Supporting information for:

Palladium Containing Periodic Mesoporous Organosilica with Imidazolium Framework (Pd@PMO-IL): An Efficient and Recyclable Catalyst for the Aerobic Oxidation of Alcohols

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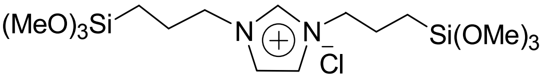
1. General information

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. Liquid NMR was obtained on a DMX-400 MHz Bruker Avance instrument using $CDCl_3$ as solvent and TMS as internal standard. Nitrogen sorption experiments were recorded using a Belsorp-BEL, Inc. analyzer at 77 K. Prior to the measurement, the materials were degassed at 373 K for 12 h. The surface areas were calculated by BET method and the pore size distributions were calculated from the adsorption branch of the isotherms using BJH method. TEM images were taken on a FEI Tecnai 12 BioTWIN microscope operated at 120 kV.

2. General procedure for the Synthesis of 1,3-bis(trimethoxysilylpropyl) imidazolium chloride (1)

Ionic liquid **1** was synthesized according to our previous reported procedure.[1, 2] In a typical experiment, sodium imidazolide (3.002 g, 30 mmol) and 3-chloropropyl-trimethoxysilane (6.082 g, 30 mmol) were added in a well dried flask containing super dry THF (100 mL) and refluxed at 65 °C for 24h under an argon atmosphere. After that, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The obtained oil was transferred to another flask containing 30 mmol of 3-chloropropyl-trimethoxysilane in absolute toluene (100 mL) and refluxed for 48h in the absence of light. Then the reaction solution was cooled to room temperature and the obtained reaction mixture was first washed carefully with toluene (5 × 50 mL) and next super dry CH_2Cl_2 was added to precipitation of NaCl. The supernatant dichloromethane solution was transferred in another well dried flask. After removal of the solvent and drying residue under reduced pressure, a yellow viscous ionic liquid (**1**) was obtained. The spectral data for IL **1** is as follows: ^{1}H-NMR (250 MHz, $CDCl_3$, 25 ºC, TMS): $\delta = 10.00$ (s, 1H, NCHN), 7.50 (d, 2H, $J = 1.7$ Hz CHCH), 4.35 (t, 4H, $J = 7.1$ Hz, NCH_2), 3.63 (s, 18H, 6 OCH_3), 2.04 (m, 4H, $CH_2CH_2CH_2$), 0.64 (t, 4H, $J = 8.1$ Hz $SiCH_2$). ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): $\delta = 136.1$ (N**C**HN), 122.2 (**C**H**C**H), 51.8 (N**C**H_2), 50.8 (O**C**H_3), 24.1 (CH_2**C**H_2CH_2), 5.8 (Si**C**H_2).



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1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride (BTMSPI)

3. General procedure for the synthesis of periodic mesoporous organosilica with ionic liquid framework (PMO-IL)

PMO-IL was prepared according to our previous reported procedure.[2, 3] In a typical synthesis, 10. 6 g KCl and 2.0 g Pluronic P123 were added to a solution of distilled water (12.6 g) and HCl (2M, 55.4 g) with stirring at 40 °C. After clear a homogeneous solution, a pre-prepared mixture of ionic liquid (1.0 g, 2.33 mmol) and tetramethoxysilane (3.2 g, 21.04 mmol) was rapidly added to reaction vessel and stirred at the same temperature for 24h. Then, the obtained mixture was transmitted into a Teflon-lined autoclave and heated at 100 °C under static conditions for 72h. The resultant material was filtered, washed completely with deionized water, and dried at room temperature. The extraction of surfactant was accomplished four times by a Soxhlet apparatus using 100 mL of ethanol and 3 mL of concentrated HCl (for each time) for 1 g of sample during 12h. The final PMO material was denoted as PMO-IL.

