Diastereoselective Alkylation of (Arene)tricarbonylchromium and Ferrocene Complexes Using a Chiral, C_2-Symmetrical 1,2-Diamine as Auxiliary

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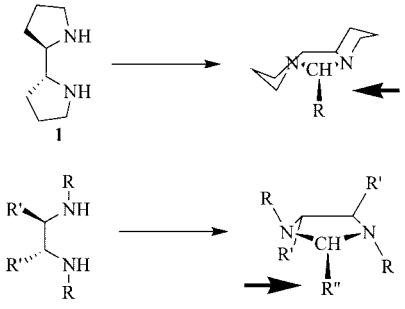
Keywords: Aminals / Chromium / Diamines / Homogeneous catalysis / Planar chirality

The aminal of (benzaldehyde)tricarbonylchromium and enantiopure bipyrrolidine undergoes diastereoselective *ortho*-metallation with butyllithium. Quenching with various electrophiles, followed by hydrolysis of the aminal, affords *ortho*-substituted (benzaldehyde)tricarbonylchromium compounds with high *ee* (91–99 %). When quenched with Ph_2PCl, a new chiral P,N-bidentate ligand is obtained, which shows efficiency in Pd- and Cu-catalysed reactions. The aminal of ferrocenecarbaldehyde could also be formed, but the *ortho*-deprotonation occurs with only moderate diastereoselectivity (70 %).

Introduction

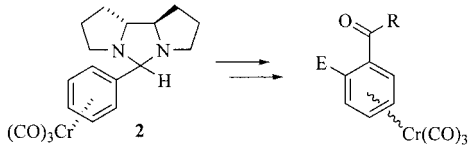
We recently reported a new, short synthesis of enantiopure bipyrrolidine **1**, a chiral 1,2-diamine with C_2 symmetry.[1] The X-ray structure of the complex with $ZnCl_2$ clearly shows the predicted stair-like conformation where all three contiguous five-membered rings adopt a *cis* ring junction.[1a] The same conformation should be expected for aminals obtained from aldehydes. This is in striking contrast with the preferred conformation of aminals obtained with other C_2-symmetrical diamines (Scheme 1).[2]



Scheme 1. Preferred conformation of aminals.

To see if this stair-like conformation is as efficient as the other conformation adopted by classical diamines, or even more so, we decided to test the 2,2′-bipyrrolidine in a diastereoselective reaction. Enantiomerically pure 1,2-diamines are useful chiral auxiliaries or ligands in many reactions, such as the Wittig reaction, the aldol reaction, the addition of organometallic reagents to hydrazones, 1,3-dipolar cycloadditions, etc.[3] We chose the diastereoselective alkylation of (arene)tricarbonylchromium complexes, using the diamine as a chiral auxiliary. (Arene)tricarbonylchromium complexes are versatile compounds[4] that can show planar chirality provided they have two different substituents in an *ortho* or *meta* relationship; these chiral complexes are useful synthons in asymmetric synthesis.[5] Beside resolution,[6] such chiral complexes may be obtained by asymmetric synthesis through enantioselective lithiation followed by electrophile trapping. This may be achieved by *ortho*-deprotonation,[7] either by a chiral base[8] or by an achiral base on an (arene)tricarbonylchromium complex bearing a chiral auxiliary.[9] Among others, chiral acetals[9b–9h] and chiral aminals[9k,9l] have already been used for this purpose. However, chiral acetals have the drawback of a difficult hydrolysis,[9c–9g] whereas chiral aminals have the drawback of a sometimes moderate *ortho* regioselectivity.[9k]

We envisioned that new aminals bearing a more basic, pyrrolidine-type nitrogen atom would be more efficient coordinating heteroatoms to perform directed *ortho*-metallation. In addition, the stair-like conformation should enhance the steric bias and increase the *ortho* versus *ortho′* selectivity (Scheme 2).



Scheme 2. Synthesis of chiral (benzaldehyde)tricarbonylchromium.

Results and Discussion

The reaction of (benzaldehyde)tricarbonylchromium with (*R*,*R*)-2,2′-bipyrrolidine (**1**) was performed as de-

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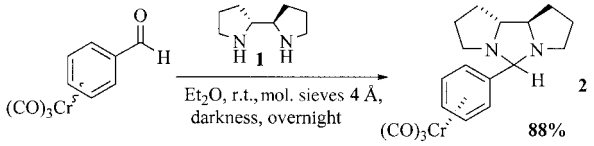
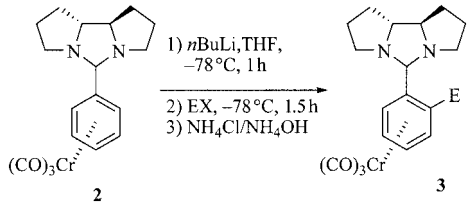
scribed for other aminals,[6h,10] the only difference being the addition of molecular sieves to ensure drier conditions and protection from sunlight due to the sensitivity of this complex. Aminal **2** (Scheme 3) could be obtained in 88% yield after recrystallisation from diethyl ether.



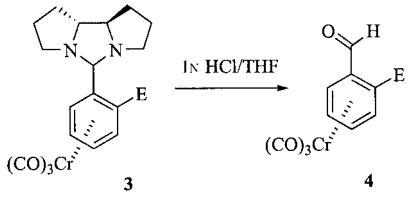
Scheme 3. Formation of aminal **2**.

The differentiation of both *ortho*-hydrogen atoms of the (arene)chromium complex **2** could be seen by ^{1}H NMR spectroscopy. As shown in the spectra in Figure 1, the starting aldehyde gives a single signal for the two *ortho*-protons (a + b) whereas two distinct signals appear for the diastereotopic protons of aminal **2**. The chemical-shift difference ($\Delta\delta \approx 0.4$ ppm) shows that the presence of the diamine could induce a diastereoselective deprotonation with a lithiated base.

