Pergamon

Tetrahedron: Asymmetry, Vol. 8, No. 11, pp. 1751–1765, 1997

Printed in Great Britain
PII: S0957-4166(97)00142-0 0957-4166/97 $17.00 + 0.00

Optically active naphthohydroquinone and naphthoquinone tricarbonyl chromium complexes via diastereoselective benzannulation with *sec.* alcohol auxiliaries[1]

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Abstract: The asymmetric benzannulation of optically active aryl or vinyl (alkoxy)carbene chromium complexes bearing chiral *sec.* alcohol auxiliaries with 3,3-dimethyl-1-butyne proceeds with moderate to high diastereoselectivities. The best results are obtained with (−)- and (+)-menthol derivatives. The stereoselectivity depends on the unsaturated carbene substituent and the solvent used. Enantiopure *S*-5-10-η^6-tricarbonyl-(2-*tert.*-butyl-1,4-naphthoquinone)chromium **25** was synthesized by intramolecular haptotropic migration of the tricarbonyl chromium fragment within the benzannulation product followed by deprotection and oxidation. © 1997 Elsevier Science Ltd

Introduction

Planar chiral tricarbonyl chromium complexes receive increasing interest as reagents in asymmetric synthesis[2]. As a consequence of the sterically demanding metal fragment the attack of nucleophiles occurs predominantly from the arene face opposite to the chromium moiety a fact which has been exploited in selective functionalization both of the arene ring and the benzylic side chains. Beside the classical route[3] to arene tricarbonyl chromium compounds based on the complexation of the preformed arene ligand an alternative access to hydroquinone complexes is provided by the chromium-mediated cocyclization of an unsaturated carbene ligand with an alkyne and a carbonyl ligand[4]. A diastereoselective control of the benzannulation which forces the tricarbonyl chromium fragment to one or the other enantiotopic arene face can be envisaged by a chiral modification of the alkyne or the carbene substitution pattern. Two studies published recently focussed on sterically demanding chiral propargyl ethers[5] and chiral unsaturated carbene substituents[6] as source of induction.

We concentrated on a more general approach exploiting readily available chiral alcohol auxiliaries as heteroatom carbene substituents. Recently, we reported on the synthetic potential of optically active menthyloxycarbene complexes[7]. We have extended these studies to alkoxy(phenyl)carbene complexes derived from terpenoid and other secondary alcohols, and we now report on their application in diastereoselective benzannulation reactions.

Synthesis of optically active alkoxycarbene complexes

The optically active carbene complexes **2–9** were synthesized via an acylation/alcoholysis sequence[8] starting from tetramethylammonium pentacarbonylbenzoylchromate **1** (Scheme 1). Their structural elucidation is mainly based on their ^{1}H- and ^{13}C-NMR-spectra. The ^{1}H-NMR-signals of complexes **5** and **7–9** are broadened at room temperature indicating a hindered rotation around the $C_{carbene}$–oxygen bond as reported recently from menthyl derivatives **2–4**[7]. Below −30°C configurationally stable E- and Z-isomers are observed the ratio of which ranges from 1:1.3 to 1:3. Their configuration has been assigned on the basis of previous investigations of the methoxy(methyl)carbene homologue[9]. In contrast, only a single isomer was detected for carbene complex **6** bearing the bulky (+)-fenchyloxy

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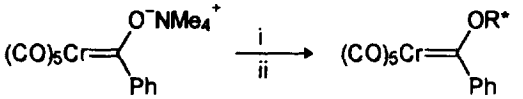
group. The upfield shift of the hydrogen next to the carbene oxygen which resembles that observed for the E-isomers of carbene complexes **2–5** and **7–9** (Table 1) suggests that complex **6** also adopts the E-configuration.



1 **2 – 9**

(–)-menthyl (–)-8-phenylmenthyl *endo*-(–)-bornyl *endo*-(+)-fenchyl

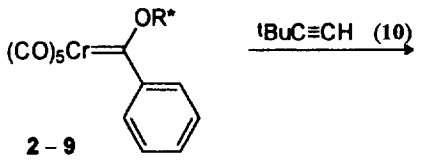
R*		yield [%]	E:Z	δ OCH (–30°C) E-isomer	Z-isomer
(–)-/(+)-menthyl	**2/3**	65	1:2	4.20	5.20
(–)-8-phenylmenthyl	**4**	33	1:2	4.50	5.50
endo-(–)-bornyl	**5**	81	1:3	4.54	5.82
endo-(+)-fenchyl	**6**	22	‡	4.19	–
(+/–)-1-phenyl-1-ethyl	**7**	40	1:1.4	5.50	6.35
(+/–)-1-naphthyl-1-ethyl	**8**	27	1:1.3	6.10	6.30
(+/–)-1-phenyl-2-methylpropyl	**9**	25	n.d.	n.d.	n.d.

Scheme 1. Synthesis of alkoxycarbene complexes **2–9**. *Reagents*: i, AcBr, –40°C, CH_2Cl_2, ii, R*OH, CH_2Cl_2, –40°C→0°C, 16 h. E:Z ratio determined by ^{1}H-NMR on the basis of the OCH-signals (n.d.: not determined). ‡Only E-isomer.

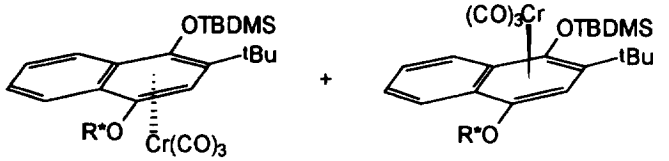
Diastereoselective benzannulation

The benzannulation reactions of the carbene complexes **2–9** were performed under identical conditions to allow a comparison of the diastereoselectivities observed. *Tert.*-butylacetylene **10** was used as terminal alkyne component to provide a regioselective incorporation into the naphthohydroquinone skeleton[10] (Scheme 2). The air-sensitive tricarbonyl chromium naphthohydroquinone complexes were stabilized by an *in situ* protection of the hydroxy functionality with *tert.* $BuMe_2SiCl$ and were isolated as silyl ethers **11–18** in moderate chemical yields.

Exceptionally high diastereoselectivities were observed in the (–)- and (+)-menthyloxy modified naphthalene complexes **11** (**a**:**b**=10:1; 81% d.e.) and **12** (**a**:**b**=1:9.2; 80% d.e.)[7]. The major diastereomers **11a** and **12b** were isolated by fractional crystallization and their absolute configurations were determined by X-ray analysis as R_p-**11a** and S_p-**12b**. Although the auxiliaries (–)-8-phenylmenthol, *endo*-(–)-borneol and especially *endo*-(+)-fenchyl alcohol are sterically more demanding, and thus are supposed to exhibit less conformational flexibility within the cyclohexane ring, lower selectivities for **13–15** were observed. For a systematic study we also included racemic *sec.* alcohol auxiliaries **16–18** which gradually differ in the steric bulk of either the aryl or the alkyl substituents. However, an increasing size of either substituent is only marginally reflected in an increasing diastereoselectivity. The selectivity even seems to decrease with an increasing sterical demand of the aryl substituent (**17** *versus* **18**).



2 – 9



11a – 18a 11b – 18b

R*		yield [%]	d.e. [%]	ratio a/b*
(–)-menthyl	2, 11	55	82	10 (11a) : 1
(+)-menthyl	3, 12	55	80	1 : 9.2 (12b)
(–)-8-phenylmenthyl	4, 13	65	50	3 : 1
endo-(–)-bornyl	5, 14	65	40	2.3 : 1
endo-(+)-fenchyl	6, 15	80	75	7 : 1
(+/–)-1-phenylethyl	7, 16	71	53	3 : 1
(+/–)-1-naphthylethyl	8, 17	51	40	2.3 : 1
(+/–)-1-phenyl-2-methylpropyl	9, 18	45	50	3 : 1

Scheme 2. Diastereoselective benzannulation. *Reagents*: i, 4 eq. HC≡CBu^t, Bu^{t}OMe, 55°C, 55 min; ii, 4 eq. ClSiMe$_2$Bu^t, 4 eq. Et$_3$N, r.t., 2 h. *Determined by ^{1}H-NMR on the basis of the 3-H signals.

Table 1. Influence of the solvent on the diastereoselective benzannulation

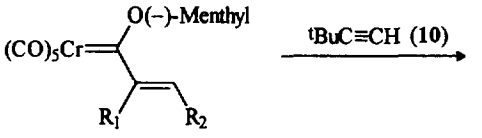
solvent	yield [%]	d.e. [%]	11a	:	11b
^{t}BuOMe	55	81	10	:	1
benzene	50	70	5.6	:	1
petroleum ether	52	57	3.7	:	1

Influence of solvent and carbene substitution pattern

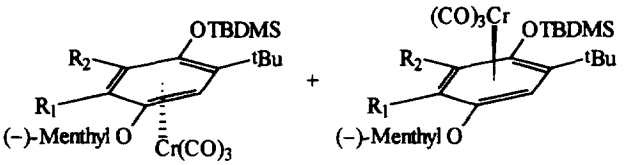
The benzannulation has been reported to depend on the coordination properties of the solvent[11]. To check the influence of the solvent on the diastereoselectivity of the benzannulation the reaction of (–)-menthyloxycarbene complex **2** and *tert.*-butylacetylene was studied using solvents of gradually modified polarity and donor ability. The results summarized in Table 1 indicate that the diastereoselectivity increases with increasing polarity and coordination ability of the solvent.

To study the influence of the unsaturated carbene side chain on the diastereoselectivity we extended our investigations to cyclic and acyclic chromium vinyl carbenes. The cyclohexenyl- and 2-propenyl carbene complexes **19** and **20** have been synthesized following a protocol already described for phenyl carbene complex **2** and have been subjected to benzannulation as outlined in Scheme 2. Under these conditions the chromium vinyl carbenes react distinctly less diastereoselective than the phenyl analogue **2**, and the d.e. values drop to 17% (**19**) and 13% (**20**), respectively (Scheme 3). A similar

dependence of the diastereoselectivity has been observed for the asymmetric benzannulation using chiral propargyl ethers[5].



