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SUPPORTING INFORMATION

# A general diastereoselective synthesis of highly functionalized ferrocenyl ambiphiles enabled at large scale by electrochemical purification

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**Electrochemistry reagents and instrumentation**

Tetraethylammonium tetrafluoroborate ($TEABF_4$) was synthesized according to the following method. Typically, in a 500 mL Erlenmeyer flask, 84.28 g of tetrafluoroboric acid, $HBF_4$ (Sigma Aldrich, 48% in $H_2O$) was mixed with 193.84 g of a solution of tetraethylammonium hydroxide, TEAOH (Alfa Aesar, 35% in $H_2O$). The reaction mixture was continuously stirred under an air atmosphere. Then, the white precipitate formed after cooling the flask in an ice bucket was isolated by filtration on a Buchner funnel. Finally, the residue was crystallized from MeOH (Carlo Erba, RPE, 99.9%) under reflux, cooled in a freezer at −18 °C, filtered on a Buchner funnel and dried at 110 °C in the stove for at least two days before use. $CH_3CN$ (SDS, Carlo Erba, HPLC gradient 99.9%) was distilled from $CaH_2$ under Ar, unless otherwise noted. NMR spectra were recorded using a BRUKER 500 MHz Avance II or 300 MHz Bruker Avance III NanoBay spectrometer. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were calibrated to TMS on the basis of the relative chemical shift of the solvent as an internal standard.

Unless stated otherwise, all manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen free argon at room temperature ($T$ = 20 °C ± 3 °C). The supporting electrolyte (tetraethylammonium tetrafluoroborate) was degassed under vacuum before use and then dissolved to a concentration of 0.1 M. Voltammetry analyses were carried out in a standard three-electrode cell, with an Autolab PGSTAT 302N potentiostat, connected to an interfaced computer that employed Electrochemistry Nova software. The reference electrode was a KCl saturated calomel electrode (SCE) separated from the analyzed solution by a sintered glass disk filled with the background solution. The auxiliary electrode was a platinum wire separated from the analyzed solution by a sintered glass disk filled with the background solution. For all voltammetry measurements, the working electrode was a platinum electrode disk ($Ø$ = 1 mm). In these conditions, when operating in acetonitrile (0.1 M $TEABF_4$), the formal potential for the ferrocene$^{(+/0)}$ couple was found to be +0.40 V *vs*. SCE.

Electrolyses were performed in a three compartment cell separated with glass frits of medium porosity with an Amel 552 potentiostat/galvanostat coupled with an Amel 721 electronic integrator. For small scale electrolysis (0.2 mmol of the crude solid to be purified ($CS_0$), $3.2\times10^{-3}$ < [**2a**] < $4.8\times10^{-3}$ M), a platinum wire spiral ($l$ = 50 cm, $Ø$ = 1 mm) is used as the working electrode, a platinum wire spiral ($l$ = 50 cm, $Ø$ = 1 mm) as the counter electrode and a saturated

calomel electrode as the reference electrode. For large scale electrolysis (21.70 g of $CS_0$, [**2a**] = $1.17\times10^{-1}$ M), a platinum grid cylinder ($\varnothing$ = 4.0 cm, $l$ = 5.0 cm) is used as the working electrode, three together-connected platinum wire spirals ($l$ = 50 cm, $\varnothing$ = 1 mm) as the counter electrode and a KCl saturated calomel electrode as the reference electrode. The anodic compartment containing the initial solution with $CS_0$ is electrolyzed at constant potential ($E_{app}$). When the current reached a stable and minimum value, the electrolysis is stopped and the anodic compartment is collected and evaporated. Work-up is performed as follow: *n*-pentane is added on the crude residue, this latter is sonicated, the resulting orange/brown solution is filtered through a sintered glass funnel and the solvent is finally evaporated. In the case of the large scale electrolysis, the worked-up solid was ultimately recrystallized from MeOH. $^1$H NMR analysis provides the final distribution in ferrocene-based compounds.

## $^1$H NMR analysis of $CS_0$ content

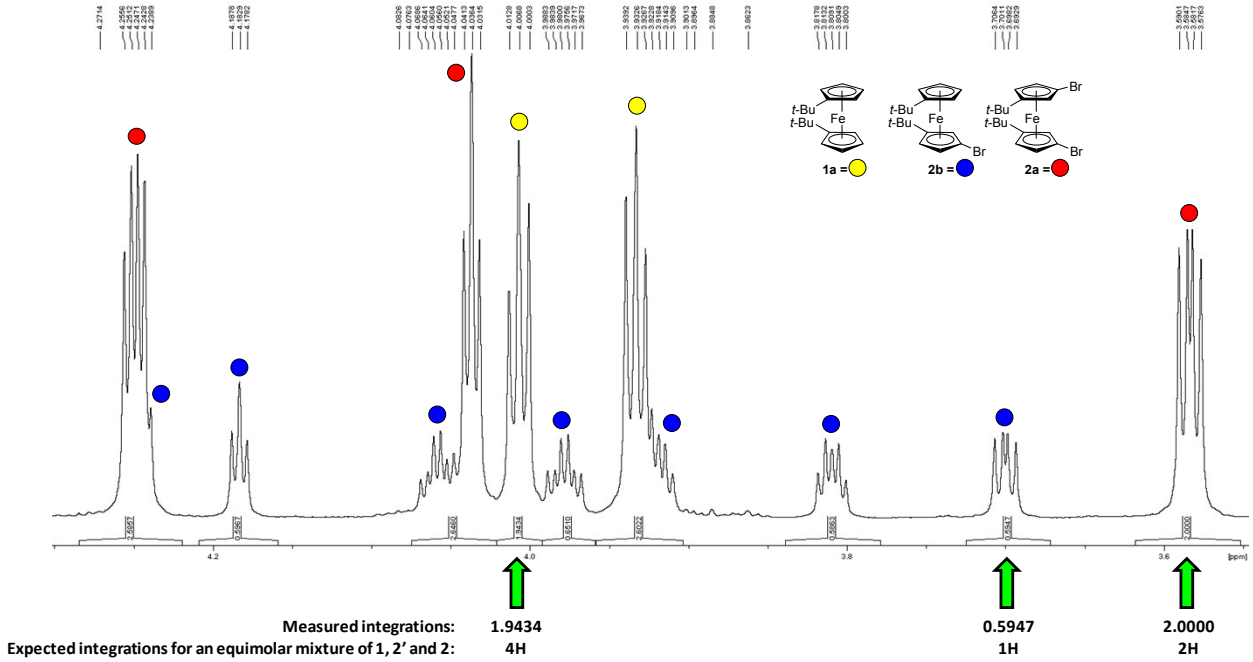



**Fig. S1** Partial $^1$H NMR spectrum of the initial crude solid to be purified ($CS_0$) focused on the cyclopentadienyl signals ($C_6D_6$, 300 MHz, 298 K). The green arrows show the integrations which are used for calculation of the molar ratio between ferrocene-based compounds (see **Table S1** below for exact composition in ferrocene products of $CS_0$).

**Table S1** Molar ratio (in ferrocene products), molar amount, molecular weight and mass of **1**, **2'** and **2** in the initial crude solid to be purified ($CS_0$), extracted from $^1$H NMR integrations shown in **Fig. S1**.

| **$CS_0$** (22.4 g; 29.9 mmol of **1b**) | **1a** | **2b** | **2a** |
|---|---|---|---|
| mol % | 23.4 | 28.4 | 48.2 |
| *n* (mmol) | 7.00 | 8.49 | 14.41 |
| *M* (g/mol) | 298.25 | 377.15 | 456.04 |
| *m* (g) | 2.08 | 3.20 | 6.57 |

## $^1$H NMR analyses of $CS_0$ content after electrolysis at 0.2 mmol scale

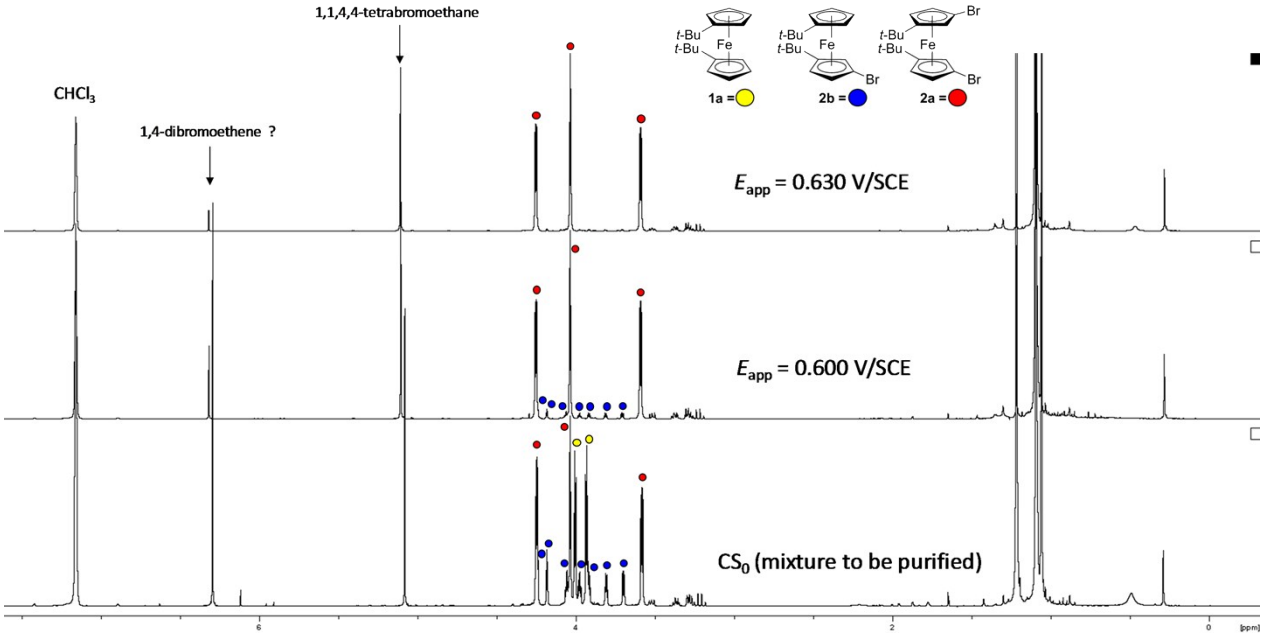



**Fig. S2** From bottom to top: $^1$H NMR spectra of the initial crude solid to be purified ($CS_0$), the crude solution after electrolysis at 0.600 V/SCE + work-up, and the crude solution after electrolysis at 0.630 V/SCE + work-up ($C_6D_6$, 300 MHz, 298 K) at 0.2 mmol scale.

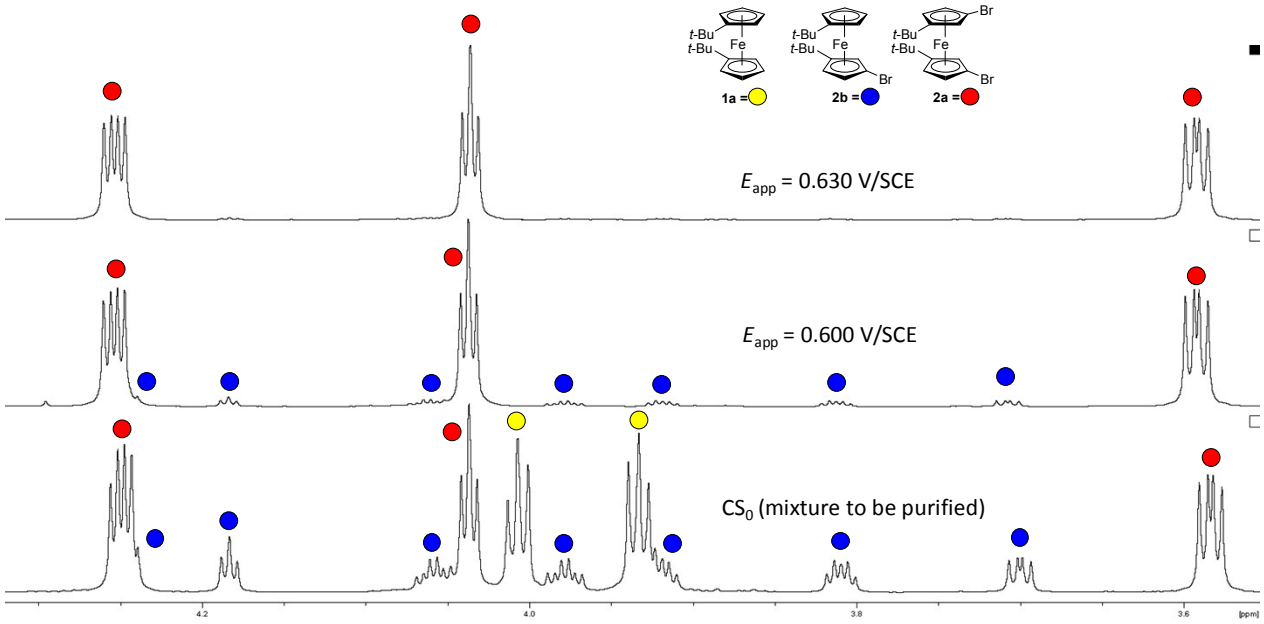



**Fig. S3** From bottom to top: partial $^1$H NMR spectra focused on cyclopentadienyl signals of the initial crude solid to be purified ($CS_0$), the crude solution after electrolysis at 0.600 V/SCE + work-up, and the crude solution after electrolysis at 0.630 V/SCE + work-up ($C_6D_6$, 300 MHz, 298 K) at 0.2 mmol scale.

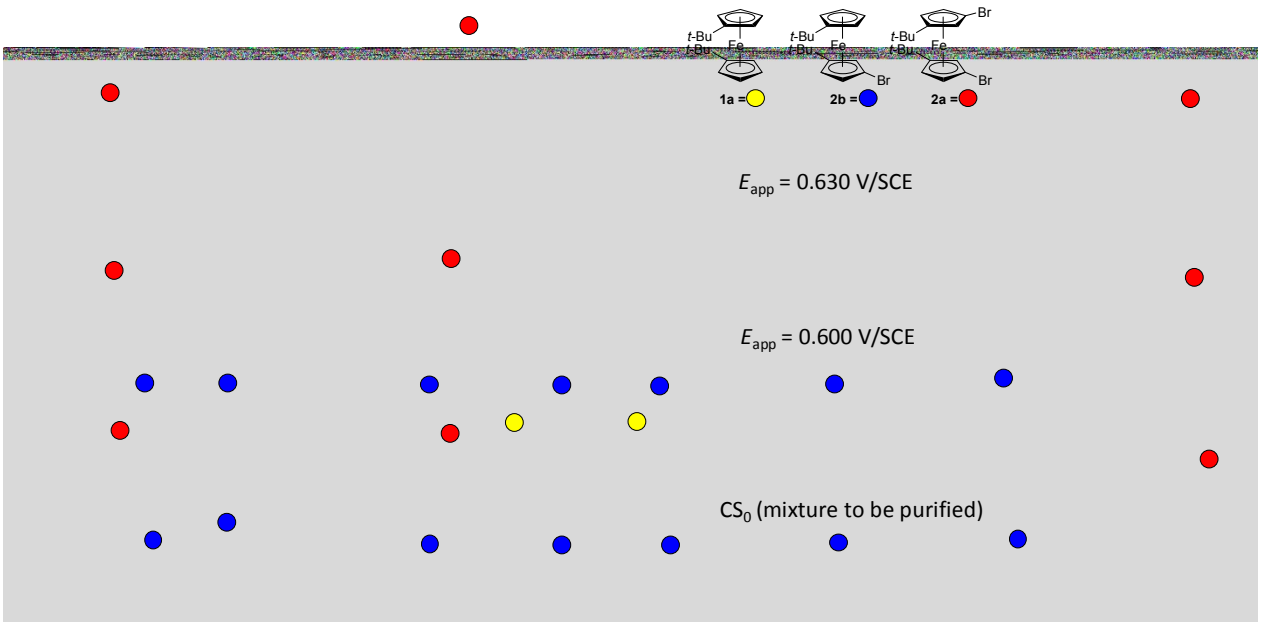



**Fig. S4** From bottom to top: partial $^1$H NMR spectra focused on the *t*-Bu signals of the initial crude solid to be purified ($CS_0$), the crude solution after electrolysis at 0.600 V/SCE + work-up, and the crude solution after electrolysis at 0.630 V/SCE + work-up ($C_6D_6$, 300 MHz, 298 K) at 0.2 mmol scale.

## Voltammetry analyses of $CS_0$

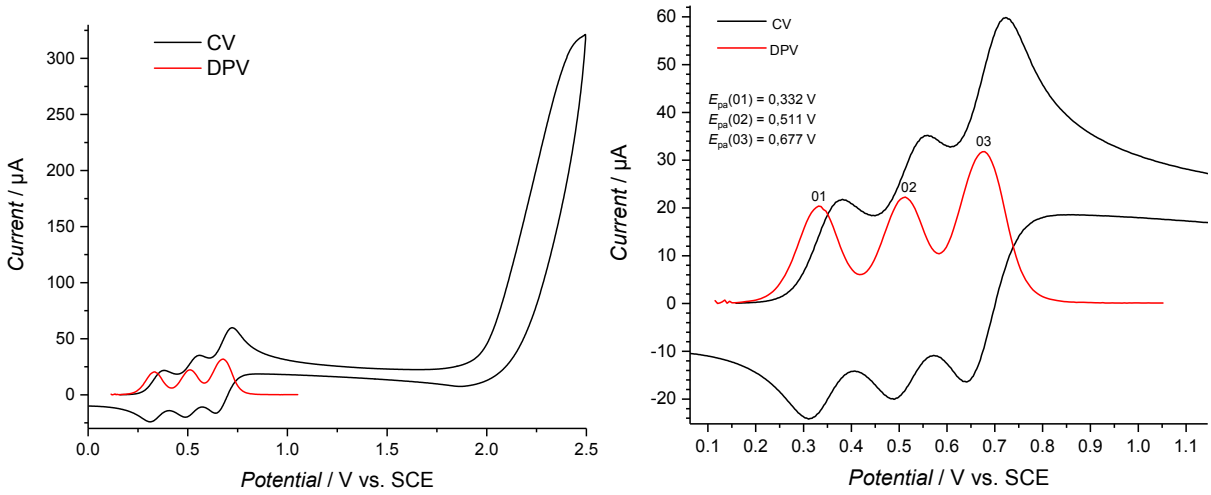



**Fig. S5** Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of a solution of $CS_0$ ($m(CS_0)$ = 147 mg; [**2a**] = $4.8\times10^{-3}$ M in $CH_3CN$ 0.1 M $TEABF_4$; $v$ = 100 mV/s and 10 mV/s for CV and DPV, respectively, working electrode: Pt ($Ø$ = 1 mm); reference electrode: SCE). Relevant parameters are gathered in **Table S2**.

**Table S2** Anodic peak potential ($E_{pa}$), cathodic peak potential ($E_{pc}$), $E_{1/2}$ (= ($E_{pa}$+$E_{pc}$)/2), $E_{pa}$-$E_{pc}$ and $E_{1/2}$ potential gaps for **1a**, **2b** and **2a** in the experimental conditions of **Fig. S8**.

| $CS_0$ | **1a** | | | | **2b** | | | | **2a** | | | | $E_{1/2}$(**2'**)-$E_{1/2}$(**1**) | $E_{1/2}$(**2**)-$E_{1/2}$(**2'**) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $E_{pa}$ (V) | $E_{pc}$ (V) | $E_{1/2}$ (V) | $E_{pa}$-$E_{pc}$ (mV) | $E_{pa}$ (V) | $E_{pc}$ (V) | $E_{1/2}$ (V) | $E_{pa}$-$E_{pc}$ (mV) | $E_{pa}$ (V) | $E_{pc}$ (V) | $E_{1/2}$ (V) | $E_{pa}$-$E_{pc}$ (mV) | (mV) | (mV) |
| CV | 0.382 | 0.311 | 0.346 | 71 | 0.558 | 0.489 | 0.524 | 69 | 0.723 | 0.640 | 0.682 | 83 | 178 | 158 |
| DPV | 0.331 | | | | 0.508 | | | | 0.669 | | | | | |

## $^1$H NMR analyses of $CS_0$ content after electrolysis at 30 mmol scale

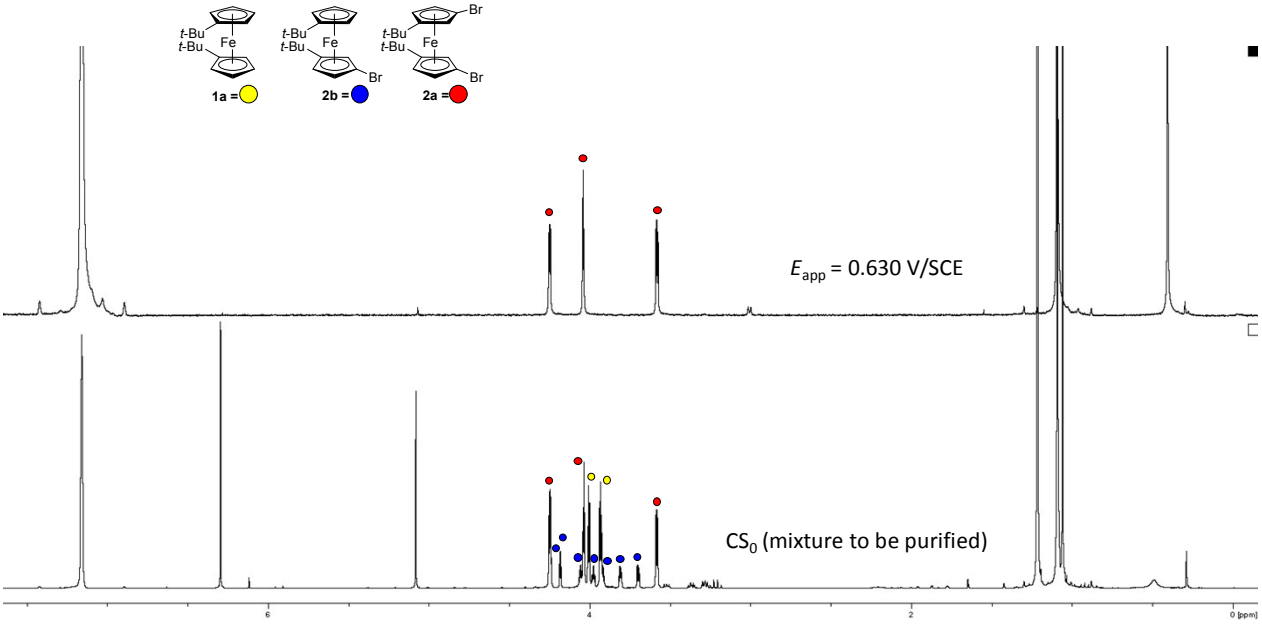



**Fig. S6** Bottom: $^1$H NMR spectrum of the initial crude solid to be purified ($CS_0$); top: $^1$H NMR spectrum obtained after electrosynthesis ($m(CS_0)$ = 21.70 g, $E_{app}$ = 0.630 V/SCE) at large scale, work-up (pentane extraction, filtration) and crystallization in MeOH ($C_6D_6$, 300 MHz, 298 K).

