# Supporting Information

# Unprecedent Formation of Methylsilylcarbonates from Ir-Catalyzed Reduction of $CO_2$ with Hydrosilanes

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# **1.** General information and experimental details

All manipulations were carried out under an argon atmosphere by Schlenk-type techniques or in a Glovebox MBraun Unilab. Organic solvents were dried by standard procedures and distilled under argon prior to use or obtained oxygen- and water-free from a solvent purification system (Innovative Technologies). $^{1}H$, $^{13}C$, $^{29}Si$ and $^{19}F$ NMR spectra were obtained on a Bruker AV-300, AV-400 or AV-500 spectrometer. Chemical shifts (δ), reported in ppm, are referenced to the residual solvent peaks and coupling constants (*J*) are reported in Hz.

**Synthesis of $[Ir(NSiMe)_2(CF_3SO_3)]_2$ (3).** Toluene (10 mL) was added to a light-protected Schlenk containing $[Ir(NSi^{Me})_2(Cl)]_2$ (300 mg, 0.268 mmol) and silver triflate (151 mg, 0.590 mmol). The mixture was stirred at room temperature for 5 hours and then filtered through Celite. Solvent was removed under reduced pressure and the solid was washed with pentane (3 x 8 mL) to afford a white solid. Yield: 320 mg (89%). $^{1}H$ NMR (300 MHz, $C_6D_6$, 298K): δ 8.73 (d, $J_{H-H}$ = 6.2 Hz, 2H, py), 6.32 (s, 2H, py), 6.02 (d, $J_{H-H}$ = 6.3 Hz, 2H, py), 1.51 (s, 6H, Me-py), 0.72 (s, 6H, Si-Me), 0.41 (s, 6H, Si-Me). $^{13}C$ NMR (75 MHz, $C_6D_6$, 298K): δ 168.7 (s, py), 152.6 (s, py), 148.7(s, py), 118.4 (s, py), 111.9 (s, py), 20.6 (s, $CH_3$-py), 3.8 (s, $CH_3$-Si), 2.4 (s, $CH_3$-Si). $^{29}Si\{^{1}H\}$ NMR plus $^{1}H$–$^{29}Si$ HMBC (60 MHz, $C_6D_6$, 298 K): δ 38.2 (Si-Ir). $^{19}F$ NMR (282 MHz, $C_6D_6$, 298K): δ -76.97 ($CF_3SO_3$). High resolution mass spectrometry ($ESI^+$): calc. *m/z* = 525.1006; found *m/z* = 525.1004 ($M^+$-$CF_3SO_3$).

**Catalytic Reactions with 1 mol% of 3.** A Young cap NMR tube was charged with 1 mol% of **3** (2.83 mg, 0.0042 mmol), 0.42 mmol of the corresponding silane (114 µL, $HSiMe(OSiMe_3)_2$; 64.4 µL, $HSiMe_2Ph$; 83.7 µL, $HSiMePh_2$) and 0.5 mL of $C_6D_6$. Argon gas was evacuated by three freeze-pump-thaw cycles. Then the tube was pressurized with $CO_2$ (3 bar) or $^{13}CO_2$ (2.7 bar) and heated at 323 K.

**Selected data for $^{13}CH_3O^{13}CO_2SiMe(OSiMe_3)_2$.** $^{1}H$ NMR plus HSQC $^{1}H$–$^{13}C$ (300 MHz, $C_6D_6$, 298 K): δ 3.33 (dd, $J_{H-C}$ = 146.9, 4.1 Hz, 3H, $CH_3OCO_2$). $^{13}C\{^{1}H\}$ plus HSQC and HMBC $^{1}H$–$^{13}C$ (75 MHz, $C_6D_6$, 298 K): δ 153.0 (d, $^{2}J_{C-C}$ = 1.7 Hz, *C*$O_3$), 54.1 (d, $^{2}J_{C-C}$ = 1.7 Hz, $CH_3O$). $^{29}Si\{^{1}H\}$ DEPT-45 NMR plus $^{1}H$–$^{29}Si$ HMBC (60 MHz, $C_6D_6$, 298 K): −55.8 (br, $CH_3OCO_2SiMe(O\underline{Si}Me_3)_2$).

**Selected data for $^{13}CH_3O^{13}CO_2SiMe_2Ph$**. $^{1}H$ NMR plus HSQC $^{1}H$–$^{13}C$ (300 MHz, $C_6D_6$, 298 K): δ 3.30 (dd, $^{1}J_{H-C}$ = 147.1 Hz, $^{3}J_{H-C}$ = 4.1 Hz, 3H, $CH_3OCO_2$). $^{13}C\{^{1}H\}$ plus HSQC and HMBC $^{1}H$–$^{13}C$ (75 MHz, $C_6D_6$, 298 K): δ 154.1 (d, $^{2}J_{C-C}$ = 1.7 Hz, *C*$O_3$), 54.2 (d, $^{2}J_{C-C}$ = 1.7 Hz, $CH_3O$). $^{29}Si\{^{1}H\}$ DEPT-45 NMR plus $^{1}H$–$^{29}Si$ HMBC (60 MHz, $C_6D_6$, 298 K): 14.3 (d, $^{2}J_{Si-C}$ = 0.9 Hz, $CH_3OCO_2$*Si*$Me_2Ph$).

**Selected data for $^{13}CH_3O^{13}CO_2SiMePh_2$**. $^{1}H$ NMR plus HSQC $^{1}H$–$^{13}C$ (300 MHz, $C_6D_6$, 298 K): δ 3.23 (dd, $^{1}J_{H-C}$ = 147.1 Hz, $^{3}J_{H-C}$ = 4.1 Hz, 3H, $CH_3OCO_2$). $^{13}C\{^{1}H\}$ plus HSQC and HMBC $^{1}H$–$^{13}C$ (75 MHz, $C_6D_6$, 298 K): δ 153.9 (d, $^{2}J_{C-C}$ = 1.7 Hz, *C*$O_3$), 54.3 (d, $^{2}J_{C-C}$ = 1.7 Hz, $CH_3O$). $^{29}Si\{^{1}H\}$ DEPT-45 NMR plus $^{1}H$–$^{29}Si$ HMBC (60 MHz, $C_6D_6$, 298 K): 2.07 (d, $^{2}J_{Si-C}$ = 1.1 Hz, $CH_3OCO_2$*Si*$MePh_2$).

