Supporting Information

G. Hilt, W. Hess and K. Harms

“Asymmetric Cobalt-catalyzed Neutral Diels-Alder Reactions of a Boron-functionalized 1,3-Diene with Alkynes and Allylboration with Aldehydes”

General procedure for the cobalt-catalyzed Diels-Alder / allylboration reaction sequence

Anhydrous zinc iodide (60 mol%), zinc dust (60 mol%) and $\text{CoBr}_2(\text{dppe})$ (10 mol%) were stirred under argon in 0.5 mL DCM until the green suspension turned brown (5-10 min). Then, the boron diene **1** (1.0 eq.) in DCM ($c = 200 \text{ mg / mL}$) and the appropriate alkyne **2** (1.0 eq.) were added and the mixture was stirred at room temperature. After 30 min the aldehyde (1.0 eq.) was added and the reaction was stirred at room temperature for 15 h. The suspension was diluted with MTBE and washed with 1 M aqueous NaOH and saturated NaHSO_3 solution. After drying with MgSO_4 the solution was filtered over a short pad of silica gel and then the solvent was removed under vacuum. The residue was then purified by flash column chromatography (pentane/MTBE).

General procedure for the asymmetric cobalt-catalyzed Diels-Alder / allylboration reaction sequence

Instead of the 10 mol% of the $\text{CoBr}_2(\text{dppe})$ complex the according cobalt complexes $[\text{CoBr}_2(\text{chiral ligand})]$ were applied (10 mol%). Otherwise the general procedure was followed as outlined above. The enantiomeric excess was determined by chiral HPLC analysis: Dynamax HPLC-system; column: Chiracel OD-H; n -hexane: i PrOH = 9:1; flow: 0.7 mL/min; UV-detector 230 nm.

(4-Chlorophenyl)-(1-methyl-5-trimethylsilyl-cyclohexa-2,4-dien-1-yl)-methanol (**5a**)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and $\text{CoBr}_2(\text{dppe})$ (31 mg, 0.05 mmol) in 0.5 mL DCM. Then the boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μL), trimethylsilyl acetylene (70 μL , 0.5 mmol) and 4-chlorobenzaldehyde (70 mg, 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 40:1) the desired product **5a** (84 mg, 0.27 mmol, 55%) was obtained as a colorless oil.

^1H NMR (300 MHz, CDCl_3): $\delta = 7.29\text{--}7.25$ (m, 2H, H_{ar}), $7.23\text{--}7.20$ (m, 2H, H_{ar}), $6.17\text{--}6.14$ (m, 1H, $\text{HC}=\text{CTMS}$), 6.00 (dd, 1H, $J = 9.4, 4.0 \text{ Hz}$, $\text{CH}=\text{CH}-\text{CH}=\text{CTMS}$), 5.35 (d, 1H, $J = 9.6 \text{ Hz}$, $\text{CH}=\text{CH}-\text{CH}=\text{CTMS}$), 4.53 (s, 1H, $\text{CH}-\text{O}$), 2.60 (dd, 1H, $J = 17.2, 1.7 \text{ Hz}$, CHH), 1.94 (bs, 1H, OH), 1.90 (dd, 1H, $J = 17.0 \text{ Hz}, 1.7 \text{ Hz}$, CHH), 0.88 (s, 1H, Me), 0.08 (s, 9H, TMS).

^{13}C NMR (75 MHz, CDCl_3): $\delta = 139.8$ (C), 138.5 (C), 134.3 (CH), 133.0 (C), 130.4 (CH), 129.2 (CH), 127.6 (CH), 124.8 (CH), 76.9 (CH), 38.6 (C), 33.5 (CH_2), 20.7 (CH_3), -2.5 (CH_3).

IR (film, cm^{-1}): 3449 (m), 3028 (w), 2955 (s), 1489 (s), 1408 (w), 1247 (s), 1091 (m), 1053 (m), 1013 (m), 837 (s), 739 (m).

MS (EI): m/z 305 (1, $[\text{M}-\text{H}]^+$), 289 (1, $[\text{M}-\text{OH}]^+$), 273 (1), 257 (1), 245 (1), 231 (1), 213 (2), 166 (7), 149 (8), 106 (11), 92 (6), 73 (100, $[\text{TMS}]^+$).

HRMS (EI): m/z calculated for $\text{C}_{17}\text{H}_{23}\text{OSiCl}$: 306.1207 $[\text{M}]^+$, found m/z 306.1196 .

