Supplementary Material (ESI) for Chemical Communications

Unanticipated Formation of *ortho* Sulfone Substituted Phenols by Anionic Thia-Fries Rearrangement of Aryl Triflate Tricarbonylchromium Complexes

Zhirong Zhao, Rudolf Wartchow, and Holger Butenschön*

Supplementary Material

General Procedure for the Synthesis of Phenol Tricarbonylchromium Complexes (GP1)

All operations are carried out under exclusion of air using standard Schlenk technique with argon as the inert gas. The phenol and 1.1 equiv. of hexacarbonylchromium are heated at reflux in dibutyl ether and THF (10:1) for 2 to 3 days. After cooling to 25 °C, the reaction mixture is carefully filtered through a P4 frit covered with a 2 cm thick layer of silica gel. The solvents are removed at reduced pressure, and the crude product is purified by flash chromatography at SiO_2, eluting with *tert*-butyl methyl ether/petroleum ether (1:1 to 4:1). The tricarbonylchromium phenol complexes are very sensitive and decompose quickly in air.

Tricarbonyl(phenol)chromium (0) (1)[1-3]

GP1, 1.13 g (12.0 mmol) of phenol, 2.90 g (13.2 mmol) of hexacarbonylchromium in 40 mL of dibutyl ether and 4 mL of THF, 2 d. 2.48 g (10.8 mmol, 90%) of **1** was obtained as a yellow solid, m. p. 43 °C (dec.). ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 4.85 (t, 1H, 4-H, $J_{H,H}$ = 6.0 Hz), 5.13 [d, 2H, 2(6)-H, $J_{H,H}$ = 6.5 Hz], 5.58 (t, 2H, 3(5)-H, $J_{H,H}$ = 6.3 Hz), 6.89 (s, 1H, OH) ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$, BB) δ 79.8 [C-2(6)], 85.1 (C-4), 95.9 [C-3(5)], 140.6 (C-1), 233.7 (CO) ppm; MS (70 eV) *m/z* (%) 230 (82) [M^+], 202 (17) [M^+ - CO], 174 (8) [M^+ - 2CO], 146 (72) [M^+ - 3CO], 94 (100) [M^+ - $Cr(CO)_3$], 80 (31), 66 (65), 52 (92).

Tricarbonyl(4-methoxyphenol)chromium(0) (2)

GP1, 2.10 g (16.9 mmol) of 4-methoxyphenol, 4.09 g (18.6 mmol) of hexacarbonylchromium, in 60 mL of dibutyl ether and 6 mL of THF, 60 h. 3.21 g (12.3 mmol, 73%) of **2** was obtained as a yellow solid, m. p. 52 °C (dec.). IR (ATR) ν/cm^{-1} 3095 (br), 2977 (w), 1946 (s, CO), 1839 (s, CO), 1556 (w), 1535 (m), 1491 (m), 1235 (m), 1181 (m), 1145 (w), 1081 (w), 1018 (m), 916 (w), 880 (w), 825 (w), 737 (m), 668 (s), 620 (s); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 3.60 (s, 3H, 7-H), 5.25 [d, 2H, 3(5)-H, $J_{H,H}$ = 7.0 Hz], 5.32 [d, 2H, 2(6)-H, $J_{H,H}$ = 6.9 Hz], 7.12 (s, 1H, OH) ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ 56.3 (C-7), 80.9 [C-2(6)], 81.0 [C-3(5)], 134.1 (C-1), 135.9 (C-4), 234.3 (CO) ppm; MS (70 eV) *m/z* (%) 260 (66) [M^+], 204 (45) [M^+ - 2CO], 176 (73) [M^+ - 3CO], 124 (72) [M^+ - Cr $(CO)_3$], 109 (75) [M^+ - $Cr(CO)_3$ - CH_3], 93 (8), 81 (67), 72 (24); HRMS ($C_{10}H_8CrO_5$) calcd. 259.9777, found. 259.9776.

Tricarbonyl(4-methylphenol)chromium(0) (3)[4]

GP1, 2.00 g (18.5 mmol) of 4-methylphenol, 4.48 g (20.3 mmol) of hexacarbonylchromium in 70 mL of dibutyl ether and 7 mL of THF, 54h. 2.94 g (12.0 mmol, 65%) of **3** was obtained as yellow oil. IR (ATR) ν/cm^{-1} 3463 (br), 1941 (s, CO), 1885 (s, CO), 1793 (s, CO), 1557 (m), 1475 (m), 1449 (m), 1398 (w), 1383 (w), 1309 (m), 1263 (m), 1201 (m), 1152 (m), 1088 (w), 1039 (w), 879 (w), 828 (w), 740 (w), 768 (m), 669 (m), 628 (m); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 2.06 (s, 3H, 7-H), 4.87 (s, 1H, OH), 5.15 [d, 2H, 2(6)-H, $J_{H,H}$ = 6.0 Hz], 5.46 [d, 2H, 3(5)-H, $J_{H,H}$ = 6.0 Hz] ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ 19.8 (C-7), 80.4 [C-2(6)] 96.0 [C-3(5)], 101.7 (C-4), 137.5 (C-1), 233.9 (CO) ppm; MS (70 eV) *m/z* (%) 244 (35) [M$^+$], 188 (13) [M$^+$ - 2CO], 160 (65) [M$^+$ - 3CO], 107 (70) [M$^+$ - Cr (CO)$_3$], 90 (9), 77 (23), 69 (8), 52 (100) [Cr]; HRMS ($C_{10}H_8$ CrO_4) found. 243.9826, calcd. 243.9828.

Tricarbonyl(2-trimethylsilylphenol)chromium(0) (4)

GP1, 2.53 g (15.2 mmol) of 2-trimethylsilylphenol,[5] 3.68 g (16.7 mmol) of hexacarbonylchromium, 30 h; 2.21 g (7.3 mmol, 48%) of **4** was obtained as yellow solid, m. p. 41°C (dec.). IR (ATR) ν/cm^{-1} = 3513 (w), 2959 (w), 1943 (s, CO), 1876 (s, CO), 1822 (s, CO), 1523 (w), 1512 (w), 1465 (m), 1373 (m), 1280 (m), 1257 (m), 1246 (w), 1177 (w), 1154 (m), 1108 (w), 1068 (m), 1022 (w), 949 (w), 871 (s), 845 (m), 820 (w), 763 (w), 756 (w), 691 (w), 668 (m), 631 (s); ^{1}H-NMR (400.1 MHz, acetone-*d*$_6$) δ 0.35 (s, 9H, 7-H), 4.99 (m, ^3J = 5.5 Hz, ^5J = 0.6 Hz, 1H, 3-H), 5.29 (dd, *J* = 0.6, 6.2 Hz, 1H, 4-H), 5.77 [dd, *J* = 1.4, 4.8 Hz, 1H, 5-H], 5.91 (m, ^3J = 5.5 Hz, ^4J = 1.5 Hz, 1H, 3-H) ppm; ^{13}C-NMR (100.6 MHz, acetone-*d*$_6$, DEPT) δ 0.11 (C-7), 80.9 (C-6), 86.9 (C-4), 88.8 (+, C-2), 99.6 (C-5), 104.1 (C-3), 148.2 (+, C-1), 236.2 (+, CO) ppm; MS (70 eV) *m/z* (%) 302 (43) [M$^+$], 246 (21) [M$^+$ – 2CO], 218 (95) [M$^+$ - 3CO], 202 (28) [M$^+$ - 3CO - CH$_3$], 187 (100) [M$^+$ - 3CO - 2CH$_3$], 166 (26) [M$^+$ - Cr (CO)$_3$], 151 (92) [M$^+$ - Cr (CO)$_3$ - 3CH$_3$], 133 (45), 123 (51) [M$^+$ - Cr (CO)$_3$ – Si(CH$_3$)$_3$], 91 (46), 75 (28), 65 (12), 52 (82); HRMS ($C_{12}H_{14}CrO_4Si$) found. 302.0067 calcd. 302.0066.

(2-Allyl-4-methoxyphenol)tricarbonylchromium(0) (5)

GP1, 0.82 g (5.0 mmol) of 2-allyl-4-methoxyphenol, 1.21 g (5.5 mmol) of hexacarbonyl chromium in 40 mL of dibutyl ether and 4 mL of THF, 48 h. 1.32 g (4.4 mmol, 88%) of **5** was obtained as a yellow oil. IR (ATR) ν/cm^{-1} 3450 (br), 3087 (w), 2978 (w), 1939 (s, CO), 1828 (s, CO), 1640 (w), 1560 (w), 1540 (w), 1488 (w), 1462 (m), 1408 (m), 1396 (w), 1322 (w), 1272 (m), 1241 (m), 1195 (m), 1142 (m), 1099 (m), 1052 (w), 1021 (w), 993 (m), 955 (w), 923 (m), 853 (w), 794 (m), 751 (w), 671 (s), 651 (w), 629 (s); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 3.21 (m, 2H, 7-H), 3.86 (s, 3H, 10-H), 4.97 (d, 1H, $J_{H,H}$ = 6.5 Hz, 6-H), 5.12 (d, 1H, $J_{H,H}$ = 1.5 Hz, 9-H), 5.16-5.19 (m, 1H, 5-H), 5.26 (d, 1H, $J_{H,H}$ = 1.5 Hz, 9-H), 5.32 (s, 1H, OH), 5.47 (d, 1H, $J_{H,H}$ = 6.5 Hz, 3-H), 5.81-5.91 (m, 1H, 8-H) ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ 38.5 (C-7), 57.4 (C-10), 78.8 (C-3), 81.1 (C-6), 88.5 (C-5), 104.4 (C-4), 118.6 (C-9), 129.7 (C-1), 129.3 (C-2), 135.1 (C-8), 234.1 (CO) ppm; MS (70 eV) *m/z* (%) 300 (59) [M^+], 244 (22) [M^+ - 2CO], 216 (94) [M^+ - 3CO], 164 (100) [M^+ - Cr $(CO)_3$], 149 (72) [M^+ - $Cr(CO)_3$ - CH_3], 137 (78), 121 (54), 103 (67), 91 (62), 77 (74), 65 (43); HRMS ($C_{13}H_{12}CrO_5$) found. 300.0090, calcd. 300.0090.

