Synthesis of [3]Ferrocenophane-bridged Cp/amido Zirconium Complexes and ansa-Zirconocene Complexes and their Use in Catalytic Polymerisation Reactions

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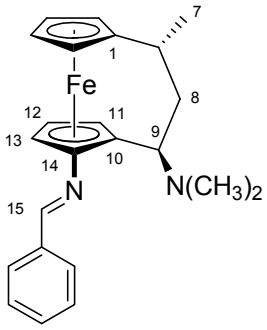
X-ray crystal structure analysis: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction SORTAV (R.H. Blessing, *Acta Cryst.* **1995**, *A51*, 33-37; R.H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421-426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics XP (BrukerAXS, 2000). R-values are given for the observed reflections, wR^2-values for all refelctions. Thermal ellipsoids are shown with 50 % probability.

Preparation of Compound **4**



Benzaldehyd (5.0 ml, 49.5 mmol, 5.7 equiv) was added to a solution of **3** (2.6 g, 8.72 mmol) in tetrahydrofuran (20 ml) at room temperature. The color of the suspension turned from yellow to deep red. After 1h the solvent was removed *in vacuo* and the crude product was purified by flash chromatography (methanol) to get **4** as a deep red powder (3.1 g, 8.02 mmol, 92%). Suitable crystals for X-ray diffraction were obtained by diffusion of pentane into a saturated solution of **4** in dichloromethane.

^{1}H NMR (600 MHz, [D_2]-dichloromethane, 298 K): δ = 1.31 (d, $^3J_{(H,H)}$ = 7.0 Hz, 3H, 7-H), 2.10 (dm, $^2J_{(H,H)}$ = 12.9 Hz, 1H, 8-H), 2.24 (s, 6H, NMe_2), 2.88 (m, 1H, 6-H), 3.34 (dm, $^3J_{(H,H)}$ = 11.8 Hz, 1H, 9-H), 3.55 (ddd, $^2J_{(H,H)}$ = 12.9 Hz, $^3J_{(H,H)}$ = 11.8 Hz, $^3J_{(H,H)}$ = 4.3 Hz, 1H, 8'-H), 3.76, 3.84, 4.13, 4.26 (each m, each 1H, C_5H_4), 4.13 (m, 1H, 13-H), 4.15 (m, 1H, 11-H), 4.49 (m, 1H, 12-H), 7.45 (m, 3H, *p*,*m*-C_6H_5), 7.84 (m, 2H, *o*-C_6H_5), 8.53 (s, 1H, 15-H).

^{13}C{^{1}H} NMR (151 MHz, [D_2]-dichloromethane, 298 K): δ = 17.2 (C7), 28.5 (C6), 43.3 (br, NMe_2), 44.2 (C8), 59.0 (C12), 59.8 (br, C9), 66.8 (br, C13), 66.7, 68.7, 70.2, 75.2 (C_5H_4),

73.4 (C11), 78.3 (br, C10), 95.3 (C1), 104.7 (C14), 128.2 (*o*-C_6H_5), 129.1 (*m*-C_6H_5), 130.7 (*p*-C_6H_5), 137.7 (*i*-C_6H_5), 156.8 (C15).

^{1}H,^{1}H 1D-TOCSY (600 MHz, [D_2]-dichloromethane, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.29 / 2.10, 2.88, 3.34, 3.55 (7-H / 8-H, 6-H, 9-H, 8'-H), 3.76 / 3.84, 4.13, 4.26 (C_5H_4), 4.49 / 4.13, 4.15 (12-H / 13-H, 11-H).

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, [D_2]-dichloromethane, 298 K): δ (^{1}H) / δ (^{1}H) = 1.31 / 2.88 (7-H / 6-H), 2.10 / 2.88, 3.34, 3.55 (8-H / 6-H, 9-H, 8'-H), 2.88 / 3.55 (6-H / 8'-H), 3.34 / 3.55 (9-H / 8'-H), 3.76 / 3.84, 4.13, 4.26 (C_5H_4), 3.84 / 4.13, 4.26 (C_5H_4), 4.13 / 4.15, 4.26, 4.49 (13-H, C_5H_4 / 11-H, 12-H, C_5H_4), 4.15 / 4.49 (11-H / 12-H), 7.45 / 7.84 (*p,m*-C_6H_5 / *o*-C_6H_5).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, [D_2]-dichloromethane, 298 K): δ (^{1}H) / δ (^{13}C) = 1.31 / 17.2 (7-H / C7), 2.10, 3.55 / 44.2 (8-H, 8'-H / C8), 2.24 / 43.3 (NMe_2), 2.88 / 28.5 (6-H / C6), 3.34 / 59.8 (9-H / C9), 3.76 / 75.2 (C_5H_4), 3.84 / 66.7 (C_5H_4), 4.13 / 68.7(C_5H_4), 4.26 / 70.2 (C_5H_4), 4.13 / 66.9, 68.7 (13-H / C13), 4.15 / 73.4 (11-H / C11), 4.49 / 59.0 (12-H / C12), 7.45 / 129.1 (*m*-C_6H_5), 7.45 / 130.7 (*p*-C_6H_5), 7.84 / 128.2 (*o*-C_6H_5), 8.53 / 156.8 (15-H / C15).

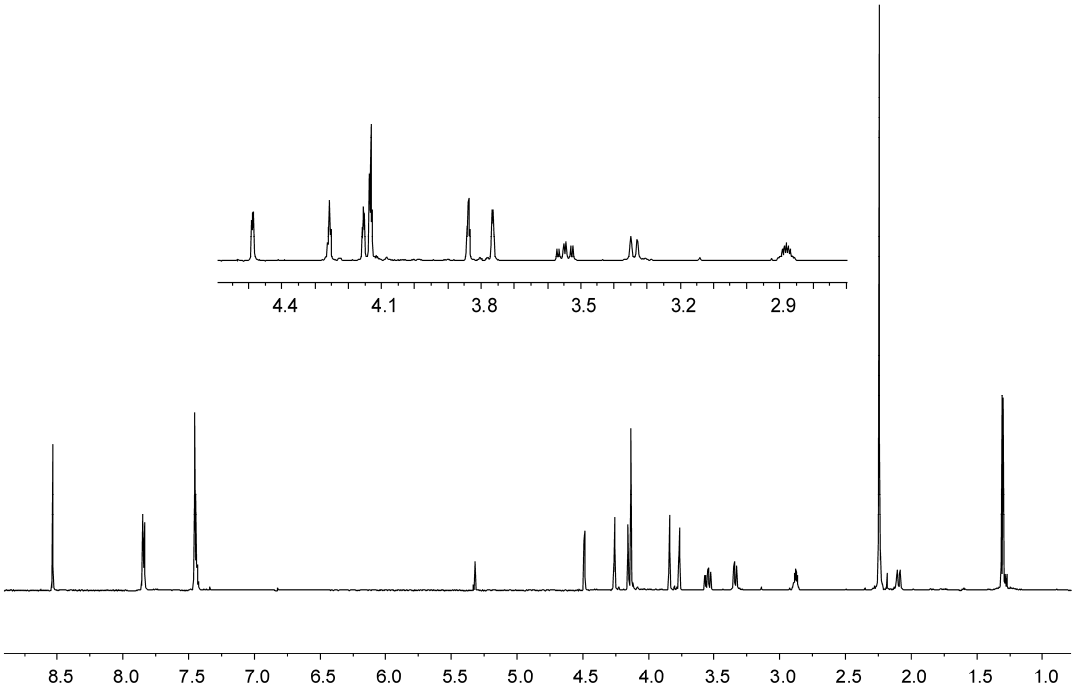
^{1}H,^{13}C GHMBC (600 MHz / 150 MHz, [D_2]-dichloromethane, 298 K): δ (^{1}H) / δ (^{13}C) = 1.31 / 28.5, 44.2, 95.3 (7-H / C6, C8, C1), 2.10 / 28.5, 59.8, 78.6, 95.3 (8-H / C6, C9 C10, C1), 3.34 / 28.5, 43.3, 44.2, 73.4, 78.6, 104.7 (9-H / C6, NMe_2, C8, C11, C10, C14), 3.55 / 17.2, 28.5, 59.8, 78.6, 95.3 (8'-H / C7, C6, C9, C10, C1), 4.13 / 59.0, 66.7, 70.2, 73.4, 75.2, 78.3, 95.3, 104.7 (13-H, C_5H_4 / C12, C11, C10, C1, C14, C_5H_4), 4.15 / 66.9, 59.0, 78.3, 104.7 (11-H / C13, C12, C10, C14), 4.26 / 66.7, 68.7, 75.2, 95.3 (C_5H_4 / C_5H_4, C1), 4.49 / 66.9, 73.4, 78.3, 104.7 (12-H / C13, C11, C10, C14), 7.45 / 128.2, 129.1, 137.7 / (*p,m*-C_6H_5 / *o*-C_6H_5, *m*-C_6H_5, *i*-C_6H_5), 7.84 / 128.2, 129.1, 130.7, 156.8 (*o*-C_6H_5 / *o*-C_6H_5, *m*-C_6H_5, *p*-C_6H_5, C15), 8.53 / 104.7, 128.2, 137.7 (15-H / C14, *o*-C_6H_5, *i*-C_6H_5).

Elemental Analysis: $C_{23}H_{26}FeN_2$ (386.3 g/mol) requires C 71.51, H 6.78, N 7.25, found: C 70.6, H 6.70, N 6.98.

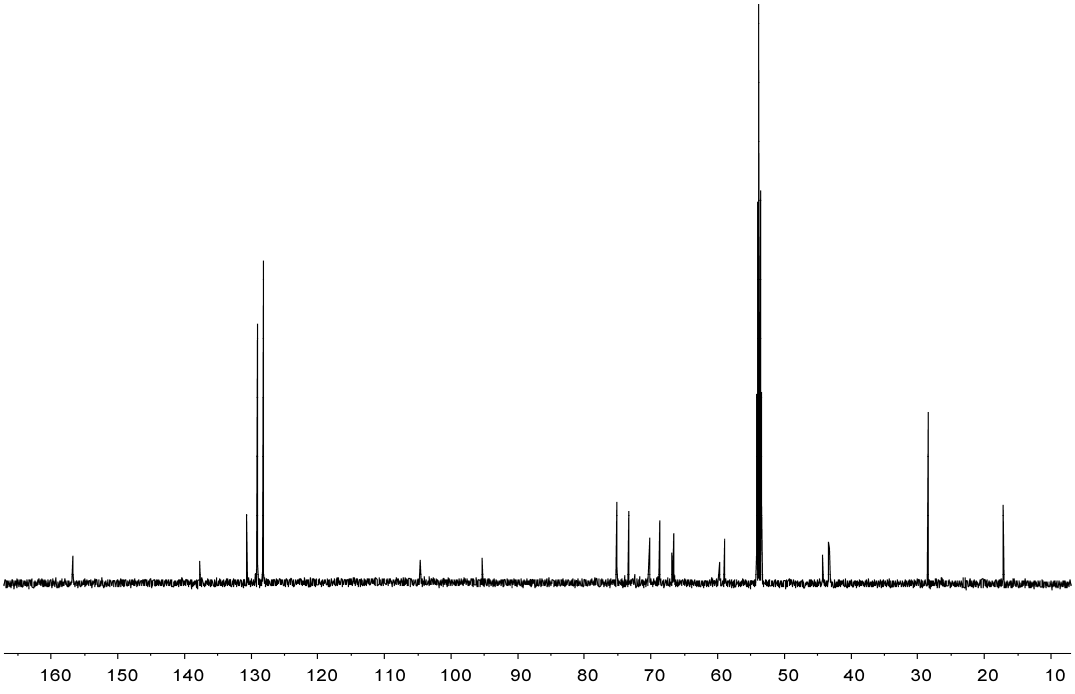
Melting Point: 131°C.

Mass Spectrometry (ESI, ES^+ for 386.14, methanol) 387.15 $[M+H]^+$.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3030 w, 2969 w, 2928 w, 2874 w, 2828 w, 1611 w, 1575 w, 1494 w, 1470 w, 1452 m, 1436 w, 1392 w, 1311 w, 1235 w, 1212 w, 1170 w, 1158 w, 1104 w, 1073 w, 1047 m, 1038 m, 999 w, 980 w, 959 m, 918 w, 860 m, 845 m, 821 m.

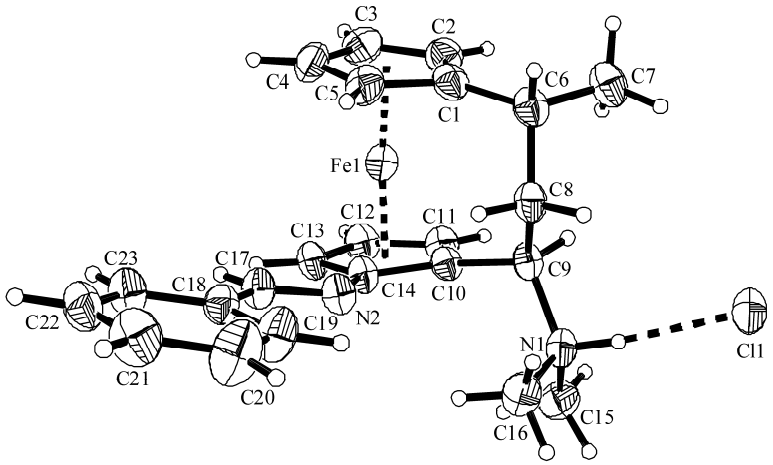


^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of **4**

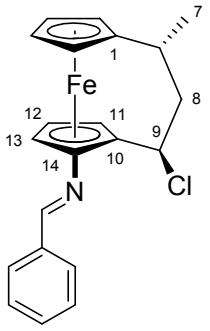


$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) of **4**

X-ray crystal structure analysis of 4 × HCl: formula $C_{23}H_{27}ClFeN_2$, M = 422.77, red crystal 0.30 x 0.20 x 0.15 mm, a = 9.4638(3), b = 12.4287(4), c = 17.3060(7) Å, β = 97.385(1) º, V = 2018.69(12) Å^3, ρ_{calc} = 1.391 g cm^{-3}, μ= 0.889 mm^{-1}, empirical absorption correction (0.776 ≤ T ≤ 0.878), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ= 0.71073 Å, T = 223(2) K, ω and φ scans, 16549 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 4786 independent (R_{int} = 0.072) and 3002 observed reflections [$I \geq 2\ \sigma(I)$], 247 refined parameters, R = 0.050, wR^2 = 0.123, max. (min.) residual electron density 0.44 (-0.41) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Preparation of Compound **5**



Methyl chloroformate (3.24 ml, 3.95 mg, 41.9 mmol, 6 equiv) was added to a solution of the tertiary amino[3]ferrocenophane **4** (2.70 g, 6.99 mmol) in anhydrous toluene (20 ml). After stirrig at room temperature for 2 hours all volatiles were removed. The deep red oil was washed with pentane (10 ml) and dried *in vacuo* to give the product as a red powder (1.80 g, 4.77 mmol, 68%). Suitable crystals for X-ray diffraction were obtained by evaporation of a saturated solution of **5** in toluene.

^{1}H NMR ([D_2]-dichloromethane, 600 MHz, 298 K): δ = 1.33 (d, $^{3}J_{(H,H)}$ = 7.3 Hz, 3H, 7-H), 2.45 (dt, $^{3}J_{(H,H)}$ = $^{3}J_{(H,H)}$ = 2.9 Hz, $^{2}J_{(H,H)}$ = 13.3 Hz, 1H, 8-H_{eq}), 2.86 (m, 1H, 6-H), 3.88 (m, 2H, 8-H_{ax}, C_5H_4), 3.90 (m, 1H, C_5H_4), 4.18 (m, 2H, 12-H, C_5H_4), 4.26 (m, 1H, 11-H), 4.30 (m, 1H, C_5H_4), 4.55 (m, 1H, 13-H), 4.97 (dd, $^{3}J_{(H,H)}$ = 2.9 Hz, $^{3}J_{(H,H)}$ = 12.4 Hz, 1H, 9-H), 7.48 (m, 3H, *m*-C_6H_5, *p*-C_6H_5), 7.92 (m, 2H, *o*-C_6H_5), 8.55 (s, 1H, 15-H).

^{13}C{^{1}H} NMR ([D_2] dichloromethane, 151 MHz, 298 K): δ = 16.8 (C7), 29.5 (C6), 51.2 (C8), 56.1 (C9), 59.7 (C13), 66.7 (C12), 67.4, 69.1, 70.8, 75.3 (C_5H_4), 69.8 (C11), 80.5 (C10), 94.2 (C1), 104.4 (C14), 128.5 (*o*-C_6H_5), 129.1, 131.0 (*m*-C_6H_5, *p*-C_6H_5), 137.4 (*i*-C_6H_5), 157.7 (C15).

^{1}H,^{1}H 1D-TOCSY ([D_2]-dichloromethane, 600 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.33 / 2.45, 2.86, 3.88, 4.97 (7-H / 8-H_{eq}, 6-H, 8-H_{ax}, 9-H), 4.26 / 4.18, 4.55 (C11 / C12, C13), 7.92 / 7.48 (*o*-C_6H_5 / *m*-C_6H_5, *p*-C_6H_5).

^{1}H,^{1}H GCOSY ([D_2]-dichloromethane, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.33 / 2.86 (7-H / 6-H), 2.45 / 2.86, 3.88, 4.97 (8-H_{eq} / 6-H, 8-H_{ax}, 9-H), 2.86 / 3.88 (6-H / 8-H_{ax}), 3.88 / 3.90, 4.18, 4.30, 4.97 (8-H_{ax}, C_5H_4 / C_5H_4, 9-H), 3.90 / 4.18, 4.30 (C_5H_4), 4.18 / 4.26, 4.30, 4.55 (12-H, C_5H_4 / 11-H, C_5H_4, 13-H), 4.26 / 4.55 (11-H / 13-H), 7.48 / 7.92 (*m*-C_6H_5, *p*-C_6H_5 / *o*-C_6H_5).

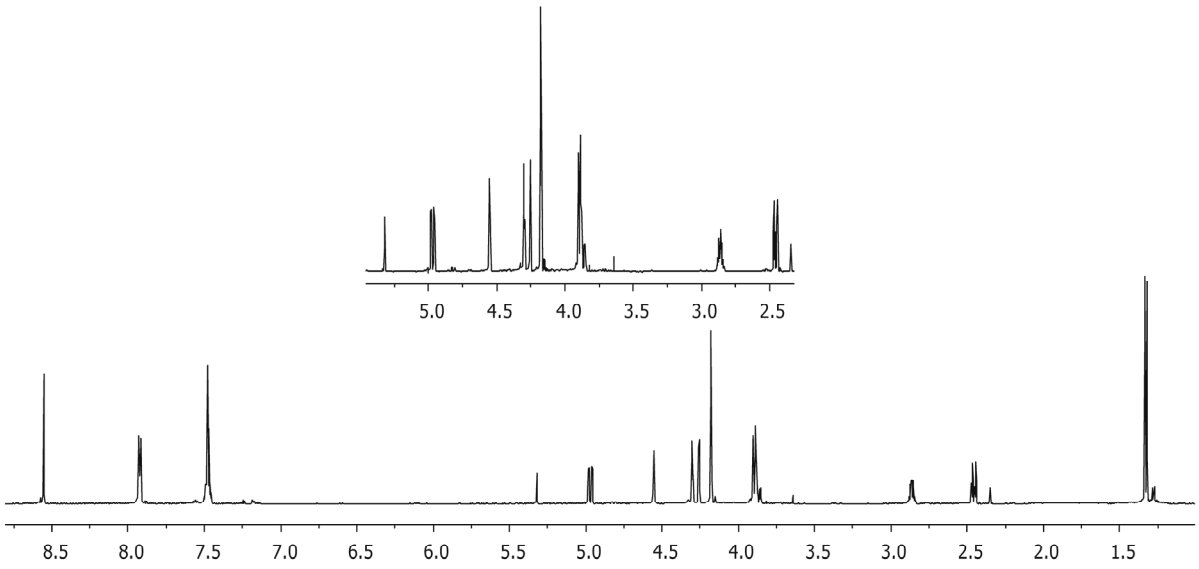
^{1}H,^{13}C GHSQC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.33 / 16.8 (7-H / C7), 2.45, 3.88 / 51.2 (8-H_{eq}, 8-H_{ax} / C8), 2.86 / 29.5 (6-H / C6), 3.88 / 67.4 (C_5H_4), 3.90 / 75.3 (C_5H_4), 4.18 / 66.7, 69.1 (12-H, C_5H_4 / C12, C_5H_4), 4.26 / 69.8 (11-H / C11), 4.30 / 70.8 (C_5H_4), 4.55 / 59.7 (13-H / C13), 4.97 / 56.1 (9-H / C9), 7.48 / 129.1, 131.0 (*m*-C_6H_5, *p*-C_6H_5), 7.92 / 128.5 (*o*-C_6H_5), 8.55 / 157.7 (15-H / C15).

^{1}H,^{13}C GHMBC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.33 / 29.5, 51.2, 94.2 (7-H / C6, C8, C1), 2.45 / 29.5, 56.1, 94.2 (8-H_{eq} / C6, C9, C10, C1), 3.88 / 16.8, 29.5, 56.1, 69.1, 70.8, 75.3, 80.5, 94.2 (8-H_{ax}, C_5H_4 / C7, C6, C9, C_5H_4, C10, C1), 3.90 / 70.8, 75.3, 94.2 (C_5H_4 / C_5H_4, C1), 4.18 / 59.7, 67.4, 69.8, 70.8, 75.3, 80.5, 94.2, 104.4 (12-H, C_5H_4 / C13, C11, C_5H_4, C10, C1, C14), 4.30 / 67.4, 69.1, 75.3, 94.2 (C_5H_4 / C_5H_4, C1), 4.55 / 66.7, 69.8, 80.5, 104.4 (13-H / C12, C11, C10, C14), 4.97 / 51.2, 69.8, 80.5, 104.4 (9-H / C8, C11, C10, C14), 7.48 / 128.5, 137.4 (*m*-C_6H_5, *p*-C_6H_5 / *o*-C_6H_5, *i*-C_6H_5), 7.92 / 128.5, 131.0, 157.7 (*o*-C_6H_5 /*o*-C_6H_5, *m*-C_6H_5, *p*-C_6H_5, C15), 8.55 / 104.4, 128.5, 137.4 (15-H / C-14, *o*-C_6H_5, *i*-C_6H_5).

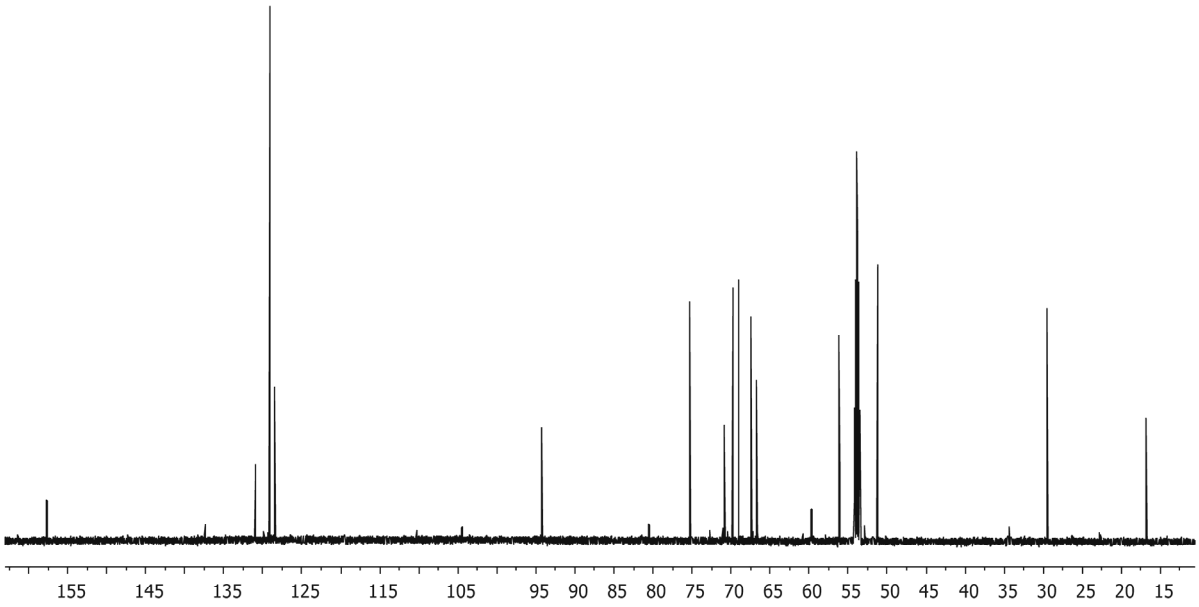
Elemental Analysis: $C_{21}H_{20}ClFeN$ (377.69 g/mol) requires C 66.78, H 5.34, N 3.71, found: C 66.12, H 5.46, N 3.87.

Melting Point: 132°C.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3082 w, 3058 w, 3022 w, 2960 w, 2931 w, 2879 w, 1733 w, 1700 w, 1615 m, 1575 m, 1494 m, 1467 m, 1449 m, 1431 w, 1391 m ,1375 m, 1326 m, 1309 m, 1296 w, 1280 m, 1246 w, 1218 m, 1212 m, 1169 w, 1117 m, 1105 m, 1071 m, 1044 m, 1034 m, 1026 s, 1004 w, 986 w, 969 m, 940 m, 883 m, 866 w, 842 s, 824 w.

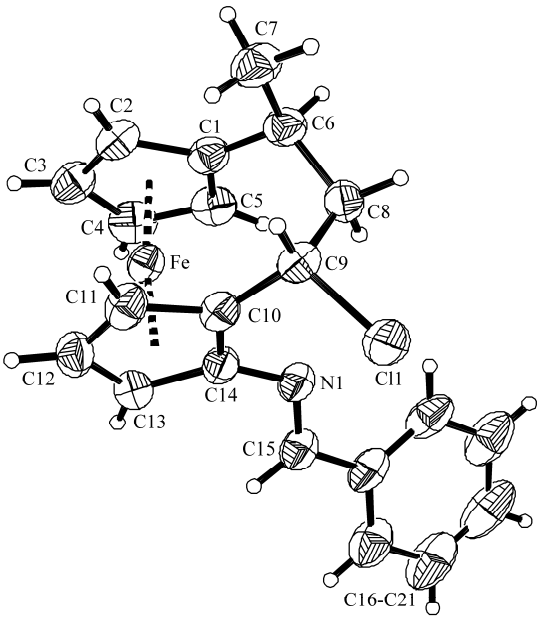


^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of **5**



$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) of **5**

X-ray crystal structure analysis: Crystal data for $C_{21}H_{20}ClFeN$ (**5**), M = 377.68, monoclinic, space group $P2_1/c$ (No. 14), a = 11.4469(3), b = 13.7506(4), c = 11.5357(3) Å, β = 107.176(1)°, V = 1734.76(8) Å^3, D_c = 1.446 g cm^{-3}, μ = 1.024 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 223(2) K, 8833 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 4017 independent (R_{int} = 0.042), and 3496 observed reflections [I ≥ 2σ(I)], 218 refined parameters, R = 0.054, wR^2 = 0.120.

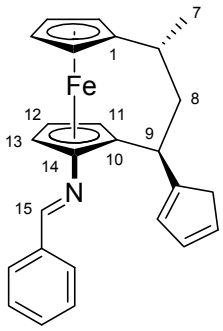


Preparation of compound **6a/b**

Compound **5** (1.80 g, 4.77 mmol) and cyclopentadienyl sodium (1.26 g, 14.3 mmol, 3 equiv) were mixed in a Schlenk flask and suspended at 0°C in prechilled anhydrous diethyl ether (100 ml). The reaction mixture was allowed to warm to ambient temperature and stirred for additional 3 h. The reaction was quenched by addition of water (0.5 ml). After 20 min of stirring magnesium sulfate was added and the solvent was removed *in vacuo*. The residue was extracted with pentane (5×20 ml) and after evaporation of the solvent under vacuum the analytically pure product was obtained as a deep red powder (1.20 g, 2.95 mmol, 62%).

An isomer mixture was obtained (ratio = 1:1.4).

Minor isomer



^{1}H NMR ([D_2]-dichloromethane, 500 MHz, 298 K): δ = 1.30 (d, $^3J_{(H,H)}$ = 7.2 Hz, 3H, 7-H), 2.30 (m, 1H, 8-H), 2.82 (m, 1H, 6-H), 3.01 (m, 2H, $C_5H_5^{CH2}$), 3.42 (m, 2H, 9-H, 8'-H), 3.73 (m, 1H, $C_5H_4^{\alpha}$), 3.90 (m, 1H, $C_5H_4^{\beta}$), 4.10 (m, 2H, $C_5H_4^{\alpha}$, 12-H), 4.21 (m, 1H, 11-H), 4.27 (m, 1H, $C_5H_4^{\beta}$), 4.44 (m, 1H, 13-H), 6.18 (m, 1H, C_5H_5), 6.31 (m, 1H, C_5H_5), 6.36 (m, 1H, C_5H_5), 7.44 (m, 3H, *m*-C_6H_5, *p*-C_6H_5), 7.81 (m, 2H, *o*-C_6H_5), 8.44 (s, 1H, 15-H).

^{13}C{^{1}H} NMR ([D_2] dichloromethane, 126 MHz, 298 K): δ = 16.89 (C7), 27.3 (C6), 32.2 (C9), 43.5 ($C_5H_5^{CH2}$), 47.5 (C8), 58.3 (C13), 65.9 (C12), 67.0 ($C_5H_4^{\beta}$), 68.7 ($C_5H_4^{\alpha}$), 70.1 ($C_5H_4^{\beta}$), 71.5 (C11), 75.0 ($C_5H_4^{\alpha}$), 86.7 (C10), 94.2 (C1), 102.6 (C14), 126.7 (C_5H_5), 131.0 (C_5H_5), 132.3 (C_5H_5), 128.1 (*o*-C_6H_5), 129.0 (*m*-C_6H_5), 130.53 (*p*-C_6H_5), 137.76 (*i*-C_6H_5), 153.3 (*i*-C_5H_5), 156.2 (C15).

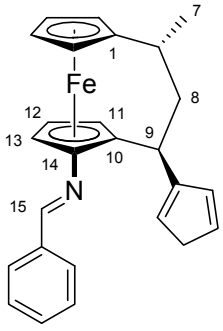
^{1}H,^{1}H 1D-TOCSY ([D_2]-dichloromethane, 500 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.30, 131 / 2.30; 2.32, 2.82, 3.36, 3.42 (7-H / 8-H, 6-H, 9-H, 8'-H), 3.73 / 3.90, 4.10, 4.27 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$).

^{1}H,^{1}H GCOSY ([D_2]-dichloromethane, 500 MHz / 500 MHz, 298 K) : δ (^{1}H) / δ (^{1}H) = 1.30 / 2.82 (7-H / 6-H), 2.30 / 2.82, 3.42 (8-H / 6-H, 9-H), 2.82 / 3.42 (6-H / 8'-H), 3.01 / 6.18, 6.31, 6.36 ($C_5H_5^{CH2}$ / C_5H_5), 3.73 / 3.90, 4.10, 4.27 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$), 3.90 / 4.10, 4.27, ($C_5H_4^{\beta}$ / $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$), 4.10 / 4.21, 4.27, 4.44 (12-H, $C_5H_4^{\alpha}$ / 11-H, $C_5H_4^{\beta}$,13-H,), 4.21 / 4.44 (11-H / 13-H), 6.18 / 6.36 (C_5H_5), 7.44 / 7.81 (*m*-C_6H_5, *p*-C_6H_5 / *o*-C_6H_5).

^{1}H,^{13}C GHSQC ([D_2]-dichloromethane, 500 MHz / 126 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.30 / 16.89 (7-H / C7), 2.30, 3.42 / 47.5 (8-H, 8'-H / C8), 2.82 / 27.3 (6-H / C6), 3.01 / 43.5 ($C_5H_5^{CH2}$), 3.42 / 32.2 (9-H / C9), 3.73 / 75.0 ($C_5H_4^{\alpha}$), 3.90 / 67.0 ($C_5H_4^{\beta}$), 4.10 / 65.9, 68.7 (12-H, $C_5H_4^{\alpha}$ / C12, $C_5H_4^{\alpha}$), 4.21 / 71.5 (11-H / C11), 4.27 / 70.1 ($C_5H_4^{\beta}$), 4.44 / 58.3 (13-H / C13), 6.18 / 131.0 (C_5H_5), 6.31 / 126.7 (C_5H_5), 6.36 / 132.3 (C_5H_5), 7.44 / 129.0, 130.53 (*m*-C_6H_5, *p*-C_6H_5), 7.81 / 128.1 (*o*-C_6H_5), 8.44 / 156.2 (H-15 / C15).

^{1}H,^{13}C GHMBC ([D_2]-dichloromethane, 500 MHz / 126 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.30 / 27.3, 47.5, 68.7, 94.2 (7-H / C6, C8, $C_5H_4^{\alpha}$, C1), 2.30 / 16.89, 27.3, 32.2, 43.5, 71.5, 86.7, 94.2, 102.6, 126.7, 153.3 (8-H / C7, C6, C9, CH_2, C11, C10, C1, C14, C_5H_5, *i*-C_5H_5), 3.01 / 126.7, 131.0, 132.3, 153.3 ($C_5H_5^{CH2}$ / C_5H_5), 3.42 / 16.89, 27.3, 32.2, 43.5, 47.5, 71.5, 86.7, 94.2, 102.6, 126.7, 153.3 (8'-H, 9-H / C7, C6, C9, CH_2, C8, C11, C10, C1, C14, C_5H_5, *i*-C_5H_5), 3.73 / 67.0, 68.7, 70.1, 94.2 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$, C1), 3.90 / 68.7, 70.1, 75.0, 94.2 ($C_5H_4^{\beta}$ / $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, C1), 4.10 / 58.3, 67.0, 70.1, 71.5, 75.0, 86.7, 94.2, 102.6 ($C_5H_4^{\alpha}$, 12-H / C13, $C_5H_4^{\beta}$, $C_5H_4^{\beta}$, C11, C(2,5), C10, C1, C14), 4.21 / 58.3, 65.9, 86.7, 102.6 (11-H / C13, C12, C10, C14), 4.27 / 67.0, 68.7, 75.0, 94.2 ($C_5H_4^{\beta}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\alpha}$, C1), 4.44 / 65.9, 71.5, 86.7, 102.6 (13-H / C12, C11, C10, C14), 6.18 / 43.5, 126.7, 132.3, 153.3 (C_5H_5 / C_5H_5, *i*-C_5H_5), 6.31 / 43.5, 131.0, 132.3, 153.3 (C_5H_5 / C_5H_5, *i*-C_5H_5), 6.36 / 43.5, 126.7, 131.0, 153.3 (C_5H_5 / C_5H_5, *i*-C_5H_5), 7.44 / 128.1, 129.0, 137.76 (*m*-C_6H_5, *p*-C_6H_5 / *o*-C_6H_5, *m*-C_6H_5, *i*-C_6H_5), 7.81 / 128.1, 130.53, 156.2 (*o*-C_6H_5 / *o*-C_6H_5, *p*-C_6H_5, C15), 8.44 / 102.6, 128.1, 137.76 (15-H / C14, *o*-C_6H_5, *i*-C_6H_5).

