# Supporting Information for Manuscript Entitled with

# One-Component Phosphonium Borane Lewis Pair Serves as Dual Initiator and Catalyst in the Ring-Opening Alternating Copolymerization of Anhydrides and Epoxides

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## 1. Experimental sections

### Chemicals

Unless otherwise stated, all chemicals are used without further purification. Propylene oxide (PO), acetonitrile, ethanol, ethyl acetate, chloroform and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium hydride (NaH), calcium hydride ($CaH_2$) and deuterated solvents were purchased from Macklin Co., Ltd. Cyclohexene oxide (CHO), 3-bromopropene , 4-Bromo-1-butene , 5-Bromo-1-pentene, 6-Bromo-1-hexene, 5-iodo-1-pentene, 9-borabicyclo[3.3.1]nonane (9-BBN) were purchased from Energy Chemical Co., Ltd. Phthalic anhydride (PA)，maleic anhydride (MA) and succinic anhydride (SA) were purchased from Energy Chemical Co., Ltd. Tetrahydrofuran (THF), n-hexane were purchased as SuperDry solvent from Energy Chemical Co., Ltd. Chloroform, $CDCl_3$, PO and CHO were dried over $CaH_2$ for 48 h, distilled and stored under nitrogen atmosphere. PA was first dissolved in acetic anhydride and stirred at 120 ºC overnight before recrystallization at room temperature and further purified by sublimation under high vacuum before use. MA and SA were treated by sublimation under high vacuum before use. Amberlite(R) IRA-400 (Cl) resin was purchased from Energy Chemical Co., and washed with methanol before using. The ammonium borane catalysts **R1**-**R3**, **B1** were synthesized according to the literature.[1]

### Methods

### NMR

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer ($^1$H NMR 400 MHz, $^{13}$C NMR 100 MHz, 128 MHz $^{11}$B NMR, 162 MHz $^{31}$P NMR) at 298 K. $^1$H and $^{13}$C NMR Chemical shifts were reported in δ (ppm) with the residual deuterated solvent peak as reference [$^1$H: TMS in $CDCl_3$ = 0 ppm; $^{13}$C: $CDCl_3$ = 77.16 ppm; $^{11}$B: $BF_3$*$Et_2O$ (external standard) = 0 ppm, $^{31}$P: 85% $H_3PO_4$ (external standards) =

0 ppm]. Data are reported as follows: Chemical shift in ppm, multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad signals, etc.), coupling constant *J* in Hz, integration, and (where applicable) interpretation. The substitution pattern of phenyl group and assignments of phenyl carbon in $^{13}C$ NMR were named as follows: ortho- (*o*-Ph), meta- (*m*-Ph), para- (*p*-Ph) and ipso- (*i*-Ph).

**MALDI-ToF**

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were conducted on a Bruker Microflex LRF MS spectrometer equipped with a 337 nm nitrogen laser operating at a positive ion, linear mode (modified according to experiments). The polymer samples (10 mg $mL^{-1}$), trans -2[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, 25 mg $mL^{-1}$) and $CF_3COONa$ (5 mg $mL^{-1}$) were dissolved in THF and mixed in a volume ratio of 20:5:5 (Sample concentration, matrix type, ionic salt and volume ratio are modified according to experimental conditions).

**GPC**

Gel permeation chromatography (GPC) experiments were performed on an Agilent HPLC system equipped with a model 1260 Hip degasser, a model 1260 Iso pump and a model 1260 differential refractometer detector with using THF as mobile phase at a flow rate of 1.0 mL $min^{-1}$ at 40 °C. One PLgel 5 μm guard column and three Mz-Gel SDplus columns ($10^3$Å,$10^4$Å and $10^5$Å, linear range of $M_W$ = 1000 – $2*10^6$ Da) were connected in series. The molecular weight and dispersity were calculated using 6 polystyrene standards with narrow molecular weight distribution as references. The sample concentration used for GPC analyses was 5-10 mg $mL^{-1}$.

**XRD**

X-ray diffraction (XRD) was carried out to measure the structure of single crystals. The data of Co1 and Fe1 was collected on Super Nova diffractometer with Mo K-alpha X-ray source (λ = 0.71073 Å) at 150 K.

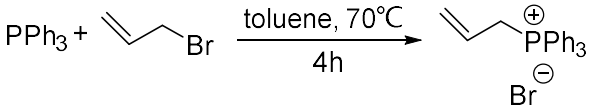
The collected data were solved using the SUPERFLIP72 program and refined by the SHELX-97 and OLEX274 programs.

**XPS**

The X-ray photoelectron spectroscopy (XPS) was measured with a Thermo Scientific ESCALAB 250Xi spectrometer (Al Kα radiation, hv = 1486.6 eV) equipped with an electron flood gun. The carbon 1s binding energy of graphite in the carbon tape (284.6 eV) was used to calibrate the binding energy. All spectra from XPS were analyzed by using Thermo Scientific Advantage Data System software

## Synthesis procedure

### Synthesis of quaternary phosphonium salt L1




Triphenylphosphine (0.262 g, 1mmol, 1 equiv.) and 3-bromopropene (0.13 mL, 1.5 mmol, 1.5 equiv.) were dissolved in toluene (5 m L) and heated at 70 ℃ for 4 h. Monitoring the $^{31}P$ NMR spectroscopy revealed full conversion. The reaction mixture was concentrated in vacuo to afford the crude product that was further purified by washing with $Et_2O$ for three times. The white solid was collected by vacuum filtration and was dried in vacuo for 12 h at 40 °C. The isolated yield was 92% (353.0 mg, 0.92 mmol). $^{1}H$ NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.88 (m, 6H, *o*-$Ph^H$), 7.79 (m, 3H, *p*-$Ph^H$), 7.69 (m, 6H, *m*-$Ph^H$), 5.69 (m, 2H, =$CH_2$), 5.40 (m, 1H, CH=), 4.89 (dd, $^{3}J$ = 15.5, 6.9 Hz, 2H, $CH_2$). $^{13}C\{^{1}H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 135.1 (d, $^{4}J_{PC}$ = 2.9 Hz, *p*-$Ph^C$), 133.9 (d, $^{3}J_{PC}$ = 9.9 Hz, *m*-$Ph^C$), 130.4 (d, $^{2}J_{PC}$ = 12.8 Hz, *o*-$Ph^C$), 126.2 (d, $^{2}J_{PC}$ = 13.1 Hz, =CH), 123.0 (d, $^{3}J_{PC}$ = 9.6 Hz, $CH_2$=), 117.8 (d, $^{1}J_{PC}$ = 85.9 Hz, *i*-$Ph^C$), 28.8 (d, $^{1}J_{PC}$ = 50.1 Hz, $CH_2$). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 21.2 (s).

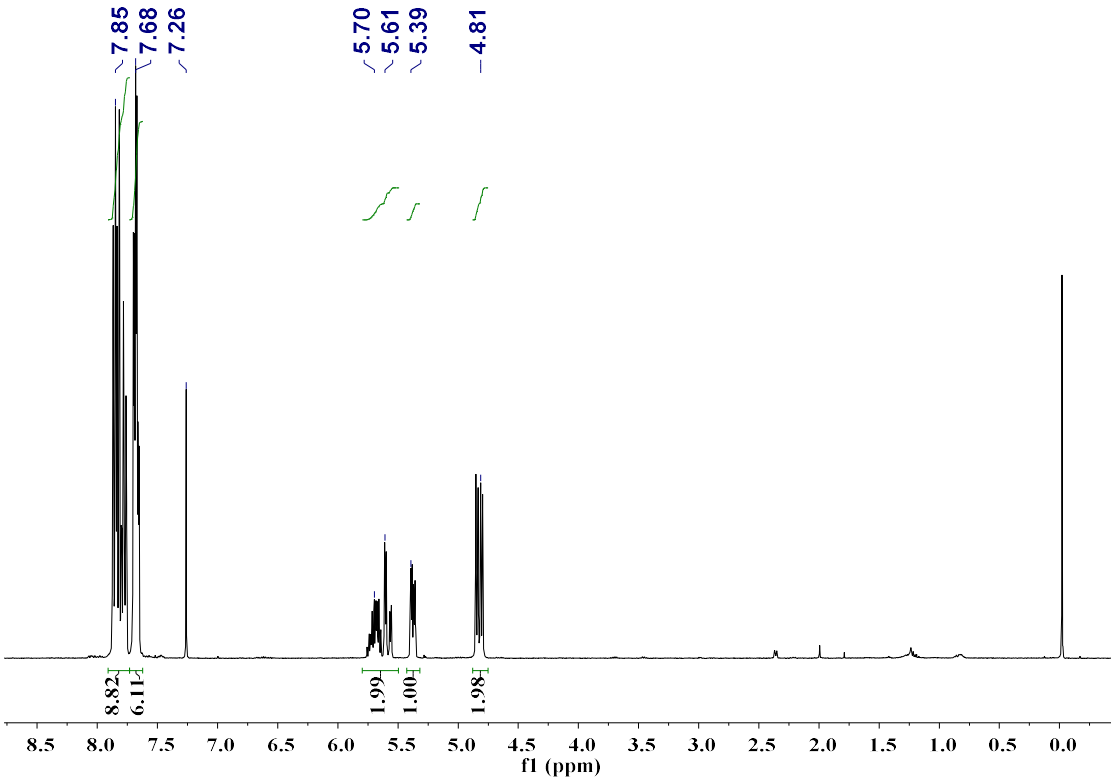



Figure S1. $^{1}$H NMR spectrum of **L1** (400 MHz, $CDCl_3$, 298 K)

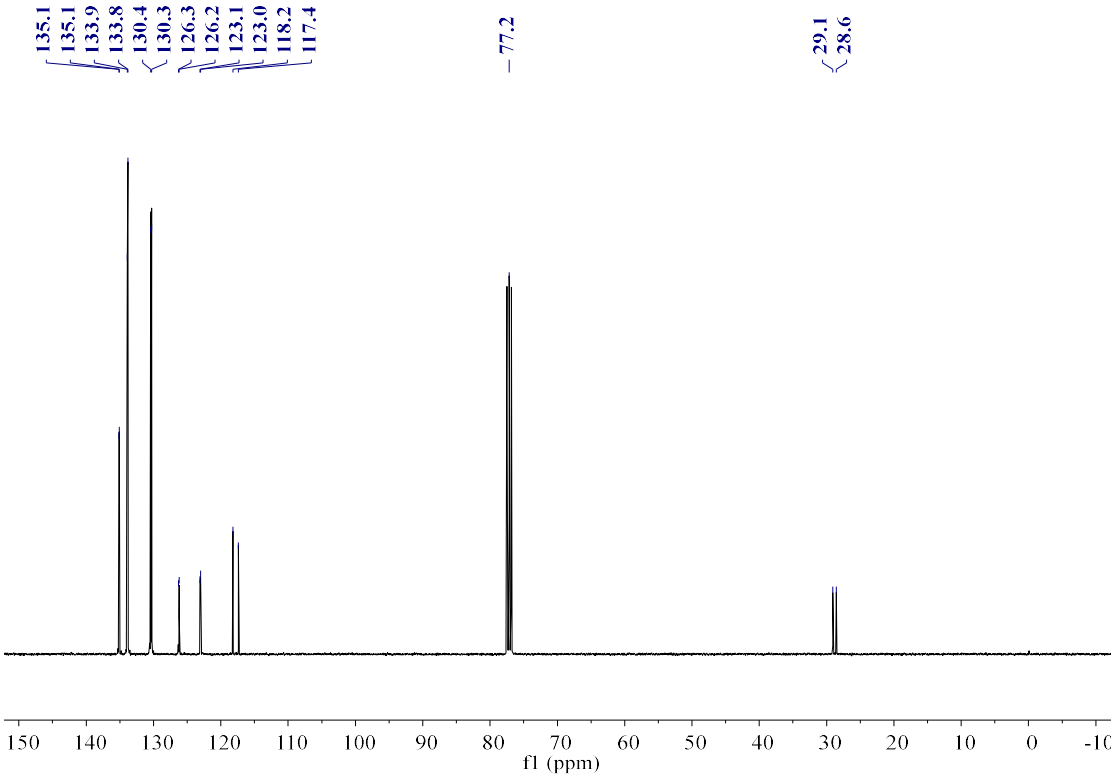



Figure S2. $^{13}$C{$^{1}$H} spectrum of **L1** (100 MHz, $CDCl_3$, 298 K)

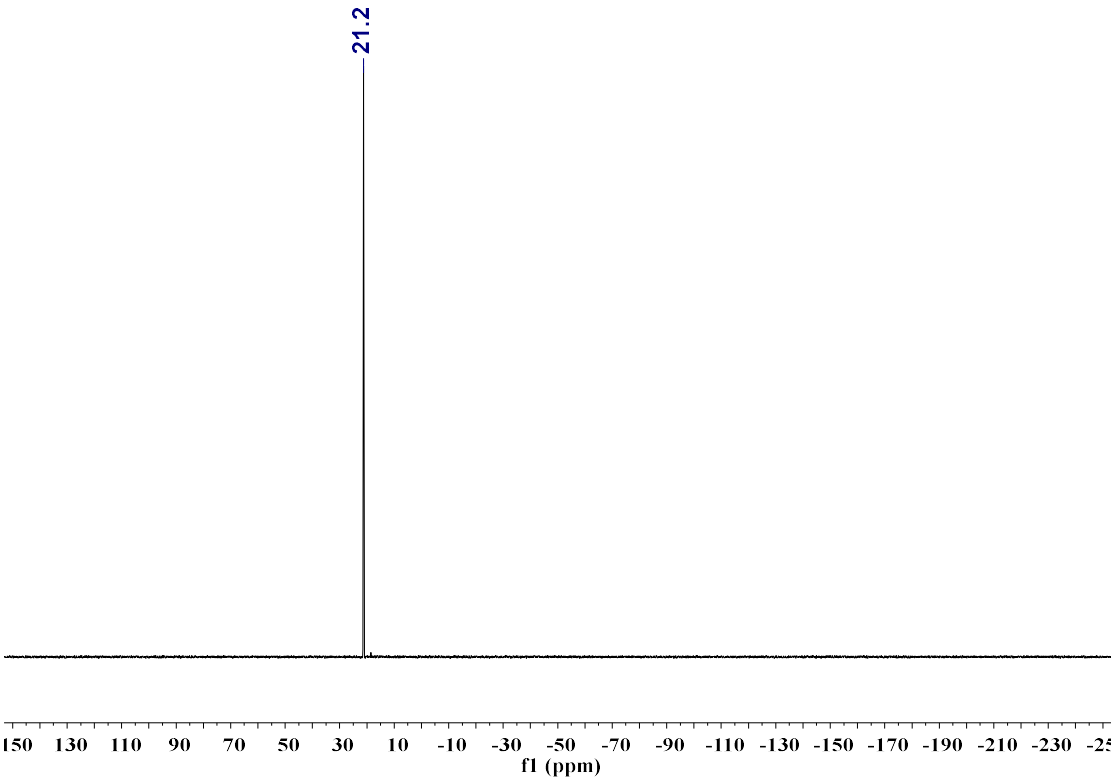
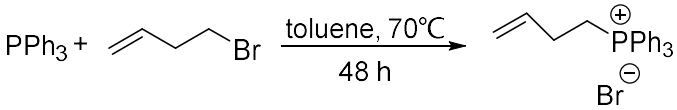



Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **L1** (162 MHz, $CDCl_3$, 298 K)

**Synthesis of quaternary ammonium salt L2**




Triphenylphosphine (0.262 g, 1 mmol, 1 equiv.) and 4-bromo-1-butene (0.15 mL, 1.5mmol, 1.5 equiv.) were dissolved in toluene (5 mL) and heated at 70 ℃ for 48 h. Monitoring the $^{31}P$ NMR spectroscopy revealed full conversion. The reaction mixture was concentrated to half and ether was added with three times of the original volume. Then, the mixture was put into the refrigerator at -30℃ overnight. The white precipitates were quickly filtered and washed with cold ether three times. The collected white solid was dried in vacuum at 40℃ for 12 h. The isolated yield was 94% (374.0 mg, 0.94 mmol). $^{1}H$ NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.90 (m, 6H, *o*-$Ph^H$), 7.79 (m, 3H, *p*-$Ph^H$), 7.70 (m, 6H, *m*-$Ph^H$), 6.02 (m, 1H, CH=), 5.02 (m, 2H, =$CH_2$), 3.99 (m, 2H, allyl-$CH_2$), 2.45 (m, 2H, $PCH_2$). $^{13}C\{^{1}H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 135.2 (d, $^{4}J_{PC}$ = 2.9 Hz, *p*-$Ph^C$), 134.9 (d, $^{1}J_{PC}$ = 15.0 Hz, *i*-$Ph^C$), 133.7 (d, $^{3}J_{PC}$ =

10.1 Hz, *m*-Ph$^{C}$), 130.6 (d, $^{2}J_{PC}$ = 12.7 Hz, *o*-Ph$^{C}$), 118.5 (s, $CH_2$=), 117.5 (d, $^{3}J_{PC}$ = 16.9 Hz, =CH), 26.6 (d, $^{2}J_{PC}$ = 3.5 Hz, $CH_2$), 22.40 (d, $^{1}J_{PC}$ = 49.8 Hz, $PCH_2$). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.5 (s). 21.2 (s).

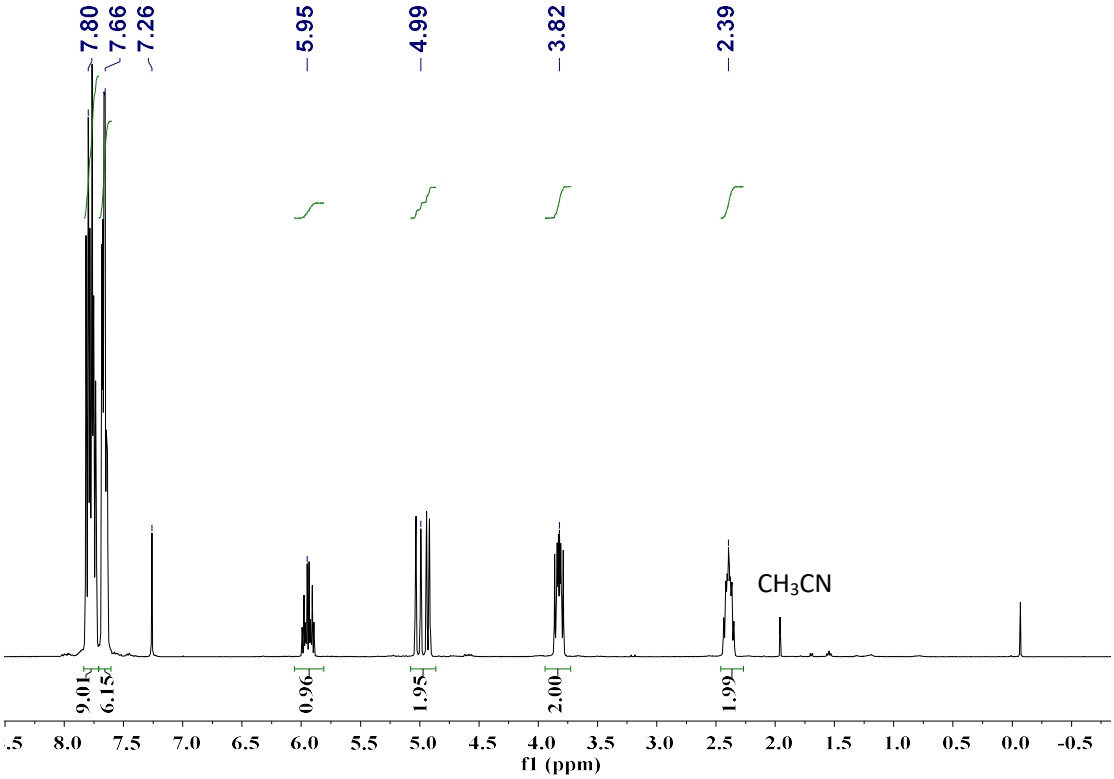



Figure S4. $^{1}H$ NMR spectrum of **L2** (400 MHz, $CDCl_3$, 298 K)

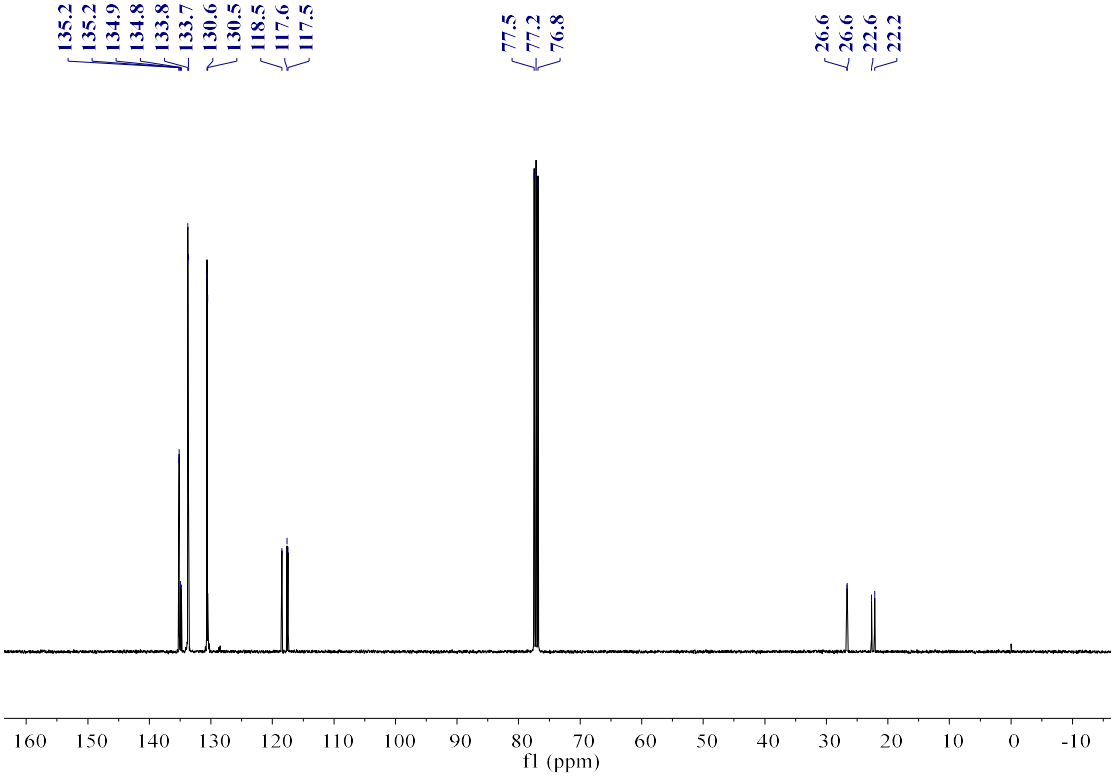


Figure S5. $^{13}C\{^{1}H\}$ spectrum of **L2** (100 MHz, $CDCl_3$, 298 K)

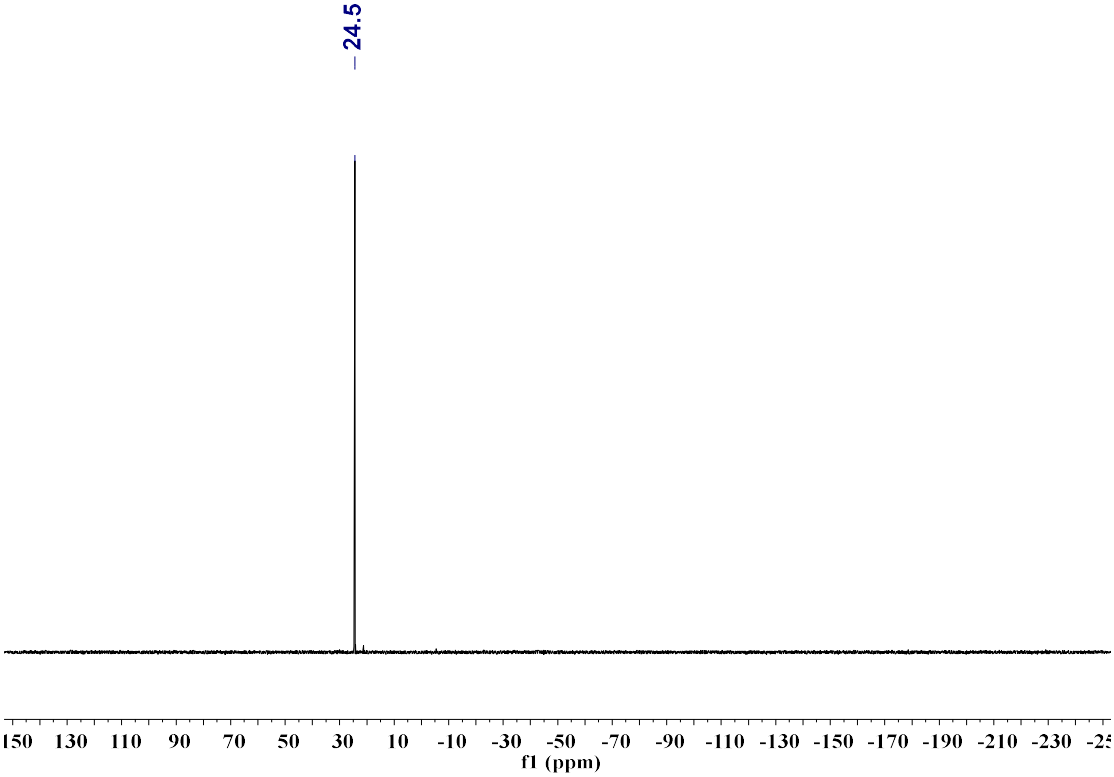
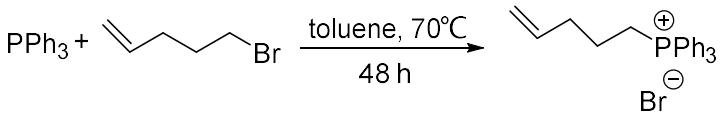



Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **L2** (162 MHz, $CDCl_3$, 298 K)

**Synthesis of quaternary ammonium salts L3**




Tripheylphosphine (0.262 g, 1 mmol, 1 equiv.) and 5-bromo-1-pentene (0.18 mL, 1.5 mmol, 1.5 equiv.) were dissolved in toluene (5mL) and heated at 70 ℃ for 48 h. Monitoring the $^{31}P$ NMR spectroscopy revealed full conversion. The reaction mixture was added with ether three times of the original volume. The mixture was put into the refrigerator at -30℃ overnight. The white soild was filtered through vacuum while it was cold and washed with ether three times. The collected white solid was dried in vacuum at 40℃ for 12 h. The isolated yield was 92% (379.0 mg, 0.92 mmol).

$^{1}H$ NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.87 (m, 6H, *o*-$Ph^H$), 7.78 (m, 3H, *p*-$Ph^H$), 7.69 (m, 6H, *m*-$Ph^H$), 5.71 (m, 1H, CH=), 5.01 (m, 2H, =$CH_2$), 3.91 (m, 2H, allyl-$CH_2$), 2.46 (m, 2H, P$CH_2$), 1.73 (m, 2H, $CH_2$).

$^{13}C\{^{1}H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 136.3 (s, *p*-$Ph^C$), 135.1 (d, $^{4}J_{PC}$ = 3.2 Hz, =CH), 133.6 (d, $^{3}J_{PC}$ = 10.1 Hz, *m*-$Ph^C$), 130.6 (d, $^{2}J_{PC}$ = 12.8 Hz, *o*-$Ph^C$), 118.6 (s, $CH_2$=), 117.4 (d, $^{1}J_{PC}$ = 75.3 Hz, *i*-$Ph^C$), 33.8 (d, $^{2}J_{PC}$ = 16.5 Hz, $CH_2$), 22.1 (d, $^{1}J_{PC}$ = 37.9 Hz, $PCH_2$), 21.8 (d, $^{3}J_{PC}$ = 8.8 Hz, $CH_2$). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.7 (s).

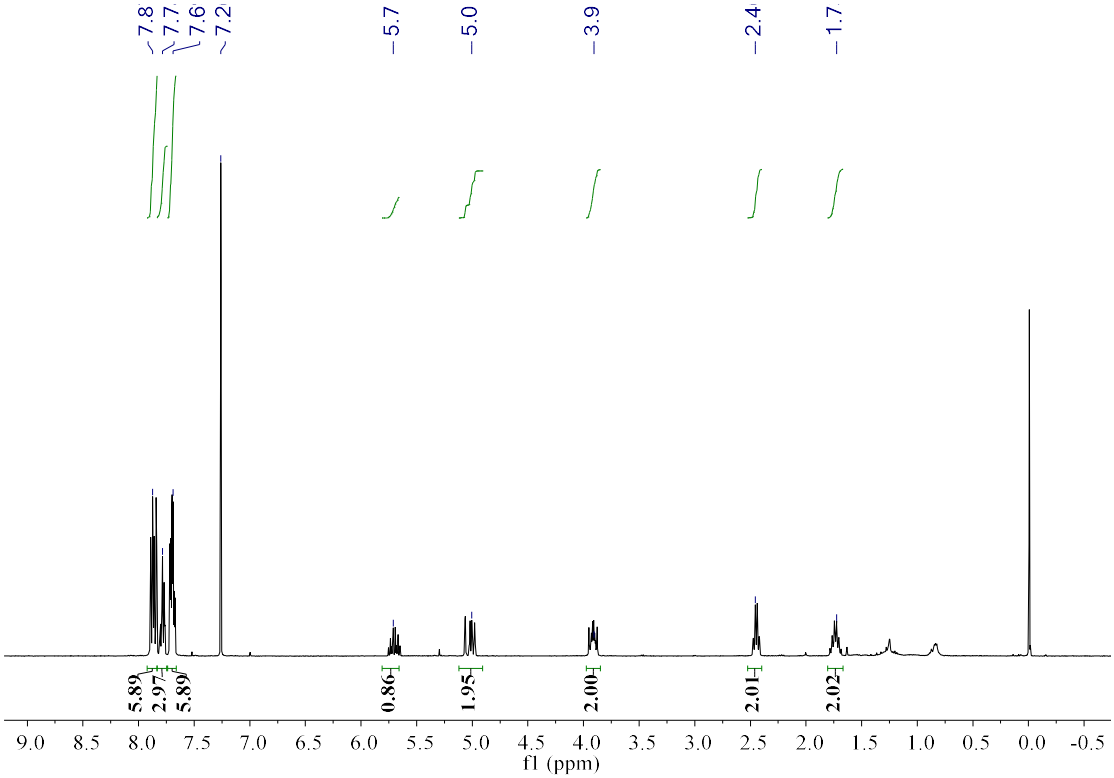



Figure S7. $^{1}H$ NMR spectrum of **L3** (400 MHz, $CDCl_3$, 298 K)

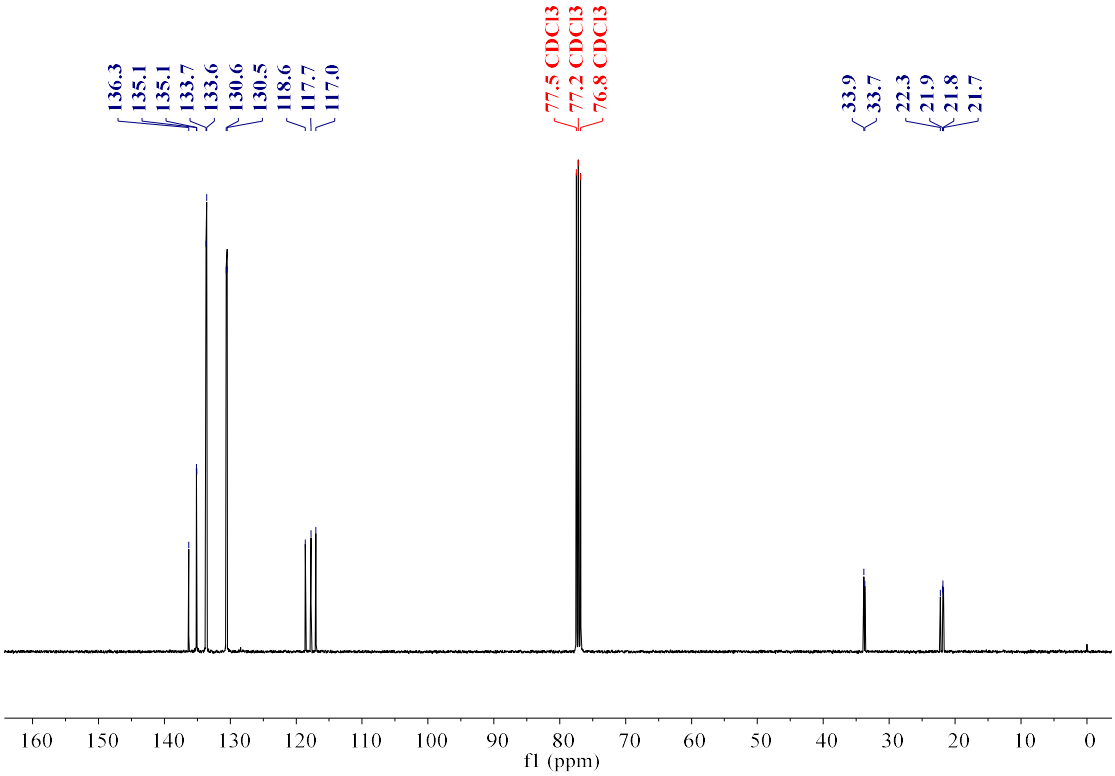



Figure S8. $^{13}C\{^{1}H\}$ spectrum of **L3** (100 MHz, $CDCl_3$, 298 K)

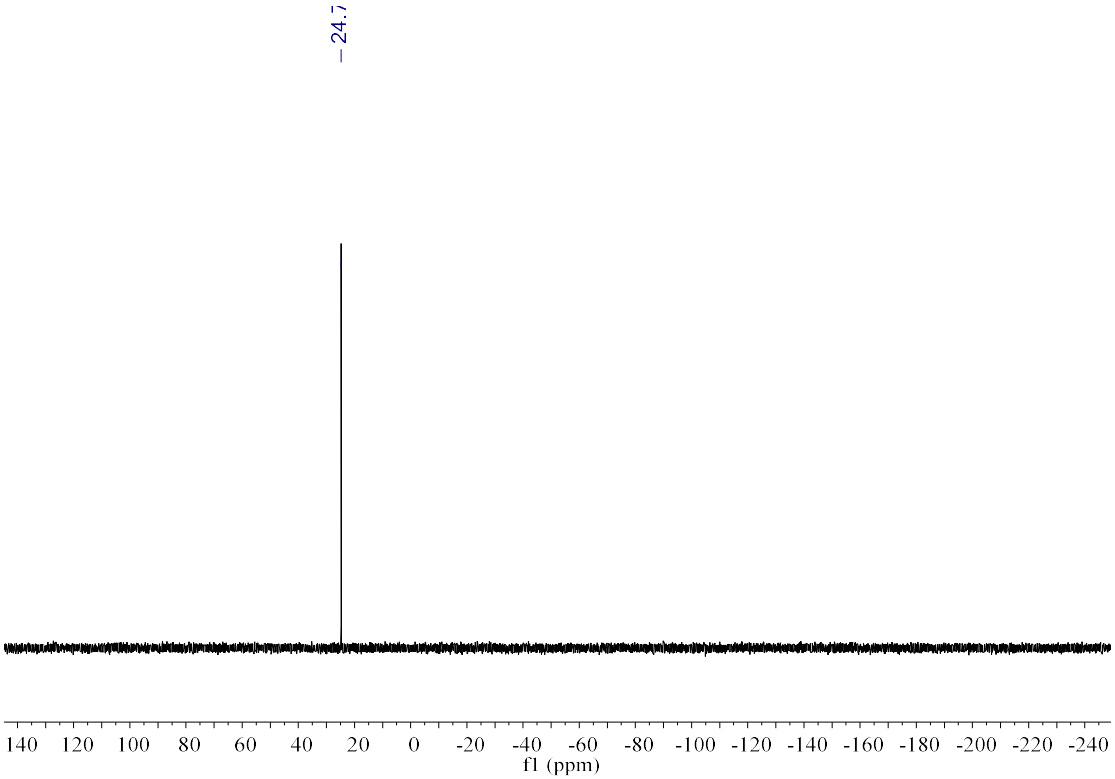
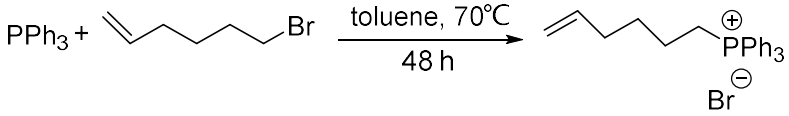



Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **L3** (162 MHz, $CDCl_3$, 298 K)

**Synthesis of quaternary ammonium salts L4**




Triphenylphosphine (0.262 g, 1 mmol, 1 equiv.) and 6-bromo-1-hexene (0.2 mL, 1.5 mmol, 1.5 equiv.) were dissolved in toluene (5 mL) and heated at 70 ℃ for 48 h. Monitoring the $^{31}$P NMR spectroscopy revealed full conversion. The reaction mixture was added with ether three times of the original volume and put into the refrigerator at -30℃ overnight. The white soild was filtered through vacuum while it was cold and washed with ether three times. The collected white solid was dried in vacuum at 40℃ for 12 h. The isolated yield was 91% (387.0 mg, 0.91 mmol).

$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.87 (m, 6H, *o*-$Ph^H$), 7.78 (m, 3H, *p*-$Ph^H$), 7.69 (m, 6H, *m*-$Ph^H$), 5.68 (m, 1H, CH=), 4.89 (m, 2H, $=CH_2$), 3.90 (m, 2H, allyl-$CH_2$), 2.07 (q, *J* = 7.0 Hz, 2H, $PCH_2$), 1.78 (m, 2H, $CH_2$), 1.61 (m, 2H, $CH_2$). $^{13}C\{^{1}H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 137.6 (s, *p*-$Ph^C$), 135.1 (d, $^{5}J_{PC}$ = 3.0 Hz, =CH), 133.6 (d, $^{3}J_{PC}$ = 10.0 Hz, *m*-$Ph^C$), 130.5 (d, $^{2}J_{PC}$ = 12.5 Hz, *o*-$Ph^C$), 118.2 (d, $^{1}J_{PC}$ = 75.3 Hz, *i*-$Ph^C$), 115.3 (s, $CH_2$=), 32.9 (s, $^{=CH}CH_2$), 29.2 (d, $^{2}J_{PC}$ = 16.0 Hz, $CH_2$), 22.6 (d, $^{1}J_{PC}$ = 50.1 Hz, $PCH_2$), 21.8 (d, $^{3}J_{PC}$ = 4.3 Hz, $CH_2$). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.6 (s).

