Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Supporting information (11 pages)

Catalytic Hydrochlorination of Unactivated Olefins with TsCl

Boris Gaspar and Erick M. Carreira*
Laboratorium für Organische Chemie, ETH Hönggerberg, CH-8093 Zürich, Switzerland.
carreira@org.chem.ethz.ch

General. All reactions were carried out under an atmosphere of argon or nitrogen. For flash chromatography technical grade solvents were used, which were distilled prior to use. Solvents for reactions were analytical grade purchased from Merck or Baker and used without further purifications.

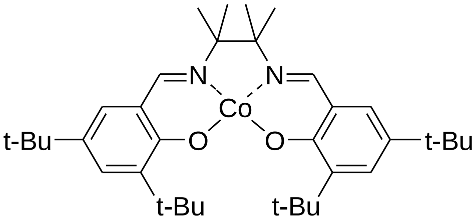
Chromatographic purification was performed as flash chromatography using Brunschwig silica 32-63, 60Å, using hexanes/diethylether, hexanes/ethyl acetate or hexanes/methylene chloride as eluent with 0.3-0.5 bar pressure. TLC was performed on Merck silica gel 60 F_{254} TLC glass plates and visualized with UV light and permanganate stain.

^{1}H-NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration, interpretation). ^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a VARIAN Mercury 75 MHz spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm as standard.

Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I FT-IR spectrophotometer as thin films unless stated otherwise and are reported as cm^{-1} (w=weak, m=medium, s=strong, sh=shoulder).

Mass spectrometric measurements were performed by the mass spectrometry service of the LOC at the ETHZ on a Finnigan TSQ 7000 ESI spectrometer for low resolution measurements and High resolution mass spectra were obtained on a VG-TRIBRID for electron impact ionization (EI) and Ion spec Ultima 4.7 spectrometer for MALDI. Elemental analysis was performed by the Mikroelementaranalytisches Laboratorium der ETHZ.

1,1,2,2-Tetramethyl-1,2-ethanediamino-*N,N*`-bis(3,5-di-*tert*-butylsalicylidene)-cobalt(II) (5)



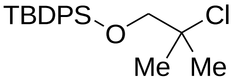
Ligand (**7**)[1] (500 mg, 0.911 mmol, 1.0 equiv.) in EtOH (20 ml) was heated to reflux under argon. After 10 minutes Co(OAc)$_2$ (obtained by drying its hydrate under vacuum at 70 °C for 3 hours, 227 mg, 0.911 mmol, 1.0 equiv.) was added and the mixture became purple. The reaction mixture was refluxed for 2 hours, cooled to RT and the precipitate filtered. The purple solid was washed with cold EtOH (10 ml) and dried under high vacuum to give 443 mg (80%) of the cobalt(II) complex **5**.

HRMS (MALDI): calcd for $C_{36}H_{54}CoN_2O_2^+$ (M) 605.3512 Found 605.3523.

IR ν 2950 (s), 2907 (m), 2359 (w), 1578 (s), 1522 (s), 1461 (m), 1422 (m), 1381 (s), 1323 (m), 1249 (s), 1204 (m), 1176 (m), 1141 (s), 1027 (w), 934 (w), 904 (w), 864 (w), 829 (w), 785 (w), 748 (w), 699 (w), 634 (w);

Anal. calcd for $C_{36}H_{54}CoN_2O_2$: C 71.38, H 8.98, N 4.62 Found: C 71.09, H 9.01, N 4.63

Tert-butyl(2-chloro-2-methylpropoxy)diphenylsilane (3)



General Procedure A:

Catalyst **5** (6.0 mg, 0.01 mmol, 2 mol%) was dissolved in EtOH (2 ml) at RT under argon. After 2 min, *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane[2] (156 mg, 0.5 mmol, 1.0 equiv.) was added followed by *p*-TsCl (99% ACROS, 116 mg, 0.6 mmol, 1.2 equiv.) and $PhSiH_3$ (98% ACROS, 62 µl, 0.5 mmol, 1.0 equiv.). Another portion of EtOH (1 ml) was added. The resulting green, homogeneous solution was stirred at RT and the reaction was monitored by TLC (hexane:CH_2Cl_2 =7:1). After completion (2.5 hours) the solvent was evaporated and the crude mixture purified by flash chromatography (hexane: CH_2Cl_2 =7:1) to afford *tert*-butyl(2-chloro-2-methylpropoxy)diphenylsilane (**3**) (167 mg, 96%) as a colorless oil.

