Electronic Supplementary Material (ESI) for Dalton Transactions.

C_1-symmetric Si-bridged (2-indenyl)(1-indenyl) *ansa*-metallocenes as efficient ethene/1-hexene copolymerization catalysts

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Supporting information

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Table of contents

Synthesis

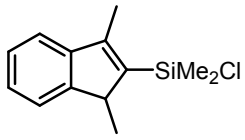
General

All manipulations with air and moisture sensitive compounds were performed either under atmosphere of purified argon using a standard Schlenk technique or in a controlled-atmosphere (nitrogen) glovebox (VAC). NMR spectra were recorded at Bruker AVANCE 400 and Bruker AVANCE-II 600 spectrometers. NOESY experiments were conducted with 250 ms mixing time. Chemical shifts were measured relative to TMS or to residual ^{1}H resonances of the deuterated solvents. C and H microanalyses were made using a Carlo Erba 1106 analyzer. HRMS spectra were measured on Orbitrap Elite instrument. All reagents and solvents were purchased from commercial sources and used as received. Ethereal solvents (THF and diethyl ether) were stored over solid KOH for 24 h and then distilled from sodium/benzophenone under argon atmosphere prior to use. Hydrocarbon solvents (toluene, hexane, methylcyclohexane) were stored over MS 4Å for 24 h prior to use. NMR solvents ($CDCl_3$, CD_2Cl_2) were purchased from DEUTERO and stored over MS 4Å. When used for sensitive compounds, they were additionally degassed by freeze-pump-thaw technique.

Starting indenes

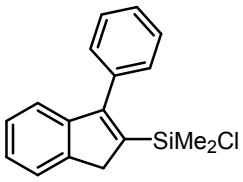
1*H*-Indene (**3**) and 9*H*-fluorene (**15**) were obtained from commercial sources; indenes**4** and **7** were obtained from corresponding ketones according to the literature procedure.[1]Indenes**5** and **6** were synthesized from indan-1-one according to the literature procedures,[2-3]indenes **8–10** and **16** were synthesized by Suzuki coupling between 2-bromo-1*H*-indene and corresponding boronic acids.[4] Indenes **11–14**, **17** and **19** were obtained from the corresponding ketones by Grignard reagent addition – dehydration sequence.[5] Indene **18**[6], 1,3-dimethyl-2-bromo-1*H*-indene[7], 2-bromo-3-phenyl-1*H*-indene[8], and pro-ligand **L26**[9] complex **C26**[9] were obtained as described.

Chlorosilanes



Chloro(1,3-dimethyl-1*H*-inden-2-yl)dimethylsilane (1-SiMe$_2$Cl). To a solution of 1,3-dimethyl-2-bromo-1*H*-indene (50.0 g, 224 mmol, 1 eq) in ether (1300 ml) *t*BuLi (354 ml, 673 mmol, 3 eq) was added at –80°C. Cooling bath was removed, and the mixture was allowed to warm to 0°C. At that point, the double metalation was complete (GC-MS). Then, this mixture was cooled to –80°C, and THF (250 ml) was added followed by $Me_2Si(H)Cl$ (24.6 ml, 224 mmol, 1 eq). The formed mixture was stirred overnight in the cooling bath so the mixture was slowly warmed to ambient temperature. Further on, a aqueous solution of NH_4Cl was added, the organic phase was separated, washed with water and dried over Na_2SO_4. Solvents were then evaporated in vacuo, and the residue was dissolved in hexane. This solution was passed through a pad of silica gel 60 (40–63 um) to remove (1,3-dimethylinden-2-yl)(ethoxy)dimethylsilane which was one of the side-products. Further on, the filtrate was evaporated in vacuo. The obtained crude (1,3-dimethyl-1*H*-inden-2-yl)(dimethyl)silane was used on the next step without additional purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (m, 1H), 7.38–7.31 (m, 2H), 7.27 (td, 1H, J = 7.0 Hz, J = 1.8 Hz), 4.53 (sept, 1H, J = 3.9 Hz), 3.57 (m, 1H), 2.30 (d, 3H, J = 1.9 Hz), 1.38 (d, 3H, J = 7.5 Hz), 0.39 (d, 3H, J = 3.9 Hz), 0.36 (d, 3H, J = 3.9 Hz). To the crude (1,3-dimethyl-1*H*-inden-2-yl)(dimethyl)silanedissloved in THF (50 ml) hexachloroethane (27.0 g, 111 mmol, 0.5 eq) and $PdCl_2$ (0.39 g, 2.20 mmol, 0.01 eq) were added. The obtained mixture was stirred overnight at room temperature, and then all volatiles were removed in vacuo. The residue was distilled in vacuo. This procedure gave 41.0 g (77%) of the title product as a colorless liquid, b.p. 72°C/2 mbar. ^{1}H NMR

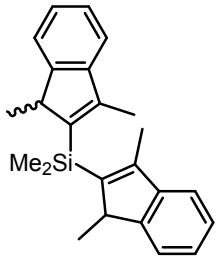
(400 MHz, $CDCl_3$): δ 7.41 (m, 1H), 7.35 (m, 1H), 7.31 (td, 1H, *J* = 7.2 Hz, *J* = 1.2 Hz), 7.26 (td, 1H, *J* = 7.1 Hz, *J* = 1.5 Hz), 3.66 (m, 1H), 2.31 (d, 3H, *J* = 2.0 Hz), 1.38 (d, 3H, *J* = 7.5 Hz), 0.70 (s, 3H), 0.69 (s, 3H).



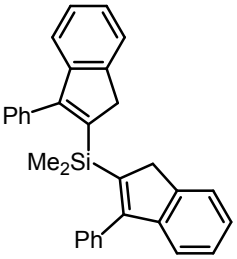
Chlorodimethyl(3-phenyl-1*H*-inden-2-yl)silane (2-$SiMe_2Cl$). To a solution of 2-bromo-3-phenyl-1*H*-indene[8] (27.0 g, 100 mmol, 1 eq.) in ether (1000 ml) *t*BuLi (176 ml, 300 mmol, 3 eq.) was added at –80°C. Cooling bath was removed, and the mixture was allowed to warm to 0°C. Then, this mixture was cooled to –80°C, and THF (250 ml) was added followed by $Me_2Si(H)Cl$ (9.45 g, 100 mmol, 1 eq.). The formed mixture was stirred overnight in the cooling bath so the mixture was slowly warmed to ambient temperature. Further on, a aqueous solution of NH_4Cl was added, the organic phase was separated, washed with water and dried over Na_2SO_4. Solvents were then evaporated in vacuo, and the residue was dissolved in hexane. This solution was passed through a pad of silica gel 60 (40–63 um). The filtrate was evaporated in vacuo. The residue was distilled in vacuo, b.p. 113–127°C/2 mbar. This procedure gave 19.8 g (63%) of the title product as a colorless liquid. It was contaminated with ~21% (w/w) of 3-phenyl-1*H*-indene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.61 (m, 1H), 7.42–7.53 (m, 5H), 7.32–7.35 (m, 3H), 4.36–4.41 (sept, 1H, *J* = 3.8 Hz), 3.66 (s, 2H), 0.20 (d, 6H, *J* = 3.8 Hz). To the above obtained crude dimethyl(3-phenyl-1*H*-indene-2-yl)silane (15.0 g, 47.0 mmol, 1 eq) dissolved in THF (50 ml) hexachloroethane (5.60 g, 24.0 mmol, 0.5 eq) and $PdCl_2$ (84.0 mg, 0.47 mmol, 0.01 eq) were added. The obtained mixture was stirred for 1 h (until the exothermic reaction ceased), and then all volatiles were removed in vacuo. The residue was distilled in vacuo to give 13.0 g (96%) of the title product as a colorless liquid, b.p. 138–142°C/2 mbar. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.61 (m, 1H), 7.42–7.51 (m, 5H), 7.31–7.33 (m, 2H), 7.23–7.25 (m, 1H), 3.77 (m, 2H), 0.39 (s, 6H).

Chloro(1*H*-inden-2-yl)dimethylsilane (Ind$SiMe_2Cl$). To a solution of 2-bromo-1*H*-indene (10.0 g, 51.0 mmol, 1 eq.) in ether (250 ml) cooled to –80°C *t*BuLi (96 ml, 153 mmol, 3 eq.) was added. Cooling bath was removed, and the mixture was allowed to warm to 0°C. Then, this mixture was cooled to –80°C, and THF (50 ml) was added followed by $Me_2Si(H)Cl$ (4.83 g, 51.0 mmol, 1 eq). The formed mixture was stirred overnight in the cooling bath so the mixture was slowly warmed to ambient temperature. Further on, a aqueous solution of NH_4Cl was added, the organic phase was separated, washed with water and dried over Na_2SO_4. Solvents were then evaporated in vacuo, and the residue was dissolved in hexane. This solution was passed through a pad of silica gel 60 (40–63 um). The filtrate was evaporated in vacuo. The residue (6.50 g, 37.0 mmol, 1 eq) was dissolved in THF (10 ml) and hexachloroethane (4.40 g, 18.5 mmol, 0.5 eq) and $PdCl_2$ (66.0 mg, 0.37 mmol, 0.01 eq) were added. The obtained mixture was stirred for 1 h (until the exothermic reaction ceased), and then all volatiles were removed in vacuo. The residue was distilled in vacuo to give 3.70 g (35%) of the title product (contaminated with ca. 25% of chloro(2,3-dihydro-1*H*-inden-2-yl)dimethylsilane) as a colorless liquid, b.p. 87–95°C/2 mbar. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.52 (d, 1H, *J* = 7.3 Hz), 7.46 (d, 1H, *J* = 7.5 Hz), 7.22–7.32 (m, 3H), 3.57 (br.s, 2H), 0.60 (s, 6H).

Pro-ligands



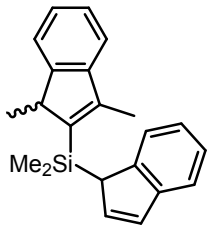
Bis(1,3-dimethyl-1*H*-inden-2-yl)dimethylsilane (L1). To a solution of 1,3-dimethyl-2-bromo-1*H*-indene[7] (5.30 g, 23.7 mmol, 1 eq) in ether (120 ml) *t*BuLi (71 ml, 71.1 mmol, 3 eq) was added at –80°C. Cooling bath was removed, and the mixture was allowed to warm to 0°C. At that point the double metalation was complete (GC-MS). Then, this mixture was cooled to –80°C, and Me_2SiCl_2 (1.43 ml, 11.9 mmol, 0.5 eq) was added. The formed mixture was stirred overnight in the cooling bath so the mixture was slowly warmed to ambient temperature. Further on, a aqueous solution of NH_4Cl was added, the organic phase was separated, washed with water and dried over Na_2SO_4. Solvents were then evaporated in vacuo, and the residue was purified by flash chromatography on silica gel 60 (40–63 um) using hexane-dichloromethane mixture (10:1, v/v) as eluent to afford 7.1 g (87%) of the title compound as yellow oil. HRMS (ESI): calcd. for $C_{24}H_{29}Si$ $[M+H]^+$: 345.2033; found 345.2040. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.48 (m, 2H), 7.33–7.37 (m, 4H), 7.25–7.30 (m, 2H), 3.62–3.73 (m, 2H), 2.23 (d, 3H, J = 1.8 Hz), 2.18 (d, 3H, J = 1.8 Hz), 1.38 (d, 3H, J = 7.5 Hz), 1.38 (d, 3H, J = 7.5 Hz), 0.61 (s 3H), 0.58 (s+s, 6H), 0.54 (s, 3H).



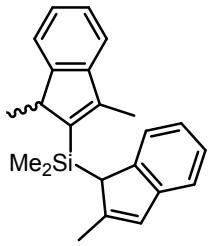
Dimethylbis(3-phenyl-1H-inden-2-yl)silane (L2). *t*BuLi (65.0 ml, 111 mmol, 3 eq) was added dropwise to a solution of 2-bromo-3-phenyl-1*H*-indene (10.0 g, 36.9 mmol, 1 eq) in dry ether (250 ml) at –80°C, and the formed mixture was stirred for 1 h at –80°C. Me_2SiCl_2 (2.38 g, 18.5 mmol, 0.5 eq) was added at –80°C, the obtained mixture was allowed to warm slowly to room temperature and stirred overnight. The resulting mixture was poured into water, the organic layer was separated, and the aqueous layer was extracted with ether (2×100 ml). The combined extract was dried over anhydrous sodium sulfate and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40–63 um) using hexane-dichloromethane mixture (10:1, vol.) as eluent to afford 1.60 g (20%) of the title compound as viscous oil. HRMS (ESI): calcd. for $C_{32}H_{29}Si$ $[M+H]^+$: 441.2033; found 441.2036. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.49 (m, 2H), 7.22–7.31 (m, 14H), 7.12–7.15 (m, 2H), 3.39 (s, 4H), –0.04 (s, 6H).

General procedure 1 for synthesis of pro-ligands. *n*-Butyllithium in hexanes (1 eq) was added dropwise to a solution of an indene (1 eq) in dry ether at ambient temperature and the formed mixture was stirred overnight. Chlorosilane **1-SiMe$_2$Cl**, **2-SiMe$_2$Cl** or **IndSiMe$_2$Cl** (1 eq) was added at –80°C, the obtained mixture was allowed to warm slowly to room temperature and then stirred overnight. The resulting mixture was poured into water, the organic layer was separated, and the aqueous layer was extracted with ether. The combined extract was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40–63 um) using hexane-dichloromethane mixture (10:1, v/v) as eluent.

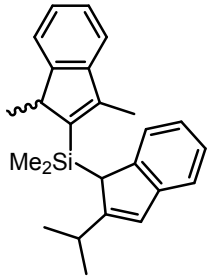
General procedure 2 for synthesis of pro-ligands. *n*-Butyllitium in hexanes (1 eq) was added dropwise to a solution of an indene (1 eq) in dry ether at ambient temperature and the formed mixture was stirred overnight. 4-Dimethylaminopyridine (DMAP, 0.02 eq) followed by chlorosilane**1-SiMe$_2$Cl** or **2-SiMe$_2$Cl** (1 eq) were added at –80°C.The obtained mixture was allowed to warm slowly to room temperature and then stirred overnight. The resulting mixture was poured into water, the organic layer was separated, and the aqueous layer was extracted with ether. The combined extract was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40–63 um) using hexane-dichloromethane mixture (10:1, v/v) as eluent.



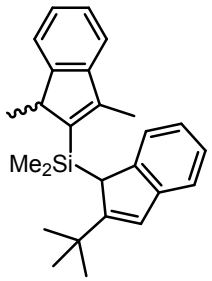
(1,3-Dimethyl-1*H*-inden-2-yl)(1*H*-inden-1-yl)dimethylsilane (L3). According to *General procedure 1*, 5.50 g (81%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from 2.50 g (21.6 mmol) of **3** in 100 ml of ether, 8.6 ml (21.6 mmol, 2.5 M) of *n*BuLi, and 5.10 g (21.6 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{22}H_{25}Si$ $[M+H]^+$: 317.1720; found: 317.1714. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.48 (m, 14H), 7.16 (t, 1H, J = 7.5 Hz), 7.09 (t, 1H, J = 7.5 Hz), 6.93–6.97 (m, 2H), 6.68 (dd, 1H, J = 5.2 Hz, J = 1.9 Hz), 6.60 (dd, 1H, J = 5.2 Hz, J = 1.9 Hz), 3.86 (m, 2H), 3.55–3.61 (m, 2H), 2.26 (d, 3H, J = 1.8 Hz), 2.22 (d, 3H, J = 2.0 Hz), 1.38 (d, 3H, J = 7.5 Hz), 1.36 (d, 3H, J = 7.5 Hz), 0.34 (s, 3H), 0.24 (s, 3H), –0.02 (s, 3H), –0.09 (s, 3H).



(1,3-Dimethyl-1*H*-inden-2-yl)(2-methyl-1*H*-inden-1-yl)dimethylsilane (L4). According to *General procedure 1*, 5.49 g (86%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from 2.50 g (19.2 mmol) of **4** in 70 ml of dry ether, 7.7 ml (19.2 mmol, 2.5 M) of *n*BuLi and 4.55 g (19.2 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{23}H_{27}Si$ $[M+H]^+$: 331.1877; found: 331.1882. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.10–7.37 (m, 12H), 7.03 (td, 1H, J = 7.3 Hz, J = 1.0 Hz), 6.93 (td, 1H, J = 7.3 Hz, J = 1.0 Hz), 6.57 (m, 2H), 3.70 (s, 1H), 3.66 (s, 1H), 3.57 (m, 2H), 2.31 (d, 3H, J = 1.8 Hz), 2.19 (s, 3H), 2.11 (d, 3H, J = 2.0 Hz), 2.01 (s, 3H), 1.41 (d, 3H, J = 7.5 Hz), 1.28 (d, 3H, J = 7.5 Hz), 0.34 (s, 3H), 0.30 (s, 3H), –0.05 (s, 3H), –0.11 (s, 3H).

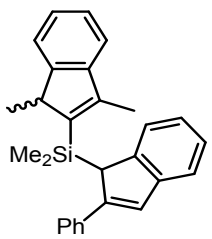


(1,3-Dimethyl-1*H*-inden-2-yl)(2-isopropyl-1*H*-inden-1-yl)dimethylsilane (L5). According to *General procedure 1*, 2.10 g (98%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from 1.00 g (6.30 mmol) of **5** in 50 ml of dry ether, 2.6 ml (6.30 mmol, 2.44 M) of *n*BuLi and 1.50 g (6.30 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{25}H_{31}Si$ $[M+H]^+$: 359.2190; found: 359.2192. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.47 (m, 2H), 7.16–7.39 (m, 11H), 7.12 (d, 1H, J = 7.5 Hz), 7.06 (t, 1H, J = 7.4 Hz), 6.95 (t, 1H, J = 7.5 Hz), 6.64 (s, 1H), 6.62 (s, 1H), 3.90–3.91 (m), 3.53–3.61 (m, 2H), 2.81 (m, 1H), 2.66 (m, 1H), 2.33 (br.s, 3H), 2.15 (br.s, 3H), 1.42 (d, 3H, J = 7.4 Hz), 1.31 (s, 3H), 1.30 (s, 3H), 1.27 (d, 3H, J = 6.5 Hz), 1.19 (d, 3H, J = 6.9 Hz), 1.04 (d, 3H, J = 6.8 Hz), 0.33 (s, 3H), 0.30 (s, 3H), –0.10 (s+s, 6H).

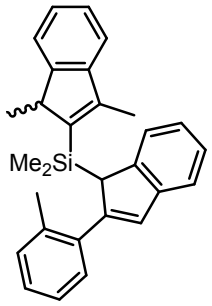


(1,3-Dimethyl-1*H*-inden-2-yl)(2-(*tert*-butyl)-1*H*-inden-1-yl)dimethylsilane (L6). According to *General procedure 2*, 3.50 g (81%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from 2.00 g (11.6 mmol) of **6** in 60 ml of dry ether, 8.7 ml (11.6 mmol, 2.5 M) of *n*BuLi, 0.03 g (0.23 mmol) of DMAP and 2.74 g (11.6 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{26}H_{33}Si$ $[M+H]^+$: 373.2346; found: 373.2343. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, 1H, J = 7.3 Hz), 7.26–7.42 (m, 10H), 7.12–7.20 (m, 2H), 6.98 (td, 1H J = 7.5 Hz, J = 1.0 Hz), 6.93 (d, 1H, J = 7.6 Hz) 6.83 (td, 1H J = 7.5 Hz, J = 1.0 Hz), 6.79 (s, 1H), 6.74 (s, 1H), 4.04 (s, 1H), 3.94 (s, 1H), 3.48–3.61 (m, 2H), 2.45 (d, 3H, J = 1.9 Hz), 2.09 (d, 3H, J = 1.9 Hz), 1.43 (d, 3H, J = 7.5 Hz), 1.37 (s, 9H), 1.24 (s, 9H), 1.14 (d, 3H, J = 7.4 Hz), 0.59 (s, 3H), 0.12 (s, 3H), 0.09 (s, 3H), –0.35 (s, 3H).

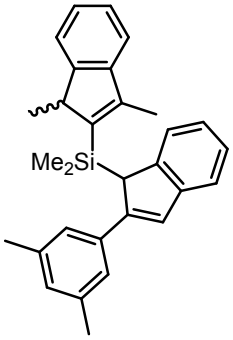
(1,3-Dimethyl-1*H*-inden-2-yl)(2-phenyl-1*H*-inden-1-yl)dimethylsilane (L7). According to *General procedure 1*, 3.16 g (62%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from 2.5 g (13.0 mmol) of **7** in 50 ml of dry ether, 5.3 ml (13.0 mmol, 2.5 M) of *n*BuLi and 3.08 g (13.0 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{28}H_{29}Si$ $[M+H]^+$: 393.2033; found: 393.2040. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 2H), 7.46 (d, 2H, J = 7.6 Hz), 7.06–7.43 (m, 23H), 7.00 (td, 1H, J = 7.3 Hz, J = 1.0 Hz), 4.43 (s, 1H), 4.42 (s, 1H), 3.45 (m, 1H), 3.02 (m, 1H), 2.20 (d,



3H, *J* = 1.6 Hz), 2.09 (d, 3H, *J* = 1.6 Hz), 1.34 (d, 3H, *J* = 7.5 Hz), 1.14 (d, 3H, *J* = 7.5 Hz), 0.08 (s, 3H), 0.04 (s, 3H), –0.22 (s, 3H), –0.35 (s, 3H).