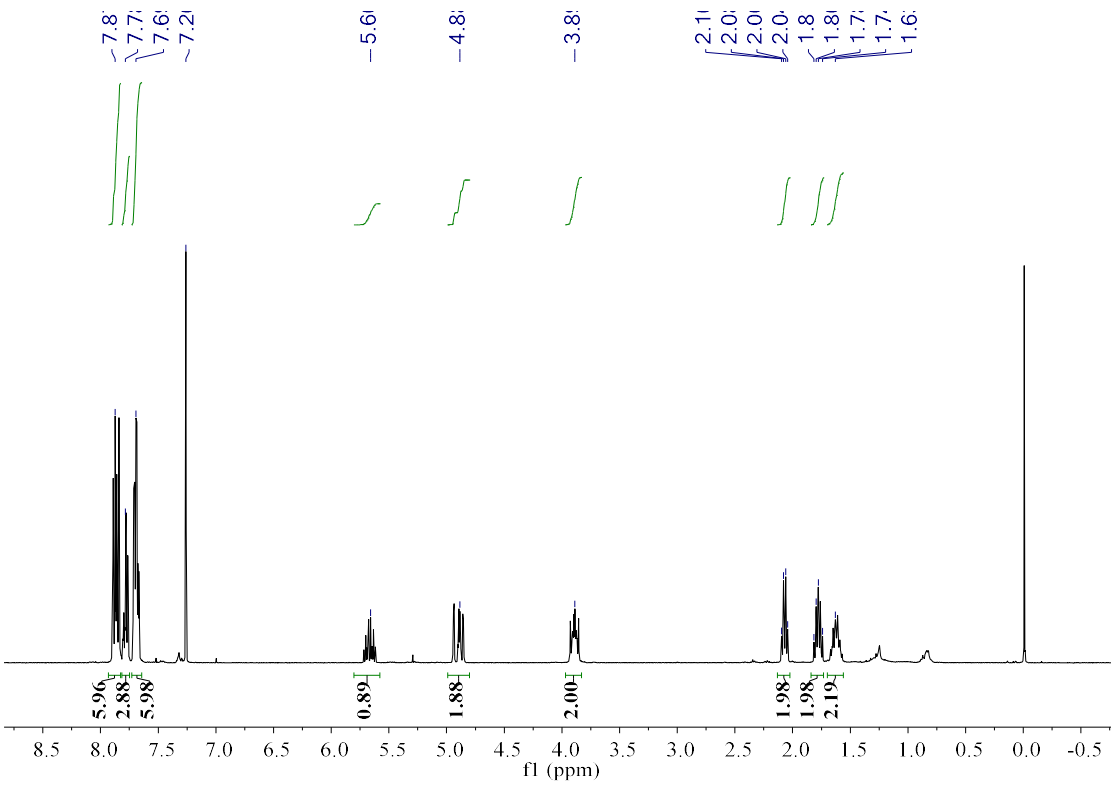



Figure S10. $^{1}H$ NMR spectrum of **L4** (400 MHz, $CDCl_3$, 298 K)

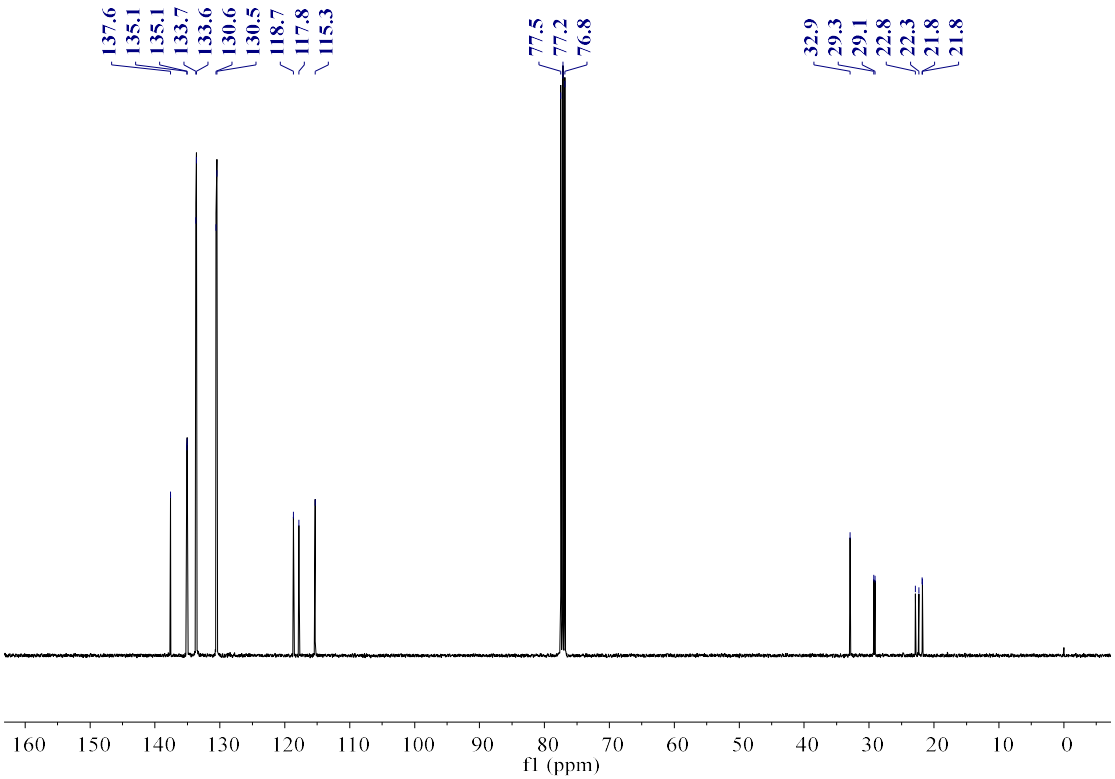



Figure S11. $^{13}C\{^{1}H\}$ spectrum of **L4** (100 MHz, $CDCl_3$, 298 K)

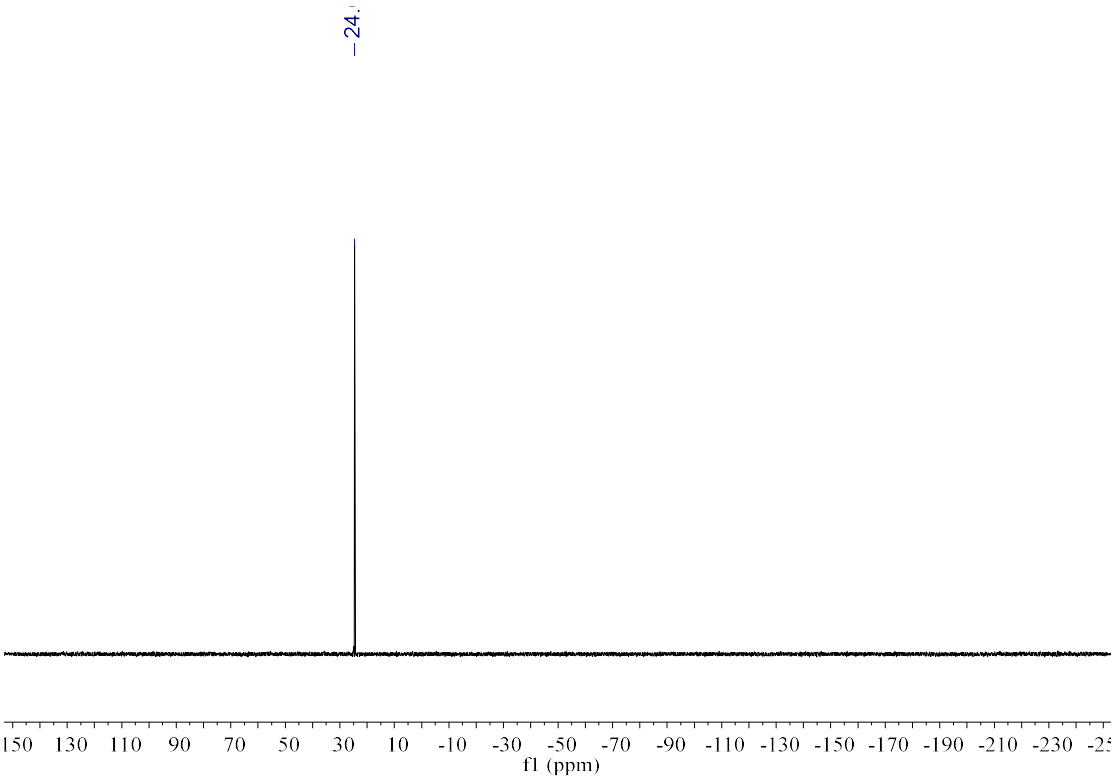
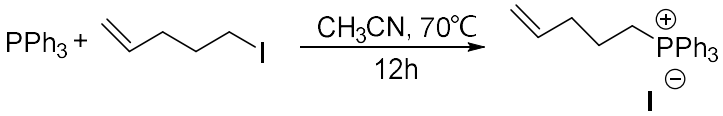



Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **L4** (162 MHz, $CDCl_3$, 298 K)

**Synthesis of quaternary ammonium salts L5**




Triphenylphosphine (0.089 g, 0.34 mmol, 1 equiv.) and 5-iodo-1-pentene (0.065 mL, 0.51 mmol, 1.5 equiv.) were dissolved in acetonitrile (3 mL) and heated at 70 ℃ for 48 h. Monitoring the $^{31}P$ NMR spectroscopy revealed full conversion. The reaction mixture was added with ether three times of the original volume and put into the refrigerator at -30℃ overnight. The white soild was filtered through vacuum while it was cold and washed with ether three times. The collected white solid was dried in vacuum at 40℃ for 12 h. The isolated yield was 97% (151.2 mg, 0.33 mmol).

$^{1}H$ NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.84 (m, 9H, *o*-$Ph^H$ and *p*-$Ph^H$), 7.71 (m, 6H, *m*-$Ph^H$), 5.70 (m, 1H, CH=), 5.03 (m, 2H, =$CH_2$), 3.76 (m, 2H, allyl-$CH_2$), 2.45 (q, *J* = 7.0 Hz, 2H, $PCH_2$), 1.74 (m, 2H, $CH_2$).

$^{13}C\{^{1}H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 136.2 (s, *p*-$Ph^C$), 135.3 (d,

$^{4}J_{PC}$ = 2.9 Hz, =CH), 133.7 (d, $^{3}J_{PC}$ = 10.1 Hz, *m*-Ph$^{C}$), 130.7 (d, $^{2}J_{PC}$ = 12.7 Hz, *o*-Ph$^{C}$), 117.3 (s, $CH_2$=), 118.0 (d, $^{1}J_{PC}$ = 86.3 Hz, *i*-Ph$^{C}$), 33.8 (d, $^{2}J_{PC}$ = 16.3 Hz, $CH_2$), 22.4 (d, $^{1}J_{PC}$ = 51.0 Hz, $PCH_2$), 21.9 (d, $^{3}J_{PC}$ = 4.1 Hz, $CH_2$). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.5 (s).

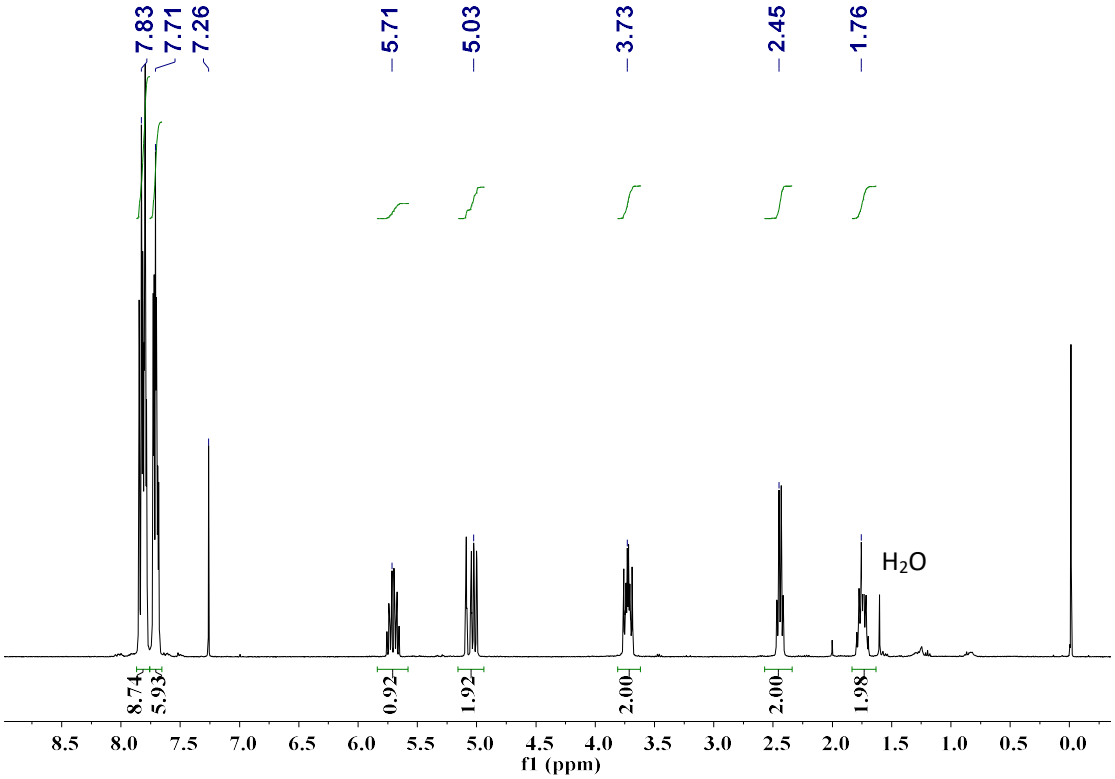



Figure S13. $^{1}H$ NMR spectrum of **L5** (400 MHz, $CDCl_3$, 298 K)

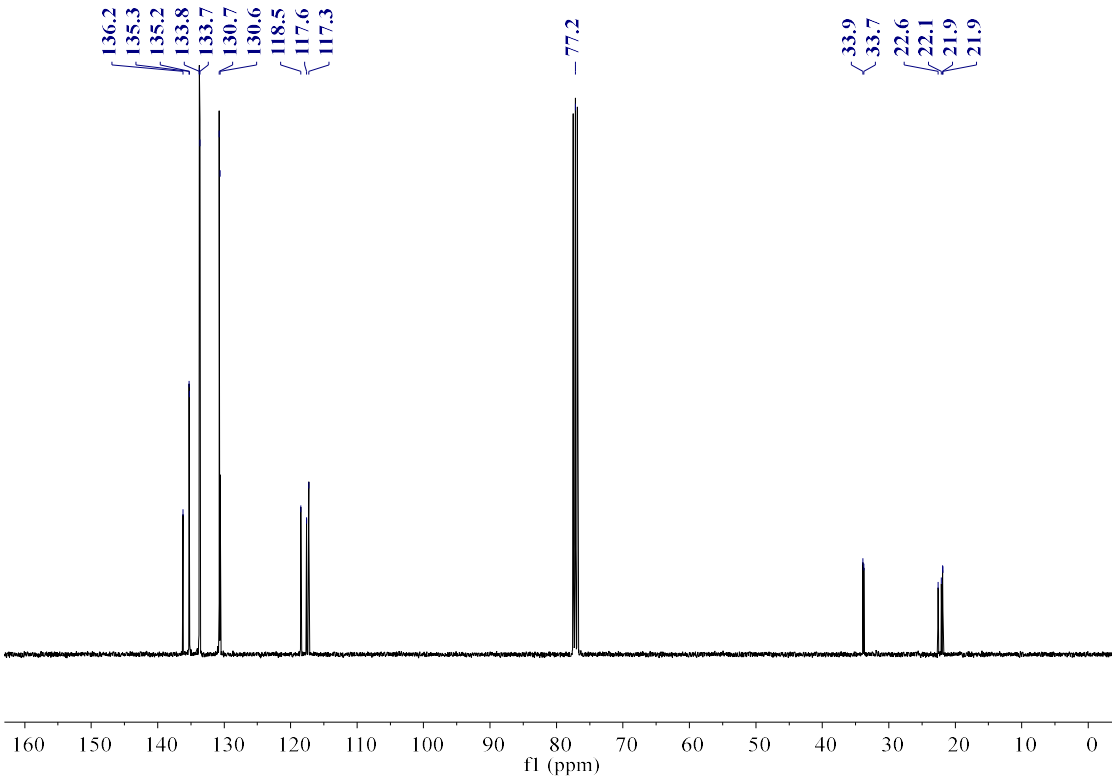



Figure S14. $^{13}C\{^{1}H\}$ spectrum of **L5** (100 MHz, $CDCl_3$, 298 K)

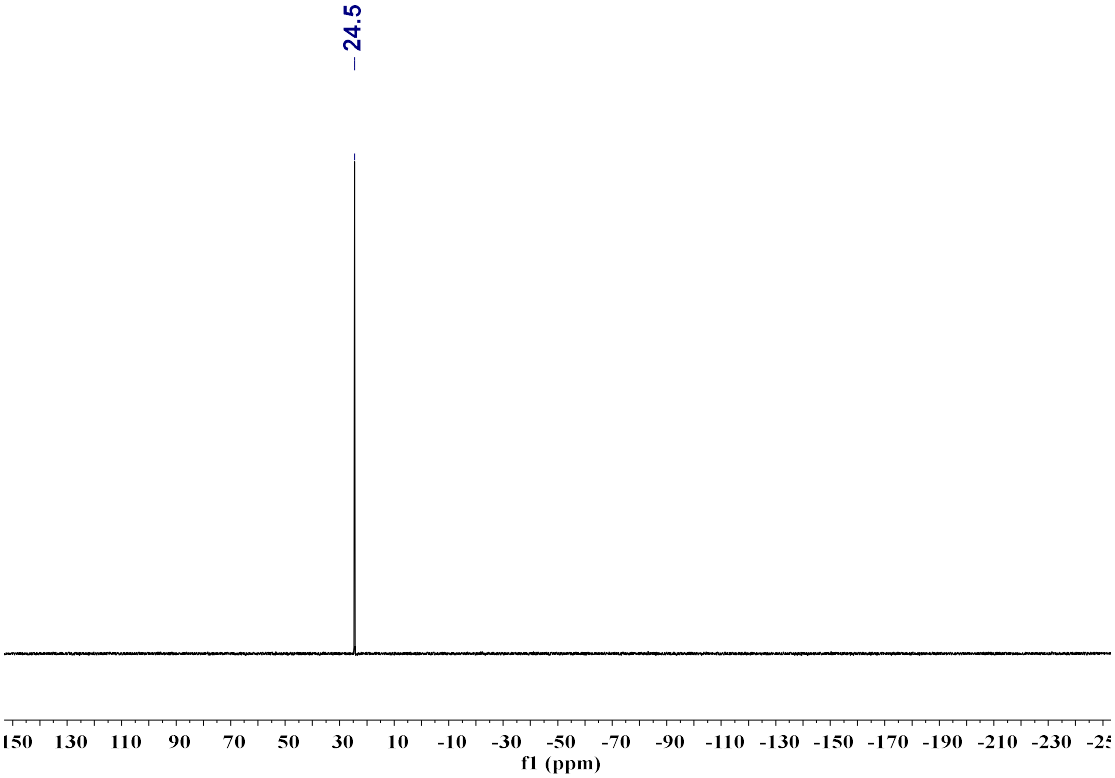
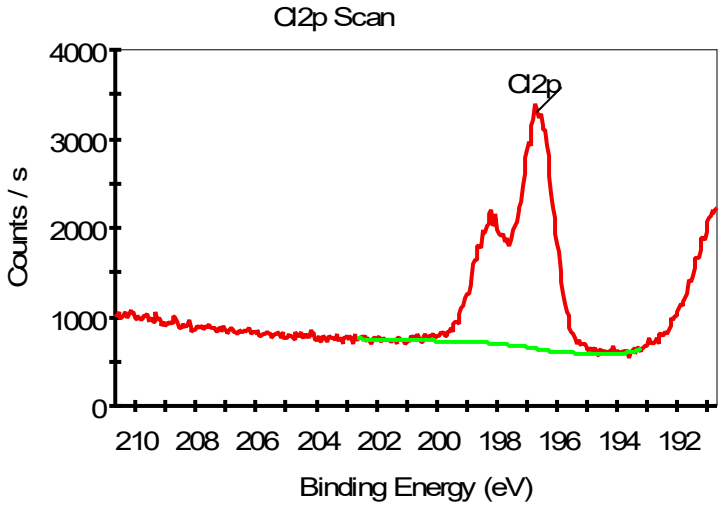



Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **L5** (162 MHz, $CDCl_3$, 298 K)

**Synthesis of quaternary ammonium salts L6**

**L3** (300 mg, 0.8 mmol) was dissolved in methanol and eluted through a column containing Amberlite IRA-400 (Cl) ion-exchange resin (3 g) at a

drop rate of 1 mL/min. Solvent was removed and product was dried in vacuo at 50 °C to yield a white solid in quantitative yield (264.0 mg, 0.72 mmol). The complete exchange was confirmed by X-ray photoelectron spectroscopy. Only chloride was detected and no detection of Br was observed.




$^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.88 (m, 6H, *o*-$Ph^H$), 7.78 (m, 3H, *p*-$Ph^H$), 7.70 (m, 6H, *m*-$Ph^H$), 5.69 (m, 1H, CH=), 5.00 (m, 2H, $=CH_2$), 3.97 (m, 2H, allyl-$CH_2$), 2.42 (m, 2H, $PCH_2$), 1.72 (m, 2H, $CH_2$). $^{13}C\{^1H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 136.5 (s, *p*-$Ph^C$), 135.1 (d, $^4J_{PC}$ = 3.0 Hz, =CH), 133.8 (d, $^3J_{PC}$ = 10.0 Hz, *m*-$Ph^C$), 130.6 (d, $^2J_{PC}$ = 12.6 Hz, *o*-$Ph^C$), 117.0 (s, $CH_2$=), 118.5 (d, $^1J_{PC}$ = 85.9 Hz, *i*-$Ph^C$), 33.9 (d, $^2J_{PC}$ = 16.4 Hz, $CH_2$), 22.1 (d, $^3J_{PC}$ = 7.8 Hz, $CH_2$), 21.8 (d, $^1J_{PC}$ = 38.8 Hz, $PCH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.8 (s).

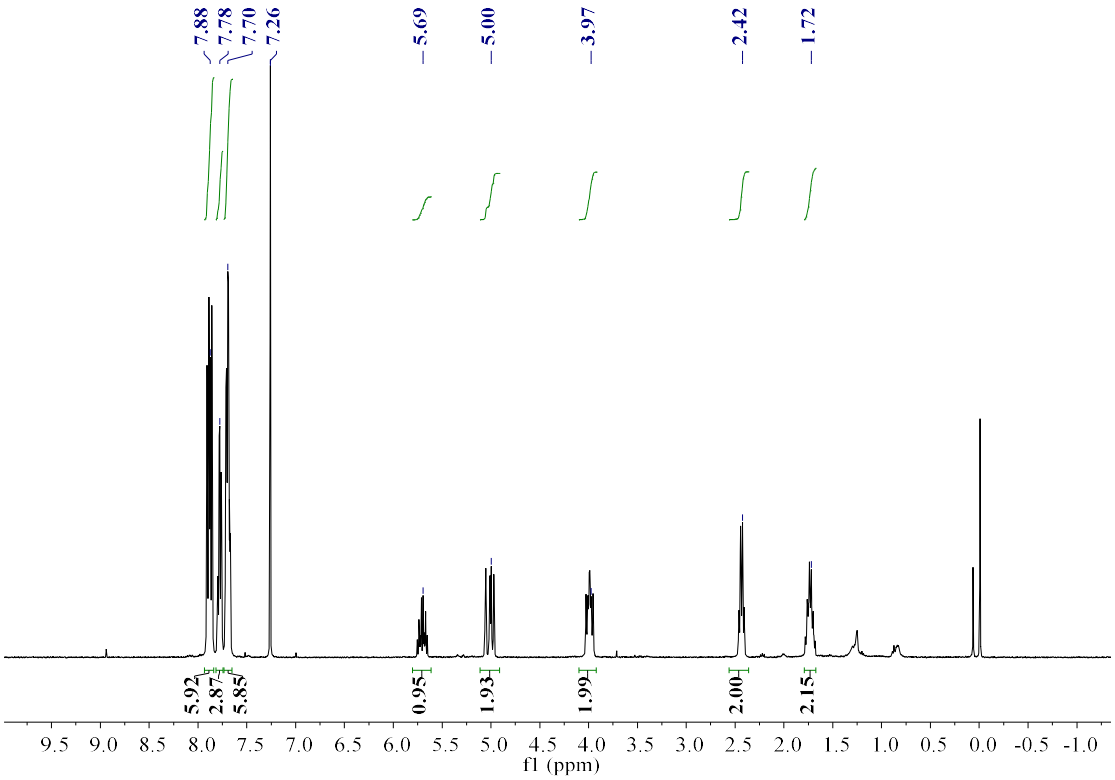



Figure S16. $^{1}$H NMR spectrum of **L6** (400 MHz, $CDCl_3$, 298 K)

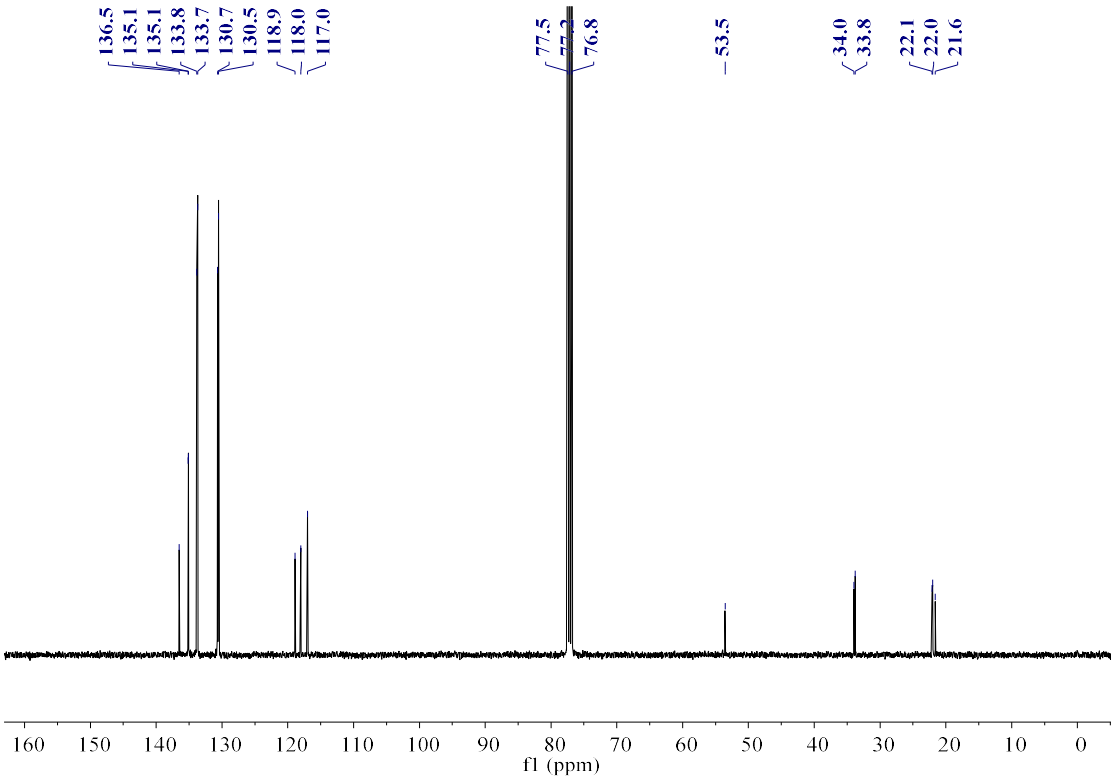



Figure S17. $^{13}$C{$^{1}$H} spectrum of **L6** (100 MHz, $CDCl_3$, 298 K)

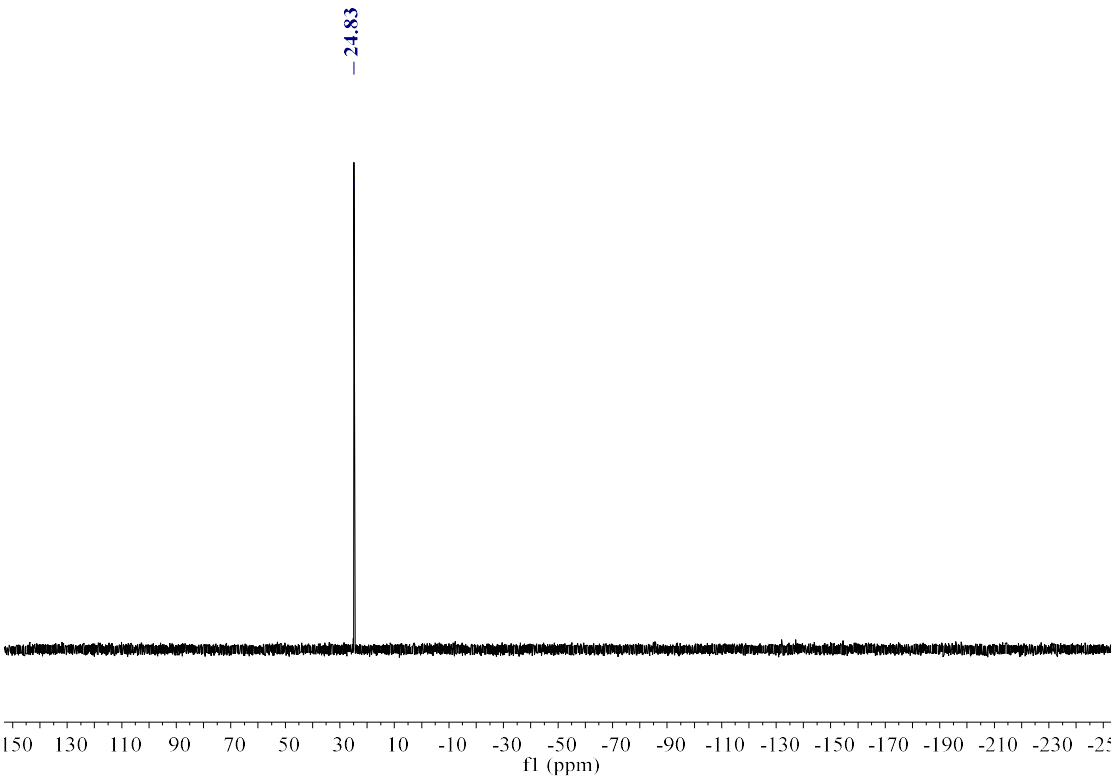
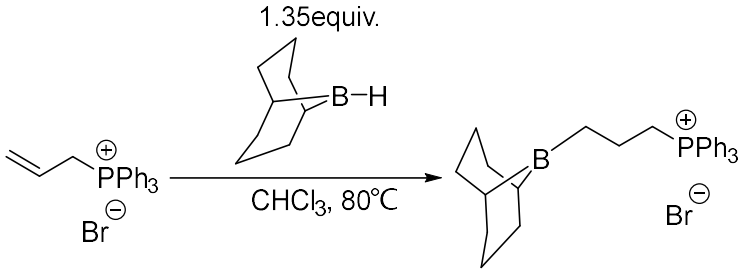



Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **L6** (162 MHz, $CDCl_3$, 298 K)

# Synthesis of organoboron catalysts

### Synthesis of C3 phosphonium borane catalyst 1




To a teflon valve sealed Schlenk vessel, C3 phosphonium salt **L1** (192 mg, 0.5 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane (9-BBN) (82.0 mg, 0.675 mmol, 1.35 equiv.) was charged in a glovebox. 8 mL $CHCl_3$ was added and the solution was heated at 80 ℃ for 24h. Monitoring the $^{1}H$ NMR spectroscopy revealed full conversion. The reaction mixture was concentrated in vacuo to afford the crude solid product that was further purified by washing it with n-hexane three times. The white solid product was dried for 12 h in vacuo at 40 °C to give the product as a white powder. The isolated yield was 92% (235.0 mg, 0.46 mmol). $^{1}H$ NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.90 (m, 6H, *o*-$Ph^{H}$), 7.78 (m,

3H, *p*-Ph$^{H}$), 7.69 (m, 6H, *m*-Ph$^{H}$), 3.93 (m, 2H, $PCH_2$, 1.82-1.53 (m, 15H, bicyclo-H), 1.37, 1.25 (m, 2H, $CH_2$), 1.15 (m, 2H, $BCH_2$). $^{13}C\{^1H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 135.1 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Ph$^{C}$), 133.8 (d, $^3J_{PC}$ = 10.0 Hz, *m*-Ph$^{C}$), 130.6 (d, $^2J_{PC}$ = 12.4 Hz, *o*-Ph$^{C}$), 118.6 (d, $^1J_{PC}$ = 85.4 Hz, *i*-Ph$^{C}$), 33.5 (s, bicyclo-C), 33.1 (s, bicyclo-C). 30.9 (br, $BCH_2$), 25.3 (d, $^1J_{PC}$ = 47.4 Hz, $PCH_2$), 23.2 (s, bicyclo-C), 23.1 (s, bicyclo-C), 18.2 (d, $^2J_{PC}$ = 4.7 Hz, $CH_2$). $^{11}B\{^1H\}$NMR (128 MHz, $CDCl_3$, 298 K) δ (ppm) = 86.6 (br), 59.1 (br). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.0 (s). **Elemental analysis**: calc. for $C_{29}H_{35}BBrP^+$ (504.1747 g/mol): C, 68.93; H, 6.98. Found: C, 68.77; H, 7.05. **Mass Spectrometry (ESI-HRMS):** calculated for $C_{29}H_{35}BP^+$: 425.2564; found: 425.2569.

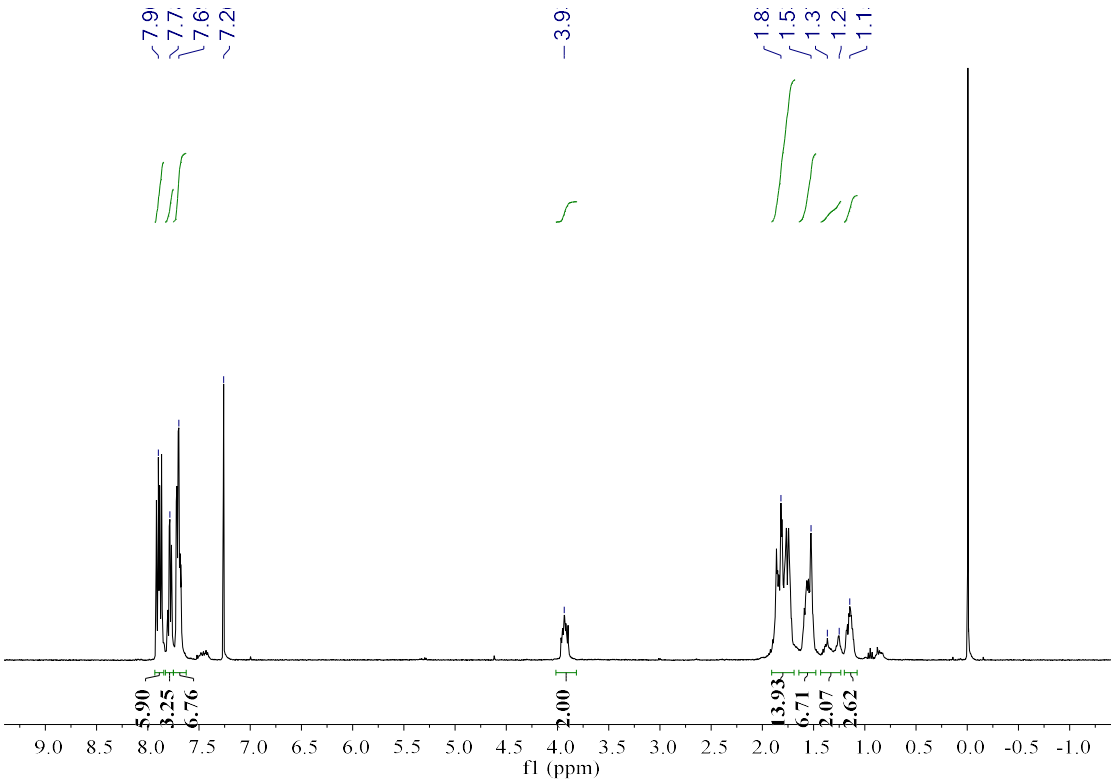



Figure S19. $^1H$ NMR spectrum of **1** (400 MHz, $CDCl_3$, 298 K)

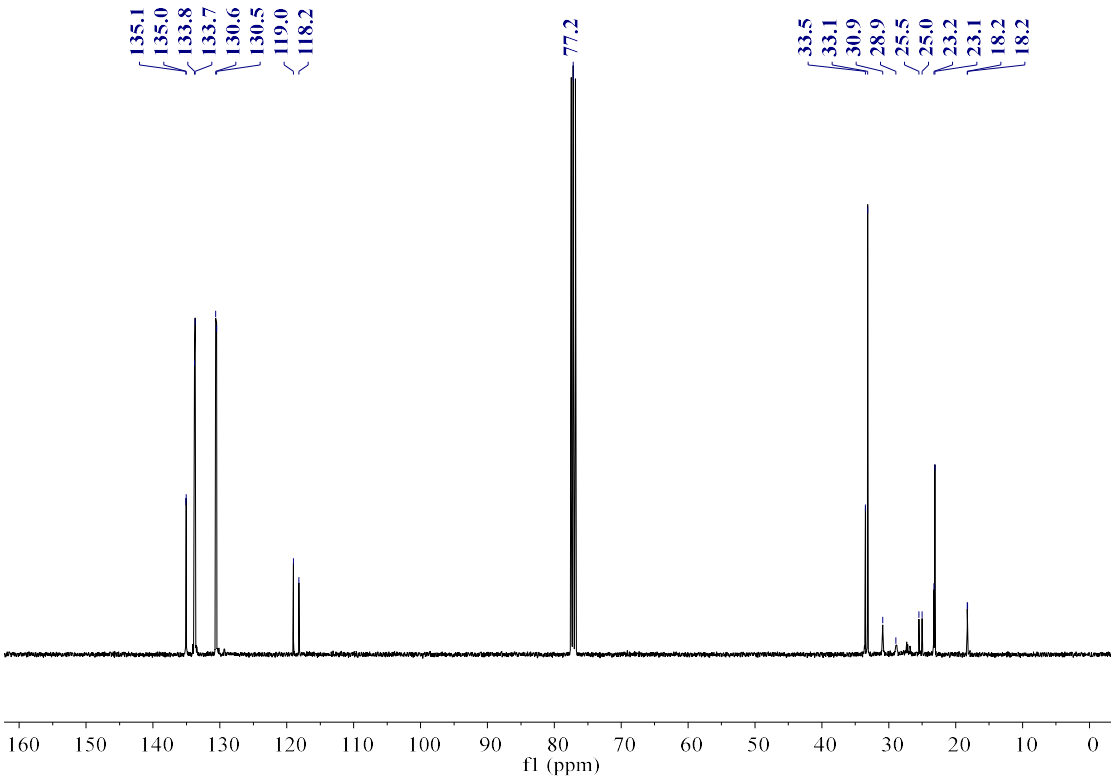



Figure S20. $^{13}C\{^{1}H\}$ spectrum of **1** (100 MHz, $CDCl_3$, 298 K)

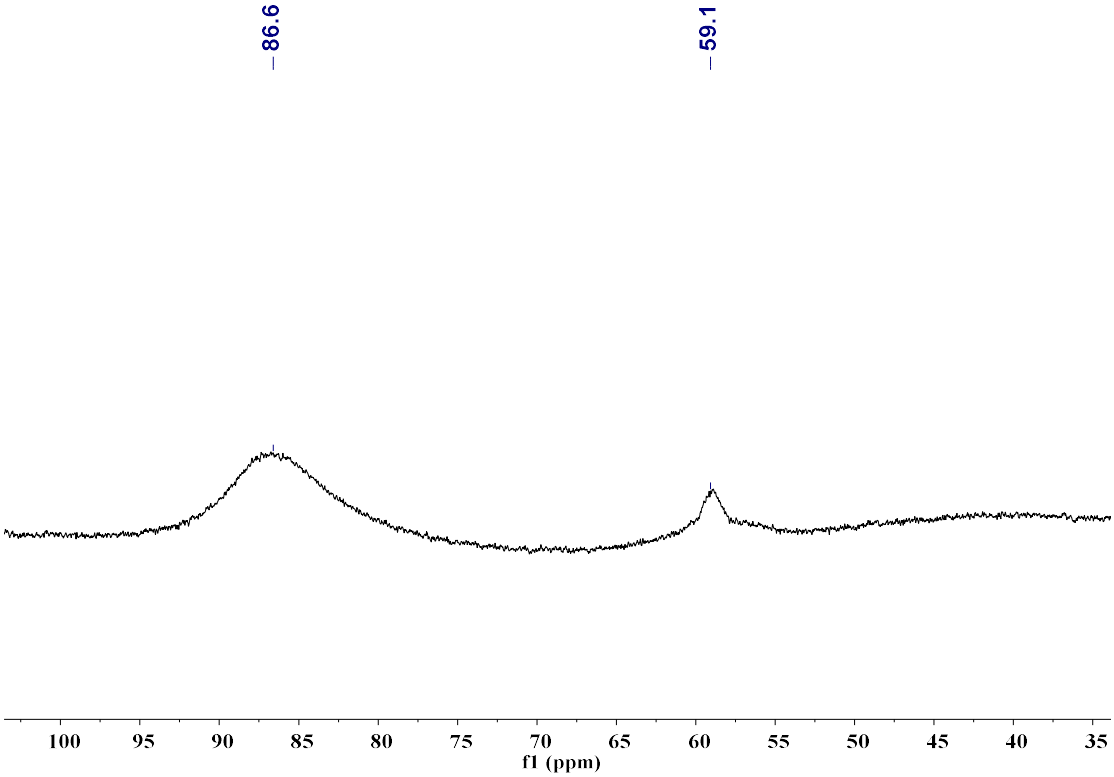



Figure S21. $^{11}B\{^{1}H\}$ NMR spectrum of **1** (128 MHz, $CDCl_3$, 298 K)

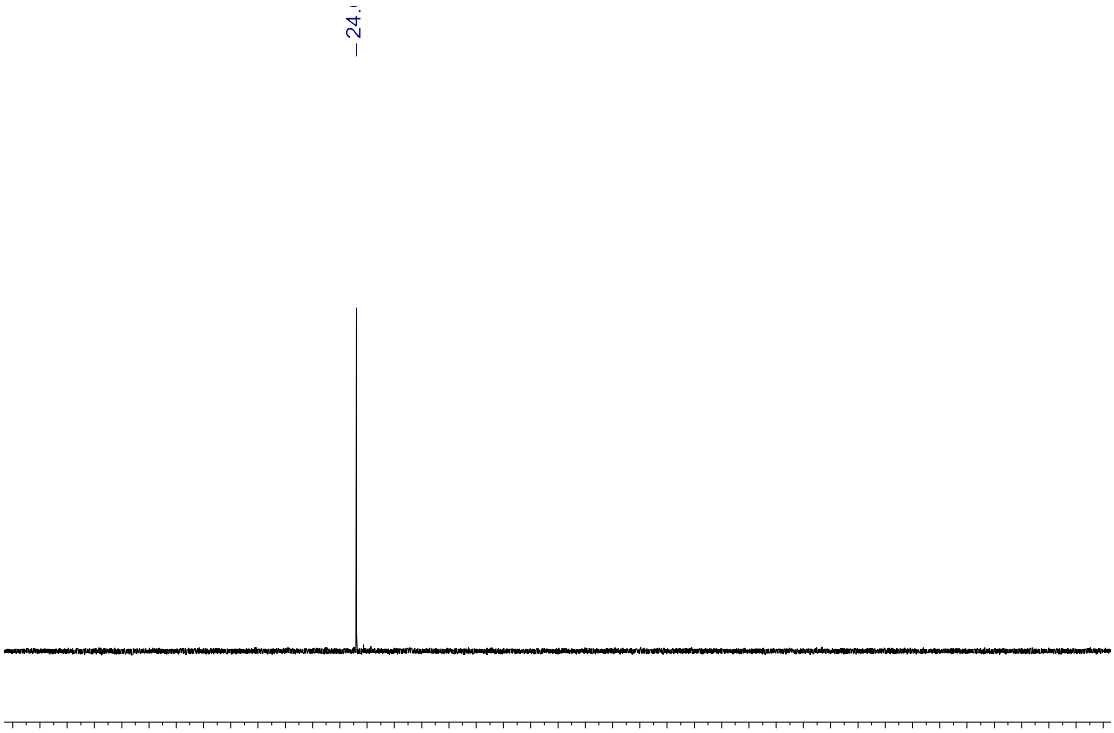
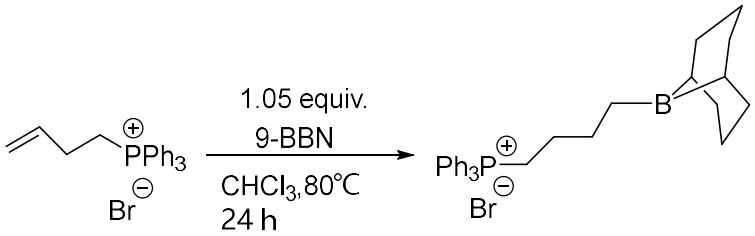



Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of **1** (162 MHz, $CDCl_3$, 298 K)

**Synthesis of C4 phosphonium borane catalyst 2** .




To a teflon valve sealed Schlenk vessel, C4 phosphonium salt **L2** (0.250 g, 0.63 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane (9-BBN) (80.7 mg , 0.66 mmol, 1.05 equiv.) was charged in a glovebox. 8 mL $CHCl_3$ was added and the solution was heated at 80 ℃ for 24h. Monitoring the $^{1}H$ NMR spectroscopy revealed full conversion. The reaction mixture was concentrated in vacuo to afford the crude solid product that was further purified by washing it with n-hexane three times. The white solid product was dried for 12 h in vacuo at 40 °C to give the product as a white powder. The isolated yield was 95% (311.0 mg, 0.60 mmol). $^{1}H$ NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.87 (m, 6H, *o*-$Ph^H$), 7.78 (m, 3H, *p*-$Ph^H$), 7.70 (m, 6H, *m*-$Ph^H$), 3.86 (m, 2H, $PCH_2$, 1.84-1.54 (m, 15H, bicyclo-H), 1.54 (m, 2H, $PCH_2\mathbf{CH_2}$), 1.35 (m, 2H, $BCH_2$), 1.11 (m, 2H, $BCH_2\mathbf{CH_2}$). $^{13}C\{^{1}H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 135.0 (d, $^{4}J_{PC}$ =

2.8 Hz, *p*-Ph$^{C}$), 133.7 (d, $^{3}J_{PC}$ = 10.0 Hz, *m*-Ph$^{C}$), 130.5 (d, $^{2}J_{PC}$ = 12.5 Hz, *o*-Ph$^{C}$), 118.5 (d, $^{1}J_{PC}$ = 85.8 Hz, *i*-Ph$^{C}$), 33.2 (s, bicyclo-C), 33.1 (s, bicyclo-C). 30.9 (br, $BCH_2$), 27.5 (m, $CH_2$), 25.7 (d, $^{1}J_{PC}$ = 16.1 Hz, $PCH_2$), 25.5 (d, $^{2}J_{PC}$ = 4.7 Hz, $CH_2$), 23.2 (s, bicyclo-C), 22.6 (s, bicyclo-C). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$, 298 K) δ (ppm) = 86.5 (br), 58.5 (br). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.5 (s). **Elemental analysis**: calc. for $C_{30}H_{37}BBrP$ (518.1909 g/mol): C, 69.39; H, 7.18. Found: C, 69.51; H, 6.98. **Mass Spectrometry (ESI-HRMS):** calculated for $C_{30}H_{37}BP^{+}$: 439.2720; found: 439.2714.

