Electronic Supplementary Information

Palladium immobilized on functionalized hypercrosslinked polymers: A highly active and recyclable catalyst for Suzuki-Miyaura coupling reactions in water

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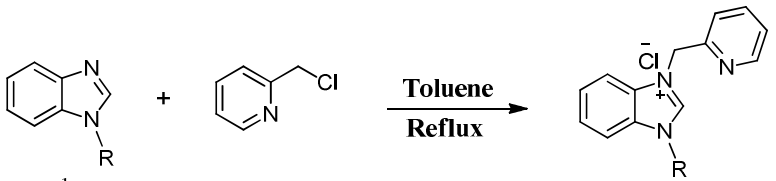
I.General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. FT-IR spectra were recorded under ambient conditions in the wavenumber range of 4000-400 cm^{-1} using an FT-IR Bruker (EQUINOX 55) spectrometer. Nitrogen adsorption-desorption was assessed using a Surface and Pore Size Analysis Instrument (3H-2000PM1, Beishide Instrument-S&T Co., Ltd., China) at 77.3K. All samples were out gassed under vacuum at 80◦C for 5 h prior to the measurement. The special surface area was calculated by the BET method. The micropore volume derived using a t-plot method based on the Halsey thickness equation. The pore size distribution was obtained by applying the BJH formalism to both the adsorption and desorption branch of the isotherm. XPS was performed on a thermo ESCALAB 250XI by using Al Ka radiation as excitation source. TGA was performed on a thermogravimetric analyser (DSC Q2000) under N_2 environment with a temperature rate of 10°C/min from room temperature to 800°C. The structure and morphology of the HCP and HCP-Pd were observed using transmission electron microscopy (TEM, FEI Tecnai G20) and scanning electron microscopy (SEM, zeiss, sigma HD). The content of Pd was measured by inductively coupled plasma emission spectrometry (ICP-AES, Agilent, Icpoes 730). The products were purified by recrystallization and column chromatography over silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C at 500 MHz and 125 MHz, respectively, with TMS as internal standard.

II. Synthesis and analytical data of NHC

Typical procedure for the preparation of **NHC** (**NHC-I** as example): To a solution of 1-benzyl-1H-benzo[d]imidazole (5.0 mmol) in toluene (5 mL) at room temperature was added (chloromethyl)benzene (6.0 mmol) in one portion. The mixture was stirred under refluxing for 20 hours. After the substrate 1-benzyl-1H-benzo[d]imidazole was consumed as indicated by TLC, the mixture was cooled to room temperature and then filtrated. The crude product was washed with ethyl acetate for three times(3 ×20mL). Then the solid was dried at 60°C under vacuum to give **NHC-I** as a brown solid, and the yield of **NHC-I** reached 94%.



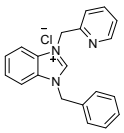
NHC[1]-I, R=Bn
NHC[1]-II, R=Ph
NHC[1]-III, R=Me

NHC-I, R=Bn
NHC-II, R=Ph
NHC-III, R=Me

1-benzyl-1H-benzo[d]imidazole (**NHC[1]-I**)[1] and 1-phenyl-1H-benzo[d]imidazole (**NHC[1]-II**)[2] was prepared as described previously.

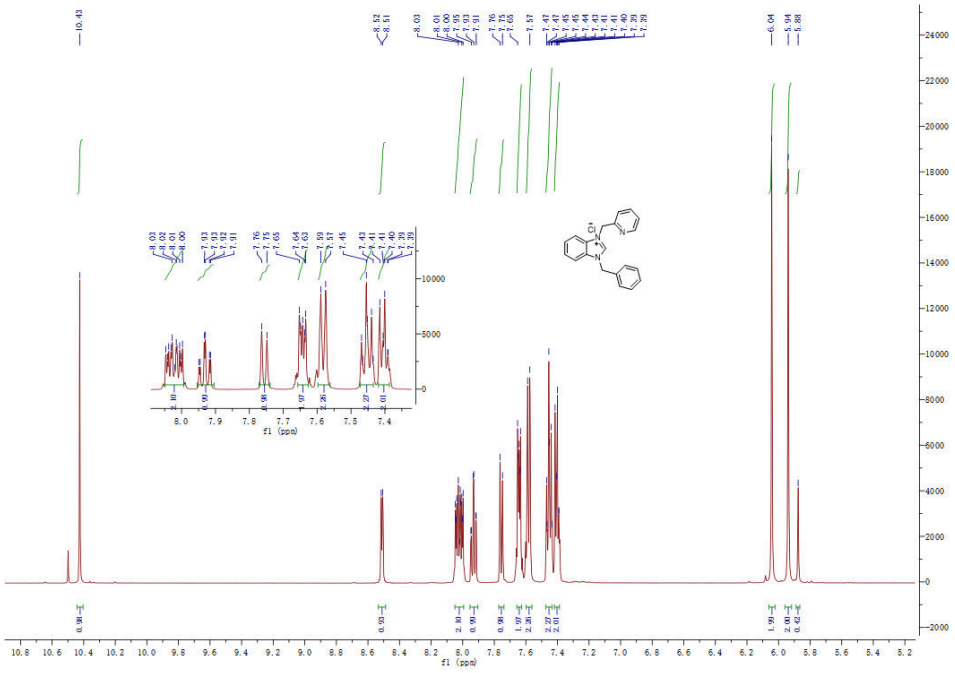
1. Xu S , Song K , Li T , et al. Palladium catalyst coordinated in knitting N-heterocyclic carbene porous polymers for efficient Suzuki–Miyaura coupling reactions[J]. Journal of Materials Chemistry A, 2015, 3， 1272-1278.

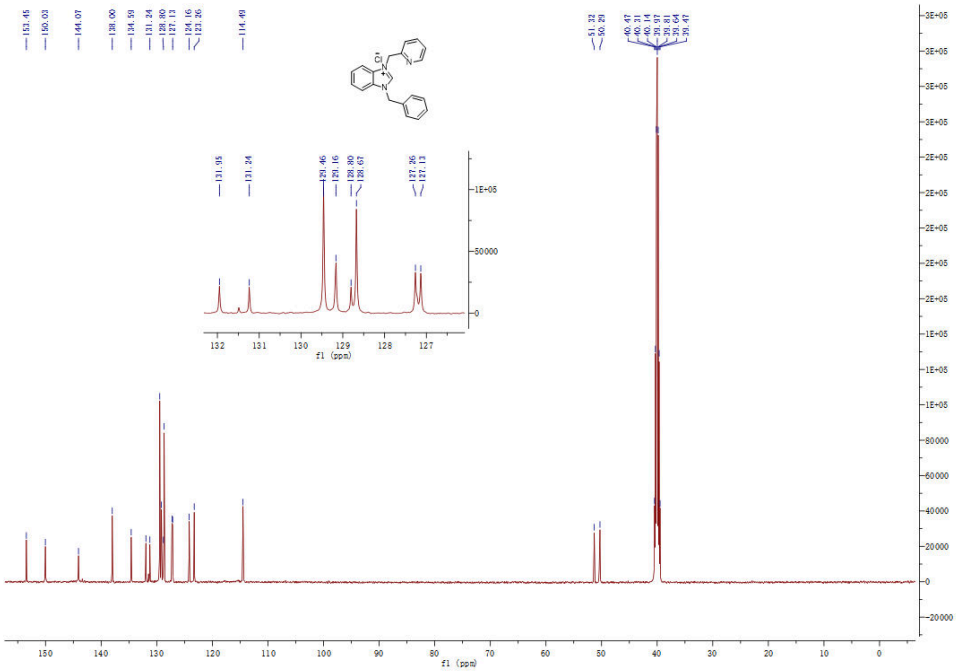
2. Kwong F Y , Buchwald S L . Mild and Efficient Copper-Catalyzed Amination of Aryl Bromides with Primary Alkylamines[J]. Organic Letters, 2003, 5(6):793-796.



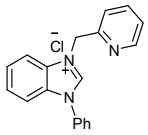
NHC-I:

Brown solid: ^{1}H NMR (500 MHz, DMSO) δ = 10.43 (s, 1H), 8.51 (d, *J* = 4.6 Hz, 1H), 8.05-7.99 (m, 2H), 7.93 (td, *J* = 7.7, 1.7 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.66-7.63 (m, 2H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.47-7.43 (m, 2H), 7.42-7.39 (m, 2H), 6.04 (s, 2H), 5.94 (s, 2H); ^{13}C NMR (125 MHz, DMSO) δ = 50.0, 51.3, 127.1, 127.3, 128.7, 128.8, 129.2, 129.5, 131.2, 132.0, 134.6, 138.0, 144.1, 150.0, 153.5. IR (KBr) 3431, 2974, 1561, 1460, 1375, 1198, 765, 706, 637.

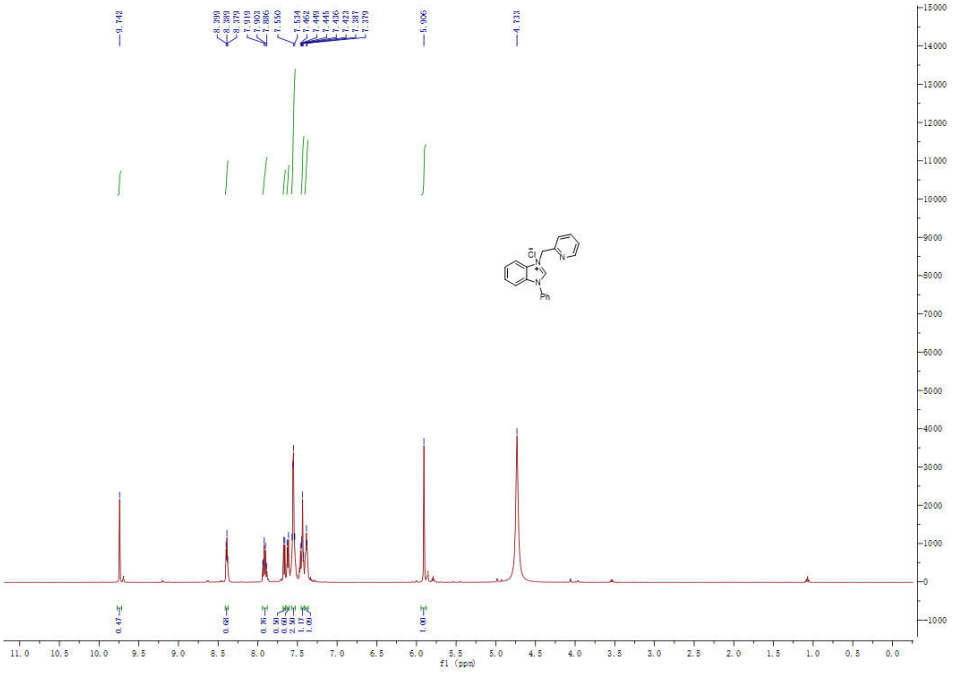


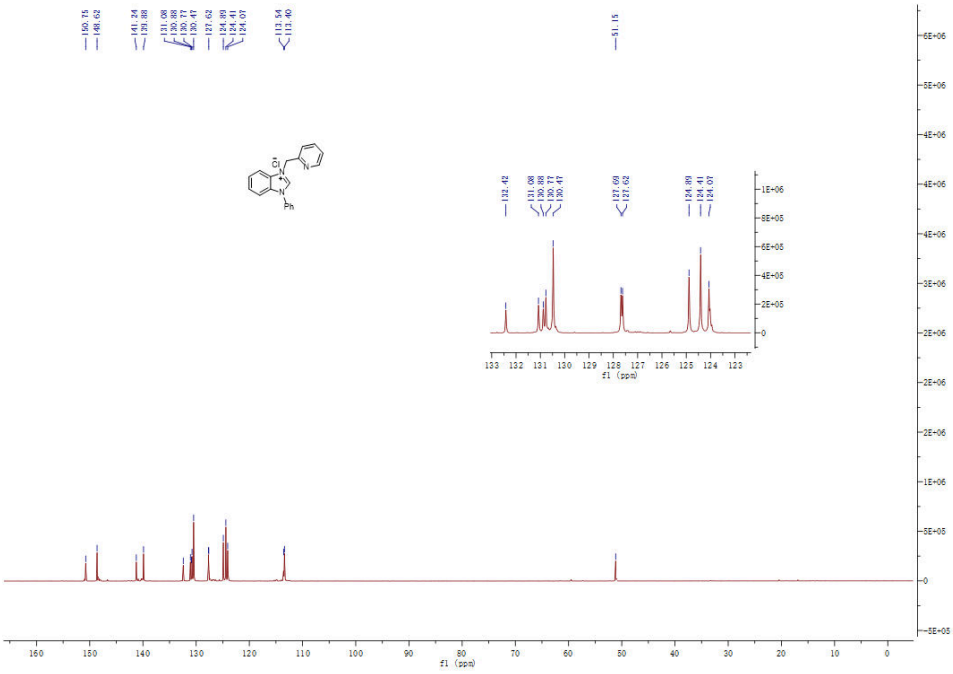


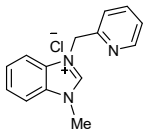
NHC-II:



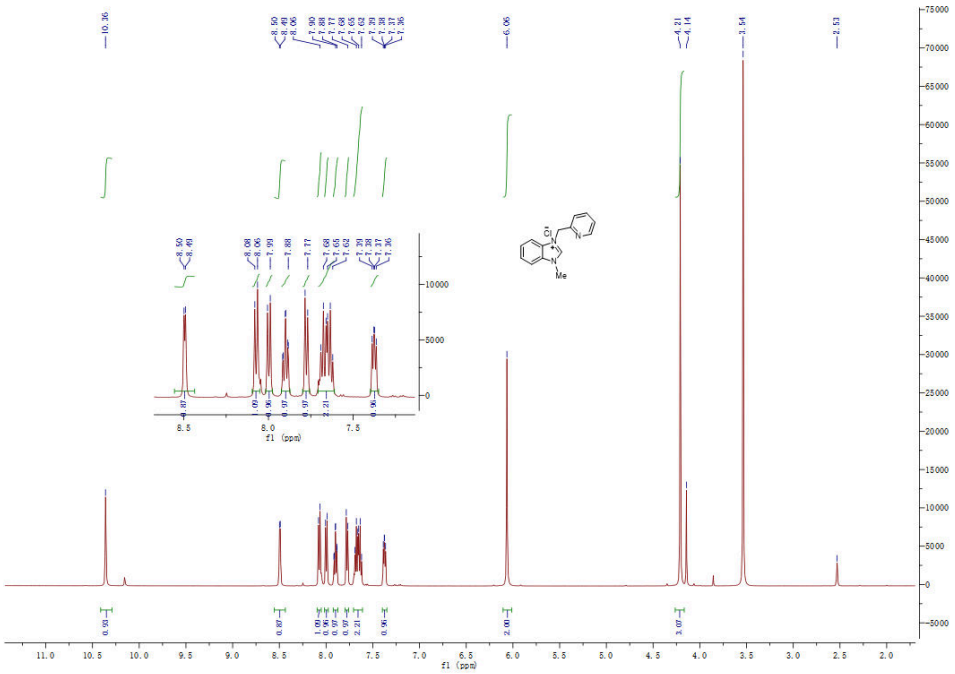
Brown solid: ^{1}H NMR (500 MHz, D_2O) δ =δ 9.74 (s, 1H), 8.39 (t, *J* = 5.0 Hz, 1H), 7.94-7.88 (m, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.57-7.53 (m, 5H), 7.44 (dd, *J* = 8.9, 4.0 Hz, 2H), 7.38 (d, *J* = 3.9 Hz, 2H), 5.91 (s, 2H); ^{13}C NMR (125 MHz, D_2O) δ = 150.75, 148.62, 141.24, 139.88, 132.42, 131.08, 130.88, 130.77, 130.47, 127.69, 127.62, 124.89, 124.41, 124.07, 113.54, 113.40, 51.15; IR (KBr) 3379, 3039, 1556, 1474, 1246, 758, 696.

