Electronic Supplementary Material (ESI) for Chemical Science. This journal is © The Royal Society of Chemistry 2019

Supporting Information

Template Catalysis by Manganese Pincer Complexes: Oxaand Aza-Michael Additions to Unsaturated Nitriles

Shan Tang, David Milstein*

Department of Organic Chemistry, the Weizmann Institute of Science, Rehovot 76100, Israel.

Corresponding author: david.milstein@weizmann.ac.il

General information	2
Detailed description of products	3
Figure S1	9
Synthesis and characterization of complex A	10
Copies of product NMR spectra	14
References	30

General information

All of the reactions were performed in an atmosphere of purified nitrogen in a Braun glovebox or using standard Schlenk techniques, unless otherwise noted. All of the solvents were reagent grade or better. All non-deuterated solvents were purified according to standard procedures under argon atmosphere. All of the commercially available reagents were used as received. Complexes [Mn]-1¹, [Mn]-2² and [Mn]-3³, compound 1f⁴ were synthesized according to reported procedures. GC analysis was performed on HP 6890 with Hp-5 column, flame ionization detector, and helium as carrier gas. NMR spectra were recorded using Bruker Advance III 300 MHz, Advance III 400 MHz, or Advance 500 MHz spectrometers at 298 K. Chemical shifts were referenced to the residual solvent peaks (¹H, ¹³C) or an external standard of phosphoric acid (85% solution in D_2O) at 0.0 ppm (³¹P). Chemical shifts are reported in parts per million, and coupling constants (J) are reported in hertz. NMR assignments of complex A were assisted by ¹³C-DEPTQ, ¹H-13C HSQC, and ¹H-¹³C HMBC data. In the ¹³C-DEPTO NMR spectrum, primary and tertiary carbon signals are phased down (d) and secondary and quaternary carbon signals are phased up (u). IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrophotometer as thin films on KBr disks. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass ZQ V4.1 spectrometer by the Chemical Research Support Unit of the Weizmann Institute of Science.

Detailed description of products

OⁱPr

3-Isopropoxybutanenitrile (**3a**):⁴ In a glove box, complex [**Mn**]-**2** (0.9 mg, 0.0020 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) or allyl cyanide (161 μ L, 2.0 mmol) and isopropanol (2.0 mL, 26.2 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, the mixture was analyzed by ¹H NMR using mesitylene as an internal standard (96% with crotononitrile, 92% with allyl cyanide). ¹H NMR (400 MHz, CDCl₃) δ 3.87 – 3.74 (m, 1H), 3.74 – 3.60 (m, 1H), 2.53 – 2.36 (m, 2H), 1.26 (d, *J* = 6.2 Hz, 3H), 1.19 – 1.12 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 117.68, 70.13, 68.46, 25.54, 22.61, 22.32, 20.69.

O[/]Pr

3-Isopropoxypentanenitrile (3b):⁴ In a glove box, complex **[Mn]-2** (0.9 mg, 0.0020 mmol) was added to a mixture of 2-pentenenitrile (282 μ L of 70% solution, 2.0 mmol) and 3-pentenenitrile (194 μ L, 2.0 mmol) and isopropanol (2.0 mL, 26.2 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, the mixture was analyzed by ¹H NMR using mesitylene as an internal standard (83% with 2-pentenenitrile, 66% with 3-pentenenitrile). ¹H NMR (400 MHz, CDCl₃) δ 3.70 (hept, *J* = 6.1 Hz, 1H, OCH(CH₃)₂), 3.55 (p, *J* = 6.0 Hz, 1H), 2.46 (dd, *J* = 5.8, 1.7 Hz, 2H), 1.65 – 1.55 (m, 2H), 1.19 (d, *J* = 6.1 Hz, 3H), 1.15 (d, *J* = 6.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 117.88, 73.80, 70.80, 27.78, 23.36, 22.73, 22.32, 9.47.

