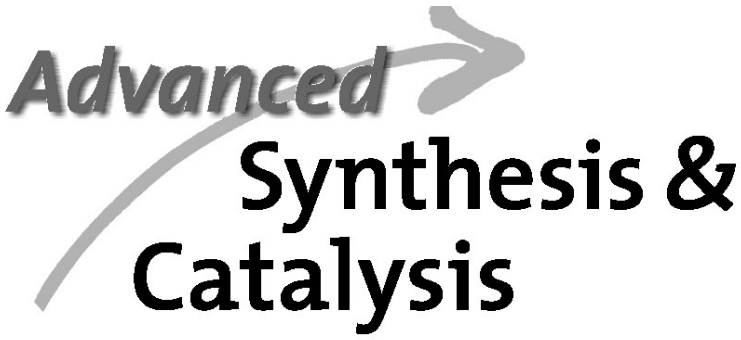

Supporting Information

Supporting Information for

Hybrid Bridged Silsesquioxane as Recyclable Metathesis Catalyst Derived from a Bis-silylated Hoveyda-type Ligand.

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Characterization data of compounds 4-8, 12 and 14.

2,3-Bis(3-*tert*-butyldimethylsiloxypropoxy)benzaldehyde, 4.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.47 (s, 1H), 7.43 (dd, 1H, *J* = 7.5 and 2.0 Hz), 7.15 (m, 2H), 4.27 (t, 2H, *J* = 6.4 Hz), 4.15 (t, 2H, *J* = 6.3 Hz), 3.84 (t, 4H, *J* = 6.3 Hz), 2.07 (quint, 2H, *J* = 6.1 Hz), 2.02 (quint, 2H, *J* = 6.4 Hz), 0.91 (s, 18H), 0.08 (s, 6H), 0.07 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 190.2, 152.2, 151.9, 129.8, 123.6, 118.8, 118.7, 71.5, 65.4, 59.4, 59.2, 33.1, 32.2, 25.6, 18.0, -5,6; IR (ATR): ν = 2953, 2928, 2882, 2856, 1687, 1583, 1470, 1375, 1310, 1248, 1080, 1005, 953, 833, 773, 662 cm^{-1}; MS: *m/z* = 367 (29, M – $C_6H_{15}Si$), 173 (65), 151 (7), 131 (24), 126 (46), 115 (20), 101 (9), 89 (54), 73 (100), 59 (12), 41 (6).

2,3-Bis(3-*tert*-butyldimethylsiloxypropoxy)styrene, 5.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.16-6.98 (m, 3H), 6.88 (dd, 1H, *J* = 8.05 and 1.6 Hz), 5.75 (dd, 1H, *J* = 16.3 and 1.4 Hz), 5.29 (dd, 1H, *J* = 9.6 and 1.4 Hz), 4.10 (t, 2H, *J* = 6.3 Hz), 4.06 (t, 2H, *J* = 6.2 Hz), 3.86 (t, 2H, *J* = 6.3 Hz), 3.85 (t, 2H, *J* = 6.1 Hz), 2.05 (quint, 2H, *J* = 6.1 Hz, 2.00 (quint, 2H, *J* = 6.3 Hz), 0.93 (s, 9H), 0.92 (s, 9H), 0.09 (s, 6H), 0.08 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 152.2, 145.8, 131.7, 131.3, 123.4, 117.4, 114.4, 112.5, 70.1, 65.1, 59.9, 59.4, 33.4, 32.4, 25.7, 18.0, -4.58, -5.63; IR (ATR): ν = 2953, 2928, 2856, 1575, 1461, 1388, 1361, 1296, 1254, 1205, 1082, 1005, 906, 833, 773, 743, 662 cm^{-1}; ESI-MS: 503 $[M + Na]^+$; HRMS: *m/z* = 480.3091 (calcd. for $C_{26}H_{48}Si_2O_4$: 480.3094).

