

Electronic supplementary information

## Fabrication of a Plasmonic Au-Pd Alloy Nanoparticles for Photocatalytic Suzuki–Miyaura Reaction at Ambient Conditions

*Dongxu Han, Zongbi Bao, Huabin Xing, Yiwen Yang, Qilong Ren, and Zhiguo Zhang\**

Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and  
Biological Engineering, Zhejiang University, Zheda Road 38, Hangzhou 310027, China

\*E-mail: [zhiguo.zhang@zju.edu.cn](mailto:zhiguo.zhang@zju.edu.cn)

## Contents

Experimental Procedures .....	S3
Chemicals and Materials.....	S3
Synthesis of the Au-Pd/TiO <sub>2</sub> Catalyst .....	S3
General procedure for the synthesis of the Pd/TiO <sub>2</sub> , Au/TiO <sub>2</sub> , Cu-Pd/TiO <sub>2</sub> , Au-Ni/TiO <sub>2</sub> , and Cu-Ni/TiO <sub>2</sub> Samples .....	S3
Photocatalytic Suzuki-Miyaura Coupling Reaction .....	S3
Characterization .....	S4
The HPLC method .....	S4
Result and discussion .....	S5
Figure S1. A line profile analysis of EDS for a typical Au-Pd alloy NP of the Au-Pd/TiO <sub>2</sub> catalyst .....	S5
Figure S2. Elemental maps of Au, Pd and Ti of the Au-Pd/TiO <sub>2</sub> catalyst.....	S5
Figure S3. (A) Photograph and (B) X-ray diffraction (XRD) spectra of the Au-Pd/TiO <sub>2</sub> catalyst with comparisons with pure Au/TiO <sub>2</sub> , Pd/TiO <sub>2</sub> , and TiO <sub>2</sub> .....	S5
Figure S4. XPS result of Au 4f of the Au/TiO <sub>2</sub> sample.....	S6
Figure S5. A line profile analysis of EDS for a typical Au-Pd alloy NP of the Au-Pd/TiO <sub>2</sub> catalyst after four circles.....	S6
Figure S6. XPS results of (A) Ti 2p, (B) O 1s of the fresh Au-Pd/TiO <sub>2</sub> catalyst and (C) Ti 2p, (D) O 1s of that after four rounds recycles.....	S7
NMR spectra of biphenyl products .....	S8

## Experimental Procedures

### Chemicals and Materials

All chemicals (AR grade) were used as received. TiO<sub>2</sub> P25 was supplied from Degussa, Huls Corporation, Germany. The H<sub>2</sub>AuCl<sub>4</sub> solution was prepared by dissolving 1 g of H<sub>2</sub>AuCl<sub>4</sub> into 50 mL H<sub>2</sub>O and was stored in the volumetric flask. The PdCl<sub>2</sub> solution was prepared the same way using 1 M HCl as the solvent. Both solutions were stored in the refrigerator at 4 °C prior to use.

### Synthesis of the Au-Pd/TiO<sub>2</sub> Catalyst

The catalyst was prepared by a one-step impregnation–reduction method. First, 833 μL of the PdCl<sub>2</sub> solution and 1045 μL of H<sub>2</sub>AuCl<sub>4</sub> solution were added into 50 mL of distilled water with stirring. P25 TiO<sub>2</sub> powder (1000 mg) was then dispersed into the mixed solution, and the slurry was placed in an oil bath with stirring to maintain a temperature of 80 °C. After impregnation of H<sub>2</sub>AuCl<sub>4</sub> and PdCl<sub>2</sub> on TiO<sub>2</sub> for 1 h, 1.0 M of NaOH solution was added to tune the pH value to approximately 10. Then, 20 mL aqueous NaBH<sub>4</sub> solution (113mg) was added dropwise to the suspension. After ageing for 10 h, the solid product was collected by vacuum filtration, and then washed thoroughly with distilled water, followed by vacuum drying at 60 °C overnight.

### Synthesis of the Pd/TiO<sub>2</sub>, Au/TiO<sub>2</sub>, Cu-Pd/TiO<sub>2</sub>, Au-Ni/TiO<sub>2</sub>, and Cu-Ni/TiO<sub>2</sub> Samples

Pd/TiO<sub>2</sub> and Au/TiO<sub>2</sub> samples were synthesized according to the same procedure of Au-Pd/TiO<sub>2</sub> with only one Pd or Au precursor. As for the other bimetallic samples, at first, for Cu-Pd/TiO<sub>2</sub>, 833μL of the PdCl<sub>2</sub> solution, 0.404 mmol CuCl<sub>2</sub>; for Au-Ni/TiO<sub>2</sub>, 1045μL H<sub>2</sub>AuCl<sub>4</sub> solution and 0.437 mmol NiCl<sub>2</sub>; and for Cu-Ni/TiO<sub>2</sub>, 0.404 mmol CuCl<sub>2</sub> and 0.437 mmol NiCl<sub>2</sub> were added into 50 mL of distilled water via stirring. Then, 1000 mg of TiO<sub>2</sub> P25 powder was dispersed into the mixed solution via vigorous stirring and then put the suspension in an oil bath to maintain at 80 °C. The following steps were the same with the synthetic process of Au-Pd/TiO<sub>2</sub>.