Tricarbonyl(5-methyl-2-isopropylphenol)chromium(0) (6)

GP1, 1.50 g (10.0 mmol) 5-methyl-2-isopropylphenol, 2.42 g (11.0 mmol) hexacarbonyl-chromium in 40 mL of dibutyl ether and 4 mL of THF, 2 d. 2.32 g (8.1 mmol, 81 %) of **6** were obtained as a yellow oil. IR (ATR) ν/cm^{-1} 3498 (br), 2970 (w), 1937 (s, CO), 1861 (s, CO), 1821 (s, CO), 1550 (w), 1528 (w), 1489 (w), 1449 (w), 1397 (m), 1378 (m), 1351 (w), 1283 (m), 1222 (w), 1181 (w), 1158 (m), 1112 (w), 1084 (w), 949 (w), 883 (w), 842 (w), 743 (w), 709 (w), 672 (m), 631 (s); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 1.21 (d, 3H, *J* = 6.4 Hz, 8-H or 9-H), 1.29 (d, 3H, *J* = 6.4 Hz, 8-H or 9-H), 2.21 (s, 3H, 10-H), 2.98 (m, 1H, 7-H), 4.57 (s, 1H, 6-H), 4.73 (d, 1H, $J_{H,H}$ = 6.2 Hz, 4-H), 4.94 (s, 1H, OH), 5.58 (d, 1H, $J_{H,H}$ = 6.2 Hz, 3-H) ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ 20.3 (C-10), 21.6 (C-8 or C-9), 24.1 (C-9 or C-8), 26.7 (C-7), 80.8 (C-6), 86.3 (C-4), 93.5 (C-3), 104.7 (C-5), 110.0 (C-2), 137.9 (C-1), 234.2 (CO) ppm; MS (70 eV) *m/z* (%) 286 (43) [M^+], 230 (25) [M^+ - 2CO], 202 (85) [M^+ - 3CO], 150 (75) [M^+ - Cr $(CO)_3$], 135 (100) [M^+ - $Cr(CO)_3$ -CH_3], 115 (50), 107 (33), 201 (96), 91 (60), 77 (35), 65 (21); HRMS ($C_{13}H_{14}O_4Cr$) calcd. 286.0297, found. 286.0296.

Tricarbonyl(2-methyl-5-isopropylphenol)chromium(0) (7)

GP1, 1.50 g (10.0 mmol) of 2-methyl-5-isopropylphenol reacted with 2.42 g (11.0 mmol) hexacarbonylchromium in 40 mL of dibutyl ether and 4 mL of THF, 2 d. 2.12 g (7.4 mmol, 74 %) of **7** was obtained as a yellow oil. IR (ATR) ν/cm^{-1} 3486 (br), 2965 (w), 1945 (s, CO), 1853 (s, CO), 1693 (w), 1536 (w), 1461 (w), 1449 (w), 1402 (w), 1381 (w), 1366 (w), 1282 (w), 1260 (w), 1167 (w), 1095 (w), 996 (w), 934 (w), 850 (w), 816 (w), 753 (w), 669 (m), 630 (m); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 1.21, 1.24 [t, 6H, *J* = 6.4 Hz, 9(10)-H], 2.17 (s, 3H, 7-H), 2.63 (m, 1H, 8-H), 4.85 (d, 1H, *J* = 6.4 Hz, 3-H), 5.15 (s, 1H, 6-H), 5.55 (d, 1H, *J* = 6.4 Hz, 4-H), 6.26 (s, 1H, OH) ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ 15.3 (C-7), 22.8 (C-9 or C-10), 23.1 (C-10 or C-9), 32.3 (C-8), 80.1 (C-6), 85.3 (C-4), 94.6 (C-2), 97.5 (C-3), 121.2 (C-5), 138.5 (C-1), 235.0 (CO) ppm; MS (70 eV) *m/z* (%) 286 (43) [M$^+$], 230 (25) [M$^+$ - 2CO], 202 (85) [M$^+$ - 3CO], 150 (75) [M$^+$ - Cr $(CO)_3$], 135 (100) [M$^+$ - $Cr(CO)_3$ - CH_3], 115 (50), 107 (33), 201 (96), 91 (60), 77 (35), 65 (21); HRMS ($C_{13}H_{14}O_4Cr$) calcd. 286.0297, found. 286.0296.

Tricarbonyl(2-fluorophenol)chromium(0) (8)

GP1, 0.74 g (6.6 mmol) of 2-fluorophenol reacted with 1.60 g (7.3 mmol) of hexacarbonylchromium in 40 mL of dibutyl ether and 4 mL of THF, 40 h. 1.28 g (5.2 mmol, 78 %) of **8** was obtained as yellow oil. IR (ATR) ν/cm^{-1} 3091 (w), 2978 (w), 1956 (s, CO), 1848 (s, CO), 1706 (w), 1616 (w), 1531 (w), 1502 (w), 1474 (m), 1428 (w), 1391 (w), 1247 (m), 1169 (w), 1077 (w), 1043 (w), 881 (w), 858 (w), 818 (w), 754 (m), 730 (w), 661 (s), 622 (s). -^{1}H NMR (400.1 MHz, acetone-d_6) δ 5.23 (m, 1H, 6-H), 5.48 (m, 1H, 3-H), 5.66 (m, 1H, 4-H), 6.12 (m, 1H, 5-H), 9.71 (br, 1H, OH) ppm;^{13}C NMR (100.6 MHz, acetone-d_6) δ 83.7 (C-6), 86.5 (C-3), 87.3 (C-4), 93.9 (C-5), 132.6 (C-1), 135.8 (d, C-2, $^1J_{C\text{-}F}$ = 258.6 Hz), 235.0

(C-7) ppm; MS (70 eV) *m/z* (%) 248 (30) [M$^+$], 220 (6) [M$^+$ - CO], 192 (7) [M$^+$ - 2CO], 164 (36) [M$^+$ - 3CO], 112 (100) [M$^+$ - Cr(CO)$_3$], 92 (32), 83 (16), 71 (13), 64 (57), 52 (95) [^{52}Cr]; HRMS ($C_9H_5CrFO_4$) calcd. 247.9577, found. 247.9576.

Tricarbonyl(1,4-dihydroxybenzene)chromium (24)[6]

GP1, 1.40 g (12.7 mmol) of 1,4-dihydroxybenzene, 3.07 g (14.0 mmol) hexacarbonylchromium in 40 mL of dibutyl ether and 4 mL of THF, 60 h. 2.44 g (9.9 mmol, 78 %) of **24** was obtained as a yellow solid, m. p. 35 °C (dec.).

IR (ATR) ν/cm^{-1} 3143 (br), 1953 (s, CO), 1855 (s, CO), 1653 (w), 1560 (w), 1516 (m), 1516 (m), 1472 (s), 1365 (w), 1246 (m), 1215 (m), 1195 (s), 1097 (w), 1077 (w), 1042 (w), 1011 (w), 877 (w), 833 (s), 760 (s), 675 (s), 631 (s); ^{1}H-NMR (400.1 MHz, CDCl$_3$) δ 5.47 [s, 4H, 2(3,4,5)-H], 8.65 (br, 2H, OH) ppm; ^{13}C-NMR (100.6 MHz, CDCl$_3$) δ 84.0 [C-2(3,5,6)], 136.2 [C-1(4)], 237.1 (CO) ppm; MS (70 eV) *m/z* (%) = 246 (34) [M$^+$], 190 (12) [M$^+$ - 2CO], 162 (51) [M$^+$ - 3CO], 110 (100) [M$^+$ - Cr (CO)$_3$], 94 (14), 81 (74), 63 (28), 52 (83); HRMS ($C_9H_6O_5Cr$) calcd. 245.9620, found. 245.9621.

Tricarbonyl(1,3,5-trihydroxybenzene)chromium (25)

GP1, 2.00 g (15.9 mmol) of 1,3,5-trihydroxybenzene, 3.84 g (17.5 mmol) of hexacarbonylchromium in 60 mL of dibutyl ether and 6 mL of THF, 2 d. 2.79 g (10.6 mmol, 67 %) of **25** was obtained as a yellow solid, m. p. 30°C (dec.).

IR (ATR) ν/cm^{-1} 3092 (br), 2976 (w), 1945 (s, CO), 1850 (s, CO), 1614 (w), 1548 (w), 1477 (w), 1388 (w), 1369 (w), 1265 (w), 1240 (w), 1196 (w), 1154 (m) 1061 (m) 1044 (w), 1019 (w), 990 (m), 916 (w), 880 (w), 838 (m), 719 (m), 681(s), 632 (s); ^{1}H-NMR (400.1 MHz, CDCl$_3$) δ 5.02 [s, 3H, 2(4,6)-H], 9.01 (br, 3H, OH) ppm; ^{13}C-NMR (100.6 MHz, CDCl$_3$) δ 69.1 [C-2(4,6)], 143.5 [C-1(3,5)], 237.7 (CO) ppm; MS (70 eV) *m/z* (%) 262 (41)

[M^+], 234 (12) [M^+ - CO], 206 (15) [M^+ - 2CO], 178 (60) [M^+ - 3CO], 126 (73) [M^+ - Cr $(CO)_3$], 110 (19), 97 (33), 80 (51), 69 (63), 52 (100); HRMS ($C_9H_6O_6Cr$) calcd. 261.9569, found. 261.9570.

