Unusual Carbamate-directed CH-activation at an Annulated Ferrocenophane Framework

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Supporting Information

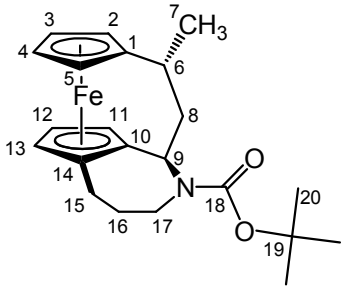
Table of Contents

General Information. All reactions with air- and moisture sensitive compounds were carried out under argon atmosphere with Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds. Elemental analyses: Foss-Heraeus CHNO-Rapid. NMR: Bruker AC 200 P (^{1}H, 200 MHz), Varian 500 MHz INOVA (^{1}H, 500 MHz; ^{13}C, 126 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz). Assignments of the resonances are supported by 2D experiments. Melting points / decomposition temperature: DSC 2010 (TA-Instruments) apparatus. Determined by the baseline method. IR: Varian 3100 FT-IR (ExcaliburSeries) spectrometer. X-ray crystal structure analysis: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a 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 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). Graphics show the thermal ellipsoids with 50 % probability, *R* values are given for the observed reflections, wR^2 values for all reflections.

Materials. Compounds **5** [P. Liptau, S. Knüppel, G. Kehr, O. Kataeva, R. Fröhlich, G. Erker, *J. Organomet. Chem*. **2001**, *637-639*, 621-630], **6** [J.-B. Sortais, T. Voss, G. Kehr, R. Fröhlich, G. Erker, *Chem. Commun.* **2009**, 7417-7418], **7** [R. B. Boers, Y. P. Randulfe, H. N. S. v. d. Haas, M. v. Rossum-Baaen, J. Lugtenburg, *Eur. J. Org. Chem.* **2002**, 2094-2108], **8-10** and **14** [T. Voss, J.-B. Sortais, R. Fröhlich, G. Kehr, G. Erker, *Organometallics*, submitted] were prepared according to literature procedures.

Preparation of compound 4. Procedure A: Triethylamine (100 µL, 73.0 mg, 0.72 mmol) and di-*tert*-butyldicarbonate (148 mg, 0.68 mmol) were added to a solution of **13** (200 mg, 0.68 mmol) in CH_2Cl_2 (50 mL) at 0 °C. The reaction mixture was stirred at room temperature overnight, toluene (10 mL) was added and all volatiles were removed *in vacuo*. After column chromatography at silica gel using dichloromethane as eluent, product **4** (188 mg, 0.48 mmol, 71%) was obtained as yellow powder.

Procedure B: Compound **17** (75 mg, 0.19 mmol) was dissolved in a mixture of MeOH (2 mL) and THF (2 mL) and hydrogenated for 5 h in the presence of Pd-C catalyst (6 mg, 10% Pd, 0.006 mmol Pd, 3 mol%) at $p(H_2) = 2.7$ bar. The catalyst was separated by filtration and the solvent removed *in vacuo* to yield the Boc-protected amine **4** (70 mg, 0.18 mmol, 95%). Crystals suitable for the X-ray crystal structure analysis were obtained by evaporation from a saturated etheral solution.



^{1}H NMR (500 MHz, [D_8]-toluene, 348 K): δ = 4.98 (br m, 1H, 9-H); 4.18 (br d, ^3J = 14.4 Hz, 1H, 17-H); 4.05 (m, 1H, 4-H); 3.86 (m, 1H, 2-H); 3.84 (br, 1H, 11-H); 3.78 (m, 1H, 3-H); 3.68 (m, 1H, 13-H); 3.65 (m, 1H, 12-H); 3.25 (m, 1H, 5-H); 2.96 (m, 1H, 17-H'); 2.57 (m, 1H, 8-H); 2.55 (m, 1H, 6-H); 2.52 (m, 1H, 15-H); 2.19 (dt, ^3J = 15.1 Hz, 3.8 Hz, 1H, 15-H'); 1.68 (dt, ^3J = 13.1 Hz, 3.9 Hz, 1H, 8-H'); 1.42 (m, 2H, 16-H); 1.33 (s, 9H, 20-H); 1.10 (d, ^3J = 7.4 Hz, 3H, 7-H).

^{13}C{^{1}H} NMR (126 MHz, [D_8]-toluene, 348 K): δ = 155.3 (C-18); 92.6 (C-1); 88.5 (C-14); 83.0 (C-10); 79.0 (C-19); 74.7 (C-5); 71.4 (C-13); 70.4 (C-11); 69.6 (C-4); 68.2 (C-2); 66.8 (C-3); 65.3 (C-12); 48.0 (C-9); 45.2 (C-8); 44.1 (C-17); 30.2 (C-16); 29.7 (C-15); 28.7 (C-20); 28.4 (C-6); 16.5 (C-7).

^{1}H TOCSY (500 MHz, [D_8]-toluene, 348 K): δ^1H_{irr} / δ^1H_{res} = 4.18 / 2.96, 2.52, 1.42 (17-H / 17-H', 15-H, 16-H); 4.05 / 3.86, 3.78, 3.25 (4-H / 2-H, 3-H, 5-H); 3.86 / 4.05, 3.78, 3.25 (2-H / 4-H, 3-H, 5-H); 3.84 / 3.68, 3.65 (11-H / 13-H, 12-H); 3.78 / 4.05, 3.86, 3.25 (3-H / 4-H, 2-H, 5-H); 3.68 / 3.84, 3.65 (13-H / 11-H, 12-H); 3.65 / 3.84, 3.68 (12-H / 11-H, 13-H); 3.25 / 4.05, 3.86, 3.78 (5-H / 4-H, 2-H, 3-H); 2.96 / 4.18, 2.19, 1.42 (17-H' / 17-H, 15-H', 16-H); 2.19 / 2.52, 1.42 (15-H' / 15-H, 16-H); 1.42 / 4.18, 2.96, 2.52, 2.19 (16-H / 17-H, 17-H', 15-H, 15-H'); 1.10 / 4.98, 2.58, 2.57, 1.68 (7-H / 9-H, 8-H, 6-H, 8-H').

^{1}H NOE (500 MHz, [D$_8$]-toluene, 348 K): δ^1H_{irr} / δ^1H_{res} = 3.86 / 3.78, 1.10 (2-H / 3-H, 7-H); 2.96 / 4.18, 2.52 (17-H' / 17-H, 15-H); 2.19 / 2.52, 1.42 (15-H' / 15-H, 16-H); 1.68 / 2.57 (8-H' / 8-H); 1.10 / 4.98, 3.86, 2.57, 1.68 (7-H / 9-H, 2-H, 8-H, 8-H').

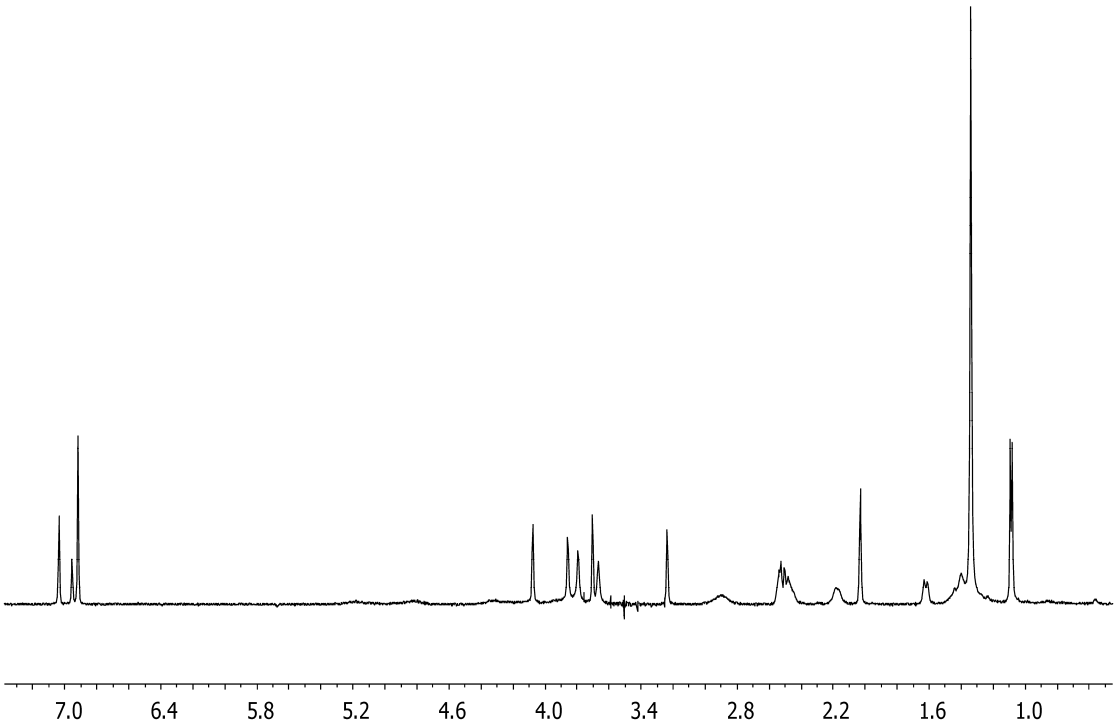
^{1}H, ^{1}H GCOSY (500 MHz, [D$_8$]-toluene, 348 K): δ = 4.98 / 2.57 (9-H / 8-H); 4.18 / 2.96, 1.42 (17-H / 17-H', 16-H); 4.05 / 3.86, 3.78, 3.25 (4-H / 2-H, 3-H, 5-H); 3.86 / 4.05, 3.78, 3.25 (2-H / 4-H, 3-H, 5-H); 3.84 / 3.68, 3.65 (11-H / 13-H, 12-H); 3.78 / 4.05, 3.86, 3.25 (3-H / 4-H, 2-H, 5-H); 3.68 / 3.84, 3.65 (13-H / 11-H, 12-H); 3.65 / 3.84, 3.68 (12-H / 11-H, 13-H); 3.25 / 4.05, 3.86, 3.78 (5-H / 4-H, 2-H, 3-H); 2.96 / 4.18, 1.42 (17-H' / 17-H, 16-H); 2.57 / 4.98, 1.68 (8-H / 9-H, 8-H'); 2.55 / 1.68, 1.10 (6-H / 8-H', 7-H); 2.52 / 2.19, 1.42 (15-H / 15-H', 16-H); 2.19 / 2.52, 1.42 (15-H' / 15-H, 16-H); 1.68 / 2.57, 2.55 (8-H' / 8-H, 6-H); 1.42 / 4.18, 2.96, 2.52, 2.19 (16-H / 17-H, 17-H', 15-H, 15-H'); 1.10 / 2.55 (7-H / 6-H).

^{1}H, ^{13}C GHSQC (500 MHz / 126 MHz, [D$_8$]-toluene, 348 K): δ^1H / $\delta^{13}C$ = 4.98 / 48.0 (9); 4.18 / 44.1 (17); 4.05 / 69.6 (4); 3.86 / 68.2 (2); 3.84 / 70.4 (11); 3.78 / 66.8 (3); 3.68 / 71.4 (13); 3.65 / 65.3 (12); 3.25 / 74.7 (5); 2.96 / 44.1 (17); 2.57 / 45.2 (8); 2.55 / 28.4 (6); 2.52 / 29.7 (15); 2.19 / 29.7 (15); 1.68 / 45.2 (8); 1.42 / 30.2 (16); 1.33 / 28.7 (20); 1.10 / 16.5 (7).

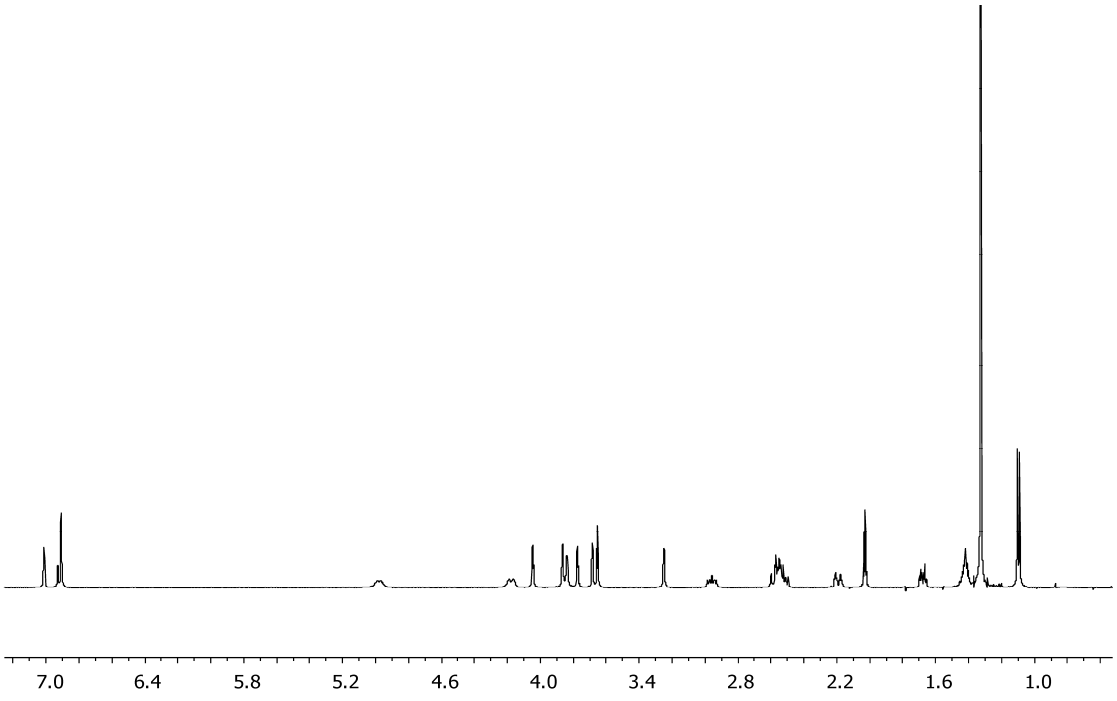
^{1}H, ^{13}C GHMBC (500 MHz / 126 MHz, [D$_8$]-toluene, 348 K): δ^1H / $\delta^{13}C$ = 4.05 / 92.6, 74.7, 68.2, 66.8 (4-H / C-1, C-5, C-2, C-3); 3.86 / 92.6, 74.7, 69.6, 66.8 (2-H / C-1, C-5, C-4, C-3); 3.84 / 88.5, 83.0, 71.4, 65.3 (11-H / C-14, C-10, C-13, C-12); 3.78 / 92.6, 74.7, 69.6, 68.2 (3-H / C-1, C-5, C-4, C-2); 3.68 / 88.5, 83.0, 70.4, 65.3 (13-H / C-14, C-10, C-11, C-12); 3.65 / 88.5, 83.0, 71.4, 70.4 (12-H / C-14, C-10, C-13, C-11); 3.25 / 92.6, 69.2, 68.2, 66.8 (5-H / C-1, C-4, C-2, C-3); 2.57 / 28.4, 16.5 (8-H / C-6, C-7); 2.55 / 45.2, 16.5 (6-H / C-8, C-7); 2.52 / 88.5, 83.0, 71.4, 44.1, 30.2 (15-H / C-14, C-10, C-13, C-17, C-16); 1.68 / 92.6, 83.0, 48.0, 28.4 (8-H' / C-1, C-10, C-9, C-6); 1.33 / 155.3, 79.0 (20-H / C-18, C-19); 1.10 / 92.6, 45.2, 28.4 (7-H / C-1, C-8, C-6).

