

Organocatalysts with carbon-centered activity for CO₂ reduction with boranes

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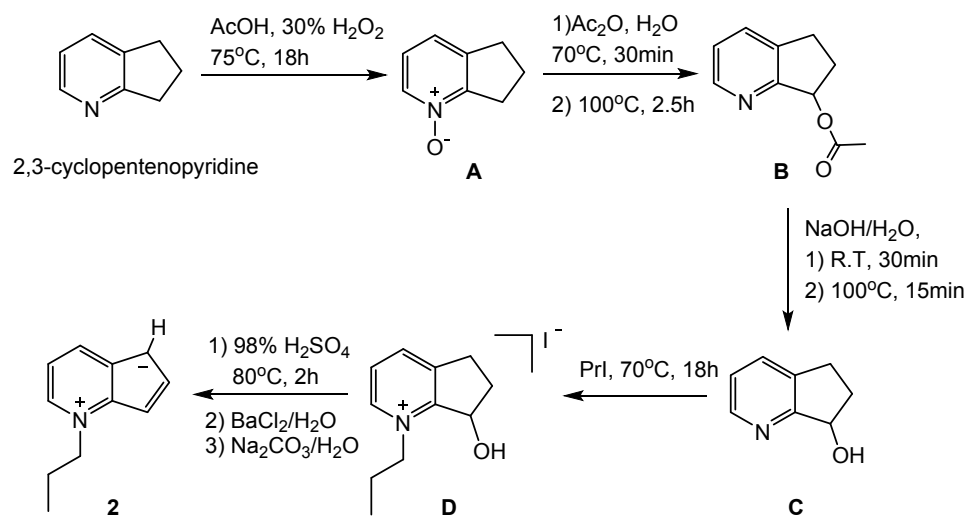
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General Considerations

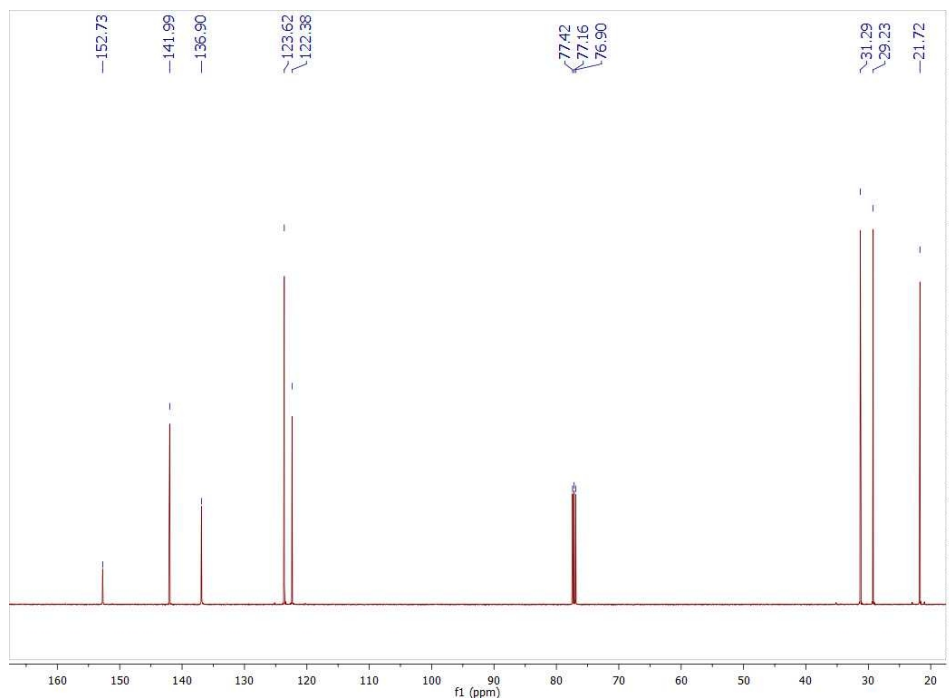
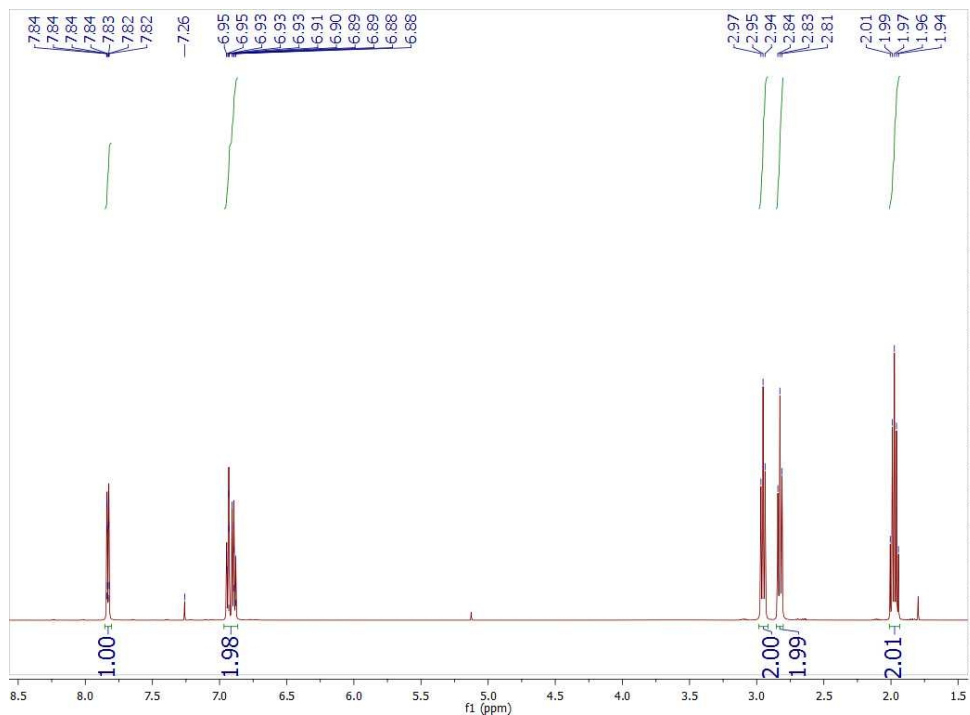
The syntheses of **A–D**, **2**, and **3** were done in air. All manipulations involving boranes were carried out under a dinitrogen atmosphere using a glovebox or Schlenk techniques. Compound **1**¹ and intermediates **A–C**² were prepared using modified literature methods. Compounds **2**, **3** and intermediate **D** are new compounds. All other chemicals were purchased from commercial source. All glassware was dried overnight in a 150 °C oven or by flame before use. The J. Young NMR tubes were dried in a 60 °C oven overnight. Catalytic reactions under 1.5 atm of CO₂ were conducted in sealed Schlenk bombs. CO₂ was purchased from Linde (Grade 4.0) and used as received. THF was dried over Na/benzophenone and distilled under dinitrogen before use. CH₂Cl₂, Et₂O, toluene, pentane, and hexanes were dried by passing through a Pure Solv InnovativeTechnology Grubbs-type solvent purification system and degassed through three freeze–pump–thaw cycles. DMSO-d₆ was dried with CaH₂ at 60 °C overnight, vacuum distilled and stored over molecular sieves. CDCl₃ was dried with P₂O₅ at 60 °C overnight, distilled under dinitrogen and stored over molecular sieves. C₆D₆ and C₆D₅Br were degassed through three freeze–pump–thaw cycles and dried over molecular sieves. ¹H, ¹¹B, and ¹³C NMR data were collected on a Varian 400 MHz, Bruker Avance III 400 MHz, Agilent DD2–500 MHz or Agilent DD2–600 MHz NMR spectrometer. The chemical shifts were reported in ppm and referenced with the residual solvent signals. gHSQC, gCOSY and gHMBC NMR experiments were performed to assign signals properly. Elemental analyses were performed by ANALEST in our department at the University of Toronto. The commercial HBcat was vacuum-distilled at 50 °C. The purity of the redistilled HBcat was determined by ¹H NMR with hexamethylbenzene as the internal standard to be ranging from 65% to 70% between batches. The measured purity of HBcat is specified in each individual experiment below.



Scheme S1. Synthesis of compound **2**

Synthesis of A:

2,3-Cyclopentenopyridine (5.0 g, 0.037 mol), acetic acid (25 mL, 0.437 mol), and 30% H₂O₂ (4.15 mL, 0.0411 mol) were combined in a round bottom flask and heated at 75 °C for 18 h, during which 30% H₂O₂ (3.35 mL, 0.0332 mol) was added at 3 h. The solution gradually changed color from pale brown to pale yellow. Volatiles were removed on a rotary evaporator. The remaining dark brown liquid was transferred into a K₂CO₃ aqueous solution (12 g of K₂CO₃ in 90 mL of H₂O), which was then extracted with CH₂Cl₂ (400 mL x 3). The combined CH₂Cl₂ layer was washed with brine and dried over MgSO₄. The removal of CH₂Cl₂ gave **A** as a white solid (4.6 g, 82% yield). ¹H NMR (CDCl₃, 500 MHz) δ: 7.83 (dd, J = 6.3, 1.0 Hz, 1H, H1), 6.94 (dd, J = 7.6, 1.3 Hz, 1H, H3), 6.89 (dd, J = 7.6, 6.4 Hz, 1H, H2), 2.95 (t, J = 7.7 Hz, 2H, H6), 2.83 (t, J = 7.7 Hz, 2H, H4), 2.0 (quintet, J = 8.75 Hz, 2H, H5). ¹³C NMR (CDCl₃, 125 MHz) δ: 152.73(C7), 141.99(C8), 136.9(C1), 123.62(C2), 122.38(C3), 31.29(C4), 29.23(C6), 21.72(C5).



Synthesis of B:

A (4.6 g, 0.034 mol), H₂O (0.3 mL, 5.4 mmol), and acetic anhydride (34 mL, 0.36 mol) were mixed in 100 mL round bottom flask. The pink solution was stirred at room temperature for 30 min and then heated at 70 °C for 30 min. The colour of the solution gradually turned to dark purple. The solution was then heated at 100 °C for 2.5 h. Volatiles were removed on a rotary evaporator. The remaining black oil was added to a K₂CO₃ aqueous solution (10 g of K₂CO₃ in 70 mL of H₂O), which was then extracted with CH₂Cl₂ (500 mL x 3). The combined CH₂Cl₂ layer was washed with brine and dried over MgSO₄. The removal of CH₂Cl₂ gave **B** as a brown oil (80.4% yield). ¹H NMR (CDCl₃, 500 MHz) δ: 8.51 (d, J = 4.2 Hz, 1H, H1), 7.60 (dd, J = 7.7, 0.6 Hz, 1H, H3), 7.19 (dd, J = 7.7, 4.9 Hz, 1H, H2), 6.13 (dd, J = 7.5, 5.0 Hz, 1H, H6), 3.07 (m, 1H, H4), 2.89 (m, 1H, H4'), 2.65 (m, 1H, H5), 2.12 (s, 3H, H10), 2.05 (m, 1H, H5'). ¹³C NMR (CDCl₃, 125 MHz) δ: 170.88(C9), 160.53(C7), 148.95(C1), 137.46(C8), 133.17(C3), 123.41(C2), 77.32(C6), 30.85(C5), 27.87(C4), 21.31(C10).

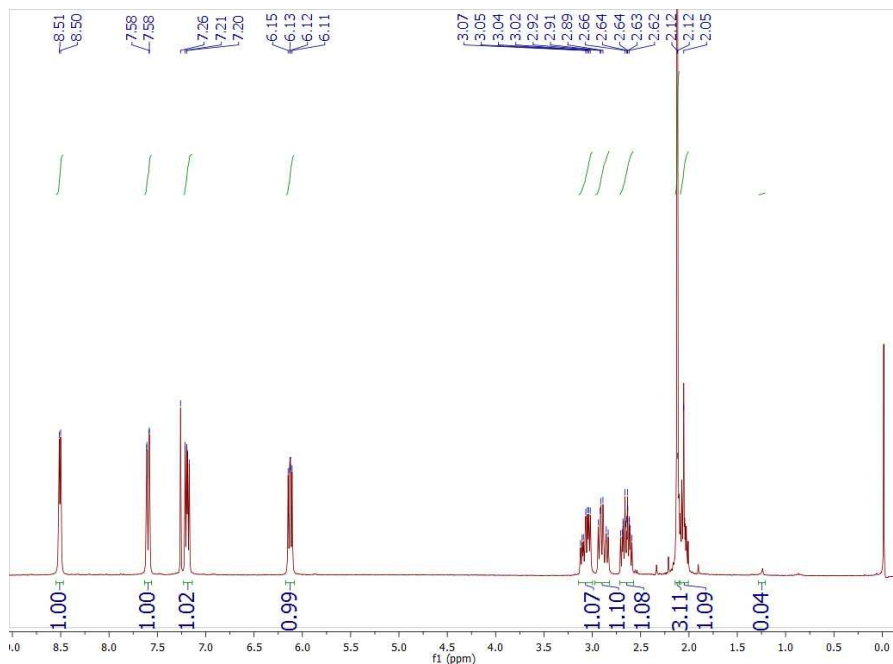


Figure S3. ¹H NMR spectrum of **B** in CDCl₃

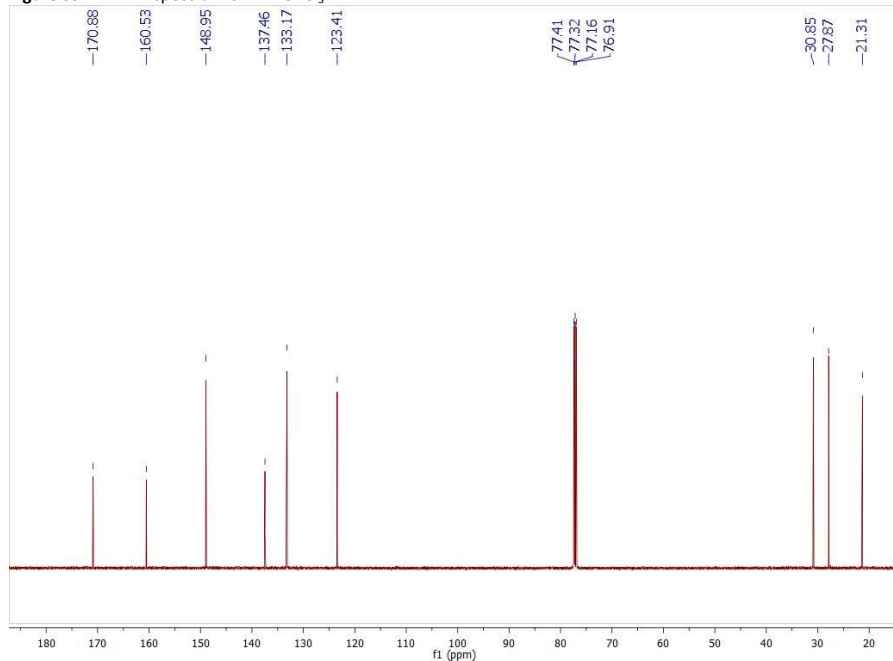


Figure S4. ¹³C NMR spectrum of **B** in CDCl₃

Synthesis of C:

B (7.05 g, 0.0398 mol) and NaOH (2.15 g, 0.0538 mol) were mixed with 19.4 mL of H₂O in a 50 mL round bottom flask. The solution was stirred at room temperature for 30 min and then heated at 100 °C for 15 min. The dark solution was cooled down and added to a K₂CO₃ aqueous solution (20 g of K₂CO₃ in 300 mL of H₂O), which was then extracted with CH₂Cl₂ (830 mL x 3). The combined CH₂Cl₂ layer was washed with brine and dried over MgSO₄. The removal of CH₂Cl₂ on a rotary evaporator gave the crude product as a brown solid. Recrystallization from cyclohexane gave pure **C** as a pale-yellow solid (4.61 g, 86.3% yield). ¹H NMR (CDCl₃, 500 MHz) δ: 8.42 (d, J = 4.8 Hz, 1H, H1), 7.58 (dd, J = 7.6, 1.3 Hz, 1H, H3), 7.15 (dd, J = 7.6, 4.9 Hz, 1H, H2), 5.26 (dd, J = 7.4, 6.1 Hz, 1H, H6), 4.98 (s, 1H, OH), 3.06 (ddd, J = 16.2, 8.9, 4.1 Hz, 1H, H4), 2.83 (m, 1H, H4'), 2.56 (m, 1H, H5), 2.07 (dddd, J = 13.3, 8.9, 7.2, 6.1 Hz, 1H, H5'). ¹³C NMR (CDCl₃, 125 MHz) δ: 164.99(C7), 147.78(C1), 136.72(C8), 133.67(C3), 122.90(C2), 74.42(C6), 32.95(C5), 27.65(C4).

