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Enantioselective synthesis and use in catalytic asymmetric addition of diethylzinc to benzaldehyde of new chiral cyclic hydroxyamino ferrocene and chromium complexes: influence of the complexation on the enantioselectivity

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Abstract

The optically active (arene)chromium complexes (+)-(*S*,1*S*)-**7–13**, (+)-(*S*,1*S*)-**20** and ferrocenyl amino alcohol (+)-(*S*,1*S*)-**14–17** were synthesized from enantiomerically pure tricarbonyl(1-indanone)chromium (ee>98), tricarbonyl(1-tetralone)chromium (ee>99) and 1,2-(α-oxotetramethylene)ferrocene (ee>98). These compounds were used as chiral catalysts in the asymmetric addition of diethylzinc to benzaldehyde: 1-phenylpropanol has been obtained in up to 70% enantiomeric excess. The influence of the metallic group on the enantioselectivities has been studied.

1. Introduction

In the last decade, the development of enantioselective reactions and the role of the asymmetric catalysts in them has seen enormous growth.[1] For example, the enantioselective alkylation with dialkylzinc of prochiral carbonyl compounds such as aldehydes, using optically active amino alcohols as catalysts has received special attention.[2] Ferrocenyl derivatives exhibiting a planar chirality have also been proven to be highly enantioselective ligands for a variety of catalytic asymmetric reactions.[3] Another class of compounds, tricarbonyl(η^6-arene)chromium complexes have been less studied as chiral auxiliairies.[4] However, several 1,2-disubstituted ferrocenyl[5] or tricarbonyl(η^6-arene)chromium[6] amino alcohols have shown good enantioselectivities in the alkylation of aldehydes.

In a preliminary communication,[7] we have reported the synthesis of chiral substituted indanol chromium complexes and their application as catalysts for the addition of diethylzinc to benzaldehyde.

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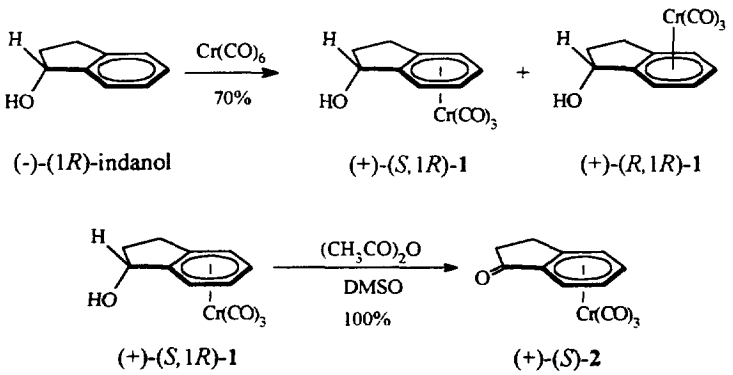
We have shown that the presence of a tricarbonyl chromium unit induced a significant increase of the enantioselectivity. In this paper, we report the enantioselective synthesis of novel cyclic tricarbonyl(η^6-arene)chromium and ferrocenyl amino alcohols and their effectiveness as chiral ligands.

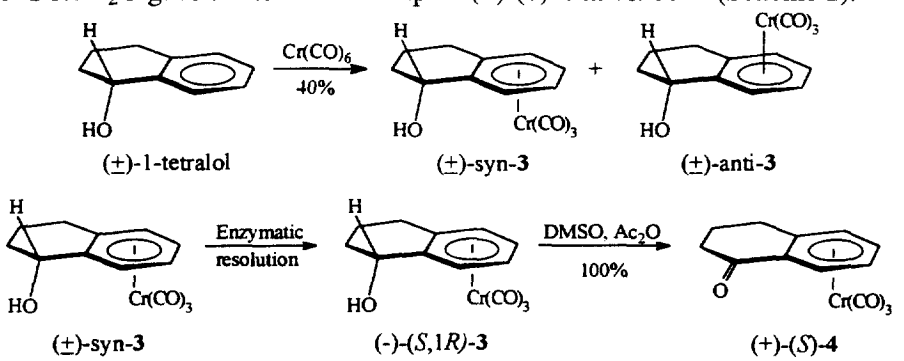
2. Results and discussion

We first established a synthesis of the homochiral 1-indanone–chromium complex (+)-(*S*)-**2**.[8] Thermolysis of chromium hexacarbonyl with enantiomerically pure (−)-(1*R*)-indanol led to an 80/20 mixture of *syn*-[(+)-(*S*,1*R*)]-**1** and *anti*-[(+)-(*R*,1*R*)]-**1** indanol complexes in 70% yield. The diastereomers[9] were separated by silica gel column chromatography. A quantitative oxidation of the (+)-(*S*,1*R*)-**1** in the presence of DMSO/Ac_2O[10] gave the indanone complex (+)-(*S*)-**2** in ee>98% (Scheme 1).



Scheme 1.

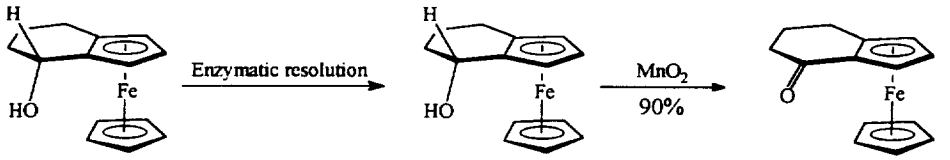
The synthesis of the homochiral 1-tetralone–chromium complex (+)-(*S*)-**4** in ee>99% was performed by complexation of the racemic tetralol followed by an enzymatic resolution. The thermolysis of chromium hexacarbonyl with racemic 1-tetralol led to a 90/10 mixture of *syn*- and *anti*-1-tetralol complexes **3** in 40% global yield.[11] Both racemic diastereomers were separated by silica gel column chromatography. After the enzymatic resolution with CCL (*Candida cylindracea* lipase), the *syn*-[(−)-(*S*,1*R*)]-1-tetralol **3** was obtained with ee>99%.[12,13] A quantitative oxidation of (−)-(*S*,1*R*)-**3** in the presence of DMSO/Ac_2O gave the tetralone complex (+)-(*S*)-**4** in ee>99% (Scheme 2).



Scheme 2.

The synthesis of the (±)-1,2-(α-hydroxytetramethylene)ferrocene **5** from ferrocene was performed as described in the literature.[14] After an enzymatic kinetic resolution of the alcohol by using

CCL lipase,[15] the oxidation of the alcohol function in the presence of MnO_2 gave (+)-1,2-(α-oxotetramethylene)ferrocene (+)-(*S*)-**6** in ee>98% (Scheme 3).



(±)-**5** (+)-(*S*,1*R*)-**5** (+)-(*S*)-**6**

Scheme 3.

The complexes (+)-(*S*)-**2,** (+)-(*S*)-**4** and (+)-(*S*)-**6** were then converted to (+)-(*S*,1*S*)-amino alcohol complexes **7–17** and **21**. Thus, the complexes (+)-(*S*,1*S*)-**7–17** were obtained in one step through the reaction of (+)-(*S*)-**2**, (+)-(*S*)-**4**, and (+)-(*S*)-**6** with the appropriate nucleophile (Table 1). Accordingly, (+)-(*S*,1*S*)-**7**, (+)-(*S*,1*S*)-**11** and (+)-(*S*,1*S*)-**14** were synthesized at −78°C through reaction between the corresponding ketone **2**, **4** and **6** and 2-lithiopyridine obtained from 2-bromopyridine and *n*-butyllithium.[16] Addition of 2-picolyllithium gave, after workup, (+)-(*S*,1*S*)-**8**, (+)-(*S*,1*S*)-**12** and (+)-(*S*,1*S*)-**15**.[17] Finally, the addition of 2-(N,N-dimethylamino)phenyllithium obtained from the reaction of dimethylaniline and *n*-butyllithium/TMEDA[17] gave the complexes (+)-(*S*,1*S*)-**9**, (+)-(*S*,1*S*)-**13** and (+)-(*S*,1*S*)-**16**. Futhermore, the amino alcohol complexes (+)-(*S*,1*S*)-**10** and (+)-(*S*,1*S*)-**17** were obtained at −78°C through the reaction between the ketone complexes (+)-(1*S*)-**1** or (+)-(1*S*)-**6** with 2-lithio(N,N-dimethylbenzylamine),[17] obtained from 2-bromo-N,N-dimethylbenzylamine and *n*-butyllithium. The condensation of the 2-(dimethylaminomethyl)phenyllithium with the ketone (+)-(1*S*)-**4** was unsuccessful. The yields have been summarized in Table 1. The moderate yields have been attributed to the enhanced acidity of the methylene group adjacent to the ketone.

