 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**38**]$BF_4$ | 1 | DCM | r.t. | – | – | 1200 | – | 78 (*S*) | 41 |
| 172 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**38**]$BF_4$ | 1 | EtOAc | r.t. | – | – | 2000 | – | 76 (*S*) | 41 |
| 173 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**39**]$BF_4$ | 1 | MeOH | r.t. | – | – | 3000 | – | 74 (*S*) | 41 |
| 174 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*S*,4*S*)-**39**]$BF_4$ | 1 | DCM | r.t. | – | – | 1500 | – | 78 (*S*) | 41 |
| 175 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 0 | 7 | 100 | 14 | 100 | 79.0 (*R*) | 39 |
| 176 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 100 | 14 | 100 | 77.0 (*R*) | 39 |
| 177 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 17.2 | Acetone | 25 | 7 | 100 | 14 | 100 | 78.0 (*R*) | 39 |
| 178 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | MeOH | 25 | 7 | 100 | 14 | 100 | 74.0 (*R*) | 39 |
| 179 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | THF | 25 | 7 | 100 | 14 | 100 | 62.0 (*R*) | 39 |
| 180 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | DCM | 25 | 7 | 100 | 14 | 100 | 72.0 (*R*) | 39 |
| 181 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 97.1 (*R*) | 18, 19 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 182 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.67 [b] | 50 | 75 | 50 | 81 (*R*) | 8 |
| 183 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.016 [b] | 50 | 3 125 | 50 | 89 (*R*) | 8, 10 |
| 184 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.67 [b] | 500 | 746 | 50 | 81 (*S*) | 15 |
| 185 | Ph | $CO_2Me$ | NHBz | Rh(COD)(*R*)-**9** | 1 | MeOH | 25 | 0.28 [b] | 500 | 1 786 | 50 | 87 (*S*) | 15 |
| 186 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**12**]$BF_4$ | 1 | MeOH | 25 | 0.033 [b] | 50 | 1 515 | 50 | 27 (*R*) | 8 |
| 187 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**13**]$BF_4$ | 1 | MeOH | 25 | 0.063 [b] | 50 | 794 | 50 | 40 (*R*) | 8 |
| 188 | Ph | $CO_2Me$ | NHBz | RhCl(*S*)-**13** | 1 | MeOH | 25 | 0.35 [b] | 50 | 143 | 50 | 41 (*R*) | 8 |
| 189 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**14**]$BF_4$ | 1 | MeOH | 25 | 0.033 [b] | 50 | 1 515 | 50 | 87 (*R*) | 8 |
| 190 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**15**]$BF_4$ | 1 | MeOH | 25 | 0.033 [b] | 50 | 1515 | 50 | 92 (*R*) | 8 |
| 191 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**16**]$BF_4$ | 1 | MeOH | 25 | 0.033 [b] | 50 | 1515 | 50 | 88 (*R*) | 8 |
| 192 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(1*S*,3*S*,5*S*)-**28**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 73 (*S*) | 40 |
| 193 | Ph | $CO_2Me$ | NHBz | [Rh(COD)(1*R*,3*R*,5*R*)-**28**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 71 (*R*) | 40 |
| 194 | Ph | $CO_2Me$ | NHCbz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 2 [b] | 50 | 25 | 50 | 88 (*R*) | 10 |
| 195 | Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.83 [b] | 50 | 60 | 50 | 93 (*R*) | 10 |
| 196 | Ph | NHCOMe | $CO_2H$ | [Rh(COD)(*S*)-**2**]$ClO_4$ | 1 | EtOH/ PhH (2:1) | 20 | 0.17–0.5 | 200 | 400–1176 | 100 | 70 (*R*) | 32 |
| 197 | Ph | NHCOMe | $CO_2H$ | [Rh(COD)(*S*)-**29**]$ClO_4$ | 1 | EtOH/ PhH (2:1) | 20 | 0.17–0.5 | 200 | 400–1176 | 100 | 86 (*S*) | 32 |
| 198 | Ph | NHCOMe | $CO_2Me$ | [Rh(COD)(*S*)-**2**]$ClO_4$ | 1 | EtOH/ PhH (2:1) | 20 | 0.17–0.5 | 200 | 400–1176 | 100 | 48 (*R*) | 32 |
| 199 | Ph | NHBz | $CO_2H$ | [Rh(COD)(*S*)-**2**]$ClO_4$ | 1 | EtOH/ PhH (2:1) | 20 | 0.17–0.5 | 200 | 400–1176 | 100 | 53 (*R*) | 32 |
| 200 | Ph | NHBz | $CO_2H$ | [Rh(COD)(*S*)-**29**]$ClO_4$ | 1 | EtOH/ PhH (2:1) | 20 | 0.17–0.5 | 200 | 400–1176 | 100 | 61 (*S*) | 32 |
| 201 | Ph | $MePO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.33 [b] | 25 | 76 | 50 | 77 (*Sc*) [g] | 12, 16 |
| 202 | Ph | $PhPO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.23 [b] | 25 | 109 | 50 | 56 (*Sc*) [g] | 12 |
| 203 | Ph | $PhPO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.33 | 95 | 288 | 95 | 65 (*Sc*) [g] | 16 |
| 204 | Ph | $PhPO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.63 [b] | 25 | 40 | 50 | 76 (*Sc*) [g] | 12 |

**Table 27.1** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | $P[H_2]$ [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 205 | Ph | $PhPO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.93 | 96 | 103 | 96 | 69 (*Sc*)[g] | 16 |
| 206 | Ph | $PhPO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 1.17[b] | 25 | 21 | 50 | 75 (*Sc*)[g] | 12 |
| 207 | Ph | $PhPO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 2.18[b] | 50 | 23 | 50 | 71 (*Sc*)[g] | 12 |
| 208 | Ph | $PhPO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.67[b] | 25 | 37 | 50 | 31 (*Sc*)[g] | 12 |
| 209 | Ph | $PhPO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.67[b] | 25 | 37 | 50 | 79 (*Sc*)[g] | 12 |
| 210 | Ph | $PhPO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 2.18 | – | – | – | 71 (*Sc*)[g] | 16 |
| 211 | Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.23[i] | 95 | 413 | 95[h] | 90 (*S*)[j] | 14 |
| 212 | Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.23[i] | 94 | 409 | 94[h] | 89 (*R*)[j] | 14 |
| 213 | Ph | $PO(OMe)_2$ | NHBz | [Rh(COD) (*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 2.33[i] | 950 | 408 | 95[h] | 89 (*S*)[j] | 14 |
| 214 | Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | PhH | 25 | 1.33[i] | 95 | 71 | 95[h] | 82 (*S*)[j] | 14 |
| 215 | Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | THF | 25 | 0.6[i] | 94 | 157 | 94[h] | 83 (*S*)[j] | 14 |
| 216 | Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**15**]$BF_4$ | 1 | MeOH | 25 | 0.2[i] | 97 | 485 | 97[h] | 91 (*S*)[j] | 14 |
| 217 | Ph | $PO(OEt)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.23[i] | 96 | 417 | 96[h] | 92 (*S*)[j] | 14 |
| 218 | Ph | $PO(O^iPr)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 1.03[i] | 95 | 92 | 95[h] | 91 (*S*)[j] | 14 |
| 219 | $C_6F_5$ | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.17[b] | 50 | 294 | 50 | 86 (*S*) | 42 |
| 220 | *o*-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 92.3 (*R*) | 18 |
| 221 | *o*-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | Acetone | 25 | 1 | 100 | 100 | 100 | 98.4 (*R*) | 18 |
| 222 | *o*-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 95–100 | 42 (*R*) | 39 |
| 223 | *m*-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 95.1(*R*) | 18 |
| 224 | *m*-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 95–100 | 85 (*R*) | 39 |
| 225 | *p*-Cl-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05[b] | 100 | 2000 | 50 | 90 (*R*) | 11 |
| 226 | *p*-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 97.8 (*R*) | 18, 19 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 227 | *p*-Cl-Ph | $CO_2Me$ | NHBz | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 97.0 (*R*) | 18, 19 |
| 228 | *p*-Cl-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05[b] | 100 | 2000 | 50 | 89 (*R*) | 11 |
| 229 | *p*-Cl-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 95–100 | 84 (*R*) | 39 |
| 230 | *p*-Cl-Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.17[i] | 96 | 565 | 96[h] | 90 (*S*)[j] | 14 |
| 231 | *p*-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 98.0 (*R*) | 18, 19 |
| 232 | *p*-Br-Ph | $CO_2Me$ | NHBz | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 96.5 (*R*) | 18, 19 |
| 233 | *o*-F-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.022[b] | 100 | 4545 | 50 | 91 (*R*) | 42 |
| 234 | *o*-F-Ph | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.017[b] | 100 | 5882 | 50 | 91 (*S*) | 42 |
| 235 | *o*-F-Ph | $CO_2H$ | NHBz | [(2*S*,3*S*)-**35**-CuCl]/[Ru(-COD)Cl]$_2$ (2 : 1) | 1 | MeOH | 25 | 0.17 | 100 | 588 | 50 | 75 (*R*) | 42 |
| 236 | *o*-F-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.018 | 50 | 2778 | 50 | 90.4 (*S*) | 42 |
| 237 | *o*-F-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.018 | 100 | 5556 | 50 | 89 (*S*) | 42 |
| 238 | *o*-F-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.025 | 50 | 2000 | 50 | 86.4 (*R*) | 42 |
| 239 | *o*-F-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.022 | 100 | 4545 | 50 | 88 (*R*) | 42 |
| 240 | *o*-F-Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.23[i] | 97 | 421 | 97[h] | 92 (*S*)[j] | 14 |
| 241 | *m*-F-Ph | $CO_2H$ | NHBz | [(1*S*,2*S*)-**35**-CuCl]/[Ru(COD)Cl]$_2$ (2 : 1) | 1 | MeOH | 25 | 0.22 | 100 | 455 | 50 | 71 (*R*) | 42 |
| 242 | *m*-F-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.022 | 100 | 4545 | 50 | 88 (*R*) | 42 |
| 243 | *m*-F-Ph | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.017 | 100 | 5882 | 50 | 90 (*S*) | 42 |
| 244 | *m*-F-Ph | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.33 | 500 | 1515 | 50 | 89 (*S*) | 42 |
| 245 | *m*-F-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.028 | 100 | 3571 | 50 | 89 (*R*) | 42 |
| 246 | *m*-F-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.027 | 100 | 3703 | 50 | 88 (*S*) | 42 |
| 247 | *m*-F-Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.27[i] | 96 | 356 | 96[h] | 90 (*S*)[j] | 14 |
| 248 | *p*-F-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.017 | 100 | 5882 | 50 | 88 (*R*) | 42 |
| 249 | *p*-F-Ph | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.017 | 100 | 5882 | 50 | 88 (*S*) | 42 |
| 250 | *p*-F-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.28 | 1000 | 3571 | 50 | 90 (*R*) | 42 |
| 251 | *p*-F-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 2.67 | 1500 | 562 | 50 | 86 (*R*) | 42 |
| 252 | *p*-F-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ Deuteration | 1 | MeOH | 25 | 0.017 | 25 | 1471 | 50 | 90 (*R*) | 42 |
| 253 | *p*-F-Ph | $CO_2H$ | NHBz | [(1*S*,2*S*)-**35**-CuCl]/[Ru(-COD)Cl]$_2$ (2 : 1) | 1 | MeOH | 25 | 0.15 | 100 | 667 | 50 | 75 (*R*) | 42 |

**Table 27.1** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 254 | *p*-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 97.2 (*R*) | 18, 19 |
| 255 | *p*-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 95–100 | 80 (*R*) | 39 |
| 256 | *p*-F-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.043 [b] | 100 | 2326 | 50 | 89 (*R*) | 42 |
| 257 | *p*-F-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.038 [b] | 100 | 2632 | 50 | 90 (*S*) | 42 |
| 258 | *p*-F-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.15 [b] | 50 | 333 | 50 | 92 (*R*) | 7, 9 |
| 259 | *p*-F-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.07 [b] | 50 | 714 | 50 | 94 (*R*) | 7, 9 |
| 260 | *p*-F-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*R*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.07 [b] | 50 | 714 | 50 | 94 (*S*) | 7, 9 |
| 261 | *p*-F-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*R*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.13 [b] | 50 | 385 | 50 | 87 (*S*) | 7, 17 |
| 262 | *p*-F-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.13 [b] | 50 | 385 | 50 | 86 (*R*) | 17 |
| 263 | *p*-F-Ph | $PhPO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 1 [b] | 25 | 25 | 50 | 64 (*Sc*) [g] | 12 |
| 264 | *p*-F-Ph | $PhPO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 1 | 95 | 95 | 95 | 64 (*Sc*) [g] | 16 |
| 265 | *p*-F-Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.23 [i] | 96 | 417 | 96 [h] | 89 (*S*) [j] | 14 |
| 266 | *p*-$CF_3$-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.017 [b] | 100 | 5882 | 50 | 90 (*R*) | 42 |
| 267 | *p*-$CF_3$-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.1 [b] | 50 | 500 | 50 | 93 (*R*) | 7, 9 |
| 268 | *p*-$CF_3$-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.07 [b] | 50 | 714 | 50 | 95 (*R*) | 7, 9 |
| 269 | *p*-$CF_3$-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*R*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.08 [b] | 50 | 625 | 50 | 94 (*S*) | 7, 9, 17 |
| 270 | *p*-$CF_3$-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*R*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.17 [b] | 50 | 294 | 50 | 86 (*S*) | 7 |
| 271 | *p*-$CF_3$-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.17 [b] | 50 | 294 | 50 | 85 (*R*) | 17 |
| 272 | *p*-$CF_3$-Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.17 [i] | 95 | 559 | 95 [h] | 90 (*S*) [j] | 14 |
| 273 | *p*-CN-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 95 (*R*) | 11 |
| 274 | *p*-$NO_2$-Ph | $CO_2H$ | NHBz | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 97.4 (*R*) | 18, 19 |
| 275 | *p*-$NO_2$-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 91 (*R*) | 11 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 276 | *p*-$NO_2$-Ph | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 90 (*S*) | 11 |
| 277 | *p*-$NO_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 97.5 (*R*) | 18, 19 |
| 278 | *p*-$NO_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 95–100 | 90 (*R*) | 39 |
| 279 | *p*-$NO_2$-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 80 (*R*) | 11 |
| 280 | *p*-$NO_2$-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.1 [b] | 50 | 500 | 50 | 92 (*R*) | 7, 9 |
| 281 | *p*-$NO_2$-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.08 [b] | 50 | 625 | 50 | 93 (*R*) | 7, 9 |
| 282 | *p*-$NO_2$-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*R*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.1 [b] | 50 | 500 | 50 | 94 (*S*) | 7, 9, 17 |
| 283 | *p*-$NO_2$-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*R*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.15 [b] | 50 | 385 | 50 | 85 (*S*) | 7, 17 |
| 284 | *p*-$NO_2$-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.15 [b] | 50 | 333 | 50 | 85 (*R*) | 17 |
| 285 | *p*-$NO_2$-Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.17 [i] | 95 | 559 | 95 [h] | 91 (*S*) [j] | 14 |
| 286 | *p*-$NO_2$-Ph | $PhPO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.75 | 95 | 127 | 95 | 60 (*Sc*) [g] | 16 |
| 287 | *o*-HO-Ph | $CO_2Me$ | NHBz | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 96.3 (*R*) | 18, 19 |
| 288 | *p*-MeO-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 90 (*R*) | 11 |
| 289 | *p*-MeO-Ph | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 92 (*S*) | 11 |
| 290 | *p*-MeO-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 88 (*R*) | 11 |
| 291 | *p*-MeO-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 91 (*S*) | 11 |
| 292 | *p*-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 97.3 (*R*) | 18, 19 |
| 293 | *p*-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 95–100 | 82 (*R*) | 39 |
| 294 | *p*-AcO-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 95.6 (*R*) | 18, 19 |
| 295 | *p*-AcO-Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 95–100 | 80 (*R*) | 39 |
| 296 | *p*-$NMe_2$-Ph | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 50 | 1000 | 50 | 72 (*S*) | 11 |
| 297 | *p*-$NMe_2$-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 85 (*S*) | 11 |
| 298 | *o*-Me-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 86 (*S*) | 11 |
| 299 | *p*-Me-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 89 (*S*) | 11 |
| 300 | *p*-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 97.3 (*R*) | 18, 19 |
| 301 | *p*-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 95–100 | 62 (*R*) | 39 |

**Table 27.1** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 302 | *p*-Me-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.12 [b] | 50 | 417 | 50 | 93 (*R*) | 7, 9 |
| 303 | *p*-Me-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*R*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.18 | 50 | 278 | 50 | 85 (*S*) | 7, 17 |
| 304 | *p*-Me-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.16 [b] | 50 | 313 | 50 | 84 (*R*) | 17 |
| 305 | 4-$^i$Pr-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 92 (*R*) | 11 |
| 306 | 4-$^i$Pr-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 89 (*S*) | 11 |
| 307 | 4-$^i$Pr-Ph | $PhPO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 2.35 [b] | 25 | 11 | 50 | 60 (*Sc*) [g] | 12 |
| 308 | 4-$^i$Pr-Ph | $PhPO_2Et$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 4.5 | 95 | 21 | 95 | 60 (*Sc*) [g] | 16 |
| 309 | 4-$^i$Pr-Ph | $PO(OMe)_2$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.4 [i] | 95 | 238 | 95 [h] | 87 (*S*) [j] | 14 |
| 310 | *p*-$^t$Bu-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**10**]$BF_4$ | 1 | MeOH | 25 | 0.12 [b] | 50 | 417 | 50 | 92 (*R*) | 7, 9 |
| 311 | *p*-$^t$Bu-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*R*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.25 [b] | 50 | 200 | 50 | 86 (*S*) | 7, 17 |
| 312 | *p*-$^t$Bu-Ph | $CO_2Me$ | NHBoc | [Rh(COD)(*S*)-**11**]$BF_4$ | 1 | MeOH | 25 | 0.25 [b] | 50 | 200 | 50 | 85 (*R*) | 17 |
| 313 | 2,4-dimethyl-Ph | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 79 (*R*) | 11 |
| 314 | 2,4-dimethyl-Ph | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 82 (*S*) | 11 |
| 315 | 1-naphthyl | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 86 (*R*) | 11 |
| 316 | 1-naphthyl | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 88 (*S*) | 11 |
| 317 | 2-naphthyl | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 87 (*R*) | 11 |
| 318 | 2-naphthyl | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 92 (*S*) | 11 |
| 319 | 2-naphthyl | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 89 (*R*) | 11 |
| 320 | 2-naphthyl | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 100 | 2000 | 50 | 89 (*S*) [e] | 11 |
| 321 | 9-phenanthryl | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 50 | 000 | 50 | 65 (*R*) | 11 |
| 322 | 9-phenanthryl | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 25 | 500 | 50 | 63 (*S*) | 11 |
| 323 | 3-OMe-4-OAc-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 50 | 100 | 100 | 98.1 (*R*) | 18, 19 |
| 324 | 3-OAc-4-OMe-Ph | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 97.4 (*S*) | 18 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 325 | 3-Me-4-OAc-Ph | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 95–100 | 75 (*R*) | 39 |
| 326 | 3-OH-4-OMe-Ph | $CO_2H$ | NHBz | Rh(COD)(*S*)-**9** | 1 | MeOH | 25 | 0.083 [b] | 50 | 602 | 50 | 83 (*R*) | 15 |
| 327 | 3,4-$(OMe)_2$Ph | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 50 | 1000 | 50 | 90 (*R*) | 15 |
| 328 | 3,4-$(OMe)_2$Ph | $CO_2H$ | NHBz | Rh(COD)(*S*)-**9** | 1 | MeOH | 25 | 0.12 [b] | 50 | 417 | 50 | 82 (*R*) | 15 |
| 329 | 3,4-$(OMe)_2$Ph | $CO_2H$ | NHBz | [(*R*)-**9**+CuCl]/[Ru(COD)$Cl]_2$ | 1 | MeOH | 25 | 0.45 [b] | 250 | 556 | 50 | 87 (*S*) | 15 |
| 330 | 3,4-$(OMe)_2$Ph | $CO_2Me$ | NHAc | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.067 [b] | 50 | 746 | 50 | 87 (*S*) | 15 |
| 331 | 3,4-$(OMe)_2$Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**9**]$BF_4$ | 1 | MeOH | 25 | 0.5 [b] | 500 | 1000 | 50 | 81 (*R*) [m,p] | 15 |
| 332 | 3,4-$(OMe)_2$Ph | $CO_2Me$ | NHBz | Rh(COD)(*S*)-**9** | 1 | MeOH | 25 | 0.2 [b] | 50 | 250 | 50 | 84 (*R*) | 15 |
| 333 | 3,4-$(OMe)_2$Ph | $CO_2Me$ | NHBz | Rh(COD)(*S*)-**9** | 1 | PhH | 25 | 1.75 [b] | 50 | 29 | 50 | 8 (*R*) | 15 |
| 334 | 2-Cl-3-OAc-4-OMe-Ph | $CO_2Me$ | NHBz | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 98.0 (*R*) | 18 |
| 335 | 4-OMe-3-OAc-Ph | NHCOMe | $CO_2H$ | [Rh(COD)(*S*)-**2**]$ClO_4$ | 1 | EtOH/PhH (2:1) | 20 | 0.17-0.5 | 200 | 400-1176 | 100 | 83 (*R*) | 32 |
| 336 | 4-OMe-3-OAc-Ph | NHCOMe | $CO_2H$ | [Rh(COD)(*S*)-**29**]$ClO_4$ | 1 | EtOH/PhH (2:1) | 20 | 0.17-0.5 | 200 | 400-1176 | 100 | 82 (*S*) | 32 |
| 337 | 3,4-methylene-dioxyphenyl | $CO_2H$ | NHAc | Rh(COD)(*S*)-**9** | 1 | PhH | 25 | 0.12 [b] | 50 | 417 | 50 | 67 (*R*) | 15 |
| 338 | 3,4-methylene-dioxyphenyl | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 97.5 (*R*) | 18 |
| 339 | 3,4-methylene-dioxyphenyl | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 95–100 | 76 (*R*) | 39 |
| 340 | 3,4-methylene-dioxyphenyl | NHCOMe | $CO_2H$ | [Rh(COD)(*S*)-**2**]$ClO_4$ | 1 | EtOH/PhH (2:1) | 20 | 0.17–0.5 | 200 | 400–1176 | 100 | 78 (*R*) | 32 |
| 341 | 3,4-methylene-dioxyphenyl | NHCOMe | $CO_2H$ | [Rh(COD)(*S*)-**29**]$ClO_4$ | 1 | EtOH/PhH (2:1) | 20 | 0.17–0.5 | 200 | 400–1176 | 100 | 81 (*S*) | 32 |
| 342 | 2-furyl | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 91.1 (*R*) | 18 |
| 343 | 2-furyl | $CO_2Me$ | NHAc | [Rh(COD)(*exo*-**40**)]$BF_4$ | 34.5 | Acetone | 25 | 7 | 95–100 | 13.6–14.3 | 5–100 | 83 (*R*) | 39 |

**Table 27.1** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | $P[H_2]$ [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 344 | Thiophen-2-yl | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.033 [b] | 50 | 1515 | 50 | 90 (*R*) | 4 |
| 345 | Thiophen-2-yl | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.43 [b] | 500 | 1163 | 50 | 89 (*R*) | 4 |
| 346 | Thiophen-2-yl | $CO_2H$ | NHAc | [Rh(COD)(*R*)-**9**]$^+$ | 1 | MeOH | 25 | 0.033 [b] | 50 | 1515 | 50 | 90 (*S*) | 4 |
| 347 | Thiophen-2-yl | $CO_2H$ | NHAc | [Rh(COD)(1*S*,2*S*)-**35**]$^+$ | 1 | MeOH | 25 | 0.058 [b] | 50 | 862 | 50 | 78 (*R*) | 4 |
| 348 | Thiophen-2-yl | $CO_2H$ | NHBz | [Rh(COD)(1*S*,2*S*)-**35**]$^+$ | 1 | MeOH | 25 | 0.067 [b] | 50 | 746 | 50 | 80 (*R*) | 4 |
| 349 | Thiophen-2-yl | $CO_2H$ | NHBz | [Rh(COD)(*R*)-**9**)]$^+$ | 1 | MeOH | 25 | 0.042 [b] | 50 | 1190 | 50 | 90 (*S*) | 4 |
| 350 | Thiophen-2-yl | $CO_2Me$ | NHAc | [Rh(COD(*S*)-**9**)]$^+$ | 1 | MeOH | 25 | 0.05 [b] | 50 | 1000 | 50 | 88 (*R*) | 4 |
| 351 | Thiophen-2-yl | $CO_2Me$ | NHAc | [Rh(COD(*S*)-**9**)]$^+$ | 1 | MeOH | 25 | 0.33 [b] | 250 | 758 | 50 | 86 (*R*) | 4 |
| 352 | Thiophen-2-yl | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*R*,5*R*)-**28**]$BF_4$ | 1 | MeOH | 25 | 0.1 [b] | 50 | 500 | 50 | 63 (*R*) | 40 |
| 353 | Thiophen-2-yl | $CO_2Me$ | NHAc | [Rh(COD) (+)(1*S*,2*S*)-**35**]$^+$ | 1 | MeOH | 25 | 0.067 [b] | 50 | 746 | 50 | 77 (*R*) | 4 |
| 354 | Thiophen-2-yl | $CO_2Me$ | NHBz | [Rh(COD)(1*S*,2*S*)-**35**]$^+$ | 1 | MeOH | 25 | 0.083 | 50 | 602 | 50 | 75 (*R*) | 4 |
| 355 | Thiophen-2-yl | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**)]$^+$ | 1 | MeOH | 25 | 0.67 [b] | 50 | 746 | 50 | 90 (*S*) | 4 |
| 356 | Thiophen-3-yl | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 88 (*R*) | 4 |
| 357 | Thiophen-3-yl | $CO_2H$ | NHAc | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.13 [b] | 500 | 3846 | 50 | 84 (*R*) | 4 |
| 358 | Thiophen-3-yl | $CO_2H$ | NHAc | [Rh(COD)(1*S*,2*S*)-**35**]$^+$ | 1 | MeOH | 25 | 0.042 [b] | 50 | 1190 | 50 | 70 (*R*) | 4 |
| 359 | Thiophen-3-yl | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 85 (*R*) | 4 |
| 360 | Thiophen-3-yl | $CO_2H$ | NHBz | [Rh(COD)(*S*)-**9**]$^+$ | 1 | MeOH | 25 | 0.058 [b] | 250 | 4310 | 50 | 84 (*R*) | 4 |
| 361 | Thiophen-3-yl | $CO_2H$ | NHBz | [Rh(COD)(+)(1*S*,2*S*)-**35**]$^+$ | 1 | MeOH | 25 | 0.042 [b] | 50 | 1190 | 50 | 65 (*R*) | 4 |
| 362 | Thiophen-3-yl | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**9**)]$^+$ | 1 | MeOH | 25 | 0.02 [b] | 50 | 2500 | 50 | 86 (*R*) | 4 |
| 363 | Thiophen-3-yl | $CO_2Me$ | NHAc | [Rh(COD)(*S*)-**9**)]$^+$ | 1 | MeOH | 25 | 0.25 [b] | 250 | 1000 | 50 | 83 (*R*) | 4 |
| 364 | Thiophen-3-yl | $CO_2Me$ | NHAc | [Rh(COD)(1*R*,3*R*,5*R*)**28**]$BF_4$ | 1 | MeOH | 25 | 0.017 [b] | 50 | 2941 | 50 | 64 (*R*) | 40 |
| 365 | Thiophen-3-yl | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*S*)-**35**]$^+$ | 1 | MeOH | 25 | 0.033 [b] | 50 | 1515 | 50 | 72 (*R*) | 4 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 366 | Thiophen-3-yl | $CO_2Me$ | NHBz | [Rh(COD)(*S*-**9**)]$^+$ | 1 | MeOH | 25 | 0.025 [b] | 50 | 2000 | 50 | 85 (*R*) | 4 | |
| 367 | Thiophen-3-yl | $CO_2Me$ | NHBz | [Rh(COD)(1*R*,3*R*,5*R*)-**28**]$BF_4$ | 1 | MeOH | 25 | 0.05 [b] | 50 | 1000 | 50 | 64 (*R*) | 40 | |
| 368 | Thiophen-3-yl | $CO_2Me$ | NHBz | [Rh(COD)(+)(1*S*,2*S*)-**35**]$^+$ | 1 | MeOH | 25 | 0.042 [b] | 50 | 1190 | 50 | 70 (*R*) | 4 | |
| 369 | Pyridin-3-yl | $CO_2H$ | NHAc | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.033 [b] | 50 | 1515 | 50 | 89 (*R*) | 5 | |
| 370 | Pyridin-3-yl | $CO_2H$ | NHAc | [Rh(COD)(*R*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.05 [b] | 50 | 1000 | 50 | 90 (*S*) | 6 | |
| 371 | Pyridin-3-yl | $CO_2H$ | NHAc | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.27 [b] | 250 | 926 | 50 | 85 (*R*) | 5, 6 | |
| 372 | Pyridin-3-yl | $CO_2H$ | NHAc | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.45 [b] | 500 | 1111 | 50 | 78 (*R*) | 5, 6 | |
| 373 | Pyridin-3-yl | $CO_2H$ | NHAc | [Rh(COD)(+)(1*S*,2*S*)-**35**] $BF_4$ [d] | 1 | MeOH | 25 | 0.083 [b] | 50 | 602 | 50 | 86 (*R*) | 5 | |
| 374 | Pyridin-3-yl | $CO_2H$ | NHBz | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.67 [b] | 50 | 746 | 50 | 86 (*R*) [f] | 5, 6 | |
| 375 | Pyridin-3-yl | $CO_2H$ | NHBz | [Rh(COD)(*R*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.05 [b] | 50 | 1000 | 50 | 86 (*S*) | 6 | |
| 376 | Pyridin-3-yl | $CO_2H$ | NHBz | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.18 [b] | 50 | 1389 | 50 | 87 (*R*) | 6 | |
| 377 | Pyridin-3-yl | $CO_2H$ | NHBz | [Rh(COD)(1*S*,2*S*)-**35**]$BF_4$ [d] | 1 | MeOH | 25 | 0.1 [b] | 50 | 500 | 50 | 60 (*R*) | 6 | |
| 378 | Pyridin-3-yl | $CO_2Me$ | NHAc | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.05 [b] | 50 | 1000 | 50 | 90 (*R*) | 6 | |
| 379 | Pyridin-3-yl | $CO_2Me$ | NHAc | [Rh(COD)(*R*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.033 [b] | 50 | 1515 | 50 | 89 (*S*) | 5, 6 | |
| 380 | Pyridin-3-yl | $CO_2Me$ | NHAc | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.5 [b] | 500 | 1000 | 50 | 83 (*R*) | 5, 6 | |
| 381 | Pyridin-3-yl | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*S*)-**35**] $BF_4$ [d] | 1 | MeOH | 25 | 0.067 [b] | 50 | 746 | 50 | 84 (*R*) | 5 | |
| 382 | Pyridin-3-yl | $CO_2Me$ | NHBz | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.1 [b] | 50 | 500 | 50 | 88 (*R*) | 5, 6 | |
| 383 | Pyridin-3-yl | $CO_2Me$ | NHBz | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.42 [b] | 250 | 595 | 50 | 84 (*R*) | 5, 6 | |
| 384 | Pyridin-3-yl | $CO_2Me$ | NHBz | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.67 [b] | 500 | 746 | 50 | 81 (*R*) | 5, 6 | |
| 385 | Pyridin-3-yl | $CO_2Me$ | NHBz | [Rh(COD)(1*R*,3*R*,5*R*)-**28**]$BF_4$ [d] | 1 | MeOH | 25 | 0.12 [b] | 50 | 417 | 50 | 59 (*R*) | 40 | |
| 386 | Pyridin-3-yl | $CO_2Me$ | NHBz | [Rh(COD)(1*S*,2*S*)-**35**] $BF_4$ | 1 | MeOH | 25 | 0.18 [b] | 50 | 278 | 50 | 70 (*R*) | 5 | |
| 387 | Pyridin-4-yl | $CO_2H$ | NHAc | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.033 [b] | 50 | 1515 | 50 | 89 (*S*) | 5, 6 | |
| 388 | Pyridin-4-yl | $CO_2H$ | NHAc | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.25 [b] | 250 | 1000 | 50 | 84 (*R*) | 5, 6 | |
| 389 | Pyridin-4-yl | $CO_2H$ | NHAc | [Rh(COD)(1*S*,2*S*)-**35**] $BF_4$ [d] | 1 | MeOH | 25 | 0.1 [b] | 50 | 500 | 50 | 82 (*R*) | 5 | |
| 390 | Pyridin-4-yl | $CO_2H$ | NHBz | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.05 [b] | 50 | 1000 | 50 | 87 (*R*) | 5, 6 | |
| 391 | Pyridin-4-yl | $CO_2H$ | NHBz | Rh(COD)(1*S*,2*S*)-**35**]$BF_4$ [d] | 1 | MeOH | 25 | 0.083 [b] | 50 | 602 | 50 | 74 (*R*) | 5, 6 | |
| 392 | Pyridin-4-yl | $CO_2Me$ | NHAc | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.033 [b] | 50 | 11515 | 50 | 89 (*R*) | 5, 6 | |
| 393 | Pyridin-4-yl | $CO_2Me$ | NHAc | [Rh(COD)(*S*-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.42 [b] | 500 | 1190 | 50 | 86 (*R*) | 5, 6 | |

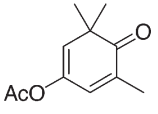
Table 27.1 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | $P[H_2]$ [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 394 | Pyridin-4-yl | $CO_2Me$ | NHAc | [Rh(COD)(1*S*,2*S*)-**35**]$BF_4$ [d] | 1 | MeOH | 25 | 0.067 [b] | 50 | 746 | 50 | 74 (*R*) | 5 |
| 395 | Pyridin-4-yl | $CO_2Me$ | NHBz | [Rh(COD)(*R*)-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.05 [b] | 50 | 1000 | 50 | 90 (*S*) | 5, 6 |
| 396 | Pyridin-4-yl | $CO_2Me$ | NHBz | [Rh(COD)(*S*)-**9**]$BF_4$ [d] | 1 | MeOH | 25 | 0.42 [b] | 500 | 1190 | 50 | 86 (*R*) | 5 |
| 397 | Pyridin-4-yl | $CO_2Me$ | NHBz | [Rh(COD)(1*R*,3*R*,5*R*)-**28**]$BF_4$ [d] | 1 | MeOH | 25 | 0.12 [b] | 50 | 417 | 50 | 59 (*R*) | 40 |
| 398 | Pyridin-4-yl | $CO_2Me$ | NHBz | [Rh(COD)(1*S*,2*S*)-**35**] $BF_4$ | 1 | MeOH | 25 | 0.1 [b] | 50 | 500 | 50 | 72 (*R*) | 6 |
| 399 | $PhCH_2$ | $CO_2H$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | r.t. | 4 | 81 | 20.3 | 81 | 2.9 (*S*) [c] | 30 |
| 400 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*S*,2*R*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 93.1 (*R*) | 18 |
| 401 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$BF_4$ | 50 | MeOH | 25 | 1 | 100 | 100 | 100 | 92.5 (*S*) | 18, 30 |
| 402 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | EtOH | r.t. | 1 | 100 | 100 | 100 | 77.1 (*S*) | 30 |
| 403 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | IPA | r.t. | 1 | 100 | 100 | 100 | 83.9 (*S*) | 30 |
| 404 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | THF | r.t. | 1 | 100 | 100 | 100 | 88.3 (*S*) | 30 |
| 405 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | $CH_2Cl_2$ | r.t. | 1 | 76.1 | 76.1 | 76.1 | 52.4 (*S*) | 30 |
| 406 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | Acetone | r.t. | 1 | 89.3 | 89.3 | 89.3 | 79.0 (*S*) | 30 |
| 407 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | PhH | r.t. | 1 | 100 | 100 | 100 | 80.2 (*S*) | 30 |
| 408 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 3 | MeOH | r.t. | 5 | 100 | 20 | 100 | 94.6 (*S*) | 30 |
| 409 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 20 | MeOH | r.t. | 3 | 100 | 33 | 100 | 95.2 (*S*) | 30 |
| 410 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | r.t. | 1 | 100 | 100 | 100 | 95.7 (*S*) | 30 |
| 411 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | –10 | 4 | 100 | 25 | 100 | 93.6 (*S*) | 30 |
| 412 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | 10 | 1 | 100 | 100 | 100 | 95.7 (*S*) | 30 |
| 413 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | 30 | 1 | 100 | 100 | 100 | 93.3 (*S*) | 30 |
| 414 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | 50 | 0.5 | 100 | 200 | 100 | 70.8 (*S*) | 30 |
| 415 | $PhCH_2$ | $CO_2Et$ | NHAc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | r.t. | 1 | 19 | 19 | 19 | 85.0 (*S*) | 30 |
| 416 | $PhCH_2$ | $CO_2Et$ | NHBz | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | r.t. | 1 | 100 | 100 | 100 | 94.6 (*S*) | 30 |
| 417 | $PhCH_2$ | $CO_2Et$ | NHCbz | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | r.t. | 1 | 20 | 20 | 20 | 58.4 (*S*) | 30 |
| 418 | $PhCH_2$ | $CO_2Et$ | $NHCO_2CH_2$-$CH(CH_3)_2$ | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | r.t. | 1 | 94 | 94 | 94 | 93.1 (*S*) | 30 |

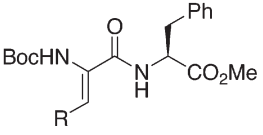
| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 419 | $PhCH_2$ | $CO_2Et$ | NHBoc | [Rh(COD)(1*R*,2*S*)-**7**]$ClO_4$ | 50 | MeOH | r.t. | 4 | 43 | 10.8 | 43 | 78.1 (*S*) | 30 |
| 420 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)(*S*)-**1**]$ClO_4$ | 1 | EtOH | 20 | – | – | – | – | 10 (*R*)[a] | 2a,b |
| 421 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)(1*R*,2*S*)-**3**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 64 (*S*) | 36 |
| 422 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)(1*R*,2*S*)-**3**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 59 (*S*) | 36 |
| 423 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)(1*R*)-**4**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 3 (*S*) | 36 |
| 424 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)(1*R*)-**4**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 0 | 36 |
| 425 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)(1*R*,2*R*)-**5**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 12 (*R*) | 36 |
| 426 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)(1*R*,2*R*)-**5**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 8 (*R*) | 36 |
| 427 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)(2*R*)-**6**]$BF_4$ | 1 | Dioxane | 25 | – | – | – | – | 31 (*R*) | 36 |
| 428 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)(2*R*)-**6**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 14 (*R*) | 36 |
| 429 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)(*R*)-**9**]$BF_4$ | 1 | $CD_3OD$ | 25 | – | – | – | – | 70 (*S*) | 13 |
| 430 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)(*R*)-**13**]$BF_4$ | 1 | $CD_3OD$ | 25 | – | – | – | – | 40 (*S*) | 13 |
| 431 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)(*R*)-**14**]$BF_4$ | 1 | $CD_3OD$ | 25 | – | – | – | – | 78 (*S*) | 13 |
| 432 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)(*R*)-**15**]$BF_4$ | 1 | $CD_3OD$ | 25 | – | – | – | – | 80 (*S*) | 13 |
| 433 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)(*R*)-**16**]$BF_4$ | 1 | $CD_3OD$ | 25 | – | – | – | – | 25 (*S*) | 13 |
| 434 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)(*S*)-**29**]$ClO_4$ | 1 | EtOH | 20 | – | – | – | – | 20 (*R*)[a] | 2a,b |

**a)** Optical yield.
**b)** t/2 for uptake 50% of theoretical hydrogen volume.
**c)** ee determination of the corresponding ester using diazomethane.
**d)** Addition of 1.5 equiv. $HBF_4$ .
**e)** ee determination after recrystallization.
**f)** Partial reaction with methanol to produce the corresponding ester.
**g)** The ee-values with respect to the $\alpha$-carbon atom can be determined from the enantiomeric excesses of the diastereomer pairs of the ester.
**h)** Crude yield after evaporation of solvent.
**i)** Approx. reaction time=approx. time for uptake of half of the $H_2$ volume×2.
**j)** Configuration (*S*) corresponds to the D-configuration of amino carboxylic acids.
**k)** Catalyst [RhCOD(*R*)-**9**]$^+$ – half-year exposure to air.
**l)** Preformed ligand-RhCl(Benzene).
**m)** Preformed complex.
**n)** Exposed to air.
**o)** Stirred for 1 h in 50% methanol/water.
**p)** Stock solution in benzene after 10 days (29 mL methanol + 1 mL stock solution).
**q)** Ligand stored for one month on air.
**r)** Catalyst solution agitated for 30 min with air.