2, 19, 20



11a, 21a, 22a **11b, 21b, 22b**

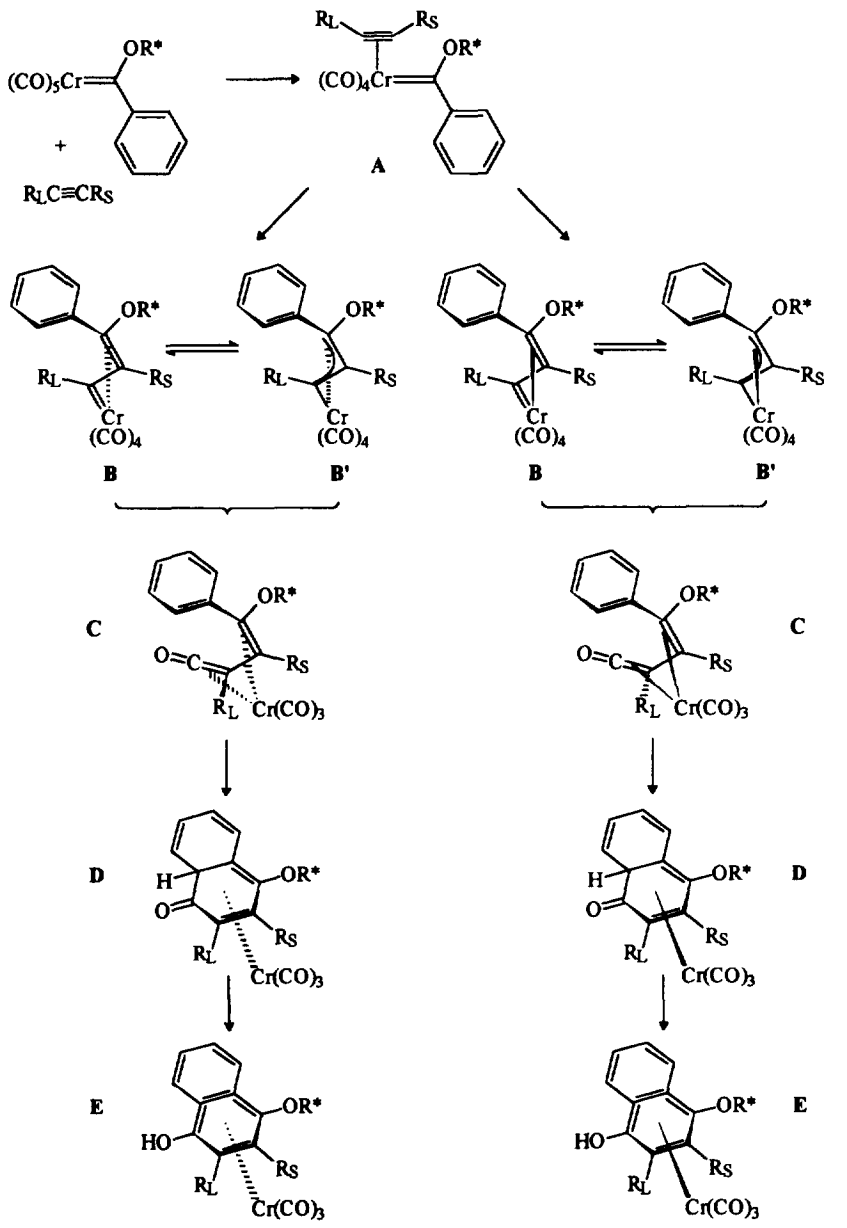
R_1/R_2		yield [%]	d.e. [%]	a	:	b
C_4H_4	**2/11**	55	81	10	:	1
C_4H_8	**19/21**	59	17	1.4	:	1
CH_3/H	**20/22**	63	13	1.3	:	1

Scheme 3. Influence of carbene substitution pattern on the benzannulation.

Discussion

The course of the benzannulation has been examined earlier by a kinetic investigation[12] and by trapping experiments of presumed intermediates[13] the role of which has been supported later by the isolation and structural characterization of stable analogues[14,15]. Based on these studies a mechanism has been suggested which involves a sequence of alkyne coordination (**A**), alkyne insertion into the chromium carbene bond (**B**, **B'**), carbon monoxide insertion (**C**), electrocyclization (**D**) and tautomerization (**E**) and has been supported by Extended Hückel molecular orbital calculations[16] and recent DFT studies[17] (Scheme 4).

The first step which allows for a differentiation of the evolving two enantiotopic faces along the reaction path leading to the annulation product is the alkyne–carbene coupling to form the η^1-η^3-vinylcarbene intermediate (**B**,**B'**) during which the chiral auxiliary may encourage the metal to coordinate either to the top or to the bottom face. It is tempting to speculate that this early stereodifferentiation is maintained throughout the benzannulation sequence. However, the inherent conformational flexibility of the auxiliaries used makes a reliable prediction of the stereochemical outcome difficult. Moreover, it seems that the steric bulk of the auxiliary is not the only aspect which finally controls the preferred coordination of the $Cr(CO)_3$-fragment to one or the other arene face. This is suggested by the fact that the incorporation of the (−)- or (+)-menthyloxy group results in a higher diastereomeric excess than observed for sterically more demanding and less flexible terpene auxiliaries. It further appears that the diastereoselectivity of the benzannulation is increased by the presence of an aromatic carbene side chain. We speculate whether this may be a consequence of a π-interaction between the chromium centre and the carbene carbon substituent which may stabilize the configuration of the transition state and which is supposed to be more efficient for an aryl than for a vinyl group.

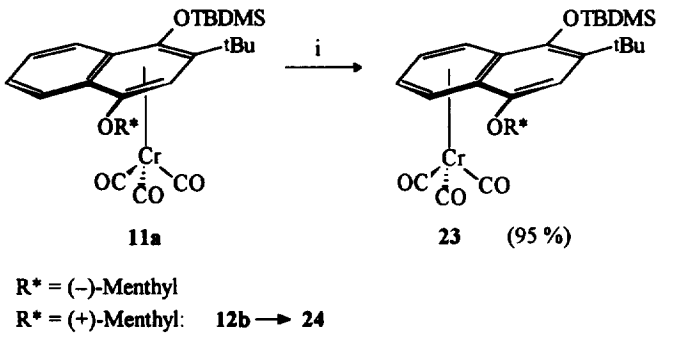


Scheme 4. Suggested mechanism for the benzannulation.

Metal migration and oxidation

Since the benzannulation of chiral alkoxy(phenyl)carbene complexes offers an access to stereodefined 1-4:9,10-η^6-naphthalene $Cr(CO)_3$-complexes we focussed our attention on the stereochemistry of the haptotropic metal migration[7]. An early EHMO study suggested that the $Cr(CO)_3$ shift to the adjacent aromatic ring occurs intramolecularly and follows a track close to the periphery rather than the shortest path[18]. Upon warming to 90°C in di-*n*-butyl ether the pure diastereomers **11a** and **12b** rearrange to give the 5-10-η^6-naphthalene complexes **23** and **24** as single diastereomers (Scheme 5). Their CD-spectra contain a mirror plane which characterizes the rearrangement products as enantiomers (Figure 1). This result strongly suggests that the haptotropic migration of the $Cr(CO)_3$-

fragment proceeds along the same face of the naphthalene skeleton, and thus provides experimental evidence for an intramolecular process with retention of configuration within the planar chiral arene chromium moiety.



Scheme 5. Haptotropic metal migration; *Conditions*: i, Bu_2O, 90°C, 20 min, 95%.

5-10-η^6-Naphthohydroquinone monoether $Cr(CO)_3$ complexes undergo oxidation without loss of the metal unit to give naphthoquinone $Cr(CO)_3$ complexes[19]. Silyl deprotection of **23** followed by oxidation on air effects the cleavage of the (−)-menthyl auxiliary and generates enantiopure tricarbonyl[*S*-5-10-η^6-(2-*tert*.butyl-1,4-naphthoquinone)]chromium **25** in low yield along with a major amount of uncoordinated quinone **26** (Scheme 6). A comparison of CD-spectra of hydroquinone complex **23** and quinone complex **25** strongly suggests that the oxidation occurs with retention of configuration at the arene chromium fragment (Figure 2). The intensive dark violet colour of naphthoquinone complex **25** hampers an accurate determination of its optical rotation.

In conclusion, the diastereoselective benzannulation of optically active phenylcarbene complexes — especially from readily available (−)- and (+)-menthol auxiliaries — offers a new approach to three different types of enantiopure tricarbonyl chromium arene complexes which represent interesting building blocks in asymmetric synthesis.

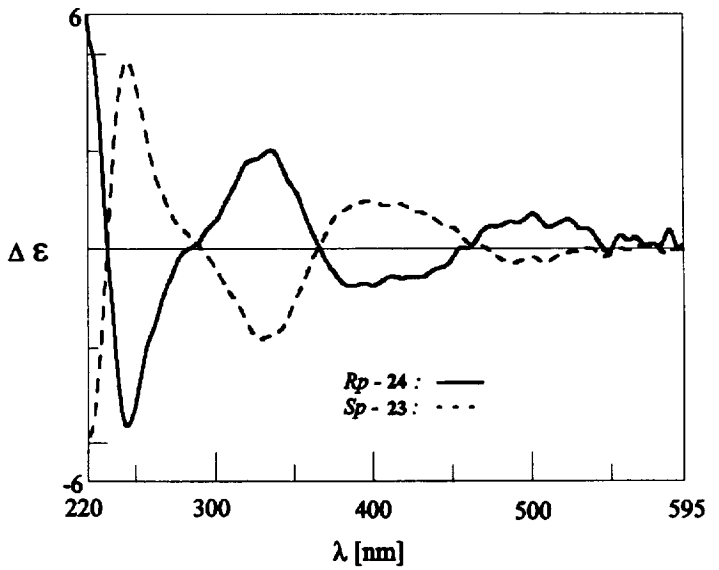
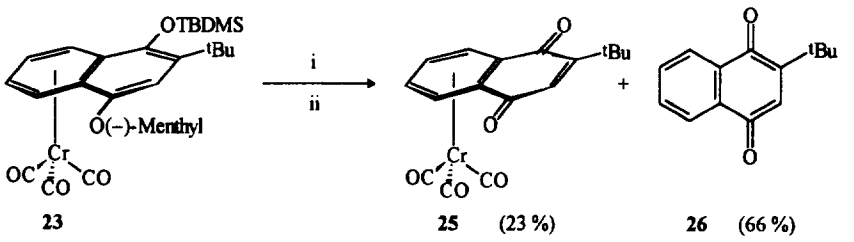


Figure 1. CD-spectra of 5-10-η^6-naphthalene complexes S_p-**23** and R_p-**24** ($c=10^{-3}$ [mol^{-1}], CH_2Cl_2).