Major isomer



^{1}H NMR ([D_2]-dichloromethane, 500 MHz, 298 K): δ = 1.31 (d, $^{3}J_{(H,H)}$ = 7.21 Hz, 3H, 7-H), 2.32 (m, 1H, 8-H), 2.82 (m, 1H, 6-H), 2.89 (m, 2H, $C_5H_5^{CH2}$), 3.36 (m, 1H, 9-H), 3.42 (m, 1H, 8'-H), 3.73 (m, 1H, ($C_5H_4^{\alpha}$), 3.90 (m, 1H, $C_5H_4^{\beta}$), 4.10 (m, 2H, $C_5H_4^{\alpha}$, 12-H), 4.23 (m, 1H, 11-H), 4.27 (m, 1H, $C_5H_4^{\beta}$), 4.44 (m, 1H, 13-H), 6.15 (m, 1H, C_5H_5), 6.31 (m, 1H, C_5H_5), 6.64 (m, 1H, C_5H_5), 7.44 (m, 3H, *m*-C_6H_5, *p*-C_6H_5), 7.81 (m, 2H, *o*-C_6H_5), 8.42 (s, 1H, 15-H).

^{13}C{^{1}H} NMR ([D_2] dichloromethane, 126 MHz, 298 K): δ = 16.91 (C7), 27.1 (C6), 31.5 (C9), 41.3 ($C_5H_5^{CH2}$), 46.6 (C8), 58.3 (C13), 65.9 (C12), 67.0 ($C_5H_4^{\beta}$), 68.7 ($C_5H_4^{\alpha}$), 70.1 ($C_5H_4^{\beta}$), 71.7 (C11), 75.0 ($C_5H_4^{\alpha}$), 85.9 (C10), 94.2 (C1), 103.0 (C14), 126.1 (C_5H_5), 133.1

(C_5H_5), 135.3 (C_5H_5), 128.1 (*o*-C_6H_5), 129.1 (*m*-C_6H_5), 130.49 (*p*-C_6H_5), 137.8 (i-C_6H_5), 150.1 (*i*-C_5H_5), 156.3 (C15).

^{1}H,^{1}H 1D-TOCSY ([D_2]-dichloromethane, 500 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.30, 1.31 / 2.30 und 2.32, 2.82, 3.36, 3.42 (7-H / 8-H, 6-H, 9-H, 8'-H), 3.73 / 3.90, 4.10, 4.27 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$).

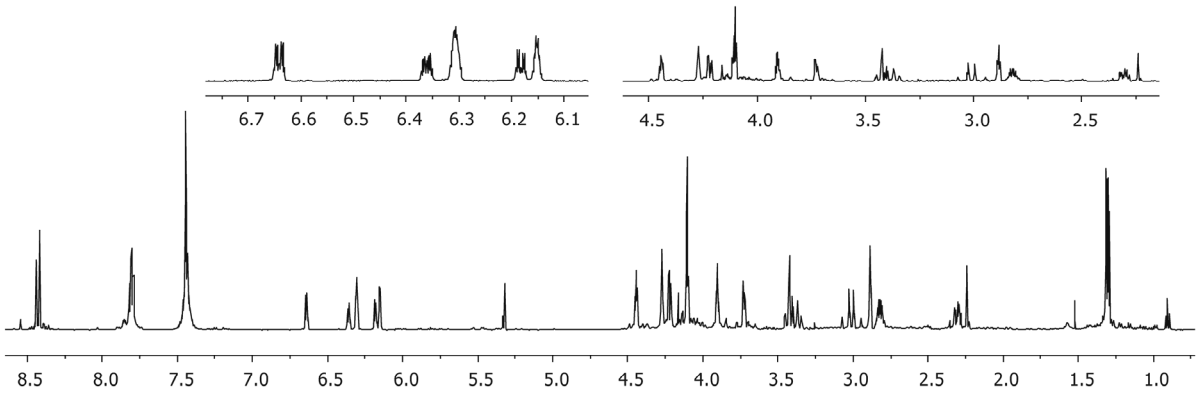
^{1}H,^{1}H GCOSY ([D_2]-dichloromethane, 500 MHz / 500 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.31 / 2.82 (7-H / 6-H), 2.32 / 2.82, 3.36, 3.42 (8-H / 6-H, 9-H, 8'-H), 2.82 / 3.42 (6-H / 8'-H), 2.89 / 6.15, 6.31, 6.64 ($C_5H_5^{CH2}$ / C_5H_5), 3.36 / 3.42 (9-H / 8'-H), 3.73 / 3.90, 4.10, 4.27 ($C_5H_4^{\alpha}$ $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$), 3.90 / 4.10, 4.27 ($C_5H_4^{\beta}$ / $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$), 4.10, 4.21, 4.27, 4.44 (12-H, $C_5H_4^{\alpha}$ / 11-H, $C_5H_4^{\beta}$, 13-H), 4.23 / 4.44 (11-H / 13-H), 6.15 / 6.31, 6.64 (C_5H_5), 6.31 / 6.64 (C_5H_5), 7.44 / 7.81 (*m*-C_6H_5, *p*-C_6H_5 / *o*-C_6H_5).

^{1}H,^{13}C GHSQC ([D_2]-dichloromethane, 500 MHz / 126 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.31 / 16.91 (7-H / C7), 2.32, 3.42 / 46.6 (8-H, 8'-H / C8), 2.82 / 27.1 (6-H / C6), 2.89 / 41.3 ($C_5H_5^{CH2}$), 3.36 / 31.5 (9-H / C9), 3.73 / 75.0 ($C_5H_4^{\alpha}$), 3.90 / 67.0 ($C_5H_4^{\beta}$), 4.10 / 65.9, 68.7 (12-H, $C_5H_4^{\alpha}$ / C12, $C_5H_4^{\alpha}$), 4.23 / 71.7 (11-H / C11), 4.27 / 70.1 ($C_5H_4^{\beta}$), 4.44 / 58.3 (13-H / C13), 6.15 / 126.1 (C_5H_5), 6.31 / 133.1 (C_5H_5), 6.64 / 135.3 (C_5H_5), 7.44 / 129.1, 130.49 (*m*-C_6H_5, *p*-C_6H_5), 7.81 / 128.1 (*o*-C_6H_5), 8.42 / 156.3 (H-15 / C15).

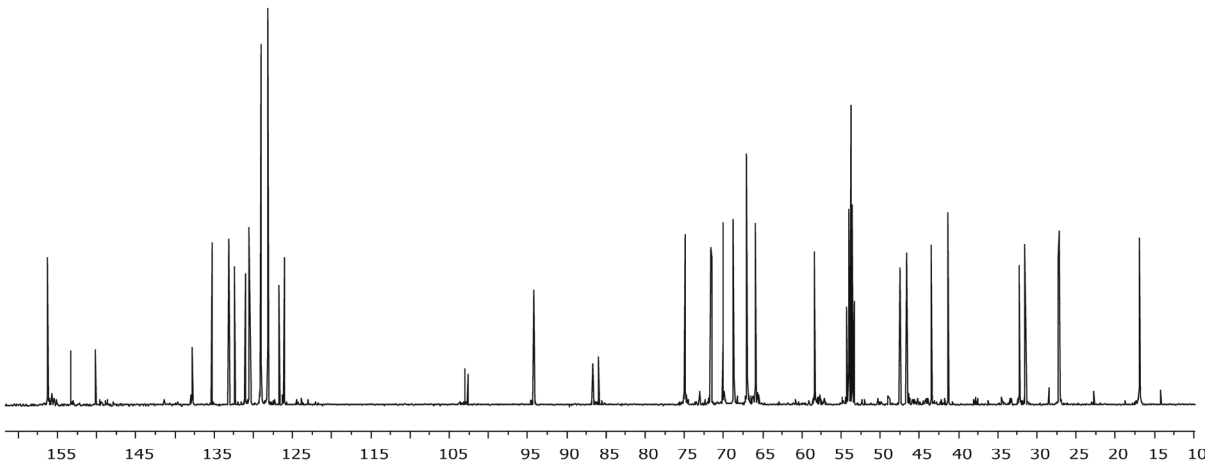
^{1}H,^{13}C GHMBC ([D_2]-dichloromethane, 500 MHz / 126 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.31 / 27.1, 46.6, 68.7, 94.2 (7-H / C6, C8, $C_5H_4^{\alpha}$, C1), 2.32 / 16.91, 27.1, 31.5, 71.7, 85.9, 94.2, 103.0, 150.1 (8-H / C7, C6, C9, C11, C10, C1, C14, *i*-C_5H_5), 2.89 / 126.1, 133.1, 135.3, 150.1 ($C_5H_5^{CH2}$ / C_5H_5, *i*-C_5H_5), 3.36 / 27.1, 46.5, 71.7, 85.9, 103.0, 126.1, 135.3, 150.1 (9-H / C6, C8, C11, C10, C14, C_5H_5, C_5H_5, *i*-C_5H_5), 3.42 / 16.91, 27.1, 31.5, 85.9, 94.2, (8'-H, / C7, C6, C9, C10, C1), 3.73 / 67.0, 68.7, 70.1, 94.2 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$, C1), 3.90 / 68.7, 70.1, 75.0, 94.1 ($C_5H_4^{\beta}$ / $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, C1), 4.10 / 58.3, 67.0, 70.1, 71.7, 75.0, 85.9, 94.2, 103.0 ($C_5H_4^{\alpha}$, 12-H / C13, $C_5H_4^{\beta}$, $C_5H_4^{\beta}$, C11, $C_5H_4^{\alpha}$, C10, C1, C14), 4.21 / 58.3, 65.9, 85.9, 103.0 (11-H / C13, C12, C10, C14), 4.27 / 67.0, 68.7, 75.0, 94.2 ($C_5H_4^{\beta}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\alpha}$, C1), 4.44 / 65.9, 71.7, 85.7, 103.6 (13-H / C12, C11, C10, C14), 6.15 / 133.1, 135.3, 150.1 (C_5H_5 / C_5H_5, *i*-C_5H_5), 6.31 / 126.1, 135.3, 150.1 (C_5H_5 / C_5H_5, *i*-C_5H_5), 6.36 / 126.1, 133.1, 150.1 (C_5H_5 / C_5H_5, *i*-C_5H_5), 7.44 / 128.1, 129.1, 137.8 (*m*-C_6H_5, *p*-C_6H_5 / *o*-C_6H_5, *m*-C_6H_5, *i*-C_6H_5), 7.81 / 128.1, 130.49, 156.3 (*o*-C_6H_5 / *o*-C_6H_5, *m*-C_6H_5, *p*-C_6H_5, C15), 8.42 / 103.0, 128.1, 137.8 (15-H / C14, *o*-C_6H_5, *i*-C_6H_5).

Elemental Analysis $C_{26}H_{25}FeN$ (407.33 g/mol) requires C 76.66, H 6.19, N 3.44 found C 76.01, H 6.25, N 3.49.

Melting Point 63°C.

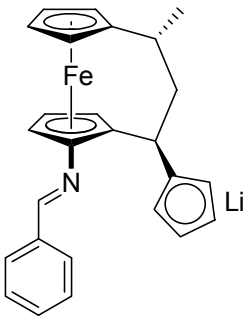


^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) of **6a/b**



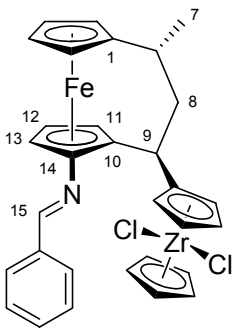
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) of **6a/b**

Preparation of Compound **7**



Compound **6a/b** (400 mg, 0.98 mmol) was dissolved in anhydrous tetrahydrofuran (20 ml) and methyllithium (21.6 mg, 0.98 mmol, 1 equiv) dissolved in tetrahydrofuran was added at room temperature. After stirring for 3 h the solvent was removed *in vacuo* and the residue was suspended in pentane and stirred overnight. The red precipitation was collected on a glas frit and washed with pentane (3×10 ml) and dried under vacuum to give the crude product, which was used without any further purification (350 mg, 0.84 mmol, 86%).

Preparation of compound **8**



Compound **7** (200 mg, 0.49 mmol) and $CpZrCl_3$·dme (188 mg, 0.49 mmol, 1 equiv) were mixed in a Schlenk flask at −78 °C and suspended in prechilled anhydrous toluene (10 ml). Then tetrahydrofuran (1 ml) was added and the suspension was allowed to warm to room temperatur by stirring overnight. The solvent was removed *in vacuo* and the residue was suspended in dichloromethane and filtrated through Celite. All volatiles were evaporated in vacuum from the filtrate. The residue was suspended in pentane and by dropwise addition of dichloromethane a clear solution was obtained, which was stored at −25°C overnight to get a red precipitate. The precipitated solid was collected by filtration and dried *in vacuo* to yield **8** as red crystalls (80 mg, 0.13 mmol, 27%).

^{1}H NMR ([D_2]-dichloromethane, 600 MHz, 298 K): δ = 1.32 (d, $^3J_{(H,H)}$ = 7.3 Hz, 3H, 7-H), 2.33 (m, 1H, 8-H), 2.79 (m, 1H, 6-H), 3.31 (m, 1H, 8'-H), 3.68, 3.90, 4.13, 4.29 (each m, each 1H, C_5H_4), 3.79 (m, 1H, 9-H), 4.15 (m, 1H, 12-H), 4.31 (m, 1H, 11-H), 4.53 (m, 1H, 13-H), 6.08 (m, 1H, $C_5H_4^{Zr}$), 6.30 (s, 5H, Cp), 6.33 (m, 1H, $C_5H_4^{Zr}$), 6.46 (m, 1H, $C_5H_4^{Zr}$), 6.57 (m, 1H, $C_5H_4^{Zr}$), 7.44 (m, 2H, *m*-C_6H_5), 7.45 (m, 1H, *p*-C_6H_5), 7.78 (m, 2H, *o*-C_6H_5), 8.51 (m, 1H, 15-H).

^{13}C{^{1}H} NMR ([D_2] dichloromethane, 151 MHz, 298 K): δ = 16.8 (C7), 27.5 (C6), 32.0 (C9), 48.4 (C8), 58.9 (C13), 66.4 (C12), 67.3 (C_5H_4), 69.0 (C_5H_4), 70.3 (C_5H_4), 72.4 (C11), 75.1 (C_5H_4), 85.0 (C10), 94.1 (C1), 102.5 (C14), 110.5 ($C_5H_4^{Zr}$), 115.2 ($C_5H_4^{Zr}$), 116.1 (Cp), 117.8

($C_5H_4^{Zr}$), 118.4 ($C_5H_4^{Zr}$), 128.2 (*o*-C_6H_5), 129.2 (*m*-C_6H_5), 130.7 (*p*-C_6H_5), 137.6 (*i*-C_6H_5), 138.1 (*i*-$C_5H_4^{Zr}$), 156.7 (C15).

^{1}H,^{1}H GCOSY ([D_2]-dichloromethane, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.32 / 2.79 (7-H / 6-H), 2.33 / 2.79, 3.31, 3.79 (8-H / 6-H, 8'-H, 9-H), 2.79 / 3.31 (6-H / 8`-H), 3.31 / 3.79 (8'-H / 9-H), 3.68 / 3.90, 4.13, 4.29 (C_5H_4), 3.90 / 4.13, 4.29 (C_5H_4), 4.13 / 4.29 (C_5H_4), 4.15 / 4.31, 4.53 (12-H / 11-H, 13-H), 4.31 / 4.53 (11-H / 13-H), 6.08 / 6.33, 6.46, 6.57 ($C_5H_4^{Zr}$), 6.33 / 6.46, 6.57 ($C_5H_4^{Zr}$), 6.46 / 6.57 ($C_5H_4^{Zr}$), 7.44, 7.45 / 7.78 (*m*-C_6H_5, *p*-C_6H_5 / *o*-C_6H_5).

^{1}H,^{13}C GHSQC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.32 / 16.8 (7-H / C7), 2.33, 3.31 / 48.4 (8-H, 8'-H / C8), 2.79 / 27.5 (6-H / C6), 3.68 / 75.1 (C_5H_4), 3.79 / 32.0 (9-H / C9), 3.90 / 67.3 (C_5H_4), 4.13 / 69.0 (C_5H_4), 4.15 / 66.4 (12-H / C12), 4.29 / 70.3 (C_5H_4), 4.31 / 72.4 (11-H / C11), 4.53 / 58.9 (13-H / C13), 6.08 / 110.5 ($C_5H_4^{Zr}$), 6.30 / 116.1 (Cp), 6.33 / 115.2 ($C_5H_4^{Zr}$), 6.46 / 117.8 ($C_5H_4^{Zr}$), 6.57 / 118.4 ($C_5H_4^{Zr}$), 7.44 / 129.2 (*m*-C_6H_5), 7.45 / 130.7 (*p*-C_6H_5), 7.78 / 128.2 (*o*-C_6H_5), 8.51 / 156.7 (15-H / C15).

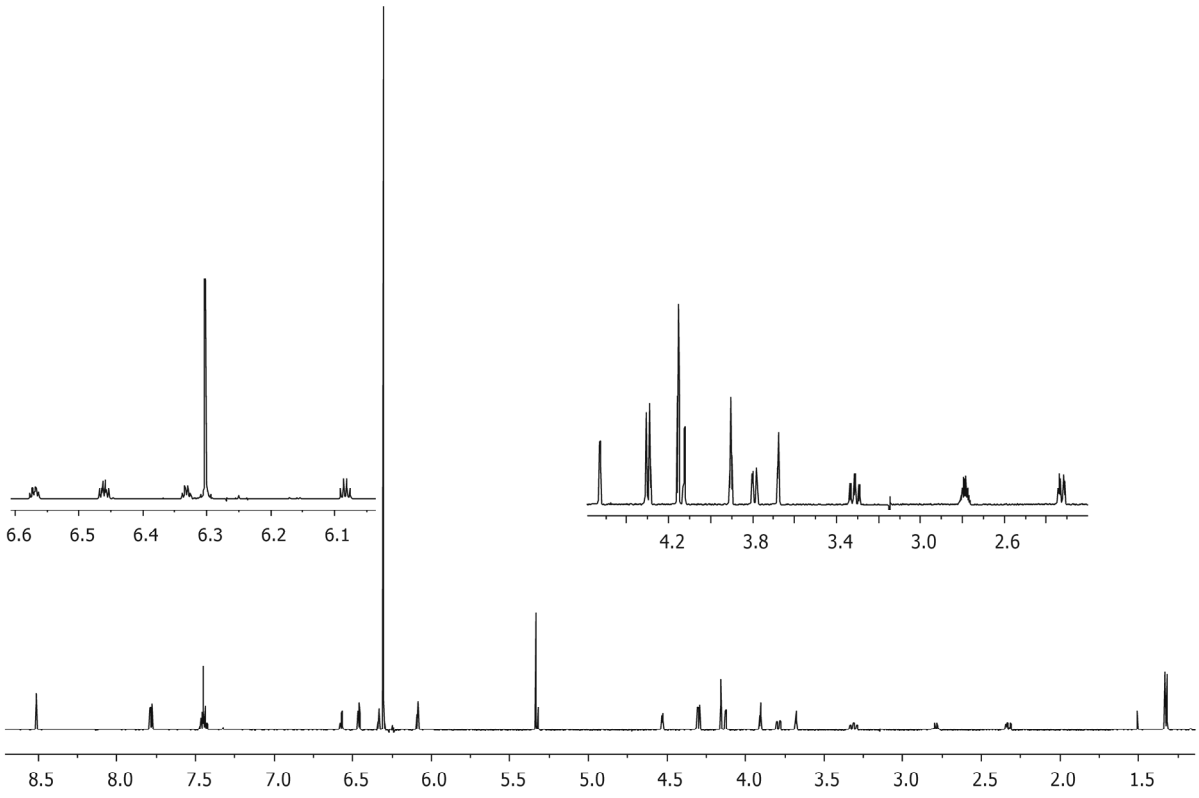
^{1}H,^{13}C GHMBC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.32 / 27.5, 48.4, 94.1 (7-H / C6, C8, C1), 2.33 / 85.0, 94.1 (8-H / C10, C1), 2.79 / 32.0 (6-H / C9), 3.31 / 16.8, 27.5, 32.0, 85.0, 94.1 (8'-H / C7, C6, C9, C10, C1), 3.68 / 67.3, 69.0, 70.3, 94.1 (C_5H_4 / C_5H_4, C1), 3.79 / 27.5, 48.4, 72.4, 85.0, 102.5, 115.2, 118.4, 138.1 (9-H / C6, C8, C11, C10, C14, $C_5H_4^{Zr}$, $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 3.90 / 69.0, 70.3, 75.1, 94.1 (C_5H_4 / C_5H_4, C1), 4.13 / 67.3, 70.3, 75.1, 94.1 (C_5H_4 / C_5H_4, C1), 4.15 / 58.9, 72.4, 85.0, 102.5 (12-H / C13, C11, C10, C14), 4.29 / 67.3, 69.0, 75.1, 94.1 (C_5H_4 / C_5H_4, C1), 4.31 / 58.9, 66.4, 85.0, 102.5 (11-H / C13, C12, C10, C14), 4.53 / 66.4, 72.4, 85.0, 102.5 (13-H / C12, C11, C10, C14), 6.30 / 116.1 (Cp), 6.33 / 117.8 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$), 6.46 / 115.2 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$), 7.44 / 129.2, 137.6 (*m*-C_6H_5 / *m*-C_6H_5, *i*-C_6H_5), 7.45 / 128.2 (*p*-C_6H_5 / *o*-C_6H_5), 7.78 / 128.2, 130.7, 156.7 (*o*-C_6H_5 / *o*-C_6H_5, *p*-C_6H_5, C15), 8.51 / 102.5, 128.2, 137.6, (15-H / C14, *o*-C_6H_5, *i*-C_6H_5).

Elemental Analysis: $C_{31}H_{29}Cl_2FeNZr$ +1/2 CH_2Cl_2 (633.54 g/mol + 42.47 g/mol) requires C 55.97, H 4.47, N 2.07, found: C 56.53, H 4.61, N 2.64.

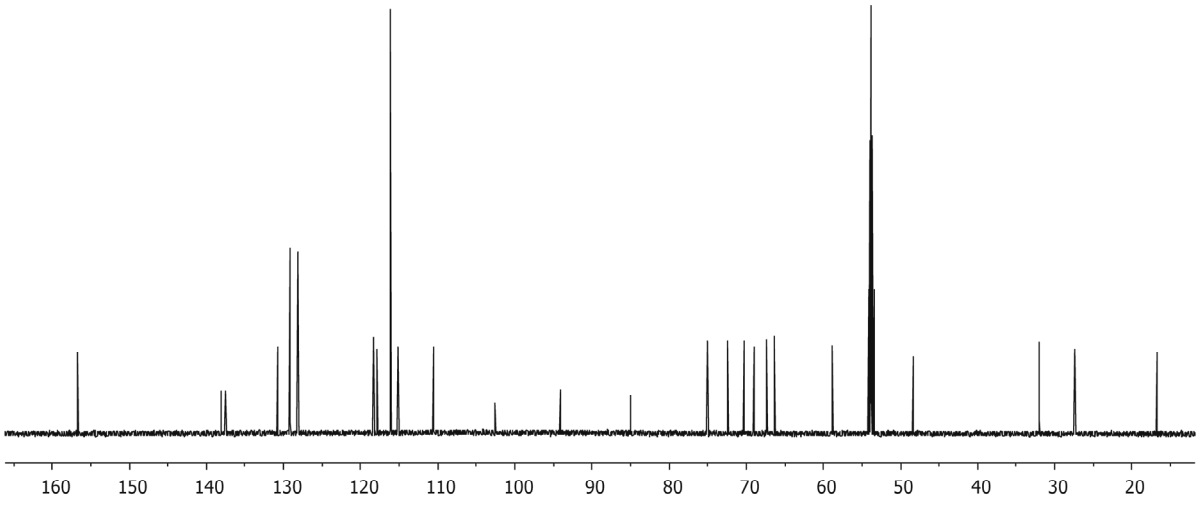
Melting Point: 167.1°C.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3935 w, 3088 w, 2958 w, 2919 w, 2869 w, 1957 w, 1745 w, 1612 m, 1574 m, 1563 m, 1494 w, 1468 m, 1450 m, 1391 w, 1373 m, 1325 m, 1308

m, 1245 w, 1231 w, 1214 w, 1167 w, 1104 m, 1075 m, 1022 s, 961 m, 915 m, 879 m, 823 s, 754 m.

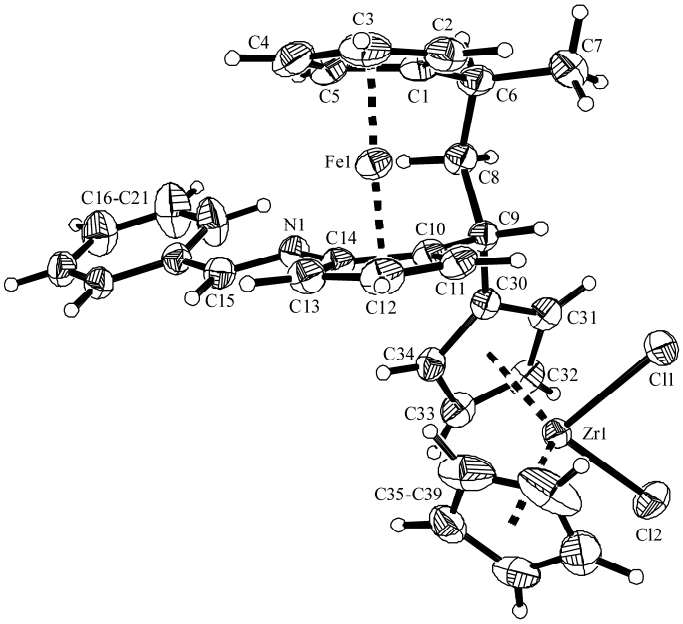


^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of **8**

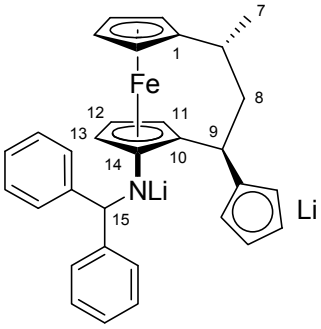


^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K) of **8**

X-ray crystal structure analysis: Crystal data for $C_{31}H_{29}Cl_2FeNZr$ * ½ CH_2Cl_2(**8**), M = 675.98, monoclinic, space group $C2/c$ (No. 15), a = 26.8528(2), b = 12.6309(1), c = 19.1447(3) Å, β = 116.986(1)°, V = 5786.38(11) Å^3, D_c = 1.552 g cm^{-3}, μ = 1.161 mm^{-1}, Z = 8, λ = 0.71073 Å, T = 223(2) K, 20203 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 7093 independent (R_{int} = 0.029), and 6026 observed reflections [I ≥ 2σ(I)], 348 refined parameters, R = 0.036, wR^2 = 0.098.



Preparation **9a**



A solution of **6a/b** (190 mg, 0.47 mmol) in anhydrous pentane (10 ml) was treated with phenyllithium (0.95 ml, 2 M in diethylether, 1.88 mmol, 4 equiv) at room temperature. The reaction mixture was stirred overnight. The precipitation was collected on a glass frit and washed with pentane (3×10 ml). The solid on the filter was dried *in vacuo* to yield the product as an orange powder (210 mg, 0.42 mmol, 89%).

^{1}H NMR ([D$_8$]-tetrahydrofurane, 500 MHz, 298 K): δ = 1.23 (d, $^{3}J_{(H,H)}$ = 7.2 Hz, 3H, 7-H), 2.52 (m, 1H, 8-H), 2.73 (m, 1H, 6-H), 2.85 (m, 1H 13-H), 3.15 (m, 2H, 9-H, 8'-H), 3.25 (m, 1H, 12-H), 3.30 (m, 1H, $C_5H_4^{\alpha}$), 3.33 (m, 1H, $C_5H_4^{\beta}$), 3.38 (m, 1H, 11-H), 3.44 (m, 1H, $C_5H_4^{\alpha}$), 3.65 (m, 1H, $C_5H_4^{\beta}$), 4.96 (s, 1H, 15-H), 5.69 (m, 2H, $C_5H_4^{Li}$), 5.83 (b, 2H, $C_5H_4^{Li}$), 6.96 (m, 2H, *p*-C_6H_5, *p*-C_6H_5'), 7.08 (m, 4H, *m*-C_6H_5, *m*-C_6H_5'), 7.11 (m, 2H, *o*-C_6H_5), 7.27 (m, 2H, *o*-C_6H_5').

^{13}C{^{1}H} NMR ([D$_8$]-tetrahydrofurane, 126 MHz, 298 K): δ =17.6 (C7), 29.0 (C6), 30.4 (C9), 46.5 (C8), 49.1 (C13), 58.3 (C12), 62.3 ($C_5H_4^{\beta}$), 63.9($C_5H_4^{\alpha}$), 66.1 (C11), 69.5 ($C_5H_4^{\beta}$), 70.6 (C15), 72.6 (C10), 74.7 ($C_5H_4^{\alpha}$), 91.2 (C1), 102.8 ($C_5H_4^{Li}$), 103.0 ($C_5H_4^{Li}$), 122.7 (*i*-$C_5H_4^{Li}$), 125.0, 125.1 (*p*-C_6H_5, *p*-C_6H_5'), 127.5, 127.9 (*m*-C_6H_5, *m*-C_6H_5'), 128.8 (*o*-C_6H_5), 129.6 (*o*-C_6H_5'), 131.4 (C14), 151.9, 152.0 (*i*-C_6H_5, *i*-C_6H_5').

^{1}H,^{1}H 1D-TOCSY ([D$_8$]-tetrahydrofuran, 500 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.23 / 2.52, 2.73, 3.15 (7-H / 8-H, 6-H, 9-H, 8'-H), 2.85 / 3.25, 3.38 (13-H / 12-H, 11-H).

^{1}H,^{1}H GCOSY ([D$_8$]-tetrahydrofuran, 500 MHz / 500 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.23 / 2.73 (7-H / 6-H), 2.52 / 2.73, 3.15 (8-H / 6-H, 9-H, 8'-H), 2.85 / 3.25, 3.38 (13-H / 12-H, 11-H), 3.25 / 3.38 (12-H / 11-H), 3.30 / 3.33, 3.44, 3.65 ($C_5H_4^{\alpha}$, / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$), $C_5H_4^{\beta}$), 3.33 / 3.44, 3.65 ($C_5H_4^{\beta}$ / $C_5H_4^{\alpha}$), $C_5H_4^{\beta}$), 3.44 / 3.65 ($C_5H_4^{\alpha}$, / $C_5H_4^{\beta}$), 5.69 / 5.83 ($C_5H_4^{Li}$), 6.96 / 7.11, 7.46 (*p*-C_6H_5 / *m*-C_6H_5, *o*-C_6H_5), 6.96 / 7.08 (*m*-C_6H_5 / *o*-C_6H_5; *m*-C_6H_5' / *o*-C_6H_5'), 7.08 / 7.11, 7.27 (*m*-C_6H_5 / *o*-C_6H_5', *o*-C_6H_5).

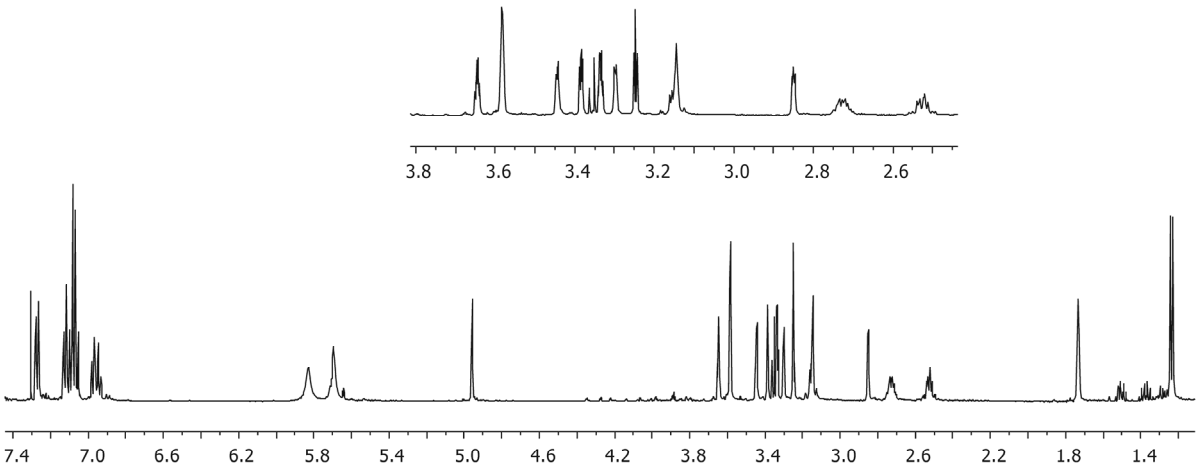
^{1}H,^{13}C GHSQC ([D$_8$]-tetrahydrofuran, 500 MHz / 126 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.23 / 17.6 (7-H / C7), 2.52, 3.15 / 46.5 (8-H, 8'-H / C8), 2.73 / 29.0 (6-H / C6), 2.85 / 49.1 (13-H / C13), 3.15 / 30.4 (9-H / C9), 3.25 / 58.3 (12-H / C12), 3.30 / 74.7 ($C_5H_4^{\alpha}$), 3.33 / 62.3 ($C_5H_4^{\beta}$), 3.38 / 66.1 (11-H / C11), 3.44 / 63.9 ($C_5H_4^{\alpha}$), 3.60/ 69.5 ($C_5H_4^{\beta}$), 4.96 / 70.6 (15-H /

C15), 5.69 / 102.8 ($C_5H_4^{Li}$), 6.96 / 125.0, 125.1 (*p*-C_6H_5, *p*-C_6H_5'), 7.08 / 127.5, 127.9 (*m*-C_6H_5, *m*-C_6H_5'), 7.11 / 128.8 (*o*-C_6H_5), 7.27 / 129.6 (*o*-C_6H_5).

