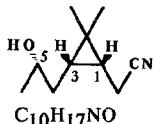


**STEREOCHEMISTRY ABSTRACTS**

A.V.Tkachev, A.V.Rukavishnikov, Yu.V.Gatilov, I.Yu.Bagrijanskaja

*Tetrahedron: Asymmetry* 1992, 3, 1165



2,2-Dimethyl-3-(2-hydroxypropyl)-cyclopropaneacetonitrile

$$[\alpha]_{580}^{22} + 7.9 \text{ (c } 5.31, \text{ CHCl}_3\text{)}$$

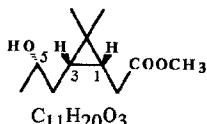
Source of chirality: diastereoselective baker's yeast-induced reduction of the corresponding ketone.

Absolute configuration: 1R,3S,SS  
(assigned by X-Ray analysis of p-toluenesulfonyl derivative).

(SS):(SR)>98:2 (by  $^1H$  and  $^{13}C$  nmr)

A.V.Tkachev, A.V.Rukavishnikov, Yu.V.Gatilov, I.Yu.Bagrijanskaja

*Tetrahedron: Asymmetry* 1992, 3, 1165



Methyl 2,2-dimethyl-3-(2-hydroxypropyl)-cyclopropaneacetate

$$[\alpha]_{580}^{22} + 5.0 \text{ (c } 4.02, \text{ CHCl}_3\text{)}$$

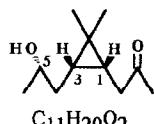
Source of chirality: diastereoselective baker's yeast-induced reduction of the corresponding ketone.

Absolute configuration: 1R,3S,SS  
(assigned by chemical correlation).

(SS):(SR)>98:2 (by  $^1H$  and  $^{13}C$  nmr)

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*Tetrahedron: Asymmetry* 1992, 3, 1165



2,2-Dimethyl-3-(2-hydroxypropyl)-1-(2-oxo-propyl)-cyclopropane

$$[\alpha]_{580}^{19} + 23.7 \text{ (c } 5.73, \text{ CHCl}_3\text{)}$$

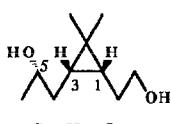
Source of chirality: diastereoselective baker's yeast-induced reduction of the corresponding ketone.

Absolute configuration: 1R,3S,SS  
(assigned by chemical correlation).

(SS):(SR)>98:2 (by  $^1H$  and  $^{13}C$  nmr)

A.V.Tkachev, A.V.Rukavishnikov, Yu.V.Gatilov, I.Yu.Bagrijanskaja

*Tetrahedron: Asymmetry* 1992, 3, 1165



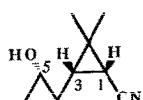
2,2-Dimethyl-1-(2-hydroxyethyl)-3-(2-hydroxypropyl)cyclopropane

$$[\alpha]_{580}^{23} + 6.8 \text{ (c } 6.01, \text{ CHCl}_3\text{)}$$

Source of chirality: diastereoselective baker's yeast-induced reduction of the corresponding ketone.

Absolute configuration: 1R,3S,SS  
(assigned by chemical correlation).

(SS):(SR)>98:2 (by  $^1H$  and  $^{13}C$  nmr)

 $C_9H_{15}NO$ 

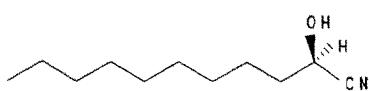
2,2-Dimethyl-3-(2-hydroxypropyl)-cyclopropanecarbonitrile

 $[\alpha]_{D}^{23} + 12.5 \text{ (c } 9.29, \text{ CHCl}_3\text{)}$ 

Source of chirality: diastereoselective baker's yeast-induced reduction of the corresponding ketone.

Absolute configuration: 1R,3S,5S

(assigned by chemical correlation).