General procedure B:

$Co(BF_4)_2•6H_2O$ (10 mg, 0.03 mmol, 6 mol %) and ligand **6**[3](14 mg, 0.03 mmol, 6 mol%) were dissolved in EtOH (2 ml) at RT under argon. After 2 min, *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (156 mg, 0.5 mmol, 1.0 equiv.) was added to the solution followed by *p*-TsCl (99% ACROS, 116 mg, 0.6

---

[1] For the preparation of ligand **7** see: G. A. Morris, H. Zhou, C. L. Stern, S. T. Nguyen, *Inorg. Chem.* **2001**, *40*, 3222-3227.

[2] J. Waser, H. Nambu, E. M. Carreira, *J. Am. Chem. Soc.* **2005**, *127*, 23, 8294-8295.

[3] J. Waser, B. Gaspar, H. Nambu, E. M. Carreira, *J. Am. Chem. Soc.* **2006**, *128*, 11693-11712.

mmol, 1.2 equiv) and TBHP (5.5 M solution in decane, 25 μl, 0.14 mmol, 0.28 equiv). Finally $PhSiH_3$ (98% ACROS, 62 μl, 0.5 mmol, 1.0 equiv.) was added and another portion of EtOH (0.5 ml). The resulting mixture was stirred at RT and the reaction was monitored by TLC (hexane:CH_2Cl_2 =7:1). After completion (5 hours) the solvent was evaporated and the crude mixture purified by flash chromatography (hexane: CH_2Cl_2 =7:1) to afford *tert*-butyl(2-chloro-2-methylpropoxy)diphenylsilane (**3**) (126 mg, 73 %) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70-7.67 (m, 4H), 7.45-7.37 (m, 6H), 3.66 (s, 2H, OCH_2), 1.60 (s, 6H, 2xCH_3), 1.09 (s, 9H, $C(CH_3)_3$);

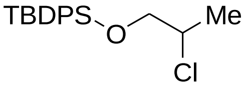
^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.52, 133.09, 129.64, 127.59, 72.72, 69.38, 29.13, 26.88, 19.50;

IR ν 3072 (w), 3051 (w), 2961 (m), 2932 (m), 2894 (m), 2858 (m), 1590 (w), 1472 (m), 1428 (m), 1391 (w), 1366 (w), 1190 (w), 1114 (s), 1008 (w), 998 (w), 827 (m), 740 (m), 701 (s), 611 (m), 578 (w), 505 (m);

HRMS (EI): calcd for $C_{20}H_{27}ClOSi^+$ (M-C_4H_9) 289.0810 Found 289.0807;

Anal. calcd for $C_{20}H_{27}OSiCl$: C 69.23, H 7.84, Found: C 69.21, H 7.76;

***Tert*-butyl(2-chloropropoxy)diphenylsilane (4)**



Chloride **4** (50 mg, 30 %, 85 % purity) was obtained as a colorless oil following the General procedure A (catalyst loading 5 %) with prop-2-enyloxy(*tert*-butyl)diphenylsilane[3] (148 mg, 0.5 mmol, 1.0 equiv.) in 24 hours after purification by flash chromatography (Hexane: CH_2Cl_2 =9:1).

Chloride **4** (136 mg, 82 %) was obtained as a colorless oil following the General procedure B (catalyst loading 12 %) with prop-2-enyloxy(*tert*-butyl)diphenylsilane (148 mg, 0.5 mmol, 1.0 equiv.) in 6 hours after purification by flash chromatography (Hexane: CH_2Cl_2 =7:1).

