Supplementary Material (ESI) for Chemical Communications
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1,2-Olefin Addition of a Frustrated Amine/Borane Lewis Pair

Jean-Baptiste Sortais, Tanja Voß, Gerald Kehr, Roland Fröhlich , Gerhard Erker

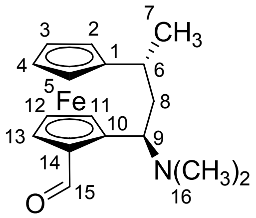
Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, 48149
Münster, Germany

Supporting Information

General Procedures. All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried with the procedure according to Grubbs (Pangborn, A. B., Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520) or were distilled from appropriate drying agents and stored under an argon atmosphere. The following instruments were used for physical characterization of the compounds: NMR spectra: *Bruker* ARX 300 spectrometer (^{19}F: 282.4 MHz, ^{11}B: 96.3 MHz), *Bruker* AV 400 spectrometer (^{1}H 400MHz, ^{13}C 101 MHz), *Varian* Inova 500 (^{1}H: 499.9 MHz, ^{13}C: 125.7 MHz, ^{19}F: 470.3 MHz, ^{11}B: 160.4 MHz) and *Varian* UnityPlus 600 (^{1}H: 599.9 MHz, ^{13}C: 150.8 MHz, ^{19}F: 564.4 MHz, ^{11}B: 192.4 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift δ is given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shift δ is given relative to $CFCl_3$ (external reference); ^{11}B NMR: chemical shift δ is given relative to $BF_3{\cdot}Et_2O$ (external reference). NMR assignments are supported by additional 2D NMR experiments. All coupling constants *J* are given in Hz. Elemental analyses were performed on a *Elementar Vario El III*.

X-Ray Crystal Structure Analyses. 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 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 SCHAKAL (E. Keller, Univ. Freiburg, 1997).

Materials. *rac-trans*-1,1'-[1-(dimethylamino)butan-1,3-diyl]ferrocene (**1**) (Liptau, P., Knüppel, S., Kehr, G., Kataeva, O., Fröhlich, R., Erker G. *J. Organomet. Chem.* **2001**, *637-639*, 621-630) and $B(C_6F_5)_3$ (Massey, A. G., Park, A. J., *J. Organomet. Chem.* **1964**, *2*(3), 245-250; Pohlmann, J. L.W., Brinkmann, F. E., *Z. Naturforsch.* **1965**, *20b* (1), 5-11) were prepared according to literature procedures.



rac-trans-1'-Formyl-2',1''-[1-(dimethylamino)butan-1,3-diyl]ferrocene (2)[1]

rac-trans-[3]Ferrocenophane **1** (8.50 g, 30.0 mmol) dissolved in 120 mL anhydrous diethylether was reacted with *tert*-butyllithium (30 mL, 1.5 M solution in n-pentane, 45.0 mmol, 1.5 equiv) under argon. 15 min after complete addition dimethyl formamide (3.70 mL, 48.0 mmol, 1.6 equiv) was added at room temperature. The mixture was stirred for another 45 min before addition of aqueous sodium bicarbonate (50 mL), whereupon the intensive red color of the solution indicated the formation of the conjugated aldehyde from hydrolysis of the lithiohemiaminal. The suspension was transferred to a separatory funnel, the layers were separated and the aqueous phase was extracted with diethyl ether (30 mL). The combined organic layers were washed with water and brine (30 mL each), dried (magnesium sulfate), concentrated and dried in vacuo to give a deep red oil (9.28 g, 29.8 mmol, 99%) as crude product. Crystals suitable for X-ray diffraction were grown by slow evaporation of an etheral solution. Analytically pure material was obtained from repetitive recrystallization (8.21 g, 26.4 mmol, 88%).

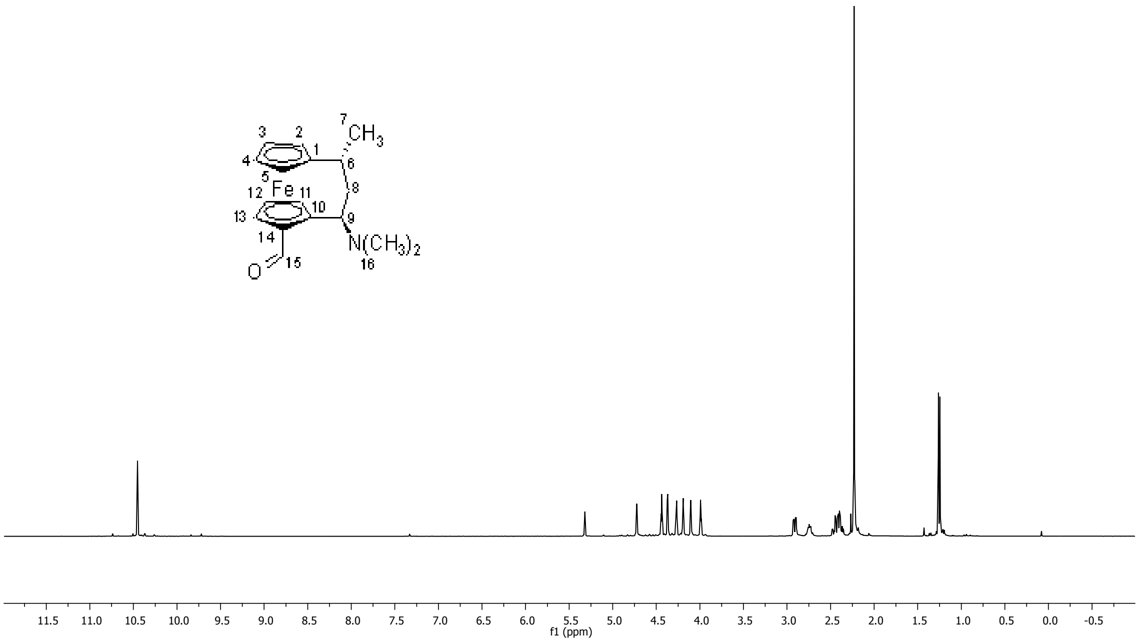
[1] L. Tebben, G. Kehr, R. Fröhlich, G. Erker, *Eur. J. Inorg. Chem,* **2008**, 2654-2658.

Elemental Analysis Calcd. for $C_{17}H_{21}NOFe$: C 65.61, H 6.80, N 4.50; found C 65.53, H 6.85, N 4.21.

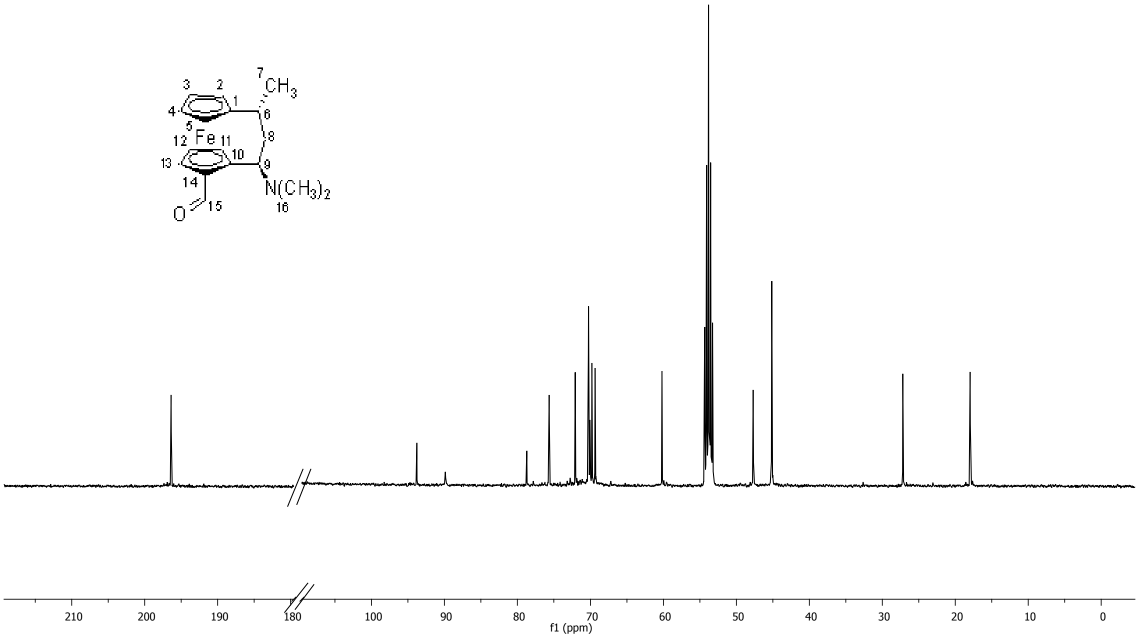
^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ = 10.45 (s, 1H, H_{15}), 4.72 (m, 1H, H_{13}), 4.43 (m, 1H, H_{12}), 4.36 (m, 1H, H_{11}), 4.26 (m, 1H, H_2), 4.19 (m, 1H, H_3), 4.10 (m, 1H, H_5), 3.98 (m, 1H, H_4), 2.91 (dd, J = 9.9 Hz, 3.8 Hz, 1H, H_9), 2.74 (m, 1H, H_6), 2.45 (ddd, J = 13.8 Hz, 9.9 Hz, 3.4 Hz, 1H, H_8), 2.38 (ddd, J = 13.8 Hz, 5.2 Hz, 3.8 Hz, 1H, H'_8), 2.22 (s, 6H, H_{16}), 1.25 (d, J = 7.2 Hz, 3H, H_7).

