

Ring-Closing Metathesis of Sterically Congested
Functionalized Zirconocenes – Ethene
Polymerization Catalysts Derived from Related
Bridged and Open Metallocenes

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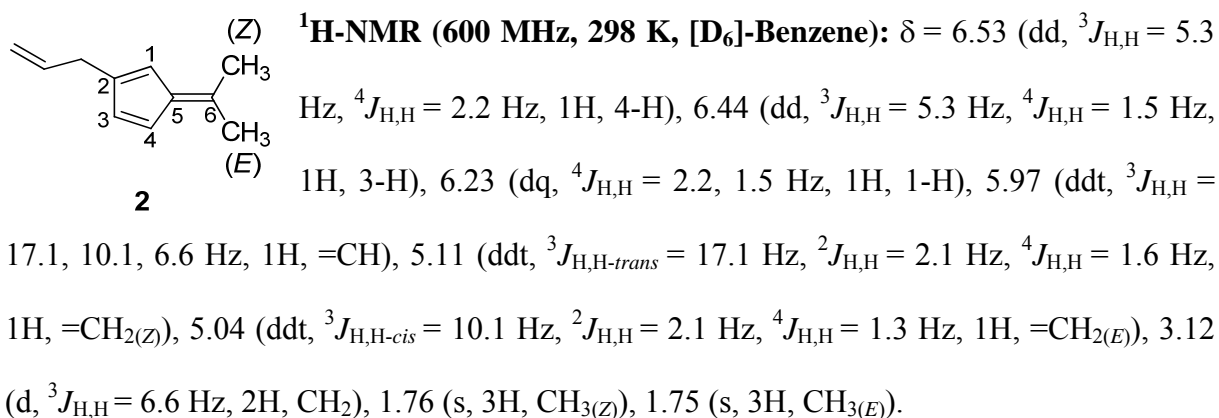
SUPPORTING INFORMATION

Experimental Section

General Information. Reactions with air- and moisture-sensitive compounds were carried out under an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled from appropriate drying agents under argon prior to use. The following instruments were used for physical characterization of the compounds. Melting points: TA-instruments DSC Q-20. Elemental analyses: Foss-Heraeus CHN-O-Rapid. NMR: Bruker AC 200 P (^1H , 200 MHz; ^{13}C , 50 MHz), Varian Inova 500 (^1H , 500 MHz; ^{13}C , 126 MHz), Varian UnityPlus 600 (^1H , 600 MHz; ^{13}C , 151 MHz). Assignments of the resonances were supported by 2D experiments. X-ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (B.V. Nonius, 1998), data reduction Denzo-SMN (Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307), absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr.*, 1995, **A51**, 33; R. H. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421) and Denzo (Z. Otwinowski, D. Borek, W. Majewski and W. Minor, *Acta Crystallogr.*, 2003, **A59**, 228), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467), structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112), graphics SCHAKAL (E. Keller, Univ. Freiburg, 1997).

The mixture of allylcyclopentadiene isomers **1** was prepared according to modified literature procedures.⁹

Preparation of compound 2. The allylcyclopentadiene isomer mixture **1** (20.2 g, 190 mmol) and pyrrolidine (9.4 mL, 114 mmol) were dissolved in methanol (75 mL). Acetone (5.6 mL, 76 mmol) was added and the reaction mixture was stirred for 4 h at room temperature. Subsequently, the resulting reaction mixture was quenched by adding acetic acid (7.0 mL, 122 mmol), pentane (75 mL) and water (75 mL). The organic phase was separated by extraction and washed twice with water (2×40 mL). After drying over sodium sulfate and filtering through silica gel, the solvents were removed in vacuo to afford the fulvene as a yellow oil in a quantitative yield.



¹³C{¹H}-NMR (151 MHz, 298 K, [D₆]-Benzene): δ = 145.4 (C-6), 144.4 (C-2), 143.2 (C-5), 136.9 (=CH), 132.7 (C-3), 121.9 (C-4), 116.6 (C-1), 115.7 (=CH₂), 35.1 (CH₂), 22.4 (CH_{3(Z)}), 22.3 (CH_{3(E)}).

¹H,¹H-GCOSY (600 MHz / 600 MHz, 298 K, [D₆]-Benzene): δ (¹H) / δ (¹H) = 6.53 / 6.44, 6.23 (4-H / 3-H, 1-H), 6.44 / 6.23 (3-H / 1-H), 6.23 / 3.12 (1-H / CH₂), 5.97 / 5.11, 5.04, 3.12 (=CH / =CH_{2(Z)}, =CH_{2(E)}, CH₂), 5.11 / 5.04, 3.12 (=CH_{2(Z)} / =CH_{2(E)}, CH₂), 5.04 / 3.12 (=CH_{2(E)} / CH₂), 3.12 / 1.75 (CH₂ / CH_{3(E)}).

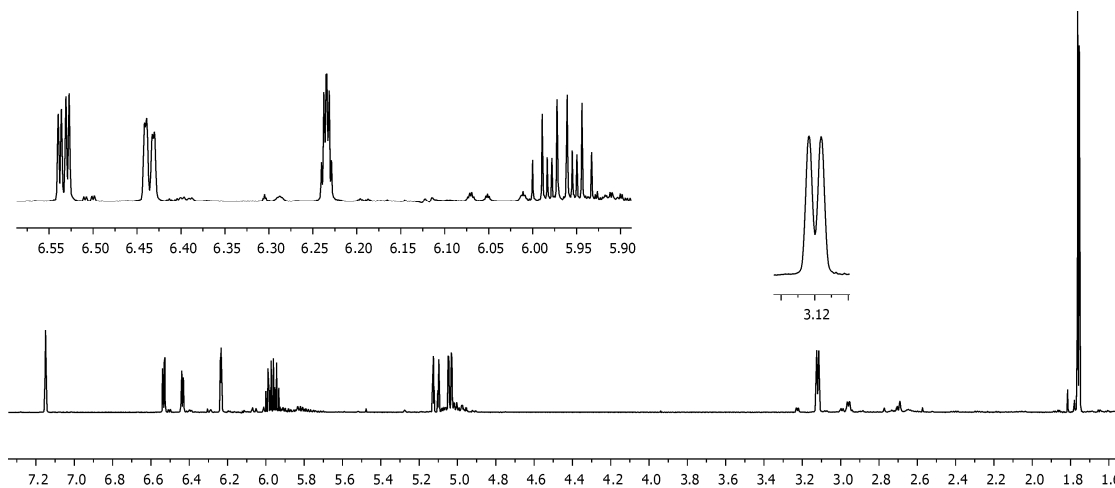
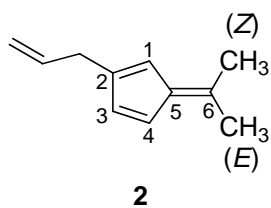
¹H,¹³C-GHSQC (600 MHz / 151 MHz, 298 K, [D₆]-Benzene): δ (¹H) / δ (¹³C) = 6.53 / 121.9 (4-H / C-4), 6.44 / 132.7 (3-H / C-3), 6.23 / 116.6 (1-H / C-1), 5.97 / 136.9 (=CH / =CH), 5.11, 5.04 / 115.7 (=CH_{2(Z)}, =CH_{2(E)} / =CH₂), 3.12 / 35.1 (CH₂ / CH₂), 1.76 / 22.4 (CH_{3(Z)} / CH_{3(Z)}), 1.75 / 22.3 (CH_{3(E)} / CH_{3(E)}).

^1H , ^{13}C -GHMBC (600 MHz / 151 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 6.53 / 144.4, 143.2, 132.7, 116.6$ (4-H / C-2, C-5, C-3, C-1), $6.44 / 144.4, 143.2, 121.9, 116.6$ (3-H / C-2, C-5, C-4, C-1), $6.23 / 144.4, 143.2, 132.7, 121.9, 35.1$ (1-H / C-2, C-5, C-3, C-4, CH_2), $5.97 / 144.4, 35.1$ ($=\text{CH} / \text{C-2}, \text{CH}_2$), $5.11 / 136.9, 35.1$ ($=\text{CH}_{2(\text{Z})} / =\text{CH}, \text{CH}_2$), $5.04 / 35.1$ ($=\text{CH}_{2(\text{E})} / \text{CH}_2$), $3.12 / 144.4, 136.9, 132.7, 116.6, 115.7$ ($\text{CH}_2 / \text{C-2}, =\text{CH}, \text{C-3}, \text{C-1}, =\text{CH}_2$), $1.76 / 145.4, 143.2, 121.9, 22.3$ ($\text{CH}_{3(\text{Z})} / \text{C-6}, \text{C-5}, \text{C-4}, \text{CH}_{3(\text{E})}$), $1.75 / 145.4, 143.2, 116.6, 22.4$ ($\text{CH}_{3(\text{E})} / \text{C-6}, \text{C-5}, \text{C-1}, \text{CH}_{3(\text{Z})}$).

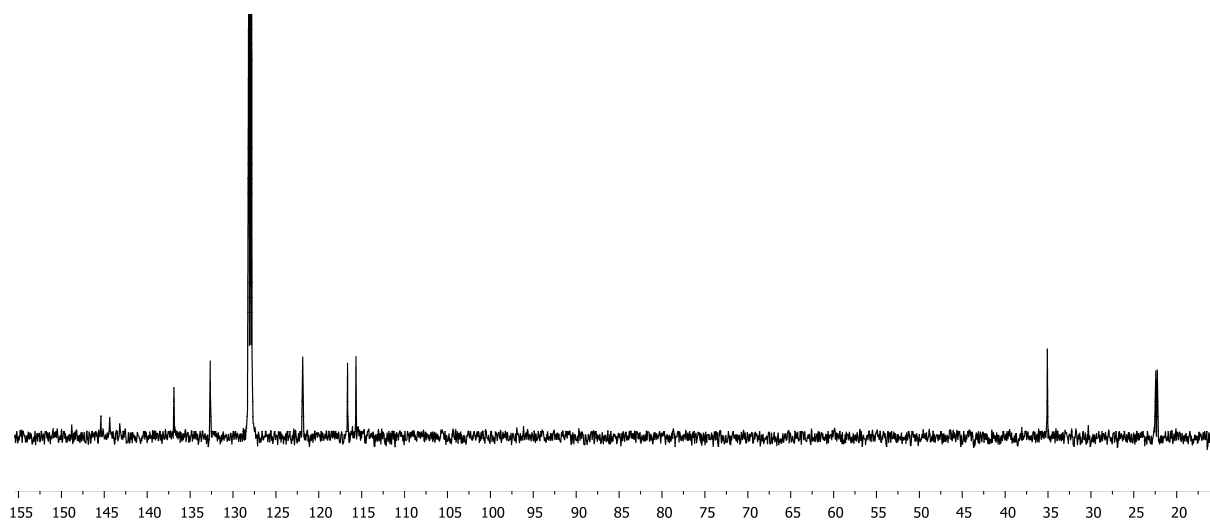
$^1\text{H}\{^1\text{H}\}$ -TOCSY (600 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H})_{\text{irr.}} / \delta (^1\text{H})_{\text{res.}} = 6.53 / 6.44, 6.23$ (4-H / 3-H, 1-H), $6.44 / 6.53, 6.23, 3.12$ (3-H / 4-H, 1-H, CH_2), $6.23 / 6.53, 6.44, 3.12$ (1-H / 4-H, 3-H, CH_2), $5.97 / 5.11, 5.04, 3.12$ ($=\text{CH} / =\text{CH}_{2(\text{Z})}, =\text{CH}_{2(\text{E})}, \text{CH}_2$), $5.11 / 5.97, 5.04, 3.12$ ($=\text{CH}_{2(\text{Z})} / =\text{CH}, =\text{CH}_{2(\text{E})}, \text{CH}_2$), $5.04 / 5.97, 5.11, 3.12$ ($=\text{CH}_{2(\text{E})} / =\text{CH}, =\text{CH}_{2(\text{Z})}, \text{CH}_2$), $3.12 / 6.44, 6.23, 5.97, 5.11, 5.04$ ($\text{CH}_2 / 3\text{-H}, 1\text{-H}, =\text{CH}, =\text{CH}_{2(\text{Z})}, =\text{CH}_{2(\text{E})}$), $1.76 / 1.75$ ($\text{CH}_{3(\text{Z})} / \text{CH}_{3(\text{E})}$).

