Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Designing highly efficient Rh/CPOL-bp&PPh_3 heterogenous catalysts for hydroformylation of internal and terminal olefins

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1. Supporting Figures

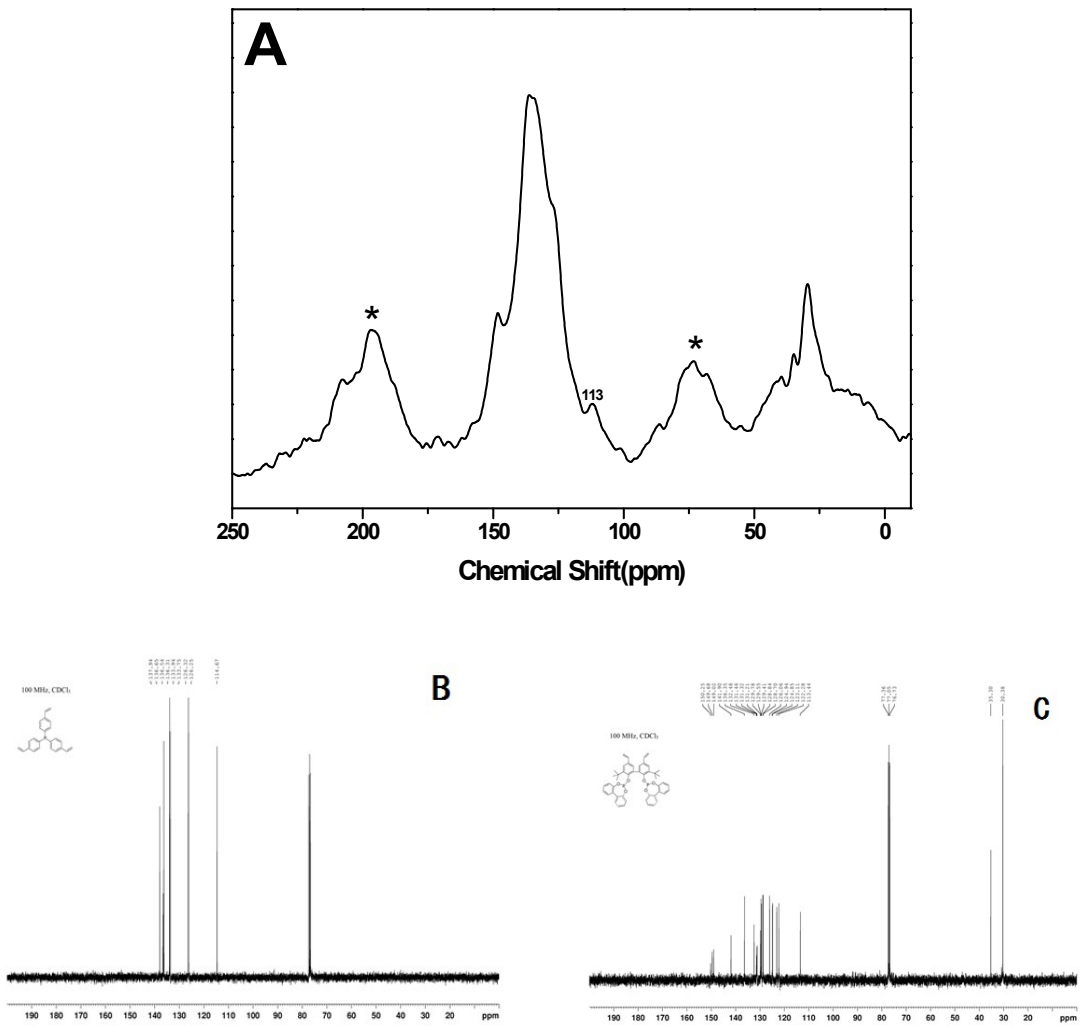
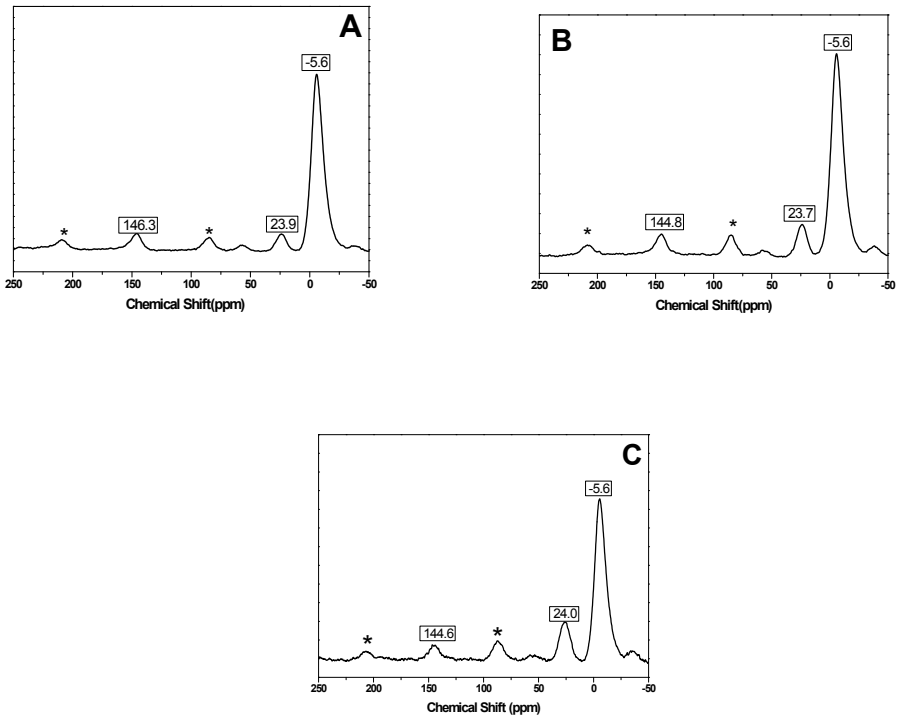


Figure S1. (A) ^{13}C MAS NMR spectrum of CPOL-bp&PPh_3, (B) ^{13}C NMR spectrum of tris(4-vinphenyl)phosphane and (C) ^{13}C NMR spectrum of vinyl biphephos.

The peaks at 113 ppm in CPOL-bp&PPh_3, which can be assigned to unpolymerized vinyl groups, is quite small compared with the corresponding monomers (B, C), indicating that CPOL-bp&PPh_3 has high degree of polymerization. The peaks at * are side bands.



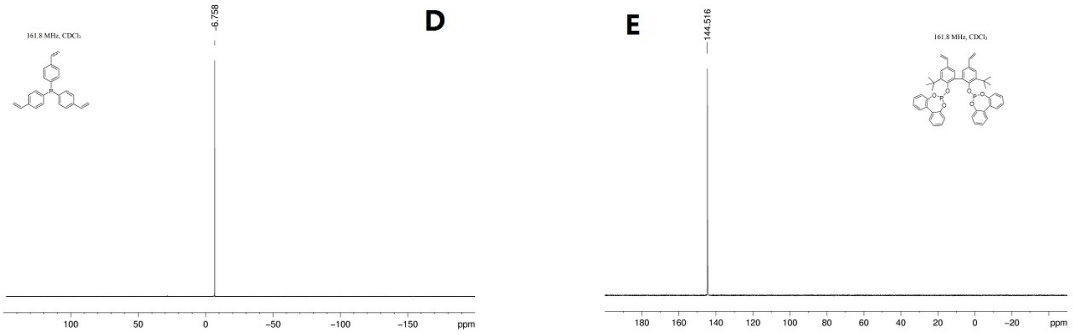


Figure S2. ^{31}P MAS NMR spectra of (A) CPOL-bp&PPh_3, (B) 0.14 % wt Rh/CPOL-bp&PPh_3 and (C) 2.0 % wt Rh/CPOL-bp&PPh_3, ^{31}P NMR spectra of (D) tris(4-vinphenyl)phosphane and (E) vinyl biphephos.

The peaks at * are side bands. The ^{31}P MAS NMR spectrum of fresh CPOL-bp&PPh_3 exhibits an additional small peak at 23.9 ppm corresponding to an oxidation state of phosphorus (P=O), which indicates that slight oxidation of P atom took place during the polymerization. Remarkably, the ^{31}P MAS NMR spectrum of fresh 0.14 % wt Rh/CPOL-bp&PPh_3 shows that the peak at 23.7 ppm could be assigned to both oxidation state of phosphorus (P=O) and those PPh_3 coordinated with Rh as well. 2.0 % wt Rh/CPOL-bp&PPh_3 shows higher peak at 24.0 ppm than 0.14 % wt Rh/CPOL-bp&PPh_3, indicating more PPh_3 units are coordinated with Rh. Besides, compared with the peak at 146.3 ppm in CPOL-bp&PPh_3, 0.14% wt Rh/CPOL-bp&PPh_3 gives relatively low-field peak at 144.8 ppm, 2.0 % wt Rh/CPOL-bp&PPh_3 gives relatively low-field peak at 144.6 ppm. The low-field shift can be ascribed to the biphephos units coordinated with Rh.

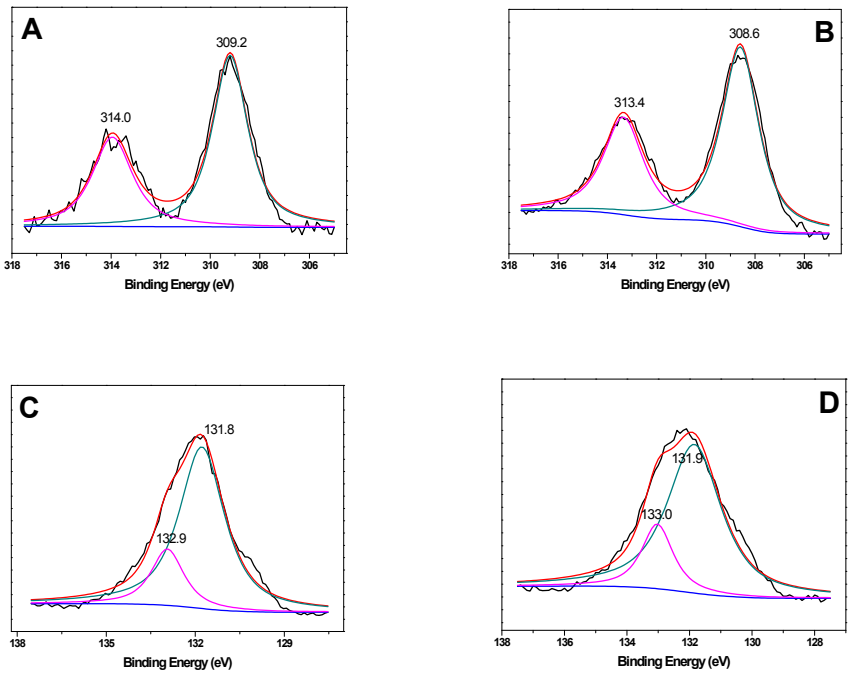


Figure S3. (A) Rh3d XPS spectra of $Rh(CO)_2(acac)$, (B) Rh3d XPS spectra of 0.14% Rh/CPOL-bp&PPh_3, (C) P2p XPS spectra of CPOL-bp&PPh_3, (E) P2p XPS spectra of 0.14% Rh/CPOL-bp&PPh_3.

XPS of $Rh(CO)_2(acac)$ shows the binding energies of $Rh3d_{3/2}$ and $Rh3d_{5/2}$ at 314.0 eV and 309.2 eV respectively. In 0.14% Rh/CPOL-bp&PPh_3 catalyst, the binding energies of $Rh3d_{3/2}$ and $Rh3d_{5/2}$ decrease to 313.4 eV and 308.6 eV, showing the successful coordination of $Rh(CO)_2$acac with CPOL-bp&PPh_3 carrier. Interestingly, compared with XPS spectra of P2p in CPOL-bp&PPh_3 (two kinds of P species: PPh_3 units at 131.8 eV, biphphos units at 132.9 eV), 0.14% Rh/CPOL-bp&PPh_3 give relatively higher binding energy (131.9 eV, 133.0 eV), indicating the successful coordination of Rh with two kinds of P species in the polymer skeleton.