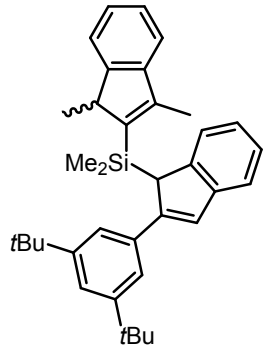


(1,3-Dimethyl-1*H*-inden-2-yl)(2-(*o*-tolyl)-1*H*-inden-1-yl)dimethylsilane (L8). According to *General procedure 1*, 2.10 g (98%) of the title compound as a ca. 1.5:1 mixture of diastereomers was obtained from 1.00 g (6.30 mmol) of **8** in 30 ml of dry ether, 2.6 ml (6.30 mmol, 2.44 M) of *n*BuLi and 1.50 g (6.30 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{29}H_{31}Si$ $[M+H]^+$: 407.2190; found: 407.2194. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.02–7.48 (m, 23H), 6.99 (td, 1H, *J* = 7.5 Hz, *J* = 1.0 Hz), 6.96 (s, 1H), 6.93 (s, 1H), 4.47 (s, 1H), 4.42 (s, 1H), 3.46 (m, 1H), 3.15 (m, 1H), 2.51 (s, 3H), 2.45 (s, 3H), 2.27 (d, 3H, *J* = 1.9 Hz), 2.08 (d, 3H, *J* = 1.9 Hz), 1.40 (d, 3H, *J* = 7.5 Hz), 1.08 (d, 3H, *J* = 7.5 Hz), –0.05 (s, 3H), –0.18 (s, 3H), –0.25 (s, 3H), –0.34 (s, 3H).

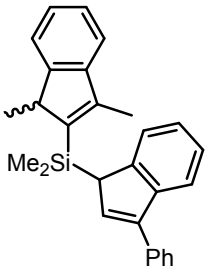


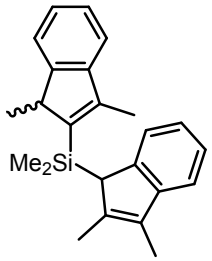
(1,3-Dimethyl-1*H*-inden-2-yl)(2-(3,5-dimethylphenyl)-1*H*-inden-1-yl)dimethylsilane (L9). According to *General procedure 1*, 1.85 g (64%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from 1.50 g (6.80 mmol) of **9** in 40 ml of dry ether, 2.8 ml (6.80 mmol, 2.45 M) of *n*BuLi and 1.60 g (6.80 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{30}H_{33}Si$ $[M+H]^+$: 421.2346; found: 421.2344. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.43–7.46 (m, 2H), 7.38–7.41 (m, 2H), 7.08–7.34 (m, 15H), 6.97–7.01 (m, 3H), 6.88 (s, 1H), 6.68 (s, 1H), 4.38 (s, 2H), 3.44 (m, 1H), 2.92 (m, 1H), 2.31 (s, 6H), 2.22 (d, 3H, *J* = 1.7 Hz), 2.10 (d, 3H, *J* = 1.7 Hz), 2.04 (s, 6H), 1.30 (d, 3H, *J* = 7.4 Hz), 1.15 (d, 3H, *J* = 7.5 Hz), 0.19 (s, 3H), 0.05 (s, 3H), –0.27 (s, 3H), –0.28 (s, 3H).

(1,3-Dimethyl-1*H*-inden-2-yl)(2-(3,5-di-*tert*-butylphenyl)-1*H*-inden-1-yl)-dimethylsilane (L10). According to *General procedure 1*, 1.50 g (60%) of the title compound as a ca. 2:3 mixture of diastereomers was obtained from 1.50 g (5.00 mmol) of **10** in 40 ml of dry ether, 2.50 ml (5.00 mmol, 2.45 M) of *n*BuLi and 1.20 g (5.00 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{36}H_{45}Si$ $[M+H]^+$: 505.3285; found: 505.3293. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.15–7.45 (m, 20H), 7.05–7.10 (m, 3H), 6.99 (t, 1H, *J* = 7.4 Hz), 4.46 (s, 1H), 4.44 (s, 1H), 3.42 (m, 1H), 3.12 (m, 1H), 2.12 (d, 3H, *J* = 1.8 Hz), 2.09 (d, 3H, *J* = 1.8 Hz), 1.36 (s, 18H), 1.29 (d, 3H, *J* = 7.5 Hz), 1.36 (s, 18H), 1.17 (d, 3H, *J* = 7.5 Hz), –0.01 (s, 3H), –0.07 (s, 3H), –0.16 (s, 3H), –0.33 (s, 3H).

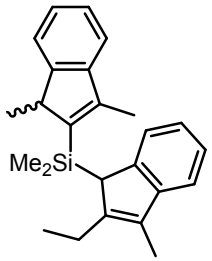


(1,3-Dimethyl-1*H*-inden-2-yl)(3-phenyl-1*H*-inden-1-yl)dimethylsilane (L11). According to *General procedure 1*, 5.45 g (89%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from **11** in 100 ml of dry ether, 6.2 ml (15.6 mmol, 2.5 M) of *n*BuLi and 3.70 g (15.6 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{28}H_{29}Si$ $[M+H]^+$: 393.2033; found: 393.2040. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.67–7.71 (m, 2H), 7.60–7.63 (m, 4H), 7.20–7.50 (m, 19H), 7.17 (t, 1H, *J* = 7.3 Hz), 6.74 (d, 1H, *J* = 2.0 Hz), 6.67 (d, 1H, *J* = 2.0 Hz), 3.99 (m, 2H), 3.60 (m, 2H), 2.32 (d, 3H, *J* = 1.8 Hz), 2.23 (d, 3H, *J* = 2.0 Hz), 1.42 (d, 3H, *J* = 7.5 Hz), 1.37 (d, 3H, *J* = 7.3 Hz), 0.38 (s, 3H), 0.32 (s, 3H), 0.04 (s, 3H), –0.03 (s, 3H).

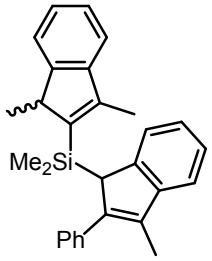




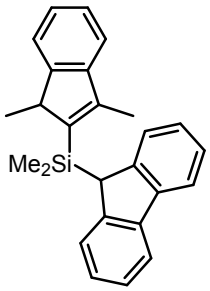
(1,3-Dimethyl-1*H*-inden-2-yl)(2,3-dimethyl-1*H*-inden-1-yl)dimethylsilane (L12). According to *General procedure 1*, 2.10 g (61%) of the title compound as a ca. 2:3 mixture of diastereomers was obtained from 1.50 g (10.0 mmol) of **12** in 50 ml of dry ether, 4.1 ml (10.0 mmol, 2.45 M) of *n*BuLi and 2.37 g (10.0 mmol) of **1-SiMe$_2$Cl**. HRMS: calcd. for $C_{24}H_{29}Si$ $[M+H]^+$: 345.2033; found: 345.2035. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.47 (m. 2H), 7.22–7.38 (m, 11H), 7.14 (d, 1H, J = 7.4 Hz), 7.08 (td, 1H, J = 7.3 Hz, J = 1.2 Hz), 6.99 (td, 1H, J = 7.3 Hz, J = 1.0 Hz), 3.67 (s, 1H), 3.63 (s, 1H), 3.54–3.62 (m, 2H), 2.32 (d, 3H, J = 1.9 Hz), 2.14 (d, 3H, J = 1.9 Hz), 2.11–2.15 (m, 9H), 1.99 (s, 3H), 1.43 (d, 3H, J = 7.5 Hz), 1.30 (d, 3H, J = 7.4 Hz), 0.33 (s, 3H), 0.32 (s, 3H), –0.097 (s, 3H), –0.100 (s, 3H).



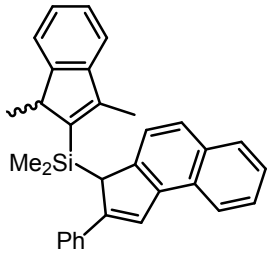
(1,3-Dimethyl-1*H*-inden-2-yl)(2-ethyl-3-methyl-1*H*-inden-1-yl)dimethylsilane (L13). According to *General procedure 1*, 2.10 g (62%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from 1.50 g (9.50 mmol) of **13** in 50 ml of dry ether, 3.9 ml (9.50 mmol, 2.45 M) of *n*BuLi and 2.25 g (9.50 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{25}H_{31}Si$ $[M+H]^+$: 359.2190; found: 359.2186. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.19–7.37 (m, 11H), 7.10 (d, 1H, J = 7.5 Hz), 7.06 (t, 1H, J = 7.4 Hz), 6.95 (t, 1H, J = 7.4 Hz), 3.79 (s, 1H), 3.77 (s, 1H), 3.50–3.57 (m, 2H), 22.67–2.76 (m, 1H), .58–2.67 (m, 1H), 2.34–2.43 (m, 1H), 2.28 (s, 3H), 2.19–2.27 (m 1H), 2.11 (s+s+s, 9H), 1.38 (d, 3H, J = 7.5 Hz), 1.27 (d, 3H, J = 7.3 Hz), 1.13 (t, 3H, J = 7.5 Hz), 0.97 (t, 3H, J = 7.4 Hz), 0.31 (s, 3H), 0.26 (s, 3H), –0.13 (s, 3H), –0.17 (s, 3H).



(1,3-Dimethyl-1*H*-inden-2-yl)(3-methyl-2-phenyl-1*H*-inden-1-yl)dimethylsilane (L14). According to *General procedure 1*, 2.70 g (92%) of the title compound as a ca. 2:3 mixture of diastereomers was obtained from 1.50 g (7.27 mmol) of **14** in 50 ml of dry ether, 3.0 ml (7.27 mmol, 2.5 M) of *n*BuLi and 1.72 g (7.27 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{29}H_{31}Si$ $[M+H]^+$: 407.2190; found: 407.2198. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00–7.45 (m, 26H), 4.33 (m, 1H), 4.26 (m, 1H), 3.44 (m, 1H), 3.03 (m, 1H), 2.31 (d, 3H, J = 1.8 Hz), 2.29 (d, 3H, J = 1.8 Hz), 2.27 (d, 3H, J = 1.8 Hz), 2.04 (d, 3H, J = 1.8 Hz), 1.39 (d, 3H, J = 7.6 Hz), 1.05 (d, 3H, J = 7.6 Hz), 0.03 (s, 3H), –0.22 (s, 3H), –0.30 (s, 3H), –0.39 (s, 3H).

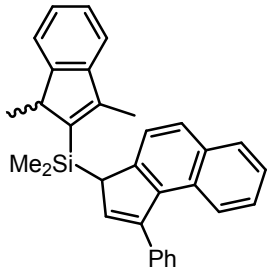


(1,3-Dimethyl-1*H*-inden-2-yl)(9*H*-fluoren-9-yl)dimethylsilane (L15). According to *General procedure 1*, 2.10 g (93%) of the title compound was obtained from 1.00 g (6.00 mmol) of **15** in 60 ml of dry ether, 2.5 ml (6.00 mmol, 2.5 M) of *n*BuLi, and 1.42 g (6.00 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{26}H_{27}Si$ $[M+H]^+$: 367.1877; found: 367.1880. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.86 (m, 2H), 7.48 (d, 1H, J = 7.5 Hz), 7.43 (d, 1H, J = 7.2 Hz), 7.23–7.38 (m, 7H), 7.15 (t, 1H, J = 7.5 Hz), 4.18 (s, 1H), 3.53 (q, 1H, J = 7.4 Hz), 2.13 (s, 3H), 1.32 (d, 3H, J = 7.4 Hz), 0.31 (s, 3H), –0.26 (s, 3H).

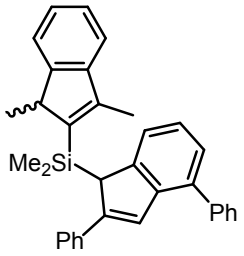


(1,3-Dimethyl-1*H*-inden-2-yl)(2-phenyl-3*H*-cyclopenta[*a*]naphthalen-3-yl)-dimethylsilane (L16). According to *General procedure 1*, 0.70 g (39%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from 1.00 g (4.10 mmol) of **16** in 40 ml of dry ether, 1.7 ml (4.10 mmol, 2.45 M) of *n*BuLi and 0.97 g (4.10 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{32}H_{31}Si$ $[M+H]^+$: 443.2190; found: 443.2198. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, 2H, J = 8.1 Hz), 7.87 (t, 2H, J = 8.8 Hz), 7.76 (s, 1H), 7.75 (s, 1H), 7.09–7.65 (m, 26H), 4.67 (s, 1H), 4.65 (s, 1H), 3.47 (m, 1H), 3.04 (m, 1H), 2.24 (d, 3H, J = 1.7 Hz), 2.09 (d, 3H, J =

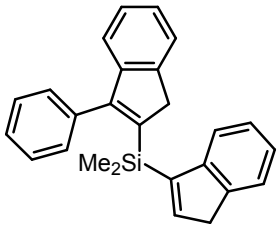
1.7 Hz), 1.37 (d, 3H, *J* = 7.5 Hz), 1.14 (d, 3H, *J* = 7.5 Hz), 0.08 (s, H), –0.01 (s, 3H), –0.25 (s, 3H), –0.40 (s, 3H).



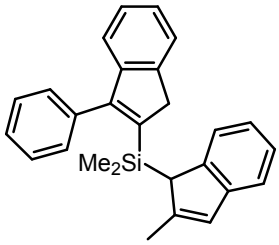
(1,3-Dimethyl-1*H*-inden-2-yl)(1-phenyl-3*H*-cyclopenta[a]naphthalen-3-yl)-dimethylsilane (L17). According to *General procedure 1*, 5.68 g (89%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from 3.50 g (14.4 mmol) of **17** in 70 ml of dry ether, 5.8 ml (14.4 mmol, 2.5 M) of *n*BuLi and 3.42 g (14.4 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{32}H_{31}Si$ $[M+H]^+$: 443.2190; found: 443.2187. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.89 (m, *2H*), 7.80 (m, 2H), 7.70 (d, 1H, *J* = 8.5 Hz), 7.60–7.64 (m, 2H), 7.20–7.50 (m, 23H), 6.67 (d, 1H, *J* = 1.8 Hz), 6.60 (d, 1H, *J* = 1.8 Hz), 4.17 (d, 1H, *J* = 1.8 Hz), 4.16 (d, 1H, *J* = 1.8 Hz), 3.65–3.69 (m, 2H), 2.32 (d, 3H, *J* = 2.0 Hz), 2.19 (d, 3H, *J* = 1.8 Hz), 1.41 (d, 3H, *J* = 7.5 Hz), 1.37 (d, 3H, *J* = 7.5 Hz), 0.40 (s, 3H), 0.36 (s, 3H), 0.04 (s, 3H), –0.02 (s, 3H).



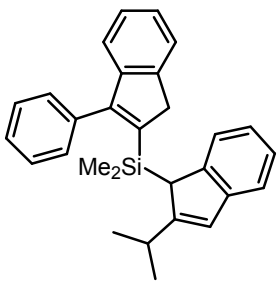
(1,3-Dimethyl-1*H*-inden-2-yl)(2,4-diphenyl-1*H*-inden-1-yl)dimethylsilane (L18). According to *General procedure 1*, 1.10 g (67%) of the title compound as a ca. 1:1 mixture of diastereomers was obtained from 0.95 g (3.54 mmol) of **17** in 40 ml of dry ether, 1.5 ml (3.54 mmol, 2.5 M) of *n*BuLi and 0.84 g (3.54 mmol) of **1-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{34}H_{33}Si$ $[M+H]^+$: 469.2346; found: 469.2351. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.07–7.59 (m, 36H), 4.53 (s, 1H), 4.52 (s, 1H), 3.49 (m, 1H), 3.01 (m, 1H), 2.19 (d, 3H, *J* = 1.7 Hz), 2.12 (d, 3H, *J* = 1.7 Hz), 1.37 (d, 3H, *J* = 7.5 Hz), 1.16 (d, 3H, *J* = 7.5 Hz), 0.11 (s, 3H), 0.02 (s, 3H), –0.14 (s, 3H), –0.26 (s, 3H).



(3-Phenyl-1*H*-inden-2-yl)(1*H*-inden-1-yl)dimethylsilane (L19). According to *General procedure 1*, 5.50 g (81%) of the title compound was obtained from 2.50 g (21.6 mmol) of **3** in 100 ml of ether, 8.6 ml (21.6 mmol, 2.5 M) of *n*BuLi, and 5.10 g (21.6 mmol) of **2-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{26}H_{25}Si$ $[M+H]^+$: 365.1720; found: 365.1718. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.49 (t, 2H, *J* = 6.3 Hz), 7.14–7.34 (m, 11H), 6.72 (t, 1H, *J* = 1.8 Hz), 3.62 (s, 2H), 3.39 (m, 2H), 0.29 (s, 6H).

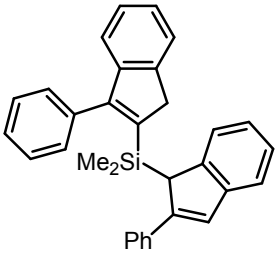


(3-Phenyl-1*H*-inden-2-yl)(2-methyl-1*H*-inden-1-yl)dimethylsilane (L20). According to *General procedure 1*, 4.20 g (72%) of the title compound was obtained from 2.00 g (15.4 mmol) of **4** in 60 ml of ether, 6.1 ml (15.4 mmol, 2.5 M) of *n*BuLi, and 4.38 g (15.4 mmol) of **2-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{27}H_{27}Si$ $[M+H]^+$: 379.1877; found: 379.1881. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.52 (m, 1H), 7.34–7.45 (m, 5H), 7.24–7.30 (m, 3H), 7.15–7.18 (m, 3H), 6.99 (t, 1H, *J* = 7.5 Hz), 6.51 (br.s, 1H), 3.47 (s, 2H), 3.37 (s, 1H), 2.06 (br.s, 3H), –0.08 (s, 3H), –0.14 (s, 3H).

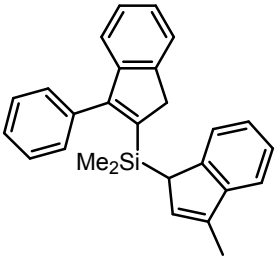


(3-Phenyl-1*H*-inden-2-yl)(2-isopropyl-1*H*-inden-1-yl)dimethylsilane (L21). According to *General procedure 2*, 3.50 g (78%) of the title compound was obtained from 1.75 g (11.0 mmol) of **5** in 60 ml of dry ether, 4.5 ml (11.0 mmol, 2.5 M) of *n*BuLi, 0.03 g (0.22 mmol) of DMAP and 3.16 g (11.0 mmol) of **2-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{29}H_{30}Si$ $[M+H]^+$: 407.2190; found: 407.2191. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.53 (m, 1H), 7.31–7.45 (m, 6H) 7.29 (dd, 1H, *J* = 7.3 Hz, *J* = 1.4 Hz), 7.27 (dd, 1H, *J* = 7.1 Hz, *J* = 1.6 Hz), 7.12–7.19

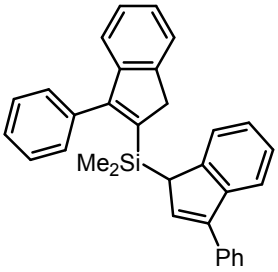
(m, 3H), 6.98 (td, 1H, *J* = 7.4 Hz, *J* = 1.1 Hz), 6.55 (s, 1H), 3.60 (s, 1H), 3.45 (s, 2H), 2.63 (m, 1H), 1.26 (d, 3H, *J* = 6.7 Hz), 1.00 (d, 3H, *J* = 6.9 Hz), –0.04 (s, 3H), –0.24 (s, 3H).



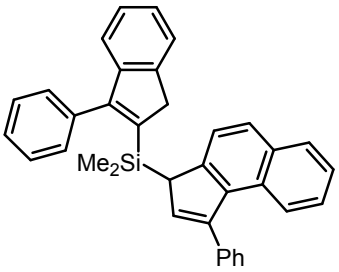
(3-Phenyl-1*H*-inden-2-yl)(2-phenyl-1*H*-inden-1-yl)dimethylsilane (L22). According to *General procedure 1*, 5.00 g (72%) of the title compound was obtained from 3.00 g (15.6 mmol) of **7** in 100 ml of ether, 6.2 ml (15.6 mmol, 2.5 M) of *n*BuLi, and 4.44 g (15.6 mmol) of **2-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{32}H_{29}Si$ $[M+H]^+$: 441.2033; found: 441.2038. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.14–7.47 (m, 17H), 7.07 (s, 1H), 7.02 (t, 1H, *J* = 7.3 Hz), 4.10 (s, 1H), 3.35 (d, 2H, *J* = 23.1 Hz), 3.20 (d, 2H, *J* = 23.1 Hz), –0.29 (s, 3H), –0.52 (s, 3H).



(3-Phenyl-1*H*-inden-2-yl)(3-methyl-1*H*-inden-1-yl)dimethylsilane (L23). According to *General procedure 1*, 2.70 g (47%) of the title compound was obtained from 2.00 g (15.4 mmol) of **19** in 60 ml of ether, 6.2 ml (15.4 mmol, 2.5 M) of *n*BuLi, and 4.38 g (15.4 mmol) of **2-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{27}H_{27}Si$ $[M+H]^+$: 379.1877; found: 379.1873. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.52 (m, 1H), 7.34–7.43 (m, 6H), 7.23–7.28 (m, 4H), 7.10–7.16 (m, 2H), 6.19 (m, 1H), 3.48 (br.s, 2H), 3.38 (m, 1H), 2.18 (m, 3H), –0.15 (s, 3H), –0.17 (s, 3H).