Following our previous work,[8k] the diastereoselective deprotonation (Scheme 4) was carried out with *n*BuLi as base in dry tetrahydrofuran at –78 °C for 1 h, followed by addition of different electrophiles at –78 °C. After 1.5 h, the reaction mixture was warmed to –50 °C and it was hydrolysed with a 1:1 aqueous solution of saturated NH_4Cl/NH_4OH. Extraction with oxygen-free solvent afforded aminals **3a**–**3e** (Scheme 5). The results are summarised in Table 1. The basic quench was essential to keep the aminal moiety.



Scheme 4. Diastereoselective lithiation and trapping with electrophiles.



Scheme 5. Hydrolysis of aminals **3**.

Table 1. Diastereoselective deprotonation and electrophile trapping.[a]

	Base	EX	Products	Yield and selectivity
1	*n*BuLi	MeI	**3a**	95%, *de* > 95%[a]
2	*n*BuLi	Me_3SnCl	**3b**	88%, *ee* = 91%[b]
3	*n*BuLi	Me_3SiCl	**3c**	77%, *ee* = 91%[b]
4	*n*BuLi	$(Ph)_2PCl$	**3d**	85%, *de* > 99%[c]
5	*n*BuLi	$(PhS)_2$	**3e**	95%, *de* > 95%[a]

[a] *de* determined by ^{1}H NMR spectroscopy. [b] *ee* determined by chiral HPLC on the corresponding aldehyde **4** (diamine **1** of *ee* 91%). [c] *de* determined by ^{31}P NMR spectroscopy.

Quantitative conversion to the corresponding aldehydes **4a**–**4d** could be achieved with a 1 N HCl wash, in a few seconds, during the extractive work up. However, due to their instability, aldehydes **4d** and **4e** could not be isolated.

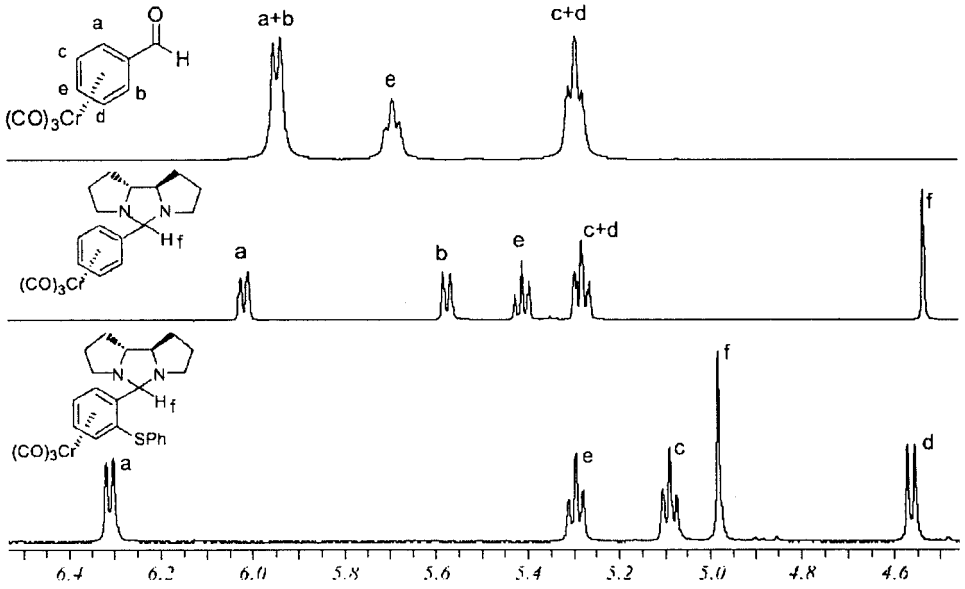
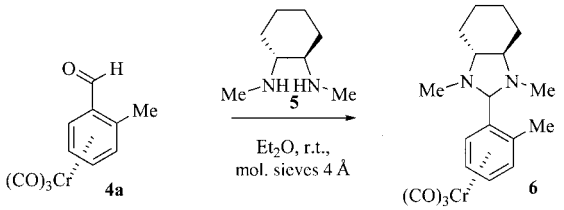


Figure 1. ^{1}H NMR spectra of (benzaldehyde)tricarbonychromium, its aminal **2**, and product **3e**.

As can be seen from these results, excellent diastereocontrol is exerted by the 2,2′-bipyrrolidine-derived aminal. In most cases, quantitative conversion was observed, with diastereoselectivities >95% (by ^{1}H NMR spectroscopy), or >99% with Ph_2PCl as electrophile (^{31}P NMR spectroscopy). With Me_3SiCl and Me_3SnCl, it was difficult to measure the *de* by ^{1}H NMR spectroscopy due to broadening of the signals, so both aminals **3b** and **3c** were hydrolysed to aldehydes **4b** and **4c**, and the *ee* determined by chiral HPLC (chiracel OD). In all cases no other regioisomers were detected by ^{1}H NMR spectroscopy. All aminal products **3** could be purified by chromatography with deoxygenated solvents and basic eluent.

The ^{1}H NMR spectrum of **3e** is shown in Figure 1. It can be seen that only one *ortho*-hydrogen signal remains, whereas the *meta*-hydrogen "d" signal has changed from a triplet to a doublet.

The absolute configuration and *ee* of **3a** were determined after hydrolysis to aldehyde **4a**. Comparison of its optical rotation with literature data was performed after formation of aminal **6** with (*R*,*R*)-*N*,*N*′-dimethylcyclohexane-1,2-diamine (**5**; Scheme 6).[6h]



Scheme 6. Determination of absolute configuration from known aminal **6**.

After recrystallisation from diethyl ether, suitable crystals of product **3d**, which contains a diphenylphosphane moiety, could be isolated; the X-ray structure is shown in Figure 2. This structure clearly shows the same absolute configuration as found for **3a**. The stair-like conformation of the 2,2′-bipyrrolidine-derived aminal induces an sp^3 hybridisation of the nitrogen atoms, with a free lone-pair readily accessible. Of the two nitrogen atoms, one is in the plane of the aromatic ring of the arene, whereas the other one is out of this plane. It is probably the out-of-plane nitrogen atom that coordinates the lithium atom of *n*BuLi, thus directing the *ortho*-metallation at this position.

