Diastereoselective Synthesis of Tricarbonyl(thiophene)chromium Complexes

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2,3-Disubstituted 2-hydroxyalkylthiophenes **9** and **10** were synthesized in a five-step sequence and their diastereoselective complexation with the $Cr(CO)_3$ fragment leading to the corresponding tricarbonyl(thiophene)chromium complexes **11** and **12** was investigated. The diastereoselectivity achieved in the complexation reaction was up to 85% d.e. and depends primarily on the bulkiness of the substituent in the 3-position of the thiophene. The relative configuration of the stereogenic center and the planar element of chirality of complex **11a** was determined by X-ray diffraction analysis.

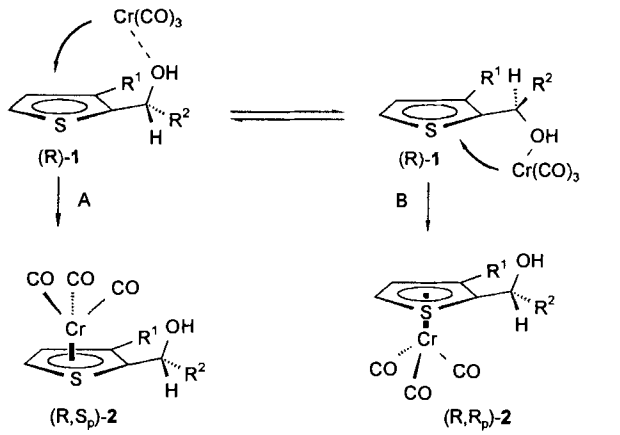
The diastereoselective synthesis of planar chiral (π-arene)tricarbonylchromium complexes has attracted considerable attention as these complexes play an important role in various asymmetric syntheses[1]. The synthesis of enantiomerically enriched planar chiral (π-arene)tricarbonylchromium complexes via diastereoselective complexation of a chiral disubstituted benzene derivative with the $Cr(CO)_3$ fragment has been successfully performed with diastereoselectivities up to >98% d.e.[1b,2]. Our interest in tricarbonyl(thiophene)chromium complexes[3] prompted us to investigate the diastereoselective complexation of chiral thiophenes.

Results and Discussion

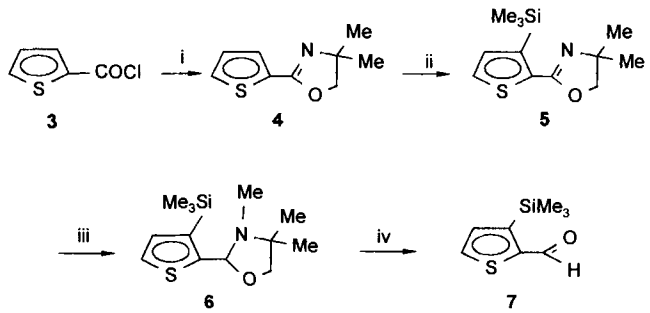
The π-complexation of racemic 2-(α-hydroxyalkyl)thiophenes bearing an additional substituent in the 3-position by a metal fragment leads to two diastereomeric products **2**, both as racemic mixtures. Because the metal fragment is supposed to be directed to the thiophene ring through *pre*-coordination to the hydroxy group, the presence of a bulky substituent on the stereogenic center in α-position of the substituent should lead to preferential attack of one of the two diastereotopic faces of the thiophene ring (Scheme 1). High levels of diastereoselectivity have been achieved in analogous complexation reactions with substituted hydroxyalkyl benzene derivatives[2a].

A Me_3Si group was chosen as a sterically demanding substituent for the 3-position and the synthesis of 2-formyl-3-trimethylsilylthiophene **7** is depicted in Scheme 2. Metalation of the thiophene at C-3 was enabled by introduction of an *ortho*-directing group into the 2-position. Oxazolines gave the best results as *ortho*-directing group[4] leading – after deprotonation and subsequent treatment with Me_3SiCl – to a mixture of 2-oxazolinyl-3-trimethylsilylthiophene **5** and 2-oxazolinyl-5-trimethylsilylthiophene (ratio 21:1). Treatment with MeI gave the respective methiodides from which the pure 2,3-disubstituted product could be separated by crystallization from methanol. After deprotection pure 2-formyl-3-trimethylsilylthiophene **7** was isolated in 35% overall yield.