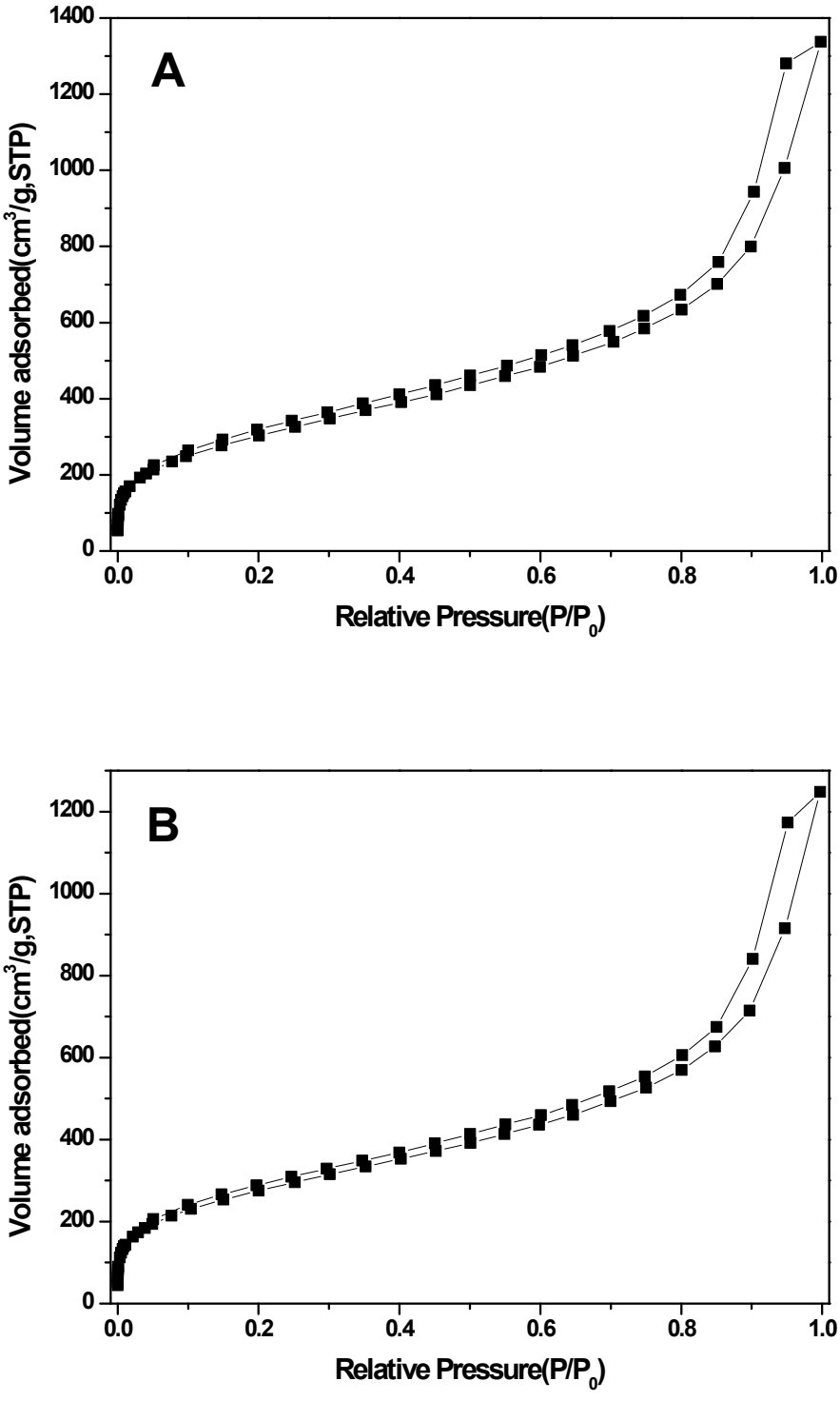


Figure S4. Nitrogen sorption isotherms of (A) CPOL-bp&PPh_3 and (B) Rh/CPOL-bp&PPh_3.

Figure S4 indicates that N_2 sorption isotherm of both CPOL-bp&PPh_3 and Rh/CPOL-bp&PPh_3 give the curve of type-I plus type-IV, showing that the two samples possess both micropores and mesoporous.

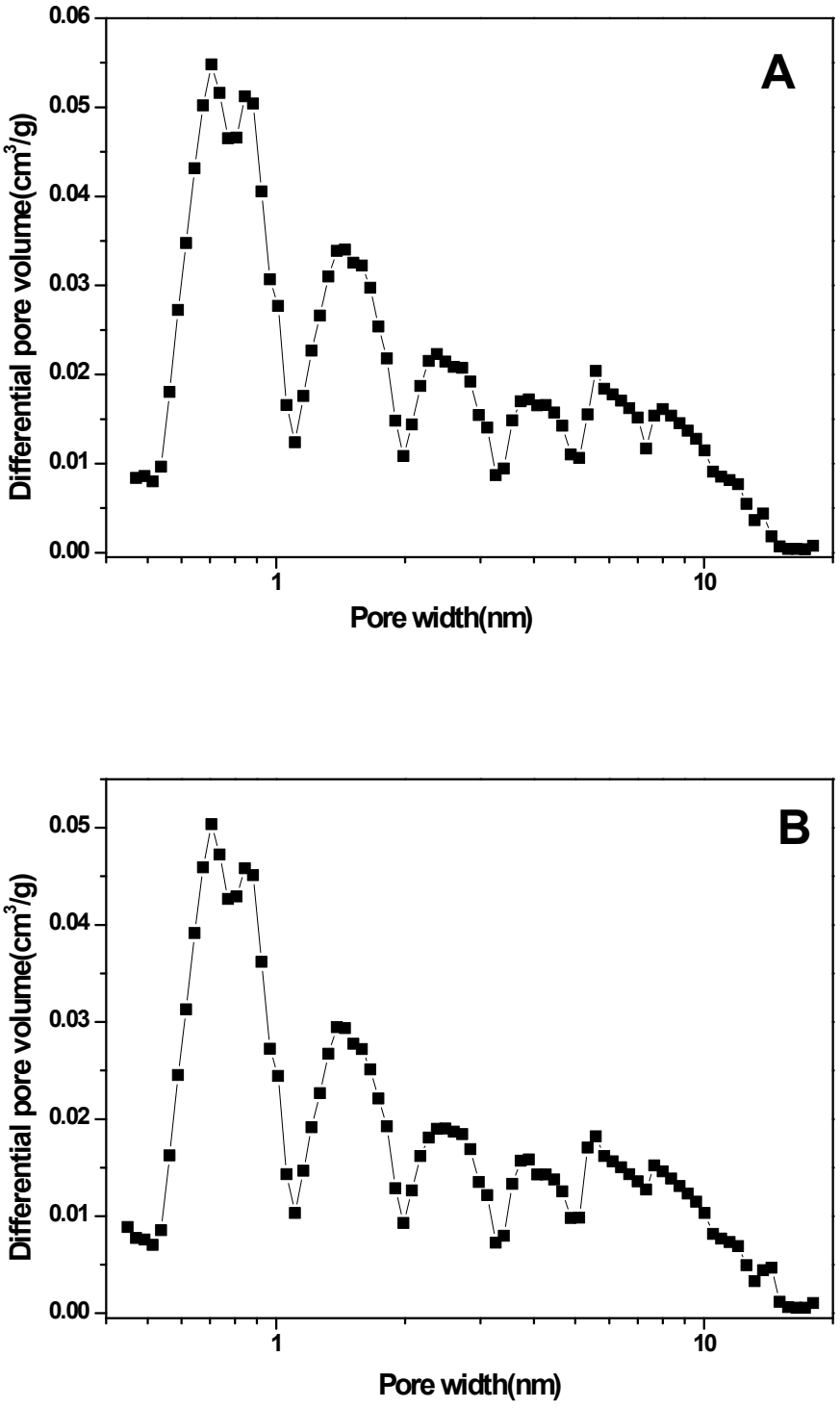


Figure S5. Pore size distribution of (A) CPOL-bp&PPh_3 and (B) Rh/CPOL-bp&PPh_3.

Pore size distribution is calculated from non-local density functional theory (NLDFT). Figure S5 indicates that both CPOL-bp&PPh_3 and Rh/CPOL-bp&PPh_3 possess hierarchical porosity.

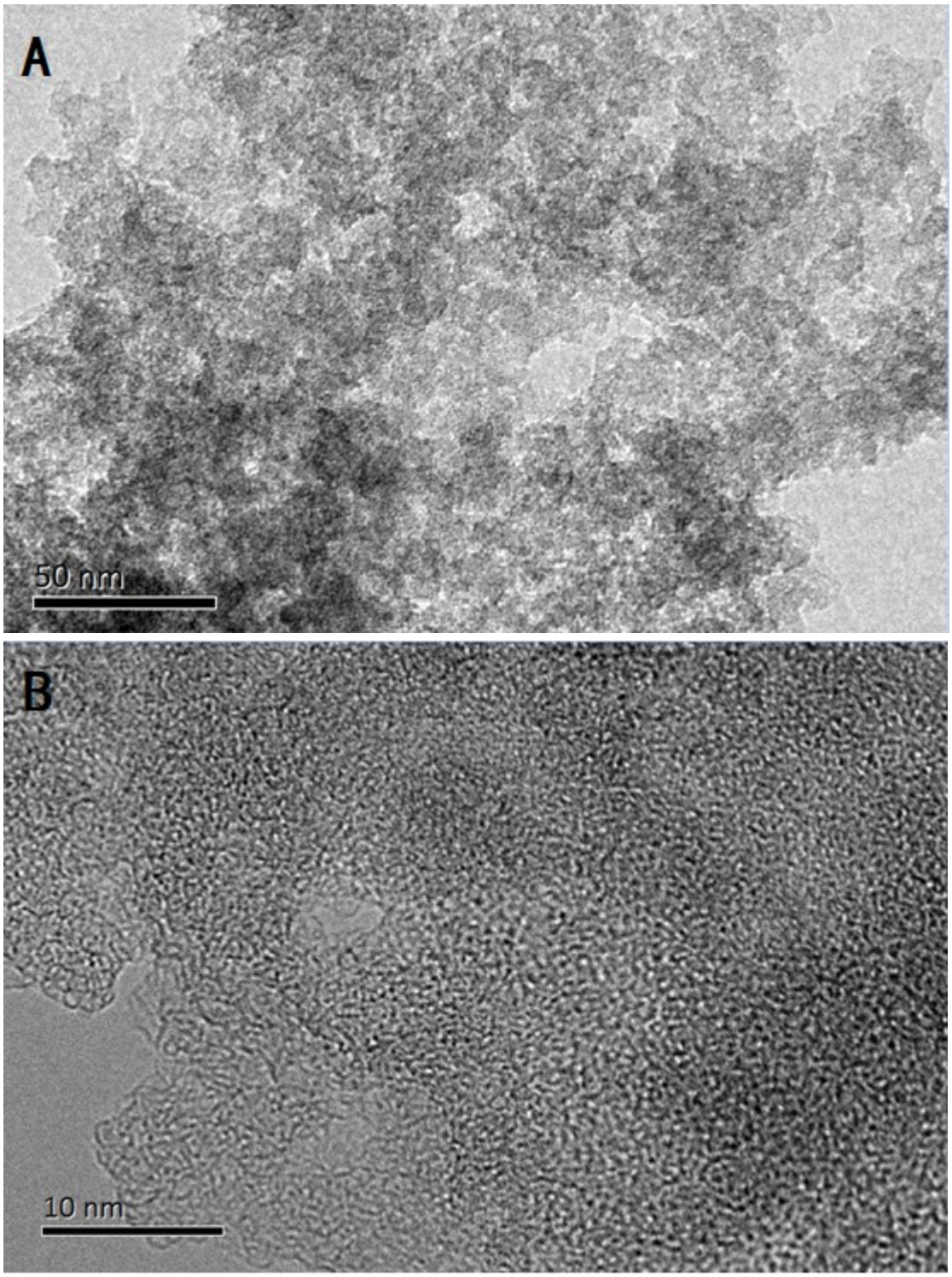


Figure S6. TEM images of CPOL-bp&PPh_3.

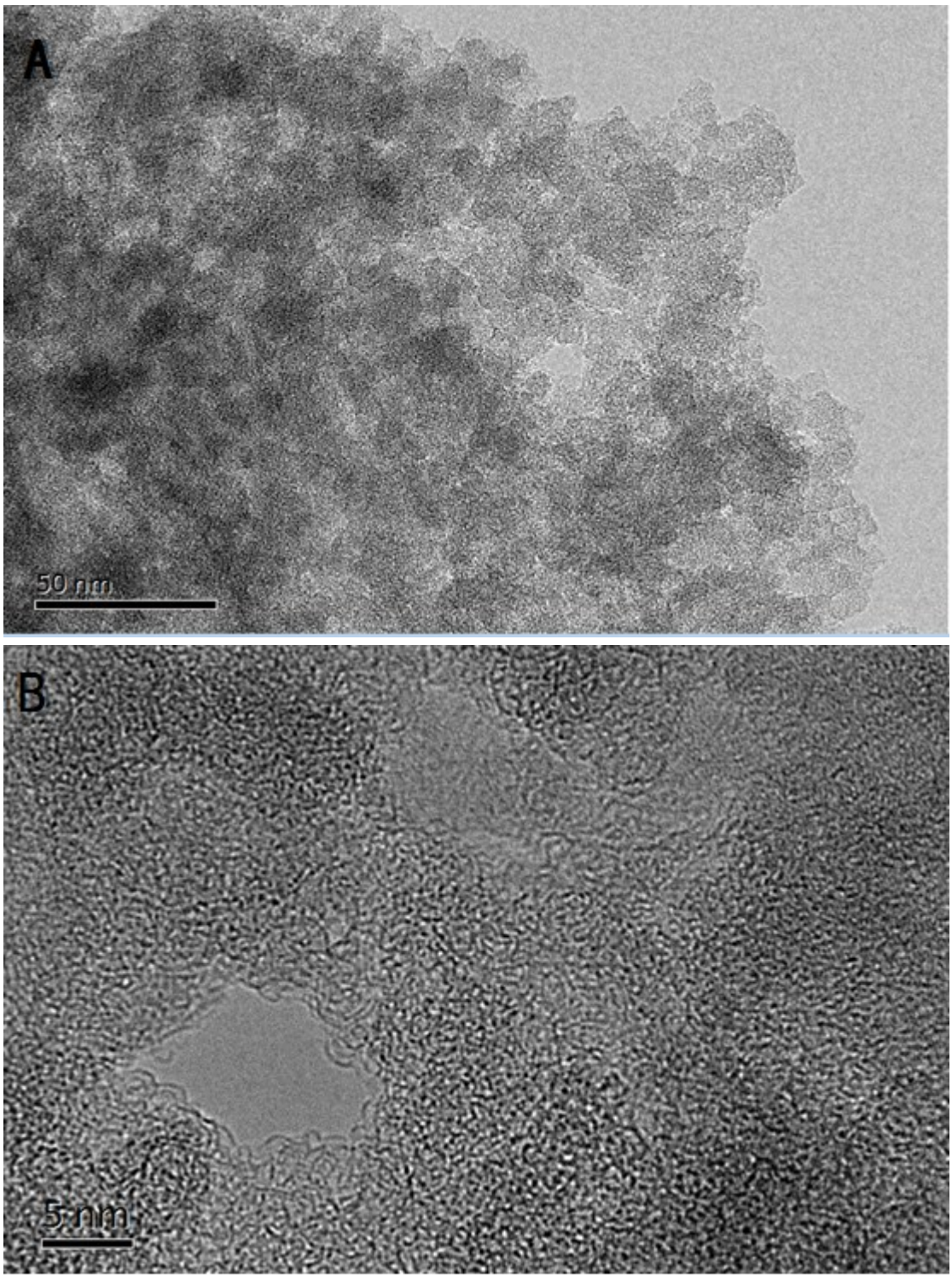


Figure S7. TEM images of Rh/CPOL-bp&PPh_3.

