α-Arylation of 2-Arylacetates and Benzofuran-2-one with Tricarbonyl(fluoroarene)chromium Complexes

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Dedicated to Professor Dr. Manfred Christl on the occasion of his 60th birthday

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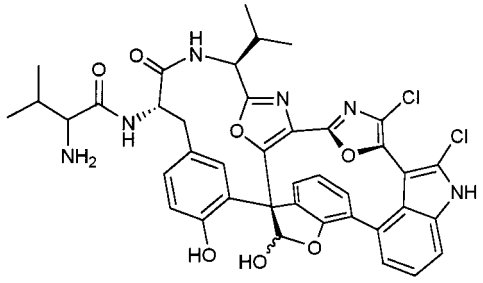
In order to synthesise fragments of the natural product diazonamide A, α-arylation of 2-arylacetates **3** and benzofuran-2-one with the aid of the tricarbonyl(fluoroarene)chromium complex ***rac*-2** was investigated. After decomplexation of the products ***rac*-4** and ***rac*-6**, it was possible to obtain 2,2-diarylacetates ***rac*-5** and the 3-arylbenzofuran-2-one ***rac*-7**.

Introduction

In the course of our efforts towards the total synthesis of diazonamide A,[1] we have addressed the problem of the construction of benzofuran systems with oxygen functions in position 2 and quaternary centres bearing aryl substituents at position 3. Benzofuran-2-ones and the corresponding open-chained 2-(2-hydroxyphenyl)acetic acid derivatives could be envisaged as suitable starting materials in which the quaternary centre could be established by treatment of the corresponding enolates with electrophiles. Since known syntheses of 2-aryl-2-(2-hydroxyphenyl)acetic acid derivatives by arylation only provide access to symmetrical products[2] and syntheses of 3-arylbenzofuran-2-ones[3−6] are rare, we looked for new ways to prepare such products. It is known that complexation of aromatic compounds with tricarbonylchromium reduces the electron density in the aromatic nucleus, thus considerably enhancing nucleophilic substitution of suitable leaving groups, such as chloride and − in particular − fluoride attached to the ring .[7] Furthermore, tricarbonylchromium complexes may possess a plane of asymmetry, thus permitting diastereoselective reactions. Aryl groups have been introduced with the aid of tricarbonylchromium complexes into malonates, benzyl cyanide, α-imino esters, or protected amino esters by way of intermediate enolates.[8,9] We report here on the application of this method to the introduction of the 2-methoxy-5-methylphenyl group into benzofuranone and (2-aryl)acetates **3**.



Diazonamide A

Results and Discussion

The 2-methoxy-5-methylphenyl group served as a model for tyrosine, which is found in the structure of diazonamide A. The synthesis started with 2-fluoro-1-methoxy-4-methylbenzene (**1**; Scheme 1), available through a photochemical version[10a] of the Schiemann reaction of the corresponding aniline.[10b] Treatment of **1** with hexacarbonylchromium under reflux in dibutyl ether/THF (3:1) afforded the tricarbonylchromium complex ***rac*-2**. This underwent the intended nucleophilic substitution of fluoride with enolates of 2-arylacetates **3** in KOH/DMSO at room temperature after 20 min. The resulting tricarbonyl(diarylacetate)chromium complexes ***rac*-4** could be isolated, but were sensitive to light. X-ray crystal analysis of ***rac*-4c** (see Figure 1) revealed an eclipsed conformation of one CO ligand of the tripod and the methoxy group of the arene ring. The decomplexation of chromium complexes ***rac*-4** in almost quantitative yields was possible by exposure to sunlight in the presence of air. In this way it was possible to obtain diarylacetates ***rac*-5a−c** with protected hydroxy groups at the *o*-positions (R^1 = H; R^2 = OMOM or OBn). Products ***rac*-5b** and ***rac*-5c** each possess an additional bromo substituent at position 3, which might be usable in later cross-coupling reactions to establish a bond to the indole ring of the diazo-

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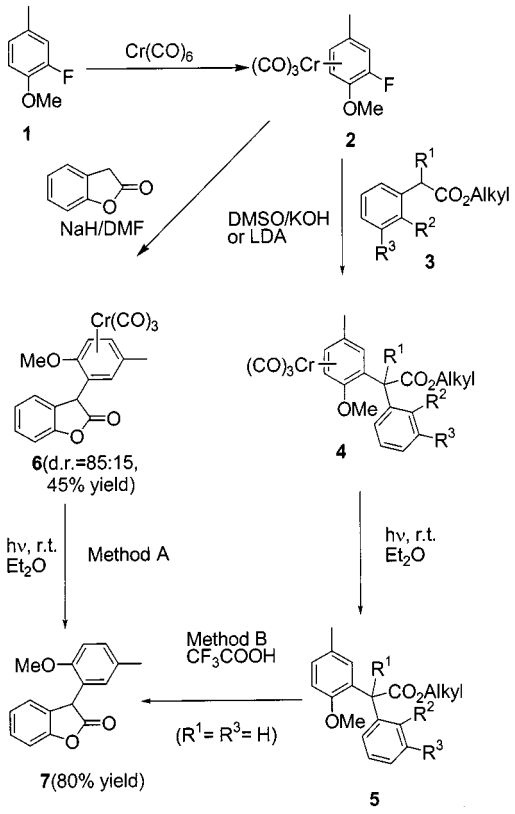
namide structure. The application of tricarbonylchromium complexes in the synthesis of corresponding protected (*o*-hydroxyphenyl)acetates **3** with secondary α-carbon atoms ($R^1 \neq H$, $R^2 = OMOM$) failed. However, the envisaged quaternary carbon atom could be built up in 2-arylacetates without substituents in the *o*-position of the phenyl ring ($R^1 \neq H$, $R^2 = H$; formation of ***rac*-4e** and ***rac*-4f**). Modest diastereoselectivities were observed in the formation of the diarylacetates ***rac*-4**, but, remarkably, the 2-MOMO-ethyl-substituted product ***rac*-4f** was obtained as a single diastereomer. Presumably, the chelating properties of the 2-MOMO-ethyl group in combination with reaction conditions favouring one of the two possible stereoisomeric intermediate enolates are responsible for this excellent stereoselectivity. In analogy to known aldol reactions[11] of methyl phenylacetate in the presence of LDA/HMPA, it may be expected that the (*E*)-enolate is also formed in our case. A synthesis of optically active tricarbonyl(diarylacetate)chromium complexes **4** might be feasible through the use of enantiopure tricarbonylchromium complex **2**, which could be produced through the corresponding phenol. On the other hand, diastereoselective formation of optically active tricarbonylchromium complexes similar to **2** might also be expected, if optically active fluorotyrosine derivatives were used as necessary as starting materials for the diazonamide A skeleton.