General Procedure for the Triflation of Tricarbonyl(phenol)chromium(0) Complexes (GP2)

All operations are carried out under exclusion of air using standard Schlenk technique with argon as the inert gas. To a stirred solution of the phenol tricarbonylchromium complex in anhydrous THF and pyridine (3:1) 1.2 equiv. of trifluoromethanesulfonic anhydride is dropwise added at –78°C. The reaction is allowed to return to 25 °C over 1 h and is then stirred for 24 to 60 h. The color of solution changes from yellow to dark orange. The reaction mixture is quenched with 30 mL of water and extracted with 3 x 30 mL of ethyl acetate. The collected organic layers are washed with water till the aqueous layer remains colourless, dried over anhydrous $MgSO_4$ and filtered through a P4 frit. After solvent removal at reduced pressure, the crude product is purified by flash chromatography at SiO_2, eluting with *tert*-butyl methyl ether/petroleum ether (1:4 to 1:1).

Tricarbonyl(phenyltriflurομethylsulfonate)chromium(0) (9)

GP2, 1.15 g (5.0 mmol) of **1**, 20 mL of THF, 7 mL of pyridine, 1.69 g (6.0 mmol) trifluoromethanesulfonic anhydride, 24 h, flash chromatography with *tert*-butyl methyl ether/petroleum ether (1:3). 1.25 g (3.45 mmol, 69%) of product **9** was obtained as yellow solid, m. p. 72°C

IR (ATR) ν/cm^{-1} 3099 (w), 1971 (s, CO), 1880 (s, CO), 1500 (w), 1430 (s), 1250 (m), 1029 (s), 1129 (s), 992 (w), 891 (w), 863 (m), 814 (m), 741 (m), 683 (w); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 5.03 (t, 1H, *J* = 3.3 Hz, 4-H), 5.46 [d, 4H, *J* = 3.1 Hz, 2(6)-H, 3(5)-H] ppm; ^{13}C-

NMR (100.6 MHz, $CDCl_3$, DEPT) δ 84.3 [–, C-2(6)], 88.4 (–, C-4), 91.3 [C-3(5)], 118.6 (+, q, $^1J_{C-F}$ = 321.0 Hz, C-7), 130.9 (+, C-1), 230.2 (+, CO) ppm. MS (70 eV) m/z (%) 363 (17) [M^+], 306 (11) [M^+ - 2CO], 278 (8) [M^+ -3CO], 226 (16) [M^+ - Cr $(CO)_3$], 209 (10),164 (8),145 (100), 93 (13) [M^+ - $Cr(CO)_3$ – OH - (SO_2F_3)], 77 (17), 69 (24); LC-MS (ESI) $C_{10}H_5O_6F_3SCr$ [–H] calcd. 360.9086, found. 360.9095.

Tricarbonyl(4-methoxyphenyltrifluromethylsulfonate)chromium(0) (10)

GP2, 2.10 g (8.1 mmol) of **2**, 30 mL of THF, 10 mL of pyridine, 2.73 g (9.7 mmol) of trifluoromethanesulfonic anhydride, 20 h. Flash chromatography, eluting with *tert*-butyl methyl ether/petroleum ether (1:2). 2.37 g (6.1 mmol, 75%) of **10** was obtained as a yellow solid, m. p. 44°C. IR (ATR) ν/cm^{-1} 3379 (w), 2951 (w), 1974 (s, CO), 1886 (s, CO), 1531 (w), 1509 (m), 1472 (m), 1429 (s), 1369 (w), 1212 (s), 1134 (s), 1101 (m), 865 (m), 822 (s), 770 (w), 731 (m), 665 (w); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 3.68 (s, 3H, 7-H), 5.10 [d, 2H, *J* = 4.8 Hz, 3(5)-H], 5.72 [d, 2H, *J* = 4.6 Hz, 2(6)-H] ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT) δ 56.2 (–, C-7), 74.8 [–, C-3(5)], 87.4 [–, C-2(6)], 118.5 (+, q, $^1J_{C-F}$ = 321.2 Hz, C-8), 122.3 (+, C-1), 140.7 (+, C-4), 230.2 (+, CO) ppm; MS (70 eV) *m/z* (%) 392 (45) [M^+], 335 (17) [M^+ - 2CO], 307 (36) [M^+ - 3CO], 239 (16) [M^+ - Cr $(CO)_3$ - CH_3], 194 (76),175 (100),124 (32), 95 (13) [M^+ - $Cr(CO)_3$ - OCH_3 - (SO_2F_3)], 81 (15); LC-MS (ESI) $C_{11}H_7O_7F_3SCr$ [–H] calcd. 390.9191, found. 390.9185.

Tricarbonyl(4-methylphenyltrifluromethylsulfonate)chromium(0) (11)

GP2, 1.30 g (5.3 mmol) of **3**, 20 mL of THF, 7 mL of pyridine, 1.80 g (6.4 mmol) of trifluoromethanesulfonic anhydride, 24 h, , flash chromatography eluting with *tert*-butyl methyl ether/petroleum ether (1:1). 1.44 g (3.8 mmol, 72%) of **11** was obtained as a yellow oil. IR (ATR) ν/cm^{-1} 3098 (w), 2917 (w), 1972 (s, CO), 1878 (s, CO), 1524 (w), 1465 (w), 1426 (m), 1386 (s), 1249 (w), 1209 (s), 1132 (s), 1096 (w), 1035 (w), 862 (s), 802 (w), 770 (w), 719 (m), 653(m), 608 (w); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 2.11 (s, 3H, 7-H), 5.27 [s, 2H, 3(5)-H], 5.56 [s, 2H, 2(6)-H] ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$, DEPT) δ 19.5 (–, C-7), 86.0 (–, C-3, C-5), 91.2 [–, C-2(6)], 106.8 (+, C-1), 118.4 (+, q, $^1J_{C\text{-}F}$ = 321.1 Hz, C-8), 128.1 (+, C-4), 230.6 (+, CO) ppm; MS (70 eV) m/z (%) 376 (42) [M$^+$], 320 (16) [M$^+$ - 2CO], 292 (25) [M$^+$ - 3CO], 223 (13) [M$^+$ - Cr $(CO)_3$ - CH_3], 187 (10),178 (70), 159 (100), 107 (7), 91 (11), 77 (29), 69 (10), 52 (85); HRMS ($C_{11}H_6O_6F_3SCr$) calcd. 375.9321, found. 375.9322.

Tricarbonyl(2-trimethylsilylphenyltrifluromethylsulfonate)chromium(0) (12)

1.80 g (6.0 mmol) of **4**, 30 mL of THF, 10 mL of pyridine, 2.02 g (7.2 mmol) of trifluoromethanesulfonic anhydride, 24 h, flash chromatography eluting with *tert*-butyl methyl ether/petroleum ether (1:1). 1.01 g (2.3 mmol, 39%) of **12** was obtained as a yellow oil.

IR (ATR) ν/cm^{-1} 2960 (w), 1975 (s, CO), 1891 (s, CO), 1504 (w), 1421 (m), 1356 (w), 1251 (m), 1211 (s), 1130 (s), 1101 (w), 1061 (m), 880 (s), 839 (s), 814 (m), 744 (m), 695 (w); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 0.43 (s, 9H, 7-H), 4.90 (t, 1H, *J* = 6.0 Hz, 6-H), 5.51 (m, 2H, 4-H, 5-H), 5.64 (t, 1H, *J* = 6.4 Hz, 3-H) ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$, DEPT) δ = –0.66 (–, C-7), 82.6 (–, C-6), 87.4 (–, C-4), 91.0 (+, C-2), 93.8 (–, C-5), 98.2 (–, C-3), 118.3 (+, q, C-7, $^1J_{C\text{-}F}$ = 320.2 Hz), 137.4 (+, C-1), 231.1 (+, CO) ppm; MS (70 eV) *m/z* (%) 434 (49) [M$^+$], 378 (8) [M$^+$ -2CO], 350 (62) [M$^+$ - 3CO], 283 (10) [M$^+$ - Cr $(CO)_3$ - CH_3], 236 (26), 217 (89), 201 (80), 187 (70), 150 (18), 135 (23),126 (35), 96 (26), 73 (25), 52 (100) [^{52}Cr]; LC-MS (ESI) $C_{13}H_{13}O_6F_3SSiCr$ [–H] calcd. 433.9559, found. 433.9561.

(2-Allyl-4-methoxyphenyltrifluromethylsulfonate)tricarbonylchromium(0) (13)

GP2, 1.68 g (5.6 mmol) of **5**, 30 mL of THF, 10 mL of pyridine, 1.89 g (6.7 mmol) of trifluoromethanesulfonic anhydride, 30 h, flash chromatography, eluting with *tert*-butyl methyl ether/petroleum ether (1:1). 2.13 g (4.9 mmol, 88%) of **13** was obtained as a yellow oil. IR (ATR) ν/cm^{-1} 2962 (w), 1969 (s, CO), 1882 (s, CO), 1641 (w), 1606 (w), 1532 (w), 1504 (w), 1466 (m), 1259 (s), 1209 (m), 1172 (m), 1134 (m) 1096 (s), 1018 (s), 927 (w), 857 (m), 796 (s), 735 (w), 663 (w), 616 (w); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 3.07 (m, 2H, 7-H), 3.87 (s, 3H, 10-H), 4.75 (d, 1H, *J* = 6.4 Hz, 6-H), 5.05 (s, 1H, 3-H), 5.19-5.26 (m, 2H, 9-H), 5.77 (d, 1H, *J* = 6.5 Hz, 5-H), 5.86-5.95 (m, 1H, 8-H) ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$, DEPT, HMQC) δ = 38.5 (+, C-7), 56.7 (–, C-10), 74.1 (–, C-3), 82.7 (–, C-6), 88.5 (–, C-5), 110.3 (+, C-4), 116.8 (+, C-1), 119.4 (+, C-9), 133.7 (–, C-8), 136.7 (+, C-2), 115.2 (+, q, C-11, $^1J_{C\text{-}F}$ = 320.7 Hz), 230.5 (+, CO) ppm; MS (70 eV) *m/z* (%) = 432 (47) [M^+], 376 (10) [M^+ - 2CO], 348 (40) [M^+ - 3CO], 296 (67) [M^+ - Cr $(CO)_3$], 234 (95), 219 (73), 200 (84), 173 (36), 163 (100), 135 (41), 103 (76), 91 (78), 77 (65), 69 (79); HRMS ($C_{14}H_{11}O_7F_3SCr$) calcd. 431.9583, found 431.9581.

