Supporting Information for:

Phosphazenes: Efficient Organocatalysts for the Catalytic Hydrosilylation of Carbon Dioxide

Marc-André Courtemanche,[a] Marc-André Légaré[a], Étienne Rochette[a], and Frédéric-Georges Fontaine*[a]

Département de Chimie, Université Laval, 1045 Avenue de la Médecine
Québec, QC, Canada, G1V 0A6.

*Email : frederic.fontaine@chm.ulaval.ca

Contents

S0: General experimental:

While no particular precautions were made to avoid contact with air for most of the catalytic reactions, the phosphazene bases and the preparation of the catalytic experiments have been handled under an inert atmosphere of dinitrogen. Reactions were carried either in a sealed J-Young NMR tube, in which case NMR conversions are indicated, or in standard oven dried vials or schlenk vessels. Benzene-d_6 was purified by vacuum distillation from Na/K alloy, bone dry CO_2 was purchased from Praxair and used as received. $^{13}CO_2$ (99% isotope label) was purchased from Cambridge Isotope Laboratories and stored over $CaCl_2$. Phosphazene bases, solvents, DMF-*d7* and silanes were purchased from Sigma Aldrich and used as received without further purification

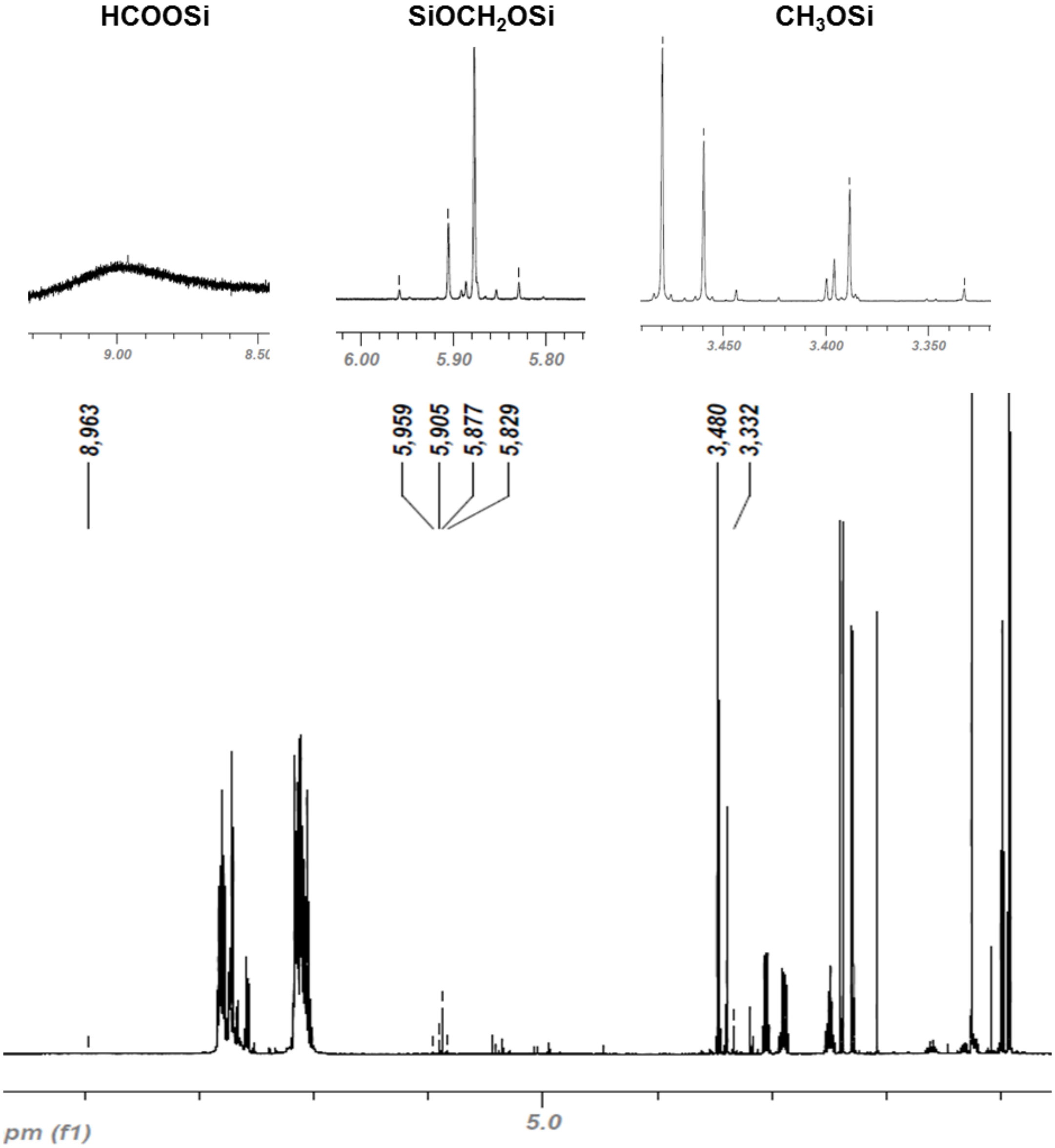
NMR spectra were recorded on Agilent Technologies NMR spectrometer at 500 MHz (^1H), 125.758 MHz (^{13}C), 202.456 MHz (^{31}P) 160.46 MHz, a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^1H), 100.580 MHz (^{13}C), 161.923 MHz (^{31}P), or on a Bruker NMR AC-300 at 300MHz (^1H), 75.435 MHz (^{13}C), 121.442 MHz (^{31}P). ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are referenced to residual protons in deuterated solvent. Multiplicities are reported as singlet (s), broad singlet (s, br) doublet (d), triplet (t), multiplet (m). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. gHSQC experiments were performed in order to confirm C-H correlations. GC-MS characterization was carried out using a Thermo Scientific trace GC ultra coupled with a ITQ 900 mass spectrometer using electronic impact (EI) ionization.

WARNING: Condensation of high pressure of CO_2 might lead to an explosion of the glassware. Care should be taken.

S1: Initial test experiment:

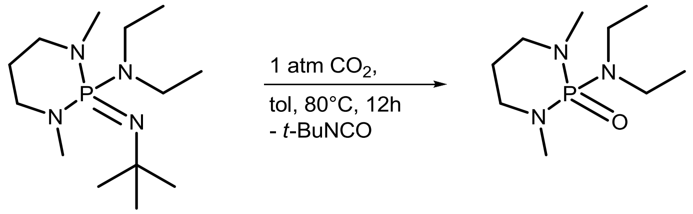
7.8 mg (0.028 mmol) of **1** along with 26.2 mg (0.142 mmol) of Ph_2SiH_2 were dissolved in benzene-d_6 and introduced into a gas tight J-Young NMR tube. CO_2 was added by freezing the solution in a liquid nitrogen bath and leaving the sample under vacuum for *ca* 3 minutes. The liquid nitrogen bath was removed and the sample was left to warm up for 20 seconds after which CO_2 was introduced into the tube. The sample was then heated at 80°C in an oil bath after which it was analyzed by NMR spectroscopy.

Figure S1: Spectrum of the reaction described in **S1** and select regions, showing the formation of CO_2 reduction products

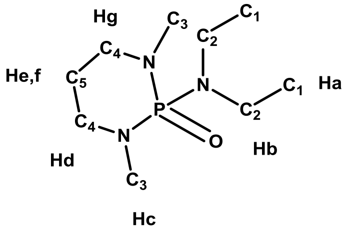


S2: Rearrangement of **1** to **4**

200 mg of **1** (0.73 mmol) were placed in a sealable schlenk tube along with 1mL of toluene. The solution was frozen in liquid nitrogen and CO_2 was introduced following the procedure described in **S1**. The reaction was heated at 80 °C for 12 hours after which the volatiles were removed in vacuo, yielding pure **4** as colorless oil, 150mg, Yield = 94% (crude)

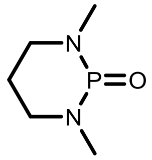


1 **4**

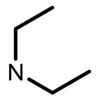


4: ^{1}H NMR 500MHZ: δ 3.07 (m, 4H, H_d); 2.9 (m, 2H, H_d or H_g); 2.48 (m, 2H, H_d or H_g); 2.39 (d, $^3J_{P\text{-}H}$:11.0Hz, 6H, H_c); 1.60 (m, 1H, He or Hf);1.20 (m, 1H, He or Hf); 0.99 (t, $^3J_{H\text{-}H}$=7.1 Hz, 6H, Ha).^{13}C {^{1}H} (126 MHz): δ 51.0 (s, 2C, C_3); 39.7 (d, $^2J_{P\text{-}C}$=5.3Hz, 2C, C_2); 35.5 (s, 2C, C_4); 26.3 (s, 1C, C_5); 14.4 (s, 2C, C_1). ^{31}P {^{1}H} (202MHz): δ 21.8 (s, 1P).

