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Tricarbonyl(η^6Arene)Chromium(0) Complexes as Chiral Auxiliaries: Asymmetric Synthesis of β-Aminoesters and β-Lactams by Reformatsky Condensation

Clara Baldoli, Paola Del Buttero*, Emanuela Licandro, Antonio Papagni

Dipartimento di Chimica Organica e Industriale dell'Universita'- Centro CNR- Via Venezian, 21 - 20133 Milano-Italy.

Tullio Pilati

CNR-Centro per lo Studio delle Relazioni fra Struttura e Reattivita' Chimica. Via C. Golgi, 19 -20133 Milano-Italy

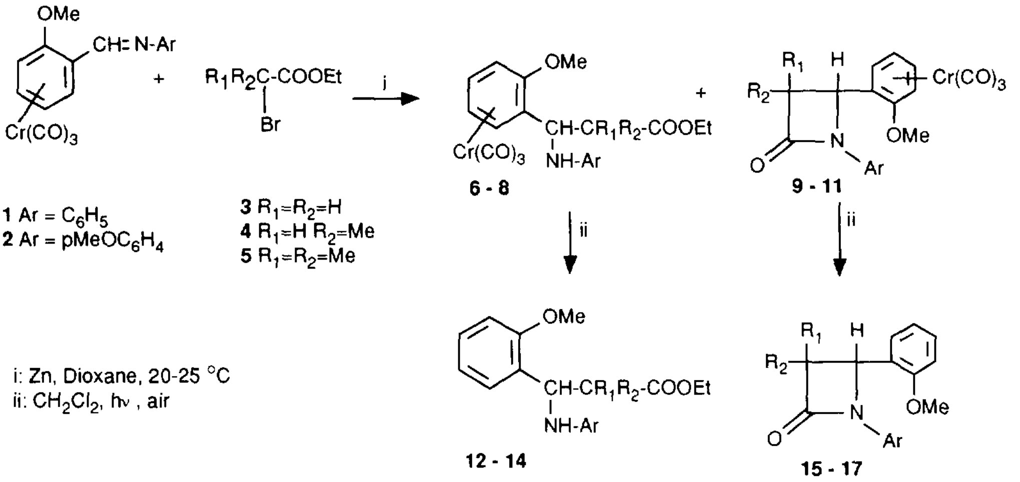
Abstract: Highly stereoselective syntheses (e.e. > 98%) of β-aminoesters and β-lactams were accomplished using enantiomerically pure tricarbonyl (η^6benzaldimine)chromium complexes in a Reformatsky type reaction promoted by ultrasound. A correlation between the configuration of complexed imines and absolute configuration of β-lactam derivatives is reported.

The addition of Reformatsky reagents to the Schiff bases of aldehydes or ketones for the synthesis of the β-lactam rings was first reported by Gilman and Speeter.[1] Apart from some papers directed to elucidate the mechanism and factors influencing the stereochemistry[2,3] of Reformatsky reactions, little attention has been dedicated to its enantioselective version expecially for the synthesis of azetidinone rings.

Recently we have succesfully employed homochiral complexes of benzaldimines and cinnamaldimines for the synthesis of β-lactam rings by condensation with lithium ester-enolates[4,5] and by [2+2] cycloaddition reaction with ketenes.[6] With the aim of extending the use of the above chiral auxiliaries toward the stereoselective synthesis of products of potential biological activity, we have examined the Reformatsky reaction as promising procedure of entry to β-aminoesters and β-lactams in optically pure form.

In this paper we report our results on the enantioselective synthesis of β-aminoesters and β-lactams, using optically pure tricarbonyl [*N*-(2-methoxybenzilidene)aniline]chromium **1**[4] or tricarbonyl [*N*-(2-methoxybenzilidene)-4-methoxyaniline]chromium **2**[6] and appropriate α-bromoesters in the presence of zinc and ultrasound irradiation. The beneficial effects of ultrasound irradiation in promoting the Reformatsky type reactions is generally accepted.[7] A mixture of Zn wool (preliminarly activated by washing it with H_2SO_4), (-) or (+)-benzaldimines **1**, **2** and α-bromoesters **3-5** in dry dioxane was maintained at 20-25 °C under sonication for 6-8 h using a commercially available cleaning bath as a convenient source of ultrasound.(Scheme1)

