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Electronic Supplementary Information

Highly Lewis-Acidic Pd(IV) Surfaces in Pd@SiO_2 Nanocatalysts for Hydroalkoxylation Reactions

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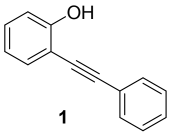
Experimental Section

Chemicals: Palladium(II) acetylacetonate ($Pd(acac)_2$, 99%), oleylamine (OAm, 70%), trioctylphosphine (TOP, 90%), igepal CO-630, tetramethyl orthosilicate (TMOS, 98%), octadecyltrimethoxysilane (C_{18}TMS, 90%), and (diacetoxyiodo)benzene ($PhI(OAc)_2$) were purchased from Aldrich. Palladium(II) acetate ($Pd(OAc)_2$, > 98%) and N-chlorosuccinimide (NCS, > 98%) were purchased from TCI and Acros Organics. Ammonium hydroxide (NH_4OH, 28% in water), cyclohexane (99.5%), hexane (99.5%), and toluene (99.5%) were purchased from Junsei. The chemicals were used as received without further purification.

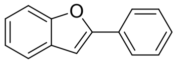
Preparation of Pd NPs and Pd@SiO_2 Yolk-Shell NPs: The Pd@SiO_2 NPs were synthesized by a modified method from the previous literature.[S1] A mixture of $Pd(acac)_2$ (91 mg, 0.30 mmol), TOP (1.0 mL, 2.3 mmol), and OAm (10 mL) was heated to 503 K for 20 min under a nitrogen atmosphere, and was aged at the same temperature for additional 40 min. The reaction mixture was cooled down to room temperature, and the Pd NPs were collected by centrifugation in ethanol. The black precipitates were redispersed in cyclohexane (50 mL). A mixture of igepal CO-630 (8.0 mL), an aqueous ammonia solution (0.80 mL, 28% in water) and cyclohexane (25 mL) was stirred at room temperature for 20 min. The Pd dispersion in cyclohexane (25 mL), TMOS (1.0 mL), and C_{18}TMS (1.0 mL) were subsequently added to the mixture, and then the resulting mixture was stirred for 1 h at room temperature. The Pd@SiO_2 NPs were precipitated in methanol (45 mL) and thoroughly washed with ethanol. The aqueous colloidal dispersion of the Pd@SiO_2 NPs (20 mL) was stirred under the hydrothermal condition at 383 K for 12 h, thoroughly washed with ethanol and de-ionized water, and dried in vacuo. The resulting powder was calcined at 773 K for 4 h under a hydrogen flow of 200 cm^3/min to yield a dark brown product, Pd@SiO_2 yolk-shell NPs. The Pd loading amount in the sample was 2.4 wt%, measured by ICP-OES.

Surfactant Treatment of Pd@pSiO_2 Yolk-Shell NPs (Table 2, entry 6): A mixture of the Pd@SiO_2 NPs (10 mg, 2.3 x 10^{-3} mmol Pd), OAm (5.0 mL, 15 mmol), and TOP (0.50 mL, 1.1 mmol) was vigorously stirred under N_2 atmosphere at 503 K for 18 h. The resulting NPs were separated and washed with ethanol by centrifugation.

*General Procedure for Hydroalkoylation of 2-phenylethynylphenol (**1**) to 2-phenylbenzofuran (**2**)*: Iodobenzene dichloride ($PhICl_2$) and 2-phenylethynylphenol were synthesized according to the literatures.[S2,S3] A side product, 3-chloro-2-phenylbenzofuran (**3**) was confirmed by matching NMR spectra in the literature.[S4] To an oven-dried sealed vial equipped with a stir bar were added Pd catalyst (1 mol% with respect to the substrate concentration), $PhICl_2$ (10-100 mol%), 2-phenylethynylphenol (**1**. 4.9 mg, 0.025mmol), and toluene (1.0 mL). The mixture was heated to 140 °C or stirred at room temperature. After 12 h, the reaction mixture was filtered, washed with toluene, and concentrated under the reduced pressure. The crude mixture was directly analysed by ^{1}H NMR spectroscopy.

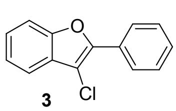


Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 6.7, 3.0 Hz, 2H), 7.43 (dd, J = 7.7, 1.7 Hz, 1H), 7.40 – 7.35 (m, 3H), 6.98 (d, J = 8.3 Hz, 1H), 6.91 (td, J = 7.5, 1.1 Hz, 1H), 5.83 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.6, 131.7, 130.6, 128.6, 122.5, 120.5, 114.9, 109.7, 95.5, 83.2.



2

Light yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 7.2 Hz, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.1 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 7.04(s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.1, 155.1, 130.7, 129.4, 128.9, 128.7, 125.1, 124.4, 123.1, 121.0, 111.3, 101.4.


3

Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 8.5 Hz, 3H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.8, 149.1, 129.4, 129.0, 128.9, 128.3, 126.4, 125.7, 123.5, 119.1, 111.6.

General Procedure for Recycling Experiments: To an oven-dried sealed vial equipped with a stir bar were added Pd catalyst (1 mol% with respect to the substrate concentration), $PhICl_2$ (25 mol%), 2-phenylethynylphenol (**1**. 9.8 mg, 0.05mmol), and toluene (1.0 mL). The mixture was heated to 140 ^{o}C. After 12 h, the reaction mixture was cooled and subjected to centrifugation for 5 minutes. The toluene layer was then removed via syringe and toluene (1 mL) was added. The reaction vial was again subjected to centrifugation for 5 min. After repeating this procedure once more, the supernatants were combined and the solvent was removed under reduced pressure to give the crude mixture, which was directly analysed by ^{1}H NMR spectroscopy. Recycling of the catalyst was achieved by simply adding more of the reactant **1** (9.8 mg), $PhICl_2$ (25 mol%), and toluene (1 mL).