Elemental Analysis: $C_{22}H_{29}FeNO_2$ requires C: 66.84, H: 7.39, N: 3.54; found C: 66.43, H: 6.77, N: 3.30.

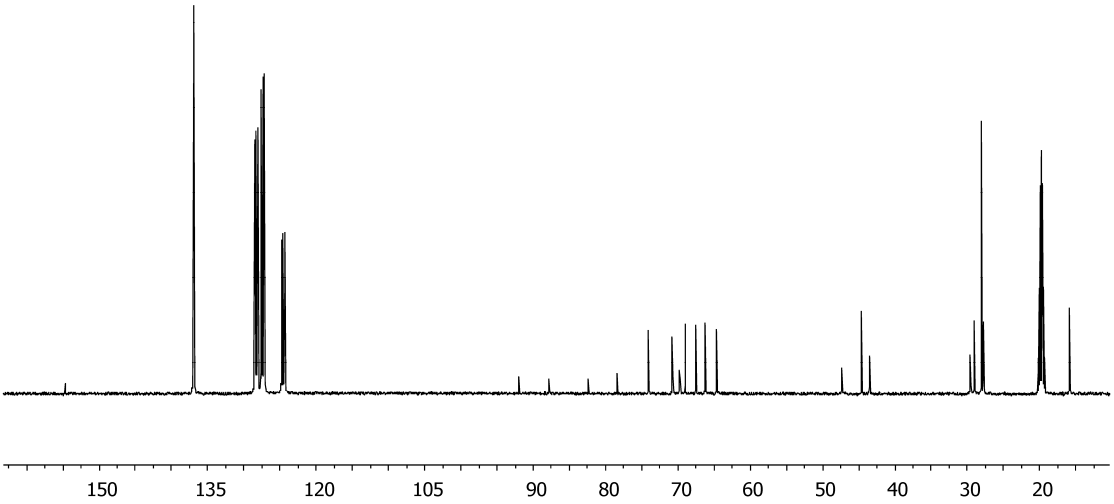
Infrared Spectroscopy: $\tilde{\nu}$ (ATR / cm^{-1}) = 2964 (m), 2914 (w), 2866 (w), 1680 (s), 1453 (m), 1392 (m), 1361 (m), 1296 (m), 1255 (m), 1169 (s), 1152 (m), 1099 (m), 1043 (m), 1025 (m), 940 (m), 887 (w).



^{1}H NMR (500 MHz, 298 K) in [D_8]-toluene of compound **4**.

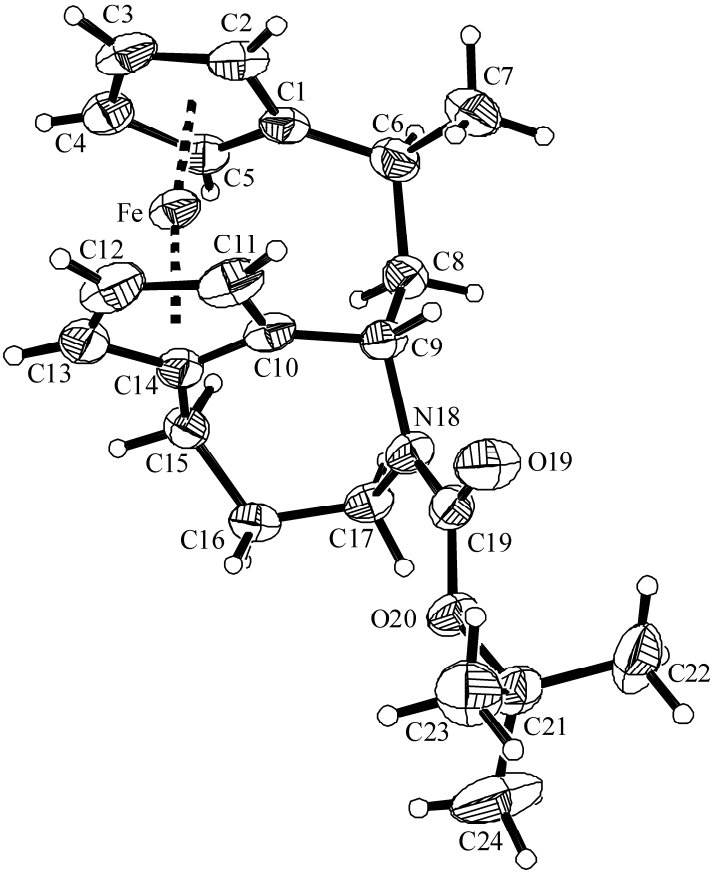


^{1}H NMR (500 MHz, 348 K) in [D_8]-toluene of compound **4**.

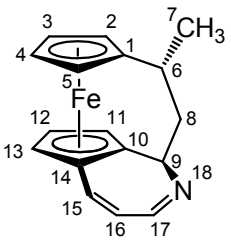


$^{13}C\{^{1}H\}$ NMR (126 MHz, 348 K) in [D_8]-toluene of compound **4**.

Crystal data for $C_{22}H_{29}FeNO_2$ (**4**), M = 395.31, triclinic, P1bar (No. 2), a = 9.7521(2), b = 9.9436(2), c = 10.8684(3) Å, α = 111.070(1), β = 99.023(1), γ = 94.053(1)°, V = 962.01(4) Å^3, D_c = 1.365 g cm^{-3}, μ = 0.800 mm^{-1}, F(000) = 420, Z = 2, λ = 0.71073 Å, T = 223(2) K, 8318 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 4473 independent (R_{int} = 0.041), and 4042 observed reflections [I ≥ 2σ(I)], 239 refined parameters, R = 0.049, wR^2 = 0.116, GoF = 1.066.



Preparation of compound 12. In a 200 mL teflon screw-capped ampoule, a solution of **10** (1.72 g, 5.10 mmol) in acetonitrile (10 mL) was treated with methyl iodide (3.20 mL, 7.24 g, 51.0 mmol, 10 eq.), where upon the orange trimethylammonium salt started to precipitate. After one hour of stirring at room temperature all volatiles were removed *in vacuo* and the residue was suspended in a 2:1 mixture of benzene and aqueous ammonia (75 mL). The ampoule was closed tightly and the suspension heated to 110 °C until the aqueous layer turned colorless (approximately 4 h). The reaction mixture was cooled to room temperature, the ampoule depressurized carefully, the solvents removed *in vacuo* and the resulting residue dissolved in dichloromethane (50 mL). After washing with 1M sodium hydroxide solution, water and brine (30 mL each), the organic layer was evaporated to dryness. The remaining solid was dissolved in diethylether (60 mL), dried over $MgSO_4$ and concentrated to yield the product as dark red powder in 95% yield (1.41 g, 4.85 mmol).



^{1}H NMR (500 MHz, [D$_6$]-benzene, 298 K): δ = 7.77 (d, ^3J = 3.7 Hz, 1H, 17-H); 6.32 (d, ^3J = 11.1 Hz, 1H, 15-H); 5.68 (dd, ^3J = 11.1 Hz, 3.7 Hz, 1H, 16-H); 5.09 (dd, ^3J = 11.8 Hz, 3.9 Hz, 1H, 9-H); 4.11 (m, 1H, C_5H_4); 4.03 (m, 1H, 12-H); 3.93 (m, 1H, 11-H); 3.92 (m, 1H, 13-H); 3.88, 3.81, 3.68 (each m, each 1H, C_5H_4); 2.37 (ddd, ^2J = 13.4 Hz, ^3J = 11.8 Hz, 3.1 Hz, 1H, 8-H); 2.31 (m, 1H, 6-H); 2.02 (ddd, ^2J = 13.4 Hz, ^3J = 4.4 Hz, 3.9 Hz, 1H, 8-H'); 1.05 (d, ^3J = 7.1 Hz, 3H, 7-H).

^{13}C{^{1}H} NMR (126 MHz, [D$_6$]-benzene, 298 K): δ = 157.8 (C-17); 137.2 (C-15); 123.4 (C-16); 94.4 (C-1); 81.6 (C-14); 80.5 (C-10); 71.7 (C_5H_4); 71.6 (C-11); 70.2 (C-12); 70.0 (C-13); 69.2, 68.6 (C_5H_4); 68.3 (C_5H_4); 53.6 (C-9); 44.0 (C-8); 27.0 (C-6); 16.6 (C-7).

^{1}H TOCSY (500 MHz, [D$_6$]-benzene, 298 K): δ^1H_{irr} / δ^1H_{res} = 7.77 / 6.32, 5.68 (17-H / 15-H, 16-H); 5.09 / 2.37, 2.31, 2.023, 1.05 (9-H / 8-H, 6-H, 8-H', 7-H); 4.11 / 3.88, 3.81, 3.68 (C_5H_4); 4.03 / 3.93, 3.92 (12-H / 11-H, 13-H); 3.93 / 4.03, 3.92 (11-H / 12-H, 13-H); 3.88 / 4.11, 3.81, 3.68 (C_5H_4); 3.81 / 4.11, 3.88, 3.68 (C_5H_4); 3.68 / 4.11, 3.88, 3.81 (C_5H_4); 2.37 / 5.09, 2.31, 2.02, 1.05 (8-H / 9-H, 6-H, 8-H', 7-H); 2.31 / 5.09, 2.02, 1.05 (6-H / 9-H, 8-H', 7-H); 2.02 / 5.09, 2.37, 2.31, 1.05 (8-H' / 9-H, 8-H, 6-H, 7-H); 1.05 / 5.09, 2.37, 2.31 (7-H / 9-H, 8-H, 6-H).

^{1}H, ^{1}H GCOSY (500 MHz, [D$_6$]-benzene, 298 K): δ = 7.77 / 5.68 (17-H / 16-H); 6.32 / 5.68 (15-H / 16-H); 5.68 / 7.77, 6.32 (16-H / 17-H, 15-H); 5.09 / 2.37, 2.02 (9-H / 8-H, 8-H'); 4.11 / 3.88, 3.81, 3.68 (C_5H_4); 4.03 / 3.93, 3.92 (12-H / 11-H, 13-H); 3.93 / 4.03 (11-H /

12-H); 3.88 / 4.11, 3.81, 3.68 (C_5H_4); 3.81 / 4.11, 3.88, 3.68 (C_5H_4); 3.68 / 4.11, 3.88, 3.81 (C_5H_4); 2.37 / 5.09, 2.02 (8-H / 9-H, 8-H'); 2.31 / 1.05 (6-H / 7-H); 2.02 / 5.09, 2.37 (8-H' / 9-H, 8-H); 1.05 / 2.31 (7-H / 6-H).

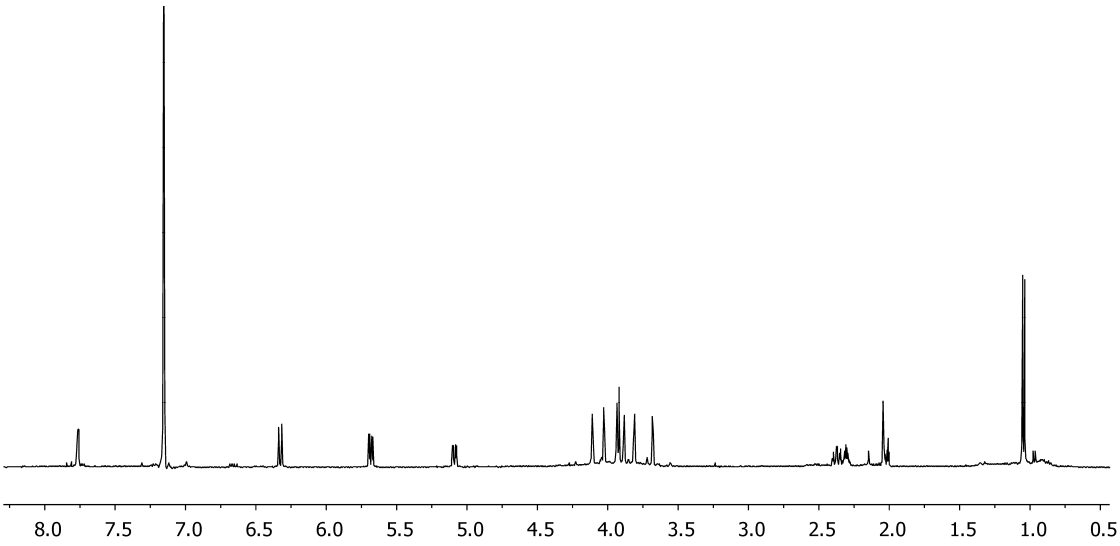
^{1}H, ^{13}C GHSQC (500 MHz / 126 MHz, [D_6]-benzene, 298 K): δ^1H / δ^{13}C = 7.77 / 157.8 (17); 6.32 / 137.2 (15); 5.68 / 123.4 (16); 5.09 / 53.6 (9); 4.11 / 69.2 (C_5H_4); 4.03 / 70.2 (12); 3.93 / 71.6 (11); 3.92 / 70.0 (13); 3.88 / 68.6 (C_5H_4); 3.81 / 68.3 (C_5H_4); 3.68 / 71.7 (C_5H_4); 2.37 / 44.0 (8); 2.31 / 27.0 (6); 2.02 / 44.0 (8); 1.05 / 16.6 (7).