MS (EI):



calcd:147.14
found:147.21



calcd:72.13
found:72.17

Figure S2A: ^{1}H NMR spectra of **4**

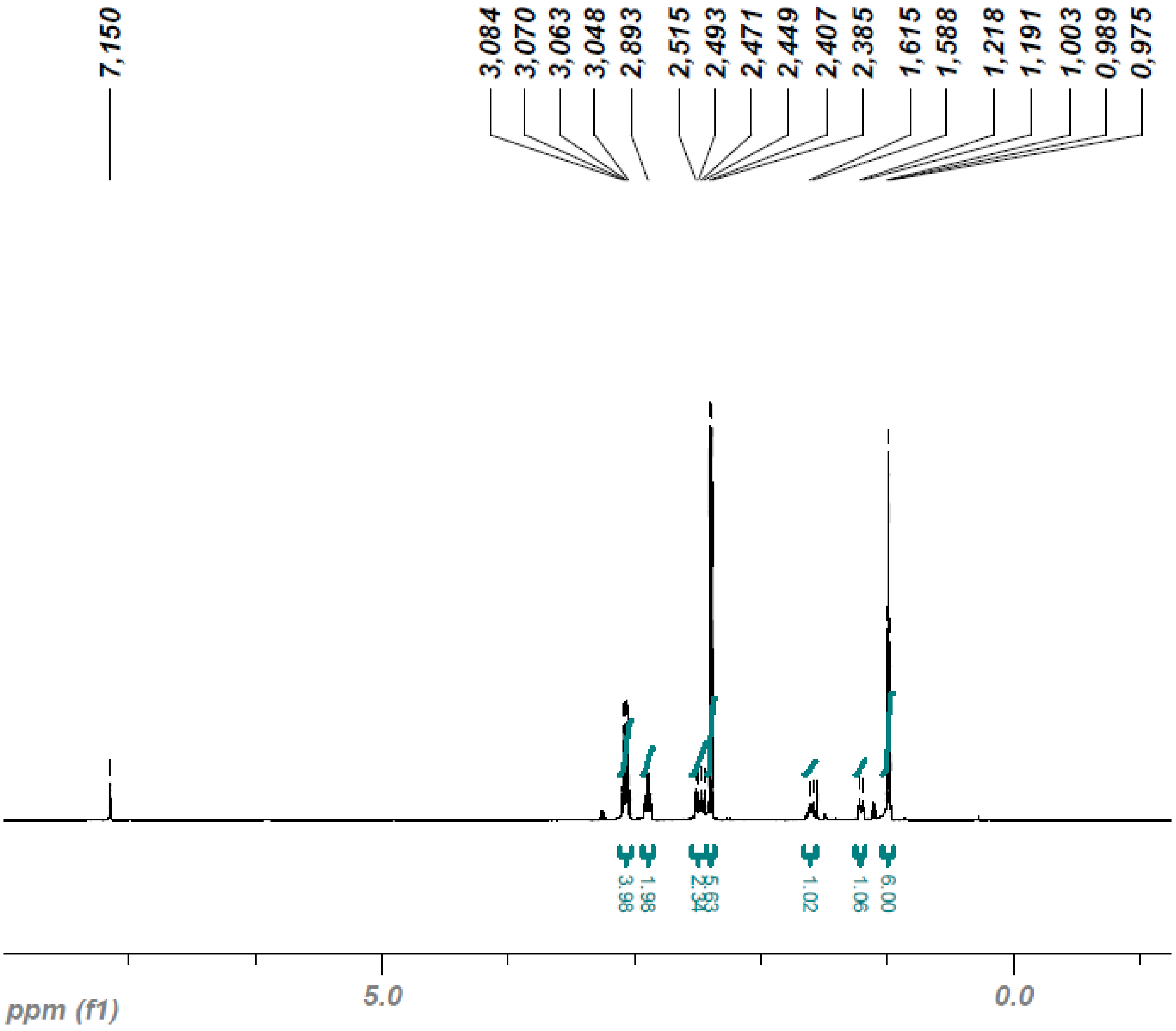


Figure S2B: $^{31}P\ \{^{1}H\}$ NMR spectra of **4**

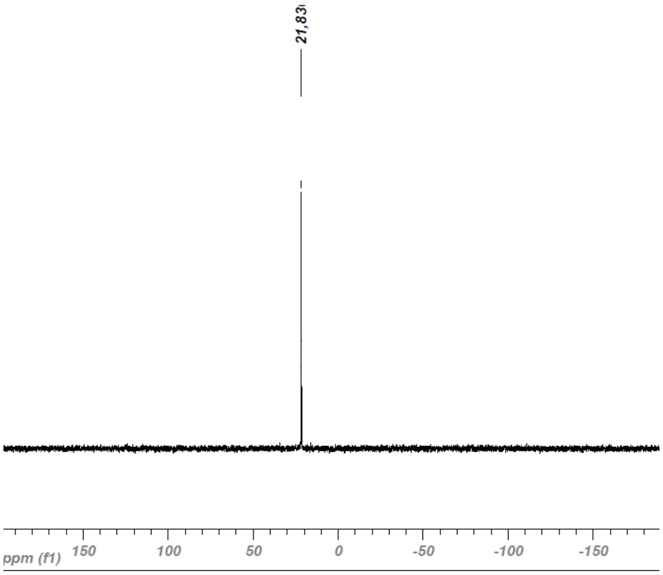
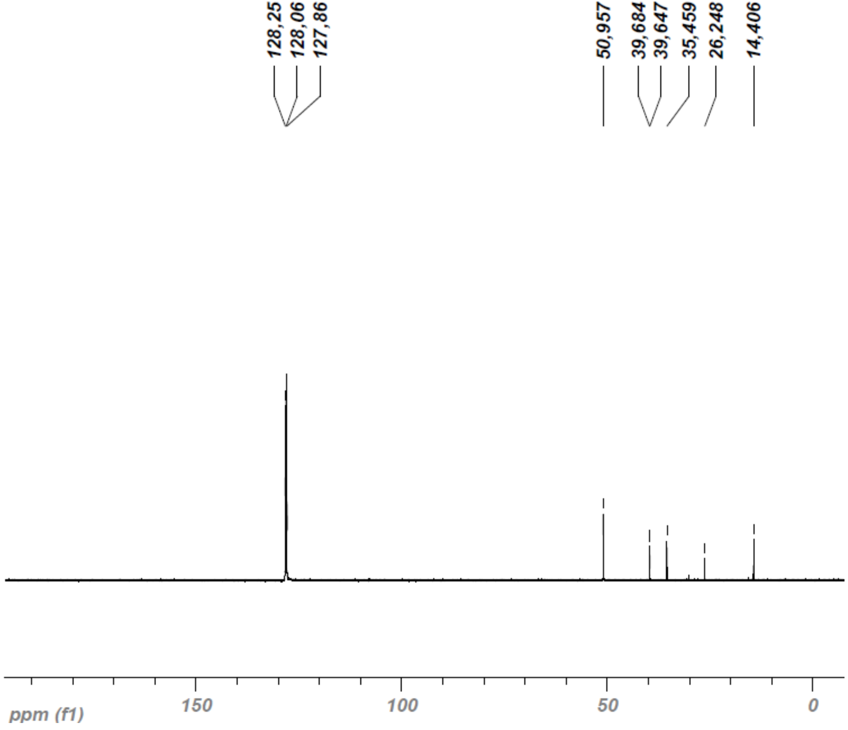
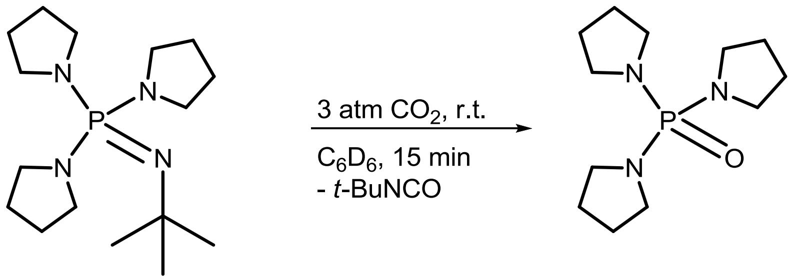


Figure S2C: $^{13}C\ \{^{1}H\}$ NMR spectra of **4**

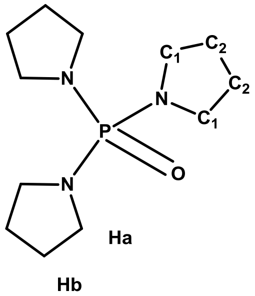


S3: Reaction of **2** with CO_2



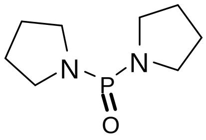
2 **5**

6.5 mg (0.021 mmol) of **2** were dissolved in 0.4 mL of benzene-d_6 and exposed to CO_2 following the procedure described in **S1**. The compound was left to react for 15 minutes after which the volatiles were removed in vacuo and the sample redissolved in benzene-d_6. Yield =quantitative (by NMR).

