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Carbohydrate Functionalized Oxacyclopentylidene Complexes[1]

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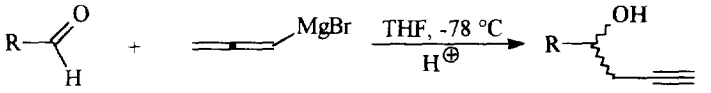
Abstract: Carbohydrate functionalized 2-oxacyclopentylidene complexes of chromium and tungsten **5a/b** - **8c/d** are synthesized by cycloisomerization of butynols **1a/b** - **4a/b** at a pentacarbonylmetal template. Their α-CH-acidity is exploited to generate compounds **9a** and **10a** bearing *exo*-alkylidene groups. Ring-opening aminolysis of **7a** leads to aminocarbene complex **11a** which - under Mitsunobu conditions - undergoes cyclization to give chromium azacyclopentylidene **12a**. © 1997 Elsevier Science Ltd.

Polyfunctionalized tetrahydrofurans are useful building blocks in organic synthesis.[2] They are used as chiral auxiliaries,[3] in the synthesis of oligo-tetrahydrofurans[4] and polyether antibiotics,[5] and are ubiquitous as furanoses. We became interested in the organometallic chemistry of sugars, and we now report on the synthesis of carbohydrate-functionalized oxacyclopentylidene complexes which is based on the cycloisomerization of butynols at coordinatively unsaturated group VI transition metal templates.[6] Fischer-type carbene complexes are known as stable but highly reactive compounds[7] which have been used in Michael-[8], Aldol-[9] and cycloaddition reactions.[10] The need to perform these reactions stereoselectively has recently caused growing interest in metal carbenes bearing a chiral carbene side chain.[10a,b] In this context, mainly amino acids,[11] amines[12] and terpene alcohols[13] have been employed; the use of carbohydrates in the chiral modification of the carbene ligand, however, is still restricted to only a few examples.[14] Butynols, required as oxacyclopentylidene precursors, are generally obtained *via* addition of *propargyl* organometallics[15] to aldehydes or ketones. In our approach, however, *allenyl* magnesium bromide[16] was the reagent of choice since it is known to undergo clean γ-addition to carbonyl compounds (Scheme 1).



1a/b - 4a/b

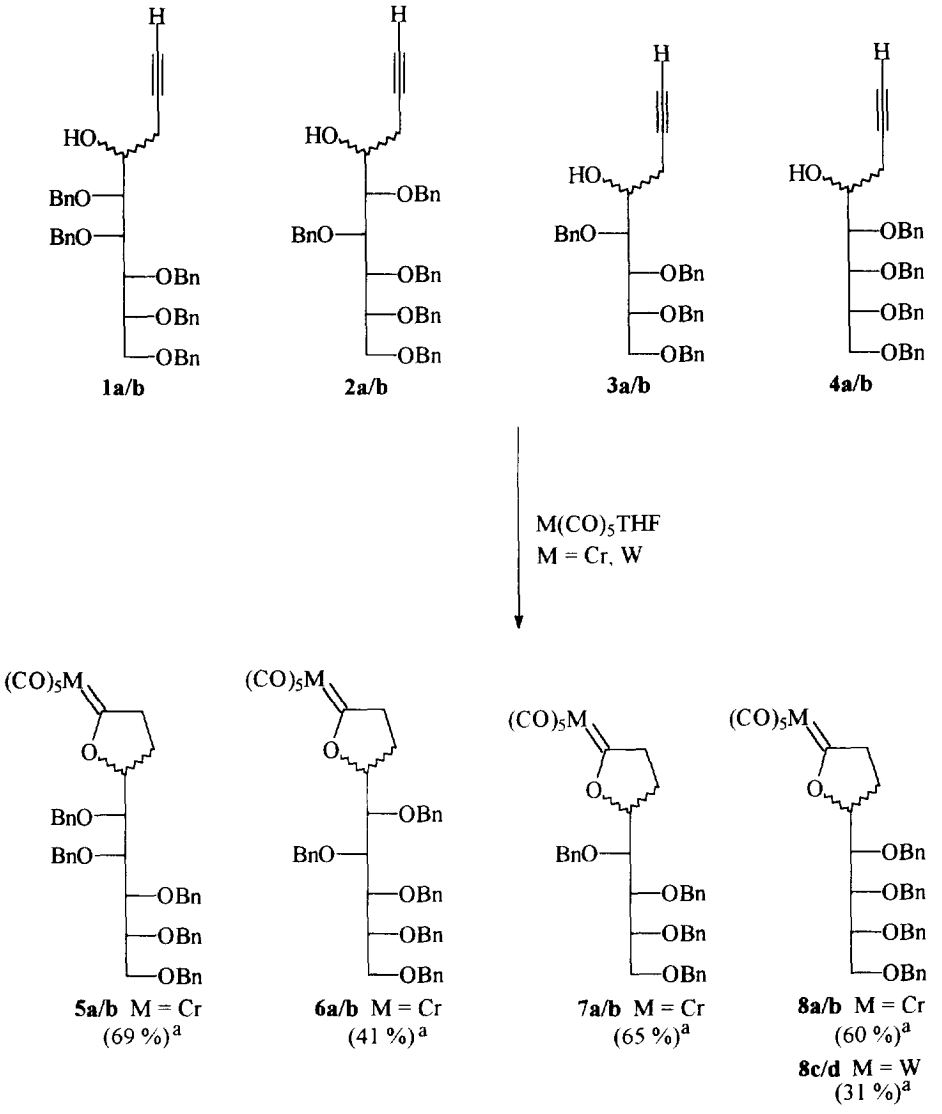
Scheme 1

Table 1. Yields and Diastereomeric Ratios of Synthesized Alkynols

alkynol	R	% yield[a]	diastereomeric ratio[b]
1a/b	perbenzyloxy-"*manno*"	82	3.6:1
2a/b	perbenzyloxy-"*gluco*"	67	1:1
3a/b	perbenzyloxy-"*arabino*"	75	1:1
4a/b	perbenzyloxy-"*ribo*"	89	4.6:1

[a]isolated yield, [b]determined by ^{1}H NMR spectroscopy

Addition of the Grignard reagent to the carbohydrate aldehyde requires protection of the free hydroxyl groups. This is achieved by thioacetalization[17] of the unprotected sugars followed by benzylation and dethioacetalization.[18] Propargylation of the aldehydes affords the alkynols **1a/b - 4a/b**, in very good yields but in low diastereoselectivity. In the *gluco*- and *arabino*-series both diastereomeric alcohols **2 a/b** and **3 a/b** are formed in a 1 : 1 ratio whereas for the mannose and ribose derivatives **1a/b** and **4a/b** a 3.6 : 1 and 4.6 : 1 preference, respectively, is observed. As demonstrated for the *gluco*-derivatives, a separation of the diastereomers is possible using chromatographic techniques but, generally, is easier to perform at the metal carbene stage. For the cycloisomerization of the alkynols we used pentacarbonyl[tetrahydrofuran]chromium(0) and -tungsten(0) generated by UV irradiation of the corresponding metal hexacarbonyls in THF at -10 °C.[19] At the pentacarbonyl-metal template the cyclization of the diastereomeric butynols **1a/b - 4a/b** affords the oxacyclopentylidene complexes **5a/b - 8c/d** in moderate to good yields (Scheme 2). Remarkably, the reactivity of the two diastereomers is significantly different, an observation which was made for all sugar moieties we used.