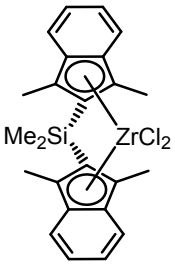


(3-Phenyl-1*H*-inden-1-yl)(3-phenyl-1*H*-inden-2-yl)dimethylsilane (L24). According to *General procedure 1*, 5.30 g (77%) of the title compound was obtained from 3.00 g (15.6 mmol) of **11** in 100 ml of ether, 6.2 ml (15.6 mmol, 2.5 M) of *n*BuLi, and 4.44 g (15.6 mmol) of **2-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{32}H_{29}Si$ $[M+H]^+$: 441.2033; found: 441.2042. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.62 (d, 1H, *J* = 7.4 Hz), 7.51–7.54 (m, 3H), 7.31–7.43 (m, 9H) 7.22–7.28 (m, 3H), 7.13–7.18 (m, 2H), 6.57 (d, 1H, *J* = 1.7 Hz), 3.62 (d, 1H, *J* = 1.7 Hz), 3.52 (s, 2H), –0.10 (s, 3H), –0.13 (s, 3H).



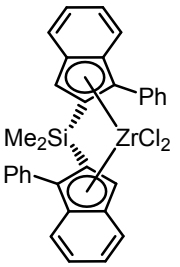
(3-Phenyl-1*H*-inden-2-yl)(1-phenyl-3*H*-cyclopenta[*a*]naphthalen-3-yl)dimethylsilane (L25). According to *General procedure 1*, 5.10 g (73%) of the title compound was obtained from 3.50 g (14.4 mmol) of **17** in 100 ml of ether, 5.8 ml (14.4 mmol, 2.5 M) of *n*BuLi, and 4.10 g (14.4 mmol) of **2-SiMe$_2$Cl**. HRMS (ESI): calcd. for $C_{36}H_{31}Si$ $[M+H]^+$: 491.2190; found: 491.2184. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.87 (d, 1H, *J* = 8.2 Hz), 7.75 (d, 1H, *J* = 8.6 Hz), 7.63 (d, 1H, *J* = 8.4 Hz), 7.52–7.54 (m, 2H), 7.33–7.47 (m, 12H), 7.27–7.29 (m, 2H), 7.16–7.21 (m, 2H), 6.54 (d, 1H, *J* = 1.7 Hz), 3.84 (d, 1H, *J* = 1.7 Hz), 3.57 (s, 2H), –0.06 (s, 3H), –0.11 (s, 3H).

Complexes

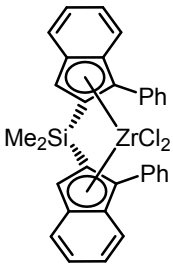


C1. *n*-Butyllithium in hexanes (9.0 ml, 22.4 mmol, 2 eq) was added dropwise to a solution of **L1** (3.87 g, 11.2 mmol, 1 eq) in ether at r. t., and the formed mixture was stirred overnight. Further on, $ZrCl_4$ (2.60 g, 11.2 mmol, 1 eq) was added at –80°C, and the obtained mixture was allowed to warm slowly to room temperature and then stirred overnight. The resulting mixture was evaporated to dryness, toluene was added to the residue, and the obtained suspension was evaporated to dryness again. Toluene was added to the residue followed by MeMgBr (3.7 ml, 112 mmol, 10 eq) and the resulting suspension was stirred overnight at 90°C. The reaction mixture was evaporated to dryness, redissolved in toluene and filtered through a pad of Celite 503. The obtained filtrate was evaporated until the precipitation started. Crystals precipitated from this solution were collected, washed with toluene, and then dried in vacuum. Yield of the title compound (yellow solid) was 2.20 g (42%). The product contained 4 eq of cocrystallized toluene. Anal. calc. for $C_{26}H_{32}SiZr$ + 4PhMe: C, 77.92; H, 7.75. Found: C, 77.70; H, 7.81. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, 4H, J = 6.7 Hz, J = 3.0 Hz), 7.07–7.10 (m, 4H), 2.20 (s, 12H), 0.72 (s, 6H), –0.73 (s, 6H). ^{13}C NMR (100 MHz, C_6D_6): δ 130.4, 123.6, 122.9, 114.0, 102.5, 42.2, 14.2, 2.8.

General procedure 3 for synthesis of complexes. *n*-Butyllithium in hexanes (2 eq) was added dropwise to a solution of pro-ligand **L2–L26** (1 eq) in ether at r. t., and the formed mixture was stirred overnight. Further on, $ZrCl_4$ (1 eq) was added at –80°C, and the obtained mixture was allowed to warm slowly to room temperature and then stirred overnight. The resulting mixture was evaporated to dryness, toluene was added to the residue, and the obtained suspension was evaporated to dryness again. Toluene was added to the residue, and the resulting suspension was filtered through a pad of Celite 503 (hot filtration may be necessary in case of a product with low solubility in toluene). The obtained filtrate was evaporated until the precipitation started. Crystals precipitated from this solution overnight at r. t. were collected, washed with small amount of cold toluene, and then dried in vacuum.

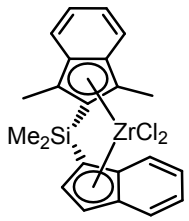


rac-**C2**

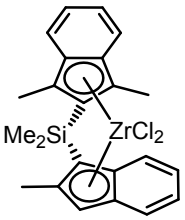


meso-**C2**

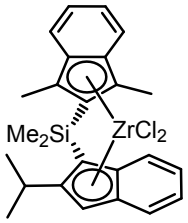
rac-**C2** and *meso*-**C2.** According to *General procedure 3,* 0.70 g (16%) of *meso*-**C2** and 0.3 g (7%) of *rac*-**C2** were obtained from 3.15 g (7.10 mmol) of **L2** in 150 ml of dry ether, 5.7 ml (14.2 mmol, 2.5 M) of *n*BuLi and 1.66 g (7.10 mmol) of $ZrCl_4$. *Meso*-**C2** was obtained as described in *General procedure 3* whereas *rac*-**C2** was isolated by evaporation of the mother liquor with subsequent washing of resulting solid with a mixture of pentane–ether. *Meso*-**C2**: anal. calc. for $C_{32}H_{26}Cl_2SiZr$: C, 63.98; H, 4.36. Found: C, 64.32; H, 4.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (t, 4H, J = 6.6 Hz), 7.40 (d, 4H, J = 7.1 Hz), 7.18–7.26 (m, 4H), 7.05–7.14 (m, 6H), 6.39 (s, 2H), 0.99 (s, 3H), 0.57 (s, 3H).^{13}C NMR (100 MHz, C_6D_6): δ 134.3, 138.8, 133.7, 132.1, 128.3, 127.9, 127.4, 127.2, 126.7, 126.6, 123.0, 111.5, 106.5, 3.0, –2.6. *Rac*-**C2**: anal. calc. for $C_{32}H_{26}Cl_2SiZr$: C 63.98; H, 4.36. Found: C, 64.11; H, 4.48. ^{1}H NMR (400 MHz, C_6D_6): δ 7.80 (d, J = 7.3 Hz, 4H), 7.60 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.28 (t, J = 7.6 Hz, 4H) 7.20 (d, J = 7.3 Hz, 2H), 6.98–6.89 (m, 4H), 5.99 (s, 2H), 0.28 (s, 6H). ^{13}C NMR (100 MHz, C_6D_6): δ 135.5, 134.3, 133.1, 132.2, 128.4, 128.3, 128.2, 127.3, 126.6, 126.2, 123.3, 113.1, 106.2, –0.7.



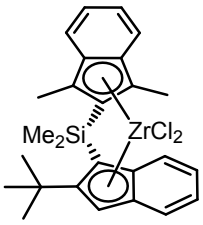
C3. According to *General procedure 3,* 5.00 g (61%) of the title compound was obtained from 5.50 g (17.4 mmol) of **L3** in 150 ml of dry ether, 13.9 ml (34.8 mmol, 2.5 M) of *n*BuLi and 4.05 g (17.4 mmol) of $ZrCl_4$. Anal. calc. for $C_{22}H_{22}Cl_2SiZr$: C, 55.44; H, 4.65. Found: C, 55.72; H, 4.74. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.70 (dd, J = 8.7 Hz, J = 1.0 Hz, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.31–7.35 (m, 1H), 7.25–7.29 (m, 1H), 7.14–7.22 (m, 2H), 7.09 (m, 1H), 6.24 (d, J = 3.4 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 3H), 1.27 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 134.1, 133.5, 133.2, 128.4, 127.6, 126.8, 126.5, 126.2, 125.6, 125.2, 124.1, 123.7, 121.1, 118.3, 117.9, 115.3, 105.7, 92.1, 15.0, 14.6, 0.5, 0.2.



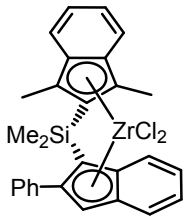
C4. According to *General procedure 3,* 3.60 g (48%) of the title compound was obtained from 5.10 g (15.0 mmol) of **L4** in 200 ml of dry ether, 12.4 ml (30.0 mmol, 2.5 M) of *n*BuLi and 3.50 g (15.0 mmol) of $ZrCl_4$. Anal. calc. for $C_{23}H_{24}Cl_2SiZr$: C, 56.30; H, 4.93. Found: C, 56.58; H, 4.98. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.83 (d, 1H, J = 8.7 Hz), 7.56 (d, 1H, J = 8.5 Hz), 7.46 (d, 1H, J = 8.5 Hz), 7.09–7.31 (m, 5H), 6.74 (s, 1H), 2.59 (s, 3H), 2.42 (s, 3H), 2.36 (s, 3H), 1.30 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 136.8, 135.9, 132.7, 129.5, 128.7, 127.1, 126.5, 125.90, 125.87, 125.7, 125.3, 124.30, 124.28, 122.0, 119.9, 119.2, 104.6, 88.3, 18.8, 15.9, 15.7, 3.03, 2.96.



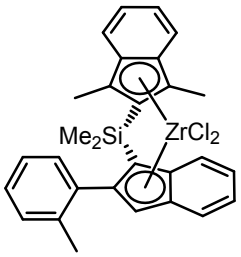
C5. According to General Procedure 3 1.20 g (41%) of the title compound was obtained from 2.00 g (5.60 mmol) of **L5** in 50 ml of dry ether, 4.4 ml (11.2 mmol, 2.5 M) of *n*BuLi and 1.30 g (5.60 mmol) of $ZrCl_4$. Anal. calc. for $C_{25}H_{28}Cl_2SiZr$: C, 57.89; H, 5.44. Found: C, 58.05; H, 5.52. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, 1H, J = 8.9 Hz), 7.51 (dt, 1H, J = 8.5 Hz, J = 1.0 Hz), 7.47 (dt, 1H, J = 8.5 Hz, J = 1.0 Hz), 7.35 (dt, 1H, J = 8.4 Hz, J = 1.0 Hz), 7.19–7.36 (m, 3H), 7.04–7.08 (m, 1H), 6.88 (s, 1H), 3.21–3.30 (m, 1H), 2.51 (s, 3H), 2.35 (s, 3H), 1.43 (d, 3H, J = 6.7 Hz), 1.29 (s, 3H), 1.20 (s, 3H), 1.20 (d, 3H, J = 6.7 Hz). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 149.4, 135.0, 134.9, 133.6, 128.2, 127.0, 126.53, 126.47, 126.0, 125.59, 125.55, 124.33, 124.31, 120.0, 118.0, 116.0, 104.8, 86.6, 30.5, 29.7, 20.1, 15.8, 14.9, 3.7, 3.2.



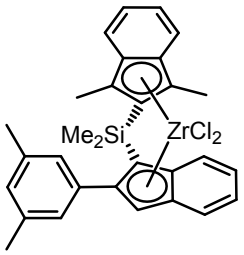
C6. According to *General procedure 3,* 1.64 g (57%) of the title compound was obtained from 2.00 g (5.40 mmol) of **L6** in 60 ml of dry ether, 4.4 ml (10.8 mmol, 2.5 M) of *n*BuLi and 1.25 g (5.40 mmol) of $ZrCl_4$. Anal. calc. for $C_{26}H_{30}Cl_2SiZr$: C, 58.62; H, 5.68. Found: C, 58.91; H, 5.74. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, 1H, J = 8.8 Hz), 7.56–7.60 (m, 1H), 7.48 (d, 1H, J = 8.4 Hz), 7.16–7.27 (m, 4H), 7.07–7.11 (m, 1H), 6.85 (s, 1H), 2.57 (s, 3H), 2.38 (s, 3H), 1.39 (s, 9H), 1.36 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 158.5, 137.5, 136.3, 132.0, 129.4, 127.9, 126.2, 126.1, 126.0, 125.7, 124.3, 124.1, 123.7, 123.1, 119.9, 116.4, 102.7, 85.4, 37.0, 33.9, 17.09, 16.7, 6.8, 5.3.



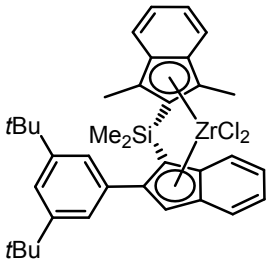
C7. According to *General procedure 3,* 4.90 g (68%) of the title compound was obtained from 5.10 g (13.0 mmol) of **L7** in 200 ml of dry ether, 10.4 ml (26.0 mmol, 2.5 M) of *n*BuLi and 3.03 g (13.0 mmol) of $ZrCl_4$. The product contained 0.5 eq of cocrystallized toluene. Anal. calc. for $C_{28}H_{26}Cl_2SiZr$ + 0.5 PhMe: C, 63.18; H, 5.05. Found: C, 62.84; H, 4.98. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.91 (dd, 1H, J = 8.8 Hz, J = 0.9 Hz), 7.78–7.80 (m, 2H), 7.54 (d, 1H, J = 8.5 Hz), 7.10–7.47 (m, 9H), 7.00 (s, 1H), 2.37 (s, 3H), 1.76 (s, 3H), 1.35 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 135.1, 134.04, 133.94, 133.7, 131.2, 129.2, 128.6, 128.4, 128.3, 127.1, 126.6, 126.2, 126.00, 125.94, 125.6, 125.4, 123.9, 123.8, 120.9, 117.4, 104.3, 86.5, 15.5, 15.0, 5.9, 3.0.



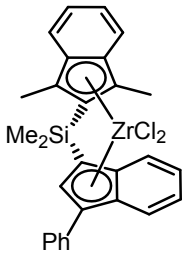
C8. According to *General procedure 3,* 1.30 g (43%) of the title compound was obtained from 2.20 g (5.40 mmol) of **L8** in 50 ml of dry ether, 4.3 ml (10.8 mmol, 2.5 M) of *n*BuLi and 1.26 g (5.40 mmol) of $ZrCl_4$. Anal. calc. for $C_{29}H_{28}Cl_2SiZr$: C, 61.46; H, 4.98. Found: C, 61.73; H, 5.04. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 1H, *J* = 7.1 Hz), 7.82 (d, 1H, *J* = 8.6 Hz), 7.54 (d, 1H, *J* = 8.6 Hz), 7.51 (d, 1H, *J* = 8.6 Hz), 7.41 (d, 1H, *J* = 8.6 Hz), 7.20–7.36 (m, 6H), 7.08–7.12 (m, 1H), 6.83 (s, 1H), 2.39 (s, 3H), 2.17 (s, 3H), 2.06 (s, 3H), 1.27 (s, 3H), 0.57 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 141.3, 139.2, 136.6, 135.1, 134.7, 133.9, 131.1, 130.5, 129.0, 127.3, 126.84, 126.76, 126.2, 125.9, 125.7, 124.5, 124.4, 121.8, 121.6, 118.8, 105.2, 89.6, 21.7, 16.03, 15.98, 2.4, 1.6.



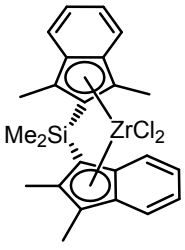
C9. According to *General procedure 3,* 1.20 g (47%) of the title compound was obtained from 1.85 g (4.40 mmol) of **L9** in 50 ml of dry ether, 3.6 ml (8.80 mmol, 2.5 M) of *n*BuLi and 1.00 g (4.40 mmol) of $ZrCl_4$. Anal. calc. for $C_{30}H_{30}Cl_2SiZr$: C, 62.04; H, 5.21. Found: C, 62.21; H, 5.37. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, 1H, *J* = 8.8 Hz), 7.52 (d, 1H, *J* = 8.5 Hz), 7.39–7.44 (m, 4H), 7.17–7.34 (m, 3H), 7.07–7.12 (m, 1H), 7.02 (s, 1H), 7.00 (s, 1H), 2.36–2.37 (m, 9H), 1.78 (s, 3H), 1.33 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 140.9, 137.5, 135.4, 134.31, 134.29, 134.0, 130.1, 129.6, 129.3, 128.9, 127.3, 127.1, 126.9, 126.3, 125.9, 125.83, 125.75, 124.2, 123.9, 120.6, 104.4, 86.6, 21.2, 15.4, 14.9, 5.5, 2.6.



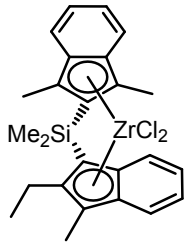
C10. According to *General procedure 3,* 0.55 g (33%) of the title compound was obtained from 1.50 g (2.97 mmol) of **L10** in 50 ml of dry ether, 2.4 ml (5.90 mmol, 2.5 M) of *n*BuLi and 0.69 g (2.97 mmol) of $ZrCl_4$. Anal. calc. for $C_{36}H_{42}Cl_2SiZr$: C, 65.03; H, 6.37. Found: C, 65.20; H, 6.52. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 1H, *J* = 8.8 Hz), 7.52 (d, 1H, *J* = 8.5 Hz), 7.42–7.45 (m, 3H), 7.14–7.34 (m, 4H), 7.11 (m, 1H), 7.01 (s, 1H), 2.37 (s, 3H), 1.80 (s, 3H), 1.37 (s, 18H), 1.33 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 143.0, 138.4, 134.8, 134.4, 134.0, 129.4, 129.1, 128.6, 127.3, 126.6, 126.5, 126.1, 125.7, 125.5, 124.4, 124.2, 123.0, 121.5, 121.3, 117.9, 105.1, 87.2, 35.4, 31.7, 15.6, 15.2, 5.8, 2.9.



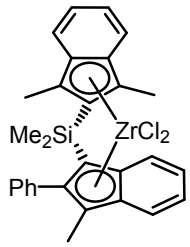
C11. According to *General procedure 3,* 3.65 g (56%) of the title compound was obtained from 4.65 g (11.8 mmol) of **L11** in 200 ml of dry ether, 9.5 ml (23.6 mmol, 2.5 M) of *n*BuLi and 2.76 g (11.8 mmol) of $ZrCl_4$. Anal. calc. for $C_{28}H_{26}Cl_2SiZr$: C, 60.84; H, 4.74. Found: C, 61.03; H, 4.97. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.80 (m, 2H), 7.40–7.49 (m, 7H), 7.33 (m, 1H), 7.18–7.25 (m, 3H), 6.20 (s, 1H), 2.45 (s, 3H), 2.39 (s, 3H), 1.33 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 134.9, 133.5, 133.2, 133.0, 129.8, 129.4, 128.7, 128.3, 128.2, 128.1, 126.7, 125.9, 125.6, 125.5, 124.7, 124.4, 123.9, 119.1, 117.5, 116.6, 104.9, 91.5, 15.4, 14.9, 1.1, 1.0.



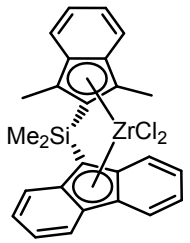
C12. According to *General procedure 3,* 1.20 g (39%) of the title compound was obtained from 2.10 g (6.00 mmol) of **L12** in 50 ml of dry ether, 5.0 ml (12.0 mmol, 2.5 M) of *n*BuLi and 1.42 g (6.00 mmol) of $ZrCl_4$. Anal. calc. for $C_{24}H_{26}Cl_2SiZr$: C, 57.12; H, 5.19. Found: C, 57.14; H, 5.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 1H, *J* = 8.7 Hz), 7.58 (d, 1H, *J* = 8.1 Hz), 7.39 (d, 1H, *J* = 8.7 Hz), 7.20–7.33 (m, 4H), 7.06 (m, 1H), 2.50 (s, 3H), 2.39 (s, 3H), 2.27 (s, 3H), 2.22 (s, 3H), 1.30 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (100 MHz, *o*-$Cl_2C_6D_4$): δ 135.2, 134.8, 132.9, 131.9, 127.6, 126.2, 126.1, 126.0, 125.2, 125.0, 124.5, 123.8, 123.7, 123.5, 117.69, 117.66, 102.8, 84.5, 15.4, 15.3, 14.9, 11.2, 2.7, 2.5.