Scheme 6. Synthesis of optically active naphthoquinone complex **25**; *Reagents* and *conditions*: i, 1.5 eq. $^{n}Bu_4NF$, THF, 0°C, 2 h; ii; O_2, THF, r.t., 15 h.

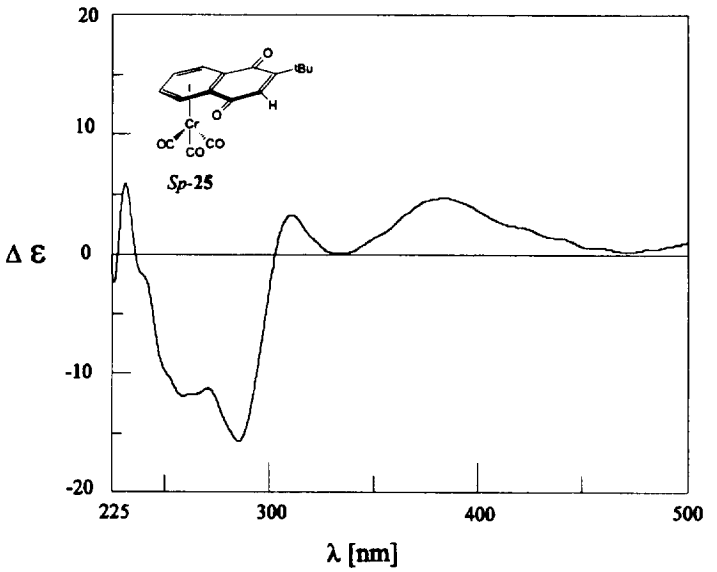


Figure 2. CD-spectrum of naphthoquinone complex *Sp*-**25** (c=10^{-3} [mol^{-1}], CH_2Cl_2).

Experimental section

All operations were performed under argon. Solvents were dried by distillation from sodium–potassium alloy and sodium hydride; petroleum ether (PE) 40–60°C. Silica gel (Merck, 0.063–0.200 mm) was degassed at high vacuum and stored under argon. —^{1}H- and ^{13}C-NMR: Bruker AMX-500, AM-400, AM-250. Chemical shifts refer to those of residual solvent signals based on δ_{TMS}=0.00. —FT-IR: Nicolet Magna 550. —MS: Kratos MS 50 and Hewlett Packard 5972. —Elemental analysis: Heraeus CHN-O-Rapid.

General procedure for the synthesis of carbene complexes 2–9, 19 and 20

10 mmol (0.9 mL) Acetyl bromide were added to a solution of 10 mmol (3.71 g) tetramethylammonium pentacarbonyl(benzoyl)chromate in 20 mL CH_2Cl_2 at −50°C. After stirring the reaction mixture for 0.5 h at this temperature a solution of 12 mmol of the chiral alcohol in 25 mL CH_2Cl_2 was added dropwise over 1 h at −40°C. The reaction mixture was stirred for 3 h and allowed to reach room temperature during stirring overnight. The solvent was evaporated under reduced pressure, the brown residue was taken up in petroleum ether and filtered through silica gel. Evaporation of the solvent provided an oily residue which was subjected to column chromatography (PE/CH_2Cl_2 5/1, −10°C). The carbene complexes **2–9**, **19** and **20** were isolated as red oils.

Pentacarbonyl[(1R,2S,5R)-(−)-menthyloxybenzylidene]chromium(0) **2** *and pentacarbonyl[(1S,2R,5S)-(+)-menthyloxybenzylidene]chromium(0)* **3**

Yield: **2**: 2.84 g (6.5 mmol, 65%), **3**: 2.62 g (6 mmol, 60%), red oils; R_f=0.60 (PE/CH_2Cl_2, 5/1); IR (PE): ν [ν(C=O)]=2062 (m, A_1), 1984 (w, B), 1960 (s, A_2), 1952 (vs, E), 1928 (m); ^{1}H-NMR (250 MHz, $CDCl_3$, −30°C): E/Z=1/3: δ=0.49/0.72 (d, $^3J_{H,H}$=6.4 Hz, 2 CH_3), 0.87 (d, $^3J_{H,H}$=6.4 Hz, br, 2 CH_3), 0.93 (d, $^3J_{H,H}$=6.4 Hz, br, 2 CH_3), 1.00–2.30 (m, 6 CH_2, 6 CH), 4.20/5.20 (m, 2 HCO), 6.72/6.84 (d, $^3J_{H,H}$=7.5 Hz, 4 ArH), 7.25 (m, 4 ArH), 7.38–7.46 (m, 2 ArH); ^{13}C-NMR (100 MHz, $CDCl_3$, −40°C): E/Z-isomers: δ=16.1/16.3 (2 CH_3), 21.3/21.6 (2 CH_3), 22.1/22.2 (2 CH_3), 22.3/22.8 (2 CH), 25.8/26.8 (2 CH_2), 30.9/31.2 (2 CH_2), 33.3/33.6 (2 CH_2), 41.6 (2 CH), 47.4 (2 CH), 91.8/92.4 (2 HCO), 117.2, 120.0, 123.3, 128.0, 128.0, 128.3, 128.5, 130.3, 151.3, 156.2 (12 ArC), 216.0/216.3 (2 *trans*-CO), 224.2/225.6 (2 *cis*-CO), 344.8/350.0 (2 Cr=C); MS (70 eV): *m/z* (%)=436 (17) [M^+], 408 (17) [M^+–CO], 380 (34) [M^+–2CO], 352 (5) [M^+–3CO], 324 (20) [M^+–4CO], 296 (82) [M^+–5CO]; HR-MS: calcd.: 436.0978, found: 436.0966; $C_{22}H_{24}O_6Cr$ (436.4): calcd.: C 60.55, H 5.54; found: **2**: C 60.50, H 5.68; **3**: C 60.32, H 5.53.

Pentacarbonyl[(1R,2S,5R)-(−)-8-phenylmenthyloxybenzylidene]chromium(0) **4**

Yield: 0.84 g (1.6 mmol, 31%, related to 5 mmol **1**), red oil; R_f=0.52 (PE/CH_2Cl_2=9/1); IR (PE): ν [ν(C=O)]=2062 (m, A_1), 1985 (w, B), 1962 (s, A_2), 1952 (vs, E), 1927 (m); ^{1}H-NMR (250 MHz, $CDCl_3$, −30°C): E/Z=1/2: δ=0.80/0.95 (d, $^3J_{H,H}$=7.0 Hz, 2 CH_3), 1.15/1.20 (d, 2 CH_3), 1.40/1.50 (d, 2 CH_3), 1.00–1.80 (m, 2 CH, 6 CH_2), 2.20/2.50 (m, 2 CH), 4.50/5.50 (m, 2 HCO), 6.70–7.50 (m, 20 ArH); ^{13}C-NMR (62.5 MHz, $CDCl_3$, −30°C): E/Z-isomers: δ=21.4/21.7 (2 CH_3), 25.8 (2 CH_3), 26.5 (2 CH_2), 27.3 (2 CH_3), 31.1/31.9 (2 CH_2), 33.4/33.9 (2 CH), 39.9/40.5 (2 $C(CH_3)_2$Ar), 42.3/43.5 (2 CH_2), 50.1/51.1 (2 CH), 91.0/93.1 (2 HCO), 117.3/118.9 (2 *para*-ArCH), 122.7–129.7 (18 ArCH), 149.9/150.1 (2 *ipso*-ArC), 215.8/216.2 (2 *cis*-CO), 223.8/225.3 (2 *trans*-CO), 345.3/351.1 (2 Cr=C); MS (70 eV): *m/z* (%)=512 (1) [M^+], 484 (1) [M^+–CO], 456 (1) [M^+–2CO], 428 (15) [M^+–3CO], 400 (12) [M^+–4CO], 372 (68) [M^+–5CO], 119 (100) [$C_3H_6C_6H_5^+$]; $C_{28}H_{28}O_6Cr$ (512.4): calcd.: C 65.24, H 5.51; found: C 65.62, H 5.50.

Pentacarbonyl[(1S-endo)-(−)-bornyloxybenzylidene]chromium(0) **5**

Yield: 2.45 g (5.7 mmol, 81%), red oil; R_f=0.50 (PE/CH_2Cl_2=5/1); IR (PE): ν [ν(C=O)]=2062 (m, A_1), 1987 (w, B), 1960 (sh, E), 1952 (vs, A_1), 1930 (sh, m); ^{1}H-NMR (500 MHz, $CDCl_3$, −30°C): E/Z=1/3: δ=0.98/0.95, 0.83/0.78 (s, 4 CH_3), 1.17/1.04 (s, 2 CH_3), 1.20–2.20 (m, 6 CH_2), 2.70/2.51 (t, $^3J_{HH}$=11 Hz, 2 CH), 4.54/5.82 (d, $^3J_{HH}$=8.9 Hz, 2 HCO), 6.90/6.62 (s, 4 ArCH), 7.43 (m, 6 ArCH); ^{13}C-NMR (125 MHz, $CDCl_3$, −30°C): E/Z-isomers: δ=13.1/13.3 (2 CH_3), 18.5/18.7, 19.4/19.9 (4 CH_3), 26.7/26.9 (2 CH_2), 27.8/27.9 (2 CH_2), 37.1/37.4 (2 CH_2), 44.5/44.6 (2 CH), 47.7/48.4 (2 $C(CH_3)_2$), 50.1/50.4 (2 $C(CH_3)$), 95.9/96.0 (2 HCO), 116.8/120.2 (2 *para*-ArCH), 124.9/127.8, 127.9/130.94 (4 *ortho*-, 4 *meta*-ArCH), 151.9/154.6 (2 *ipso*-ArC), 216.0 (2 *cis*-CO), 224.0/225.3 (2 *trans*-CO), 343.2/350.9 (2 Cr=C); MS (70 eV): *m/z* (%)=434 (2) [M^+], 406 (4) [M^+–CO], 378 (4) [M^+–2CO], 350 (1) [M^+–3CO], 322 (22) [M^+–4CO], 294 (69) [M^+–5CO]; HR-MS: calcd.: 434.0821, found: 434.0821; $C_{22}H_{22}O_6Cr$ (434.4): calcd.: C 60.83, H 5.10, found: C 61.13, H 5.17.

