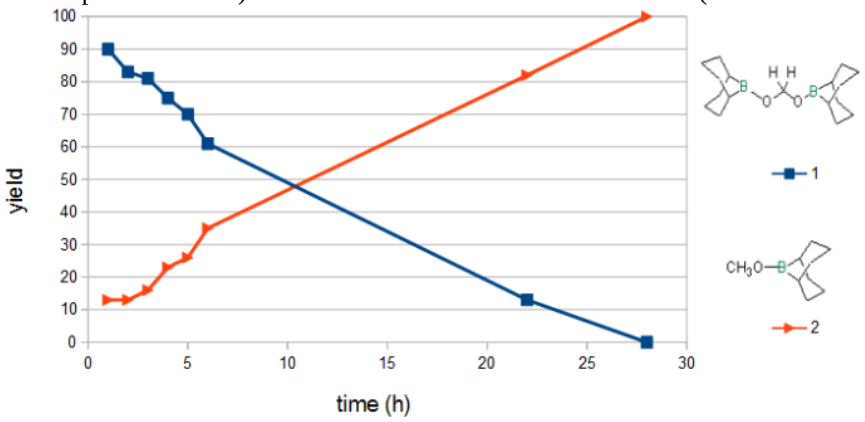
Electronic Supplementary Information

Synergistic Effects in Ambiphilic Phosphino-Borane Catalysts for the Hydroboration of CO_2

Anis Tlili, Arnaud Voituriez, Angela Marinetti,* Pierre Thuéry, Thibault Cantat**

Figure S1.

Catalytic reduction of CO_2 to methoxyborane **CH_3OBBN**. Distribution of the reduction products $H_2C(OBBN)_2$, and CH_3OBBN (%) over time (hour) in the catalytic reduction of CO_2 (1 bar) with 9-BBN, in the presence of 3-$BMes_2$ (1 mol% with respect to 9-BBN). Formation of HCOO–BBN is not shown (conversion <5 %).



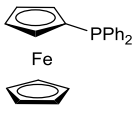
General Experimental Procedures.

All the reactions and manipulations were performed at 20°C in a recirculating mBraun LabMaster DP inert-atmosphere (Ar) drybox and with vacuum Schlenk lines. Glassware was dried overnight at 60°C before use. ^1H and ^{13}C NMR spectra were obtained by using a Bruker DPX 200 MHz spectrometer. ^{11}B NMR spectra were obtained by using a Bruker Avance 400 MHz spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to solvent impurities. Unless otherwise noted, reagents were purchased from commercial suppliers and dried over molecular sieves (4 Å) prior to use. The molecular sieves (4 Å; Aldrich) were dried under a dynamic vacuum at 250 °C for 48 h prior to use. THF, THF-d8, toluene, pentane, and [D6]benzene were dried over a sodium(0)/benzophenone mixture and distilled before use. CD_3CN and CD_2Cl_2 were dried over CaH_2 and distilled before use. Carbon dioxide was purchased from Messer in a 5.5 purity gas bottle.

Typical procedure for the catalytic hydroboration of CO_2 to methoxyborane:

The typical procedure is detailed for the conversion of CO_2 into methoxyborane with 1-dimesitylboryl-10-diphenylphosphinoferrocene **3-$BMes_2$** as catalyst and $(9\text{-BBN})_2$ as the reductant (Table 1). A 2.5 mL NMR tube equipped with a J. Young valve was charged with **3-$BMes_2$** (3.0 mg, 0.0048 mmol), $(9\text{-BBN})_2$ (58.6 mg, 0.240 mmol), and THF-d8 (0.40 mL). The reaction mixture was exposed to an atmosphere of CO_2 (1 bar), and the flask was sealed. The formation of CH_3OBBN was followed by ^1H NMR spectroscopic analysis in [D8]THF with mesitylene as an internal standard. Selected ^1H and ^{13}C NMR spectroscopic data ([D8]THF) for: HCOOBBN (δ = 8.24 (H<u>C</u>OO) and 163.2 ppm (<u>H</u>COO)), $H_2C(OBBN)_2$ (δ = 5.54 (H_2<u>C</u>$(OBBN)_2$) and 86.5 ppm (H_2<u>C</u>$(OBBN)_2$)), and CH_3OBBN (δ = 3.71 (CH_3<u>O</u>BBN) and 53.4 ppm (<u>C</u>H_3OBBN)).

1. (diphenylphosphine)ferrocene, $FcPPh_2$ (1).[1]



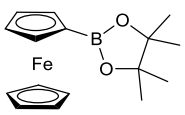
After standard cycles of evacuation and back-filling with dry and pure argon, a Schlenk tube equipped with a magnetic stirring bar was charged with ferrocene (372 mg, 2.0 mmol), *t*BuOK (22.4 mg, 0.2 mmol) and dry THF (4 ml). Afterwards, the solution was cooled down to -78°C and *t*BuLi (2.35 mL, 4.0 mmol, 1.7 M in hexane) was added dropwise. After 15 min at -78°C, the mixture was warmed to -25°C and stirred for 1 hour. Afterwards, a solution of chlorodiphenylphosphine (2.5 mmol, 448 µL) in 4 ml of dry THF was added dropwise. The solution was slowly warmed to room temperature. The reaction was quenched after 2 hours with water. The reaction mixture was diluted with CH_2Cl_2, the layers were separated and the aqueous layer was extracted 5 times. The combined organic fractions were dried over Na_2SO_4 and evaporated to give the crude product, which was purified by flash column chromatography using petroleum ether/ ethyl acetate (9:1) as eluent. The product was isolated as an orange powder in 94 % yield. The product was recrystallized in CH_2Cl_2. The analytical data correspond to those in the cited references.

^{1}H NMR ($CDCl_3$) δ (ppm): 4.10 (s, 5H), 4.17 (brs, 2H), 4.37 (brs, 2H), 7.35 (m, 10H).

^{31}P NMR ($CDCl_3$) = -16.2.

HRMS: calc. for $[M+H]^+$ $C_{22}H_{20}FeP$: 371.0652, found: 371.0634.

2. (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene: 2-Bpin[2]