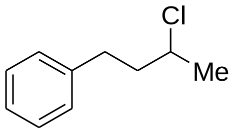
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68-7.66 (m, 4H), 7.44-7.36 (m, 6H), 4.10-3.99 (m, 1H, CHCl), 3.79 (dd, ^3J=5.4 Hz, ^2J=10.5 Hz, 1H, OCH_A), 3.64 (dd, ^3J=6.6 Hz, ^2J=10.5 Hz, 1H, OCH_B), 1.52 (d, ^3J=6.6 Hz, 3H, CH_3), 1.08 (s, 9H, $C(CH_3)_3$);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.56, 133.22, 129.77, 127.71, 68.92, 57.51, 26.75, 21.48, 19.29;

IR ν 3071 (w), 3050 (w), 2959 (m), 2931 (m), 2893 (m), 2858 (m), 1590 (w), 1472 (m), 1427 (m), 1390 (m), 1361 (w), 1302 (w), 1264 (w), 1222 (w), 1188 (w), 1146 (w), 1113 (s), 1009 (m), 937 (w), 889 (w), 824 (m), 807 (m), 740 (m), 701 (s), 614 (m), 569 (w), 506 (s);

HRMS (EI): calcd for $C_{19}H_{25}ClOSi^+$ (M-C_4H_9) 275.0653 Found 275.0657;

3-Chlorobutylbenzene (9)



Chloride **9** (39 mg, 46 %, 85 % purity) was obtained as a colorless oil following the General procedure A (catalyst loading 2 %) with 4-phenylbutene (99% Aldrich, 75 μl, 0.5 mmol, 1.0 equiv.) in 22 hours after purification by flash chromatography (Hexane: CH_2Cl_2 =7:1).

Chloride **9** (77 mg, 92 %) was obtained as a colorless oil following the General procedure B (catalyst loading 6 %) with 4-phenylbutene (99% Aldrich, 75 μl, 0.5 mmol, 1.0 equiv.) in 3 hours after purification by flash chromatography (Hexane: CH_2Cl_2 =7:1).

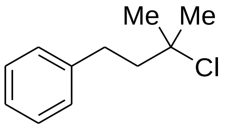
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33-7.19 (m, 5H), 4.06-3.95 (m, 1H, CHCl), 2.92-2.71 (m, 2H), 2.06-1.99 (m, 2H), 1.54 (d, ^3J=6.6 Hz, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.92, 128.39, 128.33, 125.92, 57.95, 41.96, 32.94, 25.50;

IR ν 3064 (w), 3028 (w), 2971 (w), 2927 (w), 2863 (w), 2361 (w), 1604 (w), 1496 (w), 1454 (m), 1379 (w), 1275 (w), 1117 (w), 1030 (w), 820 (w), 748 (m), 699 (s), 612 (w), 574 (w), 506 (w), 454 (w);

HRMS (EI): calcd for $C_{10}H_{13}Cl^+$ (M) 168.0700 Found 168.0700

3-Chloro-3-methylbutylbenzene (10)



Chloride **10** (73 mg, 80 %) was obtained as a colorless oil following the General procedure A (catalyst loading 2 %) with 3-methylbut-3-enylbenzene[3] (73 mg, 0.5 mmol, 1.0 equiv.) in 2 hours after purification by flash chromatography (Hexane: CH_2Cl_2 =7:1).

Chloride **10** (76 mg, 83%) was obtained as a colorless oil following the General procedure B (catalyst loading 6 %) with 3-methylbut-3-enylbenzene (73 mg, 0.5 mmol, 1.0 equiv.) in 3 hours after purification by flash chromatography (Hexane: CH_2Cl_2 =7:1).