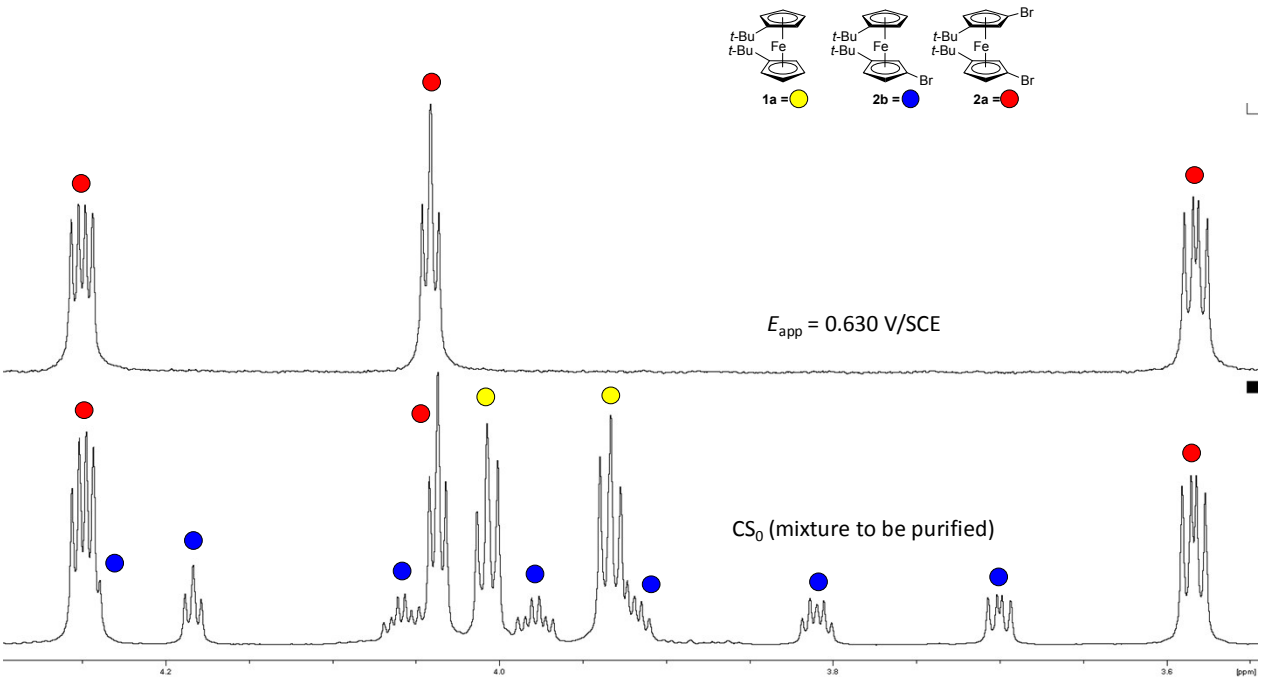



**Fig. S7** Bottom: partial $^1$H NMR spectrum focused on the cyclopentadienyl signals of the initial crude solid to be purified ($CS_0$); top: $^1$H NMR spectrum obtained after electrosynthesis ($m(CS_0)$ = 21.70 g, $E_{app}$ = 0.630 V/SCE) at large scale, work-up up (pentane extraction, filtration) and crystallization in MeOH ($C_6D_6$, 300 MHz, 298 K).

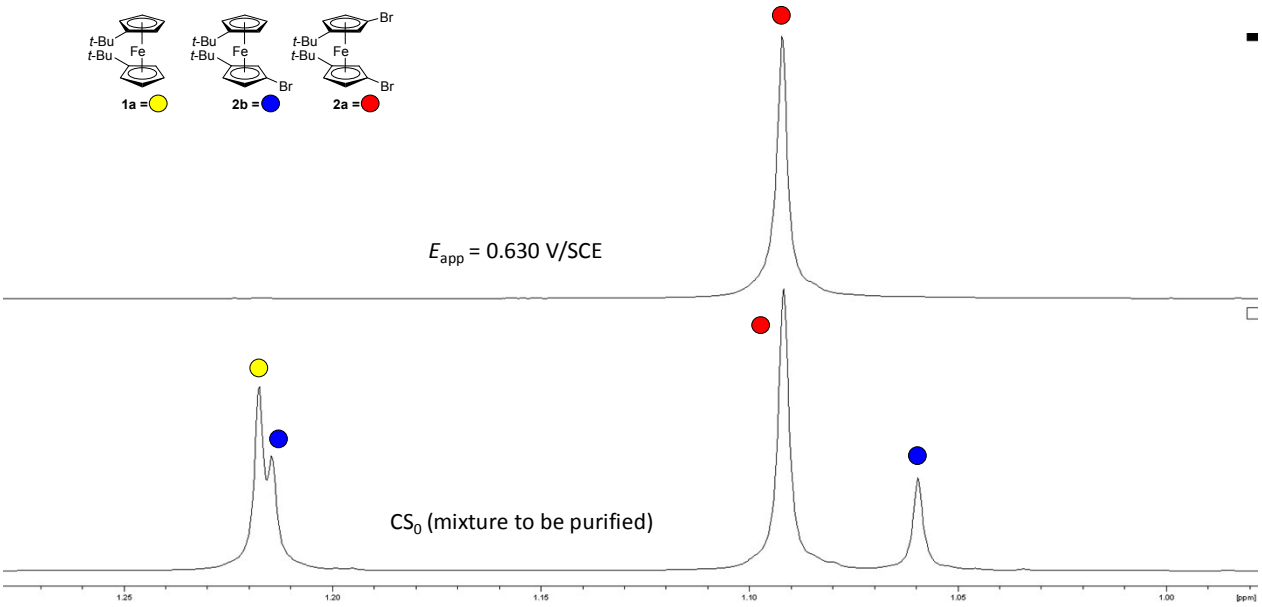



**Fig. S8** Bottom: partial $^1$H NMR spectrum focused on the *t*-Bu signals of the initial crude solid to be purified ($CS_0$); top: $^1$H NMR spectrum obtained after electrosynthesis ($m(CS_0)$ = 21.70 g, $E_{app}$ = 0.630 V/SCE) at large scale, work-up (pentane extraction, filtration) and crystallization in MeOH ($C_6D_6$, 300 MHz, 298 K).

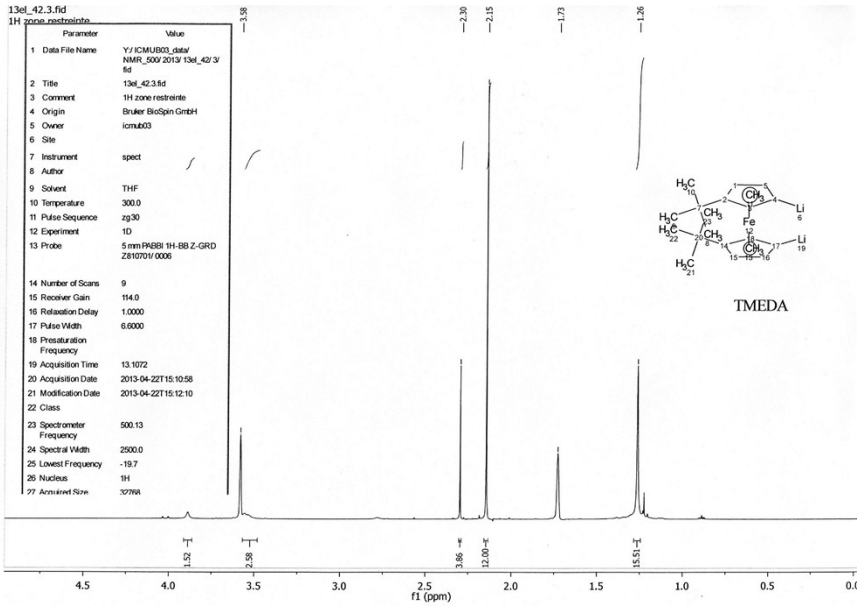
**General methods and synthesis**

All reactions were performed under argon atmosphere using Schlenk techniques or glovebox. Toluene, hexane, pentane, THF, DME and $Et_2O$, were degassed and distilled from sodium benzophenone treatment under argon atmosphere prior to use. Toluene, pentane, THF and $Et_2O$ have also been obtained from a solvent purification system. Dichloromethane and acetonitrile were distilled from calcium hydride under argon. Benzene-*d6*, THF-*d8* and DCM-*d2* ($CD_2Cl_2$) were dried over 3 Å molecular sieves. The identity and purity of the products were established at the "Pôle Chimie Moléculaire" (Welience, uB–Filiale) using multinuclear NMR, elemental analysis and high-resolution mass spectrometry. Elemental analysis was performed on an Analyzer CHNS/O Thermo Electron Flash EA 1112 Series and ICP-AES iCAP Thermo. Exact masses were obtained from a LTQ-Orbitrap XL (THERMO). $^1$H (δ in ppm) spectra (300.13, 500.13 and 600.13 MHz) and 11B NMR (δ in ppm) spectra (96.3 and 160.5 MHz) and $^{13}$C NMR (δ in ppm) spectra (75.5, 125.8 and 150.9 MHz) and $^{31}$P NMR (δ in ppm) spectra (121.5, 202.5 and 243.0 MHz), including identification by 2D NMR experiments COSY, HMQC and HMBC sequences, were recorded at 300 K unless otherwise mentioned on a Bruker 300 Avance, Bruker 500 Avance DRX, or Bruker 600 Avance II spectrometer.

**Synthesis of *rac*-1,1'-dibromo-3,3'-di(*tert*-butyl)-ferrocene, 2a.**

To a solution of 1,1'-di(*tert*-butyl)-ferrocene **1a** (10.40 g, 35 mmol)[a] and *N,N,N',N'*-tetramethylethylenediamine (12.7 mL, 85 mmol, 2.4 eq.) in 50 mL of pentane at –60 °C was added dropwise in 25 min a solution of *tert*-butyllithium in pentane (50 mL, 80 mmol, 1.6 M, 2.3 eq.). The reaction mixture was stirred for 3.5 h allowing slowly rise up to –10 °C then it was stirred 24 h at room temperature. After cooling at –20 °C, 11.28 g (26.5 mmol, 76% yield) of an orange precipitate **1b** was obtained by filtration. The highly pyrophoric compound **1b** was directly used in the following reaction. $^1$H NMR in THF-d8 (copy below), suggested a ratio *ca.* 1:1 for TMEDA: *t*-BuFcLi$_2$. For TMEDA $CH_2$ signal δ = 2.30 ppm (4 H, integration 3.86), for Me from TMEDA δ = 2.15 ppm (12 H, integration 12), for Me from *t*-Bu δ = 1.26 ppm (18 H, integration 15.5) and for H-$C_P$ δ = 3.5-3.9 ppm (6 H, integration 4.1). Under these conditions the adduct ratio in **1b** was estimated to be 1.16 TMEDA: 1 *t*-BuFcLi$_2$ based on Me groups.

[a] D. L. Compton and T. B. Rauchfuss, *Organometallics* **1994**, *13* (11), 4367.




To a solution of **1b** (1.13 g, 2.6 mmol) in 5 mL of $Et_2O$ at –80 °C was added dropwise in 1 h a solution of 1,1,2,2-tetrabromoethane (0.8 mL, 6.7 mmol, 2.6 eq.) in 20 mL of $Et_2O$. The reaction mixture was stirred for 2 h allowing slowly rise up to –30 °C, then it was stirred 16 h at room temperature. The mixture was dropped into water, then extracted with AcOEt, washed by water, by brine and dried over $MgSO_4$ giving a dark brown oil which was solubilized in a few mL of hexane, and quickly eluted on alumina giving a brown oil. Crystallization in MeOH gave **2a** as a brown crystalline solid (1.0 g, 2.2 mmol, 85% yield). X-Ray structure of **2a** was resolved.

***Larger scale synthesis***: under similar conditions, the reaction of 29.9 mmol of **1b** gave 21.70 g of a brown oil containing a mixture of **2a** (48% NMR yield), *t*-$Bu_2$FcBr **2b**, *t*-$Bu_2$Fc **1a** and 1,1,2,2-tetrabromoethane. Selective electrochemical oxidation of **2b** and **1a** was performed to purify **2a**. To 21.70 g of this brown oil under argon was added 250 mL of tetraethylammonium tetrafluoroborate (5.44 g, 25 mmol, 0.1 M) solution in acetonitrile. **2b** and **1a** were oxidized in **2b**+ and **1a**+ at 0.630 V/SCE during 7 h 10 min (Q = 2223 C). After evaporation of solvent, the organics **2a** and 1,1,2,2-tetrabromoethane were extracted with pentane. Crystallisation in pentane gave **2a** as brown crystalline solid (5.0 g, 10.9 mmol, 75% yield, 99%+ purity, no chromatography).

$^1$H NMR (600 MHz, $C_6D_6$): δ 4.25 (2 H, dd, *J* 2.6, 1.3, Cp-C*H*), 4.04 (2 H, t, *J* 1.5, Cp-C*H*), 3.59 (2 H, dd, *J* 2.6, 1.6, Cp-C*H*), and 1.09 (18 H, s, *t-Bu*). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$): δ 102.66, 78.27, 73.40, 70.70, 66.04, 31.45, and 30.61. Elemental analysis for $C_{18}H_{24}Br_2Fe$

(456.04): calculated C (47.41 %), H (5.30%); obtained C (47.29%), H (5.12%). ESI-MS: $[M]^+$: m/z exp = 453.95814, m/z theo = 453.95917, delta = –1.607 ppm. M. p. 68 °C.

**Synthesis of 1-bromo-3,3'-di(*tert*-butyl)-1'-(diphenylphosphino)-ferrocene, 3a.**[b]

To a solution of 1,1'-dibromo-3,3'-di(*tert*-butyl)-ferrocene **2a** (1.9 g, 4.2 mmol) in 10 mL of THF was added dropwise at –50 °C in 10 min a solution of *n*-butyllithium in hexane (2.6 mL, 4.2 mmol, 1.6 M). After stirring for 1 h at –30 °C, a solution of chlorodiphenylphosphine (0.74 mL, 4.0 mmol) in 5 mL of THF was added dropwise in 10 min at room temperature. The solution was stirred during 12 h at room temperature, and then AcOEt was added. The organic phase was washed by water, by brine and dried over $MgSO_4$ giving an orange oil which was purified by chromatography on silica with a 80/20 hexane/DCM eluent giving **3a** as an orange crystalline solid (1.66 g, 3.0 mmol, 71% yield). X-Ray structure of **3a** was resolved.

$^1H\{^{31}P\}$ NMR (600 MHz, $C_6D_6$): δ 7.57 (2 H, td, *J* 7.6, 1.7, Ph), 7.49 (2 H, td, *J* 8.2, 7.7, 1.4, Ph), 7.13-7.02 (6 H, m, Ph), 4.30 (1 H, t, *J* 1.5, Cp-C*H*), 4.18 (1 H, dd, *J* 2.5, 1.3, Cp-C*H*), 4.08 (1 H, dt, *J* 2.8, 1.6, Cp-C*H*), 4.00 (1 H, dd, *J* 2.5, 1.5, Cp-C*H*), 3.98 (1 H, dt, *J* 2.7, 1.5, Cp-C*H*), 3.76 (1 H, dd, *J* 2.5, 1.6, Cp-C*H*), 1.21 (9 H, s, *t-Bu*), and 1.06 (9 H, s, *t-Bu*). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 140.4 (d, *J* 12.1), 139.9 (d, *J* 12.4), 134.7 (d, *J* 20.8), 133.9 (d, *J* 19.7), 128.9, 128.7-128.5 (m), 106.74 (d, *J* 3.8), 101.6, 78.3, 77.8 (d, *J* 10.0), 75.5 (d, *J* 17.7), 72.9 (d, *J* 9.0), 70.9, 70.2, 69.8 (d, *J* 2.5), 65.1, 31.8, 31.7, 31.0, and 30.6. $^{31}P\{^1H\}$ NMR ($C_6D_6$, 243 MHz): δ –18.7. Elemental analysis for $C_{30}H_{34}BrPFe$ (561.27): calculated C (64.19 %), H (6.11%); obtained C (64.38%), H (6.36%). ESI-MS: $[M+H]^+$: m/z exp = 561.10111, m/z theo = 561.10056, delta = 1.321 ppm. M. p. 126 °C.

**Synthesis of 1-bromo-3,3'-di(tert-butyl)-1'-(di(*iso*-propyl)phosphino)-ferrocene, 3b.**

To a solution of 1,1'-dibromo-3,3'-di(*tert*-butyl)-ferrocene **2a** (2.32 g, 5.09 mmol) in 15 mL of THF was added at –50 °C dropwise in 10 min a solution of *n*-butyllithium in hexane (3.1 mL, 5.0 mmol, 1.6 M). After stirring during 1 h at –50 °C, a solution of chlorodi(*iso*-propyl)phosphine (0.80 mL, 5.0 mmol) in 5 mL of THF was added dropwise in 5 min. The solution was stirred during 12 h at room temperature, and then DCM was added. The organic phase was washed by water, by brine and dried over $MgSO_4$ giving an orange oil which was purified by

[b] All the tetra-substituted ferrocenes reported in this work came from diastereoselectively pure *rac* precursors and conserve this stereochemistry; as such could be distinguished as planar chiral *pseudo-rac* stereoisomers, in contrast to *pseudo-meso* diastereomers which would be obtained from achiral *meso* precursors.

chromatography on silica with hexane/DCM gradient, giving **3b** as an orange crystalline solid (1.85 g, 3.76 mmol, 76% yield). X-Ray structure of **3b** was resolved.

$^{1}H\{^{31}P\}$ NMR (500 MHz, $C_6D_6$): δ 4.28-4.24 (1 H, m, Cp-C*H*), 4.24-4.21 (1 H, m, Cp-C*H*), 4.18-4.14 (1 H, m, Cp-C*H*), 3.98-3.94 (1 H, m, Cp-C*H*), 3.94-3.90 (1 H, m, Cp-C*H*), 3.79-3.74 (1 H, m, Cp-C*H*), 2.06 (1 H, hept, *J* 7.1, *i*-Pr-C*H*), 1.85 (1 H, hept, *J* 7.0, *i*-Pr-C*H*), 1.26 (9 H, s, *t-Bu*), 1.20 (9 H, s, *t-Bu*), 1.18 (3 H, d, *J* 6.9, *i*-Pr-C$H_3$), 1.14 (3 H, d, *J* 7.1, *i*-Pr-C$H_3$), 1.07 (3 H, d, *J* 7.2, *i*-Pr-C$H_3$), and 1.05 (3 H, d, *J* 7.1, *i*-Pr-C$H_3$). $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$): δ 105.3 (d, *J* 1.7), 101.4, 72.8 (d, *J* 12.4), 72.3 (d, *J* 8.0), 70.2, 69.7, 69.6, 65.3, 31.9, 31.9, 31.0, 30.8, 24.0, 23.9, 23.8, 21.2 (d, *J* 15.5), 20.8, 20.7, 20.7, 20.6, 20.4, 20.3. $^{31}P\{^{1}H\}$ NMR (202 MHz, $C_6D_6$): δ –2.0. Elemental analysis for $C_{24}H_{38}BrFeP$ (493.28): calculated C (58.44 %), H (7.76%); obtained C (57.72%), H (8.07%). ESI-MS: $[M]^+$: m/z exp = 493.13081, m/z theo = 493.13167, delta = –1.742 ppm.

**Synthesis of 1-bromo-3,3'-di(*tert*-butyl)-1'-(dimesitylphosphino)-ferrocene, 3c.**

To a solution of 1,1'-dibromo-3,3'-di(*tert*-butyl)-ferrocene **2a** (1.46 g, 3.20 mmol) in 15 mL of THF at –60 °C was added dropwise in 10 min a solution of *n*-butyllithium in hexane (2.0 mL, 3.2 mmol, 1.6 M). After stirring during 1 h at –50 °C, a commercial suspension of chlorodimesitylphosphine (1.12 g, 2.5 mmol, purity 70%) in 5 mL of THF was added dropwise in 5 min at –80 °C. The solution was stirred during 12 h allowing slowly rise up to room temperature, and then DCM was added. The organic phase was washed by water, by brine and dried over $MgSO_4$ giving an orange oil which was purified by chromatography on silica with hexane/DCM gradient giving **3c** as an orange crystalline solid (690 mg, 1.07 mmol, 43% yield). X-Ray structure of **3c** was resolved.

$^{1}H\{^{31}P\}$ NMR (600 MHz, $C_6D_6$): δ 6.76 (2 H, s, *m*-C*H*), 6.72 (2 H, s, *m*-C*H*), 4.50 (1 H, s, Cp-C*H*), 4.26 (1 H, s, Cp-C*H*), 4.19 (1 H, s, Cp-C*H*), 4.15 (1 H, s, Cp-C*H*), 3.97 (1 H, s, Cp-C*H*), 3.71 (1 H, s, Cp-C*H*), 2.61 (6 H, s, *o*-C$H_3$), 2.32 (6 H, s, *o*-C$H_3$), 2.11 (3 H, s, *p*-C$H_3$), 2.09 (3 H, s, *p*-C$H_3$), 1.20 (9 H, s, *t-Bu*), and 0.94 (9 H, s, *t-Bu*). $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$): δ143.4 (d, *J* 15.3), 141.4 (d, *J* 15.0), 138.1, 136.5, 132.7 (d, *J* 26.3), 131.8 (d, *J* 16.8), 130.4 (d, *J* 1.8), 130.2 (d, *J* 3.8), 105.8 (d, *J* 5.6), 101.0, 80.0 (d, *J* 13.7), 77.6, 72.9, 71.4, 68.3, 63.9, 31.2, 30.7, 30.6, 30.1, 23.3 (t, *J* 15.0), 20.5 (d, *J* 11.0). $^{31}P\{^{1}H\}$ NMR (243 MHz, $C_6D_6$): δ –36.6. Elemental analysis for $C_{36}H_{46}BrFeP$ (645.45): calculated C (66.99 %), H (7.18%); obtained C (66.41%), H (7.39%). ESI-MS: $[M]^+$: m/z exp = 645.19238, m/z theo = 645.19427, delta = –2.928 ppm.

**Synthesis of 1'-(dimesitylboryl)-3,3'-di(*tert*-butyl)-1-(diphenylphosphino)-ferrocene, 4a.**

To a solution of 1-bromo-3,3'-di(*tert*-butyl)-1'-(diphenylphosphino)-ferrocene **3a** (0.56 g, 1.0 mmol) in 5 mL of THF at –75 °C was added dropwise in 3 min a solution of *n*-butyllithium in hexane (0.63 mL, 1.0 mmol, 1.6 M). After stirring during 1 h at –70 °C, a solution of commercial fluorodimesitylborane (0.27 g, 1.0 mmol) in 2 mL of THF was added dropwise in 10 min. The reaction mixture was stirred for 6 h allowing slowly rise up to room temperature then it was stirred 20 h at room temperature. After removal of solvent under vacuum, the red oil was purified by chromatography on silica with a 80/20 hexane/DCM eluent, giving **4a** as a dark purple crystalline solid (0.59 g, 0.81 mmol, 81% yield).

$^{1}H\{^{31}P\}$ NMR (500 MHz, C6D6): δ 7.27-7.23 (2 H, m, Ph), 7.17 (2 H, vbr, Ph), 7.11-6.97 (6 H, m, Ph), 6.87 (4 H, s, *m*-C*H*), 4.65-4.56 (2 H, m, Cp-C*H*), 4.53 (1 H, brs, Cp-C*H*), 4.28-4.22 (1 H, m, Cp-C*H*), 4.05 (1 H, brs, Cp-C*H*), 3.85-3.81 (1 H, m, Cp-C*H*), 2.55 (12 H, brs, *o*-C$H_3$), 2.23 (6 H, s, *p*-C$H_3$), 1.15 (9 H, s, *t-Bu*), 1.09 (9 H, brs, *t-Bu*). $^{11}B$ $\{^{1}H\}$ NMR (160 MHz, $C_6D_6$): δ 80.1. $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$): δ 143.9, 141.8 (d, *J* 13.3), 139.6, 138.0 (d, *J* 11.5), 137.4, 135.8 (d, *J* 21.2), 132.6 (d, *J* 18.3), 129.2, 128.9, 128.5, 128.4 (d, *J* 2.6), 128.3, 128.2, 128.0, 107.7 (d, *J* 6.3), 106.7 (br), 80.2 (br), 78.5, 76.5 (d, *J* 9.5), 73.4, 71.8 (d, *J* 4.1), 66.5 (br), 31.0 (d, *J* 7.3), 31.8, 31.3, 30.9, 25.2 (br), 23.1, 21.2, and 14.4. $^{31}P\{^{1}H\}$ NMR (202 MHz, $C_6D_6$): δ –18.0. Elemental analysis for $C_{48}H_{56}BPFe$ (730.59): calculated C (78.91 %), H (7.73%); obtained C (79.02%), H (8.13%). ESI-MS: $[M]^+$: m/z exp = 730.35645, m/z theo = 730.35658, delta = 1.078 ppm. M. p. 222 °C.