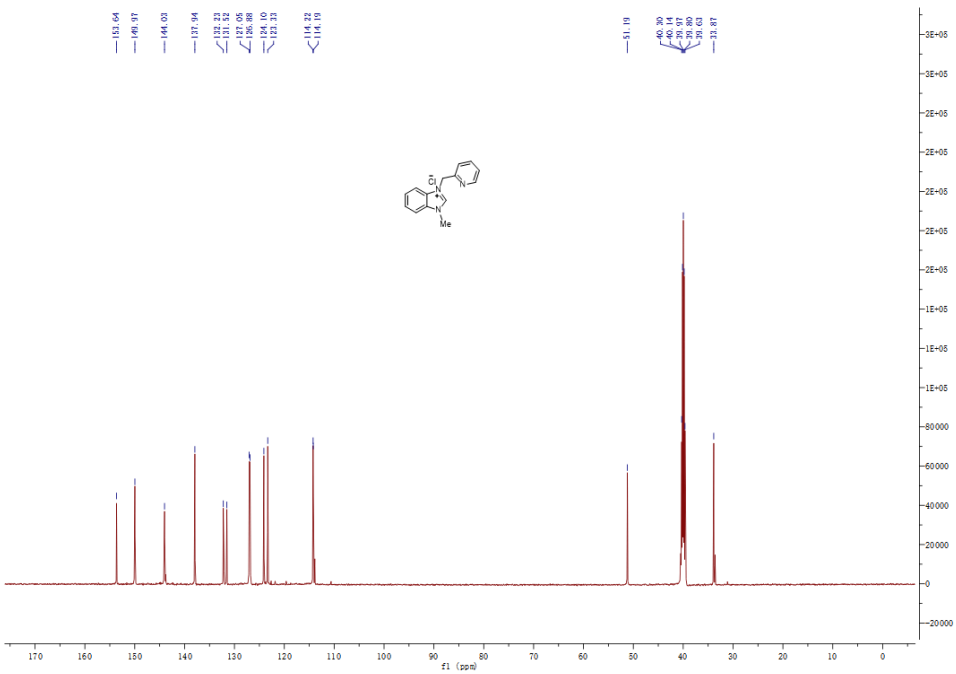




NHC-III: 

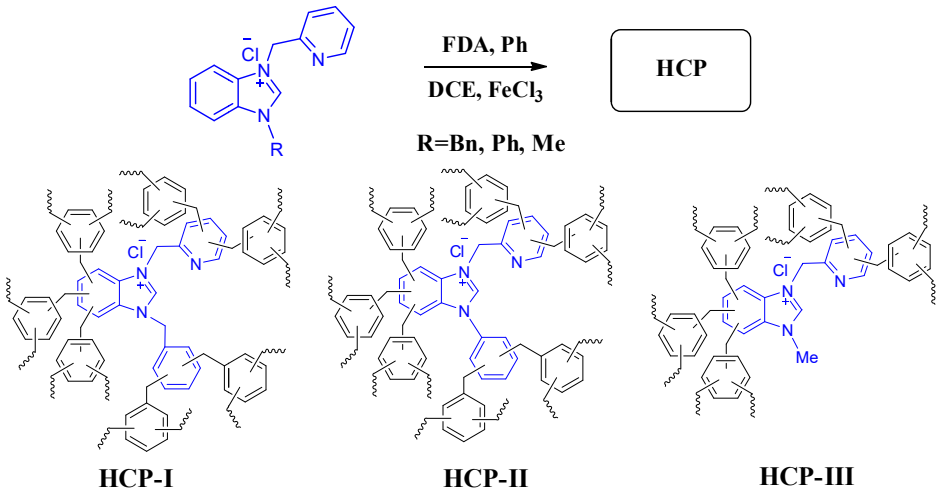
Brown solid: ^{1}H NMR (500 MHz, DMSO) δ = 10.36 (s, 1H), 8.49 (d, *J* = 4.4 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.90 (td, *J* = 7.6, 1.3 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.66 (dt, *J* = 15.3, 7.3 Hz, 2H), 7.38 (dd, *J* = 7.0, 5.1 Hz, 1H), 6.06 (s, 2H), 4.21 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ = 33.9, 51.2, 114.1, 114.2, 123.3, 124.1, 126.9, 127.1, 131.5, 132.2, 137.9, 144.0, 149.9, 153.6; IR (KBr) 3382, 3017, 1561, 1429, 1294, 1026, 767, 745, 685.



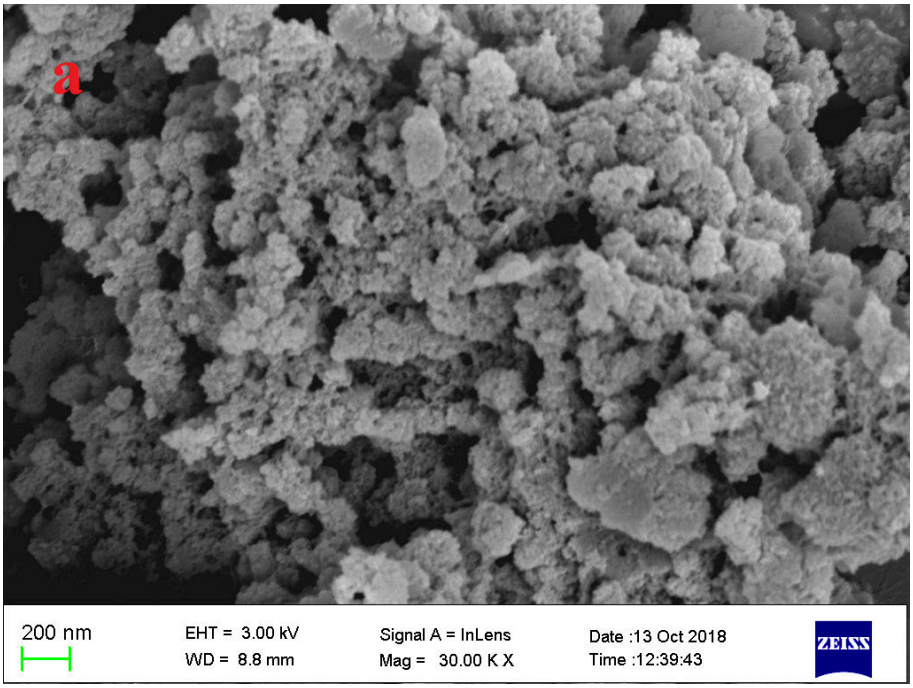


III. Synthesis and analytical data of HCP

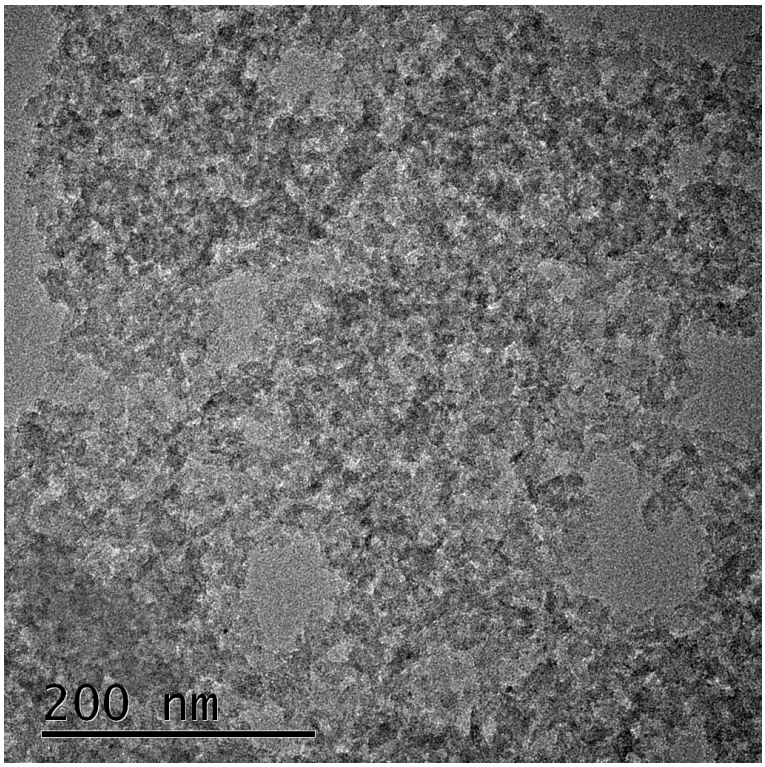
Typical procedure for the preparation of **HCP** (**HCP-I** as example): $FeCl_3$ (anhydrous, 0.09mol) was added to a solution of benzene (0.03mol), NHC-I (0.02mol), and formaldehyde dimethyl acetal (FDA, 0.09mol) in 20mL 1,2-dichloroethane (DCE). The resulting mixture was stirred at room temperature for good mixing, and then was stirred at 45°C for 5h to form original network, and then heated at 80°C for 48h to react completely. The resulting precipitate was washed three times with methanol, then washed with methanol in a Soxhlet for 48 h, and finally dried under reduced pressure at 60°C for 24h to give HCP-I.



