Supporting Information

$Ph_2PCH_2CH_2B(C_8H_{14})$ and its formaldehyde adduct as catalysts for the reduction of CO_2 with hydroboranes

Alberto Ramos,* Antonio Antiñolo, Fernando Carrillo-Hermosilla, Rafael Fernández-Galán

Centro de Innovación en Química Avanzada (ORFEO-CINQA). Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, Campus Universitario, E-13071 Ciudad Real, Spain.

*Email: Alberto.Ramos@uclm.es

CONTENTS

General remarks. All manipulations were carried out under dry nitrogen (or CO_2) using standard Schlenk and glovebox techniques. Anhydrous solvents purchased from commercial sources were stored under N_2 in Schlenk tubes equipped with J. Young-type Teflon stoppers, containing activated molecular sieves (4 Å). Microanalyses were carried out with a LECO CHNS-932 analyser. NMR spectra were recorded on Bruker 400 and 500 spectrometers in C_6D_6 at 298 K unless otherwise stated, using standard TOPSPIN 4.0 software. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are referenced to residual protons or carbons in deuterated solvent. Most of the NMR assignments in the latter spectra were supported by additional 2D experiments. ^{11}B NMR and ^{31}P{^{1}H} NMR chemical shifts are referenced to external 15% $BF_3{\cdot}OEt_2$ in $CDCl_3$ and 85% aqueous H_3PO_4 solutions, respectively. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. All reagents were purchased from the usual commercial suppliers.

Preparation of $Ph_2P(CH_2)_2BBN$ (1). Compound **1** was prepared according to literature procedures with slight modifications.[1] H-BBN (254 mg, 2.08 mmol) was added to a toluene solution (10 mL) of $Ph_2PCH{=}CH_2$ (464 mg, 2.08 mmol). Then, the mixture was stirred at 100 ºC for 3h. Afterwards, pentane (15 mL) was added at room temperature to obtain compound **1** as a white precipitate. The solid was collected by vacuum filtration, subsequently washed with pentane (2 x 5 mL), and dried under vacuum to yield compound **1** as a white powder (530 mg, 76%), slightly soluble in dichloromethane, toluene or THF and totally insoluble in pentane or hexanes. ^{1}H NMR (500 MHz): δ 7.51 (m, 4H, *o*-Ph), 7.11 (m, 4H, *m*-Ph), 7.06 (m, 2H, *p*-Ph), 2.25 (m, 2H, PC*H*$_2$CH$_2$), 1.90-1.60 (m, 12H, BBN), 1.56 (m, 2H, CH$_2$C*H*$_2$B), 1.19 (m, 2H, BBN). ^{13}C{^{1}H} NMR (126 MHz) δ 140.0 (d, J = 15.5, *ipso*-Ph), 133.3 (d, J = 18.1, *o*-Ph), 128.7 (d, J = 6.4, *m*-Ph), 128.7 (s, *p*-Ph), 33.6 (s, *C*H$_2$-BBN), 31.5 (br, *C*H-BBN), 23.7 (s, *C*H$_2$-BBN), 23.7 (br, CH$_2$*C*H$_2$B), 23.0 (d, J = 12.0, CH$_2$*C*H$_2$P). ^{31}P{1H} NMR (202 MHz) δ –10.2 (s, *P*). ^{11}B NMR (160 MHz) δ 87.3 (br, *B*).

Preparation of solutions containing (H-BBN)$Ph_2P(CH_2)_2BBN$ (1-H-BBN). H-BBN (6 mg, 0.05 mmol) was added to a suspension of compound **1** (17 mg, 0.05 mmol) in C_6D_6 (ca. 0.6 mL) in an NMR tube equipped with a J. Young valve. The adduct formation reaction was monitored by NMR and an equilibrium was reached after 24 h at room temperature, with a ratio **1-H-BBN**/**1** of 9 to 1. The adduct **1-H-BBN** was characterized by NMR from these solutions. ^{1}H NMR (400 MHz): δ 7.54 (m, 4H, *o*-Ph), 7.06 – 6.96 (m, 6H, *m/p*-Ph), 3.20 – 2.50 (m, vbr, 1H, *H*-BBN), 2.60 – 1.40 (m, 26H, BBN), 2.47 (m,

2H, PC*H*$_2$CH$_2$), 1.53 (m, 2H, CH$_2$C*H*$_2$B), 1.07 (m, 2H, BBN). ^{1}H{^{11}B} NMR (500 MHz): δ 2.83 (s, 1H, *H*-BBN). ^{13}C{^{1}H} NMR (126 MHz) δ 133.6 (d, J_{PC} = 7.6, *o*-Ph), 131.3 (d, J_{PC} = 44.7, *ipso*-Ph), 130.6 (s, *p*-Ph), 128.8 (d, J_{PC} = 8.4, *m*-Ph), 37.6, 37.4, 33.5, 32.8 (4 x s, *C*H$_2$-BBN), 31.3 (br, *C*H-BBN), 26.5, 25.7, 23.5 (3 x s, *C*H$_2$-BBN), 21.6 (br, *C*H-BBN), 20.3 (br, CH$_2$*C*H$_2$B), 19.3 (d, *J* = 28.0, P*C*H$_2$CH$_2$). ^{31}P{^{1}H} NMR (162 MHz) δ 8.4 (s, *P*). ^{11}B NMR (160 MHz): δ 86.1 (br, Δν½ = 657 Hz, BBN), –15.1 (br, Δν½ = 274 Hz, H-BBN).

Preparation of Ph$_2$P(CH$_2$)$_2$BBN(CH$_2$O) (2). Excess paraformaldehyde (70 mg, 2.22 mmol) was added to a suspension of compound **1** (340 mg, 1.02 mmol) in toluene (10 mL). The suspension was stirred at 60 ºC for 14 h to yield a slightly cloudy mixture containing compound **2**. The mixture was filtered to remove the excess paraformaldehyde. Then, the solvent from the remaining colorless solution was removed under vacuum. The white solid thus obtained was washed twice with pentane (2 x 10 mL) and dried again under vacuum to give compound **2** as a white solid (330 mg, 89%). Crystals of compound **2** suitable for an X-ray analysis were obtained from a concentrate toluene/pentane (1:1) solution at –20 ºC. Anal calc. for C$_{23}$H$_{30}$BOP (**2**): C, 75.84; H, 8.30 Found: C, 75.51; H, 8.21. ^{1}H NMR (400 MHz): δ 7.24 (m, 4H, *m*-Ph), 7.01 (m, 2H, *p*-Ph), 6.88 (m, 4H, *o*-Ph), 4.87 (d, *J* = 2.0, 2H, C*H*$_2$O), 2.80 – 2.00 (m, 12H, C*H*$_2$-BBN), 2.32 (m, 2H, PC*H*$_2$CH$_2$), 1.31 (m, 2H, C*H*-BBN), 1.11 (m, 2H, CH$_2$C*H*$_2$B). ^{13}C{^{1}H} NMR (101 MHz) δ 133.2 (d, J_{PC} = 3.0, *p*-Ph), 132.7 (d, J_{PC} = 8.1, *m*-Ph), 129.5 (d, J_{PC} = 11.1, *o*-Ph), 122.0 (d, J_{PC} = 71.5, *ipso*-Ph), 60.4 (d, J_{PC} = 47.5, P*C*H$_2$O), 34.1, 32.1, 27.4, 27.2 (4 x s, *C*H$_2$-BBN), 25.4 (br, *C*H-BBN), 18.0 (d, J_{PC} = 46.1, P*C*H$_2$CH$_2$), 12.1 (br, CH$_2$*C*H$_2$B). ^{11}B NMR (128 MHz): δ –1.2 (s, B, Δν½ = 247 Hz). ^{31}P{^{1}H} NMR (162 MHz): δ –0.4 (s, P).

Reaction of equimolar amounts of compound 2 and H-BBN with CO$_2$. *NMR scale*: A solution of compound **2** (36 mg, 0.10 mmol) and H-BBN (13 mg, 0.11 mmol) in C$_6$D$_6$ (*ca*. 0.6 mL) was charged into an NMR tube equipped with a J. Young stopper. The solution was subjected to a freeze-pump-thaw cycle: frozen with liquid N$_2$, then the headspace was evacuated under vacuum and, once the solution thawed at room temperature, CO$_2$ gas was introduced (*ca*. 1 atm). Then, the reaction was monitored by NMR spectroscopy until total consumption of the hydroborane. Small amounts of MeOBBN were formed together with a mixture of the main products: BBN(CH$_2$)$_2$(Ph$_2$P)(CH$_2$O)BBN(HCO$_2$) (**3**) and the 14-membered cycle

$BBN(CH_2)_2(Ph_2P)(CH_2O)BBN(HCO_2)BBN(HCO_2)$ (**4**), containing one and two formate units, respectively. Compound **3** starts to crystallize after 2 h, and the ratio of compound **4** in solution increases. The hydroborane is fully consumed after 15 h, and a substantial amount of colorless crystals of **3** are formed, suitable for an X-ray diffraction analysis. Only small amounts of a mixture of compounds **2-4** and MeOBBN are present in solution. Compound **3** is completely insoluble in all the usual organic solvents and was only partially characterized by signature signals in NMR spectra. *Schlenk scale*: A solution of compound **2** (50 mg, 0.14 mmol) and H-BBN (18 mg, 0.15 mmol) in toluene (*ca*. 5 mL) was charged into a Schlenk tube with a J. Young stopper. The solution was degassed under vacuum and quickly refilled with CO_2 gas (x3). After a few minutes, colourless crystals of 3 start to form. After 7 h, pentane (5 mL) is added to the mixture and the latter was kept overnight at –20 ºC to complete precipitation of compound **3**. Then, the supernatant was decanted and the white solid washed with pentane (2 x 5 mL) and dried under vacuum (38 mg, 52%). Anal calc. for $C_{32}H_{45}B_2O_3P$ (**3**): C, 72.48; H, 8.45 Found: C, 72.26; H, 8.27. *Partial NMR data for compounds **3** and **4***: ^{1}H NMR (400 MHz): δ 8.74 (s, C*H*O_2), 4.62 (s, C*H*$_2$O). $^{31}P\{^1H\}$ NMR (162 MHz) δ 25.8 (br, P, **4**), 24.2 (br, P, **3**). No signals owing to the B nuclei of **3** or **4** could be detected in the ^{11}B NMR spectrum.

Reaction of equimolar amounts of compound 2 and H-BBN with $^{13}CO_2$. A solution of compound **2** (36 mg, 0.10 mmol) and H-BBN (13 mg, 0.11 mmol) in C_6D_6 (*ca*. 0.6 mL) was charged into an NMR tube with a J. Young stopper. The solution was subjected to a freeze-pump-thaw cycle and, once thawed at room temperature, $^{13}CO_2$ gas was introduced (*ca*. 1 atm). The reaction was monitored by NMR, and the formation of $BBN(CH_2)_2(Ph_2P)(CH_2O)BBN(H^{13}CO_2)$ (**^{13}C-3**) and the macrocycle $BBN(CH_2)_2(Ph_2P)(CH_2O)BBN(H^{13}CO_2)BBN(H^{13}CO_2)$ (**^{13}C-4**) was soon detected in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra recoded after 10 min and 6 h, together with increasing amounts of MeOBBN. After 24 h at room temperature, there is a great amount of crystalline solid in the tube, presumably compound **^{13}C-3**, and only small amounts of **2** and MeOBBN and trace amounts of **^{13}C-3** and **^{13}C-4** remain in solution. *Partial NMR data for compounds **^{13}C-3** and **^{13}C-4***: ^{1}H NMR (400 MHz): δ 8.76 (d, $^1J_{CH}$ = 206.9, *H*$^{13}CO_2$), 4.63 (s, C*H*$_2$O). $^{13}C\{^1H\}$ NMR (101 MHz): δ 172.5 (br, ^{13}CH_2O). $^{31}P\{^1H\}$ NMR (162 MHz) δ 24.9 (br, P). No signals owing to the B nuclei of **^{13}C-3** or **^{13}C-4** could be detected in the ^{11}B NMR spectrum.

Reaction of compound 2 with 2 equiv of H-BBN and CO_2. *NMR scale*: A solution of compound **2** (18 mg, 0.05 mmol) and H-BBN (13 mg, 0.11 mmol) in C_6D_6 (*ca*. 0.6 mL) was charged into an NMR tube with a J. Young stopper. The solution was subjected to a freeze-pump-thaw cycle and, once thawed at room temperature, CO_2 gas was introduced (*ca.* 1 atm). Then, the reaction was monitored by NMR spectroscopy until total consumption of the hydroborane. Through the course of the reaction, formation of compounds **3** and **4**, as well as small amounts of MeOBBN, are observed by NMR spectroscopy. After 3 days, the reaction is complete and a crystalline precipitate of compound **4** is formed, with small amounts of **4** and MeOBBN remaining in solution. *Schlenk scale*: A solution of compound **2** (54 mg, 0.15 mmol) and H-BBN (37 mg, 0.30 mmol) in toluene (*ca*. 5 mL) was charged into a Schlenk tube with a J. Young stopper. The solution was degassed under vacuum and quickly refilled with CO_2 gas (x3), stirred for 1 h and left standing overnight. After 20 h, small amounts of a white crystalline precipitate are observed. Then, the mixture is placed in a refrigerator at –20 ºC and colorless crystals of **4**, suitable for an X-ray diffraction study are obtained. The crystalline product is filtered, washed with pentane (3 x 5 mL) and dried under vacuum to obtain **4** as a white solid (60 mg, 57%). Compound **4** is scarcely soluble in the usual organic solvents. Anal calc. for $C_{41}H_{60}B_3O_5P$ (**4**): C, 70.72; H, 8.69 Found: C, 70.59; H, 8.61. *Partial NMR data for compound **4***: ^{1}H NMR (500 MHz): δ 8.74 (s, 2H, *H*CO_2), 7.10 – 6.85 (m, 10H, PPh_2), 4.63 (d, 2H, J_{PH} = 3.2, C*H*$_2$O). $^{31}P\{^1H\}$ NMR (202 MHz) δ 26.0 (s, P). No signals owing to the B nuclei of **4** could be detected in the ^{11}B NMR spectrum.

Preparation of $(HCO_2)\{BBN(CH_2)_2(Ph_2P)(CH_2O)\}_2Bcat$ (5). *NMR scale*: A solution of compound **2** (36 mg, 0.10 mmol) and HBcat (11 μL, 0.10 mmol) in C_6D_6 (*ca*. 0.6 mL) was charged into an NMR tube with a J. Young stopper. The solution was subjected to a freeze-pump-thaw cycle and, once thawed at room temperature, CO_2 gas was introduced (*ca.* 1 atm). Monitoring of the reaction by NMR showed that after 15 min at room temperature the reaction is complete, with total consumption of **2** and formation of compound **5** as the major species in solution, with small amounts of MeOBcat. Compound **5** crystallizes upon standing at room temperature for hours. Once precipitated, compound **5** showed very low solubility in C_6D_6 or THF-d_8 and higher solubility, but low stability in CD_2Cl_2. *Schlenk scale*: A solution of compound **2** (50 mg, 0.14 mmol) and HBcat (17 μL, 0.16 mmol) in toluene (*ca*. 5 mL) was charged into a Schlenk tube with a J. Young stopper. The solution was degassed under vacuum and quickly refilled with CO_2 gas (x3).

and stirred for 1 h to yield a slightly cloudy solution containing compound **5**. Then, addition of pentane (5 mL) led to total precipitation of **5**. The supernatant was decanted and the white solid was washed with pentane (5 mL) to yield compound **5** as a white solid (52 mg, 78%). To obtain crystals of compound **5** suitable for an X-ray diffraction analysis, the reaction crude in toluene is carefully layered with pentane (ratio toluene/pentane 2 to 1) and placed in the refrigerator at – 20 ºC for 2 days. Compound **5** crystallizes with one molecule of toluene. Anal calc. for $C_{60}H_{73}B_3O_6P_2$ (**5**·C_7H_8): C, 73.19; H, 7.47 Found: C, 72.97; H, 7.36. ^{1}H NMR (400 MHz): δ 8.79 (s, 1H, *H*CO_2), 7.11 (m, 8H, *p*-Ph), 7.03 (m, 4H, *m*-Ph), 7.01 (br, 2H, C_6H_4), 6.88 (m, 8H, *o*-Ph), 6.78 (br, 2H, C_6H_4), 4.72 (s, 4H, C*H*$_2$O), 2.73 (m, 4H, PC*H*$_2$CH$_2$), 2.40 – 1.70 (m, 24H, C*H*$_2$-BBN), 1.23 (m, 4H, C*H*-BBN), 0.98 (m, 4H, CH$_2$C*H*$_2$B). ^{13}C{^{1}H} NMR (101 MHz): δ 173.9 (s, H*C*O_2), 149.3 (br, C-*C*$_6$H$_4$), 133.6 (s, *p*-Ph), 132.9 (d, J_{PC} = 8.0, *m*-Ph), 129.6 (d, J_{PC} = 11.4, *o*-Ph), 121.9 (br, CH-*C*$_6$H$_4$), 119.9 (d, J_{PC} = 76.8, *i*-Ph), 112.0 (br, CH-*C*$_6$H$_4$), 56.0 (d, J_{PC} = 72.1, P*C*H$_2$O), 32.6, 25.7 (2 x s, *C*H$_2$-BBN), 25.4 (s, *C*H-BBN), 16.1 (d, J_{PC} = 41.4, P*C*H$_2$CH$_2$), 13.7 (br, CH$_2$*C*H$_2$B). ^{31}P{^{1}H} NMR (162 MHz): δ 23.7 (s, P). ^{11}B NMR (128 MHz): δ 19.4 (br, Bcat, 1B), 10.8 (br, BBN, 2B). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.33 (s, 1H, C*H*O_2), 7.75 – 7.50 (m, 20H, Ph), 6.69 (br, 4H, C_6H_4), 4.76 (s, 4H, C*H*$_2$O), 2.69 (m, 4H, PC*H*$_2$CH$_2$), 1.90 – 1.30 (m, 24H, C*H*$_2$-BBN), 0.90 (m, br, 8H, C*H*-BBN + CH$_2$C*H*$_2$B). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 23.3 (br, Δν$_{½}$ = 170 Hz, P). ^{11}B NMR (160 MHz, CD_2Cl_2): δ 17.1 (br, Δν$_{½}$ = 495 Hz, Bcat, 1B), 10.0 (br, Δν$_{½}$ = 437 Hz, BBN, 2B).

Preparation of solutions of (H^{13}CO$_2$){BBN(CH$_2$)$_2$(Ph$_2$P)(CH$_2$O)}$_2$Bcat (^{13}C-5). <u>*NMR scale*</u>: A solution of compound **2** (36 mg, 0.10 mmol) and HBcat (11 μL, 0.10 mmol) in C_6D_6 (*ca*. 0.6 mL) was charged into an NMR tube with a J. Young stopper The solution was subjected to a freeze-pump-thaw cycle and, once thawed at room temperature, $^{13}CO_2$ gas was introduced (*ca*. 1 atm). The reaction is complete after 15 min at room temperature, with total consumption of **2** and formation of compound **^{13}C-5** as the major species in solution, with small amounts of CH$_3$OBcat and ^{13}CH$_3$OBcat. Compound **5** was *in situ* characterized by multinuclear NMR before total precipitation. ^{1}H NMR (500 MHz): δ 8.79 (d, *J* = 207.2, 1H, *H*^{13}CO_2), 7.11 (m, 8H, *p*-Ph), 7.03 (m, 4H, *m*-Ph), 7.01 (br, 2H, C_6H_4), 6.88 (m, 8H, *o*-Ph), 6.78 (br, 2H, C_6H_4), 4.72 (s, 4H, C*H*$_2$O), 2.73 (m, 4H, PC*H*$_2$CH$_2$), 2.40 – 1.70 (m, 24H, C*H*$_2$-BBN), 1.24 (m, 4H, C*H*-BBN), 1.00 (m, 4H, CH$_2$C*H*$_2$B).). ^{13}C{^{1}H} NMR (126 MHz) δ 173.9 (s, H^{13}*C*O_2), 151.3 (br, C-1/2-*C*$_6$H$_4$), 133.2 (s, *p*-Ph), 132.9 (d, J_{PC} = 7.7, *m*-Ph), 129.6 (d, J_{PC} = 11.3, *o*-Ph), 120.5 (br, *C*$_6$H$_4$),

119.8 (d, J_{PC} = 77.7, *i*-Ph), 111.0 (br, C_6H_4), 55.8 (d, J_{PC} = 70.5, P*C*H_2O), 32.5, 25.8 (2 x s, *C*H_2-BBN), 25.2 (s, *C*H-BBN), 16.1 (d, J_{PC} = 41.3, P*C*H_2CH_2), 13.6 (br, CH_2*C*H_2B). $^{31}P\{^1H\}$ NMR (202 MHz): δ 23.3 (s, P). ^{11}B NMR (160 MHz): δ 19.5 (br, Bcat, 1B), 10.6 (br, BBN, 2B).

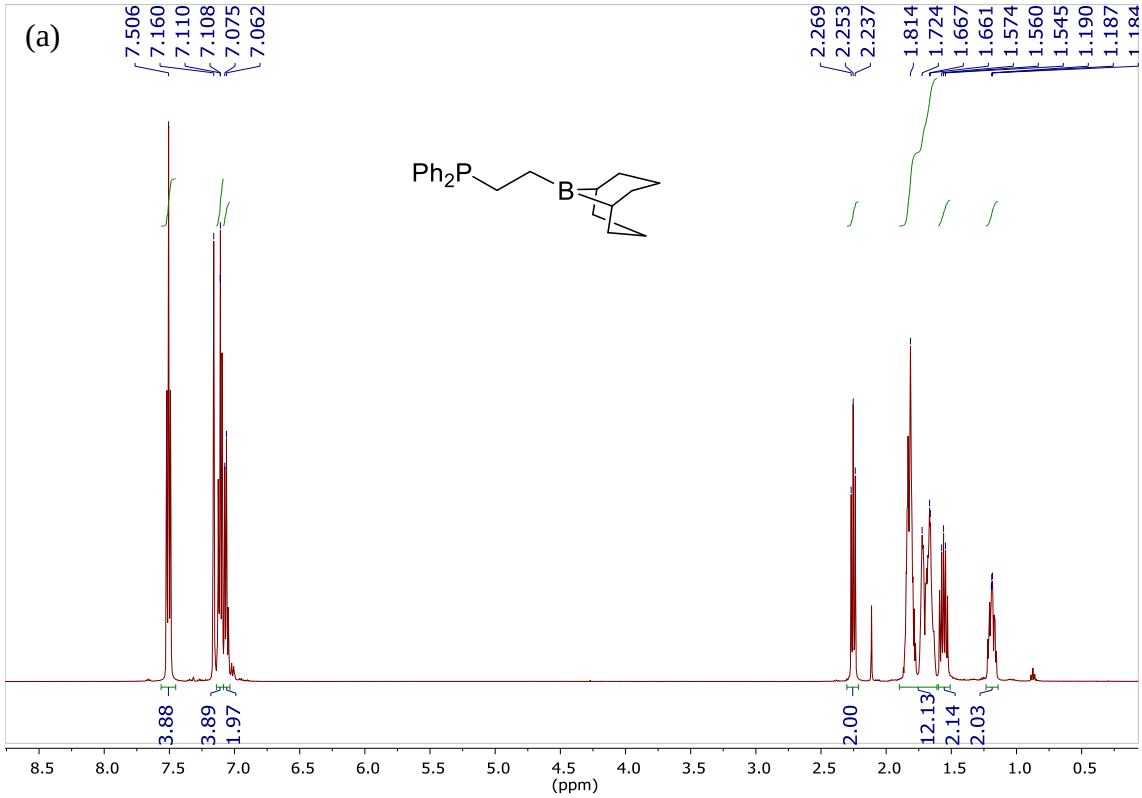
Reaction of compound 2 with 1 equiv of HBpin and CO_2. *NMR scale*: A solution of compound **2** (36 mg, 0.10 mmol) and HBpin (15 μL, 0.10 mmol) in C_6D_6 (*ca*. 0.6 mL) was charged into an NMR tube with a J. Young stopper. The solution was subjected to a freeze-pump-thaw cycle and, once thawed at room temperature, CO_2 gas was introduced (*ca.* 1 atm). Total consumption of the hydroborane takes place after 150 min to give a compound tentatively formulated as $(HCO_2)BBN(CH_2)_2(Ph_2P)(CH_2O)Bpin$ (**6**) as the major species. Small amounts of **2** (ratio **6**/**2** *ca.* 93:7), CH_3OBpin and $CH_2(OBpin)_2$ are also present in solution. Once precipitated with pentane as a white solid, compound **6** is scarcely soluble in C_6D_6 and more soluble, but unstable in CD_2Cl_2, giving increasing amounts of compound **2** with time. *Schlenk scale*: A solution of compound **2** (54 mg, 0.15 mmol) and HBpin (23 μL, 0.16 mmol) in toluene (*ca*. 3 mL) was charged into a Schlenk tube with a J. Young stopper. The solution was subjected to a freeze-pump-thaw cycle and, once thawed at room temperature, CO_2 gas was introduced (*ca.* 1 atm). After a few minutes, a white precipitate of **6** is already observed. After 30 min, the solvent was removed and the product was precipitated in a CH_2Cl_2/pentane 1:2 mixture at – 20 ºC. Characterization of the product in CD_2Cl_2 revealed the presence of *ca.* 10% of compound **2**. *NMR data for compound **6***: ^1H NMR (500 MHz, CD_2Cl_2): δ 8.32 (s, 1H, C*H*O_2), 7.79 (m, 2H, *p*-Ph), 7.74 – 7.62 (m, 8H, *o/m*-Ph), 5.11 (d, *J* = 2.8, 2H, C*H*$_2$O), 2.69 (m, 2H, PC*H*$_2$$CH_2$), 1.90 – 1.30 (m, 12H, C*H*$_2$-BBN), 1.13 (s, 12H, C*H*$_3$-pin), 0.60 (m, br, 4H, C*H*-BBN + CH_2C*H*$_2$B). $^{13}C\{^1H\}$ NMR (126 MHz,) δ 167.1 (s, H*C*O_2), 135.2 (s, *p*-Ph), 133.5 (d, J_{PC} = 8.5, *m*-Ph), 130.5 (d, J_{PC} = 11.8, *o*-Ph), 117.8 (d, J_{PC} = 80.6, *ipso*-Ph), 84.9 (s, *C*-pin), 58.4 (d, J_{PC} = 67.7, P*C*H_2O), 32.2 (br, *C*H_2-BBN), 25.9 (s, *C*H_2-BBN), 25.1 (br, *C*H-BBN), 24.6 (s, *C*H_3-pin), 16.7 (d, J_{PC} = 37.6, P*C*H_2CH_2), 14.4 (br, CH_2*C*H_2B). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 25.3 (br, $\Delta\nu_{½}$ = 170 Hz, P). ^{11}B NMR (160 MHz, CD_2Cl_2): δ 22.3 (br, $\Delta\nu_{½}$ = 270 Hz, Bpin, 1B), 1.9 (br, $\Delta\nu_{½}$ = 310 Hz, BBN, 1B).

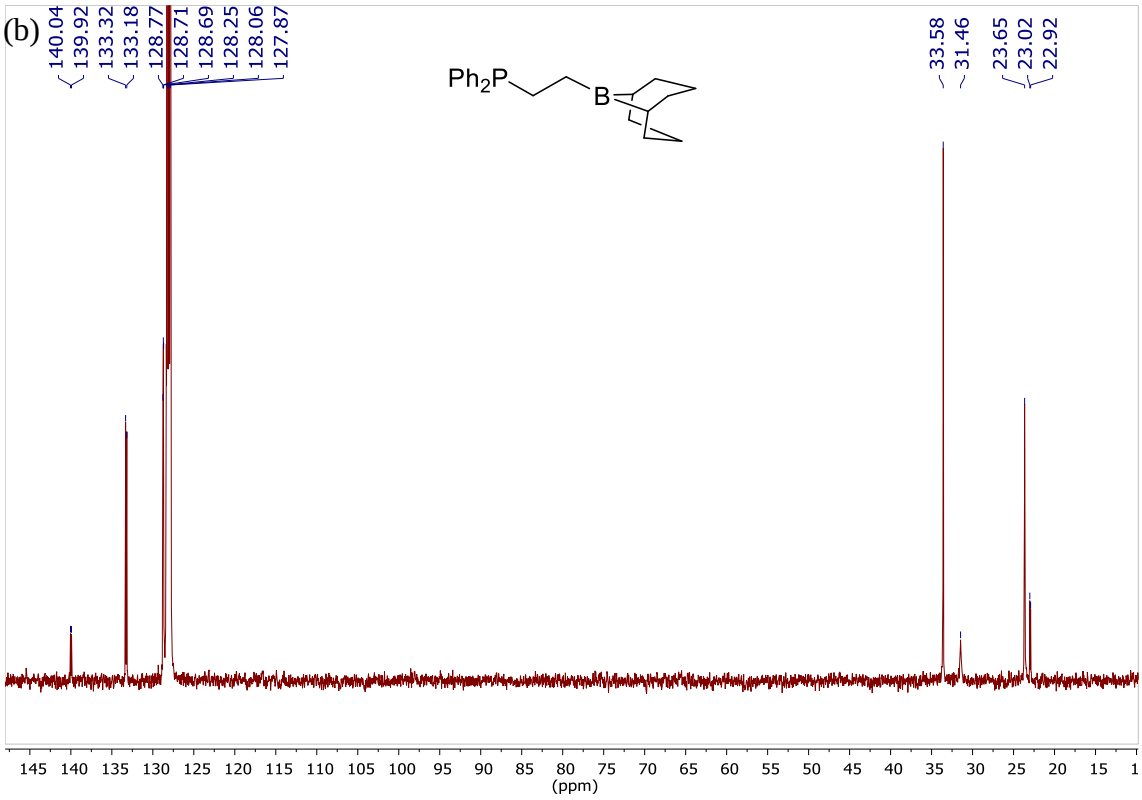
Reaction of compound 2 with 1 equiv of HBpin and $^{13}CO_2$. *NMR scale*: A solution of compound **2** (36 mg, 0.10 mmol) and HBpin (17 μL, 0.12 mmol) in C_6D_6 (*ca*. 0.6 mL) was charged into an NMR tube with a J. Young stopper. The solution was subjected to a freeze-pump-thaw cycle and, once thawed at room temperature, $^{13}CO_2$ gas was introduced

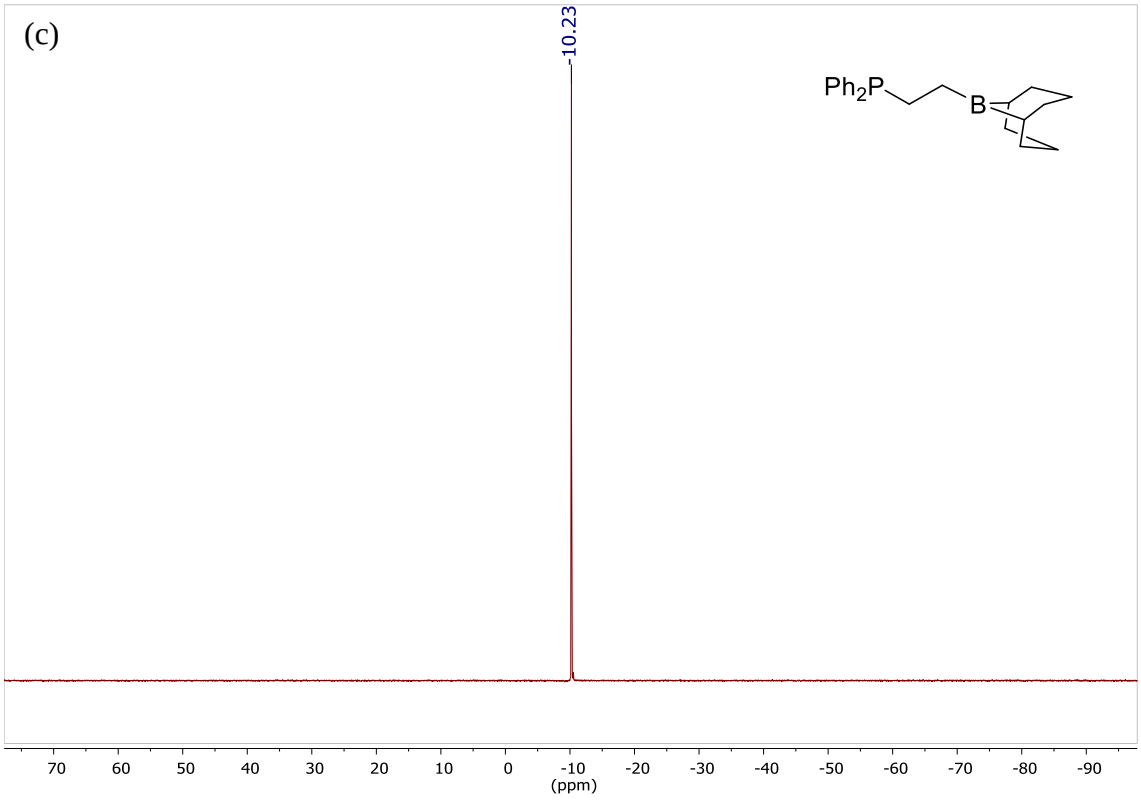
(*ca.* 1 atm). After 15 min all $^{13}CO_2$ was depleted while there is still unreacted HBpin and compound **2**, together with the major product **^{13}C-6**, as observed by NMR. Then, a second freeze-pump-thaw cycle was carried out, introducing more $^{13}CO_2$ gas afterwards. Almost instantly, vast amounts of a white precipitate, presumably of compound **^{13}C-6**, were formed inside the tube. Then, C_6D_6 was eliminated under vacuum and the solid was dissolved in CD_2Cl_2 to characterize the reaction crude *in situ*, which contains **^{13}C-6**, as the major product and minor amounts of **2**, $O(Bpin)_2$ and other unidentified products (ratio **^{13}C-6**/**2** ca. 4 to 1). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.31 (s, $^1J_{CH}$ = 197.8, 1H, $^{13}CHO_2$), 7.85 – 7.55 (m, 10H, Ph), 5.12 (d, *J* = 2.9, 2H, C*H*$_2$O), 2.68 (m, 2H, PC*H*$_2$CH$_2$), 1.90 – 1.30 (m, 12H, C*H*$_2$-BBN), 1.13 (s, 12H, C*H*$_3$-pin), 0.60 (m, br, 4H, C*H*-BBN + CH$_2$C*H*$_2$B). ^{13}C{^{1}H} NMR (126 MHz,) δ 167.3 (s, H^{13}*C*O$_2$), 135.2 (s, *p*-Ph), 133.5 (d, J_{PC} = 8.6, *p*-Ph), 130.5 (d, J_{PC} = 11.8, *o*-Ph), 117.8 (d, J_{PC} = 80.7, *ipso*-Ph), 84.9 (s, *C*-pin), 58.4 (d, J_{PC} = 67.7, P*C*H$_2$O), 32.2 (br, *C*H$_2$-BBN), 25.9 (s, *C*H$_2$-BBN), 25.1 (br, *C*H-BBN), 24.6 (s, *C*H$_3$-pin), 16.7 (d, J_{PC} = 37.1, P*C*H$_2$CH$_2$), 14.4 (br, CH$_2$*C*H$_2$B). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 25.3 (br, $\Delta\nu_{½}$ = 170 Hz, P). ^{11}B NMR (160 MHz, CD_2Cl_2): δ 22.3 (br, Bpin, 1B), 1.8 (br, BBN, 1B).

Preparation of (BH$_3$)Ph$_2$P(CH$_2$)$_2$BBN (1-BH$_3$). $BH_3{\cdot}SMe_2$ (12 μL, 0.12 mmol) was added to a suspension of compound **1** (34 mg, 0.10 mmol) in toluene (*ca*. 2 mL) at room temperature. A colorless solution containing **1-BH$_3$** was obtained after stirring for 10 min. Then, the solvent was eliminated under vacuum to obtain **1-BH$_3$** as a colorless oil. Pentane (3 mL) was added afterwards, and the mixture stirred for 5 min. The solvent was again eliminated under vacuum. This process was repeated one more time until adduct **1-BH$_3$** was obtained as a white solid (30 mg, 86%). Anal calc. for $C_{22}H_{31}B_2P$ (**6**): C, 75.91; H, 8.98. Found: C, 76.03; H, 8.85. ^{1}H NMR (400 MHz): δ 7.69 (m, 4H, *o*-Ph), 7.08 – 6.97 (m, 6H, *m/p*-Ph), 2.31 (m, 2H, PC*H*$_2$CH$_2$), 2.25 – 1.35 (vbr, 3H, B*H*$_3$), 1.90 – 1.10 (m, 16H, CH$_2$C*H*$_2$B + BBN). ^{1}H{^{11}B} NMR (400 MHz): δ 1.83 (s, 3H, B*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz) δ 132.7 (d, J_{PC} = 8.8, *o*-Ph), 131.1 (d, J_{PC} = 2.7, *p*-Ph), 130.7 (d, J_{PC} = 53.0, *ipso*-Ph), 129.0 (d, J_{PC} = 9.6, *m*-Ph), 33.7 (s, *C*H$_2$-BBN), 31.3 (br, *C*H-BBN), 23.6 (s, *C*H$_2$-BBN), 21.3 (d, J_{PC} = 36.2, P*C*H$_2$CH$_2$), 19.9 (br, CH$_2$*C*H$_2$B). ^{31}P{^{1}H} NMR (202 MHz):δ 19.3 (m, br, P).^{11}B NMR (160 MHz): δ 84.8, (br, BBN), –38.6 (qd, J_{BH} = 100, J_{BP} = 57, *B*H$_3$). ^{11}B{^{1}H} NMR (160 MHz): δ 85.2, (br, BBN), –38.6 (d, J_{BP} = 57, *B*H$_3$).

Figure S1. ^{1}H (a), $^{13}C\{^{1}H\}$ (b), $^{31}P\{^{1}H\}$ (c) and ^{11}B (d) NMR spectra for compound **1** in C_6D_6.






(c)
-10.23
Ph2P
B
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
(ppm)

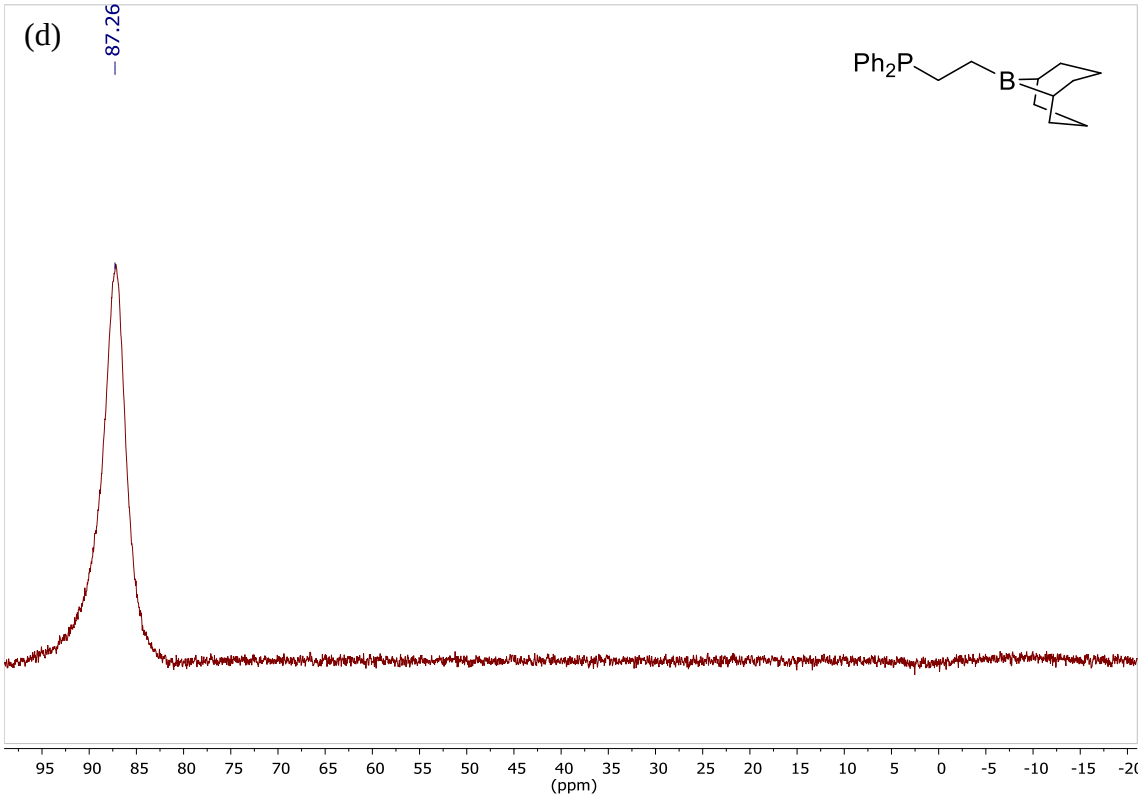
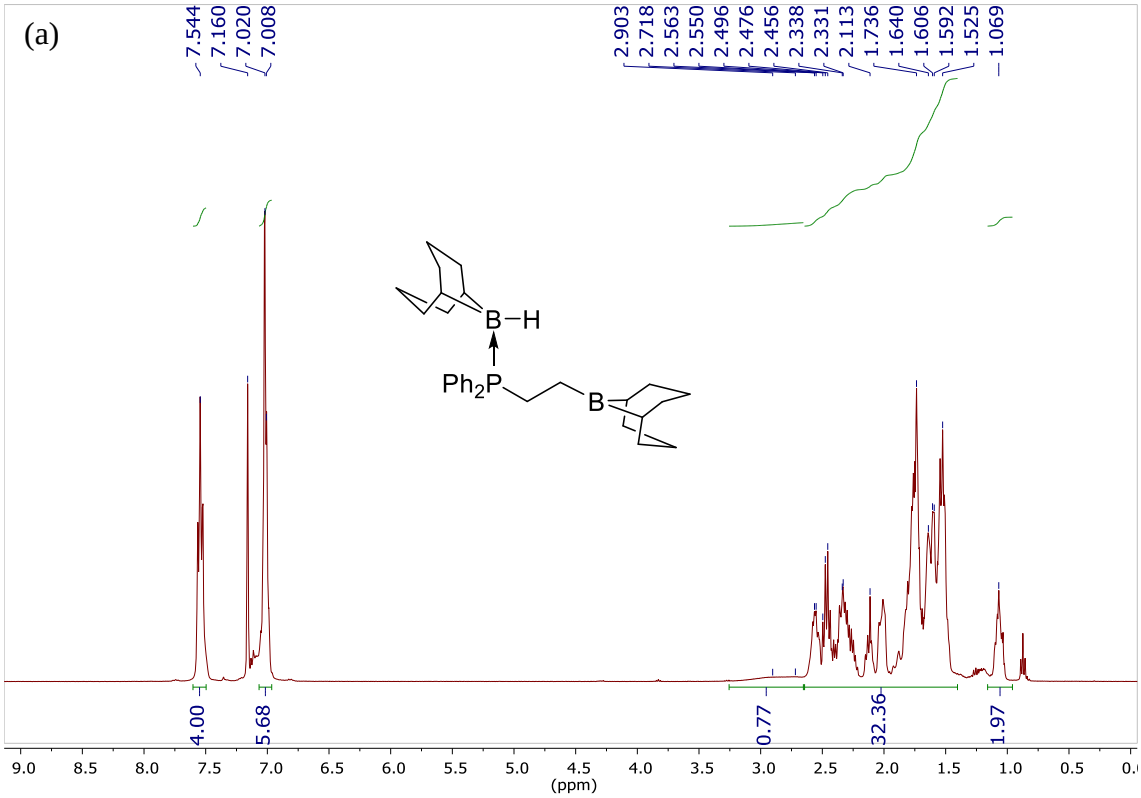
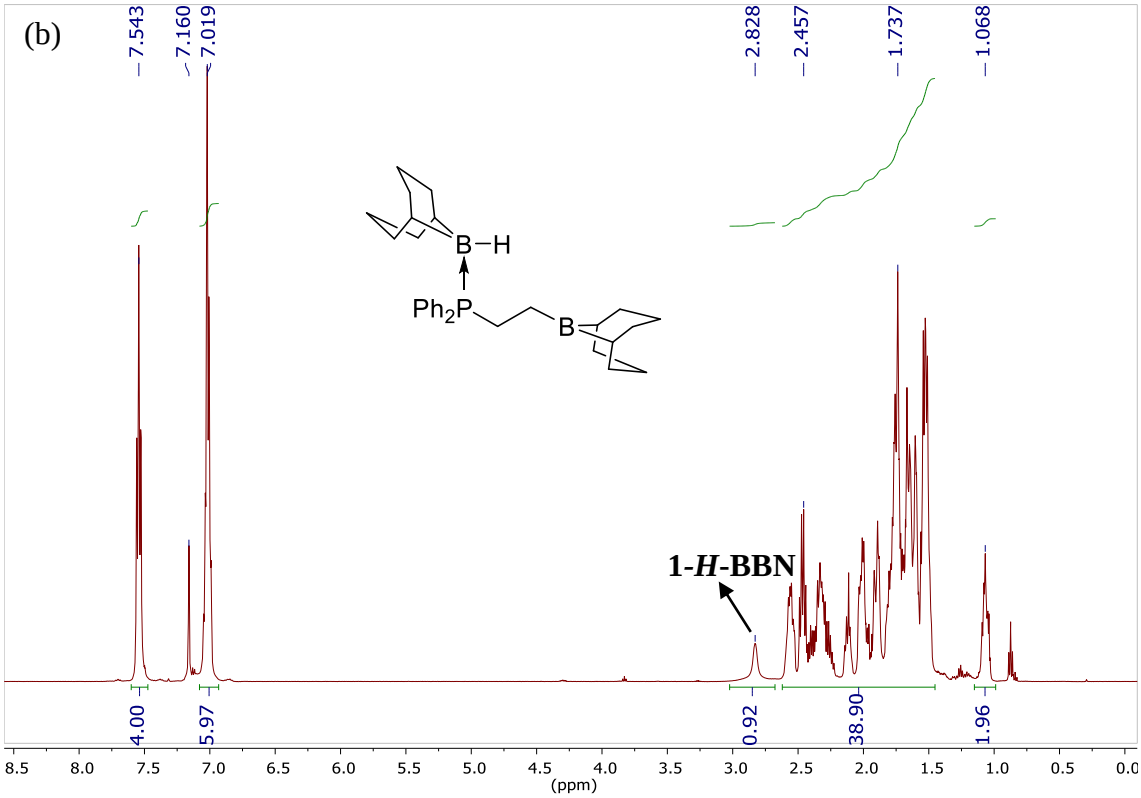
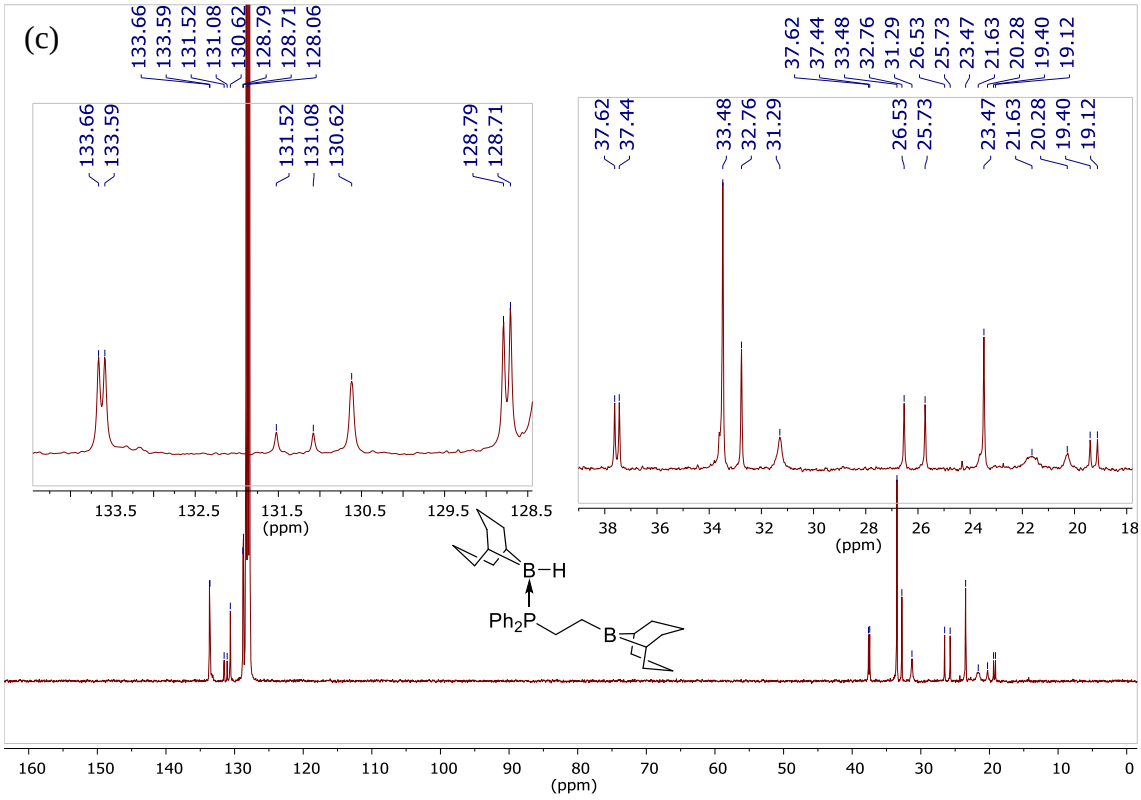
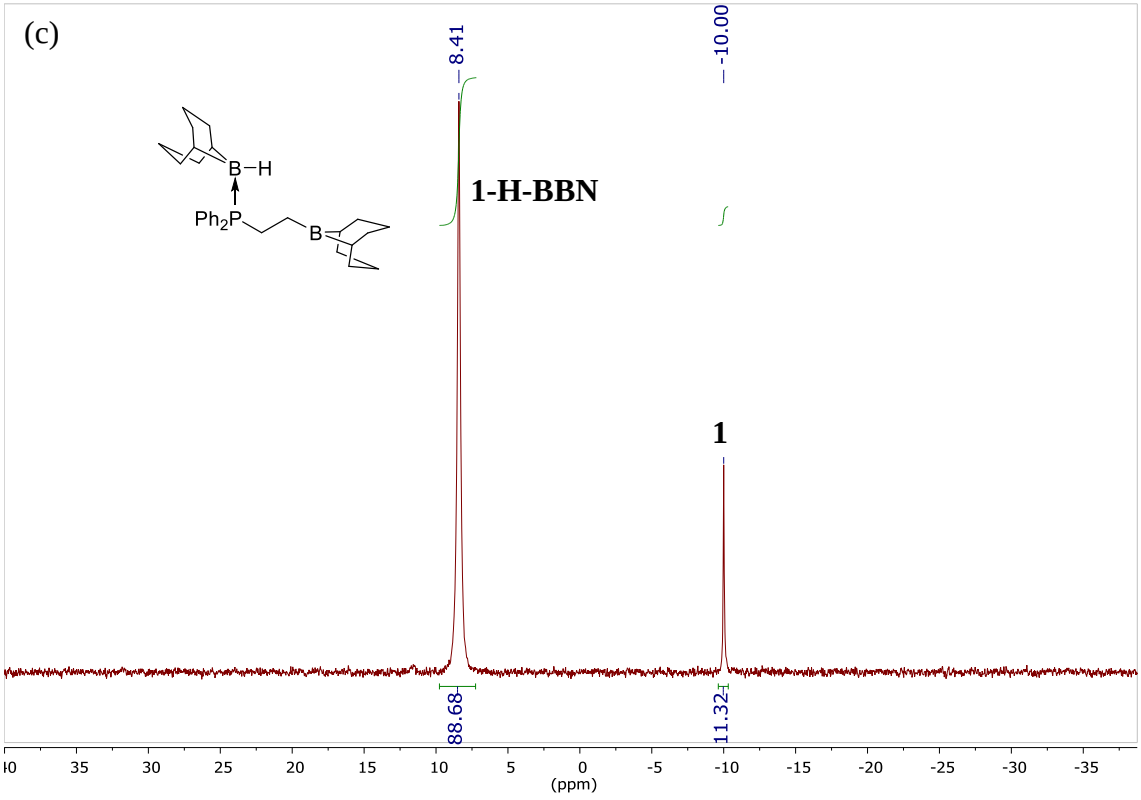

(d)
87.26
Ph2P
B
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
(ppm)

Figure S2. ^{1}H (a), $^{1}H\{^{11}B\}$ (b), $^{13}C\{^{1}H\}$ (c), $^{31}P\{^{1}H\}$ (d) and ^{11}B (e) NMR spectra for compound **1-HBBN** in C_6D_6 at 25 ºC.