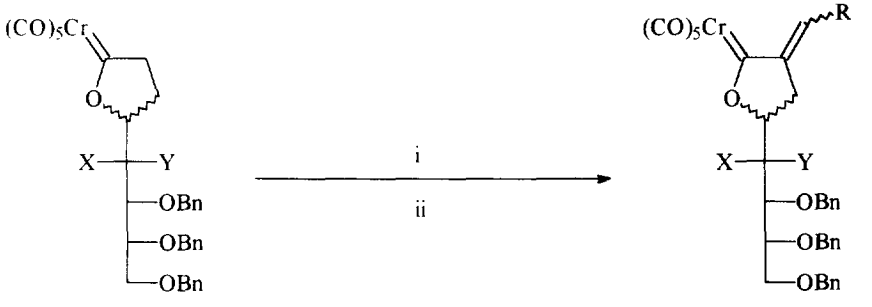


[a] isolated yield after flash chromatography

Scheme 2

The spectroscopic properties of complexes **5a/b - 8c/d** are typical for Fischer carbene complexes. Most striking are the significant down-field shifts of the carbene carbon atoms C-1 (ca. 341 ppm) in the ^{13}C NMR spectra. This indicates the presence of a new strongly electrophilic center which can be exploited for further functionalization based on either addition of nucleophiles or α-CH-acidity.[20]

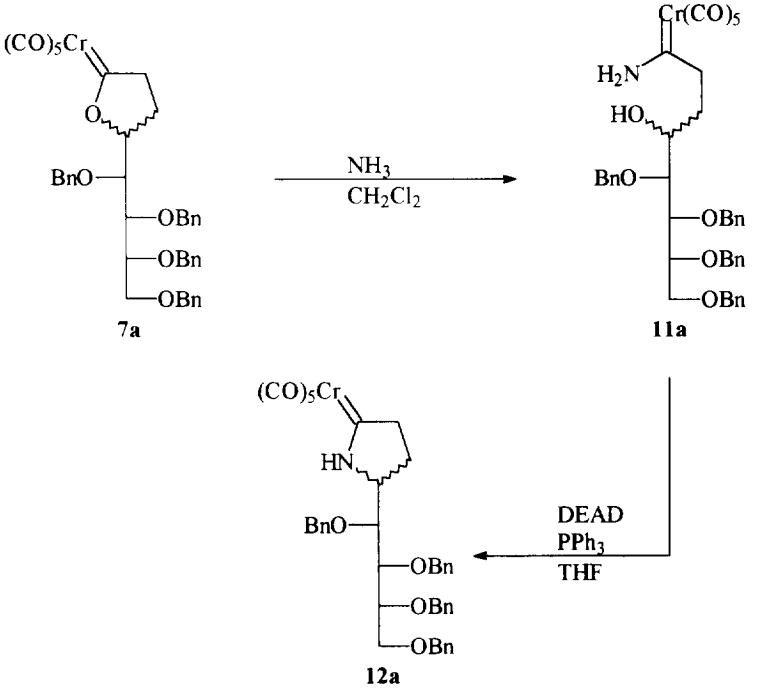
The α-CH-acidity of 2-oxacyclopentylidene complexes allows the synthesis of *exo*-alkylidene complexes (Scheme 3) that may be promising reagents for ligand- or metal-centered cycloaddition reactions.[21] Deprotonation of the ribose derivative **8a** with *n*-butyllithium at -78 °C in THF generates the conjugated base which is trapped in an aldol-type reaction with benzaldehyde activated by boron trifluoride - etherate to give pentacarbonyl[5-phenylmethylene-3-(*R/S*)-(1'-(*R*), 2'-(*R*), 3'-(*R*), 4-tetrabenzyloxybutyl)-2-oxacyclopentylidene]chromium(0) (**9a**) in 73 % yield as a mixture of diastereomers. An *exo*-methylene group is introduced following a protocol reported by Maiorana and coworkers.[22] If the carbene complex anion obtained from **7a** upon deprotonation is treated with the electrophilic C_1 source *N,N*-dimethylmethylene iminium chloride, the parent α-*exo*-methylene complex **10a** can be isolated in good yield.



Scheme 3

The electrophilicity of the carbene carbon atom can be further exploited in the addition of nucleophiles as demonstrated by the aminolysis of *arabino*-complex **7a**. Bubbling gaseous ammonia through a solution of **7a** in dichloromethane at -78 °C leads to a colour change from orange to yellow indicating the formation of aminocarbene complex **11a**. The addition of the N-nucleophile to the carbene carbon atom is followed by ring-opening and, thus, regenerates an unprotected hydroxy group at the former C-1 position of the sugar skeleton. We speculated whether the butynol cycloisomerization/aminolysis sequence could be used in an approach to azacycloalkylidene complexes. Their synthesis *via* a metal template assisted cycloisomerization of alkynylamines - similar to the metal oxacycloalkylidene route - is hampered by the superior coordination ability of

the nitrogen functionality.[23] A nucleophilic substitution of the γ-hydroxy group clearly suffers from the reduced nucleophilicity of the amino group as a consequence of the partial lone-pair donation of the nitrogen to the carbene carbon atom. However, in the presence of diethyl azodicarboxylate (DEAD) and triphenylphosphine hydroxy groups can be modified to excellent leaving groups as has been recently demonstrated for an intermolecular reaction using phthalimide.[24] This strategy also works with metal aminocarbenes, the even less "nucleophilic" isolobal analogs[25] of carboxylic amides. Thus, under Mitsunobu conditions[26] the γ-hydroxy aminocarbene complex **11a** undergoes nucleophilic cyclization to give azacyclopentylidene complex **12a** in good yield (Scheme 4). This route provides a complementary access to cyclic metal aminocarbenes. Their synthesis, so far, has been reported from γ-lactones, and has required $K_2[Cr(CO)_5]$ as a troublesome metal nucleophile.[27]



Scheme 4

EXPERIMENTAL

General: All transformations involving organometallics were performed under argon using solvents dried by standard procedures. The chromatographic workup was carried out at 0 °C with degassed solvents on silica gel (Merck 60 (0.063 - 0.200 mm)). - ^1H and ^{13}C NMR: Bruker DRX-500, AM-400

and AM-250. Chemical shifts refer to those of residual solvent signals based on $\delta_{TMS} = 0.00$. - FT-IR: Nicolet Magna 550. - Elemental analyses: Heraeus CHN-O-Rapid and Elementar Analysensysteme GmbH Vario EL. - MS (EI, 70 eV): Kratos MS 50 and Kratos Concept 1H.