(5S):(5R)>98:2 (by  $^1H$  and  $^{13}C$  nmr)

E.e. = 63 % (by chiral GLC)

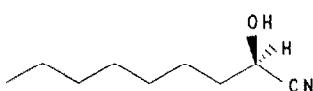
Source of chirality: (R)-

mandelonitrile lyase

Absolute configuration: (R)

 $C_{11}H_{21}NO$ 

(R)-2-Hydroxyundecanenitrile



E.e. = 87 % (by chiral GLC)

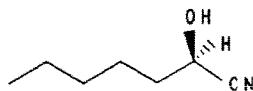
Source of chirality: (R)-

mandelonitrile lyase

Absolute configuration: (R)

 $C_9H_{17}NO$ 

(R)-2-Hydroxynonanenitrile



E.e. = 94 % (by chiral GLC)

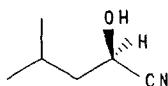
Source of chirality: (R)-

mandelonitrile lyase

Absolute configuration: (R)

 $C_7H_{13}NO$ 

(R)-2-Hydroxyheptanenitrile



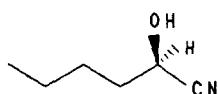
E.e. = 94 % (by chiral GLC)

Source of chirality: (*R*)-

mandelonitrile lyase

Absolute configuration: (*R*)

$C_6H_{11}NO$   
*(R)*-2-Hydroxy-4-methylpentanenitrile



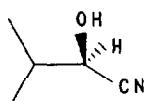
E.e. = 97 % (by chiral GLC)

Source of chirality: (*R*)-

mandelonitrile lyase

Absolute configuration: (*R*)

$C_6H_{11}NO$   
*(R)*-2-Hydroxyhexanenitrile



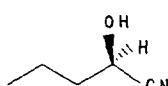
E.e. = 83 % (by chiral GLC)

Source of chirality: (*R*)-

mandelonitrile lyase

Absolute configuration: (*R*)

$C_5H_9NO$   
*(R)*-2-Hydroxy-3-methylbutanenitrile



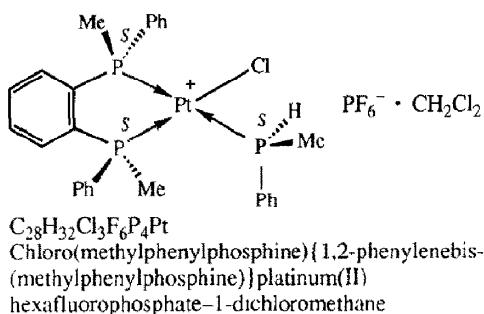
E.e. = 95 % (by chiral GLC)

Source of chirality: (*R*)-

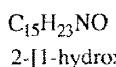
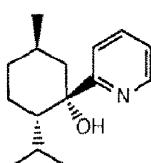
mandelonitrile lyase

Absolute configuration: (*R*)

$C_5H_9NO$   
*(R)*-2-Hydroxypentanenitrile



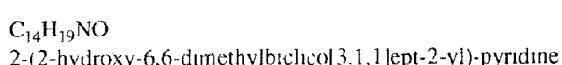
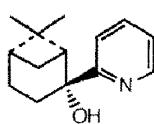
E.e. = 100%

[α]<sub>D</sub> = +56 (c 1, CH<sub>2</sub>Cl<sub>2</sub>)Absolute configuration [S-(R\*), (R\*,R\*)]  
(X-ray crystal structure)Source of chirality: [R-(R\*,R\*)]-1,2-C<sub>6</sub>H<sub>4</sub>(PMePh)<sub>2</sub>  
(N. K. Roberts and S. B. Wild,  
*J. Am. Chem. Soc.* 1979, 101, 6254.)[α]<sub>D</sub><sup>25</sup> -33.0 (c 1.6, CCl<sub>4</sub>); mp 69-70 °C

Absolute configuration: 1S, 2S, 5R

Source of chirality: (-)-menthone

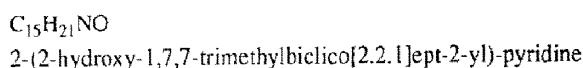
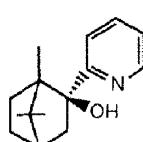
Use: catalyst for enantioselective reactions

[α]<sub>D</sub><sup>25</sup> -1.9 (c 1.6, CCl<sub>4</sub>); bp 120 °C (0.1 mbar)

Absolute configuration: 1R, 2R, 5R

Source of chirality: (+)-nopolone

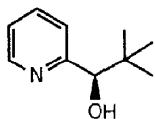
Use: catalyst for enantioselective reactions

[α]<sub>D</sub><sup>25</sup> -46.2 (c 1.6, CCl<sub>4</sub>); mp 59-60 °C

Absolute configuration: 1R, 2S, 5S

Source of chirality: (+)-camphor

Use: catalyst for enantioselective reactions



$[\alpha]^{25}_D +16.32$  (*c* 1.6, CCl<sub>4</sub>); bp 100 °C (10 mbar)

Absolute configuration: R E.e.= 91 %

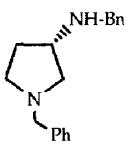
Source of chirality: asymmetric reduction with a chiral borane

Use: catalyst for enantioselective reactions

C<sub>10</sub>H<sub>15</sub>NO

2-(2,2-dimethyl-1-hydroxypropyl)pyridine

Jacques Maddaluno, Aline Corruble, Valérie Leroux, Gérard Plé,  
Lucette Duhamel and Pierre Duhamel\*.