4	5	R^1	R^2	R^3	Alkyl	yield %	d. r.
a	a	H	OMOM	H	Me	97	58:42
b	b	H	OMOM	Br	Me	84	56:44
c	c	H	OBn	Br	Me	75	64:36
	d	H	OH	H	Me	60	
e		Me	H	H	Et	53	58:42
f		CH_2CH_2O-MOM	H	H	Me	91	>95:5

Scheme 1. Synthesis of 2-arylacetates and benzofurans with the aid of tricarbonylchromium complexes

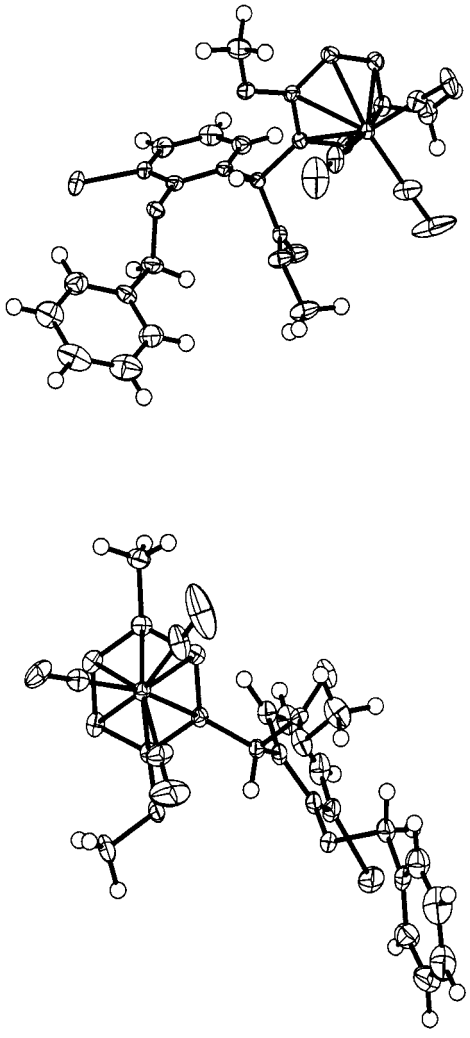


Figure 1. X-ray crystal structure analysis of **4c** in two different projections

In order to produce the benzofuran-2-one ring, the diarylacetate ***rac*-5c** was deprotected. The resulting (2-hydroxyphenyl)acetate ***rac*-5d** smoothly cyclised to 3-arylbenzofuran-2-one **7** upon heating at reflux in trifluoroacetic acid/toluene (Method B). This product (***rac*-7**) could alternatively be obtained (Method A) by arylation of benzofuran-2-one with the tricarbonylchromium complex ***rac*-2** and decomplexation of the resulting tricarbonylchromium complex ***rac*-6** in the same manner as for ***rac*-4**. Remarkably, treatment of ***rac*-2** with benzofuran-2-one proceeded with a higher diastereoselectivity (*dr* = 85:15) than observed in the arylation of the corresponding **3**. X-ray crystal analysis of

the tricarbonylchromium complex ***rac*-6** (see Figure 2) again revealed an eclipsed conformation of one CO ligand of the tripod and the methoxy group of the arene ring. The lactone ring and the arene ring are almost perpendicular to each other (dihedral angle 86°).

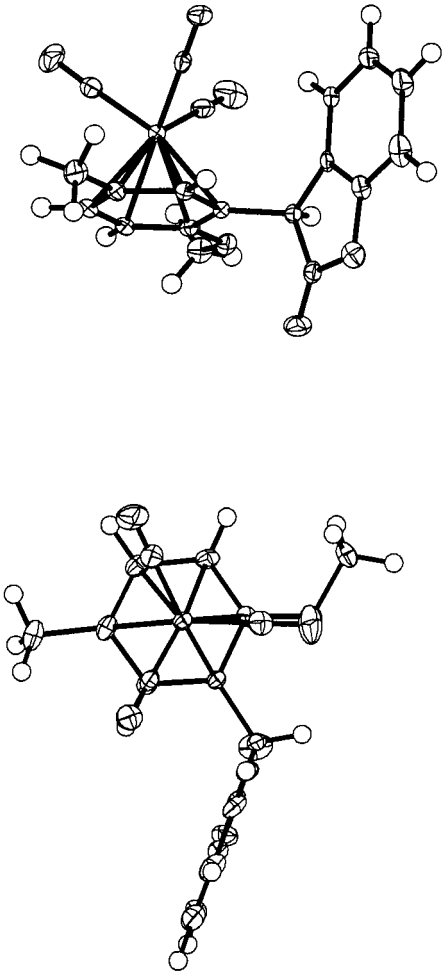


Figure 2. X-ray crystal structure analysis of **6** in two different projections

In summary, it could be demonstrated that (arene)tricarbonylchromium complexes are useful tools with which to introduce aryl rings into 2-arylacetates and benzofuranone.

Experimental Section

General Remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively, with a Bruker AC 300 in $CDCl_3$ with TMS as internal standard. Tricarbonylchromium complexes ***rac*-4** were obtained as diastereomeric mixtures, which were not separated. All spectra of ***rac*-4** were recorded from the diastereomeric mixtures. Silica (0.04−0.063 mm, Merck) was used for preparative column chromatography. If not otherwise mentioned, starting materials were purchased from commercial suppliers. All tricarbonylchromium complexes were sensitive to air and light, but could be kept in a refrigerator for prolonged periods without decomposition.