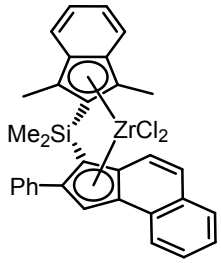
C13. According to *General procedure 3,* 1.23 g (49%) of the title compound was obtained from 2.10 g (5.85 mmol) of **L13** in 50 ml of dry ether, 4.7 ml (11.7 mmol, 2.5 M) of *n*BuLi and 1.36 g (5.85 mmol) of $ZrCl_4$. Anal. calc. for $C_{25}H_{28}Cl_2SiZr$: C, 57.89; H, 5.44. Found: C, 57.61; H, 5.40. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.84 (d, 1H, *J* = 8.8 Hz), 7.61 (m, 1H), 7.43 (d, 1H, *J* = 8.6 Hz), 7.21–7.37 (m, 4H), 7.11 (m, 1H), 2.55–2.73 (m, 2H), 2.52 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H), 1.34 (s, 3H), 1.19 (s, 3H), 1.10 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 136.3, 132.3, 129.4, 128.6, 127.4, 126.7, 126.6, 125.7, 125.6, 125.5, 125.2, 124.3, 124.2, 124.1, 119.1, 118.5, 110.4, 83.7, 23.4, 16.8, 15.7, 15.4, 11.3, 3.3, 3.0.



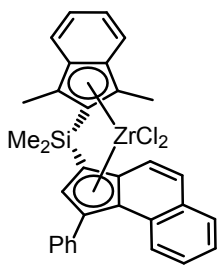
C14. According to *General procedure 3,* 1.60 g (46%) of the title compound was obtained from 2.50 g (6.10 mmol) of **L14** in 40 ml of dry ether, 4.9 ml (12.2 mmol, 2.5 M) of *n*BuLi and 1.43 g (6.10 mmol) of $ZrCl_4$. Anal. calc. for $C_{29}H_{28}Cl_2SiZr$: C, 61.46; H, 4.98. Found: C, 61.66; H, 5.18. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.86 (d, 1H, *J* = 8.9 Hz), 7.49 (d, 1H, *J* = 8.4 Hz), 7.21–7.44 (m, 10H), 7.08–7.12 (m, 1H), 2.40 (s, 3H), 2.28 (s, 3H), 1.84 (s, 3H), 1.33 (s, 3H), 0.61 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2): *δ* 139.5, 134.8, 134.6, 134.3, 133.5, 129.5, 128.9, 128.7, 128.64, 128.55, 128.2, 127.0, 126.7, 126.1, 126.0, 125.7, 125.6, 125.0, 124.5, 124.3, 120.9, 118.1, 103.5, 85.5, 15.8, 15.4, 12.1, 4.9, 3.1.



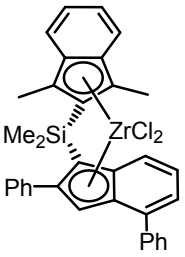
C15. According to *General procedure 3,* 0.57 g (20%) of the title compound was obtained from 2.00 g (5.50 mmol) of **L15** in 50 ml of dry ether, 4.4 ml (11.0 mmol, 2.5 M) of *n*BuLi and 1.43 g (5.50 mmol) of $ZrCl_4$. The product contained 1eq of cocrystallized toluene. Anal. calc. for $C_{26}H_{24}Cl_2SiZr$ + PhMe: C, 64.05; H, 5.21. Found: C, 63.72; H, 5.25. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.91 (d, 2H, *J* = 8.1 Hz), 7.86 (d, 2H, *J* = 8.0 Hz), 7.53 (t, 2H, *J* = 7.6 Hz), 7.16–7.34 (m, 6H), 2.44 (s, 6H), 1.40 (s, 6H). ^{13}C NMR (100 MHz, *o*-$Cl_2C_6D_4$): *δ* 129.6, 129.0, 128.2, 128.1, 126.3, 126.1, 125.3, 124.5, 123.8, 119.0, 101.8, 70.4, 15.2, 2.5.



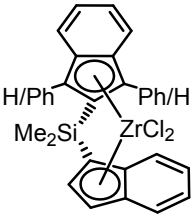
C16. According to *General procedure 3,* 2.49 g (57%) of the title compound was obtained from 3.20 g (7.22 mmol) of **L16** in 60 ml of dry ether, 5.8 ml (14.4 mmol, 2.5 M) of *n*BuLi and 1.68 g (7.22 mmol) of $ZrCl_4$. Anal. calc. for $C_{32}H_{28}Cl_2SiZr$: C, 63.76; H, 4.68. Found: C, 63.94; H, 4.75. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.97 (d, 1H, *J* = 7.9 Hz), 7.82 (d, 2H, *J* = 7.1 Hz), 7.73–7.77 (m, 2H), 7.38–7.53 (m, 9H), 7.25 (m, 1H), 7.15 (m, 1H), 2.42 (s, 3H), 1.81 (s, 3H), 1.37 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, *o*-$Cl_2C_6D_4$): *δ* 137.2, 134.4, 133.0, 132.8, 130.3, 129.4, 127.6, 127.4, 127.2, 126.8, 126.6, 126.4, 126.1, 124.7, 124.2, 122.9, 122.8, 122.6, 122.0, 119.11, 119.09, 116.0, 104.5, 90.2, 14.4, 13.9, 4.7, 1.6.



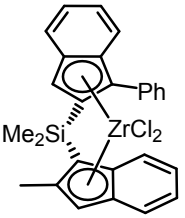
C17. According to *General procedure 3,* 4.30 g (60%) of the title compound was obtained from 5.30 g (12.0 mmol) of **L17** in 200 ml of dry ether, 9.60 ml (24.0 mmol, 2.5 M) of *n*BuLi and 2.80 g (12.0 mmol) of zirconium tetrachloride. The product contained 0.5 eq of cocrystallized toluene. Anal. calc. for $C_{32}H_{28}Cl_2SiZr$ + 0.5 PhMe: C, 65.71; H, 4.97. Found: C, 66.03; H, 4.92. ^{1}H NMR (400 MHz, *o*-$Cl_2C_6D_4$): *δ* 8.21 (d, 1H, *J* = 8.3 Hz), 7.69 (d, 2H, *J* = 7.5 Hz), 7.62 (d, 1H, *J* = 7.8 Hz), 7.47 (d, 1H, *J* = 9.2 Hz), 6.96–7.38 (m, 10H + 5H in PhMe), 6.00 (s, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 1.13 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, *o*-$Cl_2C_6D_4$): *δ* 136.9, 135.8, 133.7, 132.6, 131.2, 130.6, 129.1, 129.0, 128.9, 128.2, 128.0, 127.9, 127.8, 126.4, 125.7, 125.4, 125.2, 124.8, 123.8, 123.5, 123.1, 118.4, 117.8, 116.1, 105.7, 94.9, 15.3, 14.6, 0.62, 0.57.



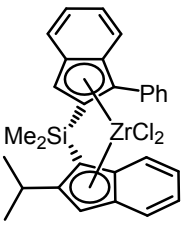
C18. According to *General procedure 3,* 0.75 g (50%) of the title compound was obtained from 1.10 g (2.50 mmol) of **L18** in 40 ml of dry ether, 2.0 ml (5.00 mmol, 2.5 M) of *n*BuLi and 0.58 g (2.50 mmol) of $ZrCl_4$. Anal. calc. for $C_{34}H_{30}Cl_2SiZr$: C, 64.94; H, 4.81. Found: C, 65.16; H, 4.87. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 1H, J = 8.6 Hz), 7.75 (d, 2H, J = 6.4 Hz), 7.47 (t, 2H, J = 8.5 Hz), 7.16–7.38 (m, 10H), 7.07 (s, 1H), 2.42 (s, 3H), 1.81 (s, 3H), 1.37 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 141.5, 139.7, 135.4, 134.3, 134.0, 133.2, 131.5, 129.7, 129.1, 128.93, 128.89, 128.5, 128.2, 128.0, 127.8, 127.6, 126.8, 126.2, 126.0, 125.6, 125.3, 124.5, 124.3, 121.8, 121.4, 120.6, 118.1, 104.8, 87.4, 15.4, 15.1, 5.9, 3.0.



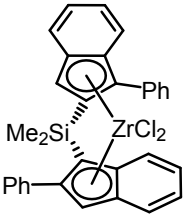
C19. According to *General procedure 3,* 1.10 g (21%) of the title compound was obtained from 3.70 g (10.1 mmol) of **L19** in 100 ml of dry ether, 8.1 ml (20.2 mmol, 2.5 M) of *n*BuLi and 2.35 g (10.1 mmol) of $ZrCl_4$. The product was ca. 1:1 mixture of two isomers (A and B) according to NMR. Anal. calc. for $C_{26}H_{22}Cl_2SiZr$: C, 59.52; H, 4.23. Found: C, 59.70; H, 4.48. ^{1}H NMR (400 MHz, CD_2Cl_2, mixture of isomers A and B): δ 7.17–7.65 (m, 11H in A + 14H in B), 6.97 (d, 1H in A, J = 3.1 Hz), 6.74–6.78 (m, 1H in A), 6.45 (d, 1H in A, J = 8.7 Hz), 6.23 (d, 1H in A, J = 3.2 Hz), 6.18 (s, 1H in A), 6.14 (s, 1H in B), 5.96 (d, 1H in B, J = 4.0 Hz), 1.10 (s, 3H in B), 0.95 (s, 3H in A), 0.93 (s, 3H in A), 0.61 (s, 3H in B). ^{13}C NMR (150 MHz, CD_2Cl_2, mixture of isomers): δ 136.4, 135.19, 135.17, 134.9, 134.2, 132.6, 132.3, 132.0, 130.3, 129.8, 129.7, 129.4, 128.9, 128.6, 128.5, 128.4, 128.19, 128.17, 128.0, 127.5, 127.03, 126.97, 126.7, 126.4, 126.3, 126.2, 125.9, 125.7, 125.0, 123.6, 123.3, 123.0, 121.0, 119.8, 119.1, 112.9, 109.0, 107.9, 107.4, 93.3, 91.8, 66.1, 1.4, 0.7, –2.5, –3.5.



Syn-**C20**. According to *General procedure 3,* 1.65 g (28%) of the title compound was obtained from 4.10 g (10.8 mmol) of **L20** in 200 ml of dry ether, 8.7 ml (21.6 mmol, 2.5 M) of *n*BuLi and 2.50 g (10.8 mmol) of $ZrCl_4$. Anal. calc. for $C_{27}H_{24}Cl_2SiZr$: C, 60.20; H, 4.49. Found: C, 60.48; H, 4.64. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.68 (d, 1H, J = 7.7 Hz), 7.50 (d, 1H, J = 8.5 Hz), 7.37–7.42 (m, 4H), 7.18–7.31 (m, 5H), 6.75 (s, 1H), 6.63–6.67 (m, 1H), 6.45 (d, 1H, J = 8.7 Hz), 6.23 (s, 1H), 2.37 (s, 3H), 1.07 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 137.4, 135.6, 135.0, 134.4, 132.6, 130.6, 129.4, 128.6, 128.3, 127.3, 127.0, 126.8, 126.6, 126.4, 126.1, 125.5, 125.2, 123.4, 121.4, 109.0, 106.8, 88.6, 19.3, 2.6, 0.1.

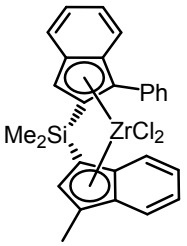


Syn-**C21**. According to *General procedure 3,* 0.58 g (25%) of the title compound was obtained from 1.70 g (4.20 mmol) of **L21** in 200 ml of dry ether, 3.4 ml (8.40 mmol, 2.5 M) of *n*BuLi and 0.97 g (4.20 mmol) of $ZrCl_4$. Anal. calc. for $C_{29}H_{28}Cl_2SiZr$: C, 61.46; H, 4.98. Found: C, 61.63; H, 5.13. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.63 (d, 1H, J = 8.4 Hz), 7.51 (d, 1H, J = 8.5 Hz), 7.39–7.43 (m, 4H), 7.33–7.36 (m, 2H), 7.23–7.28 (m, 2H), 7.19 (m, 1H), 6.86 (s, 1H), 6.66 (m, 1H), 6.52 (m, 1H), 6.15 (s, 1H), 3.02 (m, 1H), 1.49 (d, 3H, J = 6.5 Hz), 1.22 (d, 3H, J = 6.9 Hz), 1.13 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 150.0, 134.8, 134.67, 134.65, 132.5, 131.4, 128.34, 128.31, 127.6, 127.07, 127.06, 127.0, 126.7, 126.5, 126.2, 125.8, 125.7, 123.4, 115.3, 109.0, 106.1, 87.2, 31.0, 29.5, 20.6, 2.7, 0.8.

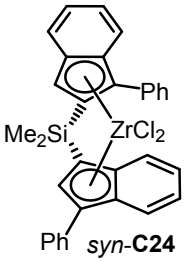


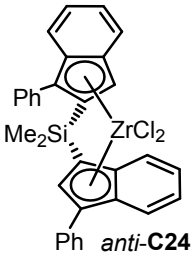
Syn-**C22**. According to *General procedure 3,* 2.10 g (31%) of the title compound was obtained from 5.00 g (11.3 mmol) of **L22** in 200 ml of dry ether, 9.10 ml (22.6 mmol, 2.5 M) of *n*BuLi and 2.65 g (11.3 mmol) of $ZrCl_4$. Anal. calc. for $C_{32}H_{26}Cl_2SiZr$: C, 63.98; H, 4.36. Found: C, 64.26; H, 4.41. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.74–7.76 (m, 2H), 7.59 (d, 2H, J = 8.5 Hz), 7.42–7.48 (m, 8H), 7.30 (m, 2H), 7.22 (m, 2H), 6.97 (s, 1H), 6.76 (m, 1H), 6.67 (m, 1H), 5.84 (s, 1H), 0.88 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (150 MHz,

CD_2Cl_2): δ 142.5, 136.0, 134.6, 134.5, 134.4, 132.5, 132.1, 131.2, 129.4, 128.8, 128.50, 128.46, 128.3, 127.5, 127.2, 126.8, 126.42, 126.39, 126.2, 126.1, 123.5, 120.3, 110.0, 105.8, 89.2, 66.1, 2.2, 1.5.

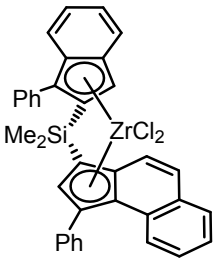


Syn-**C23**. According to *General procedure 3,* 0.70 g (17%) of the title compound was obtained from 2.60 g (6.90 mmol) of **L23** in 100 ml of dry ether, 5.5 ml (13.8 mmol, 2.5 M) of *n*BuLi and 1.60 g (6.90 mmol) of $ZrCl_4$. The product contained 0.5 eq of cocrystallized toluene. Anal. calc. for $C_{27}H_{24}Cl_2SiZr$ + 0.5 PhMe: C, 62.65; H, 4.83. Found: C, 62.44; H, 4.90. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.68 (d, 1H, J = 8.1 Hz), 7.21–7.45 (m, 10H), 6.74 (m, 1H), 6.43 (d, 1H, J = 8.9 Hz), 6.05 (s, 1H), 5.86 (s, 1H), 2.42 (s, 3H), 0.90 (s, 6H). ^{13}C NMR (100 MHz, *o*-$Cl_2C_6D_4$): δ 135.8, 134.5, 134.1, 129.5, 129.0, 128.4, 128.2, 128.0, 127.8, 126.7, 126.4, 125.8, 125.6, 125.5, 125.3, 123.3, 122.9, 107.3, 106.5, 88.6, 13.4, 1.2, -4.0.





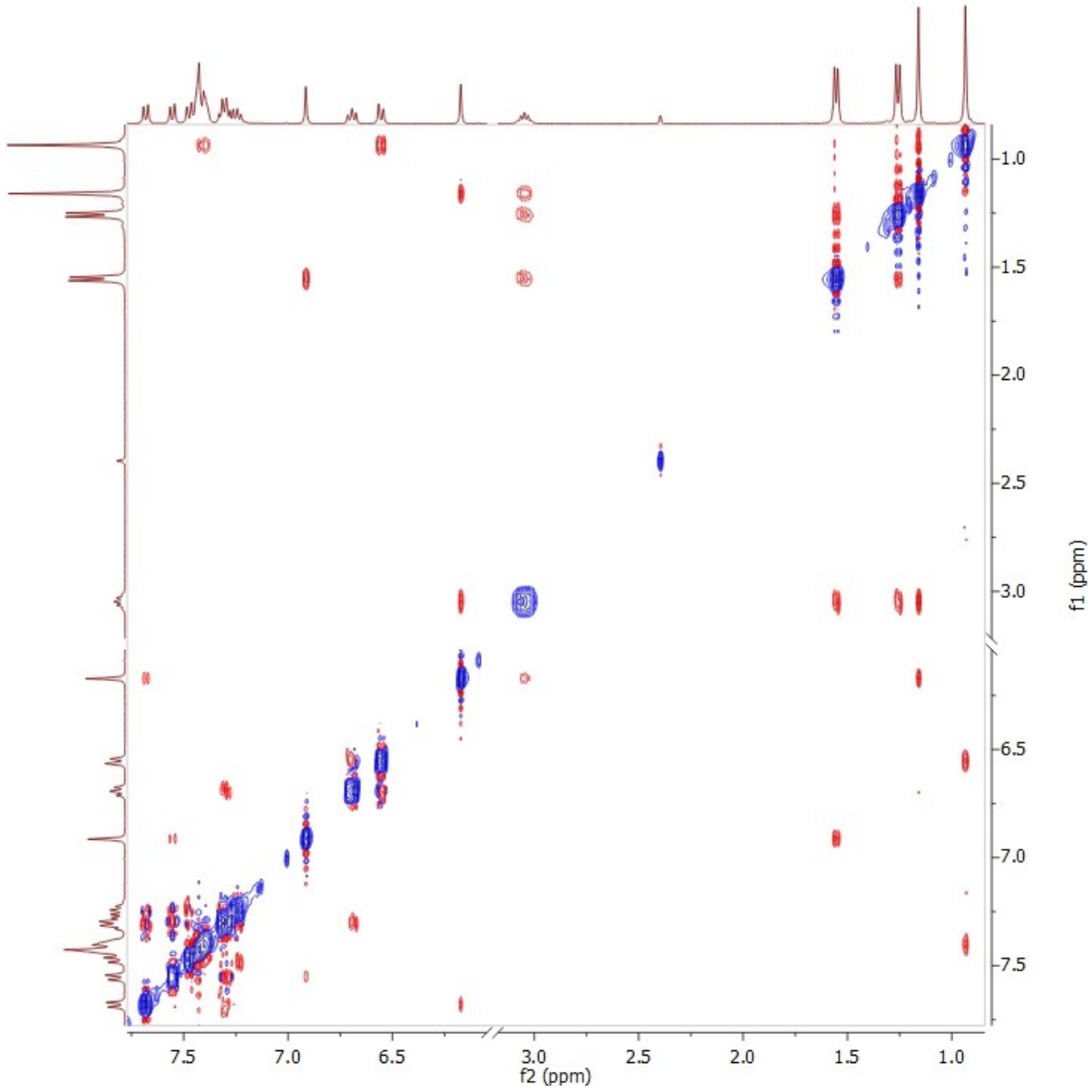
Syn-and *anti*-**C24**. According to *General procedure 3,* 1.30 g (16%) of *syn*-**C24** and 1.50 g (17%) of the isomeric *anti*-**C24** were obtained from 6.10 g (13.8 mmol) of **L24** in 200 ml of dry ether, 11.1 ml (27.7 mmol, 2.5 M) of *n*BuLi and 3.20 g (13.8 mmol) of $ZrCl_4$. *Syn*-**C24** was isolated as described in *General procedure 3*, whereas the isomeric compound *anti*-**C24** precipitated from the mother liquor. *Syn*-**C24**. Anal. calc. for $C_{32}H_{26}Cl_2SiZr$: C, 63.98; H, 4.36. Found: C 64.14; H 4.42. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.78 (d, 1H, J = 8.9 Hz), 7.66–7.68 (m, 1H), 7.34–7.51 (m, 11H), 7.21–7.25 (m, 3H), 6.75–6.79 (m, 1H), 6.45–6.47 (d, 1H, J = 8.5 Hz), 6.24 (s, 1H), 6.15 (s, 1H), 1.02 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, *o*-$Cl_2C_6D_4$): δ 134.8, 134.74, 134.68, 134.2, 131.4, 129.5, 129.4, 128.4, 128.10, 128.05, 128.0, 127.7, 127.3, 126.7, 125.7, 125.6, 125.5, 125.1, 123.5, 122.9, 118.9, 108.1, 107.2, 91.05, 1.5, –4.2. *Anti*-**C24**. Anal. calc. for $C_{32}H_{26}Cl_2SiZr$: C, 63.98; H, 4.36. Found: C, 64.33; H, 4.52. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.87 (d, 1H, J = 8.7 Hz), 7.63 (d, 1H, J = 8.7 Hz), 7.33–7.55 (m, 13H), 7.20–7.24 (m, 3H), 6.25 (s, 1H), 5.97 (s, 1H), 1.17 (s, 3H), 0.62 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 135.12, 135.07, 134.48, 134.46, 134.4, 132.6, 131.9, 130.6, 130.1, 129.8, 128.8, 128.7, 128.5, 128.4, 128.3, 127.7, 127.4, 126.5, 126.4, 126.1, 125.1, 123.6, 116.7, 111.1, 106.8, 91.2, 0.5, –2.1.



