

## ESI for

### **A facile approach to constructing Pd@PCN-Se nano-composited catalysts for selective alcohol oxidation reactions**

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### **Table of Contents**

General experimental conditions.....	S2
Experimental procedures.....	S2
Catalyst recycle & reuse.....	S3
Characterization of the products.....	S4
Copies of <sup>1</sup> H NMR spectra of the products.....	S6
XPS survey spectrum of Pd@PCN-Se.....	S10
XPS core level spectrum of Se powder.....	S11
XPS spectra of PCN, PCN-Se and Pd@PCN-Se.....	S12

## General experimental conditions

Chemicals and solvents were all purchased and used as received. All reactions were monitored by TLC. **Melting points** were measured on a WRS-2A digital instrument. **Fourier Transform infrared (FT-IR) spectra** were determined on a Bruker TENSOR-27 spectrometer. **The XRD analyses** were performed on a powder X-ray diffractometer (Bruker-D8 Advance) equipped with Cu-K $\alpha$  radiation ( $\lambda=0.15418$  nm) at 30 kV accelerating voltage while maintaining the emission current at 15 mA. **The ICP analyses** were performed on PerkinElmer Optima 7300 DV inductively coupled plasma spectrometer. Detailed procedures for ICP measurement were as follows: 20mg of as-prepared Pd@PCN-Se powders were digested by 10ml nitric acid (1M), and then the supernatant solutions were adopted to analyze the contents of Se and Pd by ICP-MS. **The XPS spectra** were determined on ThermoScientific ESCALAB 250Xi X-ray photoelectron spectrometer and Pd on PCN-Se fabricated with 10% Se feeding weight ratio was employed to strengthen the signals. **FE-SEM images** were determined on Hitachi S-4800 field emission scanning electron microscope. **HR-TEM images** were determined on Tecnai G<sup>2</sup> F30 field emission transmission electron microscope. **N<sub>2</sub> adsorption-desorption isotherms** were recorded at 77 K on a surface area analyzer (Quantachrome, Nova 4200e). **Specific surface area (S<sub>BET</sub>) and pore size/volume** were calculated from the Brunauer-Emmit-Teller (BET) theory and Barrett-Joyner-Halenda (BJH) theory, respectively. **<sup>1</sup>H NMR spectrum** was recorded on a Agilent instrument (400 MHz for <sup>1</sup>H NMR spectroscopy) by using CDCl<sub>3</sub> as solvent and Me<sub>4</sub>Si as internal standard. Chemical shifts for <sup>1</sup>H NMR were referred to Me<sub>4</sub>Si (0 ppm) and *J*-values were shown in Hz.

## Experimental procedures

### *General procedures for the fabrication of Pd@PCN-Se and Pd@PCN*

1.9 g of melamine and 0.1 g of Se powder were initially grinded together and then sent into a tube furnace, in which the temperature rose at 5 °C/min rate until reaching

500 °C. After calcining at this temperature for 3 h with N<sub>2</sub> protection, PCN-Se bulk materials were obtained and they were grinded into powders. 250 mg of PCN-Se powder was then immersed in 20 mL of aqueous PdCl<sub>2</sub> (0.01 mol/L) for 48 h. After filtration and washing with water and ethanol, the powder was dried under vacuum and could be used as the Pd@PCN-Se catalyst in alcohol oxidation reactions. Pd@PCN was prepared in similar way but without adding Se powder.

*General procedures for catalyst evaluation through the alcohol oxidation*

20 mg of Pd@PCN-Se, 0.5 mmol of diphenylmethanol, 5 mmol of H<sub>2</sub>O<sub>2</sub> (30 wt% aqueous solution) and 2 mL of 1,4-dioxane were added into a 15 mL reaction tube. The mixture was stirred at 80 °C for 48 h. After cooling to room temperature, the produced benzophenone was isolated by preparative thin layer chromatography (TLC).

**Catalyst recycle & reuse**

**Table S1.** Catalyst recycle & reuse<sup>a</sup>

Entry	Cycle NO.	Catalyst lost weight (mg) <sup>b</sup>	Product yield (%)
1	1 (first use, fresh catalyst)	4.4	96
2	2	4.6	97
3	3	4.3	95
4	4	4.7	95
5	5	4.1	94

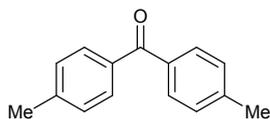
<sup>a</sup> The reaction was performed under the conditions of Table 1, entry 2 in text and 20 mg of catalyst was used for each reaction.

<sup>b</sup> The recycled catalyst was weighted to calculate the lost weight and in the next turn of reaction, the lost weight was supplied by fresh catalyst.