## **2.** NMR Characterization of complex **3**

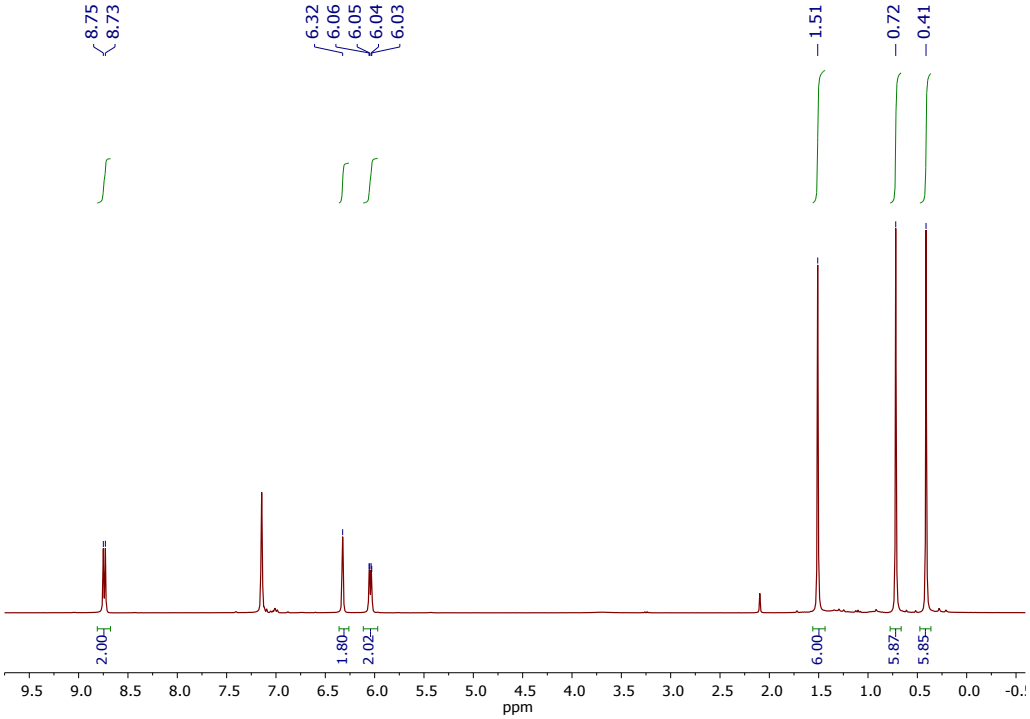


**Figure S1.** [1]H-NMR spectrum of complex **3**

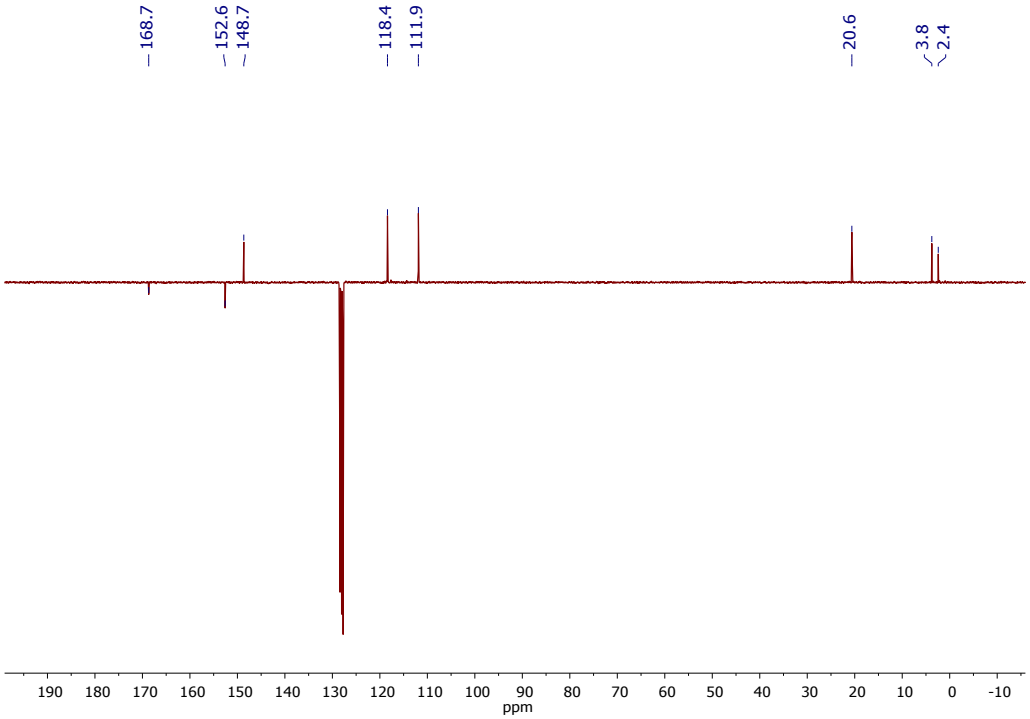


**Figure S2.** [13]C APT NMR spectrum of complex **3**

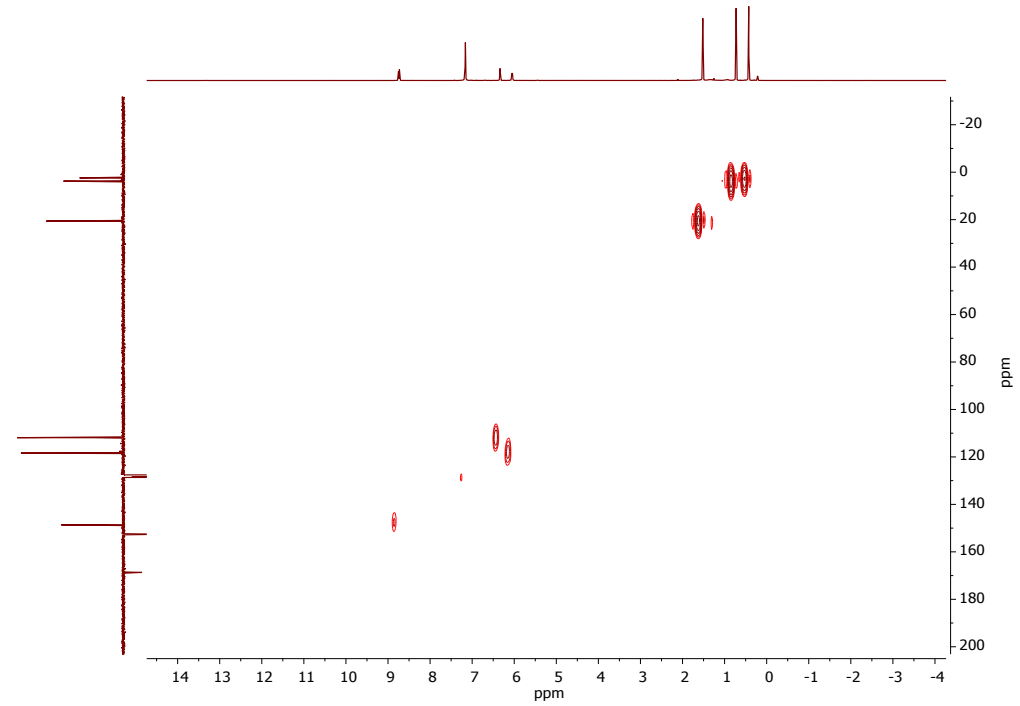


**Figure S3.** $^{1}H–^{13}C$ HSQC spectrum of complex **3**

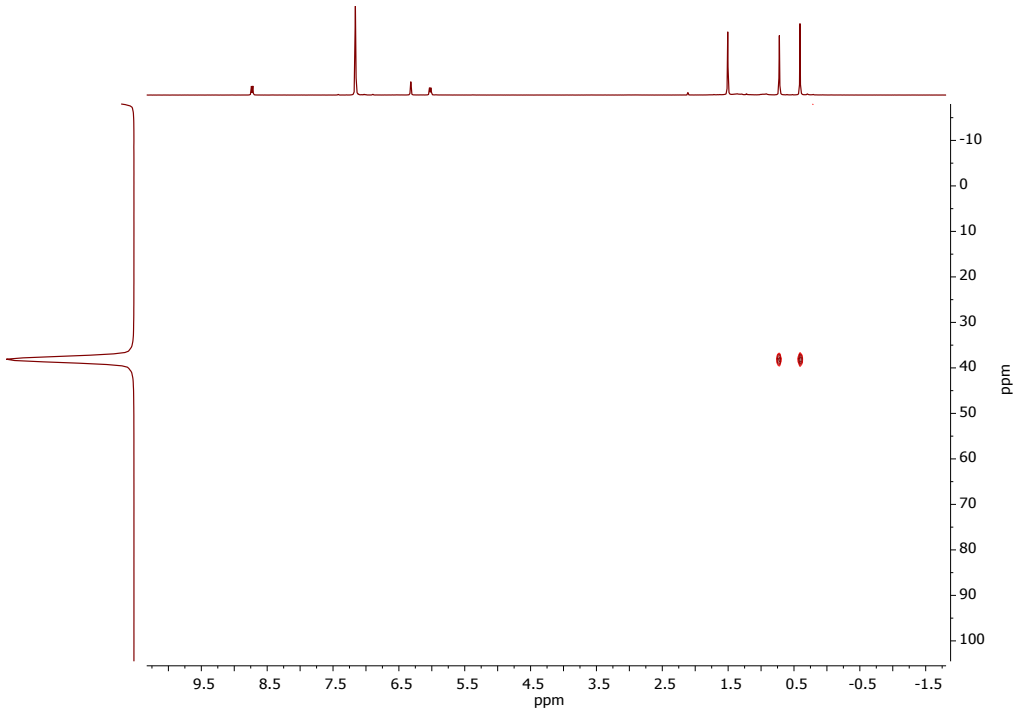


**Figure S4.** $^{1}H–^{29}Si$ HMBC spectrum of complex **3**

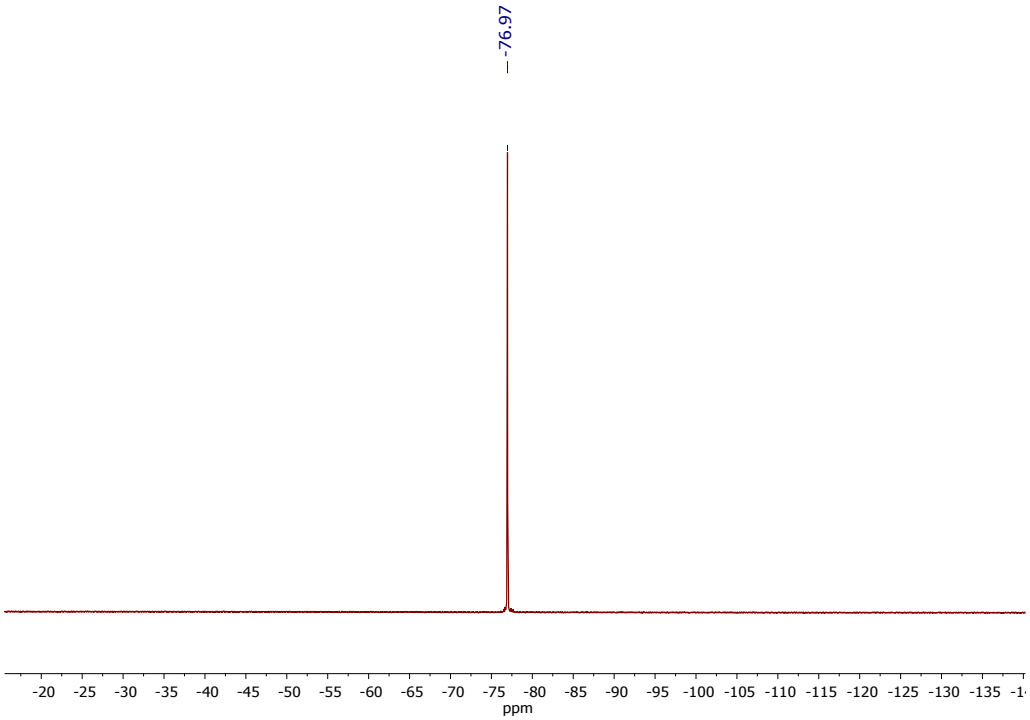


