

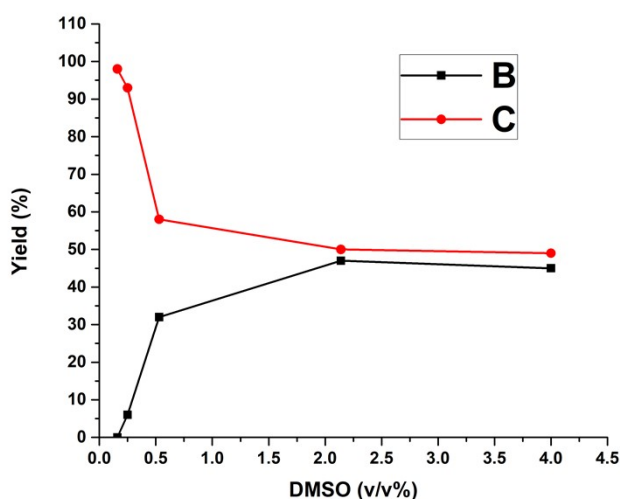
## Supplementary Information

## General experimental procedure

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk line or nitrogen-filled glove box. Petroleum ether (boiling point 40-60 °C) and other solvents were purified by distillation under a nitrogen atmosphere according to the standard procedures. Reagents were sourced from commercial suppliers and used without further purification. (9-BBN)<sub>2</sub> was synthesized according to the reported method.<sup>1</sup> <sup>1</sup>H NMR (400 MHz or 500 MHz), <sup>13</sup>C{<sup>1</sup>H} NMR (125.75 MHz) and <sup>11</sup>B NMR (160.46 MHz) were recorded at room temperature. <sup>1</sup>H NMR chemical shifts were referenced to the residual proton signal in the deuterated solvent and <sup>13</sup>C{<sup>1</sup>H} chemical shifts were referenced to the carbon signal of DMSO for samples recorded with D<sub>2</sub>O capillary or to the signal of carbon of CDCl<sub>3</sub>. For <sup>11</sup>B NMR, BF<sub>3</sub>•OEt<sub>2</sub> in CDCl<sub>3</sub> was employed as an external standard (0.0 ppm). All chemical shifts are reported in parts per million (ppm), and coupling constants are expressed in Hertz (Hz). High resolution mass spectra (ESI+/-) were obtained using Agilent AdvanceBio 6545XT LC/Q-TOF system. GC-MS analyses were performed on a Thermo Scientific TRACE 1300 system with an ISQ mass detector and the capillary column of TG-5MS (30 m × 0.25 mm × 0.25 μm, 5% phenyl methylpolysiloxane, 330/350 °C).

## Experimental procedure for monitoring of the CO<sub>2</sub> reduction in J. Young NMR tube

Inside a nitrogen filled glove box, 9-BBN (0.040 g, 0.3278 mmol), DMSO (1.7 μL, 7.3 mol%) and mesitylene (10.4 μL, 0.0749 mmol) were taken in a J. Young NMR tube, and then benzene (0.5 mL) was added. Subsequently, the NMR tube was taken out of the glove box and degassed by the freeze-pump-thaw method three times and filled with carbon dioxide, and the resulting reaction mixture was monitored by <sup>1</sup>H NMR method for every half an hour for the total of 16 h. After every half an hour, NMR tube was re-exposed to CO<sub>2</sub> (balloon, 1 atm) and spectra were recorded.



**Figure S1.** The change in the NMR yield of bis(boryl)acetal **B** and methoxyborane **C** as the % of DMSO in toluene (DMSO v/v%) changes.

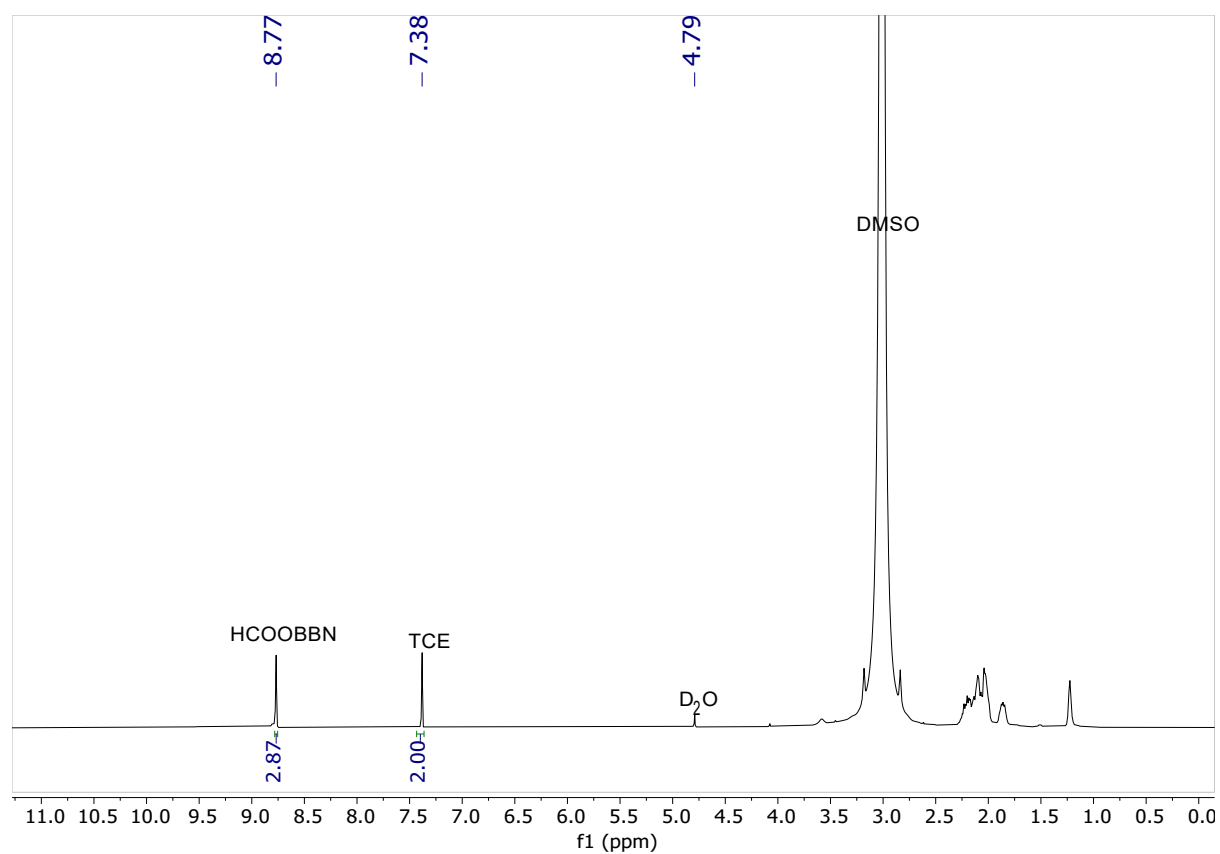
### X-ray structures and refinement data

The suitable single crystals of compound **E** were obtained by layering a toluene solution with petroleum ether. Data collection was performed using a Bruker D8 QUEST CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The space group for every structure was obtained by XPREP program. The structures were solved by SHELXT<sup>2</sup> which successfully located most of the nonhydrogen atoms. Subsequently, least-squares refinements were carried out on  $F^2$  using SHELXL Version 2018/3<sup>3</sup> to locate the remaining nonhydrogen atoms. Nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were fixed in calculated positions. The crystal structure was plotted using the ORTEP3 programme. The refinement data for the structure is summarized in Table S1. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. This data can be obtained free of charge upon quoting the depository number CCDC 2382681 from website at <http://www.ccdc.cam.ac.uk>.

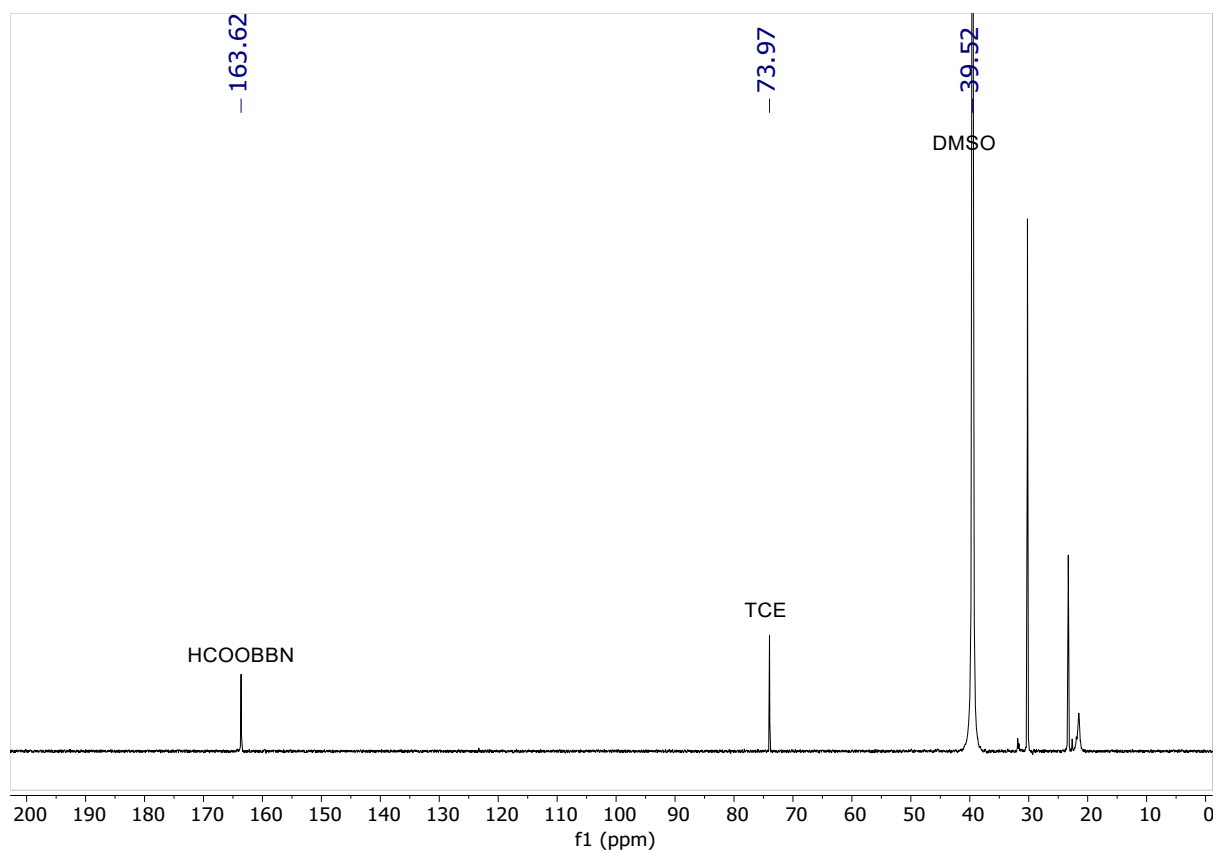
**Table S1. Crystallographic data for [HCOOBBN][DMSO] adduct, E**

Complex	E
Empirical formula	C <sub>11</sub> H <sub>21</sub> BO <sub>3</sub> S
Formula wt.	244.15
Temp, K	120.0
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	13.0315(18)
<i>b</i> , Å	6.5150(9)
<i>c</i> , Å	15.3340(19)
$\alpha$ , (°)	90
$\beta$ , (°)	98.689(4)
$\gamma$ , (°)	90
Volume, Å <sup>3</sup>	1286.9(3)
$\rho_{calc}$ , g/cm <sup>3</sup>	1.260
<i>Z</i>	4
Crystal size/mm	0.74 × 0.136 × 0.108
$\theta$ range (°)	2.687 to 24.992
$\lambda$ , Å	0.71073
<i>R</i> <sub>int</sub>	0.1306
GOF ( <i>F</i> <sup>2</sup> )	1.026
<i>R</i> <sub>1</sub>	0.0548
<i>wR</i> <sub>2</sub>	0.1094

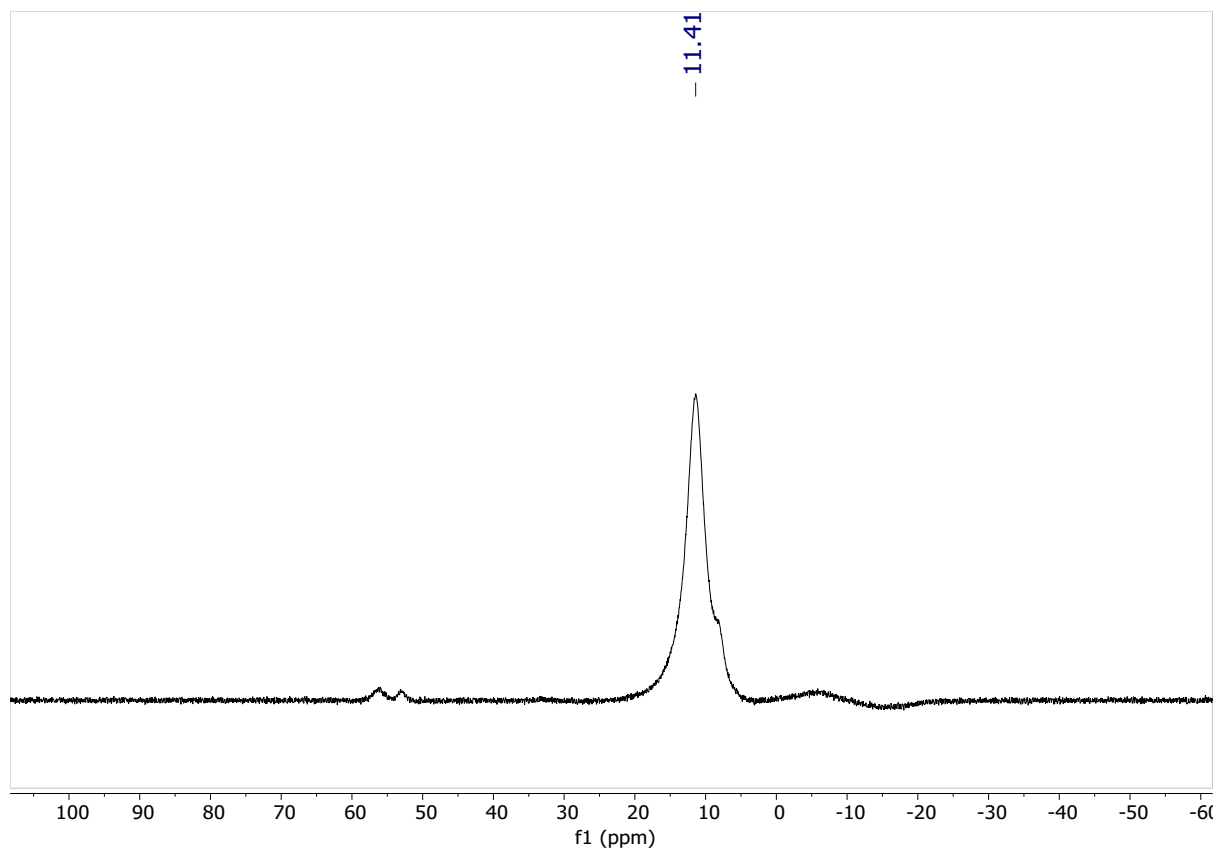
## For Table 1



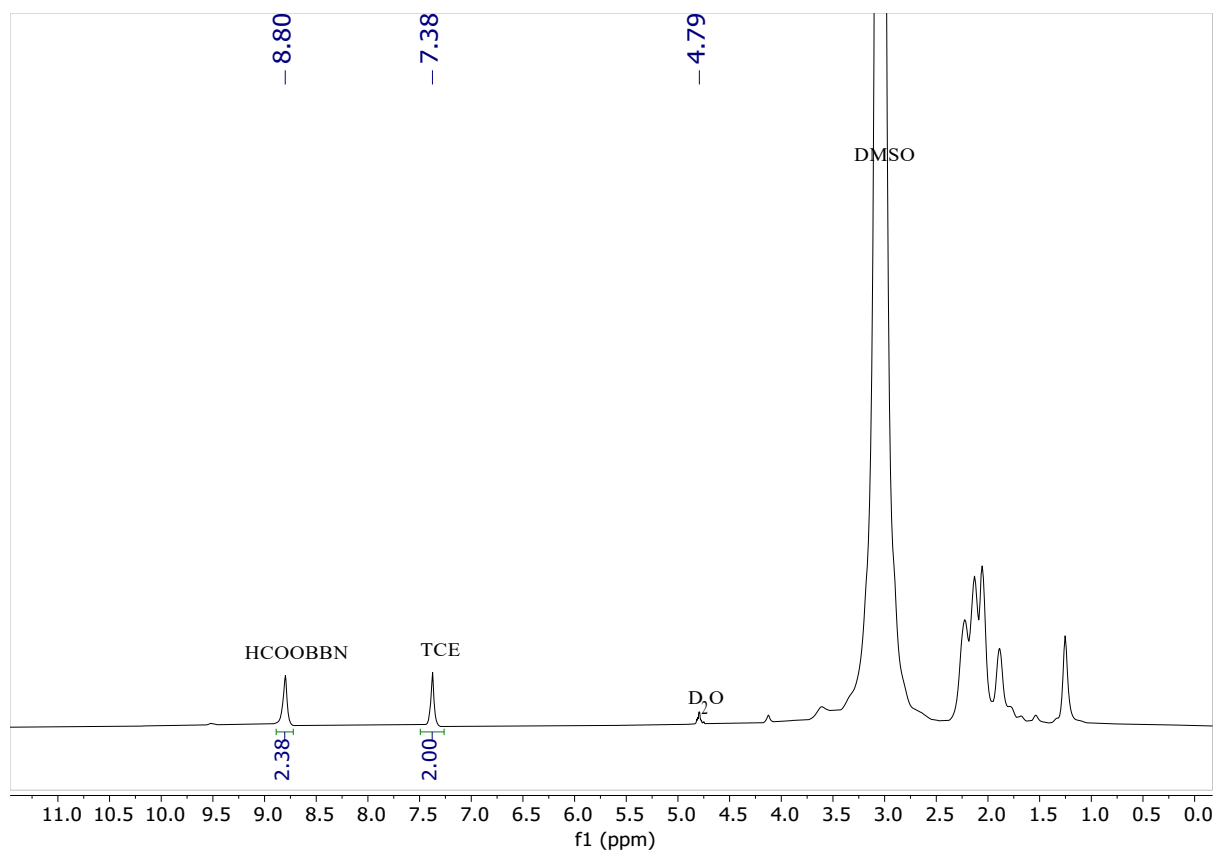
**Figure S2.** <sup>1</sup>H NMR (DMSO solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 2 h at 25 °C.



**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO solution with  $\text{D}_2\text{O}$  capillary, 125.75 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 25 °C.

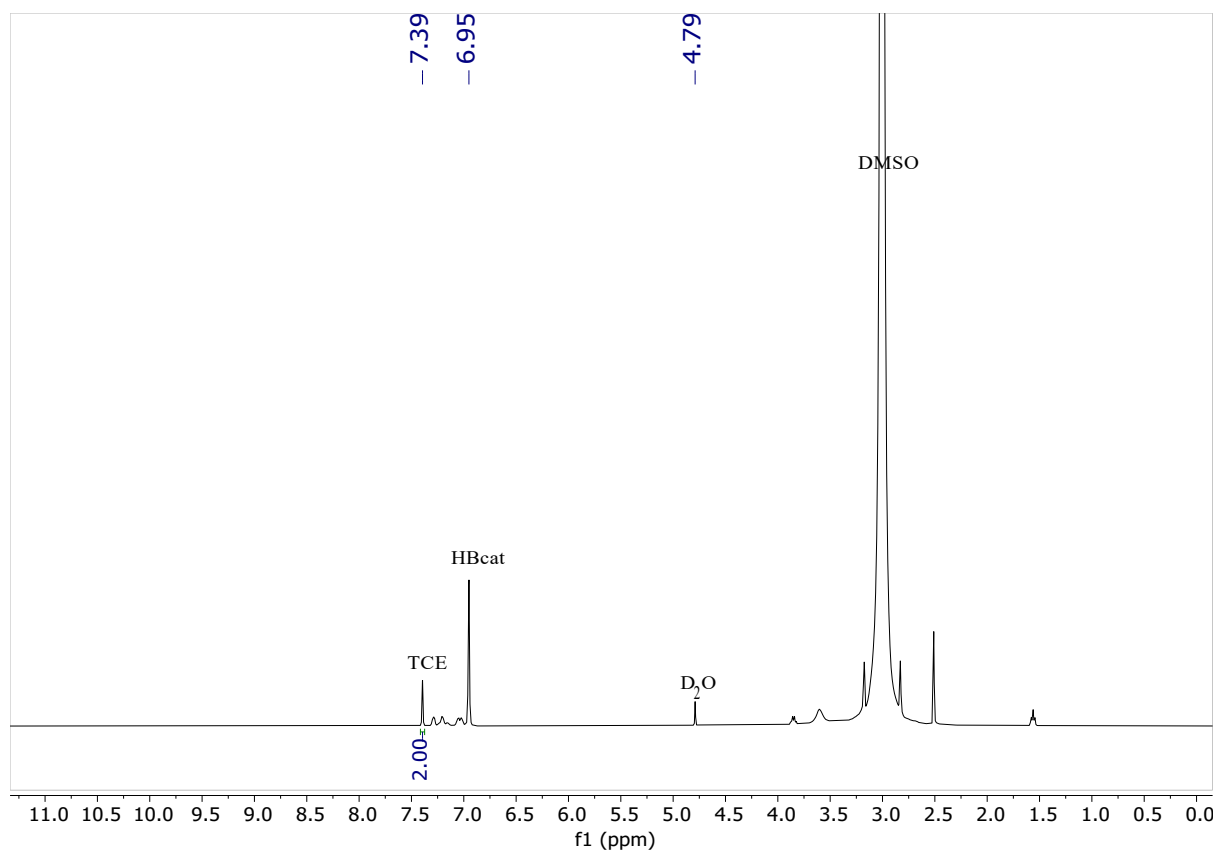


**Figure S4.**  $^{11}\text{B}$  NMR (DMSO solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 25 °C.

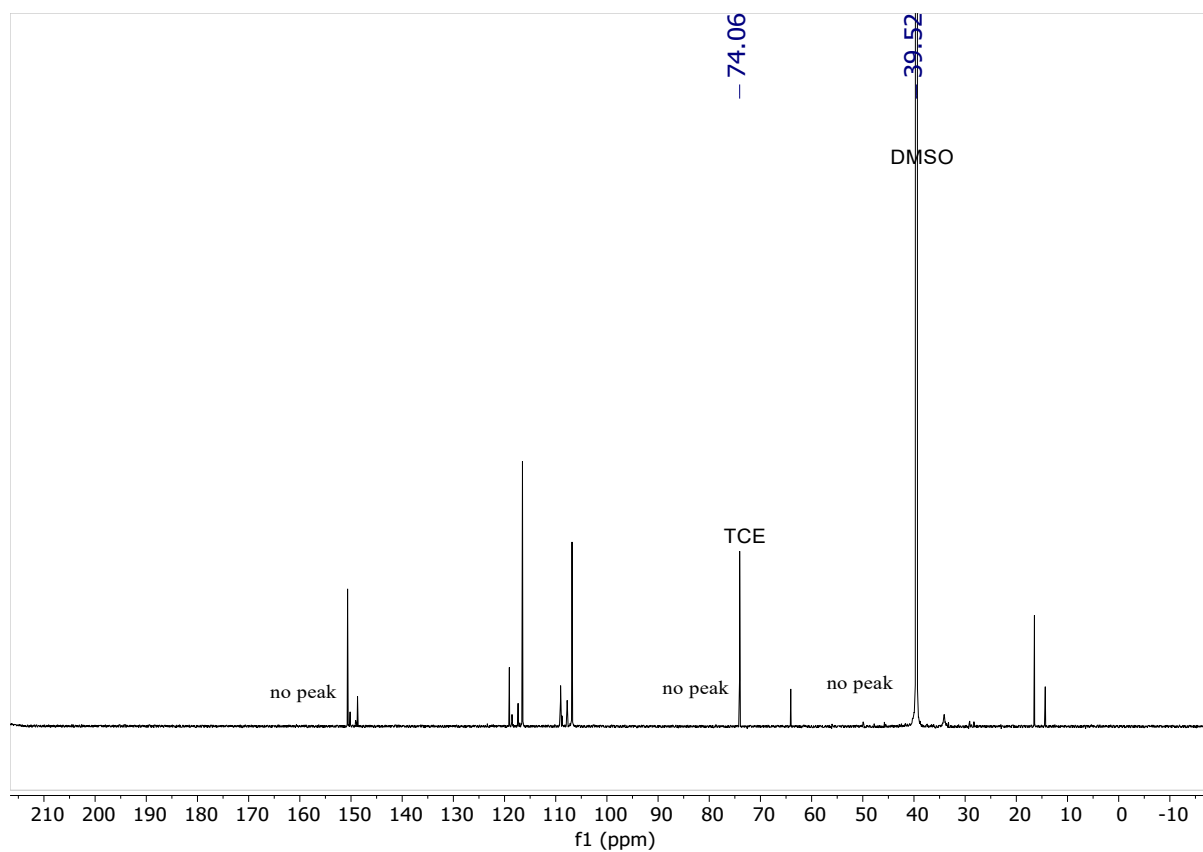


**Figure S5.**  $^1\text{H}$  NMR (DMSO solution with  $\text{D}_2\text{O}$  capillary, 500 MHz, 25  $^\circ\text{C}$ ) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (1.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 3 h at 25  $^\circ\text{C}$ .

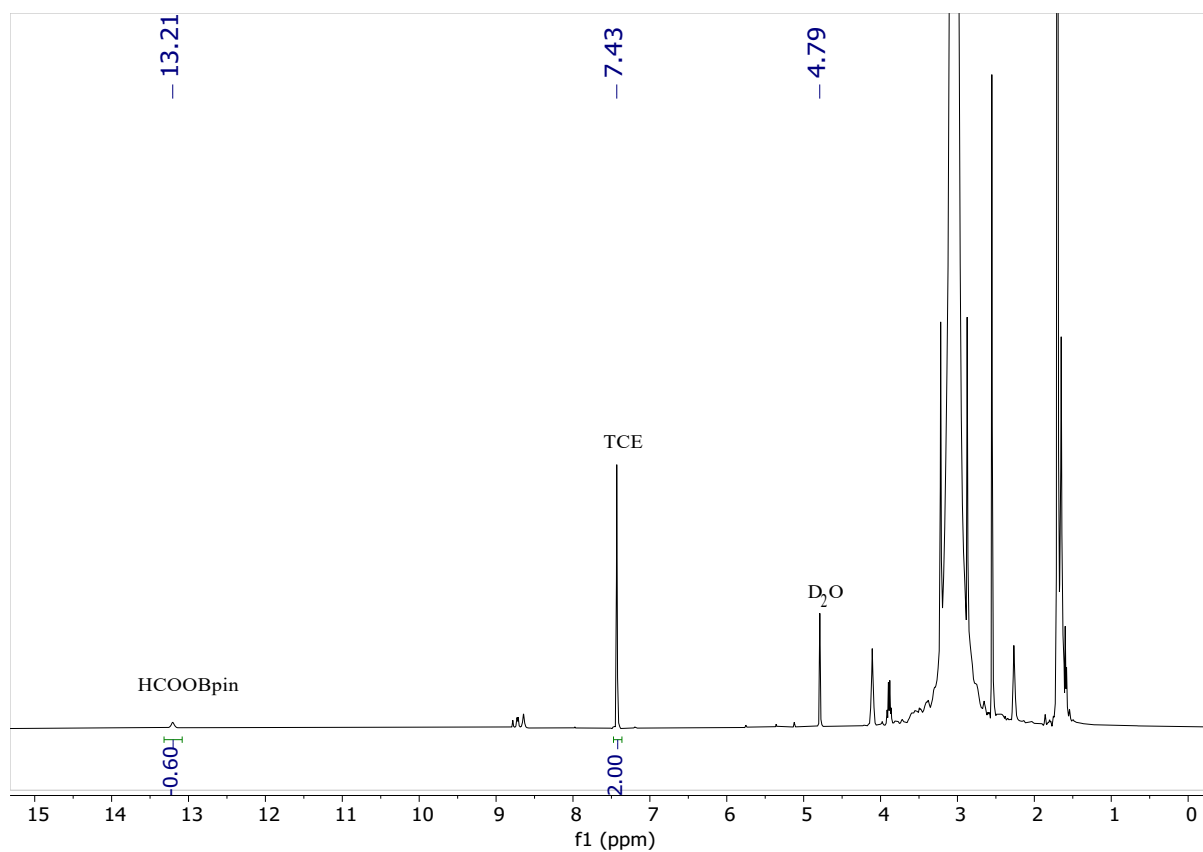




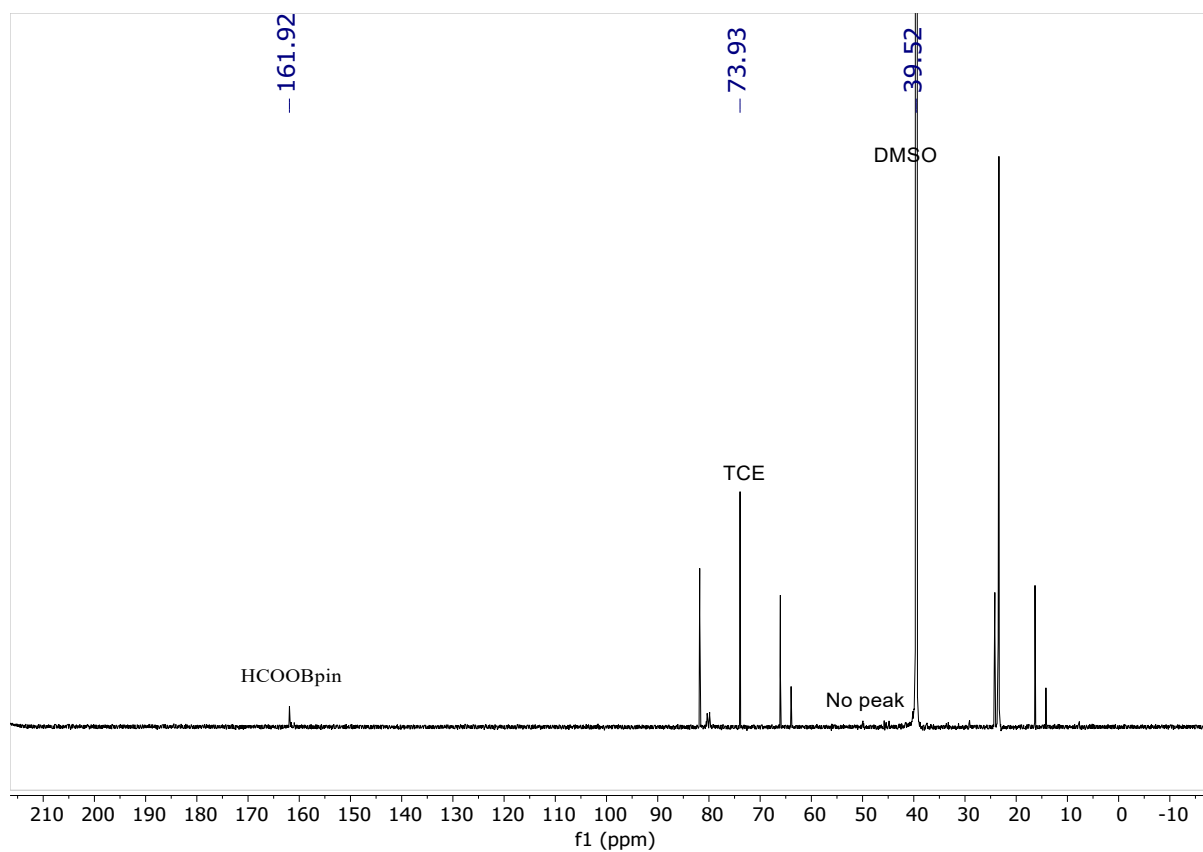
**Figure S6.**  $^1\text{H}$  NMR (DMSO solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25 °C) spectrum of reaction mixture of HBcat (1.0 mmol) and DMSO (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 3 h at 25 °C.



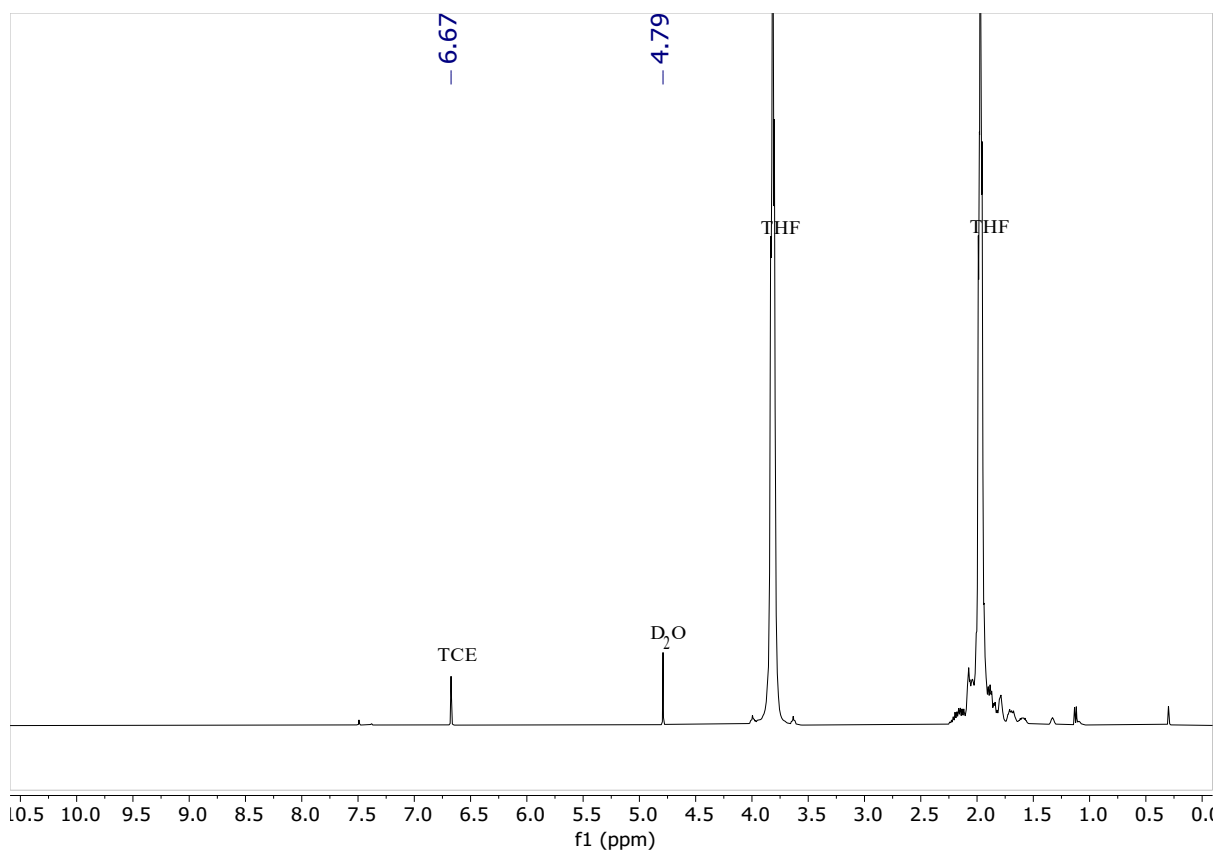
**Figure S7.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO solution with  $\text{D}_2\text{O}$  capillary, 125.75 MHz, 25 °C) spectrum of reaction mixture of HBcat (1.0 mmol) and DMSO (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 3 h at 25 °C.



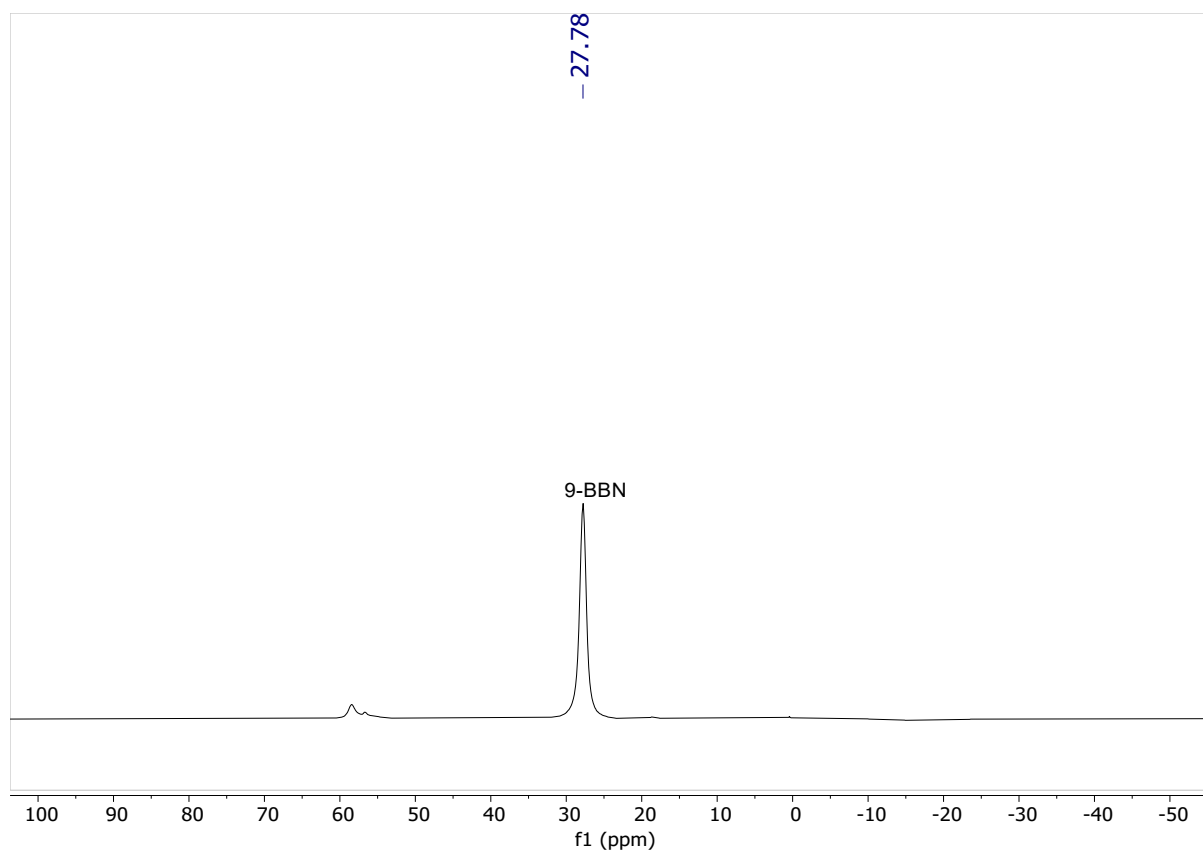
**Figure S8.** <sup>1</sup>H NMR (DMSO solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of HBpin (1.0 mmol) and DMSO (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 3 h at 25 °C.



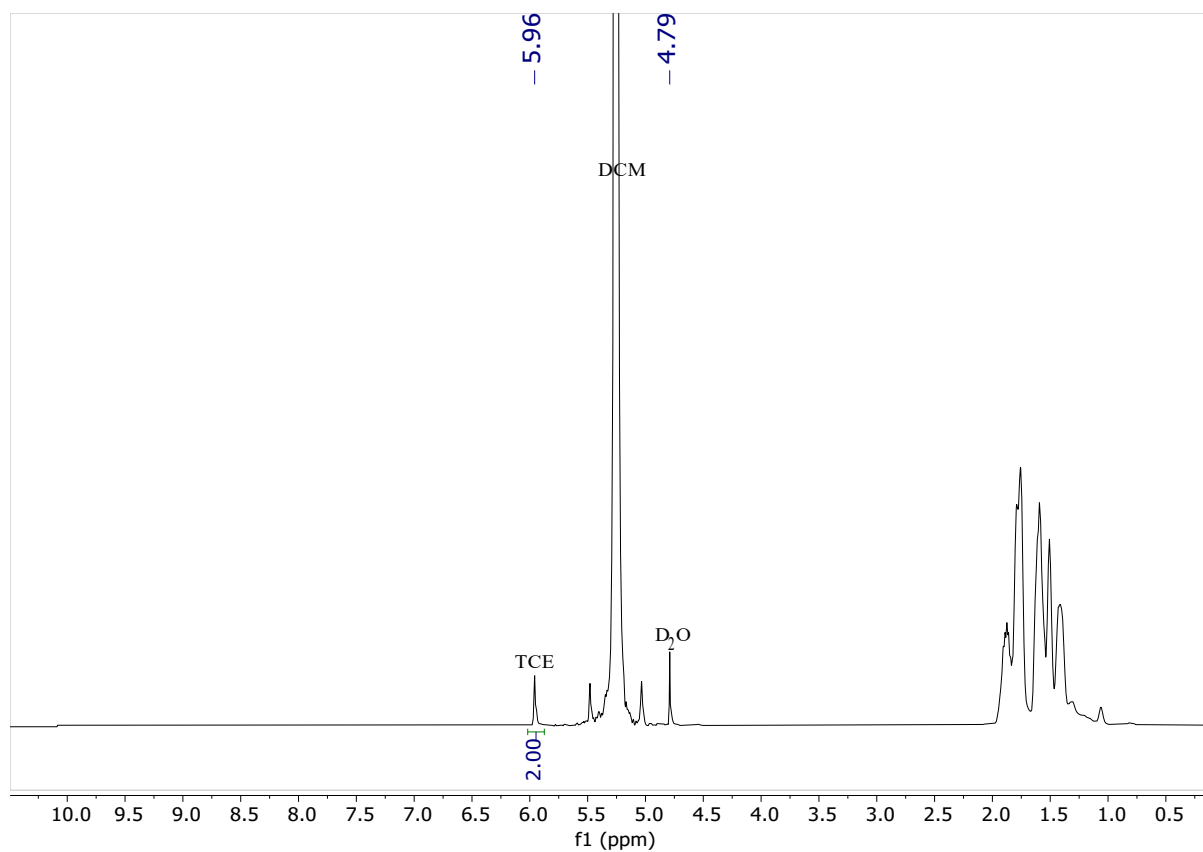
**Figure S9.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO solution with  $\text{D}_2\text{O}$  capillary, 125.75 MHz, 25 °C) spectrum of reaction mixture of HBpin (1.0 mmol) and DMSO (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 3 h at 25 °C.



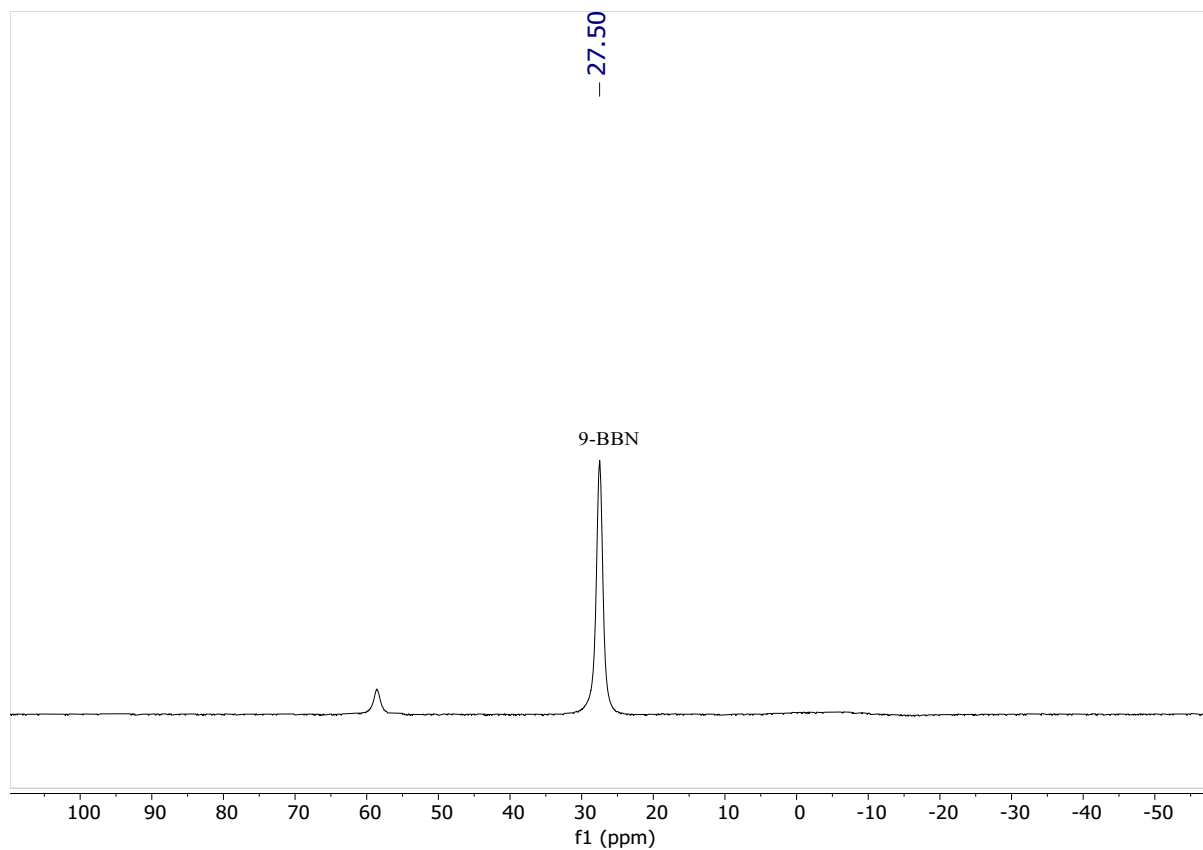
**Figure S10.** <sup>1</sup>H NMR (THF solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and THF (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 14 h at 25 °C.