$^1\text{H}\{^1\text{H}\}$ -NOE (600 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H})_{\text{irr.}} / \delta (^1\text{H})_{\text{res.}} = 6.53 / 6.44, 1.75$ (4-H / 3-H, $\text{CH}_{3(\text{E})}$), $6.44 / 6.53$ (3-H / 4-H), $6.23 / 3.12, 1.76$ (1-H / $\text{CH}_2, \text{CH}_{3(\text{Z})}$), $5.97 / 5.11, 5.04, 3.12$ ($=\text{CH} / =\text{CH}_{2(\text{Z})}, =\text{CH}_{2(\text{E})}, \text{CH}_2$), $5.11 / 5.97, 3.12$ ($=\text{CH}_{2(\text{Z})} / =\text{CH}, \text{CH}_2$), $5.04 / 5.97, 3.12$ ($=\text{CH}_{2(\text{E})} / =\text{CH}, \text{CH}_2$), $3.12 / 6.44, 6.23, 5.11, 5.04$ ($\text{CH}_2 / 3\text{-H}, 1\text{-H}, =\text{CH}_{2(\text{Z})}, =\text{CH}_{2(\text{E})}$), $1.76 / 6.23$ ($\text{CH}_{3(\text{Z})} / 1\text{-H}$), $1.75 / 6.53$ ($\text{CH}_{3(\text{E})} / 4\text{-H}$).

Elemental Analysis: $\text{C}_{11}\text{H}_{14}$ calculated: C 90.35, H 9.65; found: C 89.76, H 9.89.

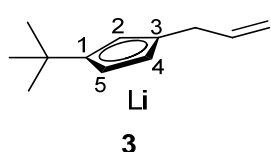


¹H-NMR spectrum of compound **2** (600 MHz, 298 K, [D₆]-Benzene)



¹³C-NMR spectrum of compound **2** (151 MHz, 298 K, [D₆]-Benzene)

Preparation of compound 3. Methyllithium (21.4 mL, 34.2 mmol, 1.6 M soln. in diethyl ether) was added dropwise to a solution of 2-allyl-6,6-dimethylfulvene (**2**) (5.0 g, 34.2 mmol) in THF (50 mL) at $-50\text{ }^{\circ}\text{C}$. The resulting reaction mixture was stirred at $-50\text{ }^{\circ}\text{C}$ for 30 minutes. All the volatiles were removed in vacuo, the residue was suspended in pentane (30 mL), and the product was separated from the suspension by filtration. After drying in vacuo, the lithium salt was isolated as a white powder (5.5 g, 32.7 mmol, 96%).



$^1\text{H-NMR}$ (600 MHz, 298 K, $[\text{D}_8]$ -Tetrahydrofuran): $\delta = 5.97$ (ddt, $^3J_{\text{H,H}} = 17.0, 10.0, 6.9$ Hz, 1H, =CH), 5.37 (m, 1H, 5-H), 5.36 (m, 1H, 2-H), 5.26 (m, 1H, 4-H), 4.90 (ddt, $^3J_{\text{H,H-trans}} = 17.0$ Hz, $^2J_{\text{H,H}} = 2.7$ Hz, $^4J_{\text{H,H}} = 1.6$ Hz, 1H, =CH_{2(Z)}), 4.74 (ddt, $^3J_{\text{H,H-cis}} = 10.0$ Hz, $^2J_{\text{H,H}} = 2.7$ Hz, $^4J_{\text{H,H}} = 1.2$ Hz, 1H, =CH_{2(E)}), 3.17 (dm, $^3J_{\text{H,H}} = 6.9$ Hz, 2H, CH₂), 1.18 (s, 9H, *t*-Bu^{Me}).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (151 MHz, 298 K, $[\text{D}_8]$ -Tetrahydrofuran): $\delta = 142.8$ (=CH), 130.1 (C-1), 115.3 (C-3), 111.3 (=CH₂), 101.1 (C-4), 100.1 (C-2), 99.1 (C-5), 36.4 (CH₂), 33.8 (*t*-Bu^{Me}), 32.3 (*t*-Bu^C).

$^1\text{H}, ^1\text{H}$ -GCOSY (600 MHz / 600 MHz, 298 K, $[\text{D}_8]$ -Tetrahydrofuran): $\delta (^1\text{H}) / \delta (^1\text{H}) = 5.97 / 4.90, 4.74, 3.17$ (=CH / =CH_{2(Z)}, =CH_{2(E)}, CH₂), 5.37 / 5.26 (5-H / 4-H), 5.36 / 5.26 (2-H / 4-H), 4.90 / 4.74, 3.17 (=CH_{2(Z)} / =CH_{2(E)}, CH₂), 4.74 / 3.17 (=CH_{2(E)} / CH₂).

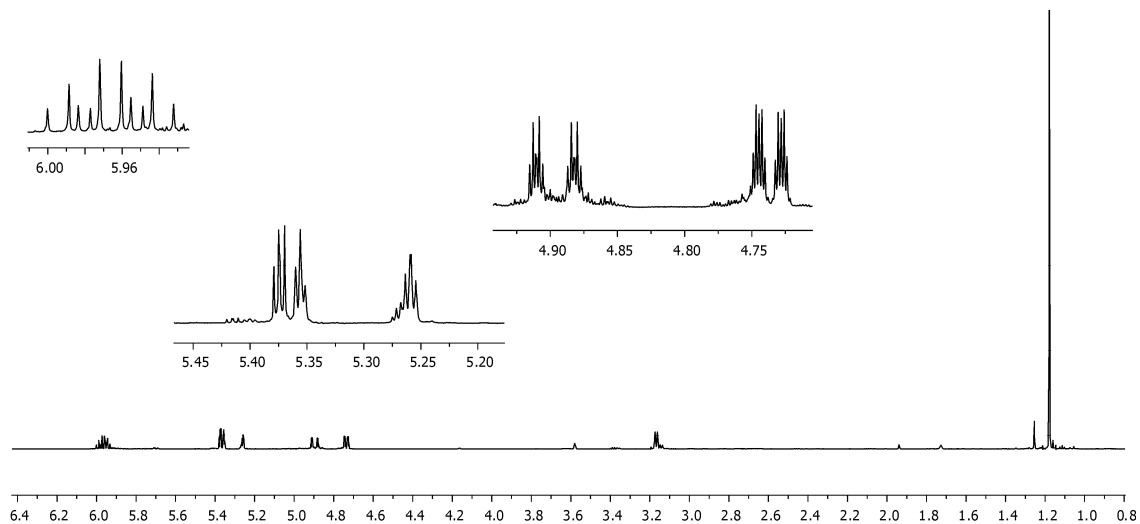
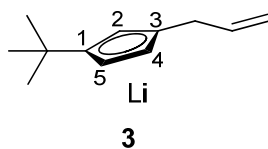
$^1\text{H}, ^{13}\text{C}$ -GHSQC (600 MHz / 151 MHz, 298 K, $[\text{D}_8]$ -Tetrahydrofuran): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 5.97 / 142.8$ (=CH / =CH), 5.37 / 99.1 (5-H / C-5), 5.36 / 100.1 (2-H / C-2), 5.26 / 101.1 (4-H / C-4), 4.90, 4.74 / 111.3 (=CH_{2(Z)}, =CH_{2(E)} / =CH₂), 3.17 / 36.4 (CH₂ / CH₂), 1.18 / 33.8 (*t*-Bu^{Me} / *t*-Bu^{Me}).

$^1\text{H}, ^{13}\text{C}$ -GHMBC (600 MHz / 151 MHz, 298 K, $[\text{D}_8]$ -Tetrahydrofuran): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 5.97 / 36.4$ (=CH / CH₂), 5.37 / 115.3, 101.1, 100.1 (5-H / C-3, C-4, C-2), 5.36 / 130.1, 115.3, 101.1, 99.1 (2-H / C-1, C-3, C-4, C-5), 5.26 / 130.1, 115.3, 100.1, 99.1 (4-H / C-1, C-3, C-2, C-5), 4.90 / 36.4 (=CH_{2(Z)} / CH₂), 4.74 / 36.4 (=CH_{2(E)} / CH₂), 3.17 / 142.8, 115.3, 111.3,

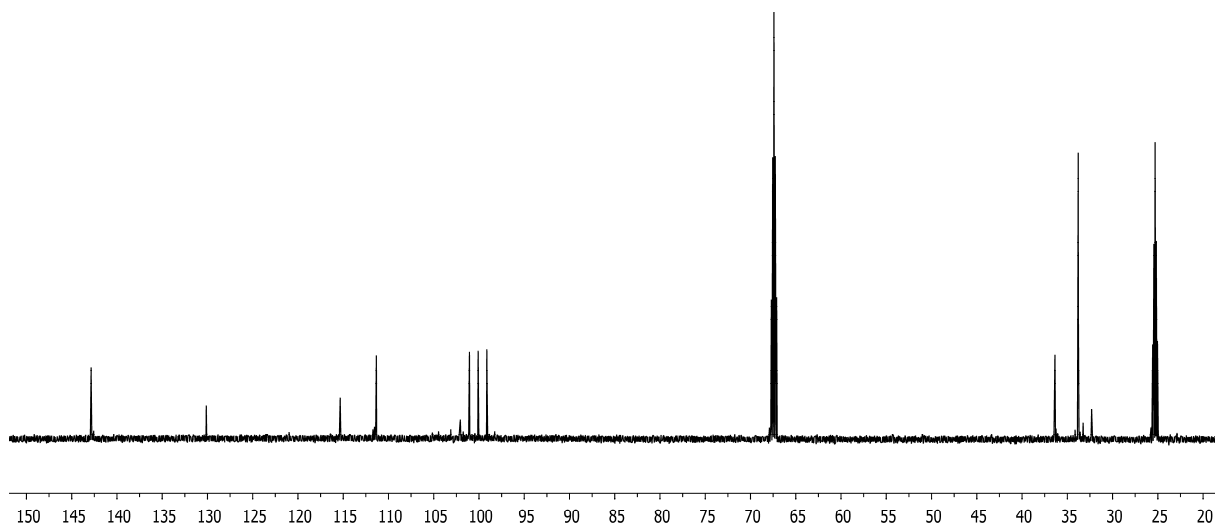
101.1, 100.1 (CH₂ / =CH, C-3, =CH₂, C-4, C-2), 1.18 / 130.1, 33.8, 32.3 (*t*-Bu^{Me} / C-1, *t*-Bu^{Me}, *t*-Bu^C).

¹H{¹H}-TOCSY (600 MHz, 298 K, [D₈]-Tetrahydrofuran): δ (¹H)_{irr.} / δ (¹H)_{res.} = 5.97 / 4.90, 4.74, 3.17 (=CH / =CH_{2(Z)}, =CH_{2(E)}, CH₂), 5.37 / 5.36, 5.26 (5-H / 2-H, 4-H), 5.36 / 5.37, 5.26 (2-H / 5-H, 4-H), 5.26 / 5.37, 5.36 (4-H / 5-H, 2-H), 4.90 / 5.97, 4.74, 3.17 (=CH_{2(Z)} / =CH, =CH_{2(E)}, CH₂), 4.74 / 5.97, 4.90, 3.17 (=CH_{2(E)} / =CH, =CH_{2(Z)}, CH₂), 3.17 / 5.97, 4.90, 4.74 (CH₂ / =CH, =CH_{2(Z)}, =CH_{2(E)}).

¹H{¹H}-NOE (600 MHz, 298 K, [D₈]-Tetrahydrofuran): δ (¹H)_{irr.} / δ (¹H)_{res.} = 5.97 / 4.74 (=CH / =CH_{2(E)}), 5.37 / 5.26 (5-H / 4-H), 5.26 / 5.37, 3.17 (4-H / 5-H, CH₂), 4.90 / 4.74 (=CH_{2(Z)} / =CH_{2(E)}), 4.74 / 5.97, 4.90 (=CH_{2(E)} / =CH, =CH_{2(Z)}), 3.17 / 5.36, 5.26 (CH₂ / 2-H, 4-H), 1.18 / 5.37, 5.36 (*t*-Bu^{Me} / 5-H, 2-H).



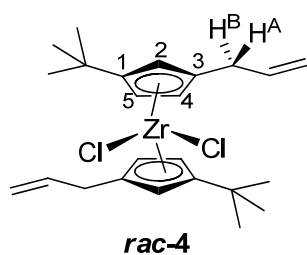
^1H -NMR spectrum of compound **3** (600 MHz, 298 K, $[\text{D}_8]$ -Tetrahydrofuran)



^{13}C -NMR spectrum of compound **3** (151 MHz, 298 K, $[\text{D}_8]$ -Tetrahydrofuran)

Preparation of compound 4. Precooled toluene (60 mL) was added to a mixture of lithium salt **3** (3.32 g, 19.7 mmol) and zirconium tetrachloride (2.30 g, 9.9 mmol) at $-78\text{ }^{\circ}\text{C}$. The resulting suspension was stirred overnight and was allowed to warm slowly to room temperature. After filtration, the solvent was removed from the filtrate in vacuo, and the residue was suspended in pentane (40 mL). The pentane solution was separated by decantation and transferred into another Schlenk-flask. The remaining white solid was dried in vacuo to afford the *rac*-isomer (0.85 g, 1.8 mmol, 18%). The pentane solution contained mostly the soluble *meso*-isomer and small amounts of the partially soluble *rac*-isomer. The remaining *rac*-isomer was separated by stepwise recrystallization of reduced volumes of pentane solution. Finally, the *meso*-isomer was isolated as a pale yellow solid (1.09 g, 2.2 mmol, 23%) after removing pentane in vacuo. Single crystals of *rac*-**4** were obtained from a concentrated solution of the compound in toluene at $-30\text{ }^{\circ}\text{C}$, while the other diastereoisomer *meso*-**4** was crystallized from its concentrated pentane solution at $-30\text{ }^{\circ}\text{C}$.