Scheme 1. *Pre*-coordination of the $Cr(CO)_3$ group and stereoselective direction to the thiophene



Scheme 2. Synthesis of 2-formyl-3-trimethylsilylthiophene 7



Treatment of aldehyde **7** with Grignard reagents R^2MgX (**a**: R^2 = Me; **b**: *i*Pr) led to the 2-hydroxyalkyl-3-trimethylsilylthiophenes **9a**, **b**. The analogous reaction of commercially available 2-formyl-3-methylthiophene **8** gave the 2-hydroxyalkyl-3-methylthiophenes **10a**, **b**.

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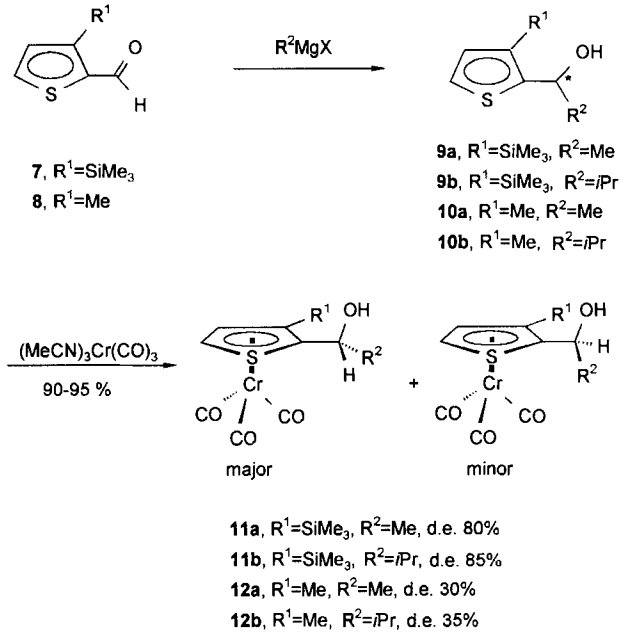
Scheme 3. Synthesis and complexation of 2-hydroxyalkyl-3-alkylthiophenes

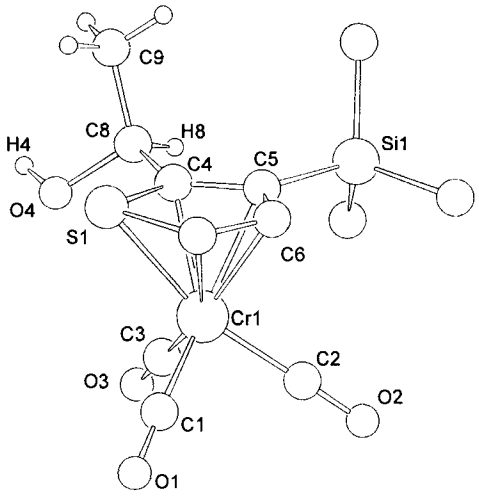


Tricarbonyl(thiophene)chromium complexes were synthesized by treatment of the thiophenes **9a**, **b** and **10a**, **b** with tris(acetonitrile)tricarbonylchromium in dioxane at room temperature[5]. Evaporation of the solvent at reduced pressure (20 torr) and subsequent dissolution of the residue in dioxane led after 2–4 repetitions to the tricarbonyl(thiophene)chromium complexes **11a**, **b** and **12a**, **b** in almost quantitative yield. The use of $(\gamma\text{-picoline})_3Cr(CO)_3/BF_3 \cdot OEt_2$ as a source of $Cr(CO)_3$ fragments[6] was less satisfactory resulting in lower yields and the formation of $(\gamma\text{-picoline})Cr(CO)_5$ as an inseparable byproduct.

The ratio of diastereomeric complexation products was determined by analysis of their integrated ^{1}H-NMR spectra. Modest diastereoselectivities were obtained for the complexation of the different 2-hydroxyalkyl-3-methylthiophenes **10a**, **b**. The d.e. was 30% for **12a** (R^2 = Me) and 35% for **12b** (R^2 = *i*Pr). Introduction of the sterically more demanding trimethylsilyl group into the 3-position of the thiophene increased the diastereoselectivity remarkably, leading to d.e. = 80% for **11a** (R^2 = Me) and 85% for **11b** (R^2 = *i*Pr). Very low diastereoselectivity (d.e. <10%) was observed for the complexation of the isomeric 5-trimethylsilyl-substituted 2-(α-hydroxyethyl)thiophene. An X-ray crystal structure determination of the major diastereomer of complex **11a** (Figure 1) revealed the relative configuration of the central and planar elements of chirality to be (S^*,S_p^*)[7]. This suggests that the complexation proceeds via pathway B in Scheme 1 with a lower activation barrier as compared to pathway A, the latter involving an unfavourable approach of the α-Me group and the substituent R^1 = $SiMe_3$.