It is also possible to see that the phosphorus group and the diamine form a cage, where a transition metal ion could fit for a catalytic asymmetric reaction. Thus, **3d** could act as a chiral P,N-bidentate ligand. Several (arene)tricarbonylchromium complexes are known to be excellent ligands in transition-metal-catalysed reactions.[11] This complex was therefore tested as a ligand in the enantioselective Pd-catalysed allylic alkylation.[12] One acyclic (**7**) and one cyclic substrate (**8**) were chosen as representative allylic acetates, with dimethyl malonate as nucleophile (Scheme 7). Both reactions were quantitative after 1 d.

Although the enantioselectivities are moderate for the adducts **9** and **10**, it is interesting to note that the same

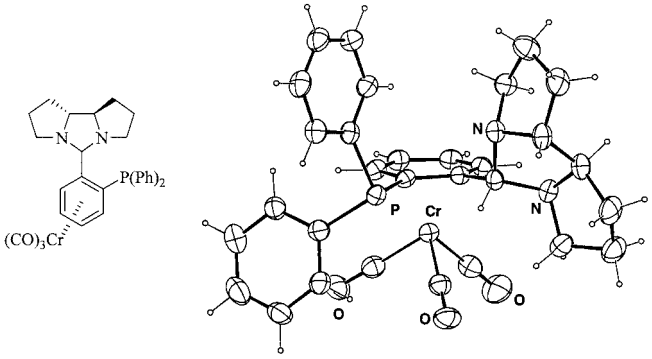
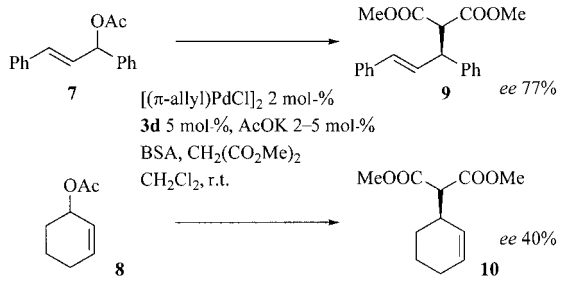
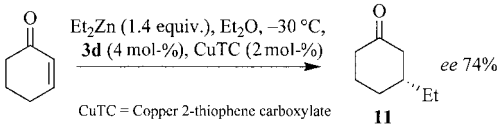


Figure 2. ORTEP representation of aminal **3d**.



Scheme 7. Allylic substitution with **3d** as chiral ligand.

ligand **3d** (Scheme 8) is efficient in both acyclic and cyclic substrates. It should also be mentioned that, in striking contrast, the analogous ligand without the tricarbonylchromium moiety affords only racemic products.

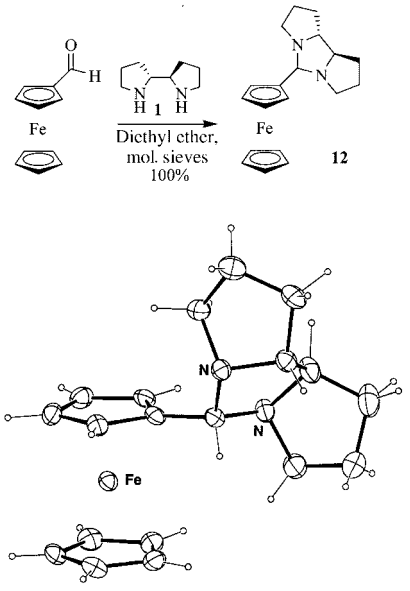


Scheme 8. Conjugate addition with **3d** as chiral ligand.

Another test reaction was the Cu-catalysed conjugate addition of diethylzinc to cyclohexenone.[13] The reaction occurred with quantitative conversion to the adduct **11**, and with 74% *ee*.[14]

These results show that we have found an easy way to prepare an interesting new chiral bidentate phosphane.

By analogy to (arene)tricarbonylchromium complexes, we expected to obtain similar results with ferrocene derivatives. Stereoselective *ortho*-deprotonations are also known with these complexes,[15] and the resulting chiral, substituted ferrocenes are excellent ligands as well.[16] Thus, ferrocenecarbaldehyde forms the corresponding aminal **12** easily under standard conditions. Furthermore, there is no need to work in the dark, as this compound is much more stable than aminal **2**. In the case of aminal **12**, it was possible to grow crystals suitable for X ray analysis (Scheme 9).



Scheme 9. Formation and ORTEP drawing of ferrocenecarbaldehyde aminal **12**.

If we assume that (benzaldehyde)tricarbonylchromium aminal (**2**) has roughly the same conformation, and if we also assume that this conformation is not very different in solution, we can see that one nitrogen atom of the aminal is in the plane of the Cp ring (or the arene ring in **2**) and very close to an α-hydrogen atom (2.69 Å); the other nitrogen atom is out of the plane, at 3.24 Å from the α′-hydrogen atom. This conformation is similar to that of the substituted aminal **3d**. It is therefore supposed that the deprotonating reagent (RLi) can be coordinated by the out-of-the-plane nitrogen atom and is thus close to the α′ hydrogen atom that is removed.

Several *ortho*-deprotonation conditions were tested with aminal **12** (Scheme 10). Unexpectedly, this reaction proved to be extremely difficult, with a reasonable conversion being achieved only with *s*BuLi in THF after raising the temperature to +20 °C. Reaction of the lithiated intermediate with Ph_2PCl, TMSCl or MeI gave intractable mixtures, whereas with diiodoethane we obtained the iodide **13** in 50% yield. Hydrolysis to the corresponding ferrocenecarbaldehyde **14** was straightforward, and its optical-rotation value (–392) showed that it was only 70% *ee*. The absolute configuration corresponds to the anticipated stereochemistry (α′-deprotonation in **12**). The low selectivity achieved with ferrocene aminal **12** may be ascribed to the high temperature needed for the *ortho*-deprotonation.