**Figure S5.** $^{19}F$ NMR spectrum of complex **3**

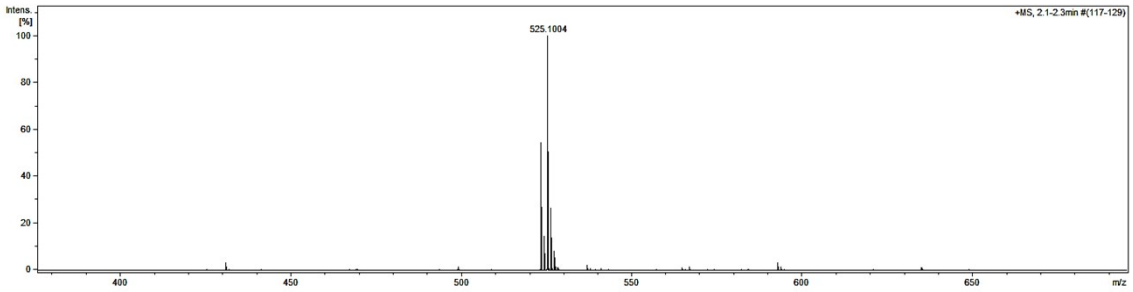


**Figure S6.** HR-MS spectrum of complex **3**

## **3.** NMR characterization of the methyl-silyl-carbonates species

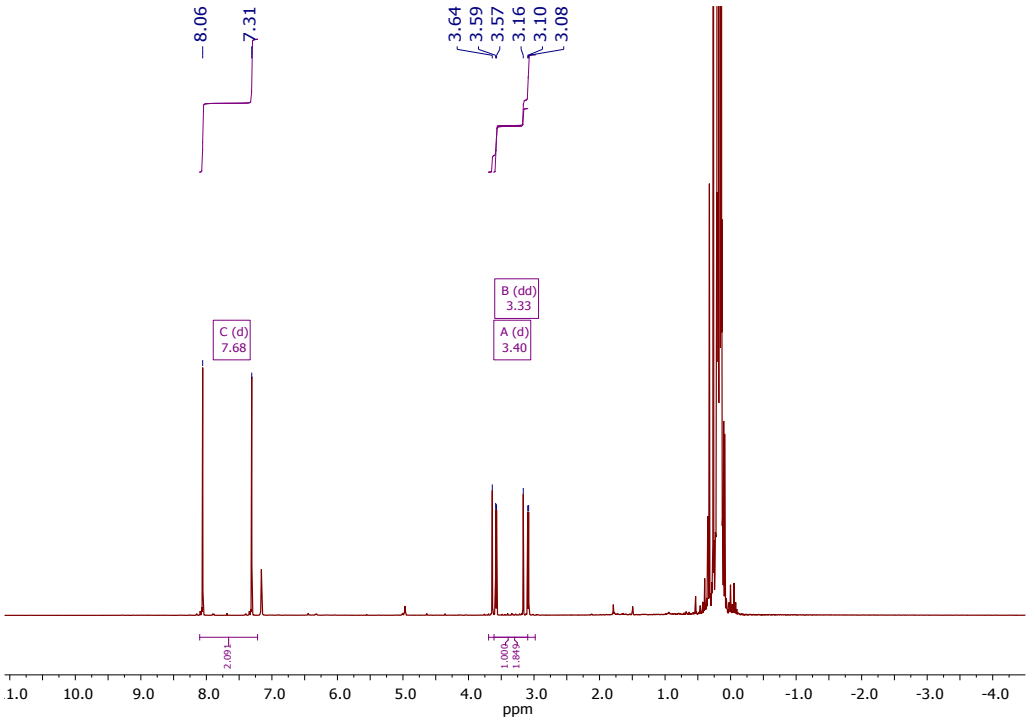


**Figure S7.** $^{1}H$ NMR from the **3**-catalyzed reaction of $^{13}CO_2$ with HMTS after 12 hours

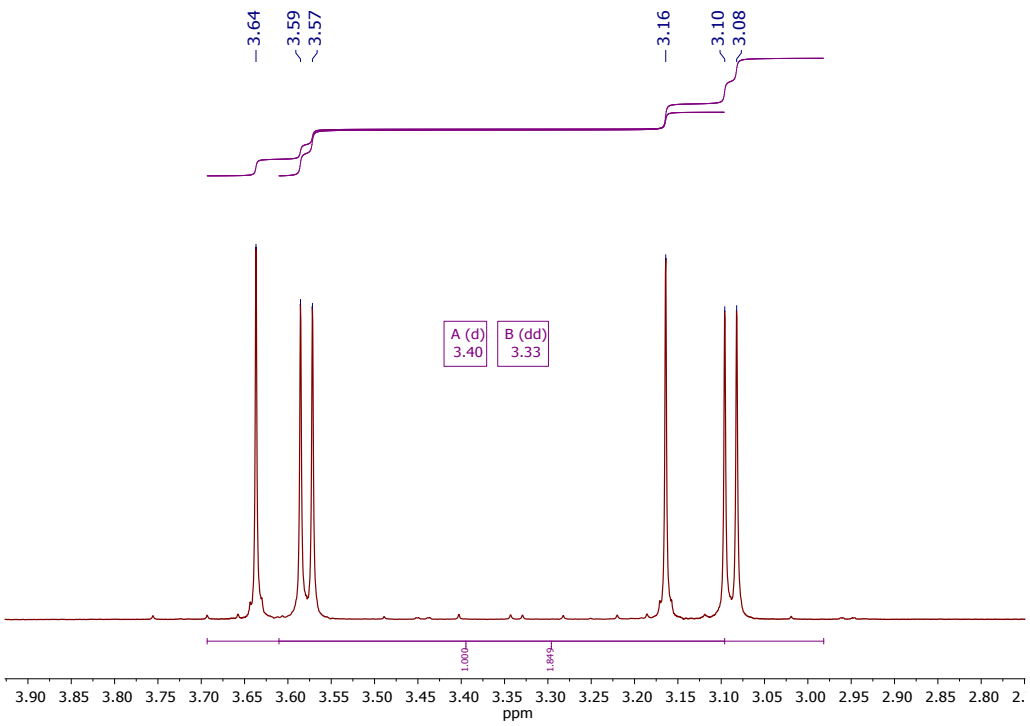


**Figure S8.** $^{1}H$ NMR detail showing the *$^{13}CH_3O$-* products. [A = $^{13}CH_3OSiMe(OSiMe_3)_2$; B = $^{13}CH_3O^{13}CO_2SiMe(OSiMe_3)_2$]