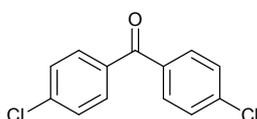
**Characterization data of the product**



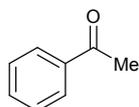
**Benzophenone:** Solid, m. p. 47.9 – 48.6 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.79 (d,  $J = 7.6$  Hz, 4H), 7.57 (t,  $J = 7.3$  Hz, 2H), 7.46 (t,  $J = 7.4$  Hz, 4H); IR  $\nu_{\text{max}}$  (KBr, film,  $\text{cm}^{-1}$ ): 3287, 3052, 1983, 1919, 1805, 1715, 1647, 1584, 1445, 1311, 1271, 1159, 1076, 995, 927, 866, 813, 762, 700, 631, 437; Known compound.<sup>1</sup>



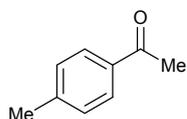
**Di-*p*-tolylmethanone:** Solid, m.p. 92.5-94.2 °C.  $^1\text{HNMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.69 (d,  $J = 7.83$  Hz, 4H), 7.26 (d,  $J = 7.89$  Hz, 4H), 2.43 (s, 6H); IR  $\nu_{\text{max}}$  (KBr, film,  $\text{cm}^{-1}$ ): 3666, 3277, 3033, 2978, 2586, 2414, 2299, 1925, 1802, 1646, 1596, 1409, 1270, 1164, 1032, 919, 835, 462; Known compound.<sup>2</sup>



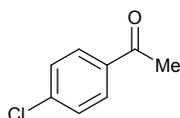
**Bis(4-chlorophenyl)methanone:** Solid, m.p. 147.1–147.8 °C.  $^1\text{HNMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.71 (d,  $J = 8.54$  Hz, 4H), 7.45 (d,  $J = 8.54$  Hz, 4H); IR  $\nu_{\text{max}}$  (KBr, film,  $\text{cm}^{-1}$ ): 3442, 3291, 3089, 2565, 2402, 2287, 1924, 1796, 1653, 1582, 1478, 1393, 1276, 1087, 1009, 968, 846, 752; Known compound.<sup>1</sup>



**Acetophenone:** Oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.87 (d,  $J = 7.6$  Hz, 2H), 7.48 (t,  $J = 6.8$  Hz, 1H), 7.37 (t,  $J = 7.3$  Hz, 2H), 2.53-2.50 (m, 3H); IR  $\nu_{\text{max}}$  (KBr, film,  $\text{cm}^{-1}$ ): 3353, 3063, 2312, 1980, 1906, 1686, 1595, 1443, 1360, 1263, 955, 761, 691, 590; Known compound.<sup>2</sup>

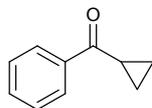


**1-(*p*-Tolyl)ethan-1-one:** Oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.85(s, 2H), 7.25 (s, 2H), 2.57 (s, 3H), 2.40 (s, 3H); IR  $\nu_{\text{max}}$  (KBr, film,  $\text{cm}^{-1}$ ): 3346, 3003, 2924, 2304, 1929, 1683, 1607, 1418, 1359, 1267, 1182, 1022, 955, 816, 582; Known compound.<sup>2</sup>

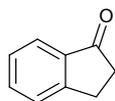


**1-(4-Chlorophenyl)ethan-1-one:** Oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm):

7.89 (d,  $J = 8.8$  Hz, 2H), 7.43 (d,  $J = 8.4$  Hz, 2H), 2.59 (s, 3H); IR  $\nu_{\max}$  (KBr, film,  $\text{cm}^{-1}$ ): 3446, 3074, 3005, 2301, 1919, 1688, 1587, 1486, 1400, 1358, 1261, 1095, 958, 829; Known compound.<sup>2</sup>



**Cyclopropyl(phenyl)methanone:** Oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.98 (d,  $J = 4.4$  Hz, 2H), 7.54-7.50 (m, 1H), 7.45-7.41 (m, 2H), 2.67-2.61 (m, 1H), 1.21-1.22 (m, 2H), 1.01-0.99 (m, 2H); IR  $\nu_{\max}$  (KBr, film,  $\text{cm}^{-1}$ ): 3066, 3010, 1667, 1589, 1448, 1385, 1224, 1172, 1033, 992, 701, 644; Known compound.<sup>1</sup>

