

Supporting Information

Iron-Mediated Coupling of Carbon Dioxide and Ethylene: Macrocyclic Metallalactones Enable Access to Various Carboxylates.

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I. General Considerations

All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere (nitrogen) dry box unless otherwise noted. All glassware was stored in a pre-heated oven prior to use. The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.¹ Sodium was purchased from Sigma-Aldrich as a solid in kerosene. Mercury was purchased from Sigma-Aldrich and purified by shaking with sugar and separating via a separatory funnel prior to use. Celite was dried at 150 °C under vacuum for 3 days prior to use. Ethylene was purchased from Matheson Tri-Gas Inc., passed through a column of 4 Å molecular sieves and Drierite, and stored in a thick walled Schlenk tube over 3 Å molecular sieves. Ethylene-d₄ was purchased from Cambridge Isotopes and stored in a thick walled Schlenk tube over 4 Å molecular sieves. CO₂ was purchased from Airgas and stored in a thick walled Schlenk tube over 3 Å molecular sieves. Hydrogen gas was purchased from Airgas National Welders and passed through a column of MnO₂ supported on vermiculite and 3 Å molecular sieves prior to use on a Schlenk manifold. Deuterium gas was purchased from Cambridge Isotope Labs (>99.8% purity), passed through a column of MnO₂ supported on vermiculite and 3 Å molecular sieves prior to use on a Schlenk manifold. All carboxylic acids were purchased from Sigma-Aldrich or Acros Organics and degassed through the freeze-pump-thaw procedure (3 cycles). (ⁱPrPDI)Fe(N₂)₂² and (ⁱPrPDI)Fe(CH₂SiMe₃)₃³ were prepared according to a literature procedure and stored at -35 °C in a N₂-filled glovebox.

¹H NMR spectra were recorded on either Bruker ADVANCE 300 or 500 spectrophotometers operating at 300.13 MHz, and 500.46 MHz, respectively. ¹³C NMR spectra were recorded on either Bruker ADVANCE 300 or 500 spectrometer operating at 75.48 MHz and 125.85 MHz, respectively. ²H NMR spectra were recorded on a Bruker ADVANCE 500 spectrometer operating at 76.78 MHz. All ¹H and ¹³C NMR chemical shifts are reported in ppm relative to SiMe₄ using the ¹H (chloroform-*d*: 7.26 ppm; benzene-*d*₆: 7.16 ppm) and ¹³C (chloroform-*d*:

77.16 ppm; benzene-*d*₆: 128.06 ppm) chemical shifts of the solvent as a standard. ¹H NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent, obsc = obscured), coupling constants (Hz), integration, assignment. ¹H NMR data for paramagnetic compounds are reported as follows: chemical shift, integration, peak width at half height (Hz). ¹³C NMR data for diamagnetic compounds are reported as follows: chemical shift, number of protons attached to carbon (e.g. CH₂), assignment.

Zero-field ⁵⁷Fe Mössbauer spectra were recorded on a SEE Co. Mössbauer spectrometer (MS4) at 80 K in constant acceleration mode. ⁵⁷Co/Rh was used as the radiation source. WMOSS software⁴ was used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The temperature of the sample was controlled by a Janis Research Co. CCS-850 He/N₂ cryostat within an accuracy of 0.3 K. Isomer shifts were determined relative to α-iron at 298 K.

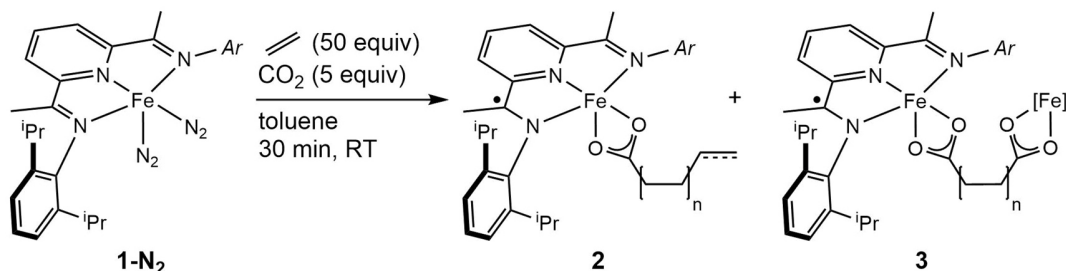
High-resolution mass spectra were measured using an Agilent 7200 GC-MS at the Princeton University Mass Spectrometry Facility. GC analyses were performed using an Agilent 7890A GC-System equipped with a Rtx®–35MS column.

Elemental analyses were performed at Robinson Microlit Laboratories, Inc., in Ledgewood, NJ. Solid-state magnetic moments were determined using a Johnson Matthey Magnetic Susceptibility Balance that was calibrated with HgCo(SCN)₄. High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS. Infrared spectroscopy was conducted on a Thermo-Nicolet iS10 FT-IR spectrometer calibrated with a polystyrene standard.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker SMART APEX DUO diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å) and a Cu X-ray tube (λ = 1.54178 Å). Preliminary data revealed the crystal system. The data

collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

II. Preparation of (*i*PrPDI)Fe(carboxylates) from CO₂ and ethylene.



CO₂/ethylene coupling with low CO₂/ethylene ratio. In a N₂-filled glovebox a 50 mL reaction vessel with a Teflon valve was charged with a solution of (*i*PrPDI)Fe(N₂)₂ (100 mg, 0.168 mmol, 1.0 equiv) in toluene (5 mL). The vessel was sealed and attached to a Schlenk line where the solution was frozen (−196 °C, liquid nitrogen), and the headspace evacuated. Ethylene (8.4 mmol, 155 mmHg in 1000 mL, 50 equiv) was measured with a calibrated gas bulb and then condensed into the reaction vessel immersed in liquid nitrogen. The same procedure was repeated with CO₂ gas (0.84 mmol, 15 mmHg in 1000 mL, 5 equiv), without thawing the reaction mixture in between the gas additions. The reaction vessel was sealed with the Teflon valve, and the reaction mixture was thawed under a cold stream of water and stirred for 30 minutes at RT. All volatiles were removed, and the resulting orange/brown residue was taken up in pentane and filtered through a short plug of Celite. All volatiles were removed to yield an orange/brown viscous oil (90 mg) which was identified as a mixture of (*i*PrPDI)Fe(carboxylates), α-olefins and *i*PrPDI.

It should be noted that all (PDI)Fe carboxylates described in this study, are not stable for prolonged periods of time in the solid state at room temperature. The decomposition product is NMR-silent but routinely identified by Mößbauer spectroscopy ($\delta = 1.34$ mm/s; $|\Delta E_Q| = 2.56$ mm/s).

NMR Spectroscopy:

Major species: **1-O₂CC₂H₅**

¹H NMR (300 MHz, C₆D₆, 25 °C): δ 367.06 (*p*-py, 1H), 178.19 (O₂CCH₂CH₃, 2H), 117.85 (*m*-py, 2H), 60.57 (O₂CCH₂CH₃, 3H), -2.60 (*m*-Ar, 4H), -16.19 (*p*-Ar, 2H), -19.10 (CH(CH₃)₂, 12H), -28.69 (CH(CH₃)₂, 12H), -112.79 (CH-(CH₃)₂, 4H), -281.80 (N=C-CH₃, 6H).

Significant peaks for homologous (ⁱPrPDI)Fe(carboxylates) (**2**) (ligand peaks are overlaying with **1-O₂CC₂H₅**):

¹H NMR (300 MHz, C₆D₆, 25 °C): δ 61.40 (O₂CCH₂CH₂CH₂CH₂CH₂...), 37.39 (O₂CCH₂CH₂CH₂CH₂CH₂...), 20.60 (O₂CCH₂CH₂CH₂CH₂CH₂...), 12.39 (O₂CCH₂CH₂CH₂CH₂CH₂...).

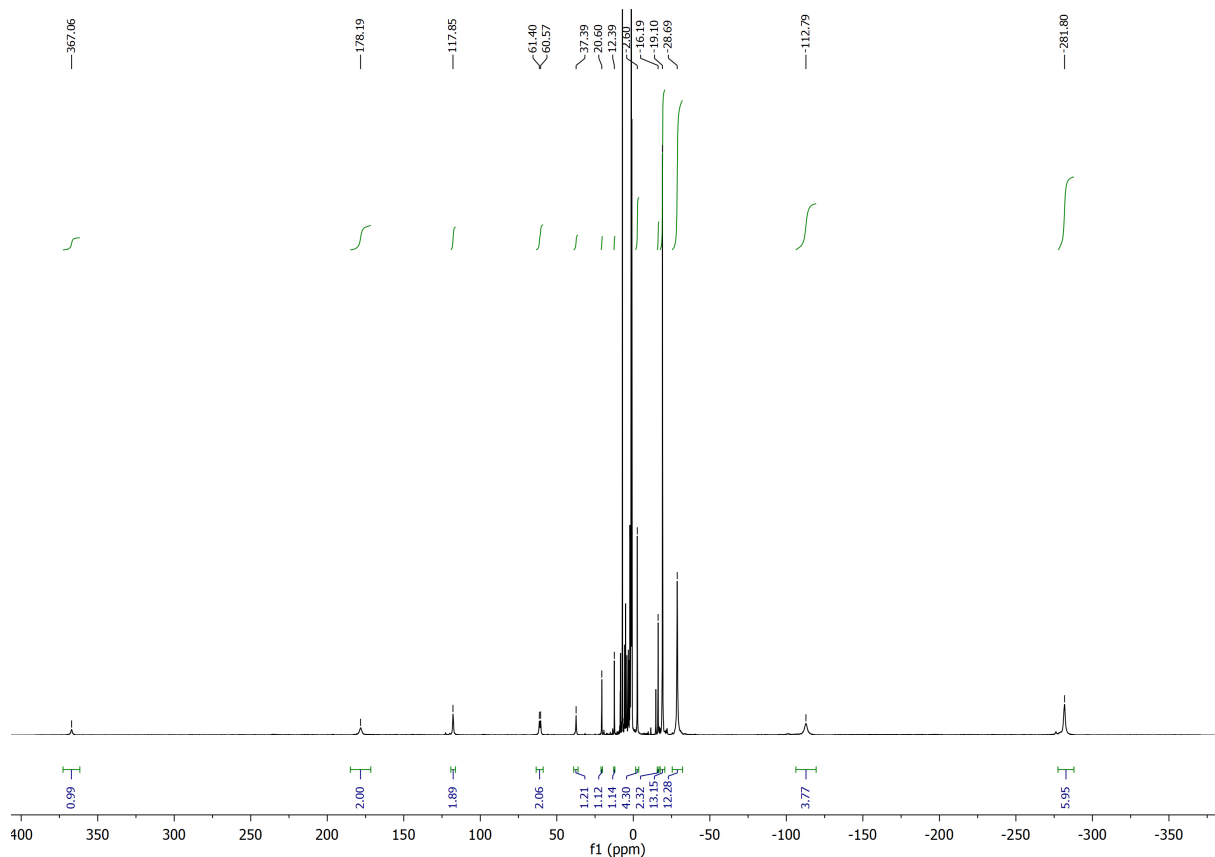


Figure S 1. ¹H NMR spectrum of the mixture of (ⁱPrPDI)Fe(carboxylates) obtained after coupling of CO₂ (5 equiv) and ethylene (50 equiv).

Mössbauer spectroscopy:

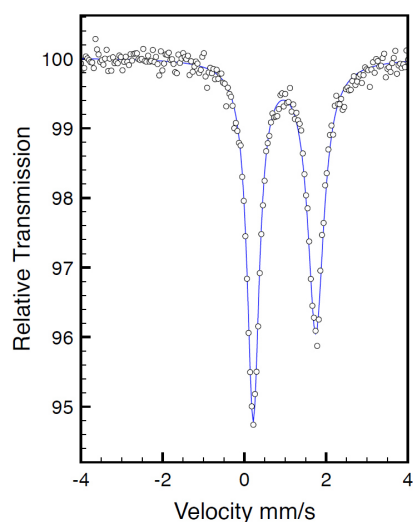


Figure S 2. Zero-field ^{57}Fe Mössbauer spectrum of the mixture of (i^{Pr} PDI)Fe(carboxylates) obtained after coupling of CO_2 (5 equiv) and ethylene (50 equiv) at 80 K in frozen toluene. Simulated parameters (blue lines) are $\delta = 0.98 \text{ mm/s}$, $|\Delta E_Q| = 1.53 \text{ mm/s}$.

GC-MS analysis of the carboxylates:

To the obtained mixture of (i^{Pr} PDI)Fe(carboxylates) (40 mg) was added a mixture of ethanol and conc. HCl aq. (1/1, 3 mL) and the resulting mixture was stirred for 48 h. Ethyl butyrate (4.0 μL , 0.030 mmol) was added as an internal standard. The solution was extracted with CH_2Cl_2 (4 x 2 mL) and the organic layer was subjected to GC-MS analysis. The detected esters and yields are summarized in Table S 1.

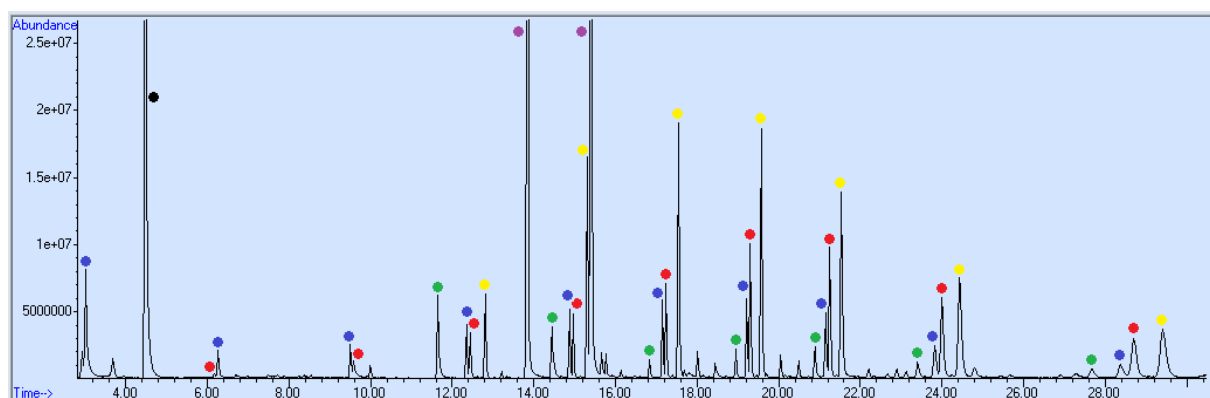


Figure S 3. GC-chromatogram of the mixture obtained after acid mediated ethanolysis of (i^{Pr} PDI)Fe(carboxylates). (blue dots: saturated carboxylates; red dots: unsaturated carboxylates; green dots: biscalboxylates; yellow dots: α -olefins; black dot: internal standard; violet dots: species associated with i^{Pr} PDI).

Table S 1. Esters detected by GC-MS.

Entry	Molecule	Mass calcd. ^a	Mass found	Yield (μmol) ^{b,c}	Yield (%) ^{c,d}
1	EtOOC-CH ₂ -CH ₃	102.07	102.07	22.18	13.20
2	EtOOC-CH ₂ -CH ₂ -CH ₃	130.0988	130.0992	1.82	1.08
3	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₃	158.1301	158.1298	1.13	0.67
4	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	186.1614	186.1610	1.34	0.80
5	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	214.1927	214.1924	1.40	0.83
6	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	242.2240	242.2238	1.32	0.79
7	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	270.2553	270.2557	1.40	0.83
8	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	298.2866	298.2874	1.38	0.82
9	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	326.3179	326.3185	1.13	0.67
10	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	354.3492	354.3489	0.78	0.46
11	EtOOC-CH ₂ -CH ₂ -CH=CH ₂	128.0832	128.0820	0.18	0.11
12	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	156.1145	156.1141	0.92	0.55
13	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	184.1458	184.1446	1.25	0.74
14	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	212.1771	212.1762	1.35	0.80
15	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	240.2084	240.2091	1.73	1.03
16	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	268.2397	268.2406	2.56	1.52
17	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	296.2709	296.2709	3.08	1.83
18	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	324.3023	324.3022	3.10	1.84
19	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	352.3336	352.3328	2.65	1.60
20	EtOOC-CH ₂ -CH ₂ -COOEt	174.0887	174.0880	4.15	2.47
21	EtOOC-CH ₂ -CH ₂ -CH ₂ -COOEt	157.0859 ^{e)}	157.0862	1.34	0.80
22	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -COOEt	185.1172 ^{e)}	185.1170	0.47	0.28
23	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -COOEt	213.1485 ^{e)}	213.1491	0.68	0.40
24	EtOOC-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -COOEt	241.1798 ^{e)}	241.1805	0.87	0.52

25		269.2111 ^{e)}	269.2116	0.59	0.35
26		297.2424 ^{e)}	297.2422	0.51	0.30

a) calcd. for $[M^+]$. b) determined through integration versus ethyl butyrate as internal standard; corrected amounts; extrapolated to the whole sample. c) determined through integration versus ethyl butyrate as internal standard; corrected yields vs. $(iPrPDI)Fe(N_2)_2$ assuming one molecule/ $[Fe]$; extrapolated to the whole sample. d) Correction factors were determined for entry 1, 3, 4, 5, 6, 7, 12, 14, 20, 21, and 23. All other correction factors were extrapolated from this data. e) calcd. for $[M-EtO^-]$.

