Supporting Information for

Porous Organic Polymer Supported Rhodium as a Heterogeneous Catalyst for Hydroformylation of Alkynes to α,β-Unsaturated Aldehydes

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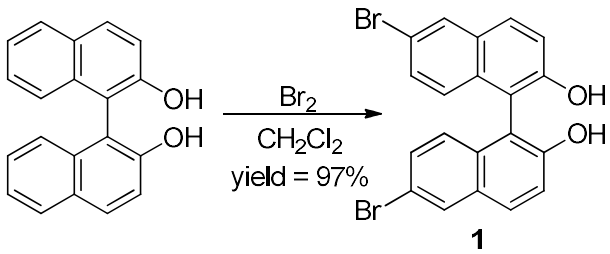
CONTENTS

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, HRMS were used to characterize all the isolated compounds. ^{1}H NMR spectra were recorded on 500 MHz and ^{13}C NMR spectra were recorded on 125 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. Solid NMR was recorded on Agilent DD2 600 MHz. HRMS (ESI) were determined on APEX III 7.0 TESLA FTMS spectrometers. ICP-MS were determined on Thermo iCAP Q. The IR spectra were measured on a Thermo (SCIENTIFC) NICOLET iS10 spectrometer. The SEM and TEM spectra were obtained on a Zeiss sigma 500 and JEOL-2100F spectrometers, respectively. N_2 sorption isotherms were obtained on a Micromeritics asap 2460. Thermogravimeric analysis was determined on NETZSCH TG 209 F1. X-ray photoelectron spectroscopy (XPS) was performed on a ThermoScientific ESCALAB 250Xi. GC analyses were measured on an Agilent 7820A system using a FID detector.

2. Synthesis and characterization of Rh/POL-BINAPa&PPh_3, Rh/POL-BPa&PPh_3, Rh/POL-PPh_3 and BINAPa (4)

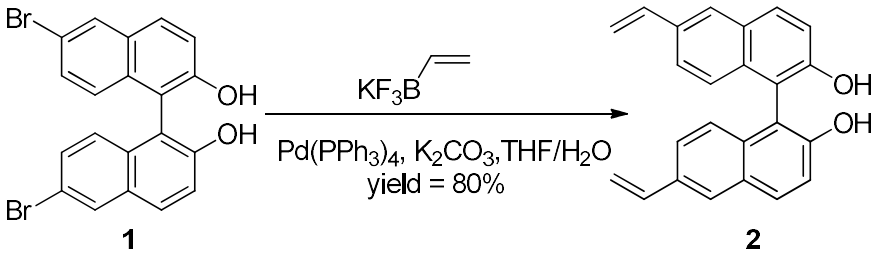


1

Synthesis of 6,6'-dibromo-[1,1'-binaphthalene]-2,2'-diol (1).

Compound **1** was obtained by following the reported literature procedure.[1] ^{1}H

NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.92 (d, *J* = 9.0 Hz, 2H), 7.43-7.39 (m, 4H), 6.99 (d, *J* = 9.0 Hz, 2H), 5.09 (s, 2H) ppm.

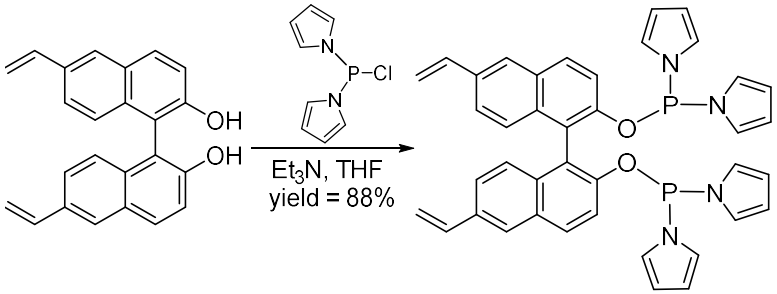


1 2

Synthesis of 6,6'-divinyl-[1,1'-binaphthalene]-2,2'-diol (2)[1].

In the nitrogen atmosphere, compound **1** (500 mg, 1.13 mmol), $C_2H_3BF_3K$ (664 mg, 4.9 mmol), K_2CO_3 (677 mg, 4.9 mmol) and $Pd(PPh_3)_4$ (25.0 mg, 0.021 mmol) were added to mixture solvent (6 mL THF and 1 mL H_2O) in Schlenk tube. The mixture was heated to reflux for 24 h, then was purified by silica gel column chromatography (PE:EA = 2:1). The light yellow solid compound **2** was obtained in 80% yield (290.0 mg).

A light yellow solid, 80% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 7.83 (s, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 7.13 (d, *J* = 9.0 Hz, 2H), 6.88 (dd, *J* = 11.0, 6.5 Hz, 2H), 5.82 (d, *J* = 17.5 Hz, 2H), 5.32 (d, *J* = 10.5 Hz, 2H), 5.16 (s, 2H) ppm.



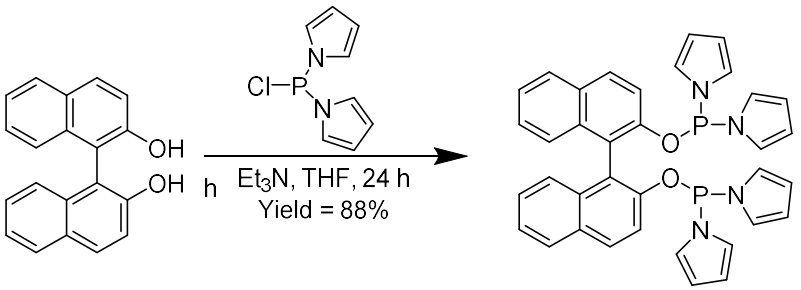
2 3 vBINAPa

Synthesis of 1,1',1'',1'''-(((6,6'-divinyl-[1,1'-binaphthalene]-2,2'-diyl)bis(oxy)) bis (phosphinetriyl)) tetrakis(1H-pyrrole) (3).

Under N_2 atmosphere, a solution of compound **2** (313.5 mg, 0.97 mmol) in THF (5.0 mL) was added dropwise to a solution of chlorodipyrrolylphosphine (424.0 mg, 2.14 mmol) and triethylamine (216.6 mg, 2.14 mmol) in THF (5.0 mL) at 0 ^oC. After 12 h of stirring at room temperature, the mixture of reaction was purified by silica gel column chromatography (PE:EA = 10:1). The white oily compound **3** was evaporated

under reduced pressure and obtained in 88% yield (557.0 mg).

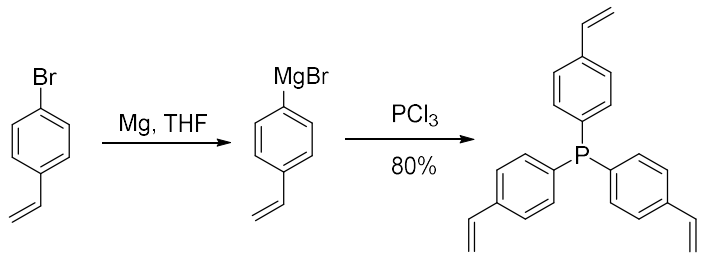
Oil, 88% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.92 (d, *J* = 7.0 Hz, 2H), 7.87 (s, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.07 (s, 2H), 7.24-7.20 (m, 2H), 6.96-6.90 (m, 2H), 6.58 (d, *J* = 25.0 Hz, 8H), 6.20 (d, *J* = 25.0 Hz, 8H), 5.88 (d, *J* = 17.0 Hz, 2H), 5.39 (d, *J* = 11.5 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.2 (d, *J* = 12.0 Hz), 136.4, 134.5, 133.2, 130.9, 130.5, 126.3, 126.0, 124.5, 122.5, 121.0 (d, *J* = 14.4 Hz), 120.9 (d, *J* = 13.9 Hz), 119.5 (d, *J* = 10.1 Hz), 114.3, 112.1 (d, *J* = 1.8 Hz) ppm; ^{31}P NMR (161 MHz, $CDCl_3$): δ 108.9 ppm; FTIR (neat): 3098.8, 2955.6, 2924.6, 2853.8, 1587.7, 1454.3, 1345.7, 1071.9, 1054.2, 987.4, 826.4, 732.8, 619.7 cm^{-1}.; HRMS (Maldi) m/z: Calcd. For $C_{40}H_{33}N_4O_2P_2^+$: 663.2073 [M+H$^+$], found: 663.2087.



4

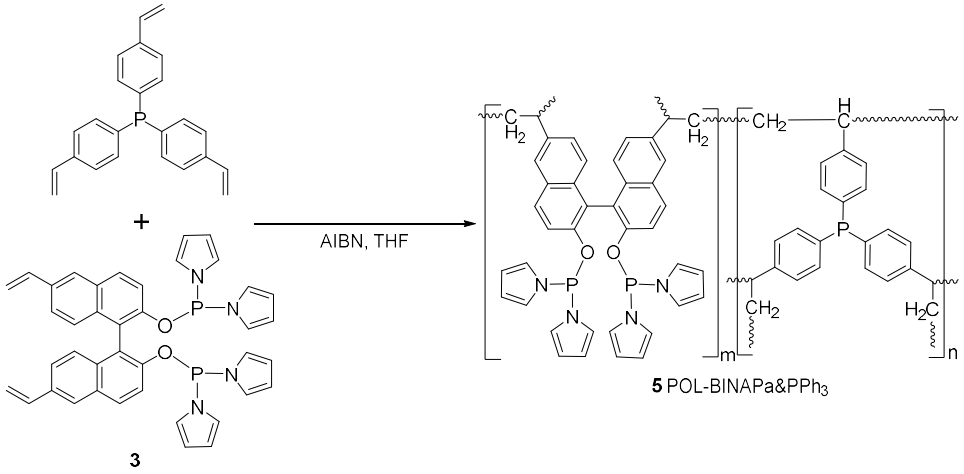
Synthesis of compound 2,2'-bis((di(1H-pyrrol-1-yl)phosphino)oxy)-1,1'-binaphthalene compound (4).

The compound **4** was obtained by following the reported literature procedure[2]. 88% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): 7.88 (d, *J* = 8.5 Hz, 4H), 7.43 (t, *J* = 7.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.23-7.21 (m, 2H), 7.13 (d, *J* = 9.0 Hz, 2H), 6.46 (d, *J* = 10.5 Hz, 8H) , 6.11 (d, *J* = 26.0 Hz, 8H) ppm.



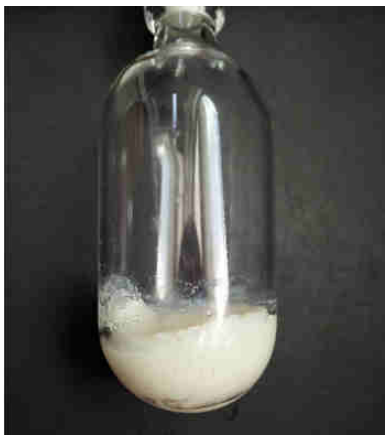
Synthesis of tris(4-vinylphenyl)phosphine.

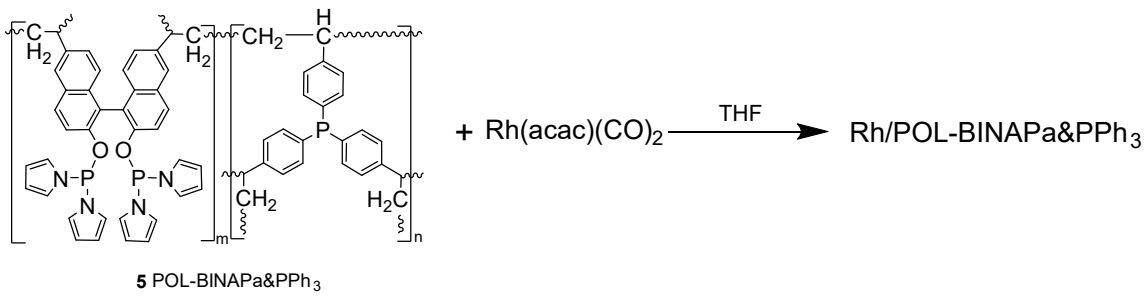
The compound was obtained by following the reported literature procedure[3]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, *J* = 10.0 Hz, 6H), 7.24-7.23 (m, 6H), 6.68 (dd, *J* = 20.0, 10.0 Hz, 3H), 5.76 (d, *J* = 20.0 Hz, 3H), 5.26 (d, *J* = 10.0 Hz, 3H) ppm.



Synthesis of POL-BINAPa&PPh$_3$(5).

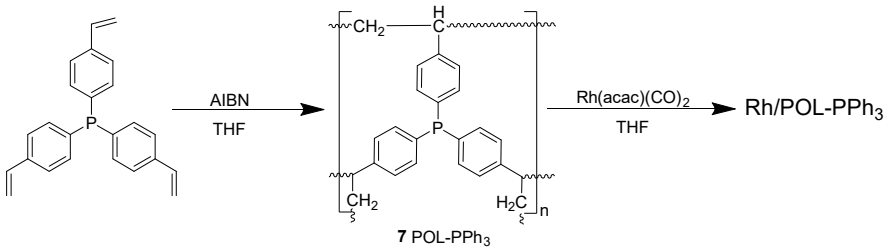
Tris(4-vinphenyl) phosphane (460.0 mg, 1.36 mmol), compound **3** (225.0 mg, 0.34 mmol) and AIBN (24.0 mg, 0.15 mmol) were dissolved in THF (11.0 mL) under N_2 atmosphere in Schlenk flask. After stirring for 10 minutes at room temperature, the mixture was heated to 100 ^{o}C for 24 h. The white solid was formed and swollen in THF. After evaporation of THF at 40 ^{o}C under vacuum, the crude product was washed by THF (3×8 mL) and separated by using a centrifuge (8000 rpm, 5 min). The copolymer POL-BPa&PPh$_3$ (0.640 g) was obtained as a light yellow solid.





Synthesis of Rh/POL-BINAPa&PPh_3.

In glove box, POL-BINAPa&PPh_3 (320.0 mg) and $Rh(acac)(CO)_2$ (14.6 mg) was added to THF (10 mL). After stirring for 24 h under N_2 at room temperature, the resulting product was separated by using centrifuge. The crude product was washed by THF (3×8 mL) and evaporation of THF under vaccum, the slight yellow catalyst Rh/POL-BINAPa&PPh_3 (300 mg) was obtained.

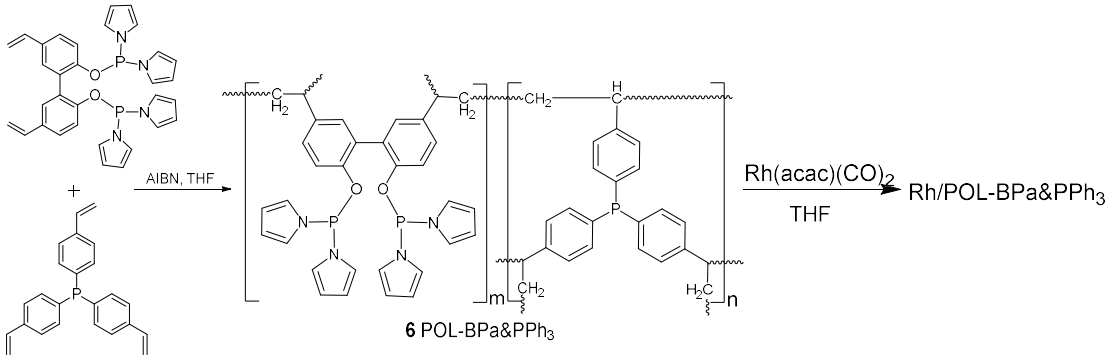


Synthesis of Rh/POL-PPh_3[4].

Tris(4-vinphenyl) phosphane (200.0 mg, 0.58 mmol) and AIBN (8.0 mg, 0.05 mmol) were dissolved in THF (8.0 mL) under N_2 atmosphere in Schlenk flask. After stirring for 10 minutes at room temperature, the mixture was heated to 100 ^oC for 20 h. The white solid was formed and swollen in THF. After evaporation of THF at 40 ^oC under vacuum, the crude product was washed by THF (3×8 mL) and separated by using a centrifuge (8000 rpm, 5 min). The POL-PPh_3 (185.0 mg) was obtained as a white solid.

In glove box, POL-PPh_3 (185.0 mg) and $Rh(acac)(CO)_2$ (12.0 mg) was added to THF (10 mL). After stirring for 24 h under N_2 at room temperature, the resulting product was separated by using centrifuge. The crude product was washed by toluene (3×8 mL) and evaporation of toluene under vaccum, the light yellow catalyst

$Rh/POL\text{-}PPh_3$ (152.4 mg) was obtained.