(1-Methyl-5-trimethylsilyl-cyclohexa-2,4-dien-1-yl)-(4-nitrophenyl)-methanol (5b)

According to the general procedure the catalyst was prepared from zinc iodide (400 mg, 1.2 mmol), zinc dust (80 mg, 1.2 mmol) and $\text{CoBr}_2(\text{dppe})$ (124 mg, 0.2 mmol) in DCM (1.0 mL). Then boron diene **1** (372 mg, 2.0 mmol) in DCM (1.86 mL), trimethylsilyl acetylene (280 μL , 2.0 mmol) and 4-nitrobenzaldehyde (302 mg, 2.0 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 15:1) the desired product **5b** (531 mg, 1.68 mmol, 84%) was obtained as a yellow oil.

^1H NMR (400 MHz, CDCl_3): δ = 8.11 (d, 2H, J = 8.8 Hz, H_{ar}), 7.45 (d, 2H, J = 8.8 Hz, H_{ar}), 6.20-6.17 (m, 1H, $\text{HC}=\text{CTMS}$), 6.02 (dd, 1H, J = 9.5, 4.9 Hz, $\text{CH}=\text{CH}-\text{CH}=\text{CTMS}$), 5.29 (d, 1H, J = 9.5 Hz, $\text{CH}=\text{CH}-\text{CH}=\text{CTMS}$), 4.68 (s, 1H, $\text{CH}-\text{O}$), 2.62 (dd, 1H, J = 17.3, 1.0 Hz, CHH), 2.10 (bs, 1H, OH), 1.92 (dd, 1H, J = 17.0, 2.1 Hz, CHH), 0.89 (s, 3H, Me), 0.08 (s, 9H, TMS).

^{13}C NMR (100 MHz, CDCl_3): δ = 149.1 (C), 147.1 (C), 138.8 (C), 133.7 (CH), 130.5 (CH), 128.6 (CH), 125.3 (CH), 122.5 (CH), 75.9 (CH), 38.5 (C), 33.9 (CH_2), 20.7 (CH_3), -2.5 (TMS).

IR (film, cm^{-1}): 3473 (m), 3022 (w), 2957 (m), 1604 (m), 1520 (s), 1347 (s), 1313 (w), 1244 (m), 1107 (w), 1054 (m), 1038 (s), 1005 (w), 886 (w), 833 (s), 743 (s), 728 (s), 702 (w).

MS (EI): m/z 317 (1, $[\text{M}^+]$), 302 (1, $[\text{M}^+-\text{Me}]$), 285 (1, $[\text{M}^+-\text{Me}-\text{OH}]$), 269 (1), 254 (1), 225 (2), 210 (2), 195 (2), 180 (2), 164 (5), 153 (30), 149 (44), 136 (9), 121 (7), 106 (7), 91 (4), 73 (100, TMS^+).

HRMS (EI): m/z calculated for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{Si}$: 317.1447 $[\text{M}^+]$, found m/z 317.1420

(1-Methyl-5-trimethylsilyl-cyclohexa-2,4-dien-1-yl)-(3-nitrophenyl)-methanol (5c)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and $\text{CoBr}_2(\text{dppe})$ (31 mg, 0.05 mmol) in DCM (0.5 mL). Then boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μL), trimethylsilyl acetylene (70 μL , 0.5 mmol) and 3-nitrobenzaldehyde (75 mg, 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 20:1) the desired product **5c** (99 mg, 0.31 mmol, 63%) was obtained as a yellow oil.

^1H NMR (300 MHz, CDCl_3): δ = 8.13 (s, 1H, H_{ar}), 8.08 (d, 1H, J = 8.1 Hz, H_{ar}), 7.61 (d, 1H, J = 7.7 Hz, H_{ar}), 7.45 (t, 1H, J = 7.9 Hz, H_{ar}), 6.17 (d, 1H, J = 4.5 Hz, H_{olef}), 6.04 (dd, 1H, J = 9.6, 4.9 Hz, H_{olef}), 5.28 (d, 1H, J = 9.4 Hz, H_{olef}), 4.67 (s, 1H, OH), 2.62 (d, 1H, J = 17.2 Hz, CHH), 2.18 (s, 1H, OH), 1.93 (dd, 1H, J = 17.2, 2.1 Hz, CHH), 0.89 (s, 3H, CH_3), 0.07 (s, 9H, TMS).

^{13}C NMR (75 MHz, CDCl_3): δ = 147.6 (C), 143.7 (C), 138.8 (C), 133.9 (CH), 133.6 (CH), 130.5 (CH), 128.2 (CH), 125.4 (CH), 122.6 (CH), 122.2 (CH), 75.8 (CH), 38.4 (C), 33.8 (CH_2), 20.7 (CH_3), -2.5 (TMS).

IR (film, cm^{-1}): 3547 (s), 3027 (w), 2956 (s), 1530 (s), 1350 (s), 1247 (s), 1053 (s), 838 (s), 726 (s).

MS (EI): m/z 317 (<1, $[\text{M}]^+$), 300 (4, $[\text{M}-\text{OH}]^+$), 284 (2), 269 (2), 254 (2), 239 (2), 229 (3), 210 (3), 194 (3), 181 (8), 165 (7), 149 (40), 136 (3), 121 (8), 105 (13), 92 (10).