Pentacarbonyl[(1R-endo)-(+)-fenchyloxybenzylidene]chromium(0) **6**

Yield: 0.80 g (1.9 mmol, 22%), red oil; R_f=0.87 (PE/CH_2Cl_2=1/1); IR (PE): ν [ν(C=O)]=2063 (m, A_1), 1987 (w, B), 1961 (s, E), 1952 (vs, A_1); ^{1}H-NMR (400 MHz, $CDCl_3$): E-isomer: δ=0.67 (s, CH_3), 1.03 (s, CH_3), 1.08 (s, CH_3), 1.32 (m, 2 CH_2, 2 *endo*-H), 1.54–1.68 (m, 2 CH_2, 2 *exo*-H), 1.76 (d, $^2J_{HH}$=3.9 Hz, CH_2, *anti*-H), 1.95 (m, CH_2, *syn*-H), 2.37 (m, CH), 4.19 (d, $^3J_{HH}$=1.6 Hz, HCO), 6.75 (d, $^3J_{HH}$=7.6 Hz, ArCH), 7.25–7.45 (m, 3 ArCH); ^{13}C-NMR (125 MHz, $CDCl_3$): E-isomer: δ=19.0 (CH_3), 21.6 (CH_3), 25.7 (CH_2), 27.7 (CH_2), 28.4 (CH_3), 40.3 ($C(CH_3)_2$), 41.1 (CH_2), 48.3 (CH), 50.1 ($C(CH_3)_3$), 102.0 (HCO), 119.2 (*para*-ArCH), 127.8, 128.2 (2 *ortho*- and 2 *meta*-ArCH), 152.0 (*ipso*-ArC), 216.2 (*cis*-CO), 225.2 (*trans*-CO), 351.5 (Cr=C); MS (70 eV): *m/z* (%)=434 (16)

[M^+], 406 (43) [M^+–CO], 378 (60), [M^+–2CO], 350 (20) [M^+–3CO], 322 (22) [M^+–4CO], 294 (100) [M^+–5CO]; HR-MS: calcd.: 434.0821, found: 434.0812; $C_{22}H_{22}O_6Cr$ (434.4): calcd.: C 60.83, H 5.10, found: C 60.94, H 5.08.

Pentacarbonyl[(±)-1-phenyl-1-ethoxybenzylidene]chromium(0) ***7***

Yield: 1.43 g, (3.6 mmol, 36%), red oil; R_f=0.38 (PE/CH_2Cl_2=8/1); IR (PE): ν [ν(C=O)]=2064 (s, A_1), 1987.2 (w, B), 1963 (vs, E), 1954 (vs, A_1); ^{1}H-NMR (500 MHz, $CDCl_3$, −30°C.): E/Z=1/1.4: δ=1.70/1.95 (s, br, 2 CH_3), 5.50/6.35 (s, 2 HCO), 6.82/6.94 (s, 4 ArCH), 7.15–7.60 (m, 16 ArCH); ^{13}C-NMR (125 MHz, $CDCl_3$, −30°C): E/Z-isomers δ =22.6/24.0 (2 CH_3), 87.6/90.8 (2 HCO), 118.4/118.6 (2 *para*-ArCH), 125.0/125.6 (2 *para*-ArCH), 125.9/126.2 (4 *ortho*-ArCH), 128.0 (4 *meta*-ArCH), 128.5/128.7 (4 *ortho*-ArCH), 129.5/131.2 (4 *meta*-ArCH), 139.3/140.3 (2 *ipso*-ArC), 151.3/154.0 (2 *ipso*-ArC), 215.8/216.0 (2 *cis*-CO), 223.7/225.3 (2 *trans*-CO), 342.0/351.7 (2 Cr=C); MS (70 eV): *m/z* (%)=402 (15) [M^+], 374 (8) [M^+–CO], 318 (40) [M^+–3CO], 297 (45) [M^+–$C_6H_5CHCH_3$], 290 (12) [M^+–4CO], 262 (88) [M^+–5CO]; HR-MS: calcd.: 402.0195, found: 402.0189; $C_{20}H_{14}O_6Cr$ (402.3): calcd.: C 59.71, H 3.51, found: C 59.89, H 3.64.

Pentacarbonyl[(±)-1-naphthyl-1-ethoxybenzylidene]chromium(0) ***8***

Yield: 1.20 g, (2.7 mmol, 27%), red solid; R_f=0.41 (PE/CH_2Cl_2=8/1); IR (PE): ν [ν(C=O)]=2064 (m, A_1), 1987 (w, B), 1954 (sh, E), 1954 (vs, A_1); ^{1}H-NMR (500 MHz, $CDCl_3$, −30°C): E/Z=1/1.3: δ=1.90/2.20 (s, br, 2 CH_3), 6.10/6.30 (s, br, 2 HCO), 6.90–8.40 (m, 24 ArCH); ^{13}C-NMR (125 MHz, $CDCl_3$, −30°C): E/Z-isomers: δ=25.0/24.5 (2 CH_3), 89.2/85.6 (2 HCO), 119.6/118.6 (2 *para*-ArCH), 123.3/122.7 (2 ArCH), 131.8–123.7 (20 ArCH), 134.1/133.9 (2 ArC), 137.5/136.7 (2 ArC), 143.6/143.1 (2 *ipso*-ArC), 155.2/152.0 (2 *ipso*-ArC), 216.5 (2 *cis*-CO), 226.0/224.5 (2 *trans*-CO), 353.1/344.8 (2 Cr=C); MS (70 eV): *m/z* (%)=368 (8) [M^+–3CO], 284 (2) [M^+–4CO], 260 (5) [M^+–$Cr(CO)_5$], 155 (100) [H_3C-$CH(C_{10}H_7)^+$], 78 (33).

Pentacarbonyl[(±)-2-methyl-1-phenyl-1-propyloxybenzylidene]chromium(0) ***9***

Yield: 1.07 g (2.5 mmol, 25%), red oil; R_f=0.75 (PE/CH_2Cl_2=5/2); IR (PE): ν [ν(C=O)]=2064 (m, $A_1{}^1$), 1987 (w, B), 1962 (s, E), 1954 (vs, $A_1{}^2$), 1926 (m); ^{1}H-NMR (500 MHz, $CDCl_3$, r.t.): δ=1.20 (s, 2 CH_3), 2.50 (s, br, $HC(CH_3)_2$), 5.20 (s, HCO), 7.20–7.60 (m, 10 ArCH); ^{13}C-NMR (125 MHz, $CDCl_3$, r.t.): δ=18.7 (2 CH_3), 35.5 ($HC(CH_3)_2$), 97.8 (HCO), 120.0 (*para*-ArCH), 127.0 (*para*-ArCH), 128.4, 128.5, 128.8, 129.0 (2 *ortho*-, 2 *meta*-ArCH), 142.1 (*ipso*-ArC), 152.0 (*ipso*-ArC), 216.5 (*cis*-CO), 225.5 (*trans*-CO), 352.9 (Cr=C); MS (70eV): *m/z* (%)=430 (1) [M^+], 402 (0.5) [M^+–CO], 346 (5) [M^+–3CO], 318 (0.5) [M^+–4CO], 290 (9) [M^+–5CO], 133 (42) [$CHCH(CH_3)_2C_6H_5^+$], 105 (100) [$C_6H_5CO^+$]; HR-MS: calcd.: 430.0508, found: 430.0506; $C_{22}H_{18}O_6Cr$ (430.4): calcd.: C 61.40, H 4.22, found: C 61.67 H 4.50.

Pentacarbonyl[1R,2S,5R-(−)-menthyloxy-2-cyclohexenylmethylidene]chromium(0) ***19***

Yield: red oil, 0.5 g (1.14 mmol, 33%); R_f=0.8 (PE/CH_2Cl_2=5/1); IR (PE): ν [ν(C=O)]=2060 (m, A_1), 1987 (w, B), 1950 (vs, A_1), 1943 (sh, E), 1927 (s); ^{1}H-NMR (500 MHz, $CDCl_3$, r.t): δ=0.70 (s, br, CH_3), 1.00 (d, $^3J_{HH}$=6.3 Hz, CH_3), 1.30 (d, $^3J_{HH}$=6.8 Hz, CH_3), 1.40–2.90 (m, 7 CH_2, 3 CH), 4.70 (s, br, 1H, HCO), 6.91 (s, 1H, =CH); ^{13}C-NMR (125 MHz, $CDCl_3$, −30°C): E/Z-isomers: δ=16.2 (2 CH_3), 21.0, 21.5, 22.0, 22.5, 24.0 (4 CH_3, 8 CH_2), 24.6/25.1 (2 CH_2), 25.3/25.6 (2 CH), 30.5/31.2 (2 CH), 33.2/33.4 (2 CH_2), 41.6/41.4 (2 CH_2), 47.2/47.0 (2 CH), 90.5/90.9 (2 HCO), 120.3/122.1 (2 C=CH), 148.5/150.0 (2 *C*=CH), 217.3 (2 *cis*-CO), 224.7/226.0 (2 *trans*-CO), 345.1/345.3 (2 Cr=C); MS (70 eV): *m/z* (%)=440 (1) [M^+], 412 (12) [M^+–CO], 384 (5) [M^+–2CO], 356 (3) [M^+–3CO], 328 (5) [M^+–4CO], 300 (45) [M^+–5CO]; HR-MS [M^+–CO]: calcd.: 412.1291, found: 412.1343.