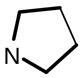


5: ^{1}H NMR 500MHZ: δ 3.11 (m, 12H, H_a); 1.5 (m, 12H, H_b).^{13}C {^{1}H} (126 MHz): δ 46.7 (d, 12C, $^2J_{P\text{-}C}$=5.3Hz); 26.7 (d, 12C, $^3J_{P\text{-}C}$=7.6 Hz). ^{31}P {^{1}H} (202MHz): δ 14.9 (s, 1P)

MS (EI):



calcd:187.10
found:187.24



calcd:70.11
found:70.12

Figure S3A: ^1H NMR of **5**

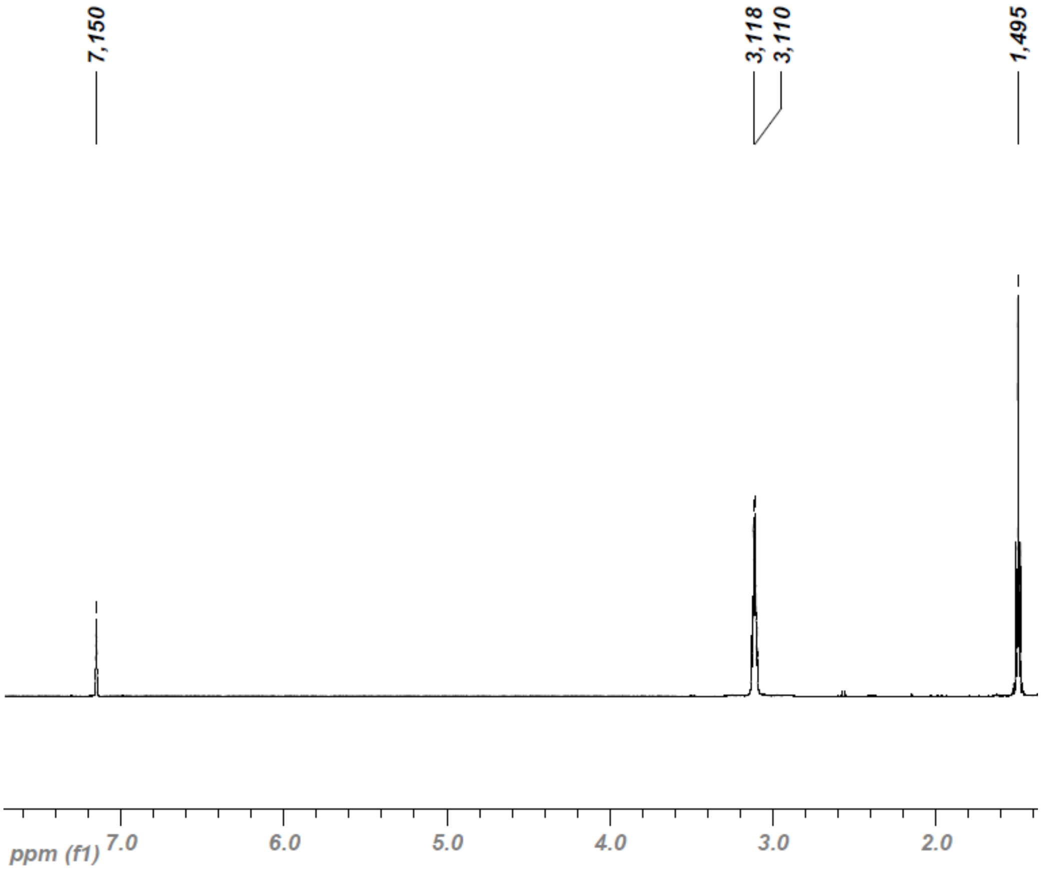


Figure S3B: $^{13}C\{^1H\}$ NMR of **5**

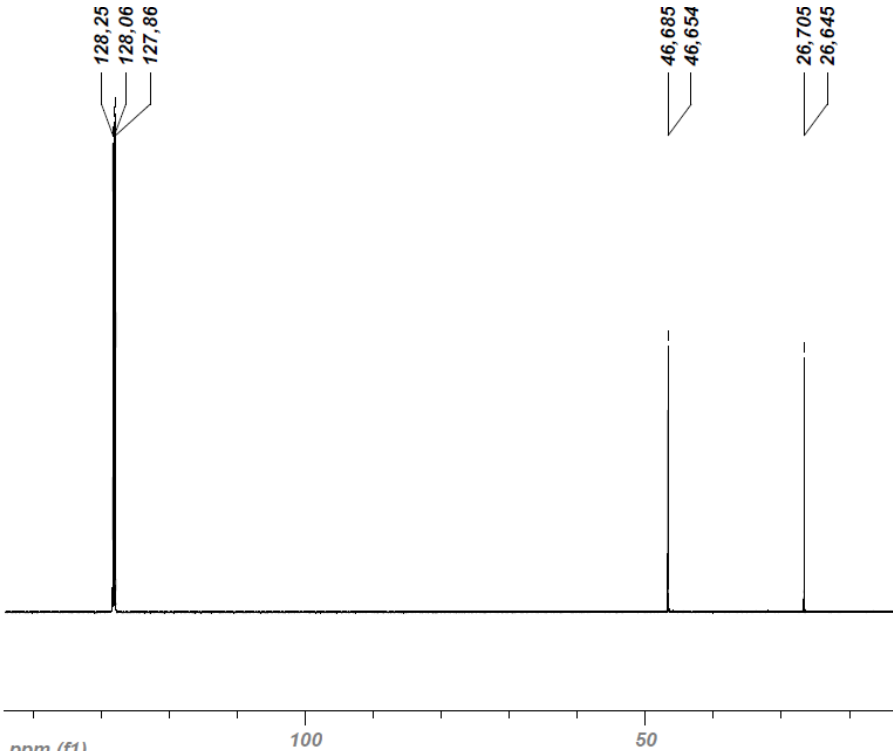
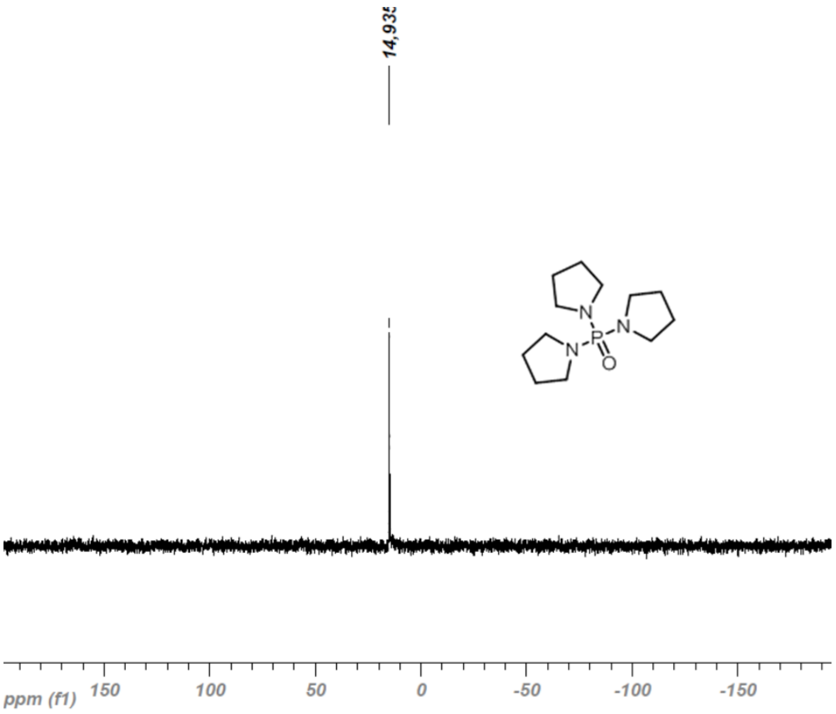
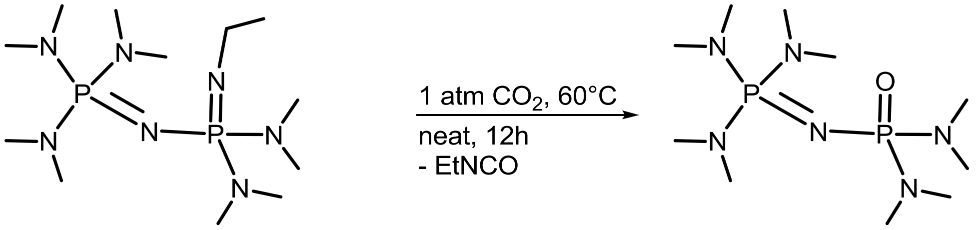


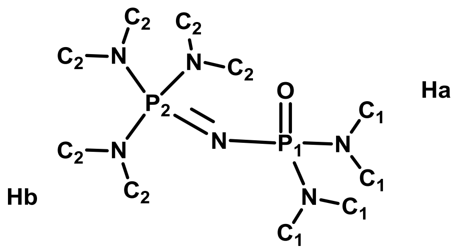
Figure S3C: $^{31}P\{^1H\}$ NMR of **5**



S4 Reaction of **3** with CO_2.