(c)
133.66
133.59
131.52
131.08
130.62
128.79
128.71
128.06
37.62
37.44
33.48
32.76
31.29
26.53
25.73
23.47
21.63
20.28
19.40
19.12
B–H
Ph2P
B
(ppm)


(c)
8.41
-10.00
1-H-BBN
1
88.68
11.32
B–H
Ph2P
B
(ppm)

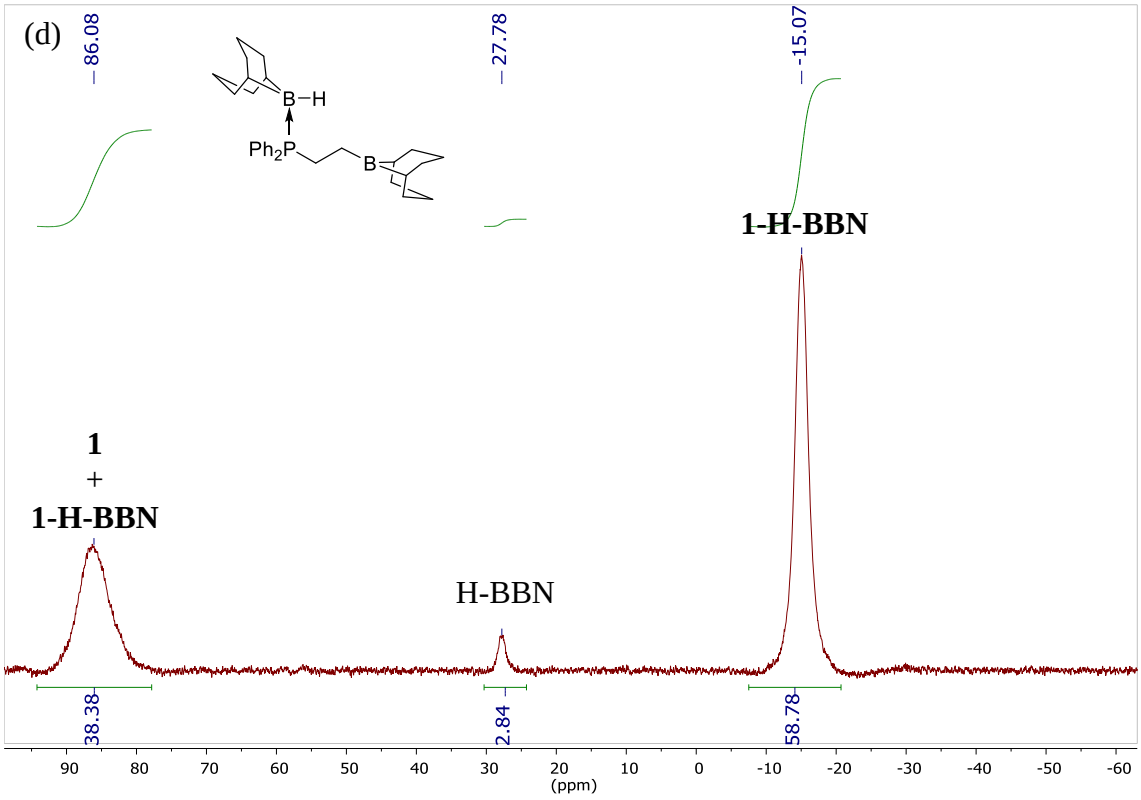
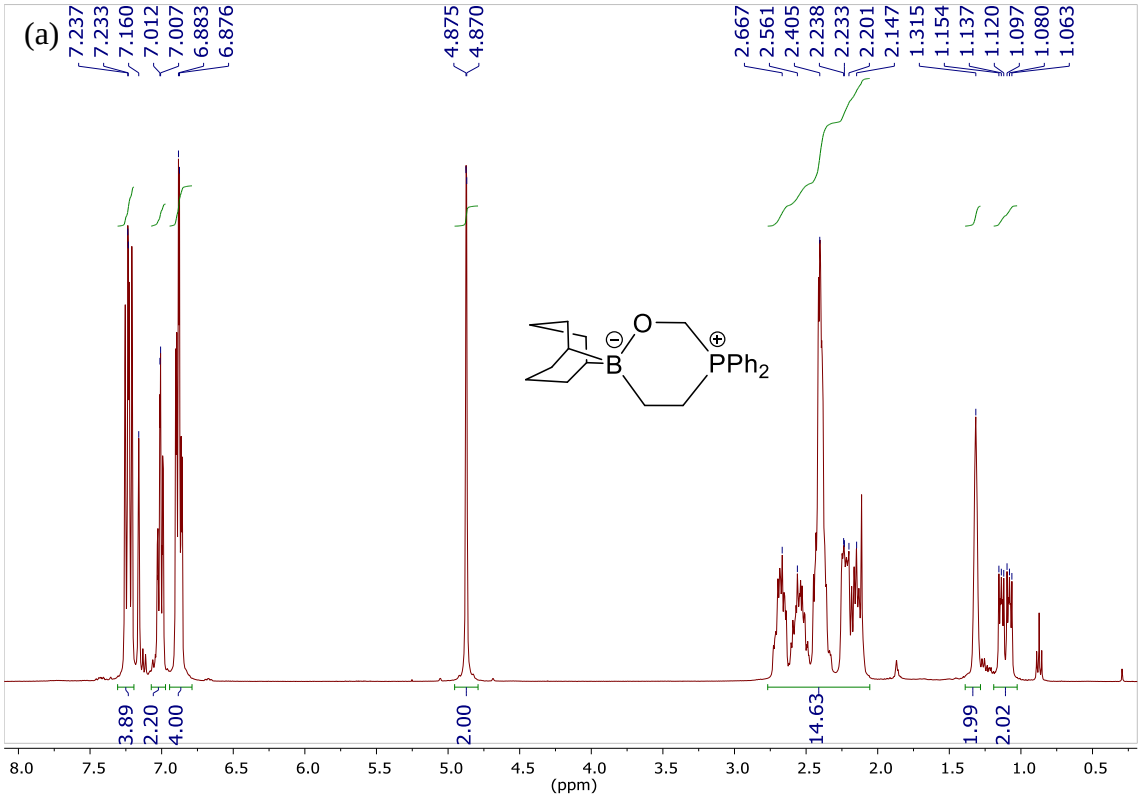
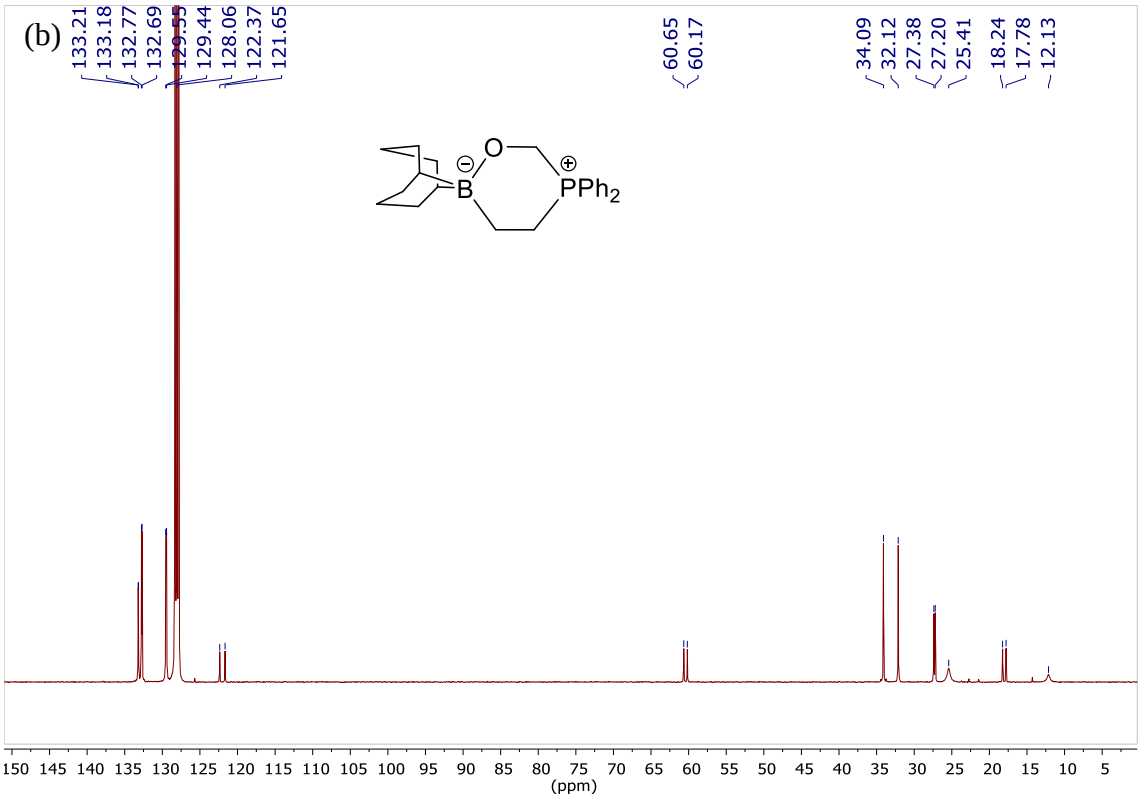
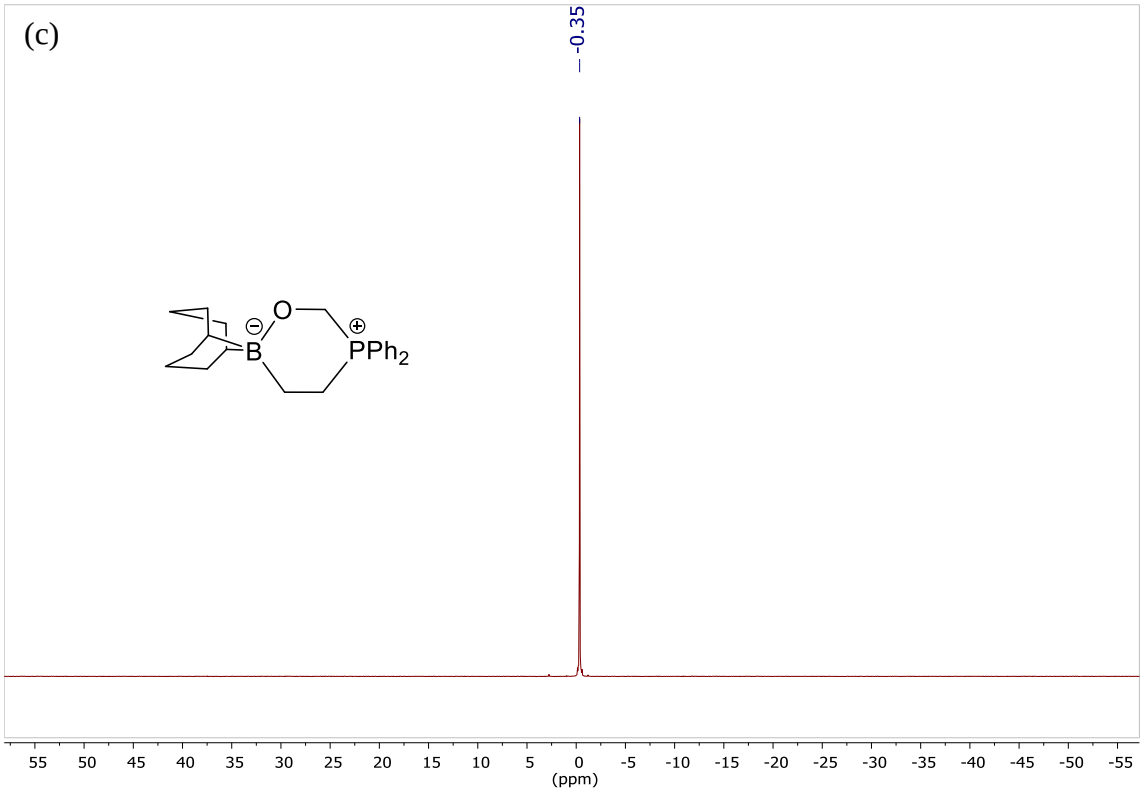

(d)
86.08
27.78
-15.07
B–H
Ph2P
B
1-H-BBN
1
+
1-H-BBN
H-BBN
38.38
2.84
58.78
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
(ppm)

Figure S3. ^{1}H (a), $^{13}C\{^{1}H\}$ (b), $^{31}P\{^{1}H\}$ (c) and ^{11}B (d) NMR spectra for compound **2** in C_6D_6.





(c)


-0.35
O
B
PPh2
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55
(ppm)

(d)

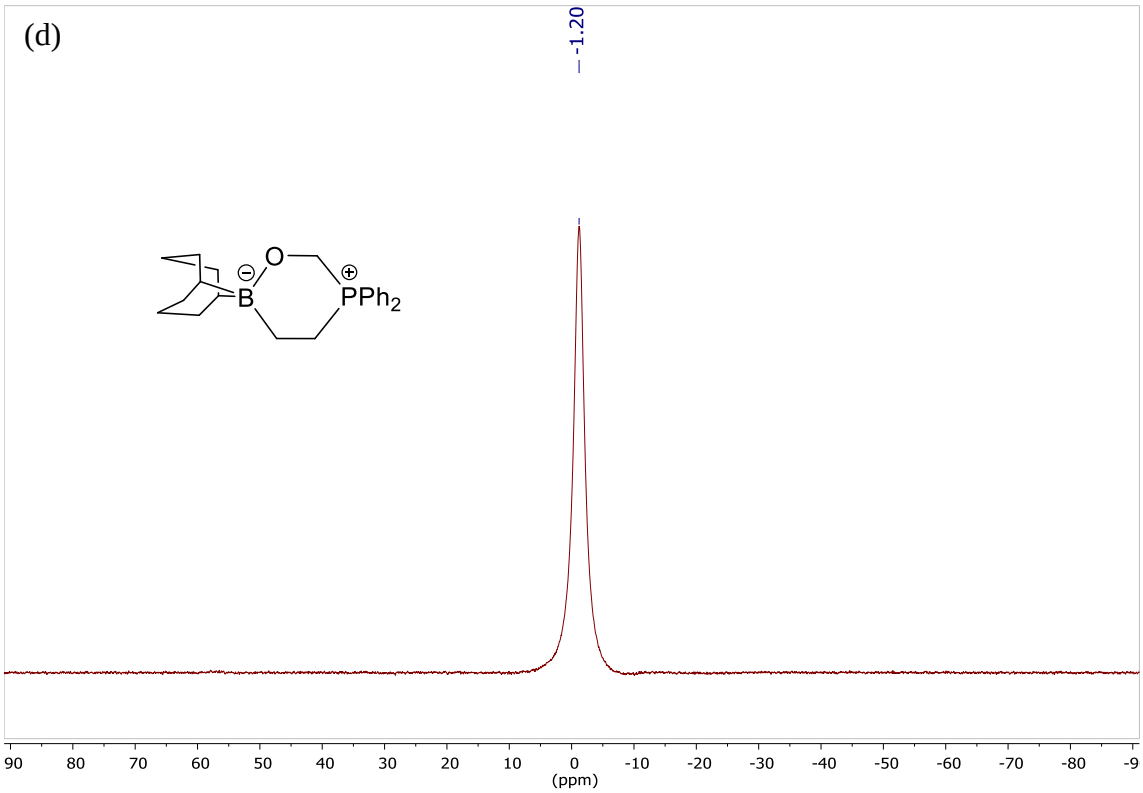
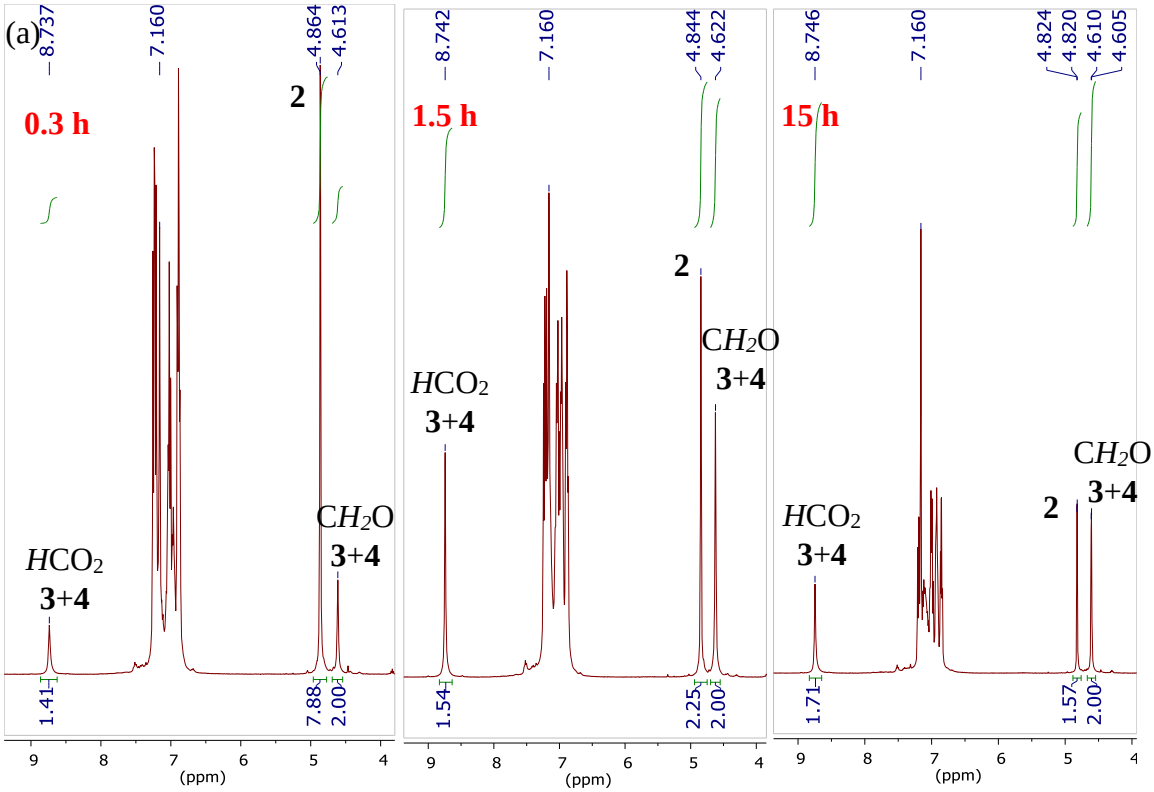
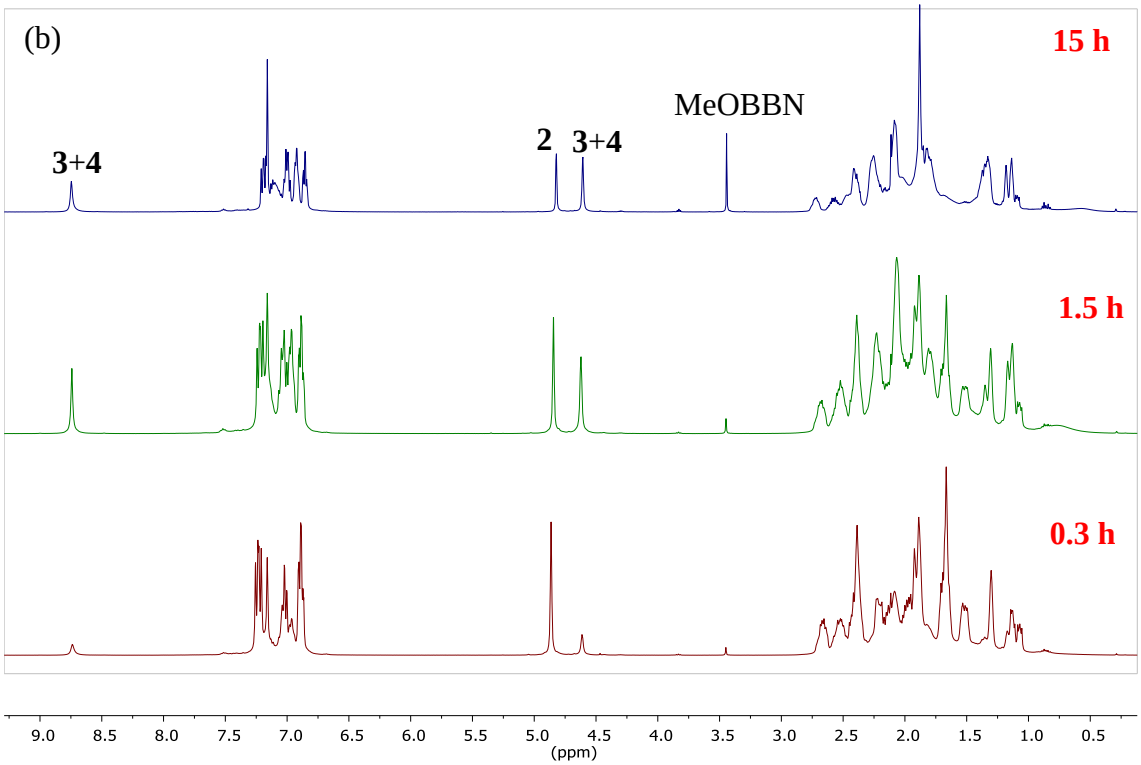
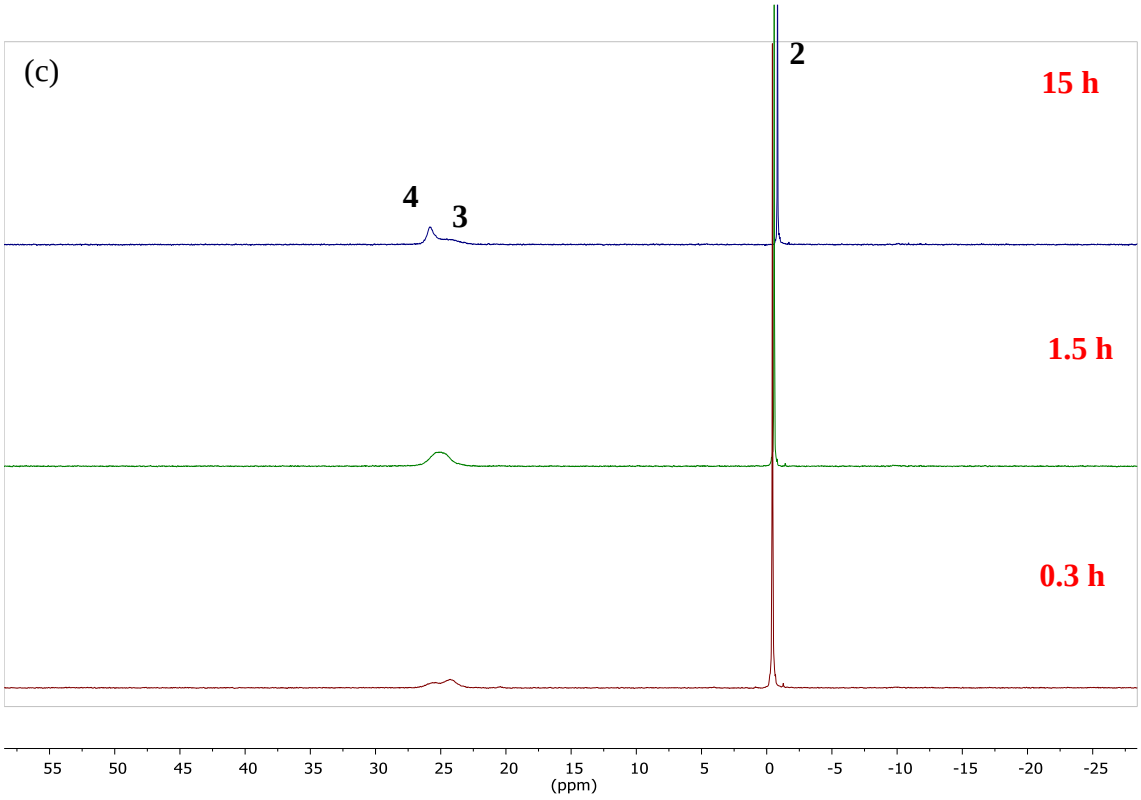

-1.20
O
B
PPh2
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -9
(ppm)

Figure S4. (a) ^{1}H NMR spectra showing the reaction between equimolar amounts of **2** and H-BBN under 1 atm of CO_2 in C_6D_6.and the integral values for the C*H*$_2$O and *H*CO$_2$ units of **3** and **4**; ^{1}H (b), ^{31}P{^{1}H} (c) and ^{11}B (c) NMR stacked plots for the same reaction.






(c)
2
15 h
4
3
1.5 h
0.3 h
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
(ppm)

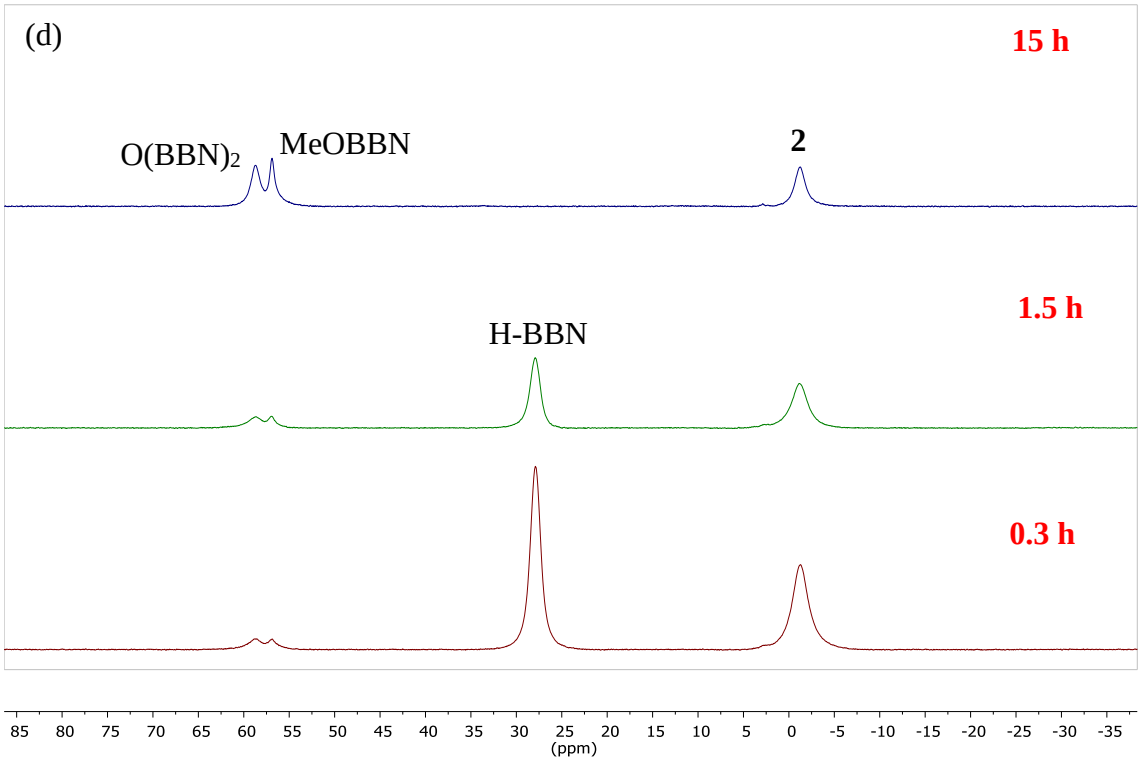
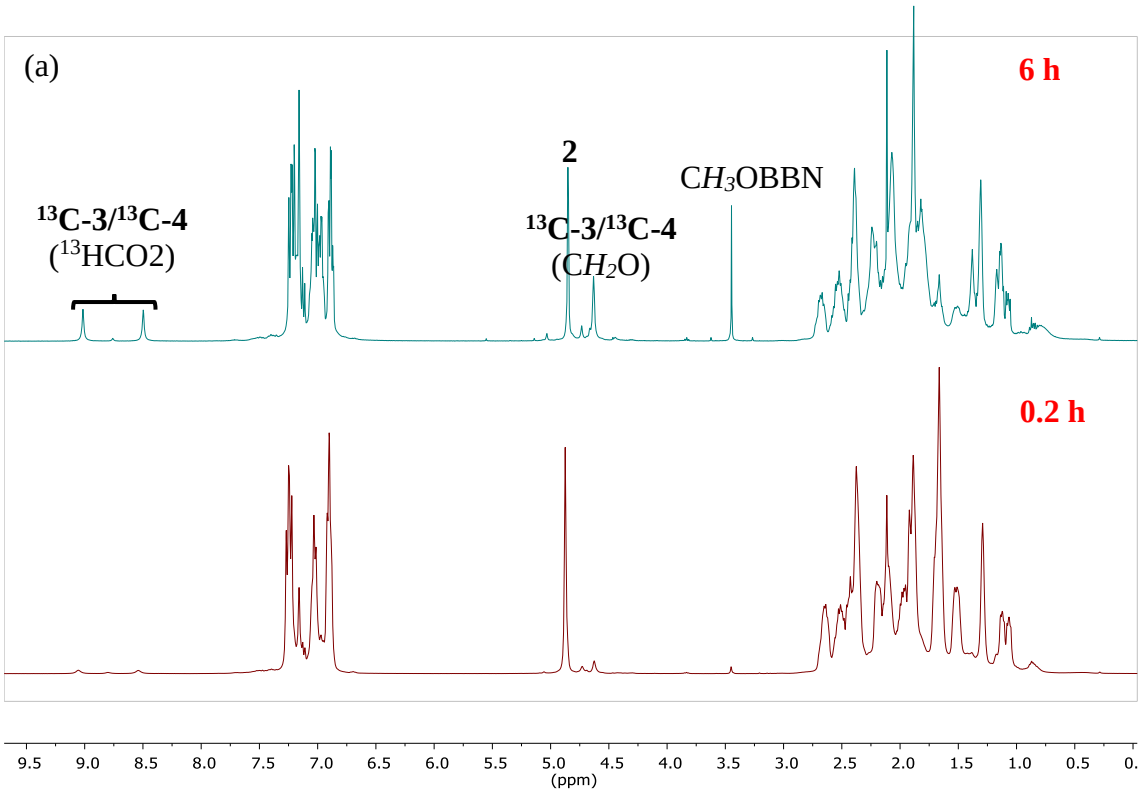
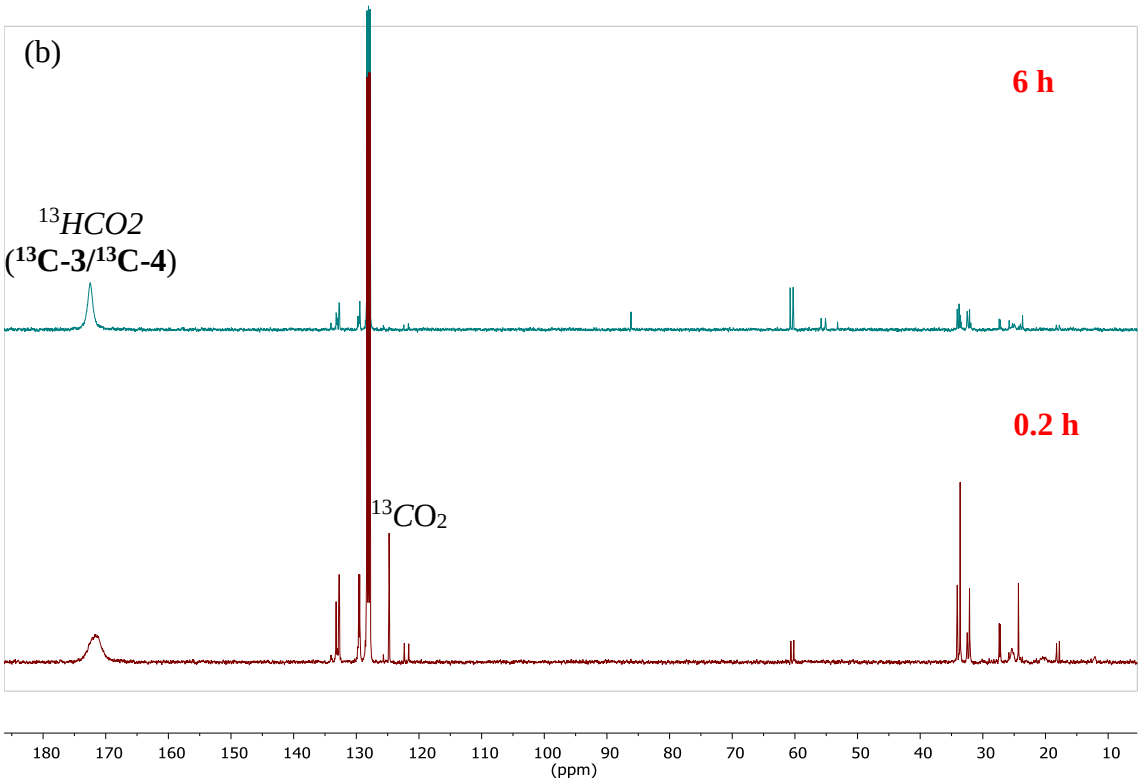
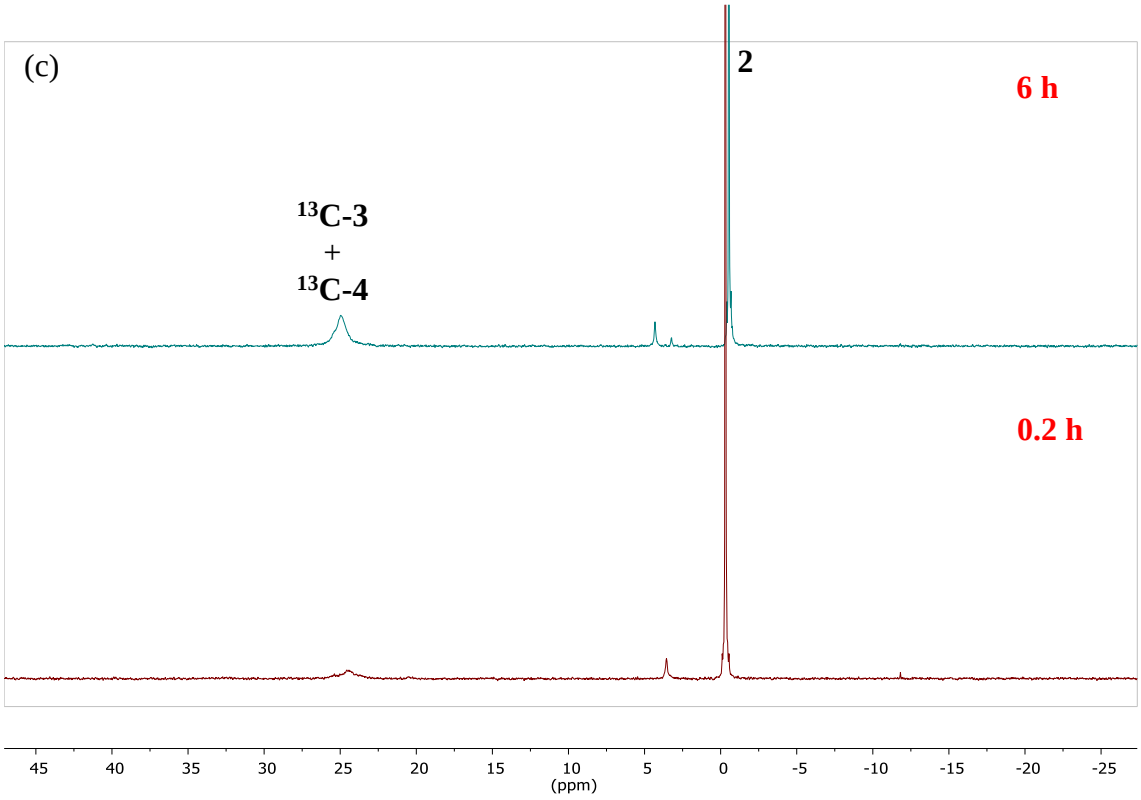

(d)
15 h
O(BBN)2
MeOBBN
2
1.5 h
H-BBN
0.3 h
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
(ppm)

Figure S5. NMR stacked plots for the reaction between equimolar amounts of **2** and H-BBN under 1 atm of $^{13}CO_2$ in C_6D_6: ^{1}H (a), $^{13}C\{^{1}H\}$ (b), $^{31}P\{^{1}H\}$ (c) and ^{11}B (d) NMR.






(c)
2
6 h
^{13}C-3
+
^{13}C-4
0.2 h
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
(ppm)

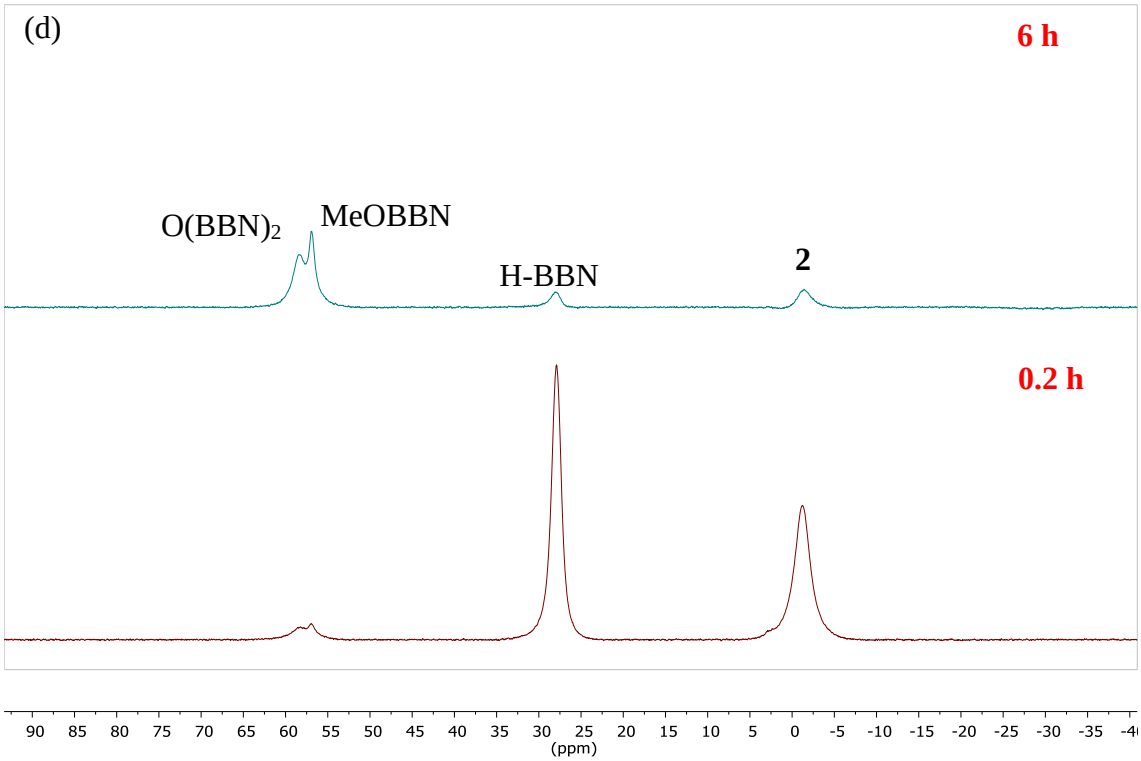
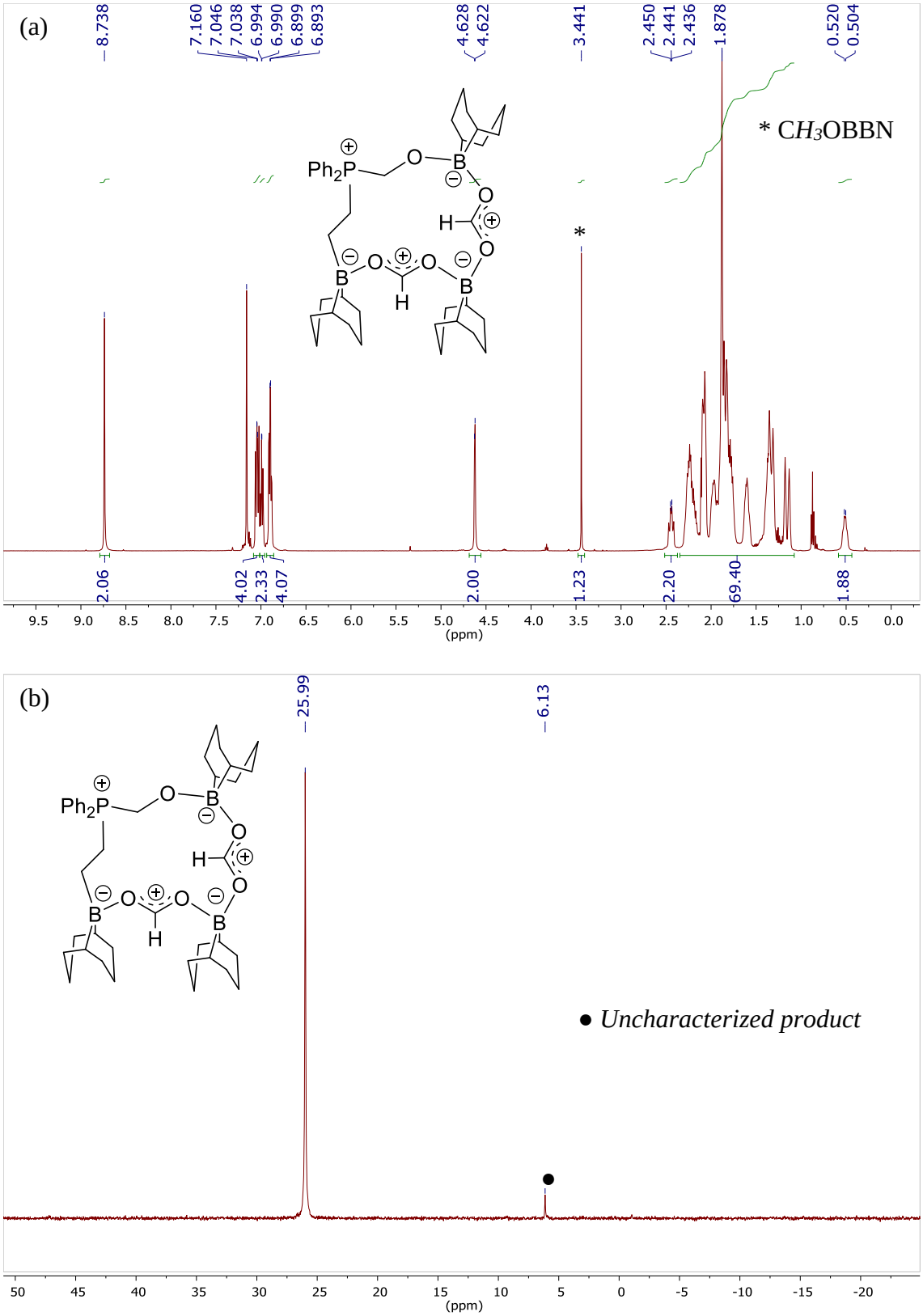

(d)
6 h
O(BBN)$_2$
MeOBBN
H-BBN
2
0.2 h
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
(ppm)

Figure S6. ^{1}H (a), $^{31}P\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for the reaction crude of **2**, H-BBN (2 equiv) and CO_2 (1 atm) after 3 days at room temperature in C_6D_6 to give compound **4**.



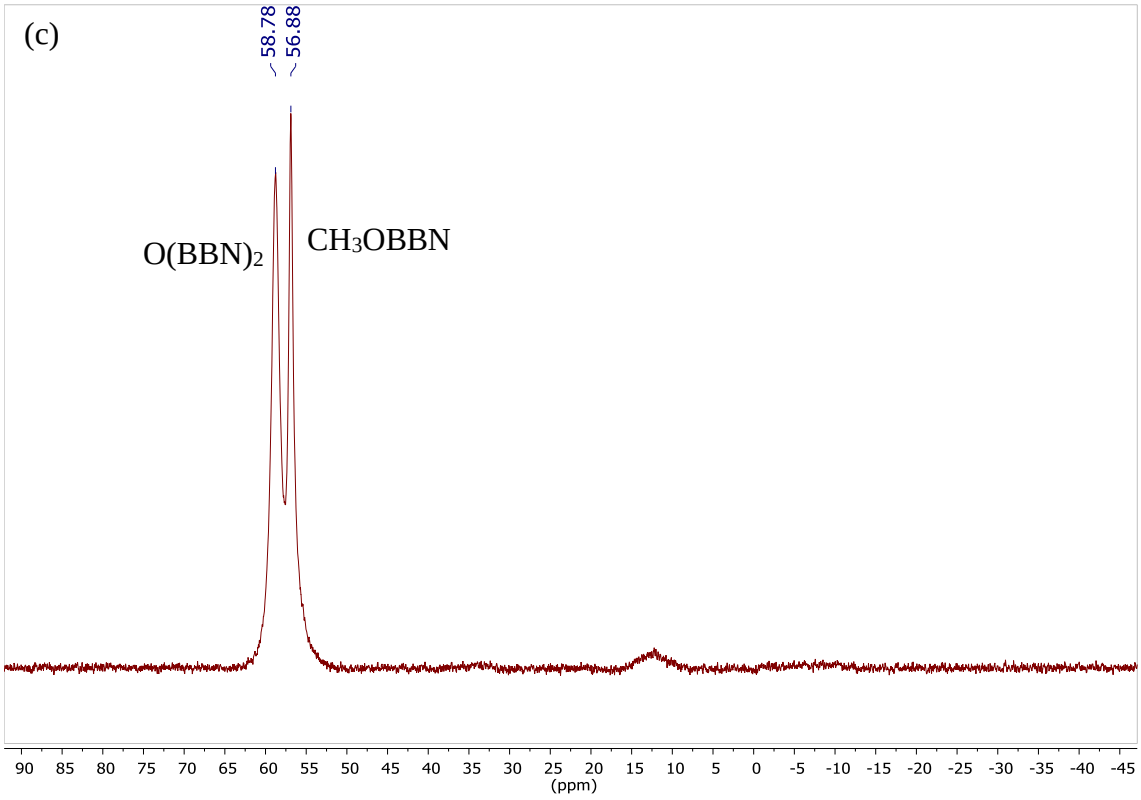
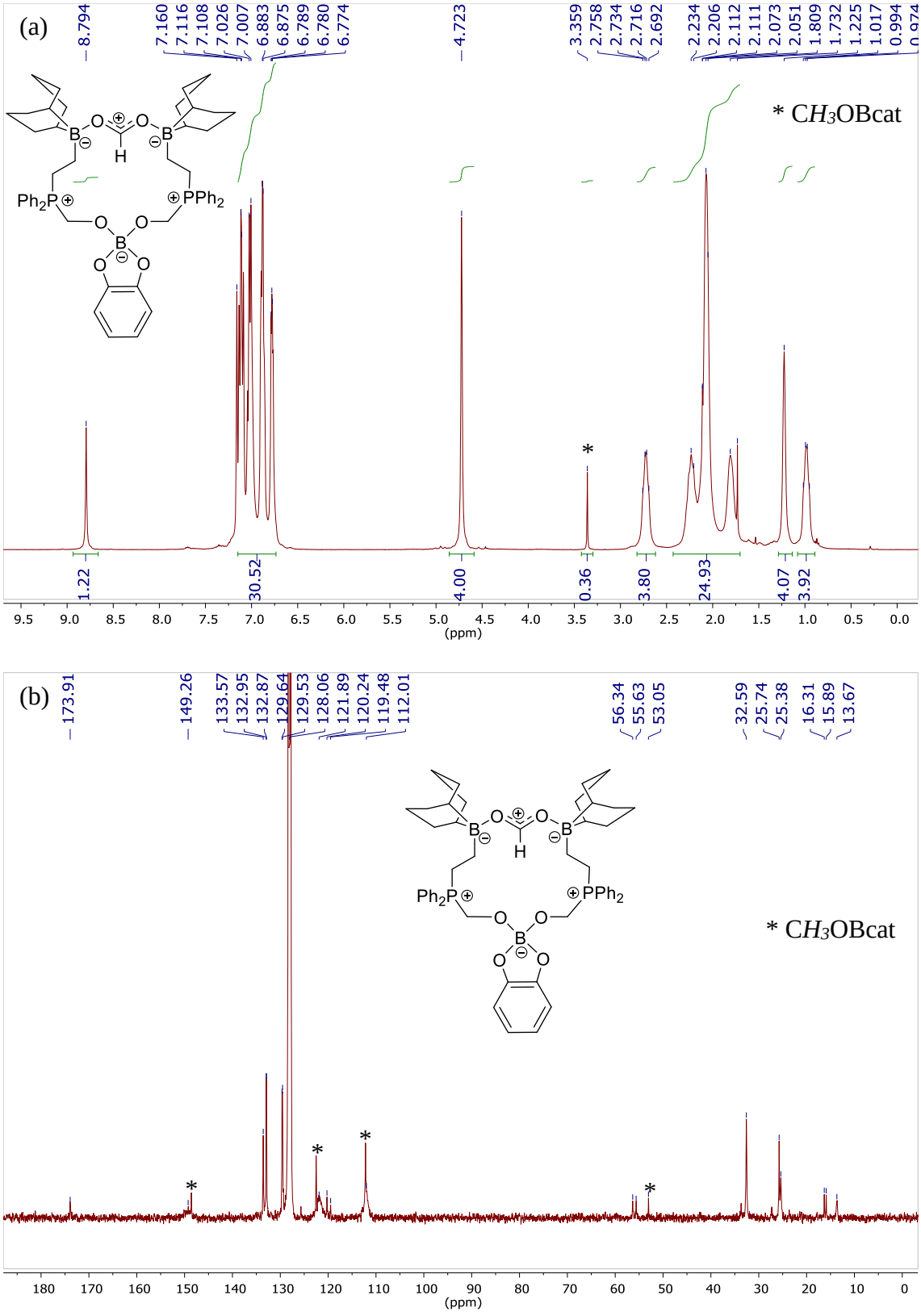
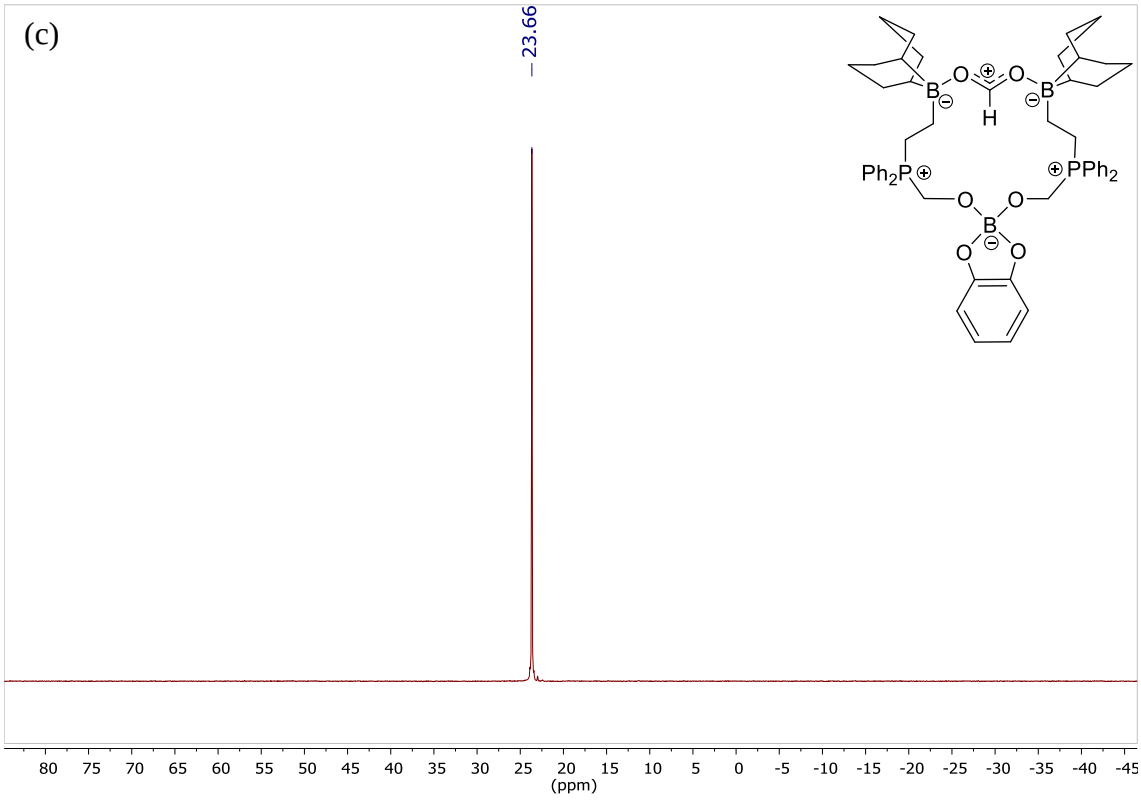
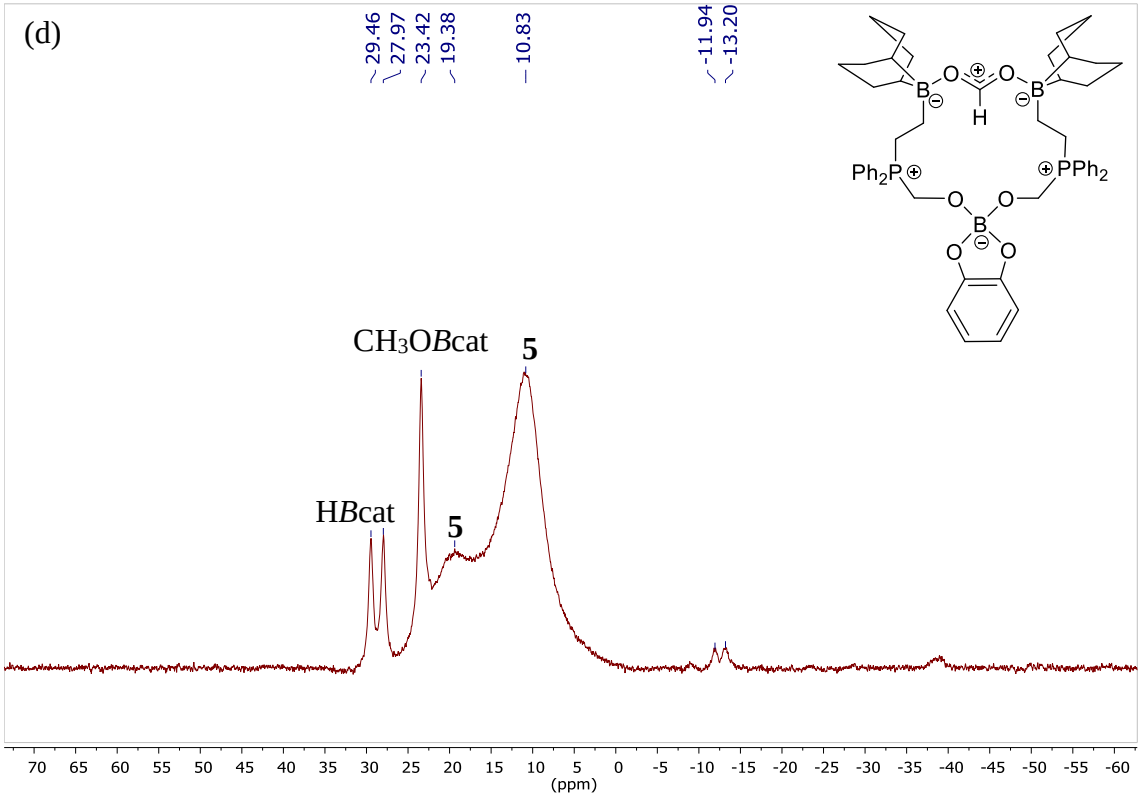
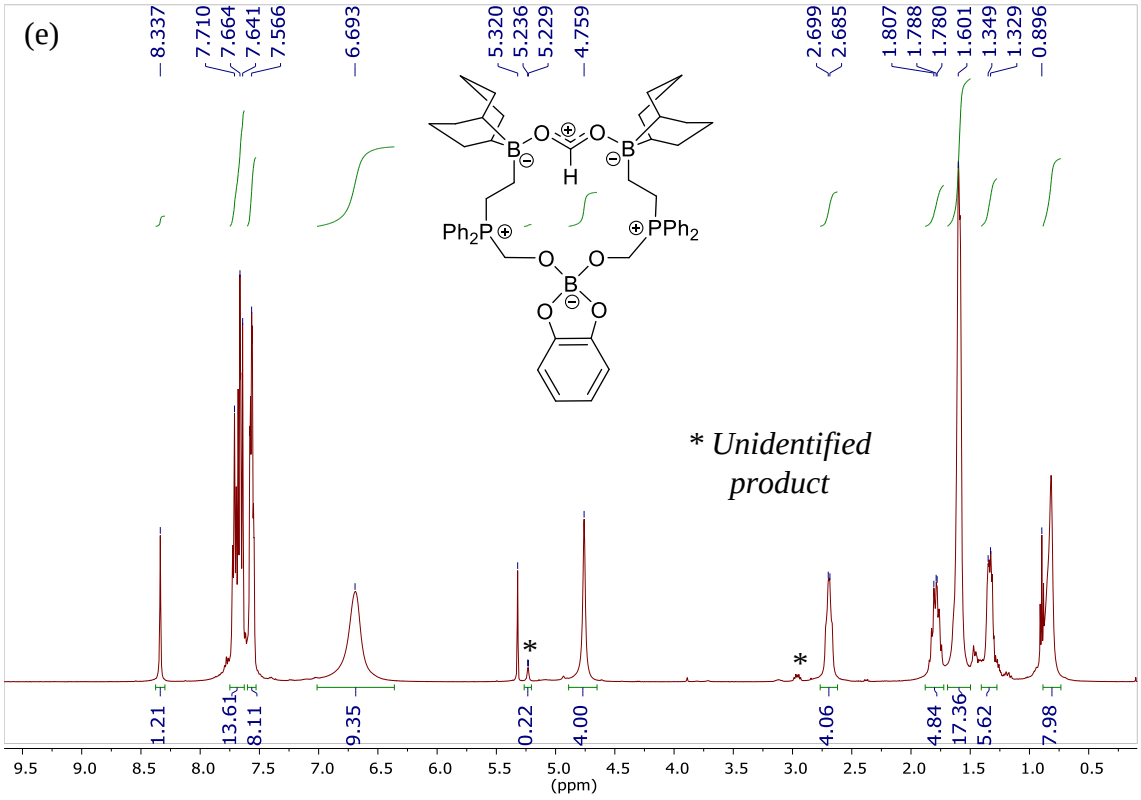

(c)
58.78
56.88
O(BBN)2
CH3OBBN
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
(ppm)

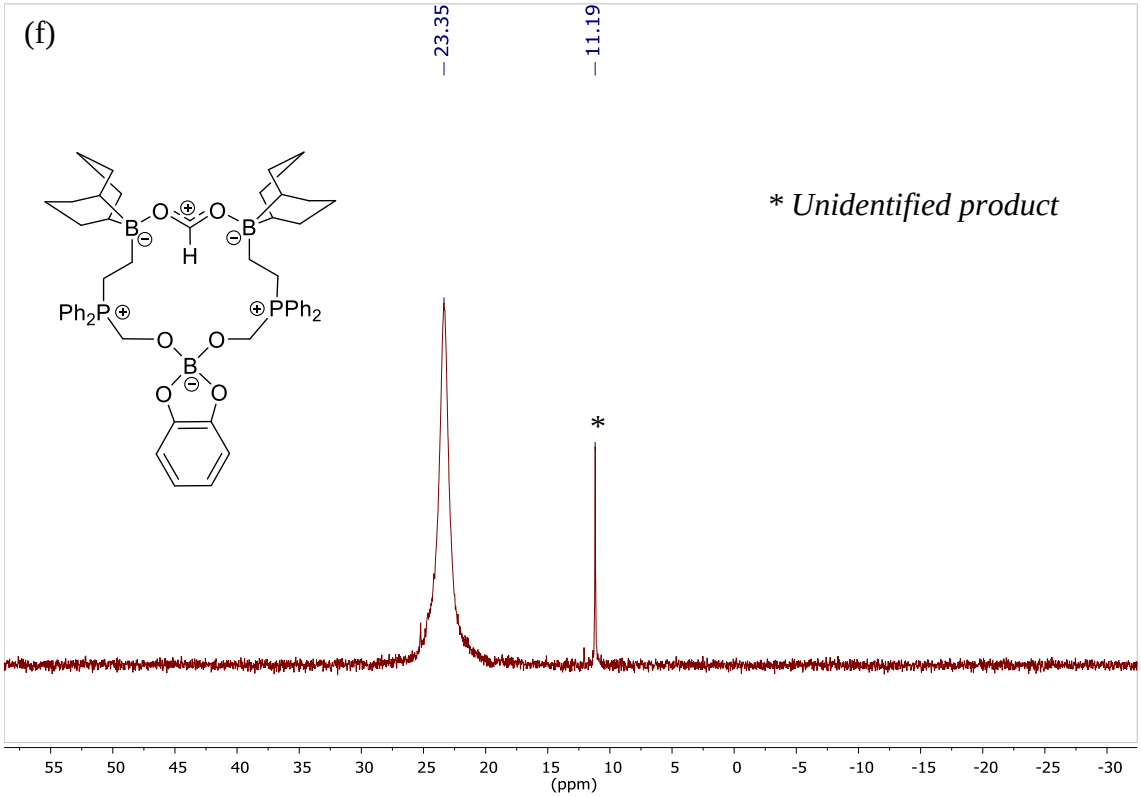
Figure S7. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) $^{31}P\{^{1}H\}$ (c) and ^{11}B (d) NMR spectra of the reaction crude of **2**, HBcat (1 equiv) and CO_2 after 15 min at room temperature in C_6D_6, containing **5** as the major species; ^{1}H (e), $^{31}P\{^{1}H\}$ (f) and ^{11}B (g) NMR of compound **5** in CD_2Cl_2.