The picolylferrocene compound (+)-(*S*,1*S*)-**15** was highly unstable in an acidic environment and led to the dehydrated complex **18**. Both complexes (+)-(*S*,1*S*)-**8** and (+)-(*S*,1*S*)-**12** were stable under similar conditions (Scheme 4).

Complex (+)-(*S*,1*S*)-**20** was obtained in three steps. First, a Reformatsky reaction was conducted with (+)-(*S*)-**2** that gave, after workup, a single complex (+)-(*S*,1*S*)-**19** in 69% yield. Then, a reduction with lithium aluminium hydride followed by a bismethylation with methyl iodide led to the complex (+)-(*S*,1*S*)-**20** in 30% overall yield (Scheme 5).

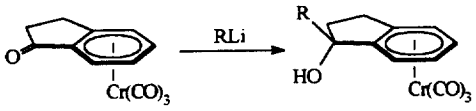
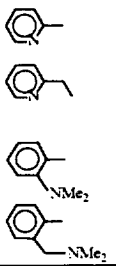
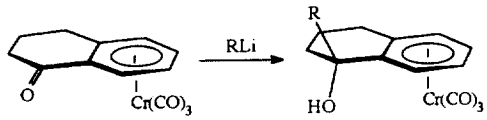
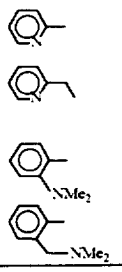
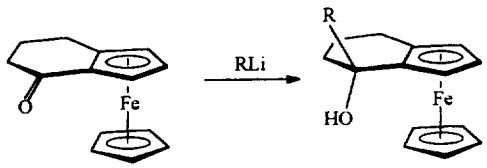
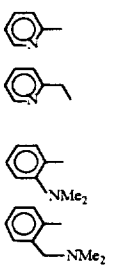
Unfortunately, under the same conditions no reaction occurred with (+)-(*S*)-**4** while the ferrocenic complex (+)-(*S*)-**6** led to the vinylic complex (+)-(*S*)-**21** in 56% yield (Scheme 6).

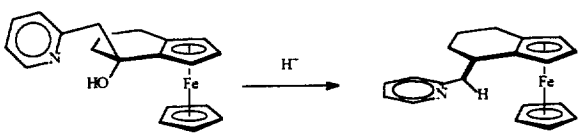
Finally, the tricarbonylchromium complexes (+)-(*S*,1*S*)-**7–13** and (+)-(*S*,1*S*)-**20** were quantitatively decomplexed by photolysis in dilute Et_2O solution to give the coresponding free ligands **22–29** (Scheme 7).

The reaction of diethylzinc with benzaldehyde was carried out in the presence of amino alcohols in order to examine the structural effect of the complexation upon enantioselectivity (Scheme 8). The reaction conditions and results are summarized in Table 2.

1-Phenylpropanol is produced with low to good enantiomeric excesses and the preferred configuration was the (*R*)-alcohol. First, we examined the catalytic activities of amino alcohols derived from indanol. In many cases, we have observed a dramatic increase of the enantioselectivities when the catalyst was complexed with a tricarbonyl chromium group as the compounds (+)-(*S*,1*S*)-**7–9** and (+)-(*S*,1*S*)-**20** (entries 1–6 and 9–10, Table 2). The gain in ee brought about by such coordination was in the 33–60% enantiomeric excess range. Here, the effect is more pronounced than in the case reported by Jones[6b] where the uncomplexed catalyst was already highly enantioselective. Moreover, Uemura[6a,6c] has obtained a similar gain (69%) in enantiomeric excess in the asymmetric ethylation of benzaldehyde

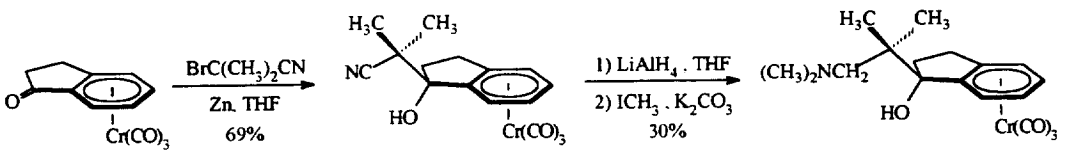
Table 1
Synthesis of amino alcohol complexes (+)-(*S*,1*S*)-**7**–**17**

Reaction	R	Catalyst	Yield (%)
 (+)-(*S*)-**2** (+)-(*S*,1*S*)-**7-10**		(+)-(*S*,1*S*)-**7**	71
		(+)-(*S*,1*S*)-**8**	30
		(+)-(*S*,1*S*)-**9**	40
		(+)-(*S*,1*S*)-**10**	40
 (+)-(*S*)-**4** (+)-(*S*,1*S*)-**11-13**		(+)-(*S*,1*S*)-**11**	68
		(+)-(*S*,1*S*)-**12**	71
		(+)-(*S*,1*S*)-**13**	15
		-	0
 (+)-(*S*)-**6** (+)-(*S*,1*S*)-**14-17**		(+)-(*S*,1*S*)-**14**	64
		(+)-(*S*,1*S*)-**15**	55
		(+)-(*S*,1*S*)-**16**	37
		(+)-(*S*,1*S*)-**17**	55



(+)-(*S*,1*S*)-**15** (+)-(*S*)-**18**

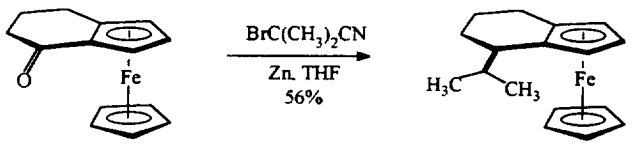
Scheme 4.



(+)-(*S*)-**2** (+)-(*S*,1*S*)-**19** (+)-(*S*,1*S*)-**20**

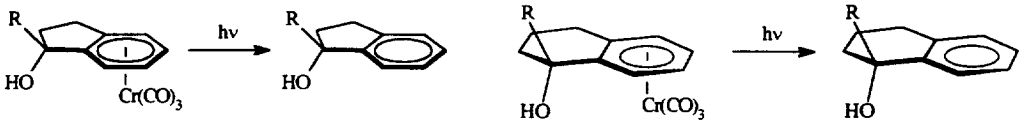
Scheme 5.

using (1,2-disubstituted arene)chromium complexes. Among these chiral chromium complexes, complex (+)-(*S*,1*S*)-**8** with a picolyl substituent gave a high degree of enantioselectivity (entry 3).



(+)-(*S*)-**6** (+)-(*S*)-**21**

Scheme 6.



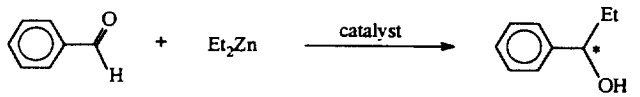
(+)-(*S*,1*R*)-**7**
(+)-(*S*,1*R*)-**8**
(+)-(*S*,1*R*)-**9**
(+)-(*S*,1*R*)-**10**
(+)-(*S*,1*R*)-**20**

(+)-(1*R*)-**22**
(+)-(1*S*)-**23**
(+)-(1*R*)-**24**
(+)-(1*R*)-**25**
(+)-(1*R*)-**26**

(+)-(*S*,1*S*)-**11**
(+)-(*S*,1*S*)-**12**
(+)-(*S*,1*S*)-**13**

(+)-(1*R*)-**27**
(+)-(1*S*)-**28**
(+)-(1*R*)-**29**

Scheme 7.