General procedure for the preparation of butynols and oxacyclopentylidene complexes as described for glucose

2, 3, 4, 5, 6-Penta-O-benzyl-1-C-(2-propynyl)-D-glucose (2)

1.13 ml (2.82 mmol) Allenyl magnesium bromide (2.5 M in diethyl ether) are added at -78 °C in one portion to a solution of 890 mg (1.41 mmol) perbenzylated D-glucose in 80 ml THF. After stirring for 1 h at - 78 °C the cooling bath is removed, and after an additional 10 min 20 ml of a half-concentrated solution of ammonium chloride are added. The organic layer is separated, and the aqueous layer is extracted three times with 30 ml portions of diethyl ether. The combined organic extracts are dried over sodium sulfate, and the solvent is evaporated to dryness. Column chromatography (SiO_2, petroleum ether/diethyl ether/dichloromethane: 4/1/1) yields 630 mg (67%) of a colourless oil containing equal amounts of two diastereomers (R_f = 0.39 (diastereomer **2a**) and R_f = 0.33 (diastereomer **2b**)).

Pentacarbonyl[3-(*R/S*)-(1'-(*R*), 2'-(*R*), 3'-(*R*), 4'-(*R*), 5'-pentabenzyloxypentyl)-2-oxacyclopentylidene]chromium(0) (6a)

1.6 ml (0.08 mmol) $Cr(CO)_5THF$ (0.05 M in THF) are added to 56 mg (0.08 mmol) of diastereomer **2a**. This mixture is concentrated to half of the volume and stirred at 20 °C for 20 h. After evaporation of the solvent the dark brown residue is purified by column chromatography (SiO_2, petroleum ether/diethyl ether: 2/1) yielding 28 mg (0.03 mmol, 40 %) of a yellow oil.

R_f (petroleum ether/diethyl ether: 2/1): 0.71; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.44 - 7.15 (m, 25 H, Ph), 4.95 (t*d, J = 8.2, 2.0 Hz, 1 H, H-3), 4.77 - 4.61 (m, 7 H, CH_2Ph), 4.57 (dd, J = 7.0, 2.0 Hz, 1 H, H-1'), 4.50 - 4.43 (m, 3 H, CH_2Ph), 4.04 (q, J = 4.6 Hz, 1 H, H-4'), 4.00 (t, J= 4.8 Hz, 1 H, H-3'), 3.98 (dd, J = 10.2, 4.0 Hz, 1 H, H-5a'), 3.84 (dd, J = 10.2, 4.6 Hz, 1 H, H-5b'), 3.72 (dd, J = 7.0, 4.7 Hz, 1 H, H-2'), 3.44 (ddd, J = 20.4, 9.9, 4.5 Hz, 1 H, H-5a), 2.79 (ddd, J = 20.4, 10.0, 7.7 Hz, 1H, H-5b), 1.67 (ddt, J = 12.5, 9.9, 7.7 Hz, 1H, H-4a), 1.11 (dddd, J = 12.5, 10.0, 8.7, 4.5 Hz, 1 H, H-4b); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 - 7.15 (m, 25 H, Ph), 4.93 (m, 1 H, H-3), 4.72 - 4.35 (m, 10 H, CH_2Ph), 4.35 (dd, J = 7.8, 1.9 Hz, 1 H, H-1'), 3.91 - 3.86 (m, 2 H, H-4', H-5a'), 3.83 - 3.72 (m, 3 H, H-3', H-5b', H-5a), 3.60 (dd, J = 7.8, 3.9 Hz, 1 H, H-2'), 3.35 (ddd, J = 20.4, 10.0, 7.4 Hz, 1 H, H-5b), 1.89 (m, 1 H, H-4a), 1.59 (m, 1 H, H-4b); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 340.68

(C-1), 223.41 (*trans*-CO), 216.62 (*cis*-CO), 138.33, 138.10, 137.97, 137.79 (5C, C-*ipso*), 128.69 - 127.71 (25 C, Ph), 99.91 (C-3), 80.07 (C-1'), 79.27 (C-2'), 78.86 (C-3'), 77.42 (C-4'), 75.25, 75.14, 73.53, 73.24, 72.44 (CH_2Ph), 69.12 (C-5'), 61.88 (C-5), 20.74 (C-4); MS (FAB, mNBA): m/z (%) = 863 (5) [M^+ + H], 778 (14) [M^+ - 3 CO], 722 (9) [M^+ - 5 CO], 632 (9) [M^+ + H - C_7H_7 - 5 CO], 580 (2) [M^+ + H - C_7H_7 - $Cr(CO)_5$]; IR (KBr): 2940 (w), 2850 (w), 2064 (m), 1983 (m), 1936 (vs), 1497 (w), 1454 (w), 1385 (w), 1207 (m), 1092 (m), 1067 (m), 1028 (m), 667 (m), 654 (m) cm^{-1}.

Pentacarbonyl[3-(*R*/*S*)-(1'-(*R*), 2'-(*R*), 3'-(*R*), 4'-(*R*), 5'-pentabenzyloxypentyl)-2-oxacyclopentylidene]chromium(0) (6b)

2.5 ml (0.125 mmol) $Cr(CO)_5THF$ (2.5 M in THF) are added to 84 mg (0.125 mmol) of diastereomer **2b**. This mixture is concentrated to half of the volume and stirred at 20 °C for 3 d. After evaporation of the solvent the dark brown residue is purified by column chromatography (SiO_2, petroleum ether/diethyl ether: 2/1) yielding 46 mg (0.053 mmol, 42 %) of a yellow oil.

R_f (petroleum ether/diethyl ether: 2/1): 0.62; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 - 7.18 (m, 25 H, Ph), 5.01 (m, 1 H, H-3), 4.82 - 4.38 (m, 10 H, CH_2Ph), 4.08 (dd, J = 7.5, 3.7 Hz, 1 H, H-2'), 3.91 - 3.89 (m, 3 H,H-3', H-4', H-5a'), 3.74 (dd, J = 11.7, 5.9 Hz, 1 H, H-5b'), 3.62 (dd, J = 7.4, 3.5 Hz, 1 H, H-1'), 3.41 (ddd, J = 20.5, 9.9, 6.3 Hz, 1 H, H-5a), 3.20 (ddd, J = 20.5, 9.9, 5.7 Hz, 1 H, H-5b), 1.10 (m, 1 H, H-4a), 0.88 (m, 1 H, H-4b); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 341.39 (C-1), 223.61 (*trans*-CO), 216.72 (*cis*-CO), 138.41, 138.13, 138.08 (C-*ipso*), 128.68 - 127.68 (Ph), 99.61 (C-3), 80.71 (C-1'), 79.67 (C-2'), 78.99 (C-3'), 77.48 (C-4'), 75.32, 74.97, 73.51, 73.09, 72.66 (CH_2Ph), 69.47 (C-5'), 61.16 (C-5), 23.01 (C-4); MS (FAB, mNBA): m/z (%) = 863 (2) [M^+ + H], 834 (1) [M^+ - CO], 778 (4) [M^+ - 3 CO], 772 (0.5) [M^+ - C_7H_7], 722 (2) [M^+ - 5 CO], 688 (1) [M^+ - C_7H_7 - 3 CO], 632 (1) [M^+ + H - C_7H_7 - 5 CO], 580 (2) [M^+ + H - C_7H_7 - $Cr(CO)_5$]; IR (KBr): 2918 (w), 2062 (m), 1983 (m), 1936 (vs), 1505 (w), 1454 (w), 1354 (w), 1206 (m), 1101 (m), 1069 (m), 1028 (m), 667 (m), 654 (m) cm^{-1}; elemental analysis (%): (mixture of diastereomers **6a/b**) calcd.: C 68.21, H 5.37, found: C 68.25, H 5.37.