We kept a sample containing *meso*-**4** in d_6 -benzene for 1 h at $60\text{ }^{\circ}\text{C}$. Subsequent $^1\text{H-NMR}$ measurement showed that under these conditions no thermally induced conversion to *rac*-**4** was observed.



$^1\text{H-NMR}$ (600 MHz, 298 K, $[\text{D}_6]\text{-Benzene}$): $\delta = 6.29$ (m, 2H, 2-H), 5.91 (m, 2H, =CH), 5.77 (m, 2H, 5-H), 5.50 (m, 2H, 4-H), 4.97 (dm, $^3J_{\text{H,H-cis}} = 10.8$ Hz, 2H, =CH_{2(E)}), 4.95 (dm, $^3J_{\text{H,H-trans}} = 16.8$ Hz, 2H, =CH_{2(Z)}}), 3.50 (ddt, $^2J_{\text{H,H}} = 16.3$ Hz, $^3J_{\text{H,H}} = 6.1$ Hz, $^4J_{\text{H,H}} = 1.5$ Hz, 2H, CH₂^A), 3.31 (ddt, $^2J_{\text{H,H}} = 16.3$ Hz, $^3J_{\text{H,H}} = 6.8$ Hz, $^4J_{\text{H,H}} = 1.1$ Hz, 2H, CH₂^B), 1.17 (s, 18H, *t*-Bu^{Me}).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (151 MHz, 298 K, $[\text{D}_6]\text{-Benzene}$): $\delta = 145.1$ (C-1), 137.2 (=CH), 135.4 (C-3), 117.7 (C-2), 116.1 (=CH₂), 107.8 (C-5), 107.7 (C-4), 35.8 (CH₂), 33.8 (*t*-Bu^C), 31.3 (*t*-Bu^{Me}).

^1H , ^1H -GCOSY (600 MHz / 600 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^1\text{H}) = 6.29 / 5.77$, 5.50, 3.50, 3.31 (2-H / 5-H, 4-H, CH_2^{A} , CH_2^{B}), 5.91 / 4.97, 4.95, 3.50, 3.31 ($=\text{CH} / =\text{CH}_{2(\text{E})}$, $=\text{CH}_{2(\text{Z})}$, CH_2^{A} , CH_2^{B}), 5.77 / 5.50 (5-H / 4-H), 5.50 / 3.50, 3.31 (4-H / CH_2^{A} , CH_2^{B}), 4.97 / 4.95, 3.50, 3.31 ($=\text{CH}_{2(\text{E})} / =\text{CH}_{2(\text{Z})}$, CH_2^{A} , CH_2^{B}), 4.95 / 3.50, 3.31 ($=\text{CH}_{2(\text{Z})} / \text{CH}_2^{\text{A}}$, CH_2^{B}), 3.50 / 3.31 ($\text{CH}_2^{\text{A}} / \text{CH}_2^{\text{B}}$).

^1H , ^{13}C -GHSQC (600 MHz / 151 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 6.29 / 117.7$ (2-H / C-2), 5.91 / 137.2 ($=\text{CH} / =\text{CH}$), 5.77 / 107.8 (5-H / C-5), 5.50 / 107.7 (4-H / C-4), 4.97, 4.95 / 116.1 ($=\text{CH}_{2(\text{E})}$, $=\text{CH}_{2(\text{Z})} / =\text{CH}_2$), 3.50, 3.31 / 35.8 (CH_2^{A} , $\text{CH}_2^{\text{B}} / \text{CH}_2$), 1.17 / 31.3 ($t\text{-Bu}^{\text{Me}} / t\text{-Bu}^{\text{Me}}$).

^1H , ^{13}C -GHMBC (600 MHz / 151 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 6.29 / 145.1$, 135.4, 107.8, 107.7 (2-H / C-1, C-3, C-5, C-4), 5.91 / 135.4, 35.8 ($=\text{CH} / \text{C-3}$, CH_2), 5.77 / 145.1, 135.4, 117.7, 107.7, 33.8 (5-H / C-1, C-3, C-2, C-4, $t\text{-Bu}^{\text{C}}$), 5.50 / 145.1, 135.4, 117.7, 107.8, 35.8 (4-H / C-1, C-3, C-2, C-5, CH_2), 4.97 / 137.2, 35.8 ($=\text{CH}_{2(\text{E})} / =\text{CH}$, CH_2), 4.95 / 137.2, 35.8 ($=\text{CH}_{2(\text{Z})} / =\text{CH}$, CH_2), 3.50 / 137.2, 135.4, 117.7, 116.1, 107.7 ($\text{CH}_2^{\text{A}} / =\text{CH}$, C-3, C-2, $=\text{CH}_2$, C-4), 3.31 / 137.2, 135.4, 117.7, 116.1, 107.7 ($\text{CH}_2^{\text{B}} / =\text{CH}$, C-3, C-2, $=\text{CH}_2$, C-4), 1.17 / 145.1, 117.7, 107.8, 33.8, 31.3 ($t\text{-Bu}^{\text{Me}} / \text{C-1}$, C-2, C-5, $t\text{-Bu}^{\text{C}}$, $t\text{-Bu}^{\text{Me}}$).

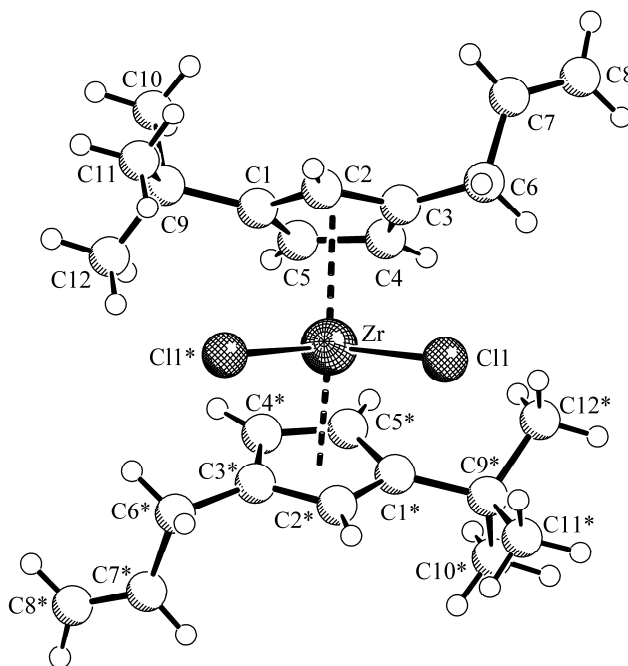
$^1\text{H}\{^1\text{H}\}$ -TOCSY (600 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H})_{\text{irr.}} / \delta (^1\text{H})_{\text{res.}} = 6.29 / 5.77$, 5.50 (2-H / 5-H, 4-H), 5.77 / 6.29, 5.50 (5-H / 2-H, 4-H), 5.50 / 6.29, 5.77 (4-H / 2-H, 5-H), 4.97 / 5.91, 4.95, 3.50, 3.31 ($=\text{CH}_{2(\text{E})} / =\text{CH}$, $=\text{CH}_{2(\text{Z})}$, CH_2^{A} , CH_2^{B}), 4.95 / 5.91, 4.97, 3.50, 3.31 ($=\text{CH}_{2(\text{Z})} / =\text{CH}$, $=\text{CH}_{2(\text{E})}$, CH_2^{A} , CH_2^{B}), 3.50 / 5.91, 4.97, 4.95, 3.31 ($\text{CH}_2^{\text{A}} / =\text{CH}$, $=\text{CH}_{2(\text{E})}$, $=\text{CH}_{2(\text{Z})}$, CH_2^{B}), 3.31 / 5.91, 4.97, 4.95, 3.50 ($\text{CH}_2^{\text{B}} / =\text{CH}$, $=\text{CH}_{2(\text{E})}$, $=\text{CH}_{2(\text{Z})}$, CH_2^{A}).

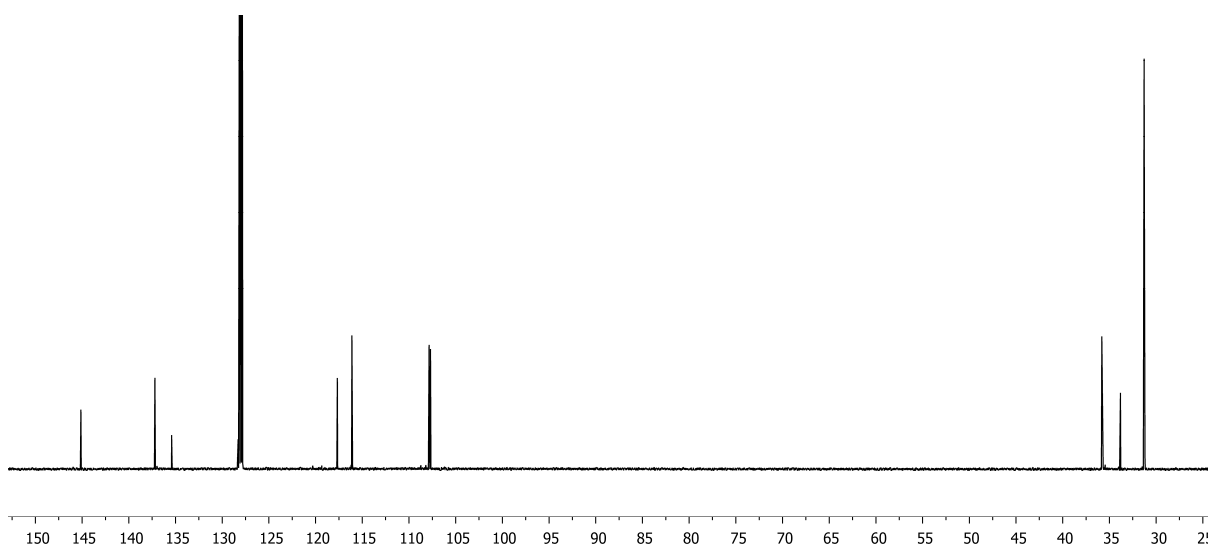
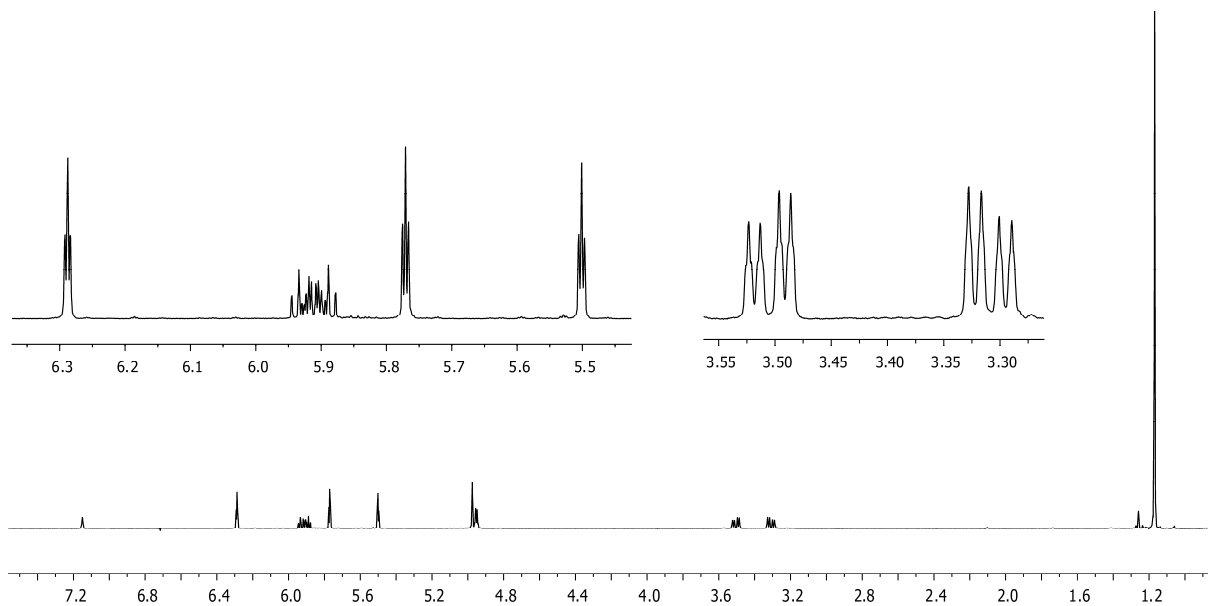
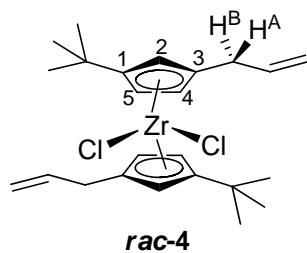
$^1\text{H}\{^1\text{H}\}$ -NOE (600 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H})_{\text{irr.}} / \delta (^1\text{H})_{\text{res.}} = 6.29 / 3.50$, 1.17 (2-H / CH_2^{A} , $t\text{-Bu}^{\text{Me}}$), 5.77 / 5.50, 1.17 (5-H / 4-H, $t\text{-Bu}^{\text{Me}}$), 5.50 / 5.77, 3.31, 1.17 (4-H / 5-H, CH_2^{B} , $t\text{-Bu}^{\text{Me}}$), 4.97 / 5.91 ($=\text{CH}_{2(\text{E})} / =\text{CH}$), 3.50 / 5.91, 3.31 ($\text{CH}_2^{\text{A}} / =\text{CH}$, CH_2^{B}), 3.31 / 5.91, 3.50 ($\text{CH}_2^{\text{B}} / =\text{CH}$, CH_2^{A}), 1.17 / 6.29, 5.77, 5.50 ($t\text{-Bu}^{\text{Me}} / 2\text{-H}$, 5-H, 4-H).