HRMS (EI): m/z calculated for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{Si}$: 317.1447 $[\text{M}^+]$, found m/z 317.1435

(1-Methyl-5-trimethylsilyl-cyclohexa-2,4-dien-1-yl)-(4-trifluoromethylphenyl)-methanol (5d)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and $\text{CoBr}_2(\text{dppe})$ (31 mg, 0.05 mmol) in DCM (0.5 mL). Then boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μL), trimethylsilyl acetylene (70 μL , 0.5 mmol) and 4-(trifluoromethyl)benzaldehyde (70 μL , 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 50:1) the product **5d** (108 mg, 0.32 mmol, 63%) was obtained as a colorless oil.

^1H NMR (400 MHz, CDCl_3): δ = 7.55 (d, 2H, J = 8.3 Hz, H_{ar}), 7.41 (d, 2H, J = 8.3 Hz, H_{ar}), 6.20-6.17 (m, 1H, $\text{HC}=\text{CTMS}$), 6.02 (dd, 1H, J = 9.6, 4.8 Hz, $\text{CH}=\text{CH}-\text{CH}=\text{CTMS}$), 5.34 (d, 1H, J = 9.4 Hz, $\text{CH}=\text{CH}-\text{CH}=\text{CTMS}$), 4.62 (s, 1H, $\text{CH}-\text{O}$), 2.63 (dd, 1H, J = 17.1, 1.3 Hz, CHH), 2.02 (bs, 1H, OH), 1.94 (dd, 1H, J = 17.1, 1.9 Hz, CHH), 0.90 (s, 3H, Me), 0.09 (s, 9H, TMS).

^{13}C NMR (100 MHz, CDCl_3): δ = 145.4 (C), 138.7 (C), 134.1 (C), 130.5 (C), 129.4 (q, J = 32.4 Hz, CCF_3), 128.2 (CH), 125.0 (CH), 124.2 (q, J = 272.0 Hz, CF_3), 124.3 (q, J = 3.8 Hz, $(\text{CH})_2\text{CCF}_3$), 76.7 (CH), 38.5 (C), 33.8 (CH_2), 20.8 (CH_3), -2.5 (TMS).

^{19}F NMR (282 MHz, CDCl_3): δ = -62.37 (s, CF_3).

IR (film, cm^{-1}): 3443 (m), 3027 (w), 2957 (m), 1619 (w), 1417 (w), 1326 (s), 1248 (m), 1165 (s), 1127 (s), 1068 (m), 1055 (w), 1016 (w), 837 (s), 744 (w), 722 (w).

MS (EI): m/z 387 (1), 354 (1), 340 (1, $[\text{M}^+]$), 322 (1), 307 (1), 280 (1), 265 (1), 249 (1), 231 (4), 173 (7), 165 (15), 156 (48), 149 (29), 135 (10), 127 (26), 73 (100, TMS^+)

HRMS (EI): m/z calculated for $\text{C}_{18}\text{H}_{23}\text{OSiF}_3$: 340.1270 $[\text{M}^+]$, found m/z 340.1487

(1-Methyl-5-trimethylsilyl-cyclohexa-2,4-dien-1-yl)-phenyl-methanol (5e)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and $\text{CoBr}_2(\text{dppe})$ (31 mg, 0.05 mmol) in DCM (0.5 mL). Then boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μL), trimethylsilyl acetylene (70 μL , 0.5 mmol) and benzaldehyde (51 μL , 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 50:1) the product **5e** (81 mg, 0.30 mmol, 60%) was obtained as a colorless oil.

^1H NMR (300 MHz, CDCl_3): δ = 7.29-7.18 (m, 5H, H_{ar}), 6.12-6.11 (m, 1H, H_{olef}), 5.95 (dd, 1H, J = 9.5, 4.9 Hz, H_{olef}), 5.37 (d, 1H, J = 9.6 Hz, H_{olef}), 4.52 (s, 1H, $\text{CH}-\text{O}$), 2.58 (dd, 1H, J = 17.0, 1.7 Hz, CHH), 1.89 (dd, 1H, J = 17.0, 1.7 Hz, CHH), 1.89 (s, 1H, OH), 0.86 (s, 3H, CH_3), 0.04 (s, 9H, TMS).

^{13}C NMR (75 MHz, CDCl_3): δ = 141.4 (C), 138.4 (C), 134.7 (CH), 130.4 (CH), 127.9 (CH), 127.5 (CH), 127.2 (CH), 124.4 (CH), 77.8 (CH), 38.6 (C), 33.6 (CH_2), 20.7 (CH_3), -2.5 (TMS).

