Supplementary Information (SI) for Catalysis Science & Technology.

Supporting Information for

Efficient synthesis of π-acidic phosphorus-containing porous polymer supported catalysts for hydroformylation of olefins

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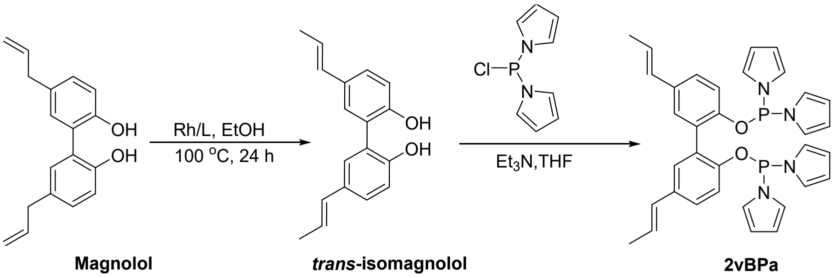
1. General methods

Unless otherwise noted, all manipulations involving air- or moisture-sensitive compounds were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Solvents were dried according to standard procedures. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on 500 MHz by using a Bruker Avance 500 spectrometer. Chemical shifts (δ values) were reported in ppm with internal TMS (^{1}H NMR), $CDCl_3$ (^{13}C NMR), or external 85% H_3PO_4 (^{31}P NMR) as the standard, respectively. ICP-MS were determined on Thermo iCAP Q. The FT-IR spectra were measured on a Thermo (SCIENTIFIC) NICOLET iS10 spectrometer. KBr pellet was used for FT-IR analysis of solid samples. The SEM and TEM spectra were obtained on a TESCAN MIRA LMS and JEOL JEM-2100Plus, respectively. N_2 sorption isotherms were obtained on a Micromeritics ASAP 2460. Thermogravimetric analysis was determined on Netzsch TG 209 F3. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi with the Al Kα radiation as X-ray source (*hv*=1486.6 eV). The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The 30 mL autoclave was used for the hydroformylation, and the autoclave was customized to Anhui Kemi Instrument Co., LTD.

2. Synthesis of catalysts

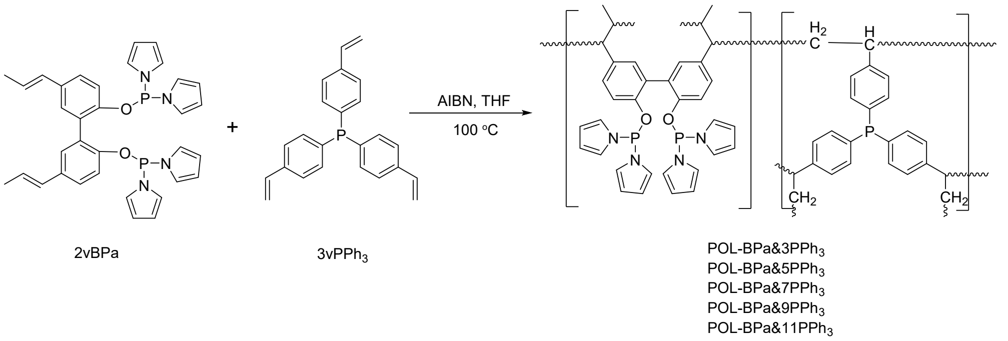
Synthesis of BPa.



Magnolol (5.3 g, 20 mmol), Rh(acac)(CO)₂ (5.0 mg, 0.02 mmol), and PPh_3 (15.7 mg, 0.06 mmol) were added to a Schlenk flask. After adding 2.0 mL of anhydrous ethanol and 50 μL of H_2O, the mixture was heated at 100 °C in an oil bath for 24 h under N_2. The mixture was purified by column chromatography on silica gel to afford the isomerization product *trans*-isomagnolol (4.8 g, 91% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (dd, J = 8.5, 2.0 Hz, 2 H), 7.23-7.22 (m, 2 H), 6.95 (d, J = 8.5 Hz, 2 H), 6.36 (d, J = 16.0 Hz, 2 H), 6.17-6.10 (m, 2 H), 5.67 (br, 2 H), 1.87 (d, J = 7 Hz, 6 H) ppm.[1]

The 1,1'-(chlorophosphoryl)bis(1H-pyrrole) (223.7 mg, 1.13 mmol) and Et_3N (227.9 mg, 2.25 mmol) were dissolved in 2.0 mL anhydrous THF under N_2. The mixture was cooled to 0 °C, the THF solution of *trans*-isomagnolol (151.8 mg, 0.57 mmol) was added via syringe, and the mixture was stirred overnight. The mixture was purified by column chromatography on silica gel to afford the 2vBPa (242.1 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.20 (m, 4H), 6.77 (d, J = 7.5 Hz, 2H), 6.71 (s, 8H), 6.37-6.31 (m, 2H), 6.22 (d, J = 2.5 Hz, 8H), 6.16-6.11 (m, 2H), 1.86 (d, J = 6.5 Hz, 8H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5 (d, J = 10 Hz), 134.5, 129.7, 128.9, 126.7, 126.0, 121.4 (d, J = 16.3 Hz), 119.4 (d, J = 12.5 Hz), 113.1 (d, J = 5.0 Hz), 112.2 (d, J = 3.8 Hz), 18.4 ppm; ^{31}P NMR (201 MHz, $CDCl_3$) δ 108.3 ppm. FTIR (neat): 3025, 2923, 1601, 1492, 1451, 1181, 1055, 737, 698 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{34}H_{33}N_4O_2P_2^+$: 591.2073, Found: 591.2072 ($M+H^+$).