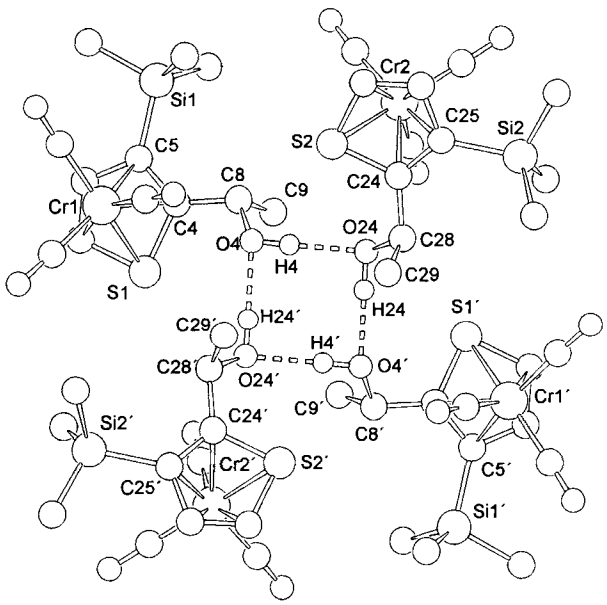
Complex **11a** crystallizes in the monoclinic space group *I2/a* with two independent molecules in the asymmetric unit, which show similar bond lengths and angles within

Figure 1. Molecular structure of **11a**



experimental error, falling in the range observed for other tricarbonyl(thiophene)chromium complexes[3]. In the crystal the molecules of **11a** form cyclic tetramers via hydrogen bonds between the hydroxy groups (Figure 2). A crystallographic C_2 axis relates pairwise opposite molecules of the tetramer.

Figure 2. Tetrameric arrangement of molecules in the structure of **11a**



These results show a strong dependence of the achieved diastereoselectivity on the size of the substituent in the 3-position. In contrast, the size of the hydroxyalkyl group has only minor influence on the d.e. Compared to the diastereoselectivities achieved in the complexation of similarly substituted benzenes[2a], the complexation of the thiophenes gave lower diastereoselectivities. This can be explained by the larger outer ring angles for the five-membered ring of the thiophene compared with the six-membered ring of the benzene derivatives which bring the ring substituents in

closer contact to each other in the latter case. Hence, the steric influence should be more pronounced in the benzene series.

Another approach to the diastereoselective complexation of thiophenes was based on acetals prepared from (+)-diethyl tartrate and 3-substituted thiophene-2-carbaldehydes[8]. After complexation the subsequent hydrolysis of the acetal group was supposed to lead to enantiomerically enriched planar chiral thiophene-2-carbaldehyde tricarbonylchromium complexes. However, the synthesis of the chiral acetal prepared from (+)-diethyl tartrate and 3-methylthiophene-2-carbaldehyde gave two atropisomers because of the hindered rotation of the thienyl group about the transannular C–C-bond, whose separation was unsatisfactory.

In summary, we have performed the first diastereoselective complexation of a chiral disubstituted thiophene with a $Cr(CO)_3$ fragment. The obtained diastereoselectivities were up to d.e. = 85%, depending primarily on the bulkiness of the substituents in the 3-position of the thiophene.

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Experimental Section

All manipulations were carried out under dry N_2 in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under N_2. – NMR: Varian Unity 500 (499.843 MHz, ^1H, int. TMS; 125.639 MHz, $^{13}C\{^1H\}$, APT, int. TMS). – MS: Finnigan MAT 95. – Elemental analysis (C, H, N): Carlo-Erba elemental analyzer, Modell 1106. – Tris(acetonitrile)tricarbonylchromium[5] and 4,5-dihydro-4,4-dimethyl-2-(2-thienyl)oxazole **4**[4] were prepared as described in the literature.

