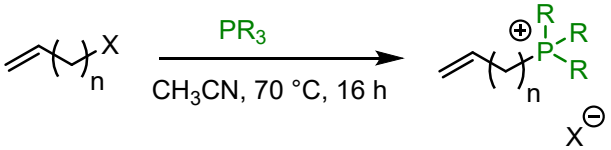
Supporting Information

Bifunctional Organoboron-Phosphonium Catalysts for Copolymerization of CO_2 and Epoxides

Materials and Methods:

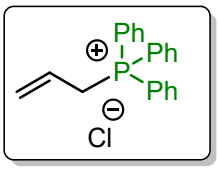
All reactions were performed under a nitrogen or argon atmosphere using standard Schlenk line and glovebox techniques. Glassware and stainless-steel reactors were dried at 150 °C for 24 hours prior to use. Solvents were purchased from commercial sources and dried using MBraun Manual Solvent purification system packed with Alcoa F200 activated alumina desiccant. Starting materials such as epoxides, phosphines, allyl bromide, allyl chloride, 5-bromo-1-pentene and 9-borabicyclo[3.3.1]nonane (9-BBN) were purchased from commercial sources. Bone-dry CO_2 was supplied from a high-pressure cylinder and equipped with a liquid dip tube purchased from Scott Specialty Gases. NMR spectra were recorded on a 400 MHz Bruker spectrometer with $CDCl_3$ as an internal standard at 7.26 ppm. Infrared spectra were taken using a Bruker Tensor 27 FT-IR spectrometer and CaF_2 sample cell with 0.02 mm path length. A Malvern modular GPC apparatus with ViscoGEL I-series columns (H&L) and THF eluent was used. M_w and M_n were calculated using data from RI, Right Angle Light Scattering (RALS) and Low Angle Light Scattering (LALS) detectors calibrated against polystyrene standards.

General procedure for the synthesis of phosphonium salts. To an oven dried Schlenk flask equipped with stir bar was added a solution of phosphines (10 mmol, 1.00 equiv) in acetonitrile (10 mL) was treated with alkenyl halide (10 mmol, 1.00 equiv) under nitrogen atmosphere. Then, the reaction mixture was then heated to 70 °C for 24 h. After completion, the mixture was concentrated in vacuo to afford the crude product that was further purified by washing with pentane (3 x 10 mL). The white solid was isolated by vacuum filtration and was dried for 12 h in vacuo at room temperature.



Scheme S1: Synthesis of phosphonium salt

Characterization data for phosphonium salts.



Allyltriphenylphosphonium chloride. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.70 (m, 9H), 7.64-7.61 (m, 6H), 5.64-5.61 (m, 1H), 5.48 (dd, *J* = 16.8, 5.2 Hz, 1H), 5.30 (dd, *J* = 10.0, 4.4 Hz, 1H), 4.74 (dd, *J* = 15.6, 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.1 (d, *J* = 3.0 Hz), 134.0 (d, *J* = 9.6 Hz), 130.4 (d, *J* = 2.8 Hz), 126.3 (d, *J* = 3.0 Hz), 123.3 (d, *J* = 9.9 Hz), 118.4 (d, *J* = 85.2 Hz), 28.9 (d, *J* = 49.8 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 21.15. ESI-MS calculated for $C_{21}H_{20}P$ $[M]^+$, 303.1297; found, 303.1290.

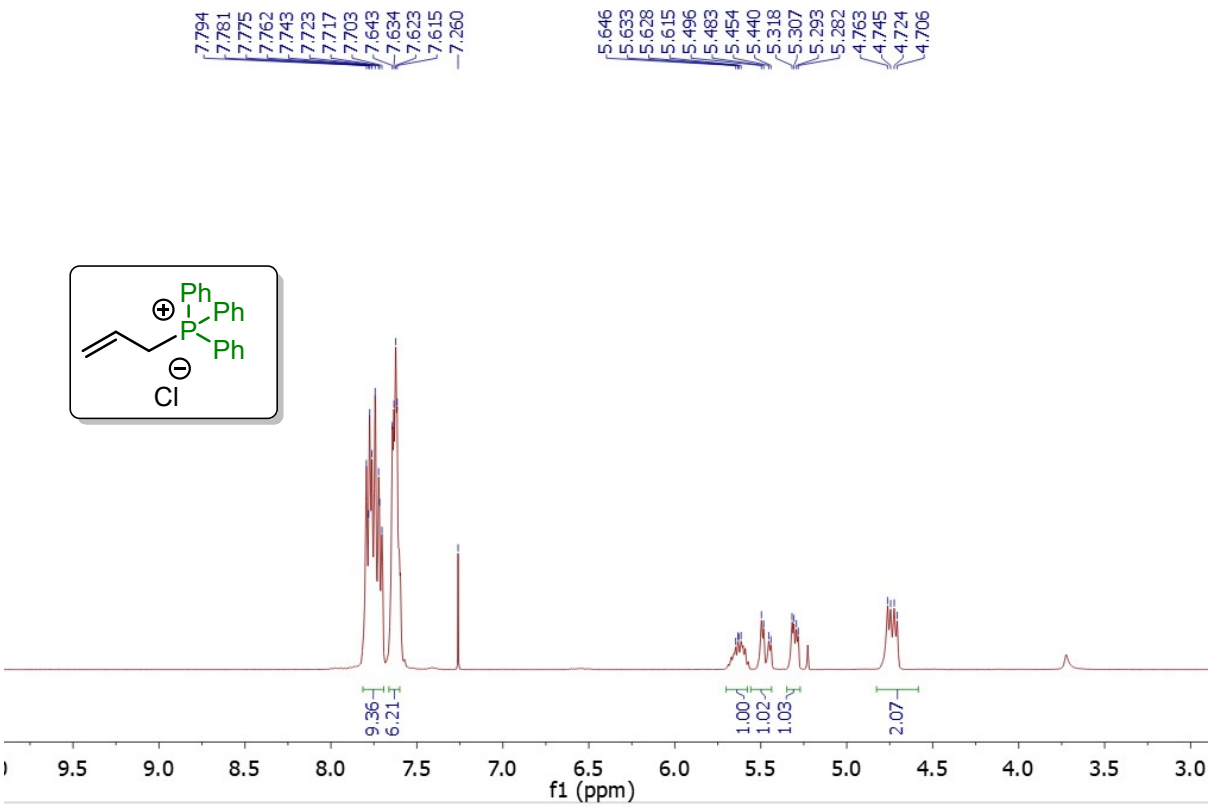


Figure S1: ^{1}H NMR of phosphonium salt ($CDCl_3$, 400 MHz).

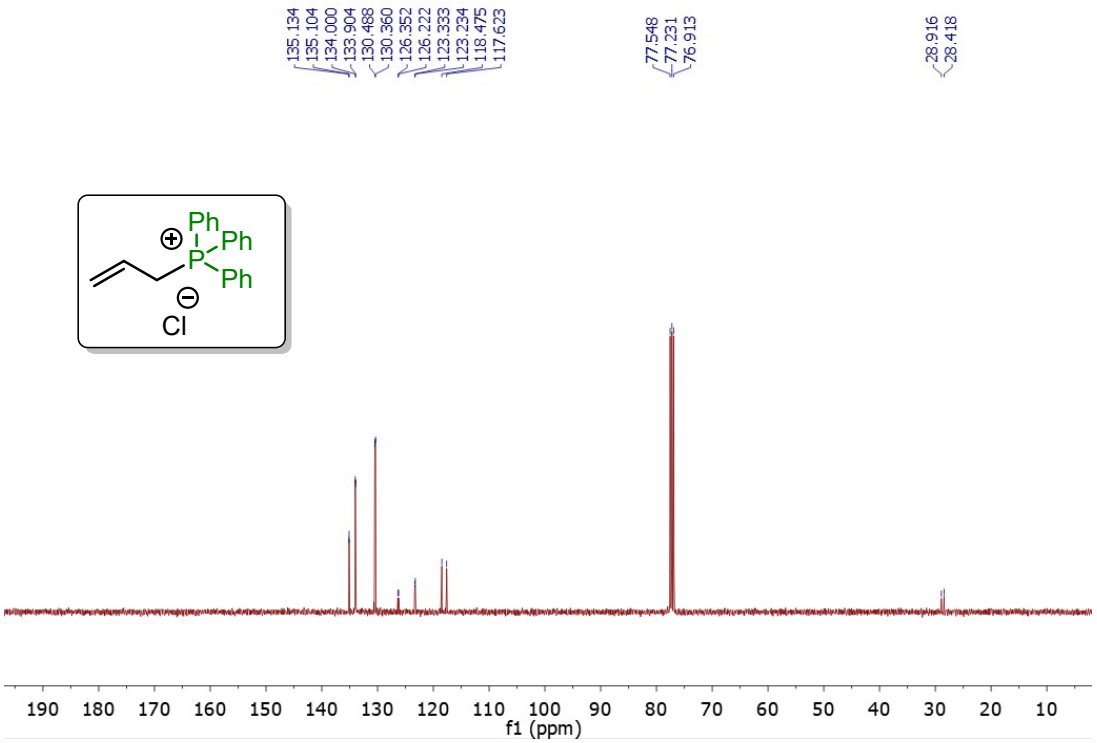


Figure S2: ^{13}C NMR of phosphonium salt ($CDCl_3$, 100 MHz).

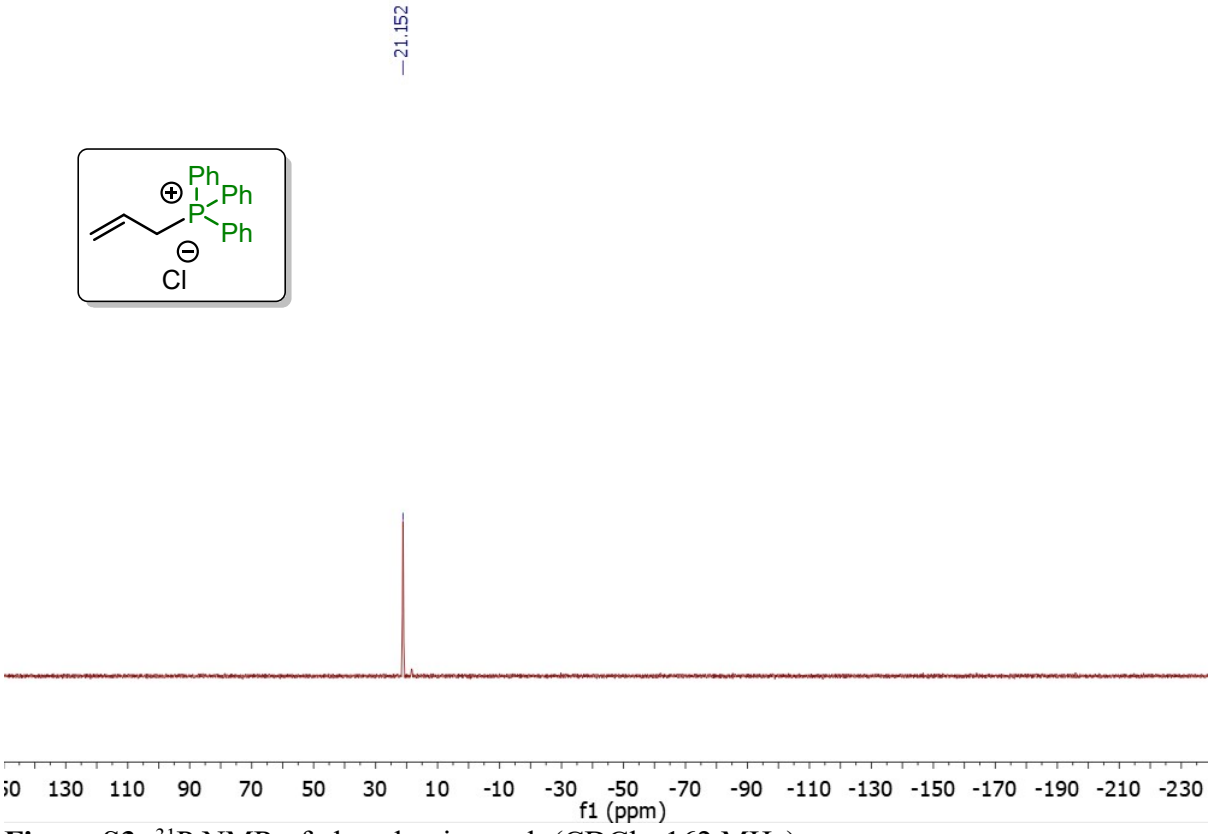


Figure S3: ^{31}P NMR of phosphonium salt ($CDCl_3$, 162 MHz).

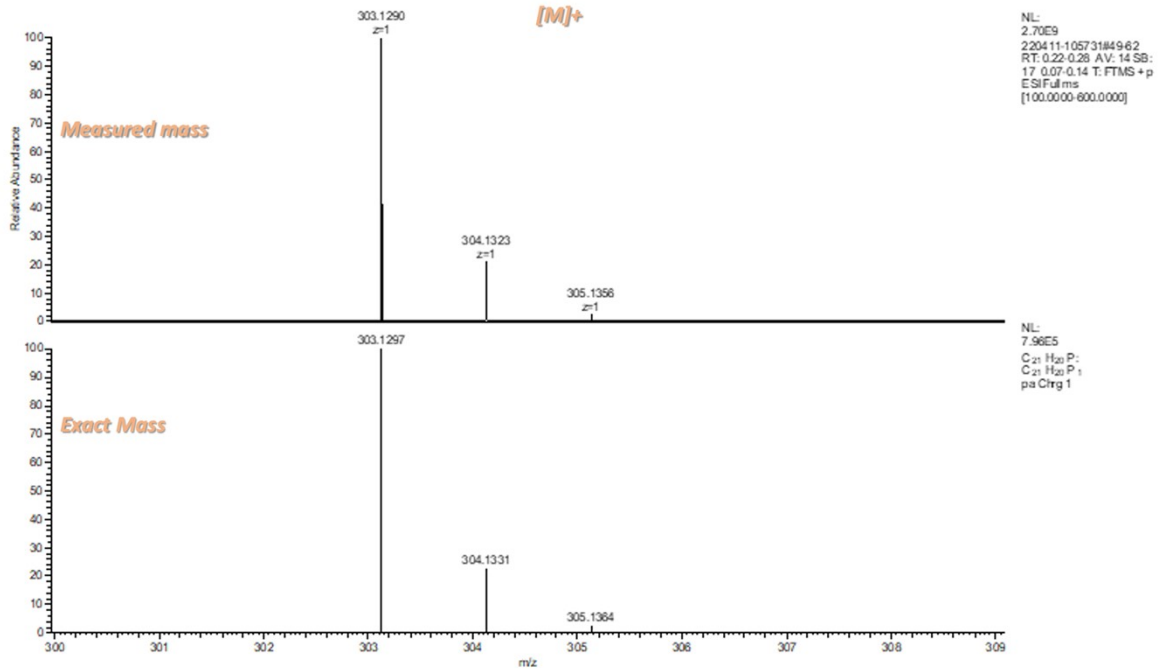
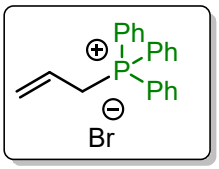


Figure S4: ESI-MS Spectrum of phosphonium salt.



Allyltriphenylphosphonium bromide. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.75 (m, 9H), 7.67-7.64 (m, 6H), 5.68-5.51 (m, 1H), 5.55-5.50 (m, 1H), 5.36-5.32 (m, 1H), 4.73-4.67 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.2 (d, J = 3.3 Hz), 134.0 (d, J = 10.1 Hz), 130.5 (d, J = 2.7 Hz), 126.4 (d, J = 3.0 Hz), 123.2 (d, J = 10.0 Hz), 118.4 (d, J = 85.7 Hz), 28.9 (d, J = 49.9 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 21.10. ESI-MS calculated for $C_{21}H_{20}P$ $[M]^+$, 303.1297; found, 303.1291.

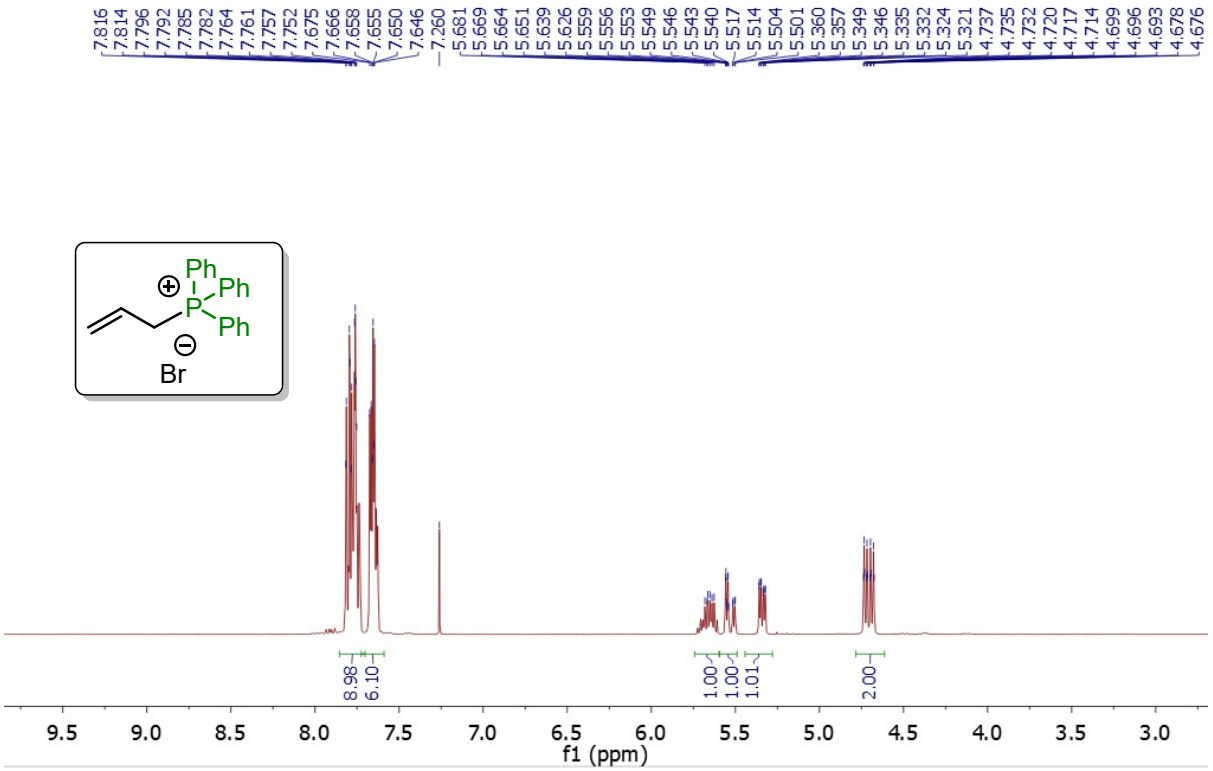


Figure S5: ^{1}H NMR of phosphonium salt ($CDCl_3$, 400 MHz).

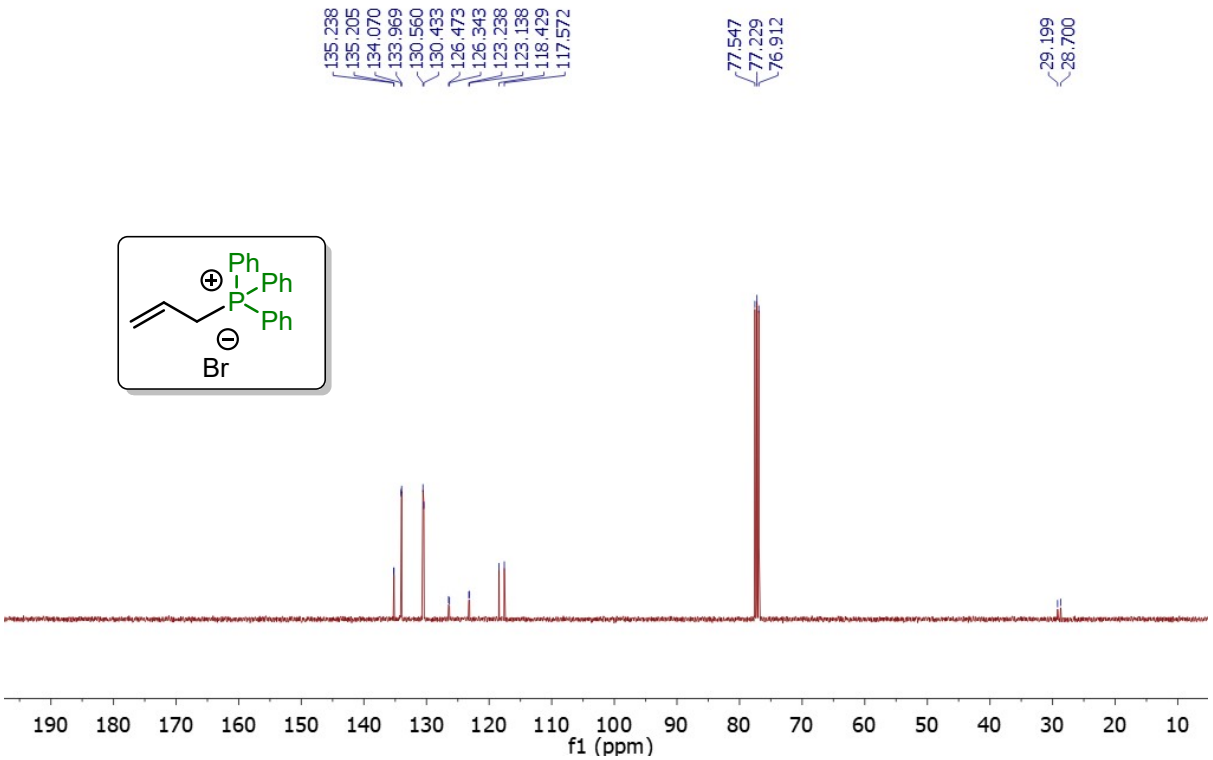


Figure S6: ^{13}C NMR of phosphonium salt ($CDCl_3$, 100 MHz).

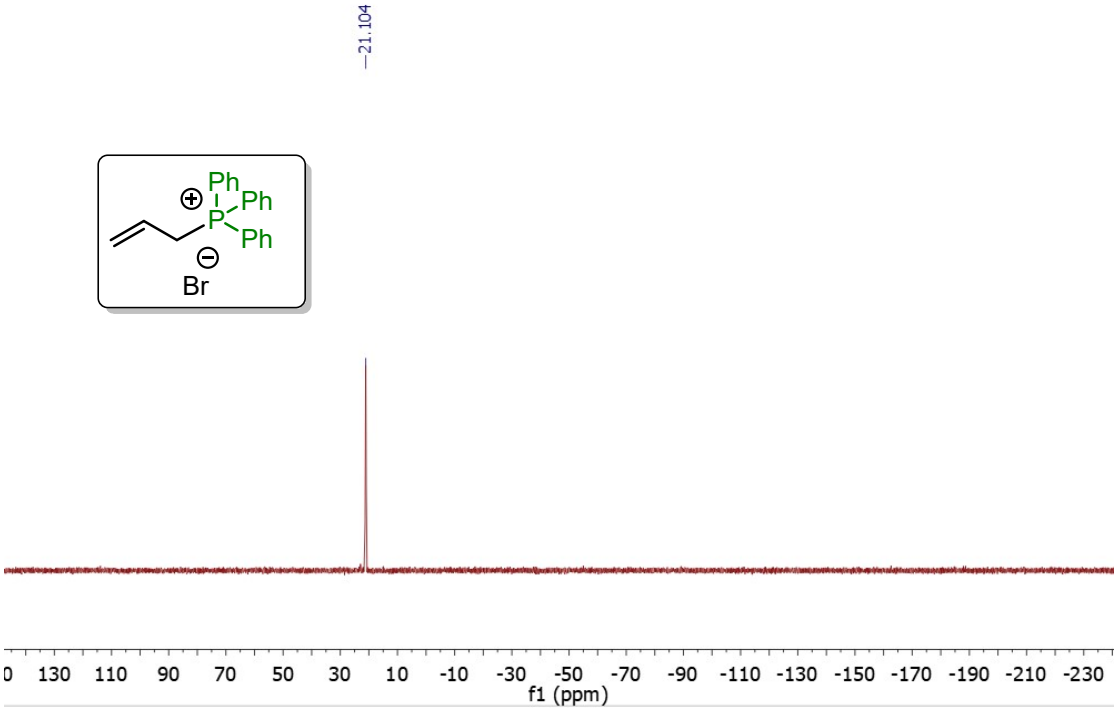


Figure S7: ^{31}P NMR of phosphonium salt ($CDCl_3$, 162 MHz).

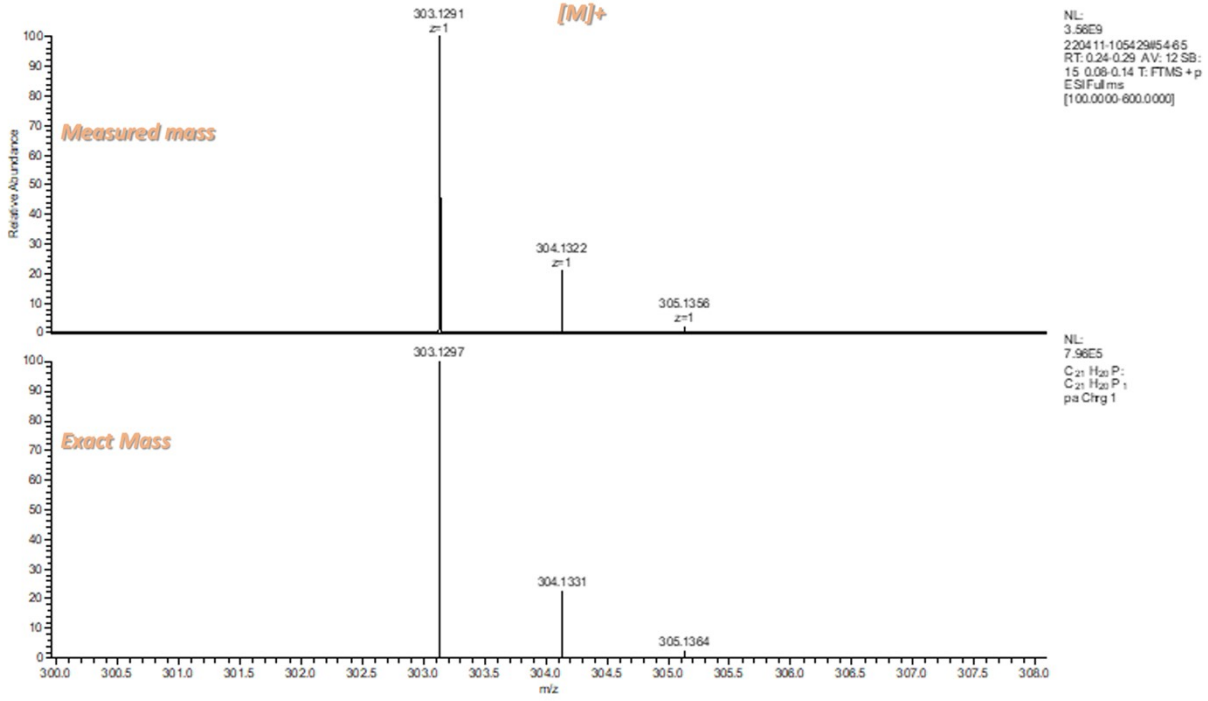
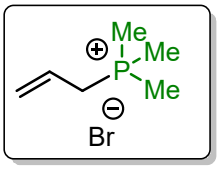


Figure S8: ESI-MS Spectrum of phosphonium salt.



