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Supporting Information:

Phosphonium Salt & ZnX_2-PPh_3 Integrated Hierarchical POPs: Tailorable Synthesis and Highly Efficient Cooperative Catalysis in CO_2 Utilization

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1. Supplementary figures

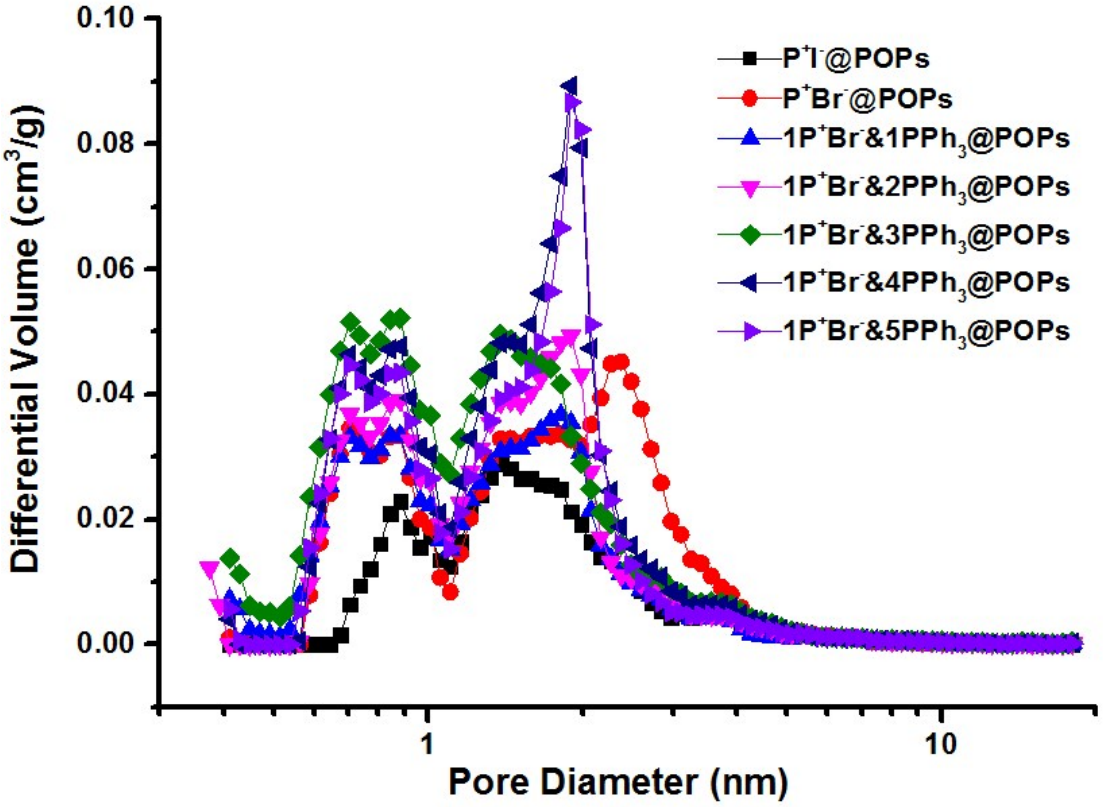


Figure S1. Pore sizes distributions of the afforded polymers.

Figure S1 showed the pore size distribution curves of the afforded porous organic polymers calculated from non-local density functional theory (NLDFT). The pore sizes were mainly distributed at 0.70, 0.85, 1.45, 2-18 nm respectively.