ⁱPrO CN

3-Isopropoxypropanenitrile (3c):⁴ In a glove box, complex **[Mn]-2** (0.9 mg, 0.0020 mmol) was added to a mixture of 3-pentenenitrile (131 μ L, 2.0 mmol) and isopropanol (2.0 mL, 26.2 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, the mixture was analyzed by ¹H NMR using mesitylene as an internal standard (quantitative). ¹H NMR (400 MHz, CDCl₃) δ 3.79 – 3.48 (m, 3H), 2.56 (t, *J* = 6.4 Hz, 2H), 1.17 (d, *J* = 6.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 117.98, 72.28, 62.67, 21.84, 19.21.

6-Cyano-5-isopropoxyhexyl acetate (3d): In a glove box, complex **[Mn]-2** (2.2 mg, 0.0050 mmol) was added to a mixture of 3-pentenenitrile (167 mg, 1.0 mmol) and isopropanol (2.0 mL, 26.2 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, the mixture was analyzed by ¹H NMR using mesitylene as an internal standard (71%). ¹H NMR (300 MHz, CDCl₃) δ 4.06 (t, J = 6.4 Hz, 2H), 3.76 – 3.51 (m, 2H), 2.53 – 2.44 (m, 2H), 2.04 (s, 3H), 1.71 – 1.45 (m, 7H), 1.19 (d, J = 6.2 Hz, 3H), 1.14 (d, J = 6.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 171.06, 117.65, 72.35, 70.83, 64.10, 34.59, 28.39, 23.65, 22.84, 22.18, 21.68. The isolated product contains some starting material. HRMS (ESI) calculated for C₁₂H₂₁NO₃ [M+K]⁺: 266.1159; found: 266.1170.



3-Ethoxybutanenitrile (3e):⁵ In a glove box, complex **[Mn]-2** (0.9 mg, 0.0020 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) and ethanol (2.0 mL, 34 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, the mixture was analyzed by ¹H NMR using mesitylene as an internal standard (quantitative). ¹H NMR (500 MHz, CDCl₃) δ 3.80 – 3.62 (m, 1H), 3.62 – 3.41 (m, 2H), 2.48 (d, *J* = 5.7 Hz, 2H), 1.27 (d, *J* = 6.2 Hz, 3H), 1.23 – 1.13 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 117.60, 70.79, 64.43, 24.92, 19.78, 15.29.



3-Methoxybutanenitrile (3p):⁵ In a glove box, complex [**Mn**]-**2** (0.9 mg, 0.0020 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) and methanol (2.0 mL, 49 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, the mixture was analyzed by ¹H NMR using mesitylene as an internal standard (84%). ¹H NMR (300 MHz, CDCl₃) δ 3.72 – 3.52 (m, 1H), 3.36 (s, 3H), 2.50 (d, *J* = 5.6 Hz, 2H), 1.29 (d, *J* = 5.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 117.53, 72.63, 56.73, 24.73, 19.23.



3-Butoxybutanenitrile (3f):⁵ In a glove box, complex [**Mn**]-**2** (0.9 mg, 0.0020 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) and *n*-butanol (2.0 mL, 22 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, the mixture was analyzed by ¹H NMR using mesitylene as an internal standard (quantitative). ¹H NMR (500 MHz, CDCl₃) δ 3.82 – 3.59 (m, 1H), 3.59 – 3.31 (m, 2H), 2.59 – 2.40 (m, 2H), 1.65 – 1.46 (m, 2H), 1.46 – 1.21 (m, 5H), 1.05 – 0.77 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 117.62, 71.10, 69.00, 31.90, 24.95, 19.80, 19.26, 13.84.