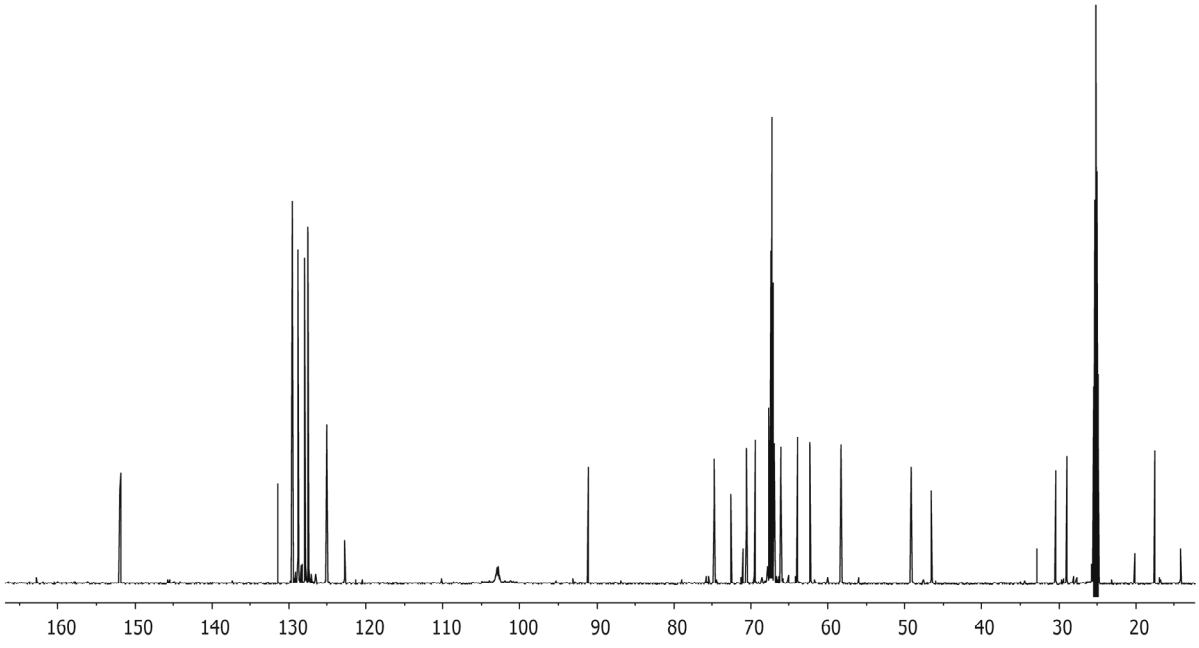
^{1}H,^{13}C GHMBC ([D_8]-tetrahydrofuran, 500 MHz / 126 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.23 / 29.0, 46.5, 91.2 (7-H / C6, C8, C1), 2.52 / 17.6, 29.0, 30.4, 72.6, 91.2, 122.7, 131.4 (8-H / C7, C6, C9, C10, C1, *i*-$C_5H_4^{Li}$, C14), 2.73 / 17.6, 30.4, 46.5, 63.9, 74.7, 91.2 (6-H / C7, C9, C8, C(2,5), C(2,5), C1), 2.85 / 58.3, 66.1, 72.6, 131.4 (13-H / C12, C11, C10, C14), 3.15 / 17.6, 29.0, 30.4, 46.5, 66.1, 72.6, 91.2, 122.7, 131.4 (8-H, 9-H / C7, C6, C9, C8, C11, C10, C1, *i*-$C_5H_4^{Li}$, C14), 3.25 / 49.1, 66.1, 72.6, 131.4 (12-H / C13, C11, C10, C14), 3.30 / 62.3, 63.9, 69.5, 91.2 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$, C1), 3.33 / 63.9, 69.5, 74.7, 91.2 ($C_5H_4^{\beta}$ / $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, C1), 3.38 / 49.1, 58.3, 72.6, 131.4 (11-H / C13, C12, C10, C14), 3.44 / 62.3, 69.5, 74.7, 91.2 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, C1), 3.65 / 62.3, 63.9, 74.7, 91.2 ($C_5H_4^{\beta}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\alpha}$, C1), 4.96 / 128.8, 129.6, 131.4, 151.9, 152.0 (15-H / *o*-C_6H_5, *o*-C_6H_5', C14, *i*-C_6H_5, *i*-C_6H_5'), 5.69 / 103.0, 122.7 ($C_5H_4^{Li}$ / $C_5H_4^{Li}$, *i*-$C_5H_4^{Li}$), 6.96 / 128.8, 129.6 (*p*-C_6H_5, *p*-C_6H_5'/ *o*-C_6H_5, *o*-C_6H_5'), 7.08 / 127.5, 127.9, 151.9, 152.0 (*m*-C_6H_5, *m*-C_6H_5' / *m*-C_6H_5, *m*-C_6H_5', *i*-C_6H_5, *i*-C_6H_5'), 7.11 / 125.1, 128.8 (*o*-C_6H_5 / *p*-C_6H_5, *o*-C_6H_5), 7.27 / 125.0, 1289.6 (*o*-C_6H_5 / *p*-C_6H_5, *o*-C_6H_5).

Melting Point: >250°C.

Infrared Spectroscopy $\widetilde{\nu}$ (KBr) / cm^{-1} = 3674 w, 3060 s, 3024 s, 2957 s, 2924 s, 2869 s, 2360 m, 2341 m, 1717 w, 1595 s, 1491 s, 1450 s, 1347 m, 1295 m, 1276 m, 1251 m, 1170 w, 1126 w, 1075 m, 1029 m, 916 m, 828 s.

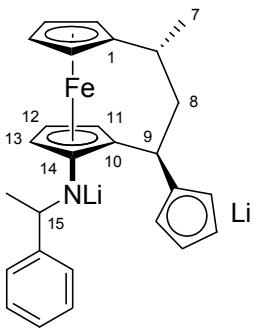


^{1}H NMR (500 MHz, D_8 THF, 298 K) of **9a**



$^{13}C\{^{1}H\}$ NMR (126 MHz, D_8 THF, 298 K) of **9a**

Preparation of compound **9b**



A solution of **6a/b** (1.13 g, 2.78 mmol) in anhydrous toluene (10 ml) was treated with methyllithium (3.48 ml, 1.6 M in diethyl ether, 5.57 mmol, 2 equiv) at 0°C. The reaction mixture was stirred for 6 h at room temperature. The precipitated solid was collected on a glass frit and washed with pentane (3×10 ml). The solid was dried on the filter *in vacuo* to yield the product as a yellow powder (1.02 g, 2.34 mmol, 84%).

^{1}H NMR ([D_8]-tetrahydrofuran, 600 MHz, 298 K): δ = 1.08 (d, $^3J_{(H,H)}$ = 6.6 Hz, 3H, Me), 1.20 (d, $^3J_{(H,H)}$ = 7.2 Hz, 3H, 7-H), 2.50 (m, 1H, 8-H), 2.69 (m, 1H, 6-H), 2.92 (m, 1H 13-H), 3.07 (m, 1H, 9-H), 3.13 (m, 2H, 8'-H, C_5H_4), 3.28 (m, 1H, C_5H_4), 3.34 (m, 1H, 12-H), 3.38 (m, 2H, 11-H, C_5H_4), 3.51 (m, 1H, C_5H_4), 3.89 (q, $^3J_{(H,H)}$ = 6.6 Hz, 1H, 15-H), 5.68 (m, 2H, $C_5H_4^{Li}$), 5.76 (br, 2H, $C_5H_4^{Li}$), 6.95 (m, 1H, *p*-C_6H_5), 7.11 (m, 2H, *m*-C_6H_5), 7.46 (m, 2H, *o*-C_6H_5).

^{13}C{^{1}H} NMR ([D_8]-tetrahydrofuran, 151 MHz, 298 K): δ =17.6 (C7), 24.6 (Me), 29.0 (C6), 30.4 (C9), 46.1 (C8), 47.3 (C13), 58.3 (C12), 59.2 (C15), 62.2, 63.7, 69.4, 74.9 (C_5H_4), 66.0 (C11), 71.5 (C10), 91.1 (C1), 102.8 ($C_5H_4^{Li}$), 123.1 (*i*-$C_5H_4^{Li}$), 124.6 (*p*-C_6H_5), 127.4 (*m*-C_6H_5), 127.9 (*o*-C_6H_5), 132.6 (C14), 154.4 (*i*-C_6H_5). [The ^{13}C signal of one $C_5H_4^{Li}$ was not observed].

^{1}H,^{1}H 1D-TOCSY ([D_8]-tetrahydrofuran, 600 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.20 / 2.50, 2.69, 3.07, 3.13 (7-H / 8-H, 6-H, 9-H, 8'-H), 2.92 / 3.34, 3.38 (13-H / 12-H, 11-H), 3.28 / 3.13, 3.38, 3.51(C_5H_4).

^{1}H,^{1}H GCOSY ([D_8]-tetrahydrofuran, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.08 / 3.89 (Me / 15-H), 1.20 / 2.69 (7-H / 6-H), 2.50 / 2.69, 3.07 (8-H / 6-H, 9-H), 2.69 / 3.13 (6-H / 8'-H), 2.92 / 3.34, 3.38 (13-H / 12-H, 11-H), 3.07 / 3.13 (9-H / 8'-H), 3.13 / 3.28, 3.38, 3.51 (C_5H_4), 3.28 / 3.38, 3.51 (C_5H_4), 3.38 / 3.51 (C_5H_4), 3.34 / 3.38 (12-H / 11-H), 6.95 / 7.11, 7.46 (*p*-C_6H_5 / *m*-C_6H_5, *o*-C_6H_5), 7.11 / 7.46 (*m*-C_6H_5 / *o*-C_6H_5).

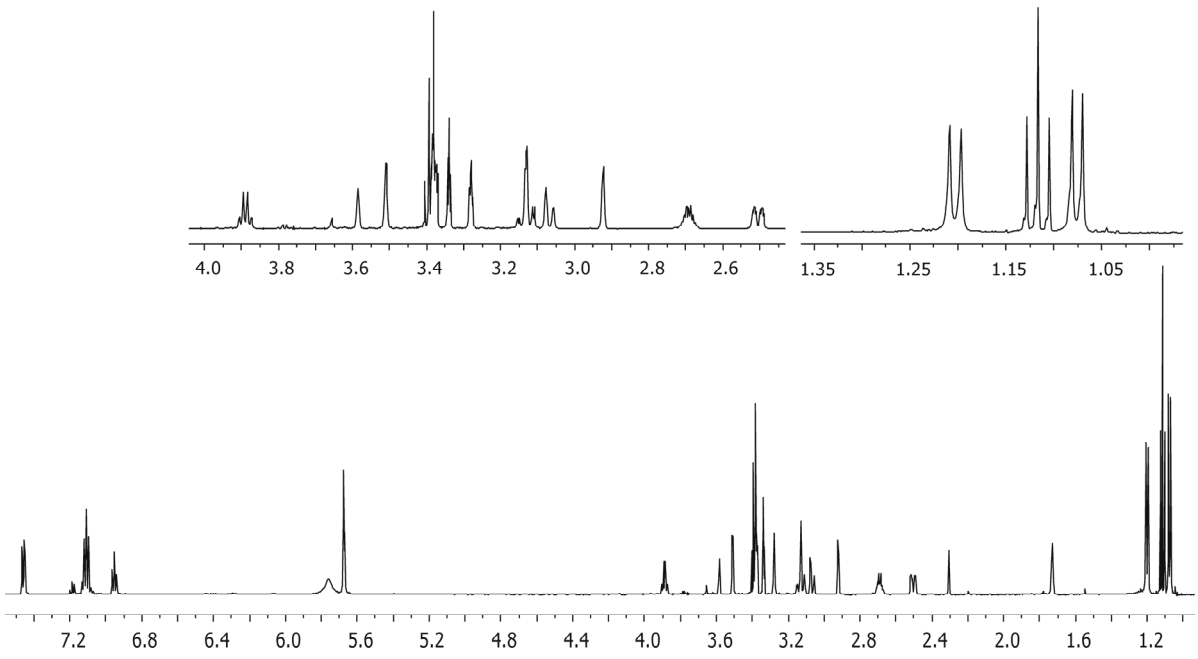
^{1}H,^{13}C GHSQC ([D_8]-tetrahydrofuran, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.08 / 24.6 (Me), 1.20 / 17.6 (7-H / C7), 2.50, 3.13 / 46.1 (8-H, 8'-H / C8), 2.69 / 29.0 (6-H / C6), 2.92 / 47.3 (13-H / C13), 3.07 / 30.4 (9-H / C9), 3.13 / 74.9 (C_5H_4), 3.28 / 62.2 (C_5H_4), 3.34 / 58.3 (12-H / C12), 3.38 / 63.7, 66.0 (C_5H_4, 11-H / C11), 3.51 / 69.4 (C_5H_4), 3.89 / 59.2 (15-H

/ C15), 5.68 / 102.8 ($C_5H_4^{Li}$), 6.95 / 124.6 (*p*-C_6H_5), 7.11 / 127.4 (*m*-C_6H_5), 7.46 / 127.9 (*o*-C_6H_5).

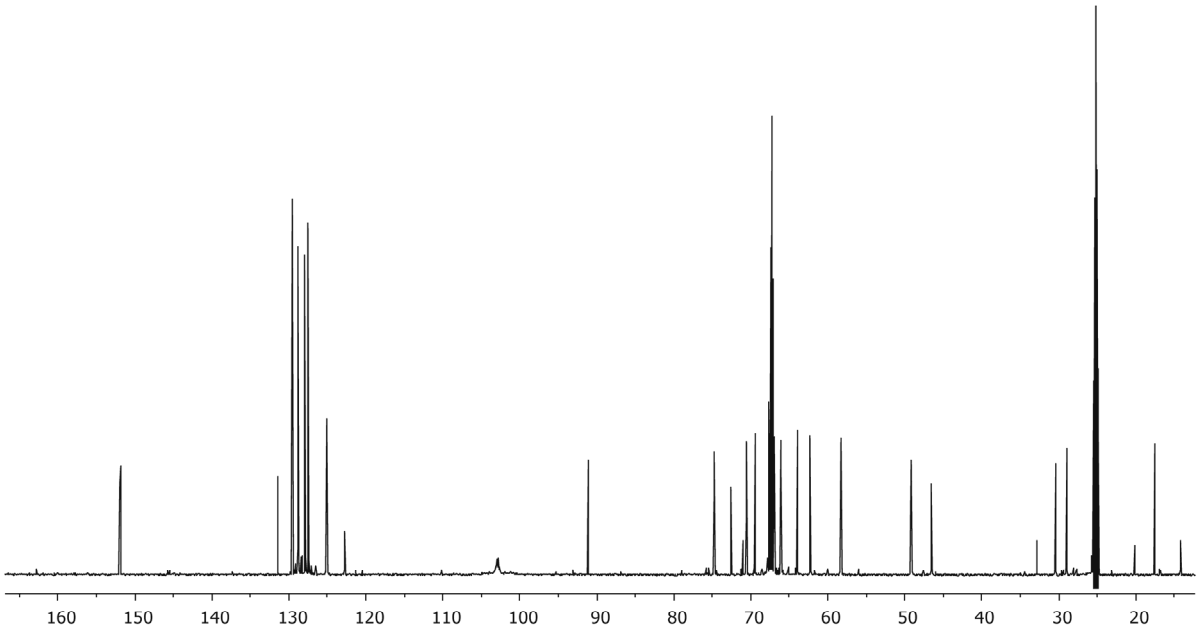
^{1}H,^{13}C GHMBC ([D_8]-tetrahydrofuran, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.08 / 59.2, 154.4 (Me / C15, *i*-C_6H_5), 1.20 / 29.0, 46.1, 91.1 (7-H / C6, C8, C1), 2.50 / 29.0, 30.4, 71.5, 91.1 (8-H / C6, C9, C10, C1), 2.69 / 17.6, 46.1, 91.1 (6-H / C7, C8, C1), 2.92 / 58.3, 66.0, 71.5, 132.6 (13-H / C12, C11, C10, C14), 3.07 / 29.0, 46.1, 66.0, 71.5, 123.1, 132.6 (9-H / C6, C8, C11, C10, *i*-$C_5H_4^{Li}$, C14), 3.13 / 17.6, 29.0, 30.4, 62.2, 63.7, 69.4, 71.5, 91.1 (8'-H, C_5H_4 / C7, C6, C9, C_5H_4, C10, C1), 3.28 / 63.7, 69.4, 74.9, 91.1 (C_5H_4 / C_5H_4, C1), 3.34 / 47.3, 66.0, 71.5, 132.6 (12-H / C13, C11, C10, C14), 3.38 / 47.3, 58.3, 62.2, 69.4, 74.9, 91.1 (11-H, C_5H_4 / C13, C12, C_5H_4, C10, C14), 3.51 / 62.2, 63.7, 74.9, 91.1 (C_5H_4 / C_5H_4, C1), 3.89 / 24.6, 127.9, 132.6, 154.4 (15-H / Me, *o*-C_6H_5, C14, *i*-C_6H_5), 5.68 / 123.1 ($C_5H_4^{Li}$), 6.95 / 127.9 (*p*-C_6H_5 / *o*-C_6H_5), 7.11 / 127.4, 154.4 (*m*-C_6H_5 / *m*-C_6H_5, *i*-C_6H_5), 7.46 / 59.2, 124.6, 127.9 (*o*-C_6H_5 / 15-H, *p*-C_6H_5, *o*-C_6H_5).

Melting Point: 168°C.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3676 w, 3363 w, 3306 w, 3084 m, 3023 w, 2959 m, 2915 m, 2871 m, 2233 w, 1944 w, 1882, w, 1810 w, 1600 m, 1491 s, 1472 s, 1453 s, 1441 s, 1388 w, 1370 m, 1350 w, 1302 m, 1253 m, 1240 m, 1209 w, 1186 w, 1173 m, 1127 m, 1084 s, 1042 s, 1025 s, 949 w, 936 s, 914 s, 864 m, 841 s, 786 s.

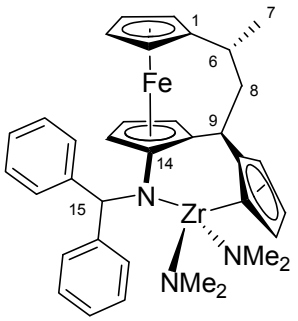


^{1}H NMR (600 MHz, D_8 THF, 298 K) of **9b**



$^{13}C\{^{1}H\}$ NMR (126 MHz, D_8 THF, 298 K) of **9b**

Preparation of **10a**



The suspension of zirconium complex $Zr(NMe_2)Cl_2 \cdot 2thf$ (793.2 mg, 2.01 mmol, 1 equiv) in anhydrous diethyl ether (40 ml) was cooled to −10 °C and added dropwise to a suspension of **9a** (1.00 g, 2.01 mmol) in anhydrous diethyl ether (40 ml). The reaction mixture was allowed to warm to room temperature by stirring overnight. The solvent was removed *in vacuo*, and the residue was suspended in pentane again. The suspension was filtered through Celite. After evaporation of the solvent *in vacuo* the product was obtained as an orange powder (1.10 mg, 1.66 mmol, 83%).

^{1}H NMR ([D_2]-dichloromethane, 600 MHz, 298 K): δ = 1.25 (d, $^3J_{(H,H)}$ = 7.2 Hz, 3H, 7-H), 2.40 (s, 12H, NMe_2), 2.68 (m, 1H, 8-H), 2.79 (m, 1H, 6-H), 2.99 (m, 1H, 8'-H), 3.08 (m, 1H, 13-H), 3.42 (m, 1H, 9-H), 3.70 (m, 1H, 12-H), 3.82 (m, 1H, C_5H_4), 3.96 (m, 1H, 11-H), 3.97 (m, 1H, C_5H_4), 4.06 (m 1H, C_5H_4), 4.19 (m, 1H, C_5H_4), 5.73 (s, 1H, 15-H), 5.98 (m, 1H, $C_5H_4^{Zr}$), 6.06 (m, 1H, $C_5H_4^{Zr}$), 6.15 (m, 1H, $C_5H_4^{Zr}$), 6.31 (m, 1H, $C_5H_4^{Zr}$), 7.18 (m, 1H, *p*-C_6H_5), 7.22 (m, 2H, *o*-C_6H_5), 7.26 (m, 1H, *p*-C_6H_5'), 7.30 (m, 2H, *m*-C_6H_5), 7.34 (m, 2H, *m*-C_6H_5'), 7.51 (m, 2H, *o*-C_6H_5').

^{13}C{^{1}H} NMR ([D_2]-dichloromethane, 151 MHz, 298 K): δ = 16.4 (C7), 26.9 (C6), 27.4 (C9), 42.7 (NMe_2), 45.4 (NMe_2), 46.4 (C8), 59.0 (C13), 63.0 (C12), 65.6 (C_5H_4), 66.9 (C11), 68.4 (C_5H_4), 70.2 (C_5H_4), 70.8 (C_5H_4), 76.3 (C15), 88.3 (C10), 92.4 (C1), 107.0 ($C_5H_4^{Zr}$), 109.6 ($C_5H_4^{Zr}$), 110.5 ($C_5H_4^{Zr}$), 111.4 ($C_5H_4^{Zr}$), 113.6 (C14), 126.4 (*p*-C_6H_5), 126.7 (*p*-C_6H_5'), 128.1 (*m*-C_6H_5), 128.5 (*m*-C_6H_5'), 128.9 (*o*-C_6H_5), 129.6 (*o*-C_6H_5'), 137.2 (*i*-$C_5H_4^{Zr}$), 146.6 (*i*-C_6H_5'), 146.8 (*i*-C_6H_5).

^{1}H,^{1}H 1D-TOCSY ([D_2]-dichloromethane, 600 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.25 / 2.68, 2.79, 2.99, 3.42 (7-H / 8-H, 6-H, 8'-H, 9-H), 3.08 / 3.70, 3.96 (13-H / 12-H, 11-H), 3.82 / 3.97, 4.06, 4.19 (C_5H_4), 7.51 / 7.26, 7.34 (*o*-C_6H_5' / *p*-C_6H_5', *m*-C_6H_5').

^{1}H,^{1}H GCOSY ([D_2]-dichloromethane, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.25 / 2.79 (7-H / 6-H), 2.68 / 2.79, 2.99, 3.42 (8-H / 6-H, 8'-H, 9-H), 2.79 / 2.99 (6-H / 8'-H), 2.99 / 3.42 (8'-H / 9-H), 3.08 / 3.70, 3.96 (13-H / 12-H, 11-H), 3.70 / 3.96 (12-H / 11-H), 3.82 / 3.97, 4.06, 4.19 (C_5H_4), 3.97 / 4.06, 4.19 (C_5H_4), 4.06 / 4.19 (C_5H_4), 5.98 / 6.06, 6.15, 6.31

($C_5H_4^{Zr}$), 6.06 / 6.15, 6.31 ($C_5H_4^{Zr}$), 6.15 / 6.31 ($C_5H_4^{Zr}$), 7.18 / 7.30 (*p*-C_6H_5 / *m*-C_6H_5), 7.22 / 7.30 (*o*-C_6H_5 / *m*-C_6H_5), 7.26 / 7.34 (*p*-C_6H_5' / *m*-C_6H_5'), 7.34 / 7.51 (*m*-C_6H_5' / *o*-C_6H_5').

^{1}H,^{13}C GHSQC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.25 / 16.4 (7-H / C7), 2.40 / 42.7, 45.4 (NMe_2), 2.68, 2.99 / 46.4 (8-H, 8'-H / C8), 2.79 / 26.9 (6-H / C6), 3.08 / 59.0 (13-H / C13), 3.42 / 27.4 (9-H / C9), 3.70 / 63.0 (12-H / C12), 3.82 / 65.6 (C_5H_4), 3.96 / 66.9 (11-H / C11), 3.97 / 70.8 (C_5H_4), 4.06 / 68.4 (C_5H_4), 4.19 / 70.2 (C_5H_4), 5.73 / 76.3 (15-H / C15), 5.98 / 111.4 ($C_5H_4^{Zr}$), 6.06 / 110.5 ($C_5H_4^{Zr}$), 6.15 / 109.6 ($C_5H_4^{Zr}$), 6.31 / 107.0 ($C_5H_4^{Zr}$), 7.18 / 126.4 (*p*-C_6H_5), 7.22 / 128.9 (*o*-C_6H_5), 7.26 / 126.7 (*p*-C_6H_5'), 7.30 / 128.1 (*m*-C_6H_5), 7.34 / 128.5 (*m*-C_6H_5'), 7.51 / 129.6 (*o*-C_6H_5').

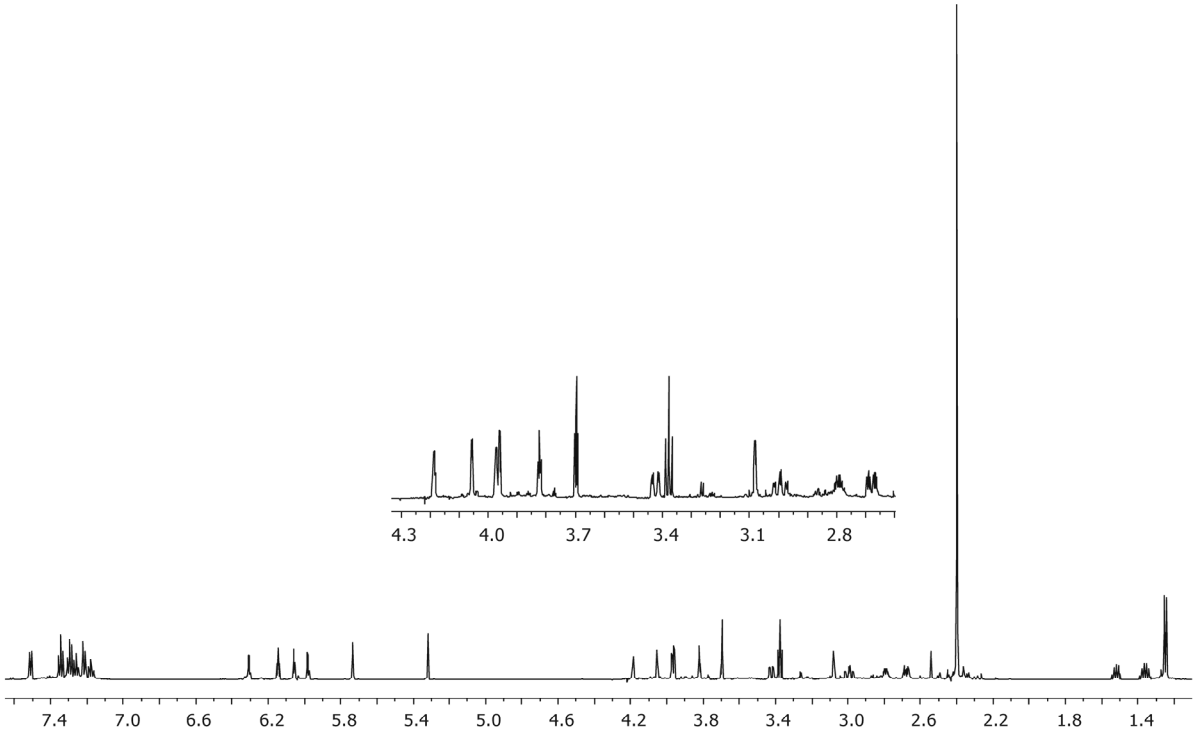
^{1}H,^{13}C GHMBC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.25 / 26.9, 46.4, 92.4 (7-H / C6, C8, C1), 2.68 / 16.4, 26.9, 88.3, 92.4, 137.2 (8-H / C7, C6, C10, C1, *i*-$C_5H_4^{Zr}$), 2.79 / 46.4, 70.8, 92.4 (6-H / C8, C_5H_4, C1), 2.99 / 16.4, 26.9, 88.3, 92.4, 137.2 (8'-H / C7, C6, C10, C1), 3.08 / 63.0, 66.9, 88.3, 113.6 (13-H / C12, C11, C10, C14), 3.42 / 26.9, 46.4, 66.9, 88.3, 107.0, 111.4, 113.3, 137.2 (9-H / C6, C8, C11, C10, $C_5H_4^{Zr}$, $C_5H_4^{Zr}$, C14, *i*-$C_5H_4^{Zr}$), 3.70 / 59.0, 66.9, 88.3, 113.6 (12-H / C13, C11, C10, C14), 3.82 / 68.4, 70.2, 70.8, 92.4 (C_5H_4, C1), 3.96 / 59.0, 63.0, 88.3, 113.6 (11-H / C13, C12, C10, C14), 3.97 / 65.6, 68.4, 70.2, 92.4 (C_5H_4 / C_5H_4, C1), 4.06 / 65.6, 70.2, 70.8, 92.4 (C_5H_4 / C_5H_4, C1), 4.19 / 65.6, 68.4, 70.8, 92.4 (C_5H_4 / C_5H_4, C1), 5.73 / 113.6, 128.1, 128.5, 128.9, 129.6, 146.6, 146.8 (15-H / C14, *m*-C_6H_5, *m*-C_6H_5', *o*-C_6H_5, *o*-C_6H_5', *i*-C_6H_5, *i*-C_6H_5'), 5.98 / 107.0 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$), 6.06 / 107, 137.2 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.15 / 107.0, 111.4, 137.2 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.31 / 111.4 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$) , 7.18 / 128.1, 128.9 (*p*-C_6H_5 / *m*-C_6H_5, *o*-C_6H_5), 7.22 / 76.3, 126.4, 128.1, 128.9 (*o*-C_6H_5 / C15, *p*-C_6H_5, *m*-C_6H_5, *o*-C_6H_5), 7.26 / 129.6 (*p*-C_6H_5' / *o*-C_6H_5'), 7.30 / 126.4, 128.1, 128.9, 146.8 (*m*-C_6H_5 / *p*-C_6H_5, *m*-C_6H_5, *o*-C_6H_5, *i*-C_6H_5), 7.34 / 128.5, 129.6, 146.6 (*m*-C_6H_5' / *m*-C_6H_5', *o*-C_6H_5', *i*-C_6H_5'), 7.51 / 76.3, 126.7, 128.5, 129.6 (*o*-C_6H_5' / C15, *p*-C_6H_5', *m*-C_6H_5', *o*-C_6H_5').

Elemental Analysis: $C_{36}H_{41}FeN_3Zr$ (662.80 g/mol) requires C 65.24, H 6.23, N 6.34 found: C 64.05, H 6.33, N 6.49.

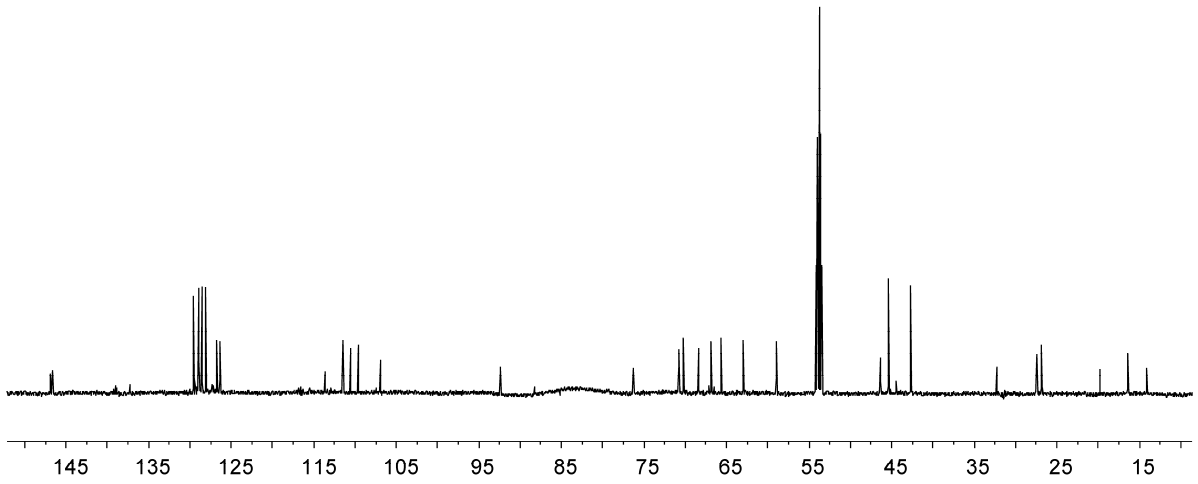
Melting Point: 109°C, decomposition.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3082 w, 3059 w, 3023 w, 2959 w, 2929 w, 2859 w, 2865 w, 2360 w, 2341 w, 1943 w, 1734 w, 1717 w, 1699 w, 1684 w, 1653 w, 1558 w, 1540

w, 1491 s,1467 s, 1450 s, 1419 s, 1372 s, 1321 m, 1242 s, 1171 m, 1123 s, 1077 w, 1035 m, 995 w, 936 s, 847 m, 795 m.

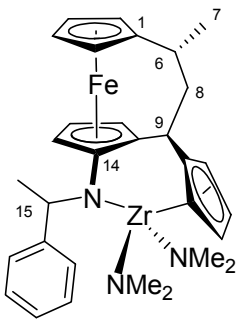


^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of **10a**



$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) of **10a**

Preparation of Compound **10b**



Compound **9b** (500 mg, 1.15 mmol) and $Zr(NMe_2)_2Cl_2$·thf (453.5 mg, 1.15 mmol, 1 equiv) were mixed in a Schlenk flask and suspended in prechilled anhydrous diethyl ether (10 ml) at 0 °C. The suspension was allowed to warm to room temperature by stirring overnight. After filtration through Celite the solvent from filtrate was removed *in vacuo* and the residue was washed with a small amount of pentane (5 ml). The residue was dried *in vacuo*. The product was obtained as a yellow powder. (250 mg, 0.42 mmol, 37%) Suitable crystals for X-ray diffraction were obtained by evaporation of a saturated solution of **10b** in toluene.