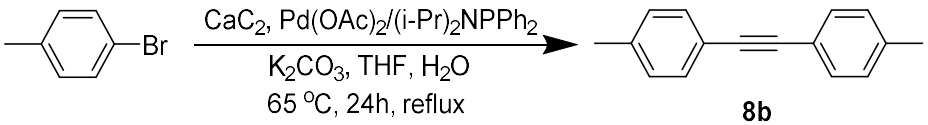


Synthesis of Rh/POL-BPa&PPh$_3$[4]. Tris(4-vinphenyl) phosphane (138.4 mg, 0.4 mmol) and vinyl phephosamidite (56.5 mg, 0.1 mmol) were dissolved in THF (6.0 mL) under N_2 atmosphere in Schlenk flask, followed by the addition of 12 mg of AIBN. After stirring for 10 minutes at room temperature, the mixture was heated to 100 ℃ for 24 h. After evaporation of THF at 40 ℃ under vacuum, the crude product was washed by THF (3×8 mL), the copolymer POL-BPa&PPh_3 (143 mg) was obtained.

In glove box, POL-BPa&PPh_3 (195.0 mg) and $Rh(acac)(CO)_2$ (20.0 mg) was added to THF (10 mL). After stirring for 24 h under N_2 at room temperature, the resulting product was separated by using centrifuge. The crude product was washed by THF (3×8 mL) and evaporation of THF under vaccum, the slight yellow catalyst Rh/POL-BPa&PPh_3 (192.0 mg) was obtained.

3. General procedure for synthesis of substrates 8.

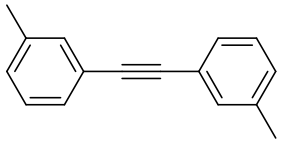
Substrates 8a, 8d, 8g, 8k, 8l and 8o were purchased from commercial suppliers.



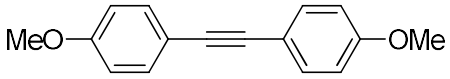
Synthesis of 1,2-di-p-tolylethyne (8b)[5]. Calcium carbide (1.24 g, 19.4 mmol), *p*-bromotoluene (1.66 g, 9.7 mmol), $(i\text{-}Pr)_2NPPh_2$ (207 mg, 0.73 mmol), $Pd(OAc)_2$ (55 mg, 0.24 mmol) and K_2CO_3 (2.68 g, 19.4 mmol) were added into undried THF (25.0 mL) under N_2 atmosphere in Schlenk flask. The mixture was heated to 65 °C. After 12 h of stirring, the mixture of reaction was purified by silica gel column

chromatography. The white solid Substrate **8b** was evaporated under reduced pressure and obtained in 65% yield (650 mg). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (d, *J* = 8.0 Hz, 4H), 7.15 (d, *J* = 7.5 Hz, 4H), 2.37 (s, 6H) ppm.

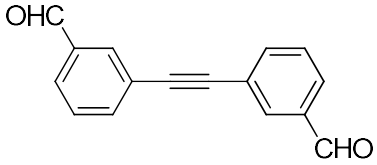
Substrates 8c, 8e, 8f, 8g, 8h and 8i were prepared by the same procedure according to **8b**.



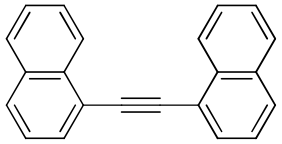
1,2-Di-m-tolylethyne (8c) [5] **.** White solid, 66% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36-7.33 (m, 4H), 7.25-7.22 (m, 2H), 7.16-7.14 (m, 2H), 2.36 (s, 6H) ppm.



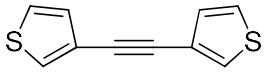
1,2-bis(4-methoxyphenyl)ethyne (8e) [5]**.** Yellow solid, 70% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 (d, *J* = 8.5 Hz, 4H), 6.87 (d, *J* = 8.5 Hz, 4H), 3.83 (s, 6H) ppm.



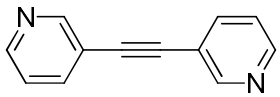
3,3'-(ethyne-1,2-diyl)dibenzaldehyde (8f) [5]**.** Yellow solid, 47% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.05 (s, 2H), 8.06 (s, 2H), 7.90-7.87 (m, 2H), 7.78-7.76 (m, 2H), 7.59-7.54 (m, 2H) ppm.



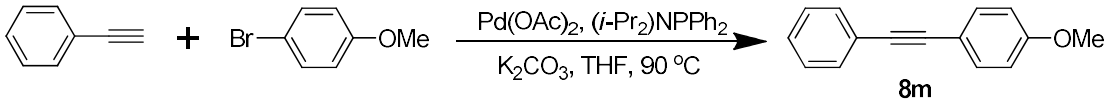
1,2-di(naphthalen-1-yl)ethyne (8g) [5]**.** White solid, 54% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.58 (d, *J* = 8.5 Hz, 2H), 7.92-7.89 (m, 6H), 7.67-7.64 (m, 2H), 7.59-7.54 (m, 4H) ppm.



1,2-di(thiophen-3-yl)ethyne (8h) [5]**.** Brown solid, 41% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (s, 2H), 7.31-7.29 (m, 2H), 7.19-7.17 (m, 2H) ppm.



1,2-di(pyridin-3-yl)ethyne (8i)[5]. Brown solid, 66% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.79 (s, 2H), 8.58 (d, *J* = 4.5 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.19-7.17 (m, 2H) ppm.



8m

Synthesis of Substrates 1-methoxy-4-(phenylethynyl)benzene (8m)[5].

Ethynylbenzene (490 mg, 4.8 mmol), 1-bromo-4-methoxybenzene (900 mg, 4.8 mmol), (*i*-Pr)$_2$NPPh$_2$ (205 mg, 0.72 mmol), Pd(OAc)$_2$ (55 mg, 0.24 mmol) and K_2CO_3 (1.33 g, 9.6 mmol) were dissolved in undried THF (20.0 mL) under N_2 atmosphere in Schlenk flask. The mixture was heated to 90 °C. After 12 h of stirring, the mixture of reaction was purified by silica gel column chromatography (PE 100%). After removing the solvent under reduced pressure, the yellow solid **8m** was obtained in 45% yield (450 mg). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59-7.53 (m, 4H), 7.39-7.36 (m, 3H), 6.93 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H) ppm.

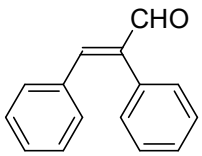
4. General procedure for the hydroformylation of Alkynes.

In a glove box, a glass vial with a magnetic stirring bar was charged with Rh/POL-BINAPa&PPh$_3$ (2.7 mg), the corresponding alkynes **8** (0.516 mmol), tolueue (1.0 mL) and *p*-xylene (30 μL, 0.25 mmol) as the internal standard. The vial was then transferred to an autoclave, which was purged with hydrogen for three times and subsequently charged with H_2 (5 atm) and CO (5 atm). The autoclave was then heated to 70 °C (oil bath) and was kept at this temperature for 20 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The mixture subsequently was analyzed by GC.After removing the solvent by vacuum, the residue was directiy purified by flash chromatography on silica gel to give the desired product **9**.

GC analysis condition for compounds of **9a**, **9b**, **9c**, **9e**, **9f**, **9h**, **9i**: SE-5, 30 m×0.32 mm×0.33 mm, flow rate 2.0 mL/min, method: ramp from 50 ℃ to 250 ℃ at a rate of

20.0 ℃/min, 250 ℃ hold for 20 min.

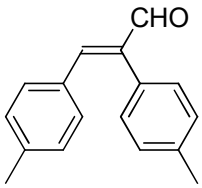
GC analysis condition for compounds of **9j**, **9k**, **9l** and **9n**: SE-5, 30 m×0.32 mm×0.33 mm, flow rate 2.0 mL/min, method: 50 ℃ hold for 5 min, and then ramp from 50 ℃ to 250 ℃ at a rate of 10.0 ℃/min, 250 ℃ hold for 5 min.



9a

(*E*)-2,3-diphenylacrylaldehyde (9a)[6]. White solid, 95.6 mg, 89% yield. The compound was purified by flash column chromatography on a silica gel with petroleum ether-ethyl acetate (10:1 V/V) as eluant.

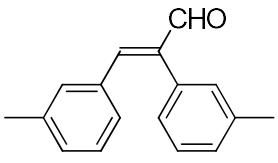
^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.77 (s, 1H), 7.42-7.38 (m, 4H), 7.29-7.28 (m, 1H), 7.25-7.19 (m, 6H) ppm.



9b

(*E*)-2,3-di-p-tolylacrylaldehyde (9b)[6] . White solid, 107.2 mg, 88% yield. The compound was purified by flash column chromatography on a silica gel with petroleum ether-ethyl acetate (10:1 V/V) as eluant.

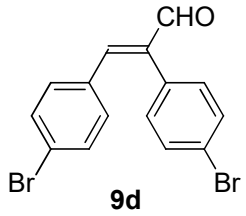
^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.71 (s, 1H), 7.30 (s, 1H), 7.20 (d, J = 6.5 Hz, 2H), 7.12 (d, J = 6.5 Hz, 2H), 7.08 (d, J = 7.5 Hz, 2H), 7.02 (d, J = 7.5 Hz, 2H), 2.37 (s, 3H), 2.28 (s, 3H) ppm.



9c

(*E*)-2,3-di-m-tolylacrylaldehyde (9c)[7] . White solid, 106.0 mg, 87% yield. The compound was purified by flash column chromatography on a silica gel with petroleum ether-ethyl acetate (15:1 V/V) as eluant.

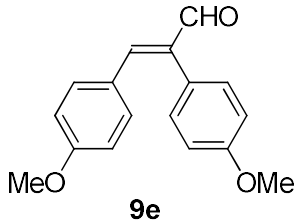
^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.71 (s, 1H), 7.29 (s, 1H), 7.26-7.25 (m, 1H), 7.17-7.16 (m, 1H), 7.07-6.95 (m, 6H), 2.32 (s, 3H), 2.20 (s, 3H) ppm.



9d

(*E*)-2,3-bis(4-bromophenyl)acrylaldehyde (9d)[6] **.** White solid, 122.7 mg, 65% yield. The compound was purified by flash column chromatography on a silica gel with petroleum ether-ethyl acetate (10:1 V/V) as eluant.

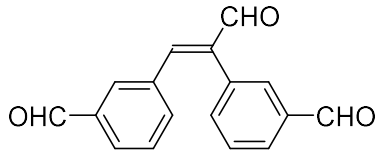
^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.72 (s, 1H), 7.53 (d, *J* = 9.5 Hz, 2H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.33 (s, 1H), 7.07-7.05 (m, 4H) ppm.



9e

(*E*)-2,3-bis(4-methoxyphenyl)acrylaldehyde (9e)[7] **.** Yellow solid, 90.0 mg, 86% yield. The compound was purified by flash column chromatography on a silica gel with petroleum ether-ethyl acetate (5:1 V/V) as eluant.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.70 (s, 1H), 7.29 (s, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 9.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 9.5 Hz, 2H), 3.84 (s, 3H), 3.78 (s, 3H) ppm.

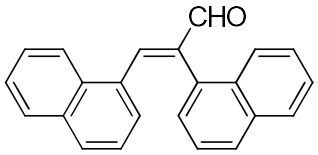


9f

(*E*)-3,3'-(3-oxoprop-1-ene-1,2-diyl)dibenzaldehyde (9f). Yellow solid, 98.2 mg, 72% yield. The compound was purified by flash column chromatography on a silica gel with petroleum ether-ethyl acetate (2:1 V/V) as eluant.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.96 (s, 1H), 9.81 (s, 1H), 9.80 (s, 1H), 7.90 (d, *J* = 7.0 Hz, 1H), 7.78 (s, 1H), 7.69 (d, *J* = 5.0 Hz, 2H), 7.58-7.54 (m, 2H), 7.43 (d, *J* = 7.0

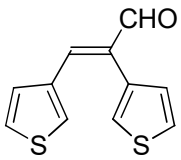
Hz, 1H), 7.36 (s, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.8, 191.6, 191.1, 148.8, 141.5, 136.8, 136.5, 135.4, 135.2, 134.4, 133.5, 131.5, 130.9, 130.6, 129.7, 129.5, 129.3 ppm; FTIR (neat): 3062.7, 2926.1, 2839.9, 2728.8, 1698.1, 1598.4, 1381.5, 1285.3, 1226.2, 1163.9, 1073.5, 913.3, 798.3, 742.7 cm^{-1}.; HRMS (ESI) m/z: Calcd. For $C_{17}H_{13}O_3^+$: 265.0863 [$M+H^+$], found: 265.0863.



9g

(*E*)-2,3-di(naphthalen-1-yl)acrylaldehyde (9g). White solid, 98.6 mg, 62% yield.The compound was purified by flash column chromatography on a silica gel with petroleum ether-ethyl acetate (10:1 V/V) as eluant.

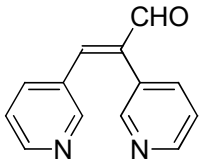
^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.08 (s, 1H), 8.48 (s, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.84-7.79 (m, 3H), 7.67-7.61 (m, 3H), 7.54-7.51 (m, 1H), 7.44-7.32 (m, 3H), 7.21-7.19 (m, 1H), 6.94-6.93 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.6, 147.8, 142.4, 133.7, 133.4, 131.7, 131.6, 131.5, 130.5, 130.3, 128.9, 128.7, 128.6, 127.9, 127.6, 127.0, 126.4, 126.2, 126.0, 125.6, 125.0, 124.9, 123.2 ppm; FTIR (neat): 3056.0, 2955.4, 2924.6, 2852.4, 2707.9, 1686.8 1611.2, 1507.3, 1463.6, 1391.4, 1338.3, 1245.5, 1174.2, 1127.2, 777.5 cm^{-1}.; HRMS (ESI) m/z: Calcd. For $C_{23}H_{17}O^+$: 309.1274 [$M+H^+$], found: 309.1278.



9h

(*E*)-2,3-di(thiophen-3-yl)acrylaldehyde (9h)[10]. Yellow solid, 69.5 mg, 61% yield. The compound was purified by flash column chromatography on a silica gel with petroleum ether-ethyl acetate (5:1 V/V) as eluant.

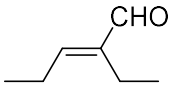
^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.70 (s, 1H), 7.43-7.40 (m, 3H), 7.31 (s, 1H) , 7.21-7.19 (m, 1H), 6.97 (d, *J* = 5.5 Hz, 1H), 6.81 (d, *J* = 5.5 Hz, 1H) ppm.



9i

(*E*)-2,3-di(pyridin-3-yl)acrylaldehyde (9i)[6]. Yellow solid, 71.6 mg, 66% yield. The compound was purified by flash column chromatography on a silica gel with petroleum ether-ethyl acetate (1:4 V/V) as eluant.

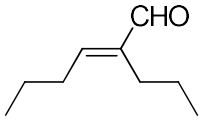
^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.80 (s, 1H), 8.63-8.51 (m, 3H), 8.38 (s, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.49 (s, 1H), 7.37-7.35 (m, 2H), 7.15-7.13 (m, 1H) ppm.



9j

(*E*)-2-ethylpent-2-enal (9j)[8]. Colourless liquid, 55.0 mg, 95% yield. The compound was purified by flash column chromatography on a silica gel with petroleum *n*-pentane-diethyl enter (20:1 V/V) as eluant.

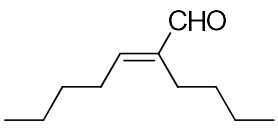
^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.30(s, 1H), 6.38 (t, *J* = 7.5 Hz, 1H), 2.36-2.29 (m, 2H), 2.20 (q, *J* = 8.0 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 8.0 Hz, 3H) ppm.



9k

(*E*)-2-propylhex-2-enal (9k)[6]. Colourless liquid, 69.5 mg, 96% yield. The compound was purified by flash column chromatography on a silica gel with petroleum *n*-pentane-diethyl enter (20:1 V/V) as eluant.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.30 (s, 1H), 6.40 (t, *J* = 8.5 Hz, 1H), 2.30-2.25 (m, 2H), 2.16 (t, *J* = 7.0 Hz, 2H), 1.49-1.45 (m, 2H), 1.34-1.29 (m, 2H), 0.91 (t, *J* = 8.5 Hz, 3H), 0.81 (t, *J* = 7.0 Hz, 3H) ppm.