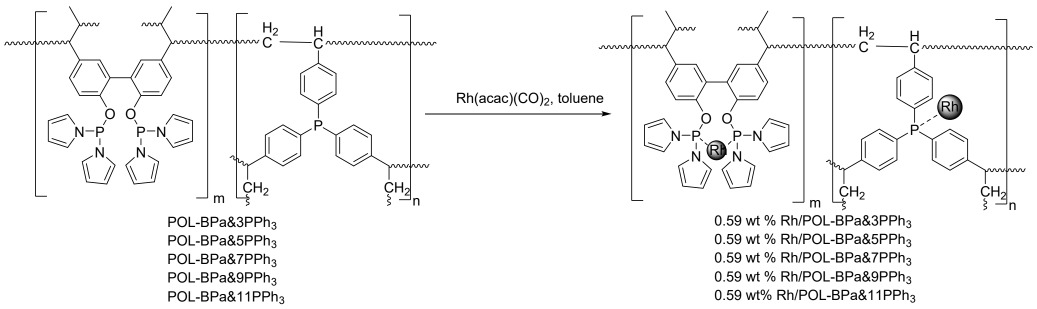
Synthesis of POLs-BPa&PPh$_3$.



Under N_2 atmosphere, 2vBPa (92.9 mg, 0.16 mmol), tris(4-vinylphenyl)phosphine (3vPPh$_3$, 163.2 mg, 0.48 mmol) and AIBN (5 mg, 0.03 mmol) were charged into a Schlenk flask. After stirring for 10 minutes at room temperature, the mixture was heated to 100 °C for 24 h. The crude product was washed by THF (3×5 mL) and separated by using a centrifuge. The copolymer POL-BPa&3PPh$_3$ (250.8 mg) was obtained.

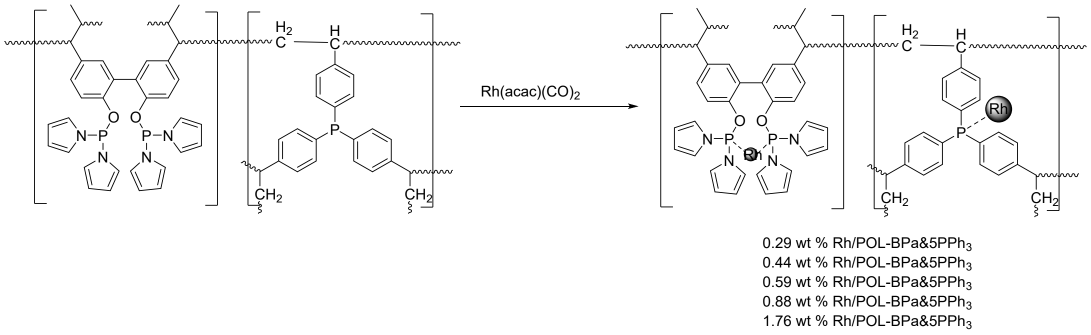
According to the synthesis process of POL-BPa&3PPh$_3$, the copolymers of POL-BPa&5PPh$_3$, POL-BPa&7PPh$_3$, POL-BPa&9PPh$_3$ and POL-BPa&11PPh$_3$ were synthesized by using 3vPPh$_3$ (163.2 mg, 0.48 mmol) and different amounts of 2vBPa (55.7, 39.8, 30.9, 25.3 mg), respectively.

Synthesis of 0.59 wt % Rh/POLs-BPa&PPh$_3$



Under N$_2$ atmosphere, 1 g of POL-BPa&5PPh$_3$, 14.8 mg of Rh(acac)(CO)$_2$ and 5 mL of toluene were charged into a Schlenk flask. The mixture was heated to 60 °C and stirred for 24 h. The solvent was subsequently removed under vacuum, affording the catalyst 0.59 wt % Rh/POL-BPa&5PPh$_3$. The preparation of other catalysts with 0.59 wt % Rh also followed the process.

Synthesis of Rh/POL-BPa&5PPh$_3$ with various Rh loading



Under N$_2$ atmosphere, 1 g of POL-BPa&5PPh$_3$, 5 mL of toluene and different amounts of Rh(acac)(CO)$_2$ (7.2, 11.0, 14.8, 22.0, 44.0 mg) were charged into a Schlenk flask, respectively. The mixture was heated to 60 °C and stirred for 24 h. The solvent was subsequently removed under vacuum, affording the catalysts of 0.29 wt % Rh/POL-BPa&5PPh$_3$, 0.44 wt %Rh/POL-BPa&5PPh$_3$, 0.59 wt % Rh/POL-BPa&5PPh$_3$, 0.88 wt % Rh/POL-BPa&5PPh$_3$, 1.76 wt % Rh/POL-BPa&5PPh$_3$.

3. Screening conditions for isomerization of magnolol

Table S1. Optimization of conditions for isomerization of magnolol.