^{1}H, ^{13}C GHMBC (500 MHz / 126 MHz, [D_6]-benzene, 298 K): δ^1H / δ^{13}C = 7.77 / 137.2, 123.4 (17-H / C-15, C-16); 6.32 / 157.8, 80.5, 70.0 (15-H / C-17, C-10, C-13); 5.68 / 157.8, 81.6 (16-H / C-17, C-14); 5.09 / 157.8, 81.6, 71.6, 44.0 (9-H / C-17, C-14, C-11, C-8); 4.03 / 81.6, 80.5, 71.6 (12-H / C-14, C-10, C-11); 3.93 / 81.6, 80.5, 70.0 (11-H / C-14, C-10, C-13); 3.92 / 81.6, 80.5, 70.0 (13-H / C-14, C-10, C-13); 3.88 / 94.4, 69.2, 68.3 (C_5H_4 / C-1, C_5H_4); 3.81 / 94.4 (C_5H_4 / C-1); 3.68 / 94.4, 69.2, 68.3 (C_5H_4 / C-1, C_5H_4); 2.37 / 94.4, 80.5, 53.6, 27.0, 16.6 (8-H / C-1, C-10, C-9, C-6, C-7); 2.31 / 53.6 (6-H / C-9); 2.02 / 94.4, 80.5, 53.6, 27.0, 16.6 (8-H' / C-1, C-10, C-9, C-6, C-7); 1.05 / 94.4, 44.0, 27.0 (7-H / C-1, C-8, C-6).

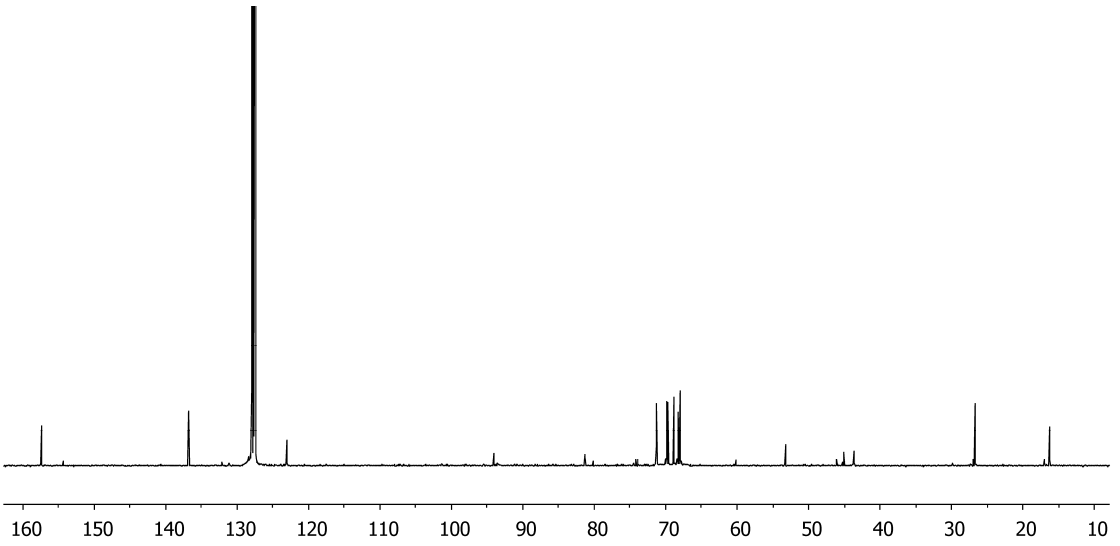
Elemental Analysis: $C_{17}H_{17}FeN$ requires C: 70.12, H: 5.88, N: 4.81; found C: 70.87, H: 6.27, N: 3.93.

Melting Point: 111 °C.

Infrared Spectroscopy: $\tilde{\nu}$ (ATR /cm^{-1}) = 3083 (w), 2959 (m), 2920 (m), 2861 (m), 1667 (m), 1628 (s), 1579 (s), 1451 (m), 1391 (m), 1375 (m), 1208 (m), 1259 (w), 1190 (w), 1118 (m), 1103 (m), 1028 (s), 997 (m), 912 (w), 856 (m), 844 (w), 802 (s).

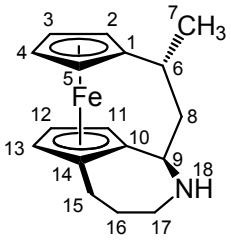


^{1}H NMR (500 MHz, 298 K) in [D_6]-benzene of compound **12**.



^{13}C{^{1}H} NMR (126 MHz, 298 K) in [D_6]-benzene of compound **12**.

Preparation of compound 13. To a solution of **12** (500 mg, 1.72 mmol) in a 1:1 mixture of THF and methanol (15 mL), Pd-C catalyst (20 mg, 10% Pd, 0.02 mmol Pd, 1mol%) was added and the resulting suspension was stirred for 10 h under a hydrogen atmosphere ($p(H_2)$ = 2.0 bar) at ambient temperature. After filtration over celite, the filtrate was concentrated to yield the product as orange oil in 80% yield (407 mg, 1.38 mmol). By storing a concentrated ethereal solution at −18 °C, single crystals suitable for the X-ray crystal structure analysis were obtained.



^{1}H NMR (600 MHz, [D$_8$]-toluene, 348 K): δ = 4.03 (m, 1H, C_5H_4); 3.84 (m, 1H, C_5H_4); 3.73 (m, 3H, C_5H_4, 2 × C_5H_3); 3.59 (m, 1H, C_5H_3); 3.39 (m, 1H, 9-H); 3.35 (m, 1H, C_5H_4); 3.00 (ddd, ^2J = 13.8 Hz, ^3J = 12.8 Hz, ^3J = 4.6 Hz, 1H, 15-H); 2.83 (ddd, ^2J = 14.0 Hz, ^3J = 8.1 Hz, ^3J = 4.8 Hz, 1H, 17-H); 2.59 (dt, ^2J = 14.0 Hz, ^3J = 7.2 Hz, 1H, 17-H'); 2.55 (m, 1H, 6-H); 2.00 (dt, ^2J = 13.8 Hz, ^3J = 3.7 Hz, 1H, 15-H'); 1.92 (dm, ^2J = 13.3 Hz, 1H, 8-H); 1.82 (ddd, ^2J = 13.3 Hz, ^3J = 10.7 Hz, 2.9 Hz, 1H, 8-H'); 1.62 (m, 1H, 16-H); 1.37 (m, 1H, 16-H'); 1.11 (d, ^3J = 7.1 Hz, 3H, 7-H); n.o. (18-H).

^{13}C{^{1}H} NMR (151 MHz, [D$_8$]-toluene, 348 K): δ = 91.3 (C-1); 90.0 (C-14); 88.7 (C-10); 77.3 (C_5H_4); 69.9 (C_5H_3); 68.5 (C_5H_4); 67.8 (C_5H_4, C_5H_3); 66.0 (C_5H_3); 65.0 (C_5H_4); 55.2 (C-9); 51.9 (C-8); 45.5 (C-17); 30.8 (C-16); 26.1 (C-15); 25.4 (C-6); 21.9 (C-7).

^{1}H TOCSY (600 MHz, [D$_8$]-toluene, 348 K): δ^1H_{irr} / δ^1H_{res} = 4.03 / 3.84, 3.73, 3.35 (C_5H_4); 3.84 / 4.03, 3.73, 3.35 (C_5H_4); 3.59 / 3.73 (C_5H_3); 3.39 / 2.56, 1.92, 1.82, 1.11 (9-H / 6-H, 8-H, 8-H', 7-H); 3.35 / 4.03, 3.84, 3.73 (C_5H_4); 3.00 / 2.83, 2.59, 2.00, 1.62, 1.37 (15-H / 17-H, 17-H', 15-H', 16-H, 16-H'); 2.83 / 3.00, 2.59, 2.00, 1.62, 1.37 (17-H / 15-H, 17-H', 15-H', 16-H, 16-H'); 2.00 / 3.00, 2.83, 2.59, 1.62, 1.37 (15-H' / 15-H, 17-H, 17-H', 16-H, 16-H'); 1.92 / 3.39, 2.55, 1.82, 1.11 (8-H / 9-H, 6-H, 8-H', 7-H); 1.37 / 3.00, 2.83, 2.59, 2.00, 1.62 (16-H' / 15-H, 17-H, 17-H', 15-H', 16-H); 1.11 / 3.39, 2.55, 1.92, 1.82 (7-H / 9-H, 6-H, 8-H, 8-H').

^{1}H, ^{1}H GCOSY (600 MHz, [D$_8$]-toluene, 348 K): δ = 4.03 / 3.84, 3.73, 3.35 (C_5H_4); 3.84 / 4.03, 3.73, 3.35 (C_5H_4); 3.73 / 4.03, 3.84, 3.59, 3.35 (C_5H_4 and C_5H_3 / C_5H_4, C_5H_4, C_5H_3, C_5H_4); 3.59 / 3.73 (C_5H_3); 3.39 / 1.92, 1.82 (9-H / 8-H, 8-H'); 3.35 / 4.03, 3.84, 3.73 (C_5H_4); 3.00 / 2.00, 1.62, 1.37 (15-H / 15-H', 16-H, 16-H'); 2.82 / 2.59, 1.62, 1.37 (17-H / 17-H', 16-H, 16-H'); 2.59 / 2.83, 1.62, 1.37 (17-H' / 17-H, 16-H, 16-H'); 2.55 / 1.82, 1.11 (6-H / 8-H', 7-H); 2.00 / 3.00, 1.62, 1.37 (15-H' / 15-H, 16-H, 16-H'); 1.92 / 3.39, 1.82 (8-H / 9-H, 8-H');

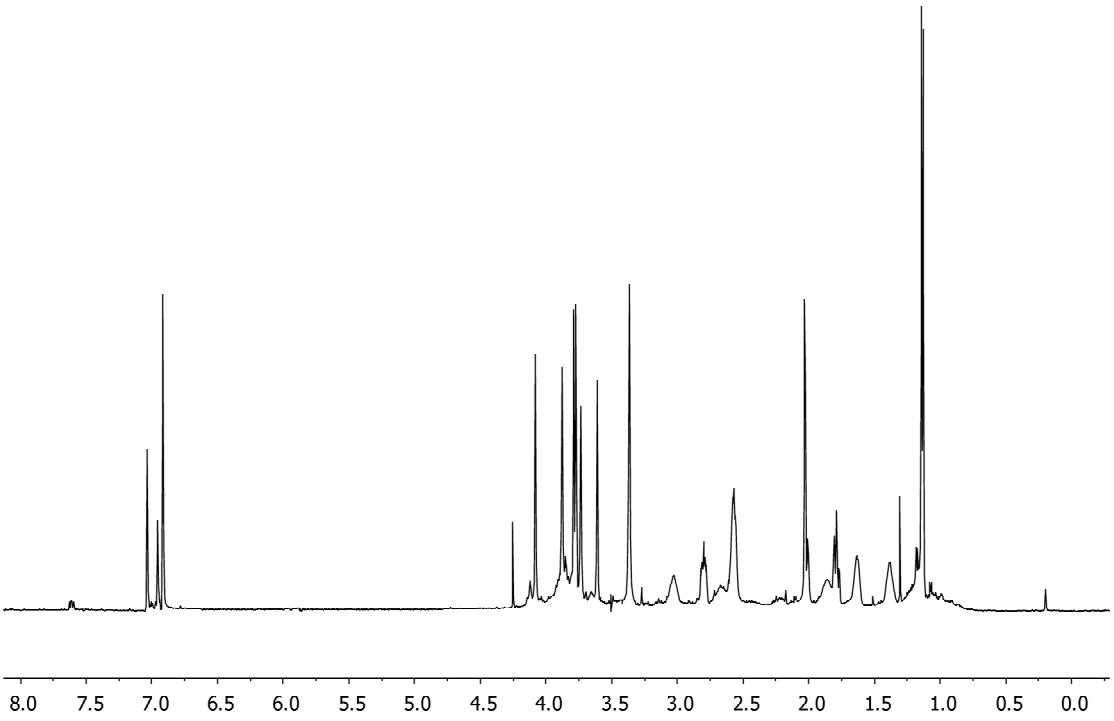
1.82 / 3.39, 2.55, 1.92 (8-H' / 9-H, 6-H, 8-H); 1.62 / 3.00, 2.83, 2.59, 2.00, 1.37 (16-H / 15-H, 17-H, 17-H', 15-H', 16-H'); 1.37 / 3.00, 2.83, 2.59, 2.00, 1.62 (16-H' / 15-H, 17-H, 17-H', 15-H', 16-H); 1.11 / 2.55 (7-H / 6-H).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, [D_8]-toluene, 348 K): δ^{1}H / δ^{13}C = 4.03 / 68.5 (C_5H_4); 3.84 / 67.8 (C_5H_4); 3.73 / 69.9 (C_5H_3); 3.73 / 66.0 (C_5H_3); 3.73 / 65.0 (C_5H_4); 3.59 / 67.8 (C_5H_3); 3.39 / 55.2 (9); 3.35 / 77.3 (C_5H_4); 3.00 / 26.1 (15); 2.83 / 45.5 (17); 2.59 / 45.5 (17); 2.55 / 25.4 (6); 2.00 / 26.1 (15); 1.92 / 51.9 (8); 1.82 / 51.9 (8); 1.62 / 30.8 (16); 1.37 / 30.8 (16); 1.11 / 21.9 (7).