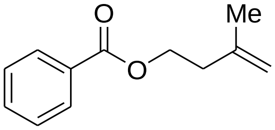
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32-7.17 (m, 5H), 2.86-2.80 (m, 2H, $PhCH_2$), 2.08-2.02 (m, 2H, CH_2), 1.65 (s, 6H, $C(CH_3)_2$);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.59, 128.32, 128.26, 125.80, 70.56, 47.98, 32.54, 31.70;

IR ν 3087 (w), 3064 (w), 3028 (w), 2973 (m), 2933 (m), 2865 (w), 1605 (w), 1498 (m), 1455 (m), 1388 (w), 1371 (m), 1233 (w), 1196 (w), 1162 (w), 1113 (m), 1072 (w), 1031 (w), 852 (w), 800 (w), 747 (m), 699 (s), 638 (w), 596 (w), 563 (m), 605 (m), 427 (m);

HRMS (EI): calcd for $C_{11}H_{15}Cl^+$ (M) 182.0857 Found 182.0856;

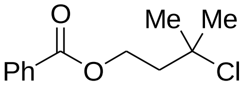
3-methylbut-3-enyl benzoate (11)[4]



Benzoyl chloride (700 µl, 6 mmol, 1.0 equiv) was added to a solution of 3-methylbut-3-en-1-ol (608 µl, 6 mmol, 1.0 equiv) in dry CH_2Cl_2 (8 ml) at 0-5 °C (ice-bath) under argon. Et_3N (1.69 ml, 12 mmol, 2.0 equiv) was added and the reaction mixture was stirred 15 min. CH_2Cl_2 (2 ml) was added and reaction mixture was stirred at RT 3.5 hours. CH_2Cl_2 (10 ml) was added and washed with 10% HCl (2x15 ml) then sat. $NaHCO_3$ (15 ml) and brine (15 ml). The solvent was evaporated and the crude product purified by flash chromatography (Hexane:CH_2Cl_2=1:4) to give **11** (1.03 g, 90%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.05-8.02 (m, 2H), 7.58-7.53 (m, 1H), 7.46-7.41 (m, 2H), 4.84 (bs, 1H, C=CH), 4,82 (bs, 1H, C=CH), 4.40 (t, 2H, ^3J=6.9 Hz, OCH_2), 2.49 (t, 2H, ^3J=6.9 Hz, CH_2), 1.82 (s, 3H, CH_3)

3-Chloro-3-methylbutyl benzoate (11)



Chloride **12** (106 mg, 93 %) was obtained as a colorless oil following the General procedure A (catalyst loading 2 %) with 3-methylbut-3-enyl benzoate (**11**) (95 mg, 0.5 mmol, 1.0 equiv.) in 4 hours after purification by flash chromatography (Hexane:CH_2Cl_2=2:3).

Chloride **12** (99 mg, 87 %) was obtained as a colorless oil following the General procedure B (catalyst loading 6 %) with 3-methylbut-3-enyl benzoate (**11**) (95 mg, 0.5 mmol, 1.0 equiv.) in 3 hours after purification by flash chromatography (Hexane:CH_2Cl_2=1:3).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.05-8.02 (m, 2H), 7.59-7.54 (m, 1H), 7.47-7.41 (m, 2H), 4.57 (t, ^3J=6.9 Hz, 2H, OCH_2), 2.26 (t, ^3J=6.9 Hz, 2H, CH_2), 1.68 (s, 6H, $C(CH_3)_2$);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.44, 132.96, 130.11, 129.51, 128.36, 68.44, 62.03, 44.04, 32.90;

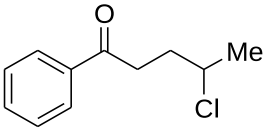
IR ν 3064 (w), 2974 (m), 2928 (w), 1720 (s), 1602 (w), 1584 (w), 1452 (m), 1388 (w), 1372 (w), 1316 (m), 1274 (s), 1221 (w), 1176 (m), 1113 (s), 1070 (m), 1027 (m), 975 (w), 807 (w), 711 (s), 687 (w), 677 (w), 572 (w), 530 (w), 442 (w);

HRMS (EI): calcd for $C_{12}H_{15}ClO_2$ (M) 226.0755 Found 226.0752;

---

[4] T. Tokuyasu, S. Kunikawa, K. J. McCullough, A. Masayuma, M. Nojima, *J. Org. Chem.* **2005**, *70*, 251-260.