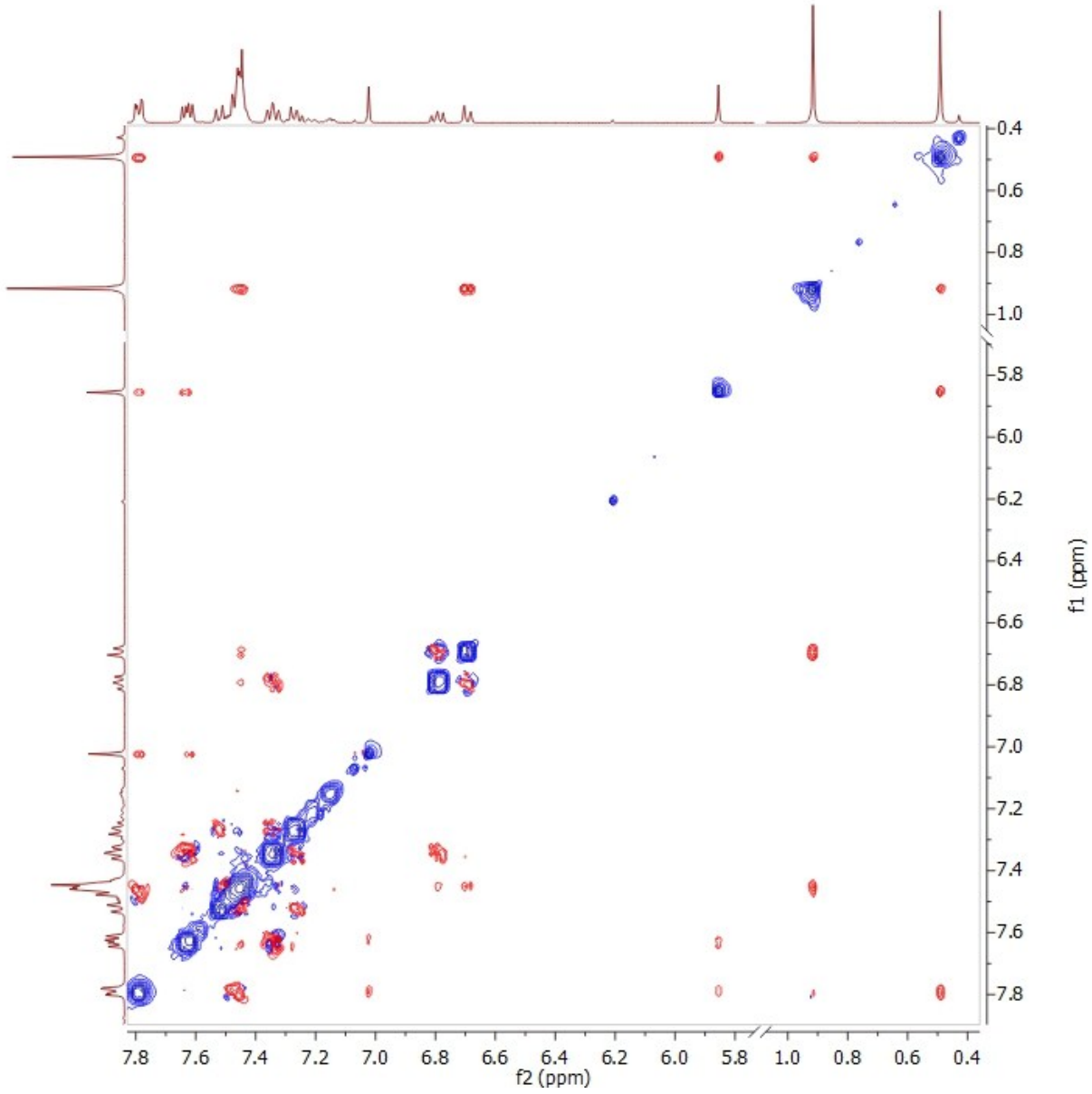
Syn-**C25**. According to *General procedure 3,* 2.20 g (28%) of the title compound was obtained from 5.15 g (10.5 mmol) of **L25** in 200 ml of dry ether, 8.4 ml (21.0 mmol, 2.5 M) of *n*BuLi and 2.45 g (10.5 mmol) of $ZrCl_4$. The product contained 1 eq of cocrystallized toluene. Anal. calc. for $C_{36}H_{28}Cl_2SiZr$ + PhMe: C, 69.51; H, 4.88. Found: C, 69.39; H, 4.75. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.16 (d, 1H, J = 8.3 Hz), 7.71–7.76 (m, 2H), 7.42–7.57 (m, 13H), 7.14–7.33 (m, 2H), 6.96 (d, 1H, J = 8.9 Hz), 6.33 (d, 1H, J = 9.0 Hz), 6.20 (s, 1H), 6.12 (s, 1H), 1.08 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 136.2, 135.0, 134.8, 134.6, 133.8, 133.6, 132.7, 132.5, 130.5, 129.9, 129.3, 128.6, 128.5, 128.4, 128.3, 128.1, 127.8, 127.3, 126.9, 126.8, 126.1, 125.1, 125.0, 124.9, 124.0, 123.2, 121.4, 109.5, 108.1, 95.1, 2.0, –3.7.

2D 1H-1H NOESY spectra

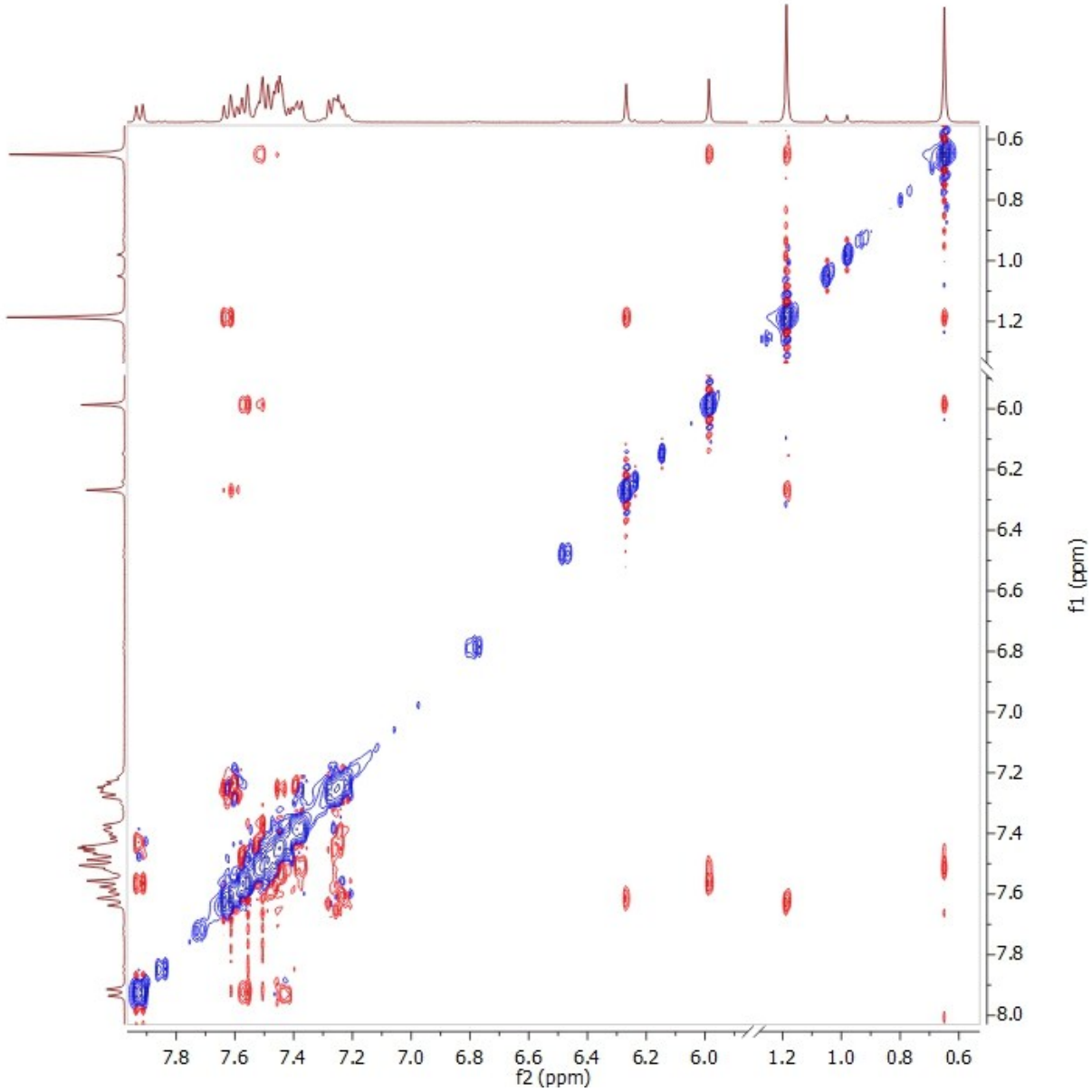
Complex **C21**



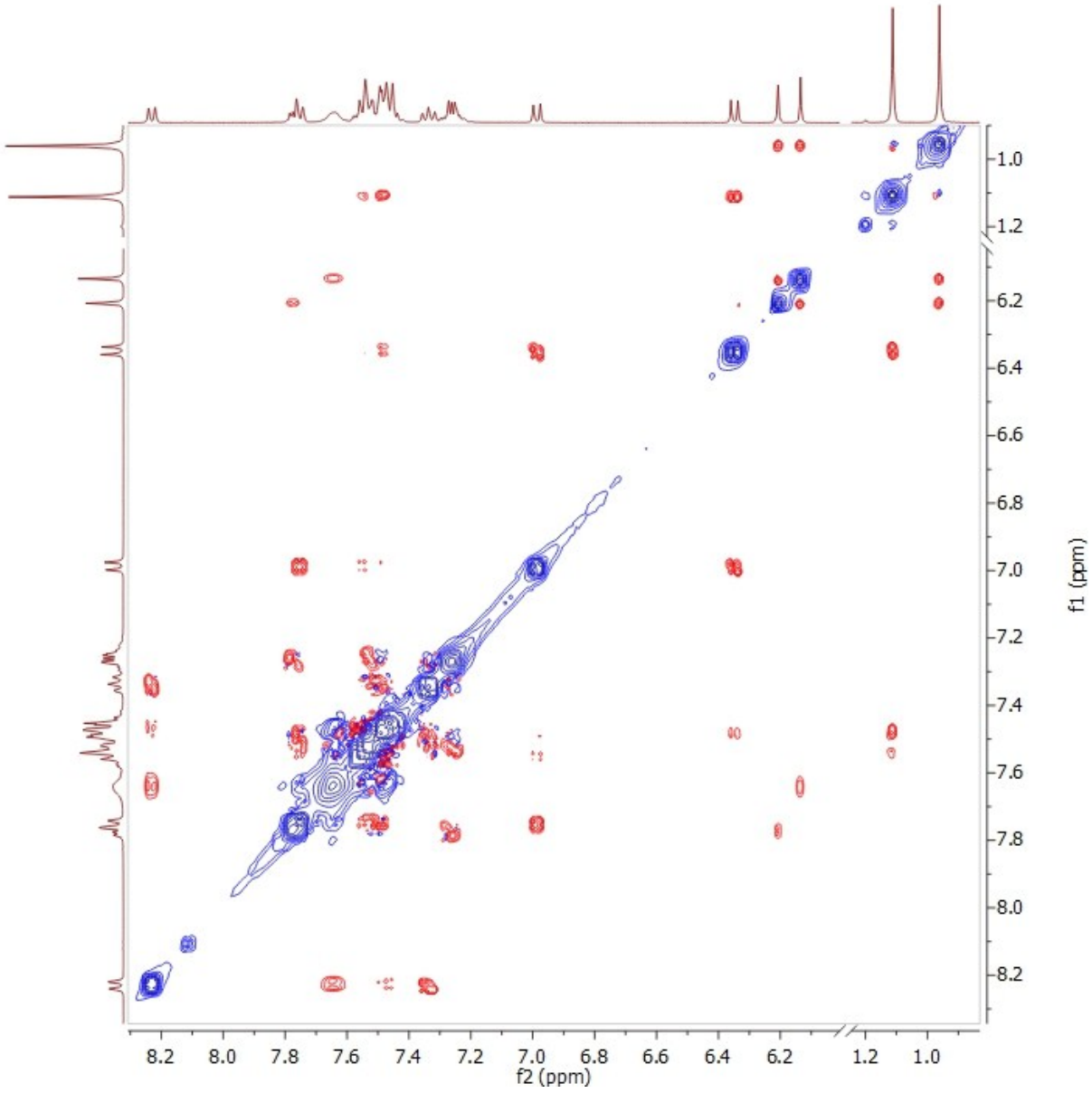
Complex *syn*-**C22**



Complex *anti*-**C24**



Complex *syn*-**C25**



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Polymerization

Detailed polymerization procedure

The polymerizations were carried out in a Parallel Pressure Reactor (PPR48). This equipment, containing 48 reactors mounted in a triple glove-box, was sold commercially by the company Symyx, thereafter by the company Freeslate. The applied polymerization protocols were as follows:

Prior to the execution of a library, the 48 PPR cells (reactors) undergo 'bake-and-purge' cycles overnight (8 h at 90-140°C with intermittent dry N_2 flow), to remove any contaminants and left-overs from previous experiments. After cooling to glove-box temperature, the stir tops are taken off, and the cells are fitted with disposable 10 mL glass inserts and PEEK stirring paddles (previously hot-dried under vacuum); the stir tops are then set back in place, the cells are loaded with the proper amounts of toluene (in the range 3.5-4.0 mL), 1-hexene (in the range 0.05 - 0.5 mL) and MAO solution (100 µL of 0.1 mol L^{-1} in toluene), thermostated at 80°C, and brought to the operating pressure of 65 psi_g with ethylene. At this point, the catalyst injection sequence is started; proper volumes of a toluene 'chaser', a solution of the precatalyst in toluene (typically in the range 0.05 - 0.02 mmol L^{-1}), and a toluene 'buffer' are uptaken into the slurry needle, and then injected into the cell of destination. The reaction is left to proceed under stirring (800 rpm) at constant temperature and pressure with continuous feed of ethylene for 5-60 min, and quenched by over-pressurizing the cell with dry air (preferred to other possible catalyst poisons because in case of cell or quench line leaks oxygen is promptly detected by the dedicated glove-box sensor).

After quenching, the cells are cooled down and vented, the stir-tops are removed, and the glass inserts containing the reaction phase are taken out and transferred to a Genevac EZ2-Plus centrifugal evaporator, where all volatiles are distilled out and the polymers are thoroughly dried overnight. Reaction yields are double-checked against on-line monomer conversion measurements by robotically weighing the dry polymers in a Bohdan Balance Automator while still in the reaction vials (subtracting the pre-recorded tare). Polymer aliquots are then sampled out for the characterizations.

Table S1. Polymerization Results (1-hexene feeding ratio 5 v/v%)

Catalyst	R_p*	M_n (kDa)	M_w (kDa)	PDI	$[H]_{cop}$ (mol%)
C1	2640	9	16	1.9	0.8
	3670	8	15	1.9	0.8
***meso*-C2**	973	38	88	2.3	1.0
	842	42	92	2.2	1.0
***rac*-C2**	78	26	53	2.0	1.6
	64	20	49	2.5	1.6
C3	1830	8	15	1.9	5.0
	2230	7	15	2.0	5.2
C4	4840	13	30	2.3	3.3
	4690	13	27	2.1	3.2
C5	1426	50	106	2.1	7.4
	1348	54	115	2.1	7.7
C6	147	34	70	2.1	2.4
	158	34	72	2.1	2.1
C7	629	34	104	3.0	8.8
	655	36	105	2.9	8.8
C8	46	33	70	2.1	7.5
	54	33	68	2.0	7.4
C9	196	45	92	2.0	9.6
	284	51	100	2.0	9.3
C10	216	35	82	2.3	10.0
	202	38	87	2.3	9.8
C11	15816	7	14	2.1	4.5
	14170	7	14	2.0	4.4
C12	5308	16	33	2.1	1.3
	5020	16	33	2.1	1.3
C13	5758	13	30	2.3	1.5
	6269	15	32	2.1	1.5
C14	979	115	243	2.1	3.7
	737	88	208	2.4	3.6
C15	416	39	86	2.2	2.5
	516	42	89	2.1	2.6
C16	815	105	284	2.7	7.7
	638	87	213	2.4	7.8
C17	9025	9	23	2.5	4.3
	4210	12	25	2.1	4.3
C18	949	70	197	2.8	10.7
	867	88	207	2.4	10.0
C19	4769	51	110	2.2	2.5
	3469	45	94	2.1	2.8
***syn*-C20**	1647	58	159	2.7	4.2
	1449	58	157	2.7	4.1
***syn*-C21**	116	55	124	2.3	4.6
	111	58	132	2.3	4.5
***syn*-C22**	38	42	105	2.5	4.8
	28	38	105	2.8	5.2
***syn*-C23**	3412	37	91	2.5	1.0
	2810	33	78	2.4	1.0
***anti*-C24**	2715	43	84	2.0	2.2
	2361	33	74	2.2	2.2
***syn*-C24**	5206	38	76	2.0	0.8
	4613	37	78	2.1	0.8
***syn*-C25**	2259	59	125	2.1	0.7
	2449	61	135	2.2	0.7
C26	197	40	99	2.5	6.4
	243	34	93	2.7	6.3

Table S2. Polymerization Results (varying 1-hexene feeding ratio)

Catalyst	1-hexene (%v/v)	R_p*	M_n (kDa)	M_w (kDa)	PDI	$[H]_{cop}$ (mol%)
C1	27	3619	9	16	1.9	3.3
		2620	8	16	2.0	3.4
***meso*-C2**	20	206	18	41	2.4	3.4
		191	19	39	2.1	3.2
***rac*-C2**	12.5	31	22	40	1.9	4.5
		37	14	28	1.9	4.5
C3	4	2750	9	17	2.0	4.2
		5040	8	17	2.1	4.1
C4	6	4050	16	31	1.9	4.0
		3980	17	32	1.9	4.1
C5	2	2986	64	143	2.2	3.5
		1622	61	141	2.3	3.6
C6	10	99	27	55	2.1	4.1
		93	21	48	2.3	5.0
C7	2	756	61	179	2.9	3.9
		958	66	182	2.8	4.0
C8	2.5	53	48	116	2.4	3.9
		70	52	115	2.2	4.0
C9	2	531	69	158	2.3	4.7
		597	88	204	2.3	4.3
C10	1.6	132	104	252	2.4	3.8
		773	69	159	2.3	3.9
C12	15	6745	11	31	2.8	3.7
		6234	13	31	2.4	3.7
C13	15	3239	15	30	2.0	3.4
		3523	14	29	2.1	3.5
C15	8	448	40	78	2.0	3.6
		317	38	94	2.4	3.4
C16	1.6	1400	104	278	2.7	3.2
		1000	144	394	2.7	3.2
C18	1.6	455	59	307	5.2	3.3
		447	91	329	3.6	3.5
C19	8	6570	49	98	2.0	3.8
		8398	51	101	2.0	3.6
***syn*-C21**	4	124	59	132	2.2	3.8
		118	51	124	2.4	3.8
***syn*-C23**	20	3853	40	79	1.9	3.0
		3295	41	82	2.0	3.0
***anti*-C24**	10	1075	40	78	1.9	1.9
		2091	37	74	2.0	1.8
***syn*-C24**	30	6257	35	73	2.1	3.7
		5497	32	73	2.3	3.8
***syn*-C25**	40	1194	61	140	2.3	2.6
		2043	60	132	2.2	2.7
C26	2.7	1192	69	154	2.2	3.8
		736	68	174	2.6	3.7

*Activity, in kg h^{-1} $mmol_{Zr}^{-1}$ $[C_2H_4]^{-1}$

Examples of ^{13}C NMR spectra of ethene/1-hexene copolymers

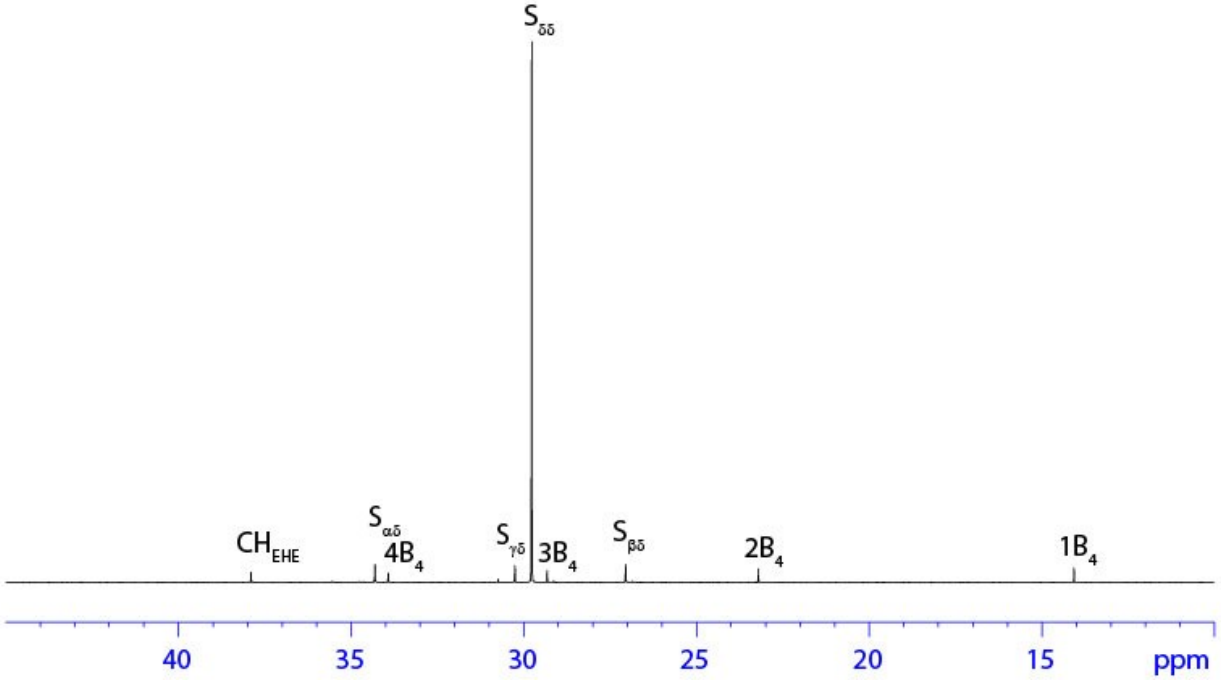


Figure S1. ^{13}C NMR spectrum of a representative sample of ethene/1-hexene copolymer (**C18**, 1.6% v/v 1-hexene feeding ratio). For resonance assignment and notation see *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29*, 201-317 and *Rubber Chem. Technol*. **1975**, *48*, 705.