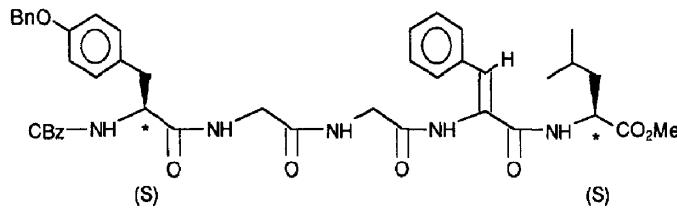
E.e.= 86% [by derivatization with (-)-α-fluoro-α-phenyl acetic acid chloride]

$[\alpha]_D^{27} = +1.7$  (*c* 2.0, CHCl<sub>3</sub>)

Source of chirality: natural [(S)-Asparagine] and asymm. synth.  
Absolute configuration 3S

C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>  
3-Benzylamino-N-benzyl-pyrrolidine

A. Hammadi, J. M. Nuzillard, J. C. Poulin and H. B. Kagan



mp = 91-93°C

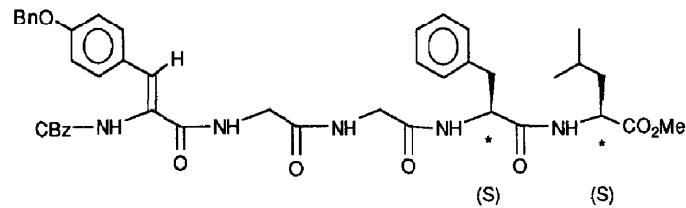
$[\alpha]_D = -9.9$  (*c* 1.0, CH<sub>3</sub>OH)

Source of chirality : (S)Tyrosine,  
(S)Leucine

C<sub>44</sub>H<sub>48</sub>N<sub>5</sub>O<sub>9</sub>

CBz-(O)Bn-(S)Tyr-(Gly)2-Δ<sup>Z</sup>Phe-(S)Leu-OMe

A. Hammadi, J. M. Nuzillard, J. C. Poulin and H. B. Kagan



mp = 124-126°C

$[\alpha]_D = 6.7$  (*c* 1.0, CH<sub>3</sub>OH)

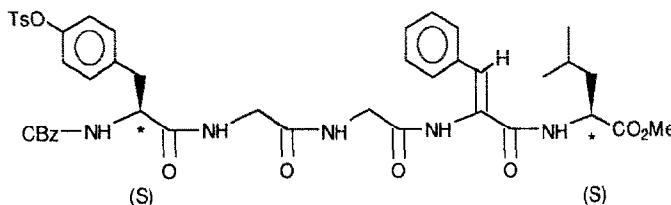
Source of chirality :  
(S)Phenylalanine, (S)Leucine

C<sub>44</sub>H<sub>48</sub>N<sub>5</sub>O<sub>9</sub>

CBz-(O)Bn-Δ<sup>Z</sup>Tyr-(Gly)2-(S)Phe-(S)Leu-OMe

A. Hammadi, J. M. Nuzillard, J. C. Poulin and H. B. Kagan

Tetrahedron: Asymmetry 1992, 3, 1247



C<sub>44</sub>H<sub>49</sub>N<sub>5</sub>O<sub>11</sub>S

CBz-(O)Ts-(S)Tyr-(Gly)<sub>2</sub>-Δ<sup>Z</sup>Phe-(S)Leu-OMe

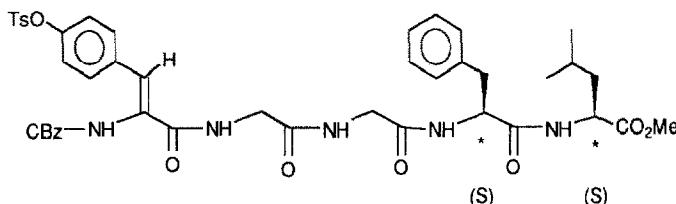
mp = 128-129°C

[α]<sub>D</sub> = -18.1 (c 1.0, CH<sub>3</sub>OH)