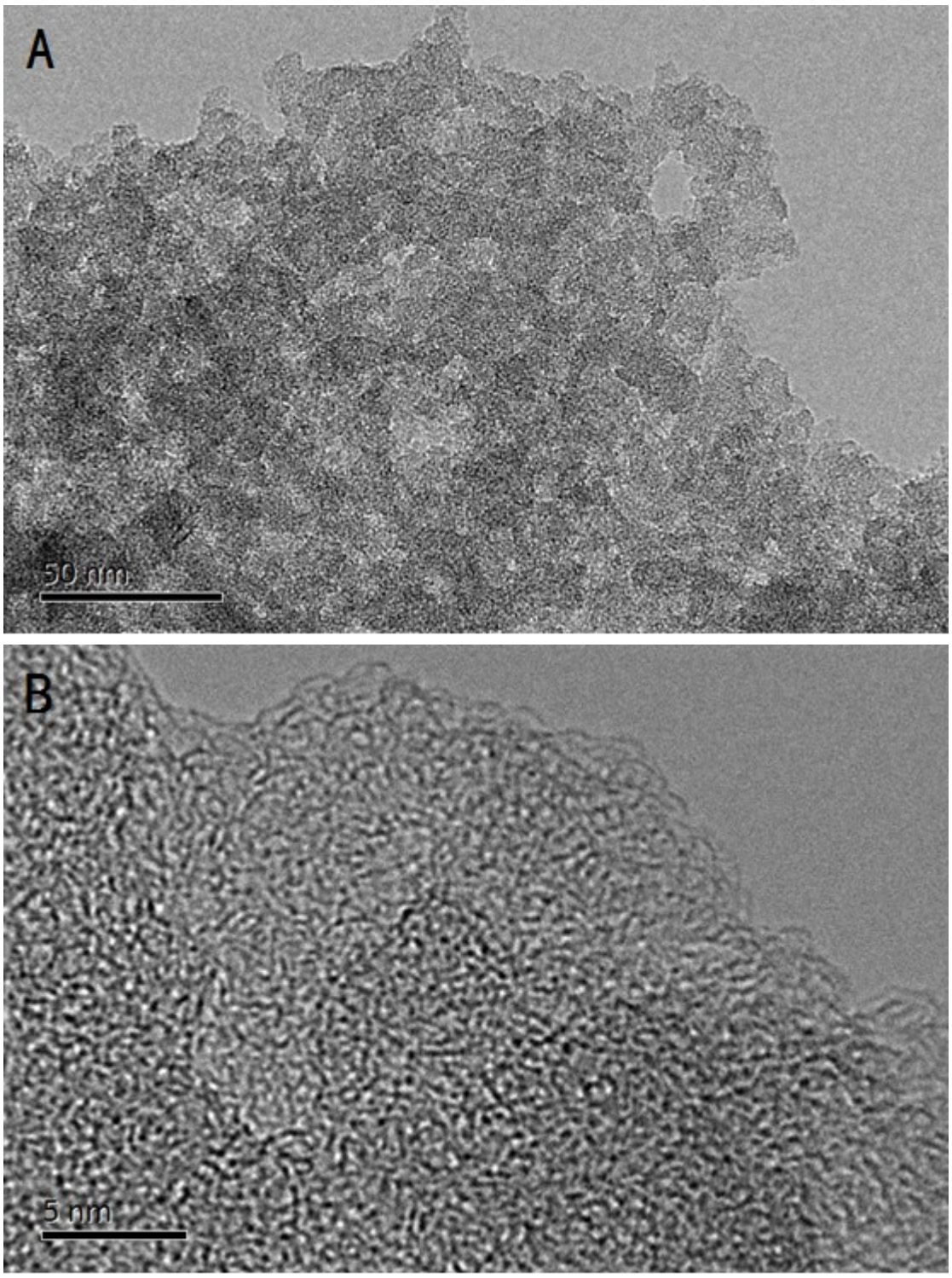
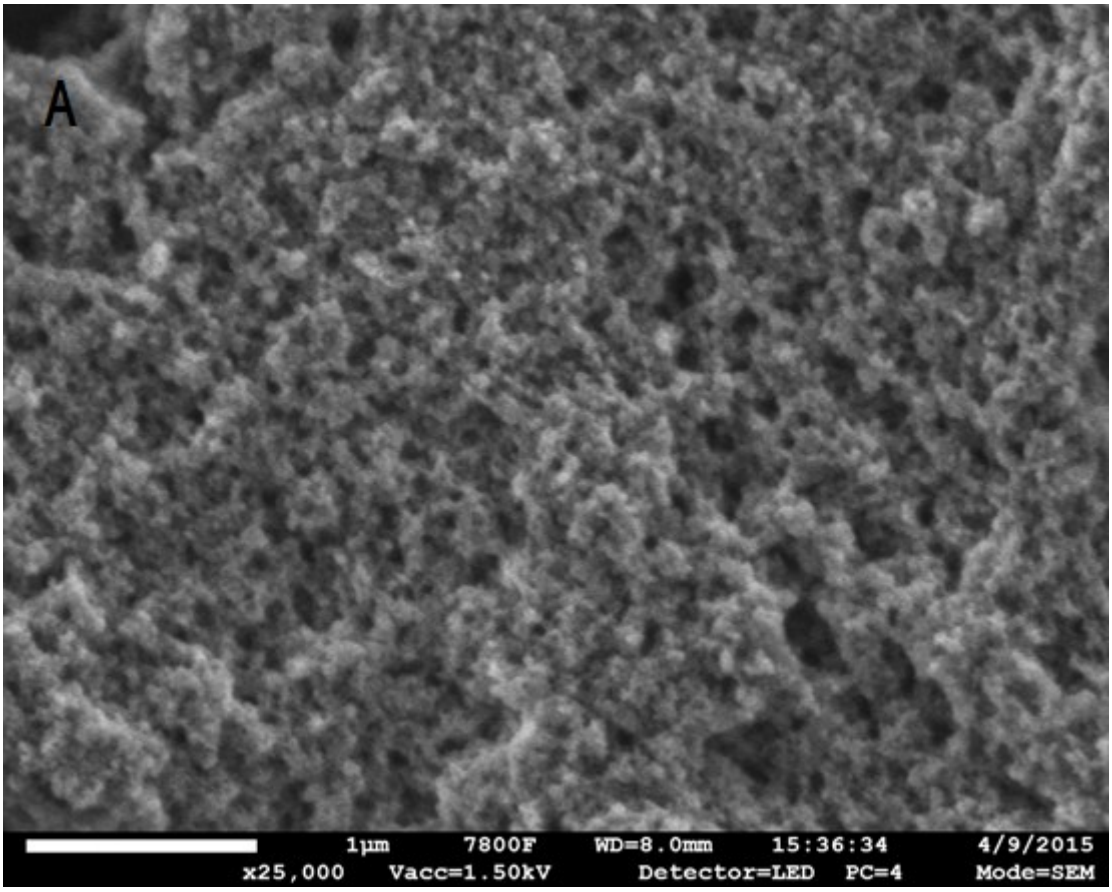


Figure S8. TEM images of Rh/CPOL-bp&PPh_3 after 6 runs.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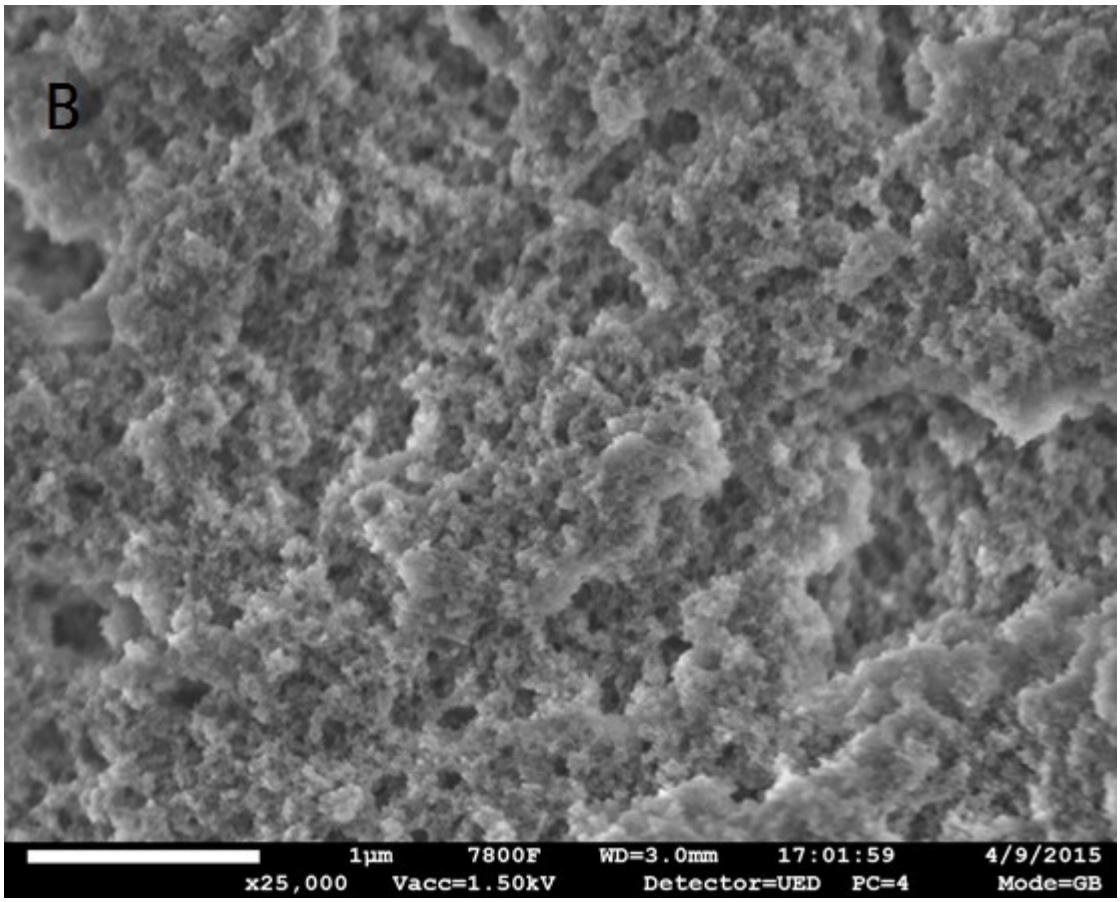
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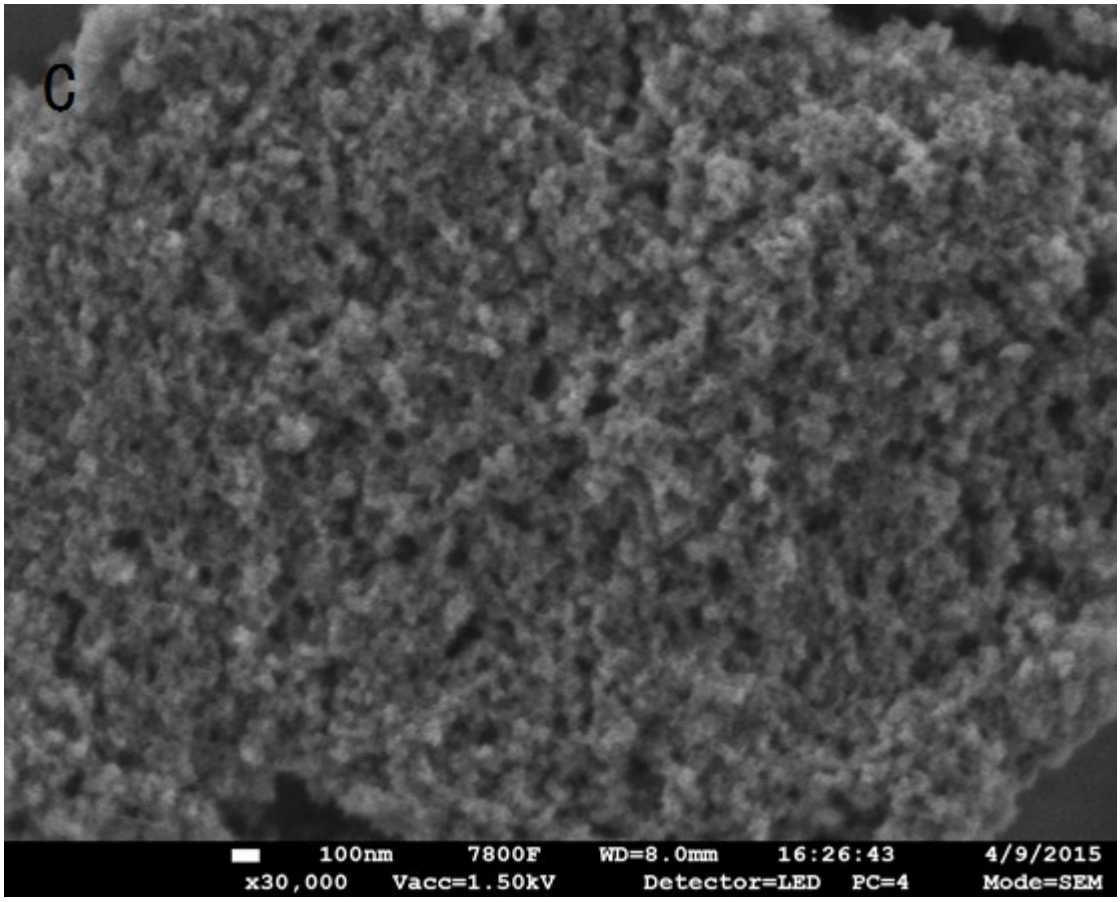
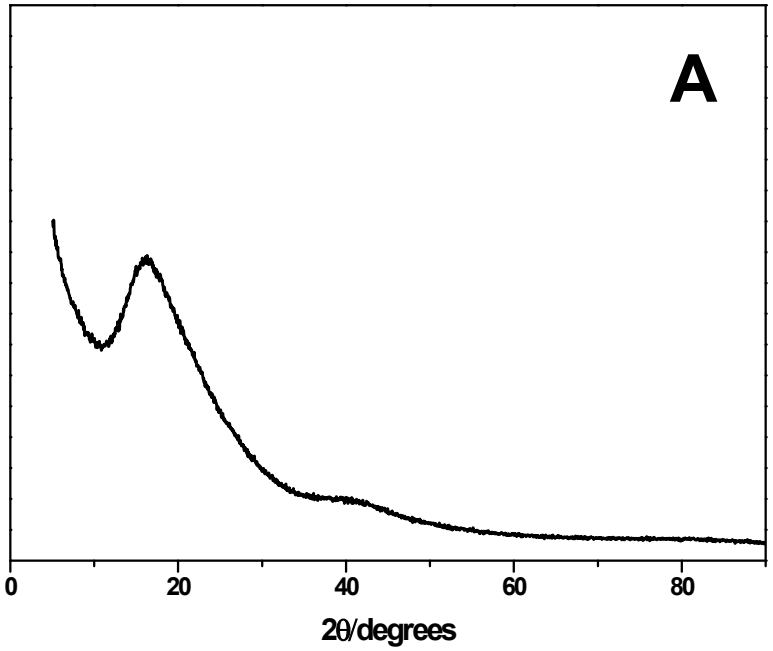