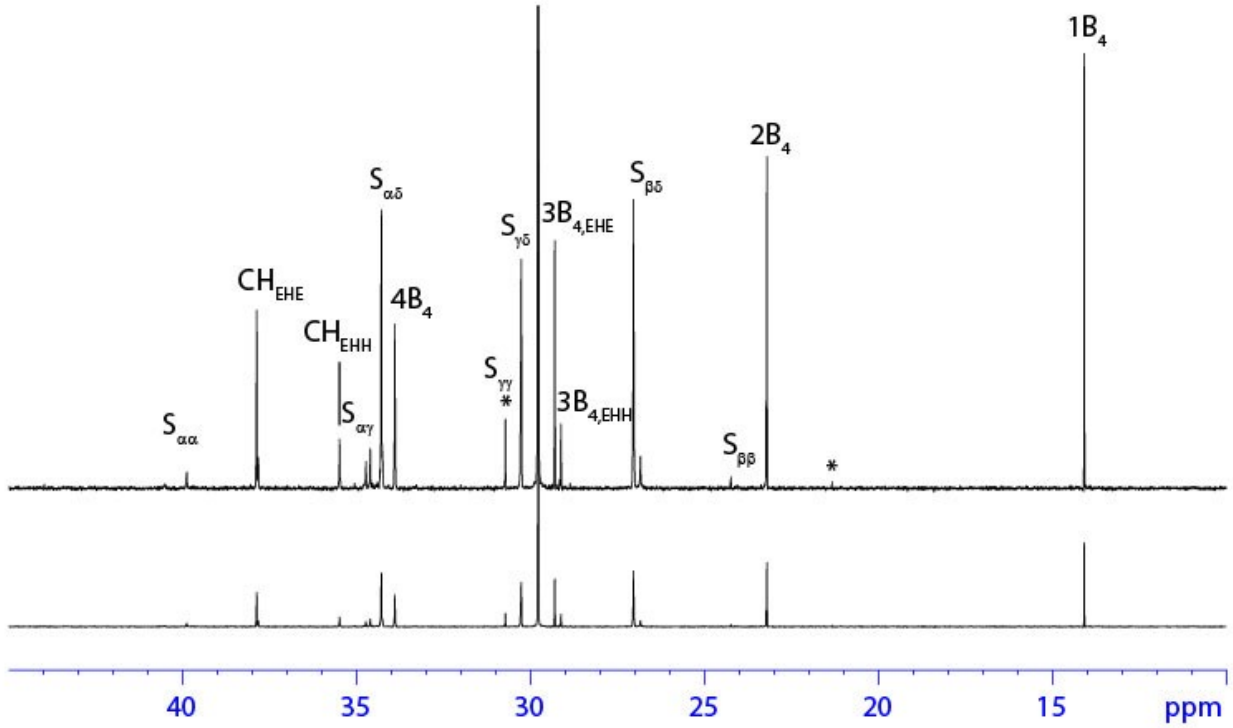


Figure S2. ^{13}C NMR spectrum of a representative sample of ethene/1-hexene copolymer (**C18**, 5 v/v% 1-hexene feeding ratio. For resonance assignment and notation see *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29*, 201-317 and *Rubber Chem. Technol*. **1975**, *48*, 705. Peaks marked with astericks are due to the stabilizier.

QSAR Models – Single Descriptor Correlations

Procedures to determine specialized descriptors

Ring aperture. The ring aperture was determined as the sum of the distances between the two front facing carbon atoms of each C5-ring of the indenyl fragments in a cross pattern.

$C_{Si\text{-}Zr}$. Sum of the distances of the Si-bound carbon atoms of the C5 rings.

Zr-Cl. Sum of Zr-Cl bond lengths.

Si-C. Sum of the bond lengths to the C5 rings

Si-C_{sp3}. Sum of the two Si-methyl bonds.

$\%V_{Bur}$. The coordinate system in SambVca was determined with Zr at the center of the sphere, Si for z-axis definition and Cl on the 2-indenyl side for xz-plane definition. This way, the 2-indenyl ligand occupies the SW quadrant. H atoms were included in the procedure, the $ZrCl_2$fragment was deleted. The sphere size used is specifically mentioned in the tables.

Table S3. Experimental Performance Indicators. $\Delta\Delta G^{\ddagger}$ at 80°C.

Catalyst	x_H	$\Delta\Delta G^{\ddagger}_{Incorporation}$	M_w	$\Delta\Delta G^{\ddagger}_{Termination}$	activity
Type I					
C3	5.1	2.10	15	3.89	2030
C4	3.3	2.41	32	4.43	4753
C5	7.6	1.82	142	5.48	1387
C6	2.3	2.66	52	4.77	153
C7	8.8	1.72	181	5.65	642
C8	7.5	1.83	116	5.34	50
C9	9.4	1.67	181	5.65	240
C10	9.9	1.63	205	5.74	209
C11	4.5	2.19	14	3.84	14993
C12	1.3	3.07	31	4.40	5164
C13	1.5	2.96	30	4.38	6014
C14	3.7	2.33	226	5.81	858
C15	2.6	2.58	86	5.12	466
C16	7.7	1.81	336	6.09	815
C17	4.3	2.22	24	4.22	6617
C18	10.4	1.60	329	6.07	908
C26	6.4	1.94	164	5.58	220
Type II					
C20	4.2	2.24	158	5.55	1548
C21	4.6	2.17	128	5.41	114
C22	5	2.11	104	5.26	33
C23	1	3.25	80	5.07	3111
C24_syn	0.8	3.41	73	5.01	4910
C24_anti	2.2	2.69	76	5.04	2538
C25	0.7	3.50	136	5.45	2354

Table S4. 1D Geometric Descriptors – Single correlations. Distances.

Descriptor No.	1	2	3	4	5	7	6
Descriptor	Si-Zr	C_{si}-Zr	Zr-Cl	Si-C	Si-C_{sp^3}	Cl-Cl	ring aperture
Catalyst							
Catalysts Type I							
C3	3.3825	5.021	4.8613	3.808	3.7974	3.783	10.6164
C4	3.3629	5.011	4.8631	3.8211	3.8034	3.779	10.6253
C5	3.3654	5.014	4.8615	3.8222	3.8061	3.726	10.638
C6	3.3499	5.01	4.8616	3.8423	3.8119	3.715	10.5807
C7	3.3782	5.03	4.8637	3.825	3.8013	3.704	10.6088
C8	3.3731	5.025	4.8625	3.8219	3.8016	3.686	10.6278
C9	3.3787	5.03	4.8643	3.8245	3.802	3.699	10.608
C10	3.376	5.003	4.8639	3.8228	3.8007	3.699	10.611
C11	3.3613	4.999	4.8517	3.8068	3.7989	3.764	10.7359
C12	3.3563	4.999	4.8658	3.8198	3.8056	3.766	10.676
C13	3.3505	4.995	4.8662	3.8211	3.8064	3.771	10.6783
C14	3.3594	5.004	4.8653	3.8225	3.8015	3.696	10.6922
C15	3.3348	4.974	4.8579	3.8109	3.8012	3.711	10.6472
C16	3.3818	5.034	4.8643	3.8275	3.8013	3.708	10.5861
C17	3.3769	5.012	4.8504	3.8077	3.7694	3.696	10.641
C18	3.3778	5.029	4.8636	3.825	3.8015	3.706	10.6184
C26	3.3712	5.03	4.8611	3.80796	3.7891	3.689	10.5148
INCORP.	0.60	0.48	0	0	0.03	0.31	0.17
MW	0.08	0.19	0.24	0.20	0.03	0.57	0.20
ACTIVITY	0.02	0.12	0.12	0.19	0.05	0.51	0.39
Catalysts Type II							
C20	3.3683	5.013	4.8618	3.8007	3.7927	3.729	10.6292
C21	3.3685	5.012	4.8596	3.8134	3.7946	3.684	10.6468
C22	3.387	5.037	4.8628	3.8166	3.7895	3.622	10.5961
C23	3.3405	4.995	4.8625	3.8016	3.7878	3.737	10.7037
C24_syn	3.3346	4.992	4.8537	3.8033	3.7878	3.747	10.7316
C24_anti	3.3598	5.008	4.8484	3.8025	3.7868	3.676	10.6457
C25	3.3587	5.007	4.8483	3.8005	3.7871	3.676	10.793
INCORP.	0.68	0.58	0.30	0.44	0.54	0.22	0.86
MW	0.33	0.18	0.05	0.01	0.41	0.04	0.01
ACTIVITY	0.70	0.75	0.26	0.91	0.30	0.57	0.42

Table S5. 1D Geometric Descriptors – Single correlations. Angles and Dihedrals.

Descriptor No.	8	9	10	11	13	14	12	15	18	20	19
Descriptor	Cl-Zr-Cl	C-Si-C	C-Si-C_{sp^3}	Si-Zr-Cl	smallest Si-Zr-Cl	largest Si-Zr-Cl	Plane angle	$ClZrSiC_{ind}$	shortest Cl-H	2nd Shortest Cl-H	Σ two shortest Cl-H
Catalyst											
Catalysts Type I											
C3	102.19	94.27	105.44	257.8	126.57	131.23	63.7	-1.16	3.113	3.156	6.269
C4	101.97	94.89	102.66	258.01	123.64	134.37	62.4	1.85	2.953	3.252	6.205
C5	100.06	94.93	101.9	259.85	128.59	131.26	62.4	3.24	2.689	3.137	5.826
C6	99.65	95.58	99.52	260.29	122.13	138.16	61.5	4.95	2.716	3.438	6.154
C7	99.21	94.79	102.42	260.69	128.57	132.12	62	4.58	2.663	3.045	5.708
C8	98.58	94.89	103.74	261.31	129.6	131.71	62.2	3.49	2.586	3.064	5.65
C9	99.02	94.8	102.32	260.86	128.29	132.57	62	4.58	2.761	3.027	5.788
C10	99.02	94.89	102.76	260.86	128.87	131.99	62	4.56	3.044	3.075	6.119
C11	101.75	94.63	105.1	258.24	127.66	130.58	64.7	-0.77	3.067	3.141	6.208
C12	101.42	94.91	101.71	258.56	124.77	133.79	63.1	3.56	2.872	3.267	6.139
C13	101.6	95.07	101.75	258.39	124.1	134.29	63	2.44	2.902	3.254	6.156
C14	98.89	94.96	102.47	261.05	130.06	130.99	63.1	4.43	2.67	3.094	5.764
C15	99.63	95.2	103.6	260.36	127.96	132.4	61.7	-1.29	3.432	3.432	6.864
C16	99.34	94.78	102.32	260.59	127.97	132.62	61.8	3.96	2.666	3.025	5.691
C17	99.3	94.09	105.82	260.68	119.34	141.34	65	-1.38	2.77	3.154	5.924
C18	99.29	94.8	102.34	260.58	128.91	131.67	62.2	4.68	2.662	3.051	5.713
C26	98.72	94.61	108.07	261.19	118.32	142.87	62.5	0.1	2.754	3.229	5.983
INCORP.	0.30	0.12	0.05	0.29	0.16	0.04	0.05	0.06	0.12	0.59	0.33
MW	0.64	0.07	0.05	0.62	0.18	0.02	0.46	0.41	0.23	0.22	0.29
ACTIVITY	0.57	0.15	0.02	0.56	0.05	0	0.53	0.20	0.08	0.01	0.06
Catalysts Type II											
C20	100.17	94.51	106.2	259.82	122.57	137.25	63	8.71	2.744	3.233	5.977
C21	98.58	94.53	105.75	261.35	125.51	135.84	63.2	9.98	2.653	2.653	5.371
C22	96.29	94.47	106.81	263.62	130.9	132.72	62.4	9.48	2.588	2.588	5.227
C23	100.45	95.08	108.75	259.54	121.33	138.21	63.8	5.99	2.76	2.98	5.74
C24_syn	101.05	95.17	108.73	258.95	119.57	139.38	64.1	5.45	2.796	3.562	6.358
C24_anti	98.61	94.47	109.06	261.37	118.68	142.69	64.8	-6.04	2.776	3.562	6.338
C25	98.63	94.71	108.74	261.34	126.05	135.29	65.6	6.12	2.687	2.681	5.368
INCORP.	0.29	0.61	0.71	0.29	0.19	0.10	0.60	0.08	0.31	0.08	0.09
MW	0.05	0.30	0.48	0.05	0.27	0.35	0.04	0.34	0.23	0.30	0.30
ACTIVITY	0.66	0.36	0.52	0.66	0.70	0.52	0.48	0.25	0.85	0.50	0.52

Table S6. Energetic Descriptors – Single correlations. Orbital Energies (E) and Occupations (Occ).

Catalyst	Descriptor No.	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37
	Descriptor	$4d_{xy}$		$4d_{xz}$		$4d_{yz}$		$4d_{x^2-y^2}$		$4d_{z^2}$		5s		$5p_x$		$5p_y$		$5p_z$	
		Occ	E	Occ	E	Occ	E	Occ	E	Occ	E	Occ	E	Occ	E	Occ	E	Occ	E
Catalysts Type I																			
C3		0.44522	-0.0524	0.41	-0.05456	0.43601	-0.0602	0.39092	-0.05126	0.44685	-0.03269	0.17825	0.9368	0.16079	0.32541	0.19316	0.3738	0.19703	0.19884
C4		0.45057	-0.03601	0.41964	-0.04935	0.36614	-0.03934	0.39453	-0.0643	0.48861	-0.048	0.17501	1.05362	0.15859	0.35337	0.19293	0.29003	0.18726	0.26116
C5		0.40822	-0.04035	0.44682	-0.03846	0.41256	-0.0512	0.40456	-0.04867	0.43437	-0.05152	0.17498	1.0473	0.1599	0.36623	0.18997	0.18386	0.18615	0.34591
C6		0.37824	-0.0512	0.46545	-0.04501	0.45887	-0.06246	0.41796	-0.03532	0.40011	-0.04356	0.17605	1.06724	0.16474	0.33796	0.18861	0.17874	0.18782	0.37191
C7		0.36912	-0.0575	0.47232	-0.03602	0.43921	-0.06276	0.428	-0.03147	0.39714	-0.04911	0.17633	1.05045	0.18192	0.25536	0.17158	0.25211	0.18396	0.37907
C8		0.36522	-0.06042	0.46587	-0.03574	0.44355	-0.06272	0.42982	-0.02813	0.39966	-0.04965	0.17639	1.04481	0.17664	0.28296	0.17708	0.22767	0.18326	0.37962
C9		0.37274	-0.05073	0.48194	-0.03858	0.44566	-0.05306	0.42028	-0.0391	0.38412	-0.05049	0.17641	1.04977	0.18529	0.23205	0.17368	0.26862	0.1779	0.38867
C10		0.3858	-0.04776	0.47644	-0.04271	0.42425	-0.03606	0.4228	-0.04871	0.396	-0.05628	0.17634	1.06162	0.18675	0.21957	0.18356	0.29001	0.16664	0.38047
C11		0.40126	-0.057	0.42259	-0.03531	0.40807	-0.03508	0.4387	-0.04862	0.43697	-0.06799	0.17345	1.03447	0.15792	0.34314	0.1805	0.31038	0.19807	0.23089
C12		0.44636	-0.03929	0.42939	-0.03357	0.38873	-0.04342	0.38403	-0.05377	0.44559	-0.04641	0.17149	1.08993	0.15057	0.35321	0.18715	0.33727	0.18834	0.20341
C13		0.42522	-0.03282	0.43989	-0.03284	0.36556	-0.03616	0.39738	-0.05523	0.46097	-0.05455	0.17096	1.09787	0.15085	0.36991	0.18791	0.24263	0.18607	0.28659
C14		0.3615	-0.05617	0.46628	-0.03664	0.42578	-0.06134	0.43209	-0.022	0.40044	-0.04357	0.17187	1.1006	0.17556	0.25479	0.16703	0.24937	0.18272	0.37987
C15		0.47362	-0.04862	0.42905	-0.04756	0.40923	-0.0414	0.35673	-0.05509	0.46609	-0.05788	0.17783	0.97746	0.17277	0.40636	0.19612	0.13093	0.17453	0.33942
C16		0.42235	-0.03874	0.37577	-0.03754	0.44261	-0.04268	0.41635	-0.05198	0.4458	-0.06321	0.17577	1.07425	0.18876	0.22602	0.15372	0.35293	0.19557	0.30766
C17		0.48276	-0.02631	0.38663	-0.0526	0.45793	-0.06428	0.36561	-0.05975	0.41664	-0.03816	0.17451	1.07889	0.15182	0.3765	0.20215	0.13496	0.18741	0.38792
C18		0.43137	-0.05553	0.4211	-0.02839	0.3975	-0.04614	0.41892	-0.0381	0.42719	-0.06362	0.17531	1.08682	0.16818	0.35889	0.17471	0.26909	0.18981	0.26136
C26		0.40755	-0.0657	0.45661	-0.02928	0.41365	-0.0742	0.42529	-0.03853	0.44839	-0.06047	0.18378	0.92268	0.1951	0.30488	0.17998	0.25151	0.19488	0.33692
INCORP.		0.15	0.17	0.03	0.02	0.19	0.05	0.25	0.13	0.22	0.07	0.22	0.03	0.42	0.33	0.21	0.02	0.01	0.13
MW		0.22	0.12	0.13	0.23	0.05	0.03	0.18	0.3	0.17	0.14	0.07	0.02	0.60	0.34	0.47	0	0.14	0.29
ACTIVITY		0.33	0.32	0.37	0.02	0.26	0.2	0.13	0.4	0.29	0	0.31	0.05	0.55	0.25	0.10	0.05	0.19	0.40
Catalysts Type II																			
C20		0.43713	-0.03631	0.3797	-0.04262	0.45048	-0.04859	0.40364	-0.06661	0.46244	-0.06141	0.17823	0.97404	0.19863	0.19911	0.15896	0.37587	0.19469	0.31646
C21		0.41121	-0.06446	0.40113	-0.06069	0.42639	-0.03447	0.42971	-0.03773	0.45872	-0.05576	0.17798	0.96414	0.18872	0.20837	0.17592	0.35774	0.18581	0.32098
C22		0.41258	-0.06617	0.4513	-0.0574	0.40803	-0.03831	0.4223	-0.04234	0.43167	-0.05785	0.1804	0.97062	0.19604	0.1906	0.18221	0.33878	0.17589	0.34115
C23		0.43049	-0.05176	0.36939	-0.04014	0.45955	-0.04136	0.41444	-0.05543	0.45912	-0.07049	0.1777	0.94853	0.19134	0.24238	0.1574	0.35395	0.20521	0.2862
C24_syn		0.40854	-0.06436	0.39128	-0.04441	0.44531	-0.03792	0.43518	-0.04471	0.4502	-0.07299	0.17738	0.96828	0.17662	0.28623	0.1683	0.31914	0.20687	0.25995
C24_anti		0.48638	-0.04036	0.3889	-0.04948	0.43874	-0.06238	0.36663	-0.05924	0.45068	-0.05457	0.17874	0.98928	0.16016	0.3642	0.20827	0.14695	0.1878	0.36643
C25		0.41931	-0.06207	0.40165	-0.05076	0.44418	-0.07159	0.43071	-0.04182	0.44176	-0.05175	0.17658	0.98124	0.16651	0.32597	0.1964	0.18484	0.19042	0.37434
INCORP.		0	0.03	0.19	0.29	0.4	0.16	0.05	0.01	0	0.13	0.56	0.01	0,31	0.40	0	0.16	0.48	0.04
MW		0.08	0.01	0.02	0.08	0.02	0.03	0.06	0	0.01	0.29	0.01	0.02	0.14	0.20	0.01	0.05	0.15	0.14
ACTIVITY		0.13	0.20	0.66	0.68	0.81	0.20	0.05	0.23	0.18	0.17	0.50	0.01	0.25	0.41	0	0.13	0.68	0.06

Table S6. Energetic Descriptors – Single correlations. Orbital Energies (E) and Occupations (Occ). (Ctd.)