$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 295 K) δ = 196.4 (C_{15}), 93.8 (C_1), 89.9 (C_{10}), 78.7 (C_{14}), 75.6 (C_{11}), 72.0 (C_{12}), 70.3 (C_2, C_3), 70.1 (C_{13}), 69.8 (C_4), 69.3 (C_5), 60.2 (C_9), 47.7 (C_8), 45.1 (C_{16}), 27.2 (C_6), 17.9 (C_7).

Mass Spectrometry (HR-ESI, MeOH) Calcd. for $C_{17}H_{21}FeNOH$ (M+): 312.1045, found: 312.1043.



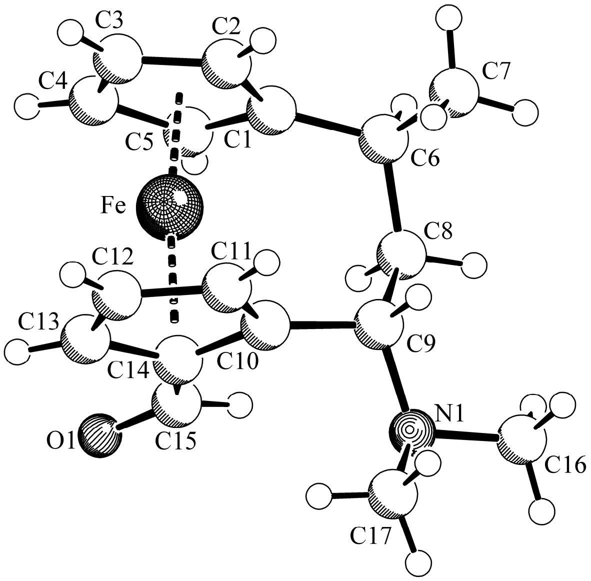
^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) of **2**.

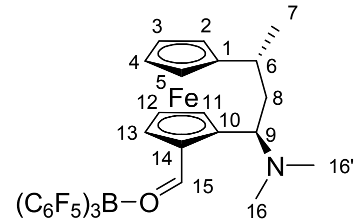


$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, 295 K) of **2.**

X-Ray Crystal Structure Analysis of 2.

Crystal data for $C_{17}H_{21}FeNO$ (**2**), *M* = 311.20, orthorhombic, space group $P2_12_12_1$ (No. 19), *a* = 7.3447(2), *b* = 14.1452(3), *c* = 14.2521(4) Å, *V* = 1480.68(7) $Å^3$, D_c = 1.396 g cm^{-3}, μ = 1.013 mm^{-1}, *Z* = 4, λ = 0.71073 Å, *T* = 223(2) K, 6229 reflections collected (±*h*, ±*k*, ±*l*), $[(\sin\theta)/\lambda]$ = 0.67 $Å^{-1}$, 3435 independent (R_{int} = 0.030) and 3302 observed reflections $[I \geq 2\sigma(I)]$, 184 refined parameters, R = 0.036, wR^2 = 0.090.
The R values are given for the observed reflections $[I \geq 2\sigma(I)]$ and wR^2 values are given for all reflections.





Compound 3

A solution of $B(C_6F_5)_3$ (255 mg, 0.49 mmol) in CH_2Cl_2 (3 mL) was added to a solution of aldehyde **2** (155 mg, 0.49 mmol) in CH_2Cl_2 (3 mL). The reaction was stirred for 30 min at RT, concentrated to c.a. 3 mL. Compound **7** was crystallized at -18°C over night, washed three times with cold CH_2Cl_2 (2 mL) at -78°C. After drying, 270 mg (67% yield) of **7** were obtained as a purple-black crystals.

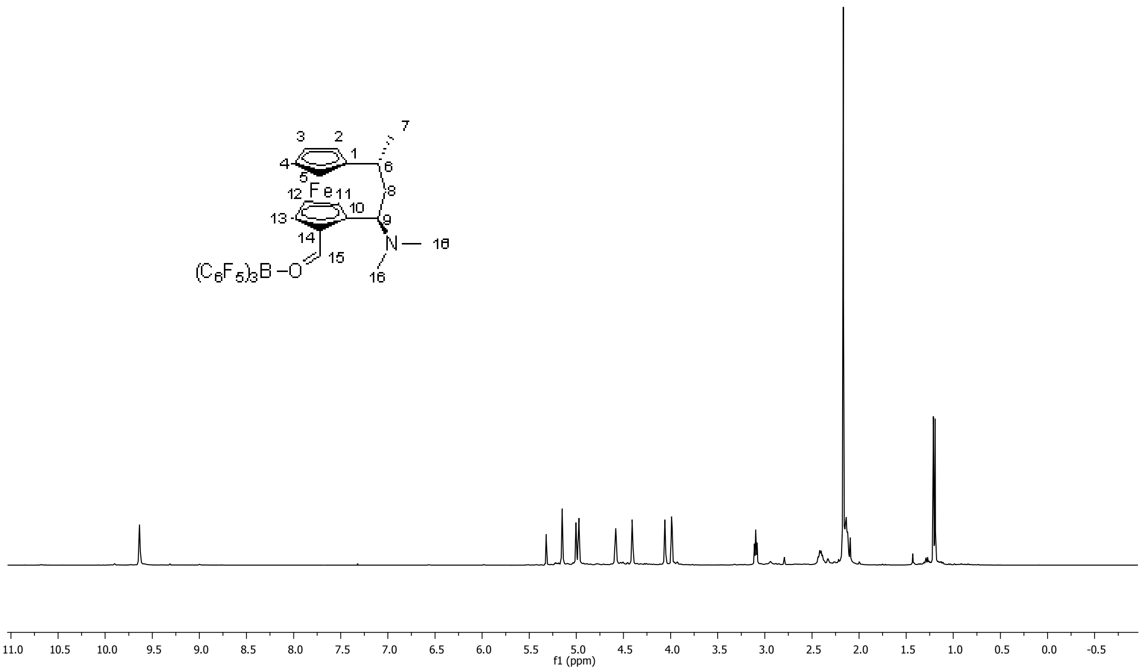
Anal. Calc. for $C_{35}H_{21}BF_{15}FeNO$: C, 51.07; H, 2.57; N,1.70. Found C,50.36; H, 2.48; N, 1.78.

^1H NMR (400 MHz, CD_2Cl_2, 298 K) δ = 9.64 (s, 1H, H_{15}), 5.15 (t, J = 2.7 Hz, 1H, H_{12}), 5.00 (m, 1H, H_{13}), 4.97 (dd, J = 2.7 Hz, 1.3 Hz, 1H, H_{11}), 4.58, 4.40, 4.06, 3.98 (each m, each 1H, C_5H_4), 3.10 (t, J = 5.5 Hz, 1H, H_9), 2.40 (m, 1H, H_6), 2.17 (s, 6H, H_{17}), 2.14 (m, 2H, H_8), 1.20 (d, J = 7.1 Hz, 3H, H_7).

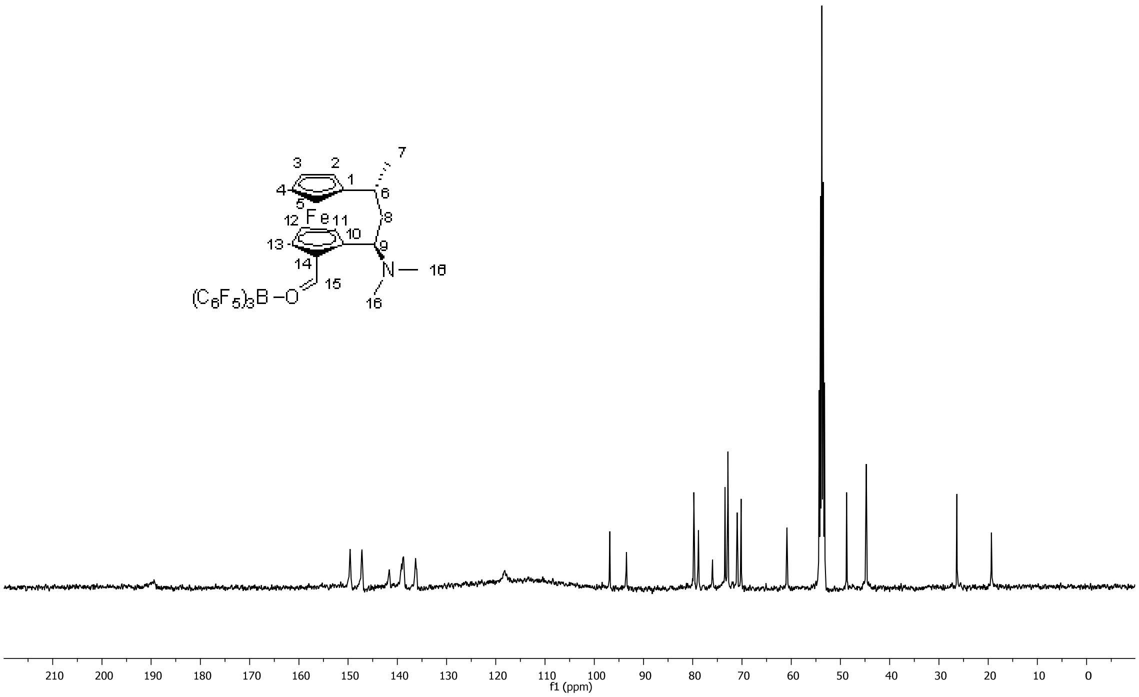
$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K) δ = 189.3 (br, C_{15}), 148.4 (dm, $^1J_{CF}$ = 240 Hz, *o*-C_6F_5), 140.4 (dm, $^1J_{CF}$ = 236 Hz, *p*-C_6F_5), 137.4 (dm, $^1J_{CF}$ = 261 Hz, *m*-C_6F_5), 118.1 (br, *i*-C_6F_5), 96.8 (C_{10}), 93.5 (C_1), 79.7 (C_{12}), 78.8 (C_{11}), 76.0 (C_{14}), 73.4, 72.9, 72.8, 70.2 (C_5H_4), 70.9 (C_{13}), 60.8 (C_9), 48.7 (C_8), 44.8 (C_{16}), 26.4 (C_6), 19.3 (C_7).