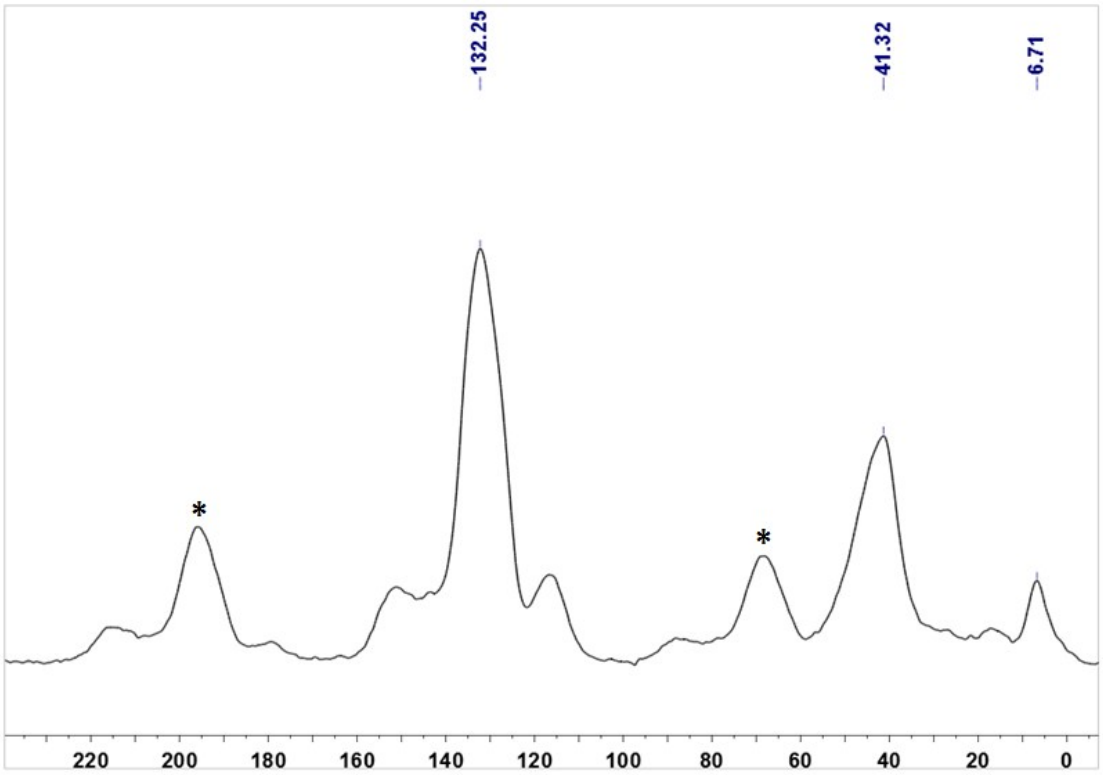


Figure S2. ^{13}C MAS NMR spectrum of $1P^{+}Br^{-}$&$1PPh_3$@POPs.

The peaks at * are side bands. Compared with the NMR spectra of the monomers $3vPPh_3$ and $3vP^{+}Br^{-}$ (see below NMR spectra), the additional peaks at 41.3 ppm was attributed to the polymerized vinyl groups. The signals ranged from 120 to 150 ppm could be attributed to the aromatic carbons.

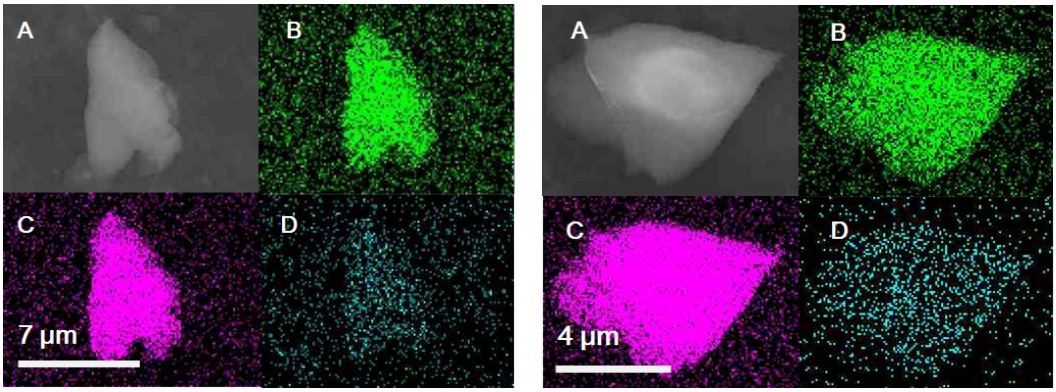


Figure S3. Elemental distribution in fresh $1P^{+}Br^{-}$&$ZnBr_2$-$1PPh_3$@POPs (left) and used $1P^{+}Br^{-}$ &$ZnBr_2$-$1PPh_3$@POPs (right) determined by SEM-EDS mapping, (A) SEM images, (B) Phosphorus, (C) Bromine and (D) Zinc.