Spectroscopic data for complexes **5a/b**, **7a/b** *and* **8a/b**

Pentacarbonyl[3-(*R*/*S*)-(1'-(*S*), 2'-(*R*), 3'-(*R*), 4'-(*R*), 5'-pentabenzyloxypentyl)-2-oxacyclopentylidene]chromium(0) (5a)

R_f (petroleum ether/diethyl ether: 2/1): 0.67; ^1H NMR (500 MHz, C_6D_6): δ = 7.50 - 7.15 (m, 25 H, Ph), 5.30 (t*d, J = 7.9 Hz,1 H, H-3), 4.85 (d, J = 11.0 Hz, 1 H, CH_2Ph), 4.71 (m, 3 H, CH_2Ph), 4.47 (m, J = 11.4, 11.6 Hz, 7 H, CH_2Ph, H-1'), 4.07 (dd, J = 4.5, 3.0 Hz, 1 H, H-3'), 3.99 (t*d, J =

5.0 Hz, 1 H, H-2'), 3.94 (m, J = 3.0 Hz, 2 H, H-4', H-5a'), 3.81 (dd, J = 11.3, 5.2 Hz, 1 H, H-5b'), 3.44 (ddd, J = 20.5, 9.6, 4.2 Hz, 1 H, H-5a), 2.70 (ddd, J = 20.6, 9.8, 8.2 Hz, 1 H, H-5b), 1.89 (m, 1 H, H-4a), 1.20 (m, 1 H, H-4b); ^{13}C NMR (100 MHz, C_6D_6): δ = 341.17 (C-1), 223.91 (*trans*-CO), 217.41 (*cis*-CO), 139.02, 138.97, 138.76, 138.32 (C-*ipso*), 128.97 - 127.90 (Ph), 101.51 (C-3), 80.71 (C-1'), 80.31 (C-2'), 80.15 (C-3'), 79.13 (C-4'), 75.11, 74.83, 73.79, 73.66, 72.29 (CH_2Ph), 69.08 (C-5'), 62.58 (C-5), 21.30 (C-4); IR (petroleum ether): 2064 (m), 1985 (w), 1946 (vs) cm^{-1}.

Pentacarbonyl[3-(*R*/*S*)-(1'-(*S*), 2'-(*R*), 3'-(*R*), 4'-(*R*), 5'-pentabenzyloxypentyl)-2-oxacyclopentylidene]chromium(0) (5b)

R_f (petroleum ether/diethyl ether: 2/1): 0.59; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.55 - 7.20 (m, 25 H, Ph), 5.25 (ddd, J = 8.2, 6.2, 2.6 Hz,1 H, H-3), 5.09 (d, J = 11.7 Hz, 1 H, CH_2Ph), 5.01 (d, J = 11.5 Hz, 1 H, CH_2Ph), 4.97 (d, J = 11.9 Hz, 1 H, CH_2Ph), 4.83 (d, J = 12.0 Hz, 1 H, CH_2Ph), 4.69 (d, J = 11.8 Hz, 1 H, CH_2Ph), 4.64 (d, J = 11.7 Hz, 1 H, CH_2Ph), 4.57 (d, J = 11.7 Hz, 1 H, CH_2Ph), 4.43 (s, 2 H, CH_2Ph), 4.36 (dd, J = 6.8, 2.9 Hz, 1 H, H-2'), 4.32 (d, J = 11.7 Hz, 1 H, CH_2Ph), 4.32 (m, J = 5.1, 2.9 Hz, 1 H, H-4'), 4.18 (dd, J = 5.1, 2.9 Hz, 1 H, H-3'), 4.09 (dd, J = 10.5, 2.9 Hz, 1 H, H-5a'), 3.89 (dd, J = 10.6, 5.2 Hz, 1 H, H-5b'), 3.77 (d, J = 6.8, 2.8 Hz, 1 H, H-1'), 3.22 (ddd, J = 20.6, 9.5, 6.8 Hz, 1 H, H-5a), 2.80 (ddd, J = 20.6, 9.5, 6.4 Hz, 1 H, H-5b), 1.22 (m, 1 H, H-4a), 0.94 (m, 1 H, H-4b); ^{13}C NMR (100 MHz, C_6D_6): δ = 341.81 (C-1), 223.95 (*trans*-CO), 217.39 (*cis*-CO), 139.34, 139.29, 139.18, 138.98, 138.33 (C-*ipso*), 128.88 - 127.77 (Ph), 99.41 (C-3), 81.13 (C-1'), 80.25 (C-2'), 79.45 (C-3'), 79.02 (C-4'), 74.97, 74.51, 73.73, 73.03, 72.56 (CH_2Ph), 70.57 (C-5'), 61.30 (C-5), 23.25 (C-4); IR (petroleum ether): 2064 (m), 1986 (w), 1946 (vs) cm^{-1}.