IR (film, cm^{-1}): 3487 (m), 3030 (w), 2952 (m), 1450 (m), 1245 (s), 1055 (m), 1013 (s), 833 (s), 749 (m), 719 (s).

MS (EI): m/z 272 (<1, $[\text{M}]^+$), 254 (1, $[\text{M}-\text{Me}]^+$), 239 (1), 179 (8), 166 (12), 149 (26), 135 (7), 107 (10), 92 (18), 73 (100, $[\text{Ph}]^+$).

HRMS (EI): m/z calculated for $\text{C}_{17}\text{H}_{24}\text{OSi}$: 272.1596 $[\text{M}^+]$, found m/z 272.1578

(1-Methyl-5-trimethylsilyl-cyclohexa-2,4-dien-1-yl)-pyridin-2-yl-methanol (5f)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and CoBr₂(dppe) (31 mg, 0.05 mmol) in DCM (0.5 mL). Then boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μ L), trimethylsilyl acetylene (70 μ L, 0.5 mmol) and 2-pyridinecarbaldehyde (48 μ L, 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 15:2) of the product **5f** (106 mg, 0.39 mmol, 78%) was obtained as an oil.

¹H NMR (300 MHz, CDCl₃): δ = 8.52-8.50 (m, 1H, H_{ar}), 7.58 (dt, 1H, J = 7.6, 1.7 Hz, H_{ar}), 7.17-7.13 (m, 2H, H_{ar}), 6.22-6.19 (m, 1H, H_{olef}), 6.02 (dd, 1H, J = 9.6, 4.9 Hz, H_{olef}), 5.35 (d, 1H, J = 9.6 Hz, H_{olef}), 4.57-4.50 (m, 2H, CHOH / OH), 2.77 (dd, 1H, J = 17.0, 0.8 Hz, CHH), 1.92 (dd, 1H, J = 17.0, 2.5 Hz, CHH), 0.77 (s, 3H, CH₃), 0.10 (s, 9H, TMS).

¹³C NMR (75 MHz, CDCl₃): δ = 159.9 (C), 147.5 (C), 139.3 (CH), 135.3 (CH), 134.9 (CH), 130.6 (CH), 124.6 (CH), 123.0 (CH), 122.1 (CH), 73.4 (CH), 38.6 (C), 34.8 (CH₂), 20.0 (CH₃), -2.4 (TMS).

IR (film, cm⁻¹): 3441 (m), 3016 (w), 2955 (s), 1593 (m), 1438 (w), 1404 (w), 1247 (m), 1054 (s), 836 (m), 749 (m), 721 (m).

MS (EI): m/z 273 (1, [M]⁺), 240 (1), 224 (1), 200 (1, [M-TMS]⁺), 181 (2), 166 (7), 149 (29), 109 (84).

HRMS (EI): m/z calculated for C₂₃H₁₆NOSi: 273.1549 [M⁺], found m/z 273.1531

(1-Methyl-5-phenyl-cyclohexa-2,4-dien-1-yl)-(4-trifluoromethylphenyl)-methanol (5g)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and CoBr₂(dppe) (31 mg, 0.05 mmol) in DCM (0.5 mL). Then boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μ L), trimethylsilyl acetylene (70 μ L, 0.5 mmol) and 4-(trifluoromethyl)benzaldehyde (70 μ L, 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 50:1) the product **5g** (52 mg, 0.15 mmol, 30%) were obtained as an oil.

¹H NMR (300 MHz, CDCl₃): δ = 7.57 (d, 2H, J = 8.3 Hz, H_{ar}), 7.44 (d, 4H, J = 7.6 Hz, H_{ar}), 7.34 (t, 2H, J = 7.0 Hz, H_{ar}), 7.28-7.23 (m, 1H, H_{ar}), 6.31 (d, 1H, J = 5.5 Hz, H_{olef}), 6.16 (dd, 1H, J = 9.4, 5.5 Hz, H_{olef}), 5.42 (d, 1H, J = 9.4 Hz, H_{olef}), 4.71 (s, 1H, CH-O), 3.17 (d, 1H, J = 17.0 Hz, CHH), 2.33 (dd, 1H, J = 17.0, 1.3 Hz, CHH), 2.03 (s, 1H, OH), 1.04 (s, 3H, CH₃).

¹³C NMR (75 MHz, CDCl₃): δ = 145.3 (C), 140.8 (C), 136.0 (C), 132.5 (CH), 129.5 (q, J = 32.1 Hz, CH), 128.4 (CH), 128.1 (CH), 127.3 (CH), 125.5 (CH), 125.1 (CH), 124.4 (q, J = 3.4 Hz, C), 124.2 (q, J = 272.2 Hz, CF₃), 119.4 (CH), 77.1 (C), 40.4 (C), 34.6 (CH₂), 21.4 (CH₃).