1) analytical data of HCP-I

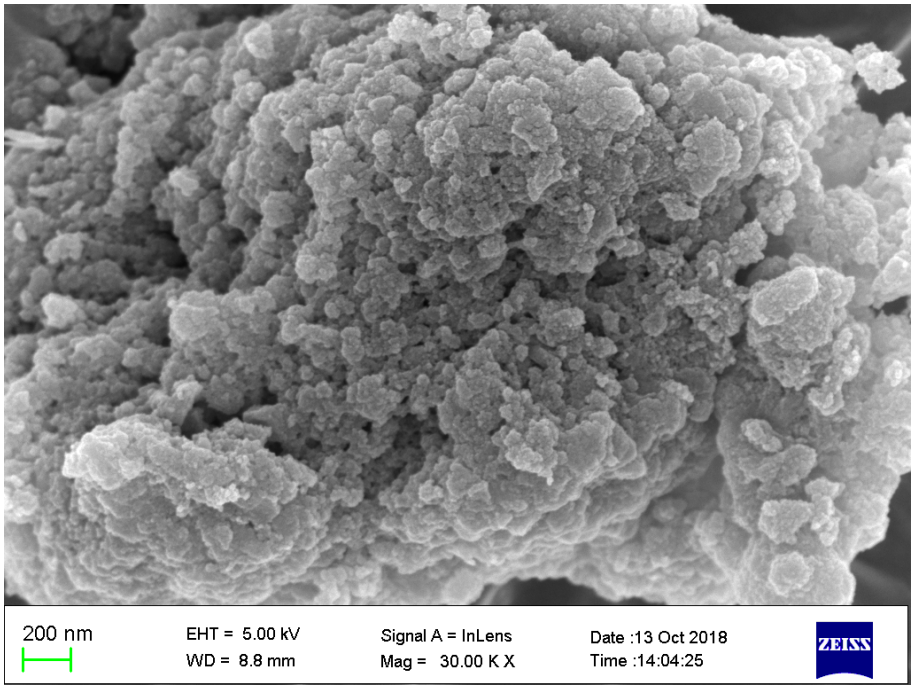


SEM imagine of HCP-I

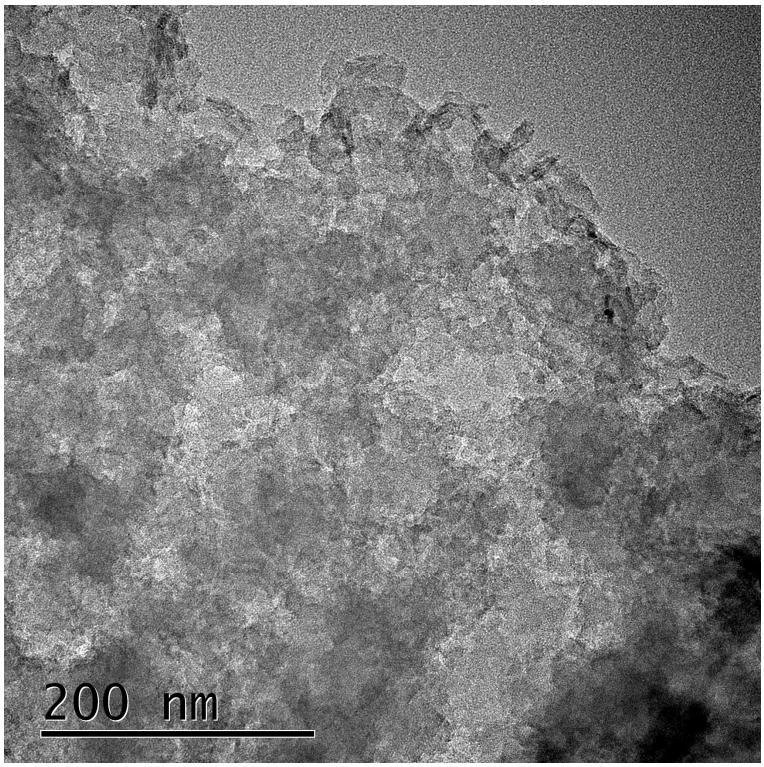


TEM imagine of HCP-I

2) analytical data of HCP-II

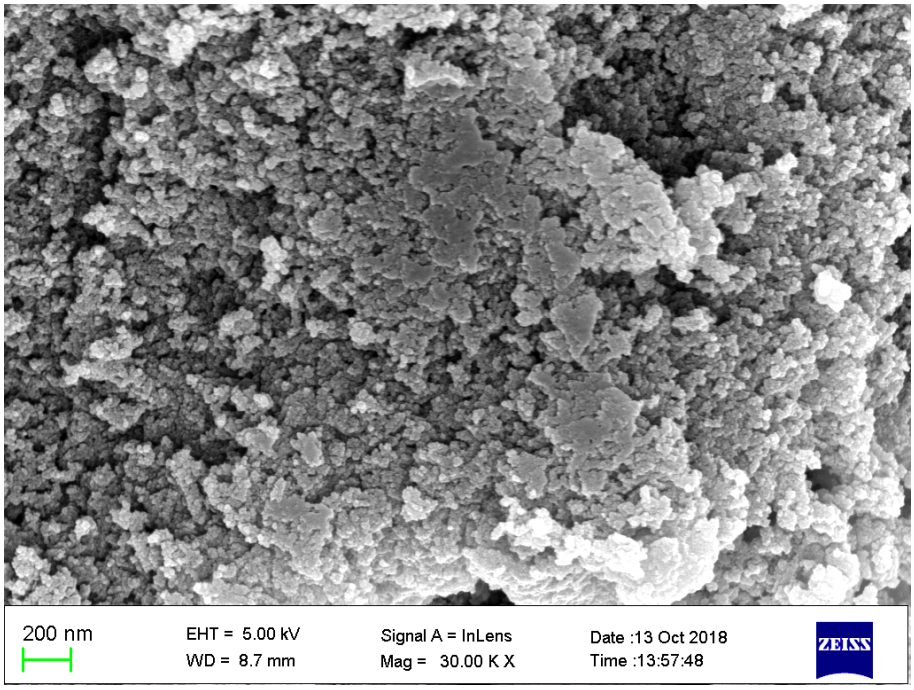


SEM imagine of HCP-II

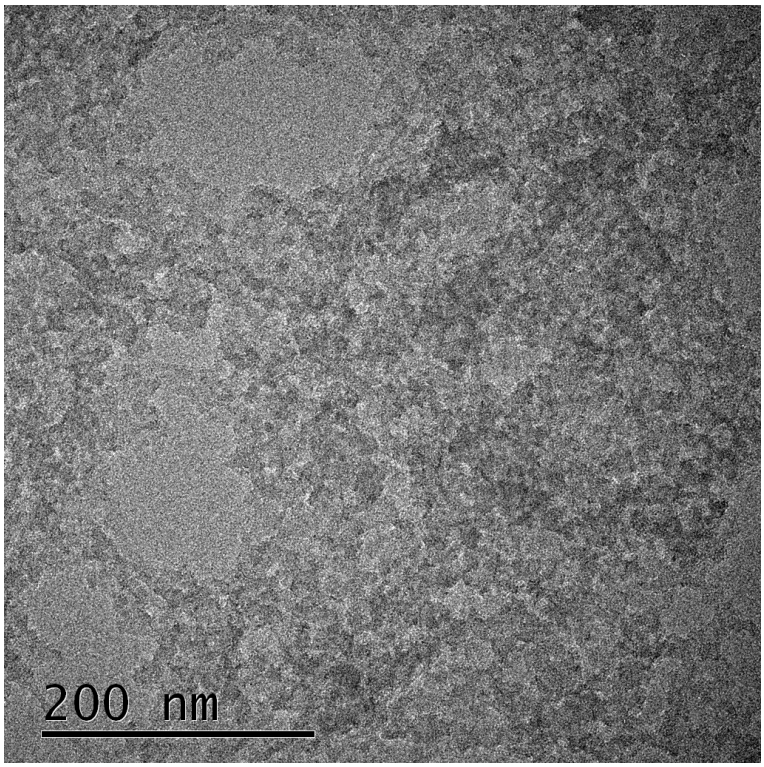


TEM imagine of HCP-II

3) analytical data of HCP-III



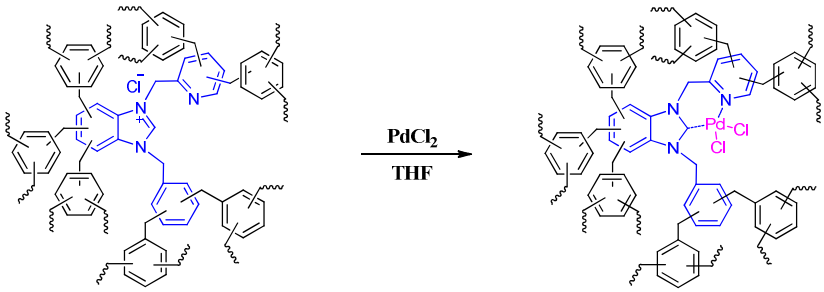
SEM imagine of HCP-III



TEM imagine of HCP-III

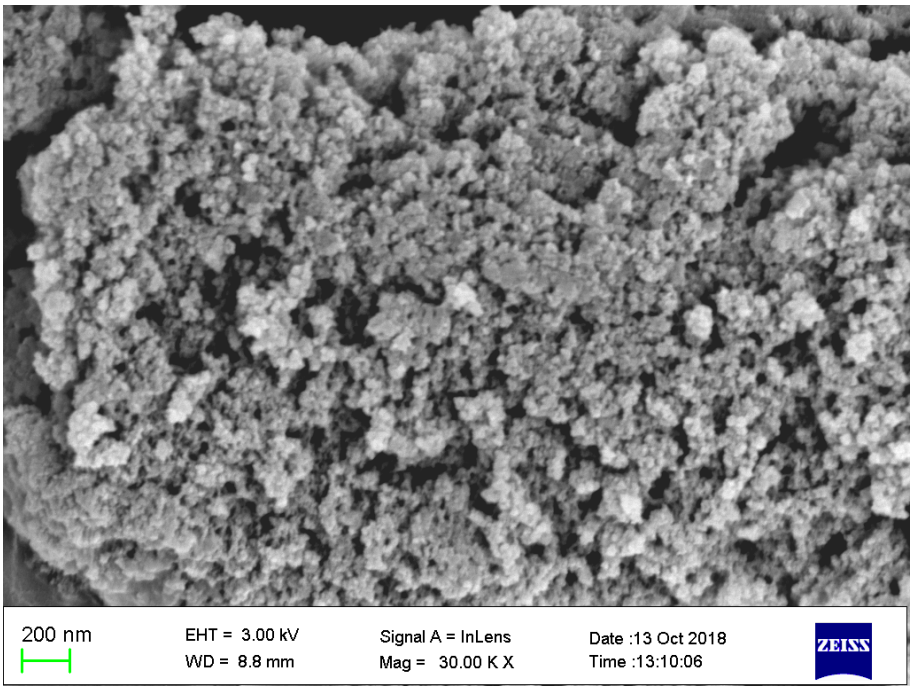
IV. Synthesis and analytical data of HCP-Pd

Typical procedure for the preparation of **HCP-Pd** (**HCP-Pd-I** as example): HCP-I(2.0g), $PdCl_2$ (0.30g) and 50mL of anhydrous tetrahydrofuran were placed in a three-necked flask. Then, the reaction mixture was stirred under refluxing for 24h. Finally, the solid was filtered and washed with methanol several times, then washed with methanol in a Soxhlet for 48h, and dried under reduced pressure at 60°C for 24h to give HCP-Pd-I.

