

## Electronic Supplementary Information

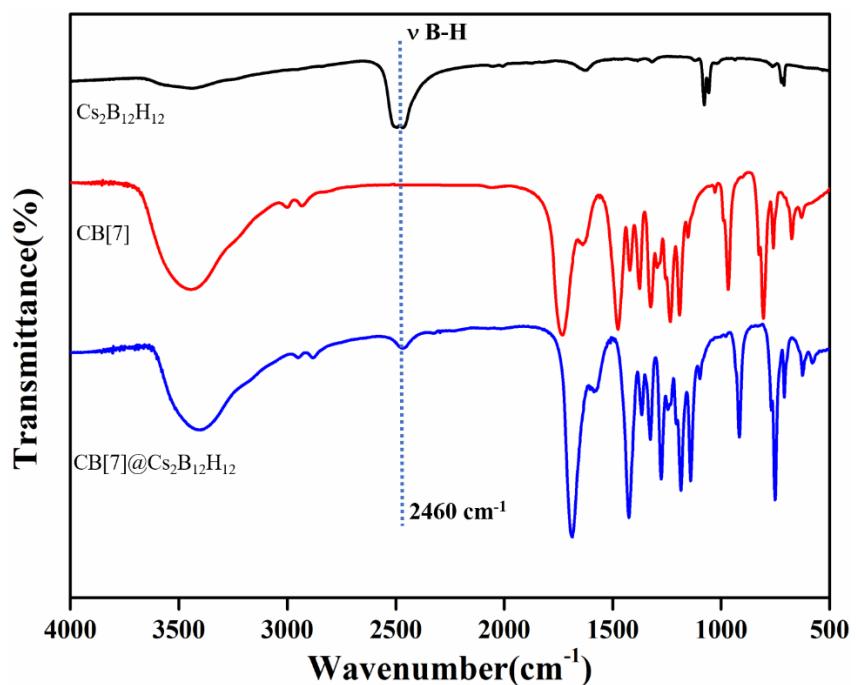
### In situ Synthesis of Ultrafine Metal Clusters triggered by Dodecaborate Supramolecular Organic Frameworks

Bin Qi, Xin Li, Liang Sun, Bo Chen, Hao Chen, Chenchen Wu, Haibo Zhang\* and Xiaohai Zhou\*

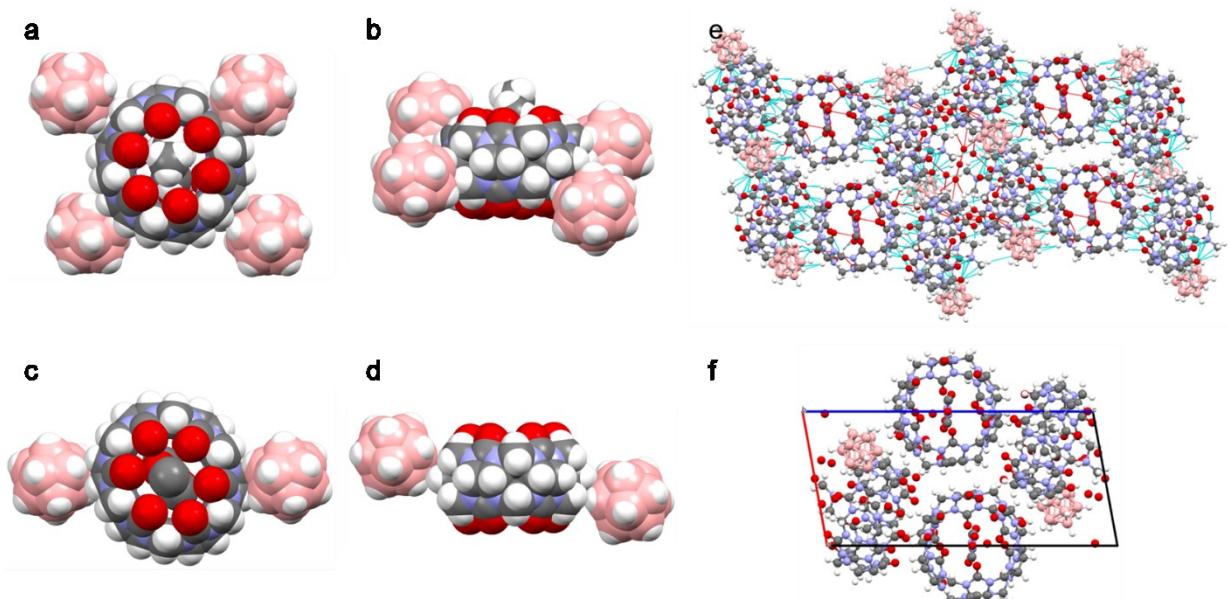
*College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China.*