4-Chloro-1-phenylpentan-1-one (13)



Chloride **13** (29 mg, 30 %) was obtained as a colorless oil following the General procedure A (catalyst loading 5 %) with 1-phenylpent-4-en-1-one[3] (80 mg, 0.5 mmol, 1.0 equiv.) in 7 hours after purification by flash chromatography two times (first Hexane:EtOAc=10:1 then Hexane:CH_2Cl_2=3:1).

Chloride **13** (82 mg, 84 %) was obtained as a colorless oil following the General procedure B (catalyst loading 12 %) with 1-phenylpent-4-en-1-one (80 mg, 0.5 mmol, 1.0 equiv.) in 6 hours after purification by flash chromatography two times (first Hexane:EtOAc=10:1 then Hexane:CH_2Cl_2=3:1).

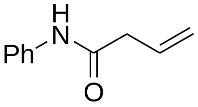
^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.00-7.97 (m 2H), 7.60-7.44 (m, 3H), 4.23-4.12 (m, 1H, CHCl), 3.30-3.13 (m, 2H, $COCH_2$), 2.34-2.23 (m, 1H, CH_A), 2.09-1.97 (m, 1H, CH_B), 1.59 (d, ^3J=6.6 Hz, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.18, 136.74, 133.14, 128.59, 127.99, 58.42, 35.52, 34.25, 25.62;

IR ν 2927 (w), 1686 (s), 1597 (m), 1580 (w), 1448 (m), 1380 (m), 1342 (m), 1278 (m), 1207 (m), 1180 (w), 1002 (w), 967 (w), 744 (m), 690 (m), 658 (w), 604 (w);

HRMS (EI): calcd for $C_{11}H_{13}ClO^+$ (M) 196.0649 Found 196.0652;

***N*-Phenylbut-3-enamide (14)**



But-3-enoic acid (444 mg, 5 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (8 ml) at RT under argon. Dimethylaminopyridine (16 mg, 0.126 mmol, 0.025 equiv) and aniline (0.92 ml, 10 mmol, 2.0 equiv) were added, the mixture was cooled to 0-5 °C (ice-bath) and DCC (1.03 g, 5 mmol, 1.0 equiv) was added. The mixture was stirred 10 min. at this temperature and then 4 hours at RT. CH_2Cl_2 (20 ml) was added and the precipitate filtered off. The resulting homogeneous solution was washed with 10% HCl (20 ml) and sat. $NaHCO_3$ (20 ml). The solvent was evaporated and the crude product purified by flash chromatography (Hexane:EtOAc=3:1) to give **14** (616 mg, 76 %) as a colorless solid. The spectroscopic data is consistent with the one reported in the literature.[5]

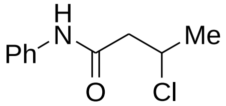
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50 (d, ^3J=7.5 Hz, 1H), 7.42 (br s, 1H, NH), 7.32 (t, ^3J=7.2 Hz, 2H); 7.11 (t, ^3J=7.2 Hz, 1H), 6.10-5.97 (m, 1H), 5.35-5.30 (m, 2H, =CH_2), 3.17 (d, ^3J=7.2 Hz, 2H, CH_2);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.57, 137.53, 130.91, 128.82, 124.27, 120.33, 119.73, 42.67;

---

[5] M. Hojo, R. Sakuragi, S. Okabe, A. Hosomi, *Chem. Comm.* **2001**, 357-358.

3-Chloro-*N*-phenylbutanamide (15)



Chloride **15** (87 mg, 88 %) was obtained as a colorless solid following the General procedure A (catalyst loading 8 %) with 3-methyl-*N*-phenylbut-3-enamide (**14**) (88 mg, 0.5 mmol, 1.0 equiv.) in 6 hours after purification by flash chromatography (Hexane:EtOAc=3:1).