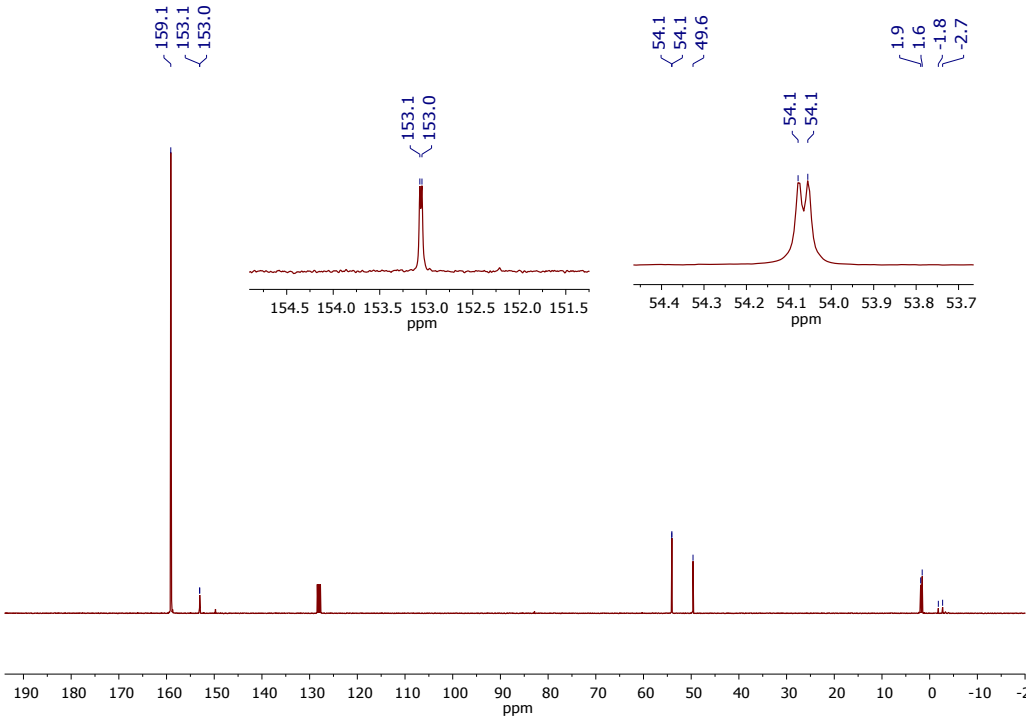


**Figure S9.** $^{13}C\{^{1}H\}$ NMR from the **3**-catalyzed reaction of $^{13}CO_2$ with HMTS after 12 hours (with details showing the $^{13}C$-$^{13}C$ coupling in the $^{13}CH_3O^{13}CO_2SiMe(OSiMe_3)_2$ compound)

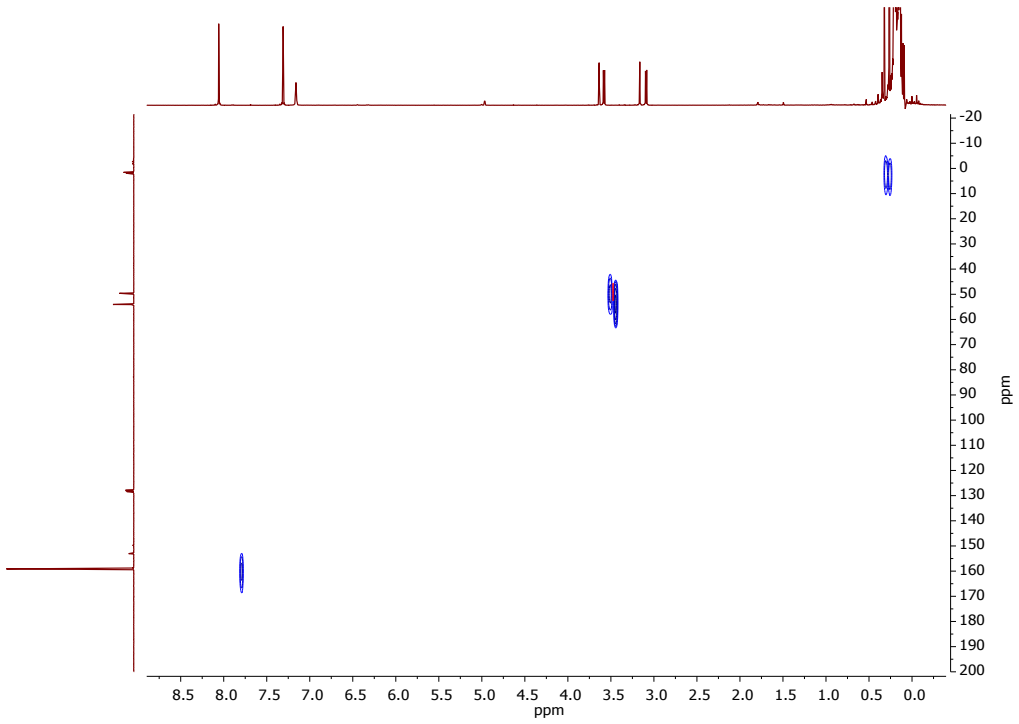


**Figure S10.** $^{1}H$–$^{13}C$ HSQC spectrum from the **3**-catalyzed reaction of $^{13}CO_2$ with HMTS

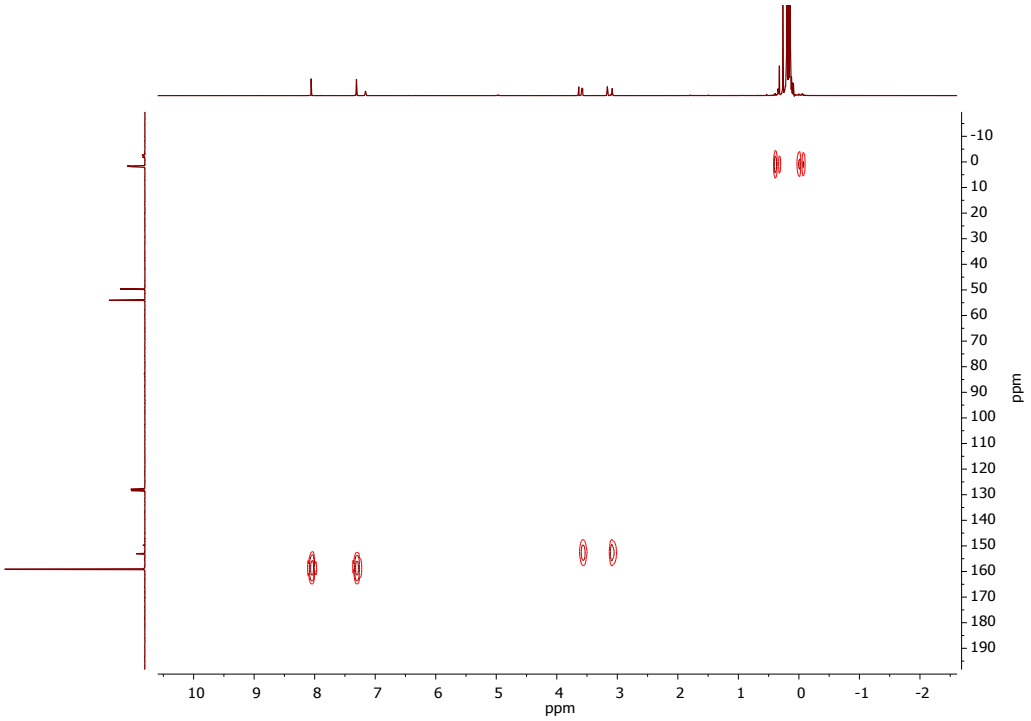


**Figure S11.** $^{1}H–^{13}C$ HMBC spectrum from the **3**-catalyzed reaction of $^{13}CO_2$ with HMTS

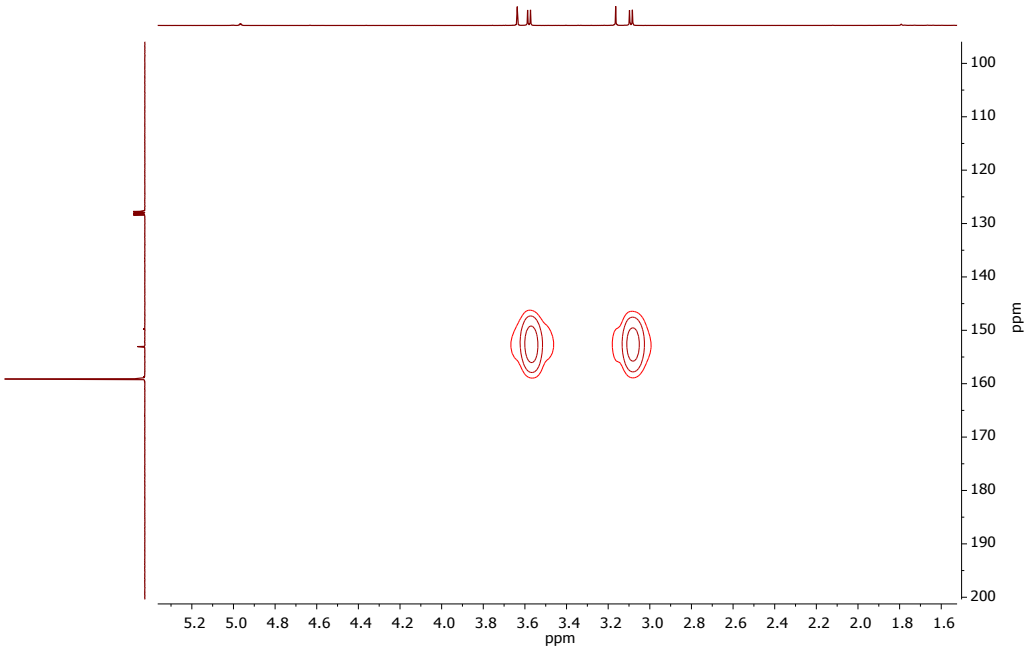


**Figure S12.** Detail from $^{1}H–^{13}C$ HMBC spectrum showing multiple bond correlation of the $CH_3O$ protons with the carbonate