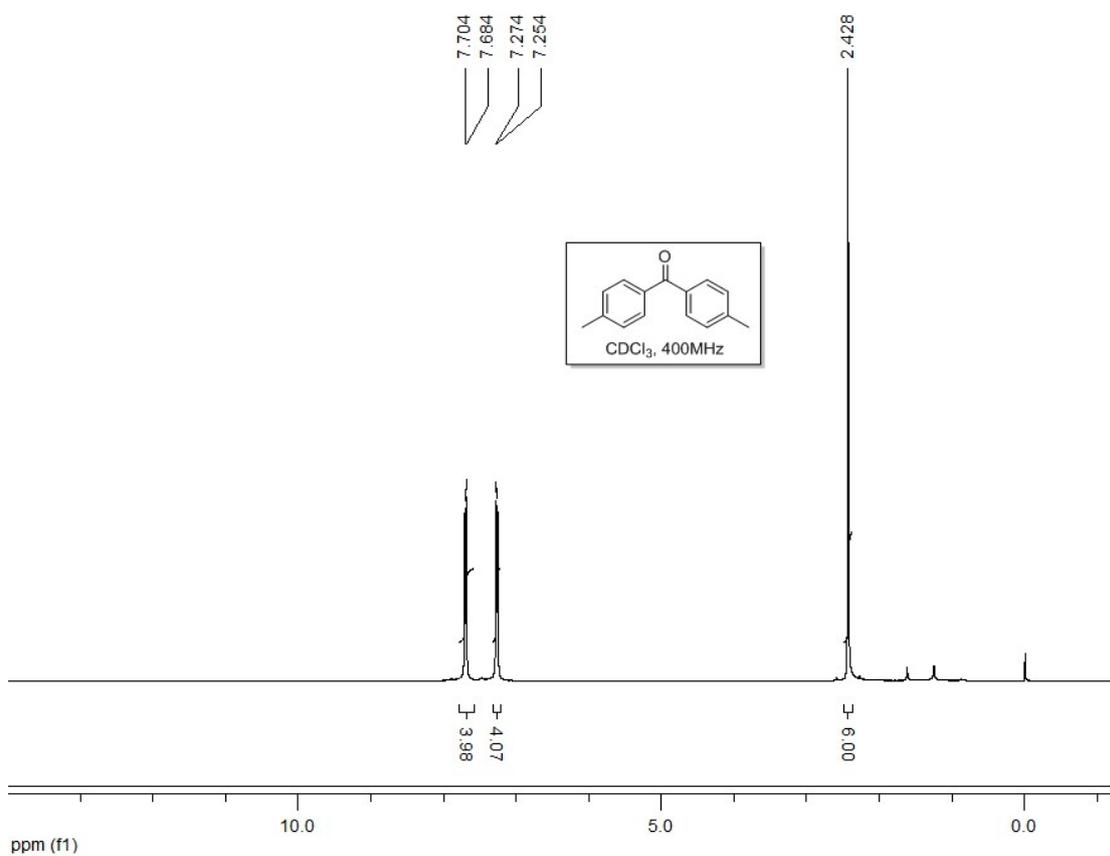
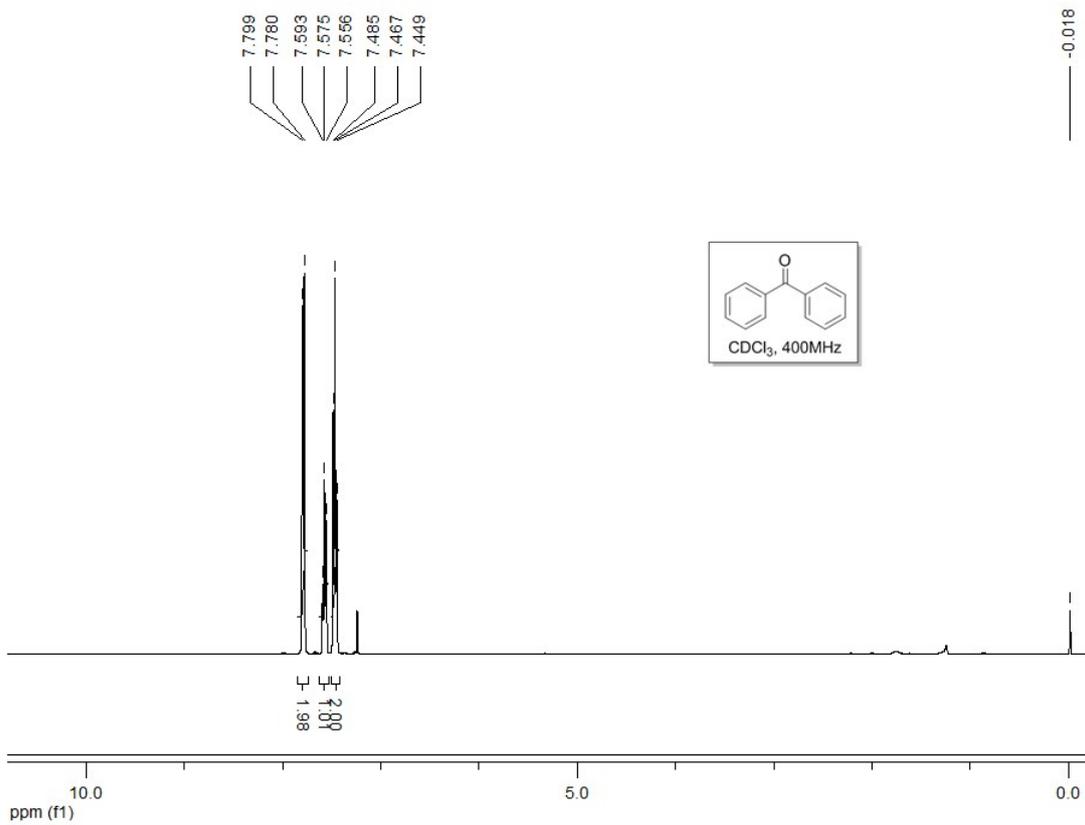