Tricarbonyl(5-methyl-2-isopropylphenyltrifluromethylsulfonate)chromium(0) (14)

1.00 g (3.5 mmol) of **6**, 20 mL of THF, 7 mL of pyridine, 1.18 g (4.2 mmol) of trifluoromethanesulfonic anhydride, 30 h, flash chromatography, eluting with *tert*-butyl methyl ether/petroleum ether (1:2). 1.08 g (2.6 mmol, 74%) of **14** was obtained as a yellow oil.

IR (ATR) ν/cm^{-1} 2978 (w), 1974 (s, CO), 1879 (s, CO), 1432 (m), 1366 (w), 1218 (s), 1132 (m), 1069 (w), 953 (w), 843 (w), 818 (m), 730 (w), 666 (m), 618 (w); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 1.27 (d, 3H, $J_{H,H}$ = 6.8 Hz, 8-H or 9-H), 1.33 (d, 3H, $J_{H,H}$ = 6.8, Hz, 8-H or 9-H), 2.27 (s, 3H, 10-H), 2.96 (m, 1H, 7-H), 4.86 (d,1H, $J_{H,H}$ = 6.2 Hz, 4-H), 5.30 (s, 1H, 6-H), 5.51 (d, 1H, $J_{H,H}$ = 6.3 Hz, 3-H) ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$, DEPT, HMQC) δ 20.2

(–, C-10), 23.1 (–, C-8 or C-9), 24.7 (–, C-8 or C-9), 26.7 (–, C-7), 84.0 (–, C-6), 88.8 (–, C-4), 90.6 (–, C-3), 108.0 (+, C-5), 109.3 (+, C-2),119.8 (+, q, $^1J_{C\text{-}F}$ = 320.3 Hz, C-11), 131.8 (+, C-1), 231.5 (+, CO) ppm; MS (70 eV) *m/z* (%) 418 (18) [M^+], 362 (11) [M^+ - 2CO], 334 (41) [M^+ - 3CO], 282 (10) [M^+ - Cr (CO)$_3$], 267 (18) [M^+ - Cr(CO)$_3$ -CH$_3$], 250 (12), 220 (88), 201 (96), 185 (100), 159 (22), 105 (36), 91 (32) [M^+- Cr(CO)$_3$- OH-(SO$_2$F$_3$)], 77(17), 69 (24); HRMS ($C_{14}H_{13}O_6F_3SCr$) calcd.417.9790, found. 417.9787.

Tricarbonyl(2-methyl-5-isopropylphenyltrifluromethylsulfonate)chromium(0) (15)

GP2, 1.20 g (4.2 mmol) of **7**, 30 mL of THF, 10 mL of pyridine, 1.42 g (5.0 mmol) of trifluoromethanesulfonic anhydride, 30 h. Flash chromatography eluting with *tert*-butyl methyl ether/petroleum ether (1:2). 0.84 g (2.0 mmol, 48%) of **15** was obtained as a yellow oil. IR (ATR) ν/cm^{-1} 2962 (w), 1970 (s, CO), 1885 (s, CO), 1623 (w), 1501 (w), 1464 (w), 1423 (m), 1249 (w), 1214 (s), 1135 (s), 1061 (m), 1036 (w), 997 (w), 929 (m), 878 (m), 812 (s), 768 (w), 738 (w), 709 (w), 683 (w), 655 (m), 605 (w); ^{1}H-NMR (400.1 MHz, CDCl$_3$) δ 1.28 (d, 3H, $J_{H,H}$ = 7.0 Hz, 9-H or 10-H), 1.29 (d, 3H, $J_{H,H}$ = 7.0 Hz, 9-H or 10-H), 2.33 (s, 3H, 7-H), 2.71 (m, 1H, 8-H), 5.11 (d, 1H, 4-H, $J_{H,H}$ = 6.1 Hz), 5.35 (d, 1H, $J_{H,H}$ = 6.2 Hz, 3-H), 5.56 (s, 1H, H-6) ppm; ^{13}C-NMR (100.6 MHz, CDCl$_3$, DEPT, HMQC) δ 15.9 (–, C-7), 23.0 (–, C-9 or C-10), 23.9 (–, C-9 or C-10), 32.2 (–, C-8), 85.1 (–, C-6), 90.0 (–, C-4), 92.1 (–, C-3), 100.2 (+, C-5), 118.6 (+, q C-11, $^1J_{C\text{-}F}$ = 320.0 Hz), 129.2 (+, C-2), 148.4 (+, C-1), 231.5 (+, CO) ppm; MS (70 eV) *m/z* (%) 418 (24) [M^+], 362 (6) [M^+ - 2CO], 334 (15) [M^+ -3CO], 265 (9) [M^+ - Cr(CO)$_3$ - CH$_3$], 220 (68), 201 (100), 185 (15), 135 (21), 91 (12) [M^+ - Cr(CO)$_3$ - OH - (SO$_2$F$_3$)], 77 (7), 69 (6), 52 (49) [Cr]; HRMS ($C_{14}H_{13}O_6F_3SCr$) calcd. 417.9790, found. 417.9791.

Tricarbonyl(2-fluorophenyltrifluoromethanesulfonate)chromium(0) (16)

GP2, 0.50 g (2.0 mmol) of tricarbonyl(2-fluorophenol)chromium(0) (**8**), 20 mL of THF, 7 mL of pyridine, 0.62 g (2.2 mmol) of trifluoromethanesulfonic anhydride, 30 h, flash chromatography eluting with *tert*-butyl methyl ether/petroleum ether (1:1). 0.40 g (1.1 mmol, 53%) of **16** was obtained as a yellow oil. IR (ATR) ν/cm^{-1} 3101 (w) cm^{-1}, 2363 (w), 1984 (s, CO), 1891 (s, CO), 1610 (w), 1517 (w), 1460 (m), 1429 (m), 1212 (s), 1129 (s), 1084 (w), 1005 (w), 877 (s), 800 (s), 770 (m), 724 (m), 650 (m), 613 (w); ^{1}H NMR (400.1 MHz, acetone-d_6) δ 5.43 (s, 1H, 3-H), 5.82 (s, 1H, 5-H), 6.08 (s, 1H, 6-H), 6.42 (s, 1H, 4-H) ppm; ^{13}C NMR (100.6 MHz, acetone-d_6, DEPT) δ = 80.9 (–, C-3), 88.1 (–, C-6), 90.0 (–, C-4), 94.4 (–, C-5), 119.3 (+, C-1), 141.2 (+, d, C-2, $^1J_{C\text{-}F}$ = 269.0 Hz), 120.1 (+, q, C-7, $^1J_{C\text{-}F}$ = 320.3 Hz), 231.2 (+, C-8) ppm; MS (70 eV) *m/z* (%) 380 (18) [M$^+$], 324 (8) [M$^+$ -2CO], 296 (62) [M$^+$ - 3CO], 227 (6) [M$^+$ - Cr(CO)$_3$ - F], 182 (36), 163 (100), 135 (73), 92 (47), 80 (12), 71 (34), 52 (75) [^{52}Cr]; HRMS $C_{10}H_4CrF_4O_6S$ calcd. 379.9070, found. 379.9069.

Tricarbonyl[phenyl-1,4-bis(trifluoromethylsulfonate)]chromium (0) (26)

GP2, 1.40 g (5.7 mmol) of **24**, 40 mL of THF, 13 mL of pyridine, 3.85 g (13.6 mmol) of trifluoromethanesulfonic anhydride, 48 h. Flash chromatography eluting with *tert*-butyl methyl ether/petroleum ether (1:2). 1.68 g (3.3 mmol, 58%) of **26** was obtained as yellow solid, m. p. 69°C.

IR (ATR) ν/cm^{-1} 3085 (w), 2963 (w), 1975 (s, CO), 1871 (s, CO), 1715 (w), 1623 (m), 1540 (m), 1489 (m), 1428 (m), 1250 (m), 1194 (s), 1159 (m), 1118 (s), 1098 (m), 903 (s), 850 (s), 799 (m), 766 (w), 744 (w), 692 (w), 666 (w); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 5.58 [s, 2(3,5,6)-H] ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$, DEPT) δ 82.7 [C-2(3,5,6)], 118.4 [+, q, $^1J_{C\text{-}F}$ = 321.1 Hz, C-7(8)], 125.5 [+, C-1(4)], 227.1 (+, CO) ppm; MS (70 eV) *m/z* (%) 510 (30) [M$^+$], 426 (48) [M$^+$ - 3CO], 374 (16) [M$^+$ - Cr (CO)$_3$], 357 (48), 312 (38), 293 (88), 229 (10), 179 (100), 160 (58),135 (19), 116 (12), 80 (33), 69 (52), 52 (89); HRMS $C_{11}H_4CrO_9F_6S_2$ calcd. 509.8606, found. 509.8606.