**Table 27.2** Asymmetric hydrogenation of other prochiral olefins.




**11**




**12**

**12a**: R = Ph
**12b**: R = *p*-$CH_3$-Ph
**12c**: R = *p*-F-Ph
**12d**: R = *p*-$CF_3$-Ph

| Entry | Catalyst | Substrate | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time h] | | | | | |
| 1 | [Rh(*R*)-**25**]$BF_4$ | 11 | 10 | EtOAc | r.t. | 18 | 100 | 5.6 | 100 | 71 (*S*) | 34 |
| 2 | [Rh(*S*)-**26**]$BF_4$ | 11 | 10 | EtOAc | r.t. | 18 | 100 | 5.6 | 100 | 71 (*R*) | 34 |
| 3 | [Rh(*S*)-**27**]$BF_4$ | 11 | 10 | EtOAc | r.t. | 18 | 100 | 5.6 | 100 | 5 (*S*) | 34 |
| 4 | [Rh(*S*)-**32**]$BF_4$ | 11 | 10 | EtOAc | r.t. | 18 | 100 | 5.6 | 100 | 30 (*R*) | 34 |
| 5 | [Rh(*S*)-**33**]$BF_4$ | 11 | 10 | EtOAc | r.t. | 18 | 100 | 5.6 | 100 | 95 (*R*) | 34 |
| 6 | [Rh(*S*)-**34**]$BF_4$ | 11 | 10 | EtOAc | r.t. | 18 | 100 | 5.6 | 100 | 31 (*R*) | 34 |
| 7 | [Rh(COD)(*R*)-**10**]$BF_4$ | 12a | 1 | MeOH | 25 | 1 | – | – | – | 77 [a] | 7 |
| 8 | [Rh(COD)(*R*)-**10**]$BF_4$ | 12b | 1 | MeOH | 25 | 1.17 | – | – | – | 76 [a] | 7 |
| 9 | [Rh(COD)(*R*)-**10**]$BF_4$ | 12c | 1 | MeOH | 25 | 1.3 | – | – | – | 78 [a] | 7 |
| 10 | [Rh(COD)(*R*)-**10**]$BF_4$ | 12d | 1 | MeOH | 25 | 1.17 | – | – | – | 91 [a] | 7 |

**a)** The ee-values with respect to the *α*-carbon atom can be determined from the enantiomeric excesses of the diastereomer pairs of the ester (see [12]).

10 000 was completed within 16 h, giving the desired product in 97% ee (Table 27.1, entry 120; 98.3% ee at SCR 100, Table 27.1, entry 118). These results were comparable to those using phosphine and phosphinite ligands (e.g., DuPhos, 99% ee [20]; DIPAMP, 96% ee [21]; TRAP, 92% ee [22]; DIOP, 55% ee [23]; CAPP, 95.6% ee [24]; BPPFA, 21% ee [25]; Ph-*β*-Glup, 91.5% ee [26]; SpirOP, 95.7% ee [27]). Further application in the hydrogenation of methyl 2-acetamido-3-(3-methoxy-4-acetoxyphenyl)-acrylate (a crucial intermediate in the synthesis of L-dopa [28]) was successfully achieved in 97.4% ee (Table 27.1, entry 324). Similarly, the enantioselective hydrogenation of ethyl (*Z*)-2-acetamido-4-phenylcrotonate gave the homophenylalanine derivative in 92.5% ee (Table 27.1, entry 401). This product is a key component of (*S*,*S*)-benazepril, an angiotensin-converting enzyme inhibitor widely used as an antihypertensive agent [29]. Jiang studied the hydrogenation of *N*-protected (*Z*)-2-aminocrotonates and found that the enantioselectivity and activity were strongly dependent on the type of *N*-protecting group used (NHAc, 95.7% ee with 100% conv.; $NHCO_2Me$, 85% ee with 19% conv.; Table 27.1, entry 412 versus 415) [30]. The results from using Rh–DPAMPP compared favorably with many commonly used chiral Rh–diphosphine catalysts (e.g., Rh–BINAP, 21.8% ee with 100% conv.; Rh–DIPAMP, 50.8% ee with 100% conv.; Rh–BDPP, 69.4% ee with 100% conv.; Rh–PPM, 14.4% ee with 7.9% conv. under the same reaction conditions).

The introduction of extra stereogenicity at the phosphorus centers is one of the methods used to increase chiral induction. Indeed, replacement of the pro-*R* phenyl with an *o*-anisyl group on the ephedrine backbone of EPHOS **17** gave **19** which was highly effective in the hydrogenation of methyl *α*-acetamidocinnamate, giving the product in 99% ee (Table 27.1, entry 147). In contrast, the use of EPHOS **17** induced only 46% ee (Table 27.1, entry 144) under the same conditions [31]. Similarly, replacement of the phenyl group with 1-naphthyl gave ligand **20** which led to 95% ee in the same reaction (Table 27.1, entry 149). It is interesting to note that the structurally similar *o*-anisyl ligands **19** and **23** derived from (+) and (–)-ephedrine, respectively, both induce high ee-values with the same (*S*) configuration of the product amino ester. This clearly shows the predominance of the chiral P center over the carbon backbone effect. However, the poor result obtained in the case of **24** bearing *o*-anisyl (*S*p) aminophosphine and (*R*p) phosphinite groups might be due to the quasi-meso structure that did not give any asymmetric induction (Fig. 27.3 c) [1, 31].

Petit reported a close analogue to ProNOP lacking the rigid pyrrolidine ring, yet, the results with both ligands in the hydrogenation of (*E*)-acetamidocinnamic acid derivatives were similar (ProNOP, 61–86% ee; NETAlaNOP, 53–83% ee) [32]. With these substrates, it is important that the problem of *E*/*Z* isomerization (as highlighted by Noyori) should be considered [33]. Ligands **25** to **27** are the only type of amidophosphine-phosphinites applied in asymmetric hydrogenation [34]. Ligand **33** was found to be highly effective in the hydrogenation of 4-oxoisophorone enol acetate (100% conversion, 95% ee (*R*): Table 27.2, entry 5; Scheme 27.1). The product, (*S*)-phorenol acetate, is an intermediate in the synthesis of the natural pigment zeaxanthin [35]. The Rh complexes with **25** or **26**

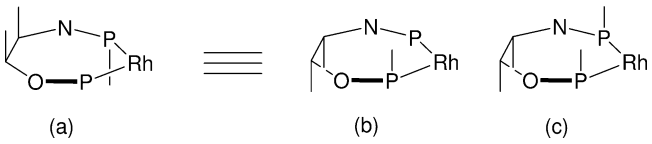
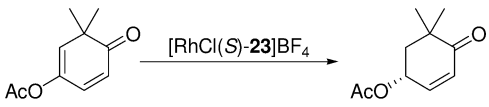



**Fig. 27.3** Quasi-meso effect in asymmetric induction.

gave 71% ee in the same reaction (Table 27.2, entries 1 and 2). The other ephedrine-based ligands, including **1** and **3** to **6** [2, 36], afforded poor to moderate enantioselectivity in the rhodium-catalyzed hydrogenation of 2-acetamido-cinnamic acid derivatives. Structural variation leading to increased rigidity of the ligand backbone is one of the promising methods to enhance enantioselectivity. Cesarotti developed an aminophosphine-phosphinite based on the rigid pyrrolidine structure of prolinol [2]. However, results with this ligand in the enantiomeric hydrogenation of dehydroamino acid derivatives were only poor to moderate. Petit [32] improved the results and obtained up to 86% ee. Interestingly, when using $[Rh(COD)(L)]ClO_4$ as catalyst, both the *Z* and *E* isomeric substrates were converted to products with the same configuration (Table 27.1, entries 93 versus 200).

During the late 1980s, Döbler and Pracejus introduced the bicyclic [2.2.1] system to provide extra conformational rigidity to the ligand backbone [37]. The synthesis of these new chiral ligands was based on the resolution of the amino alcohol obtained from the aminolysis of *exo*-norbornane epoxide [38], followed by reaction with the corresponding chlorophosphine. Indeed, the *in-situ*-prepared cationic or neutral Rh catalysts based on ligand **35** resulted in better enantioselectivity in hydrogenation of 2-acetamido-acrylic acid (up to 89% ee: Table 27.1, entry 6).

The ease of preparation of (1*S*,2*R*)-1-hydroxylmethyl-2-amino-7,7-dimethylbicyclo [2.2.1] heptane from ketopinic acid prompted us to synthesize a new AMPP ligand (i.e., *exo*-**40**) [39]. The rhodium-catalyzed enantioselective hydrogenation of 2-acetamido-acrylic acid using this ligand gave the product in 77% ee with 95–100% conversion. Electron-withdrawing groups on the *β*-substituted phenyl ring of the substrate resulted in significant enantioselectivity enhancement (Ph, 77% ee; 4-MePh, 62% ee; 4-$NO_2$Ph, 90% ee). The effect of solvents on the enantioselectivity of the reaction was also quite significant, with acetone being found the best. Döbler performed the enantiomeric hydrogenation of standard dehydroamino acid and other heteroaryl derivatives using the rhodium complex based on bicyclo [3.3.0]-octane (i.e., **28**), resulting in moderate enantioselectivities (58–73% ee) [40]. More recently, ligands **36** to **39** based on the bicyclic




**Scheme 27.1** 95% ee

[2.2.1] system were prepared [41]. The effect of the additional *P*-stereogenic center(s) was also explored with these ligands. The application of these ligands in enantiomeric hydrogenation resulted in products with up to 91% ee and TOFs ranging from 600 to 4000 $h^{-1}$. The substitution of one or both P-phenyl groups by a *p*-tolyl group resulted in a slight decrease of the enantioselectivity, regardless of the heteroatom linker (N or O) [42].

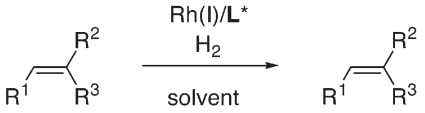
## 27.3 Bisphosphinamidite Ligands

The early development of this type of ligand was concentrated during the late 1970s and early 1980s. In 1976, the first article published on this topic was written by Giongo and co-workers, who described the initial synthesis of a chiral bisphosphinamidite **41** and its application in the enantiomeric hydrogenation of a number of dehydroamino acid derivatives [43]. The resulting enantioselectivities were comparable to the state-of-the-art ligand DIOP. In pursuing the same line of research, the Pracejus group also prepared (*S,S*)-**41** and achieved similar results [44]. Subsequently, the Giongo group further introduced other $C_2$-symmetric, 1,2-diamine-tethered bisphosphinites **42–49** with ee-values reaching 94% in the hydrogenation of (*Z*)-2-acetamidoacrylic acid (Table 27.3) [45]. Interestingly, both Giongo and Onuma noticed that when the hydrogen atoms of the amino groups were replaced with methyl groups whilst keeping the backbone chirality unchanged (as in the cases of **45** versus **46** and **47** versus **48**), a reversal of product configuration was observed. The Onuma group rationalized this by proposing a model wherein the helicity of the edge-phenyl groups on the phosphorus atoms were of opposite sense in the presence and absence of the methyl groups, respectively, as a result of a change of chirality on the nitrogen atoms. Non-$C_2$-symmetric pyrrolidine-based ligands **50–52** were also tested in asymmetric hydrogenation [47], though the results obtained were unsatisfactory. The use of a 1,4-diamino bridged bisphosphinamidite **53** was described in a recent publication in which excellent selectivity was recorded for the hydrogenation of α-acylaminocinnamic acid [48].

Surprisingly, given that many *P*-chiral ligands are efficient chiral inducers, only one example has been reported of a $C_2$-symmetric, *P*-chiral bisphosphinamidite. Ligand **54** was prepared by Wills et al. and tested in the Rh-catalyzed enantioselective hydrogenation of α-acylaminoacrylate to give disappointingly low selectivity (33% ee) and low efficiency (TON = 20, TOF = 0.4) [49].

Bisphosphinamidites which are supported by an axially chiral framework are another important class of ligands. Although reported as early as 1980 [50], no reports on the use of binaphthyl-based bisphosphinamidite in asymmetric catalysis were published during the decade thereafter. As described above, the selectivity and substrate generality in these early attempts were very limited in scope. In 1998, we unveiled that by partially hydrogenating BINAM to $H_8$-BINAM and

**Table 27.3** Bisphosphinamidite ligands.




| Entry | Substrate | | | Ligand (L) | P[$H_2$] [atm] | Solvent | Temp. [°C] | Time [h] | TON Sub:Rh | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | | | | | | | | | |
| 1 | H | Ph | NHAc | **55a** | 1.0 | THF | r.t. | 0.5 | 200 | 100 | 100 | 93 | 51a, 52 |
| 2 | H | Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 98 | 54 |
| 3 | H | Ph | NHAc | **56a** | 1.0 | THF | r.t. | 0.5 | 200 | 400 | 100 | 97 | 51b |
| 4 | H | Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 96 | 54 |
| 5 | H | 3-Cl-Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 98 | 54 |
| 6 | H | 3-Cl-Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 98 | 54 |
| 7 | H | 4-Cl-Ph | NHAc | **55a** | 1.0 | THF | r.t. | 0.5 | 200 | 400 | 100 | 95 | 51a |
| 8 | H | 4-Cl-Ph | NHAc | **56a** | 1.0 | THF | 0 | 0.5 | 200 | 400 | 100 | 97 | 51a,b |
| 9 | H | 3-Br-Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 98 | 54 |
| 10 | H | 3-Br-Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 97 | 54 |
| 11 | H | 4-Br-Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 98 | 54 |
| 12 | H | 4-Br-Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 95 | 54 |
| 13 | H | 4-F-Ph | NHAc | **55a** | 1.0 | THF | r.t. | 0.5 | 172 | 344 | 86 | 90 | 51a |
| 14 | H | 4-F-Ph | NHAc | **56a** | 1.0 | THF | 0 | 0.5 | 200 | 400 | 100 | 96 | 51a,b |
| 15 | H | 4-$CF_3$-Ph | NHAc | **55a** | 1.0 | THF | r.t. | 0.5 | 500 | 400 | 100 | 95 | 51a, 52 |
| 16 | H | 4-$CF_3$-Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 99 | 54 |
| 17 | H | 4-$CF_3$-Ph | NHAc | **56a** | 1.0 | THF | 0 | 0.5 | 200 | 400 | 100 | 99 | 51a,b |
| 18 | H | 4-$CF_3$-Ph | NHAc | **56a** | 1.0 | THF | 5 | 0.5 | 1000 | 2000 | 100 | 99 | 51a |
| 19 | H | 4-$CF_3$-Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 97 | 54 |
| 20 | H | 3-$CH_3O$-Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 97 | 54 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 21 | H | 3-$CH_3O$-Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 97 | 54 |
| 22 | H | 3-$CH_3$-Ph | NHAc | **55a** | 1.0 | THF | r.t. | 0.5 | 186 | 372 | 93 | 95 | 51b |
| 23 | H | 3-$CH_3$-Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 98 | 54 |
| 24 | H | 3-$CH_3$-Ph | NHAc | **56a** | 1.0 | THF | 0 | 0.5 | 200 | 400 | 100 | 98 | 51a,b |
| 25 | H | 3-$CH_3$-Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 98 | 54 |
| 26 | H | 4-$CH_3$-Ph | NHAc | **55a** | 1.0 | THF | r.t. | 0.5 | 500 | 1000 | 100 | 95 | 51a |
| 27 | H | 4-$CH_3$-Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 96 | 54 |
| 28 | H | 4-$CH_3$-Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 94 | 54 |
| 29 | H | 4-$CH_3$-Ph | NHAc | **56a** | 1.0 | THF | 0 | 0.5 | 200 | 400 | 100 | 97 | 51a,b |
| 30 | H | 4-$CH_3$-Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 96 | 54 |
| 31 | H | 4-$CH_3$-Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 94 | 54 |
| 32 | H | 4-Et-Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 97 | 54 |
| 33 | H | 4-Et-Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 97 | 54 |
| 34 | H | 2-furyl | NHAc | **55a** | 1.0 | THF | r.t. | 0.5 | 200 | 400 | 100 | 96 | 51a |
| 35 | H | 2-furyl | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 98 | 54 |
| 36 | H | 2-furyl | NHAc | **56a** | 1.0 | THF | 0 | 0.5 | 200 | 400 | 100 | 98 | 51a,b |
| 37 | H | 2-furyl | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 96 | 54 |
| 38 | Me | Ph | NHAc | **55b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 93 | 54 |
| 39 | Me | Ph | NHAc | **56b** | 2.0 | THF | r.t. | 0.17 | 200 | 1200 | 100 | 94 | 54 |
| 40 | Me | 4-Cl-Ph | NHAc | **56a** | 1 | THF | 0 | 2 | 200 | 100 | 100 | 80.3 | 51b |
| 41 | Me | 4-$CH_3$-Ph | NHAc | **56a** | 1 | THF | 0 | 2 | 193 | 97 | 97 | 77 | 51b |
| 42 | H | $CO_2H$ | NHAc | **41a** | 1 | MeOH | 25 | – | 570 | – | 95 | 73[a)] | 43 |
| 43 | H | $CO_2H$ | NHAc | **41a** | 1 | EtOH | 25 | – | – | – | 90–100 | 76.7 | 45b (*R*) |
| 44 | H | $CO_2H$ | NHAc | **41b** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 25.1 | 45b (*S*) |
| 45 | H | $CO_2H$ | NHAc | **42** | 25 | EtOH | 25 | – | 125 | – | 90–100 | 83[a)] | 45a |
| 46 | H | $CO_2H$ | NHAc | **42** | 5 | EtOH | 25 | – | 125 | – | 90–100 | 83.9[a)] | 45b |
| 47 | H | $CO_2H$ | NHAc | **43** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 78.9[a)] | 45b |
| 48 | H | $CO_2H$ | NHAc | **44** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 88.1 | 45b |
| 49 | H | $CO_2H$ | NHAc | **45** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 89.5 | 45b |

Table 27.3 (continued)

| Entry | Substrate | | | Ligand (L) | P[$H_2$] [atm] | Solvent | Temp. [°C] | Time [h] | TON Sub:Rh | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | | | | | | | | | |
| 50 | H | $CO_2H$ | NHAc | **46** | 5 | EtOH | 25 | – | 125 | – | 90–100 | 86.2 | 45b |
| 51 | H | $CO_2H$ | NHAc | **47a** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 24.0 | 45b |
| 52 | H | $CO_2H$ | NHAc | **48** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 90.9 | 45b |
| 53 | H | $CO_2H$ | NHAc | **49** | 5 | EtOH | 25 | – | 125 | – | 90–100 | 12.0 | 45b |
| 54 | H | $CO_2H$ | NHAc | (*S*,*S*)-**50** | 1 | EtOH | 25 | – | 125 | – | – | 33 | 47a |
| 55 | H | $CO_2H$ | NHAc | (*S*,*R*)-**50** | 1 | EtOH | 25 | – | 125 | – | – | 61 | 47a |
| 56 | H | $CO_2H$ | NHAc | **51** | 1 | EtOH | 25 | – | 125 | – | – | 68 | 47a |
| 57 | H | $CO_2H$ | NHAc | **53** | 24 | *i*PrOH | r.t. | 24 | 77 | 32 | 77 | 68 | 48 |
| 58 | H | $CO_2H$ | NHAc | **55a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 93.5 | 52 |
| 59 | H | $CO_2H$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 98 | 53, 54 |
| 60 | H | $CO_2H$ | NHAc | **56a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 99 | 51b, 52 |
| 61 | H | $CO_2H$ | NHAc | **58** | 1 | EtOH | r.t. | 1.5 | 74.5 | 50 | 15 | 78 | 55 |
| 62 | Ph | $CO_2H$ | NHAc | **41a** | 1 | MeOH | 25 | – | 300 | – | 95 | 84[a)] | 43, 45a |
| 63 | Ph | $CO_2H$ | NHBz | **41a** | 1 | MeOH | 25 | – | 50 | – | 70 | 68[a)] | 43 |
| 64 | Ph | $CO_2H$ | NHBz | **41a** | 1 | EtOH | 25 | 0.08–0.67 | – | 1008 | 90–100 | 75 | 45a |
| 65 | Ph | $CO_2H$ | NHAc | **41a** | 1 | MeOH | 25 | 0.03 | 48 | 1600 | 45 | 81.7[a)] | 44 |
| 66 | Ph | $CO_2H$ | NHAc | **41a** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 77.3 | 45b, 47a |
| 67 | Ph | $CO_2H$ | NHAc | **41b** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 40.8 | 45b, 47a |
| 68 | Ph | $CO_2H$ | NHAc | **42** | 10 | EtOH | 0 | – | 125 | – | 90–100 | 93[a)] | 45a |
| 69 | Ph | $CO_2H$ | NHAc | **42** | 5 | EtOH | 25 | – | 125 | – | 90–100 | 80.6[a)] | 45b |
| 70 | Ph | $CO_2H$ | NHAc | **43** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 74.8[a)] | 45b |
| 71 | Ph | $CO_2H$ | NHAc | **44** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 91.9 | 45b |
| 72 | Ph | $CO_2H$ | NHAc | **45** | 2 | EtOH | 25 | – | 125 | – | 90–100 | 94.4 | 45b,c, 47a |
| 73 | Ph | $CO_2H$ | NHAc | **46** | 5 | EtOH | 25 | – | 125 | – | 90–100 | 68.4 | 45b,c, 47a |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 74 | Ph | $CO_2H$ | NHAc | **47a** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 47.0 | 45b, 47a |
| 75 | Ph | $CO_2H$ | NHAc | **47a** | 7.8 | EtOH : PhH 1 : 1 | r.t. | – | – | – | – | 70 | 46 |
| 76 | Ph | $CO_2H$ | NHAc | **47b** | 7.8 | EtOH : PhH 1 : 1 | r.t. | – | – | – | – | 72 | 46 |
| 77 | Ph | $CO_2H$ | NHBz | **47a** | 7.8 | EtOH : PhH 1 : 1 | r.t. | – | – | – | – | 62 | 46 |
| 78 | Ph | $CO_2H$ | NHBz | **47b** | 7.8 | EtOH : PhH 1 : 1 | r.t. | – | – | – | – | 60 | 46 |
| 79 | Ph | $CO_2H$ | NHAc | **48** | 1 | EtOH | 25 | – | 125 | – | 90–100 | 92.1 | 45b, 46, 47a |
| 80 | Ph | $CO_2H$ | NHBz | **48** | 7.8 | EtOH | r.t. | – | – | – | – | 92 | 46 |
| 81 | Ph | $CO_2H$ | NHAc | **49** | 5 | EtOH | 25 | – | 125 | – | 90–100 | rac | 45b |
| 82 | Ph | $CO_2H$ | NHAc | (*S*,*S*)-**50** | 4.5 | EtOH | 25 | – | 125 | – | – | 35 | 47a |
| 83 | Ph | $CO_2H$ | NHAc | (*S*,*R*)-**50** | 4.5 | EtOH | 25 | – | 125 | – | – | 59 | 47a |
| 84 | Ph | $CO_2H$ | NHAc | **51** | 4.5 | EtOH | 25 | – | 125 | – | – | 69 | 47a |
| 85 | Ph | $CO_2H$ | NHAc | **53** | 1 | *i*PrOH | r.t. | 24 | 100 | 4.2 | 100 | 98 | 48 |
| 86 | Ph | $CO_2H$ | NHAc | **55a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 90.3 | 52 |
| 87 | Ph | $CO_2H$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 98 | 53, 54 |
| 88 | Ph | $CO_2H$ | NHAc | **56a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 94.2 | 52 |
| 89 | Ph | $CO_2H$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 79.6 | 56 |
| 90 | Ph | $CO_2H$ | NHAc | **58** | 1 | EtOH | r.t. | 1.5 | 500 | 333 | 100 | >98 | 55 |
| 91 | Ph | $CO_2Me$ | NHAc | **41a** | 1 | MeOH | 25 | – | 450 | – | 100 | 49[a)] | 43 |
| 92 | Ph | $CO_2Me$ | NHAc | **41a** | – | $C_6H_6$ | 25 | 0.03* | 50 | 313 | 45 | 82.5[a)] | 44 |
| 93 | Ph | $CO_2Me$ | NHAc | **41a** | 1 | EtOH | 25 | 0.08–0.67 | – | 828 | 90–100 | 55 | 45a |
| 94 | Ph | $CO_2Me$ | NHAc | **54** | 1 | MeOH | – | 48 | 20 | 0.4 | 95 | 33 | 49 |
| 95 | Ph | $CO_2Me$ | NHAc | **55a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 90 | 52 |
| 96 | Ph | $CO_2Me$ | NHAc | **55a** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 91 | 53, 54 |
| 97 | Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.5 | 5000 | 10000 | 100 | 98.6 | 53, 54 |
| 98 | Ph | $CO_2Me$ | NHAc | **55c** | 3.4 | MeOH | r.t. | 0.5 | 500 | 1000 | 100 | 13 | 53, 54 |
| 99 | Ph | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 96 | 51b, 52 |
| 100 | Ph | $CO_2Me$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 200 | 20 | 100 | 73.7 | 56 |

**Table 27.3** (continued)

| Entry | Substrate | | | Ligand (L) | P[$H_2$] [atm] | Solvent | Temp. [°C] | Time [h] | TON Sub:Rh | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | | | | | | | | | |
| 101 | Ph | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | >99 | 55 |
| 102 | Ph | $CO_2NH_2$ | NHAc | **47a** | 7.8 | EtOH:PhH 1:1 | r.t. | – | – | – | – | 92 | 46 |
| 103 | Ph | $CO_2NH_2$ | NHAc | **47b** | – | EtOH:PhH 1:1 | r.t. | – | – | – | – | 92 | 46 |
| 104 | Ph | $CO_2NH_2$ | NHAc | **47b** | – | EtOH:PhH 1:1 | r.t. | – | – | – | – | 70 | 46 |
| 105 | 2-Cl-Ph | $CO_2H$ | NHAc | **55a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 90 | 52 |
| 106 | 2-Cl-Ph | $CO_2H$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 94 | 51b, 52 |
| 107 | 2-Cl-Ph | $CO_2H$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 78.1 | 56 |
| 108 | 2-Cl-Ph | $CO_2H$ | NHAc | **58** | 1 | EtOH | r.t. | 1.5 | 500 | 333 | 100 | 96 | 55 |
| 109 | 2-Cl-Ph | $CO_2Me$ | NHAc | **55a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 90 | 52 |
| 110 | 2-Cl-Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 97 | 53, 54 |
| 111 | 2-Cl-Ph | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 97 | 52 |
| 112 | 2-Cl-Ph | $CO_2Me$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 72.0 | 56 |
| 113 | 2-Cl-Ph | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | 96 | 55 |
| 114 | 3-Cl-Ph | $CO_2H$ | NHAc | **55a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 88 | 52 |
| 115 | 3-Cl-Ph | $CO_2H$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 93 | 51b, 52 |
| 116 | 3-Cl-Ph | $CO_2H$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 76.3 | 56 |
| 117 | 3-Cl-Ph | $CO_2H$ | NHAc | **58** | 1 | EtOH | r.t. | 1.5 | 500 | 333 | 100 | 95 | 55 |
| 118 | 3-Cl-Ph | $CO_2Me$ | NHAc | **55a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 90 | 52 |
| 119 | 3-Cl-Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 97 | 53, 54 |
| 120 | 3-Cl-Ph | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 94 | 51b, 52 |
| 121 | 3-Cl-Ph | $CO_2Me$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 72.1 | 56 |
| 122 | 3-Cl-Ph | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | >99 | 55 |
| 123 | 4-Cl-Ph | $CO_2H$ | NHAc | **55a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 86 | 52 |
| 124 | 4-Cl-Ph | $CO_2H$ | NHAc | **56a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 93 | 51b, 52 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 125 | 4-Cl-Ph | $CO_2H$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 79.1 | 56 |
| 126 | 4-Cl-Ph | $CO_2Me$ | NHAc | **55a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 88 | 52 |
| 127 | 4-Cl-Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 98 | 53, 54 |
| 128 | 4-Cl-Ph | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 94 | 51b, 52 |
| 129 | 4-Cl-Ph | $CO_2Me$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 74.0 | 56 |
| 130 | 4-Cl-Ph | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | >99 | 55 |
| 131 | 4-Cl-Ph | $CO_2Me$ | NHBz | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 99 | 53 |
| 132 | 4-Br-Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 98 | 53 |
| 133 | 4-Br-Ph | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 96 | 51b, 52 |
| 134 | 4-Br-Ph | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | >99 | 55 |
| 135 | 4-Br-Ph | $CO_2Me$ | NHBz | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 96 | 51b, 52 |
| 136 | 4-F-Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 98 | 53, 54 |
| 137 | 4-F-Ph | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 93 | 51b, 52 |
| 138 | 4-F-Ph | $CO_2Me$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 73.0 | 56 |
| 139 | 4-F-Ph | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | >99 | 55 |
| 140 | 4-F-Ph | $CO_2Me$ | NHBz | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 94 | 51b, 52 |
| 141 | 4-F-Ph | $CO_2Me$ | NHBz | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 99 | 53, 54 |
| 142 | 4-$NO_2$-Ph | $CO_2H$ | NHAc | **56a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 90 | 51b, 52 |
| 143 | 4-$NO_2$-Ph | $CO_2H$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 76.4 | 56 |
| 144 | 4-$NO_2$-Ph | $CO_2Me$ | NHAc | **55a** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 82 | 53, 54 |
| 145 | 4-$NO_2$-Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 96 | 53, 54 |
| 146 | 4-$NO_2$-Ph | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 91 | 51b, 52 |
| 147 | 4-$NO_2$-Ph | $CO_2Me$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 73.4 | 56 |
| 148 | 4-$NO_2$-Ph | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | 94 | 55 |
| 149 | 4-$CH_3$-Ph | $CO_2Me$ | NHAc | **55a** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 89 | 53, 54 |
| 150 | 4-$CH_3$-Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 98 | 53, 54 |
| 151 | 4-$CH_3$-Ph | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 94 | 51b, 52 |
| 152 | 4-$CH_3$-Ph | $CO_2Me$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 200 | 20 | 100 | 71.2 | 56 |
| 153 | 4-$CH_3$-Ph | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | >98 | 55 |

**Table 27.3** (continued)

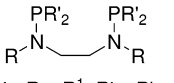
| Entry | Substrate | | | Ligand (L) | P[$H_2$] [atm] | Solvent | Temp. [°C] | Time [h] | TON Sub:Rh | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | | | | | | | | | |
| 154 | 4-$CH_3$-Ph | $CO_2Me$ | NHBz | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 95 | 51b, 52 |
| 155 | 2-$CH_3O$-Ph | $CO_2H$ | NHAc | **56a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 93 | 51b, 52 |
| 156 | 2-$CH_3O$-Ph | $CO_2H$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 79.0 | 56 |
| 157 | 2-$CH_3O$-Ph | $CO_2H$ | NHAc | **58** | 1 | EtOH | r.t. | 1.5 | 500 | 333 | 100 | 84 | 55 |
| 158 | 4-$CH_3O$-Ph | $CO_2Me$ | NHAc | **53** | 1 | *i*PrOH | r.t. | 24 | 100 | 4.2 | 100 | 91 | 48 |
| 159 | 4-$CH_3O$-Ph | $CO_2Me$ | NHAc | **55a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 93 | 52 |
| 160 | 4-$CH_3O$-Ph | $CO_2Me$ | NHAc | **55a** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 87 | 53, 54 |
| 161 | 4-$CH_3O$-Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 98 | 53, 54 |
| 162 | 4-$CH_3O$-Ph | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 93 | 51b, 52 |
| 163 | 4-$CH_3O$-Ph | $CO_2Me$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 72.7 | 56 |
| 164 | 4-$CH_3O$-Ph | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | >99 | 55 |
| 165 | 4-$CH_3O$-Ph | $CO_2Me$ | NHBz | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 95 | 51b, 52 |
| 166 | 4-AcO-Ph | $CO_2Me$ | NHAc | **55a** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 87 | 53,54 |
| 167 | 4-AcO-Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 98 | 53, 54 |
| 168 | 4-HO-Ph | $CO_2Me$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 74.6 | 56 |
| 169 | 3,4-($CH_2O_2$)-Ph | $CO_2H$ | NHAc | **41a** | 1 | MeOH | 25 | | 50 | | 90 | 75[a)] | 43 |
| 170 | 3,4-($CH_2O_2$)-Ph | $CO_2H$ | NHAc | **41a** | 1 | EtOH | 25 | | – | 612 | 90–100 | 77 | 45a |
| 171 | 3,4-($CH_2O_2$)-Ph | $CO_2H$ | NHAc | **55a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 77 | 52 |
| 172 | 3,4-($CH_2O_2$)-Ph | $CO_2H$ | NHAc | **56a** | 2.0 | EtOH | r.t. | 0.17 | 100 | 600 | 100 | 91 | 51b, 52 |
| 173 | 3,4-($CH_2O_2$)-Ph | $CO_2H$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 80.3 | 56 |
| 174 | 3,4-($CH_2O_2$)-Ph | $CO_2H$ | NHAc | **58** | 1 | EtOH | r.t. | 1.5 | 500 | 333 | 100 | 92 | 55 |
| 175 | 3,4-($CH_2O_2$)-Ph | $CO_2Me$ | NHAc | **55a** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 81 | 53 |
| 176 | 3,4-($CH_2O_2$)-Ph | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 98 | 53, 54 |
| 177 | 3,4-($CH_2O_2$)-Ph | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 93 | 51b, 52 |
| 178 | 3,4-($CH_2O_2$)-Ph | $CO_2Me$ | NHAc | **57** | 6.7 | $(CH_3)_2CO$ | 25 | 5 | 100 | 20 | 100 | 76.2 | 56 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 179 | 3,4-($CH_2O_2$)-Ph | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | >98 | 55 |
| 180 | 3-$CH_3O$,4-Ac-Ph | $CO_2H$ | NHAc | **58** | 1 | EtOH | r.t. | 1.5 | 500 | 333 | 100 | 94 | 55 |
| 181 | 3-$CH_3O$,4-AcO-Ph | $CO_2H$ | NHAc | **41a** | 1 | EtOH | 25 | – | 396 | – | 90–100 | 87 | 45a |
| 182 | 2-furyl | $CO_2Me$ | NHAc | **55a** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 84 | 53, 54 |
| 183 | 2-furyl | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 98 | 53, 54 |
| 184 | 2-furyl | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 91 | 51b, 52 |
| 185 | 2-furyl | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1.5 | 500 | 333 | 100 | >99 | 55 |
| 186 | 2-furyl | $CO_2H$ | NHBz | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 94 | 51b, 52 |
| 187 | 2-furyl | $CO_2Me$ | NHBz | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 93 | 51b, 52 |
| 188 | (*E*)-PhCH=CH | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 90 | 51b, 52 |
| 189 | H | $CO_2Et$ | OC(O)Me | **58** | 1 | THF | r.t. | 1.5 | 250 | 167 | 100 | 97 | 55 |
| 190 | H | $CO_2Me$ | NHAc | **53** | 1 | *i*PrOH | r.t. | 24 | 77 | 3.2 | 77 | 68 | 48 |
| 191 | H | $CO_2Me$ | NHAc | **55a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 93 | 51, 52 |
| 192 | H | $CO_2Me$ | NHAc | **55b** | 3.4 | MeOH | r.t. | 0.17 | 500 | 3000 | 100 | 97 | 53, 54 |
| 193 | H | $CO_2Me$ | NHAc | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 97 | 52 |
| 194 | H | $CO_2Me$ | NHAc | **58** | 1 | $(CH_3)_2CO$ | r.t. | 1 | 500 | 500 | 100 | 95 | 55 |
| 195 | *N*-Ac-3-indole | $CO_2Me$ | NHBz | **56a** | 2.0 | THF | r.t. | 0.17 | 100 | 600 | 100 | 93 | 52 |
| 196 | H | $CO_2H$ | $CH_2CO_2H$ | **41a** | 5 | EtOH | 25 | – | 50 | – | 90–100 | 12.3 | 45b |
| 197 | H | $CO_2H$ | $CH_2CO_2H$ | **41b** | 5 | EtOH | 25 | – | 50 | – | 90–100 | 35.1 | 45b |
| 198 | H | $CO_2H$ | $CH_2CO_2H$ | **42** | 5 | EtOH | 25 | – | 50 | – | 90–100 | 7.9 | 45b |
| 199 | H | $CO_2H$ | $CH_2CO_2H$ | **43** | 5 | EtOH | 25 | – | 50 | – | 90–100 | 36.6 | 45b |
| 200 | H | $CO_2H$ | $CH_2CO_2H$ | **44** | 5 | EtOH | 25 | – | 50 | – | 90–100 | 25.3 | 45b |

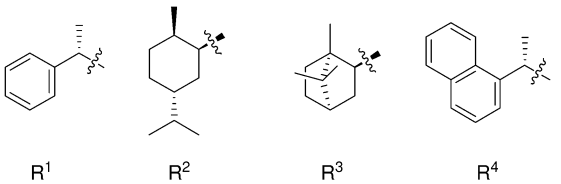
**Table 27.3** (continued)

| Entry | Substrate | | | Ligand (L) | $P[H_2]$ [atm] | Solvent | Temp. [°C] | Time [h] | TON Sub:Rh | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | | | | | | | | | |
| 201 | H | $CO_2H$ | $CH_2CO_2H$ | **45** | 5 | EtOH | 25 | – | 50 | – | 90–100 | 71.4 | 45b,c |
| 202 | H | $CO_2H$ | $CH_2CO_2H$ | **46** | 5 | EtOH | 25 | – | 50 | – | 90–100 | 5.8 | 45b,c |
| 203 | H | $CO_2H$ | $CH_2CO_2H$ | **47a** | 5 | EtOH | 25 | – | 50 | – | 90–100 | 60.3 | 45b |
| 204 | H | $CO_2H$ | $CH_2CO_2H$ | **48** | 5 | EtOH | 25 | – | 50 | – | 90–100 | 8.2 | 45b |
| 205 | H | $CO_2H$ | $CH_2CO_2H$ | **49** | 5 | EtOH | 25 | – | 50 | – | 90–100 | 5.8 | 45b |
| 206 | H | $CO_2H$ | $CH_2CO_2H$ | **58** | 1 | THF | r.t. | 1.5 | 250 | 167 | 100 | 68 | 55 |
| 207 | H | $CO_2Me$ | $CH_2CO_2Me$ | **58** | 1 | THF | r.t. | 1.5 | 250 | 167 | 100 | 93 | 55 |
| 208 | H | $CO_2Me$ | OC(O)Me | **58** | 1 | THF | r.t. | 1.5 | 250 | 167 | 100 | 96 | 55 |
| 209 | $CH_2OH$ | Me | $Me_2C{=}CH(CH_2)_2$ | **52** | 10 | $C_6H_6$ | r.t. | 8 | 48 | 6.0 | 95 | 68 | 47b |
| 210 | $CH_2OH$ | $Me_2C{=}CH(CH_2)_2$ | Me | **52** | 10 | $C_6H_6$ | r.t. | 8 | 49 | 6.1 | 97 | 61 | 47b |

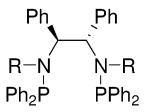
**a)** Optical yield.



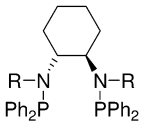
**41a** R = $R^1$, R' = $Ph_2$
**41b** R = $R^1$, R' = $Et_2$
**42** R = $R^2$, R' = $Ph_2$
**43** R = $R^3$, R' = $Ph_2$
**44** R = $R^4$, R' = $Ph_2$



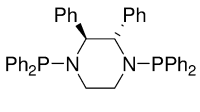
$R^1$ $R^2$ $R^3$ $R^4$



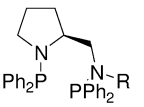
(*S*,*S*)-**45**: R = H
(*S*,*S*)-**46**: R = Me



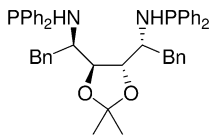
(*R*,*R*)-**47a**: R = H
(*S*,*S*)-**47b**: R = H
(*R*,*R*)-**48**: R = Me



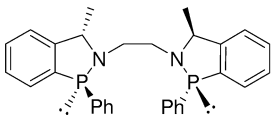
(*S*,*S*)-**49**



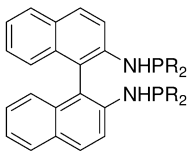
(*S*,*S*)-**50** R = (*S*)-α-methylbenzyl
(*S*,*R*)-**50** R = (*R*)-α-methylbenzyl
(*S*)-**51** R = benzyl
(*S*)-**52** R = phenyl



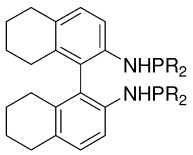
**53**



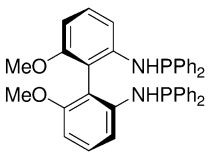
**54**



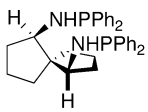
(*R*)-**55a** (*R*)-BDPAB: R = Ph
(*S*)-**55a** (*S*)-BDPAB: R = Ph
(*S*)-**55b** (*S*)-Xylyl-BDPAB: R = 3,5-$Me_2$Ph
(*R*)-**55c** (*S*)-Cy- BDPAB: R = Cy



(*R*)-**56a** (*R*)-$H_8$-BDPAB: R = Ph
(*S*)-**56a** (*S*)-$H_8$-BDPAB: R = Ph
(*S*)-**56b** (*S*)-$H_8$-Xylyl-BDPAB: R = 3,5-$Me_2$Ph



(*S*)-**57** (DMBDPPAB )



(1*R*,5*R*,6*R*)-**58** (SpiroNP)

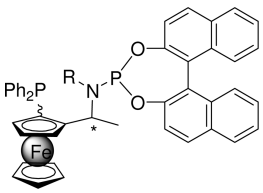
**Fig. 27.4** Bisphosphinamidite ligands.

subsequently preparing the corresponding 2,2′-bis(diphenylphosphinoamino)-1,1′-binaphthyl (BDPABs), the enantioselectivities in the hydrogenation of enamides were significantly improved in the case of (*S*)-**55a** versus (*S*)-**56a** [51]. Similarly, in the asymmetric hydrogenation of (*Z*)-2-acetamido-3-arylacrylic acids, the same observation was noted [52]. A boost in ee-value was also induced by replacing Ph with 3,5-$Me_2$Ph (**55a** versus **55b**) [53, 54]. A TOF as high as 3000 and a selectivity of up to 99% ee with the use of **55b** were observed, indicative of its high efficiency and effectiveness. In our recent findings, the conformationally rigid SpiroNP **58** also led to high enantioselectivities in the asym-

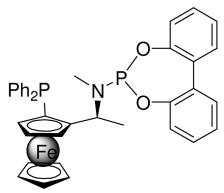
metric hydrogenation of dehydroamino acid derivatives [55]. An analogous biphenyl-based ligand **57**, however, was much less efficient than the binaphthyl-based or spiro-based counterparts [56].