(c)
23.66
Ph2P
PPh2
(ppm)


(d)
29.46
27.97
23.42
19.38
10.83
-11.94
-13.20
CH3OBcat
5
HBcat
5
Ph2P
PPh2
(ppm)


(e)
8.337
7.710
7.664
7.641
7.566
6.693
5.320
5.236
5.229
4.759
2.699
2.685
1.807
1.788
1.780
1.601
1.349
1.329
0.896
* Unidentified product
1.21
13.61
8.11
9.35
0.22
4.00
4.06
4.84
17.36
5.62
7.98
(ppm)


(f)
23.35
11.19
* Unidentified product
(ppm)

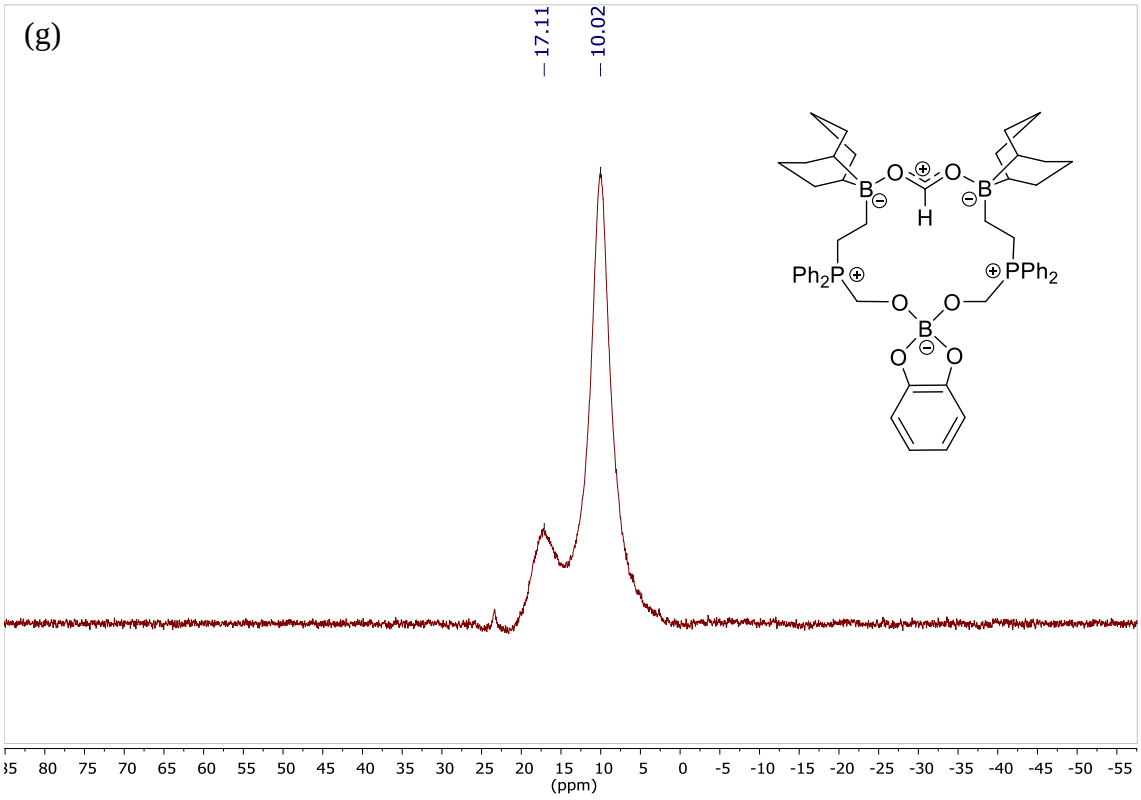
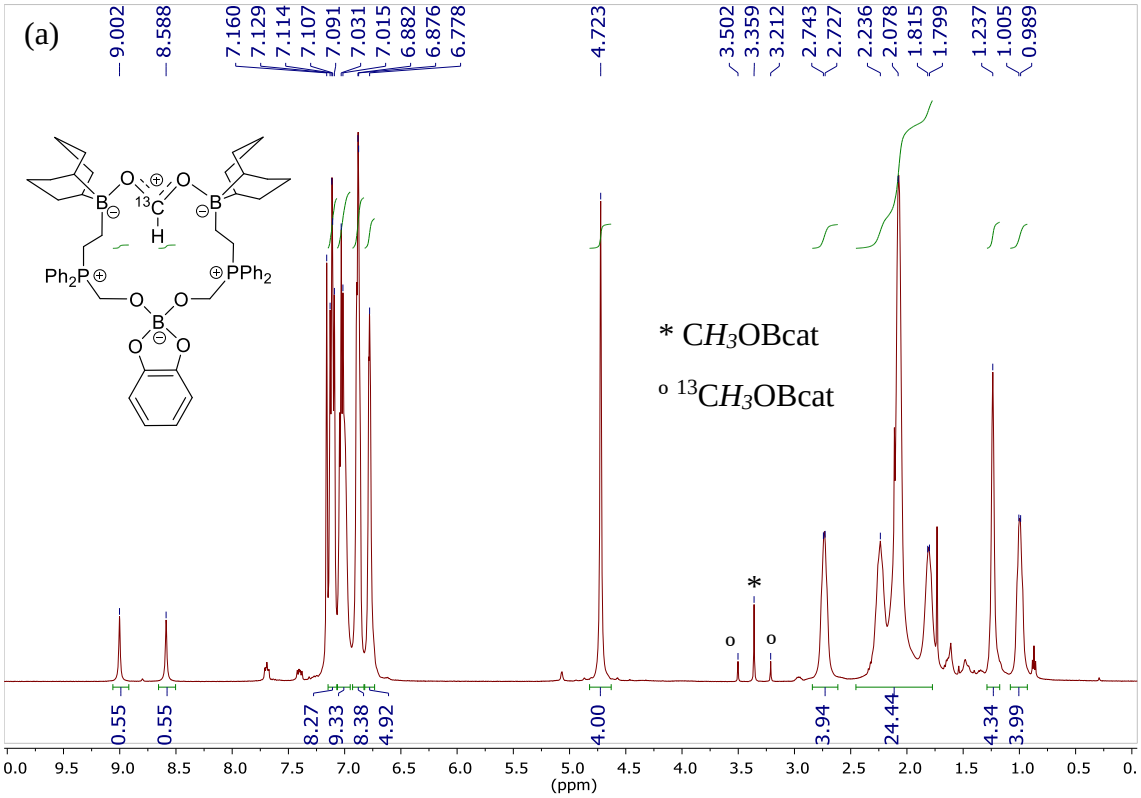
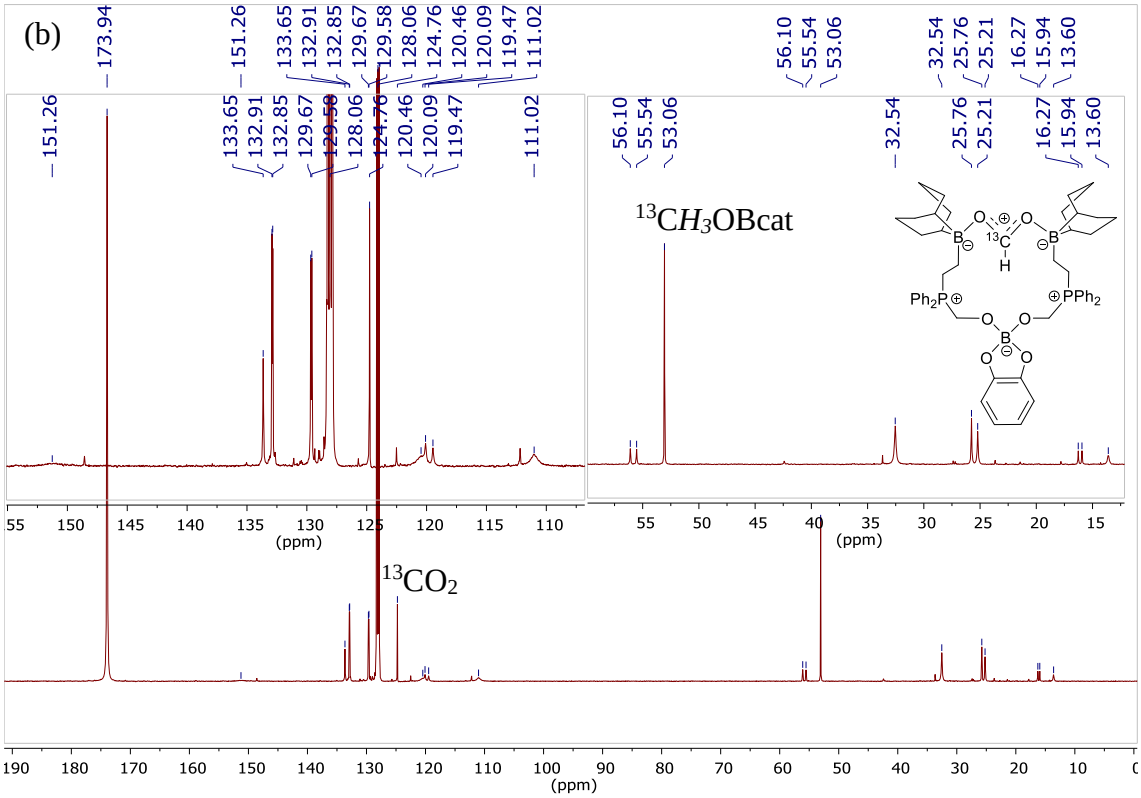
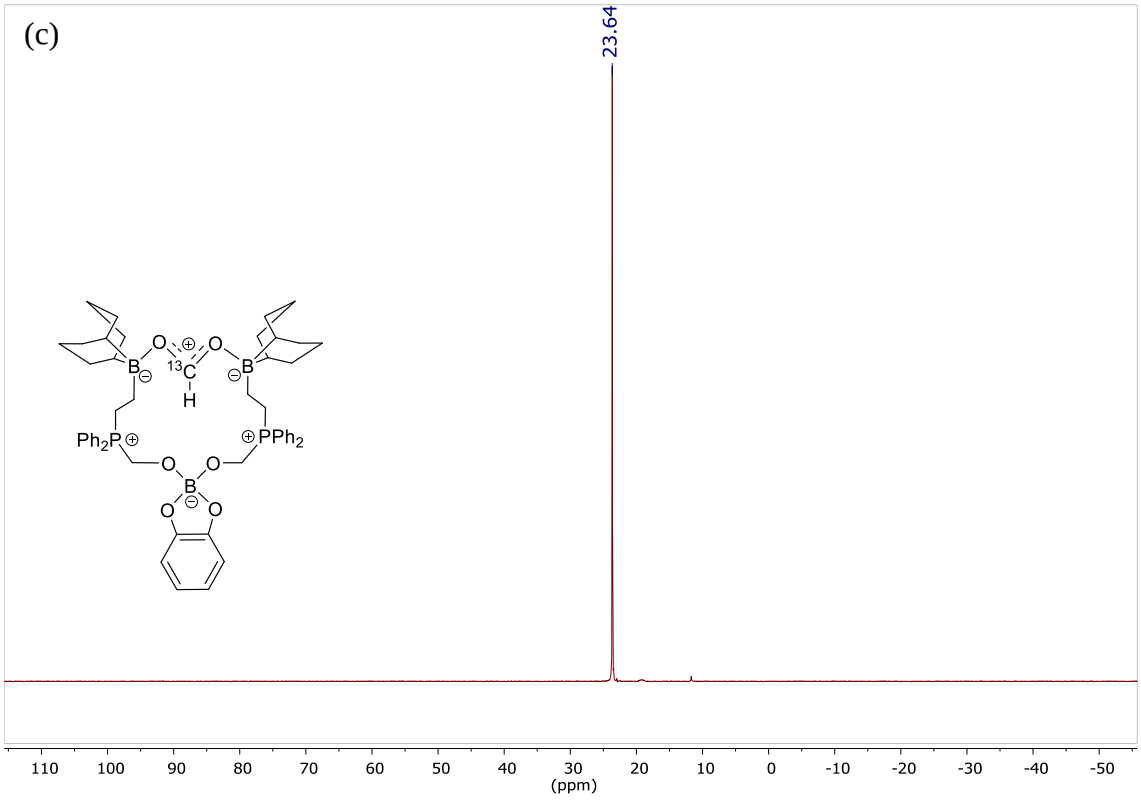

(g)
17.11
10.02
B
O
O
B
H
Ph2P
PPh2
O
O
B
O
O
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55
(ppm)

Figure S8. ^{1}H (a), $^{13}C\{^{1}H\}$ (b), $^{31}P\{^{1}H\}$ (c) and ^{11}B (d) NMR spectra of the reaction crude of **2**, HBcat (1 equiv) and $^{13}CO_2$ in C_6D_6, containing **^{13}C-5** as the major species.





(c)


23.64
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
(ppm)

(d)

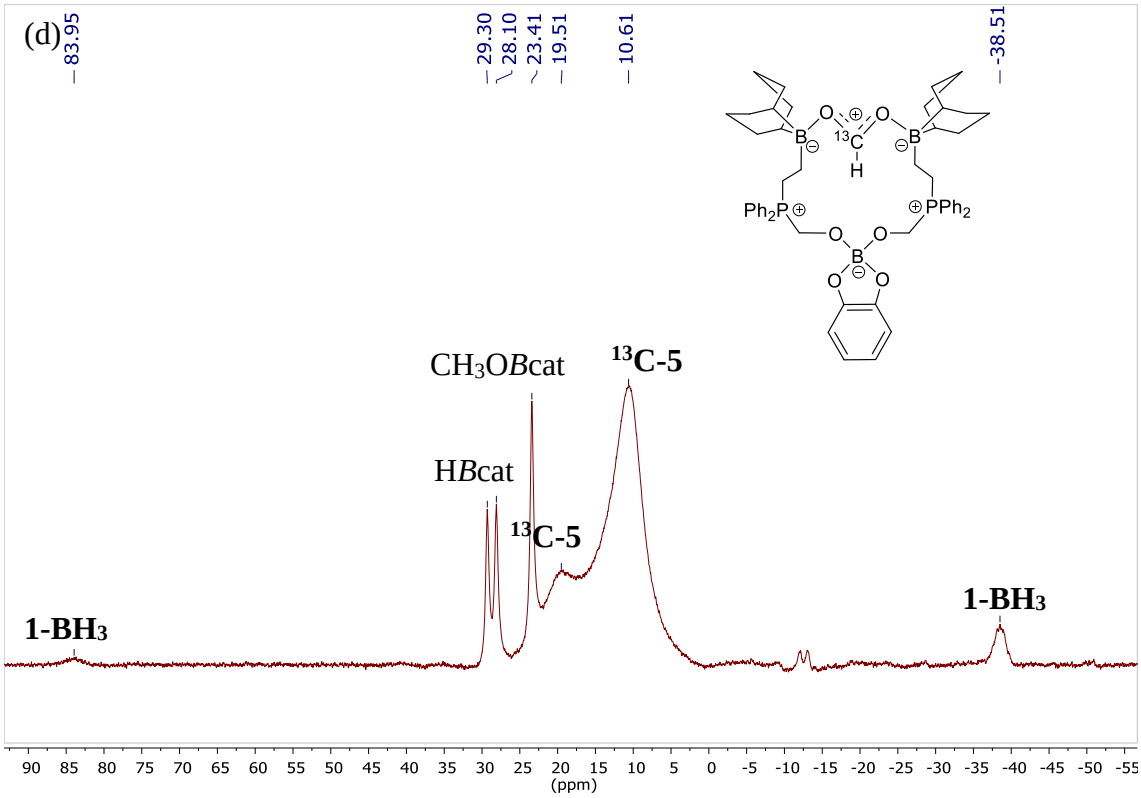
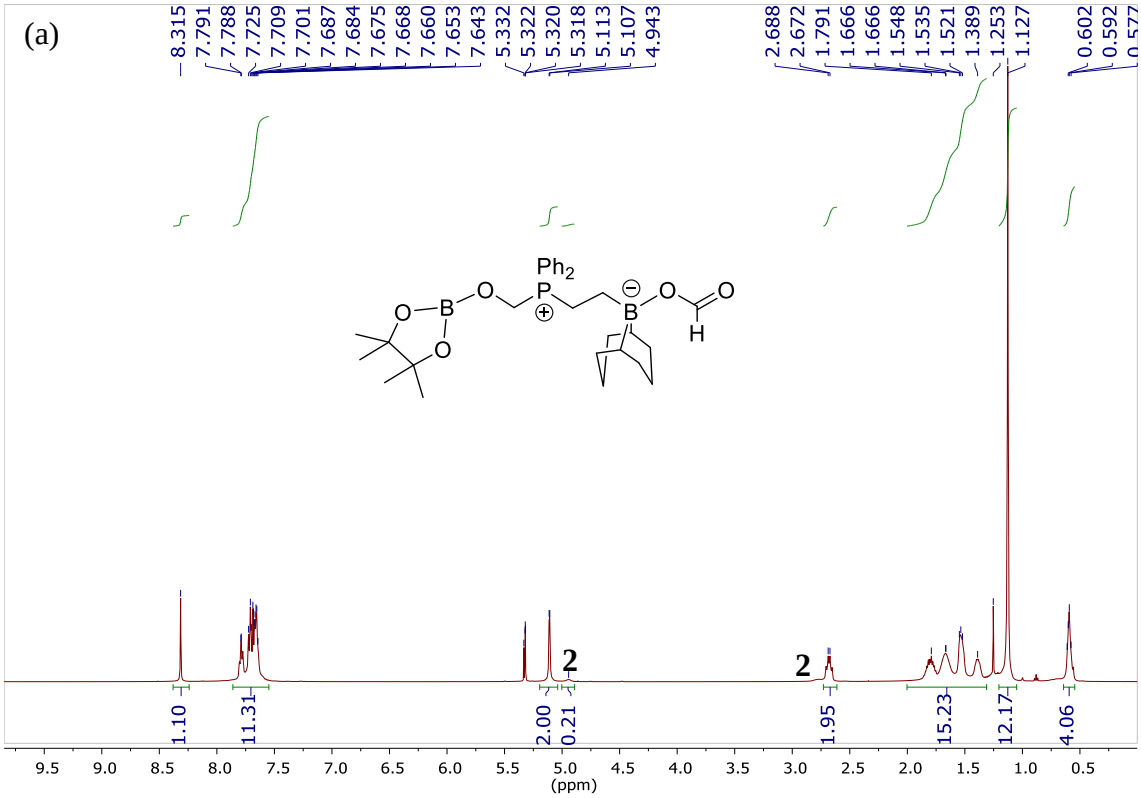
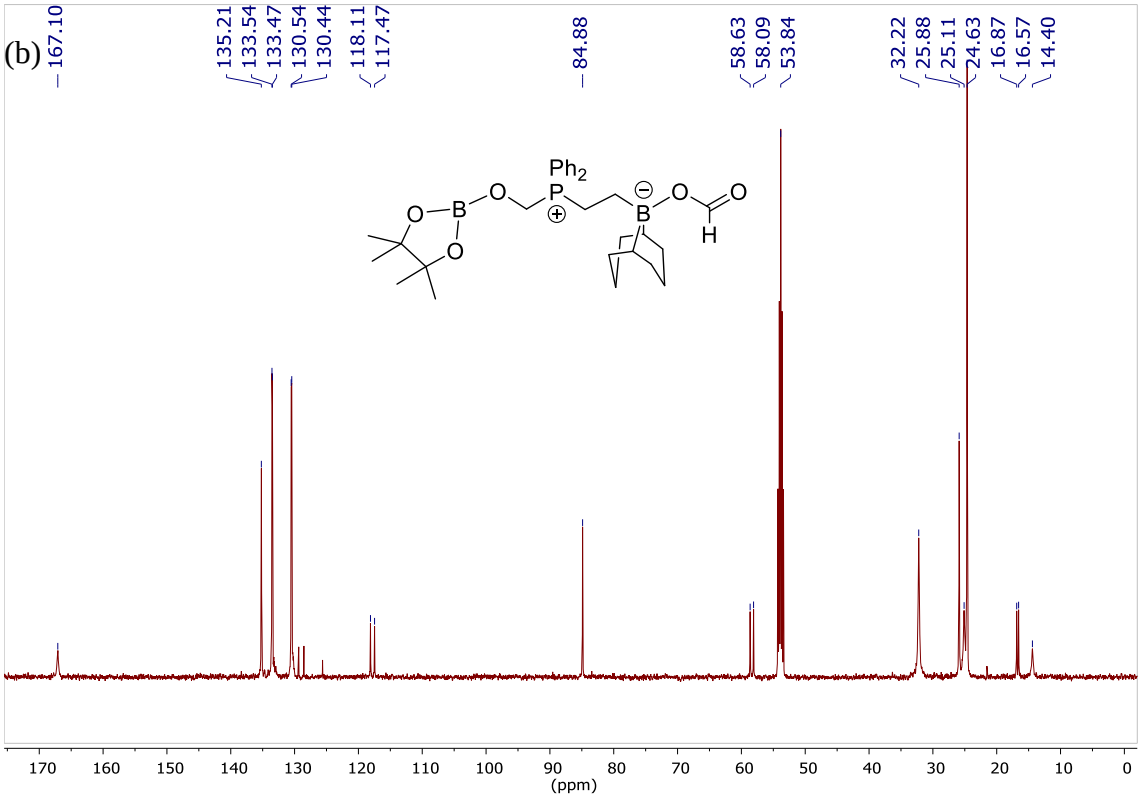
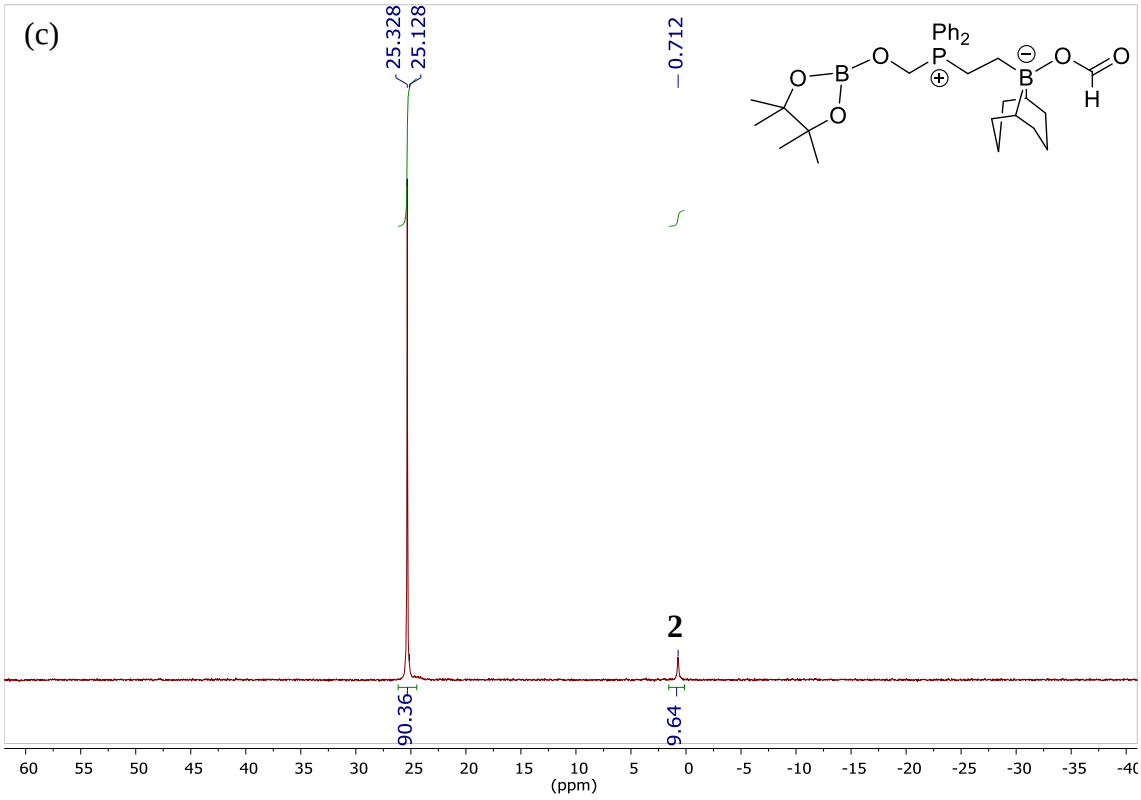

83.95
29.30
28.10
23.41
19.51
10.61
-38.51
CH3OBcat
13C-5
HBcat
13C-5
1-BH3
1-BH3
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55
(ppm)

Figure S9. ^{1}H (a), $^{13}C\{^{1}H\}$ (b), $^{31}P\{^{1}H\}$ (c) and ^{11}B (d) NMR spectra of compound **6** in CD_2Cl_2.






(c)
25.328
25.128
0.712
Ph2
P
B
O
H
2
90.36
9.64
(ppm)

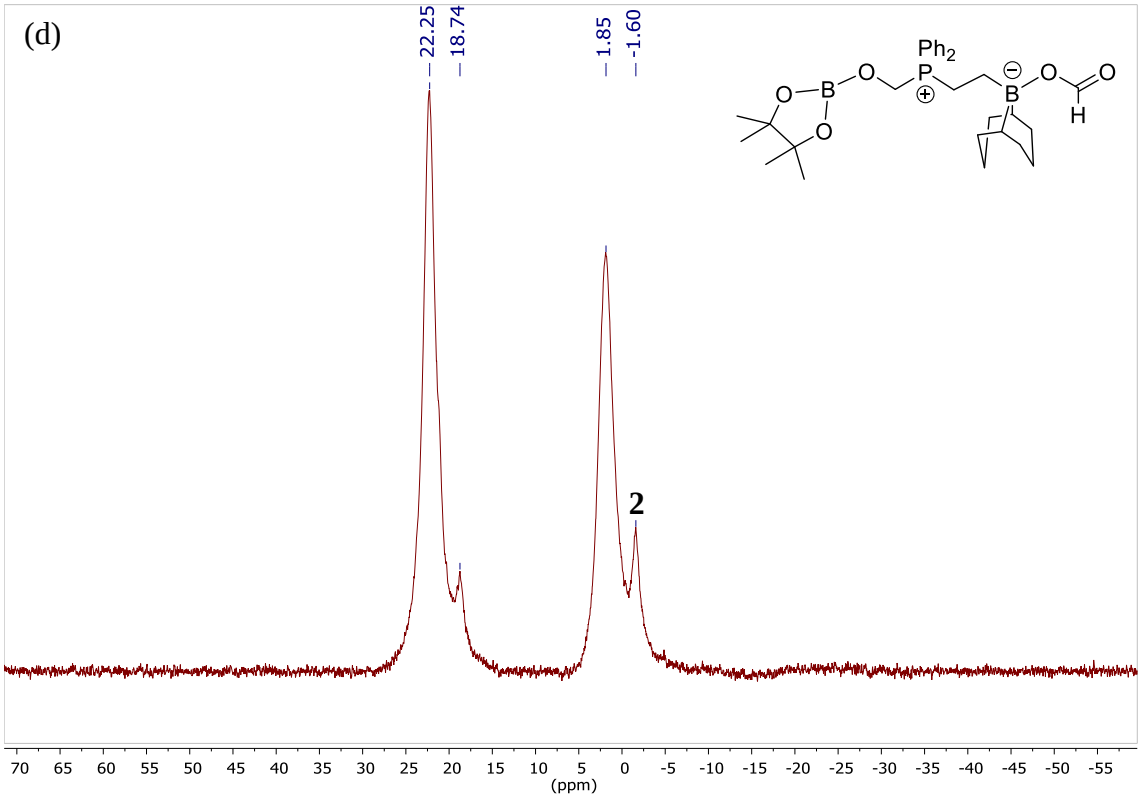
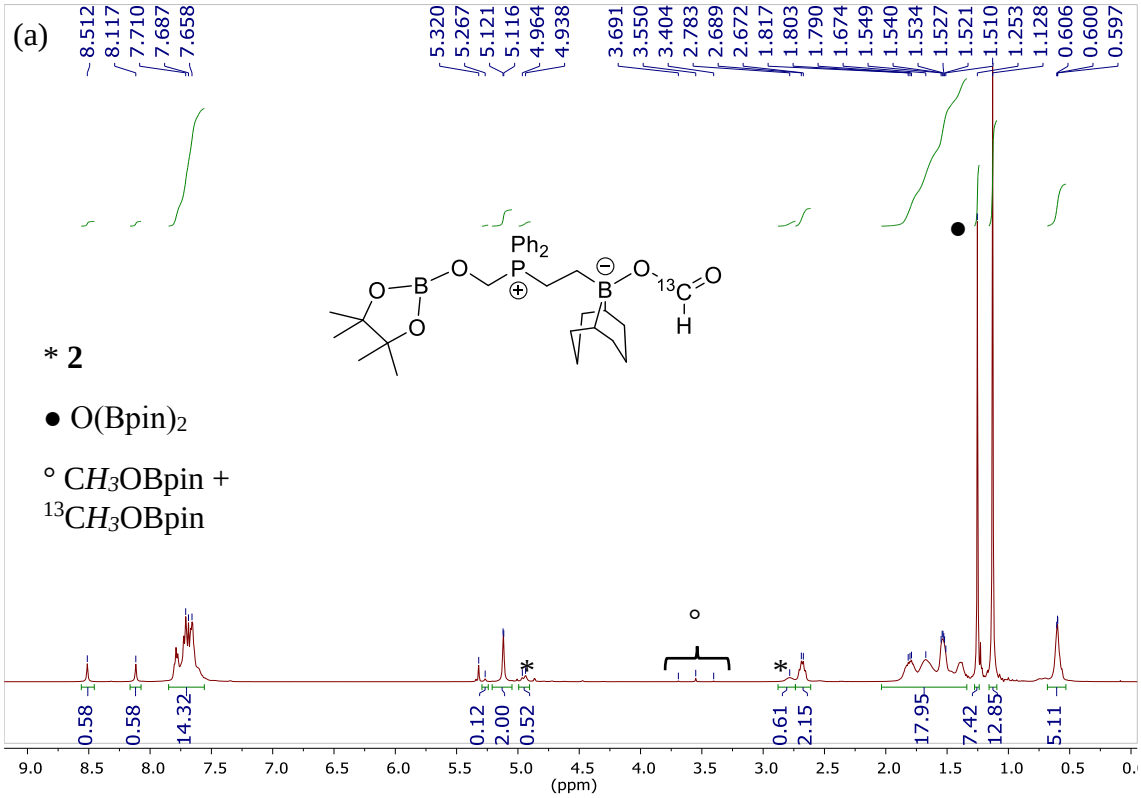
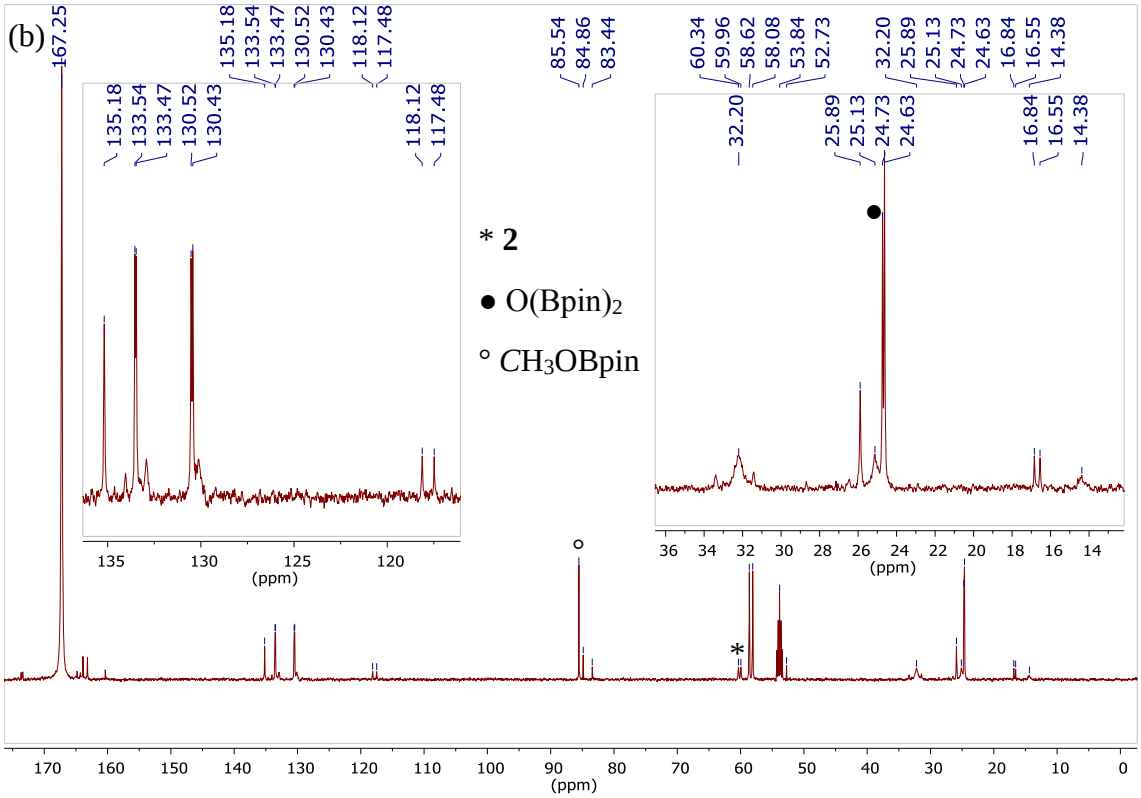
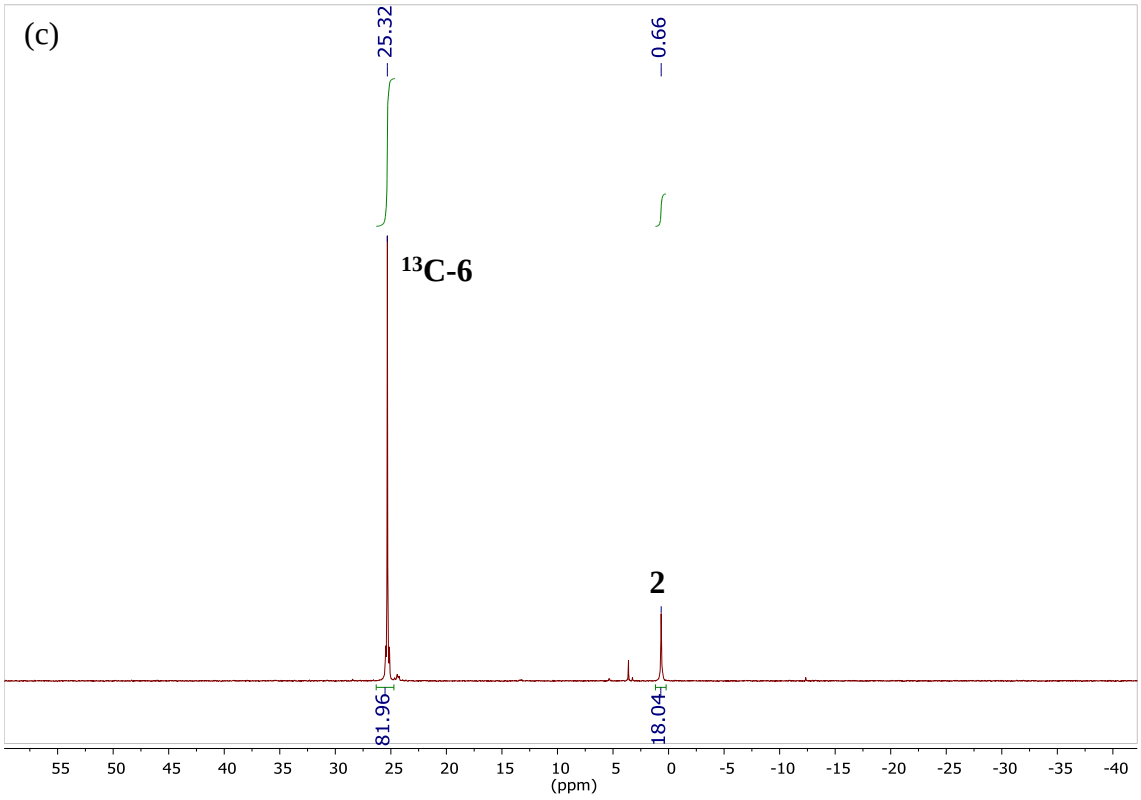

(d)
22.25
18.74
1.85
-1.60
Ph2
P
B
O
H
2
(ppm)

Figure S10. ^{1}H (a), $^{13}C\{^{1}H\}$ (b), $^{31}P\{^{1}H\}$ (c) and ^{11}B (d) NMR spectra in CD_2Cl_2 of reaction crude containing compound **^{13}C-6** as the major species.






(c)
25.32
0.66
^{13}C-6
2
81.96
18.04
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
(ppm)

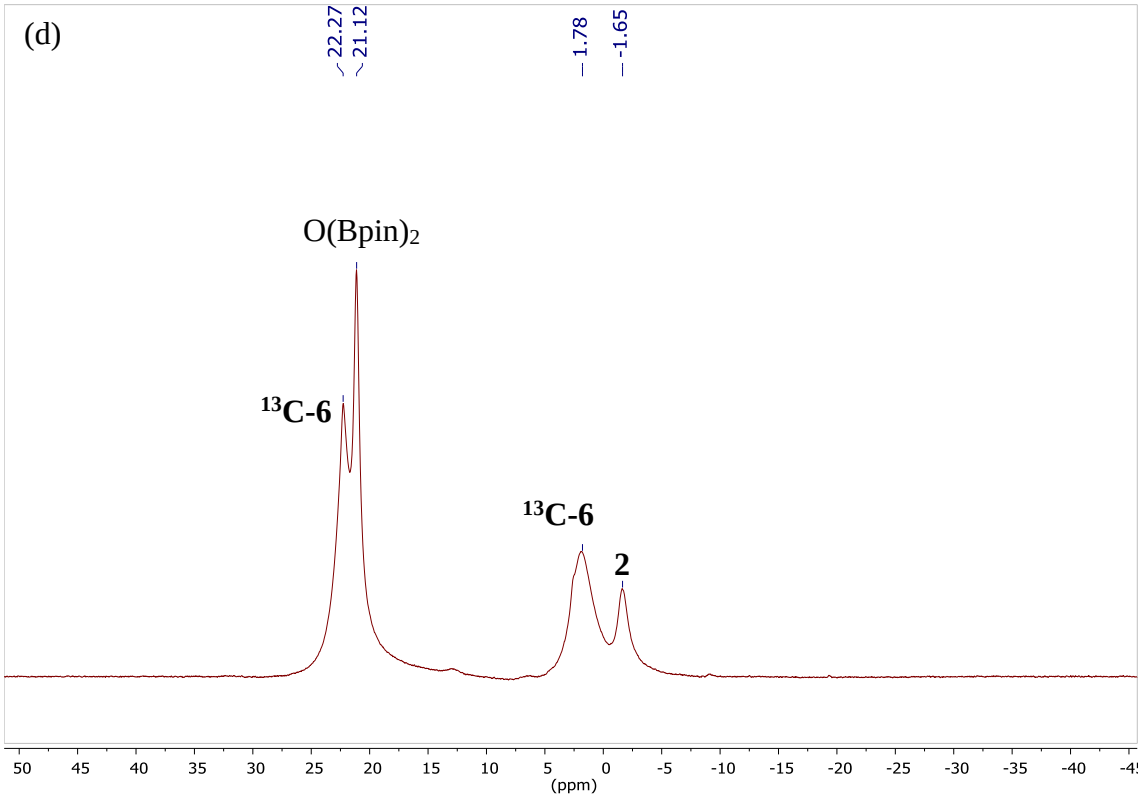
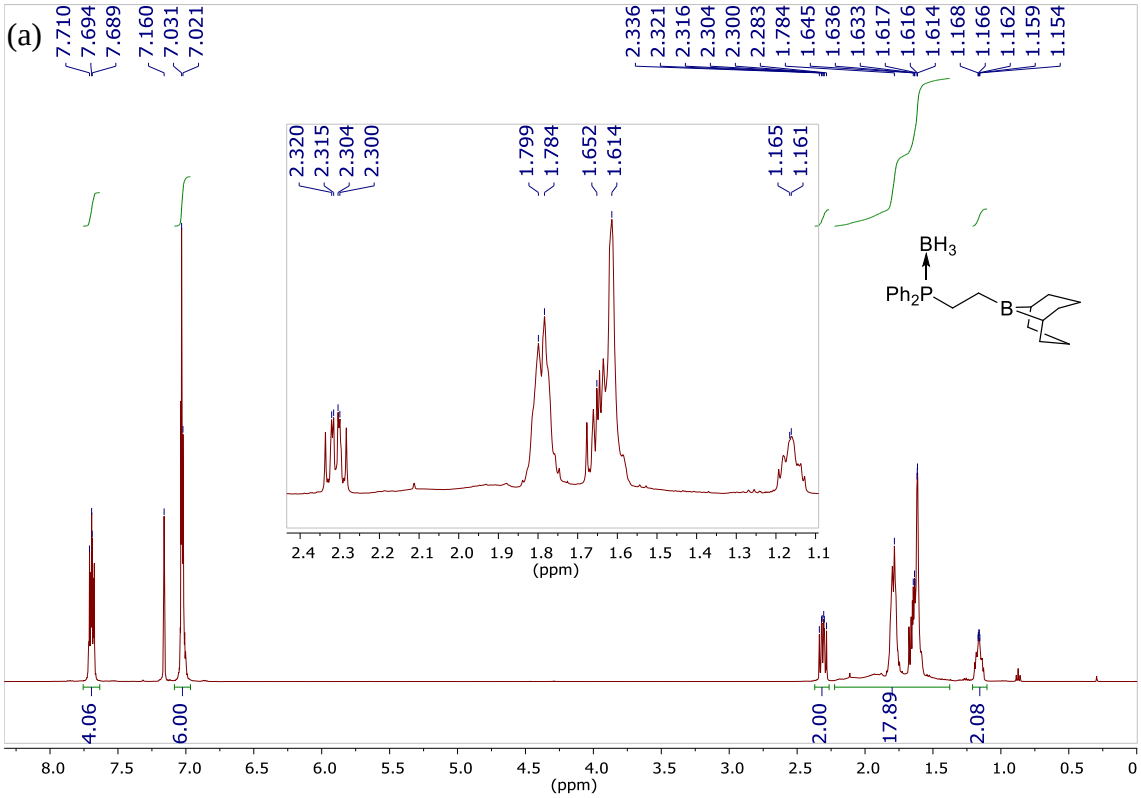
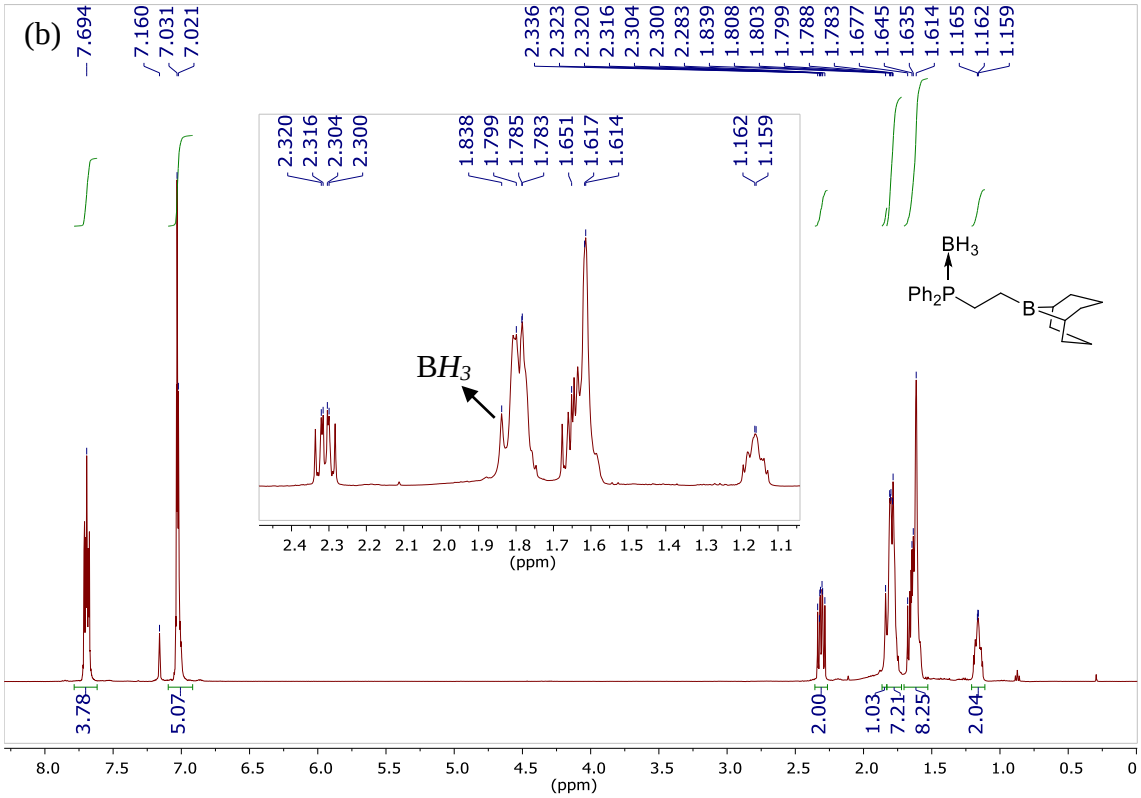
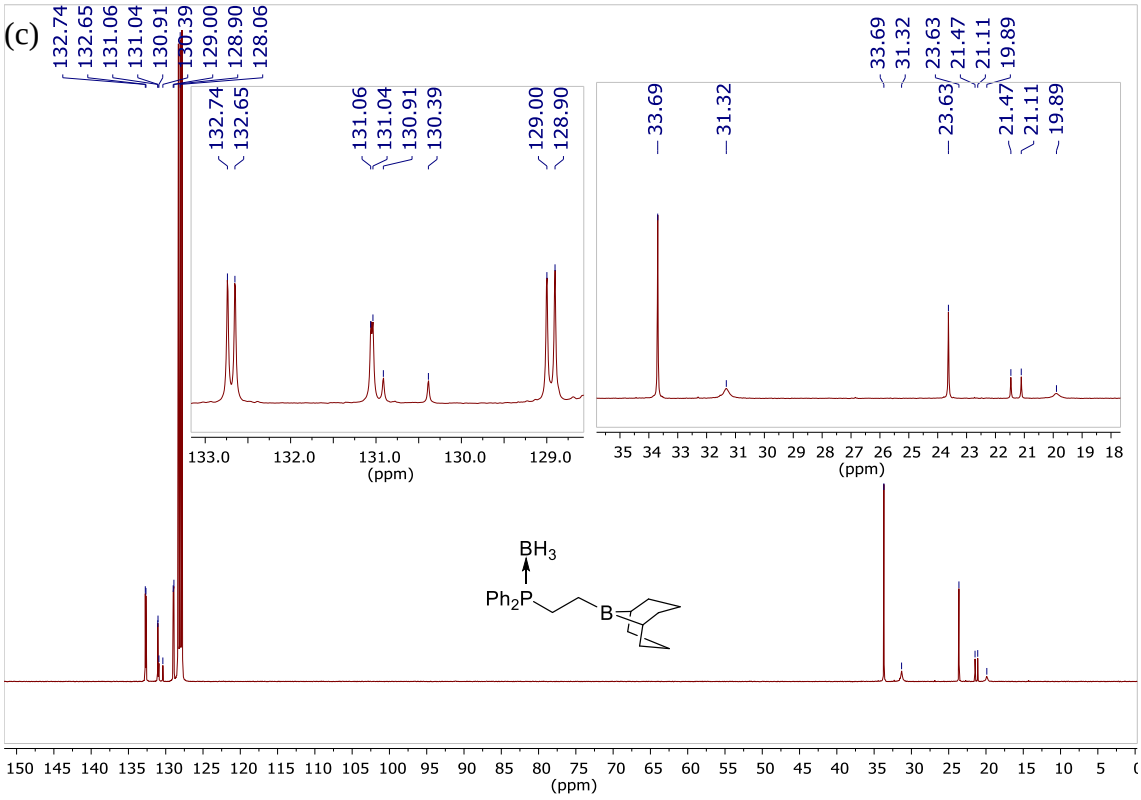
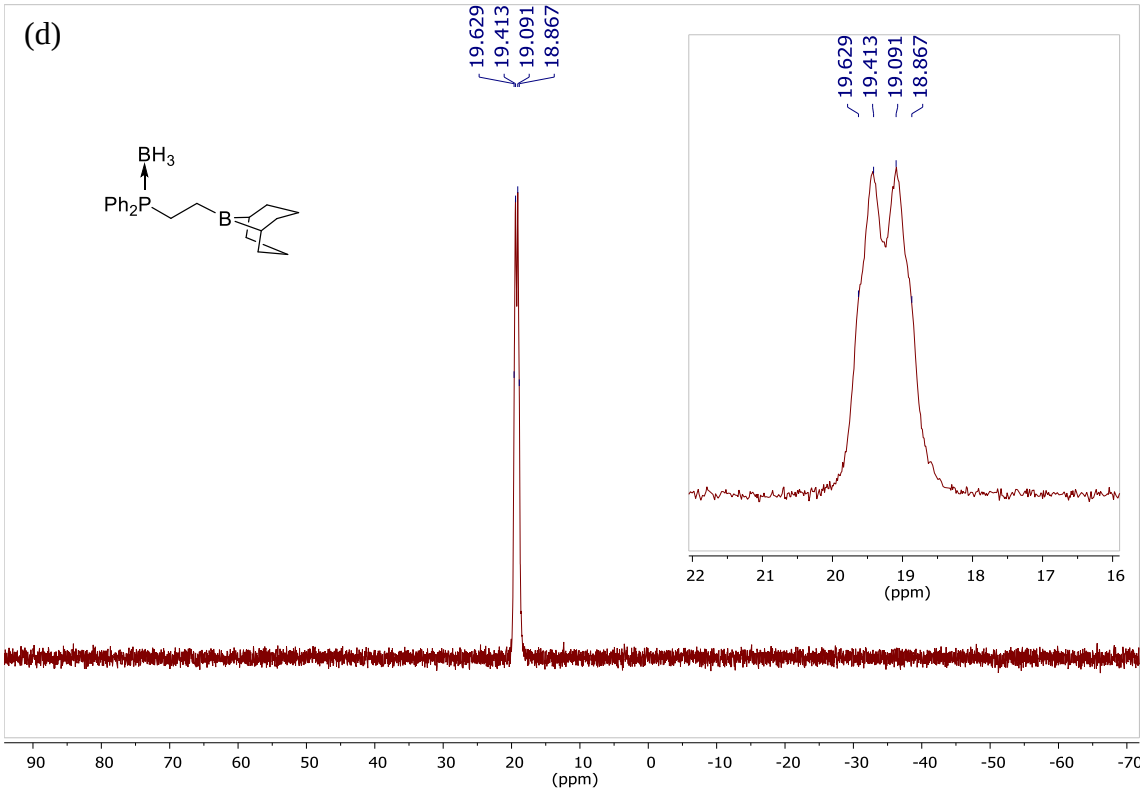

