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Tetrahedron: *Asymmetry* 15 (2004) 2247–2251
Tetrahedron: *Asymmetry*

Furanoside diphosphinites as suitable ligands for the asymmetric catalytic hydrogenation of prochiral olefins

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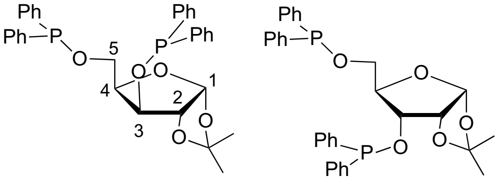
Received 2 April 2004; accepted 3 May 2004
Available online 10 July 2004

Abstract—Diphosphinite ligands, derived from inexpensive D-(+)-xylose, were tested in the rhodium- and iridium-catalyzed asymmetric hydrogenation of prochiral olefins. Our results show that the enantiomeric excesses are strongly dependent on the absolute configuration of the C-3 stereocenter of the carbohydrate backbone and on the metal source. Enantiomeric excesses of up to 78% with moderate to high activities were obtained under very mild reactions conditions with the catalytic systems [Rh(cod)(**2**)]BF_4 and [Ir(cod)(**1**)]BF_4.

1. Introduction

The increasing demand for enantiomerically pure pharmaceuticals, agrochemicals, flavors and other fine chemicals has advanced the field of asymmetric catalytic technologies.[1] Asymmetric hydrogenation utilizing molecular hydrogen to reduce prochiral olefins has become one of the most efficient asymmetric catalytic methods for constructing chiral compounds.[1] Over many years the scope of this reaction has gradually extended in terms of reactant structure and catalyst efficiency.[2] Many chiral ligands, mainly P- and N-containing ligands with either C_2- or C_1-symmetry, have been successfully applied. Diphosphines have played a dominant role among the P-ligands. However, diphosphinites, to a lesser extent, have also demonstrated their potential utility in asymmetric hydrogenation.[1,2] One of the most successful families of diphosphinites are derived from carbohydrates.[3] Despite the early success of carbohydrate phosphinite ligands in hydrogenation, reports on their use are rare.[3a,b,d,4] Recently, a new class of diphosphine,[5] phosphine–phosphite,[6] and diphosphite[7] sugar ligands, derived from D-(+)-xylose and D-(+)-glucose, with furanoside backbones have successfully been applied in the Rh-catalyzed asymmetric hydrogenation of several olefins.

Following our interest in carbohydrates as an inexpensive and highly modular chiral source for preparing ligands,[8] and encouraged by the success of the carbohydrate diphosphinite ligands and the excellent results obtained with the previously mentioned furanoside ligands, we have designed their diphosphinite **1** and **2** counterparts (Fig. 1).



1 **2**

Figure 1. Diphosphinite ligands **1**–**2**.

Herein we report the synthesis of these diphosphinite ligands **1** and **2**, their Rh(I) and Ir(I) complexes and their use in the Rh and Ir-catalyzed enantioselective hydrogenation of prochiral olefins. We have investigated the influence of the stereogenic carbon atom C-3, since ligands **1** and **2** are epimeric at C-3.

2. Results and discussion

2.1. Synthesis of the chiral diphosphinite ligands

Ligands **1** and **2** were synthesized very efficiently in one step from the corresponding alcohols **3**[9] and **4**,[10] which

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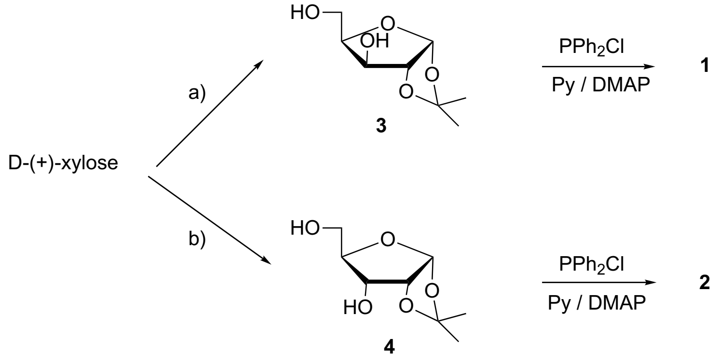
doi:10.1016/j.tetasy.2004.05.047



Scheme 1. Synthesis of ligands **1**–**2**. (a) Ref. 9; (b) Ref. 9.

were easily prepared on a large scale from inexpensive D-(+)-xylose (Scheme 1). The synthesis of ligand **1** was adapted from a previously published procedure (see Section 4).[3a] The reaction of **3** and **4** with 2 equiv of chlorodiphenylphosphine in dry THF, under nitrogen and in the presence of pyridine and 4-(dimethylamino)-pyridine (DMAP) provided the corresponding ligands in 85% and 68% yields, respectively.