## 27.4
## Mixed Phosphine-Phosphoramidites and Phosphine-Aminophosphine Ligands

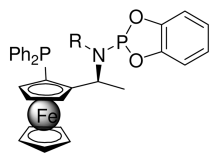
In contrast to the remarkable development of $C_2$-symmetrical ligands and $C_1$-nonsymmetrical ligands, the mixed bidentate ligands mentioned in the title were rather underdeveloped. The use of a ferrocene-based chiral backbone led to a promising class of new ligands having a wide scope and inducing good activity. Bophoz [57, 58] (Fig. 27.5, **68**) represented the first mixed phosphine-aminophosphine ligands for asymmetric catalysis with a wide scope of alkene substrates, including $\alpha,\beta$-unsaturated acids, enamides, and acetamidocinnamic acid derivatives. The TON of these catalytic asymmetric hydrogenations was gener-



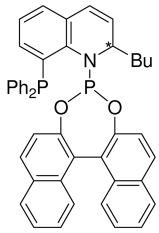
(*Rc*,*Sp*,*Sa*)-**59**: R = Me
(*Sc*,*Rp*,*Sa*)-**60**: R = Me
(*Sc*,*Rp*,*Ra*)-**61**: R = Me
(*Sc*,*Sp*,*Ra*)-**62**: R = Me
(*Sc*,*Sp*,*Sa*)-**63**: R = Me
(*Sc*,*Rp*,*Sa*)-**64**: R = H



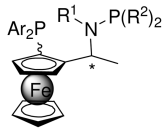
(*Sc*,*Rp*)-**65**



(*Sc*,*Rp*)-**66**



(*Sc*,*Ra*)-**83**
(*Rc*,*Ra*)-**84**



(*Rc*,*Sp*)-**67**: $R^1$ = H, $R^2$ = Ph, Ar = Ph
(*Rc*,*Sp*)-**68**: $R^1$ = Me, $R^2$ = Ph, Ar = Ph
(*Rc*,*Sp*)-**69**: $R^1$ = Et, $R^2$ = Ph, Ar = Ph
(*Rc*,*Sp*)-**70**: $R^1$ = Pr, $R^2$ = Ph, Ar = Ph
(*Rc*,*Sp*)-**71**: $R^1$ = Me, $R^2$ = $^i$Pr, Ar = Ph
(*Rc*,*Sp*)-**72**: $R^1$ = Me, $R^2$ = Cy, Ar = Ph
(*Sc*,*Rp*)-**73**: $R^1$ = Me, $R^2$ = Ph, Ar = Ph
(*Sc*,*Rp*)-**74**: $R^1$ = Et, $R^2$ = Ph, Ar = Ph
(*Sc*,*Rp*)-**75**: $R^1$ = Pr, $R^2$ = Ph, Ar = Ph
(*Sc*,*Rp*)-**76**: $R^1$ = Me, $R^2$ = Et, Ar = Ph
(*Sc*,*Rp*)-**77**: $R^1$ = Me, $R^2$ = $^i$Pr, Ar = Ph
(*Sc*,*Rp*)-**78**: $R^1$ = Me, $R^2$ = Ph, Ar = Ph
(*Rc*,*Sp*)-**79**: $R^1$ = Me, $R^2$ = 3,5-$(CH_3)_2C_6H_3$, Ar = Ph
(*Rc*,*Sp*)-**80**: $R^1$ = Me, $R^2$ = 3,5-$(CF_3)_2C_6H_3$, Ar = Ph
(*Rc*,*Sp*)-**81**: $R^1$ = Me, $R^2$ = Ph, Ar = 3,5-$(CF_3)_2C_6H_3$
(*Rc*,*Sp*)-**82**: $R^1$ = Me, $R^2$ = 3,5-$(CF_3)_2C_6H_3$, Ar = 3,5-$(CH_3)_2C_6H_3$

**Fig. 27.5** Mixed phosphine-phosphoramidites and phosphine-aminophosphine ligands.

ally in the range of 15.8 to 100. The potential of industrial usage was increased by improving its SCR to 10 000 (Table 27.4, entry 53). The shelf stability is an attractive point of this type of ligand. Somewhat surprisingly, Maligres and Krska found that **73** was unable to induce enantioselectivity in the Ru(II)-catalyzed hydrogenation of (*Z*)-α-phenoxybutenoic acid (Table 27.4, entry 96) [59].

The introduction of a third chiral element onto the chiral backbone was of interest, and we constructed a modified PPFA [60] with extra axial chirality from BINOL (Fig. 27.5, **59**) [61]. This type of ligand contains three chirality elements. Indeed, the enantioselectivity and activity remained excellent in the enantiomeric hydrogenation of α-dehydroamino acid derivatives and enamides using these ligands (Table 27.4, entries 1, 52, 67, 69–71, 79), regardless of the electronic properties of the *para*-substituting group. A similar approach was taken by Zheng's group using different diastereomers [62]. The scope was further extended to dimethyl itaconate, which was hydrogenated with a higher TON and with excellent ee and activity (Table 27.4, entry 91).

Recently, we developed three new fluorinated ferrocenyl phosphine-aminophosphine ligands derived from *N*,*N*-dimethyl-1-ferrocenylethylamine (Ugi's amine) [63]. These ligands were efficiently applied in the Rh-catalyzed hydrogenation of various aryl enamides (92.1 to 99.7% ee) and α-dehydroamino acid derivatives (98.5 to 99.7% ee), with complete conversion. The Rh–complex based on **80** led to somewhat lower enantioselectivities in the hydrogenation of arylenamides with *para*-EDG; however, the enantioselectivities were almost equally high for substrates containing *para*-EDG or *para*-EWG (98.5 to 99.7% ee) at 5 °C. These ligands also showed a remarkable air- and water-stability.

The ferrocene-based ligands have proven to be promising in most aspects of asymmetric catalysis. The only drawback was, however, the laborious resolution of Ugi's amine [64] which is used as a starting material, although this problem was solved by the facile asymmetric hydrogenation of ferrocenyl ketones using (XylylP-Phos-Ru–DPEN)$Cl_2$ (with a nonoptimized SCR of up to 100 000 on a 150-g scale; Scheme 27.2) [65]. With this method in hand, it became more flexible and almost effortless to generate a large structural diversity of ferrocene-based chiral ligands.

Mixed phosphine-phosphoramidite ligands QUINAPHOS **83** and **84**, as developed by Leitner, worked well for the Rh-catalyzed hydrogenation of itaconic acid and α-dehydroamino acid derivatives. The ligand **84** also exerted extra reactivity, leading to an average TOF of 36 000 $h^{-1}$ in the hydrogenation of dimethyl itaconate after the addition of a second batch of substrate with SCR 6000 : 1 [66]. In contrast to BINAPHOS-type ligands, the major asymmetric induction relied on the 2-position of the alkyl groups embedded in the fairly rigid heterocyclic skeleton.

**Table 27.4** Mixed phosphine–phosphoramidites and phosphine–aminophosphine ligands.

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 1 | H | Ph | NHAc | Rh-(*Rc*,*Sp*,*Sa*)-**59** | 20.7 | THF | r.t. | 7 [a] | 99 | 14.1 | >99 | 87.5 (*S*) | 61 |
| 2 | H | Ph | NHAc | Rh-(*Sc*,*Rp*,*Sa*)-**60** | 10 | DCM | r.t. | 1 | 5000 | 5000 | 100 | 99.3 (*R*) | 62 |
| 3 | H | Ph | NHAc | Rh-(*Sc*,*Rp*,*Ra*)-**61** | 10 | DCM | r.t. | 1 | 100 | 100 | 100 | 10.6 (*S*) | 62 |
| 4 | H | Ph | NHAc | Rh-(*Sc*,*Sp*,*Ra*)-**62** | 10 | DCM | r.t. | 1 | 100 | 100 | 100 | 99.6 (*S*) | 62 |
| 5 | H | Ph | NHAc | Rh-(*Sc*,*Sp*,*Sa*)-**63** | 10 | DCM | r.t. | 1 | 100 | 100 | 100 | 82.6 (*R*) | 62 |
| 6 | H | Ph | NHAc | Rh-(*Sc*,*Rp*)-**65** | 10 | DCM | r.t. | 1 | 100 | 100 | 100 | 81.5 (*S*) | 62 |
| 7 | H | Ph | NHAc | Rh-(*Sc*,*Rp*)-**66** | 10 | DCM | r.t. | 1 | 100 | 100 | 100 | 78.1 (*R*) | 62 |
| 8 | H | Ph | NHAc | Rh-(*Sc*,*Rp*)-**73** | 10 | DCM | r.t. | 1 | 100 | 100 | 100 | 61.8 (*R*) | 62 |
| 9 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**67** | 20.7 | DCM | r.t. | 10 | 100 | 10 | 100 | 70.0 (*S*) | 63 |
| 10 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**68** | 20.7 | DCM | r.t. | 8 | 100 | 12.5 | 100 | 80.6 (*S*) | 63 |
| 11 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | DCM | r.t. | 16 | 100 | 6.25 | 100 | 94.6 (*S*) | 63 |
| 12 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**81** | 20.7 | DCM | r.t. | 10 | 100 | 10 | 100 | 35.0 (*S*) | 63 |
| 13 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**82** | 20.7 | *i*-PrOH | r.t. | 16 | 100 | 6.25 | 100 | 94.4 (*S*) | 63 |
| 14 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | Toluene | r.t. | 16 | 100 | 6.25 | 100 | 93.5 (*S*) | 63 |
| 15 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | 16 | 100 | 6.25 | 100 | 96.5 (*S*) | 63 |
| 16 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**82** | 20.7 | THF | r.t. | 8 | 100 | 12.5 | 100 | 96.2 (*S*) | 63 |
| 17 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | – | 100 | – | 100 | 96.1 (*S*) [d] | 63 |
| 18 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | – | 500 | – | 100 | 95.8 (*S*) [d] | 63 |
| 19 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | – | 100 | – | 100 | 95.5 (*S*) [d] | 63 |
| 20 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | – | 100 | – | 100 | 95.2 (*S*) [d] | 63 |

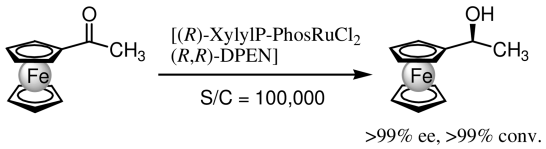
| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 21 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF/$H_2O$ 95/5 | r.t. | – | 100 | – | 100 | 95.1 (*S*) [d] | 63 |
| 22 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF/$H_2O$ 70/30 | r.t. | – | 100 | – | 100 | 77.2 (*S*) [d] | 63 |
| 23 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | 16 | 100 | 6.25 | 100 | 96.5 (*S*) | 63 |
| 24 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | 16 | 200 | 12.5 | 100 | 95.8 (*S*) | 63 |
| 25 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | 16 | 500 | 31.25 | 100 | 96.4 (*S*) | 63 |
| 26 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | 16 | 1000 | 62.5 | 100 | 95.8 (*S*) | 63 |
| 27 | H | Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | 5 | 30 | 500 | 16.67 | 100 | 98.3 (*S*) | 63 |
| 28 | H | *p*-Cl-Ph | NHAc | Rh-(*Sc*,*Rp*,*Sa*)-**60** | 10 | DCM | r.t. | 1 | 1000 | 1000 | 100 | 98.8 (*R*) | 62 |
| 29 | H | *p*-Br-Ph | NHAc | Rh-(*Sc*,*Rp*,*Sa*)-**60** | 10 | DCM | r.t. | 1 | 1000 | 1000 | 100 | 99.0 (*R*) | 62 |
| 30 | H | *p*-Br-Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | 5 | 30 | 500 | 16.67 | 100 | 99.7 (*S*) | 63 |
| 31 | H | *p*-Br-Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | 16 | 500 | 31.25 | 100 | 99.3 (*S*) | 63 |
| 32 | H | *p*-F-Ph | NHAc | Rh-(*Sc*,*Rp*,*Sa*)-**60** | 10 | DCM | r.t. | 1 | 1000 | 1000 | 100 | 98.7 (*R*) | 62 |
| 33 | H | *p*-$CF_3$-Ph | NHAc | Rh-(*Rc*,*Sp*)-**67** | 20.7 | DCM | r.t. | 10 | 100 | 10 | 100 | 73.1 (*S*) | 63 |
| 34 | H | *p*-$CF_3$-Ph | NHAc | Rh-(*Sc*,*Rp*,*Sa*)-**60** | 10 | DCM | r.t. | 1 | 1000 | 1000 | 100 | 99.2 (*R*) | 62 |
| 35 | H | *p*-$CF_3$-Ph | NHAc | Rh-(*Rc*,*Sp*)-**68** | 20.7 | DCM | r.t. | 8 | 100 | 12.5 | 100 | 79.6 (*S*) | 63 |
| 36 | H | *p*-$CF_3$-Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | 16 | 500 | 31.25 | 100 | 97.1 (*S*) | 63 |
| 37 | H | *p*-$CF_3$-Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | 5 | 30 | 500 | 16.67 | 100 | 98.6 (*S*) | 63 |
| 38 | H | *m*-$CH_3$Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | 5 | 30 | 500 | 16.67 | 100 | 98.5 (*S*) | 63 |
| 39 | H | *p*-$CH_3$Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | 16 | 500 | 31.25 | 100 | 92.1 (*S*) | 63 |
| 40 | H | *p*-$CH_3$Ph | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | 5 | 30 | 500 | 16.67 | 100 | 99.4 (*S*) | 63 |
| 41 | H | *m*-$CH_3$OPh | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | 5 | 30 | 500 | 16.67 | 100 | 99.0 (*S*) | 63 |
| 42 | H | *p*-$CH_3$OPh | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | 16 | 500 | 31.25 | 100 | 93.5 (*S*) | 63 |
| 43 | H | *p*-$CH_3$OPh | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | 5 | 30 | 500 | 16.67 | 100 | 99.3 (*S*) | 63 |
| 44 | H | $CO_2H$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 0.7 | THF | r.t. | 1 | 95 | 95 | >95 | 96 (*S*) | 57 |
| 45 | H | $CO_2H$ | NHAc | Rh-(Sc,*Rp*)-**73** | 0.69–1.38 | THF | 25 | 24 | 100 | 4.2 | 100 | 96.1 (*R*) [b] | 58 |
| 46 | H | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 0.7 | THF | r.t. | 1 | 95 | 95 | >95 | 98.5 (*S*) | 57 |
| 47 | H | $CO_2Me$ | NHAc | Rh-(Sc,*Rp*)-**73** | 0.69–1.38 | THF | 25 | 1 | 40 | 40 | 100 | 98.4 (*R*) | 58 |
| 48 | H | $CO_2Me$ | NHAc | Rh-(*Rc*,*Ra*)-**84** | 30 | DCM | r.t. | 24 | 990 | 41.3 | >99 | 97.8 (*S*) | 62 |

**Table 27.4** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 49 | H | $CO_2Me$ | $NHCO_2Bn$ | Rh-(*Rc*,*Sp*)-**68** | 0.7 | THF | r.t. | 1 | 95 | 95 | >95 | 98 (*S*) | 57, 58 |
| 50 | Me[c)] | $CO_2Me$ | NHCO (2-oxopyrrolidin-1-yl) | Rh-(*Rc*,*Sp*)-**68** | 2.8 | THF | 25 | 18 | 20.9 | 1.2 | 99 | 96.2 (*S*) | 58 |
| 51 | Ph | $CO_2H$ | NHAc | Rh- (*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 1 | 100 | 100 | 100 | 99.4 (*S*)[b)] | 57, 58 |
| 52 | Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Rp*,*Sa*)-**59** | 20.7 | THF | r.t. | 7[a)] | 99 | 14.1 | >99 | 99.0 (*S*) | 61 |
| 53 | Ph | $CO_2Me$ | NHAc | Rh-(*Sc*,*Rp*,*Sa*)-**60** | 10 | DCM | r.t. | 1 | 10000 | 10000 | 100 | 99.0 (*R*) | 62 |
| 54 | Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**67** | 0.7 | THF | r.t. | 1 | 95 | 95 | 95 | 97.2 (*S*) | 57, 58 |
| 55 | Ph | $CO_2Me$ | NHAc | Rh- (*Rc*,*Sp*)-**68** | 0.7 | THF | r.t. | 1 | 95 | 95 | >95 | 99.1 (*S*) | 57, 58 |
| 56 | Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 20.7 | THF | r.t. | – | 200 | – | 100 | 99.0 (*S*) | 63 |
| 57 | Ph | $CO_2Me$ | NHAc | Rh- (*Rc*,*Sp*)-**68** | 3.1 | THF | r.t. | 1.2 | 9630 | 8025 | 96.3 | 96.8 (*S*) | 57, 58 |
| 58 | Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**69** | 0.7 | THF | r.t. | 1 | 95 | 95 | 95 | 94.3 (*S*) | 57, 58 |
| 59 | Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**70** | 0.7 | THF | r.t. | 1 | 95 | 95 | >95 | 93.3 (*S*) | 57 |
| 60 | Ph | $CO_2Me$ | NHAc | Rh-(Sc,*Rp*)-**75** | 0.69–1.38 | THF | 25 | 1 | 100 | 100 | 100 | 93.3 (*R*) | 58 |
| 61 | Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | – | 200 | – | 100 | 99.2 (*S*) | 63 |
| 62 | Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**81** | 20.7 | THF | r.t. | – | 200 | – | 100 | 96.1 (*S*) | 63 |
| 63 | Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**82** | 20.7 | THF | r.t. | – | 200 | – | 100 | 98.5 (*S*) | 63 |
| 64 | Ph | $CO_2Me$ | NHBz | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 6 | 100 | 16.7 | 100 | 98.4 (*S*) | 58 |
| 65 | Ph | $CO_2Me$ | $NHCO_2t$-Bu | Rh-(*Rc*,*Sp*)-**68** | 0.7 | THF | r.t. | 1 | 95 | 95 | >95 | 99.5 (*S*) | 57, 58 |
| 66 | Bn | $CO_2Et$ | $NHCO_2Bn$ | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 6 | 99 | 16.5 | 99 | 98.4 (*S*) | 58 |
| 67 | *p*-Cl-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*,*Sa*)-**59** | 20.7 | THF | r.t. | 7[a)] | 99 | 14.1 | >99 | 99.0 (*S*) | 61 |
| 68 | *p*-Cl-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 2 | 50 | 25 | 100 | 98.8 (*S*) | 58 |
| 69 | *p*-Br-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*,*Sa*)-**59** | 20.7 | THF | r.t. | 7[a)] | 99 | 14.1 | >99 | 99.0 (*S*) | 61 |
| 70 | *p*-F-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*,*Sa*)-**59** | 20.7 | THF | r.t. | 7[a)] | 99 | 14.1 | >99 | 99.0 (*S*) | 61 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 71 | *p*-$NO_2$-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*,*Sa*)-**59** | 20.7 | THF | r.t. | 7 [a)] | 99 | 14.1 | >99 | 99.6 (*S*) | 61 |
| 72 | *p*-$NO_2$-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 0.5 | 100 | 200 | 100 | 97.7 (*S*) | 58 |
| 73 | *p*-$NO_2$Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 20.7 | THF | r.t. | – | 200 | – | 100 | 99.5 (*S*) | 63 |
| 74 | *p*-$NO_2$Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**80** | 20.7 | THF | r.t. | – | 200 | – | 100 | 99.7 (*S*) | 63 |
| 75 | *p*-CN-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 1 | 100 | 100 | 100 | 99.0 (*S*) | 58 |
| 76 | *o*-MeO-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 2 | 49.8 | 24.9 | 99.5 | 97.7 (*S*) | 58 |
| 77 | *m*-MeO-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 0.5 | 50 | 100 | 100 | 98.0 (*S*) | 58 |
| 78 | *p*-MeO-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 0.5 | 45 | 90 | 90 | 97.9 (*S*) | 58 |
| 79 | *p*-Me-Ph | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*,*Sa*)-**59** | 20.7 | THF | r.t. | 7 [a)] | 99 | 14.1 | >99 | 97.4 (*S*) | 61 |
| 80 | Cyclopropyl | $CO_2Me$ | NHBz | Rh-(*Sc*,*Rp*)-**73** | 0.69–1.38 | THF | 25 | 24 | 100 | 4.2 | 100 | 91.6 (*R*) | 58 |
| 81 | Cyclopropyl | $CO_2Me$ | $NHCO_2t$-Bu | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 6 | 90 | 15 | 90 | 98.6 (*S*) | 58 |
| 82 | Cyclopropyl | Bn | $NHCO_2t$-Bu | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | Acetone | 25 | 1 | 94 | 94 | 94 | >99 (*S*) | 57, 58 |
| 83 | 1-Naphthyl | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 6 | 95 | 15.8 | >95 | 99.3 (*S*) | 58 |
| 84 | 1-Naphthyl | $CO_2Me$ | $NHCO_2t$-Bu | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 6 | 95 | 15.8 | >95 | 98.2 (*S*) | 58 |
| 85 | 2-Naphthyl | $CO_2Me$ | NHAc | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 1 | 95 | 95 | >95 | 98.1 (*S*) | 58 |
| 86 | 2-Naphthyl | $CO_2Me$ | $NHCO_2t$-Bu | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 6 | 97 | 16.2 | 97 | 97.4 (*S*) | 58 |
| 87 | 3-furyl | $CO_2Me$ | NHCOPh | Rh-(*Sc*,*Rp*)-**73** | 0.69–1.38 | THF | 25 | 6 | 100 | 16.7 | 100 | 96.6 (*R*) | 58 |
| 88 | 3-furyl | $CO_2Me$ | $NHCO_2t$-Bu | Rh-(*Rc*,*Sp*)-**68** | 0.69–1.38 | THF | 25 | 6 | 98 | 16.3 | 98 | 97.2 (*S*) | 58 |
| 89 | H | $CO_2H$ | $CH_2CO_2H$ | Rh-(*Rc*,*Sp*)-**67** | 20.7 | MeOH | r.t. | 6 | 95 | 15.8 | >95 | 94.0 (*R*) | 57 |
| 90 | H | $CO_2H$ | $CH_2CO_2H$ | Rh-(*Rc*,*Sp*)-**68** | 20.7 | MeOH | r.t. | 6 | 95 | 15.8 | >95 | 97.4 (*R*) | 57 |
| 91 | H | $CO_2Me$ | $CH_2CO_2Me$ | Rh-(*Sc*,*Rp*,*Sa*)-**60** | 10 | DCM | r.t. | 0.5 | 10000 | 20000 | 100 | 99.1 (*S*) | 62 |
| 92 | H | $CO_2Me$ | $CH_2CO_2Me$ | Rh-(*Rc*,*Sp*)-**67** | 20.7 | MeOH | r.t. | 6 | 95 | 15.8 | >95 | 91.6 (*R*) | 57, 58 |
| 93 | H | $CO_2Me$ | $CH_2CO_2Me$ | Rh-(*Rc*,*Sp*)-**68** | 10 | MeOH | r.t. | 6 | 95 | 15.8 | >95 | 94.0 (*R*) | 57, 58 |
| 94 | H | $CO_2Me$ | $CH_2CO_2Me$ | Rh-(*Sc*,*Ra*)-**83** | 30 | DCM | r.t. | 24 | 990 | 41.3 | >99 | 78.8 (*R*) | 66 |
| 95 | H | $CO_2Me$ | $CH_2CO_2Me$ | Rh-(*Rc*,*Ra*)-**84** | 30 | DCM | r.t. | 24 | 990 | 41.3 | >99 | 98.8 (*R*) | 66 |
| 96 | Me | $CO_2H$ | OPh | Ru-(*Sc*,*Rp*)-**73** | 6.2 | MeOH/ EtOH/DCM 80/13/7 | 20–25 | 20 | 17.4 | 0.9 | 100 | rac | 59 |
| 97 | Ph | $CO_2H$ | $CH_2CO_2H$ | Rh-(*Rc*,*Sp*)-**67** | 20.7 | MeOH | r.t. | 6 | 95 | 15.8 | >95 | 99.0 (*R*) | 57 |
| 98 | Ph | $CO_2H$ | $CH_2CO_2H$ | Rh-(*Rc*,*Sp*)-**68** | 20.7 | MeOH | r.t. | 6 | 95 | 15.8 | >95 | 89.0 (*R*) | 57 |
| 99 | Ph | $CO_2Me$ | $CH_2CO_2Me$ | Rh-(*Rc*,*Sp*)-**67** | 20.7 | MeOH | r.t. | 6 | 95 | 15.8 | >95 | 80.0 (*R*) | 57 |

**a)** Average value.
**b)** The ee-value was determined by the corresponding methyl ester.
**c)** The ratio of *Z*/*E* is not provided.
**d)** The catalyst was prepared *in situ* in air.




**Scheme 27.2**

## 27.5
## Bisphosphinite Ligands (One P–O Bond)

A large number of bidentate phosphinites have been reported, with sugars being the most abundantly used backbone. *trans*-BDPCH **85** (Fig. 27.6) is the earliest example of a bisphosphinite used in the rhodium-catalyzed asymmetric hydrogenation of functionalized olefins inducing moderate ee-values (48.5–78.9%) [67]. A similar approach using a more rigid pentacyclic system as backbone (*trans*-BDPCP **86**) induced only poor to moderate ee-values. The best ee-value (78.9%) was obtained in the enantiomeric hydrogenation of α-acetamidoacrylic acid [68]. In 2000, Leitner developed a perfluorinated analogue **87** which induced 72% ee in the Rh-catalyzed hydrogenation of dimethyl methylsuccinate (Table 27.5, entry 934) in a supercritical $CO_2$ ($scCO_2$) and perfluorinated alcohol solvent [69]. An average TOF up to 40 000 $h^{-1}$ was obtained with this system.

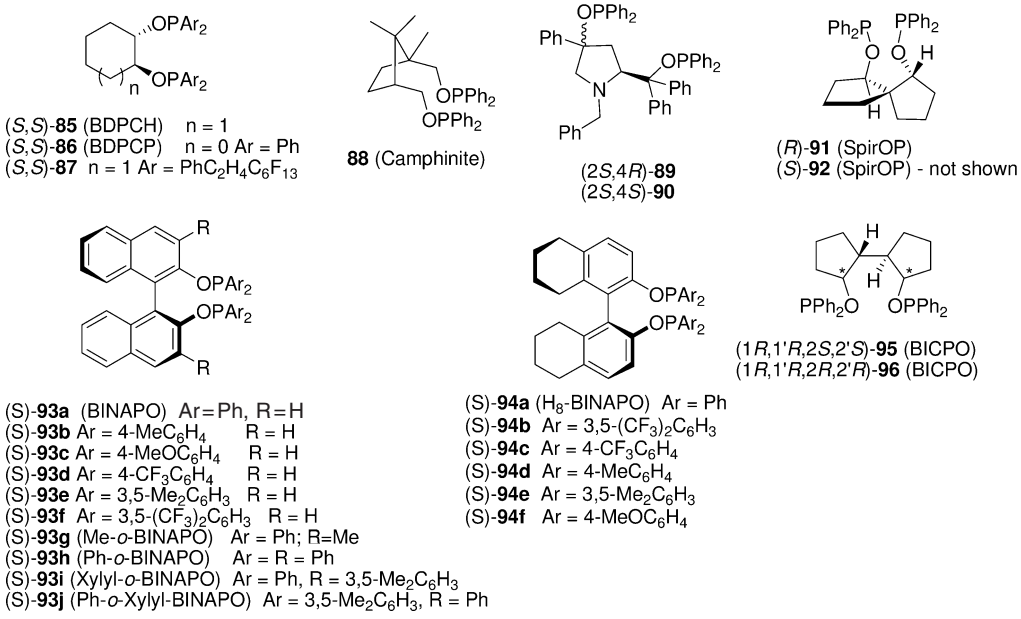



**Fig. 27.6** Bisphosphinite ligands (one P–O bond).

The binaphthyl system has served as the basis of a several classes of ligands. It has been suggested that the highly skewed position of the naphthyl rings in BINAP is the determining factor in its effectiveness in asymmetric catalytic reactions [70]. In an early study by Grubbs, the use of atropisomeric BINAPO **93a** based on the binaphthol skeleton induced 6 to 76% ee in the Rh-catalyzed hydrogenation of $\alpha$-dehydroamino acids and enamides [71]. Interestingly, we found that the partially hydrogenated $H_8$-BINAPO was more effective than BINAPO in the Rh-catalyzed hydrogenation of (*Z*)-acetamido-3-arylacrylic acids and their methyl esters (63.9–84% ee) [52]. In fact, recent research showed that chiral catalysts derived from the 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2,2′-naphthyl backbone (e.g., $H_8$-BINAP [72], $H_8$-BINOL [73, 74], $H_8$-BINAM [9], $H_8$-BDPAB [51], $H_8$-binaphthoxy [75], $H_8$-MAPs [76]) exhibited higher efficiency and enantioselectivity in asymmetric catalytic reactions than those prepared from the parent binaphthyl backbone, probably due to the steric and electronic modulation in the $H_8$-binaphthyl backbone [77]. A systematic quantification of the electronic and steric influences of these ligands were carried out by Bakos and Gergely [78]. A detrimental effect of *para*-electron-withdrawing substituents on the phenyl rings of this class of ligands was observed on enantioselectivity and activity in the hydrogenation of dimethyl itaconate (**94b** with 51.6% ee, Table 27.5, entry 939). In contrast, *para*-electron-donating groups (i.e., *p*-OMe group) enhanced the enantioselectivity (93.9% ee, Table 27.5, entry 944). Similarly, the use of **94f** (i.e., *p*-OMe group) in the hydrogenation of methyl (*Z*)-$\alpha$-acetamido-cinnamate gave 98.6% ee. The 3,3′-disubstituted bisphosphinite ligand *o*-BINAPO (**93a, b)** reported by Zhang was successfully applied in the hydrogenation of enamides (67.2–96.3% ee) and $\alpha$-dehydroamino acid derivatives (81.5–99.9% ee) [79]. The further demonstration of its application in the hydrogenation of $\beta$-aryl-substituted $\beta$-(acylamino)acrylates was also successful, leading to formation of the products with 80 to 99% ee (with **93i**) [80].

Chiral ligands **88** [81], **89** and **90** [82] with rigid backbones were found to be less effective in Rh-catalyzed hydrogenation reactions. In 1997, we introduced the novel ligand SpirOP (**91** and **92)** based on a rigid spiro backbone which mimics the binaphthyl rings in BINAP in its most effective state (skewed position), giving rise to an eight-membered chelate ring [27, 83]. Indeed, the desired hydrogenation product 2-acetamidopropionic acid was obtained in >99.9% ee, with complete conversion in 10 min using Rh–SpirOP. Similarly remarkable activity and enantioselectivity was found upon hydrogenation of the corresponding methyl ester using the same catalyst (99% ee, 99.9% conv.). The TOF of the hydrogenation of 2-acetamido-acrylic acid could be further increased to 10 000 $h^{-1}$ at ambient temperature whilst retaining 96.8% ee. The substrate's scope was also excellent (>97% ee for (*Z*)-2-acetamido-3-arylacrylic acids and 94.2–97.2% ee for the corresponding methyl esters). It is of interest to note that the Rh–SpirOP complexes in methanol showed unexpected stability based on a $^{31}$P-NMR study at ambient temperature for two days. It was further demonstrated that the use of SpirOP in the hydrogenation of $\alpha$-phenylenamide gave rise to good to excellent enantioselectivities (85.6–97.4% ee) [84].