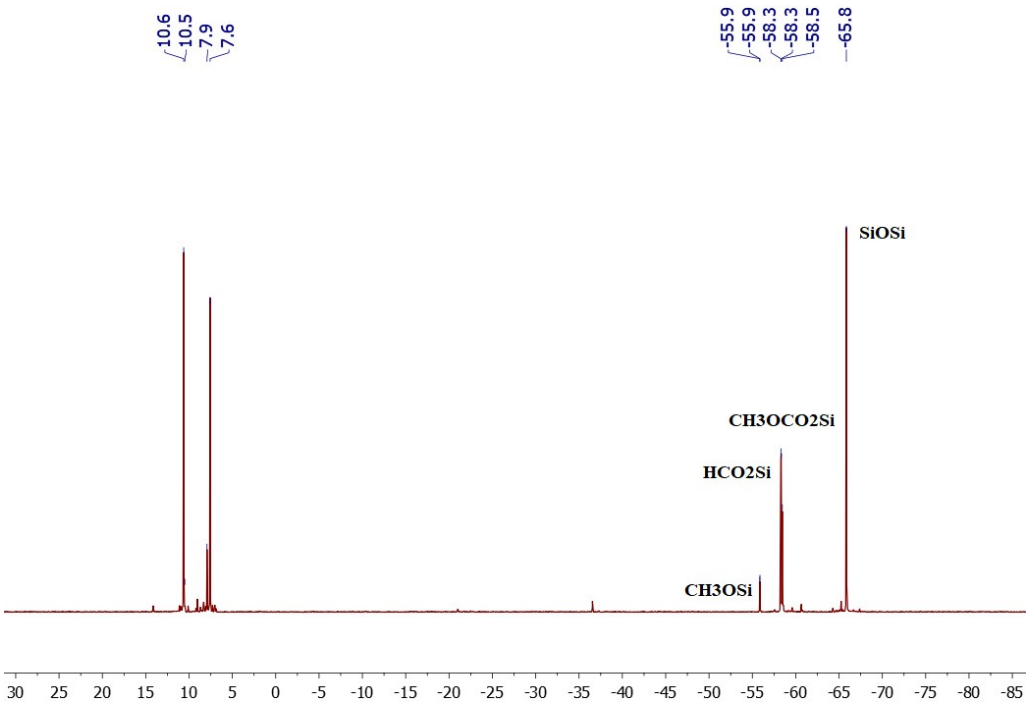


**Figure S13.** $^{29}$Si DEPT from the **3**-catalyzed reaction of $^{13}CO_2$ with HMTS

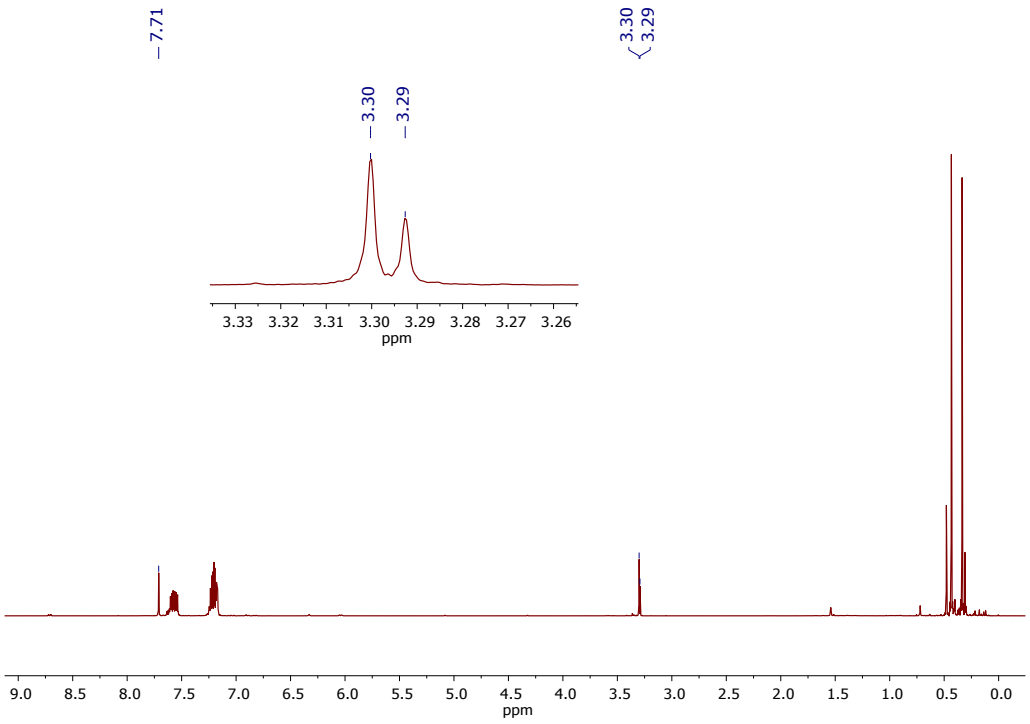


**Figure S14.** $^{1}$H NMR from the **3**-catalyzed reaction of $^{12}CO_2$ with $HSiMe_2Ph$

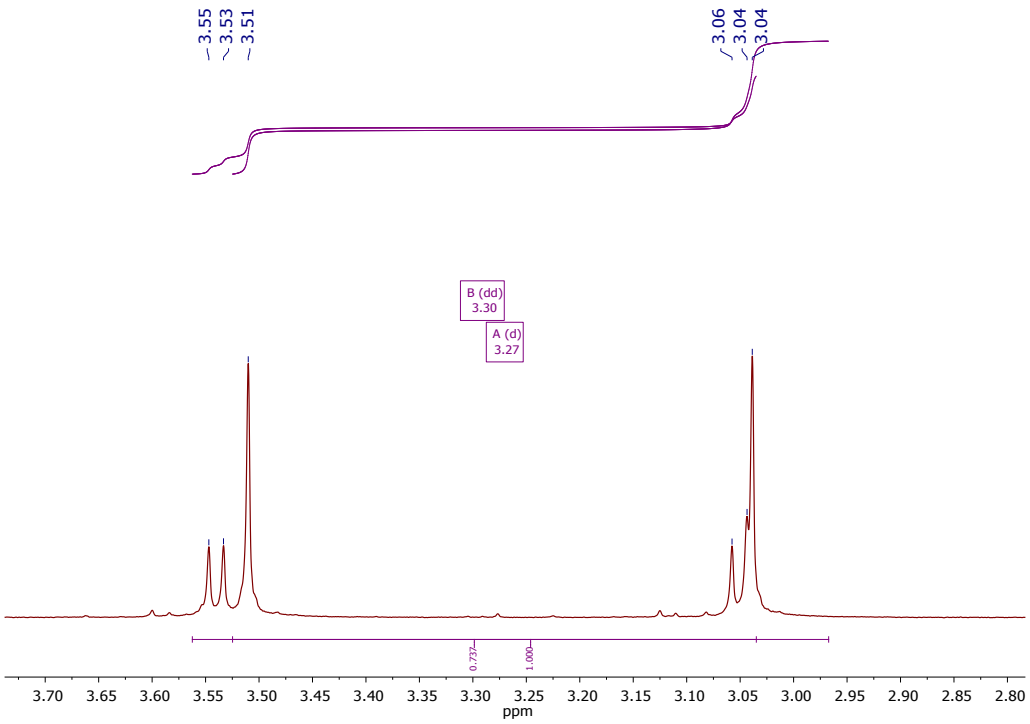


**Figure S15.** $^{1}H$ NMR detail from the **3**-catalyzed reaction of $^{13}CO_2$ with $HSiMe_2Ph$ (**A**, $^{13}CH_3OSiMe_2Ph$; **B**, $^{13}CH_3O^{13}CO_2SiMe_2Ph$)