3-Butoxypentanenitrile (3g): In a glove box, complex [**Mn**]-**2** (0.9 mg, 0.0020 mmol) was added to a mixture of 2-pentenenitrile (282 μ L of 70% solution, 2.0 mmol) and *n*-butanol (2.0 mL, 22 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, all volatile compounds were removed under vaccum to yield the final product as a pale-yellow oil (284.8 mg, 92%). Gram scale reaction: In a glove box, complex [**Mn**]-**2** (4.3 mg, 0.010 mmol) was added to a mixture of 2-pentenenitrile (1.4 mL of 70% solution, 10 mmol) and *n*-butanol (5.0 mL, 55 mmol). The reaction mixture was stirred at room temperature for 48 h. After quenching by exposure to air, all volatile components were removed under vaccum to yield the final product as a pale-yellow oil (1.34 g, 86%). ¹H NMR (300 MHz, CDCl₃) δ 3.63 – 3.37 (m, 3H), 2.50 (d, *J* = 5.7 Hz, 2H), 1.71 – 1.49 (m, 4H), 1.48 – 1.30 (m, 2H), 1.05 – 0.82 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 117.74, 76.33, 69.69, 31.92, 27.06, 22.45, 19.23, 13.78, 9.27. HRMS (ESI) calculated for C₉H₁₇NO [M+H]⁺: 156.1388; found: 156.1382.



3-(2-Methoxyethoxy)butanenitrile (3h): In a glove box, complex [Mn]-2 (0.9 mg, 0.0020 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) and *n*-

butanol (2.0 mL, 25 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, the mixture was analyzed by ¹H NMR using mesitylene as an internal standard (85%). ¹H NMR (500 MHz, CDCl₃) δ 3.81 – 3.69 (m, 1H), 3.63 (ddd, J = 9.9, 5.6, 4.0 Hz, 1H), 3.58 – 3.52 (m, 1H), 3.52 – 3.44 (m, 2H), 3.33 (s, 2H), 2.55 – 2.43 (m, 2H), 1.27 (d, J = 6.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 117.53, 71.99, 71.73, 68.48, 59.03, 24.88, 19.65. HRMS (ESI) calculated for C₇H₁₃NO₂ [M+H]⁺: 144.1025; found: 144.1030.



3-((2-Methylallyl)oxy)butanenitrile (3i): In a glove box, complex **[Mn]-2** (4.3 mg, 0.010 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) and *n*-butanol (2.0 mL, 22 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, the mixture was analyzed by ¹H NMR using mesitylene as an internal standard (97%). ¹H NMR (400 MHz, CDCl₃) δ 5.15 – 4.82 (m, 2H), 4.11 – 3.58 (m, 3H), 2.68 – 2.38 (m, 2H), 1.90 – 1.61 (m, 3H), 1.46 – 1.17 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 141.77, 117.52, 112.79, 73.01, 70.30, 25.01, 19.65, 19.46. HRMS (ESI) calculated for C₈H₁₃NO [M+H]⁺: 140.1075; found: 140.1079.



3-(Butylamino)butanenitrile (3j): In a glove box, complex **[Mn]-2** (0.9 mg, 0.0020 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) and *n*-butylamine (2.0 mL, 20 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, all volatile components were removed under vacuum to yield the final product as a colorless oil (214.0 mg, 76%). **Gram Scale reaction:** In a glove box, complex **[Mn]-2** (4.3 mg, 0.010 mmol) was added to a mixture of crotononitrile (0.82 mL, 10 mmol) and *n*-butylamine (5.0 mL, 50 mmol). The reaction mixture was stirred at room temperature for 48 h. After quenching by exposure to air, all volatile components were removed under vacuum to yield 0.87 g (62%) the final product. ¹H NMR (400 MHz, CDCl₃) δ 3.07 – 2.93 (m, 1H), 2.58 (t, *J* = 7.0 Hz, 2H), 2.42 (d, *J* = 5.5 Hz, 2H), 1.51 – 1.40 (m, 2H), 1.39 – 1.27 (m, 2H), 1.21 (d, *J* = 6.3 Hz, 3H), 0.98 (bs, 1H), 0.89 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃)

 δ 118.09, 50.10, 46.83, 32.35, 24.94, 20.66, 20.37, 13.92. HRMS (ESI) calculated for C₈H₁₆N₂ [M+H]⁺: 141.1392; found: 141.1388.