## Content

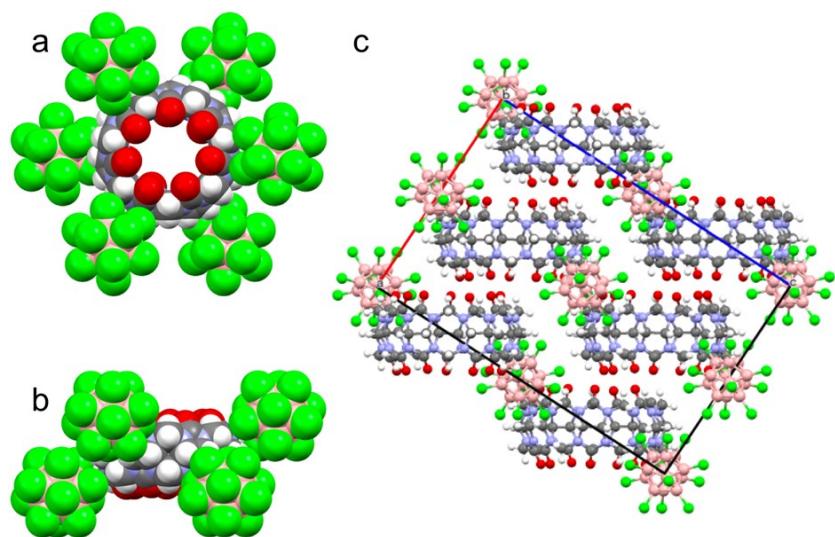
<b>Figure S1. FT-IR spectrum of pure Cs<sub>2</sub>[<i>closso</i>-B<sub>12</sub>H<sub>12</sub>], CB[7] and Cs<sub>2</sub>[<i>closso</i>-B<sub>12</sub>H<sub>12</sub>]@CB[7] assemblies.....</b>	<b>3</b>
<b>Figure S2. Views of the CB6/B<sub>12</sub>H<sub>12</sub><sup>2-</sup> complex XRD structure.....</b>	<b>4</b>
<b>Figure S3. Views of the CB7/B<sub>12</sub>Cl<sub>2</sub><sup>2-</sup> complex XRD structure.....</b>	<b>4</b>
<b>Figure S4. The photographic images of the obtained final metal/BOFs products.....</b>	<b>4</b>
<b>Figure S5. XRD results of CBn-BOFs and Au/CBn-BOFs.....</b>	<b>5</b>
<b>Figure S6. The survey XPS spectra (a) and high-resolution XPS Au 4f spectra (b) of Au-BOFs.....</b>	<b>5</b>
<b>Figure S7. XRD results of CBn-BOFs and Pd/CBn-BOFs.....</b>	<b>6</b>
<b>Figure S8. The survey XPS spectra (a) and high-resolution XPS Pd 3d spectra (b) of Pd-BOFs.....</b>	<b>6</b>
<b>Figure S9. XRD results of Ag/ BOFs.....</b>	<b>7</b>
<b>Figure S10. The survey XPS spectra (a) and high-resolution XPS Ag 3d spectra (b) of Ag/BOFs.....</b>	<b>7</b>
<b>Figure S11. XRD results of Pt/ BOFs.....</b>	<b>8</b>
<b>Figure S12. The survey XPS spectra (a) and high-resolution XPS Pt 4f spectra (b) of Pt/BOFs.....</b>	<b>8</b>
<b>Figure S13. The GC standard curves of (a) toluene and FAL, (b) toluene and FOL.....</b>	<b>9</b>
<b>Figure S14. The GC spectrum of the conversion of FAL to FOL treated with various Au/BOFs and BOFs catalysts.....</b>	<b>9</b>
<b>Figure S15. The GC spectrum of the recycling tests of FAL to FOL treated with Au/CB7-BOFs catalysts.....</b>	<b>10</b>
<b>Figure S16. The TEM image and powder XRD pattern of the Au/CB7-BOFs catalysts after 15<sup>th</sup> round of catalysis.....</b>	<b>10</b>
<b>Table S1. Comparison of the catalytic performances of Au/BOFs catalyst with already reported catalysts towards the selective reduction of FAL with FOL.....</b>	<b>10</b>
<b><sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for the products listed in Table 2 of the main text.....</b>	<b>11</b>
<b>Reference.....</b>	<b>20</b>



