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Supplementary Data for:

Phosphine Catalyzed Reduction of CO_2 with Boranes

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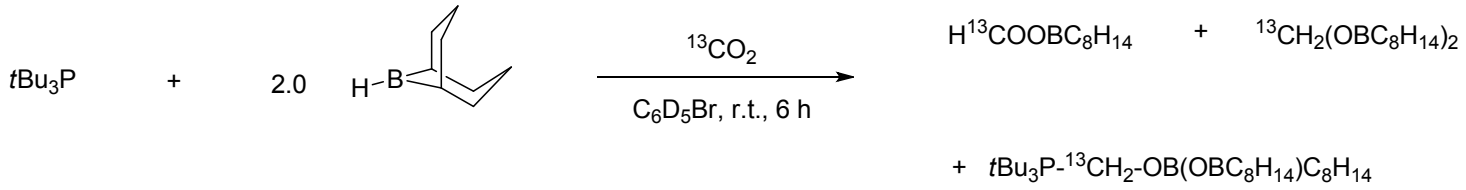
General Remarks All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing an mBraun glove box and a Schlenk vacuum-line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks (pentane, hexanes, toluene, CH_2Cl_2). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks and degassed accordingly (C_6D_5Br, C_6D_6, CD_2Cl_2, and $CDCl_3$). Toluene and pentane were stored over potassium mirrors, while bromobenzene and dichloromethane were stored over 4Å molecular sieves ^1H, ^{13}C and ^{31}P NMR spectra were recorded at 25 °C on Varian 400 MHz, Agilent 500 MHz and Bruker 400 MHz spectrometers. Chemical shifts are given relative to $SiMe_4$ and referenced to the residue solvent signal (^1H, ^{13}C) or relative to an external standard (^{31}P: 85% H_3PO_4). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. GC measurements were performed using a Chirasil-DEX CB column at 130 °C. All other reagents were purchased from Aldrich, liquids were stored over 4Å molecular sieves, gases and solutions were used as received.

Stoichiometric reactions of $(HBC_8H_{14})_2$, phosphine under an atmosphere of $^{13}CO_2$

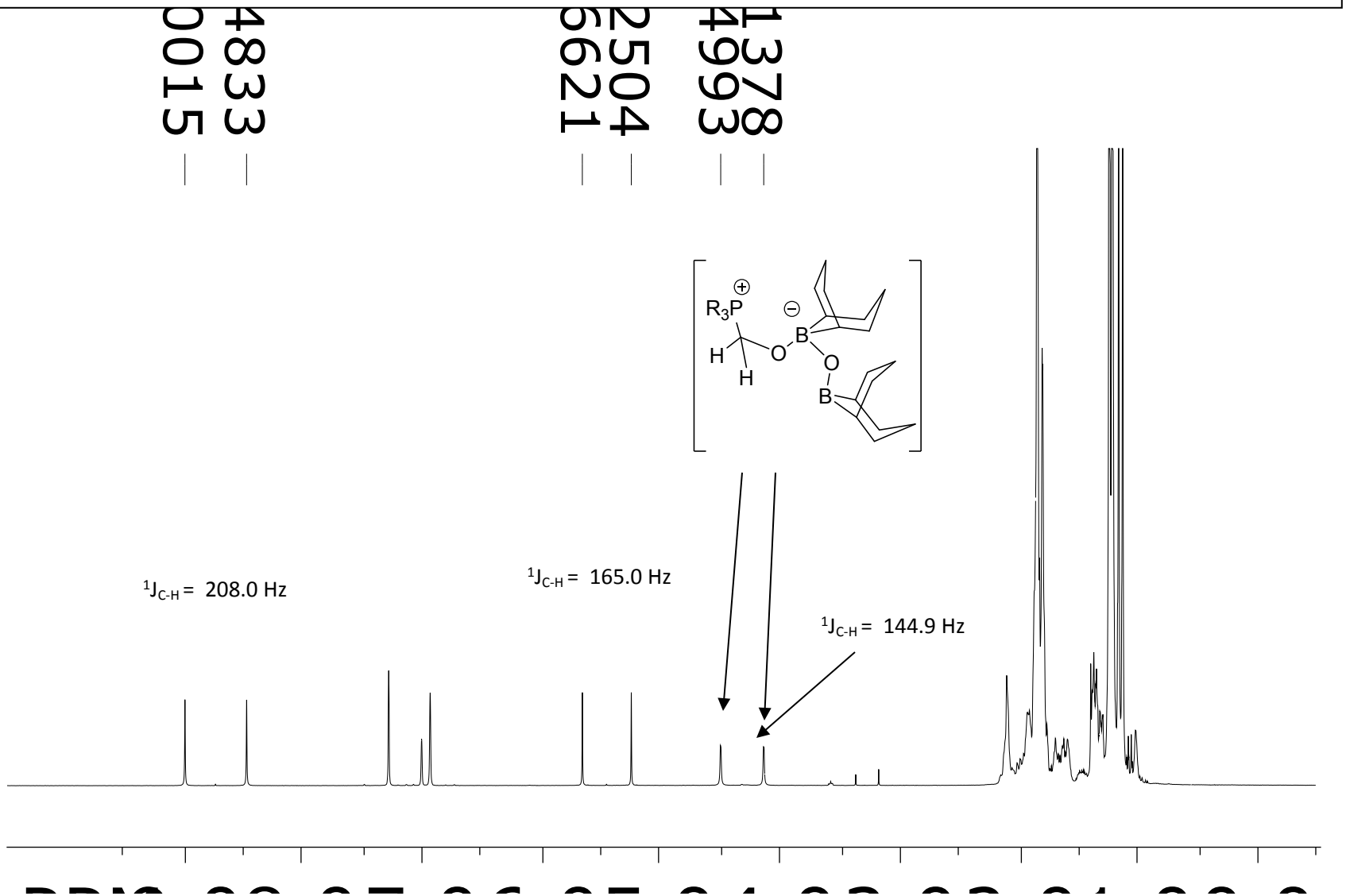
These reactions were done in a similar fashion and only one is detailed. Tris(*t*-butyl)phosphine (35 mg, 0.1730 mmol) and $(HBC_8H_{14})_2$ (23 mg, 0.0943 mmol) were dissolved in 0.80 mL of bromobenzene-d_5 in a 20 mL vial. The mixture was stirred and transferred into a J-Young tube. The sample was treated by frozen with liquid nitrogen and atmosphere replaced with $^{13}CO_2$. The sample was then warmed to room temperature affording a CO_2 pressure of 4 atm.[1] The sample was left at room temperature for 6 hours and monitored by NMR spectroscopy.



$H^{13}COOBC_8H_{14}$: ^1H NMR (C_6D_5Br, 400 MHz): 8.74 (d, $^1J^{13}_{C\text{-}H}$ = 208.0 Hz, *H*-$^{13}COOBC_8H_{14}$); $^{13}C\{^1H\}$ NMR (C_6D_5Br, 100 MHz): 169.08 (s, H-*^{13}C*$OOBC_8H_{14}$); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 169.08 (d, $^1J^{13}_{C\text{-}H}$ = 208.0 Hz, H-*^{13}C*$OOBC_8H_{14}$).
$^{13}CH_2(OBC_8H_{14})_2$: ^1H NMR (C_6D_5Br, 400 MHz): 5.46 (d, $^1J^{13}_{C\text{-}H}$ = 165.0 Hz, $^{13}CH_2(OBC_8H_{14})_2$); $^{13}C\{^1H\}$ NMR (C_6D_5Br, 100 MHz): 85.44 (s, $^{13}CH_2(OBC_8H_{14})_2$); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 85.44 (d, $^1J^{13}_{C\text{-}H}$ = 165.0 Hz, $^{13}CH_2(OBC_8H_{14})_2$).
***t*Bu$_3$P-CH$_2$-OB(OBC$_8$H$_{14}$)C$_8$H$_{14}$**: ^1H NMR (C_6D_5Br, 400 MHz): 4.32 (dd, $^1J^{13}_{C\text{-}H}$ = 144.9 Hz, $^2J_{H\text{-}P}$ = 1.2 Hz, *t*Bu$_3$P-C*H*$_2$-OB(OB C_8H_{14})C_8H_{14}); $^{31}P\{^1H\}$ NMR (C_6D_5Br, 162 MHz): 43.27 (d, $^1J^{13}_{C\text{-}P}$ = 55.7 Hz, *t*Bu$_3$P-C*H*$_2$-OB(OB C_8H_{14})C_8H_{14}); $^{13}C\{^1H\}$ NMR (C_6D_5Br, 100 MHz): 52.45 (d, $^1J^{13}_{C\text{-}P}$ = 55.7 Hz, *t*Bu$_3$P-C*H*$_2$-OB(OB C_8H_{14})C_8H_{14}); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 52.45 (td, $^1J^{13}_{C\text{-}H}$ = 144.9 Hz, $^1J^{13}_{C\text{-}P}$ = 55.7 Hz, *t*Bu$_3$P-C*H*$_2$-OB(OB C_8H_{14})C_8H_{14}).

The stoichiometric reaction between 9-BBN dimer and P*t*Bu$_3$ in the atmosphere of 4 atm $^{13}CO_2$ at room temperature for 6 hours in C_6D_5Br

^{1}H NMR spectrum (400M, C_6D_5Br)

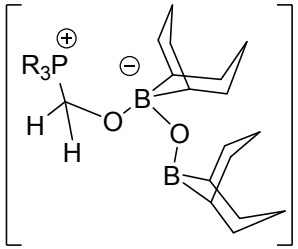


The stoichiometric reaction between 9-BBN dimer and P*t*Bu$_3$ in the atmosphere of 4 atm $^{13}CO_2$ at room temperature for 6 hours in C_6D_5Br

$^{31}P\{^1H\}$ NMR spectrum (162 M, C_6D_5Br)

86

82.5

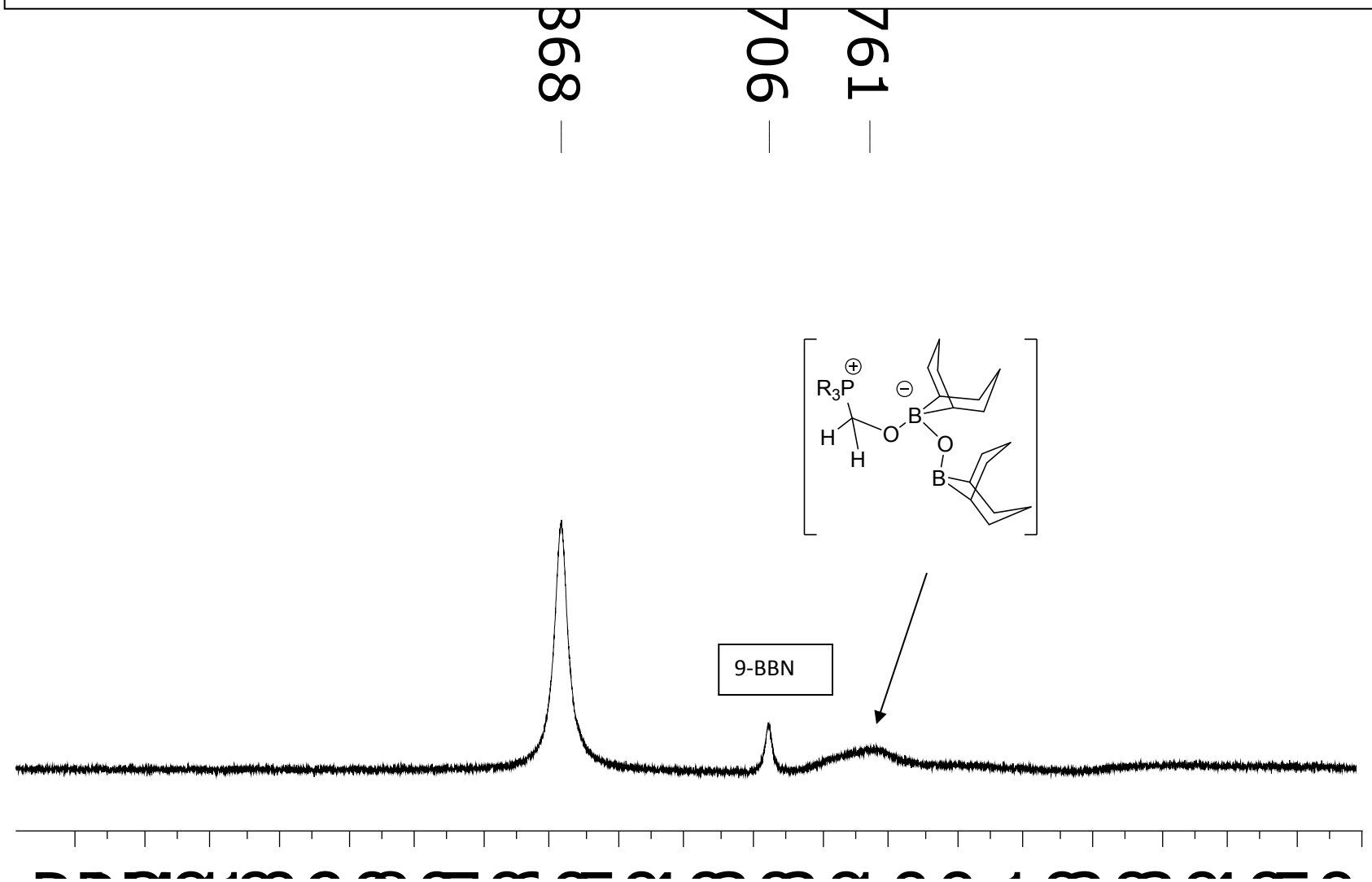


Free P*t*Bu$_3$

43.27 ppm ($^1J_{C\text{-}P}$ = 55.7 Hz)

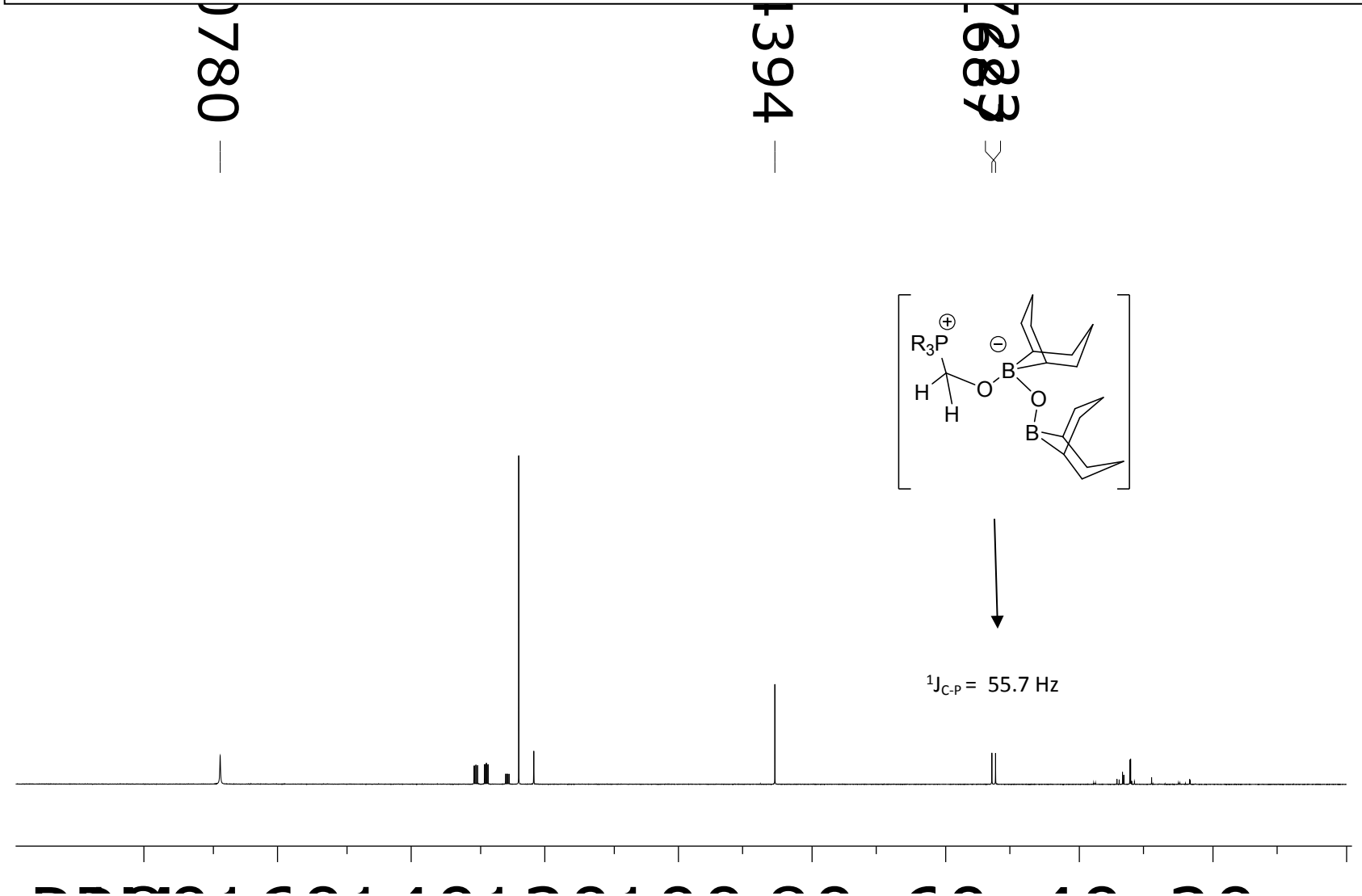
The stoichiometric reaction between 9-BBN dimer and P*t*Bu$_3$ in the atmosphere of 4 atm $^{13}CO_2$ at room temperature for 6 hours in C_6D_5Br

$^{11}B\{^1H\}$ NMR spectrum (128 M, C_6D_5Br)



The stoichiometric reaction between 9-BBN dimer and P*t*Bu$_3$ in the atmosphere of 4 atm $^{13}CO_2$ at room temperature for 6 hours in C_6D_5Br

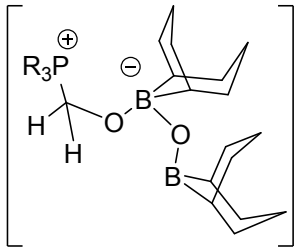
$^{13}C\{^1H\}$ NMR spectrum (100 M, C_6D_5Br)



The stoichiometric reaction between 9-BBN dimer and P*t*Bu$_3$ in the atmosphere of 4 atm $^{13}CO_2$ at room temperature for 6 hours in C_6D_5Br

^{13}C NMR spectrum (100 M, C_6D_5Br)

^{13}C {^1H}



$^1J_{C-P}$ = 55.7 Hz

^{13}C with ^1H coupling

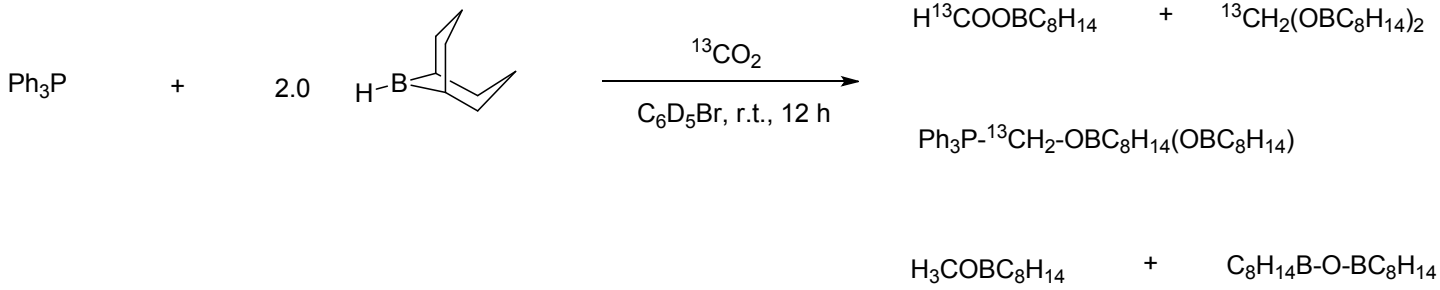
$^1J_{C-H}$ = 208.0 Hz

$^1J_{C-H}$ = 165.0 Hz

$^1J_{C-H}$ = 144.9 Hz

Stoichiometric reaction between $(HBC_8H_{14})_2$, PPh_3 in the atmosphere of $^{13}CO_2$

This reaction was performed in a similar fashion to that described above, using triphenylphosphine (22 mg, 0.0839 mmol) and $(HBC_8H_{14})_2$ (14 mg, 0.0574 mmol).



$H^{13}COOBC_8H_{14}$: ^1H NMR (C_6D_5Br, 400 MHz): 8.64 (d, $^1J^{13}_{C\text{-}H}$ = 206.5 Hz, *H*-$^{13}COOBC_8H_{14}$); $^{13}C\{^1H\}$ NMR (C_6D_5Br, 100 MHz): 169.06 (s, H-*^{13}C*$OOBC_8H_{14}$); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 169.08 (d, $^1J^{13}_{C\text{-}H}$ = 206.5 Hz, H-*^{13}C*$OOBC_8H_{14}$).

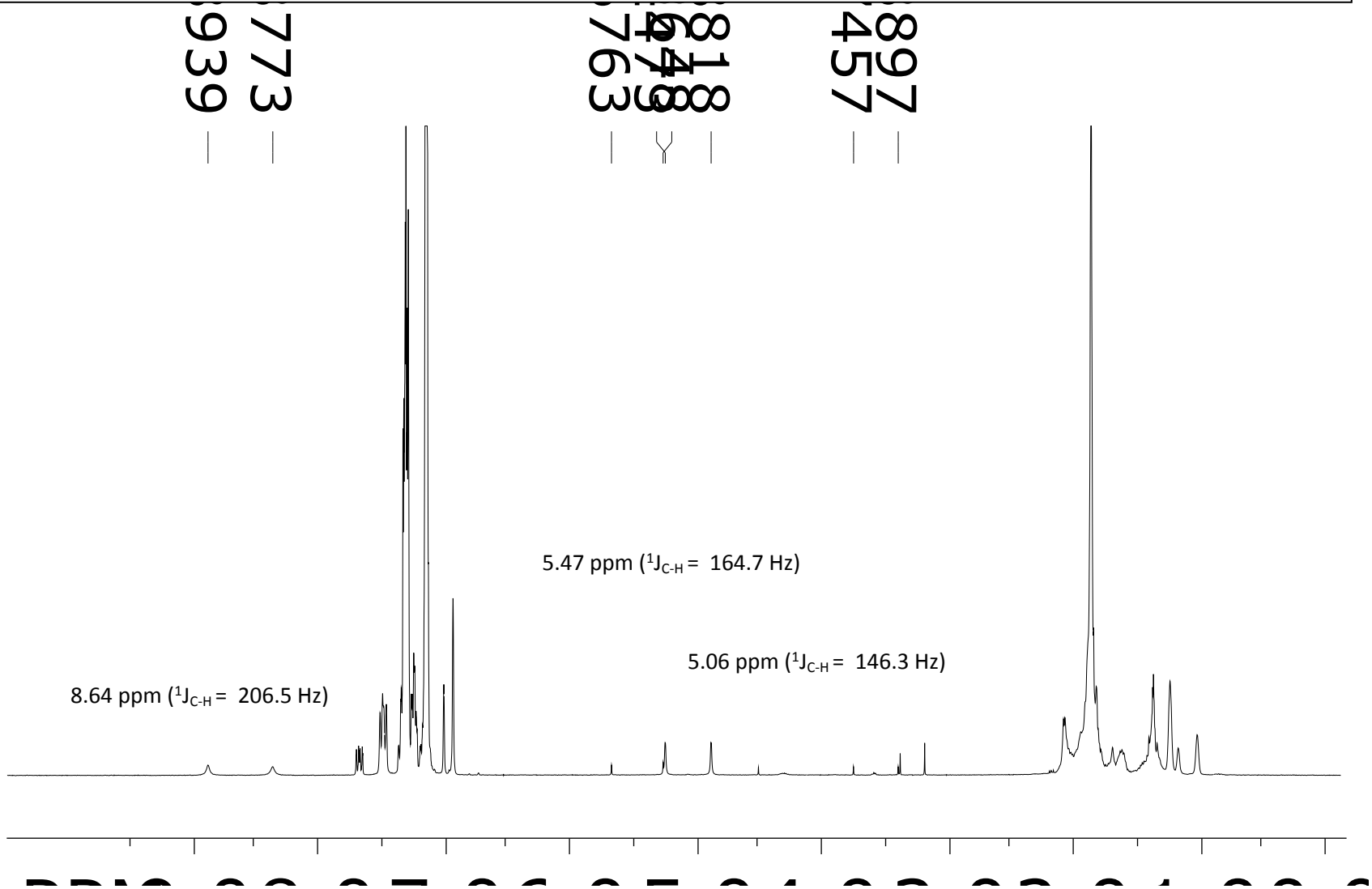
$^{13}CH_2(OBC_8H_{14})$: ^1H NMR (C_6D_5Br, 400 MHz): 5.47 (d, $^1J^{13}_{C\text{-}H}$ = 164.7 Hz, $^{13}CH_2(OBC_8H_{14})_2$); $^{13}C\{^1H\}$ NMR (C_6D_5Br, 100 MHz): 85.47 (s, $^{13}CH_2(OBC_8H_{14})_2$); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 85.47 (d, $^1J^{13}_{C\text{-}H}$ = 164.7 Hz, $^{13}CH_2(OBC_8H_{14})_2$).

Ph_3P-CH_2-$OBC_8H_{14}(OBC_8H_{14})$: ^1H NMR (C_6D_5Br, 400 MHz): 5.06 (d, $^1J^{13}_{C\text{-}H}$ = 146.3 Hz, Ph_3P-$^{13}CH_2$-$OBC_8H_{14}(OBC_8H_{14})$); $^{31}P\{^1H\}$ NMR (C_6D_5Br, 162 MHz): 17.74 (d, $^1J_{C\text{-}P}$ = 70.8 Hz, Ph_3P-$^{13}CH_2$-$OBC_8H_{14}(OBC_8H_{14})$); $^{13}C\{^1H\}$ NMR (C_6D_5Br, 100 MHz): 57.42 (d, $^1J_{C\text{-}P}$ = 70.8 Hz, Ph_3P-$^{13}CH_2$-$OBC_8H_{14}(OBC_8H_{14})$); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 57.42 (td, $^1J^{13}_{C\text{-}H}$ = 146.3 Hz, $^1J_{C\text{-}P}$ = 70.8 Hz, Ph_3P-$^{13}CH_2$-$OBC_8H_{14}(OBC_8H_{14})$).

$H_3{}^{13}COBC_8H_{14}$: ^1H NMR (C_6D_5Br, 400 MHz): 3.57 (d, $^1J^{13}_{C\text{-}H}$ = 142.4 Hz, $H_3{}^{13}COBC_8H_{14}$); $^{13}C\{^1H\}$ NMR (C_6D_5Br, 100 MHz): 52.68 (s, $H_3{}^{13}COBC_8H_{14}$); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 52.68 (q, $^1J^{13}_{C\text{-}H}$ = 142.4 Hz, $H_3{}^{13}COBC_8H_{14}$).