**Table 27.5** Enantiomeric hydrogenation using bisphosphinite, bisphosphonite, or bisphosphite.

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | $P[H_2]$ [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 1 | H | $CO_2H$ | NHAc | [Rh(1,5-hexadiene)(+)-*trans*-**85**]Cl | 50 | – | –20 | 24 | – | – | – | 78.9 (S) | 67 |
| 2 | H | $CO_2H$ | NHAc | [Rh(1,5-hexadiene)(+)-*trans*-**86**]Cl | 50 | – | –20 | 24 | – | – | – | 0 | 68a |
| 3 | H | $CO_2H$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | >99.9 (*R*) | 27 |
| 4 | H | $CO_2H$ | NHAc | [Rh(COD)**91**]$BF_4$ | 13.8 | MeOH | 25 | 1 | 10000 | 10000 | >99.9 | 96.8 (*R*) | 27 |
| 5 | H | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 94.8 (*S*) | 85 |
| 6 | H | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.0317[f] | 50 | 1579 | 50 | 72.6 | 26 |
| 7 | H | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.0167[f] | 50 | 3000 | 50 | 97.7 (*S*) | 91b |
| 8 | H | $CO_2H$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.0167[f] | 50 | 3000 | 50 | 96.5 (*S*) | 91b |
| 9 | H | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.047[f] | 50 | 1071 | 50 | 97.7 (*S*) | 26 |
| 10 | H | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.25 | 50 | 200 | 50 | 97.7 (*S*) | 26 |
| 11 | H | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 100 | MeOH | 25 | – | 100[c] | – | – | 93.9 (*S*) | 26 |
| 12 | H | $CO_2H$ | NHAc | [Rh(COD)**98b**]$BF_4$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 97 (*S*) | 98 |
| 13 | H | $CO_2H$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.9 | 95b |
| 14 | H | $CO_2H$ | NHAc | [Rh(COE)**93a**]Cl | 102 | Tol | 25 | 24 | 25 | 1 | 50[b] | 9[a] | 71 |
| 15 | H | $CO_2H$ | NHAc | [Rh(COE)**93a**]Cl | 95 | Tol/acetone 1:1 | 0 | 24 | 50 | 2 | 100[b] | 6[a] | 71 |
| 16 | H | $CO_2H$ | NHAc | [Rh(NBD)**97a**]$PF_6$ | 1 | EtOH | 30 | 0.33 | 40 | 120 | 100[b] | 67 (*S*) | 88 |
| 17 | H | $CO_2H$ | NHAc | [Rh(NBD)**97a**]$PF_6$ | 1 | EtOH | 30 | 0.33 | 100 | 300 | 100[b] | 68 (*S*) | 88 |
| 18 | H | $CO_2H$ | NHAc | [Rh(NBD)**97a**]$PF_6$ | 1 | EtOH | 0 | 0.5 | 100 | 200 | 100[b] | 74 (*S*) | 88 |
| 19 | H | $CO_2H$ | NHAc | [Rh(NBD)**97a**]$PF_6$ | 1 | EtOH | –20 | 1 | 100 | 100 | 100[b] | 80 (*S*) | 88 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 20 | H | $CO_2H$ | NHAc | [Rh(COD)**102a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 95.0 (*S*) | 95 b |
| 21 | H | $CO_2H$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 90.8 (*R*) | 95 b |
| 22 | H | $CO_2H$ | NHAc | [Rh(COD)**114a**]$BF_4$ | 1 | MeOH | 25 | 0.017 [f] | 50 | 2941 | 50 | 59 (*S*) | 99 |
| 23 | H | $CO_2H$ | NHAc | [Rh(COD)**114a**]$BF_4$ | 1 | PhH | 25 | 6.67 [f] | 50 | 8 | 50 | 48 (*S*) | 99 |
| 24 | H | $CO_2H$ | NHAc | [Rh(COD)**114a**]$BF_4$ | 1 | $H_2O$ | 25 | 7.58 [f] | 50 | 7 | 50 | 14 (*S*) | 99 |
| 25 | H | $CO_2H$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | MeOH | 25 | 0.017 [f] | 50 | 2941 | 50 | 56 (*S*) | 99 |
| 26 | H | $CO_2H$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | PhH | 25 | 8.08 [f] | 50 | 6 | 50 | 71 (*S*) | 99 |
| 27 | H | $CO_2H$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | $H_2O$+Triton X-100 (0.1 mmol) | 25 | 0.01 [f] | 50 | 500 | 50 | 42 (*S*) | 99 |
| 28 | H | $CO_2H$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | $H_2O$+Triton X-100 (0.5 mmol) | 25 | 0.05 [f] | 50 | 1000 | 50 | 42 (*S*) | 99 |
| 29 | H | $CO_2H$ | NHAc | [Rh(COD)**115a**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 86 (*S*) | 98 |
| 30 | H | $CO_2H$ | NHAc | [Rh(COD)**115a**]$SbF_6$ | 2.8 | $H_2O$ | r.t. | 19 | 100 | 5 | 100 | 14 (*S*) | 98 |
| 31 | H | $CO_2H$ | NHAc | [Rh(COD)**115b**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 90 (*S*) | 98 |
| 32 | H | $CO_2H$ | NHAc | [Rh(COD)**115c**]$BF_4$ | 2.8 | THF | r.t. | – | 150 | – | 100 | 87 (*S*) | 98 |
| 33 | H | $CO_2H$ | NHAc | [Rh(COD)**115c**]$BF_4$ | 2.8 | MeOH | r.t. | – | 150 | – | 100 | 54 (*S*) | 98 |
| 34 | H | $CO_2H$ | NHAc | [Rh(COD)**115c**]$BF_4$ | 2.8 | $H_2O$ | r.t. | – | 150 | – | 100 | 53 (*S*) | 98 |
| 35 | H | $CO_2H$ | NHAc | [Rh(COD)**115c**]$BF_4$ | 2.8 | $H_2O$/EtOAc (1:1) | r.t. | – | 100 | – | 100 | 6 (*S*) | 98 |
| 36 | H | $CO_2H$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | THF | r.t. | – | 100 | – | 100 | 93 (*S*) | 98 |
| 37 | H | $CO_2H$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | MeOH | r.t. | – | 100 | – | 100 | 37 (*S*) | 98 |
| 38 | H | $CO_2H$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | EtOH | r.t. | – | 100 | – | 100 | 89 (*S*) | 98 |
| 39 | H | $CO_2H$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | $H_2O$ | r.t. | – | 100 | – | 100 | 2 (*S*) | 98 |
| 40 | H | $CO_2H$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | $H_2O$/EtOAc (1:1) | r.t. | – | 100 | – | 100 | 2 (*S*) | 98 |
| 41 | H | $CO_2H$ | NHAc | [Rh(COD)**115e**]$BF_4$ | 2.8 | THF | r.t. | – | 150 | – | 100 | 0 | 98 |
| 42 | H | $CO_2H$ | NHAc | [Rh(COD)**119d**]$SbF_6$ | 2.8 | $H_2O$ | r.t. | 2 | 125 | 63 | 100 | 59 (*S*) | 102 |
| 43 | H | $CO_2H$ | NHAc | [Rh(COD)**119e**]$SbF_6$ | 2.8 | $H_2O$/EtOAc | r.t. | 20 | 125 | 6 | 100 | 65 (*S*) [a] | 102 |
| 44 | H | $CO_2H$ | NHAc | [Rh(COD)**128**]Cl | 10 | MeOH | r.t. | 0.25 | 230 | 920 | 100 | 26 (*S*) | 106 |
| 45 | H | $CO_2H$ | NHAc | [Rh(COD)**129**]Cl | 56 | MeOH | r.t. | 1 | 260 | 260 | 100 | 14 (*R*) | 106 |
| 46 | H | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 96.7 (*R*) | 107 |
| 47 | H | $CO_2H$ | NHAc | [Rh(COD)**141b**]$BF_4$ | 3.5 | MeOH | r.t. | 0.5 | 1000 | 2000 | >99 | 97 (*S*) | 111 |
| 48 | H | $CO_2H$ | NHAc | [Rh(COD)**166**]$BF_4$ | 51 | $H_2O$ | r.t. | 24 | 50 | 2 | 100 | 10 (*R*) [j] | 129 |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 49 | H | $CO_2Me$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 99.0 (*R*) | 27 |
| 50 | H | $CO_2Me$ | NHAc | [Rh(COE)**93a**]Cl | 99 | Tol | 0 | 53.5 | 30 | 0.6 | 60[b] | 44[a] | 71 |
| 51 | H | $CO_2Me$ | NHAc | [Rh(COE)**93a**]Cl | 91 | Tol/acetone 1:1 | 0 | 68.5 | 50 | 0.7 | 100[b] | 76[a] | 71 |
| 52 | H | $CO_2Me$ | NHAc | [Rh(COD)**93a**]$PF_6$ | 3 | Tol | r.t. | 12 | 100 | 8.3 | 100 | 73.2 (*S*) | 79 |
| 53 | H | $CO_2Me$ | NHAc | [Rh(COD)**93g**]$PF_6$ | 3 | Tol | r.t. | 12 | 100 | 8.3 | 100 | 94.8 (*S*) | 79 |
| 54 | H | $CO_2Me$ | NHAc | [Rh(COD)**93h**]$PF_6$ | 3 | Tol | r.t. | 12 | 100 | 8.3 | 100 | 99.9 (*S*) | 79 |
| 55 | H | $CO_2Me$ | NHAc | [Rh(COD)**93i**]$PF_6$ | 3 | Tol | r.t. | 12 | 100 | 8.3 | 100 | 95.4 (*S*) | 79 |
| 56 | H | $CO_2Me$ | NHAc | [Rh(COD)**93j**]$PF_6$ | 3 | Tol | r.t. | 12 | 100 | 8.3 | 100 | 93 (*S*) | 79 |
| 57 | H | $CO_2Me$ | NHAc | [Rh(COD)**94a**]$BF_4$ | 6.9 | DCM | r.t. | 0.17 | 245 | 1441 | 49 | 81 (*S*) | 52 |
| 58 | H | $CO_2Et$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.085[f] | 50 | 588 | 50 | 58.2 | 26 |
| 59 | H | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.0267[f] | 50 | 1875 | 50 | 73.4 | 26 |
| 60 | H | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.0167[f] | 50 | 3000 | 50 | 90.9 (*S*) | 91b |
| 61 | H | $CO_2Me$ | NHAc | [Rh(NBD)**97a**]$PF_6$ | 1 | EtOH | 30 | 0.167 | 100 | 600 | 100[b] | 53 (*S*) | 88 |
| 62 | H | $CO_2Me$ | NHAc | [Rh(NBD)**97a**]$PF_6$ | 1 | EtOH | 0 | 0.5 | 100 | 200 | 100[b] | 78 (*S*) | 88 |
| 63 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ | 25 | 0.33 | 50 | 150 | 50 | 44 (S) | 99 |
| 64 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $LiBF_4$ | 25 | 0.52 | 50 | 97 | 50 | 43 (S) | 99 |
| 65 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $NaBF_4$ | 25 | 0.55 | 50 | 91 | 50 | 40 (S) | 99 |
| 66 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $KBF_4$ | 25 | 0.53 | 50 | 94 | 50 | 42 (S) | 99 |
| 67 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $RbBF_4$ | 25 | 0.62 | 50 | 81 | 50 | 42 (S) | 99 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 68 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$+0.1 mmol $CsBF_4$ | 25 | 0.62 | 50 | 81 | 50 | 41 (S) | 99 |
| 69 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$+Triton X100 (0.1 mmol) | 25 | 0.067 | 50 | 750 | 50 | 69 (S) | 99 |
| 70 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$+Triton X100+ 0.1 mmol $LiBF_4$ | 25 | 0.12 | 50 | 429 | 50 | 68 (S) | 99 |
| 71 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$+Triton X100+ 0.1 mmol $NaBF_4$ | 25 | 0.1 | 50 | 500 | 50 | 68 (S) | 99 |
| 72 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$+Triton X100+ 0.1 mmol $KBF_4$ | 25 | 0.1 | 50 | 500 | 50 | 68 (S) | 99 |
| 73 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$+ Triton X100+0.1 mmol $RbBF_4$ | 25 | 0.15 | 50 | 333 | 50 | 68 (S) | 99 |
| 74 | H | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$+Triton X100+ 0.1 mmol $CsBF_4$ | 25 | 0.13 | 50 | 375 | 50 | 68 (S) | 99 |
| 75 | H | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.0333 [f] | 50 | 1500 | 50 | 95.2 (*S*) | 91 b |
| 76 | H | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.0217 [f] | 50 | 2308 | 50 | 90.9 | 26 |
| 77 | H | $CO_2Et$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.0233 [f] | 50 | 2143 | 50 | 83.0 | 26 |
| 78 | H | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.016 [f] | 50 | 3333 | 50 | 90.6 (*S*) | 91 e |
| 79 | H | $CO_2Me$ | NHAc | [Rh(COD)**98i**]$BF_4$ | 1 | MeOH | 25 | 0.0333 [f] | 50 | 1500 | 50 | 95 (*S*) | 97 |
| 80 | H | $CO_2Me$ | NHAc | [Rh(COD)**98i**]$BF_4$ | 1 | $H_2O$ | 25 | 0.467 [f] | 50 | 107 | 50 | 79 (*S*) | 97 |
| 81 | H | $CO_2Me$ | NHAc | [Rh(COD)**98i**]$BF_4$ | 1 | $H_2O$+SDS, 0.035 [g] | 25 | 0.133 [f] | 50 | 375 | 50 | 93 (*S*) | 97 |
| 82 | H | $CO_2Me$ | NHAc | [Rh(COD)**98i**]$BF_4$ | 1 | $H_2O$+SDS, 0.173 [g] | 25 | 0.0417 [f] | 50 | 1200 | 50 | 97 (*S*) | 97 |
| 83 | H | $CO_2Me$ | NHAc | [Rh(COD)**114a**]$BF_4$ | 1 | PhH | 25 | 0.017 [f] | 50 | 2941 | 50 | 41 (*S*) | 99 |
| 84 | H | $CO_2Me$ | NHAc | [Rh(COD)**114a**]$BF_4$ | 1 | $H_2O$ | 25 | 1.22 [f] | 50 | 41 | 50 | 34 (*S*) | 99 |
| 85 | H | $CO_2Me$ | NHAc | [Rh(COD)**114a**]$BF_4$ | 1 | MeOH | 25 | 0.017 [f] | 50 | 2941 | 50 | 75 (*S*) | 99 |
| 86 | H | $CO_2Me$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | MeOH | 25 | 0.017 [f] | 50 | 2941 | 50 | 71 (*S*) | 99 |
| 87 | H | $CO_2Me$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | PhH | 25 | 0.017 [f] | 50 | 2941 | 50 | 36 (*S*) | 99 |
| 88 | H | $CO_2Me$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | $H_2O$ | 25 | 0.33 [f] | 50 | 152 | 50 | 44 (*S*) | 99 |
| 89 | H | $CO_2Me$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | $H_2O$+Triton X-100 (0.1 mmol) | 25 | 0.067 [f] | 50 | 746 | 50 | 69 (*S*) | 99 |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 90 | H | $CO_2Me$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | $H_2O$+Triton X-100 (0.5 mmol) | 25 | 0.05 [f] | 50 | 1000 | 50 | 70 (*S*) | 99 |
| 91 | H | $CO_2Me$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 93 (*S*) | 98 |
| 92 | H | $CO_2Me$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | EtOH | r.t. | 1 | 150 | 150 | 100 | 89 (*S*) | 98 |
| 93 | H | $CO_2Me$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | $H_2O$/THF (3:1) | r.t. | 2 | 100 | 50 | 100 | 87 (*S*) | 98 |
| 94 | H | $CO_2Me$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | MeOH | r.t. | 3 | 100 | 33 | 100 | 37 (*S*) | 98 |
| 95 | H | $CO_2Me$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | MeOH/$H_2O$ (1:1) | r.t. | 7 | 100 | 14 | 100 | 90 (*S*) | 98 |
| 96 | H | $CO_2Me$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | MeOH/$H_2O$ (1:3) | r.t. | 3 | 100 | 33 | 100 | 74 (*S*) | 98 |
| 97 | H | $CO_2Me$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | MeOH/$H_2O$ (1:20) | r.t. | 3 | 150 | 50 | 100 | 57 (*S*) | 98 |
| 98 | H | $CO_2Me$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | $H_2O$ | r.t. | 21 | 100 | 5 | 100 | 2 (*S*) | 98 |
| 99 | H | $CO_2Me$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | $H_2O$ | r.t. | 12 | 52.5 | 4 | 35 | 58 (*S*) | 98 |
| 100 | H | $CO_2Me$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | EtOH/$H_2O$ (1:1) | r.t. | 1 | 150 | 150 | 100 | 85 (*S*) | 98 |
| 101 | H | $CO_2Me$ | NHAc | [Rh(COD)**115g**]$SbF_6$ | 2.8 | $H_2O$ | r.t. | 1 | 150 | 150 | 100 | 61 (*S*) | 98 |
| 102 | H | $CO_2Me$ | NHAc | [Rh(COD)**115g**]$SbF_6$ | 2.8 | $H_2O$ | r.t. | 3 | 100 | 33 | 97 | 65 (*S*) | 98 |
| 103 | H | $CO_2Me$ | NHAc | [Rh(COD)**115g**]$SbF_6$ | 2.8 | THF | r.t. | 1 | 150 | 150 | 100 | 86 (*S*) | 98 |
| 104 | H | $CO_2Me$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$ | r.t. | 1.5 | 50 | 33 | 100 | 80 (*S*) | 101 |
| 105 | H | $CO_2Me$ | NHAc | [Rh(COD)**119a**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | ~100 | 65 (*S*) | 102 |
| 106 | H | $CO_2Me$ | NHAc | [Rh(COD)**119b**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | ~100 | 83 (*S*) | 102 |
| 107 | H | $CO_2Me$ | NHAc | [Rh(COD)**119d**]$SbF_6$ | 2.8 | $H_2O$ | r.t. | 2 | 125 | 63 | 100 | 55 (*S*) | 102 |
| 108 | H | $CO_2Me$ | NHAc | [Rh(COD)**119e**]$SbF_6$ | 2.8 | $H_2O$ | r.t. | 2 | 125 | 63 | 100 | 49 (*S*) | 102 |
| 109 | H | $CO_2Me$ | NHAc | [Rh(COD)ent-**120**]$BF_4$ | 1 | Acetone | r.t. | – | 100 | – | 100 | 18 (*R*) | 105 |
| 110 | H | $CO_2Me$ | NHAc | [Rh(COD)**121a**]$BF_4$ | 1 | Acetone | r.t. | – | 100 | – | 100 | 5 (*R*) | 105 |
| 111 | H | $CO_2Me$ | NHAc | [Rh(COD)**121b**]$BF_4$ | 1 | Acetone | r.t. | – | 100 | – | 100 | 59 (*R*) | 105 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 112 | H | $CO_2Me$ | NHAc | [Rh(COD)**121d**]$BF_4$ | 1 | Acetone | r.t. | – | 100 | – | 100 | 26 (*R*) | 105 |
| 113 | H | $CO_2Me$ | NHAc | [Rh(COD)**122a**]$BF_4$ | 1 | Acetone | r.t. | 0.25 | 500 | 2000 | 100 | 76 (*R*) | 105 |
| 114 | H | $CO_2Me$ | NHAc | [Rh(COD)**122b**]$BF_4$ | 1 | Acetone/DCM 13:2 | r.t. | – | 100 | – | 100 | 85 (*R*) | 105 |
| 115 | H | $CO_2Me$ | NHAc | [Rh(COD)**122b**]$BF_4$ | 1 | Acetone/DCM 13:2 | –25 | 0.33 | 100 | 303 | 100 | 91 (*R*) | 105 |
| 116 | H | $CO_2Me$ | NHAc | [Rh(COD)**122c**]$BF_4$ | 1 | Acetone | r.t. | – | 100 | – | 100 | 80 (*R*) | 105 |
| 117 | H | $CO_2Me$ | NHAc | [Rh(COD)**122d**]$BF_4$ | 1 | Acetone/DCM 13:2 | r.t. | – | 100 | – | 100 | 78 (*R*) | 105 |
| 118 | H | $CO_2Me$ | NHAc | [Rh(COD)**122e**]$BF_4$ | 1 | Acetone | r.t. | – | 100 | – | 100 | 87 (*R*) | 105 |
| 119 | H | $CO_2Me$ | NHAc | [Rh(COD)**122e**]$BF_4$ | 1 | Acetone | –25 | 0.5 | 100 | 200 | 100 | 93 (*R*) | 105 |
| 120 | H | $CO_2Me$ | NHAc | [Ir(COD)**126**]$BF_4$ | 1 | DCM | 25 | 0.42 | 100 | 238 | 100 | 78 (*R*) | 104 |
| 121 | H | $CO_2Me$ | NHAc | [Rh(COD)**126**]$BF_4$ | 1 | DCM | 25 | 0.25 | 100 | 400 | 100 | 8 (*R*) | 104 |
| 122 | H | $CO_2Me$ | NHAc | [Ir(COD)**127**]$BF_4$ | 1 | DCM | 25 | 0.75 | 76 | 101 | 76 | 15 (*R*) | 104 |
| 123 | H | $CO_2Me$ | NHAc | [Rh(COD)**127**]$BF_4$ | 1 | DCM | 25 | 0.02 | 100 | 5000 | 100 | 76 (*R*) | 104 |
| 124 | H | $CO_2Me$ | NHAc | [Rh(COD)**127**]$BF_4$ | 1 | DCM | 25 | 0.75 | 96 | 128 | 96 | 81 (*R*) | 104 |
| 125 | H | $CO_2Me$ | NHAc | [Rh(COD)**133a**]$BF_4$ | 1 | IPA | r.t. | 24 | 72 | 3 | 72 | 41 | 48 |
| 126 | H | $CO_2Me$ | NHAc | [Rh(COD)**133b**]$BF_4$ | 1 | IPA | r.t. | 24 | 77 | 2 | 77 | 46 | 48 |
| 127 | H | $CO_2Me$ | NHAc | [Rh(COD)**133c**]$BF_4$ | 1 | IPA | r.t. | 24 | 80 | 3 | 80 | 48 | 48 |
| 128 | H | $CO_2Me$ | NHAc | [Rh(COD)**136**]$BF_4$ | 1.3 | DCM | r.t. | 20 | 1000 | 50 | 100 | 90 (*R*) | 109 |
| 129 | H | $CO_2Me$ | NHAc | [Rh(COD)**136**]$BF_4$ | 1.5 | DCM | 25 | 3 | 479 | 160 | 100 | 90 (*R*) | 110 |
| 130 | H | $CO_2Me$ | NHAc | [Rh(COD)**138**]$BF_4$ | 1.3 | DCM | r.t. | 20 | 1000 | 50 | 100 | 99.5 (*R*) | 109 |
| 131 | H | $CO_2Me$ | NHAc | [Rh(COD)**140**]$BF_4$ | 1.5 | DCM | 25 | 3 | 474 | 158 | 99 | 23 (*R*) | 110 |
| 132 | H | $CO_2Me$ | NHAc | [Rh(COD)**141a**]$BF_4$ | 3.5 | MeOH | r.t. | 0.5 | 1000 | 2000 | >99 | 96 (*S*) | 111 |
| 133 | H | $CO_2Me$ | NHAc | [Rh(COD)**141a**]$BF_4$ | 3.5 | MeOH/$H_2O$ 9:1 | r.t. | 3 | 1000 | 333 | >99 | 96 (*S*) | 111 |
| 134 | H | $CO_2Me$ | NHAc | [Rh(COD)**141a**]$BF_4$ | 3.5 | DCM | r.t. | 1 | 1000 | 1000 | >99 | 98 (*S*) | 111 |
| 135 | H | $CO_2Me$ | NHAc | [Rh(COD)**141a**]$BF_4$ | 3.5 | Tol | r.t. | 0.5 | 1000 | 2000 | >99 | 99 (*S*) | 111 |
| 136 | H | $CO_2Me$ | NHAc | [Rh(COD)**141b**]$BF_4$ | 3.5 | MeOH | r.t. | 0.5 | 1000 | 2000 | >99 | 99 (*S*) | 111 |
| 137 | H | $CO_2Me$ | NHAc | [Rh(COD)**141c**]$BF_4$ | 3.5 | MeOH | r.t. | 1 | 50 | 50 | 5 | – | 111 |
| 138 | H | $CO_2Me$ | NHAc | [Rh(COD)**141c**]$BF_4$ | 3.5 | MeOH | r.t. | 16 | 980 | 61 | 98 | 74 (*S*) | 111 |
| 139 | H | $CO_2Me$ | NHAc | [Rh(COD)**141d**]$BF_4$ | 3.5 | MeOH | r.t. | 21 | 250 | 12 | 25 | 46 (*S*) | 111 |
| 140 | H | $CO_2Me$ | NHAc | [Ir(COD)**142a**]$BF_4$ | 5 | DCM : MeOH 2:1 | 40 | 20 | 20 | 1 | 20 | 19 (*S*) | 117 d |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 141 | H | $CO_2Me$ | NHAc | [Ir(COD)**142a**]$BF_4$ | 5 | DCM : MeOH 2 : 1 | 40 | 20 | 9 | 0.45 | 9 | 7 (*S*) | 117 d |
| 142 | H | $CO_2Me$ | NHAc | [Ir(COD)**142a**]$BF_4$ | 1 | DCM : MeOH 2 : 1 | 40 | 20 | 31 | 1.6 | 31 | 35 (*S*) | 117 d |
| 143 | H | $CO_2Me$ | NHAc | [Rh(COD)**142a**]$BF_4$ | 5 | Tol : MeOH 2 : 1 | 40 | 20 | 94 | 4.7 | 94 | 33 (*S*) | 117 d |
| 144 | H | $CO_2Me$ | NHAc | [Ir(COD)**142b**]$BF_4$ | 5 | DCM : MeOH 2 : 1 | 40 | 20 | 10 | 0.5 | 10 | 6 (*S*) | 117 d |
| 145 | H | $CO_2Me$ | NHAc | [Ir(COD)**142b**]$BF_4$ | 1 | DCM : MeOH 2 : 1 | 40 | 20 | 22 | 1.1 | 22 | 24 (*S*) | 117 d |
| 146 | H | $CO_2Me$ | NHAc | [Rh(COD)**142b**]$BF_4$ | 5 | Tol : MeOH 2 : 1 | 40 | 20 | 99 | 5 | 99 | 35 (*S*) | 117 d |
| 147 | H | $CO_2Me$ | NHAc | [Rh(COD)**142b**]$BF_4$ | 2 | Tol : MeOH 2 : 1 | 40 | 20 | 100 | 5 | 100 | 21 (*S*) | 117 d |
| 148 | H | $CO_2Me$ | NHAc | [Rh(COD)**142b**]$BF_4$ | 5 | DCM | 40 | 20 | 100 | 5 | 100 | 10 (*S*) | 117 d |
| 149 | H | $CO_2Me$ | NHAc | [Ir(COD)**143a**]$BF_4$ | 1 | DCM : MeOH 2 : 1 | 40 | 20 | 30 | 1.5 | 30 | 37 (*R*) | 117c |
| 150 | H | $CO_2Me$ | NHAc | [Rh(COD)**143a**]$BF_4$ | 5 | Tol : MeOH 2 : 1 | 40 | 20 | 56 | 2.8 | 56 | 4 (*R*) | 117 c |
| 151 | H | $CO_2Me$ | NHAc | [Ir(COD)**143b**]$BF_4$ | 1 | DCM : MeOH 2 : 1 | 40 | 20 | 24 | 1.2 | 24 | 28 (*R*) | 117 c |
| 152 | H | $CO_2Me$ | NHAc | [Rh(COD)**143b**]$BF_4$ | 5 | Tol : MeOH 2 : 1 | 40 | 20 | 88 | 4.4 | 88 | 6 (*R*) | 117 c |
| 153 | H | $CO_2Me$ | NHAc | [Rh(COD)**144a**]$BF_4$ | 5 | DCM | 25 | 8 | 98 | 12.3 | 98 | 92 (*S*) | 117 b |
| 154 | H | $CO_2Me$ | NHAc | [Rh(COD)**144c**]$BF_4$ | 5 | DCM | 25 | 6 | 100 | 16.7 | 100 | 97 (*S*) | 117 b |
| 155 | H | $CO_2Me$ | NHAc | [Rh(COD)**144c**]$BF_4$ | 30 | DCM | 5 | 4 | 1000 | 250 | 100 | >99 (*S*) | 117 b |
| 156 | H | $CO_2Me$ | NHAc | [Rh(COD)**145a**]$BF_4$ | 5 | DCM | 25 | 8 | 100 | 12.5 | 100 | 3 (*S*) | 117 b |
| 157 | H | $CO_2Me$ | NHAc | [Rh(COD)**146a**]$BF_4$ | 5 | DCM | 25 | 8 | 97 | 12.1 | 97 | 71 (*S*) | 117 b |
| 158 | H | $CO_2Me$ | NHAc | [Rh(COD)**146c**]$BF_4$ | 5 | DCM | 25 | 8 | 92 | 11.5 | 92 | 29 (*S*) | 117 b |
| 159 | H | $CO_2Me$ | NHAc | [Rh(COD)**149a**]$BF_4$ | 0.3 | DCM | 20 | 20 | 660 | 33 | 66 | 43.8 (*S*) | 116 |
| 160 | H | $CO_2Me$ | NHAc | [Rh(COD)**149b**]$BF_4$ | 0.3 | DCM | 20 | 20 | 770 | 39 | 77 | 23.2 (*S*) | 116 |
| 161 | H | $CO_2Me$ | NHAc | [Rh(COD)**149c**]$BF_4$ | 0.3 | DCM | 20 | 20 | 1000 | 50 | >99 | 88.8 (*R*) | 116 |
| 162 | H | $CO_2Me$ | NHAc | [Rh(COD)**149e**]$BF_4$ | 0.3 | DCM | 20 | 20 | 1000 | 50 | >99 | 80.7 (*R*) | 116 |
| 163 | H | $CO_2Me$ | NHAc | [Rh(COD)**159a**]$BF_4$ | 1 | MeOH | r.t. | 4 | 97 | 24.3 | 97 | 93 (*R*) | 123 |
| 164 | H | $CO_2Me$ | NHAc | [Rh(COD)**159a**]$BF_4$ | 1 | THF | r.t. | 4 | 84 | 21 | 84 | 94 (*R*) | 123 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 165 | H | $CO_2Me$ | NHAc | [Rh(COD)**159a**]$BF_4$ | 1 | DCM/MeOH 9:1 | r.t. | 14 | 78 | 5.6 | 78 | 98 (*R*) | 123 |
| 166 | H | $CO_2Me$ | NHAc | [Rh(COD)**159a**]$BF_4$ | 1 | DCM | r.t. | 14 | 77 | 5.5 | 77 | 99 (*R*) | 123 |
| 167 | H | $CO_2Me$ | NHAc | [Rh(COD)**159b**]$BF_4$ | 1 | DCM | r.t. | 2.5 | 39 | 15.6 | 39 | 96 (*S*) | 123 |
| 168 | H | $CO_2Me$ | NHAc | [Rh(COD)**159c**]$BF_4$ | 1 | DCM | r.t. | 14 | 100 | 7.1 | 100 | 4 (*S*) | 123 |
| 169 | H | $CO_2Me$ | NHAc | [Rh(COD)**159d**]$BF_4$ | 1 | DCM | r.t. | 2.5 | 100 | 40 | 100 | 96 (*S*) | 123 |
| 170 | H | $CO_2Me$ | NHAc | [Rh(COD)**159e**]$BF_4$ | 1 | DCM | r.t. | 2.5 | 100 | 40 | 100 | 95 (*R*) | 123 |
| 171 | H | $CO_2Me$ | NHAc | [Rh(COD)**159f**]$BF_4$ | 1 | DCM | r.t. | 2.5 | 100 | 40 | 100 | 6 (*R*) | 123 |
| 172 | H | $CO_2Me$ | NHAc | [Rh(COD)**159g**]$BF_4$ | 1 | DCM | r.t. | 2.5 | 100 | 40 | 100 | 95 (*S*) | 123 |
| 173 | H | $CO_2Me$ | NHAc | [Rh(COD)**159h**]$BF_4$ | 1 | DCM | r.t. | 5 | 21 | 4.2 | 21 | 58 (*R*) | 123 |
| 174 | H | $CO_2Me$ | NHAc | [Rh(COD)**160a**]$BF_4$ | 1 | DCM | r.t. | 2.5 | 32 | 12.8 | 32 | 61 (*S*) | 123 |
| 175 | H | $CO_2Me$ | NHAc | [Rh(COD)**160b**]$BF_4$ | 1 | DCM | r.t. | 1 | 100 | 100 | 100 | 96 (*R*) | 123 |
| 176 | H | $CO_2Me$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | 100 | 8.3 | 100 | >99 (*S*) | 128 |
| 177 | H | $CO_2Me$ | NHAc | [Rh(COD)**163b**]$PF_6$ | 1 | THF | r.t. | 12 | 100 | 8.3 | 100 | 96 (*S*) | 128 |
| 178 | H | $CO_2Me$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | 100 | 8.3 | 100 | >99 (*S*) | 128 |
| 179 | H | $CO_2Me$ | NHAc | [Rh(COD)**164b**]$PF_6$ | 1 | THF | r.t. | 12 | 100 | 8.3 | 100 | 77 (*S*) | 128 |
| 180 | H | $CO_2Me$ | NHAc | [Rh(COD)**166**]$BF_4$ | 51 | $H_2O$/ EtOAc (1:1) | r.t. | 24 | 50 | 2 | 100 | 18 (*R*) | 129 |
| 181 | H | $CO_2Me$ | NHAc | [Rh(COD)**167a**]$BF_4$ | 1 | DCM | r.t. | 0.08 | 100 | >1200 | 100 | 88.2 (*S*) | 121 a, b |
| 182 | H | $CO_2Me$ | NHAc | [Rh(COD)**167b**]$BF_4$ | 1 | MeOH | 25 | 1.3 | 100 | 77 | 100 | 91 (*R*) | 121 b |
| 183 | H | $CO_2Me$ | NHAc | [Rh(COD)**167b**]$BF_4$ | 1 | DCM | 25 | 2.5 | 100 | 40 | 100 | >99 (*R*) | 121 b |
| 184 | H | $CO_2Me$ | NHAc | [Rh(COD)**167b**]$BF_4$ | 1 | Tol | 25 | 10 | 100 | 10 | 100 | 97 (*R*) | 121 b |
| 185 | H | $CO_2Me$ | NHAc | [Rh(COD)**167b**]$BF_4$ | 1 | THF | 25 | 2 | 100 | 50 | 100 | 92 (*R*) | 121 b |
| 186 | H | $CO_2Me$ | NHAc | [Rh(COD)**167b**]$BF_4$ | 1 | DCM | 25 | 2.5 | 100 | 40 | 100 | >99 (*R*) [k] | 121 b |
| 187 | H | $CO_2Me$ | NHAc | [Rh(COD)**167b**]$BF_4$ | 1 | DCM | 25 | 2.5 | 100 | 40 | 100 | >99 (*R*) [l] | 121 a, b |
| 188 | H | $CO_2Me$ | NHAc | [Rh(nbd)**167b**]$BF_4$ | 1 | DCM | 25 | 2.5 | 100 | 40 | 100 | >99 (*R*) [l] | 121 b |
| 189 | H | $CO_2Me$ | NHAc | [Rh(COD)**167c**]$BF_4$ | 1 | DCM | r.t. | 0.33 | 100 | 303 | 100 | 98.3 (*S*) | 121 a, b |
| 190 | H | $CO_2Me$ | NHAc | [Rh(COD)**167d**]$BF_4$ | 1 | DCM | r.t. | 0.33 | 100 | 303 | 100 | 97.6 (*R*) | 121 a, b |
| 191 | H | $CO_2Me$ | NHAc | [Rh(COD)**168a**]$BF_4$ | 5 | DCM | 25 | 8 | 100 | 13 | 100 | 92 (*S*) | 126 |
| 192 | H | $CO_2Me$ | NHAc | [Rh(COD)**168a**]$BF_4$ | 30 | DCM | 25 | 12 | 100 | 8 | 100 | 98 (*S*) | 126 |
| 193 | H | $CO_2Me$ | NHAc | [Rh(COD)**168b**]$BF_4$ | 5 | DCM | 25 | 8 | 71 | 9 | 71 | 82 (*S*) | 126 |
| 194 | H | $CO_2Me$ | NHAc | [Rh(COD)**168c**]$BF_4$ | 5 | DCM | 25 | 8 | 46 | 6 | 46 | 15 (*S*) | 126 |
| 195 | H | $CO_2Me$ | NHAc | [Rh(COD)**168d**]$BF_4$ | 5 | DCM | 25 | 8 | 33 | 4 | 33 | 12 (*S*) | 126 |
| 196 | H | Ph | NHAc | [Rh(COD)**91**]$BF_4$ | 6.9 | MeOH | r.t. | 0.167 | 100 | 600 | 100 | 83.3 (*R*) | 84 |

Table 27.5 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 197 | H | Ph | NHAc | [Rh(COD)**91**]$BF_4$ | 6.9 | IPA | r.t. | 0.167 | 100 | 600 | 100 | 83.5 (*R*) | 84 |
| 198 | H | Ph | NHAc | [Rh(COD)**91**]$BF_4$ | 6.9 | Acetone | r.t. | 0.167 | 100 | 600 | 100 | 83.1 (*R*) | 84 |
| 199 | H | Ph | NHAc | [Rh(COD)**91**]$BF_4$ | 6.9 | THF | r.t. | 0.167 | 100 | 600 | 100 | 81.9 (*R*) | 84 |
| 200 | H | Ph | NHAc | [Rh(COD)**91**]$BF_4$ | 6.9 | DCM | r.t. | 0.167 | 100 | 600 | 100 | 82.5 (*R*) | 84 |
| 201 | H | Ph | NHAc | [Rh(COD)**91**]$BF_4$ | 6.9 | Tol | r.t. | 0.167 | 100 | 600 | 100 | 79.3 (*R*) | 84 |
| 202 | H | Ph | NHAc | [Rh(COD)**91**]$ClO_4$ | 1 | IPA | 0 | 0.167 | 100 | 600 | 100 | 89.0 (*R*) | 84 |
| 203 | H | 4-Cl-Ph | NHAc | [Rh(COD)**91**]$ClO_4$ | 1 | IPA | 0 | 0.167 | 100 | 600 | 100 | 86.1 (*R*) | 84 |
| 204 | H | 4-F-Ph | NHAc | [Rh(COD)**91**]$ClO_4$ | 1 | IPA | 0 | 0.167 | 100 | 600 | 100 | 87.9 (*R*) | 84 |
| 205 | H | 4-$CF_3$-Ph | NHAc | [Rh(COD)**91**]$ClO_4$ | 1 | IPA | 0 | 0.167 | 100 | 600 | 100 | 90.0 (*R*) | 84 |
| 206 | H | 3-Me-Ph | NHAc | [Rh(COD)**91**]$ClO_4$ | 1 | IPA | 0 | 0.167 | 100 | 600 | 100 | 85.6 (*R*) | 84 |
| 207 | H | 4-Me-Ph | NHAc | [Rh(COD)**91**]$ClO_4$ | 1 | IPA | 0 | 0.167 | 100 | 600 | 100 | 86.5 (*R*) | 84 |
| 208 | *i*-Pr | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 45.7 (*S*) | 85 |
| 209 | *i*-Pr | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.0316 [f] | 50 | 1579 | 50 | 57.2 | 26 |
| 210 | *i*-Pr | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.0133 [f] | 50 | 3750 | 50 | 95.3 | 26 |
| 211 | *i*-Pr | $CO_2H$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 90.0 (*S*) | 95b |
| 212 | *i*-Pr | $CO_2H$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 91.0 (*S*) | 95b |
| 213 | *i*-Pr | $CO_2H$ | NHAc | [Rh(COD)**98c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 64.4 | 95b |
| 214 | *i*-Pr | $CO_2H$ | NHAc | [Rh(COD)**98d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 26.0 | 95b |
| 215 | *i*-Pr | $CO_2H$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 83.6 | 95b |
| 216 | *i*-Pr | $CO_2H$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 89.2 (*R*) | 95b |
| 217 | *i*-Pr | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.02 [f] | 50 | 2500 | 50 | 86.1 | 26 |
| 218 | *i*-Pr (*Z*) | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 92.0 | 95b |
| 219 | *i*-Pr (*Z*/*E*) | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 86.5 | 95b |
| 220 | *i*-Pr | $CO_2Me$ | NHAc | [[Rh(COD)**98d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 5.6 (*R*) | 95b |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 221 | *i*-Pr | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 87.2 (*S*) | 95 b |
| 222 | *i*-Pr | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 86.9 (*R*) | 95 b |
| 223 | *i*-Pr | $CO_2Me$ | NHAc | [Rh(COD)**103g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 86.5 (*R*) | 95 b |
| 224 | *i*-Pr (*E*) | NHAc | $CO_2Me$ | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 73.3 | 95 b |
| 225 | Bn | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 40.6 (*S*) | 95 b |
| 226 | Bn | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 67.0 (*R*) | 95 b |
| 227 | Ph | $CO_2H$ | NHAc | [Rh(1,5-hexadiene)(+)-*trans*-**85**]Cl | 50 | – | 0 | 24 | – | – | – | 68.5 (*S*) [a] | 67 |
| 228 | Ph | $CO_2H$ | NHAc | [Rh(1,5-hexadiene)d-*trans*-**86**]Cl | 50 | – | 0 | – | – | – | – | 12 (*S*) [a] | 68 a |
| 229 | Ph | $CO_2H$ | NHAc | [Rh(COD)**88**]Cl | 20.7 | PhH/EtOH 1 : 1 | 60 | 24 | 50 [c] | 2.1 | 100 [d] | 4.3 | 81 |
| 230 | Ph | $CO_2H$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 97.9 (*R*) | 27 |
| 231 | Ph | $CO_2H$ | NHAc | [Rh(COD)**93a**]$BF_4$ | 6.9 | MeOH | r.t. | 0.5 | 356 | 712 | 71.2 | 18 (*S*) | 52 |
| 232 | Ph | $CO_2H$ | NHAc | [Rh(COD)**94a**]$BF_4$ | 6.9 | MeOH | r.t. | 0.5 | 410 | 820 | 81.9 | 74.2 (*S*) | 52 |
| 233 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | DCE | r.t. | 24 | 100 | 4 | 100 | 88.2 (*S*) | 85 |
| 234 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | THF | r.t. | 24 | 100 | 4 | 100 | 89.1 (*S*) | 85 |
| 235 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | THF:$Et_3N$ = 1 : 1 | r.t. | 24 | 30 | 1 | 30 | 30.9 (*S*) | 85 |
| 236 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | MeOH | r.t. | 24 | 100 | 4 | 100 | 92.4 (*S*) | 85 |
| 237 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | MeOH : $Et_3N$ = 1 : 1 | r.t. | 24 | 100 | 4 | 100 | 67.9 (*S*) | 85 |
| 238 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | EtOH | r.t. | 24 | 100 | 4 | 100 | 92.0 (*S*) | 85 |
| 239 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | $CF_3CH_2OH$ | r.t. | 24 | 100 | 4 | 100 | 80.3 (*S*) | 85 |
| 240 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | *t*-BuOH | r.t. | 24 | 100 | 4 | 100 | 91.1 (*S*) | 85 |
| 241 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 94.7 (*S*) | 85 |
| 242 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | IPA | 0 | 24 | 100 | 4 | 100 | 96.1 (*S*) | 85 |
| 243 | Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | IPA | r.t. | 24 | 86.6 | 3.6 | 86.6 | 63.9 (*S*) | 85 |
| 244 | Ph | $CO_2H$ | NHAc | [Rh(COD)**96**]$BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4.2 | 100 | 83.5 (*R*) | 85 |
| 245 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.11 [f] | 50 | 455 | 50 | 73.2 (*S*) | 26 |
| 246 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | EtOH | 25 | 0.1 [f] | 50 | 500 | 50 | 71 (*S*) [a] | 26 |
| 247 | Ph | $CO_2H$ | NHAc | $[Rh(COD)Cl]_2$ + **97a** (neutral) | 1 | EtOH | 25 | 3 | 50 | 16.7 | 50 | 69 (*S*) | 26 |

Table 27.5 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 248 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**97a**]$PF_6$ | 1 | EtOH | 30 | 1 | 100 | 100 | 100[b] | 61 (*S*) | 88 |
| 249 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**97a**]$PF_6$ | 1 | EtOH | 0 | 1.5 | 100 | 67 | 100[b] | 75 (*S*) | 88 |
| 250 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.0333[f] | 50 | 1500 | 50 | 96.6 (*S*) | 91b |
| 251 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | PhH | 25 | 0.183[f] | 50 | 273 | 50 | 98.6 (*S*) | 91b |
| 252 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | Tol | 25 | 0.317[f] | 50 | 158 | 50 | 98.9 (*S*) | 91b |
| 253 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | Tol | 25 | 0.32 | 50 | 156 | 50 | 98.9 (*S*) | 91b |
| 254 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97a**]Cl | 50 | – | 25 | 8 | 100[c] | – | – | 46 (*S*)[a] | 89 |
| 255 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97a**]$ClO_4$ | 1 | EtOH | 25 | – | 50 | – | 100 | 61 (*S*) | 90 |
| 256 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97b**]Cl | 50 | – | 25 | 8 | 100[c] | – | – | 36 (*S*)[a] | 89 |
| 257 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ | 25 | 0.52 | 50 | 91 | 50 | 80 (S) | 99 |
| 258 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $LiBF_4$ | 25 | 0.5 | 50 | 100 | 50 | 64 (S) | 99 |
| 259 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $NaBF_4$ | 25 | 0.3 | 50 | 167 | 50 | 83 (S) | 99 |
| 260 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $KBF_4$ | 25 | 0.45 | 50 | 111 | 50 | 82 (S) | 99 |
| 261 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $RbBF_4$ | 25 | 0.33 | 50 | 150 | 50 | 82 (S) | 99 |
| 262 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $CsBF_4$ | 25 | 0.47 | 50 | 120 | 50 | 83 (S) | 99 |
| 263 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.0667[f] | 50 | 750 | 50 | 95.1 (*S*) | 91b |
| 264 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | PhH | 25 | 0.467[f] | 50 | 107 | 50 | 85.5 (*S*) | 91b |
| 265 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | Tol | 25 | 8[f] | 50 | 6.25 | 50 | 82.3 (*S*) | 91b |
| 266 | Ph | $CO_2H$ | NHAc | [Rh(COD)**97d**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 53.7 (*S*) | 26 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 267 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.0233 [f] | 50 | 2143 | 50 | 96.6 (*S*) | 26 |
| 268 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | –27 | – | – | – | – | 99.3 (*S*) | 26 |
| 269 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | –22.2 | – | – | – | – | 98.3 (*S*) | 26 |
| 270 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 0.4 | – | – | – | – | 97.7 (*S*) | 26 |
| 271 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 97.1 (*S*) | 26 |
| 272 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 55.2 | – | – | – | – | 92.7 (*S*) | 26 |
| 273 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | EtOH | 25 | 0.117 [f] | 50 | 429 | 50 | 96 (*S*) [a] | 26 |
| 274 | Ph | $CO_2H$ | NHAc | $[Rh(COD)Cl]_2$ + **98a** (neutral) | 1 | EtOH | 25 | 1.67 | 50 | 30 | 50 | 87 (*S*) [a] | 26 |
| 275 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.03 | 50 | 1667 | 50 | 96.5 (*S*) | 91e |
| 276 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 94.0 | 95a, b |
| 277 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 99.0 | 95a, b |
| 278 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 60.0 | 95a, b |
| 279 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98d**]$SbF_6$ | 2–2.8 | THF | r.t. | – | – | – | – | 71 | 95a |
| 280 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98f**]OTf | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.0 | 95b |
| 281 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98f**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 93.0 | 95b |
| 282 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.6 | 95b |
| 283 | Ph | $CO_2H$ | NHAc | [Rh(COD)**98h**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 91.0 | 95b |
| 284 | Ph | $CO_2H$ | NHAc | [Rh(COD)**100**]Cl | 50 | – | 25 | 8 | 100 [c] | – | – | 80 (*S*) [a] | 89 |
| 285 | Ph | $CO_2H$ | NHAc | [Rh(COD)**100b**]$BF_4$ | 1 | MeOH | 25 | – | 50 | – | 50 | 90 (*S*) | 91e |
| 286 | Ph | $CO_2H$ | NHAc | [Rh(COD)**101a**]$BF_4$ | 1 | MeOH | 25 | 0.0617 [f] | 50 | 810 | 50 | 94.5 (*S*) | 91c |
| 287 | Ph | $CO_2H$ | NHAc | [Rh(COD)**101b**]$BF_4$ | 1 | MeOH | 25 | 0.0633 [f] | 50 | 789 | 50 | 96.2 (*S*) | 91c |
| 288 | Ph | $CO_2H$ | NHAc | [Rh(COD)**101c**]$BF_4$ | 1 | MeOH | 25 | 0.0633 [f] | 50 | 789 | 50 | 91.4 (*S*) | 91c |
| 289 | Ph | $CO_2H$ | NHAc | [Rh(COD)**101d**]$BF_4$ | 1 | MeOH | 25 | 0.0683 [f] | 50 | 732 | 50 | 94.9 (*S*) | 91c |
| 290 | Ph | $CO_2H$ | NHAc | [Rh(COD)**101e**]$BF_4$ | 1 | MeOH | 25 | 0.0817 [f] | 50 | 612 | 50 | 90.4 (*S*) | 91c |
| 291 | Ph | $CO_2H$ | NHAc | [Rh(COD)**101f**]$BF_4$ | 1 | MeOH | 25 | 0.142 [f] | 50 | 353 | 50 | 93.6 (*S*) | 91c |
| 292 | Ph | $CO_2H$ | NHAc | [Rh(COD)**102a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 94.5 | 95b |
| 293 | Ph | $CO_2H$ | NHAc | [Rh(COD)**102a**]$BF_4$ | 2–2.8 | THF | r.t. | – | – | – | – | 98.3 | 95a |
| 294 | Ph | $CO_2H$ | NHAc | [Rh(COD)**102b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 94.5 | 95b |
| 295 | Ph | $CO_2H$ | NHAc | [Rh(COD)**103a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 95.8 | 95b |
| 296 | Ph | $CO_2H$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.0 | 95b |