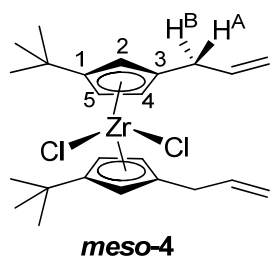
Elemental Analysis: C₂₄H₃₄ZrCl₂ calculated: C 59.48, H 7.07; found: C 58.85, H 6.85.

Melting Point: 158 °C.

X-ray Crystal Structure Analysis: Crystal data of C₂₄H₃₄Cl₂Zr (*rac-4*), *M* = 484.63, monoclinic, space group *C2/c* (No. 15), *a* = 18.4863(3), *b* = 6.6869(1), *c* = 20.7792(5) Å, β = 105.909(1)°, *V* = 2470.26(8) Å³, *D_c* = 1.303 g cm⁻³, μ = 0.668 mm⁻¹, *Z* = 4, λ = 0.71073 Å, *T* = 223(2) K, 12058 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.67 Å⁻¹, 2942 independent (*R_{int}* = 0.065), and 2570 observed reflections [*I* ≥ 2σ(*I*)], 126 refined parameters, *R* = 0.036, *wR*² = 0.081.







$^1\text{H-NMR}$ (600 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta = 6.29$ (m, 2H, 2-H), 5.85 (m, 2H, =CH), 5.76 (m, 2H, 5-H), 5.52 (m, 2H, 4-H), 4.97 (dm, $^3J_{\text{H,H-trans}} = 17.1$ Hz, 2H, =CH_{2(Z)}}), 4.95 (dm, $^3J_{\text{H,H-cis}} = 10.2$ Hz, 2H, =CH_{2(E)}}), 3.29 (ddt, $^2J_{\text{H,H}} = 16.2$ Hz, $^3J_{\text{H,H}} = 6.1$ Hz, $^4J_{\text{H,H}} = 1.5$ Hz, 2H, CH_{2^A}), 3.20 (ddt, $^2J_{\text{H,H}} = 16.2$ Hz, $^3J_{\text{H,H}} = 6.7$ Hz, $^4J_{\text{H,H}} = 1.4$ Hz, 2H, CH_{2^B}), 1.26 (s, 18H, *t*-Bu^{Me}).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (151 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta = 145.9$ (C-1), 137.0 (=CH), 131.6 (C-3), 119.4 (C-2), 116.2 (=CH₂), 108.7 (C-4), 108.2 (C-5), 35.4 (CH₂), 34.0 (*t*-Bu^C), 31.2 (*t*-Bu^{Me}).

$^1\text{H}, ^1\text{H-GCOSY}$ (600 MHz / 600 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^1\text{H}) = 6.29 / 5.76, 5.52, 3.29, 3.20$ (2-H / 5-H, 4-H, CH_{2^A}, CH_{2^B}), 5.85 / 4.97, 4.95, 3.29, 3.20 (=CH / =CH_{2(Z)}}, =CH_{2(E)}}, CH_{2^A}, CH_{2^B}), 5.76 / 5.52 (5-H / 4-H), 5.52 / 3.29, 3.20 (4-H / CH_{2^A}, CH_{2^B}), 4.97 / 4.95, 3.29, 3.20 (=CH_{2(Z)}} / =CH_{2(E)}}, CH_{2^A}, CH_{2^B}), 4.95 / 3.29, 3.20 (=CH_{2(E)}} / CH_{2^A}, CH_{2^B}), 3.29 / 3.20 (CH_{2^A} / CH_{2^B}).

$^1\text{H}, ^{13}\text{C-GHSQC}$ (600 MHz / 151 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 6.29 / 119.4$ (2-H / C-2), 5.85 / 137.0 (=CH / =CH), 5.76 / 108.2 (5-H / C-5), 5.52 / 108.7 (4-H / C-4), 4.97, 4.95 / 116.2 (=CH_{2(Z)}}, =CH_{2(E)}} / =CH₂), 3.29, 3.20 / 35.4 (CH_{2^A}, CH_{2^B} / CH₂), 1.26 / 31.2 (*t*-Bu^{Me} / *t*-Bu^{Me}).

$^1\text{H}, ^{13}\text{C-GHMBC}$ (600 MHz / 151 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 6.29 / 145.9, 131.6, 108.7, 108.2$ (2-H / C-1, C-3, C-4, C-5), 5.85 / 131.6, 35.4 (=CH / C-3, CH₂), 5.76 / 145.9, 131.6, 119.4, 108.7, 34.0 (5-H / C-1, C-3, C-2, C-4, *t*-Bu^C), 5.52 / 145.9, 131.6, 119.4, 108.2, 35.4 (4-H / C-1, C-3, C-2, C-5, CH₂), 4.97 / 137.0, 35.4 (=CH_{2(Z)}} / =CH, CH₂), 4.95 / 137.0, 35.4 (=CH_{2(E)}} / =CH, CH₂), 3.29 / 137.0, 131.6, 119.4, 116.2, 108.7 (CH_{2^A} / =CH, C-3, C-2, =CH₂, C-4), 3.20 / 137.0, 131.6, 119.4, 116.2, 108.7 (CH_{2^B} / =CH, C-3, C-2, =CH₂, C-4), 1.26 / 145.9, 119.4, 108.2, 34.0, 31.2 (*t*-Bu^{Me} / C-1, C-2, C-5, *t*-Bu^C, *t*-Bu^{Me}).

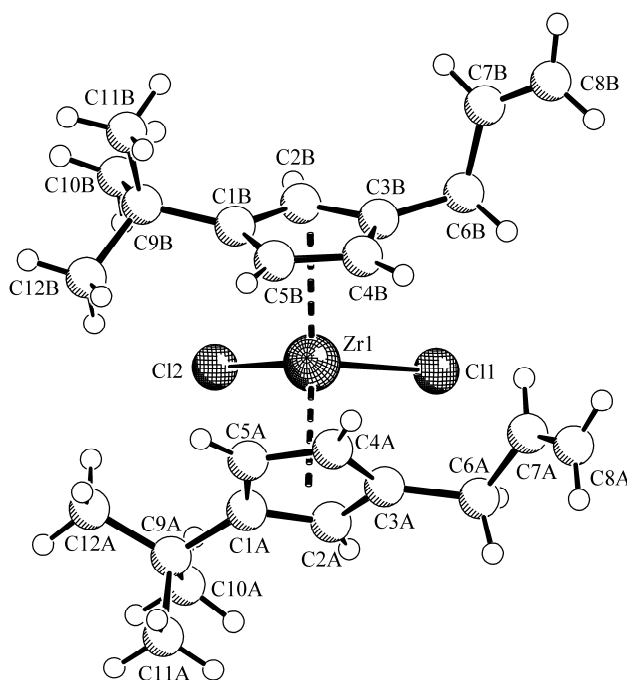
$^1\text{H}\{^1\text{H}\}$ -TOCSY (600 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H})_{\text{irr.}} / \delta (^1\text{H})_{\text{res.}} = 6.29 / 5.76, 5.52$ (2-H / 5-H, 4-H), 4.97 / 5.85, 4.95, 3.29, 3.20 ($=\text{CH}_{2(\text{Z})} / =\text{CH}, =\text{CH}_{2(\text{E})}, \text{CH}_2^{\text{A}}, \text{CH}_2^{\text{B}}$), 3.29 / 5.85, 4.97, 4.95, 3.20 ($\text{CH}_2^{\text{A}} / =\text{CH}, =\text{CH}_{2(\text{Z})}, =\text{CH}_{2(\text{E})}, \text{CH}_2^{\text{B}}$).

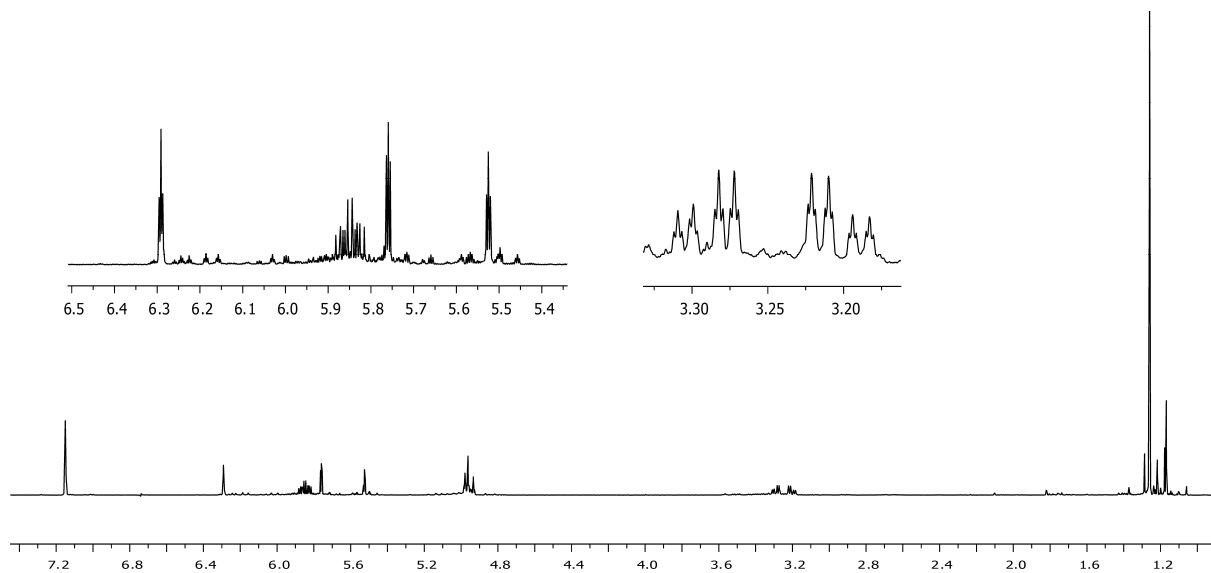
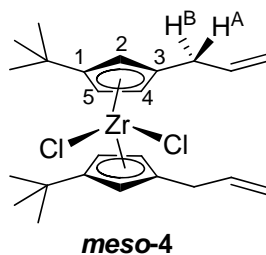
$^1\text{H}\{^1\text{H}\}$ -NOE (600 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H})_{\text{irr.}} / \delta (^1\text{H})_{\text{res.}} = 6.29 / 3.29, 1.26$ (2-H / $\text{CH}_2^{\text{A}}, t\text{-Bu}^{\text{Me}}$), 5.76 / 5.52, 1.26 (5-H / 4-H, $t\text{-Bu}^{\text{Me}}$), 5.52 / 5.76, 3.20 (4-H / 5-H, CH_2^{B}), 3.29 / 6.29, 5.85, 5.52, 4.97, 3.20 ($\text{CH}_2^{\text{A}} / 2\text{-H}, =\text{CH}, 4\text{-H}, =\text{CH}_{2(\text{Z})}, \text{CH}_2^{\text{B}}$), 1.26 / 6.29, 5.76 ($t\text{-Bu}^{\text{Me}} / 2\text{-H}, 5\text{-H}$).

Elemental Analysis: $\text{C}_{24}\text{H}_{34}\text{ZrCl}_2$ calculated: C 59.48, H 7.07; found: C 58.58, H 6.52.