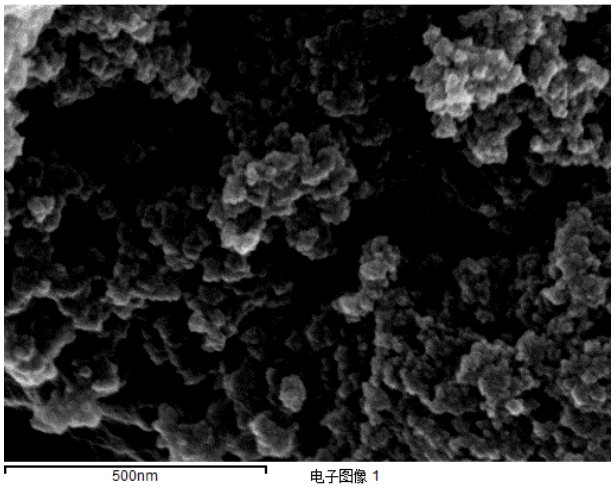


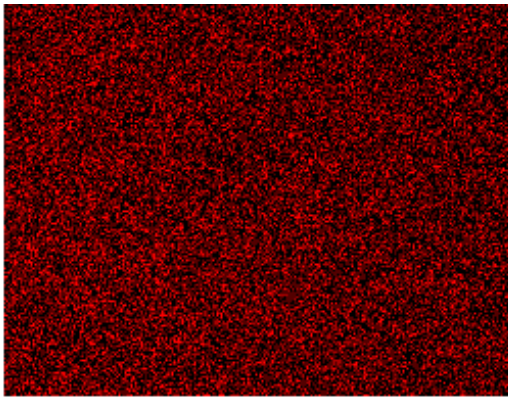
HCP-I **HCP-Pd-I**

1) analytical data of HCP-Pd-I

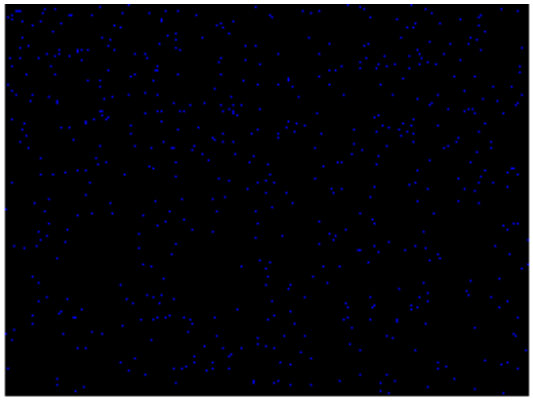


SEM imagine of HCP-Pd-I

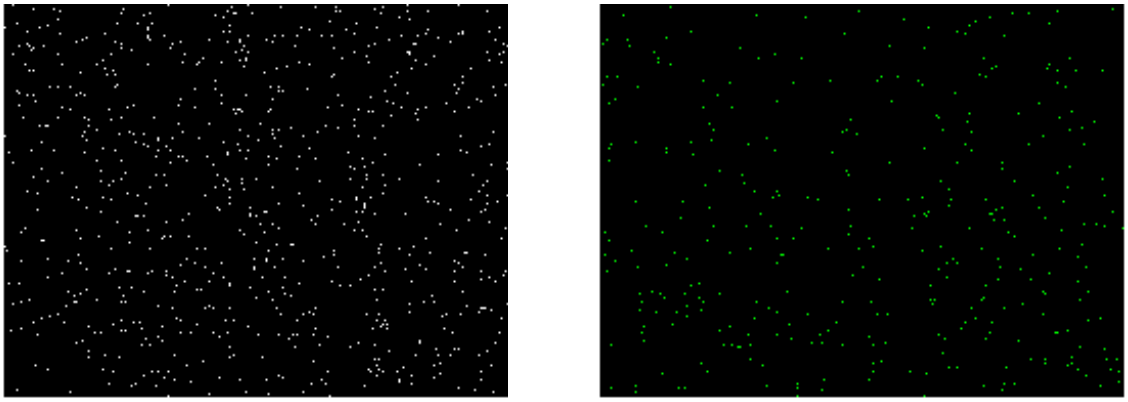




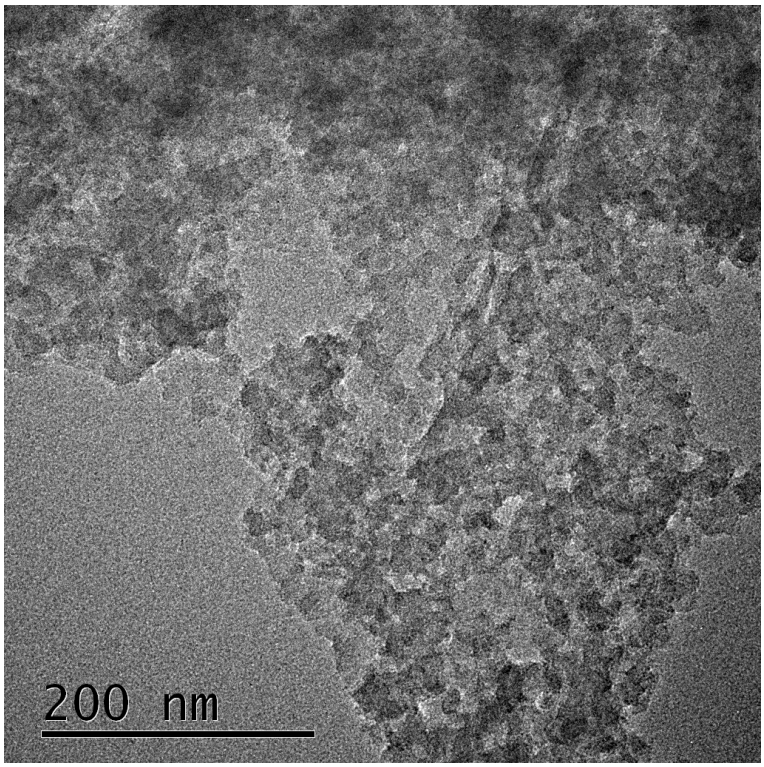
C Ka1_2



Pd La1

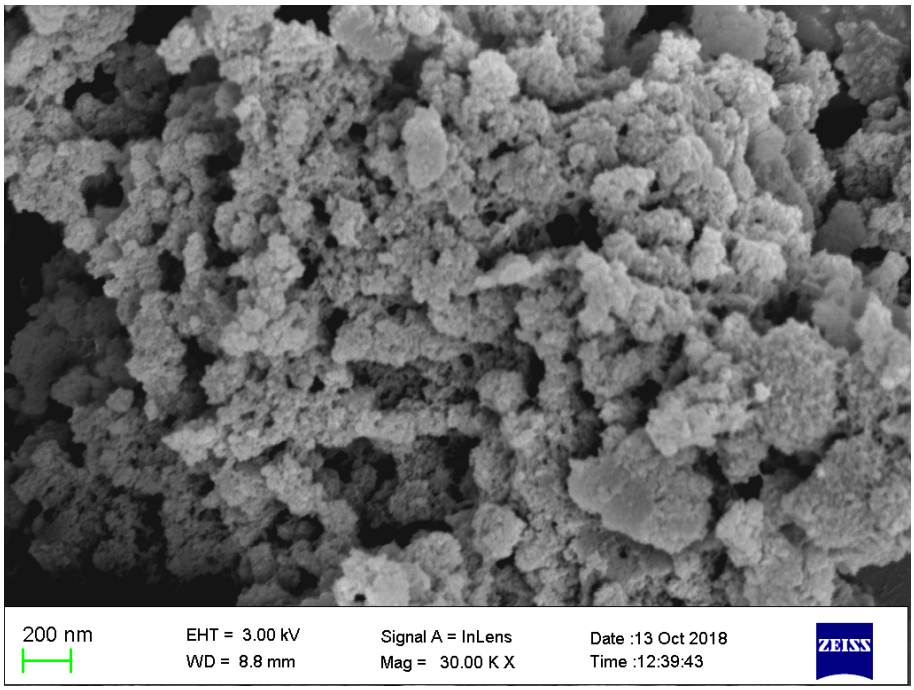


SEM elemental mapping imagine of HCP-Pd-I

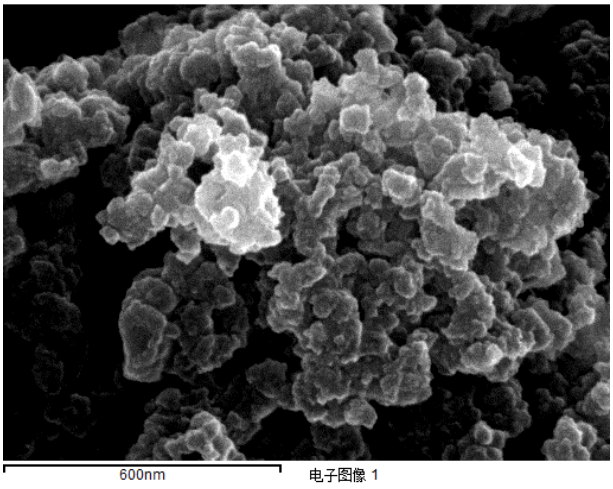


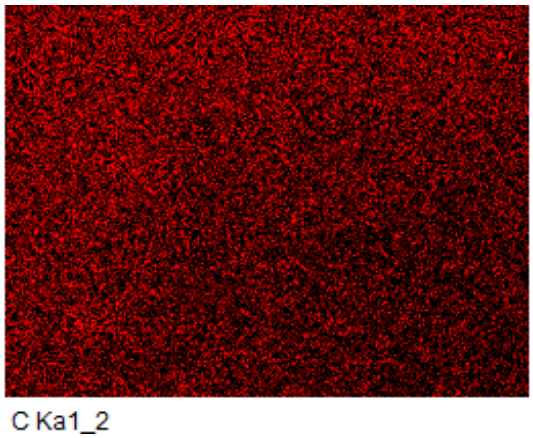
TEM imagine of HCP-Pd-I

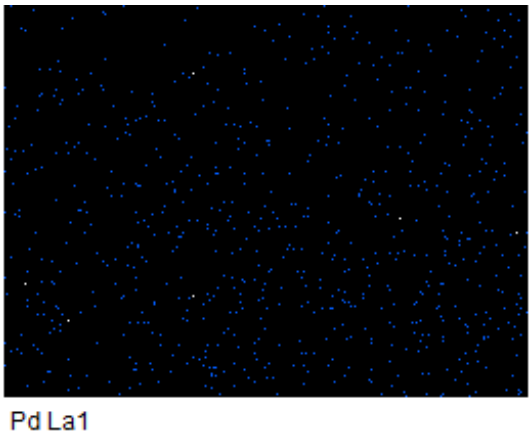
2) analytical data of HCP-Pd-II

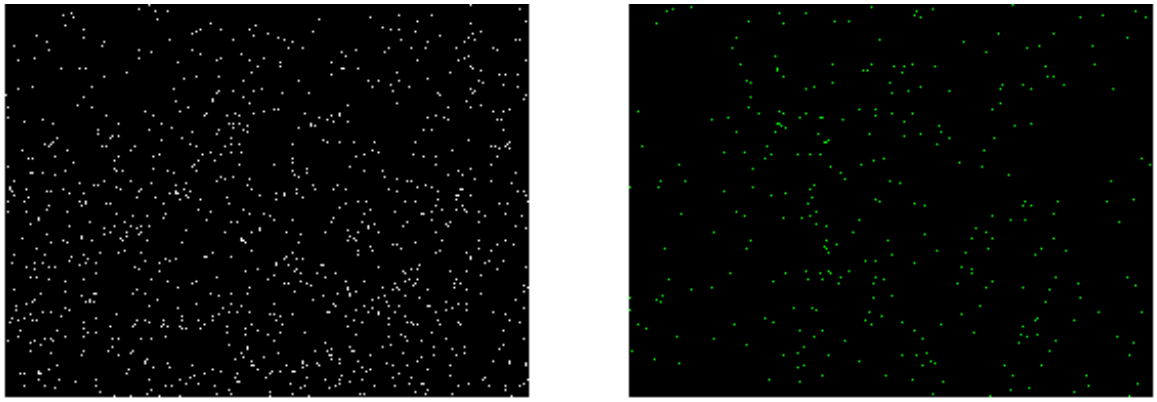


SEM imagine of HCP-Pd-II

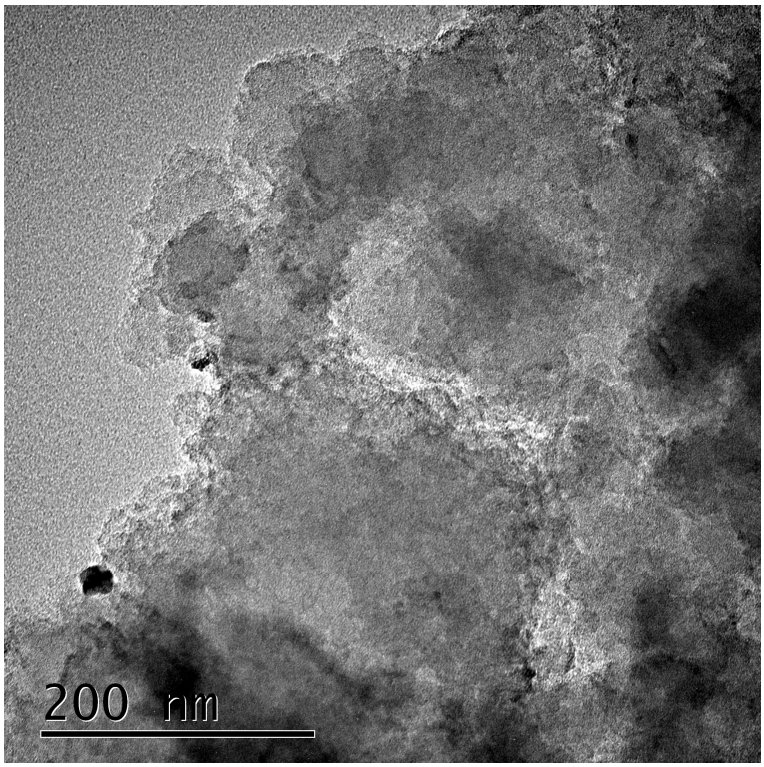






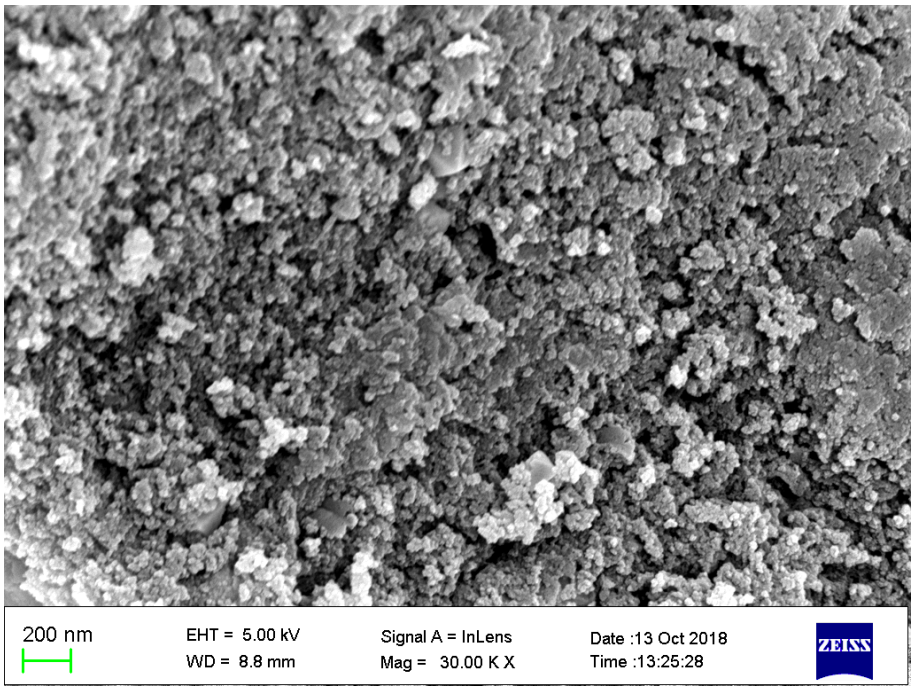


SEM elemental mapping imagine of HCP-Pd-II

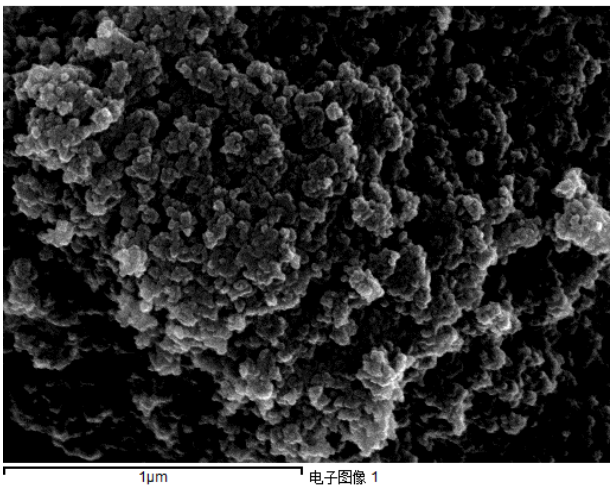


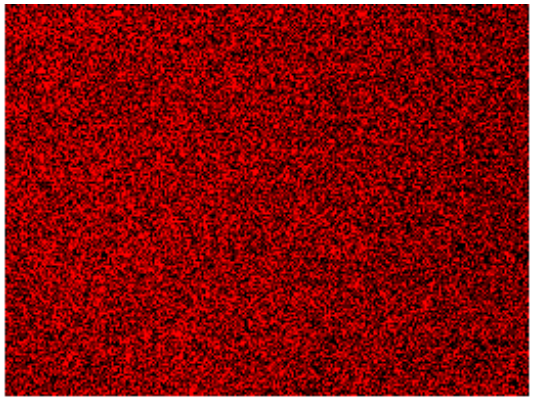