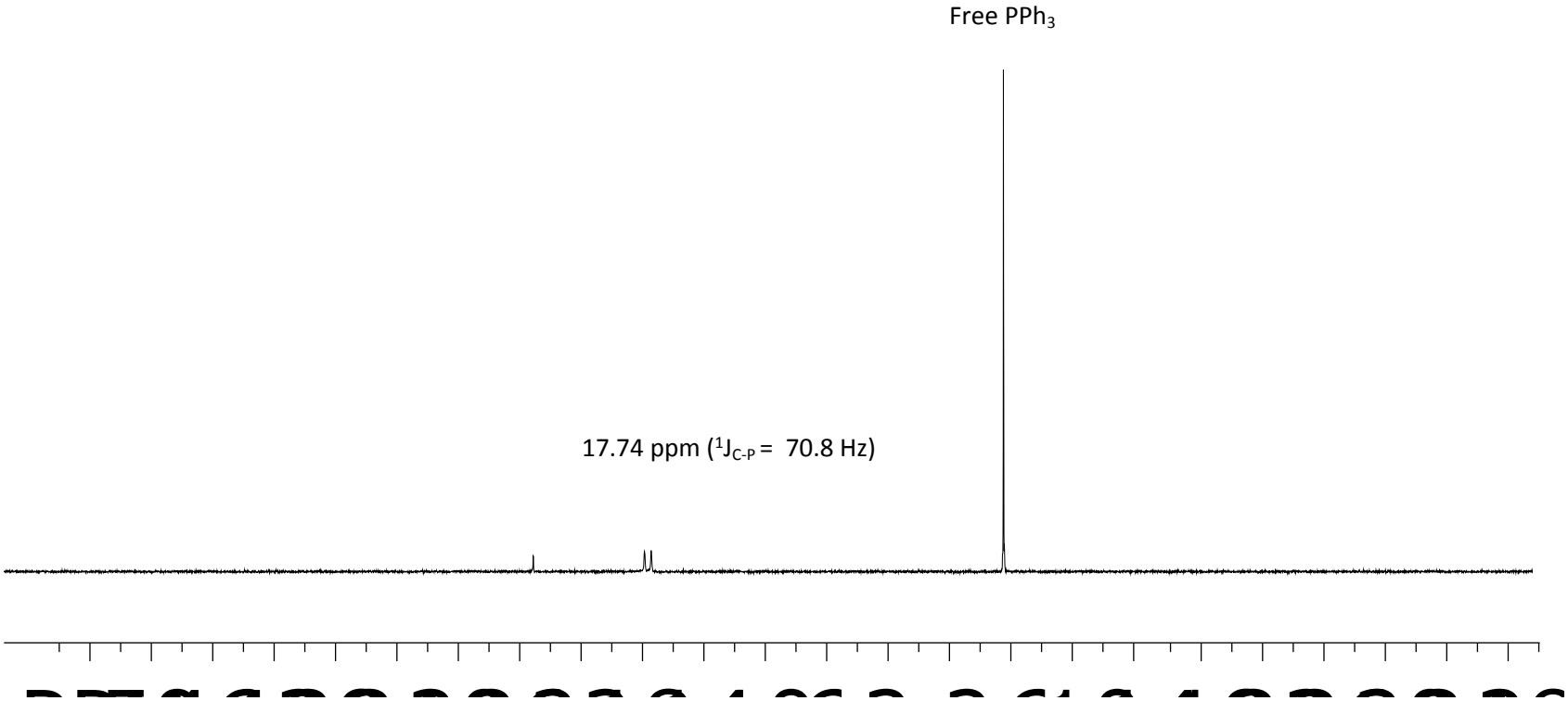
The stoichiometric reaction between 9-BBN dimer and PPh_3 in the atmosphere of 4 atm $^{13}CO_2$ at room temperature for 12 hours in C_6D_5Br

^1H NMR spectrum (400M, C_6D_5Br)



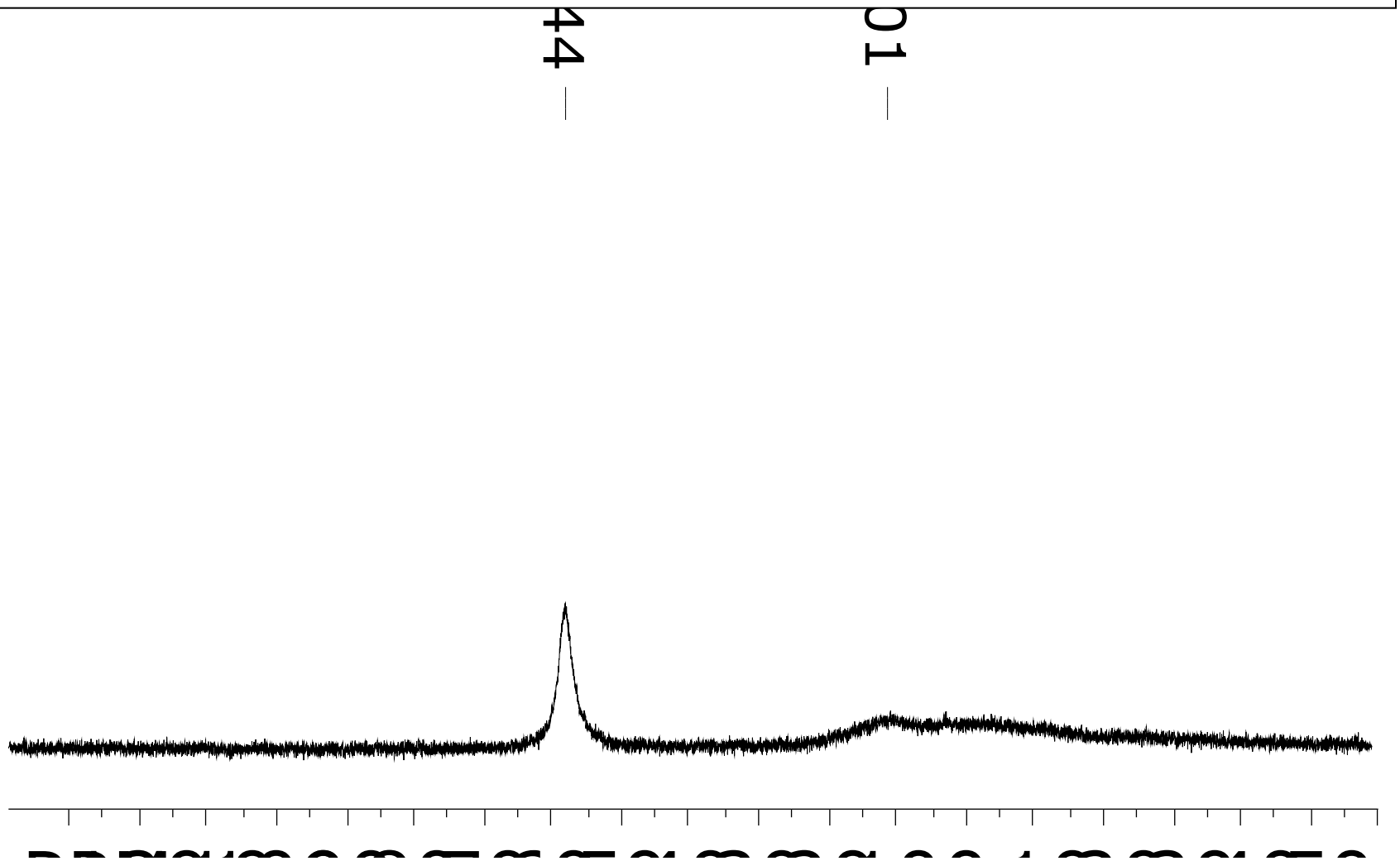
The stoichiometric reaction between 9-BBN dimer and PPh_3 in the atmosphere of 4 atm $^{13}CO_2$ at room temperature for 12 hours in C_6D_5Br

$^{31}P\{^1H\}$ NMR spectrum (162 M, C_6D_5Br)



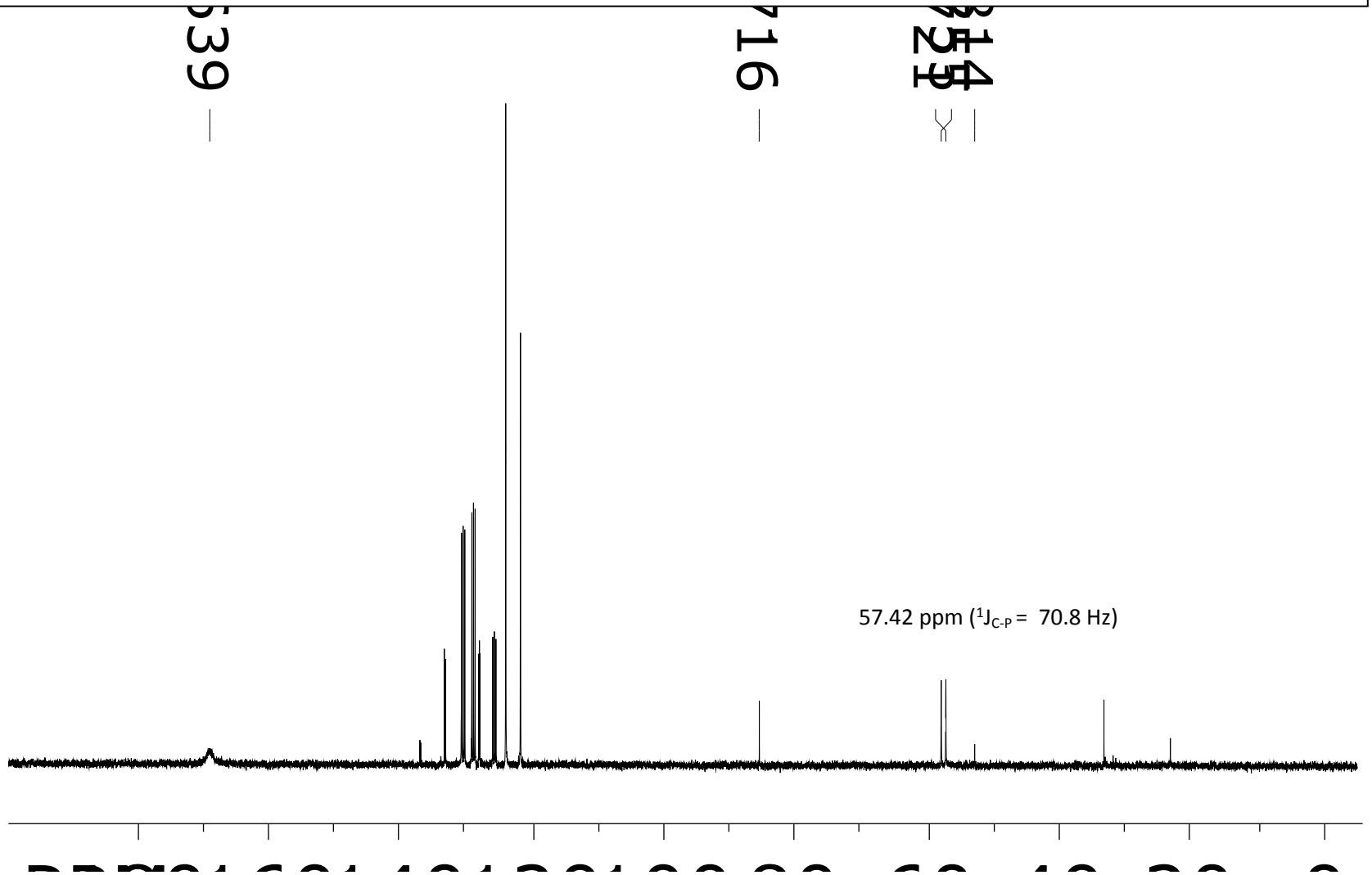
The stoichiometric reaction between 9-BBN dimer and PPh_3 in the atmosphere of 4 atm $^{13}CO_2$ at room temperature for 12 hours in C_6D_5Br

$^{11}B\{^1H\}$ NMR spectrum (128 M, C_6D_5Br)



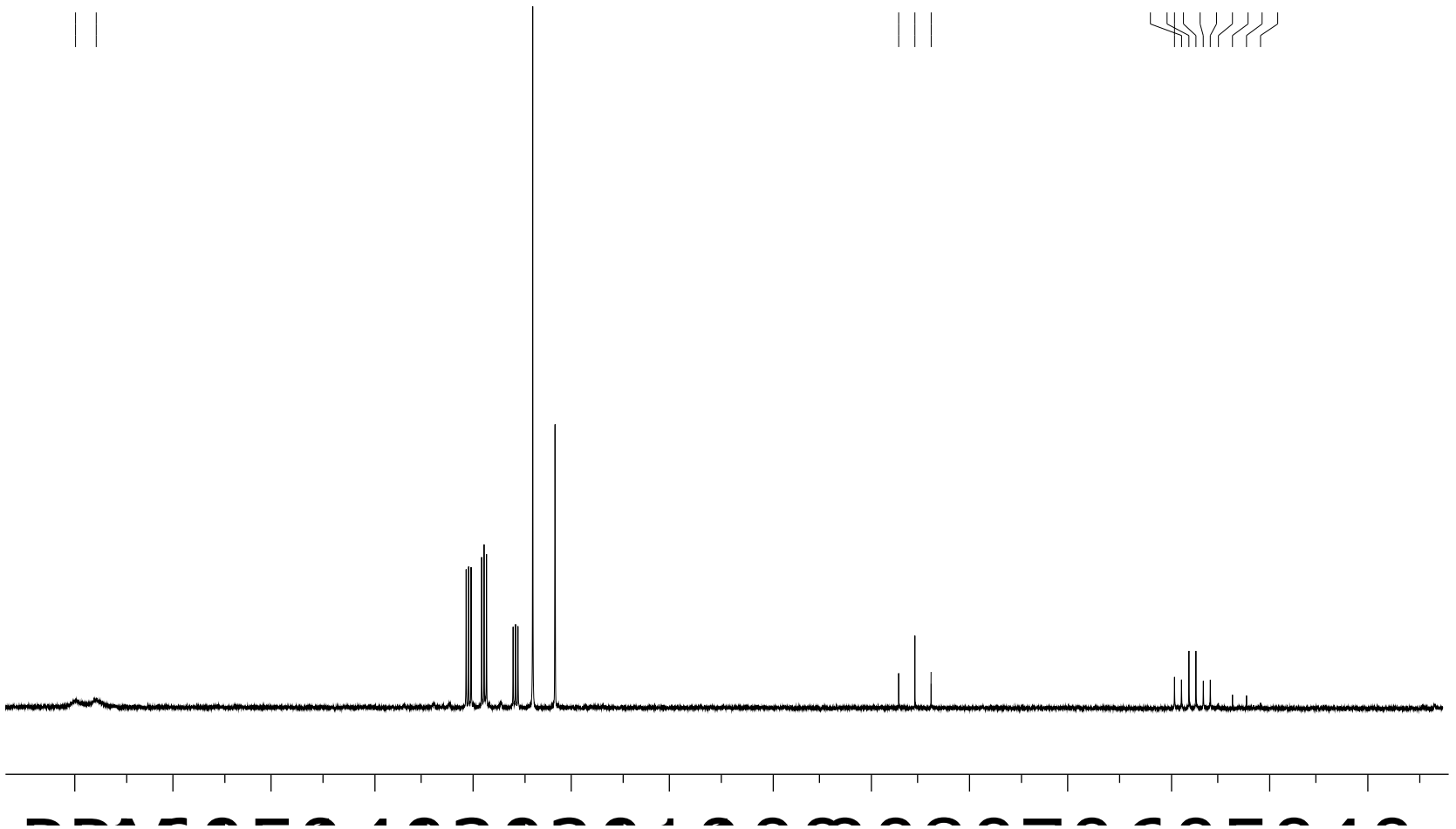
The stoichiometric reaction between 9-BBN dimer and PPh_3 in the atmosphere of 4 atm $^{13}CO_2$ at room temperature for 12 hours in C_6D_5Br

$^{13}C\{^1H\}$ NMR spectrum (100 M, C_6D_5Br)



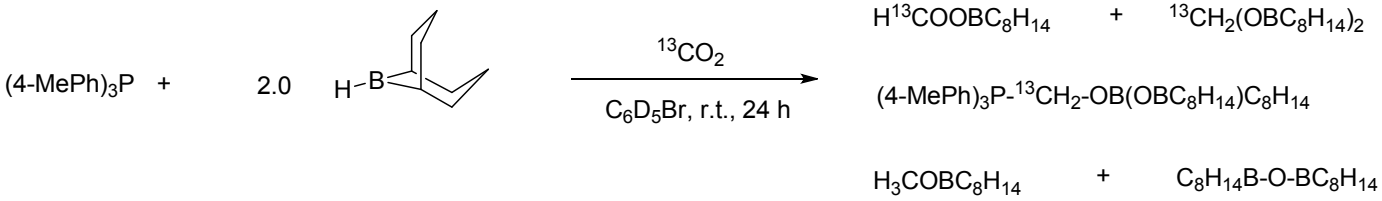
The stoichiometric reaction between 9-BBN dimer and PPh_3 in the atmosphere of 4 atm $^{13}CO_2$ at room temperature for 12 hours in C_6D_5Br

^{13}C NMR spectrum (100 M, C_6D_5Br)



Stoichiometric reaction between $(HBC_8H_{14})_2$, P(4-methylphenyl)$_3$ in the atmosphere of $^{13}CO_2$

In a similar fashion,Tri(4-methylphenyl)phosphine (31 mg, 0.1018 mmol) and $(HBC_8H_{14})_2$ (24 mg, 0.0983 mmol) were combined and reacted with CO_2.



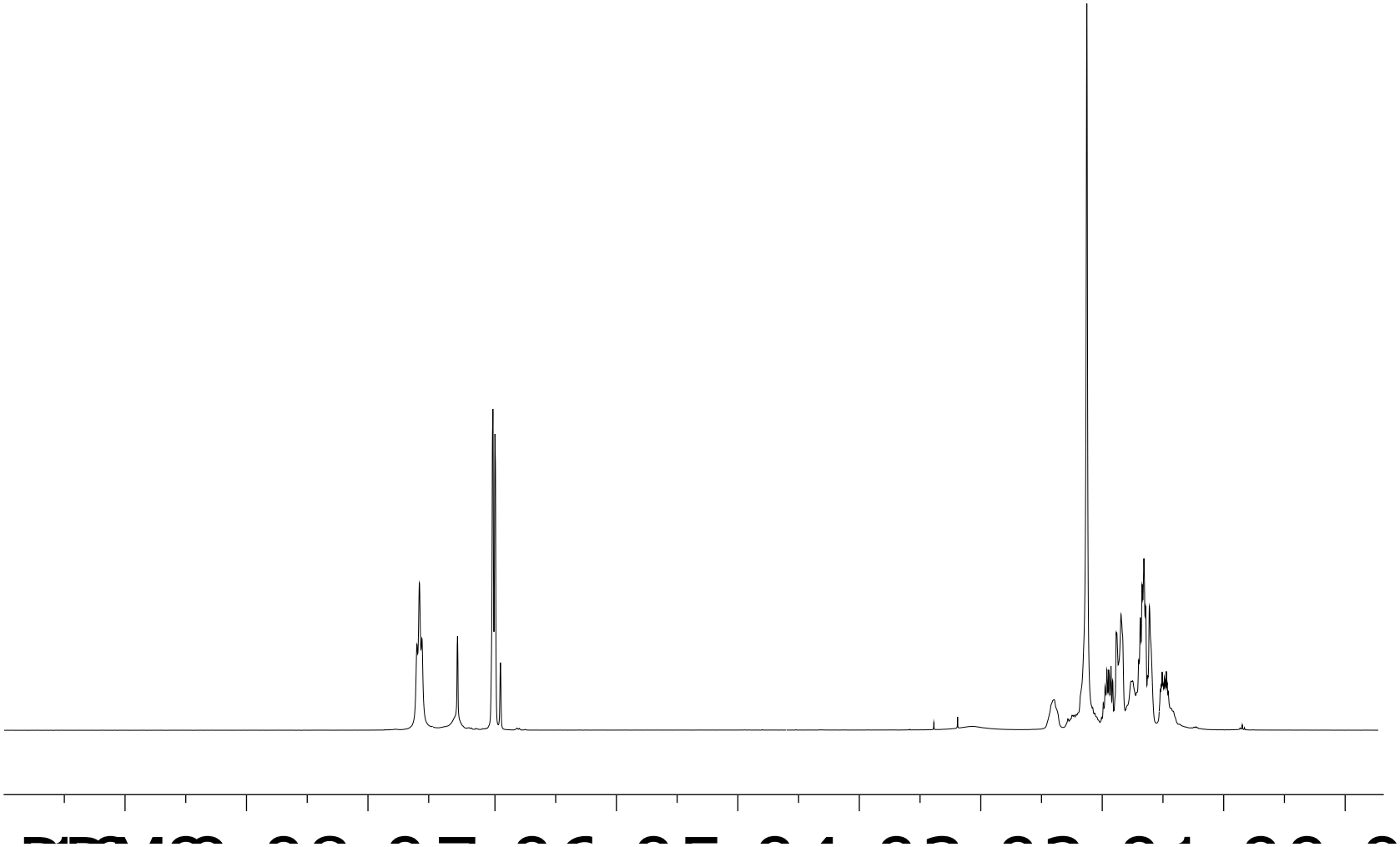
$H^{13}COOBC_8H_{14}$: ^{1}H NMR (C_6D_5Br, 400 MHz): 8.62 (d, $^1J^{13}_{C\text{-}H}$ = 208.3 Hz, *H*-^{13}COOBC$_8$H$_{14}$); ^{13}C{^{1}H} NMR (C_6D_5Br, 100 MHz): 169.80 (s, H-*^{13}C*OOBC$_8$H$_{14}$); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 169.80 (d, $^1J^{13}_{C\text{-}H}$ = 208.3 Hz, H-*^{13}C*OOBC$_8$H$_{14}$).

$^{13}CH_2(OBC_8H_{14})_2$: ^{1}H NMR (C_6D_5Br, 400 MHz): 5.47 (d, $^1J^{13}_{C\text{-}H}$ = 164.6 Hz, $^{13}CH_2(OBC_8H_{14})_2$); ^{13}C{^{1}H} NMR (C_6D_5Br, 100 MHz): 85.43 (s, *^{13}C*H$_2$(OBC$_8$H$_{14}$)$_2$); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 85.43 (d, $^1J^{13}_{C\text{-}H}$ = 164.6 Hz, *^{13}C*H$_2$(OBC$_8$H$_{14}$)$_2$).

(4-MePh)$_3$P-^{13}CH$_2$-OBC$_8$H$_{14}$(OBC$_8$H$_{14}$): ^{1}H NMR (C_6D_5Br, 400 MHz): 5.09 (d, $^1J^{13}_{C\text{-}H}$ = 146.5 Hz, (4-MePh)$_3$P-C*H*$_2$-OB (OBC$_8$H$_{14}$)C$_8$H$_{14}$); ^{31}P{^{1}H} NMR (C_6D_5Br, 162 MHz): 17.53 (d, $^1J_{C\text{-}P}$ = 71.7 Hz, (4-MePh)$_3$*P*-^{13}CH$_2$-OB (OBC$_8$H$_{14}$)C$_8$H$_{14}$); ^{13}C{^{1}H} NMR (C_6D_5Br, 100 MHz): 57.42 (d, $^1J_{C\text{-}P}$ = 71.7 Hz, (4-MePh)$_3$P-*^{13}C*H$_2$-OB(OBC$_8$H$_{14}$)C$_8$H$_{14}$); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 57.42 (td, $^1J^{13}_{C\text{-}H}$ = 146.3 Hz, $^1J_{C\text{-}P}$ = 71.7 Hz, (4-MePh)$_3$P-*^{13}C*H$_2$-OB(OBC$_8$H$_{14}$)C$_8$H$_{14}$).

$H_3{}^{13}CO\text{-}BC_8H_{14}$: ^{1}H NMR ($C_6D_5Br$, 400 MHz): 3.57 (d, $^1J^{13}_{C\text{-}H}$ = 142.5 Hz, *H*$_3{}^{13}$COBC$_8$H$_{14}$); ^{13}C{^{1}H} NMR (C_6D_5Br, 100 MHz): 52.68 (s, H$_3$*^{13}C*OBC$_8$H$_{14}$); ^{13}C NMR with proton coupling (C_6D_5Br, 100 MHz): 52.68 (q, $^1J^{13}_{C\text{-}H}$ = 142.5 Hz, H$_3$*^{13}C*OBC$_8$H$_{14}$).