Table 27.5 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 297 | Ph | $CO_2H$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | – | – | – | – | 93 | 95 a |
| 298 | Ph | $CO_2H$ | NHAc | [Rh(COD)**111**]$ClO_4$ | 1 | EtOH | 25 | 0.3 | 50 | 167 | 100 | 55 (*R*) | 90 |
| 299 | Ph | $CO_2H$ | NHAc | [Rh(COD)**111**]$ClO_4$ | 1 | EtOH | 0 | 1 | 50 | 50 | 100 | 70 (*R*) | 90 |
| 300 | Ph | $CO_2H$ | NHAc | [Rh(COD)**112b**]$BF_4$ | 1 | MeOH | 25 | 0.12 | 50 | 417 | 50 | 1 (*S*) | 91 e |
| 301 | Ph | $CO_2H$ | NHAc | [Rh(COD)**113a**]Cl | 50 | – | 25 | 8 | 100 [c] | – | – | 0 | 89 |
| 302 | Ph | $CO_2H$ | NHAc | [Rh(COD)**113b**]Cl | 50 | – | 25 | 8 | 100 [c] | – | – | 0 | 89 |
| 303 | Ph | $CO_2H$ | NHAc | [Rh(COD)**113c**]$BF_4$ | 1 | MeOH | 25 | 0.17 | 50 | 294 | 50 | 2 (*S*) | 91 e |
| 304 | Ph | $CO_2H$ | NHAc | [Rh(COD)**113d**]$BF_4$ | 1 | MeOH | 25 | 0.12 | 50 | 429 | 50 | 46 (*S*) | 91 e |
| 305 | Ph | $CO_2H$ | NHAc | [Rh(COD)**113e**]$BF_4$ | 1 | MeOH | 25 | 0.12 | 50 | 417 | 50 | 46 (*S*) | 91 e |
| 306 | Ph | $CO_2H$ | NHAc | [Rh(COD)**114a**]$BF_4$ | 1 | MeOH | 25 | 0.083 [f] | 50 | 602 | 50 | 55 (*S*) | 99 |
| 307 | Ph | $CO_2H$ | NHAc | [Rh(COD)**114a**]$BF_4$ | 1 | PhH | 25 | 0.68 [f] | 50 | 74 | 50 | 58 (*S*) | 99 |
| 308 | Ph | $CO_2H$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | MeOH | 25 | 0.05 [f] | 50 | 1000 | 50 | 52 (*S*) | 99 |
| 309 | Ph | $CO_2H$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | PhH | 25 | 0.052 [f] | 50 | 97 | 50 | 80 (*S*) | 99 |
| 310 | Ph | $CO_2H$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | THF | r.t. | – | 150 | – | 100 | 97 (*S*) | 98 |
| 311 | Ph | $CO_2H$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | $H_2O$/EtOAc (1:1) | r.t. | – | 100 | – | 100 | 7 (*S*) | 98 |
| 312 | Ph | $CO_2H$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/MeOH/ EtOAc (0.6:0.4:2) | r.t. | 3 | 100 | 33 | 100 | 96 (*S*) | 101 |
| 313 | Ph | $CO_2H$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/MeOH(3:2) | r.t. | 1.5 | 100 | 67 | 100 | 95 (*S*) | 101 |
| 314 | Ph | $CO_2H$ | NHAc | [Rh(COD)**119d**]$SbF_6$ | 2.8 | $H_2O$/THF(1:1) | r.t. | 24 | 15 | 0.6 | 12 | 65 (*S*) | 102 |
| 315 | Ph | $CO_2H$ | NHAc | [Rh(COD)**119d**]$SbF_6$ | 2.8 | THF | r.t. | 2 | 125 | 63 | 100 | 70 (*S*) | 102 |
| 316 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]$BF_4$ | 1 | EtOH | 25 | 1 | 100 | 100 | 100 | 30 (*R*) | 103 |
| 317 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 40 (*R*) | 103 |
| 318 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]$BF_4$ | 1 | THF | 0 | 1 | 100 | 100 | 100 | 52 (*R*) | 103 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 319 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]$BF_4$ | 1 | THF | –78 | 3 | 100 | 33 | 100 | 10 (*R*) | 103 |
| 320 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]$BPh_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 30 (*R*) | 103 |
| 321 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]$BPh_4$ | 1 | EtOH | 25 | 1 | 100 | 100 | 100 | 35 (*R*) | 103 |
| 322 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]Cl | 20.4 | PhH/EtOH 1:1 | 60 | 24 | 100 | 2 | 100 | 8.2 (*R*) | 103 |
| 323 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]$ClO_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 36 (*R*) | 103 |
| 324 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]$ClO_4$ | 1 | EtOH | 25 | 1 | 100 | 100 | 100 | 28 (*R*) | 103 |
| 325 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]$PF_6$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 32 (*R*) | 103 |
| 326 | Ph | $CO_2H$ | NHAc | [Rh(COD)**124**]$PF_6$ | 1 | EtOH | 25 | 1 | 100 | 100 | 100 | 30 (*R*) | 103 |
| 327 | Ph | $CO_2H$ | NHAc | [Rh(COD)**125**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 54 (*S*) | 103 |
| 328 | Ph | $CO_2H$ | NHAc | [Rh(COD)**126**]Cl | 50 | – | 25 | 1 | 100 [c] | 100 | 100 | 62 (*R*) [a] | 89 |
| 329 | Ph | $CO_2H$ | NHAc | [Rh(COD)**128**]Cl | 51 | MeOH | r.t. | 0.25 | 230 | 920 | 100 | 36 (*S*) | 106 |
| 330 | Ph | $CO_2H$ | NHAc | [Rh(COD)**129**]Cl | 51 | MeOH | r.t. | 1 | 270 | 270 | 100 | 15 (*R*) | 106 |
| 331 | Ph | $CO_2H$ | NHAc | [Rh(COD)**131**]$BF_4$ | 1 | PhH | 25 | 6 | 89.5 | 15 | 89.5 | 40.8 (*R*) | 108 |
| 332 | Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 1 | Acetone | 25 | 0.25–1 | 100 | 100–400 | 100 | 90.1 (*R*) | 107 |
| 333 | Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 6.9 | Acetone | 25 | 0.25–1 | 100 | 100–400 | 100 | 92.8 (*R*) | 107 |
| 334 | Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25–1 | 100 | 100–400 | 100 | 94.4 (*R*) | 107 |
| 335 | Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | –15 | 0.25–1 | 100 | 100–400 | 100 | 97.1 (*R*) | 107 |
| 336 | Ph | $CO_2H$ | NHAc | [Rh(COD)**133a**]$BF_4$ | 1 | IPA | r.t. | 24 | 98 | 4 | 98 | 94 [j] | 48 |
| 337 | Ph | $CO_2H$ | NHAc | [Rh(COD)**133b**]$BF_4$ | 1 | IPA | r.t. | 24 | 94 | 4 | 94 | 89 [j] | 48 |
| 338 | Ph | $CO_2H$ | NHAc | [Rh(COD)**133c**]$BF_4$ | 1 | IPA | r.t. | 24 | 94 | 4 | 98 | 97 [j] | 48 |
| 339 | Ph | $CO_2H$ | NHAc | [Rh(COD)**134**]$BF_4$ | 1 | PhH | 25 | 5.0 | 85.6 | 17 | 85.6 | 25.6 (*R*) | 108 |
| 340 | Ph | $CO_2H$ | NHAc | [Rh(COD)**135**]$BF_4$ | 1 | PhH | 25 | 7.5 | 93.4 | 12 | 93.4 | 57.1 (*R*) | 108 |
| 341 | Ph | $CO_2H$ | NHAc | [Rh(COD)**141a**]$BF_4$ | 3.5 | MeOH | r.t. | 0.5 | 1000 | 2000 | >99 | 93 (*S*) | 111 |
| 342 | Ph | $CO_2H$ | NHAc | [Rh(COD)**141b**]$BF_4$ | 3.5 | MeOH | r.t. | 0.5 | 1000 | 2000 | >99 | 99 (*S*) | 111 |
| 343 | Ph | $CO_2H$ | NHAc | [Rh(COD)**142a**]$BF_4$ | 5 | Tol:MeOH 2:1 | 40 | 20 | 100 | 5 | 100 | 31 (*S*) | 117 d |
| 344 | Ph | $CO_2H$ | NHAc | [Rh(COD)**142b**]$BF_4$ | 5 | Tol:MeOH 2:1 | 40 | 20 | 100 | 5 | 100 | 30 (*S*) | 117 d |
| 345 | Ph | $CO_2H$ | NHAc | [Ir(COD)**142b**]$BF_4$ | 5 | DCM:MeOH 2:1 | 40 | 20 | 18 | 0.9 | 18 | 15 (*S*) | 117 d |

Table 27.5 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 346 | Ph | $CO_2H$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | 99 | 8.3 | 100 | 99 (*S*) | 128 |
| 347 | Ph | $CO_2H$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 348 | Ph | $CO_2H$ | NHAc | [Rh(COD)**166**]$BF_4$ | 51 | $H_2O$/EtOAc (1:1) | r.t. | 24 | 50 | 2.1 | 100 | 50 (*R*) [i)] | 129 |
| 349 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**107**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 25 | 24 | 100 | 4 | 100 | 24.8 (*R*) | 93 |
| 350 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**107**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 25 | 24 | 47.5 | 2 | 95 | 31.0 (*R*) | 93 |
| 351 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**107**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 25 | 24 | 18.4 | 0.8 | 92 | 16.2 (*R*) | 93 |
| 352 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**107**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 40 | 24 | 95 | 4 | 95 | 14.9 (*R*) | 93 |
| 353 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**107**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 60 | 24 | 100 | 4 | 100 | 12.4 (*R*) | 93 |
| 354 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**107**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 80 | 24 | 96 | 4 | 96 | 5.3 (*R*) | 93 |
| 355 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**107**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | –15 to –20 | 7 | 53 | 8 | 53 | 62.7 (*R*) | 93 |
| 356 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**107**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | –15 to –20 | 7 | 18.8 | 3 | 94 | 27.7 (*R*) | 93 |
| 357 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**107**]$ClO_4$ | 1.97 | PhH:EtOH = 1:1 | 25 | 24 | 90 | 4 | 90 | 20.9 (*R*) | 93 |
| 358 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 25 | 24 | 100 | 4 | 100 | 63.4 (*S*) | 93 |
| 359 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 25 | 24 | 50 | 2 | 100 | 68.2 (*S*) | 93 |
| 360 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 25 | 24 | 20 | 0.9 | 100 | 44.1 (*S*) | 93 |
| 361 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 25 | 1 | 96 | 96 | 96 | 60.4 (*S*) | 93 |
| 362 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 25 | 2 | 100 | 50 | 100 | 66.9 (*S*) | 93 |
| 363 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 25 | 4 | 94 | 24 | 94 | 59.6 (*S*) | 93 |
| 364 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 40 | 24 | 100 | 4 | 100 | 45.9 (*S*) | 93 |
| 365 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 60 | 24 | 100 | 4 | 100 | 26.3 (*S*) | 93 |
| 366 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | 80 | 24 | 100 | 4 | 100 | 12.9 (*S*) | 93 |
| 367 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH:EtOH = 1:1 | –15 to –20 | 6 | 20 | 3 | 20 | 80.1 (*S*) | 93 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 368 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH : EtOH = 1 : 1 | –15 to –20 | 8 | 20 | 3 | 100 | 74.1 (*S*) | 93 |
| 369 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH : EtOH = 1 : 1 | 0 | 24 | 100 | 4 | 100 | 72.1 (*S*) | 93 |
| 370 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH : EtOH = 1 : 1 | –5 | 24 | 93 | 4 | 93 | 78.4 (*S*) | 93 |
| 371 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.48 | PhH : EtOH = 1 : 1 | –15 | 24 | 79 | 3 | 79 | 90.4 (*S*) | 93 |
| 372 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 1.09 | PhH : EtOH = 1 : 1 | 25 | 24 | 70 | 3 | 70 | 21.9 (*S*) | 93 |
| 373 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**108**]$ClO_4$ | 19.70 | PhH : EtOH = 1 : 1 | 25 | 50 | 100 | 2 | 100 | 22.9 (*S*) | 93 |
| 374 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**109**]$ClO_4$ dimer | 1.48 | – | 25 | 24 | 63 | 3 | 63 [b] | 13.8 (*R*) | 94 |
| 375 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**109**]$ClO_4$ dimer | 1.48 | – | 25 | 24 | 50 | 2 | 100 [b] | 11.6 (*R*) | 94 |
| 376 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**109**]$ClO_4$ dimer | 1.48 | – | 25 | 24 | 20 | 0.8 | 100 [b] | 14.9 (*R*) | 94 |
| 377 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**109**]$ClO_4$ dimer | 1.48 | – | 40 | 24 | 100 | 4 | 100 [b] | 8.2 (*R*) | 94 |
| 378 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**109**]$ClO_4$ dimer | 1.48 | – | 60 | 24 | 100 | 4 | 100 [b] | 1.6 (*S*) | 94 |
| 379 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**109**]$ClO_4$ dimer | 1.48 | – | 80 | 24 | 100 | 4 | 100 [b] | 2.9 (*S*) | 94 |
| 380 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**109**]$ClO_4$ dimer | 1.48 | – | –15 to –20 | 7 | 93 | 13 | 93 [b] | 26.3 (*R*) | 94 |
| 381 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**109**]$ClO_4$ dimer | 1.48 | – | –15 to –20 | 7 | 20 | 3 | 100 [b] | 29.3 (*R*) | 94 |
| 382 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**110**]$ClO_4$ dimer | 1.48 | – | 25 | 24 | 100 | 4 | 100 [b] | 4.8 (*R*) | 94 |
| 383 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**110**]$ClO_4$ dimer | 1.48 | – | 25 | 24 | 50 | 2 | 100 [b] | 6.9 (*R*) | 94 |

Table 27.5 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | $P[H_2]$ [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 384 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**110**]$ClO_4$ dimer | 1.48 | – | 25 | 24 | 19.4 | 0.8 | 97 [b] | 2.5 (*R*) | 94 |
| 385 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**110**]$ClO_4$ dimer | 1.48 | – | 40 | 24 | 100 | 4 | 100 [b] | 3.1 (*R*) | 94 |
| 386 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**110**]$ClO_4$ dimer | 1.48 | – | 60 | 24 | 100 | 4 | 100 [b] | 1.5 (*R*) | 94 |
| 387 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**110**]$ClO_4$ dimer | 1.48 | – | 80 | 24 | 100 | 4 | 100 [b] | 2.1 (*R*) | 94 |
| 388 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**110**]$ClO_4$ dimer | 1.48 | – | –15 to –20 | 7 | 92 | 13 | 92 [b] | 12.1 (*R*) | 94 |
| 389 | Ph | $CO_2H$ | NHAc | [Rh(NBD)**110**]$ClO_4$ dimer | 1.48 | – | –15 to –20 | 7 | 18.6 | 3 | 93 [b] | 9.5 (*R*) | 94 |
| 390 | Ph | $CO_2H$ | NHAc | $[RhCl(COD)]_2$ + **165** + $Et_3N$ | 1 | EtOH : PhH =1 : 1 | r.t. | 48 | 100 | 2 | 100 | 4.7 (*R*) [a] | 119 |
| 391 | Ph | $CO_2H$ | NHBz | [Rh(COD)**95**]$BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 89.2 (*S*) | 85 |
| 392 | Ph | $CO_2H$ | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.0333 | 50 | 1500 | 50 | 95.0 (*S*) | 91 b |
| 393 | Ph | $CO_2H$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 [f] | 50 | 1000 | 50 | 93.7 (*S*) | 91 b |
| 394 | Ph | $CO_2H$ | NHBz | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.117 [f] | 50 | 429 | 50 | 96 (*S*) | 26 |
| 395 | Ph | $CO_2H$ | NHBz | [Rh(COD)**98a**]$BF_4$ | 50 | MeOH | 25 | | 100 [b] | | | 95 (*S*) | 26 |
| 396 | Ph | $CO_2H$ | NHBz | [Rh(COD)**128**]Cl | 10 | MeOH | r.t. | 1 | 110 | 110 | 100 | 44 (*S*) | 106 |
| 397 | Ph | $CO_2H$ | NHBz | [Rh(COD)**129**]Cl | 51 | MeOH | r.t. | 1 | 100 | 100 | 100 | 17 (*R*) | 106 |
| 398 | Ph | $CO_2H$ | NHBz | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 399 | Ph | $CO_2H$ | NHBz | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 400 | Ph | $CO_2Me$ | NHAc | [Rh(1,5-hexadiene)d-*trans*-**86**]Cl | 50 | – | 50 | – | – | – | – | 43 (*S*) [a] | 68 a |
| 401 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**88**]Cl | 69 | PhH : EtOH =1 : 1 | 100 | 48 | 50 [c] | – | [d] | 10.3 | 81 |
| 402 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 95.7 (*R*) | 27 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 403 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**93a**]$BF_4$ | 6.9 | DCM | r.t. | 0.17 | 428 | 2518 | 85.5 | 64 (*S*) | 52 |
| 404 | Ph | $CO_2Me$ | NHAc | [Rh(COE)**93a**]Cl | 97 | Tol/acetone 1:1 | 0 | 24 | 20.5 | 0.9 | 41 [b] | 76 [a] | 71 |
| 405 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**94a**]$BF_4$ | 6.9 | DCM | r.t. | 0.17 | 500 | 2941 | 100 | 84 (*S*) | 52 |
| 406 | Ph | $CO_2Me$ | NHAc | $[Rh(COD)Cl]_2$ + **97a** (cationic) | 1 | PhH | 25 | 0.117 [f] | 50 | 429 | 50 | 6 (*S*) [a] | 26 |
| 407 | Ph | $CO_2Me$ | NHAc | $[Rh(COD)Cl]_2$ + **97a** (neutral) | 1 | EtOH | 25 | 5.17 [f] | 50 | 10 | 50 | 63 (*S*) [a] | 26 |
| 408 | Ph | $CO_2Me$ | NHAc | $[Rh(COD)Cl]_2$ + **97a** (neutral) | 1 | PhH | 25 | >83.3 [f] | 50 | 0.6 | 50 | 14 (*S*) [a] | 26 |
| 409 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.113 [f] | 50 | 441 | 50 | 72.2 (*S*) | 26 |
| 410 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | –21.3 | – | – | – | – | 82.3 (*S*) | 26 |
| 411 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 0.5 | – | – | – | – | 77.8 (*S*) | 26 |
| 412 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | EtOH | 25 | 0.1 [f] | 50 | 500 | 50 | 73 (*S*) [a] | 26, 91 e |
| 413 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 73 (*S*) | 91 a |
| 414 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.1 [f] | 50 | 500 | 50 | 91.5 (*S*) | 91 b |
| 415 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.12 | 50 | 417 | 50 | 72 (*S*) | 91 e |
| 416 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | PhH | 25 | 0.08 | 50 | 625 | 50 | 6 (*R*) | 91 e |
| 417 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]Cl | 50 | – | 25 | 8 | 100 [c] | – | – | 8 (*S*) [a] | 89 |
| 418 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$ClO_4$ | 1 | EtOH | 25 | – | 50 | – | 100 | 60( *S*) | 90 |
| 419 | Ph | $CO_2Me$ | NHAc | [Rh(NBD)**97a**]$PF_6$ | 1 | EtOH | 30 | 0.5 | 100 | 200 | 100 [b] | 60 (*S*) | 88 |
| 420 | Ph | $CO_2Me$ | NHAc | [Rh(NBD)**97a**]$PF_6$ | 1 | EtOH | 0 | 3 | 100 | 33 | 100 | 65 (*S*) | 88 |
| 421 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $LiBF_4$ | 25 | 0.033 | 50 | 1500 | 50 | 45 (S) | 99 |
| 422 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $NaBF_4$ | 25 | 0.017 | 50 | 3000 | 50 | 41 (S) | 99 |
| 423 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $KBF_4$ | 25 | 0.017 | 50 | 3000 | 50 | 41 (S) | 99 |
| 424 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $RbBF_4$ | 25 | 0.033 | 50 | 1500 | 50 | 41 (S) | 99 |
| 425 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ + 0.1 mmol $CsBF_4$ | 25 | 0.033 | 50 | 1500 | 50 | 41 (S) | 99 |

Table 27.5 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | $P[H_2]$ [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 426 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97b**]$BF_4$ | 1 | $H_2O$ | 25 | 0.033 | 50 | 1500 | 50 | 41 (S) | 99 |
| 427 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97b**]Cl | 50 | – | 25 | 8 | 100 [c] | – | – | 10 (*S*) [a] | 89 |
| 428 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.58 | 50 | 86 | 50 | 61 (*S*) | 91a |
| 429 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH + Triton X-100 | 25 | 0.07 | 50 | 714 | 50 | 87 (*S*) | 91a |
| 430 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH + Tween 20 | 25 | 0.12 | 50 | 417 | 50 | 86 (*S*) | 91a |
| 431 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH + Tween 40 | 25 | 0.1 | 50 | 500 | 50 | 86 (*S*) | 91a |
| 432 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH + Tween 60 | 25 | 0.12 | 50 | 417 | 50 | 85 (*S*) | 91a |
| 433 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH + Tween 80 | 25 | 0.13 | 50 | 385 | 50 | 87 (*S*) | 91a |
| 434 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH + Brij 56 | 25 | 0.1 | 50 | 500 | 50 | 83 (*S*) | 91a |
| 435 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH + Brij 58 | 25 | 0.08 | 50 | 625 | 50 | 85 (*S*) | 91a |
| 436 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH + Brij 76 | 25 | 0.12 | 50 | 417 | 50 | 83 (*S*) | 91a |
| 437 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH + Brij 78 | 25 | 0.1 | 50 | 500 | 50 | 82 (*S*) | 91a |
| 438 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 [f] | 50 | 1000 | 50 | 94.8 (*S*) | 91b |
| 439 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97d**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 17.2 (*S*) | 26 |
| 440 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**97d**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 63 (*S*) | 91a |
| 441 | Ph | $CO_2Me$ | NHAc | $[Rh(COD)Cl]_2$ + **98a** (cationic) | 1 | PhH | 25 | 0.117 [f] | 50 | 429 | 50 | 69 (*S*) [a] | 26 |
| 442 | Ph | $CO_2Me$ | NHAc | $[Rh(COD)Cl]_2$ + **98a** (neutral) | 1 | EtOH | 25 | 10.7 [f] | 50 | 4.69 | 50 | 79 (*S*) [a] | 26 |
| 443 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | EtOH | 25 | 0.117 [f] | 50 | 429 | 50 | 89 (*S*) [a] | 26 |
| 444 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.103 [f] | 50 | 484 | 50 | 91.1 (*S*) | 26 |
| 445 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 100 | MeOH | 25 | 0.00083 [f] | 50 | 60241 | 50 | 91.5 (*S*) | 26 |
| 446 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | –20 | – | – | – | – | 95.4 (*S*) | 26 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 447 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | –5.2 | – | – | – | – | 93.9 (*S*) | 26 |
| 448 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 10.1 | – | – | – | – | 93.2 (*S*) | 26 |
| 449 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 90.5 (*S*) | 26 |
| 450 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 40.6 | – | – | – | – | 88.0 (*S*) | 26 |
| 451 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 54.6 | – | – | – | – | 86.2 (*S*) | 26 |
| 452 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 91 (*S*) | 91a |
| 453 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.1[f] | 50 | 500 | 50 | 91.5 (*S*) | 91e |
| 454 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | $ClCH_2CH_2Cl$ | 25 | 0.08 | 50 | 625 | 50 | 90 (*S*) | 91e |
| 455 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | $CH_2Cl_2$ | 25 | 0.17 | 50 | 294 | 50 | 89 (*S*) | 91e |
| 456 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | *o*-Xylene | 25 | 0.03 | 50 | 1667 | 50 | 83 (*S*) | 91e |
| 457 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | *m*-Xylene | 25 | 0.08 | 50 | 625 | 50 | 85 (*S*) | 91e |
| 458 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | *p*-Xylene | 25 | 0.13 | 50 | 385 | 50 | 81 (*S*) | 91e |
| 459 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | EtOH | 25 | 0.083[f] | 50 | 600 | 50 | 89 (*S*) | 91e |
| 460 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | THF | 25 | 0.067[f] | 50 | 750 | 50 | 86.1 (*S*) | 91e |
| 461 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | PhH | 25 | 0.117[f] | 50 | 429 | 50 | 81.0 (*S*) | 91e |
| 462 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | Tol | 25 | 0.1[f] | 50 | 500 | 50 | 81.0 (*S*) | 91e |
| 463 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 84.7 | 95b |
| 464 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 90.2 | 95b |
| 465 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 94.4 | 95b |
| 466 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.4 | 95b |
| 467 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98c**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 6.2 | 95b |
| 468 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 2.0 | 95b |
| 469 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98d**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 7.2 | 95b |
| 470 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98e**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 9.8 | 95b |
| 471 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98e**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 2.0 | 95b |
| 472 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 98.2 | 95b |
| 473 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 99.0 | 95b |
| 474 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98h**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 81.0 | 95b |
| 475 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98i**]$BF_4$ | 1 | MeOH | 25 | 0.0567[f] | 50 | 882 | 50 | 95 (*S*) | 97 |
| 476 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98i**]$BF_4$ | 1 | $H_2O$ | 25 | 6[f] | 50 | 8 | 50 | 84 (*S*) | 97 |
| 477 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98i**]$BF_4$ | 1 | $H_2O$+SDS, 0.035[g] | 25 | 1.1[f] | 50 | 45 | 50 | 94 (*S*) | 97 |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 478 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98i**]$BF_4$ | 1 | $H_2O$+SDS, 0.173 [g] | 25 | 0.11 [f] | 50 | 469 | 50 | 97 (*S*) | 97 |
| 479 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98i**]$BF_4$ | 1 | $H_2O$+Triton X-100, 0.03 [g] | 25 | 1.083 [f] | 50 | 46 | 50 | 95 (*S*) | 97 |
| 480 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**98i**]$BF_4$ | 1 | $H_2O$+Triton X-100, 0.1 [g] | 25 | 0.33 [f] | 50 | 150 | 50 | 95 (*S*) | 97 |
| 481 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**100**]Cl | 50 | – | 25 | 8 | 100 [c] | – | – | 10 (*S*) [a] | 89 |
| 482 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**100b**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 89 (*S*) | 91 a |
| 483 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**100b**]$BF_4$ | 1 | MeOH | 25 | – | 50 | – | 50 | 80 (*S*) | 91 e |
| 484 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**101a**]$BF_4$ | 1 | MeOH | 25 | 0.09 [f] | 50 | 555 | 50 | 91.1 (*S*) | 91 e |
| 485 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**101b**]$BF_4$ | 1 | MeOH | 25 | 0.093 [f] | 50 | 536 | 50 | 91.8 (*S*) | 91 c |
| 486 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**101c**]$BF_4$ | 1 | MeOH | 25 | 0.11 [f] | 50 | 469 | 50 | 89.2 (*S*) | 91 c |
| 487 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**101d**]$BF_4$ | 1 | MeOH | 25 | 0.15 [f] | 50 | 345 | 50 | 90.8 (*S*) | 91 c |
| 488 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**101e**]$BF_4$ | 1 | MeOH | 25 | 0.12 [f] | 50 | 407 | 50 | 89.3 (*S*) | 91 c |
| 489 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**101 f**]$BF_4$ | 1 | MeOH | 25 | 0.14 [f] | 50 | 361 | 50 | 83.8 (*S*) | 91 c |
| 490 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**102a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 98.3 | 95 b |
| 491 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**102a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 98.4 | 95 b |
| 492 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**102b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 94.9 | 95 b |
| 493 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 93.0 | 95 b |
| 494 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.3 | 95 b |
| 495 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**103b**]$BF_4$ | 2–2.8 | THF | r.t. | – | – | – | – | 71.1 | 95 a |
| 496 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**103b**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 87.4 | 95 b |
| 497 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**103c**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 1.0 | 95 a, b |
| 498 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**103d**]$BF_4$ | 2–2.8 | THF | r.t. | – | – | – | – | 2.3 | 95 a, b |
| 499 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**103e**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 2.0 | 95 a, b |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 500 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**103f**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 84.7 | 95 a, b |
| 501 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**104a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 92.4 | 95 b |
| 502 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**104b**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 84.0 | 95 b |
| 503 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**104d**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 11.0 | 95 b |
| 504 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**105a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 65.1 | 95 a, b |
| 505 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**106a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 83.2 | 95 b |
| 506 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**111**]$ClO_4$ | 1 | EtOH | 25 | 24 | 50 | 2 | 100 | 52 (*R*) | 90 |
| 507 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**112a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 72.2 | 95 b |
| 508 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**112b**]$BF_4$ | 1 | MeOH | 25 | 0.07 | 50 | 714 | 50 | 1.5 (*S*) | 91 e |
| 509 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**113a**]Cl | 50 | – | 25 | 8 | 100 [c] | – | – | 46 (*S*) [a] | 89 |
| 510 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**113b**]Cl | 50 | – | 25 | 8 | 100 [c] | – | – | 20 (*S*) [a] | 89 |
| 511 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**113c**]$BF_4$ | 1 | MeOH | 25 | 0.07 | 50 | 714 | 50 | 66 (*S*) | 91 a, e |
| 512 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**113c**]$BF_4$ | 1 | MeOH | 25 | 0.067 | 50 | 750 | 50 | 66 (*S*) | 91 e |
| 513 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**113d**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 77 (*S*) | 91 a |
| 514 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**113d**]$BF_4$ | 1 | MeOH | 25 | 0.13 | 50 | 750 | 50 | 83 (*S*) | 91 e |
| 515 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**113e**]$BF_4$ | 1 | MeOH | 25 | 0.13 | 50 | 385 | 50 | 83 (*S*) | 91 a, e |
| 516 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**113f**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 59 (*S*) | 91 a |
| 517 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**114a**]$BF_4$ | 1 | MeOH | 25 | 0.083 [f] | 50 | 602 | 50 | 57 (*S*) | 99 |
| 518 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**114a**]$BF_4$ | 1 | PhH | 25 | 0.05 [f] | 50 | 1000 | 50 | 43 (*S*) | 99 |
| 519 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | MeOH | 25 | 0.05 [f] | 50 | 1000 | 50 | 53 (*S*) | 99 |
| 520 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**114b**]$BF_4$ | 1 | PhH | 25 | 0.033 [f] | 50 | 1515 | 50 | 41 (*S*) | 99 |
| 521 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**116a**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | – | 35 (*R*) | 102 |
| 522 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**116b**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | – | 30 (*R*) | 102 |
| 523 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$ | r.t. | 6 | 20 | 3 | 100 | 88 (*S*) | 101 |
| 524 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$ + 10 wt% SDS | r.t. | 1 | 100 | 100 | 100 | 99.9 (*S*) [b] | 101 |
| 525 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/EtOAc (1 : 1) | r.t. | 1.5 | 50 | 33 | 100 | 87 (*S*) | 101 |
| 526 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/MeOH/ EtOAc (0.6 : 0.4 : 1) | r.t. | 3 | 100 | 33 | 100 | 98 (*S*) | 101 |
| 527 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/MeOH (3 : 2) | r.t. | 1.5 | 100 | 67 | 100 | 94 (*S*) | 101 |
| 528 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**118**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | – | 25 (*R*) | 102 |
| 529 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**119a**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | ~100 | 69 (*S*) | 102 |

Table 27.5 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 530 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**119b**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | ~100 | 87 (*S*) | 102 |
| 531 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**119c**]$BF_4$ | 5 | $H_2O$/EtOAc (1:1) | r.t. | 1.5 | 50 | 33 | 100 | 68 (*S*) | 101 |
| 532 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**119c**]$BF_4$ | 5 | $H_2O$/MeOH/EtOAc (0.6:0.4:1) | r.t. | 3 | 100 | 33 | 100 | 76 (*S*) | 101 |
| 533 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**119c**]$BF_4$ | 5 | $H_2O$/MeOH (3:2) | r.t. | 1.5 | 100 | 67 | 100 | 75 (*S*) | 101 |
| 534 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**119d**]$BF_4$ | 5 | $H_2O$ | r.t. | 6 | 20 | 3 | 100 | 55 (*S*) | 101 |
| 535 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**119d**]$BF_4$ | 5 | $H_2O$ + 10 wt% SDS | r.t. | 1 | 100 | 100 | 100 | 90 (*S*) [b] | 101 |
| 536 | Ph | $CO_2Me$ | NHAc | [Rh(COD)ent-**120**]$BF_4$ | 1 | Acetone | r.t. | 0.08 | 100 | 1250 | 100 | 27 (*R*) | 105 |
| 537 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**121a**]$BF_4$ | 1 | Acetone | r.t. | 0.08 | 100 | 1250 | 100 | 18 (*R*) | 105 |
| 538 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**121b**]$BF_4$ | 1 | Acetone | r.t. | 0.08 | 100 | 1250 | 100 | 59 (*R*) | 105 |
| 539 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**121d**]$BF_4$ | 1 | Acetone | r.t. | 0.08 | 100 | 1250 | 100 | 32 (*R*) | 105 |
| 540 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**122a**]$BF_4$ | 1 | Acetone | r.t. | 0.08 | 95 | 1188 | 95 | 73 (*R*) | 105 |
| 541 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**122b**]$BF_4$ | 1 | Acetone/DCM 13:2 | r.t. | 0.08 | 96 | 1200 | 96 | 81 (*R*) | 105 |
| 542 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**122c**]$BF_4$ | 1 | Acetone | r.t. | 0.08 | 100 | 1250 | 100 | 77 (*R*) | 105 |
| 543 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**122d**]$BF_4$ | 1 | Acetone/DCM 13:2 | r.t. | 0.08 | 100 | 1250 | 100 | 75 (*R*) | 105 |
| 544 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**122e**]$BF_4$ | 1 | Acetone | r.t. | 0.08 | 100 | 1250 | 100 | 86 (*R*) | 105 |
| 545 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**123b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 49.0 | 95b |
| 546 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**124**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 24 (*R*) | 103 |
| 547 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**124**]Cl | 68 | PhH:EtOH = 1:1 | 100 | 48 | 100 | 2.1 | 100 | 3.4 (*R*) | 103 |
| 548 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**125**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 35 (*S*) | 103 |
| 549 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**126**]$BF_4$ | 1 | DCM | 25 | 0.02 | 100 | 5000 | 100 | 10 (*R*) | 104 |
| 550 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**126**]Cl | 50 | – | 25 | 1 | 100 [c] | 100 | 100 | 48 (*R*) [a] | 89 |
| 551 | Ph | $CO_2Me$ | NHAc | [Ir(COD)**126**]$BF_4$ | 1 | DCM | 25 | 0.42 | 100 | 238 | 100 | 20 (*R*) | 104 |
| 552 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**127**]$BF_4$ | 1 | DCM | 25 | 0.02 | 100 | 5000 | 100 | 35 (*R*) | 104 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 553 | Ph | $CO_2Me$ | NHAc | [Ir(COD)**127**]$BF_4$ | 1 | DCM | 25 | 0.75 | 100 | 133 | 100 | 10 (*R*) | 104 |
| 554 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**131**]$BF_4$ | 1 | PhH | 25 | 5.5 | 99.9 | 18 | 99.9 | 31.5 (*R*) | 108 |
| 555 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 91.6 (*R*) | 107 |
| 556 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | MeOH | 25 | 0.25 | 100 | 400 | 100 | 84 (*R*) | 107 |
| 557 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | IPA | 25 | 0.25 | 100 | 400 | 100 | 89.4 (*R*) | 107 |
| 558 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | THF | 25 | 0.25 | 100 | 400 | 100 | 86.3 (*R*) | 107 |
| 559 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | DCM | 25 | 0.25 | 100 | 400 | 100 | 86.2 (*R*) | 107 |
| 560 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | PhH | 25 | 0.25 | 100 | 400 | 100 | 82.9 (*R*) | 107 |
| 561 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**134**]$BF_4$ | 1 | PhH | 25 | 4.5 | 92.5 | 21 | 92.5 | 24.6 (*R*) | 108 |
| 562 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**135**]$BF_4$ | 1 | PhH | 25 | 7.5 | 96.6 | 13 | 96.6 | 46.2 (*R*) | 108 |
| 563 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**136**]$BF_4$ | 1.5 | MeOH | 25 | 20 | 388 | 19 | 81 | 19 (*R*) | 110 |
| 564 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**139**]$BF_4$ | 1.2 | MeOH | – | | 100 | – | 100 | 54 | 113 |
| 565 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**139**]$BF_4$ | 5 | MeOH | – | 2 | 94 | 47 | 94 | 47 | 113 |
| 566 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**140**]$BF_4$ | 1.5 | DCM | 25 | 20 | 479 | 24 | 100 | 14 (*R*) | 110 |
| 567 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**141a**]$BF_4$ | 3.5 | MeOH | r.t. | 0.5 | 1000 | 2000 | >99 | 95 (*S*) | 111 |
| 568 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**141a**]$BF_4$ | 5 | MeOH | r.t. | 2 | 5000 | 2500 | >99 | 95 (*S*) | 111 |
| 569 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**141b**]$BF_4$ | 3.5 | MeOH | r.t. | 0.5 | 980 | 1960 | 98 | 97 (*S*) | 111 |
| 570 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**141b**]$BF_4$ | 3.5 | Tol | r.t. | 2 | 1000 | 500 | >99 | 99 (*S*) | 111 |
| 571 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**141b**]$BF_4$ | 5 | MeOH | r.t. | 6 | 5000 | 833 | >99 | 98.5 (*S*) | 111 |
| 572 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**144a**]$BF_4$ | 5 | DCM | 25 | 8 | 96 | 12 | 96 | 91 (*S*) | 117 b |
| 573 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**144c**]$BF_4$ | 5 | DCM | 25 | 6 | 100 | 16.7 | 100 | 98 (*S*) | 117 b |
| 574 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**144c**]$BF_4$ | 30 | DCM | 5 | 4 | 1000 | 250 | 100 | >99 (*S*) | 117 b |
| 575 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**145a**]$BF_4$ | 5 | DCM | 25 | 8 | 100 | 12.5 | 100 | 2 (*S*) | 117 b |
| 576 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**146a**]$BF_4$ | 5 | DCM | 25 | 8 | 98 | 12.3 | 98 | 70 (*S*) | 117 b |
| 577 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**146c**]$BF_4$ | 5 | DCM | 25 | 8 | 96 | 12 | 96 | 32 (*S*) | 117 b |
| 578 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**147**]$BF_4$ | 1 | THF | 25 | – | – | – | – | 13 | 115 |
| 579 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**150a**]$BF_4$ | 1 | DCM | 25 | 2.2 | 100 | 45.5 | 100 | 30 (*S*) | 118 |
| 580 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**150b**]$BF_4$ | 1 | DCM | 25 | 3.3 | 100 | 30.3 | 100 | 18 (*R*) | 118 |
| 581 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**150c**]$BF_4$ | 1 | DCM | 25 | 4.3 | 100 | 23.3 | 100 | 30 (*R*) | 118 |
| 582 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**150d**]$BF_4$ | 1 | DCM | 25 | 3 | 100 | 33.3 | 100 | 48 (*S*) | 118 |