Scheme 8.

However, contrary to preceding papers,[6,7] the $Cr(CO)_3$ complexation of the catalyst (+)-(1*R*)-**25** decreased the enantioselectivity (entries 7 and 8). Indeed, the complex (+)-(*S*,1*S*)-**10** gave the 1-phenylpropanol in 62% ee (entry 7) while the corresponding $Cr(CO)_3$-free chiral amino alcohol (+)-(1*R*)-**25** increased the enantioselectivity to 87% ee under the same conditions (entry 8). The origin of the selectivity difference between catalysts can be explained by the model depicted in Fig. 1, which is based on that proposed by Uemuera[6c] and Watanabe.[5a] Thus, in the case of the uncomplexed catalyst (+)-(1*R*)-**25**, the molecular model suggested that the zinc alkoxide forms a seven-membered ring with a chair conformation (transition state **A**). The ethylation occurs in a six-membered cyclic transition state with an equatorial orientation of the alkyl or phenyl group of the aldehyde. Thus, nucleophilic attack of the ethyl group onto the Re face of the aldehyde leds to the (*R*)-1-phenylpropanol. On the contrary, this assembly is not possible from the complexed catalyst (+)-(*R*,1*R*)-**10**. Indeed, the presence of the tripod $Cr(CO)_3$ forces the seven-membered ring to adopt a boat conformation to avoid the steric interaction with the zinc atom (transition state **B**).

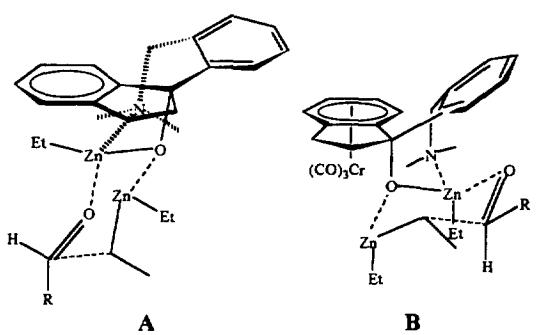
The influence of the skeleton structure was next studied by comparison of the results obtained by catalysts possessing a five-membered-ring side chain or a six-membered-ring side chain in (arene)chromium complexes. Contrary to the substituted indanol, the amino alcohols derived from tetralol showed no positive influence on the enantioselectivity with $Cr(CO)_3$ complexation. The enantioselectivities were very low (Table 2, entries 11–16) and the greatest difference (17% ee) was obtained between the amino alcohols (+)-(*S*,1*S*)-**12** and (+)-(1*S*)-**28** (entries 13 and 14). Thus, we suggest that the high flexibility of the hexane ring could explain this result. Furthermore, the selectivities of the ferrocenyl catalysts were modest (4 to 35%, entries 17–20). However with the same nitrogen substituent, the ferrocenyl aminoalcohol showed a better enantioselectivity than the corresponding chromium complex (22% ee for (+)-(*S*,1*S*)-**12** versus 35% for (+)-(*S*,1*S*)-**15**, entry 13 versus entry 18).

Surprising results were obtained in the presence of catalysts with an o-dimethylanilino group (entries 5, 6, 15, 16, 19) which led to the opposite configuration of the 1-phenylpropanol.

Table 2
Enantioselective addition of diethylzinc to benzaldehyde in presence of chiral catalyst

Entry[a]	Catalyst	time (h)	yield (%)[b]	ee (%)[c]	configuration[d]
1	(+)-(*S*,1*S*)-**7**	90	92	47	R
2	(+)-(1*R*)-**22**	90	89	9	R
3	(+)-(*S*,1*S*)-**8**	18	97	70	R
4	(+)-(1*S*)-**23**	18	96	10	R
5	(+)-(*S*,1*S*)-**9**	18	92	42	S
6	(+)-(1*R*)-**24**	18	77	19	S
7	(+)-(*S*,1*S*)-**10**	18	77	62	R
8	(+)-(1*R*)-**25**	18	95	87	R
9	(+)-(*S*,1*S*)-**20**	25	96	57	R
10	(+)-(1*R*)-**26**	25	74	0	-
11	(+)-(*S*,1*S*)-**11**	18	77	14	R
12	(+)-(1*R*)-**27**	18	73	14	R
13	(+)-(*S*,1*S*)-**12**	18	77	22	R
14	(+)-(1*S*)-**28**	18	73	5	R
15	(+)-(*S*,1*S*)-**13**	18	74	4	S
16	(+)-(1*R*)-**29**	18	76	4	S
17	(+)-(*S*,1*S*)-**14**	18	95	15	R
18	(+)-(*S*,1*S*)-**15**	18	83	35	R
19	(+)-(*S*,1*S*)-**16**	18	76	15	S
20	(+)-(*S*,1*S*)-**17**	18	76	31	R

[a] the reactions were performed at room temperature using 5% of the catalyst. [b] determined by ^{1}H NMR. [c] determined by GC analysis on FS-Cyclodex β-I/P (30 m x 0.24). [d] determined from the sign of the specific rotation.



A B

Fig. 1.

Table 3
Enantioselective addition of diethylzinc to aldehydes in presence of chiral catalysts (+)-(*S*,1*S*)-**10** and (+)-(1*R*)-**25**

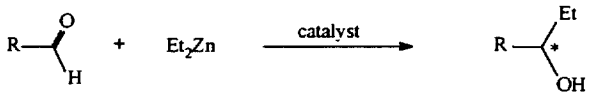
Entry[a]	R	Catalyst (mol %)	T°C	Yield [b] (%)	ee (%)[c] (config[d])
1	C_6H_5	(+)-(*S*,1*S*)-**10** (5)	0	75	58 (R)
2	C_6H_5	(+)-(*S*,1*S*)-**10** (5)	20	77	62 (R)
3	C_6H_5	(+)-(1*R*)-**25** (5)	0	99	88 (R)
4	C_6H_5	(+)-(1*R*)-**25** (5)	20	95	87 (R)
5	C_6H_5	(+)-(1*R*)-**25** (10)	20	95	90 (R)
6	pCl-C_6H_5	(+)-(1*R*)-**25** (10)	20	95	87 (R) [e]
7	pOMe-C_6H_5	(+)-(1*R*)-**25** (10)	20	97	63 (R) [f]
8	nC_6H_{13}-	(+)-(1*R*)-**25** (10)	20	99	74 (R) [g]

[a] the reactions were performed in dry toluene during 16 hours. [b] determined by ^1H NMR. [c] determined by GC analysis on FS-Cyclodex β-I/P (30 m x 0.24). [d] determined from the sign of the specific rotation. [e] $[\alpha]_D^{20}$ = +25.1 (c = 5.1, $CHCl_3$); lit.[18a] ee 100% : $[\alpha]_D^{20}$ = +28.59 (c = 5.1, C_6H_6). [f] $[\alpha]_D^{20}$ = +23.2 (c = 5.1, C_6H_6); lit.[18a] ee 100% : $[\alpha]_D^{20}$ = +36.53 (c = 5.1, C_6H_6). [g] $[\alpha]_D^{20}$ = +7.1 (c = 8.3, $CHCl_3$); lit.[18b] ee 100% : $[\alpha]_D^{20}$ = +9.6 (c = 8.3, $CHCl_3$).

Increasing the amount of (+)-(1*R*)-**25** from 5 to 10 mol% showed a slight influence on both the chemical yield and the ee. When 5 mol% of amino alcohol was used, (*R*)-1-phenylpropanol (87% ee) was obtained in 95% yield (Table 3, entry 4). The ee increased weakly to 90% when 10 mol% of (+)-(1*R*)-**25** was used (entry 5).

For (+)-(*S*,1*S*)-**10**, the influence of the temperature on enantioselectivity was also examined. Greater enantioselectivity was observed when the reaction of benzaldehyde and Et_2Zn catalysed by 5 mol% of (+)-(*S*,1*S*)-**10** was performed at 20°C (62% ee, entry 2) than when it was performed at a lower temperature 0°C (58% ee, entry 1). No effect of temperature was observed in the case of the corresponding $Cr(CO)_3$-free amino alcohol (+)-(1*R*)-**25** (87% ee at 20°C versus 88% at 0°C, entry 4 versus entry 3).