2,3-Bis(3-hydroxypropoxy)styrene, 6.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.15-6.96 (m, 3H), 6.84 (dd, 1H, *J* = 8.0 and 1.6 Hz), 5.76 (dd, 1H, *J* = 17.7 and 1.2 Hz), 5.31 (dd, 1H, *J* = 11.1 and 1.2 Hz), 4.15 (t, 2H, *J* = 5.8 Hz), 4.04 (t, 2H, *J* = 5.8 Hz), 3.90 (t, 2H, *J* = 5.8 Hz), 3.85 (t, 2H, *J* = 5.8 Hz), 3.43 (s, 2H), 2.07 (quint, 2H, *J* = 5.8 Hz), 2.00 (quint, 2H, *J* = 5.8 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 151.7, 145.3, 131.8, 130.8, 124.0, 117.8, 115.1, 112.2, 71.3, 66.3, 60.2, 59.8, 32.3, 31.7; IR (ATR) ν = 3316 (broad), 2878, 1574, 1459, 1415, 1384, 1296, 1263, 1204, 1051, 912, 795, 744 cm^{-1}; MS: *m/z* = 252 [M^+, 17], 194 (M - C_3H_6O, 13), 147 (6), 136 (M - $C_6H_{12}O_2$, 100), 107 (19), 91 (6), 77 (11); elemental analysis: calcd. for $C_{14}H_{20}O_4$: C 66.65, H 7.99; found: C 66.83, H 8.30.

***O*-(3-(2-(3-triethoxysilylpropylcarbamoyloxypropoxy)-6-vinylphenoxy)propyl *N*-(3-triethoxysilylpropyl)carbamate, 7.**

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.09-6.95 (m, 3H), 6.80 (d, 1H, *J* = 7.9 Hz), 5.72 (dd, 1H, *J* = 17.7 and 1.2 Hz), 5.33 (broad s, 1H), 5.27 (dd, 1H, *J* = 11.8 and 1.2 Hz), 5.03 (broad s, 1H), 4.27 (t, 4H, *J* = 3.9 Hz), 4.05 (t, 2H, *J* = 6.1 Hz), 3.99 (t, 2H, *J* = 6.4 Hz), 3.80 (q, 12H, *J* = 7.0 Hz), 3.15 (q, 4H, *J* = 6.4 Hz), 2.10 (apparent sept, 4H, *J* = 7.3 Hz), 1.61 (quint, 4H, *J* = 8.2 Hz), 1.21 (t, 18H, *J* = 7.0 Hz), 0.61 (t, 4H, *J* = 8.4 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 157.1, 157.0, 152.6, 146.2, 132.5, 131.6, 124.3, 118.3, 115.5, 113.0, 70.5, 65.5, 62.0, 58.9, 58.8, 43.9, 30.5, 29.5, 23.7, 18.7, 8.0; IR (ATR): ν = 3332, 2972, 2883, 1699, 1532, 1460, 1389, 1245, 1072, 951, 772 cm^{-1}; HRMS: *m/z* = 746.3842 (calcd. for $C_{34}H_{62}N_2Si_2O_{12}$: 746.3841).

Hybrid material 8a.

S_{BET} = 766 m^2 g^{-1}; IR (KBr): ν = 3418, 2983, 1698, 1538, 1079, 958, 798 cm^{-1}; ^{29}Si CP-MAS NMR: δ = -57.2 (T^2), -64.5 (T^3), -101.2 (Q^3), -109.2 (Q^4); elemental analysis: found: C 12.03, H 2.83, N 0.38, Si 33.8.

Hybrid material 8b.