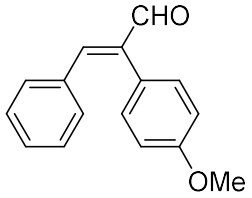


9l

(*E*)-2-butylhept-2-enal (9l)[6]. Colourless liquid, 84.2 mg, 97% yield. The compound was purified by flash column chromatography on a silica gel with petroleum

n-pentane-diethyl enter (20:1 V/V) as eluant.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.34 (s, 1H), 6.43 (t, *J* = 7.0 Hz, 1H), 2.36-2.32 (m, 2H), 2.23-2.20 (m, 2H), 1.49-1.46 (m, 2H), 1.39-1.35 (m, 2H), 1.30-1.28 (m, 4H), 0.94-0.87 (m, 6H) ppm.



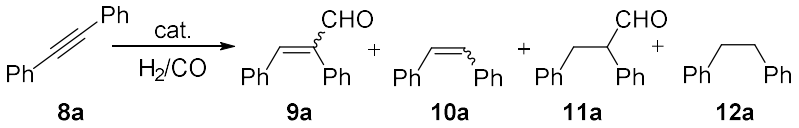
9m

(*E*)-3-(4-methoxyphenyl)-2-phenylacrylaldehyde (9m)[9]. Yellow solid, 92.2 mg, 67.5% yield. The compound was purified by flash column chromatography on a silica gel with petroleum ether-ethyl acetate (10:1 V/V) as eluant.

9n ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.74 (s, 1H), 7.33 (s, 1H), 7.27-7.23(m, 4H), 7.13 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H) ppm.

5. Screening conditions for hydroformylation of diphenylacetylene.

Table 1. Screening conditions for hydroformylation of diphenylacetylene[a]



8a **9a** **10a** **11a** **12a**

Entry	Solvent	H_2/CO (bar)	Temp. (℃)	Conv. (%)	**9a**(*E/Z*) (%)	**10a** (%)
1	Toluene	5/5	70	100	90 (60)	10
2	Toluene	5/5	60	73	67 (87)	6
3	Toluene	5/5	80	100	86 (57)	14
4	Toluene	10/10	70	93	85 (59)	8
5	Toluene	3/3	70	99	83 (55)	15
6	THF	5/5	70	100	87 (22)	13
7	CH_3CN	5/5	70	100	90 (34)	10
8	Ethyl acetate	5/5	70	99	89 (57)	10

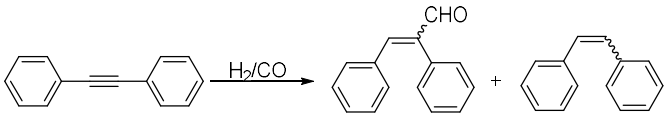
9	CH_2Cl_2	5/5	70	82	74 (133)	8
10	*n*-Hexane	5/5	70	100	80 (60)	19
11	EtOH	5/5	70	92	81 (4)	10

[a]8a (96.0 mg), 2.7 mg of Rh/POL-BINAPa&PPh_3 (Rh loading at 1.32 wt%), S/C = 1000, solvent (1.0 mL), 20 h.

6. Recycling tests of the Rh/POL-BINAPa&PPh_3 in 1,2-diphenylethyne hydroformylation.

In a glove box, a glass vial with a magnetic stirring bar was charged with Rh/POL-BINAPa&PPh_3 (28.0 mg), 1,2-diphenylethyne (950 mg, 5.33 mmol), toluene (7.0 mL) and decane (30 μL, 0.25 mmol) as the internal standard. The vial was then transferred to an autoclave, which was purged with hydrogen for three times and subsequently charged with CO (5 atm) and H_2 (5 atm). The autoclave was then heated to 70 °C (oil bath) and was kept at this temperature for 8 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The catalyst of reaction mixture was separated in air by using centrifuge and used to test next recycling reaction with the same condition and procedure. The mixture subsequently was analyzed by GC.

Table 2. Catalytic hydroformylation of 1,2-diphenylethyne.



8a 9a 10a

Recycle	Conversion (%)	**9a** (%)	**9a** (*E*/*Z*)	**10a** (%)
1	83.9	79.5	94.9	4.4
2	83.4	79.1	97.2	4.3
3	85.5	79.4	94.3	6.1
4	84.5	77.4	92.0	7.1
5	82.6	73.6	93.2	9.0
6	84.6	73.7	84.1	10.9
7	83.0	72.4	80.1	10.6
8	84.5	73.6	81.4	10.9
9	83.5	72.2	93.8	11.3

10	85.2	73.7	92.6	11.5

7. ^{13}C and ^{31}P MAS NMR spectra of compound POL-BINAPa&PPh_3

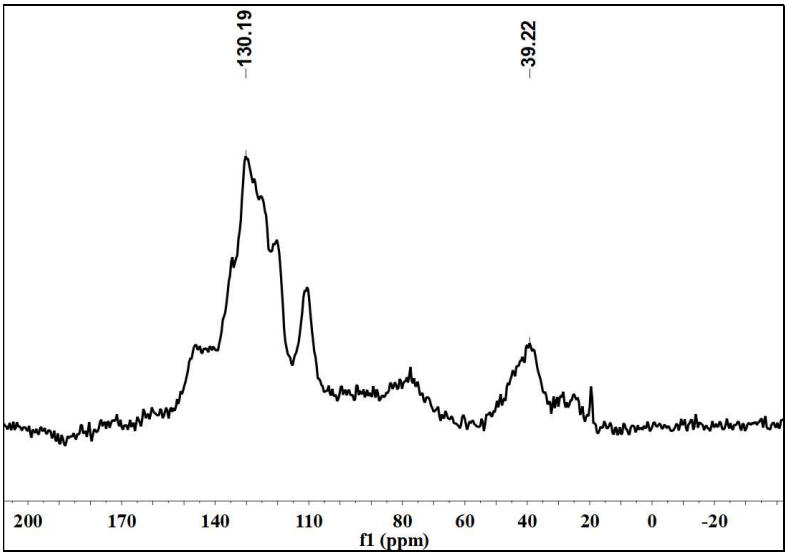


Figure S1. ^{13}C MAS NMR spectra of compound Rh/POL-BINAPa&PPh_3

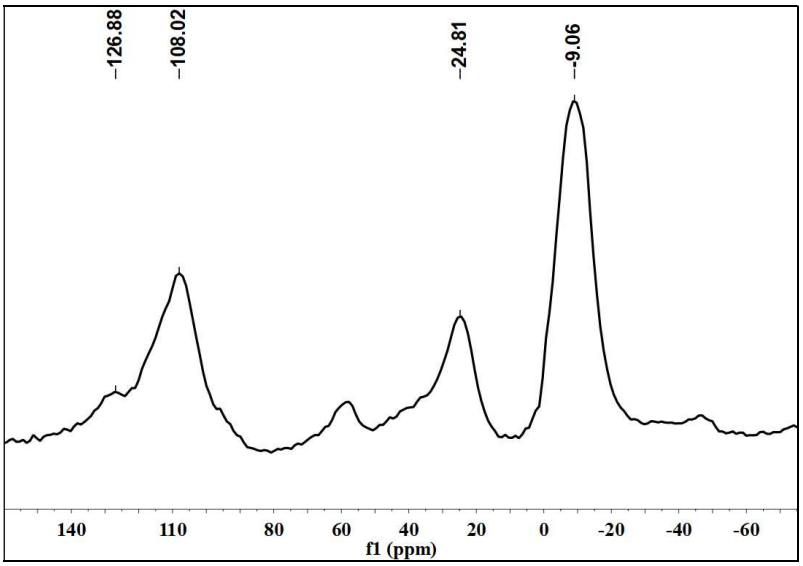


Figure S2. ^{31}P MAS NMR spectra of compound Rh/POL-BINAPa&PPh_3

8. Nitrogen sorption isotherms of POL-BINAPa&PPh_3 and Rh/POL-BINAPa&PPh_3

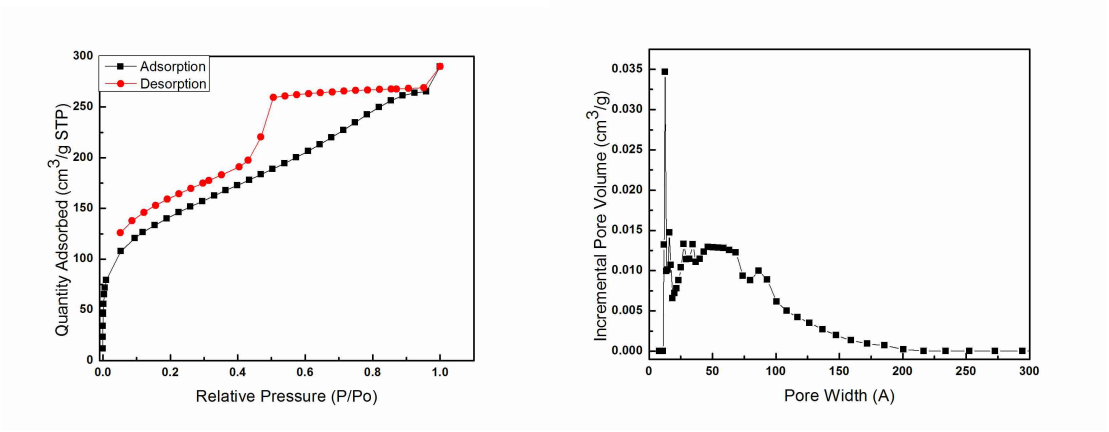


Figure S3. Nitrogen sorption isotherm and pore size distribution of POL-BINAPa&PPh_3

Pore size distribution is calculated from non-local density functional theory (NLDFT). The Brunauer-Emmett-Teller (BET) surface area and pore volume of POL-BINAPa &PPh_3 are 518.8 m^2/g and 0.42 cm^3/g, respectively.

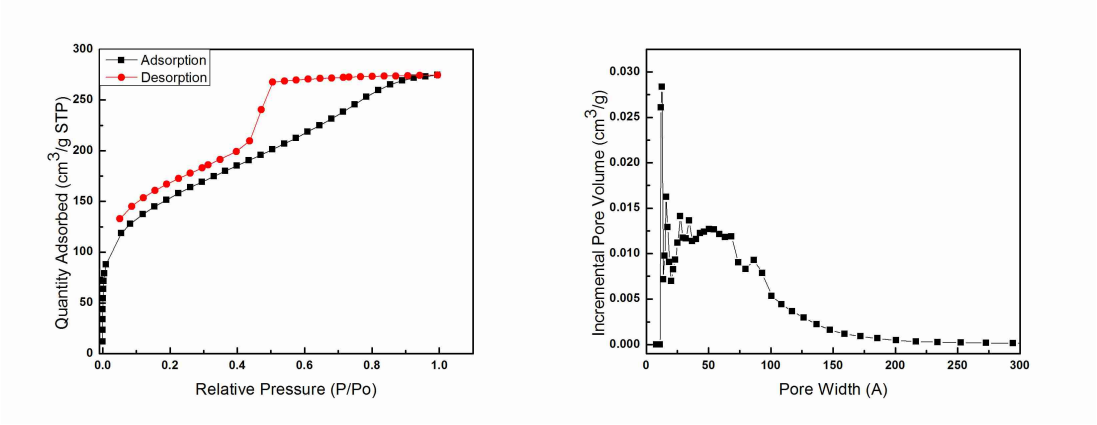


Figure S4. Nitrogen sorption isotherms and pore size distribution of Rh/POL-BINAPa&PPh_3

Pore size distribution is calculated from non-local density functional theory (NLDFT). The Brunauer-Emmett-Teller (BET) surface area and pore volume of Rh/POL-BINAPa &PPh_3 are 492.2 m^2/g and 0.41cm^3/g, respectively.

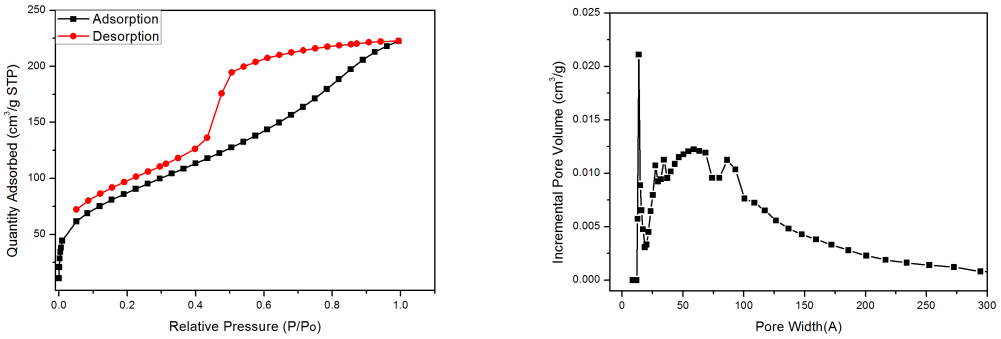


Figure S5. Nitrogen sorption isotherms and pore size distribution of the recovered Rh/POL-BINAPa&PPh_3.

Pore size distribution is calculated from non-local density functional theory (NLDFT). The Brunauer-Emmett-Teller (BET) surface area and pore volume of Rh/POL-BINAPa &PPh_3 are 317.86 m^2/g and 0.34cm^3/g, respectively.

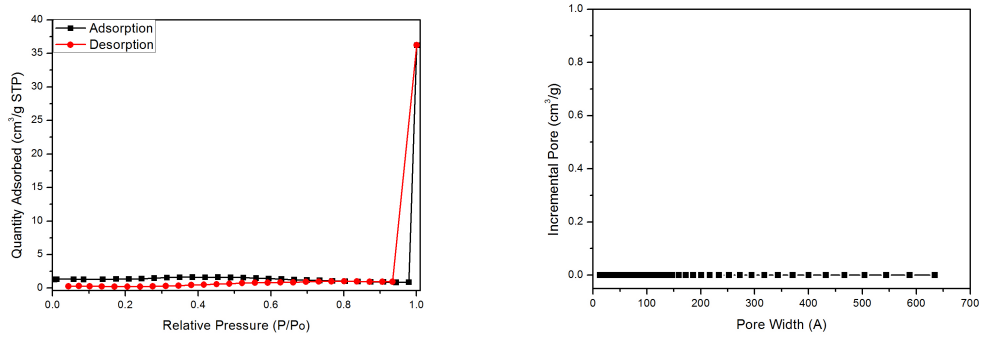


Figure S6. Nitrogen sorption isotherm and pore size distribution of POL-BINAPa&PPh_3 (vBINAPa:vPPh_3 = 1:1.5)

Pore size distribution is calculated from non-local density functional theory (NLDFT). The Brunauer-Emmett-Teller (BET) surface area and pore volume of Rh/POL-BINAPa &PPh_3 are 4.52 m^2/g and 0.0013 cm^3/g, respectively.