All the ligands were stable during purification on neutral alumina under an atmosphere of argon and they were isolated as pale yellow oils. The ^{1}H, ^{31}P, and ^{13}C NMR spectra were as expected for these C_1 ligands (see Section 4). The spectral assignments were based on information from ^{13}C–^{1}H and ^{31}P–^{1}H correlation measurements.

2.2. Synthesis of rhodium and iridium complexes

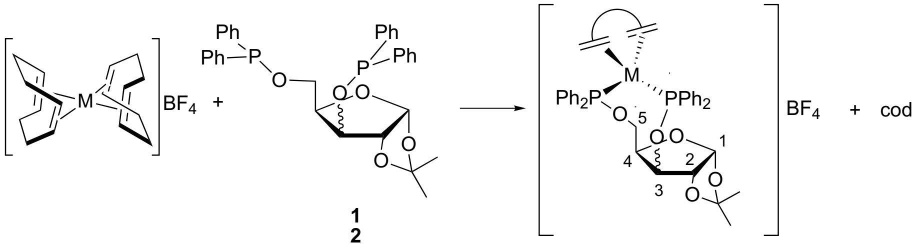
The reaction of the corresponding chiral diphosphinite ligands **1** and **2** with $[M(cod)_2]BF_4$ (M = Rh, Ir) in dichloromethane solution proceeded with the displacement of one molecule of the 1,5-cyclooctadiene ligand to afford the cationic complexes $[M(cod)(P–P)]BF_4$ **5**–**8** (Scheme 2). All attempts to isolate these complexes were unsuccessful.

The complexes were characterized in solution using ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The spectral assignments (selected data in Table 1) were based on information from ^{1}H–^{1}H COSY, ^{13}C–^{1}H, and ^{31}P–^{1}H correlation measurements.

For complexes **5**, **6**, and **8** the variable temperature ^{1}H and ^{13}C NMR measurements indicated the presence of one isomer with an overall C_1-symmetry in solution. However, for complex **7** several isomers were detected. Only two of these (denoted as **a** and **b**), in a ratio of 2:1, have been fully characterized. These different isomers may be attributed to the different conformers of the eight-membered chelate ring.[11]

Over the whole temperature range explored (from 40 to −80 °C), the ^{1}H and ^{13}C NMR of complexes **5**, **6**, and **8** showed four signals for the olefinic protons and four signals for the olefinic carbon atoms of the coordinated cyclooctadiene, as expected for a C_1-symmetrical complex. For each isomer of complex **7**, only two broad signals for the olefinic protons and one broad signal for the olefinic carbon atoms were observed. This is probably due to an overlap of the broad signals. The signals from the diphosphinite ligands produced the expected ^{1}H and ^{13}C NMR pattern for the *xylo*- and *ribo*-furanoside nucleus (Table 1, Scheme 2).

The ^{31}P NMR spectra (see Section 4) of the rhodium complexes **5** and **6** showed two signals split into clearly resolved double doublets due to the ^{31}P, ^{103}Rh and ^{31}P, ^{31}P coupling. The iridium complexes **7** and **8** showed two doublets due to the ^{31}P, ^{31}P coupling. When the tem-



	M	Diphosphinite
5	Rh	**1**
6	Rh	**2**
7	Ir	**1**
8	Ir	**2**

Scheme 2. Synthesis of rhodium and iridium complexes **5**–**8**.