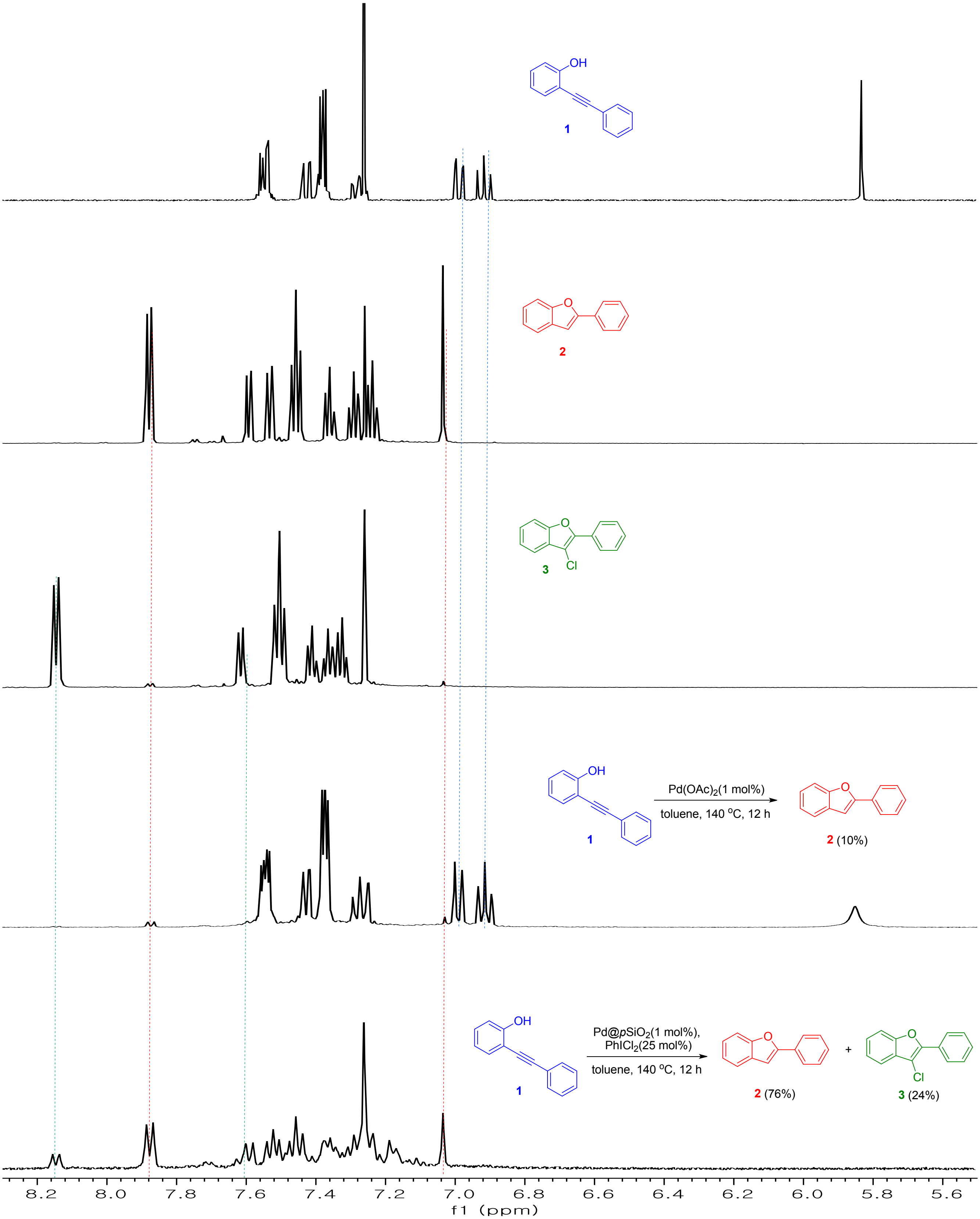
Characterization: The catalyst particles were characterized by transmission electron microscopy (TEM, Philips F30 Tecnai operated at 300 kV, KAIST; EF-TEM AE12, KBSI). The particle dispersions were drop-casted on carbon-supported 300 mesh Cu grids (TED PELLAR, INC) and the X-ray photoelectron spectra (XPS) data were recorded on Sigma Probe (XPS (UPS), Thermo VG Scientific). The Pd content of each sample was determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES, iCPA-6300 Duo ICP-OES). The ^{1}H and ^{13}C NMR spectra were recorded on either a Agilent Technologies DD2 (600 MHz for ^{1}H and 150 MHz for ^{13}C) or a Bruker Ascend 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer and are reported in ppm, relative to residual protonated solvent peak ($CDCl_3$).

[S1] J. C. Park, E. Heo, A. Kim, M. Kim, K. H. Park, H. Song, *J. Phys. Chem. C*, 2011, **115**, 15772.

[S2] D. C. Powers, D. Benitez, E. Tkatchouk, W. A. Goddard III, T. Ritter, *J. Am. Chem. Soc.*, 2010, **132**, 14092.

[S3] A. Fürstner, P. W. Davies, *J. Am. Chem. Soc.*, 2005, **127**, 15024.

[S4] Y. Liang, S. Tang, X.-D. Zhang, L.-Q. Mao, Y.-X. Xie, J.-H. Li, *Org. Lett.*, 2006, **8**, 3017.


OH
1
O
2
O
3
Cl
OH
Pd(OAc)$_2$(1 mol%)
toluene, 140 °C, 12 h
1
O
2 (10%)
OH
Pd@pSiO$_2$(1 mol%),
PhICl$_2$(25 mol%)
toluene, 140 °C, 12 h
1
O
2 (76%)
+
O
Cl
3 (24%)
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
f1 (ppm)