^{1}H NMR ([D_2]-dichlormethane, 600 MHz, 298 K): δ = 1.27 (d, $^3J_{(H,H)}$ = 7.2 Hz, 3H, 7-H), 2.00 (d, $^3J_{(H,H)}$ = 6.9 Hz, 3H, Me), 2.38 (m, 1H, 8-H), 2.44 (s, 6H, NMe_2), 2.62 (m, 1H, 8'-H), 2.75 (m, 1H, 6-H), 2.85 (s, 6H, NMe_2'), 3.03 (m, 1H, 13-H), 3.46 (m, 1H, 9-H), 3.50, 3.85, 3.95, 3.97 (each m, each 1H, C_5H_4), 3.65 (m, 1H, 12-H), 3.88 (m, 1H, 11-H), 5.21 (q, $^3J_{(H,H)}$ = 6.9 Hz, 15-H), 5.87, 6.18, 6.21, 6.27 (each m, each 1H, $C_5H_4^{Zr}$), 7.12 (m, 1H, *p*-C_6H_5), 7.18 (m, 2H, *o*-C_6H_5), 7.23 (m, 2H, *m*-C_6H_5).

^{13}C{^{1}H} NMR ([D_2]-dichloromethane, 151 MHz, 298 K): δ = 16.7 (C7), 21.3 (Me), 27.1 (C6), 27.4 (C9), 44.0 (NMe_2'), 45.7 (NMe_2), 46.4 (C8), 57.6 (C13, C15), 61.0 (C12), 66.5, 67.0, 71.0, 73.6 (C_5H_4), 67.1 (C11), 79.8 (C10), 92.4 (C1), 108.4 ($C_5H_4^{Zr}$), 108.9 ($C_5H_4^{Zr}$), 112.0 (C14), 112.7 ($C_5H_4^{Zr}$), 112.9 ($C_5H_4^{Zr}$), 125.8 (*p*-C_6H_5), 127.0 (*o*-C_6H_5), 127.9 (*m*-C_6H_5), 132.5 (*i*-$C_5H_4^{Zr}$), 146.2 (*i*-C_6H_5).

^{1}H,^{1}H 1D-TOCSY ([D_2]-dichloromethane, 600 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.27 / 2.38, 2.62, 2.75, 3.46 (7-H / 8-H, 8'-H, 6-H, 9-H), 3.65 / 3.03, 3.88 (12-H / 13-H, 11-H).

^{1}H,^{1}H GCOSY ([D_2]-dichloromethane, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.27 / 2.75 (7-H / 6-H), 2.00 / 5.21 (Me / 15-H), 2.38 / 2.62, 2.75, 3.46 (8-H / 8'-H, 6-H, 9-H), 2.62 / 2.75, 3.46 (8'-H / 6-H, 9-H), 3.03 / 3.65, 3.88 (13-H / 12-H, 11-H), 3.50 / 3.85, 3.95, 3.97 (C_5H_4), 3.65 / 3.88 (12-H / 11-H), 3.85 / 3.94, 3.97 (C_5H_4), 3.94 / 3.97 (C_5H_4), 5.87 / 6.18, 6.21, 6.27 ($C_5H_4^{Zr}$), 6.18 / 6.21, 6.27 ($C_5H_4^{Zr}$), 6.21 / 6.27 ($C_5H_4^{Zr}$), 7.12 / 7.23 (*p*-C_6H_5 / *m*-C_6H_5), 7.18 / 7.23 (*o*-C_6H_5 / *m*-C_6H_5).

^{1}H,^{13}C GHSQC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.27 / 16.7 (7-H / C7), 2.00 / 21.3 (Me), 2.38, 2.62 / 46.4 (8-H, 8'-H / C8), 2.44 / 45.7 (NMe_2), 2.75

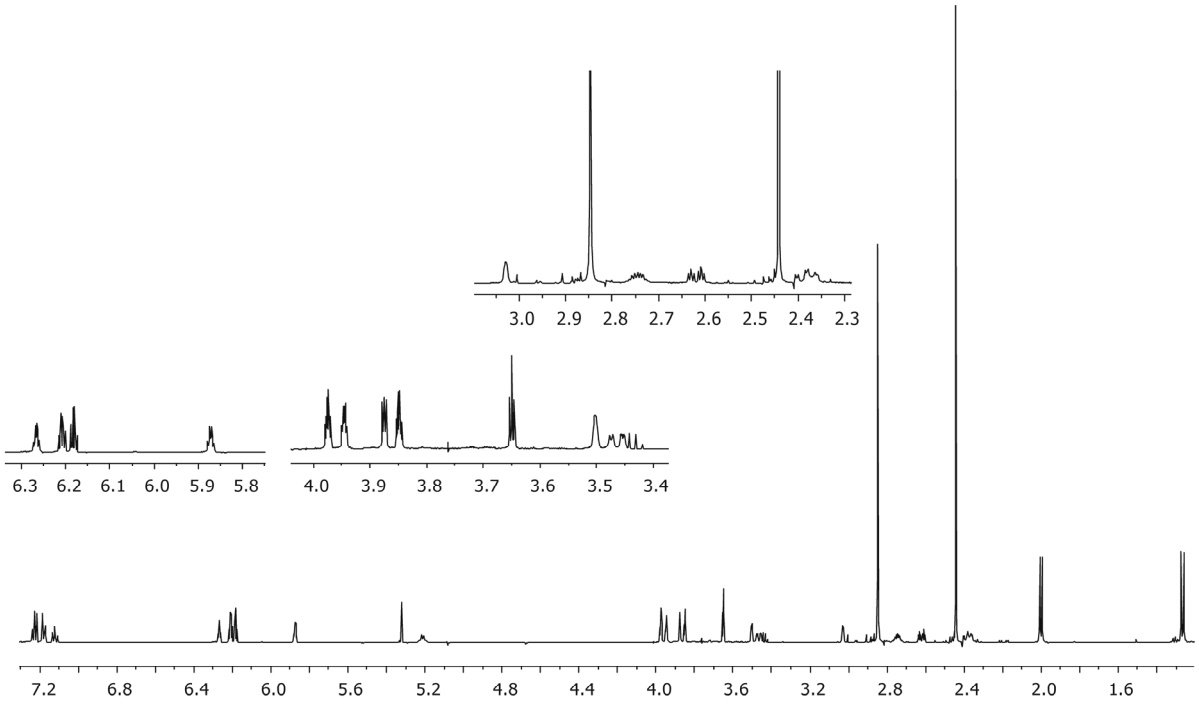
/ 27.1 (6-H / C6), 2.85 / 44.0 (NMe_2'), 3.03 / 57.6 (13-H / C13), 3.46 / 27.4 (9-H / C9), 3.50 / 73.6 (C_5H_4), 3.65 / 61.0 (12-H / C12), 3.85 / 66.5 (C_5H_4), 3.88 / 67.1 (11-H / C11), 3.95 / 67.0 (C_5H_4), 3.97 / 71.0 (C_5H_4), 5.21 / 57.6 (15-H / C15), 5.87 / 112.9 ($C_5H_4^{Zr}$), 6.18 / 108.9 ($C_5H_4^{Zr}$), 6.21 / 112.7 ($C_5H_4^{Zr}$), 6.27 / 108.4 ($C_5H_4^{Zr}$), 7.12 / 125.8 (*p*-C_6H_5), 7.18 / 127.0 (*o*-C_6H_5), 7.24 / 127.9 (*m*-C_6H_5).

^{1}H,^{13}C GHMBC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): 1.27 / 27.1, 27.4, 46.4, 92.4 (7-H / C6, C9, C8, C1), 2.00 / 57.6, 146.2 (Me / C15, *i*-C_6H_5), 2.38 / 16.7, 27.1, 27.4, (8-H / C7, C6, C9), 2.62 / 27.1, 27.4, 79.8, 92.4 (8'-H / C6, C9, C10, C1), 3.03 / 61.0, 67.1, 79.8, 112.0 (13-H / C12, C11, C10, C14), 3.46 / 67.1, 79.8, 112.0, 132.5 (9-H / C11, C10, C14, *i*-$C_5H_4^{Zr}$), 3.50 / 66.5, 67.0, 71.0, 92.4 (C_5H_4 / C_5H_4, C1), 3.65 / 57.6, 67.1, 79.8, 112.0 (12-H / C13, C11, C10, C14), 3.85 / 67.0, 71.0, 92.4 (C_5H_4 / C_5H_4, C1), 3.88 / 57.6, 61.0, 79.8, 112.0 (11-H / C13, C12, C10, C14), 3.95 / 66.5, 71.0, 73.6, 92.4 (C_5H_4 / C_5H_4, C1), 3.97 / 66.5, 67.0, 73.6, 92.4 (C_5H_4 / C_5H_4, C1), 5.21 / 21.3, 112.0, 127.0, 146.2 (15-H / Me, C14, *o*-C_6H_5, *i*-C_6H_5), 7.12 / 127.0 (*p*-C_6H_5 / *o*-C_6H_5), 7.18 / 57.6, 125.8, 127.0 (o-C_6H_5 / C15, *p*-C_6H_5, *o*-C_6H_5), 7.23 / 127.9, 146.2 (*m*-C_6H_5 / *m*-C_6H_5, *i*-C_6H_5).

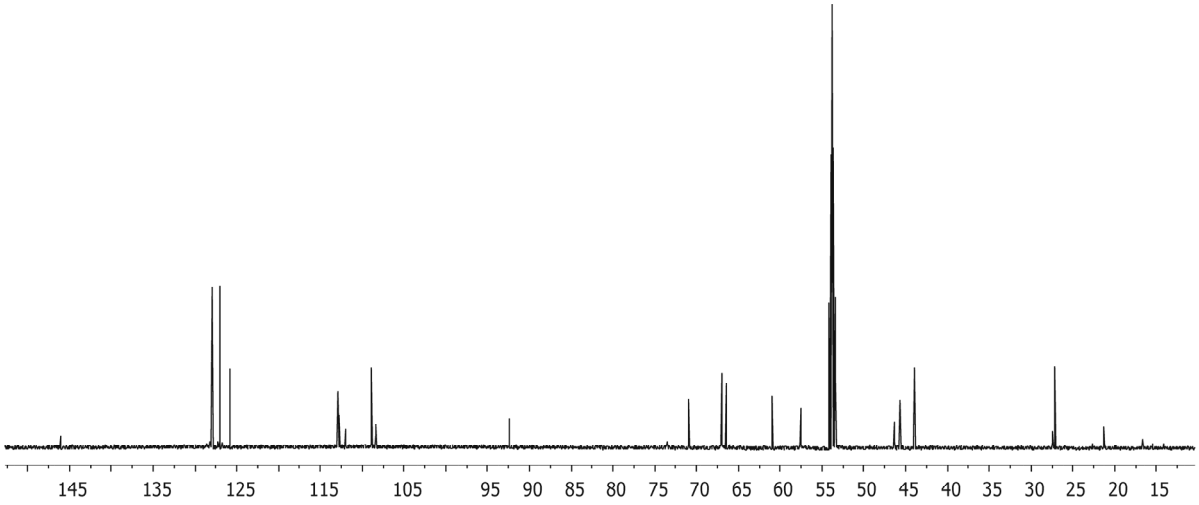
Elemental Analysis: $C_{31}H_{39}FeN_3Zr$ (600.73 g/mol) requires C 61.98, H 6.54, N 6.99 found: C 60.99, H 6.07, N 6.09.

Melting Point: >250°C.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3608 w, 3367 w, 3083 w, 3024 w, 2960 m, 2921 m, 2864 m, 1602 w, 1492 s, 1473 s, 1452 s, 1389 w, 1371 m, 1352 m, 1324 w, 1305 m 1277 w, 1257 w, 1207 w, 1172 w, 1143 m, 1101 w, 1040 s, 1027 m, 995 w, 937 w, 848 w, 789 s.

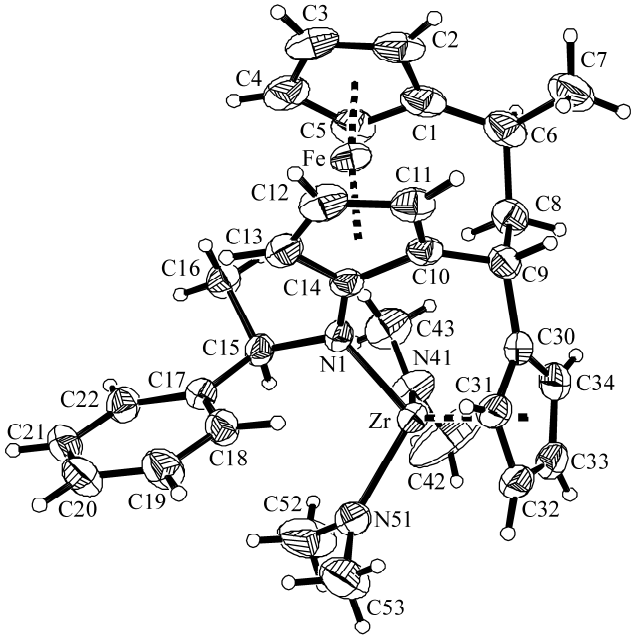


^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of **10b**

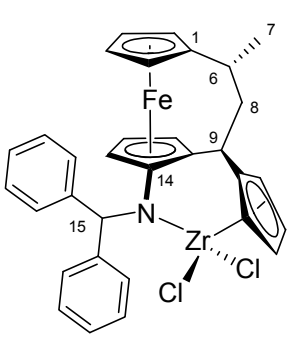


^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) of **10b**

X-ray crystal structure analysis: Crystal data for $C_{31}H_{39}FeN_3Zr$ (**10b**), M = 600.72, triclinic, space group P1bar (No. 2), a = 9.2847(2), b = 10.1003(2), c = 15.4314(4) Å, α = 93.503(1), β = 103.467(1), γ = 100.702(1)°, V = 1374.59(5) Å^3, D_c = 1.451 g cm^{-3}, μ = 0.931 mm^{-1}, Z = 2, λ = 0.71073 Å, T = 223(2) K, 12144 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 6479 independent (R_{int} = 0.041), and 5930 observed reflections [I ≥ 2σ(I)], 331 refined parameters, R = 0.044, wR^2 = 0.108.



Preparation of Compound **11a**



TMSCl (0.39 ml, 3.00 mmol, 10 equiv) was added dropwise to a solution of **10a** (200 mg, 0.30 mmol) in anhydrous toluene (10 ml) ar −20 °C. The reaction mixture was allowed to warm to room temperature by stirring overnight. The solvent was removed *in vacuo* and the obtained red oil was treated with pentane. After removal of the solvent *in vacuo* the product was obtained as a red powder (190 mg, 0.29 mmol, 97%).

An isomer mixture was obtained (ratio = 1:1).

Due to the complexity of the mixture only selected characteristic NMR data are listed. The phenyl area could not be assigned.

1. Isomer

^{1}H NMR ([D$_8$]-toluene, 500 MHz, 213 K): δ = 0.84 (d, $^{3}J_{(H,H)}$ = 7.5 Hz, 3H, 7-H), 1.83 (m, 1H, 8-H), 1.99 (m, 1H, 8'-H), 2.33 (m, 1H, 6-H), 2.89 (m, 1H, 9-H), 2.92 (m, 1H, C_5H_4), 3.13 (m, 1H, C_5H_4), 3.37 (m, 1H, 13-H), 3.53 (m, 1H, 11-H), 3.59 (m, 1H, 12-H), 3.63 (m, 2H, C_5H_4), 5.43 (m, 1H, $C_5H_4^{Zr}$), 5.78 (m, 1H, $C_5H_4^{Zr}$), 6.03 (m, 1H, $C_5H_4^{Zr}$), 6.20 (m, 1H, $C_5H_4^{Zr}$), 7.60 (s, 1H, 15-H), 6.84-7.24 (m, 8 H, C_6H_5), 7.81 (m, 2H, *o*-C_6H_5).

^{13}C{^{1}H} NMR ([D$_8$]-toluene, 126 MHz, 213 K): δ = 16.2 (C7), 26.1 (C6), 26.0 (C9), 46.8 (C8), 59.6 (C13), 61.1 (C15), 62.1 (C12), 67.3 (C_5H_4), 67.4 (C11), 67.9 (C_5H_4), 72.0 (C_5H_4), 72.4 (C_5H_4), 76.9 (C10), 91.5 (C1), 107.2 (C14), 113.9 ($C_5H_4^{Zr}$), 115.1 ($C_5H_4^{Zr}$), 115.4 ($C_5H_4^{Zr}$), 120.0 ($C_5H_4^{Zr}$), 132.5 (*i*-$C_5H_4^{Zr}$), 140.5 (*i*-C_6H_5).

^{1}H,^{1}H 1D-TOCSY ([D$_8$]-toluene, 500 MHz, 213 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 2.89 / 0.84, 1.83, 1.99, 2.33, (9-H / 7-H, 8-H, 8'-H, 6-H), 3.39 / 3.37, 3.53 (12-H / 13-H, 11-H), 6.20 / 5.43, 5.78, 6.03 ($C_5H_4^{Zr}$).

^{1}H,^{1}H GCOSY ([D$_8$]-toluene, 500 MHz / 500 MHz, 213 K): δ (^{1}H) / δ (^{1}H) = 0.84 / 2.33 (7-H / 6-H), 1.83 / 1.99, 2.33, 2.89 (8-H / 8'-H, 6-H, 9-H), 1.99 / 2.33, 2.89 (8'-H / 6-H, 9-H), 2.92 / 3.13, 3.63 (C_5H_4), 3.13 / 3.63 (C_5H_4), 3.37 / 3.53, 3.39 (13-H / 11-H, 12-H), 3.53 / 3.39 (11-H / 12-H), 5.43 / 5.78, 6.03, 6.20 ($C_5H_4^{Zr}$), 5.78 / 6.03, 6.20 ($C_5H_4^{Zr}$), 6.03 / 6.20 $C_5H_4^{Zr}$).

^{1}H,^{13}C GHSQC ([D$_8$]-toluene, 500 MHz / 126 MHz, 213 K): δ (^{1}H) / δ (^{13}C) = 0.84 / 16.2 (7-H / C7), 1.83, 1.99 / 46.8 (8-H, 8'-H / C8), 2.33 / 26.1 (6-H / C6), 2.89 / 26.0 (9-H / C9), 2.92 / 72.0 (C_5H_4), 3.13 / 72.4 (C_5H_4), 3.37 / 59.6 (13-H / C13), 3.53 / 67.4 (11-H / C11), 3.39 / 62.1 (12-H / C12), 3.63 / 67.3, 67.9 (C_5H_4), 5.43 / 115.4 ($C_5H_4^{Zr}$), 5.78 / 113.9 ($C_5H_4^{Zr}$), 6.03 / 115.1 ($C_5H_4^{Zr}$), 6.20 / 120.0 ($C_5H_4^{Zr}$), 7.60 / 61.6 (15-H / C15).

^{1}H,^{13}C GHMBC ([D$_8$]-toluene, 500 MHz / 126 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 0.84 / 26.1, 46.8, 91.5 (7-H / C6, C8, C1), 1.83 / 26.0 (8-H / C9), 1.99 / 26.0, 26.1 (8'-H / C9, C6), 2.89 / 46.8, 67.4, 76.9, 107.2, 132.5 (9-H / C8, C11, C10, C14, *i*-$C_5H_4^{Zr}$), 2.92 / 67.3, 67.9, 72.4, 91.5 (C_5H_4 / C_5H_4, C1), 3.13 / 67.3, 67.9, 72.0, 91.5 (C_5H_4 / C_5H_4, C1), 3.37 / 62.1, 67.4, 76.9, 107.2 (13-H / C12, C11, C10, C14), 3.53 / 59.6, 62.1, 76.9, 107.2 (11-H / C13, C12, C10, C14), 3.59 / 59.6, 67.4, 76.9, 107.2 (12-H / C13, C11, C10, C14), 3.63 / 67.3, 67.9, 72.0, 72.4, 91.5 (C_5H_4 / C_5H_4, C1), 5.43 / 113.9, 115.1, 120.0, 132.5 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 5.78 / 115.1, 115.4, 120.0, 132.5 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.03 / 113.9, 115.4, 120.0, 132.5 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.20 / 113.9, 115.1, 115.4, 132.5 ($C_5H_4^{Zr}$), 7.60 / 140.5 (15-H / *i*-C_6H_5).

2.Isomer

^{1}H NMR ([D$_8$]-toluene, 500 MHz, 213 K): δ = 0.85 (d, $^{3}J_{(H,H)}$ = 7.5 Hz, 3H, 7-H), 1.83 (m, 1H, 8-H), 1.99 (m, 1H, 8'-H), 2.40 (m, 1H, 6-H), 2.73 (m, 1H, 9-H), 3.29 (m, 1H, 13-H), 3.37 (m, 1H, 12-H), 3.45 (m, 1H, 11-H), 3.81 (m, 1H, C_5H_4), 3.84 (m, 1H, C_5H_4), 4.03 (m, 1H, C_5H_4), 4.29 (m, 1H, C_5H_4), 5.65 (m, 1H, $C_5H_4^{Zr}$), 5.84 (m, 1H, $C_5H_4^{Zr}$), 5.98 (s, 1H, 15-H), 6.02 (m, 1H, $C_5H_4^{Zr}$), 6.11(m, 1H, $C_5H_4^{Zr}$), 6.84-7.24 (m, 8 H, C_6H_5), 7.81 (m, 2H, *o*-C_6H_5).

^{13}C{^{1}H} NMR ([D$_8$]-toluene, 126 MHz, 213 K): δ = 16.2 (C7), 25.5 (C9), 26.2 (C6), 46.1 (C8), 59.1 (C13), 62.5 (C12), 67.1 (C_5H_4), 67.2 (C11), 68.3 (C_5H_4), 69.8 (C_5H_4), 72.4 (C_5H_4), 73.2 (C15), 80.7 (C10), 92.1 (C1), 114.5 (C14), 114.4 ($C_5H_4^{Zr}$), 114.8 ($C_5H_4^{Zr}$), 116.7 ($C_5H_4^{Zr}$), 117.2 ($C_5H_4^{Zr}$), 133.4 (*i*-$C_5H_4^{Zr}$), 142.6 (*i*-C_6H_5).

^{1}H,^{1}H 1D-TOCSY ([D8]-toluene, 500 MHz, 213 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 2.73 / 0.85, 1.83, 1.9, 2.40 (9-H / 7-H, 8-H, 8'-H, 6-H), 4.03 / 3.81, 3.84, 4.29 (C_5H_4).

^{1}H,^{1}H GCOSY ([D$_8$]-toluene, 500 MHz / 500 MHz, 213 K): δ (^{1}H) / δ (^{1}H) = 0.85 / 2.40 (7-H / 6-H), 1.83 / 1.99, 2.40, 2.73 (8-H / 8'-H, 6-H, 9-H), 1.99 / 2.40, 2.73 (8'-H / 6-H, 9-H), 3.29 / 3.37, 3.45 (13-H / 12-H, 11-H), 3.37 / 3.45 (12-H / 11-H), 3.81 / 3.84, 4.03, 4.29 (C_5H_4), 3.84

/ 4.03, 4.29 (C_5H_4), 4.03 / 4.29 (C_5H_4), 5.65 / 5.84, 6.02, 6.11 ($C_5H_4^{Zr}$), 5.84 / 6.02, 6.11 ($C_5H_4^{Zr}$), 6.02 / 6.11 ($C_5H_4^{Zr}$).

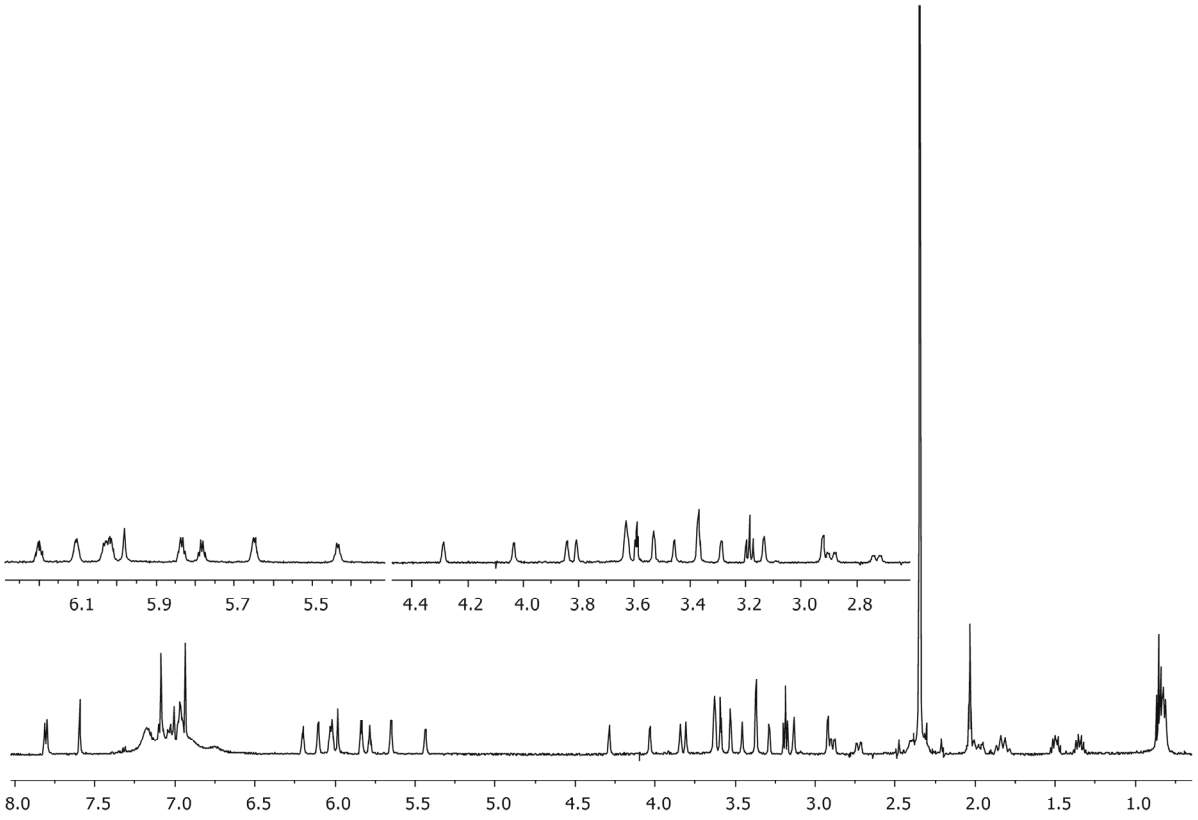
^{1}H,^{13}C GHSQC ([D_8]-toluene, 500 MHz / 126 MHz, 213 K): δ (^{1}H) / δ (^{13}C) = 0.85 / 16.2 (7-H / C7), 1.83, 1.99 / 46.1 (8-H, 8'-H / C8), 2.40 / 26.2 (6-H / C6), 2.73 / 25.5 (9-H / C9), 3.29 / 59.1 (13-H / C13), 3.37 / 62.5 (12-H / C12), 3.45 / 67.2 (11-H / C11), 3.81 / 68.3 (C_5H_4), 3.84 / 67.1 (C_5H_4), 4.03 / 72.4 (C_5H_4), 4.29 / 69.8 (C_5H_4), 5.65 / 116.7 ($C_5H_4^{Zr}$), 5.84 / 114.4 (C_5H_4), 5.98 / 73.2 (15-H / C15), 6.02 / 117.2 ($C_5H_4^{Zr}$), 6.11 / 114.8 (C_5H_4)^{Zr}.

^{1}H,^{13}C GHMBC ([D_8]-toluene, 500 MHz / 126 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 0.85 / 26.2, 46.1, 92.1 (7-H / C6, C8, C1), 1.83 / 25.5 (8-H / C9), 1.99 / 25.5, 26.2 (8'-H / C9, C6), 2.73 / 26.2, 46.1, 67.4, 80.7, 133.4 (9-H / C6, C8, C11, C10, *i*-$C_5H_4^{Zr}$), 3.29 / 62.5, 67.2, 80.7, 114.5 (13-H / C12, C11, C10, C14), 3.37 / 59.1, 67.2, 80.7, 114.5 (12-H / C13, C11, C10, C14), 3.45 / 59.1, 62.5, 80.7, 114.5 (11-H / C13, C12, C10, C14), 3.81 / 67.1, 72.4, 69.8, 92.1 (C_5H_4 / C_5H_4, C1), 3.84 / 68.3, 72.4, 69.8, 92.1 (C_5H_4 / C_5H_4, C1), 4.03 / 68.3, 67.1, 69.8, 92.1 (C_5H_4 / C_5H_4, C1), 4.29 / 68.3, 67.1, 72.4, 92.1 (C_5H_4 / C_5H_4, C1), 5.65 / 114.4, 114.8, 117.2, 133.4 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 5.84 / 114.8, 116.7, 117.2, 133.4 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.02 / 114.4, 114.8, 116.7, 133.4 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.11 / 114.4, 116.7, 117.2, 133.4 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 5.98 / 114.5, 142.6 (15-H / C14, *i*-C_6H_5).

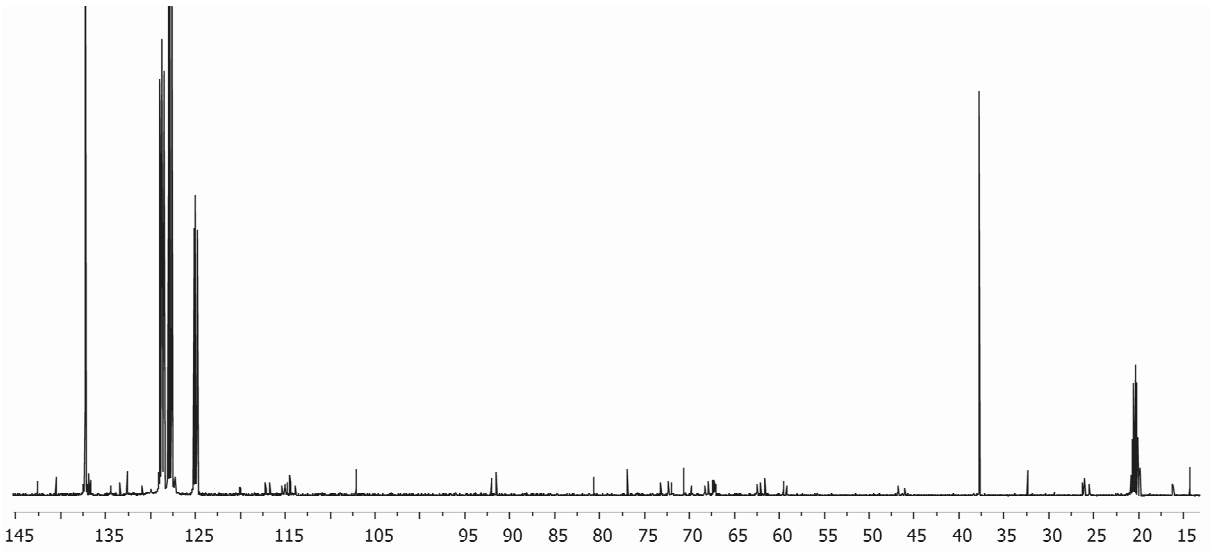
Elemental Analysis: $C_{32}H_{29}Cl_2FeNZr$ (645.55 g/mol) requires C 59.54, H 4.53, N 2.17 found: C 59.68, H 4.85, N 2.20.

Melting Point: 159°C, 192°C decomposition

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3377 b, 3087 w, 3025 w, 2960 w, 2921 w, 2848 w, 2627 w, 2359 w, 2340 w, 1950 w, 1889 w, 1814 w, 1732 w, 1684 w, 1598 m, 1540 w, 1492 s, 149 s, 1390 m, 1374 m, 1355 w, 1323 m, 1250m, 1223 m, 1175 m, 1158 m, 1126 s, 1106 s, 1042 s, 1029 s, 1008 s, 971 s, 936 s,916 s, 995 m, 866 m, 823 s.

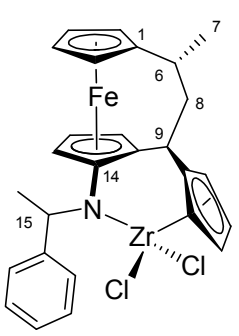


^{1}H NMR (126 MHz, D_8-toluene, 213 K) of **11a**



^{13}C{^{1}H} NMR (126 MHz, D_8-toluene, 213 K) of **11a**

Preparation of Compound **11b**



Dimethyldichlorosilane (0.3 ml, 2.4 mmol, 3 equiv) was added dropwise to a solution of **10b** (160 mg, 0.27 mmol) in anhydrous toluene (10 ml) at −10 °C and The reaction mixture was allowed to warm to room temperature by stirring overnight. The solvent was removed *in vacuo* and the obtained red oil was washed with pentane. After evaporation of the solvent and drying *in vacuo* the product was obtained as a red powder (150 mg, 0.26 mmol, 96%). Suitable crystals for X-ray diffraction were obtained by evaporation of a saturated solution of **11b** in toluene.

^{1}H NMR ([D$_6$]-benzene, 500 MHz, 298 K): δ = 0.94 (d, $^{3}J_{(H,H)}$ = 6.8 Hz, 3H, 7-H), 2.00 (d, $^{3}J_{(H,H)}$ = 6.4 Hz, 3H, Me), 2.00 (m, 1H, 8-H), 2.21 (m, 1H, 8'-H), 2.47 (m, 1H, 6-H), 2.88 (m, 1H, 13-H), 3.15 (m, 1H, 9-H), 3.45 (m, 1H, 12-H), 3.61 (m, 1H, 11-H), 3.80 (m, 2H, C_5H_4), 3.83 (m, 1H C_5H_4), 3.91 (m, 1H, C_5H_4), 5.64, 6.02, 6.23, 6.26 (4m, each 1H, $C_5H_4^{Zr}$), 6.36 (q, $^{3}J_{(H,H)}$ = 6.4 Hz, 15-H), 7.06 (m, 1H, *p*-C_6H_5), 7.16 (m, 4H, *o*-C_6H_5, *m*-C_6H_5).

^{13}C{^{1}H} NMR ([D$_6$]-benzene, 126 MHz, 298 K): δ = 16.3 (C7), 17.2 (Me), 26.5 (C6), 26.7 (C9), 47.6 (C8), 52.7 (C15), 56.5 (C13), 62.5 (C12), 67.7 (C11, C_5H_4), 68.4 (C_5H_4), 71.4 (C_5H_4), 73.5 (C_5H_4). 78.6 (C10), 92.2 (C1), 106.2 (C14), 113.6 ($C_5H_4^{Zr}$), 114.2 ($C_5H_4^{Zr}$), 116.2 ($C_5H_4^{Zr}$), 117.3 ($C_5H_4^{Zr}$), 127.52 (*p*-C_6H_5), 127.53 (*o*-C_6H_5), 128.4 (*m*-C_6H_5), 132.5 (*i*-$C_5H_4^{Zr}$), 139.6 (*i*-C_6H_5).