The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}CO_2$ at room temperature for 1.5 hours in C_6D_5Br



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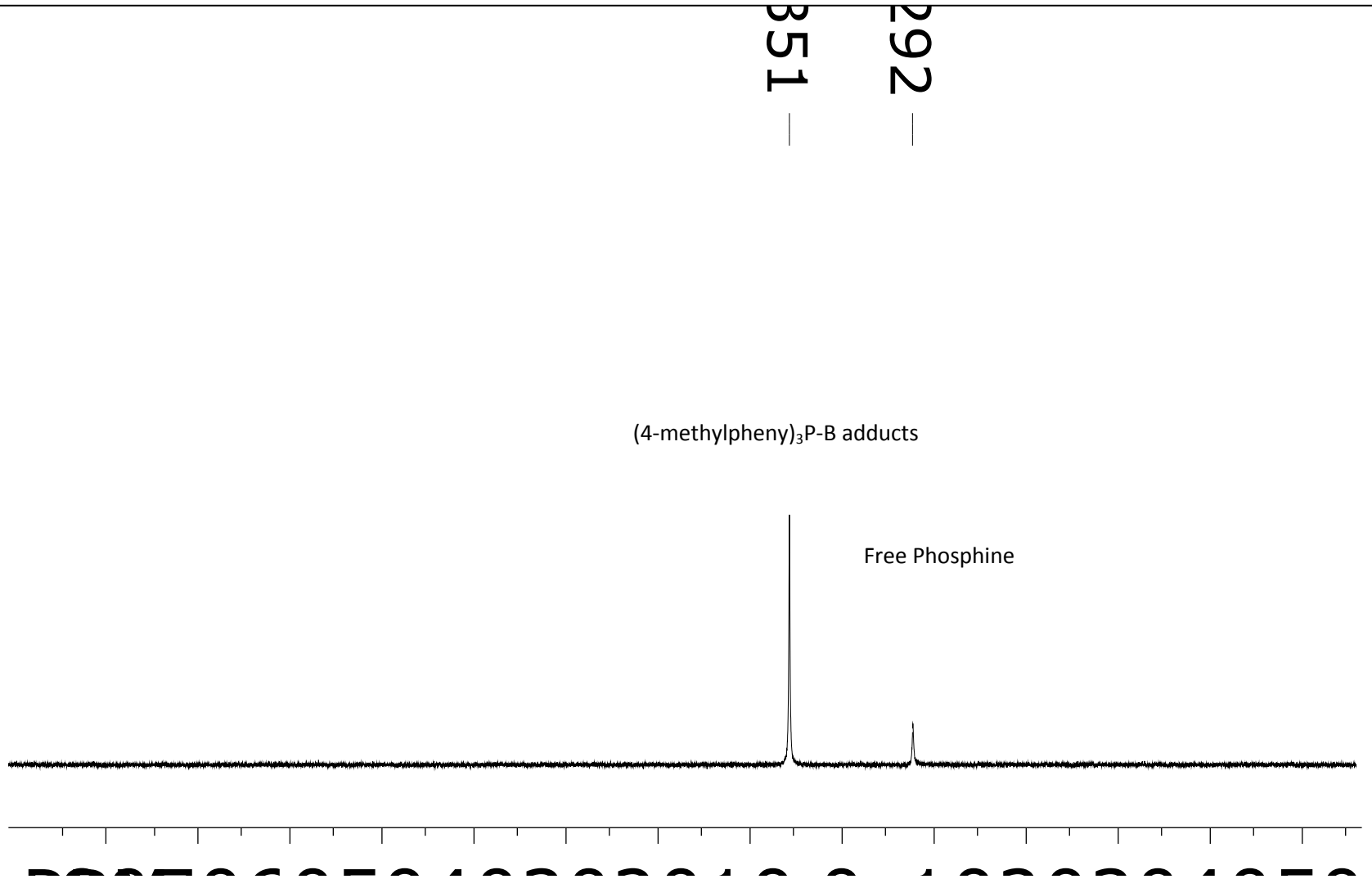

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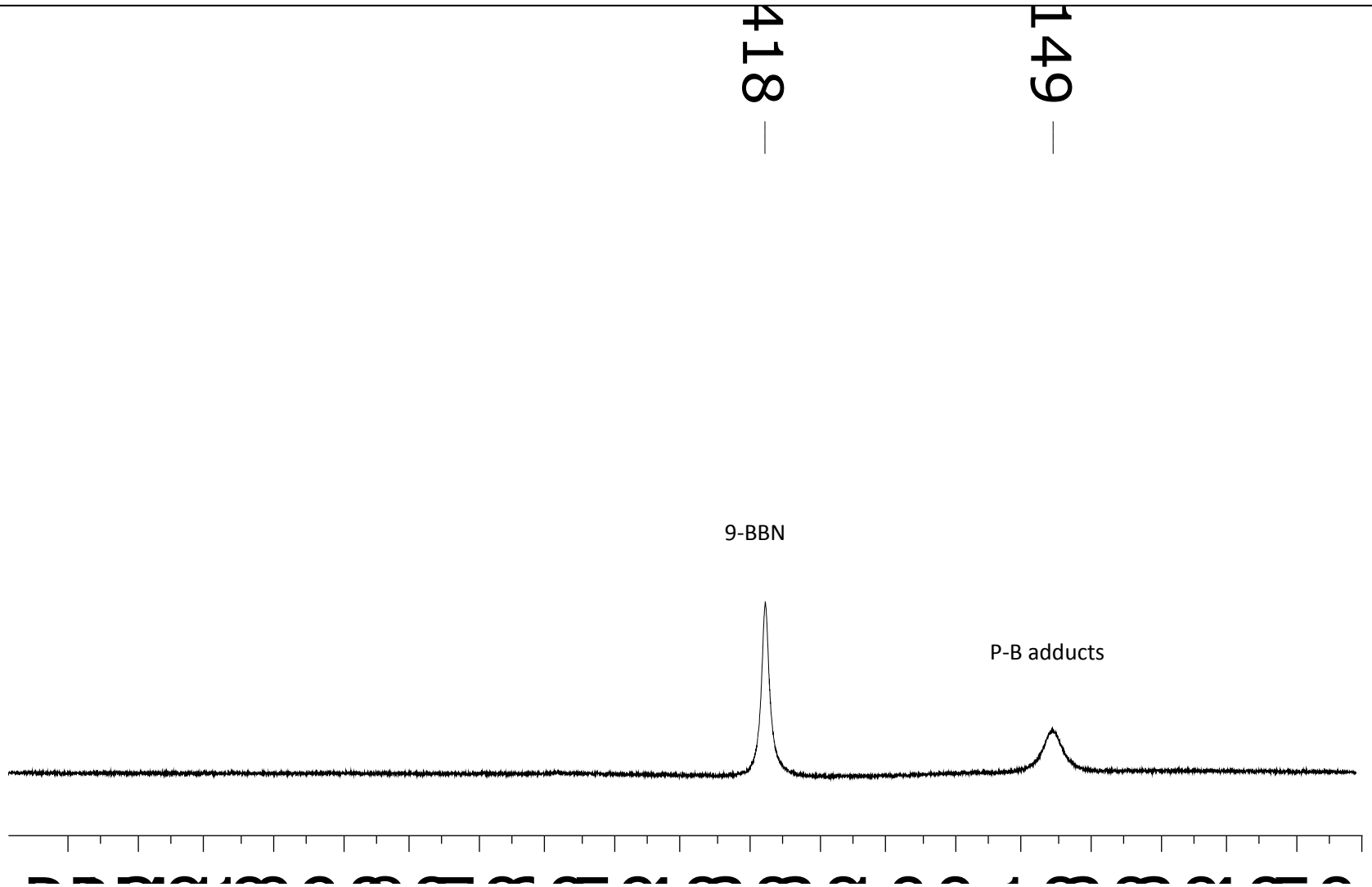

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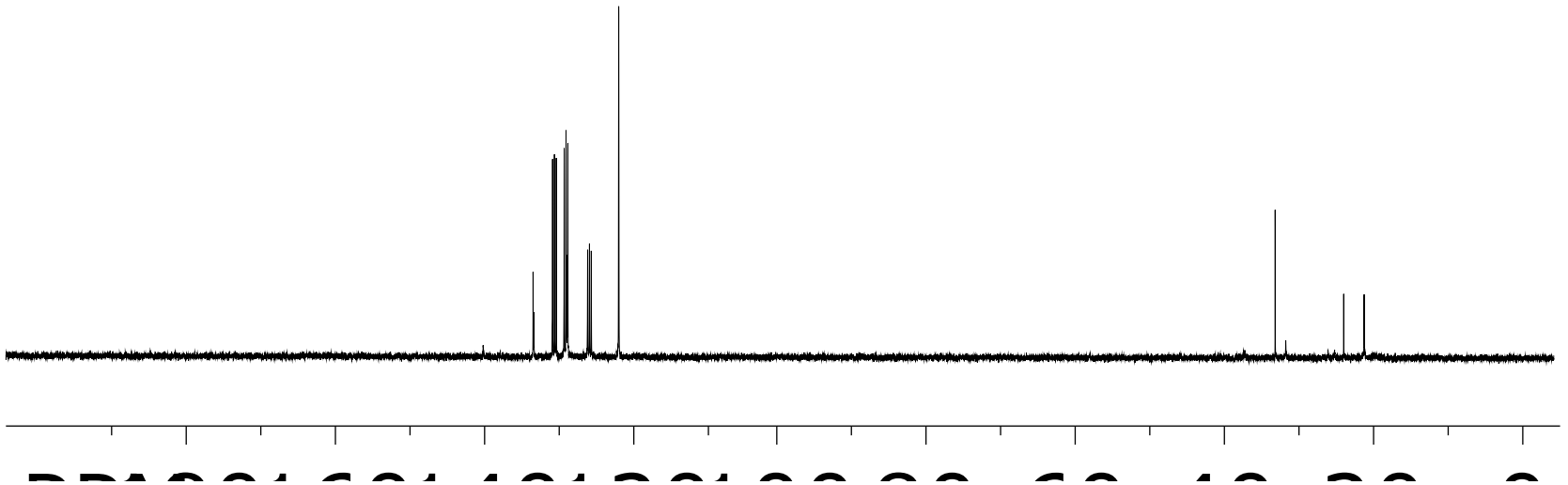
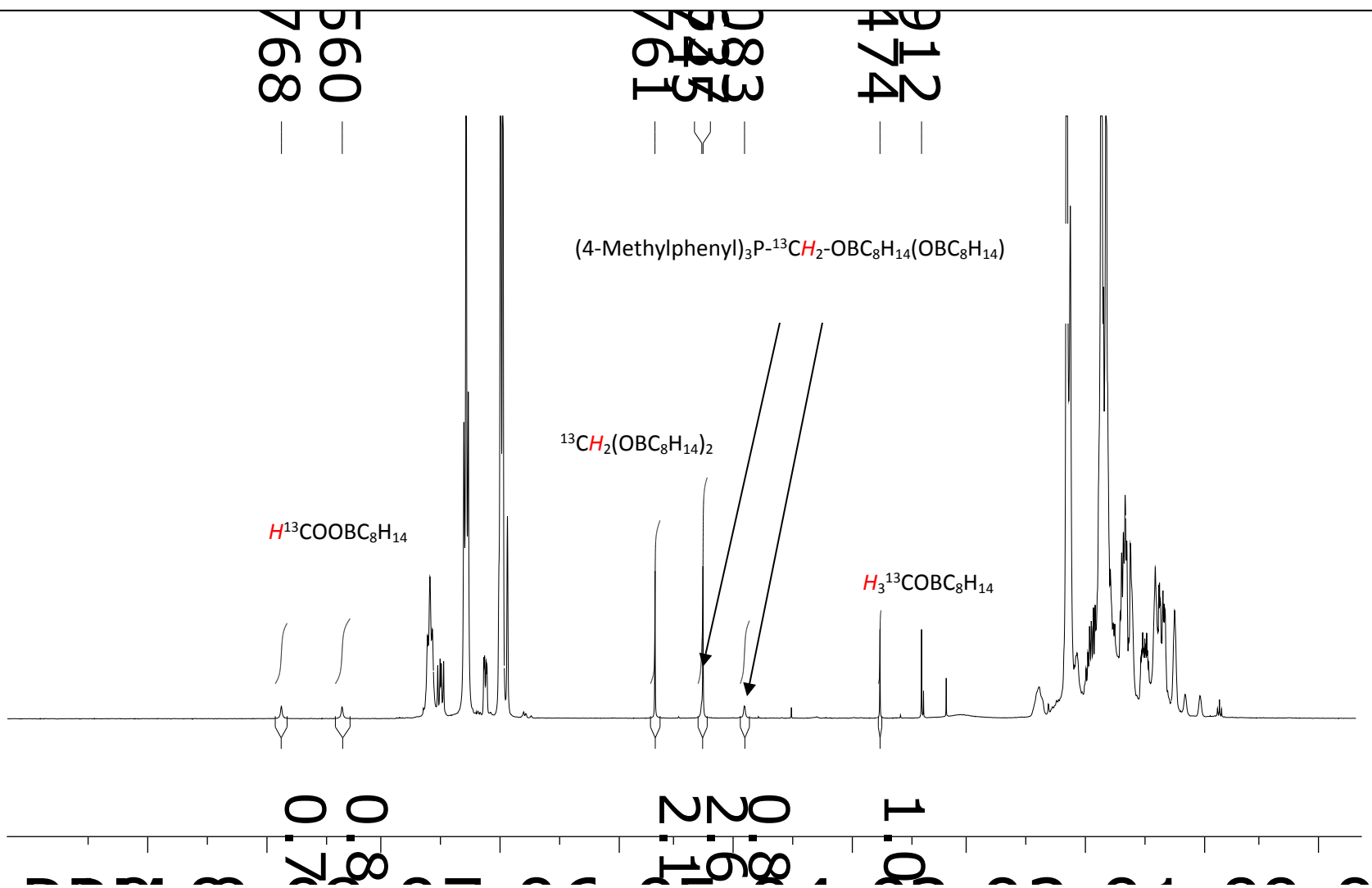
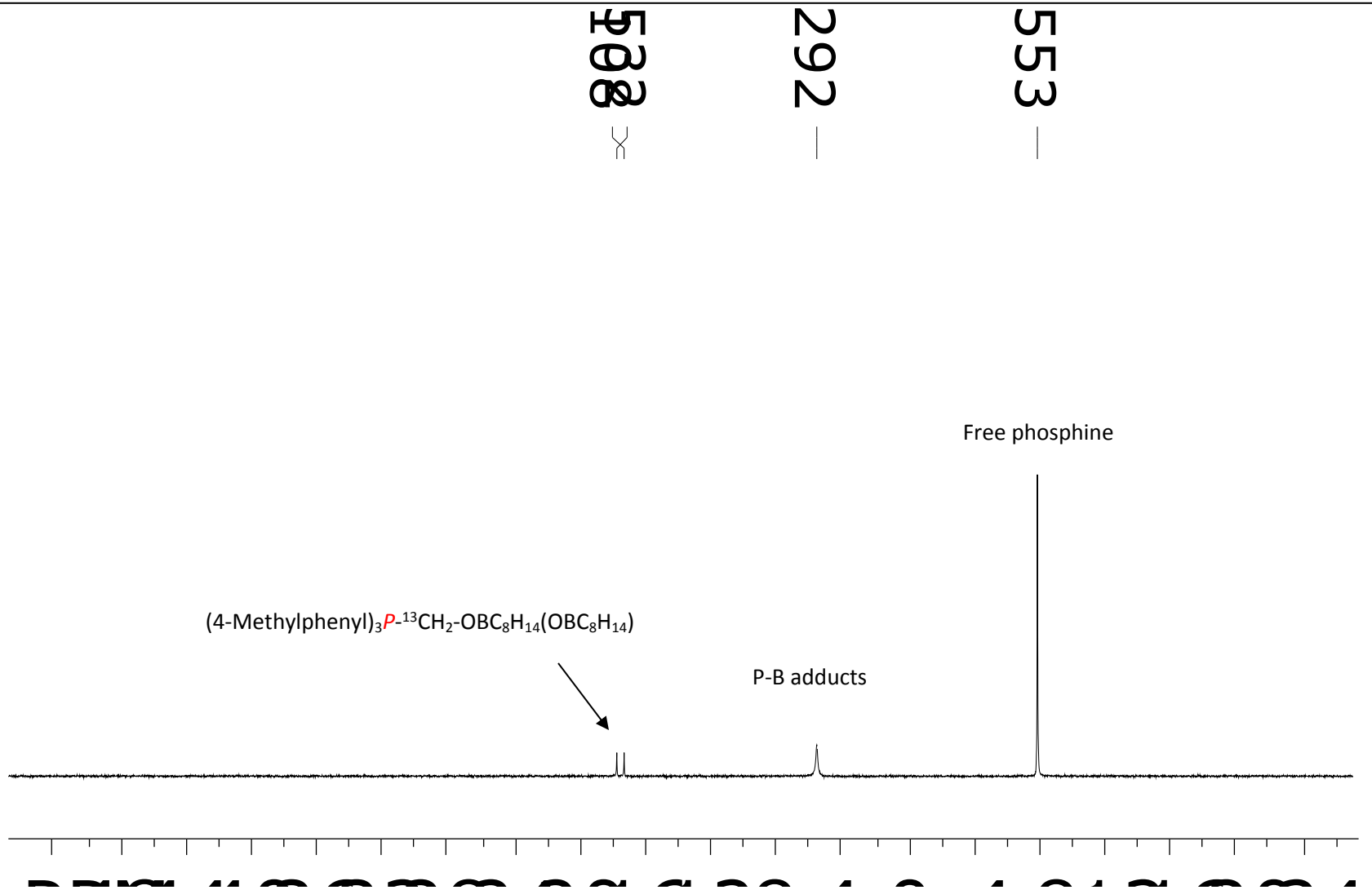


The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}CO_2$ at room temperature for 24 hours in C_6D_5Br



The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}CO_2$ at room temperature for 24 hours in C_6D_5Br



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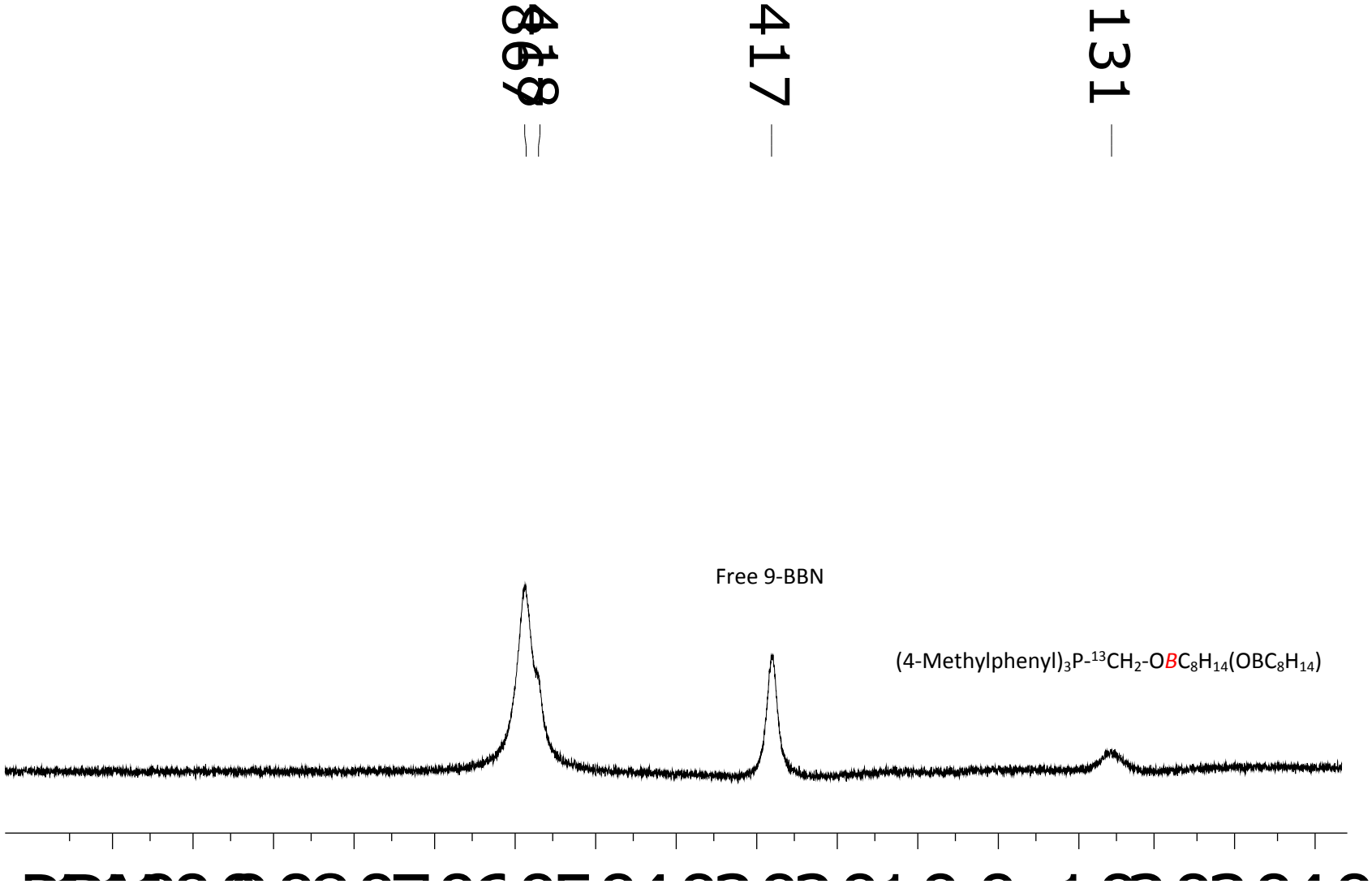
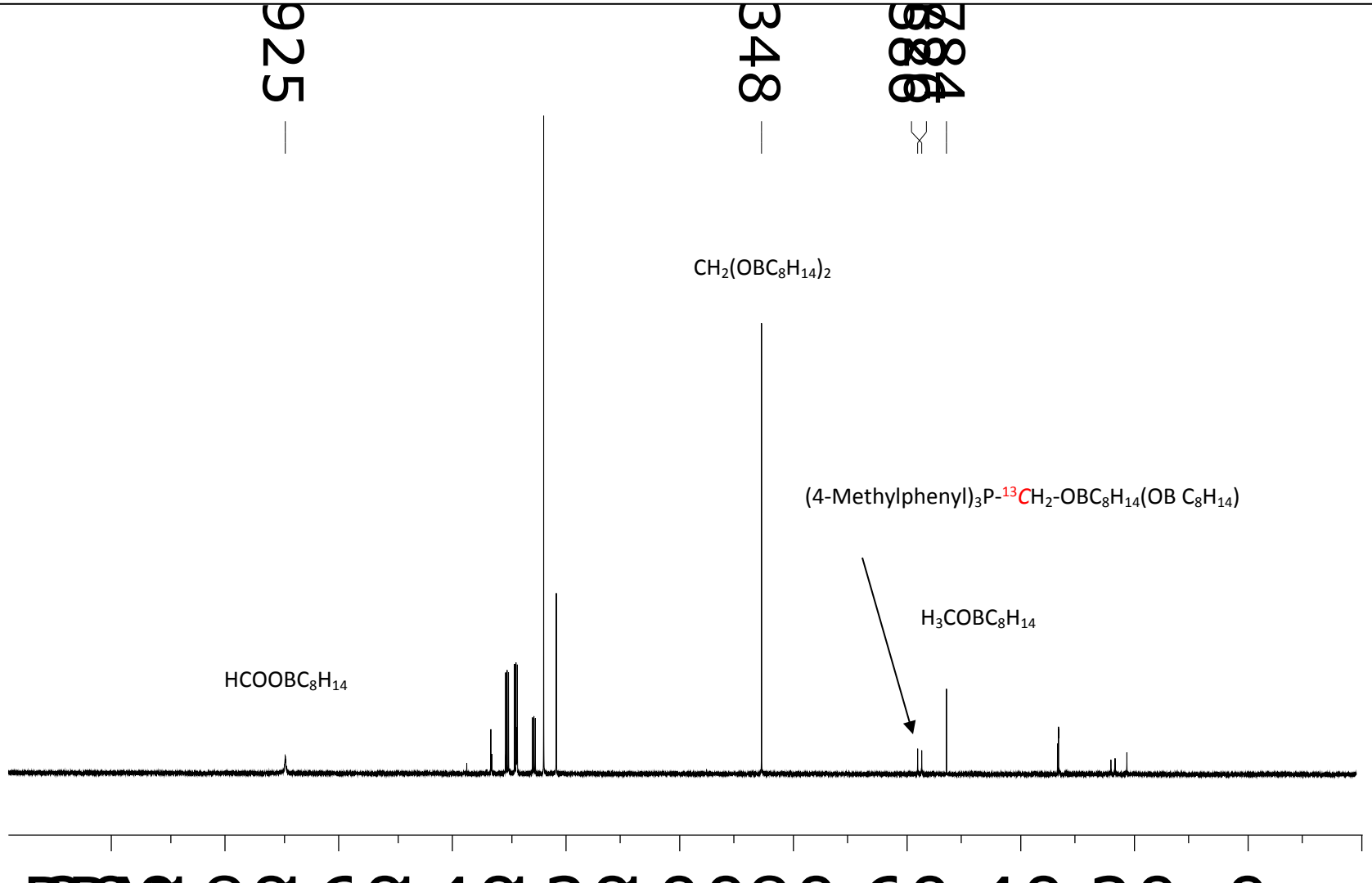


The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}CO_2$ at room temperature for 24 hours in C_6D_5Br



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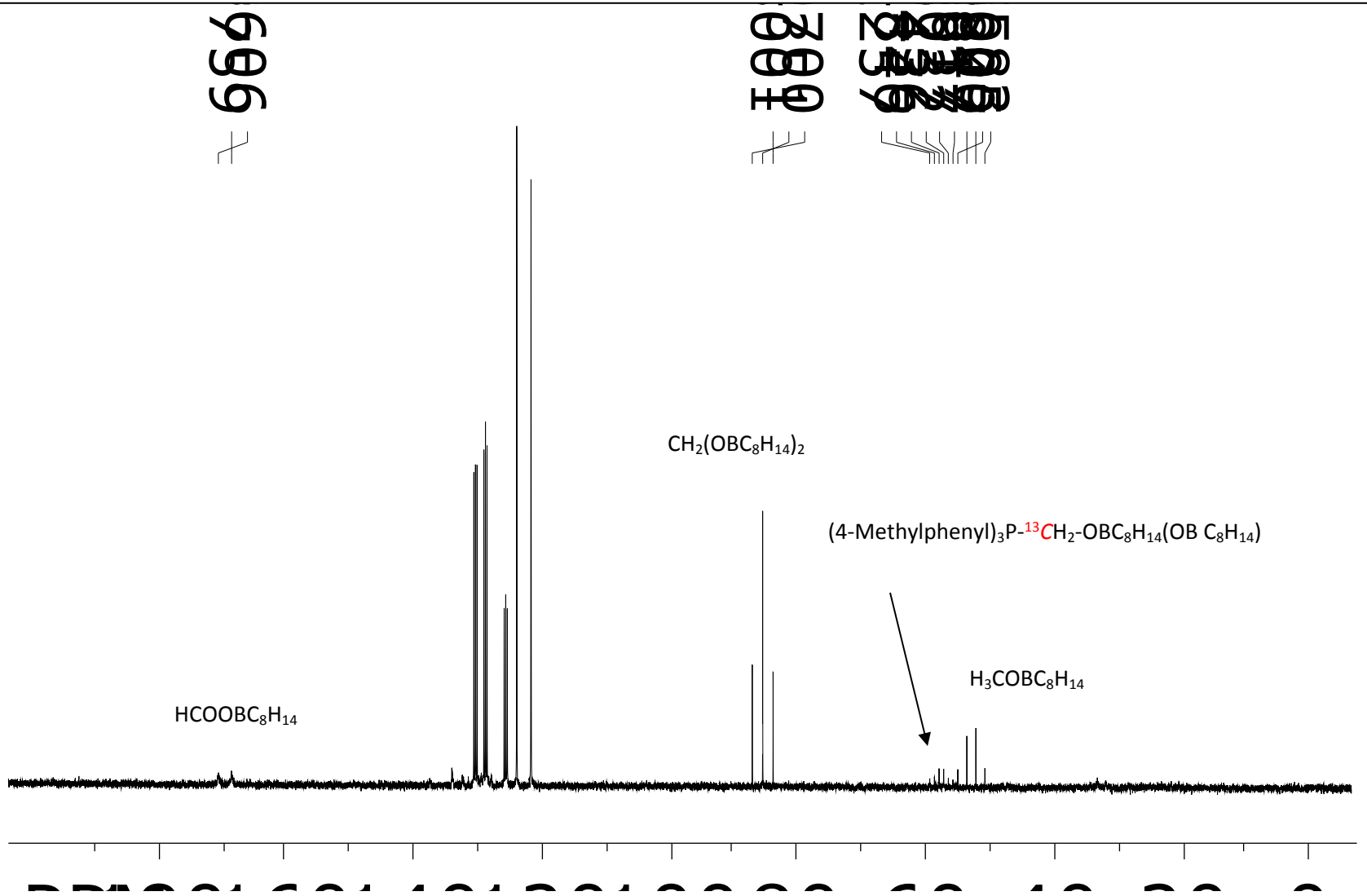