TEM imagine of HCP-Pd-II

3) analytical data of HCP-Pd-III

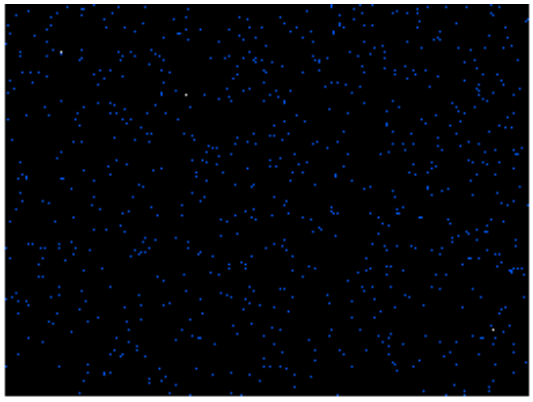


SEM imagine of HCP-Pd-III

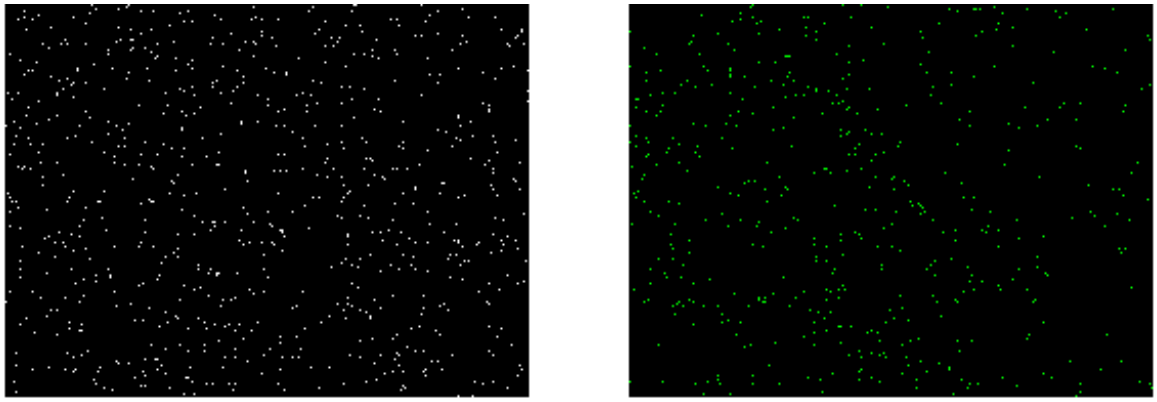




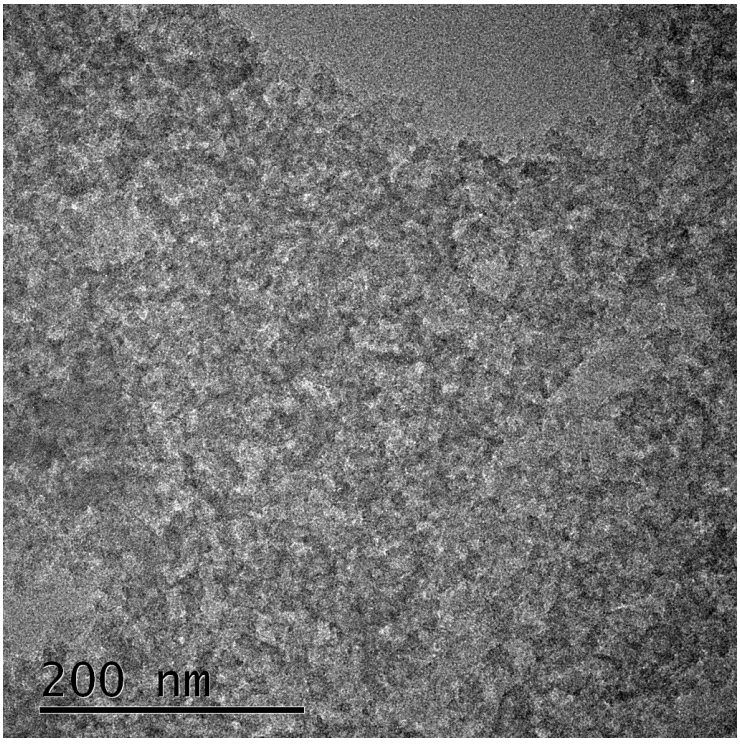
C Ka1_2



Pd La1

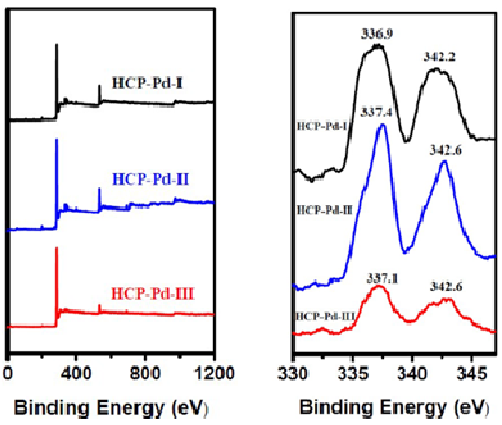


SEM elemental mapping imagine of HCP-Pd-III



TEM imagine of HCP-Pd-III

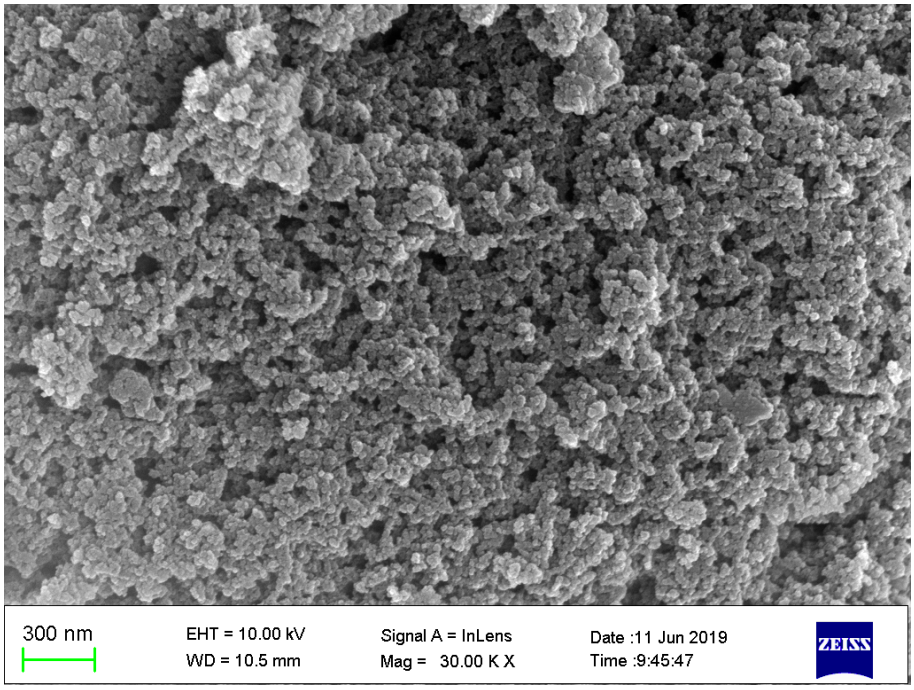
4) XPS spectra of the HCP-Pd



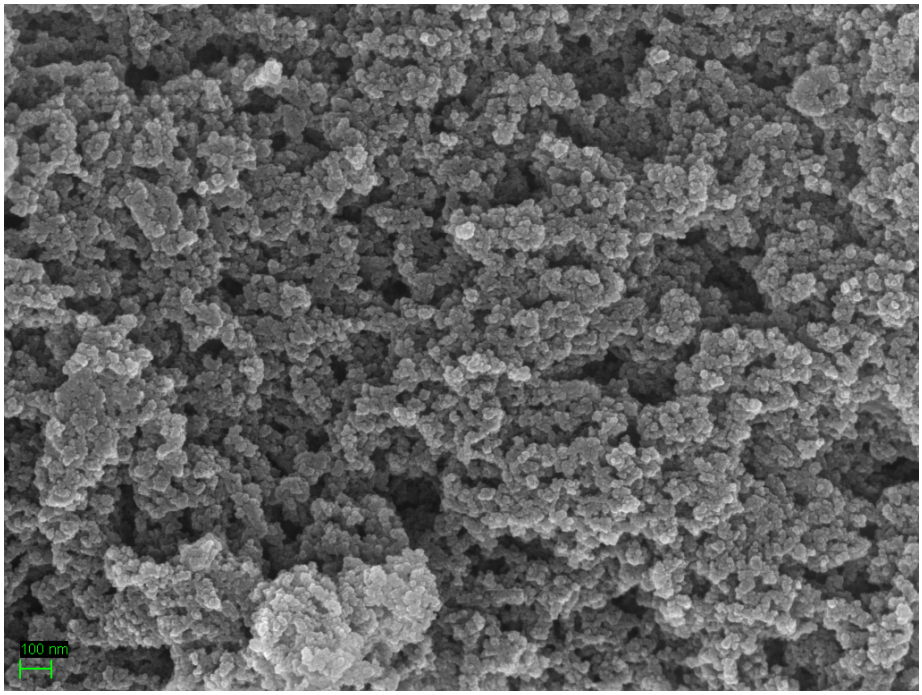
XPS spectra of the HCP-Pd

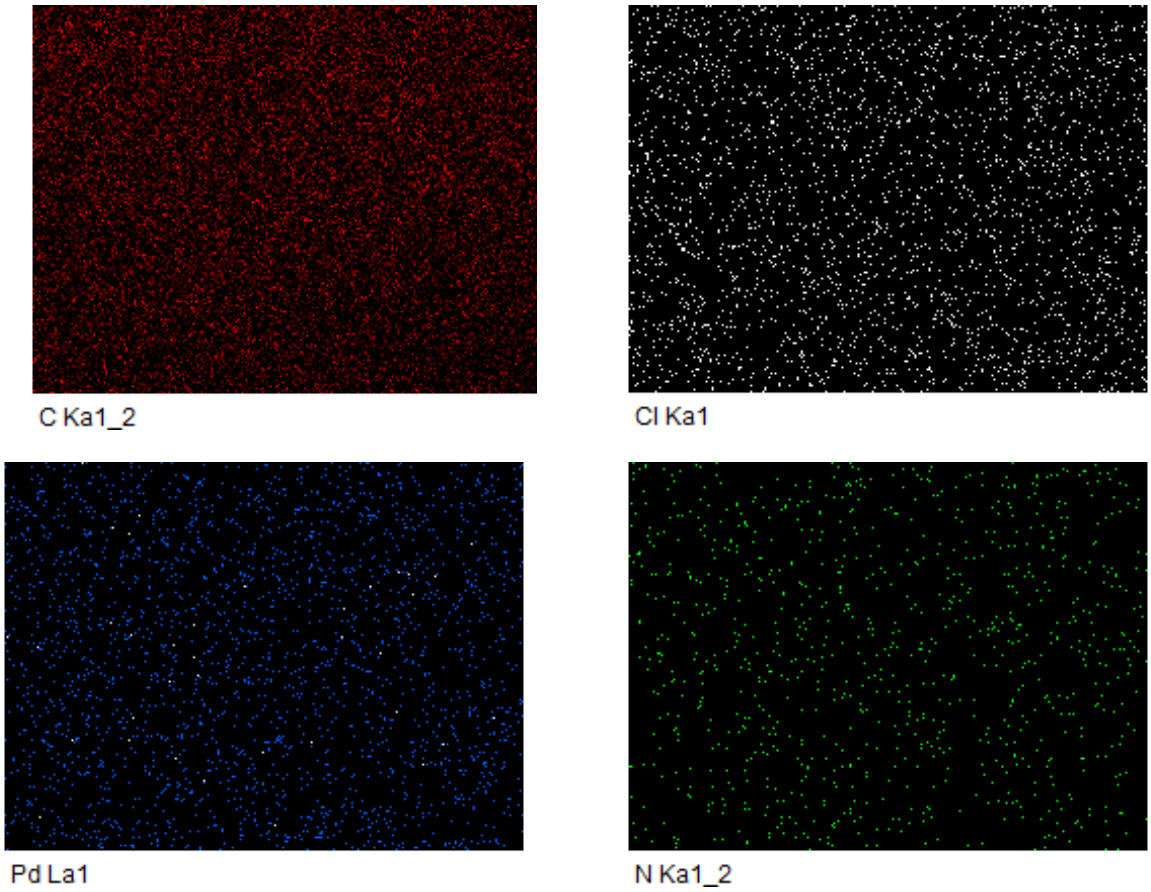
V. Analytical data of Poly-Pd and recycled HCP-Pd

1) analytical data of **Poly-Pd**



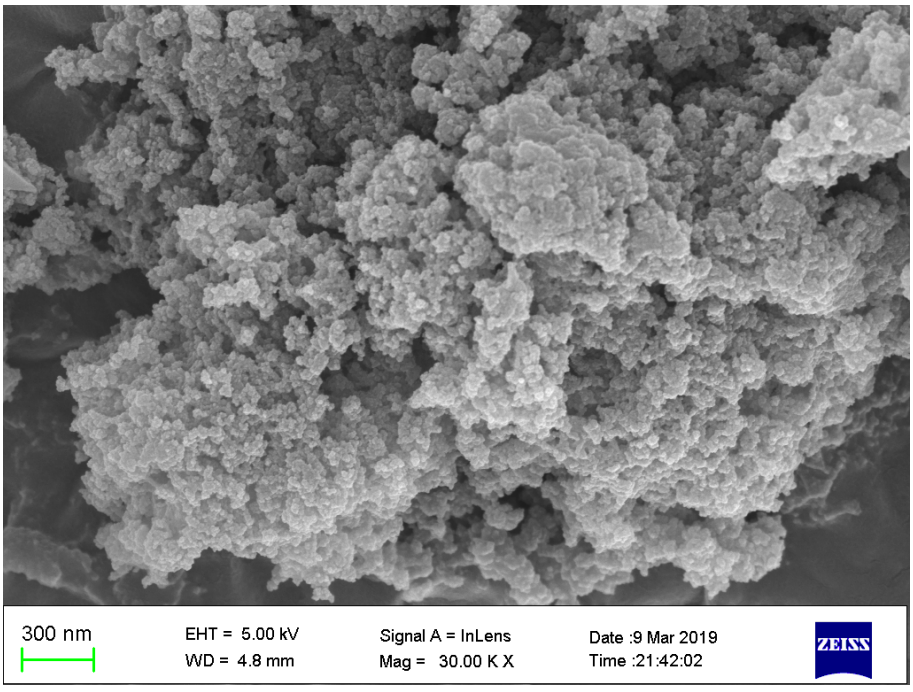
TEM imagine of Poly-Pd



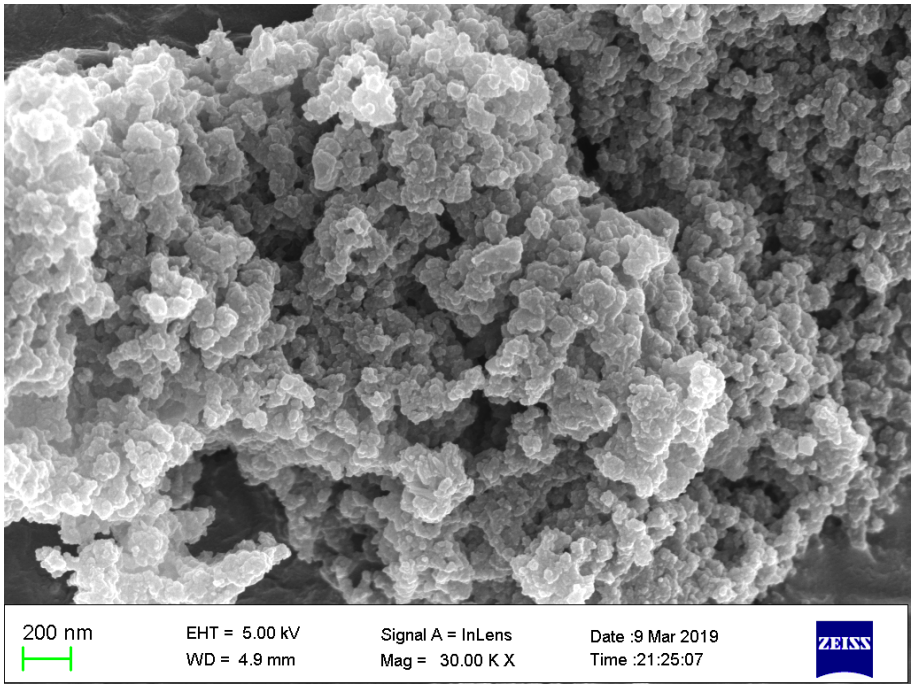


SEM elemental mapping imagine of Poly-Pd

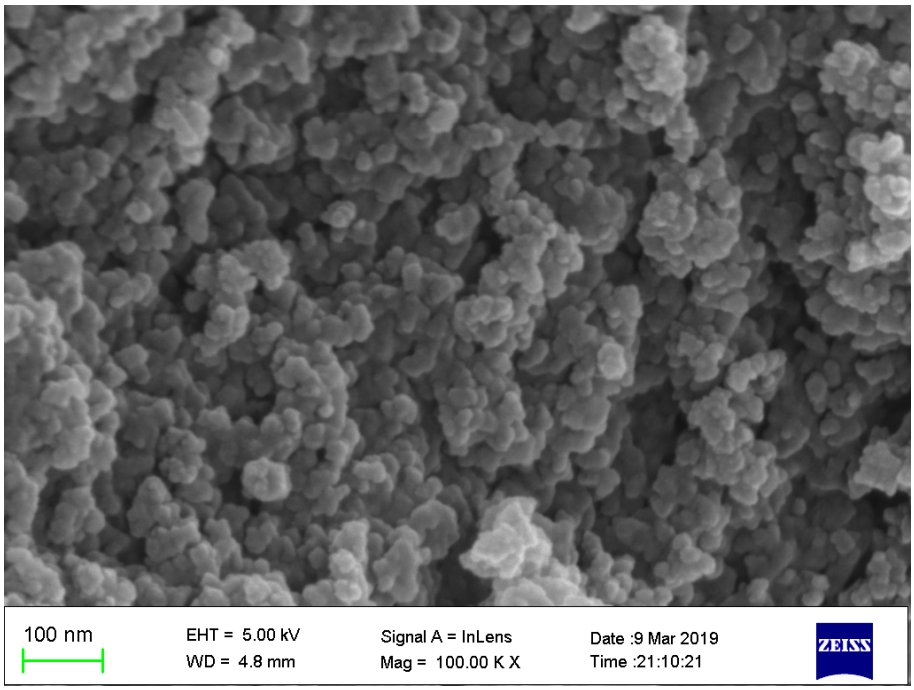
2) analytical data of **recycled HCP-Pd**