$^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2, 298 K) δ = 1.2 (s, $\nu_{1/2}$ = 220Hz).

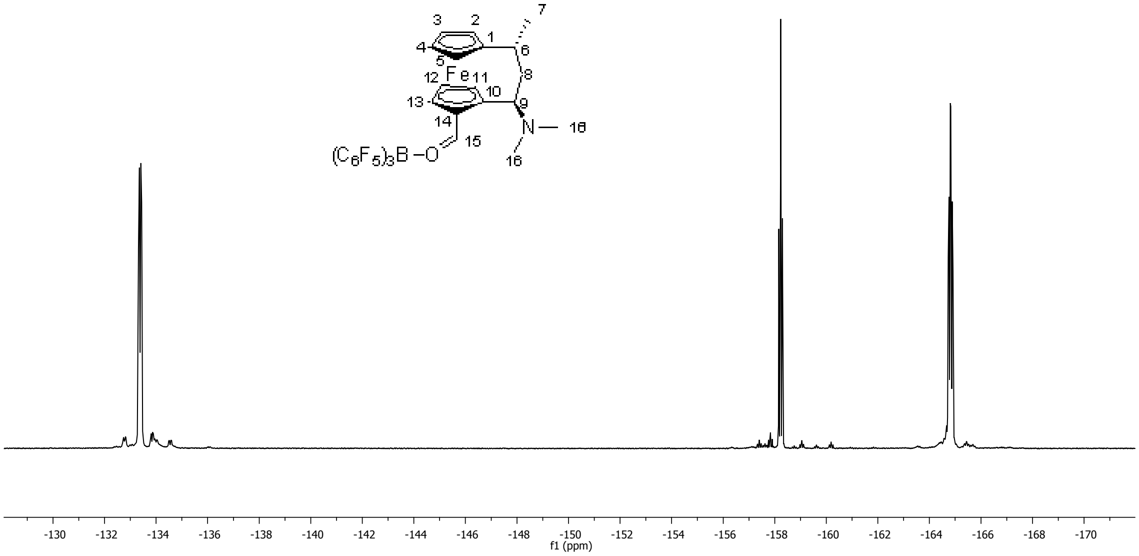
$^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2, 298 K) δ = -133.4 (m, 6F, *o*-C_6F_5), -158.2 (t, J = 20.2 Hz, 3F, *p*-C_6F_5), -164.8 (m, 6F, *m*-C_6F_5).



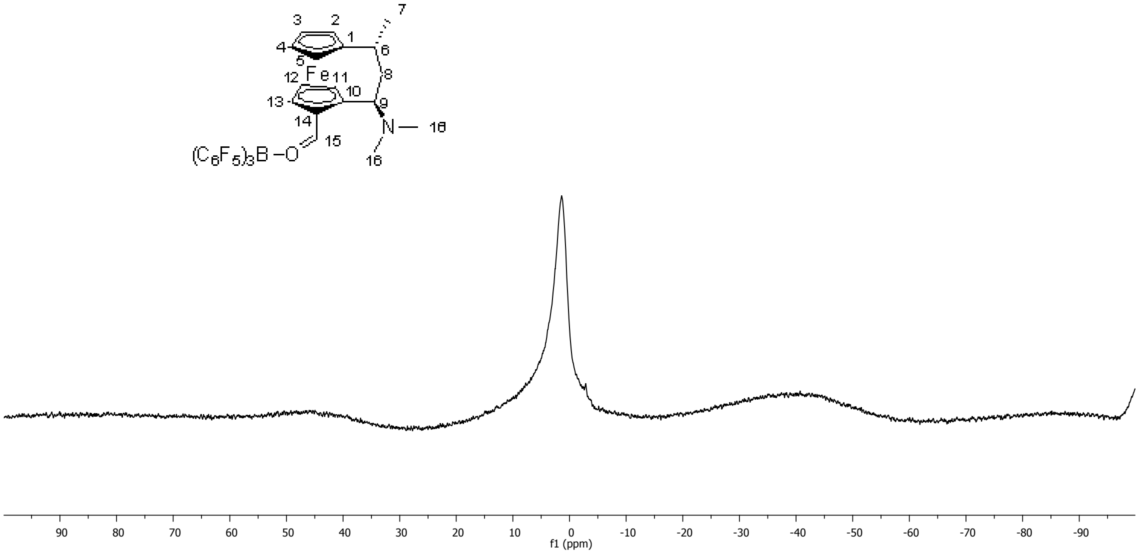
^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) of **3**.



$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 295 K) of **3.**



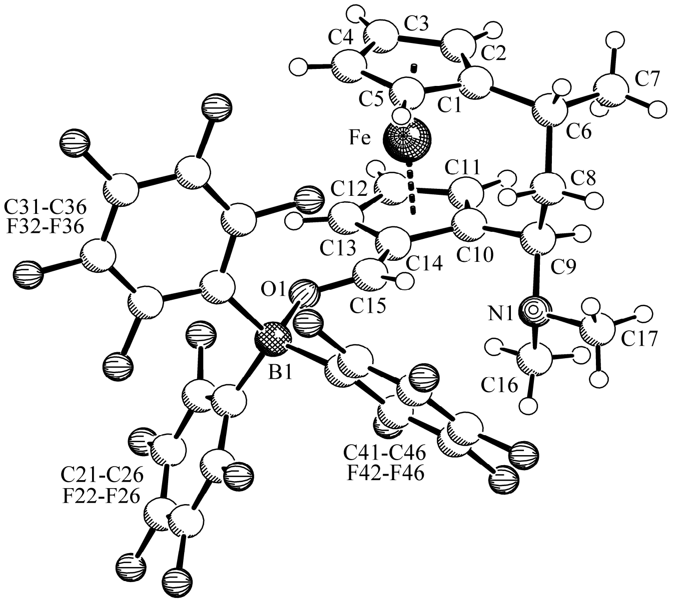
$^{19}F\{^1H\}$ NMR (282 MHz,CD_2Cl_2, 295 K) of **3.**

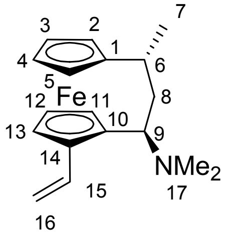


$^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2, 295 K) of **3.**

X-Ray Crystal Structure Analysis of 3.

Crystal data for $C_{35}H_{21}BF_{15}FeNO$ (**3**), *M* = 823.19, triclinic, space group *P*1bar (No. 2), *a* = 9.6199(2), *b* = 11.9463(3), *c* = 14.9994(5) Å, α = 105.859(1), β = 96.052(1), γ = 103.077(1)°, *V* = 1589.21(7) Å^3, D_c = 1.720 g cm^{-3}, μ = 0.596 mm^{-1}, *Z* = 2, λ = 0.71073 Å, *T* = 223(2) K, 13635 reflections collected (±*h*, ±*k*, ±*l*), [(*sin*θ)/λ] = 0.62 Å^{-1}, 6413 independent (R_{int} = 0.062) and 4014 observed reflections [$I \geq 2\sigma(I)$], 490 refined parameters, R = 0.061, wR^2 = 0.112.
The R values are given for the observed reflections [$I \geq 2\sigma(I)$] and wR^2 values are given for all reflections.





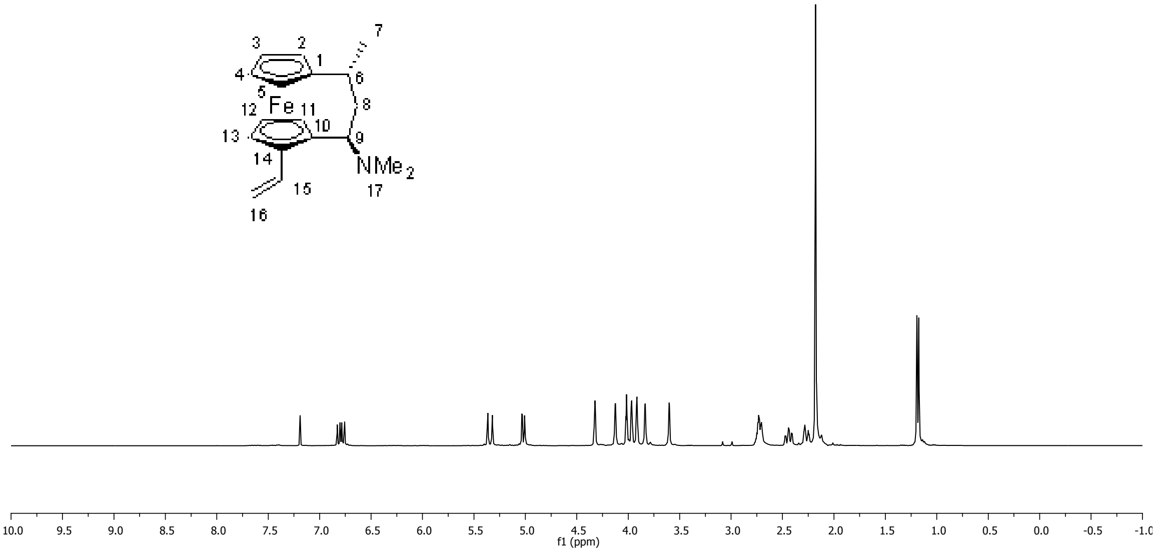
***rac-trans*-1'-Vinyl-2',1"-[1-(dimethylamino)butan-1,3-diyl]ferrocene (4)**