Mp 86-89 °C (Hexane/EtOAc);

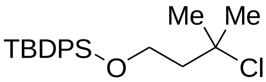
^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.52 (d, ^3J=7.8 Hz, 2H), 7.33 (t, ^3J=7.8 Hz, 3H, 2xCH$_{Ar}$ and NH), 7.13 (t, ^3J=7.5 Hz, 1H), 4.62-4.51 (m, 1H, CHCl), 2.83-2.70 (m, 2H, CH$_2$), 1.63 (d, ^3J=6.6 Hz, 3H, CH$_3$);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 167.55, 137.39, 129.02, 124.66, 120.08, 53.97, 48.33, 25.18;

IR ν 3286 (m), 1654 (s), 1600 (w), 1542 (m), 1498 (w), 1445 (w), 1316 (w), 1018 (w), 902 (w), 743 (w), 693 (m), 506 (w);

HRMS (EI) calcd for $C_{10}H_{12}ClNO^+$ (M) 197.0602 Found 197.0602;

***Tert*-butyl(3-chloro-3-methylbutoxy)diphenylsilane (16)**



Chloride **16** (135 mg, 75 %) was obtained as a colorless oil following the General procedure A (catalyst loading 5 %) with *tert*-butyl-(3-methylbut-2-enyloxy)-diphenylsilane^2 (162 mg, 0.5 mmol, 1.0 equiv.) in 4.5 hours after purification by flash chromatography (Hexane:CH$_2$Cl$_2$=10:1).

Chloride **16** (61 mg, 34 %, 60 % purity) was obtained as a colorless oil following the General procedure B (catalyst loading 6 %) with *tert*-butyl-(3-methylbut-2-enyloxy)-diphenylsilane (162 mg, 0.5 mmol, 1.0 equiv.) in 6 hours after purification by flash chromatography (Hexane:CH$_2$Cl$_2$=7:1).

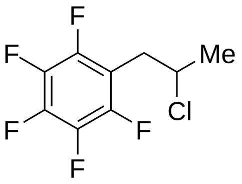
^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.69-7.66 (m, 4H), 7.46-7.36 (m, 6H), 3.89 (t, ^3J=6.9 Hz, 2H, OCH$_2$), 2.07 (t, ^3J=6.9 Hz, 2H, CH$_2$), 1.59 (s, 6H, C(CH$_3$)$_2$), 1.05 (s. 9H, C(CH$_3$)$_3$);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 135.41, 133.52, 129.52, 127.55, 69.59, 61.06, 47.98, 33.12, 26.90, 19.22;

IR ν 3072 (w), 3051 (w), 2961 (m), 2931 (m), 2890 (m), 2858 (m), 1472 (m), 1428 (m), 1388 (m), 1371 (w), 1186 (w), 1112 (s), 1049 (m), 1008 (w), 997 (w), 939 (w), 892 (w), 856 (w), 823 (m), 785 (w), 738 (m), 702 (s), 689 (m), 614 (m), 575 (w), 506 (m);

HRMS (EI): calcd for $C_{21}H_{29}ClOSi^+$ (M-C$_4$H$_9$) 303.0967 Found 303.0966;

1-(2-Chloropropyl)-2,3,4,5,6-pentafluorobenzene (17)



Chloride **17** (82 mg, 67 %) was obtained as a colorless oil following the General procedure A (catalyst loading 5 %) with allyl pentafluorobenzene (Aldrich, 107 mg, 0.5 mmol, 1.0 equiv.) in 4 hours after purification by flash chromatography (Hexane:CH_2Cl_2=5:1).

Chloride **17** (38 mg, 31 %) was obtained as a colorless oil following the General procedure B (catalyst loading 6 %) with allyl pentafluorobenzene (Aldrich, 107 mg, 0.5 mmol, 1.0 equiv.) in 4 hours after purification by flash chromatography (Hexane:CH_2Cl_2=5:1).