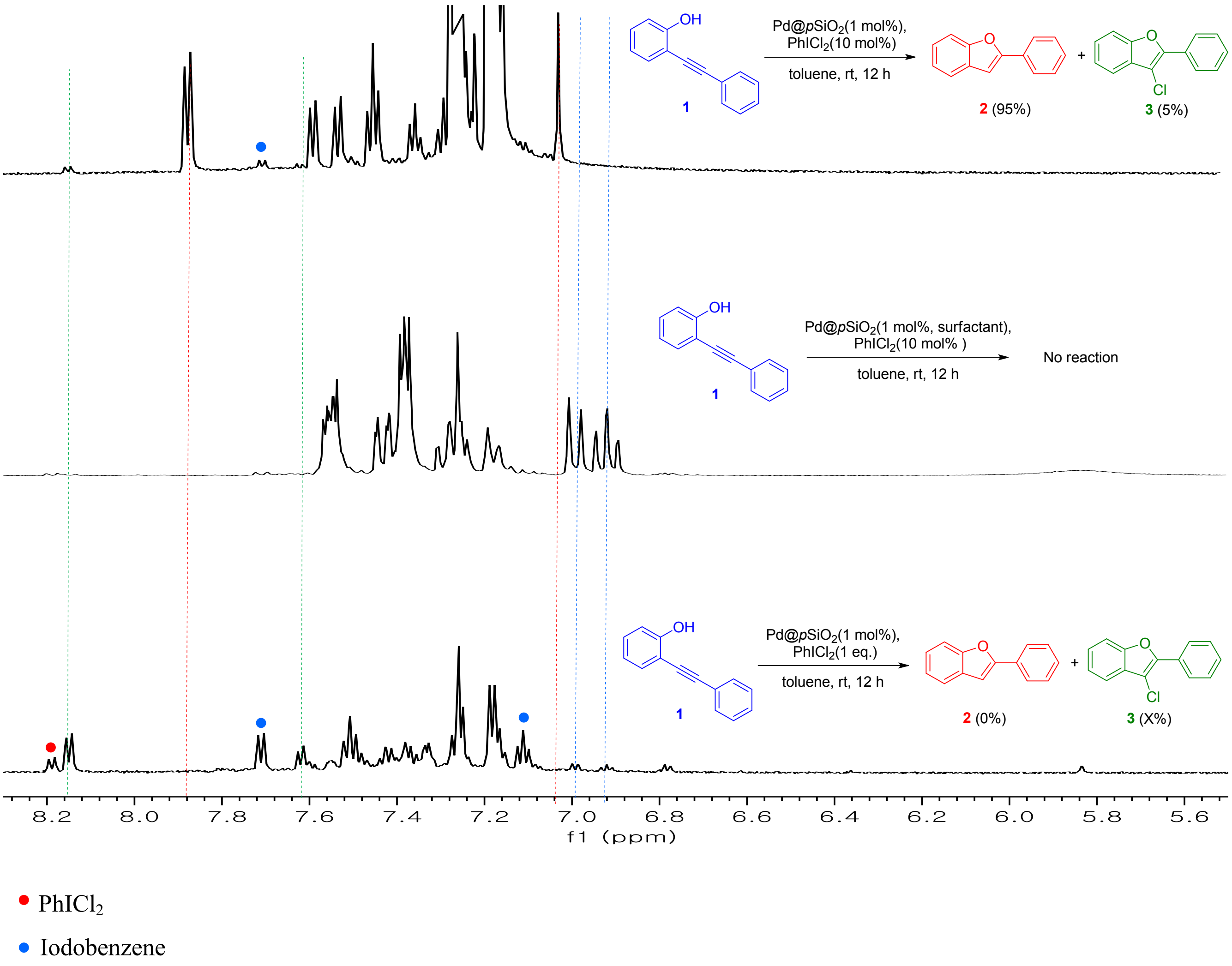


Fig. S1 Partial ^{1}H NMR spectra for the reaction of **1** to **2** and **3**.

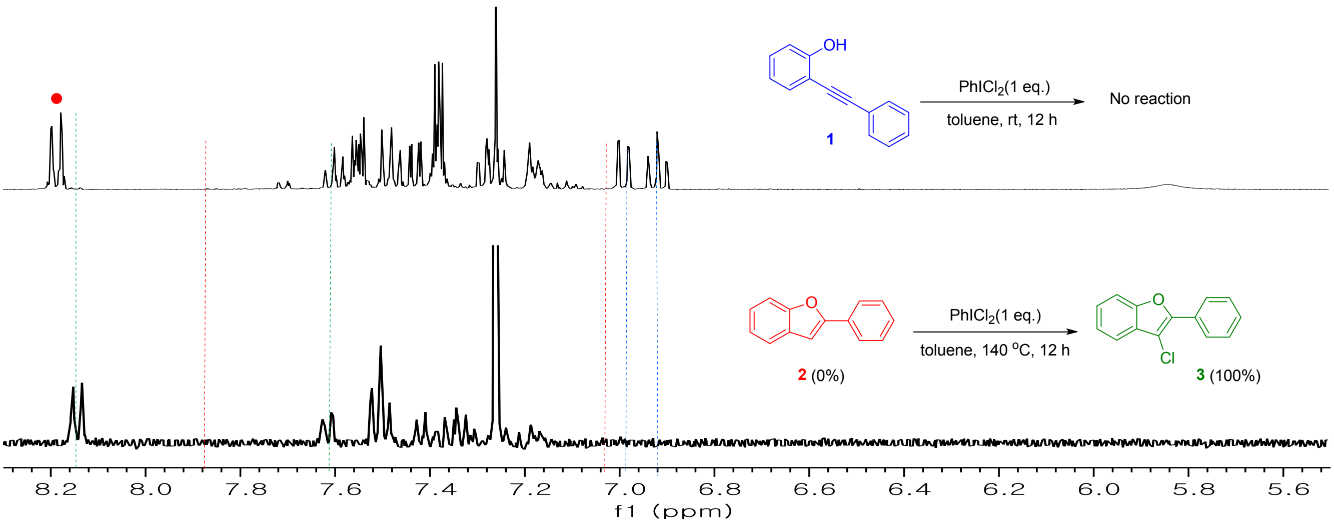
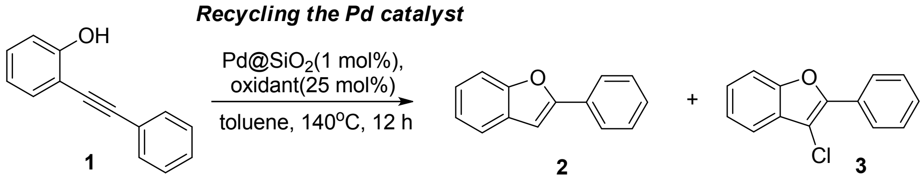


Fig. S2 Partial ^{1}H NMR spectra for chlorination of **2** to **3**.



# of cycles	Cyclization (%) (**2** + **3**)	Conversion (%) (**2**:**3**)
1	92	75:17
2	100	80:20
3	97	78:19
4	90	74:16
5	85	69:16
6	92	74:18

Fig. S3 Recycling Experiments of Pd@SiO_2 catalysts for hydroalkoxylation of **1.**

Proposed Reaction Mechanism: On the basis of the mechanisms of homogeneous catalysis,[S5-7] the reaction mechanism is proposed as Fig. S4. Unlike the base catalyzed cyclizations,[S8] the present reaction is catalyzed by Lewis acids, which activate the π-bond in **1** to form an intermediate **S1**. In accordance with our experimental results, we propose that Pd nanoparticles with Pd^{IV} surface oxidation states are the active Lewis acid catalysts. Then, the addition of phenolic oxide nucleophiles to afford the intermediate **S2**. Although the existence of **S2** is indirectly demonstrated by experiments in homogeneous catalysis, further mechanistic studies are required to provide the detailed information of **S2** in heterogeneous catalysis. Protonolysis of intermediate **S2** formed 2-phenylbenzofuran (**2**) which is converted to 3-chloro-2-phenylbenzofuran (**3**) by electrophilic chlorination reaction.

[S5] Y. Liang, S. Tang, X.-D. Zhang, L.-Q. Mao, Y.-X. Xie, J.-H. Li, *Org. Lett.*, 2006, **8**, 3017.

[S6] S. Yang, Z. Li, X. Jian, C. He, *Angew. Chem. Int. Ed.*, 2010, **48**, 3999.

[S7] A. Fürstner, P. W. Davies, *J. Am. Chem. Soc.*, 2005, **127**, 15024.

[S8] Y. Hu, K. J. Nawoschik, Y. Liao, J. Ma, R. Fathi, Z. Yang, *J. Org. Chem.*, 2004, **69**, 2235.