Pentacarbonyl[3-(*R*/*S*)-(1'-(*S*), 2'-(*R*), 3'-(*R*), 4'-tetrabenzyloxybutyl)-2-oxacyclopentylidene]-chromium(0) (7a)

R_f (petroleum ether/diethyl ether: 2/1): 0.74; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.44 - 7.17 (m, 20 H, Ph), 5.09 (t*d, J = 8.0, 1.9 Hz, 1 H, H-3), 4.75 (d, J = 12.0 Hz, 1 H, CH_2Ph), 4.64 (d, J = 11.5 Hz, 1 H, CH_2Ph), 4.63 (d, J = 11.2 Hz, 1 H, CH_2Ph), 4.60 (d, J = 11.5 Hz, 1 H, CH_2Ph), 4.58 (dd, J = 5.3, 1.9 Hz, 1 H, H-1'), 4.57 (d, J = 12.0 Hz, 1 H, CH_2Ph), 4.54 (d, J = 11.2 Hz, 1 H, CH_2Ph), 4.43 (d, J = 12.0 Hz, 1 H, CH_2Ph), 4.40 (d, J = 12.0 Hz, 1 H, CH_2Ph), 3.89 (q*, J = 4.7 Hz, 1 H, H-3'), 3.84 (t*, J = 5.0 Hz, 1 H, H-2'), 3.78 (dd, J = 10.1, 4.3 Hz, 1 H, H-4a'), 3.71 (dd, J = 10.1, 5.0 Hz, 1 H, H-4b'), 3.45 (ddd, J = 20.6, 9.7, 4.4 Hz, 1 H, H-5a), 2.78 (ddd, J = 20.6, 9.9, 7.8 Hz, 1 H, H-5b), 1.73 (ddt, J = 12.5, 9.7, 7.8 Hz, 1 H, H-4a), 1.07 (dddd, J = 12.5, 9.9, 8.2, 4.4 Hz, 1 H, H-4b); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 - 7.14 (m, 20 H, Ph), 5.09 (t*d, J = 7.9, 1.9 Hz, 1 H, H-3), 4.79

(d, J = 11.7 Hz, 1 H, CH_2Ph), 4.63 (d, J = 12.1 Hz, 1 H, CH_2Ph), 4.62 (d, J = 12.1 Hz, 1 H, CH_2Ph), 4.61 (d, J = 11.0 Hz, 1 H, CH_2Ph), 4.59 (d, J = 11.7 Hz, 1 H, CH_2Ph), 4.54 (s, 2 H, CH_2Ph), 4.53 (d, J = 11.0 Hz, 1 H, CH_2Ph), 4.50 (dd, J = 4.7, 1.9 Hz, 1 H, H-1'), 3.86 - 3.67 (m, 4 H, H-2', H,3', H-4a', H-4b', H-5a), 3.36 (ddd, J = 20.3, 9.8, 7.8 Hz, 1 H, H-5b), 1.98 (ddt, J = 12.9, 9.8, 7.8 Hz, 1 H, H-4a), 1.55 (dddd, J = 12.9, 9.8, 8.2, 4.7 Hz, 1 H, H-4b); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 341.12 (C-1), 223.42 (*trans*-CO), 216.61 (*cis*-CO), 138.04, 137.93, 137.71, 137.65 (C-*ipso*), 128.53 - 127.73 (Ph), 100.40 (C-3), 78.27 (C-1'), 78.16 (C-2'), 77.34 (C-3'), 73.78, 73.72, 73.48, 72.27 (CH_2Ph), 68.06 (C-4'), 62.02 (C-5), 20.59 (C-4); MS (FAB, mNBA): m/z (%) = 742 (9) [M^+], 658 (35) [M^+ - 3 CO], 602 (12) [M^+ - 5 CO], 568 (7) [M^+ + H - C_7H_7 - 3 CO], 511 (12) [M^+ - C_7H_7 - 5 CO], 460 (5) [M^+ + H - C_7H_7 - $Cr(CO)_5$]; IR (KBr): 2872 (w), 2064 (m), 1983 (m), 1931 (vs), 1454 (w), 1207 (w), 1110 (w), 654 (m) cm^{-1}; elemental analysis (%): calcd.: C 66.30, H 5.16, found: C 66.15, H 5.19.

Pentacarbonyl[3-(*R*/*S*)-(1'-(*S*), 2'-(*R*), 3'-(*R*), 4'-tetrabenzyloxybutyl)-2-oxacyclopentylidene]-chromium(0) (7b)

R_f (petroleum ether/diethyl ether: 2/1): 0.59; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37 - 7.17 (m, 20 H, Ph), 5.45 (ddd, J = 10.0, 6.4, 3.7 Hz, 1 H, H-3), 4.81 (d, J = 11.2 Hz, 1 H, CH_2Ph), 4.76 (d, J = 11.6 Hz, 1 H, CH_2Ph), 4.71 (d, J = 11.2 Hz, 1 H, CH_2Ph), 4.70 (d, J = 11.9 Hz, 1 H, CH_2Ph), 4.66 (d, J = 11.9 Hz, 1 H, CH_2Ph), 4.54 (d, J = 11.6 Hz, 1 H, CH_2Ph), 4.50 (s, 2 H, CH_2Ph), 4.06 (dd, J = 6.9, 3.6 Hz, 1 H, H-2'), 3.97 (m, 1 H,H-3'), 3.81 (dd, J = 10.2, 4.6 Hz, 1 H, H-4a'), 3.77 (dd, J = 6.9, 3.7 Hz, 1 H, H-1'), 3.70 (dd, J = 10.2, 5.3 Hz, 1 H, H-4b'), 3.59 (ddd, J = 20.4, 9.4, 5.9 Hz, 1 H, H-5a), 3.37 (ddd, J = 20.4, 9.8, 6.2 Hz, 1 H, H-5b), 1.79 (m, 1 H, H-4a), 1.36 (ddt, J = 12.9, 9.4, 6.3 Hz, 1 H, H-4b); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 341.35 (C-1), 223.60 (*trans*-CO), 216.68 (*cis*-CO), 138.24, 138.05, 137.76, 137.76, 137.76 (C-*ipso*), 128.59 - 127.65 (Ph), 99.24 (C-3), 80.38 (C-1'), 78.92 (C-2'), 77.75 (C-3'), 74.62, 73.98, 73.54, 72.27 (CH_2Ph), 68.89 (C-4'), 61.08 (C-5), 23.28 (C-4); MS (FAB, mNBA): m/z (%) = 742 (5) [M^+], 658 (17) [M^+ - 3 CO], 602 (2) [M^+ - 5 CO], 568 (4) [M^+ + H - C_7H_7 - 3 CO], 511 (5) [M^+ - C_7H_7 - 5 CO], 460 (9) [M^+ + H - C_7H_7 - $Cr(CO)_5$]; IR (KBr): 3032 (w), 2870 (w), 2064 (m), 1985 (m), 1935 (vs), 1497 (w), 1454 (w), 1362 (w), 1206 (m), 1099 (m), 667 (m), 656 (m)cm^{-1}; elemental analysis (%): calcd.: C 66.30, H 5.16, found: C 66.36, H 5.26.