TEM imagine of recycled HCP-Pd-I



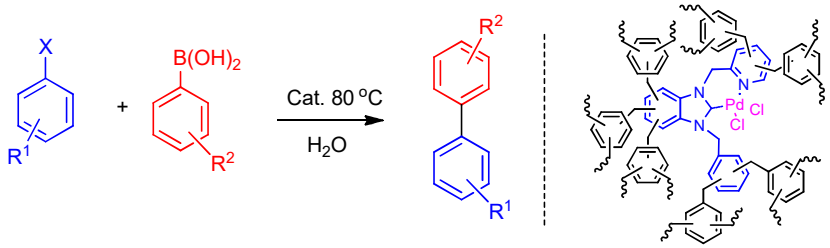
TEM imagine of recycled HCP-Pd-II



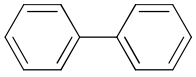
TEM imagine of recycled HCP-Pd-III

VI. Synthesis and analytical data o 3

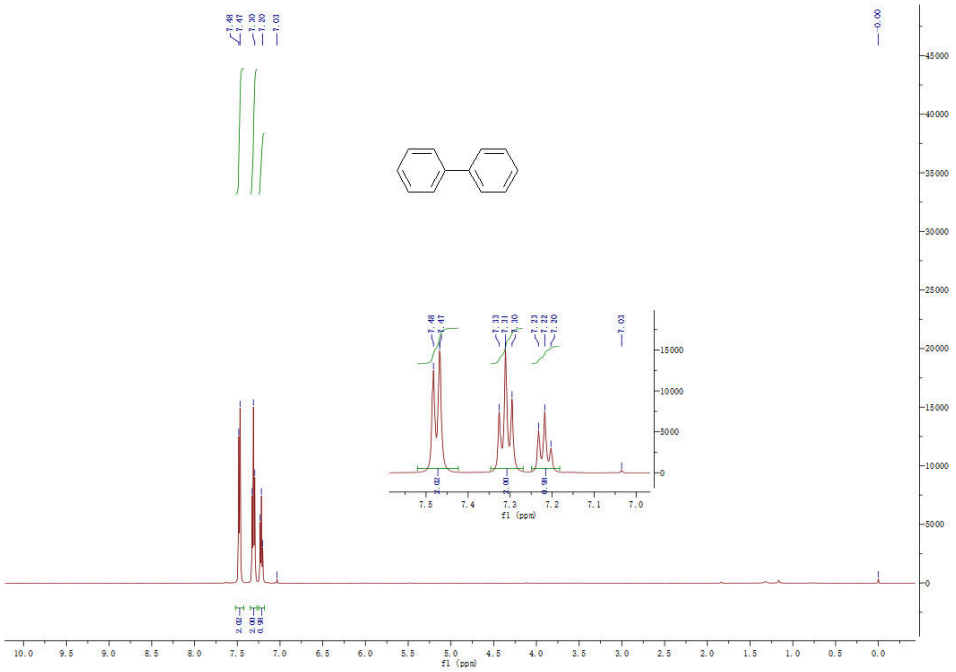
Typical procedure for the preparation of **3** (**3a** as example): **HCP-Pd-I**(40mg) was added to a solution of iodobenzene **1a** (2.5mmol), phenylboronic acid **2a** (3.3mmol), and K_3PO_4 (5.0mmol) in 20mL water. The mixture was stirred under a N_2 atmosphere at 80°C for 1.0 hour. After the substrate iodobenzene **1a** was consumed as indicated by TLC, and then poured into ice-water (100mL) under stirring. The mixture was extracted with dichloromethane (3 × 20mL), the combined organic phase was washed with water (3× 20mL), dried over $MgSO_4$, filtered and concentrated in *vacuo.* The crude product was purified by flash chromatography (silica gel, petroleum ether: diethyl ether = 20: 1) to give **3a** as a white solid (366 mg, 95%).

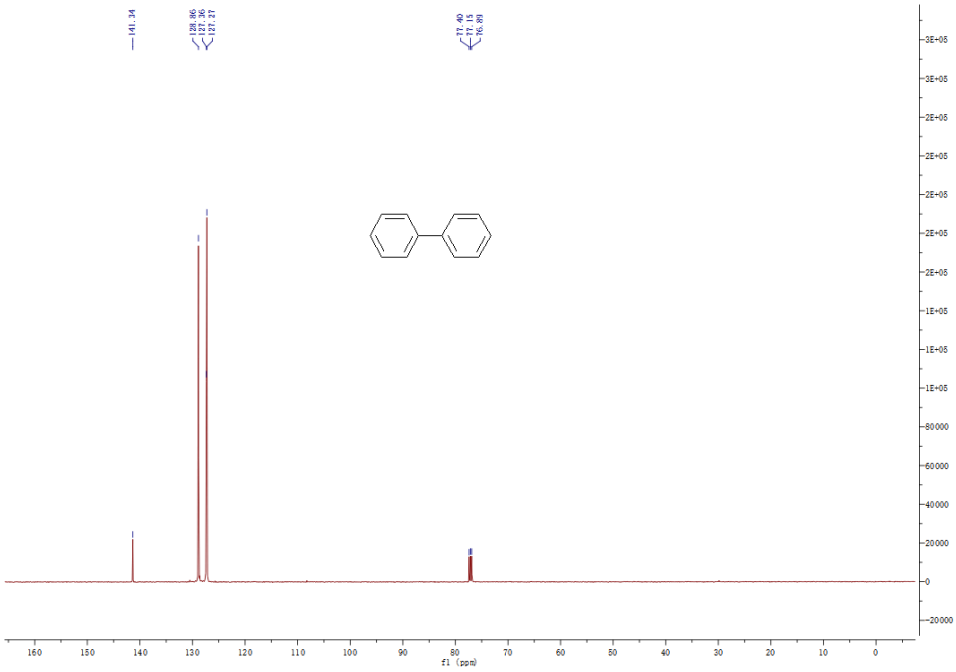


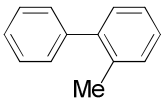
1 **2** **3** HCP-Pd-I

3a: 

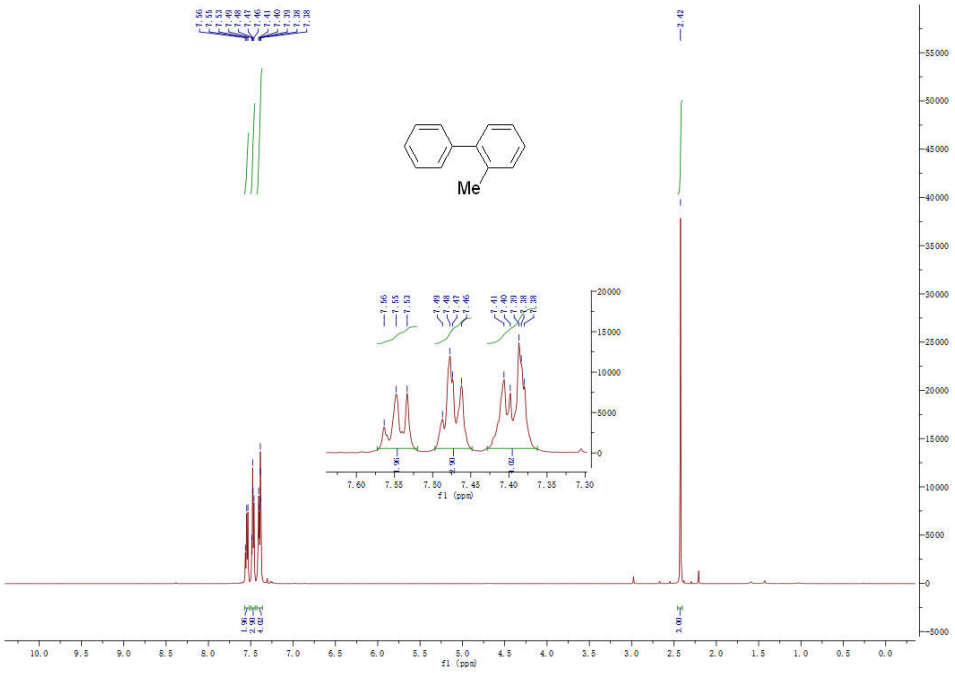
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 127.3, 127.4, 128.9, 141.3; IR (KBr) 3034, 1479, 1429, 1170, 1007, 727, 696, 611.

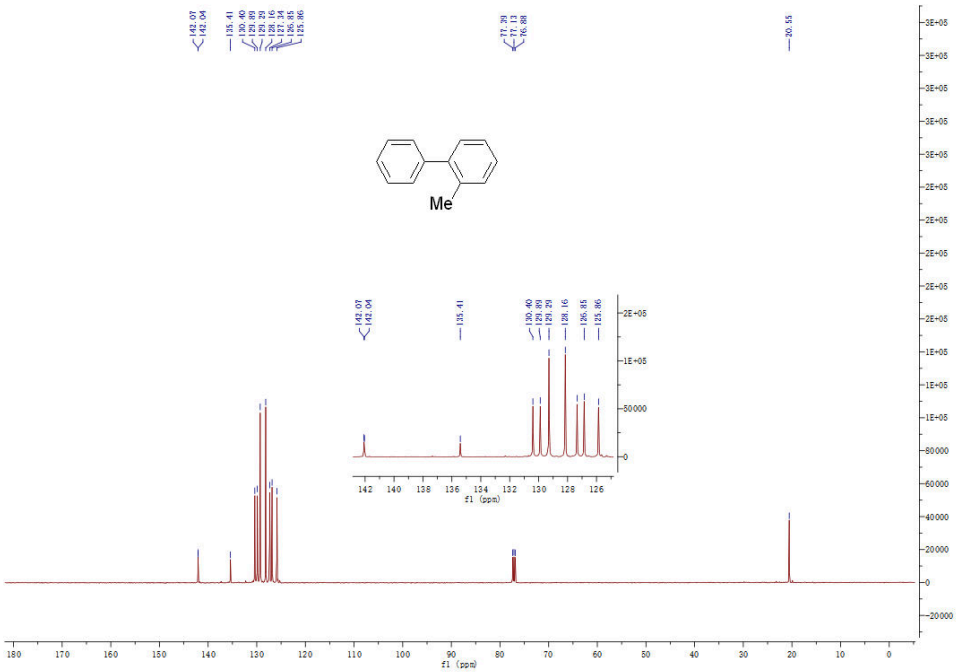


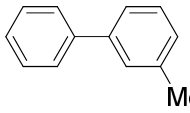


3b: 

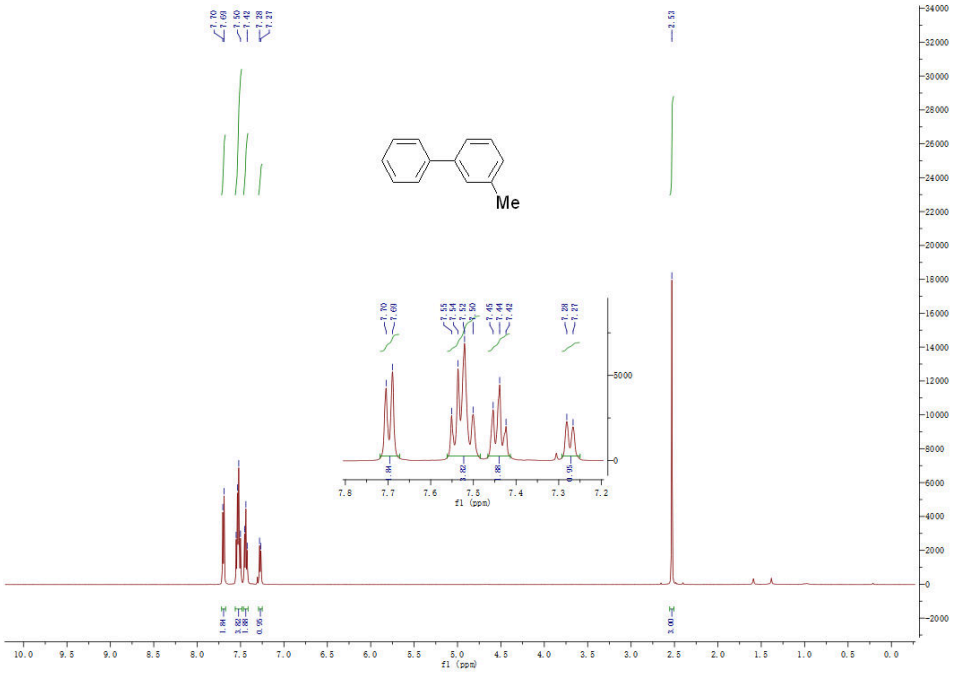
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57-7.52 (m, 2H), 7.48 (dd, *J* = 7.1, 5.4 Hz, 3H), 7.43-7.36 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 20.6, 125.9, 126.9, 128.2, 129.3, 129.9, 130.4, 135.4, 142.0, 142.1; IR (KBr) 3020, 1599, 1479, 1341, 1009, 726, 701, 617.