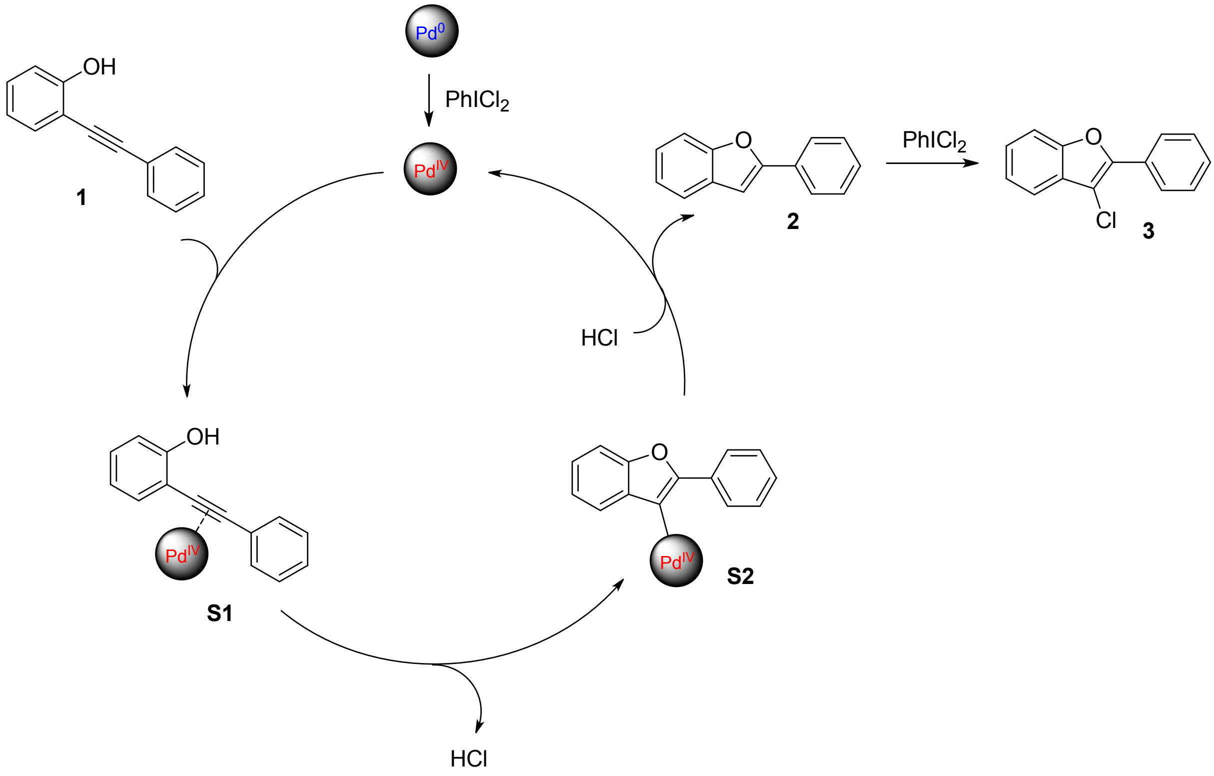


Fig. S4 Proposed reaction mechanism for hydroalkoxylation of **1.**

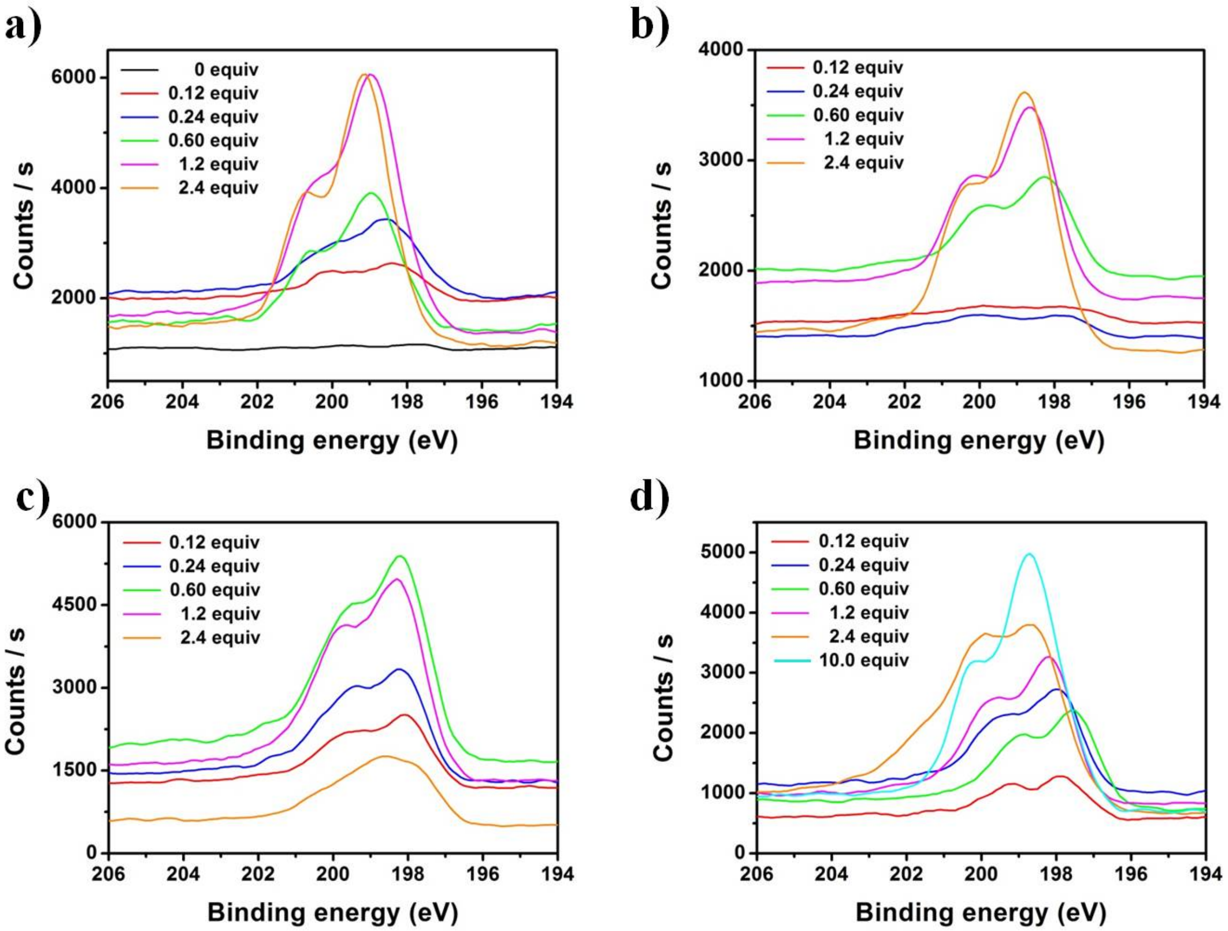


Fig. S5 The XPS spectra of the Cl 2p level for Pd NPs after the treatment with $PhICl_2$ at 140 ^{o}C (a) for 1 h and (b) for 12 h, and at room temperature (c) for 1 h and (d) for 12 h, resplectively.

