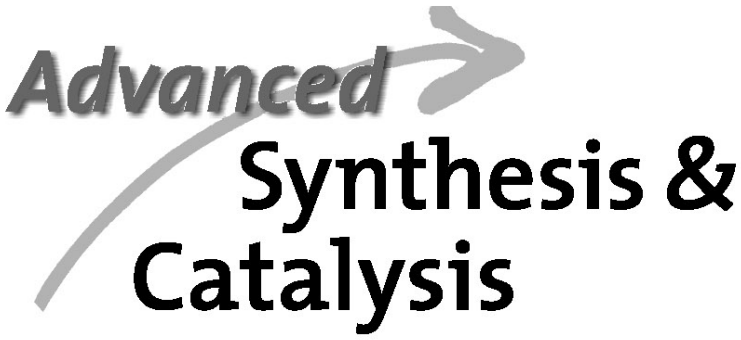

Supporting Information

Polyglycerol Supported Chromium-Salen as a High-loading Dendritic Catalyst for Stereoselective Diels-Alder Reactions

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SUPPORTING INFORMATION

1. General information

NMR-spectra were obtained on following spectrometers: Bruker ARX 300 (300 MHz spectra), Bruker DRX 400 (400 MHz spectra) or Bruker DRX 500 (500 MHz spectra). IR-spectra were obtained on a Bruker Vector22, on a Bruker IFS66 FT-IR, or on a Nicolet Avatar 320 FT-IR spectrometer in the range of 4000-500 cm^{-1}. Dialysis was performed with benzoylated cellulose dialysis tubes from Sigma-Aldrich (No. D-7884, width: 32 mm, molecular weight cut-off (MWCO) 1000 g mol^{-1}). Ultrafiltration procedures were performed in commercially available pressure and solvent resistant cells from Millipore® equipped with an ultrafiltration membrane (Koch, MPF 50, MWCO = 700 g mol^{-1}). Preparative GPC was performed on a PSS GRAL 100 Å column equipped with an Ecom spol. s r.o. LCP 4020 isocratic pump and injection system, an Ecom spol. s r.o. LCD 2083 spectrophotometric detector and preparative detecting cell, and a precolumn PSS GRAL. ICP-AES measurements were performed on an Iris Intrepid spectrometer from Thermo Elemental. Polyglycerol **3** (Mn = 8000 g mol^{-1}, 13.5 mmol OH groups g^{-1}, TMP starter unit) was prepared according to the published procedures.[1,2] Other chemicals were commercially available. For water-free procedures, the solvents were dried conventionally.

2. Characterization data

3-*tert*-Butyl-5-(chloromethyl)-2-hydroxybenzaldehyde 6:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.87 (s, 1 H), 9.87 (s, 1 H), 7.53 (s, 1 H), 7.44 (s, 1 H), 4.59 (s, 2 H), 1.43 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.9, 161.4, 139.2, 134.7, 131.9, 128.4, 120.4, 46.0, 35.1, 29.0; IR (KBr): ν = 2996, 2971, 2948, 2907, 2859, 1651 (C=O), 1615, 1596, 1481, 1466, 1435, 1381, 1357, 1323, 1266, 1236, 1213, 1164, 1148, 1027, 979,939, 909, 886, 806, 796, 772, 761, 699, 608, 551, 522, 496 cm^{-1}; FAB-MS (HR): calcd. For $C_{12}H_{15}ClO_2$ $[M+H]^+$ 226.0761, found 226.0746.

3-*tert*-Butyl-5-polyglyceryloxymethylsalicylaldehyde 7:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.75 (s, 1 H), 9.77 (s, 1 H), 7.52 – 7.21 (br, 2 H), 4.67 – 4.26 (br, 2 H), 4.11 – 3.11 (PG backbone), 1.85 (PG starter unit), 1.36 (s, 9 H), 0.77 (PG starter unit); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.2, 160.8, 138.4, 133.9, 131.1, 129.2 – 128.8 (3 C), 120.3, 80.1 – 67.0 (PG backbone and Bn-C), 37.1, 29.3; IR (KBr): ν = 3423 (OH), 2957, 2902, 2870, 1650 (C=O), 1439, 1391, 1324, 1267, 1227, 1155, 1101, 911, 773, 733 cm^{-1}.