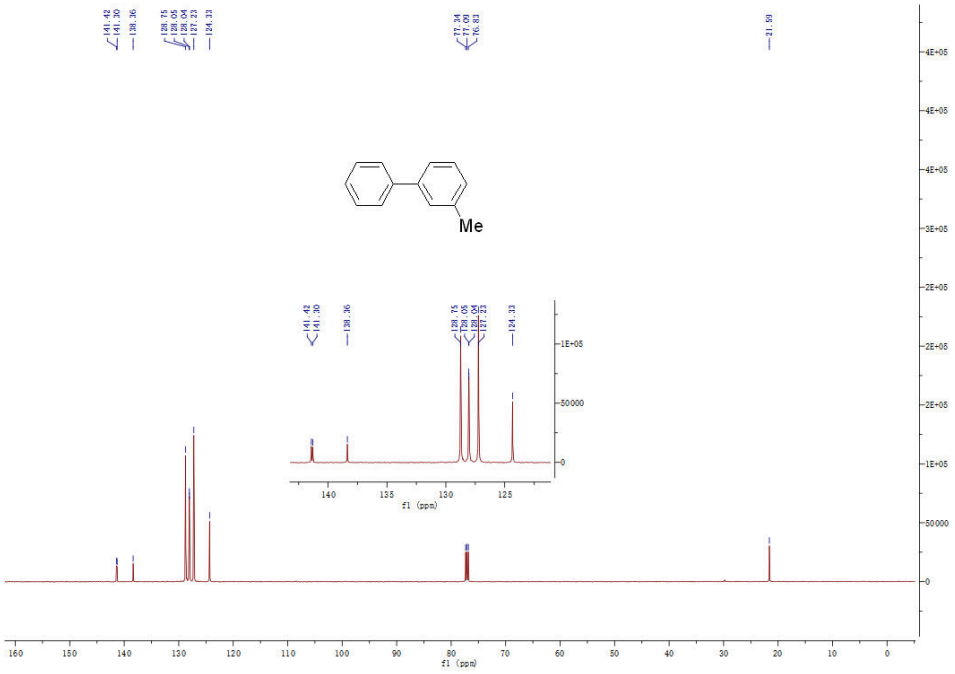


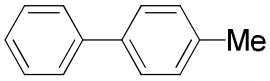


3c: 

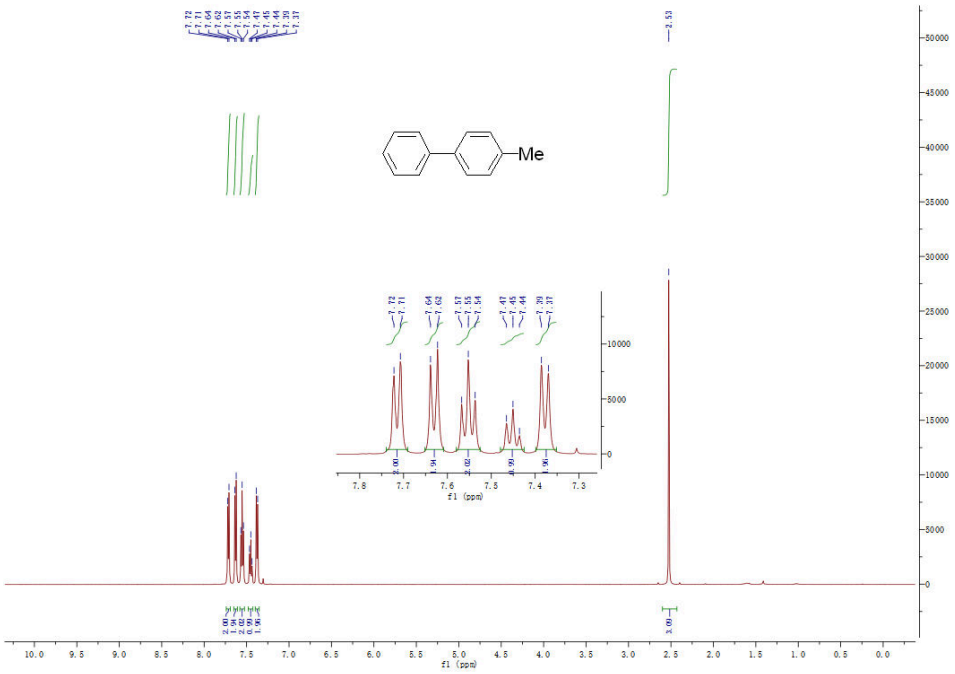
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 7.5 Hz, 2H), 7.53 (dd, *J* = 16.4, 8.7 Hz, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.6, 124.3, 127.2, 128.0, 128.1, 128.8, 138.4, 141.3, 141.4; IR (KBr) 3029, 1600, 1481, 791, 752, 697, 616.

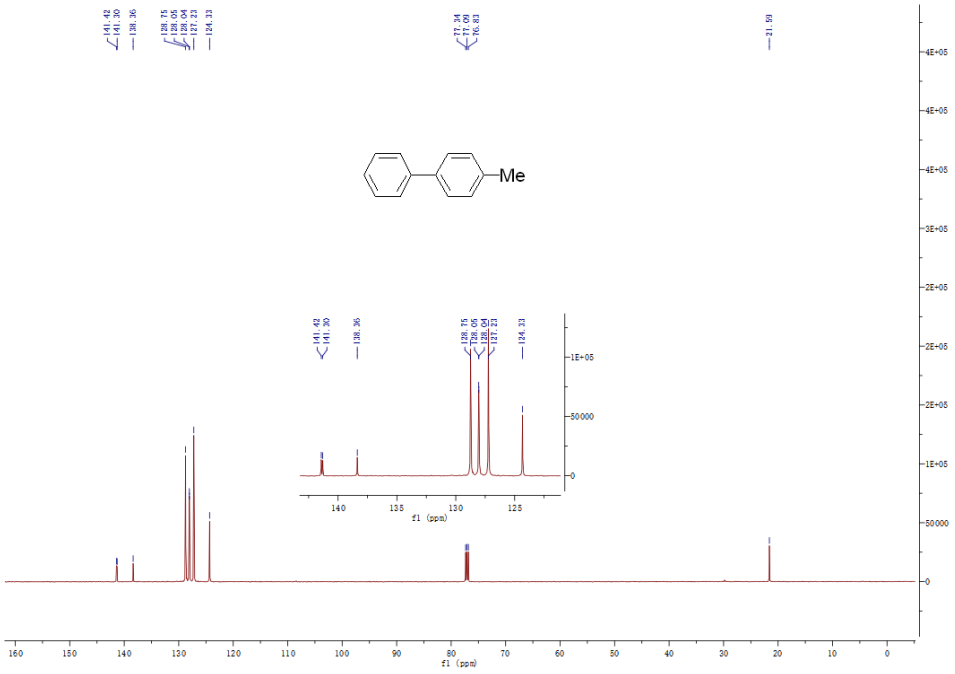




3d: 

White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 7.3 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.6, 124.3, 127.2, 128.0, 128.1, 128.8, 138.4, 141.3, 141.4; IR (KBr) 2917, 1487, 1377, 1006, 822, 754, 689.





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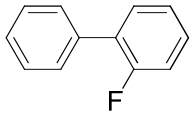
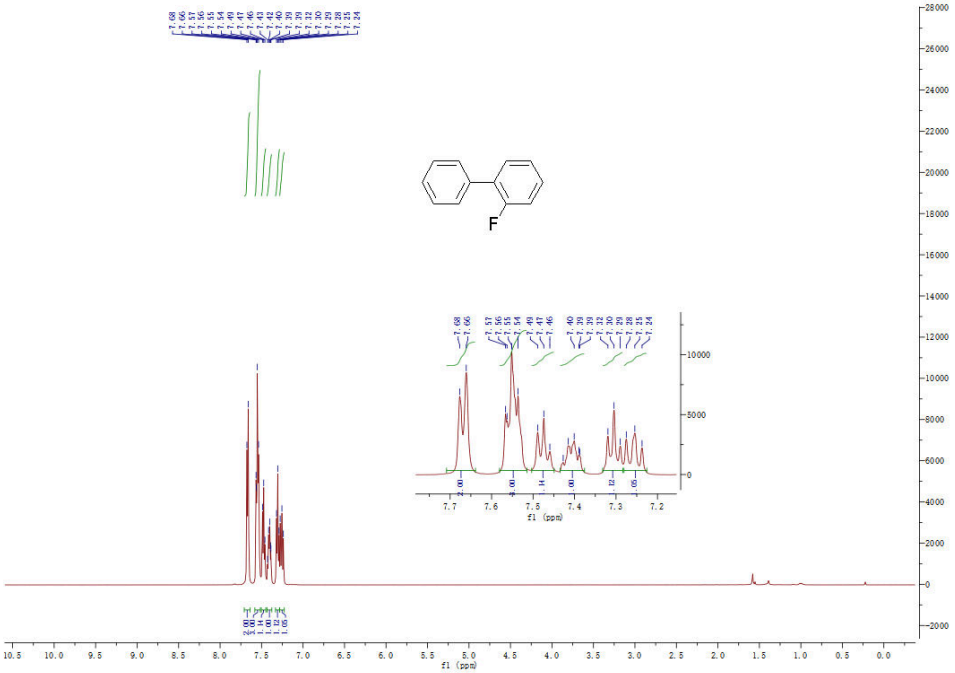
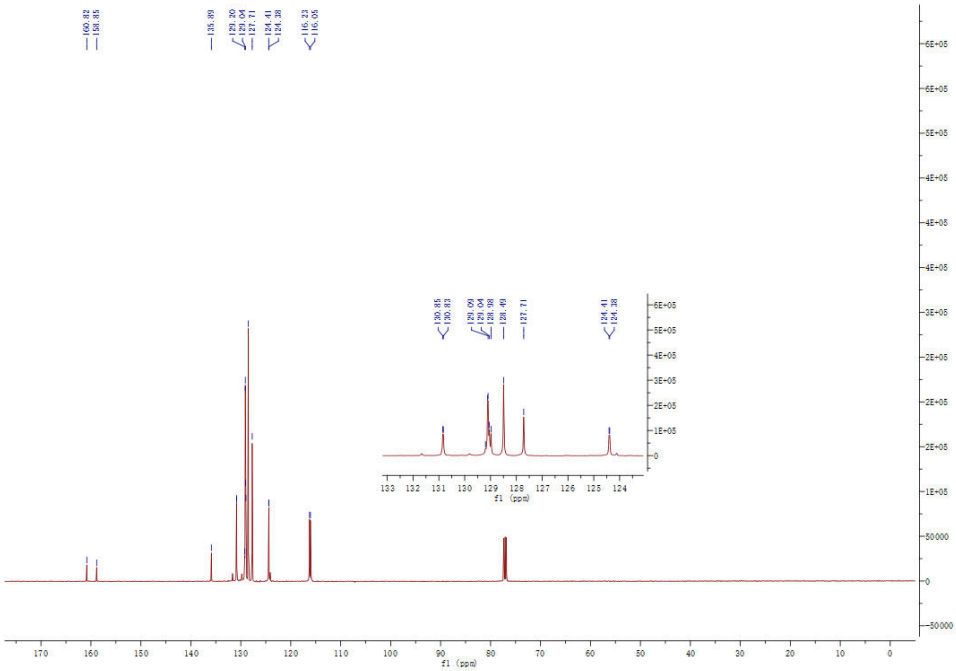
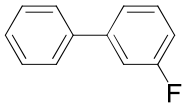


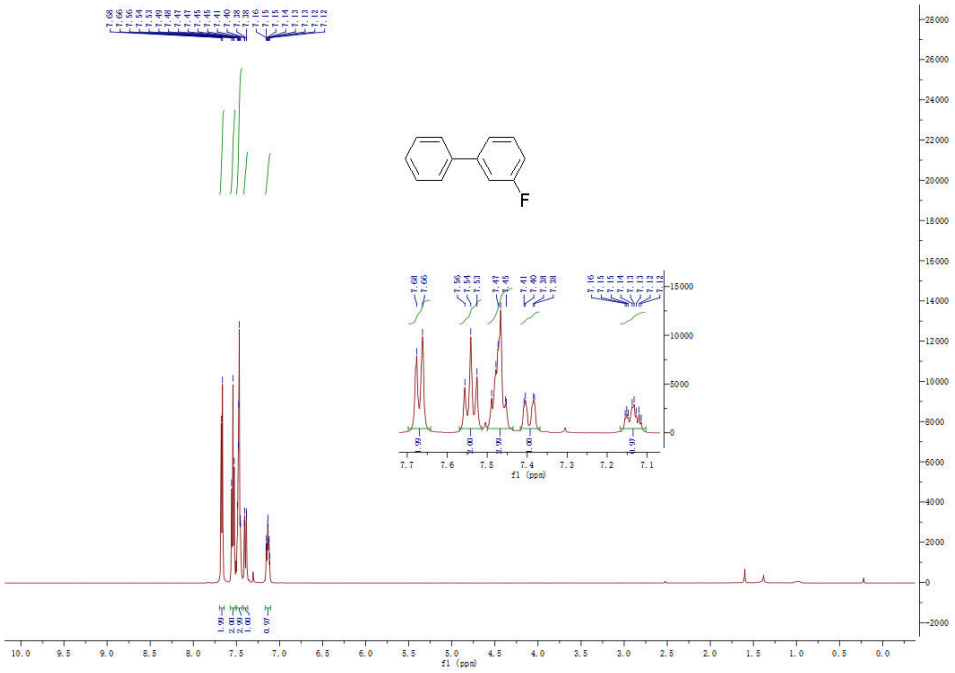
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 7.8 Hz, 2H), 7.55 (dd, *J* = 10.4, 4.7 Hz, 3H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.43-7.38 (m, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.28-7.23 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 124.4, 127.7, 128.5, 128.9, 129.0, 129.1, 130.8, 135.9, 158.6, 160.8; IR (KBr) 2924, 1476, 1435, 1202, 1106, 727, 698, 611.

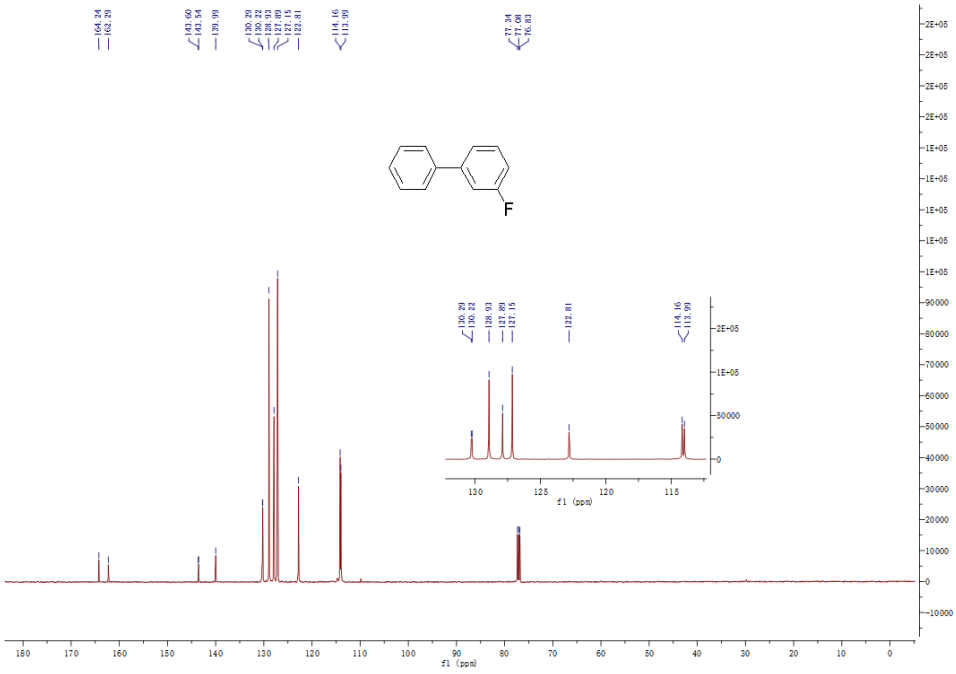


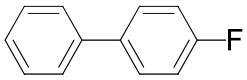


3f: 