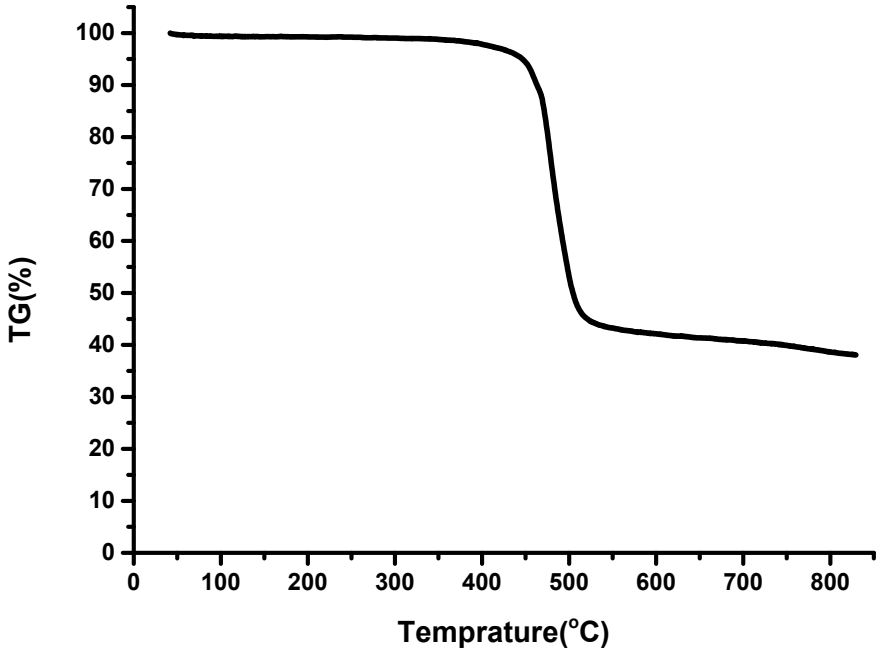


Figure S4. TG curve of the afforded $1P^{+}Br^{-}$&$1PPh_3$@POPs polymer.