2-Fluoro-1-methoxy-4-methylbenzene (1):[10a,10b] A solution of 2-methoxy-5-methyldiazonium tetrafluoroborate (9.00 g, 38.1 mmol) in $BF_3{\cdot}Et_2O$ (120 mL) was irradiated by a mercury lamp (150 W) at 0 °C until the evolution of N_2 had ceased. After dilution with Et_2O (100 mL), the solution was poured into ice/water (400 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 × 100 mL). The combined organic layers were washed with 10% aqueous K_2CO_3 (2 × 100 mL), dried with $MgSO_4$, and concentrated under vacuum. The remaining red liquid was distilled under vacuum (b.p. 74−82 °C at 15 Torr) to afford 3.90 g (73%) of the product; colourless liquid. R_f = 0.57 (hexane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3), 3.89 (s, 3 H, OCH_3), 6.87−6.95 (m, 3 H, Ar). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.4 (*C*H$_3$), 56.4 (O*C*H$_3$), 113.4 (6-*C*H, ^3J = 2.1 Hz), 116.7 (3-*C*H, ^2J = 17.7 Hz), 124.4 (5-*C*H, ^4J = 3.5 Hz), 131.0 (4-*C*, ^3J = 6.7 Hz), 145.3 (1-*C*, ^2J = 10.7 Hz), 152.2 (2-*C*F, ^1J = 244.8 Hz).

Tricarbonyl(2-fluoro-1-methoxy-4-methylbenzene)chromium (*rac*-2): A solution of **1** (3.76 g, 26.8 mmol) in dry THF (20 mL) and a solution of hexacarbonylchromium (7.09 g, 32.2 mmol) in (nBu)$_2$O (150 mL) were both placed under argon in a flame-dried flask with an efficient condenser. After flushing with argon for 30 min, dry THF (30 mL) was added. The mixture was heated to 125 °C for 3 d with exclusion of daylight. The resulting yellowish-green suspension was filtered through Celite/silica. The yellow solution was concentrated under vacuum and purified by column chromatography (hexane/EtOAc, 8:2) to yield 4.61 g (62%) of the yellow solid product, which was stored in the dark. M.p. 67−68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, CH_3), 3.65 (s, 3 H, OCH_3), 4.68 (d, 1 H, Ar, ^3J = 7.2 Hz), 5.19 (s, 1 H, *3*, Ar), 5.27 (d, 1 H, Ar, ^3J = 7.2 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.2 (*C*H$_3$), 58.6 (O*C*H$_3$), 79.6 (6-*C*H, Ar, ^3J = 2.5 Hz); 82.8 (3-*C*H, Ar, ^2J = 17.6 Hz), 87.8 (5-*C*H, Ar), 103.8 (1-*C*, Ar, ^2J = 5.3 Hz), 129.2 (4-*C*, Ar), 138.5 (2-*C*F, Ar, ^1J = 265.8 Hz), 232.9 (3 *C*, *C*O). IR (KBr): $\tilde{\nu}$ = 1956, 1862 (with shoulder), 1633 cm^{-1}. $C_{11}H_9CrFO_4$ (276.18): calcd. C 47.84, H 3.28; found C 47.87, H 3.16.

Tricarbonyl(1-methoxy-2-{(methoxycarbonyl)[2-(methoxymethoxy)-phenyl]methyl}-4-methylbenzene)chromium (*rac*-4a): The 2-arylacetate **3a** (810 mg, 3.85 mmol) and ***rac*-2** (1.00 g, 3.62 mmol) were added at room temperature to a suspension of KOH (85%, 720 mg, 10.9 mmol) in dry DMSO (13 mL). After 20 min, saturated aqueous NH_4Cl solution (10 mL) was added. The solution was extracted with EtOAc (3 × 10 mL) and the combined organic layers were dried with $MgSO_4$, concentrated and purified by column chromatography (hexane/CH_2Cl_2, 1:2) to yield 1.64 g (97% yield) of the diastereomeric mixture as a yellow solid. *dr* = 58:42. R_f = 0.20 and 0.28 (hexane/EtOAc, 1:2). M.p. 94−98 °C. ^{1}H NMR (of major diastereomer, 300 MHz, $CDCl_3$): δ = 2.04 (s, 3 H, ArCH_3), 3.40 (s, 3 H, OCH$_2$OCH_3), 3.55 (s, 3 H, COOCH_3), 3.78 (s, 3 H, ArOCH_3), 4.89 (d, 1 H, *Ar*, ^3J = 6.7 Hz), 5.15 (s, 2 H, OCH_2OCH$_3$), 5.38 (s, 1 H, *Ar*), 5.43 (d, 1 H, *Ar*, ^3J = 6.7 Hz), 5.91 (s, 1 H, ArC*H*Ar′), 6.83−7.19 (m, 4 H, *Ar′*). ^{1}H NMR (of minor diastereomer, 300 MHz, $CDCl_3$): δ = 2.10 (s, 3 H, ArCH_3), 3.45 (s, 3 H, OCH$_2$OCH_3), 3.62 (s, 3 H, COOCH_3), 3.68 (s, 3 H, ArOCH_3), 4.91 (d, 1 H, *Ar*, ^3J = 6.9 Hz), 5.15 (s, 2 H, OCH_2OCH$_3$), 5.36 (s, 1 H, *Ar*), 5.56 (d, 1 H, *Ar*, ^3J = 6.9 Hz), 5.03 (s, 1 H, ArC*H*Ar′), 6.86−7.29 (m, 4 H, *Ar′*). ^{13}C NMR (of major diastereomer, 75.5 MHz, $CDCl_3$): δ = 20.2 (Ar*C*H$_3$), 43.0 (Ar*C*HAr′), 52.3 (CO-O*C*H$_3$), 56.0 (ArO*C*H$_3$), 56.1 (OCH$_2$O*C*H$_3$), 72.8 (*C*H, Ar), 94.3 (O*C*H$_2$OCH$_3$), 94.9 (*C*H, Ar), 96.2 (*C*, Ar), 97.4 (*C*H, Ar), 99.7 (*C*, Ar), 113.7 (*C*H, Ar), 121.5 (*C*H, Ar), 127.4 (*C*, Ar), 128.4 (*C*H, Ar), 128.8 (*C*H, Ar), 140.5 (*C*OCH$_3$, Ar), 154.6 (*C*OCH$_2$, Ar), 172.2 (*C*OOCH$_3$), 233.0 (3 C, *C*≡O). ^{13}C NMR (of minor diastereomer, 75.5 MHz, $CDCl_3$): δ = 20.0 (Ar*C*H$_3$), 44.7 (Ar*C*HAr′), 52.4 (CO-O*C*H$_3$), 56.1 (ArO*C*H$_3$), 56.3 (OCH$_2$O*C*H$_3$), 72.7 (*C*H, Ar), 94.7