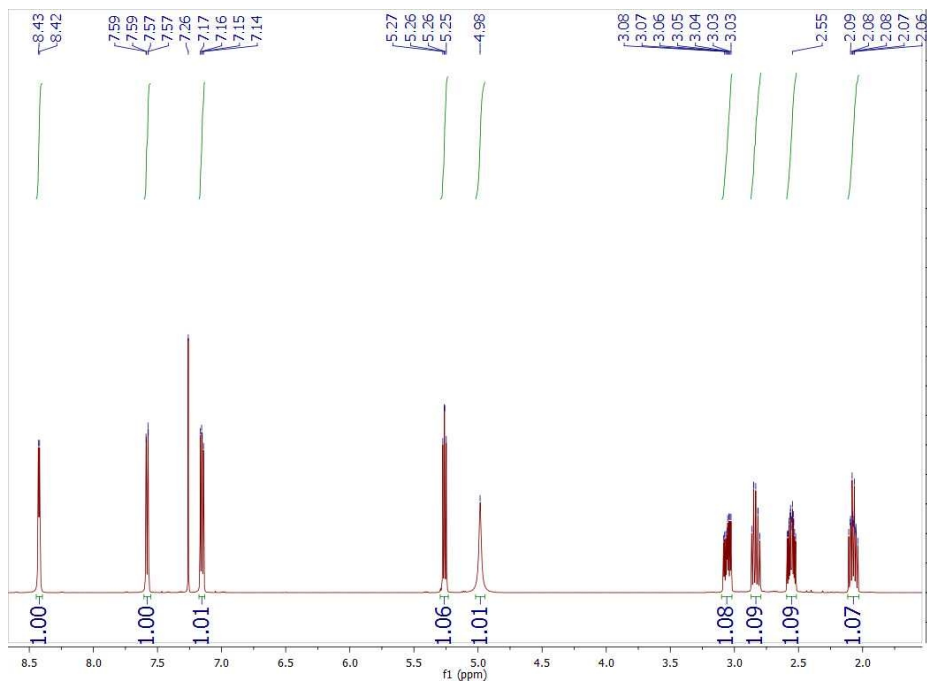


Figure S5. ¹H NMR spectrum of **C** in CDCl₃

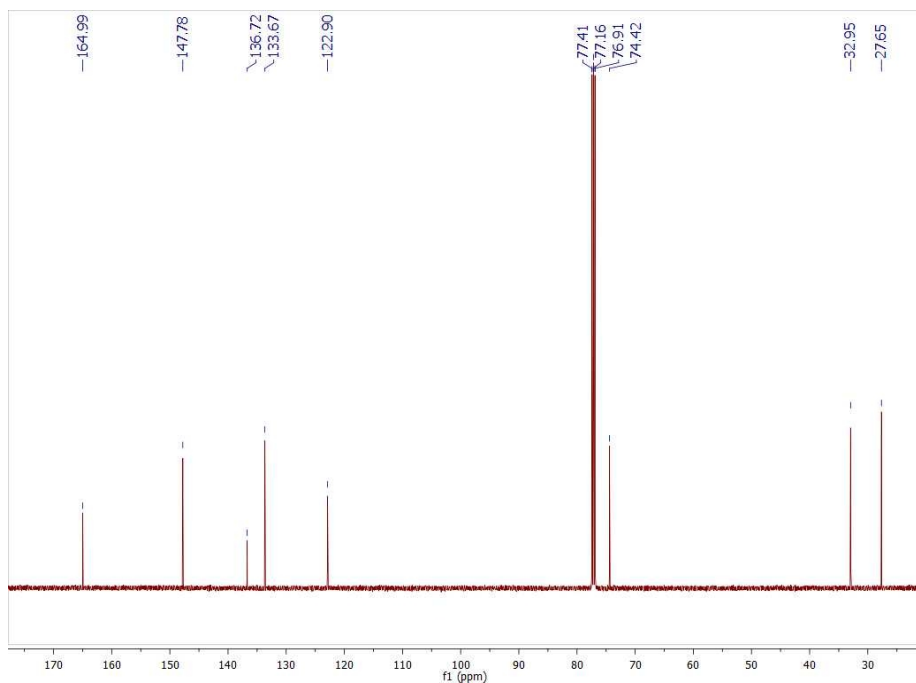
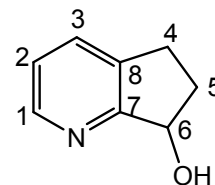


Figure S6. ¹³C NMR spectrum of **C** in CDCl₃



Synthesis of D:

C (0.56 g, 4.1 mmol) and 1-iodopropane (3 mL, 0.0274 mol) were mixed in a 25 mL round bottom flask, and heated at 70°C for 18 hours. When the reaction was complete, the colorless liquid phase turned yellow, which was decanted. The residual black-brown solid in the flask was ground and washed with 20 mL of cyclohexane. The solid was then dissolved in 300 mL of CH₂Cl₂. The resulting solution was dried over MgSO₄. The removal of CH₂Cl₂ gave **D** as a brown solid (1.13 g, 83.9% yield). ¹H NMR (CD₃CN, 500 MHz) δ: 8.60 (dd, J = 6.1, 0.6 Hz, 1H, H4), 8.31 (dd, J = 7.8, 1.0 Hz, 1H, H6), 7.84 (dd, J = 7.6, 6.3 Hz, 1H, H5), 5.62 (d, J = 4.7 Hz, 1H, H9), 4.96 (d, J = 6.9 Hz, 1H, OH), 4.76 (ddd, J = 13.0, 8.8, 6.7 Hz, 1H, H3), 4.55 (ddd, J = 13.0, 8.9, 6.8 Hz, 1H, H3'), 3.26 (ddd, J = 9.0, 5.7 Hz, 1H, H7), 3.01 (ddd, J = 9.0, 5.6 Hz, 1H, H7'), 2.58 (m, 1H, H8), 2.19 (m, 1H, H8'), 2.0 (m, 2H, H2), 0.99 (t, J = 7.4 Hz, 3H). ¹³C NMR (CD₃CN, 125 MHz) δ: 159.55(C10), 146.27(C11), 143.75(C4), 143.10(C6), 127.99(C5), 72.86(C9), 59.49(C3), 33.81(C8), 28.92(C7), 25.09(C2), 10.91(C1).

Anal. calcd for (C₁₁H₁₆NOI): C 43.29, H 5.25, N 4.59; Found: C 43.40, H 5.05, N 4.46.

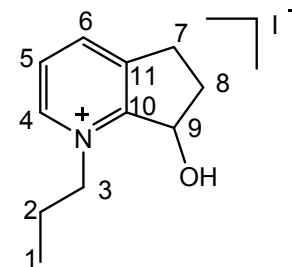
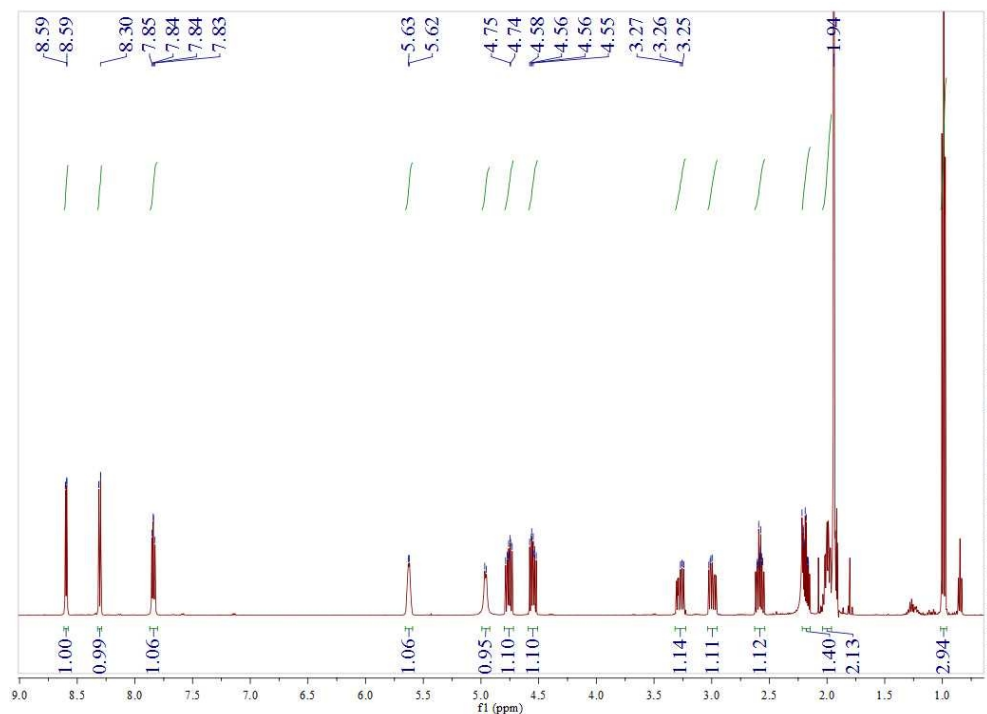


Figure S7. ¹H NMR spectrum of **D** in CD₃CN

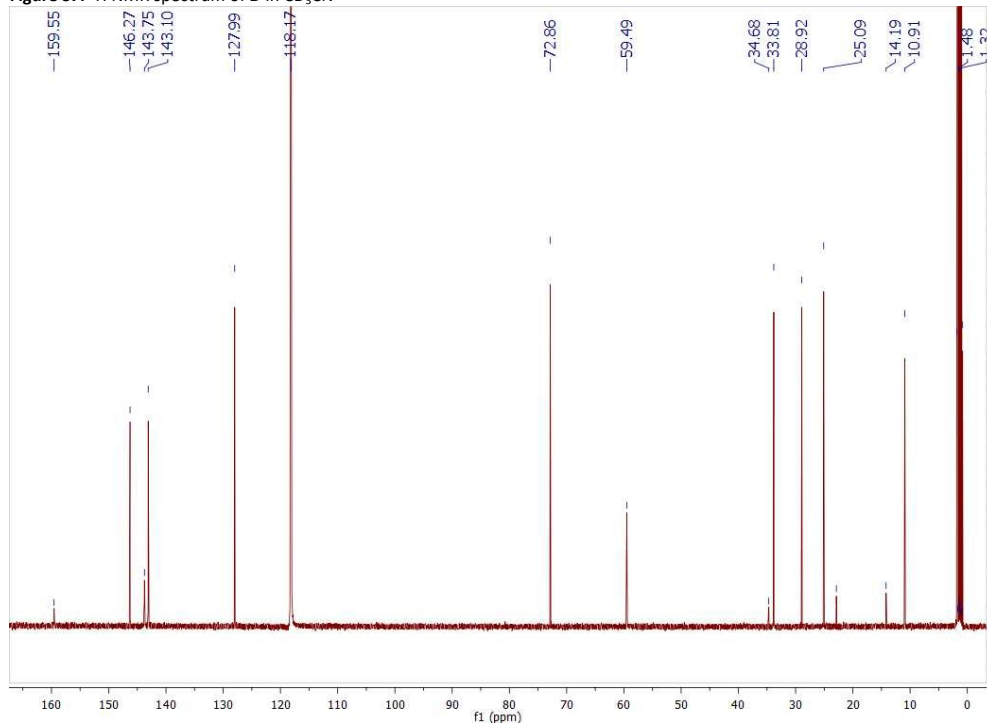
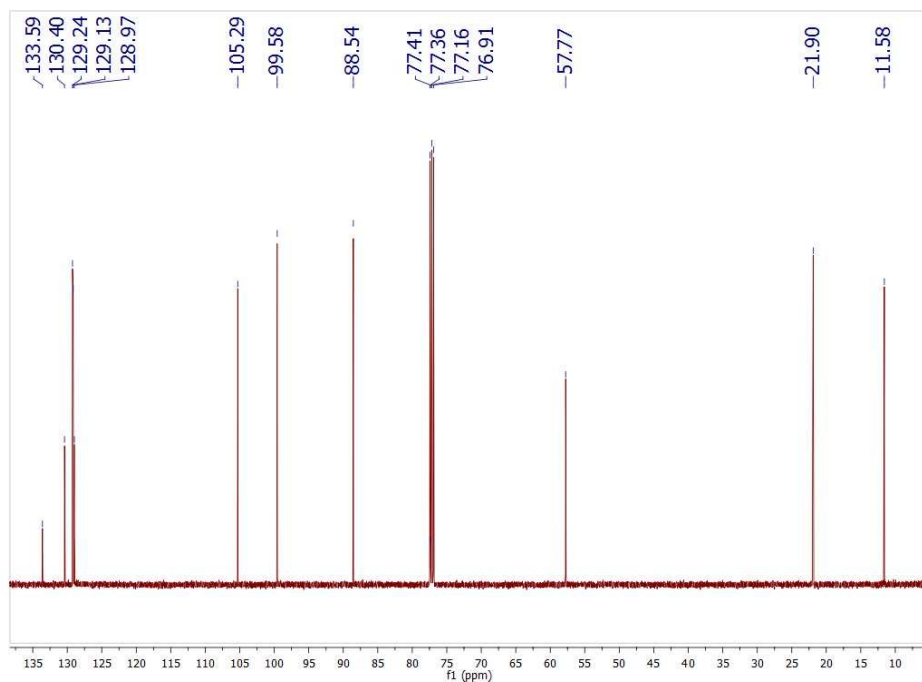
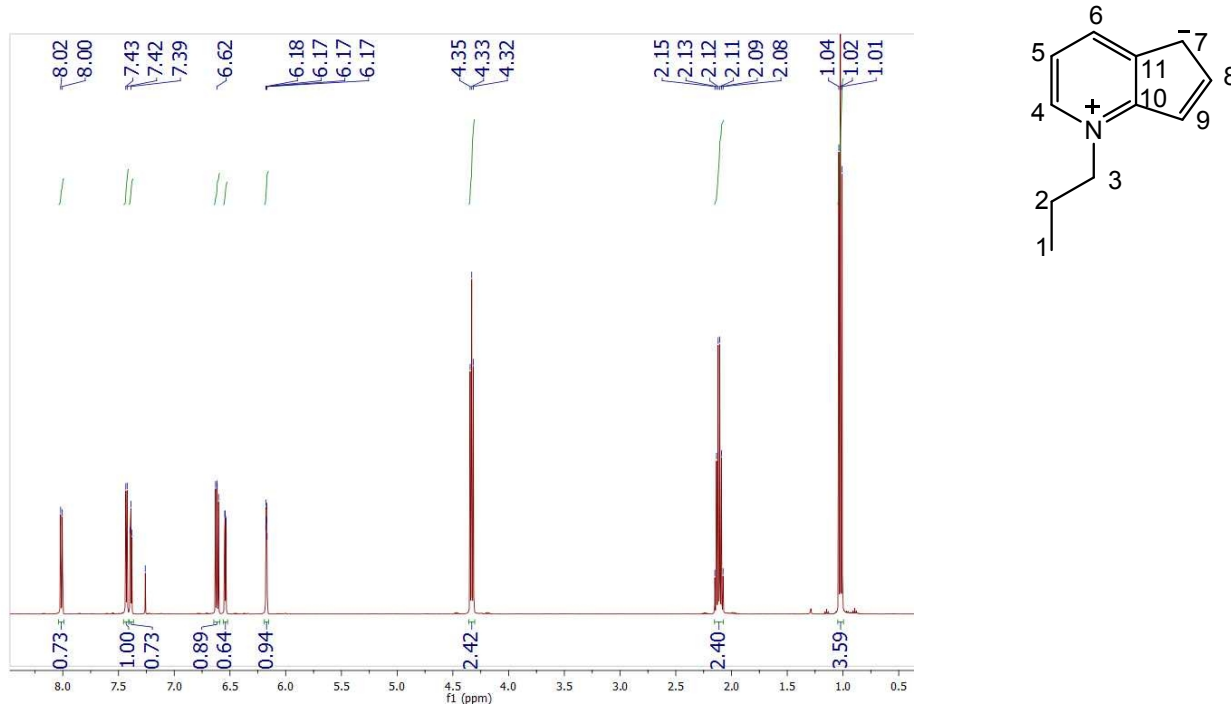