Allyltrimethylphosphonium bromide. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71-5.65 (m, 1H), 5.49-5.43 (m, 1H), 5.41-5.37 (m, 1H), 3.53 (dd, *J* = 17.2, 7.6 Hz, 2H), 2.14 (d, *J* = 14.4 Hz, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 124.9 (d, *J* = 12.7 Hz), 123.9 (d, *J* = 10.7 Hz), 29.0 (d, *J* = 51.0 Hz), 8.7 (d, *J* = 54.6 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 26.10. ESI-MS calculated for $C_6H_{14}P$ $[M]^+$, 117.0828; found, 117.0825.

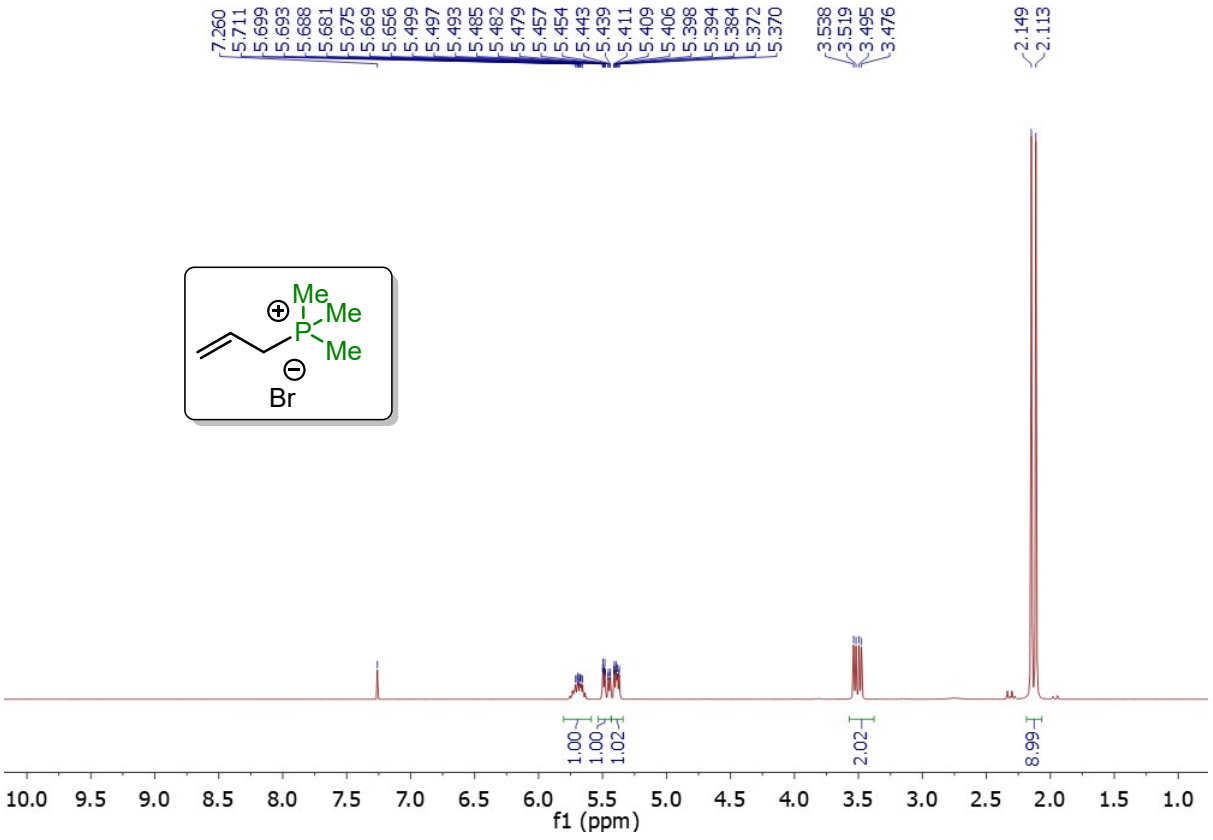


Figure S9: ^{1}H NMR of phosphonium salt ($CDCl_3$, 400 MHz).

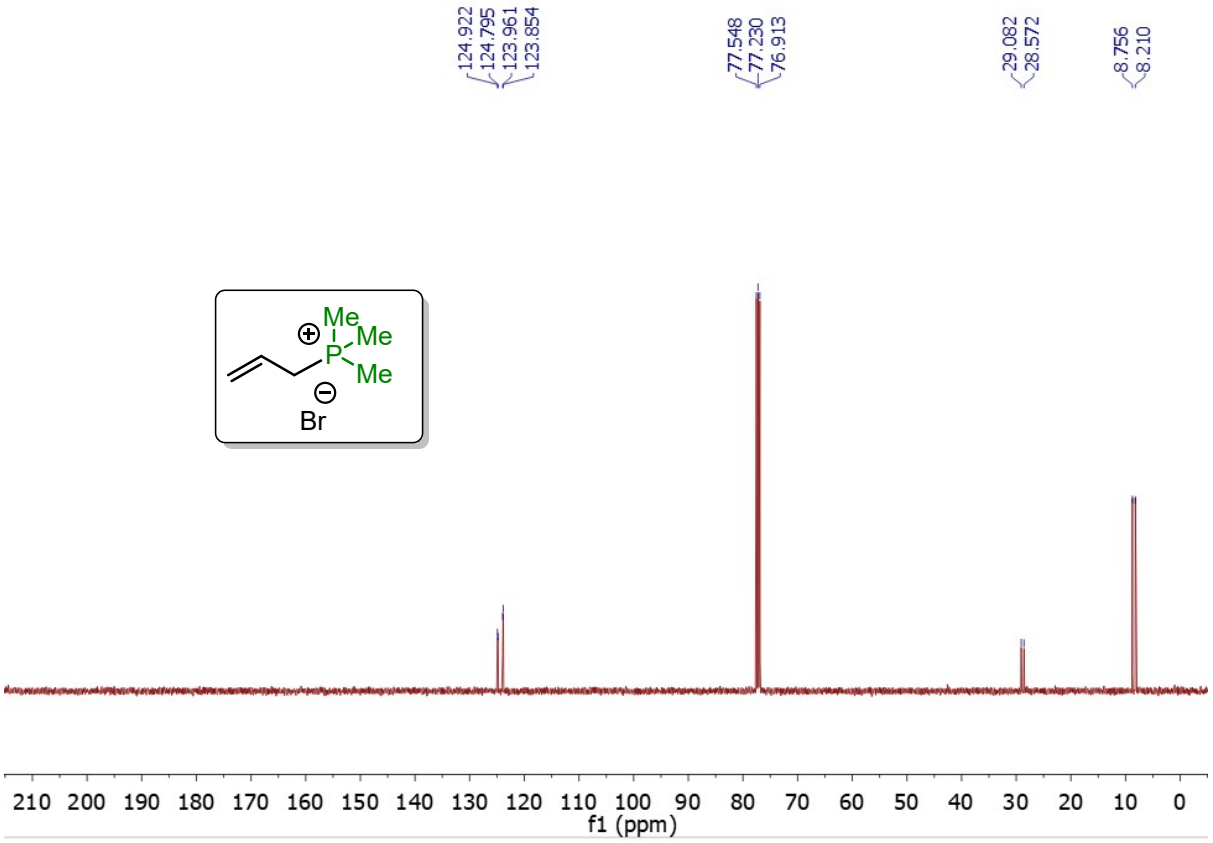


Figure S10: ^{13}C NMR of phosphonium salt ($CDCl_3$, 100 MHz).

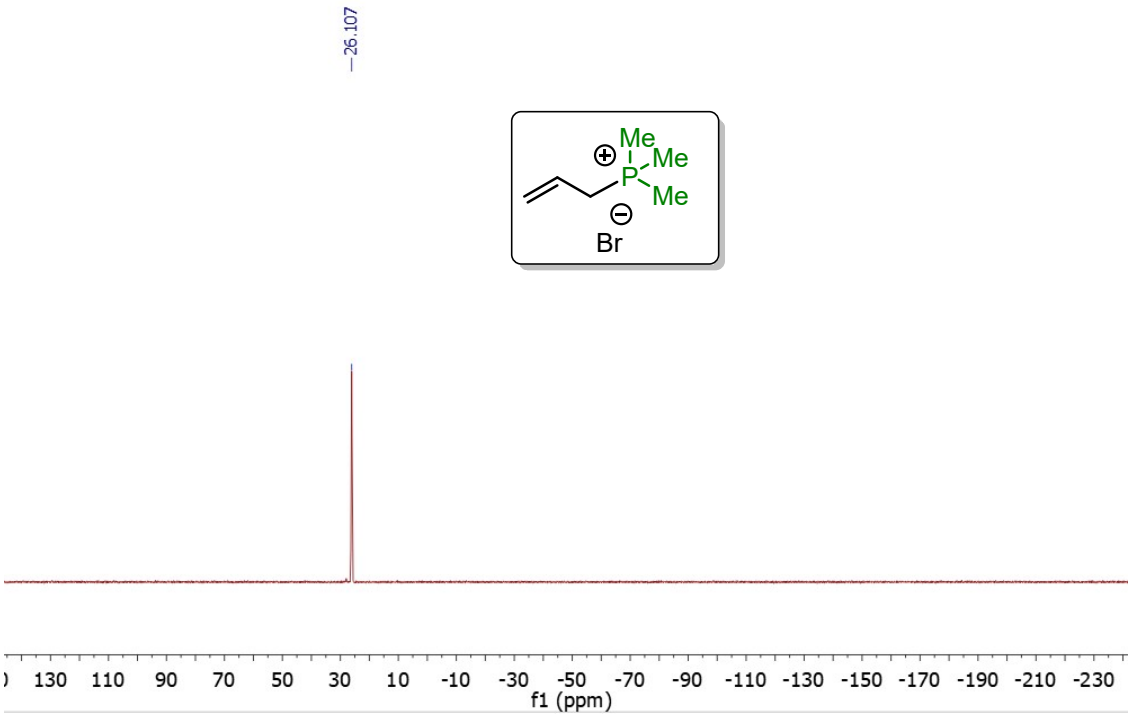


Figure S11: ^{31}P NMR of phosphonium salt ($CDCl_3$, 162 MHz).

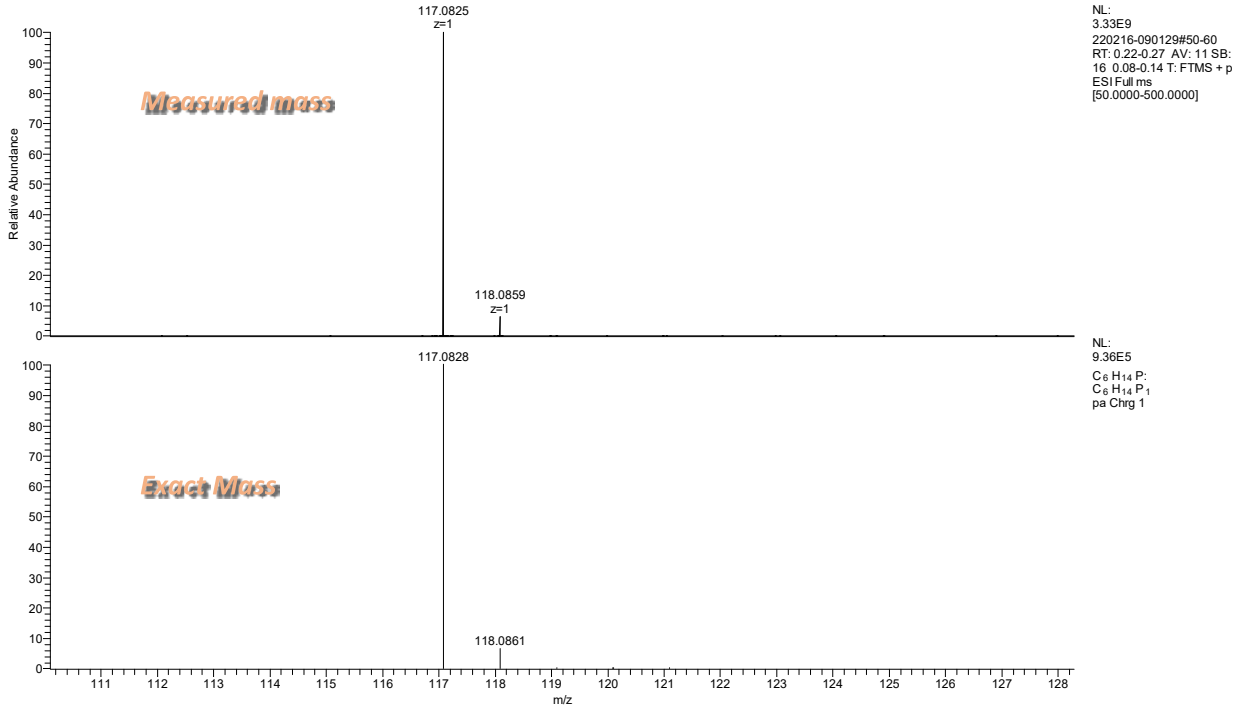
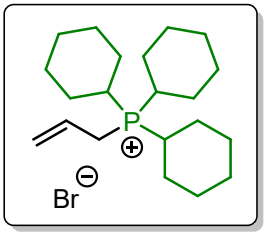


Figure S12: ESI-MS Spectrum of phosphonium salt.



Allyltricyclohexylphosphonium bromide. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73-5.68 (m, 1H), 5.56-5.50 (m, 1H), 5.38-5.35 (m, 1H), 3.48 (dd, J = 14.4, 7.2 Hz, 2H), 2.62-2.53 (m, 1H), 1.98-1.97 (m, 6H), 1.85-1.84 (m, 6H), 1.71-1.70 (m, 3H), 1.53-1.49 (m, 6H), 1.39-1.35 (m, 6 H), 1.26-1.16 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 125.1 (d, J = 8.7 Hz), 124.4 (d, J = 11.1 Hz), 30.3, 30.0, 27.2, 27.1, 26.5, 26.4, 25.4, 21.9 (d, J = 43.1 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 29.78. ESI-MS calculated for $C_{21}H_{38}P$ $[M]^+$, 321.2706; found, 321.2692.

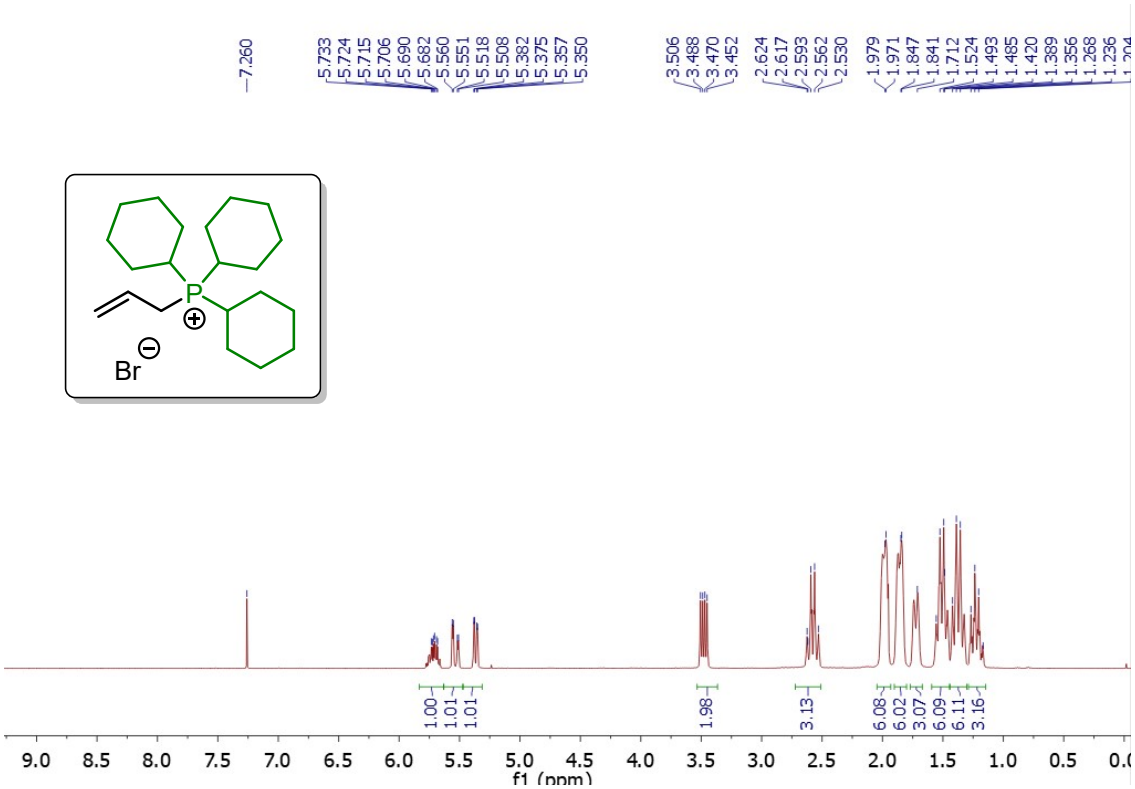


Figure S13: ^{1}H NMR of phosphonium salt ($CDCl_3$, 400 MHz).

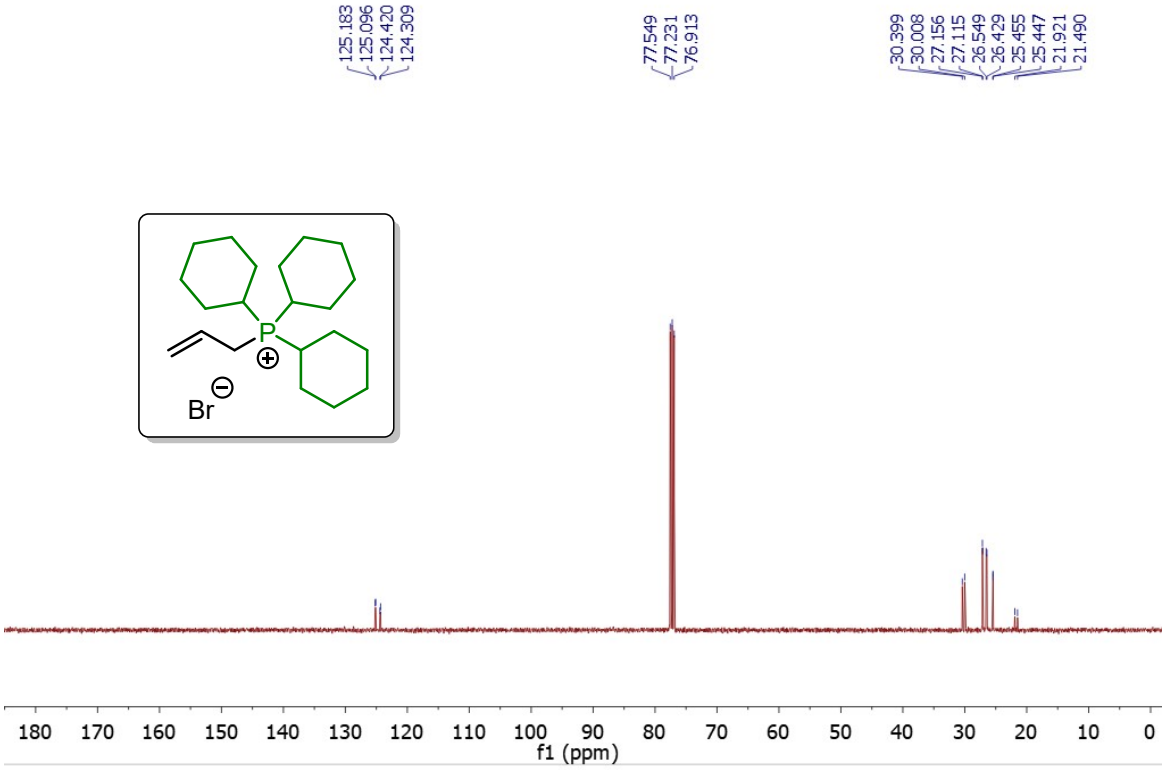


Figure S14: ^{13}C NMR of phosphonium salt ($CDCl_3$, 100 MHz).

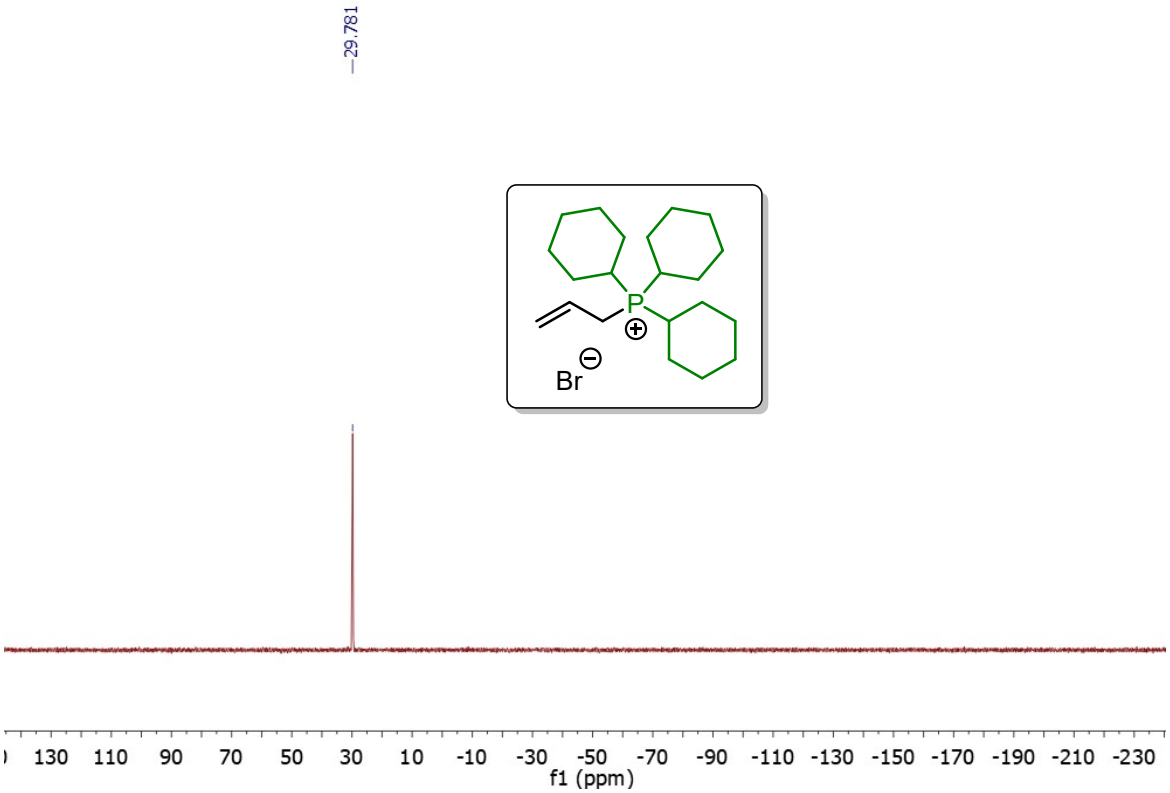


Figure S15: ^{31}P NMR of phosphonium salt ($CDCl_3$, 162 MHz).

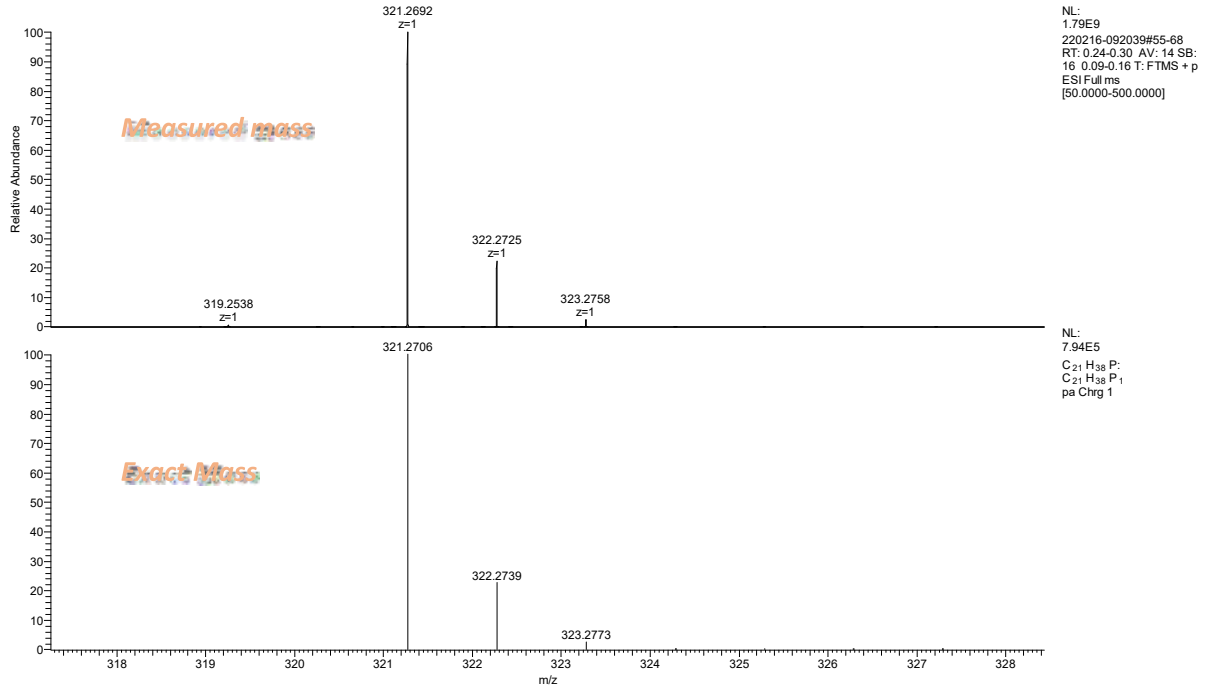
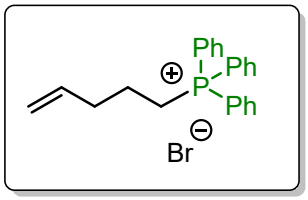


Figure S16: ESI-MS Spectrum of phosphonium salt.