(OCH_2OCH_3), 95.4 (*C*H, Ar), 97.5 (*C*, Ar), 97.9 (*C*H, Ar), 99.5 (*C*, Ar), 114.8 (*C*H, Ar), 121.9 (*C*H, Ar), 123.2 (*C*, Ar), 129.9 (*C*H, Ar), 130.5 (*C*H, Ar), 141.2 ($COCH_3$, Ar), 155.4 ($COCH_2$, Ar), 172.8 ($COOCH_3$), 233.3 (3 C, *C*≡O). MS; *m*/*z* (%): 466 (0.3) [M^+], 410 (1.0) [$M^+ - 2$ CO], 382 (6.2) [$M^+ - 3$ CO], 195 (10.3), 134 (22.0), 52 (16.5), 45 (100). IR (KBr): $\tilde{\nu}$ = 1956, 1896, 1864, 1718, 1630 cm^{-1}. $C_{22}H_{22}CrO_8$: calcd. 466.0720; found 466.0720.

(2-{[3-Bromo-2-(methoxymethoxy)phenyl](methoxycarbonyl)methyl}-1-methoxy-4-methylbenzene)tricarbonylchromium (*rac*-4b): 2-Arylacetate **3b** (1.11 g, 3.84 mmol) and ***rac*-2** (1.00 g, 3.62 mmol) were treated in a suspension of KOH (85%, 760 mg, 11.5 mmol) and dry DMSO (15 mL) as described for ***rac*-4a**. Yield: 1.65 g (84%). *dr* = 56:44. R_f = 0.82 and 0.74 (hexane/CH_2Cl_2, 1:2). Yellow crystals. M.p. 144 °C. ^{1}H NMR (of major diastereomer, 300 MHz, $CDCl_3$): δ = 2.07 (s, 3 H, ArCH_3), 3.28 (s, 3 H, OCH_2OCH_3), 3.61 (s, 3 H, $COOCH_3$), 3.77 (s, 3 H, ArOCH_3), 4.89 (d, 1 H, Ar, ^3J = 6.7 Hz), 5.15 (s, 2 H, OCH_2OCH_3), 5.40 (s, 1 H, C*H*, Ar), 5.42 (d, 1 H, Ar, ^3J = 6.7 Hz), 5.93 (s, 1 H, C*H*$COOCH_3$), 6.54−7.09 (m, 3 H, *Ar*). ^{1}H NMR (of minor diastereomer, 300 MHz, $CDCl_3$): δ = 2.14 (s, 3 H, ArCH_3), 3.58 (s, 3 H, OCH_2OCH_3), 3.63 (s, 3 H, $COOCH_3$), 3.61 (s, 3 H, ArOCH_3), 4.97 (d, 1 H, C*H*,Ar, *J* = 6.8 Hz), 5.16 (s, 2 H, OCH_2OCH_3), 5.48 (s, 1 H, C*H*, Ar), 5.61 (d, 1 H, C*H*, Ar, *J* = 6.8 Hz), 5.99 (s, 1 H, C*H*$COOCH_3$), 6.58−7.16 (m, 3 H, *Ar*). ^{13}C NMR (of major diastereomer, 75.5 MHz, $CDCl_3$): δ = 20.3 (ArCH_3), 42.4 (*C*H$COOCH_3$), 52.3 ($COOCH_3$), 56.7 (ArOCH_3), 56.9 (OCH_2OCH_3), 72.2 (*C*H, Ar), 94.3 (OCH_2OCH_3), 95.6 (*C*H, Ar), 96.6 (*C*, Ar), 97.5 (*C*H, Ar), 99.5 (*C*, Ar), 115.4 (*C*Br, Ar), 122.5 (*C*H, Ar), 126.9 (*C*, Ar), 128.0 (*C*H, Ar), 128.9 (*C*H, Ar), 140.5 ($COCH_3$, Ar), 154.6 ($COCH_2$, Ar), 172.2 ($COOCH_3$), 233.0 (3 C, *C*≡O). ^{13}C NMR (of minor diastereomer, 75.5 MHz, $CDCl_3$): δ = 18.3 (ArCH_3), 44.6 (*C*H$COOCH_3$), 52.4 ($COOCH_3$), 56.4 (ArOCH_3), 56.8 (OCH_2OCH_3), 76.9 (*C*H, Ar), 96.3 (OCH_2OCH_3), 95.9 (*C*H, Ar), 96.6 (*C*, Ar), 97.5 (*C*H, Ar), 97.5 (*C*, Ar), 114.9 (*C*Br, Ar), 123.5 (*C*H, Ar), 126.7 (*C*, Ar), 128.6 (*C*H, Ar), 129.1 (*C*H, Ar), 141.2 ($COCH_3$, Ar), 154.5 ($COCH_2$, Ar), 172.5 ($COOCH_3$), 233.1 (3 C, *C*≡O). MS; *m*/*z* (%): 546, 544 (1.0, 1.1) [M^+], 490, 488 (2.7, 2.8) [$M^+ - 2$ CO], 462, 460 (17.7, 17.2) [$M^+ - 3$ CO], 337 (10.1), 300, 298 (25.9, 25.8), 275, 273 (39.9, 39.1), 239 (13.5), 209 (20.1), 195 (66.1), 165 (41.2), 152 (23.0), 135 (64.8) [$CH_3C_6H_3(CH_2)OCH_3$], 45 (100). IR (KBr): $\tilde{\nu}$ = 1956, 1874, 1860, 1733, 1631 cm^{-1}. $C_{22}H_{21}BrCrO_8$ (545.297): calcd. C 48.46, H 3.88, Br 14.65; found C 48.47, H 4.20, Br 14.65.