Yield determination by Mößbauer spectroscopy:

In a N_2 -filled glovebox a 50 mL reaction vessel with a Teflon valve was charged with a solution of $(iPrPDI)Fe(N_2)_2$ (100 mg, 0.168 mmol, 1.0 equiv) in toluene (5 mL). The vessel was sealed and attached to a Schlenk line where the solution was frozen ($-196\text{ }^\circ\text{C}$, liquid nitrogen), and the headspace evacuated. Ethylene (8.4 mmol, 155 mmHg in 1000 mL, 50 equiv) was measured with a calibrated gas bulb and then condensed into the reaction vessel immersed in liquid nitrogen. The same procedure was repeated with CO_2 gas (0.84 mmol, 15 mmHg in 1000 mL, 5 equiv), without thawing the reaction mixture in between the gas additions. The reaction vessel was sealed with the Teflon valve, and the reaction mixture was thawed under a cold stream of water and stirred for 30 minutes at RT. The zero-field ^{57}Fe Mössbauer spectrum of the resulting solution indicated a 49% yield of $(iPrPDI)Fe(\text{carboxylates})$.

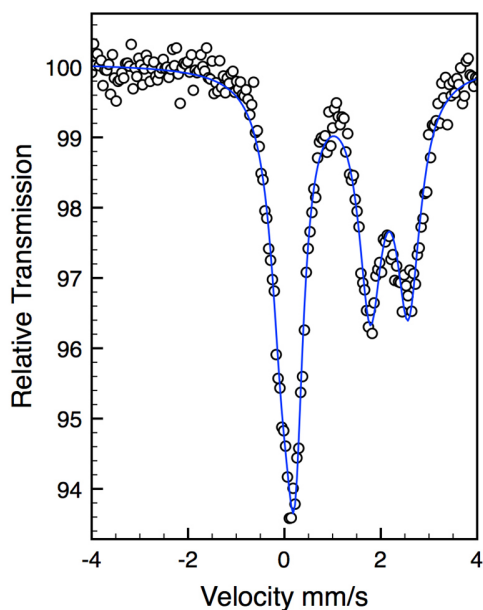
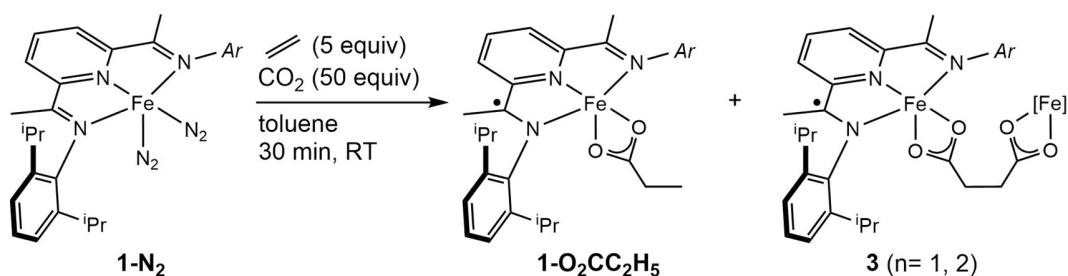


Figure S 4. Zero-field ^{57}Fe Mössbauer spectrum of the crude reaction mixture obtained after coupling of CO_2 (5 equiv) and ethylene (50 equiv) at 80 K in frozen toluene. Simulated parameters (blue lines) are $\delta = 1.00$ mm/s, $|\Delta E_Q| = 1.56$ mm/s (49%) and $\delta = 1.26$ mm/s, $|\Delta E_Q| = 2.62$ mm/s (51%).



CO_2 /ethylene coupling with high CO_2 /ethylene ratio In a N_2 -filled glovebox a 50 mL reaction vessel with a Teflon valve was charged with a solution of $(i\text{PrPDI})\text{Fe}(\text{N}_2)_2$ (100 mg, 0.168 mmol, 1.0 equiv) in toluene (5 mL). The vessel was sealed and attached to a Schlenk line where the solution was frozen (-196°C , liquid nitrogen), and the headspace evacuated. Ethylene (0.84 mmol, 15 mmHg in 1000 mL, 5 equiv) was measured with a calibrated gas bulb and then condensed into the reaction vessel immersed in liquid nitrogen. The same procedure was repeated with CO_2 gas (8.4 mmol, 155 mmHg in 1000 mL, 50 equiv), without thawing the reaction mixture in between the gas additions. The reaction vessel was sealed with the Teflon

valve, and the reaction mixture was thawed under a cold stream of water and stirred for 30 minutes at RT. All volatiles were removed, and the resulting orange/brown residue was taken up in pentane and filtered through a short plug of Celite. All volatiles were removed to yield an orange/brown solid (35 mg) which was identified as a mixture of (*i*PrPDI)Fe(carboxylates) and *i*PrPDI.

NMR Spectroscopy:

3 (n= 1):

¹H NMR (300 MHz, C₆D₆, 25 °C): δ 367.39 (*p*-py, 1H), 236.17 (O₂CCH₂CH₂CO₂, 2H), 122.82 (*m*-py, 2H), -11.45 (*p*-Ar, 2H), -14.78 (CH(CH₃)₂, 12H), -18.82 (CH(CH₃)₂, 12H), -101.59 (CH-(CH₃)₂, 4H), -276.27 (N=C-CH₃, 6H) (one peak not located).

1-O₂CC₂H₅: See above.

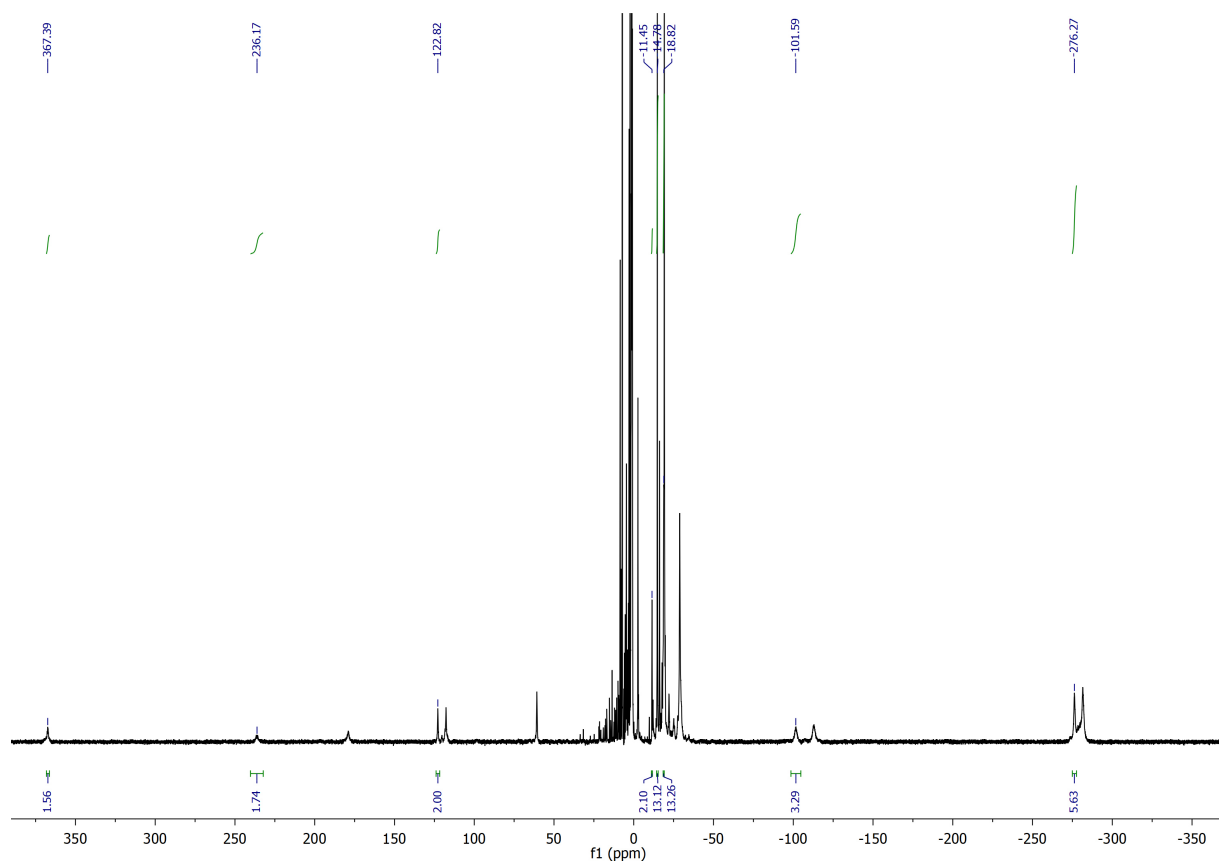


Figure S 5. ¹H NMR spectrum of the mixture of (*i*PrPDI)Fe(carboxylates) obtained after coupling of CO₂ (50 equiv) and ethylene (5 equiv).

Mössbauer spectroscopy:

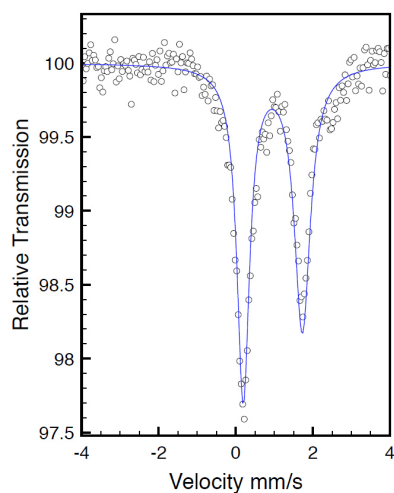


Figure S 6. Zero-field ^{57}Fe Mössbauer spectrum of the mixture of (i^{Pr} PDI)Fe(carboxylates) obtained after coupling of CO_2 (50 equiv) and ethylene (5 equiv) at 80 K in frozen toluene. Simulated parameters (blue lines) are $\delta = 0.96$ mm/s, $|\Delta E_Q| = 1.53$ mm/s.

GC-MS analysis of the carboxylates:

To the obtained mixture of (i^{Pr} PDI)Fe(carboxylates) (13 mg) was added a mixture of ethanol and conc. HCl aq. (1/1, 2 mL) and the resulting mixture was stirred for 48 h. Ethyl butyrate (2.0 μL , 0.030 mmol) was added as an internal standard. The solution was extracted with CH_2Cl_2 (4 x 2 mL) and the organic layer was ejected into a GC-MS instrument. The detected esters and yields are summarized in Table S 2.

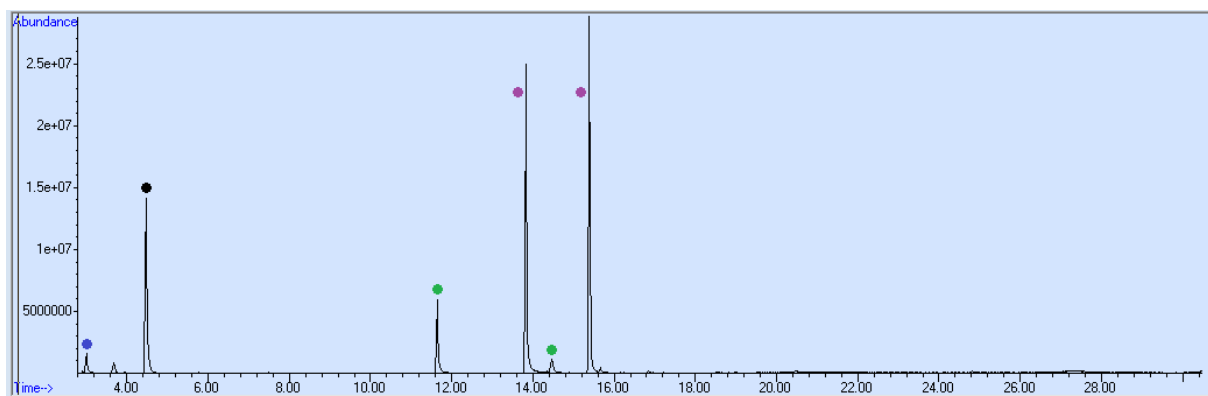


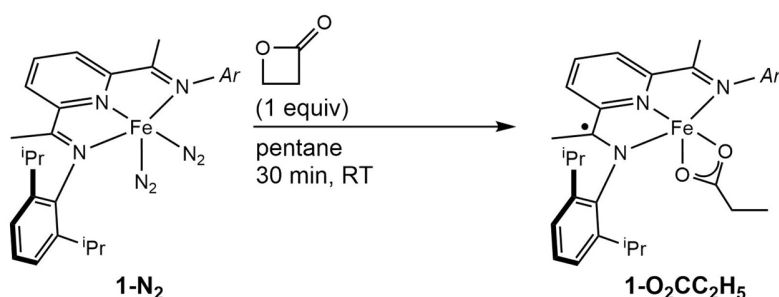
Figure S 7. GC-chromatogram of the mixture obtained after acid mediated ethanolsis of (i^{Pr} PDI)Fe(carboxylates). (blue dot: ethyl propionate; green dots: biscarboxylates; black dot: internal standard; violet dots: species associated with i^{Pr} PDI).

Table S 2. Esters detected by GC-MS.

Entry	Molecule	Yield (μmol) ^a	Yield (%) ^a
1		9.4	5.6
2		8.2	4.9
3		1.0	0.6

a) determined through integration versus ethyl butyrate as internal standard; corrected amounts; extrapolated to the whole sample. c) determined through integration versus ethyl butyrate as internal standard; corrected yields vs. (*i*PrPDI)Fe(N₂)₂ assuming one molecule/[Fe]; extrapolated to the whole sample.

III. Preparation of (*i*PrPDI)Fe(carboxylates) from β -propiolactone.



Preparation of 1-O₂CC₂H₅ from β -propiolactone. In a N₂-filled glovebox a scintillation vial was charged with a solution of (*i*PrPDI)Fe(N₂) (70 mg, 0.12 mmol, 1.0 equiv) in pentane (5 mL). β -Propiolactone (7.4 μL , 0.12 mmol, 1.0 equiv) was added and the resulting mixture was stirred for 30 min at RT and filtered. All volatiles were removed to yield 47 mg of **1-O₂CC₂H₅** (contaminated with 50% *i*PrPDI) as a dark brown solid.

¹H NMR (300 MHz, C₆D₆, 25 °C): δ 367.41 (*p*-py, 1H), 178.77 (O₂CCH₂CH₃, 2H), 117.65 (*m*-py, 2H), 60.65 (O₂CCH₂CH₃, 3H), -2.65 (*m*-Ar, 4H), -16.24 (*p*-Ar, 2H), -19.15 (CH(CH₃)₂, 12H), -28.85 (CH(CH₃)₂, 12H), -113.01 (CH-(CH₃)₂, 4H), -281.47 (N=C-CH₃, 6H).