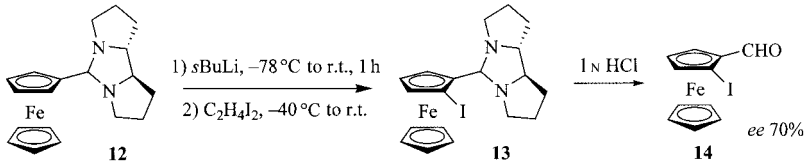
Conclusions

In summary, we have shown that (*R*,*R*)-2,2′-bipyrrolidine (**1**) is an efficient chiral auxiliary in the directed *ortho*-metallation of (arene)tricarbonylchromium complexes. This stems from the stair-like conformation of these aminals, which causes a strong bias in the steric environment of the aminal. In addition, the enhanced basicity of the pyrrolidine-type nitrogen atoms makes them excellent coordinating heteroatoms for ions of metals such as lithium.

Experimental Section

General Remarks: All reactions were carried out under nitrogen or argon using flame-dried glassware. Solvents were distilled with CaH_2 (dichloromethane, triethylamine, toluene) or Na/benzophenone (tetrahydrofuran, diethyl ether) prior to use. Commercially available solid products were generally used without purification; liquids were freshly distilled when it was deemed necessary. ^1H and ^{13}C NMR spectra were recorded with a Varian XL-200 or Bruker-AMX400 spectrometer in $CDCl_3$, or C_6D_6. Chemical shifts are given in ppm relative to TMS; coupling constants are expressed in Hertz. IR spectra were recorded with a Perkin–Elmer 1600 FT-IR spectrometer in NaCl solution cells. Optical rotations were measured in $CHCl_3$ with a Perkin–Elmer 241 polarimeter using a quartz cell (l = 10 cm), with a high-pressure sodium lamp (λ = 589 cm). Gas chromatography (GC) was performed with a Hewlett Packard 5890 instrument, and GC/MS was performed with a Hewlett Packard 6890 column OPTIMA delta-3 (30 m × 0.25 mm) and a Hewlett Packard 5973 mass-selective detectorwith EI (70 eV) as source. Supercritical-fluid chromatography (SFC) was performed with a Berger Instruments Inc. chromatograph with a Hewlett Packard 1100 DAD detector. Mass spectra were obtained with a Varian CH-4 or a Finnigan 4023 spectrometer; relative intensities are given in parenthesis.

Tricarbonylchromium(0) Complex 2: (*R*,*R*)-2,2-Bipyrrolidine (**1**; 1.45 g, 10.4 mmol) was added to a solution of (η^6-benzaldehyde) tricarbonylchromium(0)[6c] (1.67 g, 6.9 mmol) in 20 mL of dry diethyl ether. The reaction mixture was stirred at room temperature in the presence of molecular sieves (4 Å) overnight. After filtration, evaporation of the solvent and precipitation with diethyl ether gave yellow crystals of aminal **2** (1.92 g, yield 88%). M.p. 143–146 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.48–1.59 (m, 1 H), 1.68–1.95 (m, 6 H), 2.06–2.18 (m, 1 H), 2.42–2.48 (m, 1 H), 2.55–2.63 (m, 1 H), 2.74–2.81 (m, 1 H), 2.92–3.00 (m, 1 H), 3.20–3.26 (m, 1 H), 3.27–3.34 (m, 1 H), 4.54 (s, 1 H), 5.28 (t, J = 6.1 Hz, 2 H), 5.4 (t, J = 6.1 Hz, 1 H), 5.58 (d, J = 6.1 Hz, 1 H), 6.02 (d, J = 6.1 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.6, 26.3, 28.1, 30.2, 47.6, 52.8, 70.7, 70.9, 85.4, 90.3, 91.2, 93.0, 94.3, 94.5, 232.9 ppm. MS (ESI): m/z (%) = 365 (100), 363 (76), 227 (39), 169 (63), 146 (58), 129 (36). $[\alpha]_D^{21}$ = –100 (c = 0.0006, toluene).



Scheme 10. Deprotonation of ferrocene aminal **12**.

Tricarbonylchromium(0) Complex 3a: *n*BuLi (625 μL, 1 mmol of a 1.6 M solution in *n*-hexane) was added slowly, under nitrogen, to a stirred solution of imidazolidine **2** (182 mg, 0.5 mmol) in dry tetrahydrofuran (5 mL) at –80 °C and the solution was stirred at –80 °C for 1.5 h. MeI (93 μL, 3.0 mmol) was then added at –80 °C. The solution was stirred at –80 °C for 1 h, then warmed up to –50 °C. The mixture was quenched by addition of a solution of NH_4Cl/NH_3 (1:1, 10 mL), and extracted with diethyl ether (3×10 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed to yield crude product. Flash chromatography on neutral Al_2O_3 (15% Et_3N in Et_2O) gave 193 mg (*de* > 95%, yield 95%) of aminal **3a**. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95–1.09 (m, 1 H), 1.21–1.33 (m, 1 H), 1.37–1.54 (m, 6 H), 1.65–1.78 (m, 1 H), 1.93–2.06 (m, 2 H), 2.03 (s, 3 H), 2.18–2.31 (m, 1 H), 2.65–2.75 (m, 1 H), 2.81–2.89 (m, 1 H), 2.91–3.01 (m, 2 H), 4.30 (d, *J* = 6.1 Hz, 1 H), 4.33 (dt, *J* = 1.0 Hz and 6.3 Hz, 1 H), 4.53 (s, 1 H), 4.59 (dt, *J* = 1.0 Hz and 6.3 Hz, 1 H), 5.97 (d, *J* = 6.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 24.6, 26.2, 27.9, 29.9, 47.1, 52.9, 70.0, 70.3, 83.6, 88.3, 92.2, 93.5, 94.6, 108.2, 109.8, 233.7 ppm. IR: $\tilde{\nu}$ = 2930–2870, 1963, 1882, 1637, 1455, 1043–1380, 787, 763, 666, 629 cm^{-1}. $[\alpha]_D^{21}$ = –23 (*c* = 0.0011, toluene).