4,5-Dihydro-4,4-dimethyl-2-(3-trimethylsilyl-2-thienyl)oxazole (**5**): *n*-BuLi (1.6 M, 29.0 ml, 46.0 mmol) was added dropwise to a solution of **4** (7.3 g, 40.3 mmol) in 120 ml of Et_2O at −78 °C. After 30 min, the mixture was allowed to warm to 0 °C and stirred for 30 min at this temperature. Me_3SiCl (6.3 ml, 50 mmol) was added and the mixture was stirred at room temp. overnight. 30 ml of water was added, the phases were separated and the organic layer was washed with water and brine and dried with Na_2SO_4. Filtration and evaporation of the solvent in vacuo gave **5** as a pale yellow oil (9.2 g, 90%) together with less than 5% of the isomeric 5-trimethylsilyl-substituted thiophene. This oil was used in the next step without further purification. – ^1H NMR ($CDCl_3$): δ = 0.29 (s, 9H, $SiCH_3$), 1.34 [s, 6H, $C(CH_3)_2$], 4.05 (s, 2H, CH_2), 7.11 (d, *J* = 5.0 Hz, 1H, H-4), 7.35 (d, *J* = 5.0 Hz, 1H, H-5). – ^{13}C NMR ($CDCl_3$): δ = 0.1 ($SiCH_3$), 28.6 [$C(CH_3)_2$], 68.0 [$C(CH_3)_2$], 79.4 (CH_2), 127.9 (C-5), 134.2 (C-4), 145.3 (C-3), 158.6 (C-2). – $C_{12}H_{19}NOSSi$: calcd. 253.0957; found 253.0953 (MS).

3-(Trimethylsilyl)thiophene-2-carbaldehyde (**7**): A solution of **5** (10.1 g, 40.0 mmol) in 40 ml of nitromethane was treated with MeI (8.6 g, 60.0 mmol, 1.5 equiv.) and the mixture was heated at reflux for 6 h. Subsequent addition of 25 ml of ether and cooling to −20 °C yielded the *N*-methyloxazolinium salt as off-white microcrystals. Recrystallization from methanol gave the pure 3-trimethylsilyl-substituted thiophene species (9.48 g, 24.0 mmol, 60%), which was dissolved in 50 ml of methanol and treated with solid $NaBH_4$ (0.84 g, 26.4 mmol) in portions at 0 °C. After 2 h of stirring at room temp. 60 ml of water and 15.1 g (120 mmol) of oxalic acid dihydrate were carefully added and the solution was refluxed overnight, cooled to room temp. and extracted with four 30-ml portions of ether. The combined ether extracts were washed with water and brine, dried with Na_2SO_4, filtered, and the solvent was evaporated from the filtrate in vacuo to afford **7** as a colorless liquid (2.87 g, 15.5 mmol, 65%). – ^1H NMR ($CDCl_3$): δ = 0.30 (s, 9H, $SiCH_3$), 7.18 (d, *J* = 5.0 Hz, 1H, H-4), 7.64 (dd, *J* = 5.0/1.0 Hz, 1H, H-5), 9.99 (d, *J* = 1.0 Hz, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = 0.4 ($SiCH_3$), 134.2 (C-5), 135.0 (C-4), 149.2 (C-3), 152.1 (C-2), 183.3 (CHO). – $C_8H_{12}OSSi$: calcd. 183.0300; found 183.0297 (MS).