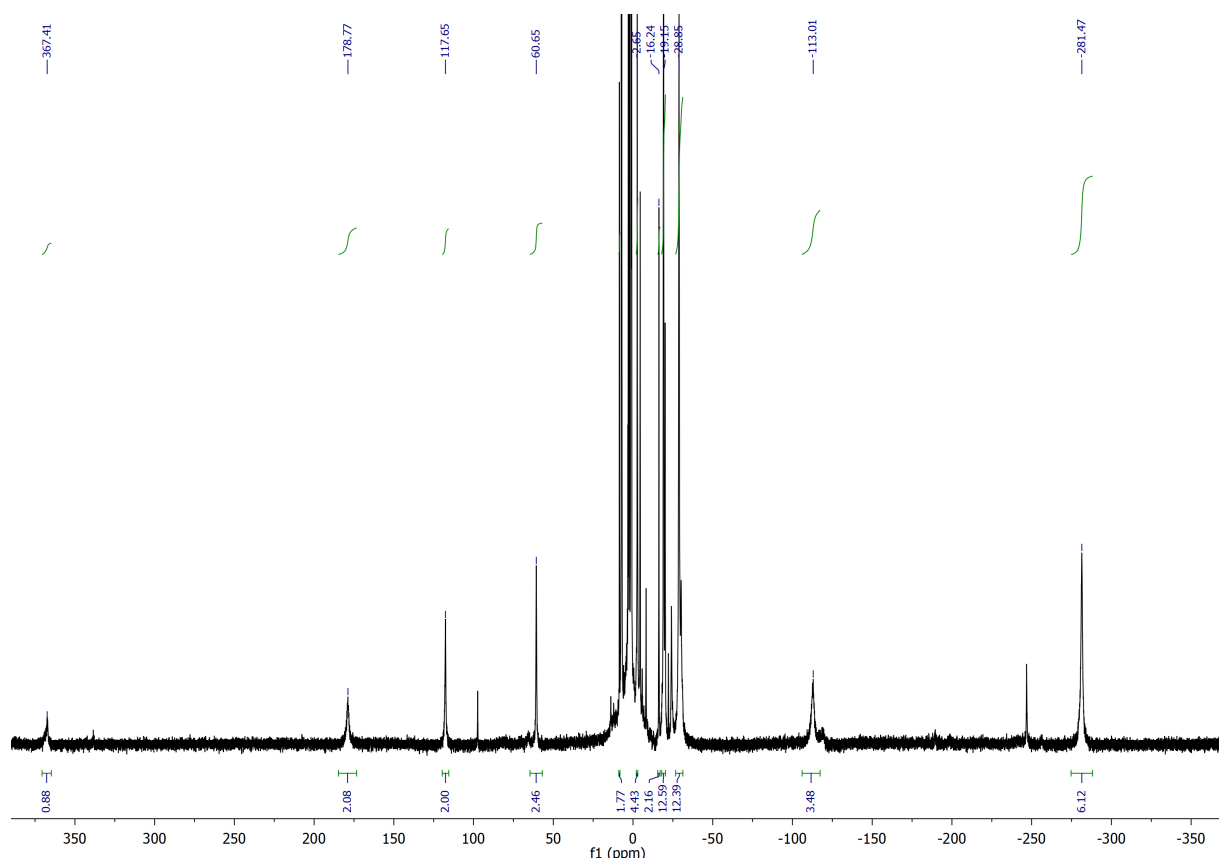
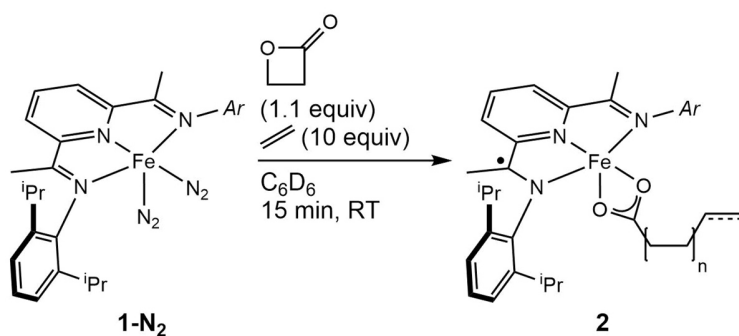


Figure S 8. ^1H NMR spectrum of **1-O₂CC₂H₅** obtained after reaction of **1-N₂** and β -propiolactone.



Observation of 2 from β -propiolactone and ethylene. In a N_2 -filled glovebox a J-Young NMR-tube was charged with a solution of $(^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$ (13 mg, 0.022 mmol, 1.0 equiv) in C_6D_6 (0.5 mL). β -Propiolactone (1.5 μL , 0.024 mmol, 1.1 equiv) was added, the tube was sealed, and the reaction mixture was frozen (-196°C , liquid nitrogen) immediately after mixing. The tube was attached to a Schlenk line and the headspace evacuated. Ethylene (0.22 mmol, 40 mmHg in 100 mL, 10 equiv) was measured with a calibrated gas bulb and then condensed into the tube

immersed in liquid nitrogen. The tube was sealed, allowed to warm to RT and slowly inverted for 15 min at RT and the reaction mixture was analyzed by ^1H NMR. The observed ^1H NMR signals are consistent with a mixture of **1-O₂CC₂H₅**, **2**, α -olefins and i^{Pr} PDI (10% determined by addition of mesitylene as internal standard).

Significant peaks for homologous (i^{Pr} PDI)Fe(carboxylates) (**2**) (ligand peaks are overlaying with **1-O₂CC₂H₅**):

^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 61.60 ($\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\dots$), 37.51 ($\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\dots$), 20.64 ($\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\dots$), 12.40 ($\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\dots$).

1-O₂CC₂H₅: See above.

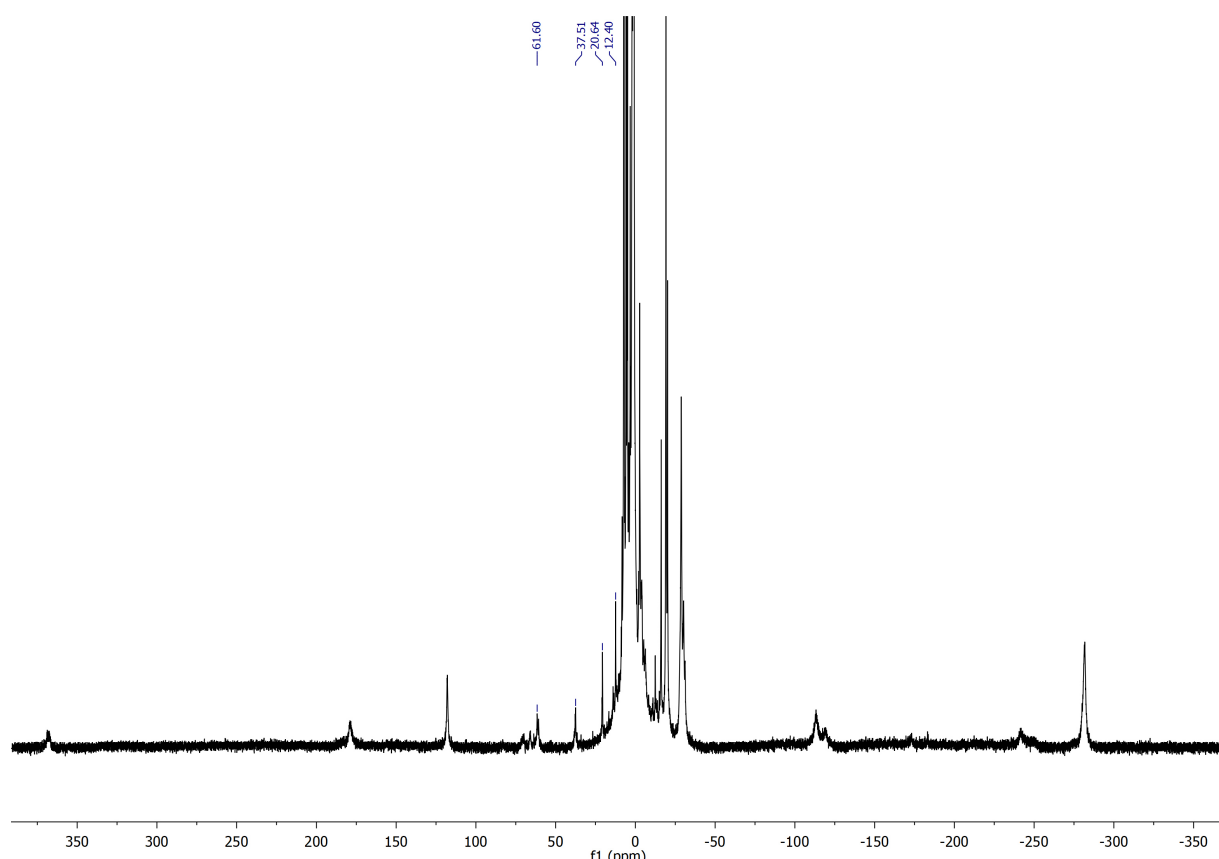
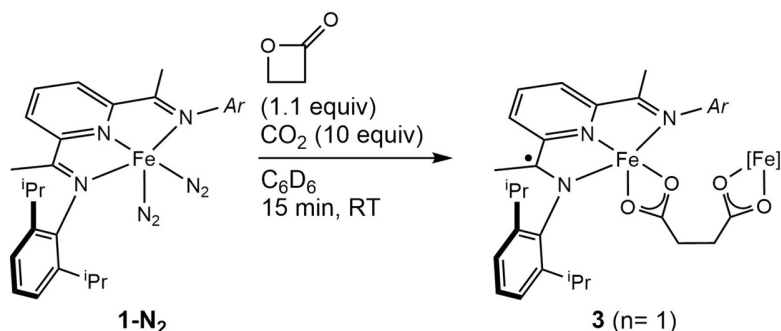


Figure S 9. ^1H NMR spectrum of the mixture of (i^{Pr} PDI)Fe(carboxylates) obtained after reaction of **1-N₂** and β -propiolactone in the presence of ethylene.



Observation of **3 (n=1) from β -propiolactone and CO_2 .** In a N_2 -filled glovebox a J-Young NMR-tube was charged with a solution of $(^{\text{iPr}}\text{PDI})\text{Fe}(\text{N}_2)_2$ (13 mg, 0.022 mmol, 1.0 equiv) in C_6D_6 (0.5 mL). β -Propiolactone (1.5 μL , 0.024 mmol, 1.1 equiv) was added, the tube was sealed, and the reaction mixture was frozen (-196°C , liquid nitrogen) immediately after mixing. The tube was attached to a Schlenk line and the headspace evacuated. CO_2 (0.22 mmol, 40 mmHg in 100 mL, 10 equiv) was measured with a calibrated gas bulb and then condensed into the tube immersed in liquid nitrogen. The tube was sealed, allowed to warm to RT and slowly inverted for 15 min at RT and the reaction mixture was analyzed by ^1H NMR. The observed ^1H NMR signals are consistent with **3 (n=1)** and $^{\text{iPr}}\text{PDI}$ (20% determined by addition of mesitylene as internal standard).

^1H NMR (300 MHz, C_6D_6 , 25°C): δ 367.21 (p -py, 1H), 236.30 ($\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2$, 2H), 122.77 (m -py, 2H), -11.46 (p -Ar, 2H), -14.78 ($\text{CH}(\text{CH}_3)_2$, 12H), -18.82 ($\text{CH}(\text{CH}_3)_2$, 12H), -101.61 ($\text{CH}(\text{CH}_3)_2$, 4H), -276.19 ($\text{N}=\text{C}-\text{CH}_3$, 6H) (one peak not located).

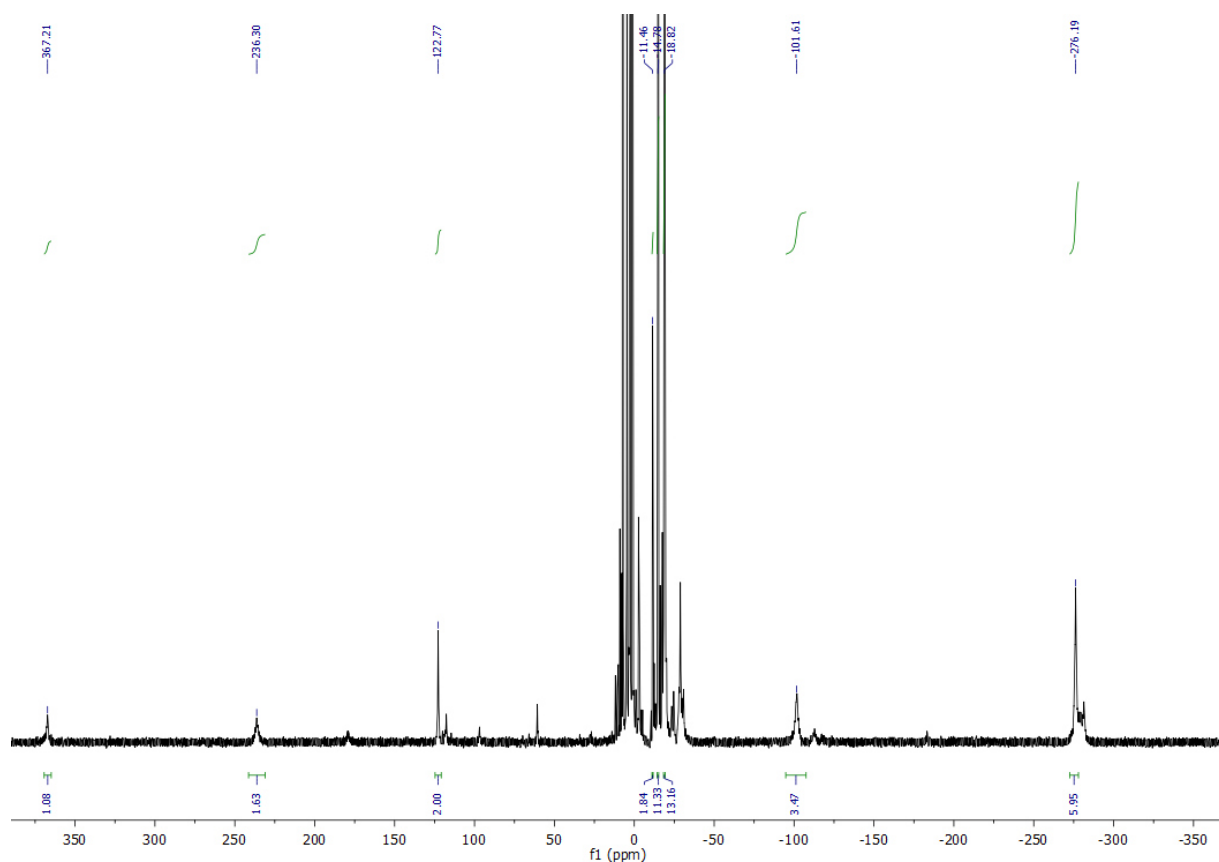
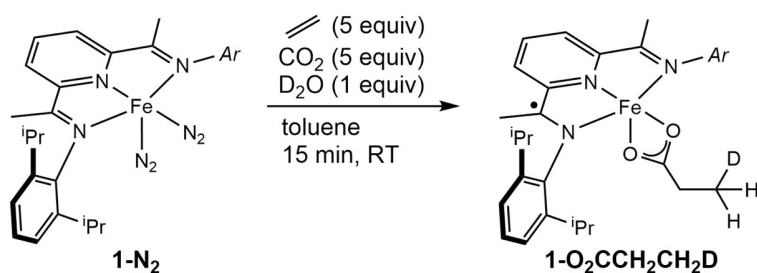


Figure S 10. ^1H NMR spectrum of **3** ($n=1$) obtained after reaction of **1-N₂** and β -propiolactone in the presence of CO_2 .

IV. Deuterium labeling studies.



Observation of $1\text{-O}_2\text{CCH}_2\text{CH}_2\text{D}$ through CO_2 /ethylene coupling in the presence of D_2O . In a N_2 -filled glovebox a J-Young NMR-tube was charged with a solution of $(^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$ (13 mg, 0.022 mmol, 1.0 equiv) in toluene (0.5 mL). The tube was sealed and attached to a Schlenk line where the solution was frozen (-196°C , liquid nitrogen), and the headspace evacuated.

Ethylene (0.11 mmol, 20 mmHg in 100 mL, 5 equiv) was measured with a calibrated gas bulb and then condensed into the tube immersed in liquid nitrogen. The same procedure was repeated with CO₂ gas (0.11 mmol, 20 mmHg in 100 mL, 5 equiv), without thawing the reaction mixture in between the gas additions. Then, D₂O (0.4 μL, 0.022 mmol, 1.0 equiv) was condensed on the frozen reaction mixture via vacuum transfer. The tube was sealed, allowed to warm to RT and slowly inverted for 15 min at RT. The reaction mixture was filtered in an N₂-filled glovebox and analyzed by ²H NMR (and ¹H NMR after solvent switch to C₆D₆). The observed ¹H and ²H NMR signals are consistent with a mixture of **1-O₂CCH₂CH₂D** and *i*PrPDI.

²H NMR (77 MHz, toluene, 25 °C): δ 60.75 (O₂CCH₂CH₂D, 1D).

¹H NMR (300 MHz, C₆D₆, 25 °C): δ 367.36 (*p*-py, 1H), 178.69 (O₂CCH₂CH₃, 2H), 117.59 (*m*-py, 2H), 60.58 (O₂CCH₂CDH₂, 2H), -2.64 (*m*-Ar, 4H), -16.24 (*p*-Ar, 2H), -19.13 (CH(CH₃)₂, 12H), -28.84 (CH(CH₃)₂, 12H), -112.65 (CH-(CH₃)₂, 4H), -281.45 (N=C-CH₃, 6H).