Table 1. Selected NMR spectroscopic data for complexes **5**–**8**[a]

	cod		Diphosphinite							
	CH_2	CH=	1	2	3	4	5	5′	CH_3	CMe_2
^1H										
5	2.31 (m) 2.43 (m) 2.57 (m)	4.62 (m), 4.70 (m) 4.84 (m), 4.99 (m)	5.88 (d)[b]	4.29 (d)[b]	4.48 (d)[c]	4.36 (m)	4.70 (dd)[d]	4.45 (dd)[d]	1.22 (s) 1.37 (s)	— —
6	2.39 (br) 2.58 (br)	4.45 (m), 4.67 (m) 4.76 (m), 4.95 (m)	5.72 (d)[e]	4.60 (t)[e]	4.44 (m)	3.68 (m)	3.96 (m)	4.08 (m)	1.36 (s) 1.23 (s)	—
7a	2.05 (br)	5.24 (br), 5.47 (br)	5.73 (d)[f]	4.40 (d)[f]	4.03 (d)[g]	4.19 (m)	3.80 (m)	3.68 (m)	1.16 (s) 1.29 (s)	—
7b	2.05 (br)	5.24 (br), 5.47 (br)	5.77 (d)[h]	4.38 (d)[h]	3.99 (d)[i]	4.21 (m)	3.90 (m)	3.57 (m)	1.14 (s) 1.26 (s)	—
8	1.26 (br) 1.44 (br)	5.23 (m), 5.24 (m) 5.25 (m), 5.47 (m)	5.36 (d)[j]	4.38 (t)[j]	4.17 (m)	4.08 (m)	3.98 (m)	3.85 (m)	1.24 (s) 1.27 (s)	—
^{13}C										
5	29.7 (br) 28.1 (br)	103.6 (dd)[k], 105.4 (dd)[l] 105.6 (dd)[k], 105.9 (dd)[l]	105.1	84.8 (d)[m]	81.1 (d)[n]	78.2 (m)	67.2 (br)	67.2 (br)	26.5 27.0	112.8
6	31.6, 31.5 29.4, 29.3	100.9 (m), 103.5 (m) 104.9 (m), 106.6 (m)	103.9	78.7 (d)[o]	79.8 (d)[p]	74.4 (br)	68.2 (m)	68.2 (m)	26.9 26.8	113.1
7a	30.4 (br)	105.4 (br)	105.2	85.6	75.4	76.0	60.3 (br)	60.3 (br)	24.6 25.8	111.5
7b	30.4 (br)	105.4 (br)	104.7	85.8	79.9	75.7	60.3 (br)	60.3 (br)	24.5 25.6	111.6
8	26.8 (m) 27.1 (m)	104.2 (m), 104.3 (m) 104.3 (m), 104.5 (m)	104.4	78.9 (d)[q]	77.8 (d)[r]	79.0 (m)	72.3 (d)[s]	72.3 (d)[s]	27.03 27.08	113.8

[a] Chemical shifts in ppm, coupling constants in Hz; room temperature except for complexes **7a** and **b** (at −20 °C); ^1H and ^{13}C NMR in CD_2Cl_2. Abbreviations: s, singlet; m, multiplet; d, doublet; t, triplet; dd, double doublet; br, broad.

[b] $^3J = 3.9$.

[c] $^3J = 3.2$.

[d] $^3J = 3.2$, $^2J = 10.9$.

[e] $^3J = 3.5$.

[f] $^3J = 3.9$.

[g] $^3J = 2.8$.

[h] $^3J = 3.6$.

[i] $^3J = 2.8$.

[j] $^3J = 3.6$.

[k] $^1J = 9.7$, $^2J = 6.6$.

[l] $^1J = 9.5$, $^2J = 6.5$.

[m] $^3J = 3.6$.

[n] $^2J = 7.2$.

[o] $^3J = 3.6$.

[p] $^2J = 4.2$.

[q] $^3J = 2.2$.

[r] $^2J = 6.7$.

[s] $^3J = 5.3$. ^1H NMR and ^{13}C NMR data for the Ph part appears at δ 7.1–7.8 ppm and δ 127–136, respectively.

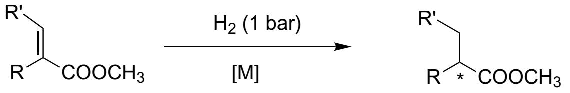
perature was lowered, none of the rhodium or iridium complexes showed any splitting, which confirms that only one isomer is present for complexes **5**, **6**, and **8**. In the case of complex **7**, it suggests that the presence of only one doublet for the two isomers is probably caused by an accidental isocronicity.