(*S*)-Tricarbonyl(η⁶-2-methylbenzaldehyde)chromium(0) (4a): A 50-mg sample of aminal **3a** (*de* > 95% by NMR, from diamine **1** of 91% *ee*) was dissolved in CH_2Cl_2 and hydrolysed with 1 N aqueous HCl solution. The organic phase was then washed with a saturated aqueous solution of Na_2CO_3 and dried with $MgSO_4$. Complex **4a** was obtained in quantitative yield and the enantiomers were separated by SFC (Chiralcel OD-H, 30% MeOH in CO_2, 2 mL min^{-1}, 30 °C) (*ee* = 91%). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3 H), 5.03 (d, *J* = 6.35 Hz, 1 H), 5.23 (t, *J* = 6.35 Hz, 1 H), 5.72 (t, *J* = 6.22 Hz, 1 H), 6.05 (d, *J* = 6.47 Hz, 1 H), 9.81 (s, 1 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 18.24, 87.68, 91.37, 93.45, 94.82, 95.49, 187.48, 230.35 ppm. $[\alpha]_D^{21}$ = +605 (*c* = 0.0016, $CHCl_3$) for 91% *ee* [ref.[6a] $[\alpha]_D^{21}$ = +665 (*c* = 0.006, $CHCl_3$) for 100% *ee*].

Tricarbonylchromium(0) Complex 3b: *n*BuLi (375 μL, 0.6 mmol of a 1.6 M solution in hexane) was added slowly, under nitrogen, to a stirred solution of imidazolidine **2** (104 mg, 0.3 mmol) in dry tetrahydrofuran (3 mL) at –80 °C. The solution was stirred at –80 °C for 1.5 h, then Me_3SnCl (179 mg, 0.9 mmol) was added. The solution was stirred at –80 °C for 1 h, then warmed up to –50 °C. The mixture was quenched by addition of a solution of NH_4Cl/NH_3 (1:1; 10 mL), and extracted with diethyl ether (3×10 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed to yield crude product. Flash chromatography on neutral Al_2O_3 (15% Et_3N in Et_2O) gave 130 mg (*de* = 91%, yield 88%) of compound **3b**. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.22 (s, 9 H), 1.45–1.55 (m, 1 H), 1.7–2.1 (m, 7 H), 2.3–2.4 (m, 1 H), 2.4–2.5 (m, 1 H), 2.67–2.75 (m, 1 H), 2.85–2.9 (m, 1 H), 3.1–3.15 (m, 1 H), 3.27–3.32 (m, 1 H), 4.49 (s, 1 H), 5.28 (t, *J* = 6.0 Hz, 1 H), 5.32 (d, *J* = 6.0 Hz, 1 H), 5.45 (t, *J* = 6.3 Hz, 1 H), 5.88 (d, *J* = 6.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –7.4, 24.2, 26.2, 28.3, 30.4, 46.9, 52.3, 70.7, 71.3, 85.6, 91.8, 93.0, 93.8, 100.8, 102.9, 116.9, 233.7 ppm. ^1H NMR (400 MHz,C_6D_6): δ = 0.37 (s, 9 H), 1.1–1.2 (m, 1 H), 1.3–1.4 (m, 1.H), 1.38–1.6 (m, 4 H), 1.6–1.68 (m, 1 H), 1.7–1.8 (m, 1 H), 2.15–2.22 (m, 1 H), 2.27–2.38 (q, *J* = 8.82 Hz 1 H), 2.8–2.92 (m, 3 H), 3.0–3.08 (m, 1 H), 4.59 (s, 1 H), 4.65 (t, *J* = 6.0 Hz, 1 H), 4.88 (t, *J* = 6.3 Hz, 1 H), 4.98 (d, *J* = 6.0 Hz, 1 H), 5.8 (d, *J* = 6.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = –7.4, 24.5, 26.7, 28.2, 30.4, 47.2, 52.8, 71.0, 71.4, 86.1, 92.1, 93.1, 93.9, 100.8, 102.5, 117.0, 234.3 ppm. IR: $\tilde{\nu}$ = 2872–2960, 1958, 1876, 1561, 1043–1456, 764–768, 665, 628, 537 cm^{-1}. MS (ESI): *m*/*z* (%) = 529 (56), 527 (42), 393 (79), 285 (100), 147 (14). $[\alpha]_D^{21}$ = +60 (*c* = 0.0005, toluene).

(*S*)-Tricarbonyl[η⁶-2-(trimethylstannyl)benzaldehyde]chromium(0) (4b): Crude aminal **3b** (prepared from diamine **1** of 91% *ee*; 74 mg, 0.14 mmol) was dissolved in 1 mL of THF and 1 mL of 1 N HCl solution, saturated with N_2, was added under an inert gas. This mixture was stirred at room temp. for 35 min. The reaction mixture was extracted with CH_2Cl_2, the organic phase was washed with a saturated aqueous solution of Na_2CO_3 and dried with $MgSO_4$. After filtration and evaporation of the solvents, 51 mg (yield 90%, *ee* 91%) of aldehyde **4b** was obtained. The enantiomeric excess was determined by HPLC [Chiralcel OD, 2% *i*PrOH in *n*-hexane, flow 0.5 mL min^{-1}, UV 254 nm: (*R*)-**4b**: t_R = 16.9; (*S*)-**4b**: t_R = 19.2]. ^1H NMR (200 MHz, C_6D_6): δ = 0.34 (s, 9 H), 4.4 (t, *J* = 6.2 Hz, 1 H), 4.50–4.61 (m, 2 H), 4.87 (d, *J* = 6.2 Hz, 1 H), 8.76 (s, 1 H) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = –7.0, 91.3, 95.3, 98.0, 98.2, 99.7, 101.7, 191.8, 231.7 ppm. $[\alpha]_D^{21}$ = +440 (*c* = 0.0005, toluene) for 91% *ee* [ref.[8h] $[\alpha]_D^{21}$ = +354 (*c* = 0.006, $CHCl_3$) for 73% *ee*].