Scheme 1



Table

Imines	R_1	R_2	Complexed β-aminoesters (yield %)	Complexed β-lactams (yield %)	Uncomplexed β-aminoesters (yield %)	Uncomplexed β-lactams (yield %)	Reaction time/h
(+)-*1S* **1**	H	H	(-) **6** (46)	(-) **9** (25)	(-) **12** (45)	(-) **15** (25)	6
(-)-1*R* **2**	H	Me	(+) **7** (40)	(+) **10cis**(40)	(+) **13** (35)	(+) **16cis**(39)	8
				(+) **10trans**(18)	--	(+) **16trans**(17)	
(+)-*1S* **1**	Me	Me	(-) **8** (63)	(-) **11** (34)	(-) **14** (62)	(-) **17** (32)	7

The usual workup and chromatographic separation on silica-gel provides, in all cases, the complexed β-aminoesters **6-8** and β-lactams **9-11**,[8] that were decomplexed to the corresponding compounds **12-14** and **15-17**, in quantitative yield.(Table)

Product **7** was obtained as a single isomer and, after decomplexation, the corresponding β-aminoester **13** was converted (LDA in THF at -78 °C)[9] in nearly quantitative yield into the *cis* β-lactam **16**. On the basis of the above result and in line with the literature,[2] the *erythro* configuration was assigned to product **7**. The *cis/trans* configuration of β-lactams **16** was inferred on the basis of proton coupling constants of H_3 and H_4 (J_{cis}= 5.7 Hz, J_{trans}= 2.2 Hz)[10] and confirmed by homonuclear NOE-difference experiments.[11]

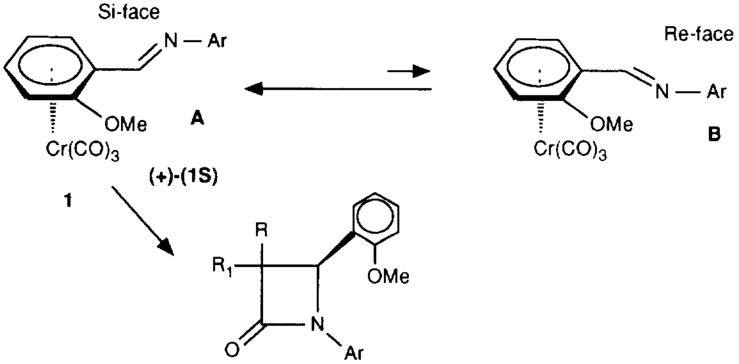
The enantiomeric excess on the uncomplexed **12-13** and **15-17**, determined by ^1H NMR using chiral

Eu(hfc)$_3$ salts, was in all cases higher than 98%. For (-)-**14** no determination of e.e. was possible because no ^{1}H NMR splitted signal was observed using Eu(hfc)$_3$ or Eu(tfc)$_3$ on racemic **14**.

Discussion

As shown in the Table, the imine complex having (+)-(*1S*) absolute configuration gave rise to β-lactams (-)-**15** and (-)-**17** and imine (-)-*(1R)* gave (+)-**16**. It is reasonable to assume that the assignment of the absolute configuration of β-lactams (and β-aminoesters) can be based on the stereochemical model accepted for reaction involving chiral tricarbonylchromium complexes. As observed for *ortho* substituted benzaldehyde complexes, also for imine (+)-(*1S*) like **1**,[6] the more stable and reactive conformation is **A** and attack of the enolate species occurs from the opposite side of the Cr(CO)$_3$ unit and on a Si-face of imine **1**.[12](Scheme 2)