2.3. Asymmetric hydrogenation

Diphosphinite ligands **1** and **2** were tested in the Rh- and Ir-catalyzed asymmetric hydrogenation of prochiral olefins **9**–**11** under mild reaction conditions (1 bar of H_2). The selected results are shown in Table 2. The catalysts were prepared in situ by adding the corresponding diphosphinite ligands to the catalyst precursor $[M(cod)_2]BF_4$ (M = Rh, Ir).

The first set of experiments, was the rhodium-catalyzed hydrogenation of methyl *N*-acetamidoacrylate **9** to scope the potential of ligands **1** and **2** (Table 2). The reaction proceeded smoothly at 1 bar of H_2 at room temperature in CH_2Cl_2. The use of ligand **1** afforded

Table 2. Asymmetric hydrogenation of prochiral substrates **9**–**11** with $[M(cod)]BF_4$/**1**–**2**, M = Rh, Ir[a]



9 R=NHCOCH$_3$; R'=H
10 R=NHCOCH$_3$; R'=Ph
11 R=CH$_2$COOCH$_3$; R'==H

Entry	M/L	Substrate	% Conv[b] (*t*/min)	% Ee[c]
1	Rh/**1**	**9**	100 (15)	8 (*R*)
2	Rh/**2**	**9**	100 (10)	76 (*R*)
3	Ir/**1**	**9**	100 (25)	78 (*R*)
4	Ir/**2**	**9**	76 (45)	15 (*R*)
5	Rh/**1**	**10**	100 (10)	10 (*R*)
6	Rh/**2**	**10**	100 (10)	35 (*R*)
7	Ir/**1**	**10**	100 (25)	20 (*R*)
8	Ir/**2**	**10**	100 (45)	10 (*R*)
9	Rh/**1**	**11**	100 (50)	9 (*S*)
10	Rh/**2**	**11**	99 (25)	15 (*R*)
11	Ir/**1**	**11**	2 (300)	3 (*R*)
12	Ir/**2**	**11**	100 (1680)	24 (*S*)
13[d]	Rh/**2**	**9**	96 (45)	81 (*R*)

[a] $[M(cod)_2]BF_4 = 0.01$ mmol. Ligand/M = 2. Substrate/M = 100. $CH_2Cl_2 = 6$ mL. $P_{H2} = 1$ bar. $T = 25$ °C.

[b] % Conversion measured by GC.

[c] % Enantiomeric excess measured by GC using a Permabond L-Chirasil-Val column for substrates **9** and **10** and a Chiraldex-G-TA for substrate **11**.

[d] $T = -25$ °C.

quantitative yields of hydrogenation product with 8% ee (entry 1). The use of the epimeric ligand **2**, whose configuration of carbon atom C-3 is opposite, had a positive effect on activity (Table 2, entry 2) and an extremely positive effect on enantioselectivity (76% ee).

Interestingly, when the $[Ir(cod)_2]BF_4$ was used as catalyst precursor, the best activity and enantioselectivity (78% ee) was obtained with ligand **1** (entry 3 vs 4).

These results clearly show that the enantiomeric excesses depend strongly on the absolute configuration of the C-3 stereocenter of the carbohydrate backbone and on the metal source. Therefore, enantioselectivities and activities were best using the catalytic systems [Rh(cod)(**2**)]BF$_4$ and [Ir(cod)(**1**)]BF$_4$.

In general, the hydrogenation of substrates **10** and **11** (Table 2, entries 5–12) follows the same trend as for **9**. However, the enantiomeric excesses substantially decreased. The use of different solvents (THF, acetone, methanol) or an increase of hydrogen pressure to 5 bar (data not shown) did not significantly improve the catalyst performance (activity and enantioselectivity).

Lowering the temperature to −25 °C resulted in an increase of the enantioselectivity (entry 2 vs 13).