(2-{[2-(Benzyloxy)-3-bromophenyl](methoxycarbonyl)methyl}-1-methoxy-4-methylbenzene)tricarbonylchromium (*rac*-4c): 2-Arylacetate **3c** (1.00 g, 2.98 mmol) and ***rac*-2** (1.29 g, 4.67 mmol) were treated in a suspension of KOH (85%, 720 mg, 10.9 mmol) and dry DMSO (7.5 mL) as described for ***rac*-4a**. Purification was by recrystallisation from hexane/EtOAc, 7:3. Yield: 1.32 g (75%). *dr* = 64:36. Yellow crystals. M.p. 153−155 °C. ^{1}H NMR (of major diastereomer, 300 MHz, $CDCl_3$): δ = 2.11 (s, 3 H, CCH_3), 3.57 (s, 3 H, $COOCH_3$), 3.74 (s, 3 H, OCH_3), 4.95 (d, 1 H, *Ar*, ^3J = 6.6 Hz), 5.06 (s, 2 H, CH_2), 5.49 (d, 1 H, *Ar*, ^3J = 6.6 Hz), 5.61 (s, 1 H, C*H*-$COOCH_3$), 5.99 (s, 1 H, *Ar*), 6.98−7.66 (m, 8 H, *Ar*). ^{1}H NMR (of minor diastereomer, 300 MHz, $CDCl_3$): δ = 1.98 (s, 3 H, CCH_3), 3.67 (s, 3 H, $COOCH_3$), 3.72 (s, 3 H, OCH_3), 4.99 (d, 1 H, *Ar*, ^3J = 6.8 Hz), 5.21 (s, 2 H, CH_2), 5.46 (d, 1 H, *Ar*, ^3J = 6.8 Hz), 5.40 (s, 1 H, C*H*-$COOCH_3$), 5.45 (s, 1 H, *Ar*), 6.95−7.54 (m, 8 H, *Ar*). ^{13}C NMR (of major diastereomer, 75.5 MHz, $CDCl_3$): δ = 20.0 (CCH_3), 43.4 (*C*H$COOCH_3$), 52.6 ($COOCH_3$), 55.9 (OCH_3), 72.7 (*C*H, Ar), 74.9 (CH_2), 94.7 (*C*H, Ar), 95.8 (C, Ar), 96.7 (*C*H, Ar), 99.7 (*C*, Ar), 117.6 (*C*Br), 125.4 (*C*H, Ar), 128.3 (*C*H, Ar), 128.4 (2 *C*H, Ar), 128.5 (2 *C*H, Ar), 128.6 (*C*H, Ar), 133.2 (*C*H, Ar), 133.7 (*C*, Ar), 136.4 (*C*, Ar), 140.2 (*C*, Ar), 153.7 (*C*, Ar), 171.4 ($COOCH_3$); 232.7 (3 C, *C*≡O). ^{13}C NMR (of minor diastereomer, 75.5 MHz, $CDCl_3$): δ = 19.9 (CCH_3), 44.7 (*C*H$COOCH_3$), 52.5 ($COOCH_3$), 56.0 (OCH_3), 72.4 (*C*H, Ar), 75.6 (CH_2), 95.4 (*C*H, Ar), 96.7 (C, Ar), 97.6 (*C*H, Ar), 99.2 (*C*, Ar), 118.2 (*C*Br), 127.9 (*C*H, Ar), 128.2 (*C*H, Ar), 128.4 (2 *C*H, Ar), 128.5 (2 *C*H, Ar), 129.0 (*C*H, Ar), 131.2 (*C*H, Ar), 134.1 (*C*, Ar), 136.6 (*C*, Ar), 140.8 (*C*, Ar), 154.3 (*C*, Ar), 172.0 ($COOCH_3$); 232.8(3 C, *C*≡O). IR (KBr): $\tilde{\nu}$ = 1954, 1873 (with shoulder), 1728, 1632 cm^{-1}. $C_{27}H_{23}BrCrO_7$: calcd. 590.0032; found 590.0034.

Tricarbonyl{2-[1-(ethoxycarbonyl)-1-phenylethyl]-1-methoxy-4-methylbenzene}chromium (*rac*-4e): A solution of LDA was prepared by adding a solution of *n*BuLi in hexane (1.6 M, 0.14 mL, 0.22 mmol) to a solution of diisopropylamine (22 mg, 0.22 mmol) in dry THF (0.5 mL) at −25 °C under argon in a flame-dried flask. After 30 min, the solution was cooled to −70 °C and a solution of ethyl 2-phenylpropionate (36 mg, 0.20 mmol) in dry THF (0.80 mL) was added. After that temperature had been maintained for 45 min, HMPA (179 mg, 1.00 mmol) and a solution of ***rac*-2** (61 mg, 0.22 mmol) in THF (3 mL) were added. The mixture was allowed to warm slowly to room temperature. Aq. NH_4Cl (7 mL) was added and the mixture was extracted with EtOAc (3 × 10 mL). The organic layer was dried with $MgSO_4$ and concentrated under vacuum to afford a yellow oil (150 mg). After column chromatography (hexane/CH_2Cl_2 3:1), 46 mg (53%) of the product was obtained (*dr* = 58:42). ^{1}H NMR (of major diastereomer, 300 MHz, $CDCl_3$): δ = 1.15 (t, 3 H, CH_2CH_3, *J* = 7.1 Hz), 1.77 (s, 3 H, ArCH_3), 1.84 (s, 3 H, CH_3), 3.59 (s, 3 H, OCH_3), 4.14 (q, *J* = 7.1 Hz, 2 H, CH_2CH_3), 4.78 (d, 1 C*H*, *J* = 7.2 Hz, Ar), 4.86 (s, 1 C*H*, Ar), 5.48 (d, 1 C*H*, *J* = 7.2 Hz, Ar), 7.28−7.72 (m, 5 C*H*, Ar). ^{1}H NMR (of minor diastereomer, 300 MHz, $CDCl_3$): δ = 1.22 (t, 3 H, CH_2CH_3, *J* = 7.0 Hz), 1.82 (s, 3 H, ArCH_3), 2.06 (s, 3 H, CH_3), 3.71 (s, 3 H, OCH_3), 4.29 (q, *J* = 7.0 Hz, 2 H, CH_2CH_3), 4.86 (s, 1 C*H*, Ar), 4.92 (d, 1 C*H*, *J* = 6.9 Hz, Ar), 5.48 (d, 1 C*H*, *J* = 6.9 Hz, Ar), 7.28−7.72 (m, 5 C*H*, Ar). ^{13}C NMR (of major diastereomer, 75.5 MHz, $CDCl_3$): δ = 14.0 (CH_2CH_3), 19.9 (ArCH_3), 25.8 (CH_3), 51.9 (C_q), 55.8 (OCH_3), 61.4 (CH_2CH_3), 72.2 (*C*H, Ar), 96.0 (*C*H, Ar), 97.1 (*C*, Ar), 98.4 (*C*H, Ar), 107.9 (*C*, Ar), 127.7 (2 *C*H, Ar), 128.0 (2 *C*H, Ar), 128.3 (*C*H, Ar), 138.9 (*C*, Ar), 140.1 (*C*, Ar), 172.7 ($COOCH_3$), 233.5 (3 C, *C*≡O). ^{13}C NMR (of minor diastereomer, 75.5 MHz, $CDCl_3$): δ = 14.0 (CH_2CH_3), 19.9 (ArCH_3), 28.3 (CH_3), 53.3 (C_q), 55.9 (OCH_3), 61.5 (CH_2CH_3), 72.6 (*C*H, Ar), 97.2 (*C*, Ar), 98.2 (*C*H, Ar), 100.8 (*C*H, Ar), 108.2 (*C*, Ar), 127.9 (2 *C*H, Ar), 128.2 (2 *C*H, Ar), 128.9 (*C*H, Ar), 139.7 (*C*, Ar), 141.5 (*C*, Ar), 173.9 ($COOCH_3$), 233.6 (3 C, *C*≡O). MS; *m*/*z* (%): 435 (0.74) [MH^+], 379 (4.0) [$MH^+ - 2$ CO], 351 (27.2) [$MH^+ - 3$ CO], 299 (11.1) [$M^+ - Cr(CO)_3$], 246 (12.7), 225 (45), 165 (11.9), 121 (16.3) [$CH_3C_6H_3OCH_3$], 105 (10.7), 103 (14.8), 97 (10.0), 91 (100), 77 (13.3) [C_6H_5], 71 (15.6), 69 (13.1), 55 (13.4), 52 (48.9), 43 (21.0), 41 (13.4), 29 (23.5). IR (film): $\tilde{\nu}$ = 1955, 1874 (br), 1728, 1600 cm^{-1}. $C_{22}H_{22}CrO_6$ (434.403): calcd. C 60.83, H 5.10; found C 60.03, H 5.24.