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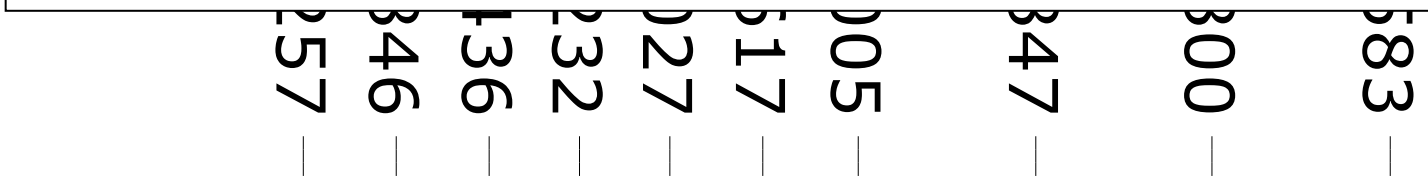
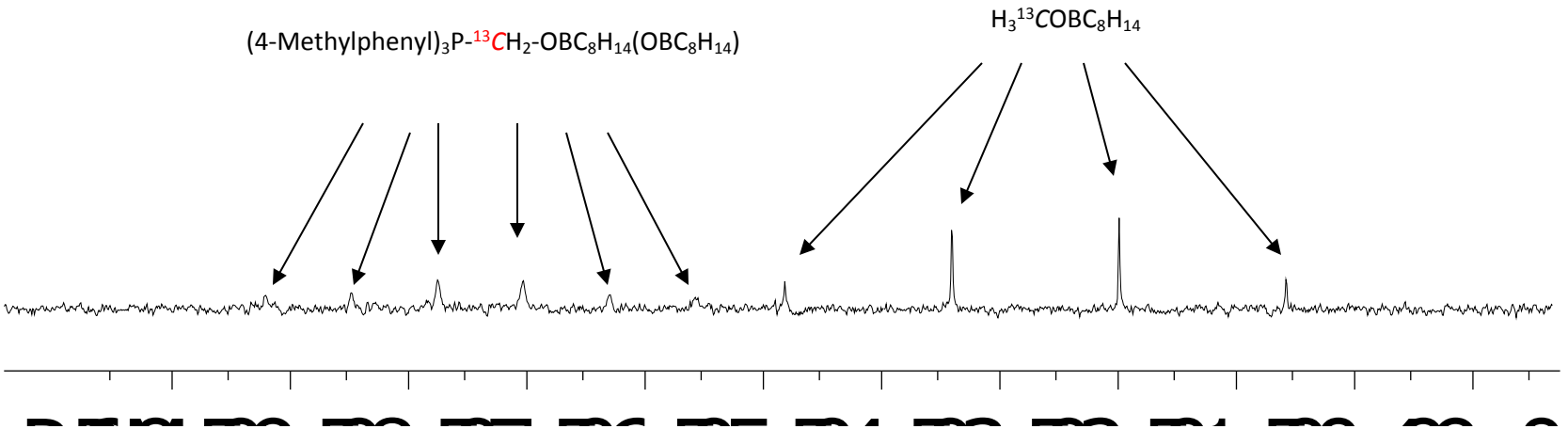
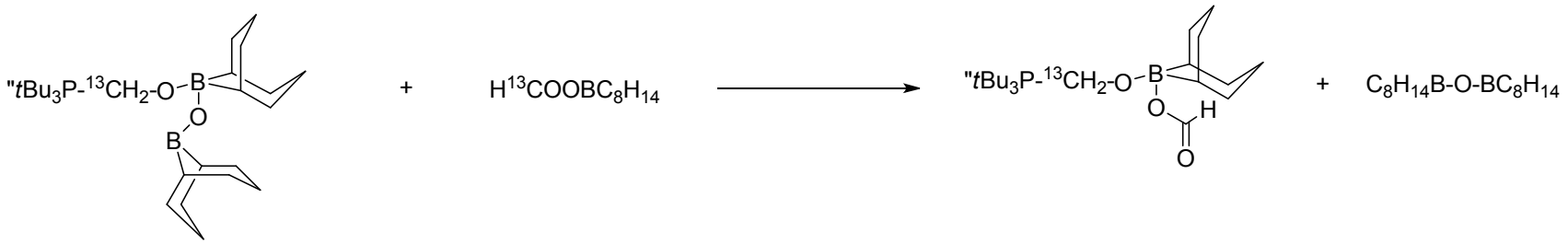




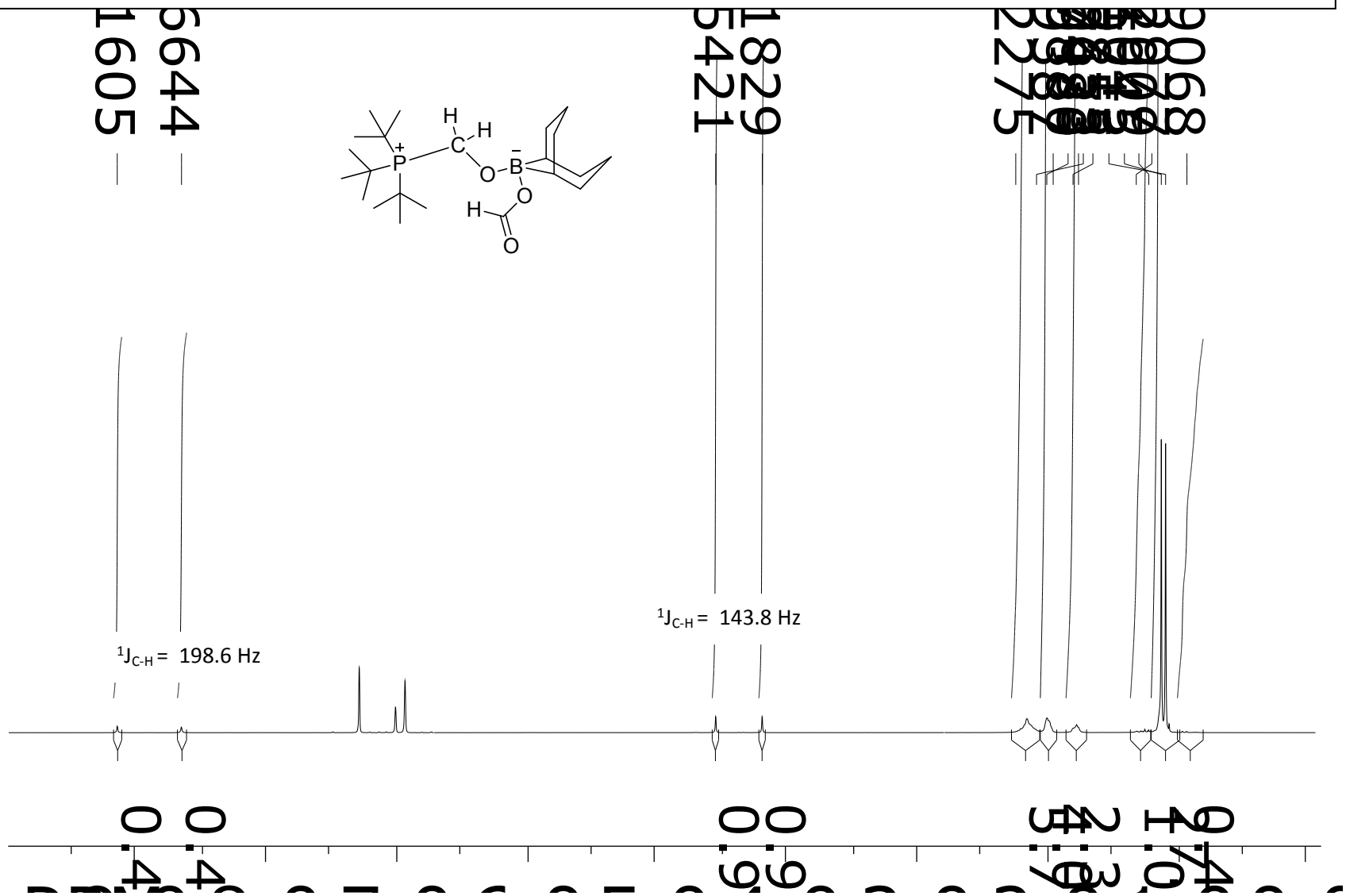
Isolation of as $(R_3PCH_2O)(HC(O)O)B(C_8H_{14})$ (R = *t*Bu 1, 4-MeC_6H_4 2)

After testing NMR spectra of the stoichiometric reaction between $(HBC_8H_{14})_2$, tris(*t*-butyl)phosphine in the atmosphere of $^{13}CO_2$, the sample above was taken into glove-box and trasferred into a 20 mL vial. The solution was layered with 8.0 mL of hexanes. The mixture was left at room temperature for overnight to obtain color less crystals (15 mg) for X-ray analysis.

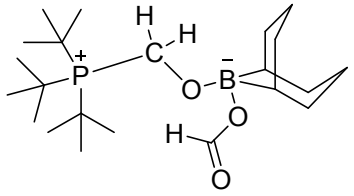
1: ^{1}H NMR (C_6D_5Br): 0.91 – 1.30 (m, 2H, C-H for (HBC_8H_{14}), overlapping with the resonance of *t*Bu), 1.09 (d, $^3J_{C-P}$ = 13.2 Hz, 27 H, 3 x $C(CH_3)_3$), 1.74-1.79 (m, 2H), 1.94-1.99 (m, 4H), 2.07-2.23 (m, 6 H), 4.36 (d, $^1J^{13}_{C-H}$ = 143.8 Hz, 2 H), 8.91 (d, $^1J^{13}_{C-H}$ = 198.6 Hz, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_5Br): 25.33, 28.64, 32.02, 36.98 (d, $^2J_{C-P}$ = 28.1 Hz), 52.41 (d, $^1J_{C-P}$ = 54.4 Hz), 165.54. $^{31}P\{^1H\}$ NMR (C_6D_5Br): 42.55 (d, $^1J_{C-P}$ = 54.4 Hz). $^{11}B\{^1H\}$ NMR (C_6D_5Br): 8.83 (s). Anal. Calcd. for $C_{22}H_{44}BO_3P$ (398.37): C, 66.33; H, 11.13; N, 0. Found: C, 65.41; H, 11.14; N, 0. (Repeated analyses resulted in consistently low carbon analysis. This is attributed to the formation of boron-carbide during combustion.)



^{1}H NMR spectrum (400M, C_6D_5Br) (species **1**)

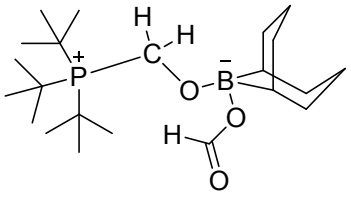


$^{31}P\{^{1}H\}$ NMR spectrum (162 M, C_6D_5Br) (species **1**)

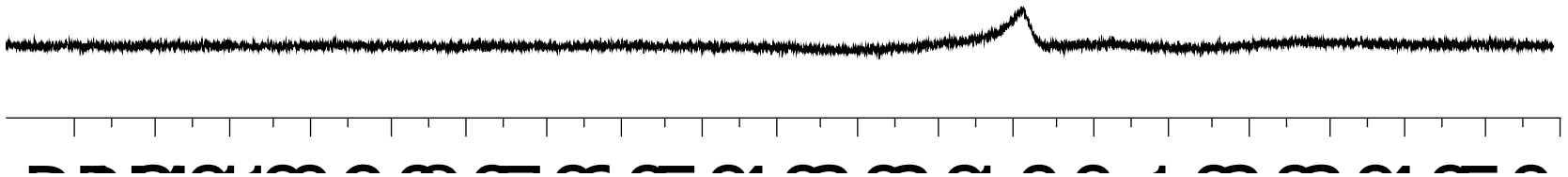


42.55 ppm ($^{1}J_{P\text{-}C}$ = 54.4 Hz)

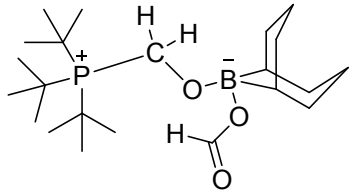
$^{11}B\{^{1}H\}$ NMR spectrum (128 M, C_6D_5Br) (species **1**)



260

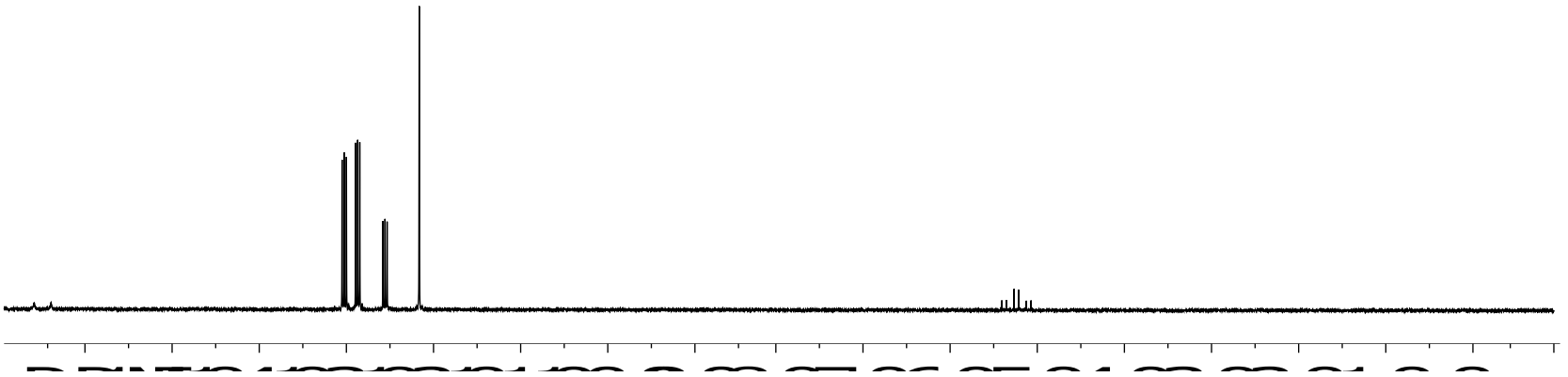


$^{13}C\{^{1}H\}$ NMR spectrum (100 M, C_6D_5Br) (species **1**)



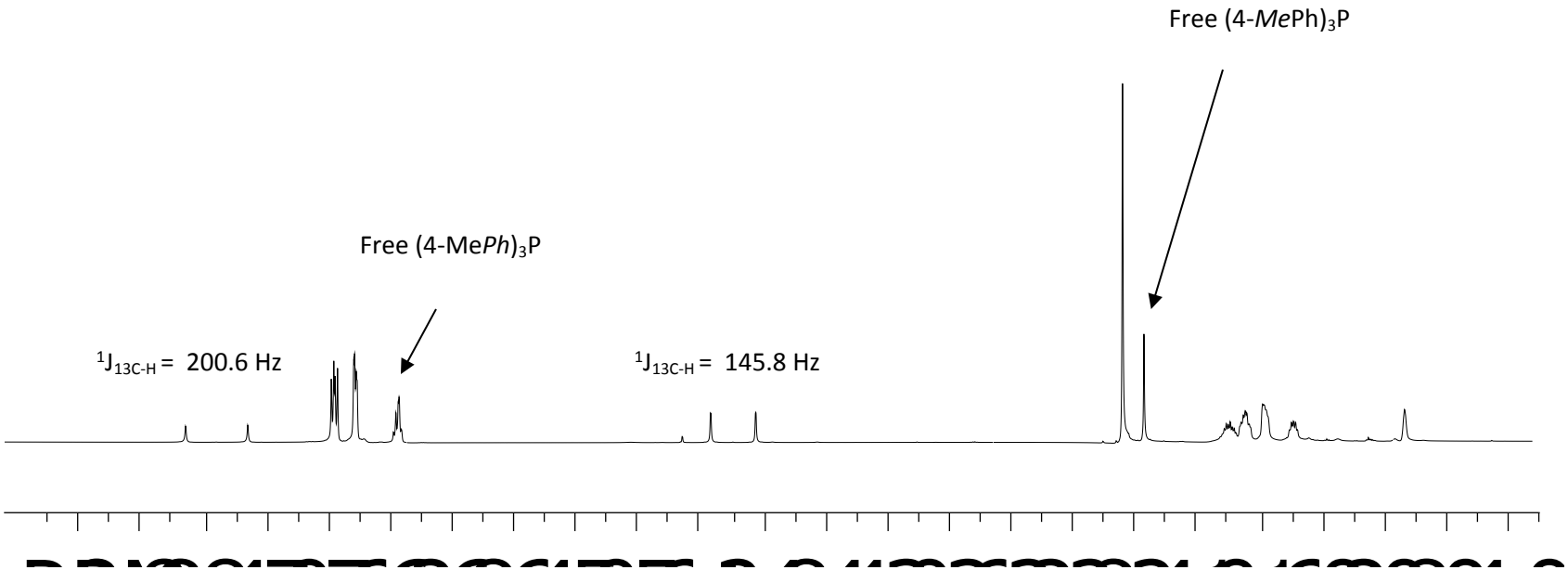
52.41 ppm ($^{1}J_{P\text{-}C}$ = 54.4 Hz)

^{13}C with ^{1}H coupling

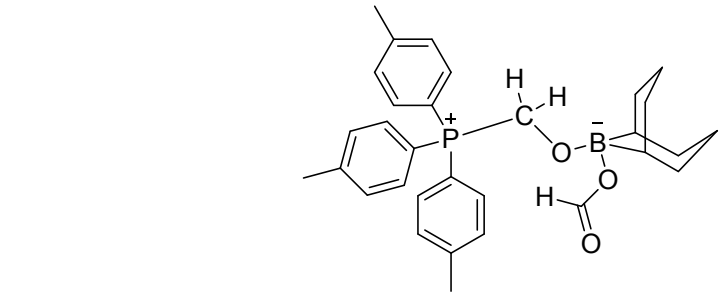


2: After testing NMR spectra of the stoichiometric reaction between $(HBC_8H_{14})_2$, P(4-methylphenyl)$_3$ in the atmosphere of $^{13}CO_2$, the sample was taken into glove-box and trasferred into a 20 mL vial. The solution was layered with 8.0 mL of hexanes. The mixture was left at room temperature for two days to obtain colorless crystals (12 mg) for X-ray analysis. (*note*: this crystal has low solubility in C_6D_5Br, therefore, CD_2Cl_2 was used for NMR spectroscopy). ^{1}H NMR (CD_2Cl_2): 0.62 – 0.72 (m, 2H, C-H for (BC_8H_{14})), 1.33 -1.93 (m, 12H, BC_8H_{14})), 2.33 (s, CH_3 for (4-MePh)$_3$P), 2.47 (s, 9 H, 3 x CH_3 on (4-MePh)$_3$P for **2**), 4.99 (d, $^1J^{13}_{C-H}$ = 145.8 Hz, 2 H, P-C*H*$_2$O on **2**), 7.15-7.20 (m, phenyl for (4-MePh)$_3$P), 7.43 (dd, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-P}$ = 2.7 Hz, 6 H, phenyl for **2**), 7.57 (dd, $^3J_{H-P}$ = 11.9 Hz, $^3J_{H-H}$ = 8.0 Hz, 6 H, phenyl for **2**), 8.33 (d, $^1J^{13}_{C-H}$ = 200.6 Hz, 1 H). ^{31}P{^{1}H} NMR (CD_2Cl_2): 16.87 (d, $^1J^{13}_{C-P}$ = 71.5 Hz), -8.20 (s, free (4-MePh)$_3$*P*). ^{11}B{^{1}H} NMR (CD_2Cl_2): 10.28 (bs). ^{13}C{^{1}H} NMR (CD_2Cl_2): 21.37 (*C*H$_3$ for (4-*Me*Ph)$_3$P), 21.97, 21.98(*C*H$_3$ for (4-*Me*Ph)$_3$PCH$_2$-O-B(OC(O)H)C$_8$H$_{14}$), 25.58, 32.31, 58.86 (d, $^1J_{C-P}$ = 71.5 Hz, P-^{13}*C*H$_2$-O), 115.53 (dd, $^1J_{C-P}$ = 86.6 Hz, $^2J^{13}_{C-C}$ = 1.8 Hz, *C*-P-^{13}CH$_2$), 131.00 (d, $^2J_{C-P}$ = 12.7 Hz, phenyl carbon on phosphine), 134.14 (d, $^3J_{C-P}$ = 9.4 Hz, phenyl carbon on phosphine), 146.46 (d, $^4J_{C-P}$ = 3.0 Hz, phenyl carbon on phosphine), 167.74 (H^{13}*C*OO). Anal. Calcd. for $C_{31}H_{38}BO_3P$ (500.41): C, 74.40; H, 7.65; N, 0. Found: C, 73.48; H, 7.61; N, 0.(Repeated analyses resulted in consistently low carbon analysis. This is attributed to the formation of boron-carbide during combustion.)

^{1}H NMR spectrum (400M, CD_2Cl_2) (species **2**)

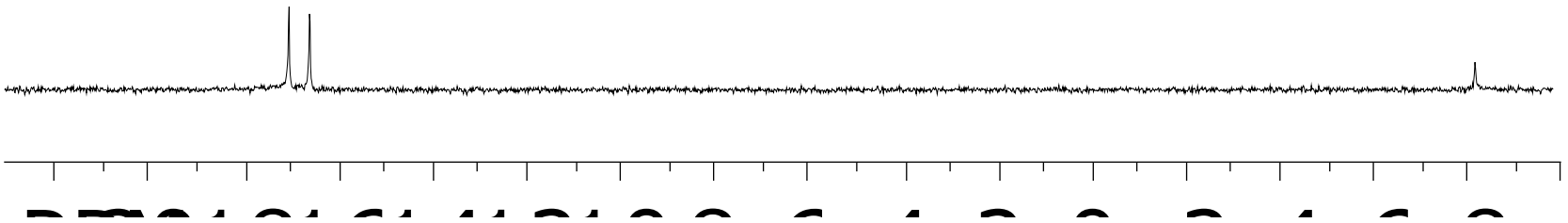


$^{31}P\{^{1}H\}$ NMR spectrum (162 M, CD_2Cl_2) (species **2**)



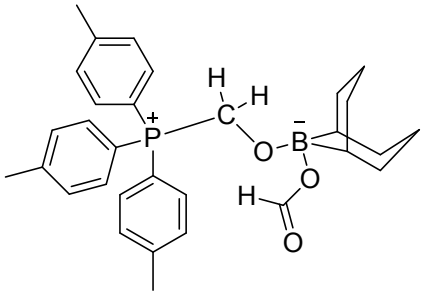
16.87 ppm ($^{1}J_{P\text{-}C}$ = 71.5 Hz)

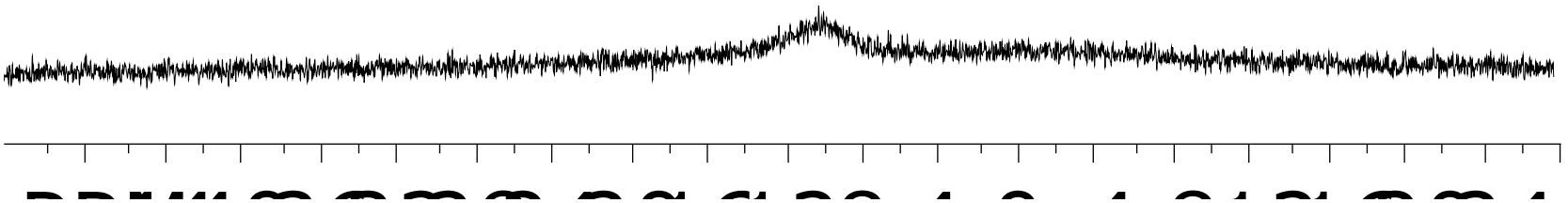
Free $(4\text{-MePh})_3P$



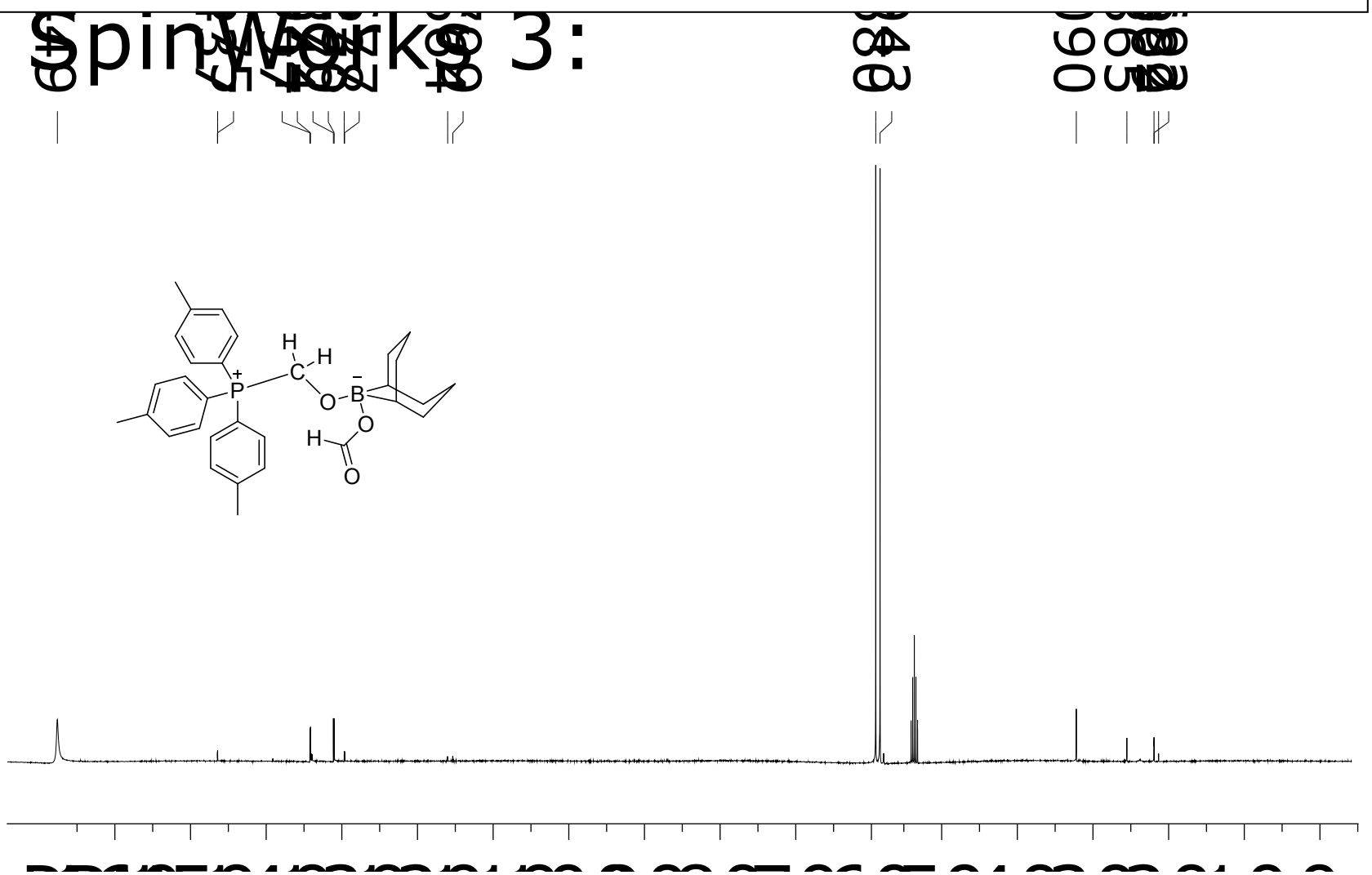
$^{11}B\{^{1}H\}$ NMR spectrum (128 M, CD_2Cl_2) (species **2**)

SpinWorks 3: bpo_b11_dec CD2





$^{13}C\{^{1}H\}$ NMR spectrum (125 M, CD_2Cl_2) (species **2**)

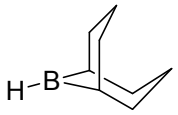


Catalytic Reactions

These reactions were done in a similar fashion and only one is detailed.

Catalyst: *t*Bu_3P

Tri(*t*-butyl)phosphine (1.5 mg, 0.00741 mmol)[2] and $(HBC_8H_{14})_2$ (23 mg, 0.0943 mmol) were dissolved in 0.70 mL of bromobenzene-d_5 in a 20 mL vial. The mixture was stirred and transferred into J-Young tube. The sample was frozen with liquid nitrogen and the atmosphere was replaced with $^{13}CO_2$. The sample was warmed to room temperature to give a pressure of CO_2 of 4 atm.[1] The sample was left at room temperature and monitored by NMR spectroscopy.