Pentacarbonyl[3-(*R/S*)-(1'-(*R*), 2'-(*R*), 3'-(*R*), 4'-tetrabenzyloxybutyl)-2-oxacyclopentylidene]-chromium(0) (8a)

R_f (petroleum ether/diethyl ether 2/1): 0.65; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.41 - 7.17 (m, 20 H, Ph), 4.89 (td, J = 7.6, 2.3 Hz, 1 H, H-3), 4.78 - 4.38 (m, 8 H, CH_2Ph), 4.33 (dd, J = 5.5, 2.3 Hz, 1 H, H-1'), 3.84 - 3.72 (m, 4 H, H-2', H-3', H-4a', H-4b'), 3.40 (ddd, J = 20.7, 9.9, 4.8 Hz, 1 H, H-5a), 2.81 (ddd, J = 20.7, 9.9, 7.3 Hz, 1 H, H-5b), 1.67 (ddt, J = 12.6, 9.9, 7.3 Hz, 1 H, H-4a), 1.01 (dddd, J = 12.6, 9.9, 8.3, 4.8 Hz, 1 H, H-4b); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 341.12 (C-1), 223.41 (*trans*-CO), 216.58 (*cis*-CO), 138.03, 137.97, 137.87 (C-*ipso*), 128.48 - 127.55 (Ph), 100.34 (C-3), 79.24 (C-1'), 79.20 (C-2'), 78.46 (C-3'), 75.05, 74.54, 74.43, 72.00 (CH_2Ph), 68.23 (C-4'), 61.80 (C-5), 20.91 (C-4); MS (FAB, mNBA, NaOAc): m/z (%) = 765 (1) [M^+ + Na], 742 (5) [M^+], 658 (31) [M^+ - 3 CO], 602 (24) [M^+ - 5 CO], 568 (10) [M^+ + H - C_7H_7 - 3 CO], 511 (23) [M^+ - C_7H_7 - 5 CO]; IR (KBr): 2868 (w), 2064 (m), 1983 (m), 1936 (vs), 1664 (w), 1497 (w), 1454 (w), 1204 (m), 1096 (m), 650 (m) cm^{-1}.

Pentacarbonyl[3-(*R/S*)-(1'-(*R*), 2'-(*R*), 3'-(*R*), 4'-tetrabenzyloxybutyl)-2-oxacyclopentylidene]-chromium(0) (8b)

R_f (petroleum ether/diethyl ether: 2/1): 0.57; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50 - 7.18 (m, 20 H, Ph), 5.09 (td, J = 7.2, 3.7 Hz, 1 H, H-3), 4.92 (d, J = 11.2 Hz, 1 H, CH_2Ph), 4.91 (d, J = 11.6 Hz, 1 H, CH_2Ph), 4.81 (d, J = 11.9 Hz, 1 H, CH_2Ph), 4.75 (d, J = 11.2 Hz, 1 H, CH_2Ph), 4.71 (d, J = 11.9 Hz, 1 H, CH_2Ph), 4.64 (d, J = 11.6 Hz, 1 H, CH_2Ph), 4.42 (s, 2 H, CH_2Ph), 4.32 (dd, J = 6.8, 4.0 Hz, 1 H, H-2'), 4.13 (m, 1 H, H-3'), 4.04 (dd, J = 9.8, 5.5 Hz, 1 H, H-4a'), 3.80 (dd, J = 9.8, 4.6 Hz, 1 H, H-4b'), 3.65 (dd, J = 6.8, 3.7 Hz, 1 H, H-1'), 3.31 (sept*, J = 20.6, 8.0 Hz, 1 H, H-5a), 2.84 (ddd, J= 20.6, 8.8, 7.2 Hz, 1 H, H-5b), 0.87 (m, 2 H, H-4a, H-4b); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 341.94 (C-1), 223.49 (*trans*-CO), 216.63 (*cis*-CO), 138.25, 138.19, 138.08 (C-*ipso*), 128.51 - 127.84 (Ph), 100.26 (C-3), 81.11 (C-1'), 79.08 (C-2'), 78.78 (C-3'), 75.32, 74.40, 73.55, 72.19 (CH_2Ph), 68.99 (C-4'), 61.21 (C-5), 23.33 (C-4); MS (FAB, mNBA, NaOAc): m/z (%) = 765 (2) [M^+ + Na], 742 (3) [M^+], 658 (9) [M^+ - 3 CO], 652 (2) [M^+ + H - C_7H_7], 603 (2) [M^+ + H - 5 CO], 568 (3) [M^+ + H - C_7H_7 - 3 CO], 511 (3) [M^+ - C_7H_7 - 5 CO], 460 (1) [M^+ + H - C_7H_7 - $Cr(CO)_5$]; IR (KBr): 2922 (w), 2062 (m), 1983 (m), 1938 (vs), 1632 (w), 1454 (w), 1207 (w), 1096 (m), 698 (m), 667 (m) cm^{-1}; elemental analysis (%): (mixture of diastereomers **8a/b**): calcd.: C 66.30, H 5.16, found: C 66.28, H 5.25.

Pentacarbonyl[3-(*R/S*)-(1'-(*R*), 2'-(*R*), 3'-(*R*), 4'-tetrabenzyloxybutyl)-2-oxacyclopentylidene]-tungsten(0) (8c)

R_f (petroleum ether/diethyl ether: 2/1): 0.76; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50 - 7.18 (m, 20 H, Ph), 5.06 (td, J = 8.2, 1.5 Hz, 1 H, H-3), 4.73 (d, J = 11.9 Hz, 1 H, CH_2Ph), 4.64 (d, J = 11.5 Hz, 1 H, CH_2Ph), 4.59 (s, 2 H, CH_2Ph), 4.57 (d, J = 11.9 Hz, 1 H, CH_2Ph), 4.54 (dd, J = 1.8 Hz, 1 H, H-1'), 4.51 (d, J = 11.5 Hz, 1 H, CH_2Ph), 4.43 (d, J = 12.0 Hz, 1 H, CH_2Ph), 4.38 (d, J = 11.9 Hz, 1 H, CH_2Ph), 3.89 (dd, J = 4.5, 4.6 Hz, 1 H, H-2'), 3.80 (dd, J = 5.4, 4.6 Hz, 1 H, H-3'), 3.77 (dd, J = 10.1, 4.5 Hz, 1 H, H-4a'), 3.71 (dd, J = 10.1, 5.2 Hz, 1 H, H-4b'), 3.18 (ddd, J = 20.7, 9.8, 4.6 Hz, 1 H, H-5a), 2.52 (ddd, J = 20.7, 9.9, 7.5 Hz, 1 H, H-5b), 1.70 (m, 1 H, H-4a), 1.04 (m, 1 H, H-4b); ^{13}C NMR (125 MHz, C_6D_6): δ = 314.19 (C-1), 204.42 (*trans*-CO), 198.01 (*cis*-CO), 138.71, 138.51, 138.21 (C-*ipso*), 128.93 - 128.02 (Ph), 101.14 (C-3), 79.10 (C-1'), 78.43 (C-2'), 78.04 (C-3'), 74.28, 73.87, 73.79, 72.74 (CH_2Ph), 69.79 (C-4'), 64.67 (C-5), 21.09 (C-4); IR (petroleum ether): 2072 (m), 1983 (w), 1948 (vs), 1938 (vs) cm^{-1}.