It is interesting that these diphosphinite ligands showed a much higher degree of enantioselectivity and higher reaction rates than their diphosphite analogues under similar reaction conditions.[5a]

3. Conclusions

Diphosphinite ligands, prepared in a few steps from the readily available D-(+)-xylose, were tested in the rhodium- and iridium-catalyzed asymmetric hydrogenation of prochiral olefins. Our results show that enantiomeric excesses depend strongly on the absolute configuration of the C-3 stereocenter of the carbohydrate backbone and on the metal source. Enantiomeric excesses of up to 78% with moderate to high activities were obtained under very mild reactions conditions with the catalytic systems [Rh(cod)(**2**)]BF$_4$ and [Ir(cod)(**1**)]BF$_4$.

Further research into more selective catalysts and other types of hydrogenation reactions is now in progress to exploit the fact that these sugar ligands can be modified so easily.

4. Experimental

4.1. General comments

All syntheses were performed using standard Schlenk techniques under argon atmosphere. Solvents were purified by standard procedures. Compounds **3** and **4** were prepared by previously described methods.[9,10] All other reagents were used as commercially available. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^1H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. All assignments in NMR spectra were determined by ^1H–^1H, ^{13}C–^1H, and ^{31}P–^1H spectra. The reaction under 1 atm of H_2 was performed in a previously described hydrogen vacuum line.[12] Gas chromatography analyses were performed in a Hewlett–Packard Model 5890A instrument. Enantiomeric excesses (ee) were measured using a fused silica capillary column 25 m × 0.25 mm Permabond L-Chirasil-Val for the determination of ee for substrates **9** and **10**, and in Chiraldex-G-TA (30 m × 0.25 mm) for substrate **11**.

4.2. Synthesis of the chiral diphosphinite ligands

4.2.1. 3,5-Dideoxy-3,5-bis(diphenylphosphinite)-1,2-*O*-isopropylidene-α-D-xylofuranose 1. A solution of 25 μL (0.11 mmol) of chlorodiphenylphosphine in 2 mL of THF was slowly added at 0 °C to a solution of 10 mg (0.05 mmol) of **3** and 6.47 mg (0.05 mmol) of DMAP in 2 mL of pyridine. The reaction mixture was stirred overnight at room temperature. Diethyl ether was then added and the pyridine salts were removed by filtration. The residue was purified by flash chromatography (eluent: toluene/NEt$_3$ 100/1, R_f 0.8) to produce 0.025 g (85%) of a pale yellow oil. Anal. Calcd for $C_{32}H_{32}O_5P_2$: C, 68.81; H, 5.77. Found: C, 68.78; H, 5.78. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 115.4 (s, P–C3), 117.4 (s, P–C5). ^1H NMR ($CDCl_3$), δ: 1.27 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 4.09 (m, 1H, H-5), 3.10 (m, 1H, H-5′), 4.38 (m, 1H, H-4), 4.42 (m, 1H, H-3), 4.60 (dd, 1H, H-2, $^3J_{2\text{-}P} = 1.6$ Hz,

$^3J_{2\text{–}3} = 3.6\,\text{Hz}$), 5.93 (d, 1H, H-1, $^3J_{1\text{–}2} = 3.6\,\text{Hz}$), 7.2–7.5 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$), δ: 26.6 (CH_3), 27.1 (CH_3), 67.3 (d, C-5, $^2J_{5\text{-P}} = 18.3\,\text{Hz}$), 80.4 (t, C-4, $^3J_{4\text{-P}} = 6.8\,\text{Hz}$, $^3J_{4\text{-P}} = 6.8\,\text{Hz}$), 82.1 (d, C-3, $^2J_{3\text{-P}} = 19.0\,\text{Hz}$), 83.9 (d, C-2,$^3J_{2\text{-P}} = 6.0\,\text{Hz}$), 105.3 (C-1), 112.3 ($CMe_2$), 128–132 (Ph).