Triphenyl(pent-4-en-1-yl)phosphonium bromide. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.71 (m, 9H), 7.69-7.61 (m, 6H), 5.61-5.57 (m, 1H), 4.97-4.89 (m, 2H), 3.68-3.60 (m, 2H), 2.32-2.30 (m, 2H), 1.67-1.63 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.2, 135.1 (d, J = 3.2 Hz), 133.6 (d, J = 9.9 Hz), 130.6 (d, J = 7.6 Hz), 118.5, 117.6 (d, J = 68.6 Hz), 33.8 (d, J = 16.5 Hz), 22.2 (d, J = 37.7 Hz), 21.7 (d, J = 8.3 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 24.29. ESI-MS calculated for $C_{23}H_{24}P$ $[M]^+$, 331.1610; found, 331.1604.

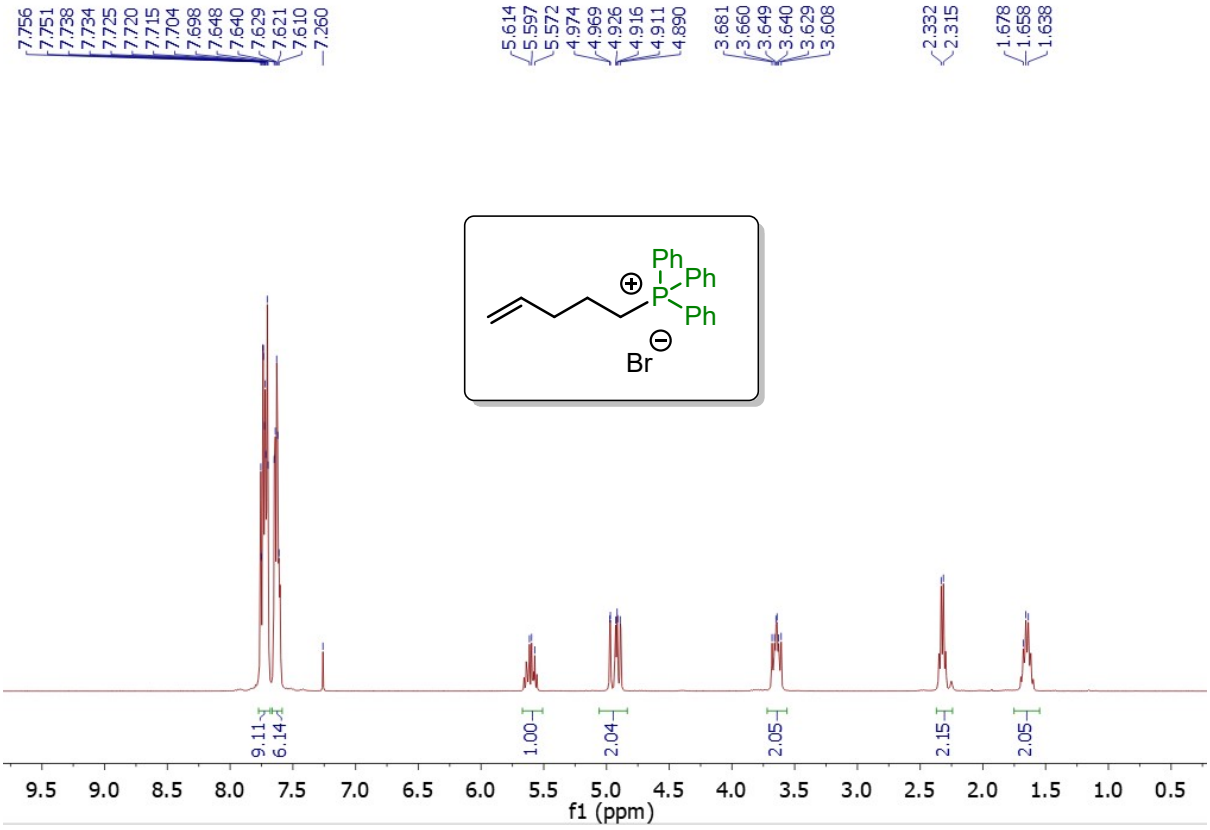


Figure S17: ^{1}H NMR of phosphonium salt ($CDCl_3$, 400 MHz).

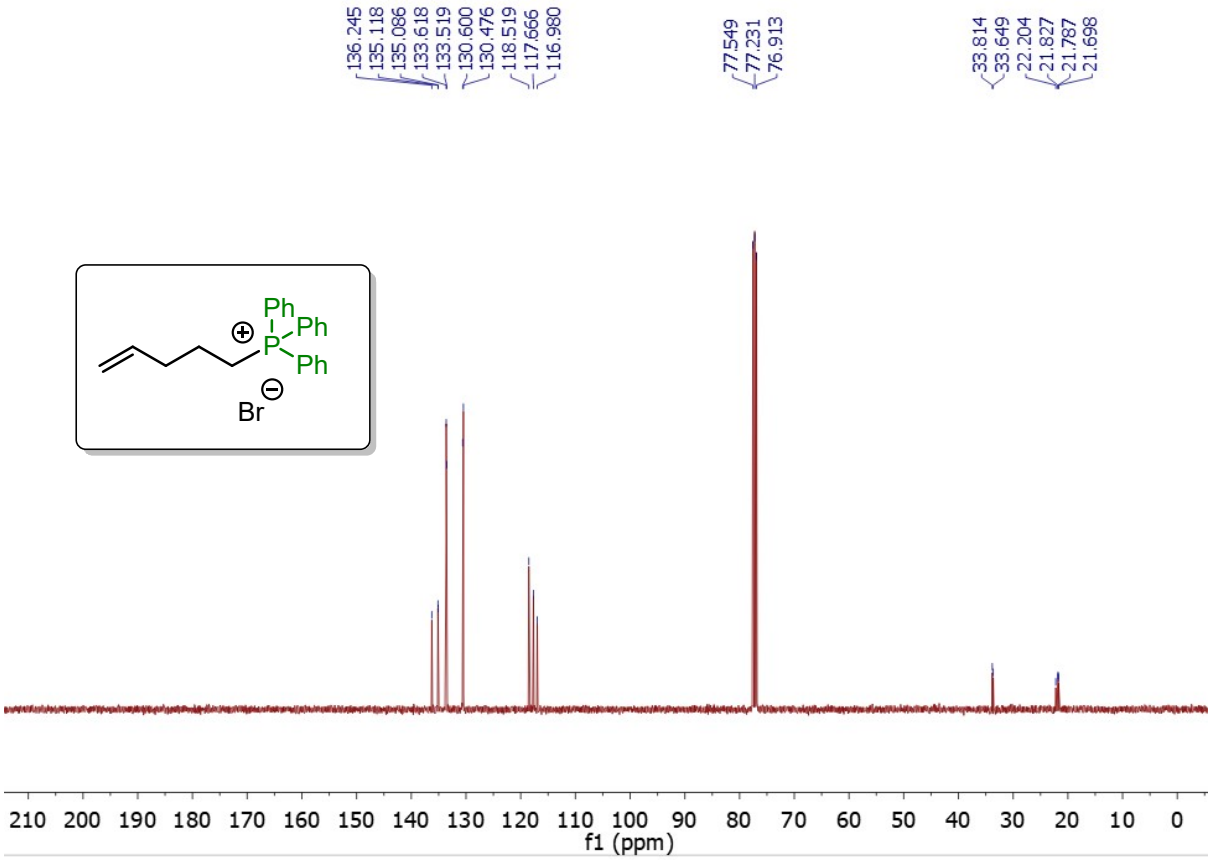


Figure S18: ^{13}C NMR of phosphonium salt ($CDCl_3$, 100 MHz).

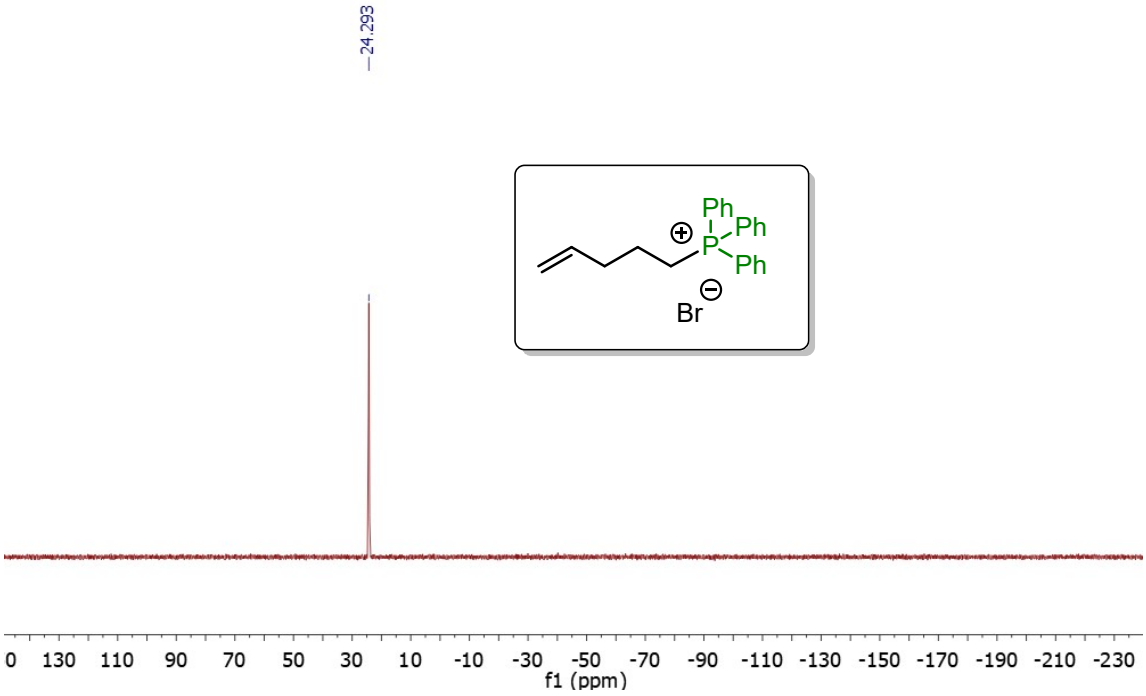


Figure S19: ^{31}P NMR of phosphonium salt ($CDCl_3$, 162 MHz).

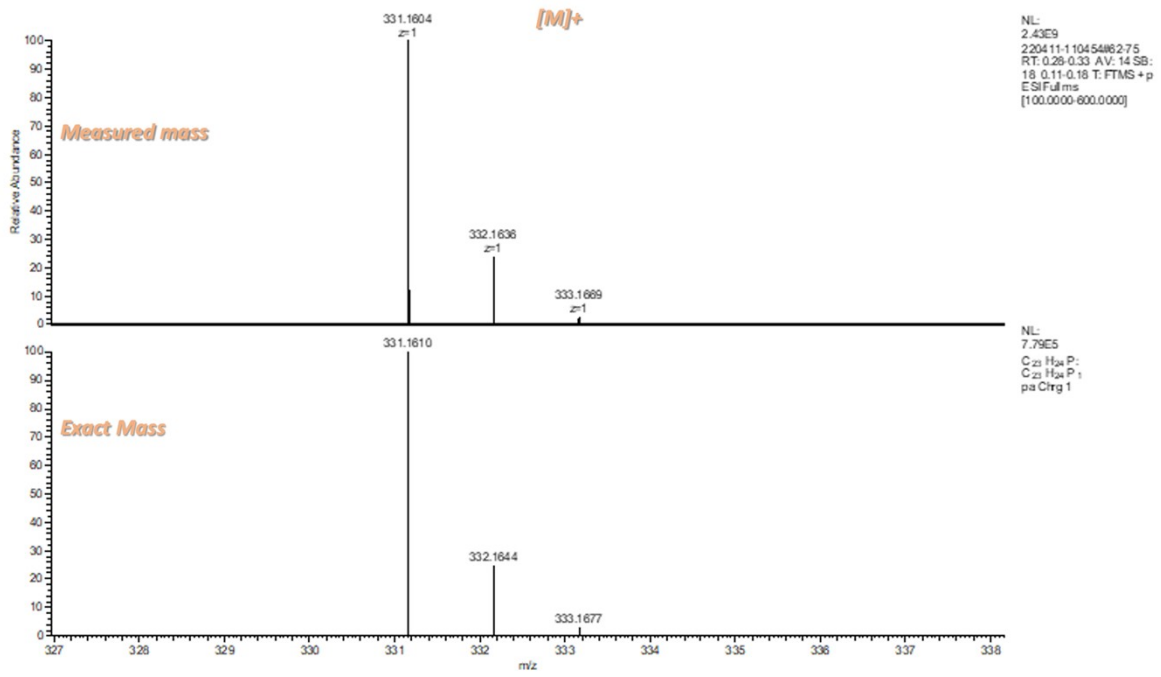
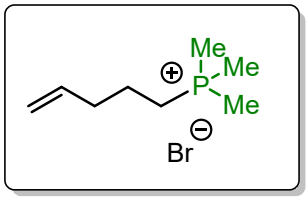


Figure S20: ESI-MS Spectrum of phosphonium salt.



Trimethyl(pent-4-en-1-yl)phosphonium bromide. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73-5.67 (m, 1H), 5.05-4.99 (m, 2H), 2.49-2.41 (m, 2H), 2.22-2.15 (m, 11H), 1.66-1.60 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 136.0, 117.1, 34.2 (d, J = 16.2 Hz), 23.4 (d, J = 52.0 Hz), 21.0 (d, J = 4.2 Hz), 9.3 (d, J = 54.2 Hz). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 27.18. ESI-MS calculated for $C_8H_{18}P$ $[M]^+$, 145.1141; found, 145.1138.

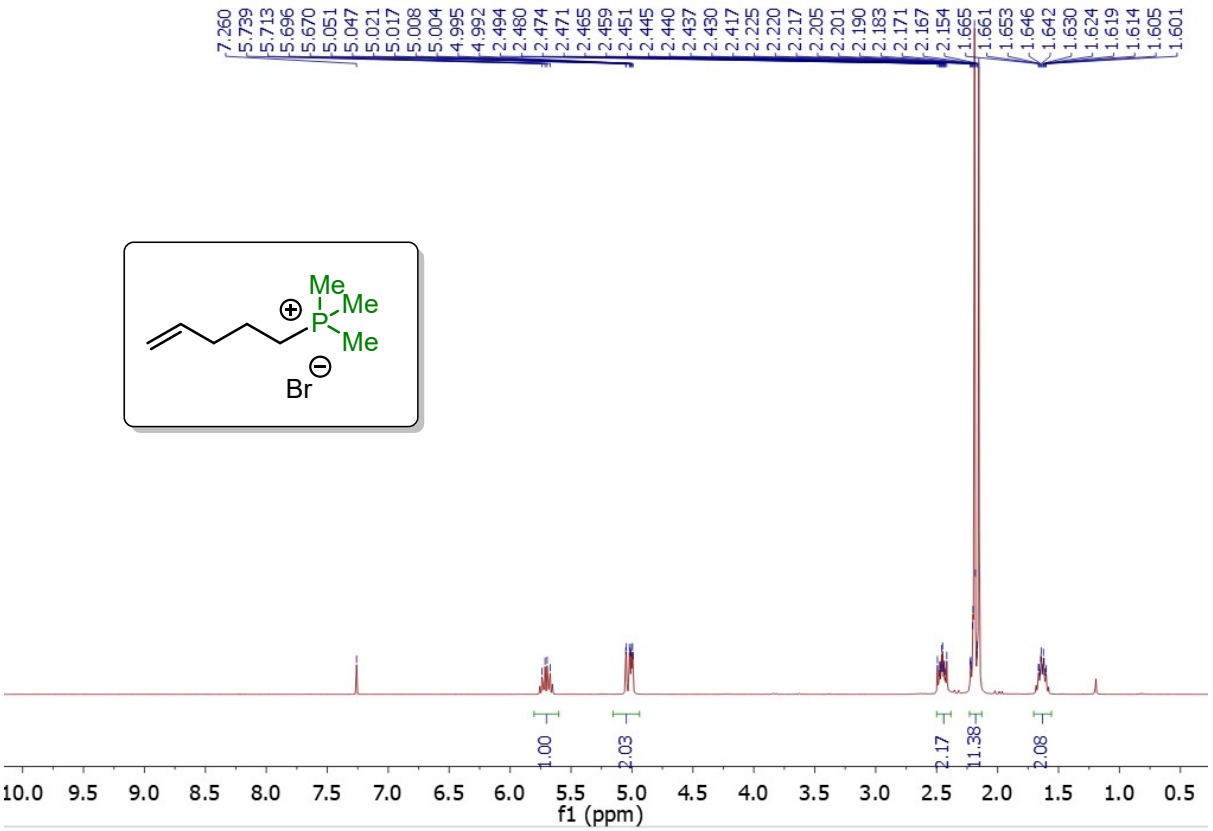


Figure S21: ^{1}H NMR of phosphonium salt ($CDCl_3$, 400 MHz).

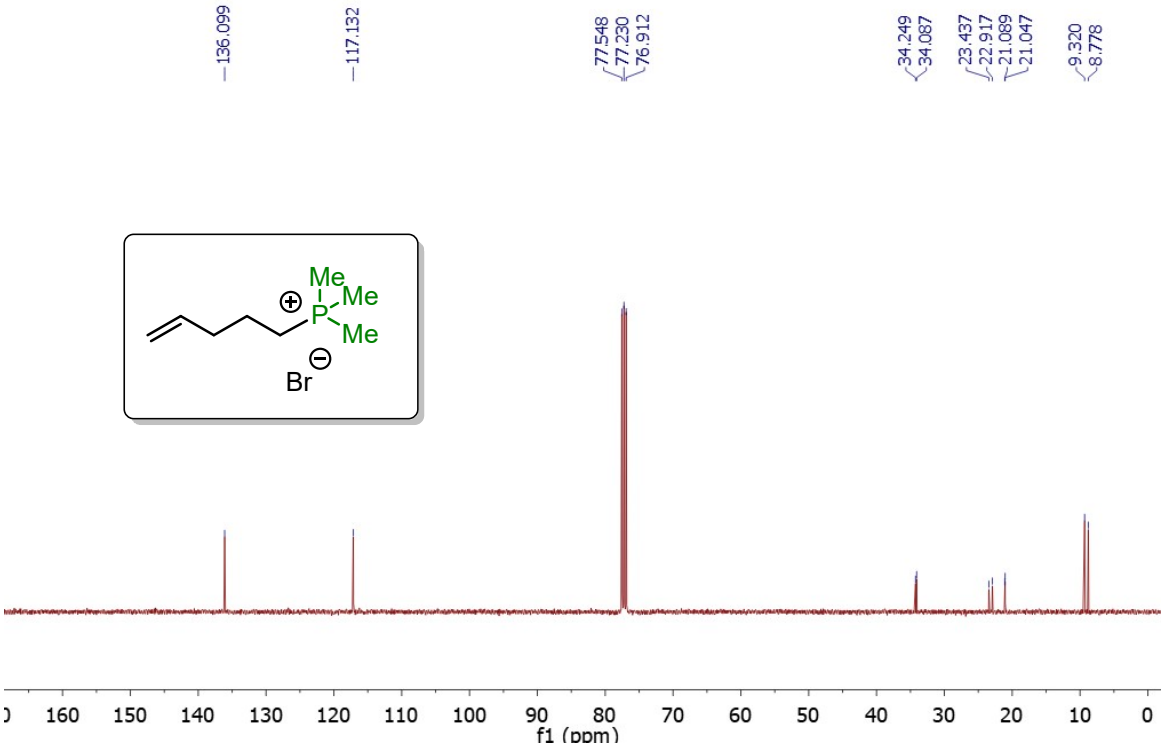


Figure S22: ^{13}C NMR of phosphonium salt ($CDCl_3$, 100 MHz).

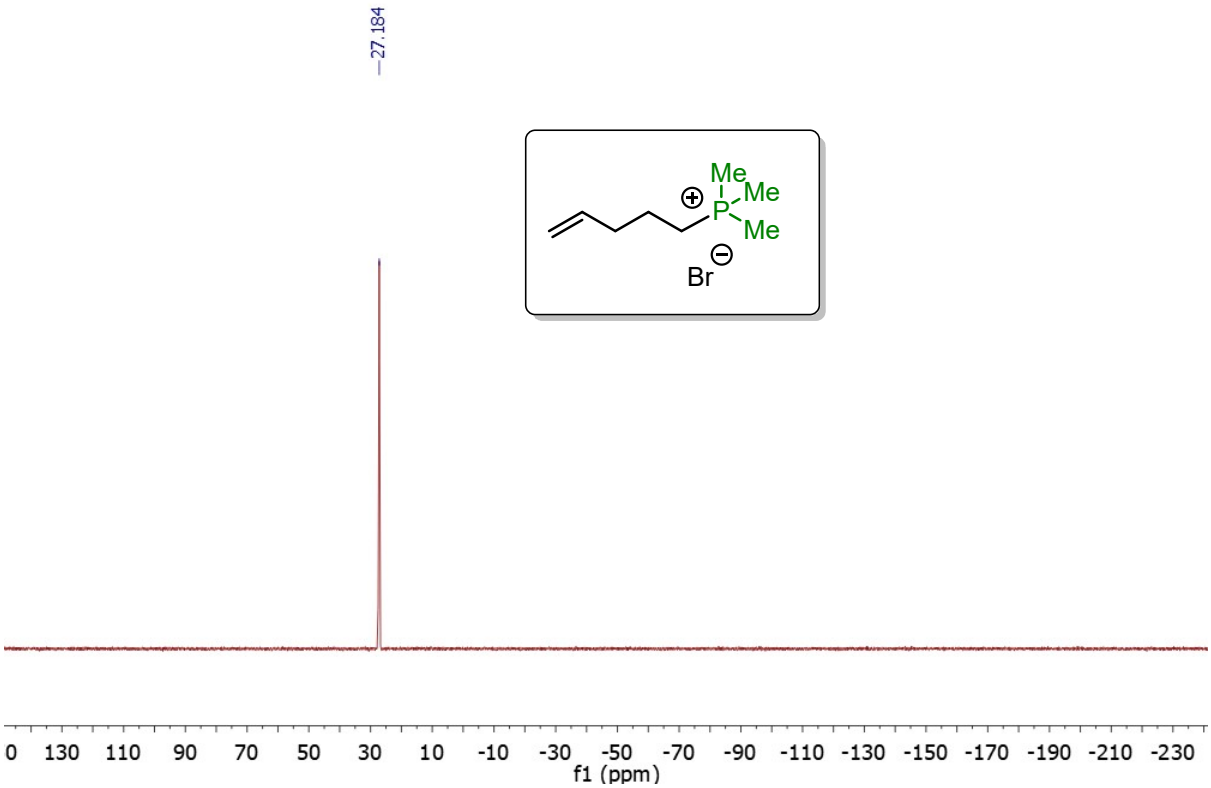


Figure S23: ^{31}P NMR of phosphonium salt ($CDCl_3$, 162 MHz).

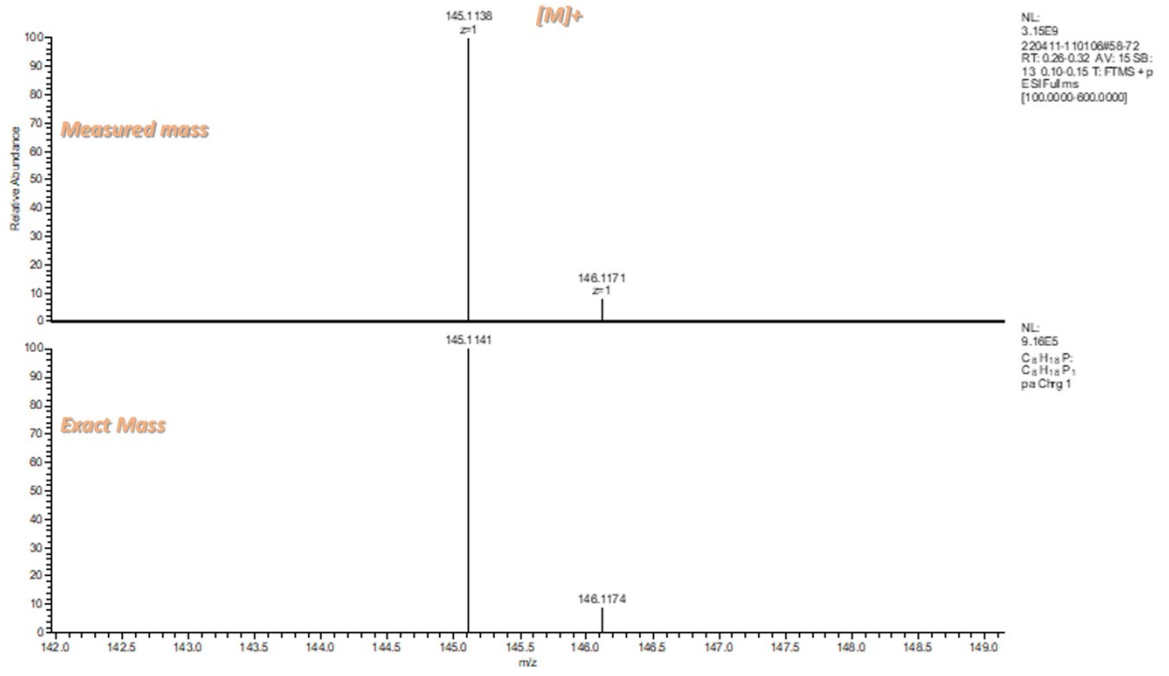
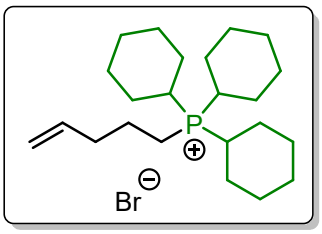


Figure S24: ESI-MS Spectrum of phosphonium salt.



Tricyclohexyl(pent-4-en-1-yl)phosphonium bromide. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63-5.61 (m, 1H), 4.99-4.92 (m, 2H), 2.50-2.46 (m, 3H), 2.27-2.26 (m, 2H), 2.17-2.15 (m, 2H), 1.87-1.76 (m, 12H), 1.66-1.62 (m, 5H), 1.37-1.34 (m, 12H), 1.17-1.13 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.8, 117.2, 34.5 (d, J = 14.2 Hz), 29.9, 29.5, 27.0, 26.3, 26.1, 25.2, 21.9 (d, J = 5.5 Hz), 15.0 (d, J = 42.9 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 31.89. ESI-MS calculated for $C_{23}H_{42}P$ [M]$^{+}$, 349.3019; found, 349.3010.