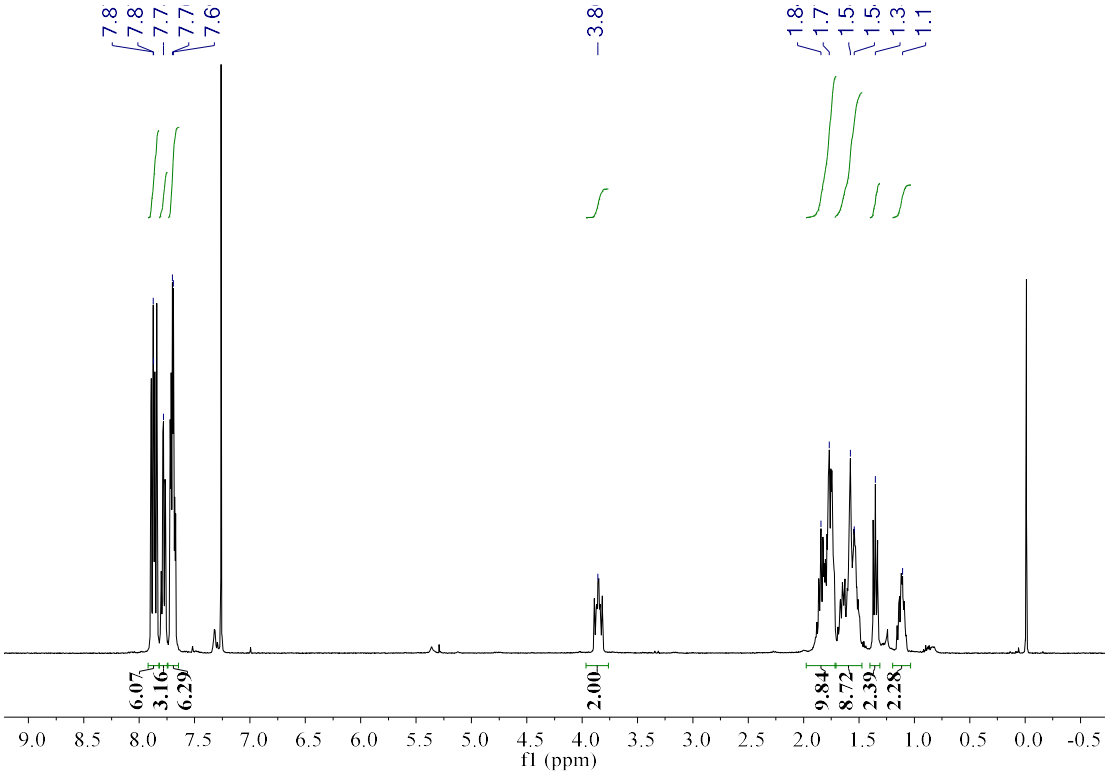



Figure S23. $^{1}H$ NMR spectrum of **2** (400 MHz, $CDCl_3$, 298 K)

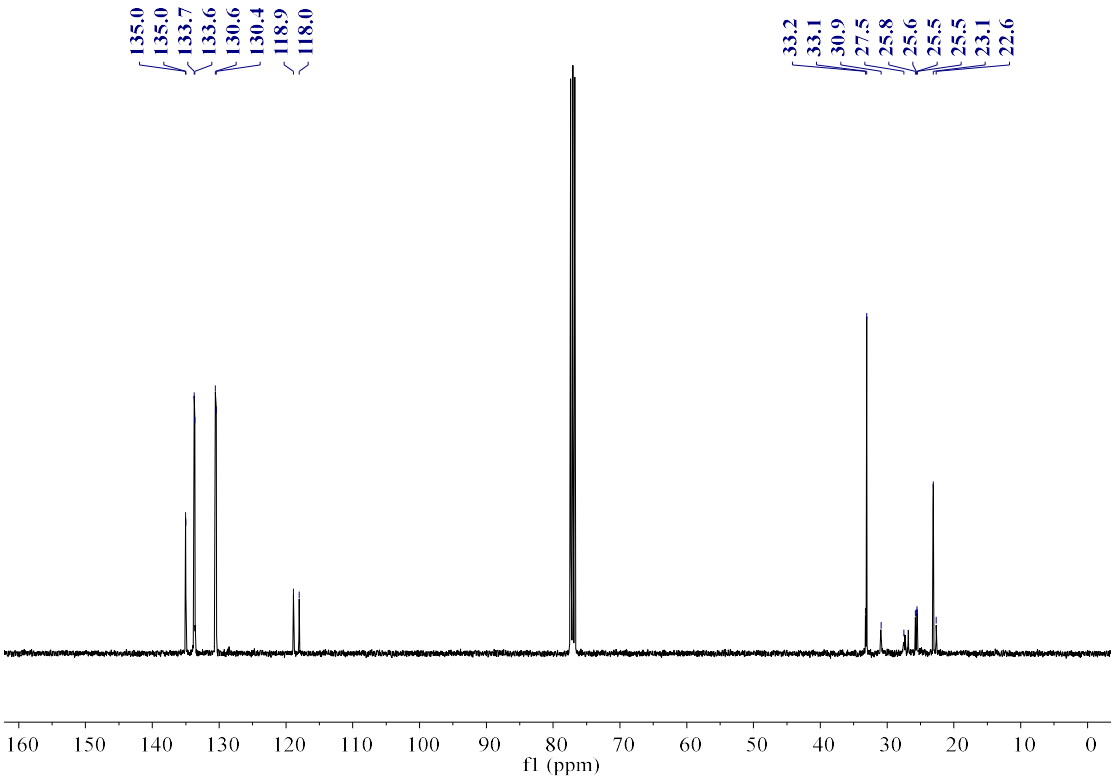



Figure S24. $^{13}C\{^{1}H\}$ spectrum of **2** (100 MHz, $CDCl_3$, 298 K)

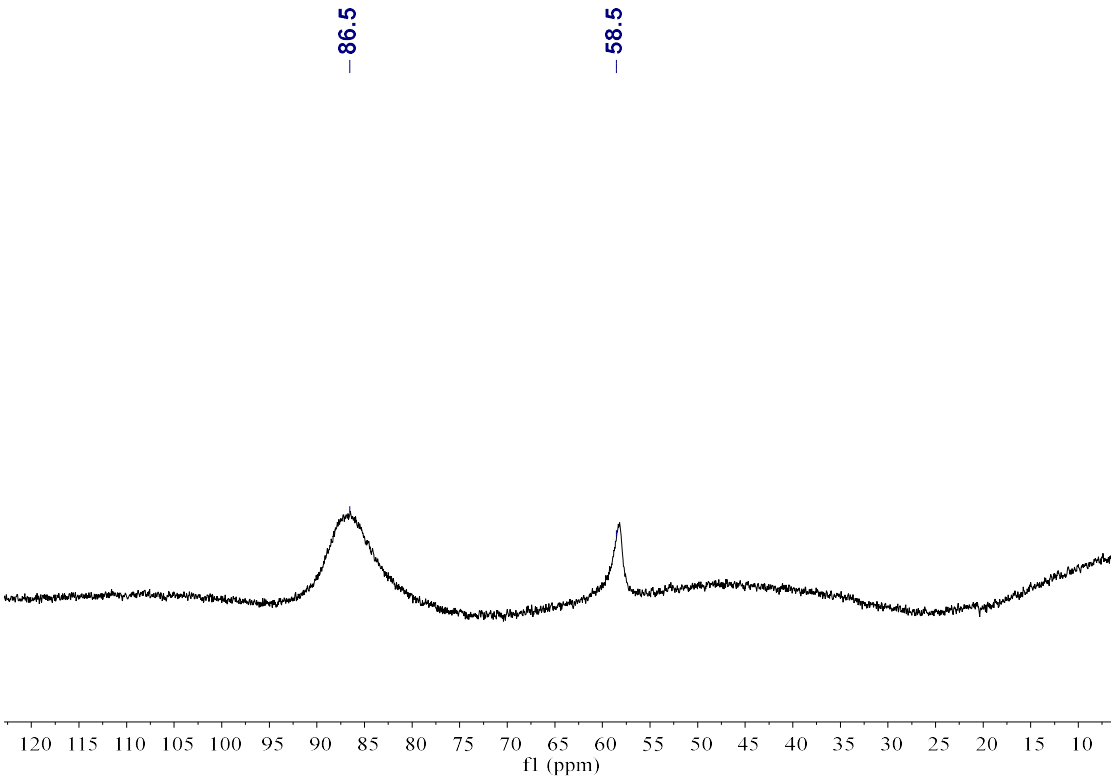



Figure S25. $^{11}B\{^{1}H\}$ NMR spectrum of **2** (128 MHz, $CDCl_3$, 298 K)

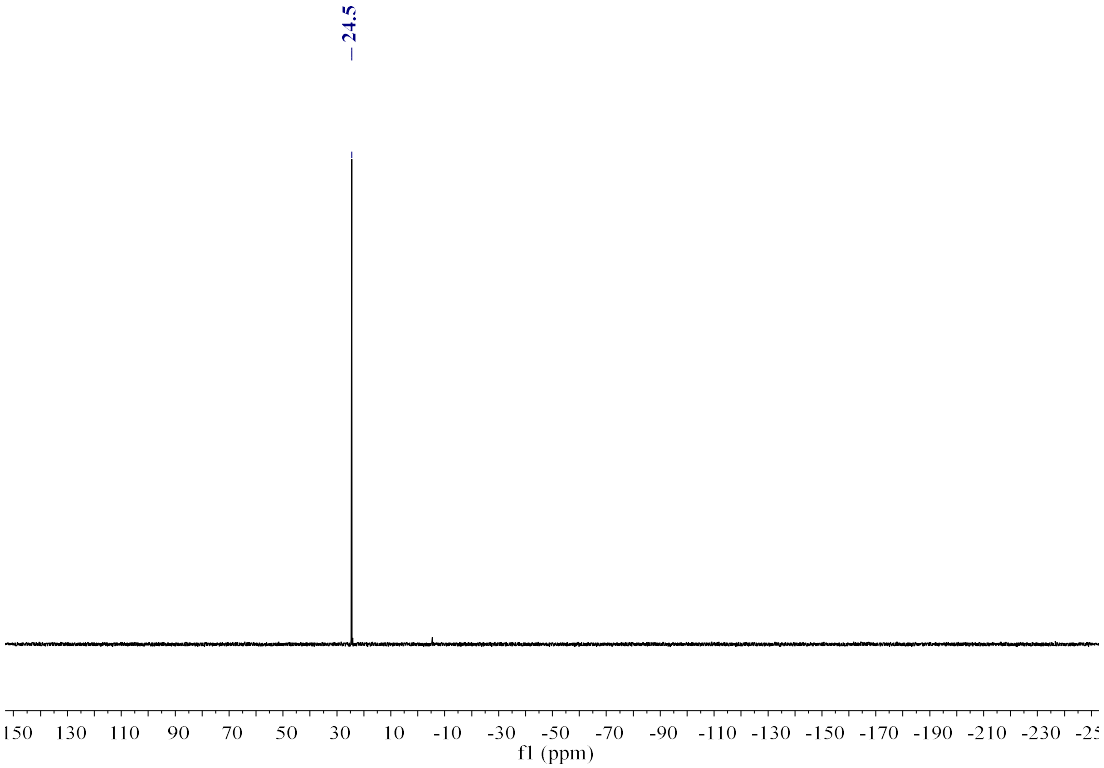
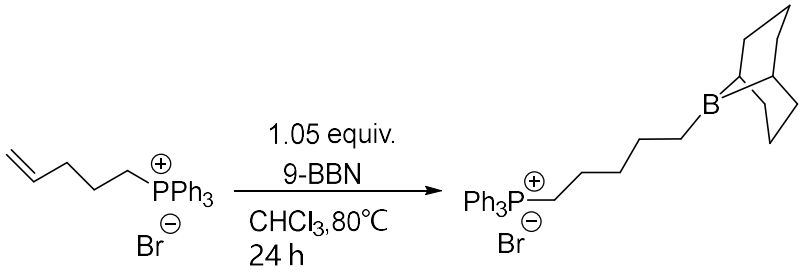



Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum of **2** (162 MHz, $CDCl_3$, 298 K)

**Synthesis of C5 phosphonium borane catalyst 3**




To a teflon valve sealed Schlenk vessel, C5 phosphonium salt **L3** (102.8 mg, 0.25 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane (9-BBN) (32 mg , 0.263 mmol, 1.05 equiv.) was charged in a glovebox. 8 mL $CHCl_3$ was added and the solution was heated at 80 ℃ for 24h. Monitoring the $^{1}H$ NMR spectroscopy revealed full conversion. The reaction mixture was concentrated in vacuo to afford the crude solid product that was further purified by washing it with n-hexane three times. The white solid product was dried for 12 h in vacuo at 40 °C to give the product as a white powder. The isolated yield was 92% (122.6 mg, 0.23 mmol). $^{1}H$ NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.89 (m, 6H, *o*-$Ph^H$), 7.79 (m, 3H, *p*-$Ph^H$), 7.70 (m, 6H, *m*-$Ph^H$), 3.88 (m, 2H, $PCH_2$, 1.79-1.60 (m, 15H,

bicyclo-H), 1.68 (m, 2H, $PCH_2\mathbf{CH_2}$), 1.46 (m, 2H, $BCH_2$), 1.29 (m, 2H, $PCH_2CH_2\mathbf{CH_2}$), 1.15 (m, 2H, $BCH_2\mathbf{CH_2}$). $^{13}C\{^1H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 135.1 (d, $^4J_{PC}$ = 3.0 Hz, *p*-$Ph^C$), 133.7 (d, $^3J_{PC}$ = 10.0 Hz, *m*-$Ph^C$), 130.6 (d, $^2J_{PC}$ = 12.6 Hz, *o*-$Ph^C$), 118.4 (d, $^1J_{PC}$ = 85.8 Hz, *i*-$Ph^C$), 33.6 (d, *J* = 15.1 Hz, $CH_2$), 33.1 (s, bicyclo-C), 31.0 (br, $BCH_2$), 27.4 (d, *J* = 9.5 Hz, $CH_2$), 27.6 (s, bicyclo-C), 24.2 (s, bicyclo-C), 23.2 (s, bicyclo-C), 22.7 (d, $CH_2$), 22.6 (d, $^1J_{PC}$ = 9.7 Hz, $PCH_2$). $^{11}B\{^1H\}$NMR (128 MHz, $CDCl_3$, 298 K) δ (ppm) = 87.8 (br), 58.0 (br). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.6 (s). **Elemental analysis**: calc. for $C_{31}H_{39}BBrP$ (532.2066 g/mol): C, 69.81; H, 7.37. Found: C, 69.75; H, 7.30. **Mass Spectrometry (ESI-HRMS):** calculated for $C_{31}H_{39}BP$: 453.2877; found: 453.2871.

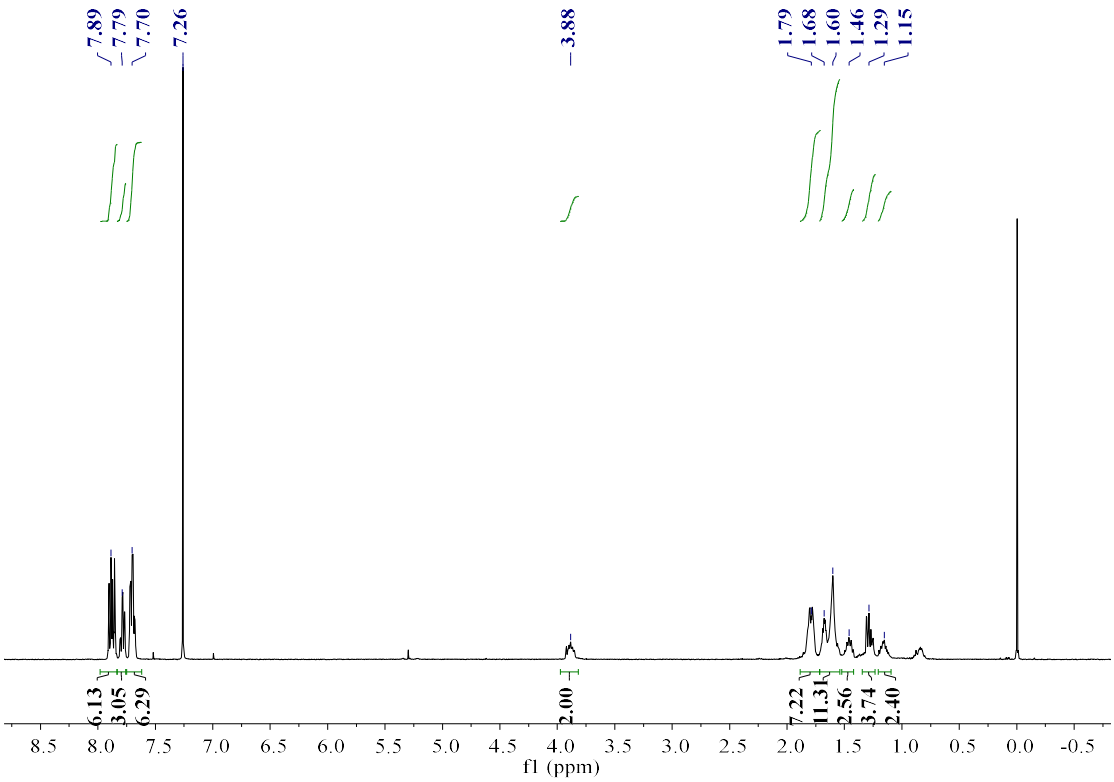



Figure S27. $^1H$ NMR spectrum of **3** (400 MHz, $CDCl_3$, 298 K)

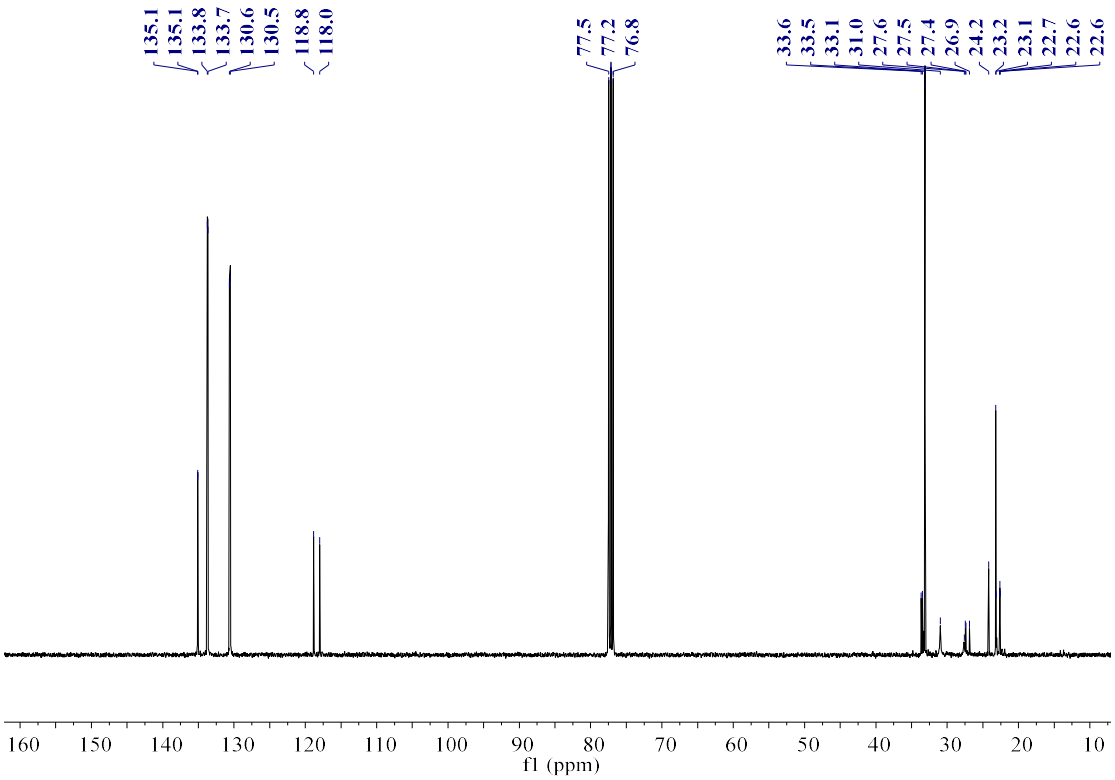



Figure S28. $^{13}C\{^{1}H\}$ spectrum of **3** (100 MHz, $CDCl_3$, 298 K)

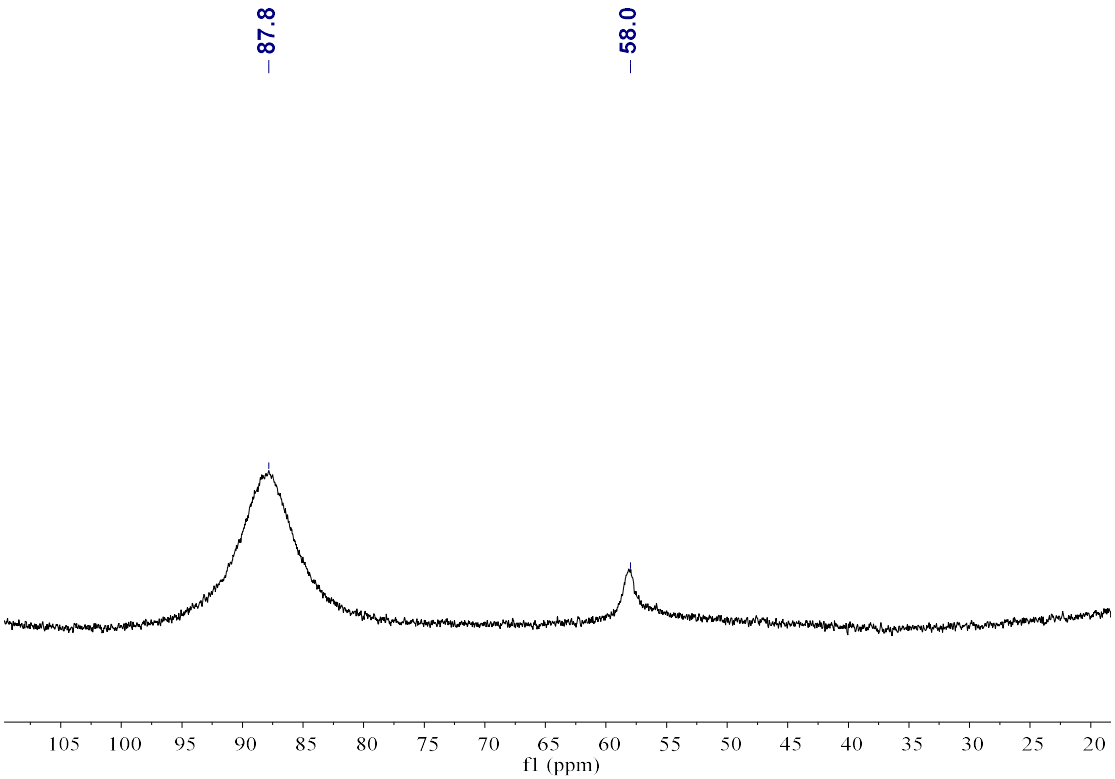



Figure S29. $^{11}B\{^{1}H\}$ NMR spectrum of **3** (128 MHz, $CDCl_3$, 298 K)

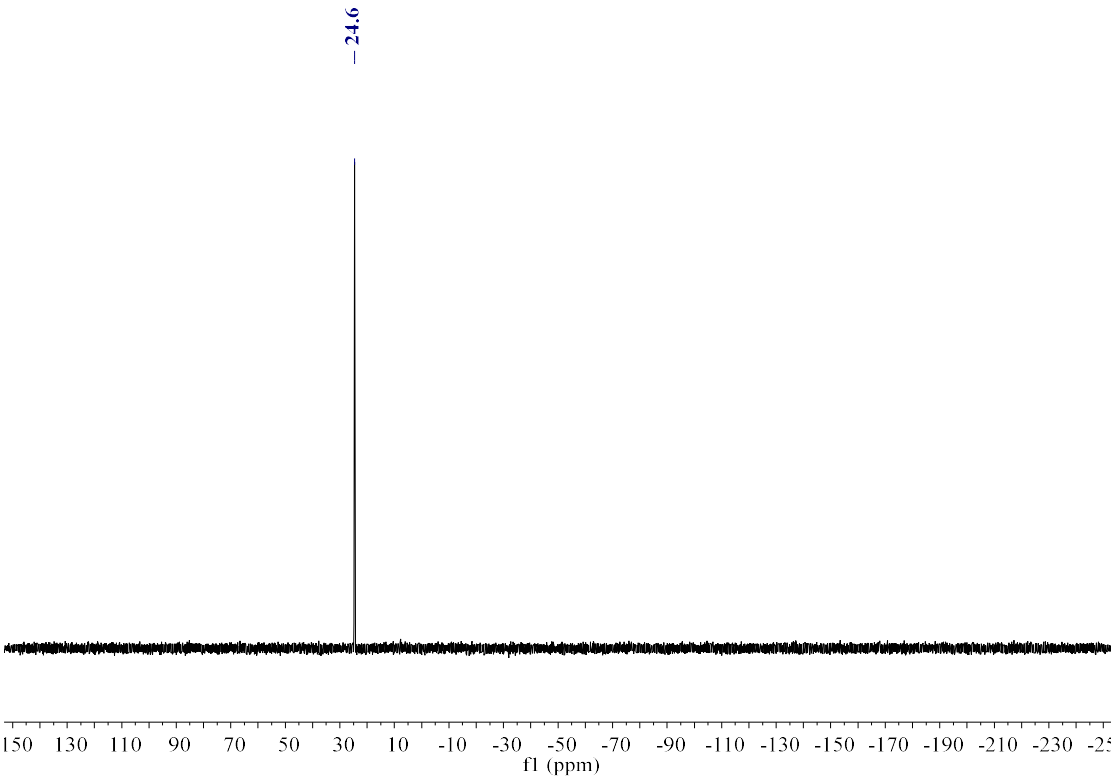
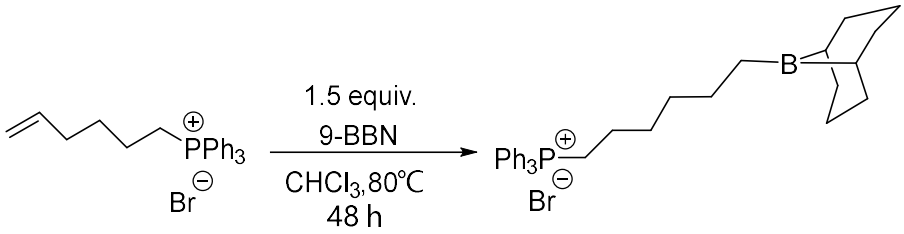



Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum of **3** (162 MHz, $CDCl_3$, 298 K)

**Synthesis of C6 phosphonium borane catalyst 4**




To a teflon valve sealed Schlenk vessel, C6 phosphonium salt **L4** (102.8 mg, 0.25 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane (9-BBN) (45.8 mg , 0.375 mmol, 1.5 equiv.) was charged in a glovebox. 8 mL $CHCl_3$ was added and the solution was heated at 80 ℃ for 24h. Monitoring the $^{1}H$ NMR spectroscopy revealed full conversion. The reaction mixture was concentrated in vacuo to afford the crude solid product that was further purified by washing it with n-hexane three times. The white solid product was dried for 12 h in vacuo at 40 °C to give the product as a white powder. The isolated yield was 92% (127.0 mg, 0.23 mmol). $^{1}H$ NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.88 (m, 6H, *o*-$Ph^H$), 7.79 (m, 3H, *p*-$Ph^H$), 7.70 (m, 6H, *m*-$Ph^H$), 3.88 (m, 2H, $PCH_2$, 1.81-1.61 (m, 15H,

bicyclo-H), 1.38 (m, $PCH_2\mathbf{CH_2}$), 1.28 (m, $PCH_2CH_2\mathbf{CH_2}$), 1.15 (m, 2H, $BCH_2$), 1.15 (m, 2H, $BCH_2\mathbf{CH_2}$). $^{13}C\{^1H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 135.1 (d, $^4J_{PC}$ = 2.9 Hz, *p*-$Ph^C$), 133.8 (d, $^3J_{PC}$ = 10.0 Hz, *m*-$Ph^C$), 130.6 (d, $^2J_{PC}$ = 12.6 Hz, *o*-$Ph^C$), 118.5 (d, $^1J_{PC}$ = 85.8 Hz, *i*-$Ph^C$), 33.3 (s, bicyclo-C), 33.2 (s, bicyclo-C), 32.4 (s, $CH_2$), 31.0 (br, $BCH_2$), 30.4 (d, *J* = 15.4 Hz, $CH_2$) 27.4 (d, *J* = 7.7 Hz, $CH_2$), 27.6 (s, bicyclo-C), 24.0 (s, bicyclo-C), 23.3 (s, bicyclo-C), 23.2 (d, $CH_2$), 22.7 (d, $^1J_{PC}$ = 9.7 Hz, $PCH_2$). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 298 K) δ (ppm) = 88.0 (br), 58.1(br). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.5 (s). **Elemental analysis**: calc. for $C_{32}H_{41}BBrP$ (546.2228 g/mol): C, 70.22; H, 7.55. Found: C, 70.10; H, 7.30. **Mass Spectrometry (ESI-HRMS):** calculated for $C_{32}H_{41}BP$: 467.3033; found: 467.3027.

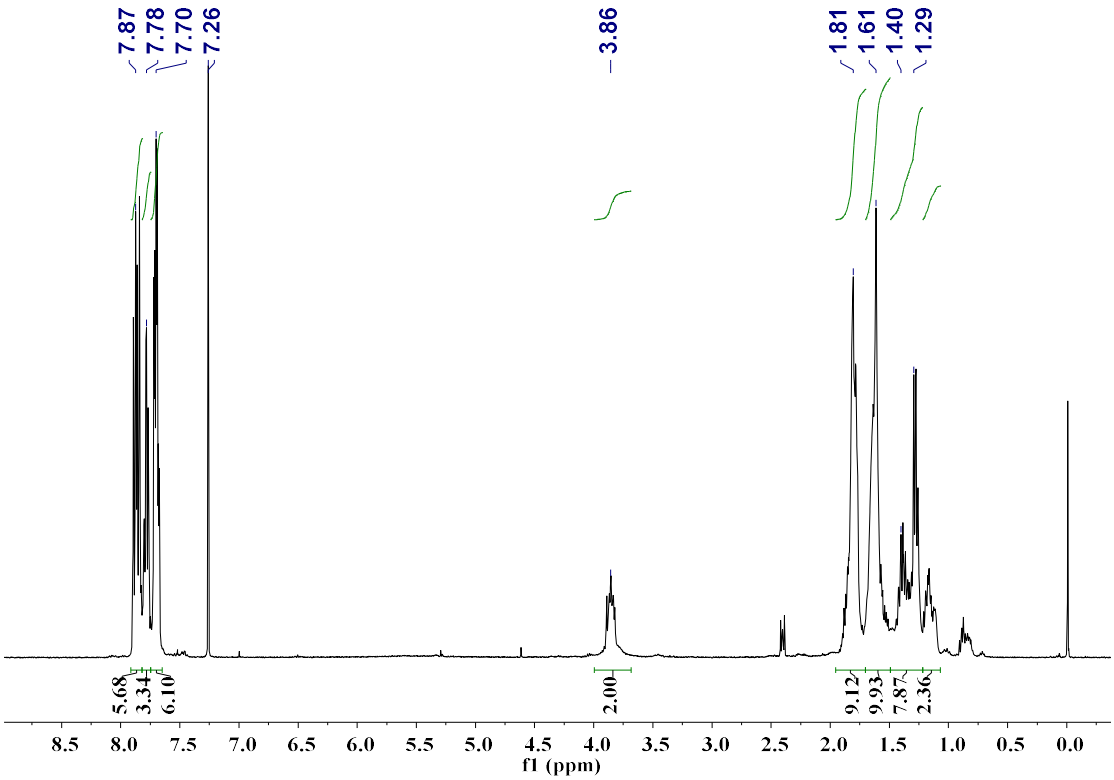



Figure S31. $^1H$ NMR spectrum of **4** (400 MHz, $CDCl_3$, 298 K)

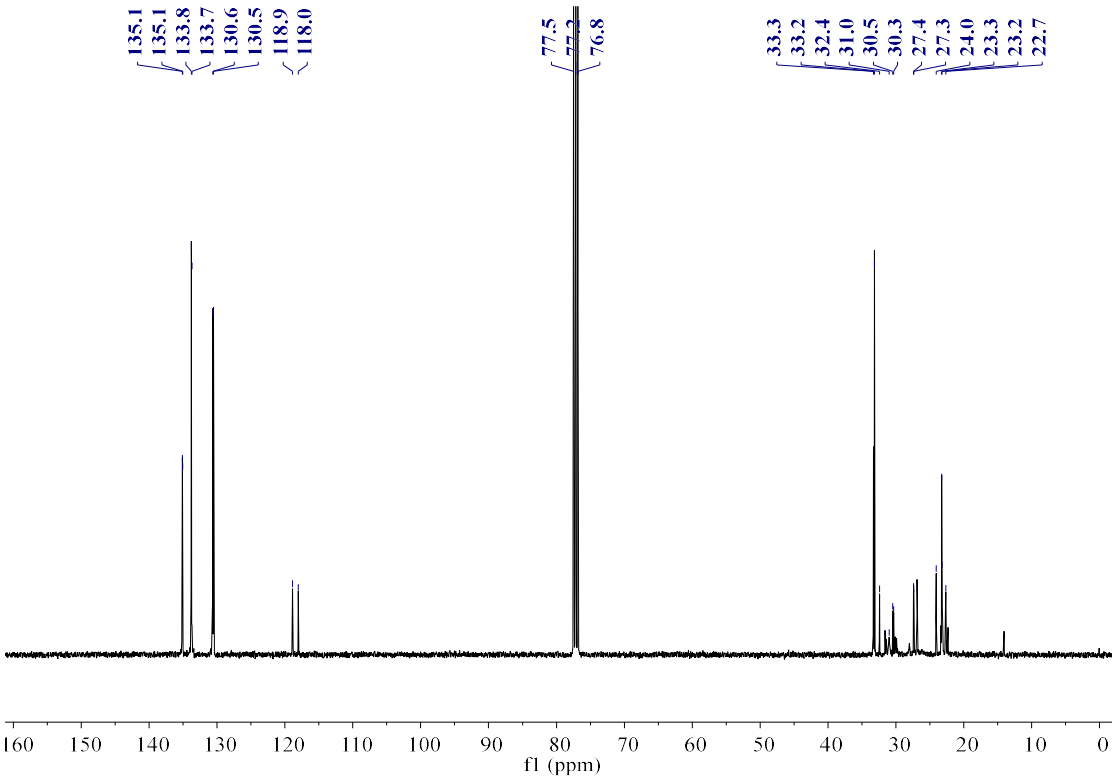



Figure S32. $^{13}C\{^{1}H\}$ spectrum of **4** (100 MHz, $CDCl_3$, 298 K)

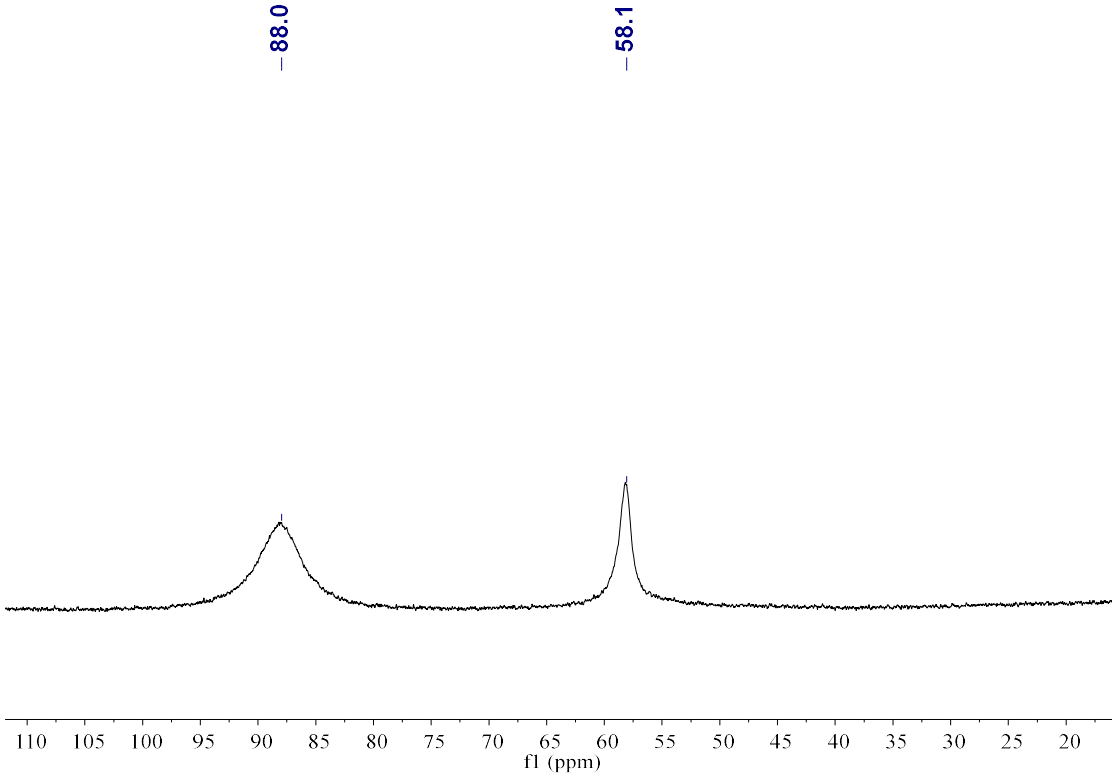



Figure S33. $^{11}B\{^{1}H\}$ NMR spectrum of **4** (128 MHz, $CDCl_3$, 298 K)

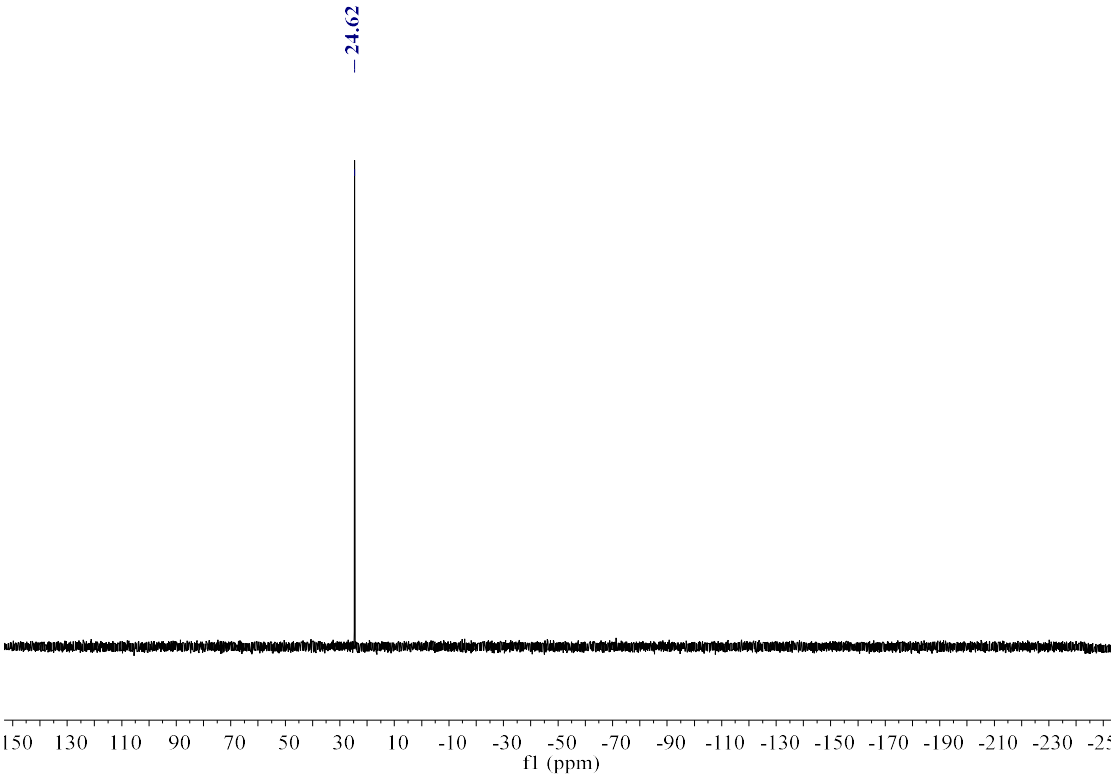
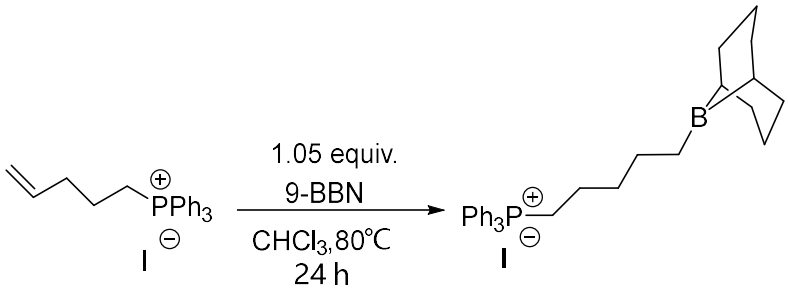



Figure S34. $^{31}P\{^{1}H\}$ NMR spectrum of **4** (162 MHz, $CDCl_3$, 298 K)

**Synthesis of C6 phosphonium borane catalyst 5**




To a teflon valve sealed Schlenk vessel, C5 phosphonium salt **L5** (366 mg, 0.8 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane (9-BBN) (102.5 mg , 0.84 mmol, 1.05 equiv.) was charged in a glovebox. 10 mL $CHCl_3$ was added and the solution was heated at 80 ℃ for 24 h. Monitoring the $^{1}H$ NMR spectroscopy revealed full conversion. The reaction mixture was concentrated in vacuo to afford the crude solid product that was further purified by washing it with n-hexane three times. The white solid product was dried for 12 h in vacuo at 40 °C to give the product as a white powder. The isolated yield was 93% (431.0 mg, 0.74 mmol). $^{1}H$

NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.82 (m, 9H, *o*-$Ph^H$ and *p*-$Ph^H$), 7.71 (m, 6H, *m*-$Ph^H$), 3.73 (m, 2H, $PCH_2$), 1.80-1.61 (m, 18H, bicyclo-H and $CH_2$), 1.48 (m, 2H, $PCH_2\mathbf{CH_2}$), 1.29 (m, 2H, $B\mathbf{CH_2}$), 1.15 (m, 2H, $BCH_2\mathbf{CH_2}$). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 298 K) δ (ppm) = 86.8 (br). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.6 (s). $^{13}C\{^1H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 135.2 (d, $^4J_{PC}$ = 3.0 Hz, *p*-$Ph^C$), 133.8 (d, $^3J_{PC}$ = 10.1 Hz, *m*-$Ph^C$), 130.7 (d, $^2J_{PC}$ = 12.5 Hz, *o*-$Ph^C$), 118.2 (d, $^1J_{PC}$ = 85.9 Hz, *i*-$Ph^C$), 33.7 (d, $^2J_{PC}$ = 15.1 Hz, $CH_2$), 33.1 (s, bicyclo-C), 31.0 (br, $BCH_2$), 27.6 ($CH_2$), 24.2 (s, bicyclo-C), 23.3 (d, $^1J_{PC}$ = 50.0 Hz, $PCH_2$), 23.2 (s, bicyclo-C), 22.6 (d, $^3J_{PC}$ = 4.5 Hz, $CH_2$). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 298 K) δ (ppm) = 87.9 (br) and 58.4 (br). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.4 (s). **Elemental analysis**: calc. for $C_{31}H_{39}BIP$ (580.1922 g/mol): C, 64.16; H, 6.77. Found: C, 63.90; H, 6.90. **Mass Spectrometry (ESI-HRMS):** calculated for $C_{31}H_{39}BP$: 453.2877; found: 453.2871.