Pentacarbonyl[1R,2S,5R-(−)-menthyloxy-2-propenylidene]chromium(0) ***20***

Yield: red oil, 0.78 g (2.0 mmol, 20%); R_f=0.75 (PE/CH_2Cl_2=5/1); IR (PE): ν [ν(C=O)]=2063 (m, A_1), 1985 (w, B), 1960 (s, E), 1952 (vs, A_1), 1929 (m); ^{1}H-NMR ($CDCl_3$, 125 MHz, r.t.): δ=0.70

(s, br, CH_3), 1.00 (s, br, 2 CH_3), 1.10–2.00 (m, 3 CH_2, 3 CH), 2.00 (s, $=CCH_3$), 4.70 (s, br, HCO), 4.90 (s, $=CH_2$); ^{13}C-NMR ($CDCl_3$, 500 MHz, −30°C): E/Z-isomers: δ=16.0/16.2 (2 CH_3), 19.8/19.5 (2=C*C*H_3), 21.2/21.3 (2 CH_3), 22.1/22.0 (2 CH_3), 22.6/22.2 (2 CH_2), 25.5 (2 CH), 31.2/30.7 (2 CH), 33.4/33.3 (2 CH_2), 41.1 (2 CH_2), 47.3/47.1 (2 CH), 91.8/91.2 (2 HCO), 110.9/108.0 (2=CH_2), 154.0/153.0 (2=*C*CH_3), 216.3/216.0 (2 *cis*-CO), 224.7/223.7 (2 *trans*-CO), 351.1/350.2 (2 Cr=C); MS (70 eV): *m/z* (%)=400 (3) [M^+], 372 (10) [M^+–CO], 344 (1) [M^+–2CO], 316 (3) [M^+–3CO], 288 (13) [M^+–4CO], 260 (100) [M^+–5CO], 138 (76), 122 (61), 95 (90); HR-MS: calcd.: 400.0978, found: 400.0981; $C_{19}H_{24}O_6Cr$ (400.4): calcd.: C 56.70, H 6.33, found: C 56.51, H 6.33.

General procedure for the synthesis of tricarbonylchromium complexes ***11a,b–18a,b, 21a,b and 22a,b***

A solution of 2 mmol **2–9, 19** and **20** and 8 mmol alkyne **10** in 5 mL *tert*-BuOMe was degassed in three cycles and warmed at 55°C for 55 minutes. After cooling to room temperature and filtration over silica gel 8 mmol TBDMSCl and 8 mmol Et_3N were added and the solution was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (PE/CH_2Cl_2=5/1, −10°C).

R-*1-4:9,10-*η^6*-Tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-(1*R*,2*S*,5*R*)-(−)-menthyl-oxynaphthalene]chromium(0)* ***11a*** *and* S-*1-4:9,10-*η^6*-tricarbonyl[1-*tert.*-butyl-dimethylsilyloxy-2-*tert.*-butyl-4-(1*S*,2*R*,5*S*)-(+)-menthyloxynaphthalene]chromium(0)* ***12b***

Yield: 0.66 g (1.1 mmol, 55%), red solid; R_f=0.27 (PE/CH_2Cl_2=5/1); d.e.=82% (**11**) and 80% (**12**) (based on ^{1}H-NMR signals for H-3: 5.71 (s)/5.60 (s) ppm); $[\alpha]_D^{25}$=+693 (**11a**), −690 (**12b**) (c=0.9, $CHCl_3$); IR (PE): ν [ν(C=O)]=1958 (s, A_1), 1890, 1877 (vs, E); ^{1}H-NMR (500 MHz, $CDCl_3$): δ=0.34, 0.53 (s, 2 $SiCH_3$), 0.80, 0.93, 1.01 (d, $^3J_{HH}$=7.0 Hz, 3 CH_3), 1.09 (s, $SiC(CH_3)_3$), 1.52 (s, $C(CH_3)_3$), 1.15–1.70 (m, 2 CH_2, CH), 1.75 (m, CH_2), 2.11 (qd, $^3J_{HH}$=7.0 Hz, $^4J_{HH}$=2.6 Hz, CH), 2.65 (m, CH), 4.00 (ddd, $^3J_{HH}$=10.6, 9.8, 5.3 Hz, HCO), 5.60 (s, $HCArCr(CO)_3$), 7.33 (ddd, $^3J_{HH}$=9.1 and 6.5 Hz, $^4J_{HH}$=1 Hz, HCAr), 7.45 (ddd, $^3J_{HH}$=8.9 and 6.5 Hz, $^4J_{HH}$=1 Hz, 1H, HCAr), 8.05 (m, 2H, HAr); ^{13}C-NMR (100 MHz, $CDCl_3$): δ=−1.0, 0.4 (2 CH_3Si), 16.9, 20.8, 22.2 (CH_3), 19.9 ($SiC(CH_3)_3$), 23.6 (CH_2), 26.0 (CH), 27.0 ($SiC(CH_3)_3$), 30.9 ($C(CH_3)_3$), 31.5 (CH), 34.2 (CH_2), 34.9 ($C(CH_3)_3$), 39.3 (CH_2), 48.1 (CH), 76.9 (OCH), 79.7 ($HCArCr(CO)_3$), 99.0, 101.0, 108.6 (3 CAr), 123.4, 125.4, 126.6, 127.8 (4 HCAr), 128.9, 130.6 (2 CAr), 234.4 ($Cr(CO)_3$); MS (70 eV): *m/z* (%)=604 (5) [M^+], 548 (1) [M^+–2CO], 520 (100) [M^+–3CO], 468 (1) [M^+–$Cr(CO)_3$]; $C_{33}H_{48}O_5SiCr$ (604.8): calcd.: C 65.53, H 8.00, found: **11a**: C 65.94, H 8.18, **12b**: C 65.43, H 7.91.

S/R-*1-4:9,10-*η^6*-Tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-(1*R*,2*S*,5*R*)-(−)-8-phenyl-menthyloxynaphthalene]chromium(0)* ***13a,b***

Yield: 0.9 g (1.3 mmol, 65%), red solid; R_f=0.15 (PE/CH_2Cl_2=5/1); d.e.=50% (based on ^{1}H-NMR signals for H-3: 5.38 (s)/5.33 (s) ppm, 3/1); IR (PE): ν [ν(C=O)]=1958 (s, A_1), 1891, 1878 (s, E); ^{1}H-NMR (500 MHz, $CDCl_3$): major diastereomer: δ=0.41, 0.59 (s, 2 $SiCH_3$), 1.02 (d, $^3J_{HH}$=7.0 Hz, CH_3), 1.14 (s, $SiC(CH_3)_3$), 1.38 (s, CH_3), 1.52 (s, CH_3), 1.55 (s, $C(CH_3)_3$), 1.20–1.90 (m, 2 CH_2, CH), 2.20 (m, CH_2), 2.77 (m, CH), 4.02 (td, $^3J_{HH}$=10.4 Hz, $^4J_{HH}$=4 Hz, HCO), 5.38 (s, $HCArCr(CO)_3$), 7.09–7.40 (m, 6 HCAr), 7.51 (m, HCAr), 8.06 (m, 2 HCAr); ^{13}C-NMR (125 MHz, $CDCl_3$): major diastereomer: δ=−0.9, 0.5 (2 CH_3Si), 18.8 (CH_3), 19.9 ($SiC(CH_3)_3$), 22.0 (CH_3), 27.1 ($SiC(CH_3)_3$), 27.7 (CH_3), 28.4 (CH), 30.8 ($C(CH_3)_3$), 31.5 (CH_2), 34.7 (CH_2), 34.9 ($C(CH_3)_3$), 38.7 (CH_2), 40.0 ($C(CH_3)_2Ar$), 51.6 (CH), 74.9 (HCO), 79.0 ($HCArCr(CO)_3$), 99.1, 100.1, 108.5 (3 CAr), 123.8, 125.2, 125.3, 125.8, 126.2, 127.4, 127.9 (9 HCAr), 128.0, 130.4, 150.0 (3 CAr), 234.4 ($Cr(CO)_3$); minor diastereomer: δ=−0.9, 1.0 (2 CH_3Si), 18.8 (CH_3), 19.9 ($SiC(CH_3)_3$), 22.1 (CH_3), 27.0 ($SiC(CH_3)_3$), 27 (CH_3), 28.2 (CH), 30.7 ($C(CH_3)_3$), 31.1 (CH_2), 34.8 (CH_2), 35.2 ($C(CH_3)_3$), 38.7 (CH_2), 40.2 ($C(CH_3)_2Ar$), 51.8 (CH), 75.0 (HCO), 75.8 ($HCArCr(CO)_3$), 99.3, 100.7, 108,7 (3 CAr), 123.8, 125.2, 125.4, 125.9, 126.2, 127.5, 128.0 (9 HCAr), 128.0, 133.4 (2 CAr), 149.6 (*ipso*-ArC), 234.4 ($Cr(CO)_3$); MS (70 eV): *m/z* (%)=680 (6) [M^+], 596 (100) [M^+–3CO], 544 (9) [M^+–$Cr(CO)_3$]; $C_{39}H_{52}O_5SiCr$ (680.2): calcd.: C 68.79, H 7.70, found: C 68.52, H 7.71.

R,S-*1-4:9,10-η⁶-Tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-(1*S-endo*)-(−)-bornyloxy)-naphthalene]chromium(0)* ***14a,b***

Yield: 0.46 g (0.8 mmol, 44%), red solid; R_f=0.26 (PE/CH_2Cl_2=5/1); d.e.=40% (based on ^{1}H-NMR signals for H-3: 5.43 (s)/5.40 (s) ppm, 1/2.3); IR (PE): ν [ν(C=O)]=1958 (vs, A_1), 1890, 1879 (s, E); ^{1}H-NMR (500 MHz, $CDCl_3$): major/minor diastereomer: δ=0.34/0.33 (s, 2 $SiCH_3$), 0.53/0.52 (s, 2 $SiCH_3$), 0.98, 1.02, 1.05 (s, 6 CH_3), 1.53/1.52 (s, 2 $SiC(CH_3)_3$), 1.54/1.56 (s, 2 $C(CH_3)_3$), 1.20–1.50 (m, 4 CH_2), 1.85/2.25 (m, 2 CH_2), 2.50/2.35 (m, 2 CH), 4.22/4.35 (dm, $^3J_{HH}$=7.7 Hz, 2 HCO), 5.44/5.47 (s, 2 $HCArCr(CO)_3$), 7.39/7.50 (m, 6 HCAr), 8.11 (m, 2 HCAr); ^{13}C-NMR (125 MHz, $CDCl_3$): major/minor diastereomer: δ=−1.0 (2 $SiCH_3$), 0.4/0.5 (2 $SiCH_3$), 13.8/14.0 (2 CH_3), 19.0/19.1 (2 CH_3), 19.5/19.6 (2 CH_3), 19.9 (2 $SiC(CH_3)_3$), 27.0 (2 $SiC(CH_3)_3$), 27.2/27.3 (2 CH_2), 27.9/27.6 (2 CH_2), 30.8/30.7 (2 $C(CH_3)_3$), 37.7/34.4 (2 CH_2), 34.7/34.8 (2 $C(CH_3)_3$), 45.3/45.2 (2 CH), 47.6/47.5 (2 CCH_3), 49.9/50.0 (2 $C(CH_3)_2$), 77.7/77.2 (2 HCO), 85.9/84.7 (2 $HCArCr(CO)_3$), 98.9/99.2 (2 CAr), 101.6/100.0 (2 CAr), 108.6/109.0 (2 CAr), 123.4/123.3 (2 HCAr), 125.7/125.6 (2 HCAr), 126.6/126.5 (2 HCAr), 127.8/127.7 (2 HCAr), 130.6/129.7 (2 CAr), 130.2/130.3 (2 CAr), 234.2/234.4 (2 $Cr(CO)_3$); MS (70 eV): *m/z* (%)=602 (4) [M^+], 546 (2) [M^+–2CO], 518 (100) [M^+–3CO], 466 (10) [M^+–$Cr(CO)_3$]; HR-MS: calcd.: 602.2520, found: 602.2522; $C_{33}H_{46}O_5SiCr$ (602.2): calcd.: C 65.75, H 7.69, found: C 65.64, H 7.74.