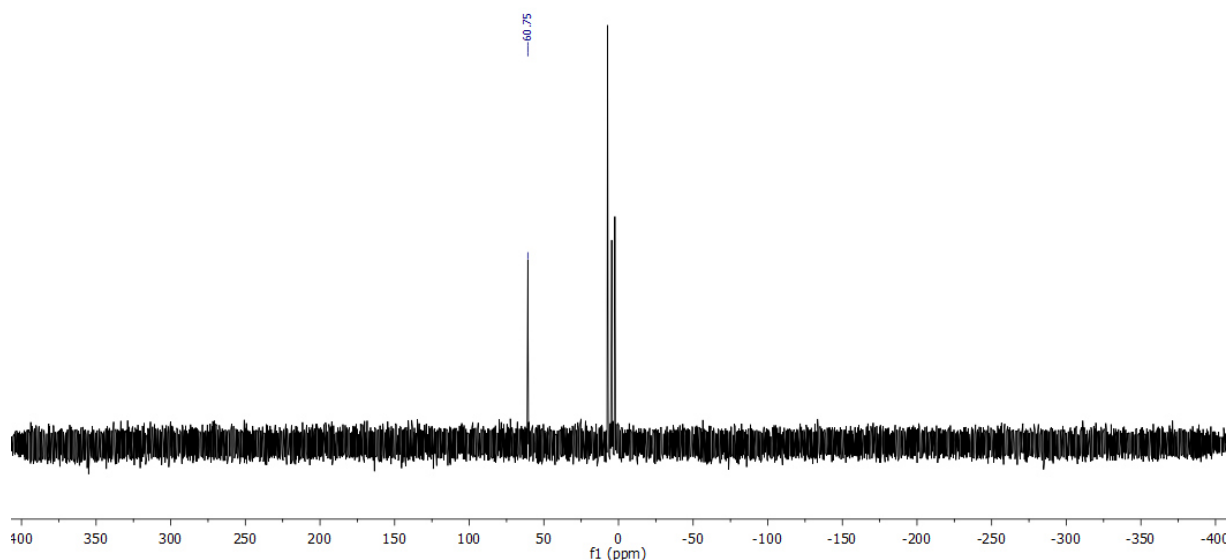


Figure S 11. ²H NMR spectrum of **1-O₂CCH₂CH₂D** obtained after coupling of CO₂ and ethylene in the presence of D₂O.

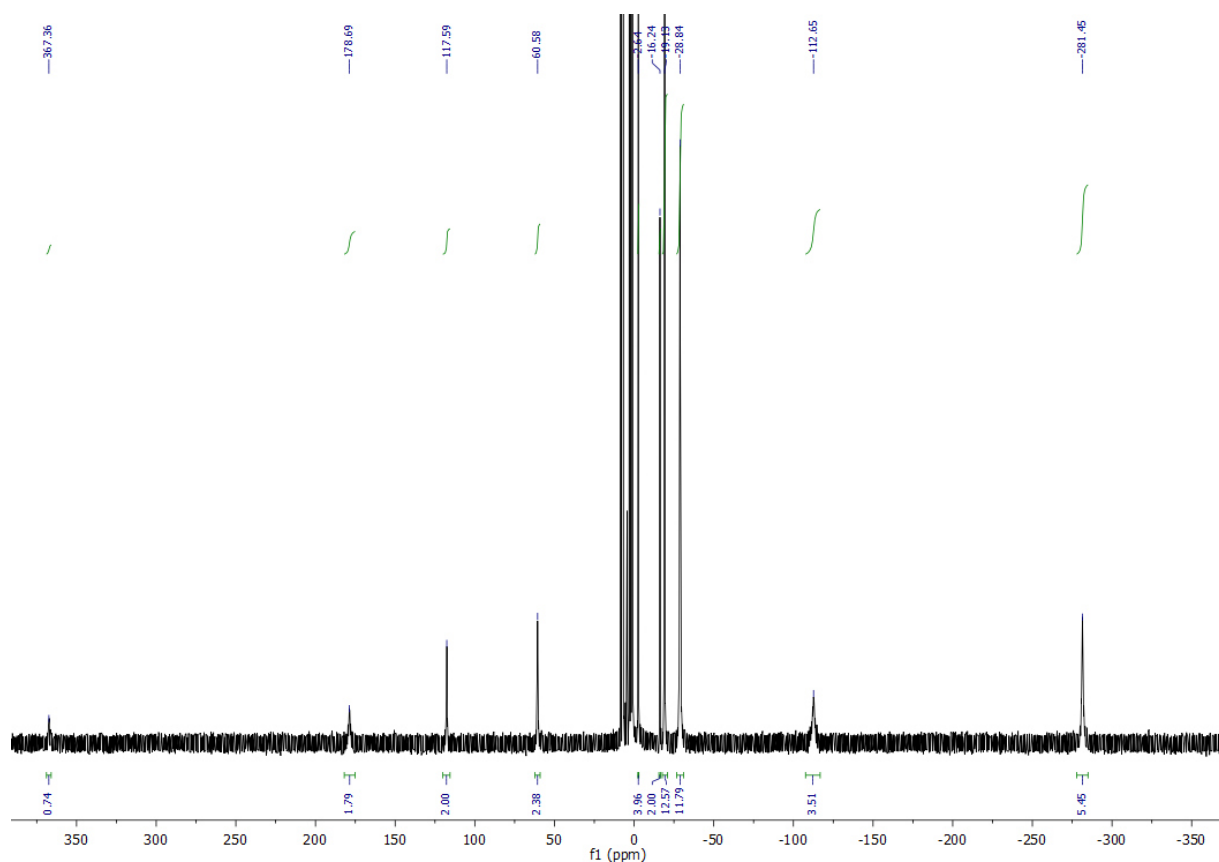
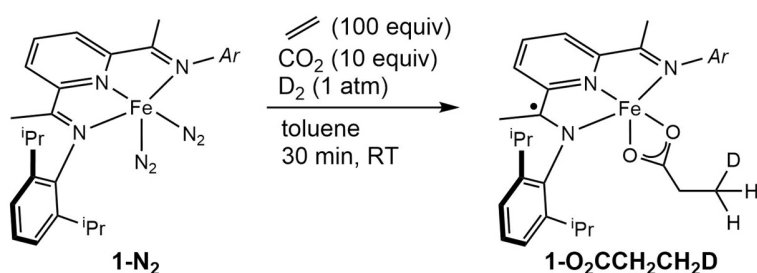


Figure S 12. ^1H NMR spectrum of $1\text{-O}_2\text{CCH}_2\text{CH}_2\text{D}$ obtained after coupling of CO_2 and ethylene in the presence of D_2O .



Observation of $1\text{-O}_2\text{CCH}_2\text{CH}_2\text{D}$ through $\text{CO}_2/\text{ethylene}$ coupling in the presence of D_2 . In a N_2 -filled glovebox a 50 mL reaction vessel with a Teflon valve was charged with a solution of $(\text{iPrPDI})\text{Fe}(\text{N}_2)_2$ (13 mg, 0.022 mmol, 1.0 equiv) in toluene (0.5 mL). The vessel was sealed and attached to a Schlenk line where the solution was frozen (-196°C , liquid nitrogen), and the headspace evacuated. Ethylene (2.2 mmol, 40 mmHg in 1000 mL, 100 equiv) was measured

with a calibrated gas bulb and then condensed into the reaction vessel immersed in liquid nitrogen. The same procedure was repeated with CO₂ gas (0.22 mmol, 4 mmHg in 1000 mL, 10 equiv), without thawing the reaction mixture in between the gas additions. The frozen reaction mixture was pressurized with D₂ (ca. 1 atm) and the reaction vessel was sealed with the Teflon valve. The reaction mixture was thawed under a cold stream of water and stirred for 30 minutes at RT. In a N₂-filled glovebox the reaction mixture was transferred to a J-Young NMR-tube and analyzed by ²H NMR. The observed ²H NMR signals are consistent with a mixture of **1-O₂CCH₂CH₂D** and traces of **1-O₂CCH₂CH₂CH₂CH₂D**.

²H NMR (77 MHz, toluene, 25 °C): δ 61.24 (O₂CCH₂CH₂D, 1D), 19.52 (O₂CCH₂CH₂CH₂CH₂D, 1D)

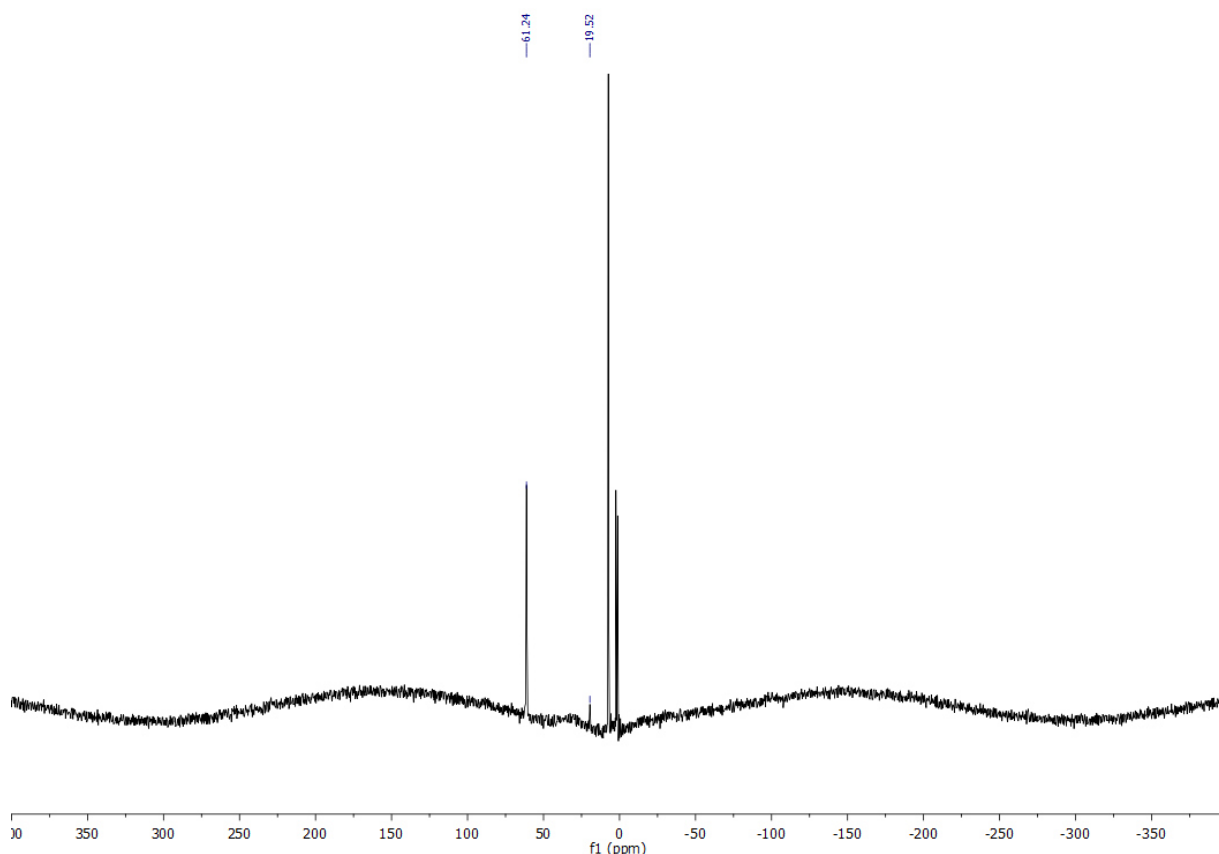
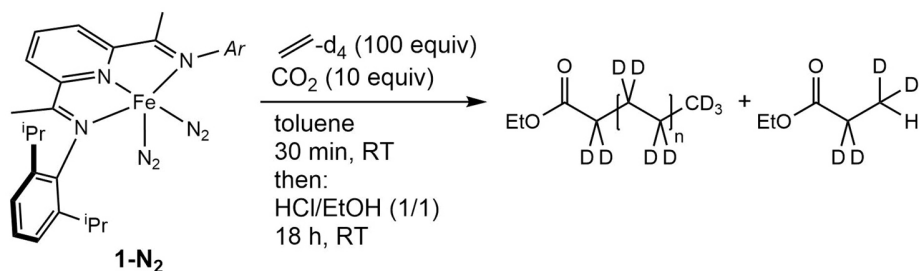


Figure S 13. ²H NMR spectrum of **1-O₂CCH₂CH₂D** and **1-O₂CCH₂CH₂CH₂CH₂D** obtained after coupling of CO₂ and ethylene in the presence of D₂.

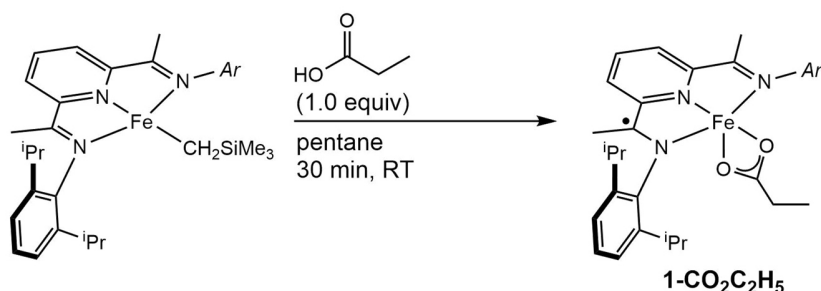


Observation of perdeuterated esters through CO₂/ethylene-d₄ coupling. In a N₂-filled glovebox a 50 mL reaction vessel with a Teflon valve was charged with a solution of (iPrPDI)Fe(N₂)₂ (13 mg, 0.022 mmol, 1.0 equiv) in toluene (0.5 mL). The vessel was sealed and attached to a Schlenk line where the solution was frozen (−196 °C, liquid nitrogen), and the headspace evacuated. Ethylene-d₄ (2.2 mmol, 40 mmHg in 1000 mL, 100 equiv) was measured with a calibrated gas bulb and then condensed into the reaction vessel immersed in liquid nitrogen. The same procedure was repeated with CO₂ gas (0.22 mmol, 4 mmHg in 1000 mL, 10 equiv), without thawing the reaction mixture in between the gas additions. The reaction vessel was sealed with the Teflon valve, and the reaction mixture was thawed under a cold stream of water and stirred for 30 minutes at RT. All volatiles were removed, and the resulting orange/brown residue was taken up in pentane and filtered through a short plug of Celite. All volatiles were removed and a mixture of ethanol and conc. HCl aq. (1/1, 2 mL) was added. The resulting mixture was stirred for 18 h, extracted with CH₂Cl₂ (4 x 1 mL) and the organic layer was subjected to GC-MS analysis.

Percentage of perdeuterated ethyl esters as a function of *n* as detected by GC-MS:

n = 0: 3%; *n* = 1: 72%; *n* = 2: 70%; *n* = 3: 72%; *n* = 4: 70%; *n* = 5: 69%; *n* = 6: 66%; *n* = 7: 67%;
n = 8: 69%; *n* = 9: 69%.

V. Preparation of (ⁱPrPDI)Fe(carboxylates) from carboxylic acids.



Preparation of 1-O₂CC₂H₅ from (ⁱPrPDI)Fe(CH₂SiMe₃) and propionic acid. In a N₂-filled glovebox a scintillation vial was charged with a solution of (ⁱPrPDI)Fe(CH₂SiMe₃) (186 mg, 0.30 mmol, 1.0 equiv) in pentane (5 mL) and the solution was cooled to −35 °C. A cooled solution (−35 °C) of propionic acid (22.0 μL, 0.30 mmol, 1.0 equiv) in pentane (2 mL) was added and the resulting mixture was allowed to warm to RT, stirred for 30 min and filtered. All volatiles were removed in vacuo to yield a mixture of **1-O₂CC₂H₅** and ⁱPrPDI. To remove most of the ⁱPrPDI impurity, a concentrated toluene solution of the residue was layered with pentane and cooled to −35 °C. Filtration and removal of all volatiles in vacuo yielded 126 mg (69% yield, contaminated with 14% ⁱPrPDI) of **1-O₂CC₂H₅** as a dark brown solid. Single crystals suitable for x-ray crystallography were obtained from an Et₂O solution at −35 °C.

Anal Calcd for C₃₆H₄₈FeN₃O₂: C, 70.81; H, 7.92; N, 6.88. Found: C, 70.68; H, 8.02; N, 6.98. Magnetic Susceptibility (Guoy, 23 °C): μ_{eff} = 3.6 μ_B. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ 366.53 (*p*-py, 1H), 178.54 (O₂CCH₂CH₃, 2H), 117.38 (*m*-py, 2H), 60.58 (O₂CCH₂CH₃, 3H), −2.61 (*m*-Ar, 4H), −16.19 (*p*-Ar, 2H), −19.10 (CH(CH₃)₂, 12H), −28.77 (CH(CH₃)₂, 12H), −112.53 (CH-(CH₃)₂, 4H), −280.84 (N=C-CH₃, 6H).