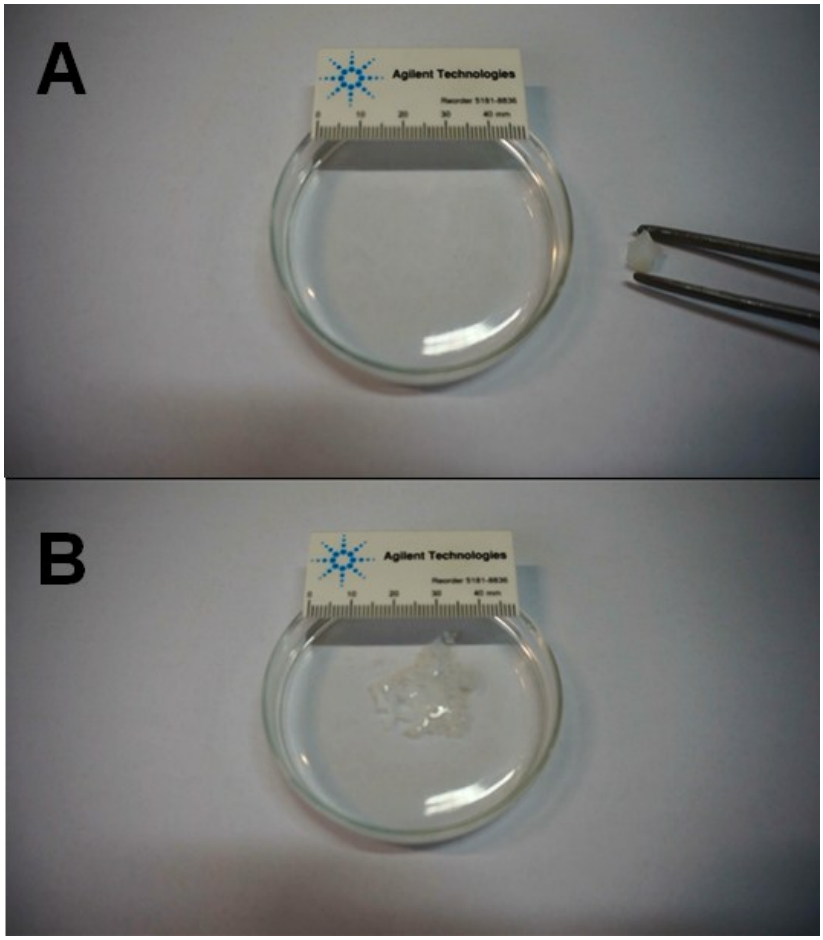


Figure S5. Photograph of the $1P^{+}Br^{-}$&$1PPh_3$@POPs in dry state (A) and in THF solution (B). The $1P^{+}Br^{-}$&$1PPh_3$@POPs could swell in other solution such as DMF, toluene, ethanol and propylene oxide as well, indicating the well-swelling property of the polymer.

The isosteric heats of adsorption (Q_{st}) of 1P$^+$Br$^-$&1PPh$_3$@POPs and P$^+$Br$^-$@POPs polymers were calculated according to Clausius-Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = Q_{\mathrm{st}} \ \mathrm{x} \ \frac{T_2 - T_1}{R \ x \ T_1 \ x \ T_2}$$

where Q_{st} is the isosteric heats of adsorption, T_i represents a temperature at which an isotherm i is measured, P_i represents a pressure at which a specific equilibrium adsorption amount is reached at T_i, R is gas constant (8.314 J K^{-1} mol^{-1}).

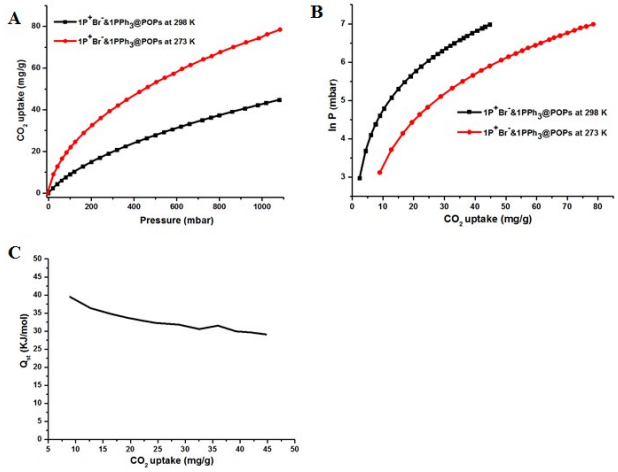


Figure S6. (A) The CO_2 isotherms of 1P$^+$Br$^-$&1PPh$_3$@POPs polymer at 298 K and 273 K; (B) The plots of lnP vs. CO_2 uptake of 1P$^+$Br$^-$&1PPh$_3$@POPs polymer at 298 K and 273 K calculated from the data in (A); (C) The plot of Q_{st} vs. CO_2 uptake calculated from the data in (B) based on Clausius-Clapeyron equation.

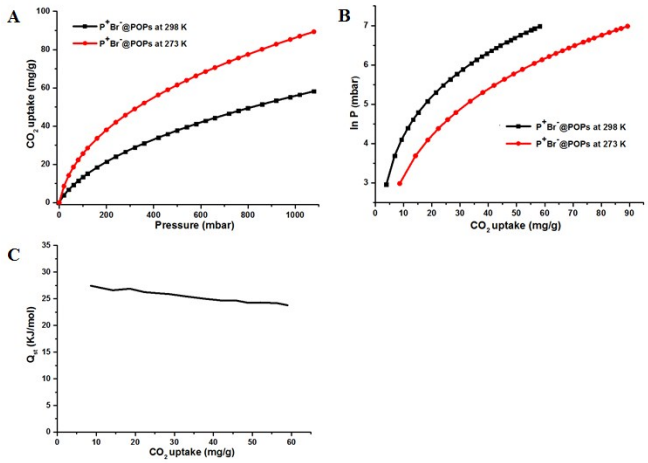


Figure S7. (A) The CO_2 isotherms of P$^+$Br$^-$@POPs polymer at 298 K and 273 K; (B) The plots of lnP vs. CO_2 uptake of P$^+$Br$^-$@POPs polymer at 298 K and 273 K calculated from the data in (A); (C) The plot of Q_{st} vs. CO_2 uptake calculated from the data in (B) based on Clausius-Clapeyron equation.