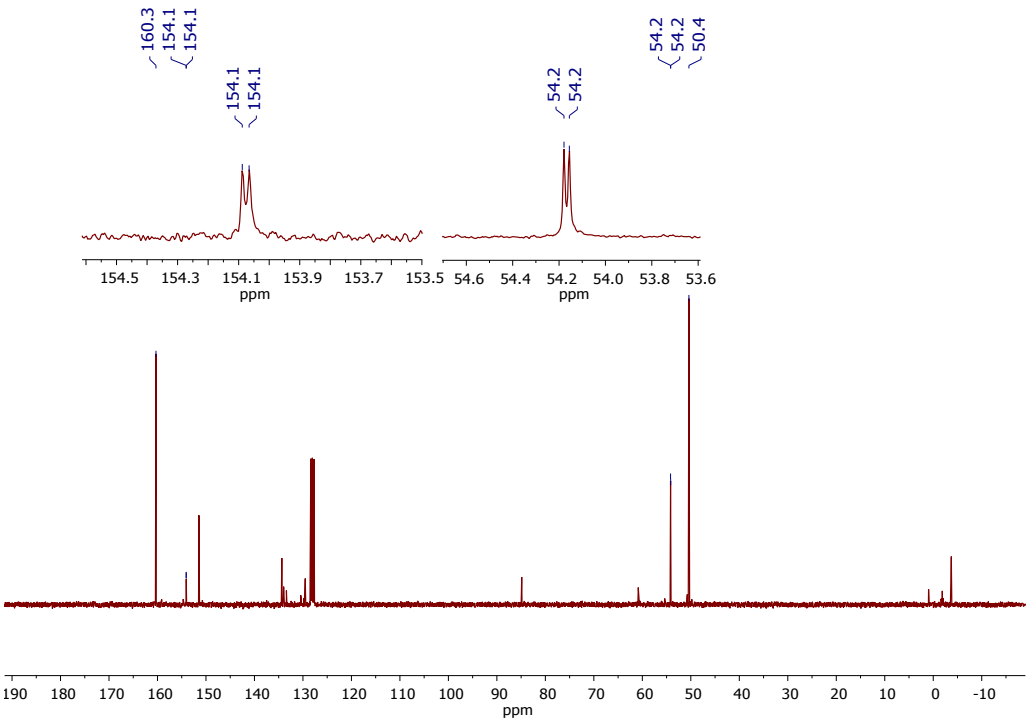


**Figure S16.** $^{13}C\{^{1}H\}$ NMR from the **3**-catalyzed reaction of $^{13}CO_2$ with $HSiMe_2Ph$ (with details showing the $^{13}C$-$^{13}C$ coupling in the $^{13}CH_3O^{13}CO_2SiMe_2Ph$ compound)