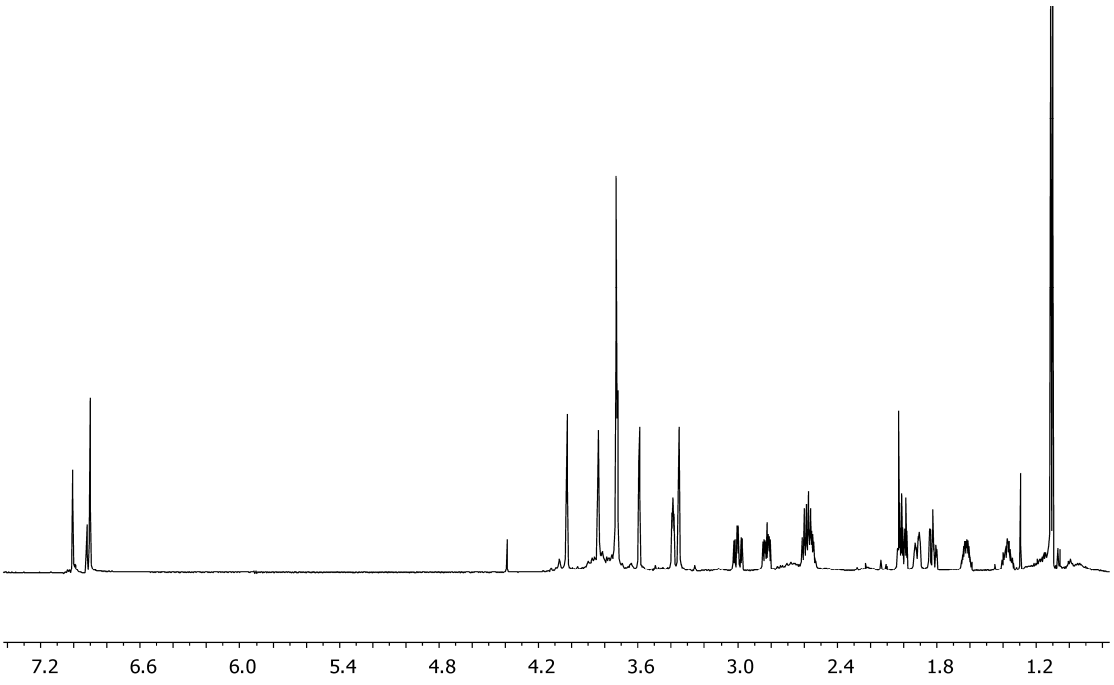
^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, [D_8]-toluene, 348 K): δ^{1}H / δ^{13}C = 4.03 / 91.3, 77.3, 67.8, 65.0 (C_5H_4 / C-1, C_5H_4); 3.84 / 91.3, 77.3, 68.5, 65.0 (C_5H_4 / C-1, C_5H_4); 3.73 / 91.3, 90.0, 88.7, 69.9, 67.8, 66.0 (C_5H_4 and C_5H_3 / C-1, C-14, C-10, C_5H_3, C_5H_3 and C_5H_4, C_5H_3); 3.59 / 90.0, 88.7, 69.9, 66.0 (C_5H_3 / C-14, C-10, C_5H_3); 3.39 / 45.5, 25.4 (9-H / C-17, C-6); 3.35 / 91.3, 67.8, 65.0 (C_5H_4 / C-1, C_5H_4); 3.00 / 90.0, 45.5, 30.8 (15-H / C-14, C-17, C-16); 2.83 / 55.2, 30.8, 26.21 (17-H / C-9, C-16, C-15); 2.59 / 55.2, 30.8, 26.1 (17-H' / C-9, C-16, C-15); 1.82 / 91.3, 88.7, 25.4 (8-H' / C-1, C-10, C-6); 1.37 / 90.0, 45.5, 26.1 (16-H' / C-14, C-17, C-15); 1.11 / 91.3, 51.9, 25.4 (7-H / C-1, C-8, C-6).

MS-ES^{+}: $[C_{17}H_{21}FeN]H^{+}$ requires: m/z = 296.1096; found: m/z = 296.1092.

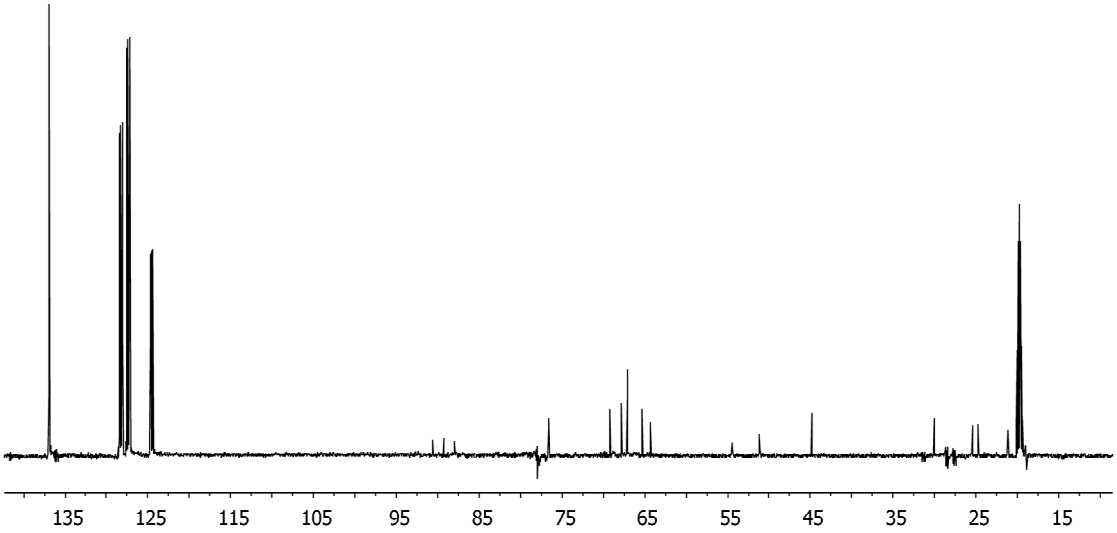
Infrared Spectroscopy: $\tilde{\nu}$ (ATR / cm^{-1}) = 3074 (w), 2948 (m), 2917 (m), 2865 (m), 2785 (w), 1362 (m), 2339 (m), 1449 (m), 1447 (m), 1428 (m), 1372 (w), 1343 (m), 1325 (m), 1266 (w), 1224 (w), 1122 (m), 1101 (m), 1022 (m), 1019 (m), 915 (w), 794 (s).



^{1}H NMR (600 MHz, 298 K) in [D_8]-toluene of compound **13**.

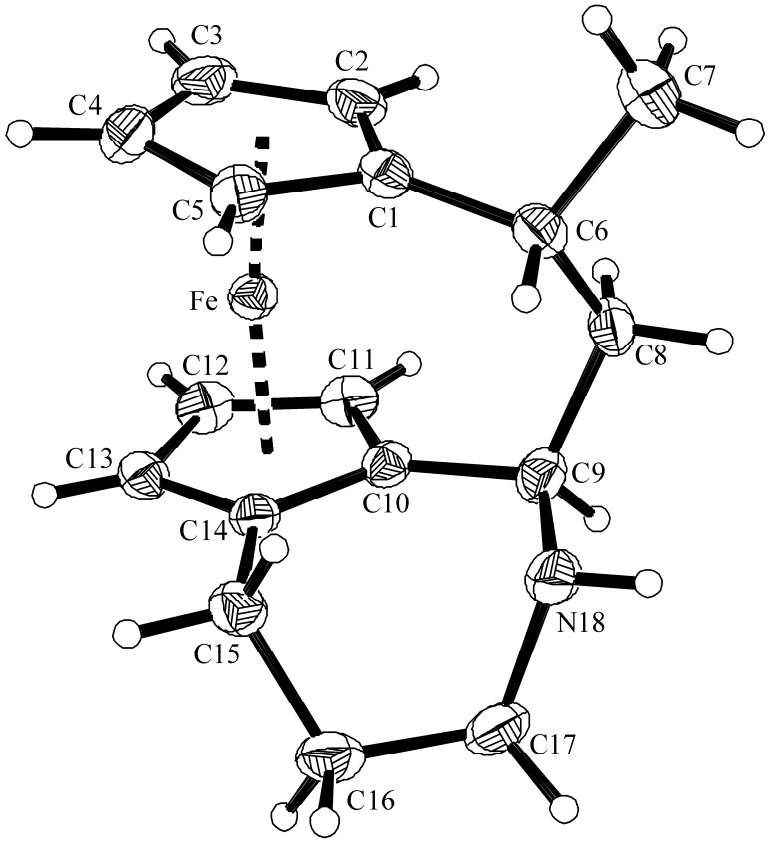


^{1}H NMR (600 MHz, 348 K) in [D_8]-toluene of compound **13**.



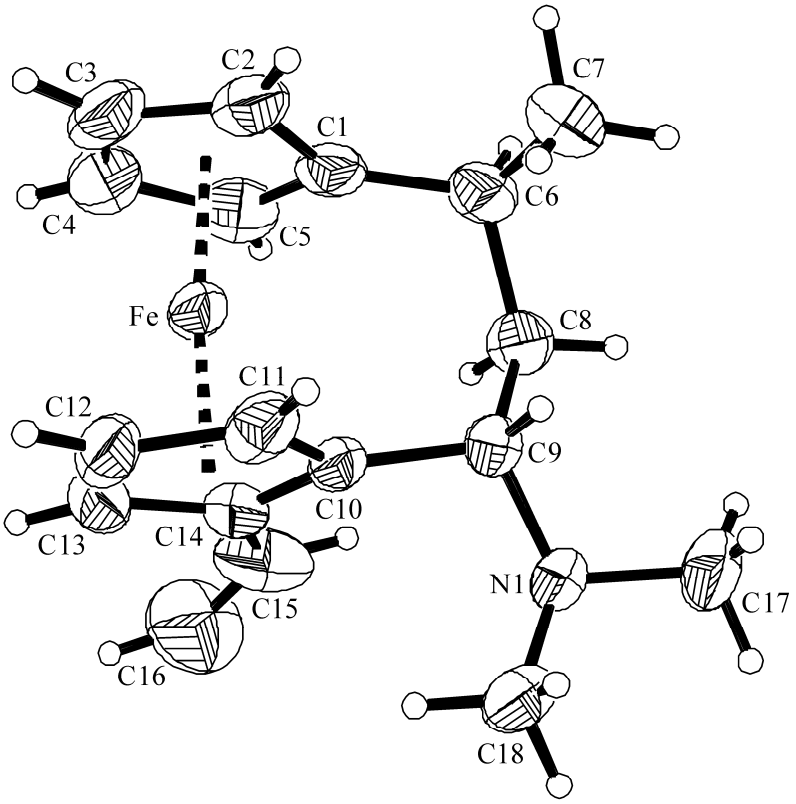
$^{13}C\{^{1}H\}$ NMR (151 MHz, 348 K) in [D_8]-toluene of compound **13**.

Crystal data for $C_{17}H_{21}FeN$ (**13**), M = 295.20, monoclinic, $P2_1/n$ (No. 14), a = 8.1066(2), b = 10.4457(2), c = 15.9844(5) Å, β = 99.924(1)°, V = 1333.29(6) Å^3, D_c = 1.471 g cm^{-3}, μ = 1.115 mm^{-1}, $F(000)$ = 624, Z = 4, λ = 0.71073 Å, T = 223(2) K, 9109 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 3172 independent (R_{int} = 0.034), and 2442 observed reflections [$I \geq 2\sigma(I)$], 177 refined parameters, R = 0.038, wR^2 = 0.077, GoF = 1.055.

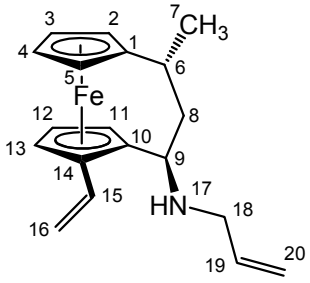


X-Ray crystal structure analysis of compound 14. Crystals suitable for the X-ray crystal structure analysis were grown from a diethylether solution at -4°C.

Crystal data for $C_{18}H_{23}FeN$ (**14**), M = 309.22, monoclinic, $P2_1/c$ (No. 14), a = 10.5831(2), b = 12.5351(2), c = 11.8169(3) Å, β = 91.632(1)°, V = 1567.00(6) Å^3, D_c = 1.311 g cm^{-3}, μ = 0.952 mm^{-1}, F(000) = 656, Z = 4, λ = 0.71073 Å, T = 223(2) K, 8985 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 3663 independent (R_{int} = 0.037), and 3172 observed reflections [I ≥ 2σ(I)], 188 refined parameters, R = 0.049, wR^2 = 0.119, GoF = 1.035.



Preparation of compound 15. Ferrocenophane **14** (886 mg, 2.87 mmol) was dissolved in CH_3CN (5 mL), treated with methyl iodide (1.8 mL, 4.07 g, 28.7 mmol, 10 eq.) and the resulting solution stirred at room temperature for 2 h. All volatiles were removed under reduced pressure, before allyl amine (0.43 mL, 327 mg, 5.74 mmol, 2 eq.), K_2CO_3 (830 mg, 6.02 mmol, 2.1 eq.) and CH_3CN (5 mL) were added. The reaction mixture was heated to 80 °C overnight and evaporated to dryness. After addition of dichloromethane (5 mL), the suspension was filtered over celite and the solvent removed *in vacuo* to yield a yellow oil (826 mg, 2.57 mmol, 90%).



^{1}H NMR (500 MHz, [D$_2$]-dichloromethane, 298 K): δ = 6.94 (dd, ^3J = 17.5 Hz, 10.8 Hz, 1H, 15-H); 5.86 (ddd, ^3J = 17.2 Hz, ^3J = 10.3 Hz, ^3J = 6.3 Hz, ^3J = 5.5 Hz, 1H, 19-H); 5.38 (dd, ^3J = 17.5 Hz, ^2J = 1.9 Hz, 1H, 16-H^A); 5.11 (dq, ^3J = 17.2 Hz, ^2J = ^4J = 1.7 Hz, 1H, 20-H^A); 5.05 (dd, ^3J = 10.8 Hz, ^2J = 1.9 Hz, 1H, 16-H'); 5.03 (dm, ^3J = 10.3 Hz, 1H, 20-H'); 4.37 (m, 1H, 13-H); 4.17 (m, 1H, $C_5H_4^{\beta}$); 4.07 (t, ^3J = 2.6 Hz, 1H, 12-H); 4.05 (m, 1H, 11-H); 4.03 (m, 1H, $C_5H_4^{\beta}$); 3.90 (m, 1H, $C_5H_4^{\alpha}$); 3.66 (m, 1H, $C_5H_4^{\alpha}$); 3.51 (dd, ^3J = 11.2 Hz, 3.3 Hz, 1H, 9-H); 3.17 (ddt, ^2J = 14.2 Hz, ^3J = 5.5 Hz, ^3J = ^4J = 1.7 Hz, 1H, 18-H); 3.12 (ddt, ^2J = 14.2 Hz, ^3J = 6.3 Hz, ^3J = ^4J = 1.7 Hz, 1H, 18-H'); 2.72 (m, 1H, 6-H); 2.55 (ddd, ^2J = 13.3 Hz, ^3J = 11.2 Hz, 3.6 Hz, 1H, 8-H); 2.12 (ddd, ^2J = 13.3 Hz, ^3J = 4.2 Hz, 3.3 Hz, 1H, 8-H'); 1.25 (d, ^3J = 7.3 Hz, 3H, 7-H); 1.15 (br, 1H, 17-H); [α, β: relative position in the C_5H_4 ligand].

^{13}C{^{1}H} NMR (126 MHz, [D$_2$]-dichloromethane, 298 K): δ = 137.9 (C-19); 135.2 (C-15); 115.3 (C-20); 112.1 (C-16); 94.2 (C-1); 83.6 (C-10); 82.6 (C-14); 74.9 ($C_5H_4^{\alpha}$); 72.5 (C-11); 69.4 ($C_5H_4^{\beta}$); 67.9 ($C_5H_4^{\beta}$); 67.8 (C-12); 67.53 (C-13); 67.50 ($C_5H_4^{\alpha}$); 51.4 (C-9); 51.2 (C-18); 49.8 (C-8); 27.5 (C-6); 17.5 (C-7); [α, β: relative position in the C_5H_4 ligand].