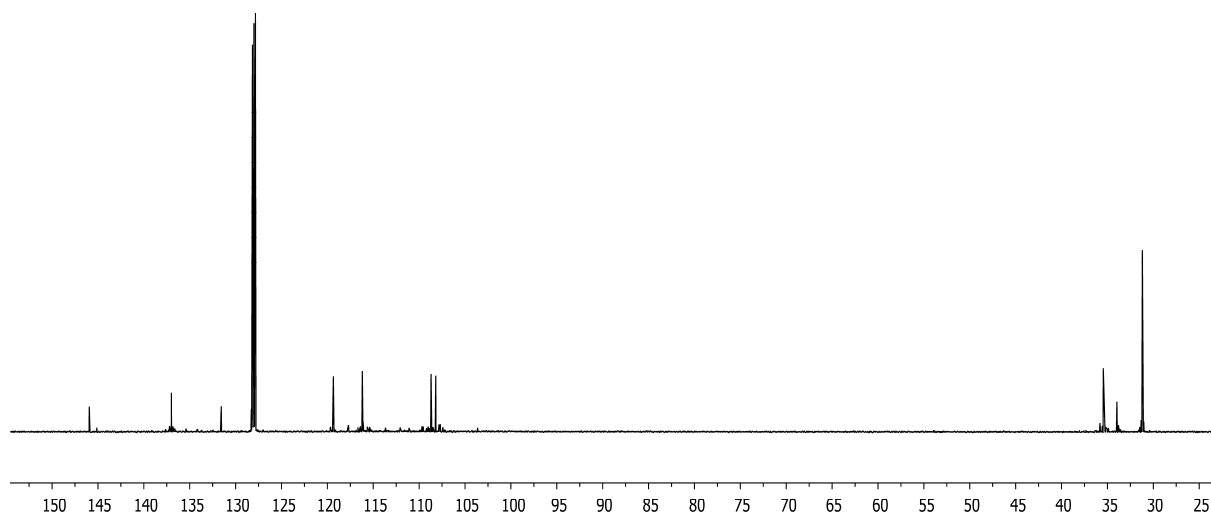
Melting Point: 72 °C.

X-ray Crystal Structure Analysis: Crystal data of $\text{C}_{24}\text{H}_{34}\text{Cl}_2\text{Zr}$ (*meso*-4), $M = 484.63$, triclinic, space group $P1\bar{1}$ (No. 2), $a = 6.7351(1)$, $b = 10.0317(2)$, $c = 18.8814(4)$ Å, $\alpha = 75.096(1)$, $\beta = 87.165(1)$, $\gamma = 79.401(2)^\circ$, $V = 1211.76(4)$ Å³, $D_c = 1.328$ g cm⁻³, $\mu = 0.681$ mm⁻¹, $Z = 2$, $\lambda = 0.71073$ Å, $T = 223(2)$ K, 11034 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å⁻¹, 5695 independent ($R_{\text{int}} = 0.052$), and 4716 observed reflections [$I \geq 2\sigma(I)$], 260 refined parameters, $R = 0.040$, $wR^2 = 0.096$.



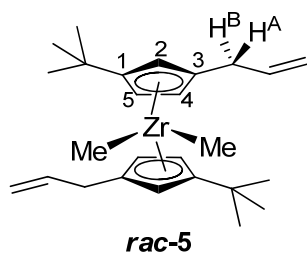


$^1\text{H-NMR}$ spectrum of compound *meso-4* (600 MHz, 298 K, $[\text{D}_6]$ -Benzene)



$^{13}\text{C-NMR}$ spectrum of compound *meso-4* (151 MHz, 298 K, $[\text{D}_6]$ -Benzene)

Preparation of compound *rac*-5. Methyllithium (0.4 mL, 0.64 mmol, 1.6 M soln. in diethyl ether) was added dropwise to a solution of *rac*-4 (150 mg, 0.31 mmol) in toluene (10 mL) at $-30\text{ }^{\circ}\text{C}$. The resulting reaction mixture was stirred overnight and was allowed to warm slowly to room temperature. LiCl was filtered off from the mixture and all the volatiles were removed in vacuo. The residue was washed with pentane (10 mL) and filtered again. The solvent was removed from the filtrate in vacuo to give the compound as a colorless oil (107 mg, 0.24 mmol, 78%).



$^1\text{H-NMR}$ (500 MHz, 298 K, $[\text{D}_6]$ -Benzene): δ = 6.22 (m, 2H, 2-H), 6.02 (m, 2H, =CH), 5.33 (m, 2H, 4-H), 5.29 (m, 2H, 5-H), 5.07 (dm, $^3J_{\text{H,H-trans}} = 17.0\text{ Hz}$, 2H, =CH_{2(Z)}}), 5.02 (dm, $^3J_{\text{H,H-cis}} = 10.1\text{ Hz}$, 2H, =CH_{2(E)}}), 3.36 (ddt, $^2J_{\text{H,H}} = 16.0\text{ Hz}$, $^3J_{\text{H,H}} = 6.2\text{ Hz}$, $^4J_{\text{H,H}} = 1.5\text{ Hz}$, 2H, CH₂^A), 3.22 (ddt, $^2J_{\text{H,H}} = 16.0\text{ Hz}$, $^3J_{\text{H,H}} = 6.4\text{ Hz}$, $^4J_{\text{H,H}} = 1.3\text{ Hz}$, 2H, CH₂^B), 1.07 (s, 18H, *t*-Bu^{Me}), -0.09 (s, 6H, Zr-Me).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz, 298 K, $[\text{D}_6]$ -Benzene): δ = 138.7 (C-1), 138.6 (=CH), 126.3 (C-3), 115.3 (=CH₂), 113.5 (C-2), 106.1 (C-4), 102.2 (C-5), 35.3 (CH₂), 34.0 (Zr-Me), 32.9 (*t*-Bu^C), 31.7 (*t*-Bu^{Me}).

$^1\text{H}, ^1\text{H-GCOSY}$ (500 MHz / 500 MHz, 298 K, $[\text{D}_6]$ -Benzene): δ (^1H) / δ (^1H) = 6.22 / 5.33, 5.29, 3.36, 3.22 (2-H / 4-H, 5-H, CH₂^A, CH₂^B), 6.02 / 5.07, 5.02, 3.36, 3.22 (=CH / =CH_{2(Z)}}, =CH_{2(E)}, CH₂^A, CH₂^B), 5.33 / 5.29, 3.36, 3.22 (4-H / 5-H, CH₂^A, CH₂^B), 5.07 / 5.02, 3.36, 3.22 (=CH_{2(Z)}} / =CH_{2(E)}, CH₂^A, CH₂^B), 5.02 / 3.36, 3.22 (=CH_{2(E)} / CH₂^A, CH₂^B), 3.36 / 3.22 (CH₂^A / CH₂^B).

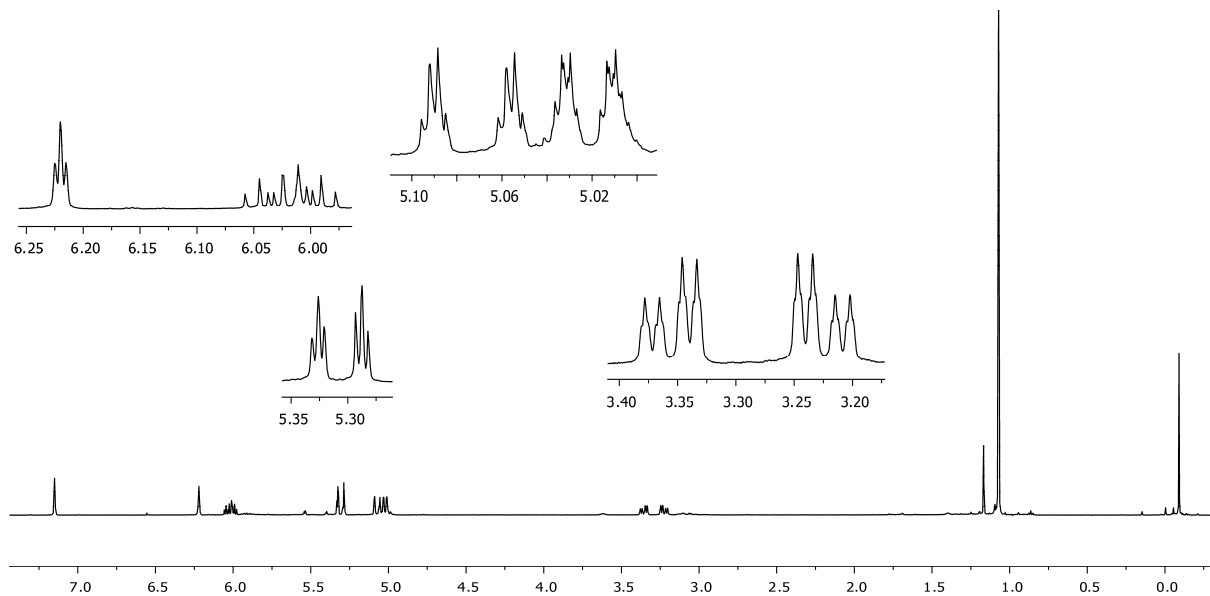
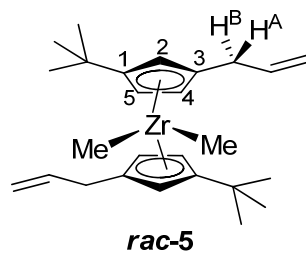
$^1\text{H}, ^{13}\text{C-GHSQC}$ (500 MHz / 126 MHz, 298 K, $[\text{D}_6]$ -Benzene): δ (^1H) / δ (^{13}C) = 6.22 / 113.5 (2-H / C-2), 6.02 / 138.6 (=CH / =CH), 5.33 / 106.1 (4-H / C-4), 5.29 / 102.2 (5-H / C-5), 5.07, 5.02 / 115.3 (=CH_{2(Z)}}, =CH_{2(E)} / =CH₂), 3.36, 3.22 / 35.3 (CH₂^A, CH₂^B / CH₂), 1.07 / 31.7 (*t*-Bu^{Me} / *t*-Bu^{Me}), -0.09 / 34.0 (Zr-Me / Zr-Me).

^1H , ^{13}C -GHMBC (500 MHz / 126 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 6.22 / 138.7, 126.3, 106.1, 102.2, 35.3, 34.0, 32.9$ (2-H / C-1, C-3, C-4, C-5, CH_2 , Zr-Me, $t\text{-Bu}^{\text{C}}$), $6.02 / 126.3, 113.5, 35.3$ ($=\text{CH} / \text{C-3, C-2, CH}_2$), $5.33 / 138.7, 126.3, 113.5, 102.2, 35.3, 32.9$ (4-H / C-1, C-3, C-2, C-5, CH_2 , $t\text{-Bu}^{\text{C}}$), $5.29 / 138.7, 126.3, 113.5, 106.1, 35.3, 32.9$ (5-H / C-1, C-3, C-2, C-4, CH_2 , $t\text{-Bu}^{\text{C}}$), $5.07 / 138.6, 35.3$ ($=\text{CH}_{2(\text{Z})} / =\text{CH, CH}_2$), $5.02 / 138.6, 35.3$ ($=\text{CH}_{2(\text{E})} / =\text{CH, CH}_2$), $3.36 / 138.6, 126.3, 115.3, 113.5, 106.1$ ($\text{CH}_2^{\text{A}} / =\text{CH, C-3, =\text{CH}_2, \text{C-2, C-4}$), $3.22 / 138.6, 126.3, 115.3, 113.5, 106.1$ ($\text{CH}_2^{\text{B}} / =\text{CH, C-3, =\text{CH}_2, \text{C-2, C-4}$), $1.07 / 138.7, 32.9, 31.7$ ($t\text{-Bu}^{\text{Me}} / \text{C-1, } t\text{-Bu}^{\text{C}}, t\text{-Bu}^{\text{Me}}$), $-0.09 / 35.3$ (Zr-Me / CH_2).