Table 27.5 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 583 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**154a**]OTf | 5 | MeOH | r.t. | 18 | 200 | 11.1 | 100 | 81 (*S*) | 127 |
| 584 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**154a**]OTf | 5 | Tol | r.t. | 18 | 200 | 11.1 | 100 | 85 (*S*) | 127 |
| 585 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**154b**]OTf | 5 | Tol | r.t. | 18 | 200 | 11.1 | 100 | 89 (*S*) | 127 |
| 586 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**154c**]OTf | 5 | Tol | r.t. | 18 | 200 | 11.1 | 100 | 50 (*R*) | 127 |
| 587 | Ph | $CO_2Me$ | NHAc | [Rh(COD)(*S*,*S*ax)-**155b**] $BF_4$ | 4.1 | DCM | r.t. | 24 | 450 | 18.8 | 90 | 70.3 (*R*) | 124 a |
| 588 | Ph | $CO_2Me$ | NHAc | [Rh(COD) (*S*,*R*ax)-**155b**]B $F_4$ | 4.1 | DCM | r.t. | 24 | 500 | 18.8 | 100 | 99.0 (*S*) | 124 a |
| 589 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**155c**]$BF_4$ | 4.1 | DCM | r.t. | 24 | 225 | 9.4 | 45 | 22.0 (*S*) | 124 a |
| 590 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**156a**]$BF_4$ | 4.1 | DCM | r.t. | 16 | 500 | 31.3 | 100 | 99.5 (*R*) | 124 a |
| 591 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**156b**]$BF_4$ | 4.1 | DCM | r.t. | 16 | 500 | 31.3 | 100 | 56.1 (*R*) | 124 a |
| 592 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**156c**]$BF_4$ | 4.1 | DCM | r.t. | 16 | 100 | 6.3 | 20 | 90.6 (*R*) | 124 a |
| 593 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**159a**]$BF_4$ | 1 | DCM | r.t. | 24 | 100 | 4.2 | 100 | 97 (*R*) | 123 |
| 594 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**159b**]$BF_4$ | 1 | DCM | r.t. | 24 | 100 | 4.2 | 100 | 92 (*S*) | 123 |
| 595 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**159c**]$BF_4$ | 1 | DCM | r.t. | 24 | 50 | 2.1 | 100 | 6 (*S*) | 123 |
| 596 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**159d**]$BF_4$ | 1 | DCM | r.t. | 12 | 100 | 8.3 | 100 | 95 (*S*) | 123 |
| 597 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**159e**]$BF_4$ | 1 | DCM | r.t. | 12 | 100 | 8.3 | 100 | 95 (*R*) | 123 |
| 598 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**159f**]$BF_4$ | 1 | DCM | r.t. | 12 | 50 | 4.2 | 100 | 3 (*R*) | 123 |
| 599 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**159g**]$BF_4$ | 1 | DCM | r.t. | 12 | 50 | 4.2 | 100 | 89 (*S*) | 123 |
| 600 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**159h**]$BF_4$ | 1 | DCM | r.t. | 24 | 85 | 3.5 | 85 | 63 (*R*) | 123 |
| 601 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**160a**]$BF_4$ | 1 | DCM | r.t. | 12 | 50 | 4.2 | 100 | 65 (*S*) | 123 |
| 602 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**160b**]$BF_4$ | 1 | DCM | r.t. | 1 | 50 | 50 | 100 | 95 (*R*) | 123 |
| 603 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 604 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 605 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**166**]$BF_4$ | 1 | DCM | r.t. | 1 | 100 | 100 | 100 | 37 (*R*) | 129 |
| 606 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**166**]$BF_4$ | 1 | DCE | r.t. | 0.5 | 100 | 200 | 100 | 69 (*R*) | 129 |
| 607 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**166**]$BF_4$ | 50 | DCE | r.t. | 2 | 88 | 44 | 88 | 33 (*R*) | 129 |
| 608 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**166**]$BF_4$ | 30 | $H_2O$ | r.t. | 24 | 40 | 1.7 | 100 | 13 (*R*) | 129 |
| 609 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**166**]$BF_4$ | 50 | $H_2O$ | r.t. | 24 | 40 | 1.7 | 100 | 72 (*R*) | 129 |
| 610 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**166**]$BF_4$ | 70 | $H_2O$ | r.t. | 24 | 40 | 1.7 | 100 | 62 (*R*) | 129 |
| 611 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**166**]$BF_4$ | 50 | MeOH | r.t. | 9 | 50 | 5.6 | 100 | 50 (*R*) | 129 |
| 612 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**166**]$BF_4$ | 50 | $H_2O$/EtOAc (1:1) | r.t. | 12(24) [h] | 50 | 4.2 | 100 (100) [i] | 73 (70) [i] (*R*) | 129 |
| 613 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**167a**]$BF_4$ | 1 | DCM | 25 | 0.17 | 100 | 588 | 100 | 84.1 (*S*) | 121 a, b |
| 614 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**167b**]$BF_4$ | 1 | DCM | 25 | 3 | 100 | 33 | 100 | 98.8 (*R*) | 121 a, b |
| 615 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**167c**]$BF_4$ | 1 | DCM | r.t. | 0.5 | 100 | 200 | 100 | 98.0 (*S*) | 121 a |
| 616 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**167c**]$BF_4$ | 1 | DCM | 25 | 0.5 | 100 | 200 | 100 | 91 (*S*) | 121 b |
| 617 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**167d**]$BF_4$ | 1 | DCM | r.t. | 0.5 | 100 | 200 | 100 | 94.3 (*R*) | 121 a, b |
| 618 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**168a**]$BF_4$ | 5 | DCM | 25 | 8 | 77 | 6 | 77 | 94 (*S*) | 126 |
| 619 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**168a**]$BF_4$ | 30 | DCM | 25 | 12 | 72 | 6 | 72 | 98 (*S*) | 126 |
| 620 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**168b**]$BF_4$ | 5 | DCM | 25 | 8 | 53 | 7 | 53 | 85 (*S*) | 126 |
| 621 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**168c**]$BF_4$ | 5 | DCM | 25 | 8 | 29 | 4 | 29 | 18 (*S*) | 126 |
| 622 | Ph | $CO_2Me$ | NHAc | [Rh(COD)**168d**]$BF_4$ | 5 | DCM | 25 | 8 | 35 | 4 | 35 | 17 (*S*) | 126 |
| 623 | Ph | $CO_2Me$ | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.1 [f] | 50 | 500 | 50 | 87.3 (*S*) | 91 b |
| 624 | Ph | $CO_2Me$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 [f] | 50 | 1000 | 50 | 91.6 (*S*) | 91 b |
| 625 | Ph | $CO_2Me$ | NHBz | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.117 [f] | 50 | 429 | 50 | 77 (*S*) | 26 |
| 626 | Ph | $CO_2Me$ | NHBz | [Rh(COD)**98a**]$BF_4$ | 50 | MeOH | 25 | – | 100 [b] | – | – | 77 (*S*) | 26 |
| 627 | Ph | $CO_2Me$ | NHBz | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/MeOH/ EtOAc (0.6:0.4:1) | r.t. | 3 | 100 | 33 | 100 | 92 (*S*) | 101 |
| 628 | Ph | $CO_2Me$ | NHBz | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/MeOH(3:2) | r.t. | 1.5 | 100 | 67 | 100 | 90 (*S*) | 101 |
| 629 | Ph | $CO_2Me$ | NHBz | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 630 | Ph | $CO_2Me$ | NHBz | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 631 | Ph | $CO_2Me$ | NHCbz | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | – | – | – | – | 57 (*S*) [a] | 10 |
| 632 | Ph | $CO_2Et$ | NHAc | [Rh(COD)**89**]$PF_6$ | 5 | EtOH | 60 | 7 | 90 | 13 | 90 | 7 (*S*) | 82 |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 633 | Ph | $CO_2Et$ | NHAc | [Rh(COD)**90**]$PF_6$ | 5 | EtOH | 60 | 3 | 85 | 28 | 85 | 12 (*S*) | 82 |
| 634 | Ph | $CO_2Et$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.27 [f)] | 50 | 187 | 50 | 58.3 | 26 |
| 635 | Ph | $CO_2Et$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.1 [f)] | 50 | 500 | 50 | 90.6 (*S*) | 91 b |
| 636 | Ph | $CO_2Et$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 [f)] | 50 | 1000 | 50 | 94.4 (*S*) | 91 b |
| 637 | Ph | $CO_2Et$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.08 [f)] | 50 | 625 | 50 | 90.2 | 26 |
| 638 | 2-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 97.3 (*R*) | 27 |
| 639 | 2-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**95**] $BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 92.9 (*S*) | 85 |
| 640 | 2-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25–1 | 100 | 100–400 | 100 | 92.3 (*R*) | 107 |
| 641 | 2-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 642 | 2-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 643 | 2-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)**94a**]$BF_4$ | 6.9 | DCM | r.t. | 0.17 | 500 | 2941 | 100 | 85 (*S*) | 52 |
| 644 | 2-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)**93h**]$PF_6$ | 3 | Tol | r.t. | 12 | 100 | 8.3 | 100 | 81.5 (*S*) | 79 |
| 645 | 2-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 646 | 2-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 647 | 3-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 97.4 (*R*) | 27 |
| 648 | 3-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**93a**]$BF_4$ | 6.9 | MeOH | r.t. | 0.5 | 282 | 564 | 56.3 | 10.5 (*S*) | 52 |
| 649 | 3-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**94a**]$BF_4$ | 6.9 | MeOH | r.t. | 0.5 | 440 | 880 | 87.9 | 37 (*S*) | 52 |
| 650 | 3-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25–1 | 100 | 100–400 | 100 | 90.3 (*R*) | 107 |
| 651 | 3-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)**93a**]$BF_4$ | 6.9 | DCM | r.t. | 0.17 | 352 | 2071 | 70.3 | 54.7 (*S*) | 52 |
| 652 | 3-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)**94a**]$BF_4$ | 6.9 | DCM | r.t. | 0.17 | 500 | 2941 | 100 | 78.3 (*S*) | 52 |
| 653 | 3-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)**166**]$BF_4$ | 51 | $H_2O$/EtOAc (1:1) | r.t. | 24 | 50 | 2 | 100 | 67 (*R*) | 129 |
| 654 | 4-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 97.3 (*R*) | 27 |
| 655 | 4-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25–1 | 100 | 100–400 | 100 | 93.3 (*R*) | 107 |
| 656 | 4-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 0–5 | 0.25–1 | 100 | 100–400 | 100 | 94.6 (*R*) | 107 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 657 | 4-Cl-Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | –15 | 0.25–1 | 100 | 100–400 | 100 | 96.3 (*R*) | 107 |
| 658 | 4-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 94.2 (*R*) | 27 |
| 659 | 4-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)**94a**]$BF_4$ | 6.9 | DCM | r.t. | 0.17 | 500 | 2941 | 100 | 80.8 (*S*) | 52 |
| 660 | 4-Cl-Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 91.3 (*R*) | 107 |
| 661 | 3-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**95**] $BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 93.5 (*S*) | 85 |
| 662 | 3-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 89 (*S*) | 98 |
| 663 | 3-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**98b**]$BF_4$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 97 (*S*) | 98 |
| 664 | 3-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | – | – | – | – | 96.4 | 95 a |
| 665 | 3-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**115a**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 74 (*S*) | 98 |
| 666 | 3-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**115b**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 95 (*S*) | 98 |
| 667 | 3-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | THF | r.t. | – | 100 | – | 100 | 96 (*S*) | 98 |
| 668 | 3-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 669 | 3-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 670 | 3-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**93h**]$PF_6$ | 3 | Tol | r.t. | 12 | 100 | 8.3 | 100 | 92.6 (*S*) | 79 |
| 671 | 3-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 89.2 | 95 b |
| 672 | 3-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.8 | 95 b |
| 673 | 3-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.4 | 95 b |
| 674 | 3-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 675 | 3-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 676 | 4-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 98.0 | 95 b |
| 677 | 4-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**98c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | | | | 47.0 | 95 b |
| 678 | 4-Br-Ph | $CO_2H$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.4 | 95 b |
| 679 | 4-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 96.3 (*R*) | 27 |
| 680 | 4-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 91.2 (*R*) | 107 |
| 681 | 4-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**154a**]OTf | 5 | MeOH | r.t. | 18 | 200 | 11.1 | 100 | 82 (*S*) | 127 |
| 682 | 4-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**154a**]OTf | 5 | Tol | r.t. | 18 | 200 | 11.1 | 100 | 87 (*S*) | 127 |
| 683 | 4-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**154b**]OTf | 5 | Tol | r.t. | 18 | 200 | 11.1 | 100 | 87 (*S*) | 127 |
| 684 | 4-Br-Ph | $CO_2Me$ | NHAc | [Rh(COD)**154c**]OTf | 5 | Tol | r.t. | 18 | 196 | 10.9 | 98 | 29 (*R*) | 127 |
| 685 | 2-F-Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 89 (*S*) | 98 |
| 686 | 2-F-Ph | $CO_2H$ | NHAc | [Rh(COD)**98b**]$BF_4$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 97 (*S*) | 98 |
| 687 | 2-F-Ph | $CO_2H$ | NHAc | [Rh(COD)**115a**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 63 (*S*) | 98 |

Table 27.5 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 688 | 2-F-Ph | $CO_2H$ | NHAc | [Rh(COD)**115b**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 96 (*S*) | 98 |
| 689 | 2-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 89.1 | 95 b |
| 690 | 2-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.8 | 95 b |
| 691 | 2-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.8 | 95 b |
| 692 | 2-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 95.6 | 95 b |
| 693 | 2-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**115a**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 66 (*S*) | 98 |
| 694 | 3-F-Ph | $CO_2H$ | NHAc | [Rh(COD)**115d**]$BF_4$ | 2.8 | THF | r.t. | – | 100 | – | 100 | 95 (*S*) | 98 |
| 695 | 3-F-Ph | $CO_2H$ | NHAc | [Rh(COD)**115e**]$BF_4$ | 2.8 | THF | r.t. | – | 100 | – | 100 | 2 (*S*) | 98 |
| 696 | 3-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 88.9 | 95 b |
| 697 | 3-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.1 | 95 b |
| 698 | 3-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.3 | 95 b |
| 699 | 4-F-Ph | $CO_2H$ | NHAc | [Rh(COD)**95**] $BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 91.1 (*S*) | 85 |
| 700 | 4-F-Ph | $CO_2H$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.4 | 95 b |
| 701 | 4-F-Ph | $CO_2H$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | 99 | 8.3 | 100 | 99 (*S*) | 128 |
| 702 | 4-F-Ph | $CO_2H$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 703 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 95.5 (*R*) | 27 |
| 704 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**93h**]$PF_6$ | 3 | Tol | r.t. | 12 | 100 | 8.3 | 100 | 93.4 (*S*) | 79 |
| 705 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 84.0 | 95b |
| 706 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 85.0 | 95 a, b |
| 707 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.2 | 95 a, b |
| 708 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 13.0 | 95 a, b |
| 709 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 9.0 | 95 a, b |
| 710 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98 f**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 89.0 | 95 b |
| 711 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 98.7 | 95 b |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 712 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98h**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 81.0 | 95 b |
| 713 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**102a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.8 | 95 b |
| 714 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.2 | 95 b |
| 715 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 73.5 | 95 b |
| 716 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | <1 | 95 b |
| 717 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 11.0 | 95 b |
| 718 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103e**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | <1 | 95 b |
| 719 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103 f**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 87.0 | 95 b |
| 720 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**104a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 92.0 | 95 b |
| 721 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 91.2 (*R*) | 107 |
| 722 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | 99 | 8.3 | 100 | 99 (*S*) | 128 |
| 723 | 4-F-Ph | $CO_2Me$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 724 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 62.0 | 95 a, b |
| 725 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | – | – | – | – | 97 | 95 a |
| 726 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 95.7 | 95 b |
| 727 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**98c**]$SbF_6$ | 2–2.8 | THF | r.t. | – | – | – | – | <1 | 95 a |
| 728 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**98c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | <3 | 95 b |
| 729 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**98d**]$SbF_6$ | 2–2.8 | THF | r.t. | – | – | – | – | 54 | 95 a |
| 730 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**98d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | <5 | 95 b |
| 731 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**98 f**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 85.0 | 95 b |
| 732 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**102a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.0 | 95 b |
| 733 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 90.0 | 95 b |
| 734 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**123a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 56.8 | 95 b |
| 735 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**123b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 53.0 | 95 b |
| 736 | 4-F-Ph | $CO_2Me$ | NHCbz | [Rh(COD)**123 f**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 57.0 | 95 b |
| 737 | 4-$NO_2$-Ph | $CO_2H$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 97.0 (*R*) | 27 |
| 738 | 4-$NO_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 90.5 (*R*) | 107 |
| 739 | 4-HO-Ph | $CO_2H$ | NHAc | [Rh(1,5-hexadiene) (+)-*trans*-**85**]Cl | 50 | – | 15 | 24 | – | – | – | 48.5 (S) [a)] | 67 |
| 740 | 4-HO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 91.5 (*R*) | 107 |
| 741 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 91.0 | 95 a, b |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 742 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.0 | 95 a, b |
| 743 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**98c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 53.0 | 95 a, b |
| 744 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**98d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 5.0 | 95 a, b |
| 745 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 95.9 | 95 b |
| 746 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**103b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 73.4 | 95 b |
| 747 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**103c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | <1 | 95 b |
| 748 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**103d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 2.3 | 95 b |
| 749 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**103e**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 2.1 | 95 b |
| 750 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**103f**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 85.3 | 95 b |
| 751 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**104a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 93.1 | 95 b |
| 752 | 3-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25–1 | 100 | – | 100 | 93.2 (*R*) | 107 |
| 753 | 3-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 88.0 | 95 b |
| 754 | 3-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.8 | 95 b |
| 755 | 3-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 21.0 | 95 b |
| 756 | 3-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 98.8 | 95 b |
| 757 | 3-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**116a**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | – | 70 (*R*) | 1, 2 |
| 758 | 3-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**116b**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | – | 40 (*R*) | 102 |
| 759 | 3-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**119a**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | ~100 | 70 (*S*) | 102 |
| 760 | 3-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**119b**]$SbF_6$ | 2.07 | THF | r.t. | – | – | – | ~100 | 92 (*S*) | 102 |
| 761 | 4-MeO-Ph | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 93.2 (*S*) | 85 |
| 762 | 4-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 96.2 (*R*) | 27 |
| 763 | 4-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**93h**]$PF_6$ | 3 | Tol | r.t. | 12 | 100 | 8.3 | 100 | 87.2 (*S*) | 79 |
| 764 | 4-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**94f**]$BF_4$ | 7 | DCM | r.t. | 0.1 | 500 | 5000 | 100 | 96.8 (*S*) | 78 |
| 765 | 4-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**94f**]$BF_4$ | 1 | DCM | r.t. | 0.42 | 488 | 1162 | 97.5 | 98.6 (*S*) | 78 |
| 766 | 4-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/MeOH/EtOAc(0.6:0.4:1) | r.t. | 3 | 100 | 33 | 100 | 98 (*S*) | 101 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 767 | 4-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/MeOH (3 : 2) | r.t. | 3 | 100 | 33 | 100 | 98 (*S*) | 101 |
| 768 | 4-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 91.4 (*R*) | 107 |
| 769 | 4-MeO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**133a**]$BF_4$ | 1 | IPA | r.t. | 24 | 97 | 4 | 97 | 90 | 48 |
| 770 | 3-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)**93h**]$SbF_6$ | 3 | THF | r.t. | 12 | 100 | 8.3 | 100 | 96.3 (*S*) | 79 |
| 771 | 4-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 95.6 (*R*) | 27 |
| 772 | 4-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)**94a**]$BF_4$ | 6.9 | DCM | r.t. | 0.17 | 500 | 2941 | 100 | 83.5 (*S*) | 52 |
| 773 | 4-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)**94d**]$BF_4$ | 7 | DCM | r.t. | 0.42 | 500 | 1190 | 100 | 92.5 (*S*) | 78 |
| 774 | 4-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 90.6 (*R*) | 107 |
| 775 | 4-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)**154a**]OTf | 5 | MeOH | r.t. | 18 | 40 | 2.2 | 20 | 73 (*S*) | 127 |
| 776 | 4-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)**154a**]OTf | 5 | Tol | r.t. | 18 | 120 | 6.7 | 60 | 85 (*S*) | 127 |
| 777 | 4-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)**154b**]OTf | 5 | Tol | r.t. | 18 | 200 | 11.1 | 100 | 85 (*S*) | 127 |
| 778 | 4-Me-Ph | $CO_2Me$ | NHAc | [Rh(COD)**154c**]OTf | 5 | Tol | r.t. | 18 | 186 | 10.3 | 93 | 34 (*R*) | 127 |
| 779 | 4-Me-Ph | $CO_2Me$ | NHBz | [Rh(COD)**94a**]$BF_4$ | 6.9 | DCM | r.t. | 0.17 | 479 | 2818 | 95.7 | 80 (*S*) | 52 |
| 780 | 4-$CF_3$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**93h**]$SbF_6$ | 3 | THF | r.t. | 12 | 100 | 8.3 | 100 | 95.7 (*S*) | 79 |
| 781 | 4-$CF_3$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**94c**]$BF_4$ | 7 | DCM | r.t. | 0.83 | 409 | 493 | 81.8 | 48.7 (*S*) | 78 |
| 782 | 2-Naphthyl | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 91.4 (*S*) | 85 |
| 783 | 2-Naphthyl | $CO_2H$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 94.0 | 95 b |
| 784 | 2-Naphthyl | $CO_2H$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 98.0 | 95 b |
| 785 | 2-Naphthyl | $CO_2H$ | NHAc | [Rh(COD)**98c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 22.0 | 95 b |
| 786 | 2-Naphthyl | $CO_2H$ | NHAc | [Rh(COD)**98d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 26.6 | 95 b |
| 787 | 2-Naphthyl | $CO_2H$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | – | – | – | – | 96 | 95 a |
| 788 | 2-Naphthyl | $CO_2H$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 789 | 2-Naphthyl | $CO_2H$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 790 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**93h**]$PF_6$ | 3 | Tol | r.t. | 12 | 100 | 8.3 | 100 | 97.3 (*S*) | 79 |
| 791 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**93h**]$SbF_6$ | 3 | THF | r.t. | 12 | 100 | 8.3 | 100 | 94.1 (*S*) | 79 |
| 792 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 86.5 | 95 b |
| 793 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.1 | 95 b |
| 794 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**98d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 10.8 | 95 b |
| 795 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.0 | 95 b |
| 796 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**104a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 93.0 | 95 b |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 797 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/MeOH/EtOAc(0.6:0.4:1) | r.t. | 3 | 100 | 33 | 100 | 96 (*S*) | 101 |
| 798 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**117**]$BF_4$ | 5 | $H_2O$/MeOH (3:2) | r.t. | 3 | 100 | 33 | 100 | 95 (*S*) | 101 |
| 799 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 800 | 2-Naphthyl | $CO_2Me$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | >99 | 8.3 | 100 | >99 (*S*) | 128 |
| 801 | 3,5-$F_2$-Ph | $CO_2H$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | – | – | – | – | 96.2 | 95 a, b |
| 802 | 3,5-$F_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 88.3 | 95 b |
| 803 | 3,5-$F_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.0 | 95 b |
| 804 | 3,5-$F_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 98.4 | 95 b |
| 805 | 3,5-$F_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 73.0 | 95 b |
| 806 | 3,5-$F_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 3.0 | 95 b |
| 807 | 3,5-$F_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 5.6 | 95 b |
| 808 | 3,5-$F_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103e**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 2.7 | 95 b |
| 809 | 3,5-$F_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103f**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 85.1 | 95 b |
| 810 | 3,5-$Me_2$-P | $CO_2Me$ | NHAc | [Rh(COD)**93e**]$BF_4$ | 7 | DCM | r.t. | 0.42 | 500 | 1190 | 100 | 93.9 (*S*) | 78 |
| 811 | 3,5-$Me_2$-P | $CO_2Me$ | NHAc | [Rh(COD)**94e**]$BF_4$ | 7 | DCM | r.t. | 0.22 | 500 | 2273 | 100 | 95.4 (*S*) | 78 |
| 812 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**94b**]$BF_4$ | 7 | DCM | r.t. | 1.75 | 147 | 84 | 29.3 | 30.9 (*S*) | 78 |
| 813 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 95.8 | 95b |
| 814 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(NBD)**98b**]$SbF_6$ | 2.8 | THF | r.t. | 0.25 | 1000 | 4000 | 100 | 96.1 (*S*) | 95 b |
| 815 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 85.2 | 95 b |
| 816 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.1 | 95 b |
| 817 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.9 | 95 b |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 818 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**102a**]$BF_4$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 93.7 | 95 b |
| 819 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.4 | 95 b |
| 820 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 77.9 | 95 b |
| 821 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103c**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 3.2 | 95 b |
| 822 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | <1 | 95 b |
| 823 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103e**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | <1 | 95 b |
| 824 | 3,5-$(CF_3)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**103f**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 83.9 | 95 b |
| 825 | 3,4-$(MeO)_2$-Ph | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.1 [f] | 50 | 500 | 50 | 96.7 (*S*) | 91 b |
| 826 | 3,4-$(MeO)_2$-Ph | $CO_2H$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.083 [f] | 50 | 600 | 50 | 94.8 (*S*) | 91 b |
| 827 | 3,4-$(MeO)_2$-Ph | $CO_2H$ | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.083 [f] | 50 | 600 | 50 | 95.1 (*S*) | 91 b |
| 828 | 3,4-$(MeO)_2$-Ph | $CO_2H$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.067 [f] | 50 | 750 | 50 | 92.0 (*S*) | 91 b |
| 829 | 3,4-$(MeO)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.37 [f] | 50 | 136 | 50 | 92.4 (*S*) | 91 b |
| 830 | 3,4-$(MeO)_2$-Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.2 [f] | 50 | 250 | 50 | 95.7 (*S*) | 91 b |
| 831 | 3,4-$(MeO)_2$-Ph | $CO_2Me$ | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.13 [f] | 50 | 375 | 50 | 87.7 (*S*) | 91 b |
| 832 | 3,4-$(MeO)_2$-Ph | $CO_2Me$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.12 [f] | 50 | 429 | 50 | 91.2 (*S*) | 91 b |
| 833 | 3,4-$(MeO)_2$-Ph | $CO_2Et$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.13 [f] | 50 | 375 | 50 | 90.6 (*S*) | 91 b |
| 834 | 3,4-$(MeO)_2$-Ph | $CO_2Et$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.083 [f] | 50 | 600 | 50 | 95.2 (*S*) | 91 b |
| 835 | 3,4-$(MeO)_2$-Ph | $CO_2Et$ | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.17 [f] | 50 | 300 | 50 | 88.9 (*S*) | 91 b |
| 836 | 3,4-$(MeO)_2$-Ph | $CO_2Et$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.13 [f] | 50 | 375 | 50 | 90.5 (*S*) | 91 b |
| 837 | 3,4-$(MeO)_2$-Ph | $CO_2i$-Pr | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.37 [f] | 50 | 136 | 50 | 91.3 (*S*) | 91 b |
| 838 | 3,4-$(MeO)_2$-Ph | $CO_2i$-Pr | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.18 [f] | 50 | 273 | 50 | 94.7 (*S*) | 91 b |
| 839 | 3,4-$(MeO)_2$-Ph | $CO_2i$-Pr | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.33 [f] | 50 | 150 | 50 | 89.1 (*S*) | 91 b |
| 840 | 3,4-$(MeO)_2$-Ph | $CO_2i$-Pr | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.23 [f] | 50 | 214 | 50 | 92.7 (*S*) | 91 b |
| 841 | 3,4-$(MeO)_2$-Ph | $CO_2$-$C_2H_4OH$ | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.17 [f] | 50 | 300 | 50 | 87.3 (*S*) | 91 b |
| 842 | 3,4-$(MeO)_2$-Ph | $CO_2$-$C_2H_4OH$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.13 [f] | 50 | 375 | 50 | 89.9 (*S*) | 91 b |
| 843 | 3-MeO-4-HO-Ph | $CO_2H$ | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.067 [f] | 50 | 750 | 50 | 96.9 (*S*) | 91 b |
| 844 | 3-MeO-4-HO-Ph | $CO_2H$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.067 [f] | 50 | 750 | 50 | 94.1 (*S*) | 91 b |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 845 | 3-MeO-4-HO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.2 [f] | 50 | 250 | 50 | 91.7 (*S*) | 91b |
| 846 | 3-MeO-4-HO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.083 [f] | 50 | 600 | 50 | 95.0 (*S*) | 91b |
| 847 | 3-MeO-4-HO-Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 90.2 (*R*) | 107 |
| 848 | 3-MeO-4-HO-Ph | $CO_2Me$ | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.18 [f] | 50 | 273 | 50 | 89.0 (*S*) | 91b |
| 849 | 3-MeO-4-HO-Ph | $CO_2Me$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.1 [f] | 50 | 500 | 50 | 92.1 (*S*) | 91b |
| 850 | 3-MeO-4-HO-Ph | $CO_2C_2H_4OH$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.22 [f] | 50 | 231 | 50 | 91.7 (*S*) | 91b |
| 851 | 3-MeO-4-HO-Ph | $CO_2C_2H_4OH$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.12 [f] | 50 | 429 | 50 | 95.5 (*S*) | 91b |
| 852 | 3-MeO-4-HO-Ph | $CO_2C_2H_4OH$ | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.27 [f] | 50 | 188 | 50 | 88.4 (*S*) | 91b |
| 853 | 3-MeO-4-HO-Ph | $CO_2C_2H_4OH$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.2 [f] | 50 | 250 | 50 | 90.2 (*S*) | 91b |
| 854 | 3-MeO-4-AcOPh | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.095 [f] | 50 | 526 | 50 | 94 (*S*) | 26 |
| 855 | 3-MeO-4-AcOPh | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.08 [f] | 50 | 625 | 50 | 71 (*S*) | 26 |
| 856 | 3-MeO-4-AcOPh | $CO_2H$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.17 [f] | 50 | 300 | 50 | 96.0 (*S*) | 91b |
| 857 | 3-MeO-4-AcOPh | $CO_2H$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.15 [f] | 50 | 333 | 50 | 95.2 (*S*) | 91b |
| 858 | 3-MeO-4-OAcPh | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 95.0 (*S*) | 85 |
| 859 | 3-MeO-4-AcOPh | $CO_2H$ | NHAc | [Rh(COD)**124**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 36 (*R*) | 103 |
| 860 | 3-MeO-4-AcOPh | $CO_2H$ | NHAc | [Rh(COD)**125**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 65 (*S*) | 103 |
| 861 | 3-MeO-4-AcOPh | $CO_2Me$ | NHAc | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.083 [f] | 50 | 600 | 50 | 92.4 (*S*) | 91b |
| 862 | 3-MeO-4-AcOPh | $CO_2Me$ | NHAc | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 [f] | 50 | 1000 | 50 | 95.6 (*S*) | 91b |
| 863 | 3-MeO-4-AcOPh | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.15 [f] | 50 | 333 | 50 | 91 (*S*) | 26 |
| 864 | 3-MeO-4-AcOPh | $CO_2Me$ | NHBz | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.083 [f] | 50 | 600 | 50 | 87.2 (*S*) | 91b |
| 865 | 3-MeO-4-AcOPh | $CO_2Me$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.067 [f] | 50 | 750 | 50 | 91.3 (*S*) | 91b |
| 866 | 3-MeO-4-AcOPh | $CO_2Et$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 0.14 [f] | 50 | 353 | 50 | 87 (*S*) | 26 |
| 867 | 3-MeO-4-AcOPh | $CO_2Et$ | NHBz | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.083 [f] | 50 | 600 | 50 | 90.5 (*S*) | 91b |
| 868 | 3,4-($OCH_2O$)-Ph | $CO_2H$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25–1 | 100 | 100–400 | 100 | 94.2 (*R*) | 107 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 869 | 3,4-($OCH_2O$)-Ph | $CO_2Me$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 94.9 (*R*) | 27 |
| 870 | 3,4-($OCH_2O$)-Ph | $CO_2Me$ | NHAc | [Rh(COD)**132**]$BF_4$ | 34.5 | Acetone | 25 | 0.25 | 100 | 400 | 100 | 93.2 (*R*) | 107 |
| 871 | 4-Ph-Ph | $CO_2Me$ | NHAc | [Rh(COD)**93h**]$SbF_6$ | 3 | THF | r.t. | 12 | 100 | 8.3 | 100 | 94.2 (*S*) | 79 |
| 872 | 2-Furyl | $CO_2Me$ | NHAc | [Rh(COD)**91**]$BF_4$ | 1 | MeOH | 25 | 0.167 | 100 | 600 | >99.9 | 97.2 (*R*) | 27 |
| 873 | 2-Furyl | $CO_2Me$ | NHBz | [Rh(COD)**94a**]$BF_4$ | 6.9 | DCM | r.t. | 0.17 | 500 | 2941 | 100 | 63.9 (*S*) | 52 |
| 874 | Thiophen-2-yl | $CO_2H$ | NHAc | [Rh(COD)**95**]$BF_4$ | 1 | IPA | r.t. | 24 | 100 | 4 | 100 | 90.1 (*S*) | 85 |
| 875 | Thiophen-2-yl | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 85 (*S*) | 98 |
| 876 | Thiophen-2-yl | $CO_2H$ | NHAc | [Rh(COD)**98b**]$BF_4$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 96 (*S*) | 98 |
| 877 | Thiophen-2-yl | $CO_2H$ | NHAc | [Rh(COD)**115a**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 91 | 30 | 91 | 26 (*S*) | 98 |
| 878 | Thiophen-2-yl | $CO_2H$ | NHAc | [Rh(COD)**115b**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 28 | 9 | 28 | 80 (*S*) | 98 |
| 879 | Thiophen-2-yl | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 85.2 | 95 b |
| 880 | Thiophen-2-yl | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 95.6 | 95 b |
| 881 | Thiophen-2-yl | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.2 | 95 b |
| 882 | Thiophen-2-yl | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96 | 95 b |
| 883 | Thiophen-2-yl | $CO_2Me$ | NHAc | [Rh(COD)**163a**]$PF_6$ | 1 | THF | r.t. | 12 | 95 | 7.9 | 100 | 95 (*S*) | 128 |
| 884 | Thiophen-2-yl | $CO_2Me$ | NHAc | [Rh(COD)**164a**]$PF_6$ | 1 | THF | r.t. | 12 | 95 | 7.9 | 100 | 95 (*S*) | 128 |
| 885 | Thiophen-3-yl | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 87 (*S*) | 98 |
| 886 | Thiophen-3-yl | $CO_2H$ | NHAc | [Rh(COD)**98b**]$BF_4$ | 2.8 | THF | r.t. | 3 | 100 | 33 | 100 | 97 (*S*) | 98 |
| 887 | Thiophen-3-yl | $CO_2H$ | NHAc | [Rh(COD)**115a**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 86 | 29 | 86 | 28 (*S*) | 98 |
| 888 | Thiophen-3-yl | $CO_2H$ | NHAc | [Rh(COD)**115b**]$SbF_6$ | 2.8 | THF | r.t. | 3 | 68 | 23 | 68 | 92 (*S*) | 98 |
| 889 | Thiophen-3-yl | $CO_2Me$ | NHAc | [Rh(COD)**98a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 86.6 | 95 b |
| 890 | Thiophen-3-yl | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 96.7 | 95 b |
| 891 | Thiophen-3-yl | $CO_2Me$ | NHAc | [Rh(COD)**98g**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 98.8 | 95 b |
| 892 | Thiophen-3-yl | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 97.0 | 95 a, b |
| 893 | H | Ph | NHAc | [Rh(COD)**93a**]$SbF_6$ | 3 | THF | r.t. | 12 | 100 | 8.3 | 100 | 28.3 (*S*) | 79 |
| 894 | H | Ph | NHAc | [Rh(COD)**93g**]$SbF_6$ | 3 | THF | r.t. | 12 | 100 | 8.3 | 100 | 67.2 (*S*) | 79 |
| 895 | H | Ph | NHAc | [Rh(COD)**93h**]$SbF_6$ | 3 | THF | r.t. | 12 | 100 | 8.3 | 100 | 94.3 (*S*) | 79 |
| 896 | H | Ph | NHAc | [Rh(COD)**93i**]$SbF_6$ | 3 | THF | r.t. | 12 | 100 | 8.3 | 100 | 89.4 (*S*) | 79 |
| 897 | H | Ph | NHAc | [Rh(COD)**93j**]$SbF_6$ | 3 | THF | r.t. | 12 | 100 | 8.3 | 100 | 90.3 (*S*) | 79 |
| 898 | $CO_2Me$ | Ph | NHAc | [Ru(*p*-cymene)**93a**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 2 (*S*) | 80 |
| 899 | $CO_2Me$ | Ph | NHAc | [Ru(*p*-cymene)**93g**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 22 (*S*) | 80 |