As shown in Figure S6 (C), the Q_{st} of prepared $1P^{+}Br^{-}\&1PPh_3$@POPs polymer decreased slowly from 40 KJ/mol to 30 KJ/mol with the increasing of CO_2 uptake form 10 mg/g to 45 mg/g. Comparatively, the Q_{st} of $P^{+}Br^{-}$@POPs decreased from 27 KJ/mol slowly to 23 KJ/mol with the increasing of CO_2 uptake form 10 mg/g to 60 mg/g (Figure 7 C). The Q_{st} data of hybrid $1P^{+}Br^{-}\&1PPh_3$@POPs polymer was higher than $P^{+}Br^{-}$@POPs under the same CO_2 uptake, showing the CO_2-philic properties of the extra doped PPh_3 units in the polymer.

To test the porosity texture of the POPs and loading catalytic pormoters, P^+Br^-&$ZnBr_2$-$1PPh_3$@POPs was chosen as a representative catalyst and the N_2 sorption isotherm of P^+Br^-&$ZnBr_2$-$1PPh_3$@POPs catalyst was attached below(Figure S8). The BET surface area was 458.2 m^2/g while the total pore volume was 0.435 cm^3/g. And the catalyst also showed the hierarchical pore size distribution. After loading Zn, the POPs maintained its microporosity.

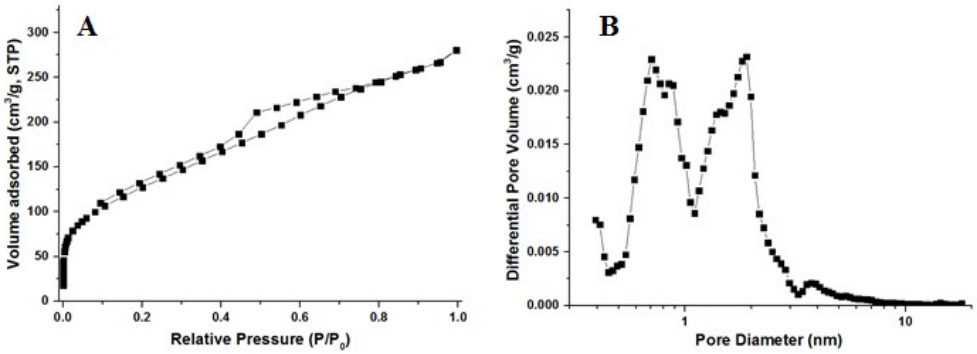
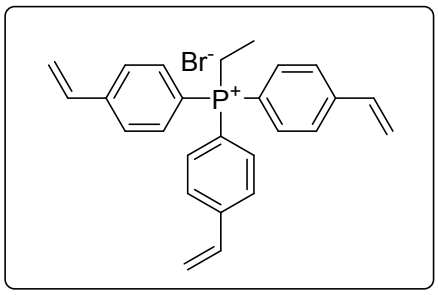
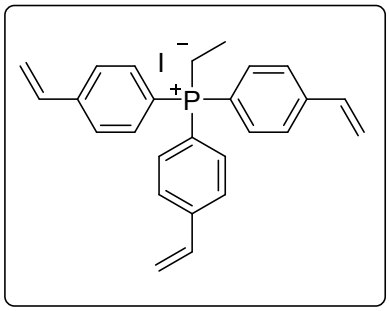


Figure S8. (A) Nitrogen sorption isotherm and (B) Pore sizes distribution of P^+Br^-&$ZnBr_2$-$1PPh_3$@POPs catalyst.