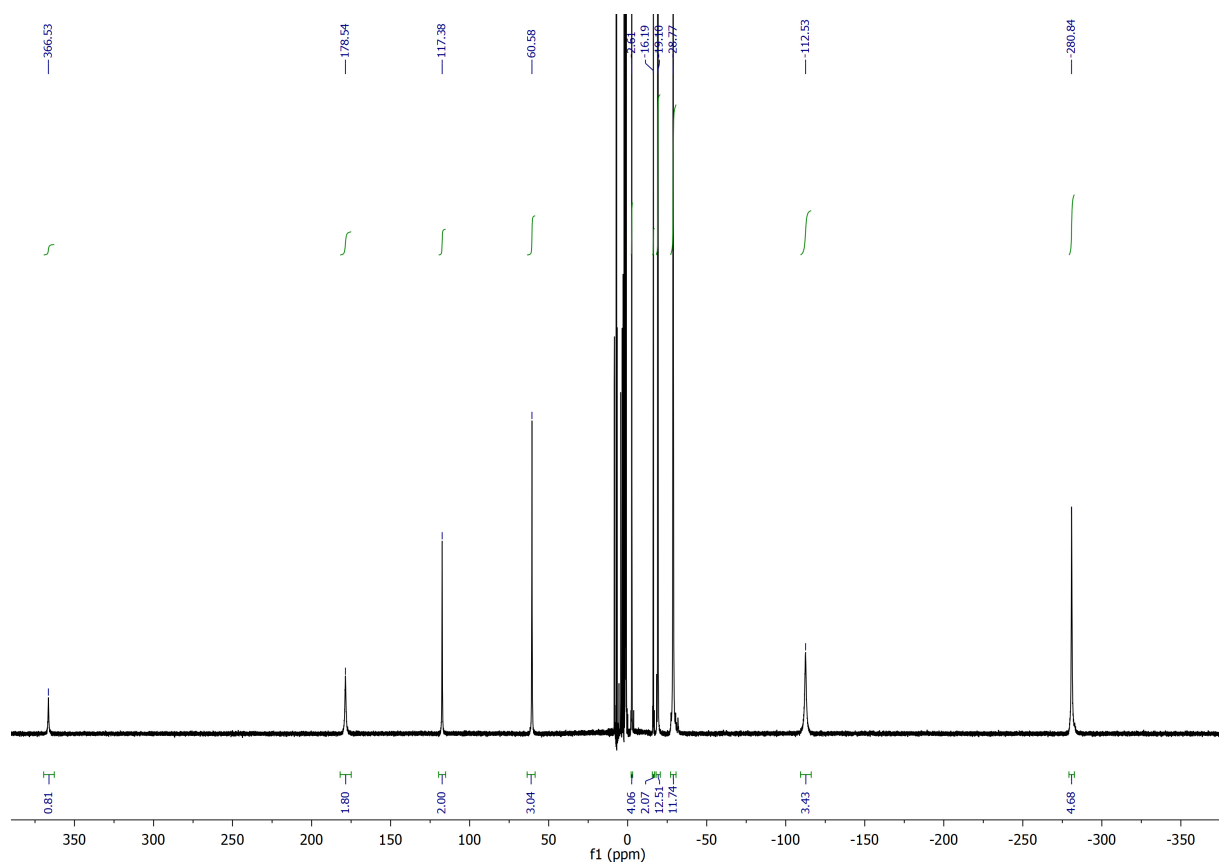


Figure S 14. ^1H NMR spectrum of $1\text{-O}_2\text{CC}_2\text{H}_5$ from $(\text{IPr})\text{PDI})\text{Fe}(\text{CH}_2\text{SiMe}_3)$ and propionic acid.

Mössbauer spectroscopy:

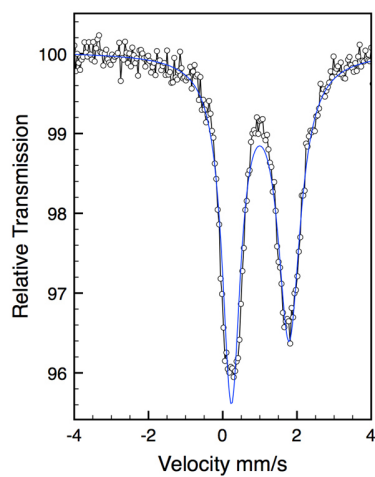
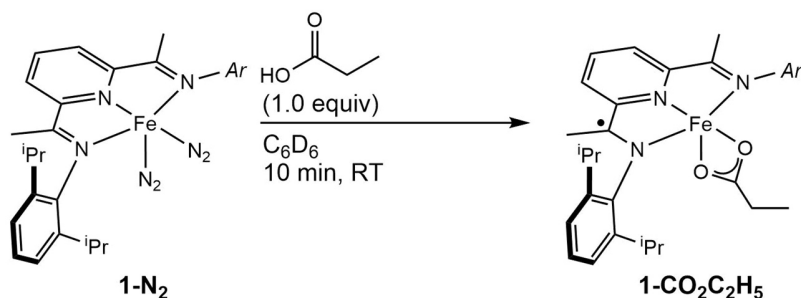


Figure S 15. Zero-field ^{57}Fe Mössbauer spectrum of $1\text{-O}_2\text{CC}_2\text{H}_5$ at 80 K in frozen toluene. Simulated parameters (blue lines) are $\delta = 1.01$ mm/s, $|\Delta E_Q| = 1.56$ mm/s.



Observation of 1-O₂CC₂H₅ from (iPrPDI)Fe(N₂)₂ (1-N₂) and propionic acid. In a N₂-filled glovebox a J-Young NMR-tube was charged with a solution of (iPrPDI)Fe(N₂)₂ (13 mg, 0.022 mmol, 1.0 equiv) in C₆D₆ (0.5 mL). Propionic acid (1.6 μL, 0.022 mmol, 1.0 equiv) was added and the tube was slowly inverted for 10 min before the resulting mixture was analyzed by ¹H NMR. The observed ¹H NMR signals are consistent with a mixture of **1-O₂CC₂H₅** and iPrPDI.

¹H NMR (300 MHz, C₆D₆, 25 °C): δ 367.42 (*p*-py, 1H), 178.91 (O₂CCH₂CH₃, 2H), 117.60 (*m*-py, 2H), 60.71 (O₂CCH₂CH₃, 3H), -2.65 (*m*-Ar, 4H), -16.23 (*p*-Ar, 2H), -19.16 (CH(CH₃)₂, 12H), -28.84 (CH(CH₃)₂, 12H), -112.92 (CH-(CH₃)₂, 4H), -281.48 (N=C-CH₃, 6H).

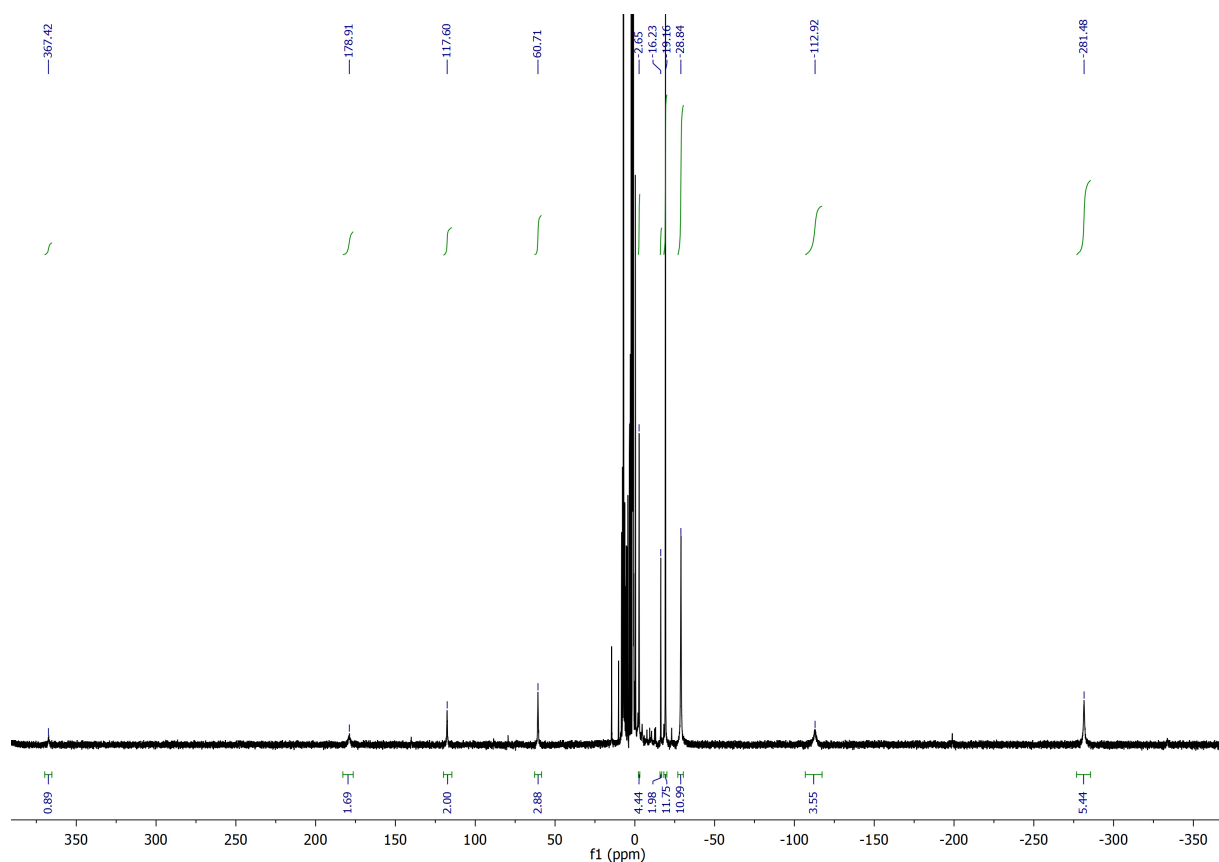
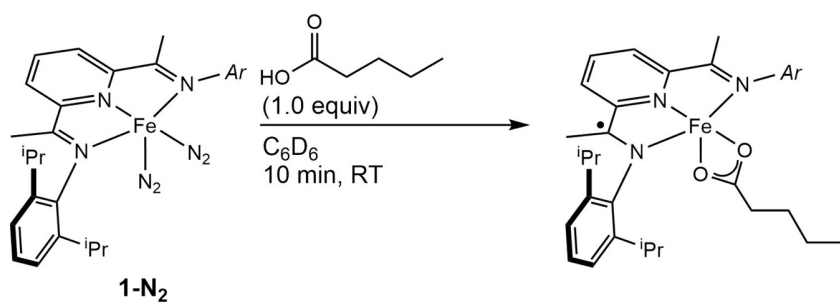


Figure S 16. ^1H NMR spectrum of $1\text{-O}_2\text{CC}_2\text{H}_5$ from 1-N_2 and propionic acid.



Observation of (*i*PrPDI)Fe(pentanoate) from (*i*PrPDI)Fe(N₂) (1-N₂**) and pentanoic acid.** In a N₂-filled glovebox a J-Young NMR-tube was charged with a solution of (*i*PrPDI)Fe(N₂)₂ (13 mg, 0.022 mmol, 1.0 equiv) in C₆D₆ (0.5 mL). Pentanoic acid (2.4 μL , 0.022 mmol, 1.0 equiv) was added and the tube was slowly inverted for 10 min before the resulting mixture was and

analyzed by ^1H NMR. The observed ^1H NMR signals are consistent with a mixture of $(i\text{PrPDI})\text{Fe}(\text{pentanoate})$ and $i\text{PrPDI}$.

^1H NMR (300 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ 367.91 (p -py, 1H), 178.32 ($\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 2H), 117.83 (m -py, 2H), 61.47 ($\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 2H), 38.43 ($\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 2H), 19.35 ($\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 3H), -2.60 (m -Ar, 4H), -16.23 (p -Ar, 2H), -19.15 ($\text{CH}(\text{CH}_3)_2$, 12H), -28.60 ($\text{CH}(\text{CH}_3)_2$, 12H), -113.47 ($\text{CH}-(\text{CH}_3)_2$, 4H), -281.73 ($\text{N}=\text{C}-\text{CH}_3$, 6H).

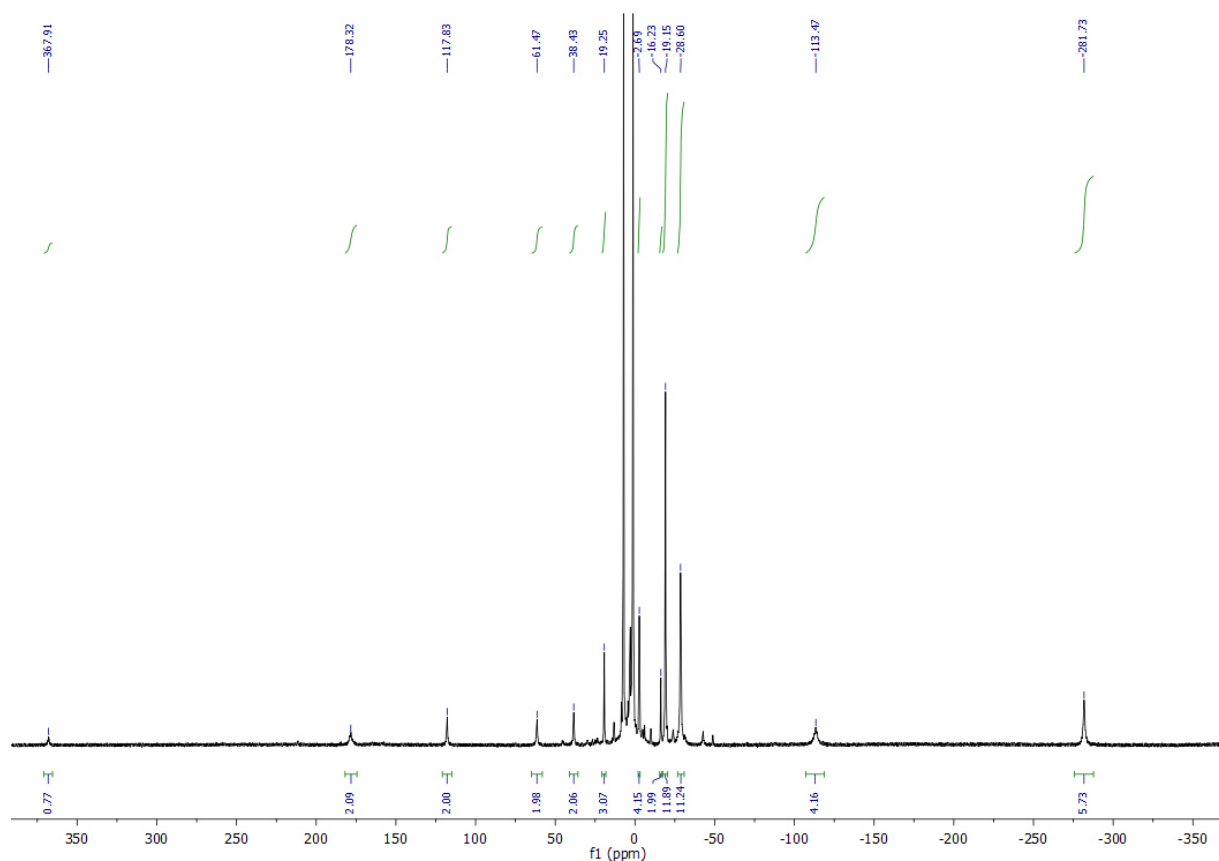
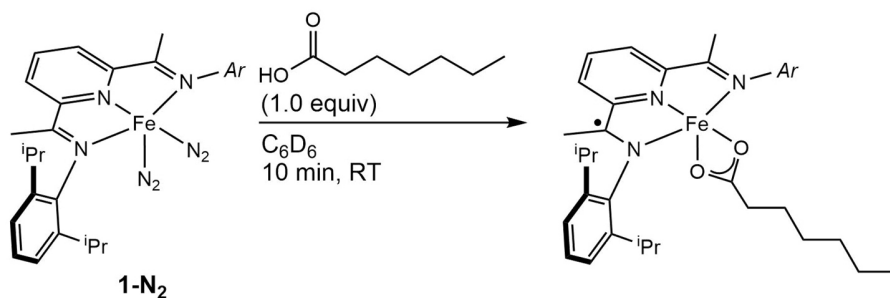


Figure S 17. ^1H NMR spectrum of $(i\text{PrPDI})\text{Fe}(\text{pentanoate})$.



Observation of (iPrPDI)Fe(heptanoate) from (iPrPDI)Fe(N₂) (1-N₂) and heptanoic acid. In a N₂-filled glovebox a J-Young NMR-tube was charged with a solution of (iPrPDI)Fe(N₂)₂ (13 mg, 0.022 mmol, 1.0 equiv) in C₆D₆ (0.5 mL). Heptanoic acid (3.1 μ L, 0.022 mmol, 1.0 equiv) was added and the tube was slowly inverted for 10 min before the resulting mixture was analyzed by ¹H NMR. The observed ¹H NMR signals are consistent with a mixture of (iPrPDI)Fe(heptanoate) and iPrPDI.

¹H NMR (300 MHz, C₆D₆, 25 °C): δ 367.57 (*p*-py, 1H), 178.53 (O₂CCH₂CH₂CH₂CH₂CH₂CH₃, 2H), 117.96 (*m*-py, 2H), 61.52 (O₂CCH₂CH₂CH₂CH₂CH₂CH₃, 2H), 37.43 (O₂CCH₂CH₂CH₂CH₂CH₂CH₃, 2H), 20.64 (O₂CCH₂CH₂CH₂CH₂CH₂CH₃, 2H), 12.33 (O₂CCH₂CH₂CH₂CH₂CH₂CH₃, 2H), 7.50 (O₂CCH₂CH₂CH₂CH₂CH₂CH₃, 3H), -2.69 (*m*-Ar, 4H), -16.22 (*p*-Ar, 2H), -19.17 (CH(CH₃)₂, 12H), -28.75 (CH(CH₃)₂, 12H), -113.21 (CH-(CH₃)₂, 4H), -281.85 (N=C-CH₃, 6H).