General Procedure for the Synthesis of 3-Substituted 2-(α-Hydroxyalkyl)thiophenes: A solution of **7** or **8** (9 mmol) in 5 ml of Et_2O was added dropwise to a solution of 10 mmol of the Grignard reagent (prepared from 10 mmol of Mg and 11 mmol of MeI or *i*PrBr in 25 ml of Et_2O) in Et_2O and the mixture was refluxed for 1 h. Ice/water was added and the pH adjusted to 7.5–8.0 by the addition of 2 M HCl. The organic layer was separated, washed with water, dried with Na_2SO_4 and evaporated to dryness in vacuo. – **9a**: 88%. – ^1H NMR ($CDCl_3$): δ = 0.45 (s, 9H, $SiCH_3$), 1.72 (d, *J* = 6.5 Hz, 3H, CCH_3), 2.12 (d, *J* = 3.0 Hz, 1H, OH), 5.44 (dq, *J* = 6.5/3.0 Hz, 1H, $CHCH_3$), 7.14 (d, *J* = 5.0 Hz, 1H, H-4), 7.39 (d, *J* = 5.0 Hz, 1H, H-5). – ^{13}C NMR ($CDCl_3$): δ = 0.4 ($SiCH_3$), 26.4 (CCH_3), 66.6 (CHOH), 123.9 (C-4), 132.6 (C-5), 136.5 (C-3), 157.2 (C-2). – $C_9H_{16}OSSi$; calcd. 200.0691; found 200.0694 (MS). – **9b**: 40%. – ^1H NMR ($CDCl_3$): δ = 0.34 (s, 9H, $SiCH_3$), 1.19 (d, *J* = 6.5 Hz, 3H, $CHCH_3$), 1.40 (d, *J* = 6.5 Hz, 3H, $CHCH_3$), 1.94 (s, 1H, OH), 2.00–2.10 [m, 1H, $(CH_3)_2CH$], 4.71 (d, *J* = 8.5 Hz, 1H, CHOH), 7.04 (d, *J* = 5.0 Hz, 1H, H-4), 7.31 (d, *J* = 5.0 Hz, 1H, H-5). – ^{13}C NMR ($CDCl_3$): δ = 0.7 ($SiCH_3$), 19.1 ($CHCH_3$), 19.9 ($CHCH_3$), 37.2 [$(CH_3)_2CH$], 75.9 (CHOH), 124.4 (C-4), 132.3 (C-5), 137.9 (C-3), 155.2 (C-2). – $C_{11}H_{20}OSSi$; calcd. 228.1004; found 228.1002 (MS). – **10a**: 92%. – ^1H NMR ($CDCl_3$): δ = 1.44 (d, *J* = 6.5 Hz, 3H, $CHCH_3$), 2.12 (s, 3H, CCH_3), 2.47 (s, 1H, OH), 5.04 (q, *J* = 6.5 Hz, 1H, CH_3CH), 6.68 (d, *J* = 5.0 Hz, 1H, H-4), 7.01 (d, *J* = 5.0 Hz, 1H, H-5). – ^{13}C NMR ($CDCl_3$): δ = 13.7 (CCH_3), 24.9 ($CHCH_3$), 64.5 (CHOH), 122.6 (C-4), 130.2 (C-5), 133.0 (C-3), 143.0 (C-2). – $C_7H_{10}OS$; calcd. 141.0374; found 141.0376 (MS). – **10b**: 88%. – ^1H NMR ($CDCl_3$): δ = 0.81 (d, *J* = 6.5 Hz, 3H, $CHCH_3$), 1.07 (d, *J* = 6.5 Hz, 3H, $CHCH_3$), 1.95–2.00 [m, 1H, $(CH_3)_2CH$], 2.19 (s, 3H, CCH_3), 2.21 (d, *J* = 1.0 Hz, 1H, OH), 4.56 (d, *J* = 8.0 Hz, 1H, CHOH), 6.75 (d, *J* = 5.0 Hz, 1H, H-4), 7.12 (d, *J* = 5.0 Hz, 1H, H-5). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (CCH_3), 18.3 ($CHCH_3$), 19.0 ($CHCH_3$), 36.5 [$(CH_3)_2CH$], 73.9 (CHOH), 123.0 (C-4), 129.7 (C-5), 133.7 (C-3), 141.2 (C-2). – $C_9H_{14}OS$; calcd. 141.0374; found 141.0376 (MS).

General Procedure for the Synthesis of Tricarbonyl(thiophene)-chromium Complexes: Tris(acetonitrile)tricarbonylchromium (1–3 mmol) was suspended in 20 ml of dry dioxane and 4 equiv. of the thiophene derivative were added as a dioxane solution. The color of the solution changed from orange to dark red. Evaporation of the solvent at reduced pressure (room temp., 40 Torr) and subsequent dissolution of the residue in dioxane gave after 2–4 repetitions the tricarbonyl(thiophene)chromium complexes.

Tricarbonyl[1-(3-trimethylsilylthiophene-2-yl)ethanol]chromium (**11a**): To a suspension of tris(acetonitrile)tricarbonylchromium (660 mg, 2.5 mmol) in dioxane was added a solution of **9a** (2.1 g, 10.0 mmol) in dioxane. Treatment according to the genral procedure gave 756 mg (90%) of **11a**. Recrystallization from Et_2O/hexane afforded red needles, suitable for X-ray diffraction analysis. – d.e. = 80%. – IR (dioxane): $\tilde{\nu}$ = 1856 cm^{-1} (CO), 1877 (CO), 1952 (CO). – **11a I** (major diastereomer): ^1H NMR (C_6D_6): δ = 0.08 (s, 9H, $SiCH_3$), 1.06 (d, *J* = 6.5 Hz, 3H, $CHCH_3$), 2.20 (d, *J* = 3.5 Hz, 1H, CHOH), 3.81 (dd, *J* = 3.5/1.0 Hz, 1H, H-5), 4.32 (qdd, *J* = 6.5/3.5/1.0 Hz, 1H, $CHCH_3$), 4.60 (d, *J* = 3.5 Hz, 1H, H-4). – ^{13}C NMR ($CDCl_3$): δ = 0.2 ($SiCH_3$), 27.5 ($CHCH_3$), 66.0