Pentacarbonyl[3-(*R/S*)-(1'-(*R*), 2'-(*R*), 3'-(*R*), 4'-tetrabenzyloxybutyl)-2-oxacyclopentylidene]-tungsten(0) (8d)

R_f (petroleum ether/diethyl ether: 2/1): 0.61; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50 - 7.15 (m, 20 H, Ph), 5.17 (dddd, J = 9.0, 5.6, 3.6, 2.5 Hz, 1 H, H-3), 4.86 (d, J = 11.3 Hz, 1 H, CH_2Ph), 4.79 (d, J = 11.7 Hz, 1 H, CH_2Ph), 4.74 (d, J = 11.3 Hz, 1 H, CH_2Ph), 4.72 (d, J = 11.8 Hz, 1 H, CH_2Ph), 4.68 (d, J = 11.8 Hz, 1 H, CH_2Ph), 4.43 (s, 2 H, CH_2Ph), 4.41 (d, J = 12.8 Hz, 1 H, CH_2Ph), 4.15 (dd, J = 6.9, 3.4 Hz, 1 H, H-2'), 4.11 (ddd, J = 5.0, 3.5 Hz, 1 H, H-3'), 3.91 (dd, J = 10.0, 5.0 Hz, 1 H, H-4a'), 3.79 (dd, J = 10.0, 5.3 Hz, 1 H, H-4b'), 3.72 (dd, J = 7.1, 3.6 Hz, 1 H, H-1'), 2.96 (dddd, J = 20.7, 9.7, 6.0 Hz, 1 H, H-5a), 2.50 (dddd, J= 20.7, 10.0, 6.0 Hz, 1 H, H-5b), 0.94 (m, 1 H, H-4a), 0.82 (m, 1 H, H-4b); ^{13}C NMR (125 MHz, C_6D_6): δ = 314.02 (C-1), 204.65 (*trans*-CO), 198.06 (*cis*-CO), 138.93, 138.88, 138.83, 138.33 (C-*ipso*), 128.92 - 127.81 (Ph), 99.90 (C-3), 80.48 (C-1'), 79.52 (C-2'), 78.32 (C-3'), 74.89, 74.21, 73.82, 72.79 (CH_2Ph), 68.18 (C-4'), 63.72 (C-5), 23.50 (C-4); IR (petroleum ether): 2071 (m), 1983 (w), 1948 (vs), 1935 (vs) cm^{-1}.

Pentacarbonyl[5-phenylmethylene-3(*R/S*)-(1'-(*R*), 2'-(*R*), 3'-(*R*), 4'-tetrabenzyloxybutyl)-2-oxa-cyclopentylidene]chromium(0) (9a)

0.11 ml (0.17 mmol) *n*-Butyllithium (1.6 M in hexane) are slowly added to a cooled (-78 °C) solution of 0.11 g (0.15 mmol) of compound **8a** in 3 ml THF. After 1 h a solution of 17 µl benzaldehyde and 20 µl boron trifluoride-etherate in 1.5 ml THF is added, and the mixture is kept for 4 h at ambient

temperature. Then the solvent is removed in vacuo, and purification by column chromatography (petroleum ether/diethyl ether: 2/1) yields 90 mg (0.11 mmol, 73 %) of a red syrup.

R_f (petroleum ether/diethyl ether: 2/1): 0.61; ^{1}H NMR (400 MHz, C_6D_6): δ = 8.30 (t*, J = 2.7 Hz, 1 H, H-6), 7.39 - 7.00 (m, 25 H, Ph), 5.12 (ddd, J = 8.7, 5.8, 1.7 Hz, 1 H, H-3), 4.64 (d, J = 11.9 Hz, 1 H, CH_2Ph), 4.59 (d, J = 11.2 Hz, 1 H, CH_2Ph), 4.55 (dd, J = 4.8, 1.7 Hz, 1 H, H-1'), 4.51 (d, J = 11.2 Hz, 1 H, CH_2Ph), 4.48 (d, J = 11.3 Hz, 1 H, CH_2Ph), 4.44 (d, J = 11.9 Hz, 1 H, CH_2Ph), 4.43 (d, J = 11.9 Hz, 1 H, CH_2Ph), 4.33 (d, J = 12.0 Hz, 1 H, CH_2Ph), 4.30 (d, J = 12.0 Hz, 1 H, CH_2Ph), 3.82 (t, J = 5.0 Hz, 1 H, H-2'), 3.73 (q, J = 4.9 Hz, 1 H, H-3'), 3.67 (dd, J = 10.2, 4.0 Hz, 1 H, H-4a'), 3.61 (dd, J = 10.2, 4.9 Hz, 1 H, H-4b'), 2.95 (ddd, J = 16.8, 5.8, 2.8 Hz, 1 H, H-4a), 2.09 (ddd, J = 16.8, 8.7, 2.6 Hz, 1 H, H-4b); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 (t*, J = 2.6 Hz, 1 H, H-6), 7.48-7.14 (m, 25 H, Ph), 5.32 (sept*, J = 8.1, 6.0, 1.6 Hz, 1 H, H-3), 4.84 - 4.55 (m, 8 H, CH_2Ph), 4.52 (dd, J = 5.0, 1.6 Hz, 1 H, H-1'), 3.89 (t, J = 5.0 Hz, 1 H, H-2'), 3.85 - 3.72 (m, 4H, H-3', H-4', H-5a', H-5b'), 3.00 (ddd, J = 16.8, 6.0, 2.8 Hz, 1 H, H-4a), 2.49 (ddd, J = 16.8, 8.1, 2.6 Hz, 1 H, H-4b); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 319.92 (C-1), 224.22 (*trans*-CO), 217.76 (*cis*-CO), 151.81 (C-6), 149.79 (C-5), 138.08, 137.93, 137.82, 137.72, 135.41 (C-*ipso*), 131.03 - 127.56 (Ph), 97.00 (C-3), 78.77 (C-1'), 78.06 (C-2'), 77.55 (C-3'), 73.91, 73.84, 73.62, 72.39 (CH_2Ph), 68.94 (C-4'), 27.09 (C-4); MS (FAB, mNBA): m/z (%) = 830 (3) [M^+], 803 (2) [M^+ + H - CO], 746 (10) [M^+ - 3 CO], 690 (50) [M^+ - 5 CO], 600 (7) [M^+ + H - C_7H_7 - 5 CO], 548 (2) [M^+ + H - C_7H_7 - $Cr(CO)_5$]; IR (KBr): 3065 (w), 3032 (w), 2922 (w), 2866 (w), 2056 (m), 1983 (m), 1935 (vs), 1622 (w), 1497 (w), 1454 (w), 1385 (w), 1169 (m), 1101 (m), 665 (m) cm^{-1}.