Entry	Catalyst	Yield.(%)	Reference
1[a]	Rh(acac)(CO)$_2$	95	-
2[b]	KOH	1.4	[2]

3[c]	HCl	0.36	[3]
4[d]	*p*-TsOH	2.4	[4]
5[e]	CF_3COOH	1.19	[5]
6[f]	$CoCl_2$	0.1	[6]
7[g]	$Ni(COD)_2$	0.9	[7]
8[h]	$Fe(acac)_3$	2.9	[8]

[a]Magnolol (100 mg, 0.06 mmol), $Rh(acac)(CO)_2$ (0.18 mg), PPh_3 (0.56 mg), EtOH (1 mL), 25 µL H_2O, heated at 100 °C in an oil bath for 24 h under N_2. [b]Magnolol (100 mg, 0.375 mmol), KOH (0.2 g, 3.75 mmol), MeOH (2.0 ml), heated at 110 °C in an oil bath for 24 h under N_2. [c]Magnolol (100 mg, 0.375 mmol), HCl (0.31 mL 35% aq. HCl, 3.75 mmol), MeOH (2.0 ml), 0 °C for 24 h under N_2. [d]Magnolol (100 mg, 0.375 mmol), *p*-TsOH (0.65 mg, 3.75 mmol), MeOH (2.0 ml), heated at 110 °C in an oil bath for 24 h under N_2. [e]Magnolol (100 mg, 0.375 mmol), CF_3COOH (28.7 µL, 0.375 mmol), MeOH (2.0 ml), stirred at rt. for 60 h under N_2. [f]Magnolol (100 mg, 0.375 mmol), $CoCl_2$ (24.5 mg, 0.188 mmol), PPh_3 (147.67 mg, 0.563 mmol), $NaBH_4$ (7 mg, 0.188 mmol), THF (2.0 ml), stirred at -10 °C for 24 h under N_2. [g]Magnolol (100 mg, 0.375 mmol), $Ni(COD)_2$ (2.1 mg, 0.0075 mmol), dppbts (12.5 mg, 0.03 mmol), HCl (3.1 µL 35% aq. HCl, 0.03 mmol), EtOH (2.0 ml), H_2O (2.0 mL), stirred at 80 °C for 24 h under N_2. [h]Magnolol (100 mg, 0.375 mmol), $Fe(acac)_3$ (6.7 mg, 0.019 mmol), PhMgBr (34.1 mg, 0.188 mmol), THF (2.0 ml), stirred at rt. for 24 h under N_2.

4. General procedure for Rh/POL-BPa&PPh_3-catalyzed hydroformylation of olefins.

In a glove box, an autoclave equipped with a magnetic stir bar was loaded with Rh/POL-BPa&PPh_3 (5.0 mg, 0.59 wt % Rh) and olefins (2.86 mmol). The autoclave was purged three times with hydrogen, followed by sequential charging of CO (10 bar) and H_2 (10 bar). The autoclave was kept in a pre-heated oil bath at 100 ºC for 5 h. After reaction, the autoclave was cooled in an ice-water bath, and the gases were slowly released in a well-ventilated fume hood. The resulting mixture was subjected to quantitative analysis by gas chromatography (GC).

5. Screening conditions for hydroformylation of 1-hexene

Table S2. Optimization of conditions for Rh/POL-BPa&5PPh_3-catalyzed hydroformylation of 1-hexene [a]

Entry	H_2/CO (bar)	Temp. (°C)	t (h)	Conv. (%)	Linear[b] (%)	l/b[c]	[H][d] (%)	Iso.[e] (%)	TON
1	10/10	90	5	94.6	78.4	82.3	0.1	15.3	9460

2	10/10	100	5	99.5	89.6	89.9	-	8.9	9950
3	10/10	110	5	99.6	84.4	75.3	-	14.1	9960
4	10/10	100	2	69.4	63.3	89.1	-	6.1	6940
5	10/10	100	4	94.6	85.7	88.7	-	7.9	9460
6	5/5	100	5	91.2	74.7	25.3	1.1	13.66	9120
7	20/20	100	5	83.5	67.0	20.3	0.6	13.2	8350

[a]5.0 mg Rh/POL-BPa&PPh$_3$ (0.59 wt % Rh), 1-hexene (0.36 mL, 2.86 mmol), S/C$_{Rh}$ = 10000, toluene as the solution (2 mL), *n*-decane as the internal standard, yields were determined by GC analysis. [b]Linear aldehyde. [c]Linear/branched aldehydes ratio. [d][H] = alkanes. [e]Iso. = isomeric alkenes.

Table S3. Rh/POLs-BPa&PPh$_3$ (0.59 wt % Rh) catalyzed the hydroformylation of 1-hexene [a]

Entry	Cat.	H$_2$/CO (bar)	Temp. (°C)	t(h)	Conv. (%)	Linear[b] (%)	l/b[c]	[H][d] (%)	Iso.[e] (%)	TON
1	Rh/POP-BPa&3PPh$_3$	10/10	100	5	90.75	79.3	61.8	-	10.2	9075
2	Rh/POP-BPa&5PPh$_3$	10/10	100	5	99.5	89.6	89.9	-	8.9	9950
3	Rh/POP-BPa&7PPh$_3$	10/10	100	5	83.1	72.5	57.8	-	9.3	8310
4	Rh/POP-BPa&9PPh$_3$	10/10	100	5	76.3	55.3	5.3	-	10.5	7630
5	Rh/POP-BPa&11PPh$_3$	10/10	100	5	72.5	40.1	2.0	0.1	12.3	7250

[a]1-Hexene (0.36 mL, 2.86 mmol), S/C$_{Rh}$ = 10000, toluene as the solution (2 mL), *n*-decane as the internal standard, yields were determined by GC analysis. [b]Linear aldehyde. [c]Linear/branched aldehydes ratio. [d][H] = alkanes. [e]Iso. = isomeric alkenes.