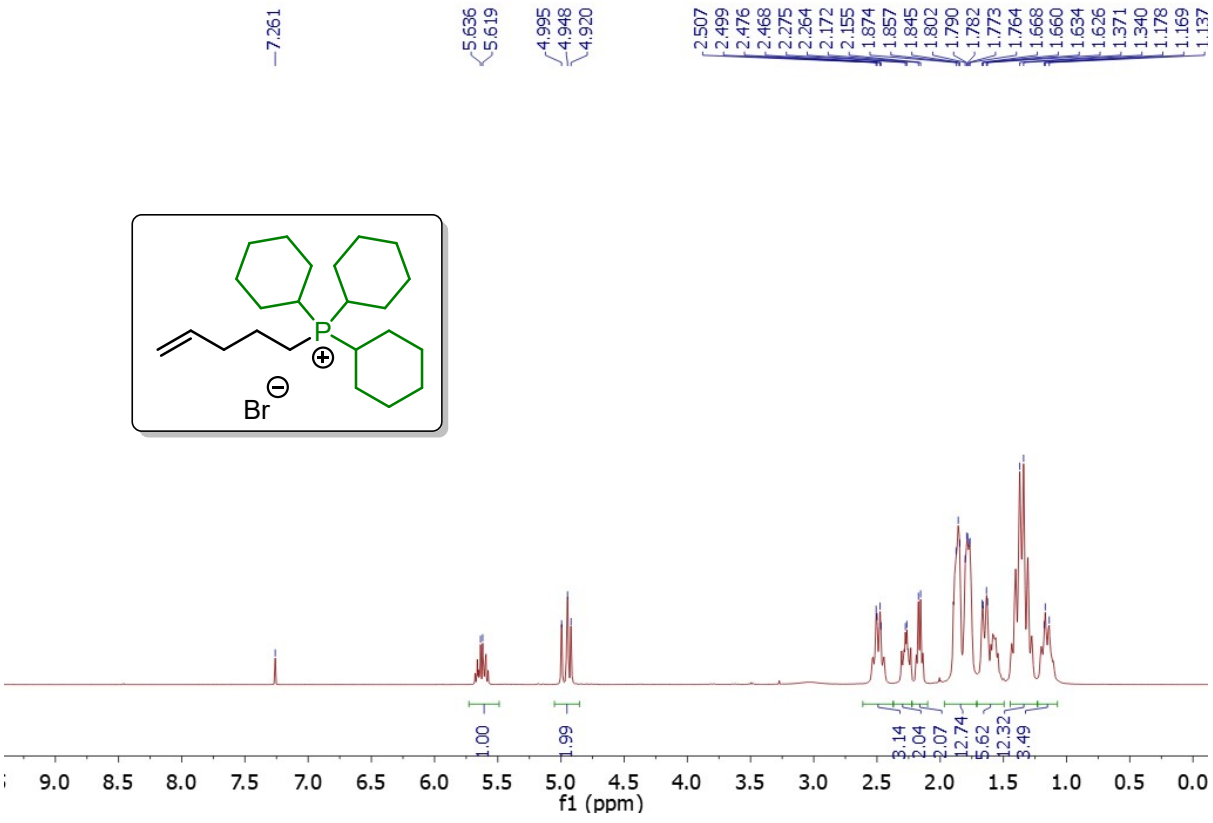


Figure S25: ^{1}H NMR of phosphonium salt ($CDCl_3$, 400 MHz).

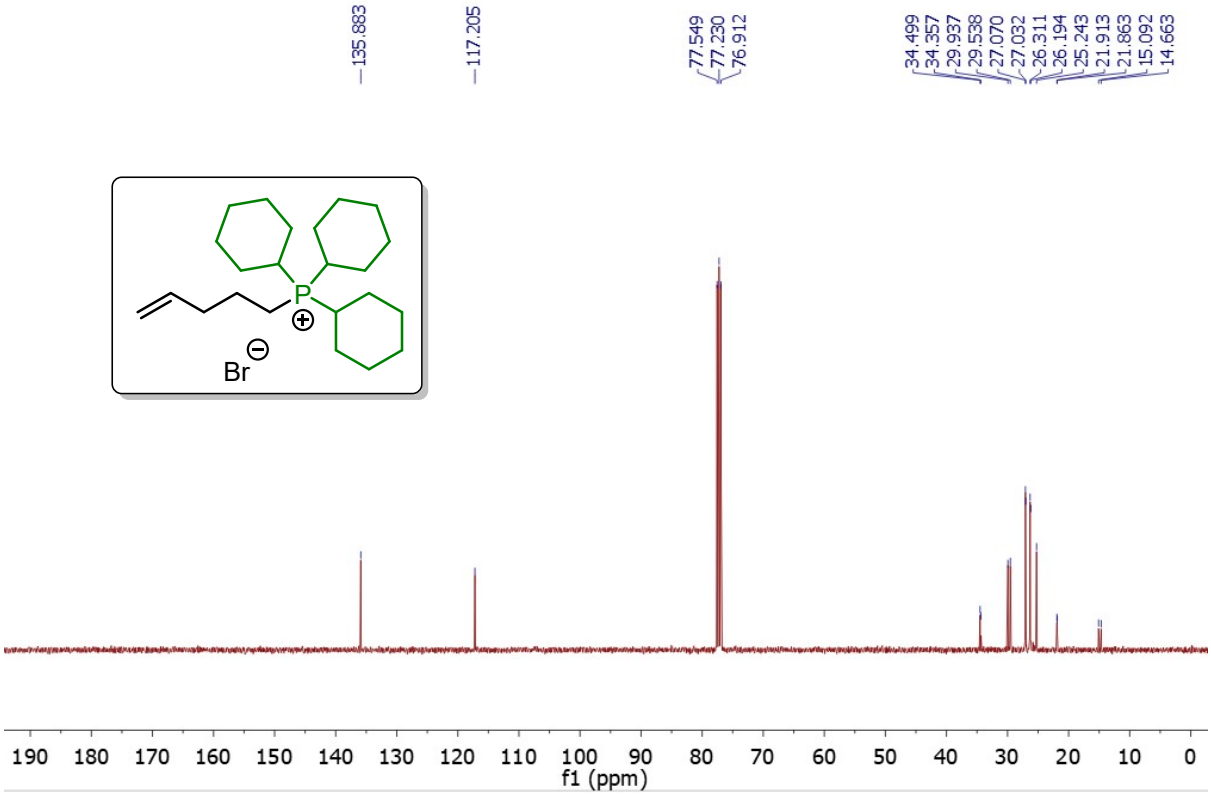


Figure S26: ^{13}C NMR of phosphonium salt ($CDCl_3$, 100 MHz).

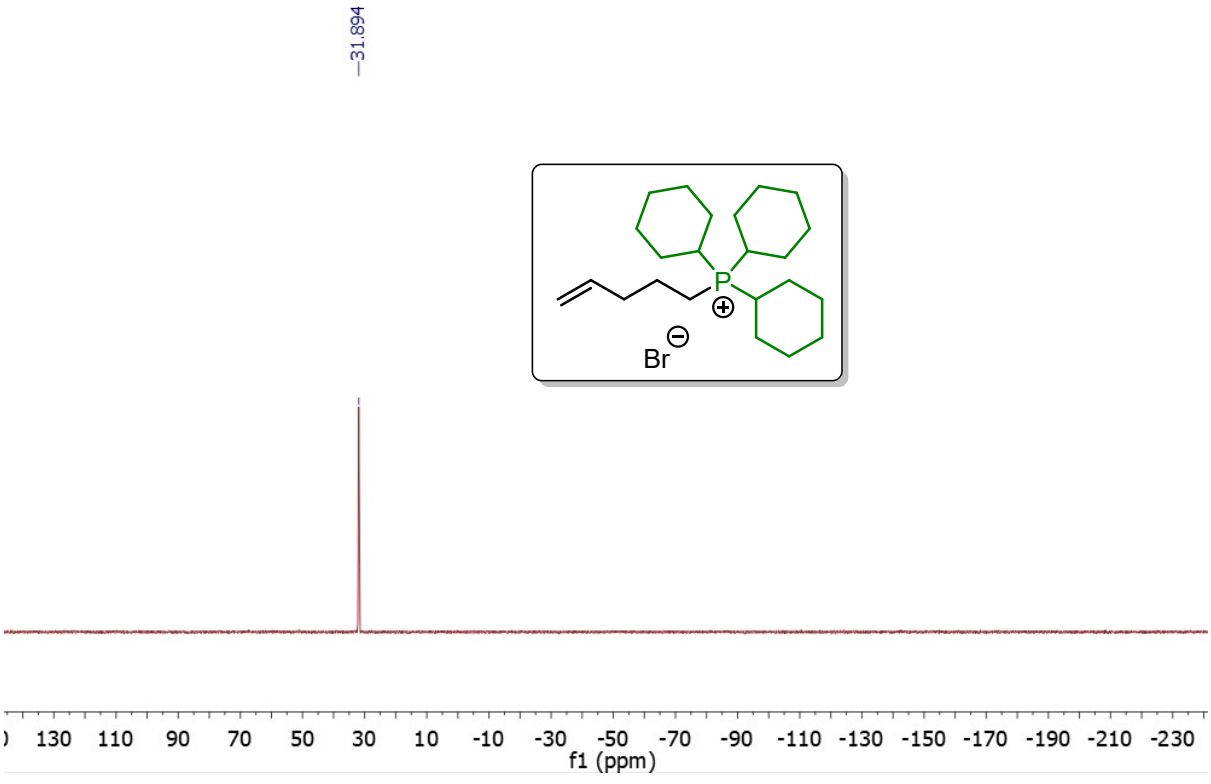


Figure S27: ^{31}P NMR of phosphonium salt ($CDCl_3$, 162 MHz).

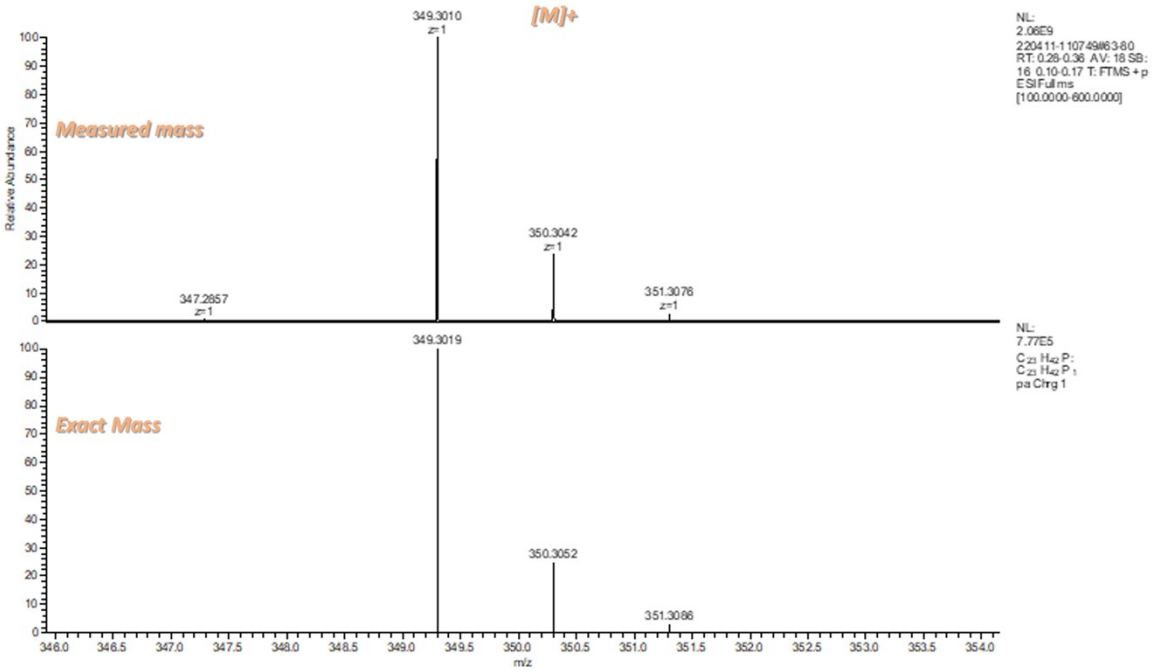
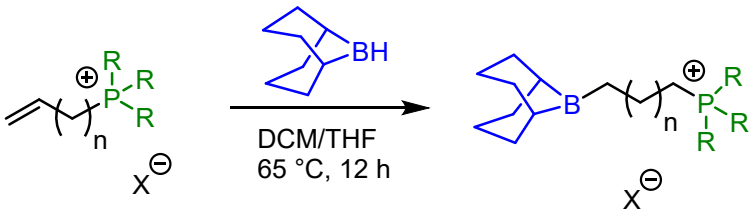


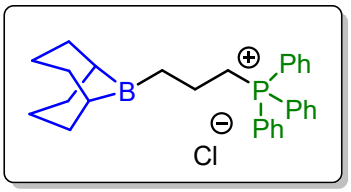
Figure S28: ESI-MS Spectrum of phosphonium salt.

General procedure for the synthesis of boron-phosphonium catalyst.

To an oven dried Schlenk flask equipped with stir bar was added the phosphonium salts (5.00 mmol, 1.00 equiv) in dichloromethane (10 mL) and 9-borabicyclo[3.3.1]nonane (9-BBN) in THF (0.5 M) (10.2 mL, 5.10 mmol, 1.02 equiv) was added via syringe under nitrogen. The reaction mixture was then heated to 65 °C for 12 h, followed by concentrated in vacuo to afford the crude solid product that was further purified by washing with dry pentane (3 x 10 mL) under argon atmosphere. The white solid product was dried for 5 h in vacuo.



Scheme S1: Synthesis of boron-phosphonium catalyst



Catalyst 1a. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.57 (m, 15H), 3.46-3.41 (m, 2H), 1.77-1.75 (m, 2H), 1.60-1.52 (m, 10H), 1.34-1.30 (m, 2H), 1.13-1.04 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 134.9 (d, J = 2.9 Hz), 133.4 (d, J = 8.9 Hz), 130.4 (d, J = 12.2 Hz), 118.9 (d, J = 87.0 Hz), 41.7, 32.8, 29.6, 26.9, 25.4, 25.0, 24.5, 23.8, 18.7. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 23.12.

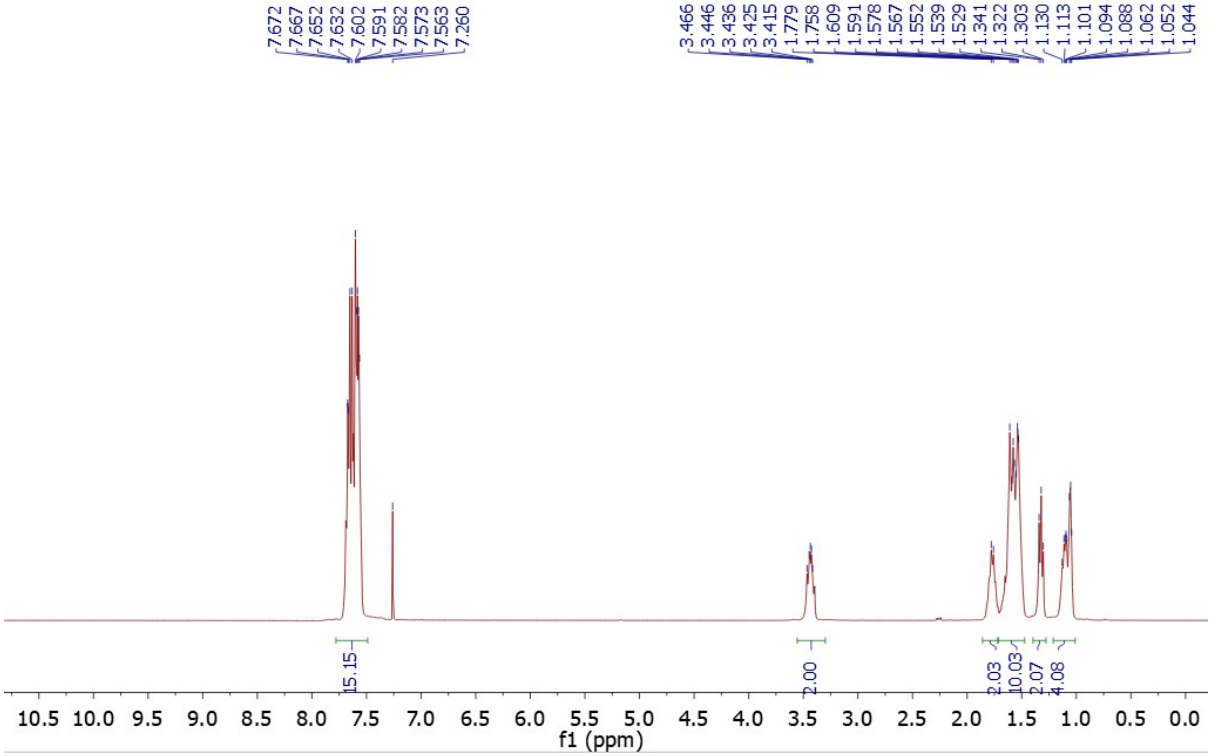


Figure S29: ^{1}H NMR of catalyst **1a** ($CDCl_3$, 400 MHz).

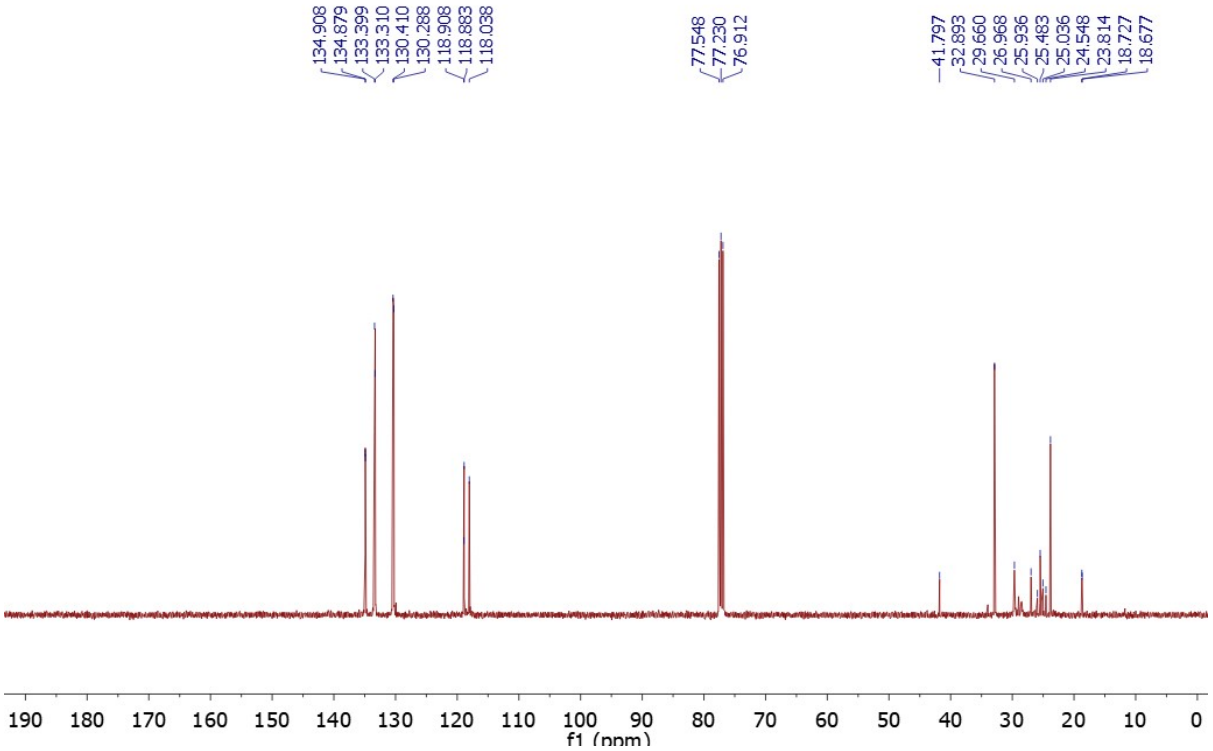


Figure S30: ^{13}C NMR of catalyst **1a** ($CDCl_3$, 100 MHz).

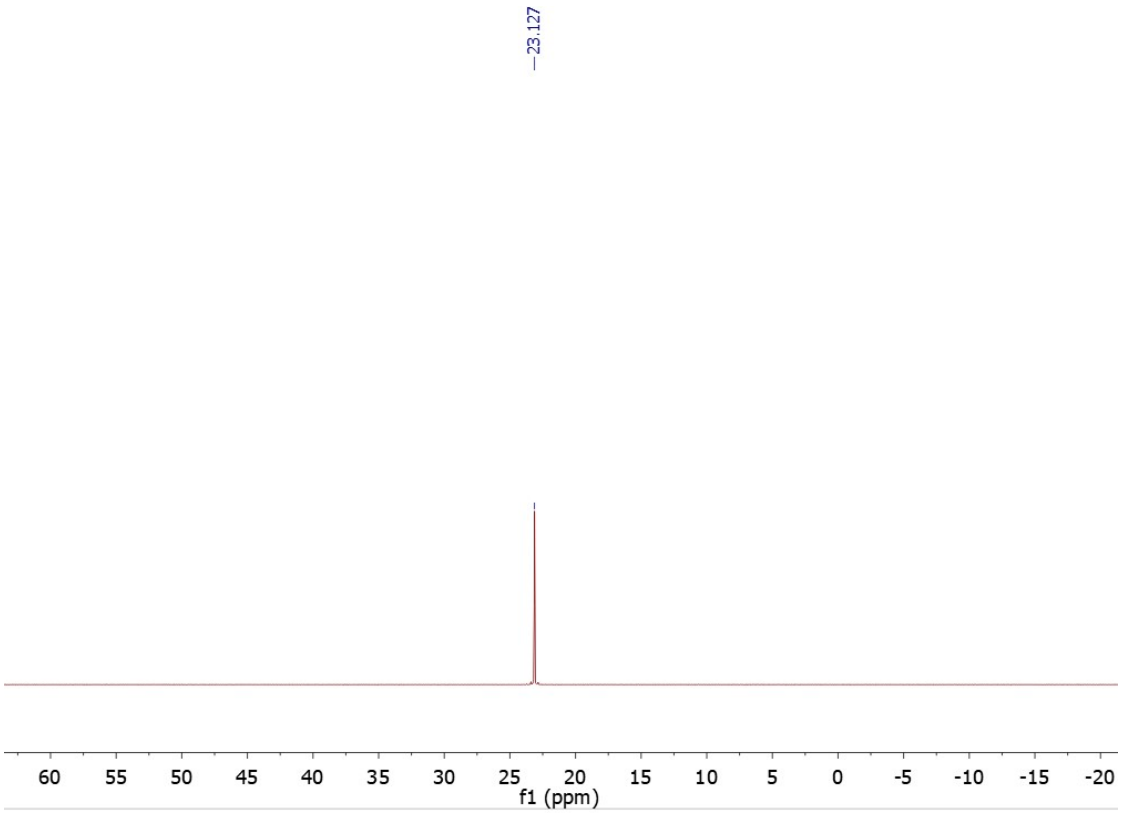
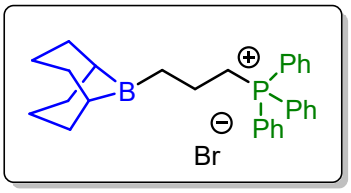


Figure S31: ^{31}P NMR of catalyst **1a** ($CDCl_3$, 162 MHz).



Catalyst 1b. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.62 (m, 15H), 3.58-3.51 (m, 2H), 1.82-1.78 (m, 2H), 1.71-1.58 (m, 10H), 1.46-1.42 (m, 2H), 1.19-1.12 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.0 (d, J = 3.0 Hz), 133.6 (d, J = 9.8 Hz), 130.5 (d, J = 12.3 Hz), 119.0 (d, J = 85.1 Hz), 33.0, 30.0, 28.7, 27.5, 26.8, 25.6, 25.1, 23.8, 18.7. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 23.31.

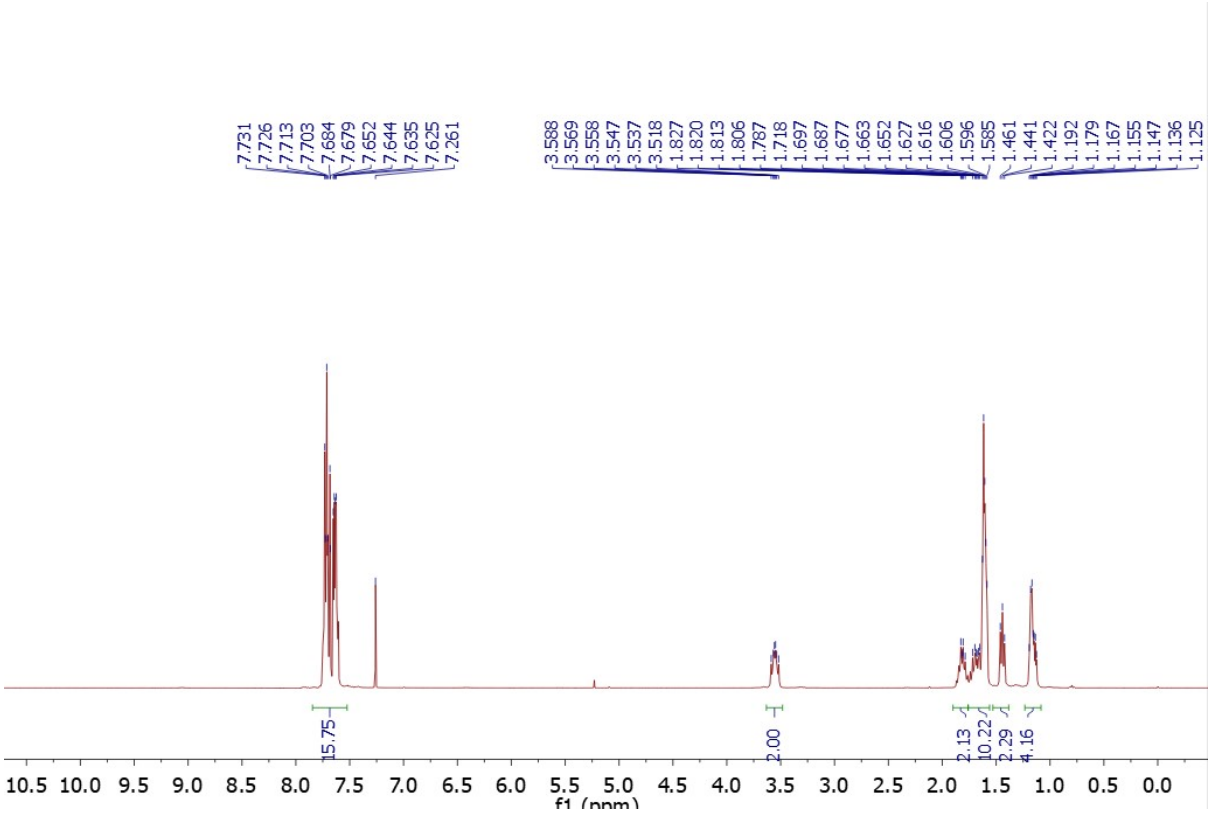


Figure S32: ^{1}H NMR of catalyst **1b** ($CDCl_3$, 400 MHz).