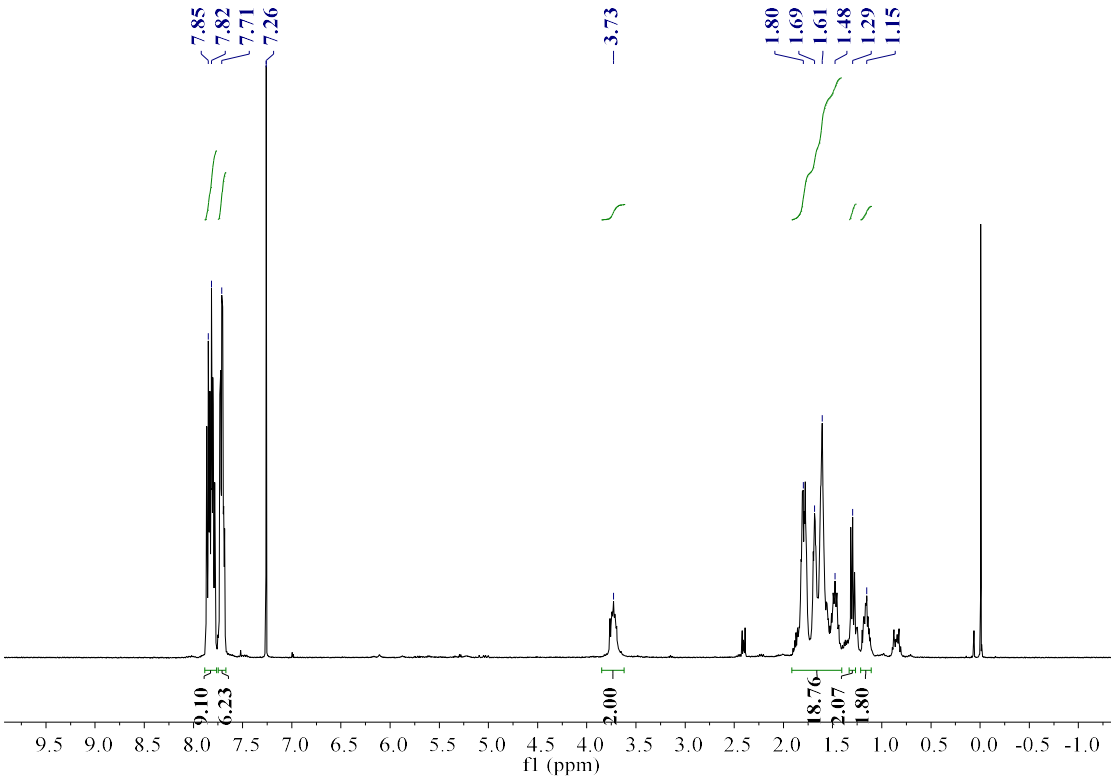



Figure S35. $^{1}H$ NMR spectrum of **5** (400 MHz, $CDCl_3$, 298 K)

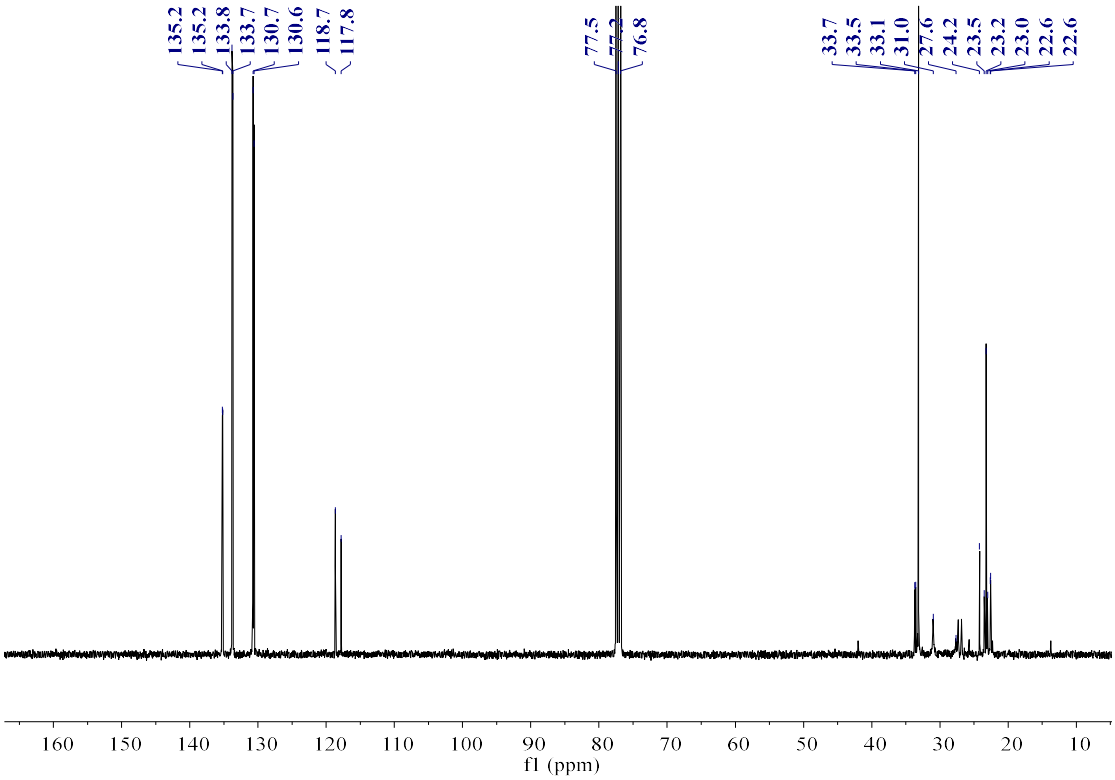



Figure S36. $^{13}C\{^{1}H\}$ spectrum of **5** (100 MHz, $CDCl_3$, 298 K)

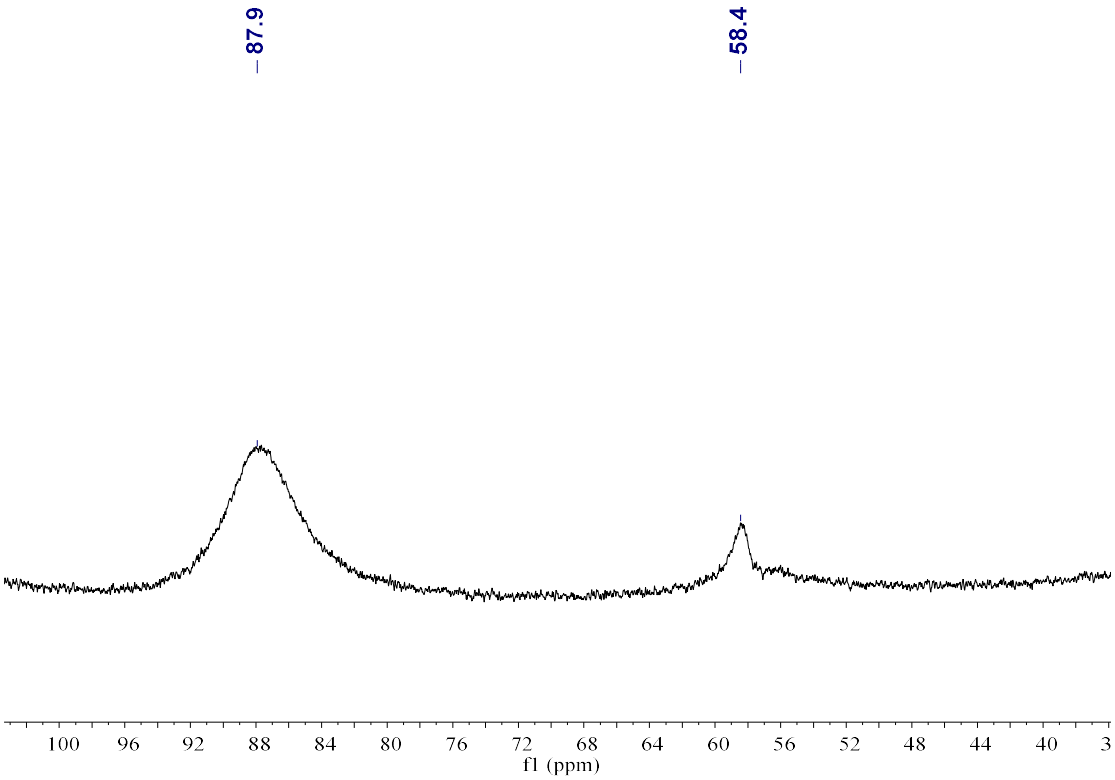



Figure S37. $^{11}B\{^{1}H\}$ NMR spectrum of **5** (128 MHz, $CDCl_3$, 298 K)

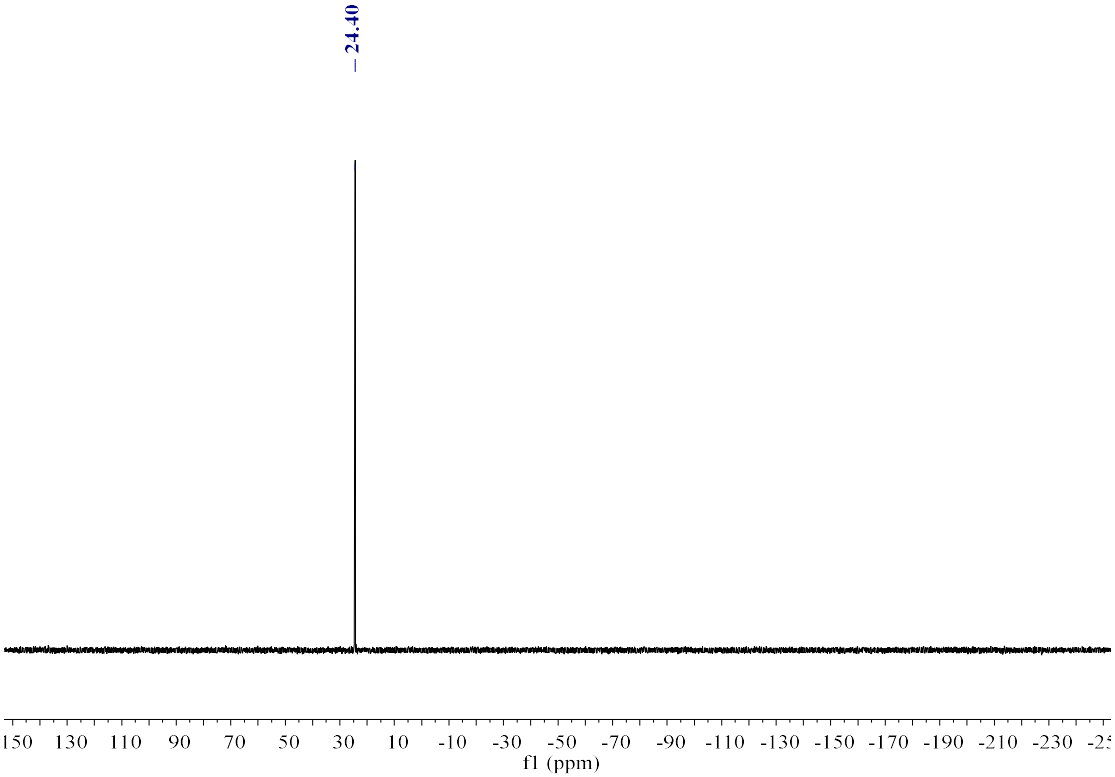
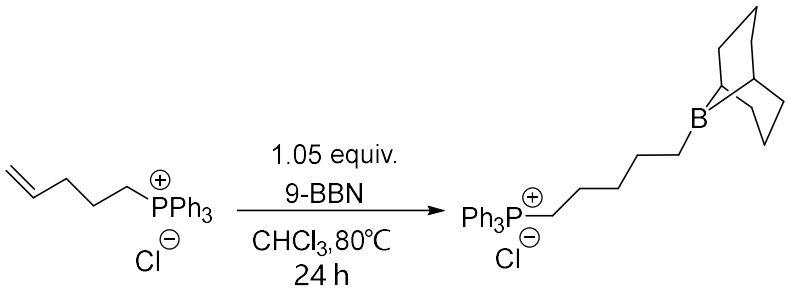
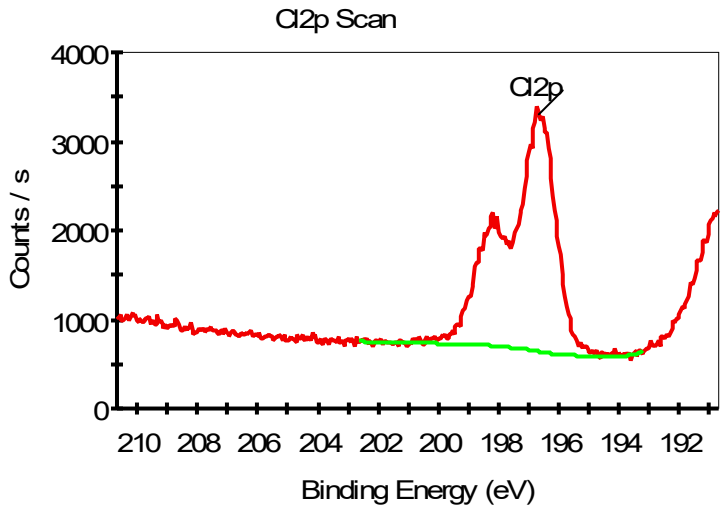



Figure S38. $^{31}P\{^{1}H\}$ NMR spectrum of **5** (162 MHz, $CDCl_3$, 298 K)

## Synthesis of C6 phosphonium borane catalyst 6




To a teflon valve sealed Schlenk vessel, C5 phosphonium salt **L6** (40.3 mg, 0.11 mmol, 1 equiv.) and 9-borabicyclo[3.3.1]nonane (9-BBN) (14.1 mg , 0.116 mmol, 1.05 equiv.) was charged in a glovebox. 6 mL $CHCl_3$ was added and the solution was heated at 80 ℃ for 24 h. Monitoring the $^1H$ NMR spectroscopy revealed full conversion. The reaction mixture was concentrated in vacuo to afford the crude solid product that was further purified by washing it with n-hexane three times. The white solid product was dried for 12 h in vacuo at 40 °C to give the product as a white powder. The isolated yield was 91% (48.0 mg, 0.10 mmol). X-ray photoelectron spectroscopy revealed that only chloride anion was deteted.




$^1H$ NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 7.88 (m, 6H, *o*-$Ph^H$), 7.79 (m, 3H, *p*-$Ph^H$), 7.71 (m, 6H, *m*-$Ph^H$), 3.93 (m, 2H, $PCH_2$, 1.81-1.60 (m, 17H, bicyclo-H and $BCH_2$), 1.46 (m, 2H, $PCH_2\mathbf{CH_2}$), 1.28 (m, 4H, $\mathbf{BCH_2}$), 1.16 (m, 2H, $BCH_2$ $\mathbf{CH_2}$). $^{13}C\{^1H\}$(100 MHz, $CDCl_3$, 298 K) δ (ppm) = 135.1 (d, $^4J_{PC}$ = 2.9 Hz, *p*-$Ph^C$), 133.7 (d, $^3J_{PC}$ = 10.0 Hz, *m*-$Ph^C$), 130.6 (d, $^2J_{PC}$ = 12.5 Hz, *o*-$Ph^C$), 118.5 (d, $^1J_{PC}$ = 85.7 Hz, *i*-$Ph^C$), 33.6 (d, *J* = 15.1 Hz, $CH_2$), 33.1 (s, bicyclo-C), 33.6 (d, $^2J_{PC}$ = 15.2 Hz, $PCH_2\mathbf{C}H_2$), 33.3 (s, bicyclo-C), 33.1 (s, bicyclo-C), 31.0 (br, $BCH_2$), 27.6 (br, $CH_2$), 24.2 (s, bicyclo-C), 23.2 (s, bicyclo-C), 22.7 (d, $^1J_{PC}$ = 49.3 Hz, $PCH_2$), 22.6 (d, $^3J_{PC}$

= 4.5 Hz, $CH_2$). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 298 K) δ (ppm) = 87.5 (br) and 57.7 (br). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) δ (ppm) = 24.6 (s). **Elemental analysis**: calc. for $C_{31}H_{39}BClP$ (488.2571 g/mol): C, 76.16; H, 8.04. Found: C, 76.40; H, 7.79. **Mass Spectrometry (ESI-HRMS):** calculated for $C_{31}H_{39}BP$: 453.2877; found: 453.2870.

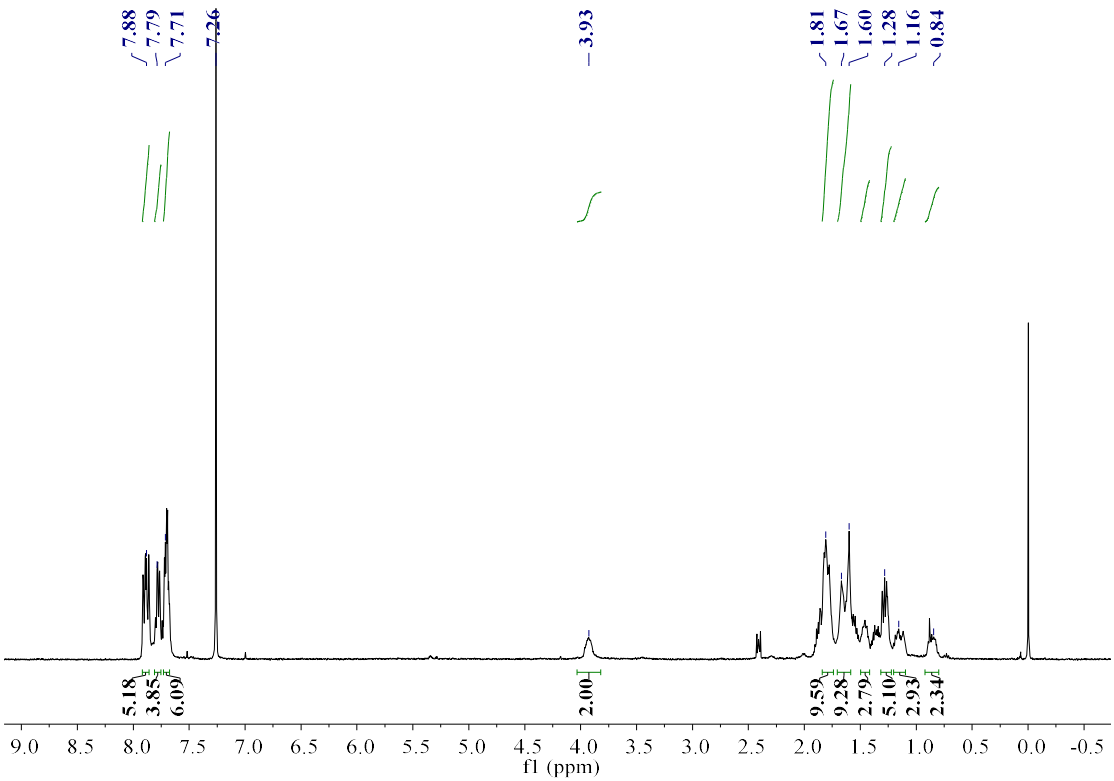



Figure S39. $^1H$ NMR spectrum of **6** (400 MHz, $CDCl_3$, 298 K)

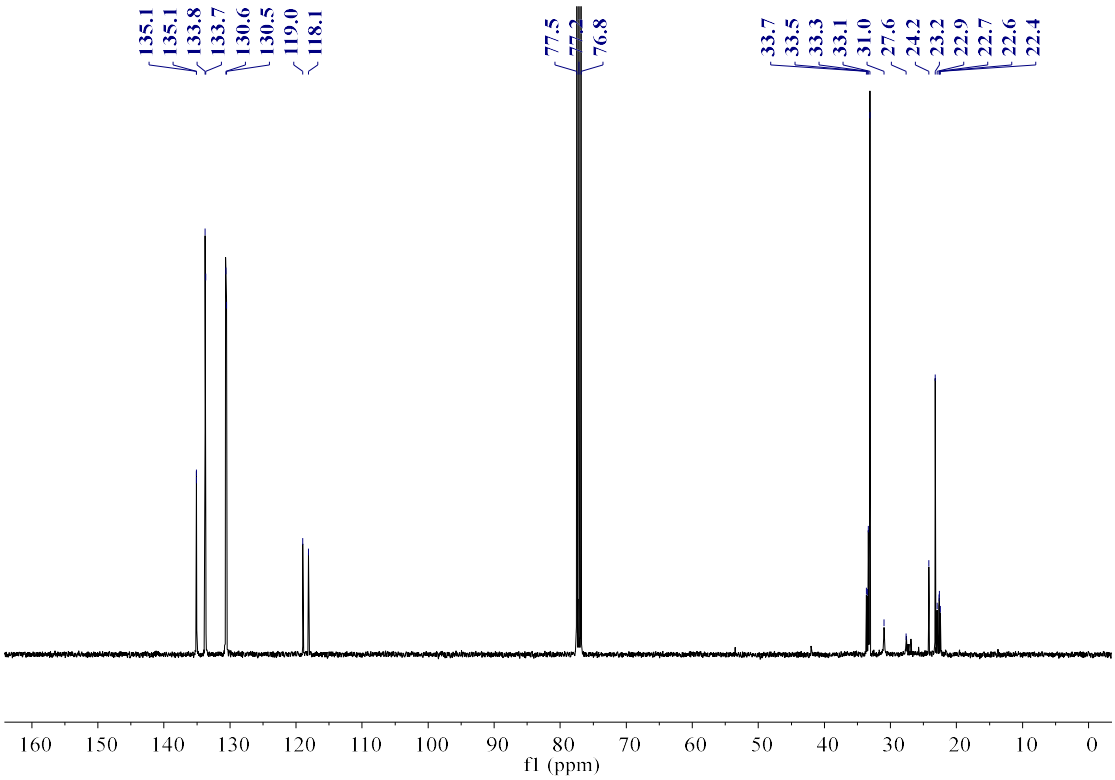



Figure S40. $^{13}C\{^{1}H\}$ spectrum of **6** (100 MHz, $CDCl_3$, 298 K)

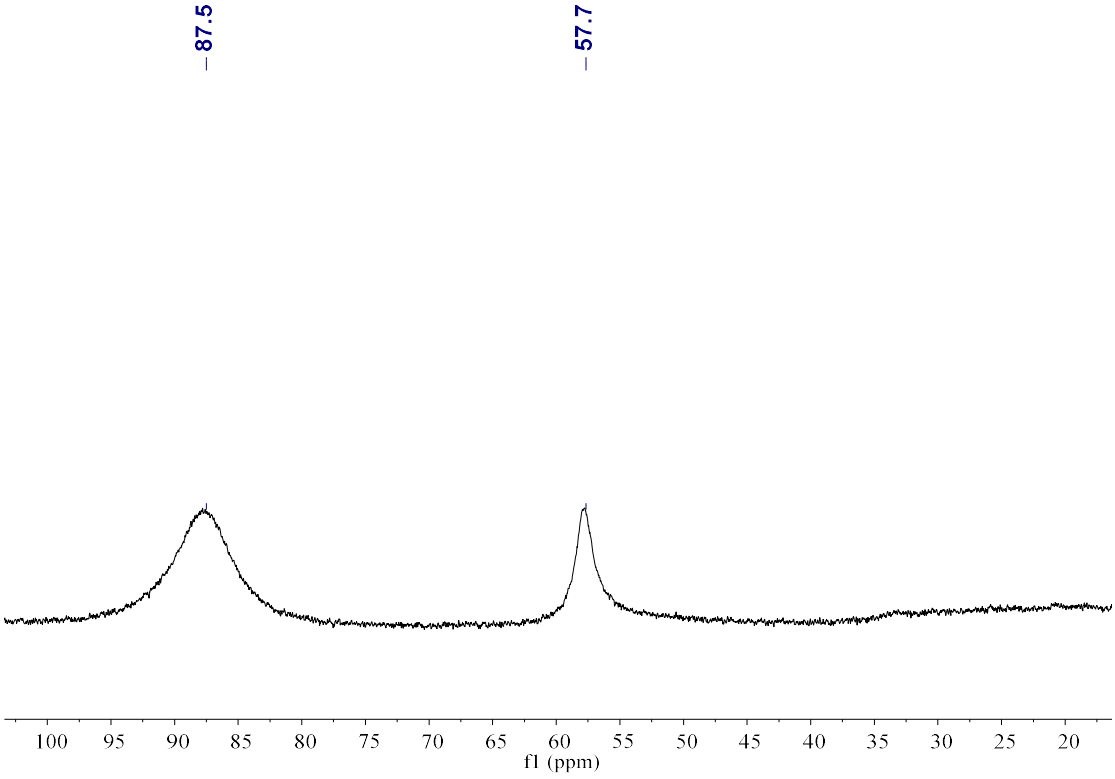



Figure S41. $^{11}B\{^{1}H\}$ NMR spectrum of **6** (128 MHz, $CDCl_3$, 298 K)

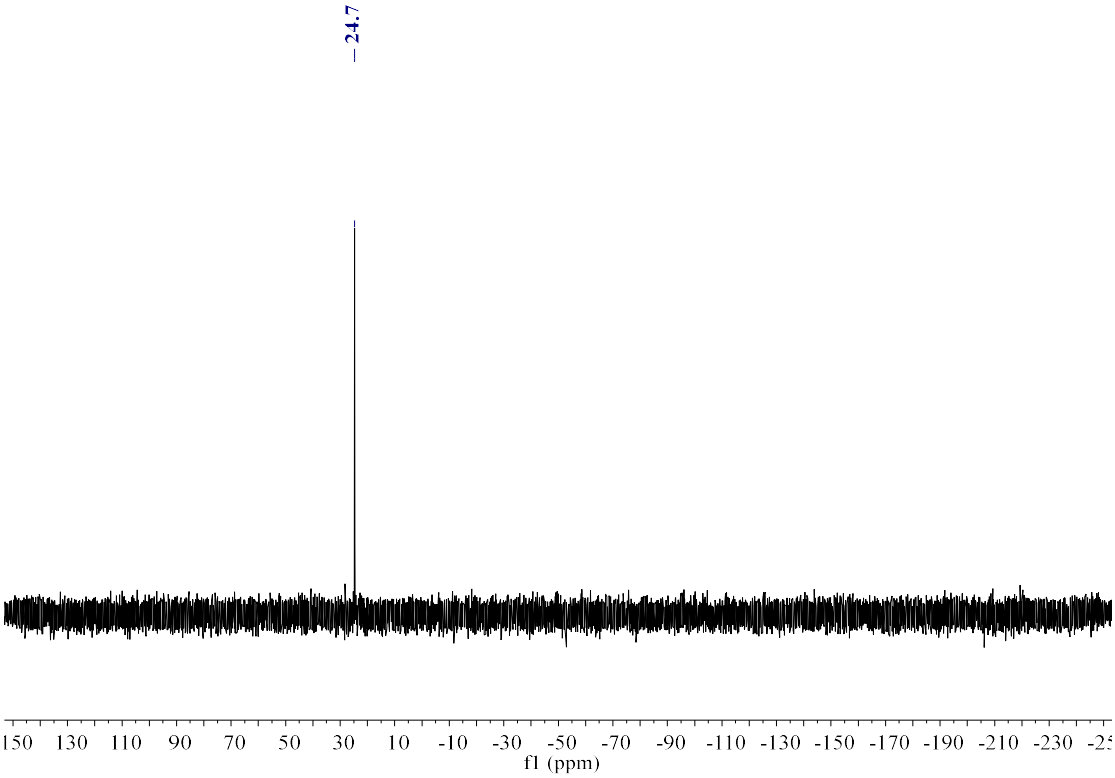



Figure S42. $^{31}P\{^{1}H\}$ NMR spectrum of **6** (162 MHz, $CDCl_3$, 298 K)

**General procedure for synthesis of polymer**

**Synthesis of poly(CHO-*alt*-PA)**

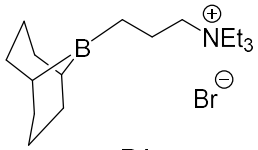
Polymerization was performed in a 10-mLpressure vial inside the glovebox for each run. In a glovebox, PA (0.6 g, 4.08 mmol), intitiator **3** (7.0 mg, 20.38 μmol), and CHO (0.8 g, 8.15 mmol) were weighed into a 10-mLpressure vial equipped with magnetic stirrer. (The excess CHO was added as an alternative for a solvent to dissolve the catalyst and PA and to ensure the smooth ROAC process.) The vial was sealed and the polymerization was stirred at 120 °C in an oil bath for 20 min. After then, the reaction was quenched by cooling to -10 °C and diluted with 3 mL $CH_2Cl_2$. And then an aliquot of the solution was taken out for the analysis of the conversion of anhydrides by $^{1}H$ NMR spectrum. The resulting poly(CHO-*alt*-PA) was obtained by precipitation from ethanol. The polymer was finally dried under vacuum at 50 °C overnight

**Table S1 Comparison of PA and CHO copolymerization results catalyzed by catalyst 1-3 and reported ammonium organoborane**

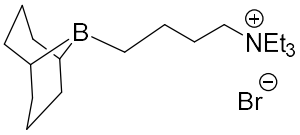
**R1-R3**

| Run | catalyst | CHO/PA/catalyst | Temperature (℃) | Time (min) | Conversion[a]% | Selectivity%[a] | $M_n$[b] (kg/mol) | $Đ$[b] |
|---|---|---|---|---|---|---|---|---|
| 1 | **1** | 400:200:1 | 120 | 20 | 55 | >98 | 12.5/5.6 | 1.04/1.07 |
| 2 | **2** | 400:200:1 | 120 | 20 | 97 | >98 | 16.2/7.7 | 1.03/1.04 |
| 3 | **3** | 400:200:1 | 120 | 20 | >99 | >98 | 18.0/8.2 | 1.04/1.06 |
| 4 | **R1** | 400:200:1 | 120 | 40 | 15 | >99 | 6.2/2.8 | 1.04/1.08 |
| 5 | **R2** | 400:200:1 | 120 | 40 | 95 | >99 | 28.4/14.2 | 1.02/1.03 |
| 6 | **R3** | 400:200:1 | 120 | 40 | >99 | >99 | 25.5/11.7 | 1.03/1.06 |

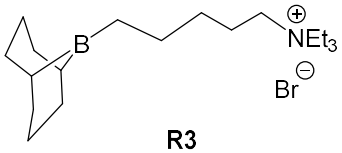
[a] The polymerization experiments were performed using 20.4 μmmol catalyst，selectivity(%) was the percentage of ester linkage in the polymer, which were both determined by $^1$H NMR spectroscopy. [b] Determined by GPC in THF, calibrated with polystyrene standards.




R1




R2




R3

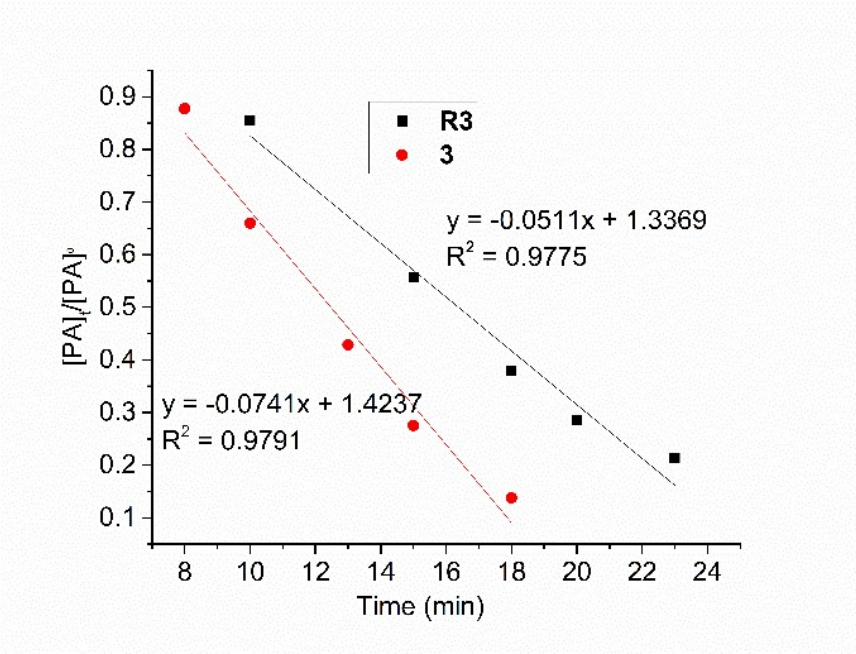


Figure S43. Comparison of reaction rate of PA/CHO copolymerization catalyzed by **3** and ammonium borane **R3** (catalyst/PA/CHO = 1:200:1000, in bulk, 120 °C).

## Kinetics Procedures

### PA concentration kinetics

PA (603 mg, 4.08 mmol), catalyst **3** (10.9 mg, 20.4 μmol) and CHO (2.08 mL, 20.4 mmol) were added to a 10-mL reaction vessel equipped with magnetic stirrer. Then the flask was immrsed in a preheateed oil bath setted at 120 °C under nitrogen atmosphere. An aliquot was taken from the reaction mixture and the conversion was monitored by $^1$H NMR at different time intervals.

**Table S2 PA concentration kinetics**

| Aliquots | $[PA]_0$ | $[PA]_t$ | $[PA]_t/[PA]_0$ | t (min) |
|---|---|---|---|---|
| 1 | 8.16 | 7.16 | 0.877451 | 8 |
| 2 | 2.94 | 1.94 | 0.659864 | 10 |
| 3 | 1.75 | 0.75 | 0.428571 | 13 |
| 4 | 1.38 | 0.38 | 0.275362 | 15 |
| 5 | 1.16 | 0.16 | 0.137931 | 18 |

### CHO concentration kinetics

PA (603 mg, 4.08 mmol), catalyst **3** (10.9 mg, 20.4 μmol), CHO (0.416 mL, 4.08 mmol) and 1.664 mL of toluene were added to a 10-mL reaction vessel equipped with magnetic stirrer. In order to keep the PA concentration constant, toluene was used. Then the flask was immersed in a preheateed oil bath setted at 120 °C under nitrogen atmosphere. An aliquot was taken from the reaction mixture and the conversion was monitored by $^1$H NMR at different time intervals.

**Table S3 CHO concentration kinetics**

| Aliquots | $[CHO]_0$ | $[CHO]_t$ | $[CHO]_t/[CHO]_0$ | t (min) |
|---|---|---|---|---|
| 1 | 1.03 | 1 | 0.970873786 | 20 |
| 2 | 1.14 | 1 | 0.877192982 | 30 |
| 3 | 1.38 | 1 | 0.724637681 | 40 |
| 4 | 1.69 | 1 | 0.591715976 | 50 |

| | | | | |
|---|---|---|---|---|
| 5 | 2.03 | 1 | 0.492610837 | 60 |
| 6 | 2.6 | 1 | 0.384615385 | 70 |
| 7 | 3.06 | 1 | 0.326797386 | 80 |
| 8 | 3.74 | 1 | 0.267379679 | 90 |

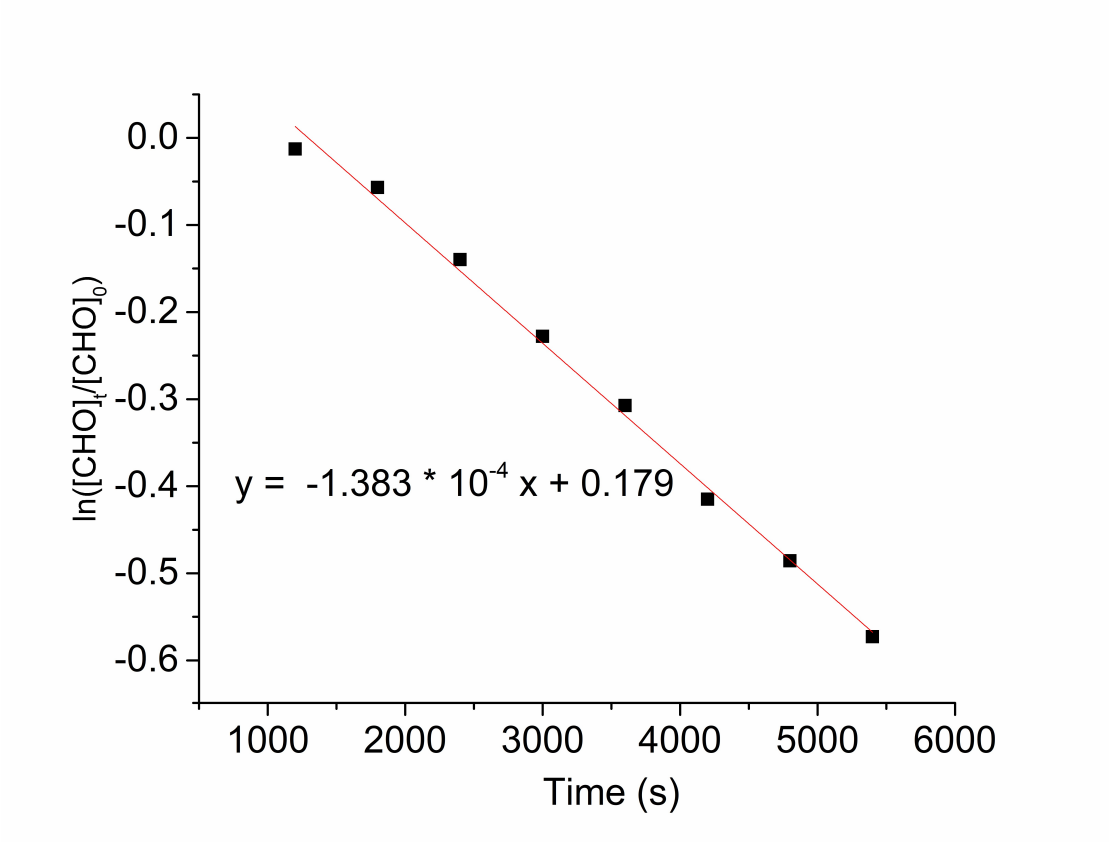



Figure S44. First-order kinetic plots of CHO concentration for ROAC of PA and CHO in solution polymerization at 120 ºC by catalyst **3**.

**Catalyst concentration kinetics**

In each run, the molar amount of catalyst **3** varied (20.4 μmol, 11.0 μmol, 5.02 μmol, 1.83 μmol) while the amount of PA and CHO kept constant. In a typical experiment , PA (603 mg, 4.08 mmol), catalyst **3** (20.4 μmol, 10.9 mg), CHO (0.831 mL, 8.15 mmol), 0.775 mL of toluene were added to a 10-mL reaction vessel equipped with magnetic stirrer. The total volume of the reaction mixture was kept in 2 mL. Then the flask was immersed in a preheateed oil bath setted at 120 °C under nitrogen atmosphere. An aliquot was taken from the reaction mixture and the conversion was monitored by $^1$H NMR at different time intervals.

**Table S4 Catalyst concentration kinetics** [**Catalyst 3**]$_0$ = 0.0102 M

| Aliquots | $[PA]_0$ | $[PA]_t$ | $[PA]_t/[PA]_0$ | t (min) |
|---|---|---|---|---|
| 1 | 4.43 | 3.43 | 0.774266 | 9 |
| 2 | 3.21 | 2.21 | 0.688474 | 10 |
| 3 | 2.63 | 1.63 | 0.619772 | 11 |
| 4 | 2.33 | 1.33 | 0.570815 | 12 |
| 5 | 2.14 | 1.14 | 0.53271 | 13 |
| 6 | 1.68 | 0.68 | 0.404762 | 14 |

**Table S5 Catalyst concentration kinetics** [**Catalyst 3**]$_0$ = 0.00550 M

| Aliquots | $[PA]_0$ | $[PA]_t$ | $[PA]_t/[PA]_0$ | t (min) |
|---|---|---|---|---|
| 1 | 8.35 | 7.35 | 0.88024 | 10 |
| 2 | 4.52 | 3.52 | 0.778761 | 13 |
| 3 | 2.86 | 1.86 | 0.65035 | 16 |
| 4 | 1.98 | 0.98 | 0.494949 | 19 |
| 5 | 1.79 | 0.79 | 0.441341 | 22 |
| 6 | 1.58 | 0.58 | 0.367089 | 25 |
| 7 | 1.52 | 0.52 | 0.342105 | 27 |

**Table S6 Catalyst concentration kinetics** [**Catalyst 3**]$_0$ = 0.00251 M

| Aliquots | $[PA]_0$ | $[PA]_t$ | $[PA]_t/[PA]_0$ | t (min) |
|---|---|---|---|---|
| 1 | 4.92 | 3.92 | 0.796748 | 12 |
| 2 | 3.44 | 2.44 | 0.709302 | 15 |
| 3 | 2.97 | 1.97 | 0.6633 | 18 |
| 4 | 2.69 | 1.69 | 0.628253 | 21 |
| 5 | 2.44 | 1.44 | 0.590164 | 24 |
| 6 | 2.26 | 1.26 | 0.557522 | 27 |
| 7 | 1.91 | 0.91 | 0.47644 | 33 |
| 8 | 1.71 | 0.71 | 0.415205 | 35 |

**Table S7 Catalyst concentration kinetics** [**Catalyst 3**]$_0$ = 0.000917 M

| Aliquots | $[PA]_0$ | $[PA]_t$ | $[PA]_t/[PA]_0$ | t (min) |
|---|---|---|---|---|
| 1 | 5.26 | 4.26 | 0.809886 | 20 |
| 2 | 4.37 | 3.37 | 0.771167 | 30 |
| 3 | 3.24 | 2.24 | 0.691358 | 50 |
| 4 | 2.56 | 1.56 | 0.609375 | 60 |
| 5 | 2.19 | 1.19 | 0.543379 | 70 |
| 6 | 1.98 | 0.98 | 0.494949 | 80 |
| 7 | 1.8 | 0.8 | 0.444444 | 90 |
| 8 | 1.69 | 0.69 | 0.408284 | 100 |

**Table S8 Catalyst concentration vs *K*app**

| $[Catalyst]_0$ | $ln[Catalyst]_0$ | *K*app | lnKapp |
|---|---|---|---|
| 0.0102 | -4.585 | 0.0675 | -2.69563 |
| 0.0055 | -5.204 | 0.0329 | -3.41428 |
| 0.00251 | -5.988 | 0.0148 | -4.21313 |
| 0.000917 | -6.995 | 0.0053 | -5.24005 |

**Reaction rate comparison**

PA (603 mg, 4.08 mmol), ammonium borane catalyst **R3** (7.6 mg, 20.4 μmol) and CHO (2.08 mL, 20.4 mmol) were added to a 10-mL reaction vessel equipped with magnetic stirrer. Then the flask was immrsed in a preheateed oil bath setted at 120 °C under nitrogen atmosphere. An aliquot was taken from the reaction mixture and the conversion was monitored by $^1$H NMR at different time intervals.