9. XPS spectra of POL-BINAPa&PPh_3, Rh/POL-BINAPa&PPh_3 and the recovered catalyst.

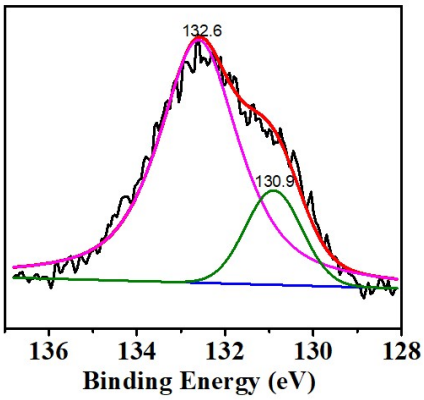


Figure S7. P2p XPS spectra of POL-BINAPa&PPh_3

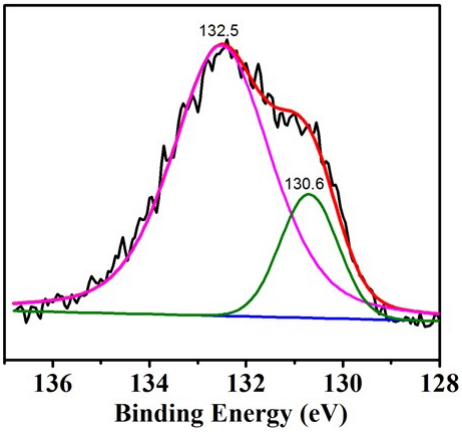


Figure S8. P2p XPS spectra of Rh/POL-BINAPa&PPh_3

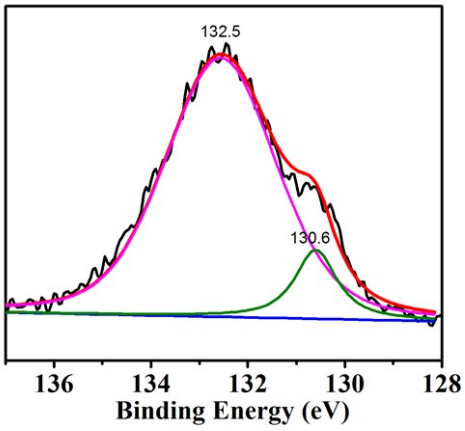


Figure S9. P2p XPS spectra of the recovered Rh/POL-BINAPa&PPh_3

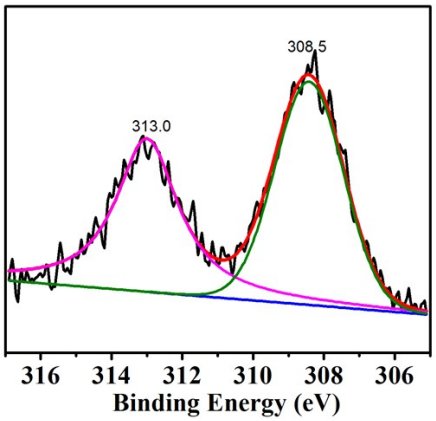


Figure S10. $Rh3d_{3/2}$ and $Rh3d_{5/2}$ XPS spectra of Rh/POL-BINAPa&PPh_3

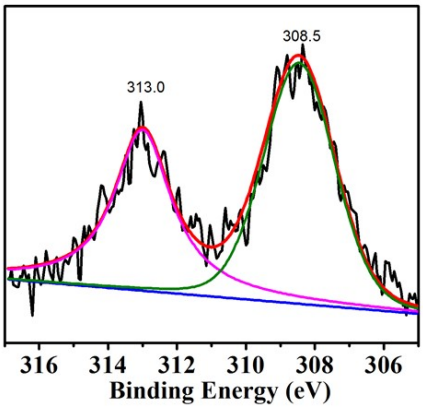


Figure S11. $Rh3d_{3/2}$ and $Rh3d_{5/2}$ XPS spectra of the recovered Rh/POL-BINAPa&PPh_3

10. FT-IR spectra of POL-BINAPa&PPh_3 Rh/POL-BINAPa&PPh_3 and the recovered catalyst.

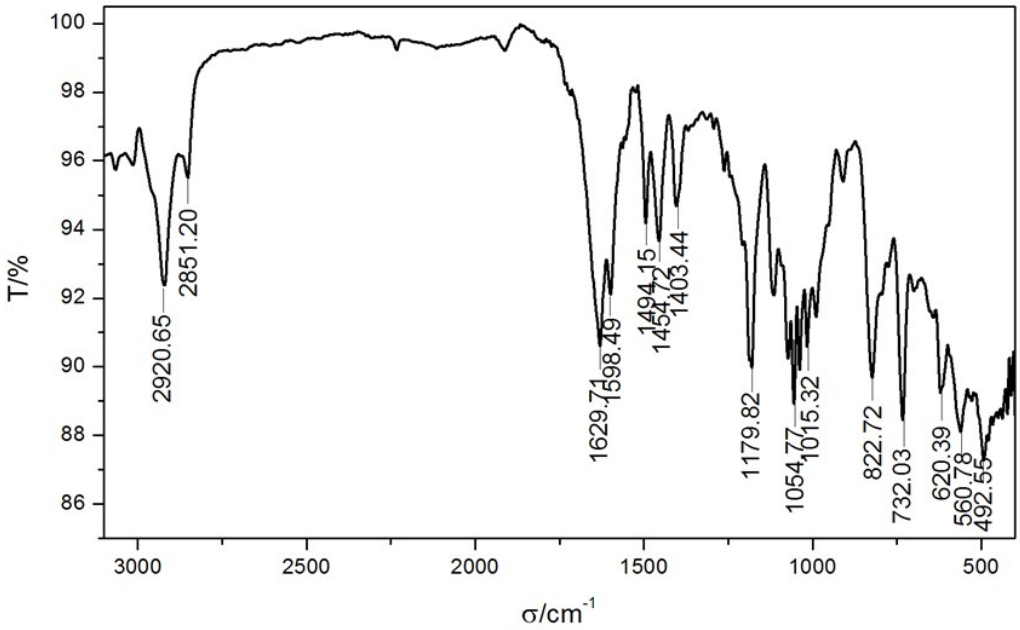


Figure S12. FT-IR spectra of POL-BINAPa&PPh_3

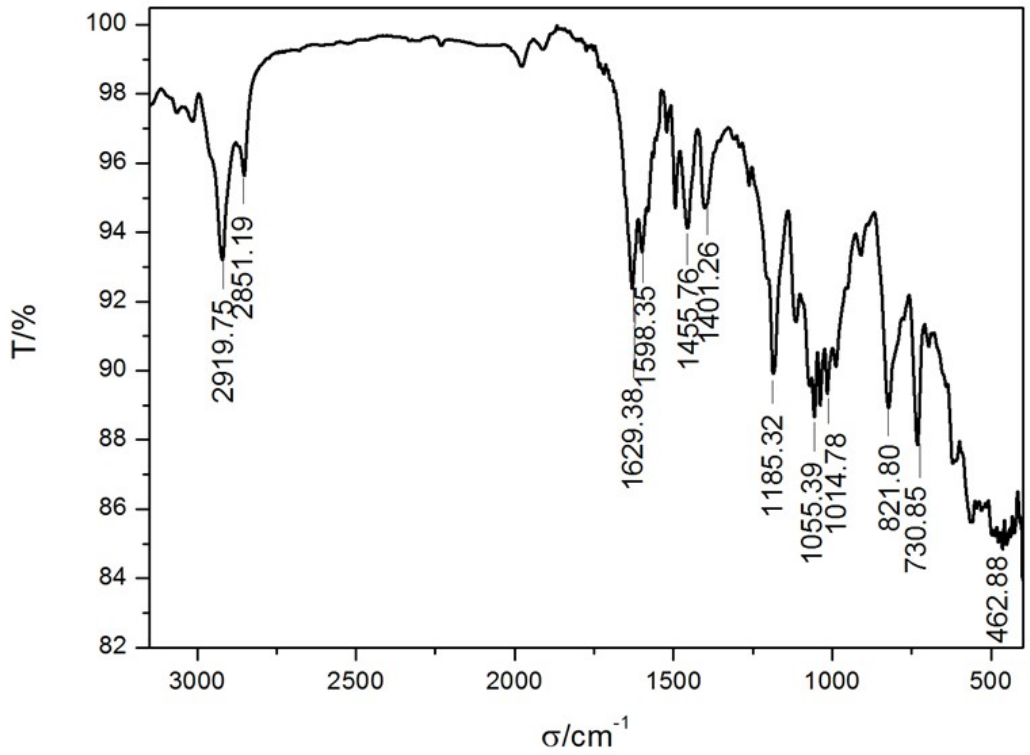


Figure S13. FT-IR spectra of Rh/POL-BINAPa&PPh_3

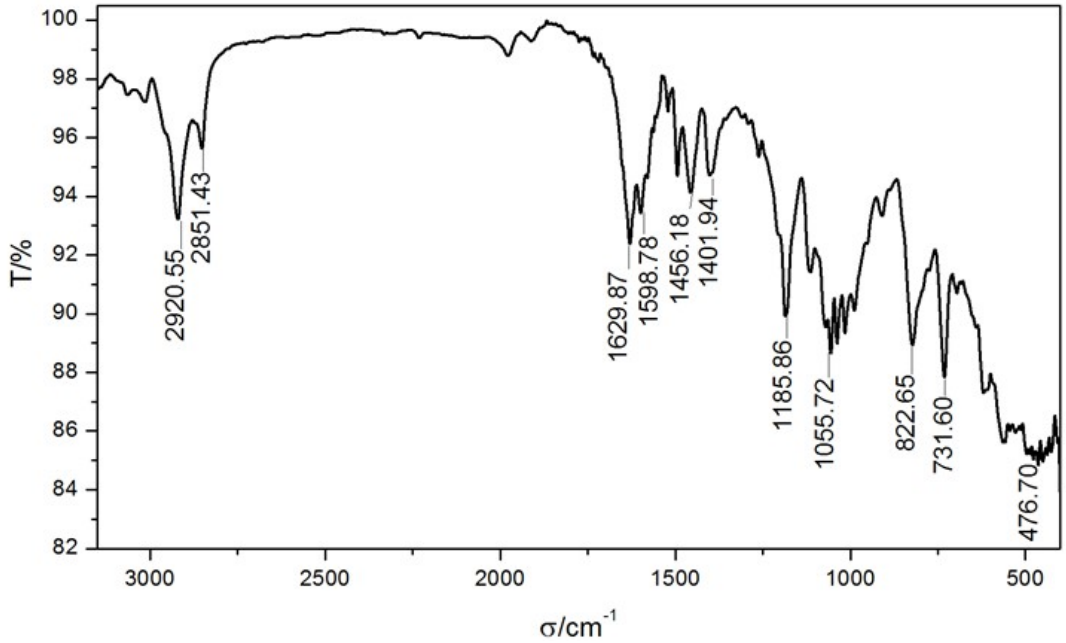


Figure S14. FT-IR spectra of the recovered Rh/POL-BINAPa&PPh_3

11. SEM and TEM images of Rh/POL-BINPa&PPh_3

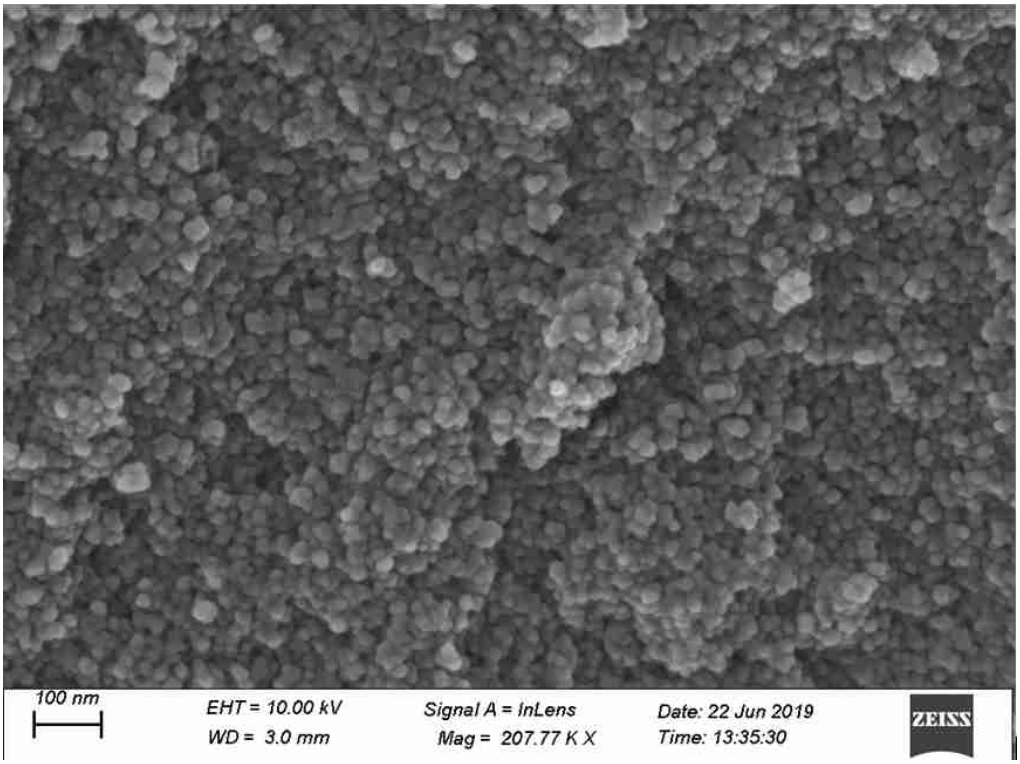
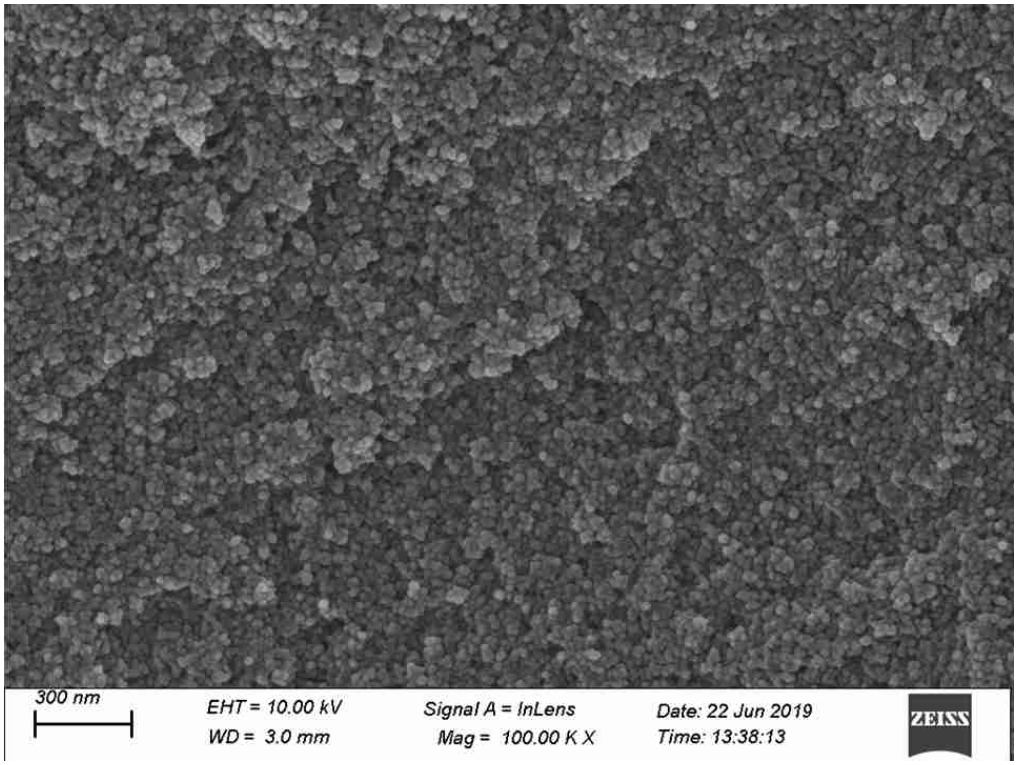
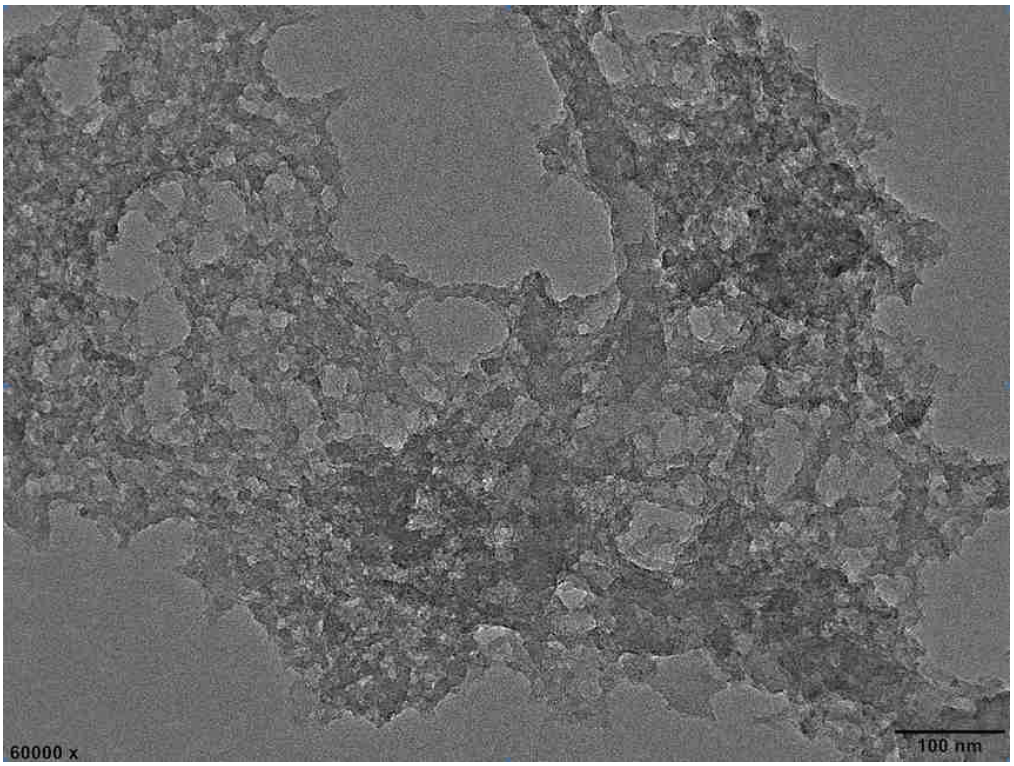
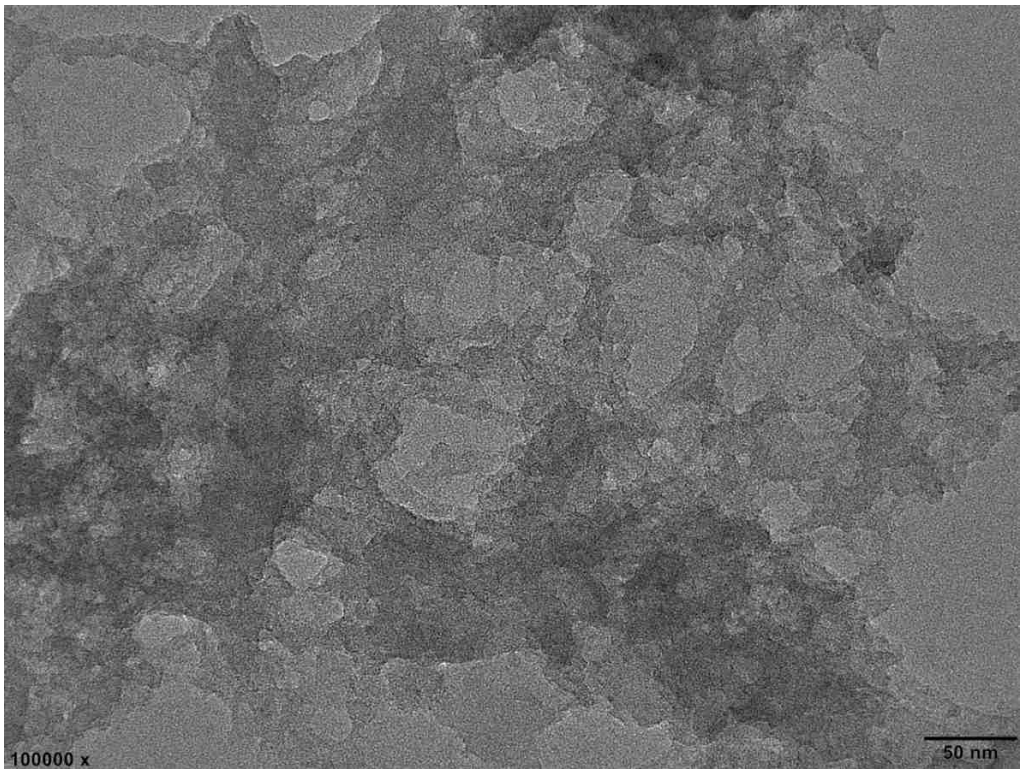