IR (film, cm⁻¹): 3441 (s), 3031 (m), 2964 (m), 2931 (m), 2874 (m), 1929 (m), 1707 (m), 1618 (m), 1493 (m), 1325 (s), 1165 (s), 1124 (s), 1067 (s), 1016 (m), 850 (s), 758 (m), 746 (m), 725 (m), 696 (m).

MS (EI): m/z 344 (1, [M]⁺), 326 (2, [M-H₂O]⁺), 311 (2), 241 (2), 215 (1), 188 (9), 169 (100, [M-F₃CC₆H₄CHO]⁺), 152 (22), 145 (17).

HRMS (EI): m/z calculated for C₂₁H₁₉OF₃: 344.1388 [M⁺], found m/z 344.1392

(1-Methyl-5-phenyl-cyclohexa-2,4-dien-1-yl)-(4-nitrophenyl)-methanol (**5h**)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and $\text{CoBr}_2(\text{dppe})$ (31 mg, 0.05 mmol) in DCM (0.5 mL). Then boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μL), phenyl acetylene (55 μL , 0.5 mmol) and 4-nitrobenzaldehyde (75 mg, 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 15:1) the product **5h** (58 mg, 0.18 mmol, 36%) was obtained as a yellow oil.

^1H NMR (300 MHz, CDCl_3): δ = 8.17-8.12 (m, 2H, H_{ar}), 7.51-7.47 (m, 2H, H_{ar}), 7.44-7.40 (m, 2H, H_{ar}), 7.36-7.31 (m, 2H, H_{ar}), 7.28-7.22 (m, 1H, H_{ar}), 6.29 (dt, 1H, J = 5.7, 0.9 Hz, H_{olef}), 6.18 (dd, 1H, J = 9.5, 5.7 Hz, H_{olef}), 5.37 (d, 1H, J = 9.5 Hz, H_{olef}), 4.77 (d, 1H, J = 2.1 Hz, CHOH), 3.07 (dd, 1H, J = 17.0, 0.8 Hz, CHH), 2.34 (dd, 1H, J = 17.0, 1.9 Hz, CHH), 2.12 (d, 1H, J = 2.8 Hz, OH), 1.04 (s, 3H, CH_3).

^{13}C NMR (75 MHz, CDCl_3): δ = 148.8 (C), 147.2 (C), 140.6 (C), 136.1 (C), 132.0 (CH), 128.5 (CH), 128.4 (CH), 127.4 (CH), 125.9 (CH), 125.1 (CH), 122.6 (CH), 119.4 (CH), 76.5 (CH), 40.4 (C), 34.7 (CH_2), 21.4 (CH_3).

HRMS (ESI): m/z calculated for $\text{C}_{20}\text{H}_{20}\text{NO}_3^+$: 322.1443 [M^+], found m/z 322.1439.

Methyl 3-{5-[Hydroxy-(4-trifluoromethylphenyl)-methyl]-5-methyl-cyclohexa-1,3-dien-1-yl} benzoate (**5i**)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and $\text{CoBr}_2(\text{dppe})$ (31 mg, 0.05 mmol) in DCM (0.5 mL). Then boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μL), methyl 3-ethynyl-benzoate (80 mg, 0.5 mmol) and 4-(trifluoromethyl)benzaldehyde (70 μL , 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 20:1) the product **5i** (72 mg, 0.18 mmol, 36%) was obtained as an oil.

^1H NMR (300 MHz, CDCl_3): δ = 8.08 (s, 1H, H_{ar}), 7.90 (d, 1H, J = 7.6 Hz, H_{ar}), 7.60-7.54 (m, 3H, H_{ar}), 7.45-7.36 (m, 3H, H_{ar}), 6.33 (d, 1H, J = 5.3 Hz, H_{olef}), 6.18-6.13 (m, 1H, H_{olef}), 5.45 (d, 1H, J = 9.6 Hz, H_{olef}), 4.71 (s, 1H, CHOH), 3.91 (s, 3H, COOMe), 3.06 (d, 1H, J = 17.0 Hz, CHH), 2.37 (d, 1H, J = 17.0 Hz, CHH), 2.16-2.00 (m, 1H, OH), 1.06 (s, 3H, CH_3).

^{13}C NMR (75 MHz, CDCl_3): δ = 167.1 (CO), 145.3 (C), 141.2 (C), 135.0 (C), 133.1 (CH), 130.3 (C), 129.6 (q, C, J = 32.5 Hz), 129.5 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 126.2 (CH), 125.3 (CH), 124.4 (q, CH, J = 3.8 Hz), 124.1 (q, C, J = 271.8 Hz, CF_3), 120.4 (CH), 77.0 (CH), 52.1 (CH_3), 40.3 (C), 34.7 (CH_2), 21.5 (CH_3).