2. Analytical data for compounds $3vP^+Br^-$ and $3vP^+I^-$

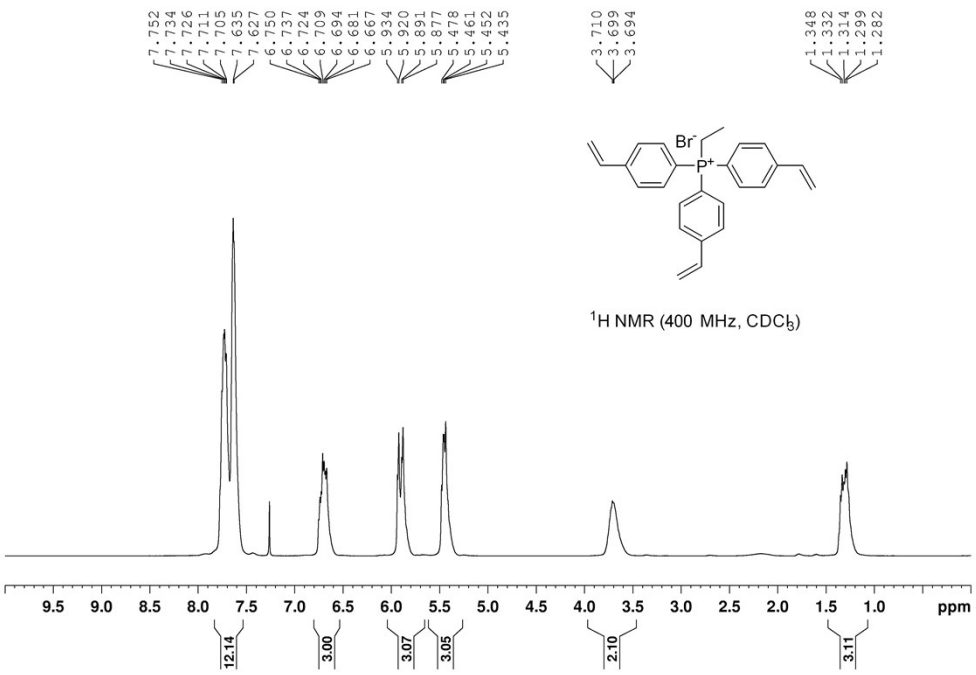


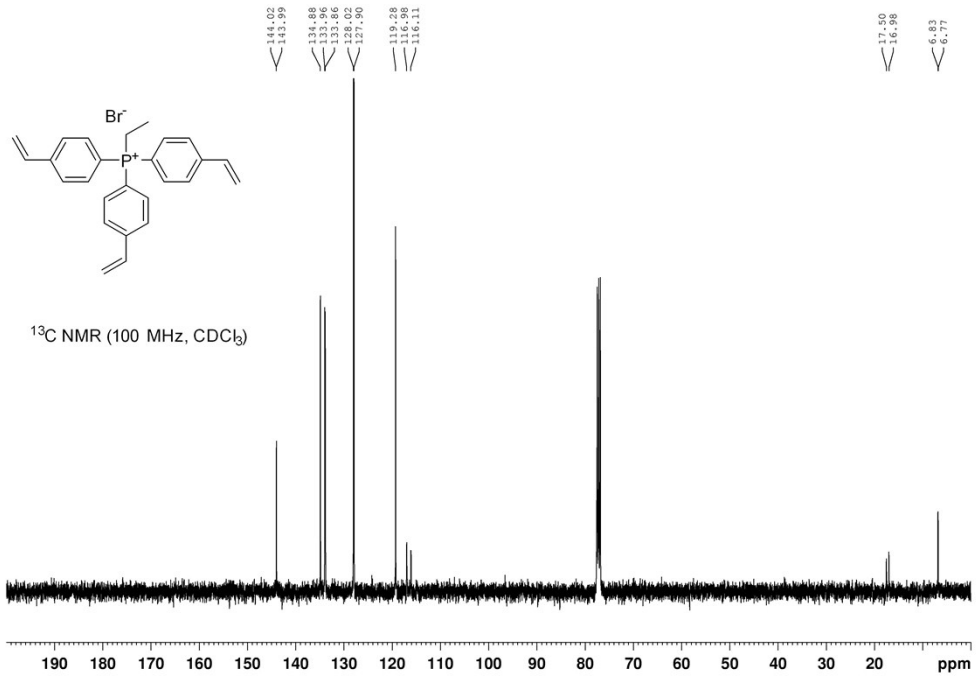
^{1}H NMR (400 MHz, $CDCl_3$) δ1.26-1.38(m, 3H), 3.58-3.78 (m, 2H), 5.35-5.50 (m, 3H), 5.81-5.96 (m, 3H), 6.60-6.78 (m, 3H), 7.54-7.98 (m, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 6.7, 6.8, 17.0, 17.5, 116.1, 117.0, 119.3, 127.9, 128.0, 133.8, 133.9, 134.9, 143.9,144.0; **^{31}P NMR** (161.8 MHz, $CDCl_3$) δ 25.3;