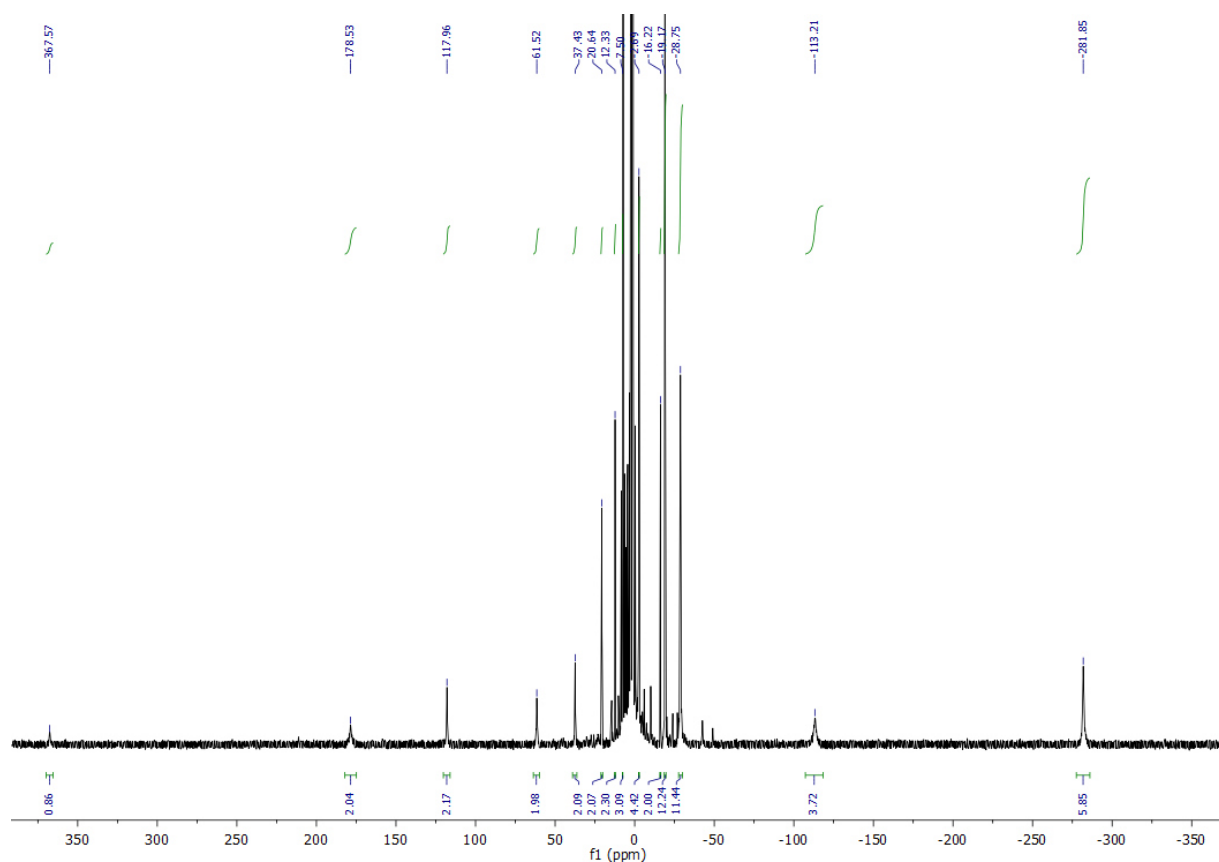
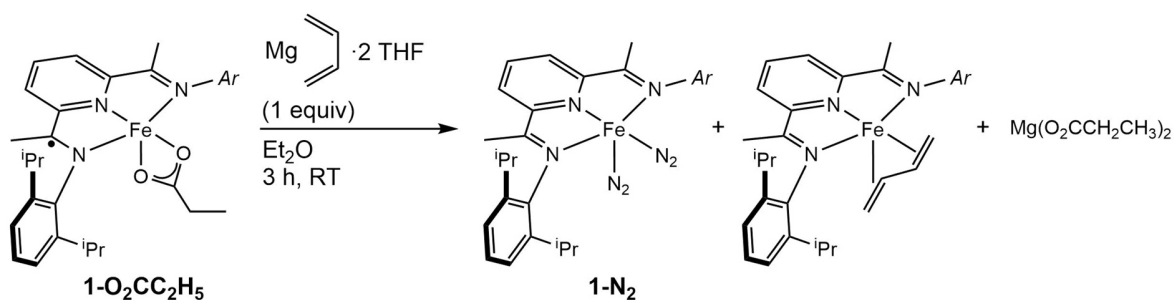


Figure S 18. ^1H NMR spectrum of $(i\text{PrPDI})\text{Fe}(\text{heptanoate})$.

VI. Reduction of $1\text{-O}_2\text{CC}_2\text{H}_5$.



Observation of $(i\text{PrPDI})\text{Fe}(\text{N}_2)_2$ (1- N_2) and $(i\text{PrPDI})\text{Fe}(\text{butadiene})$. In a N_2 -filled glovebox a scintillation vial was charged with $(i\text{PrPDI})\text{Fe}(\text{O}_2\text{CC}_2\text{H}_5)$ (10 mg, 0.016 mmol, 1.0 equiv) and $\text{Mg}(\text{butadiene}) \cdot 2\text{THF}$ (4 mg, 0.018 mmol, 1.1 equiv). Et_2O (ca. 2 mL) was added and the resulting mixture was stirred for 3 h at RT. All volatiles were removed, the residue was taken up

in C₆D₆, and the solution filtered and analyzed by ¹H NMR spectroscopy. The observed ¹H NMR signals are consistent with a mixture of (i^{Pr}PDI)Fe(N₂)₂ and (i^{Pr}PDI)Fe(butadiene).⁵

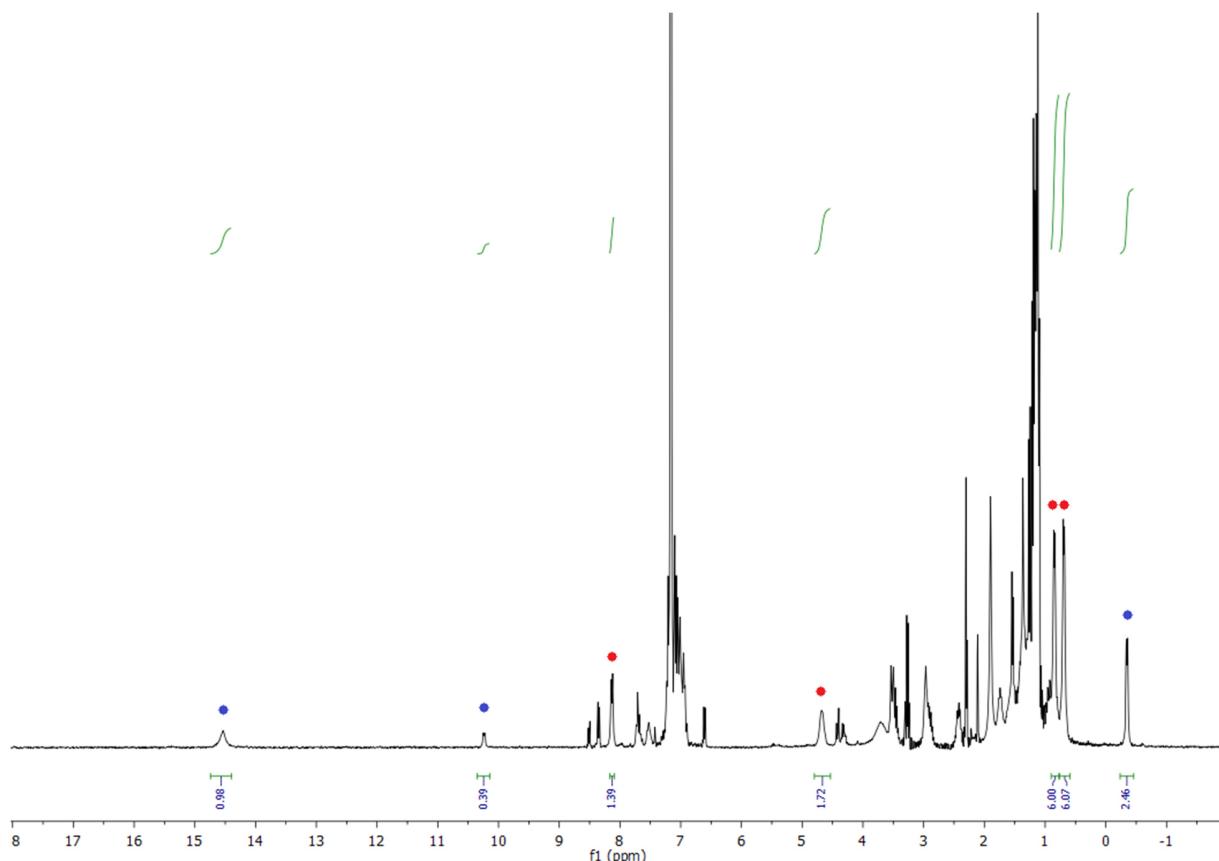


Figure S 19. ¹H NMR spectrum of the reaction mixture after reduction of (i^{Pr}PDI)Fe(propionate) with Mg(butadiene). Characteristic signals of (i^{Pr}PDI)Fe(N₂)₂ are marked with a blue circle and characteristic signals of (i^{Pr}PDI)Fe(butadiene) are marked with a red circle.

Observation of magnesium propionate. In a N₂-filled glovebox a scintillation vial was charged with (i^{Pr}PDI)Fe(O₂CC₂H₅) (10 mg, 0.016 mmol, 1.0 equiv) and Mg(butadiene)·2THF (4 mg, 0.018 mmol, 1.1 equiv). Et₂O (ca. 2 mL) was added and the resulting mixture was stirred for 3 h at RT. All volatiles were removed, the residue was extracted with D₂O, and the solution filtered and analyzed by ¹H NMR and ¹³C NMR spectroscopies.

¹H NMR (500 MHz, D₂O, 25 °C): δ 2.17 (q, J = 7.7 Hz, 2H), 1.04 (t, J = 7.7 Hz, 3H). ¹³C NMR (126 MHz, D₂O, 25 °C): δ 184.7, 30.4, 9.8.

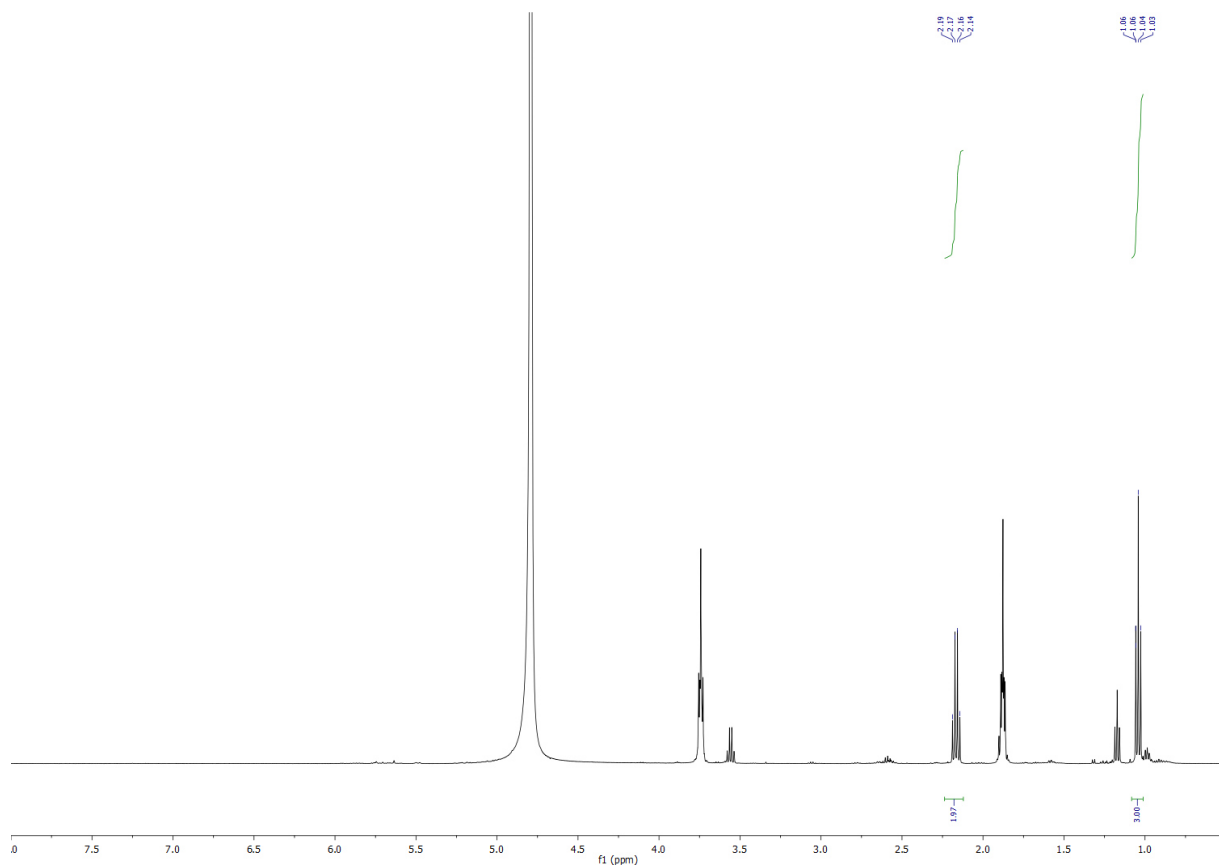


Figure S 20. ^1H NMR spectrum of magnesium propionate (with THF and Et_2O as impurities) after reduction of $(^i\text{PrPDI})\text{Fe}(\text{propionate})$ with $\text{Mg}(\text{butadiene})$.

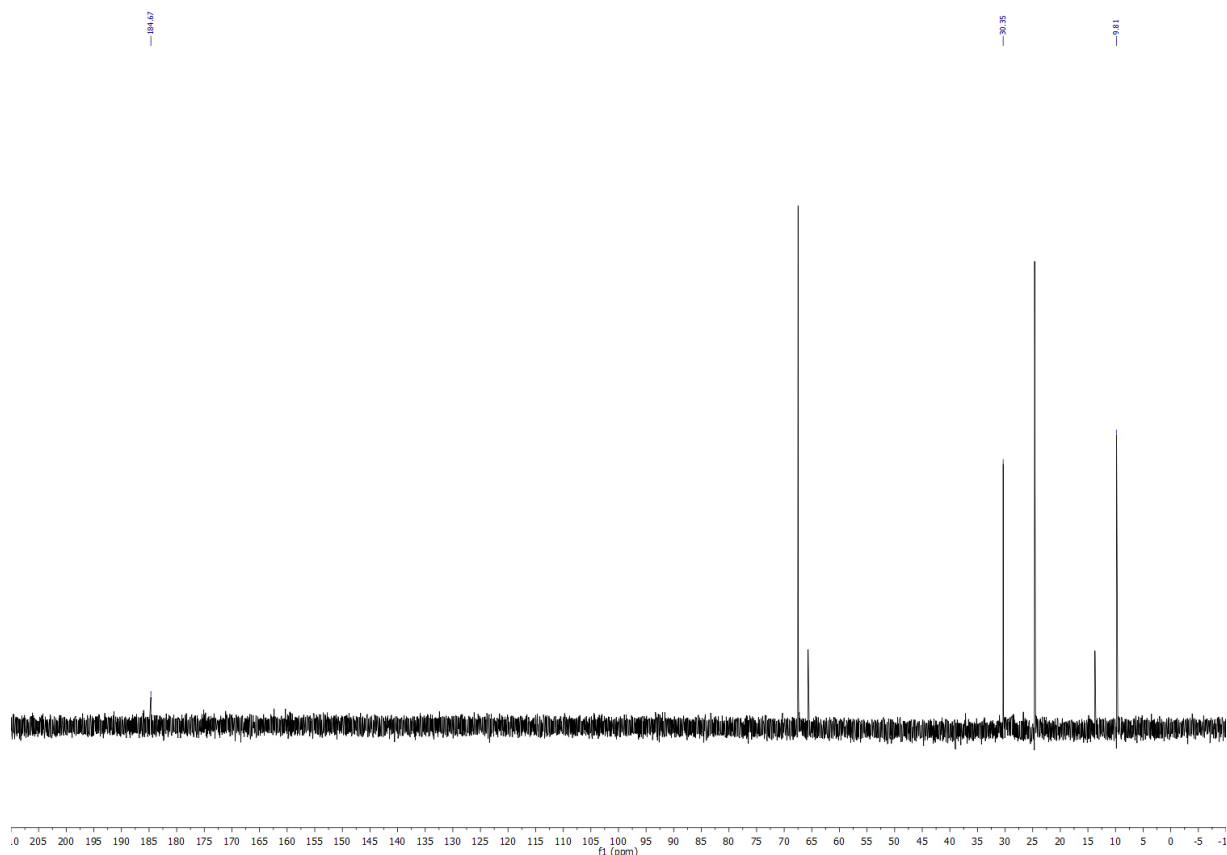


Figure S 21. ^{13}C NMR spectrum of magnesium propionate (with THF and Et_2O as impurities) after reduction of $(^i\text{PrPDI})\text{Fe}(\text{propionate})$ with $\text{Mg}(\text{butadiene})$.