Descriptor No.	38	39	40	41	42	43	44
Descriptor							
Catalyst	5s-4d_{xy} E	5s-4dz^2 E	5s-5p_xE	5s-5p_z E	Σ 5p Occ	Σ 4d Occ.	Σ 5 Occ.
Catalysts Type I							
C3	0.9892	0.96949	0.61139	0.73796	0.55098	2.129	0.72923
C4	1.08963	1.10162	0.70025	0.79246	0.53878	2.11949	0.71379
C5	1.08765	1.09882	0.68107	0.70139	0.53602	2.10653	0.711
C6	1.11844	1.1108	0.72928	0.69533	0.54117	2.12063	0.71722
C7	1.10795	1.09956	0.79509	0.67138	0.53746	2.10579	0.71379
C8	1.10523	1.09446	0.76185	0.66519	0.53698	2.10412	0.71337
C9	1.1005	1.10026	0.81772	0.6611	0.53687	2.10474	0.71328
C10	1.10938	1.1179	0.84205	0.68115	0.53695	2.10529	0.71329
C11	1.09147	1.10246	0.69133	0.80358	0.53649	2.10759	0.70994
C12	1.12922	1.13634	0.73672	0.88652	0.52606	2.0941	0.69755
C13	1.13069	1.15242	0.72796	0.81128	0.52483	2.08902	0.69579
C14	1.15677	1.14417	0.84581	0.72073	0.52531	2.08609	0.69718
C15	1.02608	1.03534	0.5711	0.63804	0.54342	2.13472	0.72125
C16	1.11299	1.13746	0.84823	0.76659	0.53805	2.10288	0.71382
C17	1.1052	1.11705	0.70239	0.69097	0.54138	2.10957	0.71589
C18	1.14235	1.15044	0.72793	0.82546	0.5327	2.09608	0.70801
C26	0.98838	0.98315	0.6178	0.58576	0.56996	2.15149	0.75374
INCORP.	0.01	0.01	0.09	0.18	0.08	0	0.11
MW	0.06	0.05	0.26	0.13	0	0.02	0
ACTIVITY	0.01	0.04	0.05	0.47	0.09	0.06	0.13
Catalysts Type II							
C20	1.01035	1.03545	0.77493	0.65758	0.55228	2.13339	0.73051
C21	1.0286	1.0199	0.75577	0.64316	0.55045	2.12716	0.72843
C22	1.03679	1.02847	0.78002	0.62947	0.55414	2.12588	0.73454
C23	1.00029	1.01902	0.70615	0.66233	0.55395	2.13299	0.73165
C24_syn	1.03264	1.04127	0.68205	0.70833	0.55179	2.13051	0.72917
C24_anti	1.02964	1.04385	0.62508	0.62285	0.55623	2.13133	0.73497
C25	1.04331	1.03299	0.65527	0.6069	0.55333	2.13761	0.72991
INCORP.	0.01	0.04	0.52	0.05	0.01	0.46	0.07
MW	0	0.06	0.27	0.17	0.20	0.04	0.14
ACTIVITY	0.08	0.21	0.48	0.12	0.03	0.58	0.04

Table S7. Energetic Descriptors – HOMO and LUMO energies.

	45	46	47
	HOMO	LUMO	LUMO-HOMO
Catalyst			
Catalysts Type I			
C3	-0.2584	-0.04965	0.20875
C4	-0.25806	-0.04861	0.20945
C5	-0.25733	-0.05042	0.20691
C6	-0.25746	-0.0516	0.20586
C7	-0.25759	-0.055	0.20259
C8	-0.25775	-0.05431	0.20344
C9	-0.25675	-0.05395	0.2028
C10	-0.25659	-0.05354	0.20305
C11	-0.25371	-0.05205	0.20166
C12	-0.25531	-0.04864	0.20667
C13	-0.25536	-0.04868	0.20668
C14	-0.25537	-0.0536	0.20177
C15	-0.24929	-0.04992	0.19937
C16	-0.25718	-0.05656	0.20062
C17	-0.25469	-0.05076	0.20393
C18	-0.2549	-0.0558	0.1991
C26	-0.26045	-0.05268	0.20777
INCORP.	0.12	0.58	0.12
MW	0.03	0.60	0.26
ACTIVITY	0.08	0.28	0.04
Catalysts Type II			
C20	-0.2615	-0.05413	0.20737
C21	-0.26106	-0.05478	0.20628
C22	-0.26108	-0.05945	0.20163
C23	-0.25925	-0.05438	0.20487
C24_syn	-0.25612	-0.05685	0.19927
C24_anti	-0.25389	-0.05275	0.20114
C25	-0.25542	-0.05824	0.19718
INCORP.	0.47	0.02	0.42
MW	0.27	0.02	0.11
ACTIVITY	0.41	0.17	0.07

Table S8. 3D Geometric Descriptors – Single correlations.

	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63
				5.0 Å							3.5 Å					
Catalyst	**%V_{Bur}**	**SW**	**NW**	**NE**	**SE**	**SW-NW**	**SE-NE**	**%V_{Bur}**	**SW**	**NW**	**NE**	**SE**	**SW-NW**	**SE-NE**	**Max**	**Min**
Catalysts Type I																
C3	56.5	40.1	62.4	60.8	62.6	22.3	1.8	68.2	65.1	70.6	68.4	68.7	5.5	0.3	5.5	0.3
C4	59.4	49.8	60.7	63	64	10.9	1	69.1	66.2	68.5	70.5	71.1	2.3	0.6	2.3	0.6
C5	61.4	58.5	60.6	62.7	63.9	2.1	1.2	69.5	68.4	68.6	70.1	71	0.2	0.9	0.9	0.9
C6	62.5	60.5	60.8	64.4	64.5	0.3	0.1	69.4	66.4	67.1	71.7	72.5	0.7	0.8	0.8	0.8
C7	61.4	58.9	61	62.3	63.6	2.1	1.3	69.9	70.7	69.1	69.6	70.4	1.6	0.8	1.6	0.8
C8	61.8	59	61.4	62.8	64.1	2.4	1.3	70.1	70.1	69	70.1	71.1	1.1	1	1.1	1
C9	61.5	59.1	61	62.3	63.5	1.9	1.2	69.9	70.8	69.1	69.6	70.3	1.7	0.7	1.7	0.7
C10	62	60.2	61.5	62.4	63.7	1.3	1.3	69.9	70.6	68.8	69.7	70.6	1.8	0.9	1.8	0.9
C11	61.4	57.4	62.1	61.6	64.5	4.7	2.9	69.7	68.6	70.5	69.2	70.4	1.9	1.2	1.9	1.2
C12	62.3	61.4	60.7	62.9	64.2	0.7	1.3	70.1	69.7	69.1	70.1	71.3	0.6	1.2	1.2	0.6
C13	62.6	62.5	61	62.8	64.3	1.5	1.5	70	69.5	69	70.4	71.3	0.5	0.9	0.9	0.5
C14	64	68.2	61.3	62.5	63.9	6.9	1.4	70.7	72.6	69.4	69.9	71	3.2	1.1	3.2	1.1
C15	56.8	49.9	62.4	63.5	51.4	12.5	12.1	68.5	69.1	69.9	66.7	68.4	0.8	1.7	1.7	0.8
C16	62.8	60.9	61.3	62	66.7	0.4	4.7	70.2	70.9	69.3	69.4	71.1	1.6	1.7	1.7	1.6
C17	62.4	61.5	64	59.3	64.9	2.5	5.6	70	72	72.1	67.2	68.6	0.1	1.4	1.4	0.1
C18	63.9	62.3	60.8	62.4	69.5	1.5	7.1	70.2	70.8	68.9	69.6	71.4	1.9	1.8	1.9	1.8
C26	56.1	59.5	56.5	47.8	60.7	3	12.9	68.8	74.2	71.4	62.9	66.6	2.8	3.7	3.7	2.8
INCORP.	0	0	0.01	0.04	0.07	0.02	0.01	0.01	0.09	0.01	0.02	0.02	0.06	0.01	0.02	0.14
MW	0.07	0.22	0.14	0.01	0.01	0.18	0.04	0.15	0.33	0.08	0	0.01	0	0.11	0.02	0.31
ACTIVITY	0.01	0.01	0.11	0.01	0.03	0.04	0.01	0	0.05	0.11	0.01	0	0	0.03	0	0.12
Catalysts Type II																
C20	58.5	50	49.7	69.2	65	0.3	4.2	69.1	66.6	65.8	72.3	71.9	0.8	0.4	0.8	0.4
C21	60.3	58.2	49	69	65.1	9.2	3.9	69.2	68.1	64.7	71.9	72.1	3.4	0.2	3.4	0.2
C22	60.5	58.1	50.5	68.4	64.9	7.6	3.5	69.9	70.7	66.1	71.2	71.8	4.6	0.6	4.6	0.6
C23	58.3	49	49.7	69.3	65.2	0.7	4.1	68.7	64.6	65.6	72.5	72.2	1	0.3	1	0.3
C24_syn	60.3	54.8	49.8	69.4	67.1	5	2.3	69.4	65.8	65.8	72.7	73.2	0	0.5	0.5	0
C24_anti	60.5	63.5	70.6	47.1	60.7	7.1	13.6	69.5	73.7	75.7	62.4	66.3	2	3.9	3.9	2
C25	60.8	55.2	49.9	68.8	69.2	5.3	0.4	68.8	64.8	65.6	71.9	73	0.8	1.1	1.1	0.8
INCORP.	0.05	0.11	0.09	0.08	0.11	0.07	0.08	0.30	0.31	0	0.02	0.06	0.56	0	0.43	0
MW	0.01	0.06	0.20	0.18	0.13	0.01	0.18	0.05	0.06	0.21	0.15	0.12	0.02	0.15	0.01	0.04
ACTIVITY	0.08	0.1	0.05	0.04	0.01	0.34	0.01	0.33	0.15	0.06	0.01	0.07	0.09	0.07	0.57	0.02

Table S8. 3D Geometric Descriptors – Single correlations (ctd.).

	64	65	66	67	68	69	70	71	72
		NPA			**Hirshfeld**			**CM5**	
Catalyst	q_{Zr}	q_{Cl}	q_{ZrCl_2}	q_{Zr}	q_{Cl}	q_{ZrCl_2}	q_{Zr}	q_{Cl}	q_{ZrCl_2}
Catalysts Type I									
C3	0.95932	-0.60001	0.35931	0.516171	-0.56162	-0.04545	0.978083	-0.71357	0.264512
C4	0.97619	-0.60339	0.3728	0.514464	-0.55516	-0.0407	0.976825	-0.70723	0.269591
C5	0.99265	-0.60496	0.38769	0.515032	-0.54222	-0.02719	0.975636	-0.69563	0.280006
C6	0.97655	-0.60003	0.37652	0.510882	-0.54155	-0.03066	0.969231	-0.69488	0.274352
C7	0.99045	-0.60452	0.38593	0.515267	-0.54326	-0.02799	0.976443	-0.69614	0.2803
C8	0.9923	-0.60385	0.38845	0.515925	-0.54178	-0.02585	0.975337	-0.69516	0.280179
C9	0.99158	-0.60572	0.38586	0.514848	-0.54458	-0.02973	0.975717	-0.69736	0.278358
C10	0.98995	-0.60533	0.38462	0.515264	-0.53774	-0.02247	0.976015	-0.6909	0.285119
C11	0.99016	-0.59314	0.39702	0.514791	-0.5439	-0.02911	0.976487	-0.69743	0.27906
C12	1.01364	-0.61542	0.39822	0.511273	-0.54421	-0.03294	0.974463	-0.69668	0.277786
C13	1.01976	-0.61475	0.40501	0.51217	-0.54389	-0.03172	0.975489	-0.69627	0.279216
C14	1.02285	-0.61579	0.40706	0.513021	-0.53073	-0.0177	0.97448	-0.6844	0.290081
C15	0.95975	-0.59645	0.3633	0.517991	-0.56499	-0.047	0.982896	-0.71746	0.26544
C16	0.99382	-0.60175	0.39207	0.511361	-0.53667	-0.02531	0.974141	-0.68934	0.284803
C17	0.98508	-0.58682	0.39826	0.511289	-0.53017	-0.01888	0.974096	-0.68448	0.289612
C18	1.00471	-0.60446	0.40025	0.515076	-0.5312	-0.01613	0.976342	-0.68426	0.292087
C26	0.9167	-0.58701	0.32969	0.519016	-0.55611	-0.03709	0.983222	-0.7085	0.274722
INCORP.	0.03	0.07	0.01	0.18	0.06	0.15	0.02	0.06	0.13
MW	0.01	0.04	0	0.04	0.13	0.21	0.04	0.13	0.22
ACTIVITY	0.08	0	0.13	0.13	0	0	0	0	0
Catalysts Type II									
C20	0.9557	-0.59658	0.35912	0.519735	-0.5473	-0.02756	0.982361	-0.70011	0.282256
C21	0.96681	-0.59603	0.37078	0.519546	-0.53063	-0.01108	0.980162	-0.6851	0.295058
C22	0.96172	-0.5971	0.36462	0.520467	-0.52868	-0.00821	0.981375	-0.68302	0.298358
C23	0.95604	-0.60024	0.3558	0.519393	-0.54381	-0.02442	0.981511	-0.6967	0.284812
C24_syn	0.9609	-0.58686	0.37404	0.520209	-0.53757	-0.01736	0.982248	-0.69129	0.29096
C24_anti	0.95519	-0.57946	0.37573	0.517534	-0.53499	-0.01746	0.979954	-0.6896	0.290351
C25	0.95674	-0.58135	0.37539	0.521349	-0.51206	0.00929	0.97783	-0.66838	0.309452
INCORP.	0.16	0.22	0.07	0.07	0.06	0.07	0.08	0.06	0.06
MW	0.01	0.05	0.03	0.21	0.06	0.07	0.06	0.06	0.06
ACTIVITY	0.46	0.21	0.01	0.03	0.05	0.05	0	0.06	0.01

QSAR Models for Catalysts of Type I and II.

Models. Regression Analysis. Catalysts Type I.

M_w Model

Regression Statistics	
Multiple R	0.9291327
R Square	0.8632876
Adjusted R Squa	0.8317385
Standard Error	0.3115237
Observations	17

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	7.966599681	2.655533	27.36336653	6.88815E-06
Residual	13	1.261611283	0.097047		
Total	16	9.228210964			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	-215.53176	95.9237222	-2.24691	0.042650198	-422.7623648	-8.3011591	-422.762365	-8.301159071
X Variable 1	-16.172315	8.143786814	-1.98585	0.068554199	-33.76589655	1.42126701	-33.7658965	1.421267008
X Variable 2	-0.4005411	0.069163303	-5.79124	6.26557E-05	-0.549959341	-0.2511229	-0.54995934	-0.251122877
X Variable 3	54.222654	19.75361851	2.744948	0.016698242	11.54755611	96.8977527	11.54755611	96.89775266

Incorporation Model

Regression Statistics	
Multiple R	0.961598007
R Square	0.924670727
Adjusted R Squ	0.899560969
Standard Error	0.146517335
Observations	17

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	3.16215094	0.790538	36.82516	1.19645E-06
Residual	12	0.257607952	0.021467		
Total	16	3.419758892			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	39.347394	10.73664027	3.664777	0.003238	15.95426444	62.74052356	15.95426444	62.74052356
X Variable 1	2.094797089	0.421203935	4.973356	0.000323	1.177072552	3.012521625	1.177072552	3.012521625
X Variable 2	-22.5319909	6.957714912	-3.23842	0.007107	-37.6915494	-7.37243241	-37.69154944	-7.372432408
X Variable 3	-217.364762	43.40808653	-5.00747	0.000305	-311.942857	-122.786666	-311.9428573	-122.7866657
X Variable 4	0.04284154	0.018531746	2.311792	0.039348	0.002464334	0.083218746	0.002464334	0.083218746

Models. Regression Analysis. Catalysts Type II.

Incorporation Model

Regression Statistics								
Multiple R	0.982739746							
R Square	0.965777408							
Adjusted R Squ	0.948666111							
Standard Error	0.138747763							
Observations	7							
ANOVA								
	df	*SS*	*MS*	*F*	*Significance F*			
Regression	2	2.173081977	1.086541	56.44093	0.001171186			
Residual	4	0.077003767	0.019251					
Total	6	2.250085745						
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	-79.9829907	9.030126433	-8.85735	0.000897	-105.054641	-54.9113403	-105.054641	-54.91134033
X Variable 1	0.186458436	0.05185039	3.596086	0.022838	0.042498676	0.330418196	0.042498676	0.330418196
X Variable 2	5.868780297	1.073161771	5.468682	0.005439	2.88920555	8.848355044	2.88920555	8.848355044

Models. Regression Analysis. Combined Catalyst Set.

M_w Model

Regression Statistics	
Multiple R	0.8643704
R Square	0.7471362
Adjusted R Squa	0.6939017
Standard Error	0.35856
Observations	24

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	7.217557758	1.804389	14.03481381	1.72104E-05
Residual	19	2.442739876	0.128565		
Total	23	9.660297634			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	-280.18573	83.33336871	-3.36223	0.003272242	-454.6044794	-105.76699	-454.604479	-105.7669889
X Variable 1	57.049162	17.08758607	3.338632	0.00345127	21.28443369	92.8138911	21.28443369	92.81389106
X Variable 2	-4.2689719	1.161003808	-3.67697	0.001601656	-6.698980841	-1.838963	-6.69898084	-1.838963046
X Variable 3	-118.67555	36.87400645	-3.21841	0.004523536	-195.8537324	-41.497367	-195.853732	-41.49736742
X Variable 4	16.599467	7.566425904	2.193832	0.040886131	0.762756077	32.4361789	0.762756077	32.43617892

Incorporation Model

Regression Statistics	
Multiple R	0.9300815
R Square	0.865051596
Adjusted R Sq	0.827565928
Standard Erro	0.238341122
Observations	24

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	6.554578	1.310916	23.07686236	3.01519E-07
Residual	18	1.022517	0.056806		
Total	23	7.577095			

	Coefficients	*andard Err*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*pper 95.0%*
Intercept	-161.8932265	49.74789	-3.25427	0.004403754	-266.409669	-57.37678438	-266.4096686	-57.3768
X Variable 1	9.346129973	1.511519	6.183269	7.76003E-06	6.170545964	12.52171398	6.170545964	12.52171
X Variable 2	-26.37952473	6.179482	-4.26889	0.000461891	-39.3621343	-13.39691513	-39.36213433	-13.3969
X Variable 3	-113.3556124	44.23907	-2.56234	0.019587396	-206.298447	-20.41277769	-206.298447	-20.4128
X Variable 4	0.079652595	0.015665	5.084627	7.73309E-05	0.046740859	0.112564331	0.046740859	0.112564
X Variable 5	22.01577073	8.418365	2.615207	0.017529412	4.329441442	39.70210003	4.329441442	39.7021

Models. Leave-one-out Cross Validation (LOOCV) Analysis.

Models. LOOCV Analysis. Abbreviations.

MEAN = mean experimental value; MAD = mean average deviation; MSE = mean squared error;

RMSE = root mean squared error; q^2 (manuscript) or Q2 (here) = cross-validated R^2

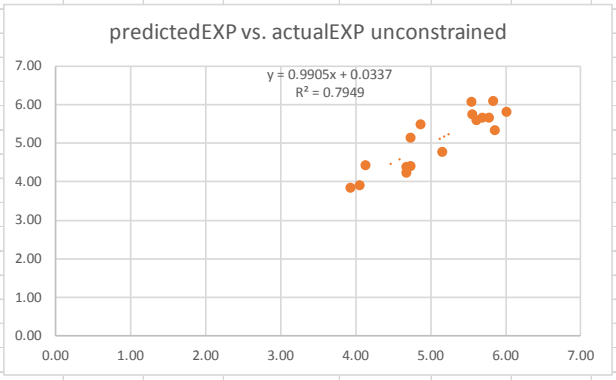
Models. LOOCV Analysis. Catalysts Type I.