4.2.2. 3,5-Dideoxy-3,5-bis(diphenylphosphinite)-1,2-*O*-isopropylidene-α-D-ribofuranose 2. Treatment of **4** (0.05 mmol) with chlorodiphenylphosphine (25 μL, 0.11 mmol) as described for compound **1** afforded diphosphinite **2**, which was purified by flash chromatography (eluent: toluene/NEt_3 100/1, R_f 0.7) to produce 0.019 g (68%) of a pale yellow oil. Anal. Calcd for $C_{32}H_{32}O_5P_2$: C, 68.81; H, 5.77. Found: C, 68.83; H, 5.76. $[\alpha]_D^{20} = +60$ (*c*, 2.0, $CHCl_3$) ^{31}P{^{1}H} NMR ($CDCl_3$), δ: 118.39 (s, P–C3), 118.42 (s, P–C5). ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 4.14 (m, 1H, H-5), 3.98 (m, 1H, H-5′), 4.23 (m, 1H, H-3), 4.26 (m, 1H, H-4), 4.52 (t, 1H, H-2, $^3J_{2\text{-P}} = 3.6\,\text{Hz}$, $^3J_{2\text{–}1} = 3.6\,\text{Hz}$), 5.42 (d, 1H, H-1, $^3J_{1\text{–}2} = 3.6\,\text{Hz}$), 7.2–7.8 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$), δ: 26.5 (CH_3), 26.6 (CH_3), 67.6 (d, C-5, $^2J_{5\text{-P}} = 19.1\,\text{Hz}$), 76.9 (d, C-3, $^2J_{3\text{-P}} = 19.0\,\text{Hz}$), 78.1 (d, C-2, $^3J_{2\text{-P}} = 3.1\,\text{Hz}$), 78.9 (t, C-4, $^3J_{4\text{-P}} = 6.8\,\text{Hz}$, $^3J_{4\text{-P}} = 6.8\,\text{Hz}$), 103.6 (C-1), 112.8 ($CMe_2$), 127–132 (Ph).

4.3. Synthesis of rhodium and iridium complexes

4.3.1. General procedure. Diphosphinite ligand (0.11 mmol) was added to a solution of $[M(cod)_2]BF_4$ (0.1 mmol M = Rh, Ir) in 2 mL of dichloromethane. After stirring for 30 min, the desired products were obtained and characterized in solution. ^{1}H and ^{13}C NMR details are reported in Table 1.

- $[Rh(cod)(\mathbf{1})]BF_4$ **5**. ^{31}P NMR (CD_2Cl_2), δ: 128.37 (dd, $^1J_{\text{P–Rh}} = 172.4\,\text{Hz}$, $^2J_{\text{P–P}} = 25.9\,\text{Hz}$, P–C5), 132.09 (dd, $^1J_{\text{P–Rh}} = 175.3\,\text{Hz}$, $^2J_{\text{P–P}} = 25.9\,\text{Hz}$, P-C3).
- $[Rh(cod)(\mathbf{2})]BF_4$ **6**. ^{31}P NMR (CD_2Cl_2), δ: 126.56 (dd, $^1J_{\text{P–Rh}} = 177.7\,\text{Hz}$, $^2J_{\text{P–P}} = 20.2\,\text{Hz}$, P–C3), 127.66 (dd, $^1J_{\text{P–Rh}} = 177.7\,\text{Hz}$, $^2J_{\text{P–P}} = 20.2\,\text{Hz}$, P–C5).
- $[Ir(cod)(\mathbf{1})]BF_4$ **7**. ^{31}P NMR (CD_2Cl_2), δ: 110.72 (d, $^2J_{\text{P–P}} = 27.4\,\text{Hz}$, P–C3), 113.98 (d, $^2J_{\text{P–P}} = 27.4\,\text{Hz}$, P–C5).
- $[Ir(cod)(\mathbf{1})]BF_4$ **8**. ^{31}P NMR (CD_2Cl_2), δ: 117.70 (d, $^2J_{\text{P–P}} = 13.3\,\text{Hz}$, P–C5), 118.34 (d, $^2J_{\text{P–P}} = 13.3\,\text{Hz}$, P–C3).

4.4. Asymmetric hydrogenation reactions

In a typical experiment, a Schlenk tube was filled with a dichloromethane solution (6 mL) of substrate (1 mmol), $[M(cod)_2]BF_4$ (4.95 mg, 0.01 mmol) and ligand (0.011 mmol). This was then purged three times with H_2 and vacuum. The reaction mixture was then shaken under H_2 (1 bar) at room temperature. To remove the catalyst, the solution was placed on a short silica gel column and eluted with CH_2Cl_2. Conversion and enantiomeric excesses were determined by gas chromatography.

Acknowledgements

We thank the Spanish Ministerio de Educación, Cultura y Deporte for their financial support (BQU2001-0656).

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