(COH), 83.4 (C-5), 101.5 (C-4), 233.6 (CO). **11a II** (minor diastereomer): ^{1}H NMR ($CDCl_3$): δ = 0.36 (br. s, 9H, $SiCH_3$), 1.59 (br. d, 3H, $CHCH_3$), 1.95 (br. s, 1H, CHO*H*), 4.91 (br. s, 1H, $CHCH_3$), 5.17 (br. s, 1H, H-5), 5.54 (br. s, 1H, H-4). – ^{13}C NMR ($CDCl_3$): δ = 0.9 ($SiCH_3$), 25.5 ($CHCH_3$), 66.5 (COH), 83.4 (C-5), 101.0 (C-4), 233.2 (CO). – MS (70 eV); *m/z* (%): 336 (30) [M^+], 308 (20) [M^+ – CO], 280 (15) [M^+ – 2 CO], 252 (60) [M^+ – 3 CO]. – $C_{12}H_{16}CrSiSO_4$ (336.4): calcd. C 42.85, H 4.79; found C 43.10, H 4.72.

X-Ray Structural Analysis of **11a**: $CrSSiO_4C_{12}H_{16}$, M = 336.40 g mol^{-1}, monoclinic space group *I2/a* (no. 15), a = 29.62(1), b = 7.140(5), c = 30.43(1) Å, β = 107.08(5)°, V = 6153(10) Å^3, Z = 16, $d_{calcd.}$ = 1.453 g cm^{-3}, μ(Mo-K_α) = 9.37 cm^{-1}, F(000) = 2784. ENRAF-Nonius CAD4, ω-scan, Mo-K_α radiation (0.71073 Å), graphite monochromator, 6624 reflections at 203 K with 3 ≤ Θ ≤ 26°, crystal size 0.05 × 0.15 × 0.30 mm^3. Structure solution with direct methods (SHELXS-86[9]). Refinement[10] with anisotropic thermal parameters for all chromium, silicon, sulfur and oxygen atoms as well as for the carbon atoms of the carbonyl ligands and isotropic thermal parameters for all other non hydrogen atoms converged at R = 0.098, R_w = 0.080 for 253 parameters and 2176 independent observations with $I > 1.0\ \sigma(I)$. Hydrogen atoms were treated as riding atoms. A final difference Fourier synthesis showed a residual density of 0.89/–0.75 eÅ^{-3}[11].

Tricarbonyl[2-methyl-1-(3-trimethylsilylthiophene-2-yl)propanol]chromium (**11b**): 470 mg (1.8 mmol) of tris(acetonitrile)-tricarbonylchromium and 1.64 g (7.2 mmol) of **9b** were allowed to react as described above to yield 622 mg (95%) of **11b**. – d.e. = 85%. – Due to broad and overlapping signals, the ^{1}H-NMR resonances could not be attributed to certain protons. – IR (dioxane): $\tilde{\nu}$ = 1854 cm^{-1} (CO), 1874 (CO), 1950 (CO). – **11b I** (major diastereomer): ^{13}C NMR ($CDCl_3$): δ = 0.8 ($SiCH_3$), 14.4 ($CHCH_3$), 20.4 ($CHCH_3$), 37.2 ($CHCH_3$), 73.4 (COH), 84.1 (C-5), 96.1 (C-3), 101.9 (C-4), 108.4 (C-2), 233.9 (CO). **11b II** (minor diastereomer): ^{13}C NMR ($CDCl_3$): δ = 0.5 ($SiCH_3$), 14.5 ($CHCH_3$), 20.5 ($CHCH_3$), 36.7 ($CHCH_3$), 73.4 (COH), 83.1 (C-5), 96.1 (C-3), 101.9 (C-4), 108.4 (C-2), 234.2 (CO). – MS (70 eV); *m/z* (%): 364 (45) [M^+], 308 (20) [M^+ – 2 CO], 280 (85) [M^+ – 3 CO]. – $C_{14}H_{20}CrSiSO_4$; calcd. 364.0251; found 364.0257 (MS).