Scheme 2



On the basis of the above consideration, the expected β-lactam **15** arising from reaction of imine (+)-(*1S*)-**1** and ethyl bromoacetate will have (*4S*) configuration. In addition the negative rotation sign of **15** can be compared with those reported in the literature[13-15] for a series of analogous β-lactams showing (*S*) configuration. Moreover the β-lactam (+)-**16** *cis* and (+)-**16** *trans*, obtained from imine (-)-(*1R*)-**2**, will have *3R,4R* and *3S,4R* configuration and are in line with recently reported stereochemical data.[16-17] [It is important to note that no change in the rotation sign of β-lactams was found from the N-aryl substituent to N-unsubstituted compounds.[4,17]] Again for β-lactam (-)-**17** synthesized from imine (+)-(*1S*)-**1**, the expected absolute configuration should be (*4R*)[18] because it is reasonable to think that no change in diastereofacial discrimination could occur passing from ethylbromoacetate to ethylbromoisobutyrate. Since at the beginning of this work, the reported (*4S*) absolute configuration for (-)*N*-phenyl-3,3 dimethyl 4-phenyl azetidin-2-one[19] did not agree with the configuration proposed by us for analogous (-)-**17**, we recorded the circular dichroism curves for **15-17** compounds. In these compounds the Cotton effect sign is connected to the relative disposition of the substituent in C-4,[13] (octant rule) and we have found at 220-250 nm a negative Cotton effect for **15** and **17** and positive for both *cis* and *trans* **16**. These data strongly support, in our opinion, that **17** has the same β-disposition of the substituent in C-4 of **15** and opposite to **16**. In addition, as we have already reported,[6] the presence of CH$_3$ or OCH$_3$ substituents on the arene ring does not influence the sign of the Cotton effect. Finally a (*4R*) configuration for (-)-**17** was confirmed by submitting to X-ray crystallographic analysis[20] the (+)-tricarbonyl[*N*-(4-methoxyphenyl) -3,3-dimethyl- 4-(2-methylphenyl) azetidin-2-one] chromium which, apart from the Cr(CO)$_3$ moiety, differs from (-)-**17** only in the *N*-aryl substituent.(Figure)

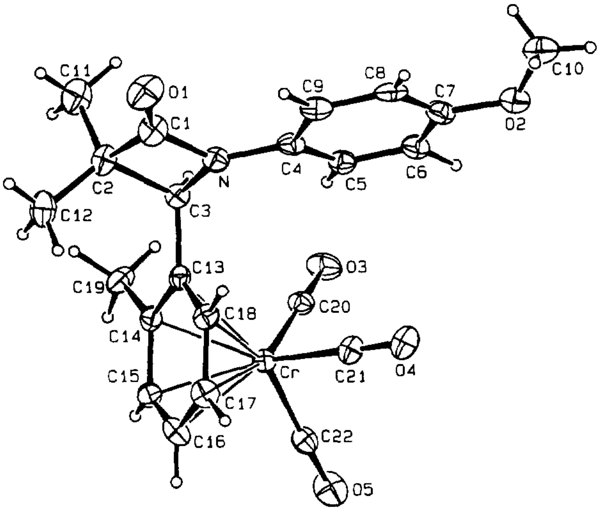


Figure: *ORTEP plot of (+)-tricarbonyl[N-(4-methoxyphenyl)-3,3-dimethyl-4(2-methylphenyl) azetidin-2-one] chromium; heavy atoms are at 20% probability level, H atoms not to scale.*

The *4R* configuration for (-)-**17** is also in good agreement with recent results by Cozzi[24] and with a report by Fujisawa.[25]

In conclusion these results represent an interesting example of the use of chiral imines in the Reformatsky type reaction; this method allows us to obtain in good yields, easily and with nearly complete enantioselection, β-aminoesters and β-lactams. We have shown that the imine (+)*1S* gives rise, independently from the type of α-bromoester, to the β-lactam with the substituent on C-4 in the β position; therefore it is possible to correlate the absolute configuration of the obtained β-lactams with the configuration of the starting tricarbonylchromium complexed chiral imines.

Experimental:

All reactions were performed under nitrogen. All of the chemicals were used as obtained from commercial sources. Column Chromatography and TLC were carried out using respectively silica gel 60 and silica gel 60 F_{254} pre-coated plates. The melting points were measured using a Büchi apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ and, unless stated otherwise, using a Varian XL 300 spectrometer. The optical rotations were measured using a Perkin-Elmer 241 Polarimeter, with a 1 dm pathlength at 25 °C. Complexed imines **1,2** are known compounds.[4,6]

Synthesis of complexed β-aminoesters (6-8) and β-lactams (9-11). General procedure:

A suspension in dry dioxane (20 mL) of the imine ($8.6\ 10^{-1}$ mmol), Zn wool ($8.6\ 10^{-1}$ mmol), a catalytic amount of KI and the appropriate α-bromoester ($8.6\ 10^{-1}$ mmol) was sonicated under an inert atmosphere (N_2) using an ultrasonic bath filled with water, keeping the temperature approximately at 25 °C by addition of ice. The reaction progress was monitored by TLC (eluent diethyl ether-light petroleum) and, if necessary, additional Zn and α-bromoester in equivalent amount were added until a good conversion of starting imine was obtained. The reaction mixture was diluted with approximately 30 mL of CH_2Cl_2, washed with 30 mL of water, afterwards with 20 mL of a 15% ammonia solution and finally with water (2x30) mL until pH= 7. After removal of the solvent under reduced pressure, the residue was purified by chromatography on silica-gel column using a mixture of diethyl ether and petroleum ether as eluent.

Decomplexation

All decomplexed products **12-17** were obtained by exposure of solution of complexes **6-11** in CH_2Cl_2 to air and sunlight for 6-10 h; the solvent was evaporated, the residue was taken up with diethyl ether and filtered over a pad of celite. After evaporation of the solvent, the pure products were made crystalline by adding diisopropyl ether.

***Tricarbonyl[2-methoxyphenyl-β-phenylamino ethylpropionate]chromium(0)* 6:**
M.p. 165 °C (diisopropyl ether), (Found C, 58.00; H, 4.84; N, 3.20%. $C_{21}H_{21}CrNO_6$ requires C, 57.93; H, 4.86; N, 3.22%). $[\alpha]_D$= -149° (c= 0.3 $CHCl_3$). ^1H NMR ($CDCl_3$) δ, 1.1 (t, 3H, $CH_2\mathit{CH_3}$, J= 7.1 Hz); 2.85 (d, 2H, $\mathit{CH_2}CH$, J= 6.0 Hz); 3.75 (s, 3H, OCH_3); 4.1 (q, 2H, $\mathit{CH_2}CH_3$, J= 7.1 Hz); 4.3 (s, 1H, NH); 4.7 (dd, 1H, arom-$Cr(CO)_3$, J= 6.35 Hz, J= 6.85 Hz); 4.88 (d, 1H, arom-$Cr(CO)_3$, J= 6.85 Hz); 4.95 (t, 1H, *CH*-CH_2, J= 6.0 Hz); 5.45 (t, 1H, arom-$Cr(CO)_3$, J= 6.35 Hz); 5.75 (d, 1H, arom-$Cr(CO)_3$, J= 6.35 Hz); 6.42-7.2 (m, 5H, arom.).

***Tricarbonyl[2-methoxyphenyl-β-(4-methoxyphenylamino)-α-methyl ethylpropionate]chromium(0)* 7:**
M.p. 119 °C (diisopropyl ether), (Found C, 57.61; H, 5.22; N, 2.90%. $C_{23}H_{25}CrNO_7$ required C, 57.62; H, 5.25; N, 2.92%). $[\alpha]_D$= +144° (c= 0.2 $CHCl_3$). ^1H NMR ($CDCl_3$) δ, 1.05 (d, 3H, CH-$\mathit{CH_3}$, J= 7.6 Hz); 1.09 (t, 3H, CH_2-$\mathit{CH_3}$, J= 7.1 Hz); 3.13 (m, 1H, *CH*-CH_3); 3.72 (s, 3H, OCH_3); 3.82 (s, 3H, OCH_3); 4.05 (q, 2H, $\mathit{CH_2}$-CH_3, J= 7.1 Hz); 4.32 (s, 1H, NH); 4.8 (t, 1H, arom-$Cr(CO)_3$, J= 5.9 Hz); 4.95 (d, 1H, *CH*-NH, J= 7.3 Hz); 5.1 (d, 1H, arom-$Cr(CO)_3$, J= 5.9 Hz); 5.53 (t, 1H,arom-$Cr(CO)_3$, J= 6.0 Hz); 5.78 (d, 1H, arom-$Cr(CO)_3$, J= 6.0 Hz); 6.62-6.68 (m, 4H, arom.).