Figure S8. ¹³C NMR spectrum of **D** in CD₃CN

Synthesis of 2:

D (0.33 g, 1.08 mmol) and 98% H₂SO₄ (0.356 mL, 6.5 mmol) were mixed in a 25 mL round bottom flask and heated at 60 °C for 2 h. The solution was cooled down followed by the addition of 10 mL of water. The solid iodine was removed through vacuum filtration. To the filtrate was added a solution of BaCl₂·2H₂O (1.69 g in 10 mL of H₂O). The white precipitate was filtered off. The resulting pale-brown aqueous filtrate was washed with 80 mL of CH₂Cl₂ and added dropwise to a solution of Na₂CO₃ (2.2 g in 10 mL of H₂O). The colorless transparent Na₂CO₃ solution turned into bright orange suspension immediately. The product was extracted with CH₂Cl₂ (200 mL x 3). The CH₂Cl₂ layer was dried over MgSO₄. The removal of CH₂Cl₂ gave pure **2** as an orange oil (0.17 g, 94.3% yield). ¹H NMR (CDCl₃, 500 MHz) δ: 8.01 (d, J = 7.4 Hz, 1H, H6), 7.43 (d, J = 6.1 Hz, 1H, H4), 7.39 (dd, J = 4.3, 4.3 Hz, 1H, H8), 6.62 (dd, J = 7.4, 6.1 Hz, 1H, H5), 6.54 (dd, J = 4.3, 1.5 Hz, 1H, H7), 6.18 (m, 1H, H9), 4.33 (t, J = 7.4 Hz, 2H, H3), 2.11 (qt, J = 7.4, 5.5 Hz, 2H, H2), 1.02 (t, J = 7.4 Hz, 3H, H1). ¹³C NMR (CDCl₃, 125 MHz) δ: 133.59(C10), 130.4(C11), 129.24(C8), 129.13(C6), 128.97(C4), 105.29(C5), 99.58(C7), 88.54(C9), 57.77(C3), 21.90(C2), 11.58(C1). ESI-MS: 159.83 [M+1].



Synthesis of 3:

A solution of **2** (11.6 mg in 0.1 mL of Et₂O) was stirred under 10 atm of CO₂ at 22.6 °C in a Parr high pressure reactor for 15 h. Unreacted **2** was washed away with 5 mL of Et₂O, yielding **3** as a yellow solid (11.0 mg, 74% yield). X-ray quality crystals of **3** were grown via slow evaporation of an Et₂O solution of **3**. ¹H NMR (DMSO-d₆, 500 MHz) δ: 11.02 (s, 1H, OH), 8.59 (d, J = 7.6 Hz, 1H, H6), 8.08 (d, J = 6.0 Hz, 1H, H4), 7.67 (d, J = 4.1 Hz, 1H, H8), 7.01 (dd, J = 7.6, 6.1 Hz, 1H, H5), 6.29 (d, J = 4.1 Hz, 1H, H9), 4.47 (t, J = 7.2 Hz, 2H, H3), 1.94 (qt, J = 7.4, 7.3 Hz, 2H, H2), 0.89 (t, J = 7.4 Hz, 3H, H1). ¹³C NMR (DMSO-d₆, 125 MHz) δ: 166.37(C12), 137.54(C10), 133.89(C8), 131.55(C4), 130.66(C6), 129.17(C11), 109.69(C5), 102.48(C7), 92.60(C9), 56.64(C3), 22.01(C2), 10.73(C1). Anal. calcd for C₁₂H₁₃NO₂: C 70.93, H 6.40, N 6.89; found: C 70.45, H 6.31, N 6.65. IR(CDCl₃ solution): ν(C=O) 1628.84cm⁻¹.

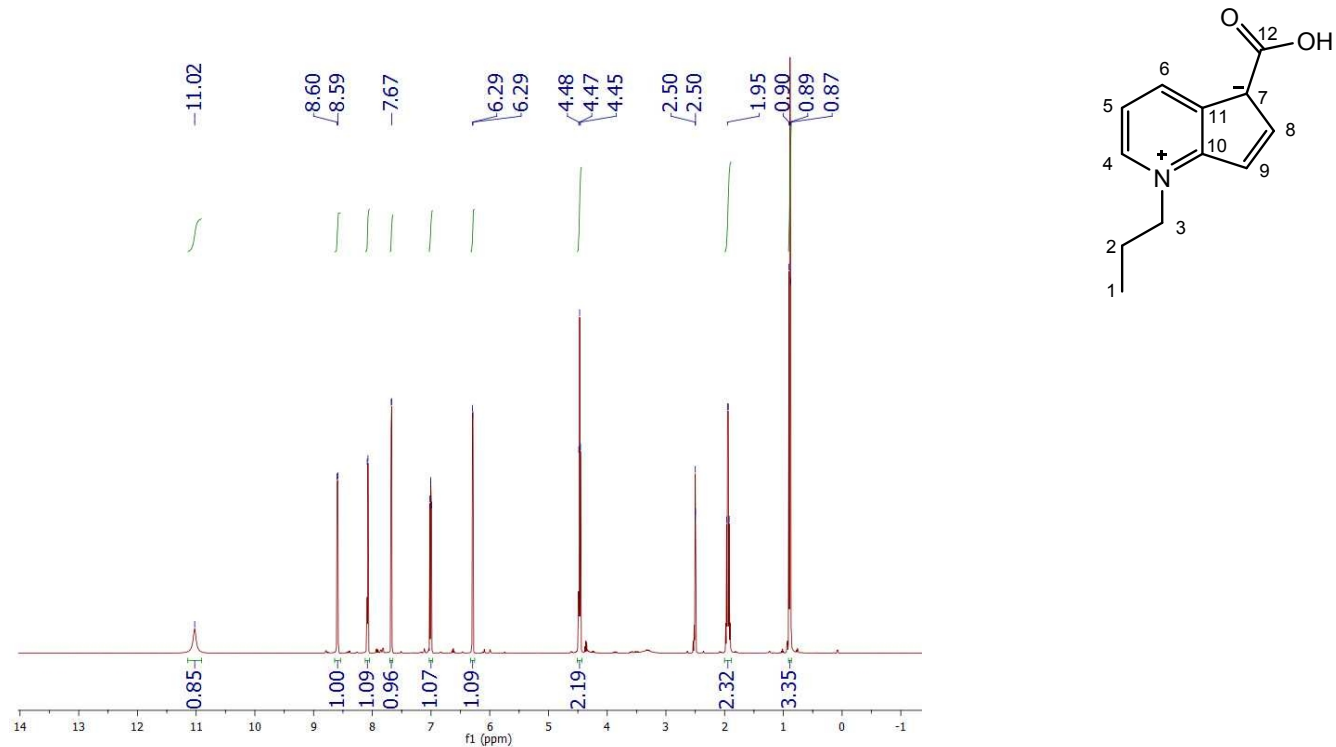


Figure S11. ¹H NMR spectrum of **3** in DMSO-d₆. The peak at 11.02 ppm in the ¹H NMR spectrum corresponds to a carboxylic acid.

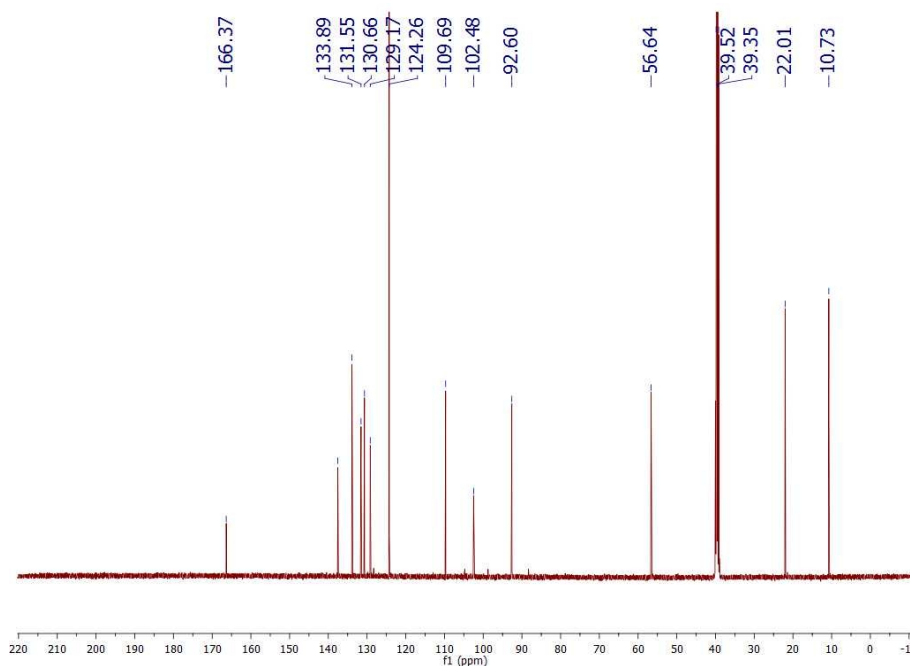


Figure S12. ¹³C NMR spectrum of **3** in DMSO-d₆. The ¹³C NMR spectrum confirms the formation of a carboxylic acid species with a new peak a 166.37 ppm.

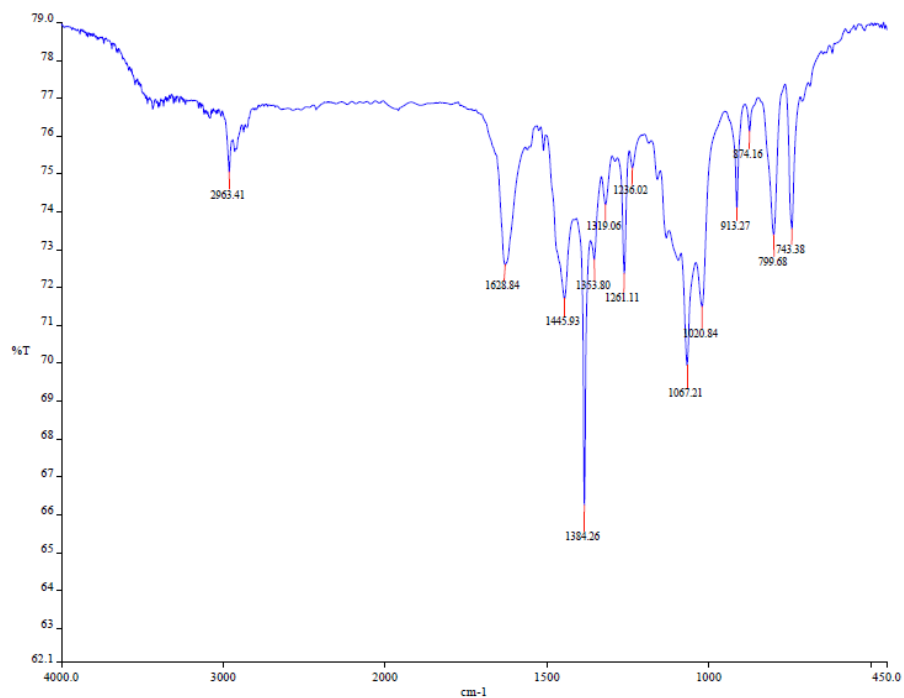


Figure S13. IR spectrum of **3** in CDCl_3

Decomposition of **3** back to **2**:

In a J. Young NMR tube, a CDCl_3 solution of **3** was heated under 1 atm of N_2 at 40°C for 3.5 h. The ^1H NMR spectrum showed over 90% of **3** decomposed back to **2**.

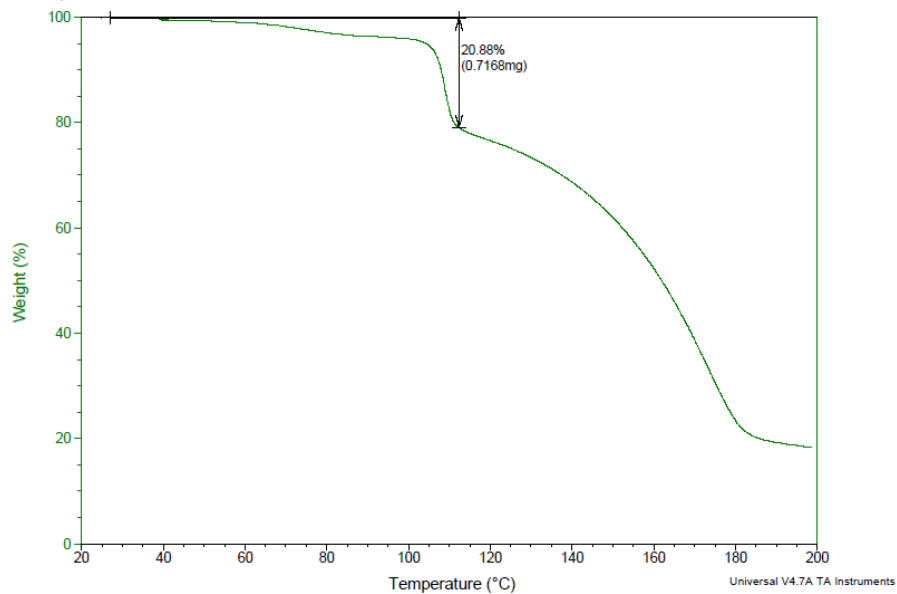


Figure S14. TGA trace of compound **3**. The 20.88% mass loss between 40°C and 110°C matches with the expected weight loss of 21.67%. TGA methods: 1. Ramp $5^\circ\text{C}/\text{min}$ to 40°C ; 2. Isothermal at 40°C for 5 min; 3. Ramp $5^\circ\text{C}/\text{min}$ to 200°C .

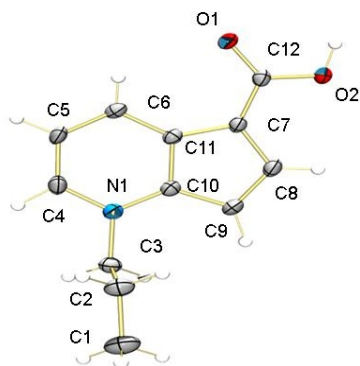


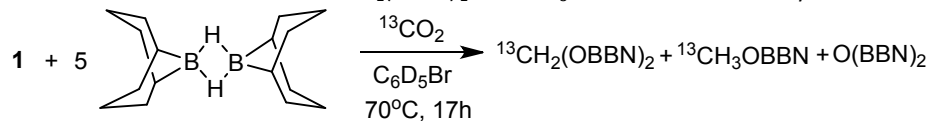
Figure S15. The molecular structure of **3**. Thermal ellipsoids are shown at 50% probability. Selected bond length[Å] and angles[°]: C7-C11, 1.427(2); C7-C8, 1.409(2); C7-C12, 1.424(2); O1-C12, 1.250(2); O2-C12, 1.338(2); N1-C4, 1.360(2); N1-C3, 1.477(2); N1-C10, 1.362(2); C11-C7-C8, 106.9(1); C11-C7-C12, 125.5(1); C8-C7-C12, 127.5(1).