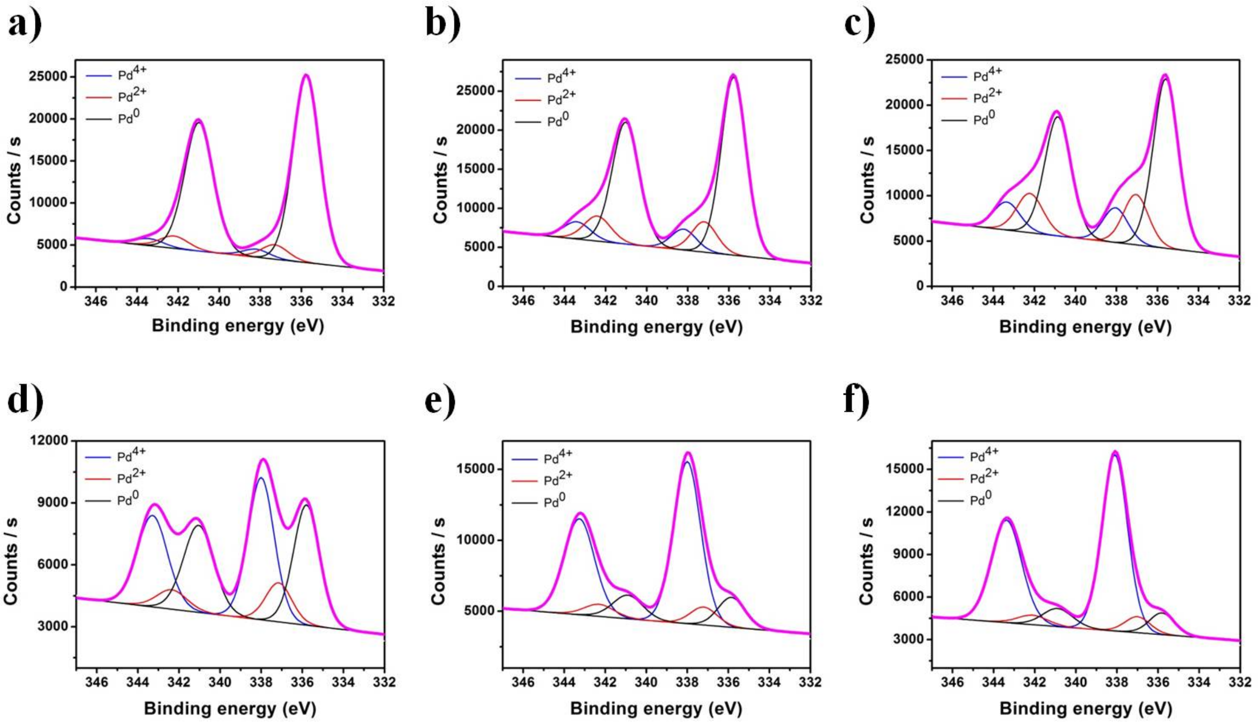


Fig. S6 The XPS spectra of the Pd 3p level for Pd NPs after the treatment with (a) 0, (b) 0.12, (c) 0.24, (d) 0.60, (e) 1.2, and (f) 2.4 equiv of $PhICl_2$ with respect to the Pd loading content at 140 °C for 1 h.

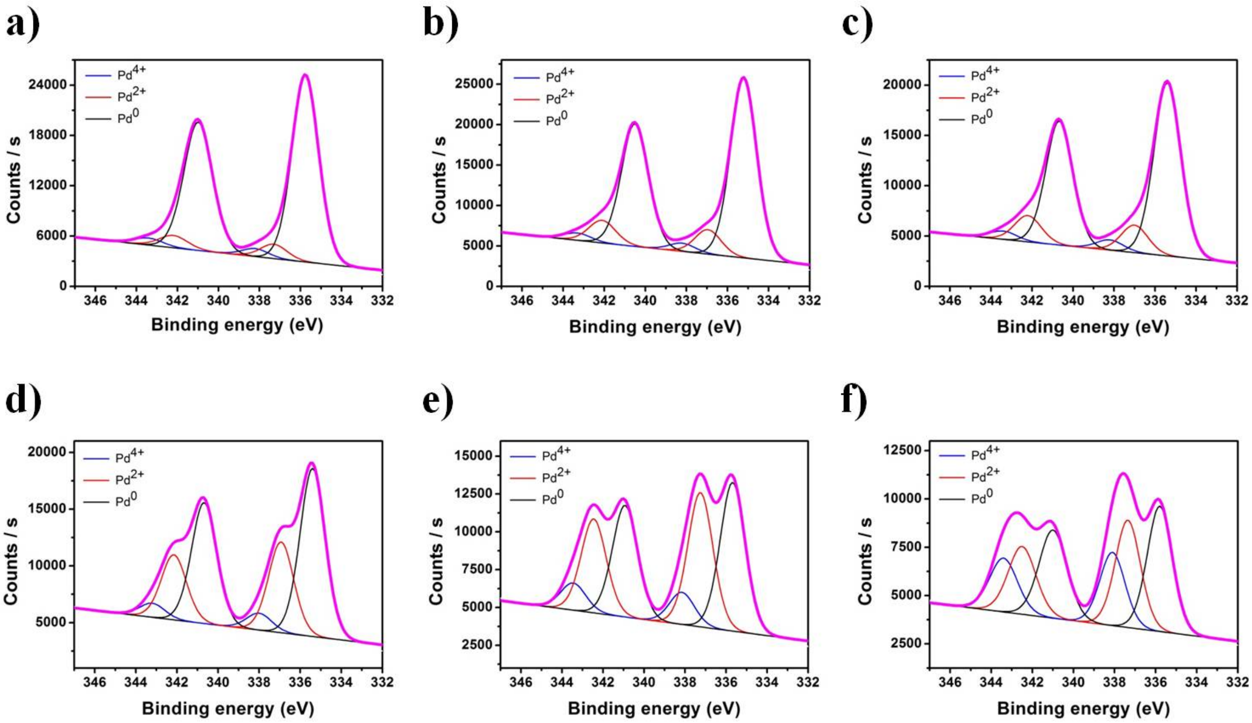


Fig. S7 The XPS spectra of the Pd 3p level for Pd NPs after the treatment with (a) 0, (b) 0.12, (c) 0.24, (d) 0.60, (e) 1.2, and (f) 2.4 equiv of $PhICl_2$ with respect to the Pd loading content at 140 ^{o}C for 12 h.