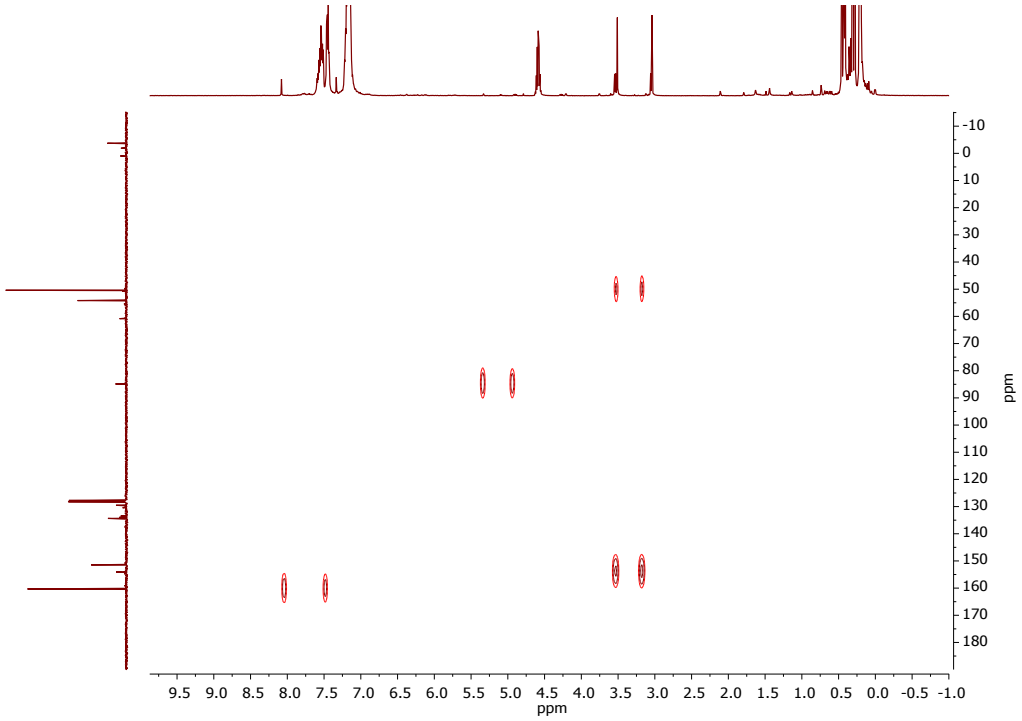


**Figure S17.** $^{1}H$–$^{13}C$ HMBC spectrum from the **3**-catalyzed reaction of $^{13}CO_2$ with $HSiMe_2Ph$

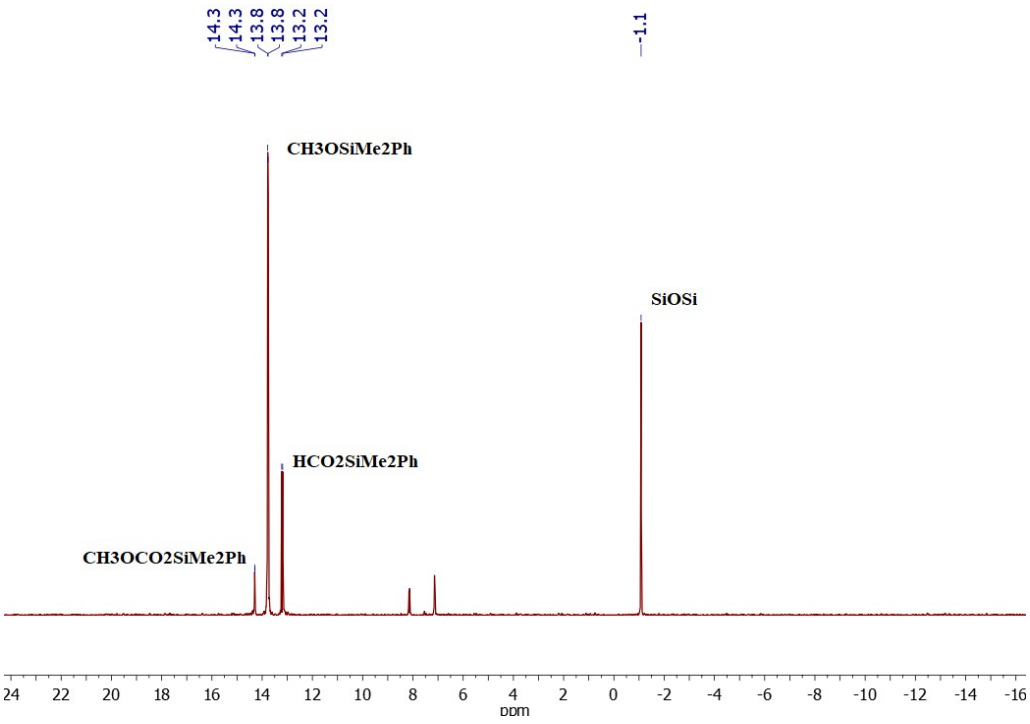


**Figure S18.** $^{29}Si$ DEPT from the **3**-catalyzed reaction of $^{13}CO_2$ with $HSiMe_2Ph$

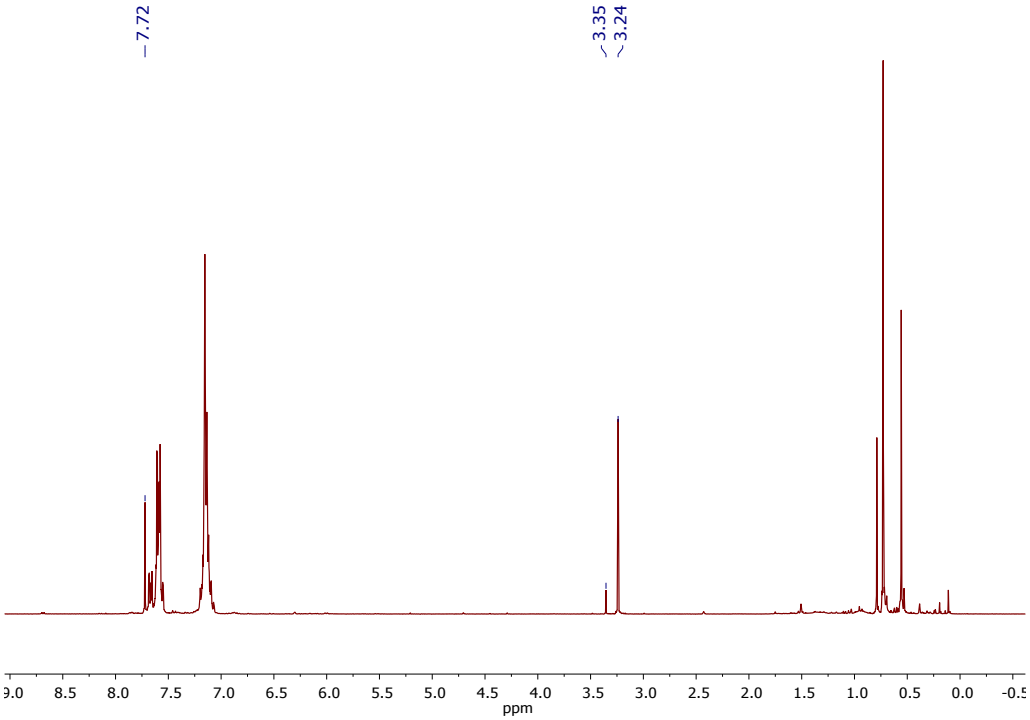


**Figure S19.** $^{1}$H NMR from the **3**-catalyzed reaction of $^{12}CO_2$ with $HSiMePh_2$

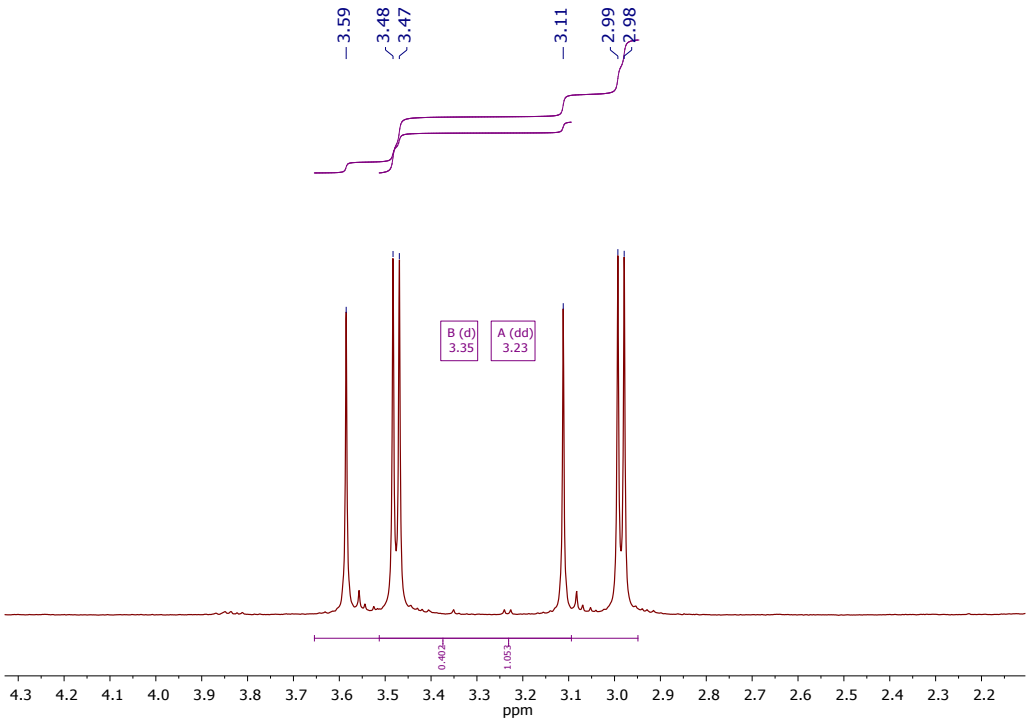


**Figure S20.** $^{1}$H NMR detail from the **3**-catalyzed reaction of $^{13}CO_2$ with $HSiMePh_2$ (**A**, $^{13}CH_3O^{13}CO_2SiMePh_2$; **B**, $^{13}CH_3OSiMePh_2$)

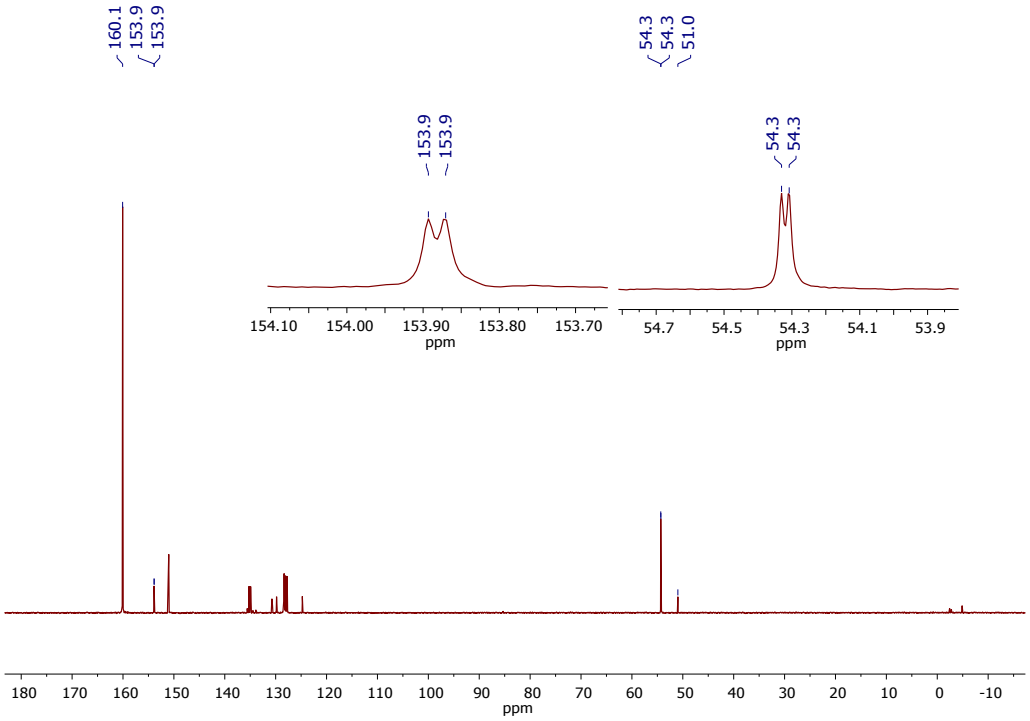


**Figure S21.** $^{13}C\{^{1}H\}$ NMR from the **3**-catalyzed reaction of $^{13}CO_2$ with $HSiMePh_2$ (with details showing the $^{13}C$-$^{13}C$ coupling in the $^{13}CH_3O^{13}CO_2SiMePh_2$ compound)