^{1}H TOCSY (500 MHz, [D$_2$]-dichloromethane, 298 K): δ^1H_{irr} / δ^1H_{res} = 6.94 / 5.38, 5.05 (15-H / 16-H^A, 16-H'); 5.86 / 5.11, 5.03, 3.17 (19-H / 20-H, 20-H', 18-H); 5.38 / 6.94, 5.05 (16-H / 15-H, 16-H'); 5.11 / 5.86, 5.03, 3.17 (20-H / 19-H, 20-H', 18-H); 4.37 / 4.07, 4.05 (13-H / 12-H, 11-H); 4.17 / 4.03, 3.90, 3.66 ($C_5H_4^{\beta}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\alpha}$); 4.07 / 4.37, 4.05 (12-H / 13-H, 11-H); 4.05 / 4.37, 4.07 (11-H / 13-H, 12-H); 3.90 / 4.17, 4.03, 3.66 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$); 3.66 / 4.17, 4.03, 3.90 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$); 3.51 / 2.72, 2.55, 2.12, 1.25 (9-H / 6-H, 8-H, 8-H', 7-H); 2.72 / 3.51, 2.55, 2.12, 1.25 (6-H / 9-H, 8-H, 8-H',

7-H); 2.12 / 3.51, 2.72, 2.55, 1.25 (8-H' / 9-H, 6-H, 8-H, 7-H); 1.25 / 3.51, 2.72, 2.55, 2.12 (7-H / 9-H, 6-H, 8-H, 8-H').

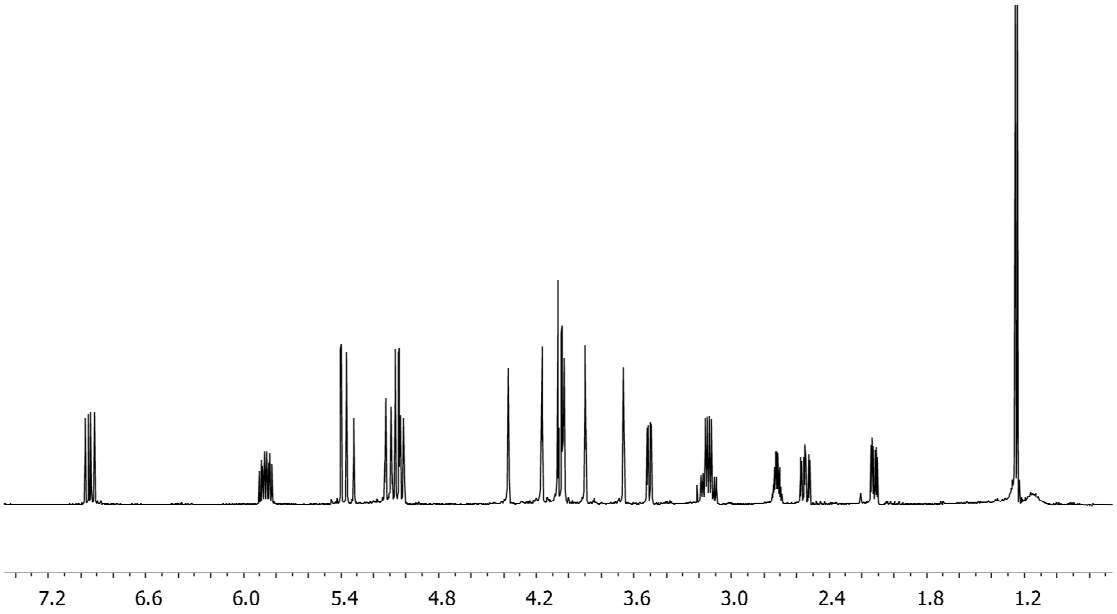
^{1}H, ^{1}H GCOSY (500 MHz, [D_2]-dichloromethane, 298 K): δ = 6.94 / 5.38, 5.05 (15-H / 16-H, 16-H'); 5.86 / 5.03, 3.17 (19-H / 20-H', 18-H); 5.38 / 6.94, 5.05 (16-H / 15-H, 16-H'); 5.11 / 5.86, 5.03 (20-H / 19-H, 20-H'); 5.05 / 6.94, 5.38 (16-H' / 15-H, 16-H); 5.03 / 5.86 (20-H' / 19-H); 4.37 / 4.07, 4.05 (13-H / 12-H, 11-H); 4.17 / 4.03, 3.90, 3.66 ($C_5H_4^{\beta}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\alpha}$); 4.07 / 4.37, 4.05 (12-H / 13-H, 11-H); 4.05 / 4.37, 4.07 (11-H / 13-H, 12-H); 4.03 / 4.17, 3.90, 3.66 ($C_5H_4^{\beta}$ / $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$, $C_5H_4^{\alpha}$); 3.90 / 4.17, 4.03, 3.66 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$); 3.66 / 4.17, 4.03, 3.90 ($C_5H_4^{\alpha}$ / $C_5H_4^{\beta}$, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$); 3.51 / 2.55, 2.12 (9-H / 8-H, 8-H'); 3.17 / 5.86, 5.11, 5.03 (18-H / 19-H, 20-H, 20-H'); 2.72 / 2.55, 2.12, 1.25 (6-H / 8-H, 8-H', 7-H); 2.55 / 3.51, 2.12 (8-H / 9-H, 8-H'); 2.12 / 3.51, 2.72, 2.55 (8-H' / 9-H, 6-H, 8-H); 1.25 / 2.72 (7-H / 6-H).

^{1}H, ^{13}C GHSQC (500 MHz / 126 MHz, [D_2]-dichloromethane, 298 K): $\delta^{1}H$ / $\delta^{13}C$ = 6.94 / 135.2 (15); 5.86 / 137.9 (19); 5.38 / 112.1 (16); 5.11 / 115.3 (20); 5.05 / 112.1 (16); 5.03 / 115.3 (20); 4.37 / 67.53 (13); 4.17 / 69.4 ($C_5H_4^{\beta}$); 4.07 / 67.8 (12); 4.05 / 72.5 (11); 4.03 / 67.9 ($C_5H_4^{\beta}$); 3.90 / 67.50 ($C_5H_4^{\alpha}$); 3.66 / 74.9 ($C_5H_4^{\alpha}$); 3.51 / 51.4 (9); 3.12 / 51.2 (18); 2.72 / 27.5 (6); 2.55 / 49.8 (8); 2.12 / 49.8 (8); 1.25 / 17.5 (7).

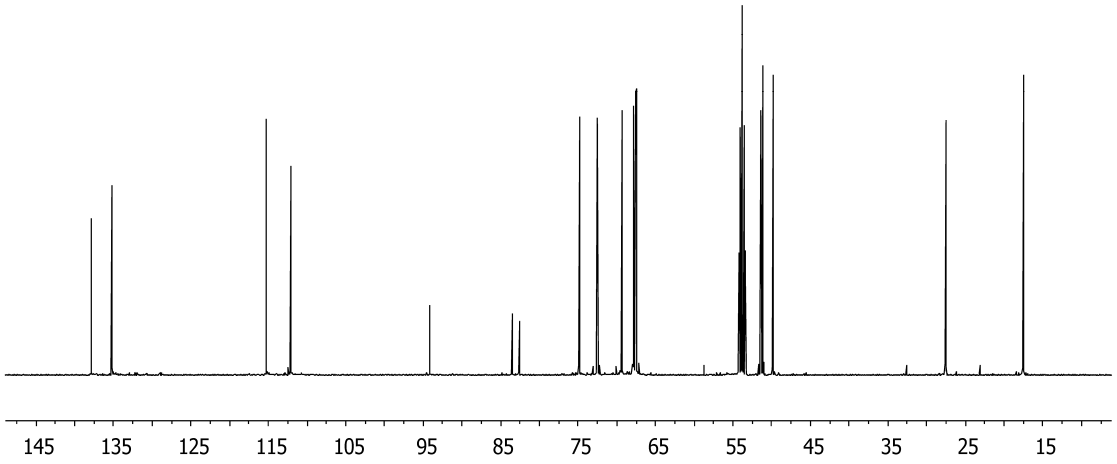
^{1}H, ^{13}C GHMBC (500 MHz / 126 MHz, [D_2]-dichloromethane, 298 K): $\delta^{1}H$ / $\delta^{13}C$ = 6.94 / 83.6, 82.6, 67.53 (15-H / C-10, C-14, C-13); 5.86 / 51.2 (19-H / C-18); 5.38 / 135.2, 82.6 (16-H / C-15, C-14); 5.11 / 51.2 (20-H / C-18); 5.05 / 82.6 (16-H' / C-14); 4.37 / 83.6, 82.6, 72.5, 67.8 (13-H / C-10, C-14, C-11, C-12); 4.17 / 94.2, 74.9, 67.9 ($C_5H_4^{\beta}$ / C-1, $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$); 4.07 / 83.6, 82.6, 72.5, 67.53 (12-H / C-10, C-14, C-11, C-13); 4.05 / 83.6, 82.6, 67.8, 67.53 (11-H / C-10, C-14, C-12, C-13); 4.03 / 94.2, 74.9, 69.4, 67.50 ($C_5H_4^{\beta}$ / C-1, $C_5H_4^{\alpha}$, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$); 3.90 / 94.2, 69.4, 67.9 ($C_5H_4^{\alpha}$ / C-1, $C_5H_4^{\beta}$, $C_5H_4^{\beta}$); 3.66 / 94.2, 69.4, 67.50 ($C_5H_4^{\alpha}$ / C-1, $C_5H_4^{\beta}$, $C_5H_4^{\alpha}$); 3.51 / 83.6, 82.6, 72.5, 51.2, 49.8, 27.5 (9-H / C-10, C-14, C-11, C-18, C-8, C-6); 3.17 / 137.9, 115.3, 51.4 (18-H / C-19, C-20, C-9); 2.72 / 94.2, 74.9, 67.50, 51.4, 49.8, 17.5 (6-H / C-1, $C_5H_4^{\alpha}$, $C_5H_4^{\alpha}$, C-9, C-8, C-7); 2.55 / 94.2, 83.6, 51.4, 27.5, 17.5 (8-H / C-1, C-10, C-9, C-6, C-7); 2.12 / 94.2, 83.6, 51.4, 27.5, 17.5 (8-H' / C-1, C-10, C-9, C-6, C-7); 1.25 / 94.2, 49.8, 27.5 (7-H / C-1, C-8, C-6).

Elemental Analysis: $C_{19}H_{23}FeN$ requires C: 71.04, H: 7.22, N: 4.36; found C: 70.64, H: 7.10, N: 4.45.

Infrared Spectroscopy: $\tilde{\nu}$ (KBr / cm^{-1}) = 3080 (m), 2962 (m), 2933 (m), 2872 (m), 2809 (m), 1624 (m), 1622 (s), 1452 (m), 1405 (m), 1375 (w), 1349 (w), 1310 (m), 1251 (m), 1143 (w), 1108 (s), 1039 (s), 994 (m), 915 (s), 840 (w), 801 (m).

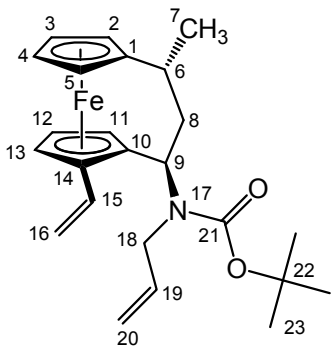


^{1}H NMR (500 MHz, 298 K) in [D_2]-dichloromethane of compound **15**.



$^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K) in [D_2]-dichloromethane of compound **15**.

Preparation of compound 16. A solution of **15** (800 mg, 2.49 mmol) in dichloromethane (20 mL) was cooled to 0 °C and treated with triethylamine (0.4 mL, 291 mg, 2.88 mmol, 1.16 eq.) and Boc_2O (544 mg, 2.49 mmol). After stirring at room temperature overnight, toluene (5 mL) was added and all volatiles removed under reduced pressure. The crude product was purified by column chromatography at silica using dichloromethane as eluent to yield the product (764 mg, 1.81 mmol, 73%). Crystals suitable for the X-ray crystal structure analysis were grown by slow evaporation of a concentrated dichloromethane solution.



^{1}H NMR (600 MHz, [D_6]-benzene, 298 K): δ = 6.83 (dd, ^3J = 17.2 Hz, 10.7 Hz, 1H, 15-H); 5.78 (ddt, ^3J = 17.2 Hz, ^3J = 10.3 Hz, ^3J = 5.2 Hz, 1H, 19-H); 5.31 (dd, ^3J = 17.2 Hz, ^2J = 1.7 Hz, 1H, 16-H); 5.10 (dq, ^3J = 17.2 Hz, ^2J = ^4J = 1.7 Hz, 1H, 20-H); 5.07 (dm, ^3J = 12.6 Hz, 1H, 9-H); 5.04 (dd, ^3J = 10.7 Hz, ^2J = 1.7 Hz, 1H, 16-H'); 4.99 (dq, ^3J = 10.3 Hz, ^2J = ^4J = 1.7 Hz, 1H, 20-H'); 4.33 (m, 1H, 13-H); 4.12 (m, 1H, C_5H_4); 4.11 (m, 1H, 11-H); 3.97 (m, 2H, 12-H, C_5H_4); 3.94 (m, 2H, 18-H); 3.78 (m, 1H, C_5H_4); 3.60 (m, 1H, C_5H_4); 2.72 (ddd, ^2J = 13.3 Hz, ^3J = 12.6 Hz, 4.4 Hz, 1H, 8-H); 2.63 (m, 1H, 6-H); 2.13 (dm, ^2J = 13.3 Hz, 1H, 8-H'); 1.44 (s, 9H, 23-H); 1.30 (d, ^3J = 7.3 Hz, 3H, 7-H).

^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 298 K): δ = 155.3 (C-21); 136.8 (C-19); 135.7 (C-15); 114.8 (C-20); 112.9 (C-16); 93.4 (C-1); 83.2 (C-14); 79.14 (C-22); 79.07 (C-10); 75.0 (C-11); 74.8 (C_5H_4); 69.9 (C_5H_4); 69.0 (C-12); 68.4 (C_5H_4); 68.0 (C-13); 67.4 (C_5H_4); 52.0 (C-9); 47.3 (C-18); 46.4 (C-8); 28.7 (C-6); 28.5 (C-23); 16.9 (C-7).