(d)
22.27
21.12
1.78
-1.65
O(Bpin)$_2$
^{13}C-6
^{13}C-6
2
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
(ppm)

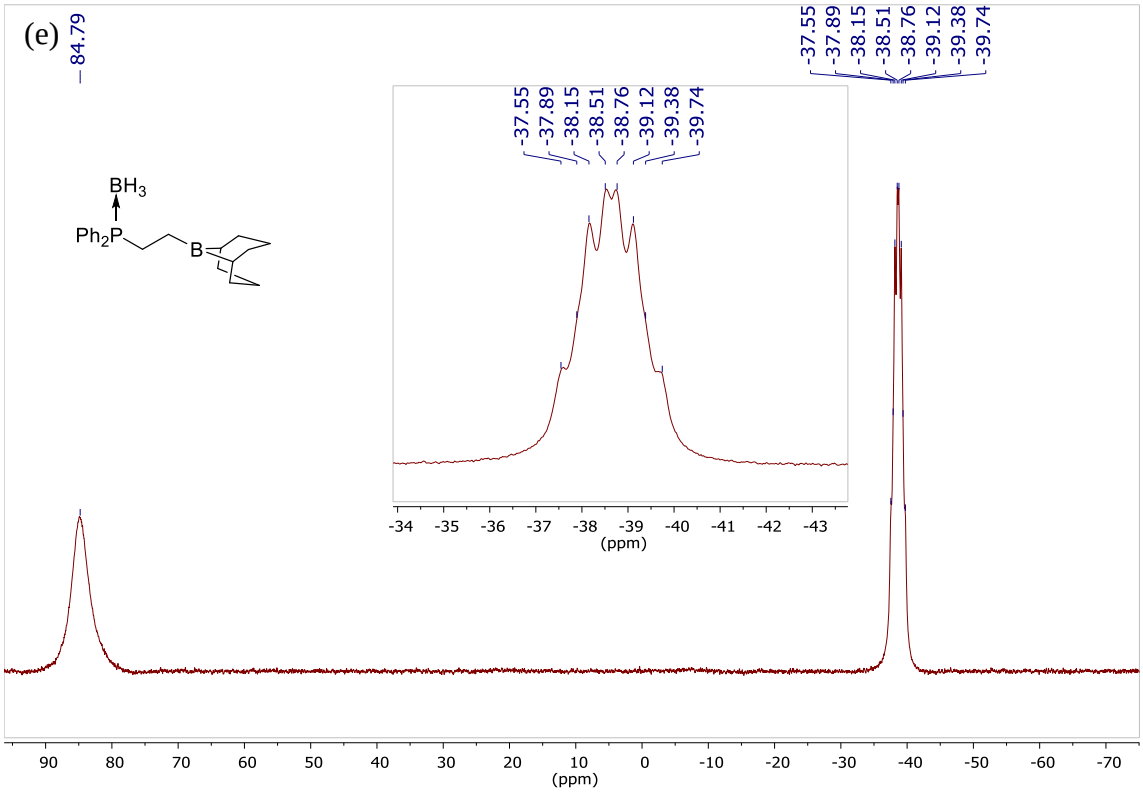
Figure S11. ^{1}H (a), $^{1}H\{^{11}B\}$ (b), $^{13}C\{^{1}H\}$ (c), $^{31}P\{^{1}H\}$ (d), ^{11}B (e) and $^{11}B\{^{1}H\}$ (f) NMR spectra for compound **1-BH$_3$** in C_6D_6.






(c)
132.74
132.65
131.06
131.04
130.91
130.39
129.00
128.90
128.06
33.69
31.32
23.63
21.47
21.11
19.89
BH3
Ph2P
B
(ppm)


(d)
19.629
19.413
19.091
18.867
BH3
Ph2P
B
(ppm)


(e)
84.79
-37.55
-37.89
-38.15
-38.51
-38.76
-39.12
-39.38
-39.74
BH3
Ph2P
B
(ppm)
(ppm)

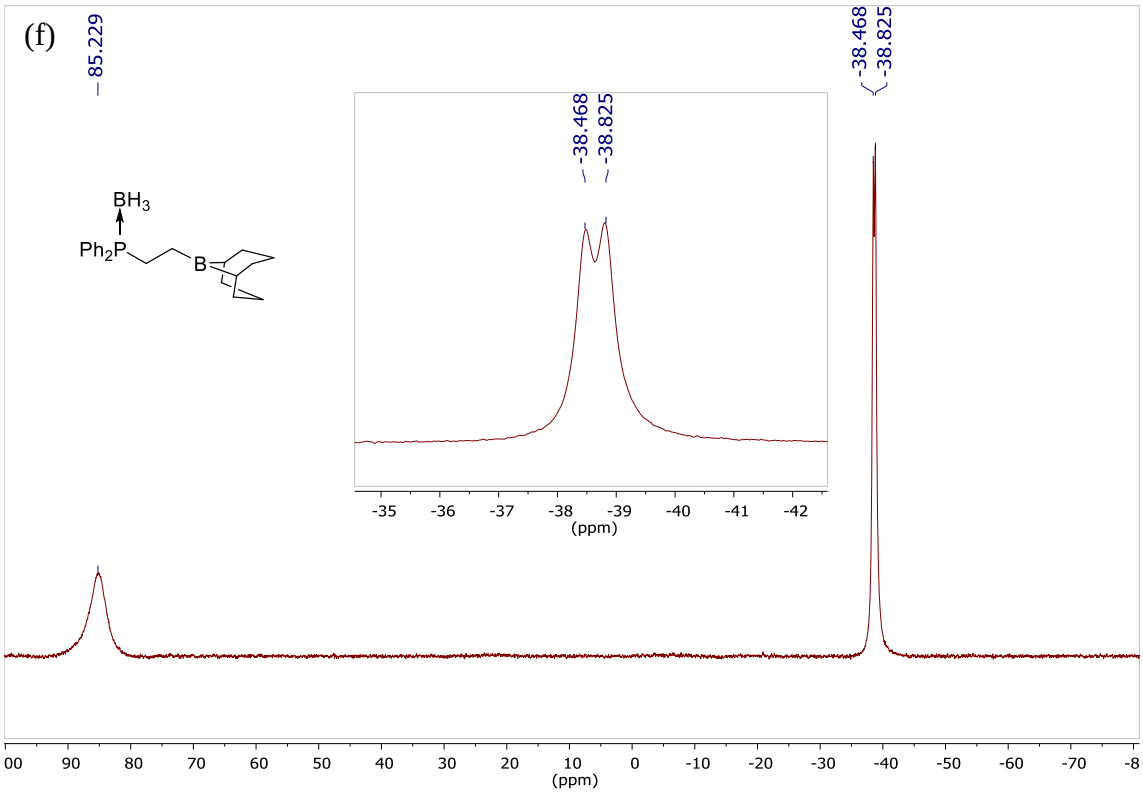
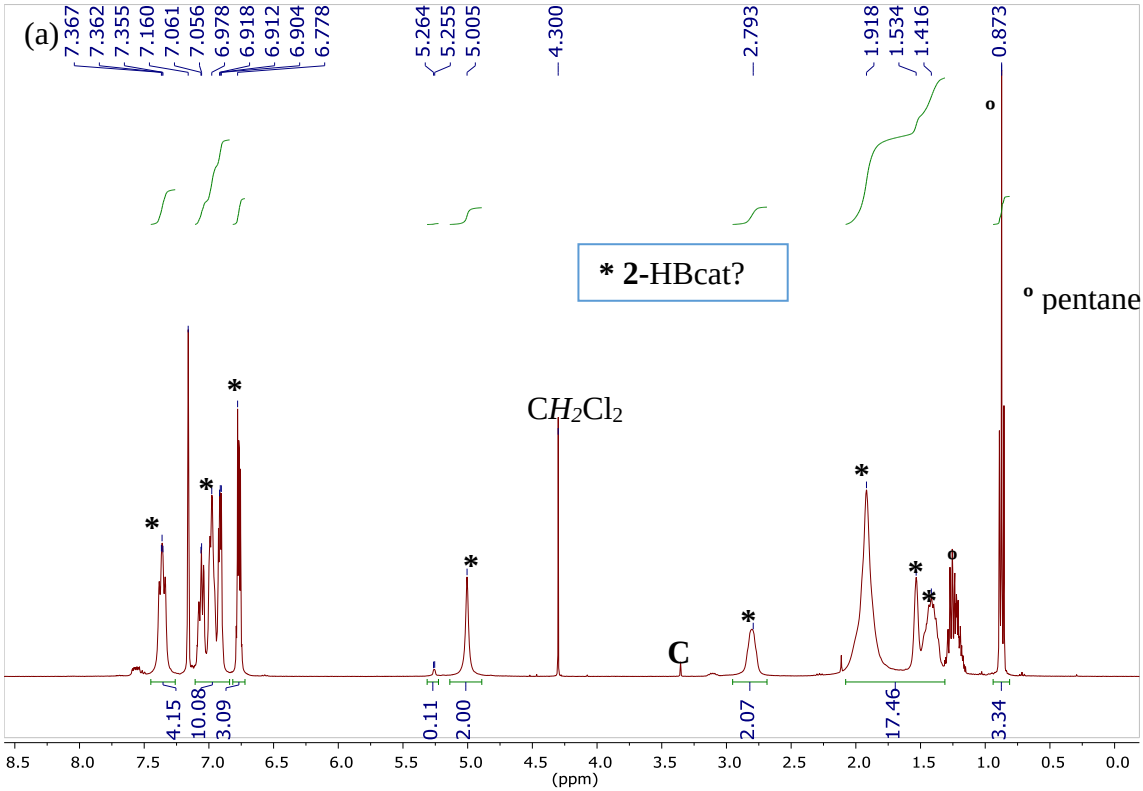
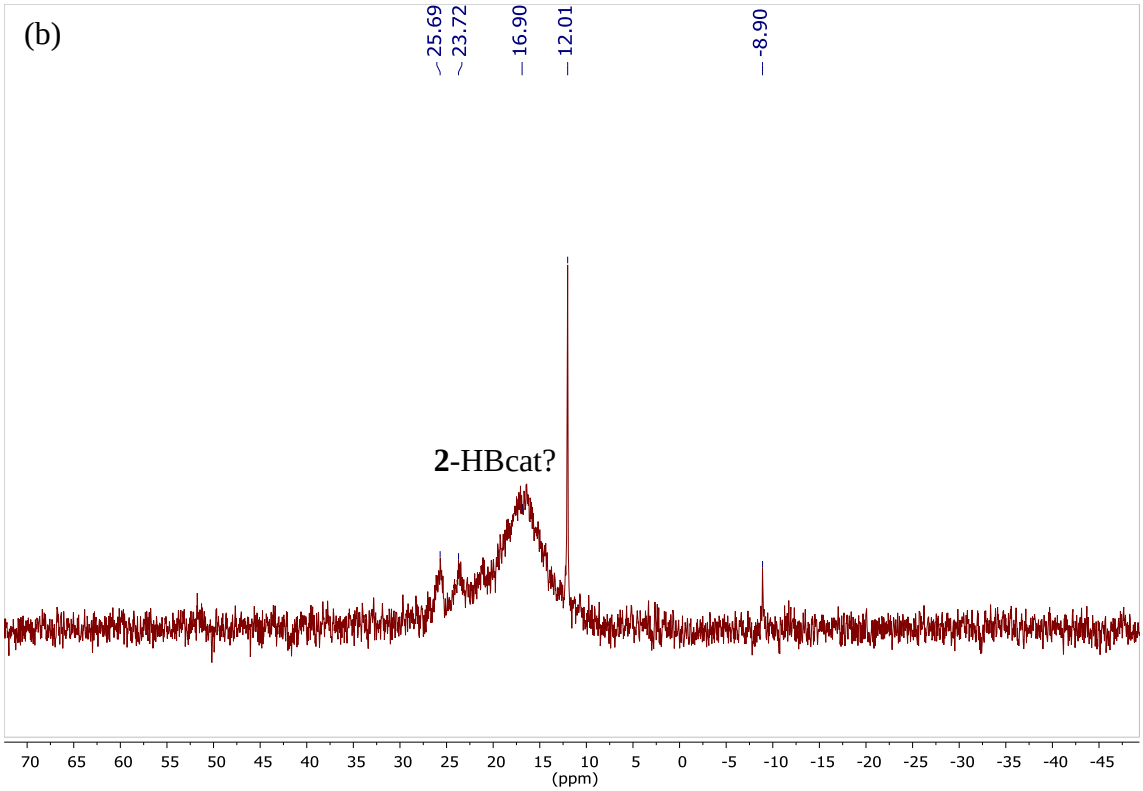

(f)
85.229
-38.468
-38.825
BH3
Ph2P
B
(ppm)
(ppm)

Figure S12. ^{1}H (a), $^{31}P\{^{1}H\}$ (b), and ^{11}B (c) NMR spectra for the impure product ("adduct **2-HBcat**?") of the reaction between compound **2** and HBcat (1 equiv) at 25 ºC in C_6D_6.





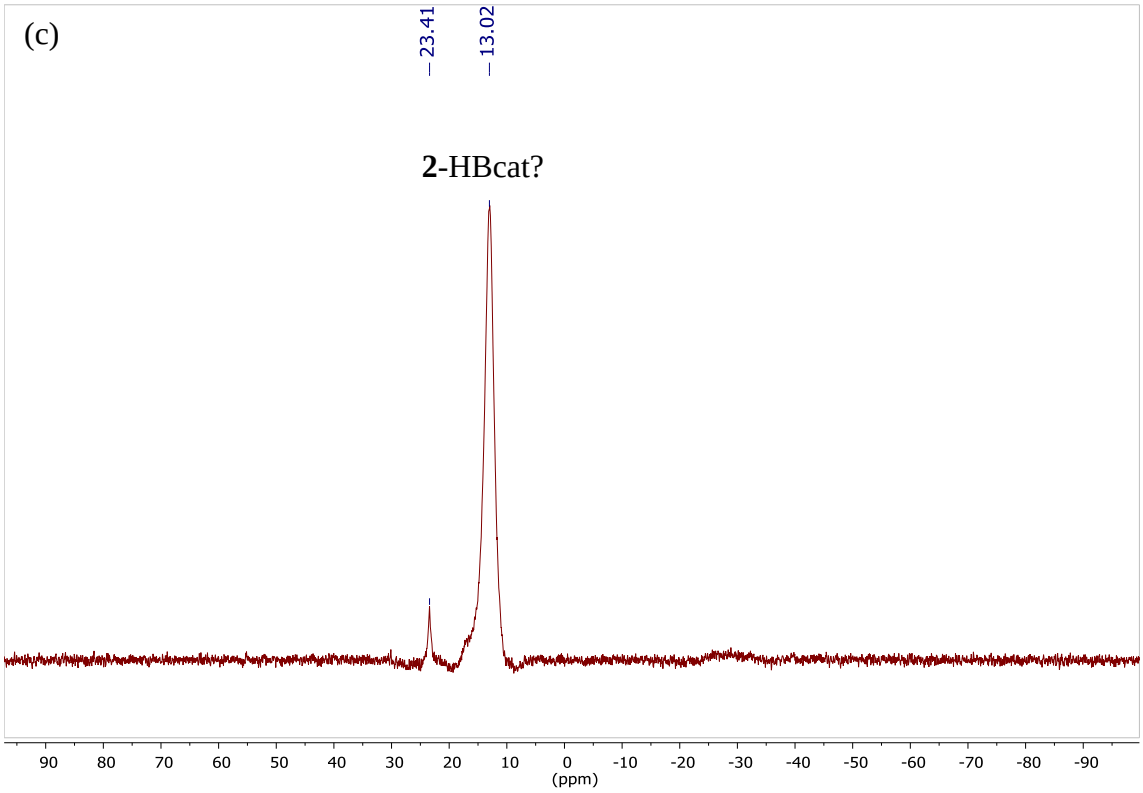
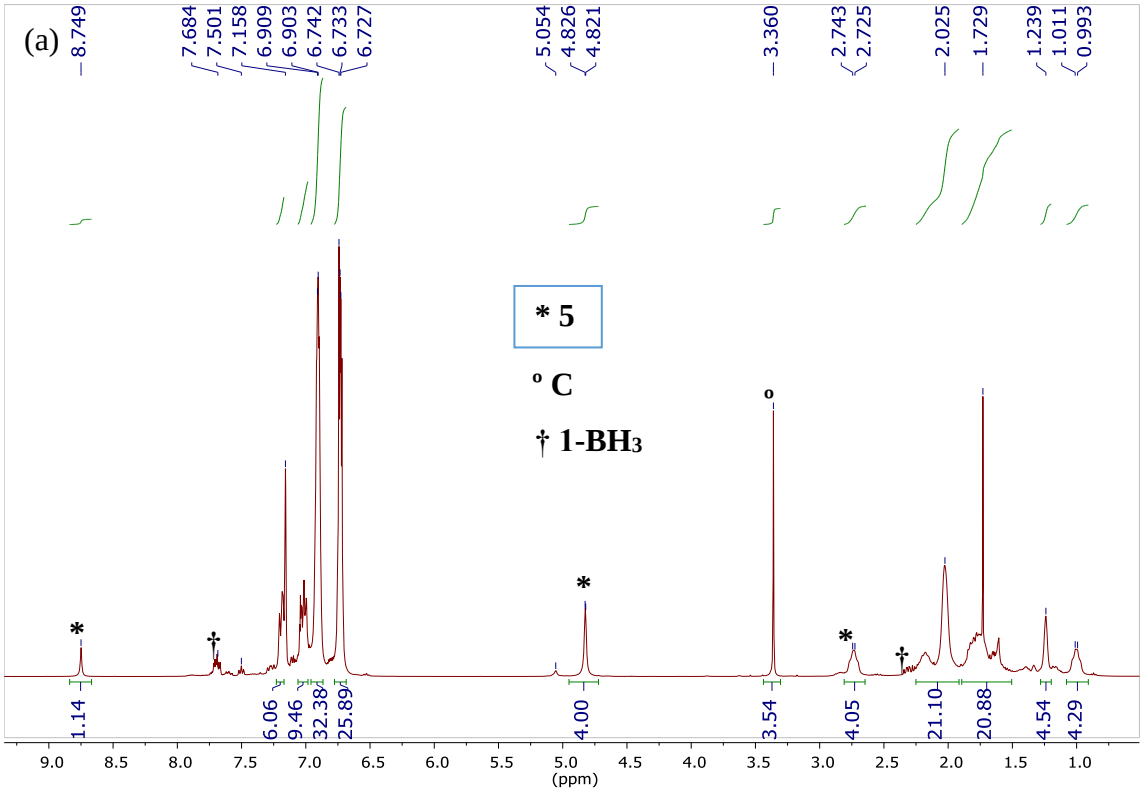
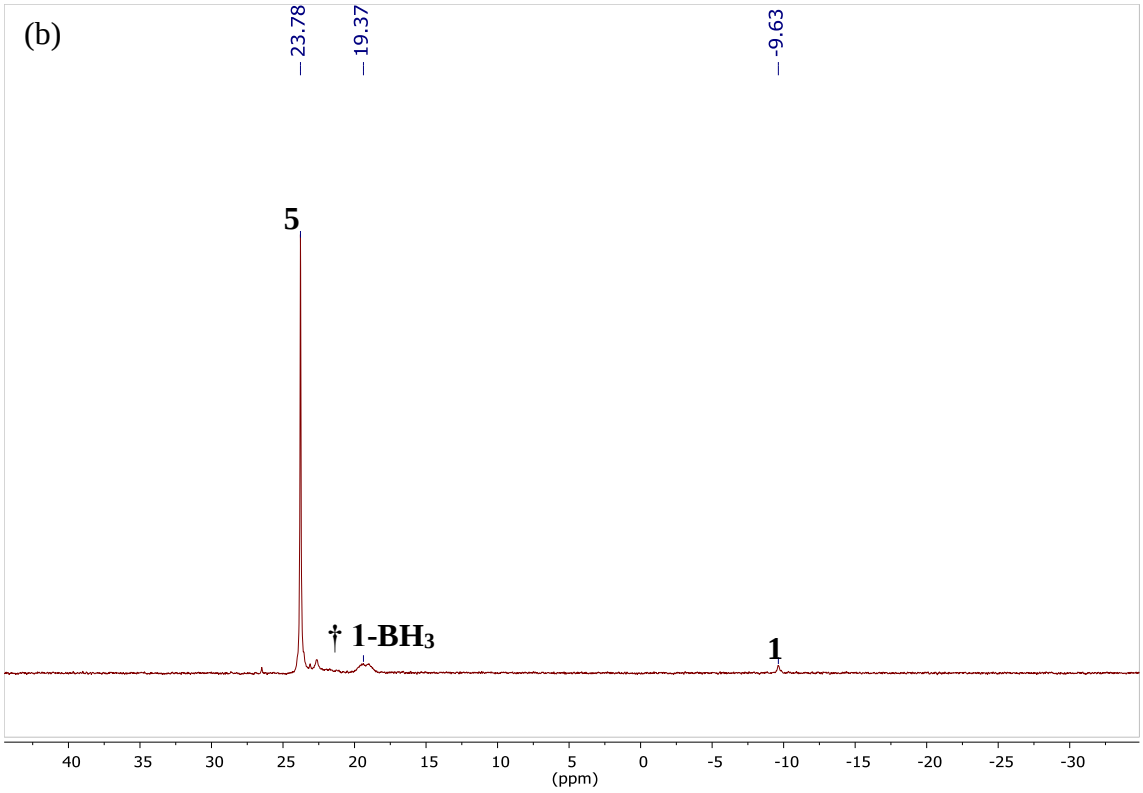

(c)
23.41
13.02
2-HBcat?
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
(ppm)

Figure S13. ^{1}H (a), $^{31}P\{^{1}H\}$ (b), and ^{11}B (c) NMR spectra for the reaction between compound **1**, HBcat (2 equiv) and CO_2 (1 atm), after 7 h at 25 ºC in C_6D_6.



† **1-BH$_3$** was formed due to the presence of small amounts of $BH_3{\cdot}SMe_2$ in HBcat.



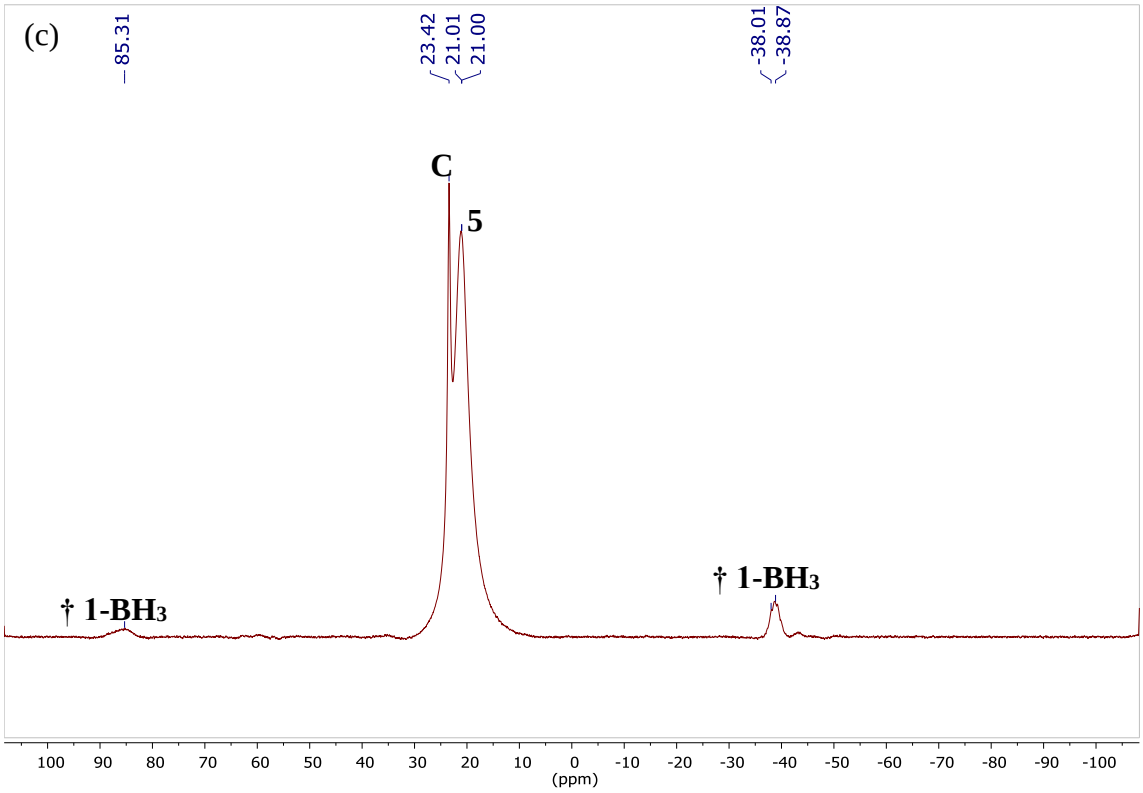
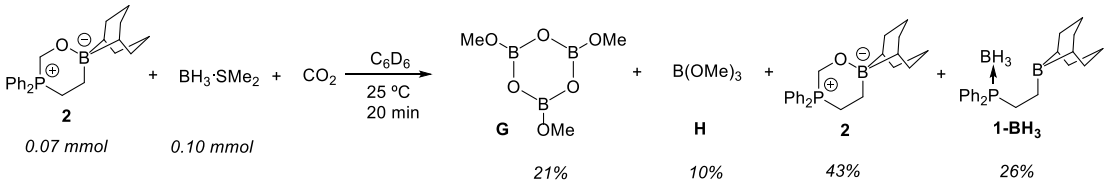
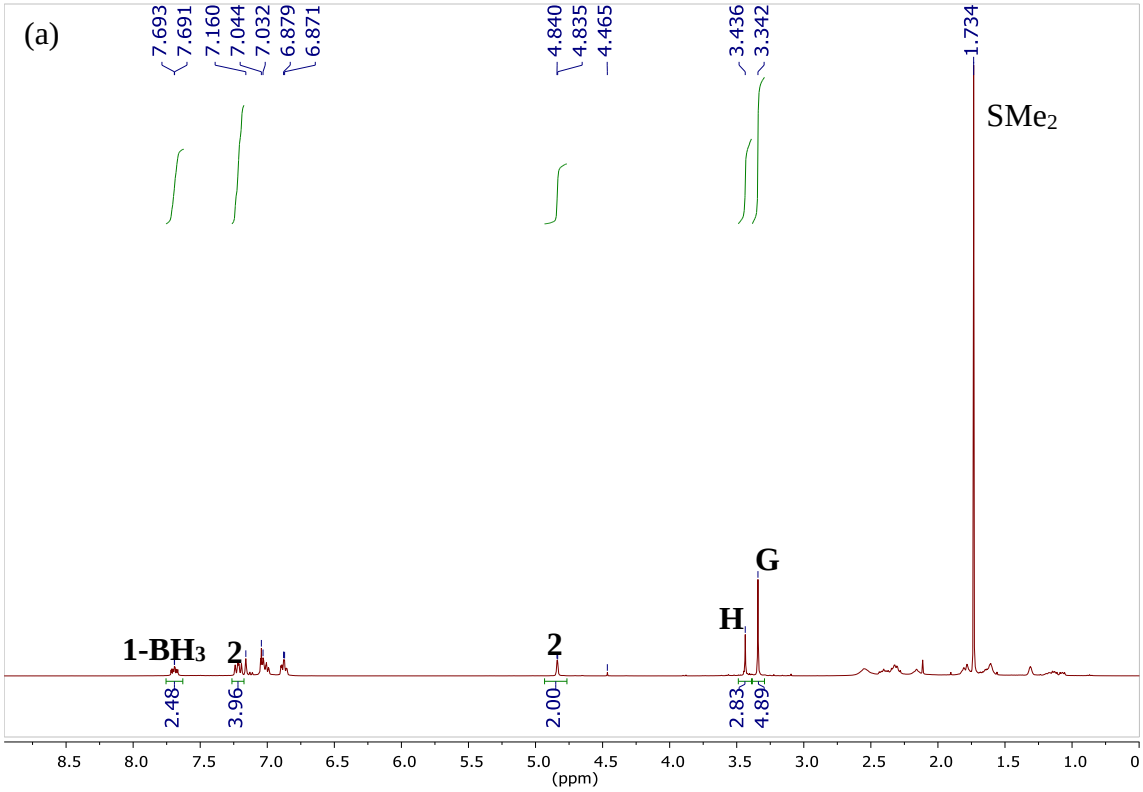
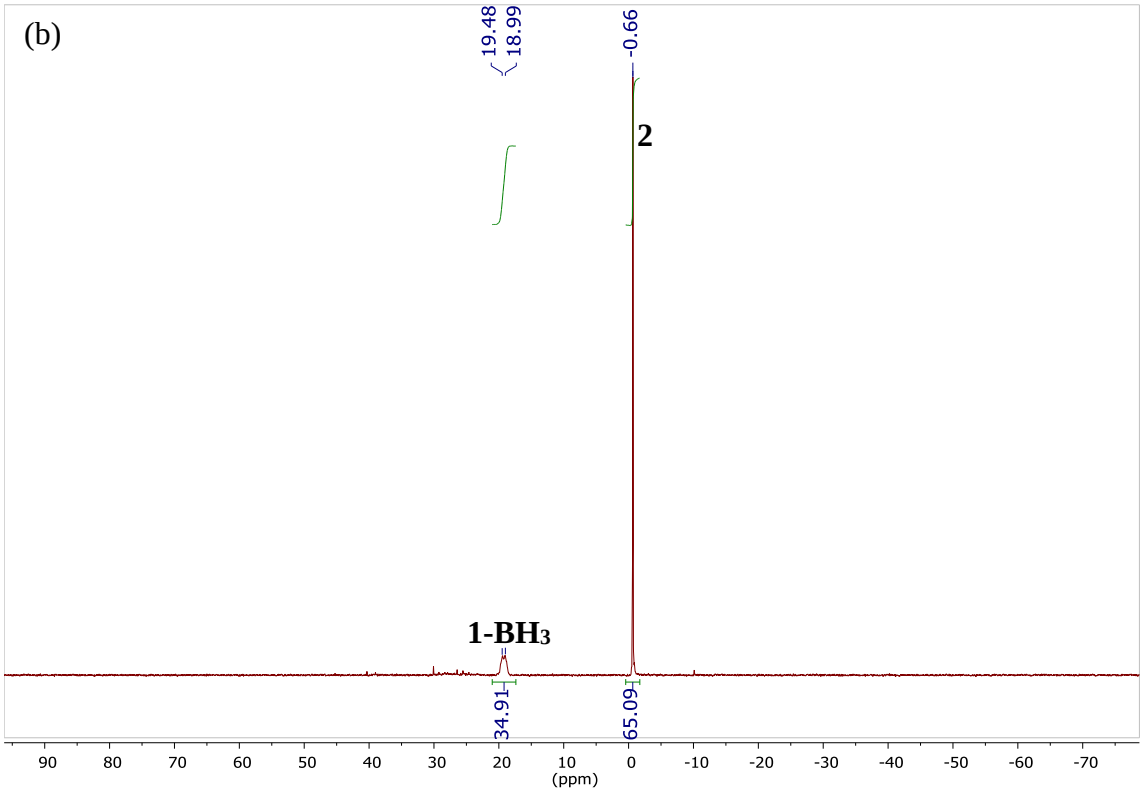

(c)
85.31
23.42
21.01
21.00
-38.01
-38.87
C
5
† 1-BH3
† 1-BH3
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
(ppm)

Figure S14. ^{1}H (a), $^{31}P\{^{1}H\}$ (b), and ^{11}B (c) NMR spectra for the reaction between compound **2**, $BH_3 \cdot SMe_2$ and CO_2 (1 atm) in an NMR tube, after 20 min at 25 ºC in C_6D_6.






(b)
19.48
18.99
-0.66
2
1-BH3
34.91
65.09
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
(ppm)

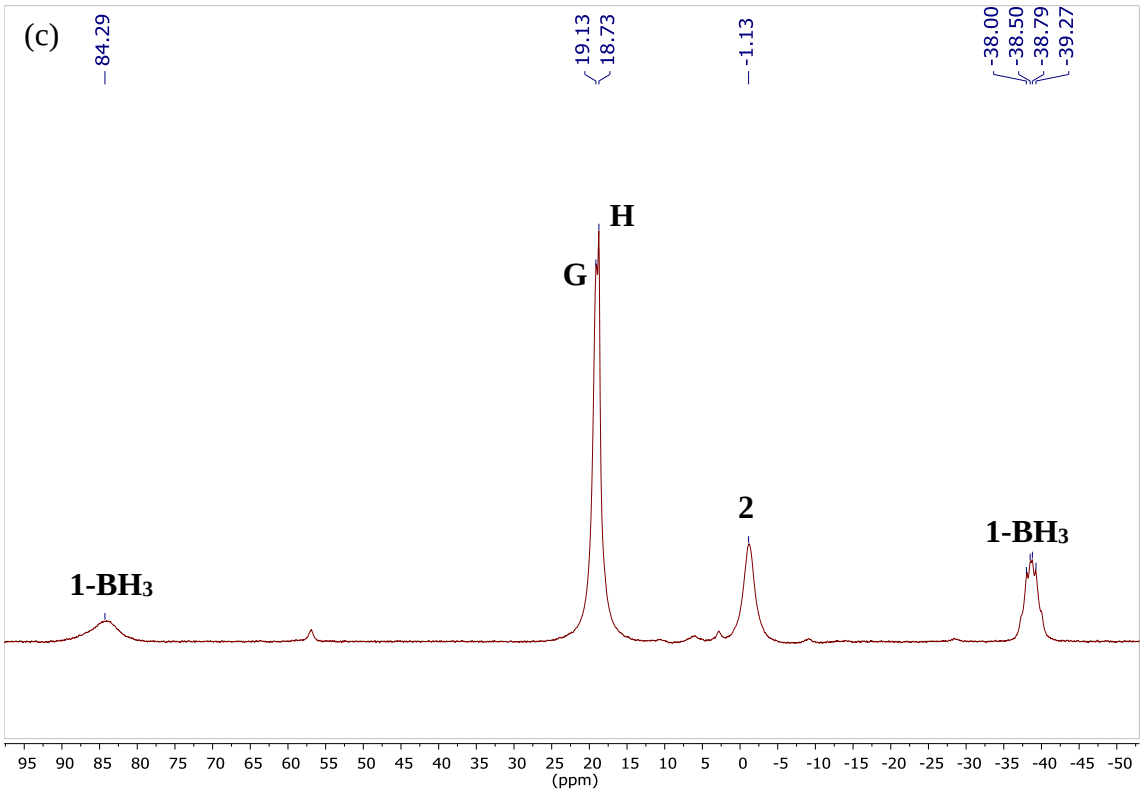
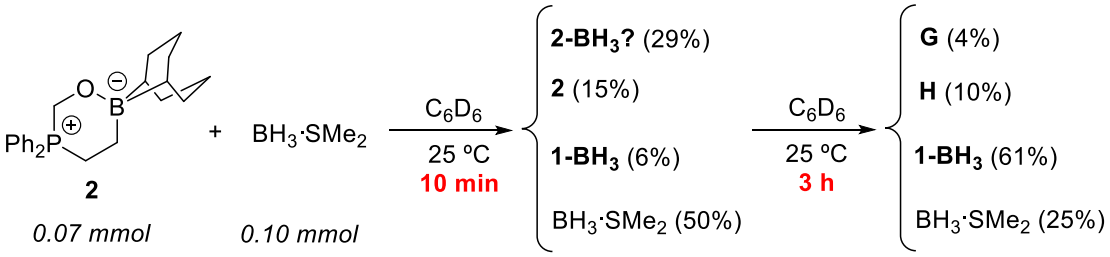
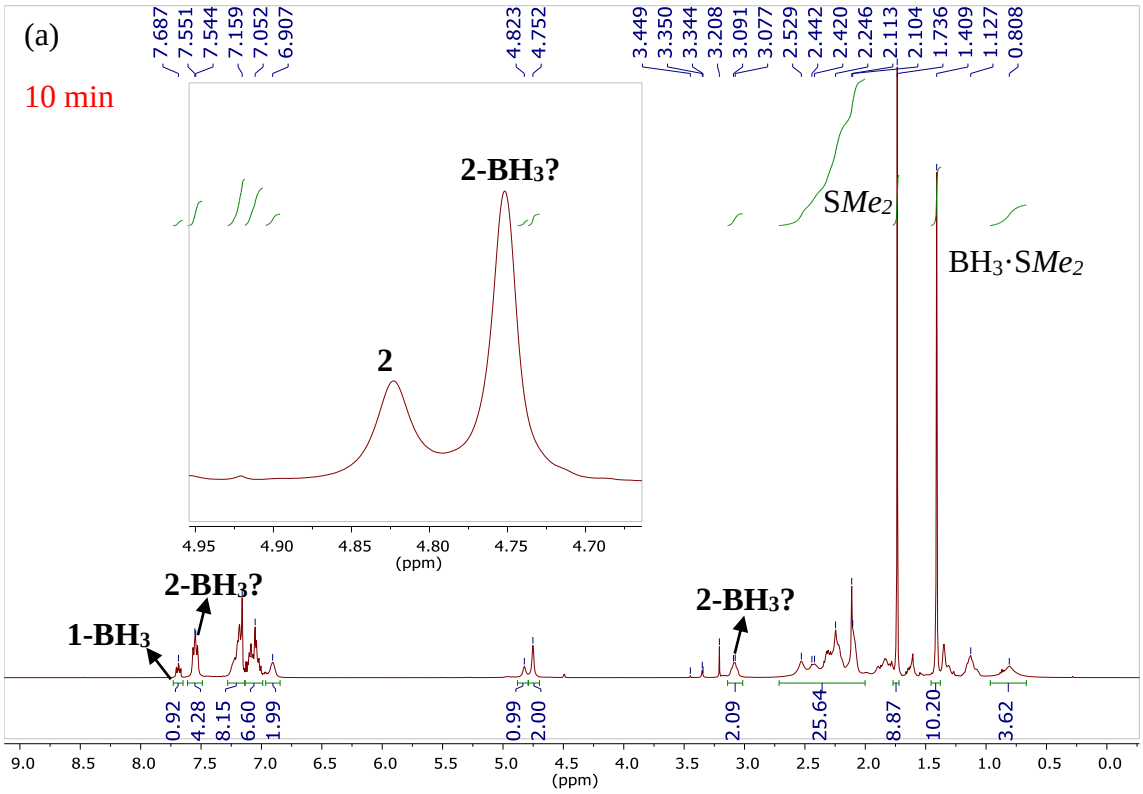
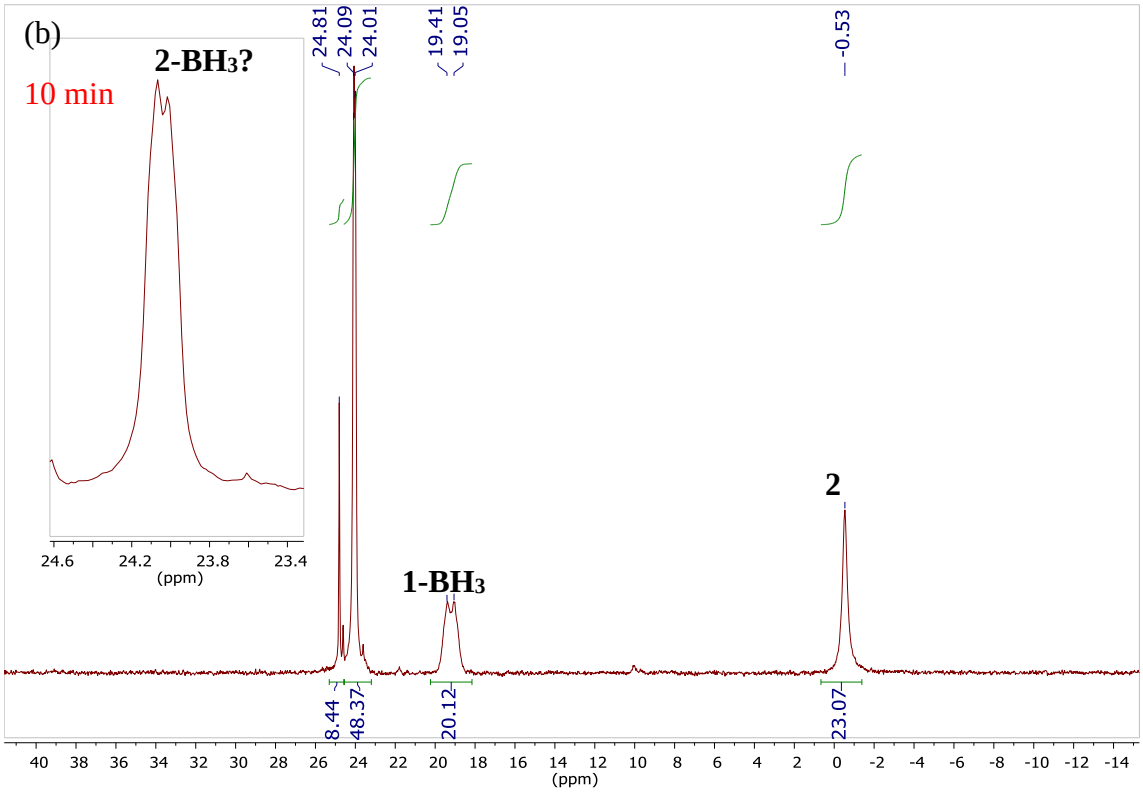
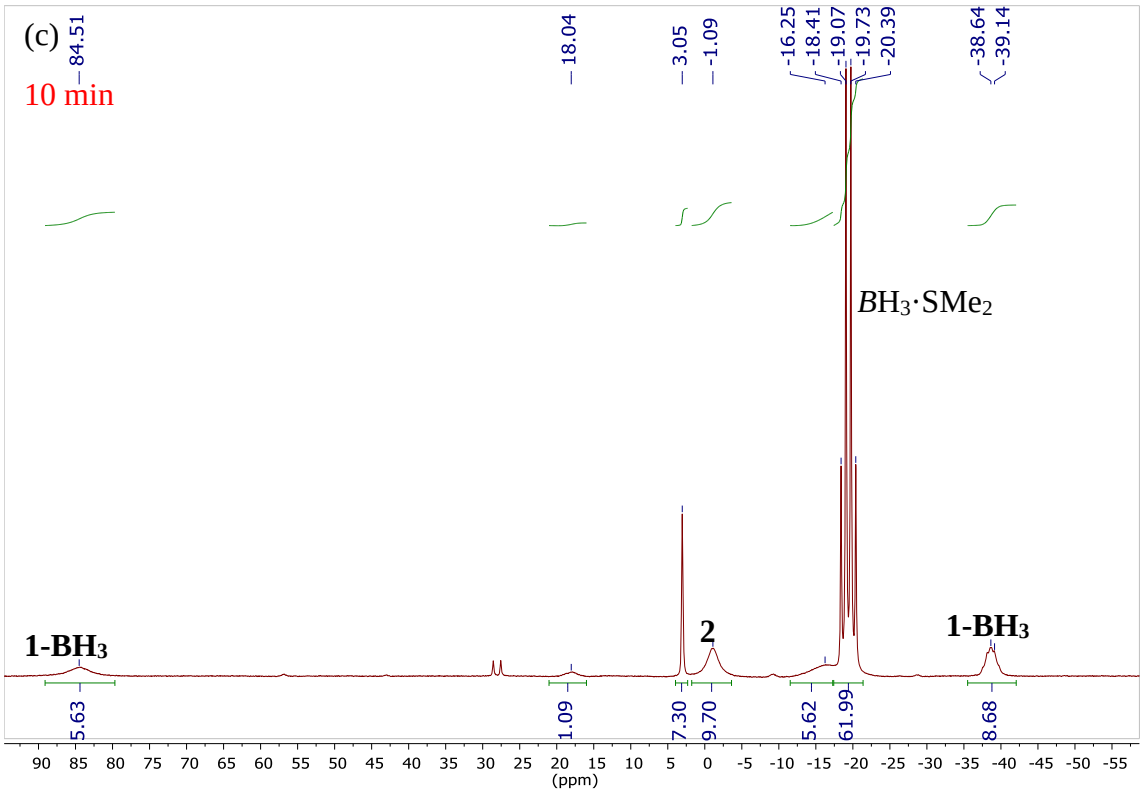

(c)
84.29
19.13
18.73
-1.13
-38.00
-38.50
-38.79
-39.27
H
G
2
1-BH3
1-BH3
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
(ppm)

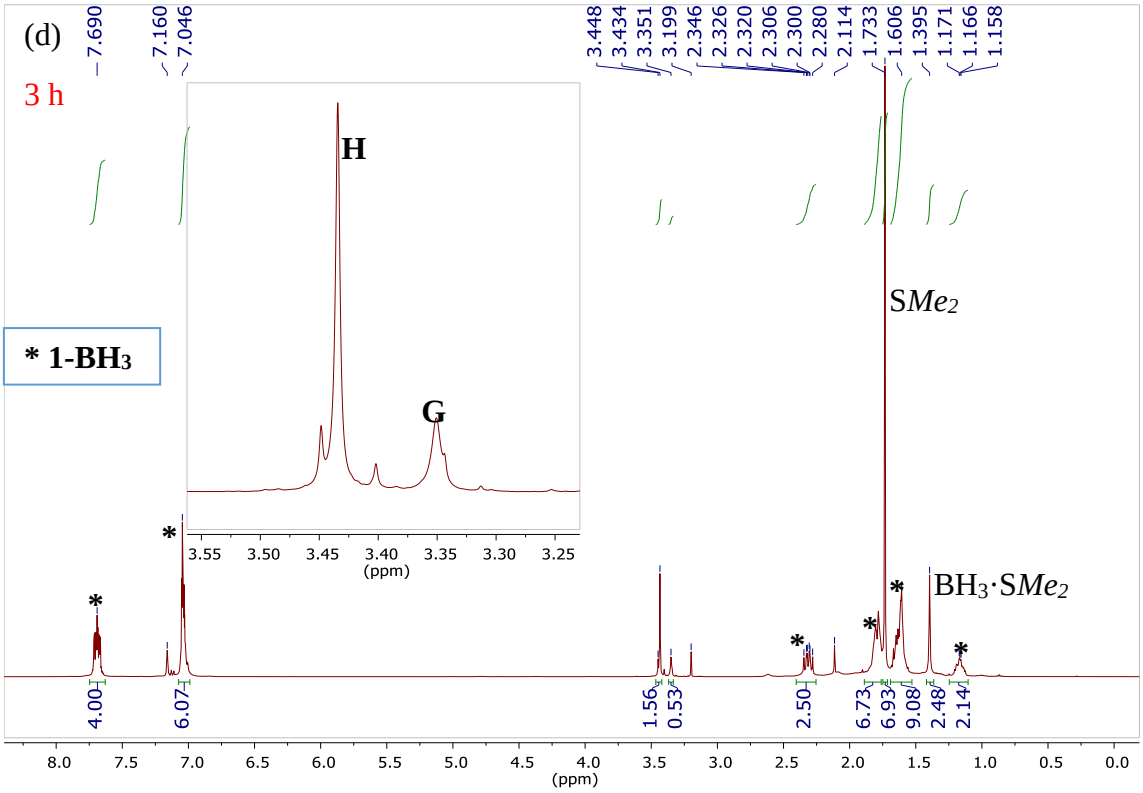
Figure S15. ^{1}H, $^{31}P\{^{1}H\}$ and ^{11}B NMR spectra for the reaction between compound **2** and $BH_3{\cdot}SMe_2$ in an NMR tube, after 10 min (a-c) and 3 h (d-f) at 25 ºC in C_6D_6.