Table 27.5 (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 900 | $CO_2Me$ | Ph | NHAc | [Ru(*p*-cymene)**93h**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 98 (*S*) | 80 |
| 901 | $CO_2Me$ | Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 99 (*S*) | 80 |
| 902 | $CO_2Me$ | Ph | NHAc | [Ru(*p*-cymene)**93j**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 97 (*S*) | 80 |
| 903 | $CO_2Et$ | Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 98 (*S*) | 80 |
| 904 | $CO_2Me$ | 2-MeO-Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 80 (*S*) | 80 |
| 905 | $CO_2Me$ | 4-MeO-Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 99 (*S*) | 80 |
| 906 | $CO_2Me$ | 2-Me-Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 96 (*S*) | 80 |
| 907 | $CO_2Me$ | 4-Me-Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 99 (*S*) | 80 |
| 908 | $CO_2Me$ | 4-Br-Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 97 (*S*) | 80 |
| 909 | $CO_2Me$ | 4-Cl-Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 97 (*S*) | 80 |
| 910 | $CO_2Me$ | 4-F-Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 99 (*S*) | 80 |
| 911 | $CO_2Et$ | 4-Br-Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 93 (*S*) | 80 |
| 912 | $CO_2Et$ | 4-Cl-Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 95 (*S*) | 80 |
| 913 | $CO_2Et$ | 4-F-Ph | NHAc | [Ru(*p*-cymene)**93i**]Cl | 5.5 | EtOH | 50 | 20 | 25 | 1.25 | 100 | 98 (*S*) | 80 |
| 914 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**142a**]$BF_4$ | 5 | DCM:MeOH 2:1 | 40 | 4 | 100 | 25 | 100 | 35 (*R*) | 117d |
| 915 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**142a**]$BF_4$ | 5 | DCM:MeOH 2:1 | 25 | 12 | 70 | 5.8 | 70 | 34 (*R*) | 117d |
| 916 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**142a**]$BF_4$ | 1 | DCM:MeOH 2:1 | 40 | 4 | 100 | 25 | 100 | 54 (*R*) | 117d |
| 917 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**142a**]$BF_4$ | 1 | DCM:MeOH 2:1 | 25 | 8 | 50 | 6.3 | 50 | 40 (*R*) | 117d |
| 918 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)**142a**]$BF_4$ | 5 | Tol:MeOH 2:1 | 40 | 6 | 70 | 11.7 | 70 | 45 (*R*) | 117d |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 919 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)**142a**]$BF_4$ | 5 | DCM : MeOH 2 : 1 | 40 | 6 | 13 | 2.2 | 13 | – | 117d |
| 920 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**142b**]$BF_4$ | 5 | DCM : MeOH 2 : 1 | 40 | 4 | 100 | 25 | 100 | 29 (*R*) | 117d |
| 921 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**142b**]$BF_4$ | 5 | DCM : MeOH 2 : 1 | 25 | 12 | 68 | 5.7 | 68 | 32 (*R*) | 117d |
| 922 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**142b**]$BF_4$ | 1 | DCM : MeOH 2 : 1 | 40 | 4 | 87 | 21.8 | 87 | 47 (*R*) | 117d |
| 923 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**142b**]$BF_4$ | 1 | DCM : MeOH 2 : 1 | 25 | 8 | 70 | 8.8 | 70 | 26 (*R*) | 117d |
| 924 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)**142b**]$BF_4$ | 5 | Tol : MeOH 2 : 1 | 40 | 6 | 99 | 16.5 | 99 | 49 (*R*) | 117d |
| 925 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**142c**]$BF_4$ | 5 | DCM : MeOH 2 : 1 | 40 | 20 | 100 | 5 | 100 | 13 (*R*) | 117d |
| 926 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**142c**]$BF_4$ | 5 | DCM : MeOH 2 : 1 | 25 | 12 | 44 | 3.7 | 44 | 11 (*R*) | 117d |
| 927 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)**142c**]$BF_4$ | 5 | Tol : MeOH 2 : 1 | 40 | 20 | 20 | 1 | 20 | 20 (*R*) | 117d |
| 928 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**143a**]$BF_4$ | 1 | DCM : MeOH 2 : 1 | 40 | 6 | 100 | 16.7 | 100 | 15 (*S*) | 117c |
| 929 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)**143a**]$BF_4$ | 5 | Tol : MeOH 2 : 1 | 40 | 20 | 100 | 5 | 100 | 11 (*R*) | 117c |
| 930 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**143b**]$BF_4$ | 1 | DCM : MeOH 2 : 1 | 40 | 6 | 100 | 16.7 | 100 | 13 (*S*) | 117c |
| 931 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)**143b**]$BF_4$ | 5 | Tol : MeOH 2 : 1 | 40 | 20 | 100 | 5 | 100 | 10 (*R*) | 117c |
| 932 | H | $CO_2H$ | $CH_2CO_2H$ | [Ir(COD)**143c**]$BF_4$ | 5 | DCM : MeOH 2 : 1 | 40 | 20 | 47 | 2.4 | 47 | 8 (*R*) | 117c |
| 933 | H | $CO_2H$ | $CH_2CO_2H$ | [Rh(COD)**143c**]$BF_4$ | 5 | Tol : MeOH 2 : 1 | 40 | 20 | 100 | 5 | 100 | 50 (*R*) | 117c |
| 934 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**87**]BARF | 30–45 | $scCO_2$ | 40–45 | 20 | 1000 | 50 | 100 | 73 (*R*) | 69 |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 935 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**93a**]$BF_4$ | 20 | DCM | r.t. | 0.28 | 500 | 1786 | 100 | 81.3 (*R*) | 78 |
| 936 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**93b**]$BF_4$ | 20 | DCM | r.t. | 0.17 | 500 | 2941 | 100 | 81.0 (*R*) | 78 |
| 937 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**93d**]$BF_4$ | 20 | DCM | r.t. | 0.5 | 500 | 1000 | 100 | 65.6 (*R*) | 78 |
| 938 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**93f**]$BF_4$ | 20 | DCM | r.t. | 1.5 | 412 | 275 | 82.3 | 50.9 (*R*) | 78 |
| 939 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**94b**]$BF_4$ | 20 | DCM | r.t. | 1.5 | 439 | 293 | 87.7 | 51.6 (*R*) | 78 |
| 940 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**94c**]$BF_4$ | 20 | DCM | r.t. | 0.33 | 500 | 1515 | 100 | 72.9 (*R*) | 78 |
| 941 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**94d**]$BF_4$ | 20 | DCM | r.t. | 0.12 | 500 | 4167 | 100 | 89.5 (*R*) | 78 |
| 942 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**94e**]$BF_4$ | 20 | DCM | r.t. | 0.15 | 500 | 3333 | 100 | 91.5 (*R*) | 78 |
| 943 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**94f**]$BF_4$ | 20 | DCM | r.t. | 0.083 | 500 | 6024 | 100 | 92.2 (*R*) | 78 |
| 944 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**94f**]$BF_4$ | 1 | DCM | r.t. | 0.42 | 500 | 1190 | 100 | 93.9 (*R*) | 78 |
| 945 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**97a**]$ClO_4$ + 0.1 $Et_3N$ | 1 | EtOH | 25 | 0.5 | 50 | 100 | 100 | 29 (*R*) | 90 |
| 946 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**97a**]$ClO_4$ + 0.2 $Et_3N$ | 1 | EtOH | 25 | 0.5 | 50 | 100 | 100 | 16 (*R*) | 90 |
| 947 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**111**]$ClO_4$ | 1 | EtOH | 25 | 0.5 | 50 | 100 | 100 | 45 (*R*) | 90 |
| 948 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**111**]$ClO_4$ | 1 | EtOH | 0 | 1 | 50 | 50 | 100 | 33 (*R*) | 90 |
| 949 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**111**]$ClO_4$ | 1 | EtOH | 25 | 0.3 | 50 | 167 | 100 | 31 (*S*) | 90 |
| 950 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**111**]$ClO_4$ | 1 | EtOH | 0 | 0.5 | 50 | 100 | 100 | 54 (*S*) | 90 |
| 951 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**111**]$ClO_4$ + 0.1 $Et_3N$ | 1 | EtOH | 25 | 0.1 | 50 | 500 | 100 | 51 (*S*) | 90 |
| 952 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**111**]$ClO_4$ + 0.2 $Et_3N$ | 1 | EtOH | 25 | 0.3 | 50 | 167 | 100 | 28 (*S*) | 90 |
| 953 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)ent-**120**]$BF_4$ | 1 | DCM | r.t. | 0.08 | 100 | 1250 | 100 | 4 (*R*) | 105 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 954 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**121a**]$BF_4$ | 1 | DCM | r.t. | 0.08 | 100 | 1250 | 100 | 53 (*R*) | 105 |
| 955 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**121b**]$BF_4$ | 1 | DCM | r.t. | 0.08 | 100 | 1250 | 100 | 9 (*R*) | 105 |
| 956 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**121d**]$BF_4$ | 1 | DCM | r.t. | 0.08 | 100 | 1250 | 100 | 19 (*R*) | 105 |
| 957 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**122a**]$BF_4$ | 1 | DCM | r.t. | 0.08 | 100 | 1250 | 100 | 48 (*S*) | 105 |
| 958 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**122b**]$BF_4$ | 1 | DCM | r.t. | 0.08 | 100 | 1250 | 100 | 48 (*S*) | 105 |
| 959 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**122b**]$BF_4$ | 1 | Acetone/DCM 13 : 2 | r.t. | 1.25 | 100 | 80 | 100 | 29 (*S*) | 105 |
| 960 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**122c**]$BF_4$ | 1 | DCM | r.t. | 0.08 | 100 | 1250 | 100 | 54 (*S*) | 105 |
| 961 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**122d**]$BF_4$ | 1 | DCM | r.t. | 0.08 | 100 | 1250 | 100 | 53 (*S*) | 105 |
| 962 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**122d**]$BF_4$ | 1 | Acetone/DCM 13 : 2 | r.t. | 1 | 100 | 100 | 100 | 63 (*S*) | 105 |
| 963 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**122e**]$BF_4$ | 1 | DCM | r.t. | 0.08 | 100 | 1250 | 100 | 51 (*S*) | 105 |
| 964 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Ir(COD)**126**]$BF_4$ | 1 | DCM | 25 | 5 | 2 | 0.4 | 2 | 3 (*R*) | 104 |
| 965 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**126**]$BF_4$ | 1 | DCM | 25 | 0.83 | 100 | 120 | 100 | 9 (*S*) | 104 |
| 966 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Ir(COD)**127**]$BF_4$ | 1 | DCM | 25 | 28 | 100 | 3.6 | 100 | 24 (*S*) | 104 |
| 967 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**127**]$BF_4$ | 1 | DCM | 25 | 0.42 | 99 | 236 | 99 | 15 (*R*) | 104 |
| 968 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**136**]$BF_4$ | 1.3 | DCM | r.t. | 20 | 2000 | 100 | 100 | 97–99 (*R*) | 109 |
| 969 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**136**]$BF_4$ | 1.3 | DCM | r.t. | 20 | 1000 | 50 | 100 | 97–99 (*R*) | 109 |
| 970 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**137a**]$BF_4$ | 20 | DCM | 23 | 0.5 | 1000 | 2000 | 100 | 59.7 (*R*) | 112 |
| 971 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**137b**]$BF_4$ | 20 | DCM | 23 | 0.17 | 1000 | 5882 | 100 | 88.5 (*R*) | 112 |
| 972 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**138**]$BF_4$ | 1.3 | DCM | r.t. | 20 | 2000 | 100 | 100 | >99.5 (*R*) | 109 |
| 973 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**138**]$BF_4$ | 1.3 | DCM | r.t. | 20 | 5380 | 269 | 100 | >99.5 (*R*) | 109 |
| 974 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**138**]$BF_4$ | 1.3 | DCM | r.t. | 20 | 1000 | 500 | 100 | >99.5 (*R*) | 109 |
| 975 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**142a**]$BF_4$ | 5 | DCM | 25 | 8 | 12 | 1.5 | 12 | 22 (*R*) | 117b |
| 976 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**143a**]$BF_4$ | 5 | DCM | 25 | 8 | 28 | 3.5 | 28 | 64 (*R*) | 117b |
| 977 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144a**]$BF_4$ | 5 | DCM | 25 | 8 | 90 | 11.3 | 90 | 90 (*R*) | 117a |
| 978 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144a**]$BF_4$ | 5 | Tol | 25 | 8 | 16 | 2 | 16 | 2 (*S*) | 117b |
| 979 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144a**]$BF_4$ | 5 | DCM | 25 | 8 | 90 | 11.3 | 90 | 90 (*R*) | 117b |
| 980 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144a**]$BF_4$ | 5 | AcOEt | 25 | 8 | 8 | 1 | 8 | 2 (*R*) | 117b |
| 981 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144a**]$BF_4$ | 5 | THF | 25 | 8 | 99 | 12.4 | 99 | 12 (*R*) | 117b |
| 982 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144a**]$BF_4$ | 1 | DCM | 25 | 20 | 100 | 5 | 100 | 10 (*R*) | 117b |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 983 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144a**]$BF_4$ | 2 | DCM | 25 | 8 | 66 | 8.3 | 66 | 90 (*R*) | 117b |
| 984 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144a**]$BF_4$ | 10 | DCM | 25 | 3 | 90 | 30 | 90 | 90 (*R*) | 117b |
| 985 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144a**]$BF_4$ | 30 | DCM | 25 | 0.8 | 100 | 125 | 100 | 91 (*R*) | 117b |
| 986 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144a**]$BF_4$ | 5 | DCM | 25 | 8 | 90 | 11.3 | 90 | 90 (*R*) | 117b |
| 987 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144b**]$BF_4$ | 5 | DCM | 25 | 8 | 82 | 10.3 | 82 | 85 (*R*) | 117a,b |
| 988 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144c**]$BF_4$ | 5 | DCM | 25 | 6 | 100 | 16.7 | 100 | 97 (*R*) | 117a,b |
| 989 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144c**]$BF_4$ | 30 | DCM | 5 | 4 | 1000 | 250 | 100 | >99 (*R*) | 117b |
| 990 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144d**]$BF_4$ | 5 | DCM | 25 | 8 | 50 | 6.3 | 50 | 50 (*S*) | 117a,b |
| 991 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144e**]$BF_4$ | 5 | DCM | 25 | 8 | 46 | 5.8 | 46 | 52 (*R*) | 117a |
| 992 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144e**]$BF_4$ | 5 | DCM | 25 | 8 | 46 | 5.8 | 46 | 52 (*R*) | 117b |
| 993 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144f**]$BF_4$ | 5 | DCM | 25 | 8 | 100 | 12.5 | 100 | 90 (*S*) | 117b |
| 994 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**144g**]$BF_4$ | 5 | DCM | 25 | 8 | 100 | 12.5 | 100 | 92 (*R*) | 117b |
| 995 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**145a**]$BF_4$ | 5 | DCM | 25 | 8 | 100 | 12.5 | 100 | 2 (*R*) | 117a,b |
| 996 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**145b**]$BF_4$ | 5 | DCM | 25 | 8 | 98 | 12.3 | 98 | 2 (*R*) | 117a,b |
| 997 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**145c**]$BF_4$ | 5 | DCM | 25 | 8 | 100 | 12.5 | 100 | 3 (*R*) | 117a,b |
| 998 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**146a**]$BF_4$ | 5 | DCM | 25 | 8 | 87 | 10.9 | 87 | 67 (*R*) | 117a,b |
| 999 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**146b**]$BF_4$ | 5 | DCM | 25 | 8 | 80 | 10 | 80 | 63 (*R*) | 117a,b |
| 1000 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**146c**]$BF_4$ | 5 | DCM | 25 | 8 | 73 | 9.1 | 73 | 29 (*R*) | 117a,b |
| 1001 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**146d**]$BF_4$ | 5 | DCM | 25 | 8 | 69 | 8.6 | 69 | 27 (*R*) | 117a,b |
| 1002 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**149a**]$BF_4$ | 0.3 | DCM | 20 | 20 | 325 | 16 | 65 | 21.0 (*S*) | 116 |
| 1003 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**149b**]$BF_4$ [k)] | 0.3 | DCM | 20 | 20 | 1000 | 50 | >99 | 87.8 (*S*) | 116 |
| 1004 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**149c**]$BF_4$ | 0.3 | DCM | –10 | 20 | 1000 | 50 | >99 | 96.2 (*R*) | 116 |
| 1005 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**149c**]$BF_4$ [k)] | 0.3 | DCM | 20 | 20 | 1000 | 50 | >99 | 94.5 (*R*) | 116 |
| 1006 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**149d**]$BF_4$ [k)] | 0.3 | DCM | 20 | 20 | 740 | 37 | 74 | 38.9 (*S*) | 116 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1007 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**149e**]$BF_4$ | 0.3 | DCM | 20 | 20 | 1000 | 50 | >99 | 96.8 (*R*) | 116 |
| 1008 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**149e**]$BF_4$ | 0.3 | DCM | –10 | 20 | 1000 | 50 | >99 | 98.2 (*R*) | 116 |
| 1009 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**149f**]$BF_4$ | 0.3 | DCM | 20 | 20 | 60 | 3 | 24 | 5.2 (*R*) | 116 |
| 1010 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**149g**]$BF_4$ | 0.3 | DCM | 20 | 20 | 1000 | 50 | >99 | 49.3 (*R*) | 116 |
| 1011 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**150a**]$BF_4$ | 1 | DCM | 25 | 0.2 | 100 | 500 | 100 | 63 (*R*) | 118 |
| 1012 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**150b**]$BF_4$ | 1 | DCM | 25 | 3.3 | 100 | 30.3 | 100 | 66 (*R*) | 118 |
| 1013 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**150c**]$BF_4$ | 1 | DCM | 25 | 3.3 | 100 | 30.3 | 100 | 14 (*R*) | 118 |
| 1014 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**150d**]$BF_4$ | 1 | DCM | 25 | 0.25 | 100 | 400 | 100 | 70 (*R*) | 118 |
| 1015 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**151**]$BF_4$ | 1.3 | DCM | 22 | 2.5 | 1000 | 400 | 100 | 88 (*R*) | 120 |
| 1016 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**151**]$BF_4$ | 1.3 | DCM | 22 | 3.2 | 1860 | 581 | 93 | 87 (*R*) | 120 |
| 1017 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**152**]$BF_4$ | 1.3 | DCM | 22 | 1.5 | 1000 | 667 | 100 | 77 (*S*) | 120 |
| 1018 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**152**]$BF_4$ | 1.3 | DCM | 22 | 1.5 | 2000 | 1333 | 100 | 79 (*S*) | 120 |
| 1019 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**153**]$BF_4$ | 1.3 | DCM | 22 | 2.5 | 1000 | 400 | 100 | 52 (*S*) | 120 |
| 1020 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**153**]$BF_4$ | 1.3 | DCM | 22 | 2.8 | 1800 | 643 | 90 | 60 (*S*) | 120 |
| 1021 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**155c**]$BF_4$ | 4.1 | DCM | r.t. | 17 | 500 | 29.4 | 100 | 49.2 (*S*) | 124b |
| 1022 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**156a**]$BF_4$ | 4.1 | DCM | r.t. | 17 | 500 | 29.4 | 100 | 99.3 (*S*) | 124b |
| 1023 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**156a**]$BF_4$ | 5.1 | DCM | r.t. | 17 | 3000 | 176.5 | 100 | 99.8 (*S*) | 124b |
| 1024 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**156a**]$BF_4$ | 4.1 | DCM | r.t. | 24 | 10000 | 416.7 | 100 | 99.6 (*S*) | 124b |
| 1025 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**156b**]$BF_4$ | 4.1 | DCM | r.t. | 17 | 500 | 29.4 | 100 | 30.8 (*R*) | 124b |
| 1026 | H | $CO_2Me$ | $CH_2CO_2Me$ | [Rh(COD)**156c**]$BF_4$ | 4.1 | DCM | r.t. | 17 | 500 | 29.4 | 100 | 1.8 (*R*) | 124b |
| 1027 | H | $CO_2H$ | Ph | [Rh(1,5-hexadiene)(+)-*trans*-**85**]Cl | 50 | – | 50 | – | – | – | – | 0.7 (S) [a] | 68a |
| 1028 | H | $CO_2H$ | Ph | [Rh(1,5-hexadiene)d-*trans*-**86**]Cl | 50 | – | 50 | – | – | – | – | 0 | 68a |
| 1029 | H | $CO_2H$ | Ph | [Rh(COD)**88**]Cl | 20.7 | PhH : EtOH = 1 : 1 | 60 | 24 | 50 [c] | – | 100 [d] | 2 | 81 |
| 1030 | H | $CO_2H$ | Ph | [Rh(COD)**97a**]$ClO_4$ | 1 | EtOH | 25 | 1 | 50 | 50 | 100 | 2 (*S*) | 90 |
| 1031 | H | $CO_2H$ | Ph | [Rh(COD)**97a**]$ClO_4$ + 0.1 $Et_3N$ | 1 | EtOH | 25 | 24 | 50 | 2 | 100 | 2 (*S*) | 90 |
| 1032 | H | $CO_2H$ | Ph | [Rh(COD)**124**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 27 (*R*) | 103 |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 1033 | H | $CO_2H$ | Ph | [Rh(COD)**124**]Cl | 20.4 | PhH : EtOH = 1 : 1 | 60 | 24 | 100 | 4 | 100 | 2.1 (*R*) | 103 |
| 1034 | H | $CO_2H$ | Ph | [Rh(COD)**125**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 17 (*S*) | 103 |
| 1035 | H | $CO_2H$ | Ph | [Rh(COD)**148**]$BF_4$ | 1 | Acetone | r.t. | 2 | – | – | >90 | 2–10 | 114 |
| 1036 | H | $CO_2Me$ | Ph | [Rh(1,5-hexadiene)(+)-*trans*-**85**]Cl | 50 | – | 50 | – | – | – | – | 4.5 (*S*) [a] | 68a |
| 1037 | H | $CO_2Me$ | Ph | [Rh(1,5-hexadiene)d-*trans*-**86**]Cl | 50 | – | 50 | – | – | – | – | 20 (*S*) [a] | 68a |
| 1038 | H | $CO_2Me$ | Ph | [Rh(COD)**88**]Cl | 69 | PhH : EtOH = 1 : 1 | 100 | 48 | 50 [c] | – | [d] | 1.0 | 81 |
| 1039 | H | $CO_2Me$ | Ph | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 9 [f] | 50 | 6 | 50 | 64 (*S*) | 26 |
| 1040 | H | $CO_2Me$ | Ph | [Rh(COD)**98a**]$BF_4$ | 50 | MeOH | 25 | – | 100 [b] | | | 64 (*S*) | 26 |
| 1041 | H | $CO_2Me$ | Ph | [Rh(COD)**124**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 12 (*R*) | 103 |
| 1042 | H | $CO_2Me$ | Ph | [Rh(COD)**124**]Cl | 68 | PhH : EtOH = 1 : 1 | 100 | 48 | 100 | 2 | 100 | 0 | 103 |
| 1043 | H | $CO_2Me$ | Ph | [Rh(COD)**125**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 10 (*S*) | 103 |
| 1044 | Ph | $CO_2H$ | Me | [Rh(COD)**88**]Cl | 20.7 | PhH : EtOH = 1 : 1 | 60 | 24 | 50 [c] | – | 100 [d] | 14.3 | 81 |
| 1045 | Ph | $CO_2H$ | Me | [Rh(COD)**124**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 54 (*R*) | 103 |
| 1046 | Ph | $CO_2H$ | Me | [Rh(COD)**124**]Cl | 20.4 | PhH : EtOH = 1 : 1 | 60 | 24 | 100 | 4 | 100 | 7.1 (*R*) | 103 |
| 1047 | Ph | $CO_2H$ | Me | [Rh(COD)**125**]$BF_4$ | 1 | THF | 25 | 1 | 100 | 100 | 100 | 48 (*S*) | 103 |
| 1048 | $CO_2H$ | Me | Ph | [Rh(COD)**97a**]$ClO_4$ | 1 | EtOH | 25 | 24 | 50 | 2 | 100 | 5 (*S*) | 90 |
| 1049 | $CO_2H$ | Me | Ph | [Rh(COD)**97a**]$ClO_4$ +0.1 $Et_3N$ | 1 | EtOH | 25 | 24 | 50 | 2 | 100 | 5 (*S*) | 90 |
| 1050 | $CO_2H$ | Ph | Me | [Rh(COD)**97a**]$ClO_4$ | 1 | EtOH | 25 | 24 | 50 | 2 | 100 | 5 (*S*) | 90 |
| 1051 | $CO_2H$ | Ph | Me | [Rh(COD)**97a**]$ClO_4$ +0.1 $Et_3N$ | 1 | EtOH | 25 | 24 | 50 | 2 | 100 | 17 (*S*) | 90 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1052 | Ph | $CO_2Me$ | Me | [Rh(COD)**88**]Cl | 20.7 | PhH : EtOH = 1 : 1 | 100 | 48 | 50 [c] | – | [d] | 4.3 | 81 |
| 1053 | Ph | $CO_2Me$ | Me | [Rh(COD)**124**]Cl | 68 | PhH : EtOH = 1 : 1 | 100 | 48 | 100 | 2 | 100 | 2.3 (*R*) | 103 |
| 1054 | Ph | $CO_2H$ | Ph | [Rh(COD)**88**]Cl | 20.7 | PhH : EtOH = 1 : 1 | 60 | 24 | 50 [c] | – | [d] | 12.0 | 81 |
| 1055 | Ph | $CO_2Me$ | Ph | [Rh(COD)**88**]Cl | 20.7 | PhH : EtOH = 1 : 1 | 100 | 48 | 50 [c] | – | [d] | 4.6 | 81 |
| 1056 | $CO_2H$ | Me | $CO_2H$ | [Rh(COD)**97a**]$ClO_4$ | 1 | EtOH | 25 | 24 | 50 | 2 | 100 | 23 (*S*) | 90 |
| 1057 | $CO_2H$ | Me | $CO_2H$ | [Rh(COD)**111**]$ClO_4$ | 1 | EtOH | 25 | 24 | 50 | 2 | 100 | 7 (*S*) | 90 |
| 1058 | $CO_2H$ | Me | $CO_2H$ | [Rh(**128**)Cl]$_2$ | 56 | MeOH | r.t. | 17 | 100 | 6 | 100 | 24 (*S*) [a] | 106 |
| 1059 | $CO_2H$ | Me | $CO_2H$ | [Rh(COD)**128**]Cl | 56 | PhH | 75 | 17 | 100 | 5.9 | 100 | 24 (*S*) | 106 |
| 1060 | $CO_2H$ | Me | $CO_2H$ | [Rh(COD)**129**]Cl | 56 | PhH | 75 | – | – | – | 0 | 0 | 106 |
| 1076 | H | Ph | $C_2H_5$ | [Rh(**129**)Cl]$_2$ | 50 | MeOH | r.t. | 15 | 140 | 9 | 100 | 37 (*R*) [a] | 106 |
| 1077 | Ph | H | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.03 | 50 | 1667 | 50 | 96.6 (*S*) | 91b |
| 1078 | Ph | H | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.07 | 50 | 714 | 50 | 95.1 (*S*) | 91b |
| 1079 | Ph | Me | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.1 | 50 | 500 | 50 | 91.5 (*S*) | 91b |
| 1080 | Ph | Me | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 | 50 | 1000 | 50 | 94.8 (*S*) | 91b |
| 1081 | Ph | Et | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.1 | 50 | 500 | 50 | 90.6 (*S*) | 91b |
| 1082 | Ph | Et | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 | 50 | 1000 | 50 | 94.4 (*S*) | 91b |
| 1083 | Ph | Et | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.1 | 50 | 500 | 50 | 90.6 (*S*) | 91b |
| 1084 | Ph | Et | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 | 50 | 1000 | 50 | 94.4 (*S*) | 91b |
| 1085 | Ph | H | Ph | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.03 | 50 | 1667 | 50 | 95.0 (*S*) | 91b |
| 1086 | Ph | H | Ph | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 | 50 | 1000 | 50 | 93.7 (*S*) | 91b |
| 1087 | Ph | Me | Ph | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.1 | 50 | 500 | 50 | 87.3 (*S*) | 91b |
| 1088 | Ph | Me | Ph | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 | 50 | 1000 | 50 | 91.6 (*S*) | 91b |
| 1089 | | | | | | | | | | | | | |
| 1090 | 3,4-$(MeO)_2$-$C_6H_3$ | H | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.1 | 50 | 500 | 50 | 96.7 (*S*) | 91b |
| 1091 | 3,4-$(MeO)_2$-$C_6H_3$ | H | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.08 | 50 | 625 | 50 | 94.8 (*S*) | 91b |
| 1092 | 3-MeO-4-AcO-$C_6H_3$ | H | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.05 | 50 | 1000 | 50 | 91.6 (*S*) | 91b |
| 1093 | 3-MeO-4-AcO-$C_6H_3$ | H | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.15 | 50 | 333 | 50 | 95.2 (*S*) | 91b |

**Table 27.5** (continued)

| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P[$H_2$] [bar] | Solvent | Temp. [°C] | Time [h] | | | | | |
| 1094 | 3,4-$(MeO)_2$-$C_6H_3$ | H | Ph | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.08 | 50 | 625 | 50 | 95.1 (*S*) | 91b |
| 1095 | 3,4-$(MeO)_2$-$C_6H_3$ | H | Ph | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.07 | 50 | 714 | 50 | 92.0 (*S*) | 91b |
| 1096 | 3-MeO-4-HO-$C_6H_3$ | H | Ph | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.07 | 50 | 714 | 50 | 96.9 (*S*) | 91b |
| 1097 | 3-MeO-4-HO-$C_6H_3$ | H | Ph | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.07 | 50 | 714 | 50 | 94.1 (*S*) | 91b |
| 1098 | 3,4-$(MeO)_2$-$C_6H_3$ | Et | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.13 | 50 | 385 | 50 | 90.6 (*S*) | 91b |
| 1099 | 3,4-$(MeO)_2$-$C_6H_3$ | Et | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.08 | 50 | 625 | 50 | 95.2 (*S*) | 91b |
| 1100 | 3,4-$(MeO)_2$-$C_6H_3$ | Et | Ph | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.17 | 50 | 294 | 50 | 88.9 (*S*) | 91b |
| 1101 | 3,4-$(MeO)_2$-$C_6H_3$ | Et | Ph | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.13 | 50 | 385 | 50 | 90.5 (*S*) | 91b |
| 1102 | 3-MeO-4-AcO-$C_6H_3$ | Et | Ph | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.08 | 50 | 625 | 50 | 87.2 (*S*) | 91b |
| 1103 | 3-MeO-4-AcO-$C_6H_3$ | Et | Ph | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.08 | 50 | 625 | 50 | 90.5 (*S*) | 91b |
| 1104 | 3,4-$(MeO)_2$-$C_6H_3$ | *i*-Pr | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.37 | 50 | 135 | 50 | 91.3 (*S*) | 91b |
| 1105 | 3,4-$(MeO)_2$-$C_6H_3$ | *i*-Pr | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.18 | 50 | 278 | 50 | 94.7 (*S*) | 91b |
| 1106 | 3,4-$(MeO)_2$-$C_6H_3$ | *i*-Pr | Ph | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.33 | 50 | 152 | 50 | 89.1 (*S*) | 91b |
| 1107 | 3,4-$(MeO)_2$-$C_6H_3$ | *i*-Pr | Ph | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.23 | 50 | 217 | 50 | 92.7 (*S*) | 91b |
| 1108 | 3,4-$(MeO)_2$-$C_6H_3$ | Me | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.37 | 50 | 135 | 50 | 92.4 (*S*) | 91b |
| 1109 | 3,4-$(MeO)_2$-$C_6H_3$ | Me | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.2 | 50 | 250 | 50 | 95.7 (*S*) | 91b |
| 1110 | 3-MeO-4-AcO-$C_6H_3$ | Me | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.08 | 50 | 625 | 50 | 92.4 (*S*) | 91b |
| 1111 | 3-MeO-4-AcO-$C_6H_3$ | Me | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.05 | 50 | 1000 | 50 | 95.6 (*S*) | 91b |
| 1112 | 3-M3O-4AcO-$C_6H_3$ | Me | Me | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.2 | 50 | 250 | 50 | 91.7 (*S*) | 91b |
| 1113 | 3-M3O-4AcO-$C_6H_3$ | Me | Me | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.08 | 50 | 625 | 50 | 95.0 (*S*) | 91b |
| 1114 | 3,4-$(MeO)_2C_6H_3$ | Me | Ph | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.13 | 50 | 385 | 50 | 87.7 (*S*) | 91b |
| 1115 | 3,4-$(MeO)_2C_6H_3$ | Me | Ph | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.12 | 50 | 417 | 50 | 91.2 (*S*) | 91b |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1116 | 3-MeO-4-AcO-$C_6H_3$ | Me | Ph | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.08 | 50 | 625 | 50 | 87.2 (*S*) | 91b |
| 1117 | 3-MeO-4-AcO-$C_6H_3$ | Me | Ph | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.07 | 50 | 714 | 50 | 91.3 (*S*) | 91b |
| 1118 | 3-MeO-4-HO-$C_6H_3$ | Me | Ph | [Rh(COD)**97a**]$BF_4$ | 1 | MeOH | 25 | 0.18 | 50 | 278 | 50 | 89.0 (*S*) | 91b |
| 1119 | 3-MeO-4-HO-$C_6H_3$ | Me | Ph | [Rh(COD)**97c**]$BF_4$ | 1 | MeOH | 25 | 0.1 | 50 | 500 | 50 | 92.1 (*S*) | 91b |

**a)** Optical yield.
**b)** Estimated by proton NMR spectra.
**c)** Substrate : catalyst ratio.
**d)** Crude reaction yields were determined by $^1$H-NMR and found to be quantitative.
**f)** t/2 for half-life time.
**g)** Surfactants.
**h)** Reaction time in the second cycle using recovered aqueous phase containing the catalyst.
**i)** Value obtained from the second cycle.
**j)** Determined as its methyl ester.
**k)** Catalysis carried out with preformed catalyst.
**l)** Ligand : metal ratio = 2

**Table 27.6** Enantiomeric hydrogenation of tetrasubstituted substrates using bisphosphinite ligands.

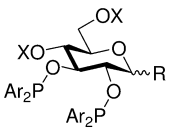
| Entry | Substrate | | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | | $P(H_2)$ [bar] | Solvent | Temp [°C] | Time [h] | | | | | |
| 1 | Me | Me | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 1 | MeOH | 25 | 16.7 [a] | 50 | 3 | 50 | 26.3 (*S*) | 91 f |
| 2 | Me | Me | $CO_2H$ | NHAc | [Rh(COD)**98a**]$BF_4$ | 100 | MeOH | 25 | 1.2 [a] | 50 | 42.9 | 50 | 21 (*S*) | 91 f |
| 3 | Me | Me | $CO_2H$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 15.5 | 95 b |
| 4 | Me | Me | $CO_2Me$ | NHAc | [Rh(COD)**98b**]$SbF_6$ | 2–2.8 | Propylene carbonate | r.t. | 2–3 | – | – | – | 28.4 (S) | 95 b |
| 5 | Me | Me | $CO_2Me$ | NHAc | [[Rh(COD)**98d**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 7.8 (R) | 95 b |
| 6 | Me | Me | $CO_2Me$ | NHAc | [Rh(COD)**103a**]$SbF_6$ | 2–2.8 | THF | r.t. | 2–3 | – | – | – | 10.1 (R) | 95 b |

**a)** t/2 for half-life time.

The enantioselectivities were found to be relatively independent of the solvent used. In 1998, Zhang reported a bisphosphinite based on a rigid bis-cyclopentyl ring system (BICPO, **95**, **96**) which induced 45.7 to 95% ee in the hydrogenation of α-dehydroamino acid derivatives [85].

Carbohydrate-based ligands represent an interesting area in the field of asymmetric catalysis (Tables 27.5 and 27.6). Apart from their unique biological properties, carbohydrates are highly functionalized inexpensive chiral-scaffolds. Various ligands derived from sugars, including glucose, galactose, mannitol, xylose, and trehalose, were synthesized and their effectiveness in asymmetric hydrogenation was differentiated by modulation of the steric and electronic properties. Claver and Diéguez summarized the application of carbohydrates in asymmetric catalysis in a recent review [86]. Other reviews relevant to this field also provided excellent information on their characterization and application [87]. Among these ligands, bidentate phosphorus donors were widely used in the form of phosphines, phosphinites, phosphites, or other mixed donor ligands.

Cullen [88], Thompson [89], Descotes [90] and Selke [91] were the early contributors to the use of a carbohydrate backbone in the Rh-catalyzed asymmetric hydrogenation of α-dehydroamino acid derivatives. A wide variety of 2,3-diphenylphosphinite pyranoside ligands (Fig. 27.7) were synthesized in order to probe the enantiodiscrimination from the stereocenters of the backbone. Among these, the best system was found by Selke to be based on β-glucopyranoside 2,3-diphosphinite ligand (i.e., **98a**), which provided up to 96% ee in the hydrogenation of 2-acetamidocinnamic acid [26, 91c]. The company VEB-ISIS produced L-DOPA in the former German Democratic Republic for many years based on an asymmetric olefin hydrogenation step using Selke's Ph -GLUP ligand [92].



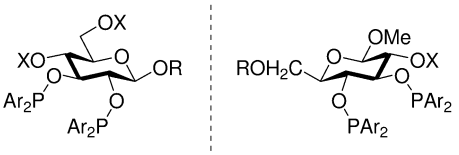

| | |
|---|---|
| **97a** (Me-α-glup) | R = α–OMe, Ar = Ph, X-X = benzylidene |
| **97b** | R = α–OMe, Ar = Ph, X-X = ethylidene |
| **97c** | R = α–OMe, Ar = Ph, X = H |
| **97d** (Ph-α-glup) | R = α–OPh, Ar = Ph, X-X = benzylidene |
| **98a** (Ph-β-glup) | R = β–OPh, Ar = Ph, X-X = benzylidene |
| **98b** | R = β–OPh, Ar = 3,5-$(CH_3)_2C_6H_3$, X-X = benzylidene |
| **98c** | R = β–OPh, Ar = 3,5-$F_2C_6H_3$, X-X = benzylidene |
| **98d** | R = β–OPh, Ar = 3,5-$(CF_3)_2C_6H_3$, X-X=benzylidene |
| **98e** | R = β–OPh, Ar = 4-$CF_3C_6H_4$, X = H |
| **98f** | R = β–OPh, Ar = 4-$MeOC_6H_4$, X = H |
| **98g** | R = β–OPh, Ar = 3,5-$(Me_3Si)_2C_6H_3$, X = H |
| **98h** | R = β–OPh, Ar = 4-$FC_6H_4$, X = H |
| **98i** | R = β–OPh, Ar = Ph, X = H |
| **98j** | R = β–OPh, Ar = Ph, X-X = isopropylidene |
| **99a** | R = β–Ph, Ar = Ph, X = H |
| **99b** | R = β–Ph, Ar = Ph, X-X = isopropylidene |
| **100a** | R = β–OMe, Ar = Ph, X-X = isopropylidene |
| **100b** | R = β–OMe, Ar = Ph, X-X = benzylidene |
| **101a** | R = β–OBn, Ar = Ph, X-X = benzylidene |
| **101b** | R = β–*O*-2-Naphthyl, Ar = Ph, X-X = benzylidene |
| **101c** | R = β–*O*-(4-$MeOC_6H_4$), Ar = Ph, X-X = benzylidene |
| **101d** | R = β–*O*-(4-$NO_2C_6H_4$), Ar = Ph, X-X = benzylidene |
| **101e** | R = β–*O*-(2-$MeOC_6H_4$), Ar = Ph, X-X = benzylidene |
| **101f** | R = β–*O*-(2-$NO_2C_6H_4$), Ar = Ph, X-X = benzylidene |

**Fig. 27.7** 2,3-Diphosphinite pyranoside ligands.

Šunjić [93] and Snatzke [94] systematically designed a series of pyranoside ligands **107–110** (see Fig. 27.10) for use in Rh-catalyzed hydrogenation. Ligand **108** proposed by Šunjić gave the highest ee-value (up to 90.4%). Thompson found poor results in the hydrogenation of (*Z*)-methyl *α*-acetamido-cinnamate (20–46% ee) using *β*-galactoside-based **113b** (see Fig. 27.10) [89]. Selke showed that *α*-galactose-based ligand **113a** induced higher enantioselectivity (86% ee) [91e].

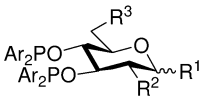
In 1994, RajanBabu carried out systematic studies on the electronic and steric properties of the diphosphinite ligands (**102–106**) [95]. It was determined that, in the Rh-catalyzed hydrogenation of a wide variety of dehydroamino acid derivatives, high enantioselectivities (ee-values up to 99% in *S*-configuration) were obtained with **98b** and **98g** bearing electron-rich substituents, whereas poor selectivity was obtained using the electron-deficient ligands. These results raised the question of the preparation of products with the *R*-configuration. Preparing the other enantiomer of **98** from L-glucose would be prohibitively expensive. Nonetheless, RajanBabu developed *pseudo*-enantiomeric diphosphinite ligands based on the relationship of the 2,3-diphenylphosphinite and its corresponding 3,4-diphosphinite ligands (**98** and **103**; Fig. 27.8). Again, electron-rich phosphinites provided up to 99% ee of the products (dehydroamino acids) with the *R*-configuration. This might be the most convenient way to synthesize both enantiomers of aromatic and heteroaromatic alanines when using sugar-based diphosphinite ligands.

Two-phase catalysis has been established as a new field of study, and has achieved industrial-scale importance in olefin hydroformylation [96]. A significant advantage is the ease of separation of catalyst and product, which may have economic and environmental impact. Thus, removal of the 4,6-*O*-protecting group in 2,3-diphosphinite ligand **98** easily generated a water-soluble catalyst. The effectiveness of using Rh–complexes of diphosphinite **98a** in an aqueous system was proved successfully. Oehme reported that use of Ph-*β*-glup with free hydroxy groups (i.e., **98i** in Fig. 27.7**)** resulted in 84% ee with 100% conversion in the hydrogenation of (*Z*)-methyl *α*-acetamidocinnamate in water (95% ee in MeOH) [97]. The enantioselectivity was further improved (up to 97% ee) using a surfactant such as sodium dodecylsulfate (SDS) or Triton X-100. Similar results were obtained in the hydrogenation of methyl *α*-acetamidoacrylate. Selke reported more experimental results with **98i**. The enantioselectivities were similar to those obtained with protected 2,3-disphosphinite ligand **98** using metha-




2,3-diphosphinite **98** 3,4-diphosphinite **103**, **104**, **112**

**Fig. 27.8** *Pseudo*-enantiomeric diphosphinite pyranoside ligands.




| | |
|---|---|
| **102a** | $R^1$ = β–OMe, $R^2$ = NHAc, $R^3$ = OTBDMS, Ar = 3,5-$(CH_3)_2C_6H_3$ |
| **102b** | $R^1$ = β–OMe, $R^2$ = NHAc, $R^3$ = OTBDMS, Ar = Ph |
| **102c** | $R^1$ = β–OMe, $R^2$ = NHAc, $R^3$ = OTBDMS, Ar = 3,5-$F_2C_6H_3$ |
| **102d** | $R^1$ = β–OMe, $R^2$ = NHAc, $R^3$ = OTBDMS, Ar = 3,5-$(CF_3)_2C_6H_3$ |
| **102e** | $R^1$ = β–OMe, $R^2$ = NHAc, $R^3$ = OTBDMS, Ar = 4-$CF_3C_6H_4$ |
| **102f** | $R^1$ = β–OMe, $R^2$ = NHAc, $R^3$ = OTBDMS, Ar = 4-$MeOC_6H_4$ |
| **103a** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OBz, Ar = 3,5-$(CH_3)_2C_6H_3$ |
| **103b** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OBz, Ar = Ph |
| **103c** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OBz, Ar = 3,5-$F_2C_6H_3$ |
| **103d** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OBz, Ar = 3,5-$(CF_3)_2C_6H_3$ |
| **103e** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OBz, Ar = 4-$CF_3C_6H_4$ |
| **103f** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OBz, Ar = 4-$MeOC_6H_4$ |
| **103g** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OBz, Ar = 3,5-$(Me_3Si)_2C_6H_3$ |
| **103h** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OBz, Ar = 4-$FC_6H_4$ |
| **104a** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OPiv, Ar = 3,5-$(CH_3)_2C_6H_3$ |
| **104b** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OPiv, Ar = Ph |
| **104c** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OPiv, Ar = 3,5-$F_2C_6H_3$ |
| **104d** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OPiv, Ar = 3,5-$(CF_3)_2C_6H_3$ |
| **104e** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OPiv, Ar = 4-$CF_3C_6H_4$ |
| **104f** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OPiv, Ar = 4-$MeOC_6H_4$ |
| **104g** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OPiv, Ar = 3,5-$(Me_3Si)_2C_6H_3$ |
| **104h** | $R^1$ = α–OMe, $R^2$ = $R^3$ = OPiv, Ar = 4-$FC_6H_4$ |
| **105a** | $R^1$ = α–OMe, $R^2$ = H, $R^3$ = OTBDMS, Ar = 3,5-$(CH_3)_2C_6H_3$ |
| **105b** | $R^1$ = α–OMe, $R^2$ = H, $R^3$ = OTBDMS, Ar = Ph |
| **105c** | $R^1$ = α–OMe, $R^2$ = H, $R^3$ = OTBDMS, Ar = 3,5-$F_2C_6H_3$ |
| **105d** | $R^1$ = α–OMe, $R^2$ = H, $R^3$ = OTBDMS, Ar = 3,5-$(CF_3)_2C_6H_3$ |
| **105e** | $R^1$ = α–OMe, $R^2$ = H, $R^3$ = OTBDMS, Ar = 4-$CF_3C_6H_4$ |
| **105f** | $R^1$ = α–OMe, $R^2$ = H, $R^3$ = OTBDMS, Ar = 4-$MeOC_6H_4$ |
| **106a** | $R^1$ = $R^2$ = H, $R^3$ = OTr, Ar = 3,5-$(CH_3)_2C_6H_3$ |
| **106b** | $R^1$ = $R^2$ = H, $R^3$ = OTr, Ar = Ph |
| **106c** | $R^1$ = $R^2$ = H, $R^3$ = OTr, Ar = 3,5-$F_2C_6H_3$ |
| **106d** | $R^1$ = $R^2$ = H, $R^3$ = OTr, Ar = 3,5-$(CF_3)_2C_6H_3$ |
| **106e** | $R^1$ = $R^2$ = H, $R^3$ = OTr, Ar = 4-$CF_3C_6H_4$ |
| **106f** | $R^1$ = $R^2$ = H, $R^3$ = OTr, Ar = 4-$MeOC_6H_4$ |

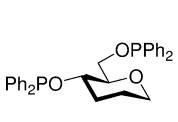
**Fig. 27.9** Bisphosphinite–3,4-diphosphinite pyranoside ligands.

nol as solvent [91a, b]. Attempts also were made by RajanBabu using modified D-salicin with pendant quaternary ammonium groups; however, the result in water (61% ee with **115g** in the hydrogenation of methyl *α*-acetamidoacrylate) [98] was inferior to that obtained in organic solvents (up to 96% ee). Attempts were also made using mannoside-based 3,4-diphosphinite **112**, but only with moderate (72.2%) ee. Glucosamine-based 3,4-diphosphinite **102a**, on the other hand, induced very high enantioselectivity (95–98.4%) in the Rh-catalyzed hydrogenation of various dehydroamino acids.

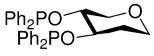
Recently, Miethchen modified diphosphinite **97d** with a crown-ether linker in the 1,4-positions in order to study the effect on enantioselectivity in Rh-catalyzed asymmetric hydrogenation reactions [99]. Introduction of the crown ether in the 1,4-position of the carbohydrate allows the enantioselectivity to be tuned, based on a strong effect of the formation of cryptate species with alkali ions.

Unfortunately, the application of this new ligand **114** (Fig. 27.10) in the hydrogenation of various dehydroamino acid derivatives gave poorer results in comparison to the parent ligand **97d**.