**Synthesis of 1'-(di(*iso*-propylboryl)-3,3'-di(*tert*-butyl)-1-(diphenylphosphino)-ferrocene, 4b.**

To a solution of 1-bromo-3,3'-di(*tert*-butyl)-1'-diphenylphosphino-ferrocene **3a** (0.562 g, 1.0 mmol) in 5 mL of THF at –75 °C was added dropwise within 3 min a solution of *n*-butyllithium in hexane (0.65 mL, 1.0 mmol, 1.6 M). After stirring during 1.5 h at –70 °C, a solution of chlorodi(*iso*-propyl)borane (0.13 g, 1.0 mmol) in 2 mL of THF was added dropwise in 10 min. The reaction mixture was stirred for 15 h allowing slowly rise up to room temperature. After removal of solvent under vacuum, **4b** was extracted with toluene as a red crystalline solid (0.52 g, 0.90 mmol, 90% yield). X-Ray structure of **4b** was resolved.

$^{1}H\{^{31}P\}$ NMR (600 MHz, $C_6D_6$): δ 7.72 (2 H, td, *J* 7.9, 1.5, Ph), 7.32 (2 H, ddd, *J* 8.2, 7.0, 1.3, Ph), 7.13-6.97 (6 H, m, Ph), 4.49-4.45 (3 H, m, Cp-C*H*), 4.37 (1 H, dt, *J* 2.7, 1.5, Cp-C*H*), 4.15 (1 H, t, *J* 2.0, Cp-C*H*), 3.88 (1 H, dt, *J* 2.5, 1.3, Cp-C*H*), 2.21 (2 H, hept, *J* 7.2, *i*-Pr-C*H*), 1.36 (6 H,

d, *J* 7.2, *i*-Pr-C*H3*), 1.28 (6 H, d, *J* 7.5, *i*-Pr-C*H3*), 1.22 (9 H, s, *t-Bu*), and 1.07 (9 H, s, *t-Bu*). $^{11}B\{^{1}H\}$ NMR (96 MHz, $C_6D_6$): δ 77. $^{13}C\{^{1}H\}$ NMR (151 MHz, $C_6D_6$): δ 141.9 (d, *J* 13.3), 138.5 (d, *J* 12.0), 135.6 (d, *J* 21.0), 134.5 (d, *J* 20.6), 133.6 (d, *J* 19.4), 132.7 (d, *J* 18.7), 129.4, 128.7 (d, *J* 7.7), 128.5 (d, *J* 5.6), 128.4, 108.7, 106.0 (d, *J* 6.0), 76.5, 76.1 (d, *J* 8.1), 73.0, 72.6, 71.3 (d, *J* 28.5), 71.1, 66.5, 31.8 (d, *J* 16.4), 30.9 (d, *J* 9.8), 23.1, 20.4, 20.2. $^{31}P\{^{1}H\}$ NMR (243 MHz, $C_6D_6$): δ –17.0. This compound is sensitive to deborylation (*see Inorg. Chem. 2017, 56, 1966−1973*); in glove box **4b** decomposes rapidly at room temperature, EA was unsatisfactory.

**Synthesis of 1'-(dimesitylboryl)-3,3'-di(*tert*-butyl)-1-(di(*iso*-propyl)phosphino)-ferrocene, 4c.**

To a solution of (1-dibromo-3,3'-di(*tert*-butyl)-1'-di(*iso*-propyl)phosphino)-ferrocene **3b** (90 mg, 0.182 mmol) in 2 mL of THF was added at –50 °C a solution of *n*-butyllithium in hexane (120 µL, 0.19 mmol, 1.6 M). After stirring during 1 h at –50 °C, a solution of commercial fluorodimesitylborane (51 mg, 0.19 mmol) in 2 mL of THF was added dropwise in 2 min. The reaction mixture was stirred for 30 min allowing slowly rise up to –10 °C then it was stirred 1 h at room temperature. After removal of solvent under vacuum, the product was extracted with pentane giving **4c** as purple oil (120 mg, 0.181 mmol, quantitative yield), single crystals for XRD were obtained after crystallization at –32 °C.

$^{1}H\{^{31}P\}$ NMR (300 MHz, $C_6D_6$): δ 6.84 (4 H, s, *m*-C*H*), 4.79-4.69 (1 H, m, Cp-C*H*), 4.69-4.63 (1 H, m, Cp-C*H*), 4.63-4.57 (1 H, m, Cp-C*H*), 4.40 (1 H, brs, Cp-C*H*), 4.17-4.07 (1 H, m, Cp-C*H*), 4.07-3.98 (1 H, m, Cp-C*H*), 2.54 (12 H, brs, *o*-C$H_3$), 2.22 (6 H, s, *p*-C$H_3$), 1.95 (1 H, hept, *J* 6.9, *i*-Pr-C*H*), 1.64 (1 H, hept, *J* 7.1, *i*-Pr-C*H*), 1.38 (9 H, s, *t-Bu*), 1.37-1.31 (3 H, m, *i*-Pr-C$H_3$), 1.10-1.00 (15H, m, *t-Bu* and *i*-Pr-C$H_3$), and 0.68 (3 H, d, *J* 6.8, *i*-Pr-C$H_3$). $^{11}B\{^{1}H\}$ NMR (96 MHz, $C_6D_6$): δ 80. $^{13}C\{^{1}H\}$ NMR (75 MHz, $C_6D_6$): 143.9, 139.3, 137.2, 128.9, 108.3, 105.7, 77.7, 75.5, 79.0, 67.6, 70.9, 69.0, 34.5, 32.6, 31.9, 31.6, 30.6, 25.0, 22.9, 22.7, 21.3, 21.2, 20.9, 20.0, 19.8, 17.6, 14.3. $^{31}P\{^{1}H\}$ NMR (121 MHz, $C_6D_6$): δ –1.8. Elemental analysis for $C_{42}H_{60}BFeP$ (662.56): calculated C (76.4 %), H (9.13%); obtained C (75.9%), H (8.77%).

**Synthesis of 1'-(dimesitylboryl)-3,3'-di(*tert*-butyl)-1-(dimesitylphosphino)-ferrocene, 4d.**

To a solution of (1-dibromo-3,3'-di(*tert*-butyl)-1'-dimesitylphosphino)-ferrocene **3c** (264 mg, 0.41 mmol) in 2 mL of THF at –60 °C was added dropwise in 3 min a solution of *n*-butyllithium in hexane (0.30 mL, 0.48 mmol, 1.6 M). After stirring during 1 h at –60 °C, a solution of commercial fluorodimesitylborane (128 mg, 0.48 mmol) in 1 mL of THF was added dropwise in 5 min. The reaction mixture was stirred for 5 h allowing slowly rise up to room temperature then

it was stirred 20 h at room temperature. Despite repeated attempts complete conversion was not achieved presumably hampered by the global hindrance of the target. After removal of solvent under vacuum, the orange oil containing **4d** (in 35% NMR yield) was purified by chromatography on silica with 80/20 hexane/DCM eluent giving 140 mg (0.172 mmol, 42% yield, 40% purity) of **4d** in a mixture with debrominated **3c** as a purple crystalline solid. Separation of **4d** from the non-borylated product was unsuccessful and only few single crystals isolation from crystallization attempts with $CH_2Cl_2$/pentane mixture allowed XRD analysis.

$^1H\{^{31}P\}$ NMR (500 MHz, $C_6D_6$): 5.12-5.02 (1 H, m, Cp-C*H*), 4.73-4.67 (1 H, m, Cp-C*H*), 4.62-4.57 (1 H, m, Cp-C*H*), 4.30-4.24 (3 H, m, Cp-C*H*), 4.24-4.18 (1 H, m, Cp-C*H*), 4.15-4.10 (1 H, m, Cp-C*H*), 1.40 (9 H, s, *t-Bu*), and 1.01 (9 H, s, *t-Bu*). Due to low purity, $^{13}C$ NMR and some $^1H$ NMR signals could not be unambiguously identified. $^{11}B\{^1H\}$NMR (160 MHz, $C_6D_6$): δ 80. $^{31}P\{^1H\}$ NMR (202 MHz, $C_6D_6$): δ –34.4 (additional signal at –37.0 ppm for debrominated **3c**).

**Synthesis of 1-bromo-3,3'-di(*tert*-butyl)-1'-formyl-ferrocene, 5a.**

To a solution of 1,1'-dibromo-3,3'-di(*tert*-butyl)-ferrocene **2a** (2.0 g, 4.39 mmol) in 20 mL of THF at –60 °C was added dropwise a solution of *n*-butyllithium in hexane (2.8 mL, 4.48 mmol, 1.6 M). After stirring during 1 h at –70 °C, *N,N*-dimethylformamide (0.5 mL, 6.14 mmol) was added. The reaction mixture was stirred for 16 h allowing slowly rise up to room temperature then it was stirred 1 h at room temperature. After removal of solvent under vacuum an orange oil was extracted by $Et_2O$, washed by water then by brine, dried over $MgSO_4$ and purified by chromatography on silica with a 100/0 and 80/20 heptane/AcOEt eluent. **5a** was isolated as an orange crystalline solid (1.07 g, 2.64 mmol, 60% yield).

$^1H$ NMR (300 MHz, $CDCl_3$): δ 10.00 (1 H, s, C(O)*H*), 4.81 (1 H, dd, *J* 2.7, 1.3, CpCHO-C*H*), 4.43 (1 H, t, *J* 1.4, CpCHO-C*H*), 4.41 (1 H, dd, *J* 2.5, 1.2, $Cp_{Br}$-C*H*), 4.39-4.31 (1 H, m, CpCHO-C*H*), 4.32 (1 H, t, *J* 1.4, CpBr-C*H*), 3.93 (1 H, dd, *J* 2.5, 1.5, CpBr-C*H*), 1.29 (9 H, s, CpCHO-*t-Bu*), and 1.17 (9 H, s, CpBr-*t-Bu*). $^{13}C\{^1H\}$ NMR (75 MHz, CDCl3): δ 194.4 (C(O)H), 108.8 (CpCHO-*C*), 103.0 (CpBr-*C*), 79.2 (CpCHO-*C*), 77.2 (CpBr-*C*), 72.5 (CpCHO-*C*H), 72.4 (CpCHO-*C*H), 71.6 (CpBr-*C*H), 69.7 (CpCHO-*C*H), 69.5 (CpBr-*C*H), 64.8 (CpBr-*C*H), 31.6 (CpBr-C($CH_3$)$_3$), 31.4 (CpCHO-C($CH_3$)$_3$), 31.1 (CpBr-*C*($CH_3$)$_3$), 30.5 (CpCHO-*C*($CH_3$)$_3$). Elemental analysis for $C_{19}H_{25}BrFeO$ (405.15): calculated C (56.33%), H (6.22%); obtained C (56.45%), H (6.32%). ESI-MS: $[M]^+$: m/z exp = 404.04339, m/z theo = 404.04327, delta = 0.293 ppm.

**Synthesis of (1-diphenylphosphino-1'-carboxaldehyde-3,3'-di-*tert*-butyl)ferrocene, 5b.**

To a solution of 1-bromo-3,3'-di(*tert*-butyl)-1'-(diphenylphosphino)-ferrocene **3a** (0.87 g, 1.55 mmol) in 7 mL of THF at –75 °C was added dropwise *n*-butyllithium (1 mL, 1.6 mmol, 1.6 N in hexane). The mixture was maintained à –70 °C for 1.5 h, then dimethylformamide (0.15 mL, 1.9 mmol) in 2 mL of THF was added dropwise. After 4 h stirring at –10 °C the solution was maintained at room temperature for 1 h. After solvent evaporation the red-orange oil obtained was purified by chromatography over silica using hexane/ethylacetate (95/5 vol/vol). Carboxaldehyde **5b** was obtained as a deep red solid in 95 yield % (0.75 g).

$^{1}$H ($C_6D_6$, 600 MHz): δ (ppm) 9.60 (brs, 1H), 7.51 (td, 2H, *J* 7.8, 1.6 Hz), 7.47 – 7.41 (m, 2H), 7.10 – 7.00 (m, 6H), 4.64 (dd, 1H, *J* 2.7, 1.3 Hz), 4.51 (t, 1H, *J* 1.5 Hz), 4.15 (q, 1H, *J* 1.6 Hz), 4.14 (t, 1H, *J* 2.0 Hz), 4.02 (q, 1H, *J* 1.7 Hz), 3.97 (dd, 1H, *J* 2.5, 1.5 Hz), 1.14 (s, 9H), 1.07 (s, 9H). $^{31}$P{$^{1}$H} ($C_6D_6$, 243 MHz): δ = –17.7. Ethylacetate traces are present ($^{1}$H NMR, t, 0.9 ppm in $C_6D_6$); Elemental analysis for $C_{31}H_{35}FeOP \cdot 1/2\ C_4H_8O_2$ (554.49): calculated C (71.48 %), H (7.08%); obtained C (71.56%), H (7.11%). ESI-MS: $[M+H]^+$: m/z exp = 511.18318, m/z theo = 511.18477, delta = –3.112 ppm.

**Synthesis of 1-bromo-3,3'-di(tert-butyl)-1'-(diethylamino)methyl-ferrocene, 6a.**

To a solution of 1-bromo-3,3'-di(*tert*-butyl)-1'-formyl-ferrocene **5a** (0.85 g, 2.1 mmol) in 15 mL of DCE at room temperature was added diethylamine (0.25 mL, 2.1 mmol). After stirring during 1 h room temperature, sodium triacetoxyborohydride (0.72 g, 3.15 mmol) was added and the reaction mixture was stirred for 24 h. After addition of 20 mL of diluted NaOH solution, the organic phase was extracted by 50 mL of DCM, washed with brine, dried over $MgSO_4$ and purified by chromatography on silica with 90/10/1 DCM/MeOH/$NEt_3$. Compound **6a** was isolated as an orange oil (0.74 g, 1.60 mmol, 76% yield).

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 4.31 (1 H, dd, *J* 2.5, 1.3, CpBr-C*H*), 4.14 (1 H, dd, *J* 2.5, 1.5, CpN-C*H*), 4.01 (1 H, t, *J* 1.4, CpBr-C*H*), 3.92-3.89 (2 H, m, CpBr-C*H* and CpN-C*H*), 3.82 (1 H, t, *J* 1.5, CpN-C*H*), 3.58 (2 H, AB, *J* 13.5, 1-C$H_2$-N), 2.47 (4 H, qd, *J* 7.1, 4.6, N-C$H_2$-$CH_3$), 1.24 (9 H, s, CpBr-*t-Bu*), 1.20 (9 H, s, CpN-*t-Bu*), and 1.06 (6 H, t, *J* 7.2, N-$CH_2$-C$H_3$). $^{13}$C{1H} NMR (75 MHz, $CDCl_3$): δ 103.97 (CpN-*C*), 100.87 (CpBr-*C*), 83.21 (CpN-*C*), 78.08 (CpBr-*C*), 73.62 (CpN-*C*H), 70.90 (CpN-*C*H), 70.21 (CpBr-*C*H), 69.02 (CpBr-*C*H), 66.72 (CpN-*C*H), 64.45 (CpBr-*C*H), 51.29 (Cp-*C*$H_2$-N), 46.59 (N-*C*$H_2$-$CH_3$), 31.68 (CpBr-C(*C*$H_3$)$_3$), 31.51 (CpN-

C($CH_3$)$_3$), 30.72 (CpN-$C$($CH_3$)$_3$), 30.60 (CpBr-$C$($CH_3$)$_3$), and 12.03 (N-$CH_2$-$CH_3$). $^{15}$N NMR (61 MHz, $CDCl_3$): δ –327.1. Elemental analysis for $C_{23}H_{36}BrFeN$ (462.28): calculated C (59.76%), H (7.85%), N (3.03%); obtained C (59.62%), H (7.44%), N (3.17%). ESI-MS: $[M]^+$: m/z exp = 462.14319, m/z theo = 462.14533, delta = –4.634 ppm.

**Synthesis of 1-bromo-3,3'-di(*tert*-butyl)-1'-(pyrrolidin-1-yl)methyl-ferrocene, 6b.**

To a solution of 1-bromo-3,3'-di(*tert*-butyl)-1'-formyl-ferrocene **5a** (0.42 g, 1.04 mmol) in 8 mL of DCE at room temperature was added pyrrolidine (0.10 mL, 2.1 mmol). After stirring during 1 h room temperature, sodium triacetoxyborohydride (0.33 g, 1.56 mmol) was added and the reaction mixture was stirred for 24 h. After addition of 10 mL of diluted NaOH solution, the organic phase was extracted by 50 mL of DCM, washed with brine, dried over $MgSO_4$ and purified by chromatography on silica neutralized by $NEt_3$ with 80/20 heptane/AcOEt. **6b** was isolated as an orange crystalline solid (0.41 g, 0.89 mmol, 86% yield).

$^1$H NMR (300 MHz, $C_6D_6$): δ 4.26 (1 H, dd, *J* 2.5, 1.3, CpBr-C*H*), 4.16 (1 H, dd, *J* 2.5, 1.4, CpN-C*H*), 3.98 (1 H, t, *J* 1.4, CpBr-C*H*), 3.93 (1 H, t, *J* 1.5, CpN-C*H*), 3.80 (1 H, dd, *J* 2.5, 1.6, CpN-C*H*), 3.69 (1 H, dd, *J* 2.5, 1.6, CpBr-C*H*), 3.57 (2 H, AB, *J* 12.6, 1-C$H_2$-N), 2.46 (4 H, ddd, *J* 6.6, 4.2, 1.3, Pyr-C$H_2$), 1.59 (4 H, p, *J* 3.4, Pyr-C$H_2$), 1.20 (9 H, s, CpN-*t-Bu*), and 1.09 (9 H, s, CpBr-*t-Bu*). $^{13}$C{1H} NMR (75 MHz, $C_6D_6$): δ 103.7 (CpN-*C*), 100.9 (CpBr-*C*), 86.0 (CpN-*C*), 78.7 (CpBr-*C*), 73.4(CpN-*C*H), 70.7 (CpN-*C*H), 70.5 (CpBr-*C*H), 69.3 (CpBr-*C*H), 66.9 (CpN-*C*H), 64.6 (CpBr-*C*H), 55.2 (Cp-$C$$H_2$-N), 54.2 (Pyr-$C$$H_2$), 31.9 (CpN-C($C$$H_3$)$_3$), 31.5 (CpBr-C($C$$H_3$)$_3$), 30.8 (CpN-$C$($CH_3$)$_3$), 30.6 (CpBr-$C$($CH_3$)$_3$), 24.0 (Pyr-$C$$H_2$). $^{15}$N NMR (61 MHz, C6D6): δ –320.7. Elemental analysis for $C_{23}H_{34}BrFeN$ (460.28): calculated C (60.02%), H (7.45%), N (3.04%); obtained C (59.89%), H (7.29%), N (3.63%). ESI-MS: $[M]^+$: m/z exp = 460.12773, m/z theo = 460.12968, delta = –4.241 ppm.

**Synthesis of 1'-(dimesitylboryl)-3,3'-di(tert-butyl)- 1-(diethylamino)methyl-ferrocene, 7a**

To a solution of 1-bromo-3,3'-di(*tert*-butyl)-1'-(diethylamino)methyl-ferrocene **6a** (0.20 g, 0.43 mmol) in 2 mL of THF at –85 °C was added a solution of *n*-butyllithium in hexane (0.27 mL, 0.43 mmol, 1.6 M). After stirring during 1 h between –85 °C and –60 °C, a solution of commercial fluorodimesitylborane (117 mg, 0.436 mmol) in 1 mL of THF was added at –85 °C. The reaction mixture was stirred for 6 h allowing slowly rise up to 0 °C, then it was stirred 15 h at room temperature. After removal of solvent under vacuum and extraction with pentane, the

purple oil was purified by chromatography on alumina with 98/2 heptane/AcOEt giving **7a** as a purple crystalline solid (42 mg, 0.066 mmol, 15% yield).

$^{1}$H NMR (300 MHz, $C_6D_6$): δ 6.83 (4 H, s, *m*-C*H*), 4.66 (1 H, dd, *J* 2.6, 1.3, $Cp^B$-C*H*), 4.63 (1 H, t, *J* 1.4, $Cp^B$-C*H*), 4.30 (1 H, dd, *J* 2.6, 1.4, $Cp^B$-C*H*), 4.22 (1 H, dd, *J* 2.4, 1.4, $Cp^N$-C*H*), 4.11 (1 H, t, *J* 1.5, $Cp^N$-C*H*), 4.01 (1 H, t, *J* 1.9, $Cp^N$-C*H*), 3.48 (2 H, AB, *J* 13.5, 1-C$H_2$-N), 2.51 (12 H, s *o*-C$H_3$), 2.43 (4 H, qd, *J* 7.1, 2.0, N-C$H_2$-$CH_3$), 2.21 (6 H, s, *p*-C$H_3$), 1.25 (9 H, d, *J* 2.3, $Cp^B$-*t-Bu*), 1.07 (9 H, s, $Cp^N$-*t-Bu*), and 0.99 (6 H, t, *J* 7.1, N-CH2-C$H_3$). $^{11}$B{$^{1}$H} NMR (160 MHz, C6D6): δ 88. $^{13}$C{$^{1}$H} NMR (75 MHz, $C_6D_6$): δ 139.2 (*o*-*C*), 137.2 (*o*-*C*), 128.9 (*m*-*C*H), 107.1 ($Cp^B$-*C*), 103.4 ($Cp^N$-*C*), 84.6 ($Cp^N$-*C*), 79.7 ($Cp^B$-*C*H), 77.2 ($Cp^B$-*C*H), 73.3 ($Cp^B$-*C*H), 70.6 ($Cp^N$-*C*H), 69.5 ($Cp^N$-*C*H), 65.7 ($Cp^N$-*C*H), 53.0 (Cp-*C*$H_2$-N), 46.8 (N-*C*H2-CH3), 32.0 ($Cp^B$-C(*C*$H_3$)$_3$), 31.8 ($Cp^N$-*C*($CH_3$)$_3$), 31.4 ($Cp^B$-*C*($CH_3$)$_3$), 30.5 ($Cp^N$-*C*($CH_3$)$_3$), 25.1 (*o*-*C*$H_3$), 21.2 (*p*-*C*$H_3$), 12.5, (N-$CH_2$-*C*$H_3$); CCp-B obscured. $^{15}$N NMR (61 MHz, $CDCl_3$): δ –329.8. Ethylacetate traces are present ($^{1}$H NMR, t, 0.9 ppm in $C_6D_6$); Elemental analysis for $C_{41}H_{58}BFeN \cdot 1/2\ C_4H_8O_2$ (675.62): calculated C (76.44%), H (9.25%); obtained C (76.37%), H (9.39%). ESI-MS: $[M]^+$: m/z exp = 631.40062, m/z theo = 631.40062, delta = –0.752 ppm.

**Synthesis of 1'-(dimesitylboryl)-3,3'-di(tert-butyl)- 1-(pyrrolidine-1-yl)methyl-ferrocene, 7b.**

To a solution of 1-bromo-3,3'-di(*tert*-butyl)-1'-(pyrrolidin-1-yl)methyl-ferrocene **6b** (0.20 g, 0.83 mmol) in 3 mL of THF at –80 °C was added a solution of *n*-butyllithium in hexane (0.55 mL, 0.88 mmol, 1.6 M). After stirring during 1 h between –85 °C and –60 °C, a solution of commercial fluorodimesitylborane (224 mg, 0.83 mmol) in 3 mL of THF was added at –85 °C. The reaction mixture was stirred for 6 h allowing slowly rise up to 0 °C then it was stirred 15 h at room temperature. After removal of solvent under vacuum, extraction with pentane gave 0.40 g of purple oil containing **7b**. This oil was purified by chromatography on alumina with a heptane/$CHCl_3$ gradient giving **7b** as a purple crystalline solid (100 mg, 0.160 mmol, 20% yield). An X-ray structure was resolved for **7b**.