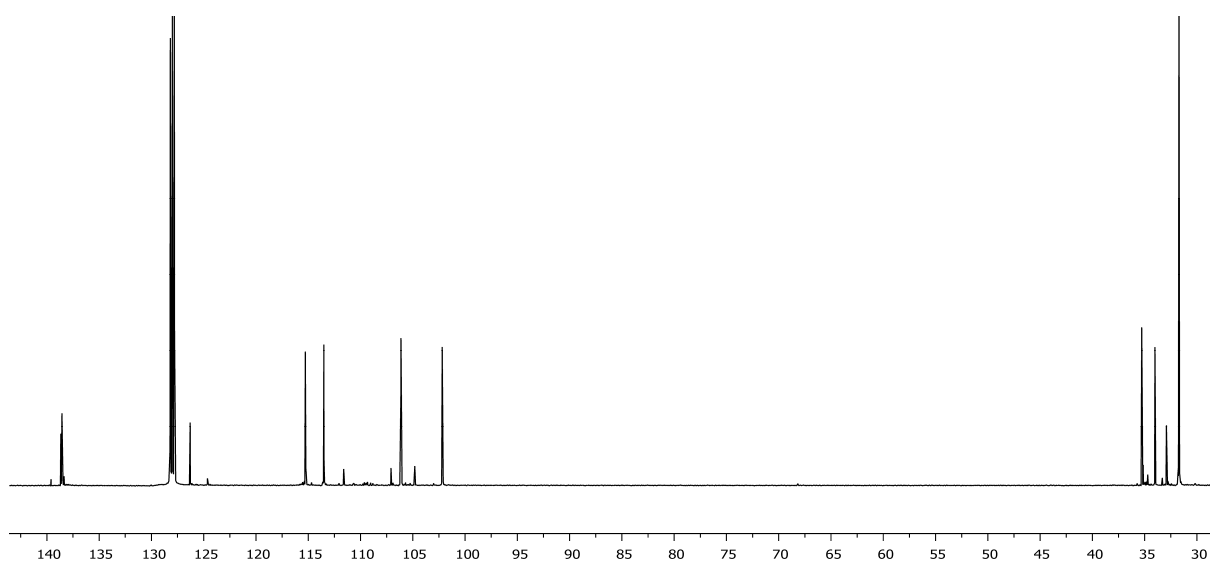
$^1\text{H}\{^1\text{H}\}$ -TOCSY (500 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H})_{\text{irr.}} / \delta (^1\text{H})_{\text{res.}} = 6.22 / 5.33, 5.29$ (2-H / 4-H, 5-H), $6.02 / 5.07, 5.02, 3.36, 3.22$ ($=\text{CH} / =\text{CH}_{2(\text{Z})}, =\text{CH}_{2(\text{E})}, \text{CH}_2^{\text{A}}, \text{CH}_2^{\text{B}}$), $5.33 / 6.22, 5.29$ (4-H / 2-H, 5-H), $5.29 / 6.22, 5.33$ (5-H / 2-H, 4-H), $5.07 / 6.02, 5.02, 3.36, 3.22$ ($=\text{CH}_{2(\text{Z})} / =\text{CH, =\text{CH}_{2(\text{E})}, \text{CH}_2^{\text{A}}, \text{CH}_2^{\text{B}}$), $5.02 / 6.02, 5.07, 3.36, 3.22$ ($=\text{CH}_{2(\text{E})} / =\text{CH, =\text{CH}_{2(\text{Z})}, \text{CH}_2^{\text{A}}, \text{CH}_2^{\text{B}}$), $3.36 / 6.02, 5.07, 5.02, 3.22$ ($\text{CH}_2^{\text{A}} / =\text{CH, =\text{CH}_{2(\text{Z})}, =\text{CH}_{2(\text{E})}, \text{CH}_2^{\text{B}}$), $3.22 / 6.02, 5.07, 5.02, 3.36$ ($\text{CH}_2^{\text{B}} / =\text{CH, =\text{CH}_{2(\text{Z})}, =\text{CH}_{2(\text{E})}, \text{CH}_2^{\text{A}}$).

$^1\text{H}\{^1\text{H}\}$ -NOE (500 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H})_{\text{irr.}} / \delta (^1\text{H})_{\text{res.}} = 6.22 / 3.36, 1.07, -0.09$ (2-H / $\text{CH}_2^{\text{A}}, t\text{-Bu}^{\text{Me}}, \text{Zr-Me}$), $5.33 / 6.22, 5.29, 3.22, 1.07, -0.09$ (4-H / 2-H, 5-H, $\text{CH}_2^{\text{B}}, t\text{-Bu}^{\text{Me}}, \text{Zr-Me}$), $5.29 / 5.33, 1.07$ (5-H / 4-H, $t\text{-Bu}^{\text{Me}}$), $5.02 / 6.02$ ($=\text{CH}_{2(\text{E})} / =\text{CH}$), $3.36 / 6.02, 3.22$ ($\text{CH}_2^{\text{A}} / =\text{CH, CH}_2^{\text{B}}$), $3.22 / 6.02, 3.36$ ($\text{CH}_2^{\text{B}} / =\text{CH, CH}_2^{\text{A}}$), $1.07 / 6.22, 5.29$ ($t\text{-Bu}^{\text{Me}} / 2\text{-H, 5-H}$), $-0.09 / 6.22, 3.36, 3.22, 1.07$ (Zr-Me / 2-H, $\text{CH}_2^{\text{A}}, \text{CH}_2^{\text{B}}, t\text{-Bu}^{\text{Me}}$).

Elemental Analysis: $\text{C}_{26}\text{H}_{40}\text{Zr}$ calculated: C 70.36, H 9.08; found: C 70.12, H 8.90.

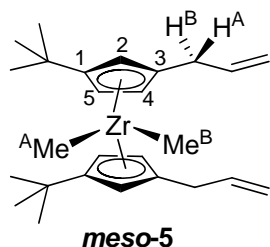


$^1\text{H-NMR}$ spectrum of compound *rac-5* (500 MHz, 298 K, $[\text{D}_6]$ -Benzene)



$^{13}\text{C-NMR}$ spectrum of compound *rac-5* (126 MHz, 298 K, $[\text{D}_6]$ -Benzene)

Preparation of compound *meso*-5. Analogous procedure as described for the preparation of *rac*-5. The reaction of methyl lithium (0.3 mL, 0.48 mmol, 1.6 M soln. in diethyl ether) and *meso*-4 (110 mg, 0.23 mmol) in toluene (10 mL) at $-30\text{ }^{\circ}\text{C}$ and subsequent purification of the compound yielded the product as a pale yellow oil (88 mg, 0.20 mmol, 87%).



$^1\text{H-NMR}$ (500 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta = 6.00$ (m, 2H, 2-H), 5.91 (m, 2H, =CH), 5.53 (m, 2H, 5-H), 5.39 (m, 2H, 4-H), 5.01 (dm, $^3J_{\text{H,H-trans}} = 17.1$ Hz, 2H, =CH_{2(Z)}}), 4.99 (dm, $^3J_{\text{H,H-cis}} = 10.1$ Hz, 2H, =CH_{2(E)}}), 3.11 (ddt, $^2J_{\text{H,H}} = 16.0$ Hz, $^3J_{\text{H,H}} = 6.1$ Hz, $^4J_{\text{H,H}} = 1.6$ Hz, 2H, CH₂^A), 3.03 (ddt, $^2J_{\text{H,H}} = 16.0$ Hz, $^3J_{\text{H,H}} = 6.4$ Hz, $^4J_{\text{H,H}} = 1.5$ Hz, 2H, CH₂^B), 1.16 (s, 18H, *t*-Bu^{Me}), -0.03 (s, 3H, Zr-Me^A), -0.08 (s, 3H, Zr-Me^B).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta = 139.6$ (C-1), 138.3 (=CH), 124.6 (C-3), 115.2 (=CH₂), 111.6 (C-2), 107.1 (C-4), 104.8 (C-5), 35.1 (CH₂), 34.7 (Zr-Me^B), 33.3 (*t*-Bu^C), 31.8 (Zr-Me^A), 31.7 (*t*-Bu^{Me}).

$^1\text{H}, ^1\text{H-GCOSY}$ (500 MHz / 500 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^1\text{H}) = 6.00 / 5.53$, 5.39 (2-H / 5-H, 4-H), 5.91 / 5.01, 4.99, 3.11, 3.03 (=CH / =CH_{2(Z)}}, =CH_{2(E)}}, CH₂^A, CH₂^B), 5.53 / 5.39 (5-H / 4-H), 5.01 / 4.99, 3.11, 3.03 (=CH_{2(Z)}} / =CH_{2(E)}}, CH₂^A, CH₂^B), 4.99 / 3.11, 3.03 (=CH_{2(E)}} / CH₂^A, CH₂^B), 3.11 / 3.03 (CH₂^A / CH₂^B), $-0.03 / -0.08$ (Zr-Me^A / Zr-Me^B).

$^1\text{H}, ^{13}\text{C-GHSQC}$ (500 MHz / 126 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 6.00 / 111.6$ (2-H / C-2), 5.91 / 138.3 (=CH / =CH), 5.53 / 104.8 (5-H / C-5), 5.39 / 107.1 (4-H / C-4), 5.01, 4.99 / 115.2 (=CH_{2(Z)}}, =CH_{2(E)}} / =CH₂), 3.11, 3.03 / 35.1 (CH₂^A, CH₂^B / CH₂), 1.16 / 31.7 (*t*-Bu^{Me} / *t*-Bu^{Me}), $-0.03 / 31.8$ (Zr-Me^A / Zr-Me^A), $-0.08 / 34.7$ (Zr-Me^B / Zr-Me^B).

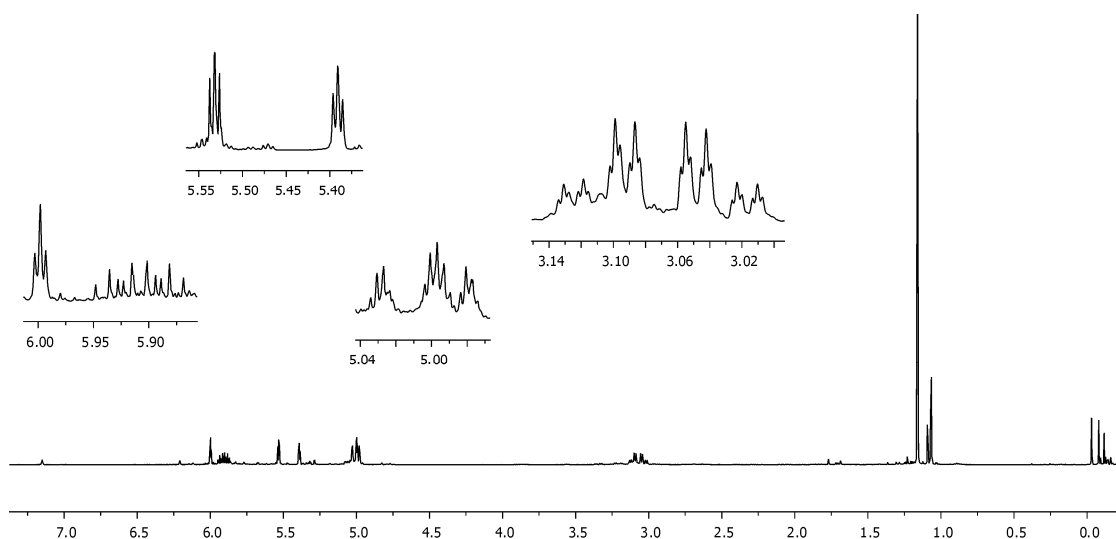
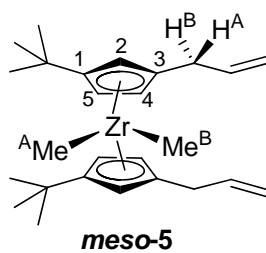
$^1\text{H}, ^{13}\text{C-GHMBC}$ (500 MHz / 126 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 6.00 / 139.6, 124.6, 107.1, 104.8, 35.1, 33.3$ (2-H / C-1, C-3, C-4, C-5, CH₂, *t*-Bu^C), 5.91 / 124.6, 35.1 (=CH / C-3, CH₂), 5.53 / 139.6, 124.6, 111.6, 107.1, 35.1, 33.3 (5-H / C-1, C-3, C-2, C-4, CH₂, *t*-Bu^C), 5.39 / 139.6, 124.6, 111.6, 104.8, 35.1, 33.3 (4-H / C-1, C-3, C-2, C-5, CH₂, *t*-

Bu^C, 5.01 / 138.3, 35.1 (=CH_{2(Z)} / =CH, CH₂), 4.99 / 138.3, 35.1 (=CH_{2(E)} / =CH, CH₂), 3.11 / 138.3, 124.6, 115.2, 111.6, 107.1 (CH_{2^A} / =CH, C-3, =CH₂, C-2, C-4), 3.03 / 138.3, 124.6, 115.2, 111.6, 107.1 (CH_{2^B} / =CH, C-3, =CH₂, C-2, C-4), 1.16 / 139.6, 104.8, 33.3, 31.7 (*t*-Bu^{Me} / C-1, C-5, *t*-Bu^C, *t*-Bu^{Me}), -0.03 / 139.6, 111.6, 107.1 (Zr-Me^A / C-1, C-2, C-4), -0.08 / 124.6, 111.6, 104.8 (Zr-Me^B / C-3, C-2, C-5).