HNⁿHex CN

3-(Hexylamino)butanenitrile (3k): In a glove box, complex **[Mn]-2** (0.9 mg, 0.002 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) and *n*-butylamine (2.0 mL, 15 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, all volatile components were removed under vacuum to yield the final product as a colorless oil (210.0 mg, 63%). ¹H NMR (400 MHz, CDCl₃) δ 3.07 – 2.95 (m, 1H), 2.63 – 2.53 (m, 2H), 2.43 (d, *J* = 5.6 Hz, 2H), 1.51 – 1.40 (m, 2H), 1.36 – 1.25 (m, 6H), 1.22 (d, *J* = 6.4 Hz, 3H), 0.98 – 0.91 (m, 1H), 0.87 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 118.03, 50.05, 47.14, 31.64, 30.17, 26.88, 24.88, 22.52, 20.61, 13.96. HRMS (ESI) calculated for C₁₀H₂₀N₂ [M+H]⁺: 169.1705; found: 169.1704.



3-(Benzylamino)butanenitrile (31):⁴ In a glove box, complex **[Mn]-2** (0.9 mg, 0.0020 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) and benzylamine (1.0 mL, 9.2 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, the mixture was analyzed by ¹H NMR using mesitylene as an internal standard (91%). ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.23 (m, 4H), 7.21 – 7.15 (m, 1H), 3.73 (s, 2H), 3.04 – 2.93 (m, 1H), 2.44 – 2.30 (m, 2H), 1.40 (bs, 1H), 1.18 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 139.59, 128.46, 127.92, 127.14, 117.95, 51.05, 49.22, 24.96, 20.48.



3-(Pyrrolidin-1-yl)butanenitrile (3m):⁶ In a glove box, complex [**Mn**]-**2** (0.9 mg, 0.0020 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) and pyrrolidine (2.0 mL, 24 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, all volatile components were removed under vacuum to yield the final product as a pale-yellow oil (210.0 mg, ~ 100%). ¹H

NMR (400 MHz, CDCl₃) δ 2.69 – 2.59 (m, 1H), 2.58 – 2.49 (m, 5H), 2.39 (dd, *J* = 16.7, 7.6 Hz, 1H), 1.80 – 1.69 (m, 4H), 1.24 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 118.39, 55.43, 51.09, 23.90, 23.49, 18.89.



3-(Piperidin-1-yl)butanenitrile (3n):⁷ In a glove box, complex **[Mn]-2** (0.9 mg, 0.0020 mmol) was added to a mixture of crotononitrile (163 μ L, 2.0 mmol) or allyl cyamide (161 μ L, 2.0 mmol) and piperidine (2.0 mL, 20 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, all volatile components were removed under vacuum to yield the final product as a pale-yellow oil (310.0 mg, ~ 100%). ¹H NMR (300 MHz, CDCl₃) δ 3.05 – 2.88 (m, 1H), 2.57 – 2.21 (m, 6H), 1.62 – 1.47 (m, 4H), 1.47 – 1.35 (m, 2H), 1.17 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 119.07, 56.73, 49.37, 26.15, 24.53, 20.51, 15.40.



3-(Piperidin-1-yl)pentanenitrile (30): In a glove box, complex **[Mn]-2** (0.9 mg, 0.0020 mmol) was added to a mixture of 2-pentenenitrile (282 µL of 70% solution, 2.0 mmol) and piperidine (2.0 mL, 20 mmol). The reaction mixture was stirred at room temperature for 24 h. After quenching by exposure to air, all volatile components were removed under vacuum to yield the final product as a pale-yellow oil (332.4 mg, ~ 100%). ¹H NMR (300 MHz, CDCl₃) δ 2.73 (p, *J* = 6.7 Hz, 1H), 2.61 – 2.24 (m, 6H), 1.62 – 1.47 (m, 6H), 1.47 – 1.35 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 119.53, 63.09, 49.34, 26.28, 24.68, 24.02, 16.94, 11.17. HRMS (ESI) calculated for C₁₀H₁₈N₂ [M+H]⁺: 167.1548; found: 167.1550.