**Figure S11.**  $^{11}\text{B}$  NMR (THF solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and THF (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for h at 25 °C.

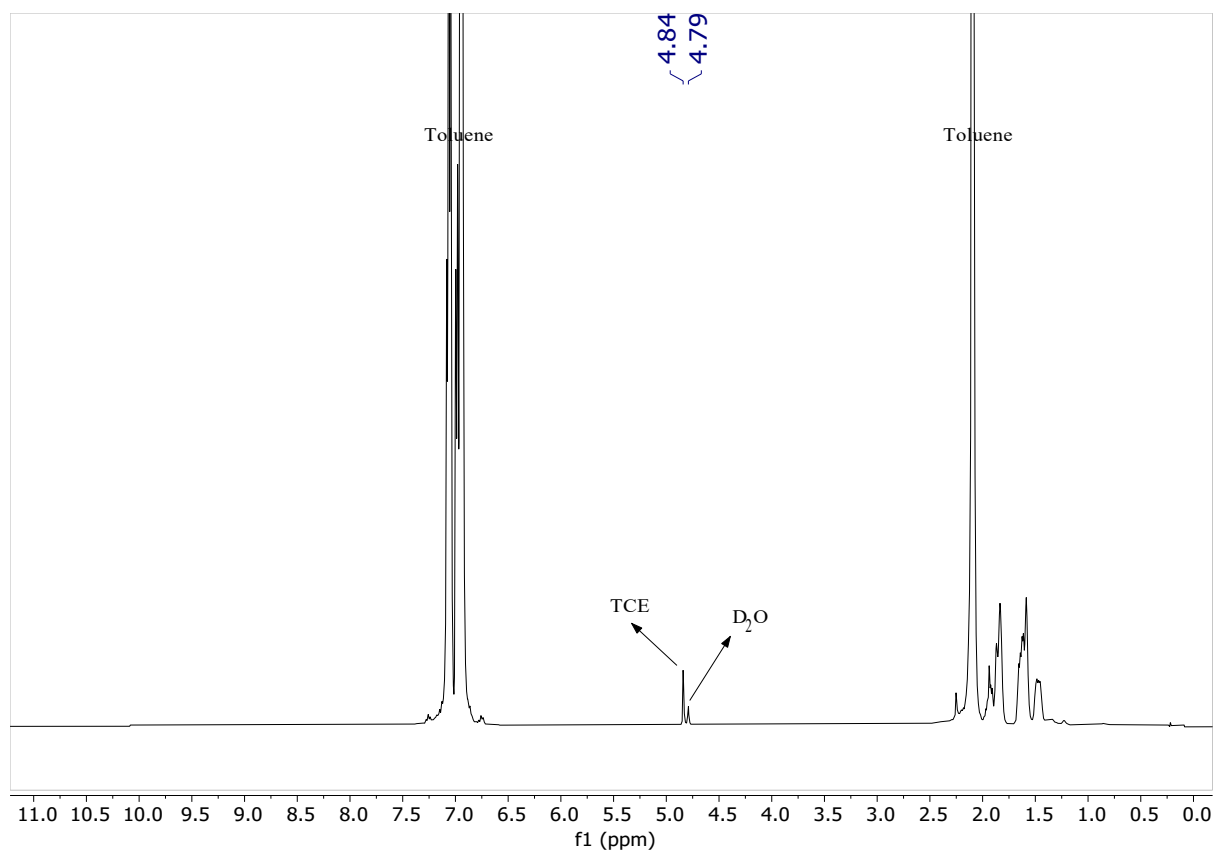


**Figure S12.** <sup>1</sup>H NMR (DCM solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DCM (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 14 h at 25 °C.

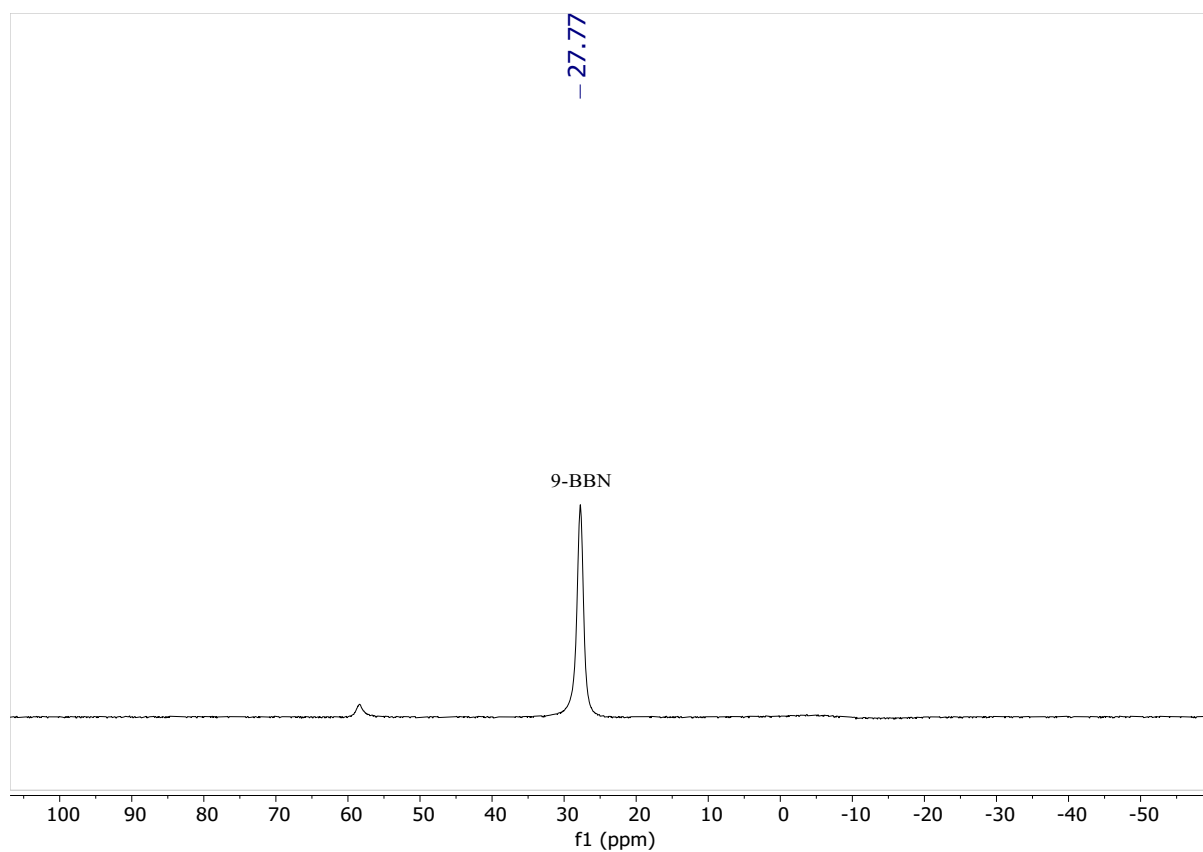


**Figure S13.**  $^{11}\text{B}$  NMR (DCM solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DCM (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 14 h at 25 °C.

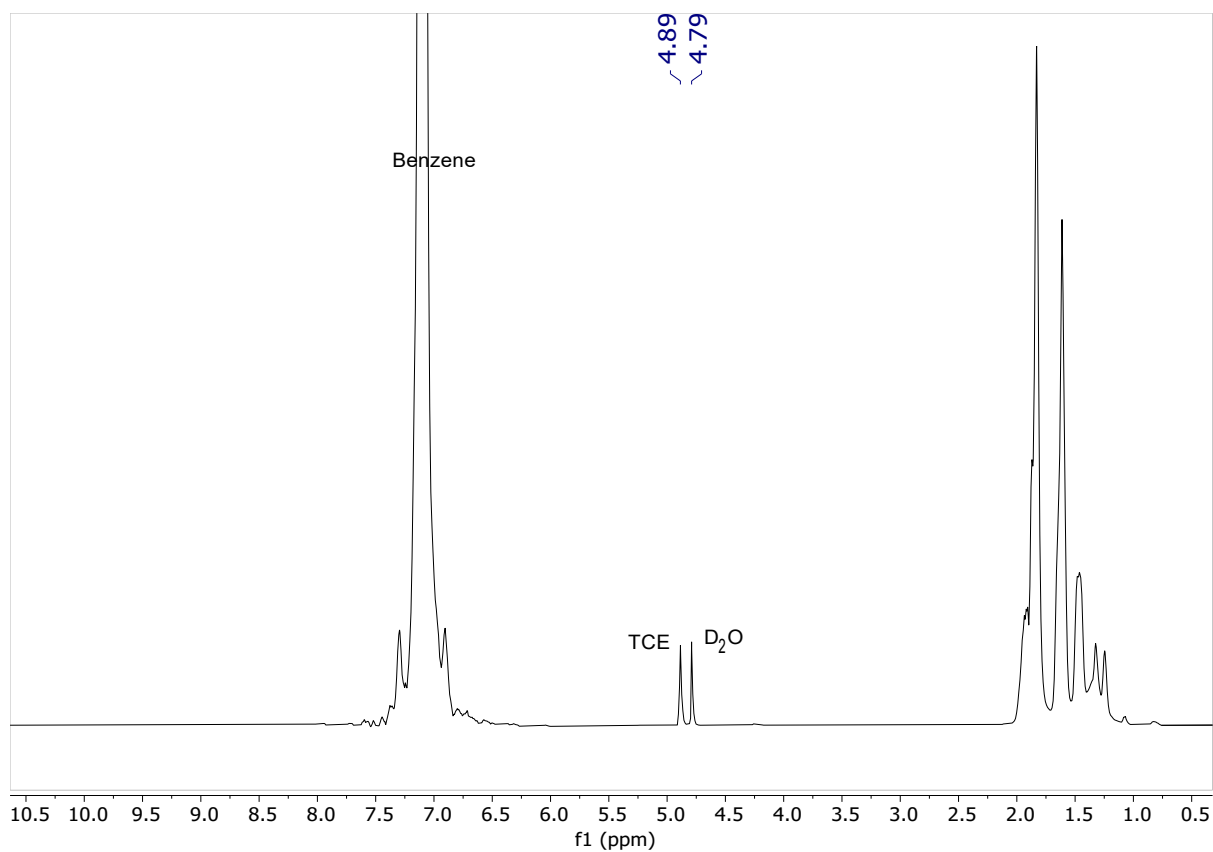




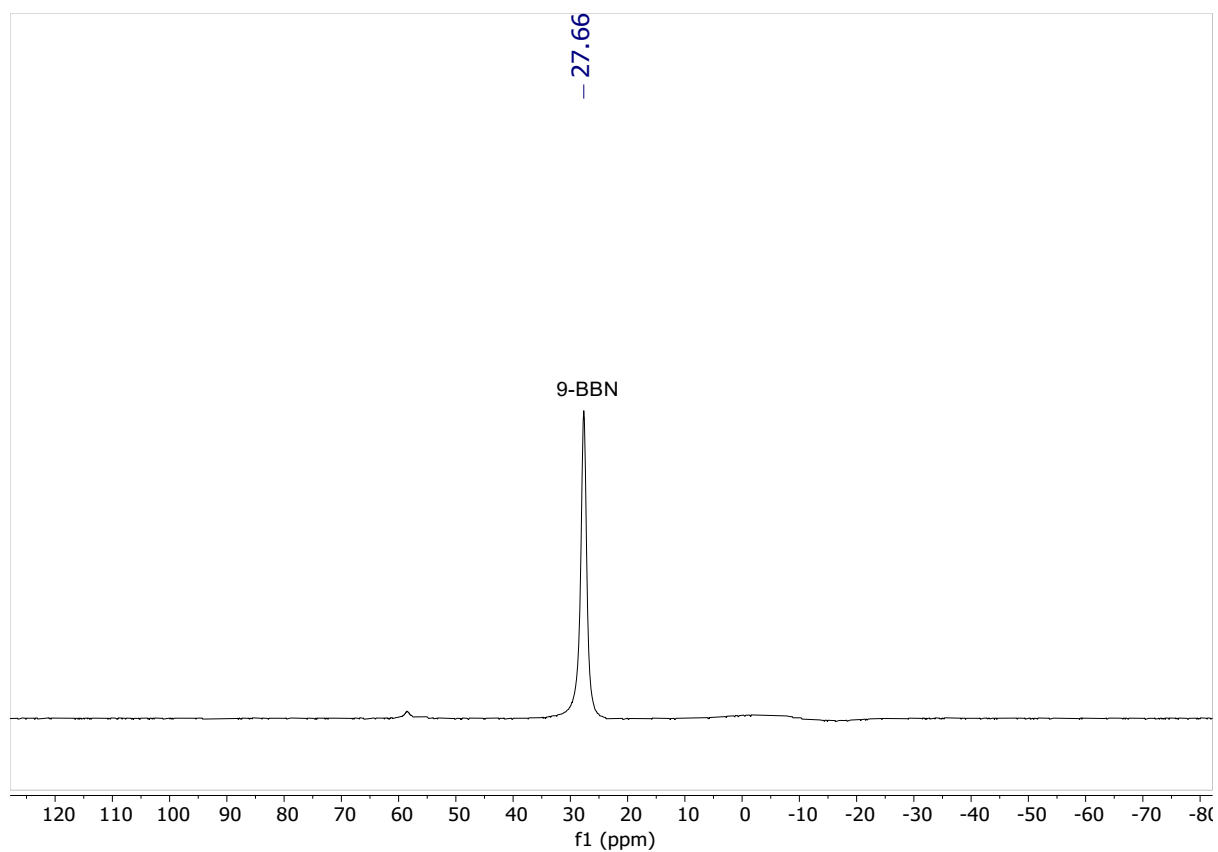
**Figure S14.** <sup>1</sup>H NMR (toluene solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and toluene (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 14 h at 25 °C.



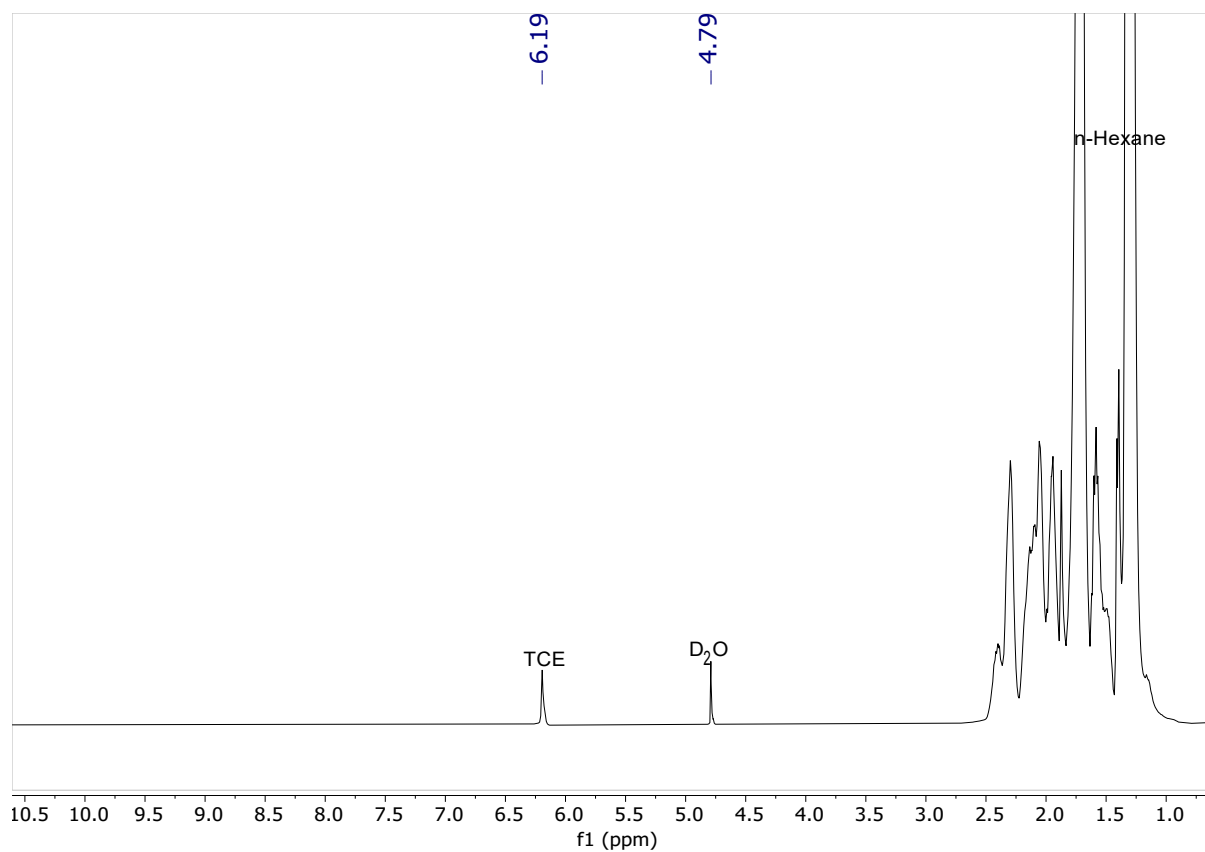
**Figure S15.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 14 h at 25 °C.



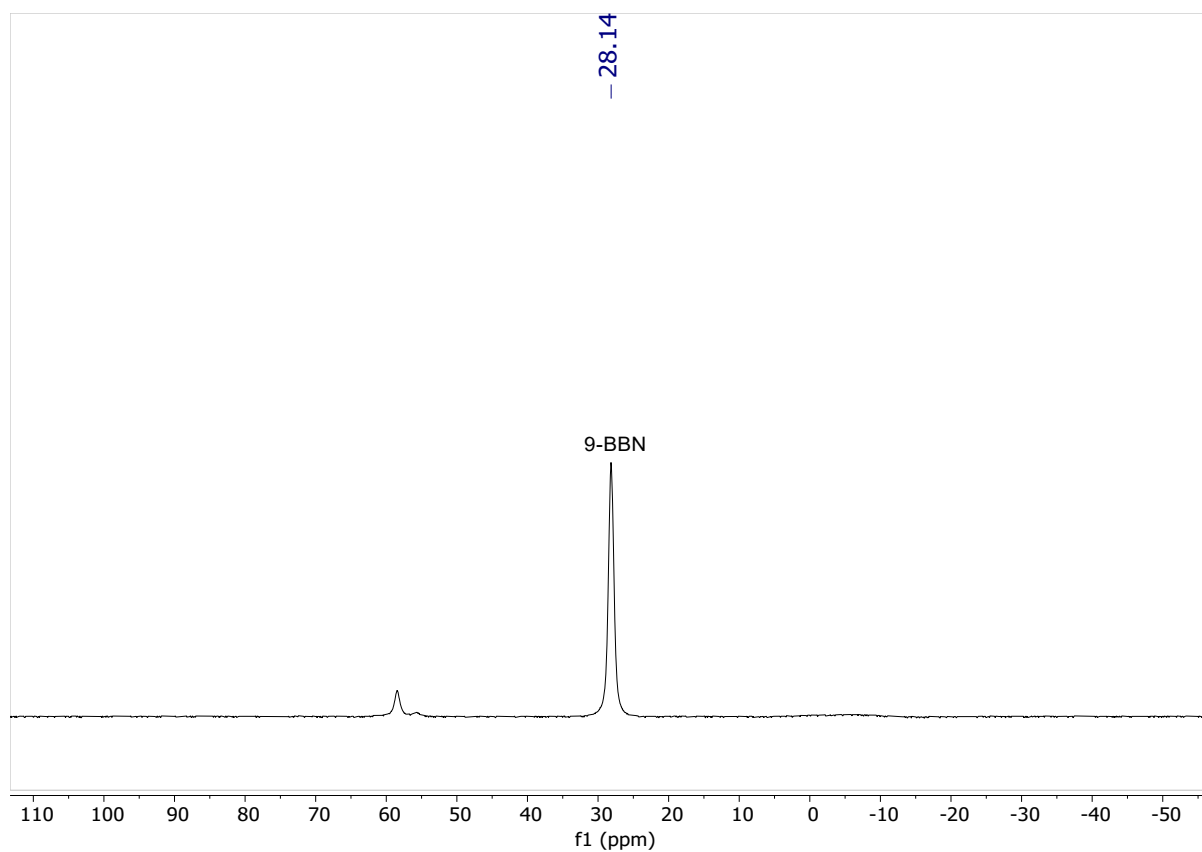
**Figure S16.** <sup>1</sup>H NMR (benzene solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and benzene (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 14 h at 25 °C.



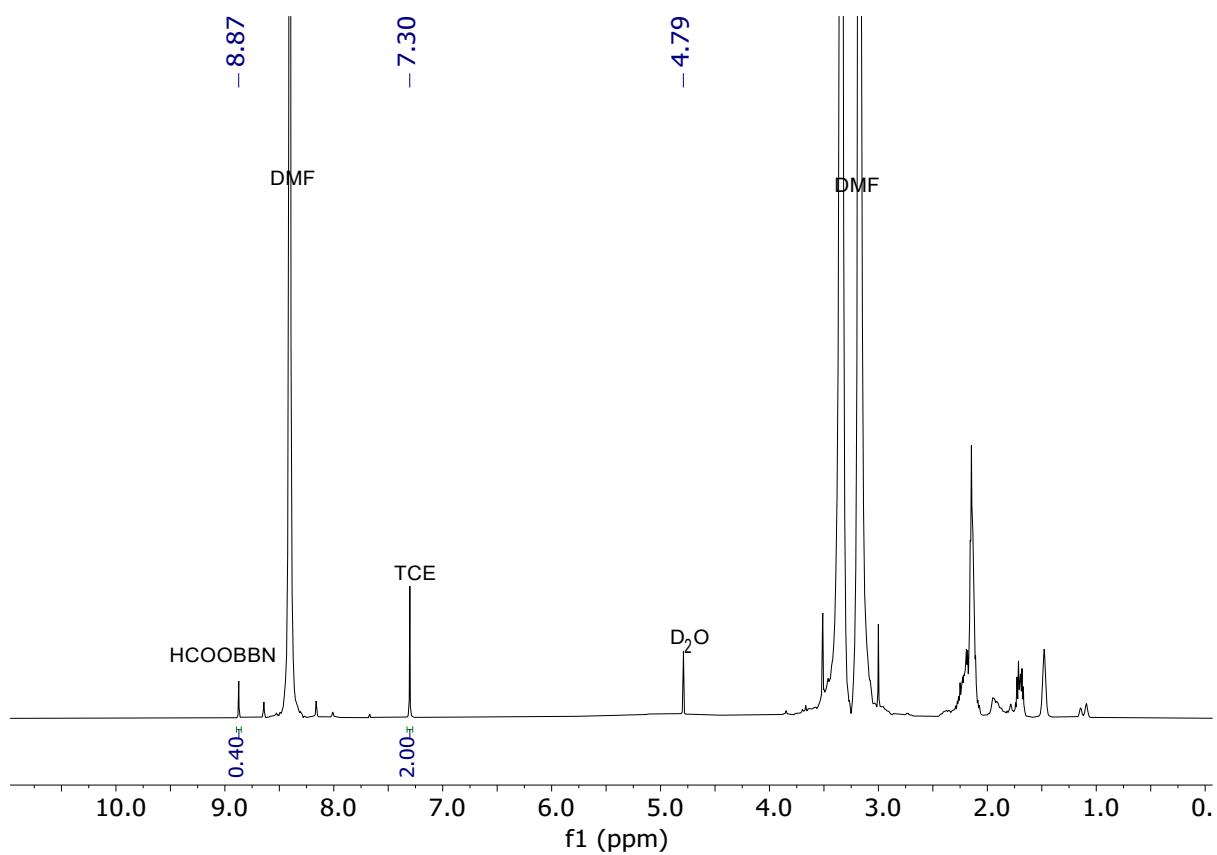
**Figure S17.**  $^{11}\text{B}$  NMR (benzene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and benzene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 14 h at 25 °C.



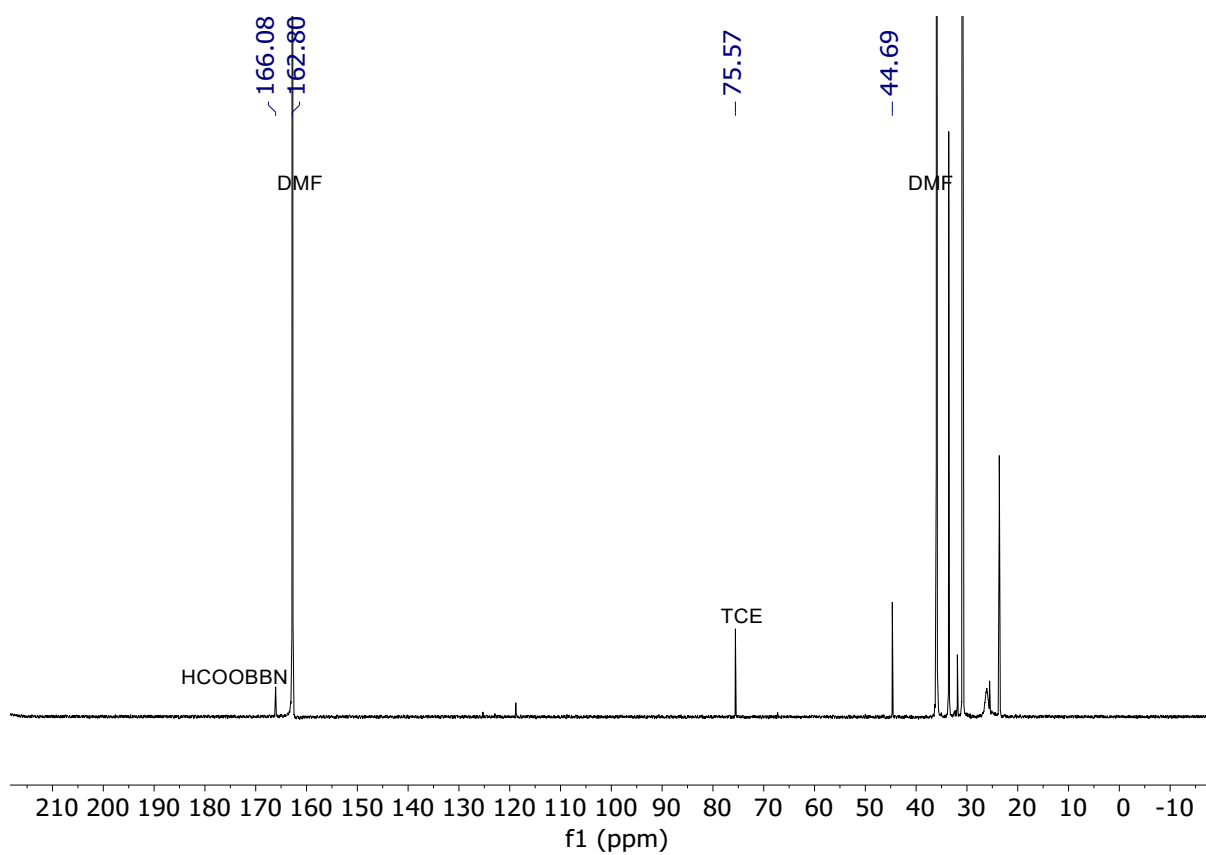
**Figure S18.** <sup>1</sup>H NMR (n-hexane solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and n-hexane (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 14 h at 25 °C.



**Figure S19.**  $^{11}\text{B}$  NMR (n-hexane solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and *n*-hexane (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 14 h at 25 °C.

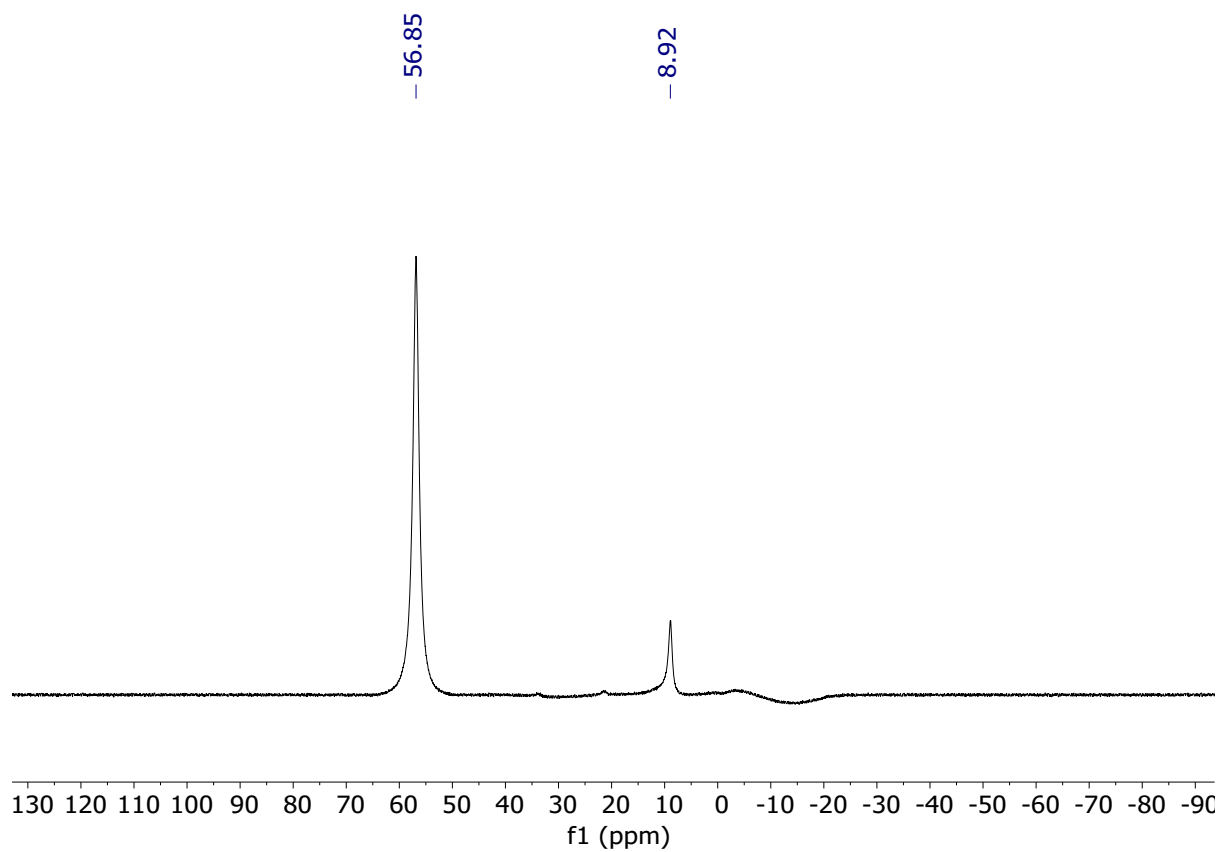


**Figure S20.** <sup>1</sup>H NMR (DMF solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMF (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 2 h at 25 °C.

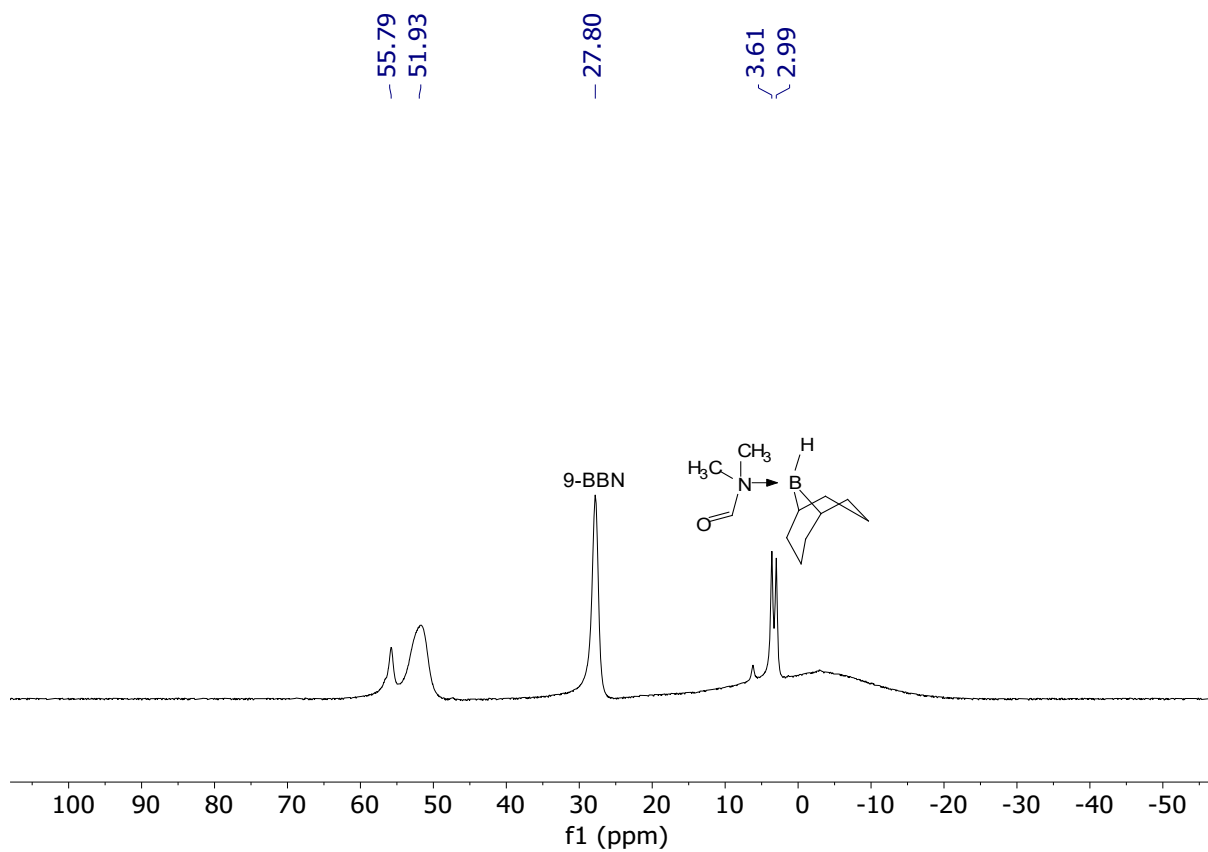


**Figure S21.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMF solution with  $\text{D}_2\text{O}$  capillary, 125.75 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMF (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 25 °C.

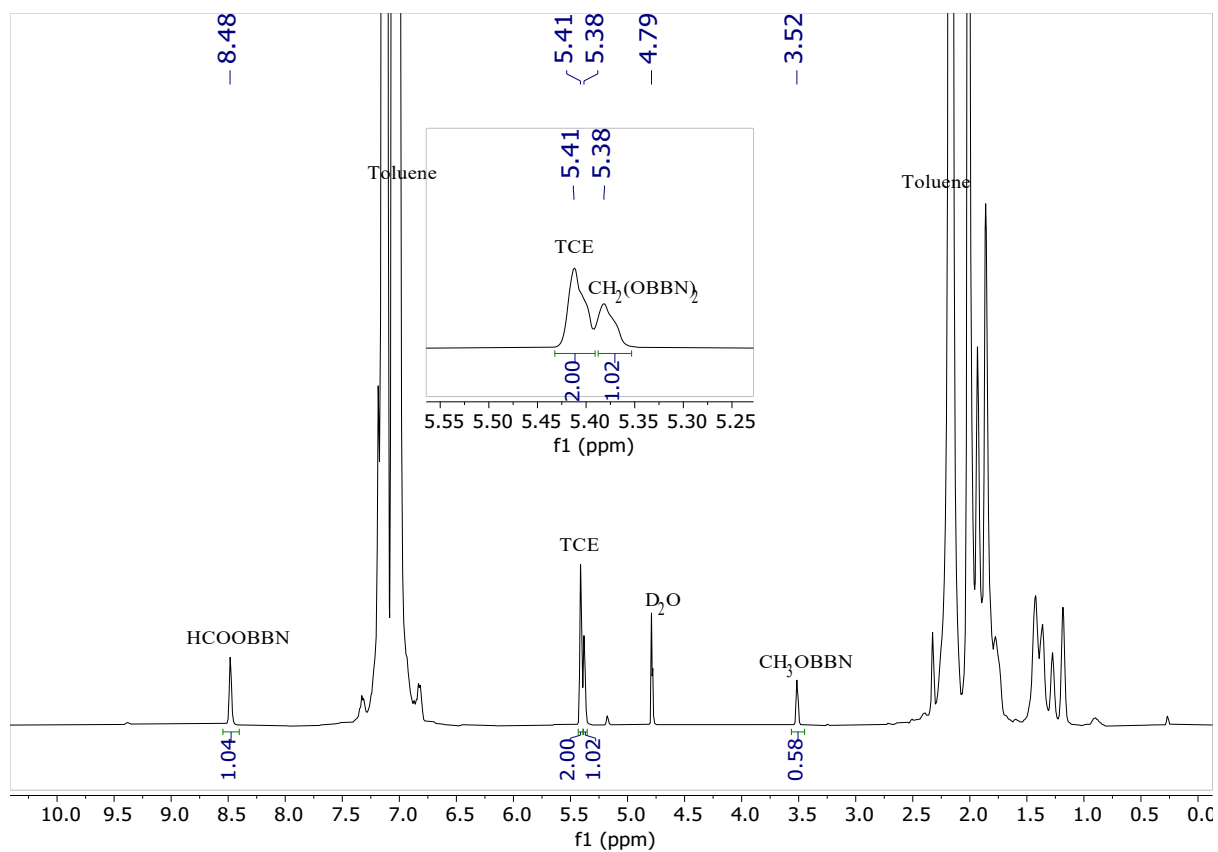




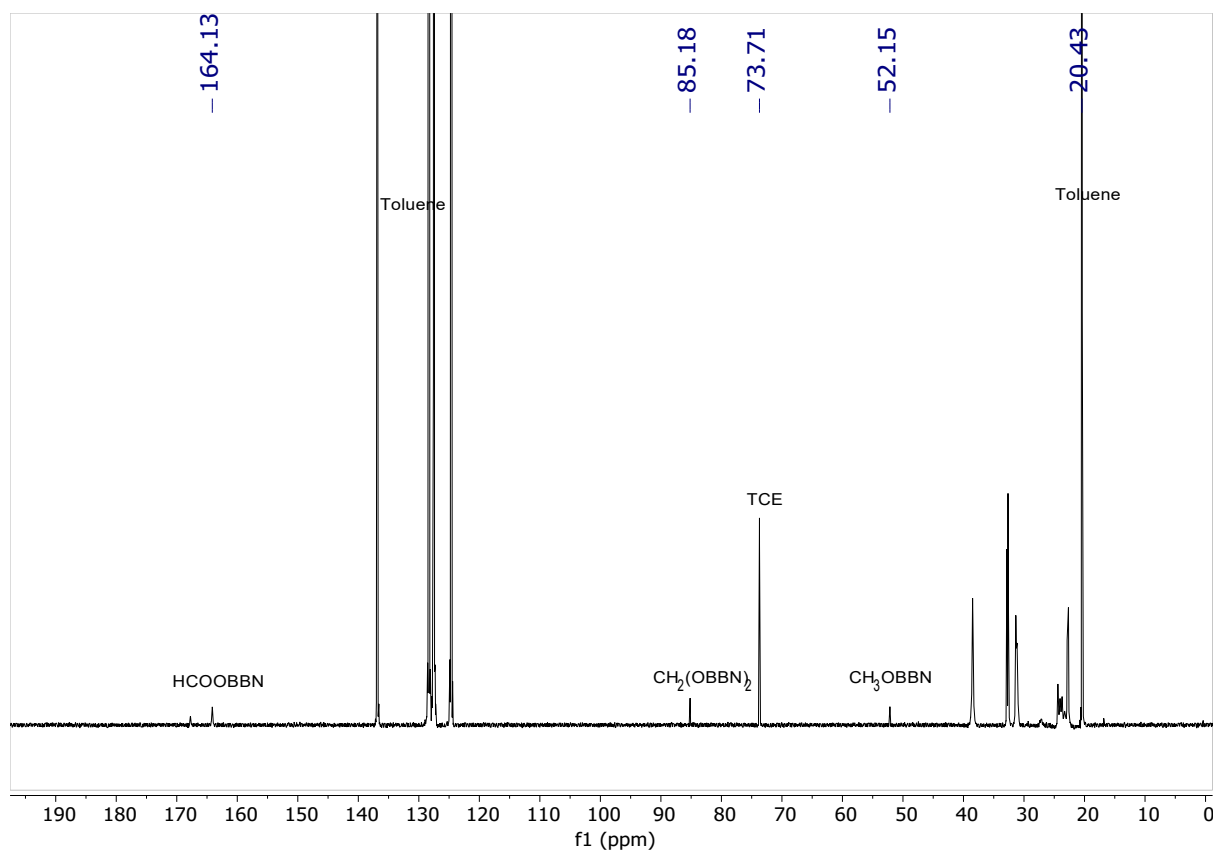
**Figure S22.**  $^{11}\text{B}$  NMR (DMF solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMF (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 25 °C.



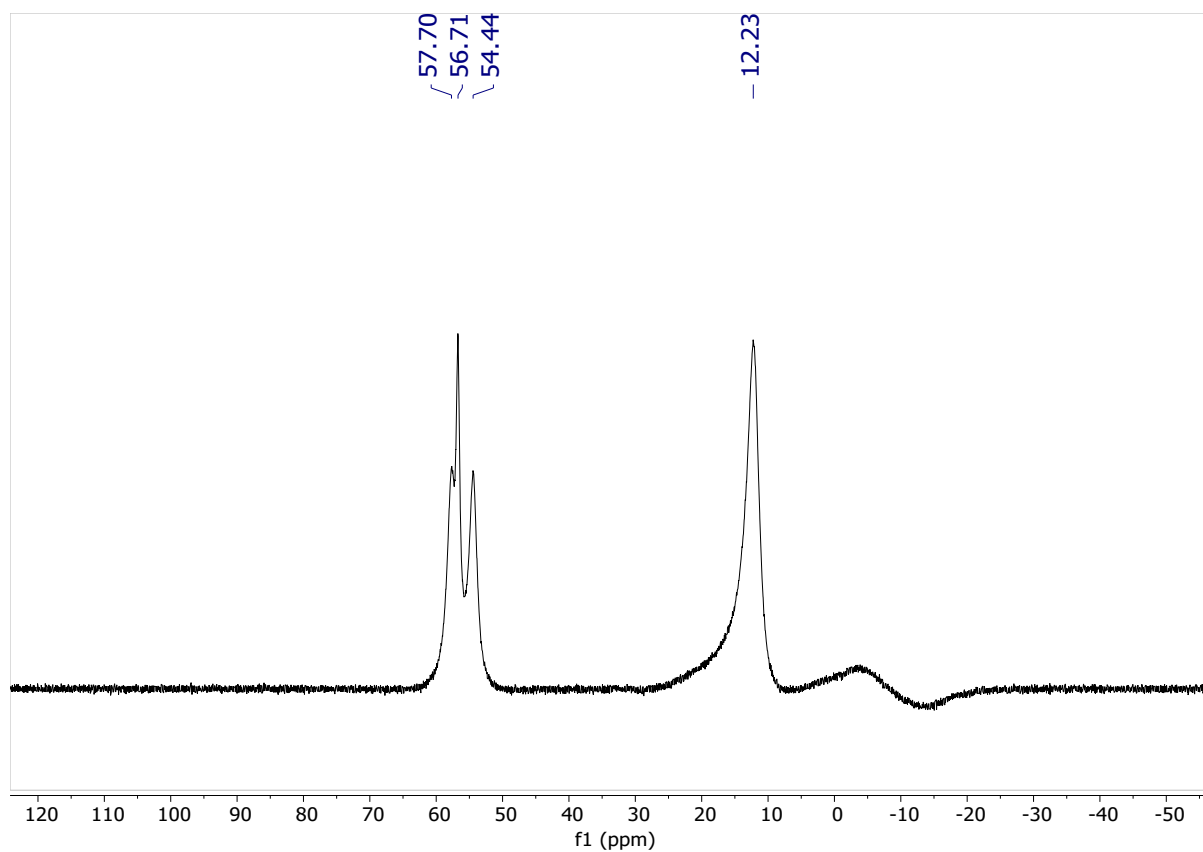
**Figure S23.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of the 1:1 molar reaction mixture of 9-BBN (0.030 g, 0.245 mmol) and DMF (19.1  $\mu\text{L}$ , 0.246 mmol) in toluene (0.5 mL) at 25 °C. Within 10 minutes spectrum was recorded.