### Photocatalytic Suzuki-Miyaura Coupling Reaction

In a typical reaction, 1 mL of water, 1 mL of ethanol, 82.9 mg (0.6 mmol) of K<sub>2</sub>CO<sub>3</sub>, 23 μL (0.2 mmol) of iodobenzene, 37.4 mg (0.3 mmol) of benzenboronic acid, and the catalyst (an equivalent amount to 0.002 mmol of Pd) were mixed via vigorous stirring. The reaction mixture was irradiated under a 5 W blue LED lamp

with magnetic stirring for 5 h. And a water bath was used to maintain the reaction in ambient temperature ( $25 \pm 5$  °C). After the reaction, the solid catalyst was separated via suction filtration and then washed thoroughly with distilled water and ethanol, followed by the removal of solvent under vacuum at 60 °C overnight. The collected sample was reused for the target reaction.

### **Characterization**

TEM, HR-TEM, STEM and EDS images were taken on a JEM 2100F transmission electron microscope at 200 kV using a copper grid coated with an ultrathin carbon film as the substrate. The optical properties of the samples were investigated by a Shimadzu UV-2600 ultraviolet-visible spectrophotometer, during which BaSO<sub>4</sub> was utilized as an internal reflectance standard. The photoluminescence spectra of the samples were recorded on an Edinburgh FLS 920 spectrophotometer, and the excitation wavelength was set at 325 nm. The crystal structures of the samples were characterized by a PANalytical X'Pert PRO X-ray diffractometer (XRD) with Cu K $\alpha$  radiation. X-ray photoelectron spectroscopy (XPS) results were obtained from a Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer using a monochromatic aluminum K $\alpha$  X-ray source at 20 kV. The binding energies of all measurements were calibrated using the C 1s peak at 284.6 eV. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a Bruker 400 MHz NMR spectrometer.

### **The HPLC method**

The products were analyzed by a Waters 1525 HPLC with a Waters 2487 Dual  $\lambda$  Absorbance Detector and a C18 column. Analytically pure biphenyl (or 4-methylbiphenyl) was used as the external standard to get the standard curves. HPLC conditions: ultraviolet visible of the detector at  $\lambda=254$  nm, column temperature at 30°C, methanol/H<sub>2</sub>O = 4/1 as mobile phase, flow rate was 1 mL/min.

## Result and discussion

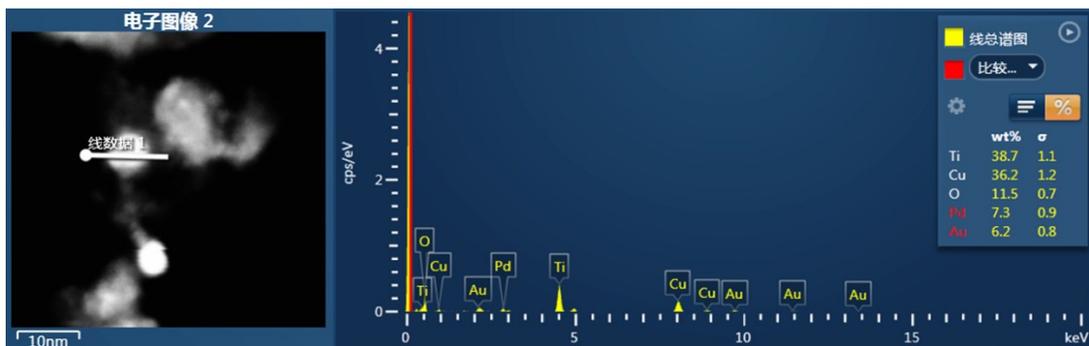


Fig. S1 A line profile analysis of EDS for a typical Au-Pd alloy NP of the Au-Pd/TiO<sub>2</sub> catalyst.