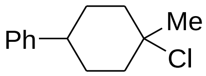
^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.29-4.18 (m, 1H, CHCl), 3.19-3.03 (m, 2H, CH_2), 1.58 (d, ^3J=6.3 Hz, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.8 (m), 143.6 (m), 141.8 (m), 139.0 (m), 135.6 (m), 111.34 (m), 55.52, 33.05, 24.98;

^{19}F NMR ($CDCl_3$, 300 MHz) δ -141.7 (m, 2F), -155.0 (m, 1F), -161.4 (m, 2F);

IR ν 2984 (w), 2934 (w), 1657 (w), 1523 (s), 1504 (s), 1457 (w), 1384 (w), 1313 (w), 1299 (w), 1196 (w), 1126 (m), 1095 (w), 1027 (m), 977 (m), 894 (w), 630 (w), 612 (w), 570 (w);

(4-Chloro-4-methylcyclohexyl)benzene (18)



Chloride **18** (90 mg, 87 %) was obtained as a mixture of two diastereoisomers **18A** and **18B** (dr=15:1) following the General procedure A (catalyst loading 2 %) with (4-methylenecyclohexyl)benzene[6] (86 mg, 0.5 mmol, 1.0 equiv) in 4 hours after purification by flash chromatography (Hexane:CH_2Cl_2=4:1).

Chloride **18** (73 mg, 70 %) was obtained as a mixture of two diastereoisomers **18A** and **18B** (dr=19:1) following the General procedure B (catalyst loading 6 %) with (4-methylenecyclohexyl)benzene (86 mg, 0.5 mmol, 1.0 equiv) in 4 hours after purification by flash chromatography (Hexane:CH_2Cl_2=5:1).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34-7.18 (m, 5H for both isomers), 2.68-2.57 (m, 1H for the minor isomer), 2.53-2.42 (m, 1H for the major isomer), 2.14-1.64 (m, 12H for both isomers), 1.68 (s, 3H, CH_3 for the major isomer);

---

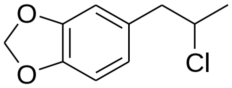
[6] (4-methylenecyclohexyl)benzene was prepared according to: A. G. M. Barret, M. J. Betts, A. Fenwick, *J. Org. Chem.* **1985**, *50*, 169-175.

^{13}C NMR (CDCl$_3$, 75 MHz) δ 146.57, 128.31, 128.26, 126.77, 126.63, 126.08, 125.98, 71.58, 43.49, 42.83, 42.55, 41.61, 34.30, 31.50, 29.96, 28.20;

IR ν 3027 (w), 2930 (s), 2862 (m), 2360 (w), 1602 (w), 1493 (m), 1439 (m), 1379 (w), 1231 (w), 1179 (w), 1120 (m), 1006 (w), 961 (m), 820 (m), 756 (m), 698 (s), 551 (m), 534 (m);

HRMS (EI) calcd for $C_{13}H_{17}Cl^+$ (M) 208.1013 Found 208.1012;

5-(2-Chloropropyl)-benzo[*d*][1,3]dioxole (19)



Chloride **19** (86 mg, 87 %) was obtained as a colorless oil following the General procedure B (catalyst loading 10 %) with Safrole (96 % Fluka, 85 mg, 0.5 mmol, 1.0 equiv.) in 7 hours after purification by flash chromatography (Hexane:EA=6:1).

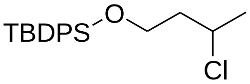
^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.77-6.64 (m, 3H), 5.94 (s, 2H, O-CH$_2$, 4.21-4.10 (m, 1H, ClCH), 2.99 (dd, 1H, ^2J=14.1 Hz, ^3J=7.2 Hz CH$_A$), 2.87 (dd, 1H, ^2J=14.1 Hz, ^3J=6.9 Hz, CH$_B$), 1.50 (d, 3H, ^3J=6.6 Hz, CH$_3$);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 147.41, 146.21, 131.58, 122.29, 109.58, 108.10, 100.87, 58.72, 46.37, 24.66;

IR ν 2894 (w), 2360 (w), 1503 (s), 1498 (s), 1443 (s), 1376 (w), 1250 (s), 1190 (m), 1098 (w), 1039 (s), 929 (m), 810 (m), 774 (w), 684 (w), 614 (w);

HRMS (EI) calcd for $C_{10}H_{11}ClO_2^+$ (M) 198.0442 Found 198.0442;

***Tert*-butyl(3-chloro-3-butoxy)diphenylsilane (20)**



Chloride **20** (126 mg, 73 %) was obtained as a colorless oil following the General procedure B (catalyst loading 12 %) with but-3-enyloxy-*tert*-butyl-diphenyl-silane[3] (155 mg, 0.5 mmol, 1.0 equiv.) in 4 hours after purification by flash chromatography (Hexane:CH$_2$Cl$_2$=7:1).