R,S-*1-4:9,10-η⁶-Tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-(1R-endo-(+)-fenchyloxy)-naphthalene]chromium(0)* ***15***

Yield: 0.16 g (0.26 mmol, 80%), red solid; R_f=0.23 (PE/CH_2Cl_2=5/1); d.e.=75% (based on ^{1}H-NMR signals for H-3: 5.68 (s)/5.51 (s) ppm, 1/7); IR (PE): ν [ν(C=O)]=1958 (vs, A_1), 1892, 1880 (s, E); ^{1}H-NMR (400 MHz, $CDCl_3$): major diastereomer: δ=0.35, 0.53 (s, 2 $SiCH_3$), 0.88 (s, CH_3), 1.11 (s, $SiC(CH_3)_3$), 1.32 (s, 2 CH_3), 1.52 (s, $C(CH_3)_3$), 1.17–2.08 (m, 3 CH_2, 1 CH), 3.71 (s, HCO), 5.51 (s, $HCArCr(CO)_3$), 7.33 (t, $^3J_{HH}$=7.7 Hz, HCAr), 7.48 (t, $^3J_{HH}$=7.5 Hz, HCAr), 8.08 (d, $^3J_{HH}$=8.8 Hz, 2 HCAr); ^{13}C-NMR (100 MHz, $CDCl_3$): major/minor diastereomer: −0.96/−0.99 (2 $SiCH_3$), 0.39/1.01 (2 $SiCH_3$), 20.0 (2 $SiC(CH_3)_3$), 20.1/20.8 (2 CH_3), 20.4/21.1 (2 CH_3), 25.6/26.1 (2 CH_2), 26.9/26.7 (2 CH_3), 25.6/26.1 (2 $SiC(CH_3)_3$), 31.0/30.5 (2 CH_2), 31.1/30.4 (2 $C(CH_3)_3$), 35.1/35.0 (2 $C(CH_3)_3$), 40.1/40.4 (2 $C(CH_3)_2$), 41.4/41.5 (2 CH_2), 49.4/48.6 (2 CH), 50.0/50.1 (2 $C(CH_3)_3$), 79.3/79.7 (2 HCO), 92.2/93.9 (2 $HCArCr(CO)_3$), 98.2/96.6 (2 CAr), 101.8/101.2 (2 CAr), 107.8/108.2 (2CAr), 123.4 (2 HCAr), 125.4/125.3 (2 HCAr), 126.9/126.8 (2 HCAr), 128.1/128.0 (2 HCAr), 130.9 (2 CAr), 131.1/131.6 (2 CAr), 234.3/234.4 (2 $Cr(CO)_3$); MS (70 eV): *m/z* (%)=602 (10) [M^+], 546 (2) [M^+–2CO], 518 (100) [M^+–3CO], 466 (12) [M^+–$Cr(CO)_3$]; HR-MS: calcd.: 602.2520, found: 602.2518; $C_{33}H_{46}O_5SiCr$ (602.8): calcd.: C 65.75, H 7.69, found: C 65.77, H 7.97.

R,S-*1-4:9,10-η⁶-Tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-((±)-1-phenyl-1-ethoxy)-naphthalene]chromium(0)* ***16a,b***

Yield: 0.73 g (0.13 mmol, 71%), red solid, R_f=0.14 and 0.10 (PE/CH_2Cl_2=3/1), d.e=50% (based on ^{1}H-NMR signals for H-3: 5.47 (s)/5.30 (s) ppm, 3/1), IR (PE): ν [ν(C=O)]=1958 (vs, A_1), 1886 (vs, E); ^{1}H-NMR (500 MHz, $CDCl_3$): major/minor diastereomer: δ=0.32 (s, 2 $SiCH_3$), 0.51/0.50 (s, 2 $SiCH_3$), 1.06/1.08 (s, 2 $C(CH_3)_3$), 1.36/1.26 (s, 2 $SiC(CH_3)_3$), 1.74/1.75 (d, $^3J_{HH}$=6.5 Hz, 2 CH_3), 5.14/5.16 (q, $^3J_{HH}$=6.5 Hz, 2 HCO), 5.47/5.30 (s, 2 $HCAr(Cr(CO)_3)$, 7.30–7.60 (m, 14 HCAr), 8.04/8.06 (d, $^3J_{HH}$=8.9 Hz, 2 HCAr), 8.13, 8.20 (m, $^3J_{HH}$=8.9 Hz, 2 HCAr); ^{13}C-NMR (500 MHz, $CDCl_3$): major/minor diastereomer: δ=−1.0/−1.1 (2 $SiCH_3$), 0.4/0.5 (2 $SiCH_3$), 20.0/19.9 (2 $SiC(CH_3)_3$), 25.0/24.5 (2 CH_3) 27.1/27.0 (2 $SiC(CH_3)_3$), 30.7/30.5 (2 $C(CH_3)_3$), 34.8/34.7 (2 $C(CH_3)_3$), 79.5/78.8 (2 HCO), 81.0/80.5 (2 $HCArCr(CO)_3$), 99.2/98.1 (2 $CArCr(CO)_3$), 100.2/102.0 (2 $CArCr(CO)_3$), 108.2/108.9 (2 $CArCr(CO)_3$), 123.7/123.2 (2 HCAr), 125.1/125.2 (2 HCAr), 126.0/125.9 (4 *ortho*-HCAr), 126.6/126.4 (2 HCAr), 127.8/127.9 (2 HCAr), 128.5/128.0 (2 *para*-HCAr), 128.7/128.9 (2 CAr), 128.9/129.0 (4 *meta*-HCAr), 131.2/130.0 (2 CAr), 140.6/143.0 (2 *ipso*-CAr), 233.8/234.2 (2 $Cr(CO)_3$); MS (70 eV): *m/z* (%)=570 (18) [M^+], 486 (100) [M^+–3CO], 434 (2) [M^+–$Cr(CO)_3$], 382

(70), 330 (25); HR-MS: calcd.: 570.1894, found: 570.1894; $C_{31}H_{38}O_5CrSi$ (570.7): calcd.: C 65.24, H 8.71, found: C 64.88, H 8.94.

R,S-*1-4:9,10-η⁶-Tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-((±)-1-naphthyl-1-ethoxy)-naphthalene]chromium(0)* ***17a,b***

Yield: 0.40 g (0.6 mmol, 55%), red solid; R_f=0.10 (PE/CH_2Cl_2=5/1); d.e.=40% (based on ^{1}H-NMR signals for H-3: 5.32 (s)/5.16 (s) ppm, 2.3/1); IR (PE): ν [ν(C=O)]=1958 (vs, A_1), 1890, 1879 (s, E); ^{1}H-NMR (500 MHz, $CDCl_3$): major/minor diastereomer: δ=0.32/0.33 (s, 2 $SiCH_3$), 0.51/0.50 (s, 2 $SiCH_3$), 1.07/1.02 (s, 2 $SiC(CH_3)_3$), 1.13/1.09 (s, $C(CH_3)_3$), 1.94/1.98 (d, $^3J_{HH}$=6.5 Hz, 2 CH_3), 5.32/5.16 (s, 2 $HCArCr(CO)_3$), 5.98/5.95 (q, $^3J_{HH}$=6.5 Hz, 2 HCO), 7.25–8.06 (m, 18 HCAr), 8.12/8.20, 8.28/8.31 (d, $^3J_{HH}$=8.5 Hz, 4 HCAr); ^{13}C-NMR (125 MHz, $CDCl_3$): major/minor diastereomer: δ=0.3/0.4 (2 $SiCH_3$), 1.1/1.0 (2 $SiCH_3$), 19.9/19.8 (2 $SiC(CH_3)_3$), 24.0/24.1 (2 CH_3), 26.9/27.0 (2 $SiC(CH_3)_3$), 30.4/30.3 ($C(CH_3)_3$), 34.5 (2 $C(CH_3)_3$), 76.2/77.7 (2 HCO), 81.5/78.9 (2 $HCArCr(CO)_3$), 97.8/99.2 (2 $CArCr(CO)_3$), 100.1/102.1 (2 $CArCr(CO)_3$), 108.2/109.0 (2 $CArCr(CO)_3$), 121.8/122.8 (HCAr), 123.1/122.5 (HCAr), 124.3/123.7 (HCAr), 124.9/125.7 (HCAr), 125.5/126.0 (HCAr), 126.2/125.9 (HCAr), 126.5/126.4 (HCAr), 126.7/126.9 (HCAr), 127.9/128.0 (HCAr), 128.8/128.4 (HCAr), 129.1/129.4 (HCAr), 129.5/128.7 (CAr), 129.9/130.0 (CAr), 131.5 (2 CAr), 134.0/133.9 (CAr), 135.5/138.4 (CAr), 233.8/234.2 (2 $Cr(CO)_3$); MS (70 eV): *m/z* (%)=620 (1) [M^+], 536 (5) [M^+–3CO], 484 (2) [M^+–$Cr(CO)_3$], 396 (9), 330 (32), 217 (13), 56 (100); HR-MS: calcd.: 620.2049, found: 620.2050; $C_{35}H_{40}O_5CrSi$ (620.8): calcd.: C 67.72, H 6.49, found: C 67.46, H 6.77.