***Tricarbonyl[2-methoxyphenyl-β-phenylamino-α,α-dimethyl ethylpropionate]chromium(0)* 8:**
M.p. 120 °C (diisopropyl ether), (Found C, 59.58; H, 5.41; N, 3.05%. $C_{23}H_{25}CrNO_6$ required C, 59.61; H, 5.44; N, 3.02%). $[\alpha]_D$= -119° (c= 0.2 $CHCl_3$). ^1H NMR ($CDCl_3$, 80 MHz) δ, 1.15 (t, 3H, CH_2-$\mathit{CH_3}$, J= 7.5 Hz), 1.28 (s, 3H, CH_3); 1.31 (s, 3H, CH_3); 3.8 (s, 3H, OCH_3); 4.05 (q, 2H, $\mathit{CH_2}$-CH_3, J= 7.5 Hz); 4.32-5.07 (m, 4H, 2 arom-$Cr(CO)_3$+ CH + NH); 5.37-5.57 (m, 2H, arom-$Cr(CO)_3$); 6.5-7.15 (m, 5H, arom.).

***(-)-(4S) Tricarbonyl[N-4-methoxyphenyl-4-(2-methoxyphenyl)azetidin-2-one] chromium(0)* 9:**
M.p. 165 °C (diisopropyl ether), (Found C, 58.66; H, 3.84; N, 3.59%. $C_{19}H_{15}CrNO_5$ requires C, 58.62; H, 3.88; N, 3.60%). $[\alpha]_D$= -179° (c= 0.2 $CHCl_3$). ^1H NMR ($CDCl_3$) δ, 2.85 (dd, 1H, CH_2, J_{gem}= 15.4 Hz, J_{trans}= 2.6 Hz); 3.52 (dd, 1H, CH_2, J_{gem}= 15.4 Hz, J_{cis}= 5.8 Hz); 3.7 (s, 3H, OCH_3); 4.79 (dd, 1H, arom-$Cr(CO)_3$, J= 6.85 Hz, J= 6.35 Hz); 4.96 (d, 1H, arom-$Cr(CO)_3$, J= 6.85 Hz); 5.11 (dd, 1H, CH, J= 2.6 Hz, J=5.8 Hz); 5.4 (t, 1H, arom-$Cr(CO)_3$, J= 6.35 Hz); 5.49 (d, 1H, arom-$Cr(CO)_3$, J= 6.35 Hz); 7-7.5 (m,

5H, arom).

(+)-(3R,4R)Tricarbonyl[N-4-methoxyphenyl-3-methyl-4-(2-methoxyphenyl) azetidin-2-one]chromium(0) **10*cis*:**
M.p. 130 °C (diisopropyl ether), (Found C, 58.18; H, 4.43; N, 3.21%. $C_{21}H_{19}CrNO_6$ requires C,58.20; H, 4.42; N, 3.23%). $[\alpha]_D$= +159° (c= 0.2 $CHCl_3$). ^1H NMR ($CDCl_3$) δ, 1.0 (d, 3H, CH_3, J= 8.1 Hz); 3.68 (m, 1H, *CH*-CH_3); 3.79 (2s, 6H, OCH_3); 4.96 (t, 1H, arom-$Cr(CO)_3$, J= 6.2 Hz); 5.03 (d, 1H, arom-$Cr(CO)_3$, J= 6.6 Hz); 5.38 (d, 1H, CH, J= 5.8 Hz); 5.39 (d, 1H, arom-$Cr(CO)_3$, J= 6.2 Hz); 5.47 (t, 1H, arom-$Cr(CO)_3$, J= 6.6 Hz); 6.9 and 7.5 (AA'BB' system, 4H, arom).

(+)-(3S,4R) Tricarbonyl[N-4-methoxyphenyl-3-methyl-4-(2-methoxyphenyl) azetidin-2-one]chromium(0) **10*trans*:**
M.p. 156 °C (diisopropyl ether), (Found C, 58.18; H, 4.39; N, 3.25%. $C_{21}H_{19}CrNO_6$ requires C, 58.20; H, 4.42; N, 3.23%). $[\alpha]_D$= +175° (c= 0.2 $CHCl_3$). ^1H NMR ($CDCl_3$) δ, 1.5 (d, 3H, CH_3, J= 7.33 Hz); 3.09 (dq, 1H, *CH*-CH_3, J= 1.83 Hz, J= 7.33 Hz); 3.78 (2s, 6H, OCH_3); 4.75 (d, 1H, CH, J= 1.83 Hz); 4.85 (t, 1H, arom-$Cr(CO)_3$, J= 6.23 Hz); 5.0 (d, 1H, arom-$Cr(CO)_3$, J= 6.59 Hz); 5.48 (m, 2H, arom-$Cr(CO)_3$); 6.9 and 7.5 (AA'BB' system, 4H, arom).