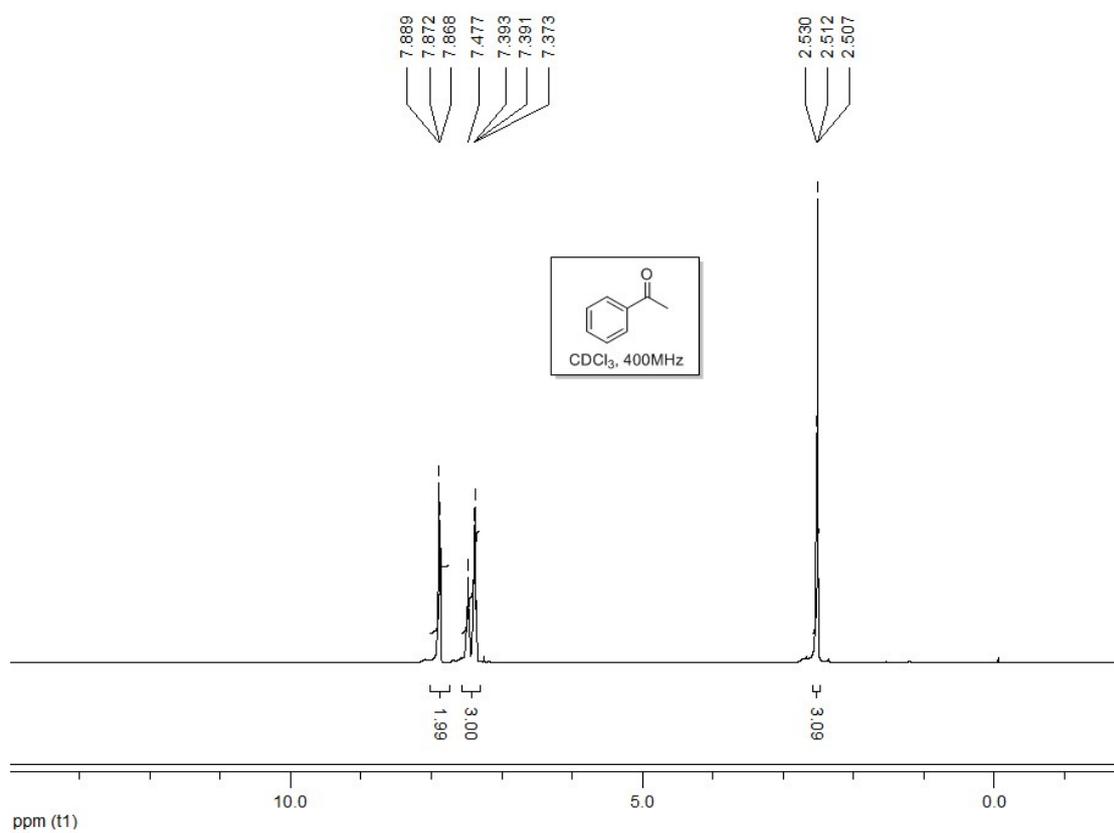
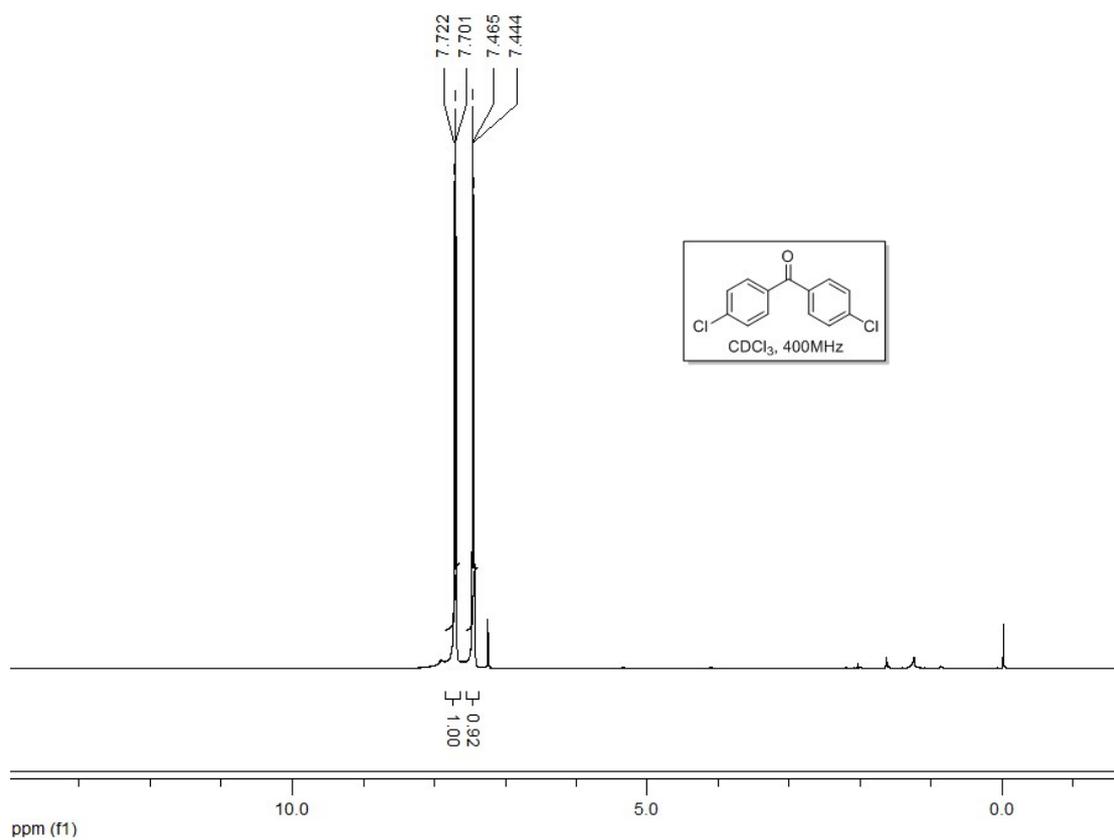
**2,3-Dihydro-1H-inden-1-one:** Solid, m. p. 41.3–42.8 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.76-7.36 (m, 4H), 3.14 (s, 2H), 2.69 (s, 2H); IR  $\nu_{\max}$  (KBr, film,  $\text{cm}^{-1}$ ): 3404, 3066, 2927, 1710, 1603, 1459, 1283, 1031, 760, 465; Known compound.<sup>1</sup>