Figure S1

³¹P{¹H} NMR spectra of the reactions between [Mn]-2 and substrates



Reaction conditions: [**Mn**]-2 (0.010 mmol), substrate (0.10 mmol), THF (0.50 mL), r.t., 5 h.

Synthesis and characterization of complex A



cis-[Mn(PNN-NH-C=CH-CH=CH-CH₃)(CO)₂] (Complex A): In a glove box, 3pentenenitrile (48 μ L, 0.50 mmol) was added to a solution of complex [Mn]-2 (21.6 mg, 0.050 mmol) in THF (1.0 mL). The reaction mixture was allowed to stir at room temperature for 5 h. Then 5.0 mL of pentane was added and the solution was kept at -38 °C in a freezer overnight to form orange crystals. The crystals were isolated by decantation and dried under vacuum. (14.4 mg, 56% yield). ³¹P{¹H} NMR (162 MHz, C_6D_6) δ 140.49. ¹H NMR (400 MHz, C_6D_6) δ 6.81 (t, ³J_{HH} = 7.7 Hz, 1H, pyridyl CH), 6.69 - 6.56 (m, 2H, pyridyl CH & NH-C=CH-CH=CH), 6.45 (d, ${}^{3}J_{HH} = 7.7$ Hz, 1H, pyridyl CH), 5.56 (dq, ${}^{3}J_{HH} = 13.5$, 6.6 Hz, 1H, NH-C=CH-CH=CH), 5.22 (d, ${}^{3}J_{HH} =$ 10.7 Hz, 1H, NH-C=CH-CH=CH), 3.99 (s, 1H, NH-C=CH-CH=CH), 3.64 (s, 1H, CHNEt₂), 3.33 (dq, ${}^{1}J_{HH} = 14.3$ Hz, ${}^{3}J_{HH} = 7.3$ Hz, 1H, N(CH₂CH₃)₂), 3.02 - 2.88 (m, 2H, CH₂P & N(CH₂CH₃)₂), 2.72 (dd, ${}^{1}J_{HH} = 16.2$ Hz, ${}^{2}J_{PH} = 10.8$ Hz, 1H, CH₂P), 2.32 $(dq, {}^{1}J_{HH} = 13.7 \text{ Hz}, {}^{3}J_{HH} = 6.9 \text{ Hz}, 1\text{H}, \text{N}(\text{CH}_{2}\text{CH}_{3})_{2}), 2.06 - 1.91 \text{ (m, 4H, NH-C=CH-})$ CH=CH-CH₃ & N(CH₂CH₃)₂), 1.27 - 1.20 (m, 9H, C(CH₃)₃), 1.15 (t, ³*J*_{HH} = 7.2 Hz, 3H, N(CH₂CH₃)₂), 0.83 - 0.69 (m, 9H, C(CH₃)₃), 0.44 (t, ${}^{3}J_{HH} = 7.1$ Hz, 3H, N(CH₂CH₃)₂). ¹³C{¹H} NMR (101 MHz, C₆D₆) δ 234.22 (d, ²J_{P-C} = 19.2 Hz, CO), 232.94 (d, ${}^{2}J_{P-C} = 17.4$ Hz, CO), 161.43 (d, ${}^{4}J_{P-C} = 2.5$ Hz, pyridyl C), 160.80 d, ${}^{2}J_{P-C} =$ 6.1 Hz, pyridyl C), 149.90 (s, NH-C=CH-CH=CH), 135.93 (s, pyridyl CH), 129.92 (s, NH-C=CH-CH=CH), 118.82 (d, ³*J*_{P-C} = 6.7 Hz, pyridyl CH), 118.45 (s, pyridyl CH), 111.30 (s, NH-C=CH-CH=CH), 91.02 (s, NH-C=CH-CH=CH), 78.12 (s, CHNEt₂), 46.79 (s, N(CH₂CH₃)₂), 45.98 (s, N(CH₂CH₃)₂), 37.31 (d, ${}^{1}J_{P-C} = 17.1$ Hz, C(CH₃)₃), 37.00 (s, C(CH₃)₃), 36.35 (d, ${}^{1}J_{P-C} = 13.3$ Hz, CH₂P), 30.71 (s, C(CH₃)₃), 29.80 (s, C(CH₃)₃), 19.32 (s, NH-C=CH-CH=CH-CH₃), 12.17 (s, N(CH₂CH₃)₂), 6.89 (s, $N(CH_2CH_3)_2$). Decomposition of complex A was observed during the measurement process. IR (KBr): $v_{CO} = 1904 \text{ cm}^{-1}$, 1825 cm⁻¹ (1:1 ratio). HRMS (ESI) calculated for C₂₆H₄₁N₃O₂PMn [M+H]⁺: 514.2395; found: 514.2389.