**Figure S24.** <sup>1</sup>H NMR (toluene solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (71 μL, 1.0 mmol) in toluene (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 1 h at 25 °C.

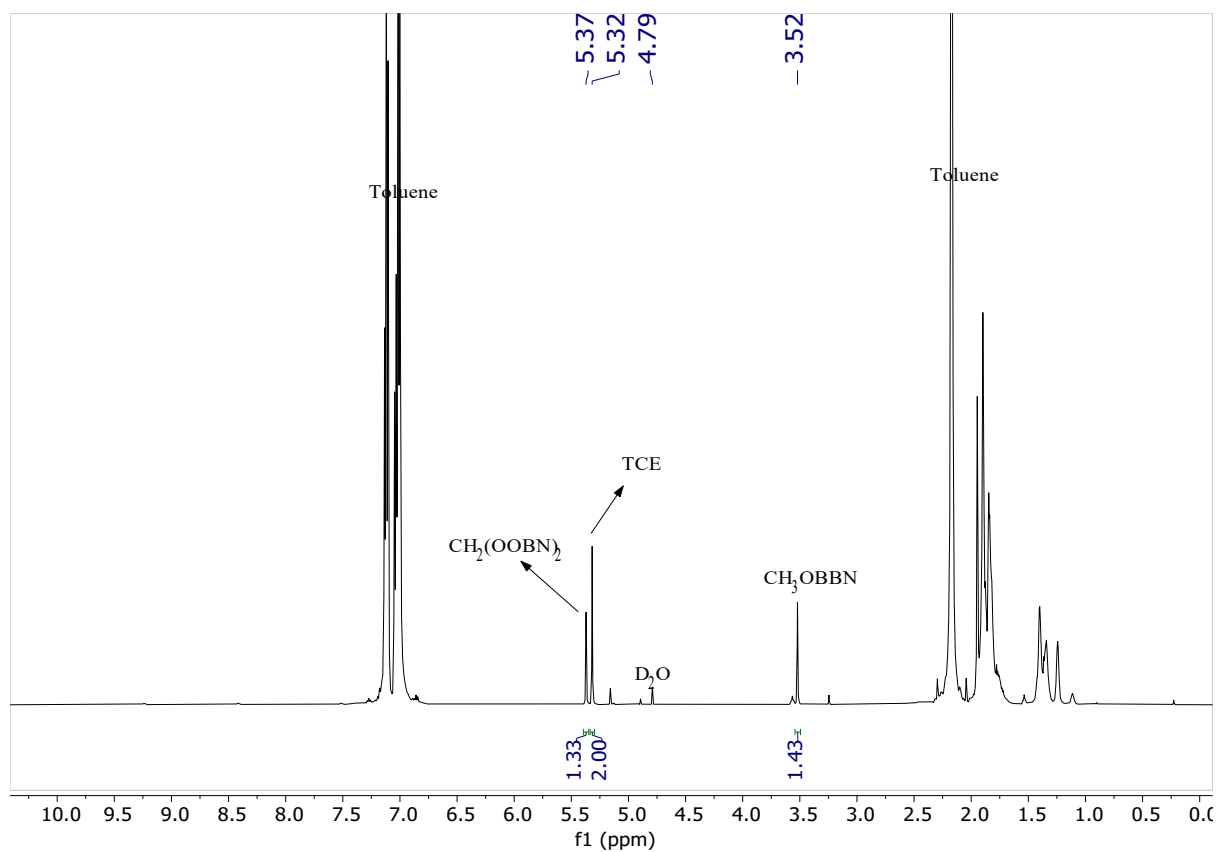


**Figure S25.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 125.75 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (71  $\mu\text{L}$ , 1.0 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 1 h at 25 °C.

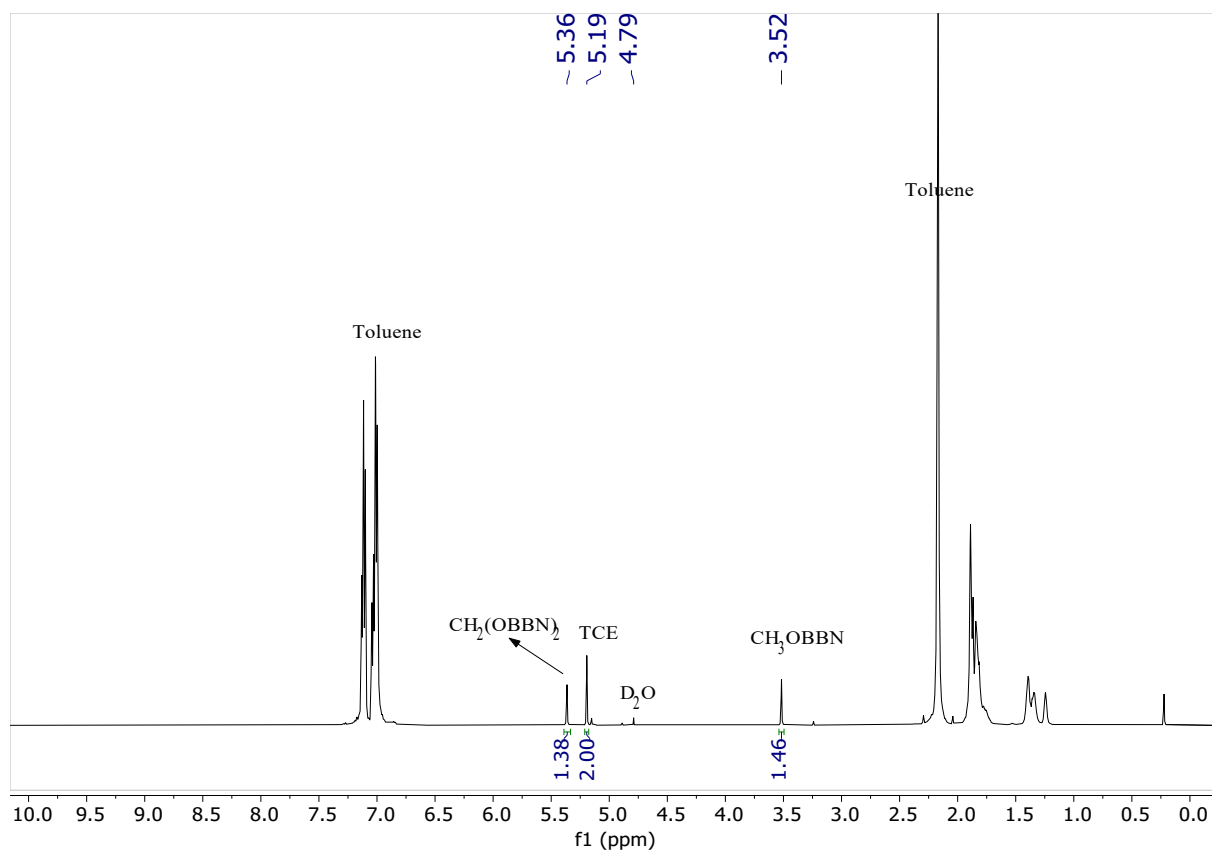


**Figure S26.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (71  $\mu\text{L}$ , 1.0 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 1 h at 25 °C.

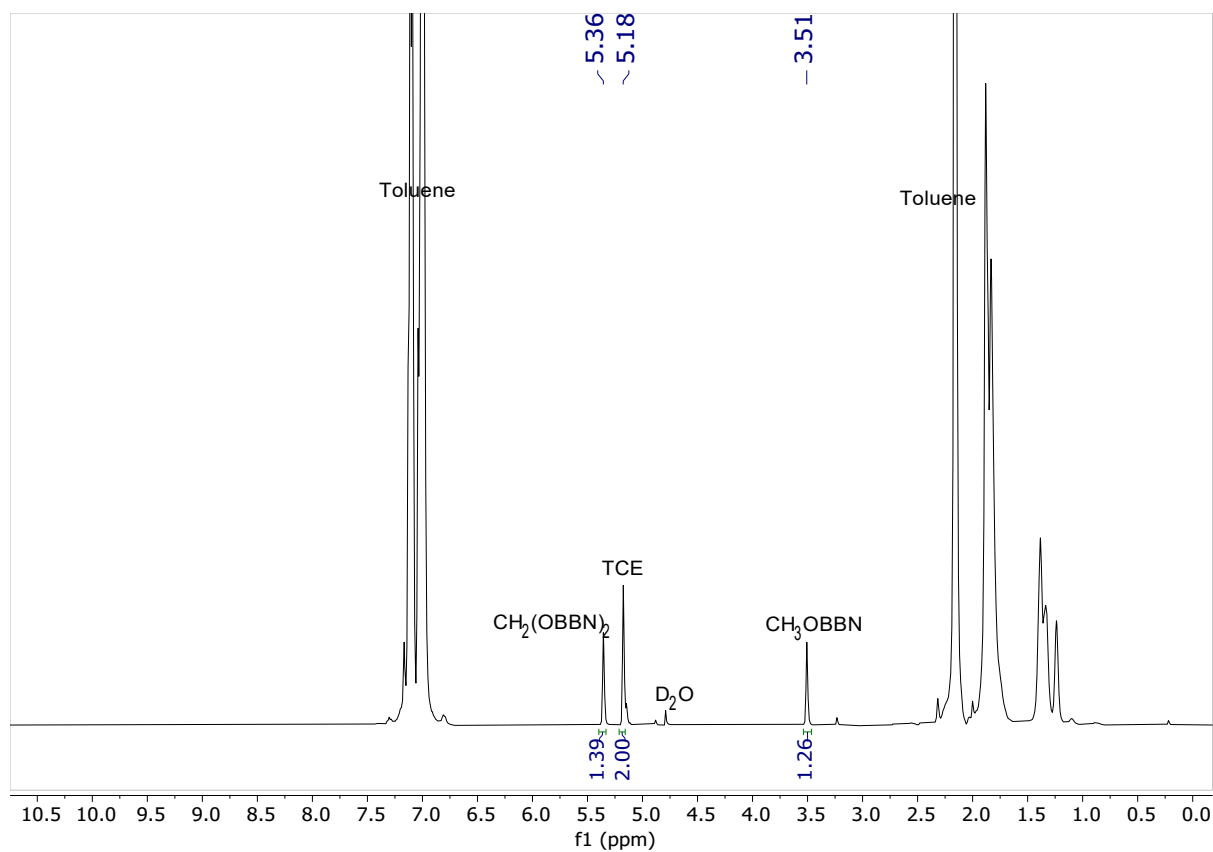
## For Table 2



**Figure S27.** <sup>1</sup>H NMR (toluene solution with D<sub>2</sub>O capillary, 500 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (20 μL, 28 mol%) in toluene (0.5 mL) under CO<sub>2</sub> (1 atm, balloon) for 3 h at 25 °C.

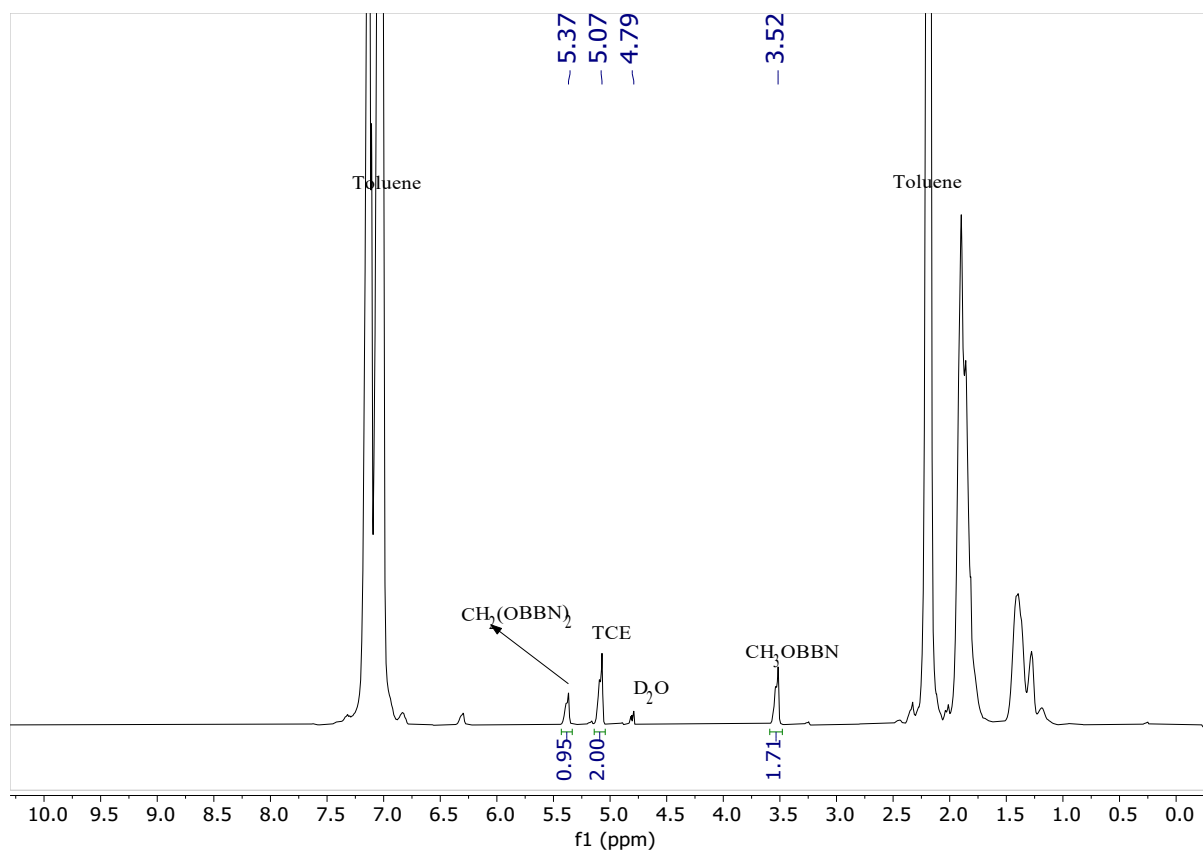


**Figure S28.** <sup>1</sup>H NMR (toluene solution with D<sub>2</sub>O capillary, 500 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (10.7 μL, 15 mol%) in toluene (0.5 mL) under CO<sub>2</sub> (1 atm, balloon) for 3 h at 25 °C.

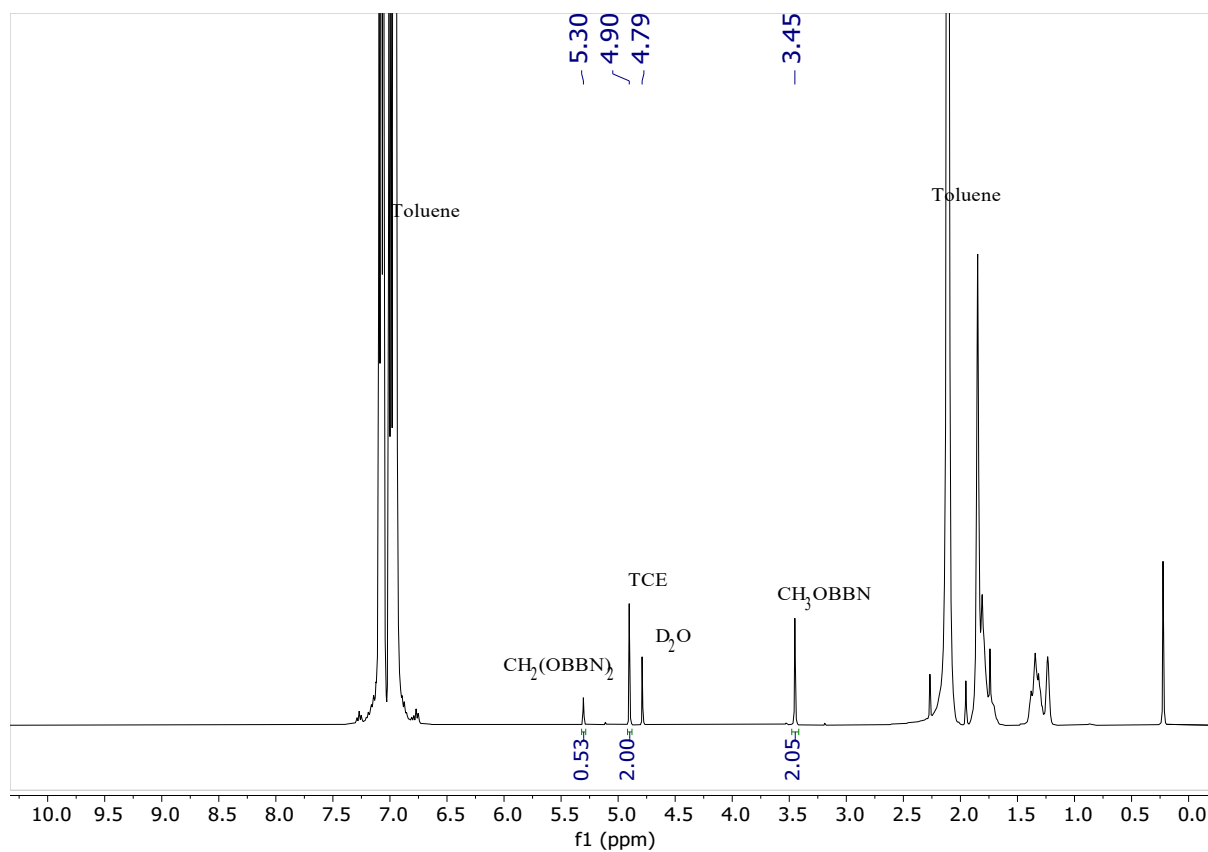


**Figure S29.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25  $^\circ\text{C}$ ) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (10.7  $\mu\text{L}$ , 15 mol%) in toluene (0.5 mL) under  $\text{CO}_2$  (1 atm, balloon) for 16 h at 25  $^\circ\text{C}$ .

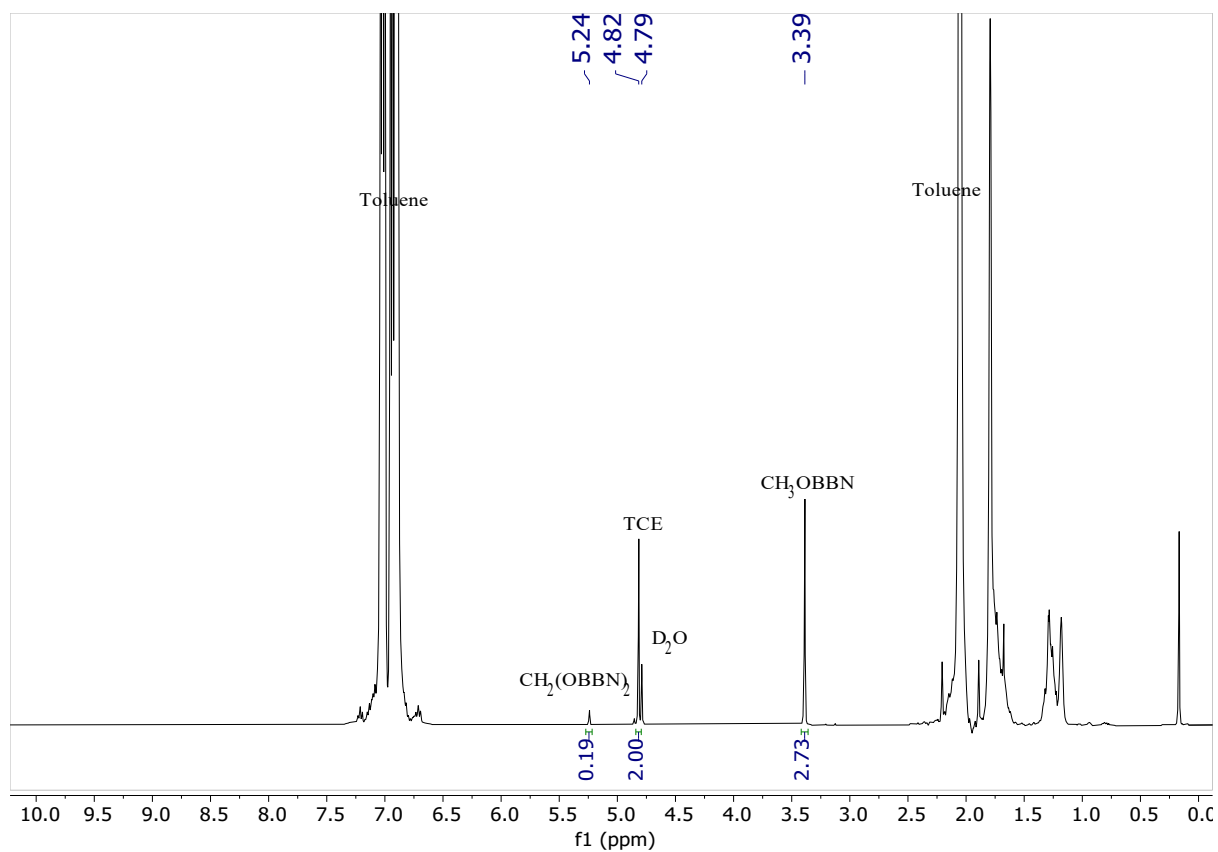




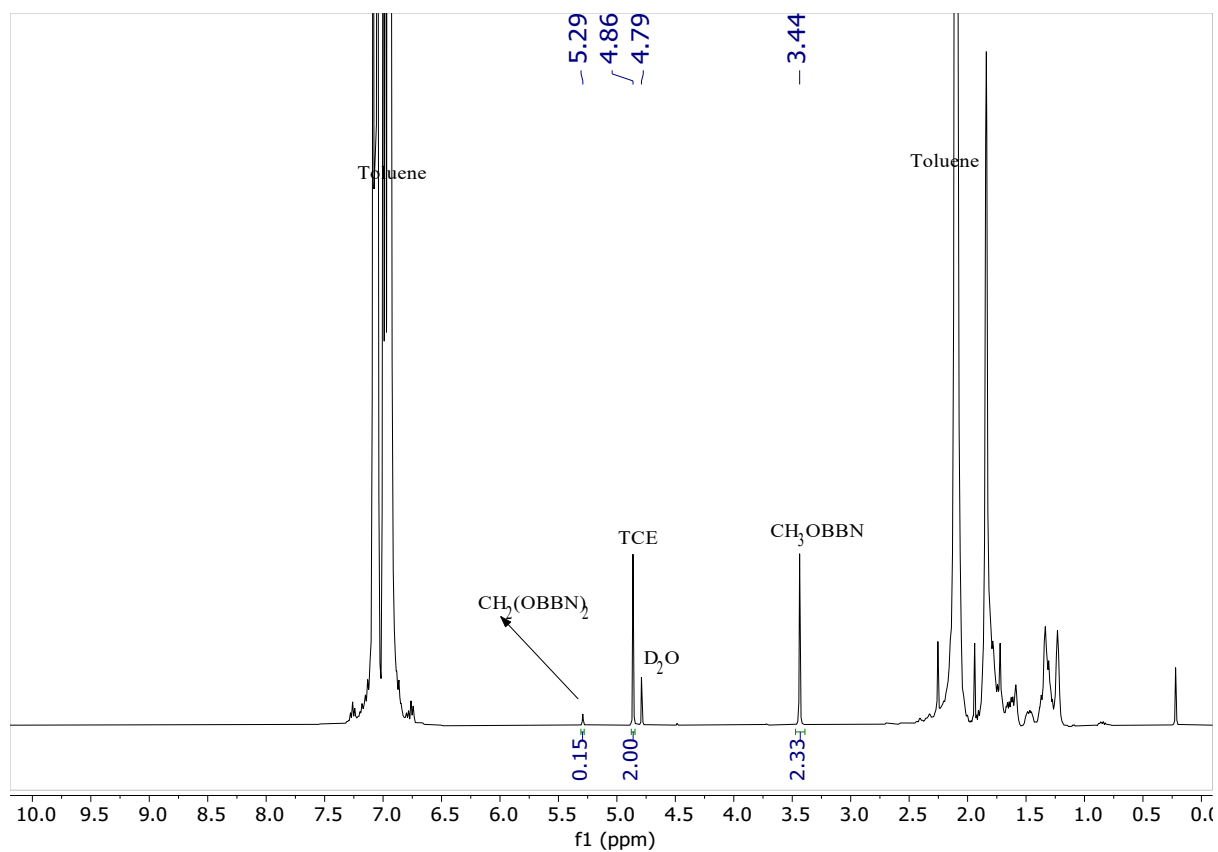
**Figure S30.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (10.7  $\mu\text{L}$ , 15 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 3 h at 25 °C.



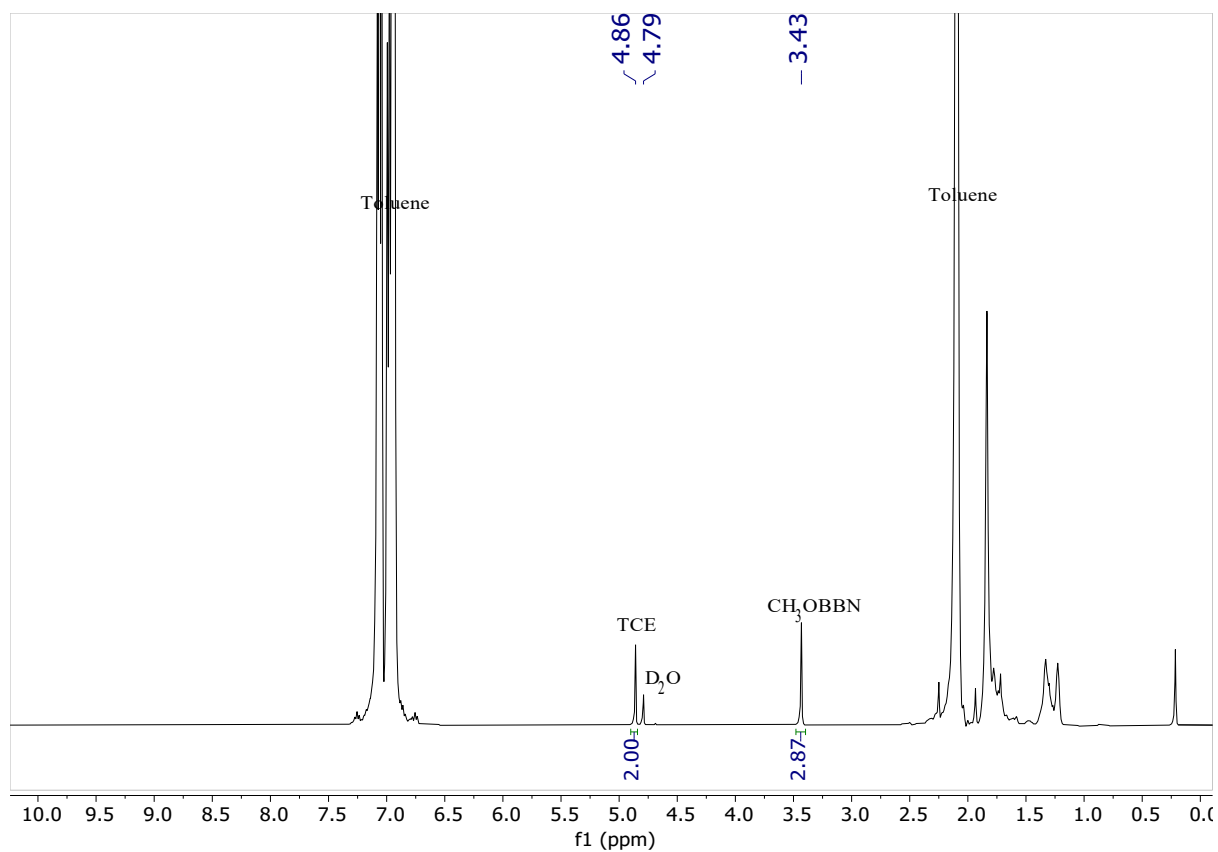
**Figure S31.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (5  $\mu\text{L}$ , 7 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 3 h at 25 °C.



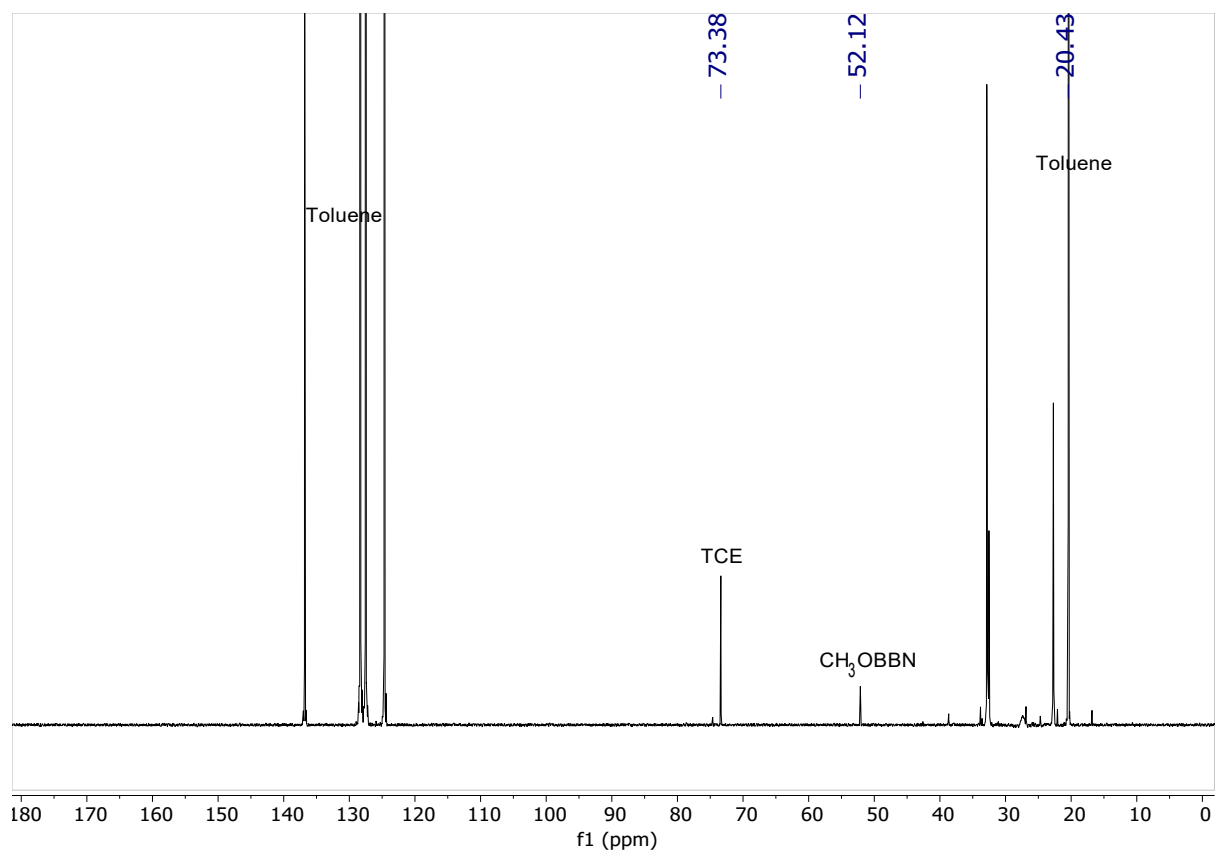
**Figure S32.** <sup>1</sup>H NMR (toluene solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (5 μL, 7 mol%) in toluene (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 6 h at 25 °C.



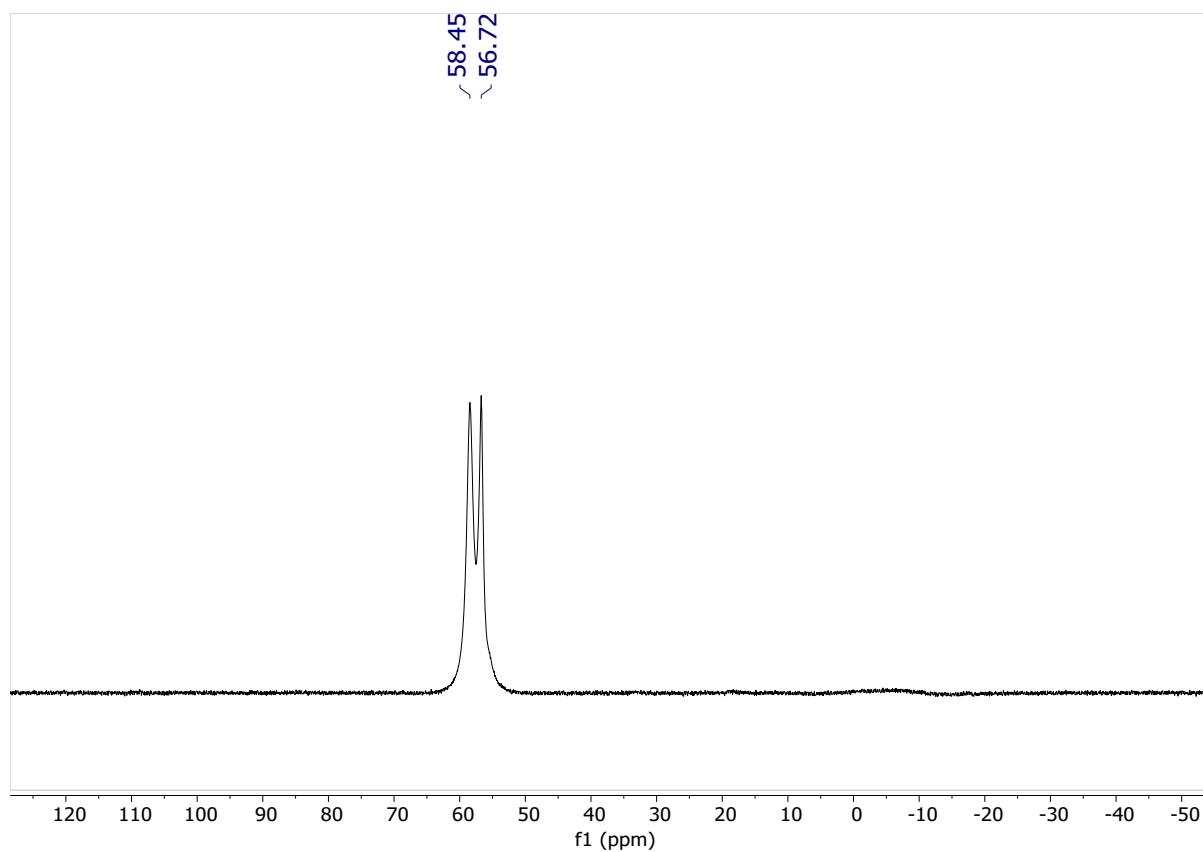
**Figure S33.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (3.2  $\mu\text{L}$ , 4.5 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 16 h at 25 °C.



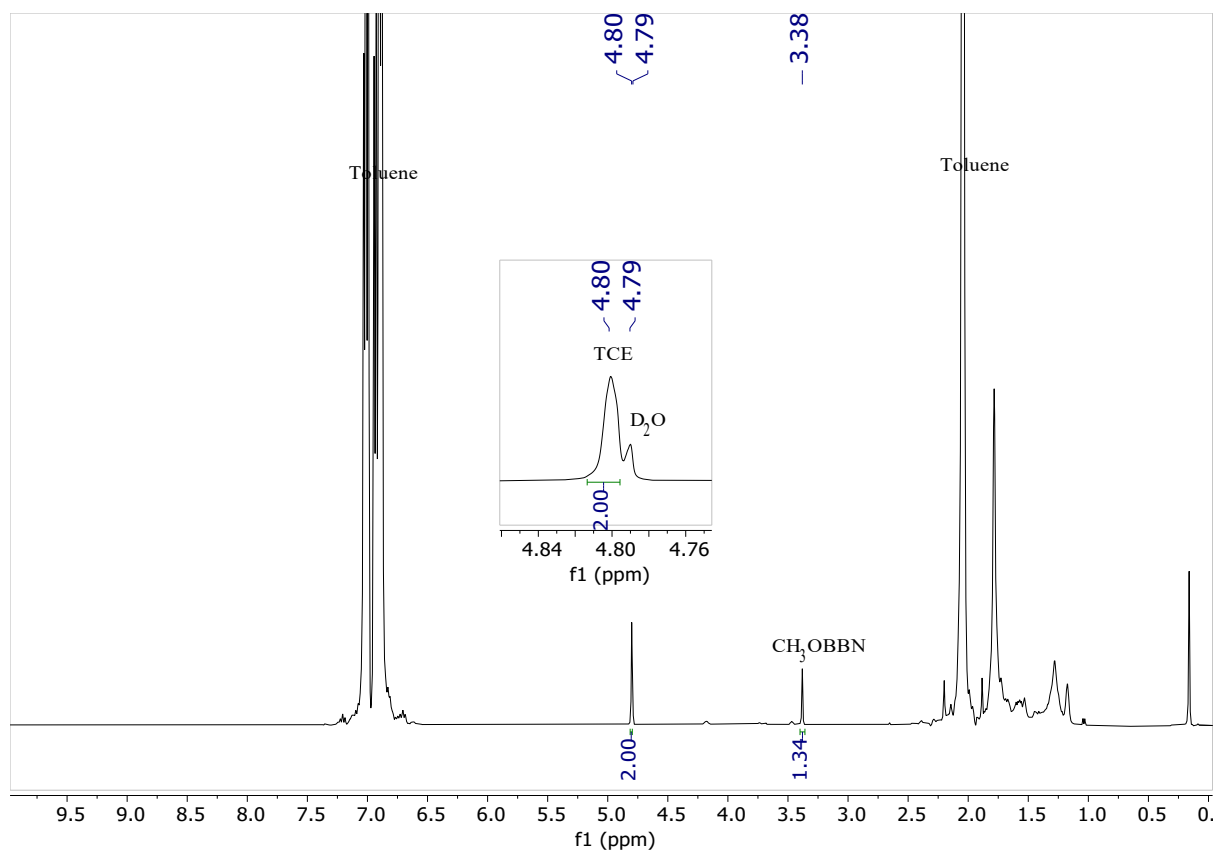
**Figure S34.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25  $^\circ\text{C}$ ) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (3.2  $\mu\text{L}$ , 4.5 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 24 h at 25  $^\circ\text{C}$ .



**Figure S35.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 125.75 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (3.2  $\mu\text{L}$ , 4.5 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 24 h at 25 °C.

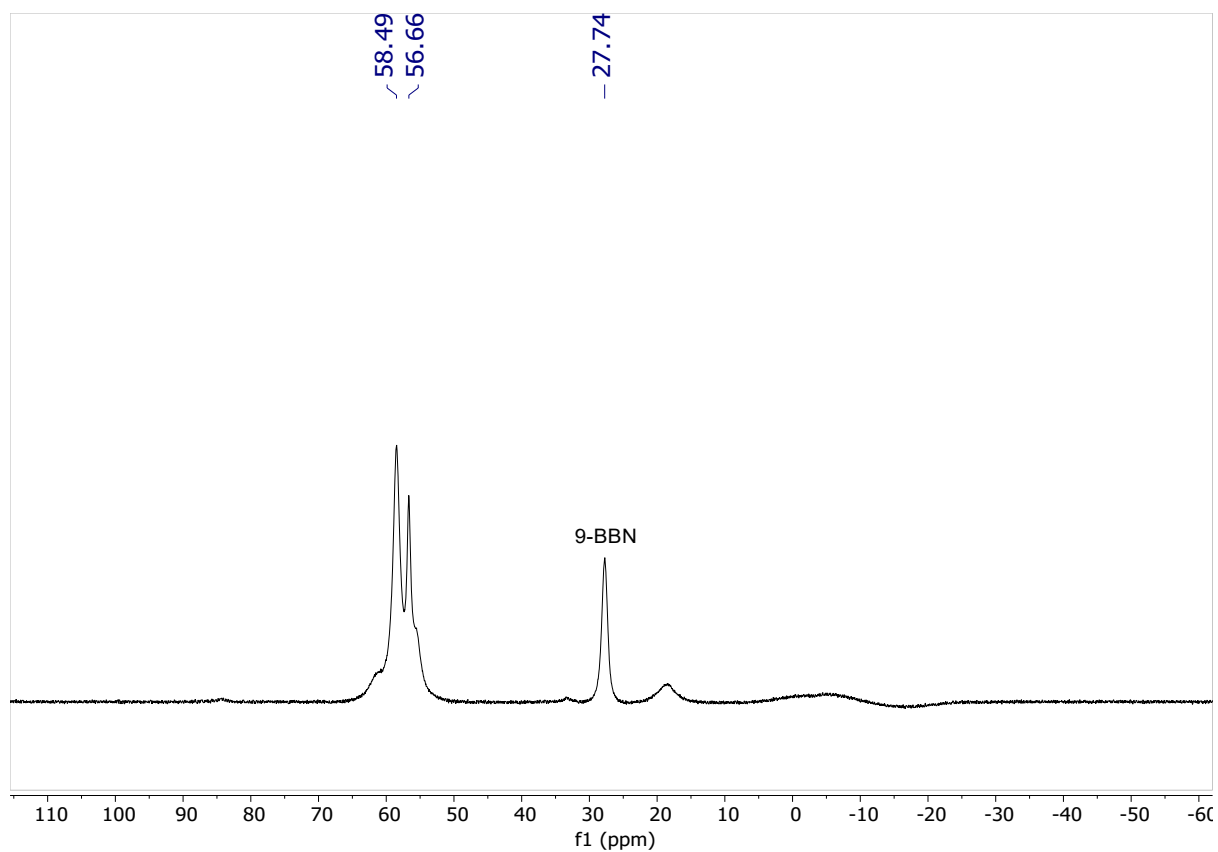


**Figure S36.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (3.2  $\mu\text{L}$ , 4.5 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 24 h at 25 °C.

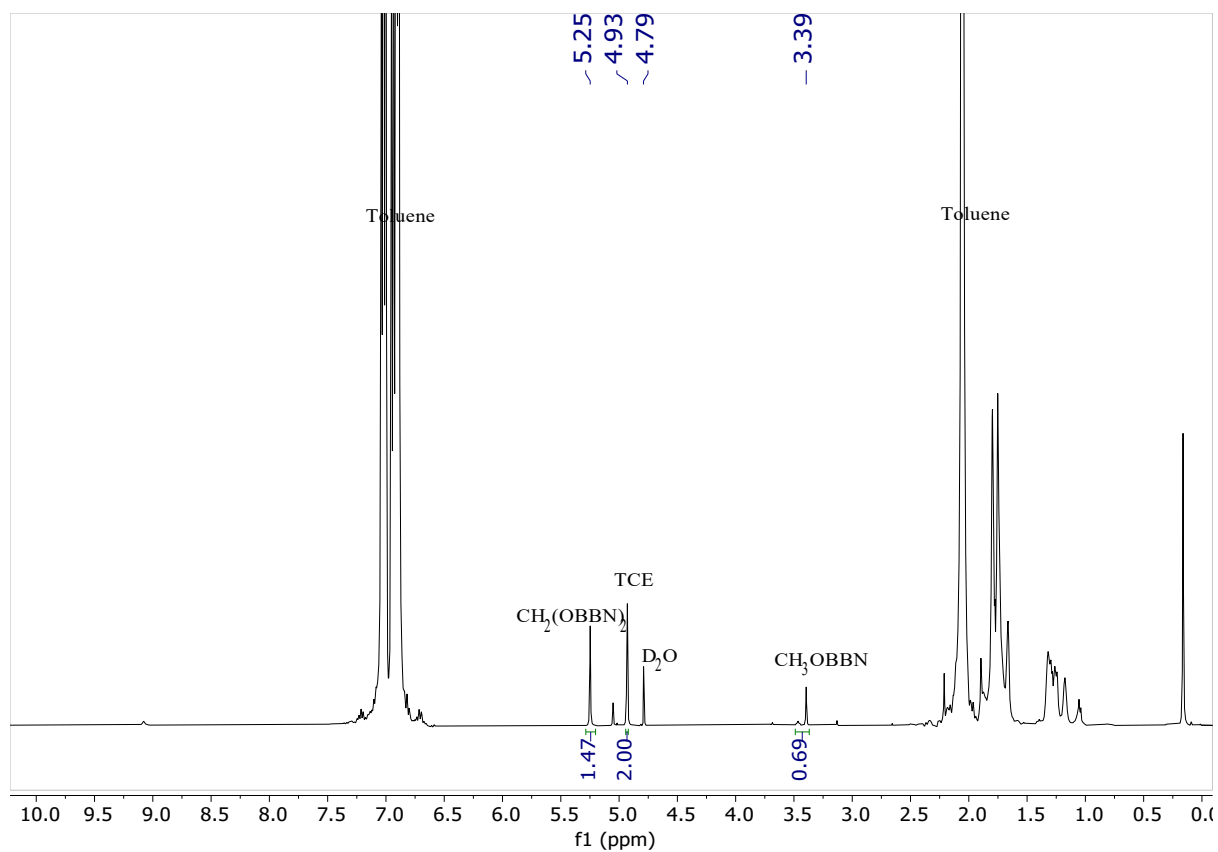


**Figure S37.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25  $^\circ\text{C}$ ) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (3.2  $\mu\text{L}$ , 4.5 mol%) in THF (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 16 h at 25  $^\circ\text{C}$ .