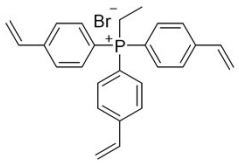


^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26-1.40(m, 3H), 3.54-3.68 (m, 2H), 5.48 (dd, 3H, J_1 = 10.7 Hz , J_2 = 3.0Hz), 5.93 (d, 3H, J = 17.0 Hz), 6.65-6.80 (m, 3H), 7.62-7.98 (m, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 6.7, 6.7, 17.3, 17.8, 115.8, 116.7, 119.3, 127.8, 128.0, 133.7, 133.8, 134.7, 143.9,144.0; **^{31}P NMR** (161.8 MHz, $CDCl_3$) δ 25.2;

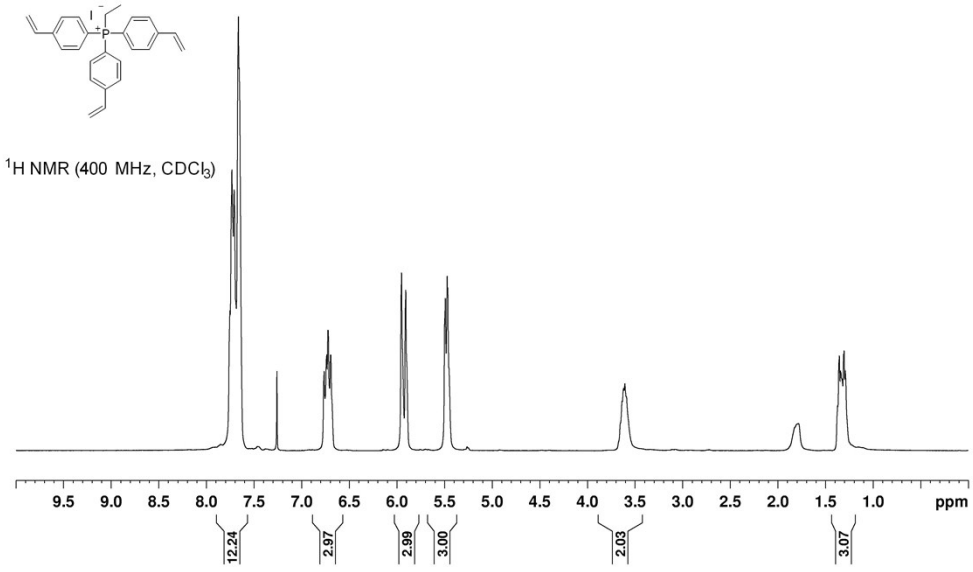
3. NMR spectra of $3vP^+Br^-$ and $3vP^+I^-$