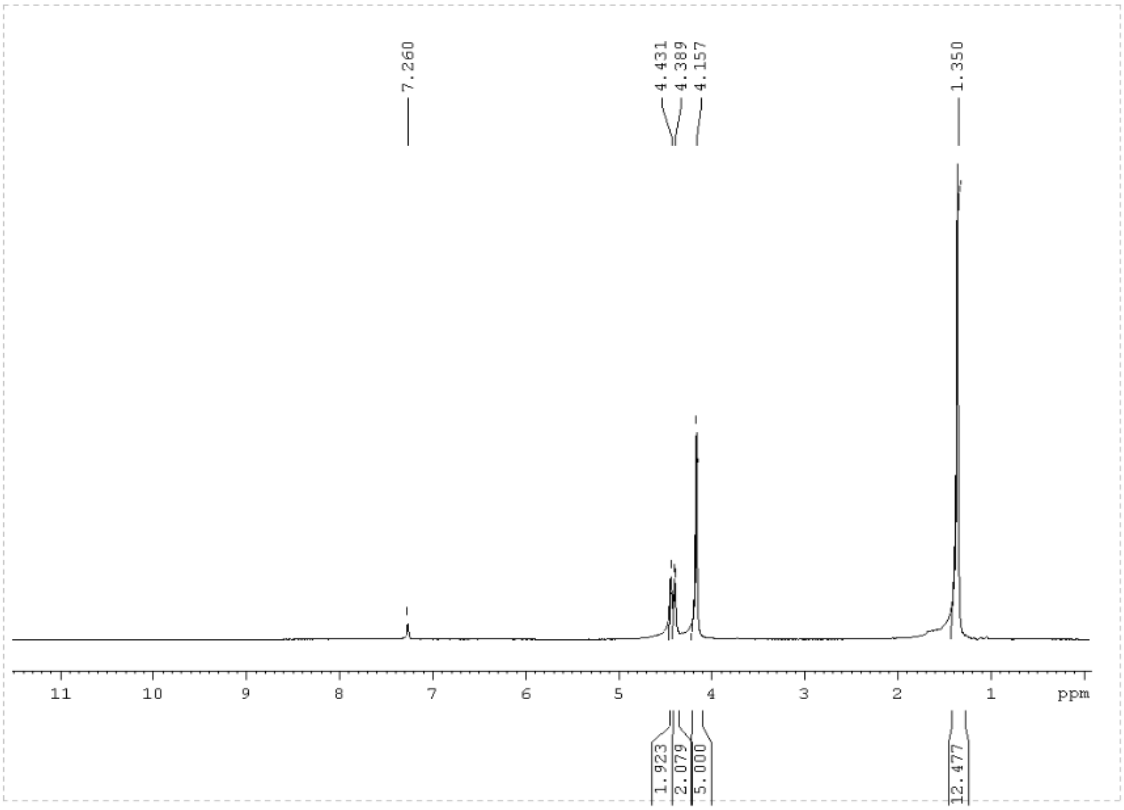


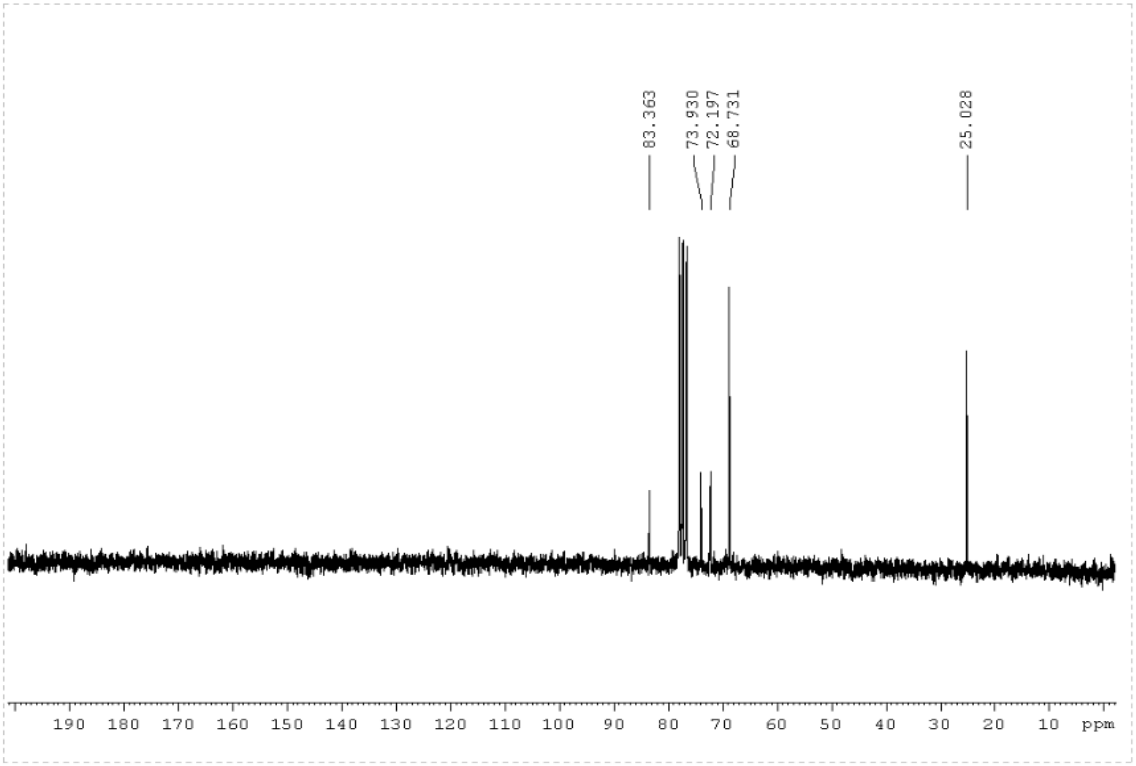
After standard cycles of evacuation and back-filling with dry and pure argon, a Schlenk tube equipped with a magnetic stirring bar was charged with ferrocene (372 mg, 2.0 mmol), *t*BuOK (22.4 mg, 0.2 mmol) in dry THF (4 ml). Afterwards, the solution was cooled down to -78°C and *t*BuLi (2.35 mL, 4.0 mmol, 1.7 M in hexane) were added dropwise. After 15 min at -78°C, the mixture was warmed to -25°C and stirred for 1 hour. Afterwards, a solution of *bis*(pinacolato)diboron (4.0 mmol, 1.01 g) in dry THF (4 mL) was added dropwise. The solution was slowly warmed to room temperature. The reaction was quenched after 2 hours with water. The reaction mixture was diluted with CH_2Cl_2, the layers were separated and the aqueous layer was extracted 5 times. The combined organic fractions were dried over Na_2SO_4 and evaporated to give the crude product, which was purified by flash column chromatography using petroleum ether/ethyl acetate (1:1) as eluent. The product was isolated as an orange powder in 25% yield. The product was recrystallized in CH_2Cl_2. The analytical data correspond to those in the cited references.

^{1}H NMR ($CDCl_3$) δ (ppm): 1.35 (s, 12H), 4.16 (s, 5H), 4.39 (brs, 2H,), 4.43 (brs, 2H).

^{13}C NMR ($CDCl_3$) δ (ppm): 25.0, 68.7, 72.2, 73.9, 83.4.

HRMS: calc. for $[M+H]^+$ $C_{16}H_{22}BFeO_2$: 313.1062, found: 313.1035.