n-BuLi (1.6 M in pentane, 17.1 mL, 27.36 mmol) was added dropwise at 0°C to a suspension of methyltriphenylphosphonium bromide (10.26 g, 28.74 mmol) in THF (400 mL). After 10 min, the suspension was warmed up to room temperature and stirred until no solid remained. Then, at -78°C, a solution of aldehyde **2** (4.259 g, 13.68 mmol) in THF (200 mL) was added dropwise to the Wittig reagent. The solution was slowly warmed up to rt overnight. After addition of 50 mL H_2O and evaporation, the residue was dissolved in Et_2O, washed with brine and dried over $MgSO_4$. The compound **4** was obtained as an orange sticky oil (3.5 g, 83% yield) after chromatography (Silica, MeOH).

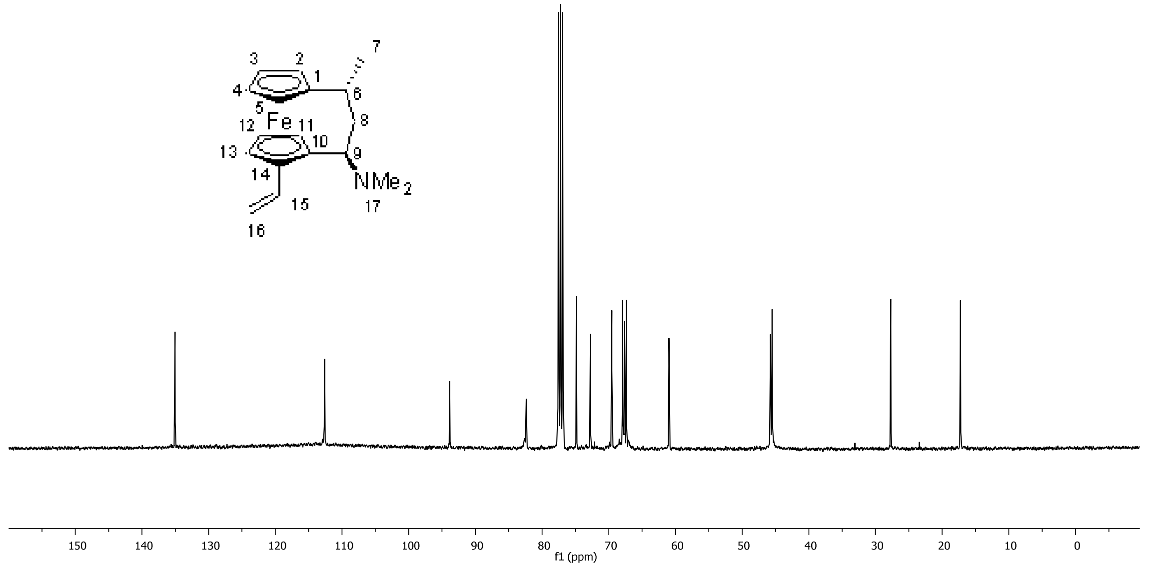
^{1}H NMR ($CDCl_3$, 400 MHz, 295 K) : δ = 6.84 (dd, J = 17.5 Hz, 10.9 Hz, 1H, H_{15}), 5.40 (dd, J = 17.5 Hz, 1.8 Hz, 1H, $H_{16(cis)}$), 5.07 (dd, J = 10.9 Hz, 1.8 Hz, 1H, $H_{16(trans)}$), 4.37 (m, 1H, H_{13}), 4.18, 4.02, 3.89, 3.65 (each m, each 1H, C_5H_4), 4.07 (t, J = 2.4 Hz, 1H, H_{12}), 3.96 (m, 1H, H_{11}), 2.78 (m, 2H, H_6 + H_9), 2.49 (ddd, J = 13.6 Hz, 11.5 Hz, 3.5 Hz, 1H, H_8), 2.32 (ddd, J = 13.6 Hz, 3.8 Hz, 2.9 Hz, 1H, H'_8), 2.23 (s, 6H, H_{17}), 1.23 (d, J = 7.3 Hz, 3H, H_7).

$^{13}C\{^1H\}$-NMR ($CDCl_3$, 101 MHz, 295 K) : δ = 134.8 (C_{15}), 112.4 (C_{16}), 93.6 (C_1), 82.4 (C_{10}), 82.2 (C_{14}), 74.6, 69.3, 67.7, 67.1 (C_5H_4), 72.5 (C_{11}), 67.6 (C_{12}), 67.4 (C_{13}), 60.7 (C_9), 45.5 (C_8), 45.3 (C_{17}), 27.5 (C_6), 17.0 (C_7).

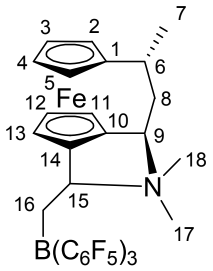
Mass Spectroscopy (HR-ESI, MeOH): Calcd. for $C_{18}H_{23}NFeH$ (MH+) 310.1253 found: 310.1246.



^{1}H NMR (400 MHz, $CDCl_3$, 295 K) of **4**.



$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 295 K) of **4**



Compound 5

Procedure A: A solution of $B(C_6F_5)_3$ (102 mg, 0.2 mmol, 1 equiv.) in CH_2Cl_2 (2 mL) was added at R.T. to a solution of **4** (62 mg, 0.2 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred 15 min at RT and colded at 5°C for 18 hours to afford **5** as yellow crystalline solid. The supernatant was removed with a syringe at -78°C, and the solid was washed three times with cold CH_2Cl_2 (3 mL) to yield analytical pure material (120 mg, 73% yield).
Procedure B: As an alternative procedure, a solution of **4** (23 mg, 0.07 mmol) in CD_2Cl_2 (0.7 mL) was added to $B(C_6F_5)_3$ (38 mg, 0.07 mmol) in a NMR tube at -78°C. NMRs recorded at -40°C show full conversion within 10 min.

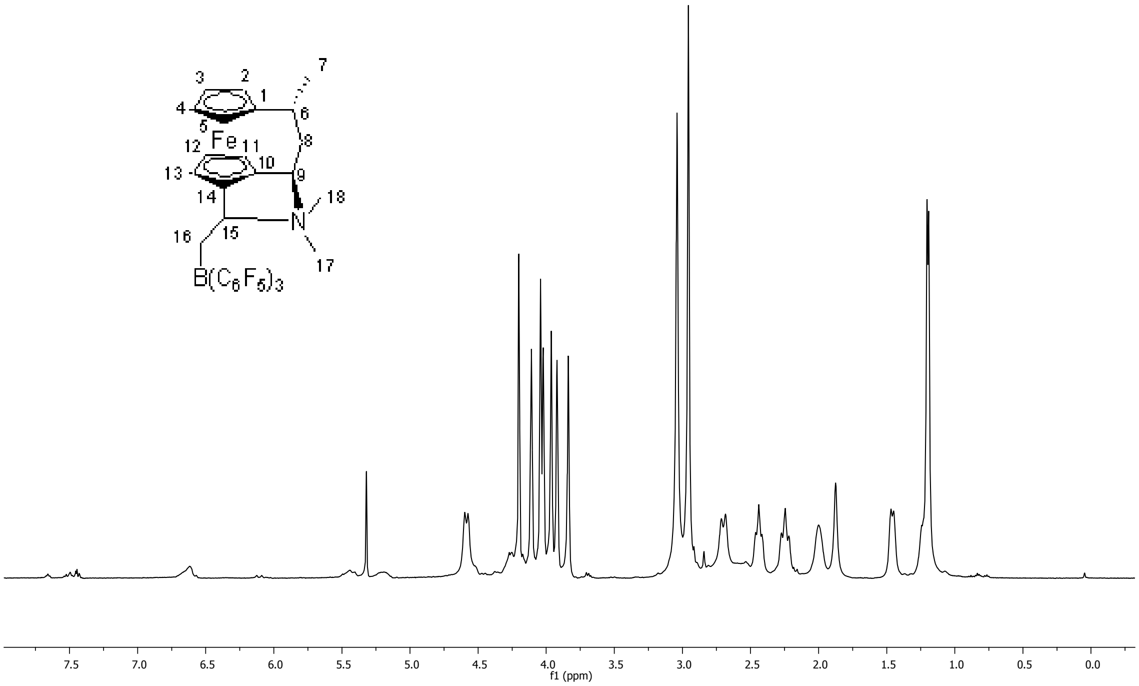
Anal. Calc. for $C_{36}H_{23}BF_{15}FeN.CH_2Cl_2$: C, 49.04; H, 2.78; N, 1.55. Found C, 48.80; H, 2.82; N, 1.62.