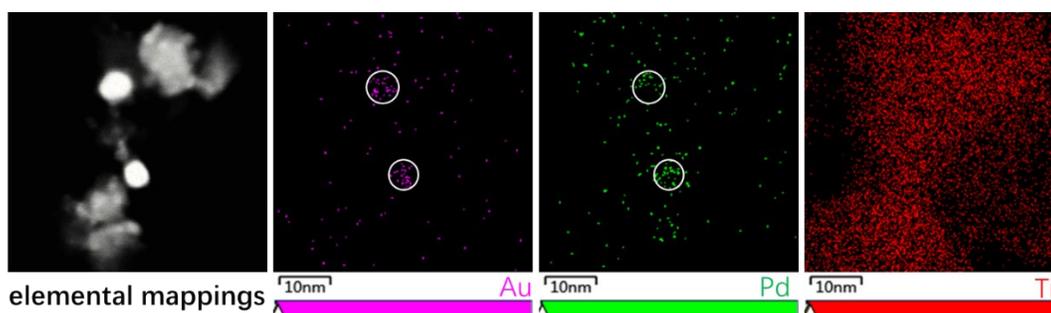


Fig. S2 Elemental maps of Au, Pd and Ti of the Au-Pd/TiO<sub>2</sub> catalyst.

Fig. S1 and Fig. S2 both showed that Au and Pd existed as binary alloy NPs on the TiO<sub>2</sub> in the Au-Pd/TiO<sub>2</sub> catalyst.

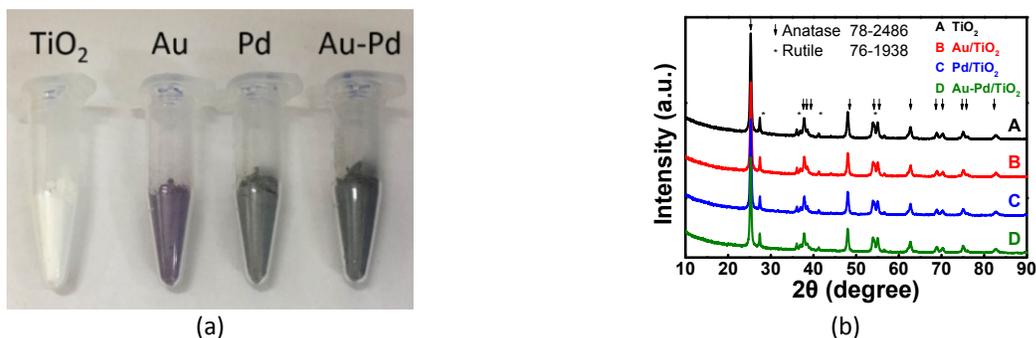
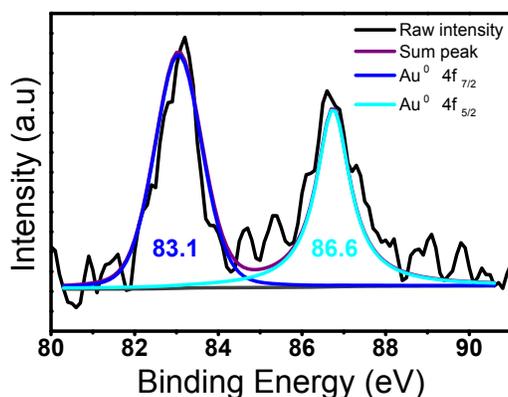


Fig. S3 (a) Photograph and (b) X-ray diffraction (XRD) spectra of the Au-Pd/TiO<sub>2</sub> catalyst with comparisons with pure Au/TiO<sub>2</sub>, Pd/TiO<sub>2</sub>, and TiO<sub>2</sub>.

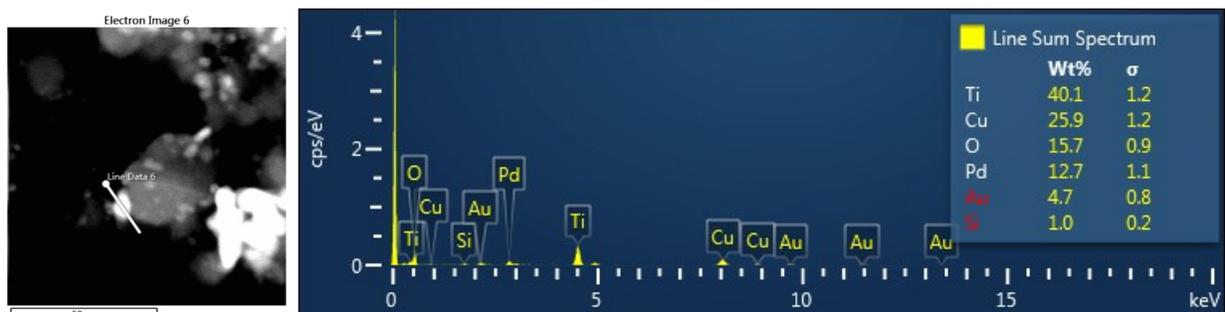
Fig. S3a shows a photograph of TiO<sub>2</sub>, Au/TiO<sub>2</sub>, Pd/TiO<sub>2</sub>, and the Au-Pd/TiO<sub>2</sub> catalyst.