The results of (+)-(1*R*)-**25** catalysed enantioselective addition of diethylzinc to other aromatic (entries 6 and 7) and aliphatic (entry 8) aldehydes are shown in Table 3 (Scheme 9). A diminution of the enantioselectivity was obtained in the ethylation of p-methoxybenzaldehyde (entry 7) and heptanal (entry 8).



Scheme 9.

3. Conclusion

New chiral amino alcohols bearing arene tricarbonylchromium or ferrocenyl moities have been prepared. In general, the presence of $Cr(CO)_3$ and the steric hindrance in the benzylic alcohol are important factors in the catalytic asymmetric ethylation of aldehydes. The synthesis of ferrocenyl derivatives homologous of indanone–$Cr(CO)_3$ and their application in catalysis are under development.

4. Experimental section

Reactions were performed in oven-dried glassware under an atmosphere of nitrogen. Air and moisture-sensitive compounds were introduced via syringe through a rubber septum. Tetrahydrofuran and toluene were distilled from sodium/benzophenone ketyl immediately before use. Dibutylether was distilled from sodium. Hexacarbonylchromium was obtained from Strem chemicals and the *Candida cylindracea* lipase (CCL, Type VII, 943 unit/mg) from Sigma. All other reagents were obtained from Aldrich and used without purification. Chromatography was performed on SiO_2 (Merck, 70–230 mesh, Kieselgel 60). ^1H NMR spectra were measured with a Bruker AC 300 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard, mass spectra with a RIBER 10-10 or Concept II H–H (Kustros Analytical, FAB) mass spectrometer, optical rotations with a Perkin–Elmer 241 polarimeter at wavelength 589 nm (sodium D line). Enantiomeric excesses were determined using a gas chromatograph equipped with a chiral column (FS-Cyclodex β-I/P, 30 m×0.24). Melting points were obtained on a Kofler apparatus and are uncorrected.

4.1. *General procedure for preparation of tricarbonyl(arene)chromium complexes*

A mixture of arene, hexacarbonylchromium in dibutylether (15 ml) and THF (3 ml) was heated at 130°C under nitrogen until the formation of the first trace of green precipitate was observed. The cooled solution was filtered through Celite and the solvent evaporated to give the crude product.

4.1.1. *(+)-(S,1R) and (+)-(R,1R)-Tricarbonyl(indanol)chromium* **1**

Thermolysis of $Cr(CO)_6$ (2.44 g, 12 mmol) with (−)-(1*R*)-indanol (1.34 g, 10 mmol) under standard conditions (72 h) followed by work-up gave a yellow oil. The residue was chromatographed on silica gel with diethylether:hexane (20:80) to give chromium complex *syn*-(+)-(*S*,1*R*)-**1** (918 mg, 34%) and *anti*-(+)-(*R*,1*R*)-**1** (216 mg, 8%).

syn-(+)-(*S*,1*R*)-Tricarbonyl(indanol)chromium **1**: $[\alpha]_D$=+61 (c=1.000, $CHCl_3$); ^1H NMR ($CDCl_3$) 5.70 (d, *J* 6.4 Hz, 1H), 5.45 (t, *J* 6.4 Hz, 1H), 5.25 (t, *J* 6.4 Hz, 1H), 5.15 (d, *J* 6.4 Hz, 1H), 5.05 (t, *J* 6.2 Hz, 1H), 2.70 (m, 2H), 2.50 (m, 1H), 1.75 (m, 1H).

anti-(+)-(*R*,1*R*)-Tricarbonyl(indanol)chromium **1**: ^1H NMR ($CDCl_3$) 5.65 (d, *J* 6.3 Hz, 1H), 5.40 (m, 2H), 5.20 (d, *J* 6.3 Hz, 1H), 5.00 (t, *J* 6.3 Hz, 1H), 3.10, 2.50, 2.35, 2.00 (4m, 4H).

4.1.2. *(±)-Tricarbonyl(1-tetralol)chromium* **3**

Thermolysis of $Cr(CO)_6$ (2.44 g, 12 mmol) with (±)-1-tetralol (1.48 g, 10 mmol) under standard conditions (72 h) followed by work-up gave a yellow oil. The residue was chromatographed on silica gel with diethylether:hexane (20:80) to give chromium complex *syn*-(±)-**3** (970 mg, 34%) and *anti*-(±)-**3** (110 mg, 4%).

syn-(±)-Tricarbonyl(1-tetralol)chromium **3**: ^1H NMR ($CDCl_3$) 5.80 (d, *J* 6.1 Hz, 1H), 5.50 (t, *J* 6.1 Hz, 1H), 5.10 (m, 2H), 4.52 (m, 1H), 2.71–2.50 (m, 2H), 2.20–1.92 (m, 2H), 1.73–1.50 (m, 2H).

anti-(±)-Tricarbonyl(1-tetralol)chromium **3**: ^1H NMR ($CDCl_3$) 5.71 (d, *J* 6.1 Hz, 1H), 5.31 (t, *J* 6.1 Hz, 1H), 5.20 (m, 1H), 5.13 (m, 1H), 4.50 (m, 1H), 2.70–2.51 (m, 2H), 2.14–1.90 (m, 2H), 1.71–1.62 (m, 2H).

4.2. General procedure for the enzymatic resolution

Racemic alcohol (0.7 mmol) was dissolved in *t*-butylmethylether (8 ml). CCL (480 mg) and vinylacetate (3 mmol) were added. The mixture was continuously stirred (300 rpm) at 45°C. After 18 h, the catalyst was removed by filtration and the solvent was evaporated under vacuum. The ester and the unreacted alcohol were isolated by silica gel column chromatography. The ester was converted into the alcohol by alkaline hydrolysis. The optically active ester was dissolved in a 1 M solution of sodium hydroxyde (10 ml) in ethanol (10 ml). After extraction, the solvent was evaporated under vacuum. Column chromatography afforded optically active alcohol.

4.2.1. Resolution of syn-(±)-tricarbonyl(1-tetralol)chromium 3

Following the general procedure, *syn*-(±)-tricarbonyl(1-tetralol)chromium **3** (199 mg, 0.7 mmol) was dissolved in *t*-butylmethylether (8 ml). CCL (480 mg) and vinylacetate (3 mmol) were added. Work-up and column chromatography gave alcohol complex (+)-(*R*,1*S*)-**3** (145 mg, 73%, ee=22%) and ester complex (85 mg, 26%, ee=99%). The alkaline hydrolysis of the ester gave the alcohol (−)-(*S*,1*R*)-**3** (52 mg, 100%). (−)-(*S*,1*R*)-**3**: $[\alpha]_D$=−20 (c=1.450, $CHCl_3$). (+)-(*R*,1*S*)-**3**: $[\alpha]_D$=+20 (c=1.450, $CHCl_3$).

^{1}H NMR analysis were in good agreement with the racemic tetralol chromium complex. The absolute configuration was established by comparison of the specific rotation of (−)-(*S*,1*R*)-**3** with literature data.[13]

4.3. General procedure for oxidation of the alcohol complex

The alcohol complex (1 mmol) was dissolved in a mixture of acetic anhydride (10 ml) and DMSO (10 ml). After stirring at room temperature, the solution was hydrolyzed by an addition of water (10 ml) and extracted with Et_2O. The organic layer was washed with a saturated aqueous $NaHCO_3$ solution. The solvent was evaporated under vacuum. The orange crystals were recrystalised by a mixture of pet. ether:diethyl ether.

4.3.1. (+)-(S)-Tricarbonyl(indanone)chromium 2

Following the general procedure, indanol complex (+)-(*S*,1*R*)-**1** (270 mg, 1 mmol) was dissolved in a mixture of acetic anhydride (10 ml) and DMSO (10 ml) for 6 h. Work-up gave the ketone complex (+)-(*S*)-**2** (241 mg, 90%) as red crystals, m.p. 142–144°C; $[\alpha]_D$=+304 (c=1.165, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 6.00 (d, *J* 6.4 Hz, 1H), 5.69 (t, *J* 6.4 Hz, 1H), 5.41 (d, *J* 6.4 Hz, 1H), 5.23 (t, *J* 6.4 Hz, 1H), 3.12 (m, 2H), 2.68 (m, 2H).