Table S4. Rh/POLs-BPa&5PPh$_3$ with various Rh loading catalyzed the hydroformylation of 1-hexene [a]

Entry	Rh (wt %)	H$_2$/CO (bar)	T (°C)	Conv. (%)	Linear[b] (%)	l/b[c]	[H][d] (%)	Iso.[e] (%)	TON
1	0.29	10/10	100	55.7	41.7	124.0	-	13.6	5570
2	0.44	10/10	100	73.5	60.6	110.1	-	12.4	7350
3	0.59	10/10	100	99.5	89.6	89.9	-	8.9	9950
4	0.88	10/10	100	98.9	85.7	65.7	0.6	11.3	9890
5	1.76	10/10	100	97.6	84.6	44.5	0.9	10.2	9760

[a]1-Hexene (0.36 mL, 2.86 mmol), S/C$_{Rh}$ = 10000, toluene as the solution (2 mL), *n*-decane as the internal standard, yields were determined by GC analysis. [b]Linear aldehyde. [c]Linear/branched

aldehydes ratio. [d][H] = alkanes. [e]Iso. = isomeric alkenes.

6. Recycling studies of the Rh/POL-BPa&5PPh$_3$ in hydroformylation of 1-hexene

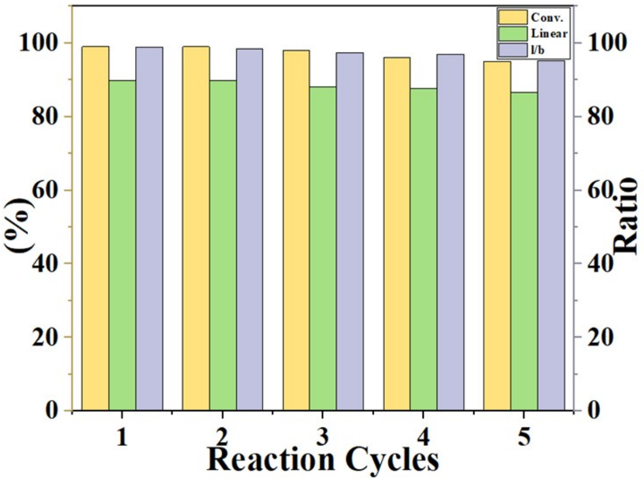


Figure S1. Recycling studies of the Rh/POL-BPa&5PPh$_3$ in hydroformylation of 1-hexene. Reaction conditions: 5 mg Rh/POL-BPa&5PPh$_3$ (0.59 wt % Rh), 1-hexene (0.36 mL), S/C = 10000, CO/H$_2$ = 10/10 bar, toluene (2.0 mL), 100 °C for 5 h.

7. The XPS spectra of the recovered Rh/POL-BPa&5PPh$_3$

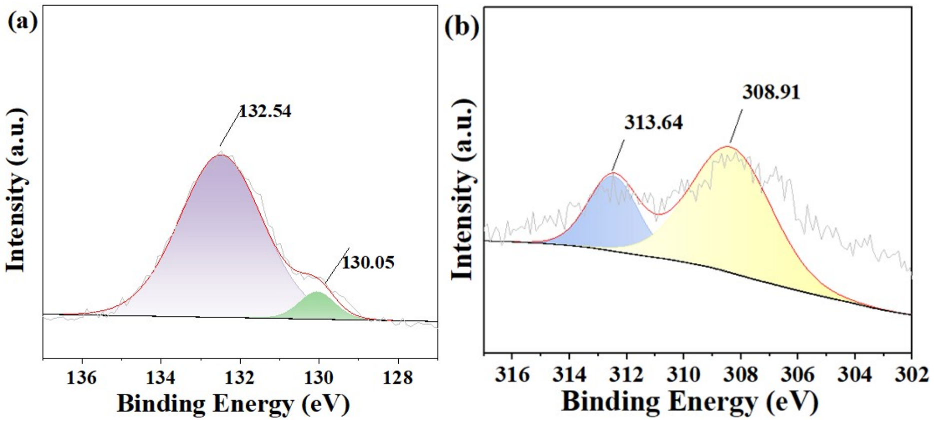
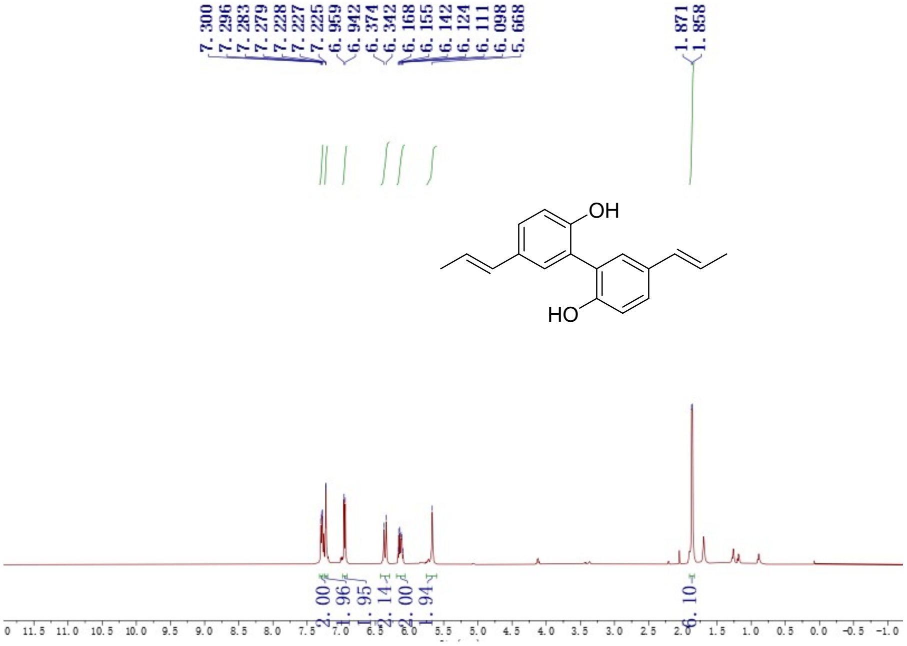