(-)-(4S) Tricarbonyl[N-phenyl-3,3-dimethyl-4-(2-methoxyphenyl) azetidin-2-one]chromium(0) **11:**
M.p. 158 °C (diisopropyl ether), (Found C, 60.38; H, 4.56; N, 3.28% $C_{21}H_{19}CrNO_5$ required C, 60.43; H, 4.59; N, 3.35%). $[\alpha]_D$= -197° (c= 0.1 $CHCl_3$). ^1H NMR ($CDCl_3$) δ 1.0 (s, 3H, CH_3); 1.6 (s, 3H, CH_3); 3.8 (s, 3H, OCH_3); 4.8-5.1 (m, 2H, arom-$Cr(CO)_3$); 5.1 (s, 1H, CH); 5.3-5.6 (m, 2H, arom-$Cr(CO))_3$); 7.0-7.7 (m, 5H, arom):

2-Methoxyphenyl-β-phenylamino ethylpropionate **12:**
M.p. 113 °C (diisopropyl ether), (Found C, 72.20; H, 6.98; N, 4.68%. $C_{18}H_{21}NO_3$ required C, 72.22; H, 7.07; N, 4.68%). $[\alpha]_D$= -71° (c= 1.0 $CHCl_3$). ^1H NMR ($CDCl_3$) δ 1.2 (t, 3H, CH_2-*CH_3*, J= 7.3 Hz); 2.85 (AB part of ABX system, 2H, CH-*CH_2*); 3.9 (s, 3H, OCH_3); 4.1 (q, 2H, *CH_2*-CH_3, J= 7.3 Hz); 4.1 (bs, 1H, NH); 5.15 (dd, 1H, *CH*-CH_2, X part of ABX system, J= 5.37 Hz, J= 6.84 Hz); 6.5-7.4 (m, 9H, Arom).

2-Methoxyphenyl-β-(4-methoxyphenylamino)-α-methyl ethylpropionate **13:**
M.p. 93 °C (diisopropyl ether), (Found C, 69.96; H,7.31; N, 4.09% $C_{20}H_{25}NO_4$ required C, 69.94; H, 7.34; N, 4.08%). $[\alpha]_D$= +6.6° (c= 1.0 $CHCl_3$). ^1H NMR ($CDCl_3$) δ 1.1 (t, 3H, CH_2-*CH_3*, J= 7.1 Hz); 1.15 (d, 3H, CH-*CH_3*, J= 7.6 Hz); 3.1 (m, 1H, *CH*-CH_3); 3.7 (s, 3H, OCH_3); 3.9 (s, 3H, OCH_3); 4.0 (q, 2H, *CH_2*-CH_3, J= 7.1 Hz); 4.3 (bs, 1H, NH); 4.9 (d, 1H, *CH*-NH, J= 6.1 Hz); 6.4-7.3 (m, 8H, arom.).

2-Methoxyphenyl-β-phenylamino-α,α-dimethyl ethylpropionate **14:**
(Found C, 73.40; H, 7.68; N, 4.30%. $C_{20}H_{25}NO_3$ required C, 73.36; H, 7.70; N, 4.28%). $[\alpha]_D$= -7.3° (c= 0.9 $CHCl_3$). ^1H NMR ($CDCl_3$) δ 1.09 (s, 3H, CH_3); 1.11 (t, 3H, CH_2-*CH_3*, J= 7.2 Hz); 1.21 (s, 3H, CH_3); 3.82 (s, 3H, OCH_3); 1.05 (q, *CH_2*-CH_3, J= 7.2 Hz); 5.0 (bs, 2H, CH + NH); 6.4-7.1 (m, 9H, arom.).