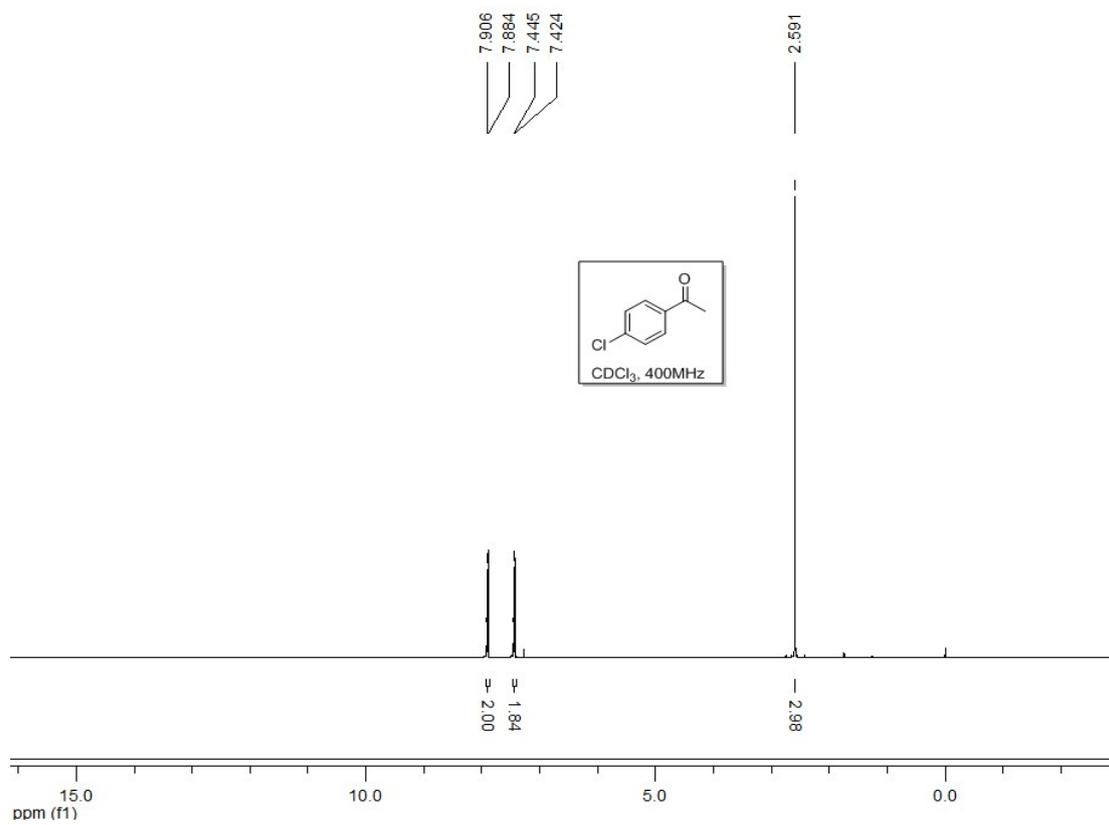
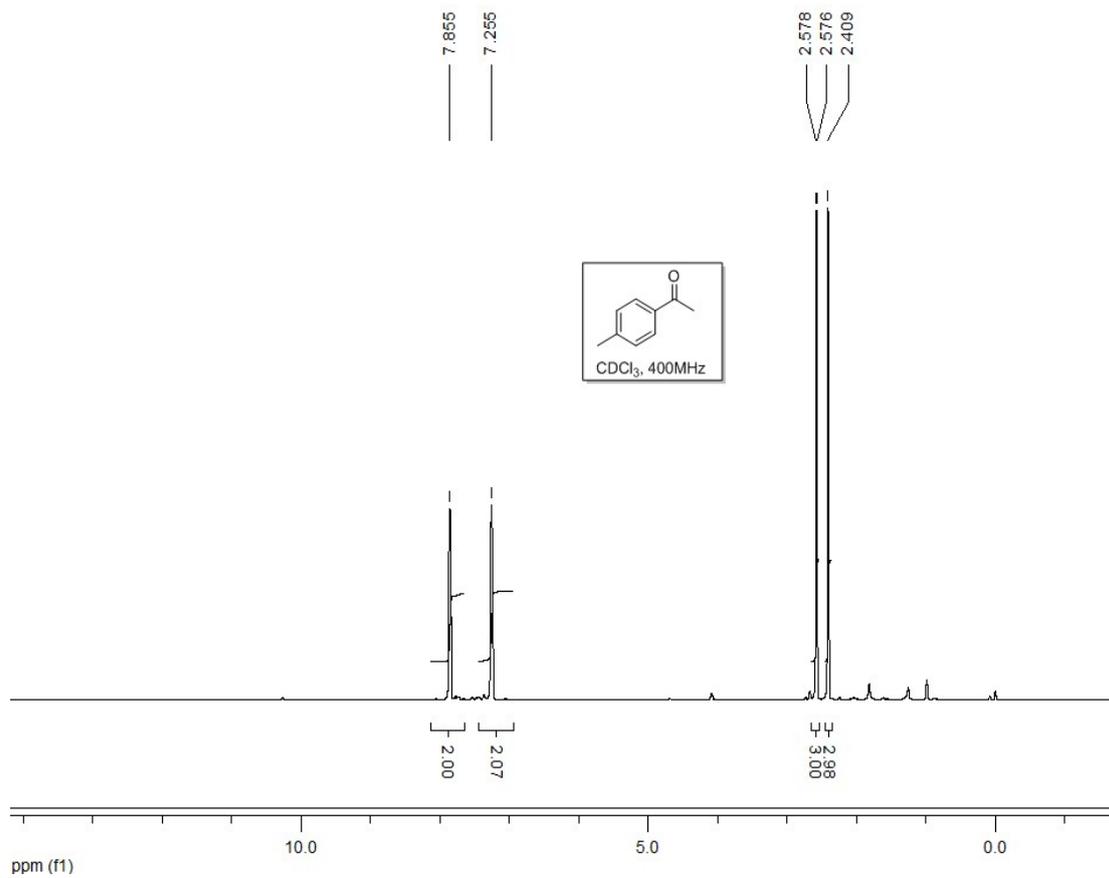
## Reference