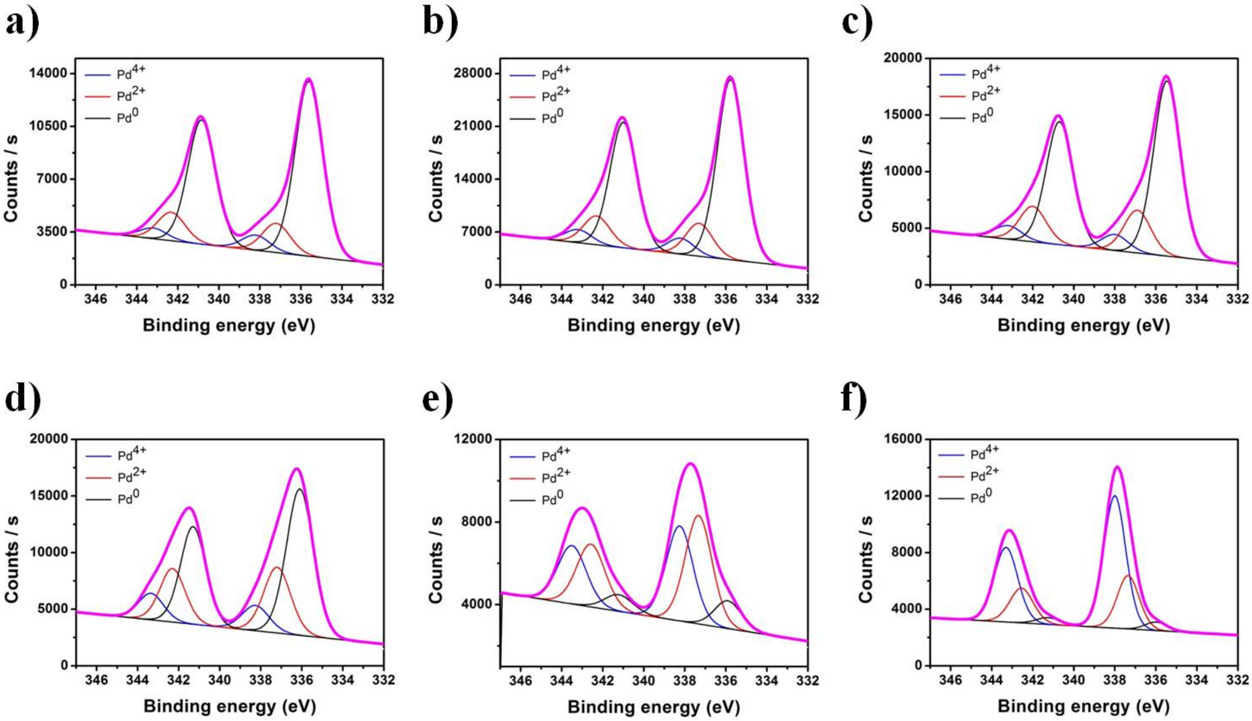
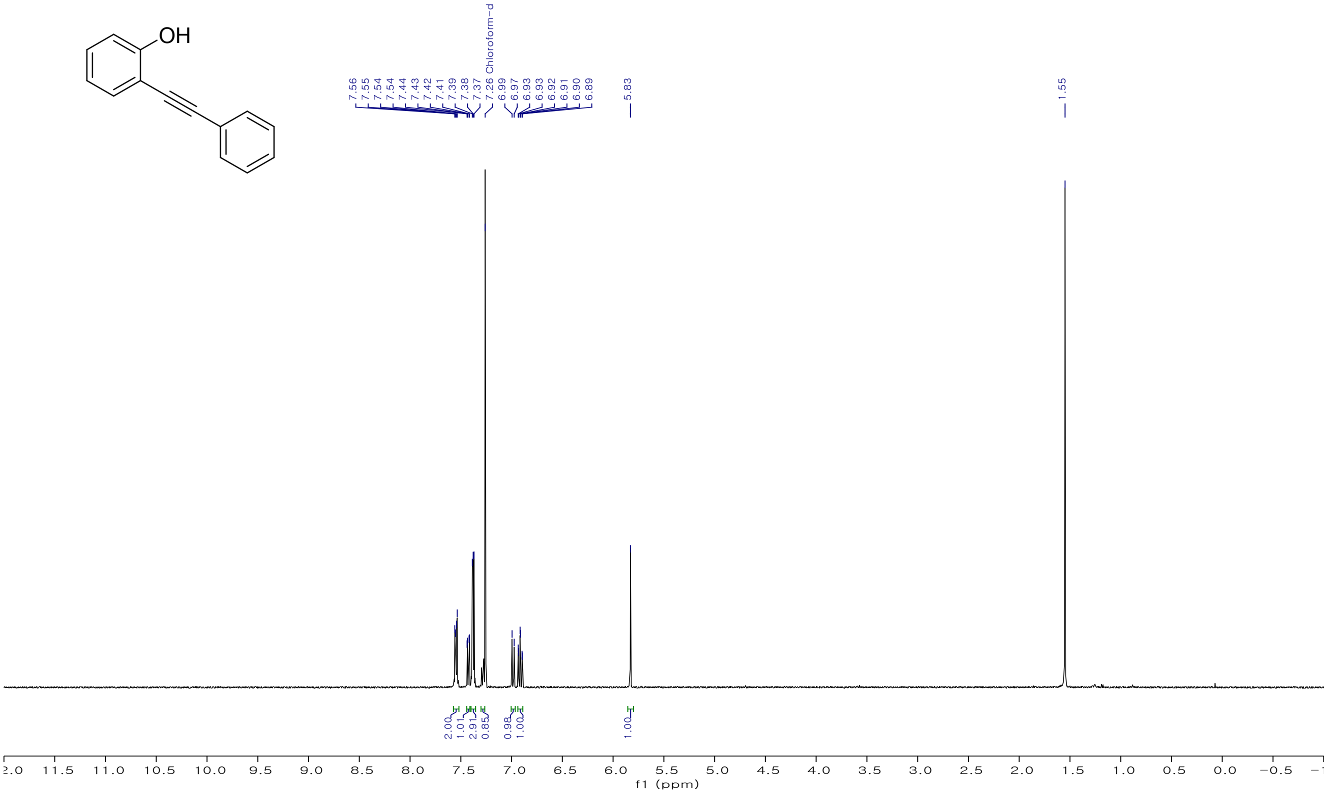
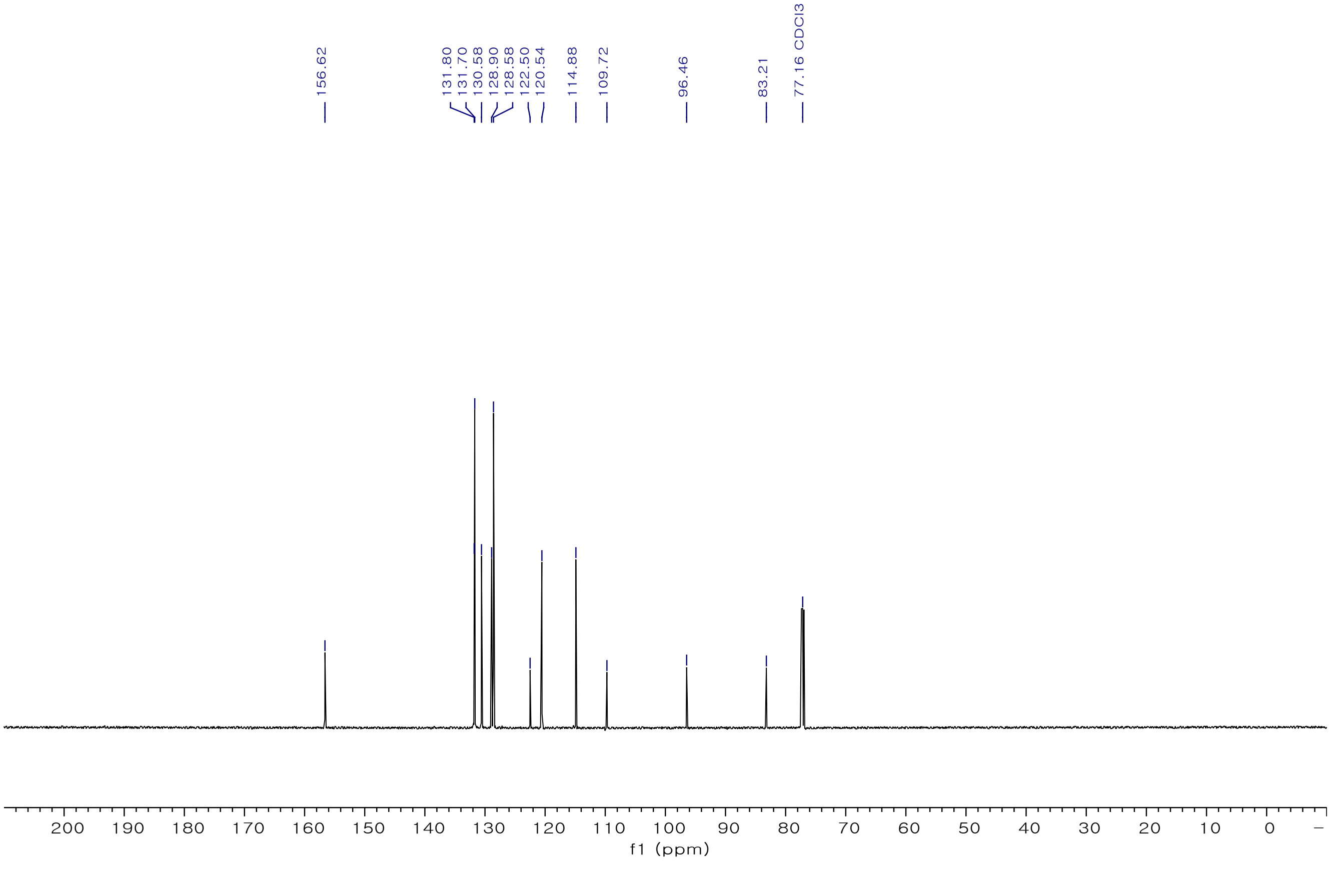