Tricarbonyl{2-[1-(methoxycarbonyl)-3-(methoxymethoxy)-1-phenylpropyl]-1-methoxy-4-methylbenzene}chromium (*rac*-4f): Diisopropylamine (20 mg, 0.20 mmol), *n*BuLi in hexane (1.6 M, 0.12 mL, 0.19 mmol), THF (1 mL), ***rac*-2** (54 mg, 0.20 mmol) in THF (2 mL), HMPA (0.16 g, 0.89 mmol), and methyl 4-(methoxymethoxy)-2-phenylbutanoate (43 mg, 0.18 mmol) in THF (1 mL) were treated as described under ***rac*-4e** to afford 81 mg (91%) of the product after chromatography with hexane/EtOAc (7:3). Yellow oil. R_f = 0.12 (hexane/EtOAc, 7:3). *dr* > 95:5. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93 (s, 3 H, CH_3), 2.68−2.87 (m, 2 H, CCH_2CH_2),

3.33 (s, 3 H, CH_2OCH_3), 3.53−3.64 (m, 1 H, $CH_2CHH'O$), 3.72 (s, 3 H, $COOCH_3$), 3.77 (s, 3 H, OCH_3), 4.22−4.25 (m, 1 H, $CH_2CHH'O$), 4.50 (d, 2 H, OCH_2O, ^2J = 1.6 Hz), 4.91 (d, 1 H, CH,Ar, ^3J = 6.7 Hz), 5.06 (d, 1 H, CH, Ar, ^4J = 1.5 Hz), 5.54 (dd, 1 H, CH, Ar,^3J = 6.7, ^4J = 1.5 Hz), 7.34−7.90 (m, 5 H, *Ar*). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.9 (CH_3), 35.8 (CCH_2CH_2), 52.3 ($COOCH_3$), 53.8 (C_q), 55.2, 56.1 (2 CH_3, OCH_3), 64.7 (CH_2CH_2O), 71.4 (CH, Ar), 96.1 (CH, Ar), 96.4 (OCH_2O), 97.8 (C, Ar), 98.6 (CH, Ar), 105.5 (*C*, Ar), 128.1, 128.4, 129.0, 130.8 (4 CH, Ar), 132.4 (*C*, Ar), 136.9 (*C*, Ar), 140.2 (CH, Ar), 172.5 ($COOCH_3$), 133.2 (3 C, C≡O). $C_{24}H_{26}O_8Cr_1$: calcd. 494.1033, found 494.1033.

General Procedure for the Decomplexation of Tricarbonylchromium Complexes *rac*-4 To Afford 2,2-Diarylacetates *rac*-5: The appropriate tricarbonylchromium complex ***rac*-4** was dissolved in THF/Et_2O (10 mL/10 mL) and was subjected to direct sunlight in the presence of air for about 1 h. A green precipitate appeared and was filtered off by pouring through a silica layer. The solution was concentrated under vacuum and the remaining colourless product was purified by chromatography.

Methyl 2-[2-(Methoxymethoxy)phenyl]-2-(2-methoxy-5-methylphenyl)acetate (*rac*-5a): Starting material ***rac*-4a** (592 mg). Yield: 378 mg (90%); colourless crystals. M.p. 79−80 °C. R_f = 0.51 (acetone/CH_2Cl_2, 1:100). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15 (s, 3 H, CCH_3), 3.33 (s, 3 H, OCH_2OCH_3), 3.63 (s, 3 H, $COOCH_3$), 3.68 (s, 3 H, OCH_3), 5.09 (dd, 2 H, OCH_2O, ^2J = 6.66 Hz), 5.56 (s, 1 H, CH), 6.70−7.16 (m, 7 H, *Ar*). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.6 (CH_3), 44.8 (CH), 52.1 ($COOCH_3$), 55.7 (OCH_3), 55.9 (OCH_3), 94.3 (OCH_2O), 110.7 (CH, Ar), 113.9 (CH, Ar), 121.7 (CH, Ar), 126.2 (C, Ar), 127.5 (C, Ar), 128.3, 128.8, 129.4, 130.0 (4 CH, Ar), 129.7 (C, Ar), 154.8 (C, Ar), 155.1 (C, Ar), 173.8 ($COOCH_3$). MS; *m*/*z* (%): 331 (9.6) [MH^+], 285 (10.4) [M^+ − MOM], 266 (12.0), 254 (18.3), 239 (19.8), 225 (17.3), 196 (18.6), 195 (50.9), 181 (11.4), 166 (11.5), 165 (69.9), 152 (11.1), 135 (17.6) [$CH_3C_6H_3(CH_2)OCH_3$], 121 (13.9) [$CH_3C_6H_3OCH_3$], 97 (32.4), 83 (38.4), 69 (37.8), 57 (47.8), 55 (42.8), 45 (100), 43 (59.4). $C_{19}H_{22}O_5$ (330.385): calcd: C 69.08 H 6.71 found C 68.87 H 6.78.