^{1}H TOCSY (600 MHz, [D_6]-benzene, 298 K): δ^1H_{irr} / δ^1H_{res} = 6.83 / 5.31, 5.04 (15-H / 16-H, 16-H'); 5.78 / 5.10, 4.99, 3.94 (19-H / 20-H, 20-H', 18-H); 5.31 / 6.83, 5.04 (16-H / 15-H, 16-H'); 5.04 / 6.83, 5.31 (16-H' / 15-H, 16-H); 4.33 / 4.11, 3.97 (13-H / 11-H, 12-H); 3.97 / 4.33, 4.12, 4.11, 3.78, 3.60 (12-H, C_5H_4 / 13-H, C_5H_4, 11-H, C_5H_4, C_5H_4); 3.78 / 4.12, 3.97, 3.60 (C_5H_4); 3.60 / 4.12, 3.97, 3.78 (C_5H_4); 2.72 / 5.07, 2.63, 2.13, 1.30 (8-H / 9-H, 6-H, 8-H', 7-H); 2.63 / 5.07, 2.72, 2.13, 1.30 (6-H / 9-H, 8-H, 8-H', 7-H); 2.14 / 5.07, 2.72, 2.63, 1.30 (8-H' / 9-H, 8-H, 6-H, 7-H); 1.30 / 5.07, 2.72, 2.63, 2.13 (7-H / 9-H, 8-H, 6-H, 8-H').

^{1}H NOE (600 MHz, [D_6]-benzene, 298 K): δ^1H_{irr} / δ^1H_{res} = 6.83 / 5.31, 5.04, 3.60 (15-H / 16-H, 16-H', C_5H_4); 5.78 / 5.07, 3.94 (19-H / 9-H, 18-H); 5.31 / 5.04, 4.33 (16-H / 16-H', 13-H); 5.04 / 6.83, 5.31 (16-H' / 15-H, 16-H); 4.99 / 5.78, 5.31, 5.04 (20-H' / 19-H, 16-H,

16-H'); 2.72 / 6.83, 3.60, 2.13 (8-H / 15-H, C_5H_4, 8-H'); 2.63 / 2.13, 1.30 (6-H / 8-H', 7-H); 1.30 / 5.07, 3.97, 2.63, 2.13 (7-H / 9-H, C_5H_4, 6-H, 8-H').

^{1}H, ^{1}H GCOSY (600 MHz, [D_6]-benzene, 298 K): δ = 6.83 / 5.31, 5.04 (15-H / 16-H, 16-H'); 5.78 / 5.10, 4.99, 3.94 (19-H / 20-H, 20-H', 18-H); 5.31 / 6.83, 5.04 (16-H / 15-H, 16-H'); 5.10 / 5.78, 4.99, 3.94 (20-H / 19-H, 20-H', 18-H); 5.07 / 2.72, 2.13 (9-H / 8-H, 8-H'); 5.04 / 6.83, 5.31 (16-H' / 15-H, 16-H); 4.99 / 5.78, 5.10, 3.94 (20-H / 19-H, 20-H', 18-H); 4.33 / 4.11, 3.97 (13-H / 11-H, 12-H); 4.12 / 3.78, 3.60 (C_5H_4); 4.11 / 4.33, 3.97 (11-H / 13-H, 12-H); 3.97 / 4.33, 4.12, 4.11, 3.78, 3.60 (12-H, C_5H_4 / 13-H, C_5H_4, 11-H, C_5H_4, C_5H_4); 3.94 / 5.78, 5.04 (18-H / 19-H, 16-H'); 3.77 / 4.12, 3.78, 3.60 (C_5H_4); 3.60 / 4.12, 3.97, 3.78 (C_5H_4); 2.72 / 5.07, 2.63, 2.13 (8-H / 9-H, 6-H, 8-H'); 2.63 / 2.72, 2.13, 1.30 (6-H / 8-H, 8-H', 7-H); 2.13 / 5.07, 2.72, 2.63 (8-H' / 9-H, 8-H, 6-H); 1.30 / 2.63 (7-H / 6-H).

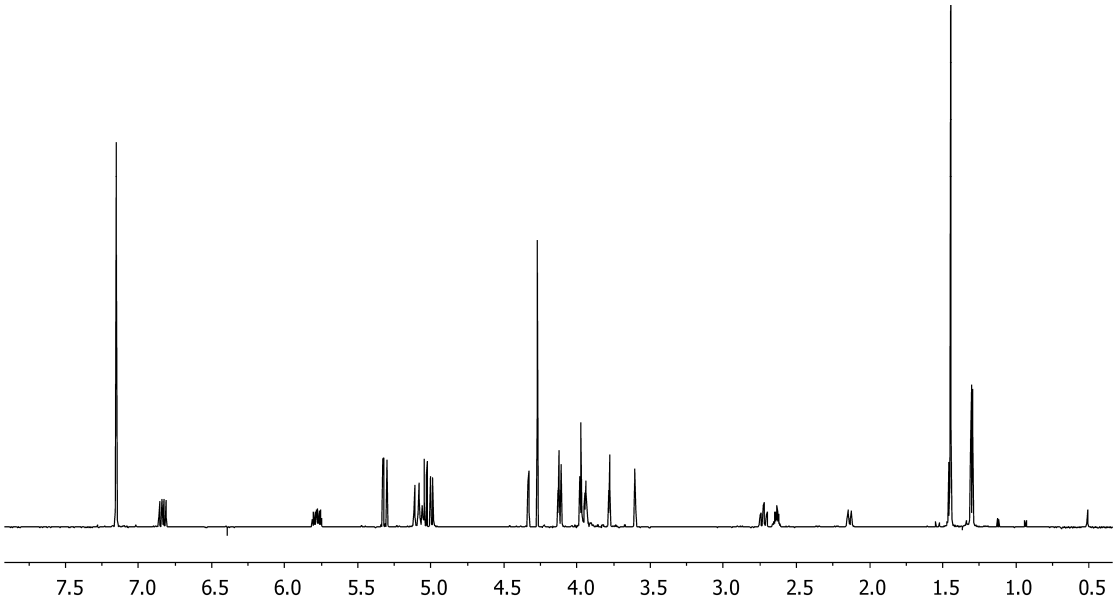
^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, [D_2]-dichloromethane, 298 K): δ^1H / δ^{13}C = 6.83 / 135.7 (15); 5.78 / 136.8 (19); 5.31 / 112.9 (16); 5.10 / 114.8 (20); 5.07 / 52.0 (9); 5.04 / 112.9 (16); 4.99 / 114.8 (20); 4.33 / 68.0 (13); 4.12 / 69.9 (C_5H_4); 4.11 / 75.0 (11); 3.97 / 69.0 (12) 3.97 / 68.4 (C_5H_4); 3.94 / 47.3 (18); 3.77 / 67.4 (C_5H_4); 3.60 / 74.8 (C_5H_4); 2.72 / 46.4 (8); 2.63 / 28.7 (6); 2.13 / 46.4 (8); 1.44 / 28.5 (23); 1.30 / 16.9 (7).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, [D_6]-benzene, 298 K): δ^1H / δ^{13}C = 6.83 / 83.2, 68.0 (15-H / C-14, C-13); 5.78 / 47.3 (19-H / C-18); 5.31 / 135.7, 83.2 (16-H / C-15, C-14); 5.10 / 136.8, 47.3 (20-H / C-19, C-18); 5.07 / 83.2, 79.07, 75.0, 46.4, 28.7 (9-H / C-14, C-10, C-11, C-8, C-6); 5.04 / 83.2 (16-H' / C-14); 4.99 / 47.3 (20-H' / C-18); 4.33 / 83.2, 79.07, 75.0, 69.0 (13-H / C-14, C-10, C-11, C-12); 4.12 / 93.4, 74.8, 68.4, 67.4 (C_5H_4 / C-1, C_5H_4); 4.11 / 83.2, 79.07, 69.0, 68.0 (11-H / C-14, C-10, C-12, C-13); 3.97 / 93.4, 83.2, 79.07, 75.0, 74.8, 69.9, 68.0, 67.4 (12-H, C_5H_4 / C-1, C-14, C-10, C-11, C_5H_4, C_5H_4, C-13, C_5H_4); 3.94 / 136.8, 114.8 (18-H / C-19, C-20); 3.78 / 93.4, 74.8, 68.4 (C_5H_4 / C-1, C_5H_4); 3.60 / 93.4, 69.9, 68.4, 67.4 (C_5H_4 / C-1, C_5H_4); 2.72 / 93.4, 79.07, 52.0, 28.7, 16.9 (8-H / C-1, C-10, C-9, C-6, C-7); 2.63 / 93.4, 74.8, 52.0 (6-H / C-1, C_5H_4, C-9); 2.13 / 93.4, 79.07, 52.0 (8-H' / C-1, C-10, C-9); 1.44 / 155.3, 79.14 (23-H / C-21, C-22); 1.30 / 93.4, 46.4 (7-H / C-1, C-8).

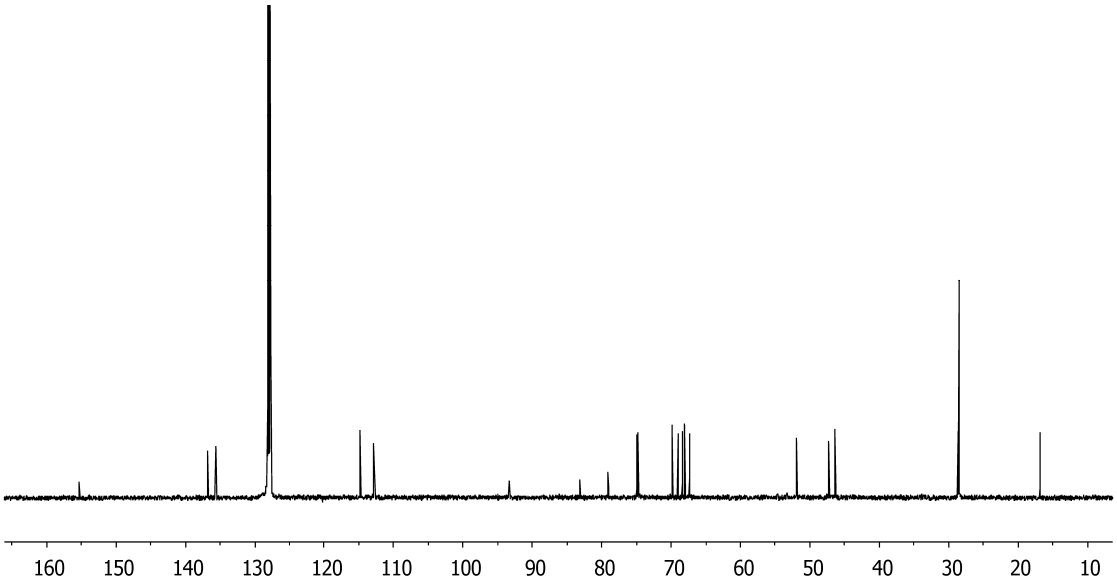
Elemental Analysis: $C_{24}H_{31}FeNO_2$ requires C: 68.41, H: 7.42, N: 3.32; found 68.16, H: 7.48, N: 3.17.

Melting Point: 65 °C.

Infrared Spectroscopy: $\tilde{\nu}$ (ATR / cm^{-1}) = 3086 (w), 2972 (m), 2930 (m), 2875 (w), 1686 (s), 1647 (w), 620 (w), 1449 (m), 1391 (m), 1378 (m), 1365 (m), 1323 (w), 1249 (m), 1169 (m), 1145 (m), 1047 (w), 1026 (w), 987 (m), 913 (m), 870 (m).

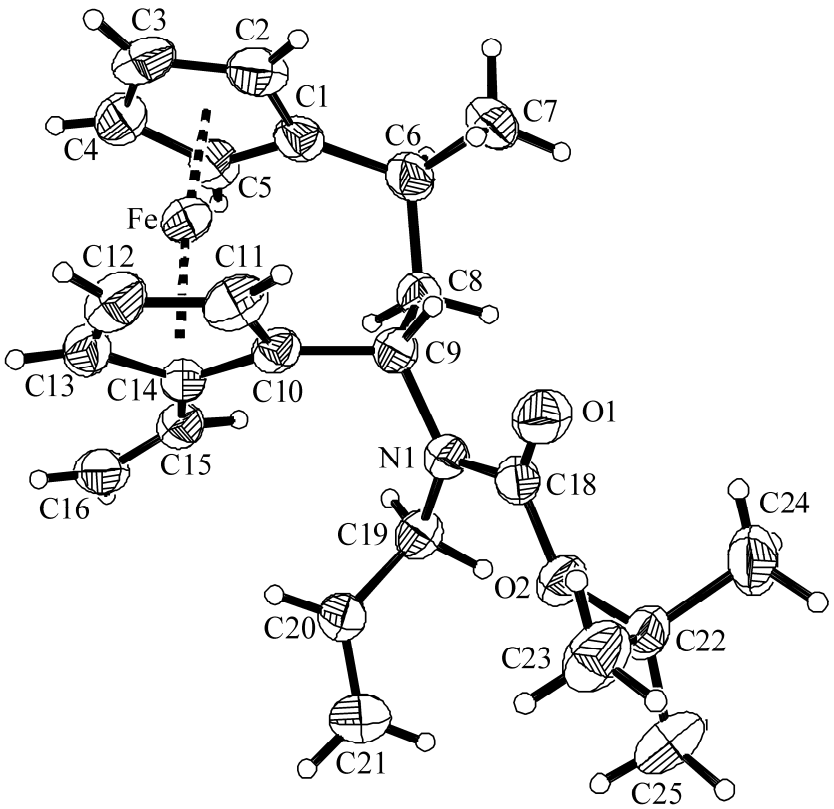


^{1}H NMR (600 MHz, 298 K) in [D_2]-dichloromethane of compound **16**.

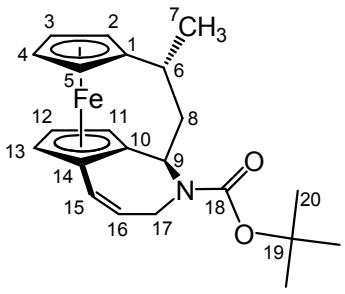


$^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K) in [D_2]-dichloromethane of compound **16**.

Crystal data for $C_{24}H_{31}FeNO_2$ (**16**), M = 421.35, monoclinic, $P2_1/n$ (No. 14), a = 8.6607(1), b = 20.8208(4), c = 11.7026(2) Å, β = 90.323(1)°, V = 2110.21(6) Å^3, D_c = 1.326 g cm^{-3}, μ = 0.734 mm^{-1}, $F(000)$ = 896, Z = 4, λ = 0.71073 Å, T = 223(2) K, 15950 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 4972 independent (R_{int} = 0.041), and 4169 observed reflections [$I \geq 2\sigma(I)$], 257 refined parameters, R = 0.045, wR^2 = 0.110, GoF = 1.040.