4.0 mol% *t*Bu_3P

$^{13}CO_2$, C_6D_5Br, r.t., 15.5 h

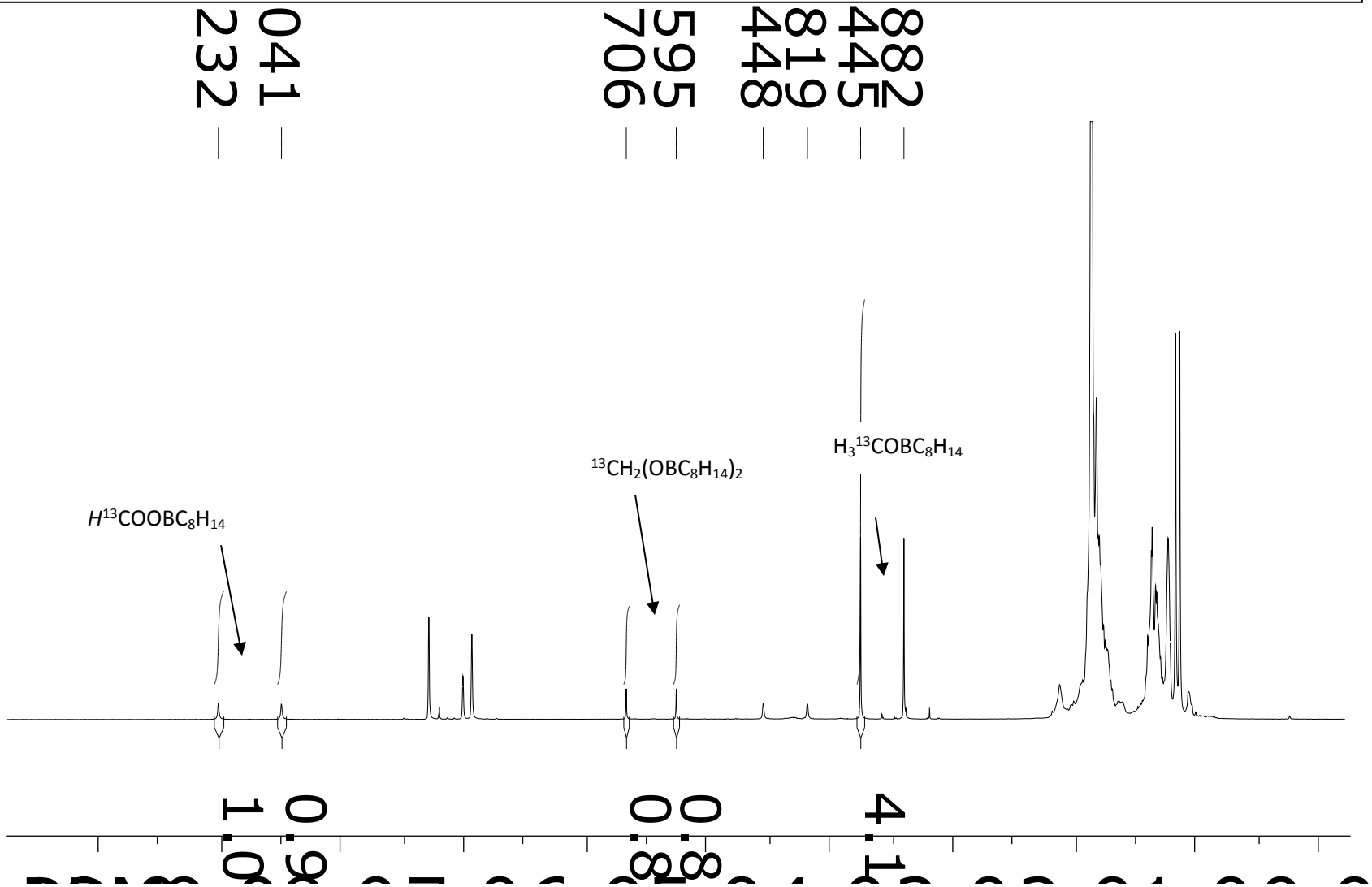
$H^{13}COOBC_8H_{14}$ + $^{13}CH_2(OBC_8H_{14})_2$

tBu_3P-$^{13}CH_2$-$OBC_8H_{14}(OBC_8H_{14})$

$H_3COBC_8H_{14}$ + $C_8H_{14}B$-O-BC_8H_{14}

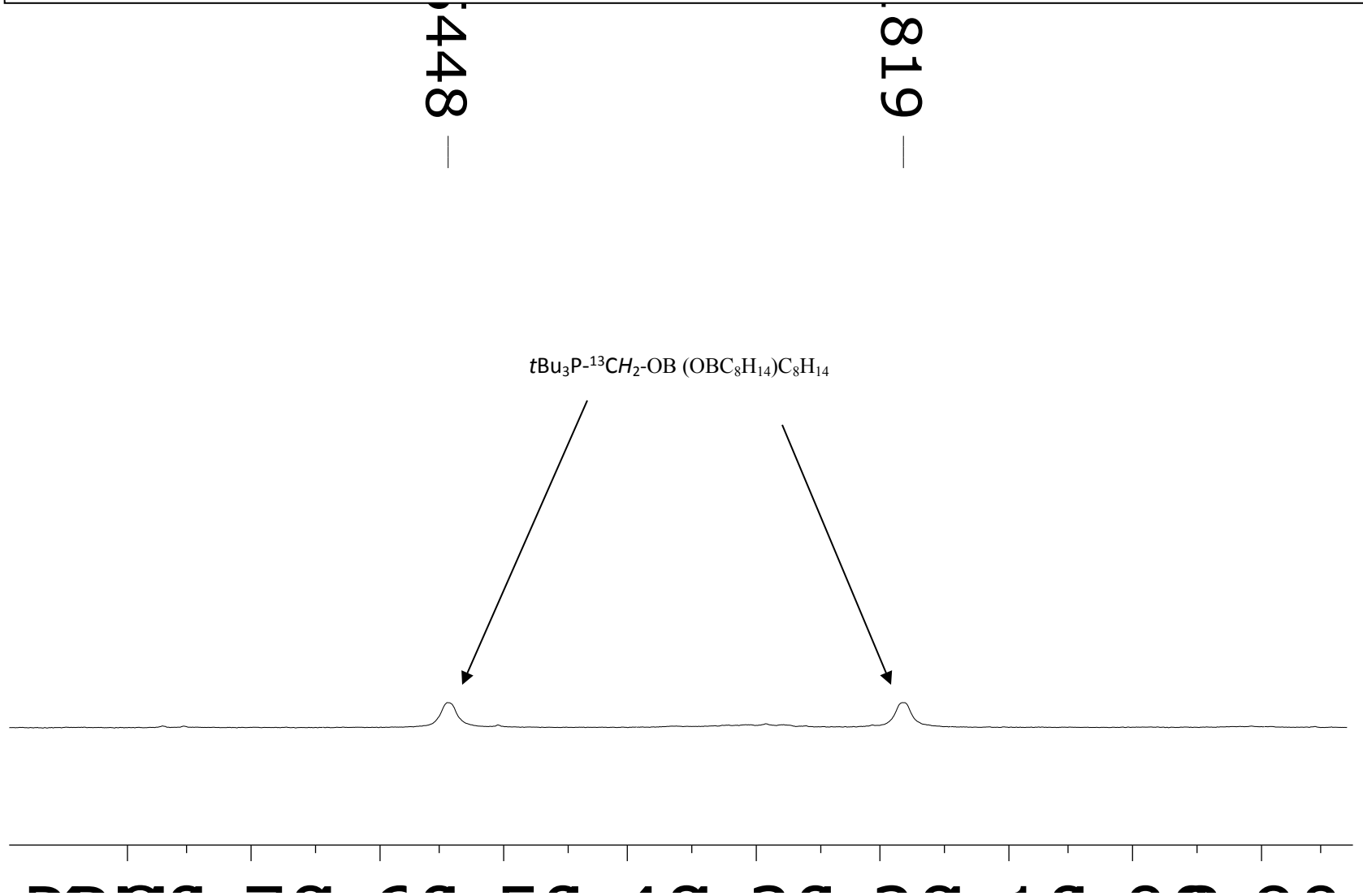
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P*t*Bu$_3$ at room temperature for 15.5 hours in C_6D_5Br

^{1}H NMR spectrum (400M, C_6D_5Br)



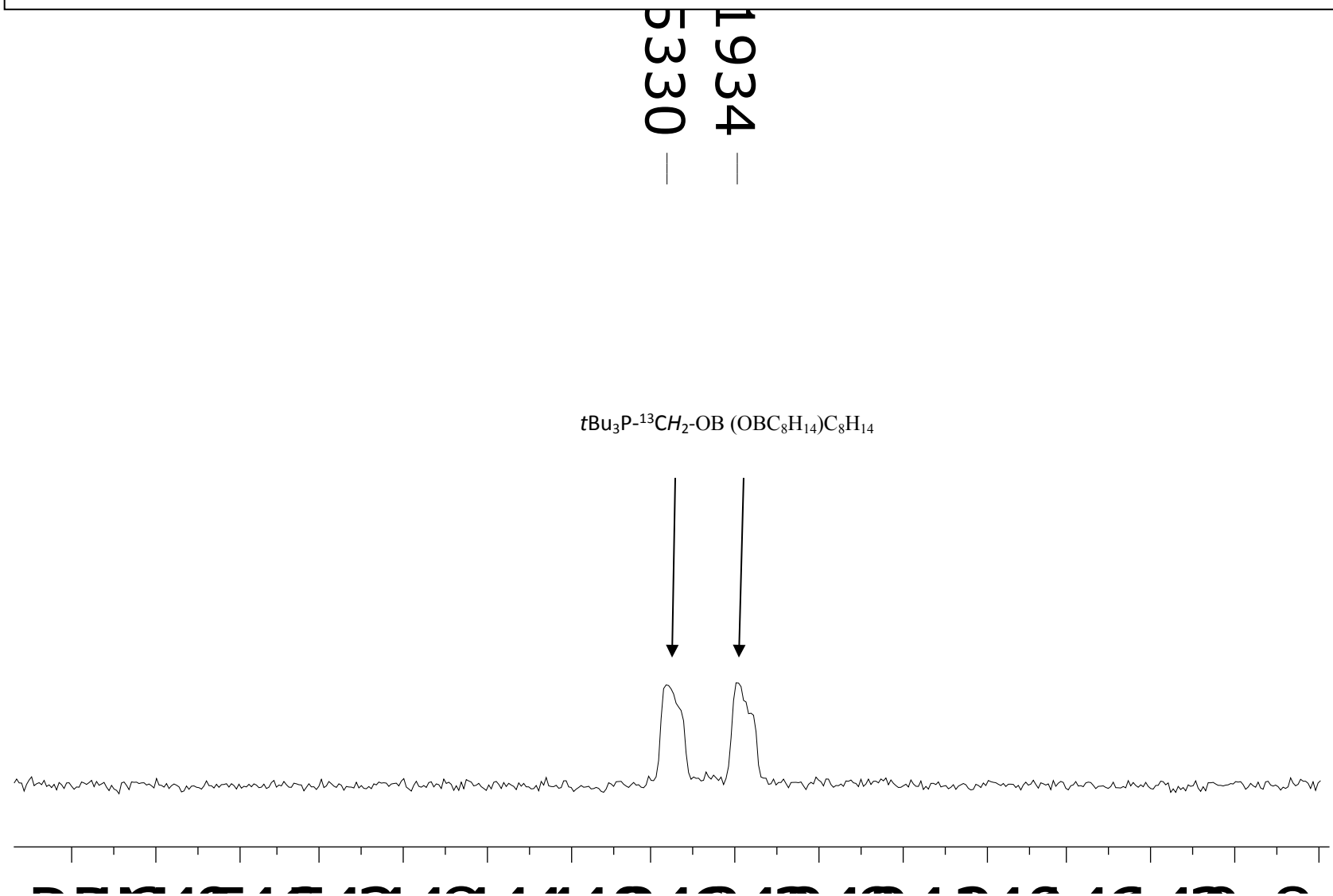
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P*t*Bu$_3$ at room temperature for 15.5 hours in C_6D_5Br

^{1}H NMR spectrum (400M, C_6D_5Br)



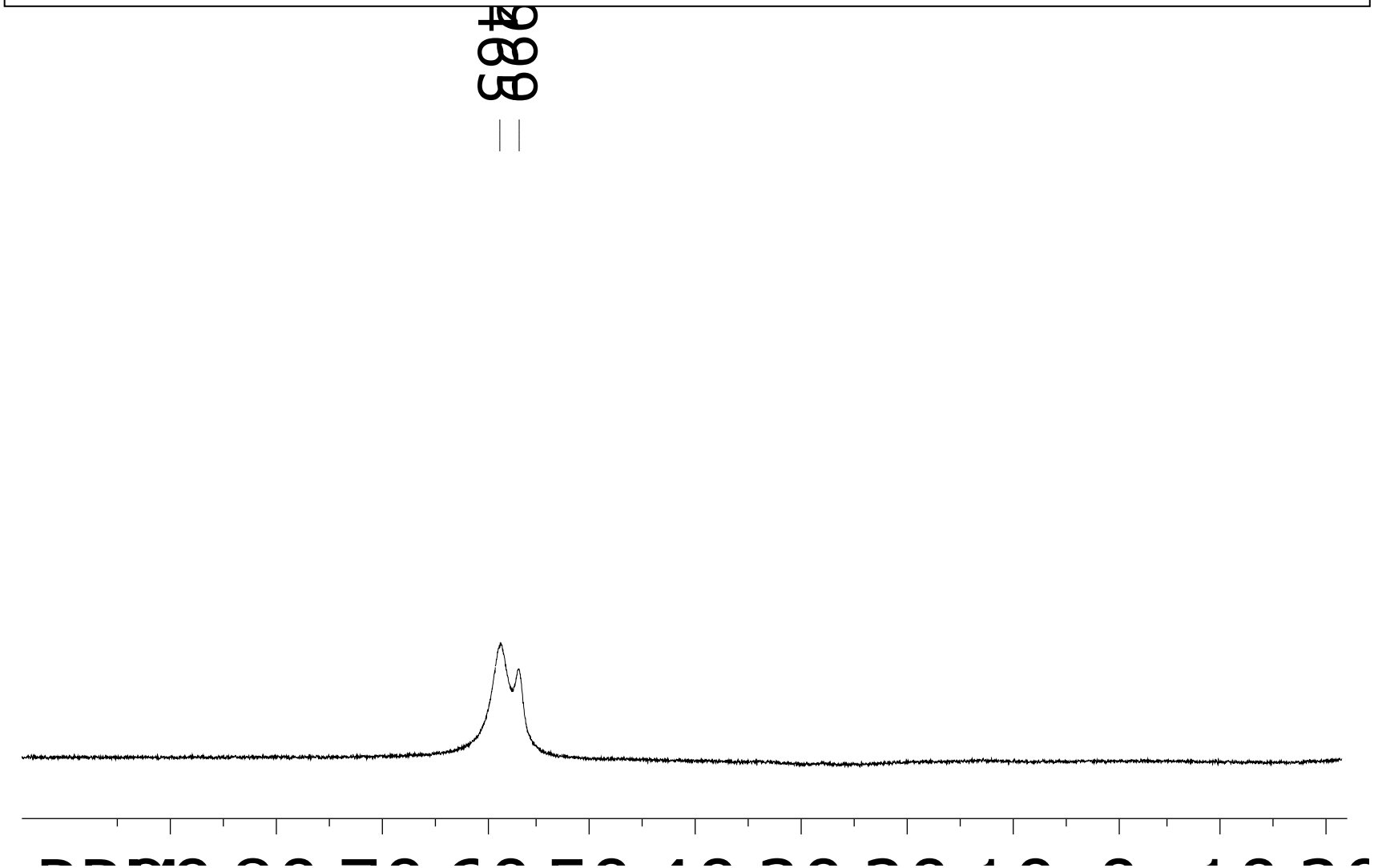
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P*t*Bu$_3$ at room temperature for 15.5 hours in C_6D_5Br

$^{31}P\{^1H\}$ NMR spectrum (162 M, C_6D_5Br)



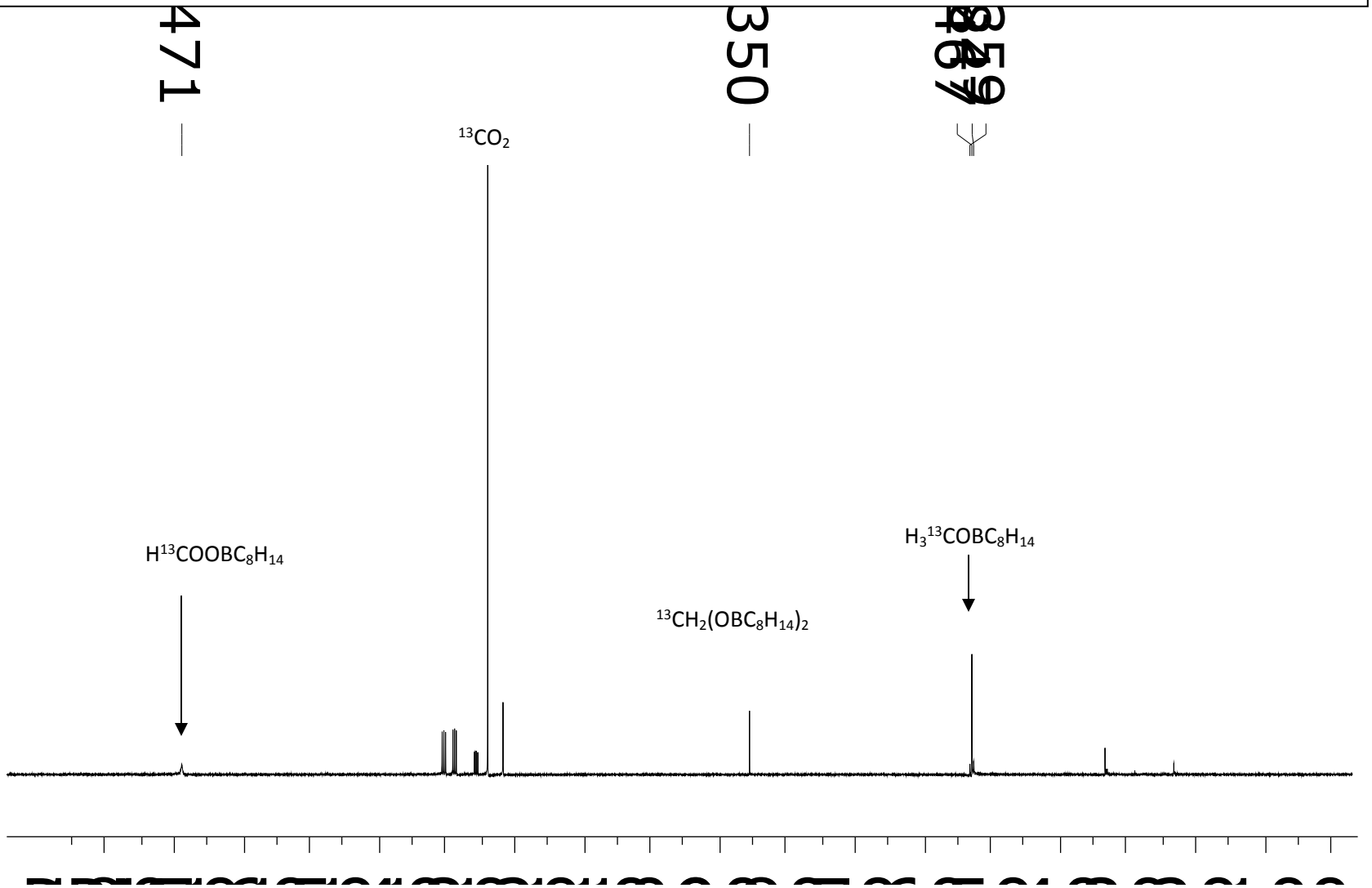
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P*t*Bu$_3$ at room temperature for 15.5 hours in C_6D_5Br

$^{11}B\{^1H\}$ NMR spectrum (128 M, C_6D_5Br)



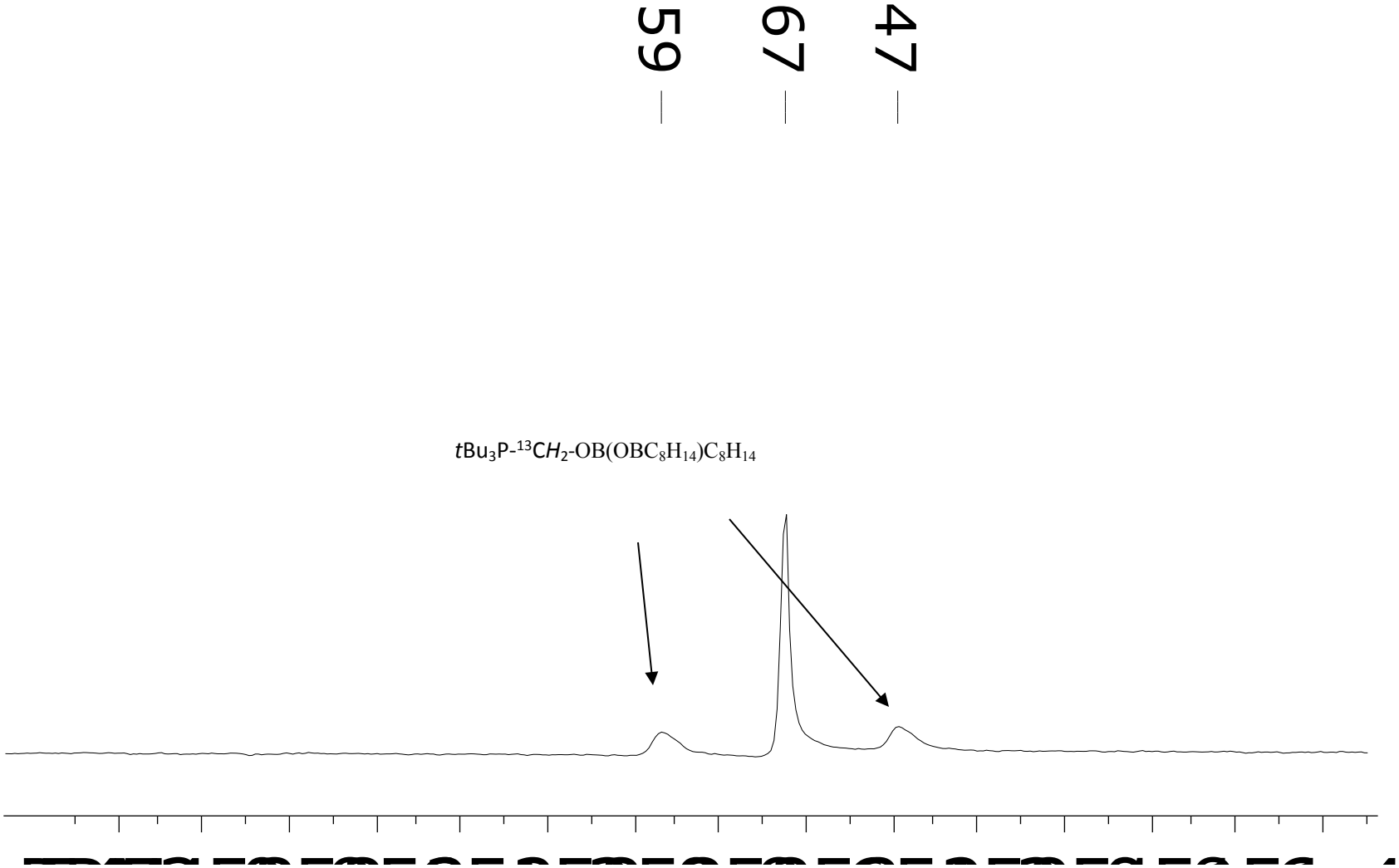
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P*t*Bu$_3$ at room temperature for 15.5 hours in C_6D_5Br

$^{13}C\{^1H\}$ NMR spectrum (100 M, C_6D_5Br)



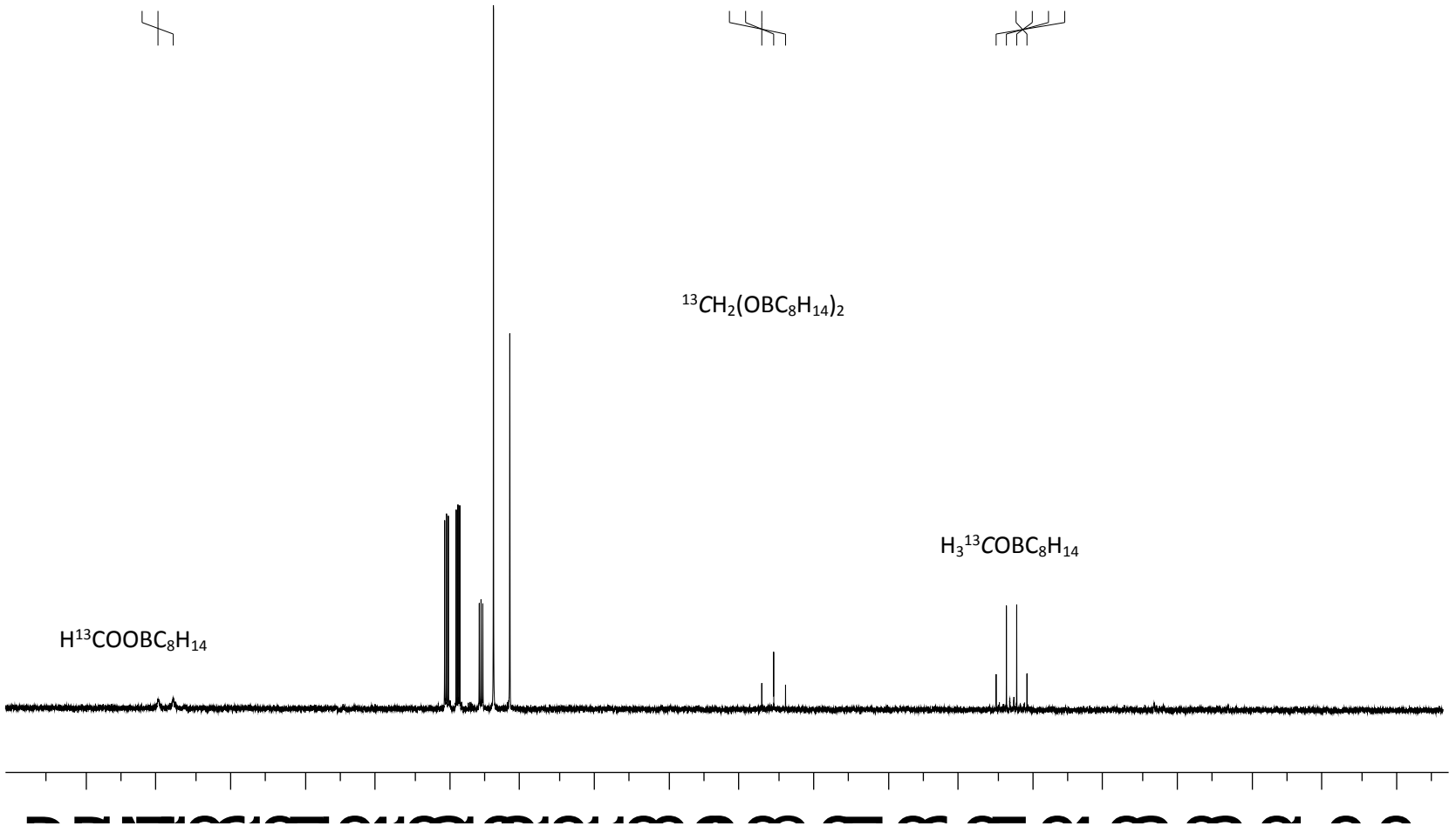
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P*t*Bu$_3$ at room temperature for 15.5 hours in C_6D_5Br

$^{13}C\{^1H\}$ NMR spectrum (100 M, C_6D_5Br)



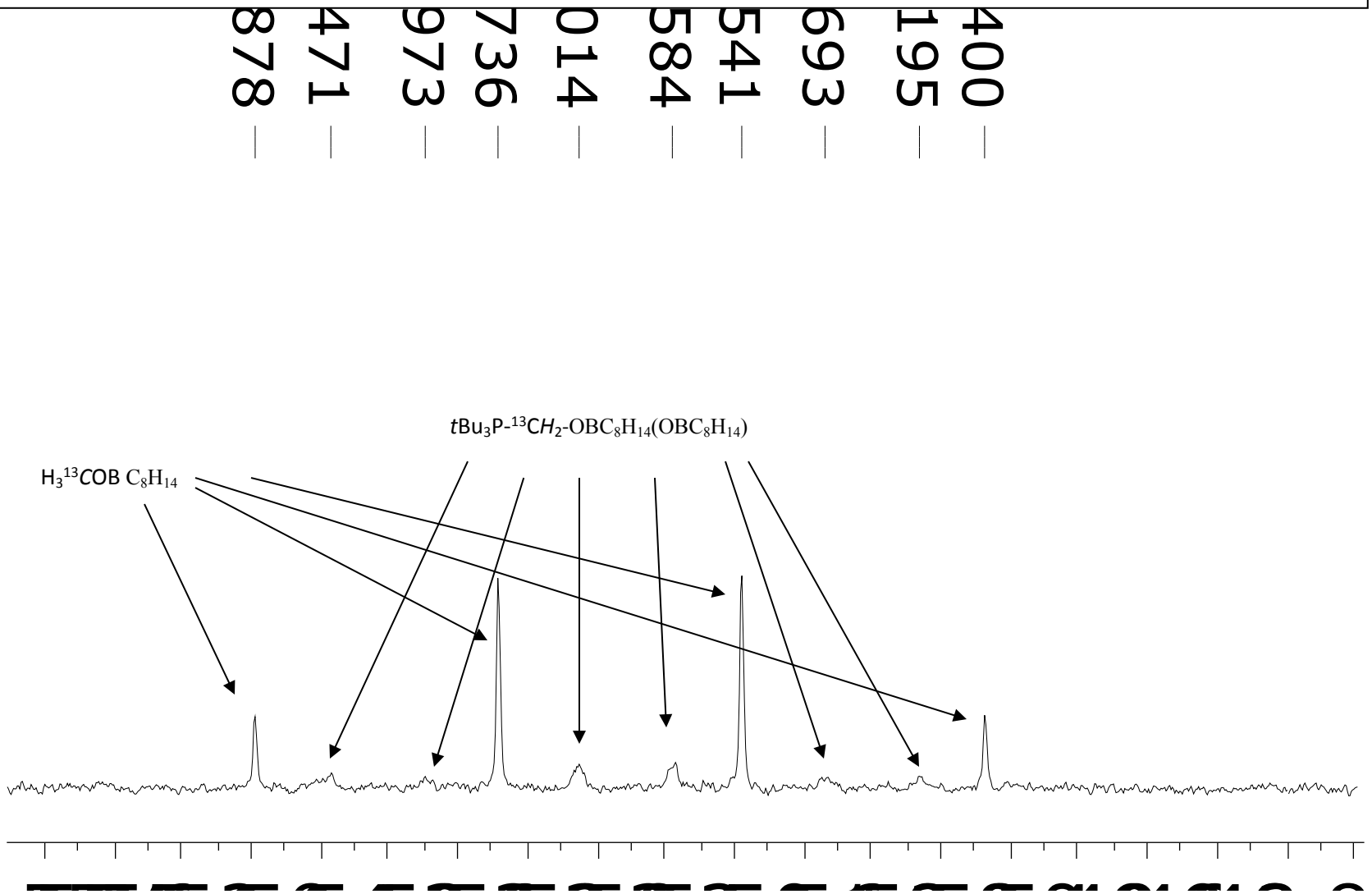
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P*t*Bu$_3$ at room temperature for 15.5 hours in C_6D_5Br

^{13}C NMR spectrum (100 M, C_6D_5Br)



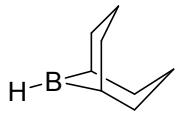
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P*t*Bu$_3$ at room temperature for 15.5 hours in C_6D_5Br

^{13}C NMR spectrum (100 M, C_6D_5Br)



Catalyst: Ph_3P

In a similar fashion triphenylphosphine (2.0 mg, 0.00763 mmol)[3], $(HBC_8H_{14})_2$ (23 mg, 0.0943 mmol) were dissolved in 0.80 mL of bromobenzene-d_5 under a $^{13}CO_2$ atmosphere.