^{1}H NMR (500 MHz, CD_2Cl_2, 233 K) δ = 4.59 (d, 1H, H_{15}), 4.20, 3.96, 3.84 (each br, each 1H, C_5H_3), 4.11 (br, 1H, H_9), 4.04, 4.02, 3.92, 1.87 (each br, each 1H, C_5H_4), 3.04 (s, 3H, H_{18}), 2.96 (s, 3H, H_{17}), 2.70 (d, 1H, H_8), 2.44 (t, 1H, H_{16}), 2.25 (t, 1H, H'_8), 2.00 (br, 1H, H_6), 1.46 (d, 1H, H'_{16}), 1.20 (d, 3H, H_7). [all resonances are broad, therefore no *J*-values were listed].

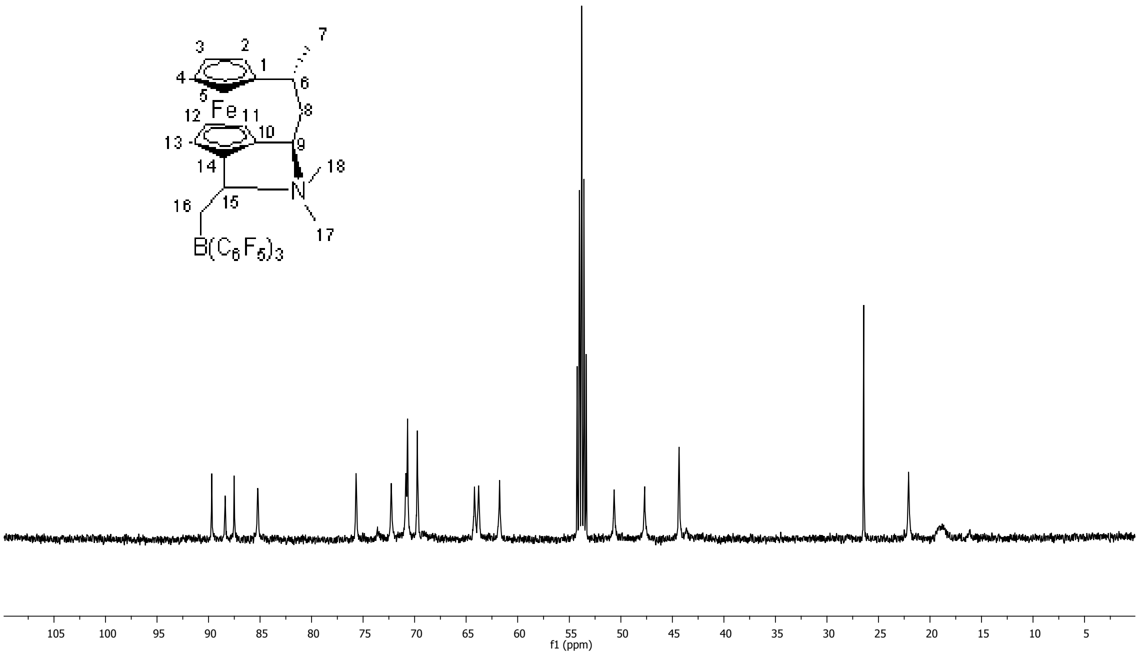
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 233 K) δ = 89.7, 88.4 (C_{10}, C_{14}), 87.5 (C_1), 85.2 (C_{15}), 75.7, 70.7, 69.7, 64.2 (C_5H_4), 72.3 (C_9), 70.9, 63.8, 61.8 (C_5H_3), 50.6 (C_{17}), 47.7 (C_8), 44.3 (C_{18}), 26.4 (C_6), 22.1 (C_7), 18.8 (br, C_{16}), n.o. (C_6F_5). [all resonances are broad].

^{19}F NMR (470 MHz, CD_2Cl_2, 233 K) δ = -131.8 (br, 6F, *o*-C_6F_5), -161.6 (br, 3F, *p*-C_6F_5), -165.8 (br, 6F, *m*-C_6F_5).

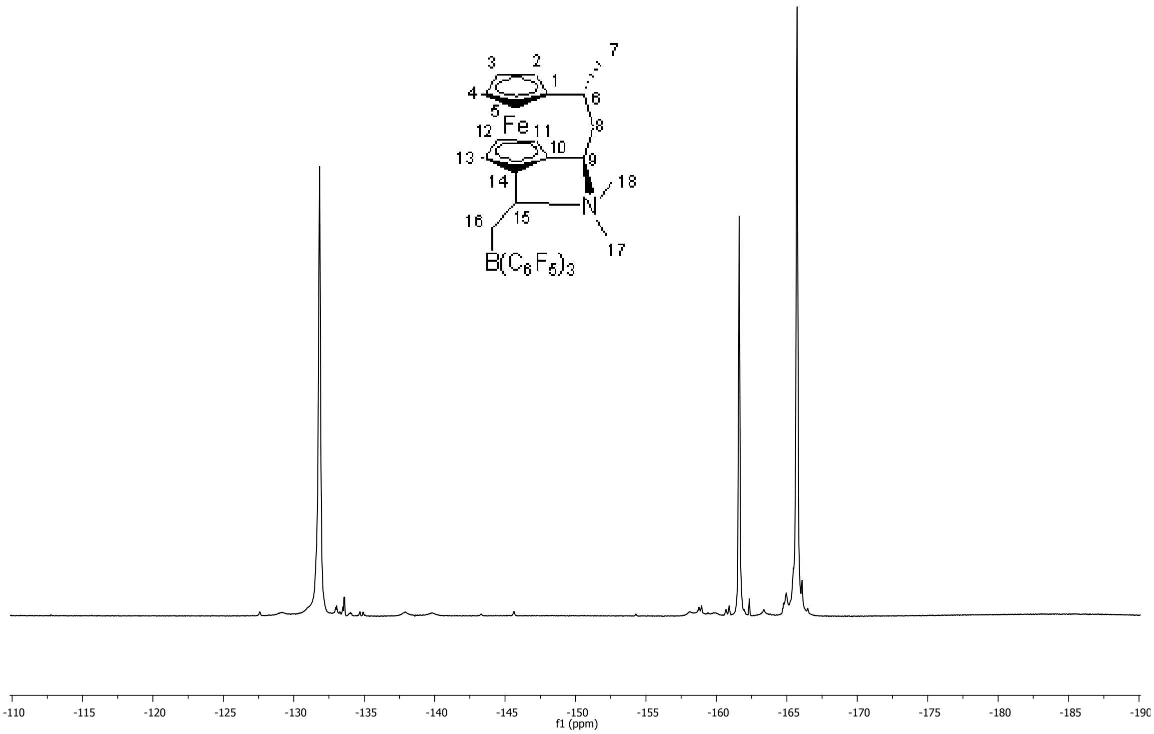
^{11}B NMR (160 MHz, CD_2Cl_2, 233 K) δ = -14.8 (s, $\nu_{1/2}$ = 60 Hz).



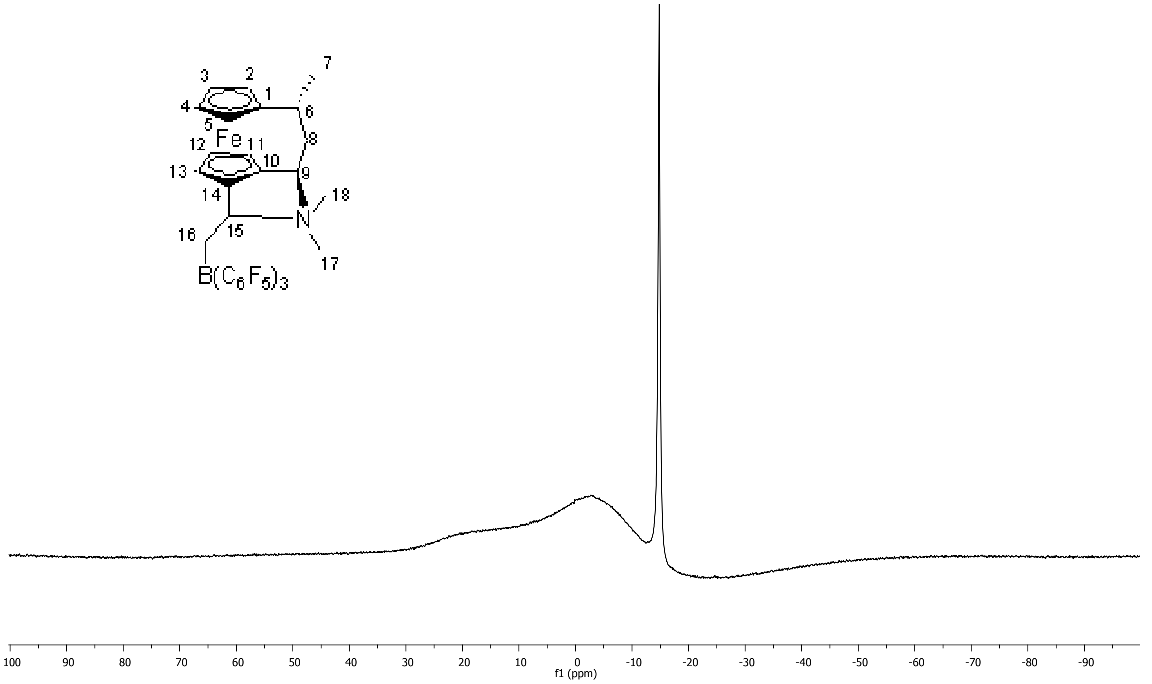
^{1}H NMR (500 MHz, CD_2Cl_2, 233 K) of **5**.



$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 233 K) of **5**.