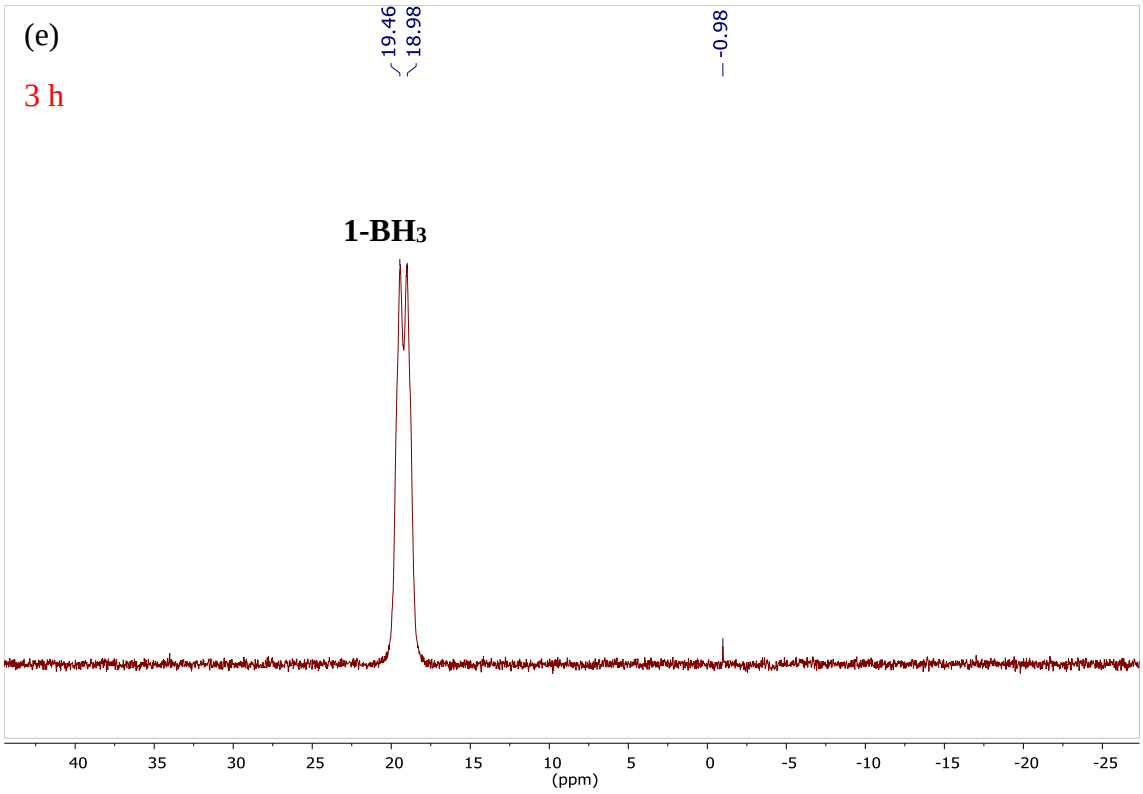





(b)
10 min
2-BH3?
24.6
24.2
23.8
23.4
(ppm)
24.81
24.09
24.01
19.41
19.05
-0.53
2
1-BH3
8.44
48.37
20.12
23.07
40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14
(ppm)


(c)
10 min
84.51
18.04
3.05
-1.09
-16.25
-18.41
-19.07
-19.73
-20.39
-38.64
-39.14
BH3·SMe2
1-BH3
2
1-BH3
5.63
1.09
7.30
9.70
5.62
61.99
8.68
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55
(ppm)


(d)
3 h
* 1-BH3
H
G
SMe2
BH3·SMe2
7.690
7.160
7.046
3.448
3.434
3.351
3.199
2.346
2.326
2.320
2.306
2.300
2.280
2.114
1.733
1.606
1.395
1.171
1.166
1.158
4.00
6.07
1.56
0.53
2.50
6.73
6.93
9.08
2.48
2.14
(ppm)


(e)
3 h
1-BH3
19.46
18.98
-0.98
(ppm)

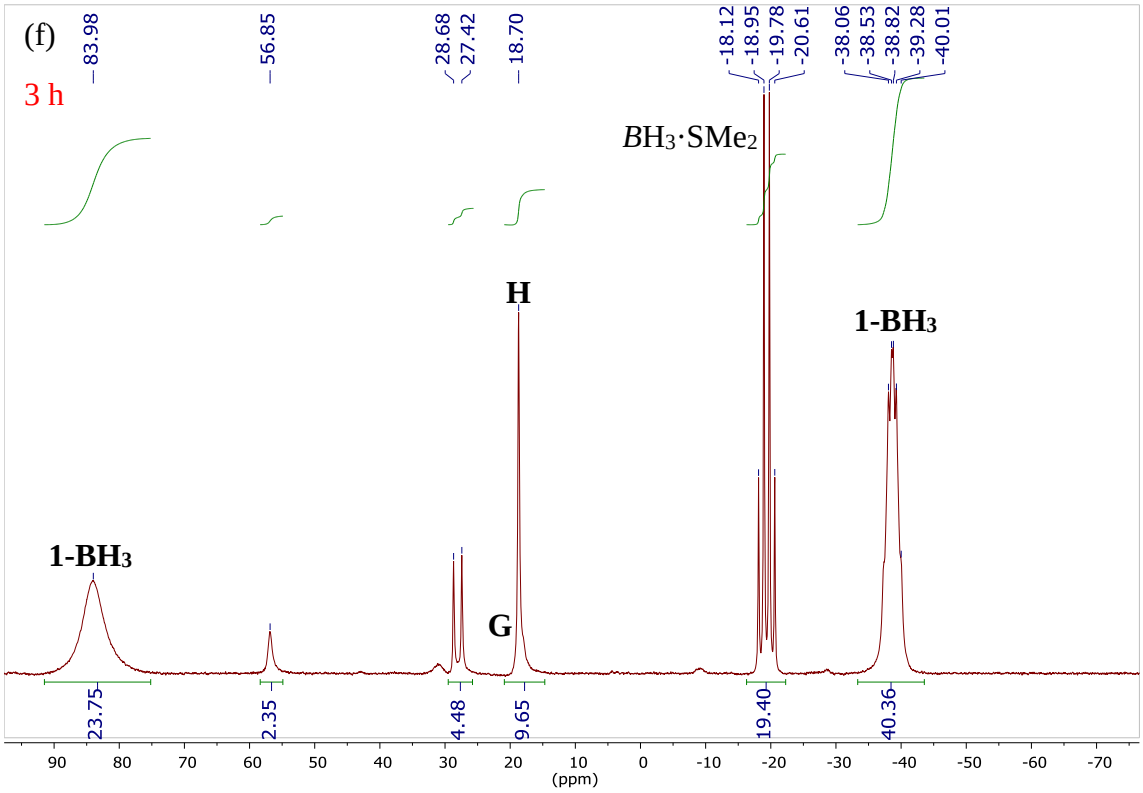
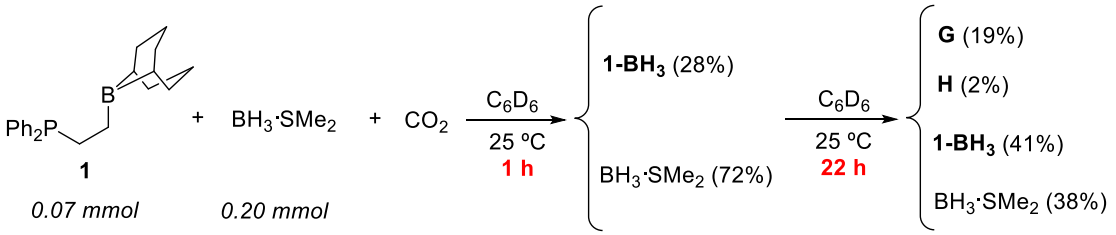
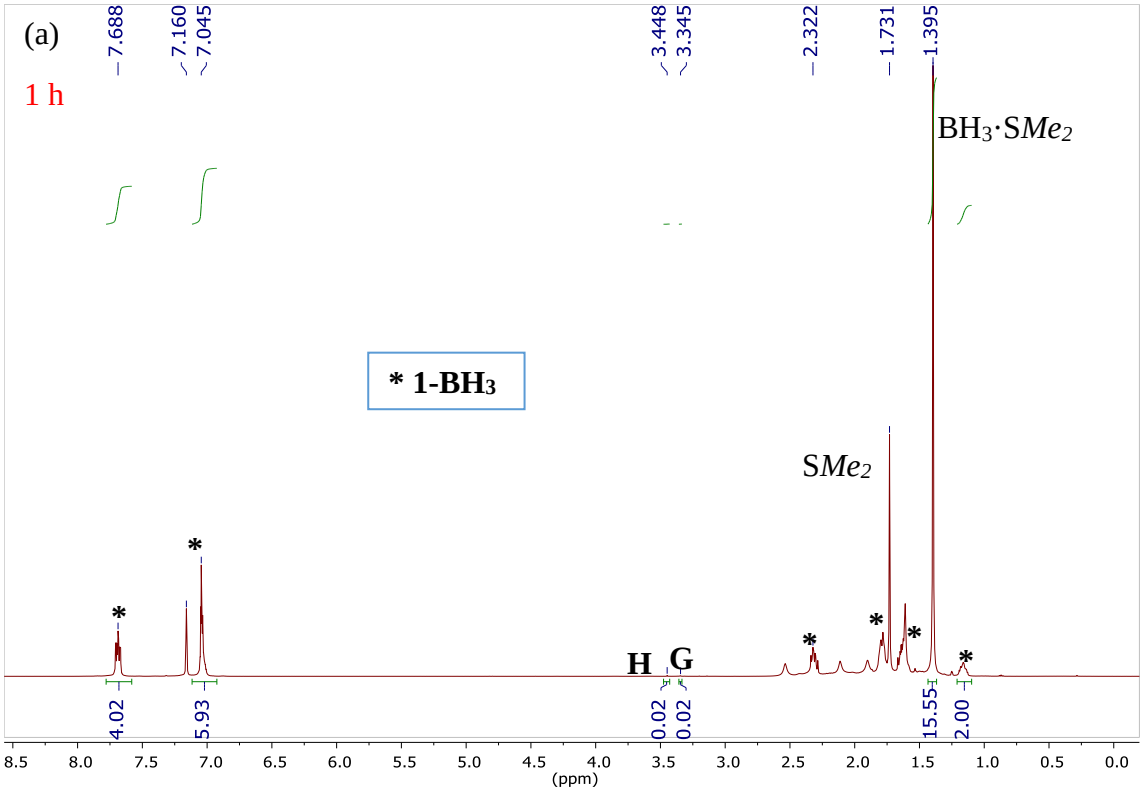
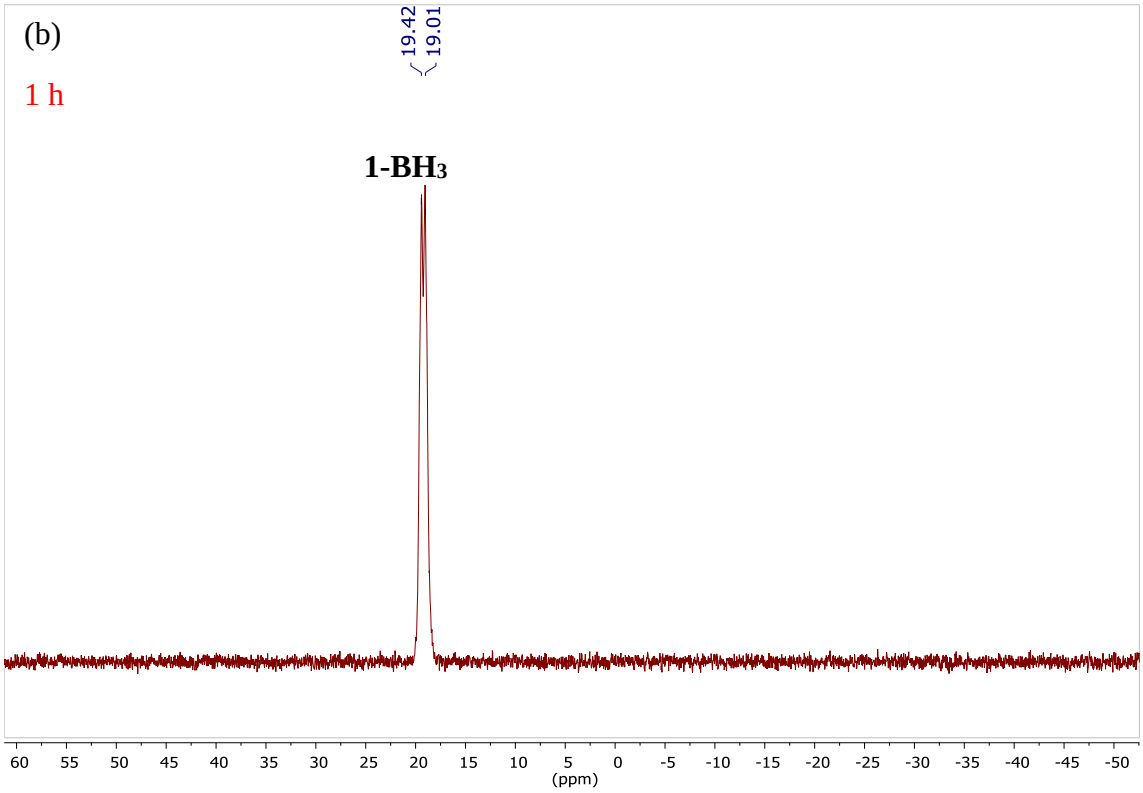
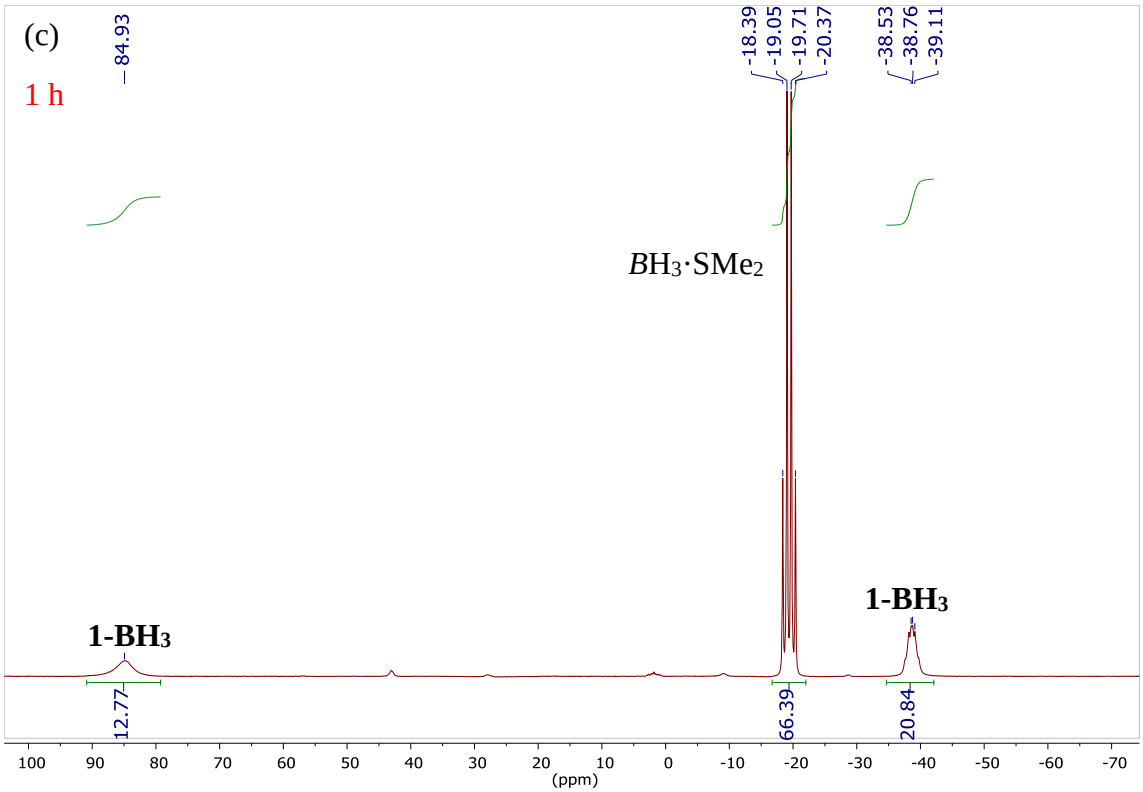

(f)
3 h
83.98
56.85
28.68
27.42
18.70
-18.12
-18.95
-19.78
-20.61
-38.06
-38.53
-38.82
-39.28
-40.01
BH3·SMe2
H
1-BH3
1-BH3
G
23.75
2.35
4.48
9.65
19.40
40.36
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
(ppm)

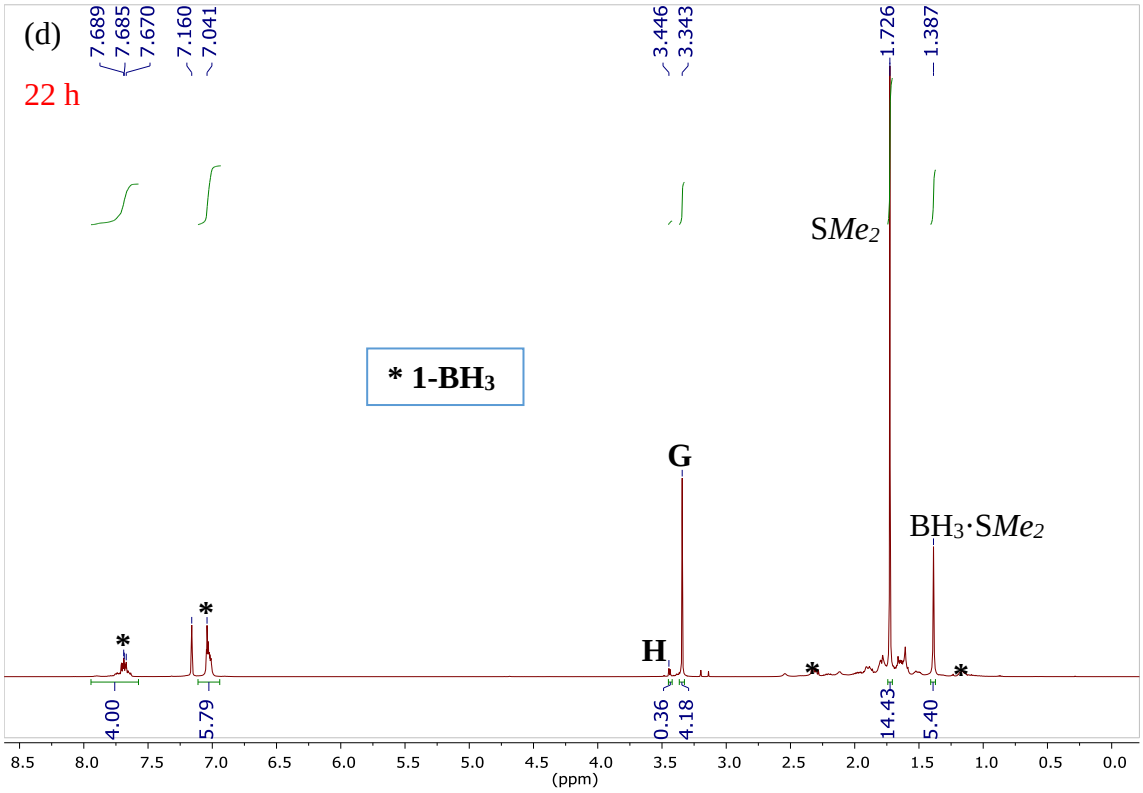
Figure S16. ^{1}H, $^{31}P\{^{1}H\}$ and ^{11}B NMR spectra for the reaction between compound **1**, $BH_3{\cdot}SMe_2$ and CO_2 (1 atm) in an NMR tube, after 1 h (a-c) and 22 h (d-f) at 25 ºC in C_6D_6.

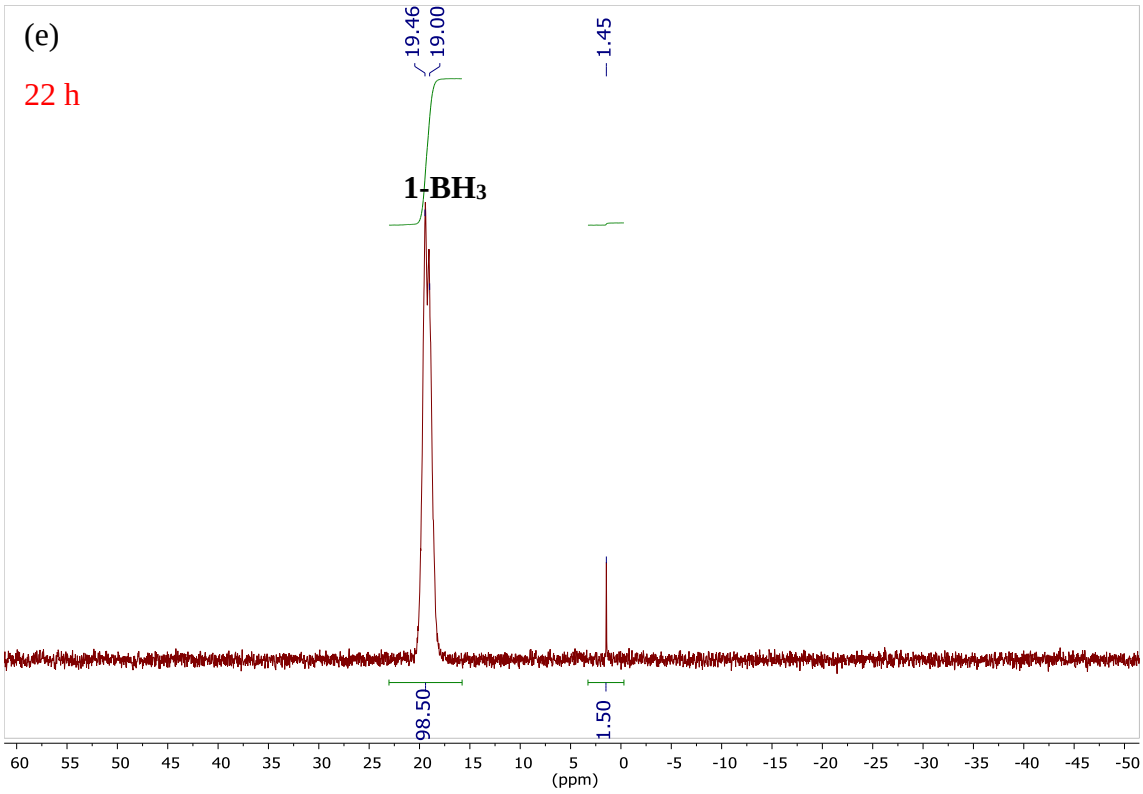


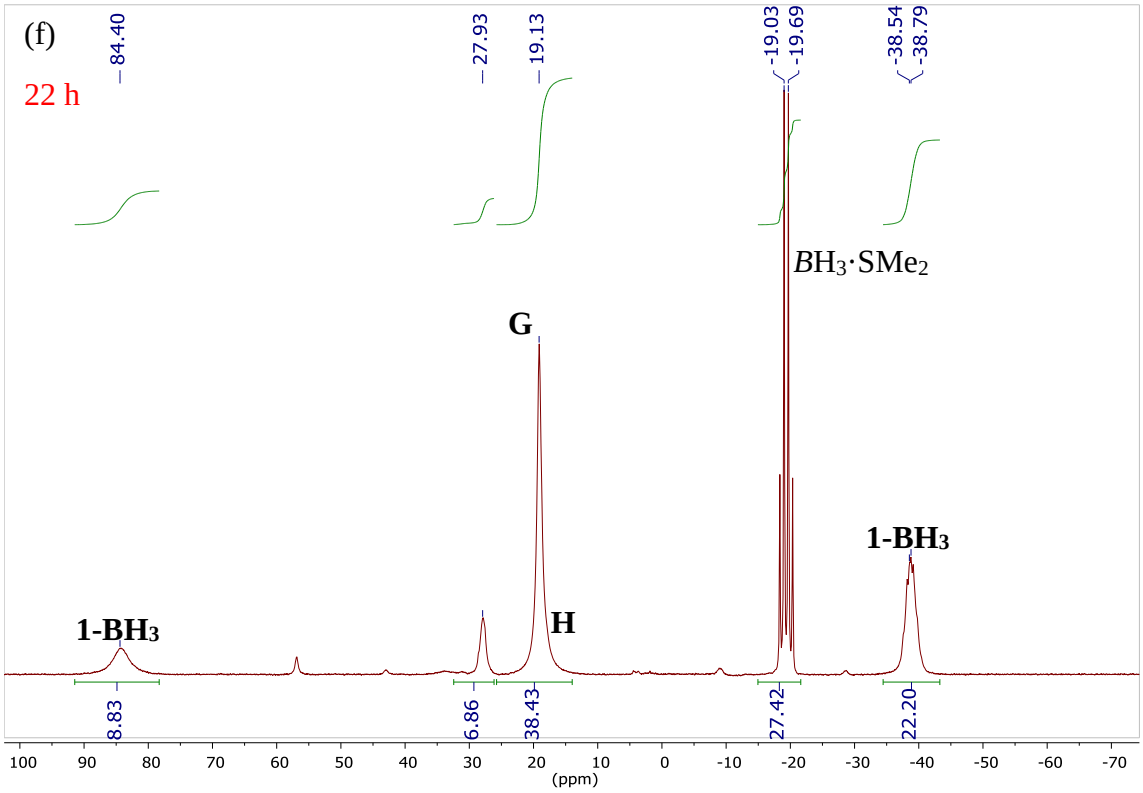



(b)
1 h
19.42
19.01
1-BH3
60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
(ppm)


(c)
1 h
84.93
-18.39
-19.05
-19.71
-20.37
-38.53
-38.76
-39.11
BH3·SMe2
1-BH3
1-BH3
12.77
66.39
20.84
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
(ppm)

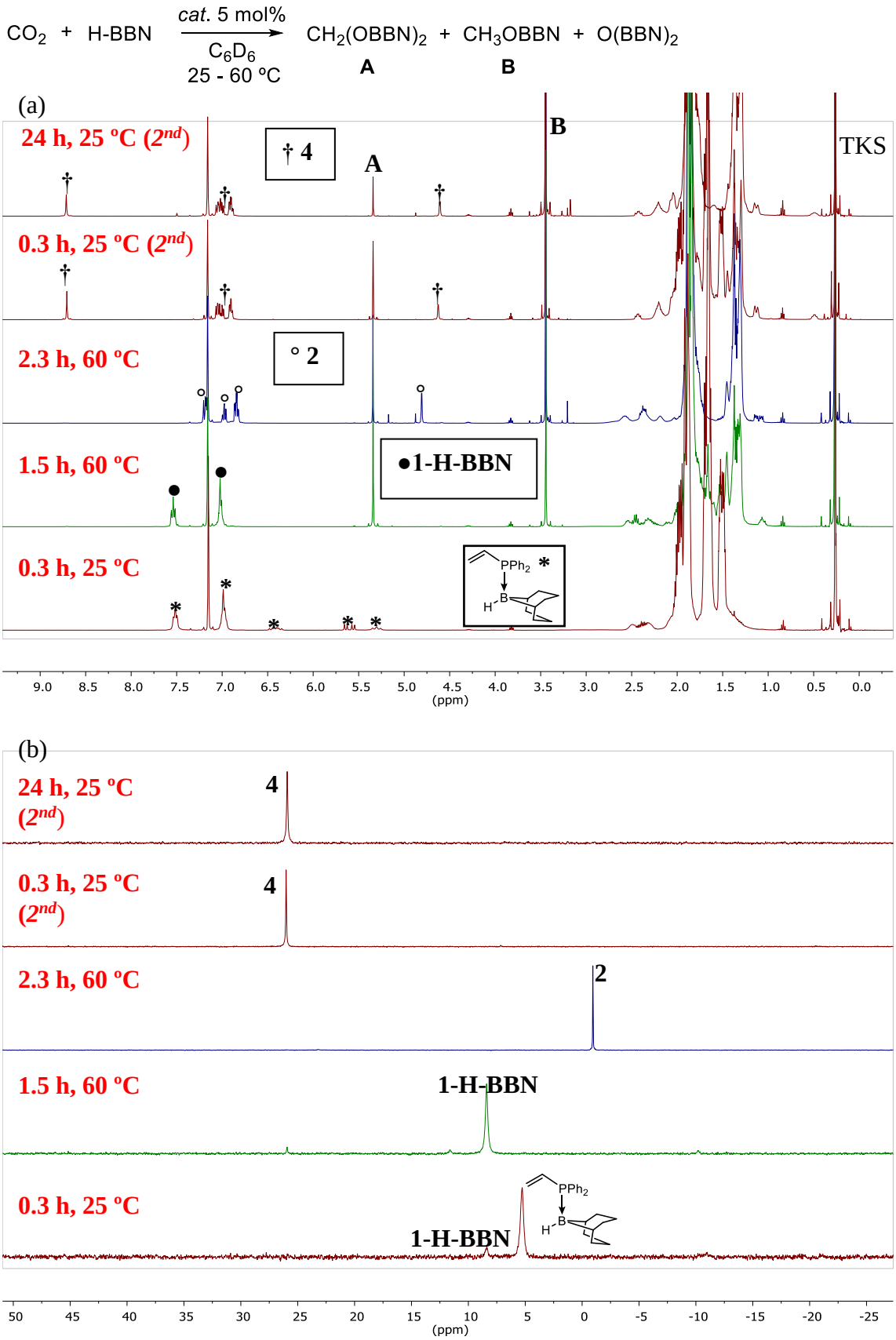

(d)
22 h
7.689
7.685
7.670
7.160
7.041
3.446
3.343
1.726
1.387
SMe2
* 1-BH3
G
BH3·SMe2
H
*
4.00
5.79
0.36
4.18
14.43
5.40
(ppm)


(e)
22 h
19.46
19.00
1.45
1-BH3
98.50
1.50
(ppm)


(f)
22 h
84.40
27.93
19.13
-19.03
-19.69
-38.54
-38.79
BH3·SMe2
G
H
1-BH3
1-BH3
8.83
6.86
38.43
27.42
22.20
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
(ppm)

Catalytic reduction of CO_2 with H-BBN, HBcat and HBpin. For the reduction of CO_2 with the latter boranes, a similar procedure was followed: in a glovebox, a solution of the corresponding hydroborane (0.20 mmol) in *ca.* 500 μL of C_6D_6 was charged to a NMR tube equipped with a J. Young valve. Subsequently, 50 μL of a 0.2 M stock solution in C_6D_6 of tetrakis(trimethylsilyl)silane (TKS, 0.01 mmol), used as an internal standard, were added to the NMR tube, followed by the appropriate volume of a stock solution of the catalyst ($Ph_2PCH{=}CH_2$, **1** or **2**) in C_6D_6 (concentration range: 0.001 – 0.2 M) amounting to a final volume of *ca.* 0.6 mL. Afterwards, the sample was subjected to a freeze-pump-thaw cycle: frozen with liquid N_2, evacuated under vacuum and, once thawed at room temperature, refilled with CO_2 (*ca*. 1 atm). Then, the sample was thoroughly shaken and was either left at room temperature, or placed in an oil bath at 60 ºC, and monitored by multinuclear NMR. The chemical shifts of the reduction products in the ^1H and ^{11}B NMR spectra, $CH_2(OBBN)_2$ (**A**) and CH_3OBBN (**B**),[2] CH_3OBcat (**C**),[3] and HCO_2Bpin (**D**),[4] $CH_2(OBpin)_2$ (**E**)[4] and CH_3OBpin (**F**)[4] compare well with those reported in the literature. The TON was calculated according to the number of C-H formed in the reduction products by integration of the corresponding signals in the ^1H NMR spectrum relative to the internal standard.

Figure S17. ^{1}H (a), $^{31}P\{^{1}H\}$ (b) and ^{11}B (c) NMR stacked plots for the catalytic reduction of CO_2 with H-BBN using Ph_2PCHCH_2 as catalyst: detection of intermediate species.



(c)

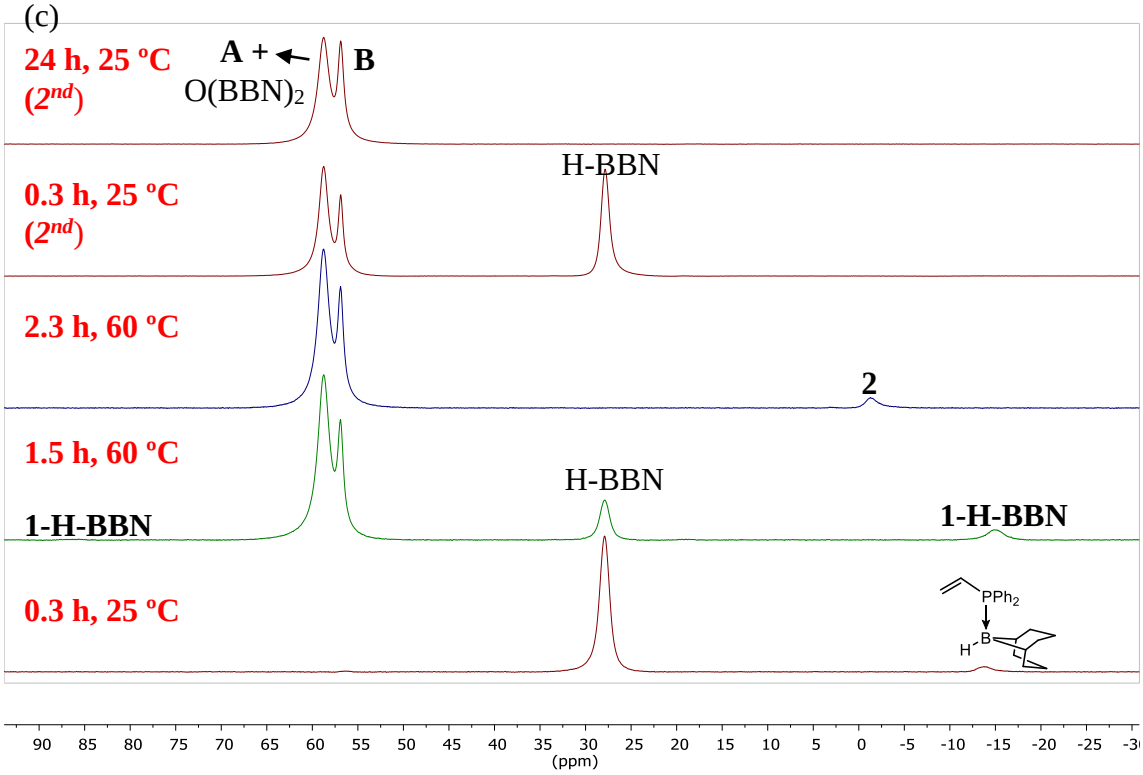
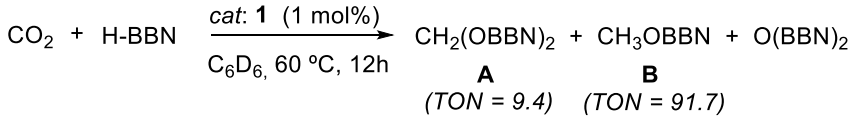
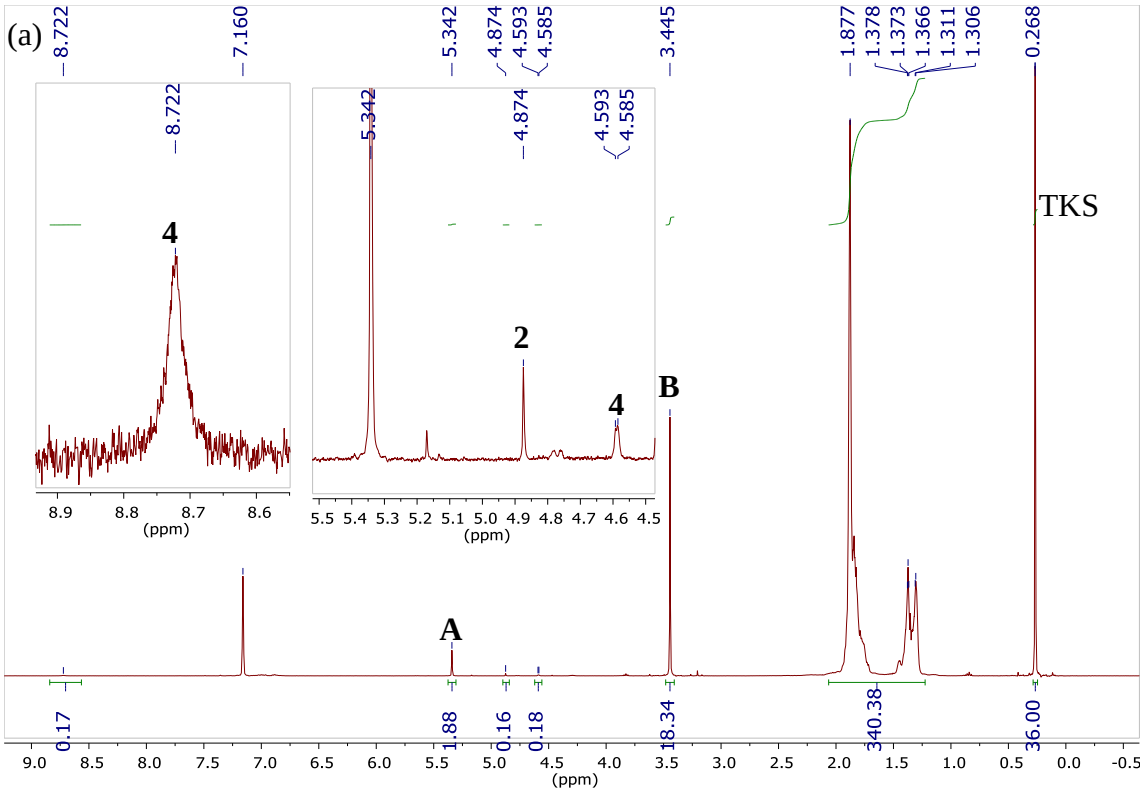
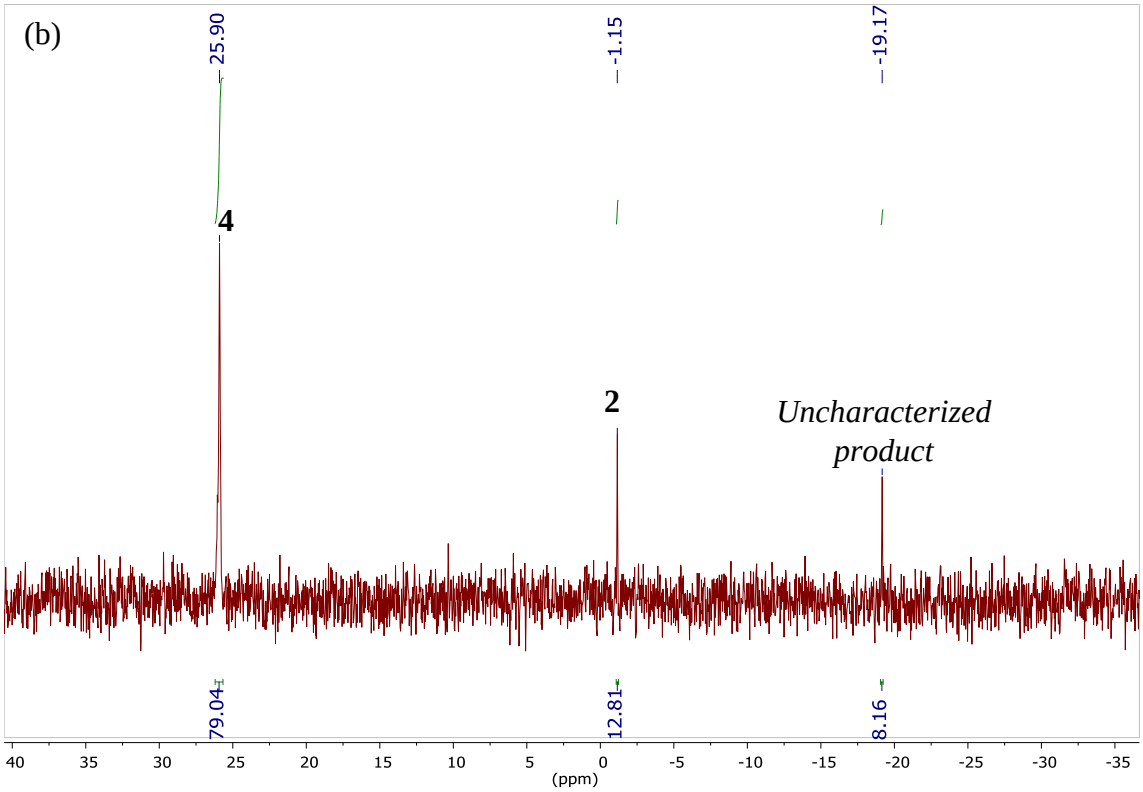

24 h, 25 °C
(2nd)
A +
O(BBN)2
B
H-BBN
0.3 h, 25 °C
(2nd)
2.3 h, 60 °C
2
1.5 h, 60 °C
H-BBN
1-H-BBN
1-H-BBN
0.3 h, 25 °C
PPh2
H
B
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
(ppm)

Figure S18. ^{1}H (a), $^{31}P\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for the catalytic reduction of CO_2 with H-BBN using compound **1** (1 mol%) as catalyst after 12h at 60 ºC.







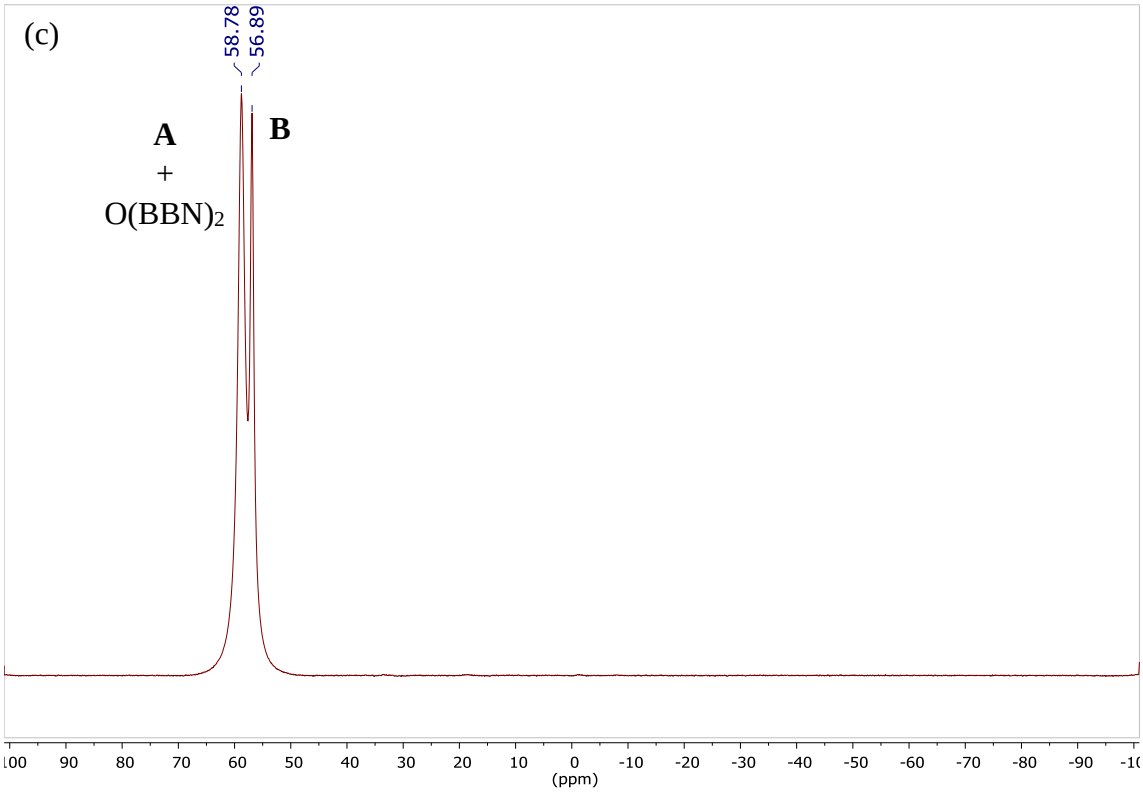
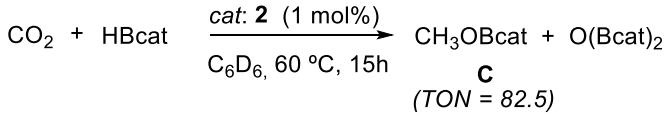
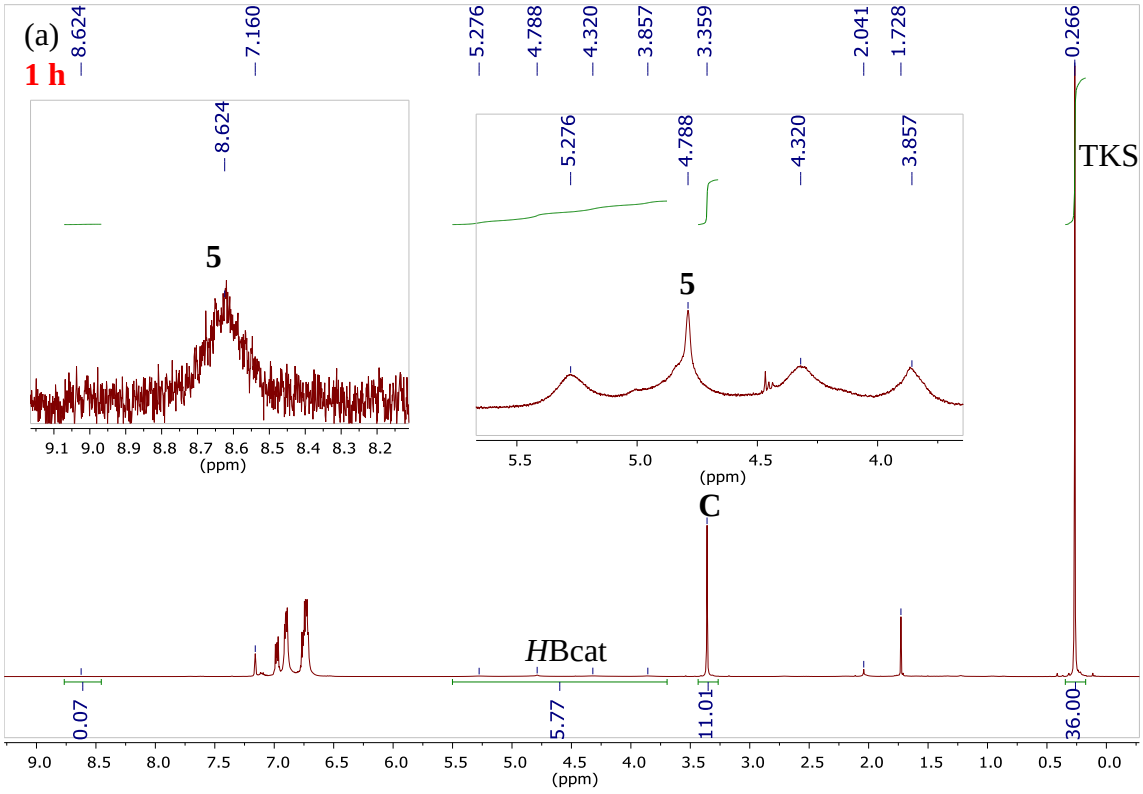
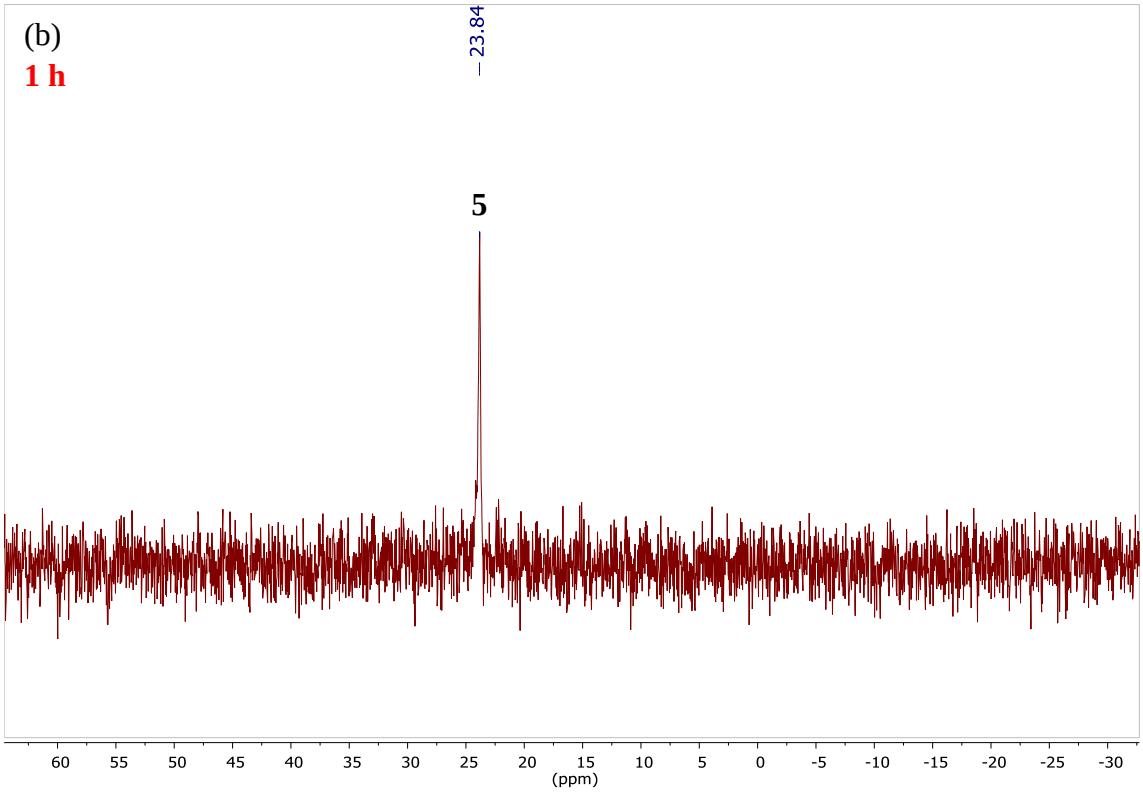
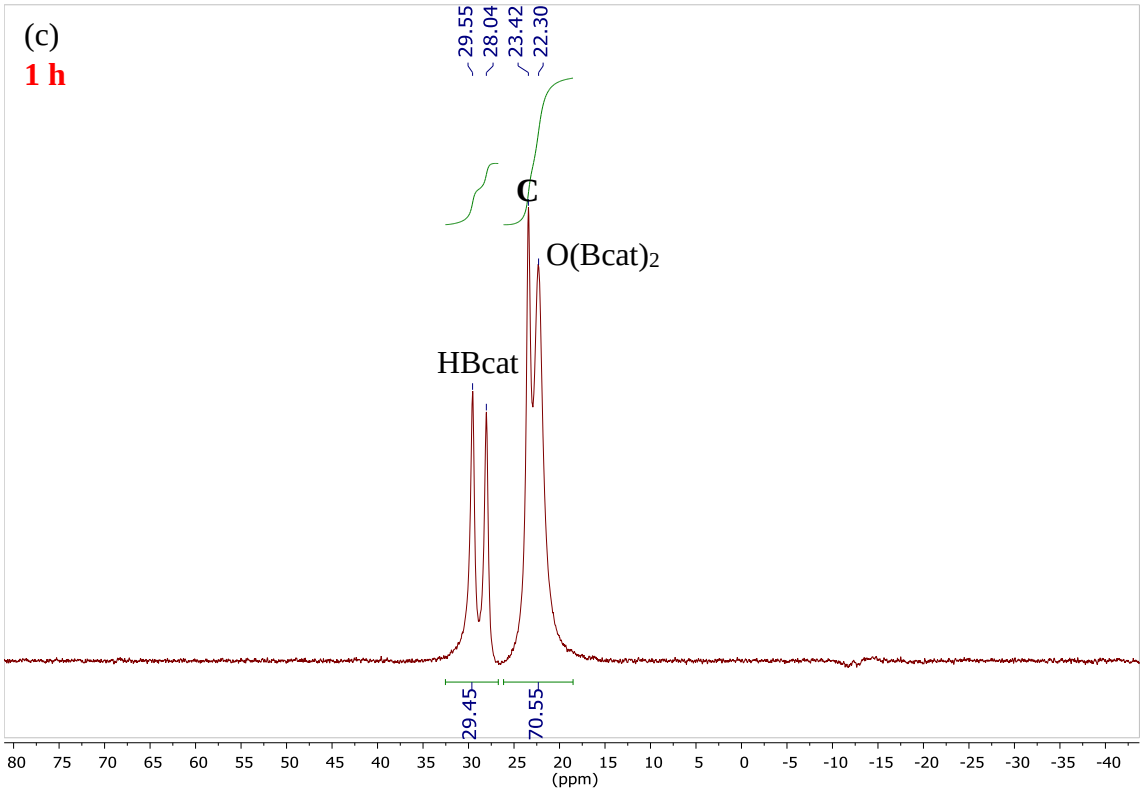

(c)
58.78
56.89
A
+
O(BBN)2
B
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
(ppm)

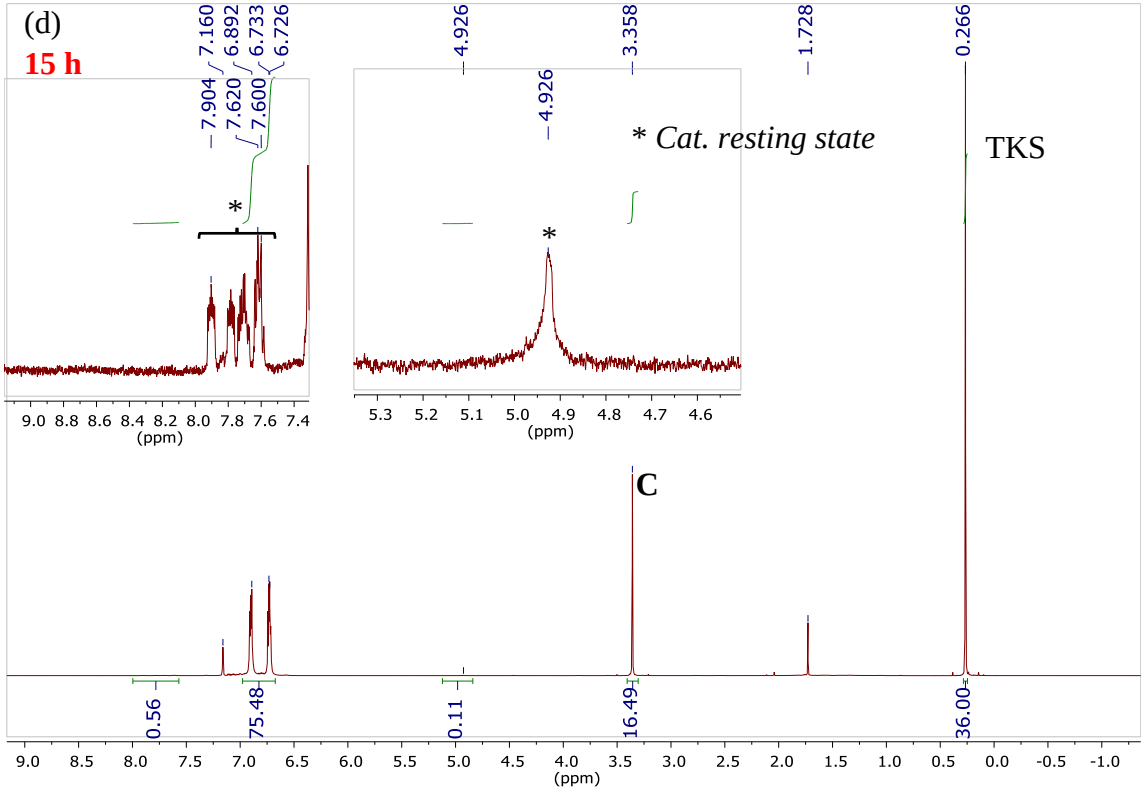
Figure S19. ^{1}H, $^{31}P\{^{1}H\}$ and ^{11}B NMR spectra for the catalytic reduction of CO_2 with HBcat using compound **2** (1 mol%) as catalyst after 1 h (a-c) and 15 h (d-f) at 60 ºC.