Methyl 2-[3-Bromo-2-(methoxymethoxy)phenyl]-2-(2-methoxy-5-methylphenyl)acetate (*rac*-5b): Starting material ***rac*-4b** (338 mg). Yield: 236 mg (93%); colourless crystals. M.p. 86 °C. R_f = 0.58 (hexane/CH_2Cl_2, 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.09 (s, 3 H, $ArCH_3$), 3.53 (s, 3 H, OCH_2OCH_3), 3.64 (s, 3 H, $COOCH_3$), 3.68 (s, 3 H, OCH_3), 5.09 (d, *J* = 5.6 Hz, 1 H, $OCHH'O$), 5.12 (d, *J* = 5.7 Hz, 1 H, $OCHH'O$), 5.69 (s, 1 H, $CHCOOCH_3$), 6.70−7.42 (m, 6 H, CH, Ar). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.6 ($ArCH_3$), 45.5 ($CHCOOCH_3$), 52.3 ($COOCH_3$), 55.6 (OCH_3), 57.8 (OCH_3), 99.9 (OCH_2O), 110.8 (CH, Ar), 117.5 (CBr, Ar), 125.6 (CH, Ar), 126.3, 129.1 (2 *C*, Ar), 129.8, 129.9, 132.6 (3 CH, Ar), 134.2 (*C*, Ar), 152.9 (*C*, Ar), 154.8 (*C*, Ar), 173.3 ($COOCH_3$). $C_{19}H_{21}BrO_5$ (409.271): calcd. C 55.76, H 5.17, Br 19.52; found C 55.85, H 5.35, Br 19.71.

Methyl 2-[2-Benzyloxy-3-bromophenyl]-2-(2-methoxy-5-methylphenyl)acetate (*rac*-5c): Starting material ***rac*-4c** (288 mg). Yield: 213 mg (96%); colourless solid. M.p. 86 °C. R_f = 0.57 (hexane/EtOAc, 7:3). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3 H, CH_3), 3.59 (s, 3 H, $COOCH_3$), 3.65 (s, 3 H, OCH_3), 4.84 (dd, 2 H, CHH', *J* = 6.2 Hz), 5.68 (s, 1 H, $CHCOOCH_3$), 6.80−7.51 (m, 11 H, *Ar*). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.6 (CH_3), 45.0 ($CHCOOCH_3$), 52.2 ($COOCH_3$), 55.5 (OCH_3), 74.8 (CH_2), 110.6 (CH, Ar), 117.6 (CBr), 125.4 (CH, Ar), 126.1 (*C*, Ar), 129.1 (*C*, Ar), 128.1 (CH, Ar), 128.2 (CH, Ar), 128.4 (2 CH, Ar), 129.2 (CH, Ar), 129.8 (2 CH, Ar), 129.9 (CH, Ar), 132.7 (CH, Ar), 134.1 (*C*, Ar), 136.8 (*C*, Ar), 153.9 (*C*, Ar), 154.8 (*C*, Ar), 173.3 ($COOCH_3$).

Methyl 2-(2-Hydroxyphenyl)-2-(2-methoxy-5-methylphenyl)acetate (*rac*-5d): A solution of ***rac*-5c** (85 mg, 0.19 mmol) in THF (5 mL) was mixed with EtOH (10 mL). Trifluoroacetic acid (3 drops) and 20% $Pd(OH)_2$/C (10 mg) were added. The mixture was hydrogenated (stirring under normal pressure at room temperature for 12 h). The reaction mixture was filtered through silica and the yellow filtrate was concentrated under vacuum. After chromatography with hexane/EtOAc (7:3), 32 mg (59%) of the pure product was obtained. Colourless oil. R_f = 0.26. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, CH_3), 3.74 (s, 3 H, $COOCH_3$), 3.80 (s, 3 H, OCH_3), 5.29 (s, 1 H, $CHCOOCH_3$), 6.70−7.17 (m, 7 H, *Ar*). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.9 (CH_3), 47.9 ($CHCOOCH_3$), 52.6 ($COOCH_3$), 55.7 (OCH_3), 110.6 (CH, Ar), 117.2 (CH, Ar), 120.6 (CH, Ar), 122.9 (*C*, Ar), 125.0 (*C*, Ar), 129.0 (CH, Ar), 129.1 (CH, Ar), 129.6 (CH, Ar), 130.1 (*C*, Ar), 130.6 (CH, Ar), 154.4 (*C*, Ar), 154.9 (*C*, Ar), 175.1 ($COOCH_3$).