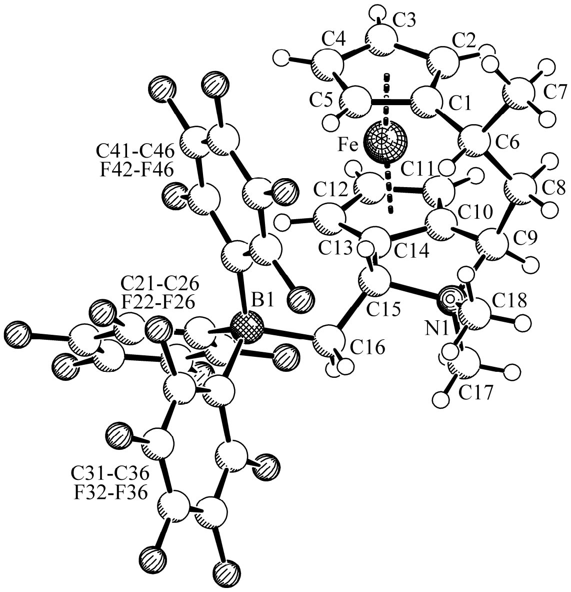
^{19}F NMR (470 MHz, CD_2Cl_2, 233 K) of **5**.

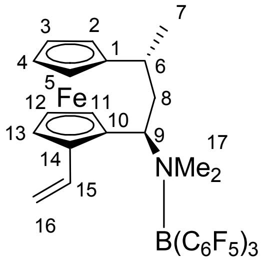


^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 233 K) of **5**.

X-Ray Crystal Structure Analysis of 5.

Crystal data for $C_{36}H_{23}BF_{15}FeN$ * CH_2Cl_2 (**5**), M = 906.14, triclinic, space group *P*1bar (No. 2), a = 9.9961(2), b = 13.2908(3), c = 14.8471(3) Å, α = 91.398(1), β = 109.054(1), γ = 105.386(1)°, V = 1784.25(5) Å^3, D_c = 1.687 g cm^{-3}, μ = 0.682 mm^{-1}, Z = 2, λ = 0.71073 Å, T = 223(2) K, 29354 reflections collected (±h, ±k, ±l), [$(sin\theta)/\lambda$] = 0.67 Å^{-1}, 8787 independent (R_{int} = 0.024) and 7250 observed reflections [$I \geq 2\sigma(I)$], 517 refined parameters, R = 0.051, wR^2 = 0.154.
The R values are given for the observed reflections [$I \geq 2\sigma(I)$] and wR^2 values are given for all reflections.





Compound 6 (NMR study)

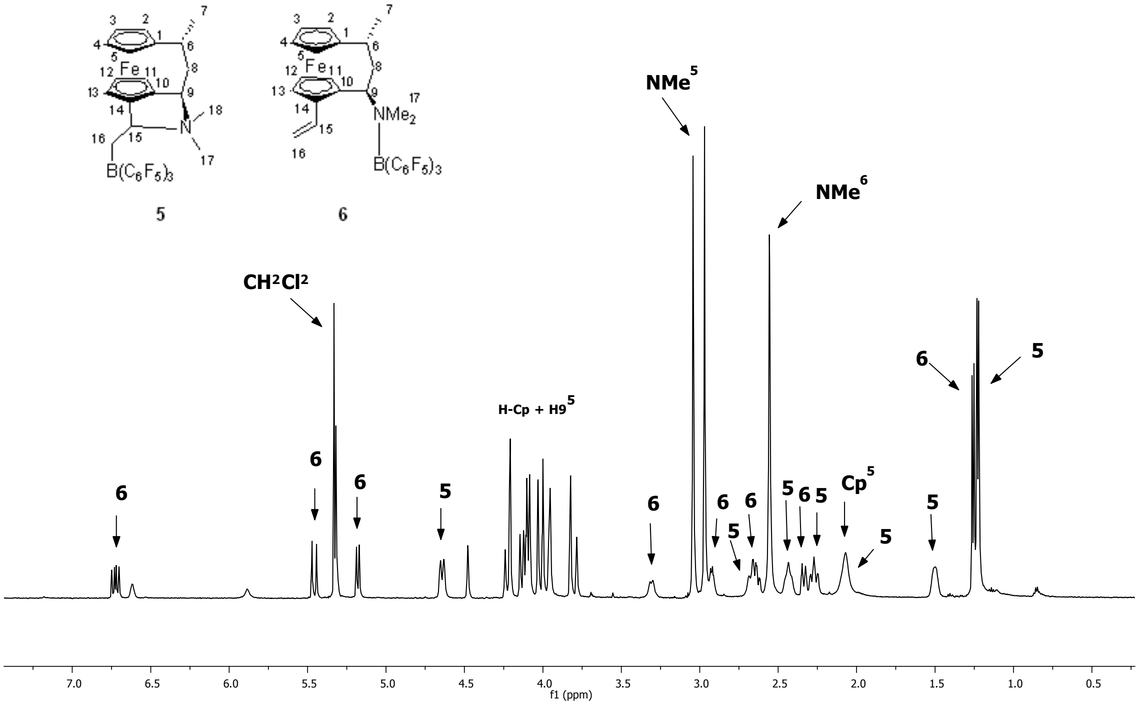
In CD_2Cl_2 solution compound **5** rearranges above -10°C to yield compound **6**. After 1h at 0°C, a sample of pure **5** is transformed in a 1:1 mixture of **5** and **6**. Above +10°C, compound **7** starts to appear slowly. After 24h at +25C°, **7** was formed in 90% conversion.

^{1}H NMR (599 MHz, CD_2Cl_2, 273 K) δ = 6.73 (dd, J = 17.2 Hz, 10.7 Hz, 1H, H_{15}), 5.46 (dd, J = 17.2 Hz, 1.0 Hz, 1H, $H_{16(cis)}$), 5.18 (d, J = 10.7, 1H, $H_{16(trans)}$), 4.48, 4.21, 4.12 (each br, each 1H, C_5H_3), 4.24, 4.15, 3.96, 3.78 (each br, each 1H, C_5H_4), 3.31 (br d, 1H, H_9), 2.93 (m, 1H, H_6), 2.64 (td, J = 13.0 Hz, 3.5 Hz, 1H, H_8), 2.56 (s, 6H, H_{17}), 2.34 (dm, J = 13.0 Hz, 1H, H'_8), 1.26 (d, J = 7.3 Hz, 3H, H_7).

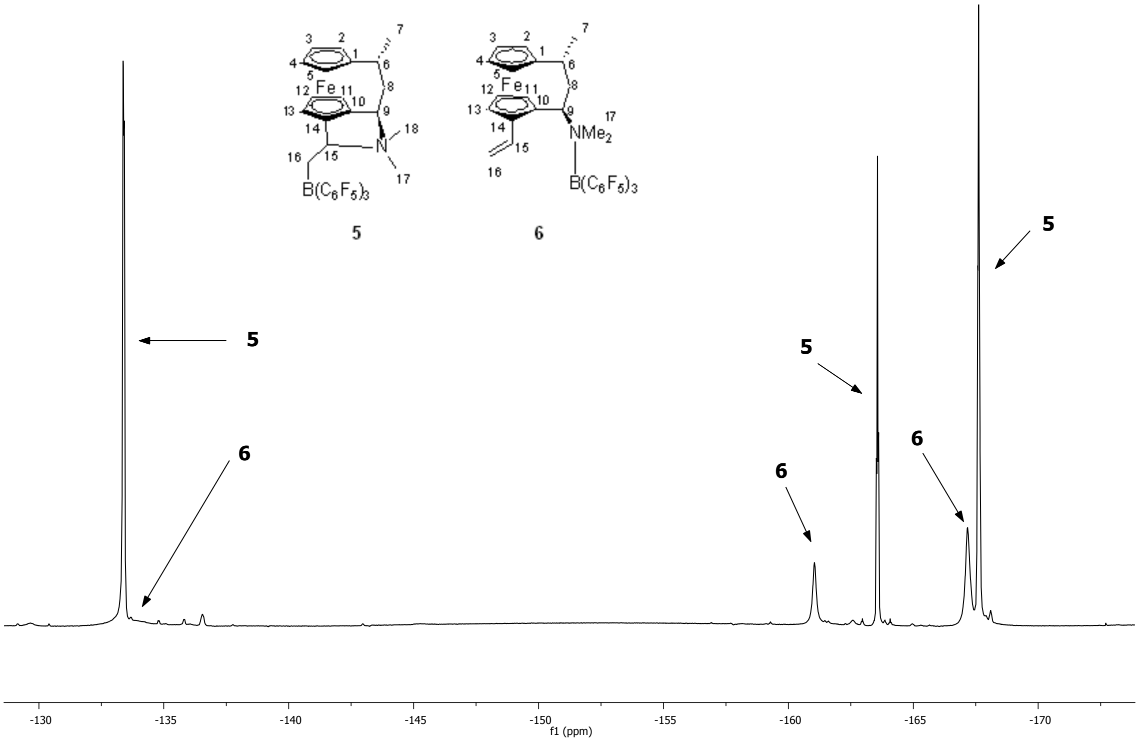
$^{13}C\{^1H\}$ NMR* (150 MHz, CD_2Cl_2) δ = 133.3 (C_{15}), 114.9 (C_{16}), 92.1 (C_1), 82.6, 73.0 (C_{14}, C_{10}), 73.9, 70.4, 68.4, 68.0 (C_5H_4), 72.6, 69.0, 68.5 (C_5H_3), 63.9 (C_9), 44.7 (C_{17}), 44.0 (C_8), 27.7 (C_6), 16.5 (C_7), n.o. (C_6F_5). [* Chemical shifts were determined from ^{1}H, ^{13}C ghsqc (273K) and ^{1}H, ^{13}C ghmbc (233K; C_1, C_{10}, and C_{14}) NMR experiments.]