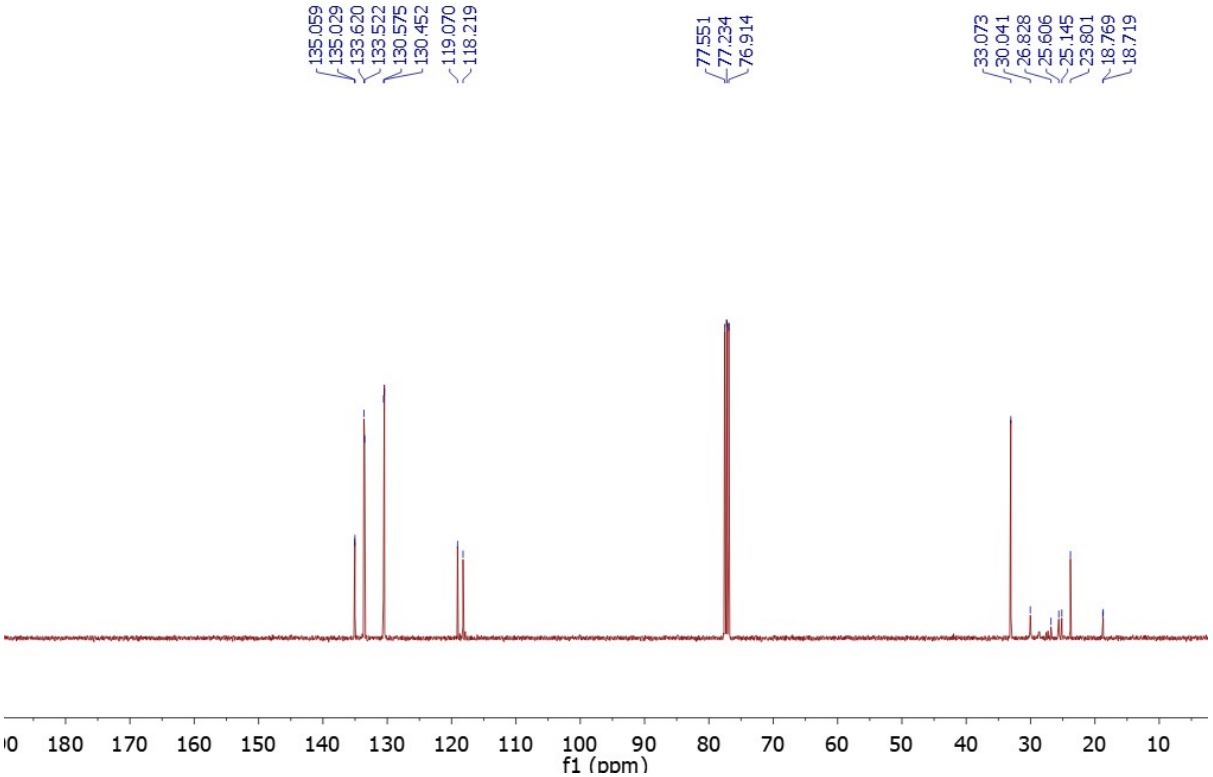


Figure S33: ^{13}C NMR of catalyst **1b** ($CDCl_3$, 100 MHz).

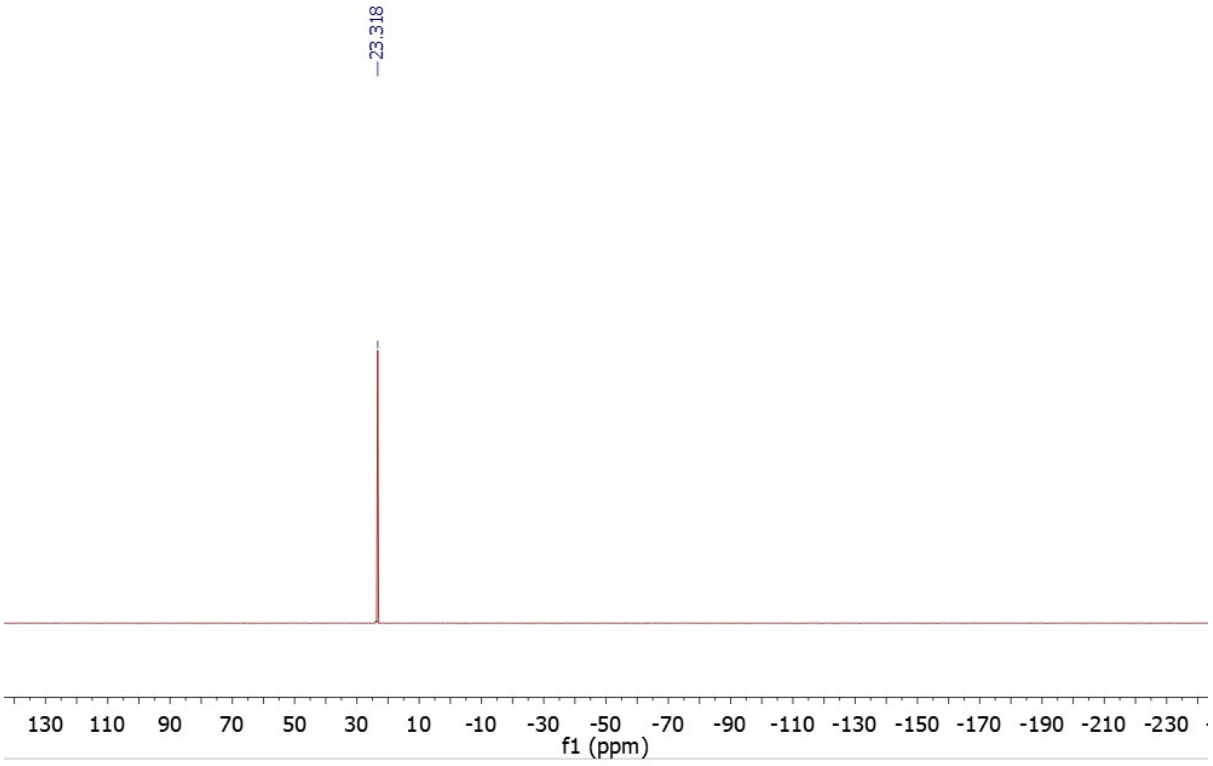
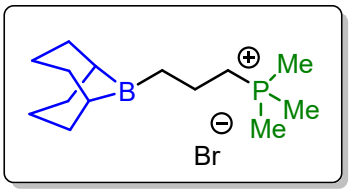


Figure S34: ^{31}P NMR of catalyst **1b** ($CDCl_3$, 162 MHz).



Catalyst 2. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55-2.47 (m, 2H), 2.23 (d, J = 14.4 Hz, 9H), 1.85-1.80 (m, 10H), 1.65-1.56 (m, 8H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 33.3, 31.1, 27.6, 27.4, 26.9, 26.8, 23.3, 9.4, 8.9. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 26.26.

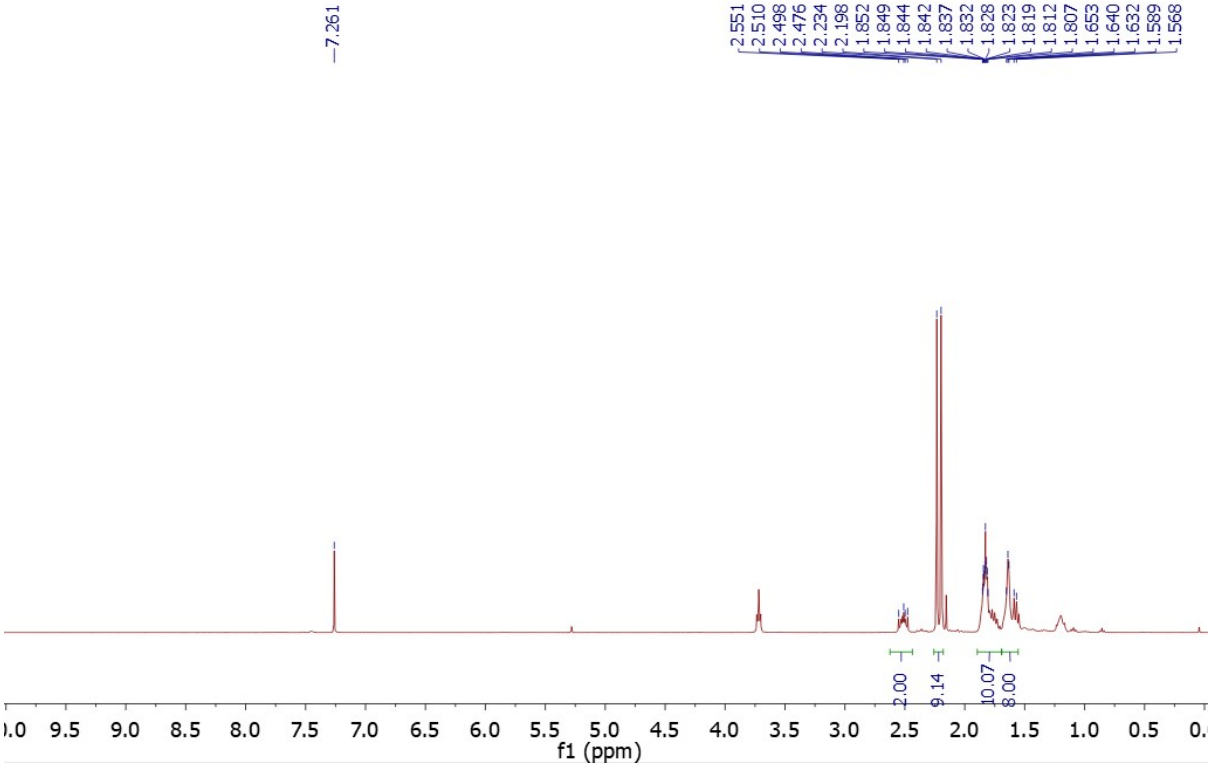


Figure S35: ^{1}H NMR of catalyst **2** ($CDCl_3$, 400 MHz).

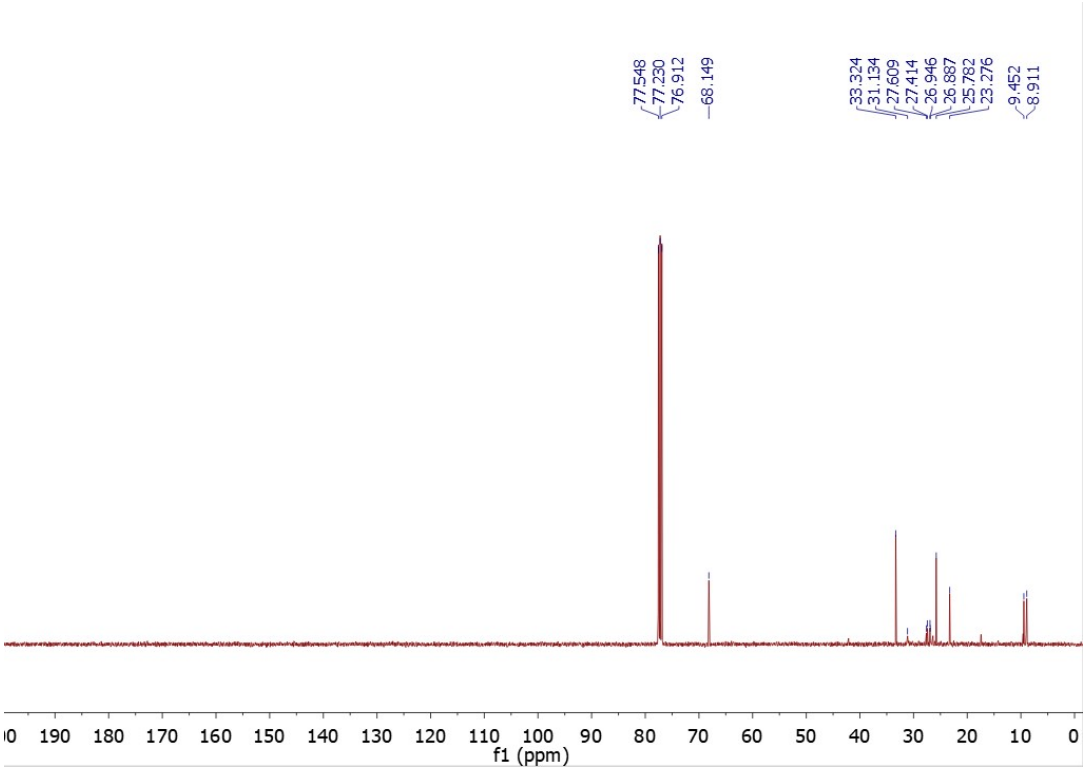


Figure S36: ^{13}C NMR of catalyst **2** ($CDCl_3$, 100 MHz).

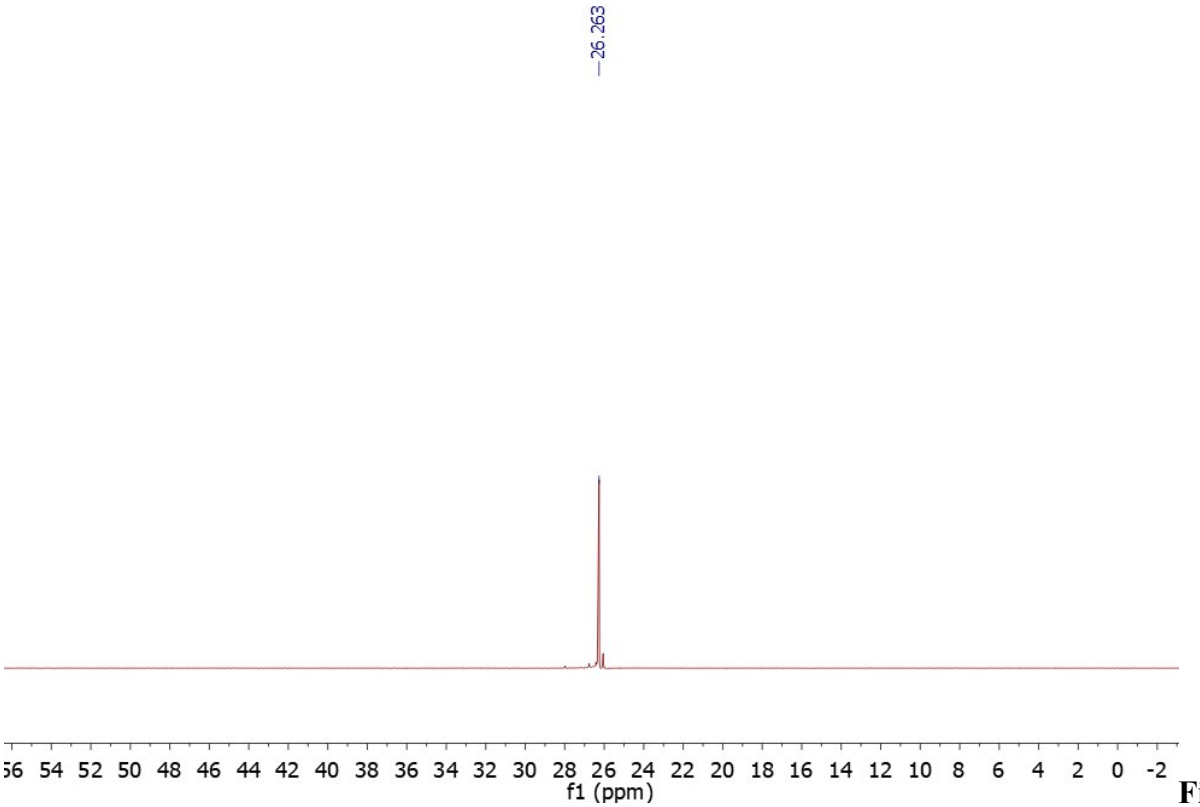
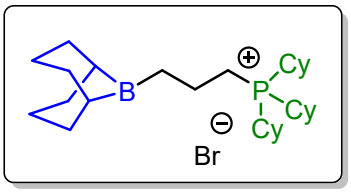


Figure S37: ^{31}P NMR of catalyst **2** ($CDCl_3$, 162 MHz).



Catalyst 4. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55-2.46 (m, 3H), 2.39-2.35 (m, 2H), 1.99-1.77 (m, 27H), 1.57-1.27 (m, 21H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 34.4, 30.3, 30.2, 29.9, 27.4, 26.7, 25.6, 24.1, 19.1, 18.7. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 31.36.

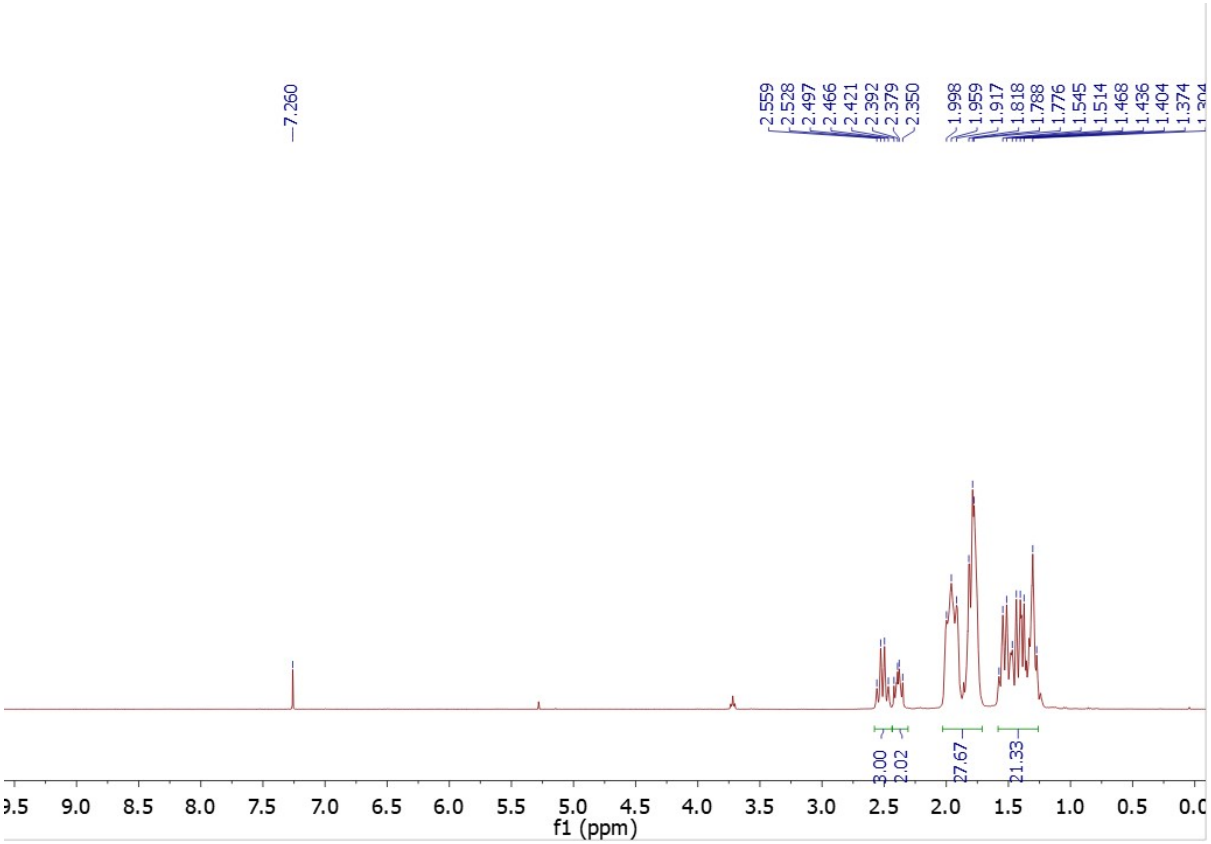


Figure S38: ^{1}H NMR of catalyst **4** ($CDCl_3$, 400 MHz).

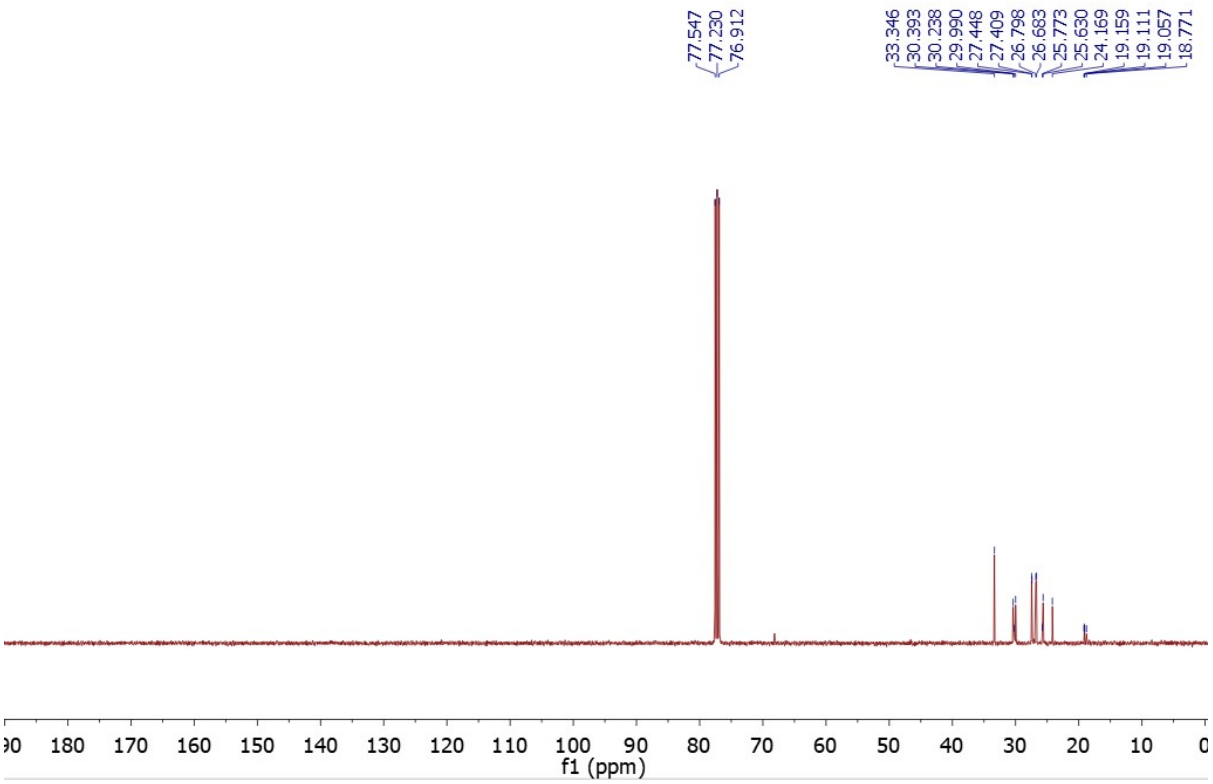


Figure S39: ^{13}C NMR of catalyst **4** ($CDCl_3$, 100 MHz).

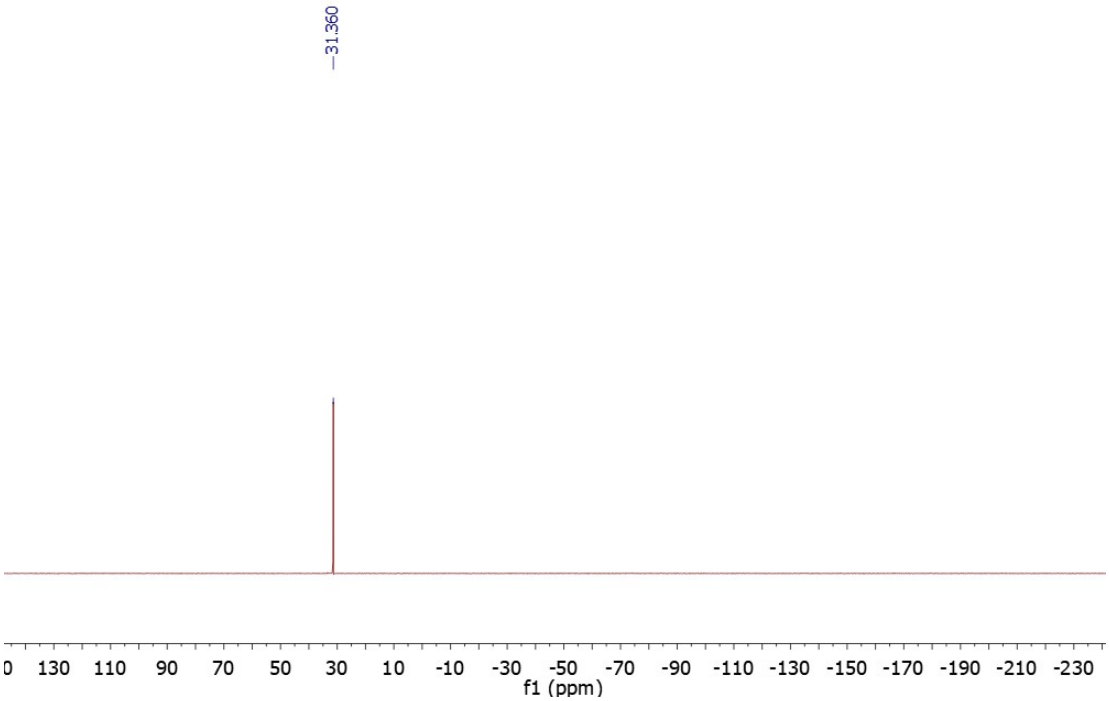
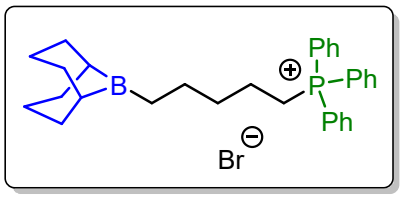


Figure S40: ^{31}P NMR of catalyst **4** ($CDCl_3$, 162 MHz).



Catalyst 5. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.69 (m, 15H), 3.86-3.84 (m, 2H), 1.82-1.78 (m, 2H), 1.79-1.58 (m, 16H), 1.47-1.43 (m, 2H), 1.29-1.27 (m, 2H), 1.15-1.14 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.0 (d, J = 3.2 Hz), 133.5 (d, J = 9.9 Hz), 130.5 (d, J = 12.3 Hz), 118.5 (d, J = 85.4 Hz), 41.8, 34.0, 32.4, 32.2, 27.2, 27.0, 26.5, 25.5, 23.0, 22.0, 13.5. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 24.24.