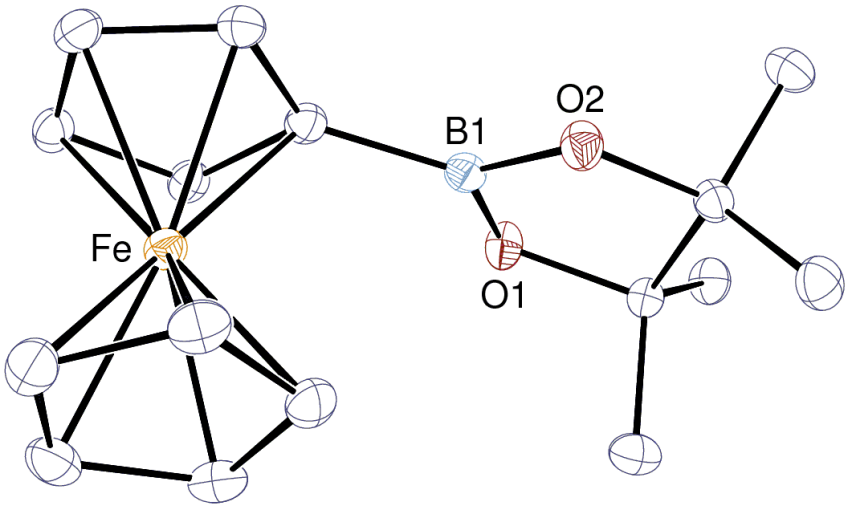




Crystallographic data collection and structure determination. The data for compound **2-Bpin** were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[3] using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The unit cell parameters were determined from ten frames, then refined on all data. The data (combination of φ- and ω-scans giving a complete data set up to θ = 30.5° and a minimum redundancy

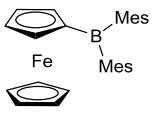
of 4 for 90% of the reflections) were processed with HKL2000.[4] Absorption effects were corrected empirically with the program SCALEPACK.[4] The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on F^2 with SHELXL-97.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3).

Crystal data for compound (2-Bpin). $C_{16}H_{21}BFeO_2$, M = 311.99, monoclinic, space group $P2_1/n$, a = 12.7414(5), b = 7.5452(3), c = 15.8499(7) Å, β = 104.524(3)°, V = 1475.06(11) Å^3, Z = 4, D_c = 1.405 g cm^{-3}, μ = 1.019 mm^{-1}, $F(000)$ = 656. Refinement of 185 parameters on 4496 independent reflections out of 56555 measured reflections (R_{int} = 0.032) led to R_1 = 0.030, wR_2 = 0.082, S = 1.073, $\Delta\rho_{max}$ = 0.35, $\Delta\rho_{min}$ = –0.48 e Å^{-3}. CCDC-1028777 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



View of compound **2-Bpin**. Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 30% probability level.

3. Dimesitylboryl-ferrocene, 2-BMes$_2$ [6]

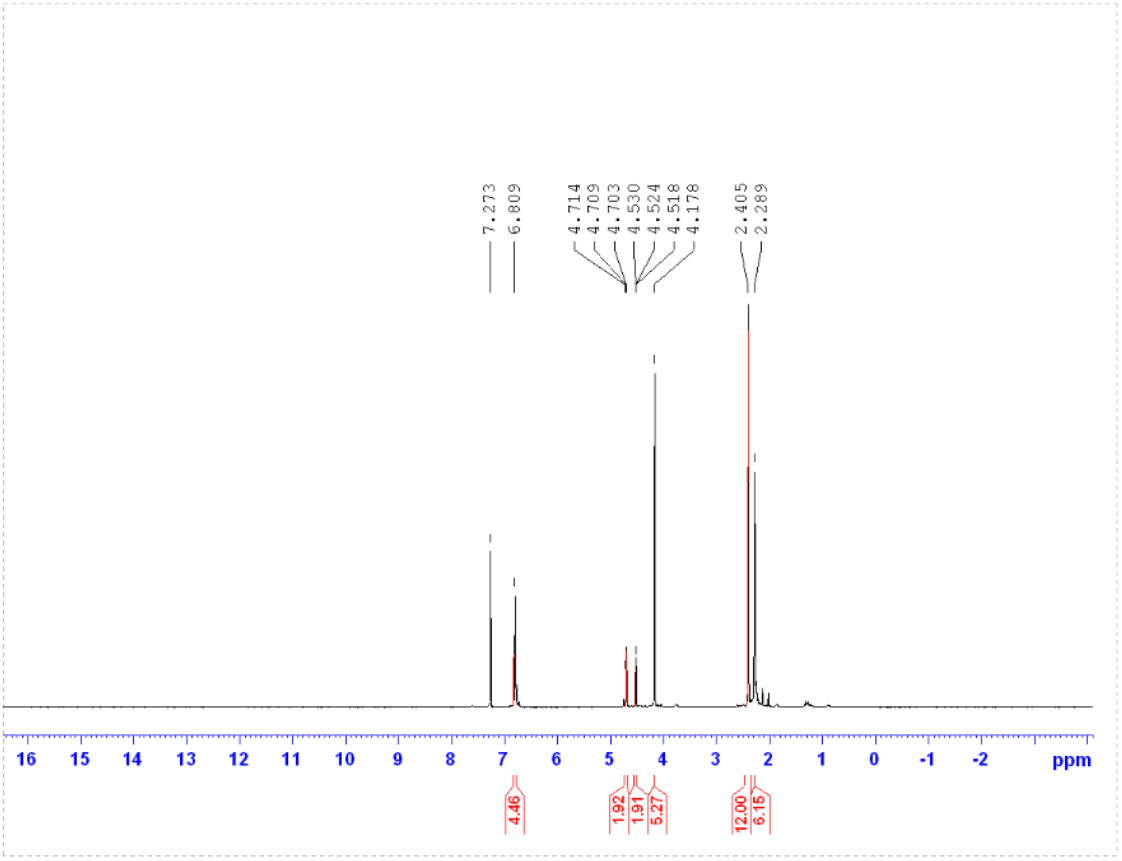


A Schlenk tube equipped with a magnetic stirring bar was charged under argon with ferrocene (372 mg, 2.0 mmol), *t*BuOK (22.4 mg, 0.2 mmol) in dry THF (4 mL). Afterwards, the solution was cooled down to -78 °C and *t*BuLi (2.35 mL, 4.0 mmol, 1.7M in hexane) was added dropwise. After 15 min at -78 °C, the mixture was warmed to -25°C and stirred for 1 hour. Afterwards, a solution of dimesitylboron fluoride (4.0 mmol, 1.07 g) in dry THF (4 mL) was added dropwise. The solution was slowly warmed to room temperature. Then, the solvent was removed under reduced pressure; the residue was dissolved in toluene (2 ml) and filtered on Buchner in glove box. The products precipitate in pentane at -40 °C as a purple powder.

^{1}**H NMR** ($CDCl_3$) δ (ppm): 2.29 (s, 6H), 2.40 (s, 12H), 4.18 (s, 5H), 4.52 (m, 2H,), 4.71 (m, 2H), 6.81 (s, 4H).

^{13}**C NMR** ($CDCl_3$) δ (ppm): 21.0, 24.3, 67.9, 69.4, 73.5, 79.3, 128.1, 136.9, 139.0.