**Table S9 PA concentration kinetics by R3**

| Aliquots | $[PA]_0$ | $[PA]_t$ | $[PA]_t/[PA]_0$ | t(min) |
|---|---|---|---|---|
| 1 | 6.91 | 5.91 | 0.8552822 | 10 |
| 2 | 2.26 | 1.26 | 0.557522124 | 15 |
| 3 | 1.61 | 0.61 | 0.378881988 | 18 |
| 4 | 1.4 | 0.4 | 0.285714286 | 20 |
| 5 | 1.27 | 0.27 | 0.212598425 | 23 |
| 6 | 1.24 | 0.24 | 0.193548387 | 25 |
| 7 | 1.21 | 0.21 | 0.173553719 | 27 |
| 8 | 1.17 | 0.17 | 0.145299145 | 30 |

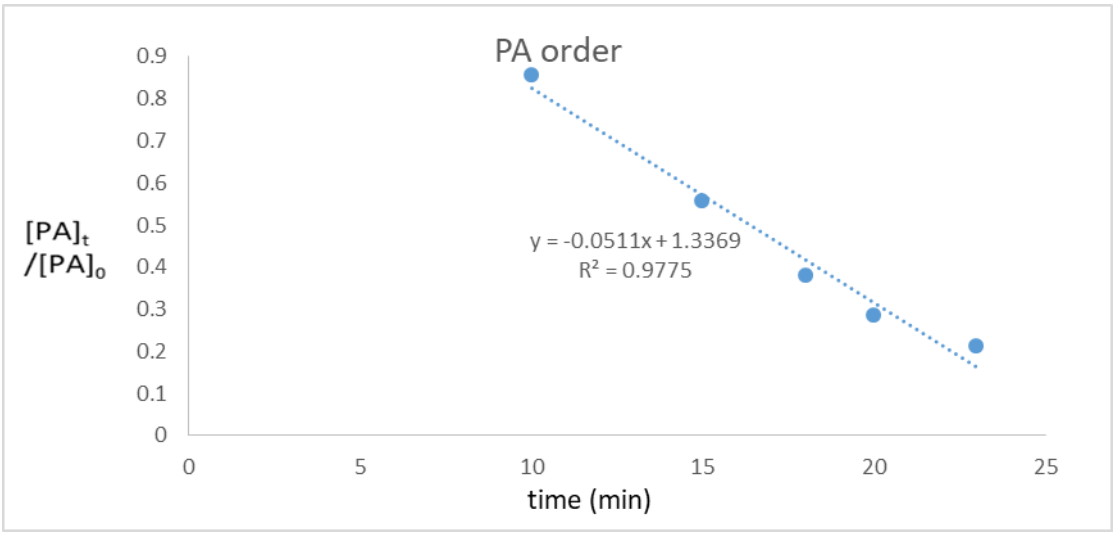



Figure S45. Zero-order kinetic plots of PA concentration for ROAC of PA and CHO in bulk at 120 ºC by catalyst **R3**. The molar ratio of ammonium salt/PA/CHO = 1/200/1000.

**Table S10 Control experiment of intermolecular B1/$Ph_4PBr$ and 3 in the ROAC of PA and CHO in a molar ratio of CHO/PA/catalyst = 400/200/1 at 120 ℃.**

| Run | catalyst | Time (min) | Conversion%[a] | Selectivity%[a] | *Mn*[b] (kg/mol) | *Đ*[b] |
|---|---|---|---|---|---|---|
| **1** | **3** | 10 | 86 | >98 | 13.0 | 1.19 |
| **2** | **B1/$Ph_4PBr$** | 10 | 20 | >98 | - | - |
| **3** | **B1/$Ph_4PBr$** | 60 | >99 | >98 | 16.1 | 1.21 |

[a] Conversion(%) is the conversion of the PA, and selectivity is the percentage of ester linkage in the polymer, which were both determined by $^1$H NMR spectroscopy. [b] Determined by GPC in THF, calibrated with polystyrene standards.

**$^1$H and $^{13}$C{$^1$H} NMR spectra of resulted poly(epoxide-*alt*-anhydride)**

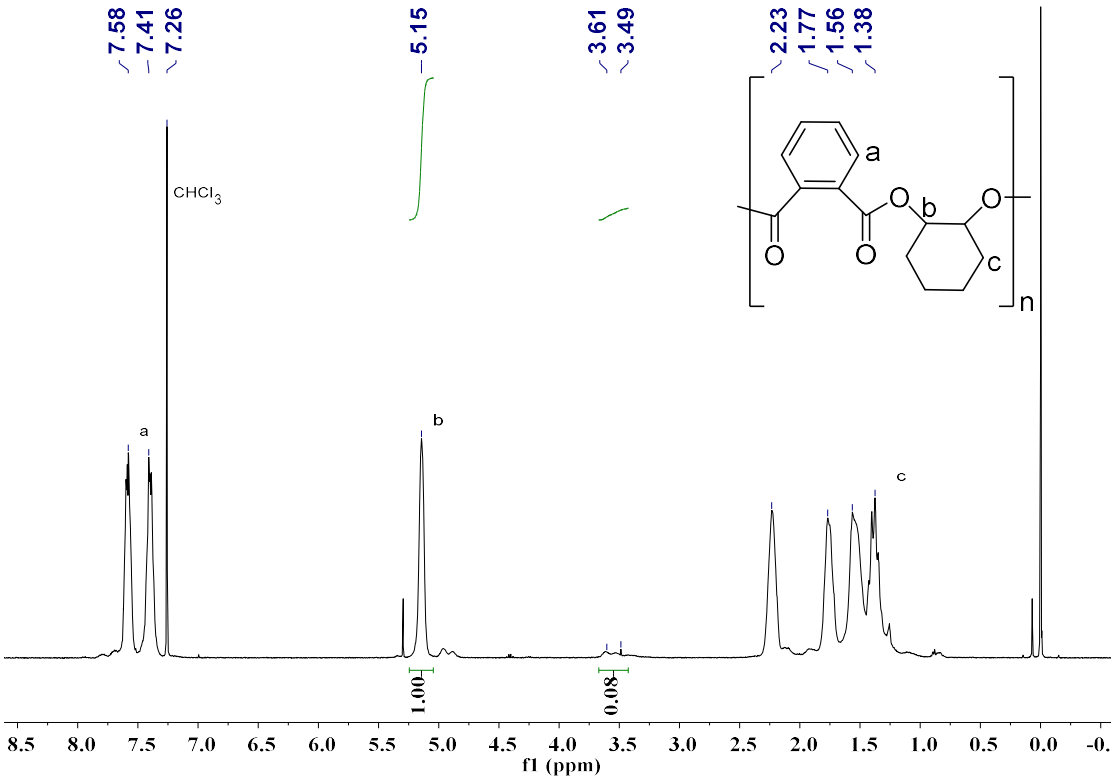



Figure S46. $^{1}$H NMR spectrum of the purified P(PA-*alt*-CHO) by catalyst **3** with CHO/PA/catalyst = 6000:5000:1 molar ratio in $CDCl_3$, table 2, run 7.

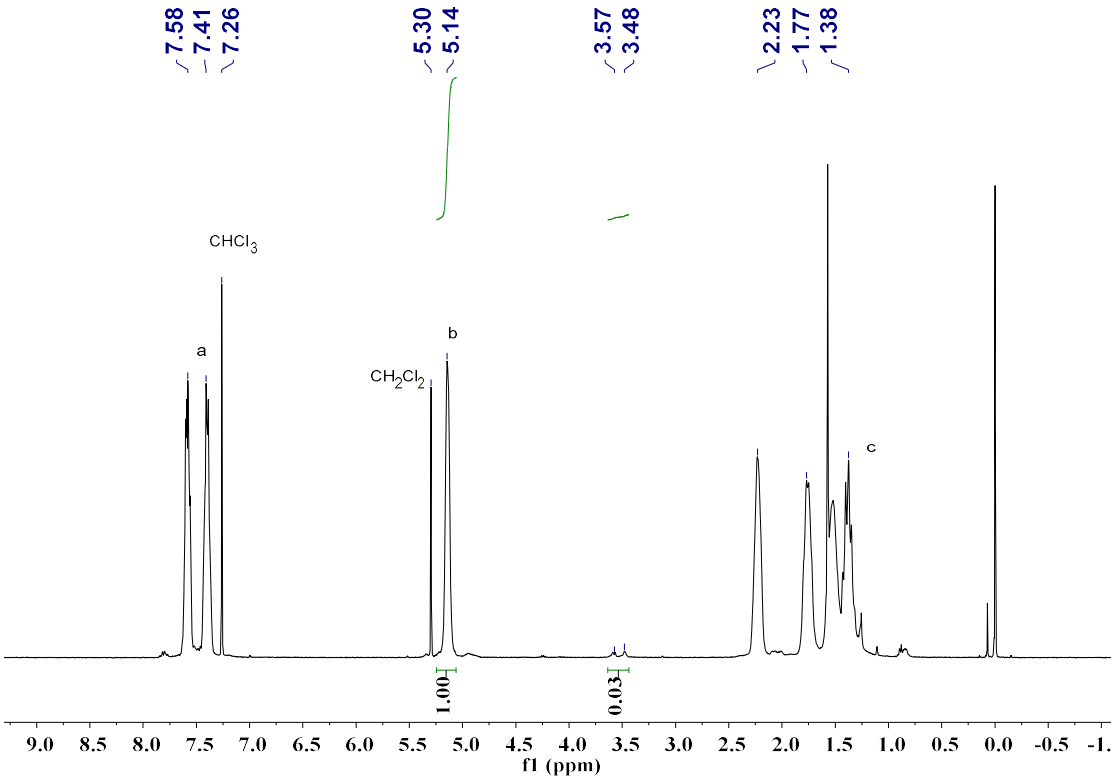



Figure S47. $^{1}$H NMR spectrum of the purified P(PA-*alt*-CHO) by catalyst **3** with CHO/PA/catalyst = 400:200:1 molar ratio in $CDCl_3$, table 1, run 3.

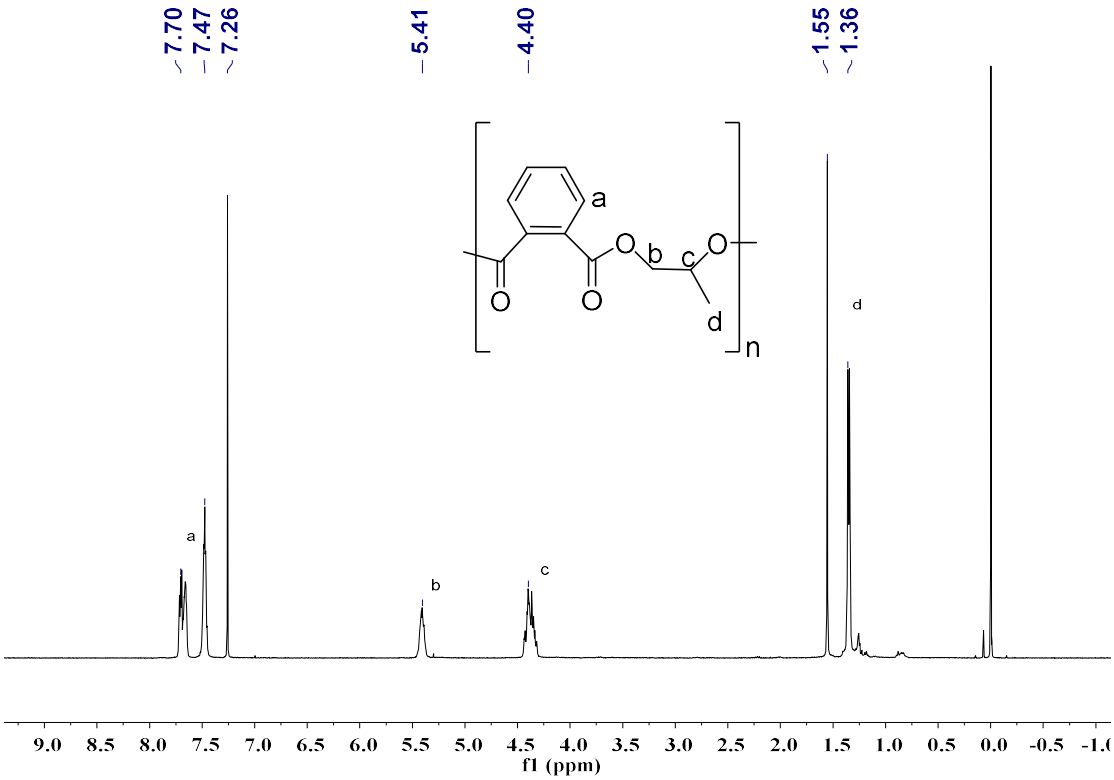



Figure S48. $^{1}$H NMR spectrum of the purified P(PA-*alt*-PO) by catalyst **3** with PO/PA/catalyst = 2000:500:1 molar ratio in $CDCl_3$, table 3, run 2.

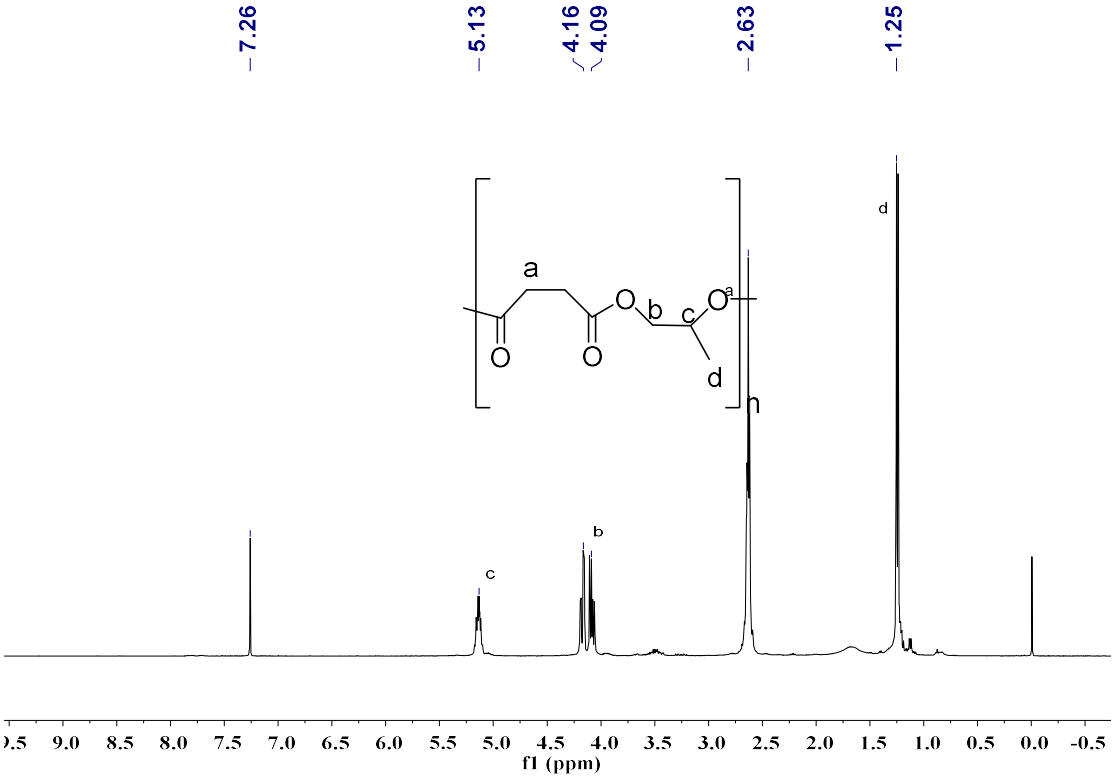



Figure S49. $^{1}$H NMR spectrum of the purified P(SA-*alt*-PO) by catalyst **3** with PO/SA/catalyst = 350:100:1 molar ratio in $CDCl_3$, table 3, run 3.

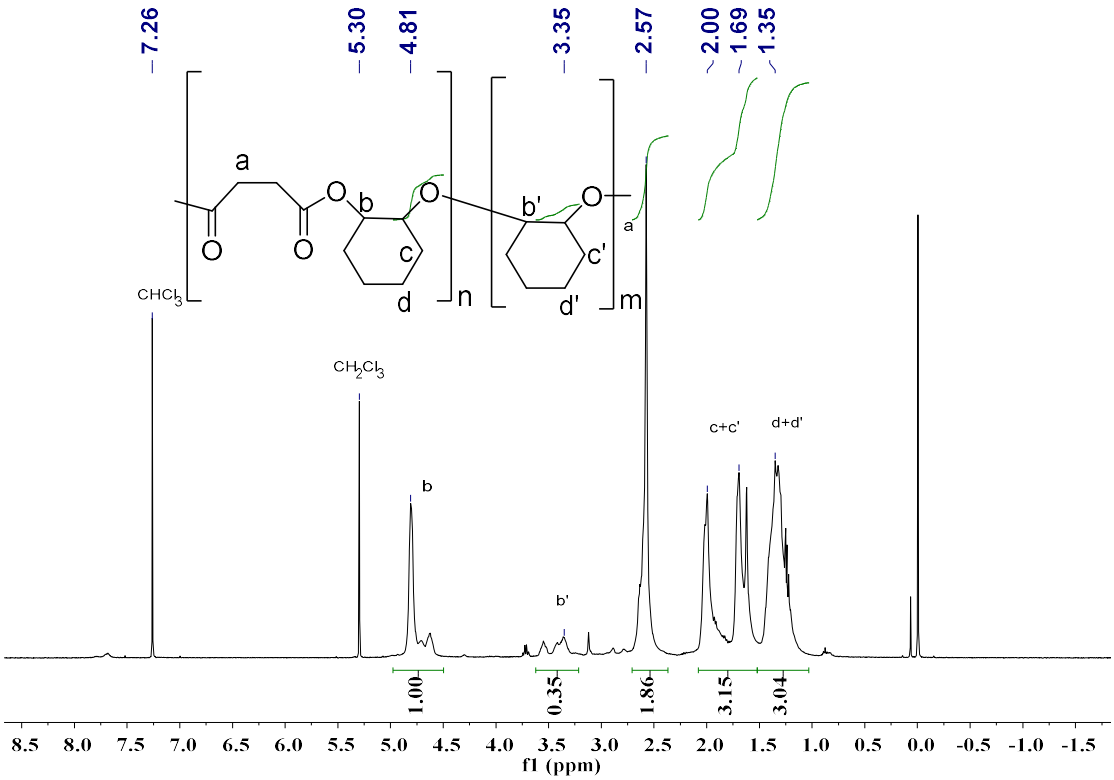



Figure S50. $^{1}$H NMR spectrum of the purified P(SA-*alt*-CHO) by catalyst **3** with CHO/SA/catalyst = 400:200:1 molar ratio in $CDCl_3$, table 3, run 5.

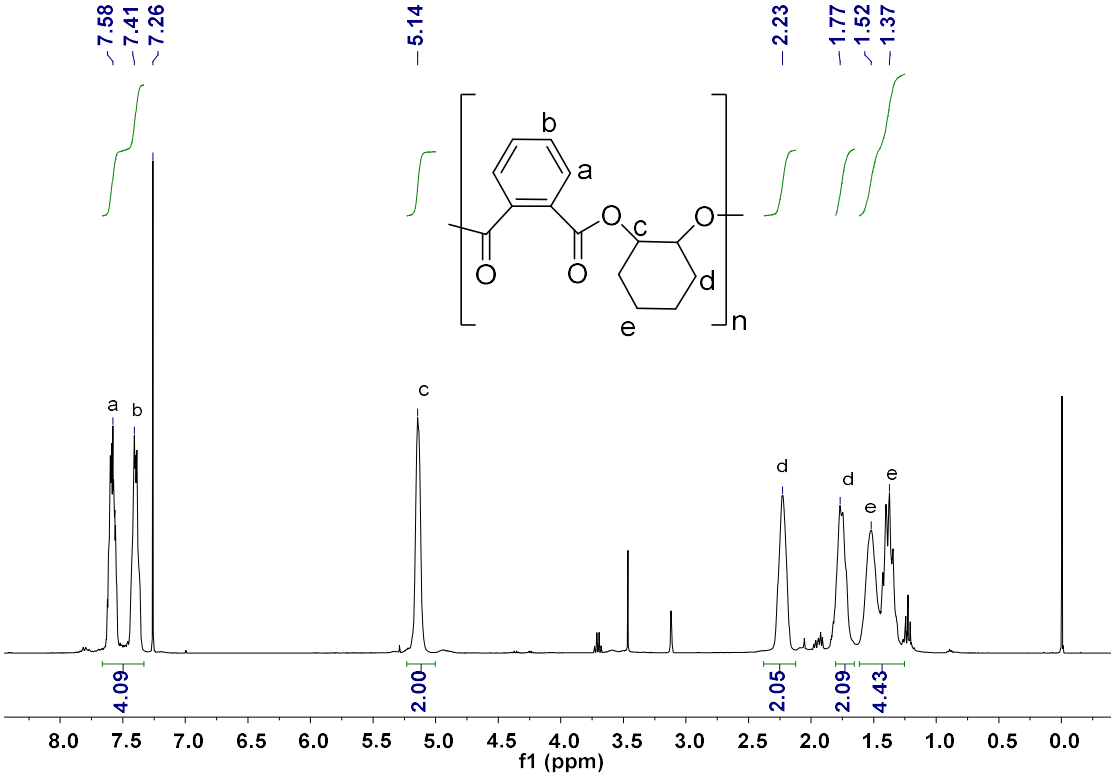



Figure S51. $^{1}$H NMR spectrum of purified P(PA-*alt*-CHO) in $CDCl_3$.

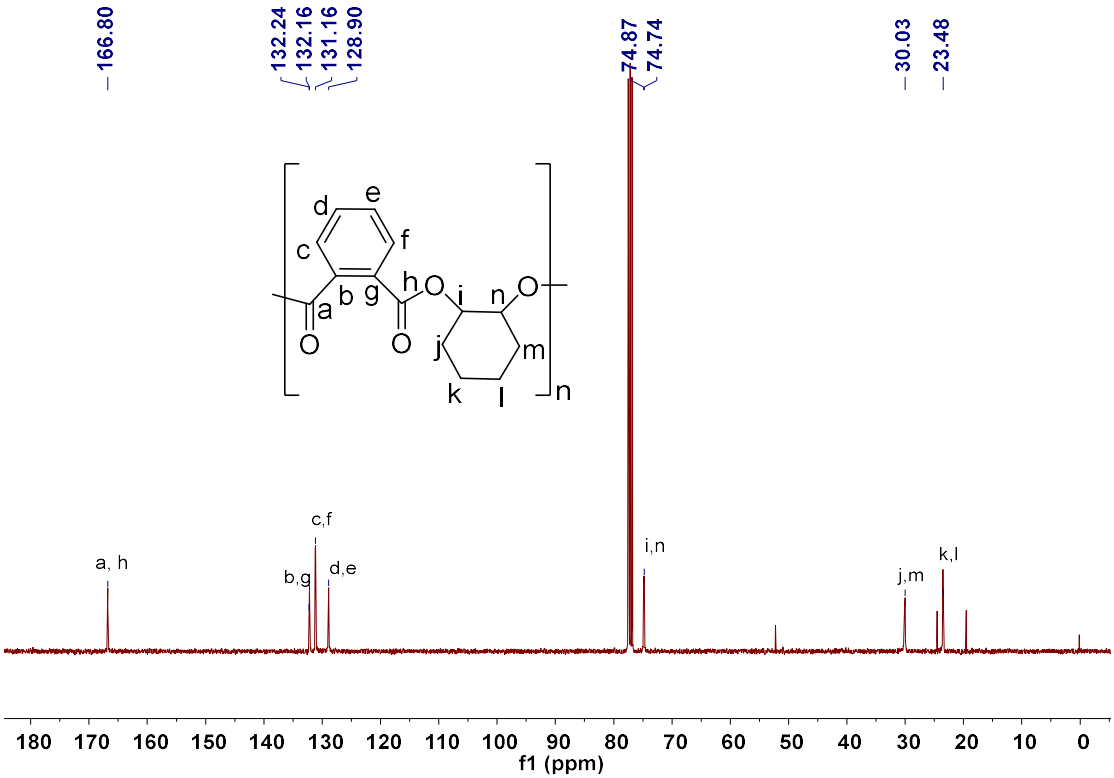



Figure S52. $^{13}C$ NMR spectrum of purified P(PA-*alt*-CHO) in $CDCl_3$.

**Selected GPC traces of the obtained poly(epoxide-*alt*-anhydride)**

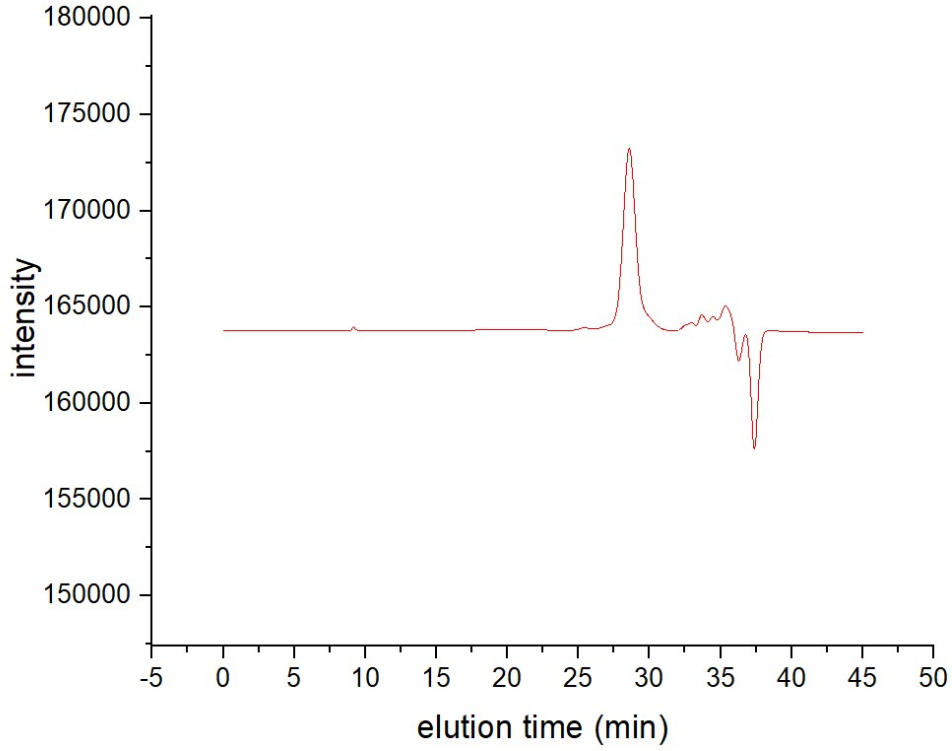



Figure S53. The GPC evolution plots of the resultant poly(PA-*alt*-CHO) obtained from table 1, run 9.

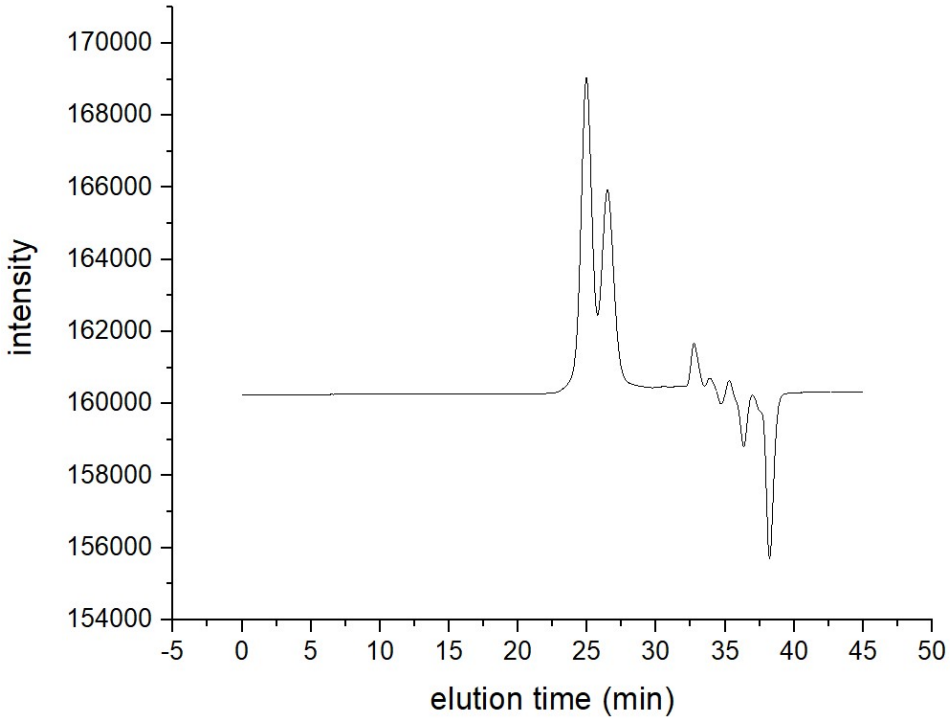



Figure S54. The GPC evolution plots of the resultant poly(PA-*alt*-CHO) obtained from table 2, run 2.

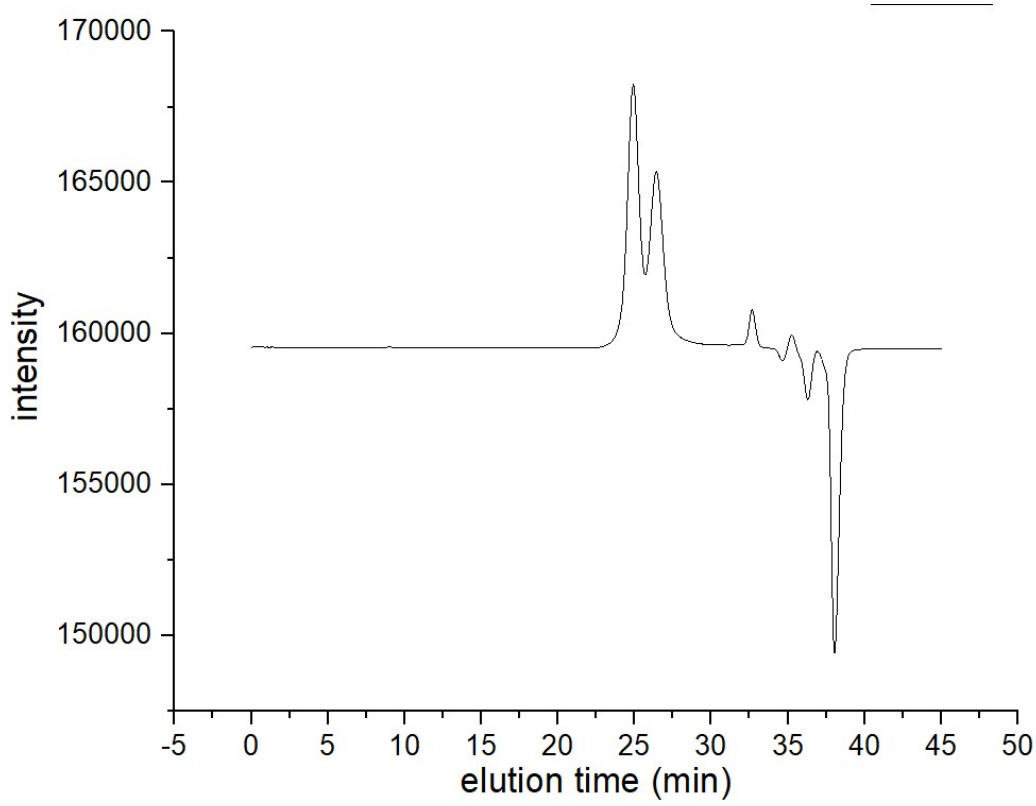



Figure S55. The GPC evolution plots of the resultant poly(PA-*alt*-CHO) obtained from table 2, run 3.

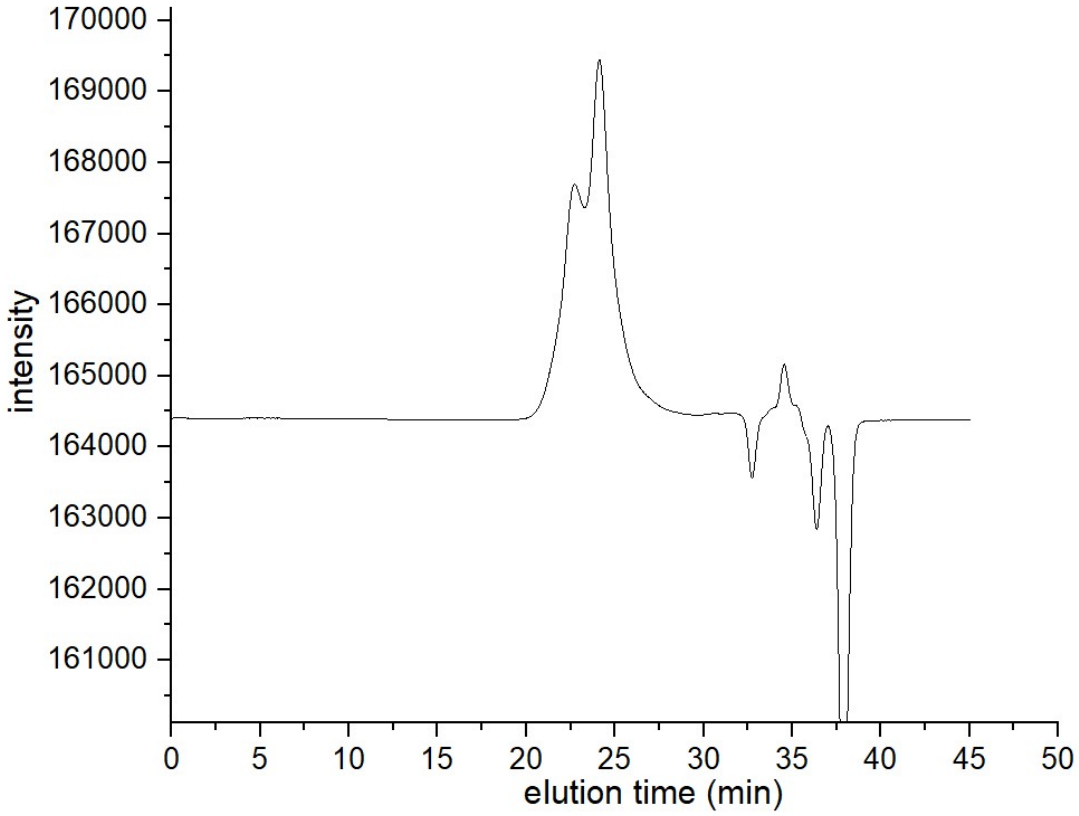



Figure S56. The GPC evolution plots of the resultant poly(PA-*alt*-CHO) obtained from table 2, run 5.

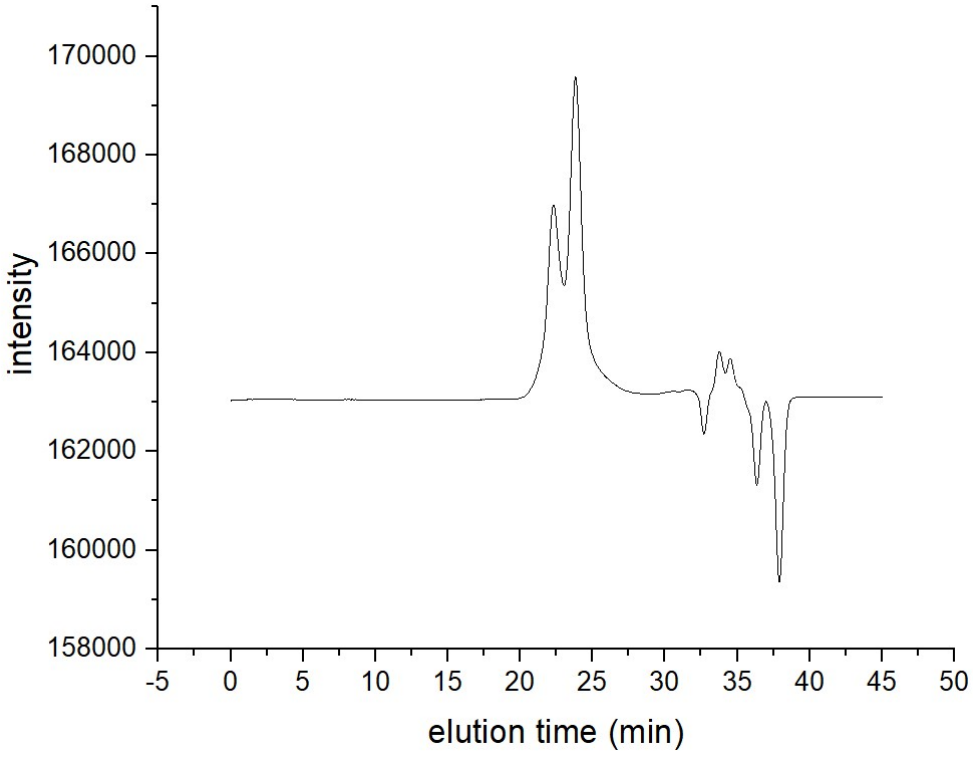



Figure S57. The GPC evolution plots of the resultant poly(PA-*alt*-CHO) obtained from table 2, run 7.

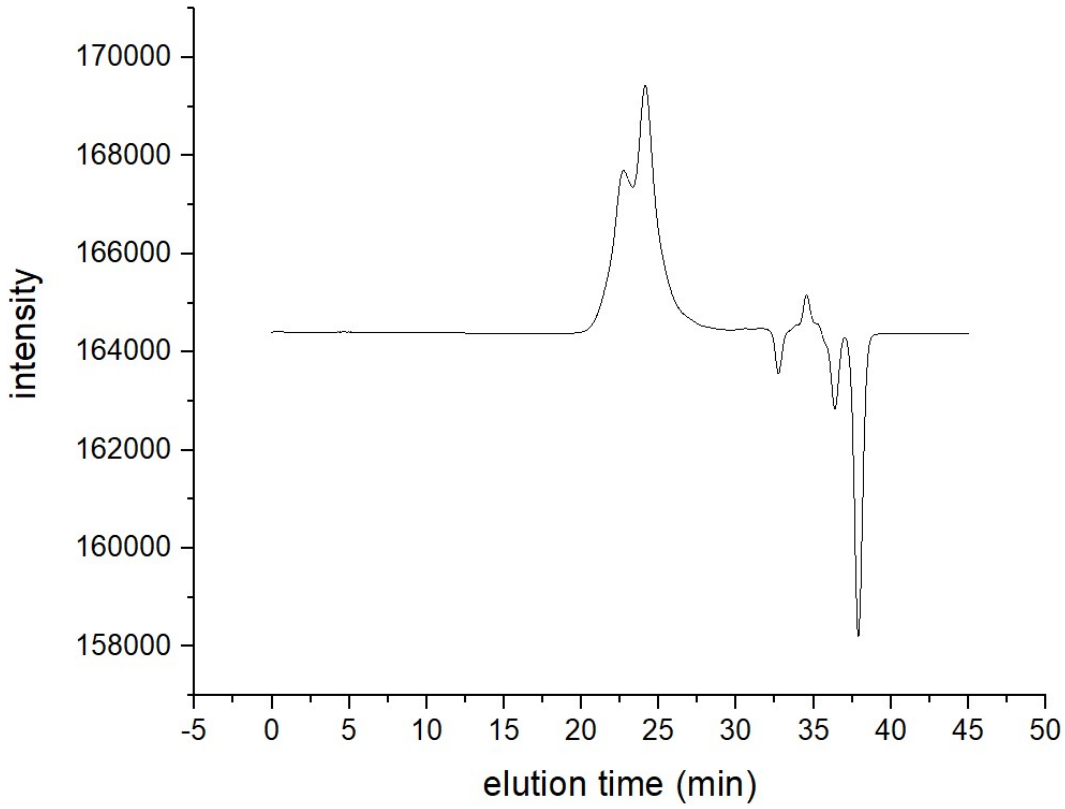



Figure S58. The GPC evolution plots of the resultant poly(PA-*alt*-CHO) obtained from table 2, run 8.

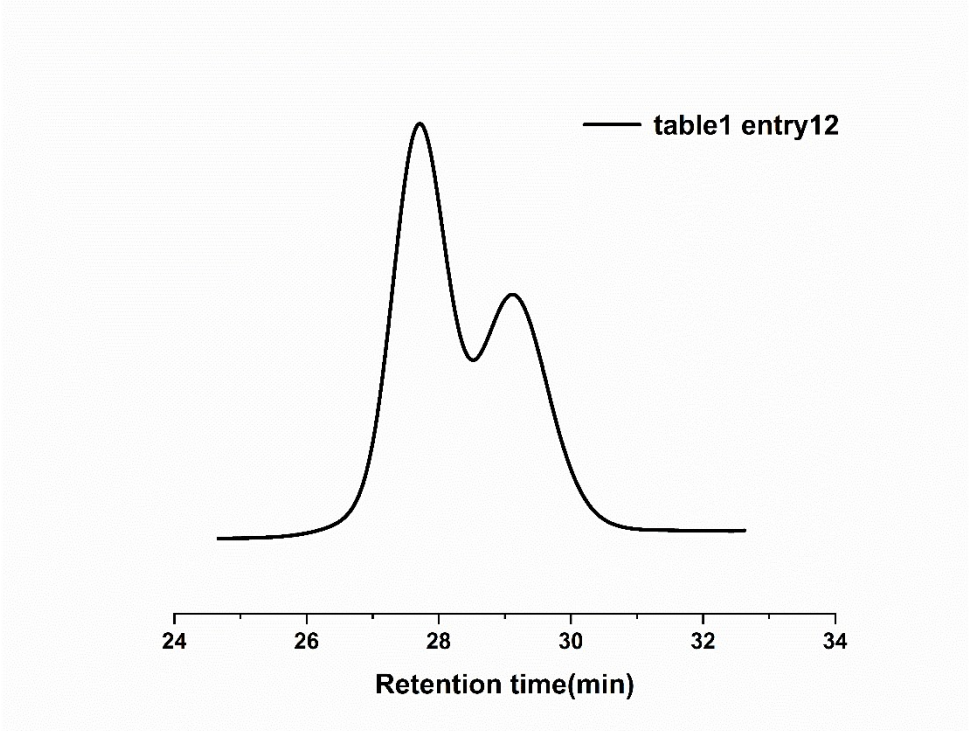



Figure S59. The GPC evolution plots of the resultant poly(PA-*alt*-CHO) obtained from table 1, run 12.