1H,1H 1D-TOCSY ([D$_6$]-Benzene, 500 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 0.94 / 2.00, 2.21, 2.47, 3.15 (7-H / 8-H, 8'-H, 6-H, 9-H), 3.45 / 2.88, 3.61 (12-H / 13-H, 11-H), 6.36 / 2.00 (15-H / Me).

^{1}H,^{1}H GCOSY ([D$_6$]-benzene, 500 MHz / 500 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 0.94 / 2.47 (7-H / 6-H), 2.00 / 2.21, 2.47, 3.15, 6.36 (Me, 8-H / 8'-H, 6-H, 9-H, 15-H), 2.21 / 2.47, 3.15 (8'-H / 6-H, 9-H), 2.88 / 3.45, 3.61 (13-H / 12-H, 11-H), 3.45 / 3.61 (12-H / 11-H), 3.80 / 3.83, 3.91 (C_5H_4), 3.83 / 3.91 (C_5H_4), 5.64 / 6.02, 6.23, 6.26 ($C_5H_4^{Zr}$), 6.02 / 6.23, 6.26 ($C_5H_4^{Zr}$), 6.23 / 6.26 ($C_5H_4^{Zr}$), 7.06 / 7.16 (*p*-C_6H_5 / *o*-C_6H_5, *m*-C_6H_5).

^{1}H,^{13}C GHSQC ([D$_6$]-benzene, 500 MHz / 126 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 0.94 / 16.3 (7-H / C7), 2.00 / 17.2 (Me), 2.00, 2.21 / 47.6 (8-H, 8'-H / C8), 2.47 / 26.5 (6-H / C6), 2.88 / 56.5 (13-H / C13), 3.15 / 26.7 (9-H / C9), 3.45 / 62.5 (12-H / C12), 3.61 / 67.7 (11-H / C11),

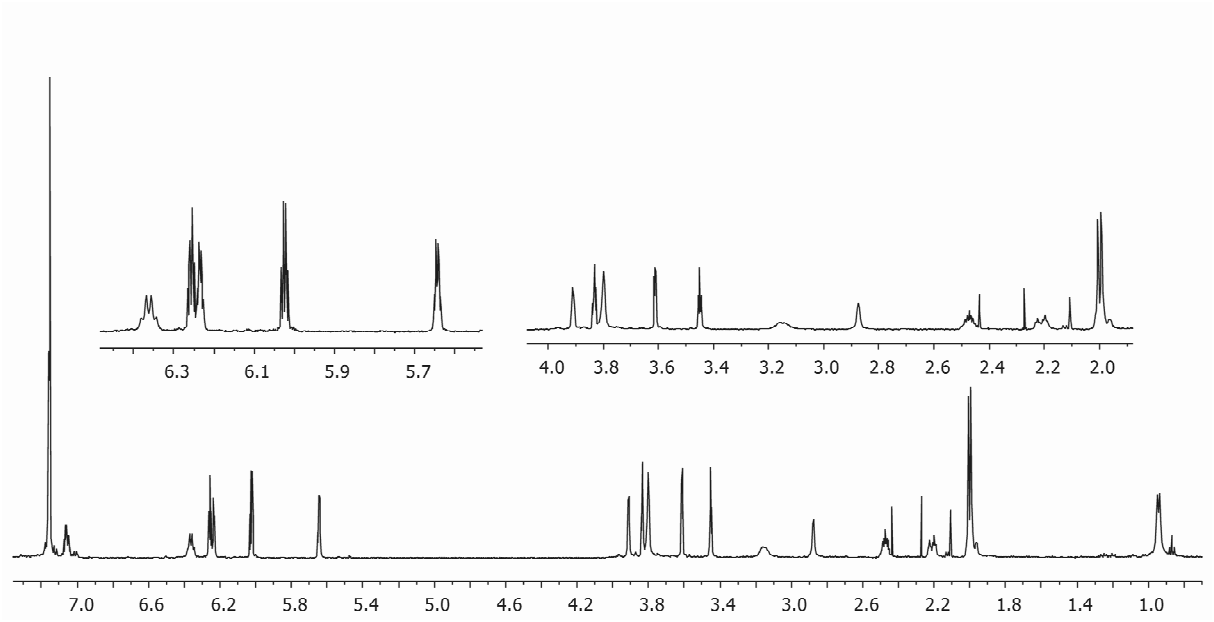
3.80 / 73.5, 67.7 (C_5H_4), 3.83 / 68.4 (C_5H_4), 3.91 / 71.4 (C_5H_4), 5.64 / 116.2 ($C_5H_4^{Zr}$), 6.02 / 113.6 ($C_5H_4^{Zr}$), 6.23 / 114.2 ($C_5H_4^{Zr}$), 6.26 / 117.3 ($C_5H_4^{Zr}$), 6.36 / 52.7 (15-H / C15), 7.06 / 127.52 (*p*-C_6H_5), 7.16 / 127.53, 128.4 (*o*-C_6H_5, *m*-C_6H_5).

^{1}H,^{13}C GHMBC ([D_6]-benzene, 500 MHz / 126 MHz, 298 K): δ (^{1}H) / δ (^{13}C) =0.94 / 26.5, 47.6, 92.2 (7-H / C6, C8, C1), 2.00 / 52.7, 139.6 (Me / C15, *i*-C_6H_5), 2.21 / 26.5, 78.6, 92.2, 132.5 (8 δ (^{1}H) / δ (^{13}C) =-H / C6, C10, C1, *i*-$C_5H_4^{Zr}$), 3.45 / 56.5, 67.7, 78.6, 106.2 (12-H / C13, C11, C10, C14), 3.61 / 56.6, 62.5, 78.6, 106.2 (11-H / C13, C12, C10, C14), 3.80 / 67.7, 68.4, 71.4, 92.2 (C_5H_4 / C_5H_4, C1), 3.83 / 71.4, 92.2 (C_5H_4 / C_5H_4, C1), 3.91 / 67.7, 68.4, 92.2 (C_5H_4 / C_5H_4, C1), 5.64 / 113.6, 114.2, 117.3, 132.5 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.02 / 114.2, 116.2, 117.3, 132.5 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.23 / 116.2, 117.3, 132.5 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.26 / 113.6, 114.2, 116.2, 132.5 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.36 / 17.2, 106.2, 127.53, 139.6 (15-H / Me, C14, o-C_6H_5, *i*-C_6H_5), 7.06 / 127.53, 128.4 (*p*-C_6H_5 / *o*-C_6H_5, *m*-C_6H_5), 7.16 / 52.7, 127.52, 127.53, 128.4, 139.6 (*o*-C_6H_5, *m*-C_6H_5 / C15, *p*-C_6H_5, *o*-C_6H_5, *m*-C_6H_5, *i*-C_6H_5).

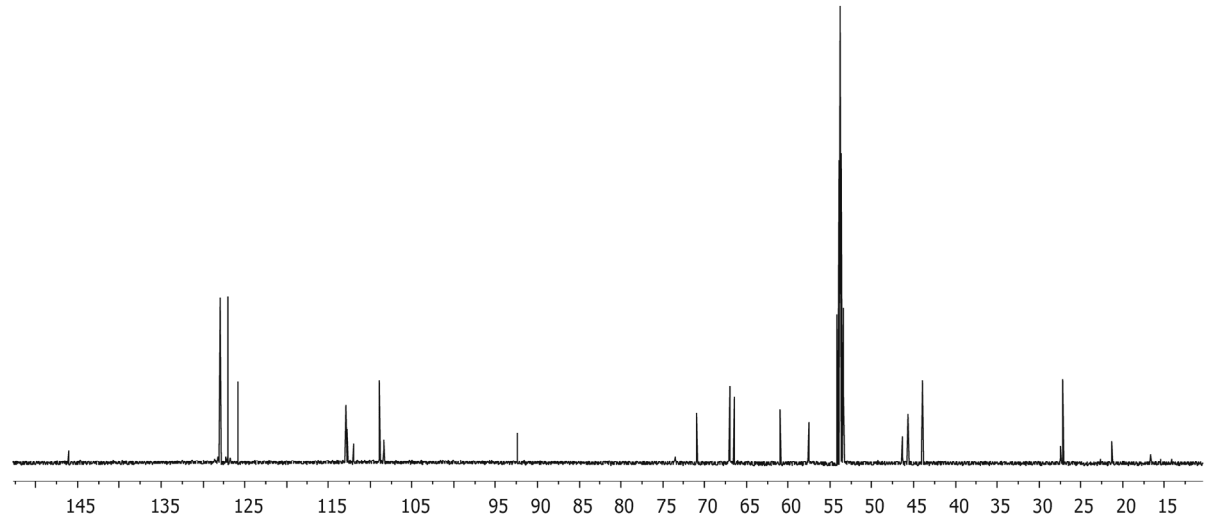
Elemental Analysis: $C_{27}H_{27}Cl_2FeZr$ (583.48 g/mol) requires C 55.58, H 4.66, N 2.40 found: C 55.25, H 5.12, N 2.96.

Melting Point: 179°C, decomposition.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3374 w, 3085 w, 3023 w, 2962 w, 2918 w, 2850 w, 1492 s, 1456 s, 1443 s, 1404 w, 1372 m, 1306 m, 1258 s, 1180 w, 1132 m, 1099 w, 1086 w, 1060 m, 1042 m, 995 w, 935 w, 917 m, 897 w, 875 w, 819 s, 764 s.

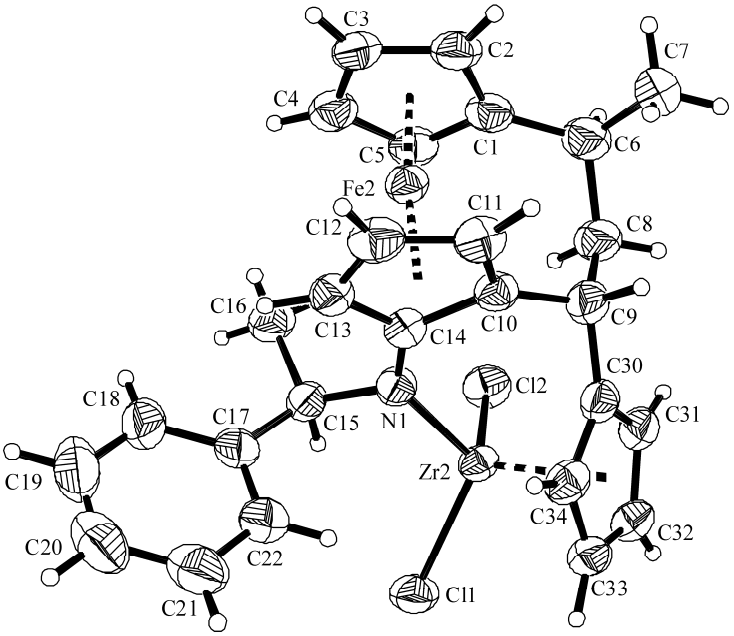


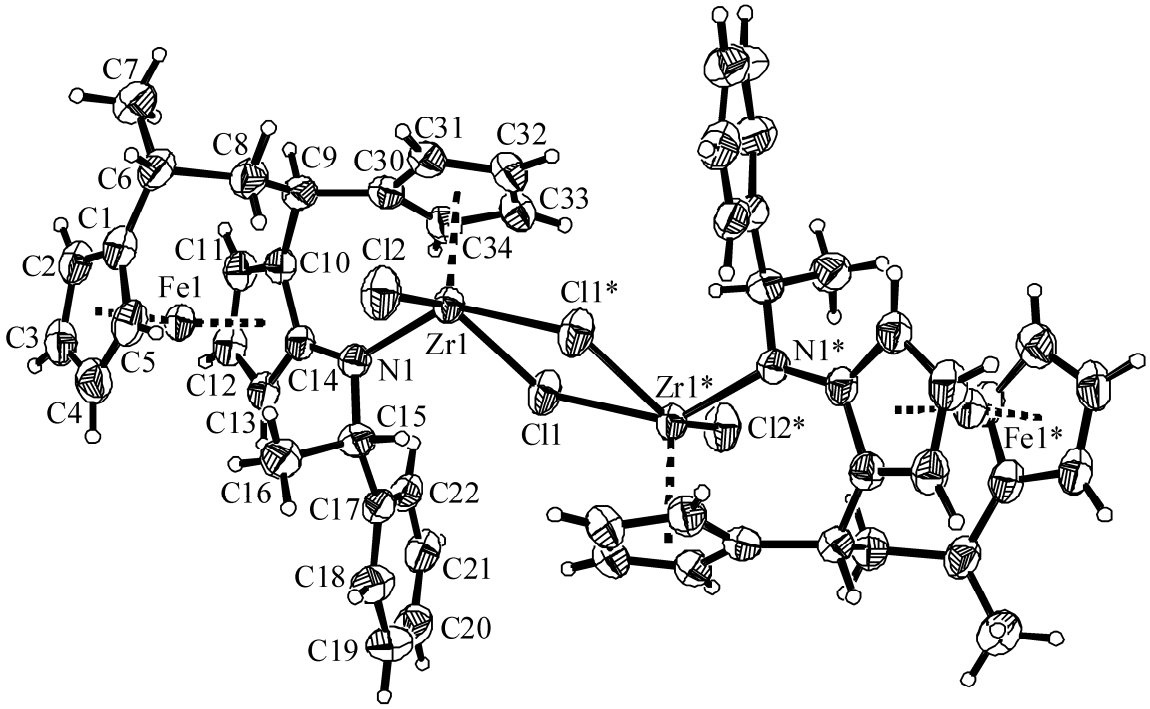
^{1}H NMR (500 MHz, D_6-Benzene, 298 K) of **11b**



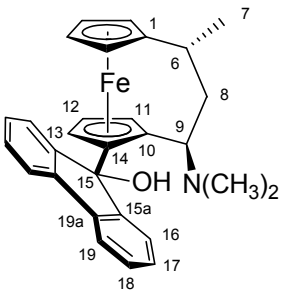
^{13}C{^{1}H} NMR (126 MHz, D_6-benzene, 213 K) of **11b**

X-ray crystal structure analysis: Crystal data for $C_{27}H_{27}Cl_2FeNZr$ (**11b**), M = 583.47, monoclinic, space group $P2_1/c$ (No. 14), a = 15.5580(3), b = 13.6033(2), c = 23.1772(4) Å, β = 106.068(1)°, V = 4713.60(14) Å^3, D_c = 1.644 g cm^{-3}, μ = 1.301 mm^{-1}, Z = 8, λ = 0.71073 Å, T = 223(2) K, 28831 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 11012 independent (R_{int} = 0.045), and 9273 observed reflections [I ≥ 2σ(I)], 581 refined parameters, R = 0.051, wR^2 = 0.125.





Preparation of Compound **13**



The [3]ferrocenophane **12** (10.0 g, 35.3 mmol) was dissolved in anhydrous diethyl ether (300 ml) and treated with *tert*-butyllithium (35.3 ml, 1.5 M in *n*-pentane, 53.0 mmol, 1.5 equiv) at 0°C. The reaction mixture was stirred for 40 min at room temperature and then fluorenone (9.55 g, 53.0 mmol, 1.5 equiv) was carefully added as a solid in several portions at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. Water was added slowly to quench excess of base. The aqueous layer was extracted with dichloromethane (3×100 ml). The combined organic phases were washed with water (3×100 ml) and dried with magnesium sulfate. Filtration and removal of the solvent *in vacuo* gave the crude product, which was purified by flash chromatography (dichloromethane:methanol, 20:1) to yield **13** as an yellow powder. (13.2 g, 28.5 mmol, 81%). Yellow crystals, suitable for X-ray diffraction, were obtained from a saturated dichloromethane/pentane solution at −8°C.

^{1}H NMR ([D_2]-dichloromethane, 600 MHz, 298 K): δ = 1.29 (d, $^3J_{(H,H)}$ = 7.4 Hz, 3H, 7-H), 2.12 (s, 6H, NMe_2), 2.50 (m, 1H, 8-H), 2.83 (m, 1H, 9-H), 2.92 (m, 1H, 6-H), 3.04 (m, 1H, 13-H), 3.20 (m, 1H, 8'-H), 3.80 (m, 1H, 12-H), 4.03 (m, 1H, 11-H), 3.82, 3.84, 4.16, 4.83 (each m, each 1H, C_5H_4), 7.09 (m, 1H, 17-H), 7.21 (m, 1H, 18-H), 7.27 (m, 1H, 16-H), 7.38 (m, 2H, 17'-H, 18'-H), 7.55 (m, 1H, 19-H), 7.63 (m, 1H, 19'-H), 8.03 (m, 1H, 16'-H), 8.28 (b, OH).

^{13}C{^{1}H} NMR ([D_2] dichloromethane, 151 MHz, 298 K): δ = 16.5 (C7), 28.0 (C6), 31.0 (NMe_2), 46.6 (C8), 61.1 (C9), 66.9 (C12), 67.7, 68.8, 70.5, 72.4 (C_5H_4), 69.7 (C13), 71.6 (C11), 82.6 (C10), 83.2 (C15), 93.2 (C1), 95.4 (C14), 119.7 (C19'), 120.1 (C19), 122.6 (C16), 126.3 (C16'), 127.3 (C17'), 127.8 (C17), 128.0 (C18), 128.9 (C18'), 137.8 (C19a), 140.7 (C19a'), 151.6 (C15a'), 156.4 (C15a).

^{1}H,^{1}H GCOSY ([D2]-dichloromethane, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.29 / 2.92 (7-H / 6H), 2.50 / 2.83, 2.92, 3.20 (8-H / 9-H, 6-H, 8'-H), 2.83 / 3.20 (9-H / 8'-H), 2.90 / 3.20 (6-H / 8'-H), 3.04 / 3.80, 4.03 (13-H / 12-H, 11-H), 3.80 / 4.03 (12-H / 11-H), 3.82 / 3.84, 4.16, 4.83 (C_5H_4 / C_5H_4), 3.84 / 4.16, 4.83 (C_5H_4 / C_5H_4), 4.16 / 4.83 (C_5H_4 / C_5H_4), 7.09 / 7.21, 7.27 (17-H / 18-H, 16-H), 7.21 / 7.55 (18-H / 19-H), 7.38 / 7.63, 8.03 (17'-H, 18'-H / 19'-H, 16'-H).

^{1}H,^{13}C GHSQC ([D2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) =.1.29 / 16.5 (7-H / C7), 2.12 / 31.0 (NMe_2), 2.50, 3.20 / 46.6 (8-H, 8'-H / C8), 2.83 / 61.1 (9-H / C9), 2.92 / 28.0 (6-H / C6), 3.04 / 69.7 (13-H / C13), 3.80 / 66.9 (12-H / C12), 4.03 / 71.6 (11-H / C11), 3.82 / 70.5 (C_5H_4), 3.84 / 67.7 (C_5H_4), 4.16 / 68.8 (C_5H_4), 4.83 / 72.4 (C_5H_4), 7.09 / 127.8 (17-H / C17), 7.21 / 128.0 (18-H / C18), 7.27 / 122.6 (16-H / C16), 7.38 / 127.3, 128.9 (17'-H, 18'-H / C17', C18'), 7.55 / 120.1 (19-H / C19), 7.63 / 119.7 (19'-H / C19'), 8.03 / 126.3 (16'-H / C16').

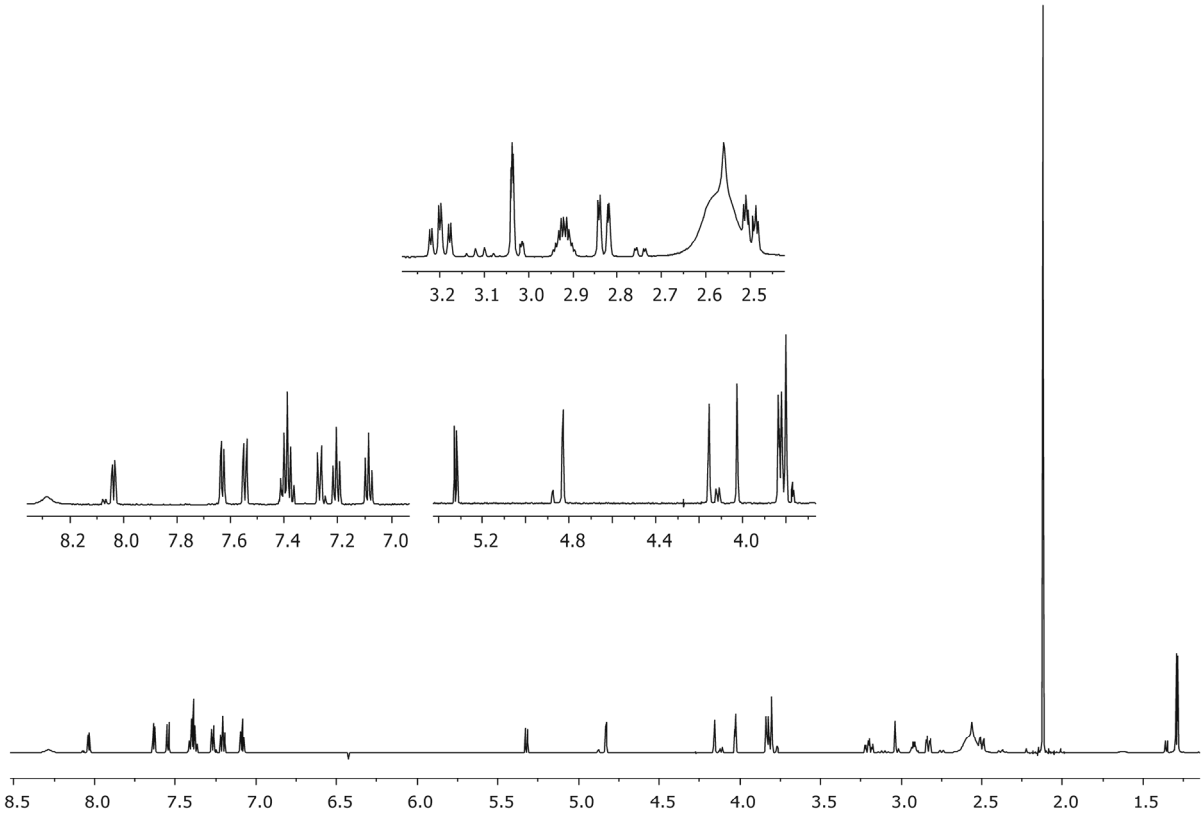
^{1}H,^{13}C GHMBC ([D2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.29 / 28.0 (7-H / C6), 2.50 / 28.0, 61.1, 82.6, 93.2 (8-H / C6, C9, C10, C1), 2.83 / 46.6, 71.6, 95.4 (9-H / C8, C11, C14), 3.04 / 66.9, 71.6, 82.6, 95.4 (13-H / C12, C11, C10, C14), 3.20 / 16.5, 28.0, 61.1, 82.6 (8'-H / C7, C6, C9, C10), 3.80 / 69.7, 71.6, 82.6, 95.4 (12-H / C13, C11, C10, C14), 4.03 / 66.9, 69.7, 82.6, 95.4 (11-H / C12, C13, C10, C14), 3.82 / 67.7, 68.8, 72.4, 93.2 (C_5H_4 / C_5H_4, C1), 3.84 / 68.8, 70.5, 72.4, 93.2 (C_5H_4 / C_5H_4, C1), 4.16 / 67.7, 70.5, 72.4 93.2 (C_5H_4 / C_5H_4, C1), 4.83 / 67.7, 68.8, 70.5, 93.2 (C_5H_4 / C_5H_4, C1), 7.09 / 120.1, 156.4 (17-H / C19, C15a), 7.21 / 122.6, 137.8 (18-H / C16, C19a), 7.27 / 83.2, 128.0, 137.8 (16-H / C15, C18, C19a), 7.38 / 119.7, 126.3, 140.7, 151.6 (17'-H, 18'-H / C19', C16', C19'a, C15a'), 7.55 / 127.8, 140.7, 156.4 (19-H / C17, C19a, C15a), 7.63 / 127.3,151.6 (19'-H / C17', C15a'), 8.03 / 83.2, 128.9, 140.7 (16'-H / C15, C18', C19'a), 8.28 (OH).

Elemental Analysis $C_{29}H_{29}FeNO$ (463.39 g/mol) requires C 75.17, H 6.31, N 3.02 found C 74.71, H 6.48, N 2.96.

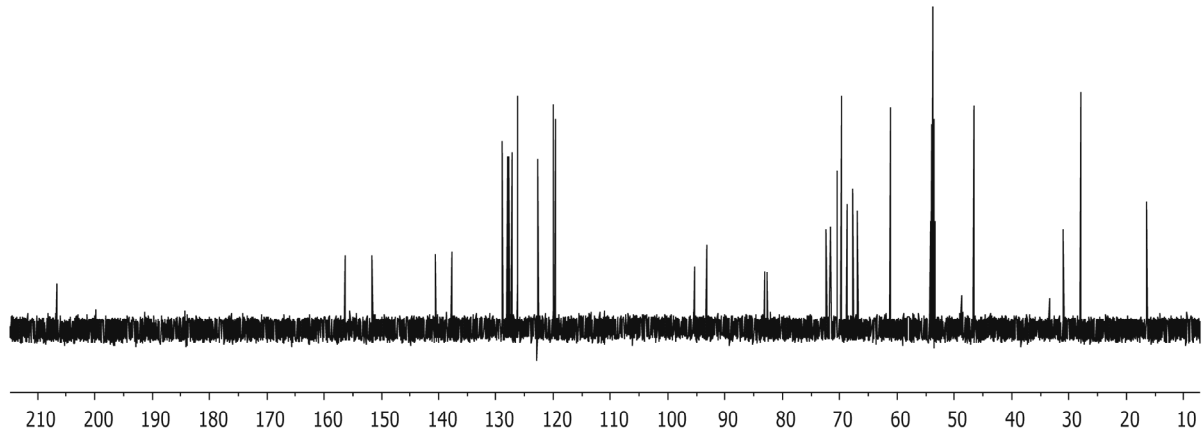
Melting Point (DSC): 198 °C

ESI-MS (ES^+, Methanol, M($C_{29}H_{29}NOFe$) = 463.2): m/z = 464.2 $[M+H]^+$.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3915 (m), 2633 (m), 2070 (m),1949 (m), 1647 (m), 1480 (s), 1155 (m), 1104 (m), 964 (m), 855 (m), 538 (s).

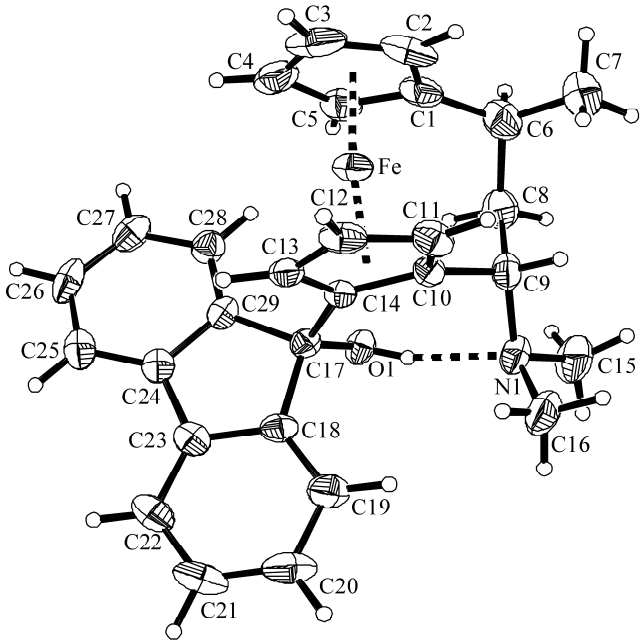


^{1}H NMR (600 MHz, CD_2Cl_2, 213 K) of **13**

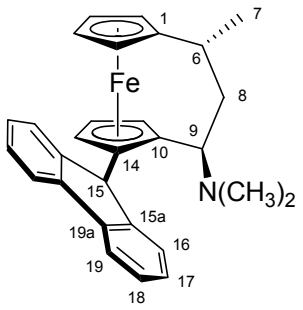


$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 213 K) of **13**

X-ray crystal structure analysis: Crystal data for $C_{29}H_{29}FeNO$ (**13**), M = 463.38, monoclinic, space group $P2_1/c$ (No. 14), a = 10.501(1), b = 13.098(1), c = 18.067(1) Å, β = 113.07(1)°, V = 2286.2(5) Å^3, D_c = 1.346 g cm^{-3}, μ = 0.681 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 198(2) K, 14863 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 5419 independent (R_{int} = 0.087), and 3495 observed reflections [I ≥ 2σ(I)], 293 refined parameters, R = 0.062, wR^2 = 0.163.



Preparation of Compound **14**



Compound **13** (10.0 g, 21.6 mmol) was dissolved in anhydrous diethyl ether (100 ml), and tetrafluoroboric acid in diethyl ether (7.40 ml, 54% in diethyl ether) was added dropwise under stirring. After 30 min the solution was filtered and the residue washed three times with of diethyl ether (60 ml) and dried under vacuum to give **FcFlu$^+$BF4$^-$**. Potassium (2.10 g, 0.05 mol) was added to graphite (5.18 g, 0.43 mol) and the mixture was heated to 150°C with periodical shaking. The color turns to bronze and after 1 h the reaction mixture was cooled to room temperature. The obtained KC_8 was suspended in anhydrous THF (100 ml) and added to the crude **FcFlu$^+$BF4$^-$**, dissolved in THF (100 ml). The mixture was heated to 55 °C for 5 days and then cooled to 0 °C and quenched with water/ethanol (20:80). The suspension was filtered and all volatiles were removed from filtrate under vacuum. The residue was extracted with diethyl ether (3×150 ml), and the combined organic layers were dried over $MgSO_4$, filtered and purified by flash chromatography (cyclohexane : triethylamine 95:5) to yield **14** as an orange powder (4.30 g, 9.61 mmol, 45%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution.

^{1}H NMR ([D_2]-dichloromethane, 500 MHz, 298 K): δ = 1.10 (d, $^3J_{(H,H)}$ = 7.4 Hz, 3H, 7-H), 2.16 (m, 1H, 8-H), 2.28 (s, 6H, NMe_2), 2.55 (m, 2H, 8'-H, 9-H), 2.63 (m, 1H, 6-H), 3.28 (m, 1H, 13-H), 3.67 (m, 1H, 12-H), 3.79 (m, 1H, 11-H), 3.90 (m, 1H, C_5H_4), 4.03 (m, 1H, C_5H_4), 4.22 (m, 2H, C_5H_4), 5.12 (s, 1H, 15-H), 7.22 (m, 1H, 18'-H), 7.27 (m, 1H, 17'-H), 7.31 (m, 1H, 17-H), 7.34 (m, 1H, 18-H), 7.61 (m, 1H, 19'-H), 7.69 (m, 1H, 19-H), 8.09 (m, 1H, 16-H), 8.75 (m, 1H, 16'-H).

^{13}C{^{1}H} NMR ([D_2] dichloromethane, 151 MHz, 298 K): δ = 17.1 (C7), 28.2 (C6), 44.4 (C8), 46.4 (NMe_2), 48.0 (C15), 62.9 (C9), 67.0 (C12), 67.3 (C_5H_4), 68.4 (C_5H_4), 70.7 (C_5H_4), 71.2 (C13), 72.7 (C_5H_4), 73.9 (C11), 81.6 (C10), 89.9 (C14), 94.1 (C1), 119.5 (C19'), 120.0 (C19), 126.4 (C17), 127.0 (C16), 127.2 (2×C, C17', C18'), 127.6 (C16'), 127.7 (C18), 140.3 (C19a'), 142.5 (C19a), 147.2 (C15a), 149.8 (C15a').

^{1}H,^{1}H 1D-TOCSY ([D_2]-dichloromethane, 500 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.10 / 2.16, 2.55, 2.63 (7-H / 8-H, 8'-H, 9-H, 6-H), 3.28 / 3.67, 3.79 (13-H / 12-H, 11-H), 3.90 / 4.03, 4.22 (C_5H_4), 7.61 / 7.22, 7.27, 8.75 (19'-H / 18'-H, 17'-H, 16'-H), 7.69 / 7.31, 7.34, 8.09 (19-H / 17-H, 18-H, 16-H).

^{1}H,^{1}H GCOSY ([D2]-dichloromethane, 500 MHz / 500 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.10 / 2.63 (7-H / 6-H), 2.16 / 2.55, 2.63 (8-H / 8'-H, 9-H, 6-H), 2.55 / 2.63 (8''-H / 6-H), 3.28 / 3.67, 3.79 (13-H / 12-H, 11-H), 3.67 / 3.79 (12-H / 11-H), 3.90 / 4.03, 4.22 (C_5H_4) / C_5H_4), 4.03 / 4.22 (C_5H_4) / C_5H_4), 7.22 / 7.27, 7.61 (18'-H / 17'-H, 19'-H), 7.27 / 8.75 (17'-H / 16'-H), 7.31 / 7.34, 8.09 (17-H / 18-H, 16-H), 7.34 / 7.69 (18-H / 19-H).

^{1}H,^{13}C GHSQC ([D2]-dichloromethane, 500 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.10 / 17.1 (7-H / C7), 2.16, 2.55 / 44.4 (8-H, 8'-H / C8), 2.28 / 46.4 (NMe_2), 2.55 / 62.9 (9-H / C9), 2.63 / 28.2 (6-H / C6), 3.28 / 71.2 (13-H / C13), 3.67 / 67.0 (12-H / C12), 3.79 / 73.9 (11-H / C11), 3.90 / 67.3 (C_5H_4), 4.03 / 68.4 (C_5H_4), 4.22 / 70.7, 72.7 (C_5H_4), 5.12 / 48.0 (15-H / C15), 7.22 / 127.2 (18'-H / C18'), 7.27 / 127.2 (17'-H / C17'), 7.31 / 126.4 (17-H / C17), 7.34 / 127.7 (18-H / C18), 7.61 / 119.5 (19'-H / C19'), 7.69 / 120.0 (19-H / C19), 8.09 / 127.0 (16-H / C16), 8.75 / 127.6 (16'-H / C16').