4. Preparation of Pd@PMO-IL catalyst

Pd@PMO-IL was also prepared according to our reported procedure.[2, 4] $Pd(OAc)_2$ (27 mg, 0.12 mmol) was added to a monodispersed solution of PMO-IL material (1g, 1.0 mmol IL/g) in DMSO (4.5 mL) under argon atmosphere. The mixture was first stirred at 60 °C for 5h, and then at 100 °C for 1h. After that, the reaction solution was cooled to room temperature and the resulting mixture was washed with CH_2Cl_2 (3×10 mL) to remove unreacted $Pd(OAc)_2$. The final material was obtained after drying by evacuation at 50 °C for 12h. The elemental analysis (EA) showed that the loading of Pd was 0.1 mmol Pd/g solid.

5. General procedure for the aerobic oxidation of alcohols in the presence of oxygen atmosphere using Pd@PMO-IL catalyst

Firstly, potassium carbonate (1 mmol), and Pd@PMO-IL catalyst (0.0025-0.01 equivalents to alcohol) were mixed in trifluorotoluene (TFT) (2.5 mL) in a two-necked flask. The flask was then evacuated (water aspirator) and refilled with pure oxygen for three times (balloon filled). After that, the alcohol (1 mmol) was injected and the resulting mixture was stirred at 95 ºC under an oxygen atmosphere (for the indicated time in the Table 2). The reaction progress was monitored via GC; after completion of the reaction, the reaction mixture was filtered off and the catalyst was washed twice with CH_2Cl_2 (5 mL). The excess of solvent was removed under reduced pressure to give the corresponding carbonyl compounds in good to excellent yields (Table 2).

6. General procedure for the aerobic oxidation of alcohols in the presence of air atmosphere using Pd@PMO-IL catalyst

Firstly, potassium carbonate (1 mmol), and Pd@PMO-IL catalyst (0.0035-0.01 equivalents to alcohol) were mixed in trifluorotoluene (TFT) (2.5 mL) in a two-necked flask. After that, the alcohol (1 mmol, in 1 mL TFT) was injected and the resulting mixture was stirred at 95 ºC under an air atmosphere (for the indicated time in the Table 2). The reaction progress was monitored via GC; after completion of the reaction, the reaction mixture was filtered off and the catalyst was washed twice with CH_2Cl_2 (5 mL). The excess of solvent was removed under reduced pressure to give the corresponding carbonyl compounds in good to excellent yields (Table 2).

7. The recovery of the Pd@PMO-IL catalyst

The aerobic oxidation over the Pd@PMO-IL catalyst was carried out under an oxygen atmosphere by treatment 0.25 mol% of the catalyst with 1-phenylethanol (5 mmol), K_2CO_3 (5 mmol) in TFT at 95 °C. The reaction progress was monitored by GC; after completion of the reaction, the resulting mixture was filtered and washed with dichloromethane thoroughly. The recovered catalyst (ROPd@PMO-IL) was then successfully reused 9 times under the same reaction conditions without any decrease in activity and selectivity.

8. Procedure for the hot filtration test

This experiment was conducted in a TFT solution containing 1 mmol 1-phenylethanol, 0.25 mol% catalyst, and 1 mmol K_2CO_3 at 95 °C under oxygen atmosphere. After ~45% of the oxidation process was completed, the reaction mixture was filtered and then filtrate was allowed to progress under oxygen atmosphere at 95 °C for 12h. The reaction progress was monitored by GC.

9. General procedure for the study of kinetic of oxidation reaction with and without poisonous agents Hg(0), poly-(4-vinylpyridine) (PVP), and SBA-propyl-SH

A solution of 4-chlorobenzyl alcohol (1 mmol) and K_2CO_3 (1 mmol), with and/or without poisoning agent (poisonous agent:Pd, 400:1) in TFT (2.5 mL) was magnetically stirred at 95 °C under molecular oxygen. Then Pd@PMO-IL catalyst (containing 0.35 mol % Pd) was rapidly added and the reaction progress was monitored by GC at every 0.5h. The results are demonstrated in Figure 1S.