$^{1}$H NMR (300 MHz, $C_6D_6$): δ 6.87 (4 H, s, *m*-C*H*), 4.66 (1 H, dd, *J* 2.6, 1.3, CpB-C*H*), 4.64 (1 H, t, *J* 1.4, CpB-C*H*), 4.30 (1 H, dd, *J* 2.6, 1.4, CpB-C*H*), 4.23 (1 H, dd, *J* 2.4, 1.4, CpN-C*H*), 4.13 (1 H, t, *J* 1.5, CpN-C*H*), 4.01 (1 H, t, *J* 1.9, CpN-C*H*), 3.47 (2 H, AB, *J* 13.5, 1-C$H_2$-N), 2.51 (12 H, s, *o*-C*H3*), 2.43 (4 H, t, *J* 6.6, Pyr-$^{\alpha}$C$H_2$), 2.21 (6 H, s, *p*-C$H_3$), 1.60 (4 H, m, Pyr-$^{\beta}$C$H_2$), 1.25

(9 H, s, CpB-*t-Bu*), and 1.07 (9 H, s, CpN-*t-Bu*). $^{11}B\{^1H\}$ NMR (160 MHz, $C_6D_6$): δ 88. $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$): δ 143.9, 139.2, 137.2, 128.9, 107.0, 103.4, 85.4, 79.7, 77.3, 73.4, 70.3, 69.4, 65.7, 55.8, 54.2, 32.0, 31.9, 31.4, 30.5, 25.1, 23.9, and 21.2. Elemental analysis for $C_{41}H_{56}BFeN$ (629.55): calculated C (78.22%), H (8.97%), N (2.22%); obtained C (78.59%), H (8.29%), N (2.02%). ESI-MS: $[M]^+$: m/z exp = 630.39482, m/z theo = 630.39280, delta = 3.204 ppm.

**Synthesis of (1-diphenylphosphino-1'-diethylaminomethyl-3,3'-di-tert-butyl)ferrocene, 8.**

To a solution of **(**1-diphenylphosphino-1'-carboxaldehyde-3,3'-di-*tert*-butyl)ferrocene **5b** (0.38 g, 0.74 mmol) in 10 mL of $CH_2Cl_2$ was added dropwise diethylamine (0.1 mL, 0.97 mmol). The mixture is stirred for 1 h at room temperature. Sodium triacetoxyborohydrure (0.23 g, 1.1 mmol) was added and stirring maintained for 20 h. The mixture was treated with 50 mL NaOH (0.1 M). The organic phase was extracted with $CH_2Cl_2$ (50 mL), and washed with brine. After drying with $MgSO_4$, filtration and solvent evaporation, we achieved purification by chromatography over alumina with hexane/ethylacetate (95/5). 1-Diphenylphosphino-1'-diethylaminomethyl-3,3'-di-*tert*-butyl)ferrocene **8** was obtained as an orange powder in 71 % yield (0.30 g).

$^1H$ ($C_6D_6$, 600 MHz): δ (ppm) = 7.60 (td, 2H, *J* 7.8, 1.5 Hz), 7.49 (td, 2H, *J* 8.2, 7.7, 1.4 Hz), 7.12–7.01 (m, 6H), 4.18 (t, 1H, *J* 1.5 Hz), 4.15–4.11 (m, 1H), 4.13–4.10 (m, 1H), 4.06 (q, 1H, *J*=1.8 Hz), 3.92–3.88 (m, 2H), 3.49–3.39 (m, 2H), 2.46 (q, 4H, *J* 7.1 Hz), 1.23 (s, 9H), 1.09 (s, 9H), 1.05 (t, 6H, *J* 7.1 Hz). $^{13}C\{^1H\}$ NMR (151 MHz, $C_6D_6$): δ 141.3, 140.1, 134.75, 133.79 (12C, Ph-*C*), 105.1, 102.5, 84.3, 75.2, 72.7, 72.6, 71.9, 69.6, 68.2, 65.7 (10C, Cp), 52.7 (1C, N-*C*$H_2$-Cp), 46.9 (2C, N-*C*$H_2$-$CH_3$), 31.0 (3C, C(*C*$H_3$)$_3$), 30.7 (3C, C(*C*$H_3$)$_3$), 12.8 (2C, N-$CH_2$-*C*$H_3$); two quaternary *C*$(CH_3)_3$ obscured (*hexane traces at 14.4, 23.1, 32.0 ppm*). NMR $^{31}P\{^1H\}$ ($C_6D_6$, 243 MHz): δ (ppm) = –17.3. Elemental analysis for $C_{35}H_{46}FeNP$ (567.57): calculated C (74.07%), H (8.17%); N (2.47); obtained C (74.54%), H (8.49%), N (2.43%). ESI-MS: $[M+H]^+$: m/z exp = 568.27803, m/z theo = 568.27901, delta = –1.717 ppm.

**Synthesis of (1-diphenylphosphino-1'-di*iso*propylphosphine-3,3'-di-*tert*-butyl)ferrocene, 9.**

To a solution of 1-bromo-3,3'-di(*tert*-butyl)-1'-(diphenylphosphino)-ferrocene, **3a** in 5 mL THF. at –75 °C was added *n*-butyllithium (0.65 mL, 1 mmol, 1.6 N in hexane). The mixture was maintained at –70 °C for 1.5h then chlorodi*iso*propylphosphine (0.15 g, 1 mmol) solution 2 mL THF was added dropwise. After 30 min at –70°C the solution was stirred for 15 h at room

temperature. Solvent evaporation gives an orange oil that was further purified by chromatography on silica using hexane/dichloromethane (8/2 vol.). 1-Diphenylphosphino-1'-di*iso*propylphosphine-3,3'-di-*tert*-butyl)ferrocene **9** was obtained as an orange powder in 85 % yield (0.52 g).

NMR $^{1}$H ($C_6D_6$, 600 MHz): δ (ppm) 7.88 (t, 2H, *J* 7.3 Hz), 7.35 (t, 2H, *J* 6.9 Hz), 7.15–6.95 (m, 6H), 4.30 – 4.26 (m, 1H), 4.19 (t, 1H, *J* 1.9 Hz), 4.15 (t, 1H, *J* 1.9 Hz), 4.08 (d, 1H, *J*=1.6 Hz), 3.97 (brs, 1H, *J* 2.3 Hz), 3.95–3.93 (m, 1H), 2.05 (m, 1H, $J_{HH}$, $J_{HP}$ 7 Hz), 1.95 (hept, 1H, *J* 7.1 Hz), 1.37 (dd, 3H, *J* 15.1, 7.1 Hz), 1.30 (s, 9H), 1.21–1.09 (m, 15H), 0.86 (dd, 3H, *J* 9.9, 6.9 Hz). $^{13}$C{$^{1}$H} ($C_6D_6$, 151 MHz): δ (ppm) δ 139.2 (2C, *ipso*-Ph), 135.8 (2C, *para*-Ph), 132.7 (4C, *ortho* or *meta*-Ph), 129.3 (4C, *ortho* or *meta*-Ph), 73.9, 73.7, 71.7, 70.4, 69.7, 68.3 (6C, Cp-*CH*), 31.2 (1C, P-*C*Cp), 32.1, 31.9 (6C, C(*C*$H_3$)$_3$), 30.9 (1C, *C*(CH$_3$)$_3$), 24.7 (1C, *C*H), 23.0 (d, 2C, *J* 145 Hz, *C*$H_3$), 20.5 (d, 2C, *J* 147 Hz, *C*$H_3$), 19.4 (1C, *C*H), quaternary Cp carbon obscured. NMR $^{31}$P{$^{1}$H} ($C_6D_6$, 243 MHz): δ (ppm) –2.3 (d, $J_{PP}$ 13 Hz), –19.4 (d, $J_{PP}$ 13 Hz). Traces of polydimethylsiloxane (PDMS from dichloromethane solvent) are visible ($^{1}$H NMR, s, 0.29 ppm in $C_6D_6$); Elementary analysis for $C_{36}H_{48}FeP_2 \cdot$ ¼ $C_2H_6OSi$ (617.10): calculated: C (71.04 %), H (8.09%); obtained C (71.03%), H (8.35%). ESI-MS: $[M+H]^+$: m/z exp = 568.27803, m/z theo = 568.27901, delta = –1.717 ppm. M. p. 108 °C.

**Single-Crystal X-ray structure determination**

The X-ray crystallographic data for **3a**, **3b**, **4a**,[c] and **4b** were collected using a Bruker/Nonius KappaCCD detector with an Oxford Cryosystems low-temperature apparatus operating at *T* = 115 K. Data were measured using φ and ω scans using MoK$_\alpha$ radiation (λ = 0.71073 Å, X-ray tube, 50 kV, 32 mA).
The total number of runs and images was based on the strategy calculation from the program Collect (Nonius BV, 1997-2000). Cell parameters were retrieved using the SCALEPACK[1] (Otwinowski, 1997) software and refined using DENZO[1] (Otwinowski, 1997). Using Olex2[2] (Dolomanov et al., 2009), the structures were solved with the ShelXS[3] (Sheldrick, 2008/2013) structure solution program, using the heavy methods solution method. The models were refined with version 2016/6 of ShelXL[4] (Sheldrick, 2015) using Least Squares minimization.

The X-ray crystallographic data for **3c, 4c, 4d and 7b** were collected using a Bruker D8 Venture triumph Mo diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at *T* = 100 K. Data were measured using MoK$_\alpha$ radiation (X-ray tube, 50kV, 30mA). The total number of

[c] **4a'** as minor conformation isomer of **4a** was refined and deposited at CSD under number 1532858.

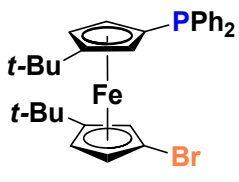
runs and images was based on the strategy calculation from the program **APEX2**[5] (Bruker). Cell parameters were retrieved and refined using the **SAINT**[6] (Bruker, V8.34A, 2013) software. Data reduction was performed using the **SAINT**[6] (Bruker, V8.34A, 2013) software which corrects for Lorentz polarisation. Using Olex2[2] (Dolomanov et al., 2009), the structure was solved with the ShelXT[7] (Sheldrick, 2015) structure solution program (except for 4d, which was solved with Sir2004[8]), using the direct solution method. The model was refined with version 2016/6 of ShelXL[4] (Sheldrick, 2015) using Least Squares minimization.

*Supplementary crystallographic data was deposited to the Cambridge Crystallographic Data Centre with the deposition numbers CCDC 1532854-1532862. These data can be obtained free of charge via https://summary.ccdc.cam.ac.uk/structure-summary-form.*

***References***

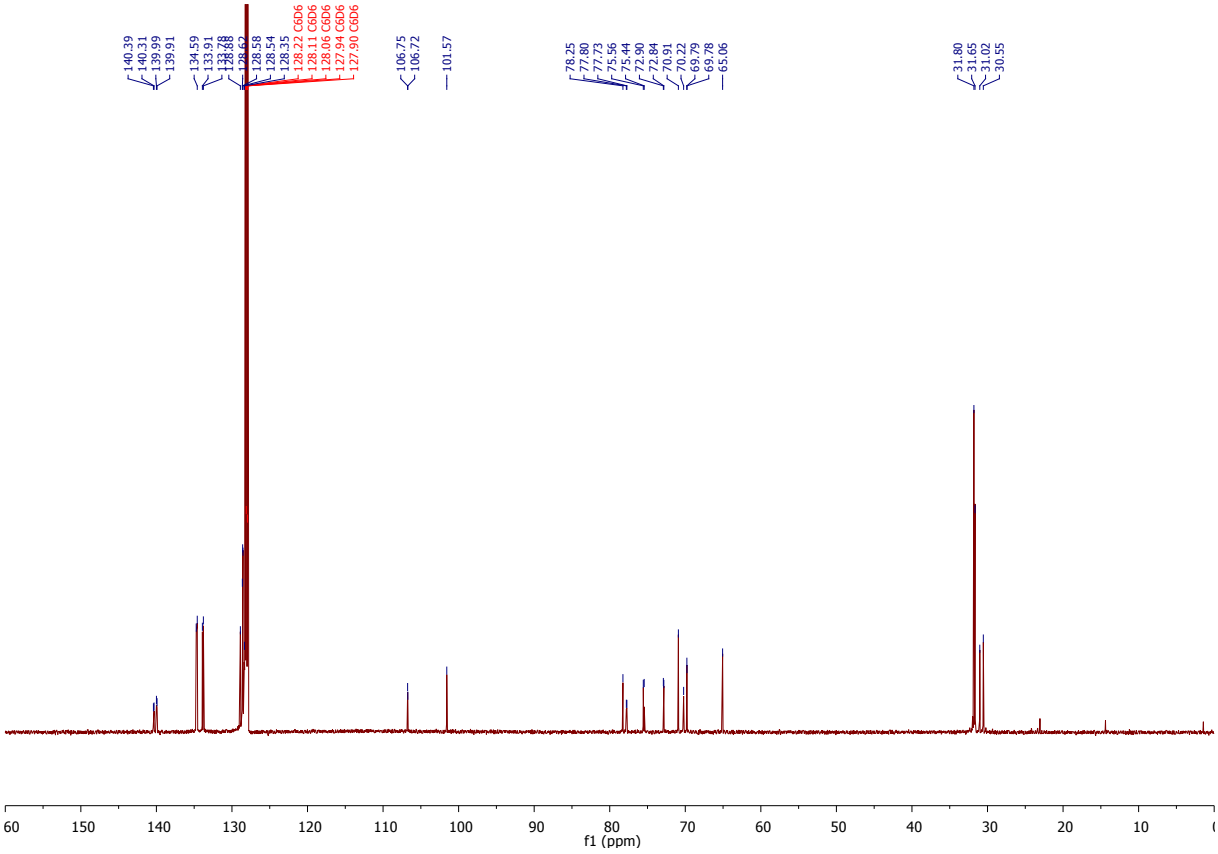

[1] Otwinowski, Z. & Minor, W. (1997). *Denzo/Scalepack, Methods in Enzymology*, Vol 276, *Macromolecular Crystallography,* Part A, edited by C. W. Carter Jr & R. M. Sweet, 307–326. New York: Academic Press.
[2] O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339–341.
[3 ] Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339–341.
[4 ] Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3–8.
[5 ] APEX2 suite for crystallographic software, Bruker axs, Madison, WI (2014).
[6] SAINT-8.34A-2013 - Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Bruker axs, Madison, WI (2013).
[7] Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3–8.
[8] Burla, M.C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G.L., De Caro, L., Giacovazzo, C., Polidori, G., Siliqi, D., Spagna, R. (2007). J. Appl. Cryst. 40, 609–613.