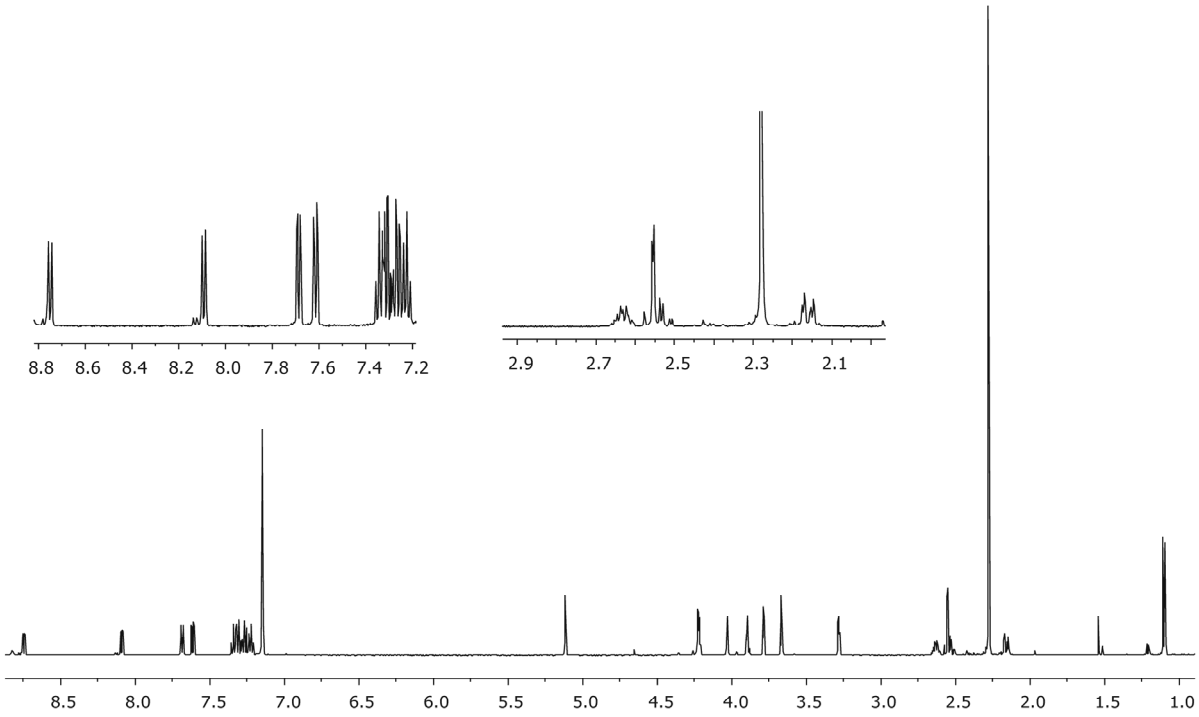
^{1}H,^{13}C GHMBC ([D2]-dichloromethane, 500 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.10 / 28.2, 44.4, 94.1 (7-H / C6, C8, C1), 2.16 / 17.1, 28.2, 46.4, 62.9, 81.6, 89.9, 94.1 (8-H / C7, C6, NMe_2, C9, C10, C14, C1), 2.28 / 62.9, (NMe_2 / C9), 2.55 / 17.1, 28.2, 44.4, 46.4, 62.9, 73.9, 81.6, 89.9 (8'-H, 9-H / C7, C6, C8, NMe_2, C9, C11, C10, C14), 2.63 / 17.1, 44.4, 62.9, 68.4, 72.7, 94.1 (6-H / C7, C8, C9, C_5H_4, C_5H_4, C1), 3.28 / 67.0, 73.9, 81.6, 89.9 (H-13 / C12, C11, C10, C14), 3.67 / 71.2, 73.9, 81.6, 89.9 (12-H / C13, C11, C10, C14), 3.79 / 67.0, 71.2, 81.6, 89.9 (11-H / C12, C13, C10, C14), 3.90 / 68.4, 70.7, 72.7, 94.1 (C_5H_4 / C_5H_4, C1), 4.03 / 67.3, 70.7, 72.7, 94.1 (C_5H_4 / C_5H_4, C1), 4.22 / 67.3, 68.4, 70.7, 72.7, 94.1 (C_5H_4 / C_5H_4, C1), 5.12 / 71.2, 81.6, 89.9, 127.0, 127.6, 140.3, 142.5, 147.2, 149.8 (15-H / C13, C10, C14, C16, C16', C19a', C19a, C15a, C15a'), 7.22 / 127.6, 140.3 (18'-H / C16', C19a'), 7.27 / 119.5, 149.8 (17'-H / C19', C15a',), 7.31 / 120.0, 142.5 (17-H / C19, C15a), 7.34 / 127.0, 142.5 (18-H / C16, C19a), 7.61 / 127.2, 149.8 (19',-H / C17', C15a'), 7.69 / 126.4, 147.2 (19-H / C17, C15a), 8.09 / 48.0, 127.7, 142.5 (16-H / C15, C18, C19a), 8.75 / 48.0, 127.2, 140.3 (16'-H / 15-H, 18'-H, C19a').

Elemental Analysis $C_{29}H_{29}FeN$ (447.39 g/mol) requires C 77.85, H 6.53, N 3.13 found C 77.34, H 6.27 N 2.78.

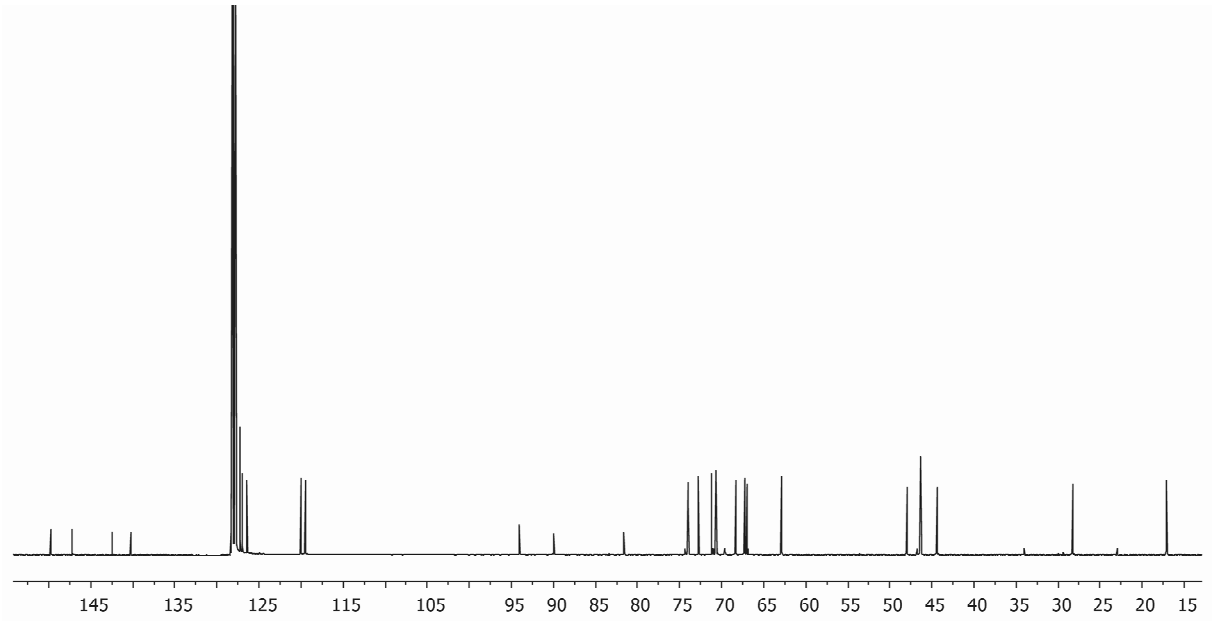
Melting Point 158 °C.

Infrared Spectroscopy $\tilde{\nu}$ (ATR)/ cm^{-1} = 2944 w, 2811 m, 2765 m, 1468 m, 1446 m, 1379 w, 1342 m, 1235 w, 1208 w, 1190 w, 1147 w, 1102 m, 1030 m, 1006 w, 967 m, 864 m, 849 m, 806 s, 740 s.

Mass Spectrometry (ESI, ES^+ for 447.165 methanol) 448.175 $[M+H]^+$.

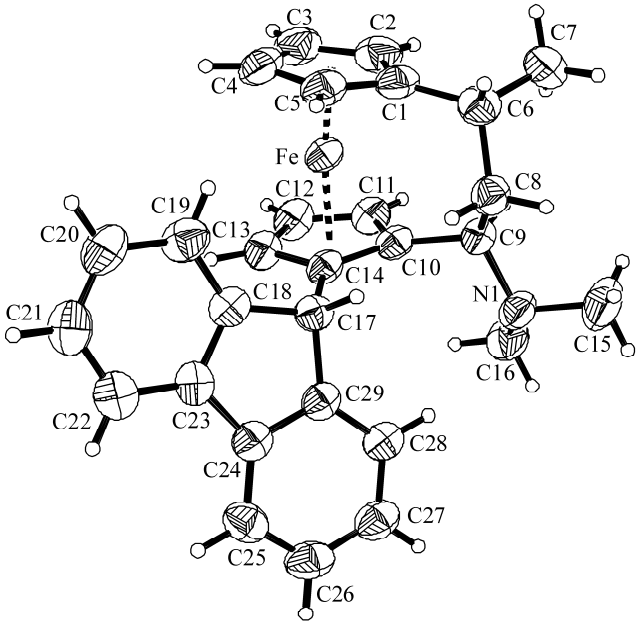


^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) of **14**

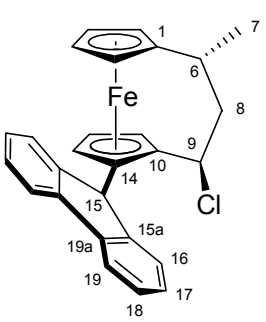


$^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) of **14**

X-ray crystal structure analysis: Crystal data for $C_{29}H_{29}FeN$ (**14**), M = 447.38, orthorhombic, space group *P*bca (No. 61), a = 9.4004(2), b = 15.8211(4), c = 29.6255(7) Å, V = 4406.0(2) Å^3, D_c = 1.349 g cm^{-3}, μ = 0.701 mm^{-1}, Z = 8, λ = 0.71073 Å, T = 223(2) K, 32361 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.667 Å^{-1}, 5422 independent (R_{int} = 0.071), and 3193 observed reflections [I ≥ 2σ(I)], 283 refined parameters, R = 0.048, wR^2 = 0.140.



Preparation of compound **15**



Methyl chloroformate (0.45 ml, 5.90 mmol, 6 equiv) was added to a solution the tertiary amino[3]ferrocenophane **14** (440 mg, 0.983 mmol) in anhydrous toluene (20 ml). After stirring at room temperature for 4 hours evaporation of all volatiles gave the crude product as a yellow oil, that solidified upon treatment with pentane (380 mg, 0.870 mmol, 89%).

^{1}H NMR ([D_2]-dichloromethane, 600 MHz, 298 K): δ = 1.36 (d, $^{3}J_{(H,H)}$ = 7.2 Hz, 3H, 7-H), 2.57 (m, 1H, 8-H), 2.90 (m, 1H, 6-H), 3.01 (m, 1H, 8'-H), 3.13 (m, 1H 13-H), 3.93 (m, 1H, 12-H), 4.09, 4.27, 4.69, 4.24 (each m, each 1H, C_5H_4), 4.17 (m, 1H, 11-H), 5.21 (m, 1H, 9-H), 5.48 (s, 1H, 15-H), 7.18 (m, 1H, 17'-H), 7.29 (m, 1H, 18'-H), 7.44 (m, 2H, 17-H, 18-H), 7.71 (m, 1H, 19'-H), 7.74 (m, 1H, 16'-H), 7.81 (m, 1H, 19-H), 8.08 (m, 1H, 16-H).

^{13}C{1H} NMR ([D_2] dichloromethane, 151 MHz, 298 K): δ = 18.5 (C7), 27.3 (C6), 46.6 (C15), 54.8 (C8), 57.1 (C9), 67.6 (C_5H_4), 67.7 (C12), 68.6 (C13), 68.9 (C_5H_4), 70.1 (C_5H_4), 70.3 (C11), 72.8 (C_5H_4), 80.5 (C10), 92.0 (C14), 92.1 (C1), 119.6 (C19'), 119.9 (C19), 126.2 (C16), 126.3 (C16'), 126.9 (C17), 127.1 (C17'), 127.2 (C18'), 127.6 (C18), 139.9 (C19a'), 141.9 (C19a), 146.6 (C15a), 149.8 (C15a').

^{1}H,^{1}H 1D-TOCSY ([D2]-dichloromethane, 600 MHz, 298 K): δ (1H)irr / δ (1H)res = 1.36 / 2.57, 2.90, 3.01, 5.21 (7-H / 8-H, 6-H, 8'-H, 9-H), 4.09 / 4.24, 4.27, 4.69 (C_5H_4), 4.17 / 3.13, 3.93 (11-H / 13-H, 12-H), 7.29 / 7.18, 7.71, 7.74 (18'-H / 17'-H, 19'-H, 16'-H), 7.81 / 7.44, 8.08 (19-H / 17-H, 18-H, 16-H).

^{1}H,^{1}H GCOSY ([D_2]-dichloromethane, 600 MHz / 600 MHz, 298 K): δ (1H) / δ (1H) = 1.36 / 2.90 (7-H / 6-H), 2.57 / 2.90, 3.01, 5.21 (8-H / 6-H, 8'-H, 9-H), 3.01 / 5.21 (8'-H / 9-H), 3.13 / 3.93, 4.17 (13-H / 12-H, 11-H), 3.93 / 4.17 (12-H / 11-H), 4.09 / 4.24, 4.27, 4.69 (C_5H_4), 4.24 / 4.27, 4.69 (C_5H_4), 4.27 / 4.69 (C_5H_4), 7.18 / 7.29, 7.74 (17'-H / 18'-H, 16'-H), 7.29 / 7.71 (18'-H / 19'-H), 7.44 / 7.44, 7.81, 8.08 (17-H, 18-H / 17-H, 18-H, 19-H, 16-H).

^{1}H,^{13}C GHSQC ([D2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.36 / 18.5 (7-H / C7), 2.57, 3.01 / 54.8 (8-H, 8'-H / C8), 2.90 / 27.3 (6-H / C6), 3.13 / 68.6 (13-H / C13), 3.93 / 67.7 (12-H / C12), 4.09 / 68.9 (C_5H_4), 4.17 / 70.3 (11-H / C11), 4.24 / 70.1 (C_5H_4), 4.27 / 67.6 (C_5H_4), 4.69 / 72.8 (C_5H_4), 5.21 / 57.1 (9-H / C9), 5.48 / 46.6 (15-H / C15), 7.18 / 127.1 (17'-H / C17'), 7.29 / 127.2 (18'-H / C18'), 7.44 / 126.9, 127.6 (17-H / C17,

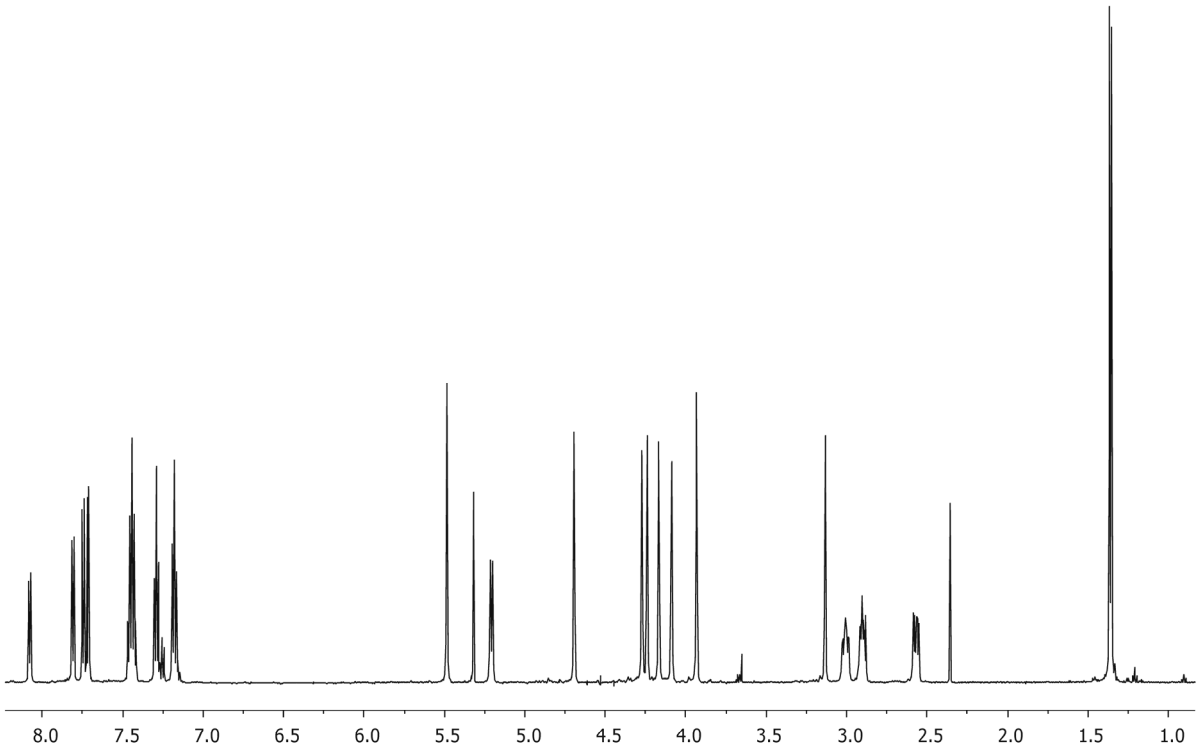
18-H / C18), 7.71 / 119.6 (19'-H / C19'), 7.74 / 126.3 (16'-H / C16'), 7.81 / 119.9 (19-H / C19), 8.08 / 126.2 (16-H / C16).

^{1}H,^{13}C GHMBC ([D_2]-dichloromethane, 600 MHz / 151MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.36 / 27.3, 54.8, 92.1 (7-H / C6, C8, C1), 2.57 / 27.3, 57.1, 80.5, 92.1 (8-H / C6, C9, C10, C1), 2.90 / 18.5, 54.8, 57.1, 67.6, 72.8, 92.1 (6-H / C7, C8, C9, C_5H_4, C_5H_4, C1), 3.01 / 27.3, 57.1, 68.9, 80.5, 92.1 (8'-H / C6, C9, C_5H_4, C10, C1), 3.13 / 46.6, 67.7, 70.3, 80.5, 92.0 (13-H / C15, C12, C11, C10, C14), 3.93 / 68.6, 70.3, 80.5, 92.0 (12-H / C13, C11, C10, C14), 4.09 / 67.6, 70.1, 72.8, 92.1 (C_5H_4 / C_5H_4, C1), 4.17 / 67.7, 68.6, 80.5, 92.0 (11-H / C12, C13, C10, C14), 4.24 / 67.6, 68.9, 72.8, 92.1 (C_5H_4 / C_5H_4, C1), 4.27 / 68.9, 70.1, 72.8, 92.1 (C_5H_4 / C_5H_4, C1), 4.69 / 67.6, 68.9, 70.1, 92.1 (C_5H_4 / C_5H_4, C1), 5.21 / 27.3, 54.8, 70.3, 80.5, 92.0 (9-H / C6, C8, C11, C10, C14), 5.48 / 68.6, 80.5, 92.0, 126.2, 126.3, 139.9, 141.9, 146.6, 149.8 (15-H / C13, C10, C14, C16, C16', C19a', C19a, C15a, C15a'), 7.18 / 119.6, 149.8 (17'-H / C19', C15a'), 7.29 / 126.3, 139.9 (18'-H / C16', C19a'), 7.44 / 119.9, 126.2, 141.9, 146.6 (17-H, 18-H / C19, C16, C19a, C15a,), 7.71 / 127.1, 141.9, 149.8 (19'-H / C17', C19a, C15a'), 7.74 / 46.6, 127.2, 139.9 (16'-H / C15, C18'', C19a'), 7.81 / 126.9, 146.6 (19-H / C17, C15a), 8.08 / 46.6, 127.6, 141.9 (16-H / C15, C18, C19a).

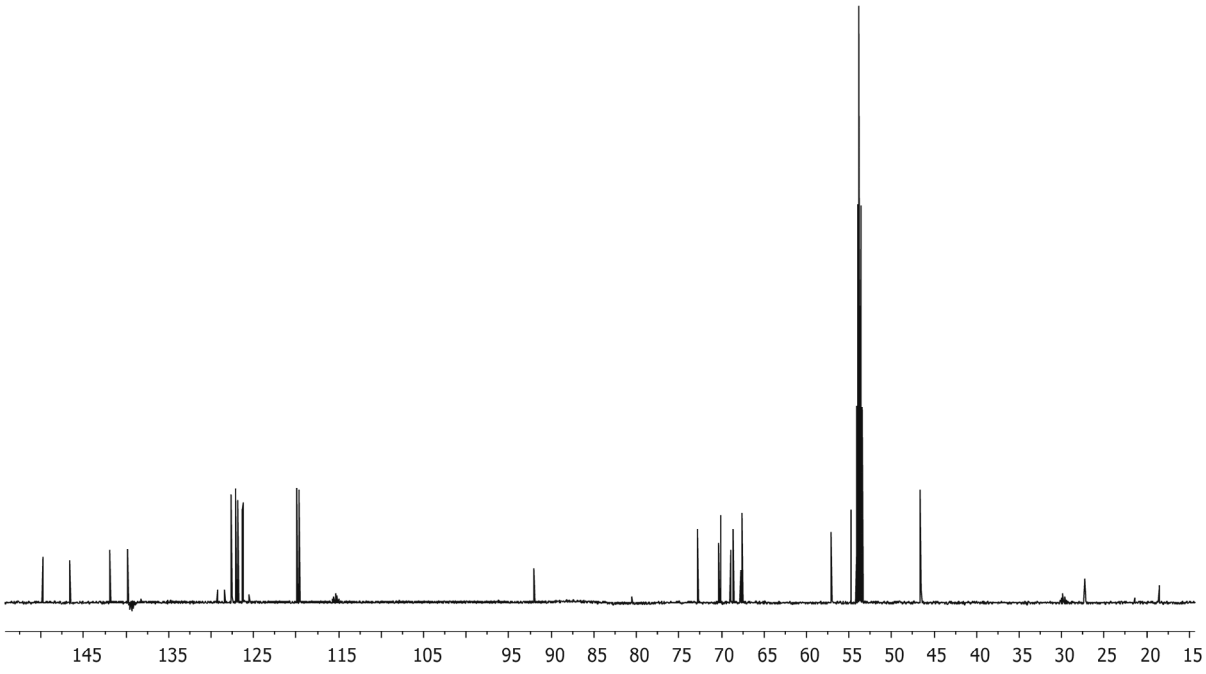
Elemental Analysis $C_{27}H_{23}ClFe$ (438.77 g/mol) requires C 73.91, H 5.28 found C 73.61, H 5.29.

Melting Point 106 °C.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3062 w, 2967 w, 2946 w, 2878 w, 2361 w, 2343 w, 1717 w, 1700 w, 1653 w, 1605 w, 1577 w, 1559 w, 1541 w, 1474 m, 1447 s, 1394 w, 1379 w, 1332 m, 1312 w, 1281 m, 1246 w, 1218 w, 1199 w, 1097 w, 1024 m, 1003 w, 986 w, 938 w, 916 m, 872 w, 846 w, 811 s.

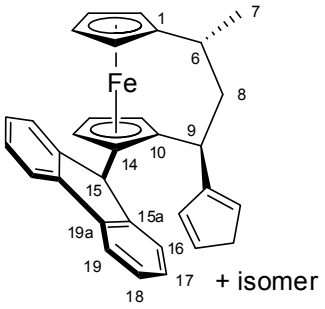


^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of **15**



^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K) of **15**

Preparation of **16a/b**



Compound **15** (1.80 g, 4.10 mmol) and cyclopentadienyl sodium (1.08 g, 12.3 mmol, 3 equiv) were placed in a Schlenk flask and suspended at 0°C in prechilled anhydrous diethyl ether (20 ml). The reaction mixture was allowed to warm to ambient temperature and stirred for additional 3 h. The reaction was quenched by the addition of water (0.5 ml). After 20 min of stiring magnesium sulfate was added and the solvent was removed *in vacuo*. The residue was extracted with pentane (5×20 ml) and after removal of the solvent from the pentane phase the analytically pure product was obtained as a yellow powder (1.51 g, 3.22 mmol, 79%).

An isomer mixture was obtained (ratio = 1:1.7).

Major isomer

^{1}H NMR ([D_2]-dichloromethane, 600 MHz, 298 K): δ = 1.29 (d, $^{3}J_{(H,H)}$ = 7.1 Hz, 3H, 7-H), 2.54 (m, 1H, 8-H), 2.85 (m, 1H, $C_5H_5^{CH2}$), 2.87 (m, 1H, 6-H), 3.01 (m, 1H, 13-H), 3.03 (m, 1H, $C_5H_5^{CH2}$'), 3.09 (m, 1H, 8'-H), 3.41 (m, 1H, 9-H), 3.86 (m, 1H, 12-H), 4.05, 4.20, 4.30, 4.64 (each m, each 1H, C_5H_4), 4.29 (m, 1H, 11-H), 4.92 (s, 1H, 15-H), 6.27, 6.59, 6.75 (each m, each 1H, C_5H_5), 6.36 (m, 1H, 16-H), 6.85 (m, 1H, 17-H), 7.15 (m, 1H, 18-H), 7.40 (m, 2H, 17'-H, 18'-H), 7.60 (m, 1H, 19-H), 7.74 (m, 1H, 19'-H), 8.13 (m, 1H, 16'-H).

^{13}C{^{1}H} NMR ([D_2] dichloromethane, 151 MHz, 298 K): δ = 16.4 (C7), 27.0 (C6), 32.2 (C9), 42.1 ($C_5H_5^{CH2}$), 46.9 (C15), 48.9 (C8), 66.5 (C12), 67.6, 68.9, 72.2, 69.98 (C_5H_4), 68.5 (C13),), 73.6 (C11), 82.7 (C10), 89.8 (C14), 93.90 (C1), 119.3 (C19), 119.8 (C19'), 125.4 (C16), 126.1 (C_5H_5), 126.6 (C16'), 126.81 (C17, C17'), 126.84 (C18), 127.58 (C18'), 134.5 (C_5H_5), 136.6 (C_5H_5), 139.6 (C19a), 142.1 (C19a'), 146.94 (C15a'), 150.0 (C15a), 150.6 (*i*-C_5H_5).

^{1}H,^{1}H 1D-TOCSY ([D2]-dichloromethane, 600 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.29 / 2.54, 2.87, 3.09, 3.41 (7-H / 8-H, 6-H, 8'-H, 9-H), 3.86 / 3.01, 4.29 (12-H / 13-H, 11-H), 6.27 / 2.85, 3.03, 6.59, 6.75 (C_5H_5 / CH_2', C_5H_5), 6.36 / 6.85, 7.15, 7.60, (16-H / 17-H, 18-H, 19-H).

^{1}H,^{1}H GCOSY ([D_2]-dichloromethane, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.29 / 2.87 (7-H / 6-H), 2.54 / 2.87, 3.09, 3.41 (8-H / 6-H, 8'-H, 9-H), 2.85 / 3.03, 6.27, 6.59, 6.75 ($C_5H_5^{CH2}$ / $C_5H_5^{CH22'}$, C_5H_5), 2.87 / 3.09 (6-H / 8'-H), 3.01 / 3.86, 4.29 (13-H / 12-H, 11-H), 3.03 / 6.27, 6.59, 6.75 (CH_2' / C_5H_5), 3.09 / 3.41 (8'-H / 9-H), 3.86 / 4.29 (12-H / 11-H), 4.05 / 4.20, 4.30, 4.64 (C_5H_4 / C_5H_4), 4.20 / 4.30, 4.64 (C_5H_4 / C_5H_4), 4.30 / 4.64 (C_5H_4 / C_5H_4), 6.27 / 6.59, 6.75 (C_5H_5 / C_5H_5), 6.36 / 6.85 (16-H / 17-H), 6.59 / 6.75 (C_5H_5 / C_5H_5), 6.85 / 7.15 (17-H / 18-H), 7.15 / 7.60 (18-H / 19-H), 7.40 / 7.74, 8.13 (17'-H, 18'-H / 19'-H, 16'-H).

^{1}H,^{13}C GHSQC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.29 / 16.4 (7-H / C7), 2.54, 3.09 / 48.9 (8-H, 8'-H / C8), 2.85, 3.03 / 42.0 ($C_5H_5^{CH2}$), 2.87 / 27.0 (6-H / C6), 3.01 / 68.5 (13-H / C13), 3.41 / 32.2 (9-H / C9), 3.86 / 66.5 (12-H / C12), 4.05 / 67.6 (C_5H_4), 4.20 / 69.98 (C_5H_4), 4.29 / 73.6 (11-H / C11), 4.30 / 68.9 (C_5H_4), 4.64 / 72.2 (C_5H_4), 4.92 / 46.9 (15-H / C15), 6.27 / 126.1 (C_5H_5), 6.59 / 134.5 (C_5H_5), 6.36 / 125.4 (16-H / C16), 6.75 / 136.6 (C_5H_5), 6.85 / 126.81 (17-H / C17), 7.15 / 126.81 (18-H / C18), 7.40 / 126.81, 127.6 (17'-H, 18'-H / C17', C18'), 7.60 / 119.3 (19-H / C19), 7.74 / 119.8 (19'-H / C19'), 8.13 / 126.6 (16'-H / C16').

^{1}H,^{13}C GHMBC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.29 / 27.0, 48.9, 93.90 (7-H / C6, C8, C1), 2.54 / 27.0, 82.7, 93.90 (8-H / C6, C10, C1), 2.85 / 126.1, 134.5, 136.6, 150.6 (CH_2 / C_5H_5), 3.01 / 66.5, 73.6, 82.7, 89.8 (13-H / C12, C11, C10, C14), 3.03 / 126.1, 134.5, 136.6, 150.6 ($C_5H_5^{CH2'}$ / C_5H_5, *i*-C_5H_5), 3.09 / 16.4, 27.0, 32.2, 82.7, 93.90 (8'-H / C7, C6, C9, C10, C1), 3.41 / 27.0, 48.9, 73.6, 82.9, 89.8, 126.1, 150.6 (9-H / C6, C8, C11, C10, C14, C_5H_5, *i*-C_5H_5), 3.86 / 68.5, 73.6, 82.7, 89.8 (12-H / C13, C11, C10, C14), 4.05 / 68.9, 69.98, 72.2, 93.90 (C_5H_4 / C_5H_4, C1), 4.20 / 67.6, 68.9, 72.2, 93.90 (C_5H_4 / C_5H_4, C1), 4.29 / 66.5, 68.5, 82.7, 89.8 (11-H / C12, C13, C10, C14), 4.30 / 67.6, 69.98, 72.2, 93.9 (C_5H_4 / C_5H_4, C1), 4.64 / 67.6, 68.5, 69.98, 93.9 (C_5H_4 / C_5H_4, C1), 4.92 / 68.5, 82.7, 89.9, 125.4, 126.6, 139.6, 142.1, 146.94, 150.0 (15-H / C13, C10, C14, C16, C16', C19a, C19a', C15a', C15a), 6.27 / 42.0, 134.5, 136.6, 150.6 ($C_5H_5^{CH2}$ / C_5H_5, *i*-C_5H_5), 6.36 / 46.9, 126.84, 139.6 (16-H / C15, C18, C19a), 6.59 / 42.0, 126.1, 136.6, 150.6 (C_5H_5 / C_5H_5, *i*-C_5H_5), 6.75 / 42.0, 126.1, 150.6 (C_5H_5 / C_5H_5, *i*-C_5H_5), 6.85 / 119.3, 150.0 (17-H / C19, C15a), 7.15 / 125.4, 139.6 (18-H / C16, C19a), 7.40 / 119.8, 126.6, 142.1, 146.94 (17'-H, 18'-H / C19', C16', C19a', C15a'), 7.60 / 126.81, 142.1, 150.0 (19-H / C17, C19a', C15a), 7.74 / 126.81, 146.94 (19'-H / C17', C15a'), 8.13 / 46.9, 127.58, 142.1 (16'-H / C15, C18', C19a').

Minor isomer

^{1}H NMR ([D$_2$]-dichloromethane, 600 MHz, 298 K): δ = 1.29 (d, $^{3}J_{(H,H)}$ = 7.1 Hz, 3H, 7-H), 2.54 (m, 1H, 8-H), 2.83 (m, 1H, 6-H), 2.98 (m, 1H, 13-H), 3.03 (m, 1H, $C_5H_5^{CH2}$), 3.09 (m, 1H, 8'-H), 3.19 (m, 1H, $C_5H_5^{CH2'}$), 3.44 (m, 1H, 9-H), 3.84 (m, 1H, 12-H), 4.04, 4.20, 4.29, 4.62 (each m, each 1H, C_5H_4), 4.23 (m, 1H, 11-H), 4.93 (s, 1H, 15-H), 6.01 (m, 1H, 16-H), 6.42, 6.45, 6.47 (each m, each 1H, C_5H_5), 6.87 (m, 1H, 17-H), 7.16 (m, 1H, 18-H), 7.40 (m, 2H, 17'-H, 18'-H), 7.61 (m, 1H, 19-H), 7.74 (m, 1H, 19'-H), 8.09 (m, 1H, 16'-H).

^{13}C{^{1}H} NMR ([D$_2$] dichloromethane, 151 MHz, 298 K): δ = 16.5 (C7), 27.1 (C6), 32.9 (C9), 45.0 ($C_5H_5^{CH2}$), 47.1 (C15), 48.8 (C8), 66.5 (C12), 67.5, 68.9 70.0, 72.3 (C_5H_4), 68.6 (C13), 73.6 (C11), 83.7 (C10), 89.7 (C14), 93.94 (C1), 119.4 (C19), 119.83 (C19'), 126 (C16), 126.7 (C16'), 126.81 (C17'), 126.9 (C18), 127.3 (C17), 127.63 (C18'), 127.0 (C_5H_5), 131.1 (C_5H_5), 133.5 (C_5H_5), 139.7 (C19a), 142.0 (C19a'), 146.95 (C15a'), 149.6 (C15a), 153.0 (*i*-C_5H_5).