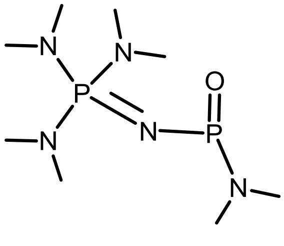
3 **6**



208 mg of **3** (0.61 mmol) was introduced in a vial (with no cap) which was deposited at the bottom of a Schlenk tube. The Schlenk tube was put under a constant flow of carbon dioxide in an oil bath maintained at 60 °C overnight. After 12 hours of reaction ,the volatiles were removed in vacuo, yielding 189 mg of crude **6** (Yield =99%).

6: ^{1}H NMR 500MHZ: δ 2.8 (d, $^3J_{P\text{-}H}$=10.8 Hz, 18H, H_b); 2.42 (d, $^3J_{P\text{-}H}$=9.4 Hz, 12H, H_b).^{13}C {^{1}H} (126 MHz): δ 38.2 (bs, 4C,C_1); 37.1 (bs, 6C, C_2). ^{31}P{^{1}H} (202MHz): δ 22.5 (d, $^2J_{P\text{-}P}$=43.0 Hz 1P, P1); 12.4 (d, $^2J_{P\text{-}P}$=43.0 Hz 1P, P2).

MS (EI): (**6** –NMe_2)



calcd: 268.15
found: 268.4

Figure S4A: ^{1}H NMR of **6**

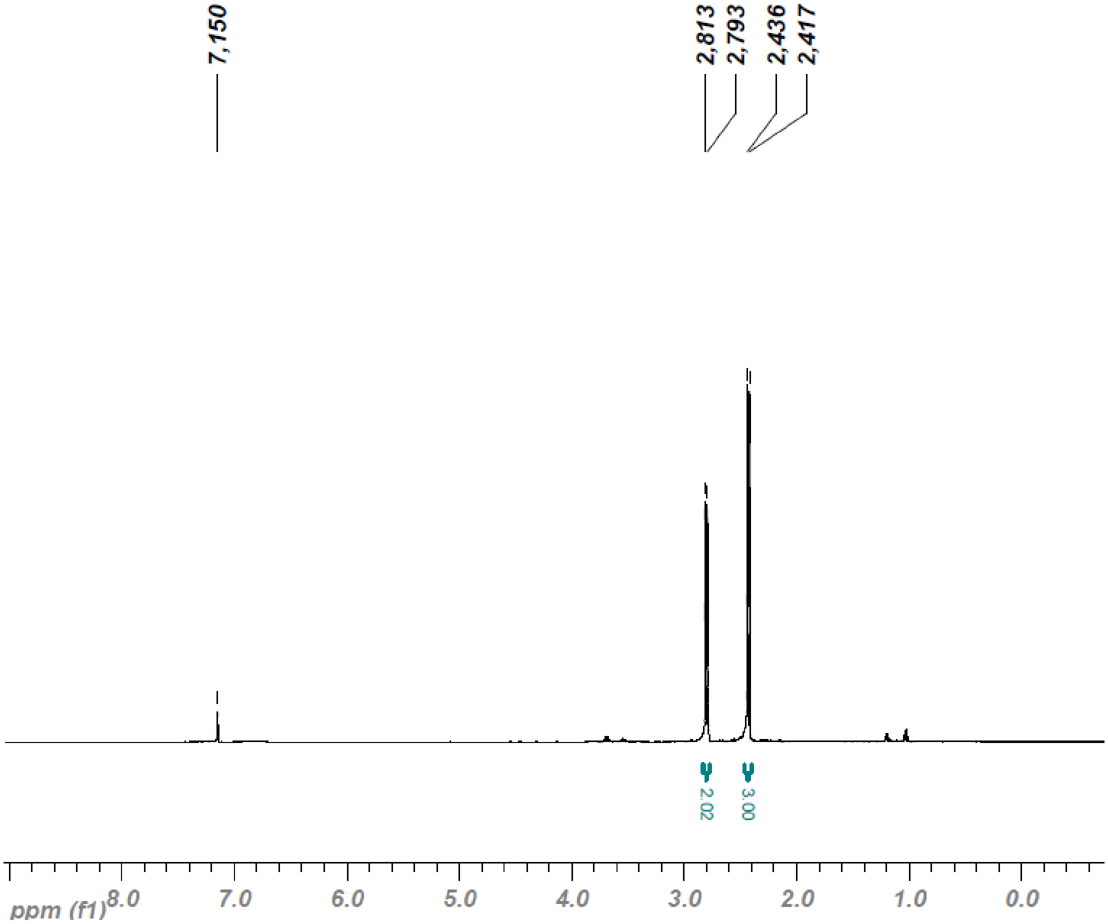


Figure S4B: $^{31}P\{^{1}H\}$ NMR of **6**

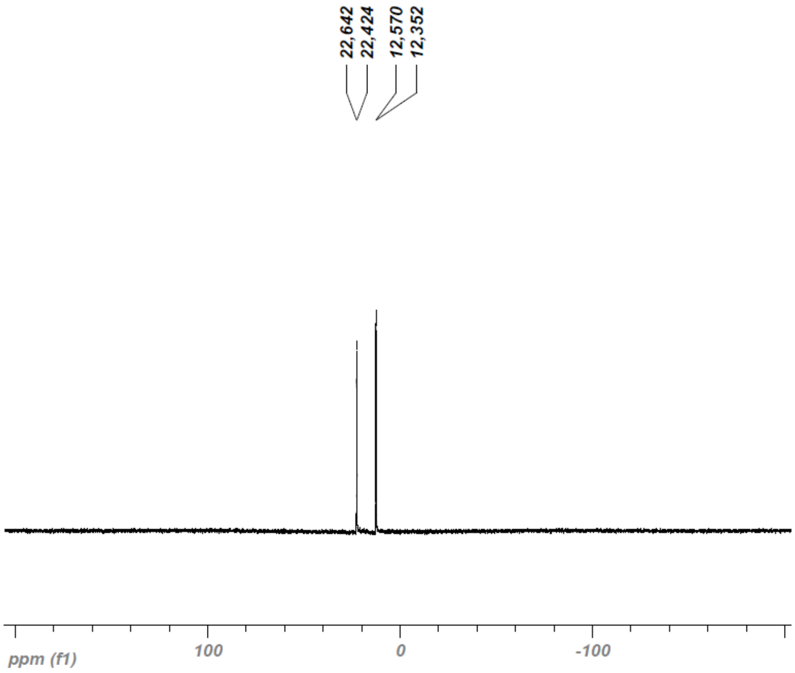
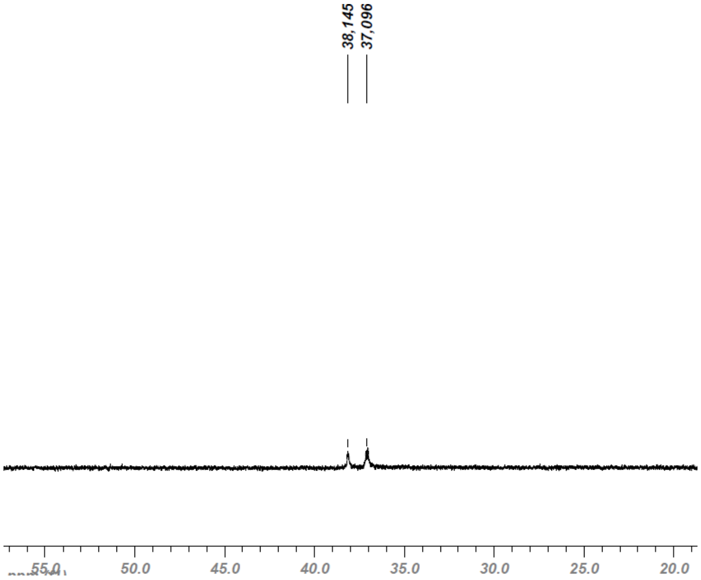


Figure S4C: $^{13}C\{^{1}H\}$ NMR of **6**



S5: Catalytic reduction using ^{13}CO2.

2.1 mg of **1** (7.6 µmol) as well as 28.7 mg (0.157 mmol) of Ph_2SiH_2 were dissolved in 0.4 ml of DMF-*d7* after which 2 µL of C_6H_{12} (internal standard) were added. The solution was transferred to a J-Young NMR tube which was frozen in a liquid nitrogen bath. The J-Young was left under vacuum for 30 minutes after which ~3 atm of $^{13}CO_2$ were condensed in the tube. The solution was left to warm at r.t. naturally and analyzed by ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy at regular intervals.

Figure S5A: ^{1}H NMR spectra after 30 minutes of the reaction described in **S5**.