Figure S15. SEM images of Rh/POL-BINAPa&PPh_3.




60000 x
100 nm


100000 x
50 nm

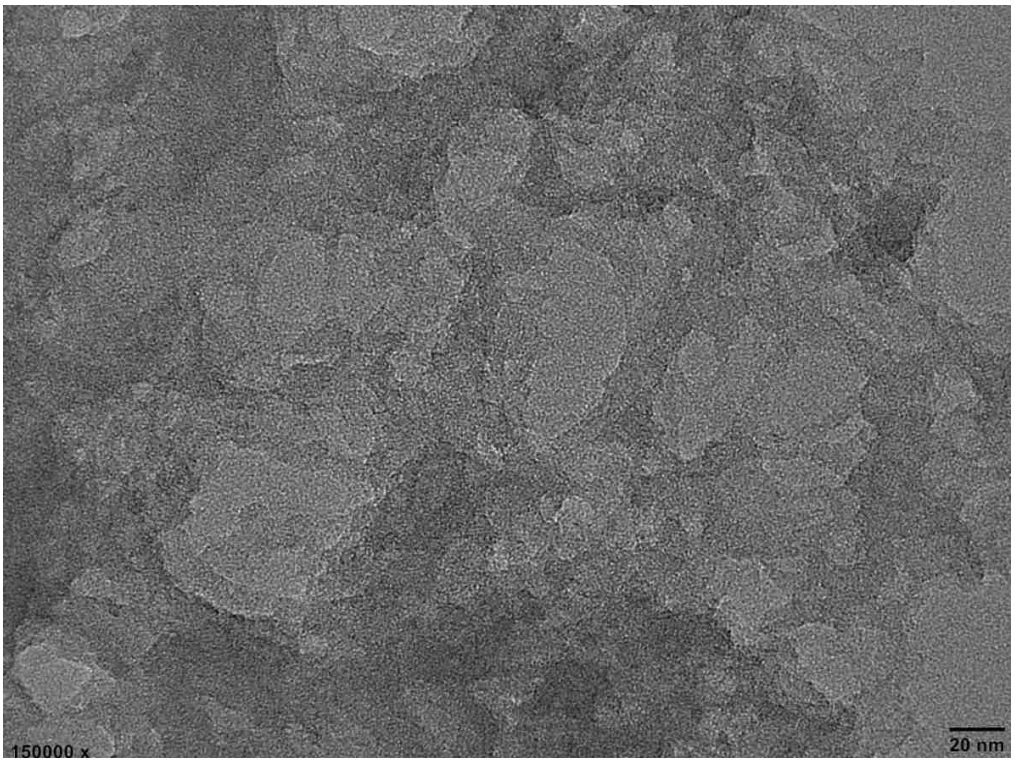
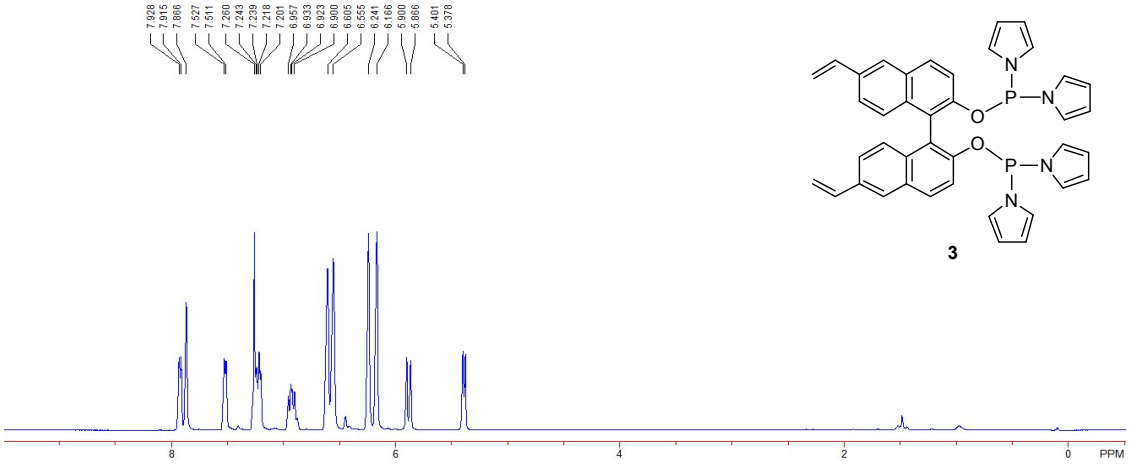
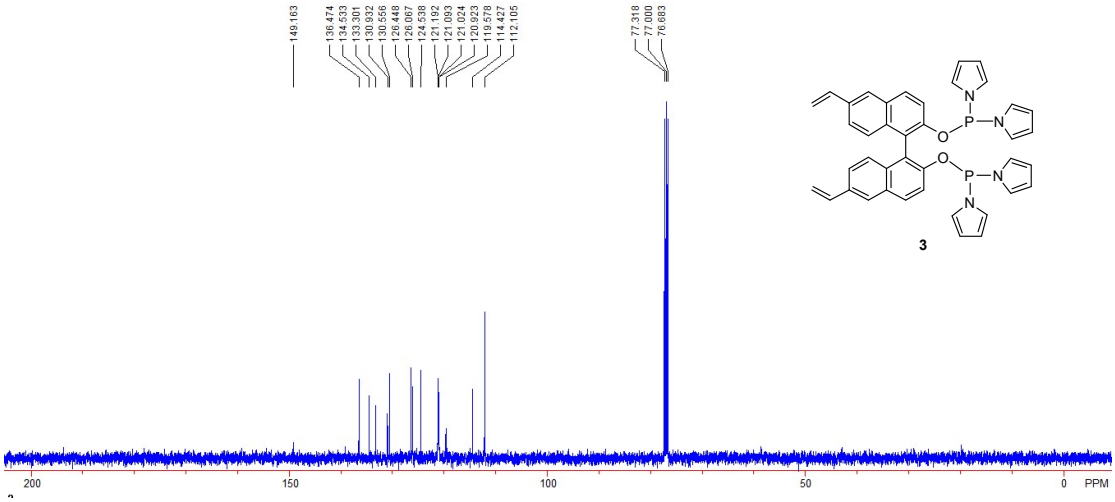
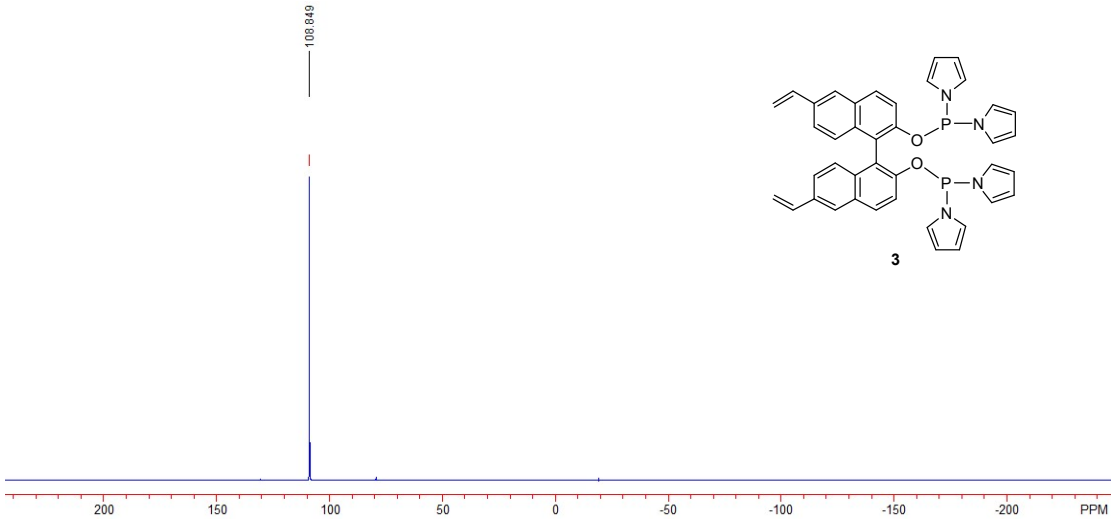


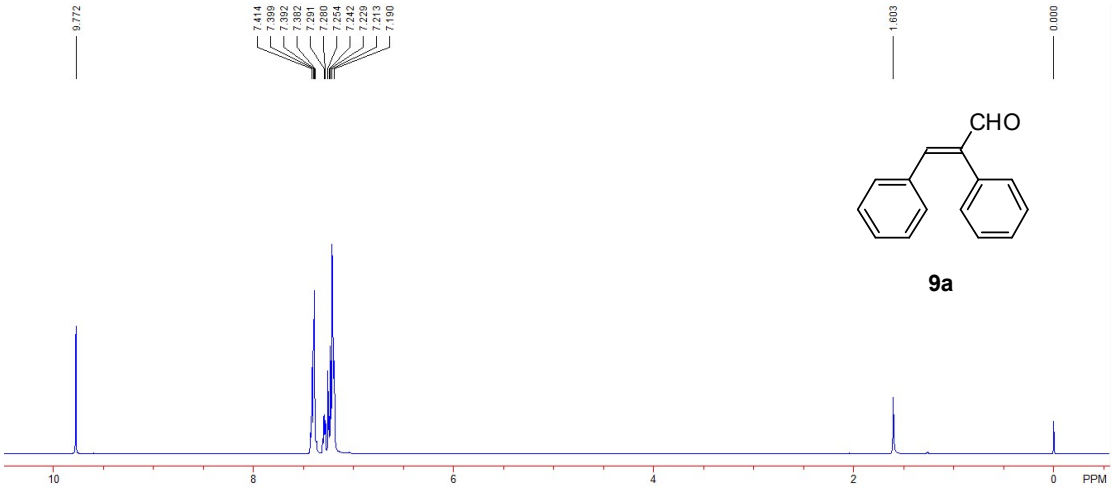
Figure S16. TEM images of Rh/POL-BINAPa&PPh_3.

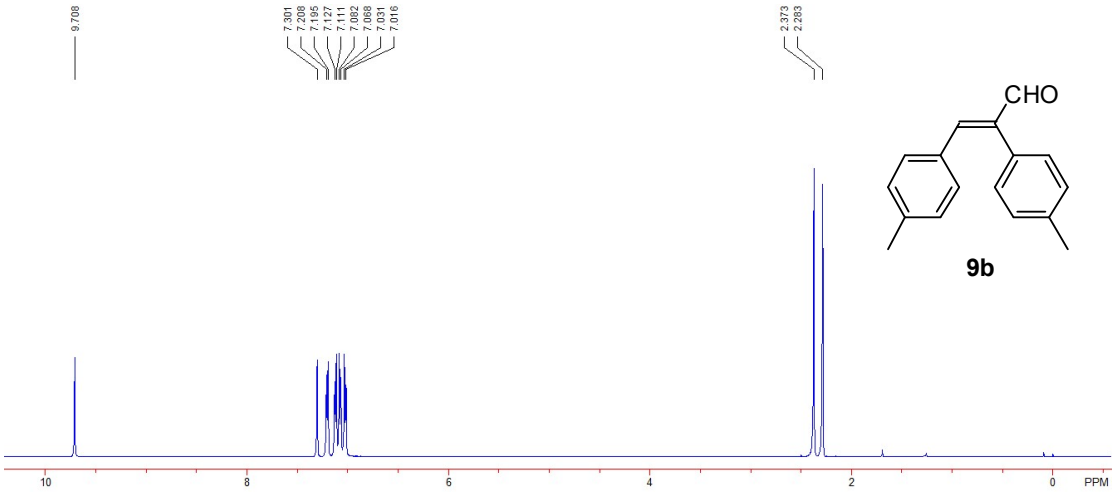
12. NMR spectra of compounds 3 and 9a-9m.