Table S1. Selected crystallographic data of 3:

3	
Formula	C ₁₂ H ₁₃ NO ₂
FW	203.23
<i>T</i> (K)	150(2)
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.1916(10)
<i>b</i> (Å)	12.6389(14)
<i>c</i> (Å)	9.1878(10)
∠ (deg)	90
∠ (deg)	100.210(6)
∠ (deg)	90
<i>V</i> (Å ³)	1050.5(2)
<i>Z</i>	4
<i>D_c</i> (g·cm ⁻³)	1.363
∠ (mm ⁻¹)	0.441
no. of refln collected	9133
no. of indept refln	2412
GOF on <i>F</i> ²	1.012
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0436 <i>wR</i> ₂ = 0.0979
<i>R</i> (all data)	<i>R</i> ₁ = 0.0802 <i>wR</i> ₂ = 0.1107

Reaction between 9-BBN and $^{13}\text{CO}_2$ in the presence of catalyst **1** at 70 °C

In a N_2 -filled glovebox 9-BBN dimer (69 mg, 0.282 mmol) was added into a J. Young NMR tube containing a solution of **1** (10.0 mg, 0.0549 mmol) in 0.6 mL of $\text{C}_6\text{D}_5\text{Br}$. The tube was treated by the "freeze pump" process once in liquid nitrogen and then immediately transferred to a $-70\text{ }^\circ\text{C}$ dry ice/ $^i\text{PrOH}$ bath and opened to 1 atm of $^{13}\text{CO}_2$ for 10 min to allow heat exchange, during which only the frozen solution-containing portion of the tube was immersed in the cold bath. The tube was then sealed and warmed up to room temperature and heated at $70\text{ }^\circ\text{C}$ for 17 h. The conversion of 9-BBN to $^{13}\text{CH}_2(\text{OBBN})_2$ and $^{13}\text{CH}_3\text{OBBN}$ was monitored by ^1H and ^{11}B NMR.



$^{13}\text{CH}_2(\text{OBBN})_2$: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$, 400 MHz) δ : 5.46 (d, $^1J_{\text{C-H}} = 164.6$ Hz, $^{13}\text{CH}_2(\text{OBBN})_2$). ^{13}C NMR ($\text{C}_6\text{D}_5\text{Br}$, 100 MHz) δ : 85.56 (t, $^1J_{\text{C-H}} = 164$ Hz, $^{13}\text{CH}_2(\text{OBBN})_2$).

$^{13}\text{CH}_3\text{OBBN}$: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$, 400 MHz) δ : 3.56 (d, $^1J_{\text{C-H}} = 142.7$ Hz, $^{13}\text{CH}_3\text{OBBN}$). ^{13}C NMR ($\text{C}_6\text{D}_5\text{Br}$, 100 MHz) δ : 52.80 (q, $^1J_{\text{C-H}} = 142$ Hz, $^{13}\text{CH}_3\text{OBBN}$).

The ^{11}B NMR spectrum showed a broad singlet at 58.59 ppm.

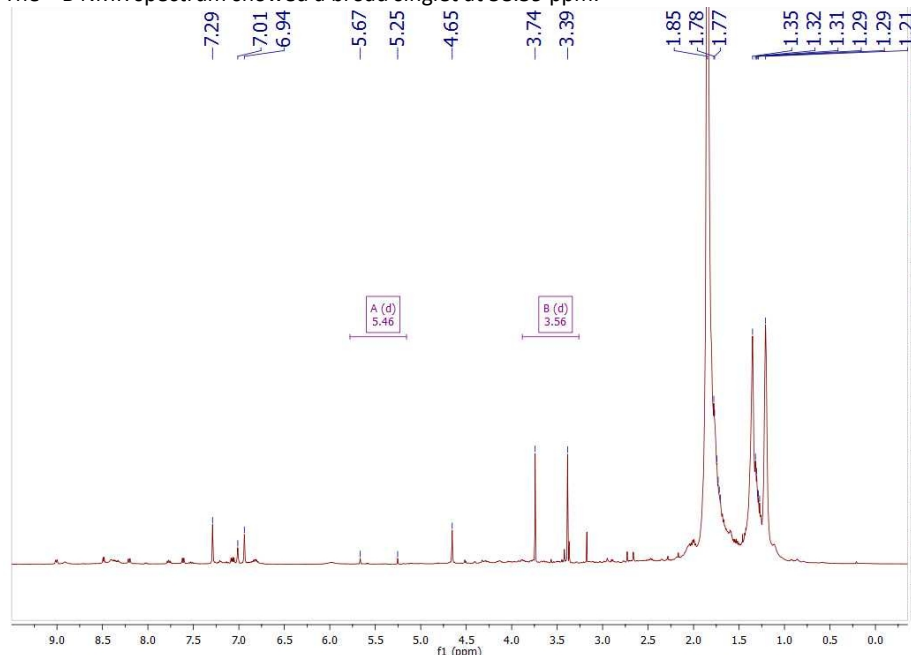


Figure S16. ^1H NMR spectrum of the final reaction mixture above.

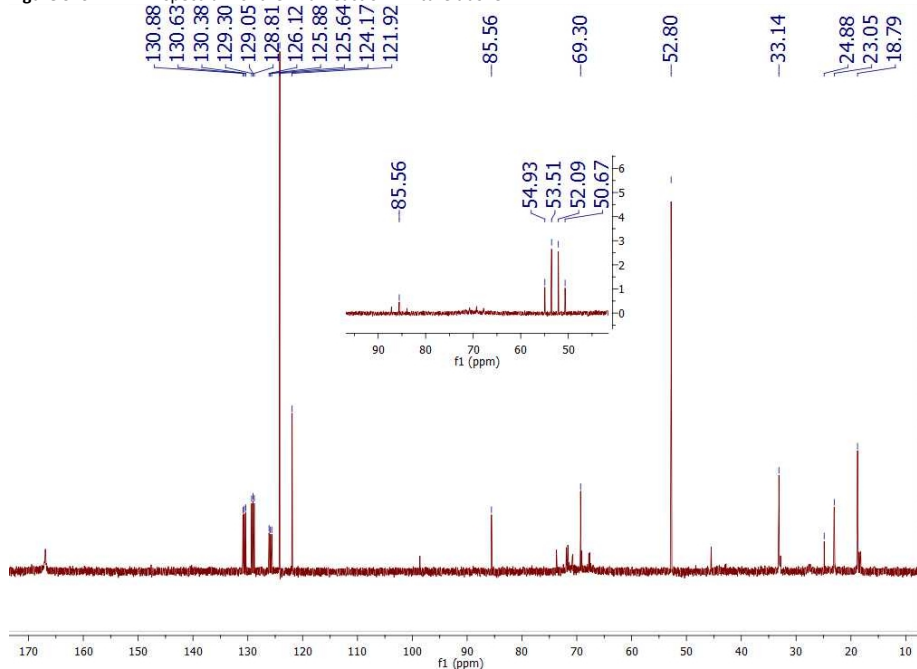
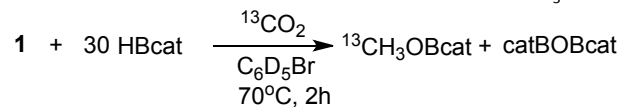


Figure S17. ^{13}C NMR spectrum of the final reaction mixture above.

Reaction between HBcat and $^{13}\text{CO}_2$ in the presence of catalyst **1** at 70 °C

In a N_2 -filled glovebox, HBcat (28.3 mg, 70% purity, 0.165 mmol) was added into a J. Young NMR tube containing a solution of **1** (1.0 mg, 0.00549 mmol in 0.6 mL of $\text{C}_6\text{D}_5\text{Br}$). The tube was treated by the “freeze pump” process once in liquid nitrogen and then immediately transferred to a $-70\text{ }^\circ\text{C}$ dry ice/ i PrOH bath and opened to 1 atm of $^{13}\text{CO}_2$ for 10 min to allow heat exchange, during which only the frozen solution-containing portion of the tube was immersed in the cold bath. The tube was then sealed and warmed up to room temperature and heated at $70\text{ }^\circ\text{C}$ for 2 h. The conversion of HBcat to $^{13}\text{CH}_3\text{OBcat}$ was monitored by ^1H and ^{11}B NMR.



$^{13}\text{CH}_3\text{OBcat}$: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$, 400 MHz) δ : 3.60 (d, $^1J_{\text{C-H}} = 145.3\text{ Hz}$, $^{13}\text{CH}_3\text{OBcat}$); ^{13}C NMR ($\text{C}_6\text{D}_5\text{Br}$, 100 MHz) δ : 52.80 (q, $^1J_{\text{C-H}} = 145\text{ Hz}$, $^{13}\text{CH}_3\text{OBcat}$).

The ^{11}B NMR spectrum showed a broad signal at 23.14 ppm.

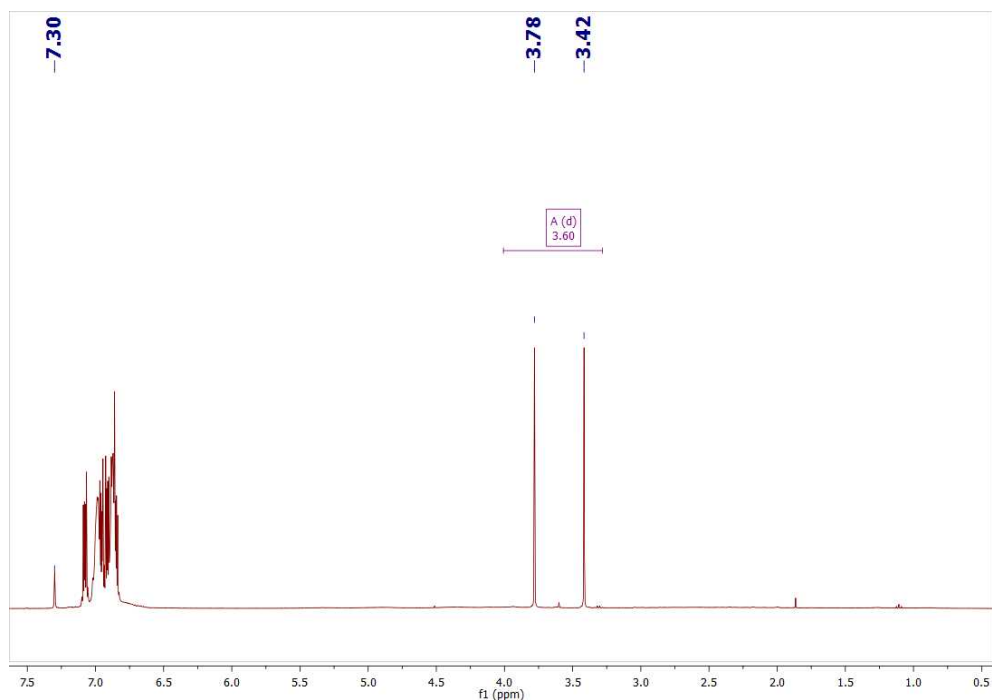


Figure S18. ^1H NMR spectrum of the final reaction mixture above

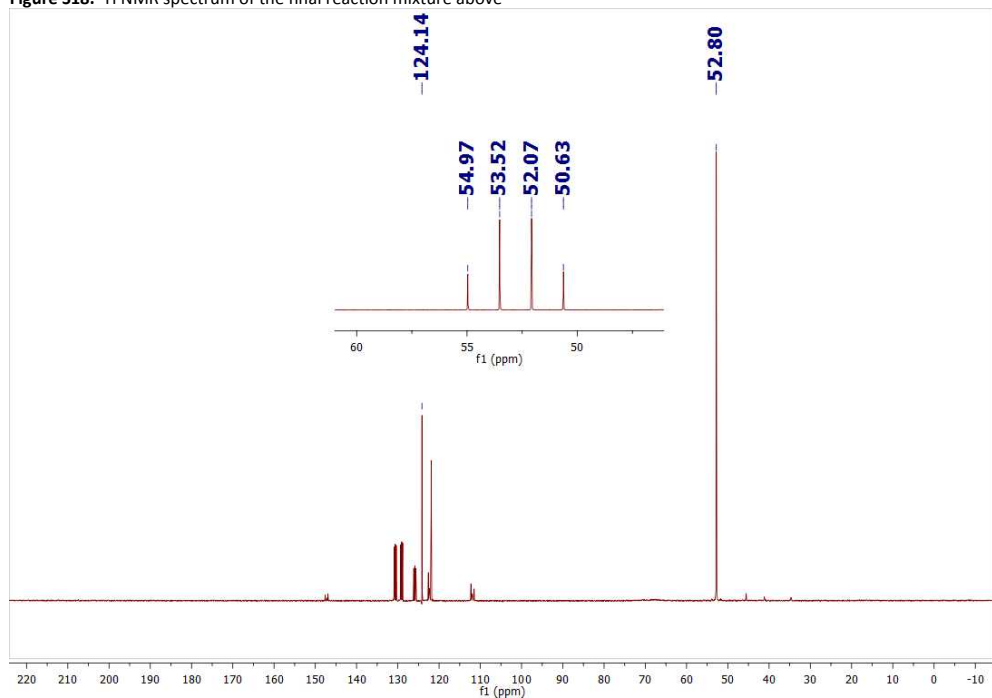
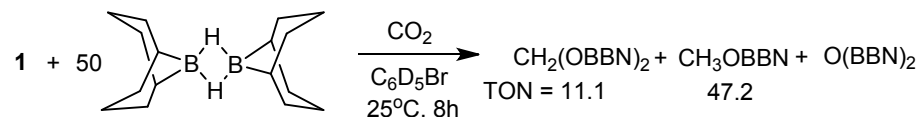


Figure S19. ^{13}C NMR spectrum of the final reaction mixture above

Reaction between 9-BBN and CO₂ in the presence of catalyst **1** at 25°C

In a N₂-filled glovebox, 9-BBN dimer (67 mg, 0.274 mmol) was added into a 50 mL Schlenk bomb containing a solution of **1** (1.0 mg, 0.00549 mmol) in 0.6 mL of C₆D₅Br. The bomb was immersed in liquid N₂ to freeze the solution; the headspace was then evacuated. The entire bomb was then immersed in a -70°C dry ice-isopropanol bath to keep the solution frozen and cool the headspace. The bomb was then opened to 1 atm of CO₂ for 10 minutes to allow the temperature to equilibrate. Subsequently the bomb was sealed and allowed to warm to 25°C quickly to achieve ~1.5 atm pressure. The reaction mixture was stirred 25 °C for 8 h. It gradually changed from a dark blue solution to an orange suspension and finally to a light yellow suspension with white precipitates. The bomb was shipped into a N₂-filled glovebox. After the release of CO₂ gas from the system, hexamethylbenzene (9.6 mg, 0.0593 mmol) was added to the mixture. The TON was calculated based on the integration of the products with respect to that of hexamethylbenzene in the ¹H NMR spectrum.



CH₂(OBBN)₂: ¹H NMR (C₆D₅Br, 400 MHz) δ: 5.46 (s, CH₂(OBBN)₂); ¹³C NMR (C₆D₅Br, 100 MHz) δ: 85.56 (CH₂(OBBN)₂).
CH₃OBBN: ¹H NMR (C₆D₅Br, 400 MHz) δ: 3.58 (s, CH₃OBBN), ¹³C NMR (C₆D₅Br, 100 MHz) δ: 52.80 (CH₃OBBN).

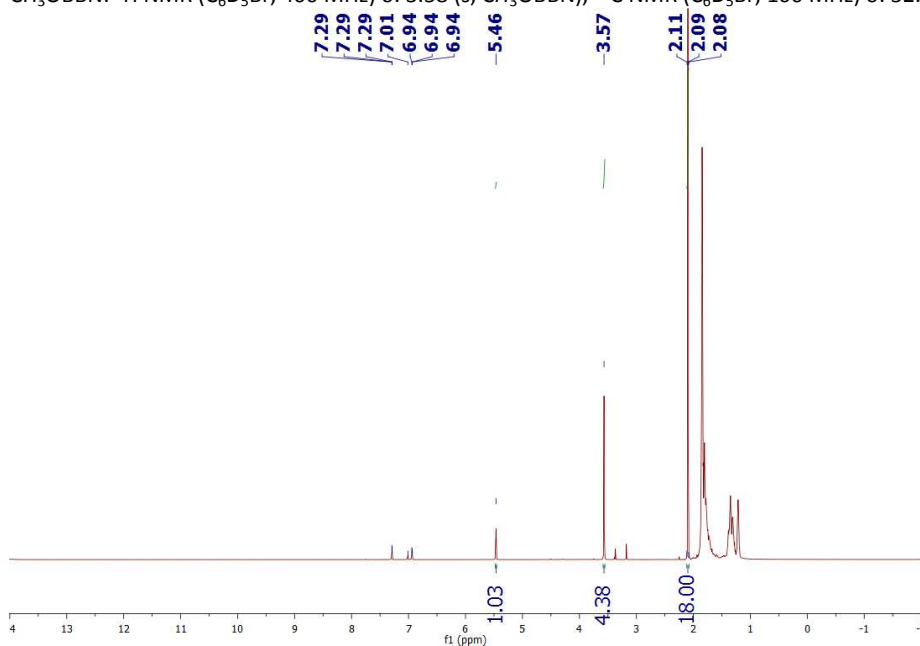


Figure S20. ¹H NMR spectrum of the final reaction mixture above.