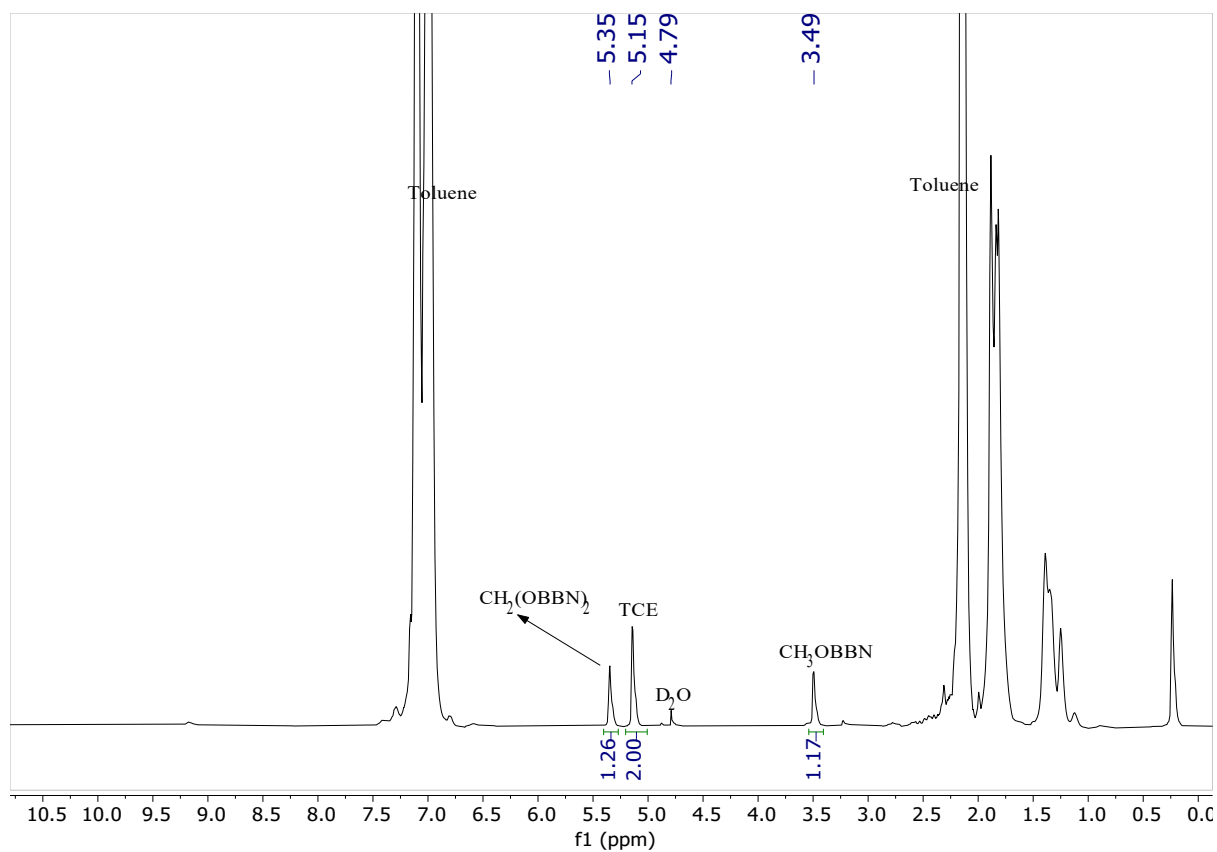




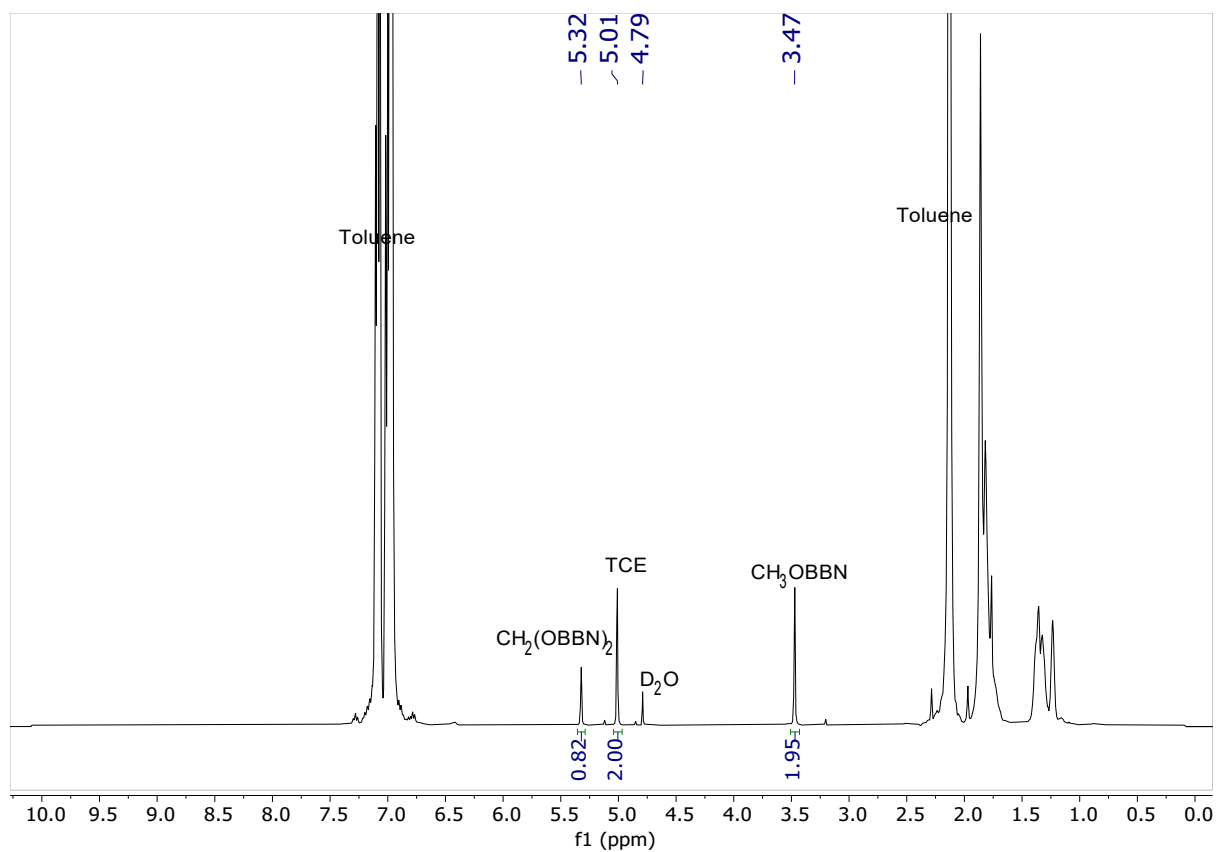
**Figure S38.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (3.2  $\mu\text{L}$ , 4.5 mol%) in THF (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 16 h at 25 °C.



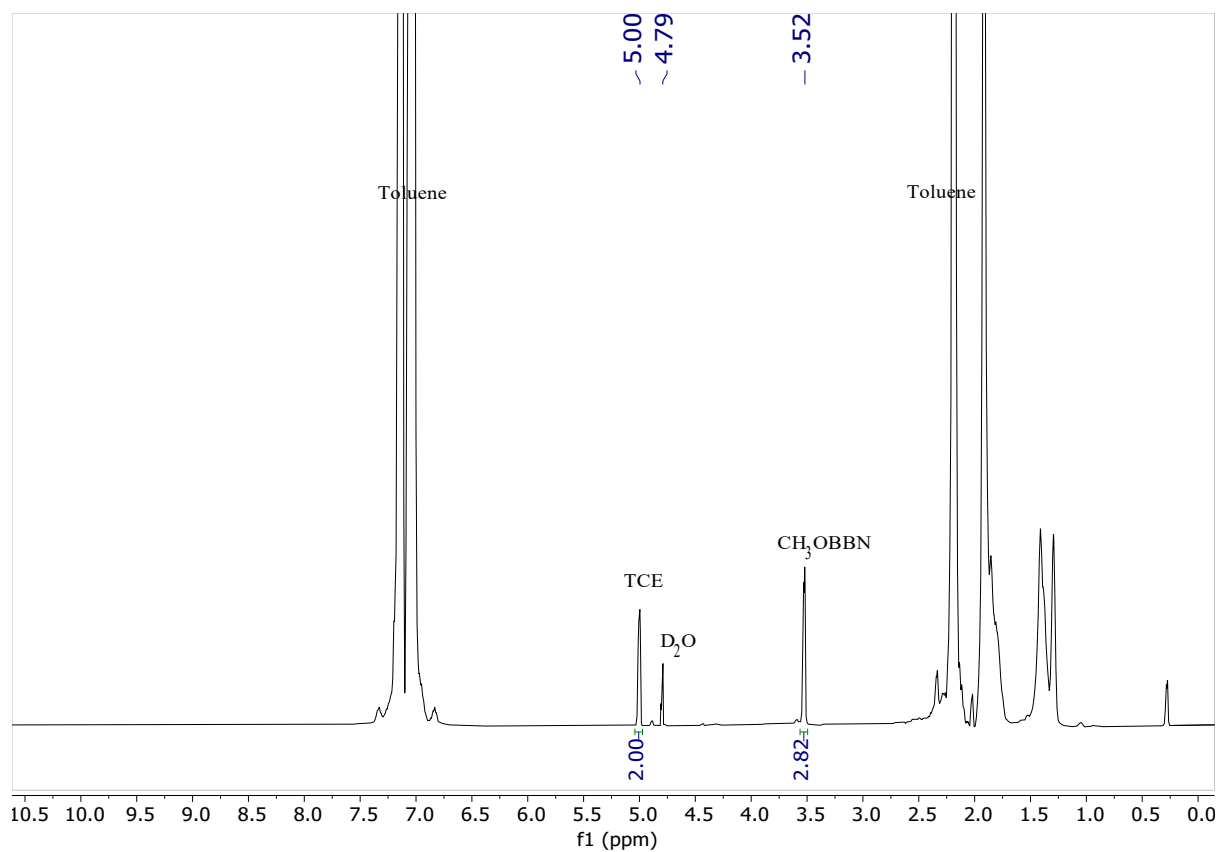
**Figure S39.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (20  $\mu\text{L}$ , 28 mol%) in THF (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 3 h at 25 °C.



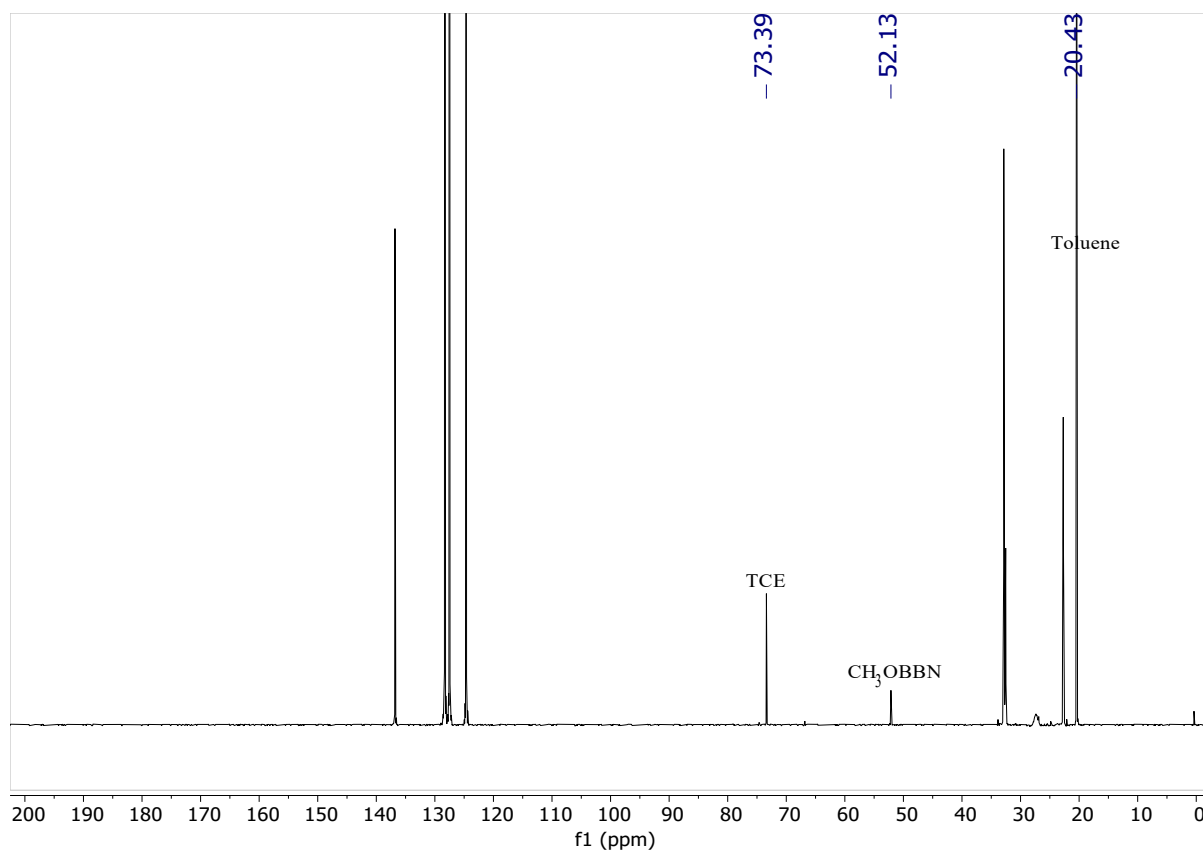
**Figure S40.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (20  $\mu\text{L}$ , 15 mol%) in THF (0.5 mL) under  $\text{CO}_2$  (1 atm, balloon) for 3 h at 25 °C.



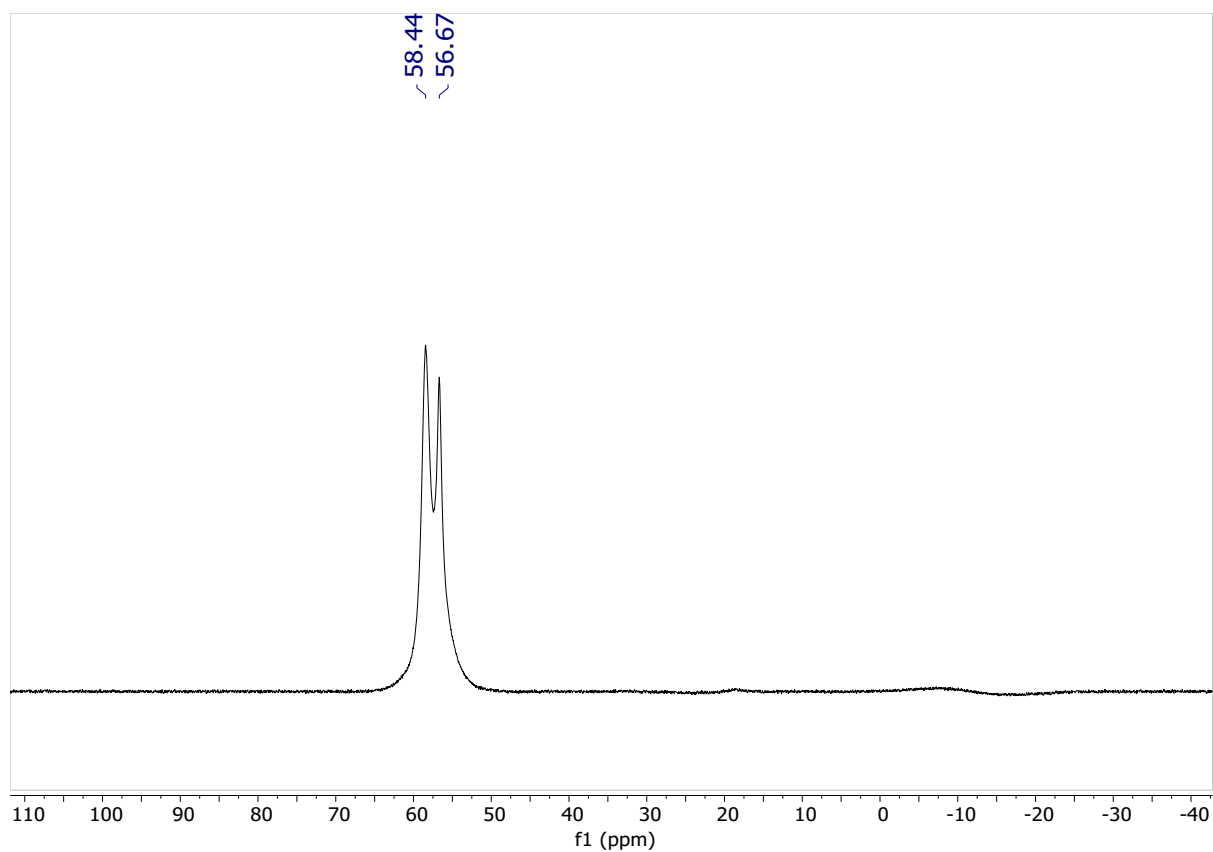
**Figure S41.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (10.7  $\mu\text{L}$ , 15 mol%) in THF (0.5 mL) under  $\text{CO}_2$  (1 atm, balloon) for 3 h at 25 °C.



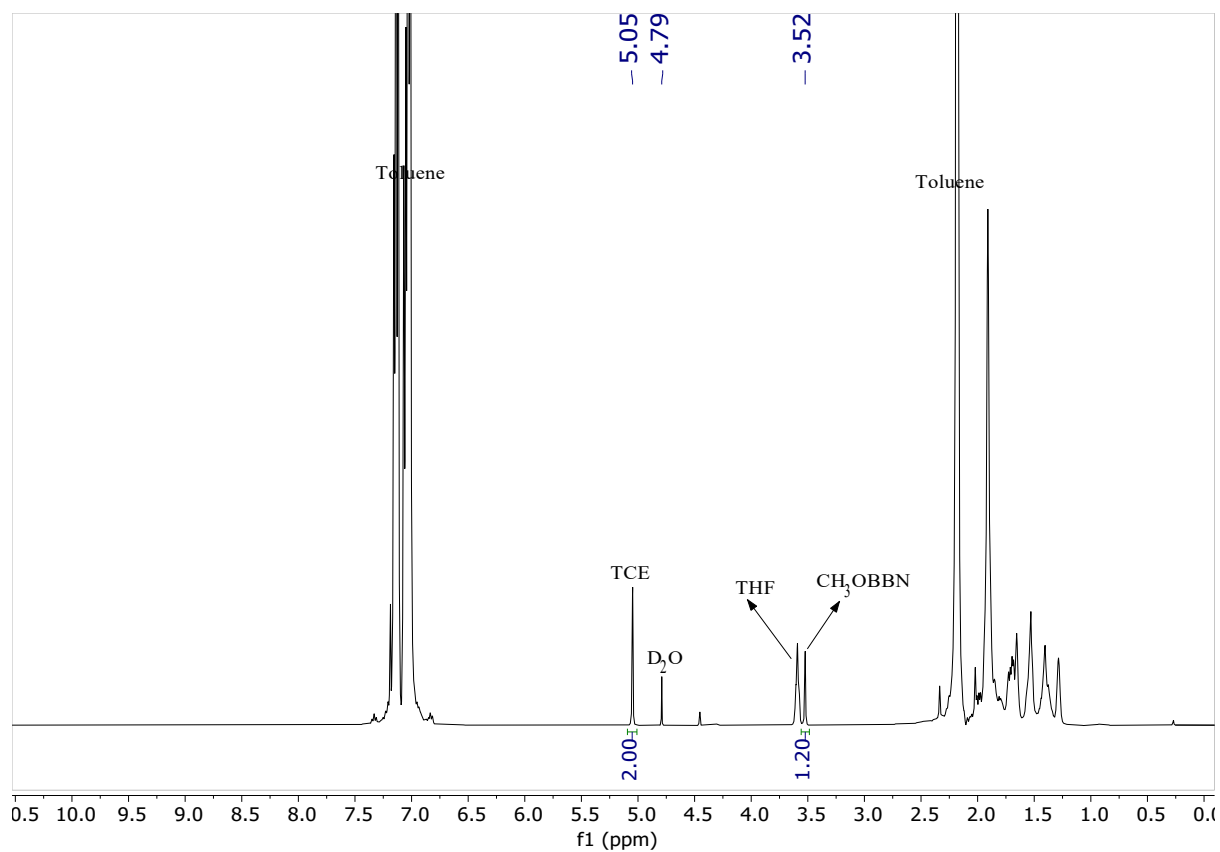
**Figure S42.** <sup>1</sup>H NMR (toluene solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (5 μL, 7 mol%) in THF (0.5 mL) under CO<sub>2</sub> (1 atm, balloon) for 6 h at 25 °C.



**Figure S43.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 125.75 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (5  $\mu\text{L}$ , 7 mol%) in THF (0.5 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25 °C.

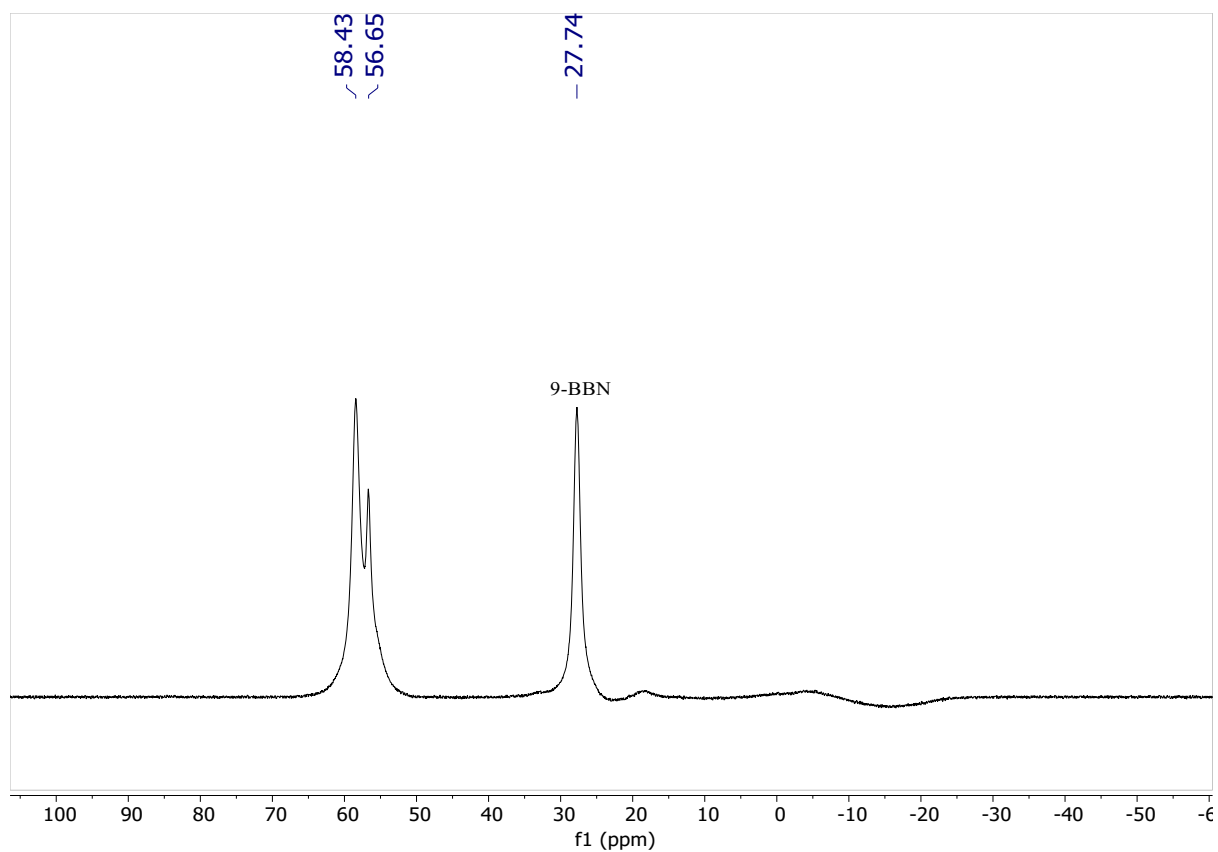


**Figure S44.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (5  $\mu\text{L}$ , 7 mol%) in THF (0.5 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25 °C.



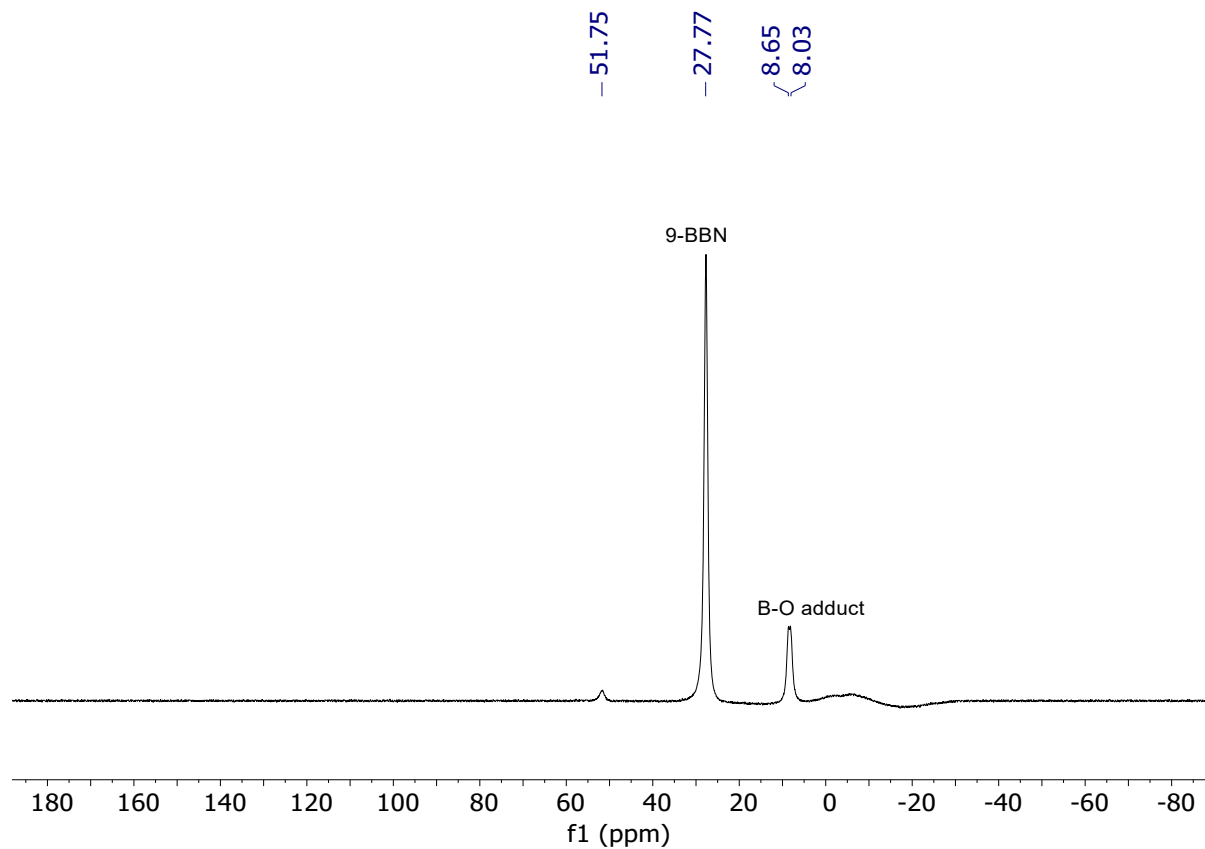
**Figure S45.** <sup>1</sup>H NMR (toluene solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (3.2 μL, 4.5 mol%) in THF (0.5 mL) under CO<sub>2</sub> (1 atm, balloon) for 16 h at 25 °C.



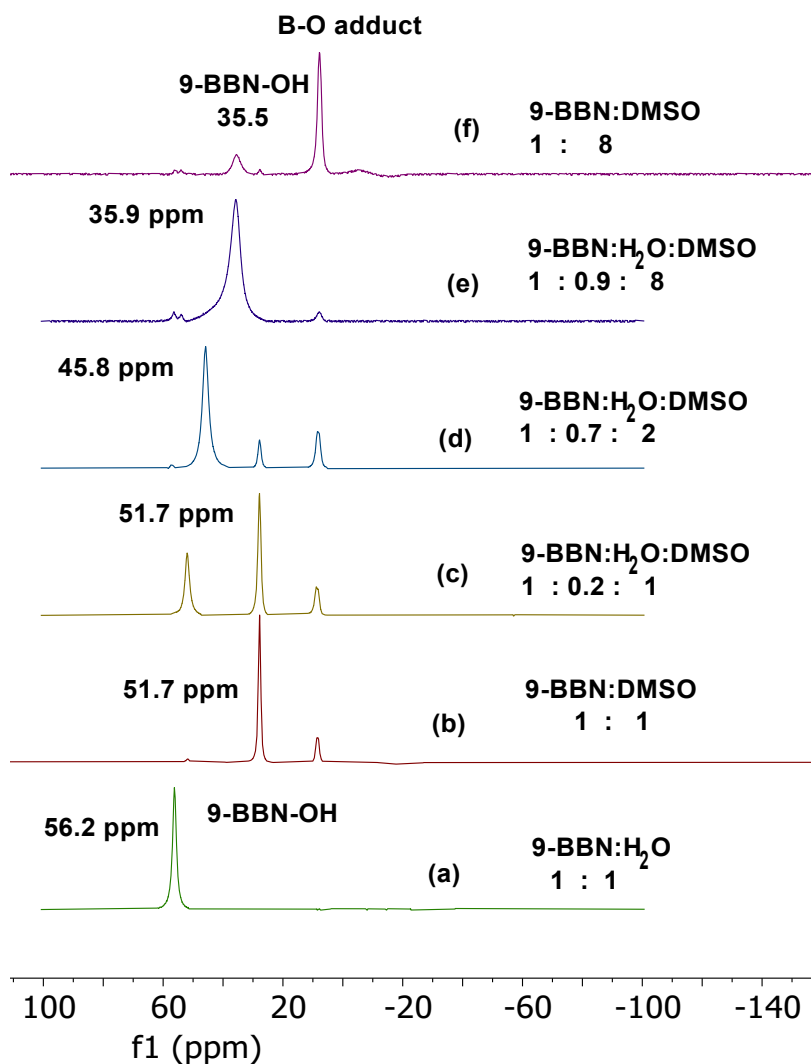


**Figure S46.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and DMSO (3.2  $\mu\text{L}$ , 4.5 mol%) in THF (0.5 mL) under  $\text{CO}_2$  (1 atm, balloon) for 16 h at 25 °C.

## Isolation of DMSO adduct of formoxyborane and mechanism NMR data



**Figure S47.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of 1:1 reaction mixture of 9-BBN (0.278 mmol) and DMSO (20  $\mu\text{L}$ , 0.281 mmol) in toluene (0.5 mL) at 25 °C.

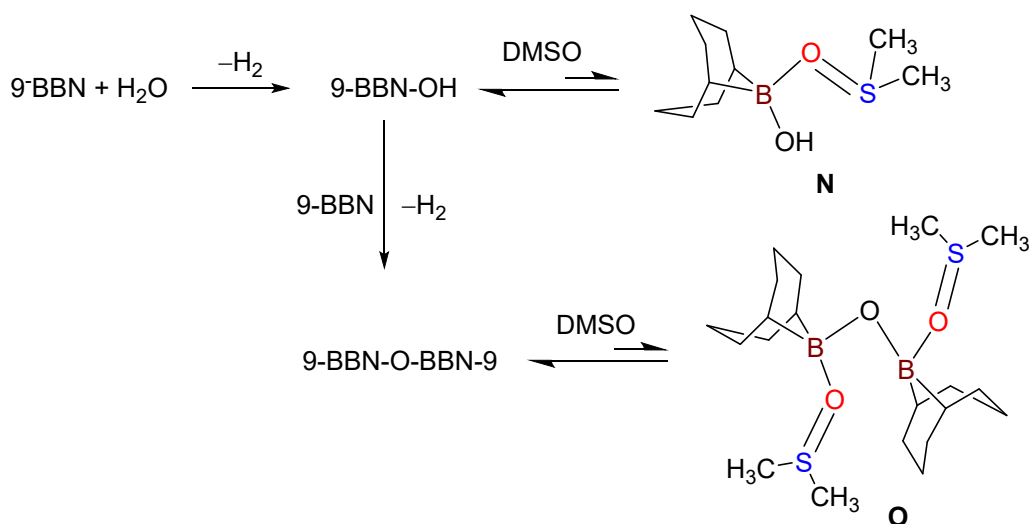


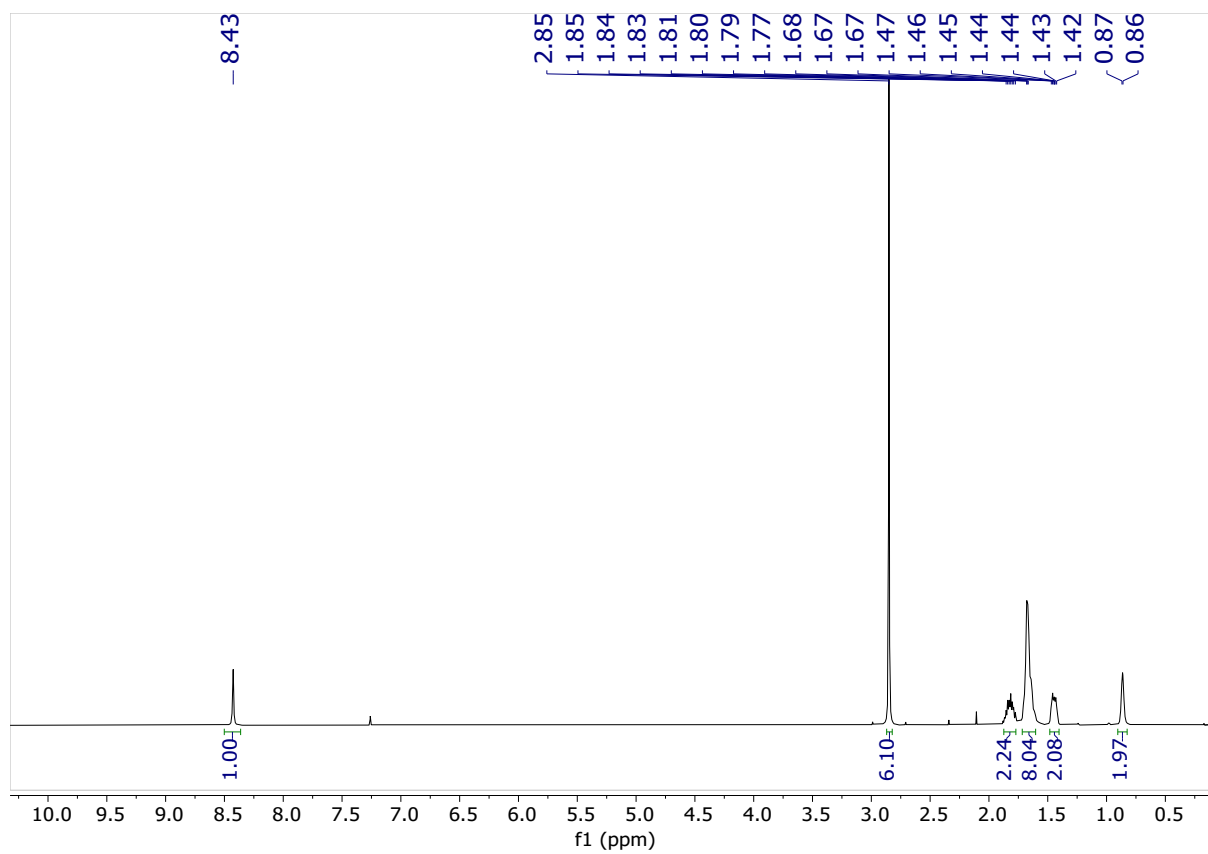
**Figure S48.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectra of 9-BBN as monomer in presence of different quantities of DMSO and water in toluene (0.5 mL) at 25 °C.

The  $^{11}\text{B}$  NMR spectrum of reaction mixture of 9-BBN and DMSO in 1:8 mole ratio in toluene, respectively, revealed a minor peak at 35.5 ppm along with peaks for free 9-BBN (27.7 ppm, minor) and a B–O adduct (7.8 ppm, major) (Fig. S48, f) which is given in the main text of the manuscript (Fig. 2, f). When this experiment was repeated with 0.9 equivalents of  $\text{H}_2\text{O}$  relative to 9-BBN, the peak near 35 ppm was intensified while the peak for B–O adduct was diminished (Fig. S48, e). This confirms that the peak around 35 ppm arises from the hydrolysis of 9-BBN, giving 9-BBN-OH. To confirm this further, a few more experiments were performed. The  $^{11}\text{B}$  NMR spectrum of the 1:1 ratio mixture of 9-BBN and DMSO in toluene showed a minor peak at 51.7 ppm along with additional peaks (free 9-BBN at 27.7 and B–O adduct 8.3 ppm) (Fig S48, b). In a separate NMR tube, one equiv of 9-BBN was taken to which 0.2 equiv of  $\text{H}_2\text{O}$ , one equiv of DMSO and toluene (0.5 mL) were added in sequence and its  $^{11}\text{B}$  NMR spectrum showed that the peak at 51.7 ppm is intensified (Fig S48, c), suggesting that this peak is due to the product of hydrolysis of 9-BBN by water. Interestingly, from two more additional experiments, we observed that the chemical shift of 9-BBN-OH is influenced by the ratio of DMSO (Fig. S48, a-f), as also observed in the spectra given in the manuscript (Fig. 2, a-f).

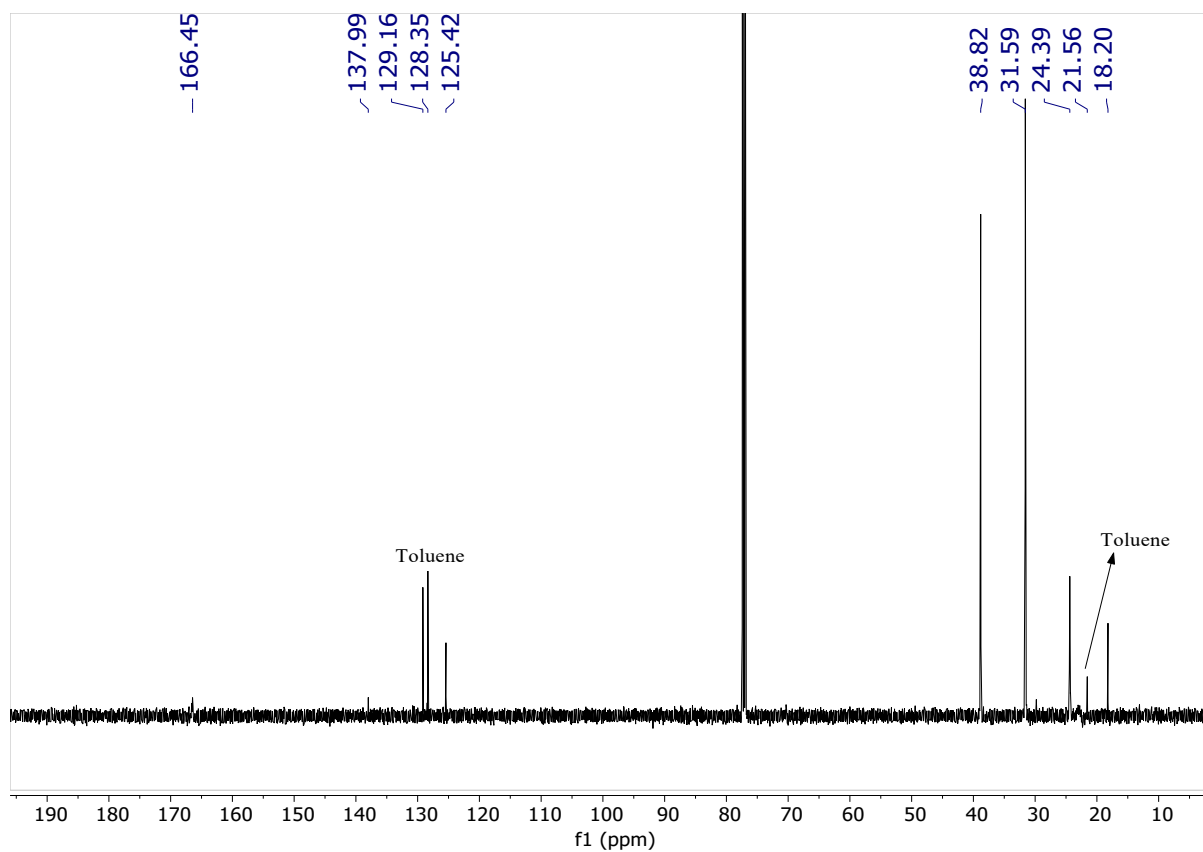
Without DMSO, the 1:1 reaction mixture of 9-BBN and H<sub>2</sub>O in toluene exhibited a peak at 56.2 ppm (Fig. S48, a) consistent with the formation of 9-BBN-OH (Ref.: K. Matos and J. A. Soderquist, *J. Org. Chem.*, 1998, 63, 461–470). However, with increasing equiv of DMSO (1, 2 and 8 equiv) relative to 9-BBN (Fig S48 c,d,e), this resonance gradually shifts to ~52 ppm, ~46 ppm, and ~36 ppm, respectively (Fig S48 c,d,e) which is closer to the minor peak at 35.5 ppm observed in Fig. S48 f, and confirms the formation of DMSO coordinated 9-BBN-OH adduct.

This can be clearly understood by the reactions given below. The presence of adventitious water in the reaction between 9-BBN and varying quantities of DMSO in benzene (Fig 2, manuscript main text) generate 9-BBN-OH and H<sub>2</sub>. 9-BBN-OH in toluene gives a resonance at 56.2 ppm. However, the presence of DMSO in the reaction shifts the resonance up field by dative bonding to 9-BBN-OH, forming an adduct 9-BBN-OH:DMSO **N**. As the number of equiv of DMSO increases, this resonance moves to 35.6 ppm (Fig S48 e). This suggests the existence of an equilibrium between the adduct 9-BBN-OH:DMSO and reactants as given below. In addition, the initially formed 9-BBN-OH can react with free 9-BBN in the reaction mixture to give 9-BBN-O-BBN-9 which can also form an adduct **O** with DMSO in an equilibrium.