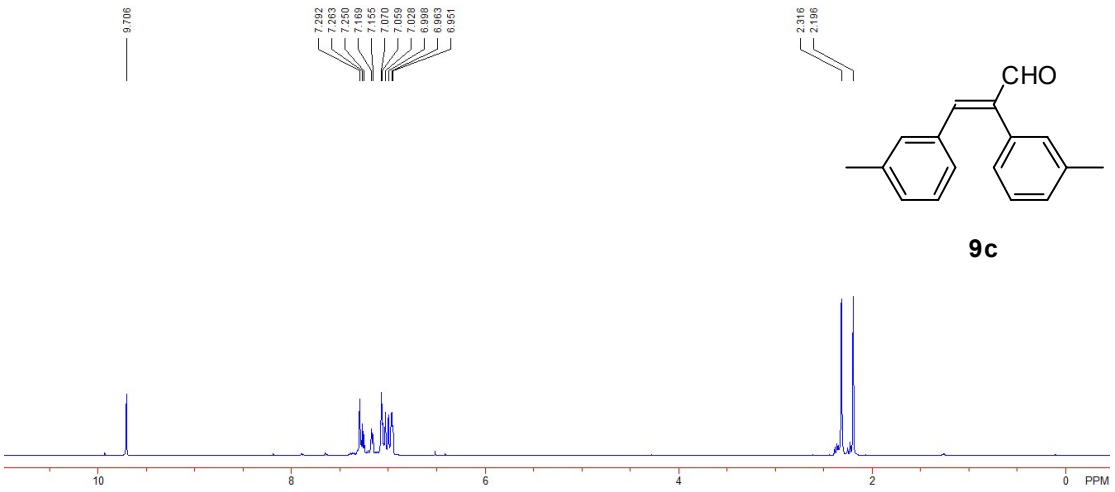


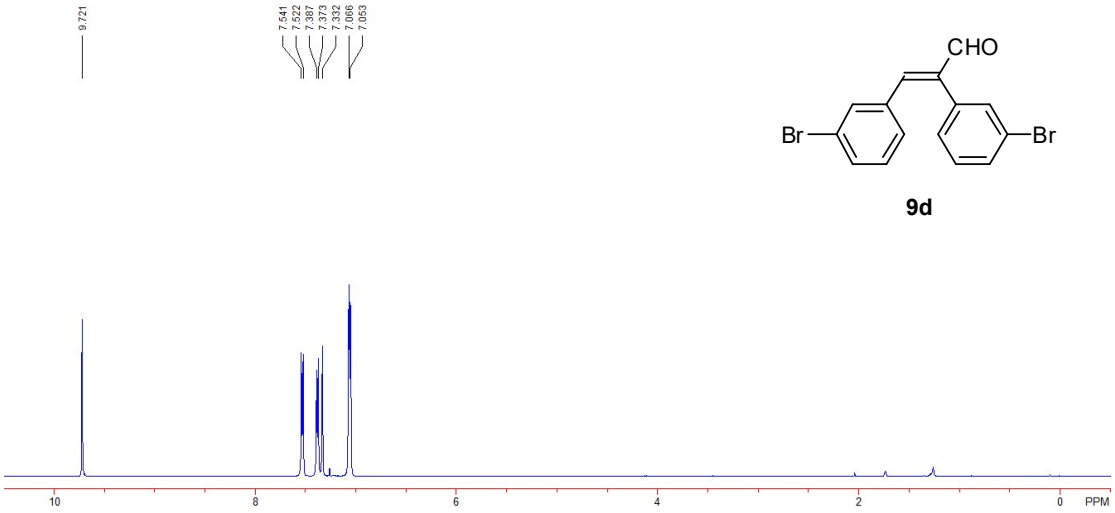




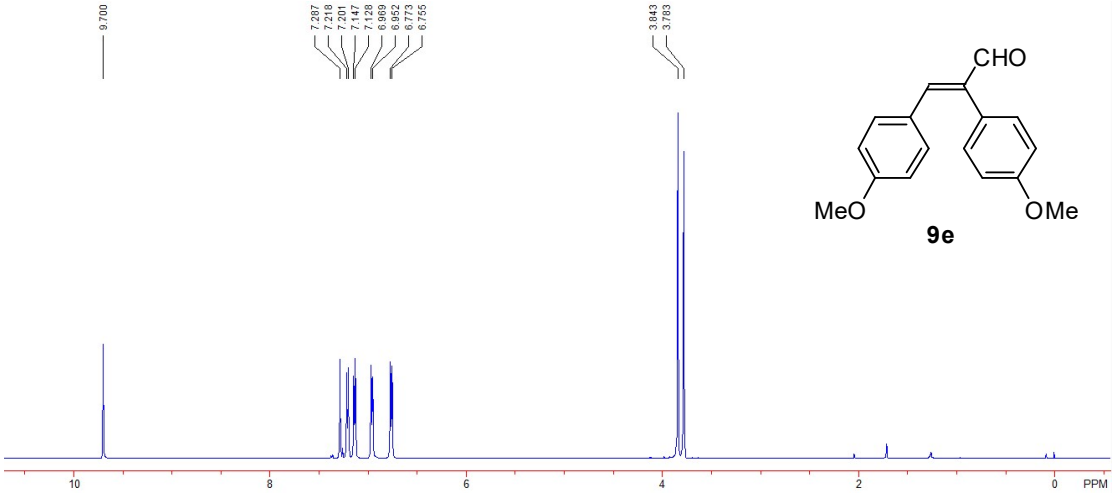

9.772
7.414
7.399
7.392
7.382
7.291
7.280
7.254
7.242
7.229
7.213
7.190
1.603
0.000
CHO
9a
10
8
6
4
2
0
PPM


9.708
7.301
7.208
7.195
7.127
7.111
7.082
7.068
7.031
7.016
2.373
2.283
CHO
9b
10
8
6
4
2
0
PPM

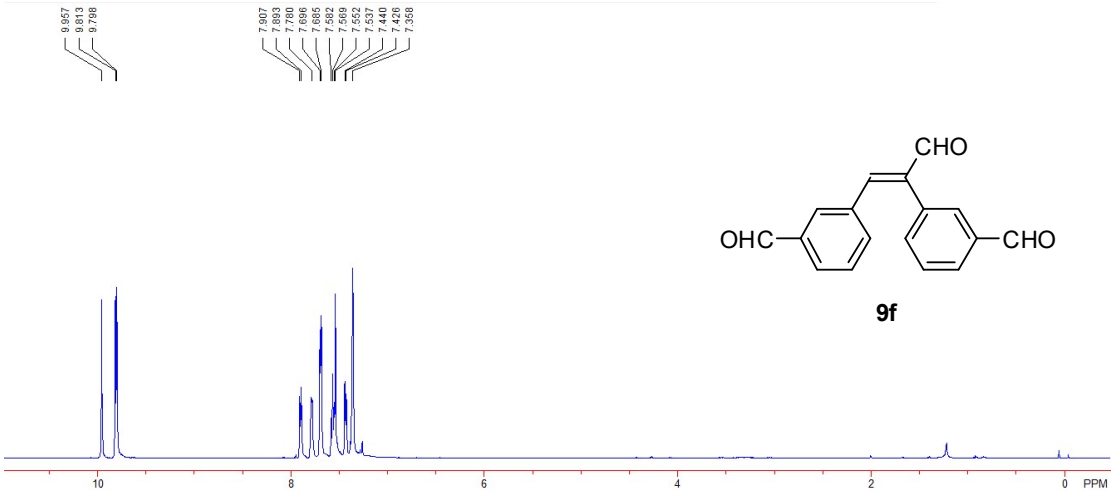

9.706
7.292
7.263
7.250
7.169
7.155
7.070
7.059
7.028
6.998
6.963
6.951
2.316
2.196
CHO
9c
10
8
6
4
2
0
PPM


9.721
7.541
7.522
7.387
7.373
7.332
7.066
7.053
CHO
Br
Br
10
8
6
4
2
0
PPM

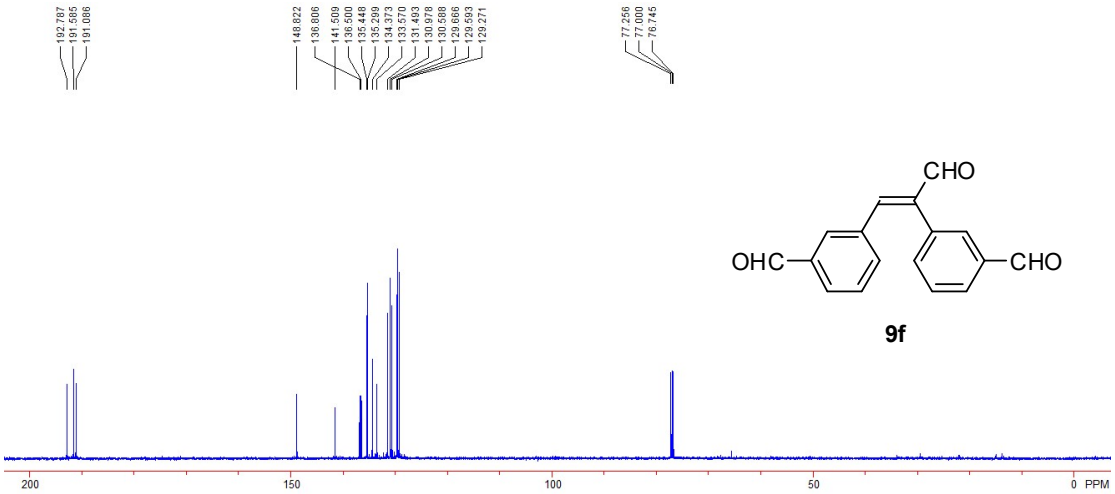
9d


9.700
7.287
7.218
7.201
7.147
7.128
6.969
6.952
6.773
6.755
3.843
3.783
CHO
MeO
OMe
10
8
6
4
2
0
PPM

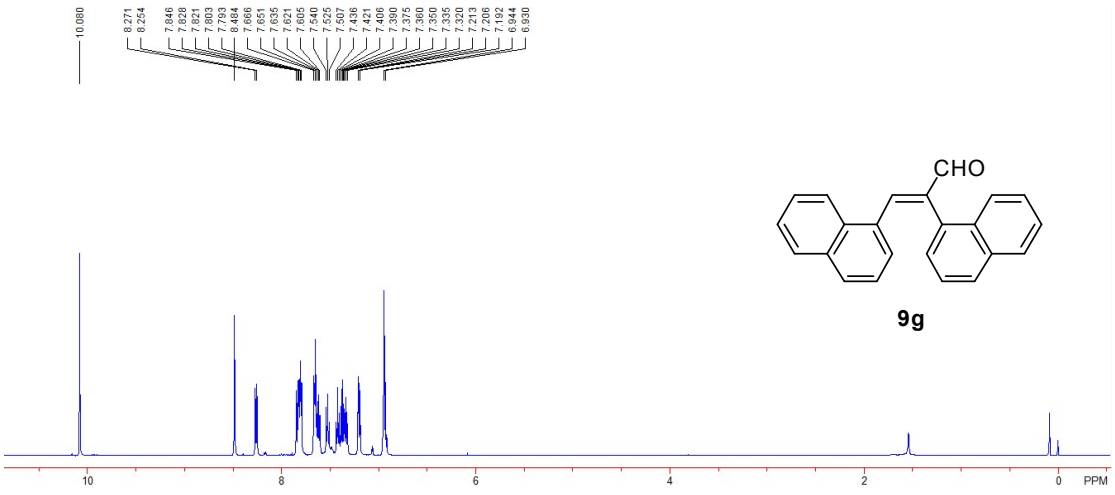
9e


9.957
9.813
9.798
7.907
7.893
7.780
7.696
7.685
7.582
7.569
7.552
7.537
7.440
7.426
7.358
CHO
OHC
CHO
10
8
6
4
2
0
PPM

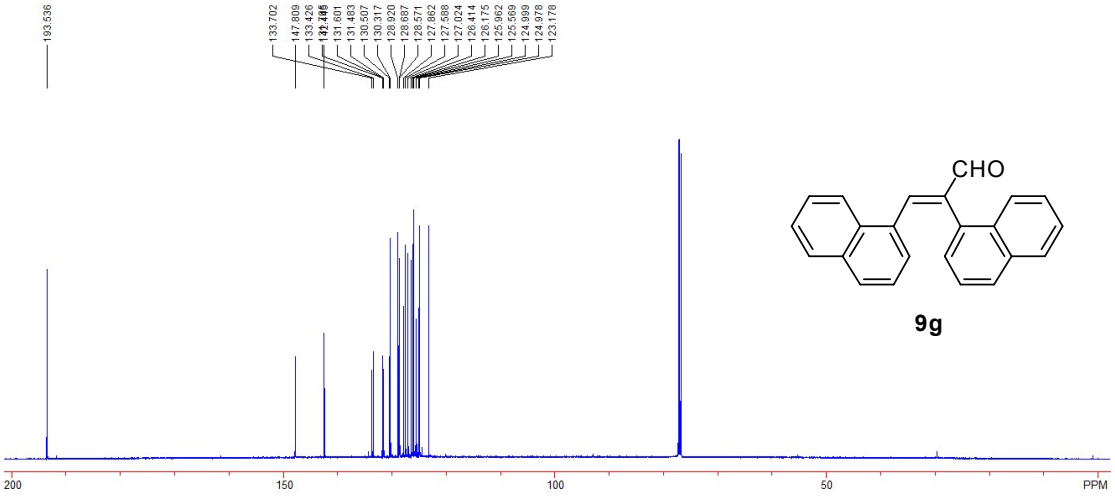
9f


192.787
191.585
191.086
148.822
136.806
141.509
136.500
135.448
135.299
134.373
133.570
131.493
130.978
130.588
129.666
129.593
129.271
77.256
77.000
76.745
CHO
OHC
CHO
200
150
100
50
0 PPM

9f


10.080
8.271
8.254
7.846
7.828
7.821
7.803
7.793
8.484
7.666
7.651
7.635
7.621
7.605
7.540
7.525
7.507
7.436
7.421
7.406
7.390
7.375
7.360
7.350
7.335
7.320
7.213
7.206
7.192
6.944
6.930
CHO
10
8
6
4
2
0 PPM

9g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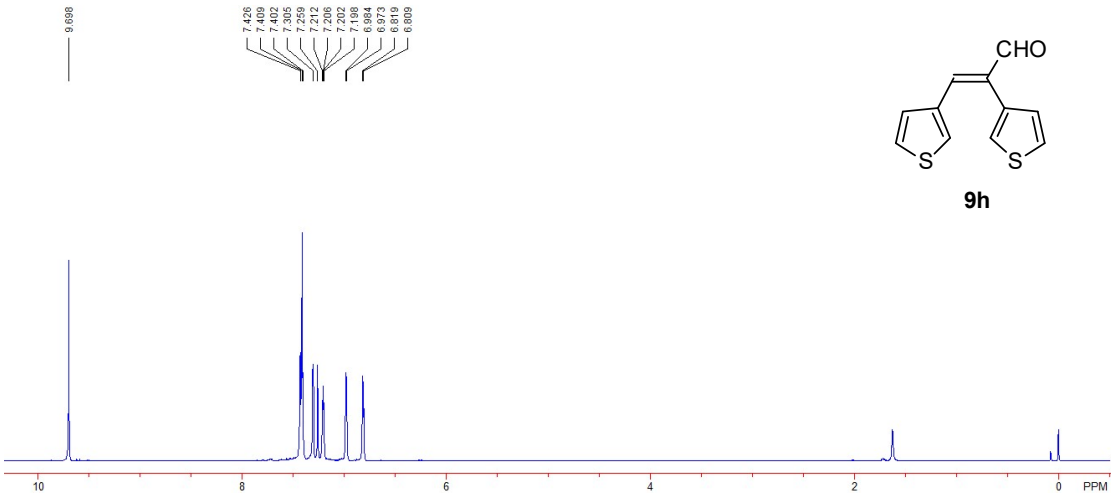
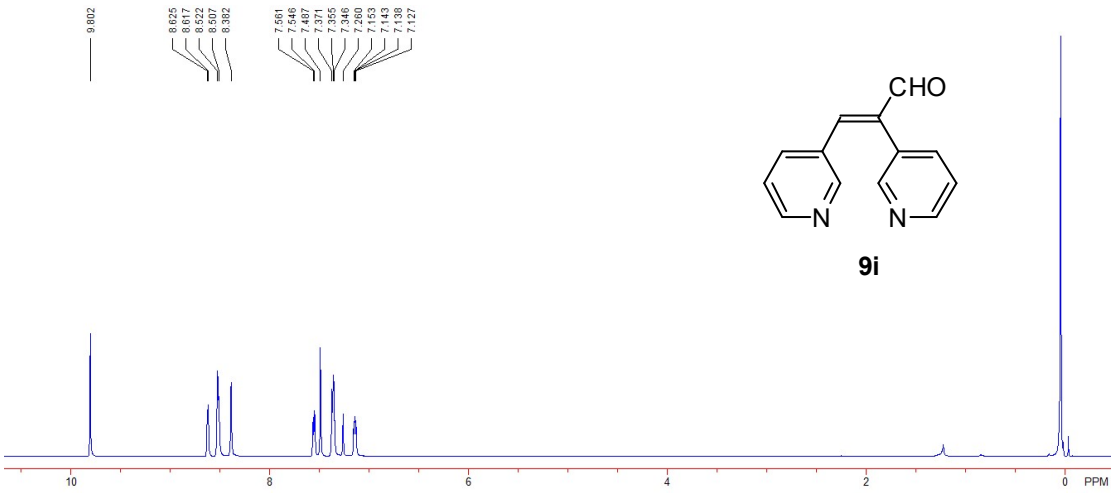
133.702
147.809
133.426
131.601
131.483
130.507
130.317
128.920
128.687
128.571
127.862
127.588
127.024
126.414
126.175
125.962
125.569
124.999
124.978
123.178
CHO
200
150
100
50
PPM