Tricarbonyl[2-(2,3-dihydro-2-oxobenzofuran-3-yl)-1-methoxy-4-methylbenzene]chromium (*rac*-6): 2,3-Dihydrobenzofuran-2-one (0.268 g, 2.00 mmol) was slowly added to a suspension of NaH (0.060 g, 2.38 mmol) in DMF (5 mL). After the evolution of H_2 had ceased, the mixture was warmed to 30 °C to obtain a clear solution. ***rac*-2** (0.552 g, 2.00 mmol) was added, and the mixture was stirred at room temperature for 30 min. Saturated aqueous NH_4Cl (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated under vacuum. The remainder was purified by column chromatography (hexane/CH_2Cl_2, 2:3) to afford 0.350 g (45%) of the product ***rac*-6** (*dr* = 85:15) and 0.166 g (30%) of the starting material ***rac*-2**. Yellow crystals. M.p. 86 °C. R_f = 0.24 (hexane/CH_2Cl_2, 2:3). ^{1}H NMR (of major diastereomer, 300 MHz, $CDCl_3$): δ = 1.90 (s, 3 H, $ArCH_3$), 3.72 (s, 3 H, $ArOCH_3$), 4.82 (s, 1 H, CH), 5.04 (d, 1 H, *Ar*, ^3J = 7.1 Hz), 5.13 (s, 1 H, *Ar*), 5.37 (d, 1 H, *Ar*, ^3J = 7.1 Hz), 7.11−7.59 (m, 4 H, *Ar*). ^{1}H NMR (of minor diastereomer, 300 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, $ArCH_3$), 3.51 (s, 3 H, $ArOCH_3$), 4.57 (s, 1 H, CH), 4.90 (d, 1 H, *Ar*, ^3J = 7.0 Hz), 5.23 (s, 1 H, *Ar*), 5.48 (d, 1 H, *Ar*, ^3J = 7.0 Hz), 7.09−7.61 (m, 4 H, *Ar*). ^{13}C NMR (of major diastereomer, 75.5 MHz, $CDCl_3$): δ = 20.1 (CH_3), 42.7 (CH), 57.0 (OCH_3), 74.3 (CH, Ar), 94.6 (CH, Ar), 94.9 (CH, Ar), 96.8 (*C*, Ar), 101.8 (*C*, Ar), 111.2 (CH, Ar), 124.4 (*C*, Ar), 125.2 (CH, Ar), 126.3 (CH, Ar), 130.4 (CH, Ar), 140.1 (*C*, Ar), 154.7 (*C*, Ar), 174.0 (*C*OO), 233.2 (3 C, *CO*). ^{13}C NMR (of minor diastereomer, 75.5 MHz, $CDCl_3$): δ = 20.1 (CH_3), 45.7 (CH), 56.5 (OCH_3), 72.8 (CH, Ar), 96.0 (CH, Ar), 96.8 (CH, Ar), 99.6 (*C*, Ar), 101.8 (*C*, Ar), 110.8 (CH, Ar), 124.7 (*C*, Ar), 126.0 (CH, Ar), 127.4 (CH, Ar), 129.6 (CH, Ar), 140.1 (*C*, Ar), 154.7 (*C*, Ar), 174.0 (*C*OO), 233.1 (3 C, *CO*). MS; *m*/*z* (%): 390 (4.1) [M^+], 334 (9.0), 306 (39), 195 (100), 171 (20), 165 (17), 139 (19), 113 (19), 97 (20), 83 (23), 57 (52), 52 (97). $C_{19}H_{14}CrO_6$ (390.307): calcd: C 58.47, H 3.62; found C 58.40, H 3.79.

2,3-Dihydro-3-(2-methoxy-5-methylphenyl)benzofuran-2-one (*rac*-7). − Method A: Decomplexation of ***rac*-6** according to the general procedure for the decomplexation of tricarbonylchromium complexes ***rac*-4** (vide supra) afforded an 80% yield. − **Method B:** A solution of ***rac*-5d** (32 mg, 0.11 mmol) in dry toluene (3 mL) was treated with trifluoroacetic acid (3 drops). The mixture was refluxed for 2.5 h. After dilution with 10 mL EtOAc, the organic layer was washed with saturated, aqueous $NaHCO_3$ solution to pH = 7 and dried with $MgSO_4$. The resulting solution was concentrated under vacuum and purified by column chromatography (hex-

ane/CH_2Cl_2, 1:2) to yield 27 mg (96%) of a white solid. M.p. 145 °C. R_f = 0.5. (hexane/CH_2Cl_2, 1:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.21 (s, 3 H, ArCH_3), 3.58 (s, 3 H, ArOCH_3), 4.85 (s, 1 H, C*H*), 6.69−7.22 (m, 7 H, *Ar*). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.4 (*C*H_3), 47.5 (*C*HCOOCH$_3$), 55.8 (O*C*H$_3$), 110.3 (*C*H, Ar), 111.6 (*C*H, Ar), 124.0 (*C*, Ar), 130.9 (*C*, Ar), 124.3 (*C*H, Ar), 124.4 (*C*H, Ar), 128.6 (*C*H, Ar), 128.2 (*C*, Ar), 128.9 (*C*H, Ar), 130.0 (*C*H, Ar), 130.4 (*C*H, Ar), 131.0 (*C*H, Ar), 153.9 (*C*, Ar), 154.9 (*C*, Ar), 176.0 (*C*OOCH$_3$). $C_{16}H_{14}O_3$: calcd. 254.09429; found 254.09425.

X-ray Crystal Structure Analysis of *rac*-4c:[12] A single crystal of ***rac*-4c** of dimensions 0.70 × 0.60 × 0.150 mm was measured with a STOE Ipds diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Crystal data: $C_{27}H_{20}BrCrO_7$, M = 588.34, triclinic, space group $P\bar{1}$, a = 8.0821(7) Å, b = 12.8159(12) Å, c = 13.8701(12) Å, α = 64.329(7)°, β = 82.180(8)°, γ = 75.936(8)°, V = 1255.3(2) Å^3, Z = 2, D_c = 1.557 g/cm^3, F(000) = 594, μ(Mo-K_α) = 2.092 mm^{-1}. At 180(2) K in the range of 1.63° < θ < 26.02°, 6338 reflections were measured, 4942 were unique ($R_{(int)}$ = 0.0211). The final residuals were $wR_{2(all)}$ = 0.0981, $R_{1(all)}$ = 0.0451 and $R_{1(obs)}$ = 0.0358. The maximum and minimum peaks in the final difmap were 0.859 and −0.532 e·Å^{-3}, respectively.

X-ray Crystal Structure Analysis of *rac*-6:[12] A single crystal of ***rac*-6** of dimensions 0.64 × 0.52 × 0.40 mm was measured with a STOE Ipds diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Crystal data: $C_{19}H_{14}CrO_6$, M = 390.30, monoclinic space group $P21/c$, a = 11.911(3) Å, b = 8.6622(16) Å, c = 16.379(4) Å, α = 90°, β = 102.23(3), γ = 90°, V = 6151.6(7) Å^3, Z = 4, D_c = 1.570 g/cm^3, F(000) = 800, μ(Mo-K_α) = 0.727 mm^{-1}. At 180(2) K in the range of 2.67° < θ < 25.80 °, 14281 reflections were measured, 3137 were unique ($R_{(int)}$ = 0.0489). The final residuals were $wR_{2(all)}$ = 0.1119, $R_{1(all)}$ = 0.0492 and $R_{1(obs)}$ = 0.0470. The maximum and minimum peaks in the final difmap were 0.518 and −0.554 e·Å^{-3}, respectively.

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[12] Crystallographic data (excluding structure factors) for the structures **4c** and **6** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-174362 (***rac*-4c**) and -174361 (***rac*-6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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