4.3.2. (+)-(S)-Tricarbonyl(tetralone)chromium 4

Following the general procedure, tetralol complex (+)-(*S*,1*R*)-**3** (284 mg, 1 mmol) was dissolved in a mixture of acetic anhydride (10 ml) and DMSO (10 ml) for 18 h. Work-up gave the ketone complex (+)-(*S*)-**4** (254 mg, 90%) as red crystals, m.p. 118–120°C; $[\alpha]_D$=+869 (c=0.99, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 6.20 (d, *J* 6.7 Hz, 1H), 5.58 (t, *J* 6.7 Hz, 1H), 5.31 (t, *J* 6.7 Hz, 1H), 5.10 (d, *J* 6.7 Hz, 1H), 3.00 (m, 1H), 2.69 (m, 2H), 2.43 (m, 1H), 2.17 (m, 2H).

4.3.3. (±)-1,2-(α-Hydroxytetramethylene)ferrocene 5

Compound **5** was prepared by methods described in the literature.[14]

4.3.4. Enzymatic resolution of (±)-1,2-(α-hydroxytetramethylene)ferrocene 5

Following the general procedure, (±)-1,2-(α-hydroxytetramethylene)ferrocene **5** (560 mg, 2.8 mmol) was dissolved in *t*-butylmethylether (35 ml). CCL (2.2 g) and vinylacetate (1.3 ml, 14 mmol) were added. Work-up and column chromatography gave alcohol complex (−)-(*R*,1*S*)-**5** (520 mg, 73%) and ester complex (225 mg, 27%). The alkaline hydrolysis of the ester gave the alcohol (+)-(*S*,1*R*)-**5** (193 mg, 100%) as a reddish yellow oil, ee=98%; $[\alpha]_D$=+42 (c=0.66, EtOH) (lit.,[15] $[\alpha]_D$=+43); ^{1}H NMR ($CDCl_3$) 4.38–4.10 (m, 9H), 2.50–1.54 (m, 6H). The ee value of (+)-(*S*,1*R*)-**5** was determinated by chiral HPLC analysis with a Daicel Chiralcel OD column.

4.3.5. Oxidation of (+)-(S,1R)-1,2-(α-hydroxytetramethylene)ferrocene 5

MnO_2 (500 mg, 5.7 mmol) was added to a solution of complex (130 mg, 0.5 mmol) in CH_2Cl_2 (20 ml). After stirring at room temperature for 2 h, the mixture was filtered through Celite and the solvent evaporated by vacuum. The ketone complex (+)-(*S*)-**6** was purified by silica gel column chromatography to yield red crystals (126 mg, 98%), m.p. 78–80°C; $[\alpha]_D$=+569 (c=0.05, EtOH); ^{1}H NMR ($CDCl_3$) 4.80 (m, 1H), 4.51 (d, *J* 2.6 Hz, 2H), 4.19 (s, 5H), 2.65 (m, 2H), 2.51–2.10 (m, 4H).

4.4. General procedure for the Reformatsky reaction

The ketone complex was dissolved in dry THF (40 ml) with zinc dust and $HgCl_2$ in a round bottomed flask equipped with a magnetic stirrer, a dropping funnel and a condenser. The resulting solution was refluxed for 5 min and isobutyrobromonitrile (0.8 ml, 8.4 mmol) was added dropwise. After refluxing for 45 min, the mixture was cooled at room temperature, quenched by an addition of a saturated solution of ammonium chloride and extracted with Et_2O. The solvent was evaporated under vacuum.

4.4.1. (+)-(S,1S)-Tricarbonyl[1-(1-cyanoisopropyl)indanol]chromium 19

Following the general procedure, complex (+)-(*S*)-**2** (405 mg, 1.51 mmol) was dissolved in dry THF (40 ml) with zinc dust (614 mg, 9 mmol) and $HgCl_2$ (30 mg). Isobutyrobromonitrile (0.8 ml, 8.4 mmol) was added. Work-up and column chromatography gave the complex (+)-(*S*,1*S*)-**19** as yellow crystals (350 mg, 69%), m.p. 134–136°C; $[\alpha]_D$=+100 (c=0.37, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 6.00 (d, *J* 6 Hz, 1H), 5.61 (t, *J* 6 Hz, 1H), 5.30 (d, *J* 6 Hz, 1H), 5.12 (t, *J* 6 Hz, 1H), 2.85 (m, 1H), 2.55 (m, 1H), 2.12 (m, 1H), 1.51 (s, 3H), 1.45 (s, 3H); MS: (m/z) 337 (M^+, 50), 281 (20), 253 (100); anal. calcd for $C_{16}H_{13}CrNO_4$: C, 56.98; H, 4.48; N, 4.15. Found: C, 56.47; H, 4.61; N, 4.13.

4.4.2. (+)-(S,1S)-Tricarbonyl[1-(2,2-dimethyl-N,N-dimethylaminoethyl)indanol]chromium 20

A solution of complex (+)-(*S*,1*S*)-**19** (260 mg, 0.77 mmol) in THF (30 ml) was added under an N_2 atmosphere to a suspension of lithium aluminium hydride (100 mg, 2.6 mmol) in dry THF (20 ml). After stirring for 1 h at room temperature, the mixture was quenched by an addition of a saturated aqueous ammonium chloride solution and extracted with Et_2O. The solvent was evaporated under vacuum. The crude product was dissolved in acetonitrile (20 ml) in the presence of potassium bicarbonate (1.1 g, 8 mmol) and methyl iodide (0.5 ml, 8 mmol). The solution was stirred for 15 h at room temperature and was quenched by a saturated solution of $NaHCO_3$. After extraction with Et_2O, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography to yield complex (+)-(*S*,1*S*)-**20** (80 mg, 30%) as yellow crystals, m.p. 166–168°C; $[\alpha]_D$=+96 (c=1.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 5.72 (d, *J* 6.1 Hz, 1H), 5.45 (t, *J* 5.9 Hz, 1H), 5.27 (d, *J* 6.0 Hz, 1H), 5.11 (t, *J* 5.9 Hz, 1H), 2.75 (m, 2H), 2.42–2.11 (m, 4H), 2.32 (s, 6H), 1.20 (s, 3H), 0.62 (s, 3H); MS: (m/z) 369 (M^+, 10), 313 (27),

285 (30), 267 (25), 227 (50); anal. calcd for $C_{18}H_{23}CrNO_4$: C, 58.54; H, 6.23; N, 3.79. Found: C, 58.89; H, 6.21; N, 3.87.

4.4.3. (+)-(S,1S)-α-Dimethylpropylidene[3](1,2)-ferrocenophane ***21***

Following the general procedure, complex (+)-(*S*)-**6** (242 mg, 0.95 mmol) was dissolved in dried THF (30 ml) with zinc dust (386 mg, 5.6 mmol) and $HgCl_2$ (18.9 mg). Isobutyrobromonitrile (0.5 ml, 5.3 mmol) was added. Work-up and column chromatography gave the complex (+)-(*S*,1*S*)-**21** as a red–orange oil (150 mg, 56%); $[\alpha]_D$=+1072 (c=1.484, Et_2O); ^1H NMR ($CDCl_3$) 4.40 (m, 1H), 4.13 (m, 1H), 4.05 (m, 1H), 4.00 (m, 5H), 2.75 (m, 2H), 2.35 (m, 1H), 2.01 (s, 3H), 1.98 (m, 3H), 1.82 (s, 1H); MS FAB: (m/z) 280 (M^+, 100), 237 (28), 121 (28); anal. calcd for $C_{17}H_{20}Fe$: C, 72.87; H, 7.19. Found: C, 72.97; H, 7.09.