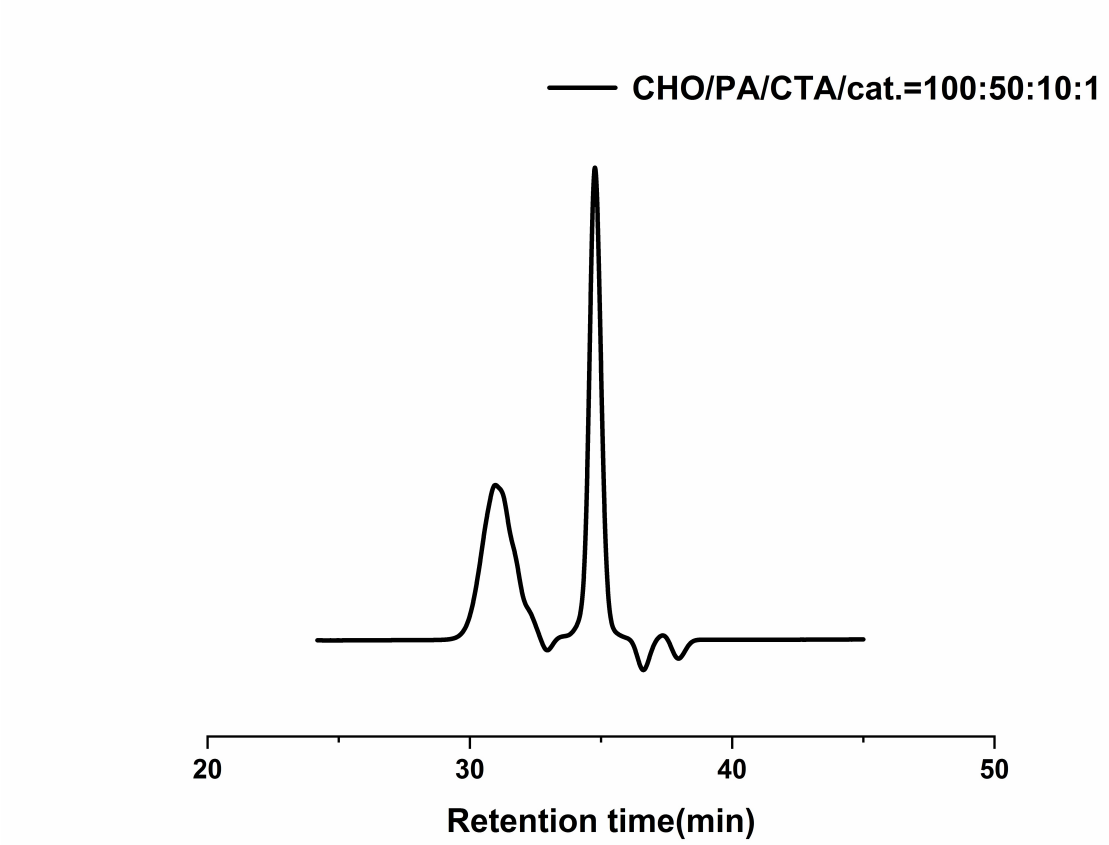



Figure S60. The GPC evolution plots of the resultant poly(PA-*alt*-CHO) obtained from table 1, run 18, CHO/PA/CHD/**3** = 100:50:10:1.

**Maldi-TOF analysis of low molecular weight of poly(CHO-*alt*-PA)**

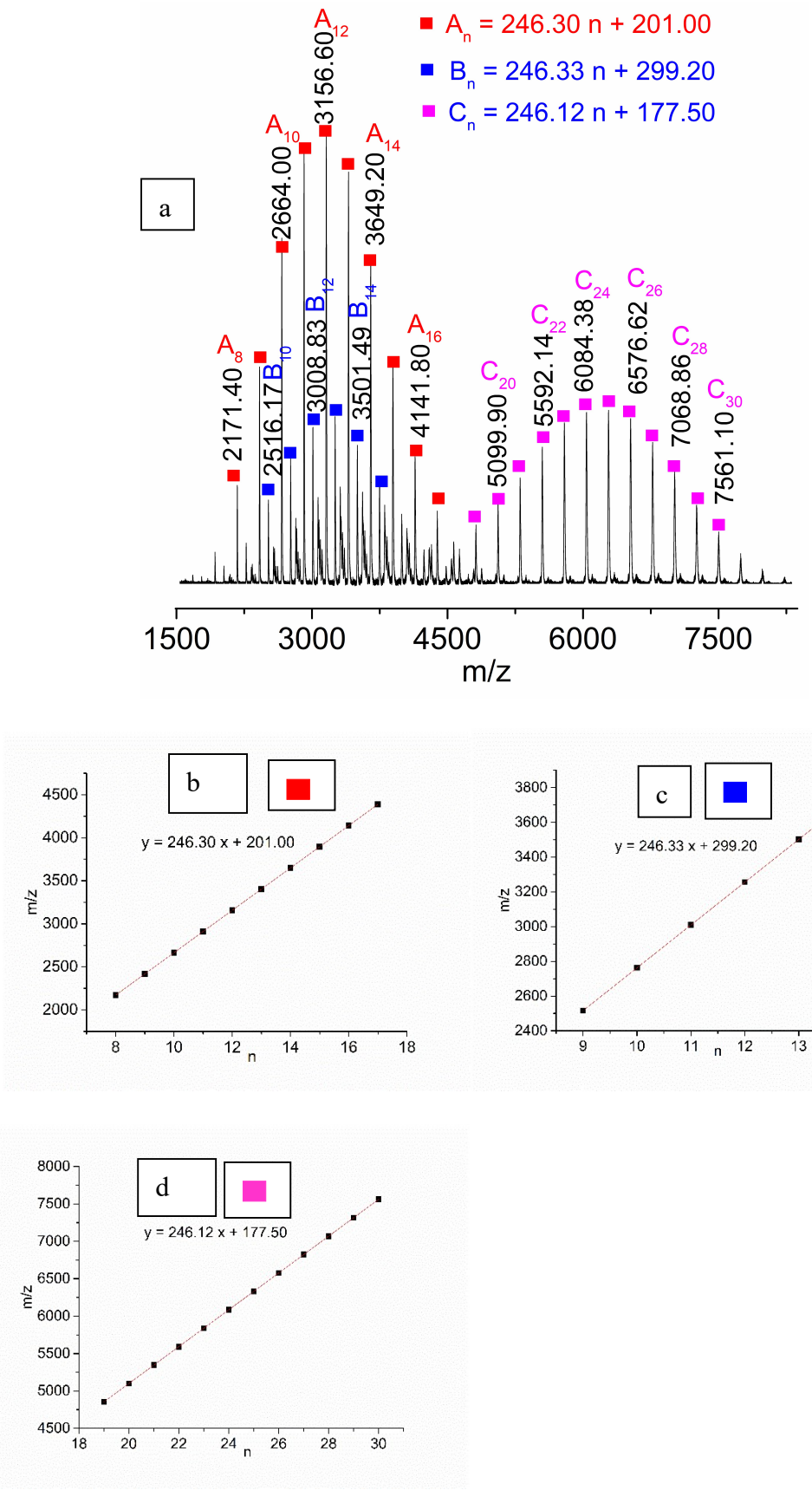



Figure S61. (a) MALDI-TOF MS of poly(PA-*alt*-CHO) obtained by using catalyst **3** （table1, run 12）. (b) The fitting relationship of m/z of Br-terminated

species vs repeating unit. (c) The fitting relationship of m/z of Br-terminated species vs repeating unit. (d) The fitting relationship of OH initiated species vs repeating unit.

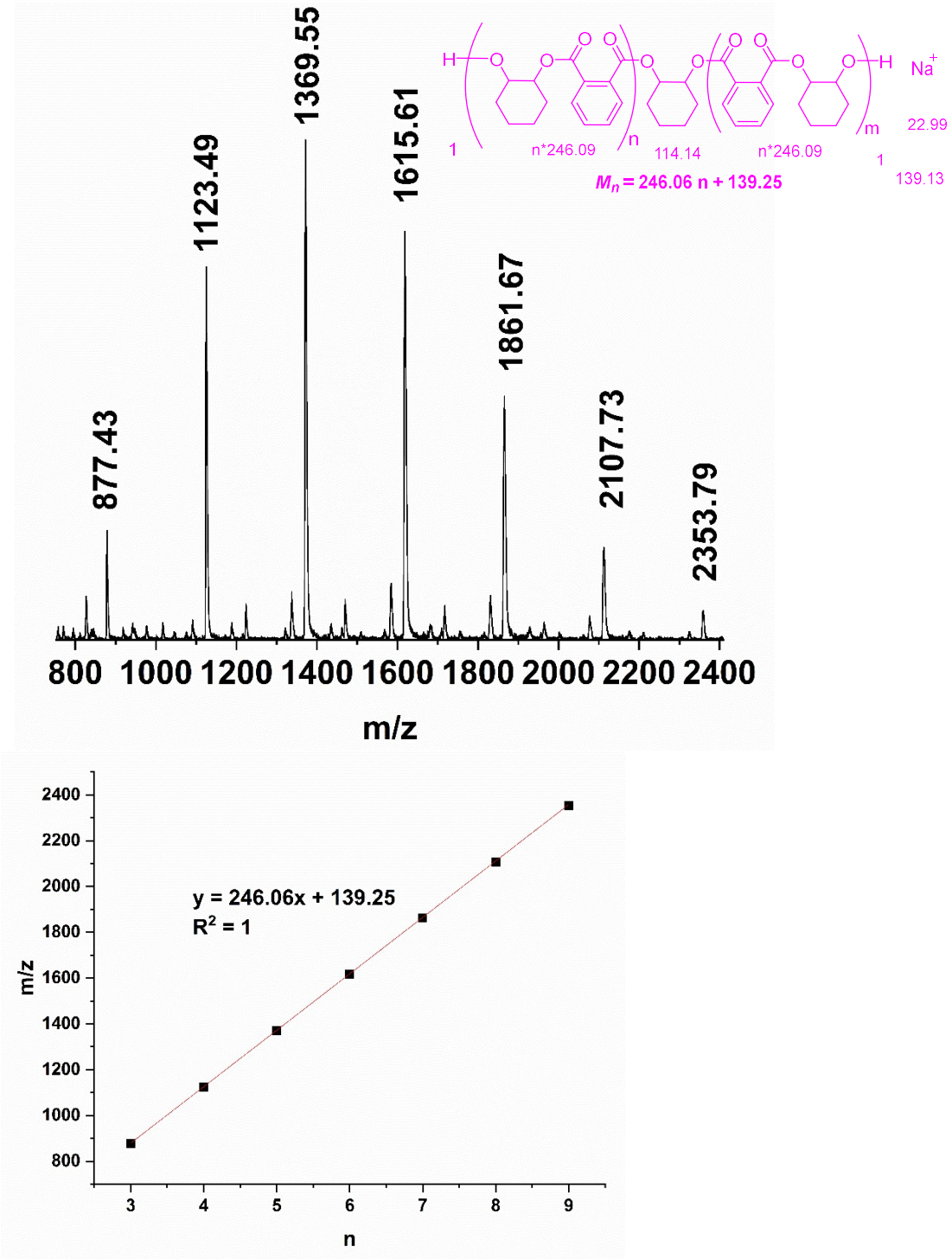



Figure S62. MALDI-TOF MS of poly(PA-*alt*-CHO) obtained from table 1, run 18.

**Additional Information**

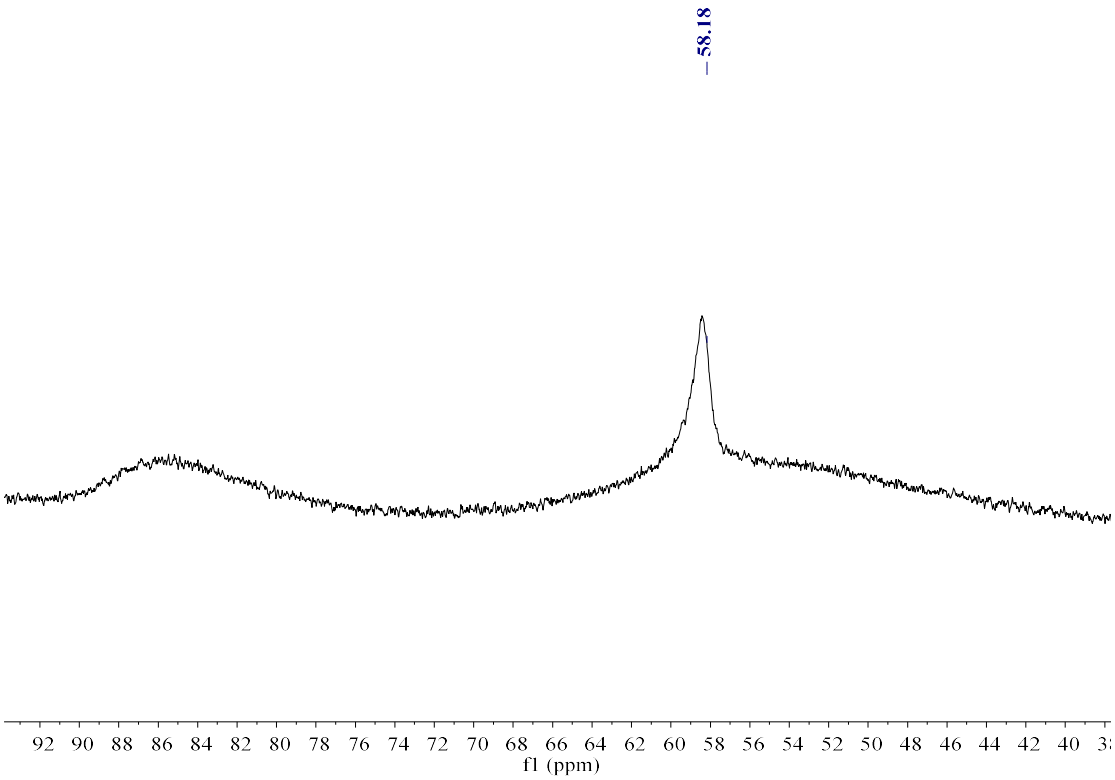



Figure S63. $^{11}B\{^{1}H\}$ NMR of catalyst **3** in THF-$d_8$

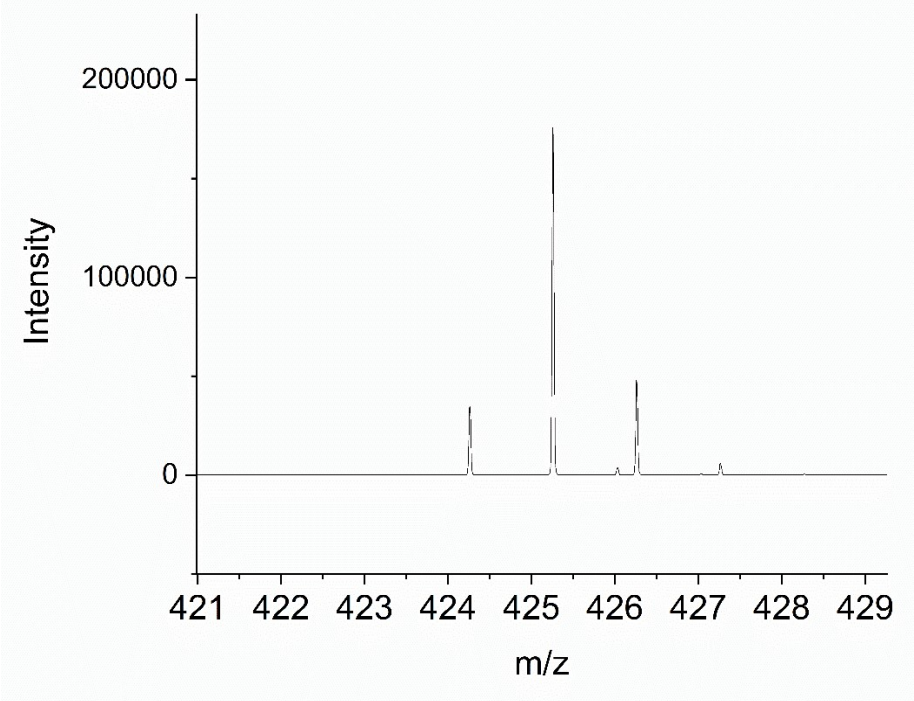



Figure S64. High resolution mass spectrum of catalyst **1**

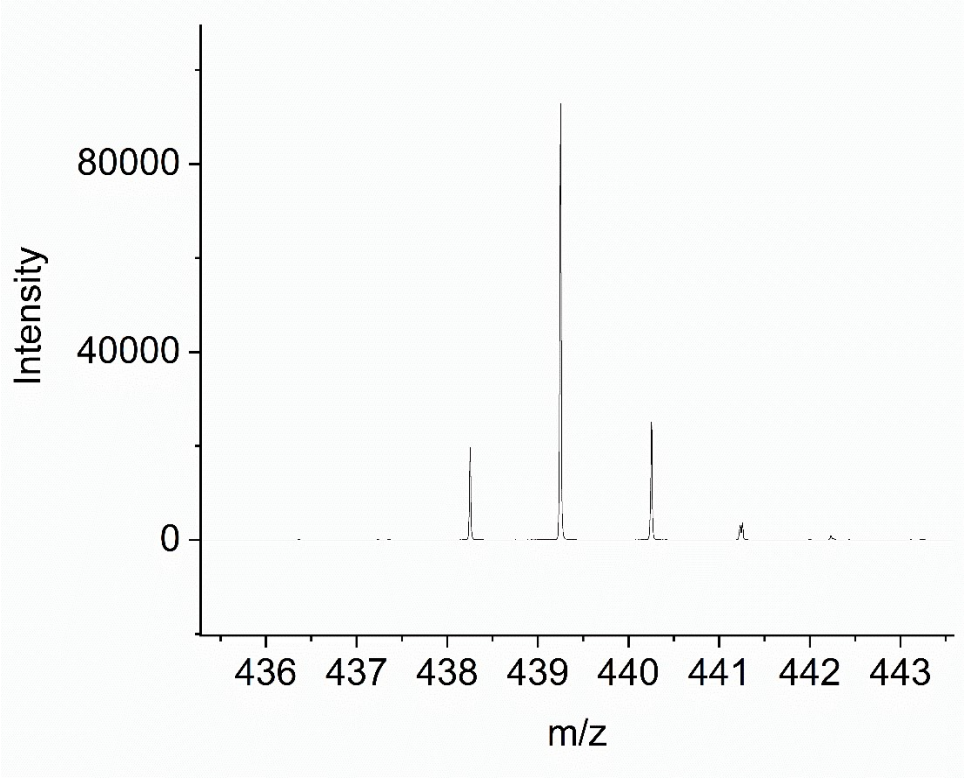



Figure S65. High resolution mass spectrum of catalyst **2**

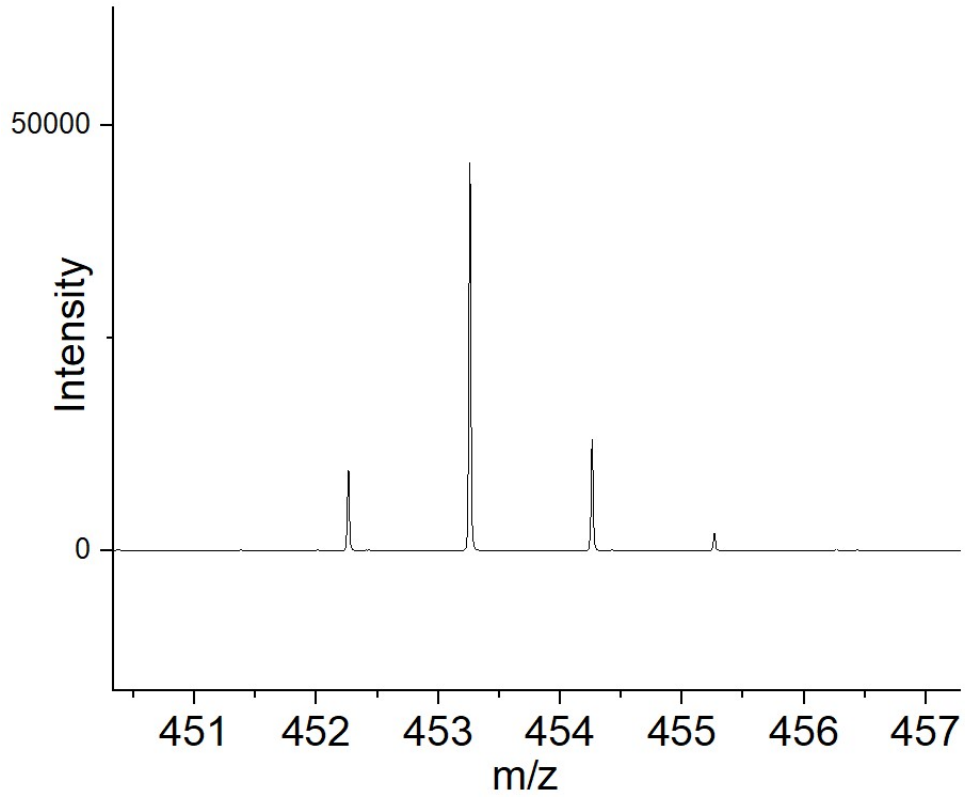



Figure S66. High resolution mass spectrum of catalyst **3**

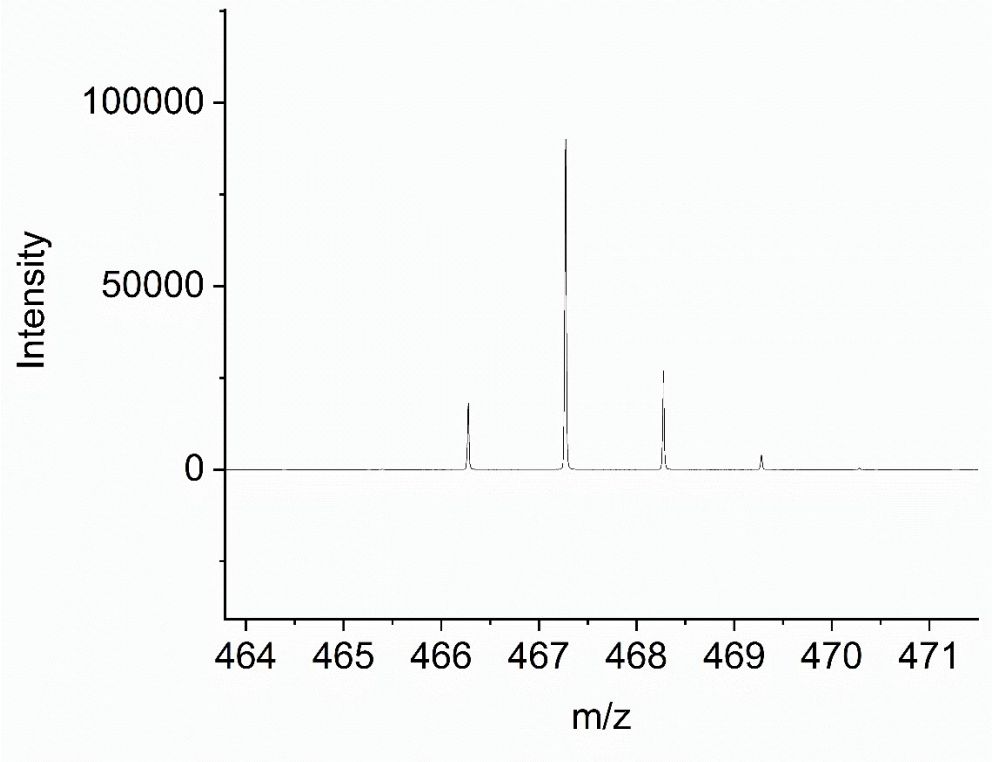



Figure S67. High resolution mass spectrum of catalyst **4**

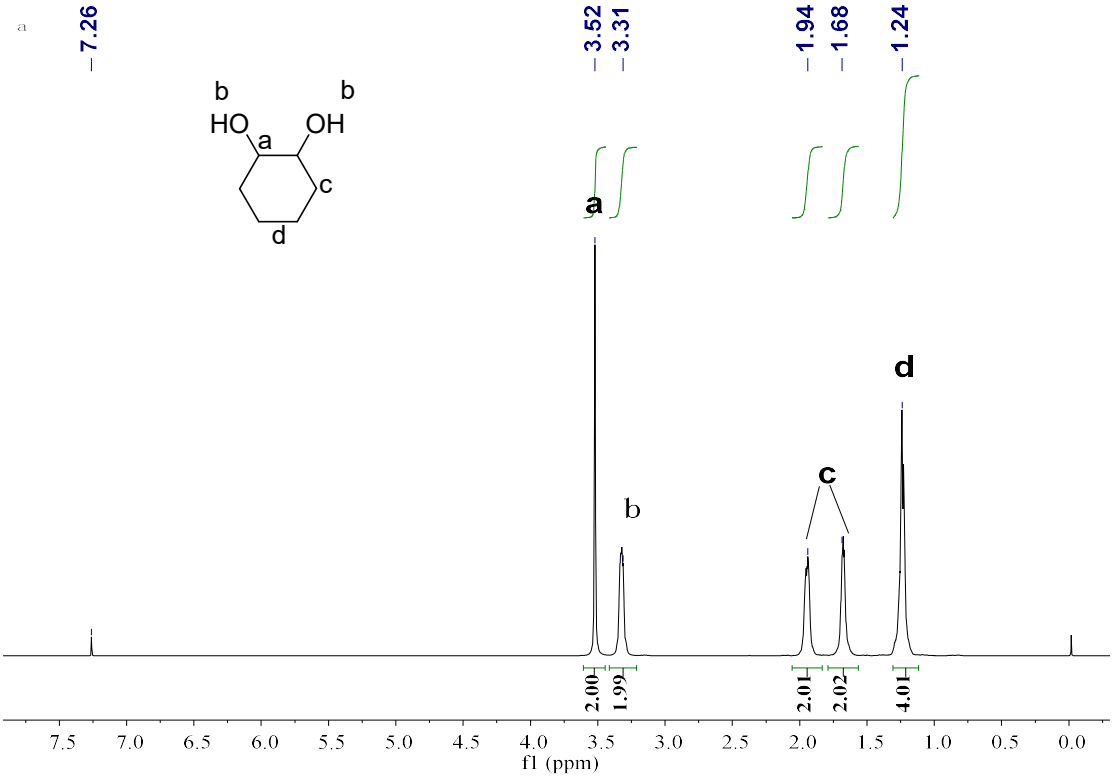



Figure S68. $^{1}H$ NMR spectrum of CHD (400 MHz, $CDCl_3$, 298 K)

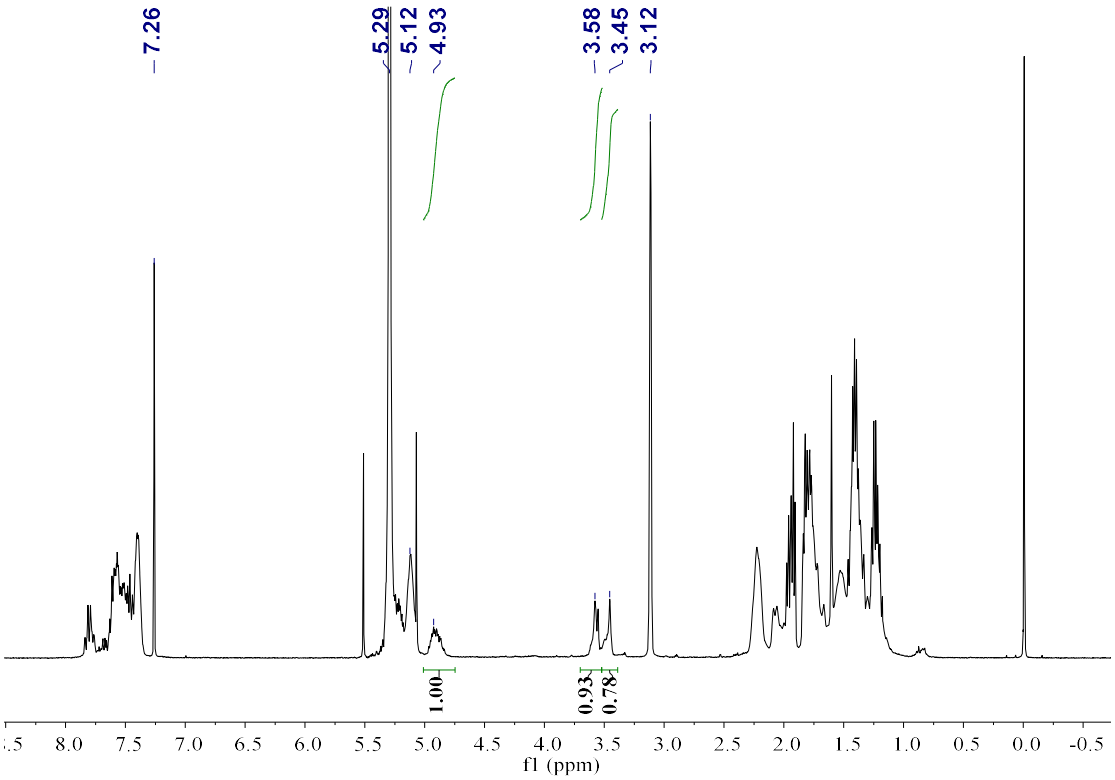



Figure S69. $^{1}$H NMR spectrum of the crude reaction mixture from table 1, run 18.

**Crystal data and structure refinement for catalyst precursors**

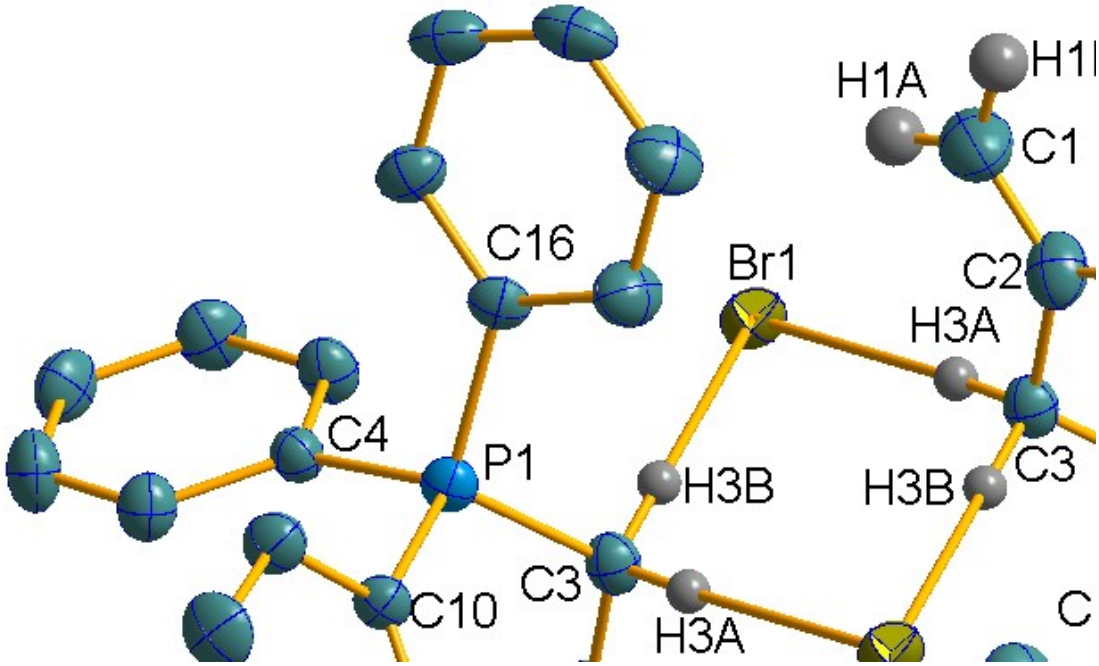



**Figure S70.** X-ray crystal structure of **L1**. Hydrogen atoms are omitted for clarity and ellipsoids drawn at 30% probability (CCDC # 2098034).

**Table S11. Crystal data and structure refinement for 2098034.**

| | |
|---|---|
| Identification code | 2098034 |
| Empirical formula | $C_{21}$ $H_{20}$ Br P |
| Formula weight | 383.25 |
| Temperature | 298(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 10.8668(11) A alpha = 90 deg.<br>b = 9.9356(9) A beta = 105.376(4) deg.<br>c = 17.4186(18) A gamma = 90 deg. |
| Volume | 1813.3(3) A^3 |
| Z, Calculated density | 4, 1.404 Mg/m^3 |
| Absorption coefficient | 2.352 mm^-1 |
| F(000) | 784 |
| Crystal size | 0.25 x 0.13 x 0.08 mm |
| Theta range for data collection | 1.94 to 25.02 deg. |
| Limiting indices | -10<=h<=12, -11<=k<=11, -18<=l<=20 |
| Reflections collected / unique | 8673/3195 [R(int) = 0.1065] |
| Completeness to theta = 25.02 | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8341 and 0.5908 |
| Refinement method | Full-matrix least-squares on F^2 |

| | |
|---|---|
| Data / restraints / parameters | 3195 / 0 / 209 |
| Goodness-of-fit on F^2 | 1.076 |
| Final R indices [I>2sigma(I)] | $R^1$ = 0.0695, $wR^2$ = 0.1626 |
| R indices (all data) | $R^1$ = 0.1057, $wR^2$ = 0.1754 |
| Extinction coefficient | 0.0040(11) |
| Largest diff. peak and hole | 0.677 and -1.583 e.A^-3 |

**Table S12. Bond lengths [Å] and angles [deg] for 2098034.**

| | |
|---|---|
| P(1)-C(16) | 1.766(6) |
| P(1)-C(3) | 1.769(6) |
| P(1)-C(4) | 1.771(6) |
| P(1)-C(10) | 1.773(6) |
| C(1)-C(2) | 1.292(10) |
| C(1)-H(1A) | 0.9300 |
| C(1)-H(1B) | 0.9300 |
| C(2)-C(3) | 1.466(9) |
| C(2)-H(2) | 0.9300 |
| C(3)-H(3A) | 0.9700 |
| C(3)-H(3B) | 0.9700 |
| C(4)-C(9) | 1.378(8) |
| C(4)-C(5) | 1.389(8) |
| C(5)-C(6) | 1.355(9) |
| C(5)-H(5) | 0.9300 |
| C(6)-C(7) | 1.356(9) |
| C(6)-H(6) | 0.9300 |
| C(7)-C(8) | 1.355(9) |
| C(7)-H(7) | 0.9300 |
| C(8)-C(9) | 1.359(8) |
| C(8)-H(8) | 0.9300 |
| C(9)-H(9) | 0.9300 |
| C(10)-C(15) | 1.372(8) |
| C(10)-C(11) | 1.375(8) |
| C(11)-C(12) | 1.362(9) |
| C(11)-H(11) | 0.9300 |
| C(12)-C(13) | 1.356(11) |
| C(12)-H(12) | 0.9300 |
| C(13)-C(14) | 1.349(10) |
| C(13)-H(13) | 0.9300 |

| | |
|---|---|
| C(14)-C(15) | 1.368(8) |
| C(14)-H(14) | 0.9300 |
| C(15)-H(15) | 0.9300 |
| C(16)-C(17) | 1.361(9) |
| C(16)-C(21) | 1.374(9) |
| C(17)-C(18) | 1.376(9) |
| C(17)-H(17) | 0.9300 |
| C(18)-C(19) | 1.363(10) |
| C(18)-H(18) | 0.9300 |
| C(19)-C(20) | 1.347(10) |
| C(19)-H(19) | 0.9300 |
| C(20)-C(21) | 1.361(10) |
| C(20)-H(20) | 0.9300 |
| C(21)-H(21) | 0.9300 |
| C(16)-P(1)-C(3) | 109.2(3) |
| C(16)-P(1)-C(4) | 108.2(3) |
| C(3)-P(1)-C(4) | 110.3(3) |
| C(16)-P(1)-C(10) | 107.1(3) |
| C(3)-P(1)-C(10) | 112.5(3) |
| C(4)-P(1)-C(10) | 109.4(3) |
| C(2)-C(1)-H(1A) | 120.0 |
| C(2)-C(1)-H(1B) | 120.0 |
| H(1A)-C(1)-H(1B) | 120.0 |
| C(1)-C(2)-C(3) | 124.5(8) |
| C(1)-C(2)-H(2) | 117.7 |
| C(3)-C(2)-H(2) | 117.7 |
| C(2)-C(3)-P(1) | 117.1(5) |
| C(2)-C(3)-H(3A) | 108.0 |
| P(1)-C(3)-H(3A) | 108.0 |
| C(2)-C(3)-H(3B) | 108.0 |
| P(1)-C(3)-H(3B) | 108.0 |
| H(3A)-C(3)-H(3B) | 107.3 |
| C(9)-C(4)-C(5) | 118.8(6) |
| C(9)-C(4)-P(1) | 118.3(5) |
| C(5)-C(4)-P(1) | 122.8(5) |
| C(6)-C(5)-C(4) | 119.8(6) |
| C(6)-C(5)-H(5) | 120.1 |
| C(4)-C(5)-H(5) | 120.1 |
| C(5)-C(6)-C(7) | 120.7(7) |
| C(5)-C(6)-H(6) | 119.7 |
| C(7)-C(6)-H(6) | 119.7 |
| C(8)-C(7)-C(6) | 120.1(7) |
| C(8)-C(7)-H(7) | 119.9 |
| C(6)-C(7)-H(7) | 119.9 |

| | |
|---|---|
| C(7)-C(8)-C(9) | 120.6(6) |
| C(7)-C(8)-H(8) | 119.7 |
| C(9)-C(8)-H(8) | 119.7 |
| C(8)-C(9)-C(4) | 120.0(6) |
| C(8)-C(9)-H(9) | 120.0 |
| C(4)-C(9)-H(9) | 120.0 |
| C(15)-C(10)-C(11) | 118.8(6) |
| C(15)-C(10)-P(1) | 122.4(5) |
| C(11)-C(10)-P(1) | 118.8(5) |
| C(12)-C(11)-C(10) | 120.9(7) |
| C(12)-C(11)-H(11) | 119.5 |
| C(10)-C(11)-H(11) | 119.5 |
| C(13)-C(12)-C(11) | 119.4(7) |
| C(13)-C(12)-H(12) | 120.3 |
| C(11)-C(12)-H(12) | 120.3 |
| C(14)-C(13)-C(12) | 120.6(6) |
| C(14)-C(13)-H(13) | 119.7 |
| C(12)-C(13)-H(13) | 119.7 |
| C(13)-C(14)-C(15) | 120.6(7) |
| C(13)-C(14)-H(14) | 119.7 |
| C(15)-C(14)-H(14) | 119.7 |
| C(14)-C(15)-C(10) | 119.7(7) |
| C(14)-C(15)-H(15) | 120.2 |
| C(10)-C(15)-H(15) | 120.2 |
| C(17)-C(16)-C(21) | 118.8(6) |
| C(17)-C(16)-P(1) | 122.6(5) |
| C(21)-C(16)-P(1) | 118.6(6) |
| C(16)-C(17)-C(18) | 120.4(7) |
| C(16)-C(17)-H(17) | 119.8 |
| C(18)-C(17)-H(17) | 119.8 |
| C(19)-C(18)-C(17) | 119.3(8) |
| C(19)-C(18)-H(18) | 120.4 |
| C(17)-C(18)-H(18) | 120.4 |
| C(20)-C(19)-C(18) | 121.0(7) |
| C(20)-C(19)-H(19) | 119.5 |
| C(18)-C(19)-H(19) | 119.5 |
| C(19)-C(20)-C(21) | 119.5(8) |
| C(19)-C(20)-H(20) | 120.2 |
| C(21)-C(20)-H(20) | 120.2 |
| C(20)-C(21)-C(16) | 121.0(8) |
| C(20)-C(21)-H(21) | 119.5 |
| C(16)-C(21)-H(21) | 119.5 |

**Table S13. Torsion angles [deg] for 2098034.**

| | |
|---|---|
| C(1)-C(2)-C(3)-P(1) | 130.8(8) |
| C(16)-P(1)-C(3)-C(2) | 168.8(5) |
| C(4)-P(1)-C(3)-C(2) | 50.1(6) |
| C(10)-P(1)-C(3)-C(2) | -72.4(6) |
| C(16)-P(1)-C(4)-C(9) | -66.3(6) |
| C(3)-P(1)-C(4)-C(9) | 53.1(6) |
| C(10)-P(1)-C(4)-C(9) | 177.4(5) |
| C(16)-P(1)-C(4)-C(5) | 111.0(6) |
| C(3)-P(1)-C(4)-C(5) | -129.6(6) |
| C(10)-P(1)-C(4)-C(5) | -5.3(7) |
| C(9)-C(4)-C(5)-C(6) | 2.1(11) |
| P(1)-C(4)-C(5)-C(6) | -175.2(6) |
| C(4)-C(5)-C(6)-C(7) | -1.2(12) |
| C(5)-C(6)-C(7)-C(8) | 0.8(13) |
| C(6)-C(7)-C(8)-C(9) | -1.5(13) |
| C(7)-C(8)-C(9)-C(4) | 2.4(12) |
| C(5)-C(4)-C(9)-C(8) | -2.7(10) |
| P(1)-C(4)-C(9)-C(8) | 174.7(6) |
| C(16)-P(1)-C(10)-C(15) | 132.2(5) |
| C(3)-P(1)-C(10)-C(15) | 12.1(6) |
| C(4)-P(1)-C(10)-C(15) | -110.8(5) |
| C(16)-P(1)-C(10)-C(11) | -48.4(6) |
| C(3)-P(1)-C(10)-C(11) | -168.4(5) |
| C(4)-P(1)-C(10)-C(11) | 68.6(5) |
| C(15)-C(10)-C(11)-C(12) | 0.6(10) |
| P(1)-C(10)-C(11)-C(12) | -178.8(5) |
| C(10)-C(11)-C(12)-C(13) | 0.0(10) |
| C(11)-C(12)-C(13)-C(14) | -1.0(11) |
| C(12)-C(13)-C(14)-C(15) | 1.4(11) |
| C(13)-C(14)-C(15)-C(10) | -0.7(10) |
| C(11)-C(10)-C(15)-C(14) | -0.2(9) |
| P(1)-C(10)-C(15)-C(14) | 179.2(5) |
| C(3)-P(1)-C(16)-C(17) | -131.2(5) |
| C(4)-P(1)-C(16)-C(17) | -11.2(6) |
| C(10)-P(1)-C(16)-C(17) | 106.6(5) |
| C(3)-P(1)-C(16)-C(21) | 52.3(6) |
| C(4)-P(1)-C(16)-C(21) | 172.3(5) |
| C(10)-P(1)-C(16)-C(21) | -69.9(6) |
| C(21)-C(16)-C(17)-C(18) | 1.1(10) |
| P(1)-C(16)-C(17)-C(18) | -175.4(5) |
| C(16)-C(17)-C(18)-C(19) | 0.3(10) |
| C(17)-C(18)-C(19)-C(20) | -1.0(11) |

| | |
|---|---|
| C(18)-C(19)-C(20)-C(21) | 0.1(12) |
| C(19)-C(20)-C(21)-C(16) | 1.4(12) |
| C(17)-C(16)-C(21)-C(20) | -2.0(10) |
| P(1)-C(16)-C(21)-C(20) | 174.6(6) |

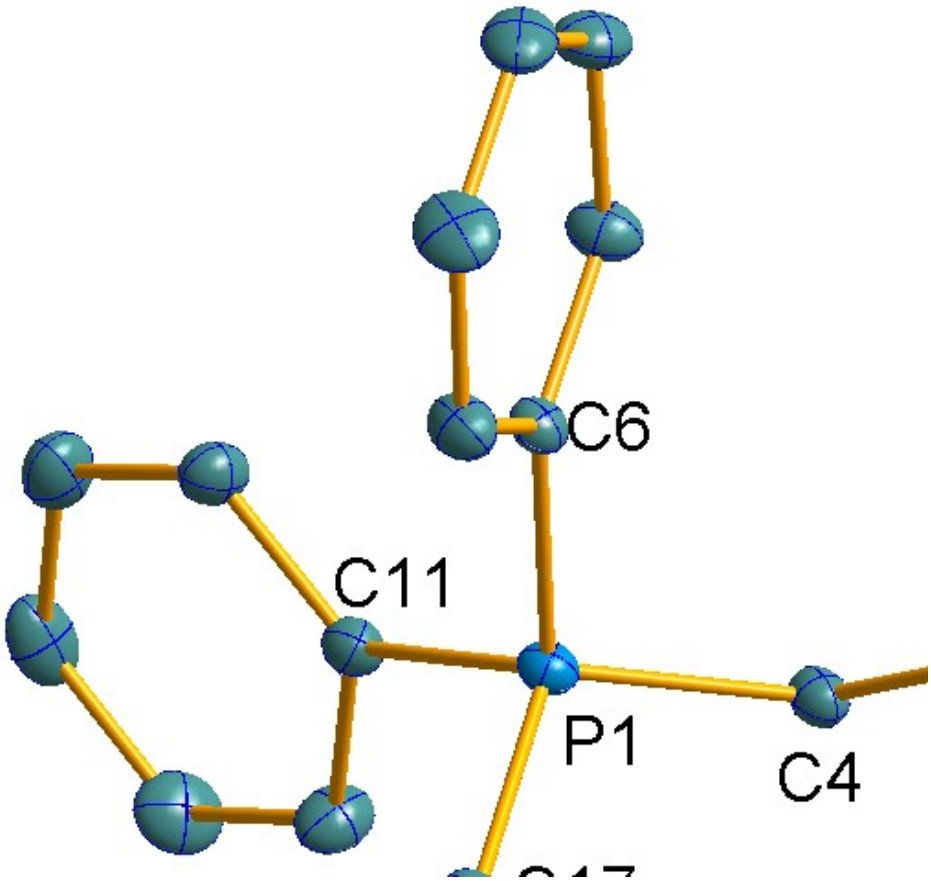



Figure S71. X-ray crystal structure of **L2**. Hydrogen atoms are omitted for clarity and ellipsoids drawn at 30% probability (CCDC # 2098035).