Tricarbonyl[phenyl-1,3,5-tris(trifluoromethylsulfonate)]chromium (0) (27)

GP2, 1.32 g (5.0 mmol) of **25**, 40 mL of THF, 13 mL of pyridine, 4.69 g (16.6 mmol) of trifluoromethanesulfonic anhydride, 60 h. Flash chromatography eluting with *tert*-butyl methyl ether/petroleum ether (1:3). 1.16 g (1.8 mmol, 35%) of **27** was obtained as a yellow solid, m. p. 67°C

IR (ATR) ν/cm^{-1} 3103 (w), 2962 (w), 2019 (s, CO), 1947 (s, CO), 1496 (w), 1438 (s), 1400 (m), 1207 (s), 1128 (s), 1091 (s), 949 (m), 850 (m), 792 (m), 752 (m), 703 (m), 668 (w); ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ 5.59 [s, 2(4,6)-H] ppm; ^{13}C-NMR (100.6 MHz, $CDCl_3$, DEPT) δ 75.2 [C-2(4,6)], 118.5 [+, q, $^1J_{C\text{-}F}$ = 321.5 Hz, C-7(8,9)], 126.8 [+, C-1(3,5)], 225.6 (+, CO) ppm; MS (70 eV) *m/z* (%) 602 (20) [M - 2CO], 574 (53) [M - 3CO], 522 (48) [M - $Cr(CO)_3$], 460 (33), 441 (68), 373 (33), 330 (49), 308 (46), 240 (43), 195 (22), 178 (52), 164 (37), 147 (43), 123 (52), 107 (29), 91 (57), 69 (100), 52 (50); HRMS $C_9H_3F_9O_9S_3$ calcd. 521.8796, found. 521.8796.

General Procedure for the Anionic Thia-Fries Rearrangement of Arylriflate Tricarbonylchromium Complexes (GP3)

All operations are carried out under exclusion of air using standard Schlenk technique with argon as the inert gas. At –78 ˚C 1.5 equiv. of butyllithium in hexane or lithium diisopropylamide (LDA) is added dropwise to the solution of the aryltriflate tricarbonylchromium complex in THF. The mixture is stirred for 2 h at –78 °C, the color changing from yellow to orange. The reaction is quenched by addition of 10 mL of saturated aqueous ammonium chloride and then extracted three times with the same volume of with ethyl acetate. The collected organic layers are washed three times with 30 mL of water, filtered through a P4 frit covered with a 2 cm thick layer of silica gel, and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product is purified by column chromatography at SiO_2 eluting with ethyl acetate, and recrystallized from hexane/THF.

Tricarbonyl(2-trifluoromethylsulfonylphenol)chromium (0) (17)

a) GP3, 500 mg (1.38 mmol) of **9**, 1.04 mL (2.1 mmol) of LDA (2M solution in THF/heptane/ethylbenzene). 450 mg (1.2 mmol, 90%) of **17** was obtained as an orange-red oil. Orange-red crystals were obtained by recrystallization from hexane/THF (3:1), m. p. 160°C (dec.).

b) At 25 °C 0.35 g (0.8 mmol) of tricarbonyl(2-trimethylsilylphenyltriflate)chromium(0) (**12**) in 10 mL of acetonitrile was added dropwise to a suspension of 5.33 g (0.8 mmol) of tetrabutylammonium fluoride on silica gel (1.5 mmol F^{-}/g) in 10 mL of acetonitrile. After stirring the mixture at 25 °C for 2 h the reaction was quenched by addition of 15 mL of water. The mixture was extracted three times with 15 mL of ethyl acetate each. The collected organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed at reduced pressure. The crude product was purified by column chromatography at SiO_2 eluting with ethyl acetate. The product was recrystallized from hexane/THF (3:1) to yield 0.249 g (0.7 mmol, 86 %) of **17** (m. p. 158°C, dec.).

IR (ATR) ν/cm^{-1} 2984 (w), 1955 (s, CO), 1856 (s, CO), 1703 (w), 1524 (s), 1469 (s), 1398 (w), 1352 (w), 1261 (w), 1193 (s), 1132 (m), 1097 (m), 1046 (m), 852 (w), 818 (w), 764 (w), 709 (m), 681 (w), 666 (w); ^{1}H-NMR (400.1 MHz, acetone-*d*$_6$) δ 4.70 (d, 1H, $J_{H, H}$ = 7.3 Hz, 6-H,), 4.93 (t, 1H, $J_{H, H}$ = 6.4 Hz, 4-H,), 5.90-5.97 (m, 2H, 3-H, 5-H), 7.34 (br, 1H, OH) ppm; ^{13}C-NMR (100.6 MHz, acetone-*d*$_6$, DEPT, HMQC) δ 80.4 (–, C-6), 83.8 (–, C-4), 85.1 (+, C-2), 99.6 (–, C-5), 103.2 (–, C-3), 122.2 (+,$^{1}J_{C\text{-}F}$ = 325.3 Hz, C-7), 161.7 (+, C-1), 235.4 (+, CO) ppm; MS (70 eV) *m/z* (%) = 363 (57) [M$^+$], 306 (36) [M$^+$ - 2CO], 278 (100) [M$^+$ - 3CO], 226 (8) [M$^+$ - Cr(CO)$_3$], 209 (98) [M$^+$ - Cr(CO)$_3$ - OH], 191 (14), 163 (16), 145 (59), 116 (11), 91 (21) [M$^+$ - Cr(CO)$_3$ - OH-(SO$_2$F$_3$)], 69 (11); HRMS ($C_{10}H_5O_6F_3SCr$) calcd. 361.9164, found. 361.9166.

Tricarbonyl(4-methoxy-2-trifluoromethylsulfonylphenol)chromium(0) (18)

GP3, 150 mg (0.4 mmol) of **10** 0.29 mL (0.57 mmol) of LDA (2M solution in THF/heptane/ethylbenzene), 123 mg (0.3 mmol, 82%) of **18** was obtained as an orange-red oil. Orange-red crystals were obtained by recrystallization in the solution of hexane/THF (3:1), m. p. 173°C (dec.).

IR (ATR) ν/cm^{-1} 2189 (w), 1976 (w, CO), 1957 (m, CO), 1854 (s, CO), 1547 (w), 1509 (m), 1439 (w), 1323 (w), 1255 (w), 1194 (m), 1041 (m), 1025 (w), 895 (w), 799 (w), 705 (m), 673 (s); ^{1}H-NMR (400.1 MHz, acetone-*d*$_6$) δ 3.60 (s, 3H, 7-H), 4.54 (d, 1H, *J* = 7.8 Hz, 6-H), 5.68 (d, 1H, *J* = 2.8 Hz, H-3), 5.99 (dd, 1H, *J* = 2.8, 5.0 Hz, H-5) ppm; ^{13}C-NMR (100.6 MHz, acetone-*d*$_6$) δ 58.3 (C-7), 80.7 (C-6), 80.0 (C-2), 83.6 (C-3), 94.0 (C-5), 122.3 (q, $^1J_{C-F}$ = 325.9 Hz, C-8), 129.1 (C-4), 160.2 (C-1), 235.9 (CO) ppm; MS (70 eV) *m/z* (%) 392 (23) [M$^+$], 336 (15) [M$^+$ - 2CO], 308 (19) [M$^+$ - 3CO], 256 (91) [M$^+$ - Cr (CO)$_3$], 240 (13) [M$^+$ - Cr(CO)$_3$ - OH], 220 (58), 185 (88), 139 (91), 108 (66), 91 (100), 80 (66), 69 (69), 52 (63); HRMS ($C_{11}H_7O_7F_3SCr$) calcd. 391.9270, found. 391.9276.

Tricarbonyl(4-methyl-2-trifluoromethylsulfonylphenol)chromium(0) (19)

GP3, 200 mg (0.5 mmol) of **11**, 0.50 mL (0.80 mmol) of BuLi (1.6 M solution in hexane). 188 mg (0.5 mmol, 94%) of **19** was obtained as a orange-red solid, m. p. 120°C (dec.). IR (ATR) ν/cm^{-1} 2988 (w), 1957 (s, CO), 1856 (s, CO), 1538 (w), 1493 (m), 1378 (w), 1349 (w), 1195 (s), 1125 (m), 1097 (m), 1050 (w), 891 (w), 841 (w), 791 (w), 708 (m), 666 (w);

^{1}H-NMR (400.1 MHz, acetone-d_6) δ 2.08 (s, 3H, 7-H), 4.73 (d, 1H, $J_{H, H}$ = 6.9 Hz, 6-H), 5.92-5.94 (m, 2H, 3-H, 5-H), 8.34 (br.,1H, OH) ppm; ^{13}C-NMR (100.6 MHz, acetone-d_6) δ 49.1 (C-7), 82.6 (C-6), 84.3 (C-2), 99.5 (C-3), 104.6 (C-5), 122.5 (q, $^1J_{C-F}$ = 327.1 Hz, C-8), 159.8 (C-1), 171.6 (C-4), 235.3 (CO) ppm; MS (70 eV) *m/z* (%) 376 (39) [M$^+$], 320 (15) [M$^+$ - 2CO], 292 (94) [M$^+$ - 3CO], 240 (28) [M$^+$ - Cr(CO)$_3$], 223 (55) [M$^+$ - Cr(CO)$_3$ - OH], 190 (17), 159 (55), 123 (40), 107 (35), 86 (100) [M$^+$ - Cr(CO)$_3$ – OH - (SO$_2$F$_3$)], 77 (41), 69 (32); HRMS ($C_{11}H_7O_6F_3SCr$) calcd.375.9321, found. 375.9321.

(2-Allyl-4-methoxy-6-trifluoromethylsulfonylphenol)tricarbonylchromium(0) (20)

GP3, 244 mg (0.6 mmol) of **13**, 0.39 mL (0.6 mmol) of BuLi (1.6 M solution in hexane). 215 mg (0.5 mmol, 88%) of **20** was obtained as a orange-yellow solid, m. p. 130°C (dec.). IR (ATR) ν/cm^{-1} 2359 (w), 2221 (w), 2055(w), 1948 (s, CO), 1836 (s, CO), 1735 (w), 1517 (m), 1437 (w), 1338 (m), 1257 (m), 1196 (m), 1138 (m), 1106 (m), 1039 (m), 797 (w), 709 (m), 683 (w), 670 (w); ^{1}H-NMR (400.1 MHz, acetone-d_6) δ 3.10 (m, 2H, 7-H), 3.82 (s, 3H, 10-H), 4.75 (d, 1H, $J_{H, H}$ = 6.4 Hz, 6-H), 5.09-5.20 (m, 2H, 9-H), 5.55 (s, 1H, 3-H), 5.85-5.91 (m, 1H, 8-H), 6.01 (s, 1H, 5-H) ppm; ^{13}C-NMR (100.6 MHz, acetone-d_6) δ 68.7 (C-7), 58.3 (C-10), 83.1 (C-2), 89.4 (C-3), 94.1 (C-5), 112.6 (C-4), 118.2 (C-9), 122.1 (q, $^1J_{C-F}$ = 327.5 Hz, C-11), 137.6 (C-8), 148.8 (C-6), 155.9 (C-1), 235.3 (CO) ppm; MS (70 eV) *m/z* (%) 432 (8) [M$^+$], 348 (34) [M$^+$ - 3CO], 296 (89) [M$^+$ - Cr(CO)$_3$], 277 (62), 220 (24), 210 (49), 171 (42), 163 (59), 148 (25), 131 (26), 12 0 (31), 105 (100), 91 (52), 77 (57); 69 (32); HRMS ($C_{14}H_{11}O_7F_3SCr$) calcd. 431.9582, found. 431.9590.