¹³C-DEPTQ NMR



¹H-¹³C HSQC



¹H-¹³C HMBC



³¹P{¹H} NMR

-140.491



Copies of NMR Spectra

¹H NMR



3a

¹H NMR



¹³C NMR









¹H NMR 3.706 3.694 3.531 3.516 3.516 3.516 3.485 2.488 2.477 1.274 1.262 1.179 o´^{Et} CN Ŵ 3.47 \ 3.15 \] 1.04 2.18-1).0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0 f1 (ppm) ¹³C NMR -117.597 --70.790 --64.434 ~24.918 ~19.784 ~15.291

3e

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

3p ¹H NMR 3.645 3.625 3.605 3.585 3.361 2.510
2.491
1.297
1.278 0 CN 0.90 2.91 2.00 ₫ 3.37 -0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0 f1 (ppm) ¹³C NMR -117.527 -72.626 -56.733 --24.730 --19.233 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 f1 (ppm)



3f



¹H NMR

3.7703.7703.77583.77583.772583.77223.77223.6503.65103.65133.65133.65133.6433.65133.6433.57553.575563.575663.5776663.5776663.5776663.5776663.577666663.57766663.577



¹³C NMR







¹H NMR





¹H NMR

$\begin{array}{c} 3.040\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.026\\ 3.025\\ 3.055\\ 3.056\\ 3.056\\ 0.0874\\ 0.0874\\ 0.0876\\ 0.0$



-118.027

¹³C NMR





¹H NMR



¹³C NMR

-139.594	128.460 127.924 127.143	 ∽51.054 ~49.225	-24.961 20.476





-118.387

¹³C NMR

¹H NMR

-55.431 -51.094	23.899 23.488 18.889
--------------------	----------------------------

.250







¹H NMR



References

- 1. Nerush, A.; Vogt, M.; Gellrich, U.; Leitus, G.; Ben-David, Y.; Milstein, D., J. Am. Chem. Soc. 2016, 138, 6985-6997.
- Espinosa-Jalapa, N. A.; Kumar, A.; Leitus, G.; Diskin-Posner, Y.; Milstein, D., J. Am. Chem. Soc. 2017, 139, 11722-11725.
- Das, U. K.; Ben-David, Y.; Diskin-Posner, Y.; Milstein, D., Angew. Chem. Int. Ed. 2018, 130, 2201-2204.
- Perdriau, S.; Zijlstra, D. S.; Heeres, H. J.; de Vries, J. G.; Otten, E., Angew. Chem. Int. Ed. 2015, 54, 4236-4240.
- 5. Jenner, G., Tetrahedron 2002, 58, 4311-4317.
- Azizi, N.; Baghi, R.; Ghafuri, H.; Bolourtchian, M.; Hashemi, M., Synlett 2010, 2010, 379-382.
- 7. Fadini, L.; Togni, A., Helv. Chim. Acta 2007, 90, 411-424.