Fig. S3b shows that XRD patterns of the Au-Pd/TiO<sub>2</sub> catalyst, Au/TiO<sub>2</sub>, Pd/TiO<sub>2</sub>, and TiO<sub>2</sub> P25 showed no differences, and all the strong diffraction peaks were easily indexed to anatase and rutile, indicating that the supported Au-Pd alloy NPs have no influence on the crystal structure of the TiO<sub>2</sub> supports.



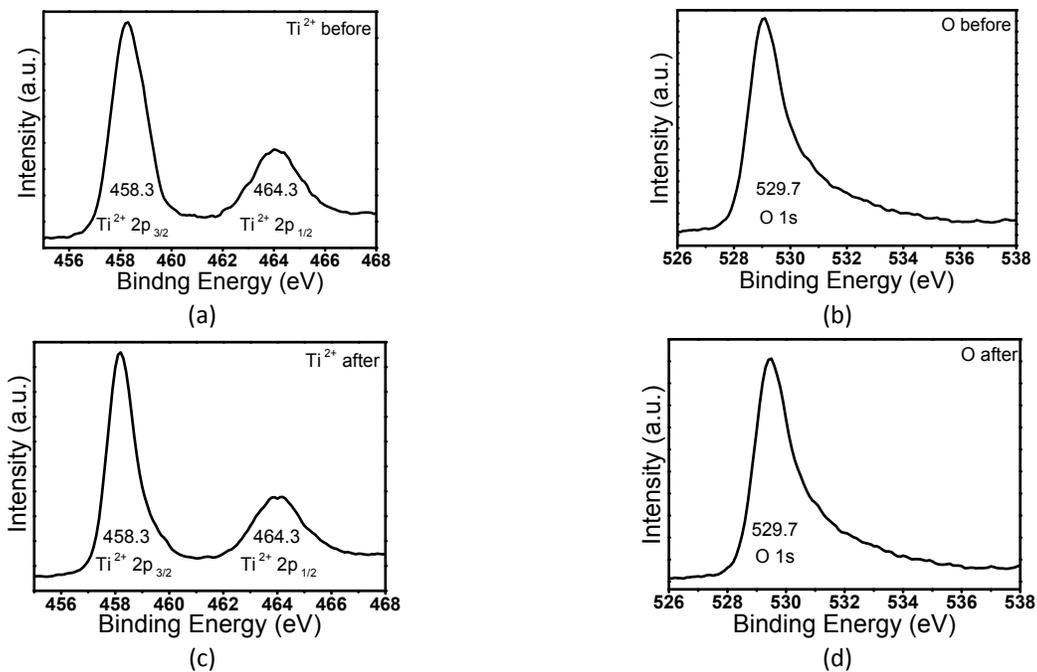
**Fig. S4** XPS result of Au 4f of the Au/TiO<sub>2</sub> sample.

Generally, the binding energy (BE) of Au<sup>0</sup> 4f<sub>7/2</sub> and Au<sup>0</sup> 4f<sub>5/2</sub> are close to 84.0 and 87.8, respectively. However, in the Au/TiO<sub>2</sub> sample, Au<sup>0</sup> 4f<sub>7/2</sub> and Au<sup>0</sup> 4f<sub>5/2</sub> were located at 83.1 and 86.6, respectively, which confirmed that electron transfer from oxygen vacancies of TiO<sub>2</sub> to the Au species could increase the electron density around Au, which resulted in the lower BE of Au.



**Fig. S5** A line profile analysis of EDS for a typical Au-Pd alloy NP of the Au-Pd/TiO<sub>2</sub> catalyst after four circles.

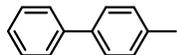
Fig. S5 was a line profile analysis of the energy dispersion X-ray spectrum for a typical Au-Pd alloy NP of the spent Au-Pd/TiO<sub>2</sub> after four circles, which showed that Au and Pd still existed as binary alloy NPs in the catalyst after recycling.



**Fig. S6** XPS results of (a) Ti 2p, (b) O 1s of the fresh Au-Pd/TiO<sub>2</sub> catalyst and (c) Ti 2p, (d) O 1s of that after four rounds recycles.