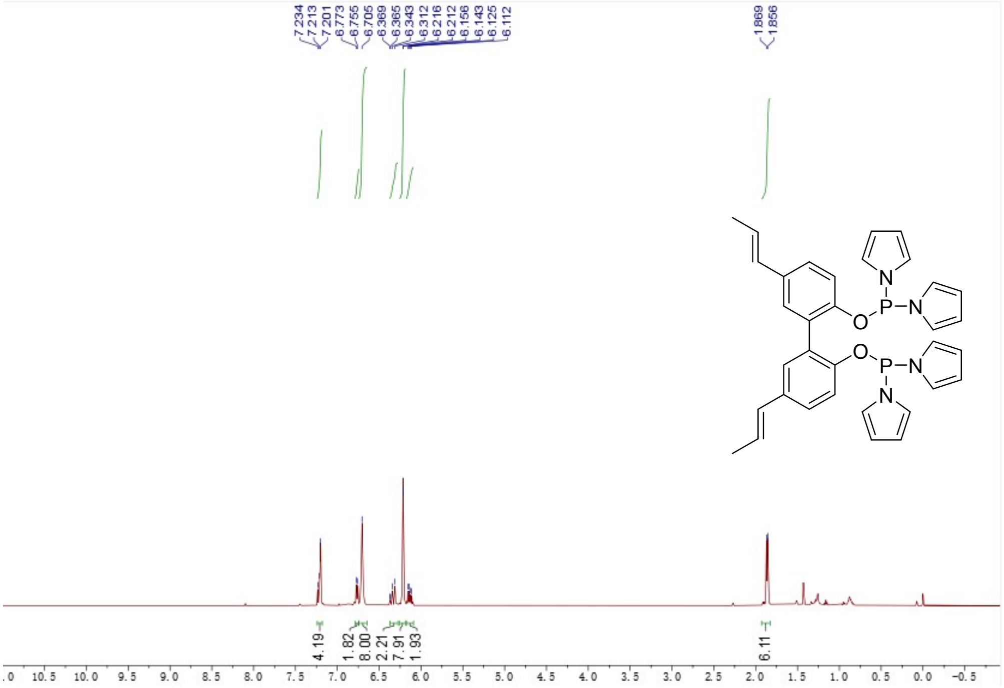
Figure S2. (a) P 2p XPS spectra, and (b) Rh 3d XPS spectra of the recovered Rh/POL-BPa&5PPh$_3$

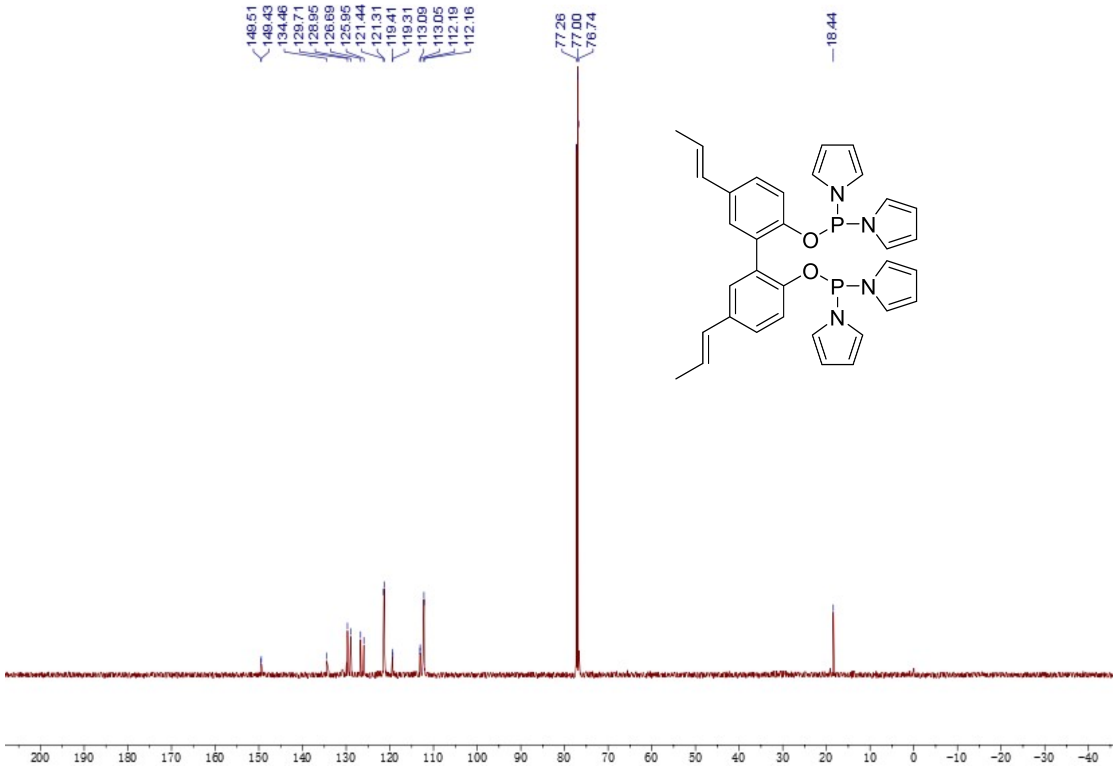
8. NMR Spectra of *trans*-isomagnolol and 2vBPa

^{1}H NMR of *trans*-isomagnolol.



^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectra, and high-resolution mass spectrometry of 2vBPa.