Tricarbonyl(5-methyl-2-isopropyl-6-trifluoromethylsulfonylphenol)chromium(0) (21)

GP3, 230 mg (0.6 mmol) of **14**, 0.52 mL (0.82 mmol) of BuLi (1.6 M solution in hexane). 184 mg (0.4 mmol, 80%) of **21** was obtained as an orange-yellow oil. IR (ATR) ν/cm^{-1}

2971 (w), 1948 (s, CO), 1830 (s, CO), 1748 (w), 1480 (m), 1343 (w), 1206 (m), 1131 (w), 1086 (w), 1049 (w), 895 (w), 805 (w), 734(w), 676(w); ^{1}H-NMR (400.1 MHz, acetone-d_6) δ 1.08 (3H, $J_{H,H}$ = 6.1 Hz, 8-H or 9-H), 1.10 (d, 3H, $J_{H,H}$ = 6.5 Hz, 8-H or 9-H), 2.39 (s, 3H, 10-H), 3.02 (m, 1H, 7-H), 4.80 (d, 1H, $J_{H,H}$ = 6.3 Hz, 3-H), 5.94 (d, 1H, $J_{H,H}$ = 6.2 Hz, 4-H) ppm; ^{13}C-NMR (100.6 MHz, acetone-d_6, DEPT) δ 21.6 (–, C-10), 22.7 (–, C-8 or C-9), 24.9 (–, C-8 or C-9), 27.4 (–, C-7), 83.9 (–, C-4), 85.1 (+, C-6); 98.8 (–, C-3), 106.9 (+, C-2); 112.5 (+, C-5), 122.4 (+, q, $^1J_{C-F}$ = 327.5 Hz, C-11), 161.2 (+, C-1), 235.6 (+, CO); MS (70 eV) *m/z* (%) 418 (42) [M$^+$], 362 (19) [M$^+$ - 2CO], 334 (100) [M$^+$ - 3CO], 282 (32) [M$^+$ - Cr (CO)$_3$], 267 (88) [M$^+$ - Cr(CO)$_3$ - CH$_3$], 250 (32), 201 (45), 150 (25), 135 (78), 105 (26), 91 (50) [M$^+$ - Cr(CO)$_3$ - OH - (SO$_2$F$_3$)], 73 (71), 61 (78); HRMS ($C_{14}H_{13}O_6F_3SCr$) calcd. 417.9790, found. 417.9792.

Tricarbonyl(2-methyl-5-isopropyl-6-trifluoromethylsulfonylphenol)chromium(0) (22)

GP3, 260 mg (0.6 mmol) of **15**, 0.58 mL (0.9 mmol) of BuLi (1.6 M solution in hexane). Differing from GP3 the mixture is stirred for 30 min at –78 °C, then warmed to 0 °C, and stirred at this temperature for 2 h. 122 mg (0.3 mmol, 47%) of **22** was obtained as a orange-yellow solid, m. p. 227°C (dec.). IR (ATR) ν/cm^{-1} 2961 (w), 1950 (s, CO), 1847 (s, CO), 1527 (w), 1506 (w), 1481 (m), 1389 (w), 1378 (w), 1330 (w), 1205 (m), 1138 (w), 1106 (m), 1007 (w), 957 (w), 841 (w), 763 (w), 719 (m), 675 (m), 631 (m), 610 (m); ^{1}H-NMR (400.1 MHz, acetone-d_6) δ 1.18 (d, 3H, $J_{H,H}$ = 7.3 Hz, 9-H or 10-H), 1.20 (d, 3H, $J_{H,H}$ = 6.9 Hz 9-H or 10-H), 1.88 (s, 3H, 7-H), 3.62 (m, 1H, 8-H), 4.84 (d, 1H, $J_{H,H}$ = 6.4 Hz, 5-H), 5.96 (d, 1H, $J_{H,H}$ = 6.4 Hz, 4-H) ppm; ^{13}C-NMR (100.6 MHz, acetone-d_6, DEPT) δ 17.4 (–, C-7), 22.6 (–, C-9 or C-10), 25.0 (–, C-9 or C-10), 28.8 (–, C-8), 78.1 (–, C-4), 85.8 (+, C-6), 102.7 (–, C-3), 96.1 (+, C-2); 112.5 (+, C-5), 122.6 (+, q, $^1J_{C-F}$ = 328.5 Hz, C-11), 164.2 (+, C-1), 236.3 (+, CO) ppm; MS (70 eV) *m/z* (%) 418 (18) [M$^+$], 362 (10) [M$^+$ - 2CO], 334 (53) [M$^+$ - 3CO], 282 (26) [M$^+$ - Cr(CO)$_3$], 267 (16) [M$^+$ - Cr(CO)$_3$ - CH$_3$], 213 (13), 201 (33), 167 (13), 150 (35), 135 (100), 123 (27), 107 (28), 91 (38) [M$^+$ - Cr(CO)$_3$ – OH - (SO$_2$CF$_3$)], 81 (57), 71 (98), 55 (87); HRMS ($C_{14}H_{13}O_6F_3SCr$) calcd. 417.9790, found 417.9789.

Tricarbonyl(2-fluoro-6-trifluoromethylsulfonylphenol)chromium(0) (23)

GP3, 250 mg (0.66 mmol) of tricarbonyl(2-fluorophenyl)chromium(0) triflate (**16**), 0.49 mL (0.79 mmol) of BuLi (1.6 M solution in hexane). 230 mg (0.5 mmol, 92%) of **23** was obtained as an orange-red oil. IR (ATR) ν/cm^{-1} 2979 (w) cm^{-1}, 2878 (w), 2336 (w), 1963 (s, CO), 1857 (s, CO), 1539 (s), 1506 (m), 1477 (w), 1353 (m), 1288 (w), 1191 (s), 1159 (m), 1133 (w), 1098 (s), 1050 (m), 967 (s), 891 (m), 847 (m), 763 (w), 700 (w), 670 (m), 658 (m), 619 (s); ^{1}H NMR (400.1 MHz, acetone-*d*$_6$) δ 4.84 (t, 1H, 3-H, *J* = 5.9 Hz), 5.73 (d, 1H, 4-H, *J* = 6.2 Hz), 6.26 (t, 1H, 5-H, *J* 6.64 Hz), 7.34 (br, 1H, OH) ppm; ^{13}C-NMR (100.6 MHz, acetone-*d*$_6$, DEPT, HMQC) δ 75.1 (–, C-3), 85.0 (+, C-6), 91.3 (–, C-4), 97.5 (–, C-5), 122.1 (+, q, C-7, $^1J_{C\text{-}F}$ = 326.4 Hz), 134.2 (+, d, C-2, $^1J_{C\text{-}F}$ = 253.8 Hz), 154.6 (+, C-1), 234.4 (+, C-8) ppm; MS (70 eV) m/z (%) 244 (18) [M$^+$ - Cr(CO)$_3$], 185 (24), 175 (10), 159 (20), 121 (14), 112 (24), 95 (28) [M$^+$ - Cr(CO)$_3$ - OH - F - (SO$_2$CF$_3$)], 83 (20), 75 (24), 69 (53), 64 (100); HRMS ($C_7H_4F_4O_3S$) calcd. 243.9817, found. 243.9818.

Tricarbonyl[2-(trifluoromethylsulfonyl)phenol-4-(trifluoromethylsulfonate)]-chromium(0) (28)

GP3, 400 mg (0.8 mmol) of **26**, 0.54 mL (0.9 mmol) of BuLi (1.6 M solution in hexane). 310 mg (0.6 mmol, 78 %) of **28** was obtained as an orange-red solid (m. p. 123 °C, dec.). IR (ATR): ν/cm^{-1} 3282 (w) , 2961 (w), 2081 (w), 1981 (s, CO), 1896 (s, CO), 1714 (w), 1535 (m), 1485 (m), 1430 (m), 1378 (w), 1357 (w), 1259 (s), 1198 (s), 1119 (s), 1096 (s), 1040 (s), 904 (m), 852 (s), 795 (s), 746 (w), 703 (w), 664 (w), 632 (w); ^{1}H-NMR (400.1 MHz, acetone-d_6) δ 4.53 (d, 1H, 6-H, J = 7.8 Hz), 6.31 (d, 1H, 3-H, J = 2.5 Hz), 6.46 (dd, 1H, 5-H, J = 2.5 Hz, 2.4 Hz), 7.34 (br., 1H, OH); ^{13}C-NMR (100.6 MHz, acetone-d_6, DEPT, HMQC) δ 78.5 (–, C-6), 79.8 (+, C-2), 92.6 (–, C-3 or C-5), 98.0 (–, C-3 or C-5), 123.4 (+, C-8, C-9, $^1J_{C-F}$ = 320.3 Hz), 122.0 (+, C-7, $^1J_{C-F}$ = 326.5 Hz), 125.0 (+, C-1), 233.0 (+, C-10); MS (70 eV) *m/z* (%) 374 (33) [$M^+ - Cr(CO)_3$], 355 (15) [$M^+ - Cr(CO)_3 - OH$], 293 (15), 255 (16), 242 (20), 220 (28), 193 (16), 149 (25), 109 (56), 97 (94), 75 (97), 64 (100), 52 (98) [^{52}Cr]; HRMS $C_8H_4O_6F_6S_2$ calcd. 373.9354, found. 373.9353.