NMR $^{1}H$, $C_6D_6$, 600 MHz

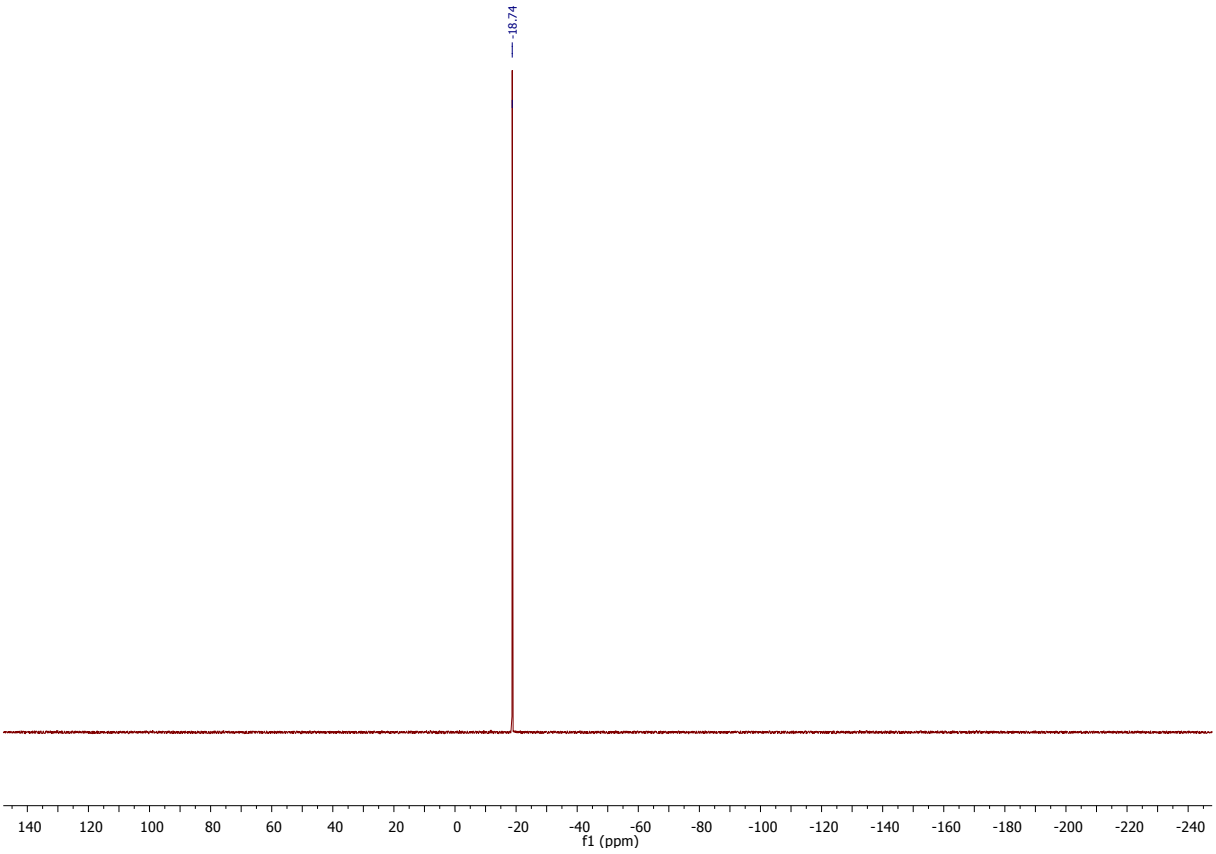



**3a**

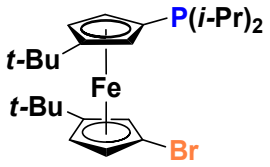
NMR $^{13}C$, $C_6D_6$, 151 MHz



NMR $^{31}P$, $C_6D_6$, 243 MHz

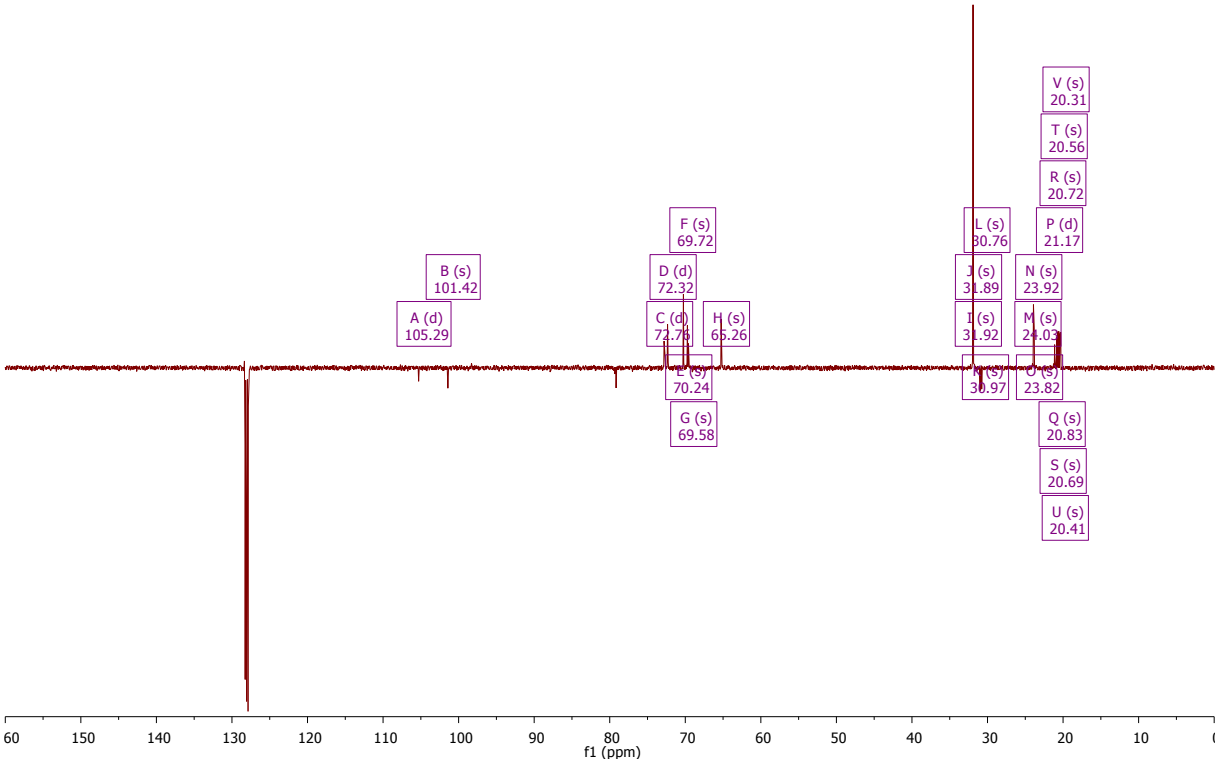


NMR $^{1}H$, $C_6D_6$, 500 MHz

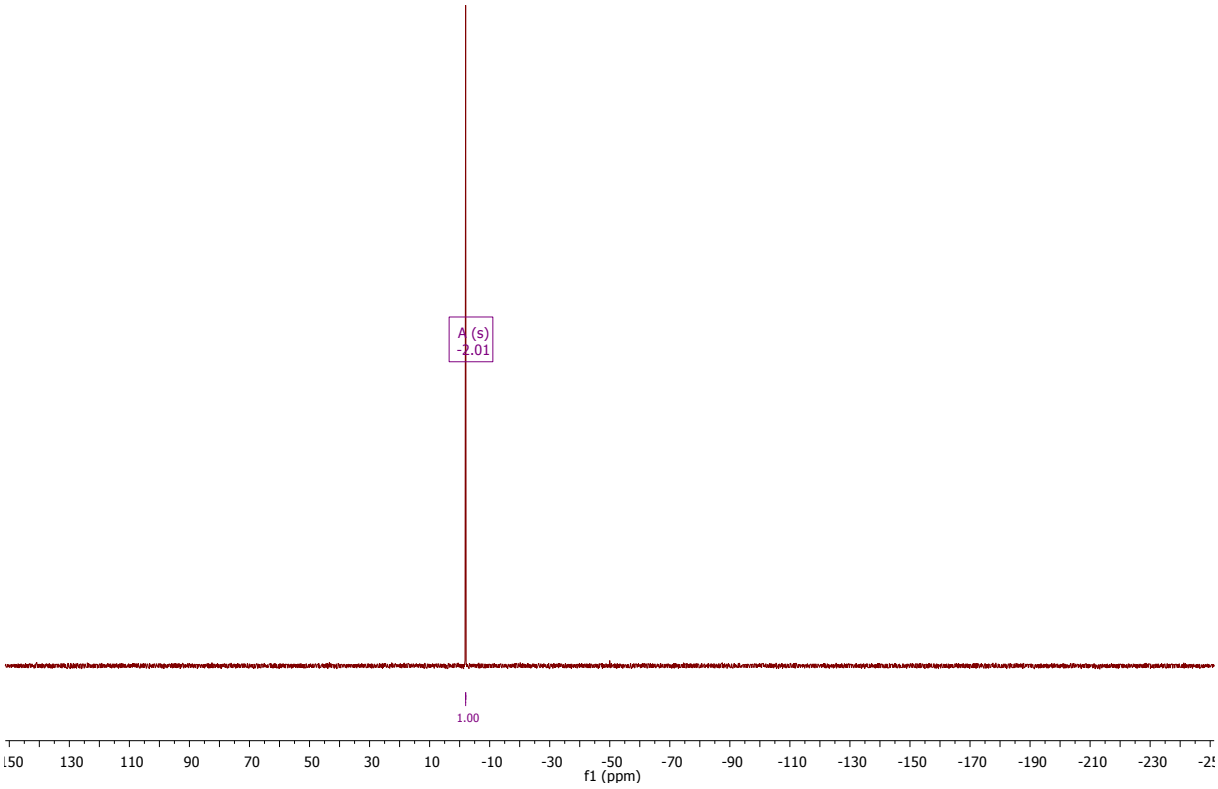



**3b**

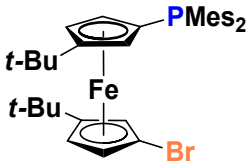
NMR $^{13}C$, $C_6D_6$, 126 MHz



NMR $^{31}P$, $C_6D_6$, 202 MHz

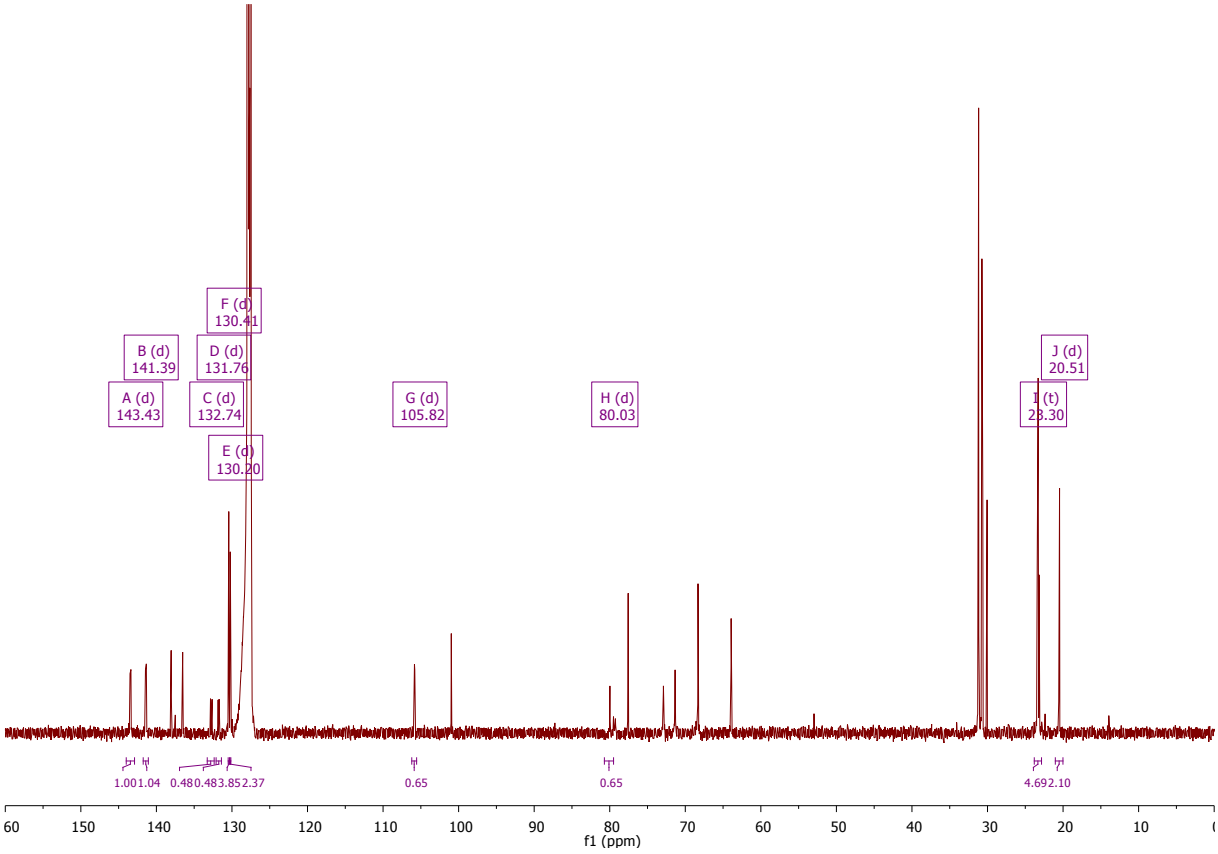


NMR $^{1}H$, $C_6D_6$, 600 MHz

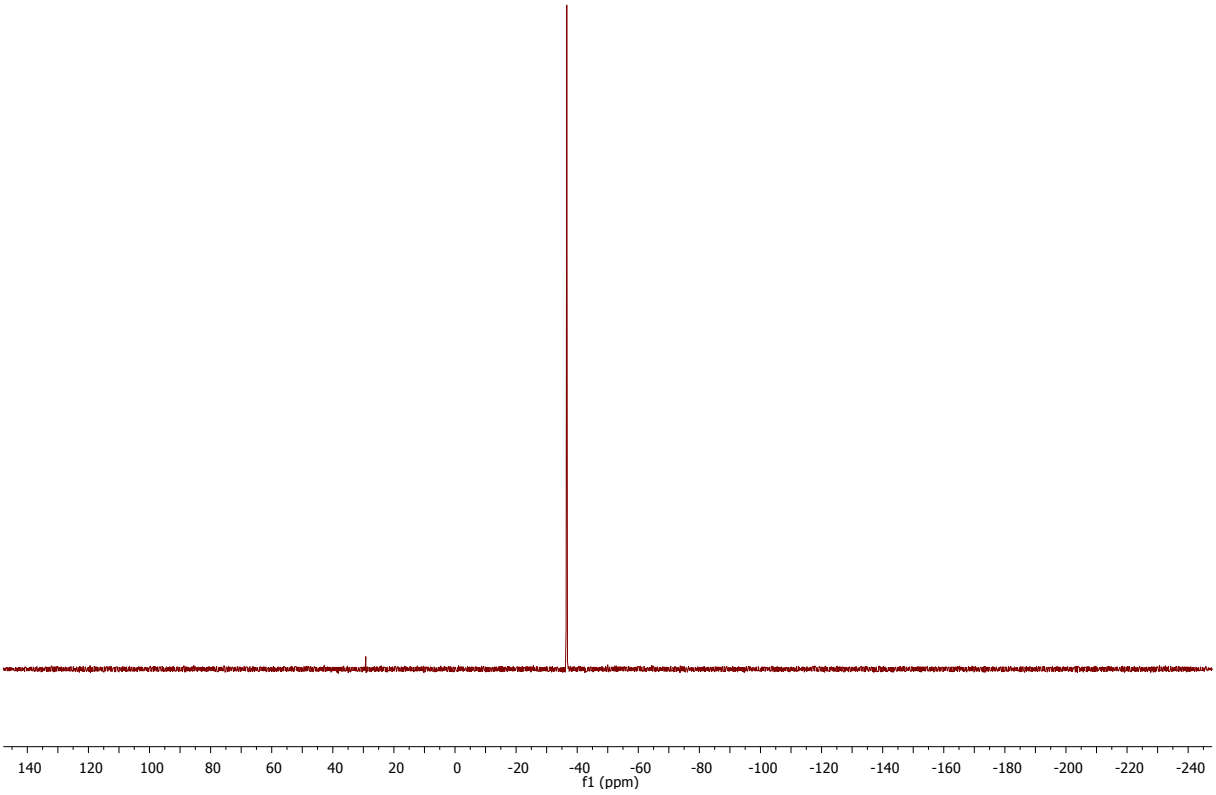



**3c**

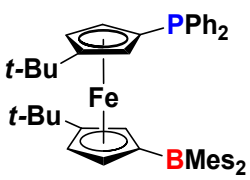
NMR $^{13}C$, $C_6D_6$, 126 MHz



NMR $^{31}P$, $C_6D_6$, 243 MHz

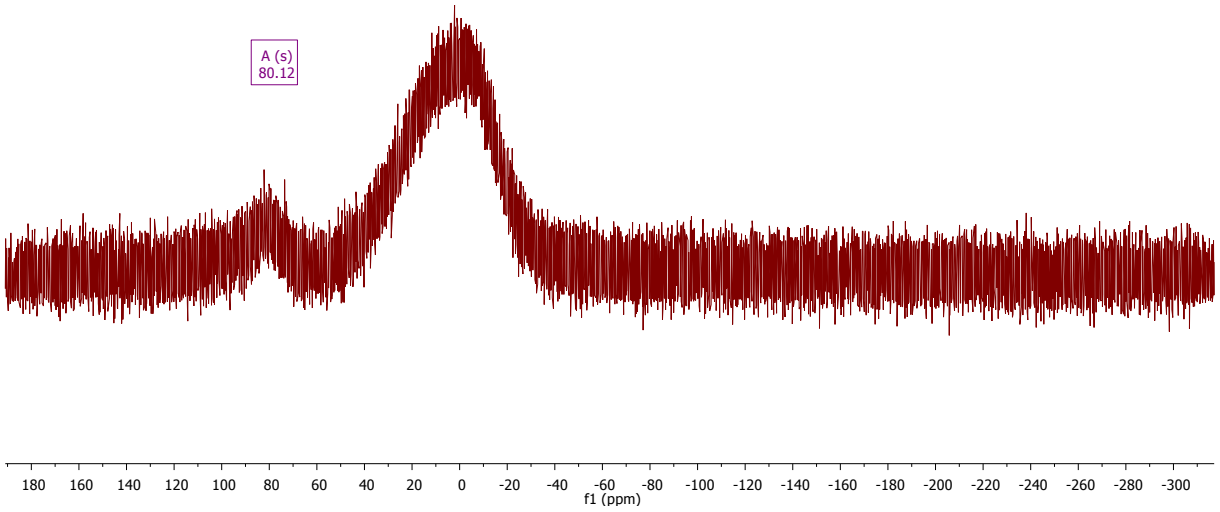


NMR $^{1}H$, $C_6D_6$, 500 MHz

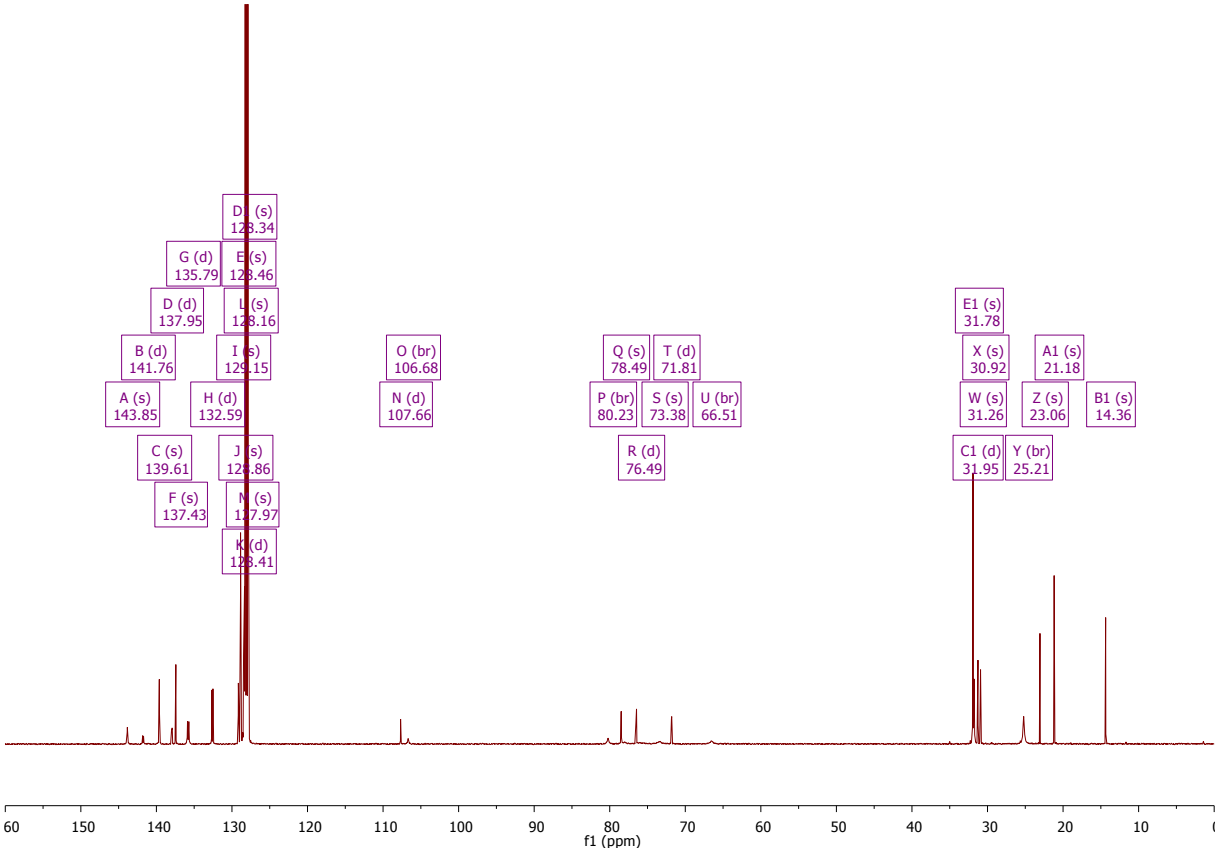



**4a**

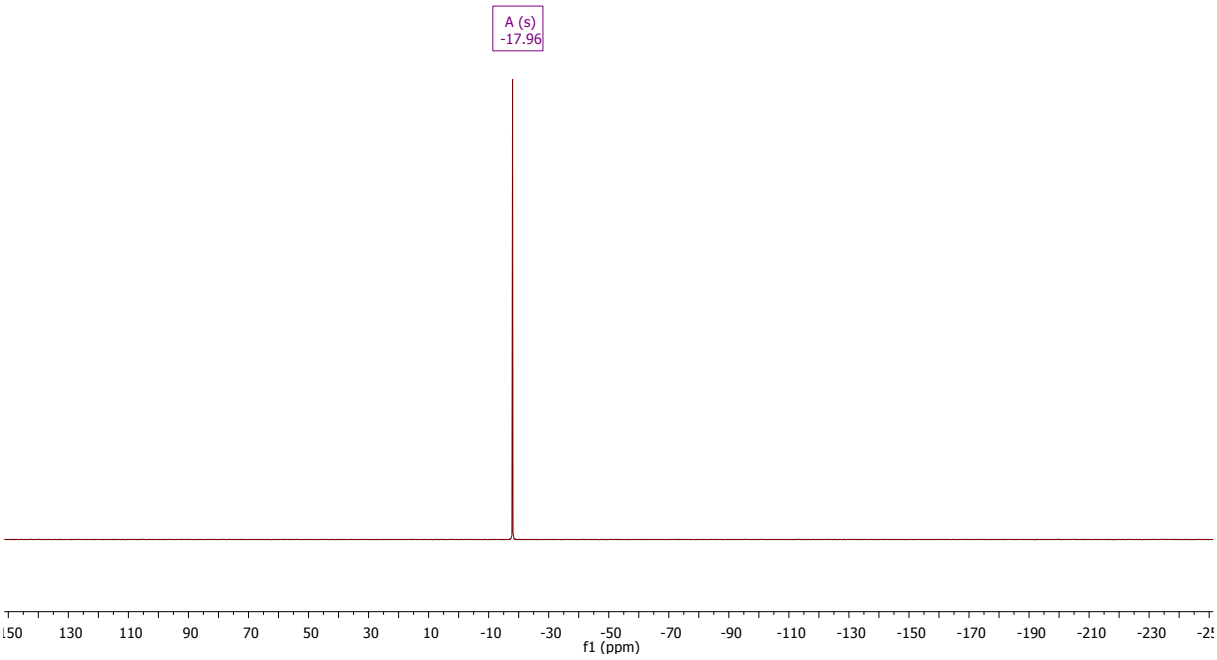
NMR $^{11}B$, $C_6D_6$, 160 MHz



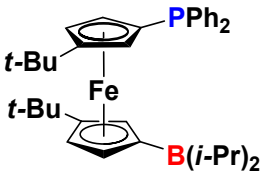
NMR $^{13}C$, $C_6D_6$, 126 MHz



NMR $^{31}P$, $C_6D_6$, 202 MHz

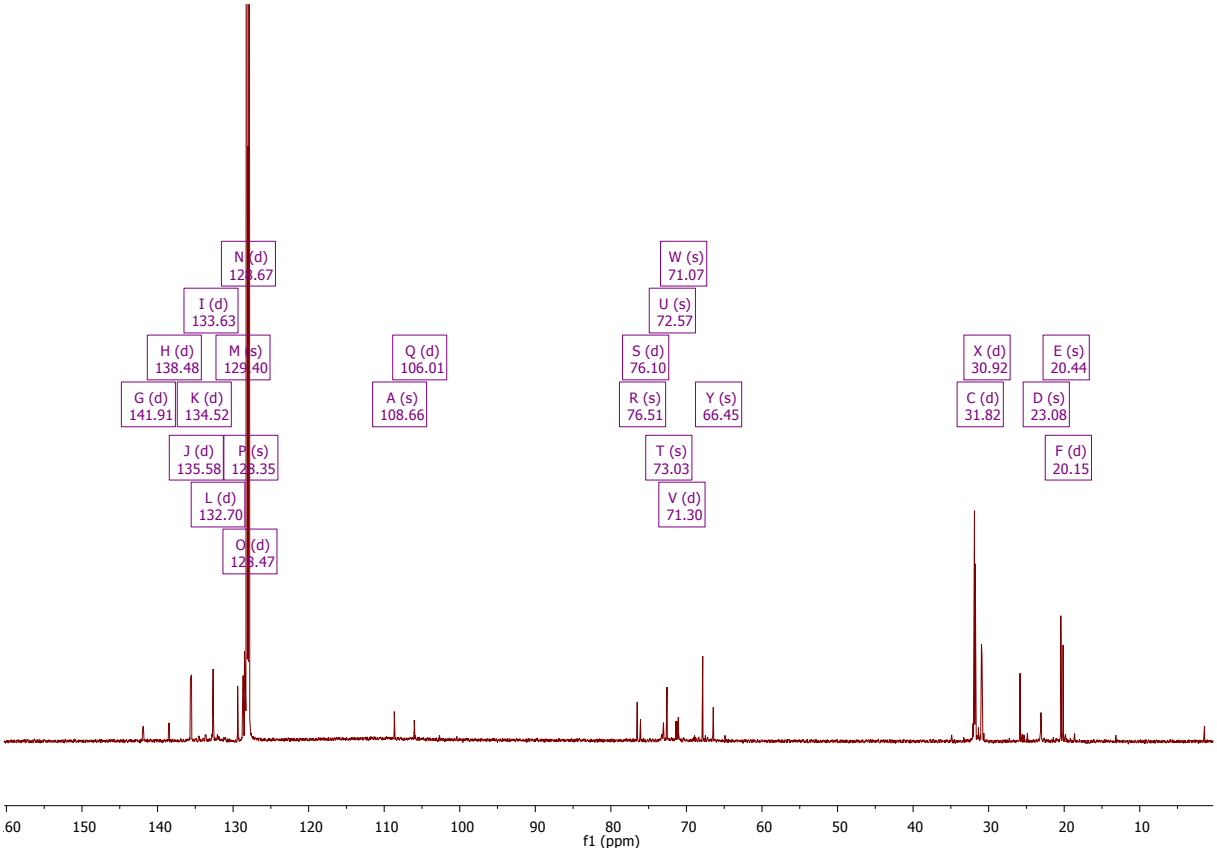


NMR $^{1}H$, $C_6D_6$, 600 MHz

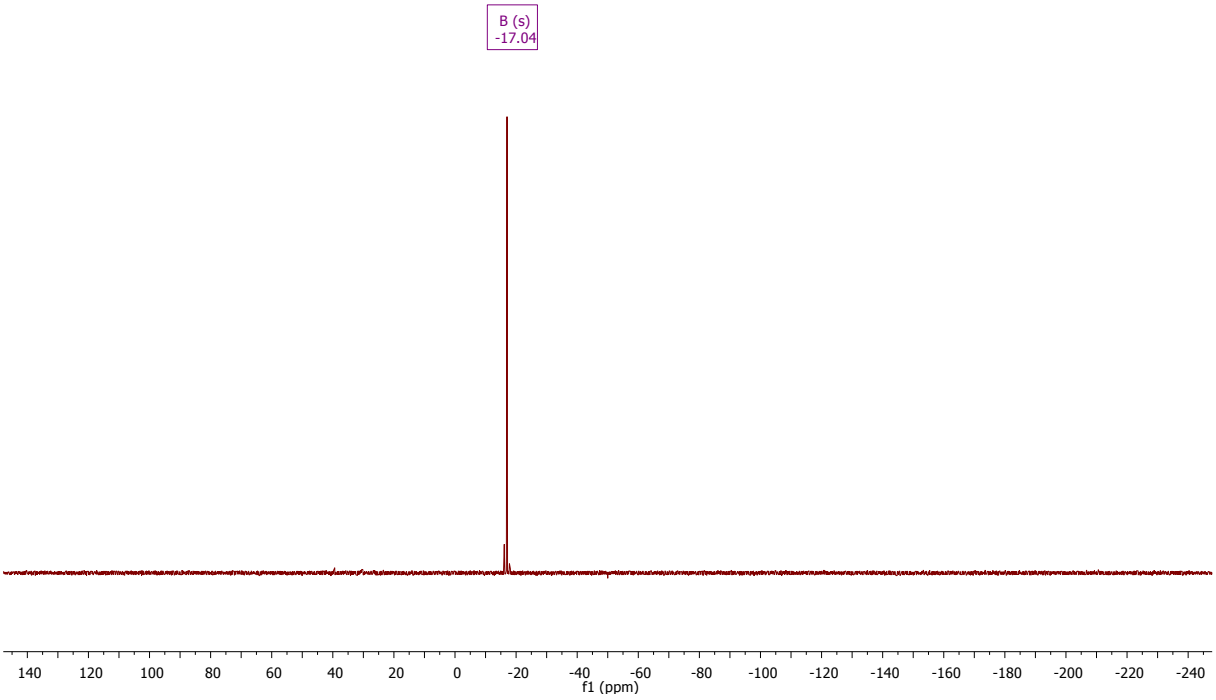



**4b**

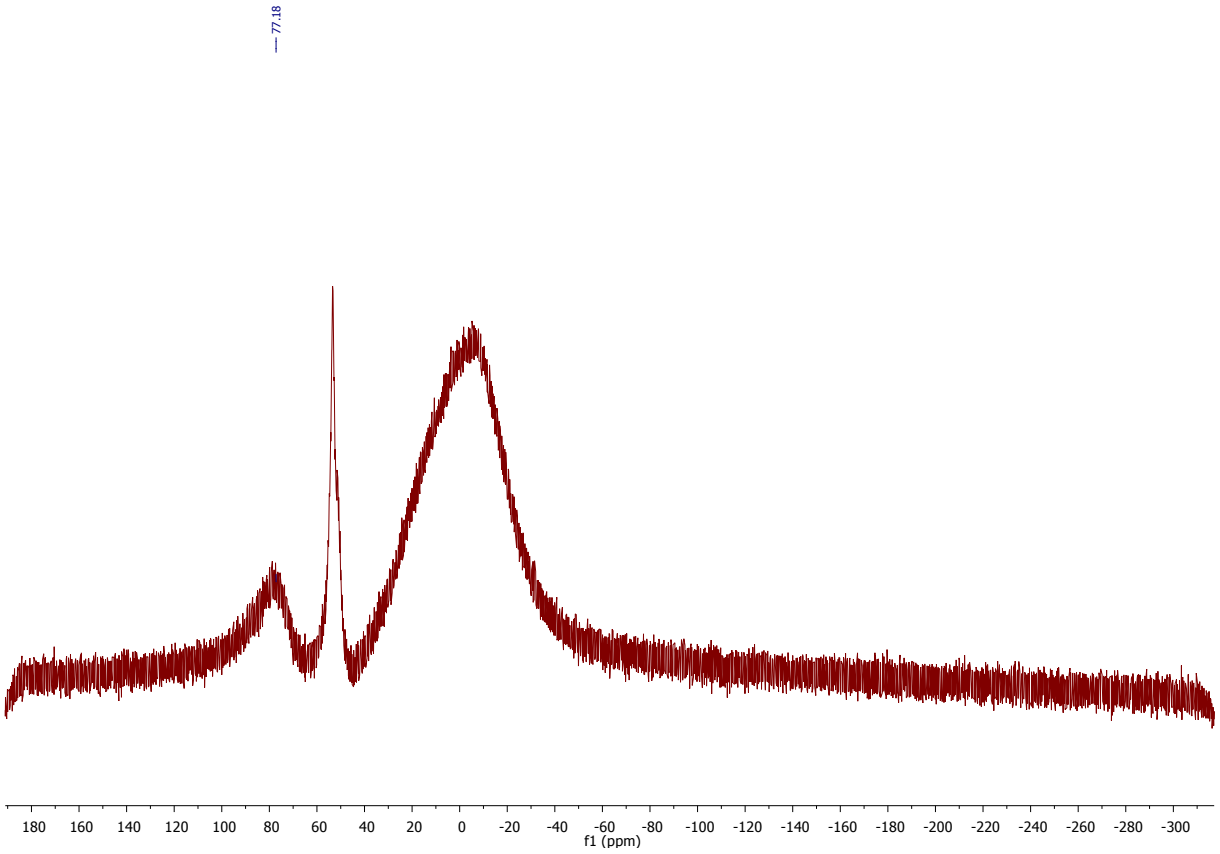
NMR $^{13}C$, $C_6D_6$, 151 MHz



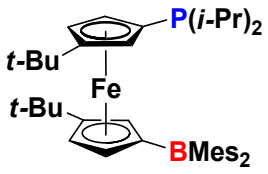
NMR $^{31}P$, $C_6D_6$, 243 MHz



NMR $^{11}B$, $C_6D_6$, 160 MHz (*deborylation to HOB(*i*-Pr)$_2$ is proposed for $\delta$ around 50 ppm, *Chem. Ber.1986, 119, 338-348.)*