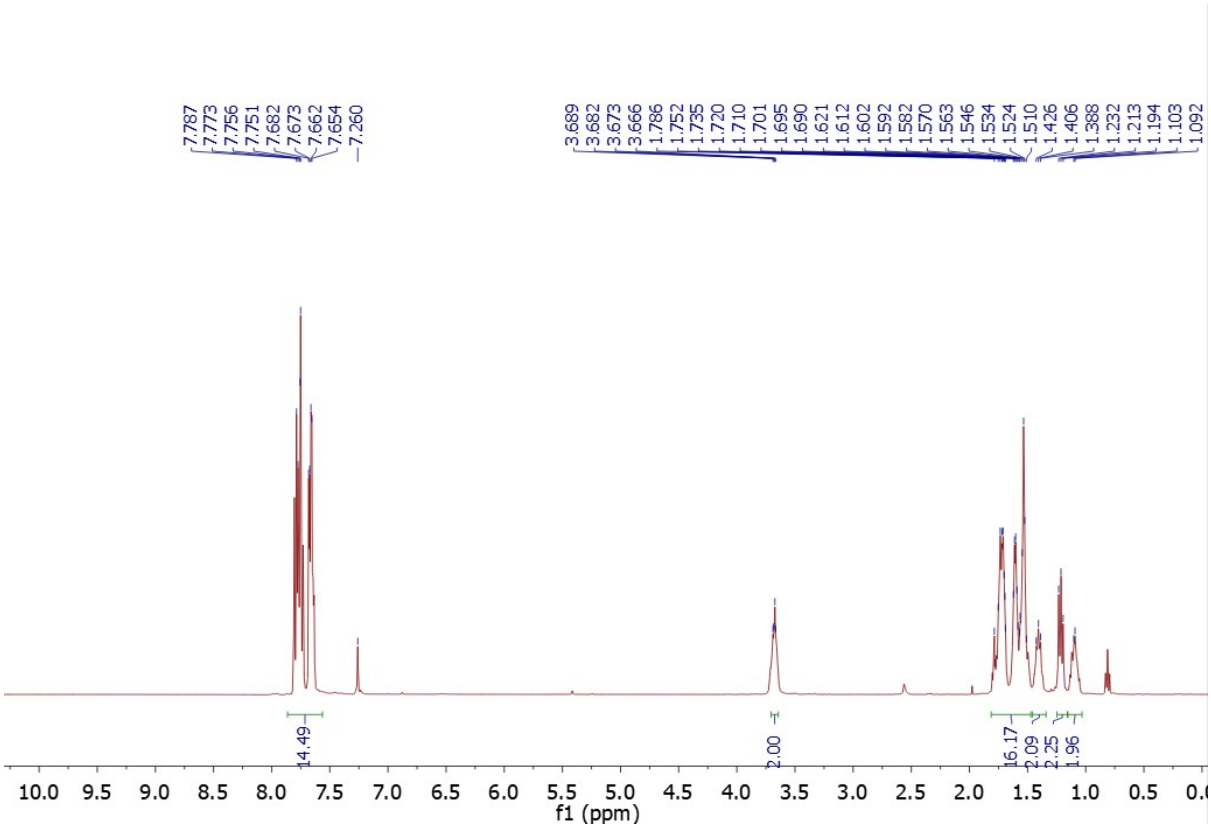


Figure S41: ^{1}H NMR of catalyst **5** ($CDCl_3$, 400 MHz).

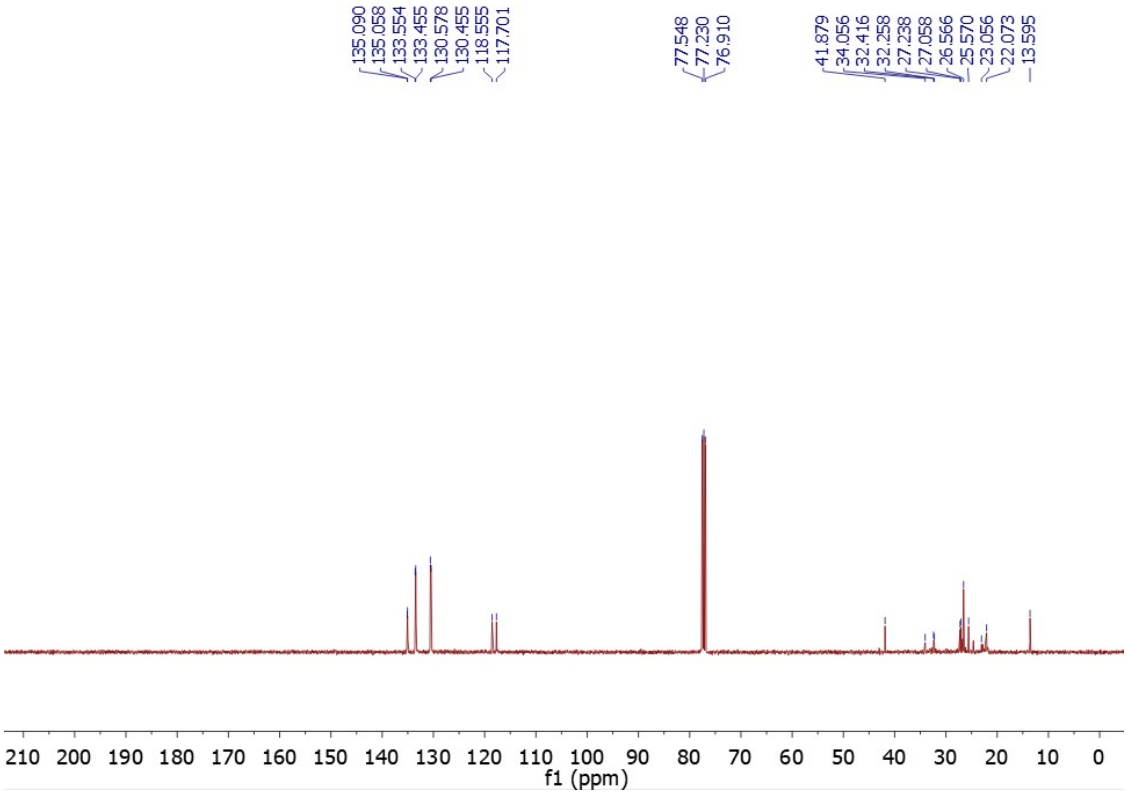


Figure S42: ^{13}C NMR of catalyst **5** ($CDCl_3$, 100 MHz).

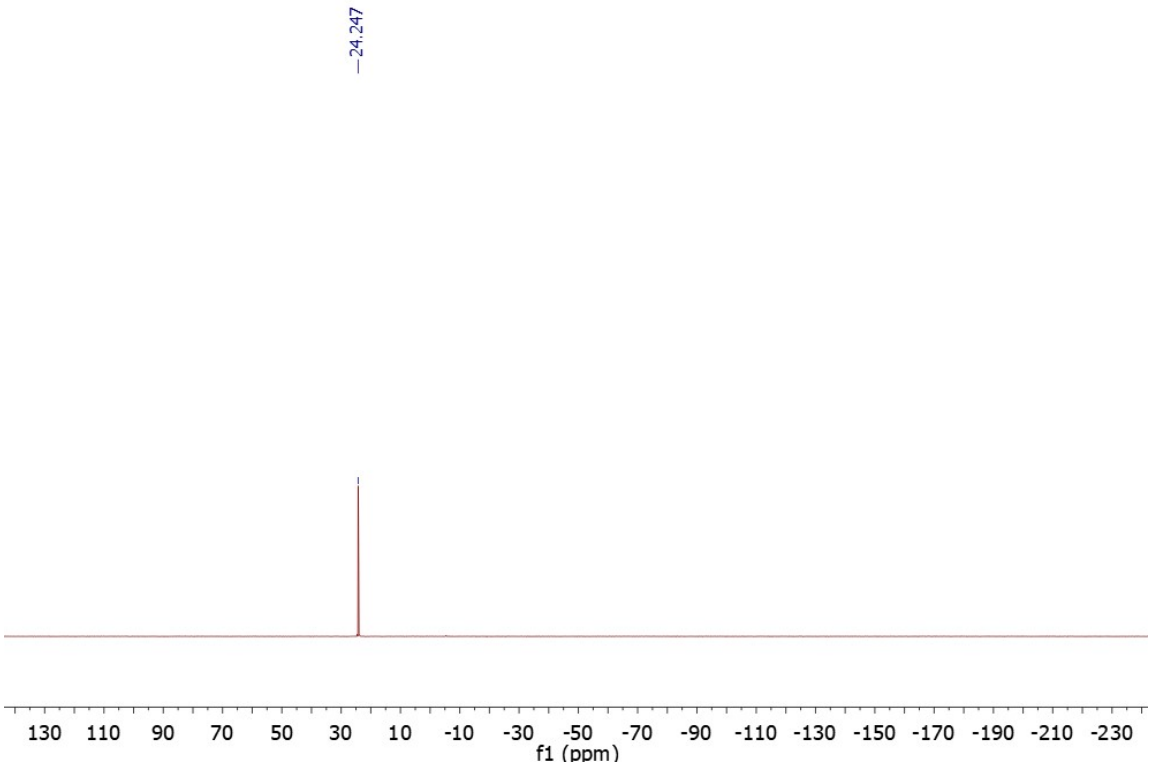
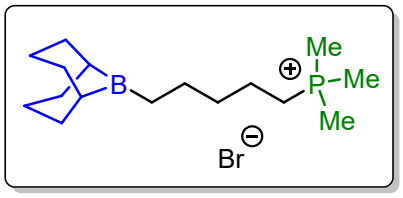


Figure S43: ^{31}P NMR of catalyst **5** ($CDCl_3$, 162 MHz).



Catalyst 6. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45-2.43 (m, 2H), 2.23 (d, J = 14.0 Hz, 9H), 1.86-1.80 (m, 5H), 1.67-1.48 (m, 12H), 1.37-1.19 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 33.3, 32.5, 32.4, 29.8, 27.5, 27.3, 26.8, 23.2, 22,7, 21.4, 20.6,19.4, 13.8, 9.1, 8.6. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 27.11.

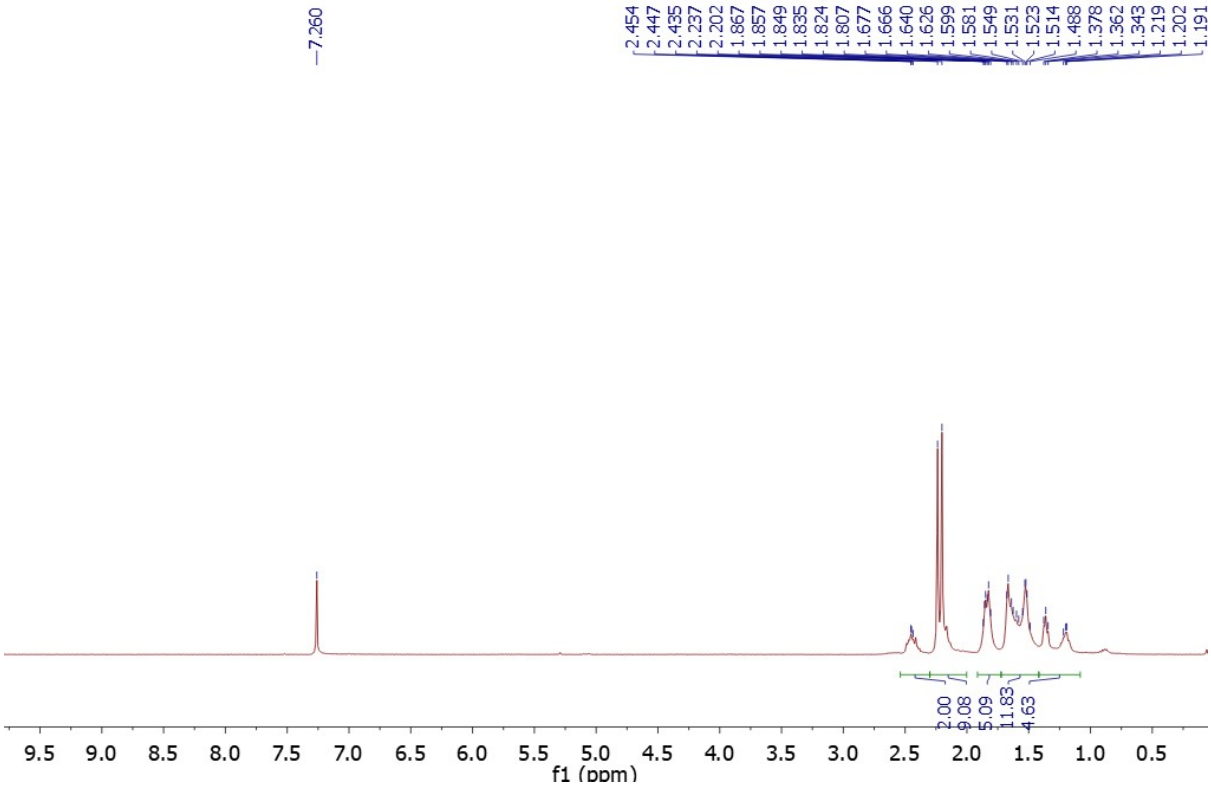


Figure S44: ^{1}H NMR of catalyst **6** ($CDCl_3$, 400 MHz).

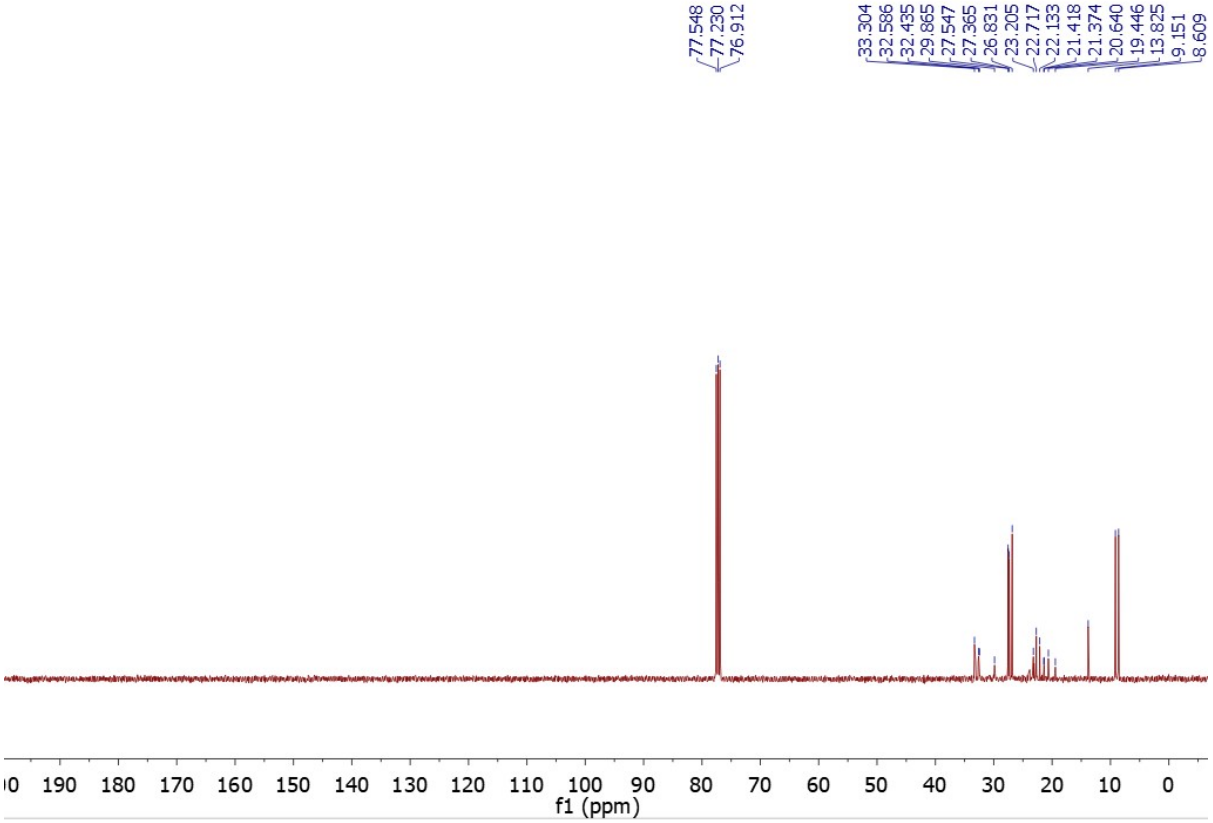


Figure S45: ^{13}C NMR of catalyst **6** ($CDCl_3$, 100 MHz).

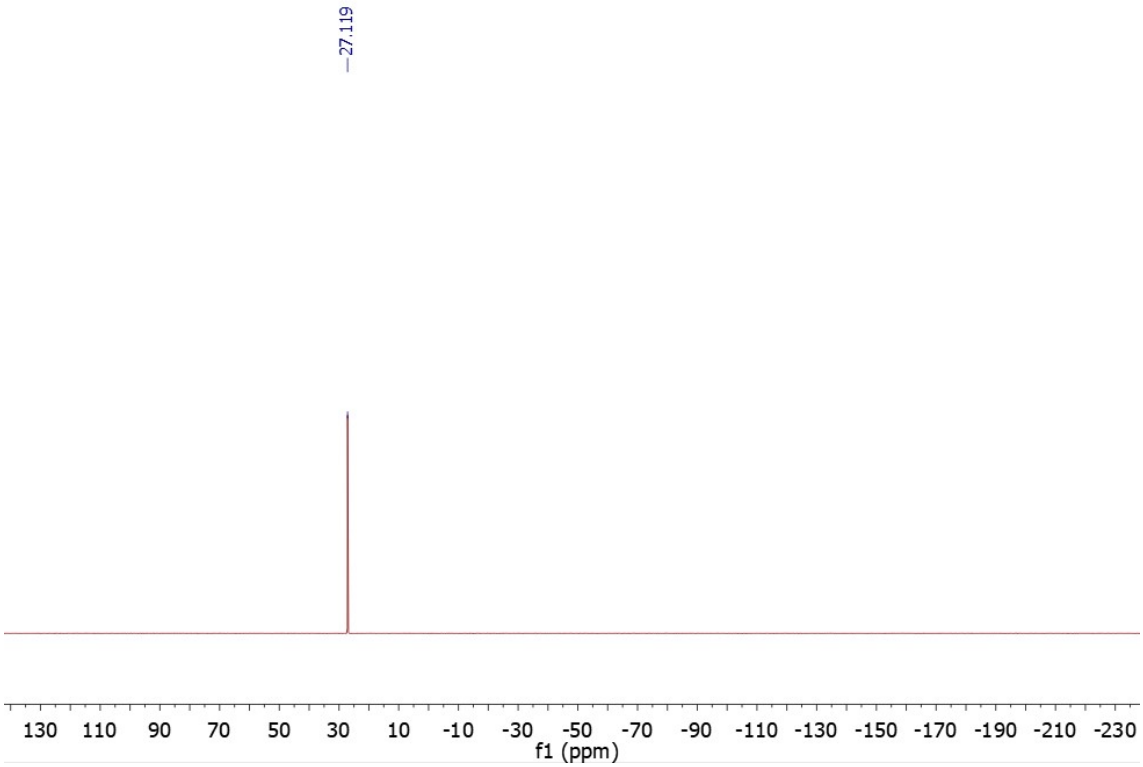
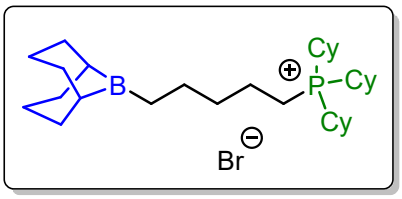


Figure S46: ^{31}P NMR of catalyst **6** ($CDCl_3$, 162 MHz).



Catalyst 7. White Solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73-2.70 (m, 3H), 2.48-2.47 (m, 2H), 2.02-1.83 (m, 23H), 1.67-1.53 (m, 24H), 1.49-1.24 (m, 5H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 34.4, 33.3, 33.2, 30.2, 29.8, 27.4, 27.3, 26.6, 26.5, 25.5, 24.2, 23.3, 16.1, 15.7. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 31.68.

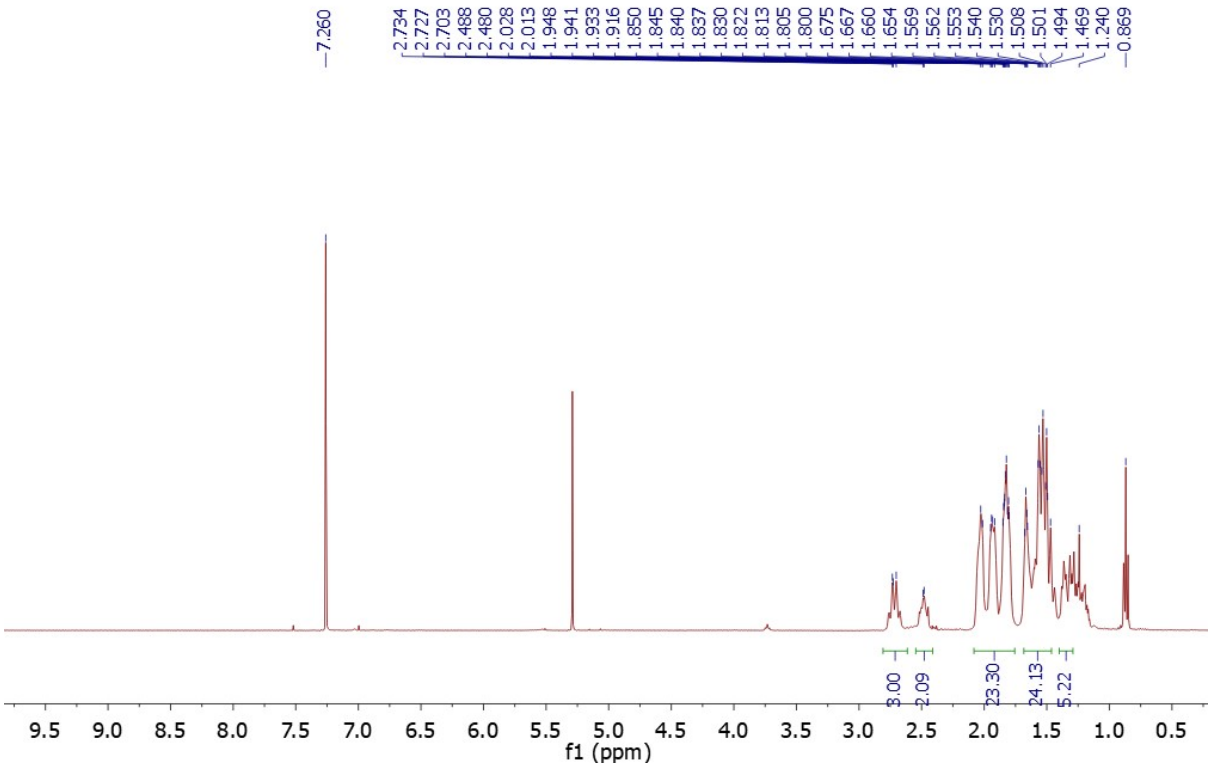


Figure S47: ^{1}H NMR of catalyst **7** ($CDCl_3$, 400 MHz).

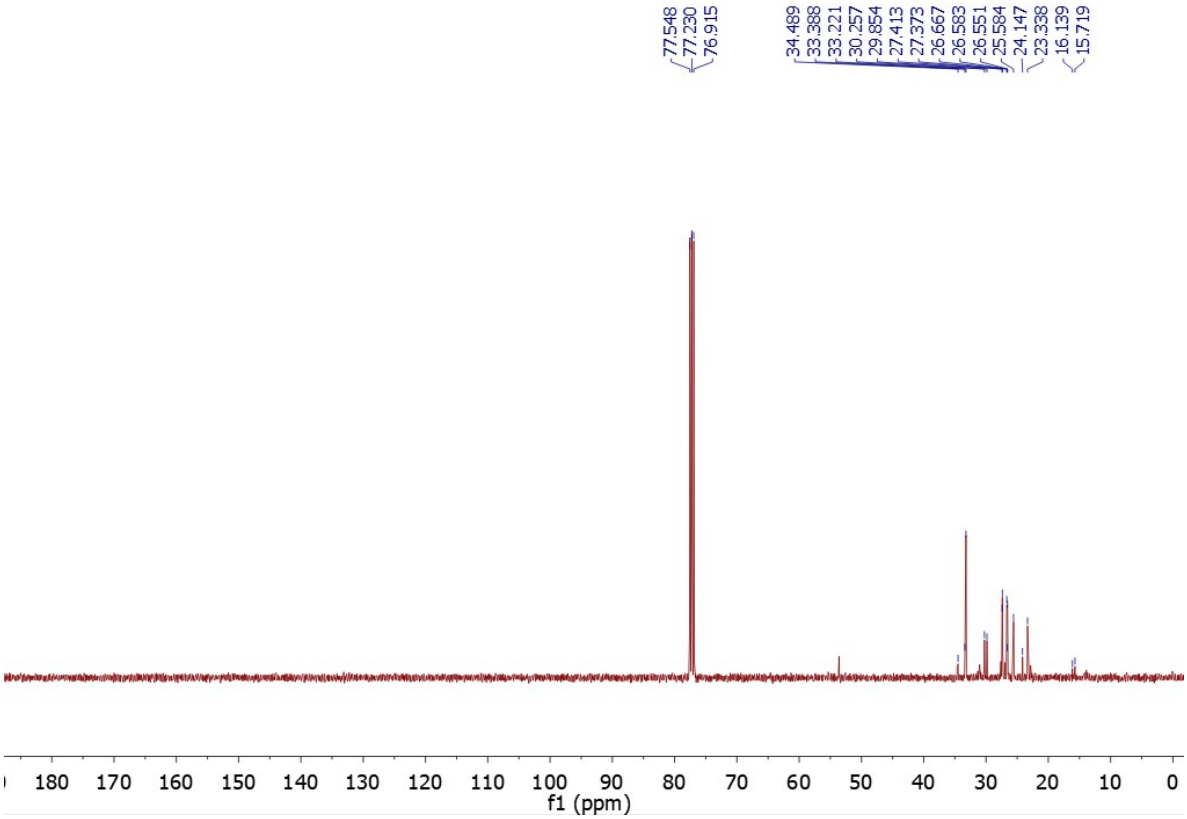


Figure S48: ^{13}C NMR of catalyst **7** ($CDCl_3$, 100 MHz).