Tricarbonylchromium(0) Complex 3c: *n*BuLi (427 μL, 0.684 mmol of a 1.6 M solution in *n*-hexane) was added slowly, under nitrogen, to a stirred solution of imidazolidine **2** (125 mg, 0.342 mmol) in dry tetrahydrofuran (3 mL) at –80 °C. The solution was stirred at –80 °C for 1.5 h and then TMSCl (173 μL, 1.03 mmol) was added at –80 °C. The solution was stirred at this temperature for 1 h and then warmed to –50 °C. The mixture was quenched by addition of a solution of NH_4Cl/NH_3 (1:1, 10 mL), and extracted with diethyl ether (3×10 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed to yield crude product. Flash chromatography on neutral Al_2O_3 (15% Et_3N in Et_2O) gave 115 mg (yield 77%) of compound **3c**. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.35 (s, 9 H), 1.45–1.55 (m, 1 H), 1.64–1.78 (m, 2 H), 1.7–1.83 (m, 4 H), 2.02–2.15 (m, 1 H), 2.25–2.35 (m, 1 H), 2.42–2.5 (m, 1 H), 2.65–2.75 (m, 1 H), 2.82–2.92 (m, 1 H), 3.1–3.18 (m, 1 H), 3.25–3.3 (m, 1 H), 4.58 (s, 1 H), 5.28 (dt, *J* = 1.0 Hz and 6.3 Hz, 1 H), 5.37 (dd, *J* = 1.0 Hz and 6.1 Hz, 1 H), 5.52 (dt, *J* = 1.0 Hz and 6.4 Hz, 1 H), 6.1 (d, *J* = 6.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.2, 24.7, 26.7, 28.3, 30.4, 47.0, 52.4, 70.5, 71.1, 84.0, 90.9, 93.0, 93.4, 99.6, 100.5, 116.1, 233.5 ppm. MS (ESI): *m*/*z* (%) = 437 (48), 373 (49), 301 (100), 285 (58), 179 (14), 160 (26).

(*R*)-Tricarbonyl[η⁶-2-(trimethylsilyl)benzaldehyde]chromium(0) (4c): Aminal **3c** (prepared from diamine **1** of 91% *ee*) was dissolved in CH_2Cl_2 and hydrolysed with 1 N HCl aqueous solution, then the organic phase was washed with a saturated aqueous solution of Na_2CO_3 and dried with $MgSO_4$. The enantiomeric excess was determined by HPLC [Chiralcel OD, 2% *i*PrOH in *n*-hexane, flow 0.5 mL min^{-1}, UV 254 nm: (*R*)-**4c**: t_R = 17.2, (*S*)-**4c**: t_R = 20.0]. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.41 (s, 9 H), 5.35–5.6 (m, 3 H), 5.78 (d, *J* = 6.3 Hz, 1 H), 9.73 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.6, 92.4, 93.2, 93.7, 97.4, 100.1, 101.2, 190.8, 230.9 ppm. $[\alpha]_D^{21}$ = +140 (*c* = 0.0015, $CHCl_3$), $[\alpha]_D^{21}$ = –147 (*c* = 0.0014, EtOH) for *ee* 91% [ref.[6c] $[\alpha]_D^{21}$ = –154 (*c* = 0.001, $CHCl_3$)].

Tricarbonylchromium(0) Complex 3d: *n*BuLi 1.6 M in hexane (1.25 mL, 2 mmol of a 1.6 M solution in *n*-hexane) was added slowly, under nitrogen, to a stirred solution of imidazolidine **2** (364 mg, 1 mmol) in dry tetrahydrofuran (10 mL) at –80 °C. The solution was stirred at –80 °C for 1.5 h and then Ph_2PCl (0.55 mL, 3 mmol) was added at –80 °C. The solution was stirred at –80 °C for 1 h and then warmed up to –50 °C. The mixture was quenched by a solution of NH_4Cl/NH_3 (1:1) (10 mL), and extracted with diethyl ether (3×10 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed to yield crude product **3d** (*de* > 99% by ^{31}P NMR). Flash chromatography on neutral Al_2O_3 (15% Et_3N in Et_2O) and recrystallisation from diethyl ether yielded 466 mg (yield 85%) of pure **3d**. ^1H NMR (400 MHz,

$CDCl_3$): δ = 0.60–0.80 (m, 1 H), 1.34–1.57 (m, 4 H), 1.66–1.93 (m, 3 H), 1.94–2.08 (m, 1 H), 2.11–2.24 (m, 1 H), 2.89 (s b, 1 H), 3.12–3.26 (m, 1 H), 4.87 (d, J = 6.3 Hz, 1 H), 5.22 (t, J = 6.1 Hz, 1 H), 5.34 (d, J = 6.0 Hz, 1 H), 5.45 (d, J = 6.3 Hz, 1 H), 6.03 (d, J = 4.6 Hz, 1 H), 7.28–7.45 (m, 10 H), 7.47–7.61 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 26.4, 28.3, 30.3, 47.4, 53.1, 70.3, 70.9, 77.2, 83.7, 91.0, 92.5, 93.6, 98.4, 105.3, 128.5, 128.9, 129.5, 134.6, 134.8, 136.2, 233.2 ppm. IR: $\tilde{\nu}$ = 2870–3056, 2366, 1983, 1887, 1410–1479, 996–1175, 623–696 cm^{-1}. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –16.38 ppm. MS (ESI): m/z (%) = 549 (19), 429 (12), 183 (18), 169 (52), 146 (78), 128 (100). $[\alpha]_D^{21}$ = –403 (c = 0.001, $CHCl_3$).