S_{BET} = 7.5 m^2 g^{-1}; IR (KBr): ν = 3342, 2937, 2884, 1702, 1577, 1542, 1415, 1461, 1267, 1201, 1136, 1045, 913, 778, 746, 695 cm^{-1}; ^{13}C CP-MAS NMR: δ = 157.6 (C=O), 152.5, 145.8, 132.0, 124.0, 117.1, 113.2 (aromatic and C=C), 62.6 (O-C), 44.3 (N-C), 29.8, 24.3 (OCH_2-C and NCH_2-C), 18.8 (residual OCH_2CH_3), 10.8 (Si-C); elemental analysis: calcd. for $C_{22}H_{32}N_2O_9Si_2$: N 5.34; found: N 5.34.

Hybrid material 8c.

S_{BET} < 1 m^2 g^{-1}; IR (KBr): ν = 3354, 3072, 2933, 1711, 1538, 1464, 1260, 1201, 1103, 1066, 953, 776, 691 cm^{-1}; ^{29}Si CP-MAS NMR: δ = -45.3 (T^1), -54.4 (T^2), -67.2 (T^3); elemental analysis: calcd. for $C_{22}H_{32}N_2O_9Si_2$: N 5.34; found: N 5.06.

Hybrid material 8d.

S_{BET} = 757 m^2 g^{-1}, pore diameter = 22-26 Å; IR (KBr): ν = 3440, 2976, 1700, 1538, 1466, 1235, 1079, 953, 798 cm^{-1}; ^{29}Si CP-MAS NMR: δ = -51.6 (T^1), -57.0 (T^2), -65.0 (T^3), -92.3 (Q^2), -100.9 (Q^3), -109.9 (Q^4); elemental analysis: found: C 11.22, H 1.96, N 0.93, Si 33.4.

Hybrid material 8aSi.

S_{BET} = 672 m^2 g^{-1}; IR (KBr): ν = 3415 (residual), 2960, 1709, 1084, 847, 759 cm^{-1}; ^{29}Si CP-MAS NMR: δ = -13.0 (Me_3SiO), -64.7 (T^3), -102.0 (Q^3), -109.7 (Q^4); elemental analysis: found: C 13.90, H 2.65, N 0.65.

Hybrid material 8dSi.

S_{BET} = 546 m^2 g^{-1}, pore diameter = 22 Å; IR (KBr): ν = 2974, 1700, 1528, 1477, 1240, 1087, 848, 759 cm^{-1}; ^{29}Si CP-MAS NMR: δ = -13.5 (Me_3SiO), -64.2 (T^3), -103.0 (Q^3), -109.9 (Q^4); elemental analysis: found: C 15.27, H 3.03, N 0.91.

***N*,*N*-Bis(2-methylallyl)-4-methylbenzenesulfonamide, 12**

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.73 (d, 2H, *J* = 8.2 Hz), 7.30 (d, 2H, *J* = 8.4 Hz), 4.89 (s, 2H), 4.80 (s, 2H), 3.72 (s, 4H), 2.44 (s, 3H), 1.63 (s, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 142.8, 139.8, 137.2, 129.2, 126,9, 114.2, 52.8, 21.2, 19.7. IR (ATR): ν = 3077, 2973, 2917, 1442, 1335, 1156, 1100, 1005, 901, 814, 777, 653 cm^{-1}.

1-Allyloxy-1, 1-diphenyl-2-propyne, 14.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.62-7.60 (m, 4H), 7.37-7.24 (m, 6H), 6.02 (ddt, 1H, *J* = 17.2, 10.4 and 5.2 Hz), 5.39 (dq apparent, 1H, *J* = 17.2 and 1.8 Hz), 5.20 (dq apparent, 1H, *J* = 10.5 and 1.5 Hz), 4.07 (dt, 2H, *J* = 5.2 and 1.5 Hz), 2.91 (s, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 142.9, 134.5, 127.9, 127.5, 126.3, 115.9, 83.0, 79.8, 77.3, 65.7. IR (ATR): ν = 3282, 3060, 3025, 2862, 1488, 1448, 1178, 1052, 1026, 917, 750, 695, 650 cm^{-1}.