4.5. General procedure for the condensation of the 2-lithiopyridine

n-Butyllithium (150 μl, 2.5 M in hexane, 0.42 mmol) was added dropwise to a solution of 2-bromopyridine (40 μl, 0.42 mmol) in dry THF (5 ml) at −78°C. After 20 min, the orange solution of 2-lithiopyridine was introduced into a solution of ketone (0.37 mmol) in dry THF (10 ml) at −78°C. The reactive mixture was stirred and allowed to reach room temperature. After 3 h, the mixture was quenched slowly by a solution of HCl (1 N, 10 ml). The reaction solution was diluted with water (10 ml) and extracted with Et_2O. The aqueous layer was neutralised by a direct addition of potassium bicarbonate and extracted with Et_2O. The solvent was evaporated under vacuum. The crude product was purified by silica gel column chromatography.

4.5.1. (+)-(S,1S)-Tricarbonyl[1-(2-pyridinyl)indanol]chromium ***7***

Following the general procedure for tricarbonylindanonechromium (+)-(*S*)-**2** (99 mg, 0.37mmol), complex (+)-(*S*,1*S*)-**7** was obtained as yellow crystals (91 mg, 71%), m.p. 116°C; $[\alpha]_D$=+20.7 (c=3.35, $CHCl_3$); ^1H NMR ($CDCl_3$) 8.53 (d, *J* 5.0 Hz, 1H), 7.75 (t, *J* 5.0 Hz, 1H), 7.21 (t, *J* 5.0 Hz, 2H), 5.50 (d, *J* 6.1 Hz, 1H), 5.41 (t, *J* 6.1 Hz, 1H), 5.34 (d, *J* 6.1 Hz, 1H), 5.17 (t, *J* 6.1 Hz, 1H), 3.00 (m, 2H), 2.51 (m, 2H); MS: (m/z) 347 (M^+, 54), 291 (79), 263 (33), 245 (40); anal. calcd for $C_{17}H_{13}CrNO_4$: C, 58.79; H, 3.77; N, 4.03. Found: C, 58.90; H, 3.90; N, 3.97.

4.5.2. (+)-(S,1S)-Tricarbonyl[1-(2-pyridinyl)-1-tetralol]chromium ***11***

Following the general procedure for tricarbonyltetraloneolchromium (+)-(*S*)-**4** (104 mg, 0.37 mmol), complex (+)-(*S*,1*S*)-**11** was obtained as a yellow oil (90 mg, 71%); $[\alpha]_D$=+184 (c=0.456, Et_2O); ^1H NMR ($CDCl_3$) 8.50 (m, 1H), 7.71 (t, *J* 7.7 Hz, 1H), 7.21 (m, 2H), 5.54 (t, *J* 6.6 Hz, 1H), 5.47 (d, *J* 6.6 Hz, 1H), 5.12 (d, *J* 6.6 Hz, 1H), 5.10 (t, *J* 6.6 Hz, 1H), 2.86 (m, 2H), 2.13 (m, 4H); MS: (m/z) 361 (M^+, 50), 305 (45), 227 (85), 206 (55); anal. calcd for $C_{18}H_{15}CrNO_4$: C, 59.83; H, 4.19; N, 3.88. Found: C, 59.27; H, 4.12; N, 3.66.

4.5.3. (+)-(S,1S)-1,2-(α-Hydroxy-α-(2-pyridinyl)tetramethylene)ferrocene ***14***

Following the general procedure for ketone (+)-(*S*)-**6** (94 mg, 0.37 mmol), complex (+)-(*S*,1*S*)-**14** was obtained as yellow crystals (70 mg, 55%), m.p. 120°C; $[\alpha]_D$=+302 (c=0.344, Et_2O); ^1H NMR ($CDCl_3$) 8.50 (d, *J* 4.8 Hz, 1H), 7.52 (d, *J* 7.8 Hz, 1H), 7.22 (d, *J* 7.8 Hz, 1H), 7.14 (m, 1H), 4.25 (s, 5H), 4.29 (s, 1H), 4.00 (m, 1H), 3.81 (m, 1H), 2.73 (m, 1H), 2.43 (m, 1H), 2.17 (m, 2H), 1.96 (m, 1H), 1.62 (m, 1H); MS: (m/z) 333 (M^+, 100), 268 (42), 194 (25); anal. calcd for $C_{19}H_{19}FeNO$: C, 68.49; H, 5.75; N, 4.20. Found C, 67.94; H, 5.74; N, 3.95.

4.6. *General procedure for the condensation of the 2-picolyllithium*

To a solution of α-picoline (45 μl, 0.45 mmol) in dry THF (5 ml) was added phenyllithium (240 μl, 1.8 M in cyclohexane, 0.43 mmol) at room temperature. After 1.5 h, the red solution of 2-picolyllithium was introduced into a solution of ketone (0.37 mmol) in dry THF (10 ml) at −78°C. The reactive mixture was stirred and allowed to reach room temperature. After the appropriate reaction time, the mixture was quenched slowly by a saturated aqueous sodium hydrogenocarbonate solution (10 ml), diluted with water (10 ml) and extracted with Et_2O. The solvent was evaporated under vacuum and the crude product was purified by silica gel column chromatography.

4.6.1. *(+)-(S,1S)-Tricarbonyl[1-(2-picolyl)indanol]chromium* **8**

Following the general procedure, 2-picolyllithium was introduced to a solution of ketone (+)-(*S*)-**2** (99 mg, 0.37 mmol) in THF (10 ml). The solution was stirred at room temperature for 15 h. Work-up and column chromatography gave the complex (+)-(*S*,1*S*)-**20** (35 mg, 26%) as a yellow oil; $[\alpha]_D$=+177 (c=2.05, Et_2O); ^1H NMR ($CDCl_3$) 8.52 (m, 1H), 7.60 (m, 1H), 7.26 (m, 1H), 7.00 (m, 1H), 5.35 (t, *J* 5.8 Hz, 1H), 5.21 (d, *J* 6.3 Hz, 1H), 5.14 (d, *J* 6.3 Hz, 1H), 5.00 (t, *J* 5.6 Hz, 1H), 3.12 (d, *J* 14 Hz, 1H), 2.91 (d, *J* 14 Hz, 1H), 2.75 (m, 2H), 2.12 (m, 2H); MS (m/z) 361 (M^+, 31), 333 (17), 305 (17), 277 (75), 275 (100); anal. calcd for $C_{18}H_{15}CrNO_4$: C, 59.84; H, 4.18; N, 3.88. Found C, 60.03; H, 4.22; N, 3.92.

4.6.2. *(+)-(S,1S)-Tricarbonyl[1-(2-picolyl)-1-tetralol]chromium* **12**

Following the general procedure, 2-picolyllithium was introduced to a solution of ketone (+)-(*S*)-**4** (104 mg, 0.37 mmol) in THF (10 ml). The solution was stirred at room temperature for 1.5 h. Work-up and column chromatography gave the complex (+)-(*S*,1*S*)-**12** (90 mg, 68%) as a yellow oil; $[\alpha]_D$=+40 (c=0.524, Et_2O); ^1H NMR ($CDCl_3$) 8.51 (d, *J* 4.0 Hz, 1H), 7.60 (t, *J* 4.0 Hz, 1H), 7.24 (t, *J* 4.0 Hz, 1H), 7.00 (d, *J* 4.0 Hz, 1H), 5.87 (t, *J* 6.0 Hz, 1H), 5.46 (d, *J* 6.0 Hz, 1H), 5.10 (m, 2H), 3.12 (s, 2H), 2.71 (m, 2H), 1.80 (m, 4H); MS (m/z) 375 (M^+, 25), 319 (30), 291 (22), 271 (33); anal. calcd for $C_{19}H_{17}CrNO$: C, 60.80; H, 4.57; N, 3.73. Found: C, 60.89; H, 4.32; N, 3.82.