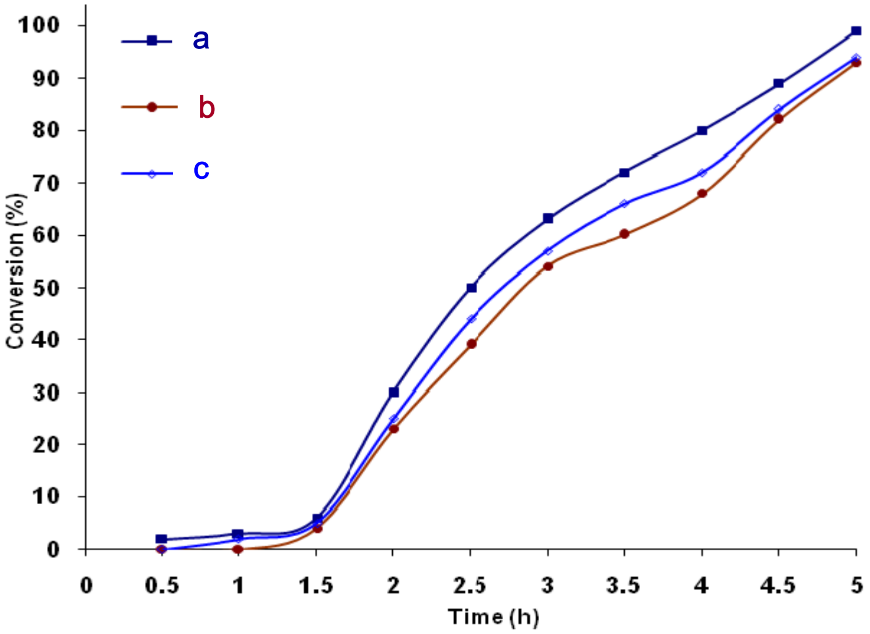


Figure 1S. Reaction progress as a function of time on the aerobic oxidation of 4-chlorobenzyl alcohol using **Pd@PMO-IL** catalyst in TFT: a) normal conditions; b) in the presence of 400 equivalents PVP; c) in the presence of 400 equivalents SBA-propyl-SH