Source of chirality : (S)Tyrosine,  
(S)Leucine

A. Hammadi, J. M. Nuzillard, J. C. Poulin and H. B. Kagan

Tetrahedron: Asymmetry 1992, 3, 1247



C<sub>44</sub>H<sub>49</sub>N<sub>5</sub>O<sub>11</sub>S

CBz-(O)Bn-Δ<sup>Z</sup>Tyr-(Gly)<sub>2</sub>-(S)Phe-(S)Leu-OMe

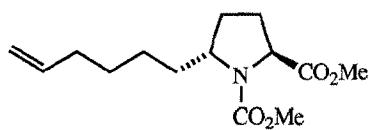
mp = 88-89°C

[α]<sub>D</sub> = 7.1 (c 1.0, CH<sub>3</sub>OH)

Source of chirality :  
(S)Phenylalanine, (S)Leucine

M. Skrinjar, C. Nilsson and L. -G. Wistrand

Tetrahedron: Asymmetry 1992, 3, 1263



C<sub>14</sub>H<sub>23</sub>NO<sub>4</sub>

(5R)-5-(5-Hexenyl)-1-methoxy-carbonyl-L-proline methyl ester

E.e. ≥ 90 %

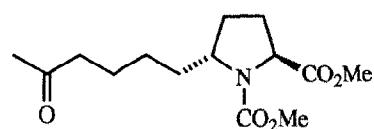
[α]<sub>D</sub><sup>25</sup> = -71.2 (c 1.0, MeOH)

Source of chirality: L-proline

Absolute configuration: 2S, 5R

M. Skrinjar, C. Nilsson and L. -G. Wistrand

Tetrahedron: Asymmetry 1992, 3, 1263



C<sub>14</sub>H<sub>23</sub>NO<sub>5</sub>

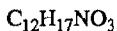
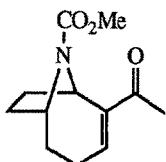
(5R)-1-Methoxycarbonyl-5-(1-(5-oxohexyl))-L-proline methyl ester

E.e. ≥ 90 %

[α]<sub>D</sub><sup>25</sup> = -84.3 (c 1.0, MeOH)

Source of chirality: L-proline

Absolute configuration: 2S, 5R

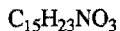
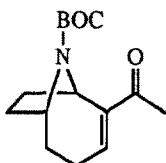


(1R)-2-Acetyl-9-methoxycarbonyl-9-azabicyclo[4.2.1]-2-nonene

E.e.  $\geq 90\%$  $[\alpha]_D^{25} = -40.9$  (c 1.0, MeOH)

Source of chirality: L-proline

Absolute configuration: 1R



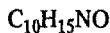
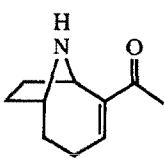
(1R)-2-Acetyl-9-t-butyloxy-carbonyl-9-azabicyclo[4.2.1]nonane

E.e. = 94 % (det. by Mosher derivative of a precursor)

 $[\alpha]_D^{25} = -46.8$  (c 0.839,  $CH_2Cl_2$ )

Source of chirality: L-proline

Absolute configuration: 1R

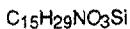
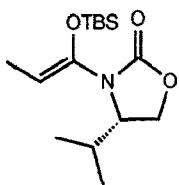


(+)-Anatoxin-a

E.e. = 94 % ( $^1H$  NMR and HPLC of Mosher derivative) $[\alpha]_D^{25} = +39.8$  (c 0.676, abs. EtOH)

Source of chirality: L-proline

Absolute configuration: 1R

(assigned on the basis of  $\alpha_D$ )

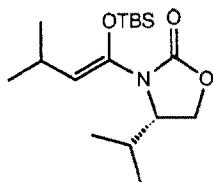
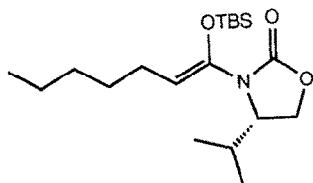
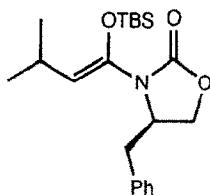
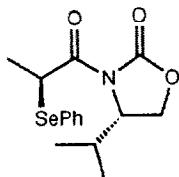
3[4S, (Z)]-{1-[{[(1,1-dimethylethyl)dimethylsilyl]oxy}-1-propenyl]-4-(1-methylethyl)-2-oxazolidinone}