4.6.3. *(+)-(S,1S)-1,2-[α-Hydroxy-α-(2-picolyl)tetramethylene]ferrocene* **15**

Following the general procedure, 2-picolyllithium was introduced to a solution of ketone (+)-(*S*)-**6** (99 mg, 0.39 mmol) in THF (10 ml). The solution was stirred at room temperature for 4 h. Work-up and column chromatography gave the complex (+)-(*S*,1*S*)-**15** (87 mg, 64%) as a yellow oil; $[\alpha]_D$=+148 (c=0.87, Et_2O); ^1H NMR ($CDCl_3$) 8.52 (dd, *J* 7.6 Hz and 1.8 Hz, 1H), 7.61 (t, *J* 7.6 Hz, 1H), 7.15 (m, 2H), 4.20 (s, 5H), 4.11 (s, 1H), 4.00 (s, 1H), 3.91 (s, 1H), 3.10 (d, *J* 13.9 Hz, 1H), 3.02 (d, *J* 13.9 Hz, 1H), 2.65 (m, 1H), 2.21 (m, 1H), 1.89 (m, 2H), 1.57 (m, 2H); MS (m/z) 347 (M^+, 100), 282 (6), 262 (100), 254 (80); anal. calcd for $C_{20}H_{21}FeNO$: C, 69.14; H, 6.10; N, 4.03. Found C, 69.41; H, 6.30; N, 4.02.

4.6.4. *(+)-(S)-(E)-α-Pyridinyl-propylidene[3](1,2)-ferrocenophane* **18**

A solution of complex (+)-(*S*,1*S*)-**15** (200 mg, 0.61 mmol) in Et_2O (50 ml) was added to a solution of HCl (1 N, 10 ml). After stirring for 5 min, the solution was extracted with Et_2O. The red aqueous layer was neutralized by an addition of potassium carbonate, extracted with Et_2O. The solvent was removed by vacuum. The product was purified by column chromatography to yield complex (+)-(*S*,1*S*)-**18** (161 mg, 80%) as red oil. $[\alpha]_D$=+748 (c=1.87, $CHCl_3$); ^1H NMR ($CDCl_3$) 8.58 (s, 1H), 7.61 (t, *J* 5 Hz, 1H), 7.20 (s, 1H), 7.00 (m, 1H), 6.75 (s, 1H), 4.63 (s, 1H), 4.31 (s, 1H), 4.20 (s, 1H), 4.12 (s, 5H), 3.39 (m, 1H),

2.45 (m, 3H), 2.01 (m, 2H); MS (m/z) 329 (M^+, 100), 262 (45), 208 (45); anal. calcd for $C_{20}H_{19}FeN$: C, 72.97; H, 5.82; N, 4.25. Found C, 73.01; H, 5.85; N, 4.12.

4.7. General procedure for the condensation of the 2-(N,N-dimethylamino)phenyllithium

n-Butyllithium (310 μl, 2.5 M in hexane, 0.8 mmol) and TMEDA (70 μl) were dissolved in dry hexane (5 ml) at room temperature. After stirring for 20 min, N,N-dimethylaniline (120 μl, 0.9 mmol) was added. After 15 h, the solution of 2-(N,N-dimethylamino)phenyllithium was added to a solution of ketone complex (0.74 mmol) in dry THF (20 ml) at room temperature. After stirring for 24 h, the mixture was quenched slowly by an aqueous solution of HCl 1 N (10 ml). The solution was diluted with water (10 ml) and extracted with Et_2O. The aqueous layer was neutralised by a direct addition of K_2CO_3 powder, extracted with Et_2O. The solvents were removed under vacuum and the crude product was purified by silica gel column chromatography.

4.7.1. (+)-(S,1S)-Tricarbonyl[1-(o-N,N-dimethylaminophenyl)indanol]chromium **9**

Following the general procedure for the ketone (+)-(*S*)-**2** (202 mg, 0.76 mmol), complex (+)-(*S*,1*S*)-**9** was obtained as yellow crystals (120 mg, 40%), m.p. 152–150°C; $[\alpha]_D$=+80 (c=1.4, Et_2O); ^1H NMR ($CDCl_3$) 7.1 (m, 2H), 6.70 (m, 2H), 5.68 (d, *J* 6.2 Hz, 1H), 5.41 (t, *J* 6.2 Hz, 1H), 5.20 (d, *J* 6.2 Hz, 1H), 5.09 (t, *J* 6.2 Hz, 1H), 2.80 (s, 6H), 2.43 (m, 4H); MS (m/z) 389 (M^+, 10), 333 (25), 305 (45), 253 (25); anal. calcd for $C_{20}H_{19}CrNO_4$: C, 61.69; H, 4.92; N, 3.60. Found: C, 60.60; H, 4.98; N, 3.60.

4.7.2. (+)-(S,1S)-Tricarbonyl[1-(o-N,N-dimethylaminophenyl)-1-tetralol]chromium **13**

Following the general procedure for the ketone (+)-(*S*)-**4** (200 mg, 0.71 mmol), complex (+)-(*S*,1*S*)-**13** was obtained as a yellow oil (43 mg, 15%); $[\alpha]_D$=+142 (c=0.324, Et_2O); ^1H NMR ($CDCl_3$) 7.18 (m, 2H), 6.73 (m, 2H), 5.60 (d, *J* 6.6 Hz, 1H), 5.41 (t, *J* 6.6 Hz, 1H), 5.19 (d, *J* 6.6 Hz, 1H), 5.10 (t, *J* 6.6 Hz, 1H), 2.21 (m, 6H), 2.68 (s, 6H); MS FAB: (m/z) 403 (52); anal. calcd for $C_{21}H_{21}CrNO_4$: C, 62.53; H, 5.25; N, 3.47. Found: C, 63.12; H, 5.63; N, 3.48.

4.7.3. (+)-(S,1S)-1,2-[α-Hydroxy-α-(o-N,N-dimethylaminophenyl)tetramethylene]ferrocene **16**

Following the general procedure for the ketone (+)-(*S*)-**6** (185 mg, 0.72 mmol), complex (+)-(*S*,1*S*)-**16** was obtained as a yellow oil (101 mg, 37%); $[\alpha]_D$=+45 (c=0.44, Et_2O); ^1H NMR ($CDCl_3$) 7.40 (d, *J* 8.0 Hz, 1H), 7.22 (d, *J* 8.0 Hz, 1H), 6.89 (d, *J* 8.0 Hz, 1H), 6.61 (d, *J* 8.0 Hz, 1H), 4.32 (s, 5H), 4.28 (s, 1H), 4.00 (s, 1H), 3.91 (s, 1H), 2.72 (s, 6H), 2.45 (s, 2H), 2.35 (s, 1H), 2.01 (s, 2H), 1.79 (s, 1H); MS FAB: (m/z) 375 (M^+, 100); 358 (20); anal. calcd for $C_{22}H_{25}FeNO$: C, 70.41; H, 6.71; N, 3.73. Found C, 70.34; H, 6.98; N, 3.78.

4.8. General procedure for the condensation of the 2-(dimethylaminomethyl)phenyllithium

A solution of 2-(dimethylaminomethyl)phenyllithium in dry THF (5 ml) was prepared from 2-bromo(N,N-dimethylaminomethyl)benzene (140 μl, 0.84 mmol) by addition of n-butyllithium (330 μl, 2.5 M in hexane, 0.82 mmol) at −78°C. After 20 min, the red solution of 2-(dimethylaminomethyl)phenyllithium was added to a solution of ketone complex (0.74 mmol) in dry THF (15 ml) at −78°C. The reactive mixture was stirred and then allowed to reach room temperature. After 15 h, the mixture was quenched slowly by the addition of an aqueous HCl solution (1 N, 5 ml), diluted with water (10 ml) and extracted with Et_2O. The aqueous layer was neutralised by

a direct addition of K_2CO_3 powder, extracted with Et_2O and the solvent was evaporated under vacuum. The crude product was purified by silica gel column chromatography.