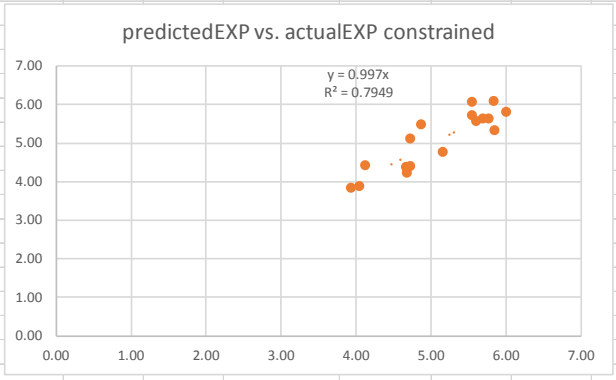
M_w Model

Catalyst	Yintercept	slopeA	slopeB	slopeC	predictedEXP	actualEXP	R2	adjR2	|Δ|	Δ2	(actualEXP-MEAN)^2
C3	-218.592	-15.9565	-0.38801	54.58814	4.04	3.89	0.84	0.80	0.153	0.023	1.426
C4	-198.611	-17.1556	-0.42125	51.20108	4.12	4.43	0.86	0.83	0.305	0.093	0.435
C5	-200.606	-19.172	-0.39111	51.0636	4.86	5.48	0.90	0.87	0.615	0.378	0.154
C6	-224.547	-14.2279	-0.41287	56.26231	5.15	4.77	0.88	0.85	0.382	0.146	0.100
C7	-215.685	-16.2948	-0.40101	54.26873	5.68	5.65	0.86	0.82	0.032	0.001	0.318
C8	-218.092	-15.8313	-0.42975	55.34335	5.85	5.34	0.89	0.86	0.511	0.261	0.062
C9	-218.472	-16.3345	-0.4041	54.90818	5.77	5.65	0.86	0.82	0.117	0.014	0.318
C10	-205.155	-17.1524	-0.38986	51.90302	5.54	5.74	0.86	0.82	0.194	0.038	0.425
C11	-197.023	-17.3654	-0.39064	50.25772	3.93	3.84	0.83	0.79	0.088	0.008	1.545
C12	-244.41	-15.2754	-0.3845	59.80294	4.72	4.40	0.86	0.83	0.321	0.103	0.465
C13	-243.829	-15.2735	-0.3846	59.68501	4.66	4.38	0.86	0.83	0.284	0.081	0.497
C14	-219.624	-17.1088	-0.40477	55.18879	6.00	5.81	0.86	0.82	0.194	0.038	0.519
C15	-223.942	-19.1391	-0.3825	55.68807	4.72	5.12	0.88	0.85	0.402	0.161	0.001
C16	-228.328	-12.0868	-0.41004	56.89371	5.83	6.09	0.85	0.81	0.258	0.066	1.001
C17	-150.912	-13.2333	-0.42813	41.39349	4.67	4.22	0.86	0.83	0.452	0.204	0.744
C18	-208.243	-15.1506	-0.39084	52.47897	5.54	6.07	0.88	0.85	0.530	0.281	0.972
C26	-215.279	-16.1479	-0.40166	54.19291	5.60	5.58	0.86	0.82	0.020	0.000	0.244
						MEAN			**MAD**	**MSE**	
						5.09			**0.29**	**0.11**	

Q^2=(actualEXP-MEAN)-SUM(Δ^2)/(actualEXP-MEAN)

Q2	**0.79**
RMSE	**0.33**



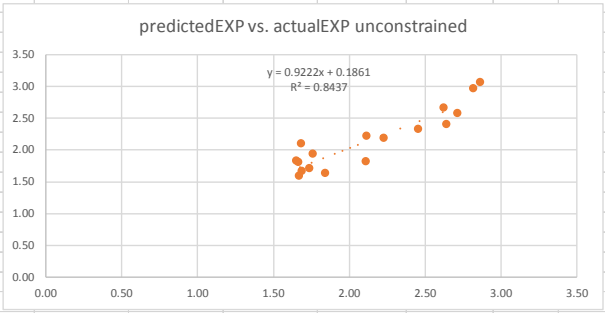


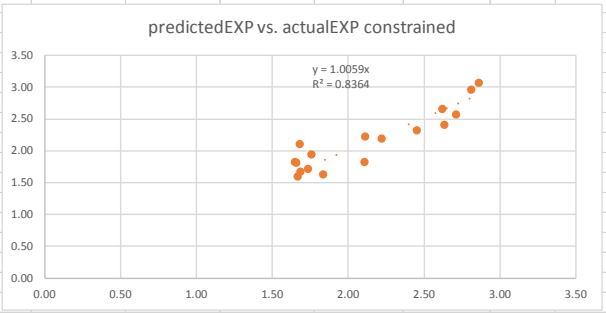
Incorporation Model

Catalyst	Yintercept	X Variable 1	X Variable 2	X Variable 3	X Variable 4	predictedEXP	actualEXP	R2	adjR2	|Δ|	Δ2	(actualEXP-MEAN)^2
C3	31.26866	2.544592	-17.64841	-200.5662	0.06870004	1.68	2.10	0.95	0.93	0.421	0.178	0.002
C4	46.10025	1.933894	-26.64718	-241.7444	0.03755998	2.63	2.41	0.93	0.91	0.226	0.051	0.067
C5	40.14823	2.017577	-22.58189	-217.955	0.03686907	2.11	1.82	0.94	0.92	0.287	0.083	0.109
C6	40.83896	2.01755	-23.46975	-223.1303	0.04460551	2.62	2.66	0.92	0.89	0.045	0.002	0.264
C7	39.33339	2.087137	-22.51754	-217.1624	0.04281589	1.73	1.72	0.92	0.89	0.017	0.000	0.188
C8	42.03507	2.100175	-24.40204	-229.9469	0.04588441	1.65	1.83	0.93	0.91	0.182	0.033	0.103
C9	39.35829	2.086683	-22.53369	-217.2647	0.04282357	1.68	1.67	0.92	0.89	0.015	0.000	0.230
C10	39.05127	2.032106	-22.33416	-214.9184	0.04285804	1.84	1.63	0.93	0.90	0.204	0.042	0.267
C11	39.46485	2.089002	-22.52466	-217.7411	0.042355	2.22	2.19	0.92	0.90	0.033	0.001	0.002
C12	34.39205	2.101537	-19.61085	-193.2055	0.0365005	2.86	3.07	0.91	0.88	0.206	0.043	0.841
C13	37.21328	2.063897	-21.49687	-205.7015	0.03965125	2.81	2.96	0.91	0.88	0.153	0.023	0.666
C14	41.68439	2.046406	-23.87894	-229.251	0.04897696	2.45	2.33	0.93	0.90	0.123	0.015	0.032
C15	36.72844	2.286697	-21.35184	-208.7529	0.04360971	2.71	2.58	0.92	0.90	0.133	0.018	0.183
C16	40.26973	2.144468	-23.26903	-222.1512	0.04334404	1.66	1.81	0.93	0.90	0.151	0.023	0.115
C17	41.32494	2.021158	-23.79881	-223.5974	0.04040729	2.11	2.22	0.93	0.90	0.111	0.012	0.005
C18	37.41174	2.121834	-21.17754	-209.3668	0.0418294	1.67	1.60	0.92	0.89	0.069	0.005	0.304
C26	37.53878	2.11465	-19.56128	-209.0056	0.0303069	1.76	1.94	0.93	0.90	0.185	0.034	0.043
							MEAN			**MAD**	**MSE**	
							2.15			**0.15**	**0.03**	

Q^2=(actualEXP-MEAN)-SUM(Δ^2)/(actualEXP-MEAN)

Q2	0.84
RMSE	0.18

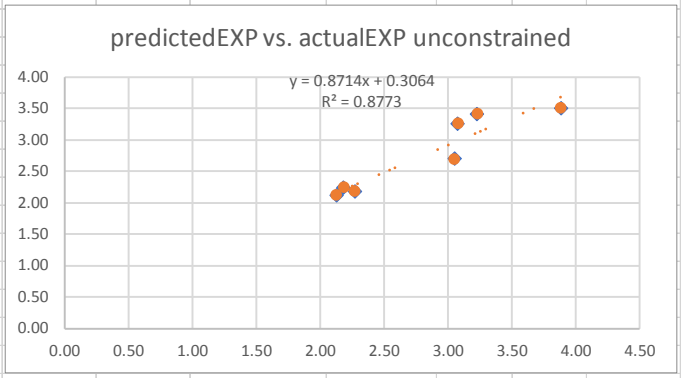


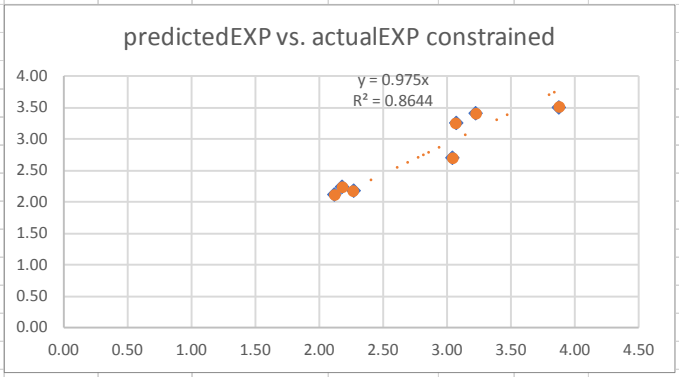


Models. LOOCV Analysis. Catalysts Type II.

Incorporation Model

Catalyst	Yintercept	slopeA	slopeB	predictedEXP	actualEXP	R2	adjR2	|Δ|	Δ2	(actualEXP-MEAN)^2
C20	-80.8426	0.193692	5.875532	2.18	2.24	0.96	0.94	0.058	0.003	0.282
C21	-79.5002	0.166297	6.028201	2.27	2.17	0.96	0.93	0.093	0.009	0.354
C22	-79.7672	0.18667	5.84653	2.12	2.12	0.96	0.93	0.006	0.000	0.428
C23	-78.7793	0.168964	5.930116	3.07	3.25	0.97	0.96	0.181	0.033	0.232
C24-syn	-76.4607	0.178563	5.6161	3.22	3.41	0.97	0.95	0.185	0.034	0.409
C24-anti	-72.843	0.272496	4.336846	3.04	2.70	0.99	0.98	0.349	0.122	0.006
C25	-97.2662	0.161097	7.748231	3.88	3.50	0.98	0.97	0.375	0.141	0.538
					MEAN			**MAD**	**MSE**	
					2.77			**0.18**	**0.05**	
				Q^2=(actualEXP-MEAN)-SUM(Δ^2)/(actualEXP-MEAN)						
				Q2	**0.85**					
				RMSE	0.22					

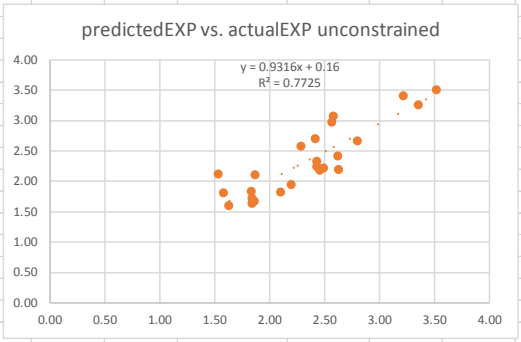


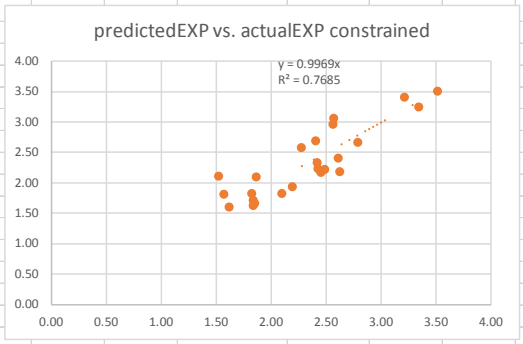


Models. LOOCV Analysis. Combined Catalysts Set.

M_w Model

Catalyst	Yintercept	slopeA	slopeB	slopeC	slopeD	slopeE	predictedEXP	actualEXP	R2	adjR2	|Δ|	Δ2	(actualEXP-MEAN)^2
C3	-177.788	9.718554	-24.9914	-104.73	0.085885	24.383	1.86	2.10	0.87	0.83	0.239	0.057	0.052
C4	-158.817	9.232259	-28.4278	-127.326	0.079658	22.37856	2.61	2.41	0.87	0.83	0.203	0.041	0.006
C5	-161.21	9.302418	-26.5978	-115.26	0.076978	22.16588	2.10	1.82	0.87	0.83	0.276	0.076	0.261
C6	-177.045	9.617425	-27.2257	-113.726	0.083402	25.20004	2.79	2.66	0.86	0.82	0.128	0.016	0.111
C7	-163.543	9.342347	-26.0668	-110.662	0.078885	22.33145	1.84	1.72	0.86	0.82	0.120	0.014	0.377
C8	-161.861	9.345928	-26.3906	-113.439	0.079672	22.01202	1.83	1.83	0.86	0.82	0.002	0.000	0.251
C9	-164.248	9.333302	-25.8346	-109.07	0.078756	22.45022	1.85	1.67	0.86	0.82	0.182	0.033	0.436
C10	-161.969	9.280692	-25.9506	-110.28	0.077887	22.09802	1.84	1.63	0.86	0.82	0.204	0.042	0.486
C11	-150.683	9.442159	-25.4718	-114.187	0.072999	18.99785	2.62	2.19	0.88	0.85	0.432	0.187	0.020
C12	-178.304	9.750005	-23.5975	-77.2199	0.077692	23.30734	2.57	3.07	0.88	0.85	0.494	0.244	0.542
C13	-173.393	9.659875	-25.1229	-87.8656	0.076346	22.964	2.56	2.97	0.87	0.84	0.403	0.163	0.403
C14	-162.177	9.371327	-26.3015	-114.636	0.079305	22.08448	2.42	2.33	0.87	0.83	0.093	0.009	0.000
C15	-165.61	9.33963	-24.8703	-109.315	0.08443	22.49918	2.28	2.58	0.87	0.84	0.300	0.090	0.061
C16	-162.753	9.538002	-27.4353	-117.497	0.08043	21.97227	1.57	1.81	0.87	0.83	0.237	0.056	0.270
C17	-145.079	8.808578	-24.1948	-116.732	0.086166	18.8201	2.49	2.22	0.87	0.83	0.265	0.070	0.012
C18	-162.017	9.34019	-26.198	-112.411	0.079531	22.00756	1.62	1.60	0.85	0.81	0.021	0.000	0.536
C26	-154.487	8.94712	-27.4	-115.674	0.082694	21.29178	2.19	1.94	0.87	0.83	0.250	0.062	0.151
C20	-147.658	9.005388	-27.1405	-121.735	0.078799	19.73066	2.42	2.24	0.87	0.83	0.186	0.035	0.008
C21	-168.711	9.557835	-26.2169	-106.952	0.080142	22.88577	2.45	2.17	0.87	0.84	0.278	0.077	0.024
C22	-148.86	9.115081	-28.9544	-150.38	0.088034	20.90888	1.52	2.12	0.90	0.87	0.592	0.350	0.046
C23	-162.838	9.448076	-27.1597	-116.32	0.080166	22.17644	3.34	3.25	0.85	0.80	0.092	0.009	0.849
C24-syn	-150.304	8.874812	-26.8689	-121.51	0.076395	20.83159	3.21	3.41	0.84	0.80	0.198	0.039	1.164
C24-anti	-163.625	9.406514	-29.0571	-126.181	0.072826	23.39822	2.41	2.69	0.87	0.83	0.289	0.083	0.133
C25	-162.582	9.378252	-26.3775	-112.936	0.079667	22.0866	3.51	3.50	0.83	0.78	0.009	0.000	1.376
							MEAN				**MAD**	**MSE**	
							2.33				**0.23**	**0.07**	
							Q^2=(actualEXP-MEAN)-SUM(Δ^2)/(actualEXP-MEAN)						
							Q2	0.77					
							RMSE	0.26					





Incorporation Model

Catalyst	Yintercept	slopeA	slopeB	slopeC	slopeD	slopeE	predictedEXP	actualEXP	R2	adjR2	|Δ|	Δ2	(actualEXP-MEAN)^2
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C5	-161.21	9.302418	-26.5978	-115.26	0.076978	22.16588	2.10	1.82	0.87	0.83	0.276	0.076	0.261
C6	-177.045	9.617425	-27.2257	-113.726	0.083402	25.20004	2.79	2.66	0.86	0.82	0.128	0.016	0.111
C7	-163.543	9.342347	-26.0668	-110.662	0.078885	22.33145	1.84	1.72	0.86	0.82	0.120	0.014	0.377
C8	-161.861	9.345928	-26.3906	-113.439	0.079672	22.01202	1.83	1.83	0.86	0.82	0.002	0.000	0.251
C9	-164.248	9.333302	-25.8346	-109.07	0.078756	22.45022	1.85	1.67	0.86	0.82	0.182	0.033	0.436
C10	-161.969	9.280692	-25.9506	-110.28	0.077887	22.09802	1.84	1.63	0.86	0.82	0.204	0.042	0.486
C11	-150.683	9.442159	-25.4718	-114.187	0.072999	18.99785	2.62	2.19	0.88	0.85	0.432	0.187	0.020
C12	-178.304	9.750005	-23.5975	-77.2199	0.077692	23.30734	2.57	3.07	0.88	0.85	0.494	0.244	0.542
C13	-173.393	9.659875	-25.1229	-87.8656	0.076346	22.964	2.56	2.97	0.87	0.84	0.403	0.163	0.403
C14	-162.177	9.371327	-26.3015	-114.636	0.079305	22.08448	2.42	2.33	0.87	0.83	0.093	0.009	0.000
C15	-165.61	9.33963	-24.8703	-109.315	0.08443	22.49918	2.28	2.58	0.87	0.84	0.300	0.090	0.061
C16	-162.753	9.538002	-27.4353	-117.497	0.08043	21.97227	1.57	1.81	0.87	0.83	0.237	0.056	0.270
C17	-145.079	8.808578	-24.1948	-116.732	0.086166	18.8201	2.49	2.22	0.87	0.83	0.265	0.070	0.012
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C26	-154.487	8.94712	-27.4	-115.674	0.082694	21.29178	2.19	1.94	0.87	0.83	0.250	0.062	0.151
C20	-147.658	9.005388	-27.1405	-121.735	0.078799	19.73066	2.42	2.24	0.87	0.83	0.186	0.035	0.008
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C22	-148.86	9.115081	-28.9544	-150.38	0.088034	20.90888	1.52	2.12	0.90	0.87	0.592	0.350	0.046
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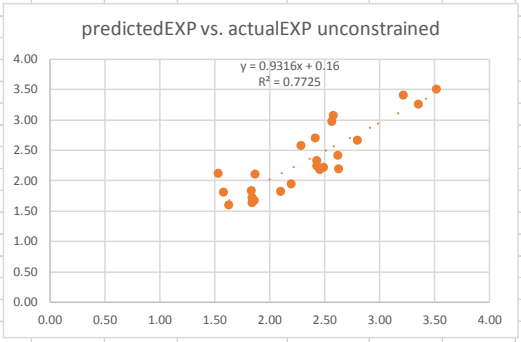
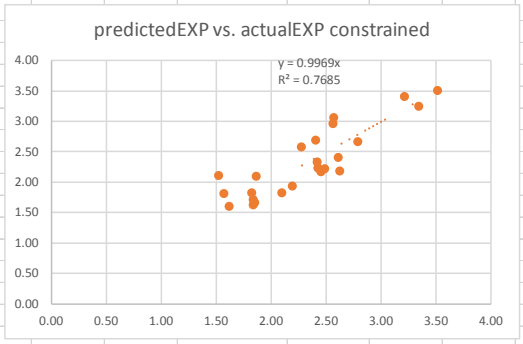
C24-syn	-150.304	8.874812	-26.8689	-121.51	0.076395	20.83159	3.21	3.41	0.84	0.80	0.198	0.039	1.164
C24-anti	-163.625	9.406514	-29.0571	-126.181	0.072826	23.39822	2.41	2.69	0.87	0.83	0.289	0.083	0.133
C25	-162.582	9.378252	-26.3775	-112.936	0.079667	22.0866	3.51	3.50	0.83	0.78	0.009	0.000	1.376
							MEAN				**MAD**	**MSE**	
							2.33				**0.23**	**0.07**	

Q^2=(actualEXP-MEAN)-SUM(Δ^2)/(actualEXP-MEAN)

Q2	0.77
RMSE	0.26





X-Ray crystallography data

Crystal structure determinations. Single crystals of complexes **C12** and *syn*-**C24** for the X-ray study were obtained by slow evaporation of solutions in toluene. Crystallographic data for these complexes were deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 1974079 and 1974080, respectively. The details of data collection and crystal structures refinement are summarized in Tables S9 and S10.

Table S9. Crystal data and structure refinement for C12

CCDC	1974079	
Empirical formula	$C_{24}H_{26}Cl_2SiZr$	
Formula weight	504.66	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.3079(6) Å	α = 75.8230(10)°.
	b = 9.6561(6) Å	β = 80.9580(10)°.
	c = 13.8605(8) Å	γ = 61.5860(10)°.
Volume	1061.11(11) $Å^3$	
Z	2	
Density (calculated)	1.579 Mg/m^3	
Absorption coefficient	0.835 mm^{-1}	
F(000)	516	
Crystal size	0.18 x 0.15 x 0.09 mm^3	
Theta range for data collection	2.446 to 29.000°.	
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-18 \le l \le 18$	
Reflections collected	16548	
Independent reflections	5632 [R(int) = 0.0250]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.7067	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5632 / 0 / 259	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0661	
R indices (all data)	R1 = 0.0339, wR2 = 0.0690	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.909 and -0.413 $e.Å^{-3}$	

Table S10. Crystal data and structure refinement for *syn*-C24

CCDC	1974080	
Empirical formula	C_{32} H_{26} Cl_2 Si Zr	
Formula weight	600.74	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.1061(4) Å	α = 90°.
	b = 10.6032(4) Å	β = 96.9880(10)°.
	c = 24.5397(10) Å	γ = 90°.
Volume	2610.07(18) $Å^3$	
Z	4	
Density (calculated)	1.529 Mg/m^3	
Absorption coefficient	0.693 mm^{-1}	
F(000)	1224	
Crystal size	0.14 x 0.08 x 0.02 mm^3	
Theta range for data collection	1.672 to 28.999°.	
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-33 \leq l \leq 33$	
Reflections collected	51545	
Independent reflections	6941 [R(int) = 0.0407]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.7067	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6941 / 0 / 327	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0271, wR2 = 0.0660	
R indices (all data)	R1 = 0.0363, wR2 = 0.0713	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.561 and -0.285 $e.Å^{-3}$	

Full Gaussian Citation

Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.