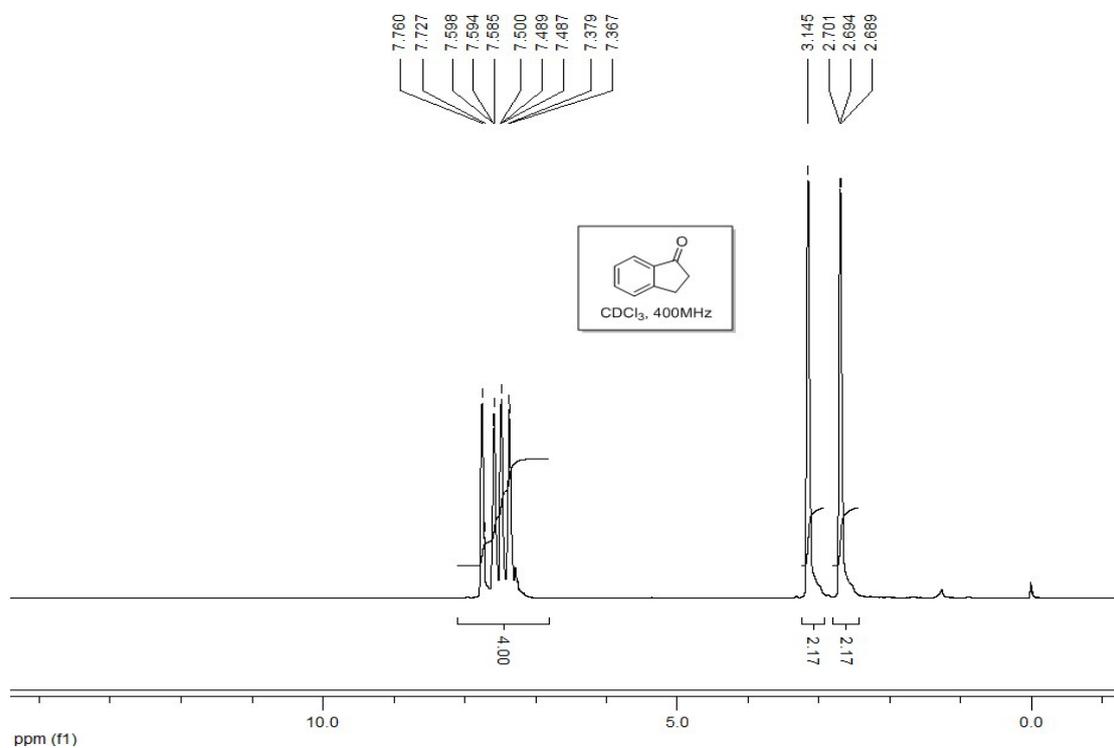
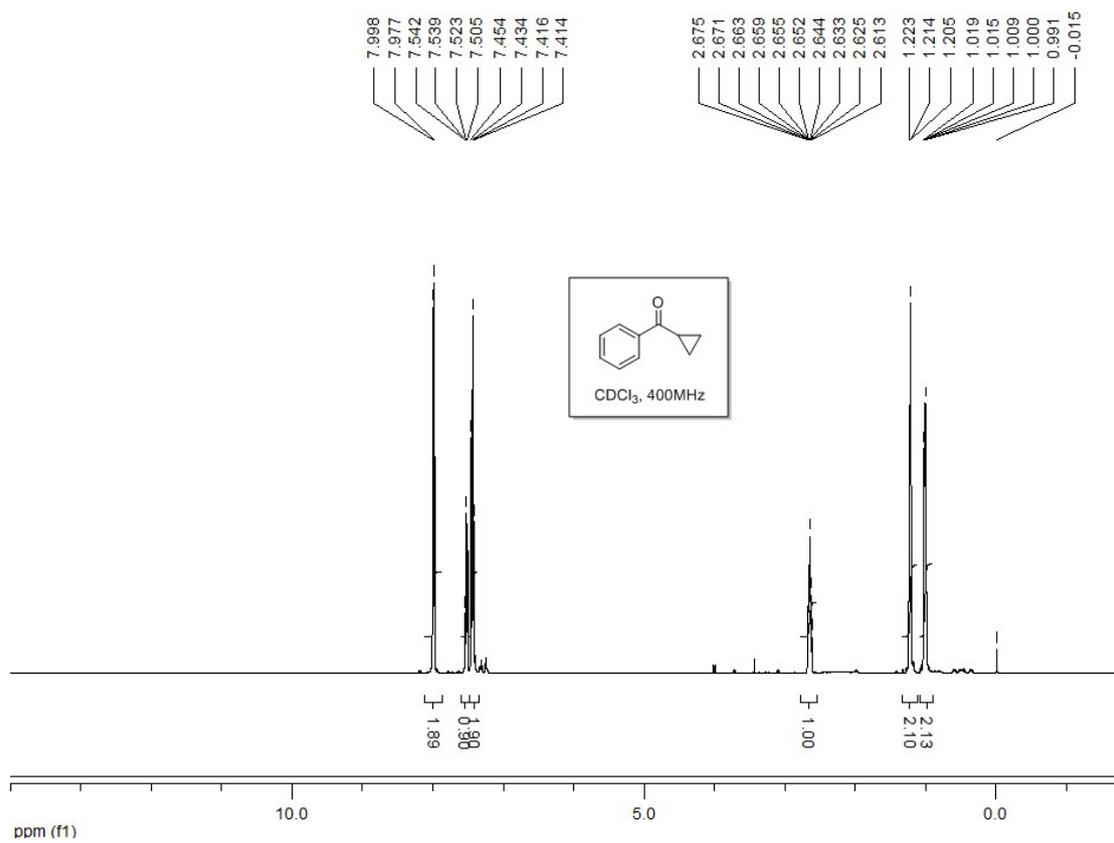
1. T. Wang, X. Jing, C. Chen and L. Yu, *J. Org. Chem.*, 2017, **82**, 9342–9349.
2. X. Jing, D. Yuan, L. Yu, *Adv. Synth. Catal.*, 2017, **359**, 1194–1201.