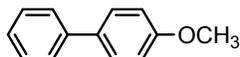
Fig. S6 showed that there was no change in either shape or binding energy of the main peaks in both Ti 2p and O 1s XPS results of the Au-Pd/TiO<sub>2</sub> catalyst after recycling.

## NMR spectra of biphenyl products



### 4-methylbiphenyl (Table2, 1):

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.57 (d, 2H), 7.49 (d, 2H), 7.42 (t, 2H), 7.32 (t, 1H), 7.25 (d, 2H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =140.81 (s), 138.00 (s), 136.67 (s), 129.14 (s), 128.37 (s), 126.64 (d,  $J$  = 2.1 Hz), 20.76 (s).



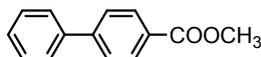
### 4-methoxybiphenyl (Table2, 2):

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.55 (m, 4H), 7.43 (t, 2H), 7.31 (t, 1H), 7.00 (t, 2H), 3.86 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =158.78 (s), 140.48 (s), 133.42 (s), 128.38 (s), 127.82 (s), 126.36 (d,  $J$  = 8.2 Hz), 113.84 (s), 55.00 (s).



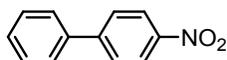
### 4-acetylbiphenyl (Table2, 3):

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =8.03 (d, 2H), 7.70 (d, 2H), 7.62 (d, 2H), 7.48 (t, 2H), 7.41 (t, 1H), 2.65 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =197.48 (s), 145.46 (s), 139.54 (s), 135.46 (s), 128.61 (d,  $J$  = 3.7 Hz), 127.90 (s), 126.92 (d,  $J$  = 4.5 Hz), 26.36 (s).



### 4-methoxycarbonylbiphenyl (Table2, 4):

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =8.10 (d, 2H), 7.68 (d, 2H), 7.62 (d, 2H), 7.47 (t, 2H), 7.40 (t, 1H), 3.94 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =166.68 (s), 145.30 (s), 139.66 (s), 129.76 (s), 128.56 (d,  $J$  = 5.2 Hz), 127.80 (s), 126.94 (s), 126.72 (s), 51.81 (s).



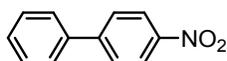
### 4-nitrobiphenyl (Table2, 5):

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =8.29 (d, 2H), 7.75 (d, 2H), 7.62 (d, 2H), 7.51 (t, 2H), 7.48 – 7.41 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 147.31 (s), 146.76 (s), 138.46 (s), 128.83 (s), 128.59 (s), 127.48 (s), 127.06 (s), 123.79 (s).



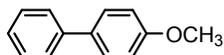
**4-acetylbiphenyl (Table2, 6):**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =8.03 (d, 2H), 7.70 (d, 2H), 7.63 (d, 2H), 7.48 (t, 2H), 7.41 (t, 1H), 2.65 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =197.48 (s), 145.46 (s), 139.53 (s), 135.49 (s), 128.63 (d,  $J$  = 3.7 Hz), 127.90 (s), 126.92 (d,  $J$  = 4.5 Hz), 26.37 (s).



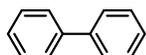
**4-nitrobiphenyl (Table2, 7):**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =8.29 (d, 2H), 7.75 (d, 2H), 7.62 (d, 2H), 7.50 (t, 2H), 7.45 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =147.32 (s), 146.76 (s), 138.46 (s), 128.83 (s), 128.59 (s), 127.48 (s), 127.06 (s), 123.79 (s).



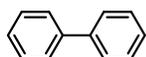
**4-methoxybiphenyl (Table2, 8):**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.55 (m, 4H), 7.42 (t, 2H), 7.31 (t, 1H), 7.00 (t, 2H), 3.86 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =158.78 (s), 140.47 (s), 133.42 (s), 128.38 (s), 127.82 (s), 126.36 (d,  $J$  = 8.2 Hz), 113.84 (s), 55.00 (s).



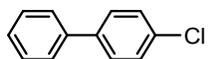
**Biphenyl (Table2, 9):**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.63 (dd, 4H), 7.48 (t, 4H), 7.39 (d, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 140.88 (s), 128.41 (s), 126.91 (s), 126.82 (s).



**Biphenyl (Table2, 10):**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 7.61 (dd, 4H), 7.47 (t, 4H), 7.37 (d, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =140.89 (s), 128.42 (s), 126.91 (s), 126.83 (s).



**4-chlorobiphenyl (Table2, 11):**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=7.55$  (m, 4H), 7.43 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta=139.65$  (s), 139.32 (s), 133.03 (s), 128.55 (d,  $J = 2.2$  Hz), 128.05 (s), 127.25 (s), 126.65 (s).