4.0 mol% Ph_3P

$^{13}CO_2$, C_6D_5Br, r.t., 19 h

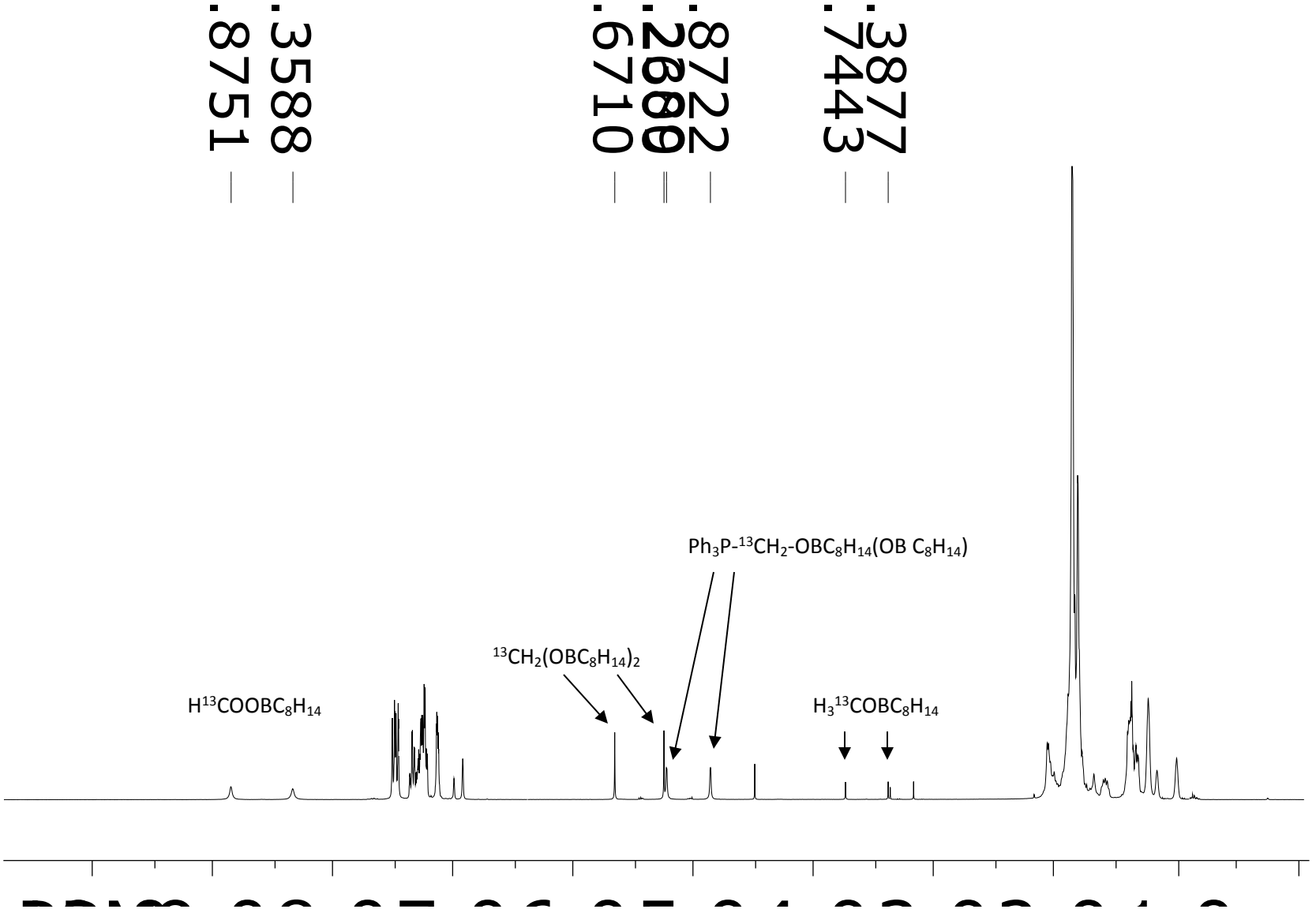
$H^{13}COOBC_8H_{14}$ + $^{13}CH_2(OBC_8H_{14})_2$

Ph_3P-$^{13}CH_2$-$OB(OBC_8H_{14})C_8H_{14}$

$H_3{}^{13}COBC_8H_{14}$ + C_8H_{14}-B-O-BC_8H_{14}

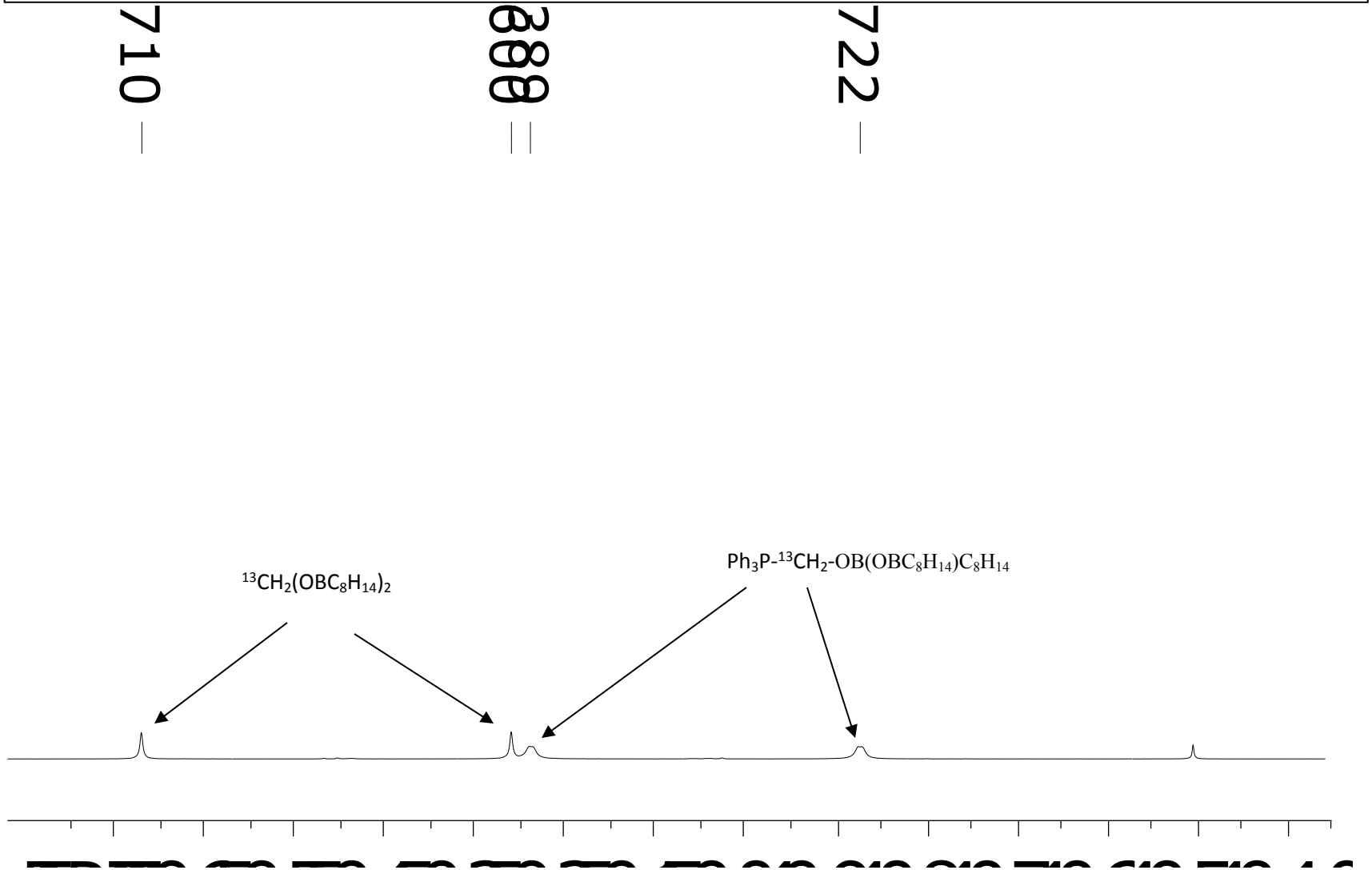
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by PPh_3 at room temperature for 19 hours in C_6D_5Br

^1H NMR spectrum (400M, C_6D_5Br)



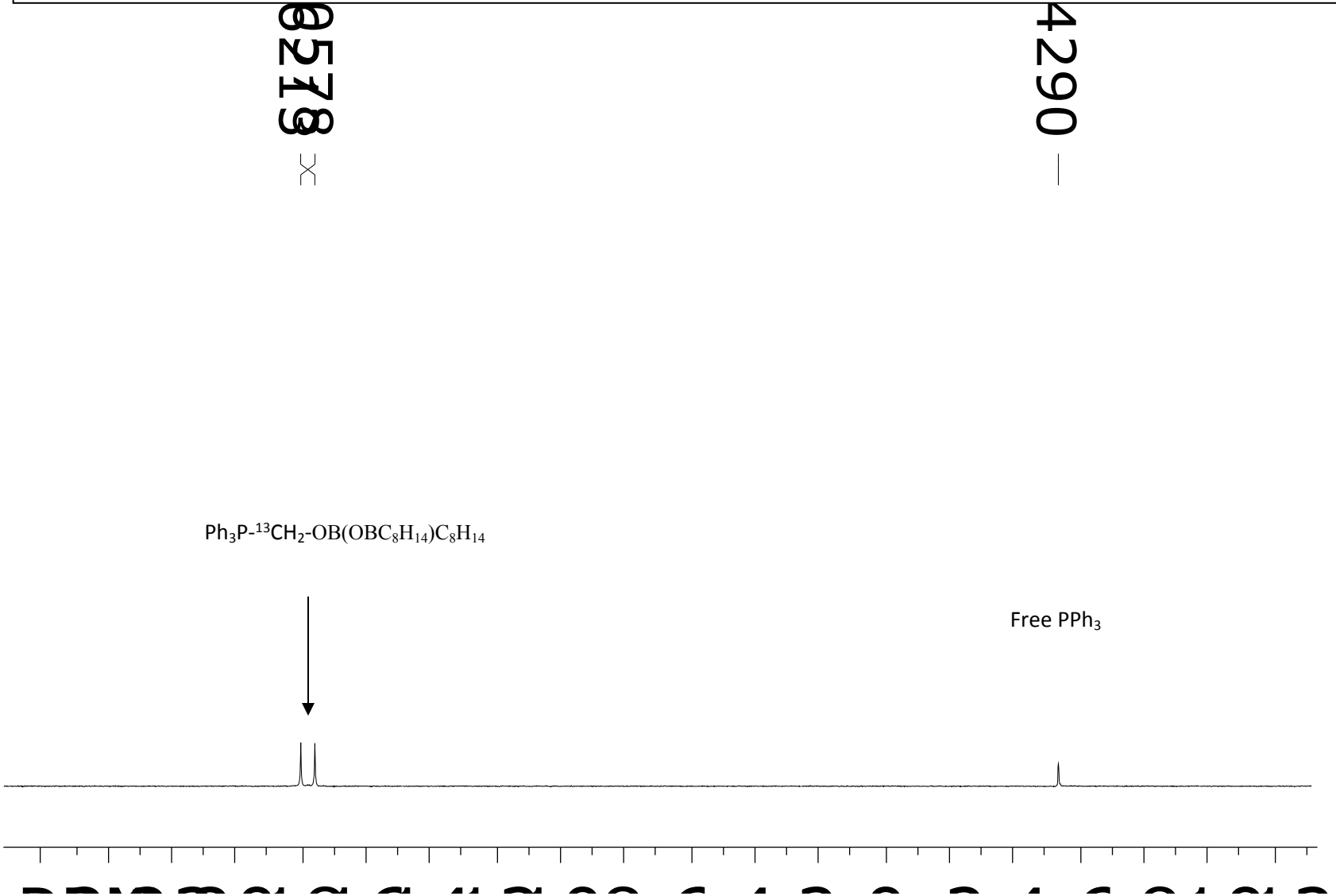
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by PPh_3 at room temperature for 19 hours in C_6D_5Br

^1H NMR spectrum (400M, C_6D_5Br)



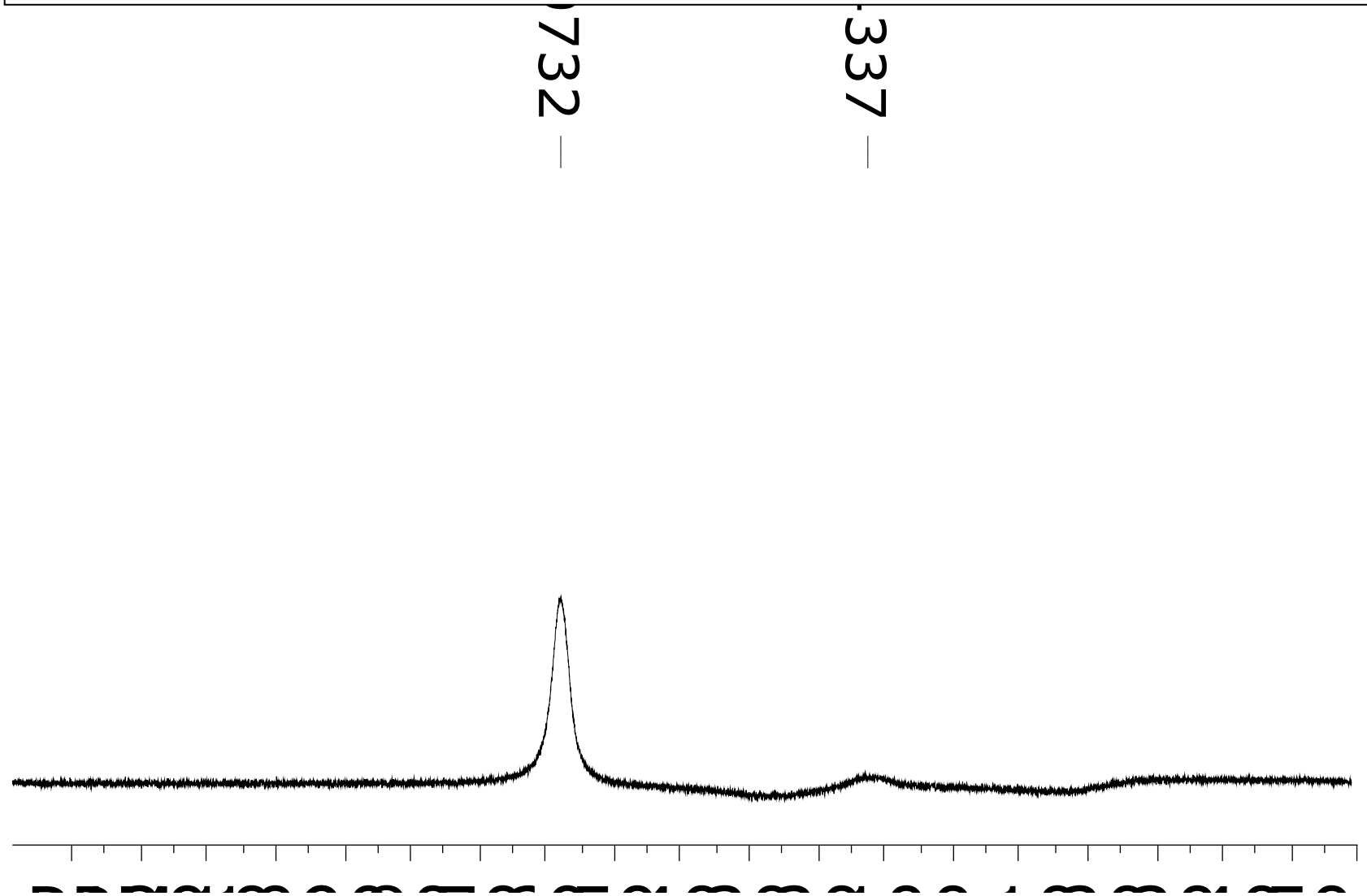
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by PPh_3 at room temperature for 19 hours in C_6D_5Br

$^{31}P\{^1H\}$ NMR spectrum (162 M, C_6D_5Br)



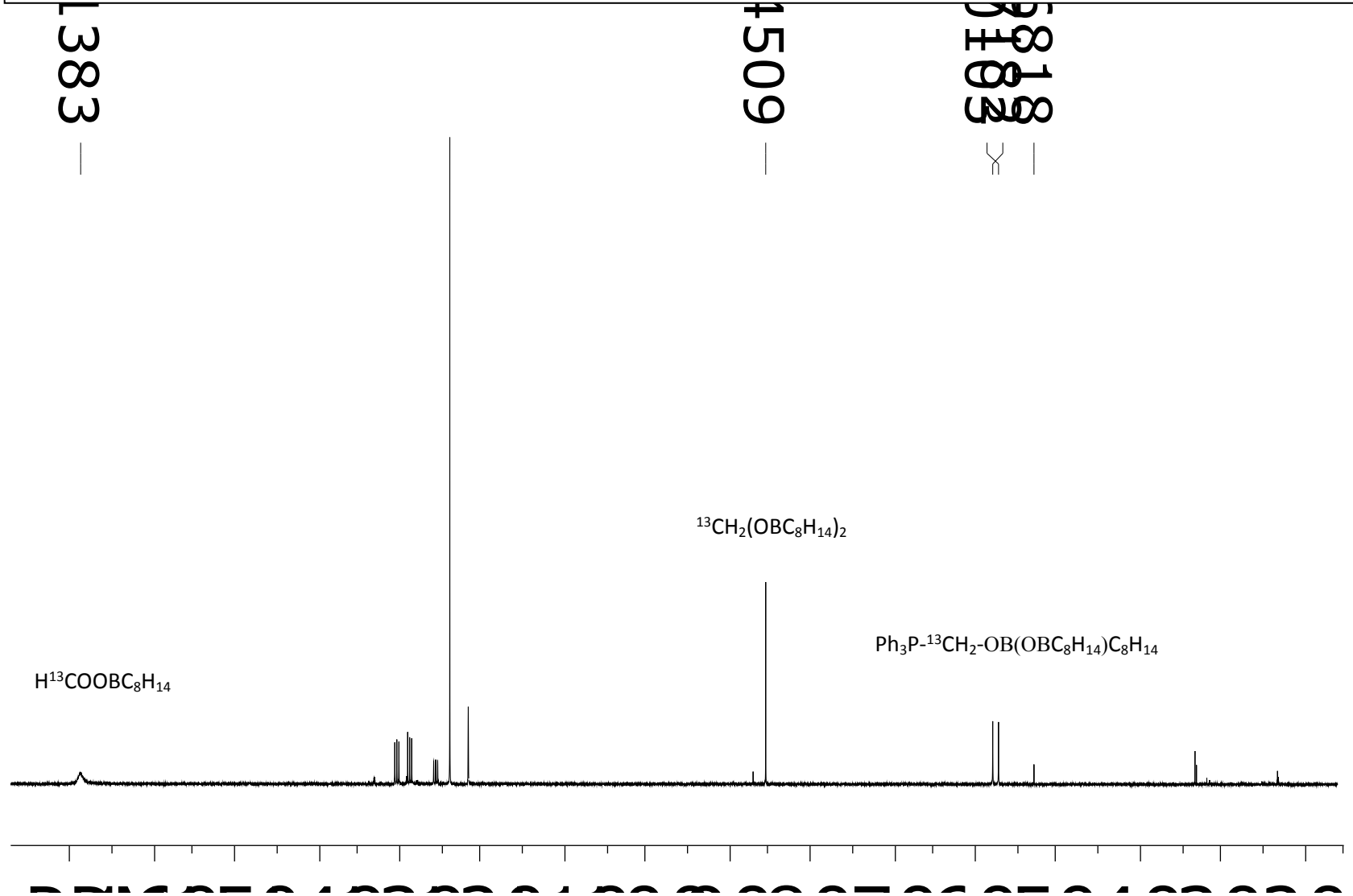
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by PPh_3 at room temperature for 19 hours in C_6D_5Br

$^{11}B\{^1H\}$ NMR spectrum (128 M, C_6D_5Br)



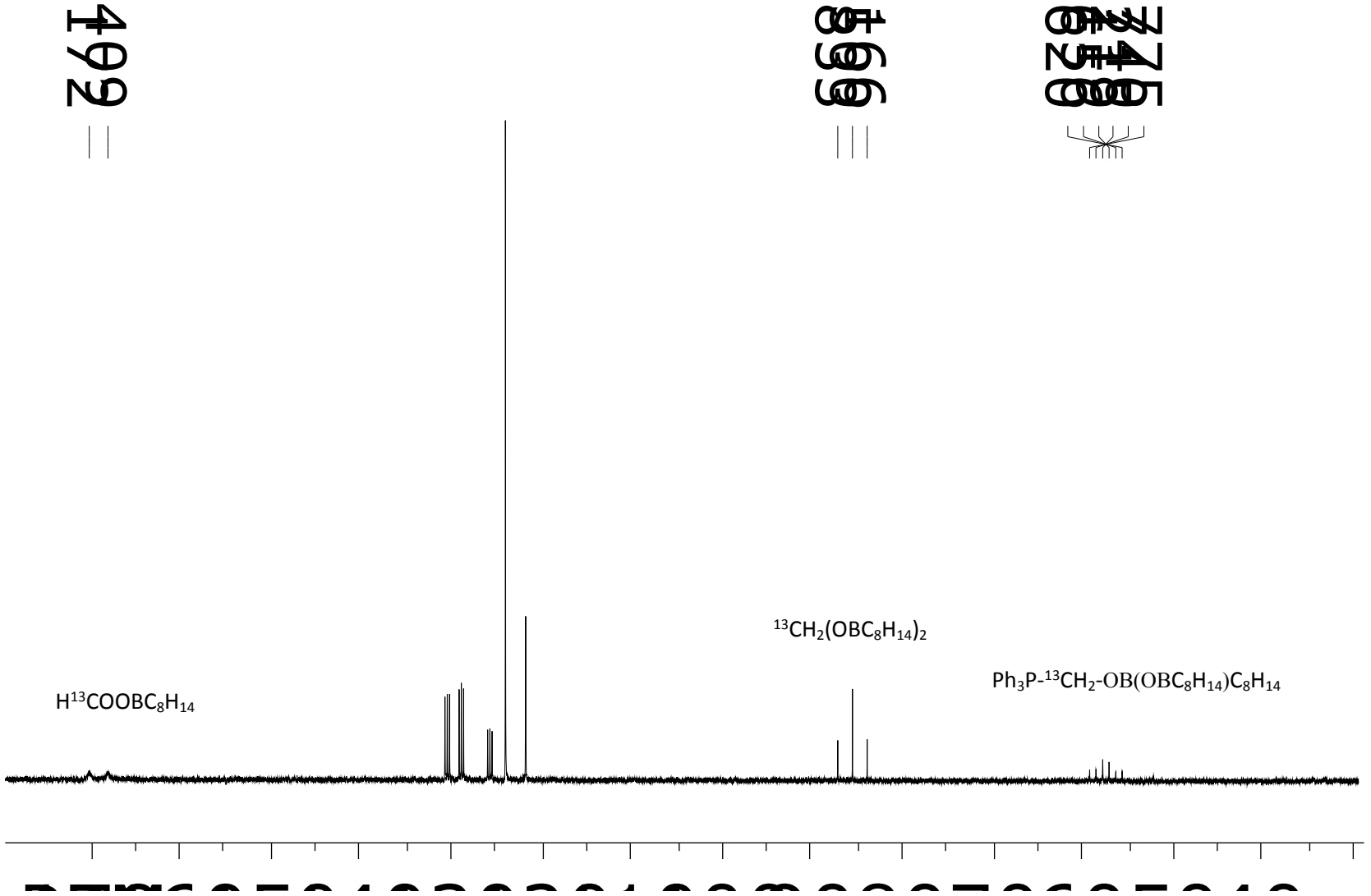
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by PPh_3 at room temperature for 19 hours in C_6D_5Br

$^{13}C\{^1H\}$ NMR spectrum (100 M, C_6D_5Br)



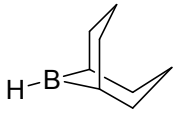
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by PPh_3 at room temperature for 19 hours in C_6D_5Br

^{13}C NMR spectrum with ^{1}H coupling (100 M, C_6D_5Br)



Catalyst: (4-$MeC_6H_4)_3P$

Similarly a solution of $(HBC_8H_{14})_2$ (23 mg, 0.0943 mmol) in 0.70 mL C_6D_5Br was added 0.1 mL of *tri*(4-methylphenyl)phosphine stock solution (0.082 M in C_6D_5Br) in a 20 mL vial was pressured with $^{13}CO_2$. The sample was then warmed up to room temperature and the pressure of CO_2 was 4 atm.[1] The sample was left at room temperature and then monitored by NMR spectroscopy. The reaction was completed in 19 h.