(*R,R*)-1,2-Diaminocyclohexane monohydrochloride 9:

^{1}H NMR (500 MHz, D_2O): δ = 2.85 (m, 2 H), 1.92 (m, 2 H), 1.65 (m, 2 H), 1.42 – 1.06 (m, 4 H); ^{13}C NMR (125 MHz, D_2O): δ = 53.7, 31.0, 23.2; IR (KBr): ν = 3439, 3383, 3284, 3030, 2939,

2858, 1599, 1516, 1476, 1384, 1087, 1036, 1012, 419 cm^{-1}; FAB-MS (HR): calcd. for $C_6H_{15}ClN_2$ $[M\text{-}HCl+H]^+$ 150.0924, found 115.1256

***N*-(3',5'-Di-*tert*-butylsalicylidene)-(*R,R*)-1,2-diaminocyclohexane monohydrochloride 11:**

^1H NMR (500 MHz, d_6-DMSO), δ = 13.42 (s, 1 H), 8.61 (s, 1 H), 8.25 (br s, 3 H), 7.33 (s, 1 H), 7.24 (s, 1 H), 3.35 (s, 1 H), 3.19 (s, 1 H), 1.86 – 1.12 (m, 26 H); ^{13}C NMR (125 MHz, d_6-DMSO) δ = 168.4, 157.4, 139.6 , 135.5, 126.6, 126.3, 118.0, 69.2, 51.3, 34.5-22.8, 31.3, 29.3; IR (KBr): ν = 3444, 2952, 2870, 1631, 1592, 1467, 1439, 1384, 1362, 1270, 1253, 1204, 1174, 1029 cm^{-1}; FAB-MS (LR): *m/z* = 331.2 $[M\text{-}HCl+H]^+$, 313.2 $[M\text{-}HCl\text{-}H_2O+H]^+$.

***N*-(3',5'-Di-*tert*-butylsalicylidene)-*N'*-(3''-*tert*butyl-5''-polyglyceryloxymethylsalicylidene)-(*R,R*)-1,2-diaminocyclohexane 12:**

^1H NMR (500 MHz, $CDCl_3$): δ = 13.94 – 13.63 (br s, 2 H), 8.52 – 7.85 (br, 2 H), 7.54 – 6.43 (br s, 4 H), 4.86 – 2.81 (PG backbone), 4.45 (br s, 1H), 4.32 (br s, 1H), 3.30 (br s, 2 H) 2.41 – 0.48 (m, 35 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.9, 165.4, 160.1, 158.0, 140.0, 137.3, 136.4, 129.5, 126.9, 126.1, 118.4, 117.9, 80.2 – 64.7 (PG backbone), 73.4, 69.5, 35.1, 34.9, 34.1, 33.2, 31.5, 29.6, 24.4; IR (KBr): ν = 3430 (OH),

2929, 2862, 2361, 2338, 1628 (C=N), 1442, 1390, 1361, 1268, 1212, 1097, 909, 878, 802, 758, 734 cm^{-1}.

***N*-(3′-*tert*-Butyl-5-polyglyceryloxymethylsalicylidene)-*N*′-(3′′,5′′-di-*tert*-butylsalicylidene)-(*R,R*)-cyclohexane-(1,2)-diaminochromium(III) chloride 13:**

IR (KBr): ν = 3334, 2948, 2865, 2360, 2341, 1619, 1538, 1457, 1434, 1385, 1341, 1316, 1236, 1204, 1166, 1097, 1028, 825, 784, 750, 721, 669, 563 cm^{-1}.

***N*-(3′,5′-Di-*tert*-butylsalicylidene)-(*R,R*)-1,2-diaminocyclohexane 14:**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.71 (s, 1H), 8.44 (s, 1 H), 7.40 (d, 1 H, *J* = 2.2 Hz), 7.11 (d, 1 H, *J* = 2.2 Hz), 2.88 (ddd, 1 H, *J* = 11.2, 9.0, 4.0 Hz), 2.80 (ddd, 1 H, *J* = 10.5, 9.2, 4.0 Hz), 1.95 – 1.01 (m, 22H).

***N*-(3′-*tert*-Butyl-5-polyglyceryloxymethylsalicylidene)-*N*′-(3′′,5′′-di-*tert*-butylsalicylidene)-(*R,R*)-cyclohexane-(1,2)-diamino-chromium(III) tetrafluoroborate 15:**

IR (KBr): ν = 3207, 2956, 2925, 2856, 1622, 1434, 1317, 1258, 1197, 1057, 800 cm^{-1}.