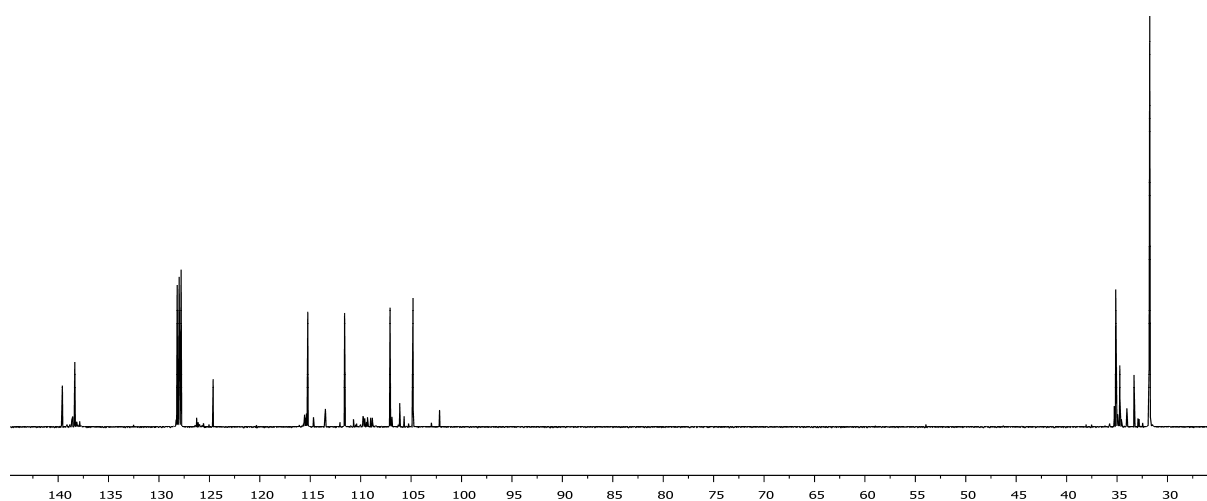
¹H{¹H}-TOCSY (500 MHz, 298 K, [D₆]-Benzene): δ (¹H)_{irr.} / δ (¹H)_{res.} = 6.00 / 5.53, 5.39 (2-H / 5-H, 4-H), 5.91 / 5.01, 4.99, 3.11, 3.03 (=CH / =CH_{2(Z)}, =CH_{2(E)}, CH_{2^A}, CH_{2^B}), 5.53 / 6.00, 5.39 (5-H / 2-H, 4-H), 5.39 / 6.00, 5.53 (4-H / 2-H, 5-H), 5.01 / 5.91, 4.99, 3.11, 3.03 (=CH_{2(Z)} / =CH, =CH_{2(E)}, CH_{2^A}, CH_{2^B}), 4.99 / 5.91, 5.01, 3.11, 3.03 (=CH_{2(E)} / =CH, =CH_{2(Z)}, CH_{2^A}, CH_{2^B}), 3.11 / 5.91, 5.01, 4.99, 3.03 (CH_{2^A} / =CH, =CH_{2(Z)}, =CH_{2(E)}, CH_{2^B}), 3.03 / 5.91, 5.01, 4.99, 3.11 (CH_{2^B} / =CH, =CH_{2(Z)}, =CH_{2(E)}, CH_{2^A}), -0.03 / -0.08 (Zr-Me^A / Zr-Me^B).

¹H{¹H}-NOE (500 MHz, 298 K, [D₆]-Benzene): δ (¹H)_{irr.} / δ (¹H)_{res.} = 6.00 / 3.11, 1.16, -0.03, -0.08 (2-H / CH_{2^A}, *t*-Bu^{Me}, Zr-Me^A, Zr-Me^B), 5.91 / 4.99, 3.03 (=CH / =CH_{2(E)}, CH_{2^B}), 5.53 / 5.39, 1.16 (5-H / 4-H, *t*-Bu^{Me}), 5.39 / 5.53, 3.03 (4-H / 5-H, CH_{2^B}), 5.01 / 5.91, 3.11, 3.03 (=CH_{2(Z)} / =CH, CH_{2^A}, CH_{2^B}), 4.99 / 5.91 (=CH_{2(E)} / =CH), 3.11 / 6.00, 5.91, -0.08 (CH_{2^A} / 2-H, =CH, Zr-Me^B), 3.03 / 5.91, 5.39, -0.08 (CH_{2^B} / =CH, 4-H, Zr-Me^B), 1.16 / 6.00, 5.53, -0.03 (*t*-Bu^{Me} / 2-H, 5-H, Zr-Me^A), -0.03 / 6.00, 5.53, 1.16 (Zr-Me^A / 2-H, 5-H, *t*-Bu^{Me}), -0.08 / 6.00, 5.39, 3.11, 3.03 (Zr-Me^B / 2-H, 4-H, CH_{2^A}, CH_{2^B}).

Elemental Analysis: C₂₆H₄₀Zr calculated: C 70.36, H 9.08; found: C 70.51, H 8.94.

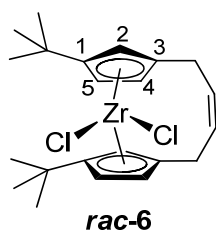


$^1\text{H-NMR}$ spectrum of compound *meso-5* (500 MHz, 298 K, $[\text{D}_6]$ -Benzene)



$^{13}\text{C-NMR}$ spectrum of compound *meso-5* (126 MHz, 298 K, $[\text{D}_6]$ -Benzene)

Preparation of compound *rac-6*. A solution of *rac-4* (250 mg, 0.52 mmol) in toluene (10 mL) was added slowly to a solution of $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}]$ “Grubbs I” catalyst (42 mg, 0.05 mmol) in toluene (50 mL) at room temperature. The resulting reaction mixture was stirred at room temperature overnight. After removing all the volatiles in vacuo, the residue was suspended in pentane. Subsequent filtration of the mixture yielded the product as a beige solid (205 mg, 0.45 mmol, 87%). Single crystals suitable for an X-ray crystal structure analysis were obtained from a concentrated solution of the compound in benzene.



^1H -NMR (500 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta = 6.16$ (each br s, each 2H, 2-H, 4-H), 6.01 (m, 2H, 5-H), 5.74 (m, 2H, =CH), 2.90 (m, 4H, CH_2), 1.28 (s, 18H, $t\text{-Bu}^{\text{Me}}$).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta = 142.5$ (C-1), 129.9 (=CH), 121.7 (C-3), 117.5, 116.4 (each br, C-2, C-4), 113.4 (C-5), 33.5 ($t\text{-Bu}^{\text{C}}$), 31.2 ($t\text{-Bu}^{\text{Me}}$), 25.6 (CH_2).

$^1\text{H},^{13}\text{C}$ -GHSQC (500 MHz / 126 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 6.16 / 117.5, 116.4$ (2-H, 4-H / C-2, C-4), 6.01 / 113.4 (5-H / C-5), 5.74 / 129.9 (=CH / =CH), 2.90 / 25.6 ($\text{CH}_2 / \text{CH}_2$), 1.28 / 31.2 ($t\text{-Bu}^{\text{Me}} / t\text{-Bu}^{\text{Me}}$).

$^1\text{H},^{13}\text{C}$ -GHMBC (500 MHz / 126 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H}) / \delta (^{13}\text{C}) = 6.16 / 142.5, 121.7, 117.5, 116.4, 113.4, 33.5, 25.6$ (2-H, 4-H / C-1, C-3, C-2, C-4, C-5, $t\text{-Bu}^{\text{C}}$, CH_2), 6.01 / 142.5, 121.7, 117.5, 116.4 (5-H / C-1, C-3, C-2, C-4), 5.74 / 121.7, 25.6 (=CH / C-3, CH_2), 2.90 / 129.9, 121.7, 117.5, 116.4 ($\text{CH}_2 / =\text{CH}$, C-3, C-2, C-4), 1.28 / 142.5, 33.5, 31.2 ($t\text{-Bu}^{\text{Me}} / \text{C-1}$, $t\text{-Bu}^{\text{C}}$, $t\text{-Bu}^{\text{Me}}$).

$^1\text{H}\{^1\text{H}\}$ -TOCSY (500 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H})_{\text{irr.}} / \delta (^1\text{H})_{\text{res.}} = 6.01 / 6.16$ (5-H / 2-H, 4-H), 2.90 / 6.16, 5.74 ($\text{CH}_2 / 2\text{-H}, 4\text{-H}, =\text{CH}$).

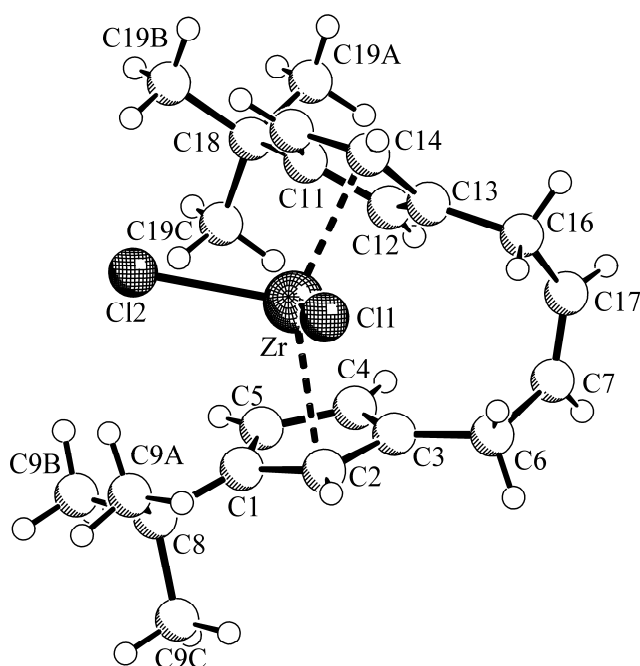
$^1\text{H}\{^1\text{H}\}$ -NOE (500 MHz, 298 K, $[\text{D}_6]$ -Benzene): $\delta (^1\text{H})_{\text{irr.}} / \delta (^1\text{H})_{\text{res.}} = 6.16 / 6.01, 5.74, 2.90, 1.28$ (2-H, 4-H / 5-H, =CH, CH_2 , $t\text{-Bu}^{\text{Me}}$), 6.01 / 6.16, 1.28 (5-H / 2-H, 4-H, $t\text{-Bu}^{\text{Me}}$), 5.74 /

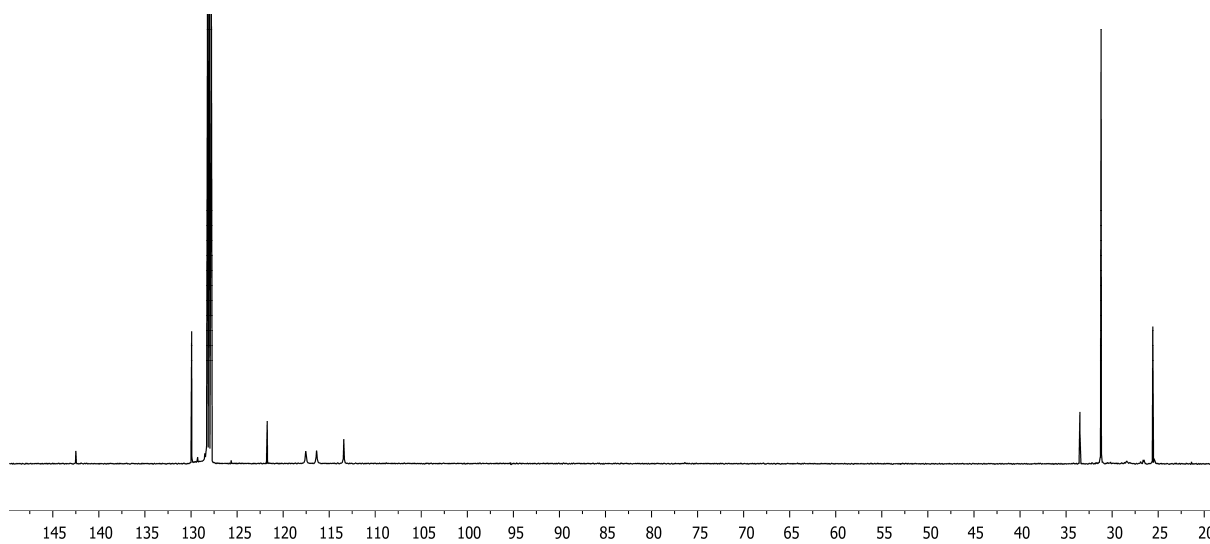
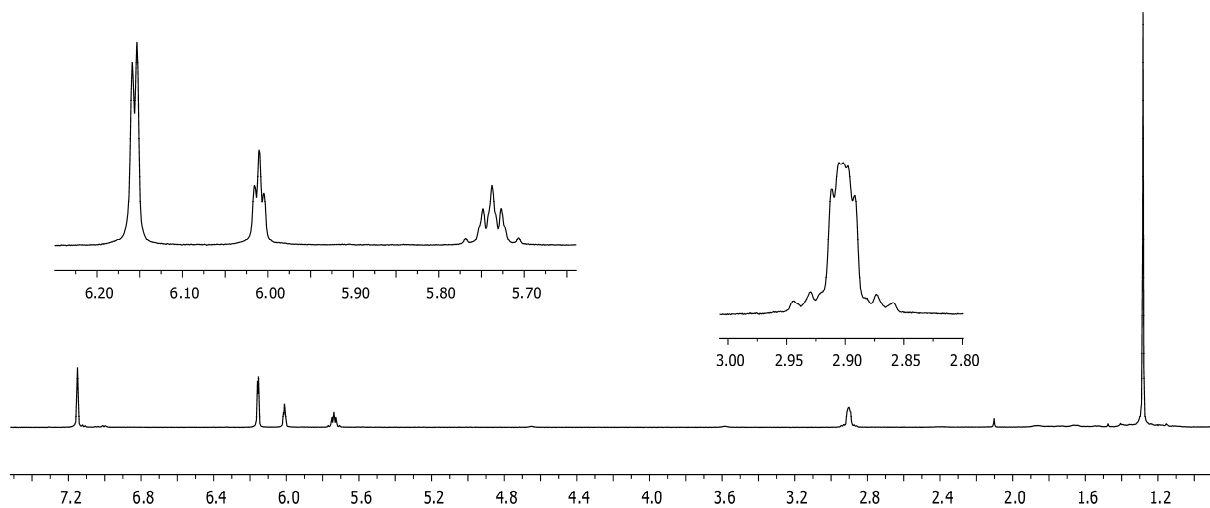
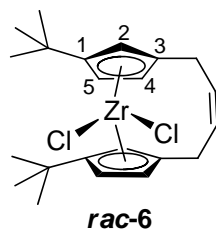
6.16, 2.90 (=CH / 2-H, 4-H, CH₂), 2.90 / 6.16, 5.74 (CH₂ / 2-H, 4-H, =CH), 1.28 / 6.16, 6.01 (*t*-Bu^{Me} / 2-H, 4-H, 5-H).