R,S-*1-4:9,10-η⁶-Tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-((±)-2-methyl-1-phenyl-1-propyloxy)naphthalene]chromium(0)* ***18a,b***

Yield of separated diastereomers: 0.08 g and 0.29 g (0.62 mmol, 45%); major diastereomer: R_f=0.15 (PE/CH_2Cl_2=3/1), minor diastereomer: R_f=0.12 (PE/CH_2Cl_2=3/1); d.e.=50% (based on ^{1}H-NMR signals for H-3: 5.41 (s)/5.29 (s) ppm, 3/1); IR (PE): ν [ν(C=O)]=1957 (vs, A_1), 1884 (vs, E); ^{1}H-NMR (500 MHz, $CDCl_3$): major diastereomer: δ=0.31, 0.50 (s, 2 $SiCH_3$), 0.92 (d, $^3J_{HH}$=6.8 Hz, CH_3), 1.05 (s, $SiC(CH_3)_3$), 1.17 (d, $^3J_{HH}$=6.7 Hz, CH_3), 1.32 (s, $C(CH_3)_3$), 2.25 (qq, $^3J_{HH}$=6.8 Hz, $HC(CH_3)_2$), 4.65 (d, $^3J_{HH}$=6 Hz, HCO), 5.41 (s, $HCArCr(CO)_3$), 7.31 (dd, $^3J_{HH}$=8.7 and 6.6 Hz, HCAr), 7.35 (m, HCAr), 7.44 (m, 4 HCAr), 7.50 (dd, $^3J_{HH}$=6.6, 8.9 Hz, HCAr), 8.03 (d, $^3J_{HH}$=8.9 Hz, HCAr), 8.18 (d, $^3J_{HH}$=8.7 Hz, HCAr); minor diastereomer: δ=0.30, 0.48 (s, 2 $SiCH_3$), 1.02 (d, $^3J_{HH}$=6.8 Hz, CH_3), 1.06 (s, $SiC(CH_3)_3$), 1.18 (s, $C(CH_3)_3$), 1.20 (s, br, CH_3), 2.24 (qq, $^3J_{HH}$=6.8 Hz, $HC(CH_3)_2$), 4.68 (d, $^3J_{HH}$=6Hz, HCO), 5.29 (s, $HCArCr(CO)_3$), 7.30–7.40 (m, 6 HCAr), 7.51 (t, $^3J_{HH}$=7.4 Hz, HCAr), 8.05 (d, $^3J_{HH}$=8.6 Hz, HCAr), 8.18 (d, $^3J_{HH}$=8.6 Hz, HCAr); ^{13}C-NMR (100 MHz, $CDCl_3$): major diastereomer: δ=−1.1, 0.2 (2 $SiCH_3$), 18.8, 18.9 (2 CH_3), 19.9 ($SiC(CH_3)_3$), 27.0 ($SiC(CH_3)_3$), 30.6 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 35.4 (CH), 81.0 (HCO), 88.5 ($HCArCr(CO)_3$), 98.0, 99.8, 108.4 (3 CAr), 123.0 (HCAr), 124.9 (HCAr), 126.7 (HCAr), 127.0 (2 *ortho*-HCAr), 127.7 (HCAr), 128.4 (*para*-HCAr), 128.6 (2 *meta*-HCAr), 129.0, 131.0 (2 CAr), 137.7 (*ipso*-CAr), 233.8 ($Cr(CO)_3$); minor diastereomer: δ=−1.2, 0.3 (2 $SiCH_3$), 18.5, 18.9 (2 CH_3), 19.8 ($SiC(CH_3)_3$), 26.9 ($SiC(CH_3)_3$), 30.5 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 35.3 (CH), 79.4 (HCO), 88.2 ($HCArCr(CO)_3$), 98.5, 102.0, 108.2 (3 CAr), 123.2 (HCAr), 125.3 (HCAr), 126.4 (2 *ortho*-HCAr), 126.7 (HCAr), 127.9 (HCAr), 128.6 (*para*-, 2 *meta*-HCAr), 129.6, 130.5 (2 CAr), 140.2 (*ipso*-CAr), 234.2 ($Cr(CO)_3$); MS (70 eV): *m/z* (%)=598 (12) [M^+], 514 (100) [M^+–3CO], 472 (14), 462 (10) [M^+–$Cr(CO)_3$], 396 (20), 330 (52), 329 (55), 217 (22); HR-MS: calcd.: 598.2202, found: 598.2207; $C_{33}H_{42}O_5CrSi$ (598.8): calcd.: C 66.20, H 7.07, found: C 65.91, H 7.05.

S/R-*1-4:9,10-η⁶-Tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-(1R,2S,5R)-(−)-menthyl-oxy-5-8-tetrahydronaphthalene]chromium(0)* ***21a,b***

Yield: 0.04 g (0.07 mmol, 59%, rel. to 0.11 mmol **19**), red solid; R_f=0.8 (PE/CH_2Cl_2=1/1); d.e.=17%, (based on ^{1}H-NMR signals for H-3: 5.52 (s), 5.44 (s) ppm, 1/1.4); IR (PE): ν [ν(C=O)]=1955 (vs,

A_1), 1877 (s, E); ^{1}H-NMR (500 MHz, $CDCl_3$): major/minor diastereomer: δ=0.39 (s, 2 $SiCH_3$), 0.44/0.45 (s, 2 $SiCH_3$), 0.80–1.00 (m, 6 CH_3), 1.04/1.10 (s, 2 $SiC(CH_3)_3$), 1.45/1.43 (s, $C(CH_3)_3$), 1.15–3.00 (m, 14 CH_2, 6 CH), 3.74/3.67 (td, $^3J_{HH}$=10.2 Hz, $^4J_{HH}$=4.5 Hz, 2 HCO), 5.52/5.43 (s, 2 $HCAr(CO)_3$); ^{13}C-NMR (125 MHz, $CDCl_3$): major/minor diastereomer: δ=0.4 (2 $SiCH_3$), 0.7/0.8 (2 $SiCH_3$), 16.1/16.4 (2 CH_3), 20.2/21.0 (2 $SiC(CH_3)_3$), 20.8/21.0 (2 CH_3), 21.8/21.9 (2 CH_2), 22.0/22.1 (2 CH_2), 22.2/22.3 (2 CH_3), 23.4/23.5 (2 CH_2), 25.7/25.8 (2 CH), 27.0/27.1 (2 CH_2), 27.4/27.5 (2 $SiC(CH_3)_3$), 29.7/29.8 (2 CH_2) 31.1/31.3 (2 $C(CH_3)_3$), 31.3/31.4 (2 CH), 34.2/34.3 (2 CH_2), 34.5/34.6 (2 $C(CH_3)_3$), 39.8/40.8 (2 CH_2), 47.9/48.3 (2 CH), 77.6/77.7 (2 HCO), 79.4/79.9 (2 $HCArCr(CO)_3$), 100.2/101.2 (2 CAr), 107.6/108.8 (2 CAr), 109.8/110.0 (2 CAr), 129.8/129.9 (2 ArC), 130.7/132.5 (2 ArC), 235.8 (2 $Cr(CO)_3$).

S/R-*1-4:9,10-η^6-Tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-(1R,2S,5R)-(−)-menthyloxy-5-methylbenzene]chromium(0)* ***22a,b***

Yield: 0.35 g (0.63 mmol, 63%, rel. to 1 mmol **20**), yellow solid; R_f=0.90 (PE/CH_2Cl_2=1/1); d.e.=13%, (based on ^{1}H-NMR signals for H-3: 5.61 (s), 5.56 (s) ppm, 1/1.3); IR (PE): ν [ν(C=O)]=1957 (vs, A^1), 1881 (s, br, E); ^{1}H-NMR (500 MHz, $CDCl_3$): major/minor diastereomer: δ=0.33/0.34 (s, 2 $SiCH_3$), 0.39 (s, 2 $SiCH_3$), 0.85 (2 d, $^3J_{HH}$=7.0 Hz, 2 CH_3), 0.90–0.96 (4 d, $^3J_{HH}$=7.0 Hz, 4 CH_3), 1.00 (s, 2 $SiC(CH_3)_3$), 1.37/1.36 (s, 2 $C(CH_3)_3$), 1.10–2.20 (m, 6 CH_2, 4 CH), 2.18/2.16 (s, 2 CH_3), 2.36 (m, 2 CH), 3.65/3.63 (m, 2 HCO), 4.90/4.88 (s, 2 6-$HCArCr(CO)_3$), 5.61/5.56 (s, 2 3-$HCArCr(CO)_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): major/minor diastereomer: δ=−4.0 (2 $SiCH_3$), −3.3/−3.2 (2 $SiCH_3$), 16.1/16.2 (2 CH_3), 16.5/16.8 (2 H_3CAr), 18.5/18.8 (2 $SiC(CH_3)_3$), 21.1 (2 CH_3), 22.3 (2 CH_3), 23.1/23.3 (2 CH_2), 25.5/25.7 (2 CH), 25.9 (2 $SiC(CH_3)_3$), 29.8/31.3 (2 CH), 30.6/30.7 (2 $C(CH_3)_3$), 34.1/34.5 (2 CH_2), 34.2/34.3 (2 $C(CH_3)_3$), 39.6/40.6 (2 CH_2), 48.0/48.1 (2 CH), 78.7/81.4 (2 HCO), 83.1/83.4 (2 $HCArCr(CO_3)$), 83.7/84.0 (2 $HCArCr(CO_3)$), 101.4/103.1(2 CAr), 107.3/108.2 (2 CAr), 128.8/129.3 (2 CAr), 135.5/135.7 (2 CAr), 235.5 (2 $Cr(CO)_3$); MS (70 eV): *m/z* (%)=568 (7) [M^+], 512 (3) [M^+–2CO], 484 (100) [M^+–3CO], 432 (10) [M^+–$Cr(CO)_3$], 346 (15), 294 (55), 237 (35); HR-MS: calcd.: 568.2676, found: 568.2688; $C_{30}H_{48}O_5SiCr$ (568.8): calcd.: C 63.35, H 8.51, found: C 63.40, H 8.57.