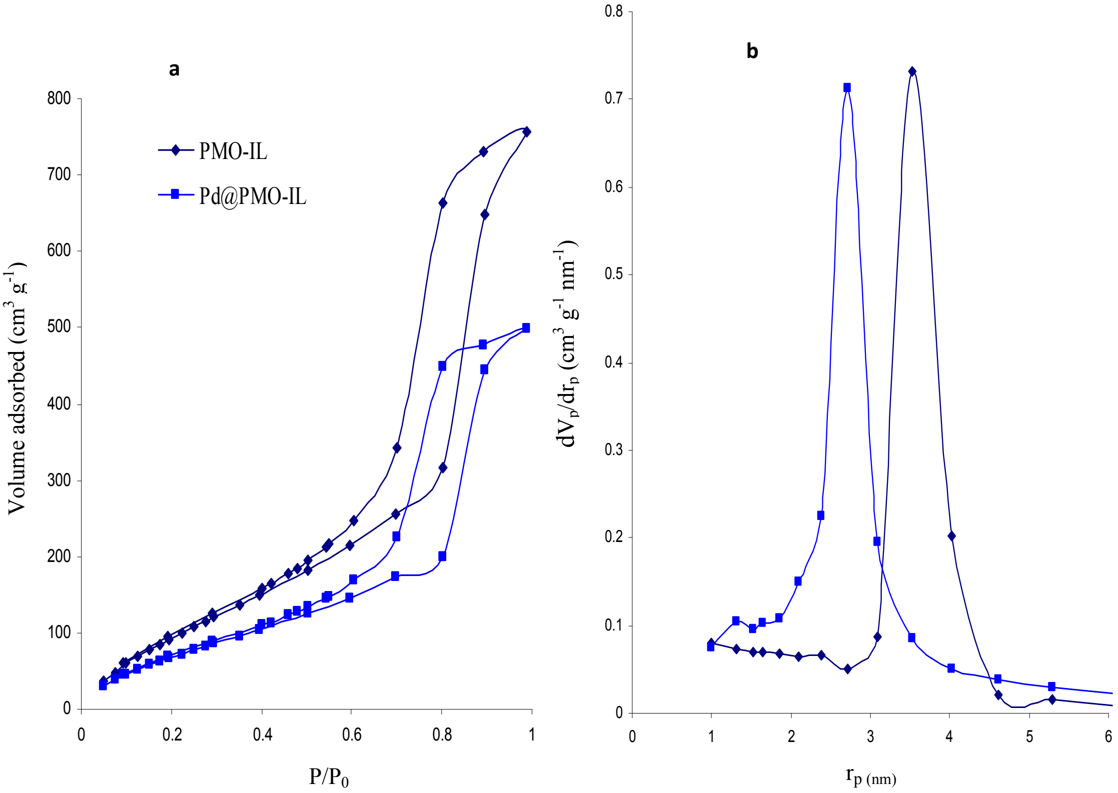


Figure 2S. Nitrogen adsorption-desorption isotherms (a) and pore size distributions (b) of the **PMO-IL** and **Pd@PMO-IL** materials. These isotherms indicate that the pore sizes of both samples are in the mesoporous range with two dimensional hexagonal structure and high uniformity of channels

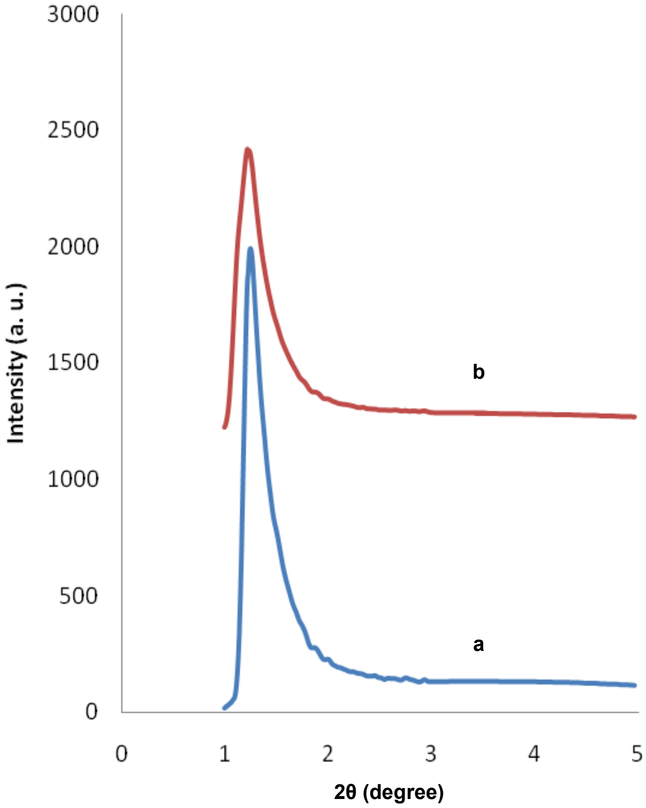


Figure 3S. Powder X-ray diffraction (PXRD) patterns of a) PMO-IL and b) Pd@PMO-IL materials