^{1}H,^{1}H GCOSY ([D$_2$]-dichloromethane, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.29 / 2.83 (7-H / 6-H), 2.54 / 2.83, 3.09, 3.44 (8-H / 6-H, 8'-H, 9-H), 2.83 / 3.09 (6-H / 8'-H), 2.98 / 3.84, 4.23 (13-H / 12-H, 11-H), 3.03 / 3.19, 6.45 ($C_5H_5^{CH2}$ / $C_5H_5^{CH2'}$, C_5H_5), 3.09 / 3.44 (8'-H / 9-H), 3.19 / 6.42, 6.45, 6.47 ($C_5H_5^{CH2'}$ / C_5H_5), 3.84 / 4.23 (12-H / 11-H), 4.04 / 4.20, 4.29, 4.62 (C_5H_4 / C_5H_4), 4.20 / 4.29, 4.62 (C_5H_4 / C_5H_4), 4.29 / 4.62 (C_5H_4 / C_5H_4), 6.01 / 6.87 (16-H / 17-H), 6.42 / 6.45 (C_5H_5 / C_5H_5), 6.45 / 6.47 (C_5H_5 / C_5H_5), 6.87 / 7.16 (17-H / 18-H), 7.16 / 7.61 (18-H / 19-H), 7.40 / 7.74, 8.09 (17'-H, 18'-H / 19'-H, 16'-H).

^{1}H,^{13}C GHSQC ([D$_2$]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.29 / 16.5 (7-H / C7), 2.54, 3.09 / 48.8 (8-H, 8'-H / C8), 2.83 / 27.1 (6-H / C6), 2.98 / 68.6 (13-H / C13), 3.03, 3.19 / 45.0 ($C_5H_5^{CH2}$), 3.44 / 32.9 (9-H / C9), 3.84 / 66.5 (12-H / C12), 4.04 / 67.5 (C_5H_4), 4.20 / 70.0 (C_5H_4), 4.23 / 73.6 (11-H / C11), 4.29 / 68.9 (C_5H_4), 4.62 / 72.3 (C_5H_4), 4.93 / 47.1 (15-H / C15), 6.42 / 131.1 (C_5H_5), 6.45 / 127.0 (C_5H_5), 6.47 / 133.5 (C_5H_5), 6.01 / 126 (16-H / C16), 6.87 / 127.3 (17-H / C17), 7.16 / 126.9 (18-H / C18), 7.40 / 126.81, 127.63 (17'-H, 18'-H / C17', C18'), 7.61 / 119.4 (19-H / C19), 7.74 / 119.83 (19'-H / C19'), 8.09 / 126.7 (16'-H / C16').

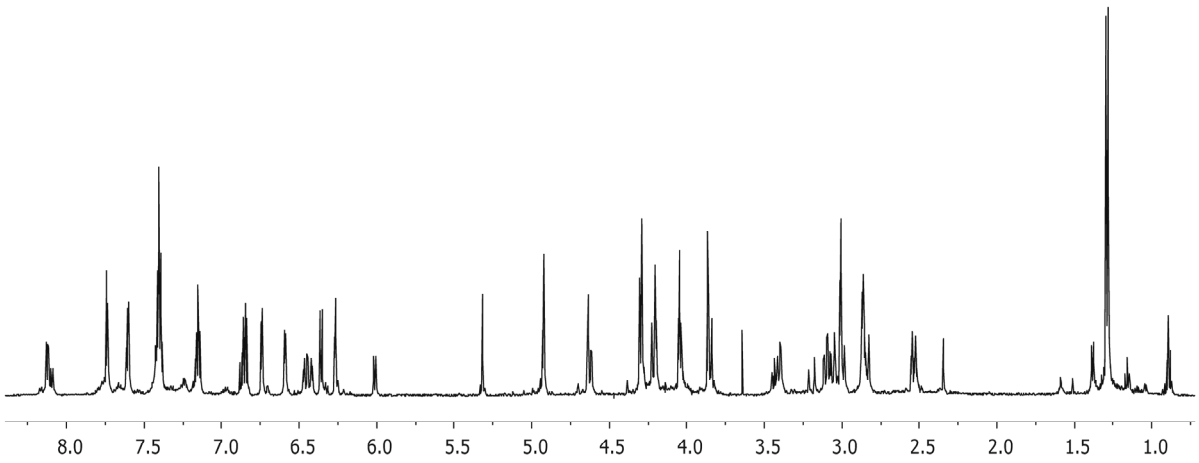
^{1}H,^{13}C GHMBC ([D$_2$]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.29 / 27.1, 48.8, 93.94 (7-H / C6, C8, C1), 2.54 / 27.1, 83.7, 93.94 (8-H / C6, C10, C1), 2.98 / 66.5, 73.6, 83.7, 89.7 (13-H / C12, C11, C10, C14), 3.03 / 127.0, 131.1, 133.5 ($C_5H_5^{CH2}$ / C_5H_5), 3.09 / 16.5, 27.1, 32.9, 83.7, 93.94 (8'-H / C7, C6, C9, C10, C1), 3.19 / 127.0, 131.1,

133.5, 153.0 ($C_5H_5^{CH2'}$ / C_5H_5, *i*-C_5H_5), 3.44 / 48.9, 73.6, 83.7, 89.7, 127.0, 153.0 (9-H / C8, C11, C10, C14, C_5H_5, *i*-C_5H_5), 3.84 / 68.6, 73.6, 83.7, 89.7 (12-H / C13, C11, C10, C14), 4.04 / 68.9, 70.00, 72.3, 93.94 (C_5H_4 / C_5H_4, C1), 4.20 / 67.5, 68.9, 72.3, 93.94 (C_5H_4 / C_5H_4, C1), 4.23 / 66.5, 68.6, 83.7 (11-H / C12, C13, C10), 4.29 / 67.5, 70.0, 72.3, 93.94 (C_5H_4 / C_5H_4, C1), 4.62 / 67.5, 68.9, 70.0, 93.94 (C_5H_4 / C_5H_4, C1), 6.42 / 45.0, 127.0, 133.5, 153.0 (C_5H_5 / CH_2, C_5H_5, *i*-C_5H_5), 6.45 / 45.0, 131.1, 133.5, 153.0 (C_5H_5 / CH_2, C_5H_5, *i*-C_5H_5), 6.47 / 45.0, 127.0, 133.5, 153.0 (C_5H_5 / CH_2, C_5H_5, *i*-C_5H_5), 4.93 / 68.6, 83.7, 89.7, 126, 126.7, 139.7, 142.0, 146.95, 149.60 (15-H / C13, C10, C14, C16, C16', C19a, C19a', C15a', C15a), 6.01 / 47.1, 126.9, 139.7 (16-H / C15, C18, C19a), 6.67 / 119.4, 149.6 (17-H / C19, C15a), 7.16 / 126, 139.7 (18-H / C16, C19a), 7.40 / 119.83, 126.7, 142.0, 146.95 (17'-H, 18'-H / C19', C16', C19a', C15a'), 7.61 / 127.3, 142.0, 149.6, (19-H / C17, C19a', C15a), 7.74 / 126.81, 146.95 (19'-H / C17', C15a'), 8.09 / 47.1, 127.63, 142.0 (16'-H / C15, C18', C19a').

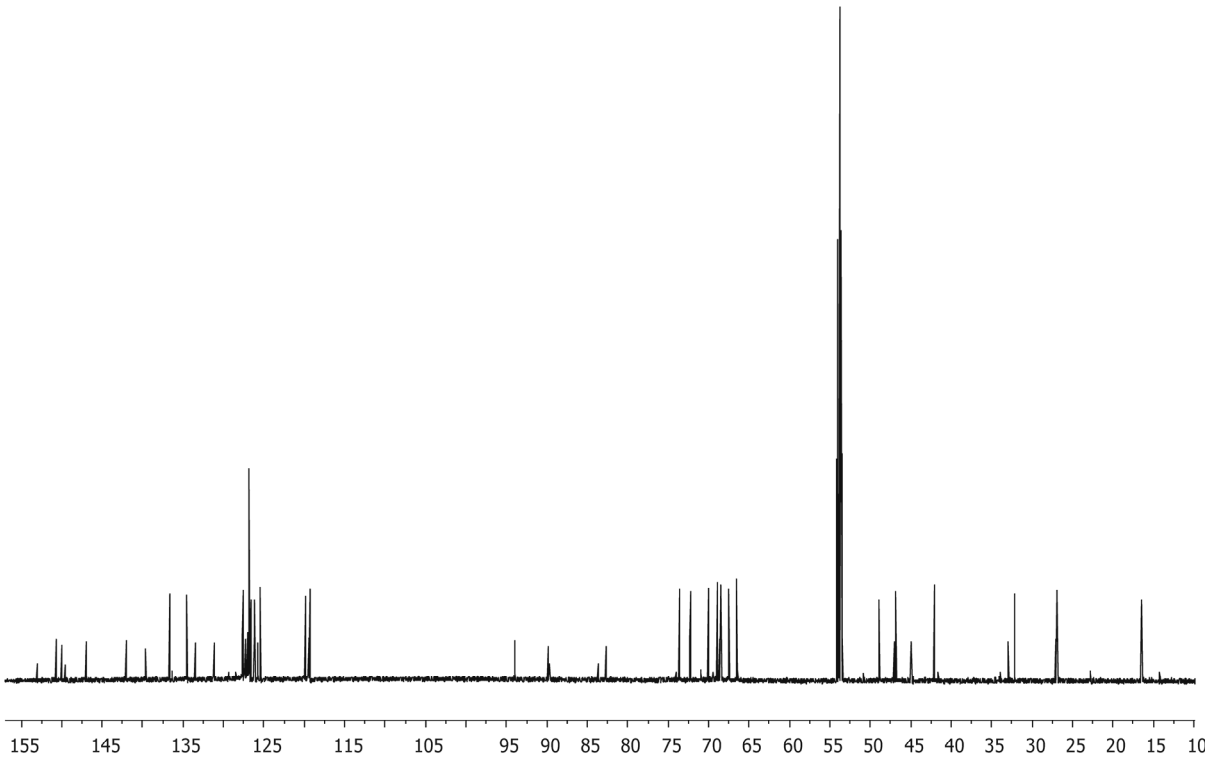
Elemental Analysis $C_{32}H_{28}Fe$ (486.41 g/mol) requires C 82.05, H 6.03 found C 81.98, H 5.64.

Melting Point 141°C.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3901 w, 3853 w, 3801 w, 3750 w, 3675 w, 3649 w, 3061 m, 3035 m, 2959 m, 2927 m, 2870 m, 2361 w, 2343 w, 1942 w, 1909 w, 1844 w, 1772 w, 1734 w, 1705 w, 1684 w, 1653 w, 1606 w, 1577 w, 1559 w, 1540 w, 1521 w, 1507 w, 1474 m, 1446 s, 1393 w, 1374 m, 1326 w, 1309 w, 1244 w, 1150 w, 1096 w, 1042 m, 1023 m, 1005 w, 983 w, 920 w, 897 m, 870 w, 845 w, 803 s.

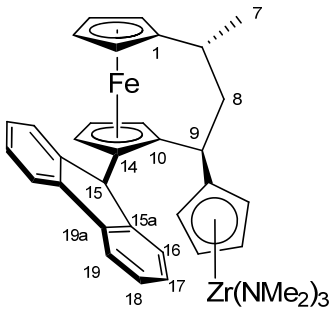


^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of **16**



$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) of **16**

Preparation of comound **17**



$Zr(NMe_2)_4$ (85.6 mg, 0.32 mmol, 1 equiv) in anhydrous tetrahydrofuran (5 ml) was added dropwise at 0 °C to a solution of **16a/b** (150 mg, 0.32 mmol) in anhydrous tetrahydrofuran (5 ml). The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. Evaporation of all volatiles gave analytically pure **17** as an orange powder (200 mg, 0.29 mmol, 90%).

^{1}H NMR ([D_2]-dichloromethane, 600 MHz, 298 K): δ = 1.31 (d, $^3J_{(H,H)}$ = 7.24 Hz, 3H, 7-H), 2.52 (m, 1H, 8-H), 2.90 (m, 1H, 6-H), 2.95 (s, 18H, NMe_2), 2.97 (m, 1H, 13-H), 3.15 (m, 1H, 8'-H), 3.74 (m, 1H, 9-H), 3.84 (m, 1H, 12-H), 4.04, 4.19, 4.31, 4.66 (each m, each 1H, C_5H_4), 4.28 (m, 1H, 11-H), 4.89 (m, 1H, 15-H), 5.53 (m, 1H, 16'-H), 6.06, 6.24, 6.27, 6.34 (each m, 4H, $C_5H_4^{Zr}$), 6.80 (m, 1H, 17'-H), 7.13 (m, 1H, 18'-H), 7.40 (m, 2H, 17-H, 18-H), 7.57 (m, 1H, 19'-H), 7.73 (m, 1H, 19-H), 8.11 (m, 1H, 16-H).

^{13}C{^{1}H} NMR ([D_2] -dichloromethane, 151 MHz, 298 K): δ = 16.6 (C7), 27.2 (C6), 31.3 (C9), 44.9 (NMe_2), 47.0 (C15), 48.9 (C8), 66.4 (C12), 67.6 (C_5H_4), 68.3 (C13), 68.9 (C_5H_4), 70.0 (C_5H_4), 72.1 (C_5H_4), 73.2 (C11), 85.1 (C10), 89.5 (C14), 93.7 (C1), 108.8 ($C_5H_4^{Zr}$), 109.6 ($C_5H_4^{Zr}$), 110.7 ($C_5H_4^{Zr}$), 112.2 ($C_5H_4^{Zr}$), 119.0 (C19'), 119.8 (C19), 126.55, 126.63 (C16, C16'), 126.75 (C18'), 126.79 (C18), 127.0 (C17), 127.6 (C17'), 133.1 (*i*-$C_5H_4^{Zr}$), 139.3 (C19a'), 142.1 (C19a), 146.9 (C15a), 149.8 (C15a').

^{1}H,^{1}H 1D-TOCSY ([D_2]-dichloromethane, 600 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.31 / 2.52, 2.90, 3.15, 3.74 (7-H / 8-H, 6-H, 8'-H, 9-H), 3.84 / 2.97, 4.28 (12-H / 13-H, 11-H), 4.04 / 4.19, 4.31, 4.66 (C_5H_4), 6.06 / 6.24, 6.27, 6.34 ($C_5H_4^{Zr}$), 7.13 / 5.53, 6.80, 7.57 (18'-H / 16'-H, 17'-H, 19'-H). [501b_031208_298k_1dtocsy.fid]

^{1}H,^{1}H GCOSY ([D_2]-dichloromethane, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.31 / 2.90 (7-H / 6-H), 2.52 / 2.90, 3.15, 3.74 (8-H / 6-H, 8'-H, 9-H), 2.90 / 3.15 (6-H / 8'-H), 2.97 / 3.84, 4.28 (13-H / 12-H, 11-H), 3.15 / 3.74 (8'-H / 9-H), 3.84 / 4.28 (12-H / 11-H), 4.04 / 4.19, 4.31, 4.66 (C_5H_4 / C_5H_4), 4.19 / 4.31, 4.66 (C_5H_4 / C_5H_4), 4.31 / 4.66 (C_5H_4 / C_5H_4), 5.53 / 6.80 (16'-H /17'-H), 6.06 / 6.24, 6.27, 6.34 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$), 6.24 / 6.27, 6.34 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$), 6.27 / 6.34 (C_5H_4 / C_5H_4), 6.80 / 7.13 (17'-H / 18'-H), 7.13 / 7.57 (18'-H / 19'-H), 7.40 / 7.40, 7.73, 8.11 (17-H, 18-H / 17-H, 18-H, 19-H, 16-H).

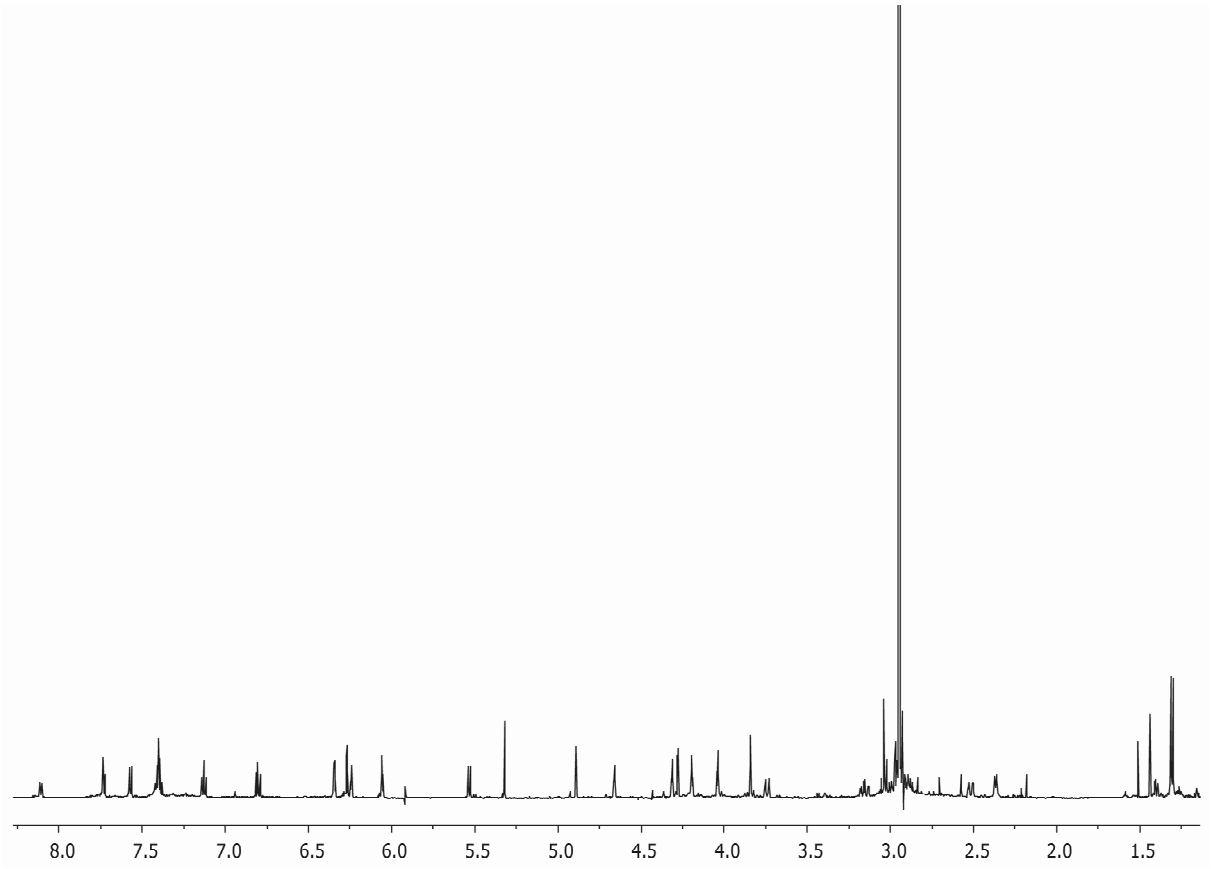
^{1}H,^{13}C GHSQC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.31 / 16.6 (7-H / C7), 2.52, 3.15 / 48.9 (8-H, 8'-H / C8), 2.90 / 27.2 (6-H / C6), 2.95 / 44.9 (NMe_2), 2.97 / 68.3 (13-H / C13), 3.74 / 31.3 (9-H / C9), 3.84 / 66.4 (12-H / C12), 4.04 / 67.6 (C_5H_4), 4.19 / 70.0 (C_5H_4), 4.28 / 73.2 (11-H / C11), 4.31 / 68.9 (C_5H_4), 4.66 / 72.1 (C_5H_4), 4.89 / 47.0 (15-H / C15), 5.53 / 126.55, 126.63 (16'-H / C16'), 6.06 / 109.6 ($C_5H_4^{Zr}$), 6.24 / 108.8 ($C_5H_4^{Zr}$), 6.27 / 110.7 ($C_5H_4^{Zr}$), 6.34 / 112.2 ($C_5H_4^{Zr}$), 6.80 / 127.0 (17'-H / C17'), 7.13 / 126.75 (18'-H / C18'), 7.40 / 126.79, 127.0 (17-H / C17, 18-H / C18), 7.57 / 119.0 (19'-H / C19'), 7.73 / 119.8 (19-H / C19), 8.11 / 126.55, 126.63 (16-H / C16).

^{1}H,^{13}C GHMBC ([D_2]-dichloromethane, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.31 / 27.2, 48.9, 93.7 (7-H / C6, C8, C1), 2.52 / 31.3, 85.1, 93.7, 133.1 (8-H / C9, C10, C1, *i*-$C_5H_4^{Zr}$), 2.90 / 31.3, 48.9 (6-H / C9, C8), 2.97 / 66.4, 73.2, 85.1, 89.5 (13-H / C12, C11, C10, C14), 3.15 / 16.6, 27.2, 31.3, 85.1, 93.7 (8'-H / C7, C6, C9, C10, C1), 3.74 / 27.2, 48.9, 73.2, 85.1, 89.5, 108.8, 112.2, 133.1 (9-H / C6, C8, C11, C10, C14, $C_5H_4^{Zr}$, $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 3.84 / 68.3, 73.2, 85.1, 89.5 (12-H / C13, C11, C10, C14), 4.04 / 68.9, 70.0, 72.1, 93.7 (C_5H_4 / C_5H_4, C1), 4.19 / 67.6, 68.9, 72.1, 93.7 (C_5H_4 / C_5H_4, C1), 4.28 / 66.4, 68.3, 85.1, 89.5 (11-H / C12, C13, C10, C14), 4.31 / 67.6, 70.0, 72.1, 93.7 (C_5H_4 / C_5H_4, C1), 4.66 / 67.4, 68.9, 70.0, 93.7 (C_5H_4 / C_5H_4, C1), 4.89 / 68.3, 85.1, 89.5, 126.55, 126.63, 139.3, 142.1, 146.9, 149.8 (15-H / C13, C10, C14, C16', C16, C19a', C19a, C15a, C15a'), 5.53 / 47.0, 126.75, 139.3 (16'-H / C15, C18', C19a'), 6.06 / 112.2, 133.1 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.24 / 110.7, 112.2, 133.1 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.27 / 109.6, 133.1 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$), 6.34 / 108.8 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$), 6.80 / 119.0, 149.8 (17'-H / C19', C15a'), 7.13 / 126.55, 126.63, 139.3 (18'-H / C16', C19a'), 7.40 / 119.8, 126.55, 126.63, 142.1, 146.9 (17-H, 18-H / C19, C16, C19a, C15a), 7.57 / 126.96, 142.1, 149.8 (19'-H / C17', C19a, C15a'), 7.73 / 126.79, 139.3, 146.9 (19-H / C17, C19a',C15a), 8.11 / 47.0, 127.75, 142.1 (16-H / C15, C18, C19a).

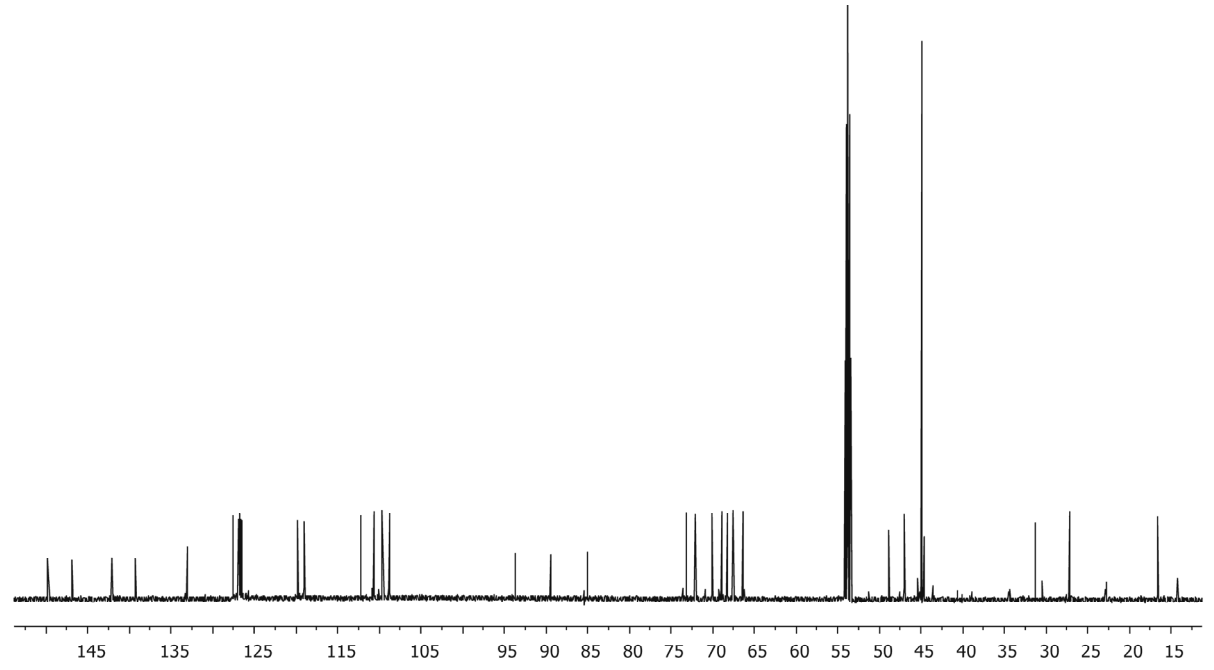
Elemental Analysis $C_{38}H_{45}FeN_3Zr$ (690.85 g/mol) requires C 66.06, H 6.57, N 6.08 found C 65.71, H 6.38, N 5.72.

Melting Point > 250 °C.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3657 w, 3062 m, 3036 w, 2957 m, 2921 m, 2854 m, 2813 m, 2762 m, 2363 w, 2075 w, 1942 w, 1908 w, 1809 w, 1740 w, 1674 w, 1606 m, 1580 m, 1475 s, 1447 s, 1421 s, 1392 w, 1374 m, 1354 w, 1325 w, 1308 w, 1296 w, 1240 s, 1141 m, 1098 m, 1041 m, 1023 m, 1005 w, 939 s, 871 w, 845 m, 803 m.

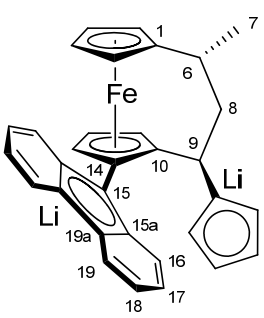


^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of **17**



^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K) of **17**

Preparation of Compound **18**



Compound **16a/b** (500 mg, 1.07 mmol) was dissolved in anhydrous toluene (10 ml) and treated with *n*-butyllithium (1.67 ml, 1.6 M in *n*-pentane, 2.67 mmol, 2.5 equiv) at 0°C. The reaction mixture was stirred for 6 h at room temperature and the resulting precipitation was collected on a glass frit, washed with pentane (3×10 ml) and dried *in vacuo* to yield the product as an orange powder (480 mg, 1.00 mmol, 93%).

^{1}H NMR ([D$_8$]-tetrahydrofuran, 600 MHz, 298 K): δ = 1.20 (d, $^{3}J_{(H,H)}$ = 7.21 Hz, 3H, 7-H), 2.24 (m, 1H, 8-H), 2.59 (m, 1H, 6-H), 3.10 (m, 1H, 8'-H), 3.74 (m, 1H, 9-H), 3.83 (m, 1H, $C_5H_4^{\beta}$), 3.96 (m, 1H, $C_5H_4^{\alpha}$), 3.98 (m, 1H, 12-H), 4.08 (m, 1H, 13-H), 4.12 (m, 1H, 11-H), 4.18 (m, 1H, $C_5H_4^{\beta}$), 4.33 (m, 1H, $C_5H_4^{\alpha}$), 5.29 (m, 2H, $C_5H_4^{Li}$), 5.53 (m, 2H, $C_5H_4^{Li}$), 6.37 (m, 2H, Flu$_{\beta}$), 6.71 (m, 2H, Flu$_{\beta}$), 7.54 (b, 2H, Flu$_{\alpha}$), 7.74 (m, 2H, Flu$_{\alpha}$).

^{13}C{^{1}H} NMR ([D$_8$]-tetrahydrofuran, 151 MHz, 298 K): δ = 19.3 (C7), 28.4 (C6), 34.3 (C9), 46.2 (C8), 64.9 (C12), 65.0 ($C_5H_4^{\beta}$), 66.8 ($C_5H_4^{\alpha}$), 70.0 ($C_5H_4^{\beta}$), 72.1 (C13), 72.6 (C11), 74.3 ($C_5H_4^{\alpha}$), 87.3 (C10), 90.4 (C14), 93.6 (C1), 101.2 ($C_5H_4^{Li}$), 103.4 ($C_5H_4^{Li}$), 109.4 (Flu$_{\beta}$), 118.1 (Flu$_{\alpha}$), 118.4 (Flu$_{\alpha}$), 119.7 (Flu$_{\beta}$), 123.0 (Flu$_q$), 123.4 (*i*-$C_5H_4^{Li}$), 136.2 (Flu$_q$), n.o. (C15).

^{1}H,^{1}H 1D-TOCSY ([D$_8$]-tetrahydrofuran, 600 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.20 / 2.24, 2.59, 3.10, 3.74 (7-H / 8-H, 6-H, 8'-H, 9-H), 4.08 / 3.98, 4.12 (13-H / 12-H, 11-H), 4.18 / 3.83, 3.96, 4.33 ($C_5H_4^{\beta}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\alpha}$), 5.29 / 5.53 ($C_5H_4^{Li}$).

^{1}H,^{1}H GCOSY ([D$_8$]-tetrahydrofuran, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.20 / 2.59 (7-H / 6-H), 2.24 / 2.59, 3.10, 3.74 (8-H / 6-H, 8'-H, 9-H), 2.59 / 3.10 (6-H / 8'-H), 3.10 / 3.74 (8'-H / 9-H), 3.83 / 3.96, 4.18, 4.33 ($C_5H_4^{\beta}$ / $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$), 3.96 / 4.18, 4.33 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$), 3.98 / 4.08, 4.12 (12-H / 13-H, 11-H), 4.08 / 4.12 (13-H / 11-H), 4.18 / 4.33 ($C_5H_4^{\beta}$ / $C_5H_4^{\alpha}$), 5.29 / 5.53 ($C_5H_4^{Li}$), 6.37 / 6.71, 7.74 (Flu$_{\beta}$ / Flu$_{\beta}$, Flu$_{\alpha}$).

^{1}H,^{13}C GHSQC ([D$_8$]-tetrahydrofuran, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.20 / 1.3 (7-H / C7), 2.24, 3.10 / 46.2 (8-H, 8'-H / C8), 2.59 / 28.4 (6-H / C6), 3.74 / 34.3 (9-H / C9), 3.83 / 65.0 ($C_5H_4^{\beta}$), 3.96 / 66.8 ($C_5H_4^{\alpha}$), 3.98 / 64.9 (12-H / C12), 4.08 / 72.1 (13-H / C13), 4.12 / 72.6 (11-H / C11), 4.18 / 70.0 ($C_5H_4^{\beta}$), 4.33 / 74.3 ($C_5H_4^{\alpha}$), 5.29 / 101.2 ($C_5H_4^{Li}$),

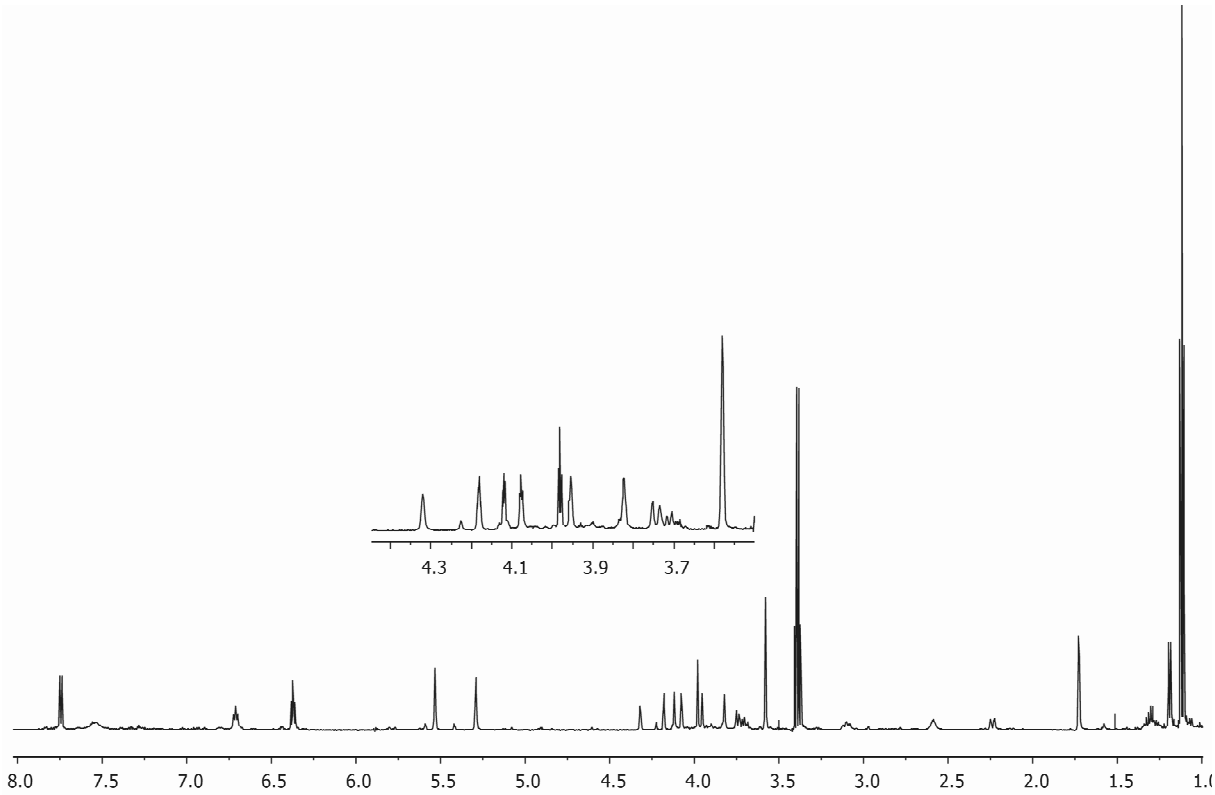
5.53 / 103.4 ($C_5H_4^{Li}$), 6.37 / 109.4 (Flu_β / Flu_β), 6.71 / 119.7 (Flu_β / Flu_β), 7.54 / 118.4 (Flu_α / Flu_α), 7.74 / 118.1 (Flu_α / Flu_α).