Tricarbonyl[1-(3-methylthiophene-2-yl)ethanol]chromium (**12a**): Tris(acetonitrile)tricarbonylchromium (790 mg, 3.0 mmol) and **10a** (1.7 g, 12.2 mmol) were treated in the above manner to give 792 mg (95%) of **12a** as red crystals. – d.e. = 30%. – IR (dioxane): $\tilde{\nu}$ = 1853 cm^{-1} (CO), 1872 (CO), 1952 (CO). – **12a I** (major diastereomer): ^{1}H NMR ($CDCl_3$): δ = 1.45 (br. s, 3H, CCH_3), 2.17 (br. s, 3H, $CHCH_3$), 2.50 (br. s, 1H, OH), 4.75 (br. s, 1H, CHOH), 5.25 (br. s, 1H, H-5), 5.53 (br. s, 1H, H-4). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (CCH_3), 25.3 ($CHCH_3$), 65.2 (COH), 83.8 (C-4), 97.2 (C-5), 103.7 (C-3), 117.0 (C-2), 233.9 (CO). **12a II** (minor diastereomer): ^{1}H-NMR ($CDCl_3$): δ = 1.51 (br. s, 3H, CCH_3), 2.04 (br. s, 3H, $CHCH_3$), 2.50 (br. s, 1H, OH), 4.39 (br. s, 1H, CHOH), 5.30 (br. s, 1H, H-5), 5.50 (br. s, 1H, H-4). – ^{13}C NMR ($CDCl_3$): δ = 14.2 (CCH_3), 23.1 ($CHCH_3$), 64.6 (COH), 84.2 (C-4), 96.5 (C-5), 101.3 (C-3), 117.0 (C-2), 233.5 (CO). – MS (70 eV); *m/z* (%): 278 (40) [M^+], 260 (2) [M^+ – H_2O], 222 (15) [M^+ – 2 CO], 194 (50) [M^+ – 3 CO], 125 (100) [M^+ – $HCr(CO)_3O$]. – $C_{10}H_{10}CrSO_4$ (278.24): calcd. C 43.17, H 3.62; found C 43.22, H 3.71.

Tricarbonyl[2-methyl-1-(3-methylthiophene-2-yl)propanol]-chromium (**12b**): Tris(acetonitrile)tricarbonylchromium (474 mg, 1.8 mmol) and **10b** (1.64 g, 7.2 mmol) were allowed to react according to the above procedure to furnish 523 mg (95%) of **12b**. – d.e. = 35%. – IR (dioxane): $\tilde{\nu}$ = 1853 cm^{-1} (CO), 1871 (CO), 1950 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.95 (br. s, 3H, CCH_3), 1.80 [br. s, 1H, $CH(CH_3)_2$], 2.20 [br. s, 6H, $CH(CH_3)_2$], 2.62 (br. s, 1H, OH), 4.4 (br. s, 1H, CHOH), 5.25 (br. s, 1H, H-5), 5.50 (br. s, 1H, H-4). – **12b I** (major diastereomer): ^{13}C NMR ($CDCl_3$): δ = 14.8 (CCH_3), 16.6 ($CHCH_3$), 19.9 ($CHCH_3$), 36.3 ($CHCH_3$), 72.9 (COH), 84.4 (C-5), 96.8 (C-4), 105.2 (C-2), 115.1 (C-3), 234.0 (CO). **12b II** (minor diastereomer): ^{13}C NMR ($CDCl_3$): δ = 14.9 (CCH_3), 16.7 ($CHCH_3$), 19.1 ($CHCH_3$), 36.2 ($CHCH_3$), 72.9 (COH), 84.1 (C-5), 96.4 (C-4), 104.8 (C-2), 115.0 (C-3), 234.1 (CO). – MS (70 eV); *m/z* (%): 306 (20) [M^+], 288 (10) [M^+ – H_2O], 250 (20) [M^+ – 2 CO], 222 (30) [M^+ – 3 CO], 127 (100) [M^+ – $Cr(CO)_3$]. – $C_{12}H_{14}CrSO_4$ (306.3): calcd. C 47.06, H 4.61; found C 46.81, H 4.68.

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