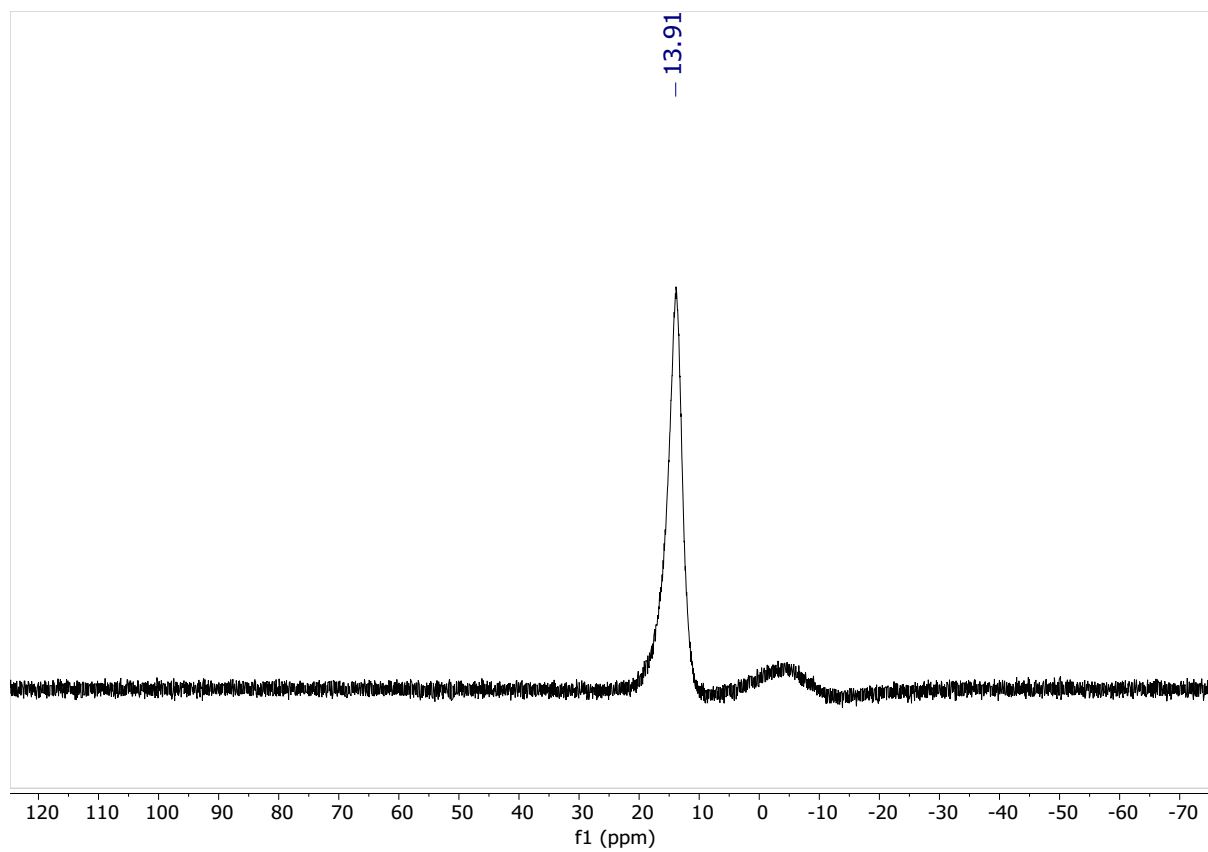




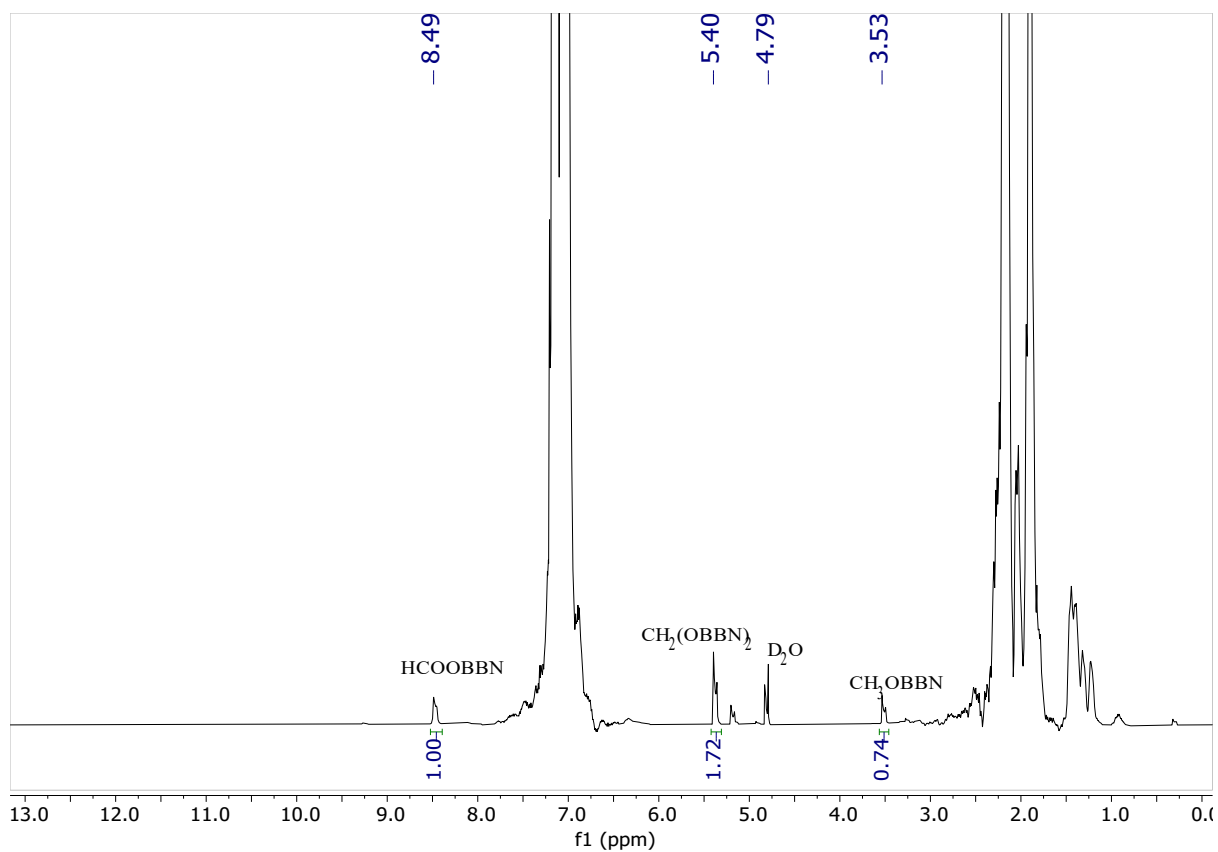
**Figure S49.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 25  $^\circ\text{C}$ ) spectrum of  $[\text{HCOBBN}][\text{DMSO}]$  (**E**).



**Figure S50.**  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125.75 MHz, 25 °C) spectrum of  $[\text{HCOBBN}][\text{DMSO}]$  (**E**).

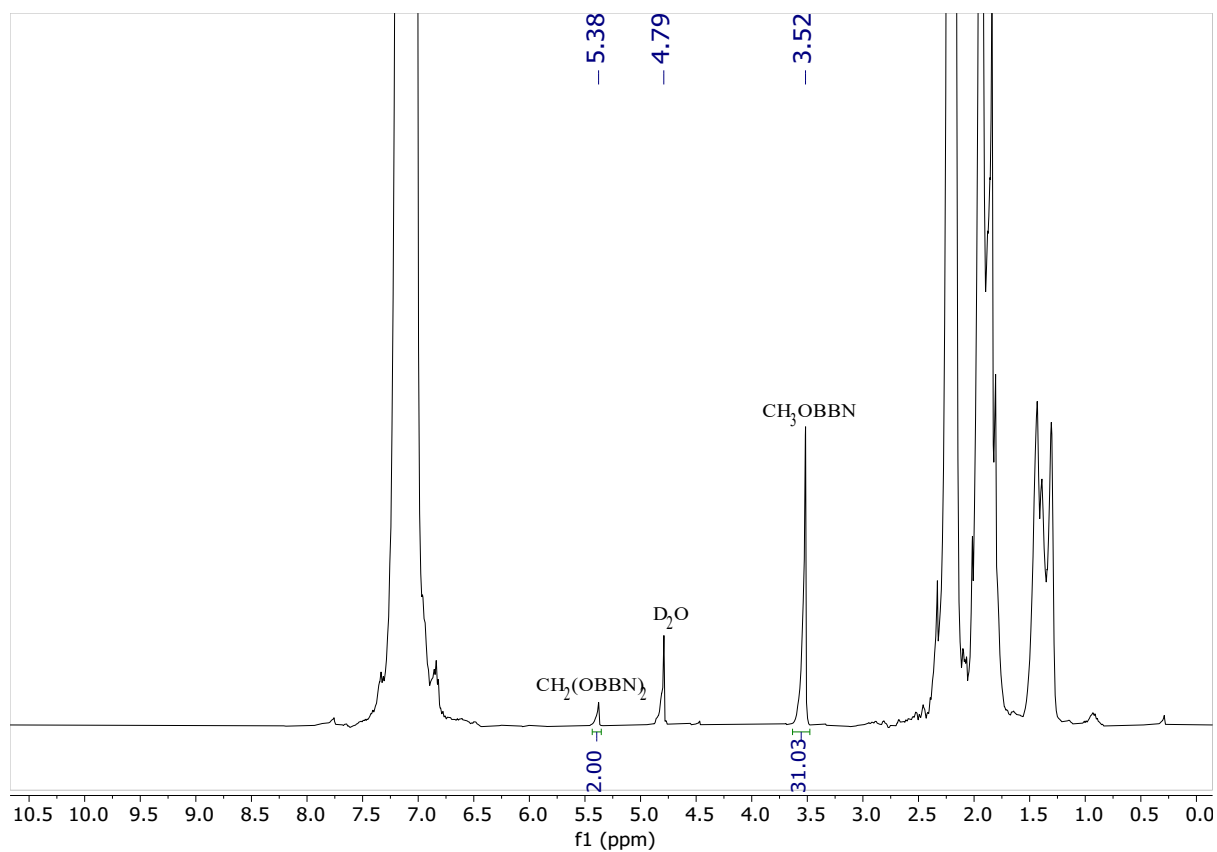


**Figure S51.**  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 160.46 MHz, 25 °C) spectrum of  $[\text{HCOOBBN}][\text{DMSO}]$  (**E**).

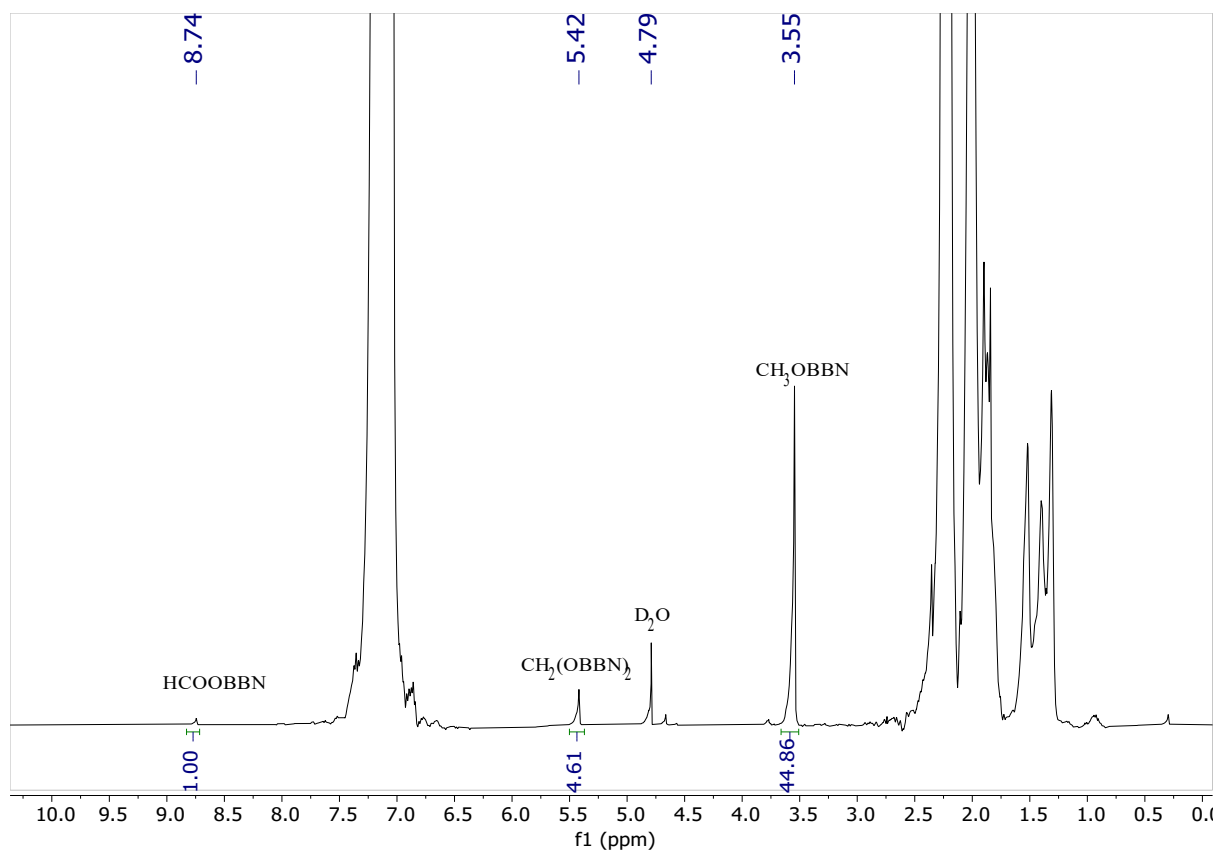


**Figure S52.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 500 MHz, 25 °C) spectrum of the 1:1 ratio reaction mixture of compound **E** (0.020 g, 0.082 mmol) and 9-BBN (0.010, 0.082 mmol) in toluene (0.5 mL) after 6 h at 25 °C.

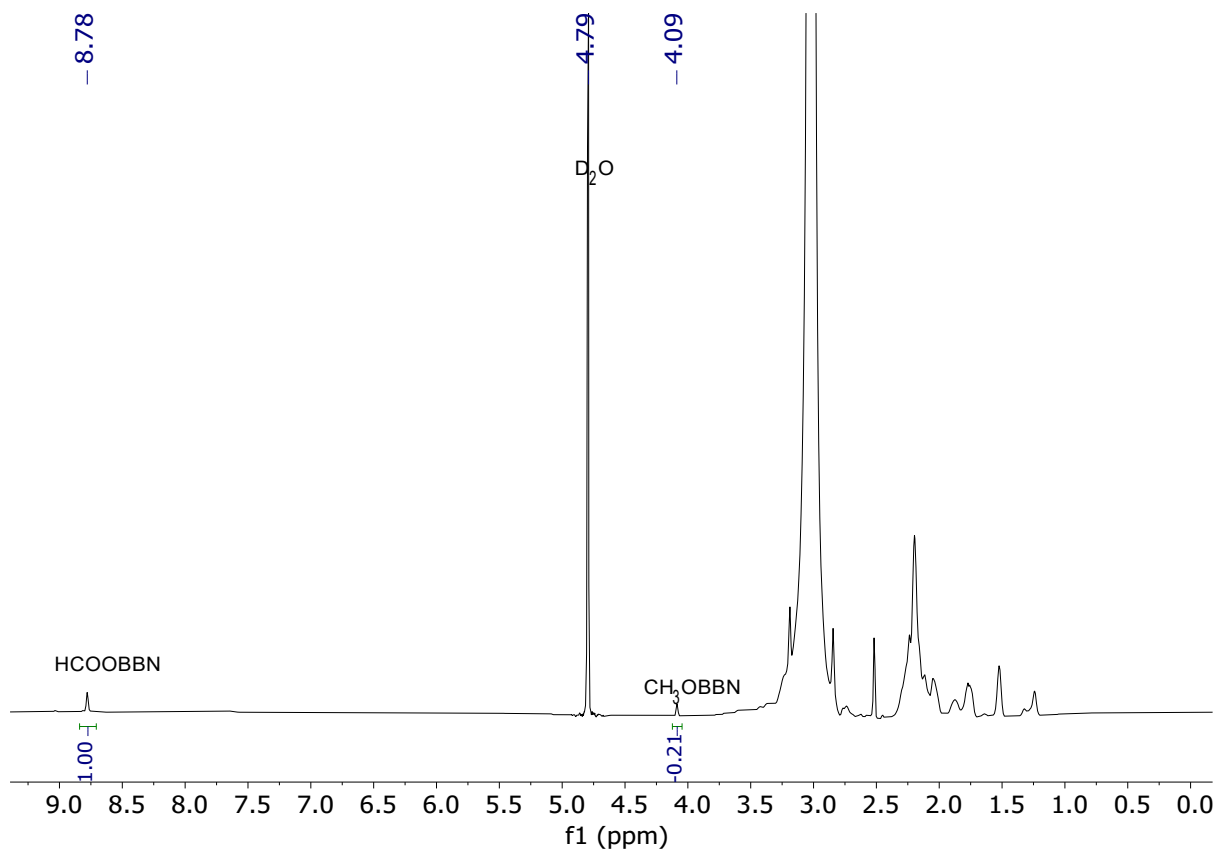




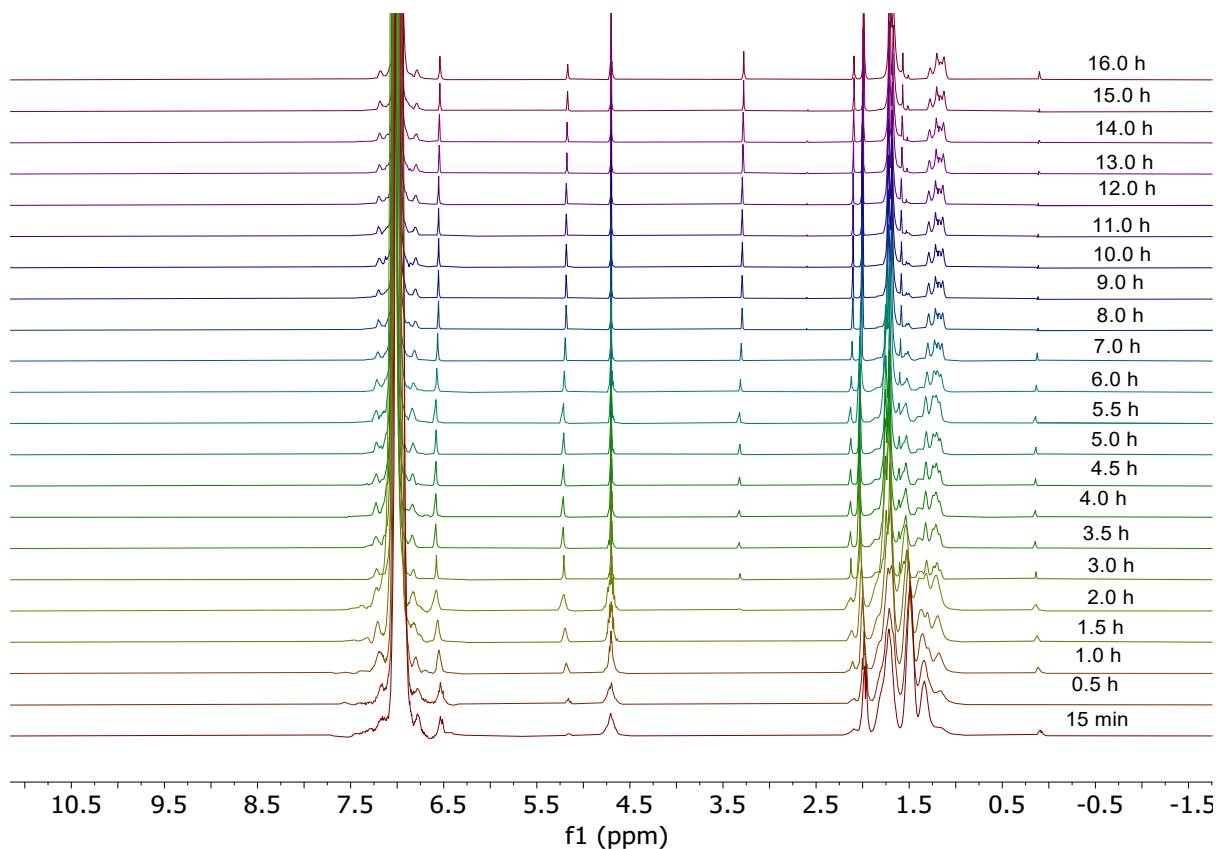
**Figure S53.** <sup>1</sup>H NMR (toluene solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of the 1:2 ratio reaction mixture of compound **E** (0.020 g, 0.082 mmol) and 9-BBN (0.020, 0.164 mmol) in toluene (0.5 mL) after 6 h at 25 °C.



**Figure S54.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25  $^\circ\text{C}$ ) spectrum of the 1:2:2 ratio reaction mixture of compound **E** (0.020 g, 0.082 mmol), 9-BBN (0.020, 0.164 mmol) and DMSO (11.7  $\mu\text{L}$ , 0.164 mmol) in toluene (0.5 mL) after 6 h at 25  $^\circ\text{C}$ .

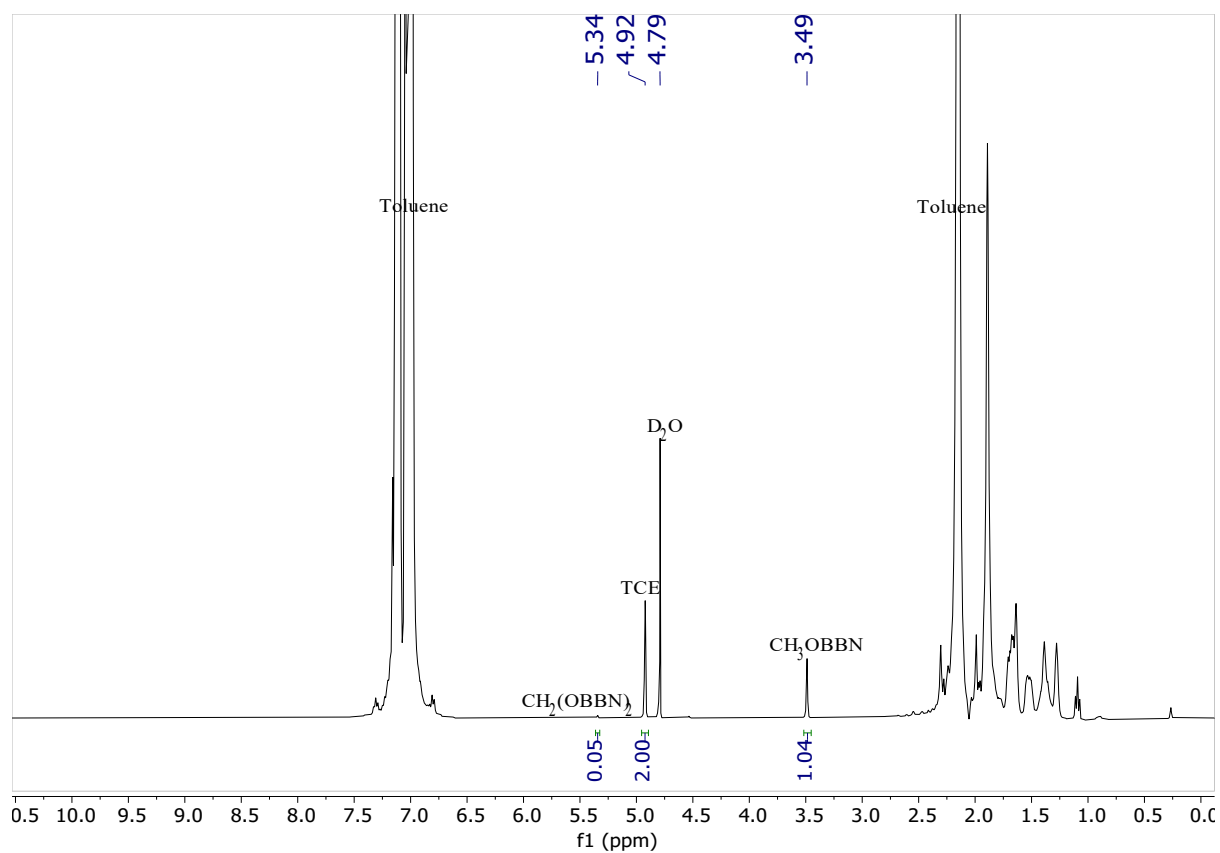


**Figure S55.** <sup>1</sup>H NMR (DMSO solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of the 1:2 ratio reaction mixture of compound **E** (0.020 g, 0.082 mmol) and 9-BBN (0.020, 0.164 mmol) in DMSO (0.5 mL) after 6 h at 25 °C.

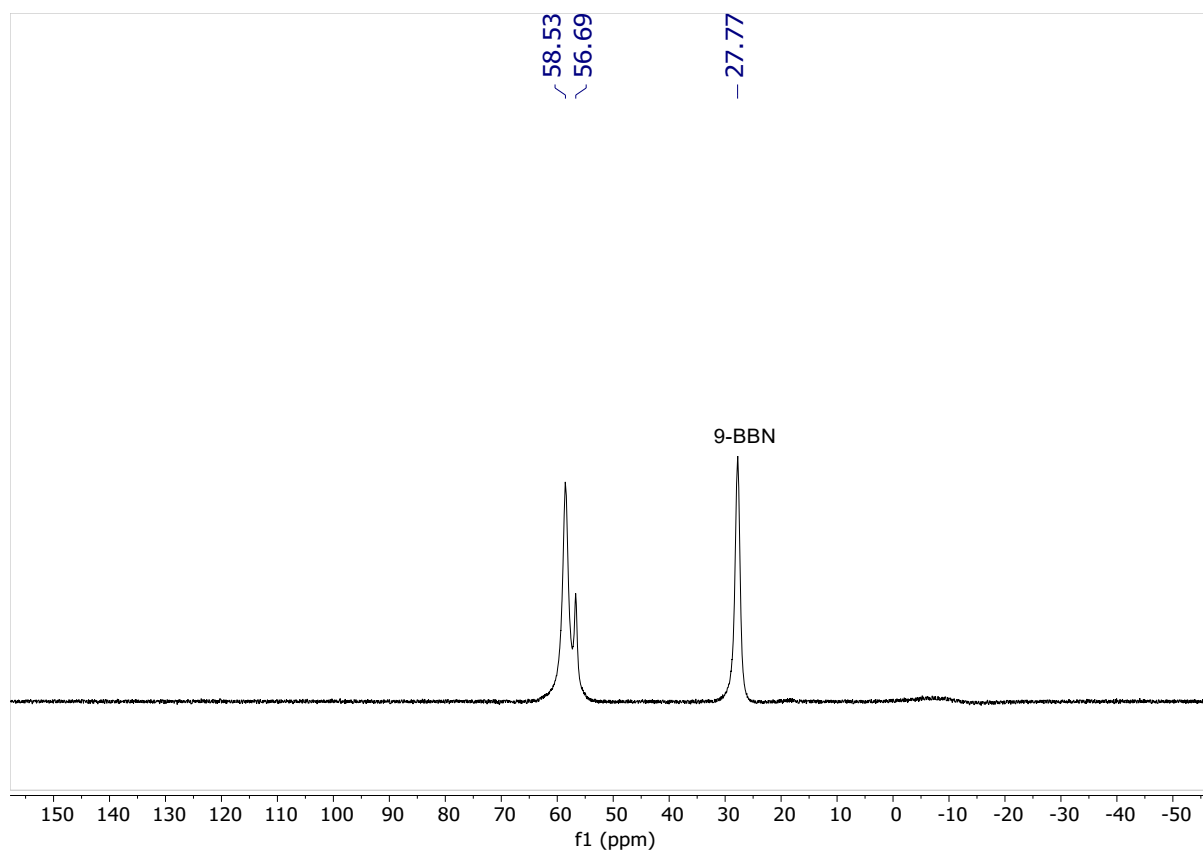


**Figure S56.** <sup>1</sup>H NMR (benzene solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (0.040 g, 0.3278 mmol), DMSO (1.7 μL, 7.3 mol%) and mesitylene (10.4 μL, 0.0749 mmol) in benzene (0.5 mL) under CO<sub>2</sub> (1 atm, balloon) for 16 h at 25 °C.

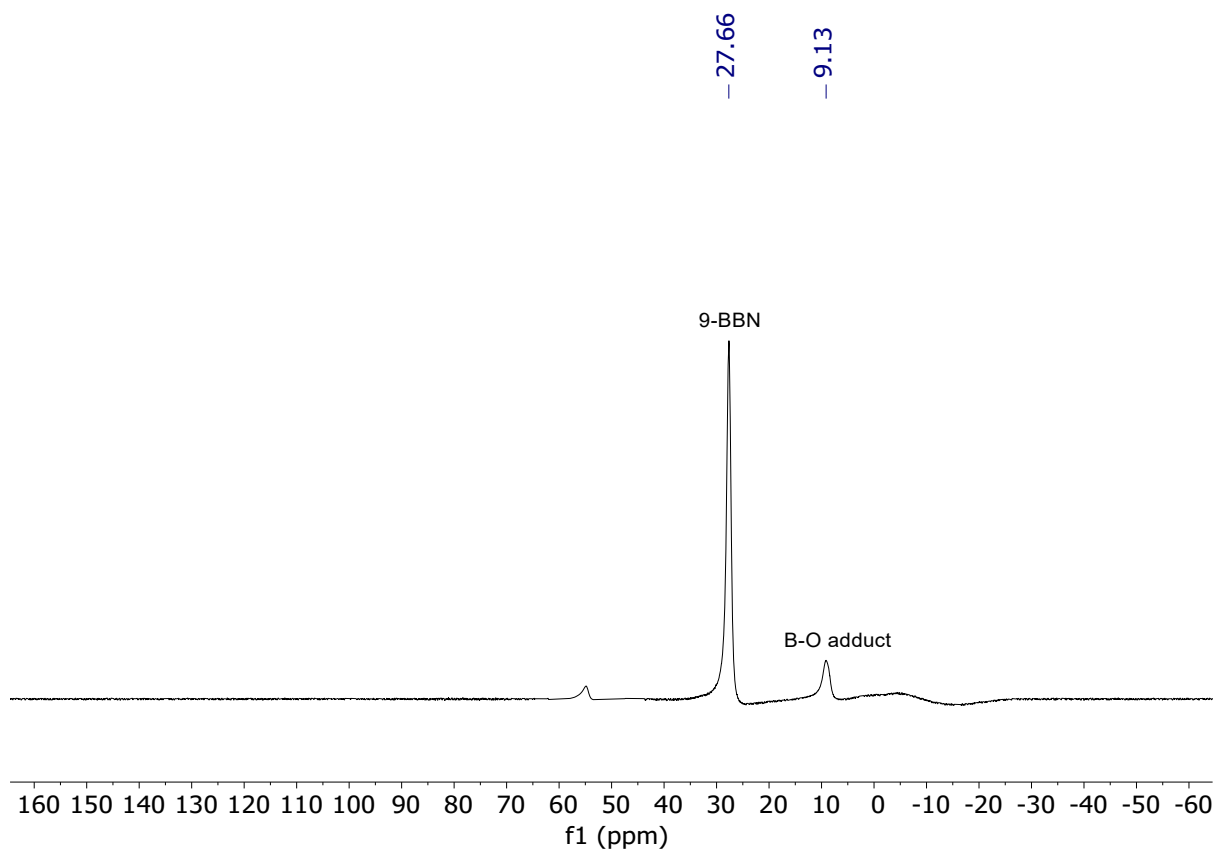
## For Table 3



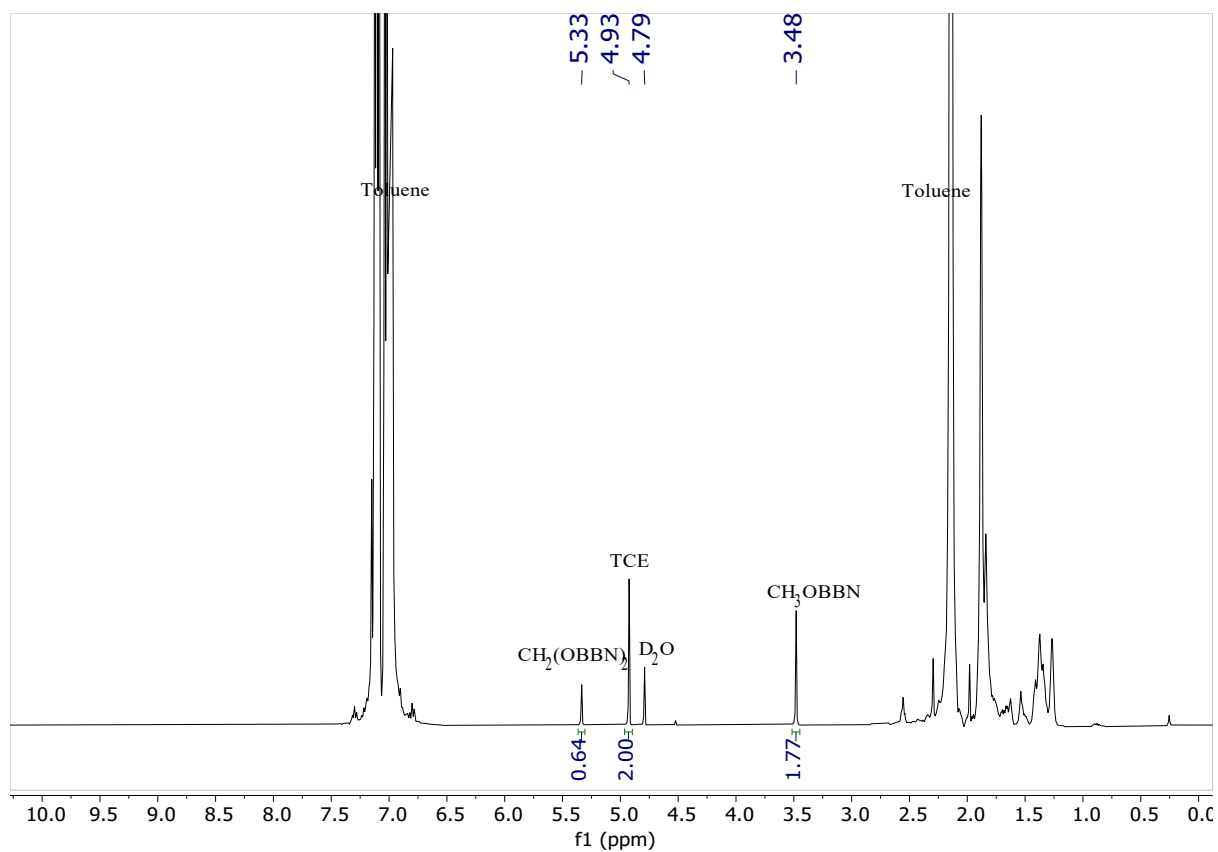
**Figure S57.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and diethylsulfoxide (DESO, 7.4  $\mu\text{L}$ , 7 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25 °C.



**Figure S58.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and diethylsulfoxide (DESO, 7.4  $\mu\text{L}$ , 7 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25 °C.

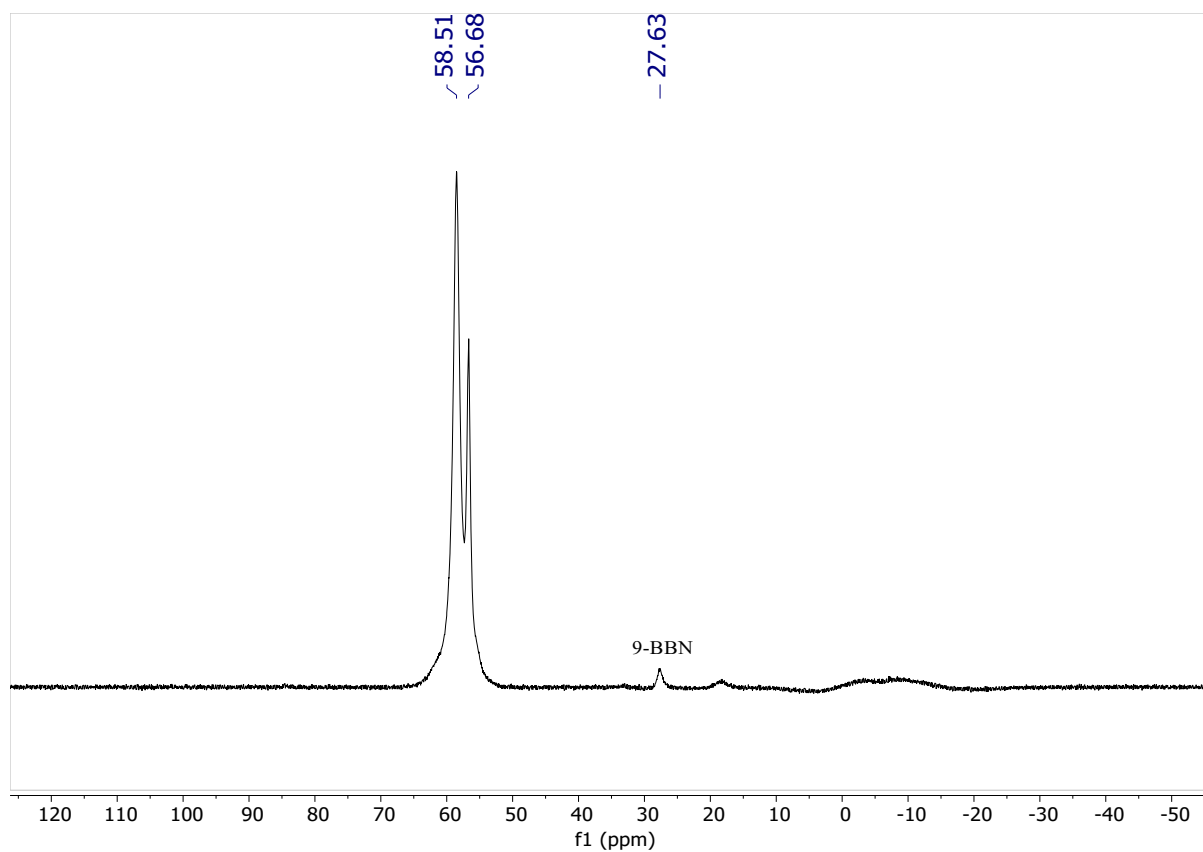


**Figure S59.**  $^{11}\text{B}$  NMR (benzene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of 1:1 molar reaction mixture of 9-BBN (0.030 g, 0.245 mmol) and diethylsulfoxide (DESO, 23.8  $\mu\text{L}$ , 0.246 mmol) in benzene (0.5 mL) at 25 °C.

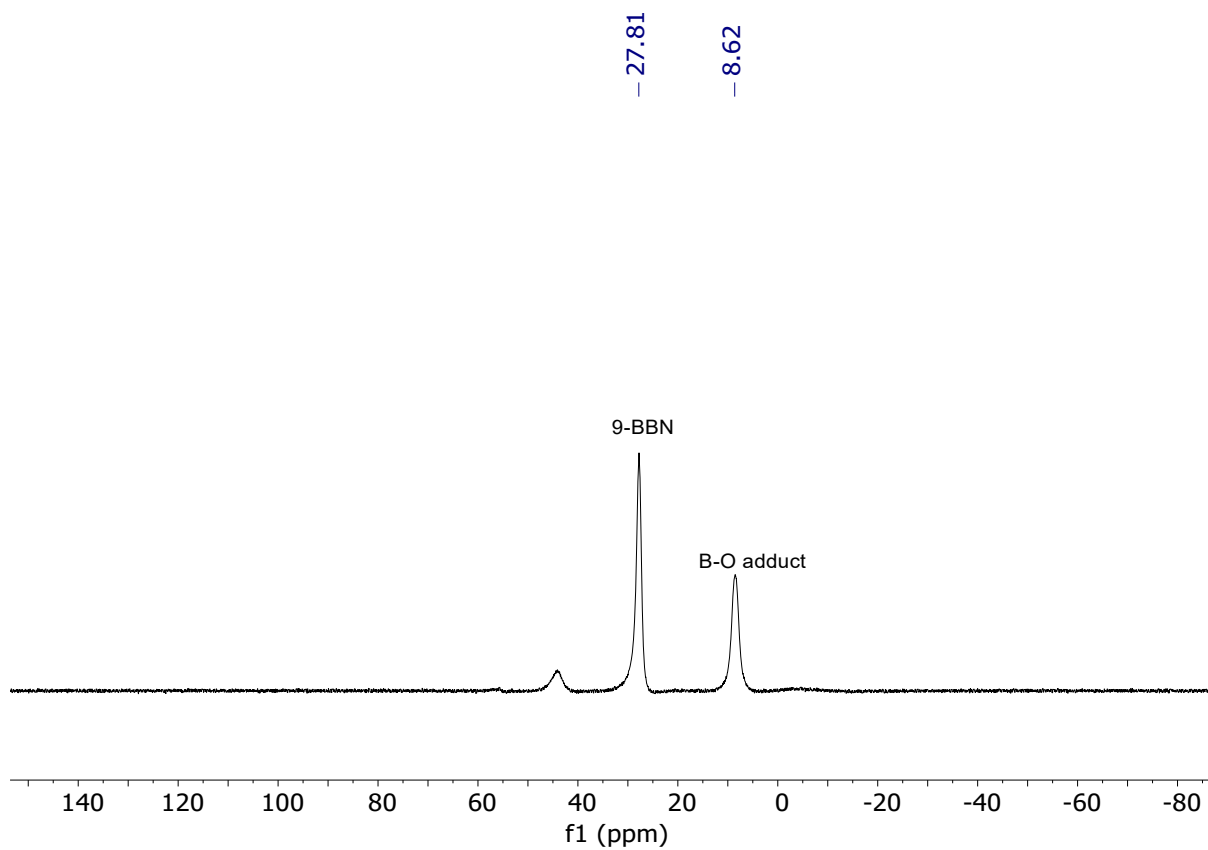


**Figure S60.** <sup>1</sup>H NMR (toluene solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and tetrahydrothiophene-1-oxide (THTO, 6.3 μL, 7 mol%) in toluene (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 6 h at 25 °C.