^{19}F NMR (564 MHz, CD_2Cl_2, 273 K) δ = -133.6 (br, 6F, *o*-C_6F_5), -161.0 (br, 3F, *p*-C_6F_5), -167.2 (br, 6F, *m*-C_6F_5).

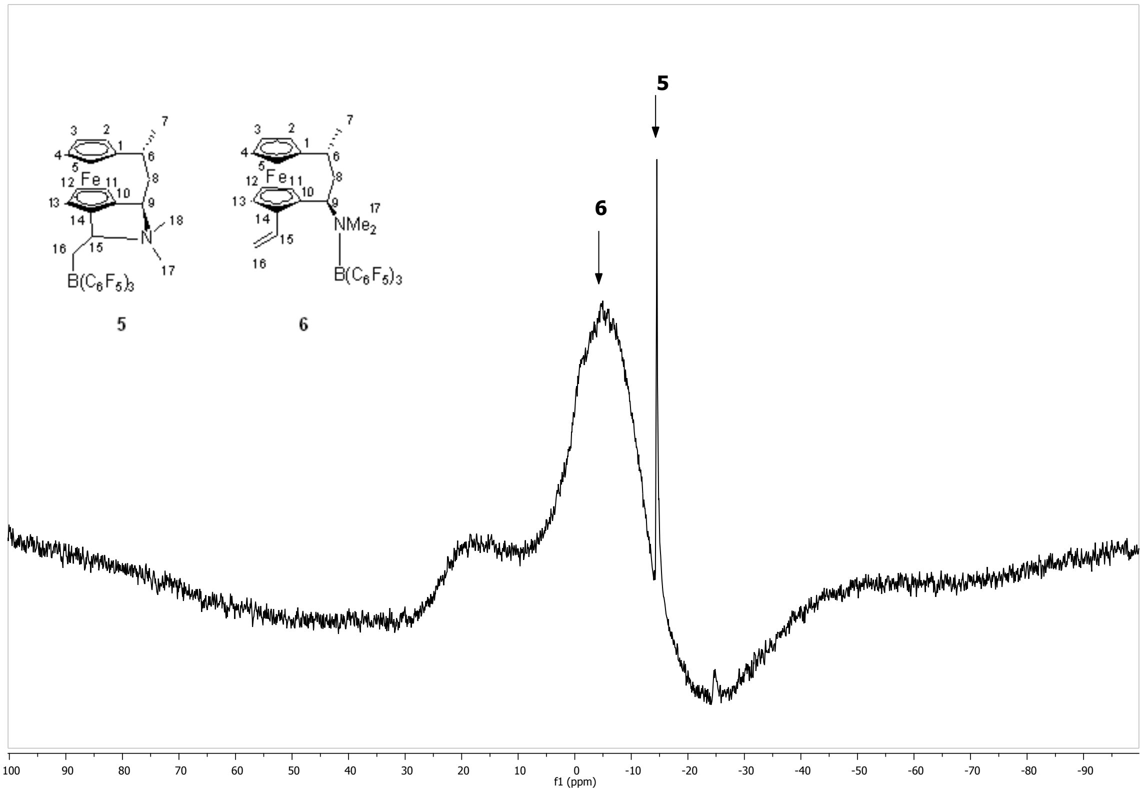
^{11}B NMR (160 MHz, CD_2Cl_2, 298K) δ = -5 (very br).



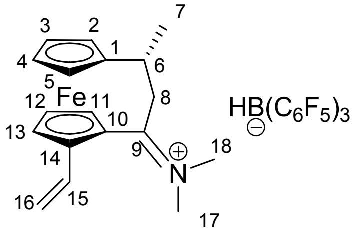
^{1}H NMR (600 MHz, CD_2Cl_2, 273 K) of a 1:1 mixture of **5** and **6**.



^{19}F NMR (564 MHz, CD_2Cl_2, 273 K) of a mixture of **5** and **6**.



$^{11}B\ \{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 298 K) of a mixture of **5** and **6**.



Compound 7

^{1}H NMR (599 MHz, CD_2Cl_2, 233 K) δ = 6.26 (dd, *J* = 17.2 Hz, 10.7 Hz, 1H, H_{15}), 5.48 (d, *J* = 17.2 Hz, 1H, $H_{16(cis)}$), 5.27 (dd, *J* = 10.7 Hz, 0.7 Hz, 1H, $H_{16(trans)}$), 5.03 (br, 1H, H_{11}), 4.88 (ddd, *J* = 2.4 Hz, 1.3 Hz, 0.5 Hz 1H, H_{13}), 4.78 (dt, *J* = 2.4 Hz, 1.3 Hz, 1H, $C_5H_4^{\alpha}$), 4.67 (td, *J* = 2.4 Hz, 0.5 Hz, 1H, H_{12}), 4.26 (dt, *J* = 2.4 Hz, 1.3 Hz, 1H, $C_5H_4^{\alpha}$), 4.13 (m, 2H, $C_5H_4^{\beta}$), 3.64 (s, 3H, H_{17}), 3.54 (t, *J* = 12.7 Hz, 1H, H_8), 3.49 (s, 3H, H_{18}), 3.26 (m, 1H, H_6), 3.09 (d, *J* = 12.7 Hz, 1H, H'_8), 1.34 (d, *J* = 7.0 Hz, 3H, H_7).

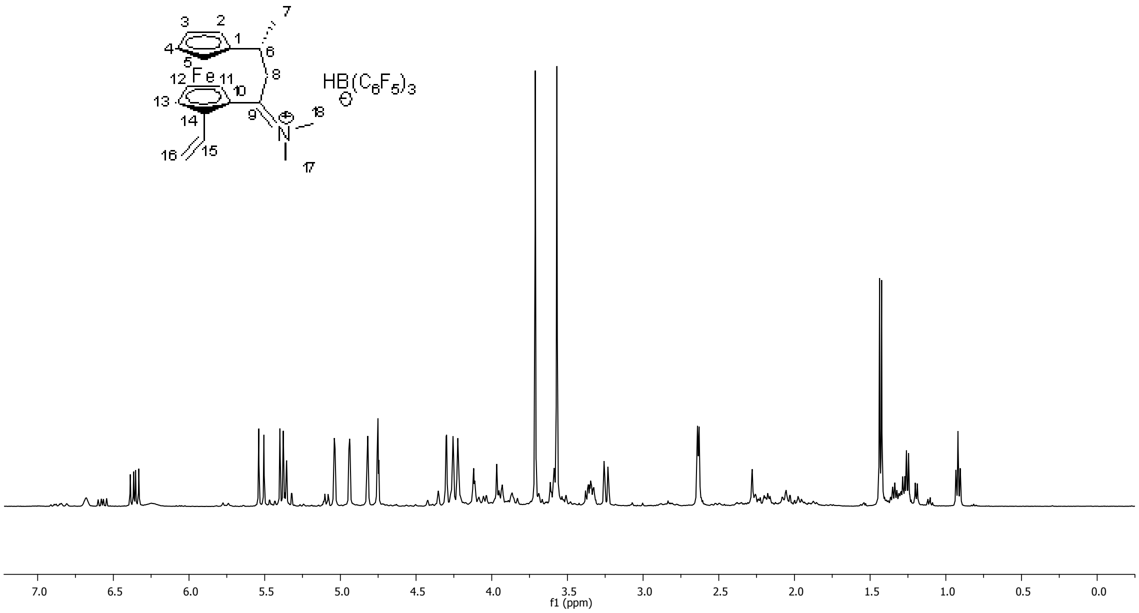
^{1}H NMR (599 MHz, CD_2Cl_2, 298 K) δ = 6.33 (dd, *J* = 17.3 Hz, 10.8 Hz, 1H, H_{15}), 5.49 (dd, *J* = 17.3 Hz, 0.7 Hz, 1H, $H_{16(cis)}$), 5.35 (dd, *J* = 10.8 Hz, 0.7 Hz, 1H, $H_{16(trans)}$), 5.01 (dd, *J* = 2.7 Hz, 1.4 Hz, 1H, H_{11}), 4.91 (ddd, *J* = 2.7 Hz, 1.4 Hz, 0.5 Hz, 1H, H_{13}), 4.79 (dt, *J* = 2.5 Hz, 1.3 Hz, 1H, $C_5H_4^{\alpha}$), 4.72 (td, *J* = 2.7 Hz, 0.5 Hz, 1H, H_{12}), 4.27 (dt, *J* = 2.5 Hz, 1.3 Hz, 1H, $C_5H_4^{\alpha}$), 4.22 (td, *J* = 2.5 Hz, 1.3 Hz, 1H, $C_5H_4^{\beta}$), 4.19 (tdd, *J* = 2.5 Hz, 1.3 Hz, 0.5 Hz,1H, $C_5H_4^{\beta}$), 3.68 (s, 3H, H_{17}), 3.56 (m, 1H, H_8), 3.54 (s, 3H, H_{18}), 3.32 (m, 1H, H_6), 3.21 (dd, *J* = 13.1 Hz, 2.4 Hz, 1H, H'_8), 1.39 (d, *J* = 6.6 Hz, 3H, H_7), n. o. ($HB(C_6F_5)_3$).