Methyl 2-(4-hydroxyphenyl) acetate 17:

^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.05 (d, 2H, *J* = 4.2 Hz), 6.74 (d, 2H, *J* = 4.2 Hz), 3.63 (s, 3H), 3.50 (s, 2H); ^{13}C-NMR (125 MHz,

$CDCl_3$) δ = 173.3, 155.6, 130.3, 125.0, 115.5, 52.1, 40.2; IR (NaCl): ν = 3399, 3024, 2954, 1717 (C=O), 1615, 1597, 1516, 1439, 1412, 1347, 1227, 1170, 1102, 1011, 827, 803, 785, 730, 618, 524, 466, 440 cm^{-1}; MS (EI, %): *m/z* = 166.0 (12, $[M]^+$), 107.0 (100).

Methyl 2-(3-*tert*-butyl-4-hydroxyphenyl) acetate 18:

^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.06 (s, 1H), 6.90 (d, 1H, *J* = 4.0 Hz), 6.51 (d, 1H, *J* = 4.0 Hz), 3.61 (s, 3H), 3.48 (s, 2H), 1.31 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 178.6, 153.6, 136.4, 128.4, 127.9, 125.1, 116.8, 52.7, 40.7, 34.4, 29.6; IR (NaCl): ν = 3436, 2955, 1719 (C=O), 1609, 1511, 1484, 1424, 1390, 1365, 1260, 1209, 1151, 1086, 1013, 894, 816, 738, 606, 498 cm^{-1}; MS (EI, %): *m/z* = 222.0 (26, $[M]^+$), 207.0 (100).

Methyl 2-(3-*tert*-buthyl-5-formyl-4-hydroxyphenyl) acetate 19:

^{1}H-NMR (500 MHz, $CDCl_3$) δ = 11.70 (s, 1H), 7.38 (d, 1H, *J* = 1.8 Hz), 7.31 (d, 1H, *J* = 1.8 Hz), 3.69 (s, 3H), 3.58 (s, 2H), 1.39 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 197.0, 171.9, 160.3, 138.6, 135.3, 132.2, 124.5, 120.5, 52.2, 40.1, 34.8, 29.1; IR (NaCl): ν = 2959, 2871, 2361, 1735 (C=O), 1653, 1511, 1437, 1391, 1362, 1328, 1267, 1203, 1016, 978, 928, 821, 799, 771, 756, 723, 709, 667, 607, 567, 548, 518 cm^{-1}; MS (EI, %): *m/z* = 249.8 (33, $[M]^+$), 234.9 (100).

2-(3-*tert*-Buthyl-5-formyl-4-hydroxyphenyl) acetic acid 20:

^{1}H-NMR (500 MHz, $CDCl_3$) δ = 11.70 (s, 1H), 9.81 (s, 1H), 7.39 (d, 1H, *J* = 1.8 Hz), 7.31 (d, 1H, *J* = 1.8 Hz), 3.61 (s, 3H), 1.38 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 196.8, 177.2, 160.3, 138.5, 135.2, 132.1, 123.7, 120.2, 39.9, 34.6, 28.9; IR (KBr): ν = 2963, 2868, 1715 (C=O), 1665, 1598, 1440, 1411, 1390, 1364, 1326, 1267, 1220, 1159, 1084, 1029, 983, 949, 926, 870, 819, 770, 706, 609, 565, 548, 513 cm^{-1}; MS (EI, %): *m/z* = 235.8 (32, $[M]^+$), 220.8 (100).

***N*-(3'-*tert*-Butyl-5-(*N*-polyglyceryl)methylamidesalicylidene)-*N'*-(3'',5''-di-*tert*-butylsalicylidene)-(*R,R*)-cyclohexane-(1,2)-diamino-chromium(III) hexafluoroantimonate 21:**

IR (KBr): ν = 3377, 2949, 2864, 1621, 1531, 1502, 1462, 1435, 1408, 1390, 1360, 1319, 1254, 1200, 1168, 1130, 1029, 836, 784, 747, 660, 562, 542 cm^{-1}.

2-Phenyl-2,3-dihydro-4*H*-pyran-4-one 22:

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (d, 1 H, *J* = 6.0 Hz), 7.45 – 7.35 (m, 5 H), 5.52 (d, 1 H, *J* = 6.0 Hz), 5.41 (dd, 1 H, *J* = 14.5, 3.4 Hz), 2.90 (dd, 1 H, *J* = 17.0, 14.5 Hz), 2.66 (dd, 1 H, *J* = 17.0, 3.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.1, 164.8, 164.2, 131.8, 129.7, 129.0, 126.9, 110.0, 83.3, 44.6; IR (KBr): ν = 3440, 2924, 1674 (C=O), 1595, 1455, 1403, 1271,

1228, 1209, 1039, 989, 933, 796, 759, 698 cm^{-1}; FAB-MS (HR): calcd. For $C_{11}H_{11}O_2$ $[M+H]^+$ 175.0681, found 175.0769.