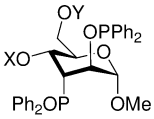
In 1998, Uemura developed novel disaccharide diphosphinite ligands **119a** and **116a (**Fig. 27.10**)** from *α,α*-trehalose. Rh-catalyzed asymmetric hydrogenation of *α*-acetamidoacrylic and cinnamic acid derivatives afforded amino acids with up to 84% ee (*S*) (with ligand **119a**) and 72% ee (*R*) (with ligand **116a**), respectively [100]. The deprotected-hydroxyl diphosphinite ligand **119e** also enabled hydroge-



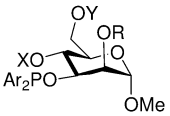
**107**



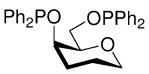
**108**



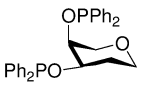
**111** X-Y = benzylidene



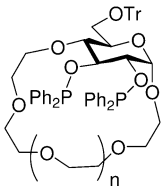
**112a** R = Y = Bn, X = $PAr_2$, Ar = 3,5-$(CH_3)_2C_6H_3$
**112b** R = $PPh_2$, X-Y = benzylidene (Me-α-manp)



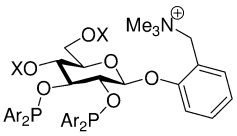
**109**



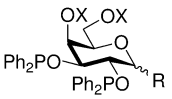
**110**



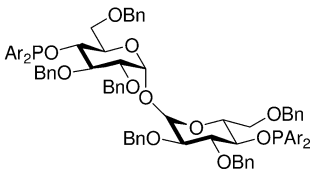
**114a** n = 1
**114b** n = 2



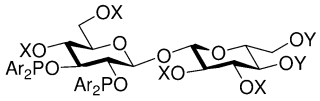
**115a** X-X = benzylidene, Ar = Ph
**115b** X-X = benzylidene, Ar = 3,5-$(CH_3)_2C_6H_3$
**115c** X-X = isopropylidene, Ar = Ph
**115d** X-X = isopropylidene, Ar = 3,5-$(CH_3)_2C_6H_3$
**115e** X-X = isopropylidene, Ar = 3,5-$(CF_3)_2C_6H_3$
**115f** X-X = H, Ar = Ph
**115g** X-X = H, Ar = 3,5-$(CH_3)_2C_6H_3$
**115h** X-X = H, Ar = 3,5-$(CF_3)_2C_6H_3$



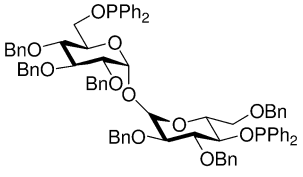
**113a** R = α-OMe, X-X = ethylidene
**113b** R = β-OMe, X-X = ethylidene
**113c** R = α-OMe, X-X = benzylidene (Me-α-galp)
**113d** R = β-OMe, X-X = benzylidene
**113e** R = β-OPh, X-X = benzylidene (Ph-β-galp)
**113f** R = α-OPh, X-X = benzylidene



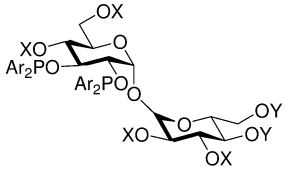
**116a** Ar = Ph
**116b** Ar = 3,5-$(CH_3)_2C_6H_3$



**117** X-X = Y-Y = H, Ar = Ph



**118**



**119a** Ar = Ph, X-X = Y-Y = cyclohexylidene
**119b** Ar = 3,5-$(CH_3)_2C_6H_3$, X-X = Y-Y = benzylidene
**119c** Ar = Ph, X-X = Y-Y = isopropylidene
**119d** Ar = Ph, X-X = Y-Y = H
**119e** Ar = 3,5-$(CH_3)_2C_6H_3$, X-X = Y-Y = H

**Fig. 27.10** Bisphosphinite–others pyranoside ligands.

nation of enamides and itaconic acid in aqueous solution with enhanced enantioselectivities (ee-values up to 99%) [101]. Similar reports by RajanBabu showed its application with moderate to good enantioselectivity [102].

In the light of the fruitful results obtained with the pyranoside-based bisphosphonites, RajanBabu also used a series of 3,4-diphosphinite ligands with a fructofuranoside backbone (i.e., **123**; Fig. 27.11) in the Rh-catalyzed hydrogenation of α-dehydroamino acids. However, the results were unsatisfactory (with only 49–57% ee) [95 b]. Similar results were found by Johnson with ligands based on α-D-glucofuranose (**124**) and α-L-idofuranose (**125**) with highest enantioselectivity (54% ee) obtained in the hydrogenation of α-methylcinnamic acid [103]. Diéguez and Ruiz described a facile synthesis of 3,4-diphosphinites **126** and **127** from D-(+)-xylose [104]. Application of these ligands in asymmetric hydrogenation showed that the enantioselectivity was strongly dependent on the absolute configuration of the C-3 stereocenter and the metal source. When ligand **126** was used in the rhodium-catalyzed hydrogenation of 2-acetamidoacrylic acid, the product was obtained with 76% ee. On the other hand, 78% ee was obtained using the Ir–**127** complex.

Díaz and Castillón reported new modular $C_2$ symmetric ligands prepared from D-glucosamine, D-glucitol and tartaric acid [105]. Ligand **122e** was found to induce the highest ee-value (93%), with full conversion in hydrogenation of methyl 2-acetamidoacrylate. In comparison to **ent-120**, the enantioselectivities of *N*-acetyl-L-alanine methyl ester induced by the catalysts based on **122** and **121** were strongly influenced by the stereocenters at positions 2 and 5 of the tetrahydrofuran ring and steric effect of the R groups. The configuration of the hydrogenation product (methyl 2-acetamidoacrylate and acetamidocinnamic acid ester) was influenced by the stereocenters at C-3 and C-4.

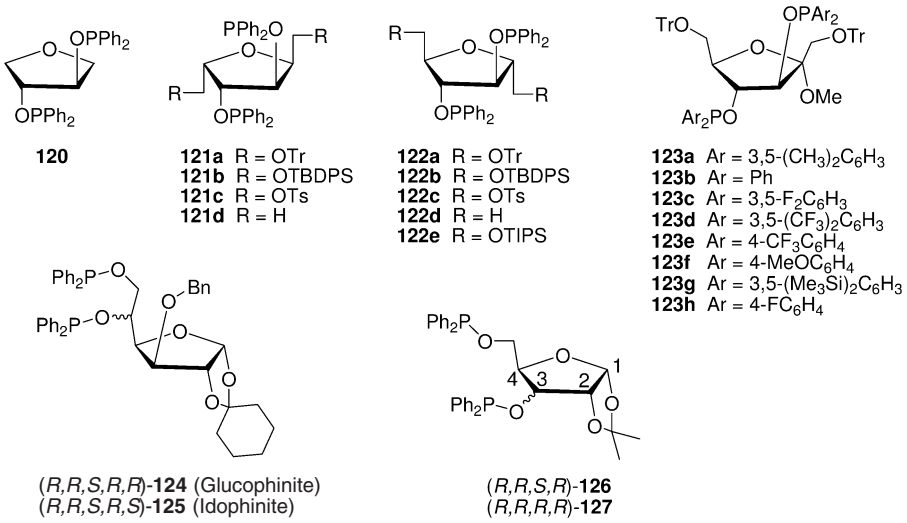



**Fig. 27.11** Bisphosphinite–furanoside ligands.

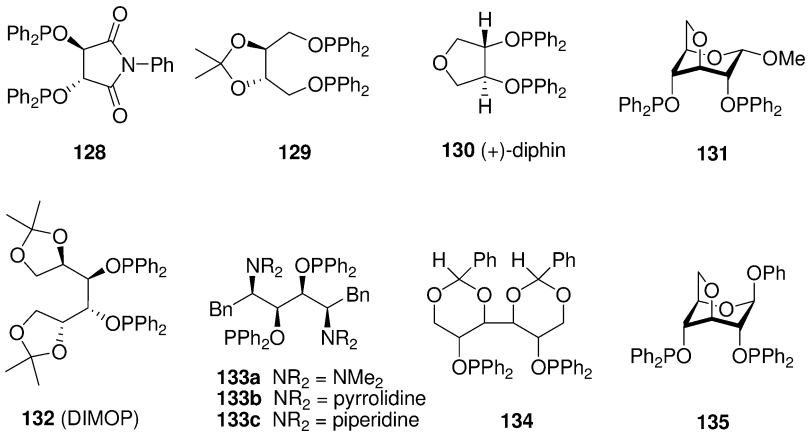



**Fig. 27.12** Bisphosphinite–other carbohydrate-derived ligands.

Increasing the ligand rigidity provides one possibility of increasing enantioselectivity. Jackson and Lovel reported a ligand [(+)-Diphin **130**; Fig. 27.12] derived from natural L-tartaric acid [68b], but use of this ligand containing a rigid tetrahydrofuran ring in the rhodium-catalyzed hydrogenation of *α*-acetamidocinnamic acid led to poor results (2% ee); in contrast, DIOP **129** induced 88% ee in the same reaction [68]. Bourson and Oliveros also developed a bisphosphonite ligand based on the *N*-phenylimide of natural L-tartaric acid **128** [106]. Unfortunately, the Rh-catalyzed hydrogenation of prochiral olefins gave unsatisfactory results with this ligand (1 to 44% ee). In 1999, we developed a new $C_2$ ligand (DIMOP **132**) from inexpensive D-mannitol, and found it to be highly effective in the Rh-catalyzed asymmetric hydrogenation of *α*-amidoacrylic acid and its derivatives [107]. For example, in the hydrogenation of 2-acetamidoacrylic acid, the product was obtained with full conversion in 15 min and 96.7% ee (SCR = 100). In all cases the desired products were found to have ee-values in excess of 90%. Lu and Jiang introduced three analogues based on D-mannitol and D-glucose, (**131**, **134**, and **135**). All ligands led to highly active catalysts with rhodium, but these were less enantioselective in the hydrogenation of *α*-acetamidocinnamic acid and its methyl ester (24.6–46.2% ee) [108]. Through structural modification of D-mannitol, Jiang and Zhang synthesized three bulky analogues (**133a–133c**), each of which induced moderate to excellent ee-values in the hydrogenation of dehydroamino acid derivatives (41–97% ee) [48].

## 27.6
## Bisphosphonite Ligands (Two P–O Bonds)

In recent years, there is no doubt that BINOL is one of the most extensively studied motifs. Incorporating a chiral binol unit into the chiral or achiral backbone constitutes a straightforward way in which to generate new chiral ligands [109].

Both ligands **138** (ferrocene backbone; Fig. 27.13) and **136** (ethylene backbone) performed very well in the hydrogenation of itaconic acid dimethyl ester (97–99.5% ee) and 2-acetamido methyl acrylate (90–99.5% ee). Pringle and Orpen reported poor results in the hydrogenation of methyl 2-acetamido acrylate with the new modified ligand **140**, although the monodentate analogues performed surprisingly well [110]. An enhancement of enantioselectivity may be achieved by combining a chiral backbone with binol in a matching sense. Switching from an achiral backbone to chiral paracyclophane was successful, as reported by Zanotti-Gerosa [111]. Ligands **141 b** and **141 c** displayed a very strong matching/mismatching effect in the Rh-catalyzed hydrogenations of methyl 2-acetamido acrylate, inducing 99% ee and 0% ee, respectively, with the stereochemistry of the product being mainly controlled by the chirality of the backbone. Rh-**141 a** was a faster catalyst (TOF 2500 $h^{-1}$) than Rh-**141 b** (TOF 833 $h^{-1}$), albeit at the expense of a few percent lower ee. Bakos used (*S,S*)-pentane-2,3-diol as the chiral backbone leading to ligands **137 a** and **b** that induced moderate to good ee-values in the hydrogenation of dimethyl 2-methylsuccinate (59.7–88.5% ee) [112]. Vogt developed a new bisphosphonite based on 9,9-dimethylxanthene (**139**) and, by applying it to

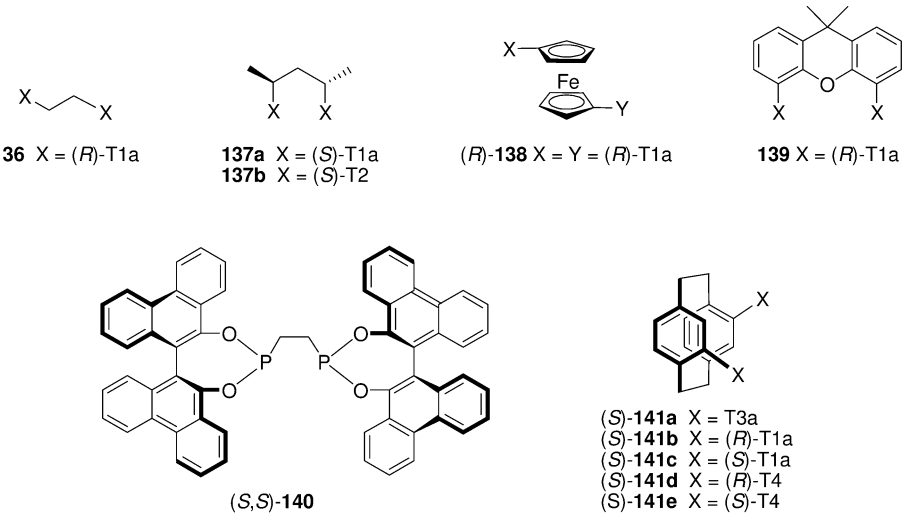


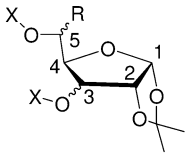

**Fig. 27.13** Bisphosphonite ligands (two P–O bonds).

the rhodium-catalyzed hydrogenation of methyl (*Z*)-2-acetamidocinnamate, obtained 54% ee with full conversion [113].

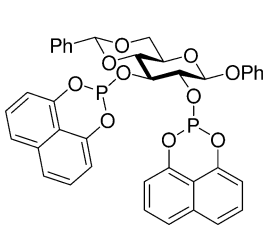
## 27.7
## Bisphosphite Ligands (Three P–O Bonds)

Wink reported the use of bisphosphite ligands in the asymmetric hydrogenation of enamides (2–10% ee) [114]. In 1998, Selke synthesized a series of analogues based on **98a**. Of these compounds, **147** (Fig. 27.14) was selected as ligand for the Rh-catalyzed hydrogenation of methyl (*Z*)-2-acetamidocinnamate, though it induced only low enantioselectivity (13% ee) [115].

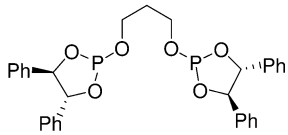
In 1999, Reetz established a class of bidentate bisphosphite ligands **149** (Fig. 27.14) based on $C_2$-symmetric 1,4:3,6-dianhydro-D-mannite [116]. These ligands induced high enantioselectivity in the hydrogenation of dimethyl itaconate (98.2% ee) and methyl *N*-2-acetamidoacrylate (88.8% ee). The results also indicated a cooperative effect between the stereogenic centers of the ligand backbone and the axial chiral binaphthyl phosphite moieties, although the sense of enantioselectivity was predominantly controlled by the binaphthyl moieties (**149e** versus **149b** and **149c**). The use of biphenyl phosphite moieties led to ligands with better performance than those carrying binaphthyls, in spite of their easy epimerization.



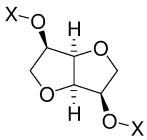
(*R*,*R*,*R*,*R*)-**142a** X = T3e, R = H
(*R*,*R*,*R*,*R*)-**142b** X = T3d, R = H
(*R*,*R*,*R*,*R*)-**142c** X = T3a, R = H
(*R*,*R*,*S*,*R*)-**143a** X = T3e, R = H
(*R*,*R*,*S*,*R*)-**143b** X = T3d, R = H
(*R*,*R*,*S*,*R*)-**143c** X = T3a, R = H
(*R*,*R*,*R*,*R*,*R*)-**144a** X = T3e, R = Me
(*R*,*R*,*R*,*R*,*R*)-**144b** X = T3d, R = Me
(*R*,*R*,*R*,*R*,*R*)-**144c** X = T3c, R = Me
(*R*,*R*,*R*,*R*,*R*)-**144d** X = (*S*)-T1a, R = Me
(*R*,*R*,*R*,*R*,*R*)-**144e** X = (*R*)-T1a, R = Me
(*R*,*R*,*R*,*R*,*R*)-**144f** X = (*S*)-T1c, R = Me
(*R*,*R*,*R*,*R*,*R*)-**144g** X = (*R*)-T1c, R = Me
(*R*,*R*,*S*,*R*,*R*)-**145a** X = T3e, R = Me
(*R*,*R*,*S*,*R*,*R*)-**145b** X = T3d, R = Me
(*R*,*R*,*S*,*R*,*R*)-**145c** X = T3c, R = Me
(*R*,*R*,*R*,*R*,*S*)-**146a** X = T3e, R = Me
(*R*,*R*,*R*,*R*,*S*)-**146b** X = T3d, R = Me
(*R*,*R*,*S*,*R*,*S*)-**146c** X = T3e, R = Me
(*R*,*R*,*S*,*R*,*S*)-**146d** X = T3d, R = Me



**147**



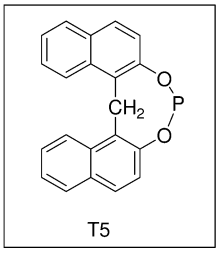
(*R*,*R*,*R*,*R*)-**148**



**149a** X = P(*O*-2-naphthyl)$_2$
**149b** X = (*S*)-T1a
**149c** X = (*R*)-T1a
**149d** X = T3a
**149e** X = T3b
**149f** X = T3e
**149g** X = T5

X–O–X

**150a** X = (*R*)-T1a
**150b** X = (*R*)-T1b
**150c** X = (*R*)-T1d
**150d** X = (*R*)-T2



T5

**Fig. 27.14** Bisphosphite ligands (three P–O bonds).

Recently, Claver and co-workers developed a series of highly effective modular $C_1$ diphosphite ligands **142–146** (Fig. 27.14) with a furanoside backbone [117]. Excellent enantioselectivities (ee-values up to >99%) and good activities were achieved in the Rh-catalyzed hydrogenation of dimethyl itaconate, methyl (*Z*)-2-acetamidocinnamate and methyl (*Z*)-2-acetamidoacrylate [117b]. Systematic variation of the stereocenters C-3 and C-5 at the ligand backbone showed that the enantiomeric excesses depended strongly on the absolute configuration of C-3 and only slightly on that of the stereocenter carbon C-5. Similar to Reetz's observation, the axially chiral binaphthyl substituent predominantly controlled the sense of the enantiodiscrimination. Bulky substituents at the *ortho*-positions of the achiral biaryl diphosphite moieties have a positive effect on enantioselectivity, especially with *o*-trimethylsilyl substituents in the biphenyl moieties of **144c**.

Börner reported the synthesis of pyrophosphites **149** with chiral binaphthyl substituents [118]. The results showed that the $H_8$-binaphthyl unit was the best for the Rh-catalyzed hydrogenation of methyl (*Z*)-2-acetamidocinnamate (48% ee) and dimethyl itaconate (70% ee).

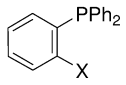
## 27.8 Other Mixed-Donor Bidentate Ligands

In 1982, Yamashita reported the application of L-talopyranoside-based phosphine-phosphinite ligand **165** (Fig. 27.15), and found that it induced low enantioselectivity (4.7–13% ee) in the hydrogenation of *α*-acetamidocinnamic acid [119]. Reetz introduced the phosphine-phosphonite ligand (**151–153**), which led to moderate enantioselectivity (52–88% ee) in the Rh-catalyzed hydrogenation of dimethyl itaconate [120]. The binaphthyl unit remained an essential element in the system.

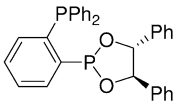
Claver and Ruiz reported excellent enantioselectivity (>99% ee) and good activities (TOF $>1200\ h^{-1}$) in the hydrogenation of methyl *N*-acetamidoacrylate and methyl *N*-acetamidocinnamate using phosphine–phosphite ligand **167** [121]. Again, ligands based on the biphenyl unit (especially with bulky *tert*-butyl groups in the *ortho* and *para positions*) showed a strong enantioinduction. Interestingly, **167** induced a higher activity and enantioselectivity than its corresponding diphosphine [122].

van Leeuwen and Claver designed a new class of chiral phosphine–phosphite ligands **159** and **160** with a stereogenic phosphine for the hydrogenation of methyl *N*-2-acetamidoacrylate and methyl *N*-2-acetamidocinnamate [123]. Up to 99% ee was achieved after systematically tuning the steric and electronic properties of the biaryl phosphite unit.

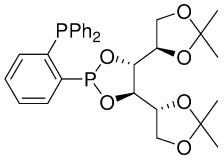
Pizzano and Suárez described a convenient preparation of a series of new chiral phosphine–phosphites based on the easy demethylation of *o*-anisyl phosphines [124]. Rh–**156a** complex was found to be the most effective catalyst for the hydrogenation of dimethyl itaconate (99.6% ee), whereas **155b** and **156a** induced >99% ee in the hydrogenation of methyl *N*-2-acetamidocinnamate. Reetz



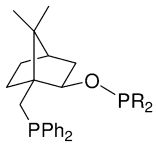
(*R*)-**151** X = (*R*)-T1a



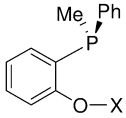
(*R*,*R*)-**152**



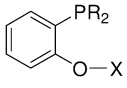
**153**



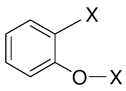
**154a** R = Ph
**154b** R = Mes
**154c** R = Cy



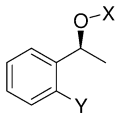
(*S*)-**155a** X = T3e
(*S*)-**155b** X = (*R*)-T4
(*S*)-**155c** X = (*S*)-T4



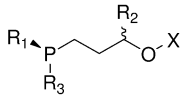
(*S*)-**156a** R = Ph, X = (*S*)-T4
(*S*)-**156b** R = Me, X = (*S*)-T4
(*S*)-**156c** R = $^{i}$Pr, X = (*S*)-T4



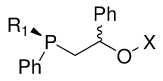
**157** X = (*R*)-T1a



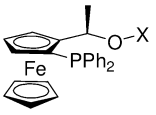
(*S*)-**158a** X = Y = (*S*)-T1a
(*S*)-**158b** X = (*R*)-T1a, Y = (*S*)-T1a
(*S*)-**158c** X = Y = (*R*)-T1a
(*S*)-**158d** X = (*S*)-T1a, Y = (*R*)-T1a



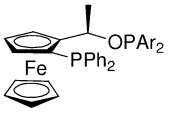
(*Sc*)-**159a** R$^1$, R$^2$, R$^3$ = Ph, X = T3e
(*Sc*)-**159b** R$^1$, R$^3$ = Ph, R$^2$ = Me, X = T3e
(*Sp*,*Sc*)-**159c** R$^1$ = 2-Anisyl, R$^2$, R$^3$ = Ph, X = T3e
(*Rp*,*Rc*)-**159d** R$^1$ = $^{t}$Bu, R$^2$, R$^3$ = Ph, X = T3e
(*Rp*,*Sc*)-**159e** R$^1$ = $^{t}$Bu, R$^2$, R$^3$ = Ph, X = T3e
(*Rp*,*racc*)-**159f** R$^1$ = $^{t}$Bu, R$^2$, R$^3$ = Ph, X = T3e
(*Rp*,*Sc*)-**159g** R$^1$ = $^{t}$Bu, R$^2$ = Me, R$^3$ = Ph, X = T3e
(*Sc*)-**159h** R$^1$, R$^3$ = $^{t}$Bu, R$^2$ = Ph, X = T3e



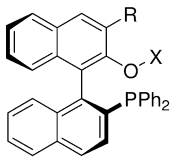
(*Rp*,*Sc*)-**160a** R$^1$ = $^{t}$Bu, X = T3e
(*Rp*,*Rc*)-**160b** R$^1$ = $^{t}$Bu, X = T3e



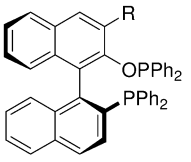
**161** X = (*S*)-T1a



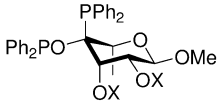
**162a** Ar = Ph
**162b** Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$



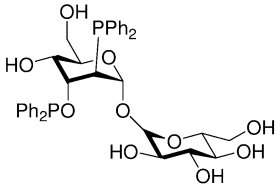
(*S*,*R*)-**163a** (*o*-BINAPHOS) X = (*R*)-T1a R = Ph
(*S*,*R*)-**163b** (BINAPHOS) X = (*R*)-T1a R = H



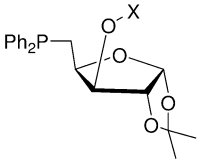
(*S*)-**164a** (*o*-BIPNITE) R = Ph
(*S*)-**164b** (BIPNITE) R = H



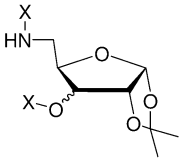
**165** X-X = isopropylidene



**166**



**167a** X = T3a
**167b** X = T3e
**167c** X = (*S*)-T1a
**167d** X = (*R*)-T1a



(*R*,*R*,*S*,*R*)-**168a** X=T3e
(*R*,*R*,*S*,*R*)-**168b** X=T3d
(*R*,*R*,*R*,*R*)-**168c** X=T3e
(*R*,*R*,*R*,*R*)-**168d** X=T3d

**Fig. 27.15** Other mixed-donor bidentate ligands.

used (*S*)-1-(2-bromophenyl)ethanol together with binol to make ligands **158a–158d**. Use of these ligands in the Rh-catalyzed hydrogenation of itaconic acid dimethyl ester gave up to 79% ee [125].

The use of phosphite–phosphoramidite ligands **168a** and **b** provided up to 98% ee in the hydrogenation of methyl (*Z*)-*N*-2-acetylaminocinnamate, but the activities were rather low when compared to **167** or to the corresponding diphosphine ligand [126].

In contrast to the extensive studies on phosphine–phosphites, the corresponding phosphine–phosphinites are rarely exploited. Laschat introduced this design with a bicyclic chiral skeleton derived from (1*S*)-(+)-camphorsulfonic acid [127]. The Rh–complex based on dimesitylphosphinite **154b** was found to be the most reactive catalyst, and was used to produce methyl *N*-2-acetamidocinnamate, with 89% ee.

In 2004, we introduced new phosphine–phosphite ligands with a ferrocenyl scaffold derived from Ugi's amine [61]. Ligand **161** was found to exhibit good enantioselectivity in the hydrogenation of methyl *N*-2-acetamidocinnamate (85–89% ee). Ligand **162b** was also found to be highly effective in the hydrogenation of methyl *N*-2-acetamidocinnamate (95.3–99.6% ee) and *N*-acetyl-*α*-arylenamides (83–91% ee).

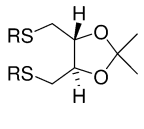
Zhang reported two new (*S*)-BINOL based ligands: phosphine–phosphite (*S,R*)-*o*-BINAPHOS **163** and phosphine–phosphinite (*S*)-*o*-BIPNITE **164** [128]. Applications of these ligands in the Rh-catalyzed hydrogenation of methyl *N*-2-acetamidocinnamate and methyl *N*-2-acetamidoacrylate induced very high enantioselectivities (>99% ee), and with a wide range of substrates.

Uemura developed a water-soluble phosphine–phosphinite ligand (derived from *α,α*-trehalose) (**166**) for the Rh-catalyzed hydrogenation of enamide derivatives; this induced only moderate enantioselectivity [129].

## 27.9
## Ligands Containing Neutral S-Donors

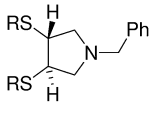
Ligands containing thioethers are stereochemically very interesting, because upon coordination, the sulfur atom becomes a stereogenic center. In the absence of any stereocontrol, the *S*-center can be either (*R*)- or (*S*)-configured. However, if one imposes an efficient stereochemical control through judicious selection of the backbone chirality, it is possible to stabilize the configuration of the sulfur atom and thereby confer chiral information to the metal center. During the past few years, a number of reports have been disclosed describing attempts to harness this special property of thioethers in the asymmetric hydrogenation of a variety of prochiral olefins.

A number of dithioethers **169–173** (Fig. 27.16) based on the chiral skeleton of some well-known phosphines such as DIOP, Deguphos and BINAP, have been reported. The use of 1,4-dithioether ligands which lack contiguous chiral centers such as (+)-Diops$R_2$ **169** [130], BINAS$R_2$ **172** [131] and **173** [132] in the Ir- or



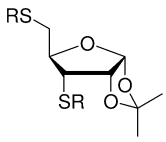
(-)-Diops$R_2$

**169a** R = Me
**169b** R = $^i$Pr
**169c** R = Ph



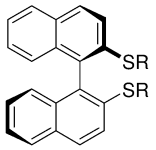
(-)-Degus$R_2$

**170a** R = Me
**170b** R = $^i$Pr
**170c** R = Ph



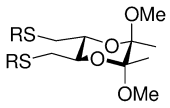
(+)-RiSS$R_2$

**171a** R = Me
**171b** R = $^i$Pr
**171c** R = Ph

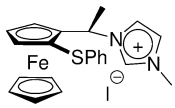


BINAS$R_2$

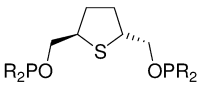
**172a** R = Me
**172b** R = $^i$Pr
**172c** R = $^t$Bu



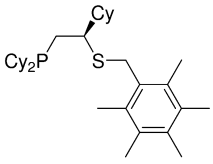
**173a** R = Ph
**173b** R = $^t$Bu



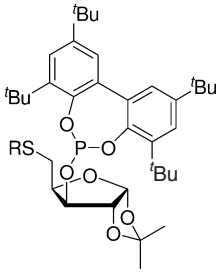
**174**



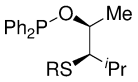
**175a** R = Et
**175b** R = Cy
**175c** R = Ph



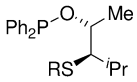
**176**



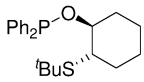
**177a** R = Me
**177b** R = $^i$Pr
**177c** R = Ph



**178a** R = Ph
**178b** R = 4-MeOPh
**178c** R = 3,5-$Me_2$Ph
**178d** R = 1-Nap
**178e** R = Bn
**178f** R = Cy
**178g** R = $^t$Bu



**179a** R = Ph
**179b** R = 4-MeOPh
**179c** R = 3,5-$Me_2$Ph
**179d** R = 1-Nap
**179e** R = Bn
**179f** R = Cy
**179g** R = $^t$Bu

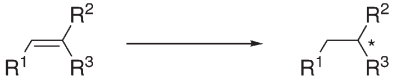


**180**

**Fig. 27.16** Thioether-containing chiral ligands in asymmetric hydrogenation.

Rh-catalyzed asymmetric hydrogenation of itaconic acid and its derivatives, dehydroamino acid derivatives and enamides led to extremely poor to moderate enantioselectivities (Table 27.7). Although NMR spectroscopic studies of the iridium(I) cyclooctadiene complexes of **169** and **172** suggested that they possessed well-defined $C_2$-symmetry, implying that both sulfur atoms have the same configuration, their corresponding *cis*-dihydridoiridium(III) adducts appeared in the NMR spectrum as either a mixture of diastereomers or $C_1$-symmetric complexes, suggestive of the configurational lability of the ligated sulfur atom under remote chiral control in the octahedral complex, thus explaining the observed

**Table 27.7** Enantiomeric hydrogenation using ligands containing a neutral S-donor.



| Entry | Substrate | | | Catalyst | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | $P(H_2)$ [bar] | Solvent | Temp [°C] | Time [h] | | | | | |
| 1 | H | Ph | NHAc | **179c**+$[Rh(COD)_2]SbF_6$ | 35.5 | THF | r.t. | 18 | 100 | 5.6 | 100 | 95 | 139 |
| 2 | Me(*E*/*Z*) | Ph | NHAc | **173a**+$[Rh(NBD)_2]SbF_6$ | 3.1 | $CH_3OH$ | r.t. | 24 | 100 | 4.0 | 95 | 21 | 132 |
| 3 | Me(*E*/*Z*) | Ph | NHAc | **173b**+$[Rh(NBD)_2]SbF_6$ | 3.1 | $CH_3OH$ | r.t. | 24 | 100 | 1.5 | 37 | 18 | 132 |
| 4 | H | $CO_2H$ | NHAc | **169c**+$[Ir(COD)_2]BF_4$ | 1 | $CH_2Cl_2$ | 20 | 12 | 40 | 3.3 | 100 | 10 | 130 |
| 5 | Me | $CO_2Me$ | NHAc | **179c** vs. **180**+$[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 97 vs. 98 | 139 |
| 6 | Et | $CO_2Me$ | NHAc | **179c** vs. **180**+$[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 94 vs. 94 | 139 |
| 7 | *i*Pr | $CO_2Me$ | NHAc | **179c** vs. **180**+$[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 89 vs. 36 | 139 |
| 8 | Ph | $CO_2H$ | NHAc | **169b**+$[Ir(COD)_2]BF_4$ | 1 | $CH_2Cl_2$ | 20 | 16 | 40 | 2.4 | 96 | 37 | 130 |
| 9 | Ph | $CO_2H$ | NHAc | **170c**+$[Ir(COD)_2]BF_4$ | 1 | $CH_2Cl_2$ | 20 | 2 | 40 | 20 | 100 | 27 | 133 |
| 10 | Ph | $CO_2Me$ | NHAc | **169c**+$[Ir(COD)_2]BF_4$ | 1 | $CH_2Cl_2$ | 20 | 48 | 40 | 0.4 | 50 | 13 | 130 |
| 11 | Ph | $CO_2Me$ | NHAc | **172a–172c** +$[Ir(COD)_2]BF_4$ | 1 | $CH_3OH$ | 25 | 0.5 | 100 | – | – | – | 131 |
| 12 | Ph | $CO_2Me$ | NHAc | **175b**+$[Rh(COD)_2]OTf$ | 4.1 | $CH_3OH$ | r.t. | O/N | 50 | – | 100 | 55 | 134 |
| 13 | Ph | $CO_2Me$ | NHAc | **176**+$[Rh(COD)_2]OTf$ | 5.5 | $CH_3OH$ | r.t. | 16 | 50 | 3.1 | 100 | 39 | 137 |
| 14 | Ph | $CO_2Me$ | NHAc | **178a**+$[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 84 | 139 |
| 15 | Ph | $CO_2Me$ | NHAc | **179a**+$[Rh(COD)_2]SbF6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 95 | 139 |
| 16 | Ph | $CO_2Me$ | NHAc | **178c**+$[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 81 | 139 |
| 17 | Ph | $CO_2Me$ | NHAc | **179c**+$[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 97 | 139 |
| 18 | Ph | $CO_2Me$ | NHAc | **178f**+$[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 84 | 139 |
| 19 | Ph | $CO_2Me$ | NHAc | **179f**+$[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | NR | | 139 |
| 20 | Ph | $CO_2Me$ | NHAc | **178g**+$[Rh(COD)2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 82 | 139 |

**Table 27.7** (continued)

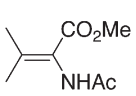
| Entry | Substrate | | | Catalyst | $P(H_2)$ [bar] | Conditions | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | | Solvent | Temp [°C] | Time [h] | | | | | |
| 21 | Ph | $CO_2Me$ | NHAc | **179g** + $[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 20 | 68 | 139 |
| 22 | Ph | $CO_2Me$ | NHAc | **179c** vs. **180** + $[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 97 vs. 97 | 139 |
| 23 | 3-Br-Ph | $CO_2Me$ | NHAc | **179c** vs. **180** + $[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 94 vs. 95 | 139 |
| 24 | 4-F,3-$NO_2$Ph | $CO_2Me$ | NHAc | **179c** vs. **180** + $[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 92 vs. 94 | 139 |
| 25 | 4-MeO-Ph | $CO_2Me$ | NHAc | **179c** vs. **180** + $[Rh(COD)_2]SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 96 vs. 98 | 139 |
| 26 | 2-thienyl | $CO_2Me$ | NHAc | **176** + $[Rh(COD)_2]OTf$ | 5.5 | $CH_3OH$ | r.t. | 16 | 50 | 3.1 | 100 | 19 | 137 |
| 27 | 4-F,3-$NO_2$Ph | $CO_2Me$ | NHAc | **176** + $[Rh(COD)_2]OTf$ | 5.5 | $CH_3OH$ | r.t. | 16 | 50 | 3.1 | 100 | 51 | 137 |
| 28 | H | $CO_2H$ | $CH_2CO_2H$ | **169b** + $[Ir(COD)_2]BF_4$ | 1 | $CH_2Cl_2$ | 20 | 6 | 40 | 6.1 | 91 | 47 | 130 |
| 29 | H | $CO_2H$ | $CH_2CO_2H$ | **170c** + $[Ir(COD_2]BF_4$ | 1 | $CH_2Cl_2$ | 20 | 12 | 40 | 3.3 | 100 | 68 | 133 |
| 30 | H | $CO_2H$ | $CH_2CO_2H$ | **171b** + $[Ir(COD_2]BF_4$ | 1 | $CH_2Cl_2$ | 20 | 12 | 100 | 8.3 | 100 | 62 | 134 |
| 31 | H | $CO_2H$ | $CH_2CO_2H$ | **172a172c** + $[Ir(COD_2]BF_4$ | 1 | $CH_3OH$ | 25 | 0.5 | 100 | | [b] | [c] | 131 |
| 32 | H | $CO_2H$ | $CH_2CO_2H$ | **177b** + $[Ir(COD_2]BF_4$ | 1 | N/A | 40 | 12 | 50 | 4.2 | 100 | 51 | 138 |
| 33 | H | $CO_2Me$ | $CH_2CO_2Me$ | **172a172c** + $[Ir(COD)_2]BF_4$ | 1 | $CH_3OH$ | 25 | 0.5 | 100 | | [b] | [c] | 131 |
| 34 | H | $CO_2Me$ | $CH_2CO_2Me$ | **174** + $[Rh(COD_2]BF_4$ | 10.1 | N/A | 50 | 12 | N/A | | 44 | 18 | 133 |

poor enantioselectivity [135, 136]. Slight improvements resulted when neighboring stereocenters were introduced, as in (–)-Degus$R_2$ **170** [133] and **171** [134] with S-substituents larger than a methyl group (Table 27.7, entries 29 and 30).

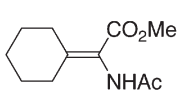
An unusual carbene-thioether hybrid ligand **174** was synthesized and applied in the rhodium-catalyzed asymmetric hydrogenation of dimethyl itaconate by Chung and co-workers; however, the selectivity and activity were low (Table 27.7, entry 34) [135].

Another major class of ligands containing a thioether functionality is the phosphorus–sulfur (P/S) mixed donor family. To date, only a few ligands of this type have been tested. The tridentate tetrahydrothiophene **175** flanked by two *trans-O*-methylene phosphinites was among the first P/S-ligands examined by Hauptman and co-workers, but only mediocre enantioselectivity was recorded in the hydrogenation of methyl *α*-acetamidoacrylate (Table 27.7, entry 12) [136]. Whilst the mode of coordination of **175** in the actual operating Rh-catalyst was unknown, the bidentate phosphine–thioethers **176**, prepared by the same team, also showed unsatisfactory results [137]. The xylofuranose-based phosphite–thioether **177** was also found to be inefficient (Table 27.7, entry 32) [138]. A breakthrough was unveiled by the Evans team [139], when Rh(I) complexes based on phosphinite–thioethers **178** and **179** were found to be highly efficient catalysts in the hydrogenation of a variety of enamide substrates. A side-by-side comparison revealed that skeleton **179** was generally more efficient than **178**, and sterically more encumbered *thio*-aryl substituents were generally superior than the less bulky ones or *thio*-alkyls. Remarkably, the meta-dialkyl effect, which was commonly noted in the phosphorus counterparts [140], also appeared to be operative here as **179** was found to be the optimal ligand (Table 27.7 entry 15). Moreover, the latter was found also to be effective in the enantioselective hydrogenation of *β,β*-disubstituted dehydroamino acids (Table 27.8, entries 1

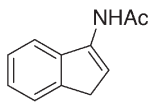
**Table 27.8** Enantiomeric hydrogenation of *β,β*-disubstituted dehydroamino acids and enamides.




**S1**




**S2**




**S3**

| Entry | Substrate | | | Catalyst] | Conditions | | | | TON | TOF [$h^{-1}$] | Conv. [%] | ee [%] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | | P($H_2$ [bar] | Solvent | Temp [°C] | Time [h] | | | | | |
| 1 | | S1 | | **179c** + [Rh($COD_2$]$SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 93 | 139 |
| 2 | | S2 | | **179c** + [Rh($COD_2$]$SbF_6$ | 1 | THF | r.t. | 18 | 100 | 5.6 | 100 | 95 | 139 |
| 3 | | S3 | | **179c** + [Rh($COD_2$]$SbF_6$ | 7.9 | THF | r.t. | 18 | 100 | 5.6 | 100 | 92 | 139 |

and 2) and enamides (Table 27.7, entry 1; Table 27.8, entry 3). The more rigid ligand **180** also proved to be comparable to **179c**. In contrast to **178g** and **179g**, the *S*-*t*Bu group in **180** exerted a positive effect in the stereodifferentiating process and induced much better reactivity. The elegant investigations of Evans and co-workers recapitulated the fact that meticulous screening of the modifiable units – the *S*-substituents in this case – was the key to finding effective ligands [141, 142].

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## Abbreviations

| | |
|---|---|
| AMPP | aminophosphine–phosphinite |
| DCE | dichloroethane |
| DCM | dichloromethane |
| IPA | isopropyl alcohol |
| r.t. | room temperature |
| $scCO_2$ | supercritical $CO_2$ |
| SCR | substrate:catalyst ratio |
| SDS | sodium dodecylsulfate |
| THF | tetrahydrofuran |
| TOF | turnover frequency |
| TON | turnover number |

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