Pentacarbonyl[3-(*R*/*S*)-(1'-(*S*), 2'-(*R*), 3'-(*R*), 4'-tetrabenzyloxybutyl)-5-methylene-2-oxacyclopentylidene]chromium(0) (10a)

0.4 ml *n*-Butyllithium (0.52 mmol, 1.3 M in n-hexane) are slowly added at -78 °C to a solution of 350 mg pentacarbonyl[3-(*R*/*S*)-(1'-(*S*), 2'-(*R*), 3'-(*R*),4'-tetrabenzyloxybutyl)-2-oxacyclopentylidene]-chromium(0) (**7a**) in 15 ml THF. After 30 min the solution is warmed to -20 °C and 92 mg (1.04 mmol) of *N*,*N*-dimethylmethylene iminium chloride are added. The colour of the reaction mixture slowly changes from yellow to red-orange. After 30 min a small amount of silica gel is added, and the solvent is removed. Purification of the residue by column chromatography (petroleum ether/diethyl ether: 2/1) at 0 °C yields 290 mg (0.38 mmol, 80 %) of a red syrup.

R_f (petroleum ether/diethyl ether: 2/1): 0.68; ^{13}C NMR (125 MHz, C_6D_6): 323.27 (C-1), 224.54 (*trans*-CO), 218.09 (*cis*-CO), 159.26 (C-5), 138.84, 138.80, 138.63 (C-*ipso*), 132.21 (C-6), 128.92 - 127.81 (Ph), 97.92 (C-3), 80.69, 79.96, 79.26, 75.57, 74.82, 73.72, 72.37 (C-1', C-2', C-3', CH_2Ph),

69.04 (C-4'), 27.4 (C-4) ppm; MS (FAB, mNBA): m/z (%) = 754 (2) [M^+], 670 (4) [M^+ - 3 CO], 614 (25) [M^+ - 5 CO], 524 (6) [M^+ + H - 5 CO - C_7H_7]; IR (KBr): 2060, 1985, 1942; (petroleum ether): 2062, 1987, 1949 cm^{-1}.

Pentacarbonyl[1-amino-5-(*R*), 6-(*R*), 7-(*R*), 8-tetrabenzyloxy-4-(*R/S*)-hydroxy-1-octylidene]chromium(0) (11a)

A solution of 545 mg (0.73 mmol) pentacarbonyl[3-(*R/S*)-(1'-(*S*), 2'-(*R*), 3'-(*R*), 4'-tetrabenzyloxybutyl)-2-oxacyclopentylidene]chromium(0) (**7a**) in 5 ml dichloromethane is cooled to - 40 °C and stirred vigorously while gaseous ammonia is bubbled through the solution. After 2 min the colour changes from orange to yellow. TLC (petroleum ether/diethyl ether/dichloromethane: 1/1/1) indicates completion of the reaction after another 3 min. The solvent is removed in vacuo, and the residue is purified at 12 °C by column chromatography (petroleum ether/diethyl ether/dichloromethane: 1/1/1) to yield 370 mg (0.50 mmol, 68.5 %) of a light yellow syrup.

R_f (petroleum ether/diethyl ether/dichloromethane: 1/1/1): 0.76; ^{1}H NMR (500 MHz, C_6D_6): δ = 8.35 (br s, 2 H, NH_2), 7.45 - 7.10 (m, 20 H, Ph), 4.78 (d, J = 11.3 Hz, 1 H, CH_2Ph), 4.65 (d, J = 11.3 Hz, 1 H, CH_2Ph), 4.59 (d, J = 11.4 Hz, 1 H, CH_2Ph), 4.50 (d, J = 11.3 Hz, 1 H, CH_2Ph), 4.49 (d, J = 11.6 Hz, 1 H, CH_2Ph), 4.45 (d, J = 11.7 Hz, 1 H, CH_2Ph), 4.41 (d, J = 12.0 Hz, 1 H, CH_2Ph), 4.40 (d, J = 11.5 Hz, 1 H, CH_2Ph), 4.07 (dd, J = 9.3, 3.8 Hz, 1 H), 3.99 (td, J = 4.2 Hz, 1 H), 3.92 (dd, J = 10.3, 3.8 Hz, 1 H), 3.84 (dd, J = 10.4, 5.5 Hz, 1 H), 3.58 (br m, 1H), 3.49 (dd, J = 6.9, 3.8 Hz, 1 H), 3.40 (d, J = 5.0 Hz, 1 H, OH), 2.84 (td, J = 6.8, 6.1 Hz, 2 H), 1.40 (m, 1 H), 1.00 (m, 1 H); ^{13}C NMR (125 MHz, C_6D_6): δ = 289.82 (C-1), 223.38 (*trans*-CO), 218.66 (*cis*-CO), 138.7 - 138.5 (C-*ipso*), 128.98 - 128.02 (Ph), 81.20, 79.63, 79.16, 74.26, 73.78, 73.55, 73.32, 71.18 (C-5, C-6, C-7, C-8, CH_2Ph), 70.05 (C-4), 51.58 (C-2), 30.96 (C-3); MS (FAB, mNBA): m/z (%) = 759 (1) [M^+], 675 (7) [M^+ - 3 CO], 619 (30) [M^+ - 5 CO], 566 (2) [M^+ - H - $Cr(CO)_5$], 528 (47) [M^+ - C_7H_7 - 5 CO], 436 (12) [M^+ - H - 2 C_7H_7 - 5 CO]; IR (KBr): 2052, 1967, 1917 cm^{-1}.

Pentacarbonyl[3-(*R/S*)-(1'-(*R*), 2'-(*R*), 3'-(*R*), 4'-tetrabenzyloxybutyl)-2-azacyclopentylidene]chromium(0) (12a)

0.25 ml (0.17 mmol) Diethyl azodicarboxylate (DEAD) and 43 mg (0.21 mmol) triphenylphosphine are added to a solution of 105 mg (0.14 mmol) pentacarbonyl[1-amino-5-(*R*), 6-(*R*), 7-(*R*), 8-tetrabenzyloxy-4-(*R/S*)-hydroxy-1-octylidene]chromium(0) (**11a**) in 10 ml THF. The solution is stirred for 12 h at ambient temperature, the solvent is removed under reduced pressure, and the

residue is purified at 0 °C by column chromatography (petroleum ether/diethyl ether: 2/1) to yield 140 mg (0.18 mmol, 80 %) of an almost colourless syrup.

R_f (petroleum ether/diethyl ether: 2/1): 0.51; ^{13}C NMR (125 MHz, C_6D_6): 270.44 (C-1), 223.73 (*trans*-CO), 219.04 (*cis*-CO), 138.35, 138.23 (C-*ipso*), 128.25 - 127.78 (Ph), 81.22, 78.43, 78.06, 76.88, 73.99, 73.72, 73.62, 72.95, 70.03 (C-1', C-2', C-3', C-4', C-3, CH_2Ph), 53.94 (C-5), 30.96 (C-4); MS (FAB, mNBA): m/z (%) = 741 (5) [M^-], 657 (38) [M^+ - 3 CO], 601 (100) [M^+ - 5 CO], 550 (17) [M^- + H - $Cr(CO)_5$], 510 (17) [M^+ - C_7H_7 - 5 CO]; IR (KBr): 2054, 1969, 1921 cm^{-1}.

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