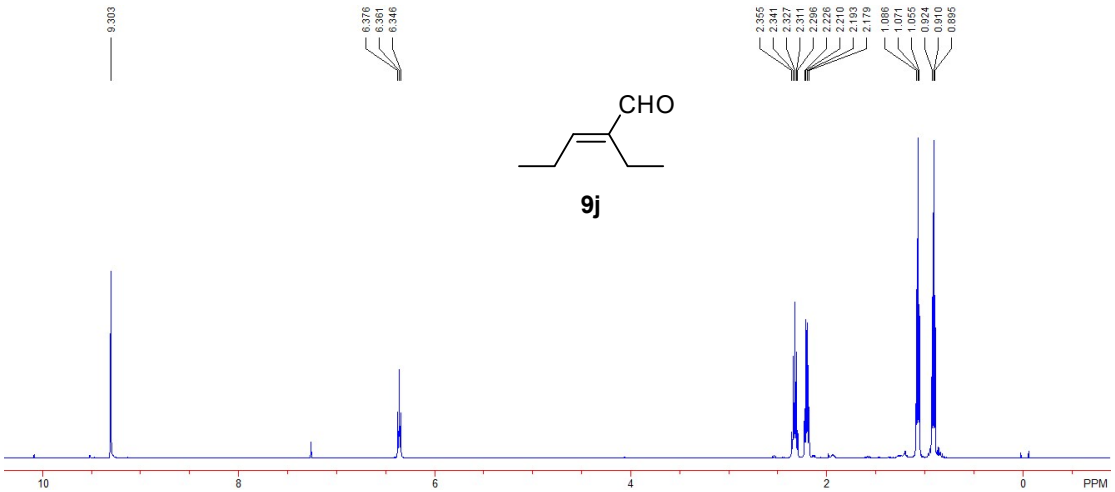
9g


9.698
7.426
7.409
7.402
7.305
7.259
7.212
7.206
7.202
7.198
6.984
6.973
6.819
6.809
CHO
S
S
10
8
6
4
2
0
PPM

9h


9.802
8.625
8.617
8.522
8.507
8.302
7.561
7.546
7.487
7.371
7.355
7.346
7.260
7.153
7.143
7.138
7.127
CHO
N
N
10
8
6
4
2
0
PPM

9i


9.303
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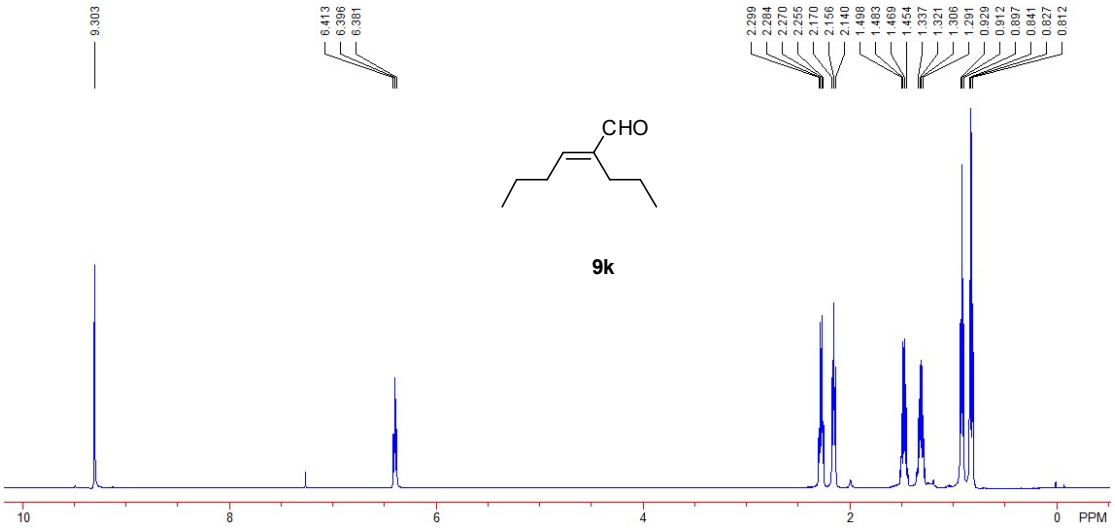
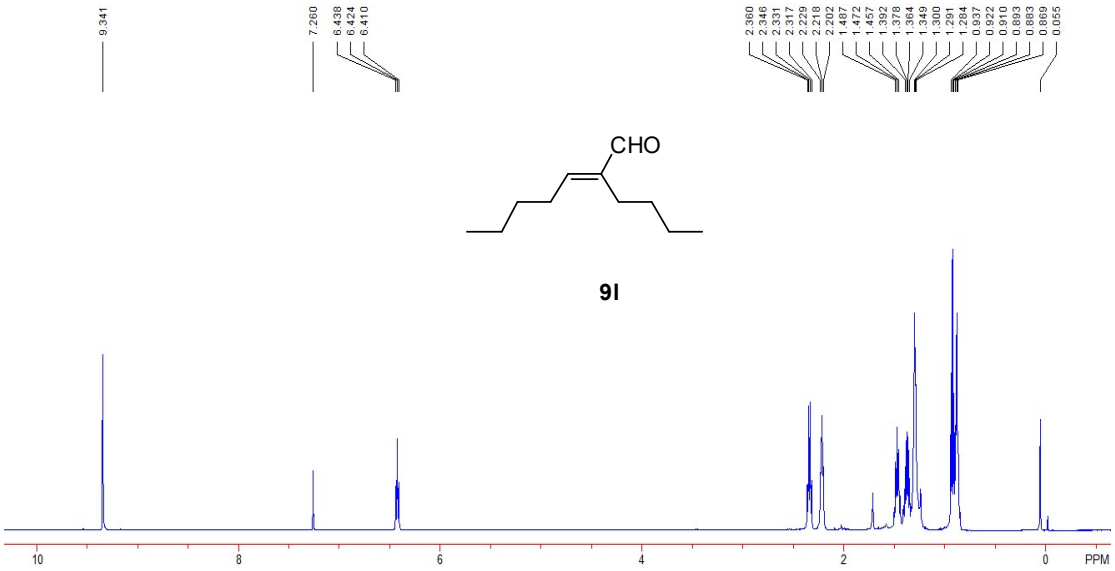
6.361
6.346
2.355
2.341
2.327
2.311
2.296
2.226
2.210
2.193
2.179
1.086
1.071
1.055
0.924
0.910
0.895
CHO
10
8
6
4
2
0
PPM

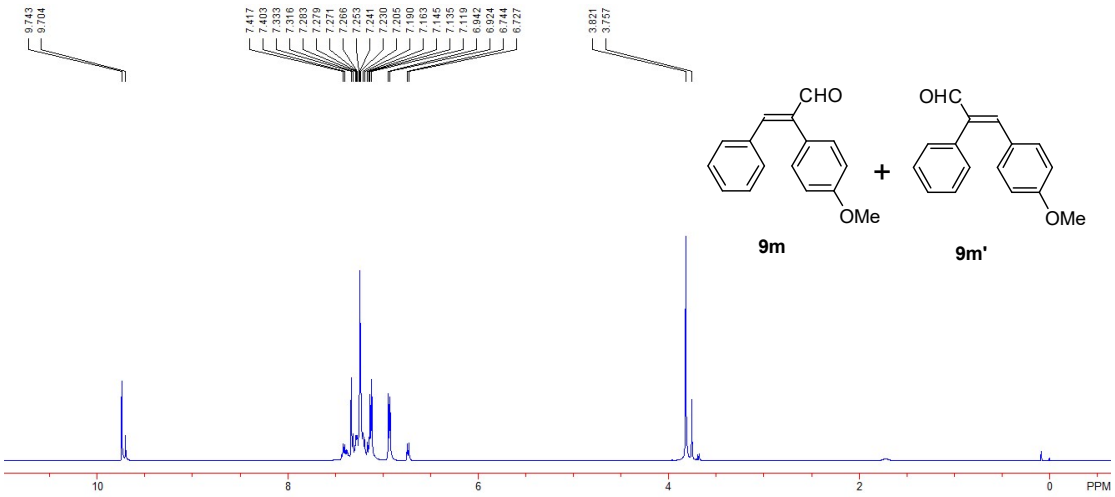
9j


9.303
6.413
6.396
6.381
2.299
2.284
2.270
2.255
2.170
2.156
2.140
1.498
1.483
1.469
1.454
1.337
1.321
1.306
1.291
0.929
0.912
0.897
0.841
0.827
0.812
CHO
10
8
6
4
2
0
PPM

9k


9.341
7.260
6.438
6.424
6.410
2.360
2.346
2.331
2.317
2.229
2.218
2.202
1.467
1.457
1.392
1.378
1.364
1.349
1.300
1.291
1.284
0.937
0.922
0.910
0.893
0.883
0.869
0.055
CHO
10
8
6
4
2
0
PPM

9l

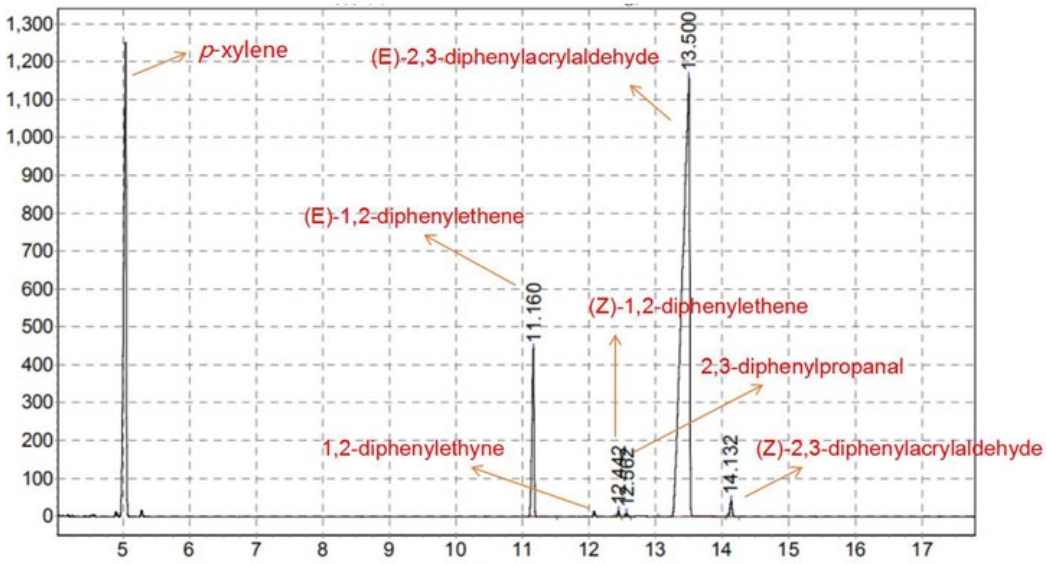

9.743
9.704
7.417
7.403
7.333
7.316
7.283
7.279
7.271
7.266
7.253
7.241
7.230
7.205
7.190
7.163
7.145
7.135
7.119
6.942
6.924
6.744
6.727
3.821
3.757
10
8
6
4
2
0
PPM

CHO
OMe
+
OHC
OMe

9m **9m'**

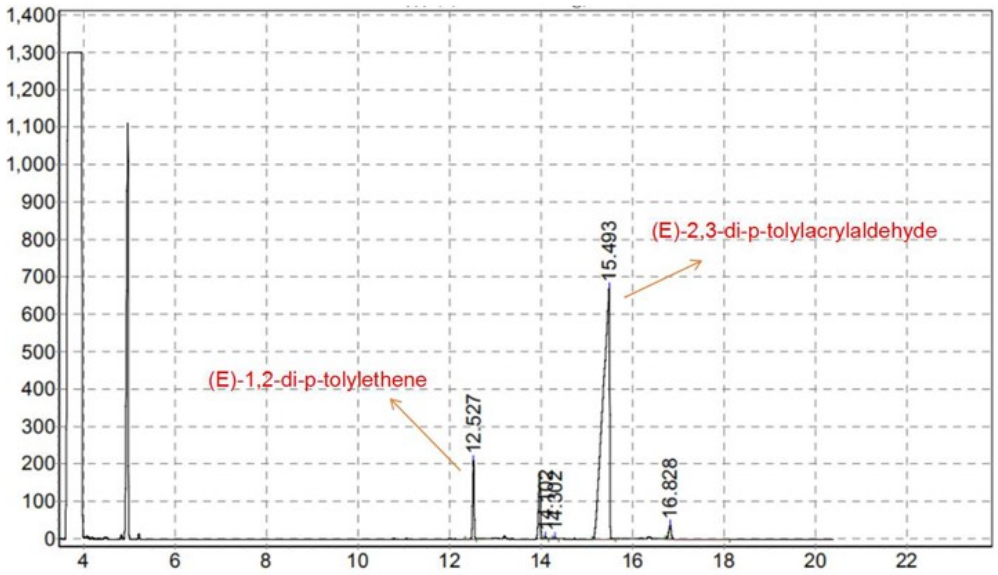
13. GC Data of compounds of 9a, 9b, 9c, 9e, 9f, 9h, 9i, 9j, 9k, 9l, 9n.

9a



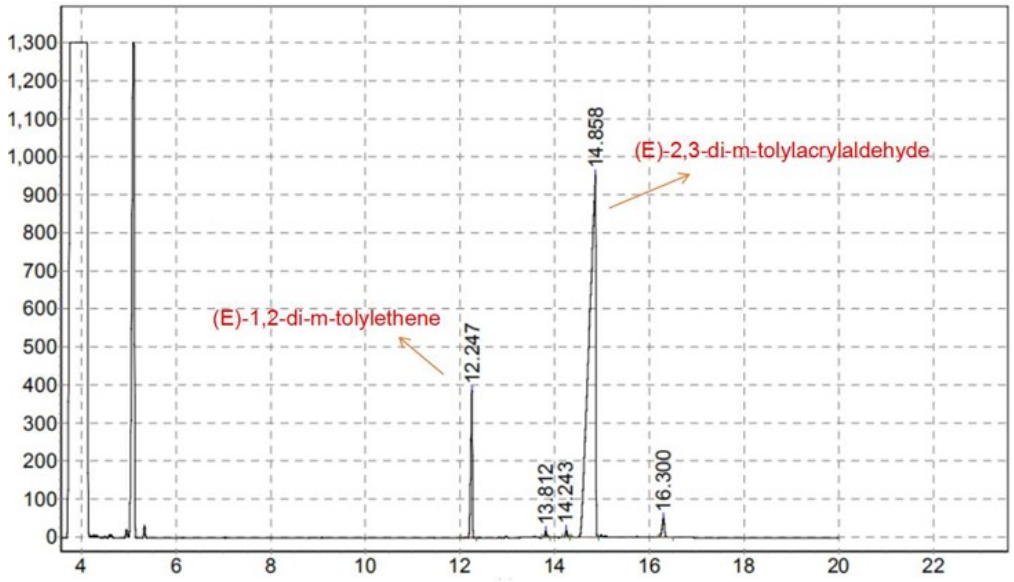
Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		11.160	443571.188	949895.250	9.6111
2		12.442	13993.969	26041.000	0.2635
3		12.562	8525.574	17101.650	0.1730
4		13.500	1159024.250	8795113.000	88.9895
5		14.132	42204.645	95160.898	0.9628
Total			1667319.625	9883311.799	100.0000

9b



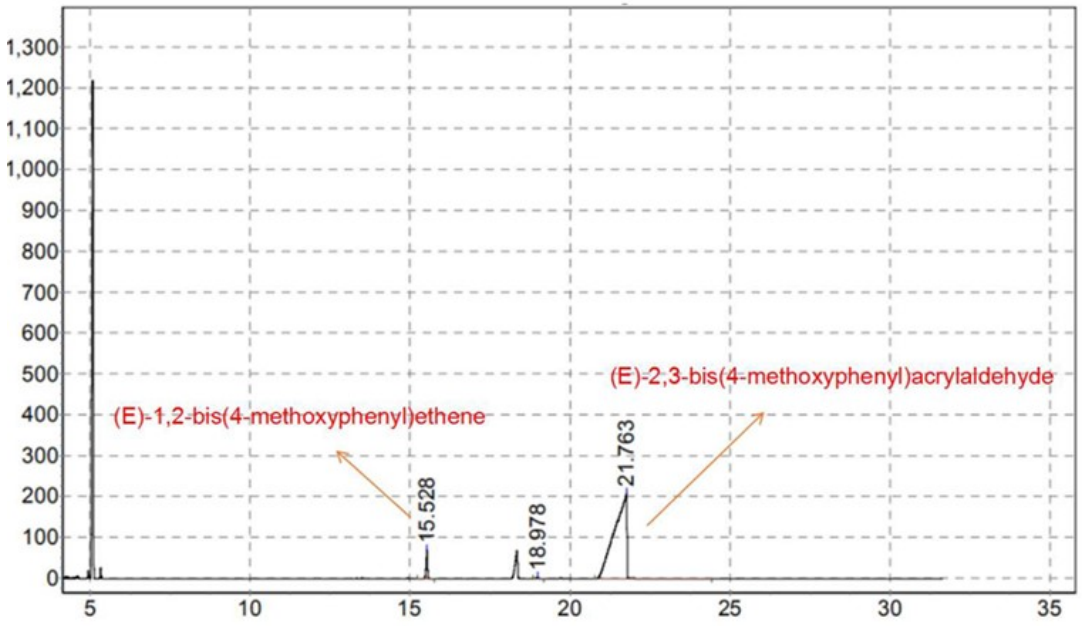
Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		12.527	210879.828	454660.156	6.1042
2		14.102	5140.141	11389.600	0.1529
3		14.302	4574.214	11116.300	0.1492
4		15.493	671315.813	6826006.500	91.6452
5		16.828	37781.520	145127.063	1.9485
Total			929691.515	7448299.618	100.0000