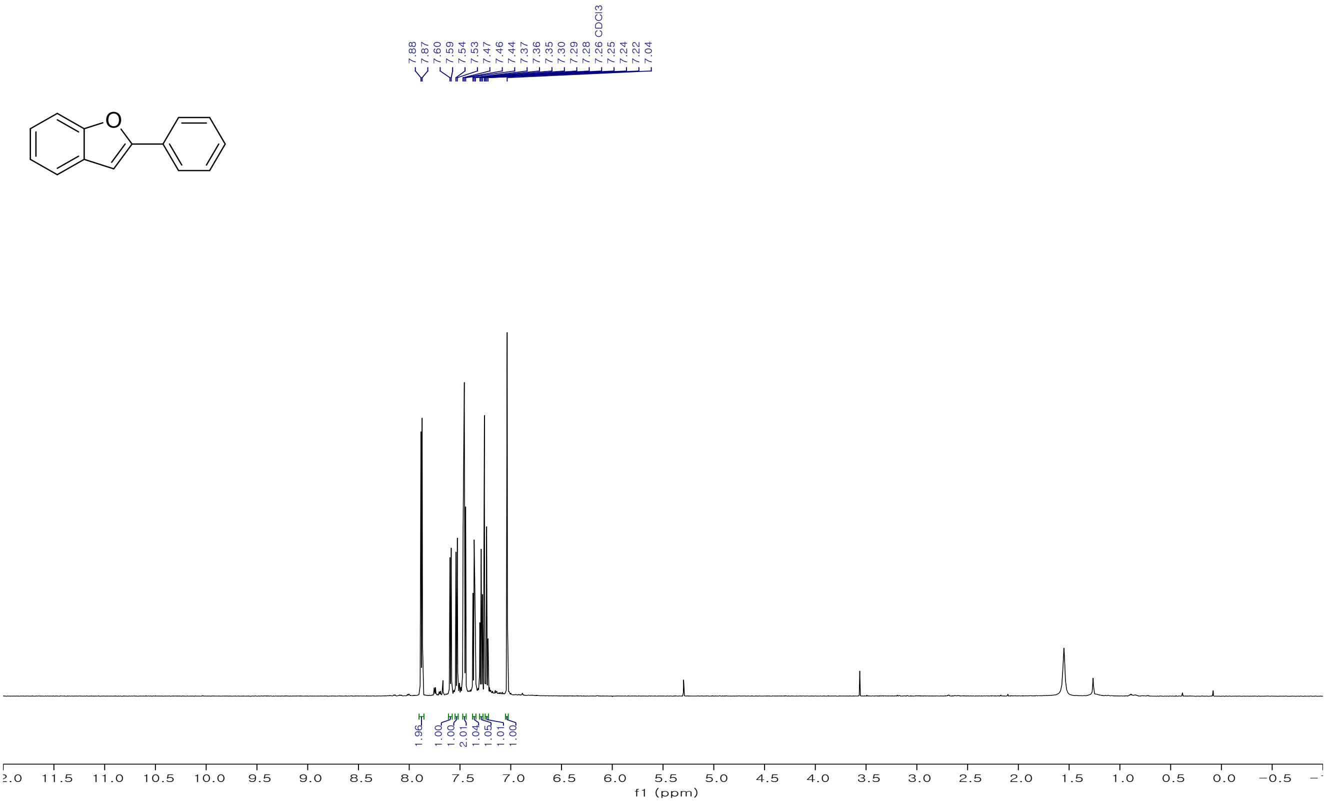
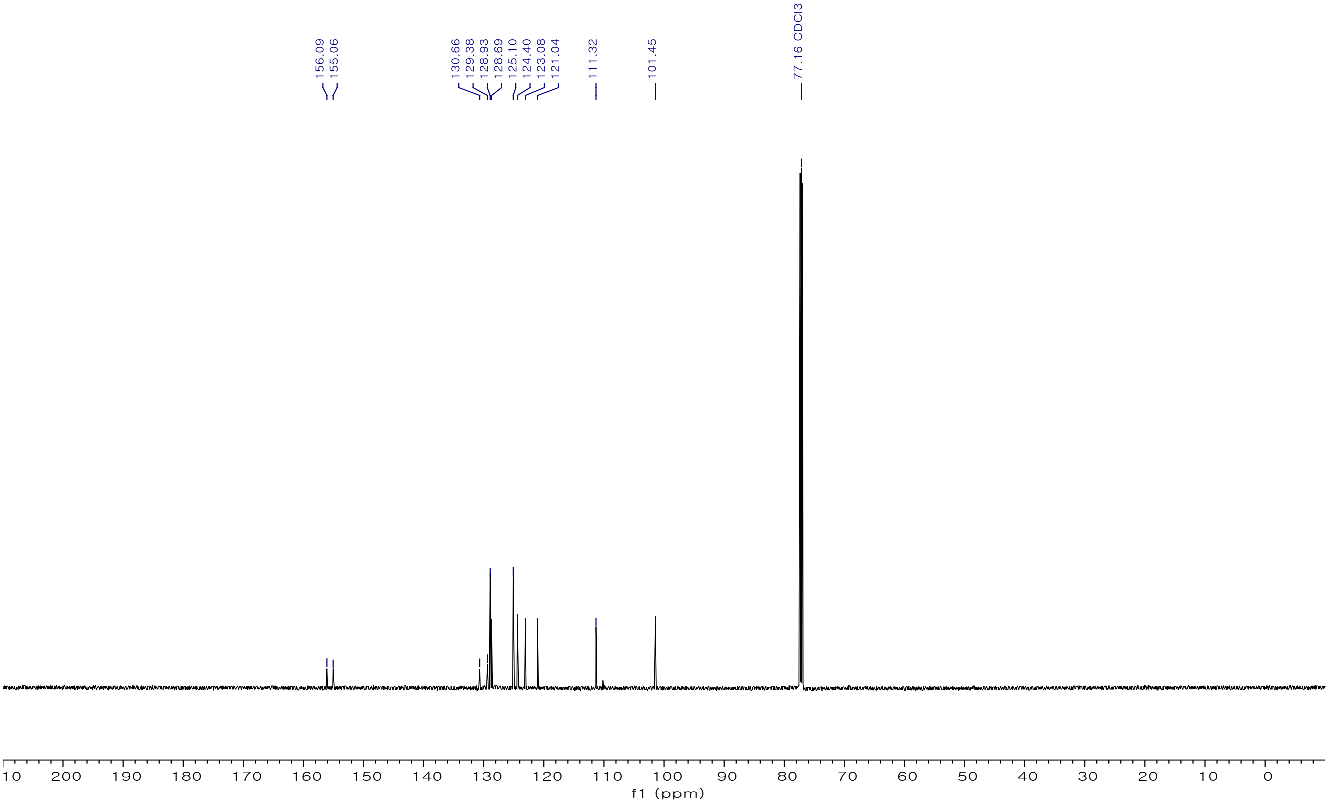