Elemental Analysis: C₂₂H₃₀ZrCl₂ calculated: C 57.87, H 6.62; found: C 57.17, H 6.13.

Melting Point: 216 °C.

X-ray Crystal Structure Analysis: Crystal data of C₂₂H₃₀Cl₂Zr (*rac*-**6**), *M* = 456.58, monoclinic, space group *P*2₁/*c* (No. 14), *a* = 10.9542(2), *b* = 7.4462(2), *c* = 26.3865(7) Å, β = 90.954(1)°, *V* = 2151.97(9) Å³, *D*_c = 1.409 g cm⁻³, μ = 0.762 mm⁻¹, *Z* = 4, λ = 0.71073 Å, *T* = 223(2) K, 14440 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.62 Å⁻¹, 4310 independent (*R*_{int} = 0.051), and 3519 observed reflections [*I* ≥ 2σ(*I*)], 232 refined parameters, *R* = 0.079, *wR*² = 0.212.



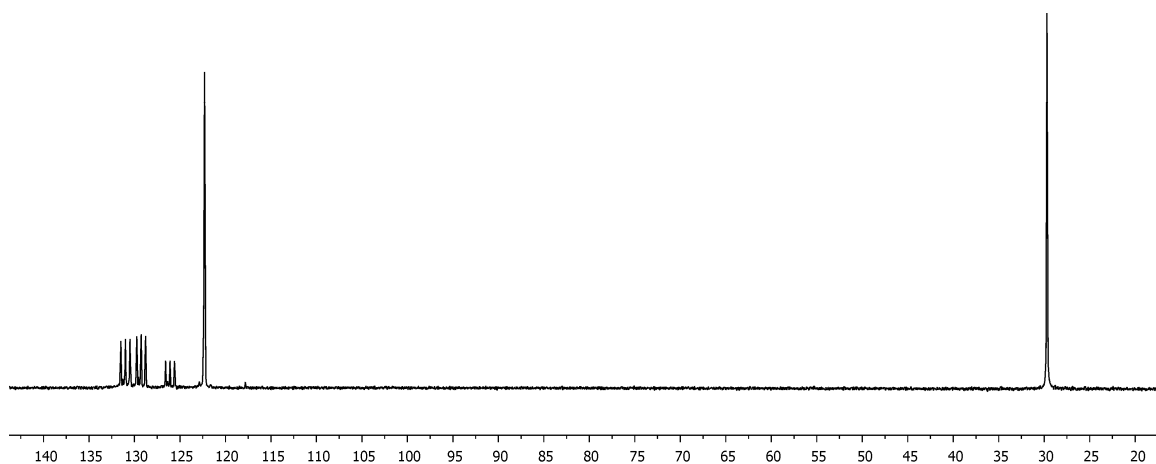


Ethene Polymerization. A 1 L Büchi glass autoclave equipped with a catalyst reservoir and stirrer was evacuated and filled with argon three times before it was charged with toluene (200 mL) and a solution of methylalumoxane (MAO) in toluene (1 mL, 10 wt. %). A precise amount of respective complex (1 μmol) was dissolved in toluene (5 mL) and loaded into the catalyst reservoir together with a solution of MAO in toluene (0.5 mL, 10 wt. %). The autoclave was brought to 40 °C and the solution was saturated with ethene at 2 bar, which was controlled by bpc 1202 (Büchi pressflow gas controller with program “bls2”) with stirring (600 rpm). After the solution was saturated with ethene (the line of consumption volume went flat), the catalyst solution in the reservoir was introduced directly into the autoclave. The polymerization reaction was stopped by terminating the transfer of ethene with the bpc controller. The resulting suspension was poured into a solution of concentrated HCl (10 mL) in methanol (200 mL). The precipitated polyethylene was collected by filtration, and dried at 80 °C in an oven overnight to constant weight. The polymer was characterized by DSC and ^{13}C NMR. The obtained polymers were highly linear polyethene.

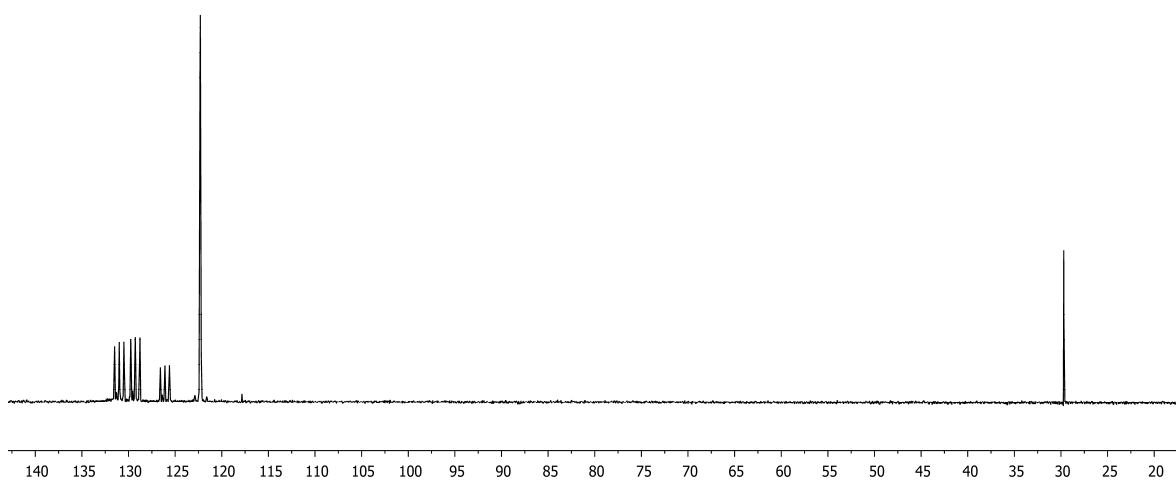
Table 1. Results of the ethene polymerization catalyzed by *rac-4*, *meso-4* and *rac-6* complex/MAO systems^a

	PE [g]	Activity^b	M.p.
<i>rac-4</i>	2.22	2220	130
<i>rac-4</i>	2.06	2060	130
<i>meso-4</i>	5.00	5000	131
<i>meso-4</i>	4.80	4800	131
<i>rac-6</i>	0.42	420	125
<i>rac-6</i>	0.38	380	125

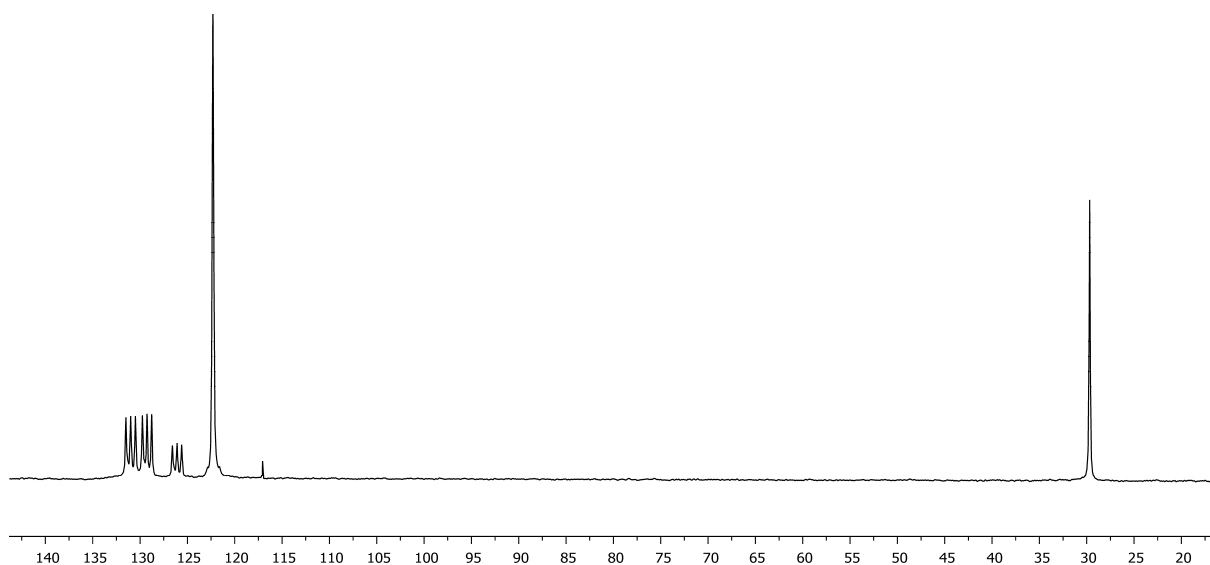
^a 1 μmol complex, 200 mL toluene, preactivated Al:Zr \approx 2400:1, reaction temperature 40 °C, 2 bar ethene; reaction time 30 min. ^b catalyst activities in kg PE / (mol[Zr] · h · bar (ethene)).



^{13}C -NMR spectrum of PE obtained by *rac*-**4** (50 MHz, 353 K, $[\text{D}_5]$ -Bromobenzene)



^{13}C -NMR spectrum of PE obtained by *meso*-**4** (50 MHz, 353 K, $[\text{D}_5]$ -Bromobenzene)



^{13}C -NMR spectrum of PE obtained by *rac*-**6** (50 MHz, 353 K, $[\text{D}_5]$ -Bromobenzene)

Propene Polymerization. A 1 L Büchi glass autoclave equipped with a catalyst reservoir and stirrer was evacuated and filled with argon three times before it was charged with toluene (200 mL) and a solution of methylalumoxane (MAO) in toluene (10 mL, 10 wt. %). A precise amount of respective complex (20 μmol) was dissolved in toluene (10 mL) and loaded into the catalyst reservoir together with a solution of MAO in toluene (10 mL, 10 wt. %). The autoclave was brought to 40 °C and the solution was saturated with propene at 2 bar, which was controlled by bpc 1202 (Büchi pressflow gas controller with program “bls2”) with stirring (600 rpm). After the solution was saturated with propene (the line of consumption volume went flat), the catalyst solution in the reservoir was introduced directly into the autoclave. The polymerization reaction was stopped by terminating the transfer of propene with the bpc controller. The polymer was extracted with toluene and dried over sodium sulfate. All the volatiles were removed in vacuo. Characterization of the obtained polypropene samples were carried out by ^{13}C NMR pentad analysis.

Table 2. Results of the propene polymerization catalyzed by *rac-4*, *meso-4* and *rac-6* complex/MAO systems^a

	PP [g]	Activity ^b	[mm]:[rm]:[rr]
<i>rac-4</i>	0.04	2	very low m.wt. atactic PP
<i>rac-4</i> ^c	0.03	3	–
<i>meso-4</i>	0.26	13	23:46:31
<i>meso-4</i> ^c	0.07	7	–
<i>rac-6</i>	0.12	6	25:42:33
<i>rac-6</i>	0.10	5	–

^a 20 μmol complex, 200 mL toluene, preactivated Al:Zr ≈ 1600:1, reaction temperature 50 °C, 2 bar propene; reaction time 30 min. ^b catalyst activities in kg PP / (mol[Zr] · h · bar (propene)). ^c 10 μmol complex.