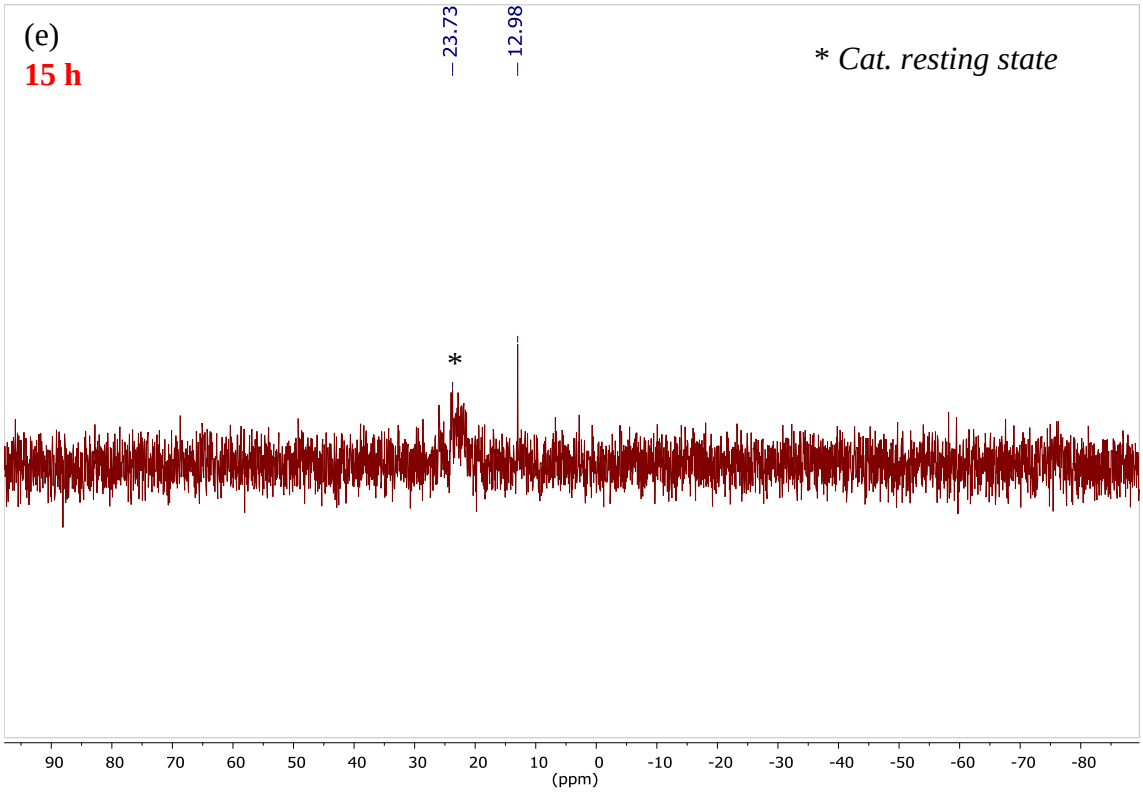







(c)
1 h
29.55
28.04
23.42
22.30
C
O(Bcat)2
HBcat
29.45
70.55
(ppm)


(d)
15 h
7.160
6.892
6.733
6.726
7.904
7.620
7.600
4.926
3.358
1.728
0.266
* Cat. resting state
TKS
C
0.56
75.48
0.11
16.49
36.00
(ppm)


(e)
15 h
23.73
12.98
* Cat. resting state
*
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
(ppm)

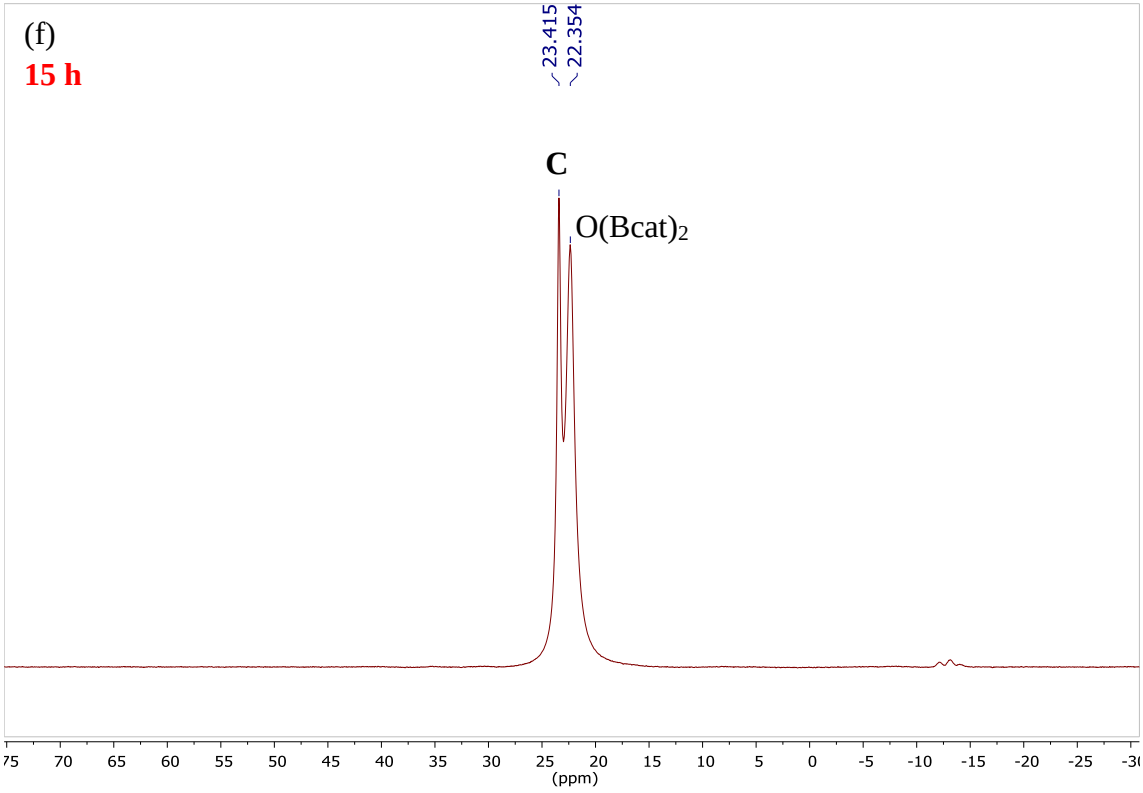
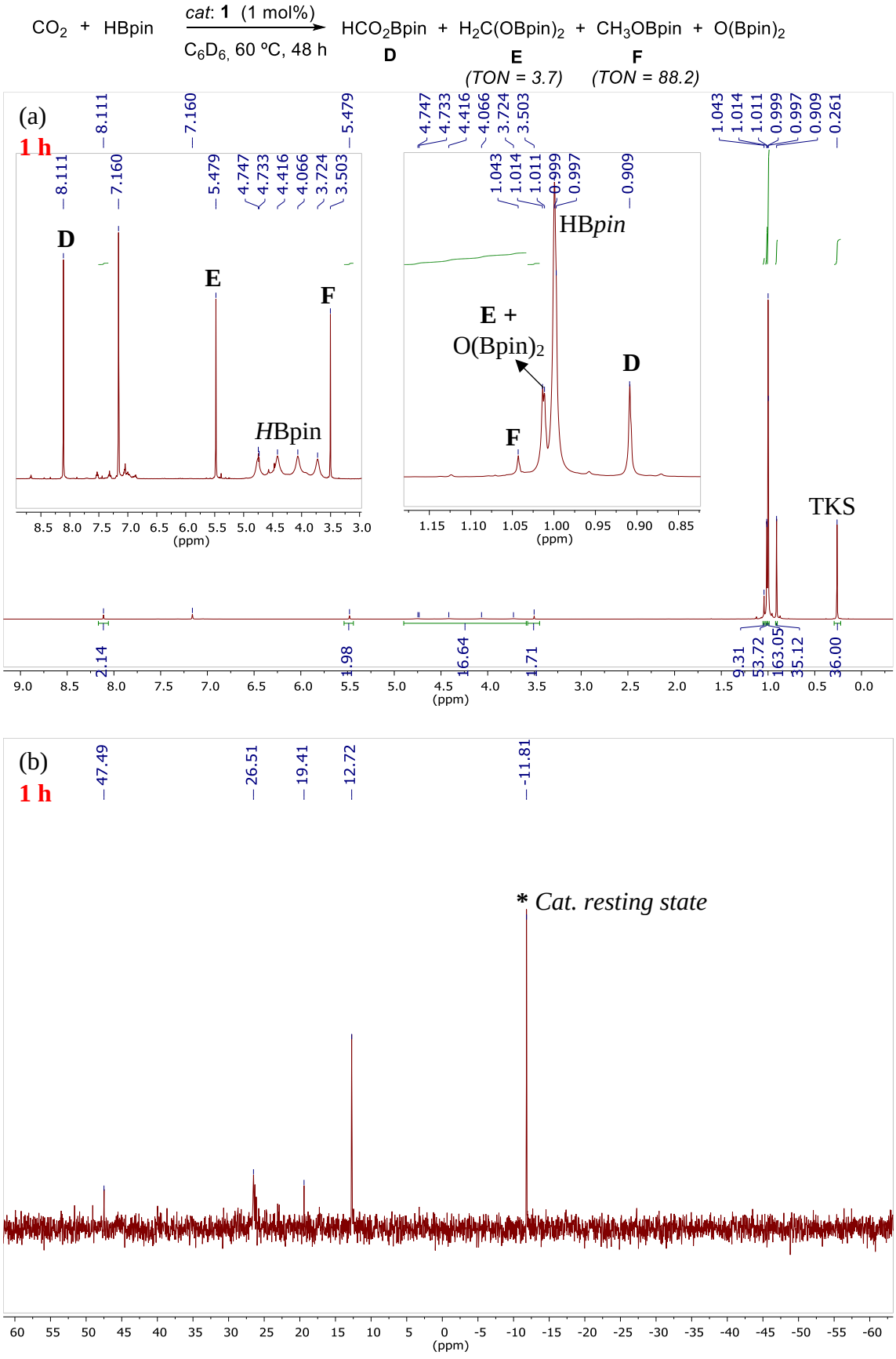
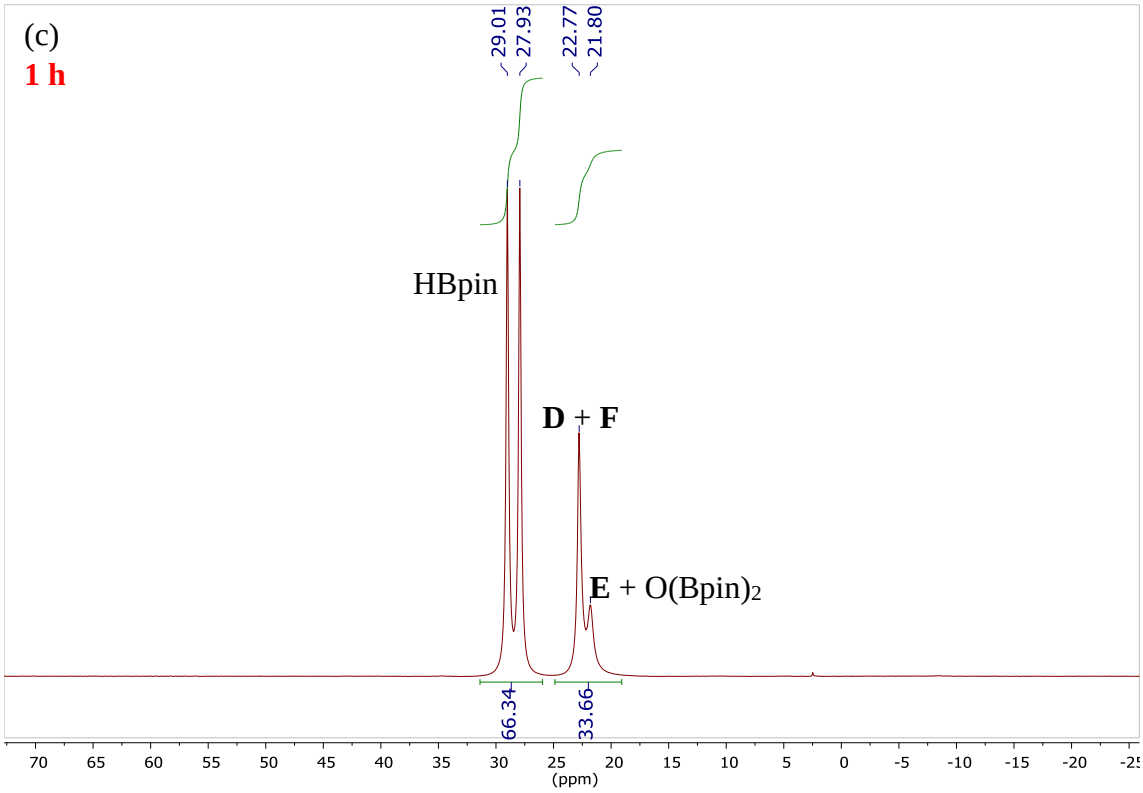
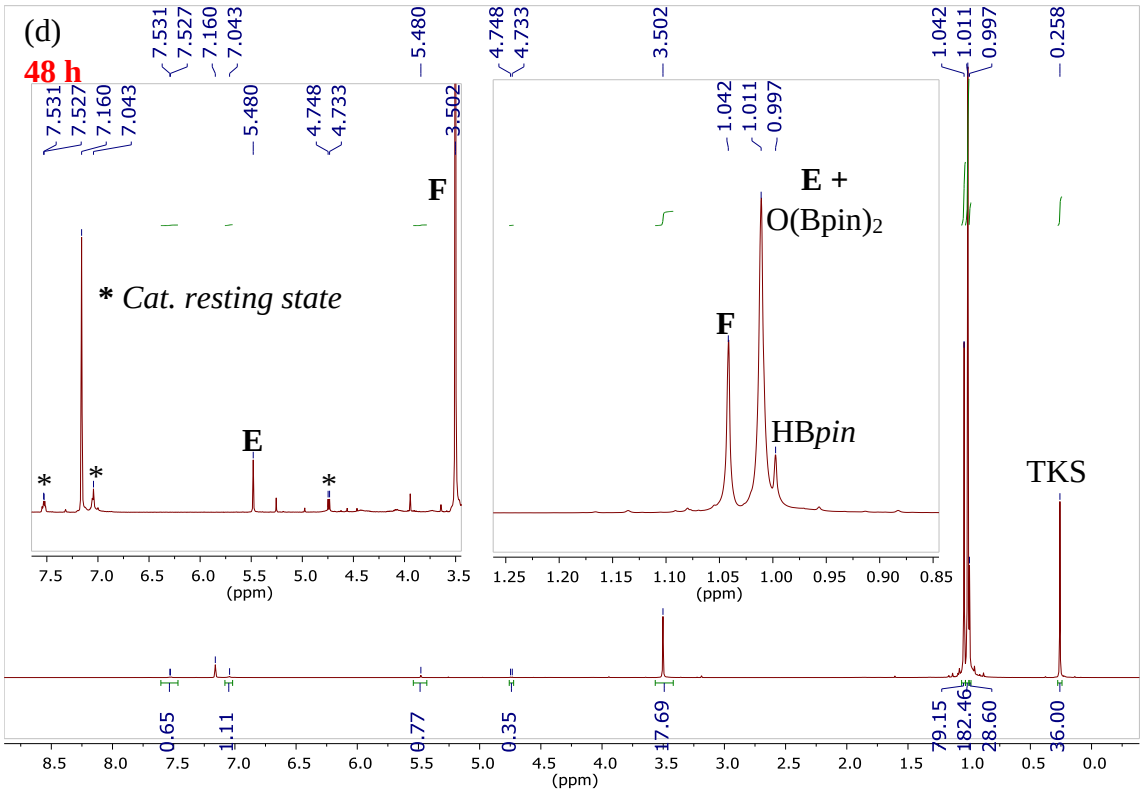
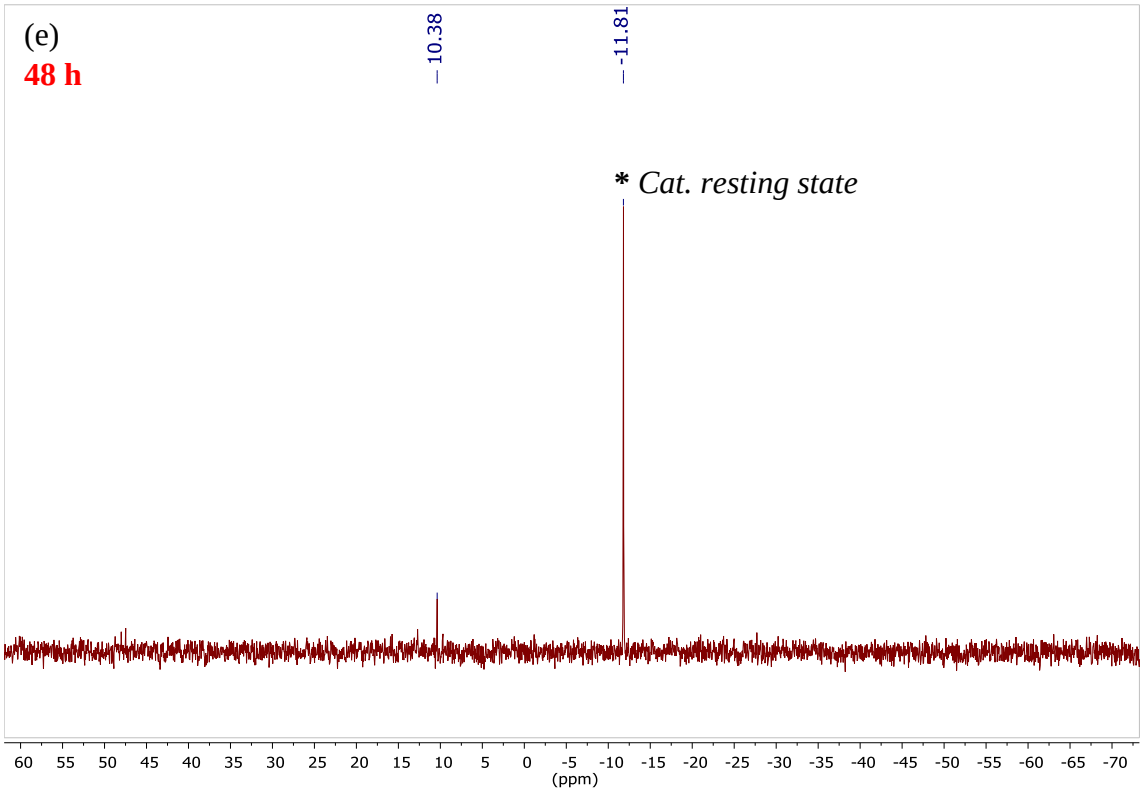

(f)
15 h
23.415
22.354
C
O(Bcat)2
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
(ppm)

Figure S20. ^{1}H, $^{31}P\{^{1}H\}$ and ^{11}B NMR spectra for the catalytic reduction of CO_2 with HBpin using compound **1** (1 mol%) as catalyst after 1 h (a-c) and 48 h (d-f) at 60 ºC.




(c)
1 h
29.01
27.93
22.77
21.80
HBpin
D + F
E + O(Bpin)2
66.34
33.66
(ppm)


(d)
48 h
7.531
7.527
7.160
7.043
5.480
4.748
4.733
3.502
1.042
1.011
0.997
0.258
F
* Cat. resting state
E
E +
O(Bpin)2
F
HBpin
TKS
0.65
1.11
0.77
0.35
17.69
79.15
182.46
28.60
36.00
(ppm)


(e)
48 h
10.38
-11.81
* Cat. resting state
60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70
(ppm)

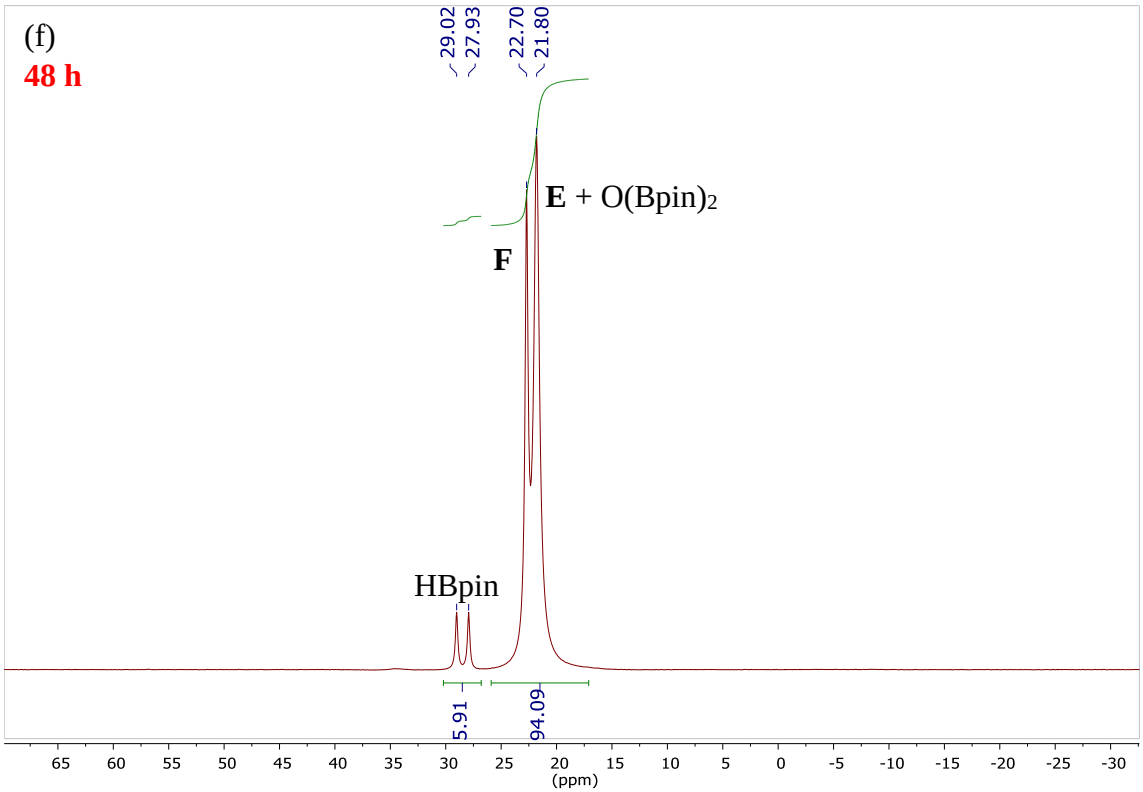
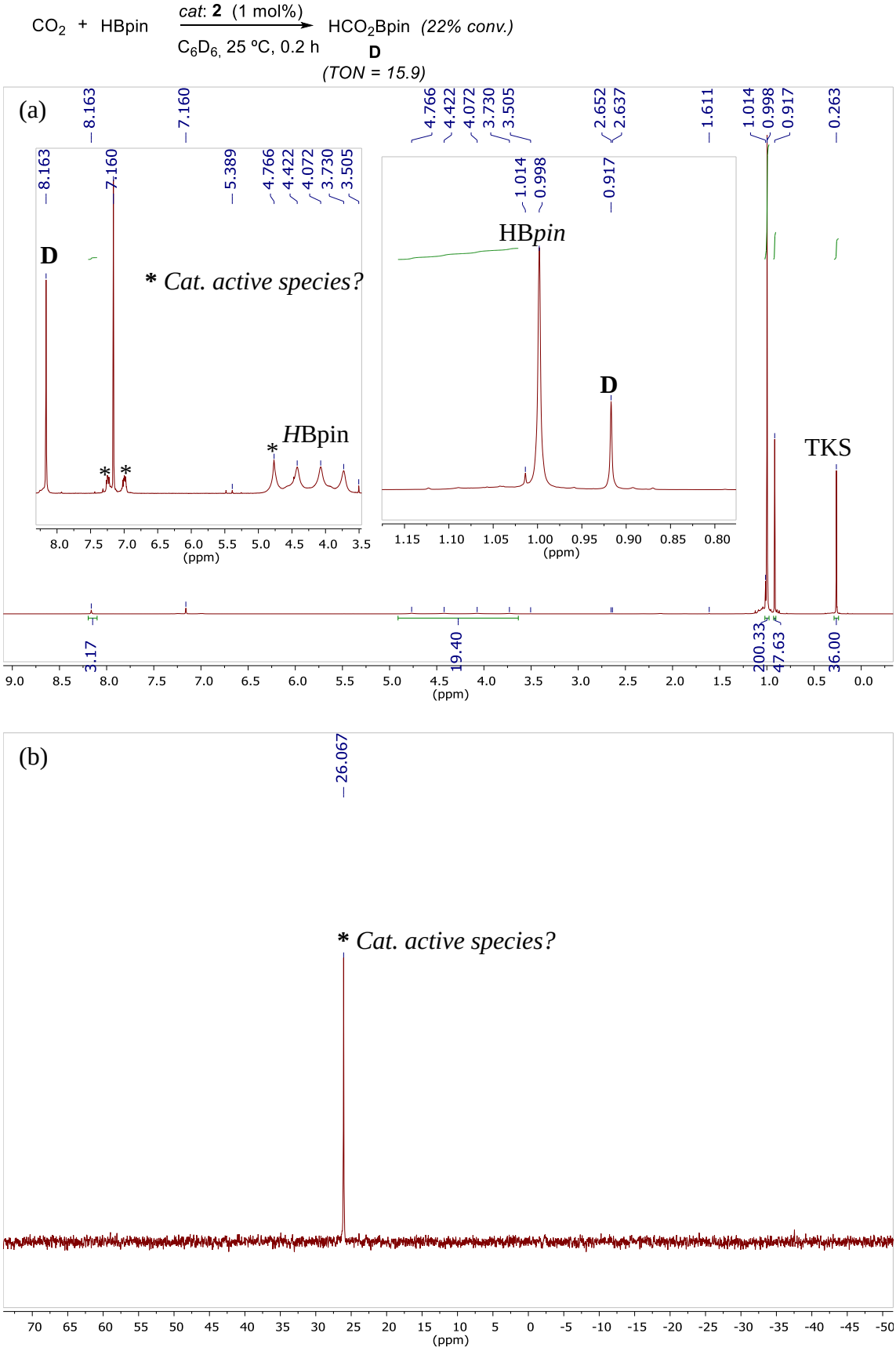
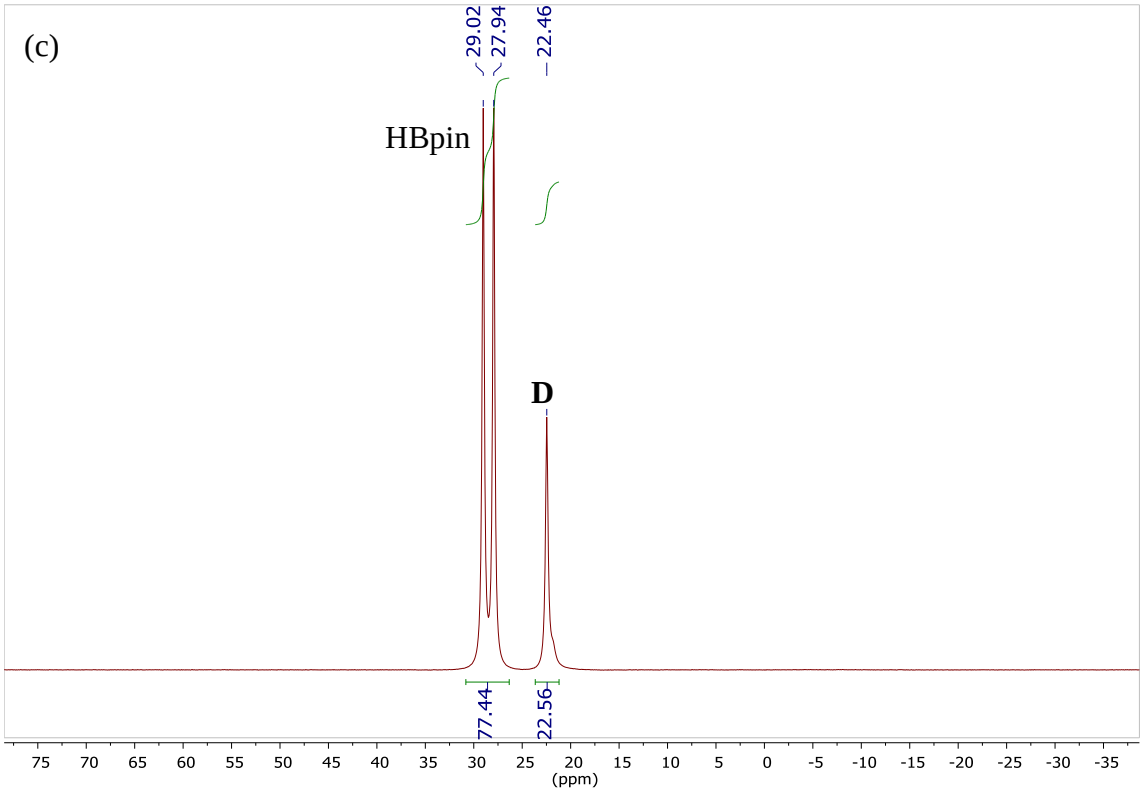

(f)
48 h
29.02
27.93
22.70
21.80
E + O(Bpin)2
F
HBpin
5.91
94.09
65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30
(ppm)

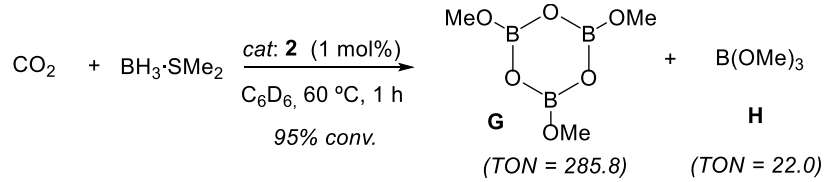
Figure S21. ^{1}H (a), $^{31}P\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for the catalytic reduction of CO_2 with HBpin using compound **2** (1 mol%) as catalyst after 0.2 h (a-c) at 25 ºC.

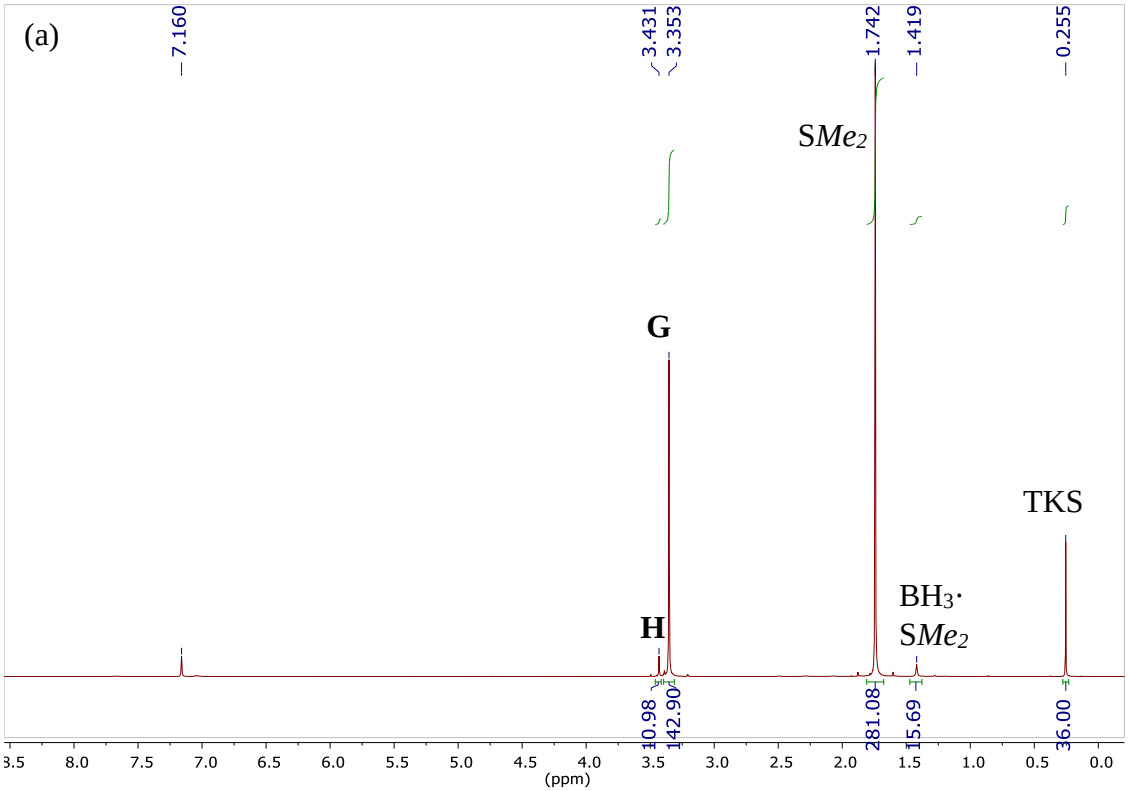


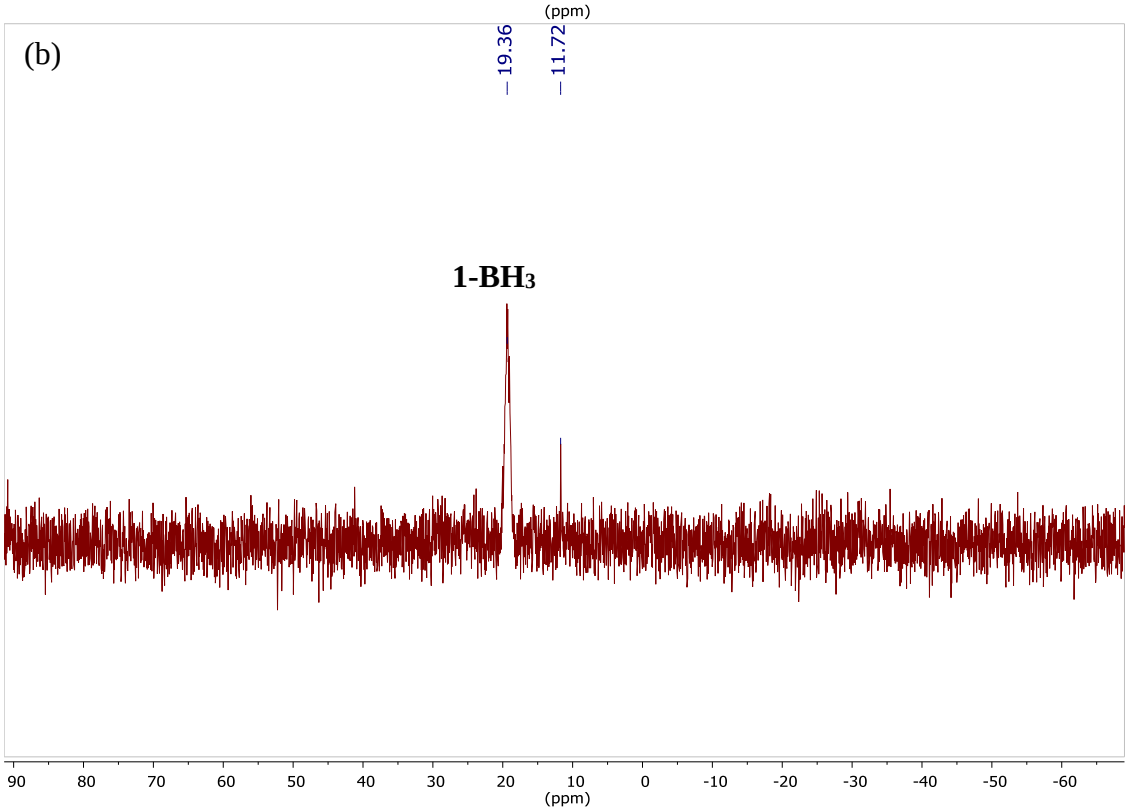

(c)
29.02
27.94
22.46
HBpin
D
77.44
22.56
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
(ppm)

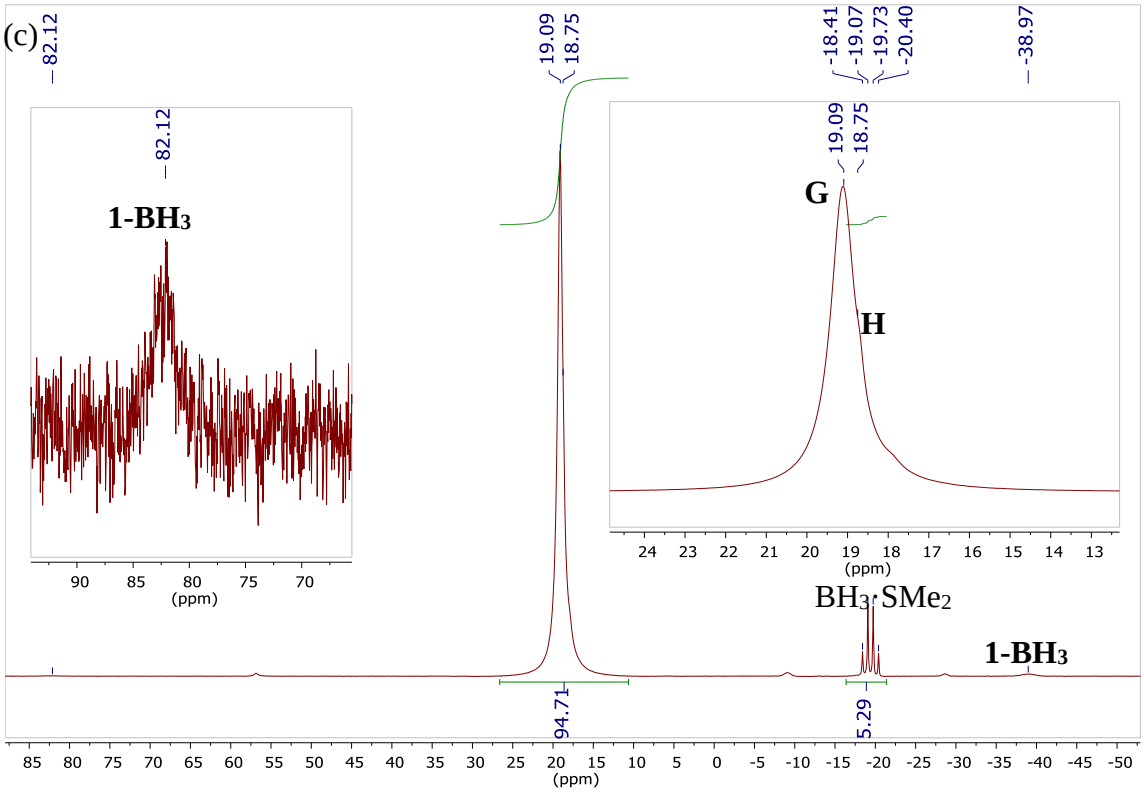
Catalytic reduction of CO_2 with $BH_3{\cdot}SMe_2$. A solution of the corresponding hydroborane (47.4 μL, 0.50 mmol) in *ca.* 650 μL of C_6D_6 was charged to a 40 mL-Schlenk tube equipped with a J. Young valve and a stir bar. Subsequently, 50 μL of a 0.2 M stock solution in C_6D_6 of TKS (0.01 mmol), used as an internal standard, were added to the NMR tube, followed by the appropriate volume of a stock solution of the catalyst ($Ph_2PCH{=}CH_2$, **1** or **2**) in C_6D_6 (concentration range: 0.001 – 0.2 M) amounting to a final volume of *ca.* 0.8 mL. Afterwards, the Schlenk was subjected to a freeze-pump-thaw cycle and, once thawed at room temperature, refilled with CO_2 (*ca*. 1 atm). Then, the solution was vigorously stirred and was either left at room temperature, or placed in an oil bath at 60 ºC and, after a fixed period, transferred to an NMR tube and monitored by multinuclear NMR. The chemical shifts of the reduction products in the ^1H and ^{11}B NMR spectra, $[OB(OMe)]_3$ (**G**) and $B(OMe)_3$ (**H**), compare well with those reported in the literature.[2a, 3b, c, 5] The TON was calculated according to the number of C-H formed in the reduction products by integration of the corresponding signals in the ^1H NMR spectrum relative to the internal standard.

Figure S22. ^{1}H (a), $^{31}P\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for the catalytic reduction of CO_2 with $BH_3{\cdot}SMe_2$ using compound **2** (1 mol%) as catalyst after 0.2 h (a-c) at 25 ºC.



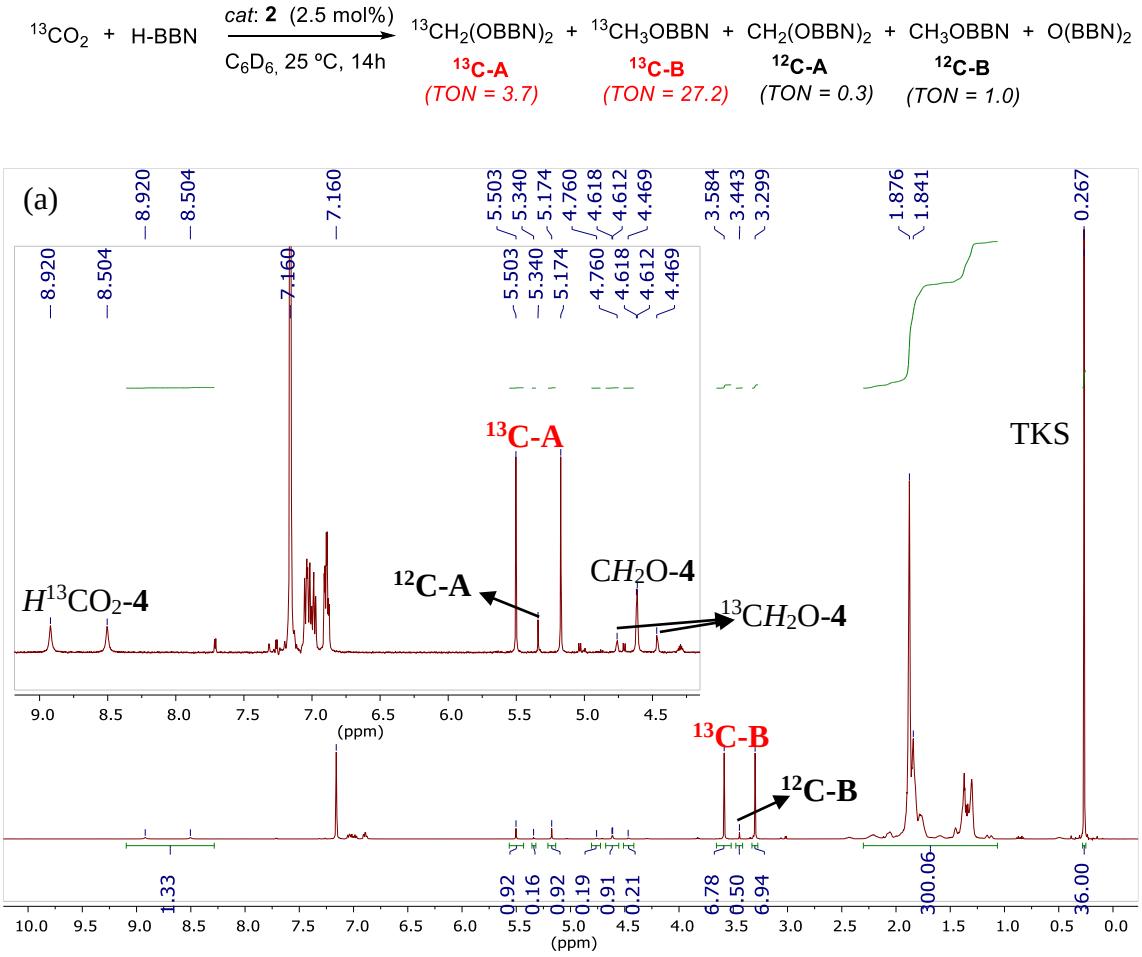


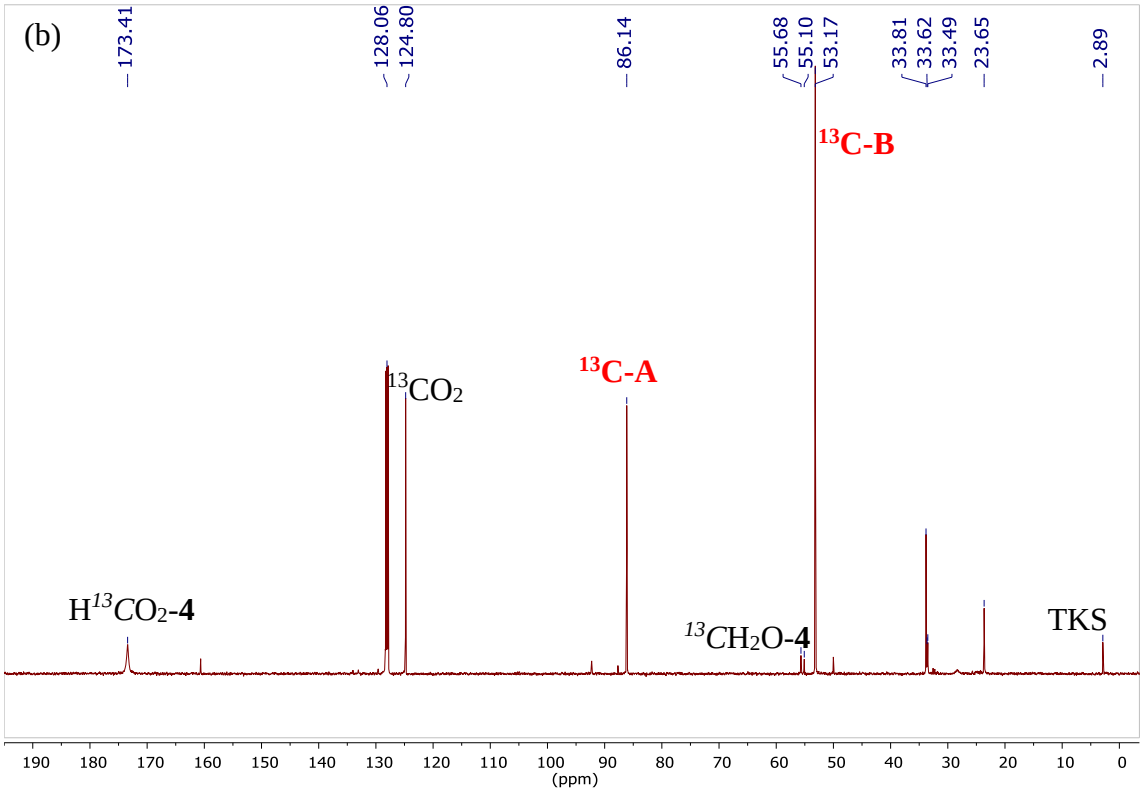


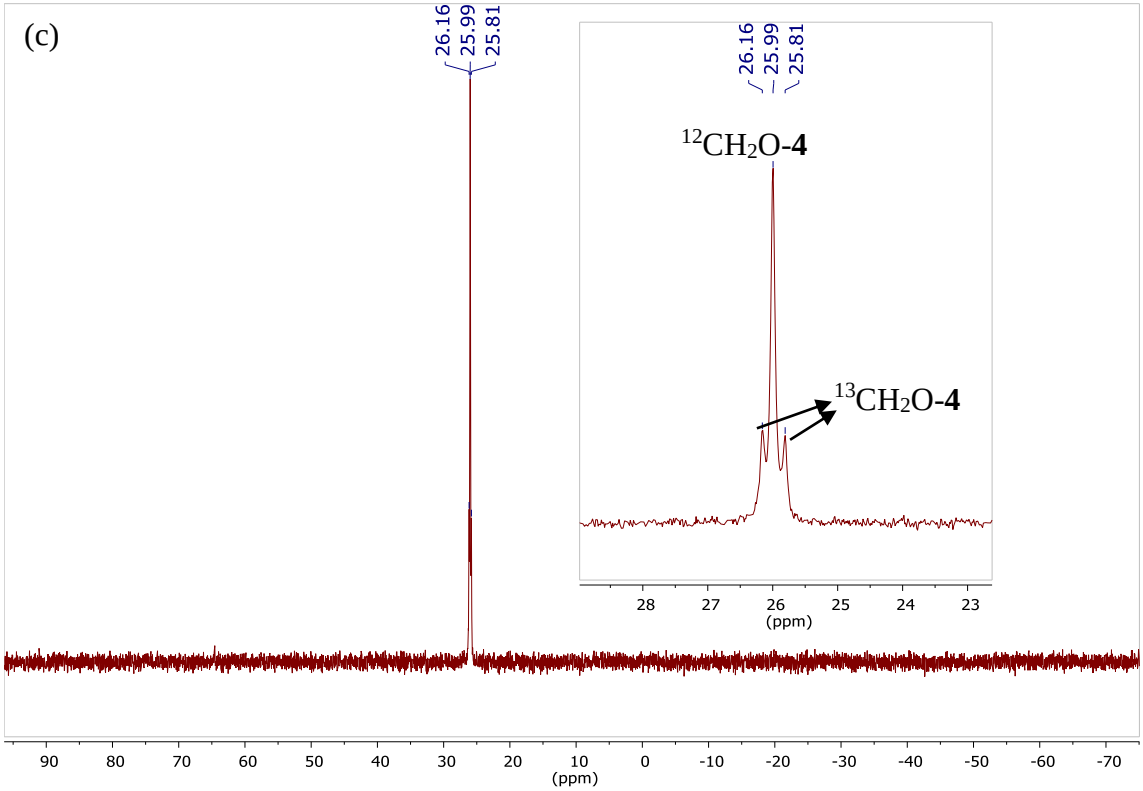

(c)
82.12
19.09
18.75
-18.41
-19.07
-19.73
-20.40
-38.97
1-BH3
G
H
BH3·SMe2
1-BH3
94.71
5.29
(ppm)

Kinetic experiments. All kinetic experiments were conducted as described in the previous section for the catalytic reduction of CO_2 with H-BBN, HBcat and HBpin. The boranes employed for the kinetic studies were H-BBN and HBcat at 25 or 60 ºC. Experiments using $^{13}CO_2$ were also conducted for H-BBN (*vide infra*). The reaction progress was monitored in all cases by ^{1}H NMR until the borane was fully or nearly consumed. The TON was calculated according to the number of C-H formed in the reduction products by integration of the corresponding signals in the ^{1}H NMR spectrum relative to the internal standard (TKS). TOF values (h^{-1}) at a given time (t_n) were obtained by dividing the increment of TON in two consecutive measurements, at t_{n-1} and t_n (h), by the increment in time. Thus, since the increments of time were relatively small, the following approximation was made: $TOF = dTON\ (dt)^{-1} \approx \Delta TON\ (\Delta t)^{-1} = [TON(t_n) - TON(t_{n-1})][t_n - t_{n-1}]^{-1}$. The concentration of the identified active species in catalysis was also measured by integration of the corresponding signals in the ^{1}H NMR spectrum relative to the internal standard (TKS).

Figure S23. ^{1}H (a), $^{13}C\{^{1}H\}$ (b), $^{31}P\{^{1}H\}$ (c) and ^{11}B (d) NMR spectra for the catalytic reduction of $^{13}CO_2$ with H-BBN using compound **2** (2.5 mol%) as catalyst at 25 ºC in C_6D_6 after kinetic experiment (14 h, 25 ºC).