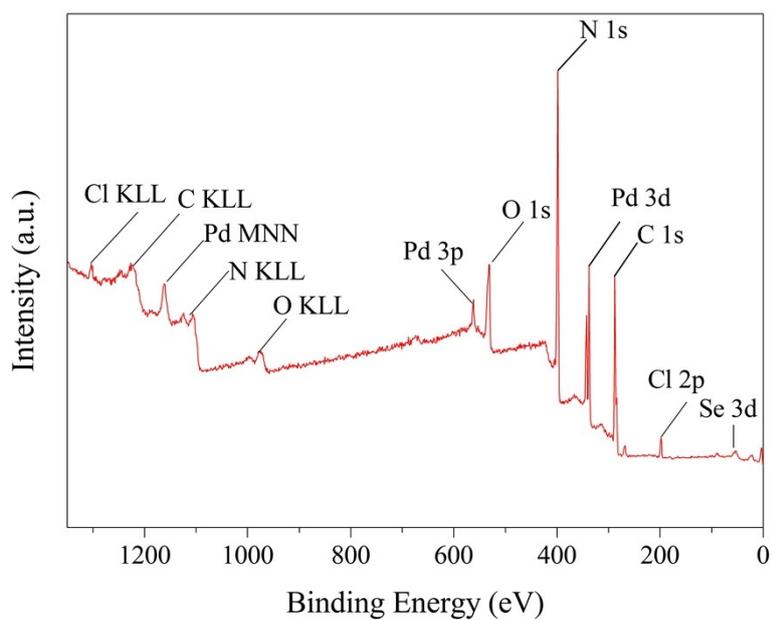
## $^1\text{H}$ NMR spectra of the products