Figure S9. SEM images of (A) CPOL-bp&PPh_3, (B) Rh/CPOL-bp&PPh_3 and (C) Rh/CPOL-bp&PPh_3 after 6 runs.

Figure S9 shows that the all the samples have hierarchical porosity.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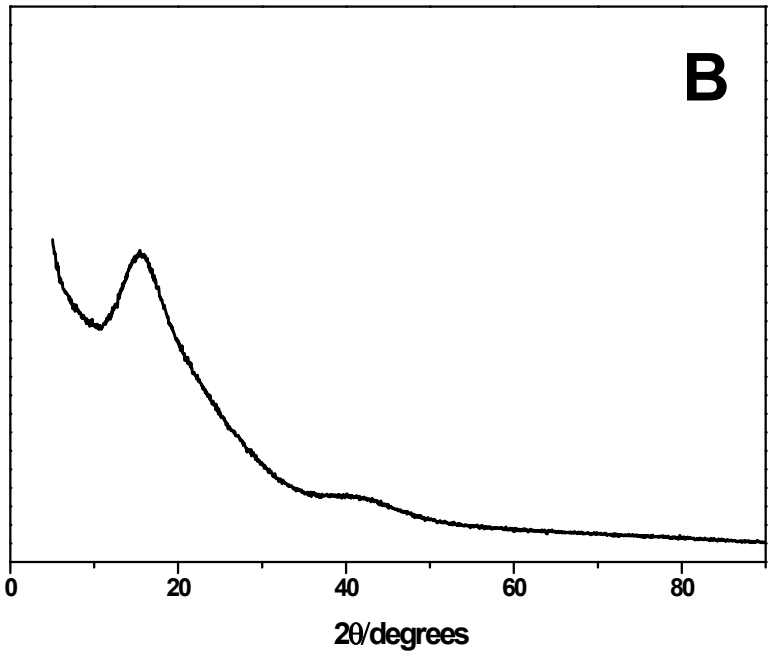
2θ/degrees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2θ/degrees

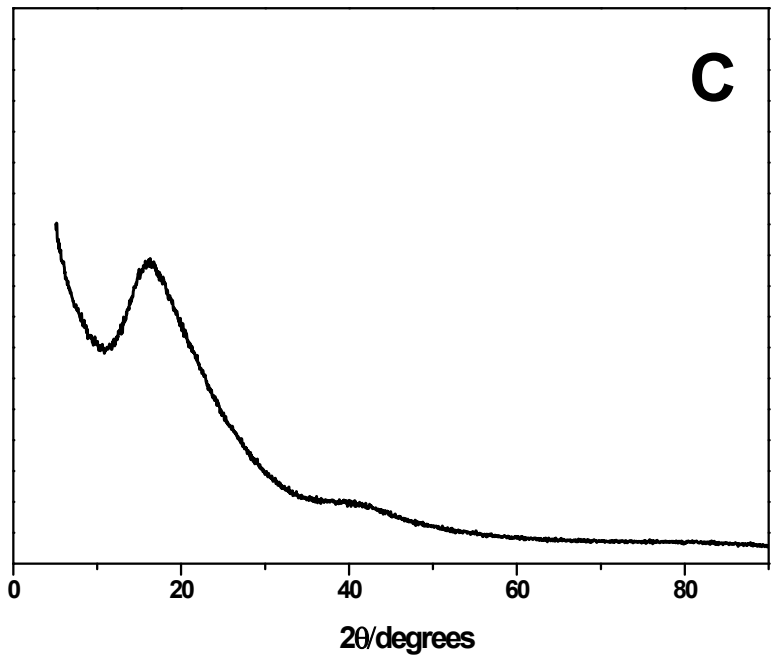


Figure S10. XRD of (A) CPOL-bp&PPh_3, (B) Rh/CPOL-bp&PPh_3 and (C) Rh/CPOL-bp&PPh_3 after 6 runs.

XRD also show that all three samples are amorphous.

2. Supporting Tables

Table S1. Rh concentration of fesh and spend catalysts

Sample	Rh content(wt.%)[a]
Rh/CPOL-bp&PPh_3 (fresh sample)	0.1385%
Rh/CPOL-bp&PPh_3 (spend sample, 6 runs)	0.1340%

[a] The lowest detectable limit of ICP-OES is 10^{-6}, “85” and “40” in Rh content are untrusted data.

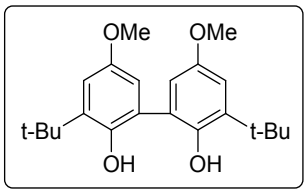
3. NMR characterizations of compounds in Scheme 1

Analytical data for compounds 1-7 and A, B

^{1}H and **^{13}C** spectra were recorded on a 500 MHz spectrometer. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to TMS in $CDCl_3$ (0 ppm) or d_6-DMSO (0 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm) or d_6-DMSO (39.5 ppm). All ^{13}C-NMR spectra were measured with complete proton decoupling except compound (A). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz.

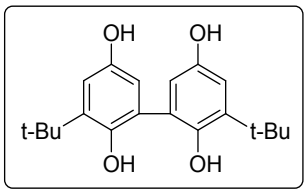
Mass spectroscopy were recorded on a Esquire 3000 Plus mass spectrometer. We were grateful to the assistance of the Department of Chemistry, Xiamen University in obtaining the MS data.

5,5'-dimethoxy-3,3'-di-*tert*-butylbiphenyl-2,2'-diol (1)



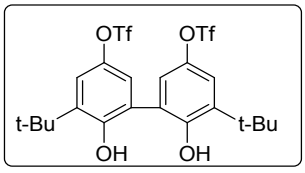
off-white powder, m.p. 220 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.43 (s, 9H), 3.77 (s, 3H), 5.04 (s, 1H) , 6.62 (d, 1H, *J* = 3.0 Hz), 6.96(d, 1H, *J* = 3.0 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 29.5, 35.2, 55.7, 111.8, 115.3, 123.3, 138.9, 145.9, 153.2.

3,3'-di-*tert*-butylbiphenyl-2,2',5,5'-tetraol (2)



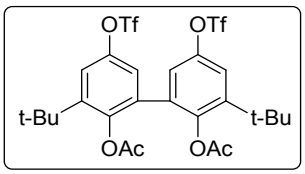
white chalky solid,m.p. 222 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.36 (s, 9H), 6.49 (d, 1H, *J* = 2.9 Hz), 6.68 (d, 1H, *J* = 2.9 Hz), 8.39 (s, 1H), 8.86 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 30.3, 35.1, 113.6, 115.4, 131.6, 140.8, 144.1, 151.4.

5,5'-di-*tert*-butyl-6,6'-dihydroxybiphenyl-3,3'-diyl bis(trifluoromethanesulfonate) (3)



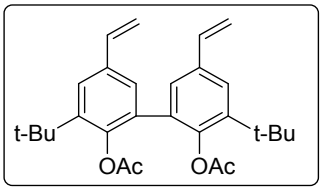
Gummy liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.45 (s, 9H), 5.44 (s, 1H), 7.04 (d, 1H, *J* = 3.1 Hz), 7.30 (d, 1H, *J* = 3.1 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 29.2, 35.5, 118.8 (q, *J* = 320.0 Hz), 121.2, 121.8, 122.5, 140.6, 142.9, 151.7.

6,6'-diacetate-5,5'-di-*tert*-butylbiphenyl-3,3'-diyl bis(trifluoromethanesulfonate) (4)



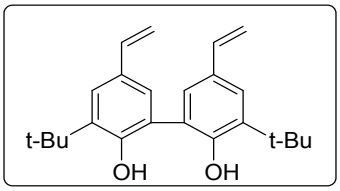
a white solid, m.p. 109 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.38 (s, 9H), 1.85 (s, 3H), 7.06 (d, 1H, *J* = 2.9 Hz), 7.36 (d, 1H, *J* = 3.1 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.4, 29.9, 35.2, 118.8 (q, *J* = 321.0 Hz), 120.9, 122.4, 133.6, 144.9, 146.4, 146.6, 167.9.

3,3'-di-*tert*-butyl-5,5'-divinylbiphenyl-2,2'-diyl diacetate (5)



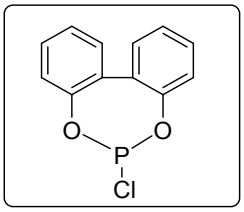
a white soild, m.p. 118 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.38 (s, 9H), 1.84 (s, 3H), 5.22 (d, 1H, *J* = 11.2 Hz), 5.70 (dd, 1H, J_1 = 17.6 Hz , J_2 = 0.6 Hz), 6.70 (dd, 1H, J_1 = 17.6 Hz , J_2 = 10.9 Hz), 7.24 (d, 1H, *J* = 1.9 Hz), 7.41 (d, 1H, *J* = 2.1Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.8, 30.4, 34.7, 114.0, 125.0, 127.9, 133.4, 135.4, 136.4, 141.3, 146.4, 168.6.

3,3'-di-*tert*-butyl-5,5'-divinylbiphenyl-2,2'-diol (6)



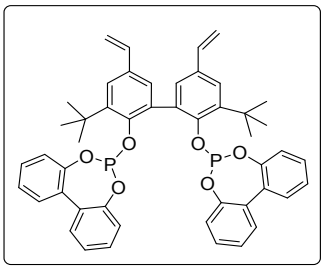
a white soild, m.p. 55 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.45 (s, 9H), 5.14 (d, 1H, *J* = 10.9 Hz), 5.30 (s, 1H), 5.62 (d, 1H, *J* = 17.6 Hz), 6.66 (dd, 1H, J_1 = 17.6 Hz , J_2 = 11.0 Hz), 7.16 (d, 1H, *J* = 1.8 Hz), 7.42 (d, 1H, *J* = 1.6 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 29.5, 35.0, 112.0, 122.5, 126.2, 126.3, 130.2, 136.3, 137.3, 152.0.