^{1}H,^{13}C GHMBC ([D_8]-tetrahydrofuran, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.20 / 28.4, 46.2, 93.6 (7-H / C6, C8, C1), 2.24 / 19.3, 28.4, 34.3, 87.3, 93.6, 123.4 (8-H / C7, C6, C9, C10, C1, *i*-C_5H_4), 2.59 / 19.3, 34.3, 66.8, 74.3, 93.6 (6-H / C7, C9, $C_5H_4^\alpha$, $C_5H_4^\alpha$, C1), 3.10 / 19.3, 28.4, 34.3, 87.3 (8'-H / C7, C6, C9, C10), 3.74 / 28.4, 46.2, 72.6, 87.3, 90.4, 103.4, 123.4 (9-H / C6, C8, C11, C10, C14, $C_5H_4^{Li}$, *i*-$C_5H_4^{Li}$), 3.83 / 66.8, 70.0, 74.3, 93.6 ($C_5H_4^\beta$ / $C_5H_4^\alpha$, $C_5H_4^\beta$, $C_5H_4^\alpha$, C1), 3.96 / 65.0, 70.0, 74.3, 93.6 ($C_5H_4^\alpha$ / $C_5H_4^\beta$, $C_5H_4^\beta$, $C_5H_4^\alpha$, C1), 3.98 / 72.1, 72.6, 87.3, 90.4 (12-H / C13, C11, C10, C14), 4.08 / 64.9, 72.6, 87.3, 90.4 (13-H / C12, C11, C10, C14), 4.12 / 64.9, 72.1, 87.3, 90.4 (11-H / C12, C13, C10, C14), 4.18 / 65.0, 66.8, 74.3, 93.6 ($C_5H_4^\beta$ / $C_5H_4^\beta$, $C_5H_4^\alpha$, $C_5H_4^\alpha$, C1), 4.33 / 65.0, 66.8, 70.0, 93.6 ($C_5H_4^\alpha$ / C(3,4), $C_5H_4^\alpha$, $C_5H_4^\beta$, C1), 5.29 / 103.4, 123.4 ($C_5H_4^{Li}$ / $C_5H_4^{Li}$, *i*-$C_5H_4^{Li}$), 5.53 / 101.2, 103.4, 123.4 ($C_5H_4^{Li}$ / $C_5H_4^{Li}$, *i*-C_5H_4), 6.37 / 118.4, 119.7, 123.0 (Flu_β / Flu_α, Flu_q), 6.71 / 118.1, 136.2 (Flu_β / Flu_α, Flu_q), 7.74 / 119.7, 123.0, 136.2 (Flu_α / Flu_β, Flu_q, Flu_q).

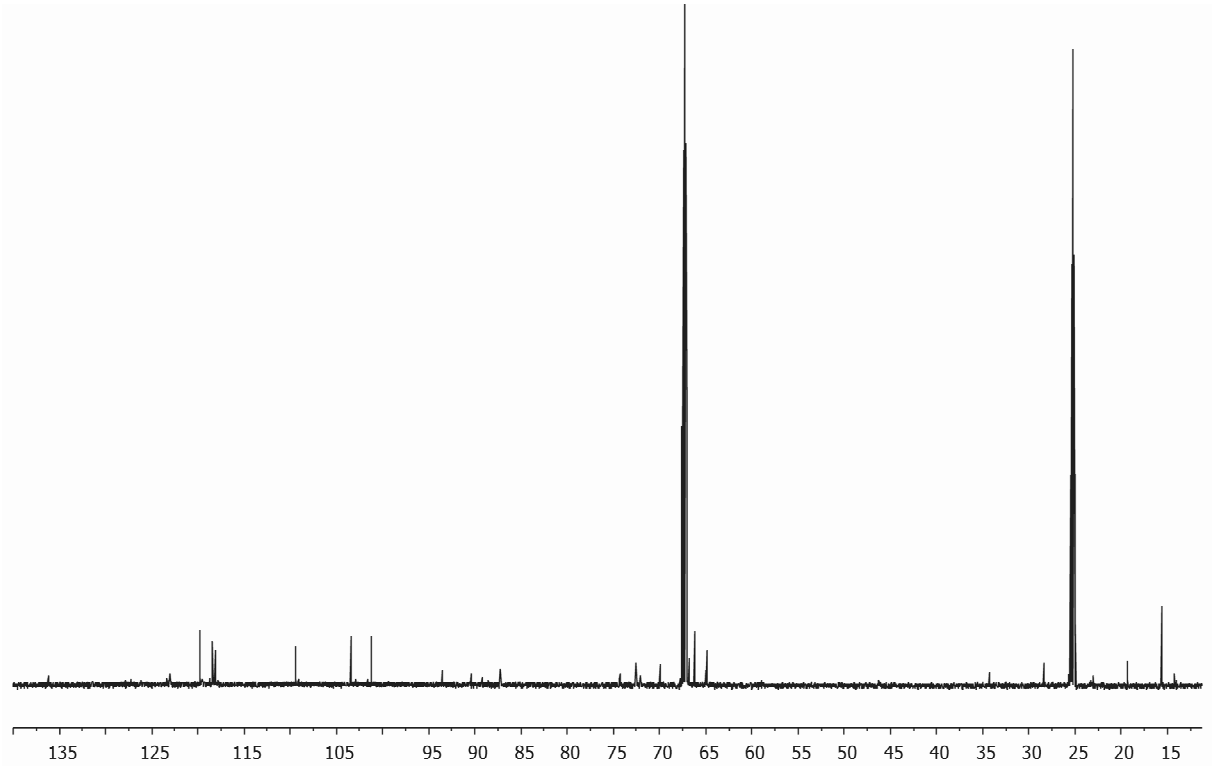
Elemental Analysis $C_{32}H_{26}FeLi_2$ (480.28 g/mol) requires C 80.03, H 5.46, found C 79.21, H 5.60.

Melting Point > 250 °C.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3676 w, 3064 m, 3037 m, 2958 m, 2920 m, 2869 m, 2360 m, 2341 w ,1943 w, 1909 w, 1700 w, 1677 w, 1603 m, 1578 m, 1571 m, 1533 w, 1475 s, 1448 s, 1373 m, 1308 s, 1215 m, 1151 w, 1110 m, 1089 m, 1044 s, 1029 s, 1004 m, 986 m, 936 w, 915 m, 898 m, 883 w, 869 w, 841 m, 803 m.

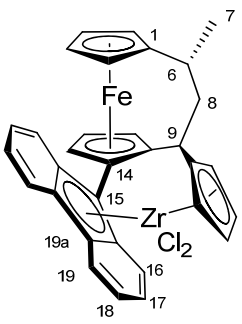


^{1}H NMR (600 MHz, D_8-THF, 298 K) of **18**



^{13}C{^{1}H} NMR (151 MHz, D_8-THF, 298 K) of **18**

Preparation of compound **20**



A supension of $Zr(NMe_2)_2Cl_2 \cdot 2thf$ (246.6 mg, 0.625 mmol, 1 equiv) suspended in anhydrous diethyl ether (10 ml) was cooled to −20 °C and a precooled suspension of **18** (300 mg, 0.625 mmol) in anhydrous diethyl ether (20 ml) was added carfully. The reaction mixture was allowed to warm to room temperature and stirred for additional 2 h. The suspension was filtered through Celite and the solvent of the filtrate was removed *in vacuo*. Toluene (20 ml), and then trimethylsilyl chloride (0.2 ml, 0.170 mg, 1.56 mmol, 2.5 equiv) were added. The reaction mixture was stirred overnight. After removel of the solvent *in vacuo* the orange residue was washed with pentane (3×5 ml) and dried under vacuum to give the product as an orange solid (307 mg, 0.488 mmol, 78%). Suitable crystals for X-ray crystallography were obtained by diffusion of pentane into a saturated solution of **20** in benzene.

^{1}H NMR ([D_6]-benzene, 500 MHz, 298 K): δ = 1.03 (d, $^3J_{(H,H)}$ = 7.0 Hz, 3H, 7-H), 2.10 (m, 2H, 8-H, 8'-H), 2.55 (m, 1H, 6-H), 3.39 (m, 1H, 9-H), 3.77, 4.04, 4.10 (each m, each 1H, C_5H_3), 3.99, 4.08, 4.22, 4.70 (each m, each 1H, C_5H_4), 5.35, 5.69, 5.93, 6.69 (each m, each 1H, $C_5H_4^{Zr}$), 6.85 (m, 1H, Flu), 7.05 (m, 1H, Flu), 8.04 (m, 1H, Flu), 7.26, 7.40, 8.18, 8.26 (each m, each 1H, Flu').

^{13}C{^{1}H} NMR ([D_6]-benzene, 126 MHz, 298 K): δ = 19.8 (br, C7), 25.1 (br, C6), 30.1 (br, C9), 50.9 (br, C8), 67.6 (br, C_5H_4), 69.3 (C_5H_4), 69.4 (C_5H_4), 74.2 (C_5H_4), 68.3, 70.2, 72.2 (each br, C_5H_3),81.3 (*i*-C_5H_4), 90.9 (C1), 94.4 (C15), 115.7, 116.8, 120.2 ($C_5H_4^{Zr}$), 124.9, 125.0, 125.7, 126.7 (Flu), 124.1 (Flu'), 125.5 (2×C, Flu'), 129.6 (Flu'), [*i*-C_5H_4, $C_5H_4^{Zr}$, *i*-$C_5H_4^{Zr}$ and the quatery Flu carbon atom were not assigned].

^{1}H,^{1}H 1D-TOCSY ([D_6]-benzene, 500 MHz, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 1.03 / 2.10, 2.55, 3.39 8 (7-H / 8-H, 8'-H, 6-H, 9-H), 3.77 / 4.04, 4.10 (C_5H_3 / C_5H_3), 3.99 / 4.08, 4.22, 4.70 (C_5H_4 / C_5H_4), 5.67 / 5.35, 5.93, 6.69 (Cp^{Zr} / Cp^{Zr}), 6.85 / 7.05, 8.04 (Flu / Flu), 7.27 / 7.40, 8.18, 8.26 (Flu' / Flu').

^{1}H,^{1}H GCOSY ([D_6]-benzen, 600 MHz / 600 MHz, 298 K): δ (^{1}H) / δ (^{1}H) = 1.03 / 2.55 (7-H / 6-H), 2.10 / 2.55, 3.39 (8-H, 8'-H / 6-H, 9-H), 3.77 / 4.04, 4.10 (C_5H_3 / C_5H_3), 4.40 / 4.10 (C_5H_3 / C_5H_3), 3.99 / 4.08, 4.22, 4.70 (C_5H_4 / C_5H_4), 4.08 / 4.22, 4.70 (C_5H_4 / C_5H_4), 4.22 / 4.70 (C_5H_4 / C_5H_4), 5.35 / 5.69, 5.3, 6.69 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$), 5.69 / 5.93, 6.69 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$),

5.93 / 6.59 ($C_5H_4^{Zr}$ / $C_5H_4^{Zr}$), 6.85 / 7.05, 8.04 (Flu / Flu), 7.05 / 8.04 (Flu / Flu), 7.26 / 7.40, 8.18 (Flu' / Flu'), 7.26 / 8.26 (Flu' / Flu'), 7.26 / 7.40, 8.18, 8.26 (Flu' / Flu').

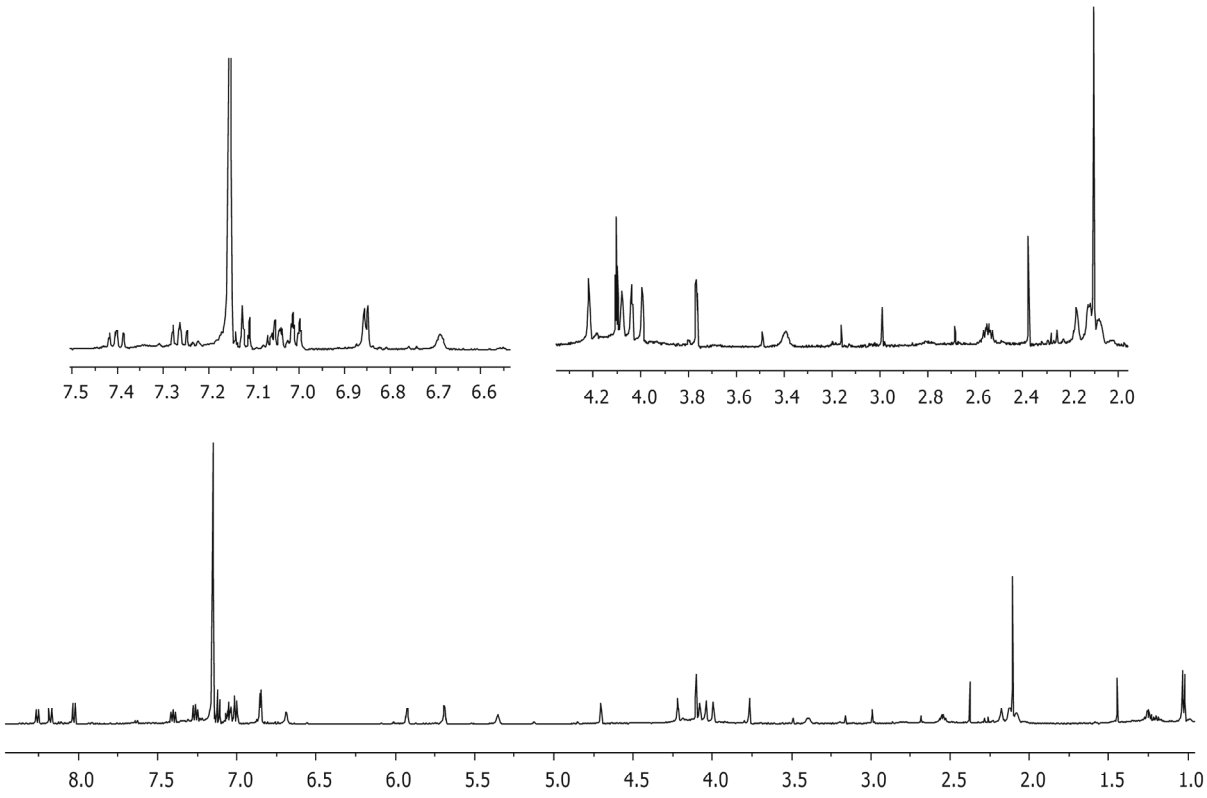
^{1}H,^{13}C GHSQC ([D_6]-benzene, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.03 / 19.8 (7-H / C7), 2.10 / 50.9 (8-H, 8'-H / C8), 2.55 / 30.1 (9-H / C9), 3.77 / 72.2 (C_5H_3), 3.99 / 67.6 (C_5H_4), 4.04 / 70.2 (C_5H_3), 4.08 / 69.4 (C_5H_4), 4.10 / 68.3 (C_5H_3), 4.22 / 69.3 (C_5H_4), 4.70 / 74.2 (C_5H_4), 5.35 / 116.8 ($C_5H_4^{Zr}$), 5.93 / 115.7 ($C_5H_4^{Zr}$), 6.69 / 120.2 ($C_5H_4^{Zr}$), 6.85 / 124.9, 126.7 (Flu), 7.05 / 125.0 (Flu), 8.04 / 125.7 (Flu), 7.26 / 125.5 (Flu), 7.40 / 129.6 (Flu), 8.18 / 125.5 (Flu), 8.26 / 124.1 (Flu).

Due to the broadness of the ^{13}C signals only the following cross-peaks were observed:
^{1}H,^{13}C GHMBC ([D_6]-benzene, 600 MHz / 151 MHz, 298 K): δ (^{1}H) / δ (^{13}C) = 1.03 / 25.2, 90.9 (7-H / C6, C1), 2.55 / 90.9 (6-H / C1), 3.77 / 81.3 (C_5H_3 / *i*-C_5H_3), 3.99 / 69.3, 74.2 (C_5H_4 / C_5H_4), 4.04 / 81.3 (C_5H_3 / *i*-C_5H_3), 4.10 / 81.3 (C_5H_3 / *i*-C_5H_3), 4.70 / 69.3, 69.4, 90.9 (C_5H_4 / C_5H_4, C1), 6.85 / 94.3, 125.0, 126.7 (Flu / C15, Flu), 7.05 / 124.9 (Flu / Flu), 8.04 / 126.7 (Flu 7 Flu), 7.26 / 124.1 (Flu' / Flu'), 7.40 / 125.5 (Flu' / Flu'), 8.18 /(125.7, 129.6 (Flu' / Flu'), 8.26 / 94.3, 125.5 (Flu' / C15, Flu').

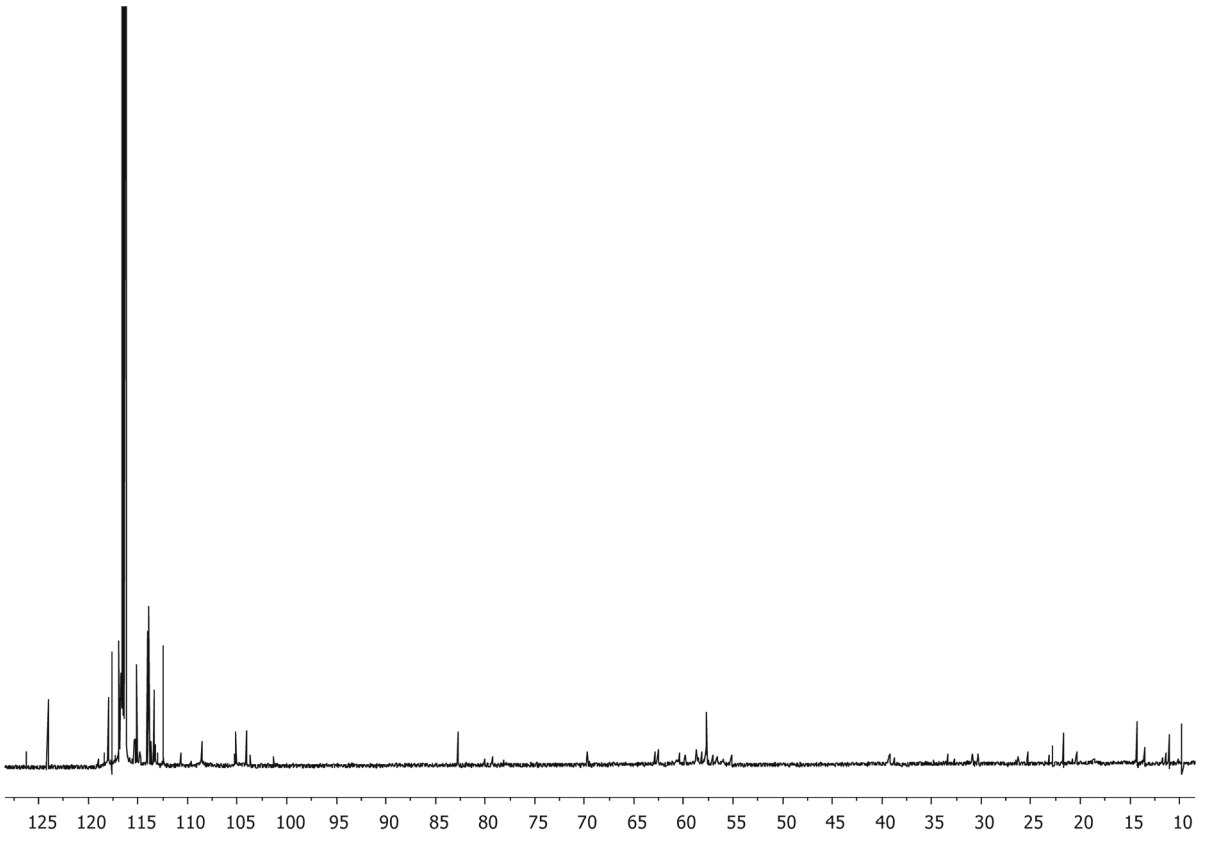
Elemental Analysis $C_{32}H_{26}Cl_2FeZr$ (628.52 g/mol) requires C 61.15, H 4.17, N found C 60.72, H 4.75.

Melting Point 158°C, decomposition.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3086 b, 2959 w, 2926 w, 2868 w, 1600 w, 1475 s, 1447 s, 1374 w, 1321 w, 1306 w, 1233 m, 1208 m, 1150 w, 1092 w, 1041 s, 1023 s, 1005 m, 939 w, 919 w, 889 m, 805 s.

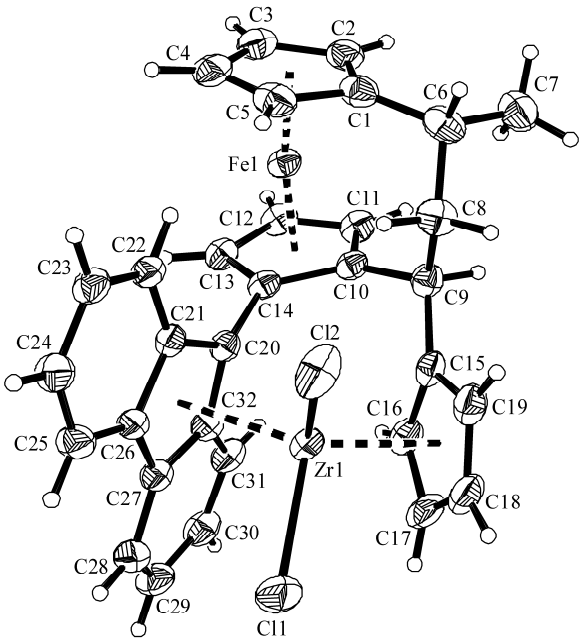


^{1}H NMR (600 MHz, C_6D_6, 298 K) of **20**



^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K) of **20**

X-ray crystal structure analysis: Crystal data for $C_{32}H_{26}Cl_2FeZr$ (**20**), M = 628.50, triclinic, space group P1bar (No. 2), a = 11.1780(2), b = 15.2159(2), c = 15.4479(3) Å, α = 76.2ß8(1), β = 83.575(1), γ = 78.305(1)°, V = 2493.11(7) Å^3, D_c = 1.674 g cm^{-3}, μ = 1.235 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 223(2) K, 23225 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 11587 independent (R_{int} = 0.044), and 10563 observed reflections [I ≥ 2σ(I)], 651 refined parameters, R = 0.042, wR^2 = 0.103.



Polymerization

Homopolymerization

Polymerization reactions were performed in a thermostated Büchi glass autoclave system. The autoclave was evacuated and charged with argon and this procedure was repeated three times. Afterwards the autoclave was charged with 200 ml of toluene and methylalumoxane [(MAO), 1.6 M solution in toluene] were added. A solution of a precatalyst in toluene was preactivated with a solution of MAO in toluene and placed into the addition funnel on the autoclave. The autoclave was evacuated for a short time and then charged with the monomer (2 bar). The monomer pressure was controlled with a bpc 1202 Büchi pressflow gas controller (with programm "bls2"). The polymerization temperature was kept constant during the polymerization with a cryostat. The mixture was stirred with a speed of 600 rpm. When the pressure had stabilized at 2 bar, the catalyst solution was added via the addition funnel into the autoclave. At the end of the polymerization run the reaction was quenched carefully by adding a mixture of methanol and 2 N aqueous HCl solution (1:1). The excess of monomer was vented.

Ethene Homopolymerization: Workup of the Polymer

After polymerization the reaction mixture was poured into methanol (1 L). The polymer preciptipated as a white solid. It was filterted and washed with methanol, water and acetone. The polymer was collected and dried overnight at 100°C. Characterization of the obtained polyethylene samples was carried out by DSC and by $^{13}C\{^{1}H\}$ NMR.

The $^{13}C\{^{1}H\}$ NMR measurement were performed at 350 K overnight using a Bruker AC200 spectrometer using a [D_5] bromobenzene solution of the polymer.

Propene Homopolymerization: Workup of the Polymer

After the polymerization experiment the reaction mixture was poured into a separating funnel and 4 N HCl (200 ml) was added. The polypropylene was extracted with toluene (3x 200 ml). Then the organic phases were combined, washed with water and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation.

Characterization of the obtained polypropylene samples were carried out using GPC and by $^{13}C\{^{1}H\}$ NMR spectroscopy. For the NMR experiment, 150 mg of the polypropylene sample

was dissolved in [D_5] bromobenzene or in a mixture of 1,2,4-trichlorobenzene (1 ml) and [D_6] benzene (0.3 ml). The $^{13}C\{^1H\}$ NMR measurements were performed at 350 K overnight using a Bruker AC200 NMR spectrometer.

Catalytic Ethylene / 1-Octene Copolymerization

Polymerization reactions were performed in a thermostated Büchi glass autoclave system. The autoclave was evacuated and charged with argon and this procedure was repeated three times. Afterwards the autoclave was charged with 200 ml of toluene and methylalumoxane [(MAO), 1.6 M solution in toluene] and the 1-octene (30 ml) was added. A solution of a precatalyst in toluene was preactivated with a solution of MAO in toluene and placed into the addition funnel on the autoclave. The autoclave was evacuated for a short periode of time and then charged with the monomer (2 bar). The monomer pressure was controlled by the bpc 1202 Büchi pressflow gas controller. The polymerization temperature was kept constant during the polymerization with a cryostat. The mixture was stirred with a speed of 600 rpm. When the pressure had stabilized at 2 bar, the solution of the catalyst was added via the addition funnel into the autoclave. At the end of the polymerization reaction the mixture was quenched by carefully adding a mixture of methanol and 2 N aqueous HCl solution (1:1). The excess of monomer was vented.

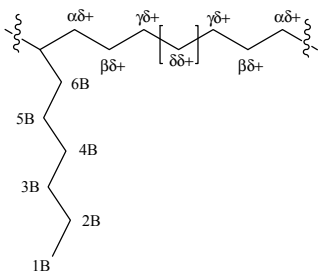
Catalytic Ethylene / 1-Octene Copolymerization: Workup of the Polymer

After polymerization the reaction mixture was filtered and the residue was washed with toluene, methanol, water and acetone. The obtained polyethylene was dried overnight at 100°C. Characterization of the obtained polyethylene samples was carried out by $^{13}C\{^1H\}$ NMR spectroscopy. The solvent of the filtrate was removed by rotary evaporation. The residue was taken up in toluene, placed in a separating funnel and 4 N HCl (200 ml) was added. The copolymer was extracted with toluene (3×200 ml). The organic phases were combined, washed with water and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation

The $^{13}C\{^{1}H\}$ NMR experiments of the copolymers were carried out in [D_6]benzene at 300 K. The ethylene:1-octene ratio was determined by integration of the respective ^{13}C NMR signals.[1]

$a = I(C_{\delta\delta+}, C_{3B}) / I(C_{\alpha\delta+}, C_{6B}) = I(C_{\delta\delta+}, C_{3B}) / I(C_{\beta\delta+}; C_{5B})$

Ethylene / Octene = [(3a-1) / 2]+2



^{13}C NMR $\{^{1}H\}$ (50.3 MHz, [D_6] benzene, 298K): δ = 37.7 (C7), 34.3 ($C_{\alpha\delta+}$, C_{6B}), 32.5 ($C_{\gamma\delta+}$, C_{4B}), 30.3 ($C_{\delta\delta+}$, C_{3B}), 27.3 ($C_{\beta\delta+}$, C_{5B}), 23.3 (C_{2B}), 14.5 (C_{1B}).

[1] J. C. Randall, *JMS-Rev. Macromol. Chem. Phys.* **1989**, **C29** (2&3), 201. b) W.-J. Wang, E. Kolodka, S. Zhu, A. E. Hamielec, *J. Polym. Sci. A* **1999**, *37*, 2949. c) W. Liu, D. G. Ray, P. L. Rinaldi, *Macromolecules* **1999**, 32, 3817.

Melting points PE

Cat	**20**	**8**	**11a**	**11b**
m.p. PE [°C]	127	129	-	128

Ethene polymerizations (activation with MAO):

cat	**cat** mg (mmol)	**Al : Zr**	**PE** [g]	**T** [°C]	**t** [min]	**Act.** [g/(mmol·h·bar)]
20	1.89 (0.003)	1500	3.2	20	30	1100
	1.89 (0.003)	1500	3.4	20	30	1100
	1.89 (0.003)	1500	5.9	20	30	2000
8	12.6 (0.02)	1600	0.2	20	60	10
	12.6 (0.02)	1600	0.3	20	60	10
11b	5.8 (0.01)	1500	1.7	20	60	100
	5.8 (0.01)	1500	1.6	20	60	100
11a	15.5 (0.02)	1300	1.18	25	15	100
	12.9 (0.02)	1300	0.80	25	60	20

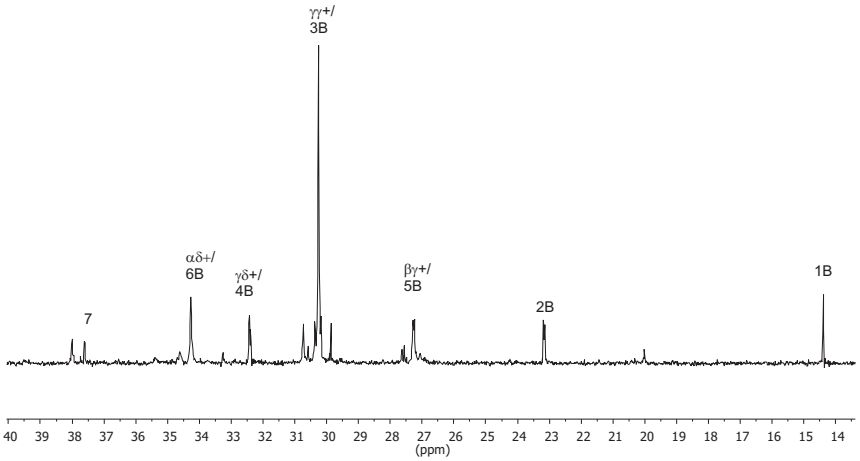
Propene polymerizations:

cat	**cat** mg(mmol)	**Al:Zr**	**PP** [g]	**T** [°C]	**t** [min]	**mmmm** [%]	**Mn**	**Mw**	**PDI**	**act.** [g/(mmol·h·bar)]
20	12.6 (0.02)	1600	8.5	20	60	5.7	35900	55700	1.6	210
	6.3 (0.01)	1600	5.5	20	60					280
	6.3 (0.01)	1600	3.5	60	60	n.a.	1800	7200	3.9	190

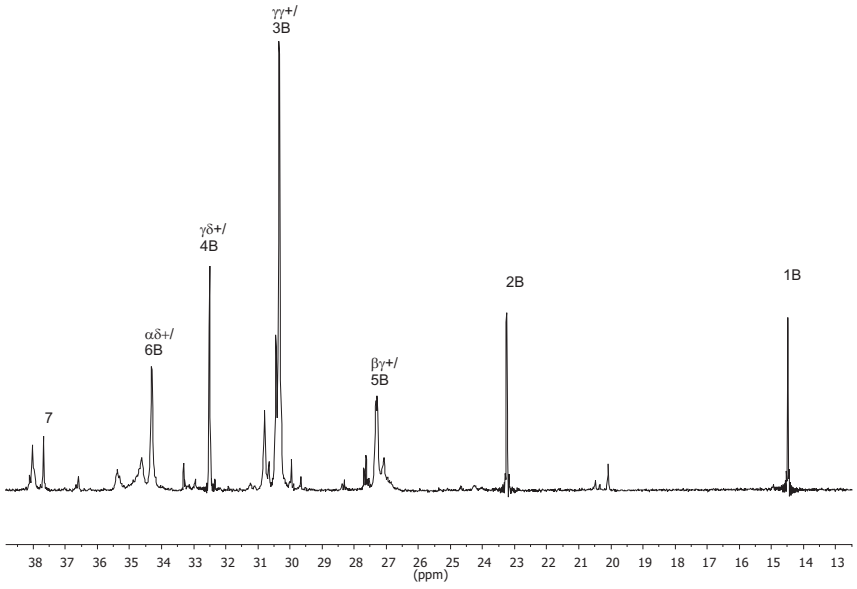
Copolymerizations:

1-Octene / ethene copolymerisations:

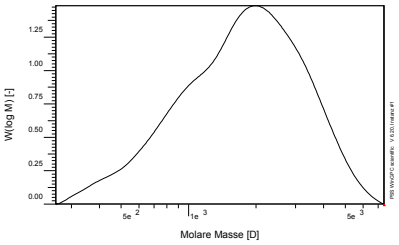
	#.	cat mg (mmol)	Al : Zr	PE [g]	CoPo [g]	T [°C]	t [min]	act. PE (CoPo) [g/(mmol·h·bar)]
11b	1	11.7 (0.02)	1500	0.7	0.4	25	60	20 (10)
	2	11.7 (0.02)	1500	0.9	0.7	25	60	20 (20)
	3	11.7 (0.02)	1500	8.0	5.8	60	40	300 (220)
	4	11.7 (0.02)	1500	8.8	5.5	60	40	330 (210)



^{13}C NMR ([D_6] benzene, 50 MHz, 298 K); CoPo 1; cat.: **11b**



^{13}C NMR ([D_6] benzene, 50 MHz, 298 K); CoPo 3; cat.: **11b**



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Integration bis : Dienstag 09.02.10 10:32:21 22.633 ml
Kalibration : PolystyreneMEM05_03_2008 39 bar.CAL
MHK - A (Kal.): 0.000E+0
Int.Stand.-K : 50.000 ml
Pumpe : HP1100
Konzentration : 1.000 g/l
Säule 1 : PSS SDV 5µ Guard
Säule 2 : SDV 5µ 1e5
Säule 3 : SDV 5µ 1e3
Detektor 1 : UV 254nm
Detektor 2 : RI
Operateur : gpcuser

Eluent : THF
MHK - K (Kal.): 1.000E+0 ml/g
Int.Stand.-M : ------- ml
Flußrate : 1.000 ml/min
Injektvolumen : 100.000 ul
Temperatur : 35.000 C
Temperatur : 35.000 C
Temperatur : 35.000 C
Versatz : 0.000 ml
Versatz : 0.150 ml
Messintervall : 1.000 sec

RI

Mn :	1.3813e3	g/mol
Mw :	2.0315e3	g/mol
Mz :	2.7218e3	g/mol
Mv :	0.000000	g/mol
D :	1.4708e0	
[n]:	0.000000	ml/g
Vp :	2.0194e1	ml
Mp :	1.9658e3	g/mol
FI :	1.990e-1	mV
< 255	0.00	
w% :	100.00	
> 7444	0.00	

Projekt : C:\WINGPC_6#1\ANLAGE1.LDA
Datum : Dienstag 09.02.10 10:48:34
Kostenstelle :
Zeichen :

GPC