Tricarbonyl[(2-trifluoromethylsulfonyl)phenol-3,5-bis(trifloromethanesulfonate)]-chromium(0) (29)

GP3, 900 mg of **27**, 1.28 mL of BuLi (1.6 M solution in hexane). 595 mg (0.9 mmol, 66 %) of **29** was obtained as a red solid (m. p. 112 °C, dec.). IR (ATR) ν/cm^{-1} 3282 (w), 2961 (w), 2124 (w), 1957 (s, CO), 1875 (s, CO), 1720 (w), 1598 (m), 1537 (m), 1510 (m), 1416 (w), 1378 (w), 1340 (w), 1262 (w), 1186 (s), 1120 (s), 1060 (m), 920 (m), 778 (w), 764 (w), 721 (w), 676 (w), 633 (w); ^{1}H-NMR (400.1 MHz, acetone-d_6) δ = 5.30 (d, 1H, 6-H, J = 6.5 Hz), 5.89 (s, 1H, 4-H), 7.69 (br.1H, OH); ^{13}C-NMR (100.6 MHz, acetone-d_6, DEPT, HMQC) δ 74.5 (–, C-6), 80.3 (+, C-2), 97.2 (–, C-4), 102.6 (+, C-5 or C-3), 106.1 (+, C-5 or C-3), 120.2 (+, C-8 or C-9, $^1J_{C-F}$ = 319.9 Hz), 120.6 (+, C-8 or C-9, $^1J_{C-F}$ = 320.0 Hz), 122.3 (+, C-7, $^1J_{C-F}$ = 326.9 Hz), 124.3 (+, C-1), 234.4 (+, C-10); MS (70 eV): *m/z* (%) 522 (36) [M^+- $Cr(CO)_3$], 373 (17), 330 (28), 240 (19), 233 (13), 176 (11), 123 (20) [$M^+ - 3\ SO_2CF_3$], 95 (12), 88 (32), 69 (100) [CF_3^+]. –HRMS $C_9H_3O_9F_9S_3$: calcd. 521.8796, found. 521.8795.

Tricarbonyl(estrone)chromium(0) (30)[7]

1017 mg (4.6 mmol) of $Cr(CO)_6$ and 1027 mg (3.8 mmol) of estrone in 44 mL of dibutyl ether / THF (10:1) was heated at 117 °C for 40 h. A yellow precipitate formed. After filtration and dissolution of the precipitate in THF the mixture was subjected to column chromatography [300x30 mm, PE, PE/TBME (6:1), PE/TMBE (2:1), EE]. 1437 mg (3.5 mmol, 93 %) of **30** was obtained as a yellow solid, mixture of diastereomers (3:5, NMR).

Signals assigned to the minor diasteromer are marked with b. IR (ATR) ν/cm^{-1} 3089 (w, O–H), 2933 (w, CH_2, CH_3), 2858 (w, CH), 1946 (s, CrCO), 1845 (s, CrCO), 1728 (s, C=O), 1543 (m, aryl-C=C), 1470 (m, aryl-C=C), 1260 (m, O–H), 1042 (m, C–OH). - ^{1}H NMR (400 MHz, acetone-d_6) δ 0.89 (s, 3 H, 18b-H), 0.90 (s, 3 H, 18-H), 1.37-1.67 (m, 7-H, 7b-H, 9-H, 9b-H, 11-H, 11b-H, 16b-H), 1.81 (t, $J_{H,H}$ = 11.73 Hz, 2 H, 16-H), 1.96-2.08 (m, 15-H), 2.17-2.27 (m, 13-H, 13b-H), 2.41-2.48 (m, 6-H), 2.77-3.01 (m, 8-H, 8b-H, 12-H), 5.14 (dd, $J_{H,H}$ = 7.03, 2.01 Hz, 1 H, 2-H), 5.21 (d, $J_{H,H}$ = 1.88 Hz, 1 H, 4b-H), 5.23 (d, $J_{H,H}$ = 1.88 Hz, 1 H, 4-H), 5.30 (dd, $J_{H,H}$ = 7.03, 2.01 Hz, 1 H, 2b-H), 5.93 (d, $J_{H,H}$ = 7.03 Hz, 1 H, 1-H), 6.09 (d, $J_{H,H}$ = 7.03 Hz, 1 H, 1b-H) ppm; ^{13}C NMR (100.6 MHz, BB, DEPT, HMQC acetone- d_6) δ 13.8 (C-18), 14.1 (C-18b), 21.9 (C-15b), 22.1 (C-15), 25.9 (C-7b), 26.2 (C-11), 26.3 (C-7), 26.7 (C-11b), 28.2 (C-12), 32.1 (C-16), 32.2 (C-16b), 36.0 (C-6), 38.4 (C-9), 39.0 (C-9b), 43.2 (C-13), 44.2 (C-13b), 50.2 (C-14b), 50.5 (C-14) 78.9 (C-2), 80.0 (C-4b), 81.4 (C-2b), 81.8 (C-4), 95.3 (C-1), 96.1 (C-1b), 105.1 (C-10b), 107.6 (C-10), 113.8 (C-5b), 114.1 (C-5), 142.5 (C-3b), 143.0 (C-3), 219.0 (C-17b), 219.1 (C-17), 235.7 (C-19b), 236.3 (C-19) ppm; MS (70 eV) *m/z* (%) 406 (58) [M^+], 350 (54) [M^+ – $(CO)_2$], 322 (100) [M^+ –$(CO)_3$], 270 (76) [M^+ –$Cr(CO)_3$, 213 (48) [M^+ –$Cr(CO)_3$ –C_3H_4O –1], 199 (23) [M^+ –$Cr(CO)_3$ –C_3H_4O –CH_3], 173 (40) [M^+ –$Cr(CO)_3$ –C_3H_4O –C_2H –1], 159 (49) [M^+ –$Cr(CO)_3$ –C_3H_4O –C_3H_3 –1], 146 (56) [M^+ –$Cr(CO)_3$ –C_3H_4O –CH_3 –C_4H_5 –1], 133 (45) [M^+ –$Cr(CO)_3$ –C_3H_4O –CH_3 –C_4H_5 –CH –1], 115 (40) [M^+ –$Cr(CO)_3$ –C_3H_4O –CH_3 –C_4H_5 –CH –OH –1], 91 (40) [M^+

–$Cr(CO)_3$ –C_3H_4O –CH_3 –C_4H_5 –C_4H_6 –1]. - LC-MS (ESI) $C_{21}H_{22}CrO_5$ [–H]: calcd. 405.0805, found 405.0794.

Tricarbonyl(3-trifluoromethylsulfonylestrone-3-trifluoromethylsulfonate)chromium(0) (31)

To a stirred solution of 1100 mg (2.7 mmol) of tricarbonyl(estron)chromium(0) (**30**) in 30 mL of anhydrous THF and 15 mL of pyridine 830 g (3.5 mmol, 1.2 equiv.) of trifluoromathanesulfonic acid anhydride was added dropwise under argon at –78 °C. The reaction mixture was allowed to warm to 25 °C over 1 h and was then stirred for 48 h. The colour of solution changed from yellow to dark orange. The reaction mixture was quenched by addition of 15 mL of water and extracted three times with 15 mL of ethyl acetate each. The collected organic layers were washed with water till the aqueous phase remained colourless, dried over anhydrous magnesium sulfate and filtered through a P4 frit. After solvent removal *in vacuo*, the crude product was purified by flash chromatography, eluting with *tert*-butyl methyl ether. 1200 mg (2.2 mmol, 84 %) of **31** was obtained as a yellow solid as a mixture of diastereomers (2:1, NMR).

Signals assigned to the minor diasteromer are marked with b. IR (ATR) ν/cm^{-1} 2939 (w), 2866 (w), 1969 (s, CO), 1888 (s, CO), 1732 (m, C=O), 1543 (m), 1457 (m), 1342 (w), 1248 (m), 1214 (m), 1137 (w), 1090 (m), 912 (m), 824 (w), 783 (w), 725 (w), 663 (w), 622 (w); ^{1}H NMR (400 MHz, acetone-d_6) δ 0.91 (s, 18b-H), 0.93 (s, 3 H, 18-H), 1.39-1.57 (m, 7-H, 7b-H, 11-H, 11b-H,), 1.64-1.73 (m, 15-H, 15b-H, 9-H, 9b-H), 1.81-1.89 (m, 16-H, 16b-H), 2.08-2.12 (m, 14-H, 14b-H), 2.26-2.39 (m, 8-H, 8b-H), 2.43-2.49 (m, 6-H, 6b-H), 2.91-3.03 (m, 12-H, 12b-H), 5.85 (dd, $J_{H,H}$ = 2.3, 2.3 Hz, 1 H, 2-H), 5.95 (d, $J_{H,H}$ = 2.2 Hz, 1H, 4-H), 5.98 (d, $J_{H,H}$ = 2.2 Hz, 4b-H), 6.01 (dd, $J_{H,H}$ = 2.2, 2.2 Hz, 2b-H), 6.09 (d, $J_{H,H}$ = 7.0 Hz, 1H, 1-H), 6.18 (d, 1b-H, $J_{H,H}$ = 7.0 Hz) ppm; ^{13}C-NMR (100.6 MHz, BB, DEPT, HMQC, acetone-d_6) δ 14.5 (C-18), 14.7 (C-18b), 22.6 (C-15b), 22.7 (C-15), 38.9 (C-9), 39.2 (C-9b), 26.3 (C-7b), 26.6 (C-11), 26.7 (C-7), 27.0 (C-11b), 28.6 (C-12), 30.6 (C-12b), 32.7 (C-16), 32.9 (C-16b), 36.6 (C-6), 36.7 (C-6b), 38.9 (C-9), 39.2 (C-9b), 43.9 (C-8), 45.0 (C-8b), 48.8 (C-13), 48.9 (C-13b), 50.9 (C-14b), 51.2 (C-14), 85.1 (C-2), 86.1 (C-2b), 87.0 (C-4b), 87.4 (C-4), 93.3 (C-1), 93.7 (C-1b), 111.5 (C-10b), 112.0 (C-5b), 112.7 (C-10), 113.8 (C-5), 120.4(q, C-19, $^1J_{C,F}$ = 319.9 Hz), 120.6 (q, C-19b, $^1J_{C,F}$ = 319.9 Hz), 133.1 (C-3b), 134.1 (C-3), 219.4 (C-17), 219.6 (C-17b), 233.6 (C-19b), 234.3 (C-19) ppm; MS (70 eV) *m/z* (%) 538 (58) [M$^+$], 482 (10) [M$^+$ – 2CO], 454 (67) [M$^+$ – 3CO], 402 (100) [M$^+$ – Cr (CO) $_3$], 385 (29), 370(38), 358 (65), 340 (86), 321(82), 305 (8), 292 (33), 269 (20), 251(55), 241 (9), 225 (45), 213 (80), 195 (23), 185 (28), 171 (26), 157 (40), 145 (31), 52(37). - LC-MS (ESI): $C_{22}H_{21}O_7F_3SCr$ [–H]: Calcd. 537.0287, found. 537.0292.