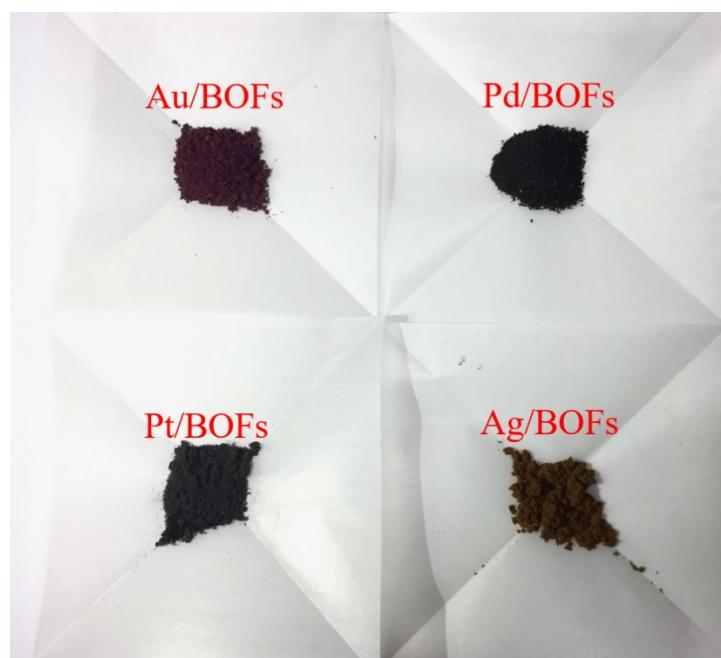
**Figure S1.** FT-IR spectrum of pure  $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{12}]$ , CB[7] and  $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{12}]@\text{CB}[7]$  assemblies.



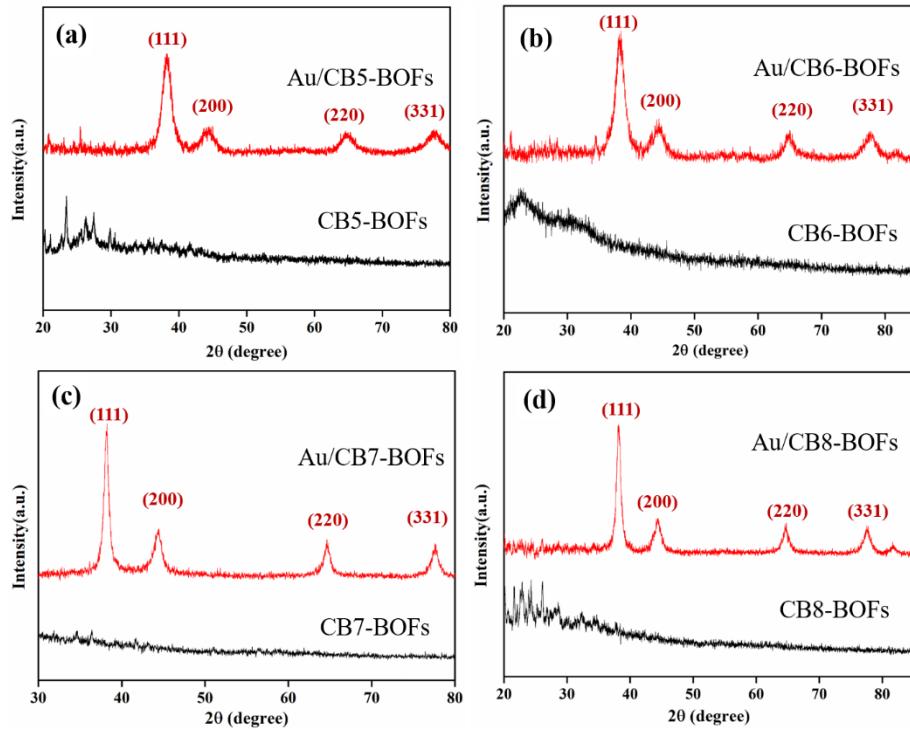
**Figure S2.** Views of the CB6/B<sub>12</sub>H<sub>12</sub><sup>2-</sup> complex XRD structure.