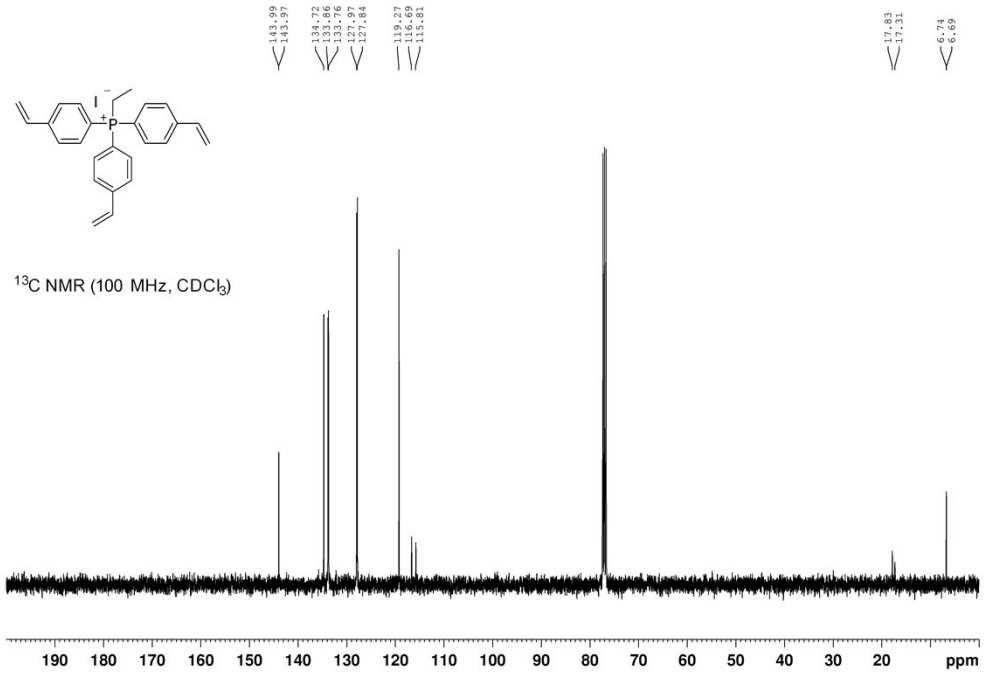




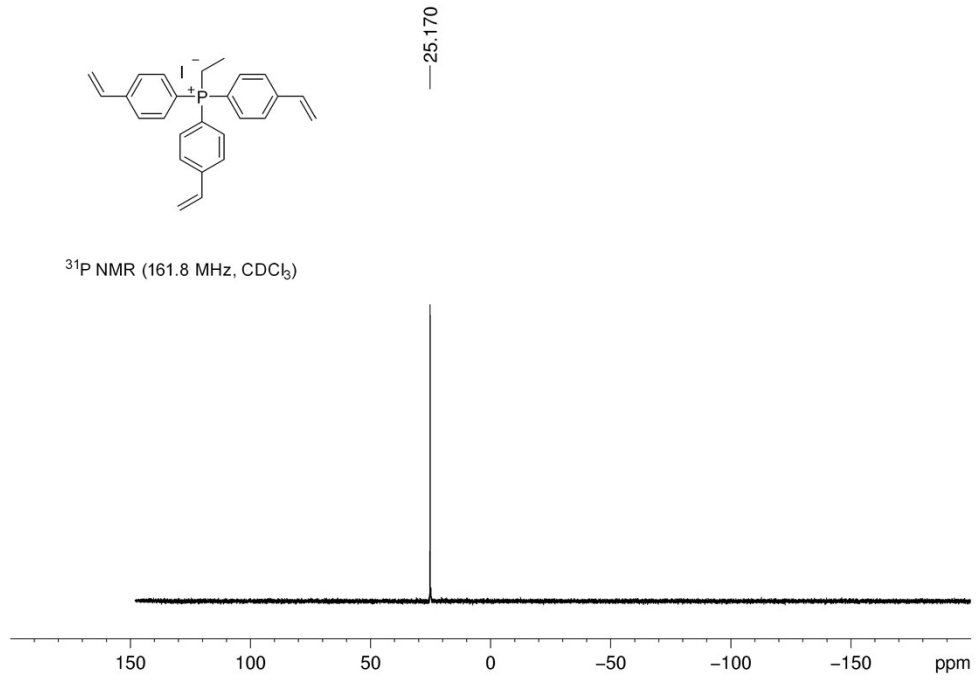
^{31}P NMR (161.8 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{31}P NMR (161.8 MHz, $CDCl_3$)