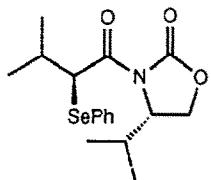
E.e. &gt;95%

 $[\alpha]_D^{21} -62$  (c 3.26 in  $CHCl_3$ )

Source of chirality: (L)-valine

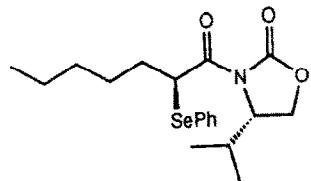
Absolute configuration: 4S

 $C_{17}H_{33}NO_3Si$  $\beta/4S, (Z)\text{-}\{1\text{-}\{(1,1\text{-dimethylethyl})dimethylsilyl\}oxy\}\text{-}3\text{-methyl-1-butene}\text{-}4\text{-}(1\text{-methylethyl)}\text{-2-oxazolidinone}$ E.e. >95%  
 $[\alpha]_D^{25} -63 (c 0.77 \text{ in CHCl}_3)$ Source of chirality: (L)-valine  
Absolute configuration: 4S $C_{19}H_{37}NO_3Si$  $\beta/4S, (Z)\text{-}\{1\text{-}\{(1,1\text{-dimethylethyl})dimethylsilyl\}oxy\}\text{-}1\text{-heptene}\text{-}4\text{-}(1\text{-methylethyl)}\text{-2-oxazolidinone}$ E.e. >95%  
 $[\alpha]_D^{25} -64 (c 1.93 \text{ in CHCl}_3)$   
Source of chirality: (L)-valine  
Absolute configuration: 4S $C_{21}H_{34}NO_3Si$  $\beta/4R, (Z)\text{-}\{1\text{-}\{(1,1\text{-dimethylethyl})dimethylsilyl\}oxy\}\text{-}3\text{-methyl-1-butene}\text{-}4\text{-}(1\text{-methylphenyl)}\text{-2-oxazolidinone}$ E.e. >95%  
 $[\alpha]_D^{25} +42 (c 1.27 \text{ in CHCl}_3)$   
Source of chirality: (D)-phenylalanine  
Absolute configuration: 4R $C_{15}H_{19}NO_3Se$  $\beta(2R,4S)\text{-}3\text{-}\{2\text{-phenylseleno-1-oxopropyl}\}\text{-}4\text{-}(1\text{-methylethyl)}\text{-2-oxazolidinone}$ D.e. 72%  
 $[\alpha]_D^{21} +145 (c 3.73 \text{ in CHCl}_3)$   
Source of chirality: Asymmetric Synthesis  
Absolute configuration: 2R,4S



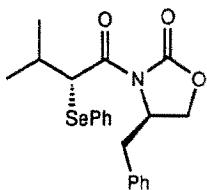
D.e. 94%  
 $[\alpha]_D^{21} +47$  (*c* 0.86 in CHCl<sub>3</sub>)

Source of chirality: Asymmetric Synthesis  
 Absolute configuration: 2R,4S

C<sub>17</sub>H<sub>23</sub>NO<sub>3</sub>Se*(3(2R),4S)-3-(2-Phenylseleno-3-methyl-1-oxobutyl)-4-(1-methylethyl)-2-oxazolidinone*

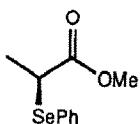
D.e. 60 %  
 $[\alpha]_D^{25} +58$  (*c* 1.52 in CHCl<sub>3</sub>)

Source of chirality: Asymmetric Synthesis  
 Absolute configuration: 2R,4S

C<sub>19</sub>H<sub>27</sub>NO<sub>3</sub>Se*(3(2R),4S)-3-(2-Phenylseleno-1-oxoheptyl)-4-(1-methylethyl)-2-oxazolidinone*

D.e. 86 %  
 $[\alpha]_D^{25} -11$  (*c* 1.16 in CHCl<sub>3</sub>)

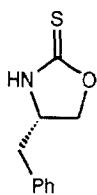
Source of chirality: Asymmetric Synthesis  
 Absolute configuration: 2S,4R

C<sub>21</sub>H<sub>23</sub>NO<sub>3</sub>Se*(3(2S),4R)-3-(2-Phenylseleno-3-methyl-1-oxobutyl)-4-(1-methylphenyl)-2-oxazolidinone*