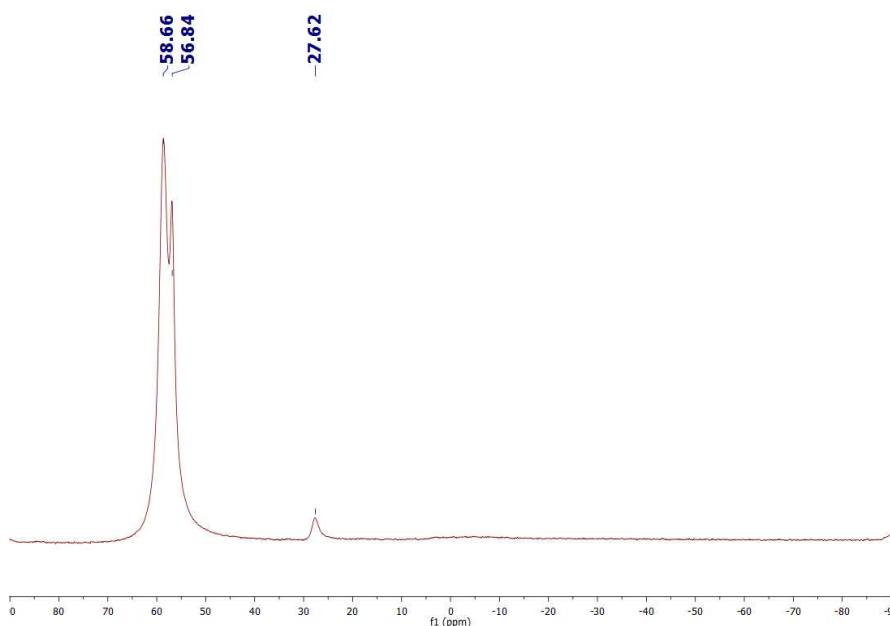


Figure S21. ¹¹B NMR spectrum of the final reaction mixture above.

Reaction between 9-BBN and CO₂ in the presence of catalyst **1** at 70 °C

In a N₂-filled glovebox, 9-BBN dimer (67 mg, 0.274 mmol) was added into a 50 mL Schlenk bomb containing a solution of **1** (1.0 mg, 0.00549 mmol) in 0.6 mL of C₆D₅Br. CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 2h. The bomb was shipped into a N₂-filled glovebox. After cooling and the release of CO₂ gas from the system, hexamethylbenzene (11.8 mg, 0.0728 mmol) was added to the mixture. The TON was calculated based on the integration of the products with respect to that of hexamethylbenzene in the ¹H NMR spectrum.

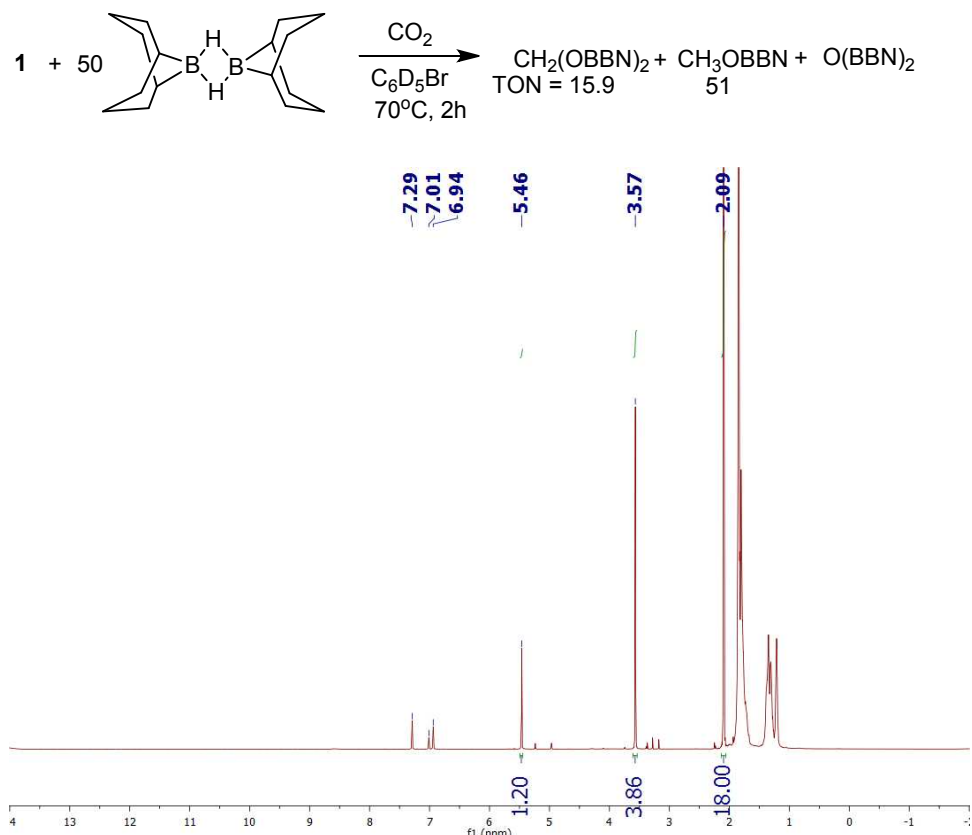


Figure S22. ¹H NMR spectrum of the final reaction mixture above

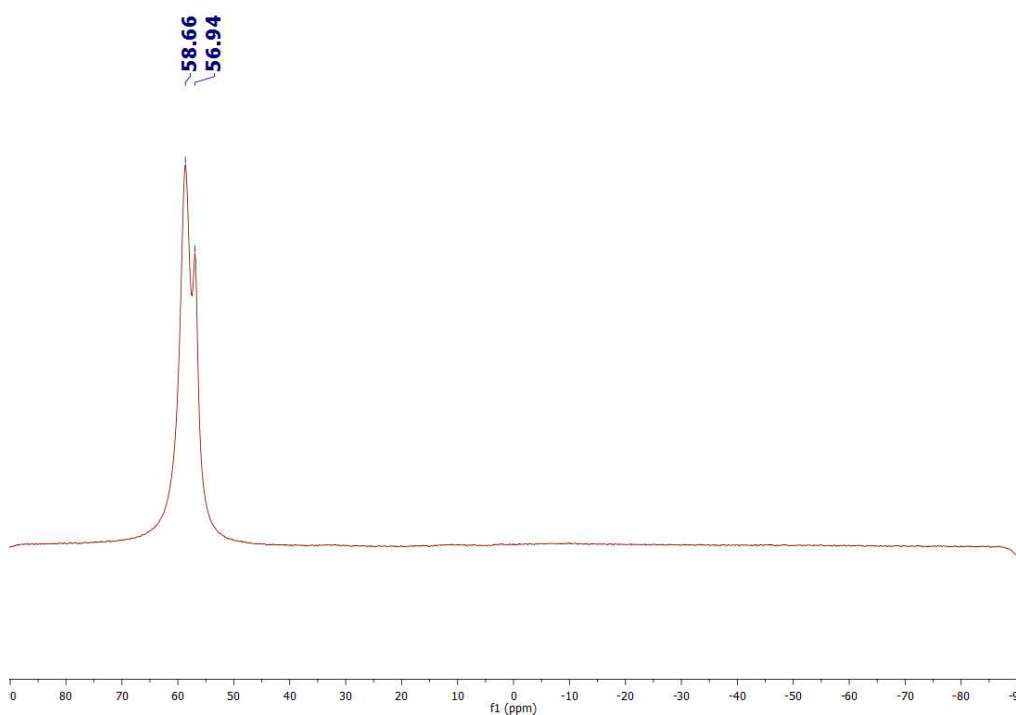
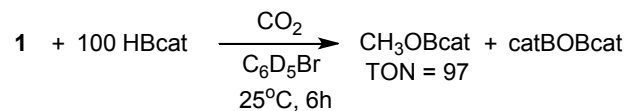


Figure S23. ¹¹B NMR spectrum of the final reaction mixture above

Reaction between HBcat and CO₂ in the presence of catalyst 1 at 25°C

In a N₂-filled glovebox, HBcat (94.7 mg, 69.6% purity, 0.549 mmol) was added into a 50 mL Schlenk bomb containing a solution of **1** (1.0 mg, 0.00549 mmol in 0.6 mL of C₆D₅Br). CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 25 °C for 6 h. It gradually changed from a dark brown solution to a light yellow suspension with white precipitates. After the release of CO₂ gas from the system, hexamethylbenzene (11.1 mg, 0.0685 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum.



CH₃OBcat: ¹H NMR (C₆D₅Br, 400 MHz) δ: 3.60 (s, CH₃OBcat); ¹³C NMR (C₆D₅Br, 100 MHz) δ: 52.80 (CH₃OBcat).
The ¹¹B NMR spectrum showed two broad signals at 23.26 and 22.47 ppm.

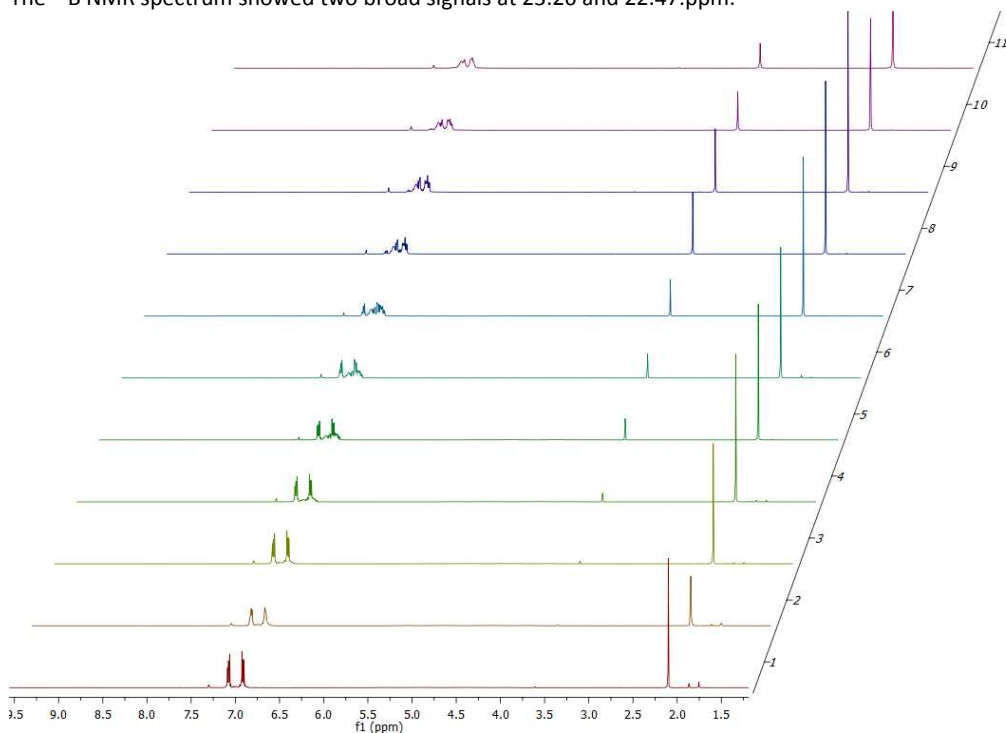


Figure S24. ¹H NMR spectra of the reaction mixture above from 5 min (bottom) to 6 h (top).

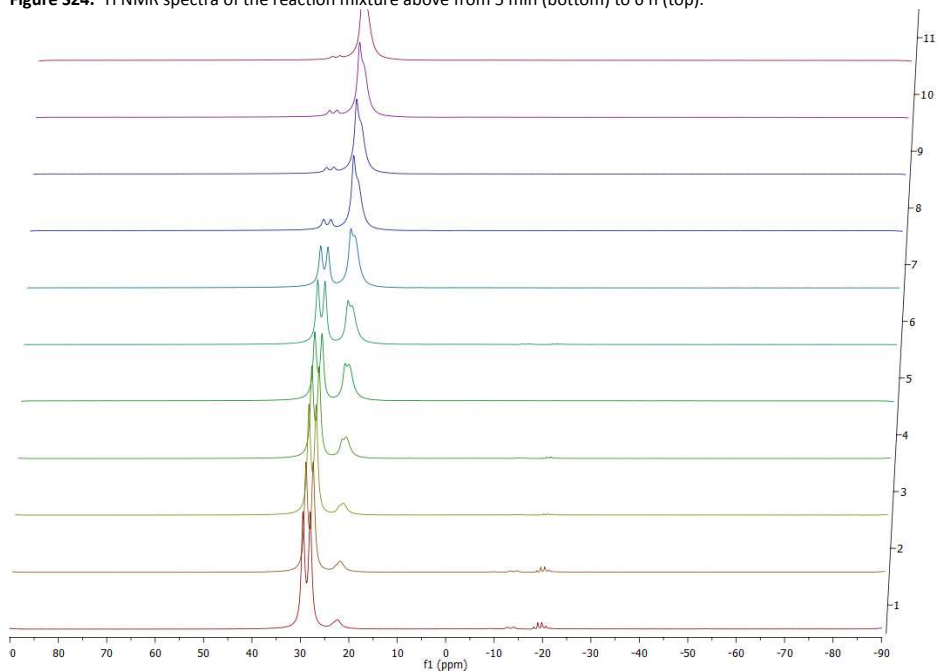


Figure S25. ¹¹B NMR spectrum of the reaction mixture above from 5 min (bottom) to 6 h (top)

Reaction between HBcat and CO₂ in the presence of catalyst 1 at 70 °C

In a N₂-filled glovebox, HBcat (101.2 mg, 65.2% purity, 0.549 mmol) was added into a 50 mL Schlenk bomb containing a solution of **1** (1.0 mg, 0.00549 mmol in 0.6 mL of C₆D₅Br). CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 2 h. The solution rapidly changed color from dark brown to light yellow. When the reaction mixture was cooled down to ambient temperature, a lot of white precipitate appeared. After the release of CO₂ gas from the system, hexamethylbenzene (0.1 mg, 0.0623 mmol) was added to the mixture. The conversion of HBcat to CH₃OBcat was monitored by ¹H NMR and ¹³B NMR. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum.