Crystal-Structure Determination: Cell dimensions and intensities were measured at 200 K with a Stoe IPDS diffractometer with graphite-monochromated Mo-K_α radiation (μ = 0.71069 Å). Data were corrected for LP and for absorption.The structure was solved by direct methods using SHELXS-97;[17] all other calculations were performed with XTAL.[18] $C_{30}H_{29}CrN_2O_3P$ (**3d**): M_r = 548.6, μ = 0.52 mm^{-1}, T_{min}/T_{max} = 0.8905/0.9416, D_x = 1.356 g cm^{-3}, tetragonal, $P4_3$, Z = 4, a = 10.4365(3), c = 24.6663(9) Å, V = 2686.7(2) Å^3; 34052 measured reflections, 5260 unique reflections of which 4324 were observable [$|F_o| > 4\sigma(F_o)$]; R_{int} for equivalent reflections 0.045. Full-matrix least-squares refinement (on F) using weight of $1/[\sigma^2(F_o) + 0.0002(F_o^2)]$ gave final values R = 0.031, wR = 0.034, for 334 variables and 4324 contributing reflections. Flack parameter:[19] x = –0.01(2). Hydrogen atoms were placed in calculated positions. CCDC-238354 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Tricarbonylchromium(0) Complex 3e: *n*BuLi (1.25 mL, 2 mmol of a 1.6 M solution in *n*-hexane) was added slowly, under nitrogen, to a stirred solution of imidazolidine **2** (364 mg, 1 mmol) in dry tetrahydrofuran (10 mL) at –80 °C. The solution was stirred at –80 °C for 1.5 h and then $(PhS)_2$ (655 mg, 3 mmol) was added at –80 °C. The solution was stirred at this temperature for 1 h and then warmed up to –50 °C. The mixture was quenched by addition of a solution of NH_4Cl/NH_3 (1:1, 10 mL), and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed to yield crude product **3e** (de > 95%). Flash chromatography on neutral Al_2O_3 (15% Et_3N in Et_2O) yielded 448 mg (yield 95%) of pure product ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53–1.69 (m, 2 H), 1.80–2.02 (m, 5 H), 2.12–2.26 (m, 1 H), 2.38–2.49 (m, 1 H), 2.56–2.68 (m, 1 H), 2.82–2.97 (m, 1 H), 2.98–3.08 (m, 1 H), 3.27–3.41 (m, 1 H), 4.56 (d, J = 6.3 Hz, 1 H), 4.98 (s, 1 H), 5.09 (t, J = 6.1 Hz, 1 H), 5.29 (t, J = 6.3 Hz, 1 H), 6.31 (d, J = 6.3 Hz, 1 H), 7.19–7.31 (m, 3 H), 7.66–7.76 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 26.4, 28.3, 30.3, 47.4, 53.1, 70.3, 70.9, 83.8, 87.8, 88.2, 92.6, 94.0, 107.2, 118.1, 127.1, 127.5, 128.8, 129.0, 129.8, 136.4, 233.2 ppm. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.10–1.24 (m, 3 H), 1.38–1.67 (m, 5 H); 1.70–1.85 (m, 1 H), 2.26–2.44 (m, 2 H), 2.95–3.07 (m, 3 H), 4.27 (dt, J = 1.0 Hz and 6.1 Hz, 1 H), 4.33–4.40 (m, 2 H), 5.12 (s, 1 H), 6.00 (dd, J = 1.0 Hz and 6.1 Hz, 1 H), 6.87–7.01 (m, 3 H), 7.66 (dd, J = 1.5 Hz and 8.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 24.7, 26.4, 27.9, 29.8, 46.9, 52.8, 70.1, 70.6, 83.7, 88.2, 88.6, 92.1, 93.3, 107.9, 117.2, 127.5, 127.7, 128.2, 129.5, 129.9, 135.8, 233.4 ppm. MS (ESI): m/z (%) = 472 (15), 359 (15), 217 (60), 197 (100), 186 (62), 159 (71), 139 (62), 127 (15). $[\alpha]_D^{21}$ = –348 (c = 0.001, $CHCl_3$).

Ferrocene Derivative 12: Ferrocenecarbaldehyde (429 mg, 2 mmol) was dissolved in 10 mL of dry diethyl ether and (*R*,*R*)-2,2′-bipyrrolidine (**1**; 280 mg, 2 mmol) was added. The reaction mixture was stirred in the presence of molecular sieves (4 Å) under N_2 at room temperature overnight. Although the conversion was quantitative, the isolated yield after crystallisation from diethyl ether was 70%. M.p. 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.2–2.0 (m, 8 H), 2.5–2.7 (m, 2 H), 2.8–3.0 (m, 4 H), 4.0–4.15 (m, 2 H), 4.1 (s, 5 H), 4.4 (s, 1 H), 4.65 (s, 1 H), 4.8 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 27.4, 29.1, 30.7, 47.9, 53.6, 66.8, 67.6, 68.1, 68.6, 69.1, 70.9, 71.3, 84.9, 89.8 ppm. $[\alpha]_D^{21}$ = –74 (c = 0.0046, $CHCl_3$).

Crystal-Structure Determination: Cell dimensions and intensities were measured at 200 K with a Stoe IPDS diffractometer with graphite-monochromated Mo-K_α radiation (μ = 0.71069 Å). Data were corrected for LP and for absorption. The structure was solved by direct methods using MULTAN 87;[20] all other calculations were performed with XTAL.[18] $[C_{19}H_{24}FeN_2]$ (**12**): M_r = 336.3, μ = 0.94 mm^{-1}, T_{min}/T_{max} = 0.7797/0.8545, D_x = 1.396 g cm^{-3}, orthorhombic, $P2_12_12_1$, Z = 4, a = 9.4335(6), b = 11.7386(8), c = 14.4525(9) Å, V = 1600.4(2) Å^3; 24851 measured reflections, 3899 unique reflections of which 3357 were observable [$|F_o| > 4\sigma(F_o)$]; R_{int} for equivalent reflections 0.028. Full-matrix least-squares refinement (on F) using weight of $1/[\sigma^2(F_o) + 0.0005(F_o^2)]$ gave final values R = 0.034, wR = 0.041, for 200 variables and 3357 contributing reflections. Flack parameter:[19] x = –0.00(2). Hydrogen atoms were retained and blocked in the last cycles. CCDC-238355 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(*S*)-2-Iodoferrocenecarbaldehyde (14): Aminal **7** (56 mg, 0.168 mmol) was dissolved in 1 mL of dry tetrahydrofuran, and 214 μL (0.214 mmol of 1 M solution in *n*-hexane) of *s*BuLi was added slowly at –78 °C. The reaction mixture was stirred at –78 °C for 2 h, then warmed up to room temperature for 1 h. 1,2-Diiodoethane (75.7 mg, 0.268 mmol) was added at –40 °C and the reaction mixture warmed to room temperature. The reaction was quenched with 0.5 mL of a 2 M solution of NaOH and extracted with diethyl ether. The organic phase was washed with a saturated solution of $N_2S_2O_3$ and dried with K_2CO_3. The crude mixture of aminals **13** (50% conversion) was then dissolved in CH_2Cl_2 and hydrolysed by two washings with a 1 N aqueous solution of HCl. The title compound was purified by flash chromatography on SiO_2 (10% Et_2O in pentane) to give 13 mg of **14**. Yield 22%, *ee* 70% (by rotation). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.3 (s, 5 H), 4.7 (m, 1 H), 4.85 (m, 1 H), 4.92 (m, 1 H), 10.05 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 70.3, 72.6, 73.8, 78.3, 79.6, 83.2, 194.4 ppm. $[\alpha]_D^{21}$ = –392 (c = 0.0013, $CHCl_3$) for 70% *ee* [ref.[15l] $[\alpha]_D^{21}$ = –558, (c = 0.0035, $CHCl_3$)].