9c



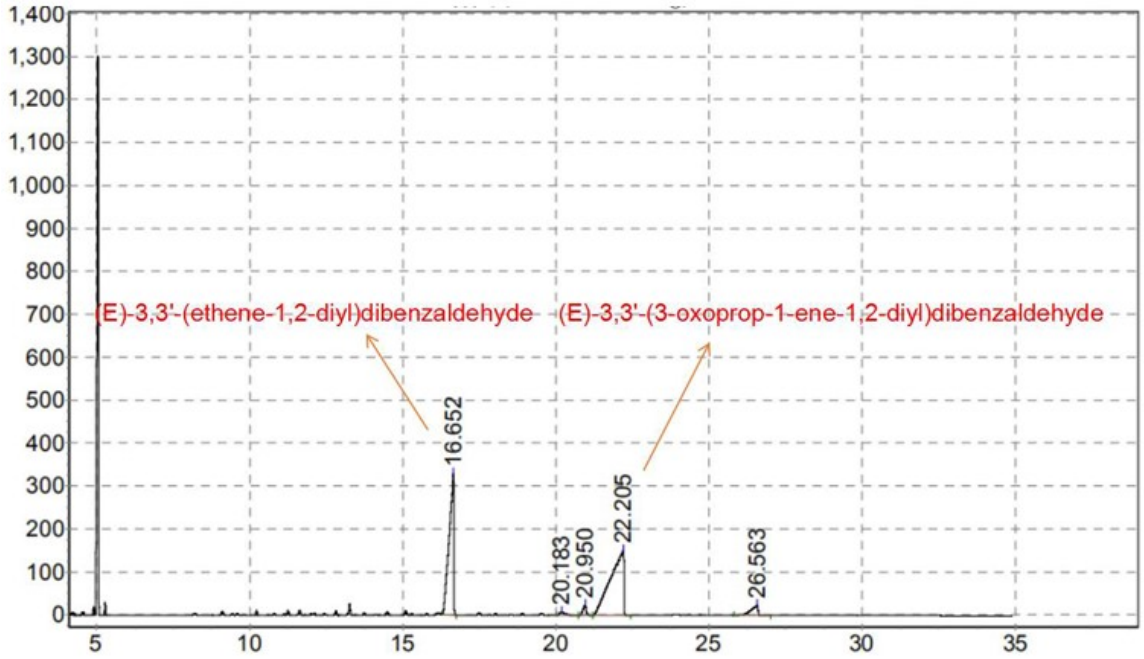
Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		12.247	386797.000	904570.375	8.6349
2		13.812	16138.693	39441.398	0.3765
3		14.243	17902.168	48033.250	0.4585
4		14.858	952810.125	9306044.000	88.8340
5		16.300	50753.941	177675.703	1.6961
Total			1424401.928	10475764.727	100.0000

9e



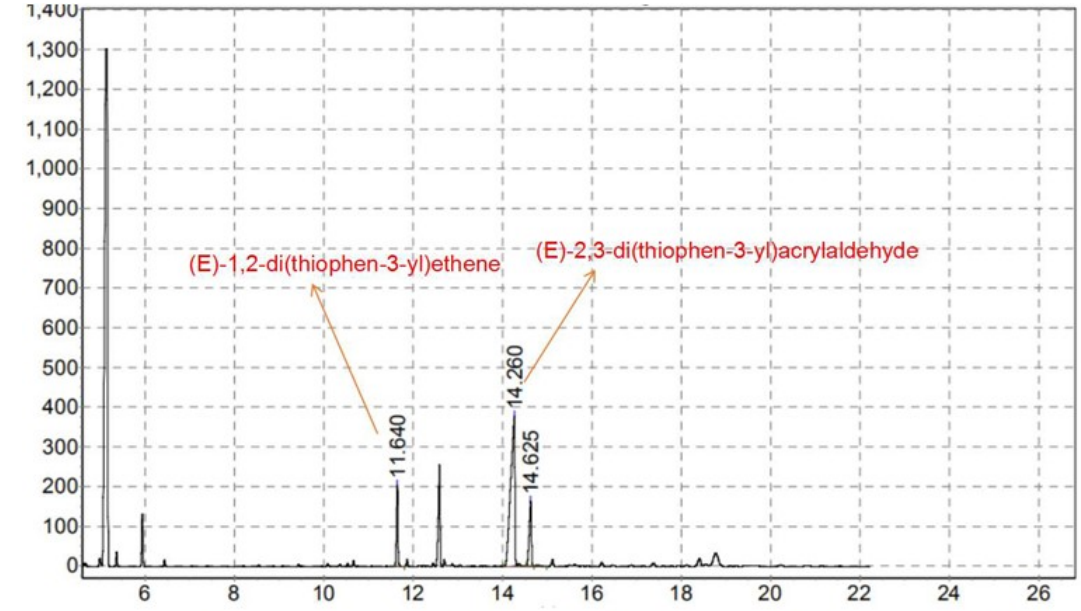
Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		15.528	69794.508	218803.297	3.7443
2		18.978	2531.736	11832.249	0.2025
3		21.763	208511.813	5613028.500	96.0532
Total			280838.056	5843664.046	100.0000

9f



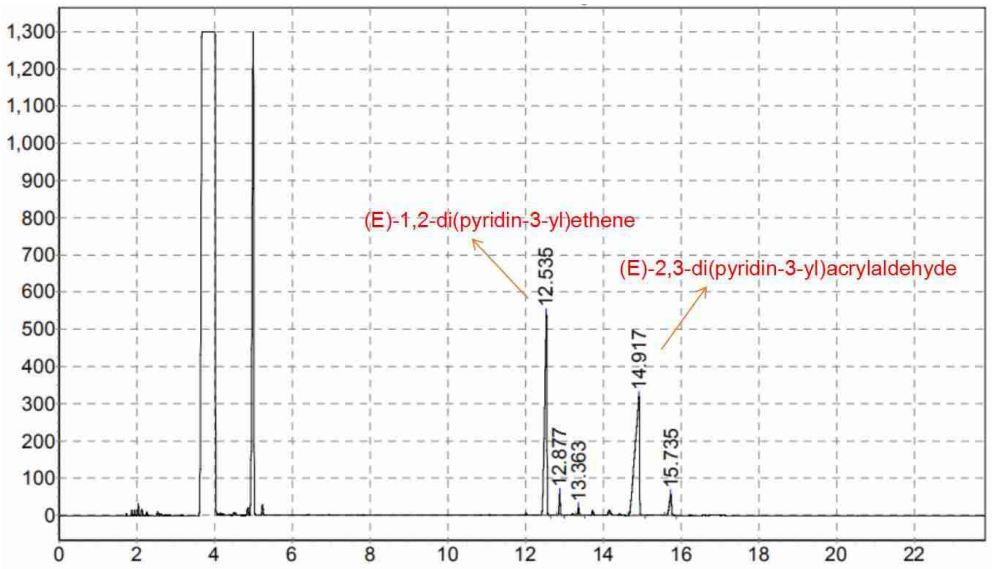
Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		16.652	328604.906	3477364.750	40.0033
2		20.183	7469.380	98562.094	1.1338
3		20.950	23593.496	177951.406	2.0471
4		22.205	151717.516	4561776.500	52.4783
5		26.563	23090.375	377038.156	4.3374
Total			534475.673	8692692.906	100.0000

9h



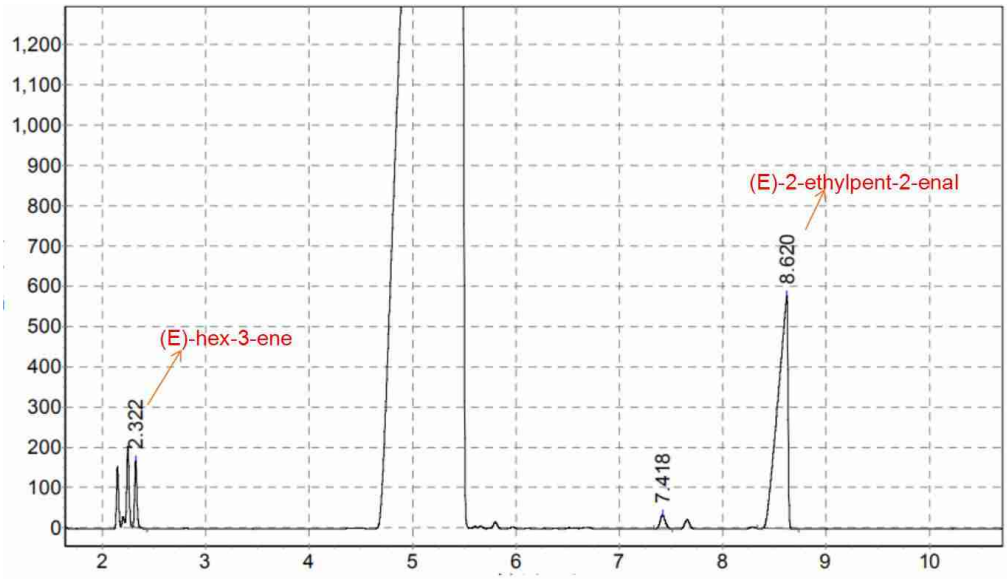
Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		11.640	203880.500	426740.719	10.5879
2		14.260	378259.563	3060020.000	75.9223
3		14.625	163636.109	543703.063	13.4898
Total			745776.172	4030463.781	100.0000

9i



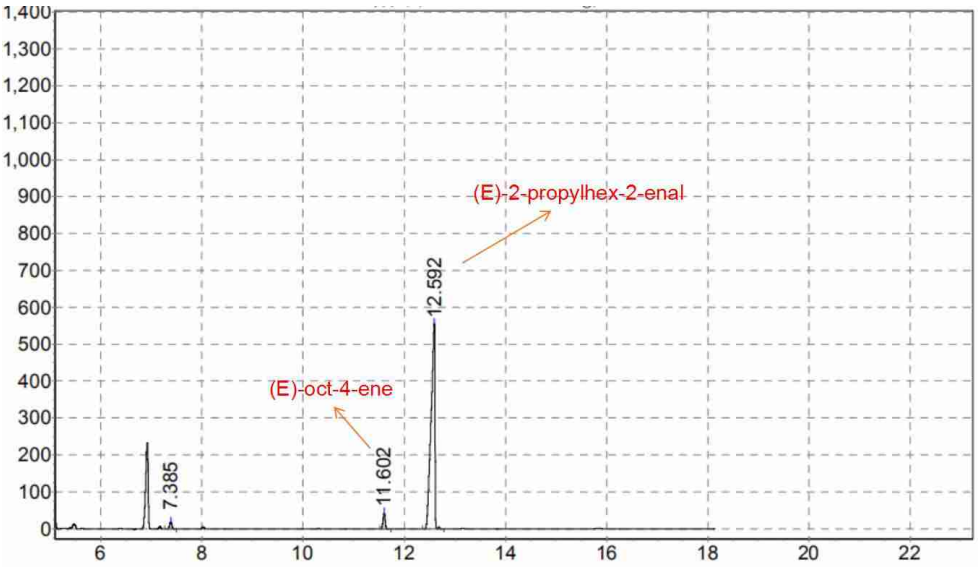
Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		12.535	542806.875	2150490.500	42.6059
2		12.877	58885.520	114675.148	2.2720
3		13.363	21394.604	47627.449	0.9436
4		14.917	320443.219	2526169.750	50.0489
5		15.735	55182.871	208439.391	4.1296
Total			998713.088	5047402.238	100.0000

9j



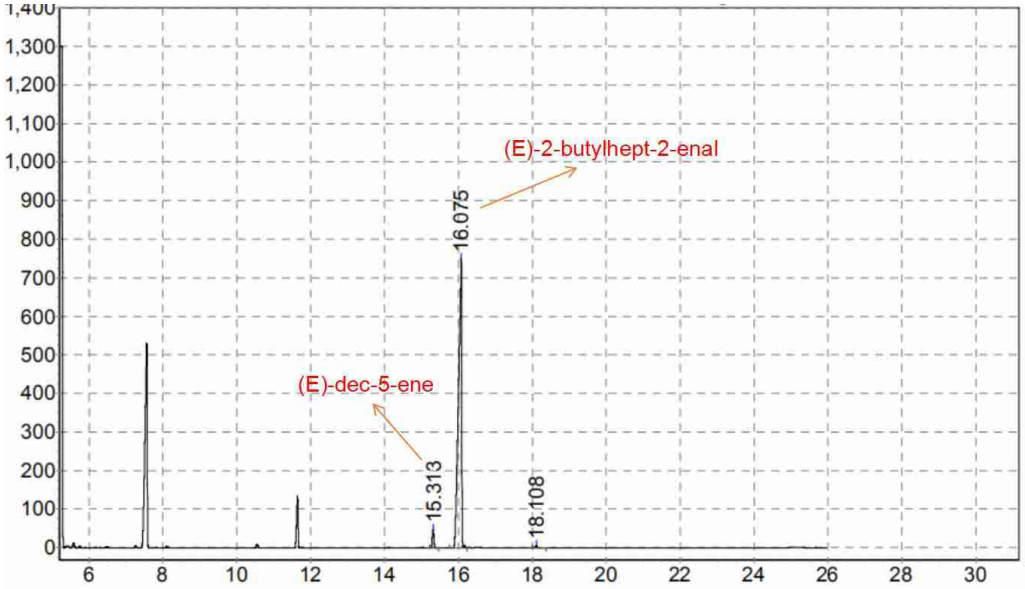
Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		2.322	165701.609	253136.453	5.9090
2		7.418	34336.867	119402.695	2.7872
3		8.620	578830.188	3911368.250	91.3038
Total			778868.664	4283907.398	100.0000

9k



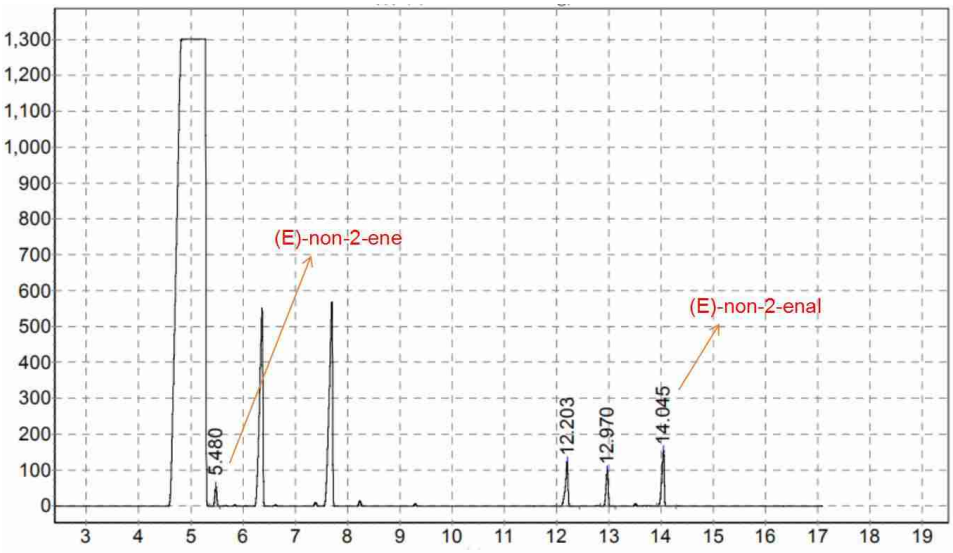
Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		7.385	18951.102	60967.102	1.9517
2		11.602	43570.102	125197.805	4.0079
3		12.592	556860.625	2937576.500	94.0403
Total			619381.828	3123741.406	100.0000

9l



Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		15.313	48870.617	139613.297	3.0042
2		16.075	751521.375	4484146.000	96.4906
3		18.108	6108.319	23477.801	0.5052
Total			806500.311	4647237.098	100.0000

9n



Peak N0.	Peak ID	Ret time	Hight	Area	Area %
1		5.480	54105.355	139325.797	10.5655
2		12.203	124478.969	423869.188	32.1432
3		12.970	99313.219	273284.531	20.7239
4		14.045	155031.906	482209.906	36.5674
Total			432929.449	1318689.422	100.0000

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