(b)
173.41
128.06
124.80
86.14
55.68
55.10
53.17
33.81
33.62
33.49
23.65
2.89
13C-B
13CO2
13C-A
H13CO2-4
13CH2O-4
TKS
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


(c)
26.16
25.99
25.81
12CH2O-4
13CH2O-4
28 27 26 25 24 23
(ppm)
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
(ppm)

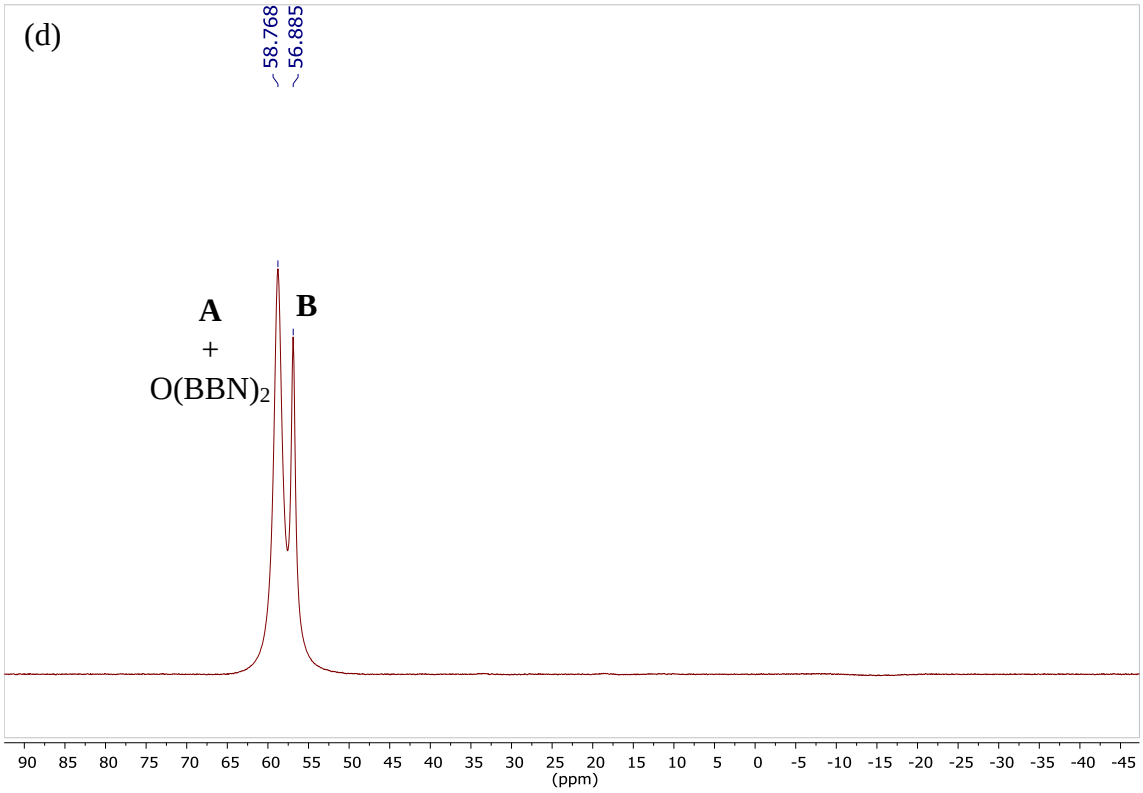
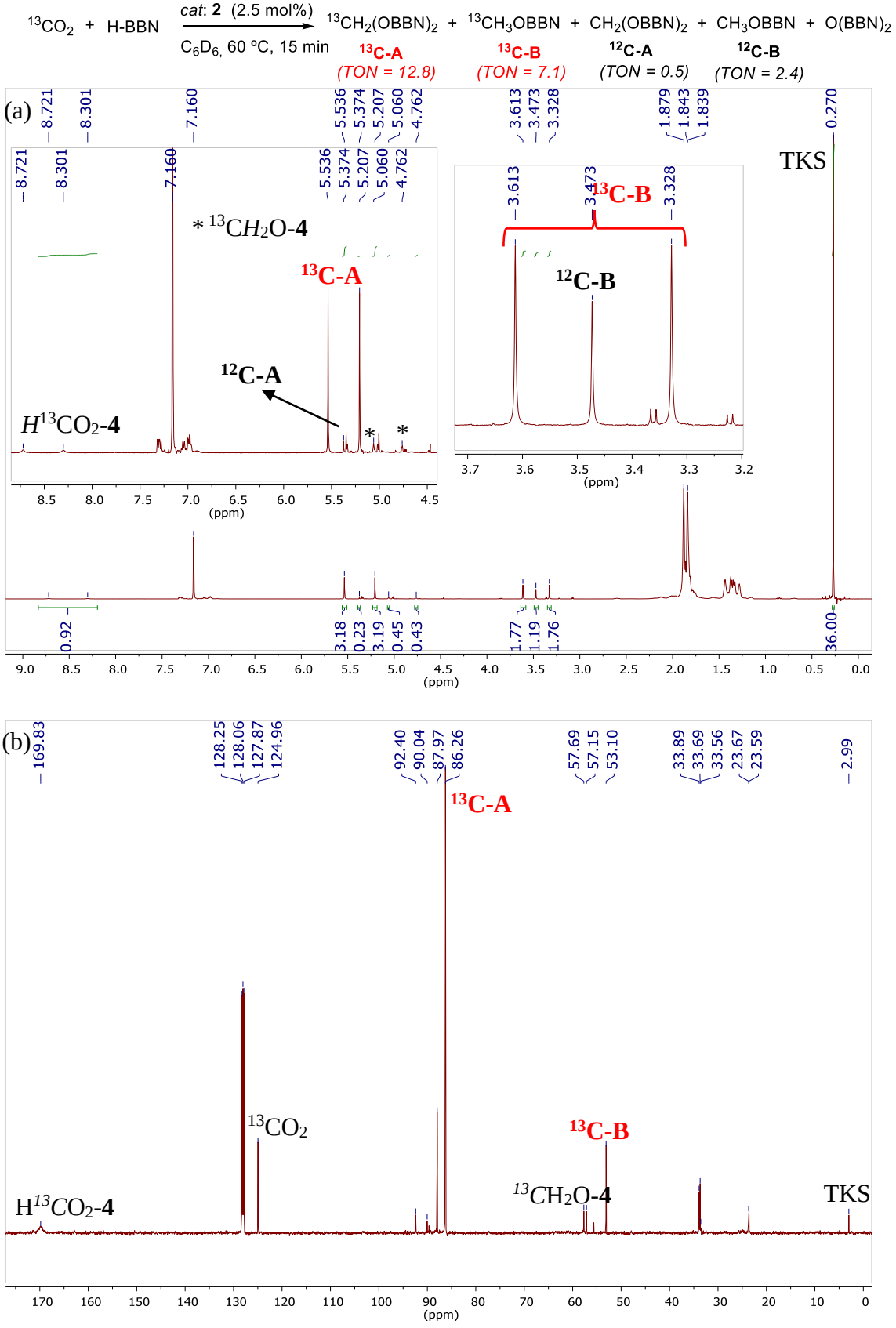
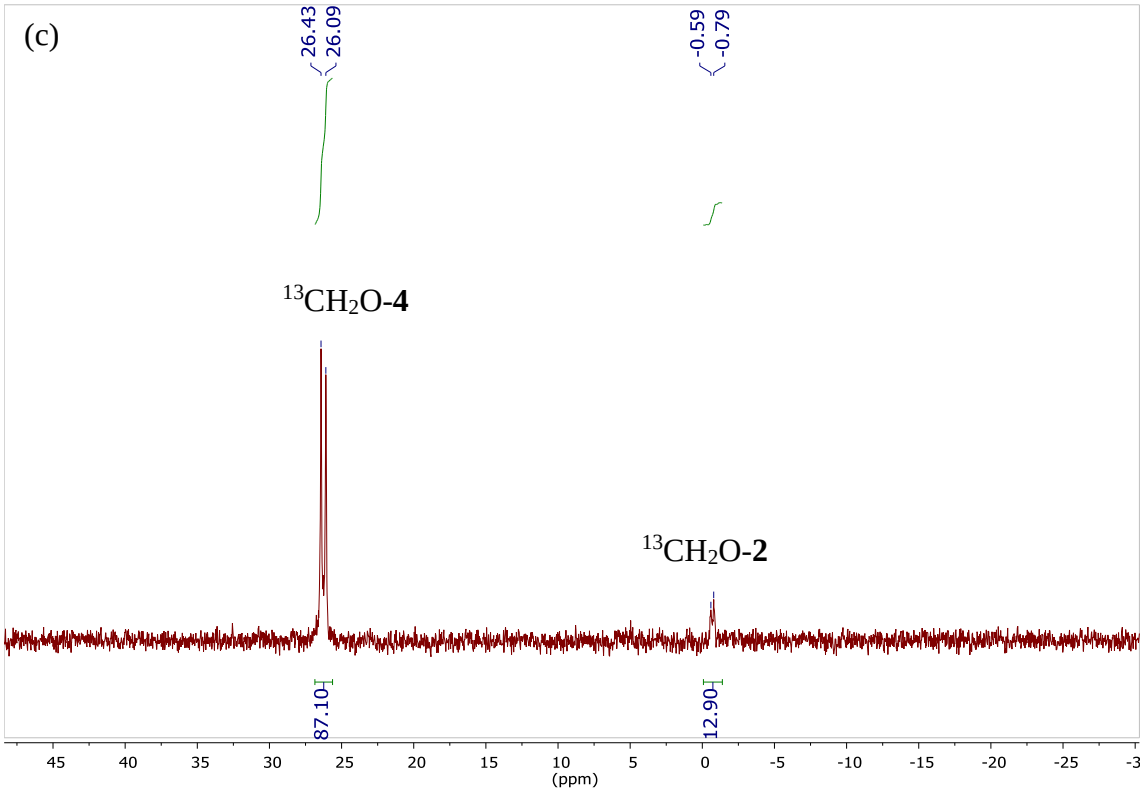

(d)
58.768
56.885
A
+
O(BBN)2
B
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
(ppm)

Figure S24. ^{1}H (a), $^{13}C\{^{1}H\}$ (b), $^{31}P\{^{1}H\}$ (c) and ^{11}B (d) NMR spectra for the catalytic reduction of $^{13}CO_2$ with H-BBN using compound **2** (2.5 mol%) as catalyst at 60 ºC in C_6D_6 after kinetic experiment (15 min, 60 ºC).




(c)
26.43
26.09
-0.59
-0.79
$^{13}CH_2O$-**4**
$^{13}CH_2O$-**2**
87.10
12.90
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -3
(ppm)

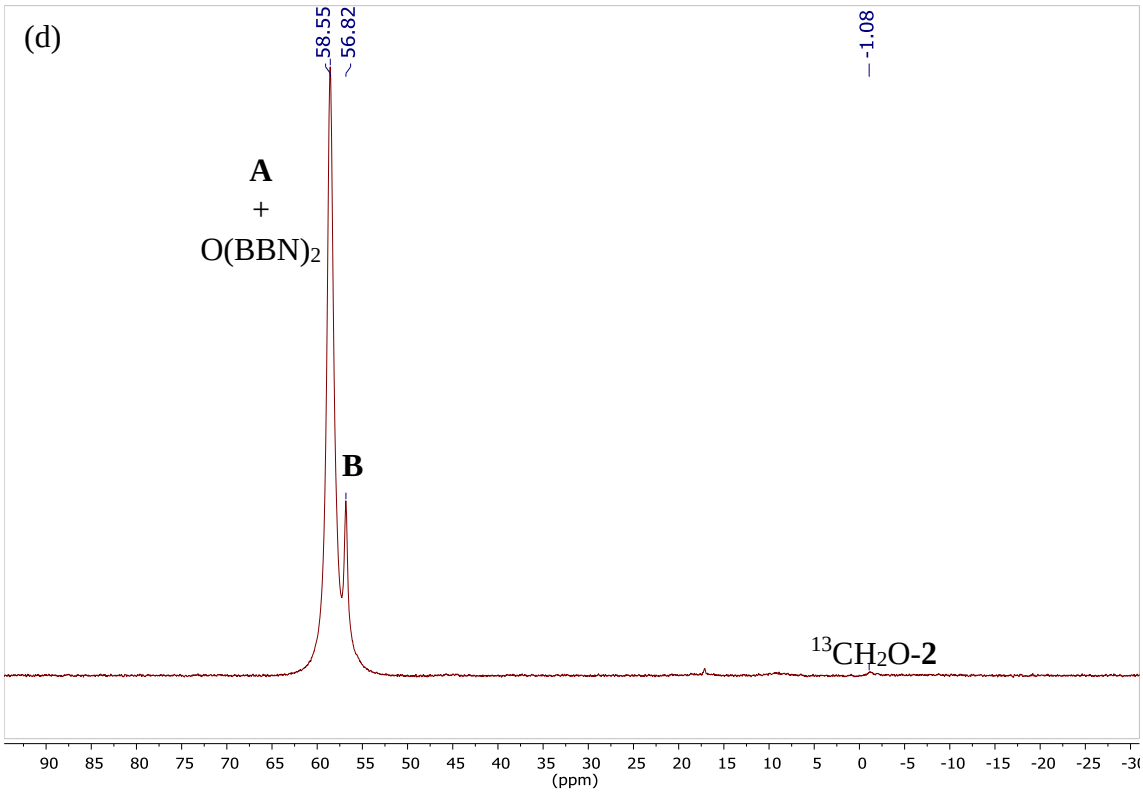
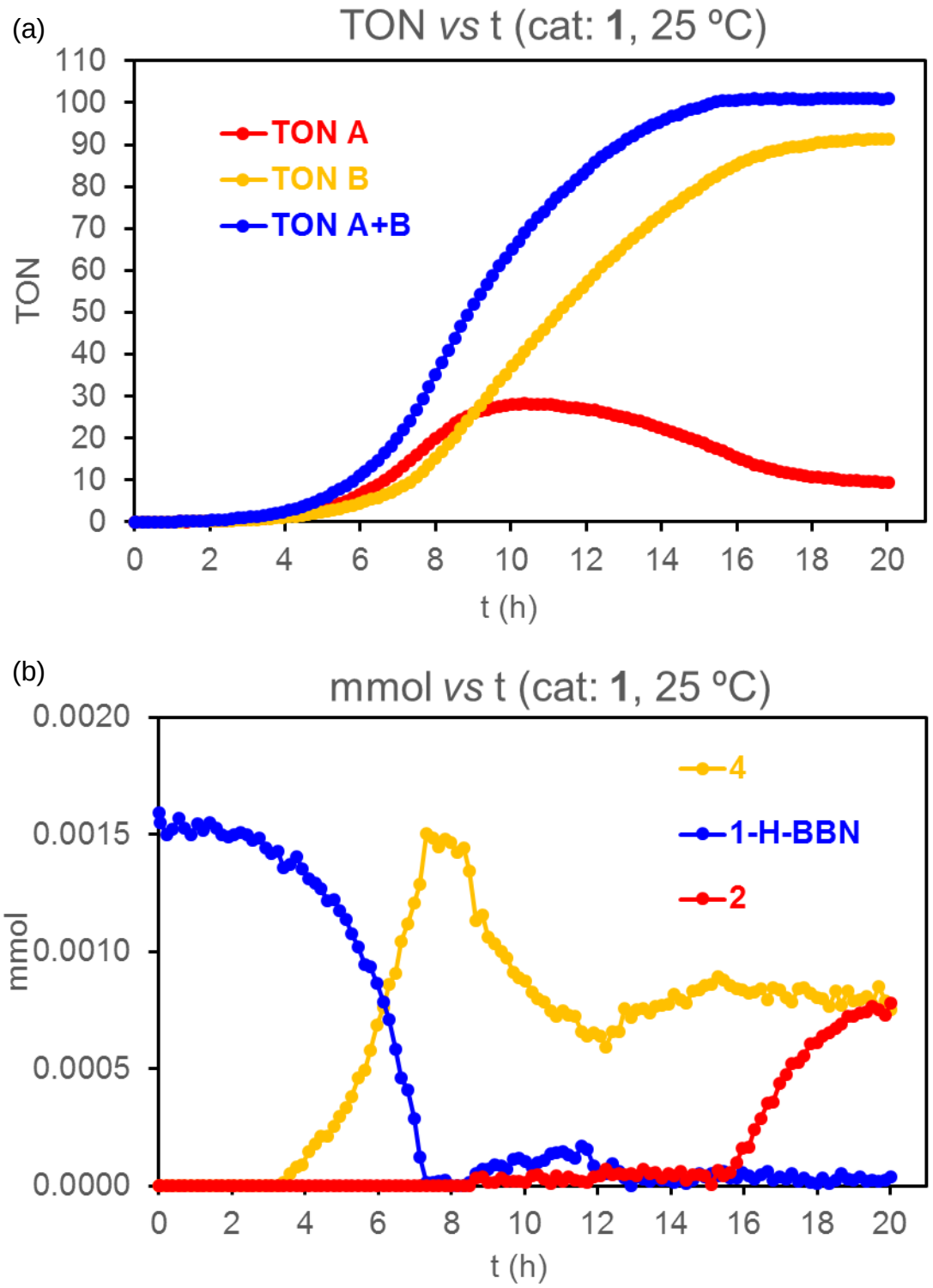
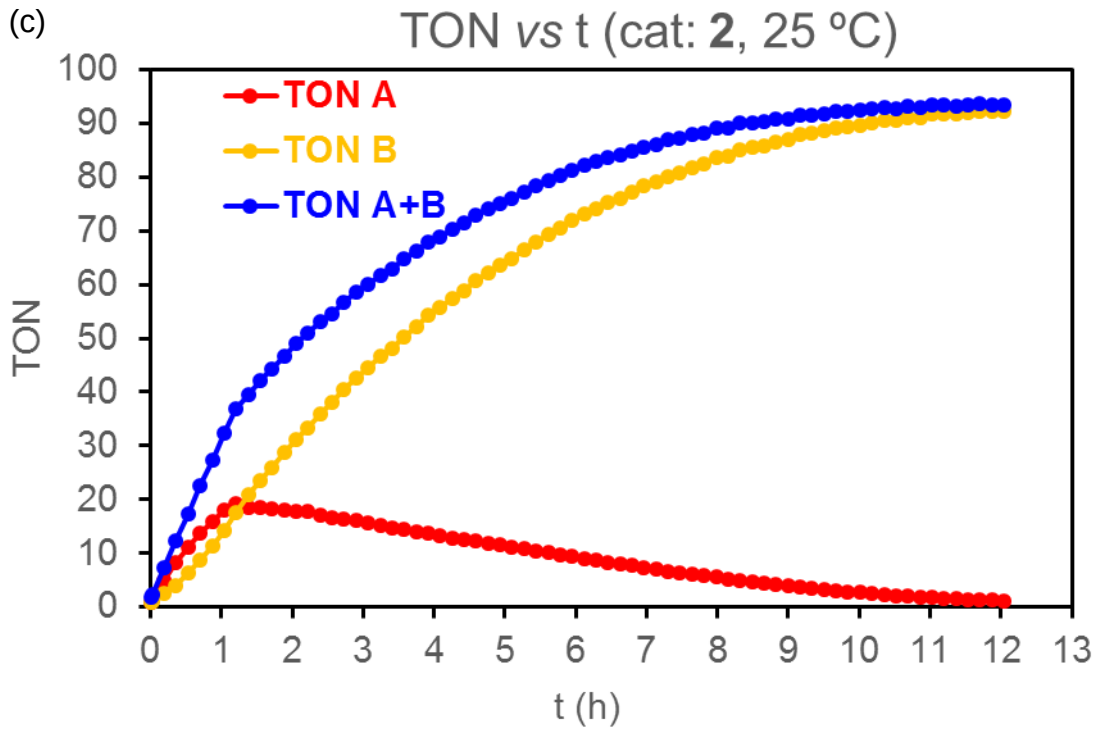

(d)
58.55
56.82
-1.08
A
+
$O(BBN)_2$
B
$^{13}CH_2O$-**2**
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -3
(ppm)

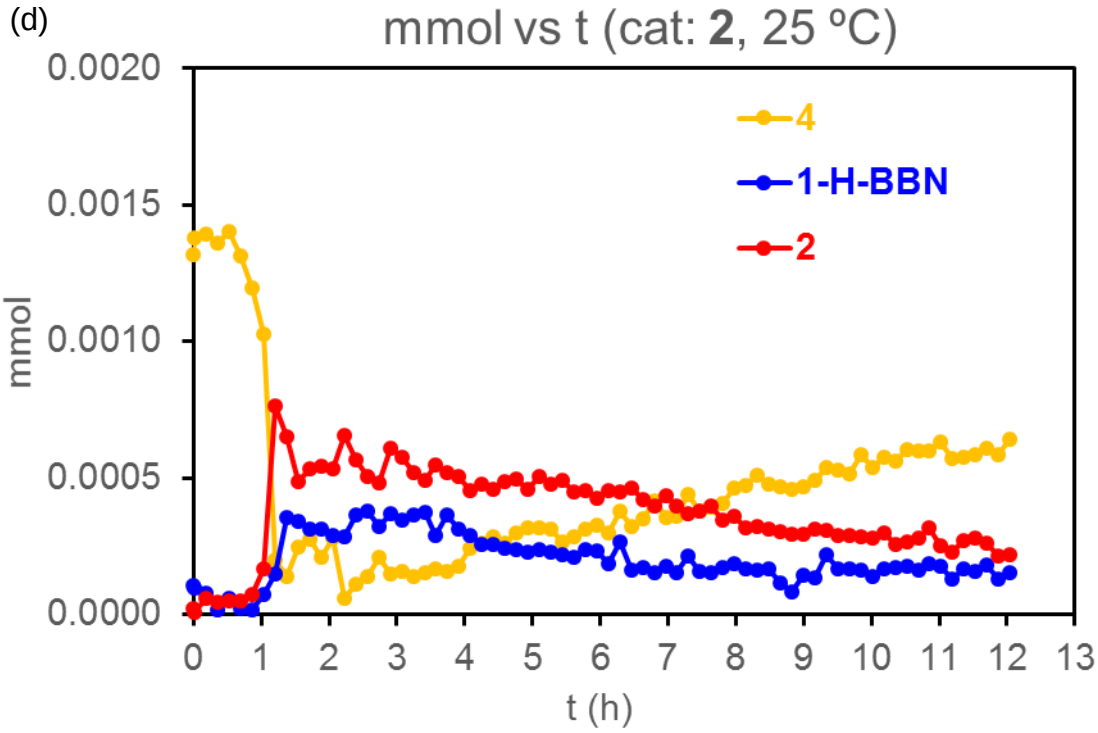
Figure S25. (a, c, e) TON for the formation of $CH_2(OBBN)_2$ (**A**, ●), CH_3OBBN (**B**, ●) and total TON (**A+B**, ●) *vs*. time (h) and (b, d, f) distribution of active species, **1-H-BBN** (●), **2** (●) and **4** (●) *vs*. time (h) for the catalytic reduction of CO_2 with H-BBN. [Reaction conditions: 1 atm CO_2, 0.6 mL C_6D_6, 0.20 mmol HBBN, 1 mol% cat, 25 ºC.]



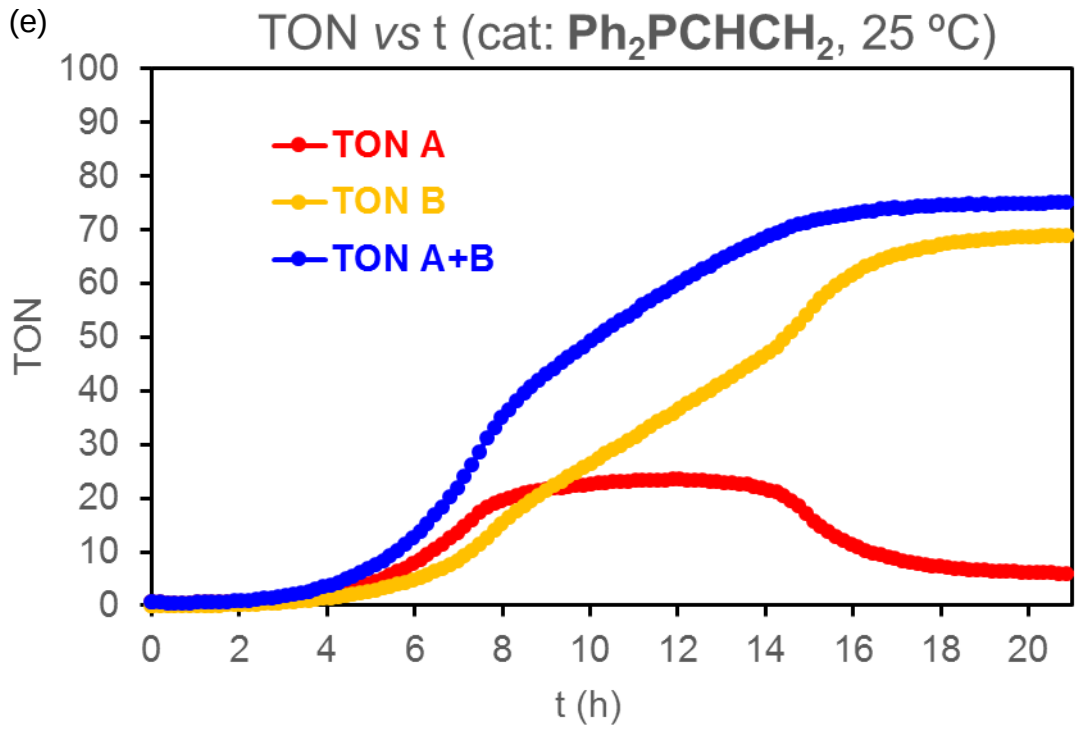
(c)


TON vs t (cat: 2, 25 ºC)
TON A
TON B
TON A+B
TON
t (h)

(d)


mmol vs t (cat: 2, 25 ºC)
4
1-H-BBN
2
mmol
t (h)

(e)


TON vs t (cat: Ph2PCHCH2, 25 ºC)
TON A
TON B
TON A+B
TON
t (h)
0
10
20
30
40
50
60
70
80
90
100
0
2
4
6
8
10
12
14
16
18
20

(f)

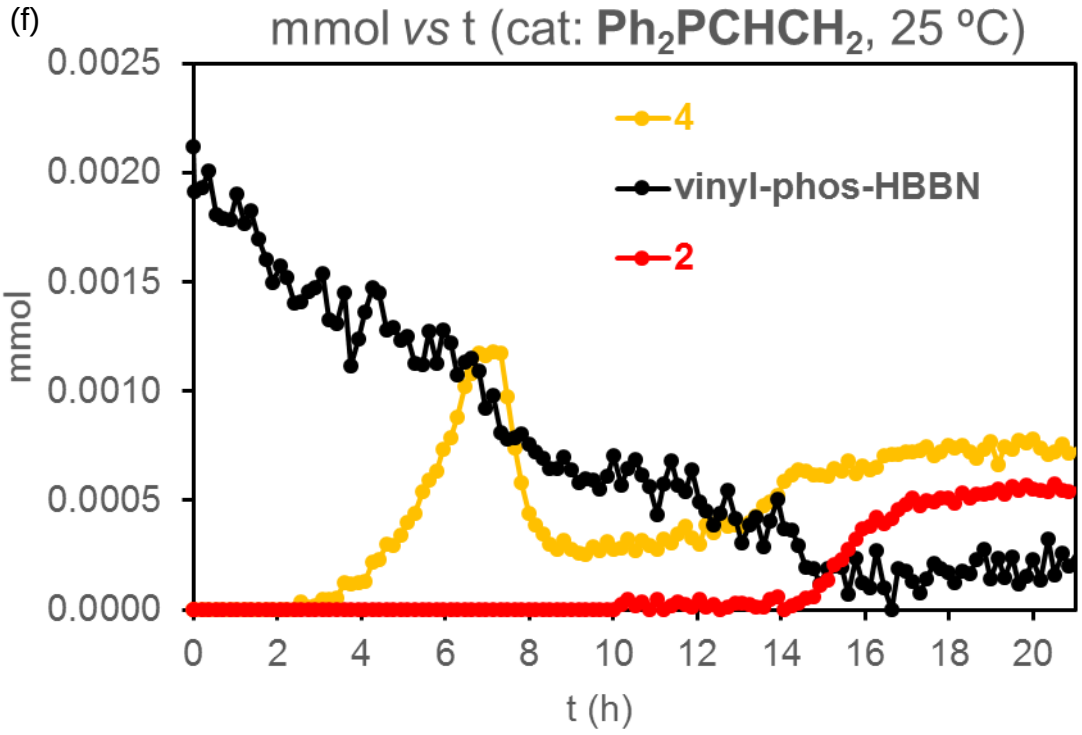
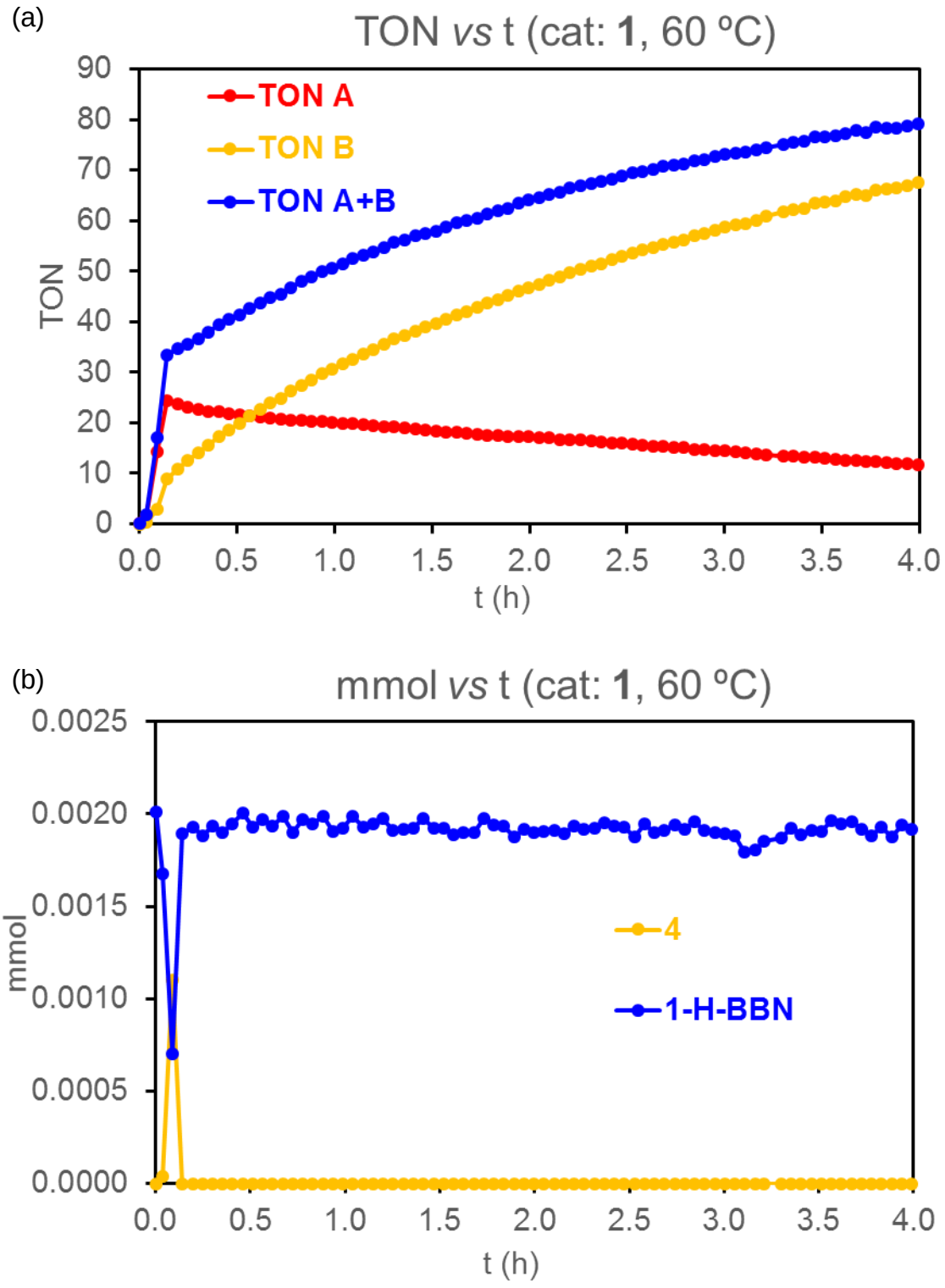
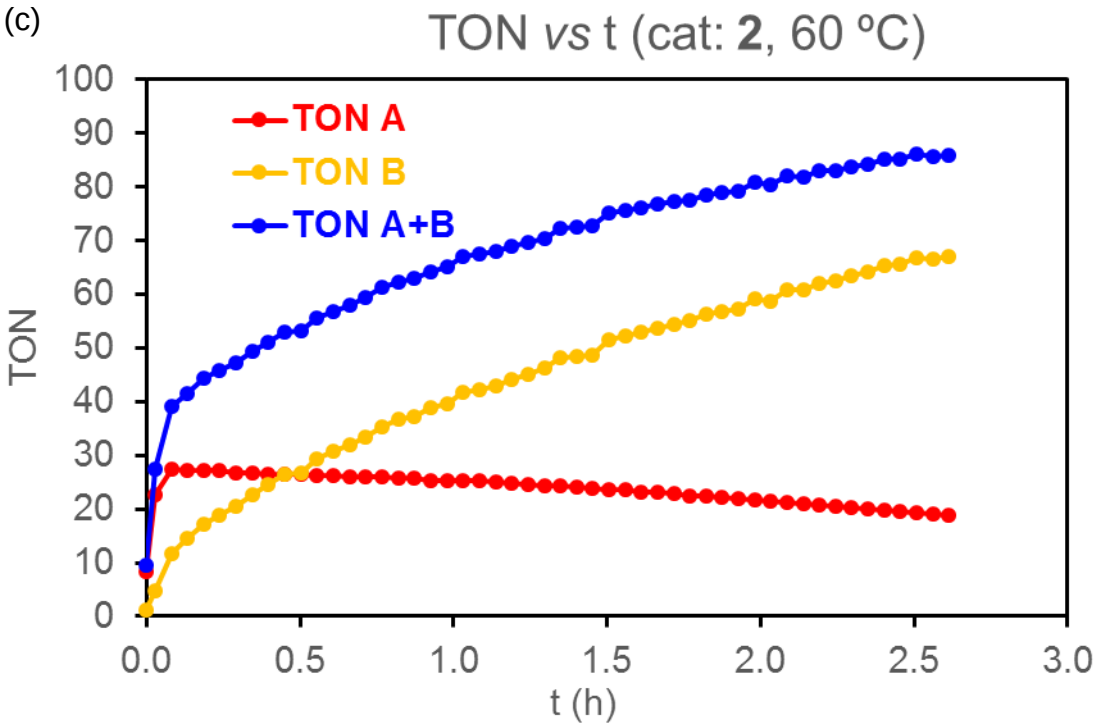

mmol vs t (cat: Ph2PCHCH2, 25 ºC)
4
vinyl-phos-HBBN
2
mmol
t (h)
0.0000
0.0005
0.0010
0.0015
0.0020
0.0025
0
2
4
6
8
10
12
14
16
18
20

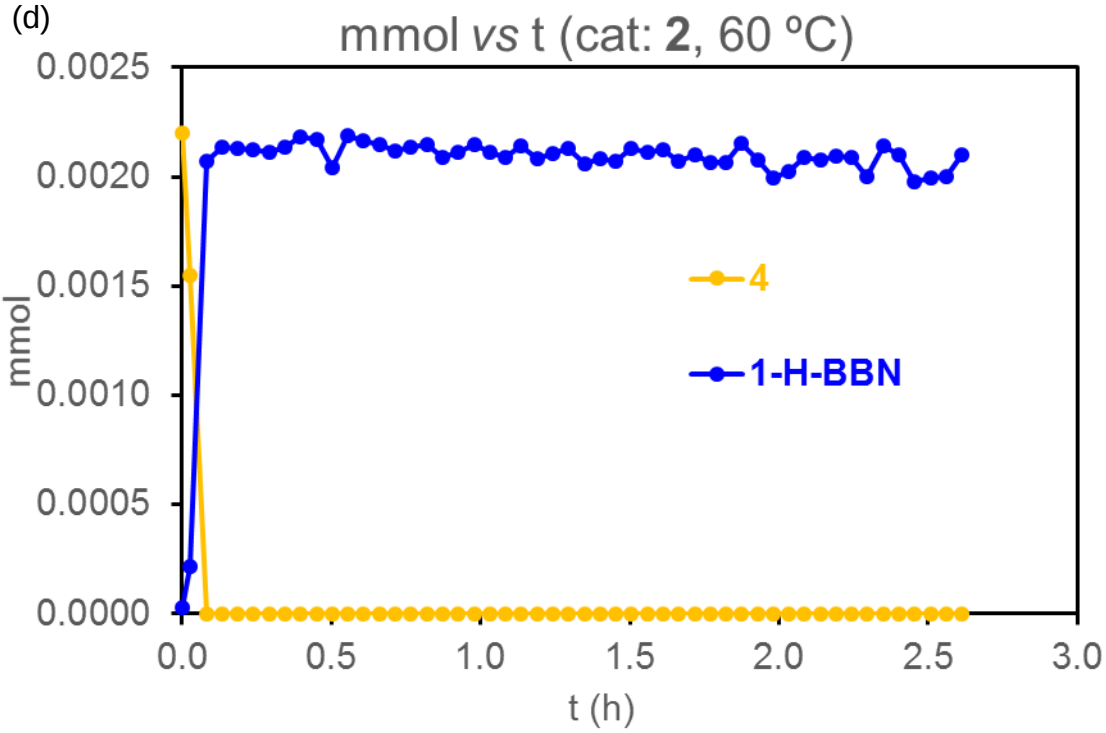
Figure S26. (a, c, e) TON for the formation of $CH_2(OBBN)_2$ (**A**, ●), CH_3OBBN (**B**, ●) and total TON (**A+B**, ●) *vs*. time (h) and (b, d, f) distribution of active species, **1-H-BBN** (●), **2** (●) and **4** (●) *vs*. time (h), for the catalytic reduction of CO_2 with H-BBN. [Reaction conditions: 1 atm CO_2, 0.6 mL C_6D_6, 0.20 mmol HBBN, 1 mol% cat, 60 ºC.]



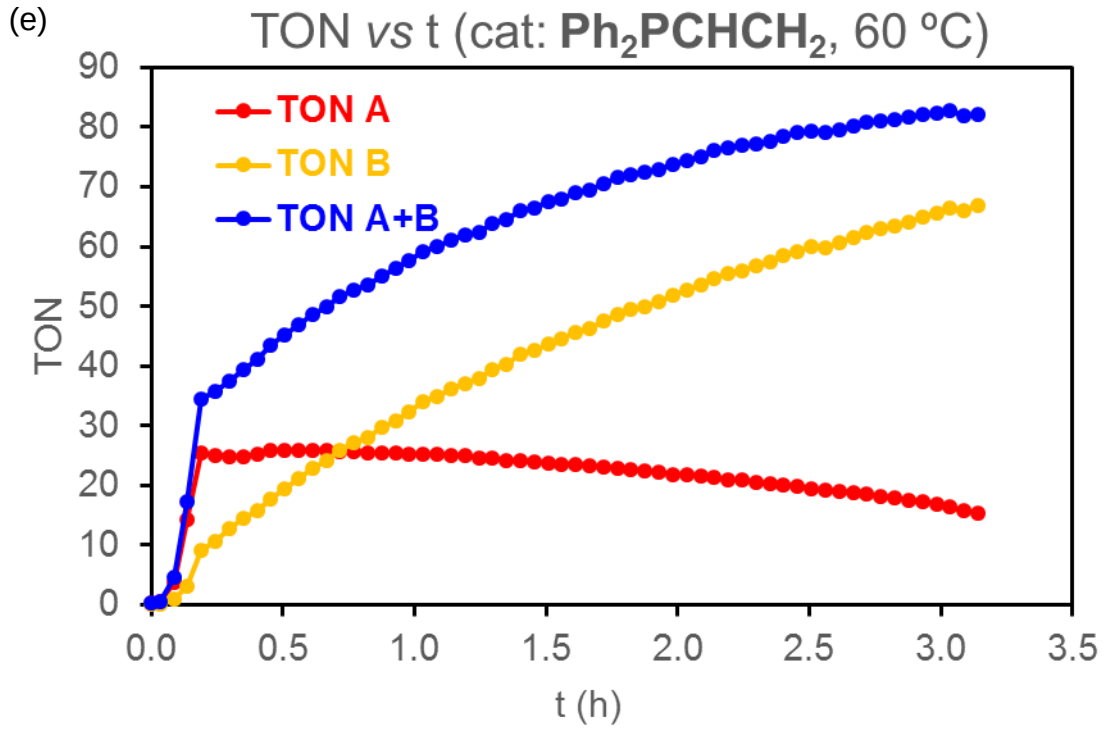
(c)


TON vs t (cat: 2, 60 ºC)
TON A
TON B
TON A+B
TON
t (h)
0
10
20
30
40
50
60
70
80
90
100
0.0
0.5
1.0
1.5
2.0
2.5
3.0

(d)


mmol vs t (cat: 2, 60 ºC)
4
1-H-BBN
mmol
t (h)
0.0000
0.0005
0.0010
0.0015
0.0020
0.0025
0.0
0.5
1.0
1.5
2.0
2.5
3.0

(e)


TON vs t (cat: Ph2PCHCH2, 60 ºC)
TON A
TON B
TON A+B
TON
t (h)
0
10
20
30
40
50
60
70
80
90
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5

(f)

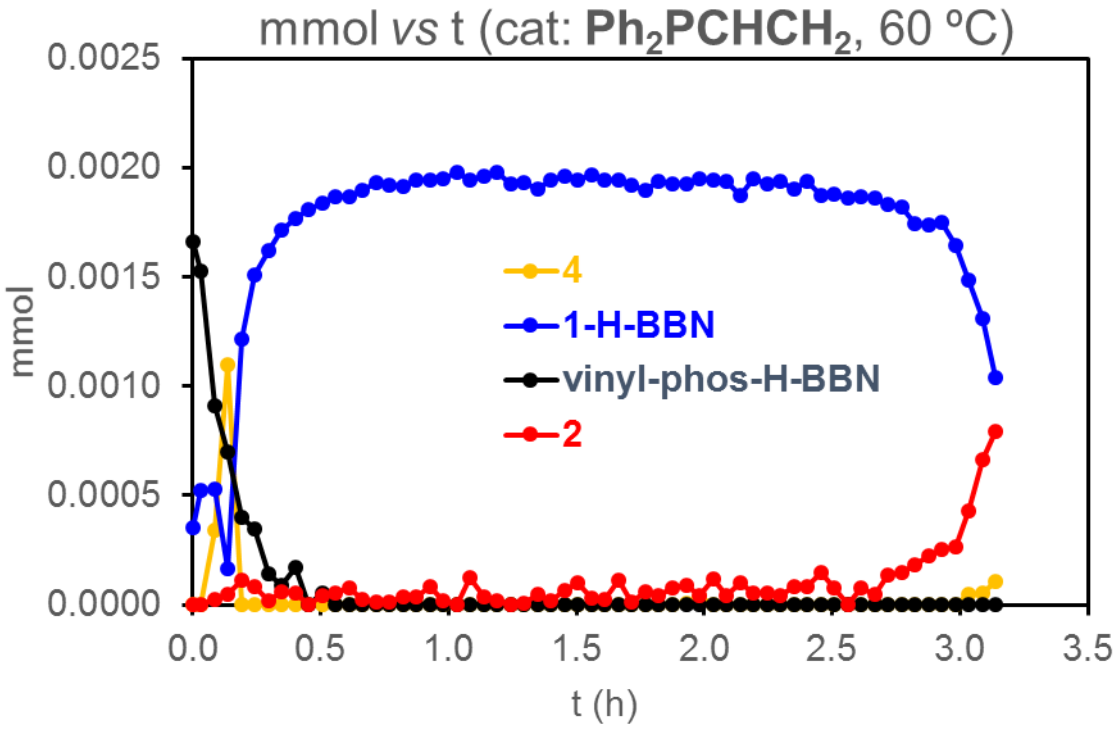
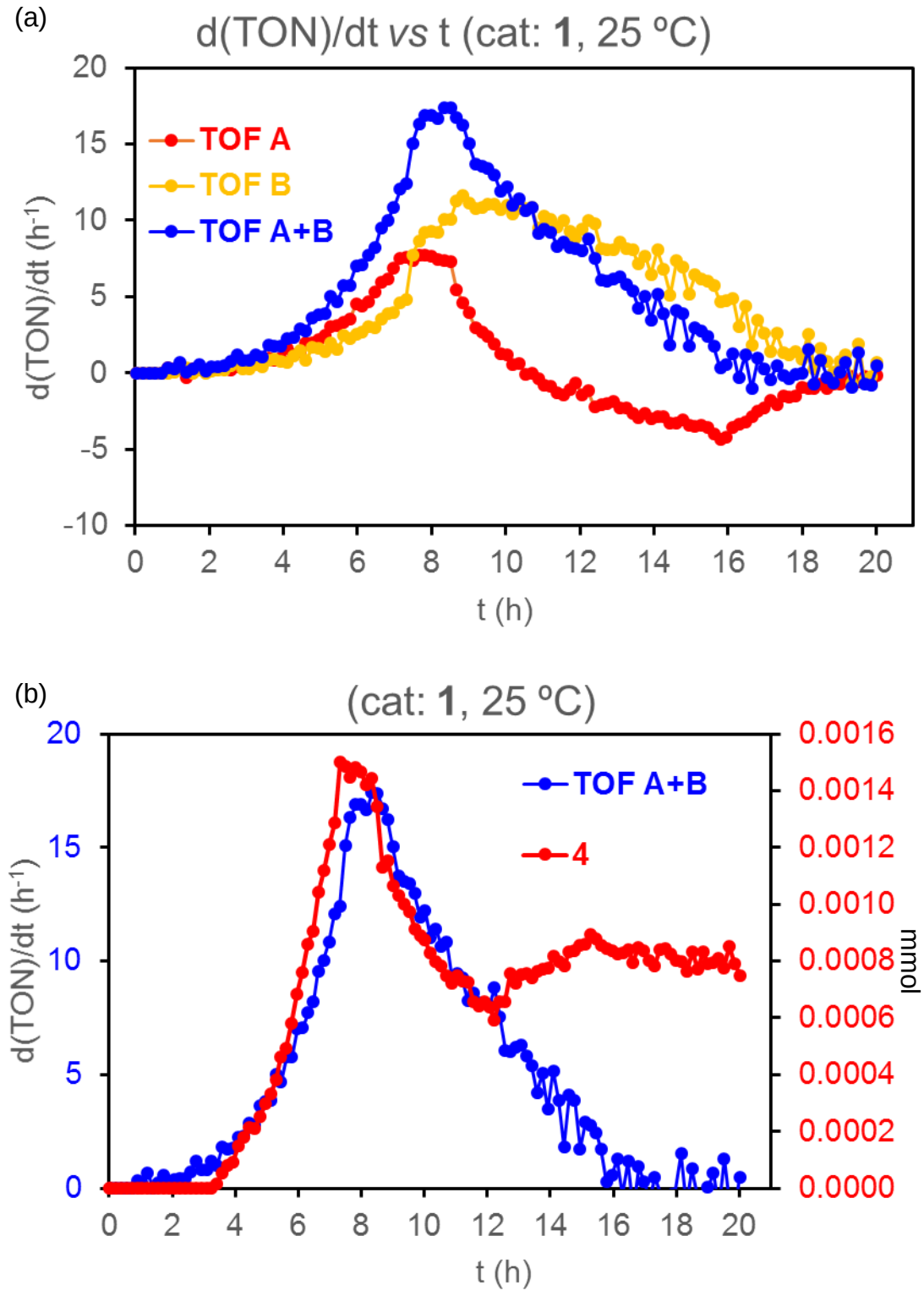
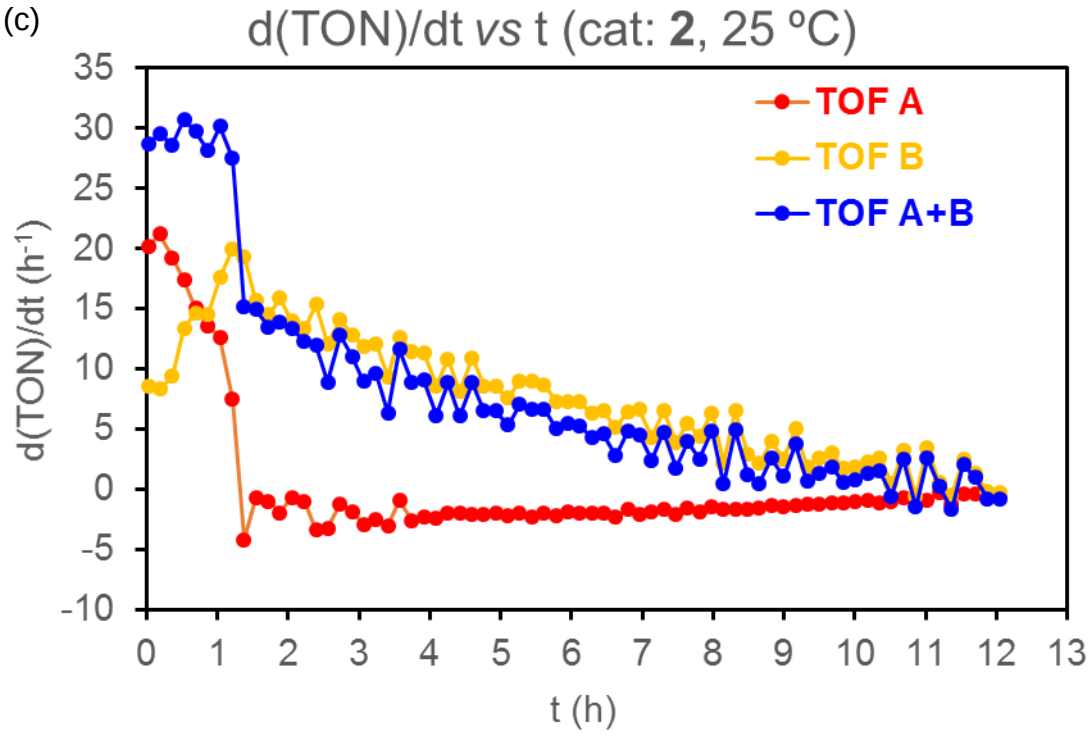

mmol vs t (cat: Ph2PCHCH2, 60 ºC)
4
1-H-BBN
vinyl-phos-H-BBN
2
mmol
t (h)
0.0000
0.0005
0.0010
0.0015
0.0020
0.0025
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5

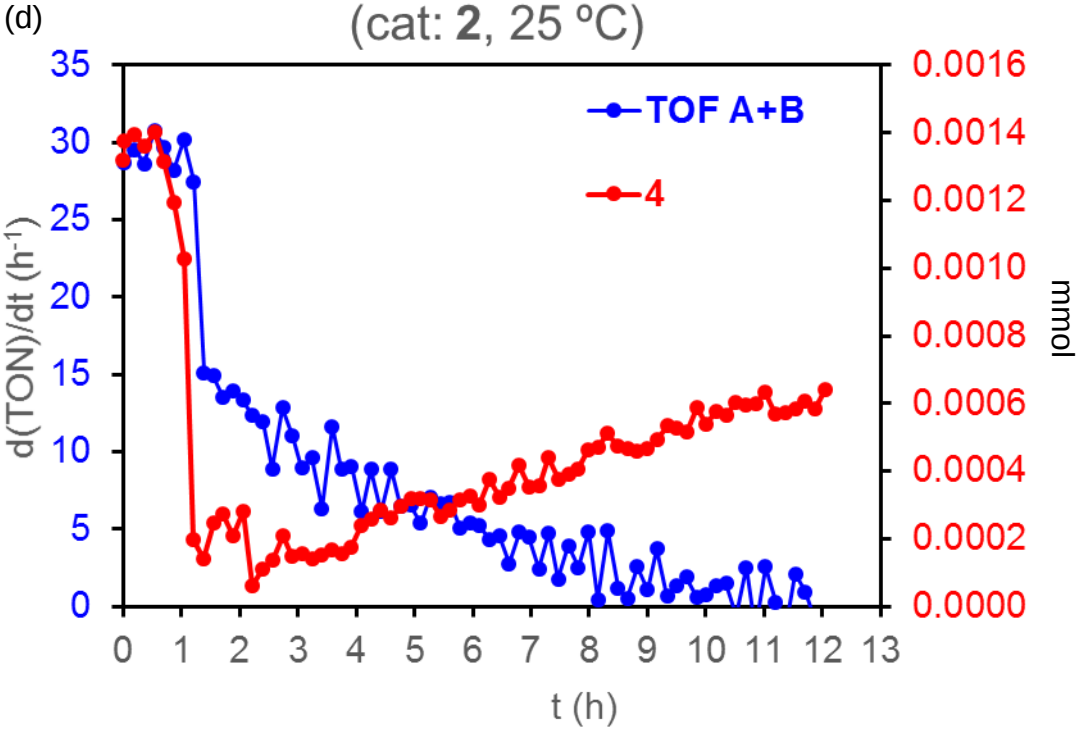
Figure S27. (a, c, e) d(TON **A**)/dt (h^{-1}, ●), d(TON **B**)/dt (h^{-1}, ●) and d(TON **A+B**)/dt (h^{-1}, ●) *vs*. time (h), and (b, d, f). plots comparing d(TON **A+B**)/dt (h^{-1}, ●) and mmol of **4** (●) *vs* time (h) for the catalytic reduction of CO_2 with H-BBN [Reaction conditions: 1 atm CO_2, 0.6 mL C_6D_6, 0.20 mmol HBBN, 1 mol%, 25 ºC]