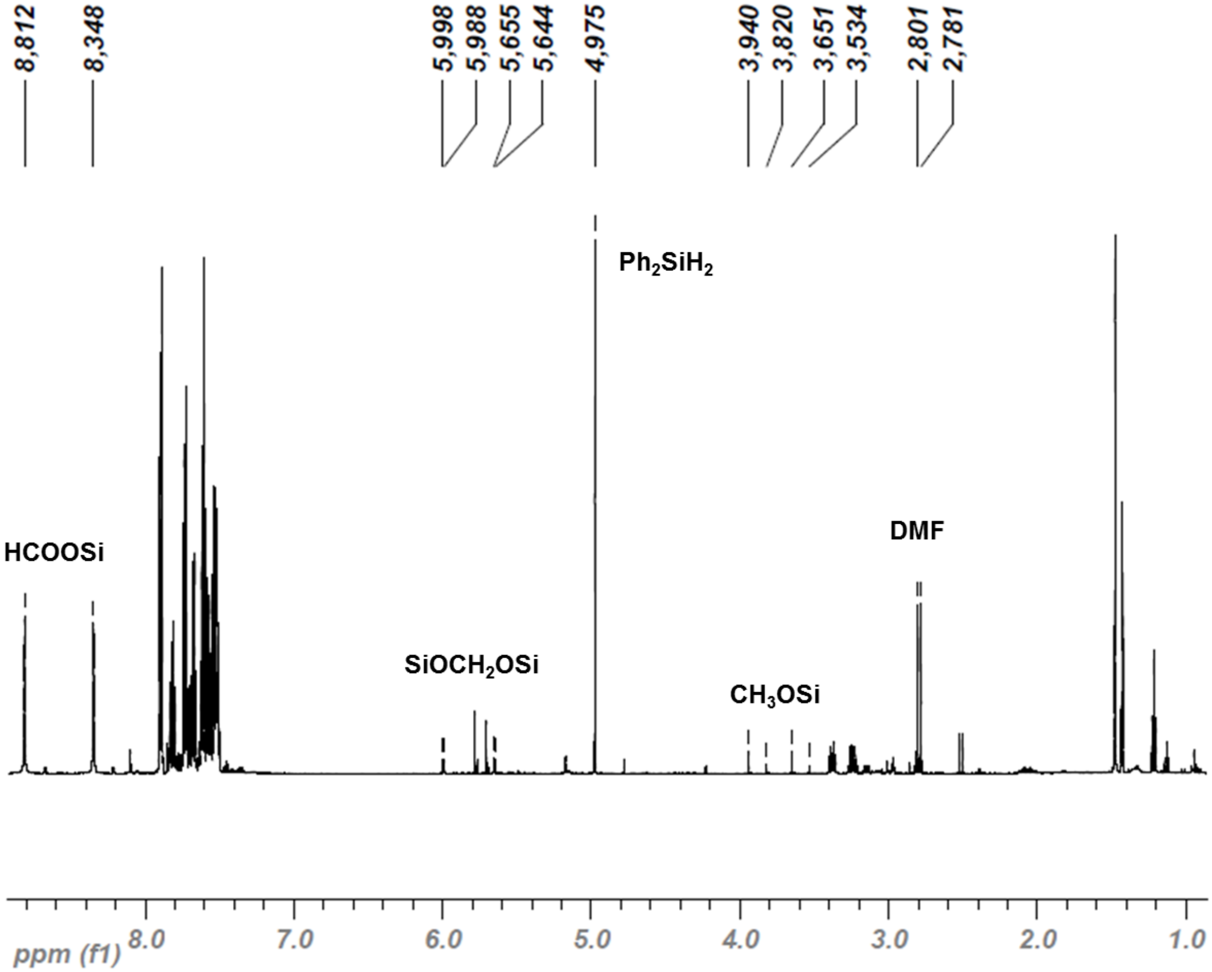


Figure S5B: $^{31}P\ \{^1H\}$ NMR spectra after 30 minutes of the reaction described in **S5**.

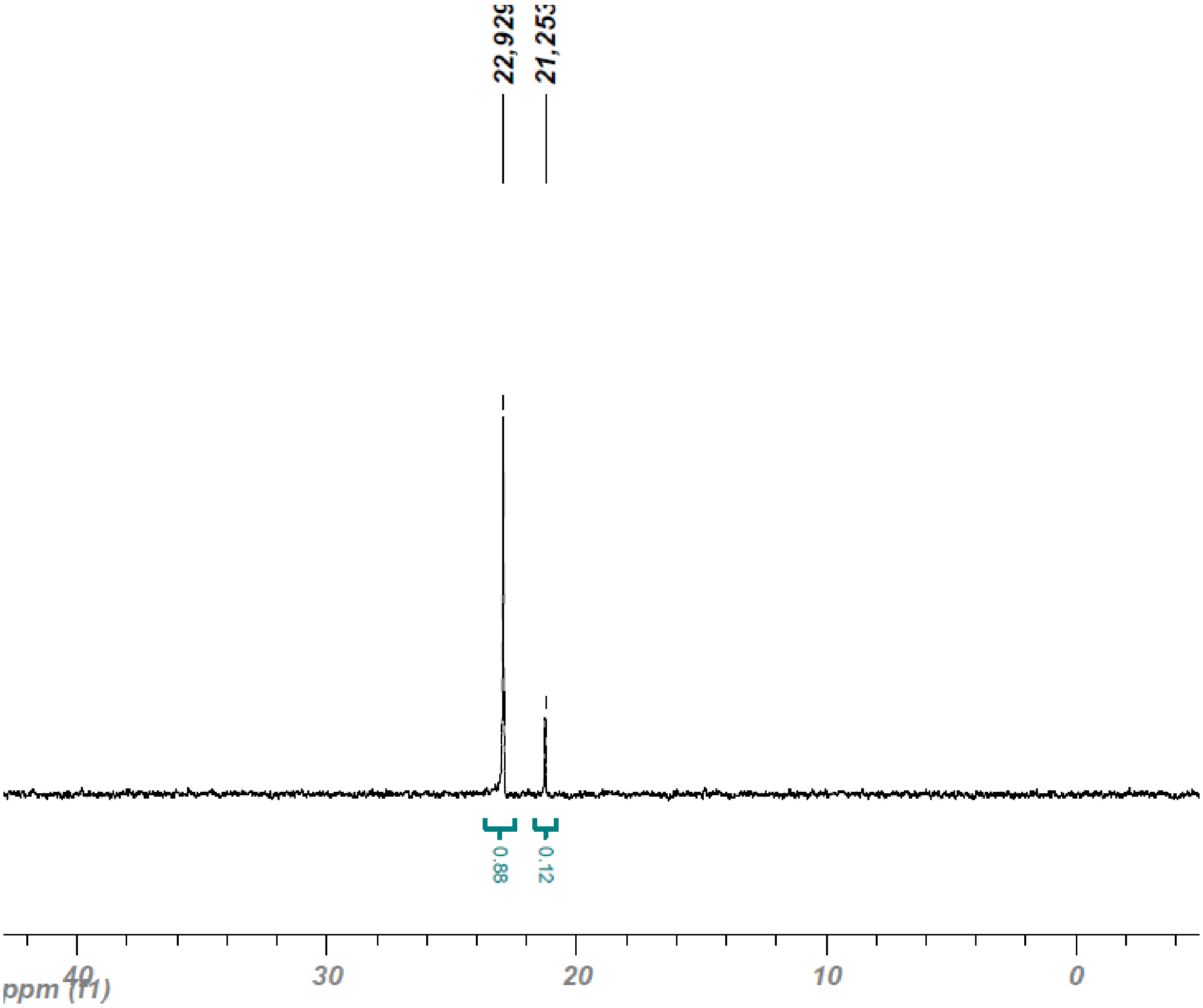
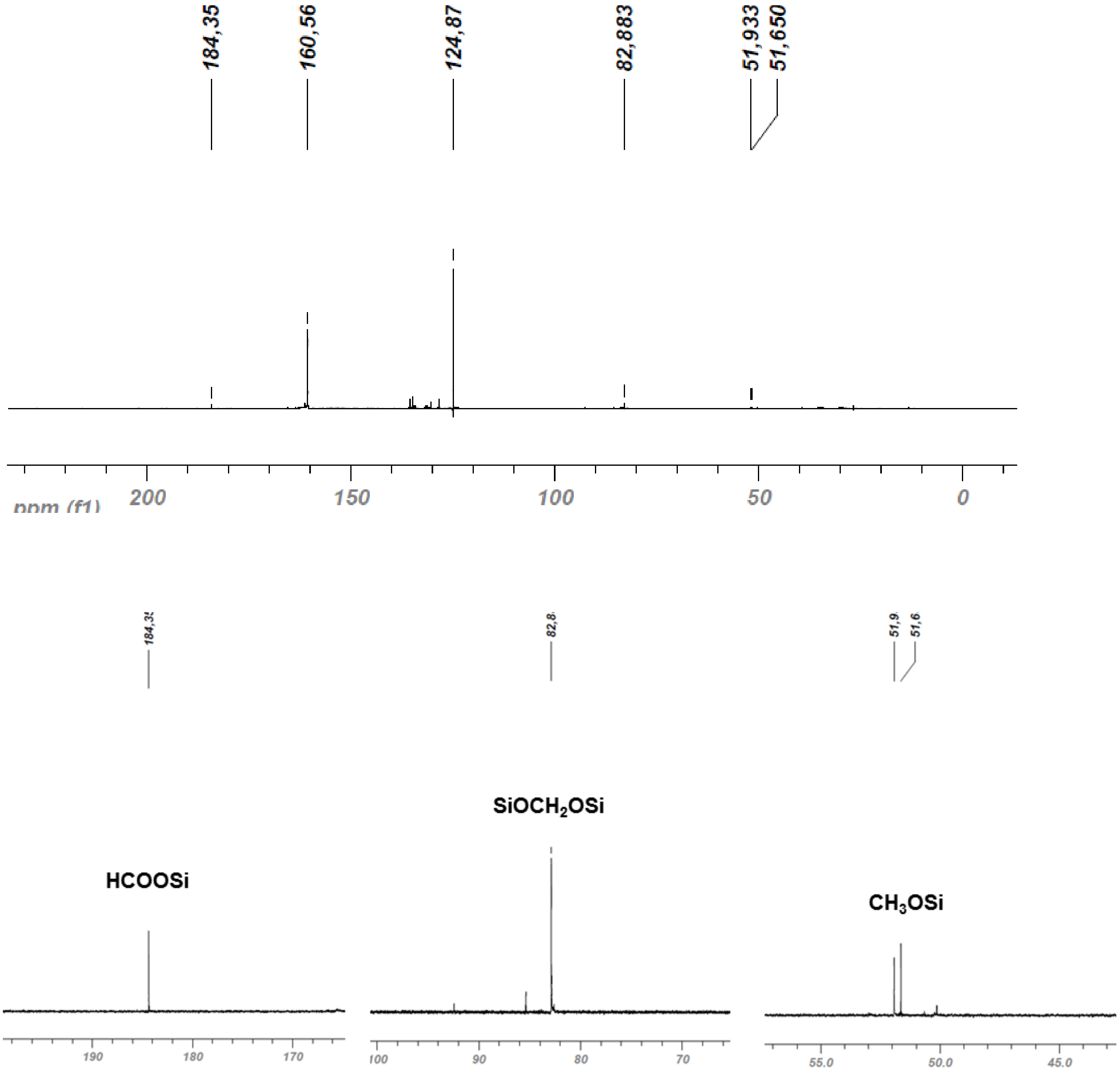
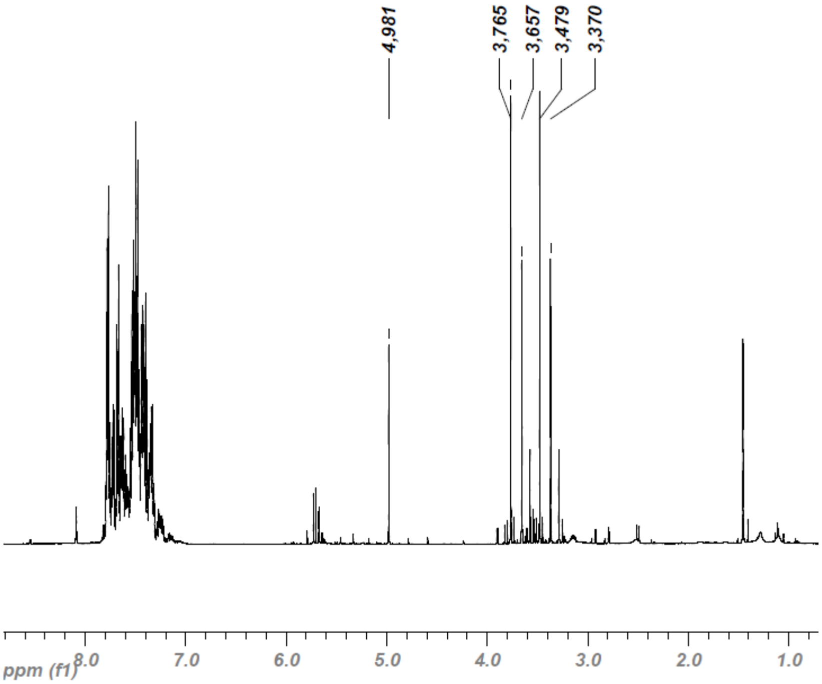