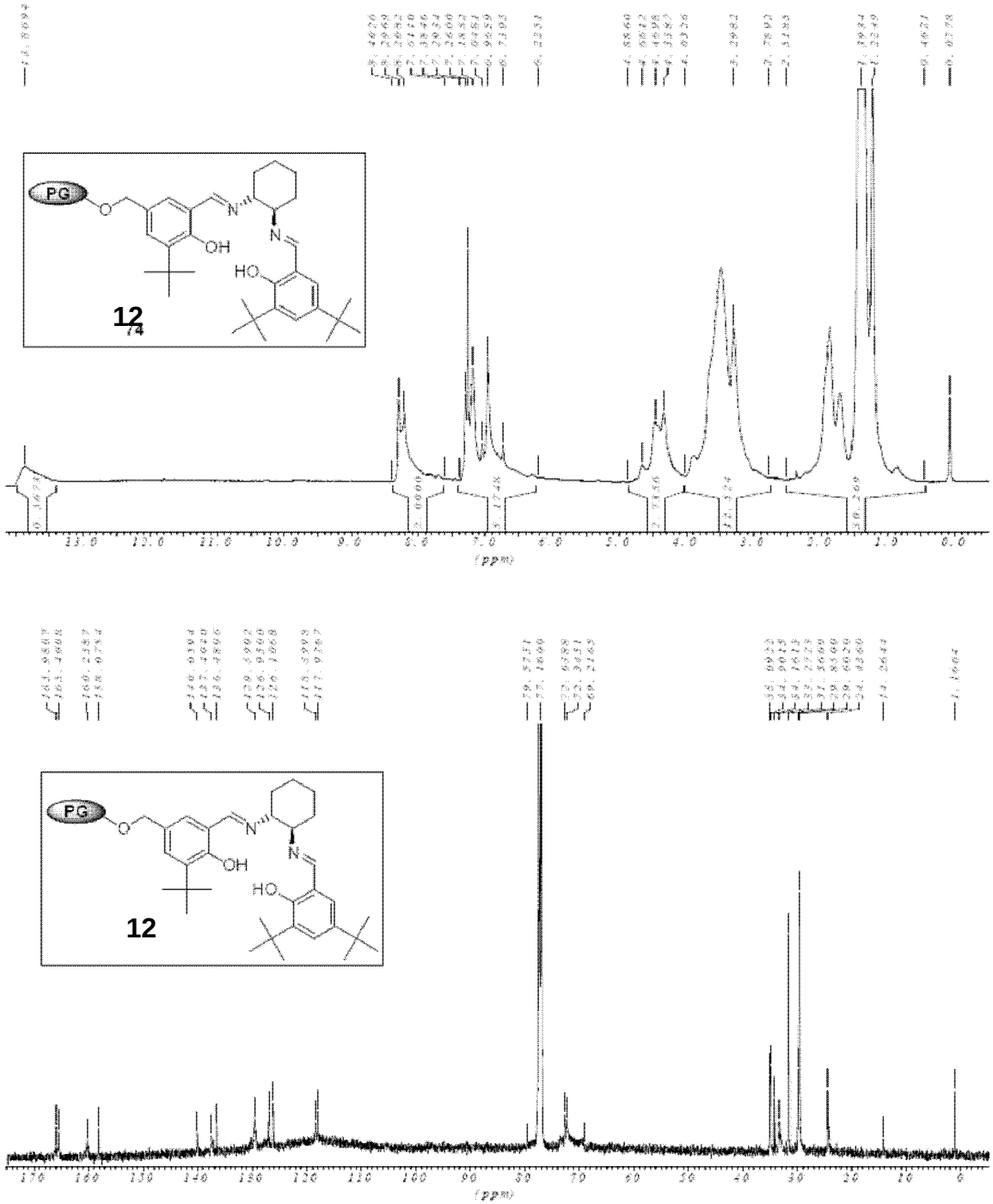

Figure S1. ^1H and ^{13}C NMR spectra of a polyglycerol supported salen ligand **10**

3. References

[1] A. Sunder, R. Hanselmann, H. Frey, R. Mülhaupt, *Macromolecules* **1999**, *32*, 4240-4246

[2] R. Haag, S. Mecking, H. Türk, Patent application DE 10211664A1, 2002.