HRMS: calc. for $[M+H]^+$ $C_{28}H_{32}BFe$: 435.1946, found: 435.1937.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6.809
4.714
4.709
4.703
4.530
4.524
4.518
4.178
2.405
2.289
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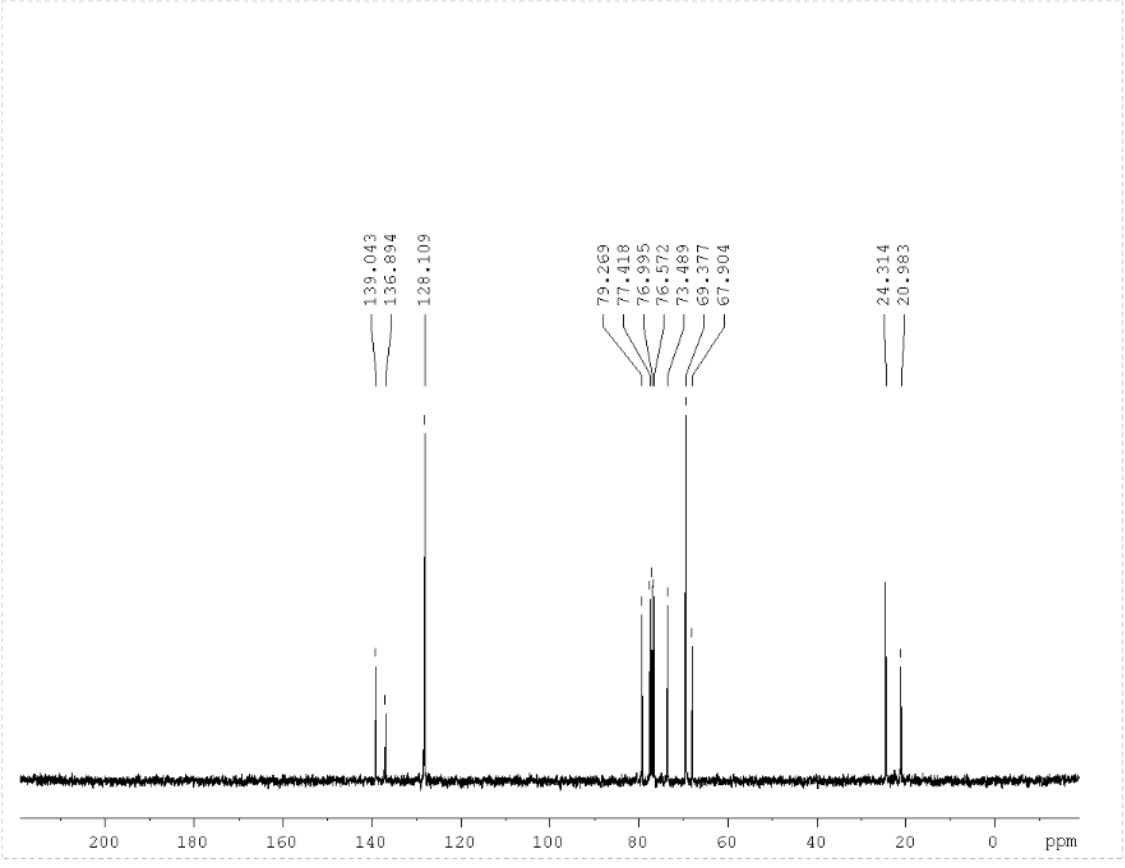
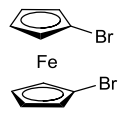
4.46
1.92
1.91
5.27
12.00
6.15


139.043
136.894
128.109
79.269
77.418
76.995
76.572
73.489
69.377
67.904
24.314
20.983
200 180 160 140 120 100 80 60 40 20 0 ppm

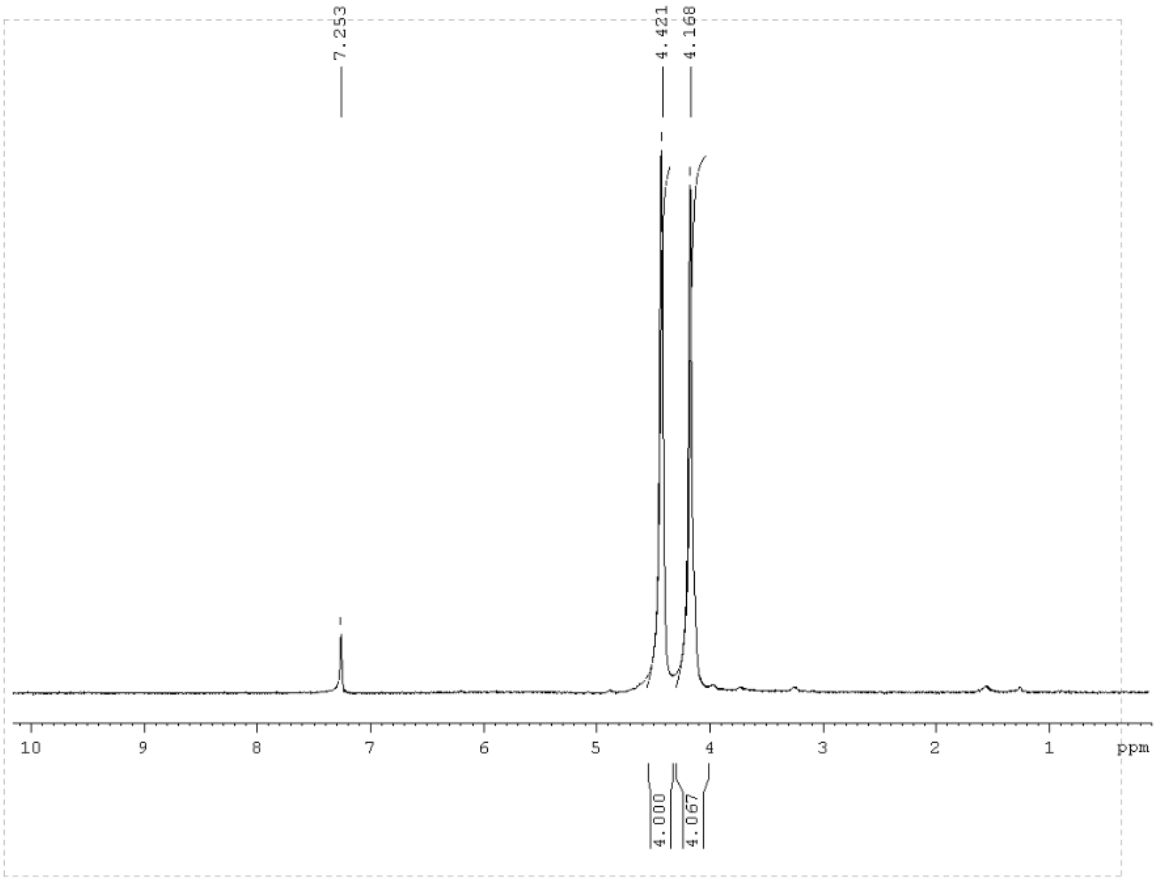
4. 1,1′-Dibromoferrocene:[7] **$FcBr_2$**