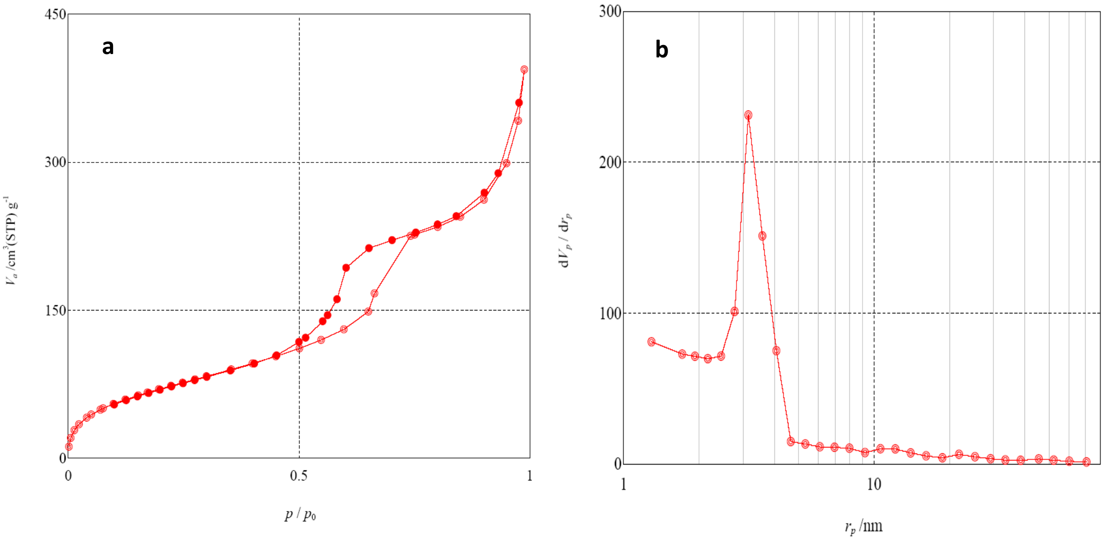


Figure 4S: Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of the SBA-15-propyl-SH. These isotherms illustrate the high regularity of functionalized mesochannels

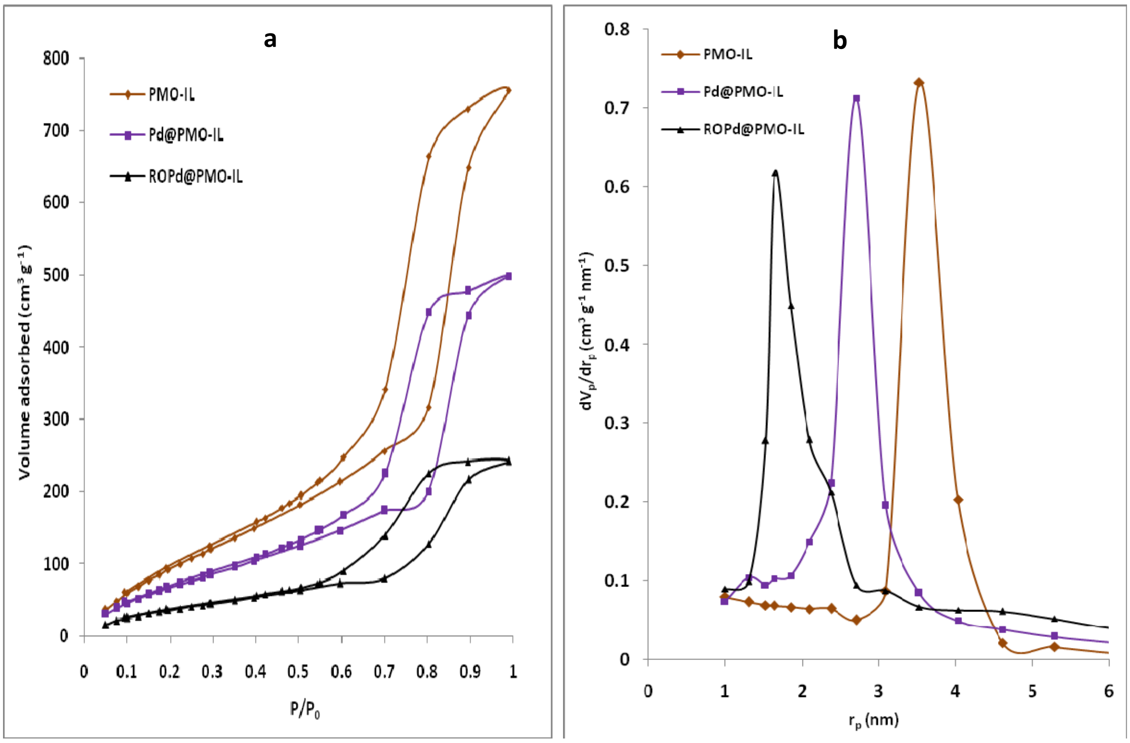
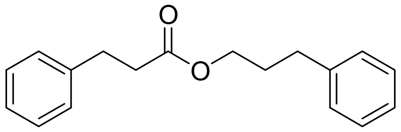


Figure 5S. Nitrogen adsorption-desorption isotherms (a) and pore size distributions (b) of the **PMO-IL**, **Pd@PMO-IL** and **ROPd@PMO-IL** materials.