^{19}F NMR (282 MHz, CDCl_3): δ = -62.42 (CF_3).

IR (film, cm^{-1}): 3468 (s), 2954 (m), 1722 (s), 1439 (w), 1325 (s), 1243 (m), 1164 (m), 1122 (s), 1067 (m), 1016 (m), 755 (s).

MS (EI): m/z 400 (3), 384 (4, [$\text{M}-\text{H}_2\text{O}$]), 361 (6), 329 (4), 258 (6), 242 (32), 226 (97, [$\text{M}-\text{F}_3\text{CC}_4\text{H}_6\text{CHO}-\text{H}$] $^+$), 211 (26), 195 (100, $\text{C}_{14}\text{H}_{11}\text{O}$), 183 (26), 173 (84), 152 (81), 145 (73).

HRMS (EI): m/z calculated for $\text{C}_{23}\text{H}_{19}\text{O}_3\text{F}_3$: 400.1286 [$\text{M}-\text{H}_2^+$], found 400.1281

(5-*tert*.-Butyl-1-methyl-cyclohexa-2,4-dien-1-yl)-(4-nitrophenyl)-methanol (5j)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and $\text{CoBr}_2(\text{dppe})$ (31 mg, 0.05 mmol) in DCM (0.5 mL). Then boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μL), 3,3-dimethyl-1-butyne (70 μL , 0.5 mmol) and 4-nitrobenzaldehyde (75 mg, 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 20:1) the product **5j** (34 mg, 0.11 mmol, 22%) was obtained as an oil.

^1H NMR (300 MHz, CDCl_3): δ = 8.15 (d, 2H, J = 8.9 Hz, H_{ar}), 7.48 (d, 2H, J = 8.5 Hz, H_{ar}), 6.02 (dd, 1H, J = 9.4, 5.5 Hz, H_{olef}), 5.74 (dt, 1H, J = 5.5, 0.9 Hz, H_{olef}), 5.08 (d, 1H, J = 9.5 Hz, H_{olef}), 4.70 (d, 1H, J = 3.0 Hz, CHOH), 2.62 (d, 1H, J = 16.8 Hz, CHH), 2.00 (d, 1H, J = 3.2 Hz, OH), 1.88 (dd, 1H, J = 16.6, 1.7 Hz, CHH), 1.07 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.90 (s, 3H, CH_3).

^{13}C NMR (75 MHz, CDCl_3): δ = 149.2 (C), 147.4 (C), 147.2 (C), 130.2 (CH), 128.7 (CH), 125.9 (CH), 122.5 (CH), 114.3 (CH), 75.6 (CH), 40.0 (C), 35.4 (C), 32.8 (CH_2), 28.3 (CH_3), 20.4 (CH_3).

IR (film, cm^{-1}): 3572 (m), 2961 (s), 1596 (m), 1514 (s), 1345 (s), 1268 (m), 1108 (m), 1033 (s), 864 (m), 802 (m), 750 (m), 727 (m).

MS (EI): m/z 300 (<1, $[\text{M}^+ - \text{H}]$), 293 (1), 284 (1), 268 (1), 253 (1), 238 (1), 226 (1), 210 (1), 196 (1), 178 (1), 165 (1), 153 (10), 133 (11), 105 (8), 93 (4), 77 (3), 65 (22), 57 (100, $[\text{Me}_3\text{C}^+]$).

HRMS (EI): m/z calculated for $\text{C}_{18}\text{H}_{22}\text{NO}_3$: 300.1600 $[\text{M}^+ - \text{H}]$, found m/z 300.1590

(5-Benzenesulfonylmethyl-1-methyl-cyclohexa-2,4-dien-1-yl)-pyridin-2-yl-methanol (5k)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and $\text{CoBr}_2(\text{dppe})$ (31 mg, 0.05 mmol) in DCM (0.5 mL). Then boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μL), (prop-2-yn-1-ylsulfonyl)-benzene (90 mg, 0.5 mmol) and 2-pyridinecarbaldehyde (50 μL , 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 1:2) the product **5k** (90 mg, 0.25 mmol, 50%) was obtained as an amorphous solid.

^1H NMR (300 MHz, CDCl_3): δ = 8.50 (d, 1H, J = 4.2 Hz, H_{ar}), 7.86 (d, 2H, J = 7.6 Hz, H_{ar}), 7.60 (q, 2H, J = 6.9 Hz, H_{ar}), 7.51 (t, 2H, J = 7.5 Hz, H_{ar}), 7.19-7.15 (m, 2H, H_{ar}), 5.85 (dd, 1H, J = 9.6, 5.3 Hz, H_{olef}), 5.64 (d, 1H, J = 4.2 Hz, H_{olef}), 5.40 (d, 1H, J = 9.6 Hz, H_{olef}), 4.56 (s, 1H, CH-O), 4.30 (bs, 1H, OH), 3.90 (d, 1H, J = 13.7 Hz, SO_2CHH), 3.79 (d, 1H, J = 13.7 Hz, SO_2CHH), 2.75 (d, 1H, J = 17.6 Hz, CHH), 2.04 (d, 1H, J = 17.6 Hz, CHH), 0.83 (s, 3H, CH_3).