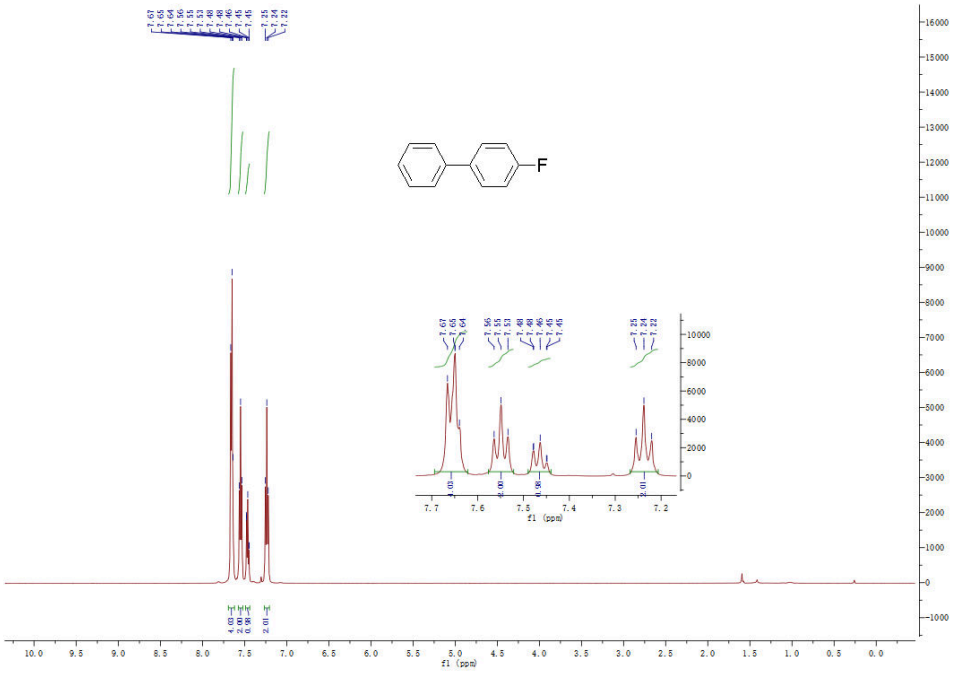
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.50-7.44 (m, 3H), 7.39 (dd, *J* = 11.6, 1.4 Hz, 1H), 7.14 (ddd, *J* = 8.8, 5.1, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 140.1, 122.8, 127.2, 127.9, 128.9, 130.2, 140.0, 143.5, 162.3, 164.2; IR (KBr) 1589, 1479, 1422, 1290, 1185, 1077, 877, 756, 695, 613.

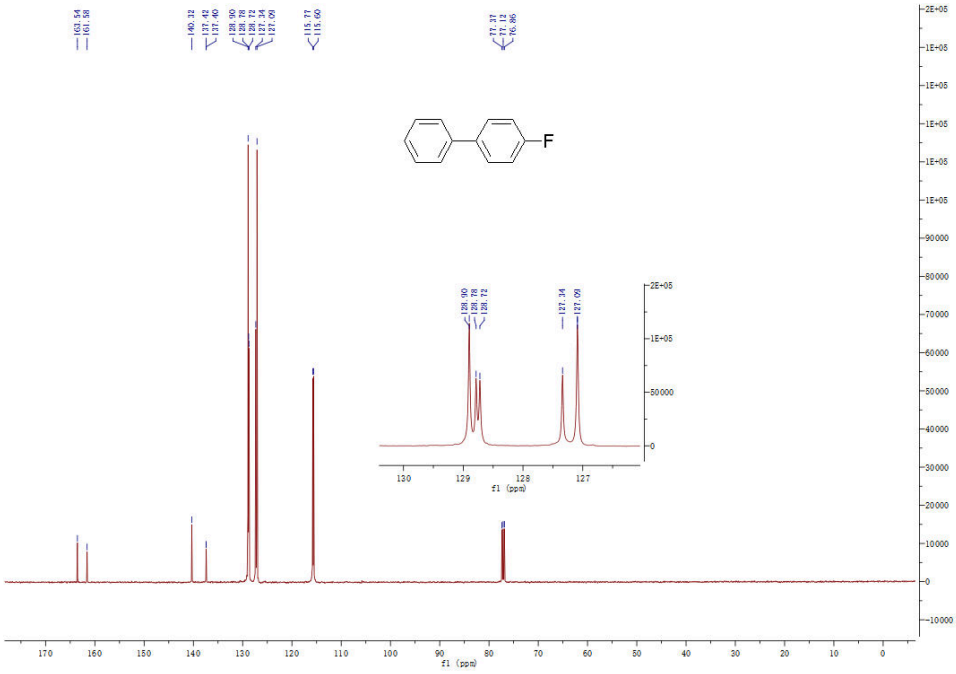


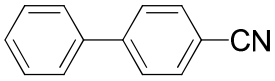


3g: 

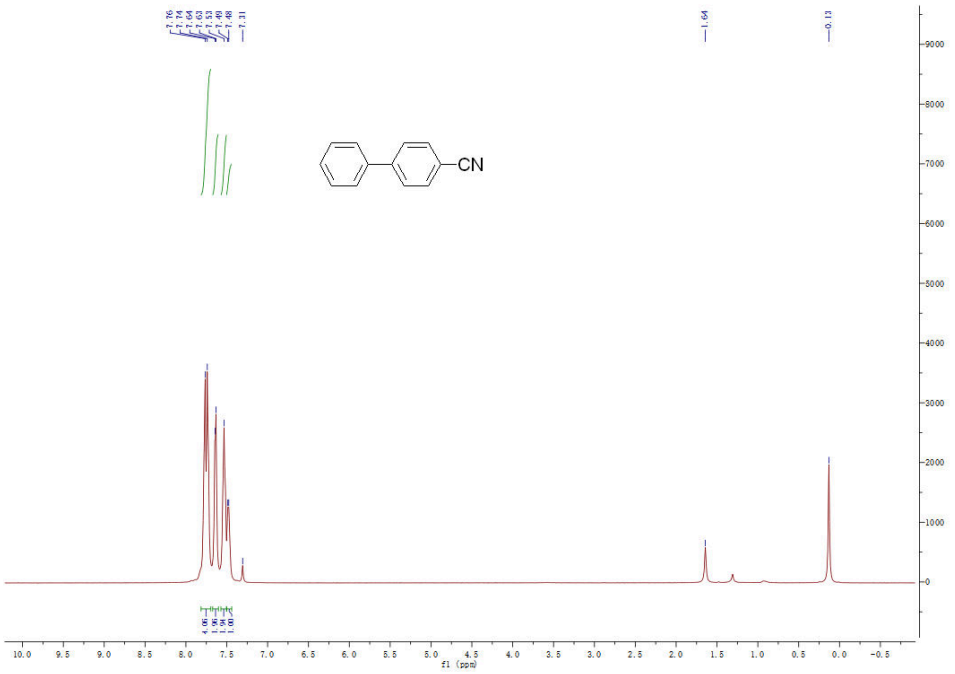
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 (t, *J* = 6.5 Hz, 4H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.49-7.44 (m, 1H), 7.24 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 115.7, 127.1, 127.3, 128.8, 137.4, 140.3, 161.6, 163.5; IR (KBr) 1598, 1519, 1484, 1236, 1195, 1006, 837, 758, 687.

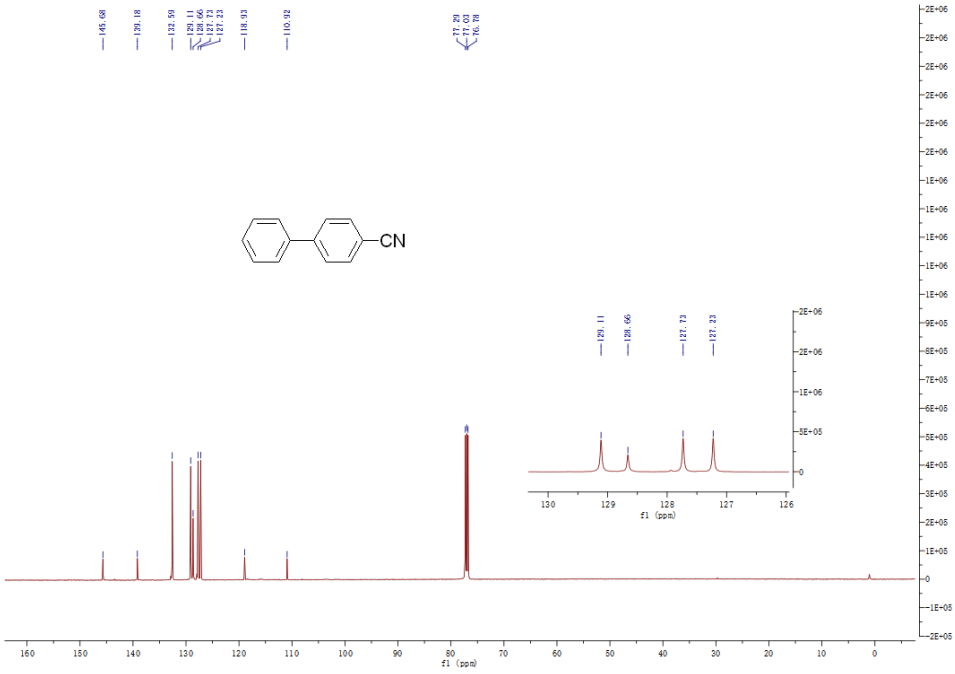


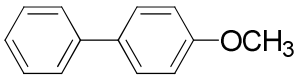


3h: 

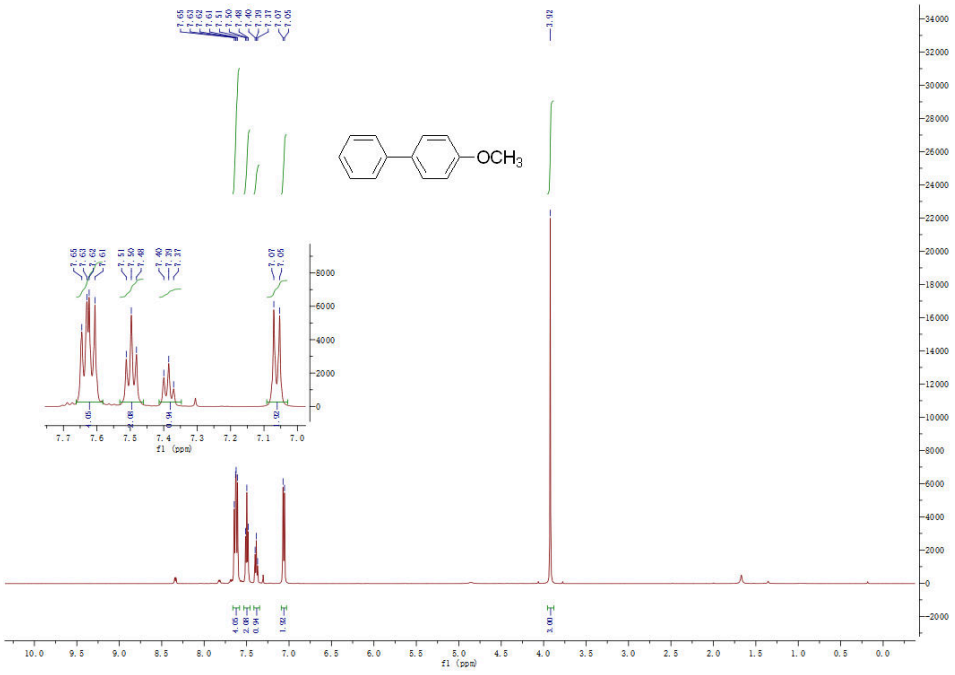
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57-7.52 (m, 2H), 7.48 (dd, *J* = 7.1, 5.4 Hz, 3H), 7.43-7.36 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 110.9, 118.9, 127.2, 127.7, 128.7, 129.1, 132.6, 139.2, 145.7; IR (KBr) 2965, 2226, 1605, 1484, 1261, 1077, 848, 769, 697.

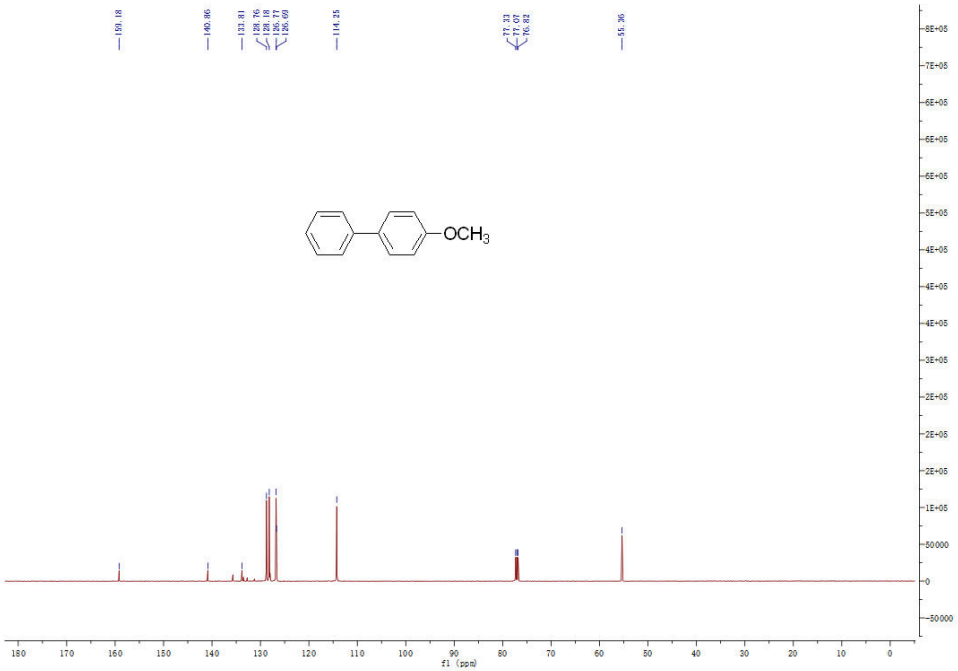


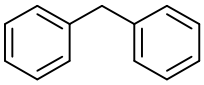


3i: 

White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 11.5, 8.2 Hz, 4H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 55.4, 114.3, 126.7, 126.8, 128.2, 128.7, 133.8, 140.9, 159.2; IR (KBr) 1605, 1485, 1248, 1199, 1036, 834, 760, 688.





3j: 

White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 - 7.38 (m, 4H), 7.32 (t, J = 6.3 Hz, 6H), 4.11 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 129.0, 128.5, 126.1, 42.0; IR (KBr) 3026, 1599, 1494, 1451, 1077, 1030, 735, 696, 608.