Independent synthesis of magnesium propionate. In a N_2 -filled glovebox a scintillation vial was charged with $\text{Mg}(\text{butadiene})\cdot 2\text{THF}$ (10 mg, 0.045 mmol, 1.0 equiv) and Et_2O (ca. 2 mL). Propionic acid (6.7 μL , 0.090 mmol, 2.0 equiv) was added and the resulting mixture was stirred for 1 h at RT. All volatiles were removed, the residue was extracted with D_2O , and the solution filtered and analyzed by ^1H NMR and ^{13}C NMR spectroscopies.

^1H NMR (500 MHz, D_2O , 25 $^\circ\text{C}$): δ 2.18 (q, J = 7.7 Hz, 1H), 1.03 (t, J = 7.7 Hz, 1H). ^{13}C NMR (126 MHz, D_2O , 25 $^\circ\text{C}$): δ 184.6, 30.4, 9.9.

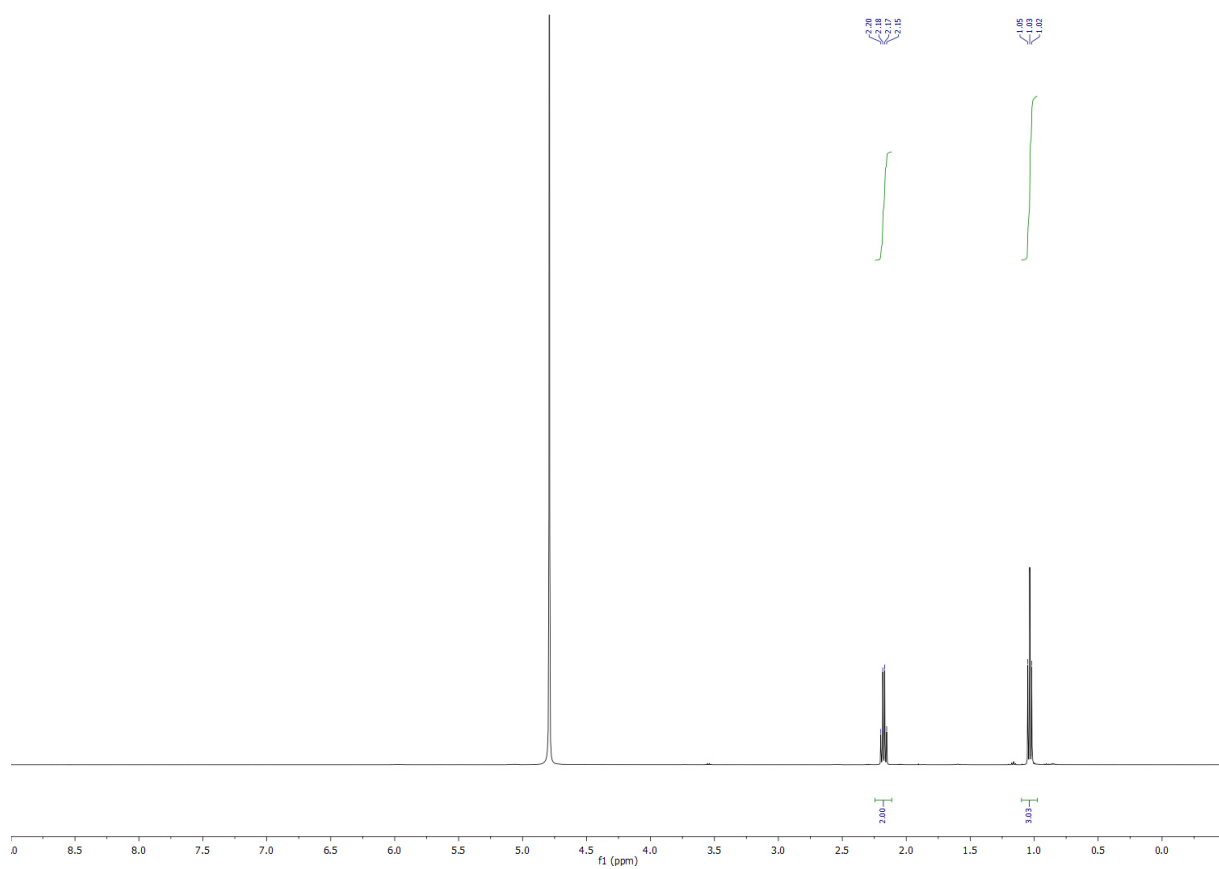


Figure S 22. ^1H NMR spectrum of magnesium propionate after reaction of propionic acid with Mg(butadiene).

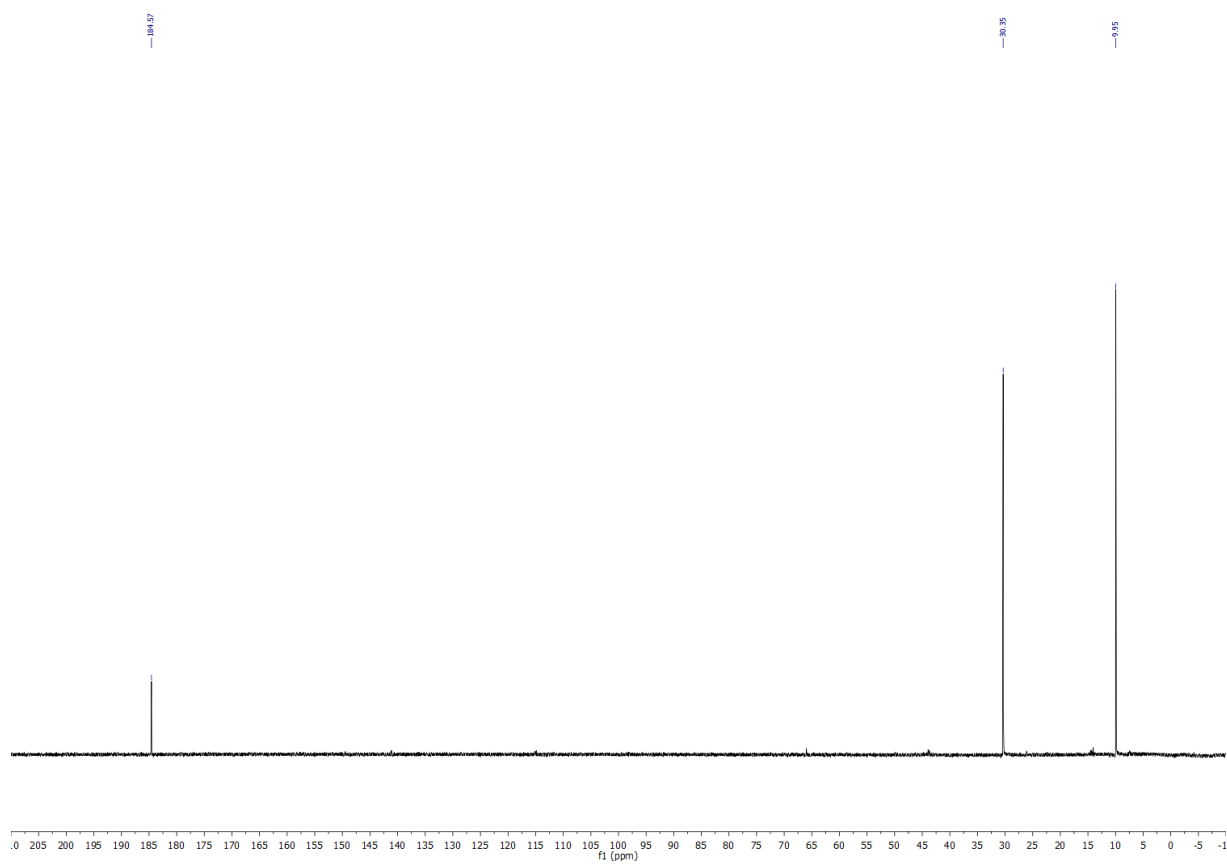


Figure S 23. ^{13}C NMR spectrum of magnesium propionate after reaction of propionic acid with Mg(butadiene).

VII. Additional Spectroscopic Data

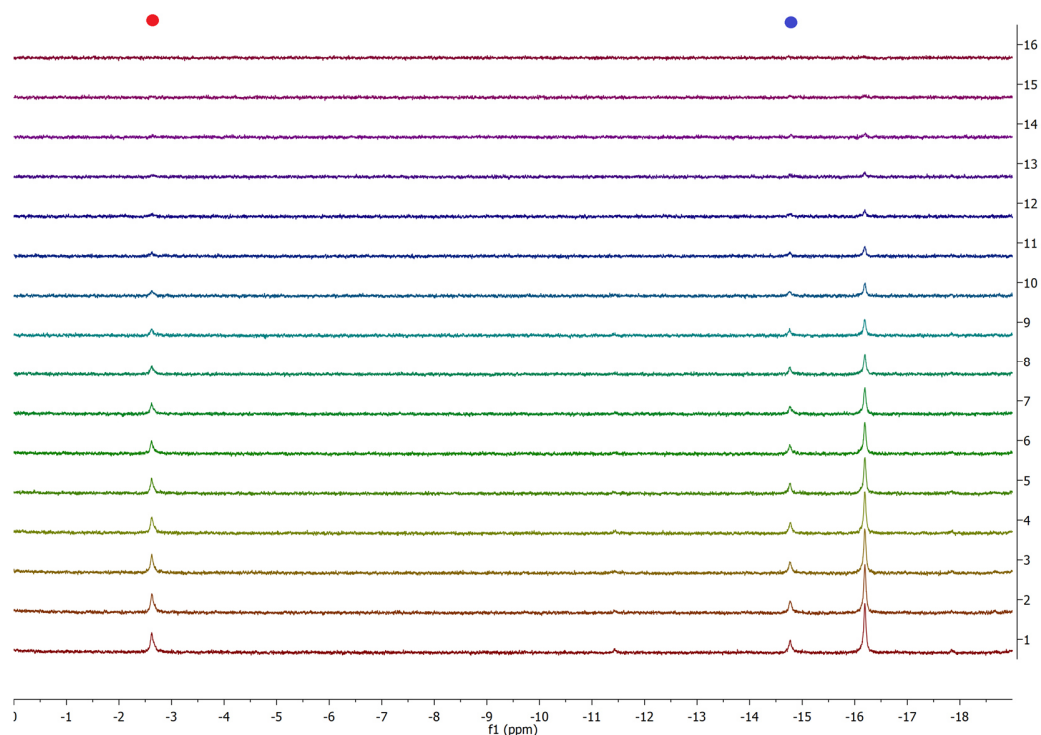


Figure S 24. DOSY Experiment of a mixture of **1-O₂CC₂H₅** (red circle) and **3** (n= 1) (blue circle) in C₆D₆ at RT.

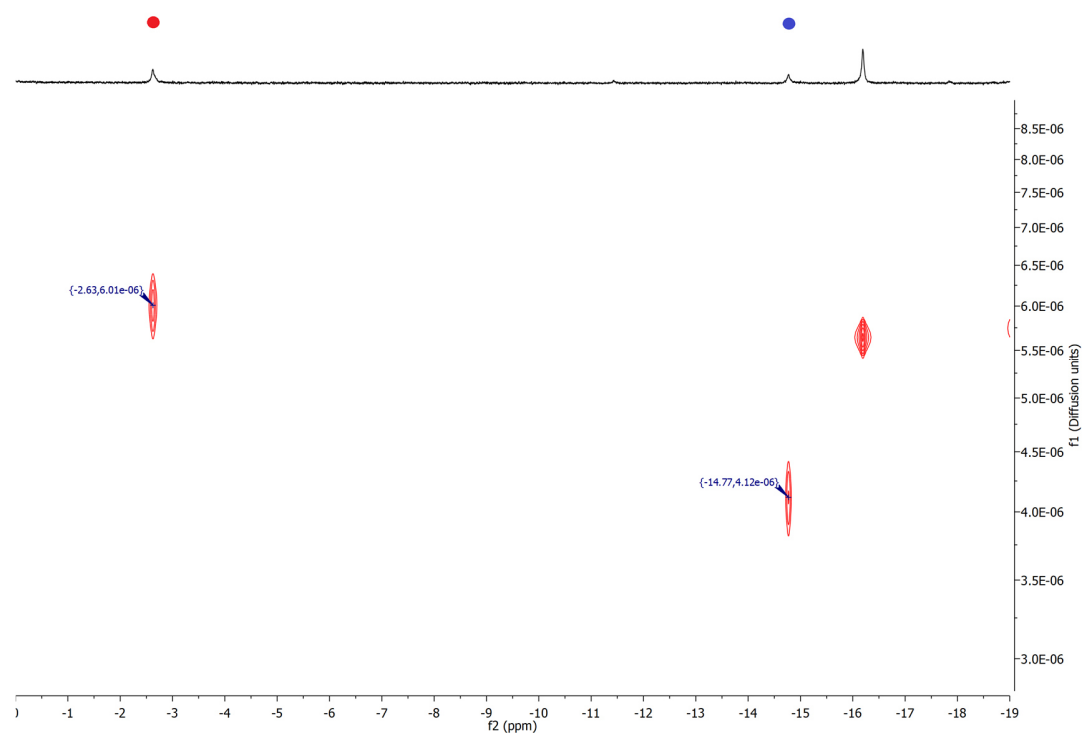


Figure S 25. DOSY Transform of a mixture of **1-O₂CC₂H₅** (red circle) and **3** (n= 1) (blue circle) in C₆D₆ at RT.

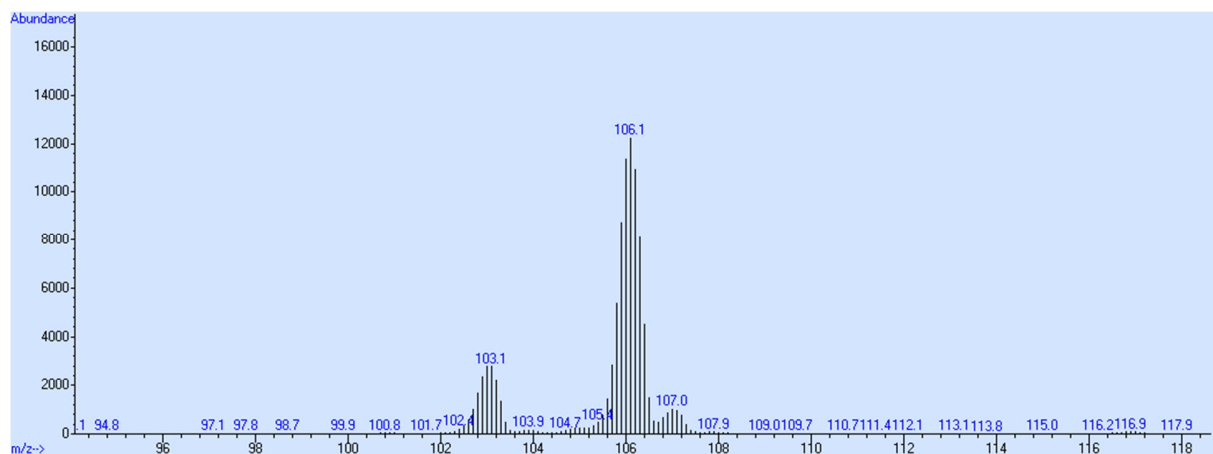


Figure S 26. Mass spectrum of the molecular peak of the ethyl ester of the C3-acid after coupling of CO₂ and ethylene-d₄ and acid mediated ethanolysis.

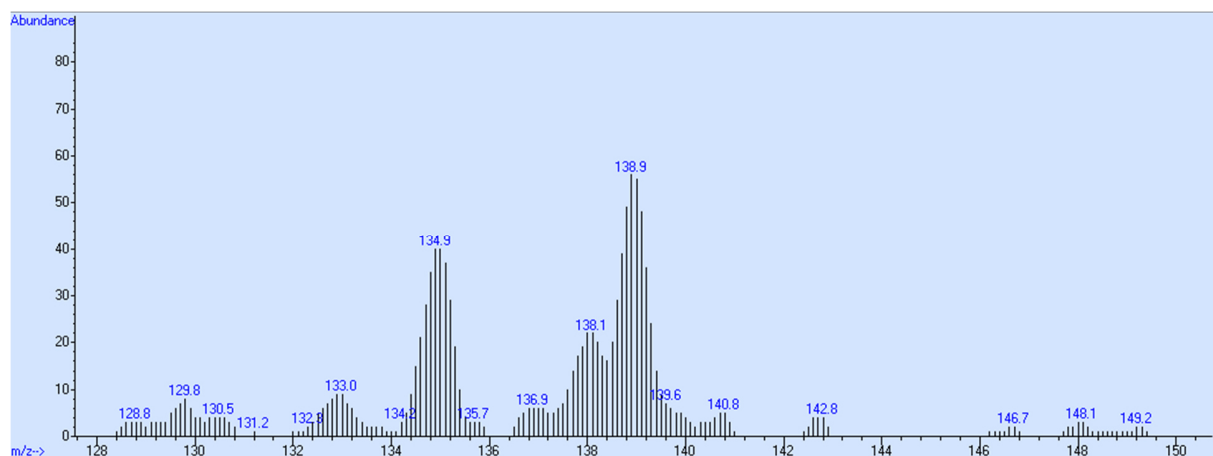


Figure S 27. Mass spectrum of the molecular peak of the ethyl ester of the C5-acid after coupling of CO₂ and ethylene-d₄ and acid mediated ethanolysis.