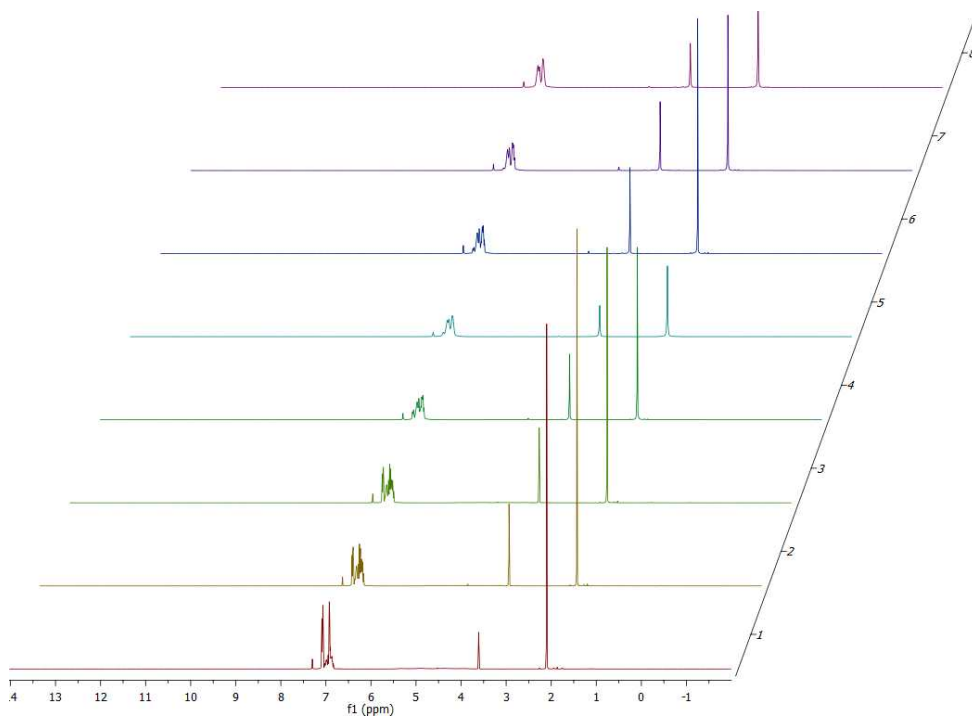
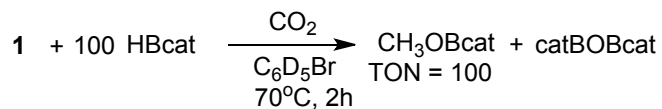


Figure S26. ¹H NMR spectrum of the reaction mixture above from 15 min (bottom) to 2 h (top)

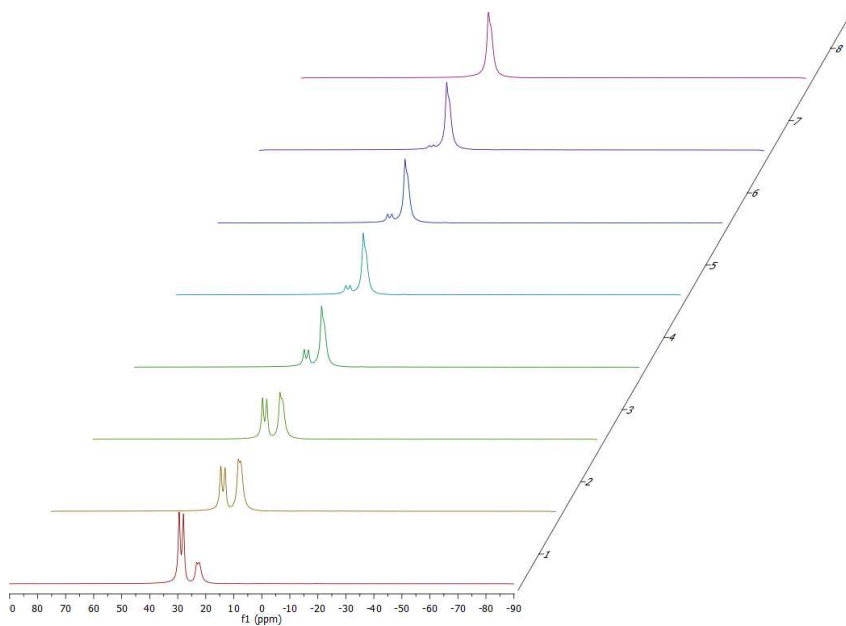


Figure S27. ¹³B NMR spectrum of the reaction mixture above from 15 min (bottom) to 2 h (top)

Reaction between HBcat and CO₂ in the presence of catalyst 1 at 70 °C

In a N₂-filled glovebox, HBcat (99.9 mg, 65.9% purity, 0.549 mmol) was added into a 50 mL Schlenk bomb containing a solution of **1** (1.0 mg, 0.00549 mmol in 0.6 mL of C₆D₅Br). CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 2 h. The solution rapidly changed color from dark brown to light yellow. When the reaction mixture was cooled to ambient temperature, a lot of white precipitates appeared. After 21.5 h, another batch of HBcat (100.0 mg, 65.9% purity, 0.549 mmol) was added into the reaction mixture. CO₂ was introduced using the same protocol as above. The reaction mixture was again stirred at 70 °C for 3 h. After cooling and the release of CO₂ gas from the system, hexamethylbenzene (11.4 mg, 0.0704 mmol) was added. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum.

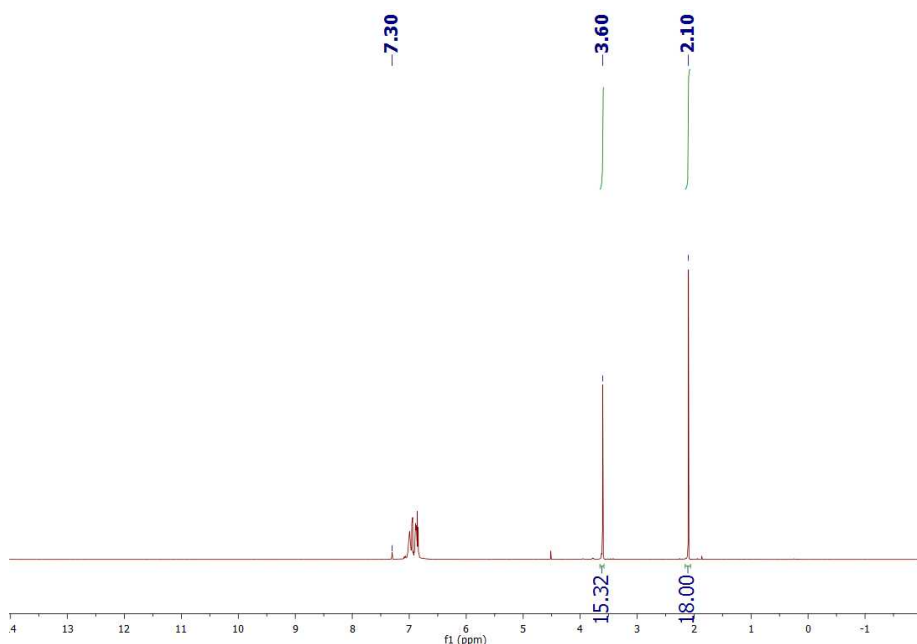
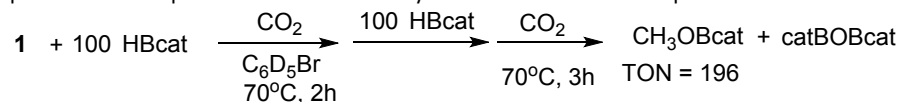


Figure S28. ¹H NMR spectrum of the final reaction mixture above

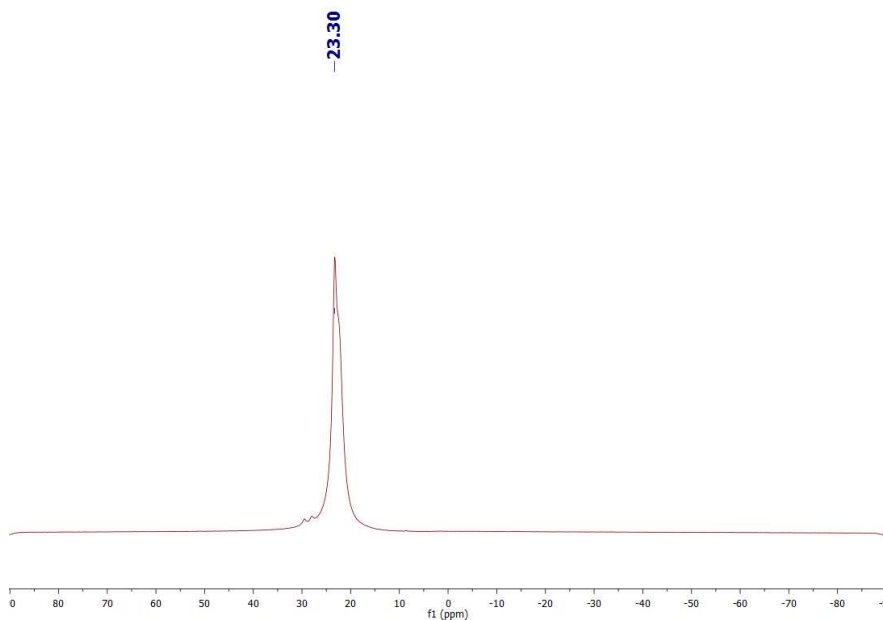
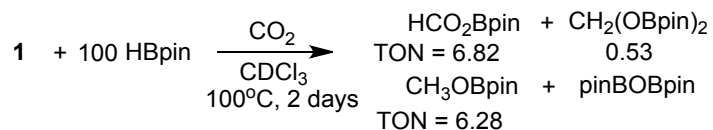


Figure S29. ¹¹B NMR spectrum of the final reaction mixture above

Reaction between HBpin and CO₂ in the presence of catalyst **1** at 100 °C

In a N₂-filled glovebox, HBpin (70.3 mg, 0.549 mmol) was added into a 50 mL Schlenk bomb containing a solution of **1** (1.0 mg, 0.00549 mmol) in 0.6 mL of CDCl₃. CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 100 °C for 48 h. The solution gradually changed color from dark blue to red and finally brown. After cooling and the release of CO₂ gas from the system, hexamethylbenzene (11.9 mg, 0.0734 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum.



HCO₂Bpin: ¹H NMR (CDCl₃, 400 MHz) δ: 8.42 (s, HCO₂Bpin)

CH₂(OBpin)₂: ¹H NMR (CDCl₃, 400 MHz) δ: 5.24 (s, CH₂(OBpin)₂)

CH₃OBpin: ¹H NMR (CDCl₃, 400 MHz) δ: 3.60 (s, CH₃OBpin)

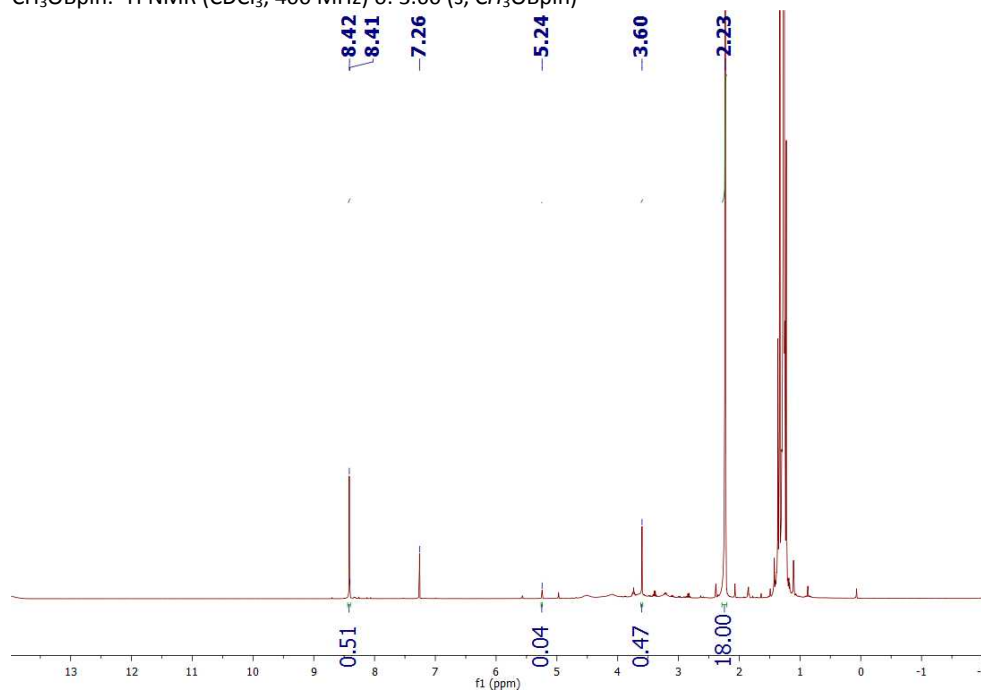


Figure S30. ¹H NMR spectrum of the final reaction mixture above

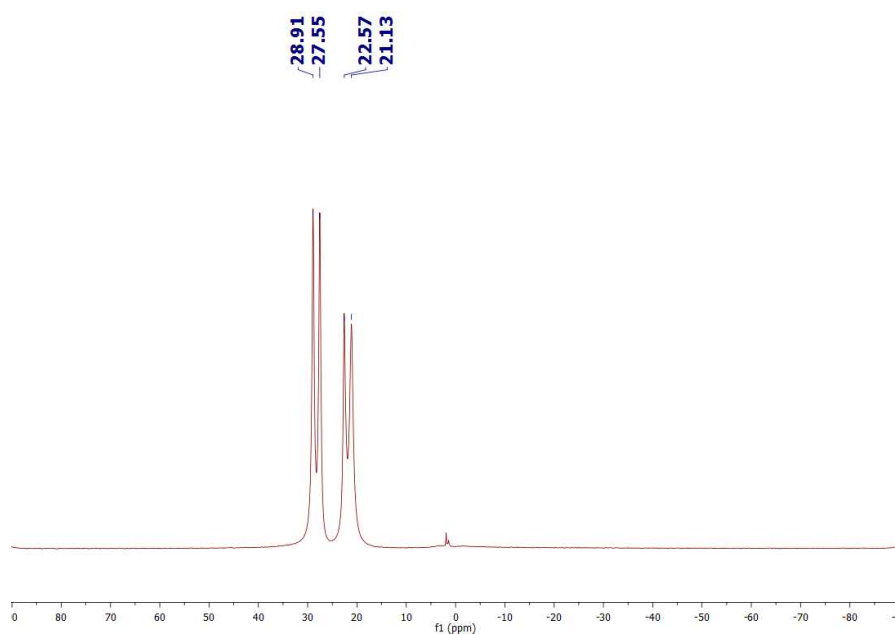
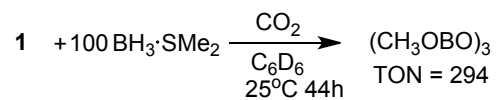


Figure S31. ¹¹B NMR spectrum of the final reaction mixture above

Reaction between $\text{BH}_3\cdot\text{SMe}_2$ and CO_2 in the presence of catalyst **1** at 25°C

In a N_2 -filled glovebox, a solution of $\text{BH}_3\cdot\text{SMe}_2$ (2.0 M in THF, 0.33 mL, 0.66 mmol) was added into a 50 mL Schlenk bomb containing a solution of **1** (1.2 mg, 0.00659 mmol in 0.6 mL of C_6D_6). CO_2 was introduced using the same protocol as above. The reaction mixture was stirred at 25°C for 44 h. After the release of CO_2 gas from the system, hexamethylbenzene (0.9 mg, 0.0056 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ^1H NMR spectrum.



$(\text{CH}_3\text{OBO})_3$: ^1H NMR (C_6D_6 , 400 MHz) δ : 3.39 (s, $(\text{CH}_3\text{OBO})_3$); ^{13}C NMR (C_6D_6 , 100 MHz) δ : 51.34 ($(\text{CH}_3\text{OBO})_3$).