S-*5-10-η^6-Tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-(1R,2S,5R)-(−)-menthyloxy-naphthalene]chromium(0)* ***23*** *and* R-*5-10-η^6-tricarbonyl[1-*tert.*-butyldimethylsilyloxy-2-*tert.*-butyl-4-(1S,2R,5S)-(+)-menthyloxy-naphthalene]chromium(0)* ***24***

1 mmol (0.6 g) **11a** or **12b** were dissolved in 5 ml di-n-butyl ether and warmed to 90°C for 20 minutes. The reaction was monitored by IR-spectroscopy. The solvent was removed under reduced pressure and after column chromatography (PE/CH_2Cl_2=5/1). 0.54 g (0.9 mmol, 90%) **23** and **24** were isolated as red solids. R_f=0.27 (PE/CH_2Cl_2=5/1); $[\alpha]_D^{25}$=+2.5 (**23**), −2.0 (**24**) (c=0.9, $CHCl_3$); IR (PE): ν [ν(C=O)]=1971 (vs, A_1), 1909, 1894 (s, E); ^{1}H-NMR (500 MHz, $CDCl_3$): δ=0.17, 0.32 (s, 2 $SiCH_3$), 0.80 (d, $^3J_{HH}$=7.0 Hz, CH_3,), 0.93 (d, $^3J_{HH}$=6.5 Hz, CH_3), 0.95 (d, $^3J_{HH}$=7.0 Hz, CH_3), 1.10 (s, $Si(CH_3)_3$), 1.38 (s, $C(CH_3)_3$), 1.40–1.60 (m, 2 CH_2), 1.68 (m, CH), 1.77 (m, CH_2), 2.18 (m, CH), 2.30 (m, CH), 4.16 (td, $^3J_{HH}$=10.4 Hz, $^3J_{HH}$=4 Hz, HCO), 5.38 (ddd, $^3J_{HH}$=6.0, $^3J_{HH}$=6.7, $^4J_{HH}$=1.0 Hz, 7-HCAr), 5.50 (ddd, $^3J_{HH}$=6.0, $^3J_{HH}$=6.7, $^4J_{HH}$=1.2 Hz, 6-HCAr), 6.30 (dd, $^3J_{HH}$=7.0, $^4J_{HH}$=1 Hz, 8-HCAr), 6.50 (d, $^3J_{HH}$=6.8, $^4J_{HH}$=1.2 Hz, 5-HCAr), 6.55 (s, 3-HCAr); ^{13}C-NMR (125 MHz, $CDCl_3$): δ=−1.4, −1.1 (2 CH_3Si), 15.2, 16.9, 18.4 (3 CH_3), 19.1 ($SiC(CH_3)_3$), 26.6 ($SiC(CH_3)_3$), 31.4 ($C(CH_3)_3$, 36.1 ($C(CH_3)_3$), 23.9, 34.5, 39.6 (3 CH_2), 26.4, 31.5, 48.0 (3 CH), 77.1 (HCO), 85.7, 86.5 (6- and 7-HCAr), 85.7, 86.5 (8- and 5-HCAr), 106.7 (3-HCAr), 96.6 105.8 (9- and 10-CAr), 136.4, 138.9, 147.5 (1-C, 2-C, and 4-CAr), 232.4 ($Cr(CO)_3$); MS (70 eV): *m/z* (%)=604 (10) [M^+], 548 (3) [M^+–2CO], 520 (100) [M^+–3CO], 468 (18) [M^+–$Cr(CO)_3$]; HR-MS: calcd.: 604.2676, found: 604.2665.

S-5-10-η^6-Tricarbonyl[2-tert.-butyl-1,4-naphthoquinone]chromium(0) 25

1.5 mmol (0.5 g) tetrabutylammonium fluoride were added to a solution of 1 mmol (0.6 g) **23** in 10 mL THF at −40°C. After 2 h at 0°C the reaction mixture was stirred at room temperature for 2 h and then on air for another 10 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (PE/CH_2Cl_2=3/1). The first band afforded 0.14 g (0.66 mmol, 66%) uncoordinated naphthoquinone **26** as a yellow oil. (−)-Menthene was isolated from the second band, and 0.08 g (0.23 mmol, 23%) naphthoquinone complex **25** were obtained from the third band as a blue solid.

IR (PE): ν [ν(C=O)]=2000 (vs, A_1), 1947 (s, E); ^{1}H-NMR (500 MHz, $CDCl_3$): 1.32 (s, $C(CH_3)_3$), 5.61 (t, $^3J_{HH}$=6.2 Hz, $HCArCr(CO)_3$), 5.74 (t, $^3J_{HH}$=6.2 Hz, $HCArCr(CO)_3$), 6.10 (d, $^3J_{HH}$=6.46 Hz, $HCArCr(CO)_3$), 6.18 (d, $^3J_{HH}$=6.36 Hz, $HCArCr(CO)_3$), 6.73 (s, 1H, HCAr); ^{13}C-NMR (125 MHz, $CDCl_3$): 29.1 ($C(CH_3)_3$), 36.0 ($C(CH_3)_3$), 89.2, 90.1, 91.3 93.2 (4 $HCArCr(CO)_3$), 91.7, 94.2 (2 $CArCr(CO)_3$), 133.7 (HCAr), 158.3 (CAr), 184.6, 184.9 (2 C=O), 229.8 ($Cr(CO)_3$); MS (70 eV): *m/z* (%)=350 (13) [M^+], 294 (9) [M^+–2CO], 266 (100) [M^+–3CO], 214 (2) [M^+–$Cr(CO)_3$], 52 (68); HR-MS: calcd.: 350.0246, found: 350.0249.

Acknowledgements

Support by the Deutsche Forschungsgemeinschaft (*SFB 334*), the Graduiertenkolleg "*Spektroskopie isolierter und kondensierter Moleküle*" and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

1. Reactions of Complex Ligands, Part 76. For Part 75, see: A. Longen, M. Nieger, F. Vögtle, K. H. Dötz, *Chem. Ber.* **1997**, in press.
2. S. G. Davies, C. L. Goodfellow, *J. Chem. Soc., Perkin Trans. I* **1990**, 393; M. Uemura, R. Miyoka, N. Nakayama, M. Shiro, Y. Hayashi, *J. Org. Chem.* **1993**, *58*, 1238; S. Maiorana, C. Baldoli, *Tetrahedron: Asym.* **1996**, *7*, 1903; E. P. Kündig, *Tetrahedron* **1996**, *52*, 7363; E. P. Kündig, L. He Xu, P. Romanens, G. Bernardinelli, *Synlett* **1996**, 270; S. G. Davies, C. L. Goodfellow, *Tetrahedron: Asym.* **1992**, *3*, 1303; S. G. Davies, L. M. A. R. B. Correia, *J. Chem. Soc., Chem. Commun.* **1996**, 1803.
3. L. S. Hegedus, *Organische Synthese mit Übergangsmetallen*, VCH, Weinheim, **1995**, p. 275 ff..
4. Reviews: K. H. Dötz, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587; W. D. Wulff in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, New York, **1991**, Vol. 5, p. 1065 ff..
5. W. D. Wulff, R. P. Hsung, *J. Am. Chem. Soc.* **1994**, *116*, 6449.
6. R. L. Beddoes, J. D. King, P. Quayle, *Tetrahedron Lett.* **1995**, *17*, 3027; R. P. Hsung, W. D. Wulff, C. A. Challener, *Synthesis* **1996**, 773.
7. K. H. Dötz, C. Stinner, M. Nieger, *J. Chem. Soc., Chem. Commun.* **1995**, 2535.
8. E. O. Fischer, T. Selmayr, F. R: Kreißl, *Chem. Ber.* **1977**, *110*, 2947; B. C. Söderberg, L. S. Hegedus, M. A. Sierra, *J. Am. Chem. Soc.* **1990**, *112*, 4364; J. Barluenga, J. M. Monserrat, J. Flórez, S. Garcia-Granda, E. Martin, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1392.
9. E. O. Fischer, C. G. Kreiter, *Angew. Chem. Int. Ed. Engl.* **1969**, *81*, 780.
10. K. H. Dötz, J. Mühlemeier, U. Schubert, O. Orama, *J. Organomet. Chem.* **1983**, *247*, 187; W. D. Wulff, P.-C. Tang, J. S. McCallum, *J. Am. Chem. Soc.* **1981**, *103*, 7677.
11. K. H. Dötz, *J. Organomet. Chem.* **1977**, *141*, 177; K. S. Chan, G. A. Peterson, T. A. Brandvold, K. L. Faron, C. A. Challener, C. Heydahl, W. D. Wulff, *J. Organomet. Chem.* **1987**, *334*, 9.
12. H. Fischer, J. Mühlemeier, R. Märkl, K. H. Dötz, *Chem. Ber.* **1982**, *151*, 1355.
13. K. H. Dötz, B. Fügen Köster, *Chem. Ber.* **1980**, *113*, 1449; K. H. Dötz, W. Sturm, *J. Organomet. Chem.* **1985**, *285*, 205.

14. J. Barluenga, F. Aznar, A. Martin, S. García-Granda, E. Pérez-Carreno, *J. Am. Chem. Soc.* **1994**, *116*, 11191; E. Chelain, A. Parlier, H. Rudler, J.-C. Daran, J. Vaissermann, *J. Organomet. Chem.* **1991**, *419*, C5; W. D. Wulff, B. M. Bax, T. A. Brandvold, K. S. Chan, A. M. Gilbert, R. P. Hsung, *Organometallics* **1994**, *13*, 102; B. A. Anderson, W. D. Wulff, *J. Am. Chem. Soc.* **1990**, *112*, 8615.
15. K. H. Dötz, T. Schäfer, F. Kroll, K. Harms, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1236; F. Hohmann, S. Siemoneit, T. Schäfer, M. Nieger, S. Kotila, K. Harms, K. H. Dötz, *Chem. Eur. J.*; in press.
16. P. Hofmann, M. Hämmerle, *Angew. Chem Int. Ed. Engl.* **1989**, *28*, 908; P. Hofmann, M. Hämmerle, G. Unfried, *New J. Chem.* **1991**, *15*, 769.
17. M. M. Gleichmann, K. H. Dötz, B. A. Heß, *J. Am. Chem. Soc.* **1996**, *118*, 10551.
18. T. A. Albright, P. Hofmann, R. Hoffmann, C. P. Lillya and P. A. Dobosh, *J. Am. Chem. Soc.* **1983**, *105*, 3396.
19. K. H. Dötz, I. Pruskil, *Chem. Ber.* **1980**, *113*, 2876.

(Received in UK 10 February 1997; accepted 25 March 1997)