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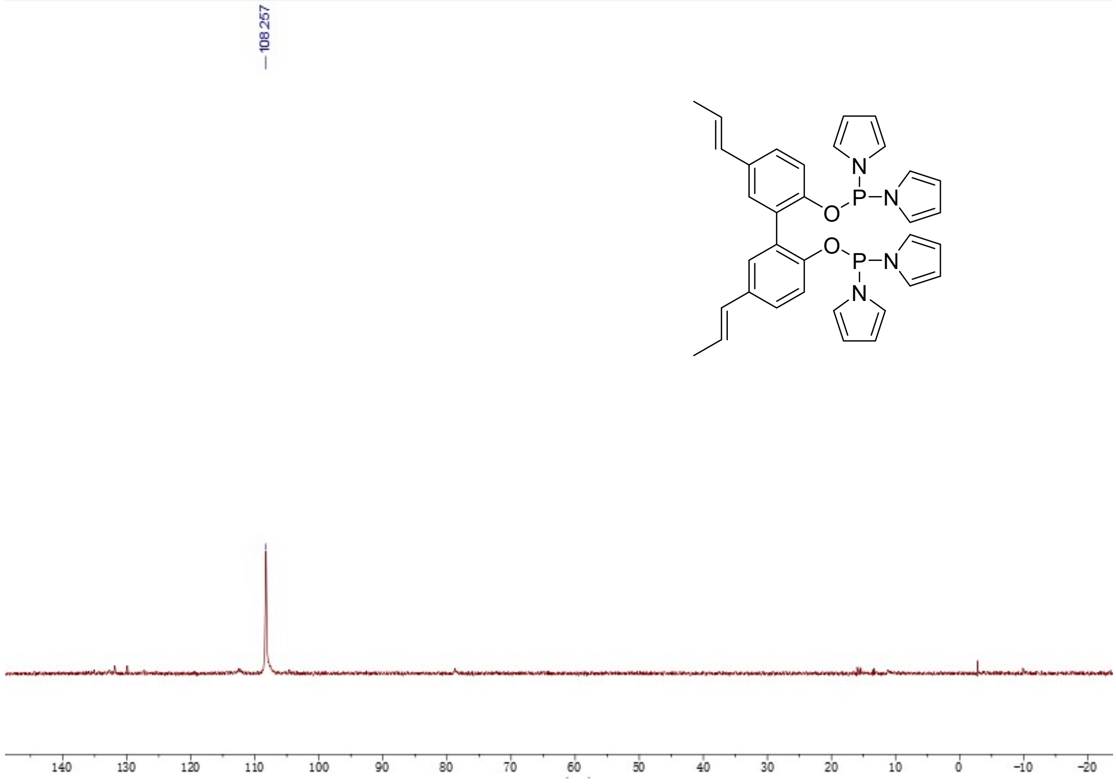
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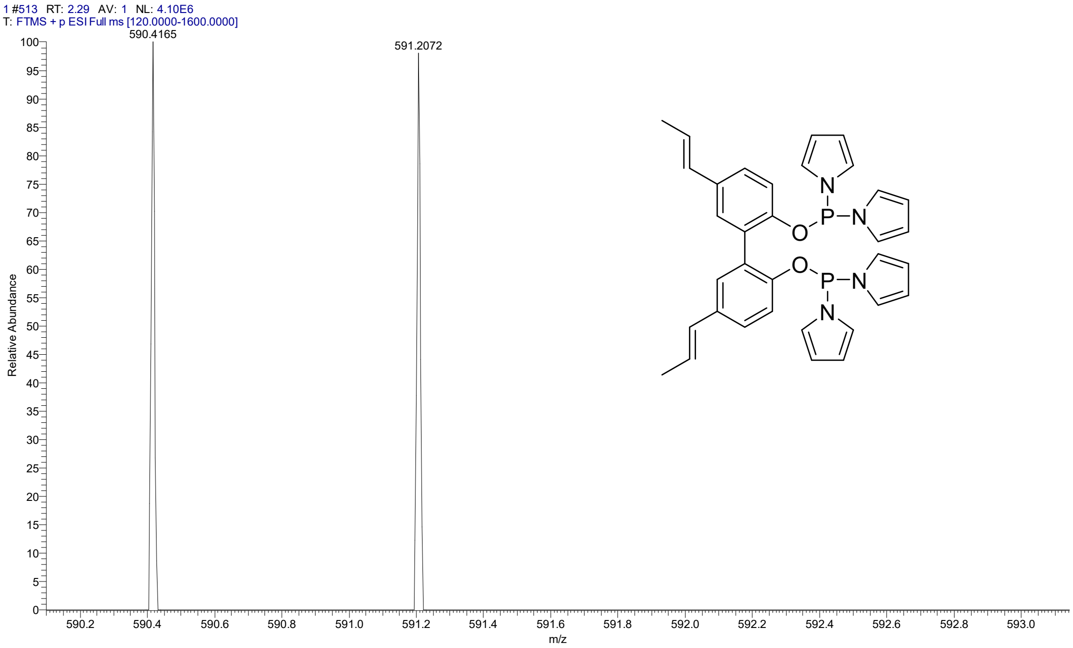
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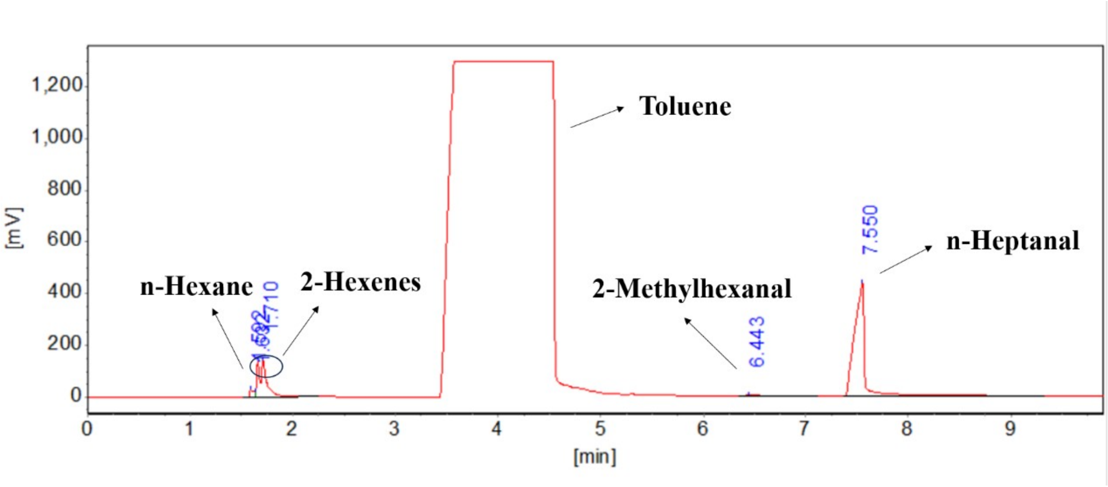