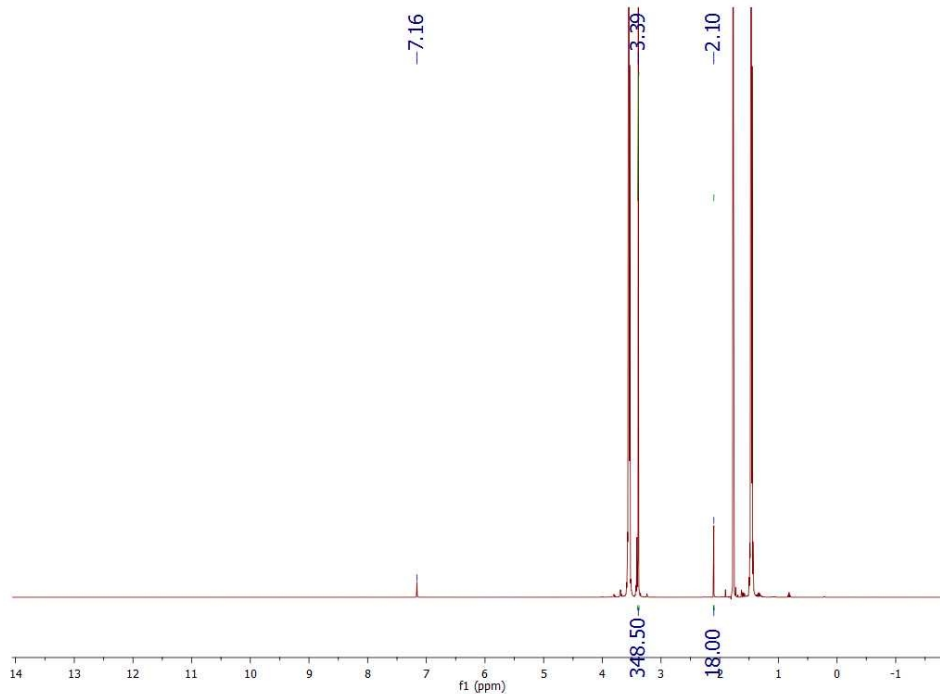


Figure S32. ^1H NMR spectrum of the final reaction mixture above

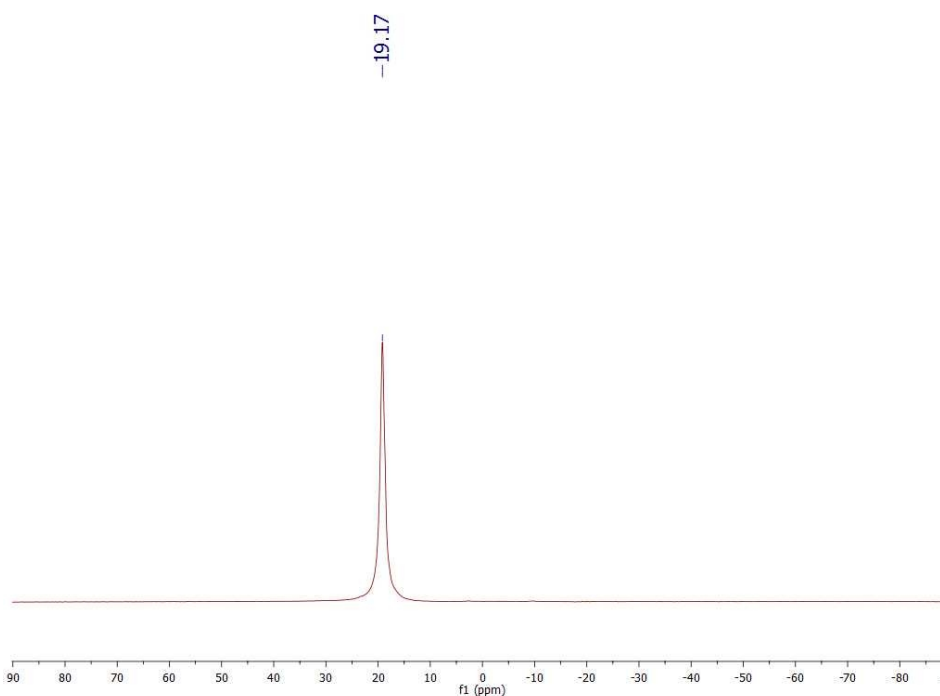
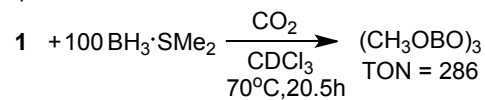


Figure S33. ^{13}C NMR spectrum of the final reaction mixture above

Reaction between $\text{BH}_3\cdot\text{SMe}_2$ and CO_2 in the presence of catalyst **1** at 70 °C

In a N_2 -filled glovebox, a solution of $\text{BH}_3\cdot\text{SMe}_2$ (2.0 M in THF, 0.275 mL, 0.549 mmol) was added into a 50 mL Schlenk bomb containing a solution of **1** (1.0 mg, 0.00549 mmol in 0.6 mL of CDCl_3). CO_2 was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 20.5 h. After cooling and the release of CO_2 gas from the system, hexamethylbenzene (1.0 mg, 0.0062 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ^1H NMR spectrum.



$(\text{CH}_3\text{OBO})_3$: ^1H NMR (CDCl_3 , 400 MHz) δ : 3.51 (s, $(\text{CH}_3\text{OBO})_3$)

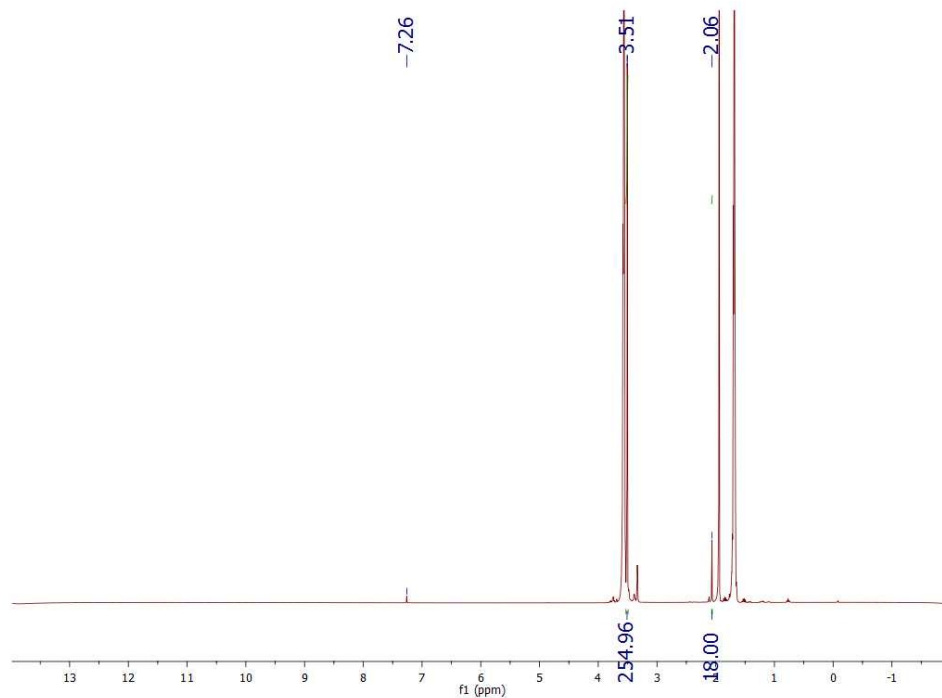


Figure S34. ^1H NMR spectrum of the final reaction mixture above

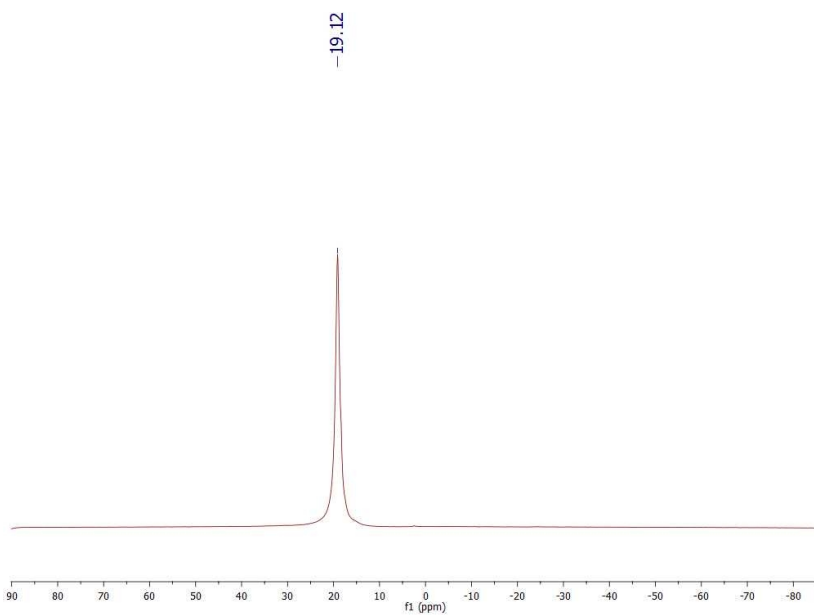
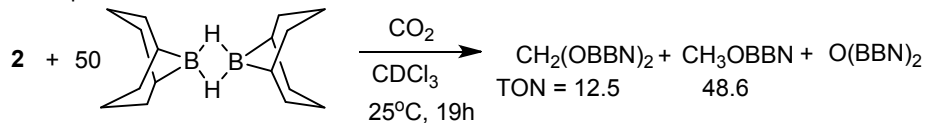


Figure S35. ^{11}B NMR spectrum of the final reaction mixture above

Reaction between 9-BBN and CO₂ in the presence of catalyst **2** at 25°C

In a N₂-filled glovebox, 9-BBN dimer (76.8 mg, 0.315 mmol) was added into a 50 mL Schlenk bomb containing a solution of **2** (1.0 mg, 0.00629 mmol) in 0.3 mL of CDCl₃. CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 25 °C for 19 h. The bomb was shipped into a N₂-filled glovebox. After releasing CO₂ gas from the system, hexamethylbenzene (13.0 mg, 0.0802 mmol) was then added to the reaction mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum.



CH₂(OBBN)₂: ¹H NMR (CDCl₃, 600 MHz) δ: 5.57 (s, CH₂(OBBN)₂); ¹³C NMR (CDCl₃, 150 MHz) δ: 86.39 (CH₂(OBBN)₂).
CH₃OBBN: ¹H NMR (CDCl₃, 600 MHz) δ: 3.77 (s, CH₃OBBN); ¹³C NMR (CDCl₃, 150 MHz) δ: 53.73 (CH₃OBBN).

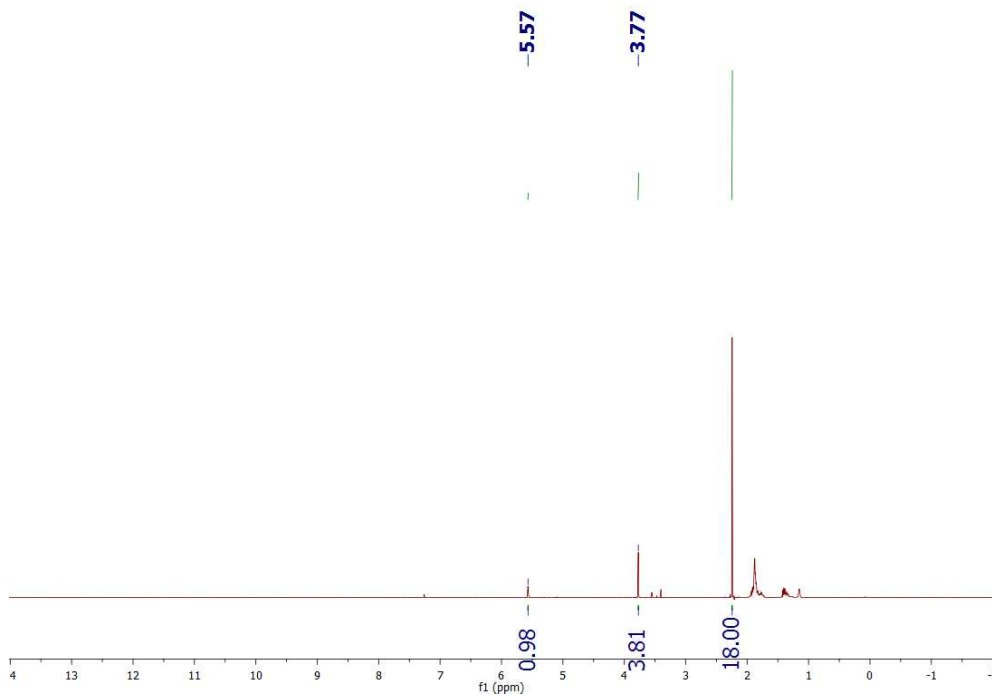


Figure S36. ¹H NMR spectrum of the final reaction mixture above

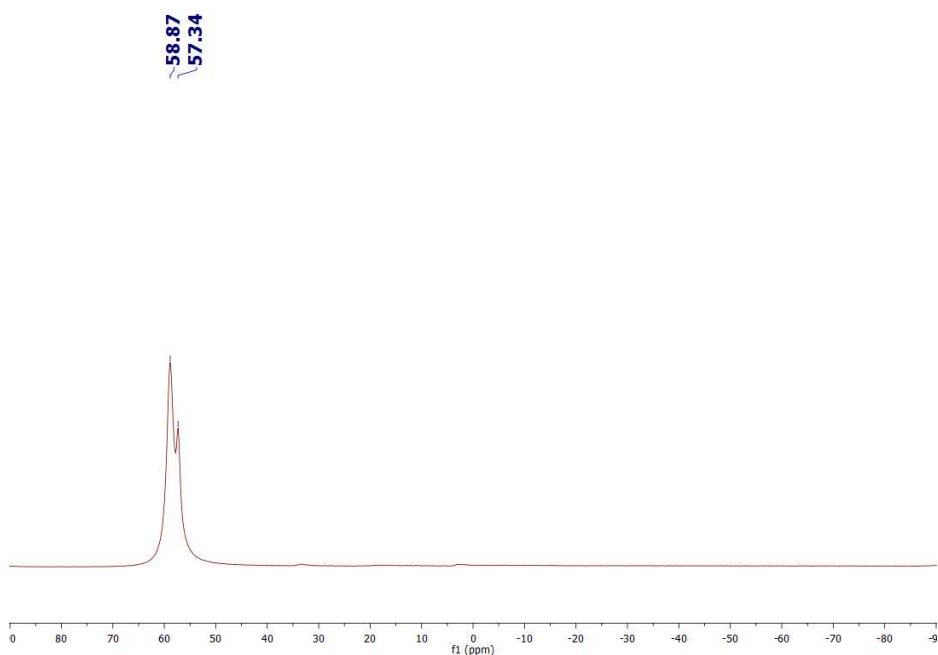


Figure S37. ¹¹B NMR spectrum of the final reaction mixture above.

Reaction between 9-BBN and CO₂ in the presence of catalyst **2** at 70 °C

In a N₂-filled glovebox, 9-BBN dimer (76.8 mg, 0.315 mmol) was added into a 50 mL Schlenk bomb containing a solution of **2** (1.0 mg, 0.00629 mmol) in 0.3 mL of CDCl₃. CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 2 h. The bomb was shipped into a N₂-filled glovebox. After cooling and releasing CO₂ gas from the system, hexamethylbenzene (14.2 mg, 0.00876 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum.

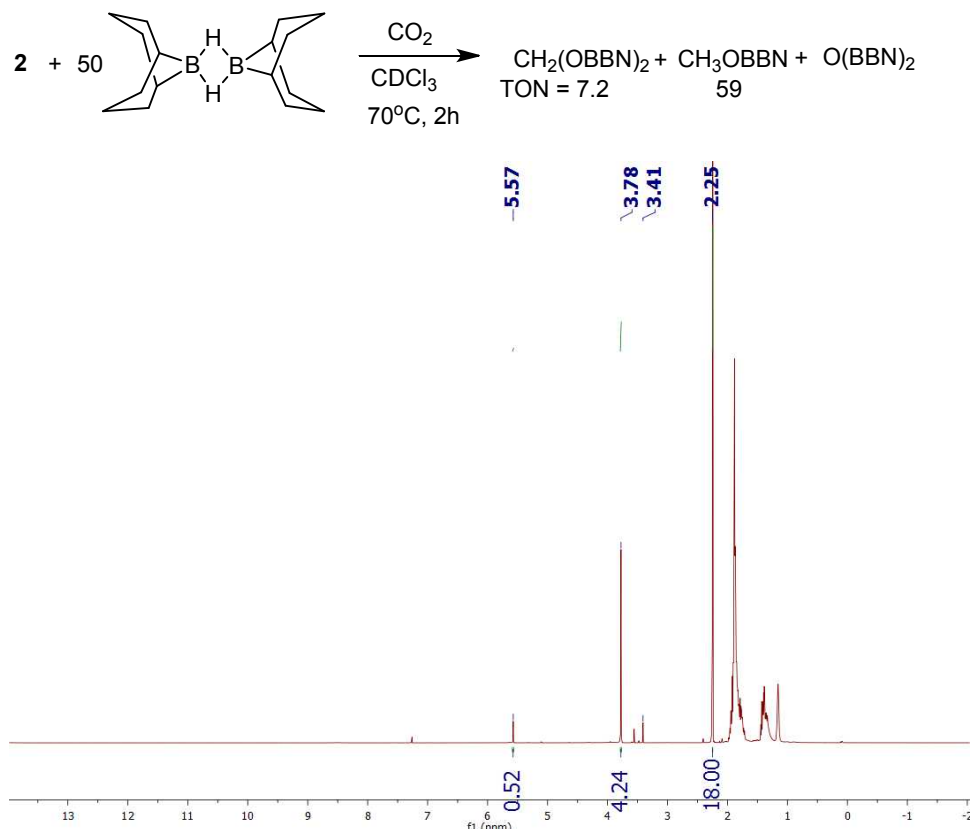


Figure S38. ¹H NMR spectrum of the final reaction mixture above

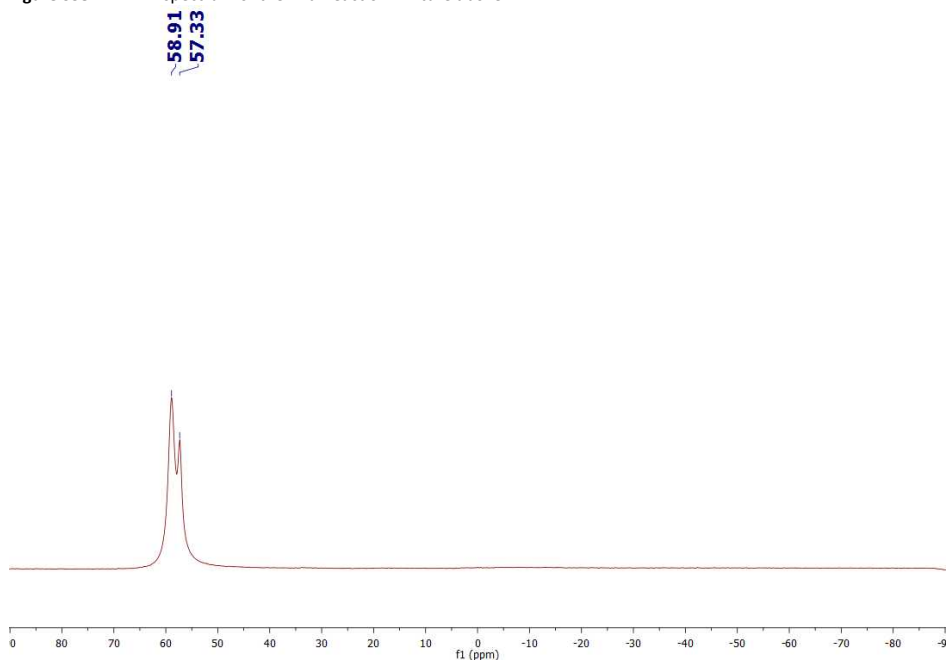
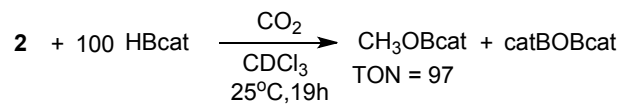