Figure S5C: $^{13}C\{^1H\}$ NMR and selected regions



Upon completion of the reaction (total consumption of silanes), the sample was degassed by a series of 3 freeze pump thaws and another loading of silane, 28.7 mg (0.157 mmol) was added to the reaction mixture. The sample was left to react for 36 hours after which the solution was once again analyzed by ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy.

Figure S5D: ^{1}H NMR spectra and select regions 36 hours after the addition of the second loading of silane



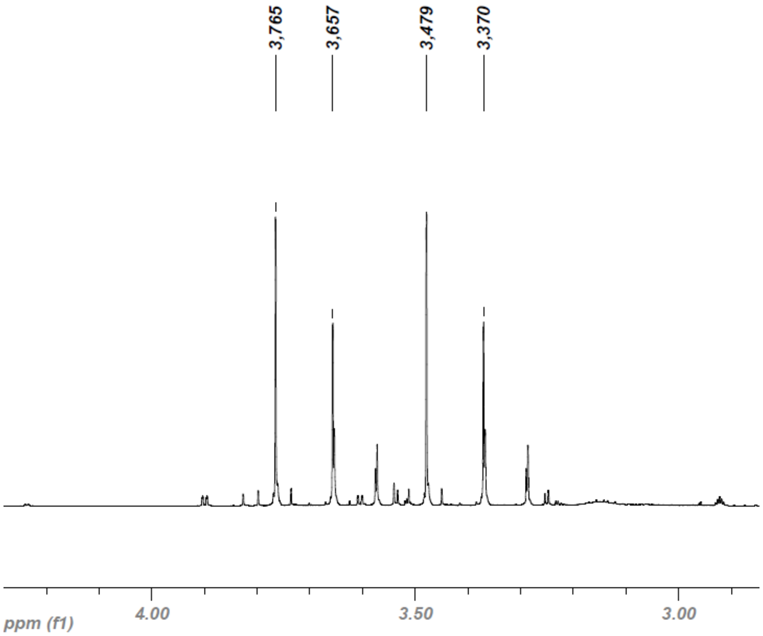


Figure S5E: $^{31}P\{^{1}H\}$ NMR spectra 36 hours the addition of the second loading of silane

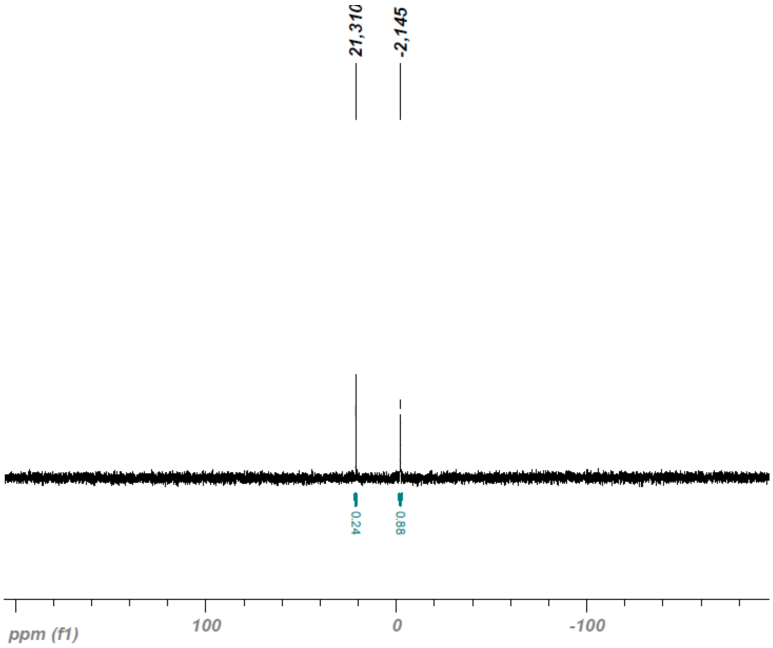
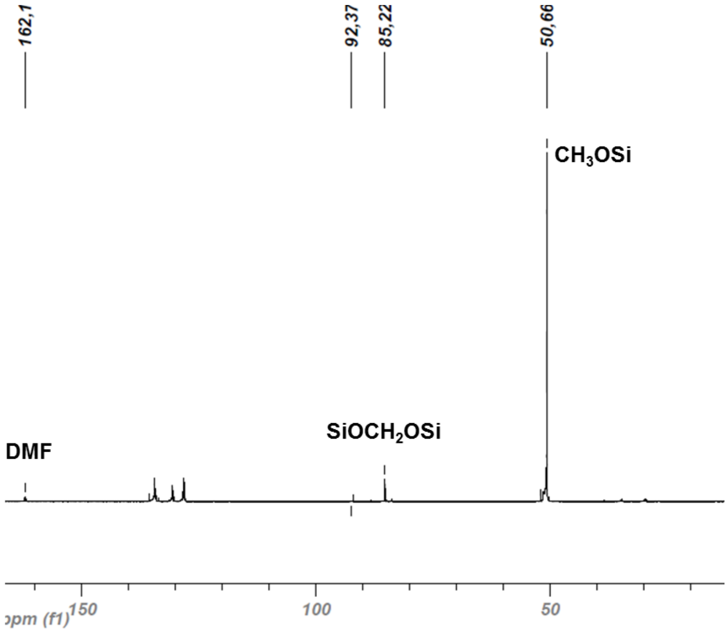


Figure S5F: $^{13}C\{^{1}H\}$ NMR spectra 36 hours after the addition of the second loading of silane



S6: Following the reaction in DMF, with various loadings of silane:

Preparation of the mother liquor: a 12.5 µmol/ml solution has been prepared by dissolving 17.0 mg of **1** in 5.0 ml (4.74 g) of DMF.