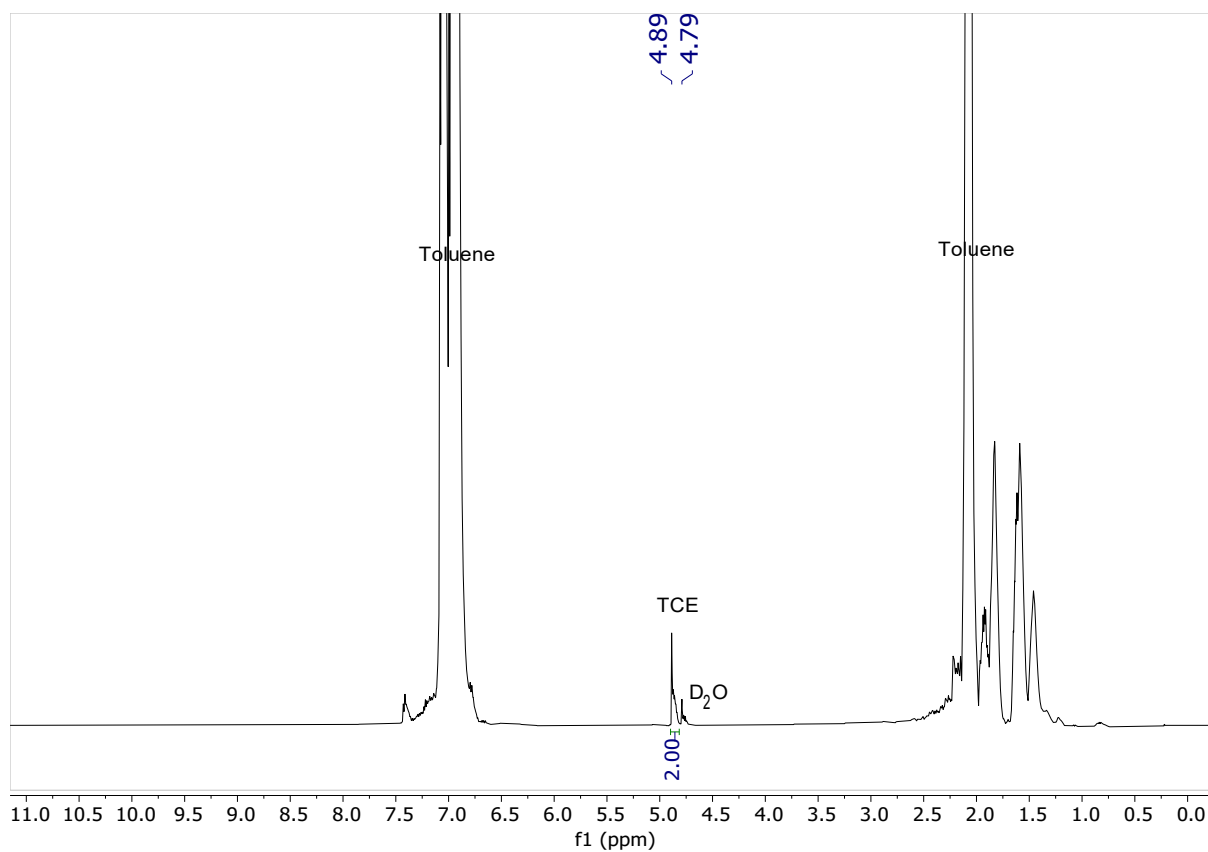




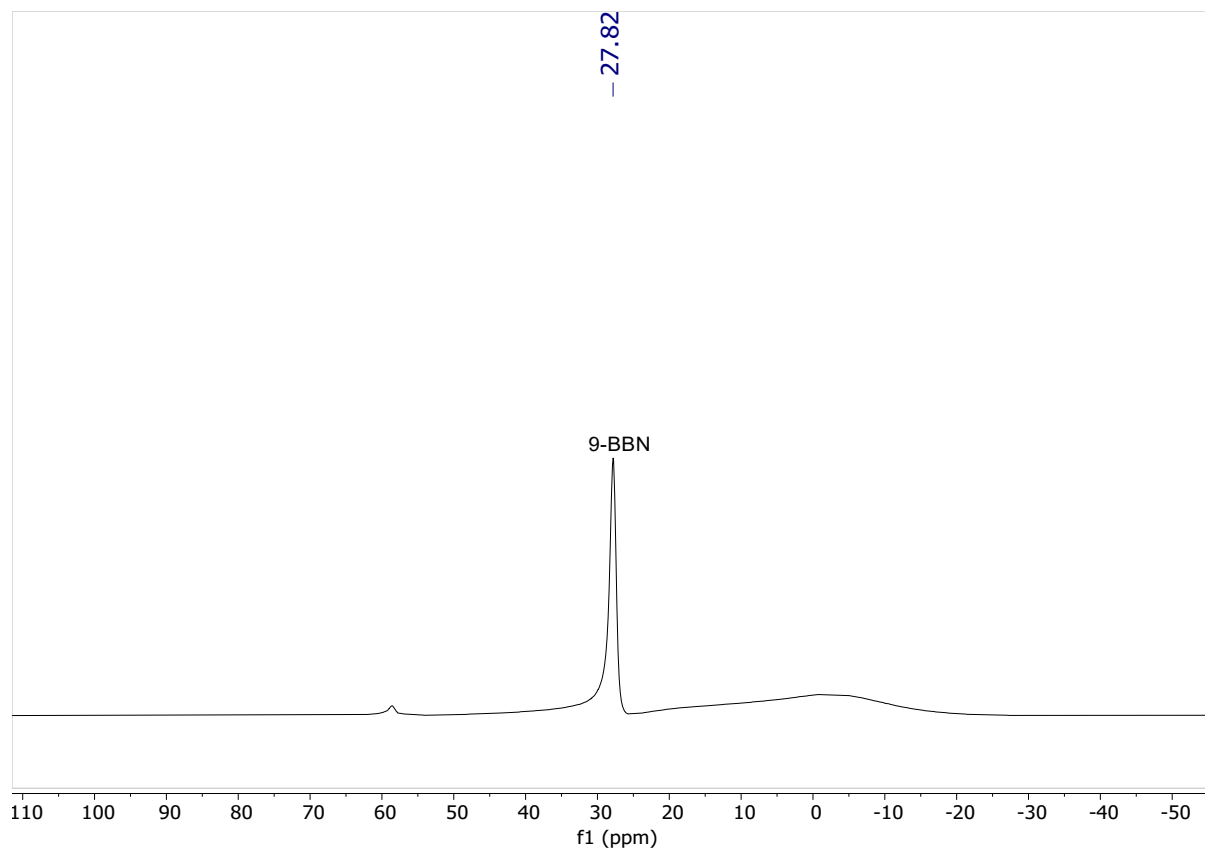
**Figure S61.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and tetrahydrothiophene-1-oxide (THTO, 6.3  $\mu\text{L}$ , 7 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25 °C.



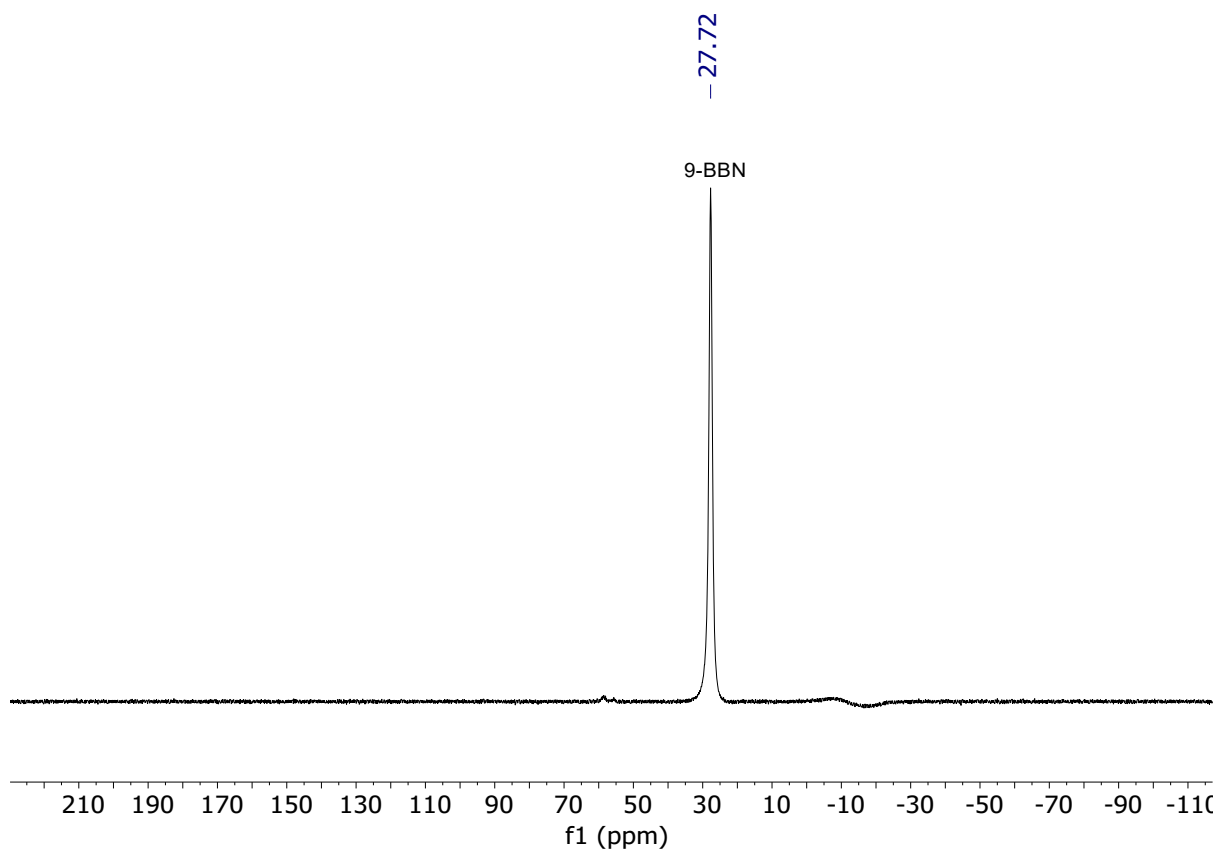
**Figure S62.**  $^{11}\text{B}$  NMR (benzene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of the 1:1 molar reaction mixture of 9-BBN (0.030 g, 0.245 mmol) and tetrahydrothiophene-1-oxide (THTO, 22.2  $\mu\text{L}$ , 0.246 mmol) in benzene (0.5 mL) at 25 °C.



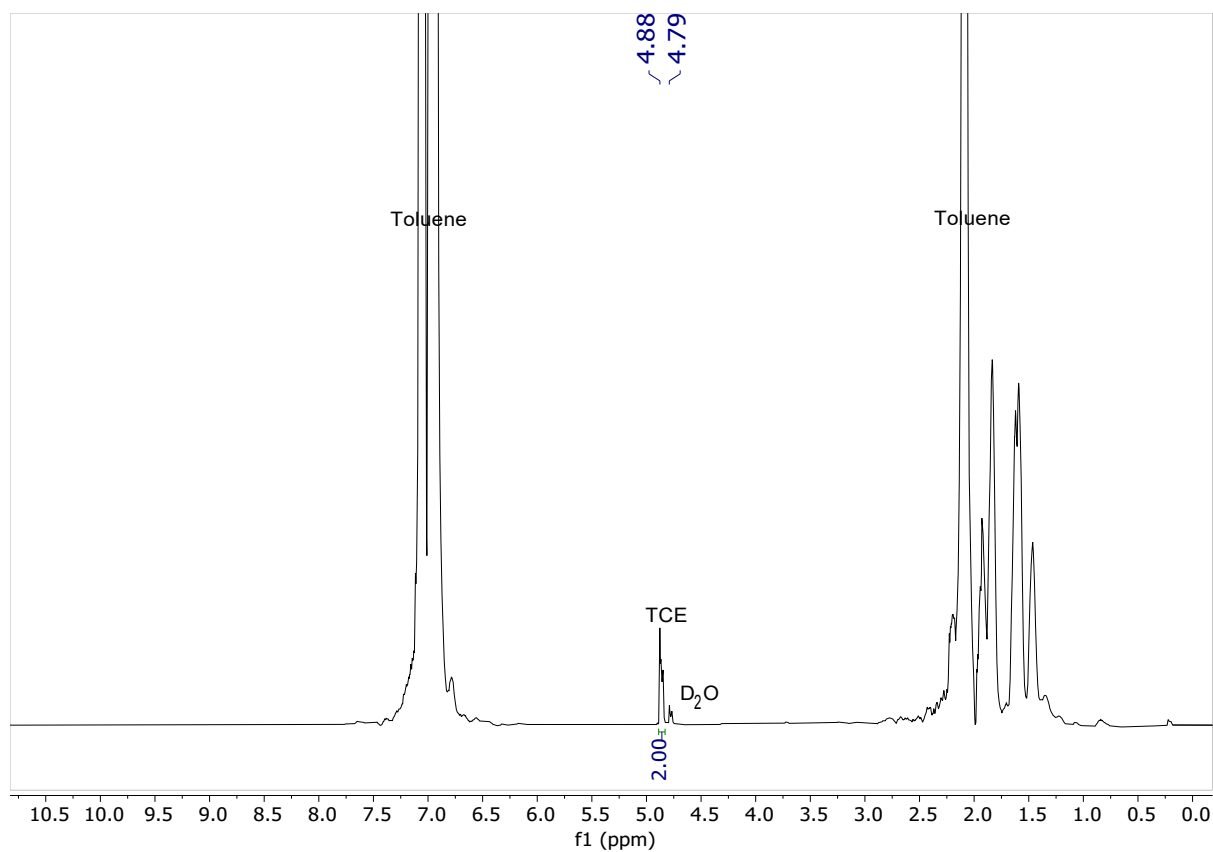
**Figure S63.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 500 MHz, 25  $^\circ\text{C}$ ) spectrum of reaction mixture of 9-BBN (1.0 mmol) and diphenylsulfoxide (DPSO, 14.2 mg, 7 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25  $^\circ\text{C}$ .



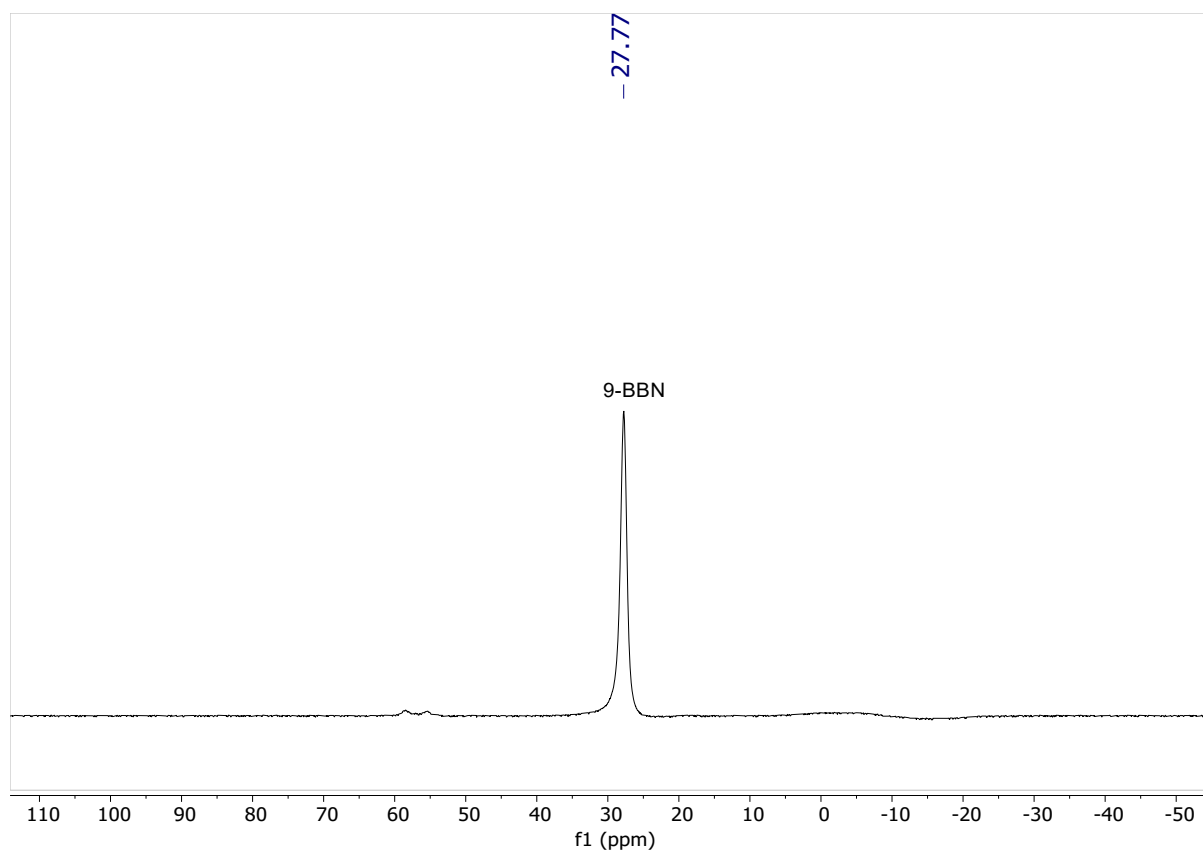
**Figure S64.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and diphenylsulfoxide (DPSO, 14.2 mg, 7 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25 °C.



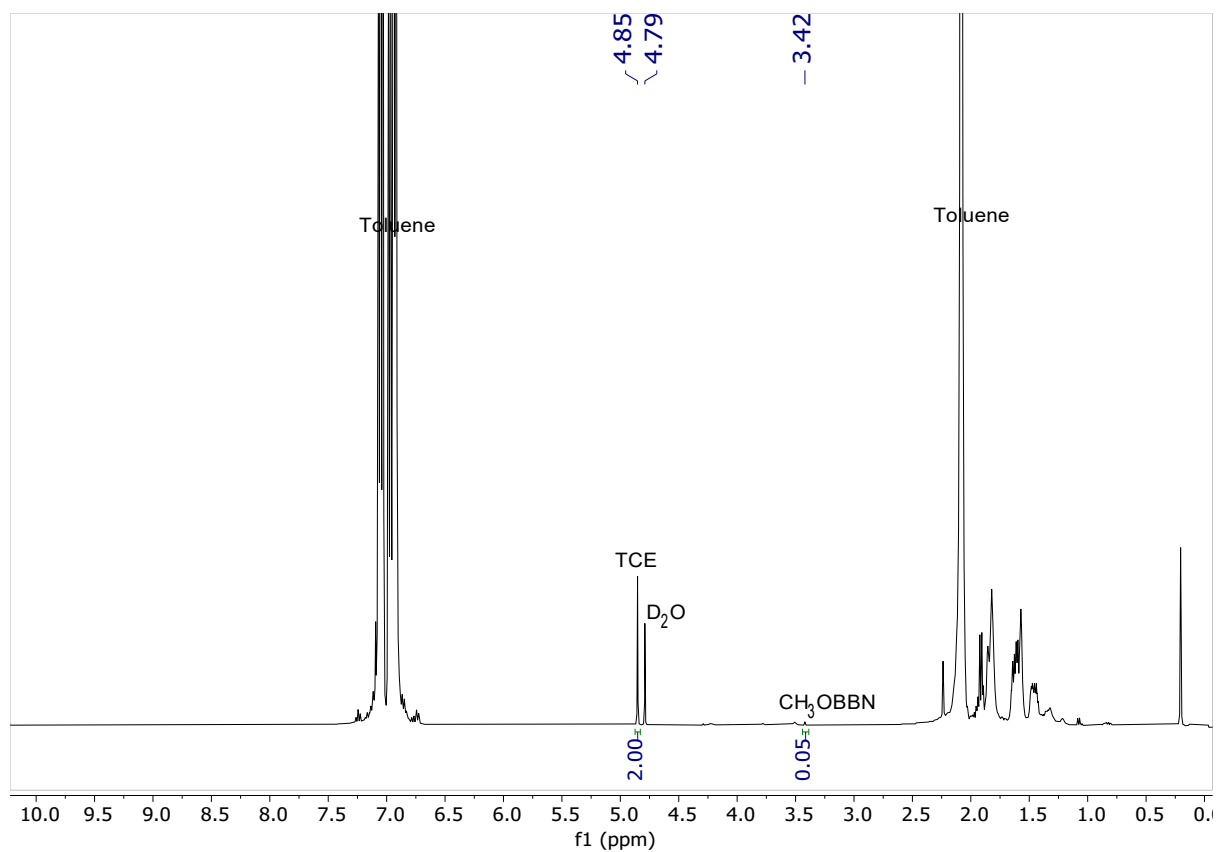
**Figure S65.**  $^{11}\text{B}$  NMR (benzene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of the 1:1 molar reaction mixture of 9-BBN (0.030 g, 0.245 mmol) and diphenylsulfoxide (DPSO, 0.050 g, 0.247) in benzene (0.5 mL) at 25 °C.



**Figure S66.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 500 MHz, 25  $^\circ\text{C}$ ) spectrum of reaction mixture of 9-BBN (1.0 mmol) and  $\text{DMSO}_2$  (6.6 mg, 7 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25  $^\circ\text{C}$ .

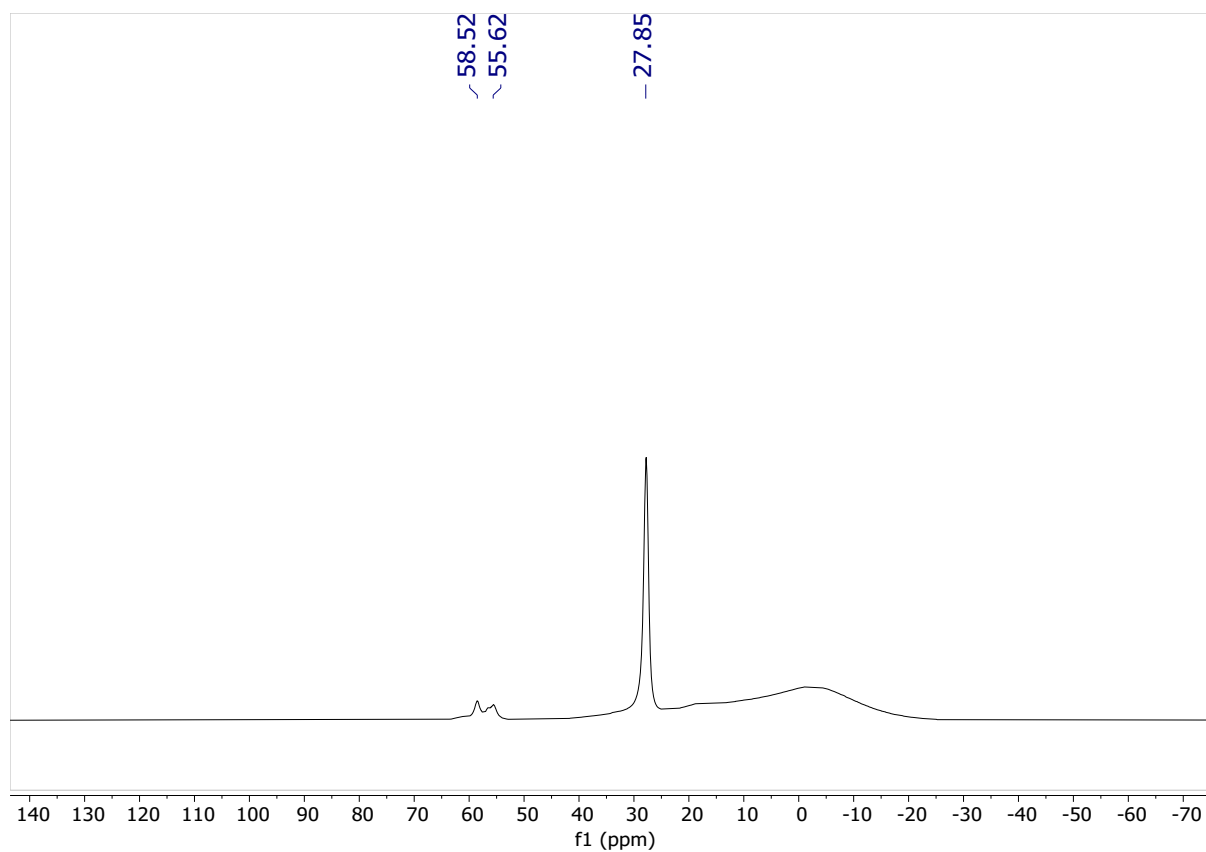


**Figure S67.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and  $\text{DMSO}_2$  (6.6 mg, 7 mol%) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25 °C.

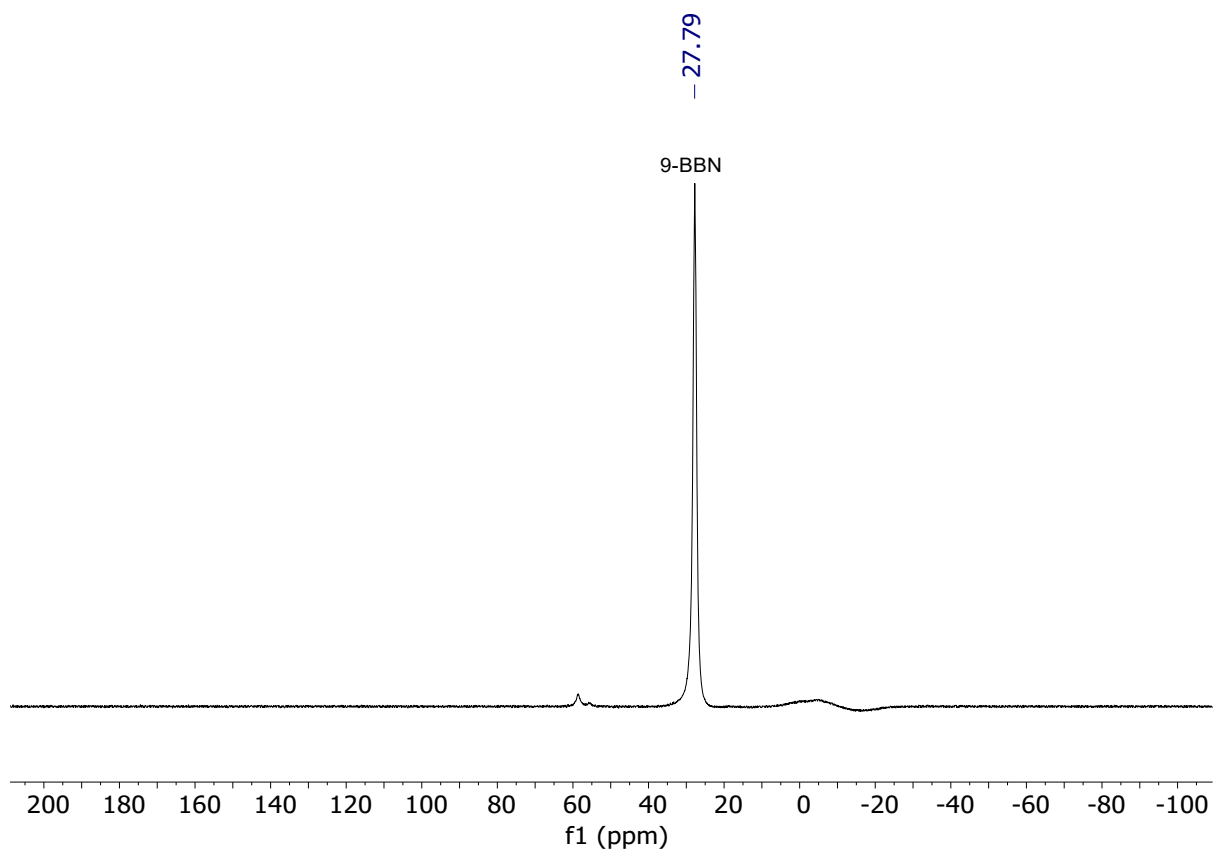


**Figure S68.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25  $^\circ\text{C}$ ) spectrum of reaction mixture of 9-BBN (1.0 mmol) and  $\text{DMSO}_2$  (6.6 mg, 7 mol%) in THF (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25  $^\circ\text{C}$ .

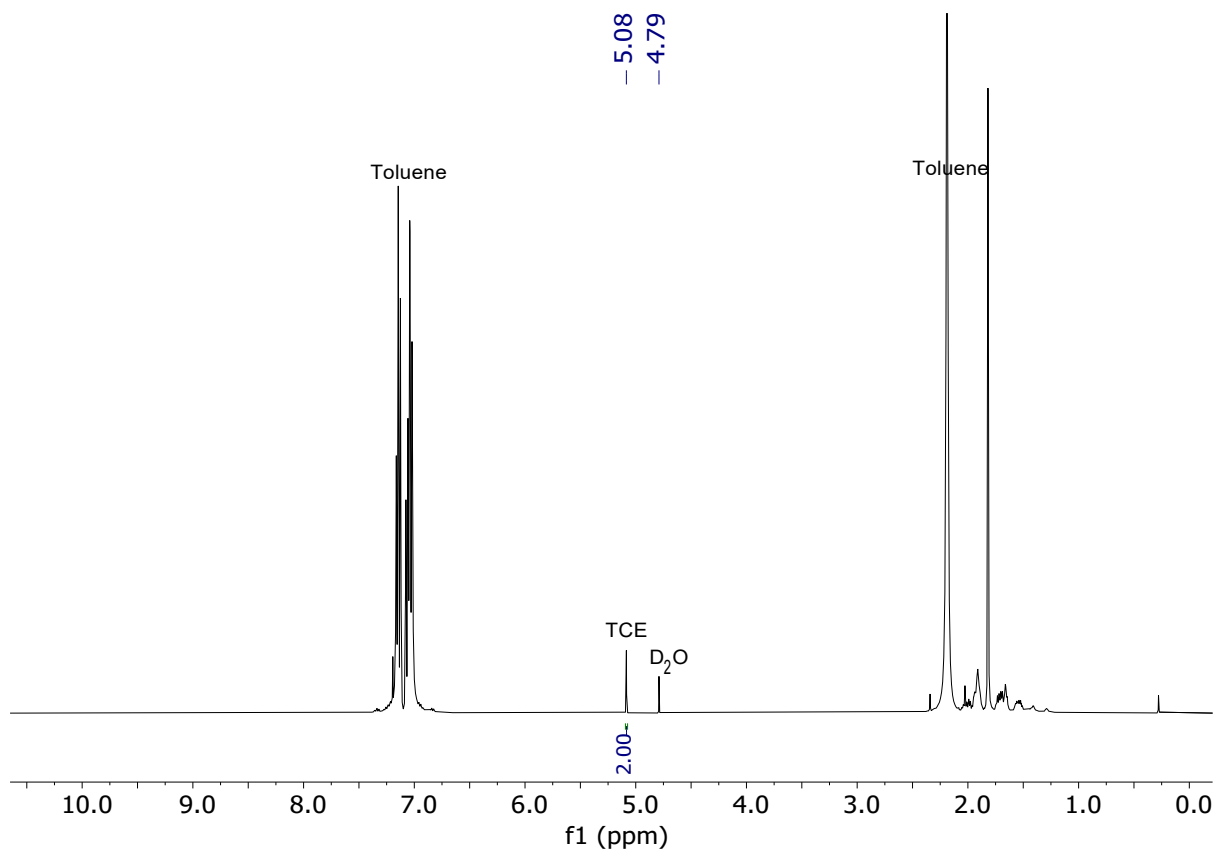




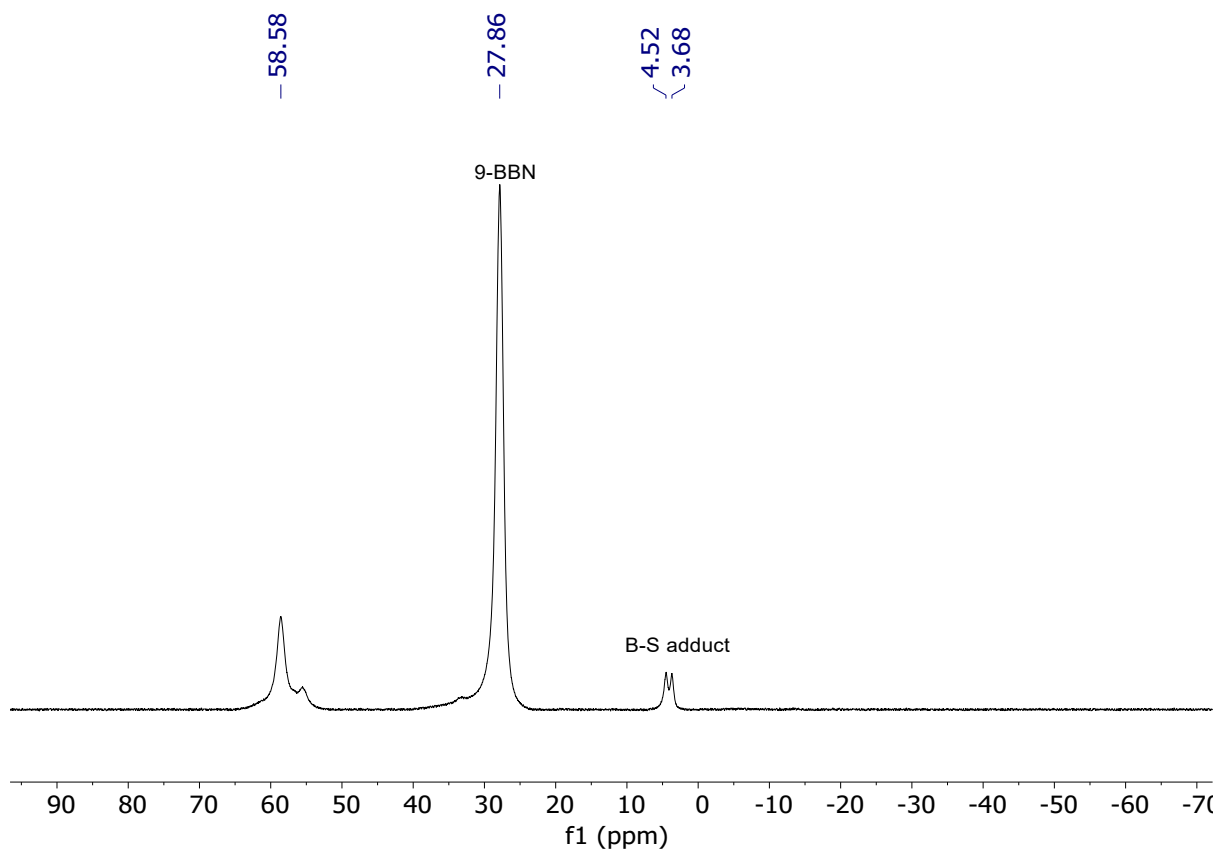
**Figure S69.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and dimethylsulfone ( $\text{DMSO}_2$ , 6.6 mg, 7 mol%) in THF (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 6 h at 25 °C.



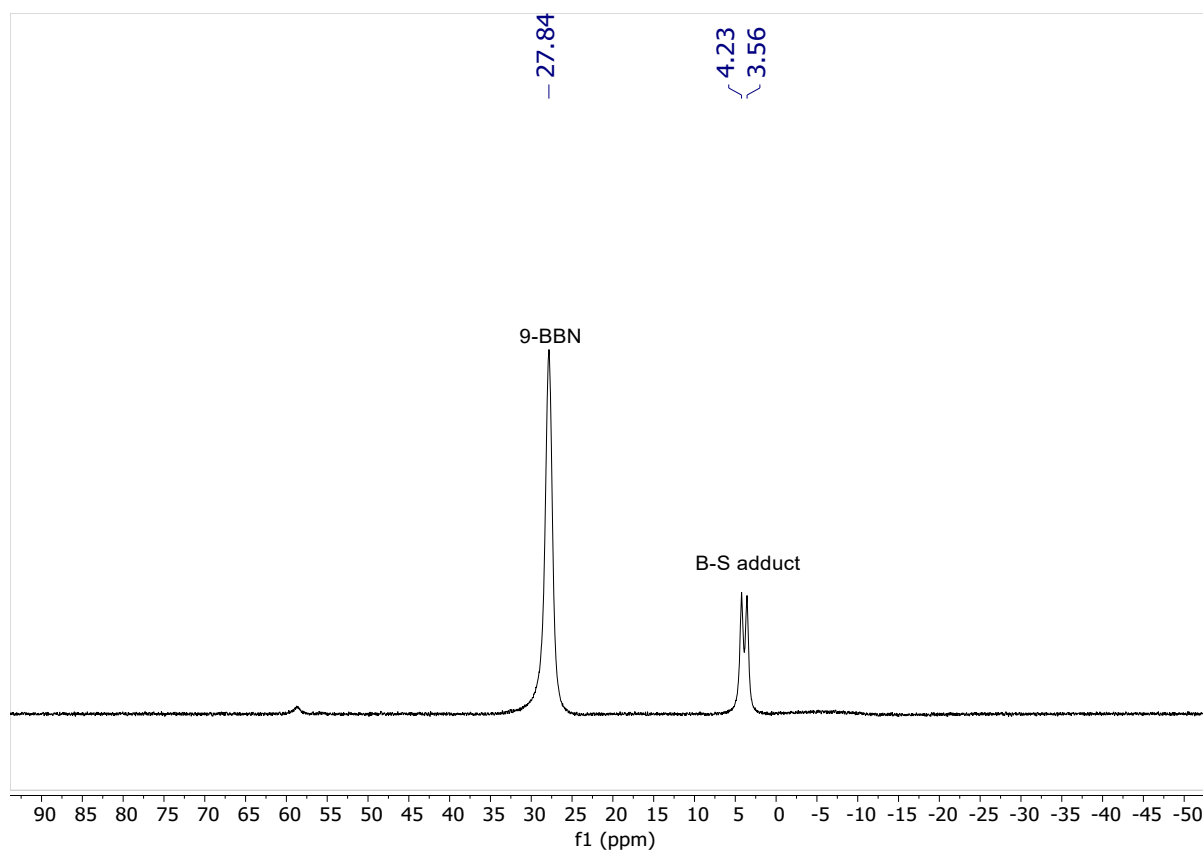
**Figure S70.**  $^{11}\text{B}$  NMR (benzene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of the 1:1 molar reaction mixture of 9-BBN (0.030 g, 0.245 mmol) and dimethylsulfone ( $\text{DMSO}_2$ , 0.023 g, 0.244) in benzene (0.5 mL) at 25 °C.



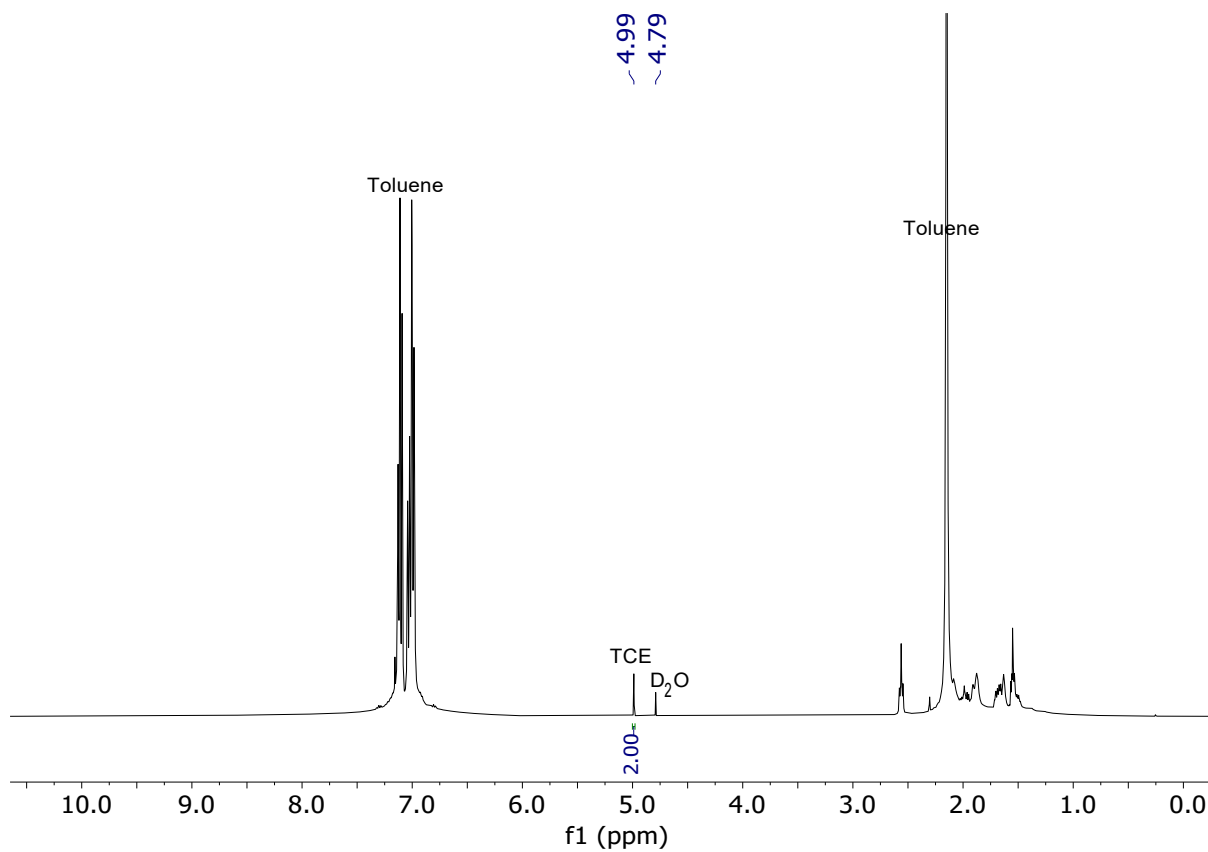
**Figure S71.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25  $^\circ\text{C}$ ) spectrum of reaction mixture of 9-BBN (1.0 mmol) and dimethylsulfide (DMS, 74.0  $\mu\text{L}$ , 1.0 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 25  $^\circ\text{C}$ . No  $\text{CO}_2$  reduced products were formed.



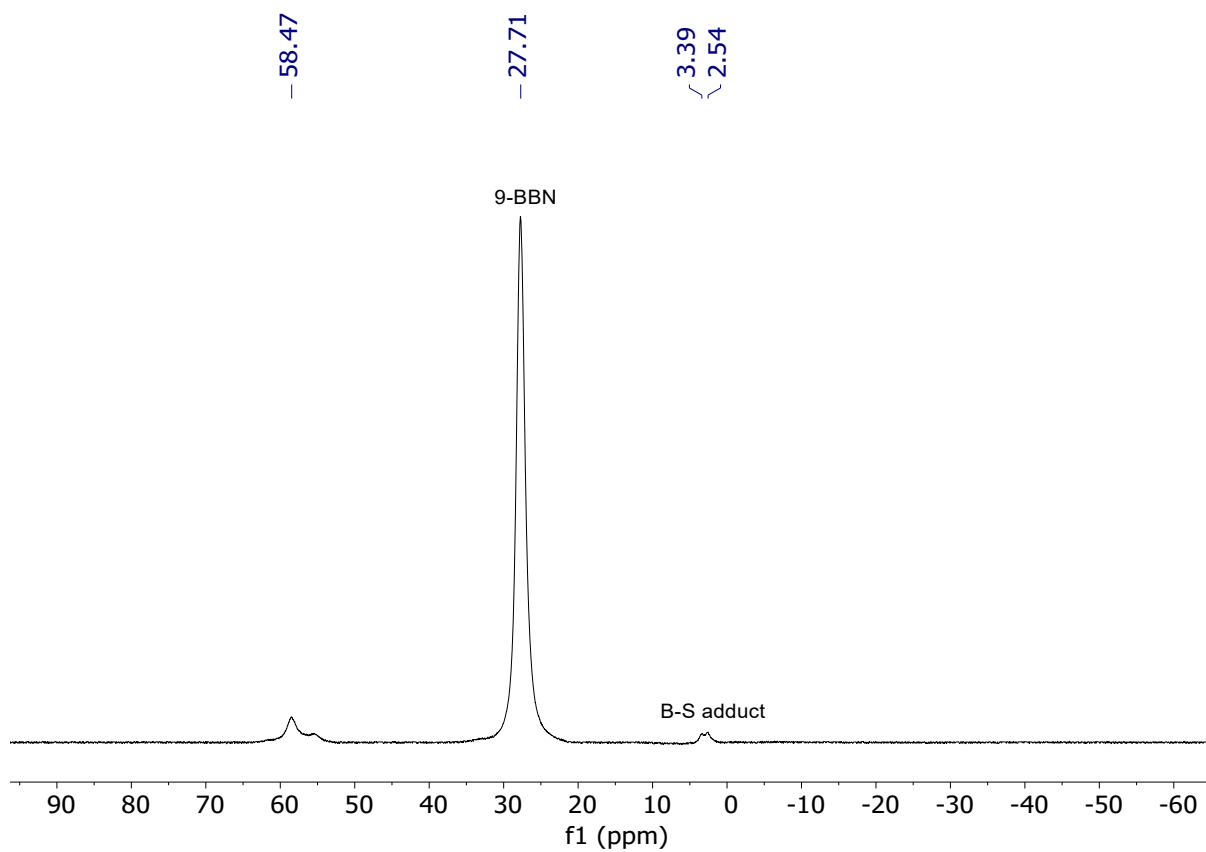
**Figure S72.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 128.37 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and dimethylsulfide (DMS, 74.0  $\mu\text{L}$ , 1.0 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 25 °C.



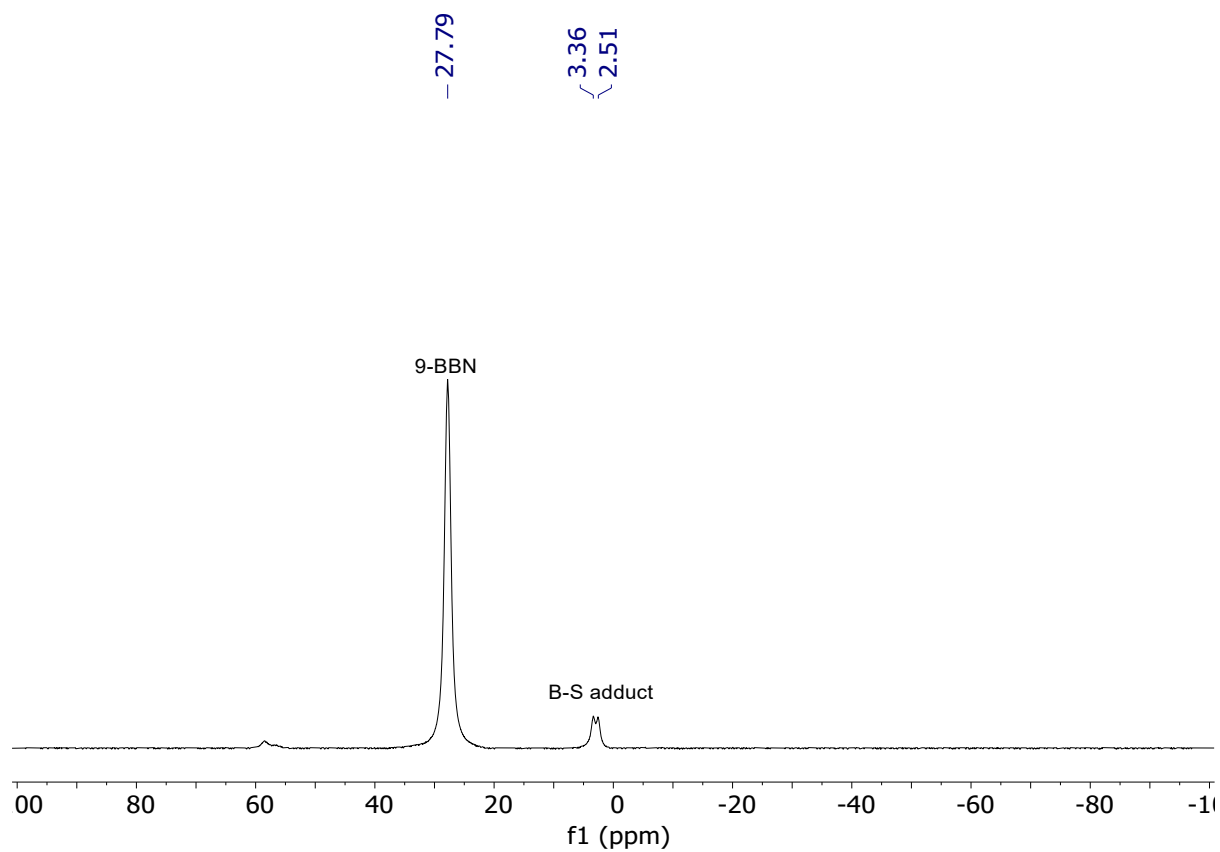
**Figure S73.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 160.46 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (0.25 mmol) and dimethylsulfide (DMS, 74.0  $\mu\text{L}$ , 1.0 mmol) in toluene (0.5 mL) at 25 °C.