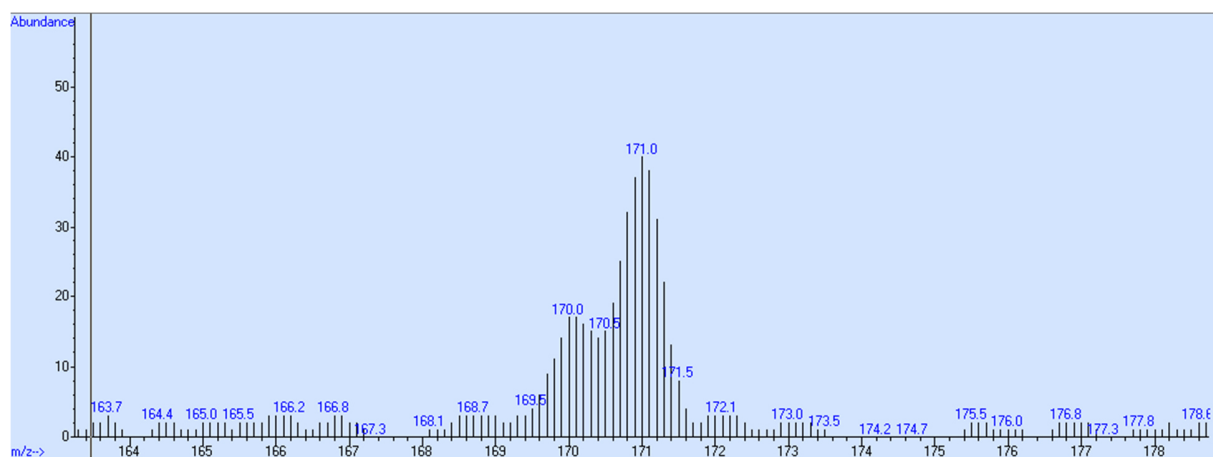


Figure S 28. Mass spectrum of the molecular peak of the ethyl ester of the C7-acid after coupling of CO₂ and ethylene-d₄ and acid mediated ethanolysis.

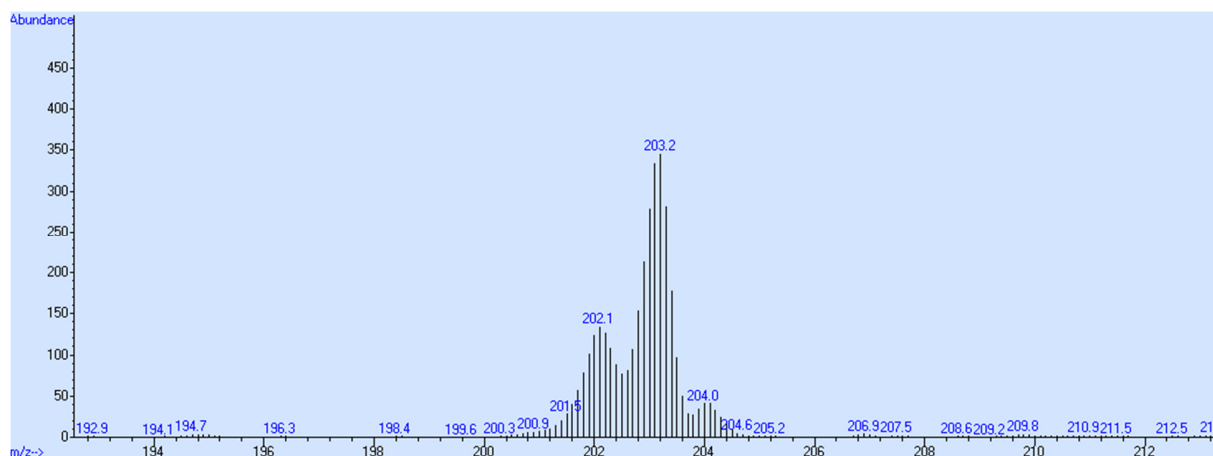


Figure S 29. Mass spectrum of the molecular peak of the ethyl ester of the C9-acid after coupling of CO₂ and ethylene-d₄ and acid mediated ethanolysis.

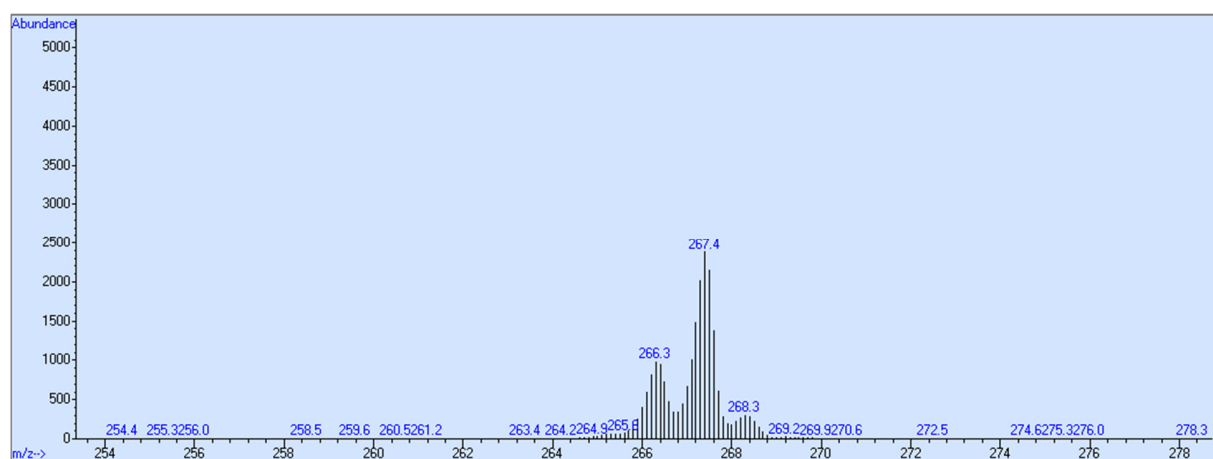


Figure S 30. Mass spectrum of the molecular peak of the ethyl ester of the C11-acid after coupling of CO₂ and ethylene-d₄ and acid mediated ethanolysis.

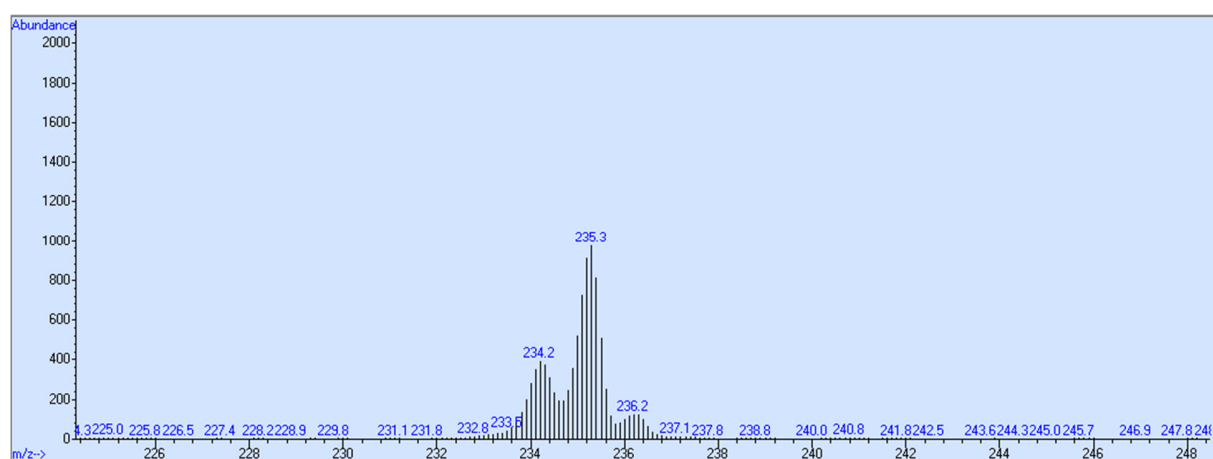


Figure S 31. Mass spectrum of the molecular peak of the ethyl ester of the C13-acid after coupling of CO₂ and ethylene-d₄ and acid mediated ethanolysis.

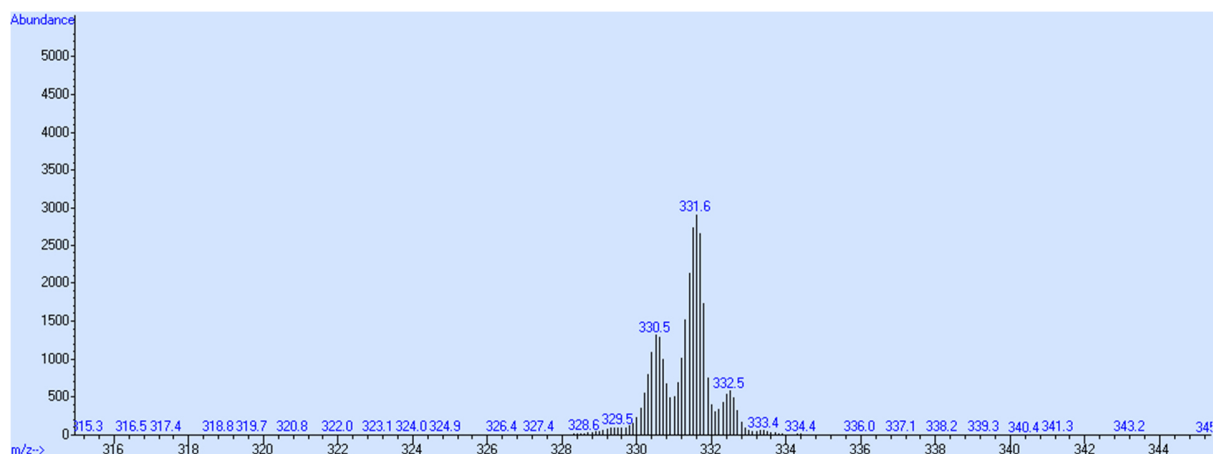


Figure S 32. Mass spectrum of the molecular peak of the ethyl ester of the C15-acid after coupling of CO₂ and ethylene-d₄ and acid mediated ethanolysis.

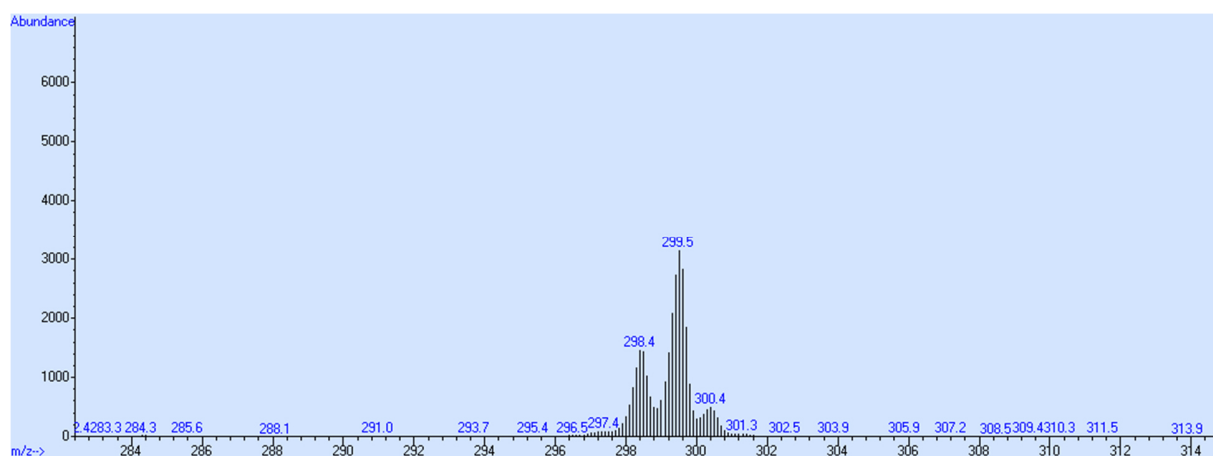


Figure S 33. Mass spectrum of the molecular peak of the ethyl ester of the C17-acid after coupling of CO₂ and ethylene-d₄ and acid mediated ethanolysis.

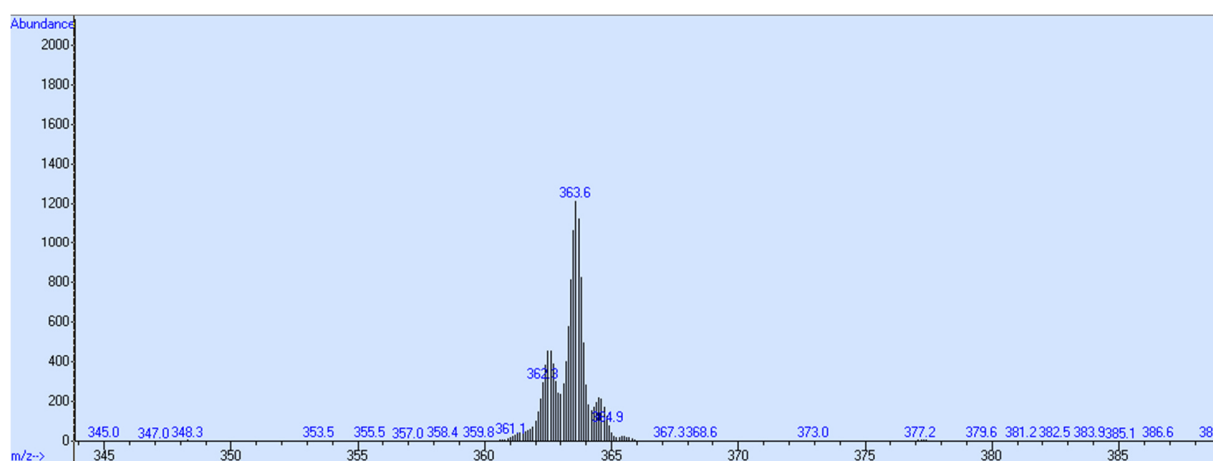


Figure S 34. Mass spectrum of the molecular peak of the ethyl ester of the C19-acid after coupling of CO₂ and ethylene-d₄ and acid mediated ethanolysis.

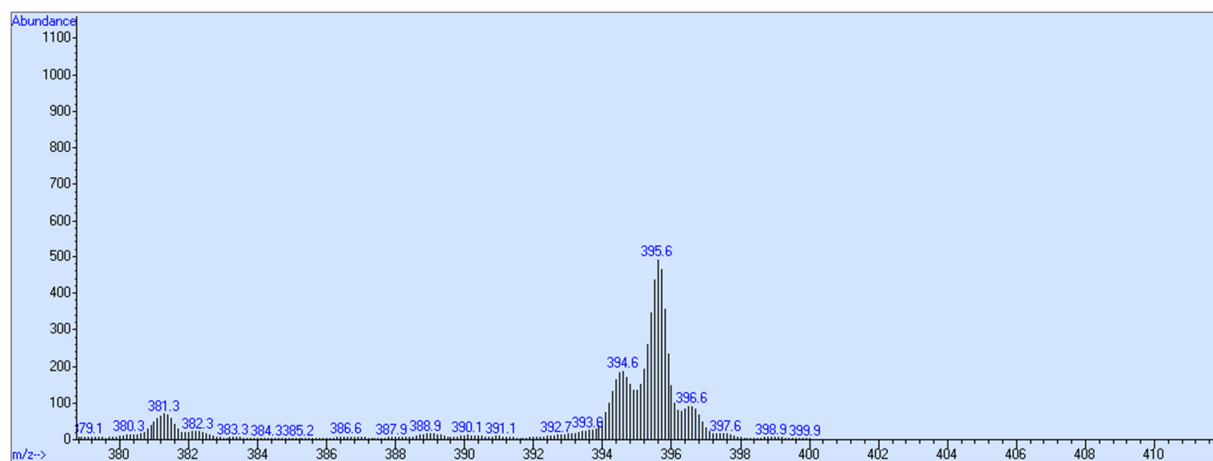


Figure S 35. Mass spectrum of the molecular peak of the ethyl ester of the C21-acid after coupling of CO₂ and ethylene-d₄ and acid mediated ethanolysis.

VIII. References

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