0.4 ml of the mother liquor described in **S8** (5.2 µmol of **1**) was introduced in a J-Young NMR tube along with 38.4 mg (0.1 mmol) (Test A), 96.0 mg (0.52 mmol) (Test B) of Ph_2SiH_2.. Then, CO_2 was added following the procedure described in S1. The samples were left to warm up at r.t. for 10 minutes before starting the acquisition at r.t. The reaction was followed by ^{1}H NMR spectroscopy and the intensity of the integration plotted agains time for both reactions in the graphs presented below:

Figure S6A: Test A

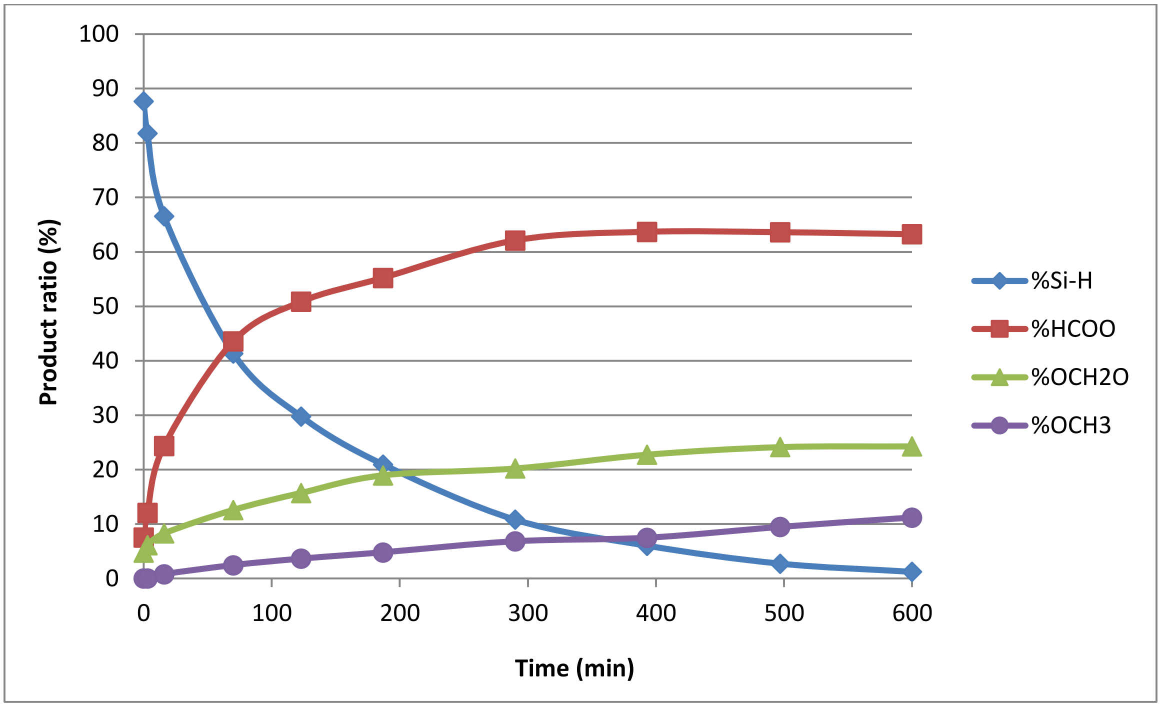
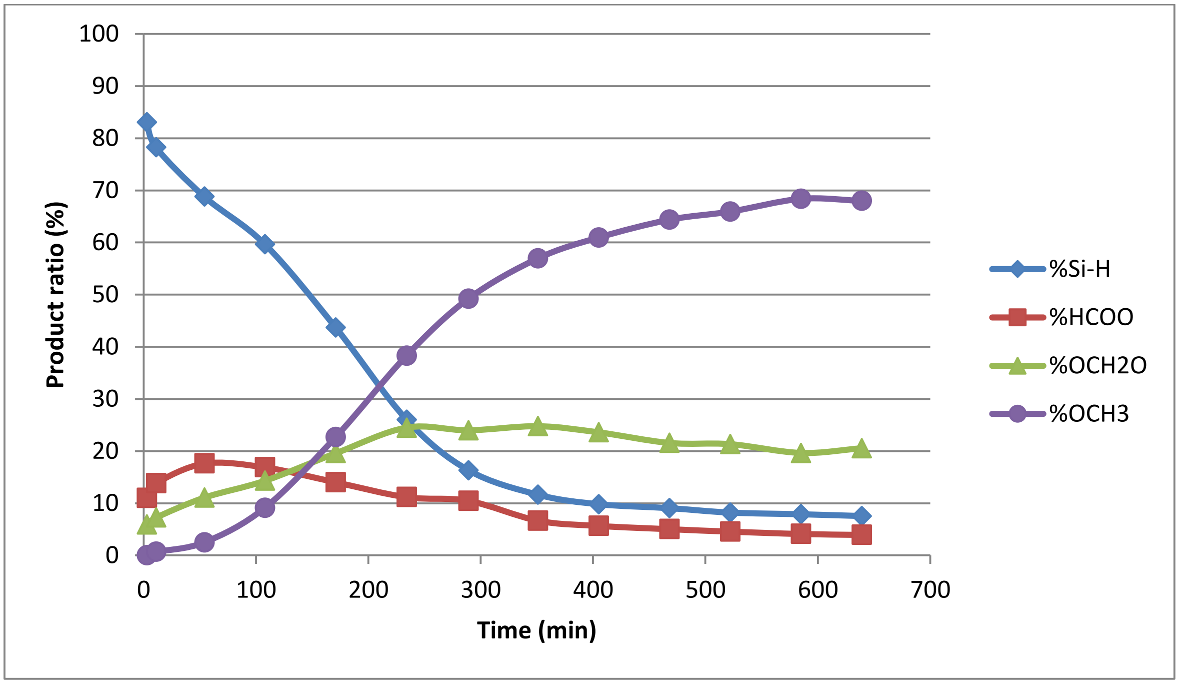