2,2'-bisphenoxyphosphorus chloride (7)



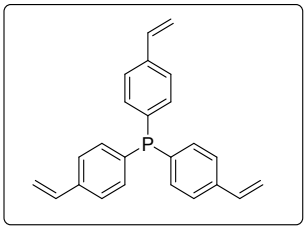
yellow liquild; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, 2H, *J* = 7.9 Hz), 7.31 (t, 2H, *J* = 7.4 Hz),7.37 (td, 2H, J_1= 7.7 Hz, J_2 = 1.6 Hz) , 7.46 (dd, 2H, J_1= 7.5 Hz, J_2 = 1.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 122.2 (d, *J* = 1.9 Hz), 126.2, 129.4, 130.1, 130.9 (d, *J* = 3.5 Hz), 149.2 (d, *J* = 5.7 Hz); **^{31}P NMR** (161.8 MHz, $CDCl_3$) δ 179.4.

6,6'-(3,3'-di-tert-butyl-5,5'-divinylbiphenyl-2,2' diyl)bis(oxy)didibenzo [1,3,2]dioxaphosphepine (A)



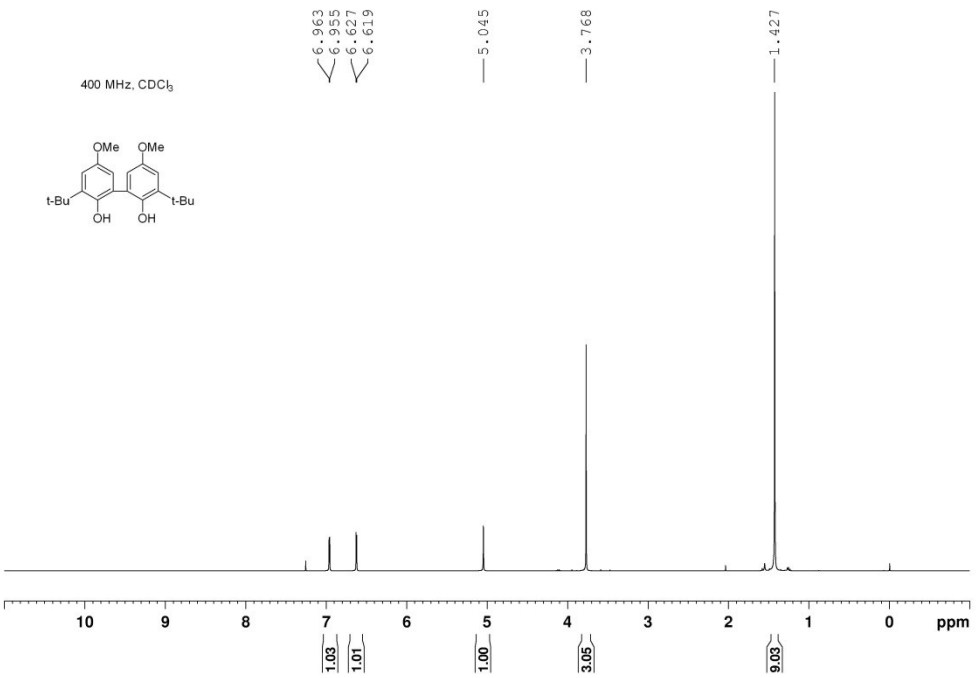
a white solid, m.p. 185 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 5.24 (dd, 1H, J_1 = 10.9 Hz, J_2 = 0.5 Hz), 5.74 (dd, 1H, J_1 = 17.6 Hz, J_2 = 0.5 Hz), 6.75 (dd, 1H, J_1 = 17.6 Hz , J_2 = 10.9 Hz), 6.72(d, 1H, J = 7.6 Hz), 7.01 (td, 1H, J_1 = 7.9 Hz , J_2 = 1.3 Hz), 7.10-7.15 (m, 2H), 7.23 (td, 1H, J_1 = 7.5 Hz , J_2 = 1.2 Hz), 7.29 (td, 1H, J_1 = 7.8 Hz , J_2 = 1.8 Hz),7.35 (dd, 1H, J_1 = 7.7 Hz , J_2 = 1.6 Hz), 7.39-7.44 (m, 2H), 7.54 (d, 1H, J = 2.3 Hz) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 30.4, 35.3, 113.4, 122.3,123.1, 124.8, 124.9, 126.1, 128.7, 128.8, 129.4, 129.6, 129.8, 131.2, 131.3, 131.5, 132.5, 136.4, 141.9, 149.0, 149.7, 150.2; **^{31}P NMR** (161.8 MHz, $CDCl_3$) δ 144.5; **HRMS** (ESI):m/z calc. for $C_{48}H_{44}O_6P_2$ $[M+H]^+$:779.2686， found:779.2697.

tris(4-vinphenyl)phosphane (B)



a white solid, m.p. 75 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.26 (d, 1H, J = 11.1 Hz), 5.76 (d, 1H, J = 17.5 Hz), 6.69 (dd, 1H, J_1 = 17.6 Hz , J_2 = 10.9 Hz), 7.25-7.29 (m, 2H), 7.35-7.37 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 114.7, 126.3 (d, 6C, J =7.0 Hz), 133.8 (d, 3C, J =19.4 Hz), 136.3, 136.6 (d, 6C, J =10.8 Hz), 137.9; **^{31}P NMR** (161.8 MHz, $CDCl_3$) δ -6.8;

NMR spectra of compounds 1-7 and A, B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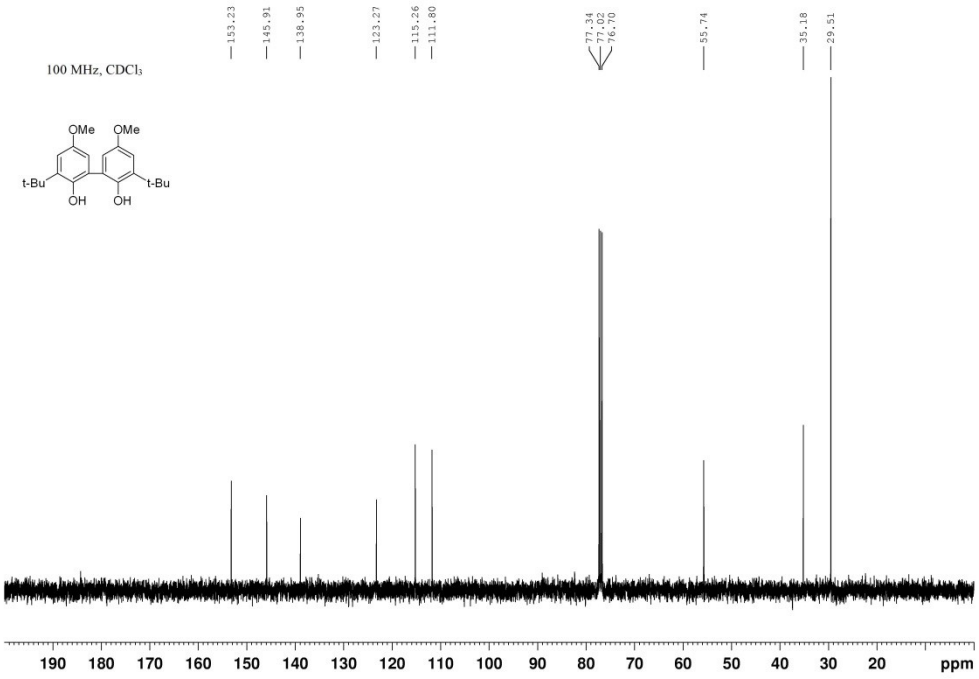
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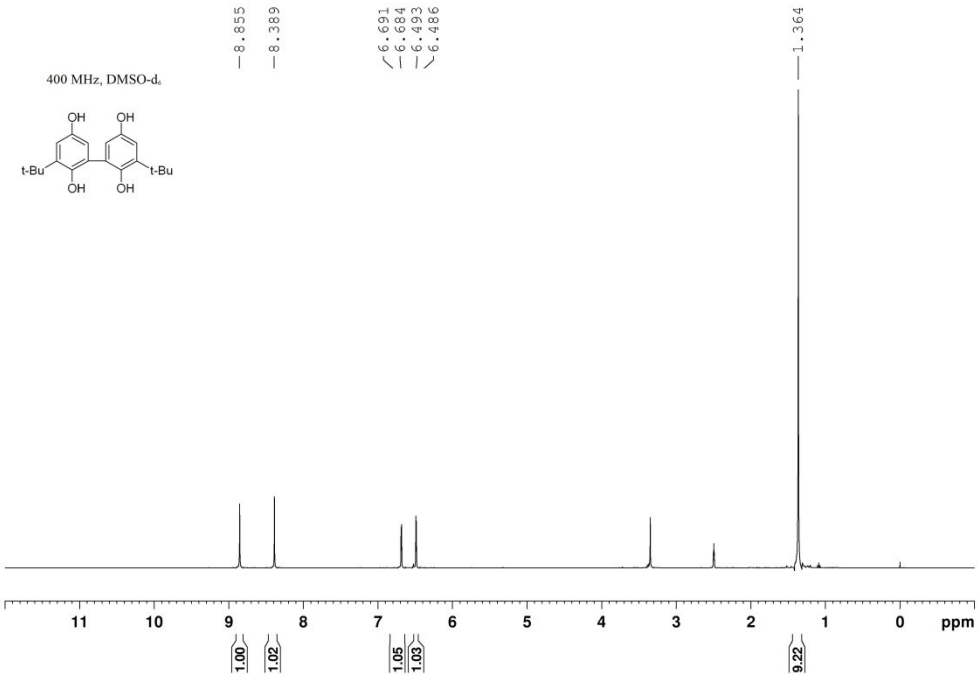
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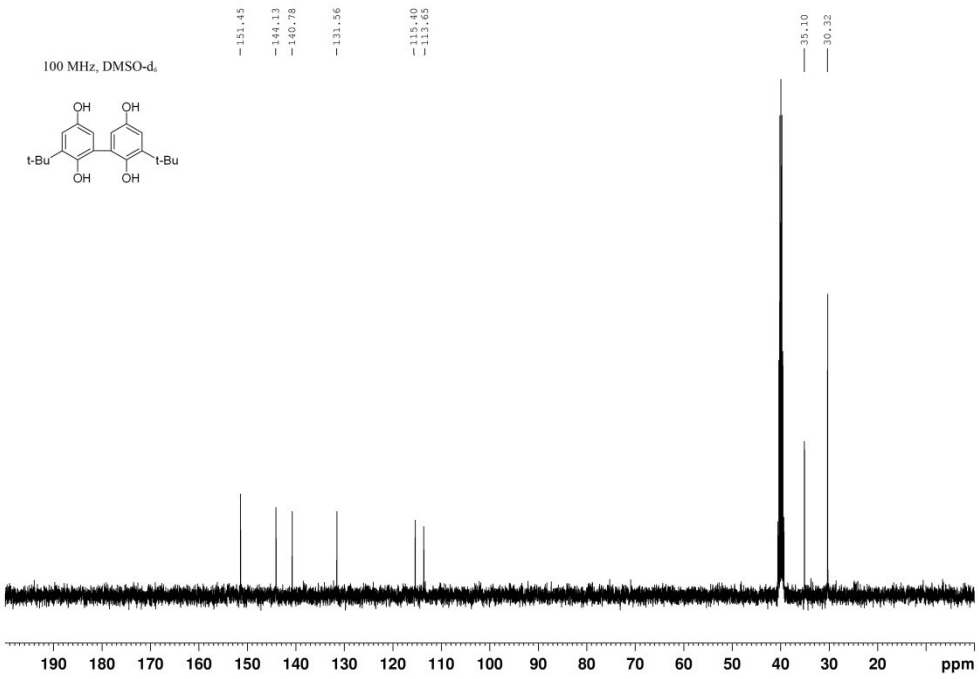
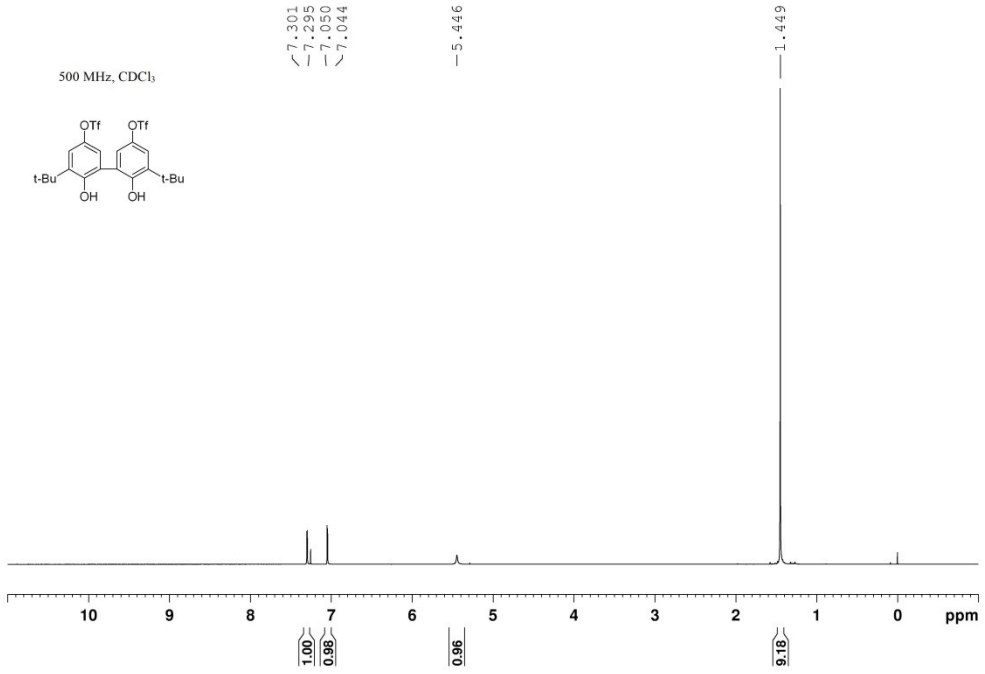
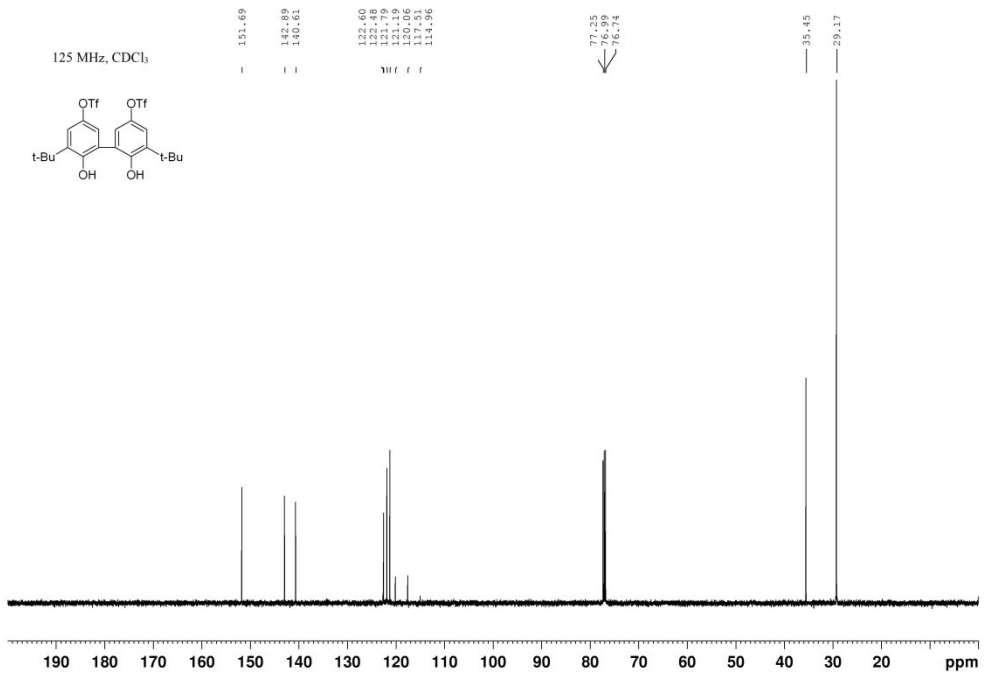
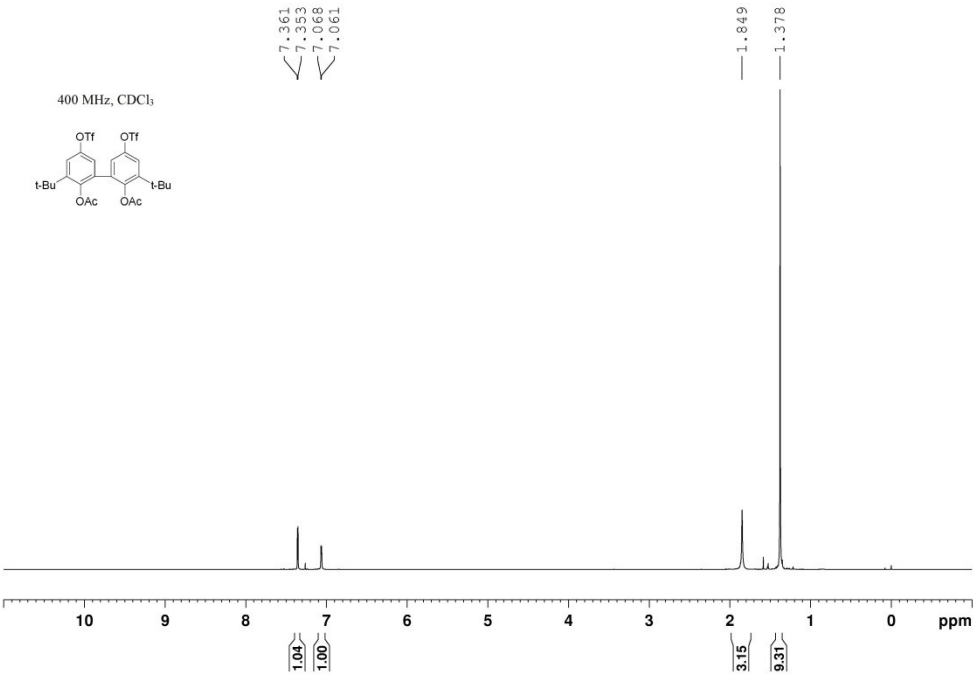
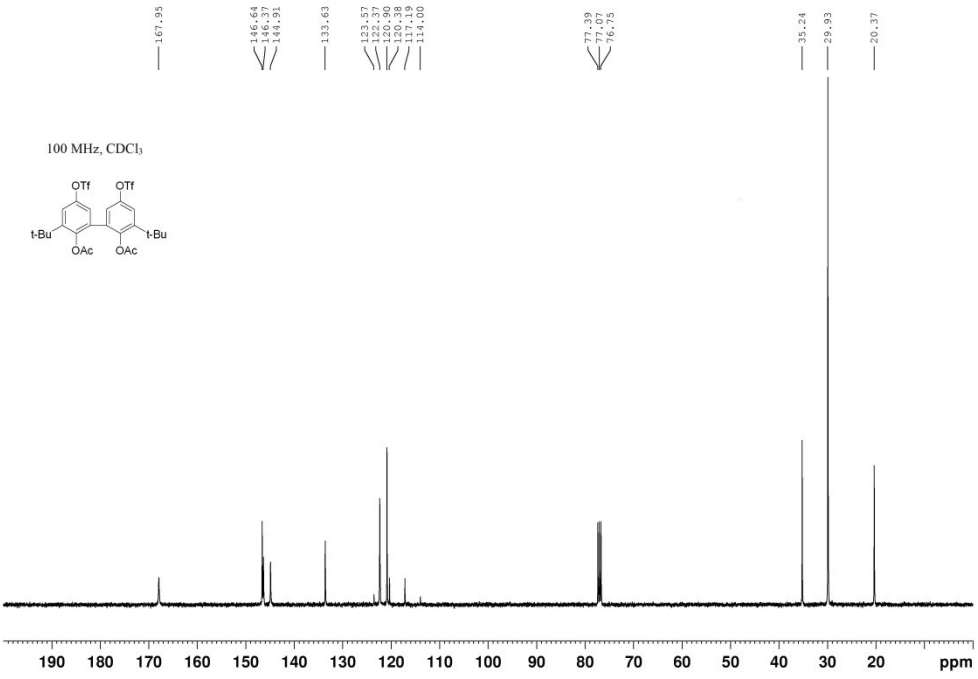
6.486
1.364
400 MHz, DMSO-d6
OH
OH
t-Bu
t-Bu
OH
OH
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
1.05
1.03
9.22