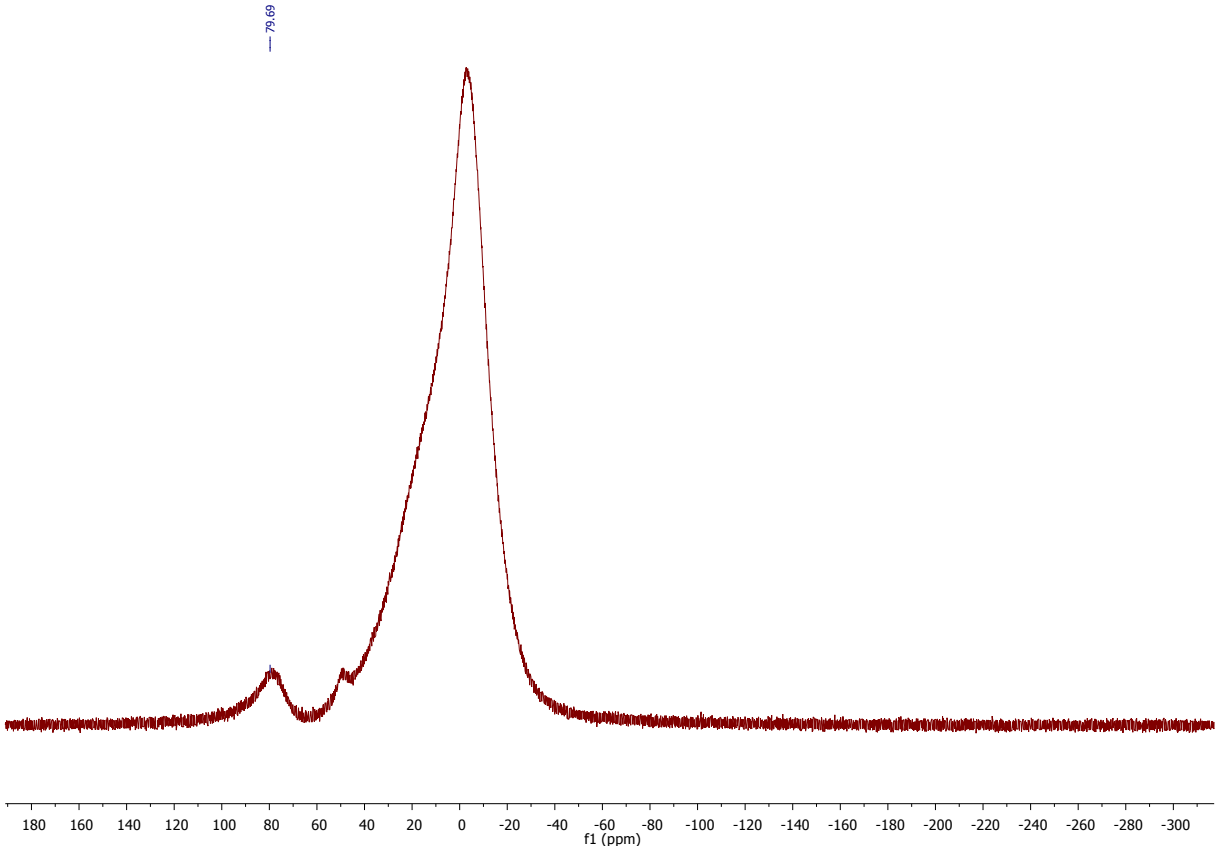


NMR $^{1}H$, $C_6D_6$, 300 MHz

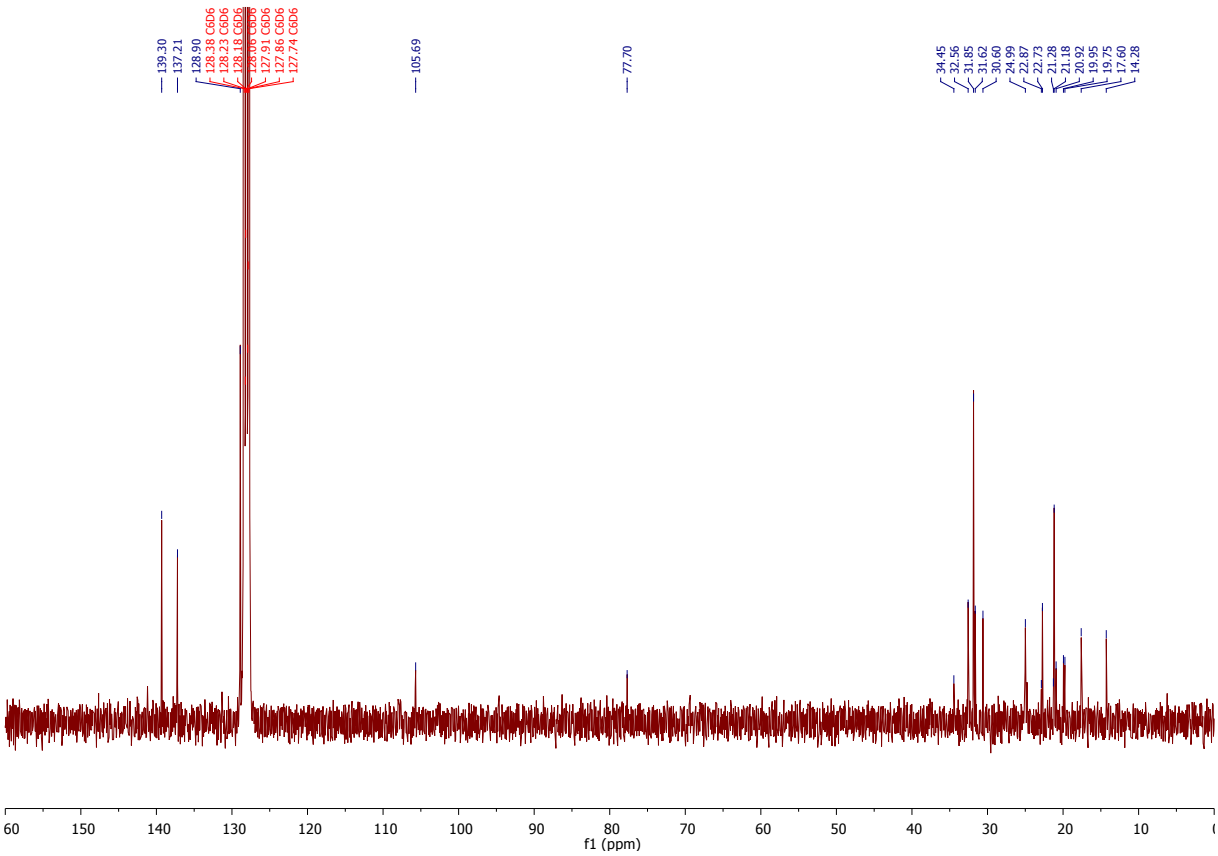



**4c**

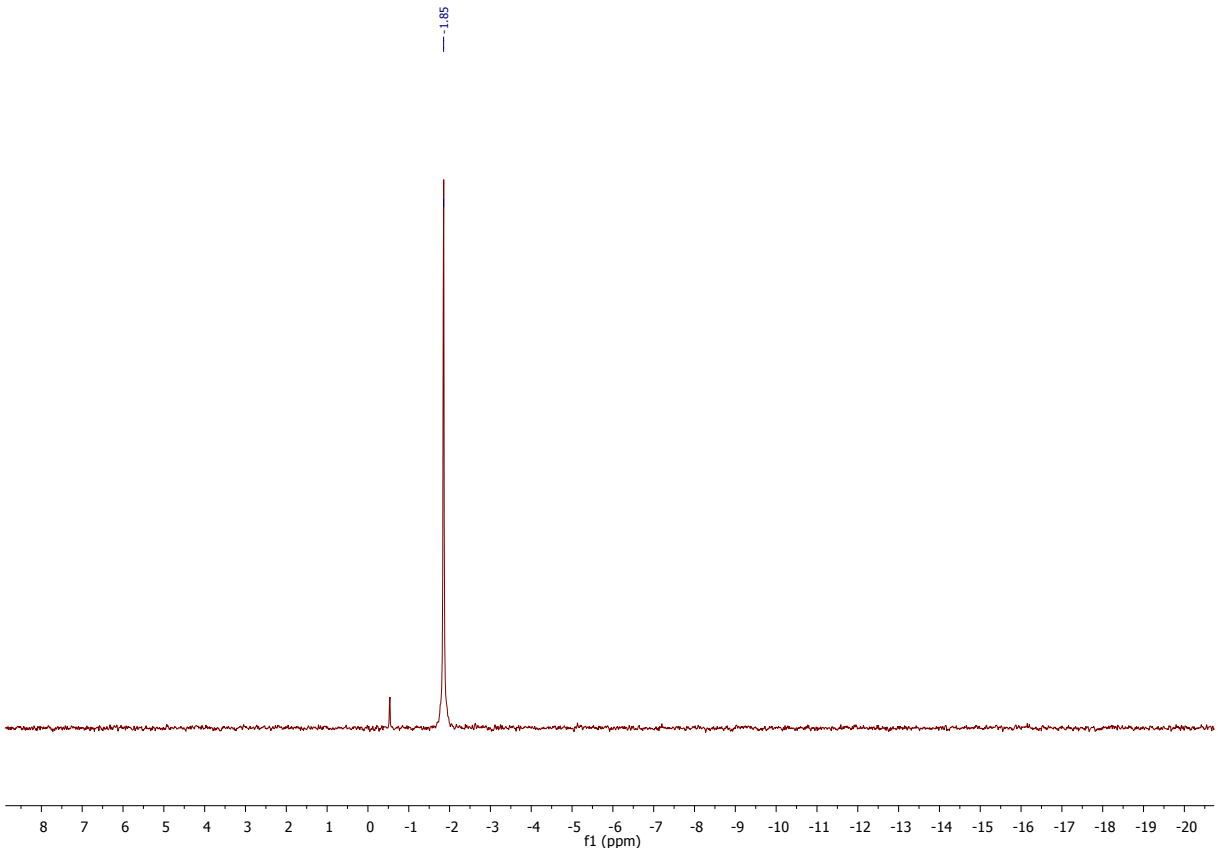
NMR $^{11}B$, $C_6D_6$, 160 MHz



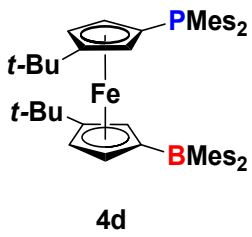
NMR $^{13}C$, $C_6D_6$, 75 MHz



NMR $^{31}P$, $C_6D_6$, 121 MHz

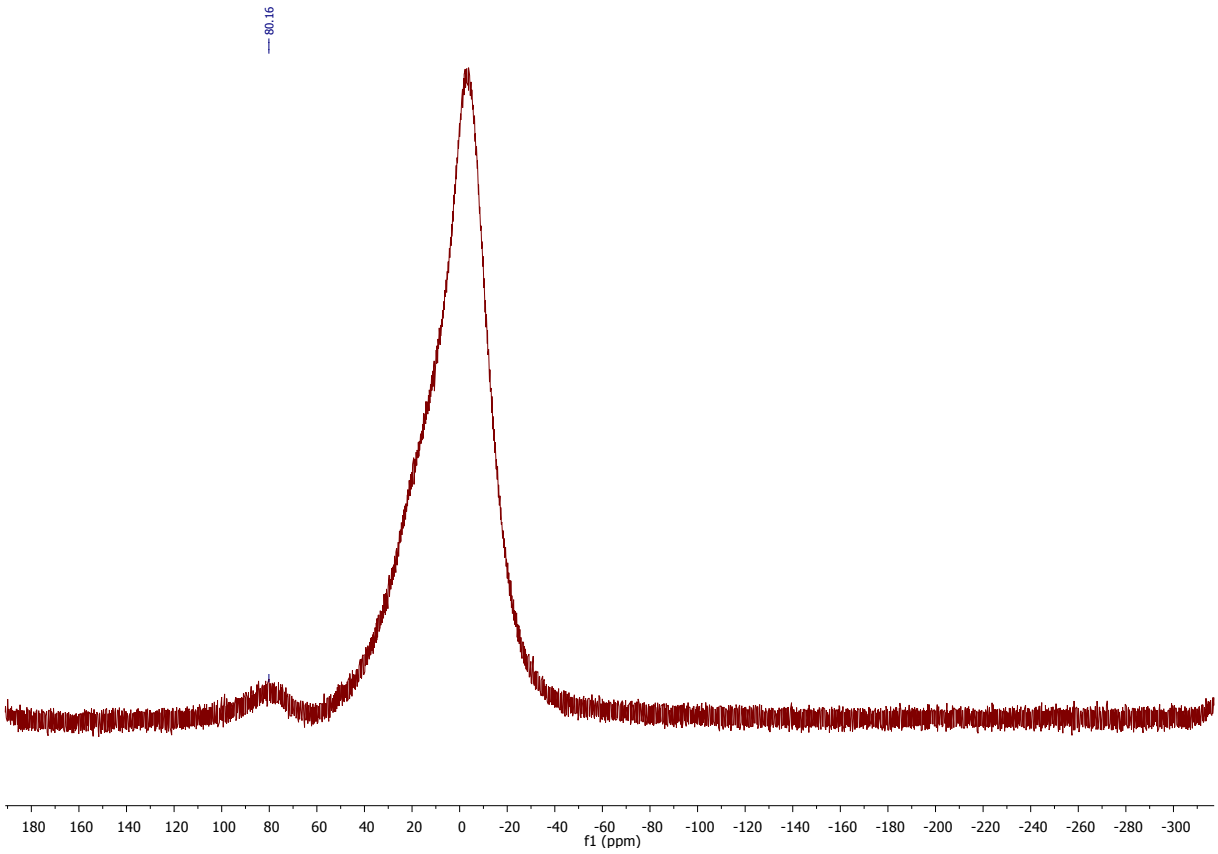


NMR $^{1}H$, $C_6D_6$, 500 MHz (*complete conversion was not achieved and **4d** is in a mixture with debrominated **3c**)