Figure S2b: Test B

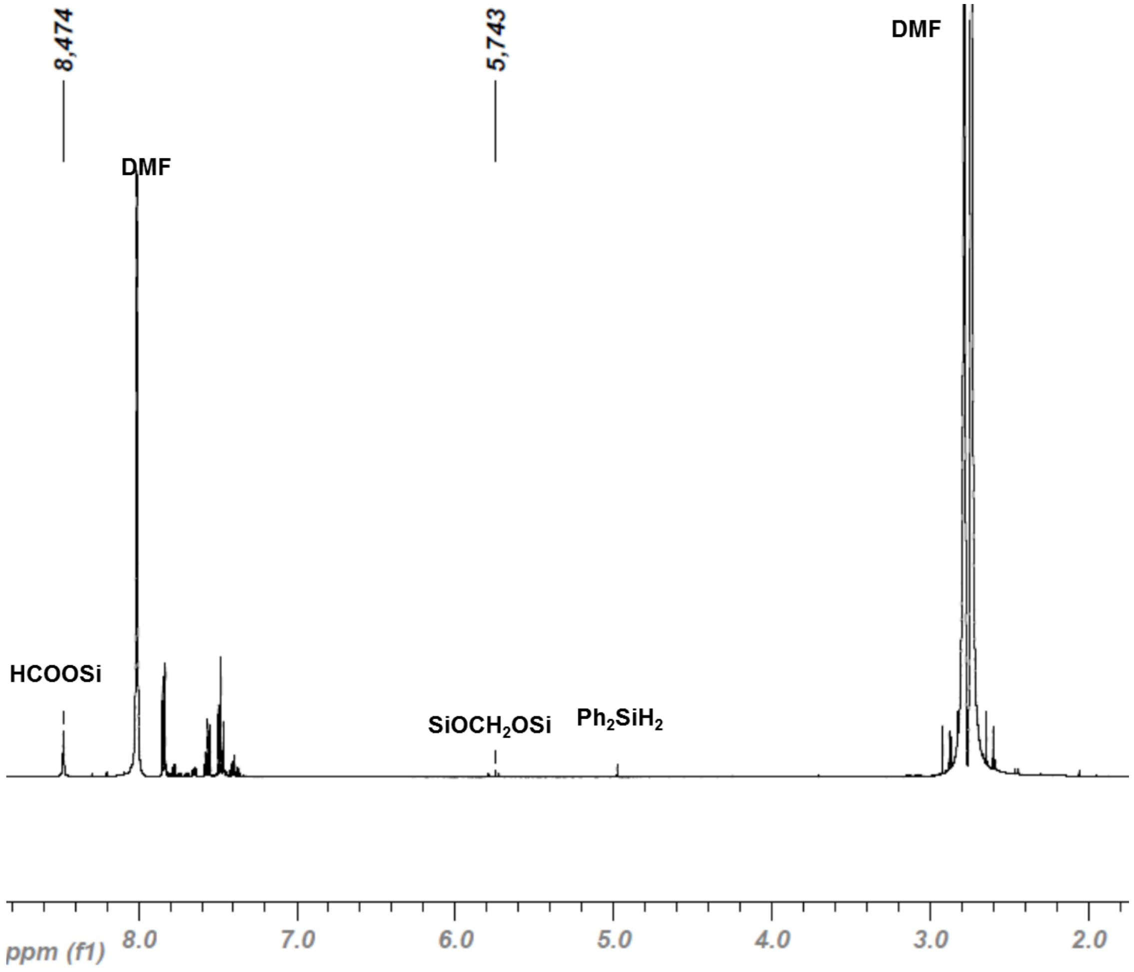


In this test, the CO_2 was depleted due to the presence of a large excess of silane, explaining why the methoxide derivatives appear as the predominant product.

S7: Reaction under 5 atm. of CO_2

0.4 ml of the mother liquor described in S8 was introduced in a 1.0 mL vial along with 38.4 mg of Ph_2SiH_2 (0.1 mmol). *ca* 0.5 mL of benzene-d_6 was added to the solution as well as a magnetic stir bar. The vial was placed inside a 170 mL Fischer porter vessel. The vessel was frozen in a liquid nitrogen bath and put under vacuum for 60 minutes, after which 5 atm was condensed in the fischer porter vase. The liquid nitrogen bath was removed and replaced with a water bath at r.t. After 2 hours of reaction, the solution was analyzed by ^1H NMR spectroscopy.

Figure S7A: ^1H NMR spectra of the reaction described above.



S8: General procedures for catalytic tests:

Mother liquor preparation:

To simplify some manipulations, a 12.5 µmol/ml solution has been prepared by dissolving 17.0 mg of **1** in 5.0 ml (4.74 g) of DMF. It will be referred as mother liquor in the rest of this section.

Various loading of Ph_2SiH_2 using 1 as catalyst (entry 1,3 and 4 of table 1 in main text):

Entry 1:
17 mg (62.5 µmol) of **1** and 460 mg (2.5 mmol) of Ph_2SiH_2 have been weighed in a vial and 5 ml of DMF have been added. The solution was then transferred to a Schlenk flask. CO_2 was added by freezing in a liquid nitrogen bath and leaving the sample under vacuum for *ca* 3 minutes. The liquid nitrogen bath was removed and sample left to warm up for *ca* 20 seconds after which CO_2 was introduced in the Schlenk flask. Sample was then allowed to warmup to r,t. in *ca* 5 min by stirring in a r.t. water bath and then left with stirring at r.t. under CO_2 flow. Aliquots were taken at different time interval, dissolved in benzene-d_6, and analysed by ^1H NMR spectroscopy. We also performed blanks, one without catalyst and one without catalyst and CO_2. The results are discussed in main text.

Entry 3: 400 µL of mother liquor (5 µmol of **1**) and 922 mg (5 mmol) of Ph_2SiH_2 have been diluted with 10 ml of DMF and the solution was then transferred to a Schlenk flask. CO_2 has been added in the same manner as for Entry 1. Aliquots were taken at different time interval, dissolved in C_6D_6, and analysed by ^1H NMR spectroscopy.

Entry 4: 80 µL of mother liquor (1 µmol of **1**) and 922 mg (5 mmol) of Ph_2SiH_2 have been diluted with 10 ml of DMF and the solution was then transferred to a Schlenk flask. CO_2 has been added in the same manner as for Entry 1. Aliquots were taken at different time interval, dissolved in benzene-d_6, and analysed by ^1H NMR spectroscopy.

Solvent screening (entry 6-8 of table 1 in main text):

3.4 mg (12.5 µmol) of **1** and 92.2 mg of Ph_2SiH_2 (0.5 mmol) have been weighted in vial and 1 ml of various solvents (DMF, CH_3CN or Toluene) have been added. Then, CO_2 was bubbled through the solution for approximately 15 seconds after what the solutions were left with stirring at r.t.under one atmosphere of CO_2 using balloons. After 4 hours of reaction, C_6D_6 was added and the solutions were analyzed by ^1H NMR spectroscopy.

In the case of CH_3CN good conversion was observed so more complete tests have been run with the same method as for DMF (see Entry 1). The first one (80eq) using 17 mg (62.5 µmol) of **1**, 460 mg (2.5 mmol) of Ph_2SiH_2 and 5 ml of CH_3CN and a second one (1000 eq) using 17 mg (62.5 µmol) of **1**, 460 mg (2.5 mmol) of Ph_2SiH_2 and 5 ml of CH_3CN. It is the results of those tests that are reported in table 1 in main text.
We also performed blanks, one without catalyst and one without catalyst and CO_2, both showing no conversion of Ph_2SiH_2 after 24h.

Silane screening (entry 3-5 of table 1 in main text):

Silanes have been screened in a similar manner using the mother liquor. 0.1 mmol of Si-H (80 eq) have been weighted in a vial and 1ml of mother liquor, (12.5 µmol of **1**) have been added. Then, CO_2 was bubbled through the solution for approximately 15 seconds after what the solutions were left with stirring under one atmosphere of CO_2 using balloons. After 4 hours of reaction, benzene-d_6 was added and the solutions were analyzed by ^1HNMR spectroscopy. Since the conversion using $(EtO)_3SiH$ and Et_3SiH were very low after only 4h, we perform another experiment with higher **1** loading in a J-Young NMR tube. Briefly, 2.8 mg of **1** (10.2 µmol) and 400 µmol of silane (65.7 mg for $(EtO)_3SiH$ and 46.5 mg for Et_3SiH) have been weighted in vials. Then 0.4 ml of DMF and 5-6 drops of C_6D_6 have been added. The solution was introduced into a gas tight J-Young NMR tube. CO_2 was added by freezing in a liquid nitrogen bath and leaving the sample under vacuum for *ca* 3 minutes. The liquid nitrogen bath was removed and sample left to warm up for *ca* 20 seconds after which *ca* 3 atm of CO_2 was introduced in the tube. The reactions were left at r.t. and monitored at various time intervals by ^1H NMR spectroscopy. The results obtained after 24h are reported in the table of the article main text.

Other phophazenes (entry 9-11 of table 1 in main text):

Catalytic activities of other phosphazenes (structure 2, 3 and 6) have been tested in J-Young NMR tube with Ph_2SiH_2. 5 µmol of phosphazene (1.6 mg for 2, 1.7 mg for 3 and, 1.6 mg for 6) and 400 µmol of Si-H (36.9 mg of Ph_2SiH_2) have been weighted in vials. Then 0.4 ml of DMF and 5-6 drops of benzene-d_6 have been added The solution was introduced into a gas tight J-Young NMR tube. CO_2 was added by freezing in a liquid nitrogen bath and leaving the sample under vacuum for *ca* 3 minutes. The liquid nitrogen bath was removed and sample left to warm up for *ca* 20 seconds after which *ca* 3 atm of CO_2 was introduced in the tube. The reactions were left at r.t. and monitored at various time intervals by ^{1}HNMR spectroscopy.

Big scale reaction in CH_3CN:

50 mg (0.18 mmol) of **1** and 1.33g of Ph_2SiH_2 (7.2 mmol) have been weighed in vial and transferred to a 100 mL schlenk tube. The compounds were dissolved in CH_3CN and stirred at r.t. for 24 hours under an atmosphere of CO_2. Then, the sample was put under a constant flow of dinitrogen after which 2,67 g of Ph_2SiH_2 (14.4 mmol) was added. The reaction was left to stir at r.t. for 48 hours. A 5mL aliquot was taken from the reaction mixture to which 1 mL of a 10% solution of NaOH in water was added. The resulting mixture was filtered and an internal standard of THF was added and the yield of methanol was determined by GC-FID spectroscopy. GC spectra were recorded on a Hewlett Packard GC-FID 6890 Series with an HP-5 (Crosslinked 5% PHME siloxane) column, using an isotherm at 40°C. Injection volumes were 1 µL. A calibration plot was obtained using three aqueous solutions of THF (1% v/v) containing methanol (0.5, 1 and 2 % v/v) to ensure linearity of the THF/MeOH signal. Yield = 69%

Figure S7A: Typical ^{1}H NMR spectra: here is shown the spectra for entry 1 in table 1 of the manuscript.