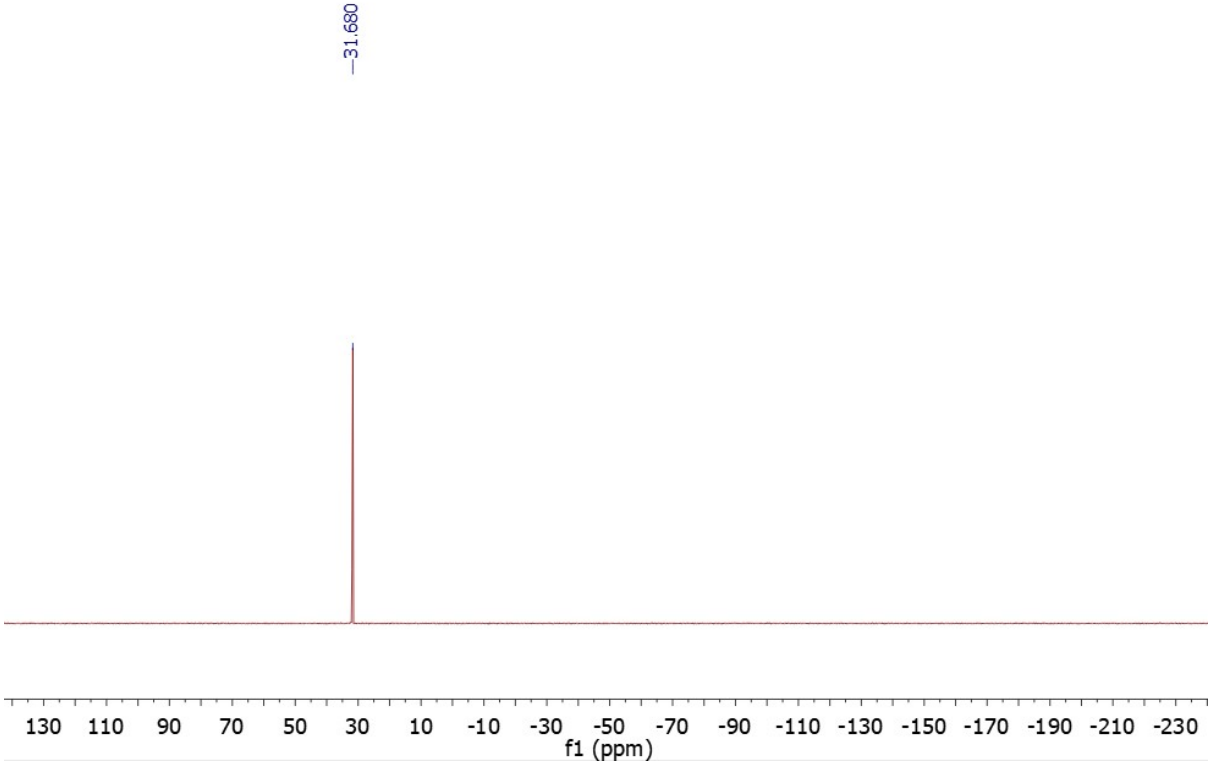


Figure S49: ^{31}P NMR of catalyst **7** ($CDCl_3$, 162 MHz).

Video 1: Comparision of the stability of ammonium and phosphonium based organocatalysts

Procedure for the copolymerization of epoxide and CO_2:

In a glovebox, a catalyst **1-7** and epoxide placed in a 15 mL stainless steel reactor equipped with magnetic stirrer under an argon atmosphere. The reactor was pressurized to 15 bar by CO_2 and heated the desired temperature. The reaction mixture was stirred for appropriate time, then the autoclave was cooled room temperature and excess CO_2 vented and quenched acidic methanolic solution (4 drops of conc. HCl/50 mL MeOH). Conversion of epoxide was determined by ^1H NMR analysis. Then, the pure polymer was obtained by precipitation from methanol and subsequently dried under vacuum for overnight.

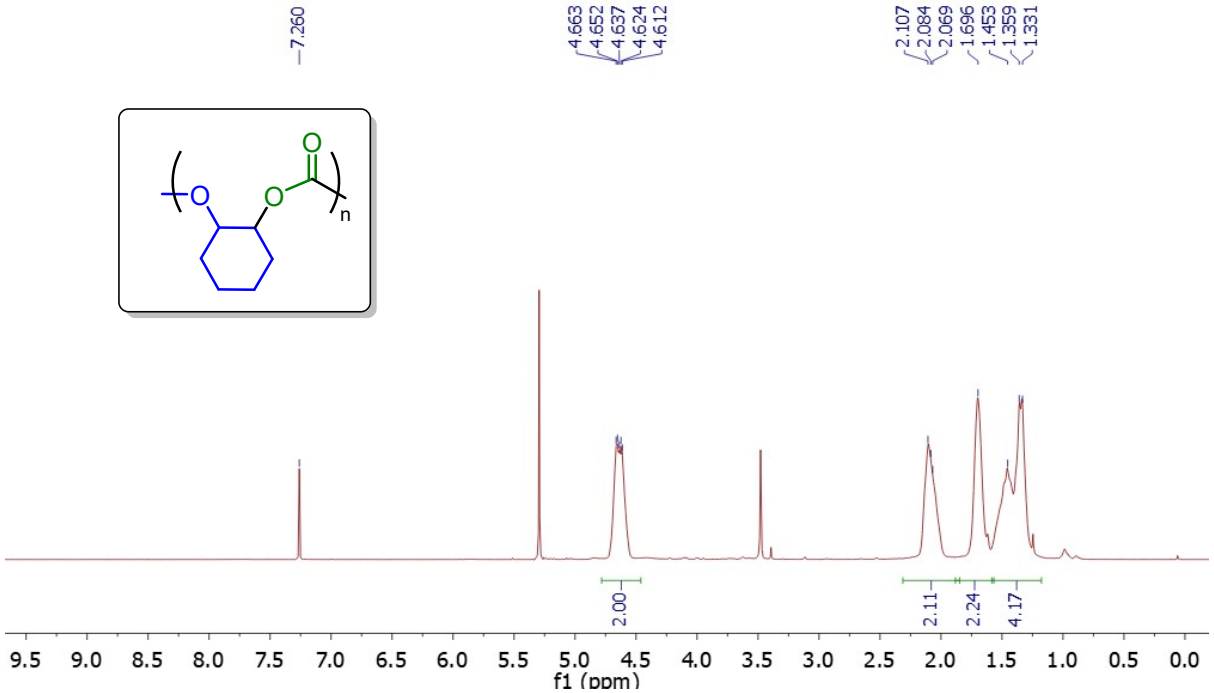


Figure S50: Representative ^{1}H NMR of copolymerization of cyclohexene oxide and CO_2 using catalyst **1b** ($CDCl_3$, 400 MHz) .

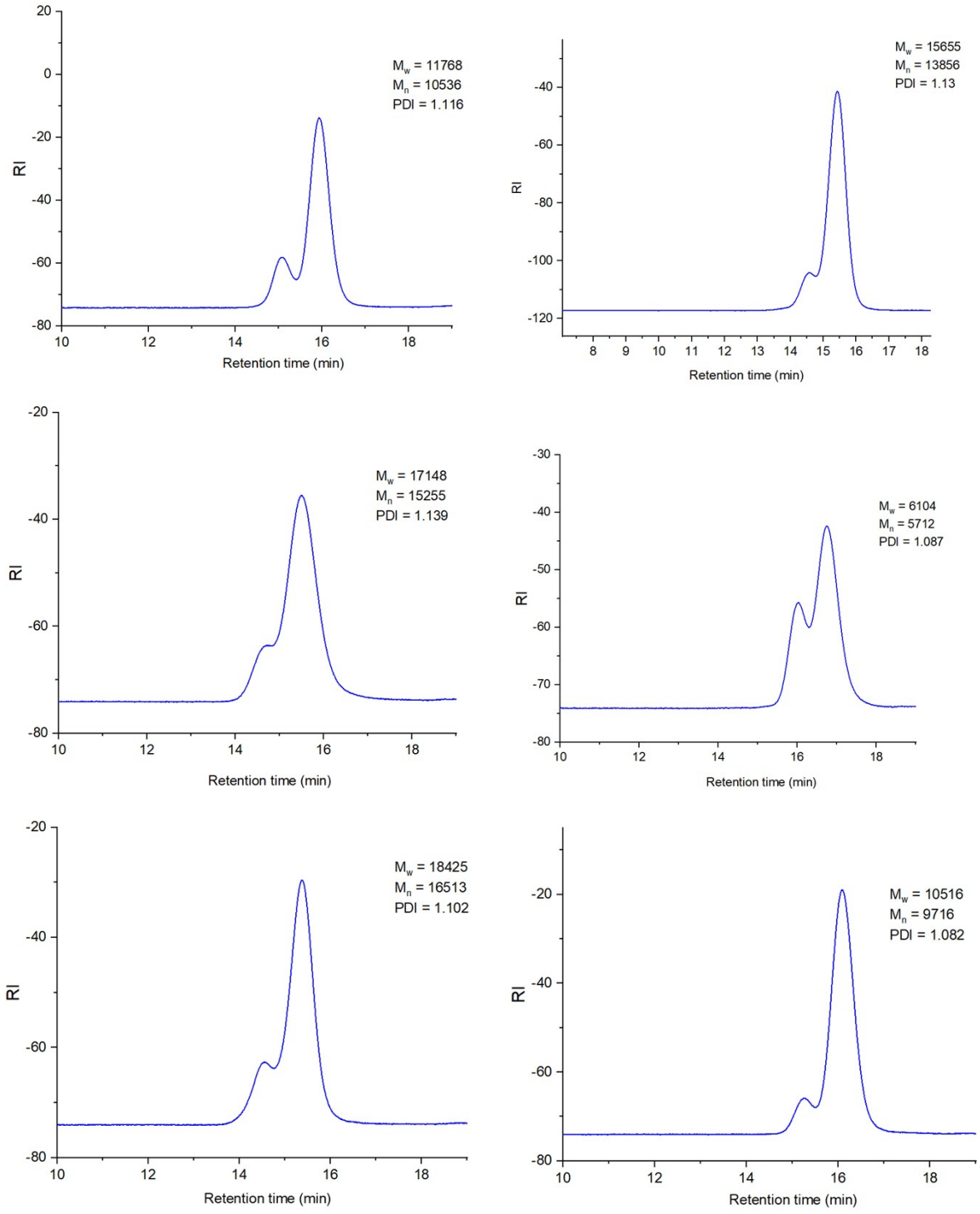


Figure S51: Representative GPC traces of PCHCs in Table 2.

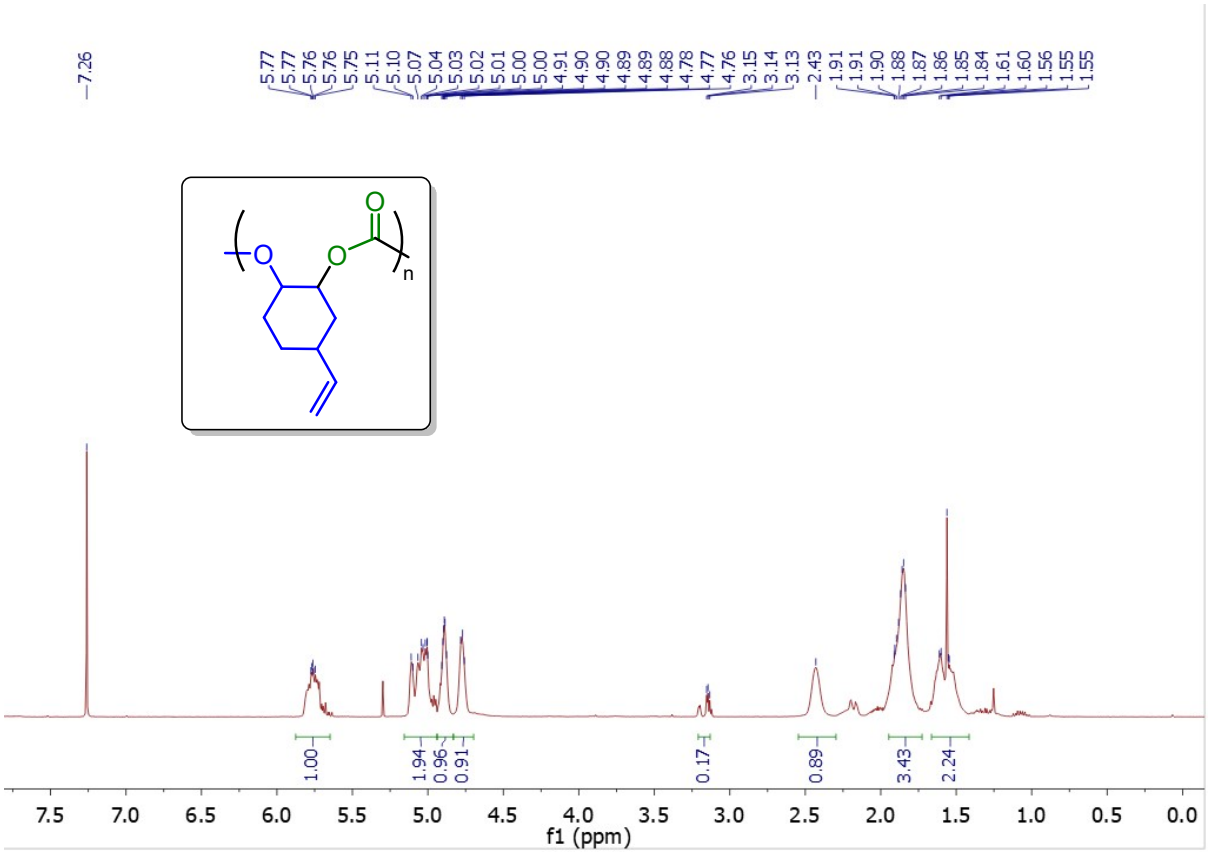


Figure S52: ^{1}H NMR of vinyl cyclohexene oxide and CO_2 using catalyst **1b** ($CDCl_3$, 400 MHz).

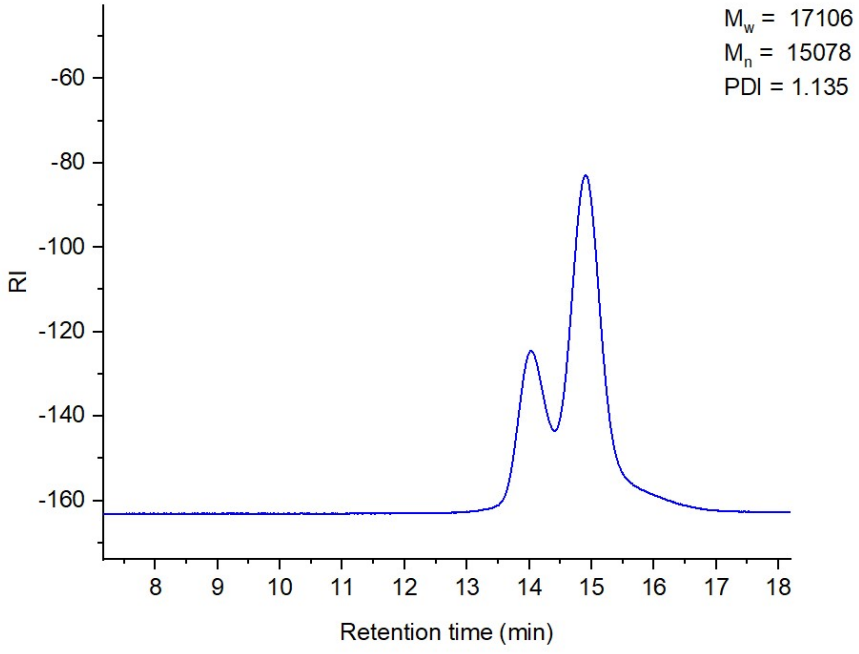


Figure S53: GPC of vinyl cyclohexene polycarbonate (PVCHC).

Procedure for the synthesis of cyclic carbonates:

In a glovebox, a catalyst **1b** and epoxide and 0.8 mL solvent (CH_2Cl_2: toluene, 1:1 v/v) were placed in a 15 mL stainless steel reactor equipped with magnetic stirrer under an argon atmosphere. The reactor was pressurized to 15 bar by CO_2 and heated the desired temperature. The reaction mixture was stirred for appropriate time, then the autoclave was cooled room temperature and excess CO_2 vented. Conversion of epoxide was determined by ^1H NMR analysis.

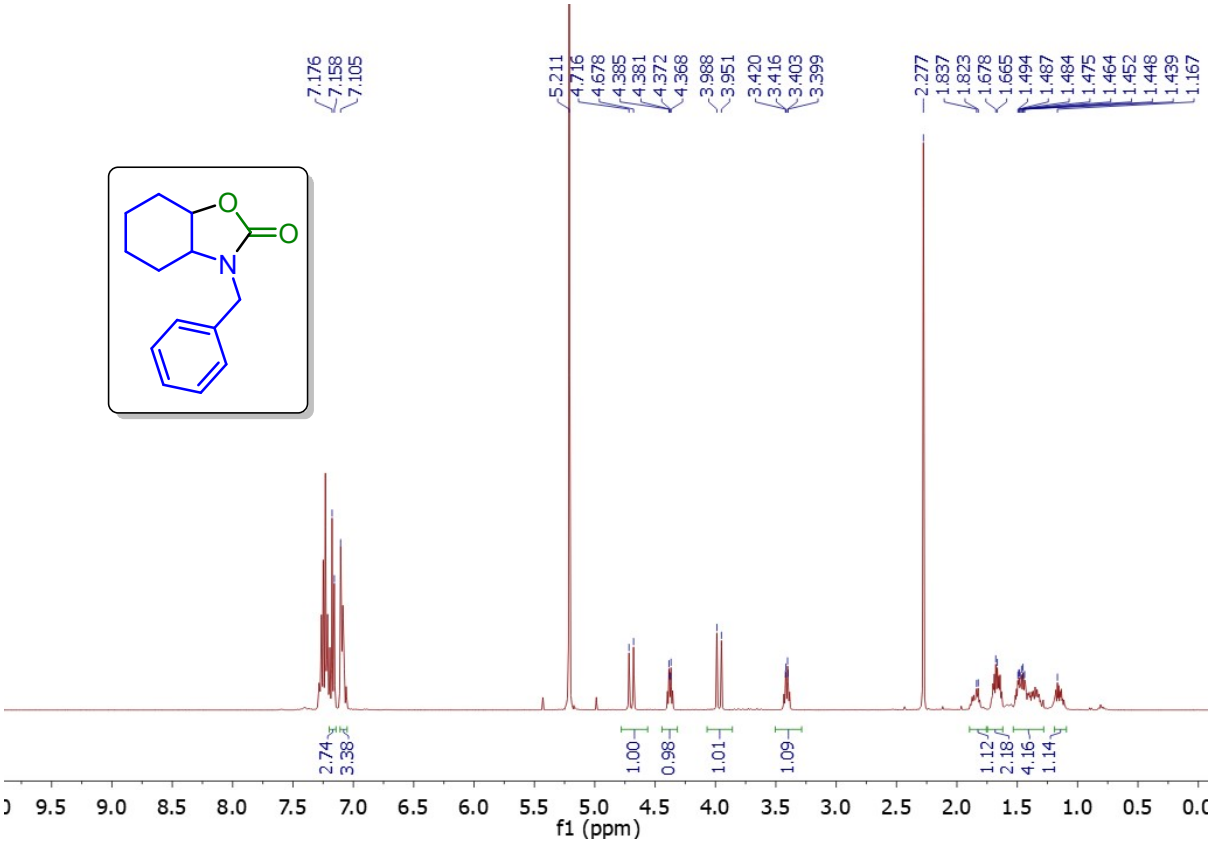


Figure S54: ^1H NMR of cyclohexane derived aziridine and CO_2 using catalyst **1b** ($CDCl_3$, 400 MHz).

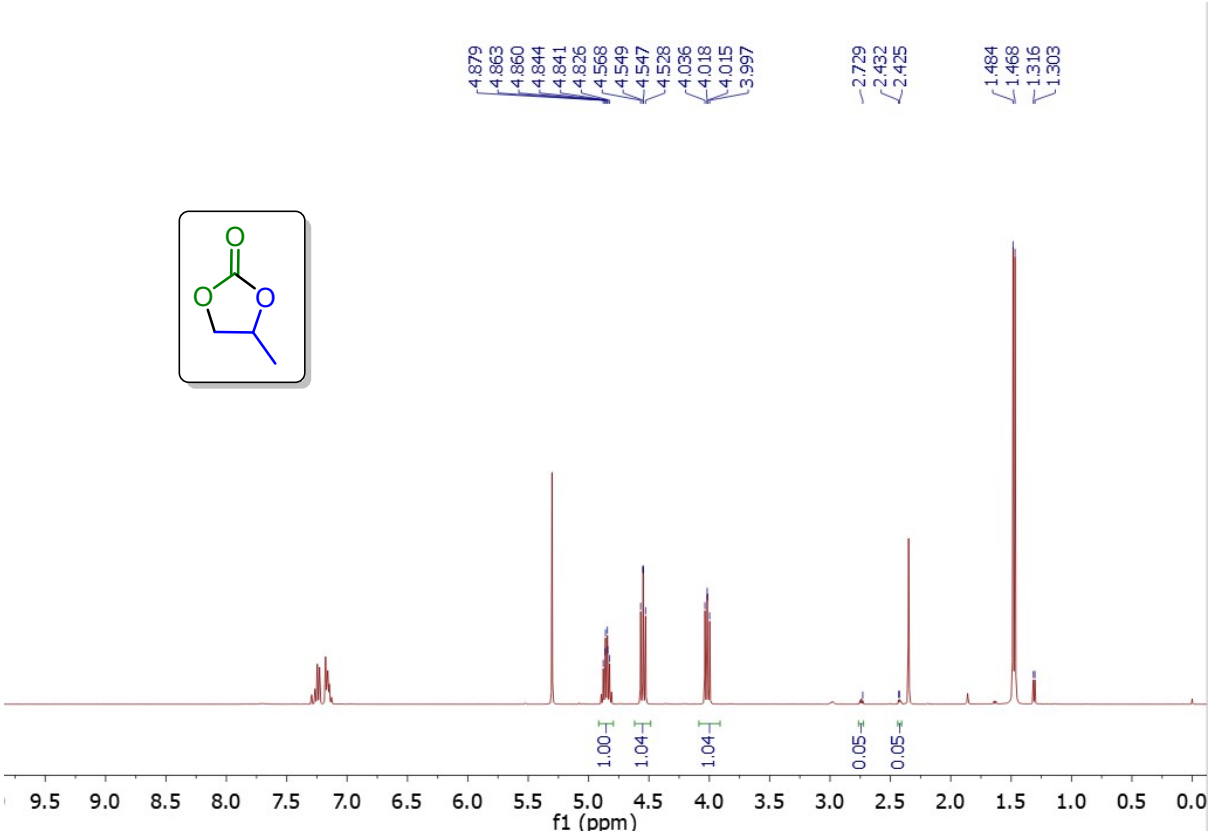


Figure S54: ^{1}H NMR of propylene oxide and CO_2 using catalyst **1b** ($CDCl_3$, 400 MHz).

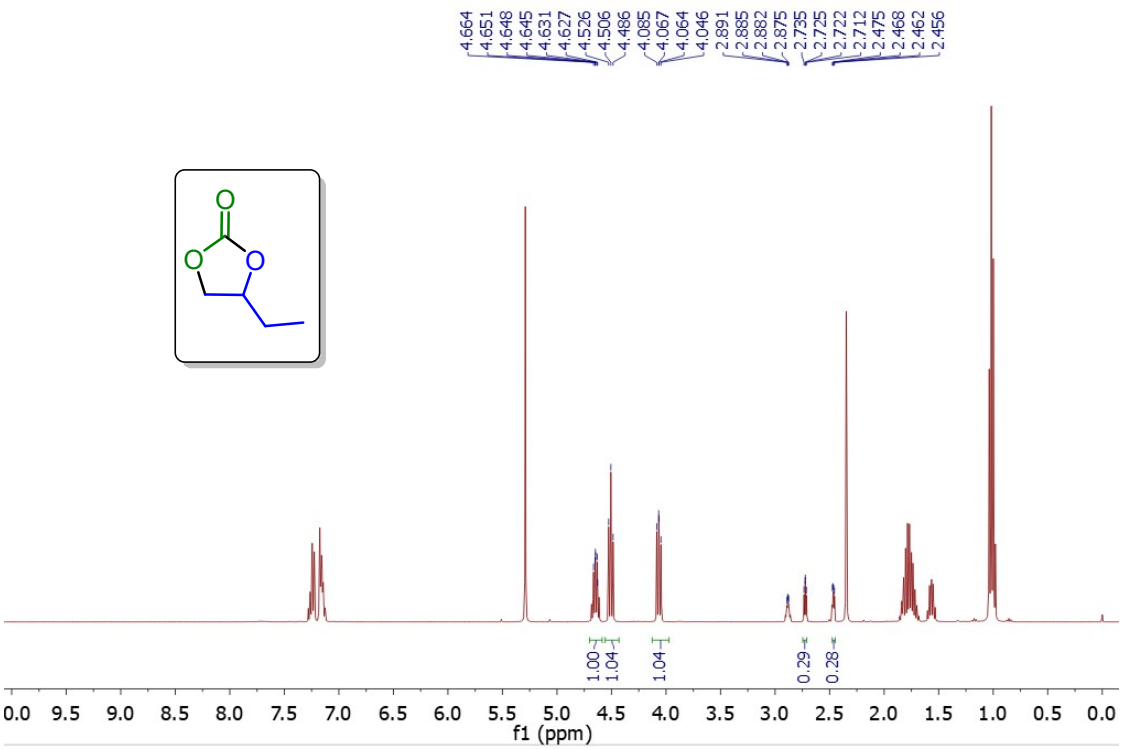


Figure S55: ^{1}H NMR of butene oxide and CO_2 using catalyst **1b** ($CDCl_3$, 400 MHz).