^{13}C NMR (75 MHz, CDCl_3): δ = 159.4 (C_{ar}), 147.7 (CH), 138.8 (C_{ar}), 135.5 (CH), 135.2 (CH), 133.6 (CH), 129.0 (CH), 128.2 (CH), 127.4 (CH), 124.5 (C_{olef}), 123.2 (CH), 122.7 (CH), 122.3 (CH), 74.7 (CH), 64.1 (CH_2), 40.3 (C), 36.5 (CH_2), 20.8 (CH_3).

IR (film cm^{-1}): 3489 (m), 3062 (w), 2964 (w), 2923 (m), 1717 (w), 1592 (m), 1446 (m), 1306 (s), 1151 (s), 1085 (m), 913 (m), 731 (s), 689 (m), 529 (m).

MS (EI): m/z (355, $[\text{M}]^+$), 300 (1), 246 (2), 214 (14, $[\text{M} - \text{PhSO}_2]^+$), 105 (100), 77 (19, $[\text{Ph}]^+$).

HRMS (EI): m/z calculated for $\text{C}_{20}\text{H}_{21}\text{NO}_3\text{S}$: 355.1242 $[\text{M}^+]$, found m/z 355.1244

(5-Butyl-1-methyl-cyclohexa-2,4-dien-1-yl)-pyridin-2-yl-methanol (5l) and (1-Butyl-5-methyl-cyclohexa-2,4-dien-1-yl)-pyridin-2-yl-methanol (6l)

According to the general procedure the catalyst was prepared from zinc iodide (100 mg, 0.3 mmol), zinc dust (20 mg, 0.3 mmol) and $\text{CoBr}_2(\text{dppe})$ (31 mg, 0.05 mmol) in DCM (0.5 mL). Then boron diene **1** (93 mg, 0.5 mmol) in DCM (465 μL), 1-hexyne (60 μL , 0.5 mmol) and 2-pyridinecarbaldehyde (50 μL , 0.5 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 20:1) the product **5l** (56 mg, 0.22 mmol, 43%, **5l:6l** = 3.0:1.0) were obtained as an oil.

^1H NMR (300 MHz, CDCl_3): **5l**: δ = 8.51 (d, 1H, J = 4.5 Hz, H_{ar}), 7.58 (dt, 1H, J = 7.6, 1.7 Hz, H_{ar}), 7.20-7.14 (m, 2H, H_{ar}), 5.95 (dd, 1H, J = 9.4, 5.1 Hz, H_{olef}), 5.66 (d, 1H, J = 4.9 Hz, H_{olef}), 5.16 (d, 1H, J = 9.5 Hz, H_{olef}), 4.61-4.51 (m, 1H, CH-O), 2.62 (d, 1H, J = 17.0 Hz, CHH), 2.17-2.01 (m, 2H, CH_2), 1.90 (d, 1H, J = 17.0 Hz, CHH), 1.76 (s, 1H, OH), 1.49-0.98 (m, 4H, CH_2CH_2), 0.89 (t, 3H, J = 7.4 Hz, CH_3), 0.78 (s, 3H, CH_3).

Additional resolved signals for **6l**: δ = 7.61-7.56 (m, 1H, H_{ar}), 5.65 (m, 1H, H_{olef}), 4.48-4.39 (m, 2H, CH-O), 2.45 (d, 1H, J = 17.8 Hz, CHH), 0.82 (t, 3H, J = 6.8 Hz, CH_3).

^{13}C NMR (75 MHz, CDCl_3): **5l**: δ = 159.8 (C), 147.5 (CH), 140.2 (C), 135.3 (CH), 130.8 (CH), 124.8 (CH), 123.1 (CH), 122.2 (CH), 117.4 (CH), 74.0 (CH), 40.0 (C), 37.1 (CH_2), 37.0 (CH_2), 29.6 (CH_2), 22.4 (CH_2), 20.5 (CH_3), 13.9 (CH_3).

^{13}C NMR (75 MHz, CDCl_3): **6l**: δ = 159.7 (C), 147.4 (CH), 135.7 (CH), 135.2 (CH), 128.8 (CH), 125.3 (CH), 123.1 (CH), 122.2 (CH), 117.7 (CH), 75.0 (CH), 43.7 (C), 34.7 (CH_2), 33.7 (CH_2), 27.2 (CH_2), 23.6 (CH_3), 23.3 (CH_2), 14.1 (CH_3).