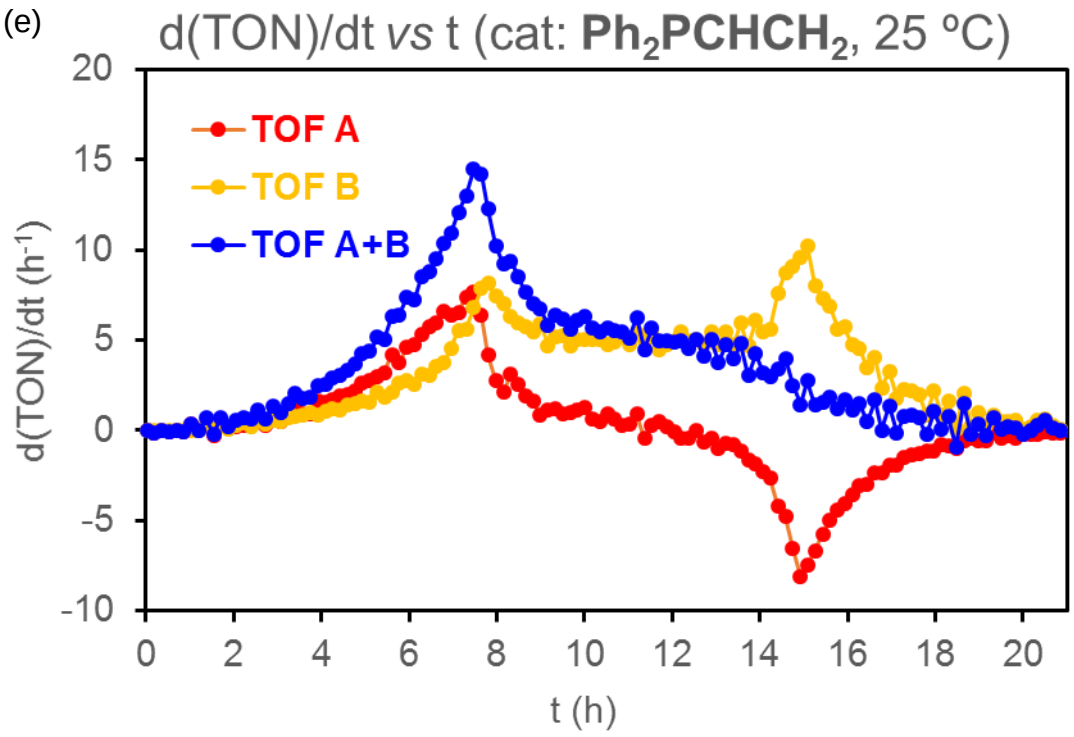
(c)


d(TON)/dt vs t (cat: 2, 25 ºC)
TOF A
TOF B
TOF A+B
d(TON)/dt (h-1)
t (h)

(d)


(cat: 2, 25 ºC)
TOF A+B
4
d(TON)/dt (h-1)
mmol
t (h)

(e)


d(TON)/dt vs t (cat: Ph2PCHCH2, 25 ºC)
TOF A
TOF B
TOF A+B
d(TON)/dt (h-1)
t (h)

(f)

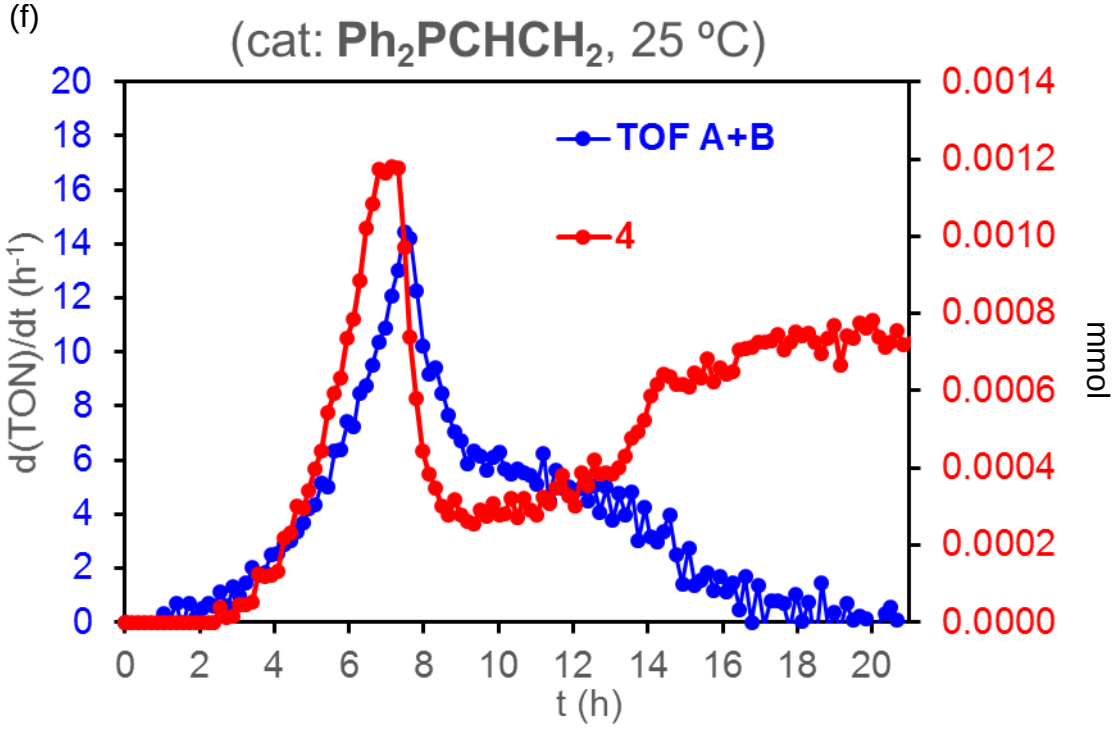
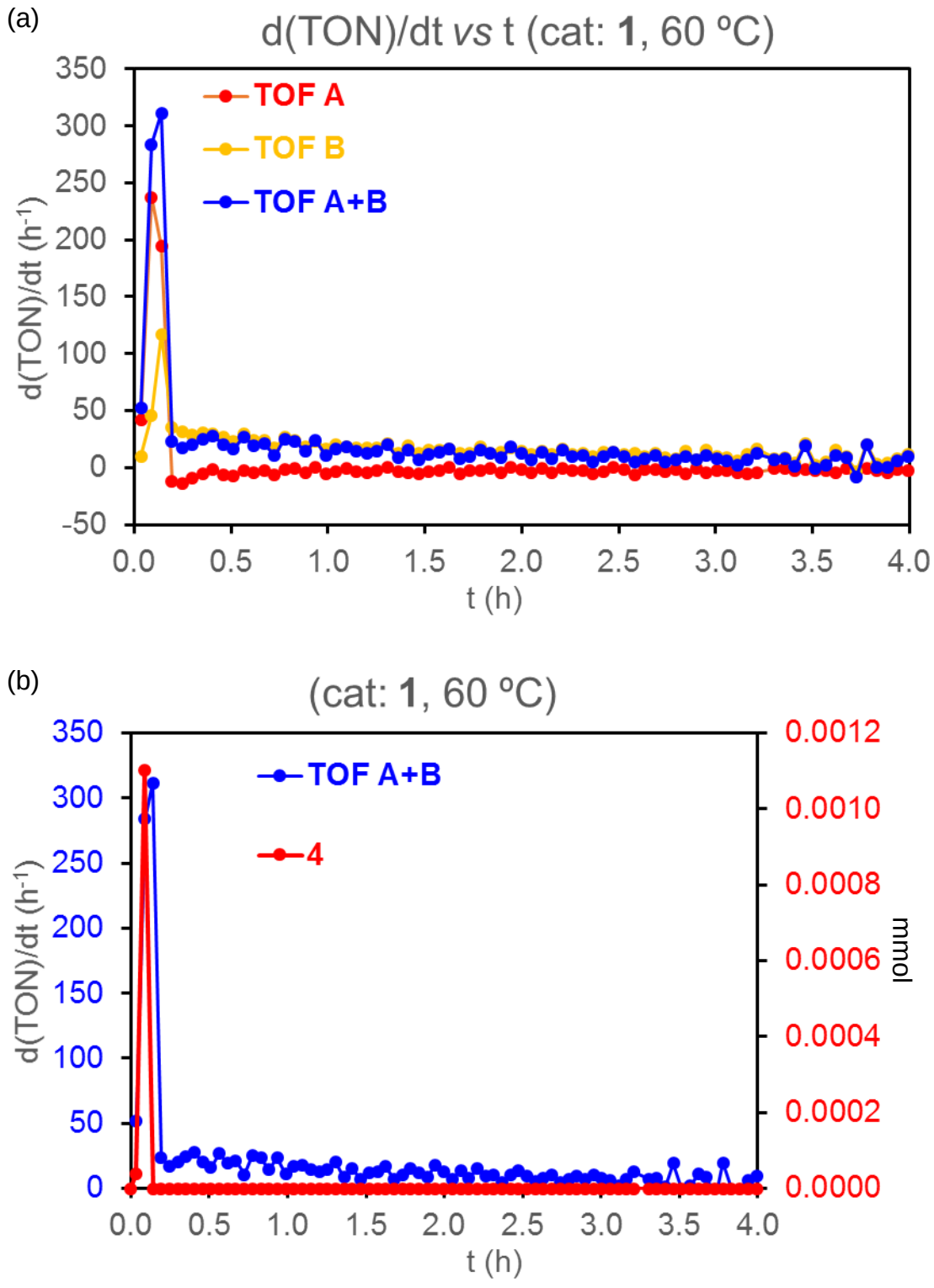
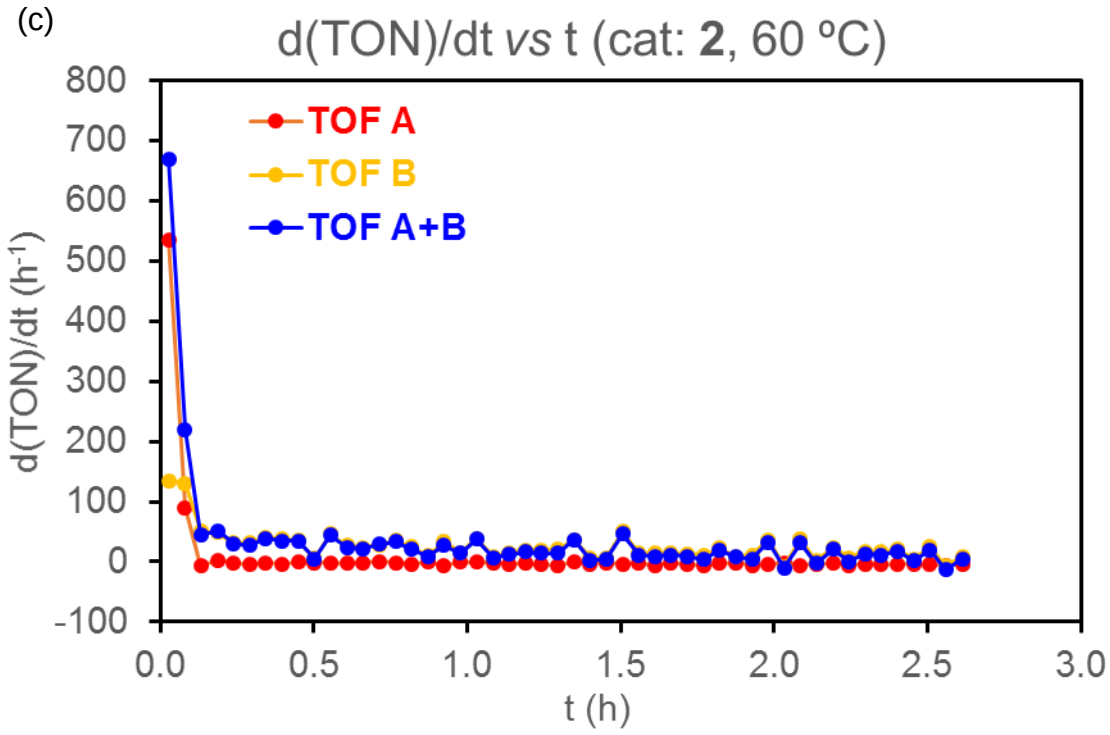

(cat: Ph2PCHCH2, 25 ºC)
TOF A+B
4
d(TON)/dt (h-1)
mmol
t (h)

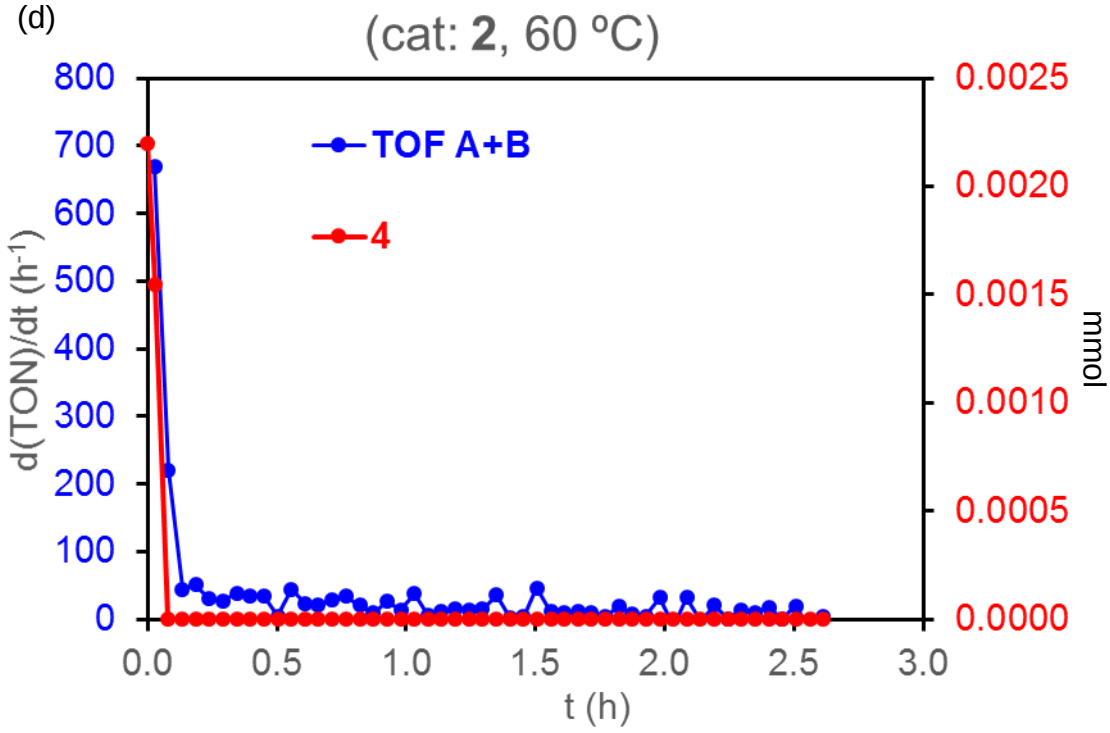
Figure S28. (a, c, e) d(TON **A**)/dt (h^{-1}, ●), d(TON **B**)/dt (h^{-1}, ●) and d(TON **A+B**)/dt (h^{-1}, ●), *vs*. time (h), and (b, d, f). plots comparing d(TON **A+B**)/dt (h^{-1}, ●) and mmol of **4** (●) *vs* time (h) for the catalytic reduction of CO_2 with H-BBN [Reaction conditions: 1 atm CO_2, 0.6 mL C_6D_6, 0.20 mmol HBBN, 1 mol%, 60 ºC]



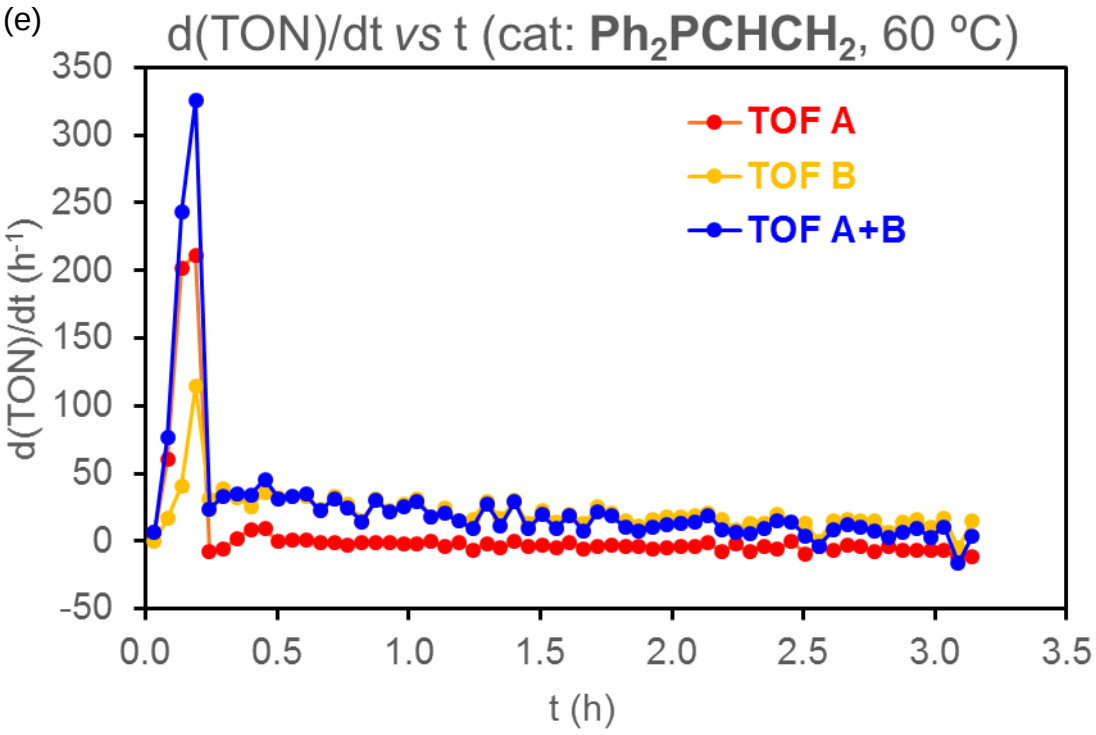
(c)


d(TON)/dt vs t (cat: 2, 60 ºC)
TOF A
TOF B
TOF A+B
d(TON)/dt (h-1)
800
700
600
500
400
300
200
100
0
-100
0.0
0.5
1.0
1.5
2.0
2.5
3.0
t (h)

(d)


(cat: 2, 60 ºC)
TOF A+B
4
d(TON)/dt (h-1)
800
700
600
500
400
300
200
100
0
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
mmol
0.0
0.5
1.0
1.5
2.0
2.5
3.0
t (h)

(e)


d(TON)/dt vs t (cat: Ph2PCHCH2, 60 ºC)
TOF A
TOF B
TOF A+B
d(TON)/dt (h-1)
t (h)

(f)

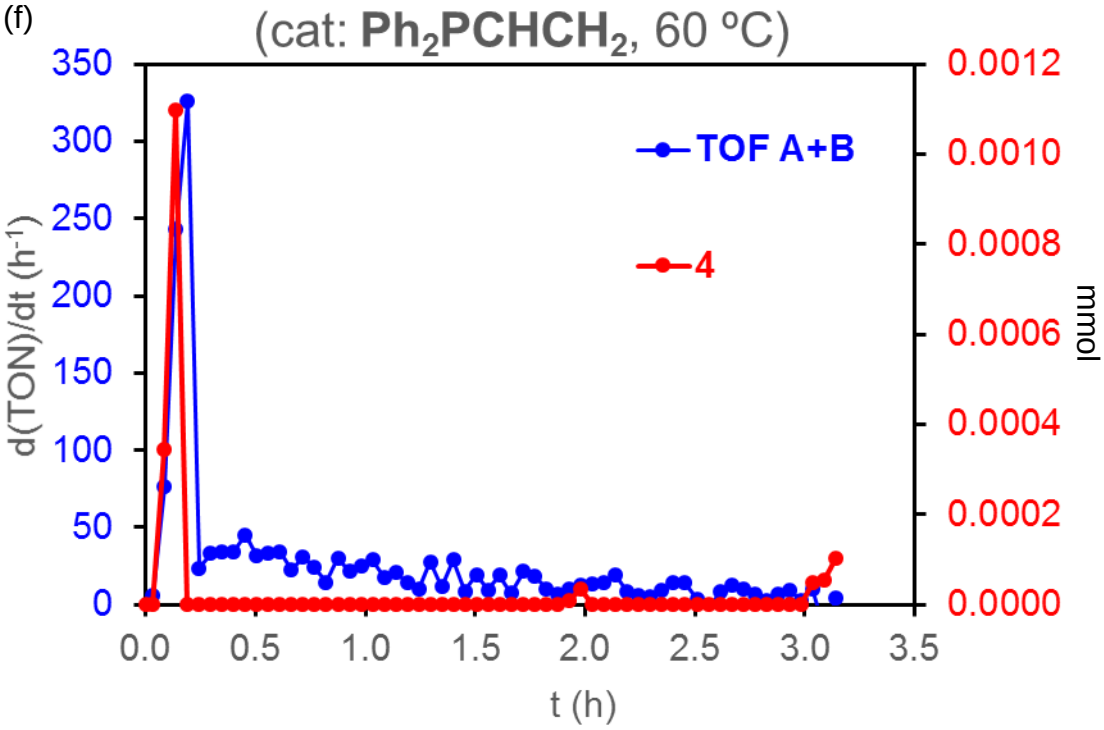
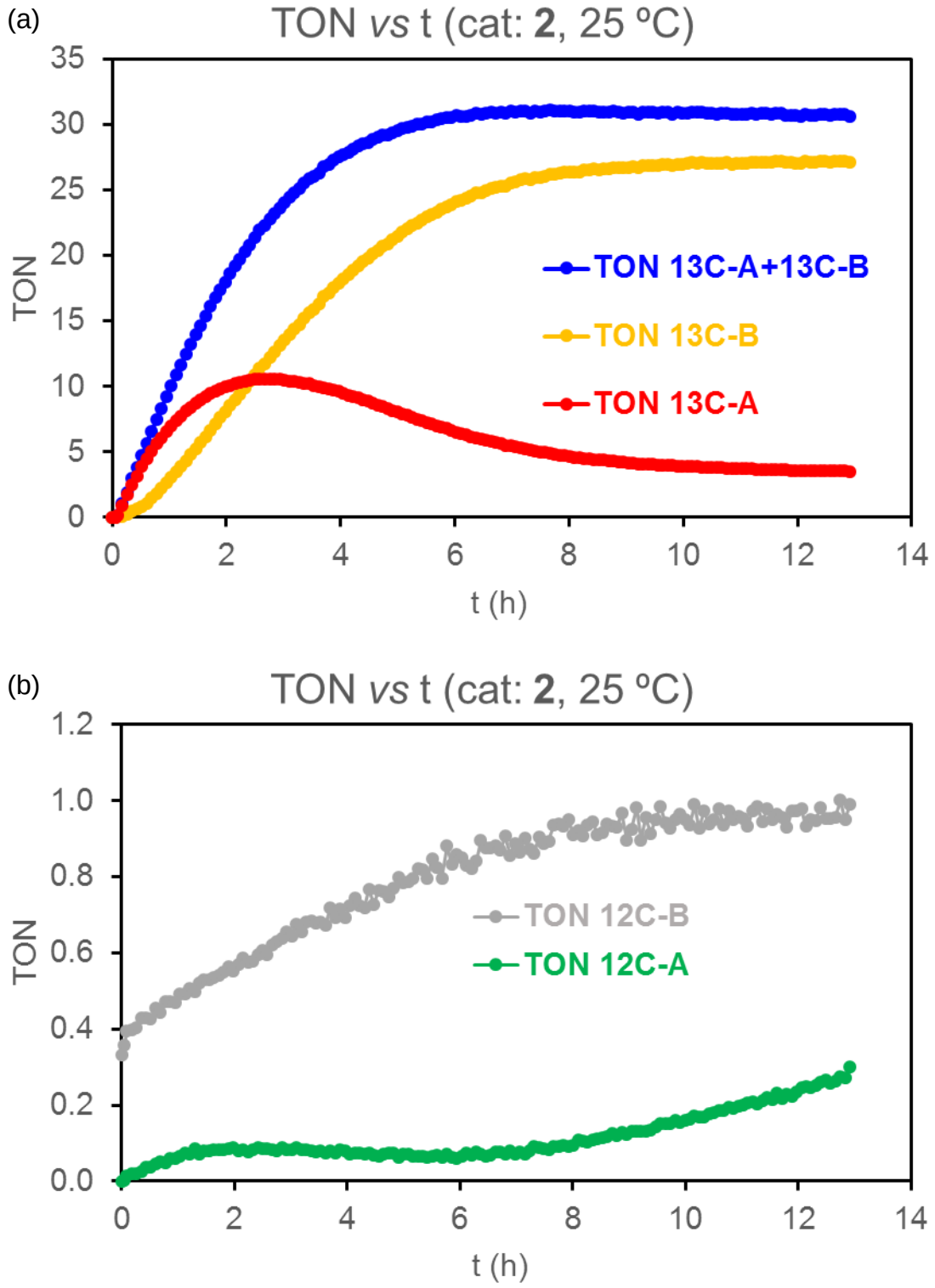

(cat: Ph2PCHCH2, 60 ºC)
TOF A+B
4
d(TON)/dt (h-1)
mmol
t (h)

Figure S29. (a) TON (**^{13}C-A+^{13}C-B**, ●), and TON for the formation of **^{13}C-A** (●) and **^{13}C-B** (●) *vs*. time (h); (b) TON for the formation of **^{12}C-A** (●) and **^{12}C-B** (●) *vs*. time (h), and (c) distribution of active species, **^{12}C-4+^{13}C-4** (●),**^{12}C-4** (●), **^{13}C-4** (●) and **2** (●) *vs*. time for the catalytic reduction of CO_2 with H-BBN. [Reaction conditions: 1 atm $^{13}CO_2$, 0.6 mL C_6D_6, 0.20 mmol HBBN, 2.5 mol% cat, 25 ºC.]



(c)

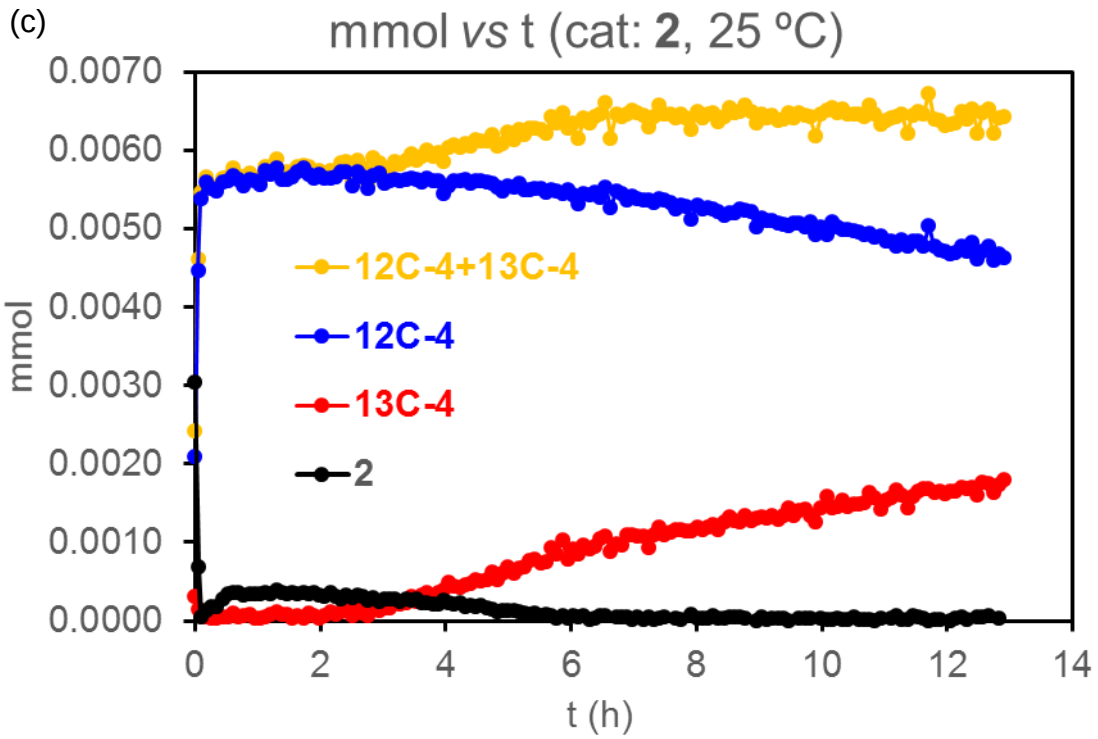
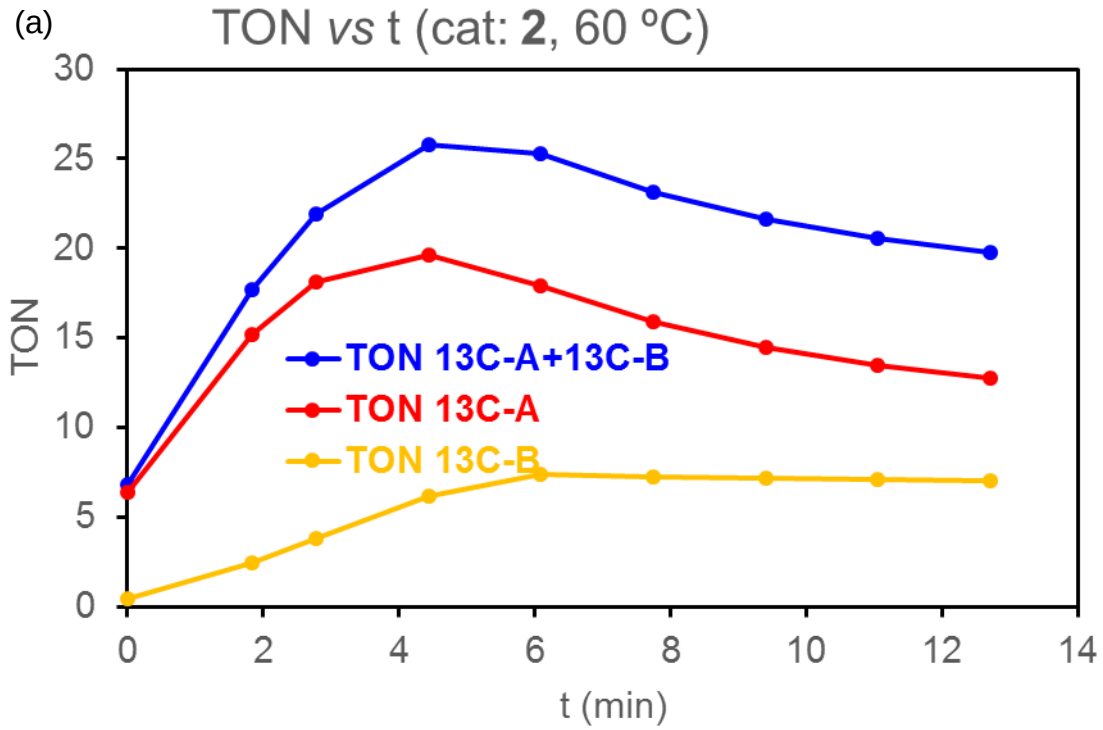
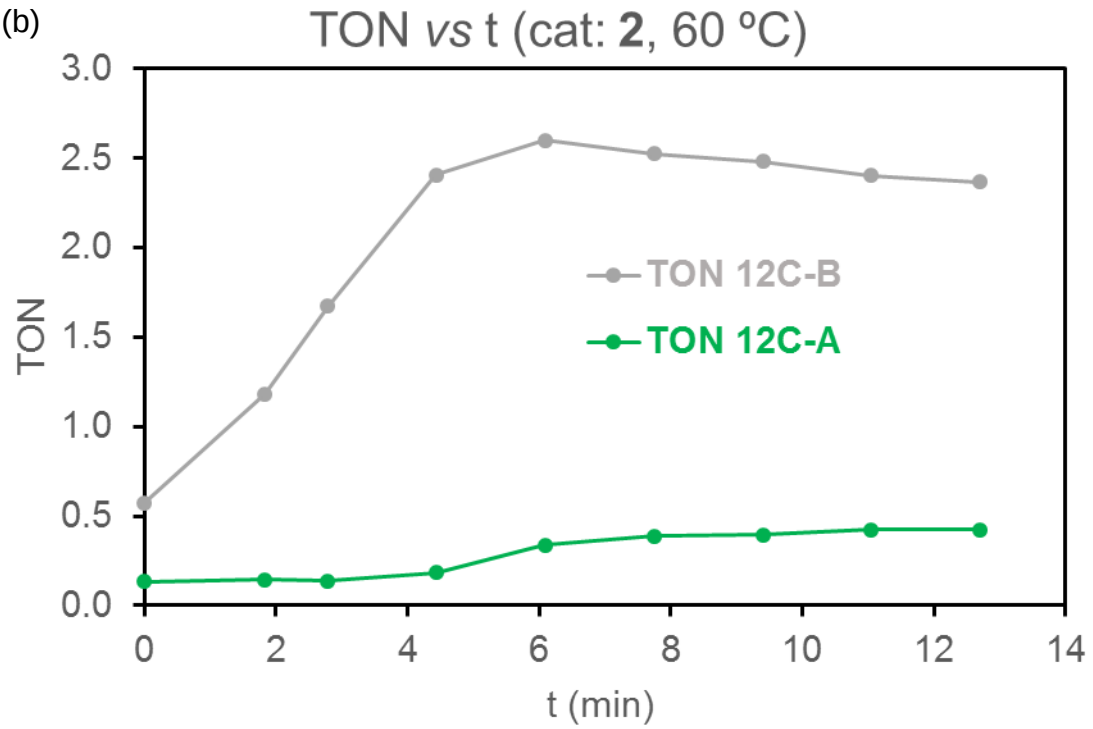

mmol vs t (cat: 2, 25 ºC)
mmol
0.0070
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0.0000
0
2
4
6
8
10
12
14
t (h)
12C-4+13C-4
12C-4
13C-4
2

Figure S30. (a) TON (**^{13}C-A+^{13}C-B**, ●), and TON for the formation of **^{13}C-A** (●) and **^{13}C-B** (●) *vs*. time (min); (b) TON for the formation of **^{12}C-A** (●) and **^{12}C-B** (●) *vs*. time (min), and (c) distribution of active species, **^{12}C-4+^{13}C-4** (●),**^{12}C-4** (●) and **^{13}C-4** (●) *vs*. time (b, d, f) for the catalytic reduction of CO_2 with H-BBN. [Reaction conditions: 1 atm $^{13}CO_2$, 0.6 mL C_6D_6, 0.20 mmol HBBN, 2.5 mol% cat, 60 ºC.]



(b)


TON vs t (cat: 2, 60 ºC)
TON
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
2
4
6
8
10
12
14
t (min)
TON 12C-B
TON 12C-A

(c)

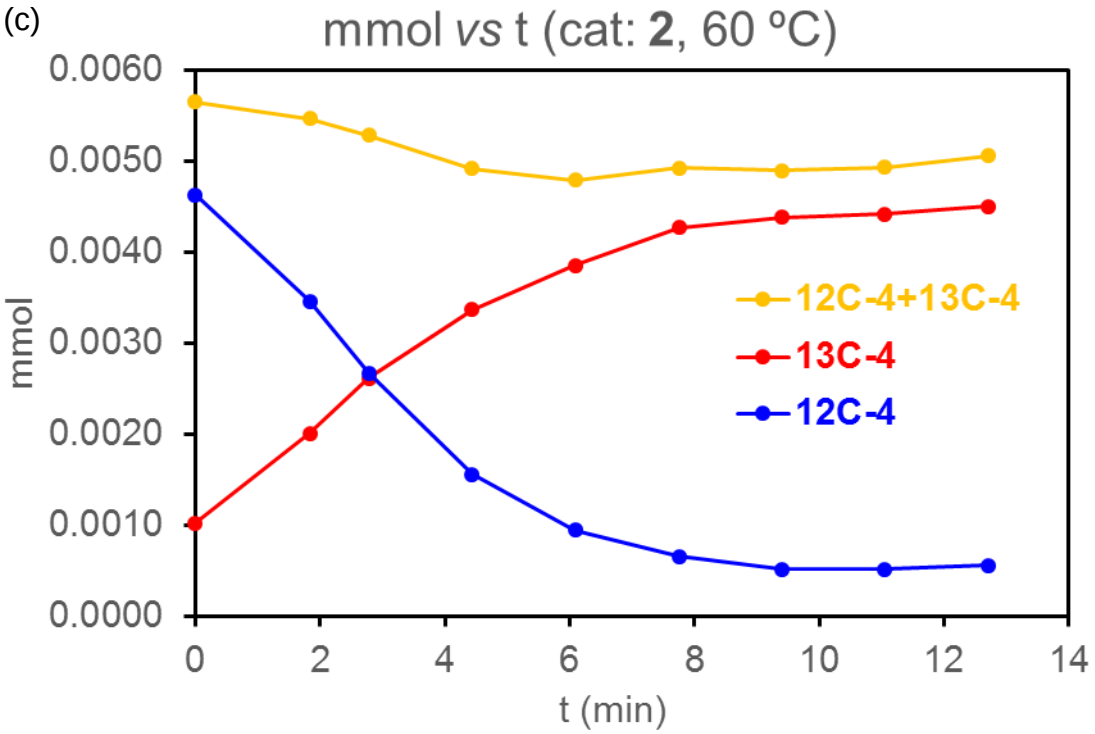
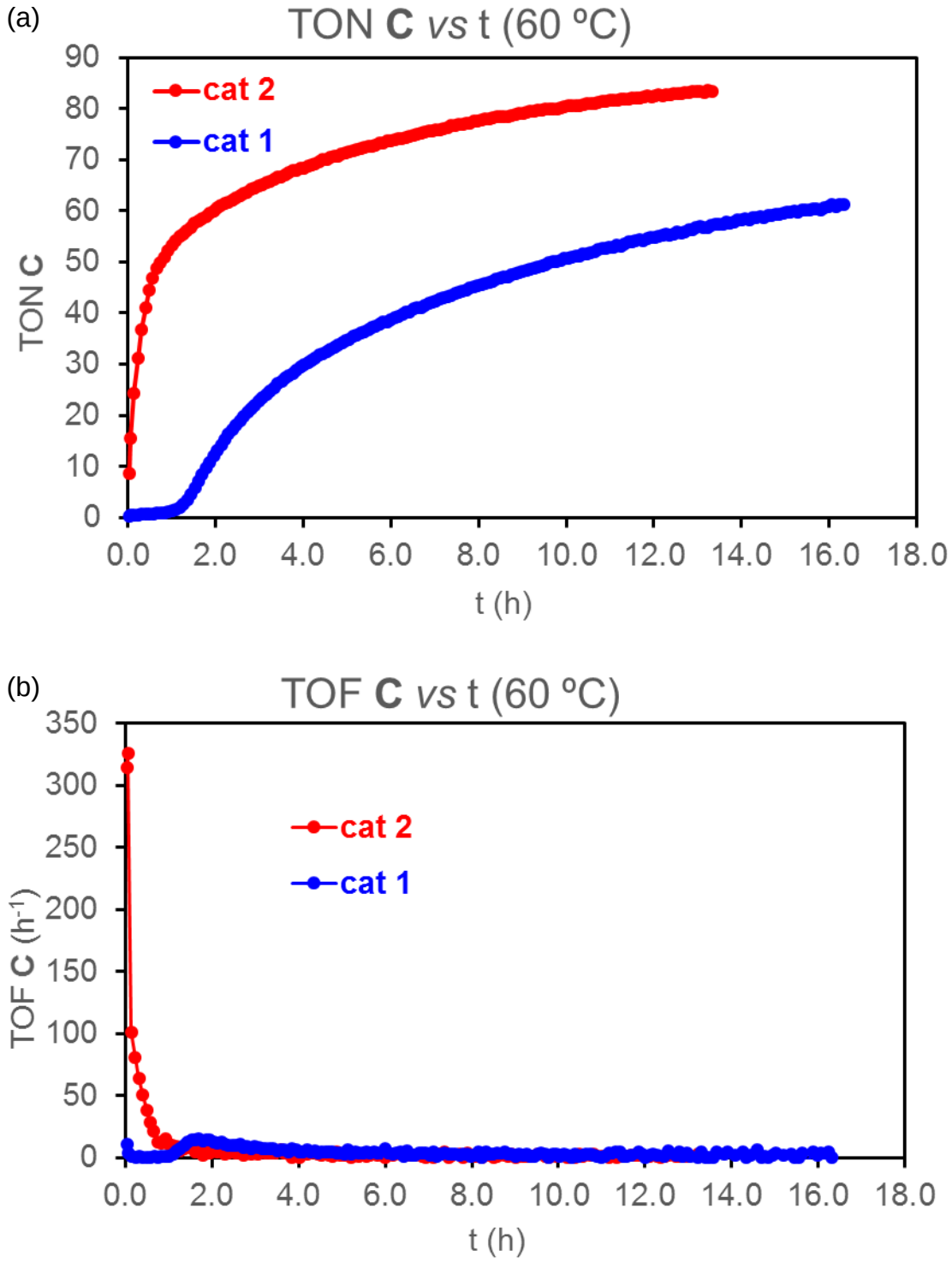
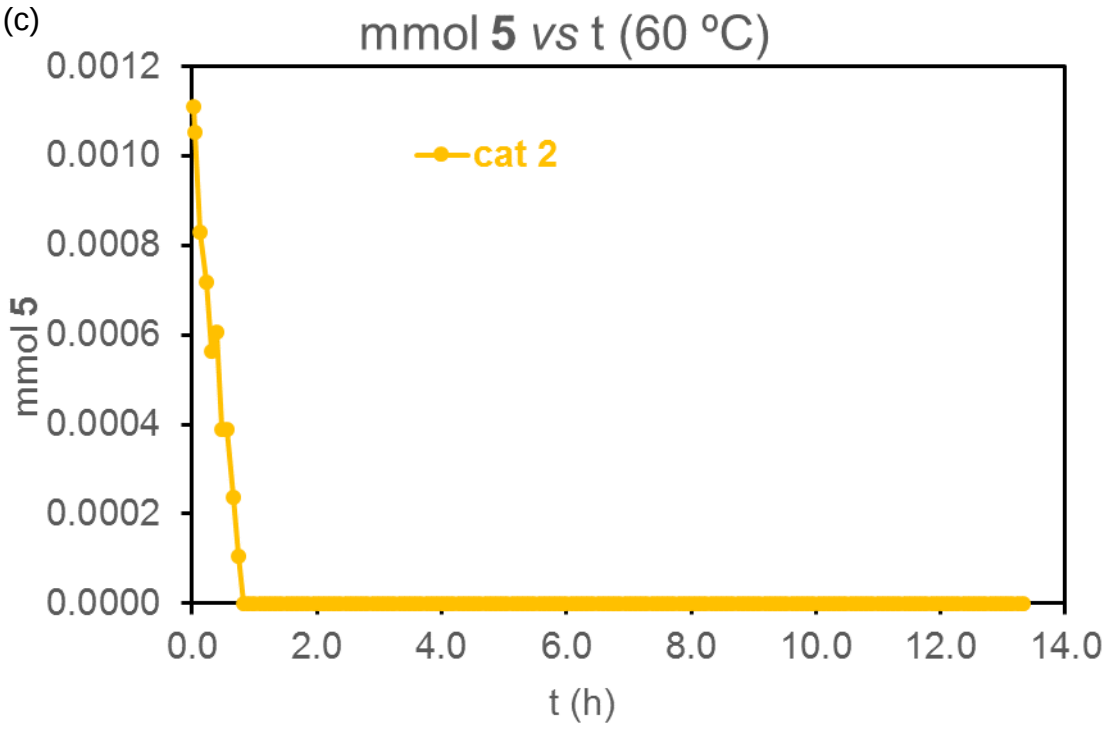

mmol vs t (cat: 2, 60 ºC)
mmol
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0.0000
0
2
4
6
8
10
12
14
t (min)
12C-4+13C-4
13C-4
12C-4

Figure S31. (a) TON for the formation of **C** *vs*. time (h) and (b) d(TON **C**)/dt (h^{-1}), *vs*. time (h) for the reduction of CO_2 with HBcat using catalyst **1** (●) and catalyst **2** (●); (c) mmol of compound **5** *vs* time (h) for the catalytic reduction of CO_2 with HBcat using catalyst **2** (●). [Reaction conditions: 1 atm CO_2, 0.6 mL C_6D_6, 0.20 mmol HBcat, 1 mol% cat, 60 ºC]



(c)


mmol 5 vs t (60 °C)
cat 2
mmol 5
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
t (h)

X-ray crystal determination. X-ray data collection of suitable single crystals of compounds **2**, **3**, **4** and **5** were performed on a Bruker KAPPA series II diffractometer with APEX II area-detector system equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Only very small single crystals of **3** could be obtained which diffracted relatively weakly. After data collection and integration with the Bruker SAINT software package,[6] absorption corrections (SADABS)[7] were applied to the collected data as well as corrections for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS-97), completed with different Fourier syntheses, and refined with full-matrix least-squares using SHELXL-97 minimizing $\omega(F_o^2 - F_c^2)^2$,[8] using Olex 2.[9] Weighted *R* factors (R_w) and all goodness of fit *S* are based on F^2; conventional *R* factors (*R*) are based on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom positions were calculated geometrically and were allowed to ride on their parent carbon or nitrogen atoms with fixed isotropic *U*. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.10 program library. Details of the structure determination and refinement of compounds are summarised in Table S1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre with deposition numbers CCDC 1995178-1995181.

Checkcif Explanation of B level alerts for Complex 3.

Datablock: fer3

Alert level B

RINTA01_ALERT_3_B

PLAT020_ALERT_3_B

Comment: The B-alerts arise from the slightly weak diffraction data used for structural determination

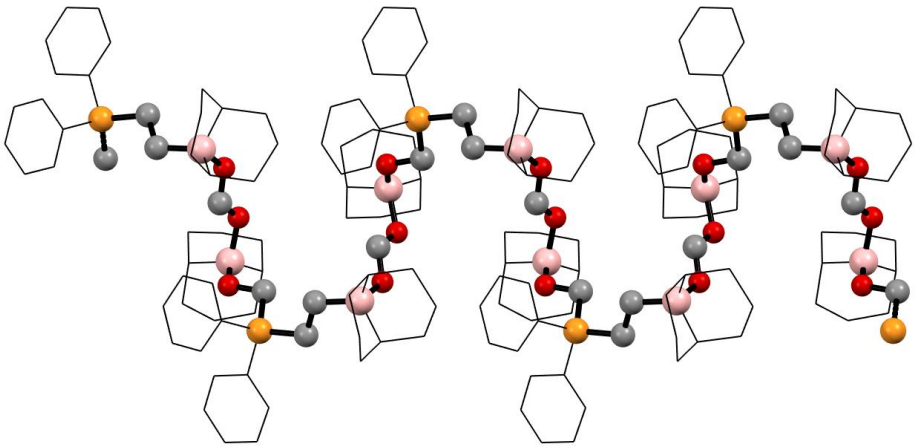
Table S1. Crystallographic data and structure refinement details for all compounds.

Compound	**2**	**3**	**4**·3(C_7H_8)	**5**·(C_7H_8)
Chem. form.	$C_{23}H_{30}BOP$	$C_{32}H_{45}B_2O_3P$	$C_{103}H_{142}B_6O_{10}P_2$	$C_{60}H_{73}B_3O_6P_2$
CCDC	1995179	1995178	1995181	1995180
Form. weight	364.25	530.27	1666.96	984.55
Cryst. system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	*P* -1	*P* 1 $2_1/c$ 1	*P* 1 $2_1/c$ 1	*Pnma*
a (Å)	12.0989(4)	11.7468(16)	13.1645(5)	12.9364(4)
b (Å)	12.1261(4)	22.222(4)	14.8261(6)	22.5508(7)
c (Å)	15.1209(5)	11.8240(18)	25.1303(10)	18.3284(5)
α (º)	76.9401(18)	90	90	90
β (º)	69.2961(18)	112.779(6)	100.5452(17)	90
γ (º)	77.158(2)	90	90	90
V (Å^3)	1996.66(12)	2845.8(8)	4822.0(3)	5346.9(3)
Z	4	4	2	4
GOF [a]	1.008	1.023	1.013	1.031
R_{int}	0.0723	0.1936	0.0864	0.1146
R_1 [b] / wR^2 [c] [I>2σ(I)]	0.0427 / 0.0868	0.0724 / 0.1512	0.0565 / 0.1300	0.0485 / 0.1209
R_1 [b] / wR^2 [c] (all data)	0.0858 / 0.1014	0.1811 / 0.1896	0.0980 / 0.1516	0.0896 / 0.1446

[a] $S = [\sum w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$ [b] $R_1 = \sum||F_0|-|F_c|| / \sum|F_0|$ [c] $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^2]^{1/2}$

$w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (F_0^2 + 2F_c^2)/3$

Figure S32. Molecular structure of compound **3** showing the helical arrangement of the polymer; H atoms were omitted for clarity and C atoms of BBN and Ph rings outside the polymeric chain have been styled wireframe also for clarity reasons. Color code: P (orange), B (pink), O (red), C (grey).



REFERENCES

1. (a) Fischbach, A.; Bazinet, P. R.; Waterman, R.; Tilley, T. D., β-Phosphinoethylboranes as Ambiphilic Ligands in Nickel−Methyl Complexes. *Organometallics* **2008**, *27*, 1135-1139; (b) Vergnaud, J.; Grellier, M.; Bouhadir, G.; Vendier, L.; Sabo-Etienne, S.; Bourissou, D., Synthesis and Reactivity of Ruthenium Arene Complexes Incorporating Novel $Ph_2PCH_2CH_2BR_2$ Ligands. Easy Access to the Four-Membered Ruthenacycle [(*p*-cymene)RuCl($\kappa^{C,P}$-$CH_2CH_2PPh_2$)]. *Organometallics* **2008**, *27*, 1140-1146; (c) Greenacre, V. K.; Ansell, M. B.; Roe, S. M.; Crossley, I. R., Synthesis, Structures and Coordination Chemistry of Singly Bridged Phosphane-Boranes with Coordinately Unsaturated Platinum Group Metals. *Eur. J. Inorg. Chem.* **2014**, *2014*, 5053-5062.

2. (a) Ramos, A.; Antiñolo, A.; Carrillo-Hermosilla, F.; Fernández-Galán, R.; Rodríguez-Diéguez, A.; García-Vivó, D., Carbodiimides as catalysts for the reduction of CO_2 with boranes. *Chem. Commun.* **2018**, *54*, 4700-4703; (b) Sau, S. C.; Bhattacharjee, R.; Vardhanapu, P. K.; Vijaykumar, G.; Datta, A.; Mandal, S. K., Metal-Free Reduction of CO_2 to Methoxyborane under Ambient Conditions through Borondiformate Formation. *Angew. Chem. Int. Ed.* **2016**, *55*, 15147-15151; (c) Yang, Y.; Xu, M.; Song, D., Organocatalysts with carbon-centered activity for CO_2 reduction with boranes. *Chem. Commun.* **2015**, *51*, 11293-11296; (d) Wang, T.; Stephan, D. W., Phosphine catalyzed reduction of CO_2 with boranes. *Chem. Commun.* **2014**, *50*, 7007-7010.

3. (a) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H., An Efficient Nickel Catalyst for the Reduction of Carbon Dioxide with a Borane. *J. Am. Chem. Soc.* **2010**, *132*, 8872-8873; (b) Povie, G.; Villa, G.; Ford, L.; Pozzi, D.; Schiesser, C. H.; Renaud, P., Role of catechol in the radical reduction of B-alkylcatecholboranes in presence of methanol. *Chem. Commun.* **2010**, *46*, 803-805; (c) Leong, B. X.; Lee, J.; Li, Y.; Yang, M. C.; Siu, C. K.; Su, M. D.; So, C. W., A Versatile NHC-Parent Silyliumylidene Cation for Catalytic Chemo- and Regioselective Hydroboration. *J. Am. Chem. Soc.* **2019**, *141*, 17629-17636.

4. (a) Espinosa, M. R.; Charboneau, D. J.; Garcia de Oliveira, A.; Hazari, N., Controlling Selectivity in the Hydroboration of Carbon Dioxide to the Formic Acid, Formaldehyde, and Methanol Oxidation Levels. *ACS Catal.* **2019**, *9*, 301-314; (b) Bontemps, S.; Vendier, L.; Sabo-Etienne, S., Borane-mediated carbon dioxide reduction

at ruthenium: formation of C_1 and C_2 compounds. *Angew. Chem. Int. Ed.* **2012**, *51*, 1671-1674.

5. (a) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G., A highly active phosphine-borane organocatalyst for the reduction of CO_2 to methanol using hydroboranes. *J. Am. Chem. Soc.* **2013**, *135*, 9326-9329; (b) Ho, S. Y. F.; So, C.-W.; Saffon-Merceron, N.; Mézailles, N., Formation of a zwitterionic boronium species from the reaction of a stable carbenoid with borane: CO_2 reduction. *Chem. Commun.* **2015**, *51*, 2107-2110.

6. *SAINT+NT Version 6.04, SAX Area-Detector Integration Program*, Bruker Analytical X-ray Instruments, Madison, WI, 1997–2001.

7. Sheldrick, G. M. *SADABS, Program for Empirical Adsorption Correction*, Institute for Inorganic Chemistry, University of Gottingen: Germany, 1996.

8. Sheldrick, G. M., SHELXT - integrated space-group and crystal-structure determination. *Acta. Crystallogr. A Found. Adv.* **2015**, *71*, 3-8.

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr*. **2009**, *42*, 339-34.