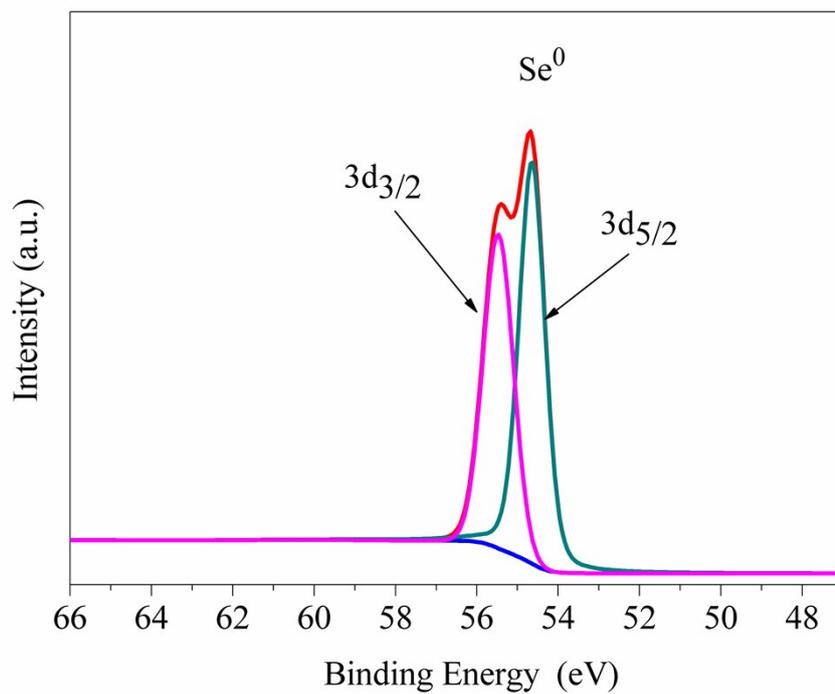




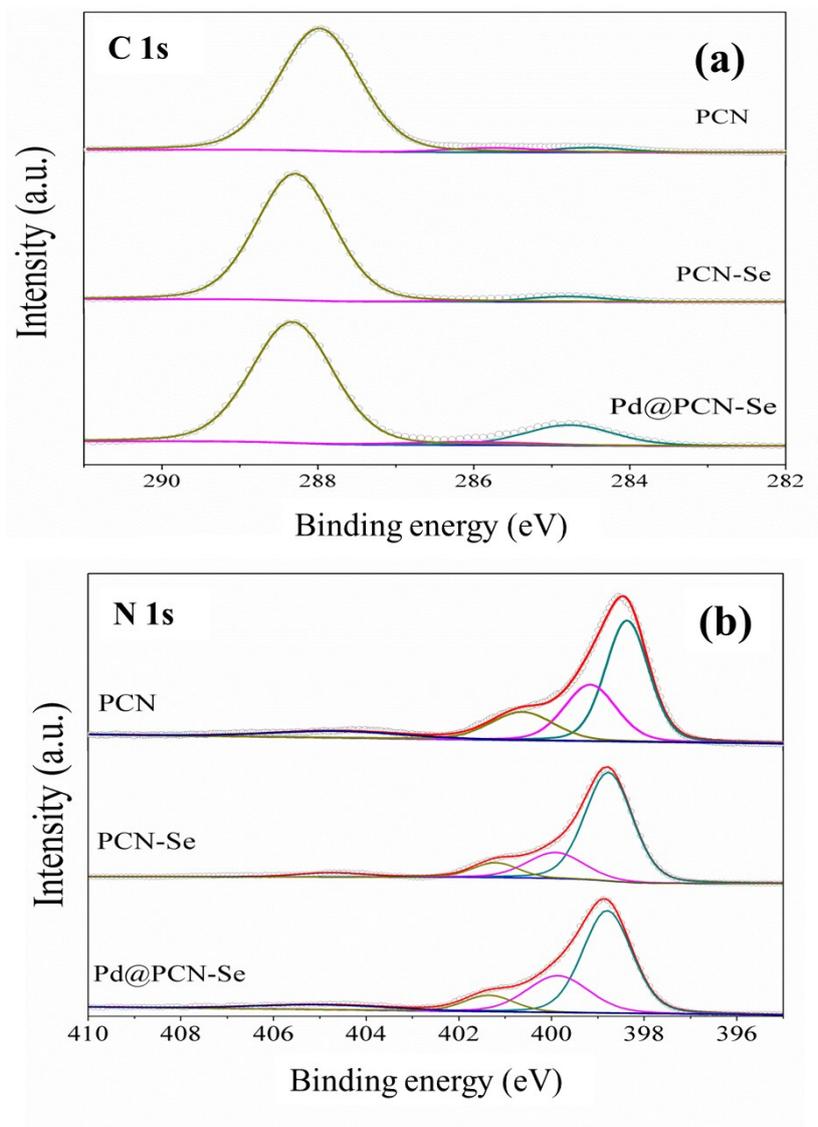




**Fig. S1** XPS survey spectrum of Pd@PCN-Se



**Fig.S2** XPS core level spectrum of Se powder



**Fig.S3** XPS spectra of PCN, PCN-Se and Pd@PCN-Se: (a) C 1s and (b) N 1s.