Figure S39. ¹¹B NMR spectrum of the final reaction mixture above

Reaction between HBcat and CO₂ in the presence of catalyst **2** at 25°C

In a N₂-filled glovebox, HBcat (107.0 mg, 70.5% purity, 0.629 mmol) was added into a 50 mL Schlenk bomb containing a solution of **2** (1.0 mg, 0.00629 mmol in 0.3 mL of CDCl₃). CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 25 °C for 19 h. After the release of CO₂ gas from the system, hexamethylbenzene (16.3mg, 0.100 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum.



CH₃OBcat: ¹H NMR (CDCl₃, 600MHz) δ: 3.90 (s, CH₃OBcat); ¹³C NMR (CDCl₃, 150 MHz) δ: 53.67 (CH₃OBcat).

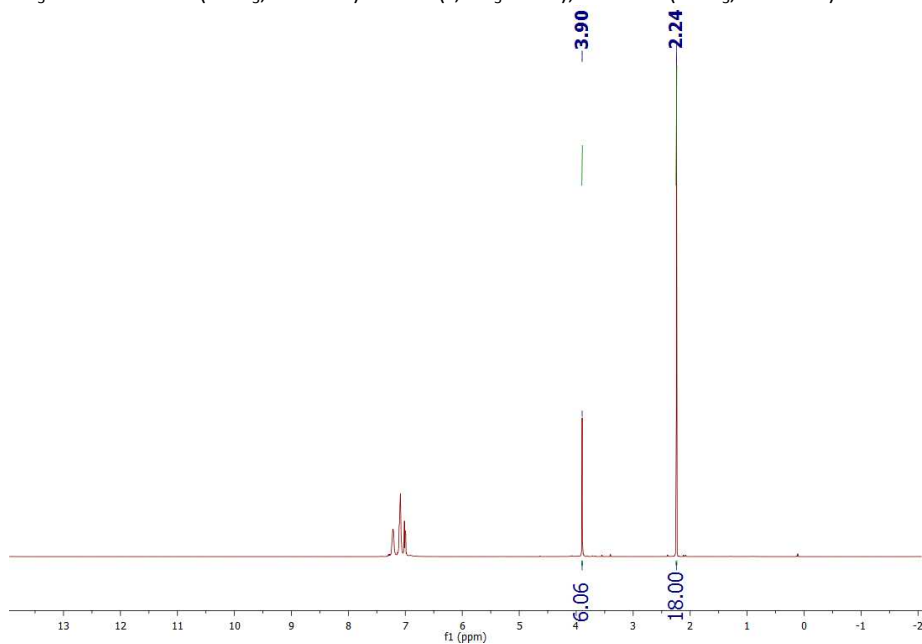


Figure S40. ¹H NMR spectrum of the final reaction mixture above

29.69
28.16
23.42
22.41

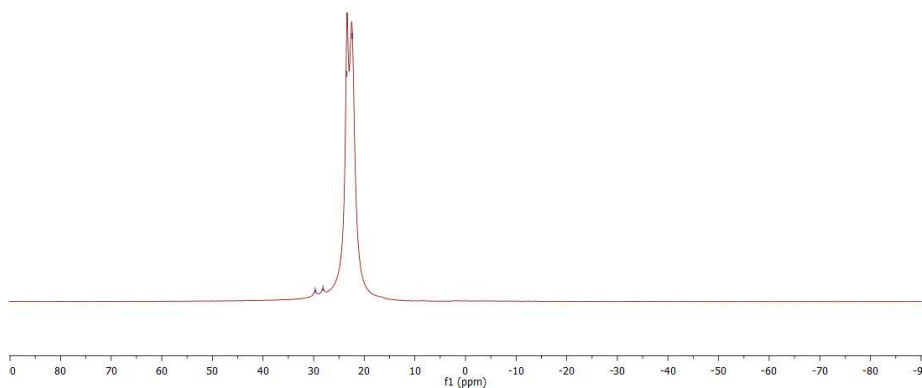
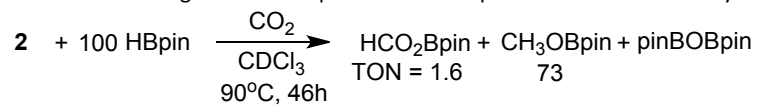


Figure S41. ¹³C NMR spectrum of the final reaction mixture above

Reaction between HBpin and CO₂ in the presence of catalyst **2** at 90 °C

In a N₂-filled glovebox, HBpin (81.1 mg, 0.629 mmol) was added into a 50 mL Schlenk bomb containing a solution of **2** (1.0 mg, 0.00629 mmol) in 0.3 mL of CDCl₃. CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 90 °C for 46 h. After cooling and the release of CO₂ gas from the system, hexamethylbenzene (13.8 mg, 0.0852 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum.



HCO₂Bpin: ¹H NMR (CDCl₃, 600 MHz) δ: 8.42 (s, HCO₂Bpin); ¹³C NMR (CDCl₃, 150 MHz) δ: 158.04 (HCO₂Bpin).

CH₃OBpin: ¹H NMR (CDCl₃, 600 MHz) δ: 3.59 (s, CH₃OBpin); ¹³C NMR (CDCl₃, 150 MHz) δ: 52.71 (CH₃OBpin).

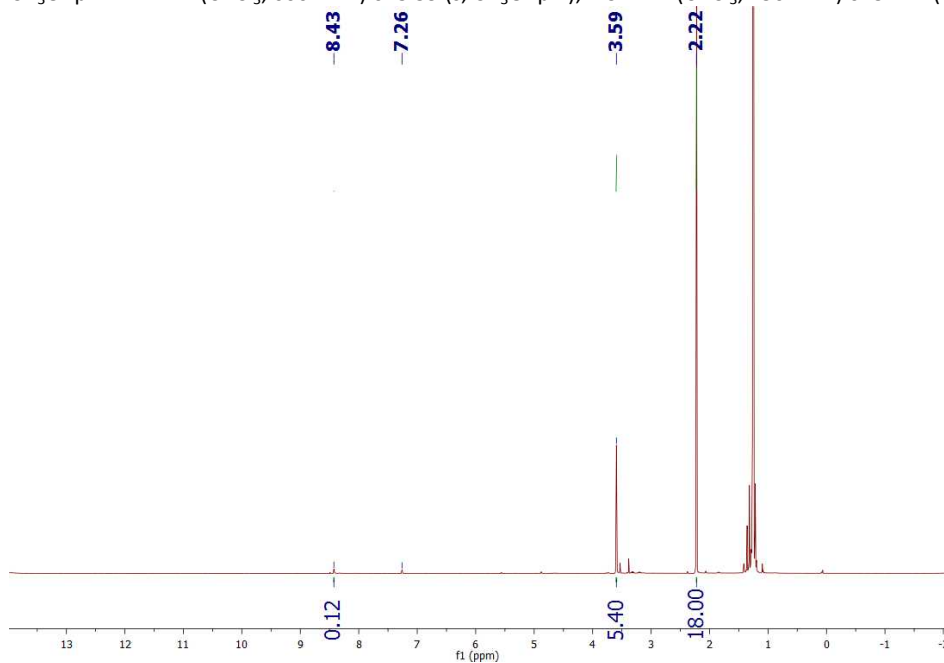


Figure S42. ¹H NMR spectrum of the final reaction mixture above

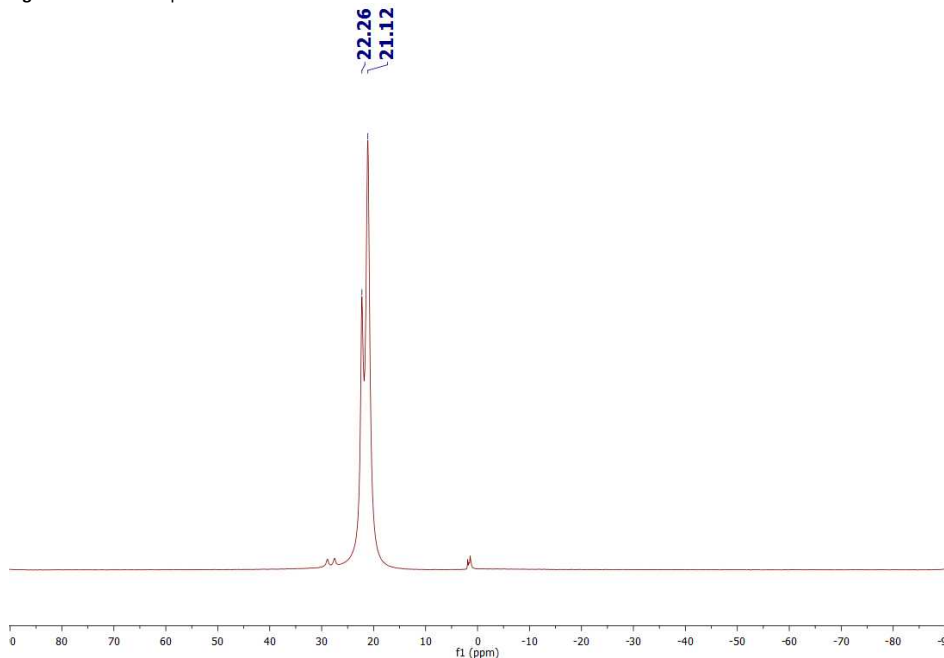
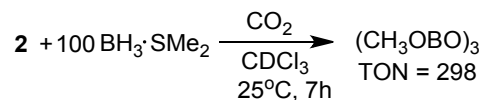


Figure S43. ¹³B NMR spectrum of the final reaction mixture above

Reaction between BH₃·SMe₂ and CO₂ in the presence of catalyst **2** at 25 °C

In a N₂-filled glovebox, a solution of BH₃·SMe₂ (2.0 M in THF, 0.31 mL, 0.629 mmol) was added into a 50 mL Schlenk bomb containing a solution of **2** (1.0 mg, 0.00629 mmol in 0.4 mL of CDCl₃). CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 25 °C for 7 h. After the release of CO₂ gas from the system, hexamethylbenzene (17.4 mg, 0.107 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum.



(CH₃OBO)₃: ¹H NMR (CDCl₃, 600 MHz) δ: 3.27 (s, (CH₃OBO)₃); ¹³C NMR (CDCl₃, 150 MHz) δ: 50.57 ((CH₃OBO)₃).

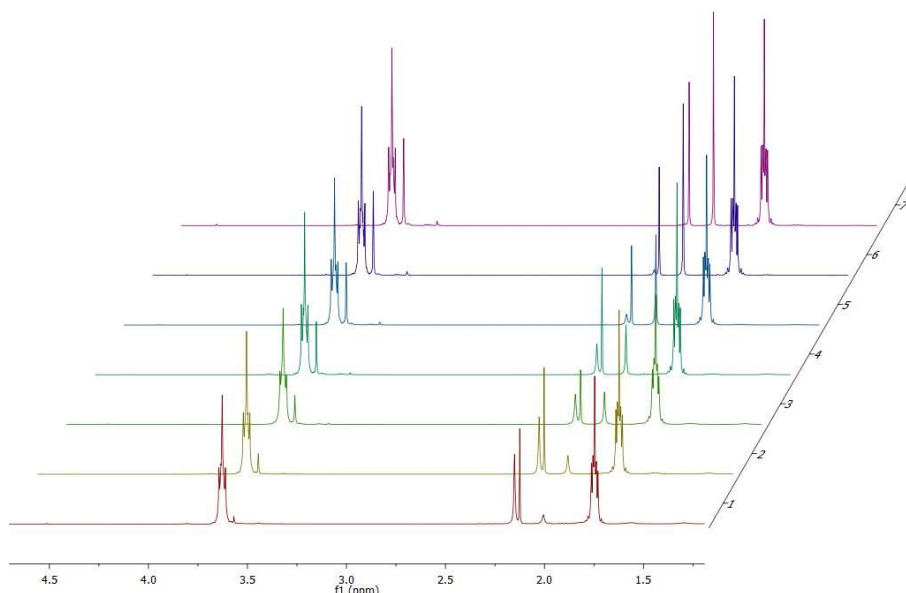


Figure S44. ¹H NMR spectra of the reaction mixture above from 1 h (bottom) to 7 h (top).

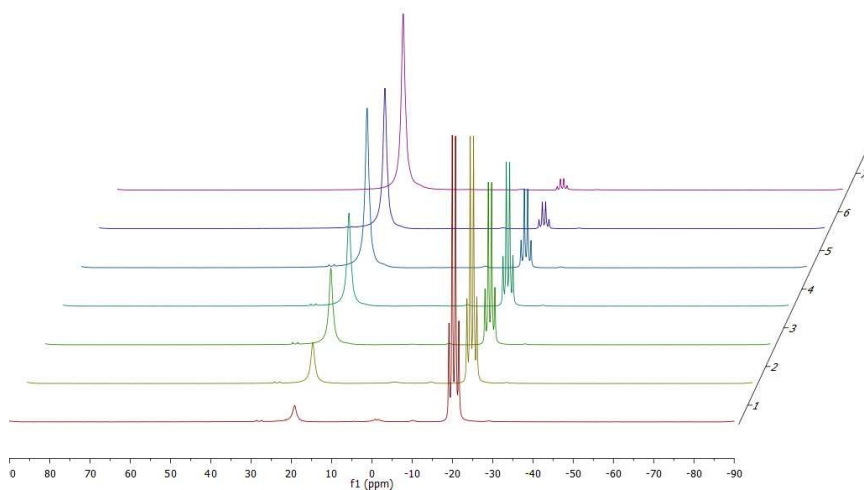


Figure S45. ¹¹B NMR spectrum of the reaction mixture above from 1 h (bottom) to 7 h (top).

Reference

- 1 V. T. Annibale, D. Song, *J. Am. Chem. Soc.*, **2013**, *135*, 161750-16183.
- 2 C. S. Giam and D. Ambrotich, *J. Chem. Soc., Chem. Commun.*, **1984**, *5*, 265-266.