E.e. 70 % [by NMR with Eu(tfc)<sub>3</sub>]  
 $[\alpha]_D^{21} -133$  (*c* 2.59 in CHCl<sub>3</sub>)

Source of chirality: Asymmetric Synthesis  
 Absolute configuration: 2R

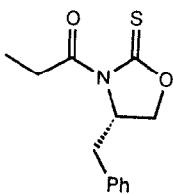
C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>Se*(2R)-2-Phenylselenopropanoic acid, methyl ester*

C<sub>10</sub>H<sub>11</sub>NOS

(4S)-4-Methylphenyl-2-oxazolidinethione

E.e. >95 %  
 $[\alpha]_D^{21} -107$  (*c* 2.89 in CHCl<sub>3</sub>)

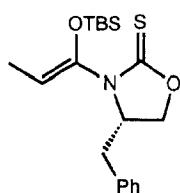
Source of chirality: (L)-phenylalaninol  
 Absolute configuration: 4S

C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub>S

(4S)-4-Methylphenyl-3-(oxopropyl)-2-oxazolidinethione

E.e. >95 %  
 $[\alpha]_D^{21} +130$  (*c* 1.69 in CHCl<sub>3</sub>)

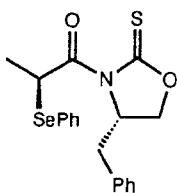
Source of chirality: (L)-phenylalaninol  
 Absolute configuration: 4S

C<sub>19</sub>H<sub>29</sub>NO<sub>2</sub>SSI

(3/4S, (Z))-1-[(1,1-dimethylethyl)dimethylsilyloxy]-1-propenyl-4-(1-methylphenyl)-2-oxazolidinethione

E.e. >95 %  
 $[\alpha]_D^{21} -30$  (*c* 2.23 in CHCl<sub>3</sub>)

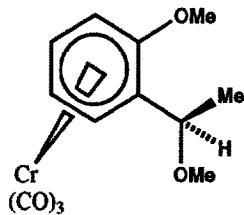
Source of chirality: (L)-phenylalaninol  
 Absolute configuration: 4S

C<sub>19</sub>H<sub>19</sub>NO<sub>2</sub>SSe

(3(2R),4S)-3-(2-Phenylseleno-1-oxopropyl)-4-(1-methylphenyl)-2-oxazolidinethione

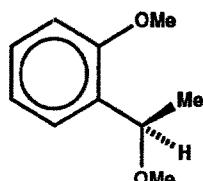
D.e. 76%  
 $[\alpha]_D^{21} +129$  (*c* 0.99 in CHCl<sub>3</sub>)

Source of chirality: Asymmetric Synthesis  
 Absolute configuration: 2R,4S



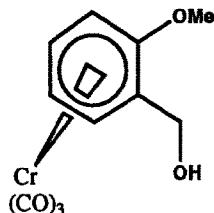
$C_{13}H_{14}CrO_5$   
Tricarbonyl( $\eta^6$ - $\alpha$ -methoxy- $\omega$ -methoxybenzyl methyl ether)chromium(0)

e.e. = 100 %  
 $[\alpha]_D^{22} = +220$  (c 0.8, CHCl<sub>3</sub>)  
 Absolute configuration R,R



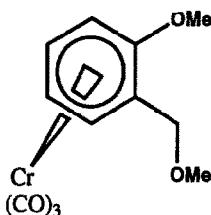
$C_{10}H_{14}CrO_2$   
α-Methyl- $\omega$ -methoxybenzyl methyl ether

e.e. = 100 %  
 $[\alpha]_D^{22} = +109$  (c 1.2, CHCl<sub>3</sub>)  
 Absolute configuration R



$C_{11}H_{10}CrO_5$   
Tricarbonyl( $\eta^6$ - $\omega$ -methoxybenzyl alcohol)chromium(0)

e.e. = 100 %  
 $[\alpha]_D^{22} = +237$  (c 1, CHCl<sub>3</sub>)  
 Absolute configuration R



$C_{12}H_{12}CrO_5$   
Tricarbonyl( $\eta^6$ - $\omega$ -methoxybenzyl methyl ether)chromium(0)

e.e. = 100 %  
 $[\alpha]_D^{22} = +200$  (c 1.3, CHCl<sub>3</sub>)  
 Absolute configuration R