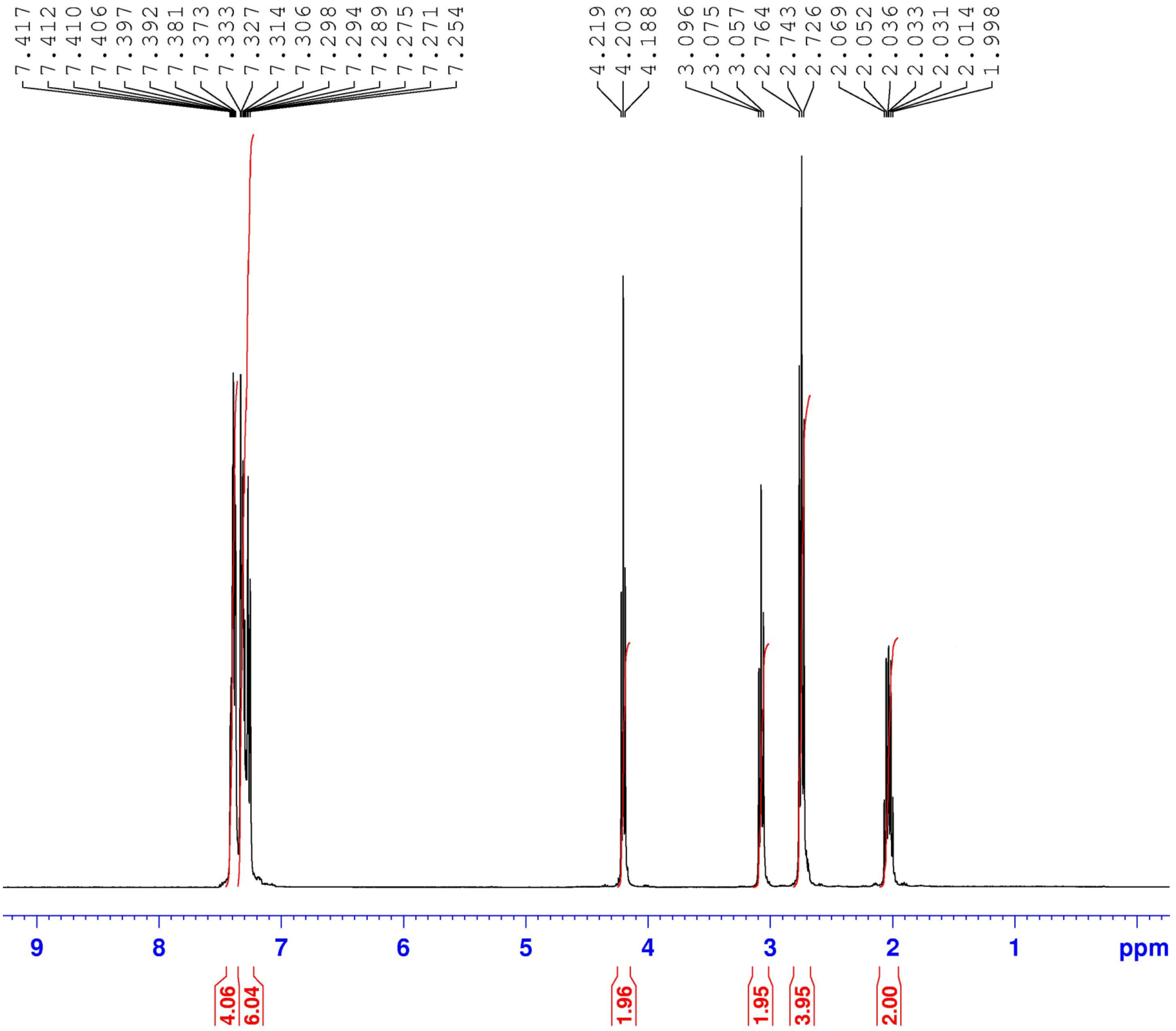
Table 1S. Structural parameters of **PMO-IL, Pd@PMO-IL** and **ROPd@PMO-IL** materials determined from nitrogen sorption experiments:

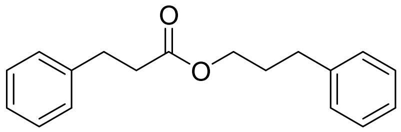
Sample	BET surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
PMO-IL	671	7.0	1.21
Pd@PMO-IL	458	5.3	0.88
ROPd@PMO-IL	303	3.3	0.58