9. GC spectra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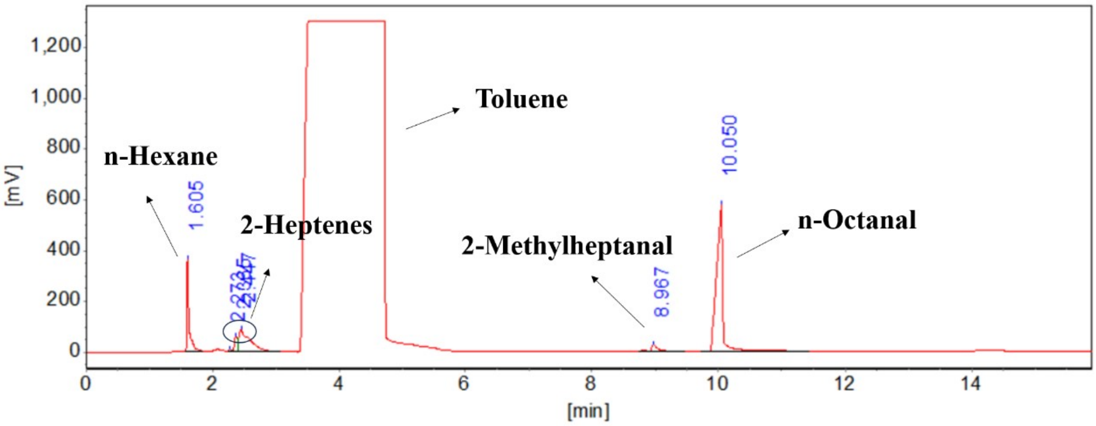
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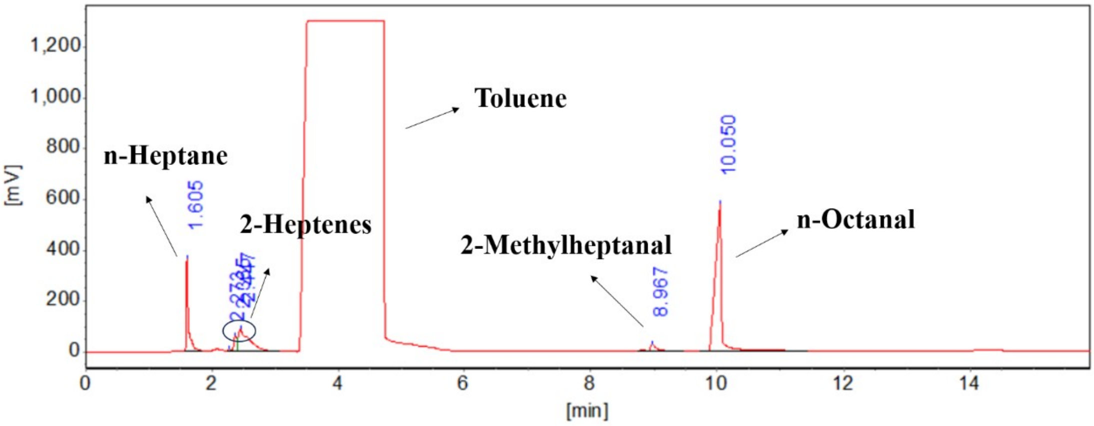
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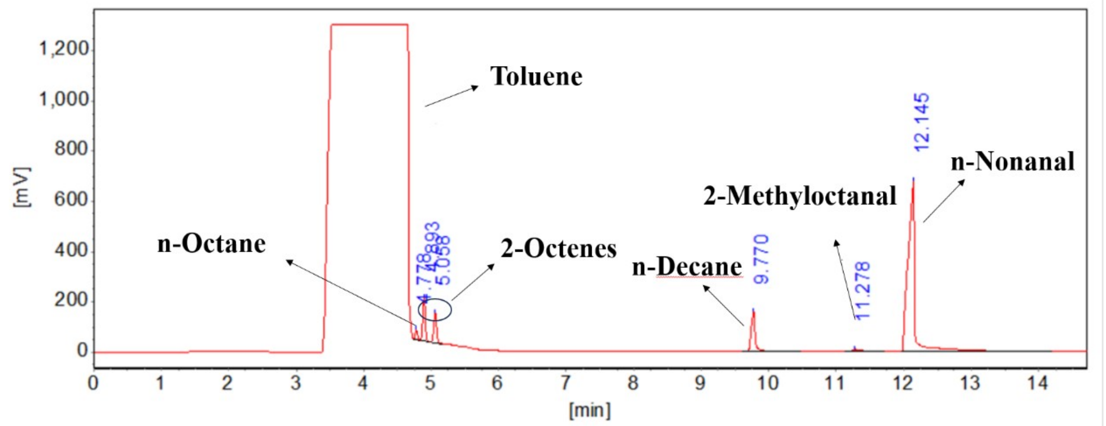