4.3 mol% $(4\text{-MePh})_3P$

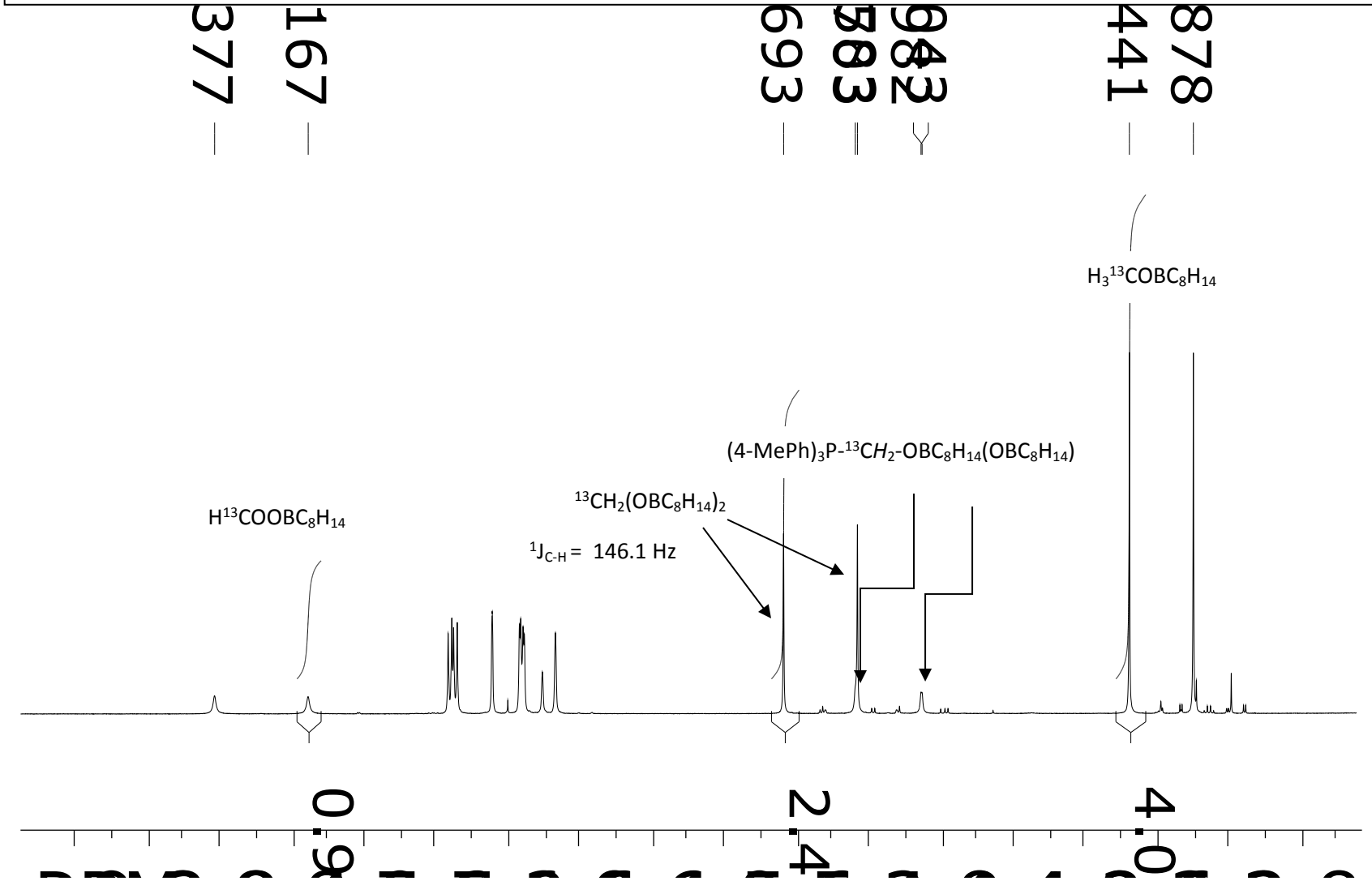
$^{13}CO_2$, C_6D_5Br, r.t., 19 h

$H^{13}COOBC_8H_{14}$ + $^{13}CH_2(OBC_8H_{14})_2$ + $(4\text{-MePh})_3P\text{-}^{13}CH_2\text{-}OBC_8H_{14}(OBC_8H_{14})$

$H_3COBC_8H_{14}$ + $C_8H_{14}B\text{-}O\text{-}BC_8H_{14}$

The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C_6D_5Br

^{1}H NMR spectrum (400M, C_6D_5Br)



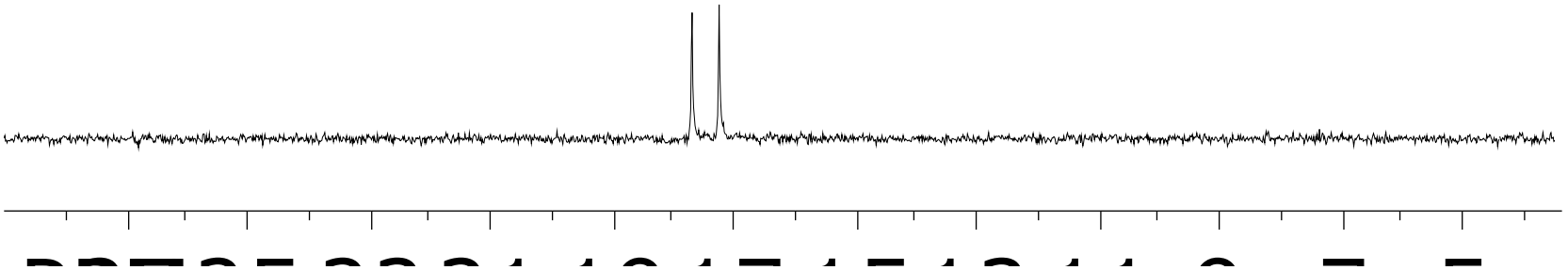
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C_6D_5Br

$^{31}P\{^1H\}$ NMR spectrum (162 M, C_6D_5Br)

96.1

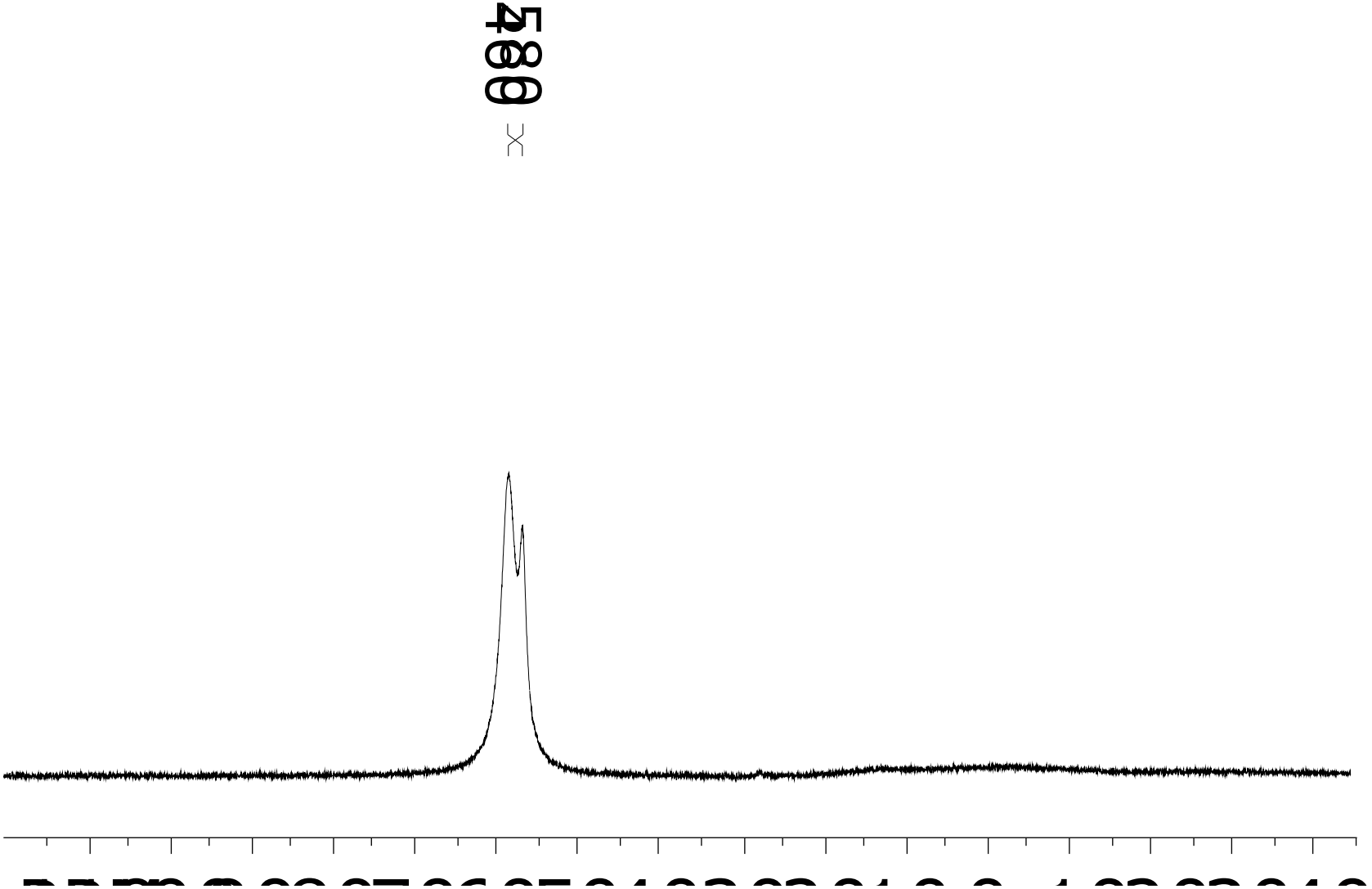
Ph_3P-$^{13}CH_2$-OBC_8H_{14} (OBC_8H_{14})

$^1J_{C\text{-}P}$ = 72.7 Hz



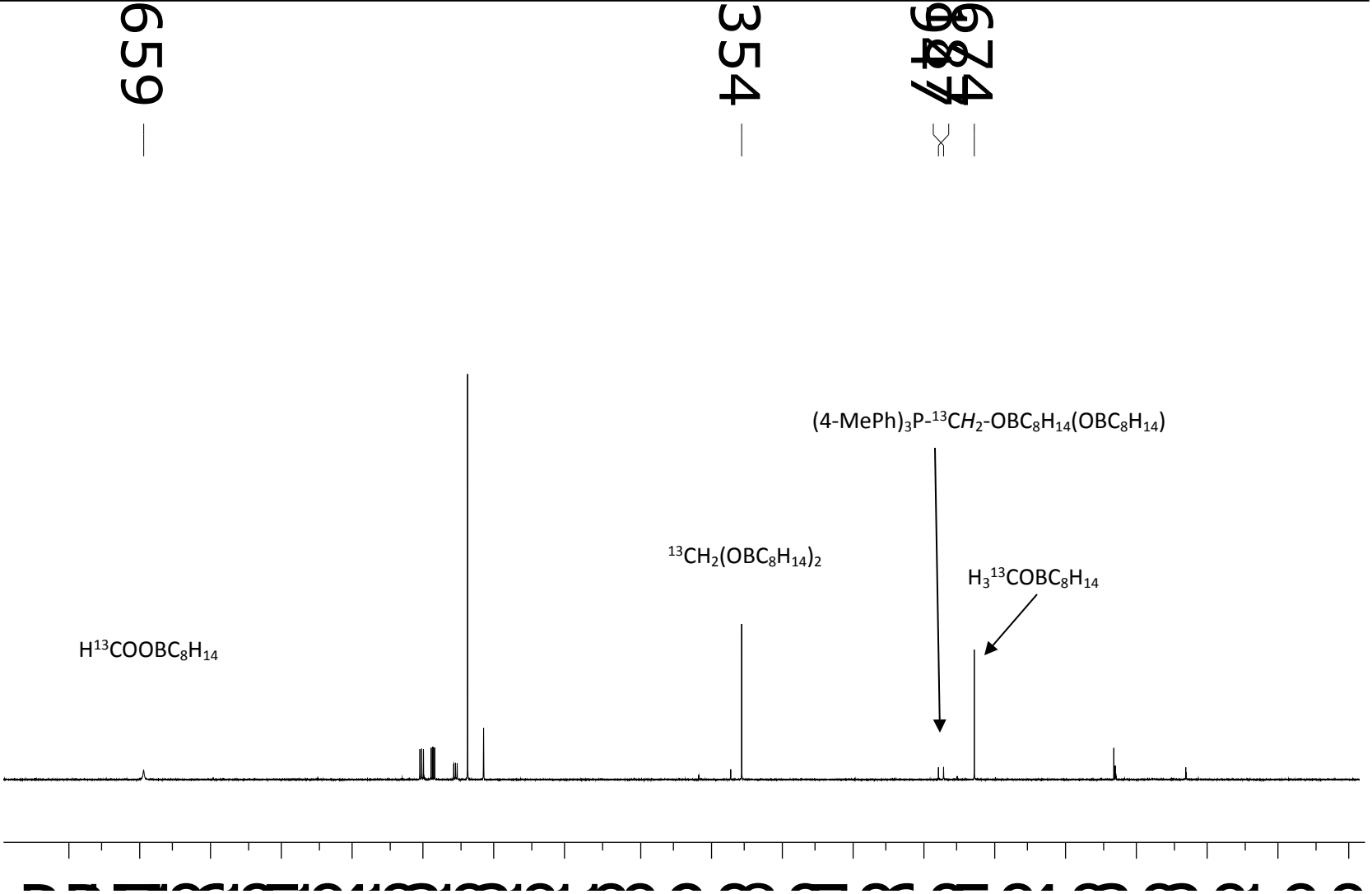
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C_6D_5Br

$^{11}B\{^1H\}$ NMR spectrum (128 M, C_6D_5Br)



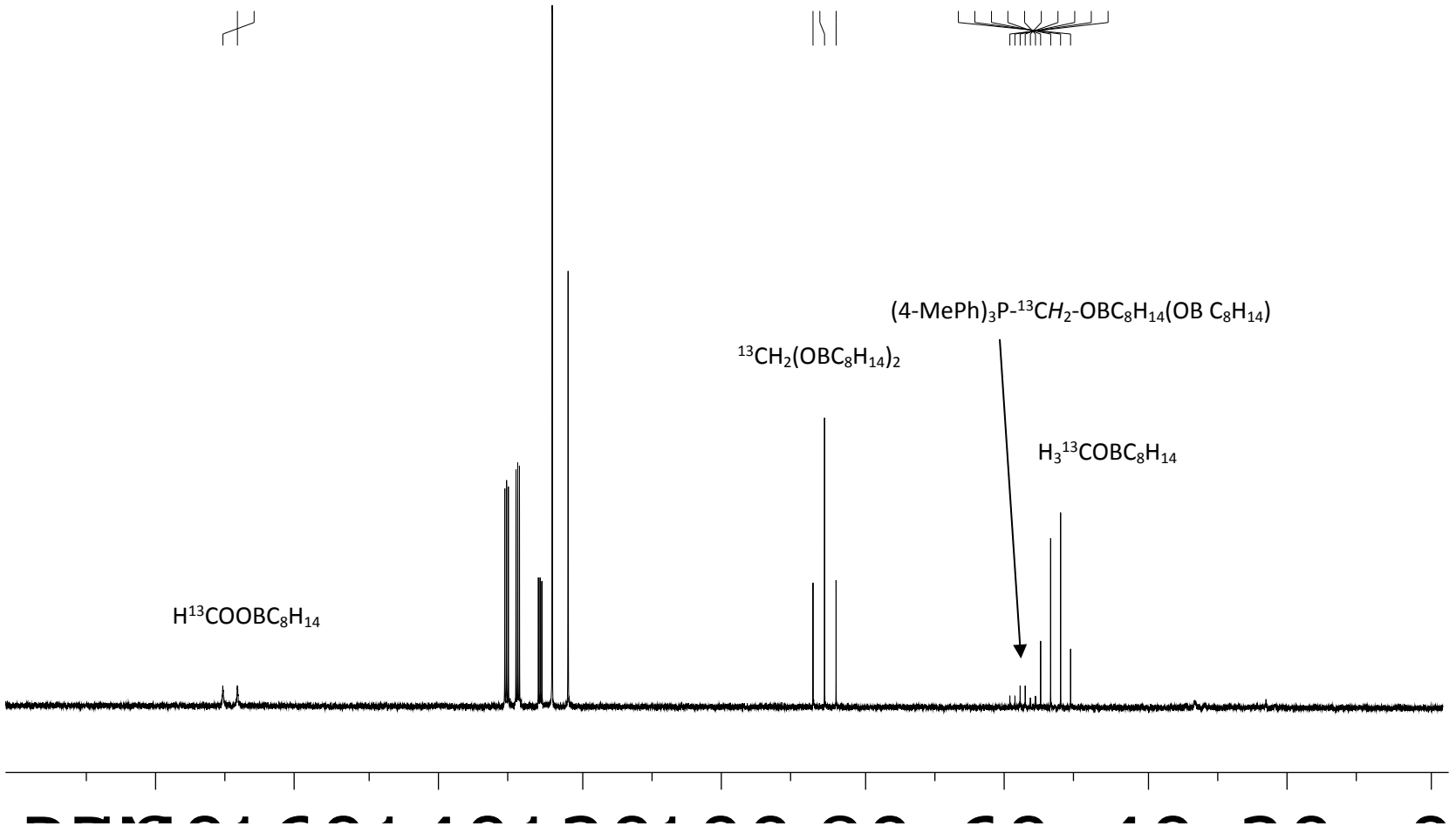
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C_6D_5Br

$^{13}C\{^1H\}$ NMR spectrum (100M, C_6D_5Br)



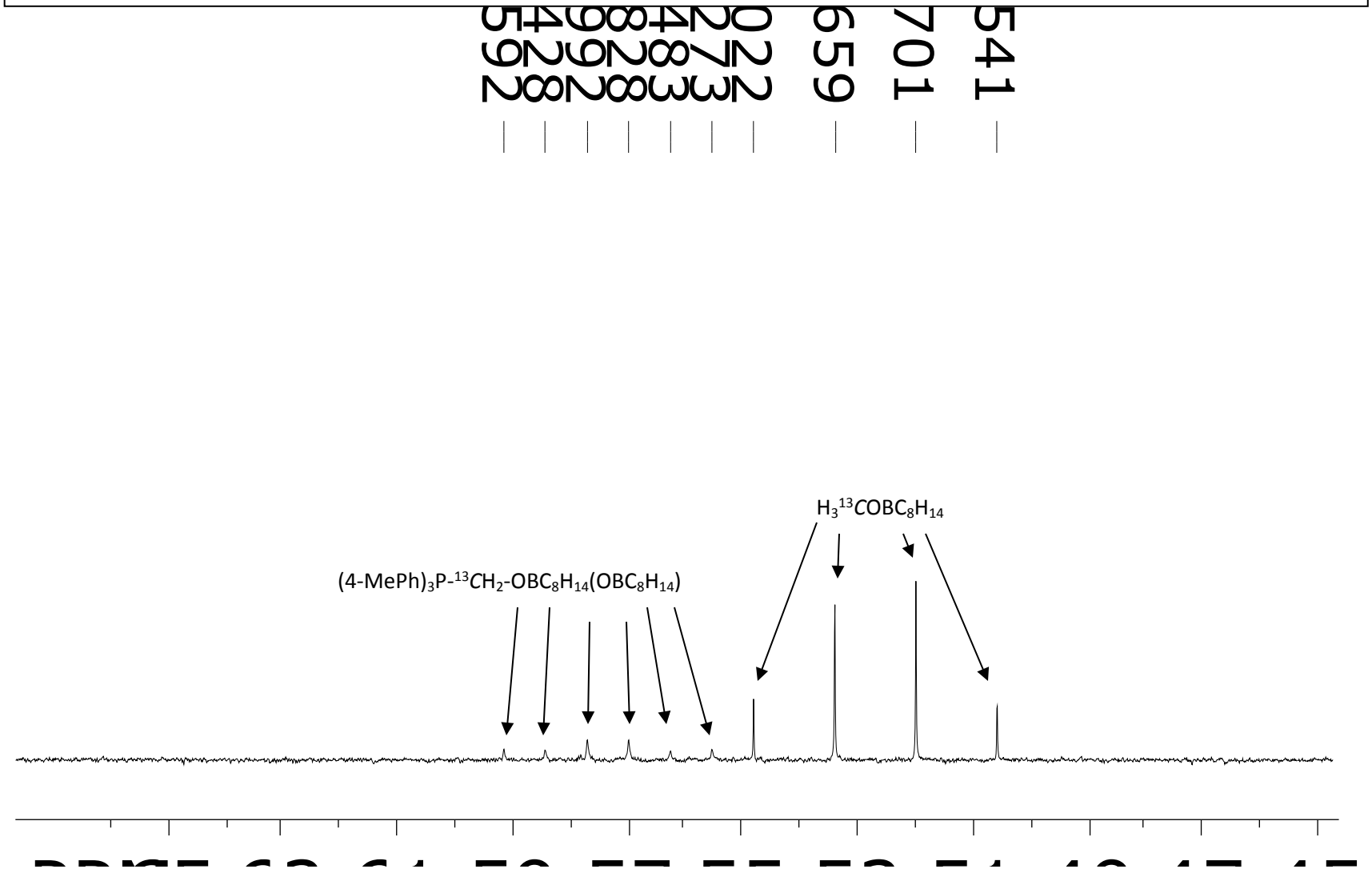
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C_6D_5Br

^{13}C NMR spectrum (100M, C_6D_5Br)



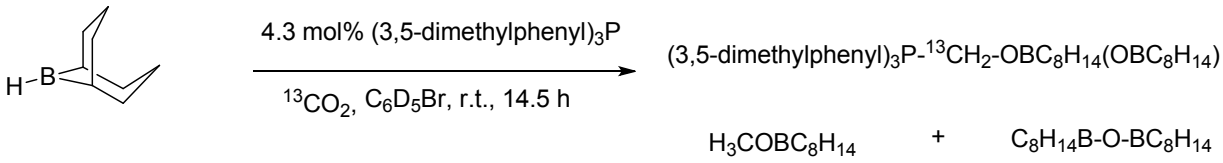
The reaction between 9-BBN dimer and $^{13}CO_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C_6D_5Br

^{13}C NMR spectrum (100M, C_6D_5Br)



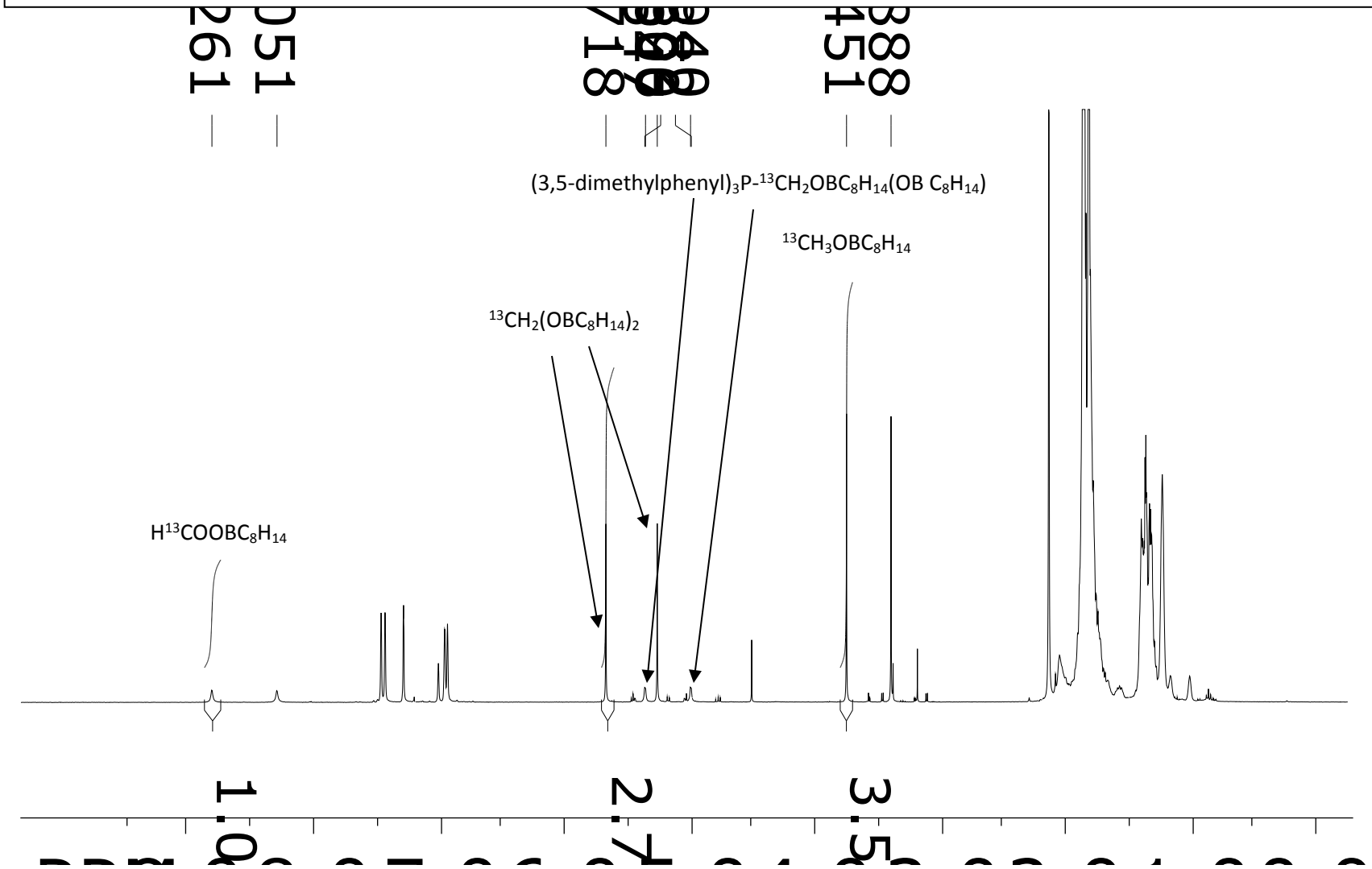
Catalyst: (3,5 $Me_2C_6H_3)_3P$

Performed as above using $(HBC_8H_{14})_2$ (23 mg, 0.0943mmol) and 0.10 mL *tri*(3,5-dimethylphenyl)phosphine stock solution (0.082 M in C_6D_5Br) under $^{13}CO_2$. The sample was then warmed up to room temperature and the pressure of CO_2 was 4 atm.[1] The sample was left at room temperature and monitored by NMR spectroscopy. The reaction was completed in 14.5 h.