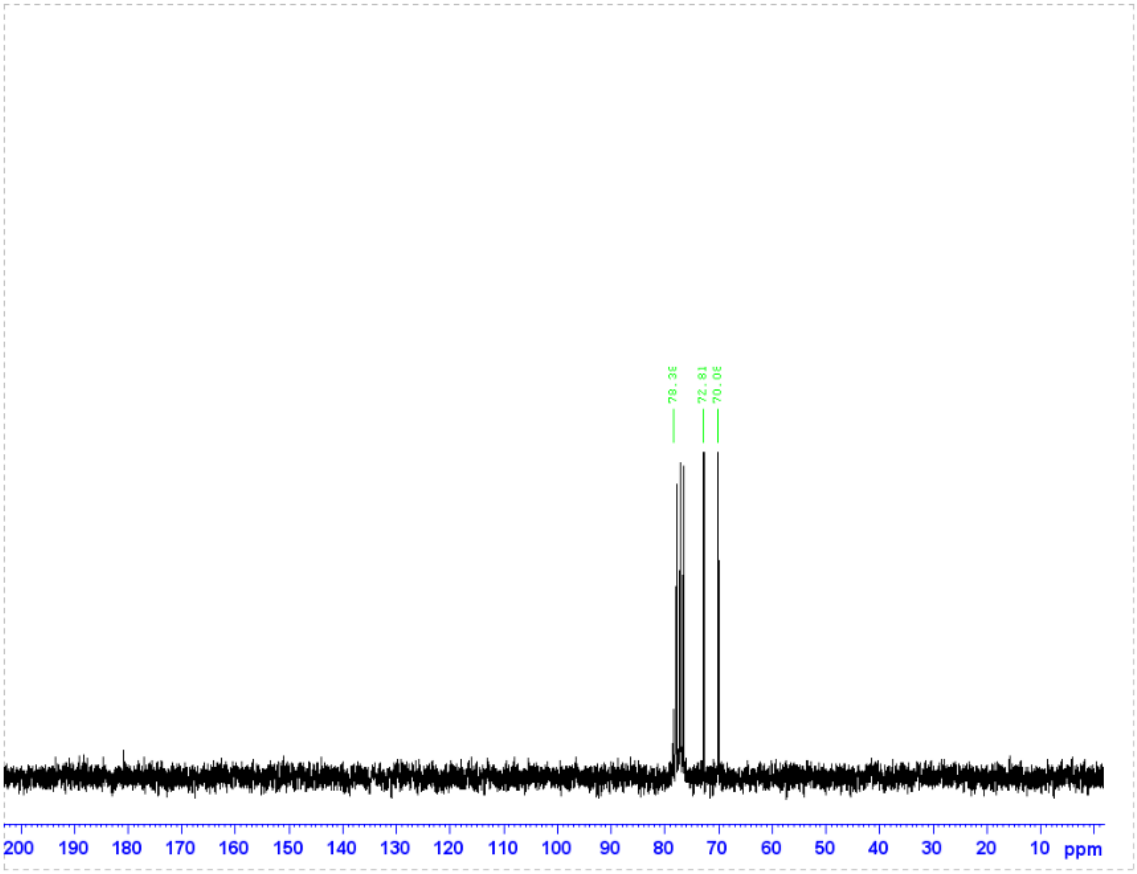


In a Schlenk tube under argon were added dropwise TMEDA (1.95 mL, 12.9 mmol) and *n*BuLi (7.39 mL, 11.84 mmol, 1.6 M in hexane) to a stirred solution of ferrocene (1.0 g, 5.38 mmol) in hexane (10 mL) at room temperature. The solution was stirred at room temperature overnight. The orange slurry was allowed to settle and the hexane layer was removed with a syringe. The remaining orange powder was washed with dry hexane (2 x 5 mL) and dissolved in dry THF (10 mL). Afterwards, the solution was cooled down to -78 °C. Then, a solution of $C_2Cl_4Br_2$ (4.38 g) in THF (8 ml) was added to the orange solution. The solution was slowly warmed to room temperature until the reaction was complete as indicated by TLC. The reaction was quenched after 2 hours with water. The reaction mixture was diluted with CH_2Cl_2. The layers were separated and the aqueous was extracted 5 times. The combined organic fractions were dried over Na_2SO_4 and evaporated to give the crude product, which was purified by flash column chromatography using petroleum ether as eluent, yielding the product as a yellow solid (87 % yield). The analytical data correspond to those in the cited references.

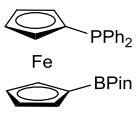
^{1}H NMR ($CDCl_3$): δ = 4.17 (bs, 4H), 4.42 (bs, 4H).

^{13}C NMR ($CDCl_3$): δ = 70.1, 72.8, 78.4.



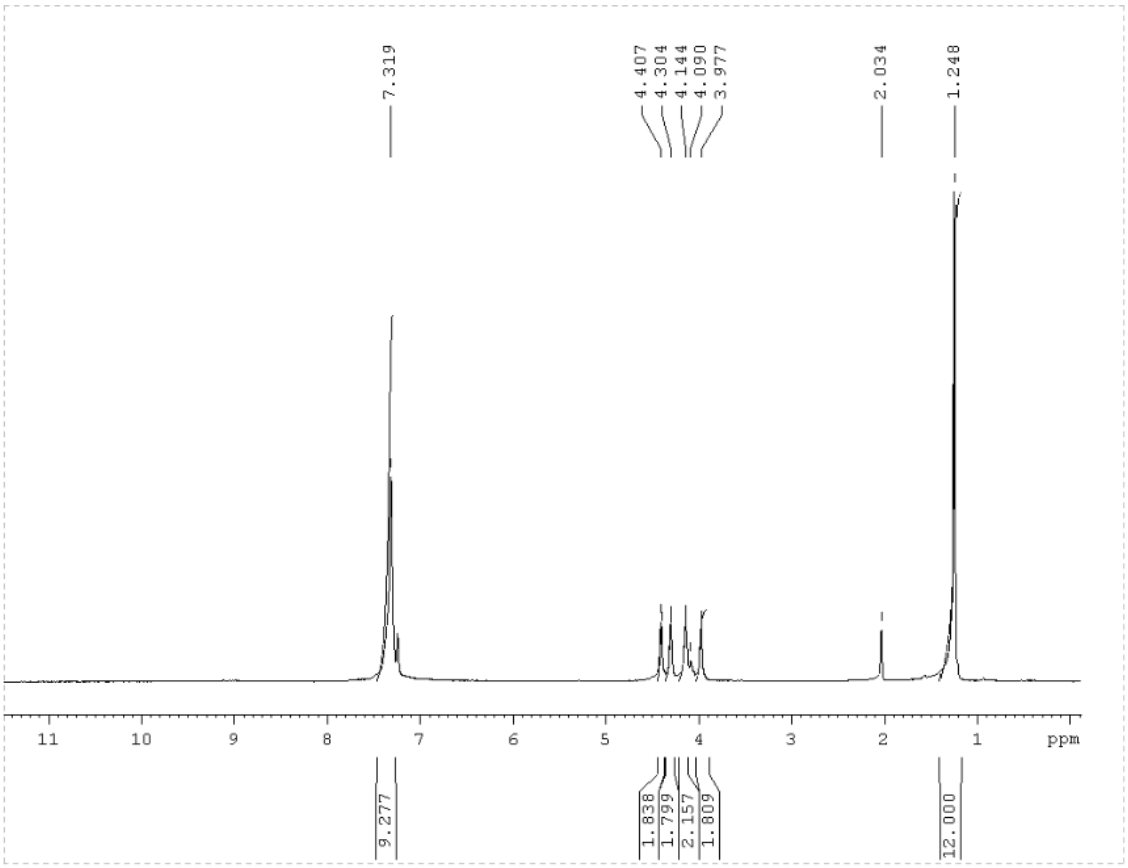


5. 1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1'-diphenylphosphino-ferrocene. 3-Bpin