Tricarbonyl-[2-(trifluoromethylsulfonyl)estrone]chromium(0) (32)

0.25 mL (0.5 mmol, 1.7 equiv.) of lithiumdiisopropylamide (LDA) (2 M solution in THF/heptane/ethylbenzene) was added dropweise to a solution of 155 mg (0.3 mmol) of tricarbonyl(trifluoromethanelsulfonylestrone)chromium (0) (**31**) in 10 mL of THF under argon at –78 ˚C. The reaction mixture was stirred at –78 °C for 2 h and for another 0.5 h after having been warmed to 25 °C. The colour of the reaction changed from yellow to orange. The reaction mixture was quenched by addition of 15 mL of saturated aqueous ammonium chloride and extracted three times with 15 mL of ethyl acetate each. The collected organic layers were washed three times with 15 mL of water each, filtered through a P4 frit covered with a 2 cm thick layer of silica gel, and dried over anhydrous magnesium sulfate. After filtration and solvent removal at reduced pressure, the crude product was purified by column chromatography ai SiO_2 (30 x 2 cm, ethyl acetate). 115 mg (0.2 mmol, 77%) of **32** was obtained as an orange-yellow solid, mixture of diastereomers (2:1, NMR).

Signals assigned to the minor diasteromer are marked with b. IR (ATR) $\tilde{\nu}$ = 2937 (w) cm^{-1}, 2864 (w), 1948 (s, CO), 1846 (s, CO), 1736 (m, C=O), 1617 (w), 1542 (m), 1485 (m), 1454 (w), 1376 (w), 1290 (w), 1265 (m), 1192 (s), 1118 (m), 1085 (m), 1043 (w), 956 (w), 925 (w), 894 (w), 863 (w), 832 (w), 783 (w), 725 (w), 705 (w), 672 (w), 630 (m), 611 (m). - ^{1}H-NMR (400 MHz, acetone- d_6) δ = 0.91 (s, 18b-H), 0.93 (s, 3 H, 18-H), 1.34-1.53 (m, 7-H, 7b-H, 11-H, 11b-H,), 1.61-1.74 (m, 15-H, 15b-H, 9-H, 9b-H), 1.81-1.86 (m, 16-H, 16b-H), 2.06-2.11 (m, 14-H, 14b-H), 2.27-2.36 (m, 8-H, 8b-H), 2.39-2.47(m, 6-H, 6b-H), 2.86-3.02 (m, 12-H, 12b-H), 4.57 (s, 4b-H), 4.62 (s, 1H, 4-H), 5.93 (s, 1H, 1-H), 6.12 (s, 1b-H) ppm. - ^{13}C-NMR (100.6 MHz, BB, DEPT, HMQC, aceton-d_6) δ = 14.6 (C-18), 14.8 (C-18b), 22.6 (C-15b), 22.8 (C-15), 26.7 (C-7b), 26.8 (C-11), 27.0 (C-7), 27.2 (C-11b), 29.4 (C-12), 30.7 (C-12b), 32.7 (C-16), 32.9 (C-16b), 36.7 (C-6), 36.8 (C-6b), 39.1 (C-9), 39.3 (C-9b), 44.0 (C-8), 45.0 (C-8b), 48.9 (C-13), 49.0 (C-13b), 51.0 (C-14b), 51.2 (C-14), 83.5 (C-4b), 85.2 (C-4), 95.3 (C-1), 96.9 (C-1b), 99.0 (C-10b), 101.2 (C-10), 119.3 (C-5), 119.4 (C-5b), 122.1 (q, C-19, $^1J_{C,F}$ = 326.9 Hz), 122.2 (q, C-19b, $^1J_{C,F}$ = 326.9 Hz), 160.8 (C-3b), 160.9 (C-3), 219.7 (C-17), 219.8 (C-17b), 235.9 (C-19b), 236.5 (C-19) ppm. -MS (EI) *m/z* (%) = 538 (38) [M^+], 482 (10) 402 (12) [$M^+ - Cr(CO)_3$], 358 (7), 279 (23), 190 (25), 167 (42), 149 (100), 140 (29), 113 (15), 104 (21), 86 (26), 69 (77), 52 (93). - HRMS: $C_{22}H_{21}O_7\,F_3SCr$ calcd. 538.0365, found. 538.0329.

2-(Trifluoromethylsulfonyl)estrone (33)

I_2 (307 mg, 1.2 mmol) in 5 mL THF was added in one portion at 0°C to **32** (162 mg, 0.3 mmol) in 5 mL of THF. After stirring for 1h at 0°C and then for 5 h at 25 °C the mixture was poured into 10 % aqueous sodium bisulfite (30 mL) and extracted with two times with 20 mL of ethyl acetate each. The combined organic layers were washed with 30 mL of saturated aqueous sodium hydrogencarbonate and 30 mL of water and dried over $MgSO_4$.

After filtration and solvent removal at reduced pressure the crude product was purified by column chromatography (THF/petroleum ether 3:1) to give 118 mg (0.3 mmol, 97%) of **33** as a light yellow solid. IR (ATR) ν/cm^{-1} = 3285 (br), 2962 (m), 2926 (m), 2857 (w), 2116 (br), 1721 (m, C=O), 1619 (w), 1581 (w), 1496 (w), 1454 (w), 1418 (m), 1374 (w), 1355 (w), 1287 (w), 1259 (s), 1208 (m), 1140 (m), 1086 (s), 1014 (s), 919 (m), 897 (w), 877 (w), 796 (s), 701 (w), 661 (w), 610 (w). - ^{1}H-NMR (400 MHz, acetone-*d*$_6$) δ 0.90 (s, 3 H, 18-H), 1.41-1.69 (m, 6H, 7-H, 11-H, 15-H), 1.78-1.99 (m, 2H, 16-H), 2.08-2.12 (m, 1H, 14-H), 2.16-2.28 (m, 2H, 8-H, 9-H), 2.33-2.48 (m, 2H, 6-H), 2.76-2.99 (m, 2H, 12-H), 6.54 (s, 1H, 4-H), 7.10 (d, 1H, 1-H, J = 8.4 Hz), 7.97 (br, 1H, OH) ppm; ^{13}C-NMR (100.6 MHz, acetone-*d*$_6$, DEPT, HMQC) δ 14.8 (–, C-18), 22.8 (+, C-11), 27.4 (+, C-7), 28.0 (+, C-15), 29.9 (+, C-12), 33.3 (+, C-16), 36.7 (+, C-6), 40.0 (–, C-9), 45.6 (–, C-8), 49.1 (+, C-13), 51.8 (–, C-14), 116.5 (–, C-4), 122.2 (+, q, C-19, $^1J_{C\text{-}F}$ = 319.1 Hz), 127.8 (–, C-1), 132.2 (+, C-10), 139.0 (+, C-5), 149.2 (+, C-2), 156.7 (+, C-3), 220.2 (+, C-17) ppm; MS (EI) *m/z* (%) = 402 (100) [M$^+$], 358 (86) , 345 (76) [M$^+$ – 3F], 304 (29), 292 (43), 270 (56) [M$^+$ – F_3CO_2S + H], 251 (52) [M$^+$ – F_3CO_2S – OH], 225 (34), 213 (82), 185 (33), 171 (21), 157 (37), 145 (29), 128 (28), 115 (40), 107 (23), 97 (56), 81(21), 69 (35) [F_3C^+], 55 (46). -HRMS $C_{19}H_{21}F_3O_7S$ calcd. 402.1113, found. 402.1110.

1 E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen and W. Semmlinger, *Chem. Ber.*, 1958, **91**, 2763-2772.

2 E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen and W. Semmlinger, *Z. Naturforsch.*, 1958, **13b**, 458.

3 G. Natta, R. Ercoli, F. Calderazzo and E. Santambrogio, *Chim. Ind. (Milan)*, 1958, **40**, 1003-1007.

4 A. Wu, E. R. Biehl and P. C. Reeves, *J. Chem. Soc., Perkin Trans. 2*, 1972, 449-451.

5 J. E. Van Epp, Jr., D. R. Boyd and G. A. Berchtold, *J. Org. Chem.*, 1981, **46**, 1817-1820.

6 H. Schumann, A. M. Arif and T. G. Richmond, *Polyhedron*, 1990, **9**, 1677-1681.

7 G. Pouskouleli, I. S. Butler and J. P. Hickey, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1659-1662.