Fig. S8 The XPS spectra of the Pd 3p level for Pd NPs after the treatment with (a) 0.12, (b) 0.24, (c) 0.60, (d) 1.2, (e) 2.4 and (f) 10 equiv of $PhICl_2$ with respect to the Pd loading content at room temperature for 12 h.


OH
7.56
7.55
7.54
7.44
7.43
7.42
7.41
7.39
7.38
7.37
7.26 Chloroform-d
6.99
6.97
6.93
6.93
6.92
6.91
6.90
6.89
5.83
1.55
2.00
1.01
2.91
0.85
0.98
1.00
1.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


156.62
131.80
131.70
130.58
128.90
128.58
122.50
120.54
114.88
109.72
96.46
83.21
77.16 CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.88
7.87
7.60
7.59
7.54
7.53
7.47
7.46
7.44
7.37
7.36
7.35
7.30
7.29
7.28
7.26 CDCl3
7.25
7.24
7.22
7.04
1.96
1.00
1.00
2.01
1.04
1.05
1.01
1.00
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


156.09
155.06
130.66
129.38
128.93
128.69
125.10
124.40
123.08
121.04
111.32
101.45
77.16 CDCl3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

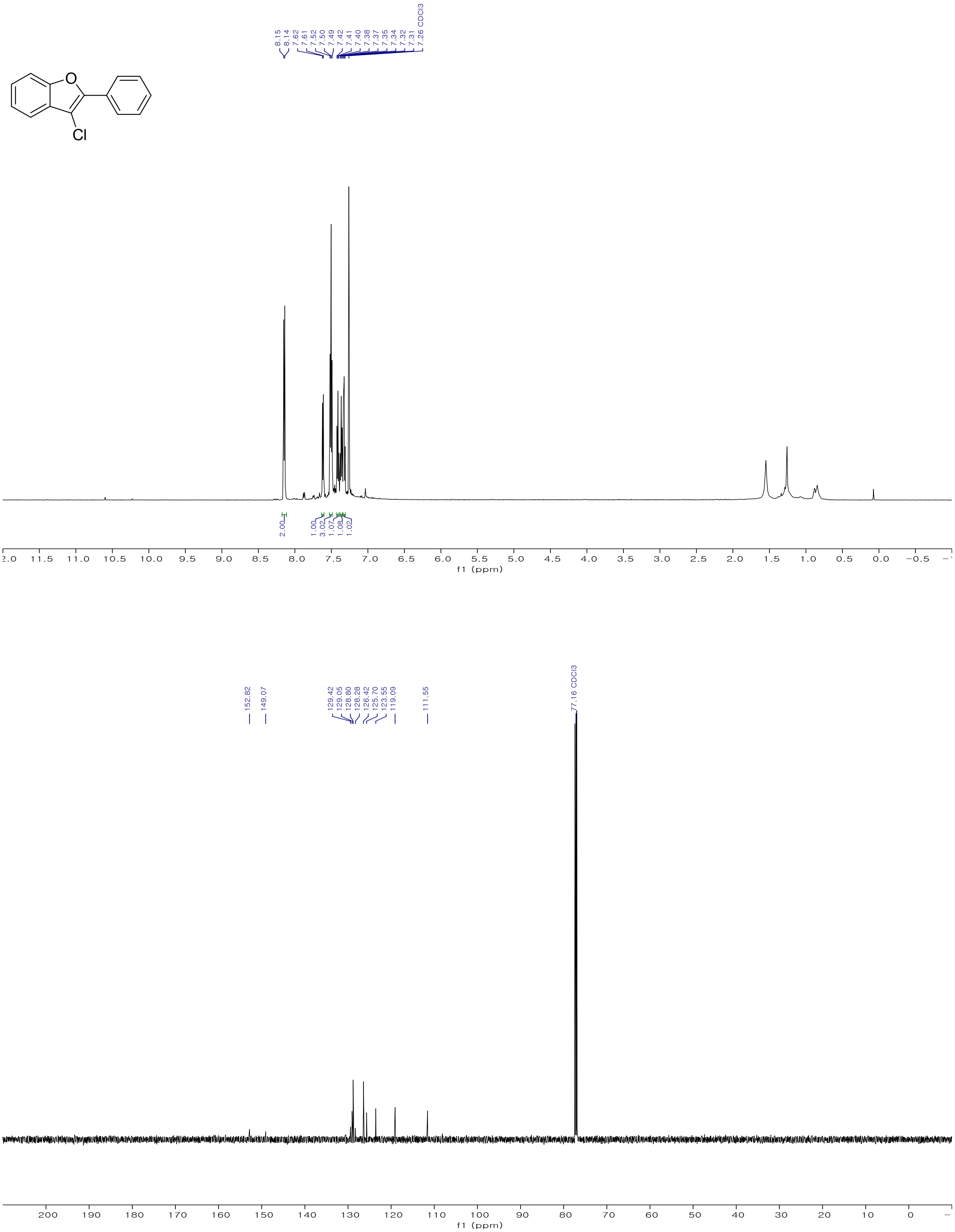


Fig. S9 ^{1}H and ^{13}C NMR spectra for **1**, **2**, and **3**.