Preparation of compound 17. Compound **16** (500 mg, 1.19 mmol) and *Grubbs* I-catalyst (50 mg, 0.06 mmol, 5 mol%) were dissolved in dichloromethane (20 mL) and heated to reflux for 2 h, before additional catalyst (50 mg, 0.06 mmol, 5 mol%) was added. After stirring at room temperature overnight, all volatiles were removed under reduced pressure and the crude product purified by column chromatography at silica using cyclohexane:ethyl acetate (10:1) as eluent. The product was obtained as orange powder (450 mg, 1.15 mmol, 97%).



^{1}H NMR (600 MHz, [D$_8$]-toluene, 363 K): δ = 5.93 (dt, ^{3}J = 11.6 Hz, ^{4}J = 1.6 Hz, 1H, 15-H); 5.32 (ddd, ^{3}J = 11.6 Hz, 4.4 Hz, 3.4 Hz, 1H, 16-H); 4.91 (br, 1H, 9-H); 4.59 (dm, ^{2}J = 18.8 Hz, 1H, 17-H); 4.05 (m, 1H, 4-H); 3.94 (m, 1H, 11-H); 3.83 (m, 1H, 13-H); 3.81 (m, 1H, 2-H); 3.79 (t, ^{3}J = 3.1 Hz, 1H, 12-H); 3.72 (m, 1H, 3-H); 3.67 (dm, ^{2}J = 18.8 Hz, 1H, 17-H'); 3.47 (m, 1H, 5-H); 2.49 (m, 2H, 6-H, 8-H); 1.84 (m, 1H, 8-H'); 1.29 (s, 9H, 20-H); 1.08 (d, ^{3}J = 7.2 Hz, 3H, 7-H).

^{13}C{^{1}H} NMR (151 MHz, [D$_8$]-toluene, 363 K): δ = 155.3 (C-18); 127.7 (C-15); 127.3 (C-16); 93.1 (C-1); 84.7, 82.1 (C-10, C-14); 79.4 (C-19); 74.2 (C-5); 70.6 (C-11,C-13); 69.7 (C-4), 67.9 (C-2), 67.8 (C-3); 67.6 (C-12); 48.1 (C-9); 45.2 (C-8); 45.1 (C-17); 28.7 (C-20); 28.1 (C-6); 16.9 (C-7).

^{1}H TOCSY (600 MHz, [D$_8$]-toluene, 363 K): $\delta^{1}H_{irr}$ / $\delta^{1}H_{res}$ = 5.93 / 5.32, 4.59, 3.67 (15-H / 16-H, 17-H, 17-H'); 5.32 / 5.93, 4.59, 3.67 (16-H / 15-H, 17-H, 17-H'); 4.91 / 2.49, 1.84, 1.08 (9-H / 6-H, 8-H, 8-H', 7-H); 4.59 / 5.93, 5.32, 3.67 (17-H / 15-H, 16-H, 17-H'); 4.05 / 3.81, 3.72, 3.47 (4-H / 2-H, 3-H, 5-H); 3.94 / 3.83, 3.79 (11-H / 13-H, 12-H); 3.83 / 3.94, 3.79 (13-H / 11-H, 12-H); 3.81 / 4.05, 3.72, 3.47 (2-H / 4-H, 3-H, 5-H); 3.79 / 3.94, 3.83 (12-H / 11-H, 13-H); 3.72 / 4.05, 3.81, 3.47 (3-H / 4-H, 2-H, 5-H); 3.67 / 5.93, 5.32, 4.59 (17-H' / 15-H, 16-H, 17-H); 3.47 / 4.05, 3.81, 3.72 (5-H / 4-H, 2-H, 3-H); 2.49 / 4.91, 1.84, 1.08 (6-H, 8-H / 9-H, 8-H', 7-H); 1.84 / 4.91, 2.49, 1.08 (8-H' / 9-H, 6-H, 8-H, 7-H); 1.08 / 4.91, 2.49, 1.84 (7-H / 9-H, 6-H, 8-H, 8-H').

^{1}H NOE (600 MHz, [D$_8$]-toluene, 363 K): $\delta^{1}H_{irr}$ / $\delta^{1}H_{res}$ = 5.93 / 5.32, 3.83 (15-H / 16-H, 13-H); 5.32 / 5.93, 3.67 (16-H / 15-H, 17-H'); 4.59 / 3.67 (17-H / 17-H'); 4.05 / 3.72, 3.47 (4-H / 3-H, 5-H); 2.49 / 3.67, 3.47 1.84, 1.08 (6-H, 8-H / 17-H', 5-H, 8-H', 7-H); 1.84 / 4.91, 2.49, 1.08 (8-H' / 9-H, 6-H, 8-H, 7-H); 1.08 / 4.91, 3.81, 2.49 (7-H / 9-H, 2-H, 6-H, 8-H).

^{1}H, ^{1}H GCOSY (600 MHz, [D_8]-toluene, 363 K): δ = 5.93 / 5.32, 4.59, 3.67 (15-H / 16-H, 17-H, 17-H'); 5.32 / 5.93, 4.59, 3.67 (16-H / 15-H, 17-H, 17-H'); 4.91 / 2.49, 1.84 (9-H / 6-H, 8-H, 8-H'); 4.59 / 5.93, 5.32, 3.67 (17-H / 15-H, 16-H, 17-H'); 4.05 / 3.81, 3.72, 3.47 (4-H / 2-H, 3-H, 5-H); 3.94 / 3.83, 3.79 (11-H / 13-H, 12-H); 3.83 / 3.94, 3.79 (13-H / 11-H, 12-H); 3.81 / 4.05, 3.72, 3.47 (2-H / 4-H, 3-H, 5-H); 3.79 / 3.94, 3.83 (12-H / 11-H, 13-H); 3.72 / 4.05, 3.81, 3.47 (3-H / 4-H, 2-H, 5-H); 3.67 / 5.93, 5.32, 4.59 (17-H' / 15-H, 16-H, 17-H); 3.47 / 4.05, 3.81, 3.72 (5-H / 4-H, 2-H, 3-H); 2.49 / 4.91, 1.84, 1.08 (6-H, 8-H / 9-H, 8-H', 7-H); 1.84 / 4.91, 2.49 (8-H' / 9-H, 6-H, 8-H); 1.08 / 2.49 (7-H / 6-H, 8-H).

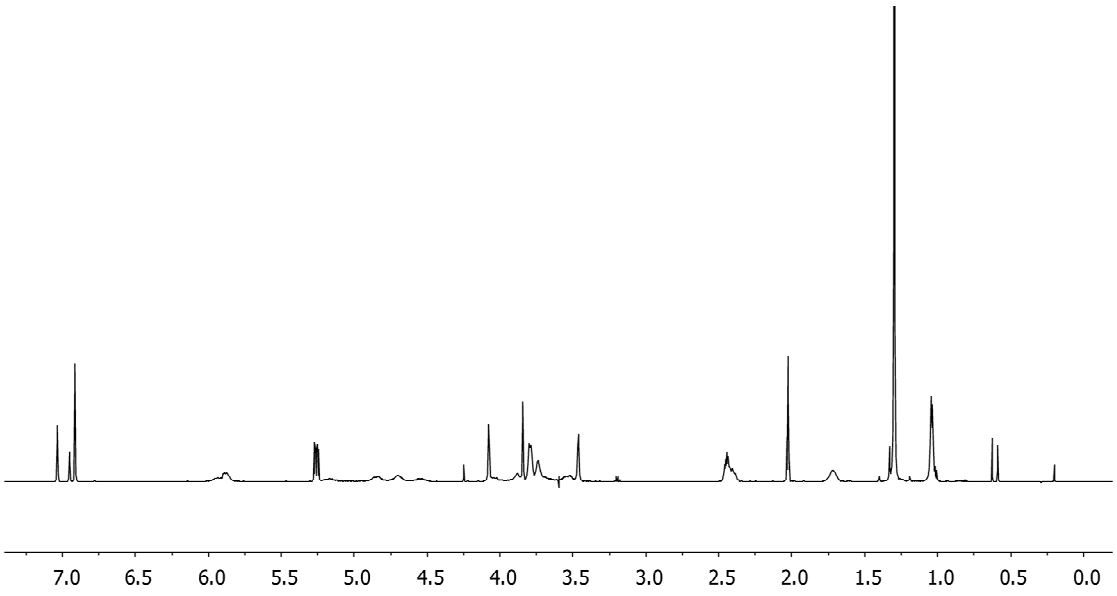
^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, [D_8]-toluene, 363 K): δ^{1}H / δ^{13}C = 5.93 / 127.7 (15); 5.32 / 127.3 (16); 4.91 / 48.1 (9); 4.59 / 44.9 (17); 4.05 / 69.7 (4); 3.94, 3.83 / 70.6 (11, 13); 3.81 / 67.9 (2); 3.79 / 67.6 (12); 3.72 / 67.8 (3); 3.67 / 45.1 (17); 3.47 / 74.2 (5); 2.49 / 28.1 (6); 2.49/ 45.2 (8); 1.84 / 45.2 (8); 1.29 / 28.7 (20); 1.08 / 16.9 (7).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, [D_8]-toluene, 363 K): δ (^{1}H) / δ (^{13}C) = 5.93 / 84.7 (15-H / C-10, C-14); 4.05 / 93.1, 74.2, 67.8 (4-H / C-1, C-5, C-3); 3.94 / 84.7, 82.1, 70.6, 67.6 (11-H / C-10, C-14, C-11, C-13, C-12); 3.83 / 84.7, 82.1, 70.6, 67.6 (13-H / C-10, C-14, C-11, C-13, C-12); 3.81 / 93.1, 74.2, 69.7, 67.8 (2-H / C-1, C-5, C-4, C-3); 3.79 / 84.7, 82.1, 70.6 (12-H / C-10, C-14, C-11, C-13); 3.72 / 93.1, 74.2 (3-H / C-1, C-5); 3.47 / 93.1, 69.7, 67.3 (5-H / C-1, C-4, C-2); 2.49 / 48.1, 28.1, 16.9 (6-H, 8-H / C-9, C-6, C-7); 1.84 / 48.1, 28.1 (8-H' / C-9, C-6); 1.29 / 79.4 (20-H / C-19); 1.08 / 93.1, 45.2, 28.1 (7-H / C-1, C-8, C-6).

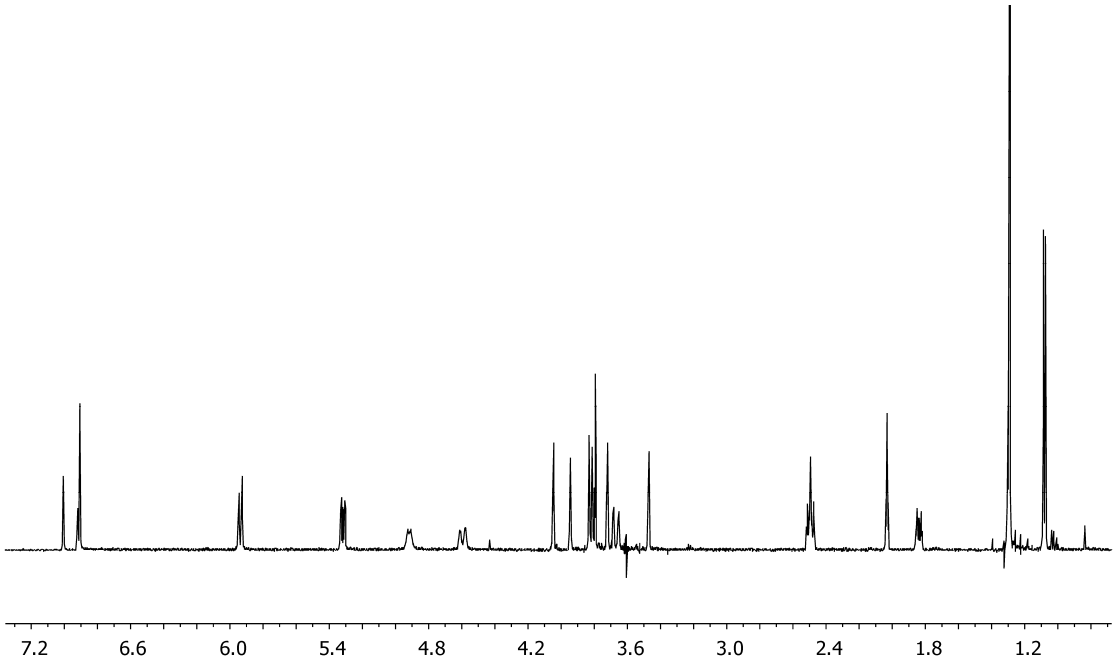
Elemental Analysis: $C_{22}H_{27}FeNO_2$ requires C: 67.18, H: 6.92, N: 3.56; found C: 66.95, H: 6.95, N: 3.25.

Melting Point: 166 °C.

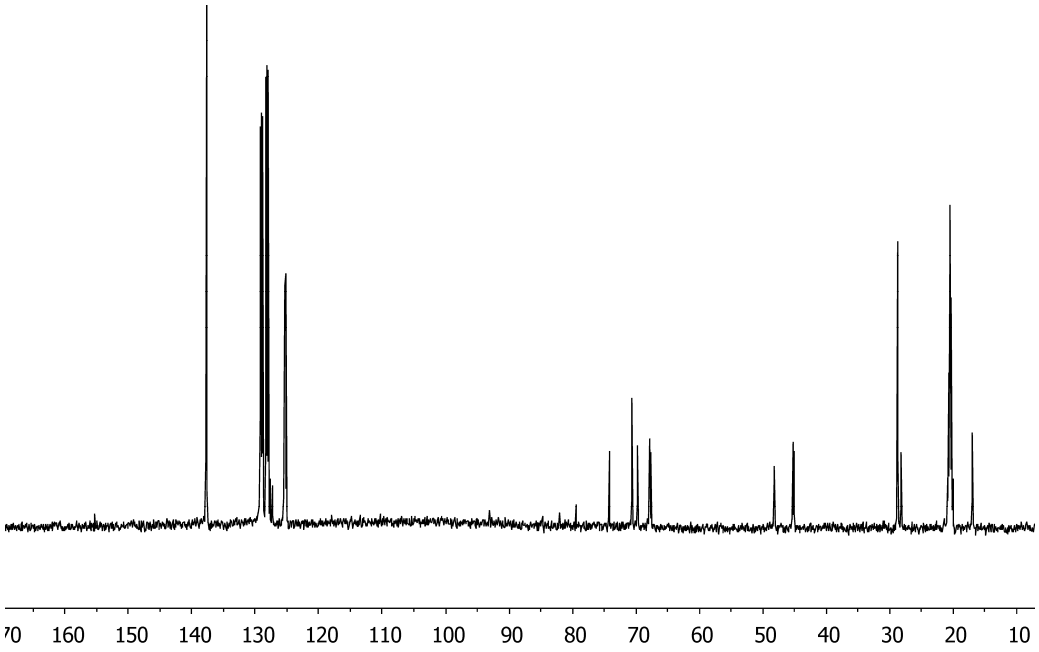
Infrared Spectroscopy: $\tilde{\nu}$ (ATR / cm^{-1}) = 3011 (w), 2976 (m), 2940 (m), 2875 (m), 2839 (m), 1683 (s), 1479 (m), 1446 (w), 1042 (m), 1365 (m), 1315 (m), 1249 (m), 1164 (m), 1092 (m), 1077 (m), 1025 (m), 992 (m), 940 (w), 917 (m), 868 (m), 846 (m), 802 (m).