After standard cycles of evacuation and back-filling with dry and pure argon, a Schlenk tube equipped with a magnetic stirring bar was charged with 1-bromo-1'diphenylphosphinoferrocene [8] (224 mg, 0.5 mmol) in dry THF (4 ml). Afterwards, the solution was cooled down to -78°C and *n*BuLi (312 µL, 0.5 mmol, 1.6 M in hexane) was added dropwise. After 15 min at -78 °C, a solution of *bis*(pinacolato)diboron (127 mg, 0.5 mmol) in 1 ml of dry THF was added. The solution was slowly warmed to room temperature. The reaction was quenched after 2 hours with water. The reaction mixture was diluted with CH_2Cl_2, the layers were separated and the aqueous layer was extracted 5 times. The combined organic fractions were dried over Na_2SO_4 and evaporated to give the crude product, which was purified by flash column chromatography using degassed solvent petroleum ether/ethyl acetate (1:1) as eluent. The product was isolated as an orange powder in 18 % yield. **It is worth noting that the product is very sensitive toward oxidation.**

^{1}H NMR ($CDCl_3$) δ (ppm): 1.25 (bs, 12H), 3.98 (s, 2H), 4.14 (s, 2H), 4.30 (s, 2H), 4.41 (s, 2H), 7.32 (m, 10H).
^{13}C NMR ($CDCl_3$) δ (ppm): 26.7, 69.2, 70.2, 75.2 (d, J_{CP} = 4 Hz), 76.1 (d, J_{CP} = 14 Hz), 84.4, 129.2 (d, J_{CP} = 6 Hz), 129.6, 134.5 (d, J_{CP} = 20 Hz), 139.4 (d, J_{CP} = 8 Hz).
^{31}P NMR ($CDCl_3$) = -17.4.
^{11}B NMR ($CDCl_3$) = 33.1.
HRMS: calc. for $[M+H]^+$ $C_{28}H_{31}BFeO_2P$: 497.1504, found: 497.1516.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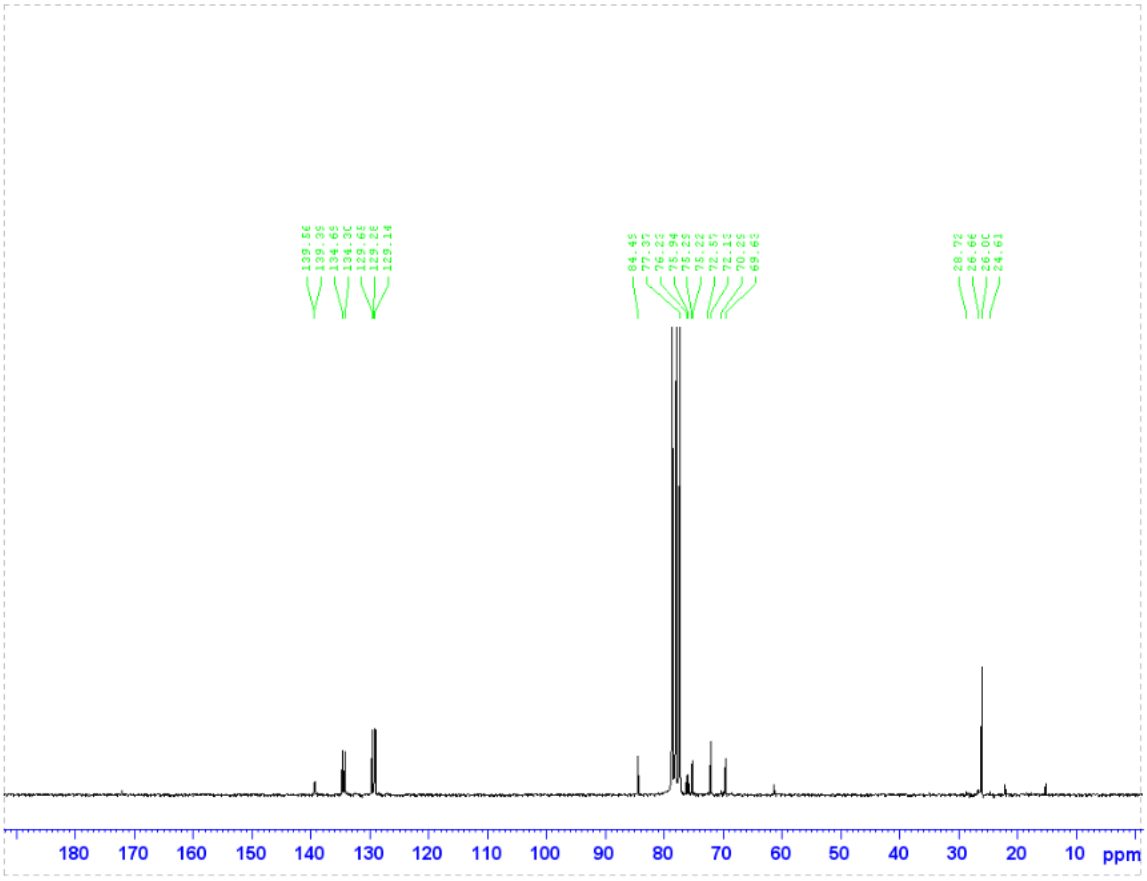
4.144
4.090
3.977
2.034
1.248
11
10
9
8
7
6
5
4
3
2
1
ppm
9.277
1.838
1.799
2.157
1.809
12.000


180
170
160
150
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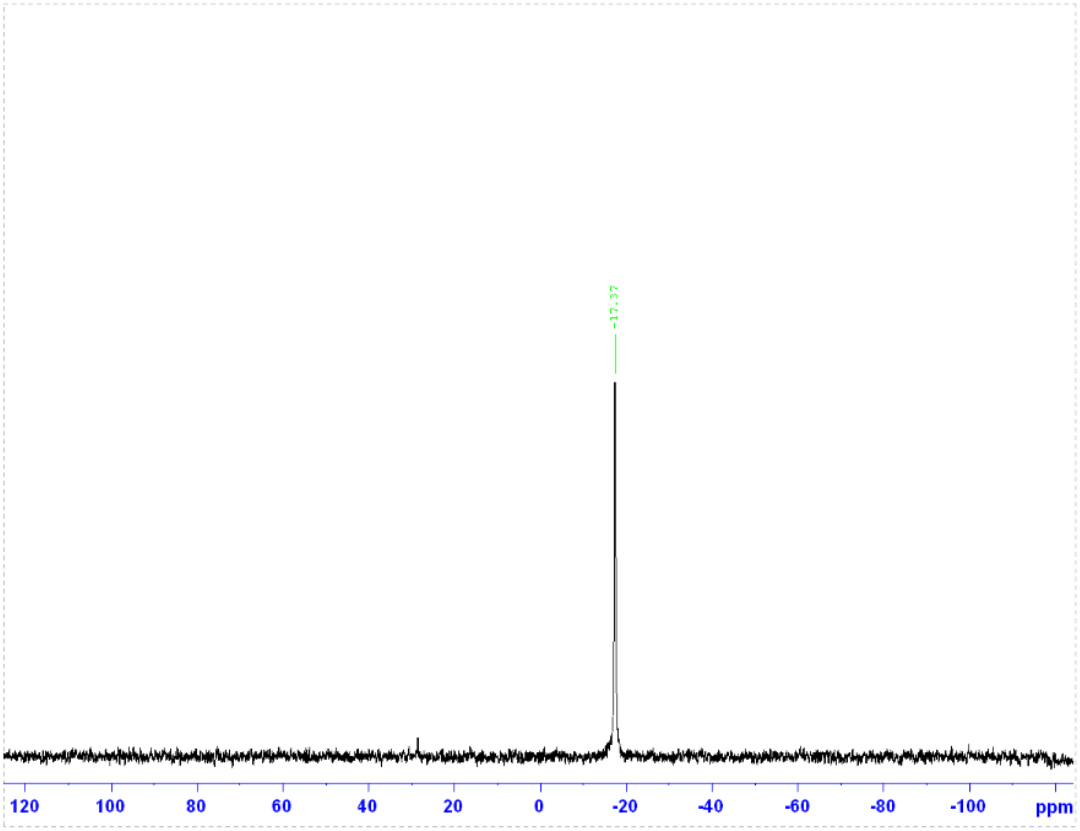
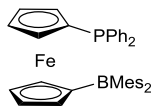
120
110
100
90
80
70
60
50
40
30
20
10
ppm