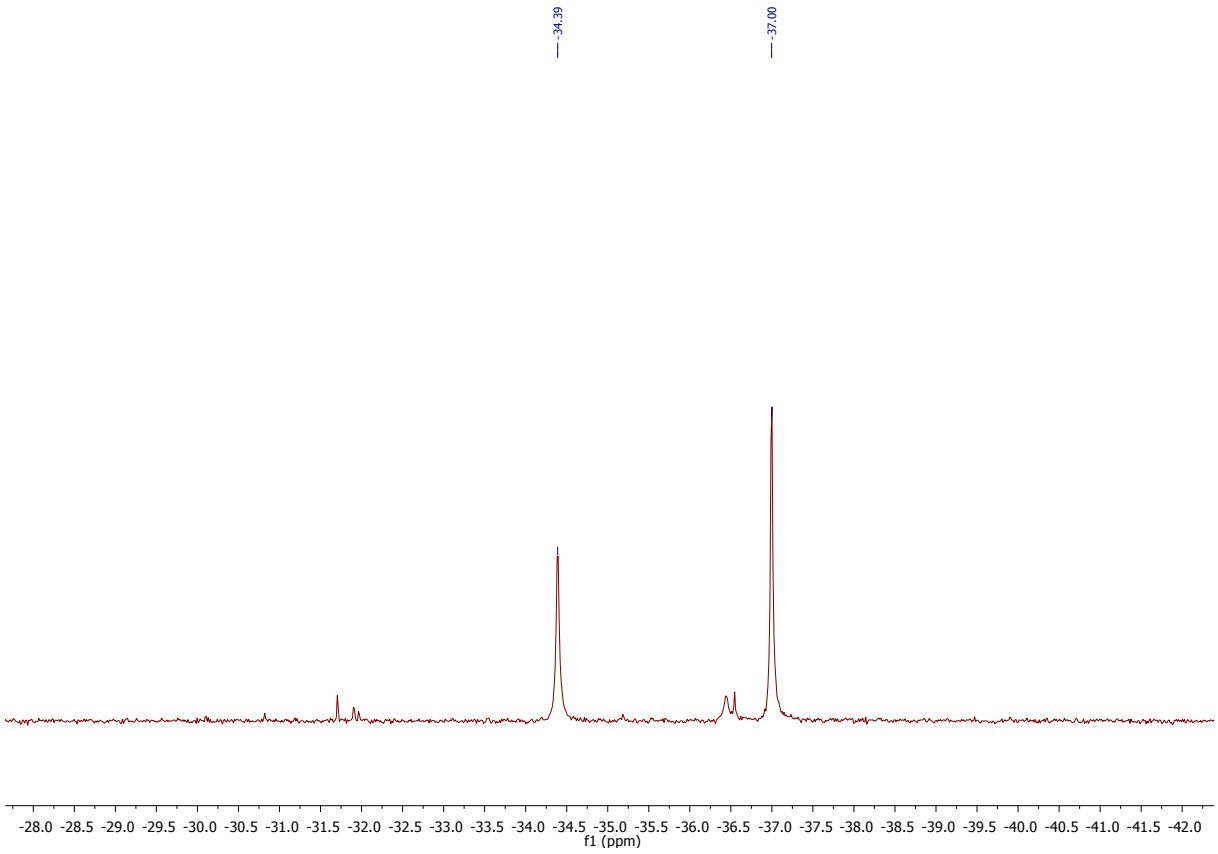



**4d**

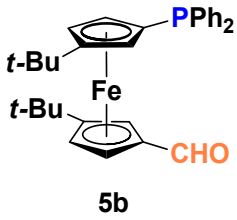
NMR $^{11}B$, $C_6D_6$, 160 MHz



NMR $^{31}P$, $C_6D_6$, 202 MHz

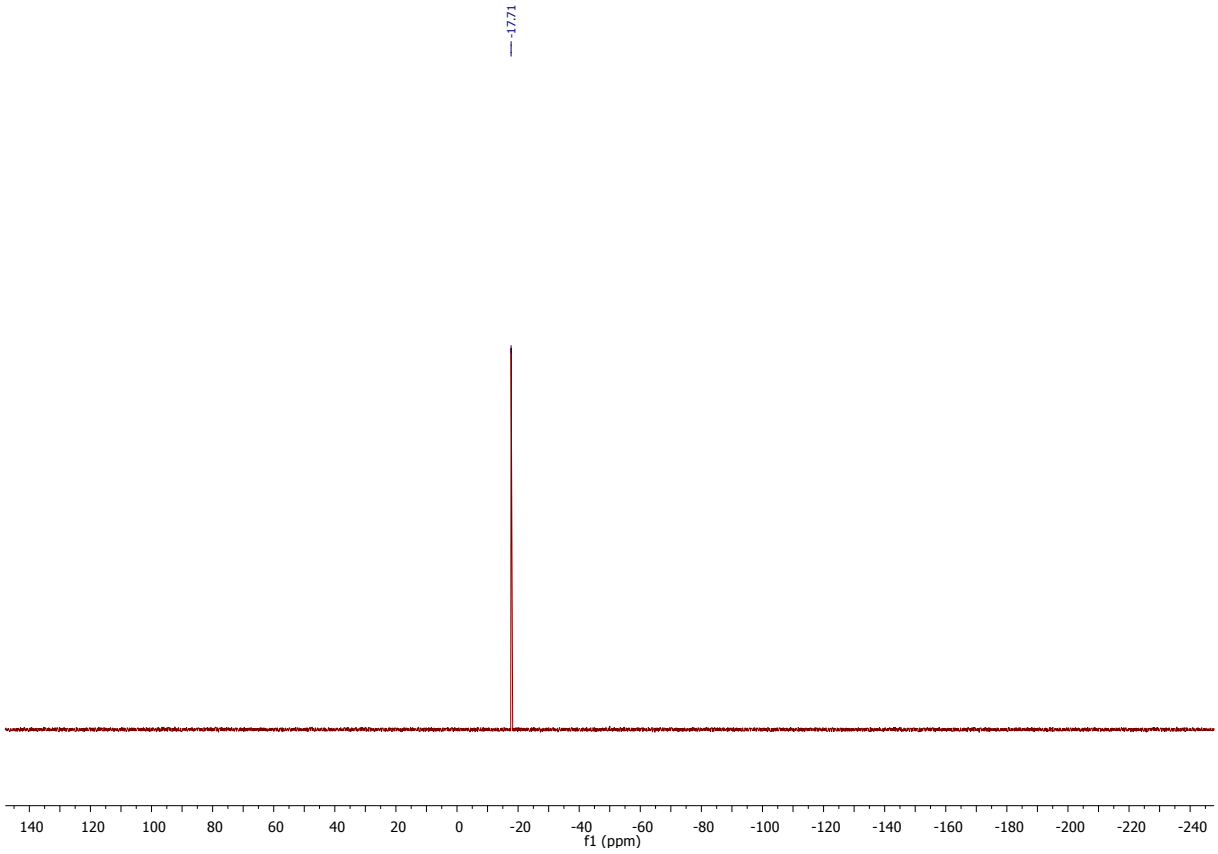


NMR $^{1}H$, $C_6D_6$, 600 MHz

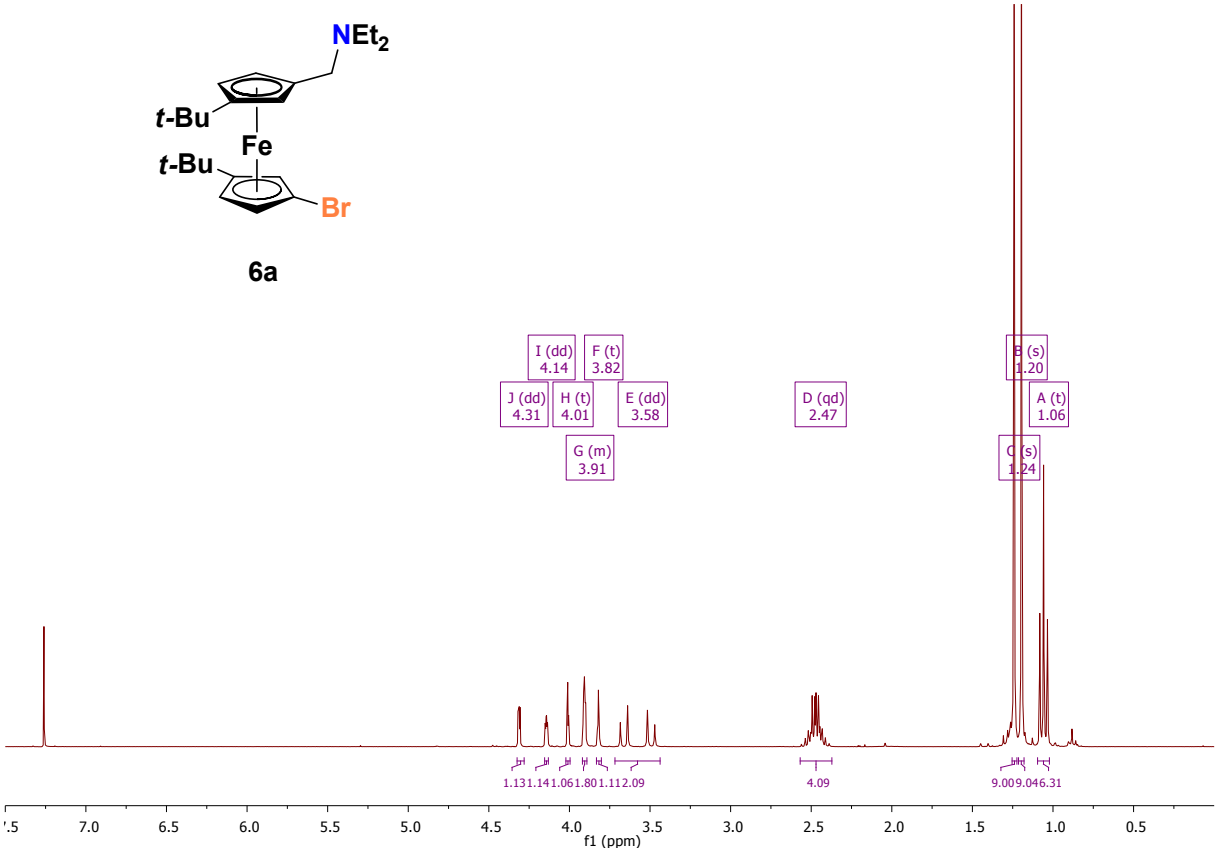



**5b**

NMR $^{31}P$, $C_6D_6$, 243 MHz

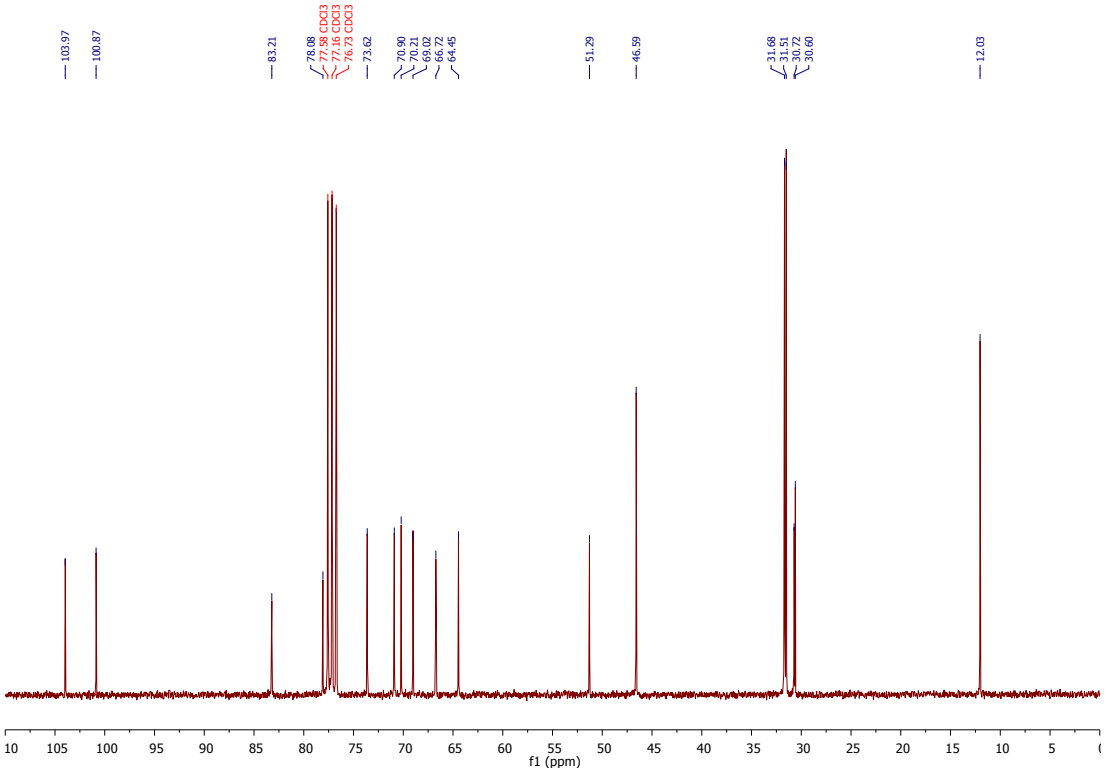


NMR $^{1}H$, $CDCl_3$, 300 MHz

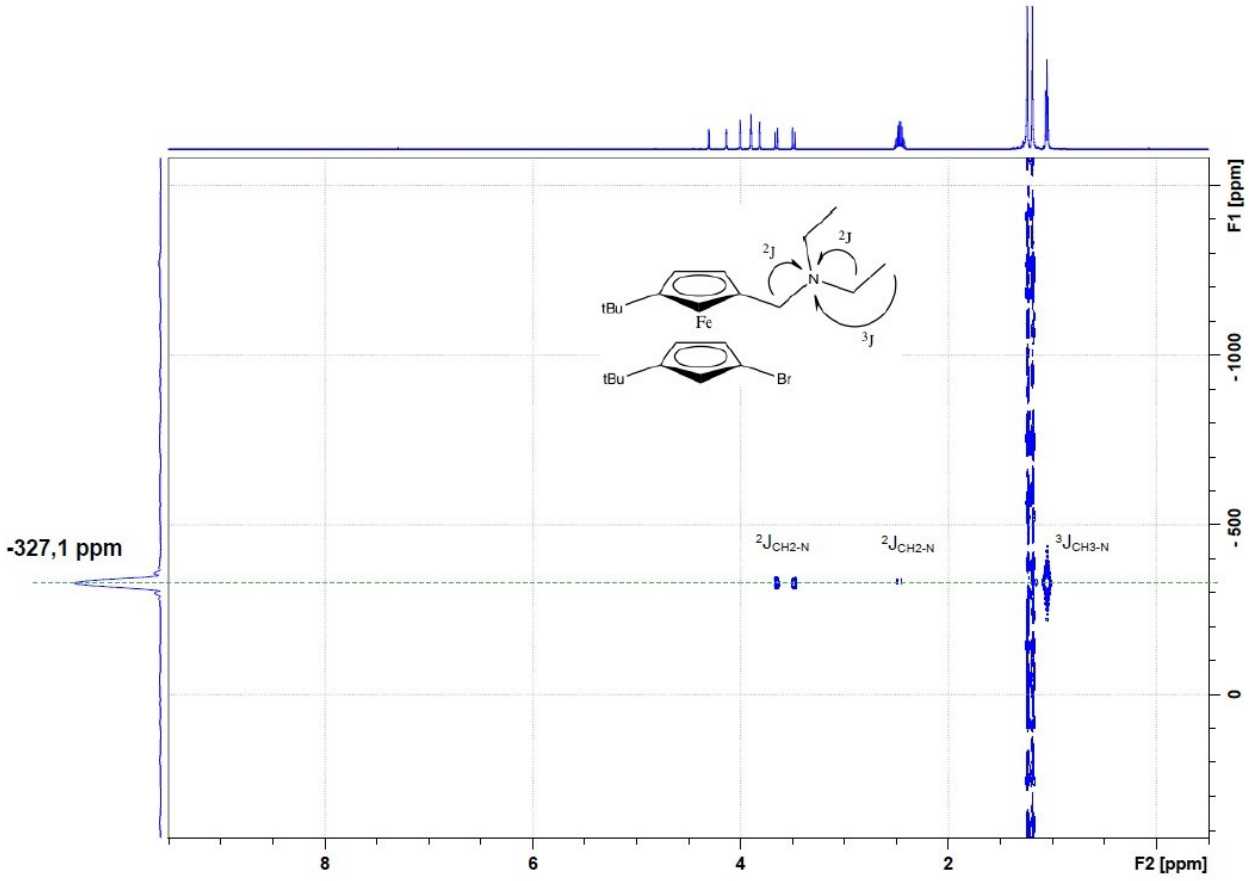



**6a**

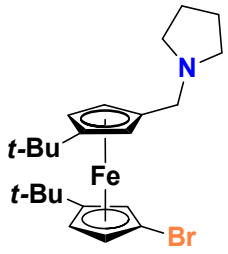
NMR $^{13}C$, $CDCl_3$, 75 MHz



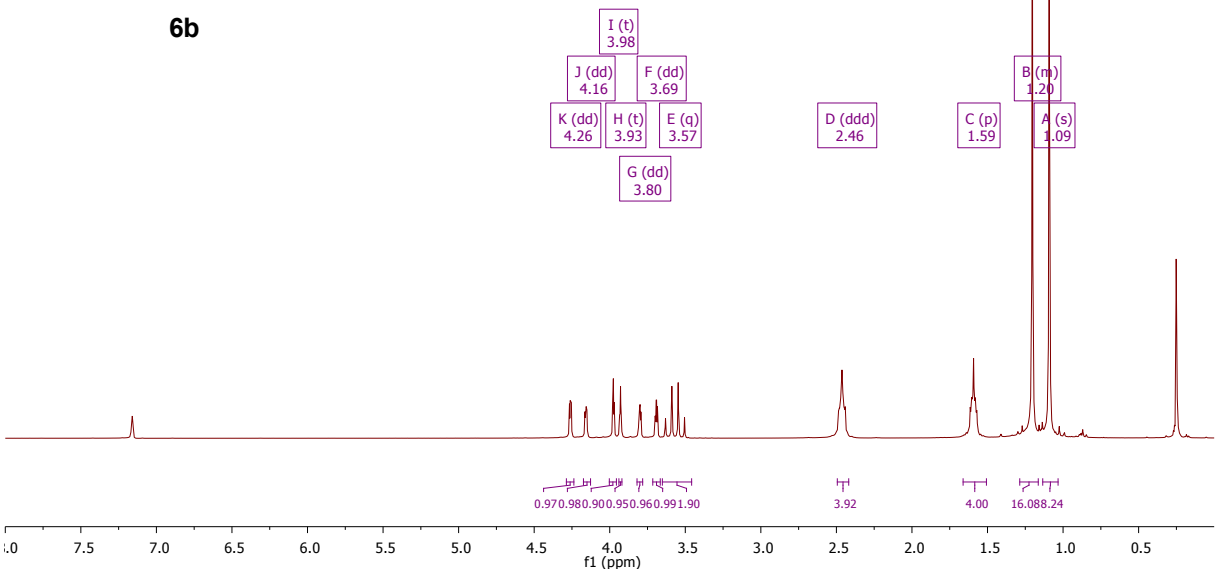
NMR $^{15}N$, $CDCl_3$, 61 MHz



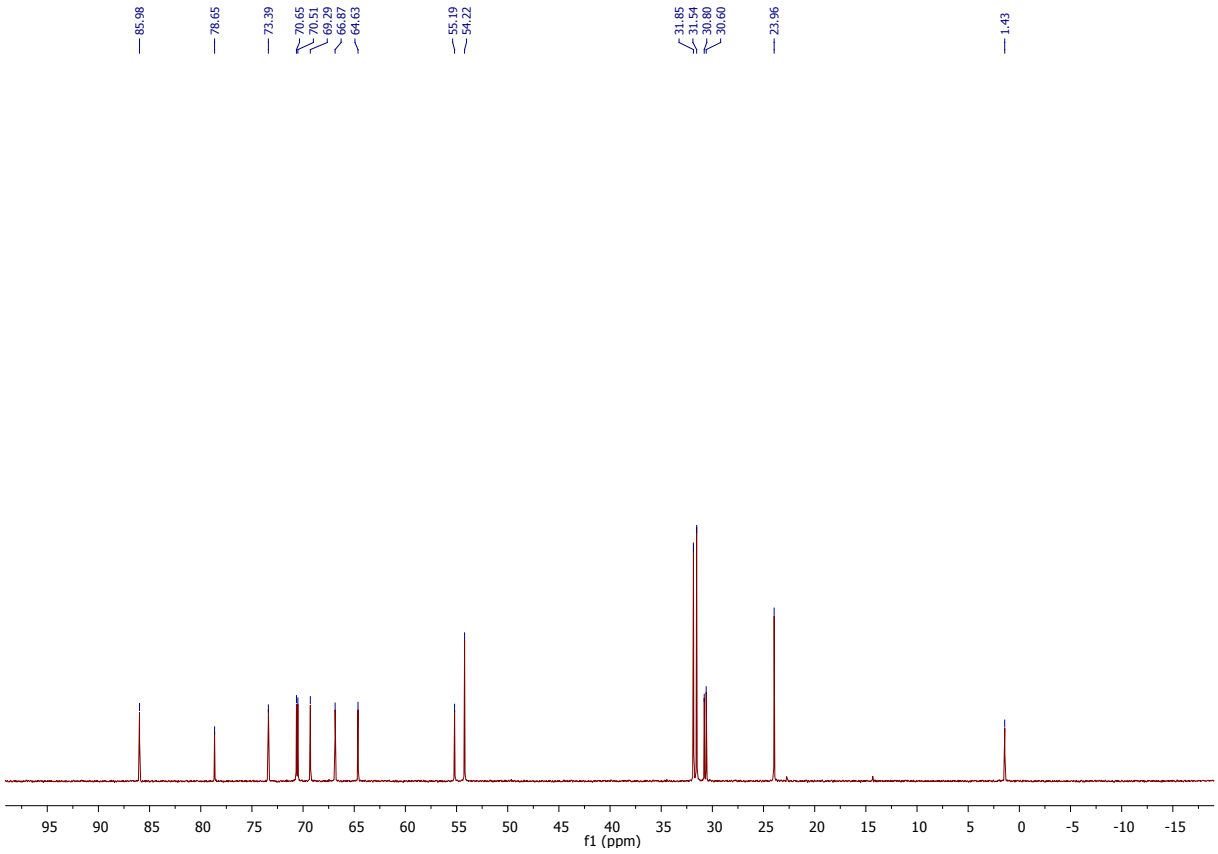
NMR $^{1}H$, $CDCl_3$, 300 MHz



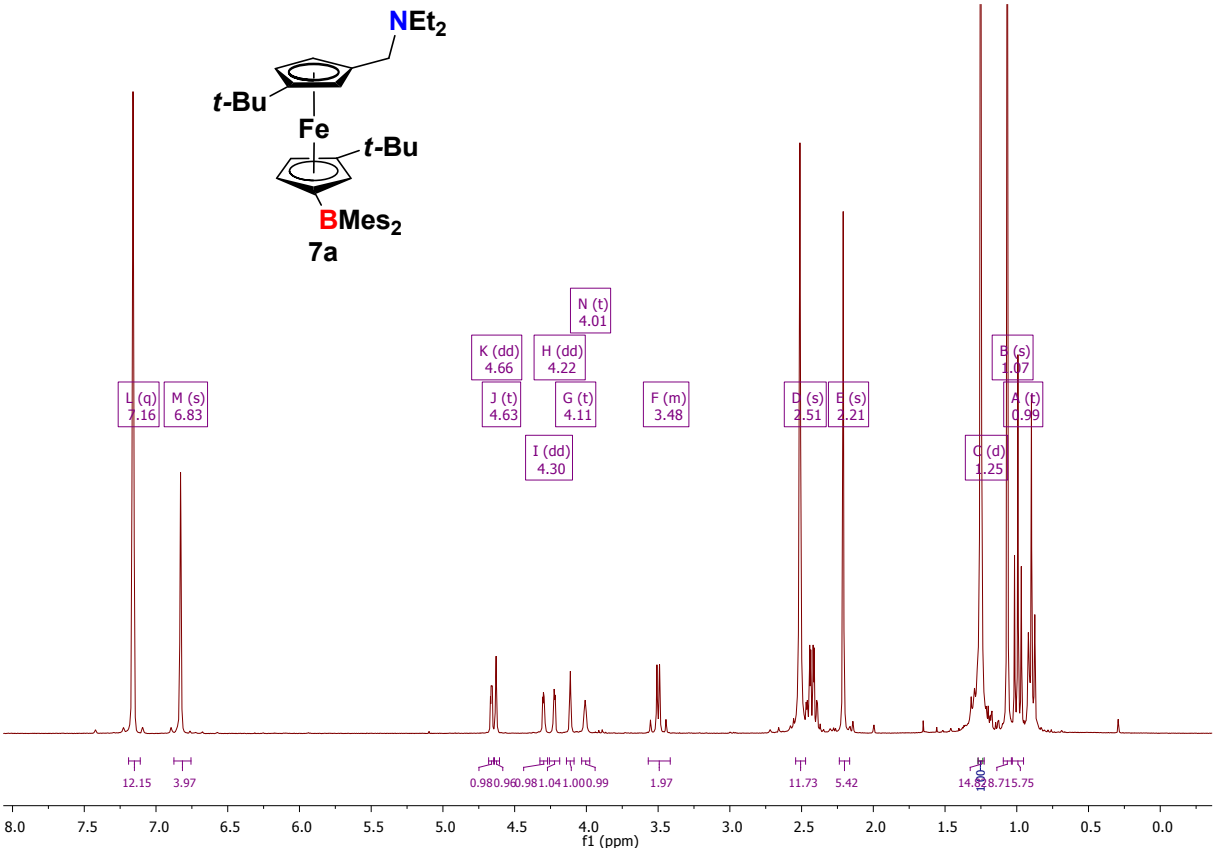

**6b**



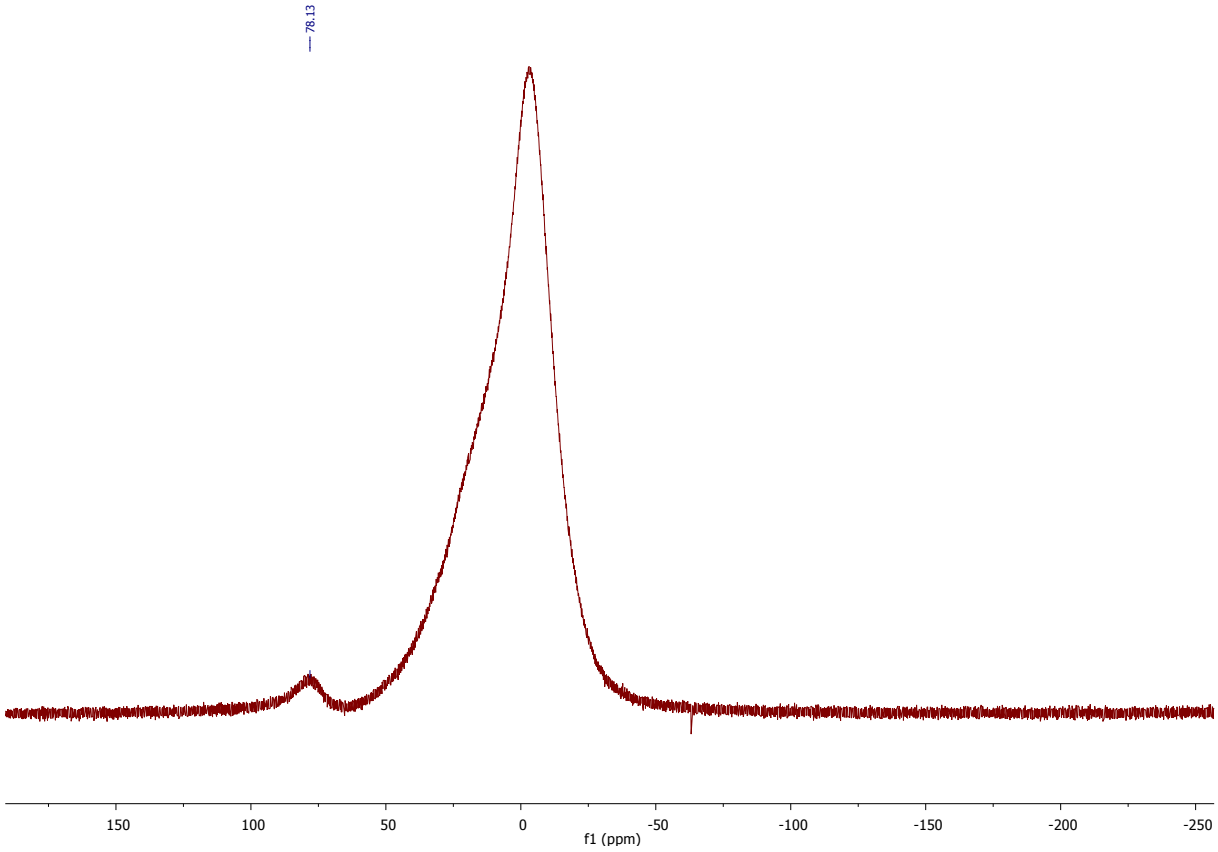
NMR $^{13}C$, $CDCl_3$, 75 MHz