**Figure S74.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25  $^\circ\text{C}$ ) spectrum of reaction mixture of 9-BBN (1.0 mmol) and tetrahydrothiophene (THT, 88.1  $\mu\text{L}$ , 1.0 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 25  $^\circ\text{C}$ . No  $\text{CO}_2$  reduced products were formed.

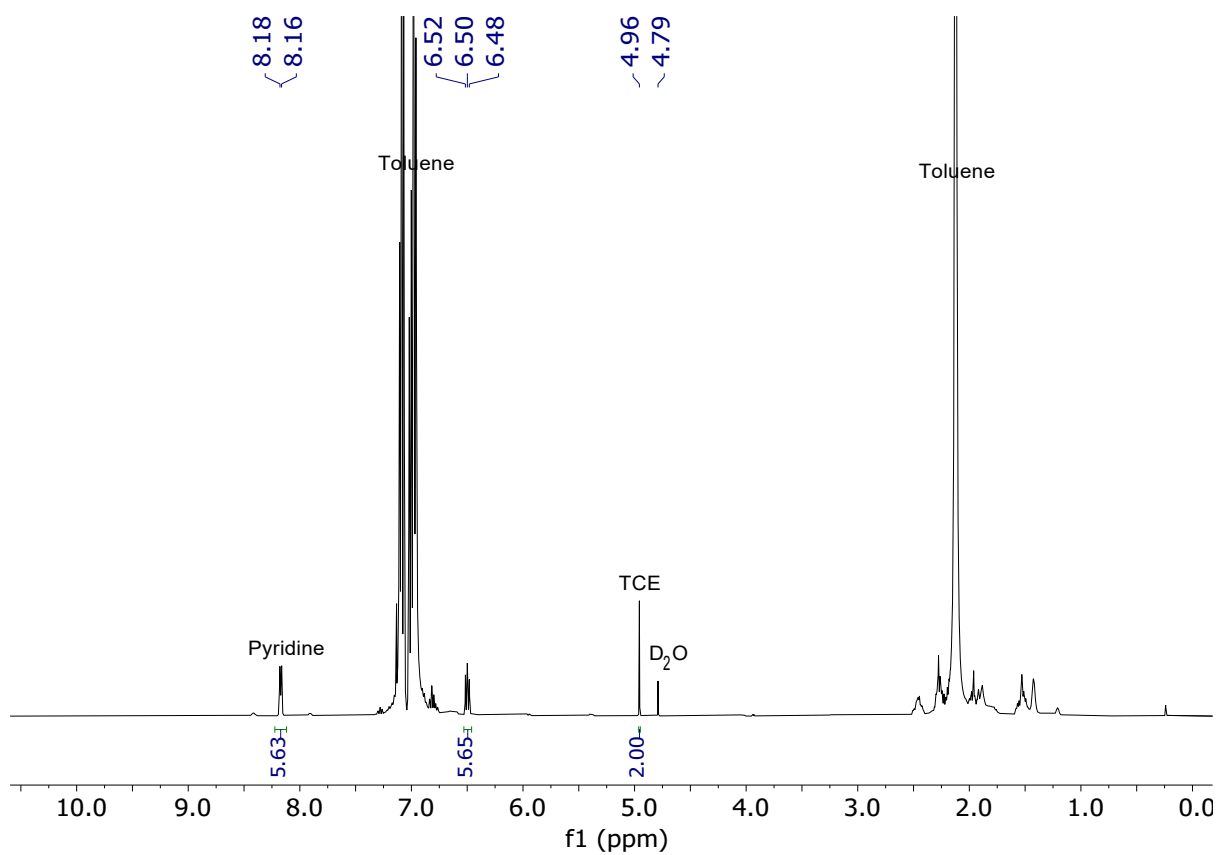


**Figure S75.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 128.37 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and tetrahydrothiophene (THT, 88.1  $\mu\text{L}$ , 1.0 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 25 °C.

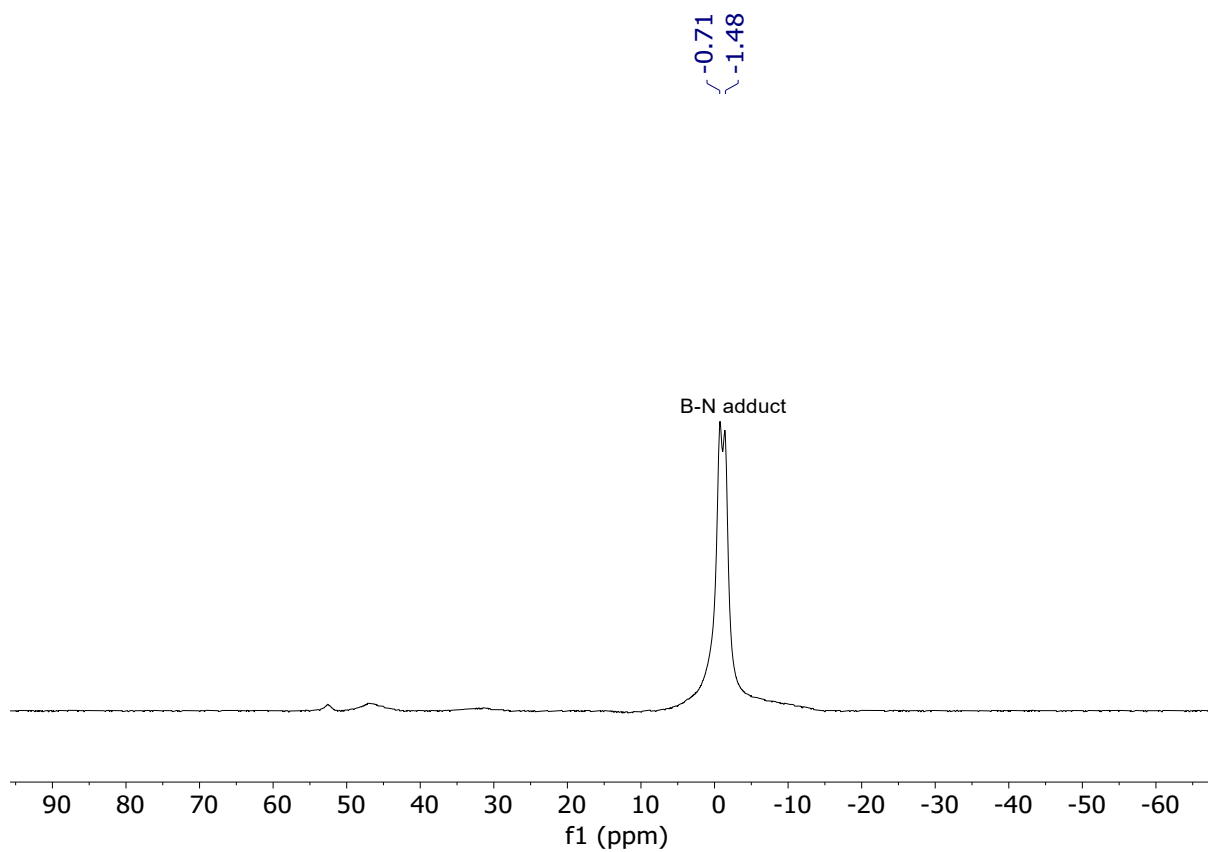


**Figure S76.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 128.37 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (0.25 mmol) and tetrahydrothiophene (THT, 88.1  $\mu\text{L}$ , 1.0 mmol) in toluene (0.5 mL) at 25 °C.

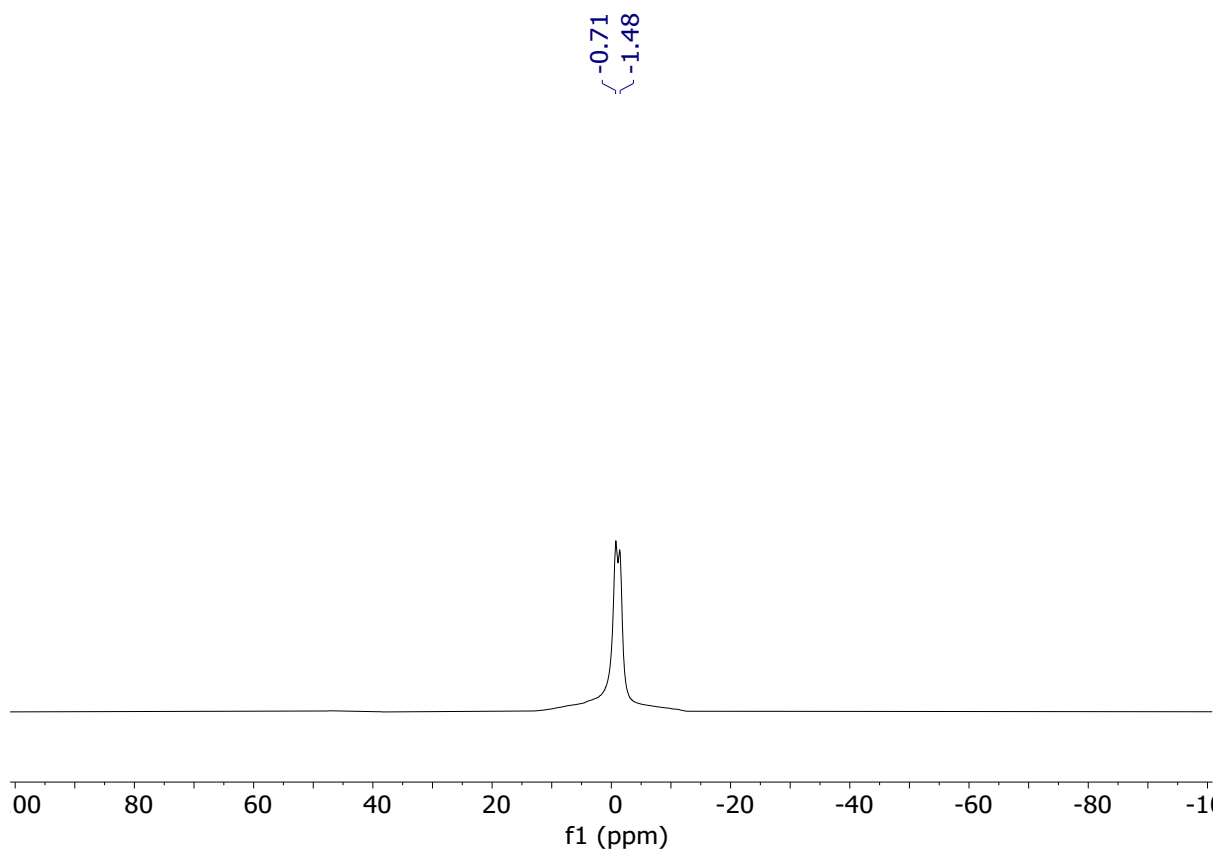




**Figure S77.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25  $^\circ\text{C}$ ) spectrum of reaction mixture of 9-BBN (1.0 mmol) and pyridine (80.6  $\mu\text{L}$ , 1.0 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 25  $^\circ\text{C}$ . No  $\text{CO}_2$  reduced products were formed.



**Figure S78.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 128.37 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (1.0 mmol) and pyridine (80.6  $\mu\text{L}$ , 1.0 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 25 °C.



**Figure S79.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 128.37 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (0.25 mmol) and pyridine (80.6  $\mu\text{L}$ , 1.0 mmol) in toluene (0.5 mL) at 25 °C.

## For C-methylenation of indoles

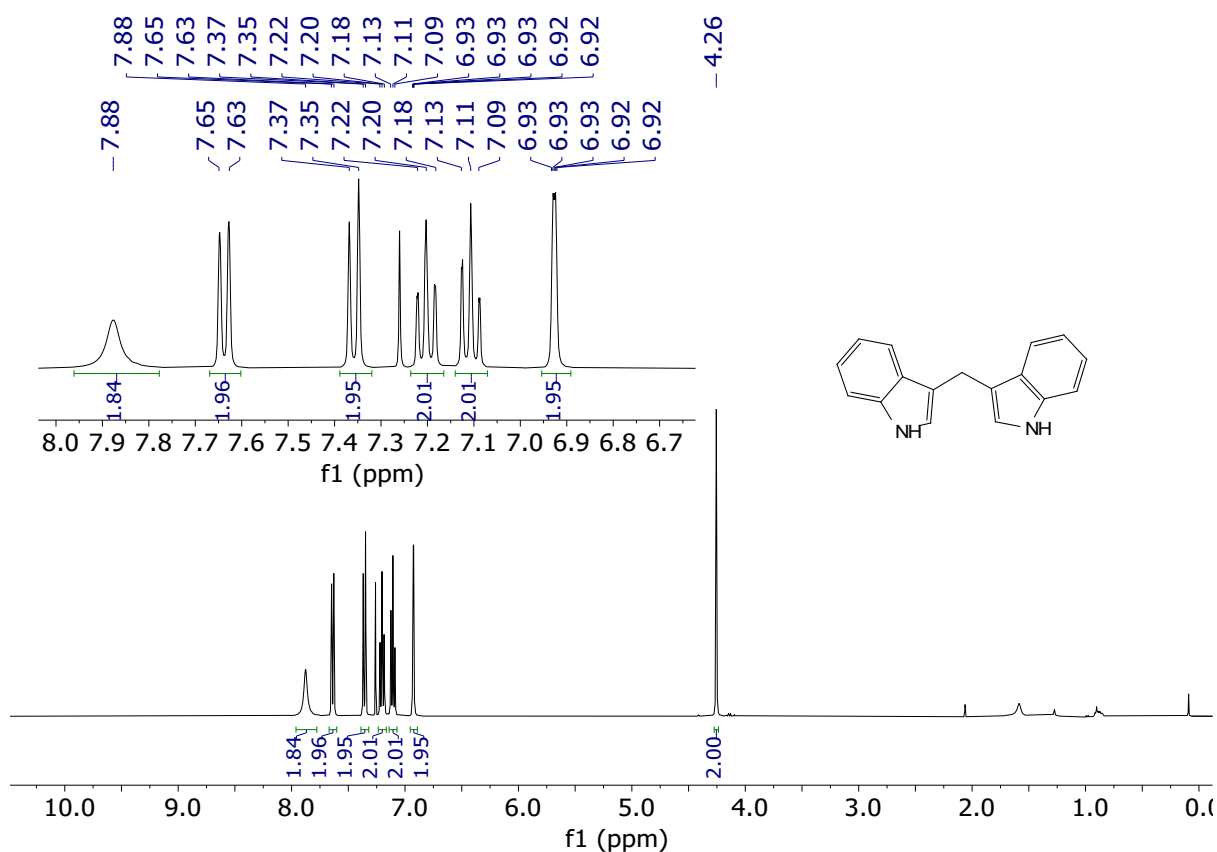


Figure S80. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C) spectrum of di(1*H*-indol-3-yl)methane.<sup>4</sup>

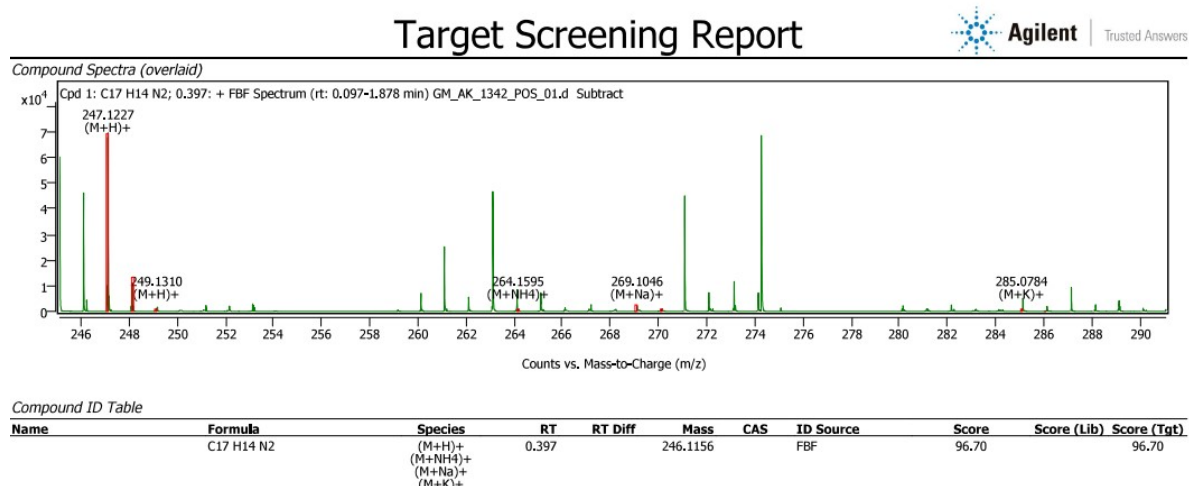
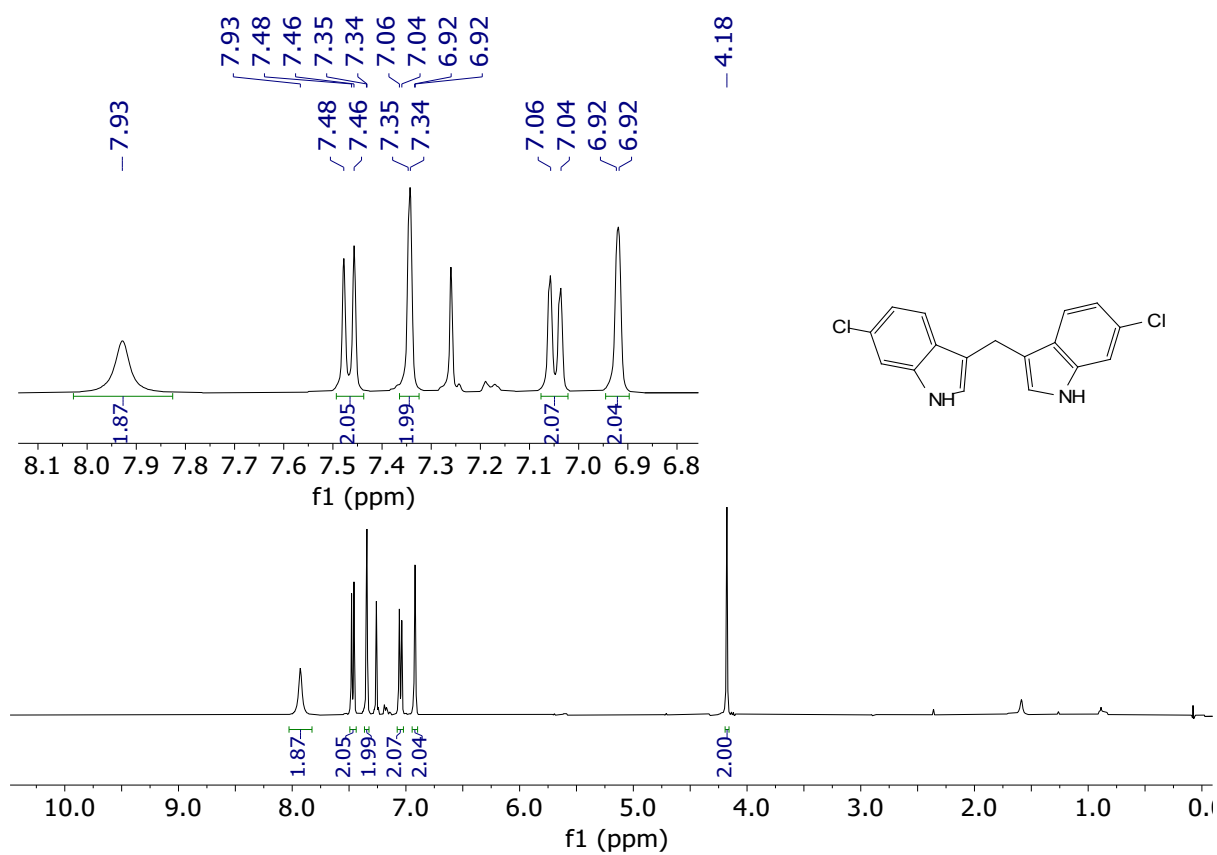
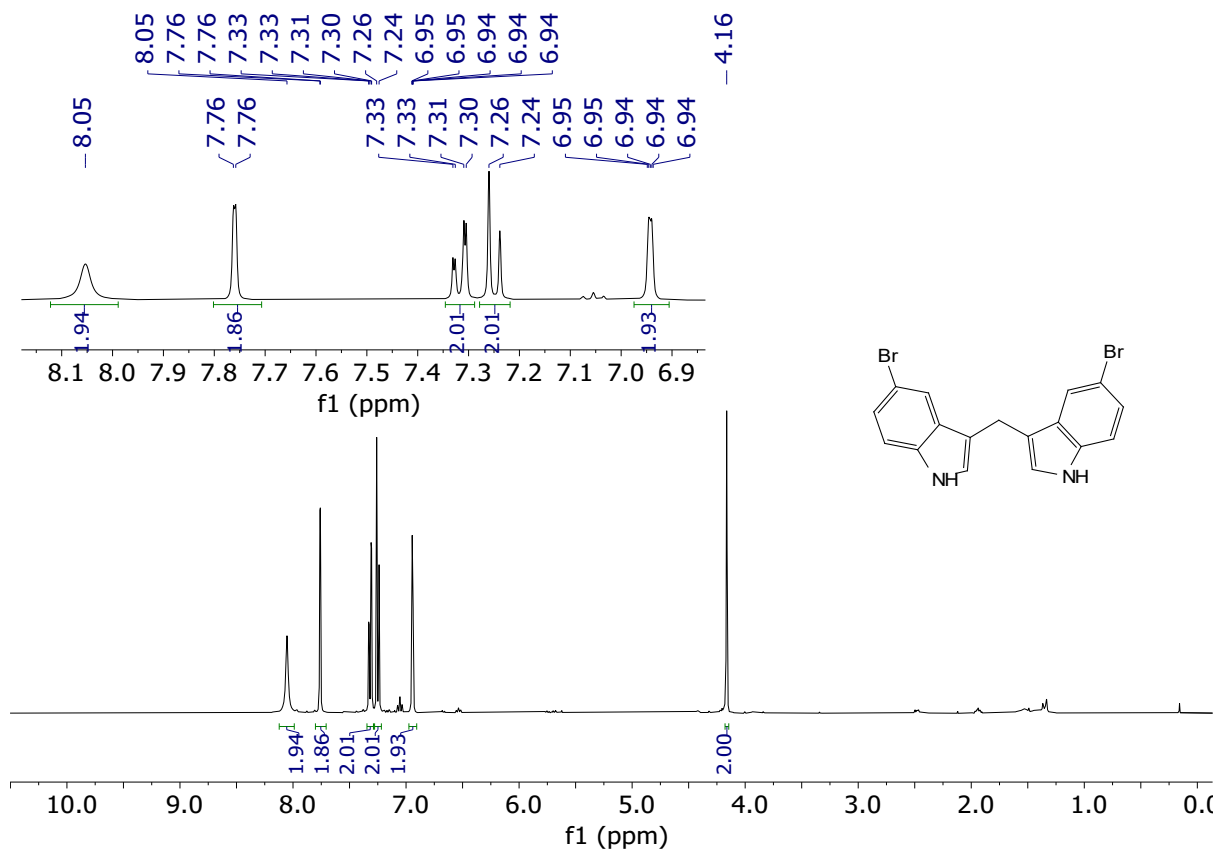
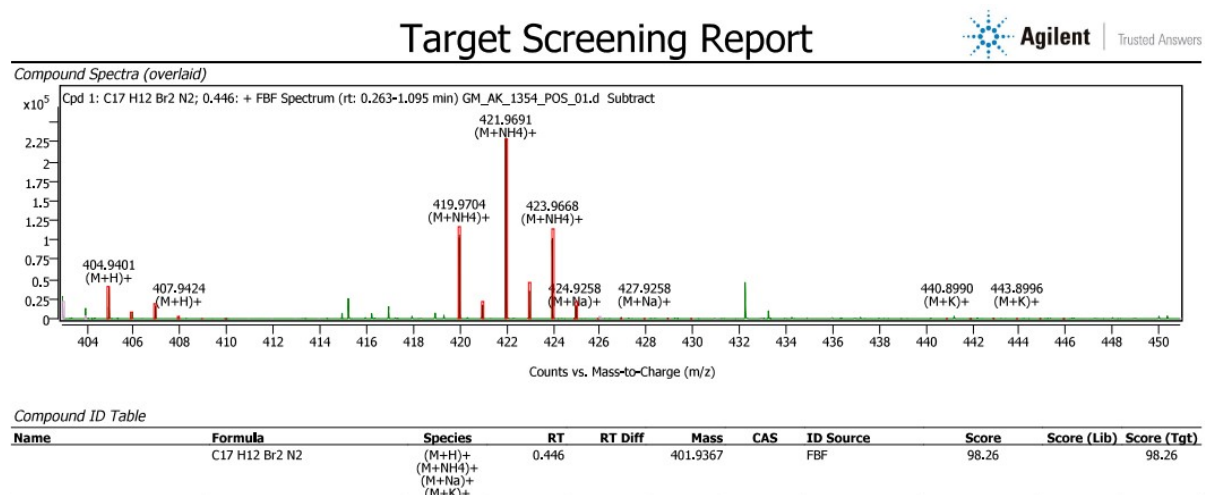


Figure S81. HRMS (ESI+) spectrum of di(1*H*-indol-3-yl)methane.

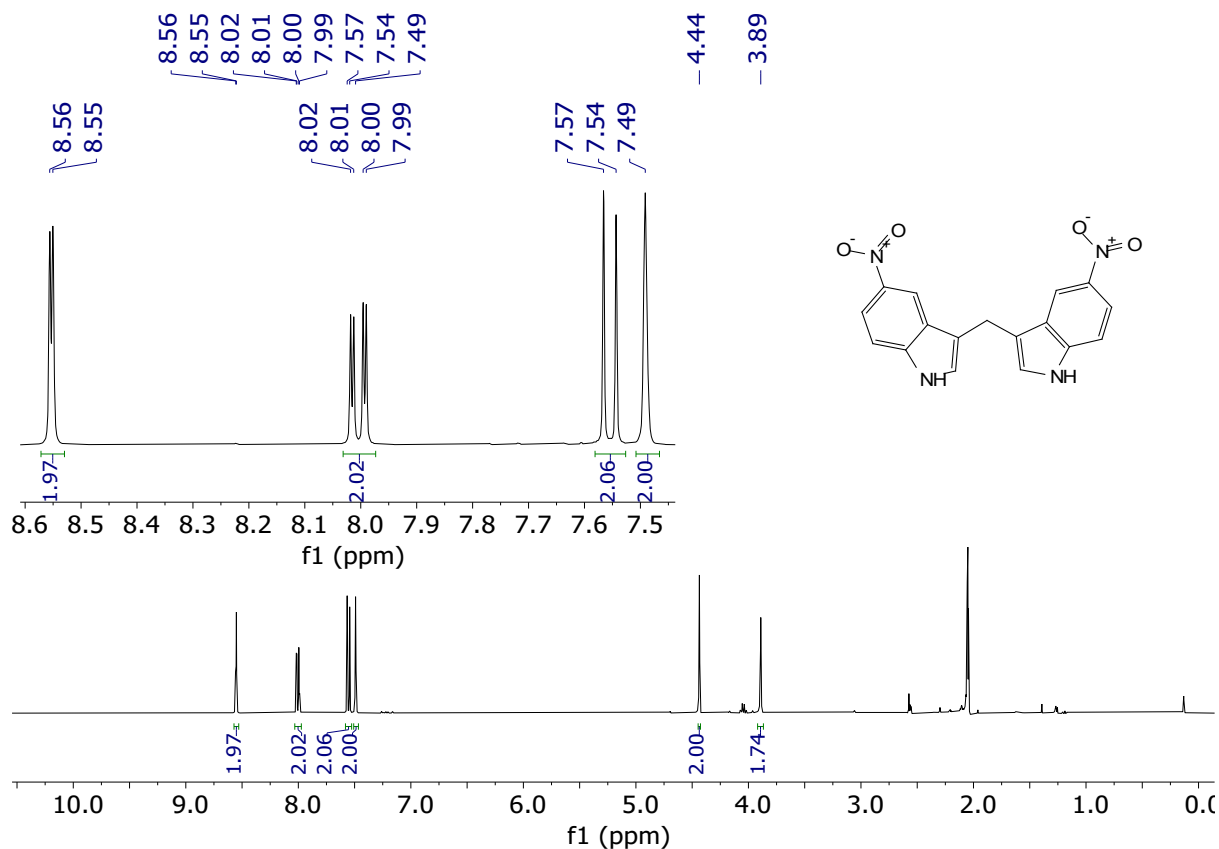




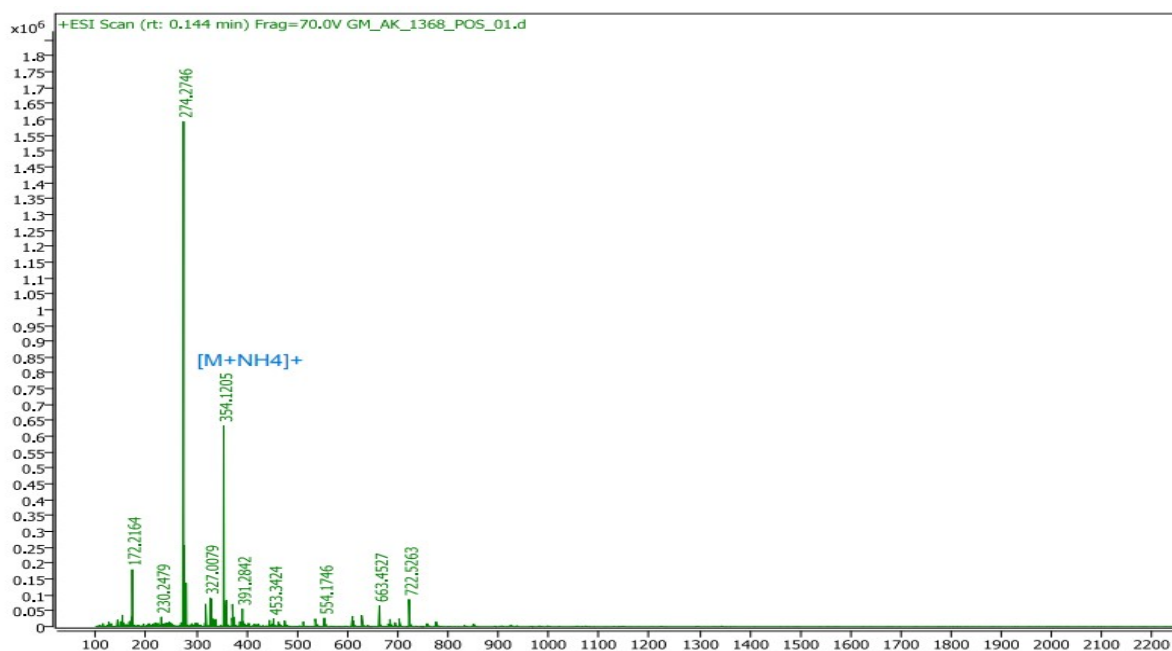
**Figure S83.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 25 °C) spectrum of bis(5-bromo-1*H*-indol-3-yl)methane.<sup>5</sup>



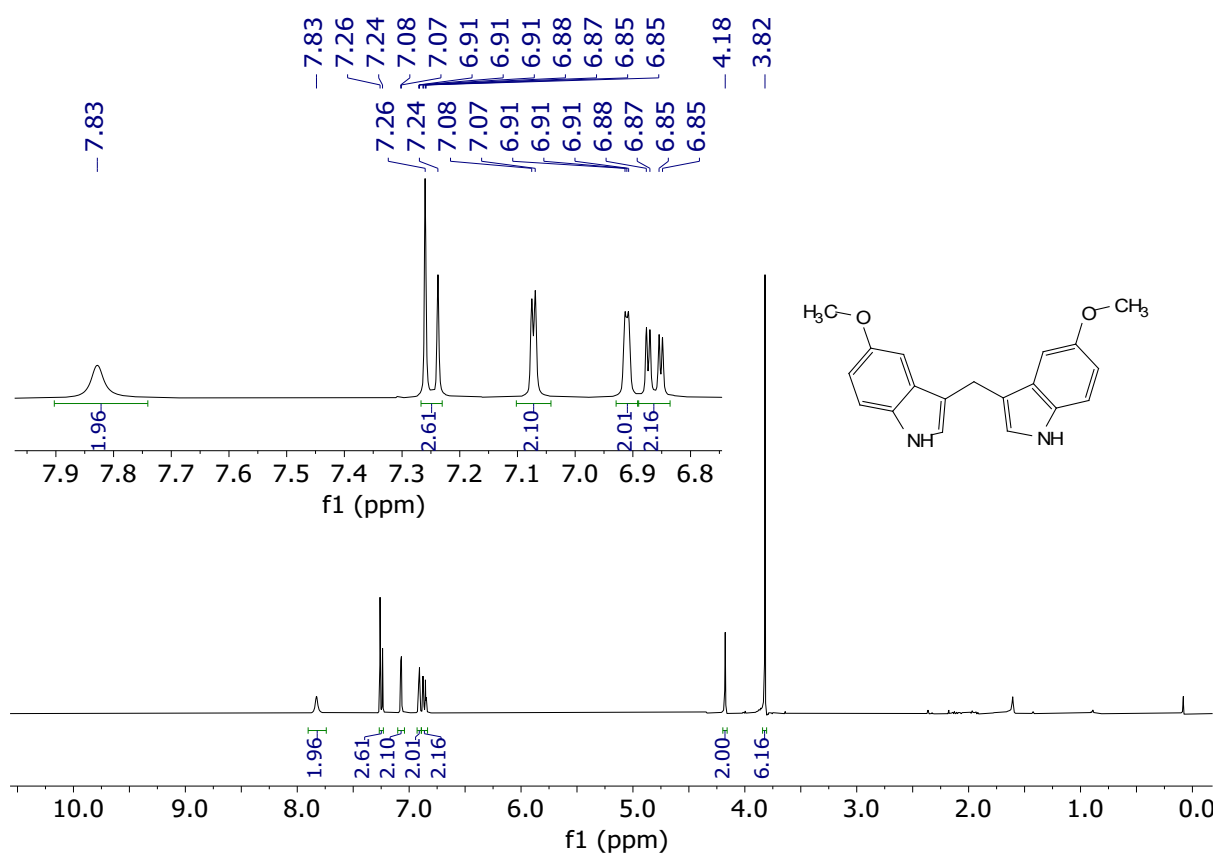
**Figure S84.** HRMS (ESI<sup>+</sup>) spectrum of bis(5-bromo-1*H*-indol-3-yl)methane.



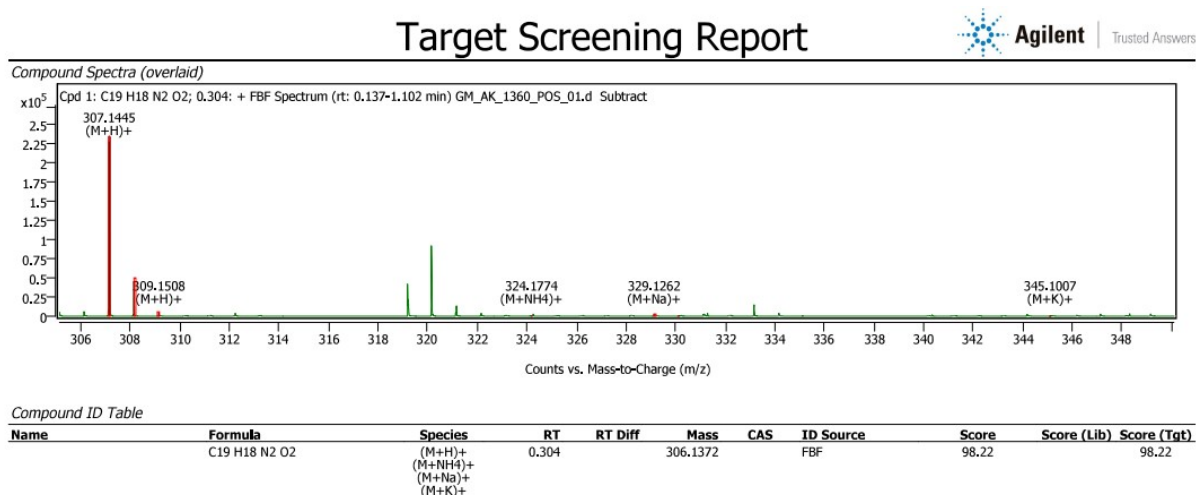
**Figure S85.** <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 400 MHz, 25 °C) spectrum of bis(5-nitro-1*H*-indol-3-yl)methane.



**Figure S86.** HRMS (ESI+) spectrum of bis(5-nitro-1*H*-indol-3-yl)methane.



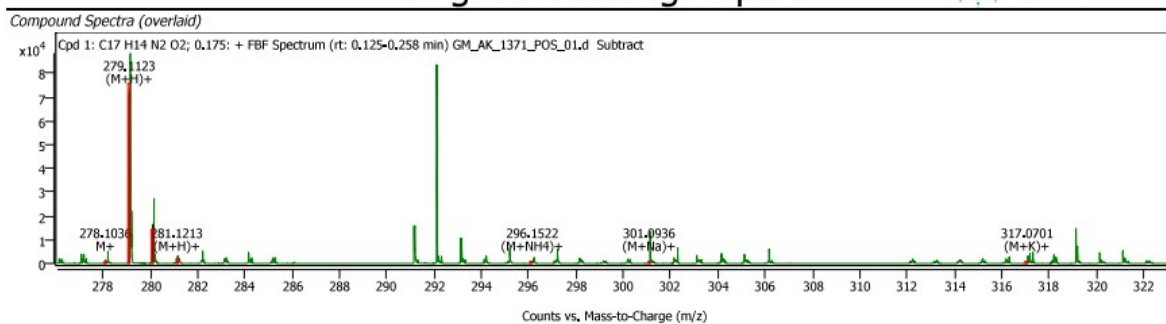
**Figure S87.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 25 °C) spectrum of bis(5-methoxy-1*H*-indol-3-yl)methane.<sup>5</sup>



**Figure S88.** HRMS (ESI+) spectrum of bis(5-methoxy-1*H*-indol-3-yl)methane.



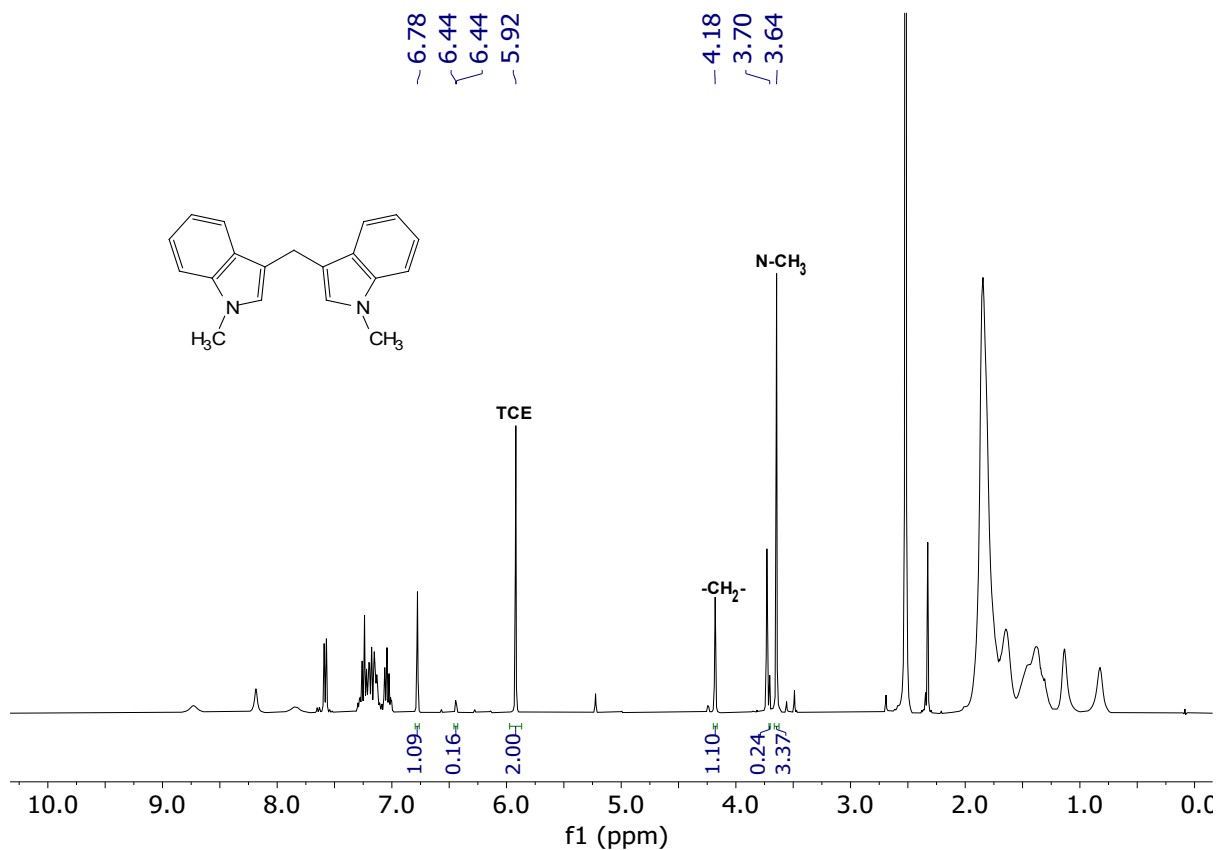
# Target Screening Report



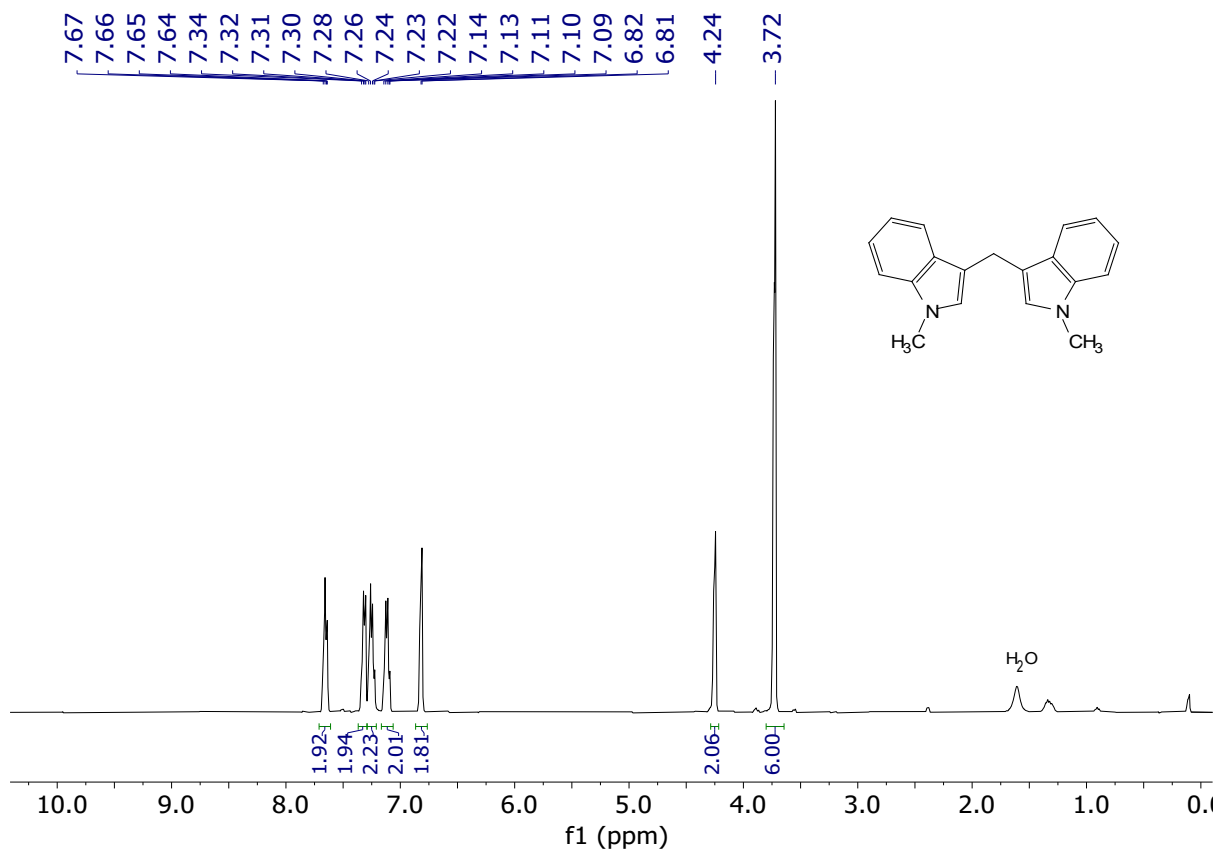
Compound ID Table

Name	Formula	Species	RT	RT Diff	Mass	CAS	ID Source	Score	Score (Lib)	Score (Tgt)
	C17 H14 N2 O2	M+ (M+H)+ (M+NH4)+ (M+Na)+ (M+K)+	0.175		278.1053		FBF	95.53		95.53

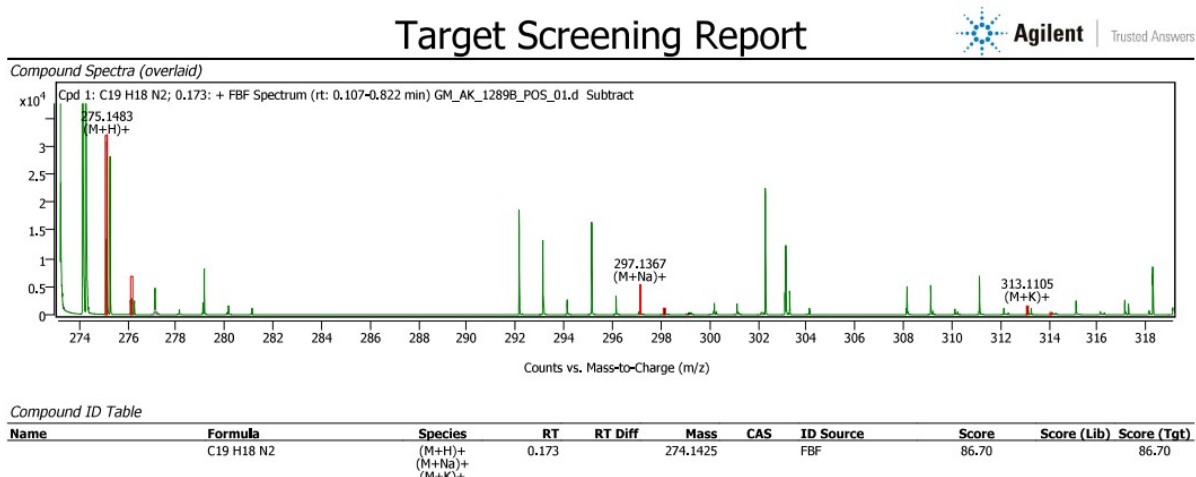
**Figure S89.** HRMS (ESI+) spectrum of bis(5-hydroxy-1*H*-indol-3-yl)methane. *m/z* calculated for [M+H]<sup>+</sup> C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 279.1128, observed 279.1123.