6. 1-Dimesitylboryl-1'-diphenylphosphino-ferrocene: 3-BMes$_2$.[9]



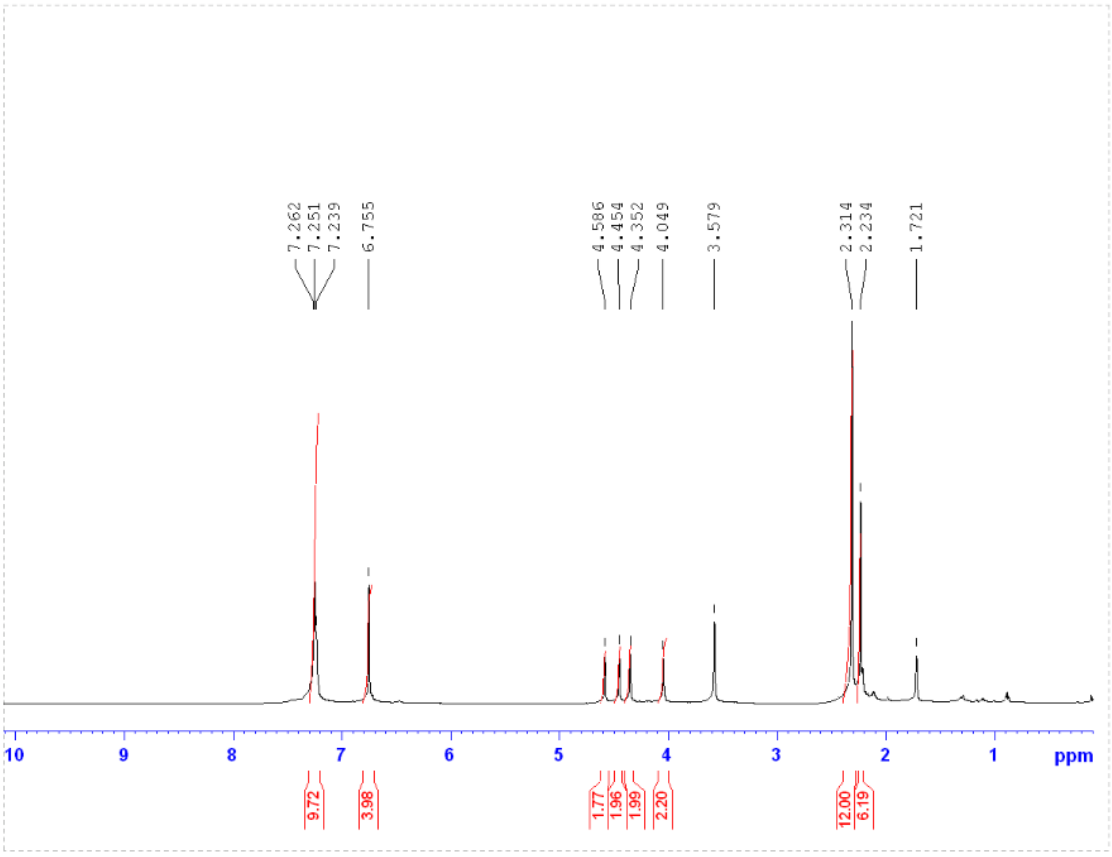
After standard cycles of evacuation and back-filling with dry and pure argon, a Schlenk tube equipped with a magnetic stirring bar was charged with 1-bromo-1'diphenylphosphinoferrocene (224 mg, 0.5 mmol) in dry THF (4 ml). Afterwards, the solution was cooled down to -78 °C and *n*BuLi (312 µL, 0.5 mmol, 1.6 M in hexane) was added dropwise. After 15 min at -78 °C, a solution of dimesitylboron fluoride (135 mg, 0.5 mmol) in 1 ml of dry THF was added. The solution was slowly warmed to room temperature. Then, the solvent was removed under reduced pressure; the residue was dissolved in toluene (2 ml) and filtered on Buchner in glove box. The product was recrystallized in pentane at -40 °C yielding the product as purple needles in 82 % yield.

^{1}H NMR (THF-d8) δ (ppm): 2.24 (s, 6H), 2.31 (s, 12H), 4.05 (s, 2H), 4.35 (s, 2H), 4.45 (s, 2H), 4.59 (s, 2H,), 6.75 (s, 4H), 7.30-7.20 (m, 10H).

^{13}C NMR (THF-d8) δ (ppm): 19.2, 22.2, 71.2 (d, J_{CP} = 3 Hz), 73.1 (d, J_{CP} = 14 Hz), 74.2, 76.7, 79.1, 126.9, 127.1 (d, J_{CP} = 16 Hz), 127.3, 132.4 (d, J_{CP} = 20 Hz), 135.7, 137.8, 138.1 (d, J_{CP} = 12 Hz), 141.7.

^{31}P NMR (THF-d8) = -19.3.