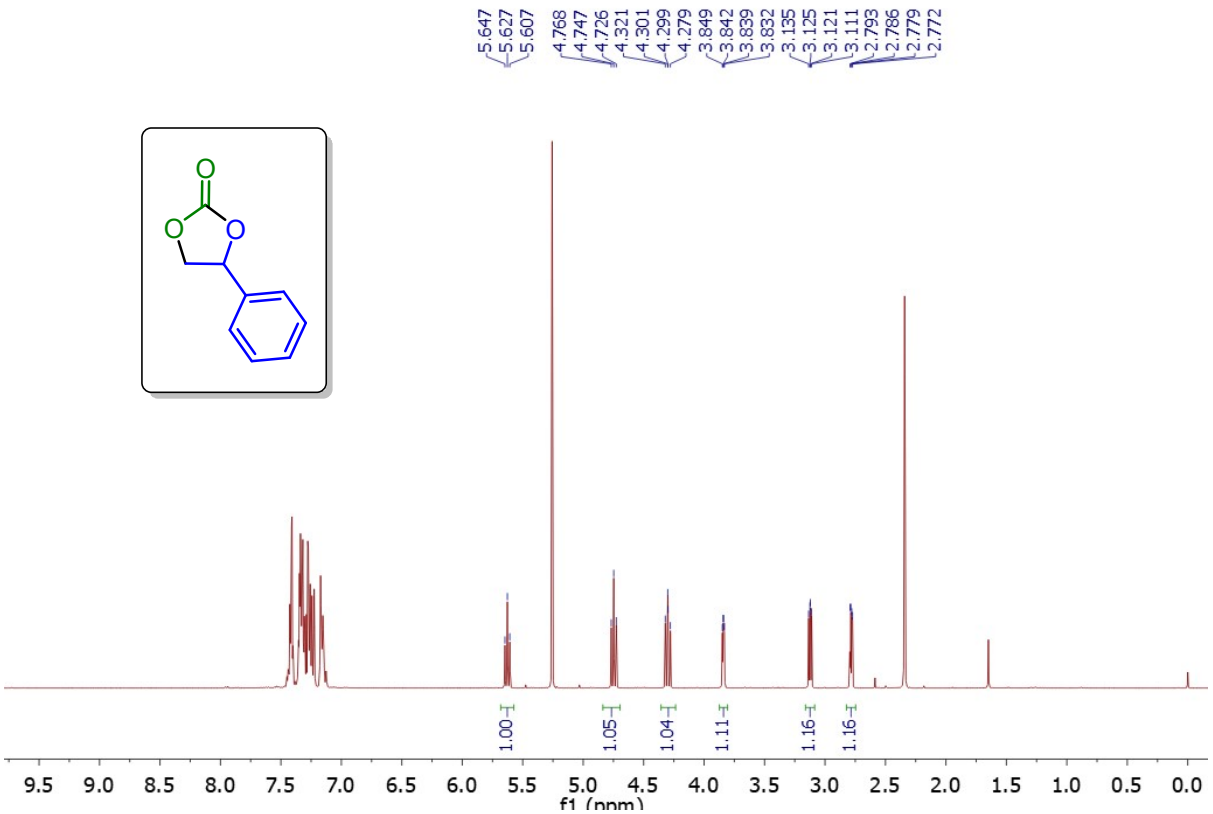


Figure S56: ^{1}H NMR of styrene oxide and CO_2 using catalyst **1b** ($CDCl_3$, 400 MHz).

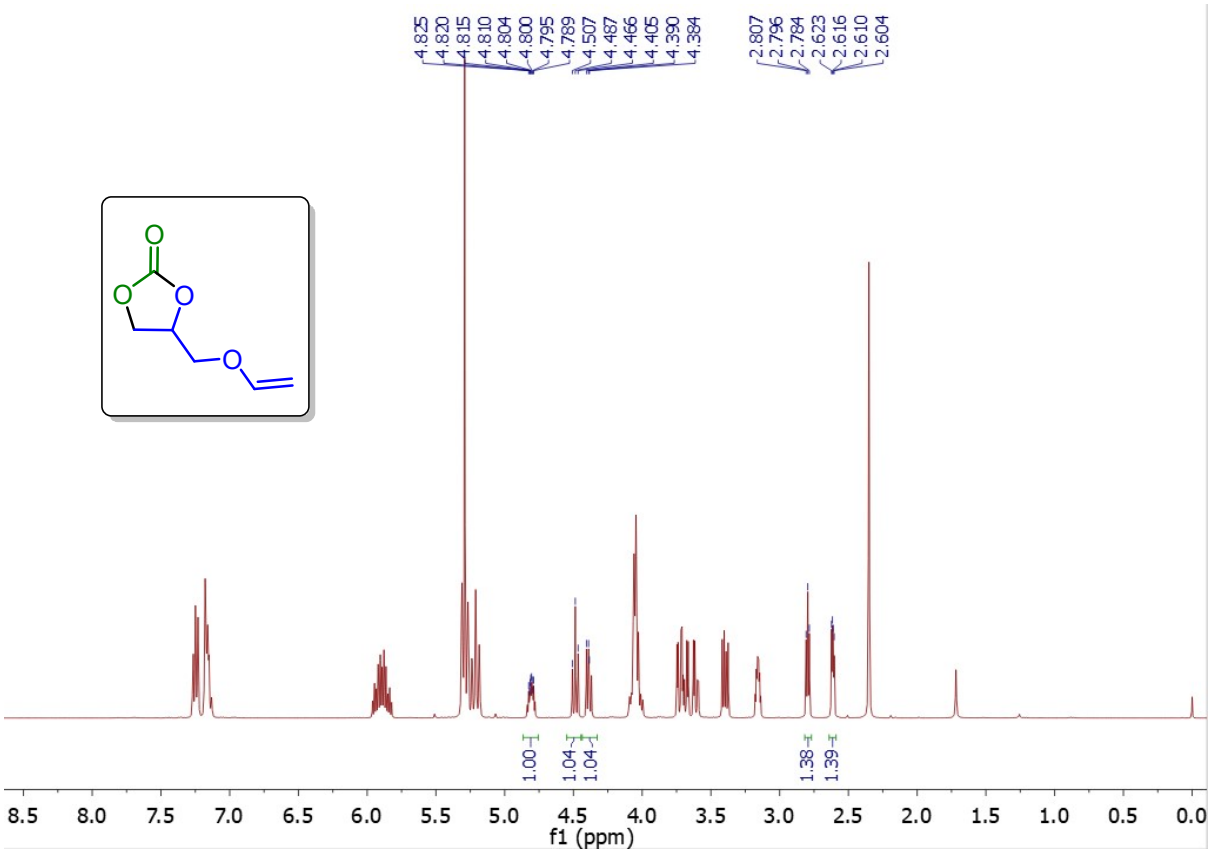


Figure S57: ^{1}H NMR of allyl glycidyl ether and CO_2 using catalyst **1b** ($CDCl_3$, 400 MHz).

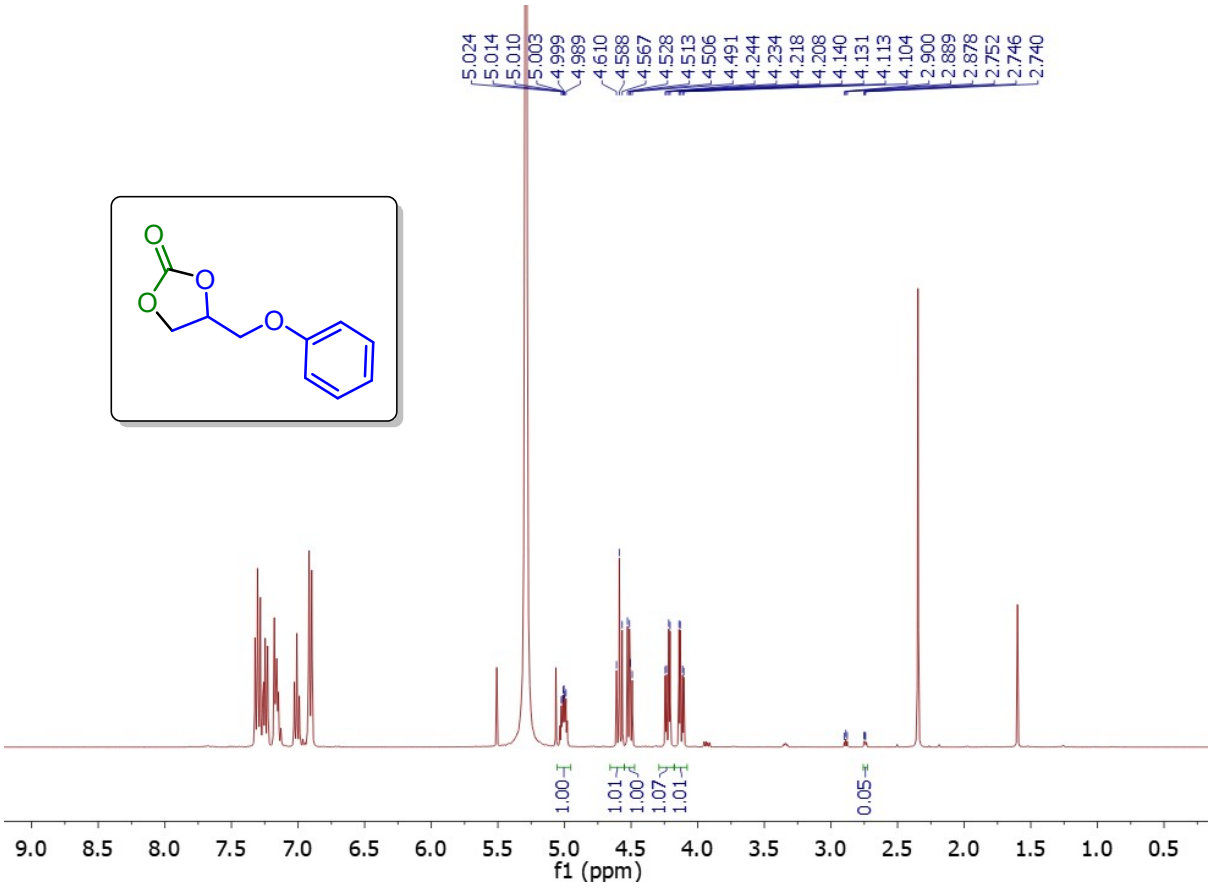


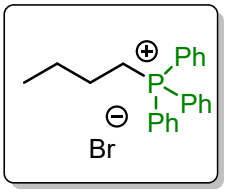
Figure S58: ^{1}H NMR of phenyl glycidyl ether and CO_2 using catalyst **1b** ($CDCl_3$, 400 MHz).

Table S1. Crystallographic data and refinement details for the crystal structure of organocatalysts

Compound	**1a**	**1b**
Empirical formula	$C_{29}H_{35}BClP$	$C_{29}H_{35}BBr_{0.5}OP$
CCDC number	**2191004**	**2191005**
FW	460.80	483
Temp, [K]	110	110
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
a, [Å]	12.0911(3)	10.0310(3)
b, [Å]	13.1217 (3)	12.2645(4)
c, [Å]	15.7545(4)	12.4476(4)
α, [°]	87.77	69.30
β, [°]	85.42	66.30
γ, [°]	89.48	73.14
V, [Å^3]	2489.64	1292.08

Z	4	2
D(calcd), [Mg/cm^3]	1.229	1.242
μ [mm^{-1}]	2.055	0.899
GOF	1.038	1.085
R1(I_0>2σ(I_0)	0.0331	0.0349
wR2 (all data)	0.0910	0.1055

Procedure for the synthesis of butyltriphenylphosphonium bromide. To an oven dried Schlenk flask equipped with stir bar was added a triphenylphosphine (10 mmol, 1.00 equiv) in acetonitrile (10 mL) was treated with 1-bromobutane (10 mmol, 1.00 equiv) under nitrogen atmosphere. Then, the reaction mixture was then heated to 70 °C for 24 h. After completion, the mixture was concentrated in vacuo to afford the crude product that was further purified by washing with pentane (3 x 10 mL). The white solid was isolated by vacuum filtration and was dried for 12 h in vacuo at room temperature.



Butyltriphenylphosphonium bromide. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.58 (m, 9H), 7.54-7.51 (m, 6H), 3.50-3.43 (m, 2H), 1.47-1.40 (m, 4H), 0.68 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 134.7 (d, *J* = 2.9 Hz), 133.2 (d, *J* = 10.0 Hz), 130.2 (d, *J* = 12.4 Hz), 118.2 (d, *J* = 85.3 Hz), 24.1 (d, *J* = 15.1 Hz), 23.4 (d, *J* = 16.4 Hz), 22.4 (d, *J* = 50.0 Hz), 13.3.

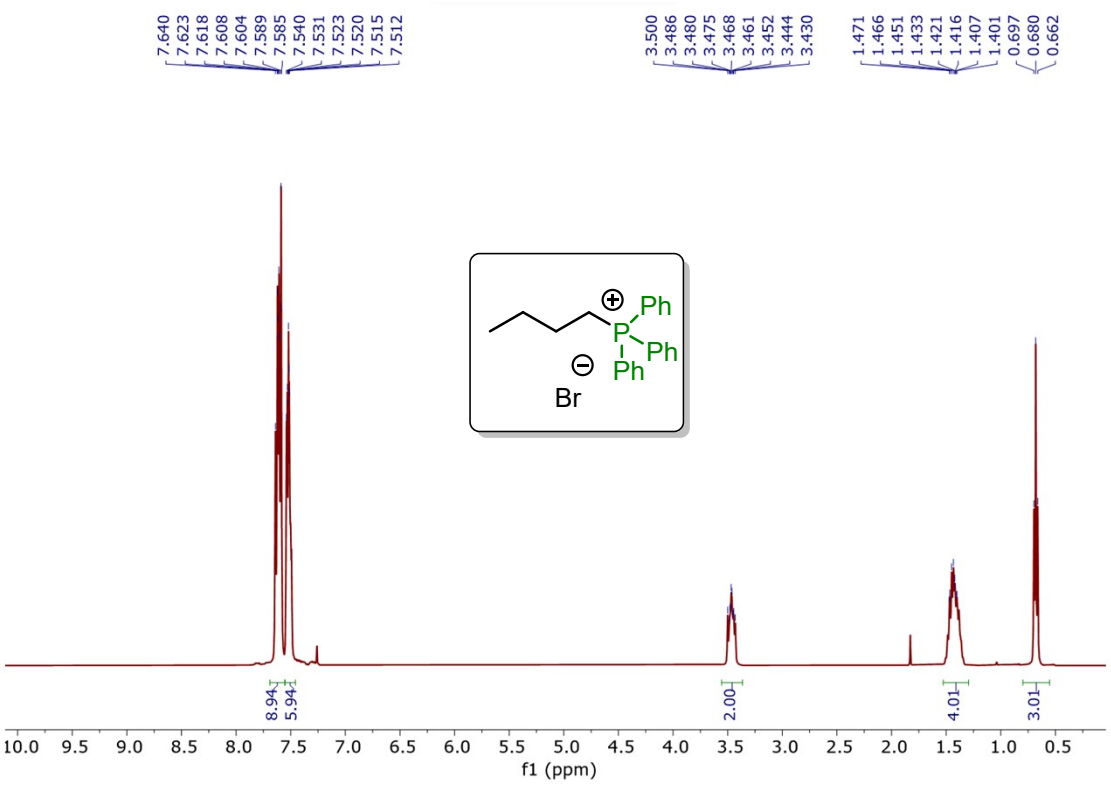


Figure S59: ^{1}H NMR of phosphonium salt ($CDCl_3$, 400 MHz).

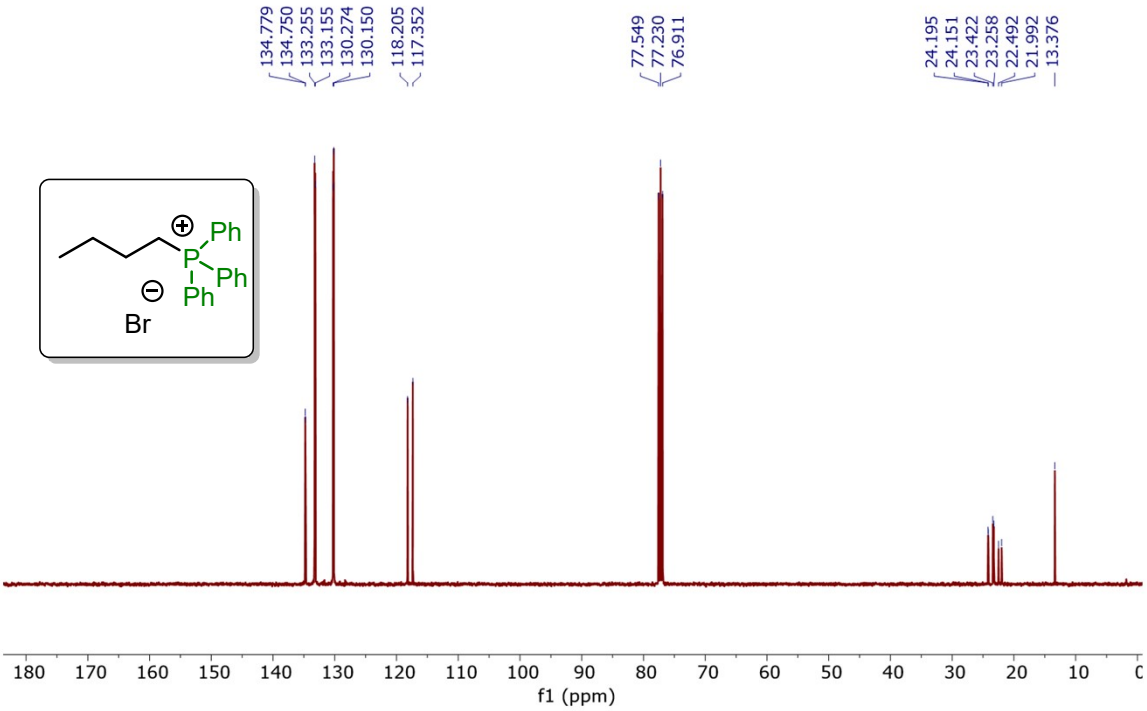
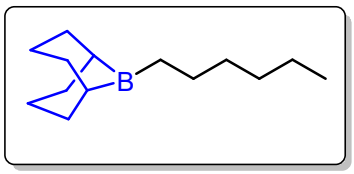


Figure S60: ^{13}C NMR of phosphonium salt ($CDCl_3$, 100 MHz).

Procedure for the synthesis of 9-hexyl-9-borabicyclo[3.3.1]nonane catalyst.

To an oven dried Schlenk flask equipped with stir bar was added the 1-hexene (5.00 mmol, 1.00 equiv) and 9-borabicyclo[3.3.1]nonane (9-BBN) in THF (0.5 M) (10.2 mL, 5.10 mmol, 1.02 equiv) was added via syringe under nitrogen. The reaction mixture was then heated to 65 °C for 12 h, followed by concentrated and dried for 5 h in vacuo to afford a alkyl borane as a colorless oil.



9-Hexyl-9-borabicyclo[3.3.1]nonane. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85-1.81 (m, 6H), 1.70-1.67 (m, 6H), 1.49-1.21 (m, 12H), 0.89-0.87 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 33.3, 32.8, 32.1, 24.6, 23.4, 22.9, 14.3.

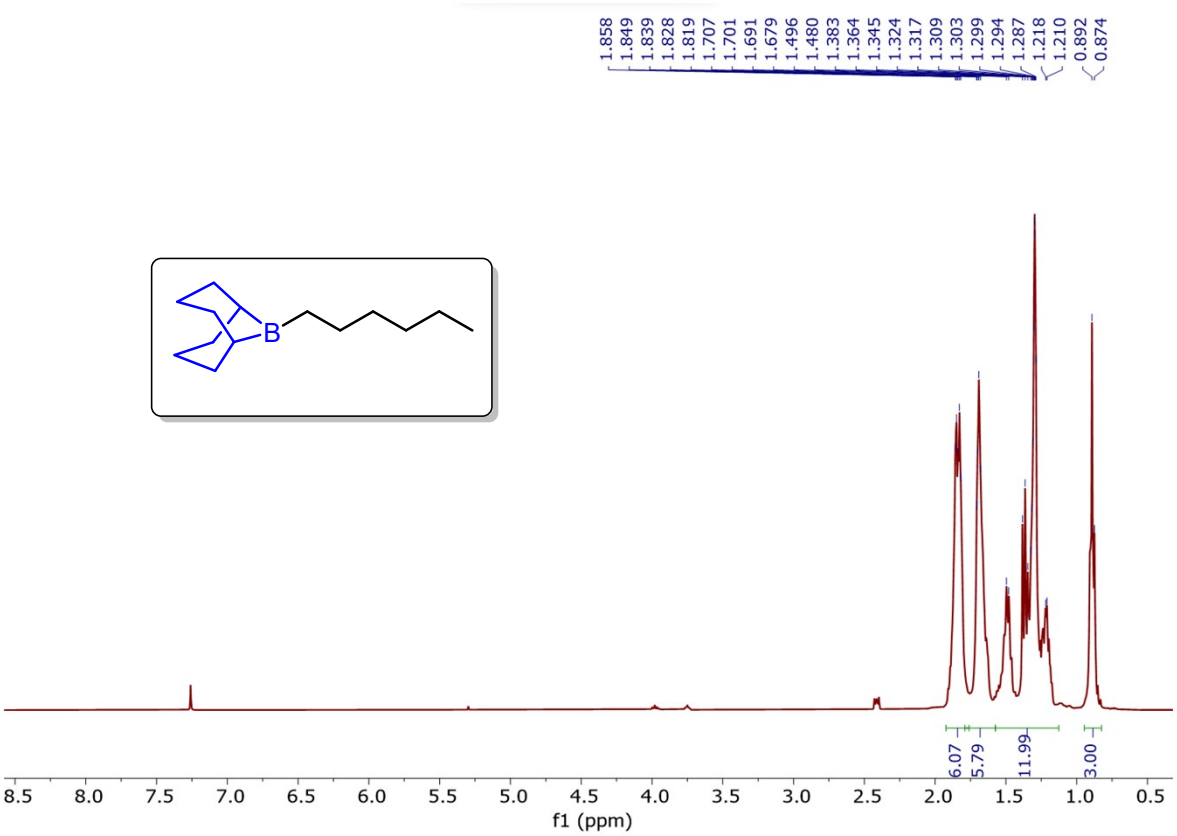


Figure S61: ^{1}H NMR of trialkyl borane ($CDCl_3$, 400 MHz).

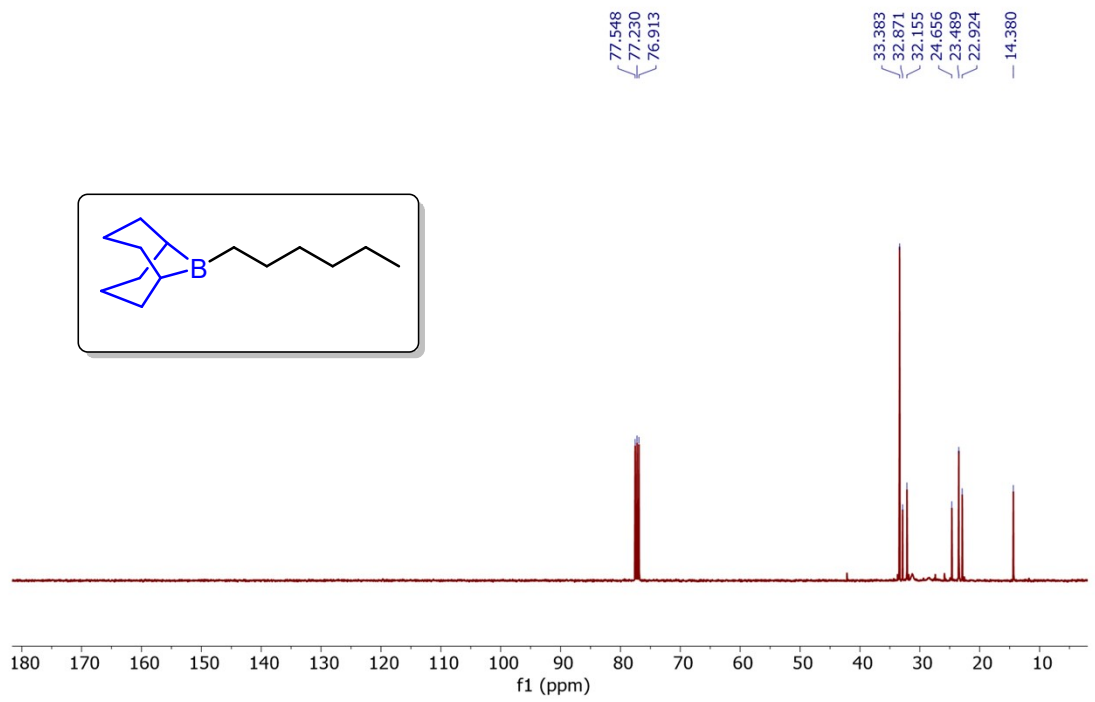


Figure S62: ^{13}C NMR of trialkyl borane ($CDCl_3$, 100 MHz).

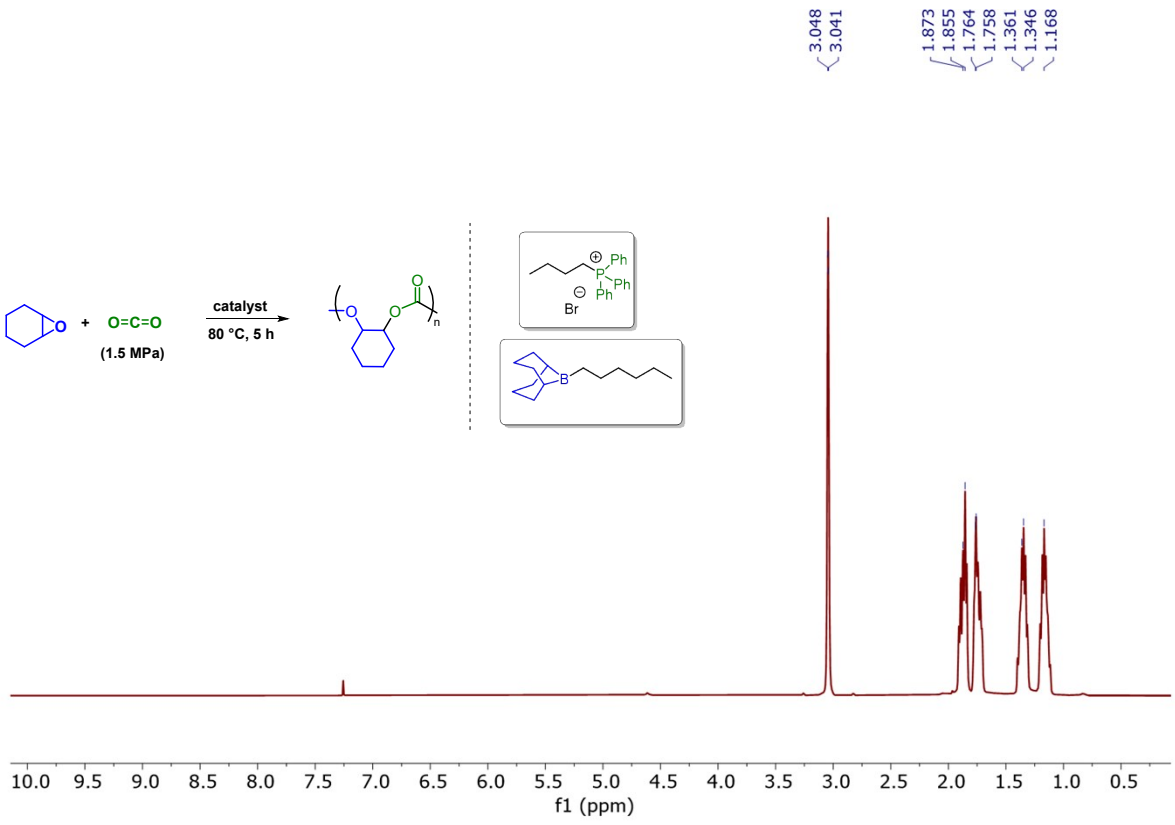


Figure S63: ^{1}H NMR of reaction mixture using trialkyl borane and phosphonium salt ($CDCl_3$, 400 MHz).