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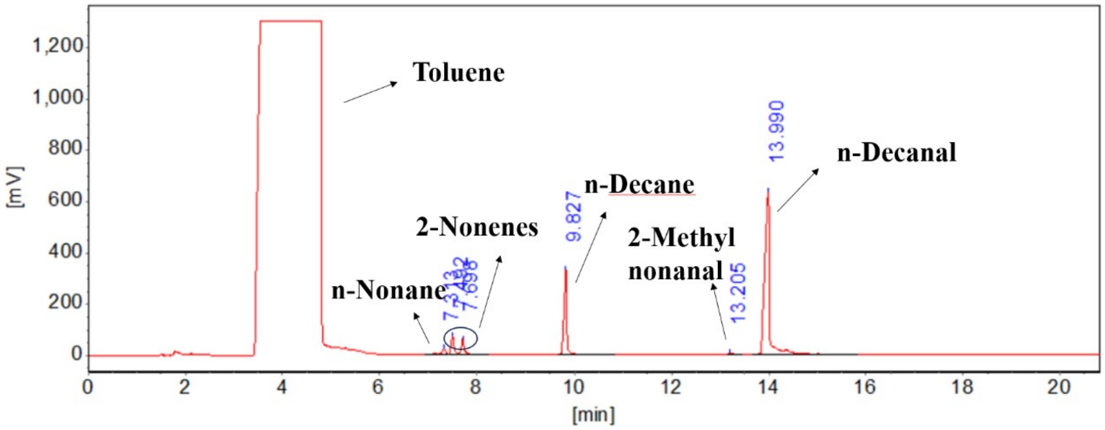
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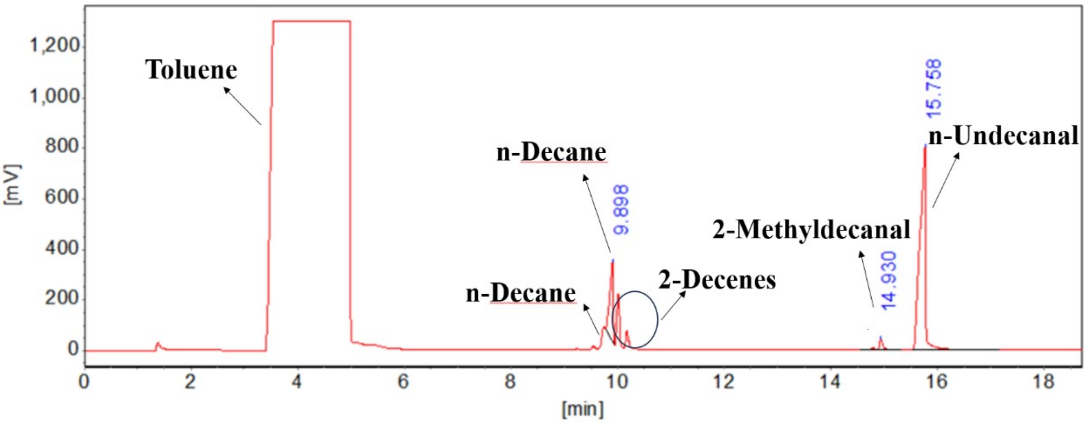
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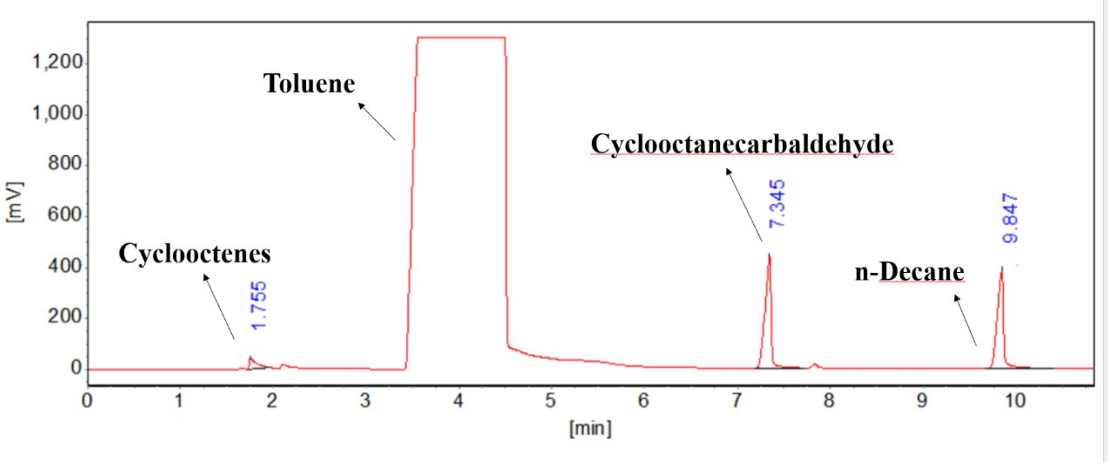

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