HRMS: calc. for $[M+H]^+$ $C_{40}H_{41}BFeP$: 619.2388, found: 619.2429.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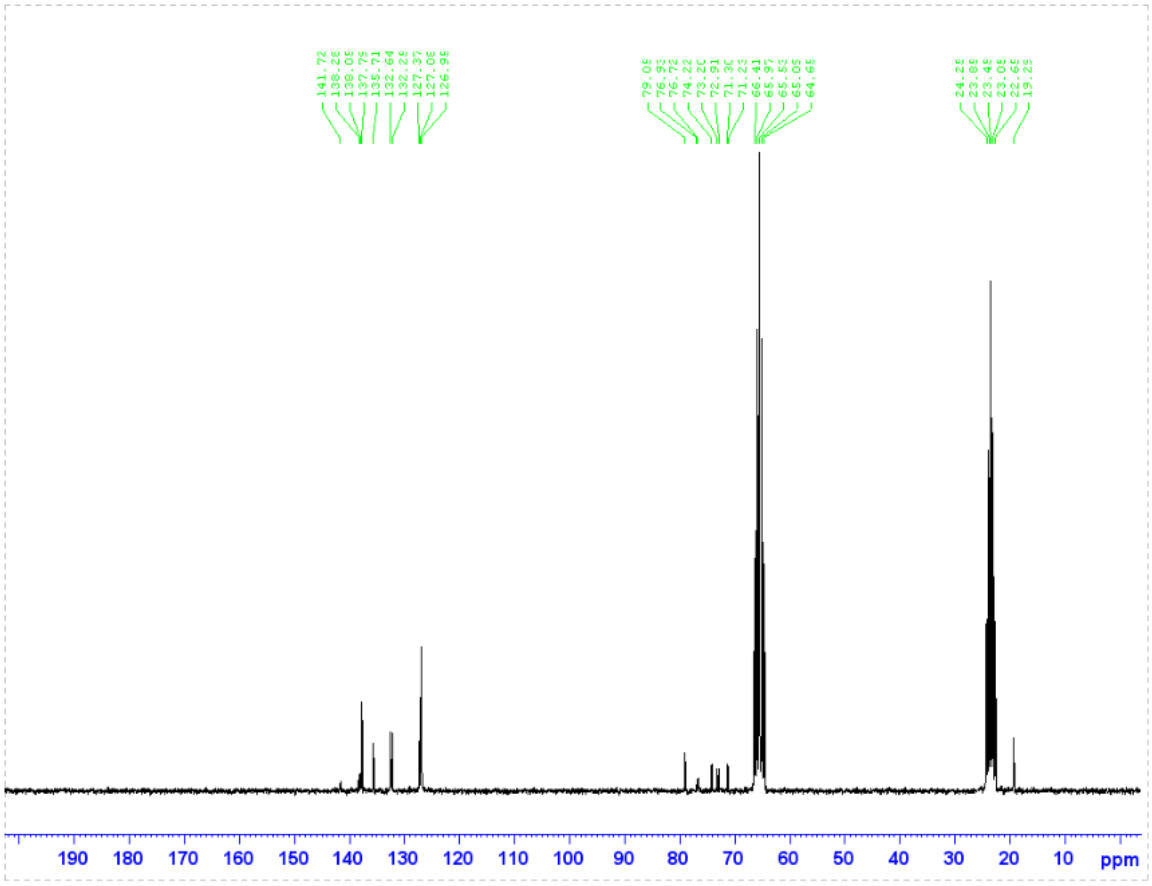
7.239
6.755
4.586
4.454
4.352
4.049
3.579
2.314
2.234
1.721
10
9
8
7
6
5
4
3
2
1
ppm
9.72
3.98
1.77
1.96
1.99
2.20
12.00
6.19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135.71
132.64
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79.05
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76.72
74.22
73.20
72.91
71.30
71.23
66.41
65.97
65.55
65.05
64.68
24.28
23.98
23.48
23.08
22.68
19.28
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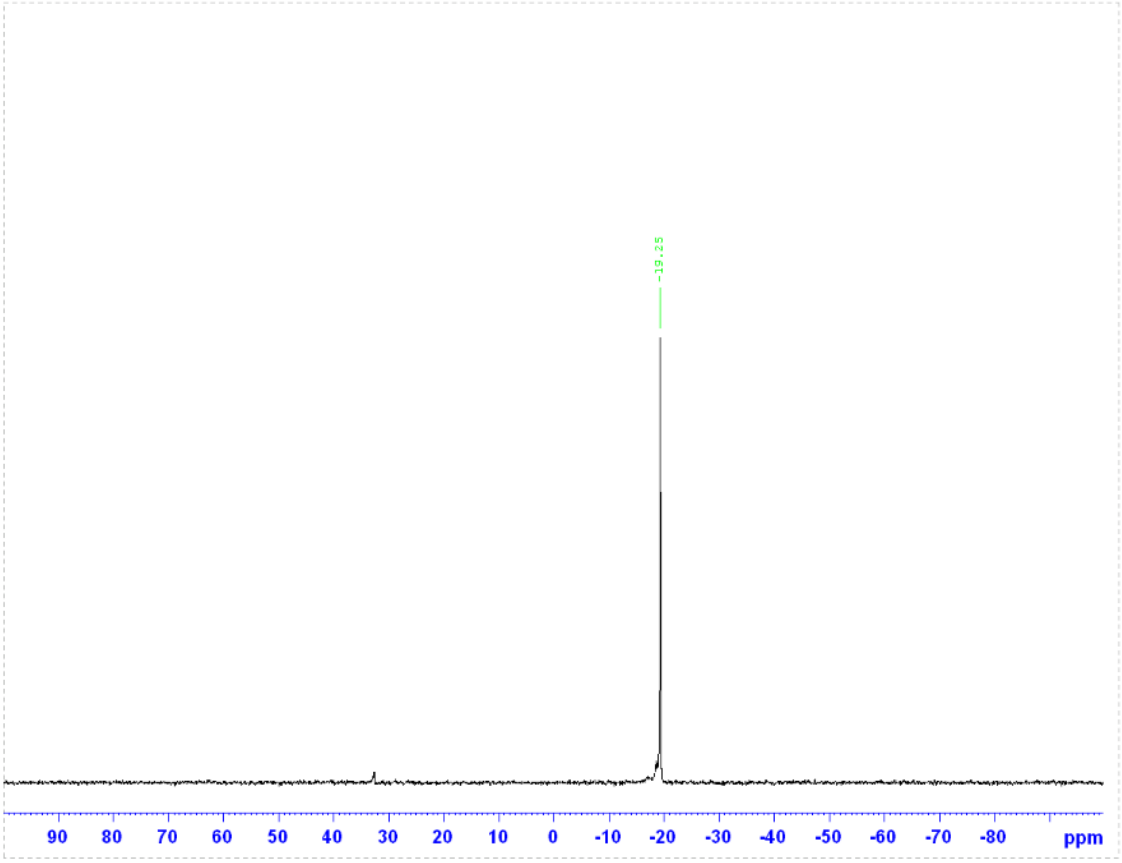
90
80
70
60
50
40
30
20
10
ppm



[1] A. K. Diallo, J. Ruiz, D. Astruc, *Org. Lett.* 2009, **11**, 2635.
[2] a) D. Anupama, K. Axel, P. Herbert, *Chem. Commun*, 2004, **13**, 1508; b) G. Wang, L. Xu, P. Li, *J. Am. Chem. Soc.* 2015, **137**, 8058.
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[4] Z. Otwinowski and W. Minor, *Methods Enzymol*., 1997, **276**, 307.
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[6] a) A. E. J. Broomsgrove, D. A. Addy, A. Di Paolo, I. R. Morgan, C. Bresner,V. Chislett, I. A. Fallis, A. L. Thompson, D. Vidovic, S. Aldridge, *Inorg. Chem.* 2010, **49**, 157. b) A. E. J. Broomsgrove, D. A. Addy, C. Bresner, I. A. Fallis, A. L. Thompson, S. Aldridge, *Chem. Eur. J.* 2008, **14**, 7525.
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