The ^{1}H- and ^{13}C-NMR spectra of 3-phenylpropyl-3-phenylpropanate obtained from aerobic oxidation of 3-phenylpropanol under desired reaction conditions

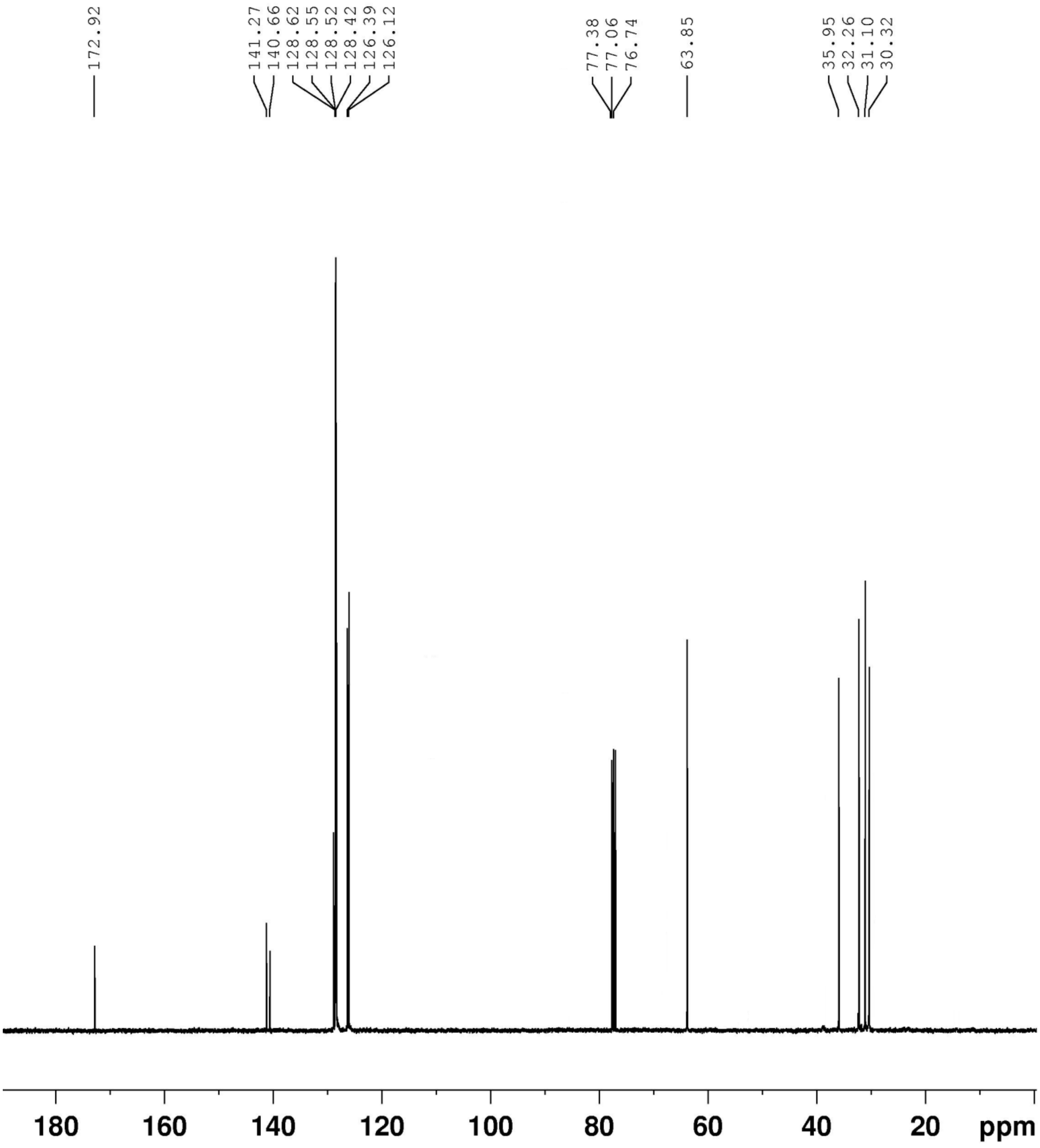


3-phenylpropyl 3-phenylpropanoate





3-phenylpropyl 3-phenylpropanoate



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