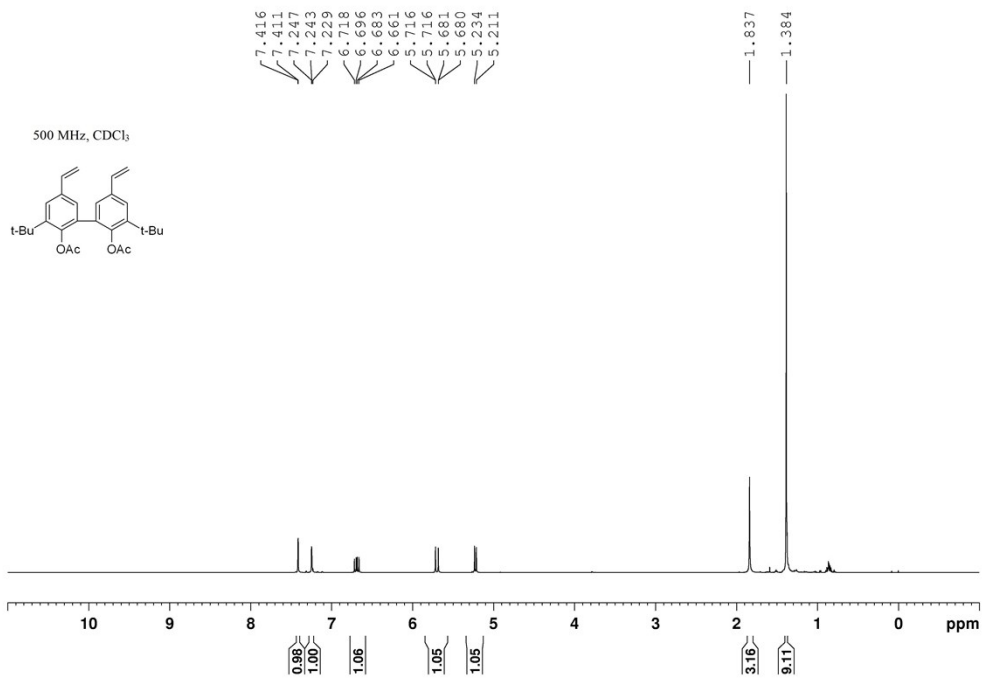

151.45
144.13
140.78
131.56
115.40
113.65
35.10
30.32
100 MHz, DMSO-d6
OH
OH
t-Bu
t-Bu
OH
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

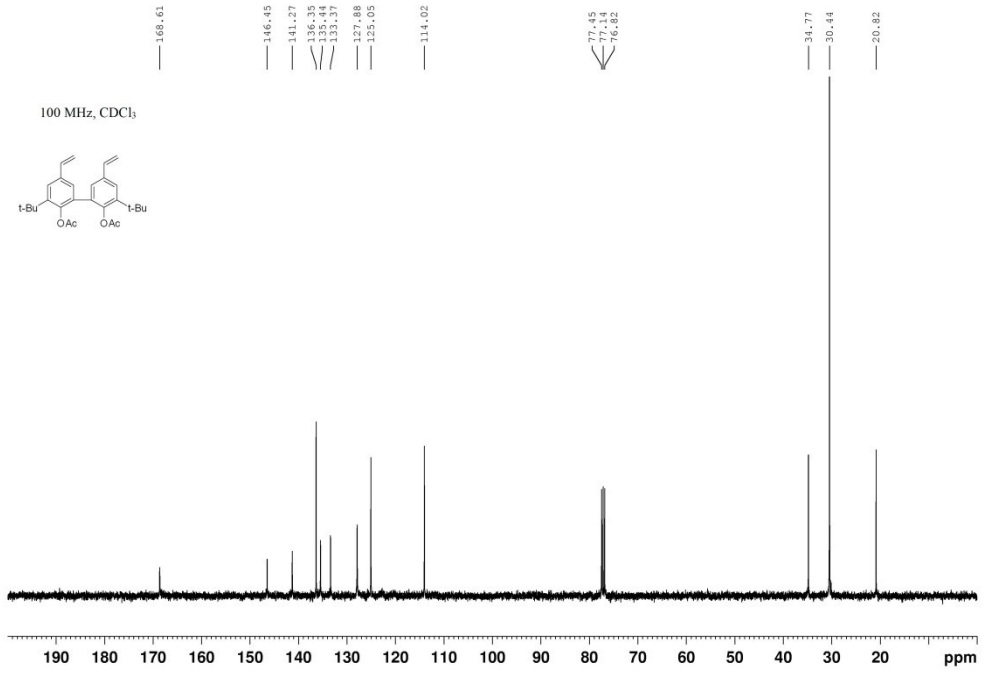

500 MHz, CDCl3
OTf
OTf
t-Bu
t-Bu
OH
OH
7.301
7.295
7.050
7.044
5.446
1.449
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
0.96
9.18

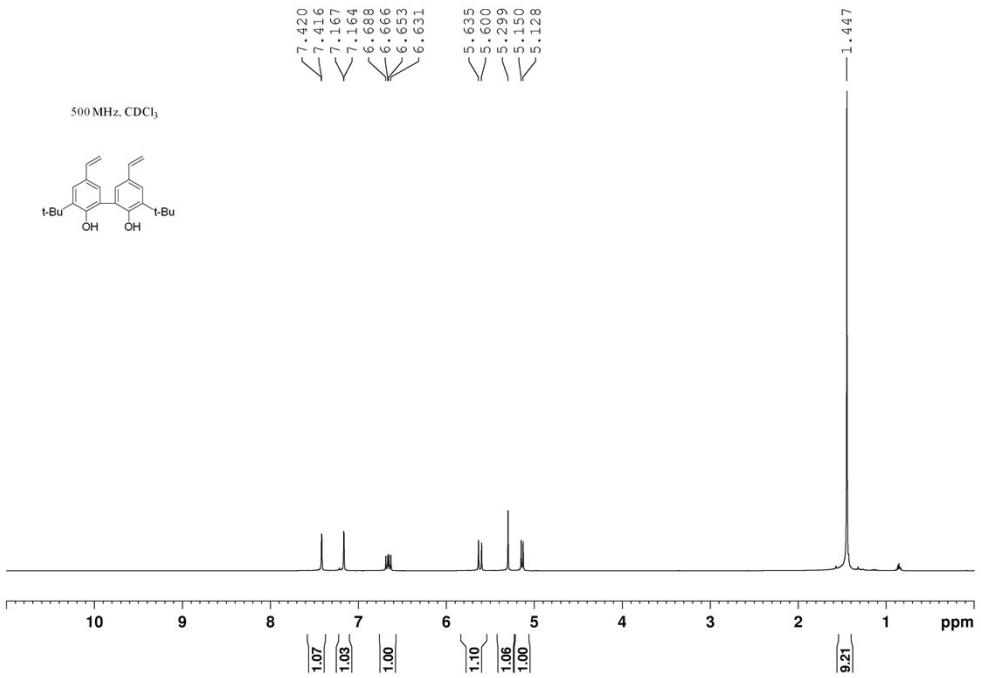

125 MHz, CDCl3
OTf
OTf
t-Bu
t-Bu
OH
OH
151.69
142.89
140.61
122.60
122.48
121.79
121.19
120.06
117.51
114.96
77.25
76.99
76.74
35.45
29.17
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