$^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) δ = 194.1 (C_9), 148.2 (dm, J_{FC} = 234, C_6F_5), 139.7 (dm, J_{FC} = 231, C_6F_5), 136.9 (dm, J_{FC} = 234 Hz, C_6F_5), 130.8 (C_{15}), 119.4 (br, C_6F_5), 117.2 (C_{16}), 94.7 (C_1), 84.2 (C_{14}), 78.7 ($C_5H_4^{\alpha}$), 76.6 (C_{11}), 74.9 (C_{12}), 72.3 ($C_5H_4^{\beta}$), 72.1 (C_{13}), 71.6 (C_{10}), 71.1 ($C_5H_4^{\beta}$), 69.0 ($C_5H_4^{\alpha}$), 50.2 (C_8), 48.9 (C_{18}), 45.5 (C_{17}), 39.1 (C_6), 22.2 (C_7).

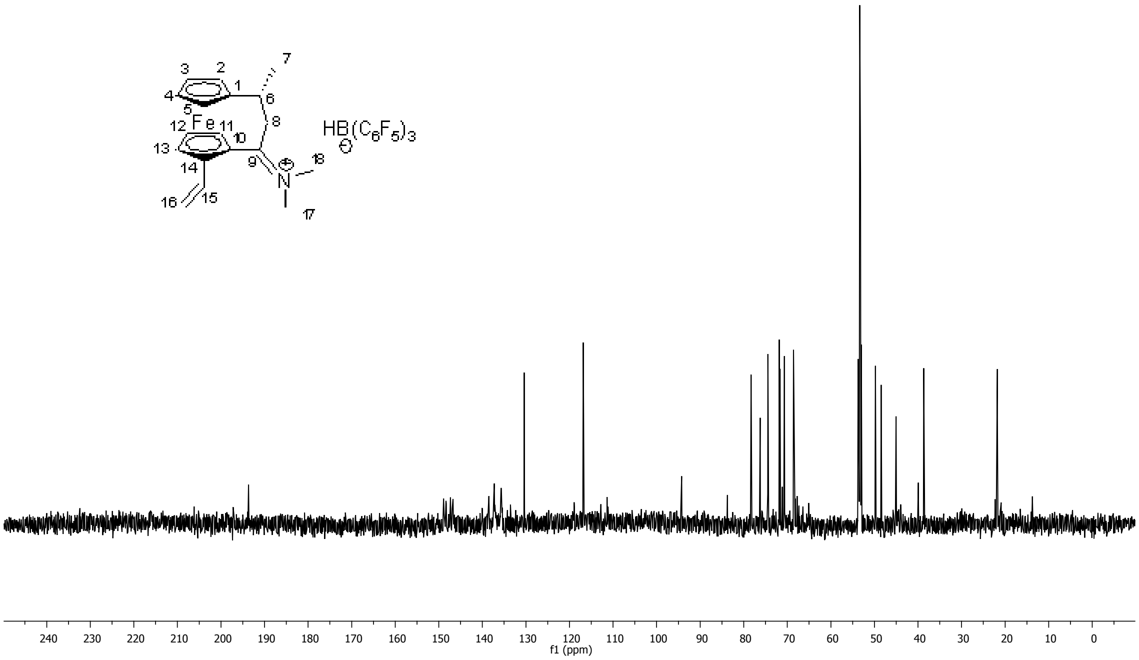
$^{19}F\{^1H\}$ NMR (564 MHz, CD_2Cl_2, 298 K) δ = -134.0 (m, 6F, *o*-C_6F_5), -164.2 (t, *J* = 20.2, 3F, *p*-C_6F_5), -167.3 (m, 6F, *m*-C_6F_5).

^{11}B NMR (96 MHz, CD_2Cl_2, 298 K) δ = -25.4 (d, *J* = 90).
$^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2, 298 K) δ = -25.4 (s, $\nu_{1/2}$ = 55 Hz).

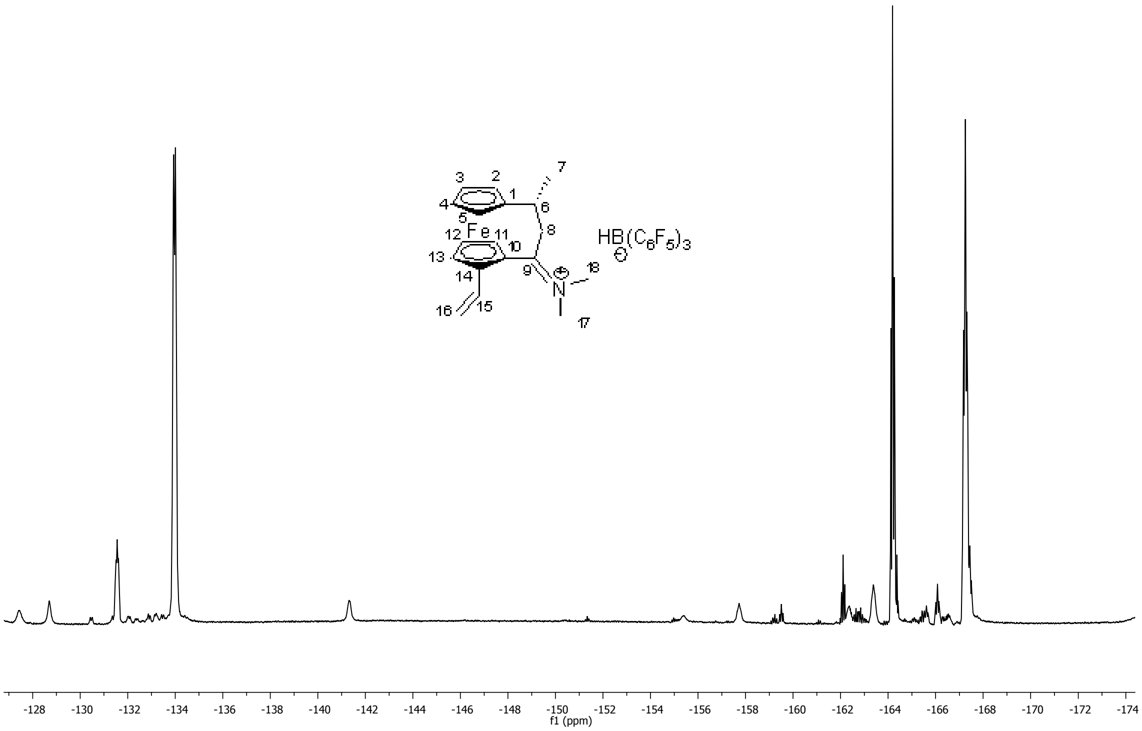
HRMS (ESI positive, MeOH) Calcd. for $C_{18}H_{22}FeN^+$: 308.1096 (M^+); Found : 308.1098.
HRMS (ESI negative, MeOH) Calcd. for $HBC_{18}F_{15}^-$: 512.9940 (M^-); Found : 512.9938.



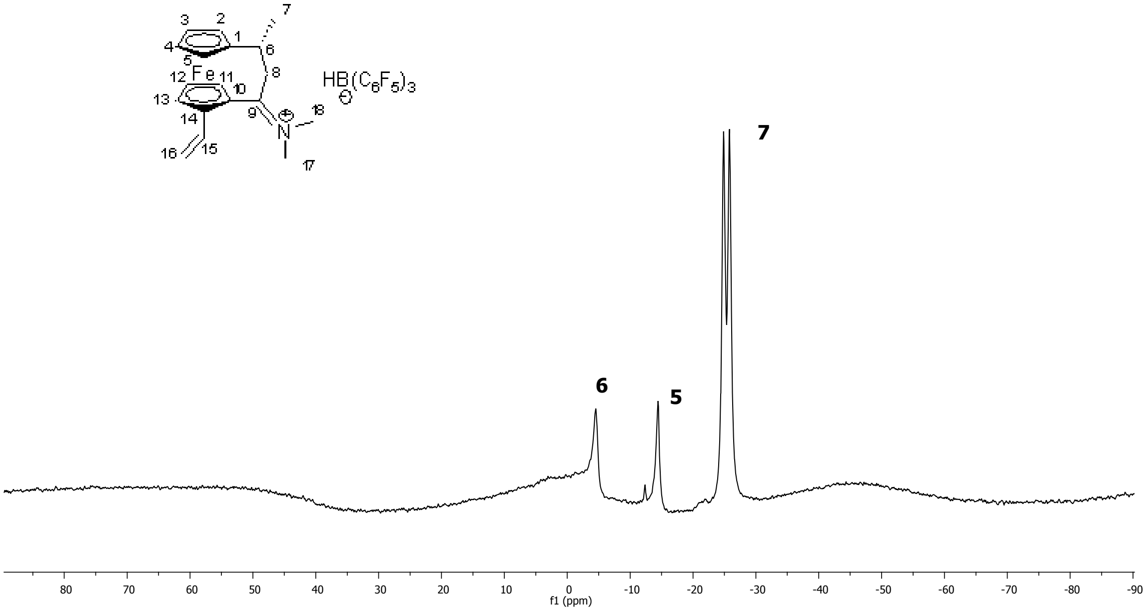
^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) of **7**.



$^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2, 298 K) of **7**.



$^{19}F\{^{1}H\}$ NMR (282 MHz, CD_2Cl_2, 289 K) of **7**.



^{11}B NMR (96 MHz, CD_2Cl_2, 289 K) of **7**.