**Figure S90.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (0.122 g, 0.999 mmol), *N*-methylindole (41.6 μL, 0.333 mmol) and DMSO (71 μL, 0.999 mmol) in toluene (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 2 h at 25 °C. After 2 h, solvent was evaporated under reduced pressure and residue was dissolved in CDCl<sub>3</sub> (0.6 mL) and 1,1,2,2-tetrachloroethane (TCE, 30.0 μL, 0.284 mmol) was added as an internal standard.

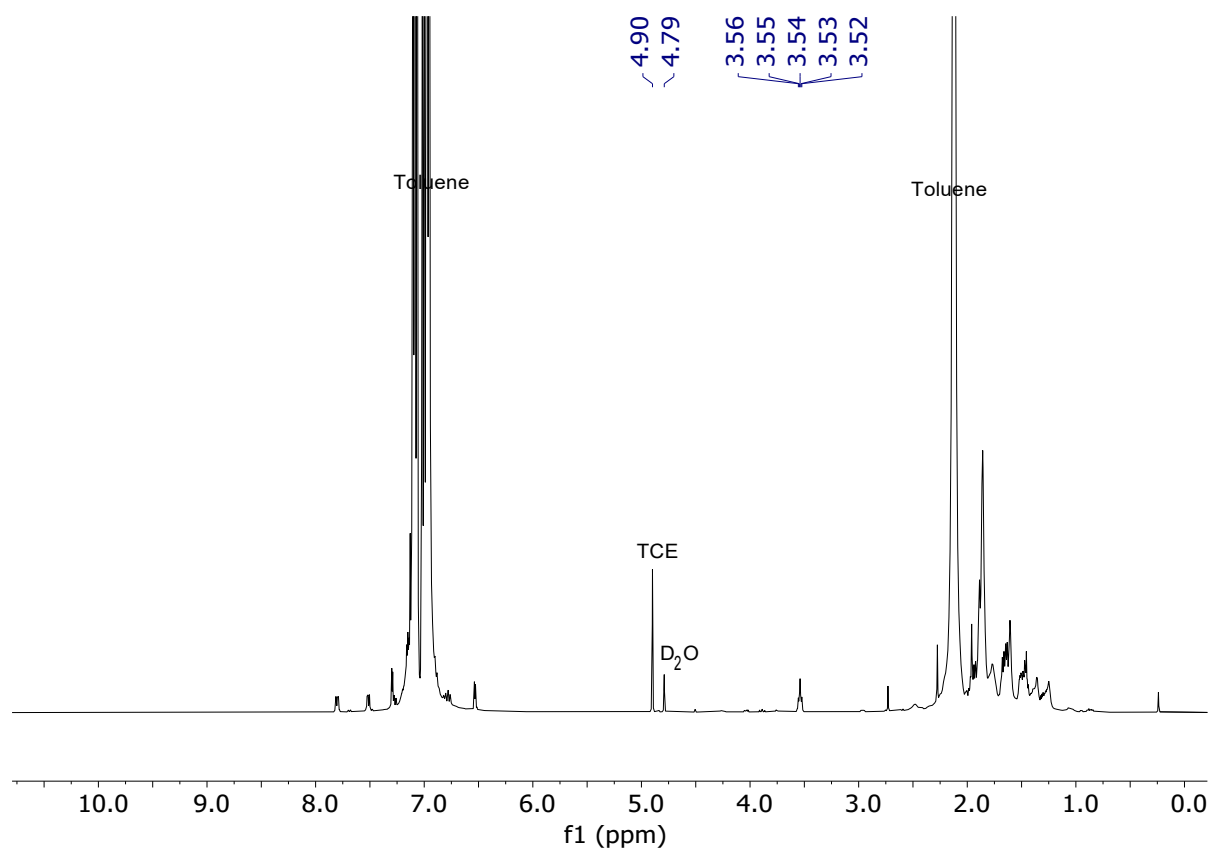


**Figure S91.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 25 °C) spectrum of 3,3'-methylenebis(1-methylindole).<sup>5</sup>

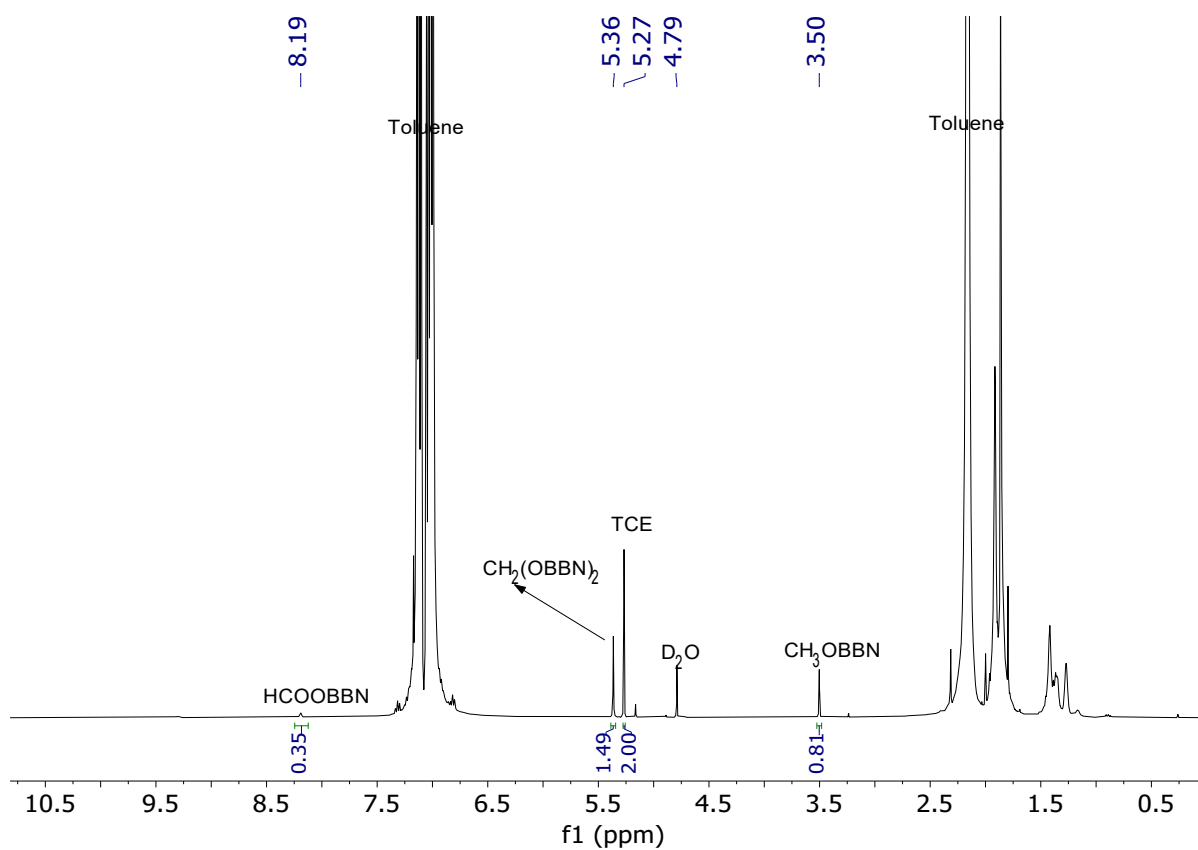


**Figure S92.** HRMS (ESI+) spectrum of 3,3'-methylenebis(1-methylindole).

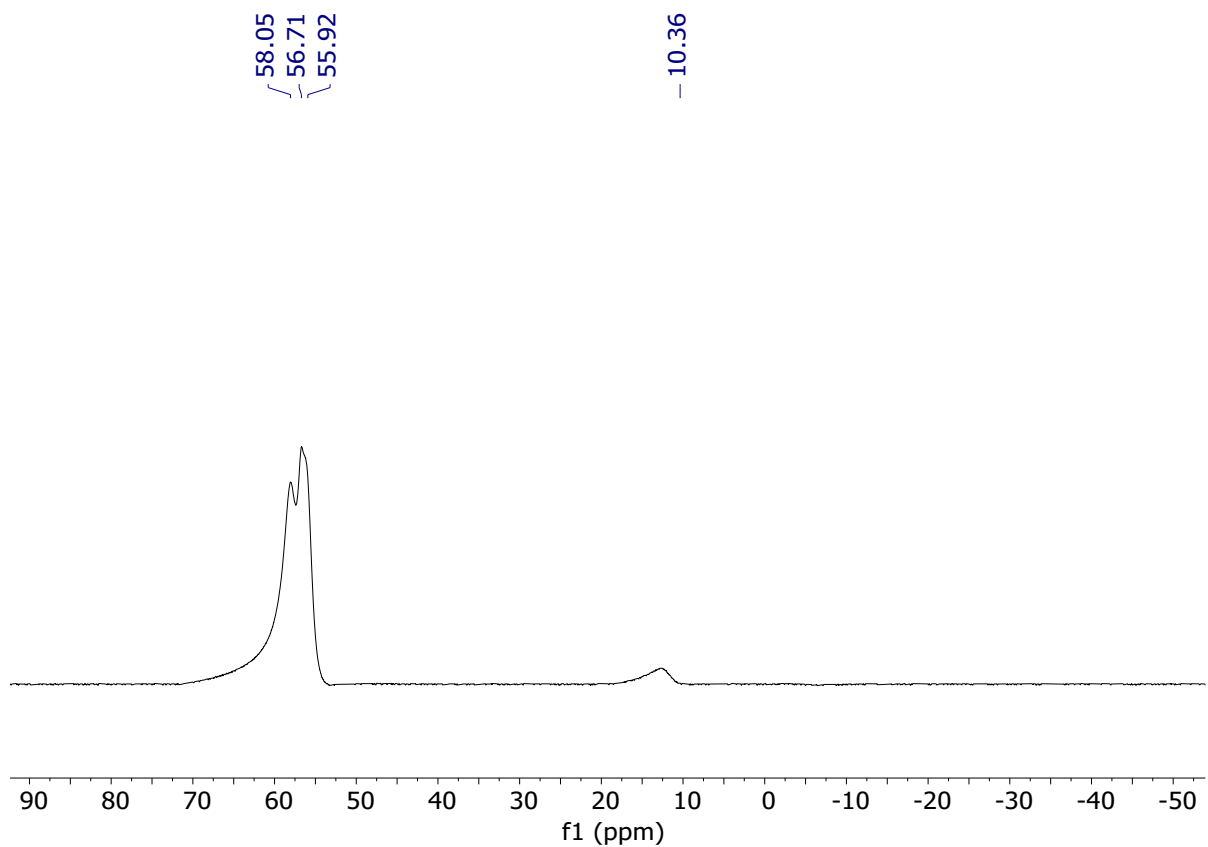
## Data for control experiments for C-methylation of indoles



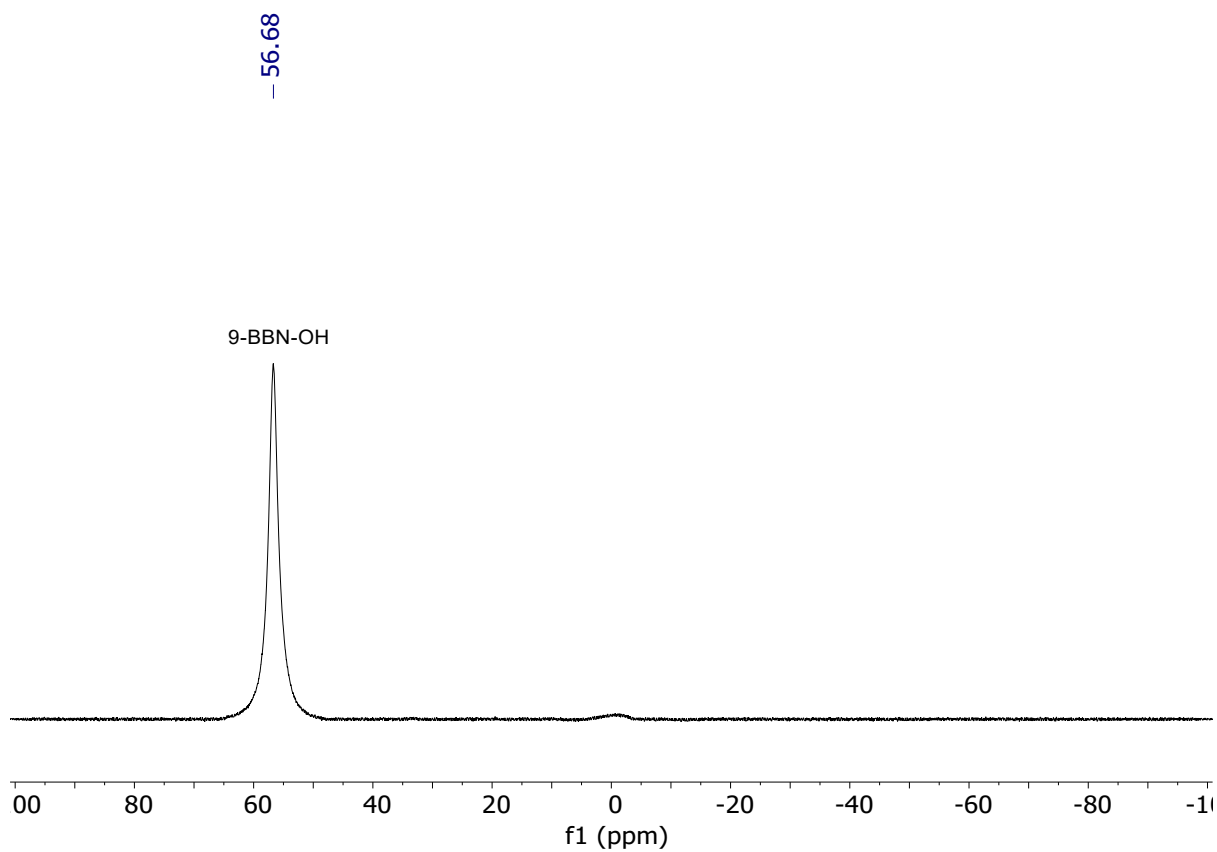
**Figure S93.**  $^1\text{H}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 400 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (0.147 g, 1.204 mmol) and indole (0.039g, 0.333 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 12 h at 80 °C. After 12 h, 1,1,2,2-tetrachloroethane (TCE, 42  $\mu\text{L}$ , 0.395 mmol) was added as an internal standard. No product formation.



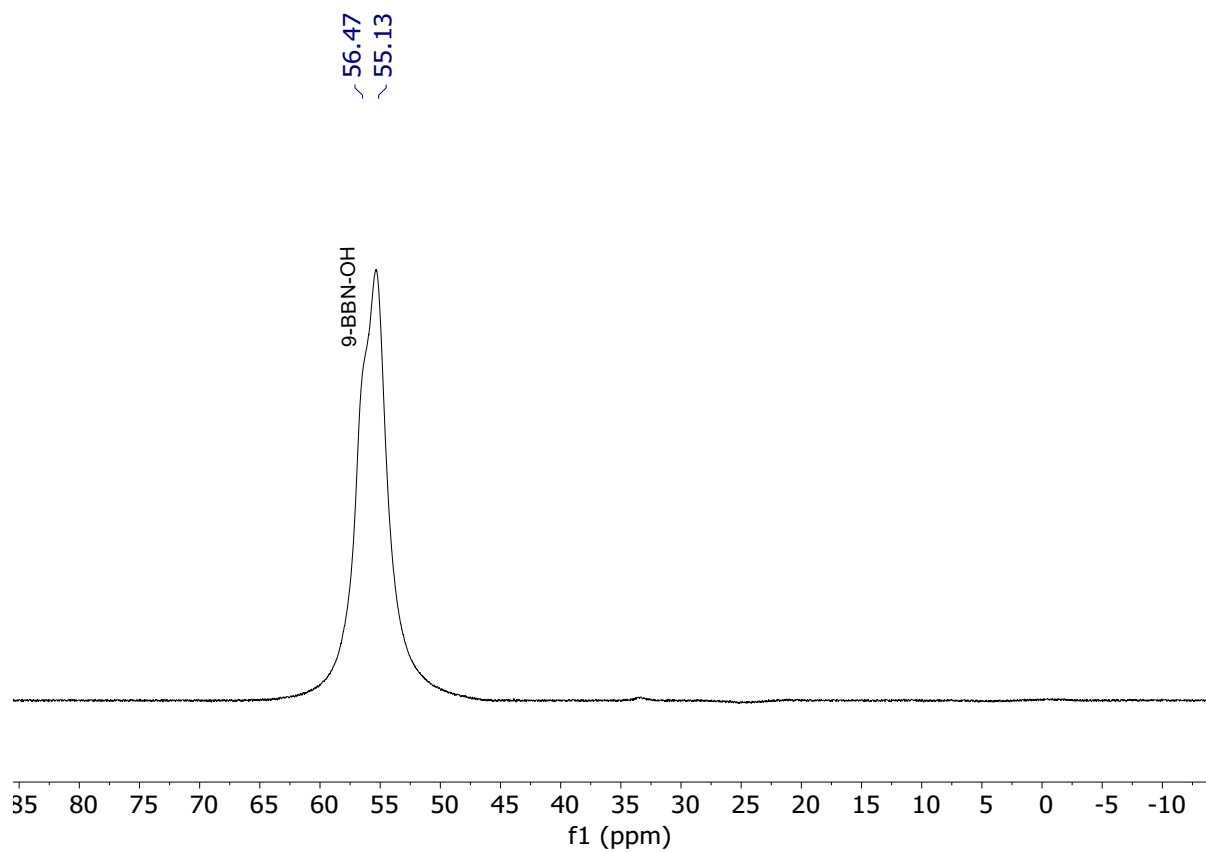
**Figure S94.** <sup>1</sup>H NMR (toluene solution with D<sub>2</sub>O capillary, 400 MHz, 25 °C) spectrum of the CO<sub>2</sub> reduction [(mixture of 9-BBN (0.147 g, 1.204 mmol) and DMSO (71 μL, 0.999 mmol) in toluene (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 2 h at 80 °C)]. After 2 h, 1,1,2,2-tetrachloroethane (TCE, 42 μL, 0.395 mmol) was added as an internal standard.



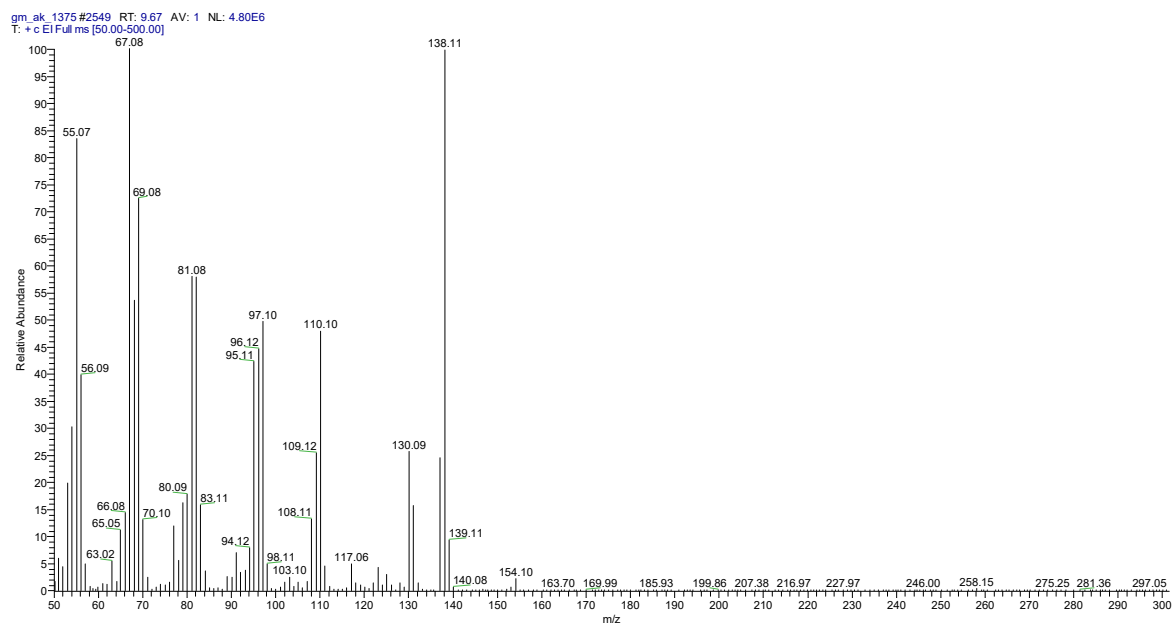
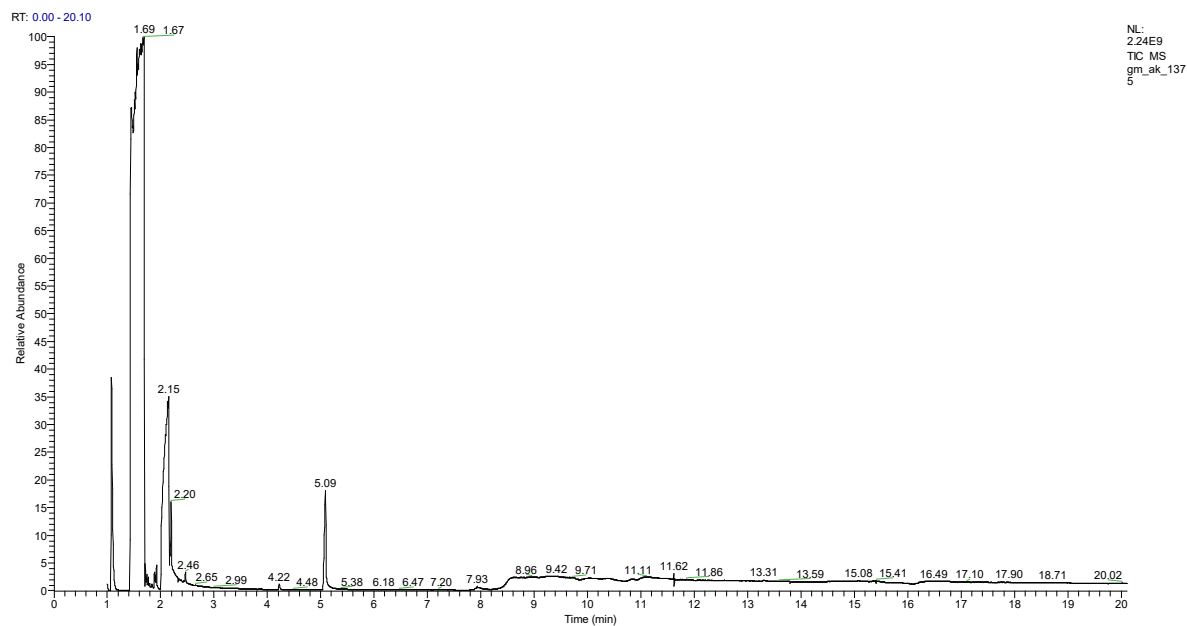
**Figure S95.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 128.37 MHz, 25 °C) spectrum of the  $\text{CO}_2$  reduction [(mixture of 9-BBN (0.147 g, 1.204 mmol) and DMSO (71  $\mu\text{L}$ , 0.999 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 2 h at 80 °C)].



**Figure S96.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 128.37 MHz, 25 °C) spectrum of reaction mixture of 9-BBN (0.6 mmol), indole (0.5 mmol), indole-3-carboxyaldehyde (0.5 mmol) and DMSO (1.0 mmol) in toluene (2.0 mL) under  $\text{N}_2$  for 4 h at 80 °C. (K. Matos and J. A. Soderquist, *J. Org. Chem.*, 1998, 63, 461–470).

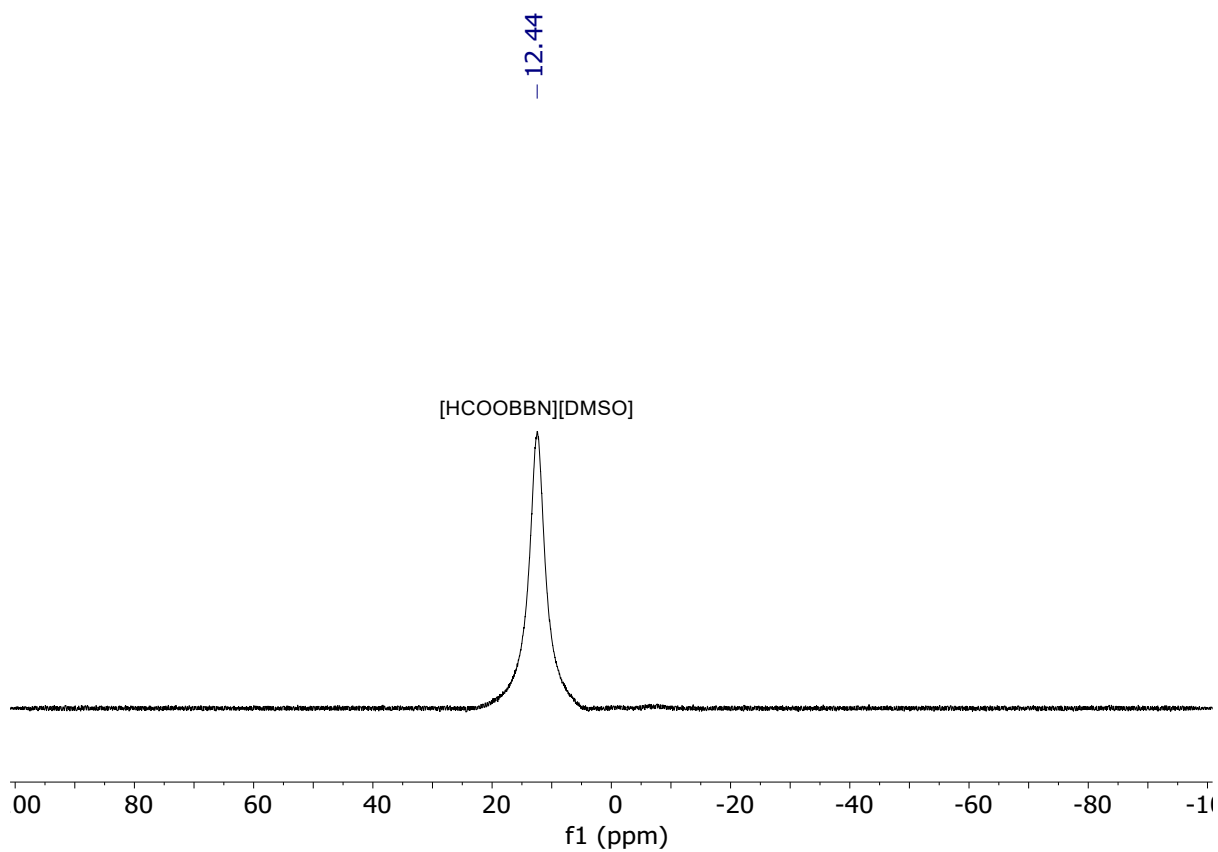


**Figure S97.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 128.37 MHz, 25 °C) spectrum of C-methylenation reaction mixture of 9-BBN (0.147 g, 1.204 mmol), indole (0.039g, 0.333 mmol) and DMSO (71  $\mu\text{L}$ , 0.999 mmol) in toluene (2.0 mL) under  $\text{CO}_2$  (1 atm, balloon) for 4 h at 80 °C). (K. Matos and J. A. Soderquist, *J. Org. Chem.*, 1998, 63, 461–470).



**Figure S98.** GC-MS spectrum of the *C*-methylenation of indole reaction [(mixture of 9-BBN (0.147 g, 1.204 mmol), indole (0.039g, 0.333 mmol) and DMSO (71  $\mu$ L, 0.999 mmol) in toluene (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 4 h at 80 °C)]. BBN-OH (C<sub>8</sub>H<sub>15</sub>BO):  $m/z$  = 138.12(cal) and 138.11 (found).



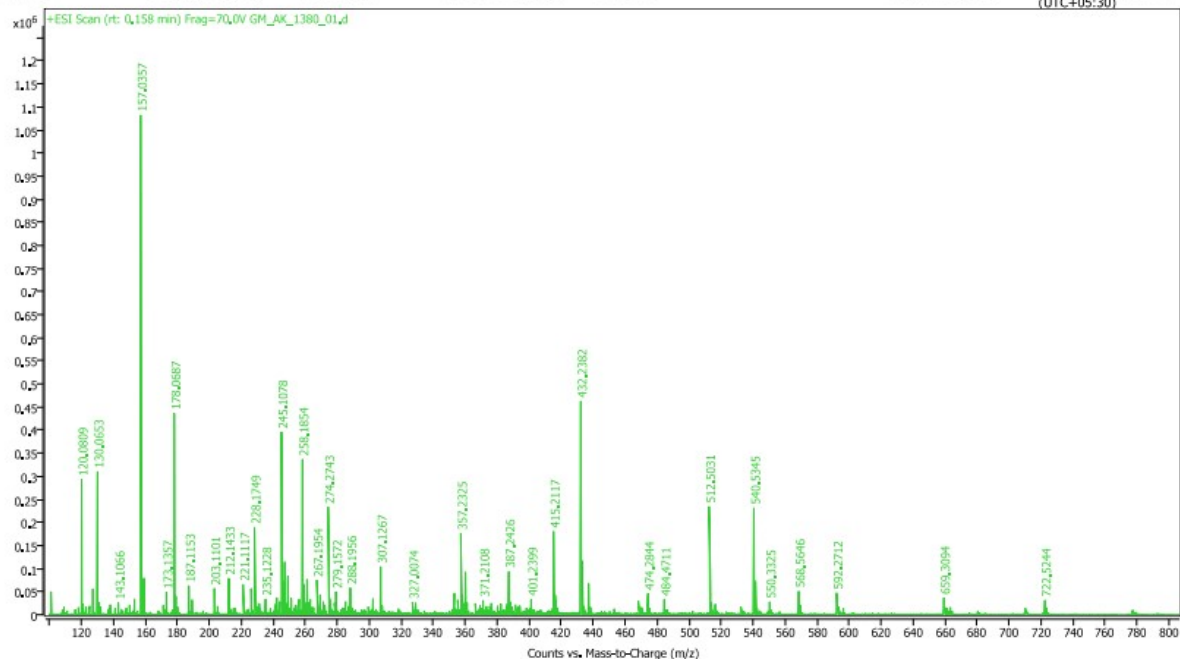


**Figure S99.**  $^{11}\text{B}$  NMR (toluene solution with  $\text{D}_2\text{O}$  capillary, 128.37 MHz, 25 °C) spectrum of reaction mixture of **E** (0.082 mmol), *N*-methylindole (0.081 mmol) in toluene (0.5 mL) under  $\text{N}_2$  for 1 h at 80 °C. This is for the reaction (v) in Fig 8.

## Spectrum Plot Report



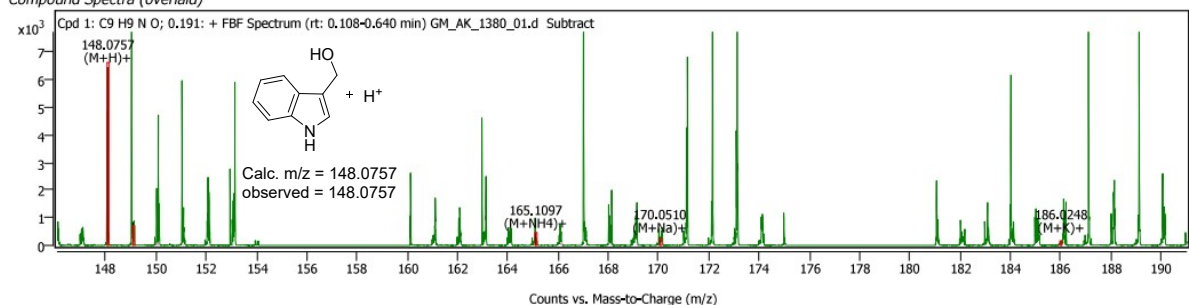
Name: GM\_AK\_1380  
 Inj. Vol. (µl): 2  
 Data File: GM\_AK\_1380\_01.d  
 Rack Pos.: Plate Pos.  
 Plate Pos.: Method (Acq)  
 MS SCAN POS\_01.m  
 Instrument: IITKGP  
 IRM Status: Success  
 Comment:  
 Operator: Acq. Time (Local): 11/7/2024 3:51:43 PM (UTC+05:30)



## Target Screening Report



## Compound Spectra (overlaid)



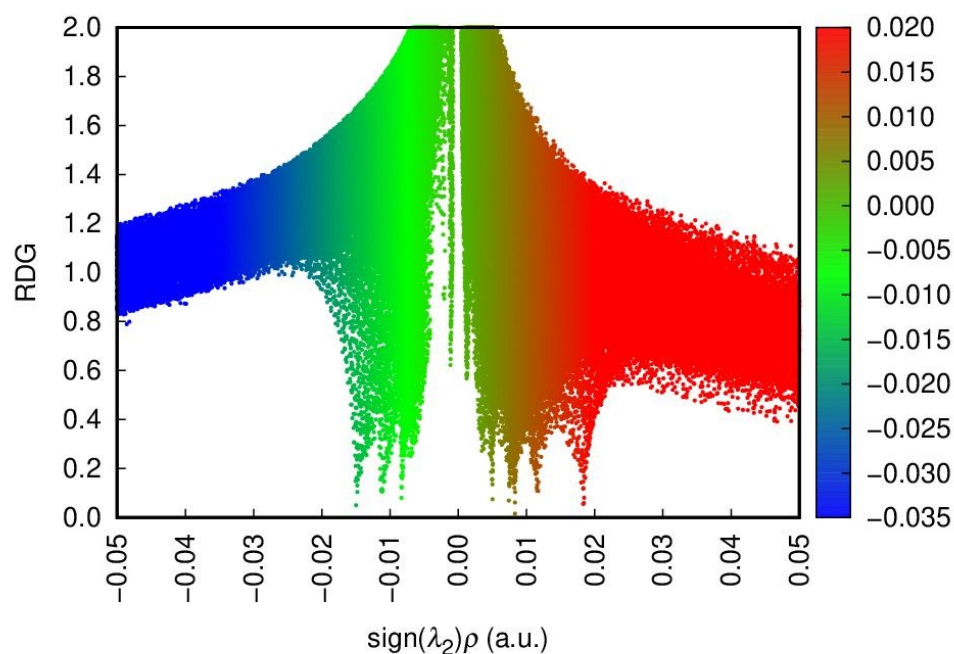
## Compound ID Table

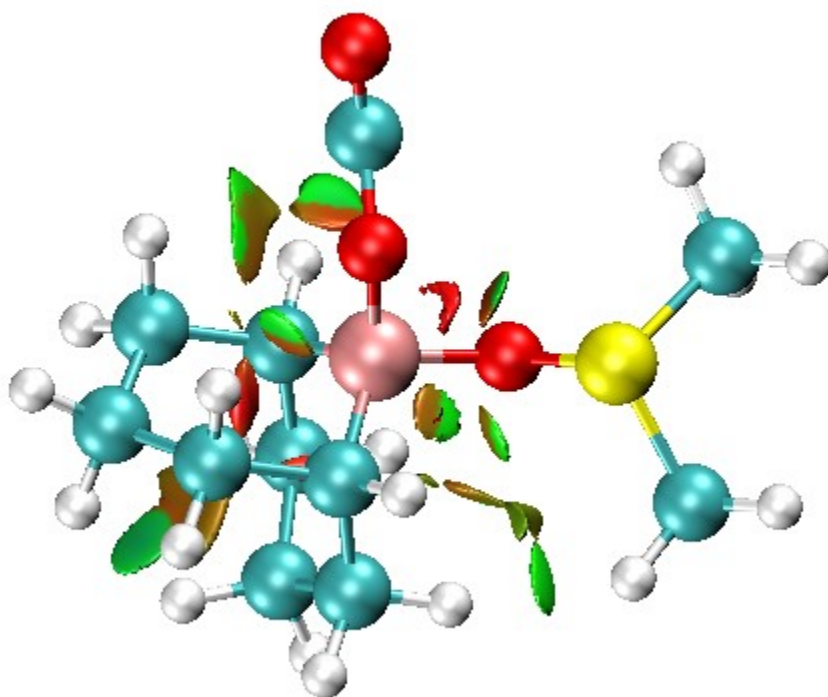
Name	Formula	Species	RT	RT Diff	Mass	CAS	ID Source	Score	Score (Lib)	Score (Tot)
	C9 H9 N O	(M+H)+ (M+NH4)+ (M+Na)+ (M+K)+	0.191		147.0685		FBF	85.54		85.54

**Figure S100.** HRMS (ESI+) spectrum of reaction mixture of 9-BBN (1.2 mmol), indole (0.333 mmol) and DMSO (1.0 mmol) in toluene (2.0 mL) under CO<sub>2</sub> (1 atm, balloon) for 1 h at 80 °C.

## Computational details

The coordinates of molecule **E** are extracted from the SC-XRD experiment, and the positions of hydrogen atoms are optimized by freezing the coordinates of non-hydrogen atoms. The H-atoms positions optimization was carried out using Gaussian 9 program, NBO analysis was carried out using NBO version 3.1. The NCI calculation was performed using Multiwfn\_3.8 program. The NCI plot was generated using VMD 1.9.4 and the scatter plot was plotted using gnuplot 6.0 and IrfanView programs. The coordinates of the hydrogen atoms position optimized structure of **E** is given below. The NBO analysis of **E** showed no second order interaction with significant energy contribution. The NCI analysis also showed weak Van der Waals interactions and steric repulsion interactions.





**Figure S101.** The molecular graph of **E** obtained from the Non-Covalent Interaction methods.

Coordinates of **E**

S	3.443200262538	3.459200264751	8.485300671585
O	3.950605302102	1.855502142211	6.024698484758
O	2.504001193082	2.324600178306	7.950100591725
O	5.672700415186	0.469706035883	5.898397475277
C	4.543995347419	0.712692055959	6.242105454067
H	3.931163298223	-0.035676002715	6.777223511453
C	1.956198148484	3.350698253751	5.584100427139
H	2.577017196902	4.246282322674	5.765657437031
C	1.508199113112	0.867097065873	6.094101456826
H	1.790529135150	-0.042263003252	6.644718533740
C	2.098703158008	3.032700229894	4.080199312811
H	1.698906132108	3.858548294339	3.475735265164
H	3.168812243781	2.979995228956	3.857263293226
C	1.632203122909	0.529701039225	4.591699348182
H	2.625874200805	0.104079007850	4.413973338152

H	0.919705068621	-0.262635020103	4.325183327847
C	2.316600177199	4.581300348476	9.263100685388
H	1.774903134249	5.100144390377	8.474015649244
H	2.889396220934	5.305346415614	9.846720748119
H	1.620933123909	4.029870307137	9.896735777055
C	0.086300006448	1.211801093831	6.546701519041
H	0.085069006285	1.293668100442	7.641124579579
H	-0.602741046524	0.390322029997	6.307021479322
C	4.141500316607	2.686800203144	9.916400744476
H	3.347750254923	2.242222171684	10.517670826418
H	4.699924361351	3.432225263980	10.485598822134
H	4.824904369790	1.914416143856	9.563749723097
C	0.520799039622	3.688802282516	6.014700474404
H	0.535630041666	4.054878308448	7.050392533374
H	0.127799009729	4.524210346723	5.418075404519
C	-0.474899036381	2.520699190671	5.955599472103
H	-0.794291060753	2.356102179316	4.925733374181
H	-1.385959105092	2.798907212986	6.499758522788
C	1.433596112015	1.721301130248	3.631902276563
H	1.830253137705	1.446475111482	2.647386203204
H	0.366305027916	1.885250142895	3.470662265132
B	2.491199188905	2.084800158230	6.398199513090

## REFERENCES

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1. J. A. Soderquist, A. Negron, 9-BORABICYCLO[3.3.1]NONANE DIMER. *Org. Synth.* 1991, **70**, 169.
2. G. M. Sheldrick, *Acta Cryst. Sect. A: Found. Crystallogr.*, 2015, **71**, 3.
3. G. M. Sheldrick, *Acta Cryst. Sect. C: Struct. Chem.*, 2015, **71**, 3.
4. Z. Guo, J. Wu, X. Wei, and C. Xi, Selective C-Methylenation of N-Unsubstituted Indoles Using CO<sub>2</sub> under NaBH<sub>4</sub>/I<sub>2</sub> System. *ChemSusChem* 2024, e202401491.
5. T. Murata, M. Hiyoshi, S. Maekawa, Y. Saiki, M. Ratanasak, J. Hasegawa, T. Ema, Deoxygenative CO<sub>2</sub> conversions with triphenylborane and phenylsilane in the presence of secondary amines or nitrogen-containing aromatics. *Green Chem.* 2022, **24**, 2385–2390.