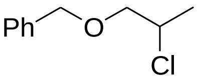
^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.69-7.65 (m, 4H), 7.44-7.37 (m, 6H), 4.40-4.29 (m, 1H, ClCH), 3.90-3.72 (m, 2H, OCH$_2$), 2.03-1.83 (m, 2H, CH$_2$), 1.54 (d, 3H, ^3J=6.6 Hz, CH$_3$), 1.06 (s, 9H, C(CH$_3$)$_3$);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 135.55, 133.70, 129.63, 127.65, 60.80, 55.35, 42.92, 26.81, 25.50, 19.21;

IR ν 3072 (w), 2959 (w), 2931 (w), 2858 (w), 1427 (w), 1428 (m), 1389 (w), 1362 (w), 1280 (w), 1204 (w), 1113 (s), 1087 (m), 988 (w), 973 (w), 899 (w), 823 (w), 737 (m), 781 (s), 613 (w), 505 (m), 488 (w), 450 (w);

HRMS (EI) calcd for $C_{20}H_{27}ClOSi^+$ (M-C$_4$H$_9$) 289.0810 Found 289.0811;

((2-Chloropropoxy)methyl)benzene (21)



Chloride **21** (26 mg, 28 %) was obtained as a colorless oil following the General procedure A (catalyst loading 4 %) with allyl benzyl ether (99% Aldrich, 78 µl, 0.5 mmol, 1.0 equiv.) in 5 hours after purification by flash chromatography (Hexane:CH_2Cl_2=2:1).

Chloride **21** (70 mg, 76 %) was obtained as a colorless oil following the General procedure B (catalyst loading 6 %) with allyl benzyl ether (99% Aldrich, 78 µl, 0.5 mmol, 1.0 equiv.) in 5 hours after purification by flash chromatography (Hexane:CH_2Cl_2=4:1).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36-7.28 (m, 5H), 4.59 (s, 2H, OCH_2), 4.20-4.10 (m, 1H, ClCH), 3.62 (dd, 1H, ^3J=6.3 Hz, ^2J=9.9 Hz, OCH_A), 3.54 (dd, 1H, ^3J=6.0 Hz, ^2J=9.9 Hz, OCH_B), 1.53 (d, 3H, ^3J=6.3 Hz, CH_3);

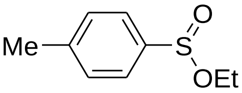
^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.69, 128.33, 127.66, 127.55, 75.24, 73.26, 55.40, 21.91;

IR ν 3031 (w), 2978 (w), 2861 (w), 1496 (w), 1454 (m), 1363 (w), 1204 (w), 1101 (s), 1028 (w), 737 (s), 697 (s), 631 (w), 468 (w);

HRMS (EI) calcd for $C_{10}H_{13}ClO^+$ (M) 184.0655 Found 184.0652;

Anal. calcd for $C_{10}H_{13}OCl$: C 65.04, H 7.10, Found: C 65.26, H 7.20

Ethyl 4-methylbenzenesulfinate (8)[7]



^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61-7.58 (m, 2H), 7.33 (d, ^3J=8.1 Hz, 2H), 4.15-4.04 (m, 1H), 3.77-3.66 (m, 1H), 2.42 (s, 3H, CH_3), 1.27 (t, ^3J=6.9 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.49, 141.66, 129.55, 125.08, 60.75, 21.60, 15.67;

IR ν 3626 (w), 3564 (w), 3383 (w), 2997 (s), 2171 (m), 1916 (w), 1694 (m), 1651 (w), 1596 (m), 1386 (m), 1130 (s), 1081 (s), 999 (m), 881 (s);

HRMS (EI) calcd for $C_9H_{12}O_2S^+$ (M) 184.0553 Found 184.0551

---

[7] T. Yoshino, S. Imori, H. Togo, *Tetrahedron* **2006**, *62*, 1309-1317.