**Table S14. Crystal data and structure refinement for 2098035.**

| | |
|---|---|
| Identification code | 2098035 |
| Empirical formula | C22 H22 Br P |
| Formula weight | 397.28 |
| Temperature | 298(2) K |

| | |
|---|---|
| Wavelength | 0.71073 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 11.3364(13) A alpha = 90 deg.<br>b = 10.3332(12) A beta = 104.699(3) deg.<br>c = 18.1348(18) A gamma = 90 deg. |
| Volume | 2054.8(4) A^3 |
| Z, Calculated density | 4, 1.284 Mg/m^3 |
| Absorption coefficient | 2.078 mm^-1 |
| F(000) | 816 |
| Crystal size | 0.40 x 0.30 x 0.27 mm |
| Theta range for data collection | 2.29 to 25.02 deg. |
| Limiting indices | -11<=h<=13, -10<=k<=12, -21<=l<=21 |
| Reflections collected / unique | 8905 / 3614 [R(int) = 0.0757] |
| Completeness to theta = 25.02 | 99.4 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.6038 and 0.4903 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3614 / 28 / 224 |
| Goodness-of-fit on F^2 | 1.044 |
| Final R indices [I>2sigma(I)] | $R^1$ = 0.0553, $wR^2$ = 0.1260 |
| R indices (all data) | $R^1$ = 0.1062, $wR^2$ = 0.1463 |

Largest diff. peak and hole 0.631 and -1.227 e.A^-3

**Table S15. Bond lengths [Å] and angles [deg] for 2098035.**

| | |
|---|---|
| P(1)-C(17) | 1.821(5) |
| P(1)-C(11) | 1.823(5) |
| P(1)-C(4) | 1.829(4) |
| P(1)-C(5) | 1.834(4) |
| C(1)-C(2) | 1.328(9) |
| C(1)-H(1A) | 0.9300 |
| C(1)-H(1B) | 0.9300 |
| C(2)-C(3) | 1.502(8) |
| C(2)-H(2) | 0.9300 |
| C(1')-C(2') | 1.310(10) |
| C(1')-H(1'1) | 0.9300 |
| C(1')-H(1'2) | 0.9300 |
| C(2')-C(3) | 1.498(9) |
| C(2')-H(2') | 0.9300 |
| C(3)-C(4) | 1.559(7) |
| C(3)-H(3A) | 0.9700 |
| C(3)-H(3B) | 0.9700 |
| C(3)-H(3'A) | 0.9700 |
| C(3)-H(3'B) | 0.9700 |
| C(4)-H(4A) | 0.9700 |
| C(4)-H(4B) | 0.9700 |
| C(5)-C(10) | 1.413(6) |
| C(5)-C(6) | 1.414(6) |
| C(6)-C(7) | 1.422(7) |
| C(6)-H(6) | 0.9300 |
| C(7)-C(8) | 1.402(8) |
| C(7)-H(7) | 0.9300 |
| C(8)-C(9) | 1.387(8) |
| C(8)-H(8) | 0.9300 |
| C(9)-C(10) | 1.401(7) |
| C(9)-H(9) | 0.9300 |
| C(10)-H(10) | 0.9300 |
| C(11)-C(12) | 1.398(6) |
| C(11)-C(16) | 1.414(6) |
| C(12)-C(13) | 1.423(7) |
| C(12)-H(12) | 0.9300 |
| C(13)-C(14) | 1.383(8) |
| C(13)-H(13) | 0.9300 |
| C(14)-C(15) | 1.382(8) |
| C(14)-H(14) | 0.9300 |

| | |
|---|---|
| C(15)-C(16) | 1.410(7) |
| C(15)-H(15) | 0.9300 |
| C(16)-H(16) | 0.9300 |
| C(17)-C(22) | 1.416(6) |
| C(17)-C(18) | 1.419(6) |
| C(18)-C(19) | 1.409(8) |
| C(18)-H(18) | 0.9300 |
| C(19)-C(20) | 1.389(9) |
| C(19)-H(19) | 0.9300 |
| C(20)-C(21) | 1.403(9) |
| C(20)-H(20) | 0.9300 |
| C(21)-C(22) | 1.413(7) |
| C(21)-H(21) | 0.9300 |
| C(22)-H(22) | 0.9300 |
| C(17)-P(1)-C(11) | 106.9(2) |
| C(17)-P(1)-C(4) | 110.7(2) |
| C(11)-P(1)-C(4) | 111.2(2) |
| C(17)-P(1)-C(5) | 110.5(2) |
| C(11)-P(1)-C(5) | 109.3(2) |
| C(4)-P(1)-C(5) | 108.3(2) |
| C(2)-C(1)-H(1A) | 120.0 |
| C(2)-C(1)-H(1B) | 120.0 |
| H(1A)-C(1)-H(1B) | 120.0 |
| C(1)-C(2)-C(3) | 119.1(10) |
| C(1)-C(2)-H(2) | 120.4 |
| C(3)-C(2)-H(2) | 120.4 |
| C(2')-C(1')-H(1'1) | 120.0 |
| C(2')-C(1')-H(1'2) | 120.0 |
| H(1'1)-C(1')-H(1'2) | 120.0 |
| C(1')-C(2')-C(3) | 135.0(16) |
| C(1')-C(2')-H(2') | 112.5 |
| C(3)-C(2')-H(2') | 112.5 |
| C(2')-C(3)-C(2) | 23.6(8) |
| C(2')-C(3)-C(4) | 105.0(8) |
| C(2)-C(3)-C(4) | 122.4(7) |
| C(2')-C(3)-H(3A) | 129.9 |
| C(2)-C(3)-H(3A) | 106.7 |
| C(4)-C(3)-H(3A) | 106.7 |
| C(2')-C(3)-H(3B) | 100.1 |
| C(2)-C(3)-H(3B) | 106.7 |
| C(4)-C(3)-H(3B) | 106.7 |
| H(3A)-C(3)-H(3B) | 106.6 |
| C(2')-C(3)-H(3'A) | 108.0 |
| C(2)-C(3)-H(3'A) | 86.1 |

| | |
|---|---|
| C(4)-C(3)-H(3'A) | 110.2 |
| H(3A)-C(3)-H(3'A) | 23.6 |
| H(3B)-C(3)-H(3'A) | 124.9 |
| C(2')-C(3)-H(3'B) | 113.8 |
| C(2)-C(3)-H(3'B) | 114.7 |
| C(4)-C(3)-H(3'B) | 111.3 |
| H(3A)-C(3)-H(3'B) | 89.1 |
| H(3B)-C(3)-H(3'B) | 17.6 |
| H(3'A)-C(3)-H(3'B) | 108.5 |
| C(3)-C(4)-P(1) | 112.9(3) |
| C(3)-C(4)-H(4A) | 109.0 |
| P(1)-C(4)-H(4A) | 109.0 |
| C(3)-C(4)-H(4B) | 109.0 |
| P(1)-C(4)-H(4B) | 109.0 |
| H(4A)-C(4)-H(4B) | 107.8 |
| C(10)-C(5)-C(6) | 119.5(4) |
| C(10)-C(5)-P(1) | 118.2(4) |
| C(6)-C(5)-P(1) | 122.2(4) |
| C(5)-C(6)-C(7) | 119.2(5) |
| C(5)-C(6)-H(6) | 120.4 |
| C(7)-C(6)-H(6) | 120.4 |
| C(8)-C(7)-C(6) | 120.1(5) |
| C(8)-C(7)-H(7) | 120.0 |
| C(6)-C(7)-H(7) | 120.0 |
| C(9)-C(8)-C(7) | 120.4(5) |
| C(9)-C(8)-H(8) | 119.8 |
| C(7)-C(8)-H(8) | 119.8 |
| C(8)-C(9)-C(10) | 120.4(5) |
| C(8)-C(9)-H(9) | 119.8 |
| C(10)-C(9)-H(9) | 119.8 |
| C(9)-C(10)-C(5) | 120.3(5) |
| C(9)-C(10)-H(10) | 119.8 |
| C(5)-C(10)-H(10) | 119.8 |
| C(12)-C(11)-C(16) | 118.7(4) |
| C(12)-C(11)-P(1) | 123.0(4) |
| C(16)-C(11)-P(1) | 118.3(4) |
| C(11)-C(12)-C(13) | 120.4(5) |
| C(11)-C(12)-H(12) | 119.8 |
| C(13)-C(12)-H(12) | 119.8 |
| C(14)-C(13)-C(12) | 120.2(5) |
| C(14)-C(13)-H(13) | 119.9 |
| C(12)-C(13)-H(13) | 119.9 |
| C(15)-C(14)-C(13) | 120.0(5) |
| C(15)-C(14)-H(14) | 120.0 |

| | |
|---|---|
| C(13)-C(14)-H(14) | 120.0 |
| C(14)-C(15)-C(16) | 120.8(5) |
| C(14)-C(15)-H(15) | 119.6 |
| C(16)-C(15)-H(15) | 119.6 |
| C(15)-C(16)-C(11) | 120.0(5) |
| C(15)-C(16)-H(16) | 120.0 |
| C(11)-C(16)-H(16) | 120.0 |
| C(22)-C(17)-C(18) | 118.8(5) |
| C(22)-C(17)-P(1) | 122.4(4) |
| C(18)-C(17)-P(1) | 118.7(4) |
| C(19)-C(18)-C(17) | 120.3(5) |
| C(19)-C(18)-H(18) | 119.8 |
| C(17)-C(18)-H(18) | 119.8 |
| C(20)-C(19)-C(18) | 120.5(6) |
| C(20)-C(19)-H(19) | 119.8 |
| C(18)-C(19)-H(19) | 119.8 |
| C(19)-C(20)-C(21) | 120.0(6) |
| C(19)-C(20)-H(20) | 120.0 |
| C(21)-C(20)-H(20) | 120.0 |
| C(20)-C(21)-C(22) | 120.5(6) |
| C(20)-C(21)-H(21) | 119.8 |
| C(22)-C(21)-H(21) | 119.8 |
| C(21)-C(22)-C(17) | 119.9(5) |
| C(21)-C(22)-H(22) | 120.1 |
| C(17)-C(22)-H(22) | 120.1 |

**Table S16. Torsion angles [deg] for 2098035.**

| | |
|---|---|
| C(1')-C(2')-C(3)-C(2) | 38(2) |
| C(1')-C(2')-C(3)-C(4) | 179(3) |
| C(1)-C(2)-C(3)-C(2') | -2(3) |
| C(1)-C(2)-C(3)-C(4) | -48.3(19) |
| C(2')-C(3)-C(4)-P(1) | 143.4(11) |
| C(2)-C(3)-C(4)-P(1) | 161.0(8) |
| C(17)-P(1)-C(4)-C(3) | -75.2(4) |
| C(11)-P(1)-C(4)-C(3) | 166.2(3) |
| C(5)-P(1)-C(4)-C(3) | 46.1(4) |
| C(17)-P(1)-C(5)-C(10) | 176.0(4) |
| C(11)-P(1)-C(5)-C(10) | -66.7(4) |
| C(4)-P(1)-C(5)-C(10) | 54.6(4) |
| C(17)-P(1)-C(5)-C(6) | -5.9(5) |
| C(11)-P(1)-C(5)-C(6) | 111.4(4) |
| C(4)-P(1)-C(5)-C(6) | -127.3(4) |

| | |
|---|---|
| C(10)-C(5)-C(6)-C(7) | -0.8(7) |
| P(1)-C(5)-C(6)-C(7) | -178.9(4) |
| C(5)-C(6)-C(7)-C(8) | 1.7(8) |
| C(6)-C(7)-C(8)-C(9) | -1.1(9) |
| C(7)-C(8)-C(9)-C(10) | -0.4(9) |
| C(8)-C(9)-C(10)-C(5) | 1.3(8) |
| C(6)-C(5)-C(10)-C(9) | -0.7(7) |
| P(1)-C(5)-C(10)-C(9) | 177.5(4) |
| C(17)-P(1)-C(11)-C(12) | 116.2(4) |
| C(4)-P(1)-C(11)-C(12) | -122.8(4) |
| C(5)-P(1)-C(11)-C(12) | -3.3(4) |
| C(17)-P(1)-C(11)-C(16) | -60.3(4) |
| C(4)-P(1)-C(11)-C(16) | 60.6(4) |
| C(5)-P(1)-C(11)-C(16) | -179.8(4) |
| C(16)-C(11)-C(12)-C(13) | -0.6(7) |
| P(1)-C(11)-C(12)-C(13) | -177.1(4) |
| C(11)-C(12)-C(13)-C(14) | 0.5(8) |
| C(12)-C(13)-C(14)-C(15) | -0.4(9) |
| C(13)-C(14)-C(15)-C(16) | 0.3(9) |
| C(14)-C(15)-C(16)-C(11) | -0.3(9) |
| C(12)-C(11)-C(16)-C(15) | 0.4(7) |
| P(1)-C(11)-C(16)-C(15) | 177.1(4) |
| C(11)-P(1)-C(17)-C(22) | 127.0(4) |
| C(4)-P(1)-C(17)-C(22) | 5.7(5) |
| C(5)-P(1)-C(17)-C(22) | -114.2(4) |
| C(11)-P(1)-C(17)-C(18) | -51.0(4) |
| C(4)-P(1)-C(17)-C(18) | -172.3(4) |
| C(5)-P(1)-C(17)-C(18) | 67.8(4) |
| C(22)-C(17)-C(18)-C(19) | 1.8(8) |
| P(1)-C(17)-C(18)-C(19) | 179.8(4) |
| C(17)-C(18)-C(19)-C(20) | -1.1(9) |
| C(18)-C(19)-C(20)-C(21) | 0.2(9) |
| C(19)-C(20)-C(21)-C(22) | -0.1(9) |
| C(20)-C(21)-C(22)-C(17) | 0.8(8) |
| C(18)-C(17)-C(22)-C(21) | -1.6(7) |
| P(1)-C(17)-C(22)-C(21) | -179.6(4) |

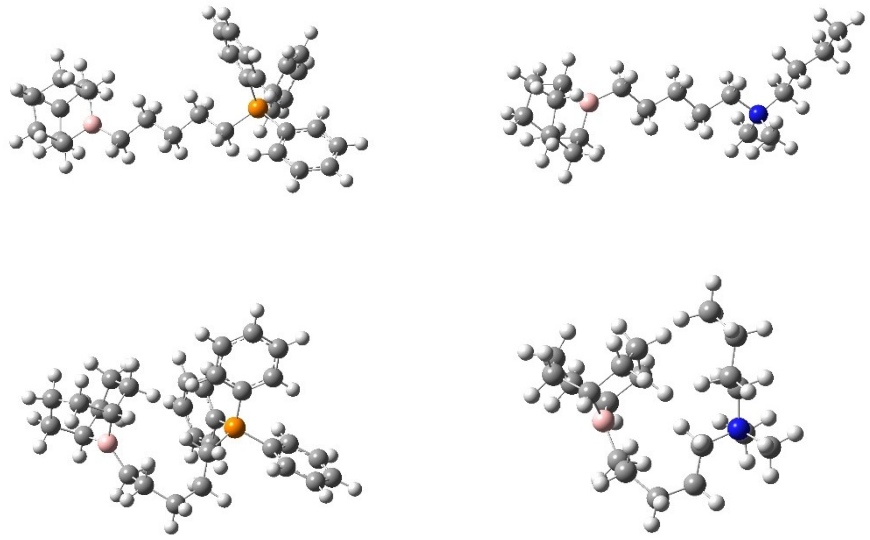
---

**Computation details**

The density functional theory (DFT) calculations were carried out to analysis the structures, interactions and reactions. All calculations were carried out using the Gaussian 09 program. The B3LYP/6-31G(d) level with D3(BJ)

correction method has been used for structure optimizations, transition states (TS) and intrinsic reaction coordinate (IRC) calculations, and subsequent frequency calculations at the same level verify the optimized structures to be ground states without imaginary frequencies (NImag = 0) and TSs have only one imaginary frequency. The single point energies were calculated at M06-2X/6-311+G(d,p) level by a self-consistent reaction field (SCRF) with SMD model, while and solvent parameter setting for CHO (ε = 11.771631) as reported.[2]

The conformers of **3** and **R3** were obtained and shown in Figure S62. Different structures of ions of **3** and **R3** are presented in Figure S62, namely the linear structures and curved structures. Based on the calculation, the curved structure is more likely to exist. The optimized size of the ions in the linear structure is shown in Figure S63.



**3** **R3**

Figure S72. Optimized structures of different ions.

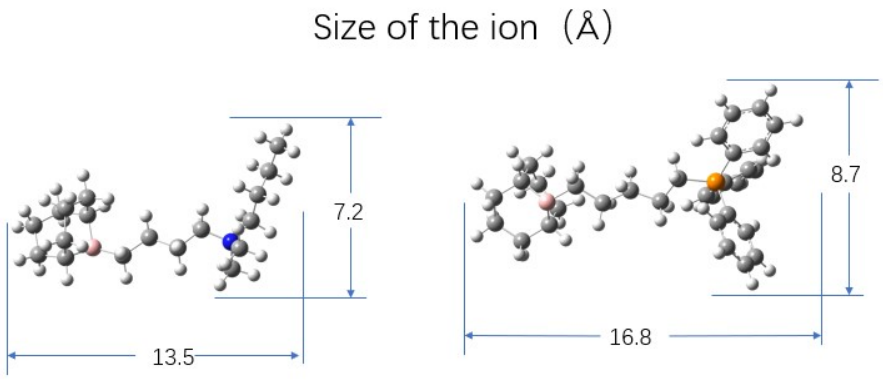
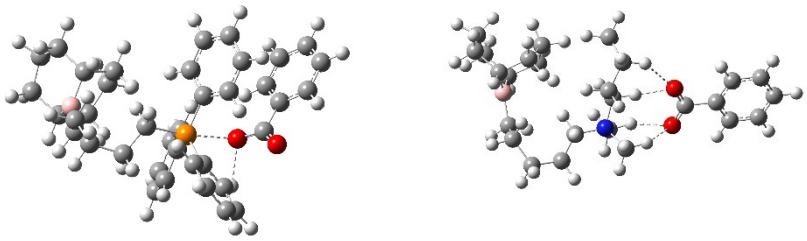



Figure S73. The optimized size of the ions in the linear structure of **3** and **R3**

The interaction structures for the coordination benzoic acid anion with different cations were shown in Figure S64.

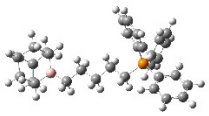


74.4 kcal/mol　　79.5 kcal/mol

Figure S74. Optimized interaction structures of **3**/**R3** and anion with interaction energy.

**Cartesian coordinates for the optimized structures**

**3** ion (in Figure S73)

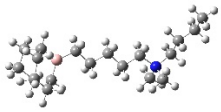


| | | | |
|---|---|---|---|
| C | -1.29038600 | 0.10466000 | -1.21011900 |
| H | -1.35748900 | 1.02928200 | -1.79444500 |
| H | -1.34295500 | -0.72339800 | -1.92697800 |
| C | 3.80680300 | 0.02497700 | -1.45045300 |
| H | 3.79156200 | 0.88782500 | -2.13852900 |
| H | 3.77222800 | -0.84547100 | -2.12835800 |

| | | | |
|---|---|---|---|
| C | 1.24544600 | 0.05841900 | -1.33334300 |
| H | 1.19848000 | -0.82008200 | -1.99256700 |
| H | 1.21674900 | 0.93832200 | -1.99137500 |
| C | 2.56405700 | 0.04421900 | -0.55398600 |
| H | 2.57729900 | -0.82954100 | 0.11264300 |
| H | 2.59959300 | 0.92257200 | 0.10565300 |
| C | 0.02037000 | 0.07034800 | -0.41152700 |
| H | 0.04050200 | -0.81555900 | 0.23505400 |
| H | 0.06827700 | 0.94510400 | 0.24692100 |
| C | 5.47506500 | 0.02026100 | 0.80765800 |
| C | 7.50001700 | 1.59459800 | 0.29725500 |
| C | 6.23431800 | 1.33786800 | 1.13783600 |
| C | 7.31702700 | 1.32067100 | -1.20771100 |
| C | 6.56339400 | 0.00468800 | -1.55500700 |
| C | 6.25374100 | -1.27748000 | 1.16495000 |
| C | 7.52020300 | -1.53680800 | 0.32625600 |
| C | 7.33037000 | -1.29579900 | -1.18324700 |
| B | 5.21599400 | 0.01247100 | -0.74394000 |
| H | 4.55447200 | 0.02017600 | 1.40729700 |
| H | 7.80862100 | 2.63894600 | 0.43285700 |
| H | 8.32676700 | 0.99457800 | 0.68445100 |
| H | 5.53643900 | 2.17452600 | 0.98237500 |
| H | 6.49350900 | 1.35825300 | 2.20587200 |
| H | 8.29793800 | 1.32907600 | -1.70294300 |
| H | 6.75223900 | 2.15556700 | -1.64871700 |
| H | 6.40914500 | -0.00558500 | -2.64330000 |
| H | 6.51665600 | -1.27067500 | 2.23228400 |
| H | 5.56668200 | -2.12661500 | 1.03086600 |
| H | 8.34134200 | -0.91963100 | 0.69834900 |
| H | 7.84120000 | -2.57451800 | 0.48245200 |
| H | 6.77240500 | -2.14494500 | -1.60539400 |
| H | 8.31012300 | -1.30541200 | -1.68078400 |
| P | -2.80751200 | 0.02159300 | -0.19107000 |
| C | -4.23513500 | 0.03800900 | -1.29319900 |
| C | -5.32840100 | -0.80003000 | -1.02827100 |
| C | -4.26292700 | 0.90546100 | -2.39836300 |
| C | -6.44215300 | -0.76691400 | -1.86515800 |
| H | -5.30637700 | -1.47606000 | -0.18023500 |
| C | -5.38142900 | 0.93146200 | -3.22750000 |
| H | -3.42419000 | 1.56043700 | -2.61300800 |
| C | -6.46934600 | 0.09630900 | -2.96147900 |
| H | -7.28636100 | -1.41786500 | -1.66195300 |
| H | -5.40238000 | 1.60005900 | -4.08206600 |
| H | -7.33787200 | 0.11761300 | -3.61221100 |

| | | | |
|---|---|---|---|
| C | -2.87306500 | 1.43103000 | 0.93332300 |
| C | -1.99710700 | 1.48074200 | 2.03257100 |
| C | -3.76582600 | 2.48590200 | 0.69601300 |
| C | -2.01359400 | 2.58680700 | 2.87730900 |
| H | -1.32199900 | 0.65611300 | 2.23614700 |
| C | -3.77318200 | 3.58894400 | 1.54879100 |
| H | -4.45430900 | 2.44361700 | -0.14080600 |
| C | -2.89834400 | 3.64105200 | 2.63431400 |
| H | -1.33958600 | 2.62458100 | 3.72708100 |
| H | -4.46643400 | 4.40372900 | 1.36648100 |
| H | -2.90870000 | 4.50077200 | 3.29695700 |
| C | -2.80421600 | -1.50264800 | 0.76849800 |
| C | -2.24740300 | -2.67009000 | 0.22186500 |
| C | -3.42241200 | -1.54062000 | 2.02817000 |
| C | -2.30255400 | -3.86296400 | 0.93814300 |
| H | -1.77393500 | -2.65423800 | -0.75460200 |
| C | -3.47618800 | -2.74057800 | 2.73508600 |
| H | -3.85138900 | -0.64024200 | 2.45514600 |
| C | -2.91568800 | -3.89830600 | 2.19278600 |
| H | -1.86655300 | -4.76354900 | 0.51806800 |
| H | -3.95220400 | -2.76917100 | 3.70993800 |
| H | -2.95549300 | -4.82997800 | 2.74834000 |

**R3** ion (in Figure S73)



| | | | |
|---|---|---|---|
| N | 4.16483100 | -1.07048400 | -0.08264800 |
| C | 3.00507700 | -0.07200500 | -0.06432100 |
| H | 3.16957900 | 0.58319700 | -0.92451300 |
| H | 3.13798100 | 0.51950300 | 0.84262500 |
| C | -1.95741300 | 0.96552100 | 0.10729500 |
| H | -1.81970900 | 1.74686100 | -0.66006200 |
| H | -1.82339400 | 1.50814600 | 1.05851000 |
| C | 0.54856100 | 0.43400600 | 0.03708900 |
| H | 0.69079100 | 0.95437500 | 0.99432000 |
| H | 0.69555400 | 1.18656800 | -0.75016500 |
| C | -0.88058900 | -0.11390400 | -0.04180200 |
| H | -1.01503300 | -0.87863700 | 0.73593600 |
| H | -1.01192700 | -0.63534200 | -0.99985500 |

| | | | |
|---|---|---|---|
| C | 5.48687300 | -0.31728600 | -0.25803600 |
| H | 6.26311200 | -1.08812800 | -0.26321500 |
| H | 5.43779200 | 0.12028700 | -1.25723700 |
| C | 1.60555800 | -0.67377500 | -0.10596100 |
| H | 1.46597500 | -1.40005500 | 0.70362000 |
| H | 1.43777400 | -1.20226900 | -1.05063600 |
| C | 4.02734500 | -2.01070700 | -1.24821100 |
| H | 4.91949200 | -2.63612200 | -1.29686800 |
| H | 3.93127700 | -1.42565000 | -2.16371500 |
| H | 3.14591800 | -2.63362000 | -1.10904700 |
| C | 4.19006300 | -1.87536100 | 1.18629400 |
| H | 4.23150400 | -1.20195500 | 2.04039400 |
| H | 5.07082100 | -2.51881000 | 1.17299000 |
| H | 3.28924700 | -2.48418700 | 1.23996600 |
| C | 5.80190400 | 0.74796000 | 0.78696100 |
| H | 5.75242700 | 0.32410600 | 1.79578000 |
| H | 5.07288600 | 1.56372900 | 0.73561000 |
| C | 7.21339500 | 1.32699500 | 0.56463700 |
| H | 7.41610200 | 2.01546900 | 1.39189400 |
| H | 7.95381800 | 0.52084200 | 0.64998800 |
| C | 7.39016200 | 2.06575500 | -0.76545500 |
| H | 8.37681300 | 2.53532200 | -0.81268700 |
| H | 6.64099900 | 2.85804100 | -0.88162400 |
| H | 7.31288700 | 1.39686000 | -1.63054100 |
| C | -3.97198000 | -0.96713600 | -0.19979000 |
| C | -5.94401100 | 0.08170500 | -1.56123800 |
| C | -4.82568700 | -0.97636800 | -1.50040400 |
| C | -5.50745300 | 1.48200900 | -1.09100800 |
| C | -4.65871100 | 1.50849800 | 0.21120500 |
| C | -4.75081300 | -1.38503100 | 1.08290100 |
| C | -5.85405200 | -0.40659400 | 1.52878000 |
| C | -5.42900300 | 1.07348200 | 1.49183000 |
| B | -3.46430200 | 0.50285200 | 0.03211400 |
| H | -3.16383400 | -1.69887300 | -0.33797200 |
| H | -6.30773100 | 0.15165000 | -2.59411400 |
| H | -6.80128500 | -0.25472300 | -0.97383800 |
| H | -4.14391100 | -0.81316400 | -2.34865100 |
| H | -5.25838800 | -1.97525400 | -1.65180400 |
| H | -6.39407600 | 2.11949700 | -0.96939800 |
| H | -4.91049300 | 1.94880200 | -1.88857400 |
| H | -4.32798100 | 2.54524000 | 0.36650900 |
| H | -5.18300100 | -2.38564500 | 0.94192300 |
| H | -4.02109100 | -1.48601500 | 1.90063300 |
| H | -6.74385800 | -0.55063700 | 0.91212700 |

| | | | |
|---|---|---|---|
| H | -6.16171800 | -0.66233200 | 2.55053100 |
| H | -4.78017100 | 1.27342100 | 2.35766300 |
| H | -6.31282000 | 1.71204000 | 1.62686000 |

**3** and anion (in Figure S74)

| | | | |
|---|---|---|---|
| C | 0.46455600 | 1.73360500 | 1.34635400 |
| H | 1.16038100 | 0.88976300 | 1.40379700 |
| H | 0.04955100 | 1.84209800 | 2.35533000 |
| C | 3.94225200 | 1.65896100 | 0.45447600 |
| H | 4.54251900 | 2.43681900 | -0.03798100 |
| H | 3.07197000 | 1.52533200 | -0.21988000 |
| C | 2.43965500 | 3.29535900 | 1.78331600 |
| H | 2.92619900 | 4.19729600 | 1.38853400 |
| H | 2.12355900 | 3.53670300 | 2.80765200 |
| C | 3.45622900 | 2.14178700 | 1.83030000 |
| H | 3.02218600 | 1.30216700 | 2.38578600 |
| H | 4.32181500 | 2.46322800 | 2.42376400 |
| C | 1.20163600 | 3.00626800 | 0.91854100 |
| H | 0.51641500 | 3.85980400 | 0.95839700 |
| H | 1.51328900 | 2.91481300 | -0.12503500 |
| C | 4.18787400 | -1.01686600 | 1.20239900 |
| C | 6.59142100 | -1.95167400 | 0.77642500 |
| C | 5.46709000 | -1.66831000 | 1.79211900 |
| C | 6.84705300 | -0.79804200 | -0.21119900 |
| C | 5.57048400 | -0.16942200 | -0.83017000 |
| C | 3.37412100 | -1.93847600 | 0.24677100 |
| C | 4.08510900 | -2.31180400 | -1.06716900 |
| C | 4.77300100 | -1.12341600 | -1.76727600 |
| B | 4.59203400 | 0.23667900 | 0.33482100 |
| H | 3.52804200 | -0.77314400 | 2.04638800 |
| H | 7.51855200 | -2.16322000 | 1.32484100 |
| H | 6.36614200 | -2.86621900 | 0.22201800 |
| H | 5.85854000 | -0.98982400 | 2.56418500 |
| H | 5.20651600 | -2.59960700 | 2.31555600 |
| H | 7.51886500 | -1.14523100 | -1.00937900 |
| H | 7.39328800 | -0.00129600 | 0.31530300 |
| H | 5.88666400 | 0.68984700 | -1.43808000 |
| H | 3.07811700 | -2.85560000 | 0.77704200 |
| H | 2.44012700 | -1.41605900 | -0.00572900 |
| H | 4.81202500 | -3.10524700 | -0.87753600 |
| H | 3.34809200 | -2.74742900 | -1.75442800 |
| H | 4.00136100 | -0.52553000 | -2.27064200 |
| H | 5.43284500 | -1.50149400 | -2.56178600 |
| P | -0.89262100 | 1.10547900 | 0.24358200 |

| | | | |
|---|---|---|---|
| C | -1.49031400 | -0.27006400 | 1.25378900 |
| C | -2.78442300 | -0.22180600 | 1.78717100 |
| C | -0.63674000 | -1.33606500 | 1.57301700 |
| C | -3.23443500 | -1.26771300 | 2.58978100 |
| H | -3.45589300 | 0.58353300 | 1.51494600 |
| C | -1.10219100 | -2.37992500 | 2.36962700 |
| H | 0.38041200 | -1.36900000 | 1.19538400 |
| C | -2.40286100 | -2.35062100 | 2.87335500 |
| H | -4.25092500 | -1.24569200 | 2.96908400 |
| H | -0.44736300 | -3.21738100 | 2.59156500 |
| H | -2.76858100 | -3.17257500 | 3.48113400 |
| C | 0.01074100 | 0.71634100 | -1.27959100 |
| C | 0.42110900 | 1.76866600 | -2.10712200 |
| C | 0.34188400 | -0.60232000 | -1.61365300 |
| C | 1.18399800 | 1.50429800 | -3.24562100 |
| H | 0.12237500 | 2.78744000 | -1.88503400 |
| C | 1.10560200 | -0.85750500 | -2.74936100 |
| H | -0.02843300 | -1.42240900 | -1.01404300 |
| C | 1.53471600 | 0.19304000 | -3.56369500 |
| H | 1.49313000 | 2.32501600 | -3.88594300 |
| H | 1.35140100 | -1.88276900 | -3.00812300 |
| H | 2.12677000 | -0.01302600 | -4.45044000 |
| C | -2.04278200 | 2.48848600 | 0.07663700 |
| C | -2.18411800 | 3.38253200 | 1.15097200 |
| C | -2.77824400 | 2.68277300 | -1.09962000 |
| C | -3.04765000 | 4.46926500 | 1.04341100 |
| H | -1.63339800 | 3.23253600 | 2.07359700 |
| C | -3.61728900 | 3.79001200 | -1.20716800 |
| H | -2.70661100 | 1.94409500 | -1.88607900 |
| C | -3.75695700 | 4.67796700 | -0.14152200 |
| H | -3.16240800 | 5.15169600 | 1.88019300 |
| H | -4.18699500 | 3.93791400 | -2.11916900 |
| H | -4.42625500 | 5.52940100 | -0.22781500 |
| C | -2.97020500 | -2.89736000 | -0.95663000 |
| C | -5.20302000 | -2.30288800 | -0.26402700 |
| C | -5.46746900 | -3.63731500 | 0.03751700 |
| C | -4.47898000 | -4.60660200 | -0.15450200 |
| C | -3.23050600 | -4.23408900 | -0.65752200 |
| H | -5.94536400 | -1.52564300 | -0.11482600 |
| H | -6.44219800 | -3.92545700 | 0.42405600 |
| H | -4.68254100 | -5.64781600 | 0.08346200 |
| H | -2.46120300 | -4.98693300 | -0.81319600 |
| C | -3.95051500 | -1.92124300 | -0.75654500 |
| C | -3.64867900 | -0.44866100 | -0.97767700 |

| | | | |
|---|---|---|---|
| O | -4.54992800 | 0.37871700 | -0.74840900 |
| O | -2.43782000 | -0.18062500 | -1.31569400 |
| H | -2.00879000 | -2.58424900 | -1.34731200 |

**R3** and anion (in Figure S74)

| | | | |
|---|---|---|---|
| N | -0.44823200 | 1.50218800 | 0.32205200 |
| C | 0.93618000 | 1.95850800 | 0.71417600 |
| H | 1.59317900 | 1.12614200 | 0.45753500 |
| H | 0.93077400 | 2.05262300 | 1.80227200 |
| C | 4.09968800 | 1.78516700 | -0.67285300 |
| H | 4.86890900 | 2.33055000 | -1.24484800 |
| H | 3.21521900 | 1.85972300 | -1.32574400 |
| C | 2.82774300 | 3.63097100 | 0.63764500 |
| H | 3.22054200 | 4.45785900 | 0.03321000 |
| H | 2.69791000 | 4.02410400 | 1.65467700 |
| C | 3.84781400 | 2.47879100 | 0.67933800 |
| H | 3.51197200 | 1.74142100 | 1.41910400 |
| H | 4.79341400 | 2.86454900 | 1.07825900 |
| C | -0.65982100 | 0.06764000 | 0.81405000 |
| H | -1.70195500 | -0.19481100 | 0.56742700 |
| H | 0.03238800 | -0.53433500 | 0.21923100 |
| C | 1.44520200 | 3.24366800 | 0.07043200 |
| H | 0.74794800 | 4.07102100 | 0.24157700 |
| H | 1.51871600 | 3.11277500 | -1.01298600 |
| C | -0.62557600 | 1.46750600 | -1.17278700 |
| H | -1.63836700 | 1.08659000 | -1.35464000 |
| H | 0.14946800 | 0.82613200 | -1.59781800 |
| H | -0.53289000 | 2.48047300 | -1.56373000 |
| C | -1.51546900 | 2.40505900 | 0.88196700 |
| H | -1.46245800 | 2.38461900 | 1.96945500 |
| H | -2.47463400 | 2.02871300 | 0.50384000 |
| H | -1.33125800 | 3.41743300 | 0.52071900 |
| C | -0.43795400 | -0.16328300 | 2.30486100 |
| H | -0.99180600 | 0.57983100 | 2.88897400 |
| H | 0.62156000 | -0.07409600 | 2.58175200 |
| C | -0.96076400 | -1.55741600 | 2.69953200 |
| H | -0.88367600 | -1.65075600 | 3.78996800 |
| H | -2.02271600 | -1.60977400 | 2.43755900 |
| C | -0.20405800 | -2.71394300 | 2.03939300 |
| H | -0.55553800 | -3.67683300 | 2.42478200 |
| H | 0.87517900 | -2.65103800 | 2.23147600 |
| H | -0.35535200 | -2.72892700 | 0.95433700 |
| C | 4.81155800 | -0.60905500 | 0.60839100 |
| C | 6.00785600 | -2.35699300 | -0.91297300 |

| | | | |
|---|---|---|---|
| C | 6.04185700 | -1.52084200 | 0.37929300 |
| C | 5.57443900 | -1.56245200 | -2.15936500 |
| C | 4.36356200 | -0.62156100 | -1.95516200 |
| C | 3.47394700 | -1.38452500 | 0.84477700 |
| C | 2.92539100 | -2.14481300 | -0.38016200 |
| C | 3.00634500 | -1.35670900 | -1.70192100 |
| B | 4.50590100 | 0.26283000 | -0.66365900 |
| H | 4.99702900 | -0.01713900 | 1.51440900 |
| H | 7.00619900 | -2.77724900 | -1.08956900 |
| H | 5.35079000 | -3.21951300 | -0.77556800 |
| H | 6.93230300 | -0.87583100 | 0.35596400 |
| H | 6.17885300 | -2.19025600 | 1.24055200 |
| H | 5.37756300 | -2.26089600 | -2.98514600 |
| H | 6.42023100 | -0.94103400 | -2.48727900 |
| H | 4.23351900 | -0.02908900 | -2.87184600 |
| H | 3.59768400 | -2.08233800 | 1.68485500 |
| H | 2.71584500 | -0.65913000 | 1.17583600 |
| H | 3.45338000 | -3.09444100 | -0.48958500 |
| H | 1.87947800 | -2.41493300 | -0.18870200 |
| H | 2.20592200 | -0.59950800 | -1.71127600 |
| H | 2.78758600 | -2.02798200 | -2.54357600 |
| C | -6.27648900 | 0.44045000 | -1.40422700 |
| C | -6.20307800 | -1.33360900 | 0.23024300 |
| C | -7.53816700 | -1.63540200 | -0.03409700 |
| C | -8.24595500 | -0.89854800 | -0.98712100 |
| C | -7.61159300 | 0.14051200 | -1.67233100 |
| H | -5.62922700 | -1.88955700 | 0.96413200 |
| H | -8.02933700 | -2.44486600 | 0.50090000 |
| H | -9.28716600 | -1.13323300 | -1.19484600 |
| H | -8.15999600 | 0.71555900 | -2.41483000 |
| C | -5.56215800 | -0.29379800 | -0.45178800 |
| C | -4.10760000 | 0.03109100 | -0.15840300 |
| O | -3.52477200 | -0.67397400 | 0.70829500 |
| O | -3.59603200 | 0.99490600 | -0.81088700 |
| H | -5.76003100 | 1.24204800 | -1.92159400 |