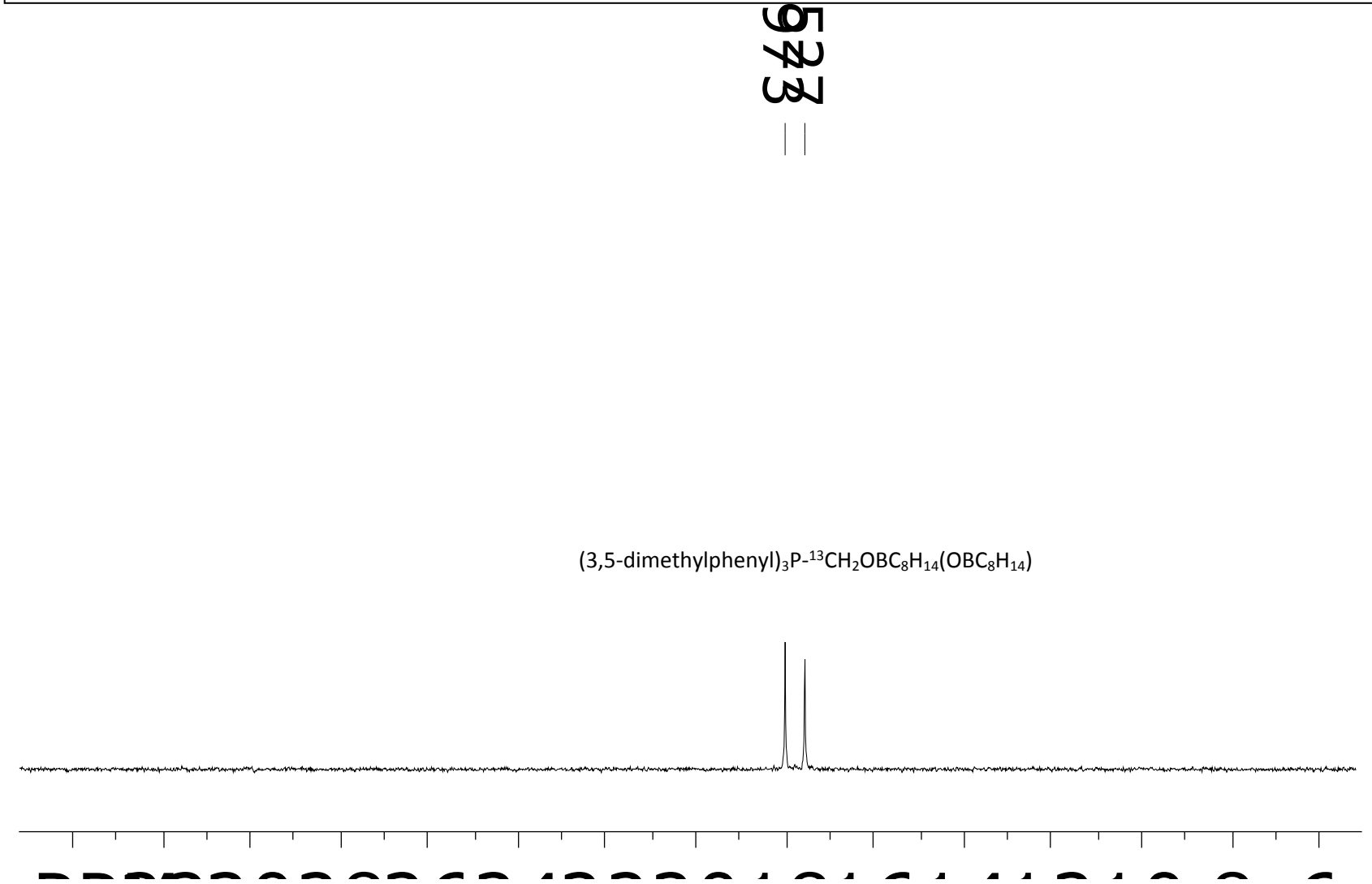
The catalytic reaction between and 9-BBN dimer and $^{13}CO_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in C_6D_5Br

^{1}H NMR spectrum (400 M, C_6D_5Br)



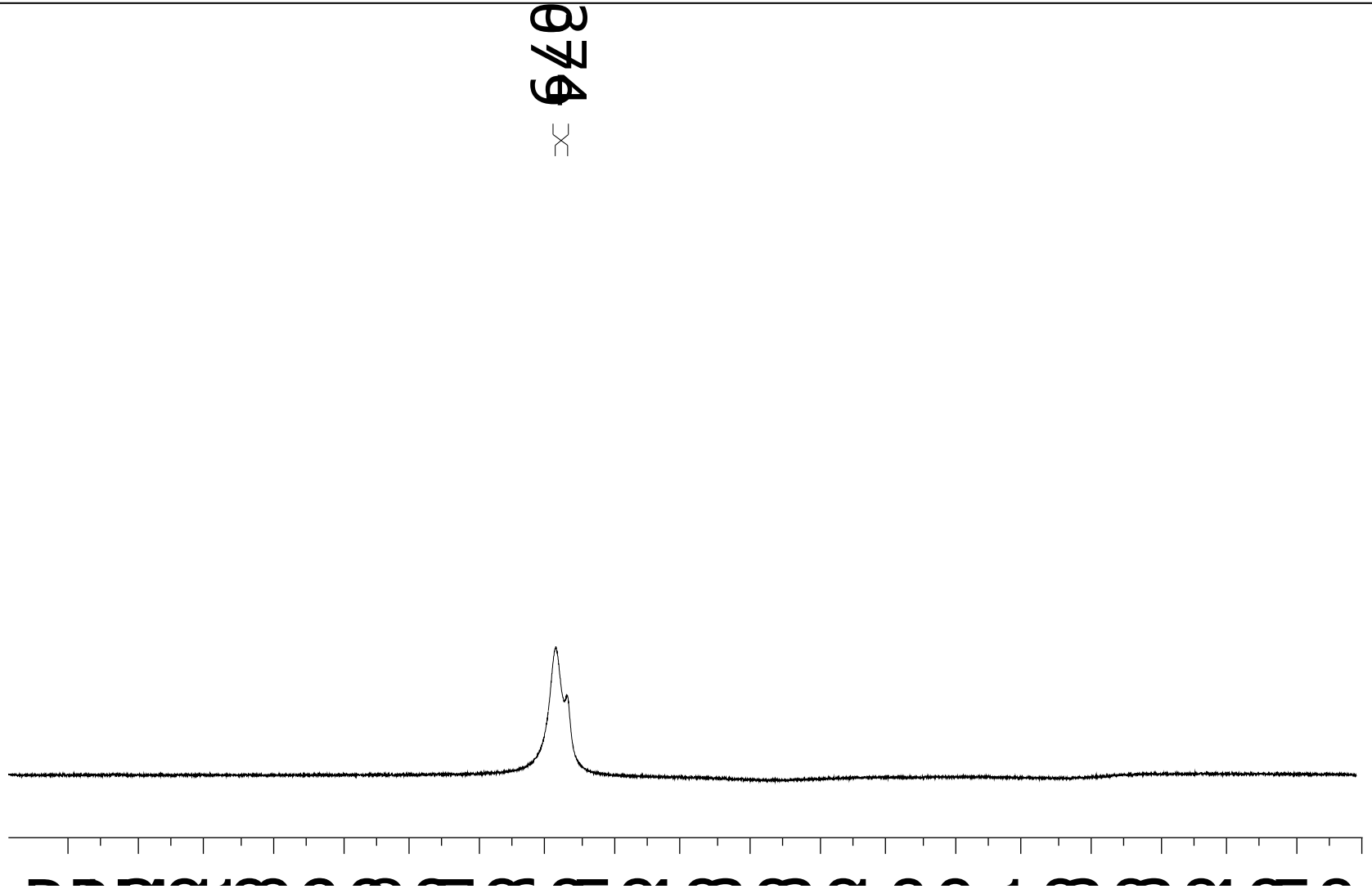
The catalytic reaction between and 9-BBN dimer and $^{13}CO_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in C_6D_5Br

^{31}P NMR spectrum (162 M, C_6D_5Br)



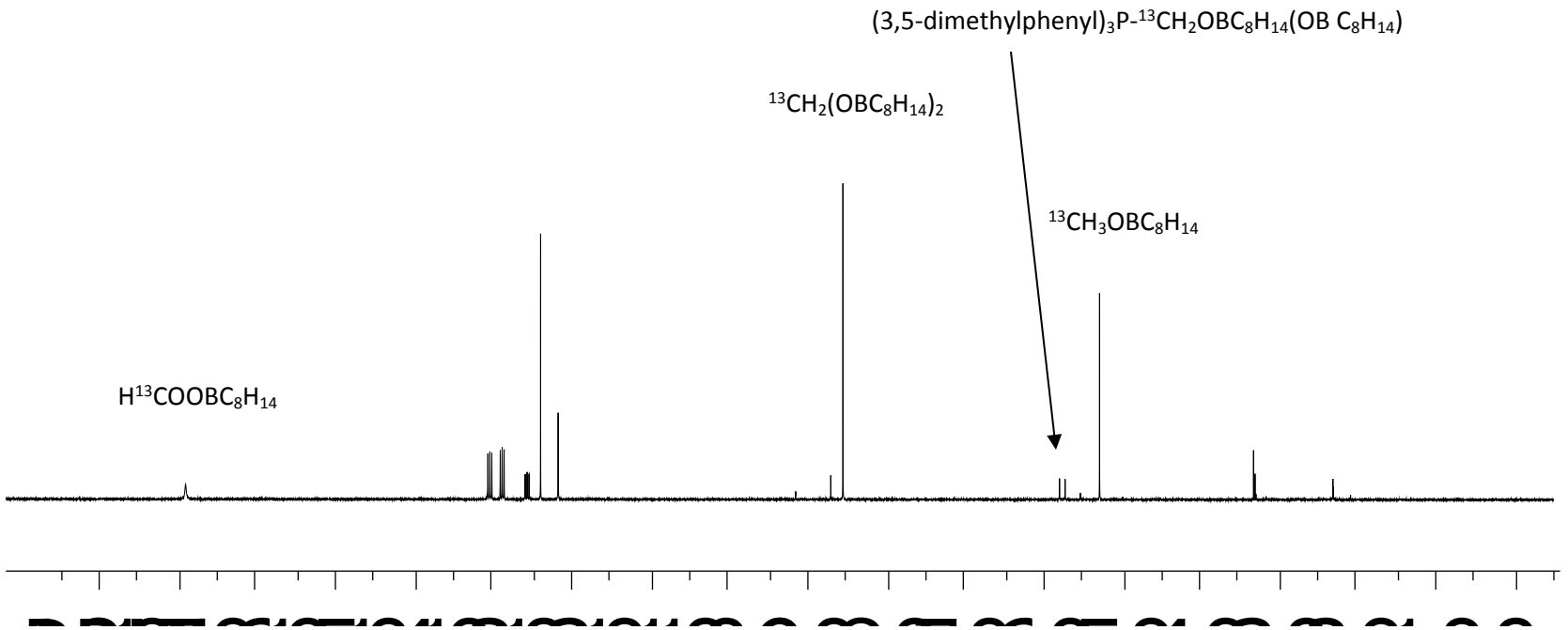
The catalytic reaction between and 9-BBN dimer and $^{13}CO_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in C_6D_5Br

^{11}B NMR spectrum (128 M, C_6D_5Br)



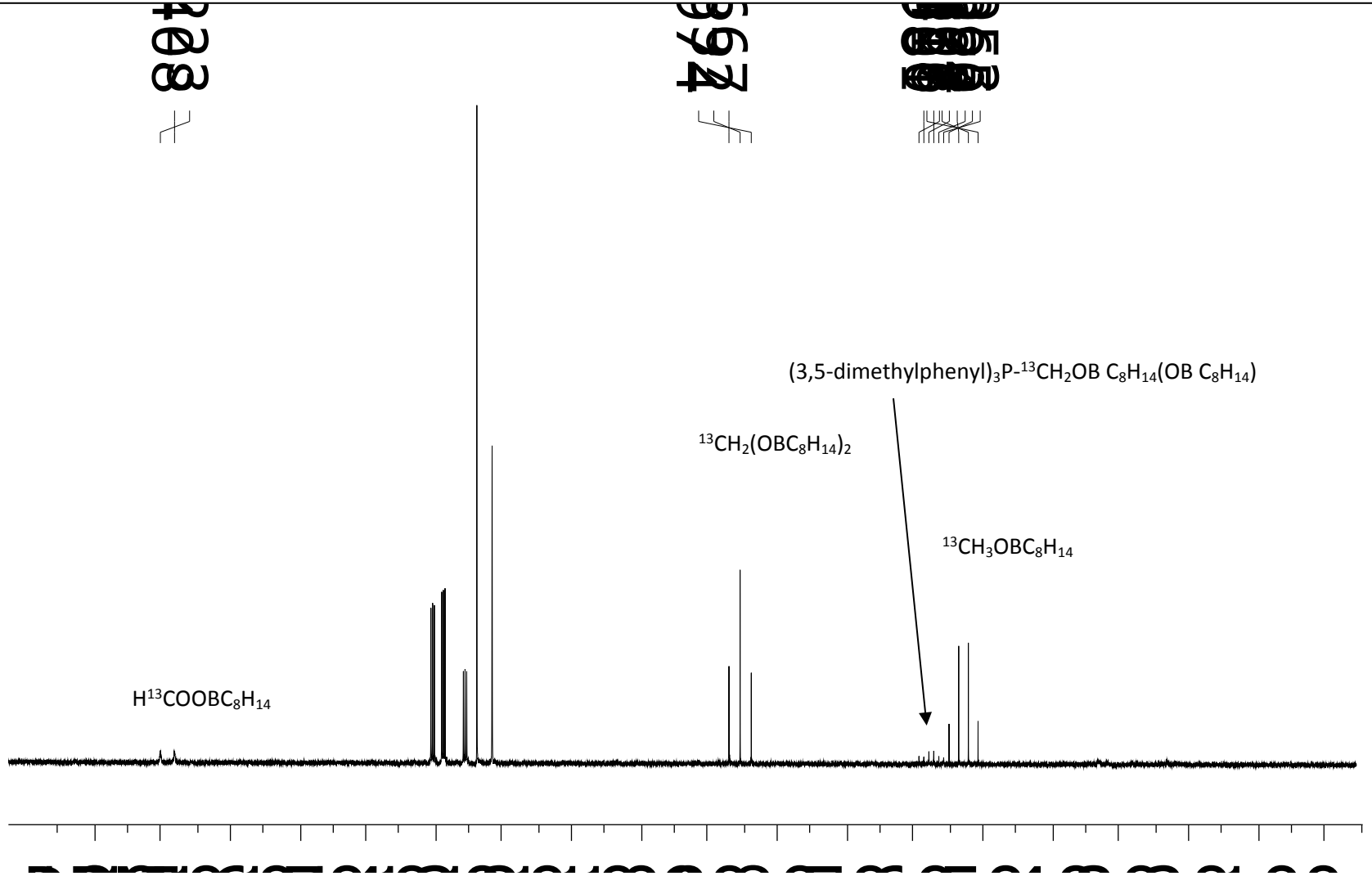
The catalytic reaction between and 9-BBN dimer and $^{13}CO_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in C_6D_5Br

$^{13}C\{^1H\}$ NMR spectrum (100 M, C_6D_5Br)



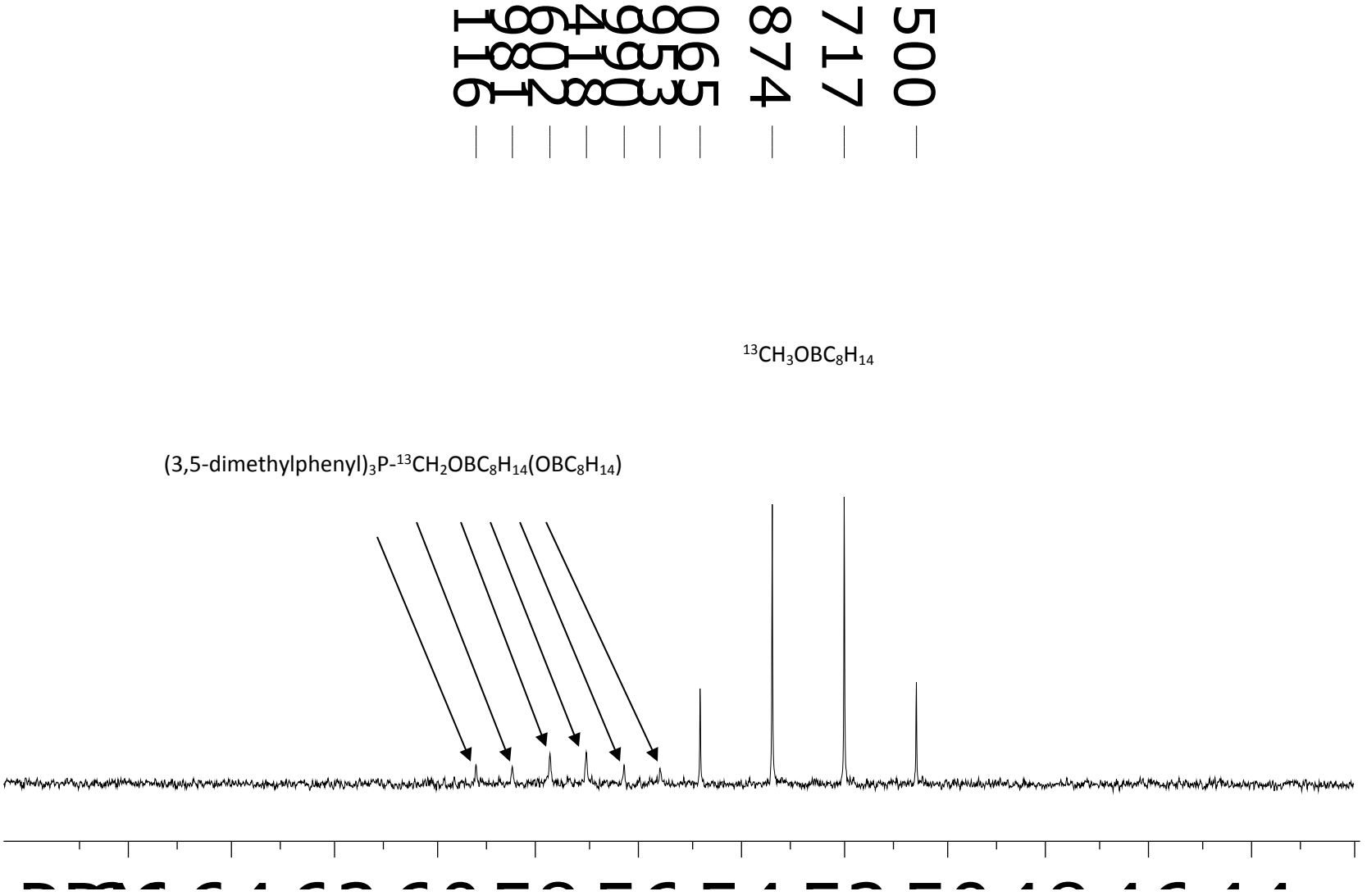
The catalytic reaction between and 9-BBN dimer and $^{13}CO_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in C_6D_5Br

$^{13}C\{^1H\}$ NMR spectrum (100 M, C_6D_5Br)



The catalytic reaction between and 9-BBN dimer and $^{13}CO_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in C_6D_5Br

$^{13}C\{^1H\}$ NMR spectrum (100 M, C_6D_5Br)



Larger scale and Lower Catalyst loardings:

The vial with $(HBC_8H_{14})_2$ (100 mg, 0.410 mmol) and PR_3 (1.0 mol% P*t*Bu_3; 1.0 mol% PPh_3; 1.0 mol% P(4-MethylPhenyl)$_3$, based on the amount of H-BC_8H_{14}) was added with 1.1 mL of C_6D_5Br. The mixture was stirred till all (HBC_8H_{14}) was dissolved before it was transferred into J-Young tube which was then tightened with Teflon cap. The sample was treated by frozen and atmosphere replaced with $^{13}CO_2$. The sample was then warmed to room temperature affording a CO_2 pressure of 5.3 atm.[1] The reactions were monitored by ^1H, ^{31}P, ^{11}B and ^{13}C NMR spectroscopy. When all $(HBC_8H_{14})_2$ was consumed after 35-36 h at room temperature, $^{13}CO_2$ was released and another 100 mg (HBC_8H_{14}) was added to the sample. The samples were left at room temperature for another one day, finding that MeO-BC_8H_{14} was the major product (96-98%) and the minor product is $CH_2(OC_8H_{14})_2$.

Table S1. The reaction with additonal (HBC_8H_{14}) to convert formate and $CH_2(OC_8H_{14})_2$ to methoxyl product

Catalysts/Time	Formate	$CH_2(OC_8H_{14})_2$	$MeOC_8H_{14}$
tBu_3P/35 h	0	2	98
Ph_3P/36 h	0	4	96
(4-MePh)$_3$P/36 h	0	2	98

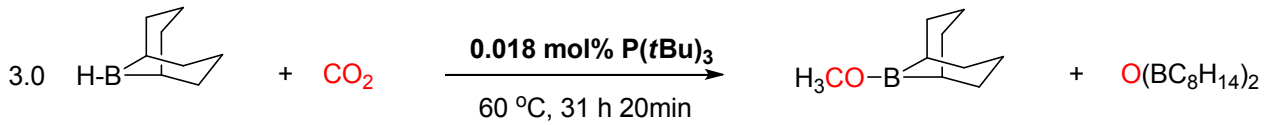
0.24 mol% P*t*Bu_3 catalyzed reduction of CO_2 with (HBC_8H_{14}) at room temperature

The vial with $(HBC_8H_{14})_2$ (100 mg, 0.410 mmol) and 0.10 mL P*t*Bu_3 stock solution (0.0198 M)[4] was added with 1.00 mL of C_6D_5Br. The mixture was stirred till all $(HBC_8H_{14})_2$ was dissolved before it was transferred into J-Young tube which was then tightened with Teflon cap. The sample was treated by frozen and atmosphere replaced with $^{13}CO_2$. The sample was then warmed to room temperature affording a CO_2 pressure of 5.3 atm.[1] The reactions were monitored by ^1H, ^{31}P, ^{11}B and ^{13}C NMR spectroscopy at 1.5 h, 4 h, 8 h, 12 h, 14 h and 16 h. The reaction was completed in 16 h.

0.0180 mol% P*t*Bu_3 catalyzed reduction of CO_2 with (HBC_8H_{14}) :

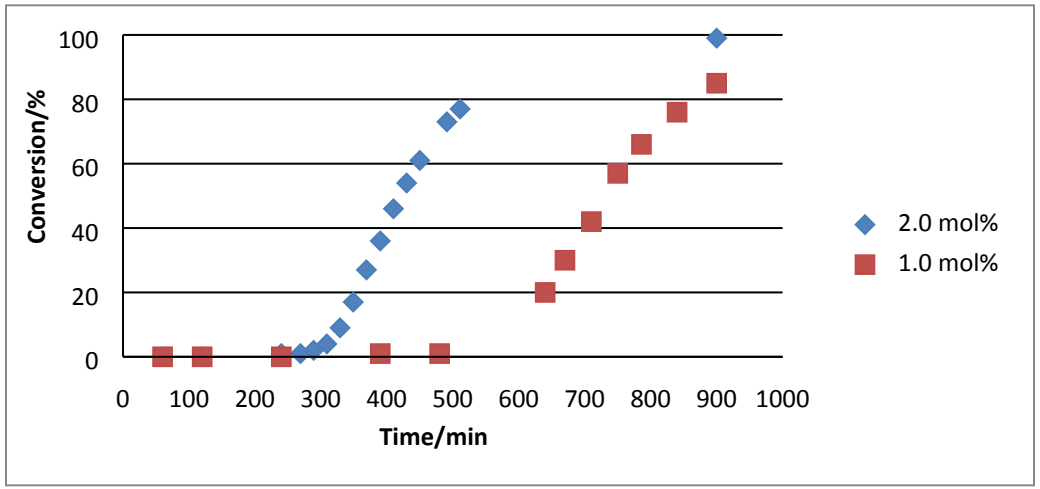
The vial with $(HBC_8H_{14})_2$ (100 mg, 0.410 mmol) was added 0.10 mL of stock solution of P*t*Bu_3 (0.00148 M)[5] in C_6D_5Br and 1.00 mL of C_6D_5Br. The mixture was stirred till all $(HBC_8H_{14})_2$ was dissolved before it was transferred into J-Young tube which was then tightened with Teflon cap. The sample was treated by frozen and atmosphere replaced with $^{13}CO_2$. The sample was then warmed to

room temperature affording a CO_2 pressure of 5.3 atm.[1] The sample was then warmed up to room temperature and heated at 60 °C and monitored by NMR spectroscopy.



1.0 mol% PPh_3 and 2.0 mol% PPh_3 catalyzed reduction of $^{13}CO_2$ with (HBC_8H_{14}) :

1.0 mol% PPh_3 reaction: The vial with $(HBC_8H_{14})_2$ (100 mg, 0.410 mmol) was added 0.10 mL of stock solution of PPh_3 (0.082 M) in C_6D_5Br and 1.00 mL of C_6D_5Br. The mixture was stirred till all (HBC_8H_{14}) was dissolved before it was transferred into J-Young tube which was then tightened with Teflon cap. The sample was treated by frozen and atmosphere replaced with $^{13}CO_2$. The sample was then warmed to room temperature affording a CO_2 pressure of 5.3 atm.[1] The sample was then warmed up to room temperature and monitored by ^{1}H, ^{31}P, ^{11}B and ^{13}C NMR spectroscopy. **2.0 mol% PPh_3 catalyzed reaction sample was prepared in the same procedure:** The vial with $(HBC_8H_{14})_2$ (100 mg, 0.410 mmol) was added 0.20 mL of stock solution of PPh_3 (0.082 M) in C_6D_5Br and 0.90 mL of C_6D_5Br.



Comparision of induction periods in reactions catalyzed 2.0 mol% and 1.0 mol% PPh_3

Footnotes

1. The amount of $^{13}CO_2$ filled was calculated to be 0.195 mmol. The volume of J-Young tube is 2.0 mL. Therefore, the pressure of $^{13}CO_2$ at the beginning was calculated as following: P= nRT/V = 0.19466 x 0.0821 x 298/1.2 = 3.97 atm when 0.8 mL of bromobenzene was used. When 1.1 mL of bromobenzene was used, the pressure of $^{13}CO_2$ at the beginning was calculated as following: P=nRT/V = 0.19466 x 0.0821 x 298/(2.0-1.1) = 5.29 atm.
2. Tri(*t*-butyl)phosphine (15.0 mg, 0.0741 mmol) was dissolved in 1.00 mL of bromobenzene-d5 and 0.10 mL of the mother solution was taken to prepare the sample.
3. Triphenylphosphine (20.0 mg, 0.0763 mmol) was dissolved in 1.00 mL of bromobenzene and 0.10 mL of the mother solution was taken to prepare the sample.
4. The stock solution was prepared in the following steps: a) 40.0 mg of tri(t-butyl)phosphine was dissolved in 1.00 mL of bromobenzene-d5 to obtain 0.198 M solution; b) 0.10 mL of the above 0.198 M solution was taken and diluted into 1.00 mL bromobenzene-d5 solution to obtain 0.0198 M solution.
5. The stock solution was prepared in the following steps: a) 30.0 mg of tri(t-butyl)phosphine was dissolved in 1.00 mL of bromobenzene-d5 to obtain 0.148 M solution; b) 0.10 mL of the above 0.148 M solution was taken and diluted into 1.00 mL bromobenzene-d5 solution to obtain 0.0148 M solution; c) 0.10 mL of the 0.0148 M solution was taken and diluted into 1.00 mL bromobenzene-d5 solution to obtain 0.00148 M solution.