(-)-(4S) N-(4-methoxyphenyl)-4-(2-methoxyphenyl) azetidin-2-one **15**:

M.p. 113 °C (diisopropyl ether), (Found C, 75.90; H, 5.96; N, 5.51% $C_{16}H_{15}NO_2$ required C, 75.87; H, 5.97; N, 5.53%). $[\alpha]_D$= -161° (c= 1.0 $CHCl_3$). ^1H NMR ($CDCl_3$) δ 2.9 (dd, 1H, CH_2, J_{gem}= 15.1 Hz, J_{trans}= 2.7 Hz); 3.51 (dd, 1H, CH_2, J_{gem}= 15.1 Hz, J_{cis}= 5.9 Hz); 3.89 (s, 3H, OCH_3); 5.53 (dd, 1H, CH, J= 5.9 Hz, J= 2.7 Hz); 6.8-7.4 (m, 9H, arom). $\Delta\varepsilon$= -10.6 (λ 225 nm, CH_3CN).

(+)-(3R4R) N-(4-methoxyphenyl)-3-methyl-4-(2-methoxyphenyl) azetidin-2-one **16** *cis:*

M.p. 133 °C (diisopropyl ether), (Found C, 72.69; H, 6.39; N, 4.69% $C_{18}H_{19}NO_3$ required C, 72.71; H, 6.44; N, 4.71%). $[\alpha]_D$= +202° (c= 1.90 $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.8 (d, 3H, CH_3, J= 7.50 Hz); 3.72 (m, 1H, *CH*-CH_3); 3.75 (s, 1H, OCH_3); 3.88 (s, 3H, OCH_3); 5.41 (d, 1H, *CH*-Ph, J= 5.8 Hz); 6.7-7.4 (m, 8H, arom). $\Delta\varepsilon$= +2.1 (λ 229 nm, CH_3CN).

(+)-(3S4R) N-(4-methoxyphenyl)-3-methyl-4-(2-methoxyphenyl) azetidin-2-one **16** ***trans:***

M.p. 78 °C (diisopropyl ether), (Found C, 72.70; H, 6.41; N 4.68% $C_{18}H_{19}NO_3$ required C, 72.71; H, 6.44; N, 4.71%). $[\alpha]_D$= +103° (c= 1.0 $CHCl_3$). ^1H NMR ($CDCl_3$) δ 1.49 (d, 3H, CH_3, J= 7.39 Hz); 3.03 (dq, 1H, *CH*-CH_3, J= 7.39 Hz, J= 2.38 Hz); 3.72 (s, 3H, OCH_3); 3.88 (s, 3H, OCH_3); 4.92 (d, 1H, *CH*-Ph, J= 2.38 Hz); 6.7-7.4 (m, 8H, arom.). $\Delta\varepsilon$= +4.1 (λ 228 nm, CH_3CN).

(-)-(4R) N-phenyl-3,3-dimethyl-4-(2-methoxyphenyl) azetidin-2-one **17**:

M.p. 100 °C (diisopropyl ether), (Found C, 76.82; H, 6.79; N, 4.97%. $C_{18}H_{19}NO_2$ required C, 76.84; H, 6.81; N, 4.98%). $[\alpha]_D$= -81° (c= 1.0 $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.8 (s, 3H, CH_3); 1.5 (s, 3H, CH_3); 3.83 (s, 3H, OCH_3); 5.07 (s, 1H, CH); 6.8-7.4 (m, 9H, arom.). $\Delta\varepsilon$= -11.6 (λ 244 nm, CH_3CN).

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(20) $C_{22}H_{21}CrNO_5$ orthorhombic, $P2_12_12_1$, M_r=431.40, a= 9.692(1), b=12.628, c=17.292(2)Å, V=2116.4 Å^3, Z=4, d_{calc}=1.354 g.cm^{-3}, μ(MoKα) =0.572 mm^{-1}; Siemens-P4 difractometer, MoKα radiation, λ=0.71069 Å; cell parameters from 47 reflectoins in the range $3.5<\Theta<15.3°$. Data collection: $4<\Theta<25°$; $0<h<11$; $0<k<15$; $-20<l<20$; 4136 reflections collected, 3971 independent, 2963 observed [with I>2.σ(I)], no absorption correction; the structure was solved by SIR92[20] and refined on F^2 by full-matrix least-squares SHELXL-93[21]. Heavy atoms anisotropic, H atoms isotropic, final R=0.0408, wR(based on F^2) = 0.0914, $\Delta\rho_{max}$=0.16 eÅ^{-3}. Absolute configuration determined by refining the Flack parameter[22] whose final value was 0.01(3).

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