4.8.1. (+)-(S,1S)-Tricarbonyl-{1-[o-(N,N-dimethylaminomethyl)phenyl]indanol}chromium ***10***

Following the general procedure for the ketone (+)-(*S*)-**2** (199 mg, 0.74 mmol), complex (+)-(*S*,1*S*)-**10** was obtained as yellow crystals (120 mg, 40%), m.p. 158–160°C; $[\alpha]_D$=+244 (c=0.422, $CHCl_3$); ^1H NMR ($CDCl_3$) 7.10 (m, 3H), 6.62 (d, *J* 7.5 Hz, 1H), 5.69 (d, *J* 6.4 Hz, 1H), 5.41 (t, *J* 6.4 Hz, 1H), 5.25 (d, *J* 6.4 Hz, 1H), 5.20 (t, *J* 6.4 Hz, 1H), 4.25 (d, *J* 12.3 Hz, 1H), 3.11 (d, *J* 12.3 Hz, 1H), 2.55 (m, 4H), 2.25 (s, 6H); MS: (m/z) 403 (M^+, 32), 375 (M, 20), 347 (M, 20), 319 (M, 22), 299 (100); anal. calcd for $C_{21}H_{21}CrNO_4$: C, 62.52; H, 5.25; N, 3.47. Found C, 62.49; H, 5.23; N, 3.42.

4.8.2. (+)-(S,1S)-1,2-[α-Hydroxy-α-(o-N,N-dimethylaminomethylphenyl)tetramethylene]ferrocene ***17***

Following the general procedure for the ketone (+)-(*S*)-**6** (190 mg, 0.74 mmol), complex (+)-(*S*,1*S*)-**17** was obtained as an orange oil (160 mg, 55%), $[\alpha]_D$=+170 (c=1.234, Et_2O); ^1H NMR ($CDCl_3$) 7.00 (m, 3H), 6.71 (m, 1H), 4.22 (s, 5H), 4.18 (m, 2H), 4.00 (m, 1H), 3.89 (m, 1H), 3.02 (d, *J* 12.5 Hz, 1H), 2.74 (m, 1H), 2.35 (m, 1H), 2.15 (m, 3H), 2.20 (s, 6H), 1.88 (m, 1H); MS FAB (m/z): 389 (M^+, 45), 370 (29), 347 (20); anal. calcd for $C_{23}H_{27}FeNO$: C, 70.96; H, 6.99; N, 3.60. Found C, 70.8; H, 7.01; N, 3.52.

4.9. General procedure for the photodecomplexation of tricarbonyl(arene)chromium complexes

Chromium aminoalcohol complex (1 mmol) was dissolved in 100 ml of Et_2O and the solution was left to stand in air and sunlight for 48 h. After filtration through Celite, the solvent was evaporated under vacuum. The crude product was purified by silica gel column chromatography. The yield was quantitative.

4.9.1. (−)-(1R)-1-(2,2-Dimethyl-N,N-dimethylaminoethyl)indanol ***26***

Colorless oil; $[\alpha]_D$=−38 (c=0.84, $CHCl_3$); ^1H NMR ($CDCl_3$) 7.31–6.90 (m, 4H), 2.70 (m, 2H), 2.35 (s, 6H), 2.41 (m, 2H), 2.35 (m, 2H), 1.21 (s, 3H), 0.64 (s, 3H); anal. calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93; N, 6.00. Found C, 77.56; H, 10.01; N, 5.56.

4.9.2. (−)-(1R)-1-(2-Pyridinyl)indanol ***22***

Colorless oil; $[\alpha]_D$=−12 (c=0.35, $CHCl_3$); ^1H NMR ($CDCl_3$) 8.60 (m, 1H), 7.61 (m, 1H), 7.25 (m, 4H), 7.19 (m, 2H), 3.20 (m, 1H), 3.01 (m, 1H), 2.55 (m, 2H); anal. calcd for $C_{14}H_{13}NO$: C, 79.62; N, 6.63. Found C, 80.53; N, 6.01.

4.9.3. (−)-(1R)-1-(2-Pyridinyl)-1-tetralol ***27***

Colorless oil; $[\alpha]_D$=−14 (c=0.46, Et_2O); ^1H NMR ($CDCl_3$) 8.50 (m, 1H), 7.59 (t, *J* 7.4 Hz, 1H), 7.12 (m, 4H), 7.00 (d, *J* 7.4 Hz, 1H), 6.89 (d, *J* 7.4 Hz, 1H), 2.91 (m, 2H), 2.14 (m, 4H); anal. calcd for $C_{15}H_{15}NO$: C, 80.00; N, 6.22. Found C, 80.19; N, 6.34.

4.9.4. (−)-(1S)-1-(2-Picolyl)indanol ***23***

Colorless oil; $[\alpha]_D$=−77 (c=0.55, Et_2O); ^1H NMR ($CDCl_3$) 8.60 (m, 1H), 7.61 (m, 1H), 7.20–6.89 (m, 6H), 3.40 (d, *J* 14 Hz, 1H), 3.11 (d, *J* 14 Hz, 1H), 3.00 (m, 1H), 2.73 (m, 1H), 2.11 (m, 2H); anal. calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found C, 80.01; H, 6.65; N. 6.22.

4.9.5. (+)-(1S)-1-(2-Picolyl)-1-tetralol 28

Colorless oil; $[\alpha]_D$=+40 (c=0.524, Et_2O); ^1H NMR ($CDCl_3$) 8.56 (m, 1H), 7.62 (m, 2H), 7.10 (m, 5H), 3.40 (d, *J* 14.5 Hz, 1H), 3.09 (d, *J* 14.5 Hz, 1H), 2.71 (m, 2H), 1.84 (m, 4H); anal. calcd for $C_{15}H_{15}NO$: C, 80.33; H, 5.85; N, 6.22. Found C, 80.69; N. 6.00.

4.9.6. (−)-(1R)-1-o-(N,N-Dimethylaminophenyl)indanol 24

Colorless oil; $[\alpha]_D$=−18 (c=0.4, Et_2O); ^1H NMR ($CDCl_3$) 7.40 (m, 1H), 7.25 (m, 5H), 7.00 (m, 1H), 6.61 (m, 1H), 3.20 (m, 1H), 2.89 (m, 1H), 2.72 (s, 6H), 2.62 (m, 1H), 2.40 (m, 1H); anal. calcd for $C_{17}H_{19}NO$: C, 80.63; N, 5.53. Found C, 80.41; N. 5.18.

4.9.7. (−)-(1R)-1-(o-N,N-Dimethylaminophenyl)-1-tetralol 29

Colorless oil; $[\alpha]_D$=−82 (c=0.324, Et_2O); ^1H NMR ($CDCl_3$) 7.55 (d, *J* 8 Hz, 1H), 7.31–7.00 (m, 6H), 6.61 (d, *J* 8 Hz, 1H), 2.91–2.61 (m, 2H), 2.68 (s, 6H), 2.55 (m, 2H), 1.90–1.59 (m, 2H); anal. calcd for $C_{17}H_{19}NO$: C, 80.89; N, 5.24. Found C, 80.00; N. 5.88.

4.9.8. (+)-(1R)-1-[o-(N,N-Dimethylaminomethyl)phenyl]indanol 25

Colorless oil; $[\alpha]_D$=+119 (c=0.200, $CHCl_3$); ^1H NMR ($CDCl_3$) 7.60–6.99 (m, 8H), 4.21 (d, *J* 12.3 Hz, 1H), 3.20 (d, *J* 12.3 Hz, 1H), 3.02 (m, 1H), 2.74 (m, 1H), 2.19 (m, 2H), 2.31 (s, 6H); anal. calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found C, 80.58; H, 7.90; N, 5.23.

4.10. General procedure for catalytic test

Aldehyde (1.1 mmol), chiral aminoalcohol complex (0.05 or 0.10 mmol) and toluene (1.5 ml) were placed in a schlenk tube with a valve and gas inlet. Diethylzinc (4 ml, 4.4 mmol, 1.1 M in toluene) was injected to the reaction mixture via a syringe. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by GC. Aqueous HCl (1 N, 10 ml) was added to quench the reaction. The mixture was extracted with Et_2O and the organic layer was washed with brine, dried over Na_2SO_4 and evaporated under vacuum. The residue was purified by column chromatography. The absolute configuration of the alcohol was determined from the sign of the specific rotation.[18]

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