^{1}H NMR (600 MHz, 298 K) in [D_8]-toluene of compound **17**.

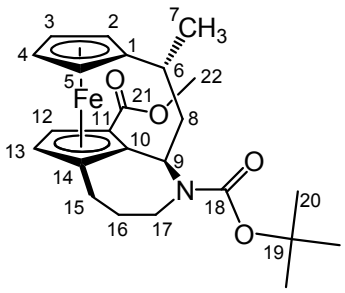


^{1}H NMR (600 MHz, 363 K) in [D_8]-toluene of compound **17**.



$^{13}C\{^{1}H\}$ NMR (151 MHz, 363 K) in $[D_8]$-toluene of compound **17**.

Preparation of compound 18. At −78 °C a solution of *N*-Boc protected amine **4** (80 mg, 0.20 mmol) in diethylether (4 mL) was treated with *sec*.-BuLi (170 µL, 1.3M in cyclohexane, 0.22 mmol, 1.1 eq.). After stirring at low temperature for 30 minutes, methyl chloroformate (17 µL, 0.22 mmol, 1.1 eq.) was added and the yellow solution warmed to room temperature. Stirring was continued for 1 h before saturated NH_4Cl solution (3 mL) was added carefully and the phases separated. The crude product was purified by column chromatography at silica using cyclohexane:ethyl acetate 10:3 as eluent to yield the γ-amino acid **18** (12.4 mg, 0.03 mmol, 15%). Besides, starting material **4** (66 mg, 0.17 mmol, 85%) was reisolated. Single crystals suitable for the X-ray crystal structure analysis were grown from a saturated solution in diethylether at room temperature.



^{1}H NMR (500 MHz, [D_2]-dichloromethane, 298 K): δ = 5.89 (br d, ^3J = 11.7 Hz, 1H, 9-H); 4.51 (d, ^3J = 2.7 Hz, 1H, 12-H); 4.18 (m, 1H, 17-H); 4.14 (m, 1H, C_5H_4); 4.12 (m, 1H, C_5H_4); 4.10 (d, 1H, ^3J = 2.7 Hz, 13-H); 3.80 (m, 1H, C_5H_4); 3.75 (s, 3H, 22-H); 3.56 (m, 1H, C_5H_4); 3.31 (m, 1H, 17-H'); 3.11 (m, 1H, 8-H); 2.92 (m, 1H, 15-H); 2.88 (m, 1H, 6-H); 2.51 (dm, ^2J = 15.4 Hz, 1H, 15-H'); 2.06 (dt, ^2J = 13.1 Hz, ^3J = 3.8 Hz, 1H, 8-H'); 1.76 (dm, ^2J = 13.6 Hz, 1H, 16-H); 1.44 (m, 1H, 16-H'); 1.39 (s, 9H, 20-H); 1.38 (d, ^3J = 6.9 Hz, 3H, 7-H).

^{13}C{^{1}H} NMR (126 MHz, [D_2]-dichloromethane, 298 K): δ = 172.4 (C-21); 95.1 (C-1); 93.1 (C-14); 85.5 (C-10); 79.6 (br, C-19); 75.2 (C_5H_4); 73.3 (C-13); 73.0 (br, C_5H_4); 70.4 (C_5H_4); 69.4 (br, C-11)[a], 69.1 (C-12); 67.6 (C_5H_4); 51.5 (C-22); 46.5 (C-8); 45.2 (br, C-9); 43.5 (br, C-17); 29.6 (br, C-16, C-15); 28.6 (C-20); 28.4 (C-6); 16.3 (C-7); n.o. (C-18) [[a] from the ghmbc experiment].

^{1}H TOCSY (500 MHz, [D_2]-dichloromethane, 298 K): δ^1H_{irr} / δ^1H_{res} = 4.51 / 4.10 (12-H / 13-H); 4.14 / 4.12, 3.80, 3.56 (C_5H_4); 3.80 / 4.14, 4.12, 3.80 (C_5H_4); 3.31 / 4.18, 2.92, 2.51, 1.76, 1.46 (17-H' / 17-H, 15-H, 15-H', 16-H, 16-H'); 2.88 / 5.89, 3.11, 2.06, 1.38 (6-H / 9-H, 8-H, 8-H', 7-H).

^{1}H, ^{1}H GCOSY (500 MHz, [D_2]-dichloromethane, 298 K): δ = 5.89 / 3.11, 2.06 (9-H / 8-H, 8-H'); 4.51 / 4.10 (12-H / 13-H); 4.18 / 3.31, 1.76 (17-H / 17-H', 16-H); 4.14 / 3.80, 3.56 (C_5H_4); 4.10 / 4.51 (13-H / 12-H); 3.80 / 4.12, 3.56 (C_5H_4); 3.56 / 4.14, 4.12, 3.80 (C_5H_4); 3.31 / 4.18, 1.44 (17-H' / 17-H, 16-H'); 3.11 / 5.98, 2.88, 2.06 (8-H / 9-H, 6-H, 8-H'); 2.92 / 2.51, 1.76, 1.44 (15-H / 15-H', 16-H, 16-H'); 2.88 / 2.06, 1.38 (6-H / 8-H', 7-H); 2.51 / 2.92,

1.76 (15-H' / 15-H, 16-H); 2.06 / 5.89, 3.11, 2.88 (8-H' / 9-H, 8-H, 6-H); 1.76 / 2.51, 1.44 (16-H / 15-H', 16-H'); 1.44 / 3.31, 2.92, 1.76 (16-H' / 17-H', 15-H, 16-H); 1.38 / 2.88 (7-H / 6-H).

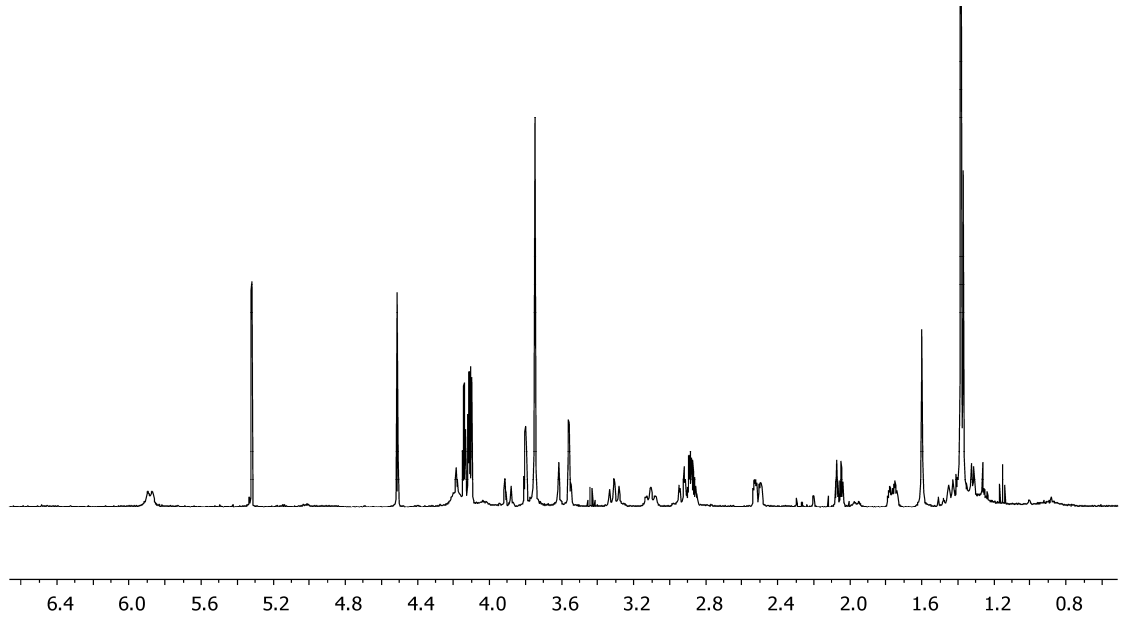
^{1}H, ^{13}C GHSQC (500 MHz / 126 MHz, [D_2]-dichloromethane, 298 K): δ^{1}H / δ^{13}C = 5.89 / 45.2 (9); 4.51 / 69.1 (12); 4.18 / 43.5 (17); 4.14 / 70.4 (C_5H_4); 4.12 / 67.6 (C_5H_4); 4.10 / 73.3 (13); 3.80 / 73.0 (C_5H_4); 3.75 / 51.5 (22); 3.56 / 75.2 (C_5H_4); 3.31 / 43.5 (17); 3.11 / 46.5 (8); 2.92 / 29.6 (15); 2.88 / 28.4 (6); 2.51 / 29.6 (15); 2.06 / 46.5 (8); 1.76 / 29.6 (16); 1.44 / 29.6 (16); 1.39 / 28.6 (20); 1.38 / 16.3 (7).

^{1}H, ^{13}C GHMBC (500 MHz / 126 MHz, [D_2]-dichloromethane, 298 K): δ^{1}H / δ^{13}C = 4.51 / 93.1, 85.5, 73.3, 69.4, 69.1 (12-H / C-14, C-10, C-13, C-11, C-12); 4.14 / 95.1, 75.2, 73.0, 67.6 (C_5H_4 / C-1, C_5H_4); 4.12 / 95.1, 75.2, 73.0, 67.6 (C_5H_4 / C-1, C_5H_4); 4.10 / 93.1, 85.5, 69.4, 69.1 (13-H / C-14, C-10, C-11, C-12); 3.80 / 95.1, 75.2, 70.4, 67.6 (C_5H_4 / C-1, C_5H_4); 3.75 / 172.4 (22-H / C-21); 3.56 / 95.1, 73.0, 70.4, 67.6 (C_5H_4 / C-1, C_5H_4); 2.92 / 93.1, 73.3 (15-H / C-14, C-13); 2.51 / 93.1, 85.5, 73.3 (15-H' / C-14, C-10, C-13); 2.06 / 95.1, 85.5, 28.4 (8-H' / C-1, C-10, C-6); 1.39 / 79.6 (20-H / C-19); 1.38 / 95.1, 46.5 (7-H / C-1, C-8).

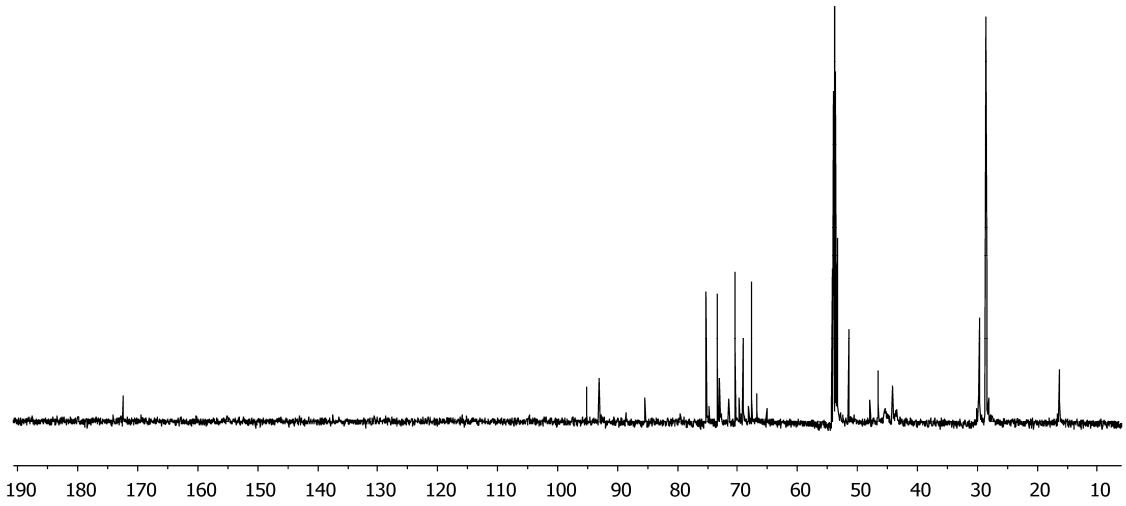
Elemental Analysis: $C_{24}H_{31}FeNO_4$ requires C: 63.58, H: 6.89, N: 3.09; found C: 63.65, H: 6.90, N: 2.93.

Melting Point: 133 °C.

Infrared Spectroscopy: $\tilde{\nu}$ (ATR / cm^{-1}) = 2961 (m), 2929 (m), 2860 (m), 2361 (w), 2337 (w), 1712 (s), 1685 (s), 1451 (s), 1396 (m), 1371 (m), 1318 (m), 1291 (m), 1247 (m), 1206 (m), 1174 (m), 1153 (m), 1127 (s), 1103 (m), 1024 (m), 988 (w), 938 (m), 921 (w), 868 (m), 863 (m), 810 (s).



^{1}H NMR (500 MHz, 298 K) in [D_2]-dichloromethane of compound **18**.



^{13}C{^{1}H} (126 MHz, 298 K) in [D_2]-dichloromethane of compound **18**.

Crystal data for $C_{24}H_{31}FeNO_4$ (**18**), M = 453.35, orthorhombic, Fdd2 (No. 43), a = 17.2035(4), b = 65.6989(16), c = 7.8148(2) Å, V = 8832.7(4) Å^3, D_c = 1.364 g cm^{-3}, μ = 0.713 mm^{-1}, F(000) = 3840, Z = 16, λ = 0.71073 Å, T = 223(2) K, 20693 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 5133 independent (R_{int} = 0.080), and 4538 observed reflections [I ≥ 2σ(I)], 277 refined parameters, R = 0.055, wR^2 = 0.138, GoF = 1.062.