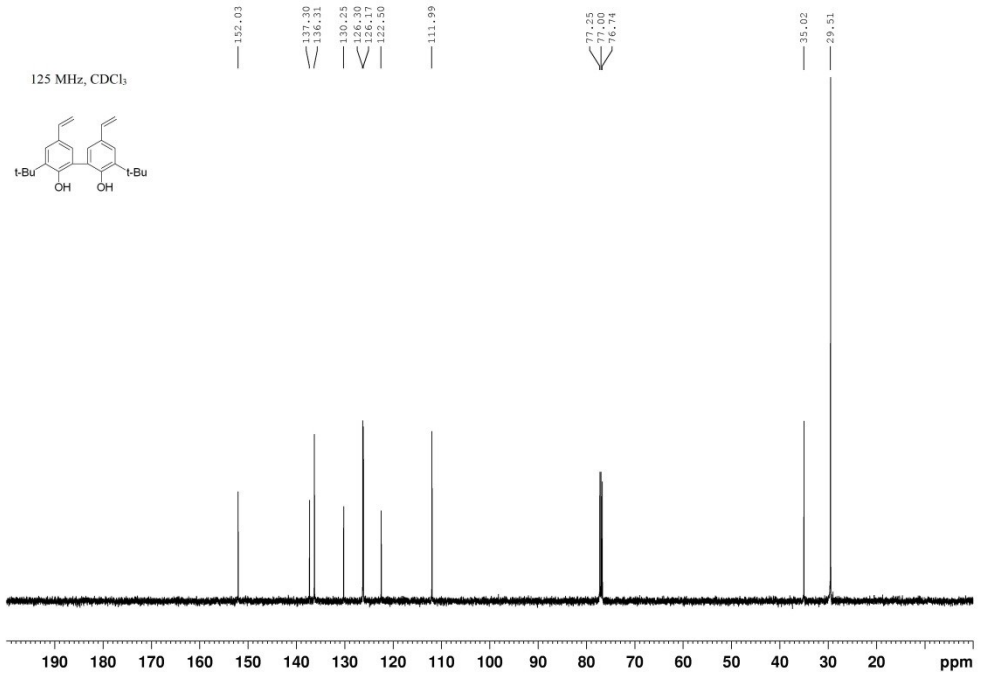

7.361
7.353
7.068
7.061
1.849
1.378
400 MHz, CDCl3
OTf
OTf
t-Bu
t-Bu
OAc
OAc
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.00
3.15
9.31

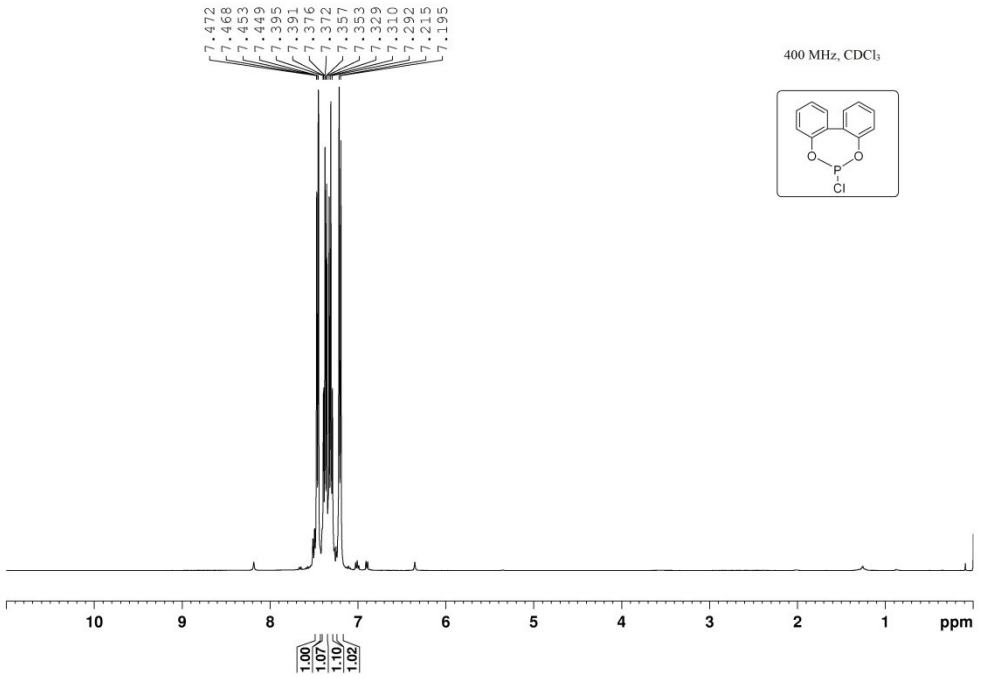

167.95
146.64
146.37
144.91
133.63
123.57
122.37
120.90
120.38
117.19
114.00
77.39
77.07
76.75
35.24
29.93
20.37
100 MHz, CDCl3
OTf
OTf
t-Bu
t-Bu
OAc
OAc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

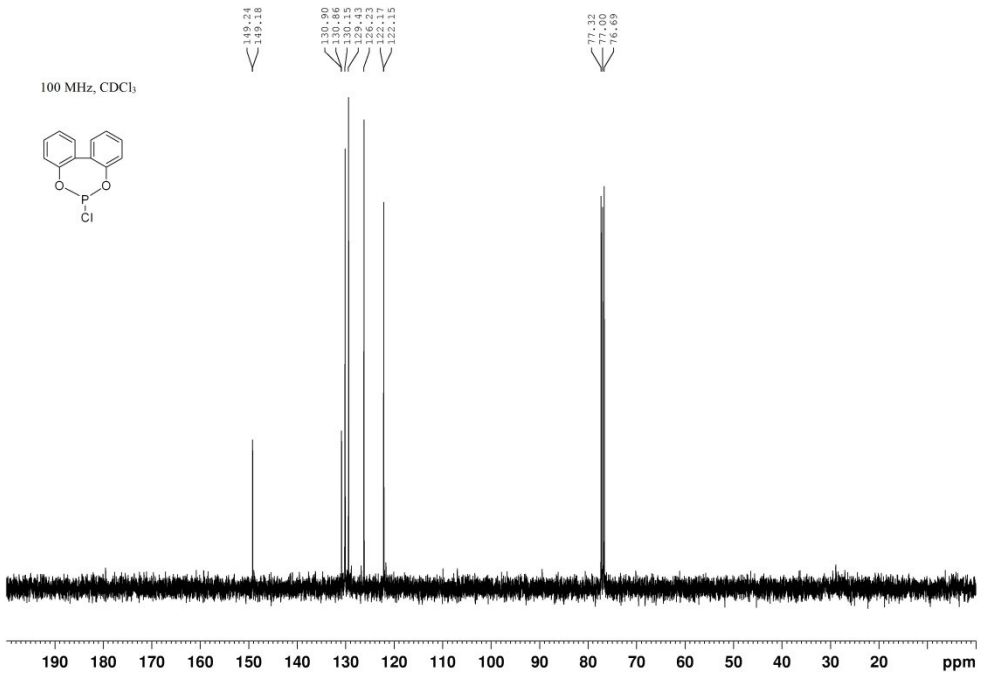

7.416
7.411
7.247
7.243
7.229
6.718
6.696
6.683
6.661
5.716
5.716
5.681
5.680
5.234
5.211
1.837
1.384
500 MHz, CDCl3
t-Bu
t-Bu
OAc
OAc
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
1.00
1.06
1.05
1.05
3.16
9.11

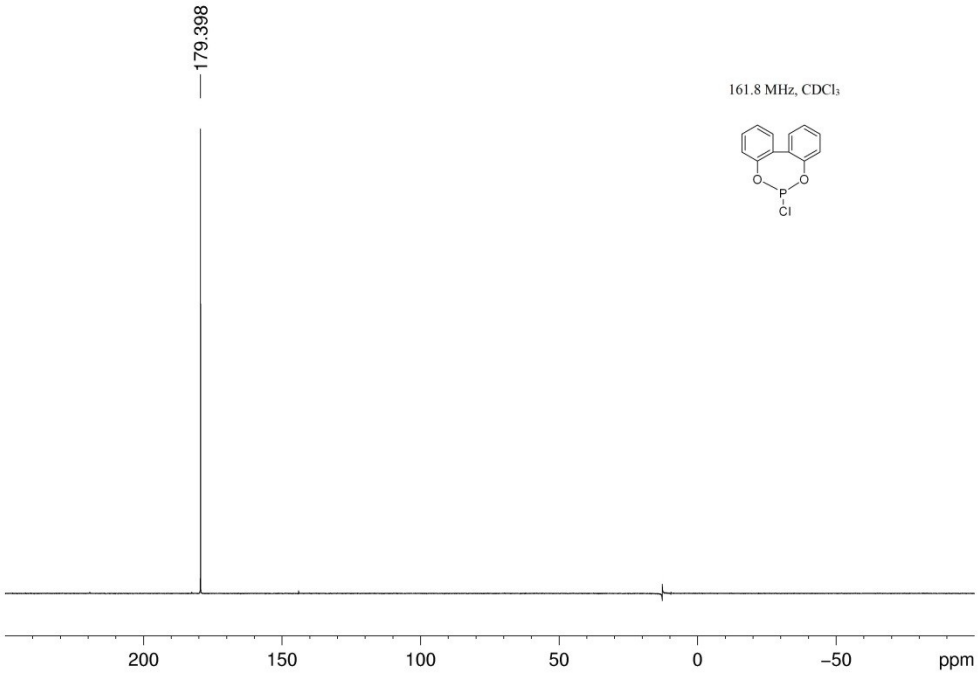

168.61
146.45
141.27
136.35
135.44
133.37
127.88
125.05
114.02
77.45
77.14
76.82
34.77
30.44
20.82
100 MHz, CDCl3
t-Bu
t-Bu
OAc
OAc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

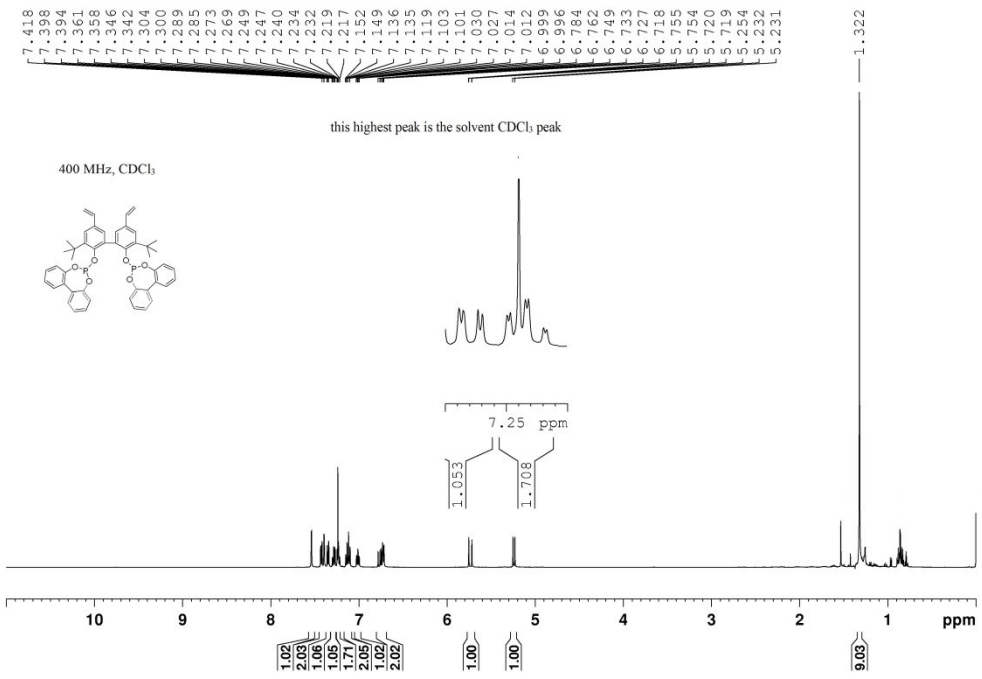

7.420
7.416
7.167
7.164
6.688
6.666
6.653
6.631
5.635
5.600
5.299
5.150
5.128
1.447
500 MHz, CDCl3
t-Bu
OH
OH
t-Bu
10
9
8
7
6
5
4
3
2
1
ppm
1.07
1.03
1.00
1.10
1.06
1.00
9.21