Pd-Catalysed Allylic Substitution with Aminal 3d as Ligand:[21] A solution of ligand **3d** (5 mol-%, 20 μmol) in dichloromethane (0.4 mL) was added to $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (2 mol-%, 2.9 mg, 8 μmol) in a 30-mL Schlenk tube equipped with a magnetic stirring bar. The suspension was degassed at 0.01 Torr by three freeze-pump-thaw cycles. The Schlenk tube was sealed with a vacuum-tight Teflon stopper, evacuated, and the solution was stirred at 50 °C for 2 h. The resulting clear, yellow solution was treated successively with a solution of the allylic acetate **7** or **8** (0.395 mmol), dimethyl malonate (111 mg, 1.185 mmol) and *N*,*O*-bis(trimethylsilyl)acetamide (243 mg, 1.185 mmol) in dichloromethane (1.5 mL) and anhydrous potassium acetate (3 mol-%, 1 mg). The solution was immediately degassed by three freeze-pump-thaw cycles and the Schlenk tube was evacuated and sealed with a vacuum-tight Teflon stopper. The reaction mixture was stirred at room temperature. After 1 d, the reaction mixture was diluted with diethyl ether (50 mL),

transferred to a separating funnel, and washed twice with ice-cold saturated aqueous NH_4Cl solution. The organic phase was dried with $MgSO_4$, concentrated in vacuo and chromatographed (cyclohexane/EtOAc, 9:1) to afford the product **9** or **10** as a colourless opaque oil.

Methyl 2-Methoxycarbonyl-3,5-diphenylpent-4-enoate (9):[22] The enantiomeric excess (77%) was determined by SFC (AD column, 3% MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.53 (s, 3 H), 3.72 (s, 3 H), 3.97 (d, J = 11.0 Hz, 1 H), 4.28 (dd, J = 10.8, 9.8 Hz, 1 H), 6.35 (dd, J = 15.8, 8.8 Hz, 1 H), 6.50 (d, J = 15.8 Hz, 1 H), 7.35–7.20 (m, 10 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 49.17 (CH), 52.44 (CH_3), 52.62 (CH_3), 57.61 (CH), 126.36 (CH), 127.15 (CH), 127.55 (CH), 127.84 (CH), 128.45 (CH), 128.70 (CH), 129.06 (CH), 131.80 (CH), 136.78 ($C_{quat.}$), 140.13 ($C_{quat.}$), 167.75 (C=O), 168.17 (C=O) ppm.

Dimethyl Cyclohex-2-en-1-ylmalonate (10):[22] The enantiomeric excess (40%) was determined by GC (Chiraldex column, isotherm 100 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (dddd, J = 19.6, 11.0, 8.5, 2.5 Hz, 1 H), 1.62–1.53 (m, 1 H), 1.81–1.69 (m, 2 H), 2.02–1.98 (m, 2 H), 2.95–2.88 (m, 1 H), 3.29 (d, J = 9.5 Hz, 1 H), 3.74 (s, 3 H), 3.75 (s, 3 H), 5.53 (dd, J = 10.4, 2.2 Hz, 1 H), 5.78 (dq, J = 10.1, 2.6 Hz, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.84 (CH_2), 24.90 (CH_2), 26.60 (CH_2), 35.36 (CH_3), 52.36 (CH), 56.83 (CH), 127.29 (CH), 129.65 (CH), 168.84 (C=O), 168.90 (C=O) ppm.

Cu-Catalysed Conjugate Addition with Aminal 3d as Ligand:[14] Ligand **3d** (0.0166 mmol) and 1 mL of Et_2O were added to a solution of copper thiophenecarboxylate (CuTC; 0.008 mmol) in Et_2O (1 mL) at room temperature under nitrogen. The solution was stirred at 25 °C for 30 min and then cooled to –30 °C. Et_2Zn (1 mL, 0.5 mmol 15% in hexane) was added dropwise such that the temperature did not rise above –30 °C. The solution was stirred for 5 min, and the Michael acceptor (0.415 mmol) was then added dropwise as a solution in 0.5 mL of Et_2O. The reaction mixture was stirred at –30 °C for 12 h before being quenched by addition of 2 N HCl. Purification by flash chromatography (R_f = 0.48; silica; hexane/AcOEt, 80:20) afforded 3-ethylcyclohexanone (**11**). The enantiomeric excess (74%) was measured by chiral GC [Lipodex E, 25 m, 50 mL s^{-1}, T = 60 °C: t_R = 24.72, major enantiomer (R); t_R = 28.15, minor enantiomer (S)]. ^{1}H NMR: δ = 2.50–0.70 (m) ppm. ^{13}C NMR: δ = 25.0 (C-7), 28.6 (C-8), 31.0 (C-4), 36.0 (C-5), 38.8 (C-3), 41.1 (C-6), 47.9 (C-2), 210.9 (C-1) ppm.

Acknowledgments

The authors thank Stephane Rosset for help, Prof. E. P. Kündig for useful discussions, Dr. S. Pache for providing the (benzaldehyde) tricarbonylchromium complex, and the Swiss National Research Foundation (no. 20-068095.02) and COST action D24/0003/01 (OFES contract no. C02.0027) for financial support.

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Received September 21, 2004