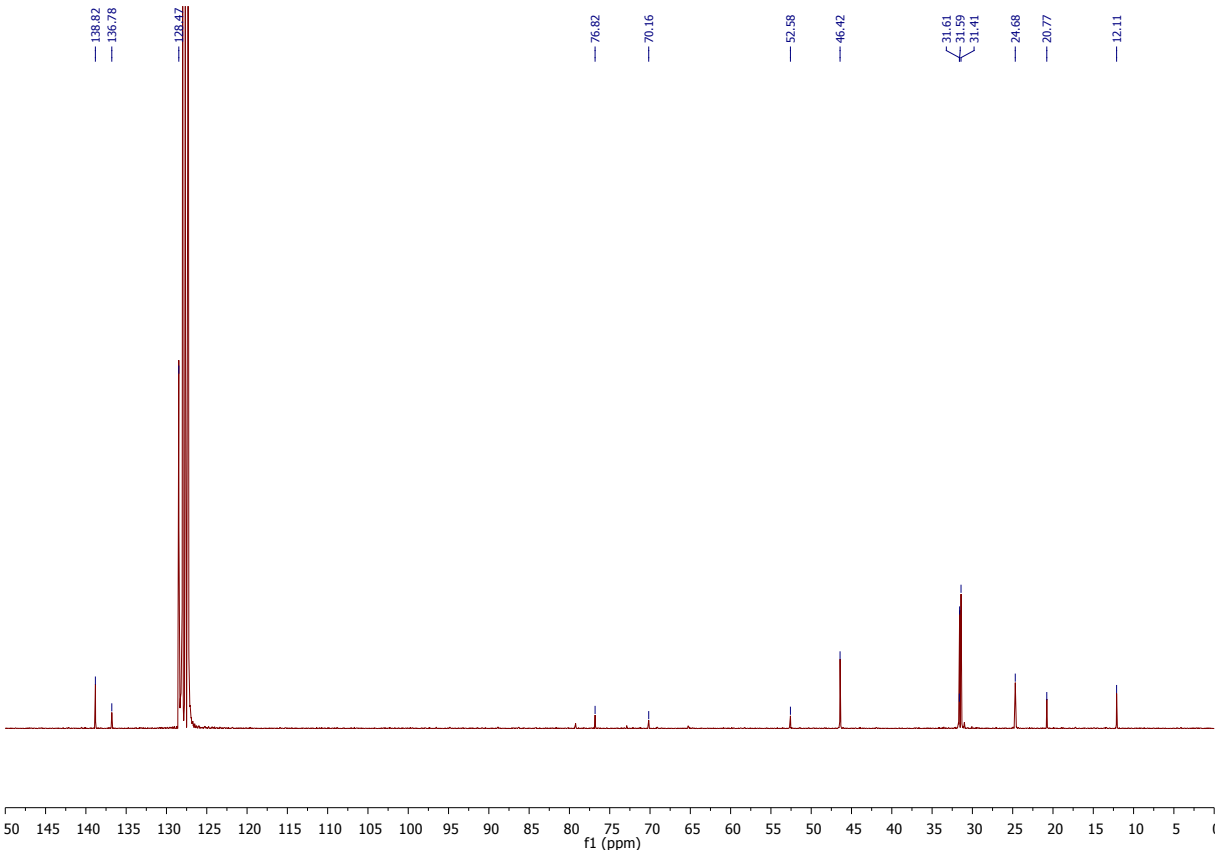
NMR $^{1}H$, $C_6D_6$, 300 MHz



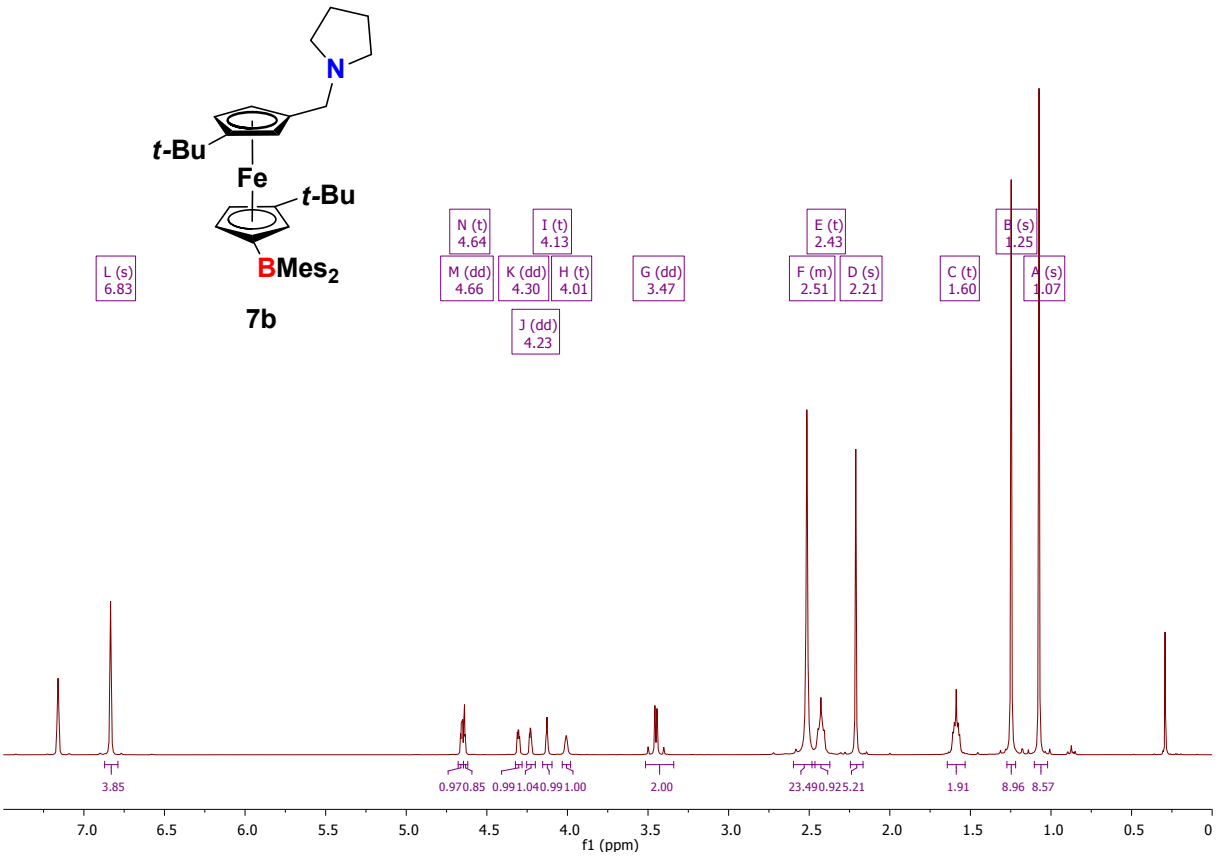
NMR $^{11}B$, $C_6D_6$, 160 MHz



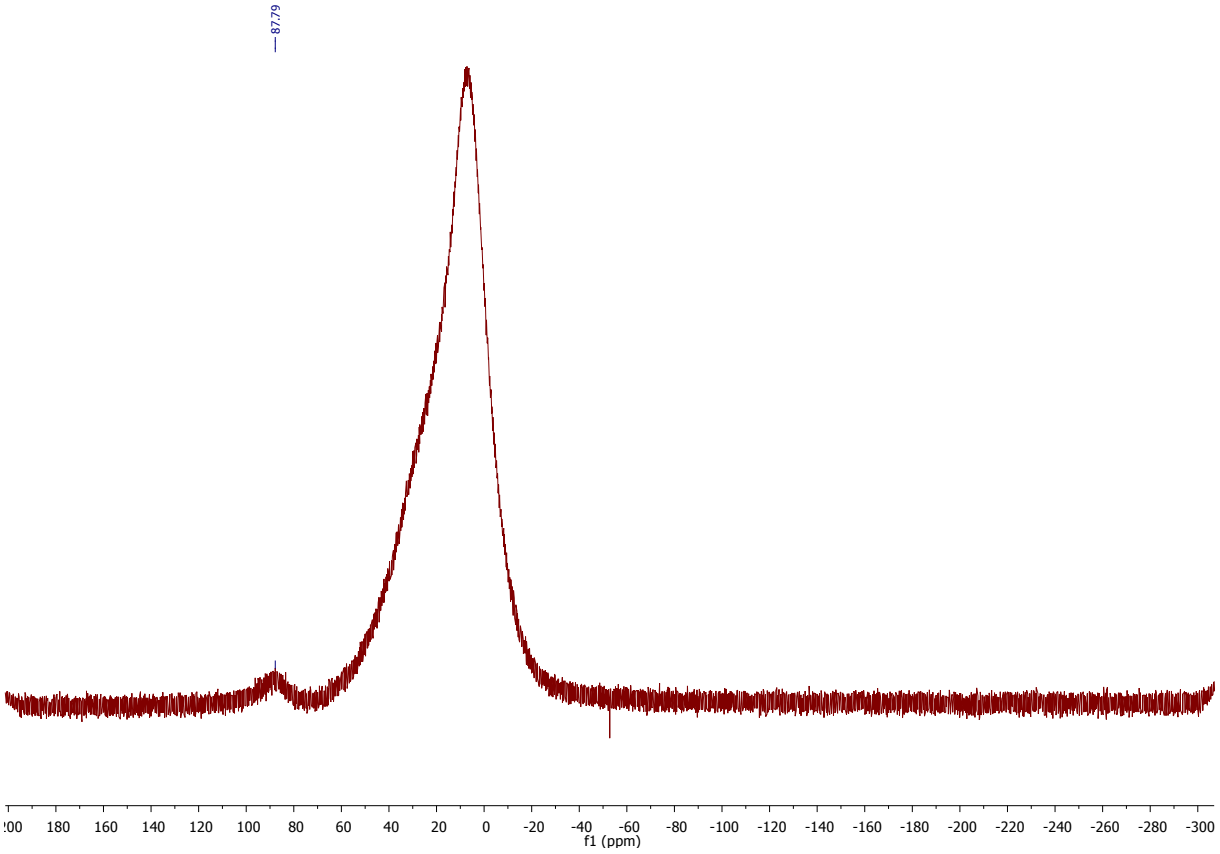
NMR $^{13}C$, $C_6D_6$, 75 MHz



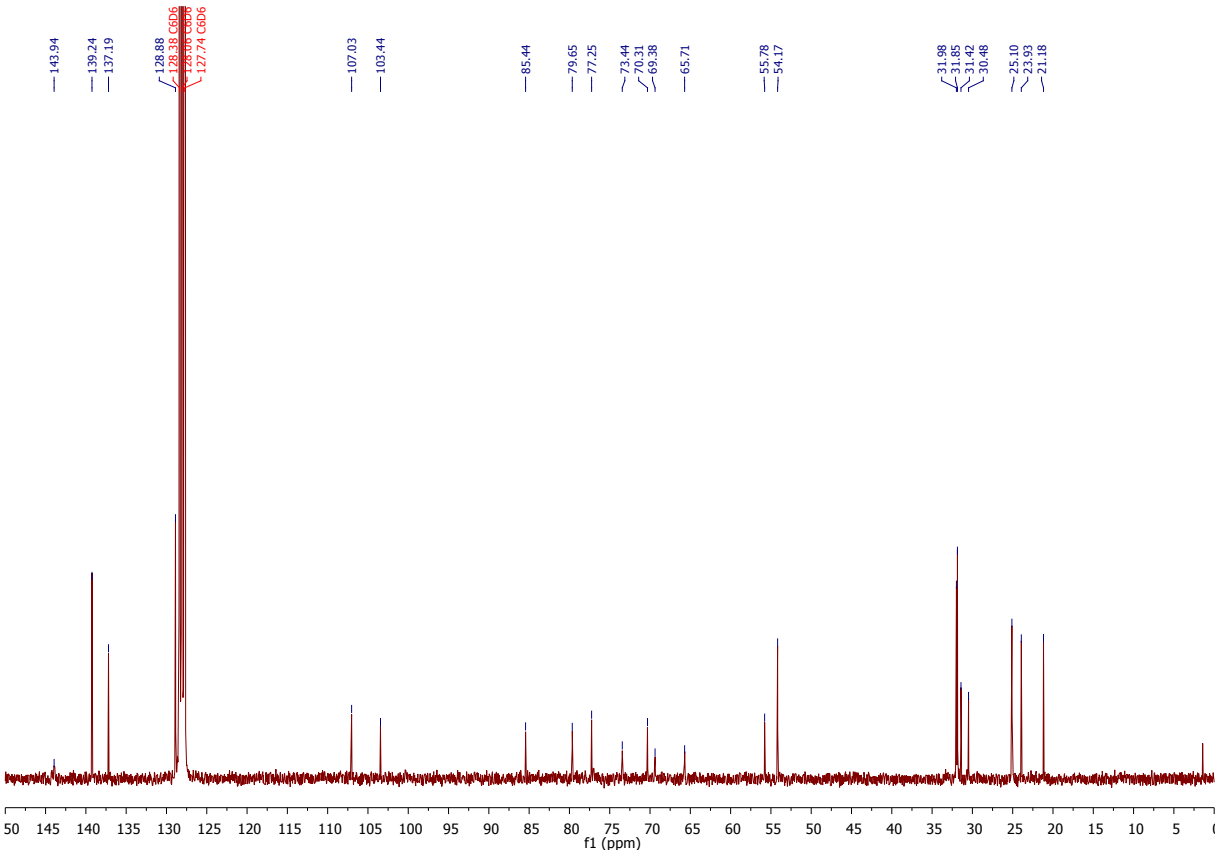
NMR $^{1}H$, $C_6D_6$, 300 MHz



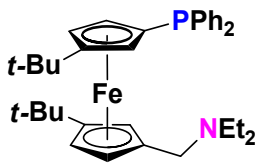
NMR $^{11}B$, $C_6D_6$, 160 MHz



NMR $^{13}C$, $C_6D_6$, 75 MHz

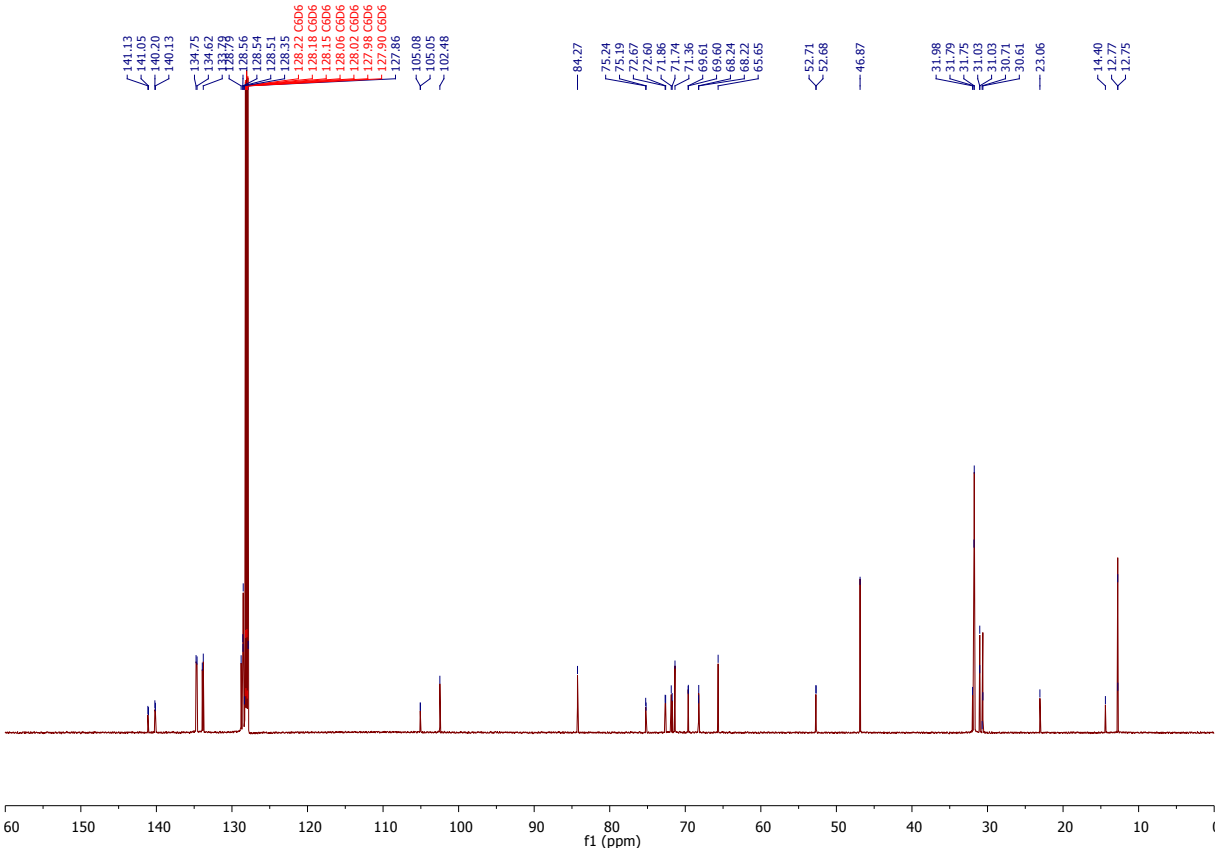


NMR $^{1}H$, $C_6D_6$, 600 MHz

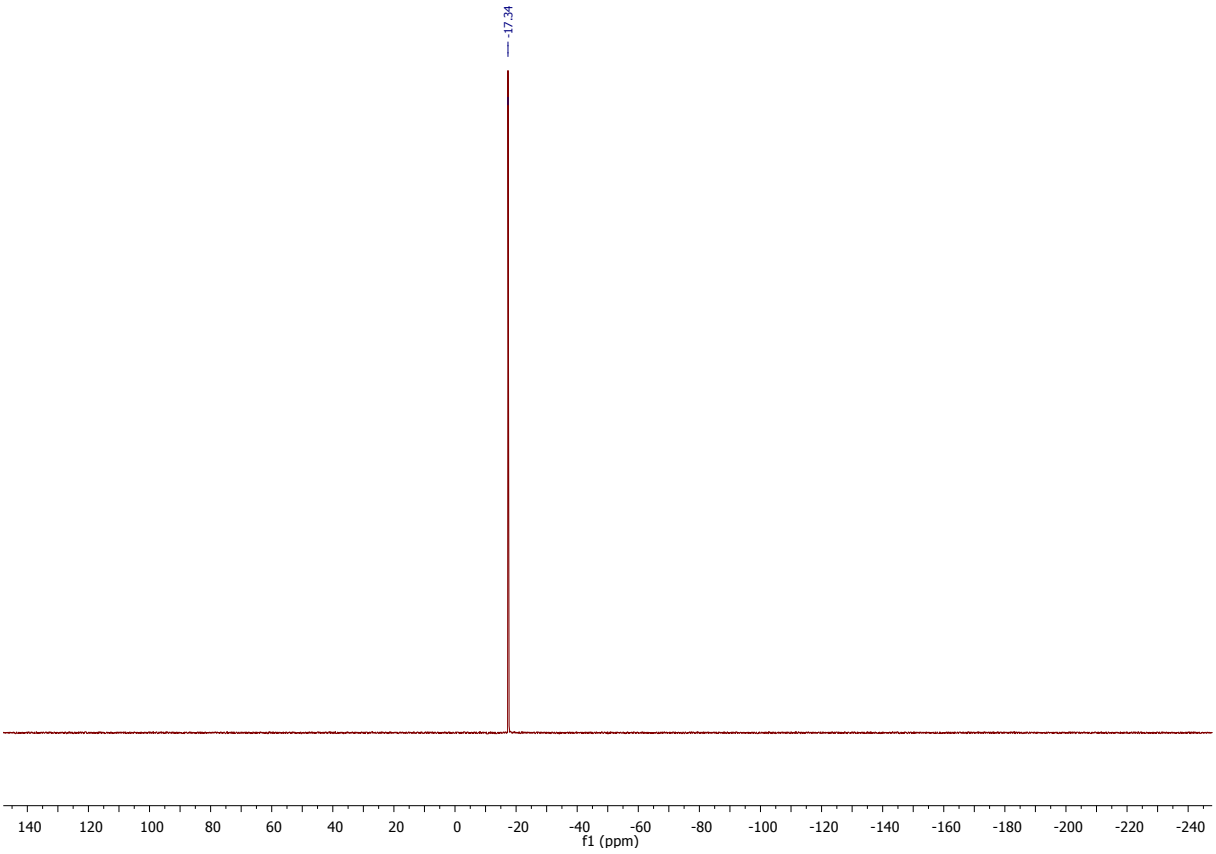



**8**

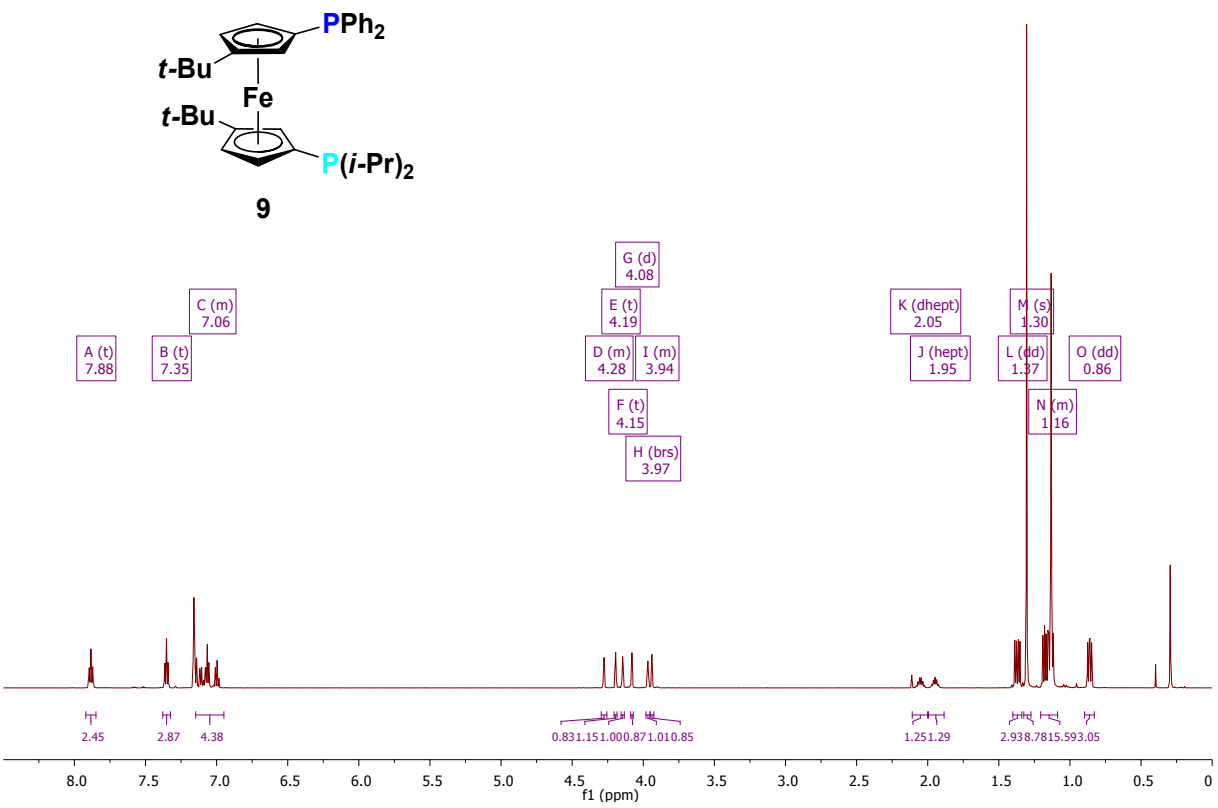
NMR $^{13}C$, $C_6D_6$, 151 MHz



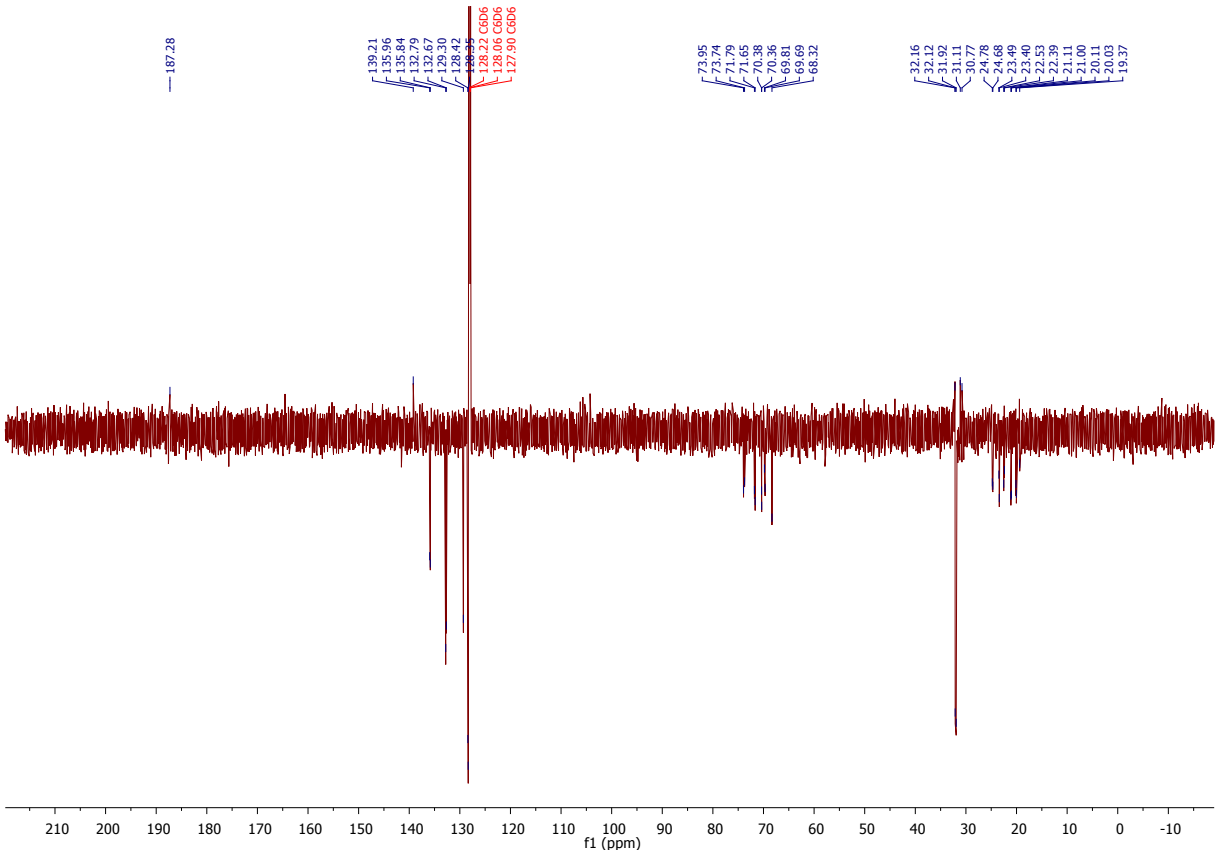
NMR $^{31}P$, $C_6D_6$, 243 MHz



NMR $^{1}H$, $C_6D_6$, 600 MHz



NMR $^{13}C$, $C_6D_6$, 151 MHz



NMR $^{31}P$, $C_6D_6$, 243 MHz