**3** (in Figure 8) reactant

| | | | |
|---|---|---|---|
| C | -1.39295600 | -1.77788800 | -1.60344300 |
| H | -1.91608500 | -2.49991300 | -2.23931100 |
| H | -0.49794400 | -2.27742000 | -1.22161300 |
| C | 1.84654300 | -1.15445200 | -1.39473300 |
| H | 1.68741300 | -2.23991600 | -1.49804900 |
| H | 1.08133400 | -0.82200900 | -0.67902500 |
| C | 0.17296600 | -0.83300200 | -3.36353400 |

| | | | |
|---|---|---|---|
| H | 0.13736800 | -1.88965100 | -3.67028300 |
| H | 0.04342800 | -0.24940200 | -4.28408000 |
| C | 1.55476500 | -0.51337600 | -2.76163400 |
| H | 1.64308400 | 0.57844700 | -2.69099200 |
| H | 2.32061100 | -0.82001100 | -3.48466800 |
| C | -1.00577300 | -0.52771400 | -2.41281800 |
| H | -0.72948500 | 0.29464300 | -1.74730600 |
| H | -1.88726600 | -0.20293700 | -2.97733000 |
| C | 4.58209900 | -0.87806900 | -1.75602000 |
| C | 4.82007300 | -3.46230300 | -1.47394800 |
| C | 4.69535300 | -2.26402200 | -2.43836900 |
| C | 3.86042600 | -3.41867900 | -0.26507700 |
| C | 3.71964400 | -2.03095200 | 0.40611500 |
| C | 5.86730500 | -0.44607600 | -1.01359100 |
| C | 6.20808000 | -1.26370000 | 0.25025400 |
| C | 5.00137700 | -1.59717500 | 1.15415300 |
| B | 3.32630600 | -0.95628500 | -0.74376800 |
| H | 4.41955700 | -0.14342600 | -2.56148300 |
| H | 4.64572400 | -4.39177800 | -2.03447700 |
| H | 5.85071700 | -3.53265400 | -1.11510400 |
| H | 3.80007100 | -2.41338800 | -3.05817100 |
| H | 5.54892100 | -2.28461100 | -3.13384800 |
| H | 4.18706700 | -4.17060600 | 0.47079300 |
| H | 2.86505200 | -3.74350200 | -0.59997800 |
| H | 2.92244400 | -2.12782400 | 1.16400100 |
| H | 6.73475200 | -0.47374700 | -1.69201200 |
| H | 5.74449500 | 0.60475800 | -0.72116700 |
| H | 6.70799200 | -2.19214300 | -0.04187200 |
| H | 6.95200800 | -0.71143900 | 0.84167600 |
| H | 4.76382900 | -0.70837500 | 1.75128100 |
| H | 5.30754100 | -2.37212200 | 1.87523900 |
| C | -1.44696200 | 5.02663300 | 0.75395500 |
| C | -1.52962400 | 3.98118000 | -1.41797700 |
| C | -2.20792700 | 5.08853700 | -1.92902500 |
| C | -2.52040700 | 6.16267400 | -1.09162200 |
| C | -2.13655800 | 6.12928300 | 0.25166200 |
| H | -1.28027400 | 3.13531200 | -2.05078700 |
| H | -2.48932200 | 5.11769100 | -2.97911400 |
| H | -3.05284900 | 7.02452800 | -1.48587200 |
| H | -2.37289800 | 6.96653200 | 0.90381900 |
| C | -1.15001200 | 3.93707100 | -0.07139300 |
| C | -0.43244300 | 2.71927500 | 0.49960100 |
| O | 0.10951300 | 2.84668400 | 1.62218500 |
| O | -0.46457200 | 1.66683500 | -0.21731200 |

| | | | |
|---|---|---|---|
| C | 3.97128800 | 2.48814600 | 2.18239400 |
| C | 2.87937700 | 1.42520700 | 2.36170400 |
| C | 2.33554300 | 0.93658300 | 1.05015900 |
| C | 2.51825900 | 1.69784000 | -0.18327400 |
| C | 3.26940800 | 3.00998000 | -0.20182000 |
| C | 3.49507200 | 3.57520000 | 1.20990600 |
| H | 3.23943700 | 0.57461000 | 2.95310700 |
| H | 2.01790800 | 1.86113700 | 2.87771800 |
| H | 4.21208000 | 2.92815500 | 3.15707700 |
| H | 4.89028200 | 2.02092700 | 1.80524300 |
| H | 4.22484900 | 2.85092000 | -0.71761700 |
| H | 2.69591600 | 3.72272000 | -0.80486600 |
| H | 4.21613800 | 4.39962000 | 1.16463700 |
| H | 2.54424700 | 3.98122200 | 1.57516800 |
| H | 1.48544800 | 0.26929600 | 1.08099300 |
| O | 3.36448000 | 0.50861500 | 0.07214300 |
| H | 1.78146900 | 1.52404500 | -0.95337100 |
| H | -1.12398100 | 4.97997500 | 1.78881500 |
| P | -2.43423800 | -1.50242200 | -0.12197500 |
| C | -1.40038100 | -1.07484200 | 1.28993700 |
| C | -1.61817900 | 0.08763700 | 2.03296700 |
| C | -0.36228200 | -1.95661100 | 1.64025900 |
| C | -0.80236600 | 0.37143400 | 3.12693300 |
| H | -2.39522500 | 0.78429100 | 1.74744600 |
| C | 0.43237400 | -1.67762100 | 2.74695200 |
| H | -0.17439800 | -2.85406500 | 1.05858400 |
| C | 0.20890800 | -0.51465100 | 3.49073100 |
| H | -0.93950900 | 1.30300700 | 3.66155300 |
| H | 1.23832500 | -2.35386100 | 3.01266600 |
| H | 0.84606000 | -0.28891800 | 4.34020400 |
| C | -3.22685400 | -3.09058100 | 0.26955300 |
| C | -3.78484400 | -3.87546700 | -0.75160700 |
| C | -3.33503500 | -3.51031600 | 1.60263600 |
| C | -4.43153700 | -5.06954800 | -0.44126900 |
| H | -3.72803600 | -3.55557800 | -1.78717800 |
| C | -3.98254700 | -4.70696500 | 1.90676100 |
| H | -2.90729500 | -2.90729100 | 2.39566400 |
| C | -4.52802700 | -5.48773100 | 0.88749400 |
| H | -4.85749900 | -5.67339700 | -1.23659600 |
| H | -4.05792100 | -5.02848400 | 2.94096700 |
| H | -5.02875400 | -6.42108800 | 1.12682300 |
| C | -3.74044000 | -0.28584900 | -0.40106900 |
| C | -3.39763200 | 1.05029400 | -0.67328000 |
| C | -5.08813700 | -0.67755700 | -0.34601500 |

| | | | |
|---|---|---|---|
| C | -4.41152900 | 1.98336300 | -0.88767600 |
| H | -2.35279200 | 1.36450700 | -0.67486100 |
| C | -6.08834400 | 0.26566700 | -0.57092700 |
| H | -5.35580800 | -1.70454900 | -0.12510500 |
| C | -5.75093400 | 1.59321100 | -0.84217400 |
| H | -4.13884200 | 3.01512200 | -1.08605700 |
| H | -7.13043000 | -0.03685900 | -0.52819800 |
| H | -6.53503900 | 2.32579100 | -1.01173700 |

**3** (in Figure 8) TS（P）

| | | | |
|---|---|---|---|
| C | 0.98058400 | -2.16823300 | 1.38086400 |
| H | 1.37639700 | -3.06070300 | 1.87930400 |
| H | 0.12714300 | -2.49564700 | 0.78131200 |
| C | -2.22179300 | -1.46173800 | 1.07096400 |
| H | -2.15805500 | -2.55361800 | 0.94740800 |
| H | -1.36708900 | -1.05813400 | 0.50930700 |
| C | -0.70678600 | -1.59281900 | 3.18662300 |
| H | -0.68958700 | -2.69034800 | 3.26828400 |
| H | -0.65079900 | -1.21429100 | 4.21542900 |
| C | -2.03600600 | -1.13688900 | 2.55766800 |
| H | -2.12767600 | -0.05483200 | 2.71027000 |
| H | -2.85896500 | -1.58342800 | 3.13061500 |
| C | 0.55237100 | -1.12224800 | 2.42508300 |
| H | 0.37608100 | -0.14815800 | 1.95486700 |
| H | 1.38589000 | -0.97846700 | 3.12132400 |
| C | -4.96820300 | -1.35001100 | 1.10640600 |
| C | -4.92673200 | -3.53827600 | -0.31350800 |
| C | -5.05694800 | -2.89364300 | 1.08441900 |
| C | -3.83837400 | -2.92324100 | -1.22104900 |
| C | -3.75367200 | -1.37780900 | -1.18794700 |
| C | -6.17449600 | -0.64303100 | 0.45196800 |
| C | -6.30307400 | -0.84006800 | -1.07206400 |
| C | -4.97747300 | -0.70715300 | -1.85170600 |
| B | -3.59004900 | -0.91359300 | 0.36792700 |
| H | -4.96594500 | -1.04750900 | 2.16612600 |
| H | -4.72739300 | -4.61342500 | -0.19713000 |
| H | -5.89120100 | -3.48033400 | -0.82610400 |
| H | -4.25609000 | -3.28775900 | 1.72635600 |
| H | -5.99991300 | -3.23913800 | 1.53768900 |
| H | -4.00420400 | -3.27734300 | -2.25159900 |
| H | -2.86150800 | -3.32937300 | -0.92257900 |
| H | -2.87281400 | -1.11224200 | -1.80337900 |
| H | -7.11965200 | -0.95661700 | 0.92399700 |
| H | -6.07275900 | 0.43110100 | 0.65449400 |

| | | | |
|---|---|---|---|
| H | -6.74627200 | -1.81928800 | -1.27685700 |
| H | -7.02298800 | -0.11014100 | -1.46948700 |
| H | -4.76180600 | 0.36092600 | -1.97852300 |
| H | -5.12846800 | -1.09944000 | -2.87085600 |
| C | 1.44197800 | 4.60401500 | -1.31452700 |
| C | 3.01241200 | 3.66004800 | 0.25037100 |
| C | 4.03027200 | 4.44428600 | -0.29196300 |
| C | 3.75542800 | 5.30825800 | -1.35431100 |
| C | 2.45503300 | 5.39083300 | -1.86033500 |
| H | 3.21148500 | 2.98697800 | 1.07457300 |
| H | 5.03755800 | 4.38357200 | 0.11311600 |
| H | 4.54730800 | 5.91859300 | -1.78073700 |
| H | 2.23414200 | 6.06951600 | -2.68046700 |
| C | 1.71396700 | 3.72128600 | -0.26302600 |
| C | 0.61565300 | 2.80759500 | 0.26189300 |
| O | -0.52420200 | 2.97280700 | -0.26105200 |
| O | 0.92152500 | 1.95833200 | 1.14401400 |
| C | -4.27581300 | 3.56347400 | 0.41764900 |
| C | -3.83660000 | 2.78766400 | -0.83192600 |
| C | -2.98737000 | 1.58202900 | -0.48875400 |
| C | -2.10959000 | 1.66268900 | 0.66386800 |
| C | -2.35880300 | 2.62956600 | 1.78593200 |
| C | -3.07083400 | 3.90112900 | 1.30574600 |
| H | -4.70497400 | 2.46890500 | -1.41939800 |
| H | -3.21975200 | 3.43252700 | -1.47165200 |
| H | -4.79396700 | 4.48073000 | 0.11349400 |
| H | -4.99587000 | 2.95875600 | 0.98272900 |
| H | -2.97007300 | 2.11713000 | 2.53863900 |
| H | -1.39451300 | 2.85499900 | 2.24732700 |
| H | -3.38725400 | 4.49475800 | 2.17171900 |
| H | -2.35390500 | 4.50149200 | 0.73493600 |
| H | -2.58918700 | 1.05406100 | -1.35323500 |
| O | -3.57490000 | 0.69863600 | 0.49182200 |
| H | -1.31006300 | 0.94932000 | 0.74664100 |
| H | 0.42701000 | 4.64043600 | -1.69483900 |
| P | 2.26107400 | -1.63146700 | 0.19524700 |
| C | 1.60750400 | -0.48154100 | -1.02105800 |
| C | 2.39017500 | 0.59162800 | -1.46567100 |
| C | 0.34432900 | -0.71897700 | -1.58699300 |
| C | 1.90270400 | 1.43446100 | -2.46145300 |
| H | 3.35557300 | 0.79339200 | -1.01678700 |
| C | -0.13659400 | 0.13533900 | -2.57418000 |
| H | -0.27053500 | -1.55039100 | -1.26153600 |
| C | 0.63766900 | 1.21429100 | -3.00433400 |

| | | | |
|---|---|---|---|
| H | 2.49519800 | 2.28499200 | -2.77840700 |
| H | -1.12182600 | -0.04036600 | -2.99378600 |
| H | 0.24854400 | 1.89258300 | -3.75706900 |
| C | 2.82331500 | -3.11061000 | -0.69343800 |
| C | 3.10724400 | -4.29541700 | 0.00463000 |
| C | 2.98995500 | -3.06638300 | -2.08447100 |
| C | 3.55198700 | -5.42090200 | -0.68474800 |
| H | 2.99011300 | -4.34256900 | 1.08275500 |
| C | 3.43394500 | -4.19750000 | -2.76800800 |
| H | 2.76545400 | -2.15506100 | -2.62775700 |
| C | 3.71392100 | -5.37297300 | -2.07115700 |
| H | 3.76737000 | -6.33527800 | -0.14061700 |
| H | 3.55636900 | -4.15943100 | -3.84600500 |
| H | 4.05579000 | -6.25342000 | -2.60690000 |
| C | 3.65913100 | -0.90177400 | 1.07311000 |
| C | 3.47680700 | 0.33363600 | 1.71935300 |
| C | 4.88887600 | -1.57275300 | 1.14654100 |
| C | 4.53584600 | 0.87517400 | 2.44682200 |
| H | 2.54015700 | 0.88684000 | 1.62503200 |
| C | 5.93591900 | -1.01471900 | 1.87743000 |
| H | 5.03107100 | -2.51757400 | 0.63370300 |
| C | 5.75812700 | 0.20595000 | 2.53072000 |
| H | 4.40056300 | 1.82986000 | 2.94625700 |
| H | 6.88914400 | -1.53170800 | 1.93234200 |
| H | 6.57554800 | 0.63849100 | 3.10045600 |

**3** (in Figure 8) product

| | | | |
|---|---|---|---|
| C | 1.15873100 | -2.08348300 | 1.43361100 |
| H | 1.60202500 | -2.96705400 | 1.90714200 |
| H | 0.31050200 | -2.43337400 | 0.83851100 |
| C | -1.99990800 | -1.50002200 | 1.05871400 |
| H | -1.75566100 | -2.55547300 | 0.85586600 |
| H | -1.21105000 | -0.90938800 | 0.56609000 |
| C | -0.56279100 | -1.63447300 | 3.23619600 |
| H | -0.47173700 | -2.72863100 | 3.31497200 |
| H | -0.55089900 | -1.25749100 | 4.26755300 |
| C | -1.90560300 | -1.26845700 | 2.56955900 |
| H | -2.12301600 | -0.21413100 | 2.78303900 |
| H | -2.69847600 | -1.83443200 | 3.07485500 |
| C | 0.68286100 | -1.08644100 | 2.50438500 |
| H | 0.45189500 | -0.11576800 | 2.05572900 |
| H | 1.50491500 | -0.91858000 | 3.20967600 |
| C | -4.72134700 | -1.85068200 | 1.02311700 |
| C | -4.26215800 | -3.94656700 | -0.46156800 |

| | | | |
|---|---|---|---|
| C | -4.52978200 | -3.38076900 | 0.95063900 |
| C | -3.29199100 | -3.11470400 | -1.32961000 |
| C | -3.47551900 | -1.58343500 | -1.23563700 |
| C | -6.02095400 | -1.34676600 | 0.36225900 |
| C | -6.07667900 | -1.50205000 | -1.17116300 |
| C | -4.77974300 | -1.09510600 | -1.90119400 |
| B | -3.43845100 | -1.10064200 | 0.34433800 |
| H | -4.80128300 | -1.59327200 | 2.09319600 |
| H | -3.87423600 | -4.97289300 | -0.37315000 |
| H | -5.21384200 | -4.04695000 | -0.99228100 |
| H | -3.68004900 | -3.64622700 | 1.59732200 |
| H | -5.39976100 | -3.91228100 | 1.37223200 |
| H | -3.38296300 | -3.45936900 | -2.37444900 |
| H | -2.26156400 | -3.35924100 | -1.02964300 |
| H | -2.64706600 | -1.14663000 | -1.82857100 |
| H | -6.90885800 | -1.84041300 | 0.79373300 |
| H | -6.10857400 | -0.27985700 | 0.60157300 |
| H | -6.32774400 | -2.53696200 | -1.42698300 |
| H | -6.90953000 | -0.89965000 | -1.56402800 |
| H | -4.74443300 | 0.00021000 | -1.94109900 |
| H | -4.84475300 | -1.43802500 | -2.94893800 |
| C | 0.52100300 | 4.53207300 | -1.33777600 |
| C | 2.46062000 | 3.96325300 | -0.00411200 |
| C | 3.24920300 | 4.79938700 | -0.78995400 |
| C | 2.67621300 | 5.49979600 | -1.85504500 |
| C | 1.31118100 | 5.36906300 | -2.12304200 |
| H | 2.88892900 | 3.40372900 | 0.81984900 |
| H | 4.30850900 | 4.90719000 | -0.57438800 |
| H | 3.29075000 | 6.15109500 | -2.47029300 |
| H | 0.86340600 | 5.91959900 | -2.94535700 |
| C | 1.09688200 | 3.81731000 | -0.28099100 |
| C | 0.30344800 | 2.84857800 | 0.53092000 |
| O | -0.97075900 | 2.81018600 | 0.16845000 |
| O | 0.80223000 | 2.16363600 | 1.41778500 |
| C | -4.47595300 | 3.21859300 | 0.37008200 |
| C | -3.73228400 | 2.46186300 | -0.73711400 |
| C | -2.87381200 | 1.32639400 | -0.14946000 |
| C | -1.88756600 | 1.90313400 | 0.88525400 |
| C | -2.59822700 | 2.68957600 | 1.97994700 |
| C | -3.49413500 | 3.79334400 | 1.40121800 |
| H | -4.44332300 | 2.02733200 | -1.44660600 |
| H | -3.08934600 | 3.15671800 | -1.29743800 |
| H | -5.08852300 | 4.02213300 | -0.05855400 |
| H | -5.15537600 | 2.51637100 | 0.86600500 |

| | | | |
|---|---|---|---|
| H | -3.21448200 | 1.96281000 | 2.52004500 |
| H | -1.86147800 | 3.09533100 | 2.68437900 |
| H | -4.03634900 | 4.29296900 | 2.21384100 |
| H | -2.86531500 | 4.55811000 | 0.92371100 |
| H | -2.27880500 | 0.87234900 | -0.95745600 |
| O | -3.68204000 | 0.39742600 | 0.49501700 |
| H | -1.28215800 | 1.10731800 | 1.30651400 |
| H | -0.53630000 | 4.41226300 | -1.54254900 |
| P | 2.38993300 | -1.46549600 | 0.23948000 |
| C | 1.66191800 | -0.33944900 | -0.96168400 |
| C | 2.39300200 | 0.76935100 | -1.41437900 |
| C | 0.41222700 | -0.64051000 | -1.52712900 |
| C | 1.86752200 | 1.58055200 | -2.41665900 |
| H | 3.35301700 | 1.01119700 | -0.97321400 |
| C | -0.10704200 | 0.18334000 | -2.52316100 |
| H | -0.17037000 | -1.49156400 | -1.19469500 |
| C | 0.61773100 | 1.29108700 | -2.96511000 |
| H | 2.41934700 | 2.45619800 | -2.74142700 |
| H | -1.08561200 | -0.04174500 | -2.93337200 |
| H | 0.20124400 | 1.93958800 | -3.72965100 |
| C | 3.03327700 | -2.89618100 | -0.67013100 |
| C | 3.41135900 | -4.05970900 | 0.01943900 |
| C | 3.15961900 | -2.84086500 | -2.06497000 |
| C | 3.91055300 | -5.15354300 | -0.68316000 |
| H | 3.32189900 | -4.11544400 | 1.09992700 |
| C | 3.65737700 | -3.94128900 | -2.76132000 |
| H | 2.86079700 | -1.94742800 | -2.60188800 |
| C | 4.03177300 | -5.09553300 | -2.07340700 |
| H | 4.19770500 | -6.05243200 | -0.14656800 |
| H | 3.74619400 | -3.89676600 | -3.84229800 |
| H | 4.41421300 | -5.95262800 | -2.61937700 |
| C | 3.75895600 | -0.64207000 | 1.08630000 |
| C | 3.51266100 | 0.57100600 | 1.75315800 |
| C | 5.04255300 | -1.20568300 | 1.09417300 |
| C | 4.55535900 | 1.20076700 | 2.42954500 |
| H | 2.53165700 | 1.03562500 | 1.72653400 |
| C | 6.07574400 | -0.56395400 | 1.77582000 |
| H | 5.23664500 | -2.13383200 | 0.56818000 |
| C | 5.83274700 | 0.63610700 | 2.44483800 |
| H | 4.36387500 | 2.13641000 | 2.94631000 |
| H | 7.06949800 | -1.00122900 | 1.77989600 |
| H | 6.63959300 | 1.13327400 | 2.97529500 |

**R3** (in Figure 8) reactant

| | | | |
|---|---|---|---|
| N | -3.41526200 | -2.62088100 | 0.82415400 |
| C | -2.26854700 | -2.69309700 | -0.18745200 |
| H | -1.93396100 | -1.65569700 | -0.29437400 |
| H | -2.72437400 | -3.01029900 | -1.12845500 |
| C | 1.37234100 | -1.81294200 | 0.13851800 |
| H | 1.67013600 | -2.69294500 | 0.72859500 |
| H | 0.63405400 | -1.30027600 | 0.77488100 |
| C | -0.07349100 | -3.66399700 | -0.92694100 |
| H | 0.65968500 | -4.43757900 | -0.66398000 |
| H | -0.54310600 | -3.98968500 | -1.86709800 |
| C | 0.67489300 | -2.33614500 | -1.13426200 |
| H | -0.01789600 | -1.58584600 | -1.53741700 |
| H | 1.41241700 | -2.50571200 | -1.92664600 |
| C | -4.39879400 | -1.54498000 | 0.36145300 |
| H | -5.05616900 | -1.35853800 | 1.21599400 |
| H | -3.77445700 | -0.66558900 | 0.17921800 |
| C | -1.13498100 | -3.63699700 | 0.18668500 |
| H | -1.50761600 | -4.65688800 | 0.34611200 |
| H | -0.65362400 | -3.30992700 | 1.11207400 |
| C | -2.87821400 | -2.18905700 | 2.16497300 |
| H | -3.72774100 | -2.05899500 | 2.83842300 |
| H | -2.32436300 | -1.24599800 | 2.03736800 |
| H | -2.22708900 | -2.97350600 | 2.54853200 |
| C | -4.10314500 | -3.93810600 | 0.96756900 |
| H | -4.40655100 | -4.29909200 | -0.01463700 |
| H | -4.98055400 | -3.80602300 | 1.60367900 |
| H | -3.42043400 | -4.65118500 | 1.42730700 |
| C | -5.23489900 | -1.89404300 | -0.86705200 |
| H | -5.95982700 | -2.68041400 | -0.62521100 |
| H | -4.60423600 | -2.27271200 | -1.67950700 |
| C | -5.97983500 | -0.64179700 | -1.37071600 |
| H | -6.80434100 | -0.96851900 | -2.01596600 |
| H | -6.44756400 | -0.13327400 | -0.51594700 |
| C | -5.08059100 | 0.33452800 | -2.13697200 |
| H | -5.64104300 | 1.23238100 | -2.41969700 |
| H | -4.71146600 | -0.13068300 | -3.05945000 |
| H | -4.20645900 | 0.64123000 | -1.55365200 |
| C | 3.69847700 | -1.27297800 | -1.27249300 |
| C | 4.95373700 | -2.91431900 | 0.32062000 |
| C | 4.23653100 | -2.70578500 | -1.03028900 |
| C | 4.24712900 | -2.27530000 | 1.53633800 |
| C | 3.67300300 | -0.85695700 | 1.29025700 |
| C | 4.80843200 | -0.21165800 | -1.43476200 |
| C | 5.62297500 | 0.09591000 | -0.16078400 |

| | | | |
|---|---|---|---|
| C | 4.78262700 | 0.20689700 | 1.12856000 |
| B | 2.73124900 | -0.93232800 | -0.02505500 |
| H | 3.15320200 | -1.30018200 | -2.23018100 |
| H | 5.06921500 | -3.99248800 | 0.50070700 |
| H | 5.97286300 | -2.52436500 | 0.24903700 |
| H | 3.38813000 | -3.40313100 | -1.08517800 |
| H | 4.92125300 | -3.00248800 | -1.84005800 |
| H | 4.95148300 | -2.25914800 | 2.38255800 |
| H | 3.42457400 | -2.93266800 | 1.84916200 |
| H | 3.09912500 | -0.59023100 | 2.19429500 |
| H | 5.50617500 | -0.50219600 | -2.23604600 |
| H | 4.33123000 | 0.71790700 | -1.77218300 |
| H | 6.39395600 | -0.66909900 | -0.02765300 |
| H | 6.17404200 | 1.03545900 | -0.30831900 |
| H | 4.31227000 | 1.19716700 | 1.14365100 |
| H | 5.46278300 | 0.18589900 | 1.99462600 |
| C | -2.15570700 | 3.21948400 | -0.57139700 |
| C | -1.51158000 | 3.27127000 | 1.75407600 |
| C | -1.50393100 | 4.66525000 | 1.72284000 |
| C | -1.82190500 | 5.34000700 | 0.54094400 |
| C | -2.15013600 | 4.61375200 | -0.60674100 |
| H | -1.27016800 | 2.72215900 | 2.65818500 |
| H | -1.25113000 | 5.22792500 | 2.61789900 |
| H | -1.81426200 | 6.42650600 | 0.51491900 |
| H | -2.39947000 | 5.13554900 | -1.52719700 |
| C | -1.83197400 | 2.53741600 | 0.60698400 |
| C | -1.82773400 | 1.01838400 | 0.64559300 |
| O | -1.47022500 | 0.47052900 | 1.72149100 |
| O | -2.17705100 | 0.42198300 | -0.42148100 |
| C | 1.73638800 | 3.88289500 | -0.14871900 |
| C | 1.88764500 | 2.82924300 | 0.96102400 |
| C | 1.37303200 | 1.46341000 | 0.56179600 |
| C | 1.00715100 | 1.15476800 | -0.82963100 |
| C | 1.13465700 | 2.18795200 | -1.91586600 |
| C | 2.09268300 | 3.32377900 | -1.53167300 |
| H | 2.93828900 | 2.72393800 | 1.25402800 |
| H | 1.33987100 | 3.14795600 | 1.85288900 |
| H | 0.69950000 | 4.23656400 | -0.16519100 |
| H | 2.36384200 | 4.75016300 | 0.08722600 |
| H | 1.44934700 | 1.69681900 | -2.84481400 |
| H | 0.12769500 | 2.58917000 | -2.08496600 |
| H | 3.12463400 | 2.95185200 | -1.53402800 |
| H | 2.03505800 | 4.11594300 | -2.28679100 |
| H | 0.91830200 | 0.84959600 | 1.33153000 |

| | | | |
|---|---|---|---|
| O | 2.29272300 | 0.68960000 | -0.29776100 |
| H | 0.29158900 | 0.35745800 | -0.98566400 |
| H | -2.40721800 | 2.63391100 | -1.44925700 |

**R3** (in Figure 8) TS（N）

| | | | |
|---|---|---|---|
| N | -2.33232400 | -2.80572500 | -0.16191500 |
| C | -1.06488100 | -3.20550400 | -0.92382900 |
| H | -1.19711600 | -4.26054500 | -1.18253700 |
| H | -0.24959300 | -3.13285600 | -0.20436600 |
| C | 1.81043800 | -1.40615100 | -0.64005700 |
| H | 2.12983800 | -2.37619400 | -0.23089900 |
| H | 0.81812200 | -1.22757000 | -0.19180800 |
| C | 0.68139500 | -2.61984000 | -2.65435800 |
| H | 1.02175600 | -3.61925200 | -2.34225300 |
| H | 0.68517300 | -2.63341500 | -3.75107500 |
| C | 1.67489600 | -1.55601900 | -2.16042000 |
| H | 1.39216900 | -0.59327300 | -2.60720400 |
| H | 2.66101200 | -1.79138900 | -2.57875600 |
| C | -2.09755200 | -1.55311700 | 0.68144100 |
| H | -1.69104400 | -0.82261400 | -0.01175500 |
| H | -3.09491600 | -1.20782000 | 0.96476900 |
| C | -0.77211200 | -2.38833600 | -2.17982700 |
| H | -0.94892400 | -1.32074100 | -2.01535700 |
| H | -1.47290900 | -2.69034200 | -2.96523300 |
| C | -2.74667100 | -3.95037000 | 0.70525800 |
| H | -1.89611700 | -4.27835400 | 1.30164600 |
| H | -3.08770200 | -4.76609800 | 0.06593000 |
| H | -3.55754900 | -3.62461400 | 1.35909300 |
| C | -3.45019900 | -2.48487100 | -1.11965500 |
| H | -3.54626800 | -3.30546700 | -1.83268100 |
| H | -3.21852400 | -1.53687800 | -1.61340300 |
| H | -4.36842800 | -2.37723700 | -0.54031200 |
| C | -1.21629600 | -1.69063600 | 1.91300900 |
| H | -0.19018000 | -1.95807600 | 1.63812400 |
| H | -1.58996400 | -2.46190800 | 2.59729900 |
| C | -1.20770100 | -0.33736300 | 2.64693700 |
| H | -0.90557000 | 0.44871600 | 1.94580000 |
| H | -2.23478300 | -0.08943400 | 2.94631500 |
| C | -0.29407500 | -0.34650900 | 3.87243800 |
| H | 0.74302900 | -0.55742000 | 3.59069200 |
| H | -0.60925600 | -1.10720300 | 4.59727100 |
| H | -0.31141100 | 0.62456800 | 4.37789500 |
| C | 4.29259600 | -0.23972700 | -0.85648200 |
| C | 5.08978500 | -1.92372500 | 0.96788100 |

| | | | |
|---|---|---|---|
| C | 4.98031300 | -1.58633800 | -0.53474400 |
| C | 3.82758600 | -1.61182000 | 1.80145200 |
| C | 3.13380400 | -0.26886300 | 1.46486000 |
| C | 5.10647300 | 1.00030500 | -0.42648700 |
| C | 5.26026900 | 1.19276700 | 1.09579400 |
| C | 3.96934100 | 0.95201500 | 1.90744200 |
| B | 2.83644000 | -0.23292800 | -0.13720000 |
| H | 4.20016000 | -0.18425300 | -1.95326600 |
| H | 5.33715700 | -2.98920200 | 1.08048100 |
| H | 5.94089700 | -1.38612200 | 1.39516900 |
| H | 4.41050100 | -2.38602300 | -1.03018400 |
| H | 5.99015400 | -1.62507600 | -0.97360700 |
| H | 4.09846000 | -1.64580800 | 2.86907300 |
| H | 3.10076000 | -2.42321500 | 1.65525800 |
| H | 2.20468600 | -0.25134500 | 2.06305800 |
| H | 6.11098700 | 0.98726600 | -0.87954900 |
| H | 4.59690300 | 1.88183700 | -0.83627900 |
| H | 6.05032000 | 0.53382600 | 1.46879100 |
| H | 5.61933900 | 2.21278700 | 1.29399200 |
| H | 3.34165500 | 1.84737200 | 1.82531700 |
| H | 4.23353200 | 0.87401900 | 2.97461900 |
| C | -4.04116000 | 1.87003000 | 1.11835500 |
| C | -5.00146800 | 0.75172900 | -0.79455500 |
| C | -6.24744500 | 0.74516100 | -0.16829400 |
| C | -6.38865700 | 1.28850100 | 1.11142400 |
| C | -5.28312100 | 1.85260500 | 1.75272800 |
| H | -4.87022400 | 0.33792800 | -1.78907900 |
| H | -7.11032100 | 0.32295100 | -0.67739500 |
| H | -7.35786300 | 1.27958800 | 1.60308400 |
| H | -5.39205700 | 2.28339500 | 2.74466300 |
| C | -3.88801600 | 1.30845200 | -0.15456700 |
| C | -2.51501000 | 1.24124900 | -0.79970400 |
| O | -1.60780400 | 1.94261600 | -0.26070900 |
| O | -2.36590900 | 0.43802000 | -1.76302500 |
| C | 1.60909600 | 4.07759800 | -0.86868200 |
| C | 1.38366200 | 3.32045300 | 0.44673900 |
| C | 1.17697400 | 1.83448700 | 0.22503400 |
| C | 0.45972900 | 1.42984500 | -0.97422000 |
| C | 0.41317000 | 2.28778100 | -2.20217900 |
| C | 0.48305000 | 3.78329000 | -1.86831000 |
| H | 2.22175000 | 3.47418300 | 1.13432300 |
| H | 0.47633100 | 3.69307700 | 0.94022300 |
| H | 1.66697700 | 5.15339100 | -0.66568300 |
| H | 2.57385200 | 3.77668200 | -1.29530600 |

| | | | |
|---|---|---|---|
| H | 1.26085900 | 1.99990200 | -2.83635800 |
| H | -0.50117300 | 2.03184800 | -2.74290700 |
| H | 0.62510900 | 4.35886600 | -2.79043300 |
| H | -0.47713800 | 4.08602400 | -1.43480100 |
| H | 0.93884700 | 1.28609000 | 1.13612500 |
| O | 2.20200800 | 1.19449900 | -0.55658600 |
| H | 0.08762100 | 0.42450900 | -1.03158600 |
| H | -3.17050000 | 2.31209100 | 1.59047900 |

**R3** (in Figure 8) product

| | | | |
|---|---|---|---|
| N | 1.09042900 | 2.74685500 | 1.24660600 |
| C | 0.60390700 | 2.60801600 | -0.19166700 |
| H | 0.96074800 | 1.62874500 | -0.50046200 |
| H | 1.13128100 | 3.37319800 | -0.76508300 |
| C | -0.63546900 | -0.10908100 | -1.71745700 |
| H | -1.27746800 | -0.75364200 | -2.33382400 |
| H | -1.25506300 | 0.10199900 | -0.84328700 |
| C | -1.20824400 | 2.42505400 | -1.90628500 |
| H | -2.28974000 | 2.26212700 | -1.98819900 |
| H | -0.97886300 | 3.32818200 | -2.49107000 |
| C | -0.44192300 | 1.22206900 | -2.49099100 |
| H | 0.61822100 | 1.49770100 | -2.55040300 |
| H | -0.75314000 | 1.11344700 | -3.53809600 |
| C | 2.57254700 | 2.39242500 | 1.29177300 |
| H | 2.86912500 | 2.50491600 | 2.33960400 |
| H | 2.61343700 | 1.33272200 | 1.03218700 |
| C | -0.89695300 | 2.70131900 | -0.41683000 |
| H | -1.28931000 | 3.68750600 | -0.13735000 |
| H | -1.40951200 | 1.96499900 | 0.19952500 |
| C | 0.38792400 | 1.73838600 | 2.11730700 |
| H | 0.86892300 | 1.74932600 | 3.09786900 |
| H | 0.49172500 | 0.76262600 | 1.62528500 |
| H | -0.66462100 | 1.99526100 | 2.21251500 |
| C | 0.84180200 | 4.12191800 | 1.76944900 |
| H | 1.31598000 | 4.85520900 | 1.11767000 |
| H | 1.25164200 | 4.19478100 | 2.77854100 |
| H | -0.23347200 | 4.29261800 | 1.79513800 |
| C | 3.48700500 | 3.21436300 | 0.38981000 |
| H | 3.32212400 | 4.28698500 | 0.54732000 |
| H | 3.27184300 | 2.99754100 | -0.66138500 |
| C | 4.96698400 | 2.89492300 | 0.66879900 |
| H | 5.57477600 | 3.59050000 | 0.07802000 |
| H | 5.19289900 | 3.11032200 | 1.72268500 |
| C | 5.36488100 | 1.45645300 | 0.32763400 |

| | | | |
|---|---|---|---|
| H | 6.43933600 | 1.30720800 | 0.47625800 |
| H | 5.13146400 | 1.22114000 | -0.71611400 |
| H | 4.84157400 | 0.72076800 | 0.94618000 |
| C | 2.16999900 | -0.49367600 | -1.52857800 |
| C | 2.02085600 | -1.91165700 | -3.72633400 |
| C | 2.39066300 | -0.57032200 | -3.06051900 |
| C | 0.71619300 | -2.52740300 | -3.19543000 |
| C | 0.60946700 | -2.54333800 | -1.65405800 |
| C | 3.20151600 | -1.32438400 | -0.73768400 |
| C | 3.12959900 | -2.84540100 | -0.98104200 |
| C | 1.70298200 | -3.44274600 | -1.02689500 |
| B | 0.65045600 | -0.98969300 | -1.11234400 |
| H | 2.37298200 | 0.56303600 | -1.25931400 |
| H | 1.93771400 | -1.75877100 | -4.81221500 |
| H | 2.83624800 | -2.62969300 | -3.59811100 |
| H | 1.78617700 | 0.21072300 | -3.53656600 |
| H | 3.43792000 | -0.32984900 | -3.31210600 |
| H | 0.62173900 | -3.54797300 | -3.60092400 |
| H | -0.13110600 | -1.96096300 | -3.60435100 |
| H | -0.36195200 | -3.01880900 | -1.42714800 |
| H | 4.23111100 | -0.99812700 | -0.95973800 |
| H | 3.03493900 | -1.12783200 | 0.32987200 |
| H | 3.65170600 | -3.07287200 | -1.91548800 |
| H | 3.70881000 | -3.36009700 | -0.19985400 |
| H | 1.40771000 | -3.69522700 | -0.00306600 |
| H | 1.75275400 | -4.40941500 | -1.55501100 |
| C | -4.55493500 | 1.54287200 | 0.09539500 |
| C | -4.02549800 | -0.57614400 | -0.95865100 |
| C | -4.89683200 | -0.26891700 | -2.00048600 |
| C | -5.59386900 | 0.94134400 | -1.99878400 |
| C | -5.42374800 | 1.84744200 | -0.94875500 |
| H | -3.46011900 | -1.49953400 | -0.96243100 |
| H | -5.02389700 | -0.96935500 | -2.82048500 |
| H | -6.26791600 | 1.17994600 | -2.81688300 |
| H | -5.96647900 | 2.78841100 | -0.94698700 |
| C | -3.85167600 | 0.33229500 | 0.09272200 |
| C | -2.88949700 | 0.08174000 | 1.19976100 |
| O | -2.27793500 | -1.10153900 | 1.08793900 |
| O | -2.67271000 | 0.89287100 | 2.09216700 |
| C | 0.56522000 | -3.43566600 | 3.22942200 |
| C | 1.07122100 | -2.31661800 | 2.31332500 |
| C | 0.02593700 | -1.87381900 | 1.26745500 |
| C | -1.23551000 | -1.44168600 | 2.03866700 |
| C | -1.77948000 | -2.55256200 | 2.93672000 |

| | | | |
|---|---|---|---|
| C | -0.72234200 | -3.01428600 | 3.94654100 |
| H | 1.34599200 | -1.43751000 | 2.91688500 |
| H | 1.97641100 | -2.62369600 | 1.78298700 |
| H | 0.36736900 | -4.33282900 | 2.62582900 |
| H | 1.33630100 | -3.71287500 | 3.95918900 |
| H | -2.68101600 | -2.19318500 | 3.44711100 |
| H | -2.08253600 | -3.39567500 | 2.30189200 |
| H | -0.49783900 | -2.18961700 | 4.63891400 |
| H | -1.11968200 | -3.83567900 | 4.55488700 |
| H | -0.26826600 | -2.74865500 | 0.67338900 |
| O | 0.55314500 | -0.86823800 | 0.45349300 |
| H | -1.03154000 | -0.55216800 | 2.63721000 |
| H | -4.39908200 | 2.23034800 | 0.91968700 |

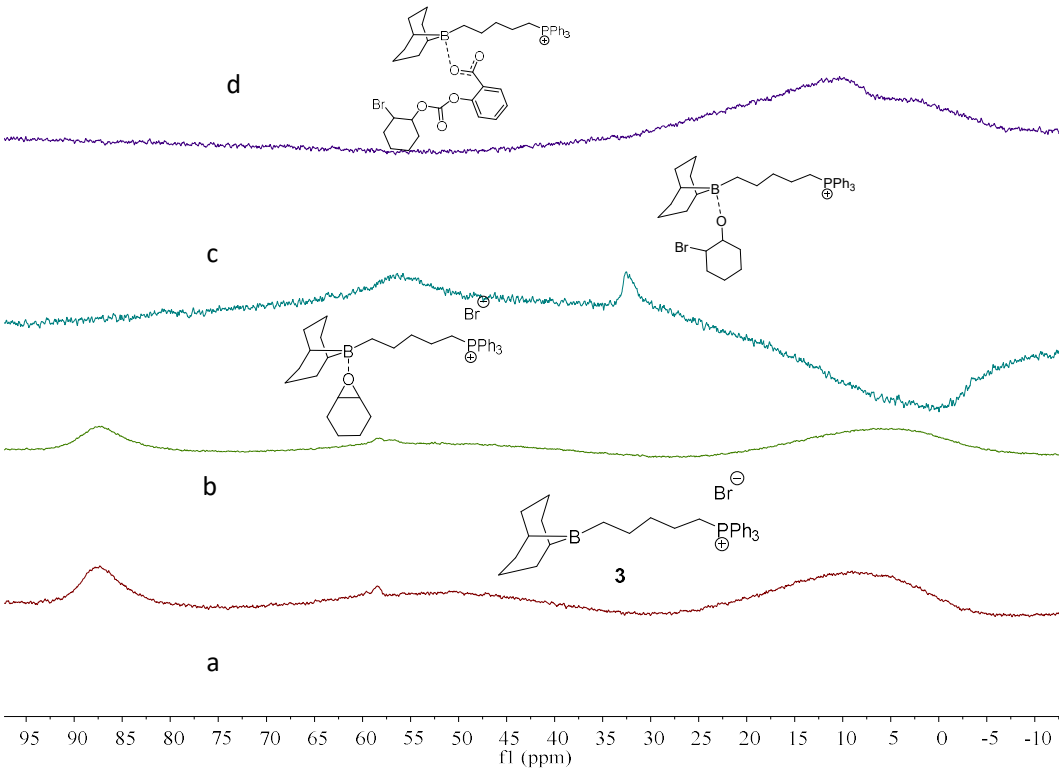



Figure S75. $^{11}B\{^{1}H\}$ NMR spectra of key intermediates for **3**-mediated ROAC of CHO and PA. a-d donated bottom to upper spectra. (a) **3** in $CDCl_3$, (b) **3**/CHO (1/2 molar ratio) in $CDCl_3$, (c) **3**/CHO (1/2 molar ratio) in THF–$d_8$, and (d) **3**/CHO/PA (1/1/2 molar ratio) in THF–$d_8$, 128 MHz, 298 K, the signal of proposed species overlapped with the resonance generated from borosilicate glass.

## References

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2 Xie, R.; Zhang Y.-Y.; Yang G.-W.; Zhu X.-F.; Li B.; Wu G.-P. *Angew. Chem. Int. Ed.* **2021**, *60*, 19253-19262.