MS (EI): m/z 257 (1, $[\text{M}]^+$), 240 (1), 224 (1), 196 (1), 182 (2), 167 (2), 149 (9), 131 (1), 119 (2), 109 (100), 93 (25).

HRMS (EI): m/z calculated for $\text{C}_{17}\text{H}_{23}\text{NO}$: 257.1783 $[\text{M}^+]$, found m/z 257.1780

(5-Benzenesulfonylmethyl-1-methyl-cyclohexa-2,4-dien-1-yl)-(4-trifluoromethylphenyl)-methanol (5m)

According to the general procedure the catalyst was prepared from zinc iodide (400 mg, 1.2 mmol), zinc dust (80 mg, 1.2 mmol) and $\text{CoBr}_2(\text{dppe})$ (124 mg, 0.2 mmol) in DCM (1.0 mL). Then boron diene **1** (372 mg, 2.0 mmol) in DCM (1.86 mL), (prop-2-yn-1-ylsulfonyl)-benzene (360 mg, 2.0 mmol) and 4-(trifluoromethyl)benzaldehyde (280 μL , 2.0 mmol) were added and the reaction mixture was stirred for 15 h. After work up and purification by flash column chromatography (pentane/MTBE = 4:1 to 2:1) the product **5m** (419 mg, 1.0 mmol, 50%) was obtained as an amorphous solid.

^1H NMR (300 MHz, CDCl_3): δ = 7.91 (d, 2H, J = 8.3 Hz, H_{ar}), 7.70-7.65 (m, 1H, H_{ar}), 7.59-7.52 (m, 4H, H_{ar}), 7.40 (d, 2H, J = 8.1 Hz, H_{ar}), 5.94 (dd, 1H, J = 9.6, 4.3 Hz, H_{olef}), 5.81-5.78 (m, 1H, H_{olef}), 5.26 (d, 1H, J = 9.6 Hz, H_{olef}), 4.74 (d, 1H, J = 4.3 Hz, CH-O), 3.92 (d, 1H, J = 13.4 Hz, CHHSO_2), 3.78 (d, 1H, J = 13.2 Hz, CHHSO_2), 3.66-3.63 (m, 1H, OH), 2.88 (d, 1H, J = 17.4 Hz, CHH), 2.15 (d, 1H, J = 17.4 Hz, CHH), 0.90 (s, 3H, CH_3).

^{13}C NMR (75 MHz, CDCl_3): δ = 145.6 (2 x C, C), 138.8 (C), 136.5 (C), 133.9 (CH), 130.7 (q, J = 271.7 Hz, CF_3), 129.3 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 124.1 (q, J = 3.9 Hz, H_{ar}), 123.7 (CH), 73.3 (CH), 63.5 (CH_2), 39.9 (C), 36.5 (CH_2), 20.1 (CH_3).

The signal of the quaternary aromatic carbon adjacent to the trifluoromethyl group is not resolved.

^{19}F NMR (282 MHz, CDCl_3): $\delta = -62.72$ (s, CF_3).

IR (film, cm^{-1}): 3483 (s), 3036 (w), 2967 (w), 2878 (w), 1616 (m), 1523 (w), 1479 (w), 1449 (w), 1411 (w), 1362 (w), 1325 (s), 1290 (m), 1246 (m), 1163 (m), 1143 (m), 1109 (m), 1109 (m), 1065 (w), 855 (w), 794 (w), 737 (m), 615 (m).

MS (EI): m/z 384, (1, $[\text{M}-\text{F}-\text{H}_2]^+$), 317 (2), 262 (4), 247 (10), 175 (15), 143 (33), 127 (20), 105 (100), 91 (66), 77 (17, $[\text{Ph}]^+$).

HRMS (EI): m/z calculated for $\text{C}_{22}\text{H}_{19}\text{FO}_3\text{S}$ $[\text{M}^+-\text{H}_2]$: 420.1007, found m/z 420.1028.

The crystal structure of **5m** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 610153

5a

5b

5c

5d

5e

5f

5g

5h

5i

5j

5k

5m

Chiral HPLC-analysis of 5m

Date: Mon, 2704Aug0519562001 22:31 UhA

Data: 10% B - 0.7ml - 5-27AUG56-009

Sample: Chiracel OD-H

A: n-Hexan

B: iPrOH (10.0 %)

Fluß: 0.7 ml/min, 230nm, p= 34, T=30 °C

w- NORPHOS (sulfon)

Method: 10% B - 0.7ml - 50min - 230nm

Sampling Int: 0.1 Seconds

Data:

Analysis: Channel A

Peak No.	Time	Type	Height(μ V)	Area(μ V-sec)	Area%
1	24.350	N	124149	6227458	13.367
2	28.855	N	565897	40358032	86.632
Total Area				46585490	99.999