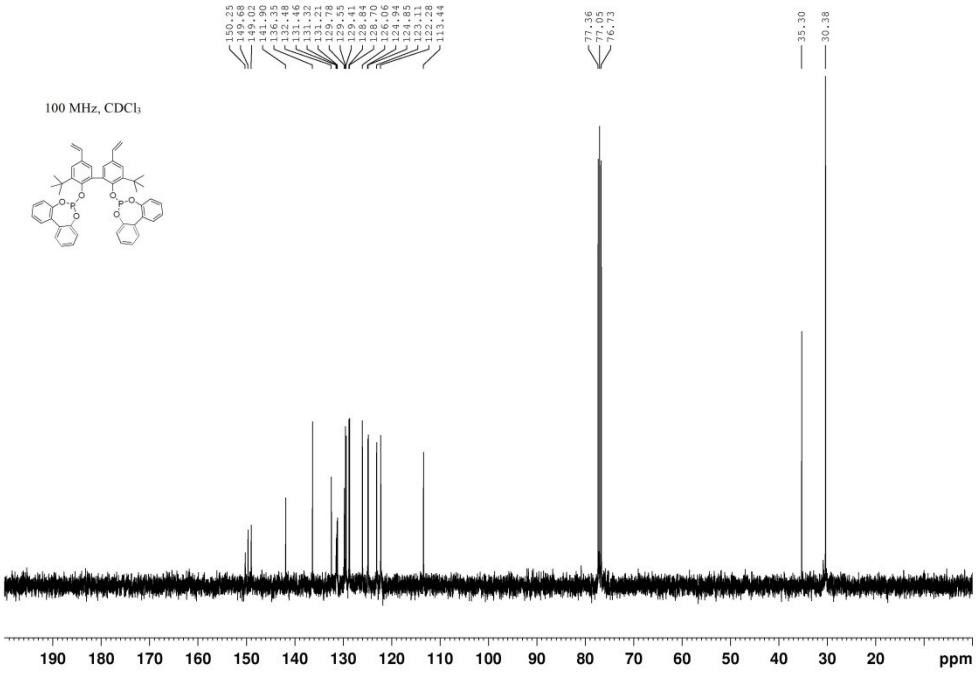

152.03
137.30
136.31
130.25
126.30
126.17
122.50
111.99
77.25
77.00
76.74
35.02
29.51
125 MHz, CDCl3
t-Bu
OH
OH
t-Bu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

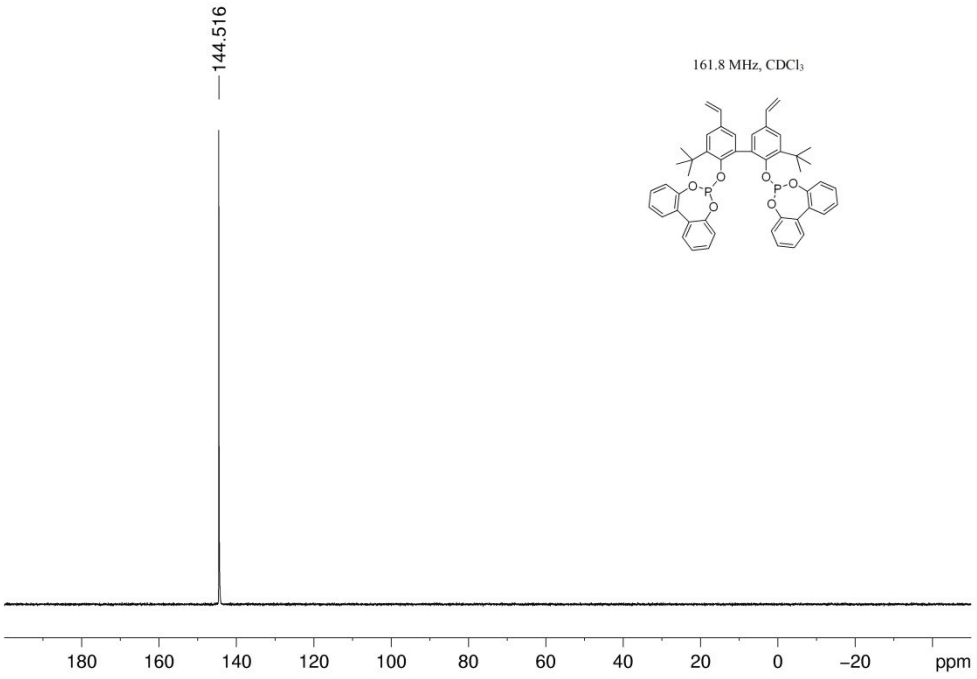

7.472
7.468
7.453
7.449
7.395
7.391
7.376
7.372
7.357
7.353
7.329
7.310
7.292
7.215
7.195
400 MHz, CDCl3
O
P
O
Cl
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.07
1.10
1.02

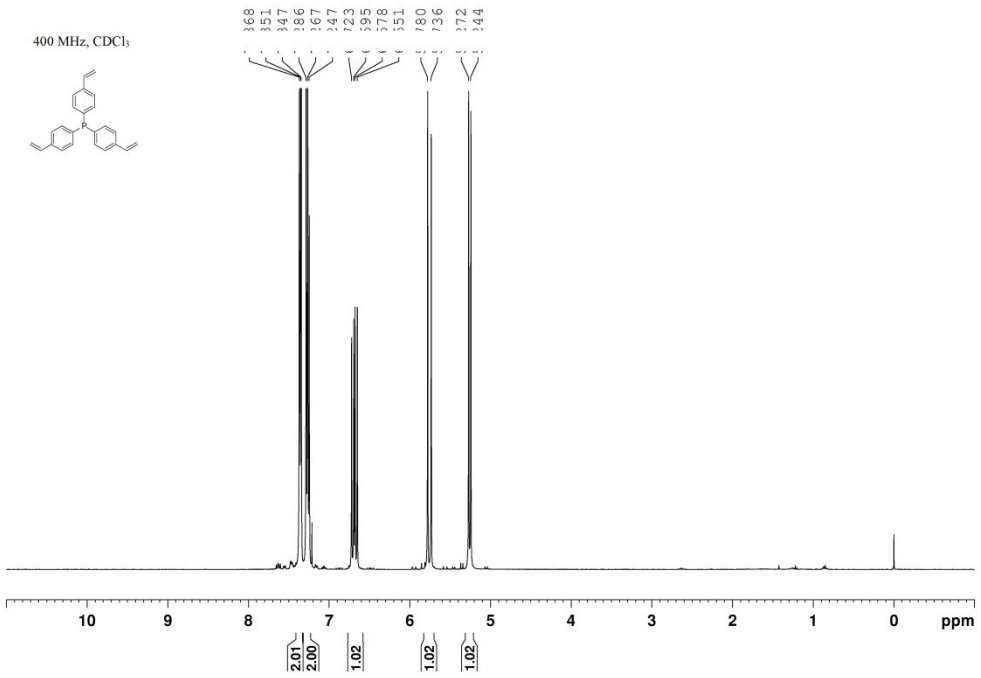

149.24
149.18
130.90
130.86
130.15
129.43
128.23
122.17
122.15
77.32
77.00
76.69
100 MHz, CDCl3
O
P
O
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

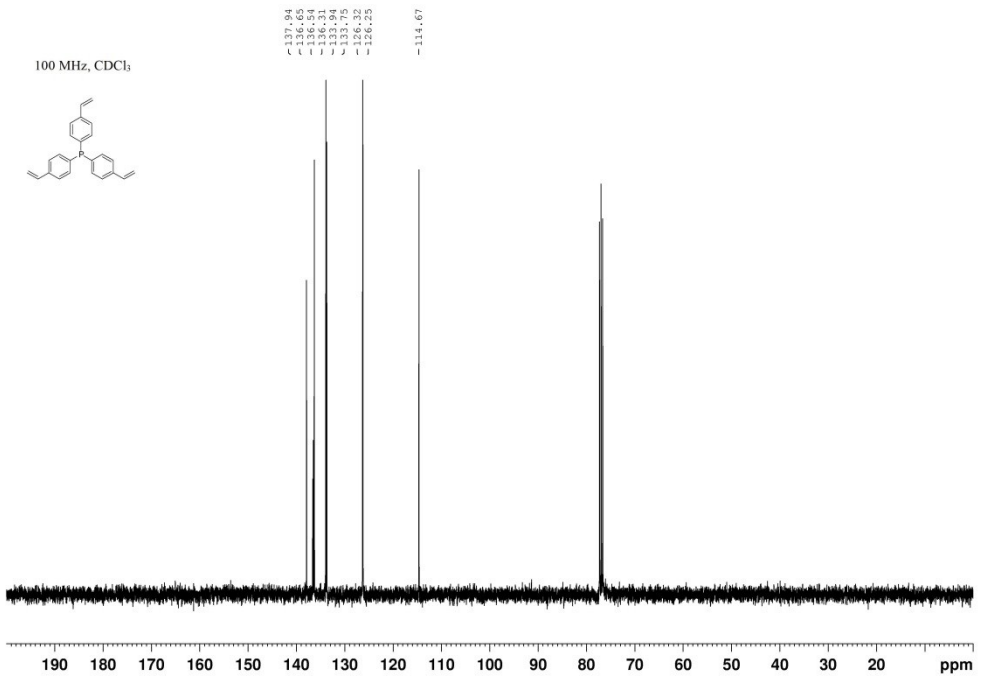

179.398
161.8 MHz, CDCl3
200
150
100
50
0
−50
ppm

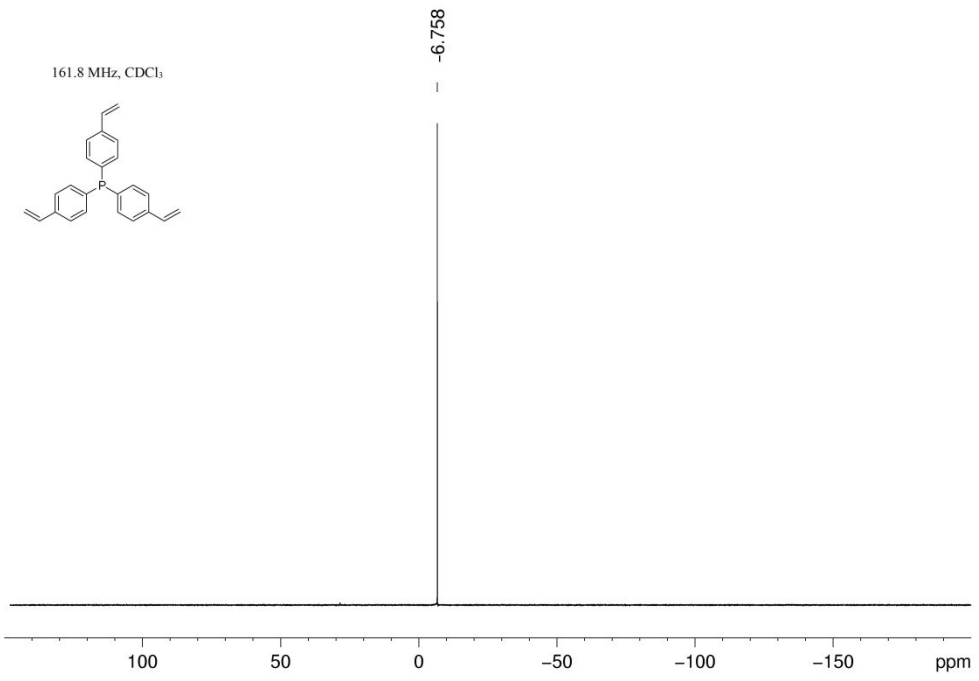

7.418
7.398
7.394
7.361
7.358
7.346
7.342
7.304
7.300
7.289
7.285
7.273
7.269
7.249
7.247
7.240
7.234
7.232
7.219
7.217
7.152
7.149
7.136
7.135
7.119
7.103
7.101
7.030
7.027
7.014
7.012
6.999
6.996
6.784
6.762
6.749
6.733
6.727
6.718
5.755
5.754
5.720
5.719
5.254
5.232
5.231
1.322
this highest peak is the solvent CDCl3 peak
400 MHz, CDCl3
7.25 ppm
1.053
1.708
10
9
8
7
6
5
4
3
2
1
ppm
1.02
2.03
1.06
1.05
1.71
2.05
1.02
2.02
1.00
1.00
9.03


150.25
149.68
149.02
141.90
136.35
132.48
131.46
131.32
131.21
129.78
129.55
128.91
128.84
128.70
126.06
124.94
124.85
123.11
122.28
113.44
77.36
77.05
76.73
35.30
30.38
100 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


144.516
161.8 MHz, CDCl3
180 160 140 120 100 80 60 40 20 0 −20 ppm


400 MHz, CDCl3
7.368
7.351
7.347
7.336
7.267
7.247
6.723
6.695
5.278
5.251
5.780
5.736
5.272
5.244
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
2.00
1.02
1.02
1.02


100 MHz, CDCl3
137.94
136.65
136.44
136.31
133.94
133.75
126.32
126.25
114.67
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


161.8 MHz, CDCl3
-6.758
100
50
0
−50
−100
−150
ppm