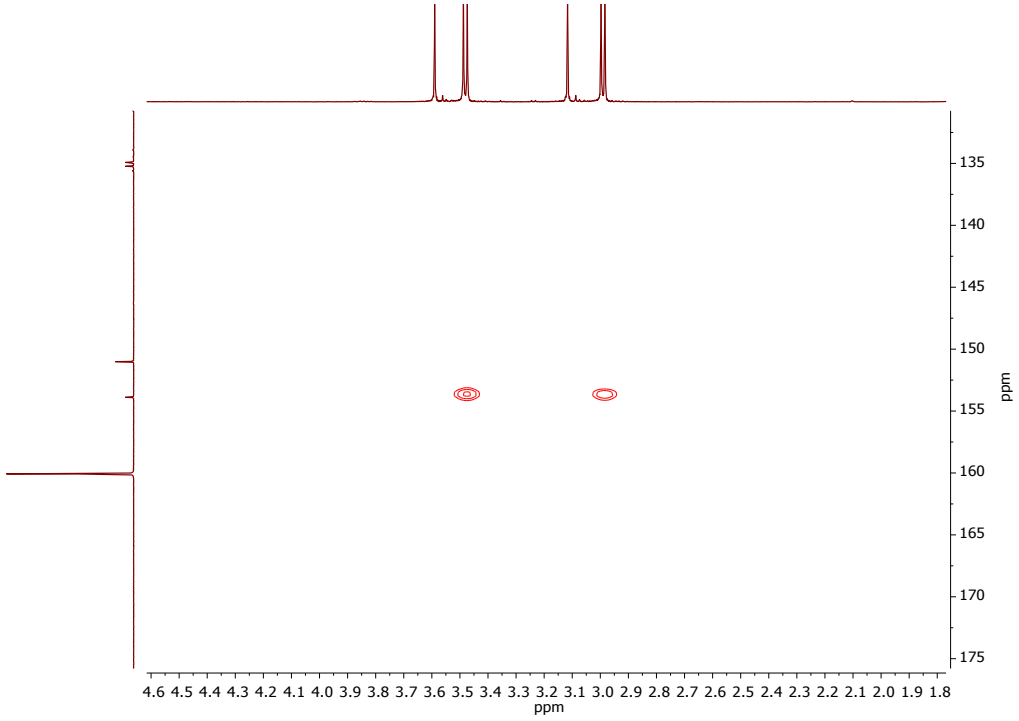


**Figure S22.** $^{1}H$–$^{13}C$ HMBC spectrum from the **3**-catalyzed reaction of $^{13}CO_2$ with $HSiMePh_2$

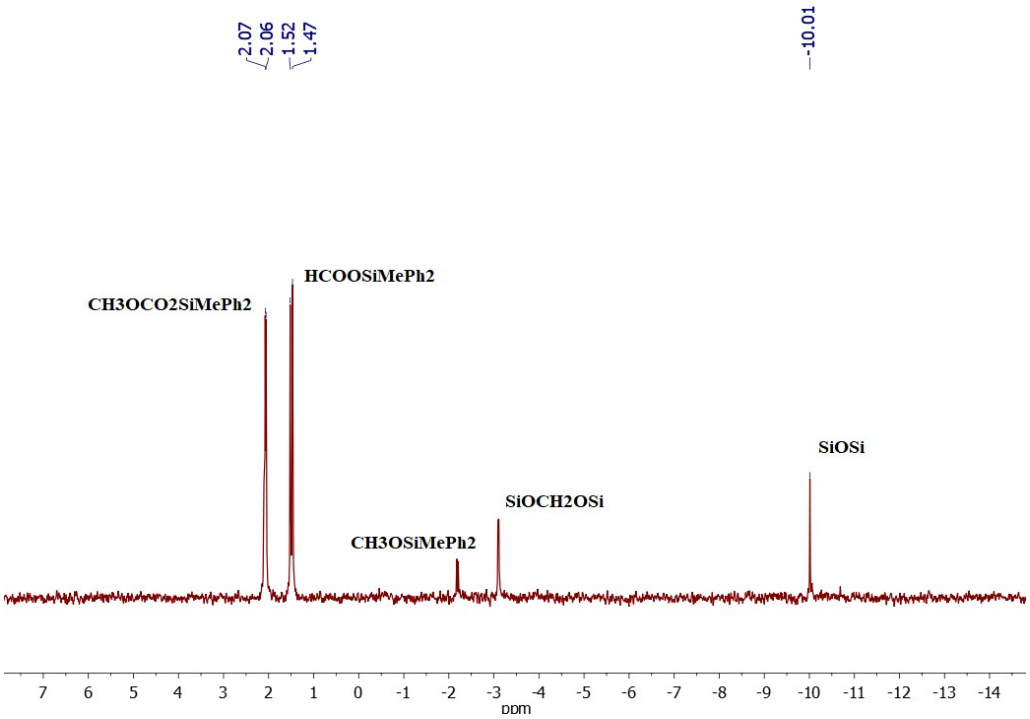


**Figure S23.** $^{29}$Si DEPT from the **3**-catalyzed reaction of $^{13}CO_2$ with $HSiMePh_2$

## **4.** Control Experiment

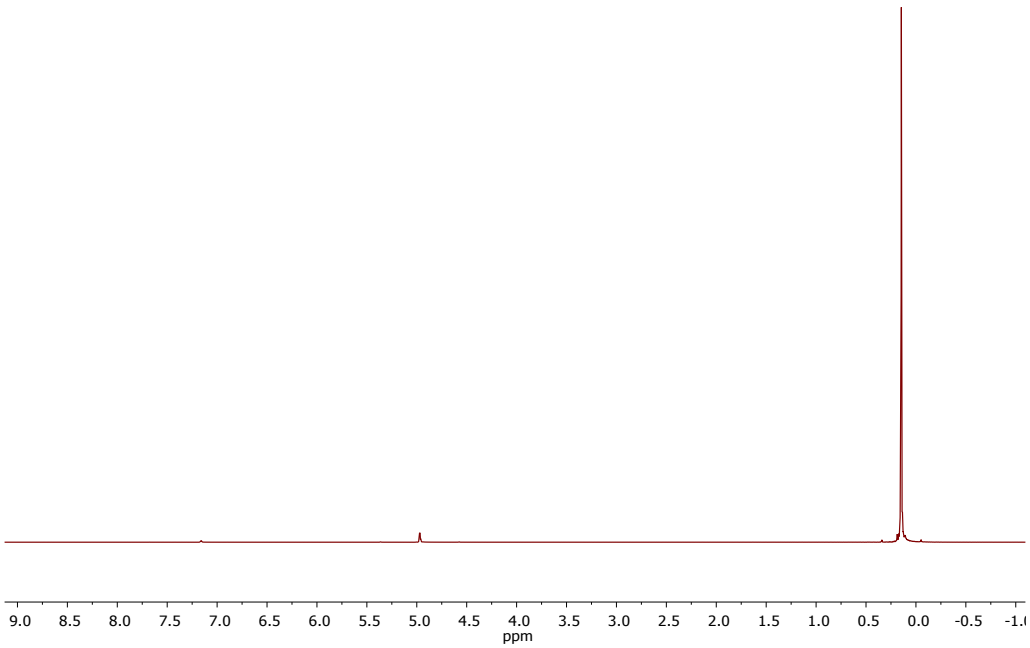


**Figure S24.** $^{1}$H NMR from the mixture of $CO_2$ and $HSiMe(OSiMe_3)_2$ in absence of **3** in $C_6D_6$ after 24h at 323K

## **5.** Crystal Structure Determination of Complex **3**

Single crystal X-ray diffraction data were collected at 100(2) K with graphite-monochromated Mo Kα radiation (λ=0.71072 Å) using narrow frame rotation (Δω=0.3°) on a Bruker Smart APEX diffractometer. Measured intensities were integrated and corrected for absorption effects with SAINT+[S1] and SABABS[S2] programs, included in APEX2 package. The structure was solved with direct methods with SHELXS-2013[S3] and refined by full-matrix least-squares refinement on $F^2$ with SHELXL-2018[S4] program, included in WingX package.[S5] The disordered solvent region has been analyzed with SQUEEZE program.[S6]

CCDC 1972218 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Crystal data compound **3**. $C_{34}H_{48}F_6Ir_2N_4O_{10}S_2Si_4 \cdot 0.5(H_2O)$; $M$ = 1364.65; colourless prism 0.140 x 0.240 x 0.330 mm$^3$; triclinic $P\bar{1}$, $a$ = 9.0468(5), $b$ = 12.0453(6), $c$ = 12.0619(7) Å, $\alpha$=66.4720(10), $\beta$=88.5460(10), $\gamma$ = 88.7690(10)°, $V$ = 1204.65(11) Å$^3$; $Z$ = 1; $D_c$ = 1.881 g/cm$^3$; $\mu$ = 5.783 mm$^{-1}$; $T_{min}/T_{max}$: 0.1676/0.5996; 23425/5849 reflections measured/unique ($R_{int}$ = 0.0179), number of data/restraint /parameters 5849/0/286, $R_1(F^2)$ = 0.0131 (5771 reflections, $I > 2\sigma(I)$) and w$R(F^2)$ = 0.0324 (all data), final $GoF$ = 1.034, largest difference peak: 0.988 e.Å$^{-3}$.

**Crystallographic references**


S1 SAINT+, version 6.01: Area-Detector Integration Software, Bruker AXS, Madison 2001.

S2 SADABS 2016/02. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr*. 2015, **48**, 3-10.

S2 (a) G. M. Sheldrick, *Acta Crystallogr*. *A* 1990, **46**, 467-473; (b) G. M. Sheldrick, *Acta Crystallogr*. *A* 2008, **64**, 112-122.

S3 G. M. Sheldrick, *Acta Crystallogr*. *C* 2015, **71**, 3-8.

S4 L. J. Farrugia, *J. Appl. Crystallogr*. 2012, **45**, 849-854.

S5 P. van der Sluis, A. L. Spek, *Acta Crystalogr.* 1990, **A46**, 194−201.


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