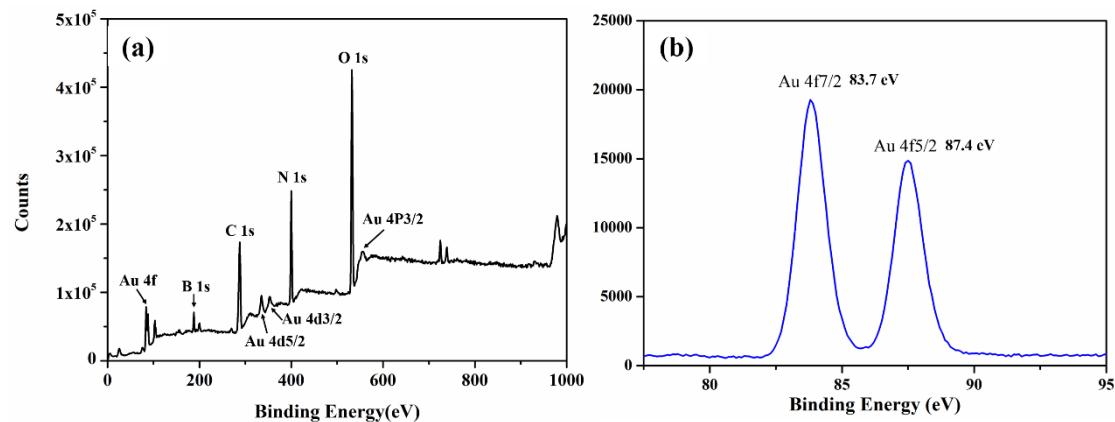
**Figure S3.** Views of the CB<sub>7</sub>/B<sub>12</sub>Cl<sub>12</sub><sup>2-</sup> complex XRD structure.



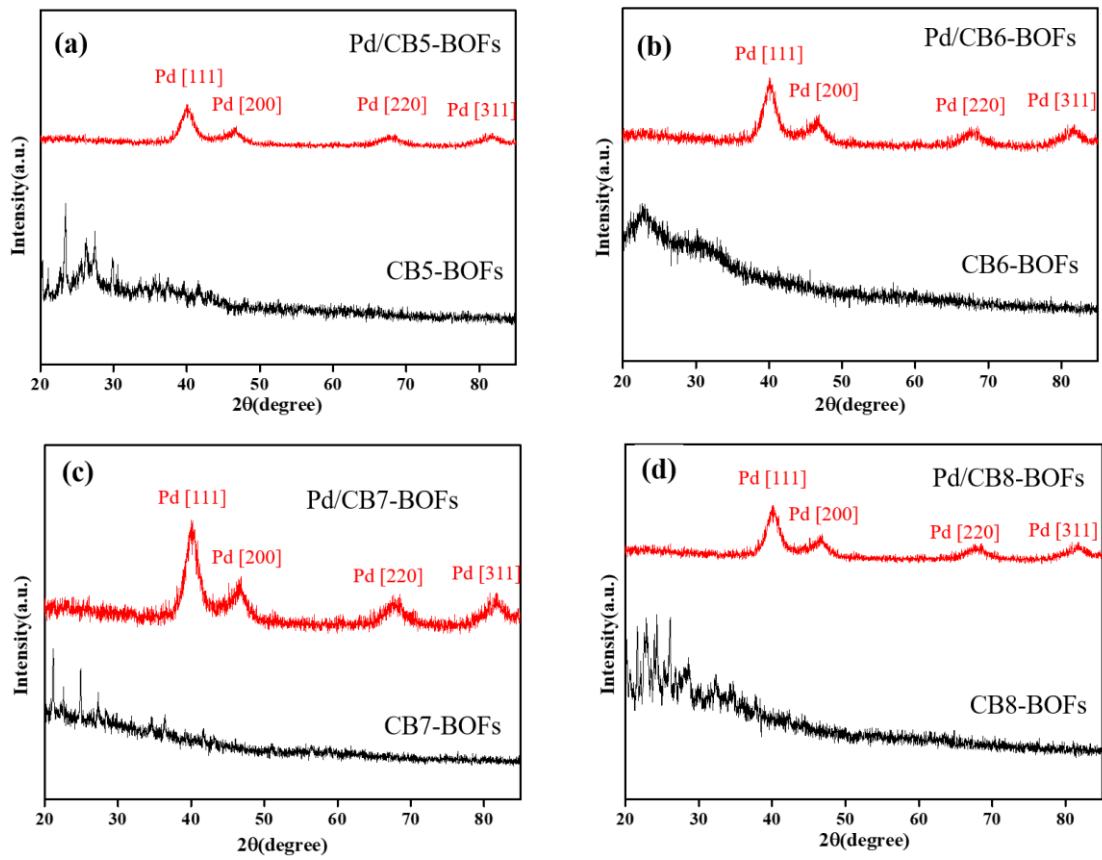
**Figure S4.** The photographic images of (a) the metal/BOFs reaction systems standing for 0.5 h, (b) the obtained final metal/BOFs products.



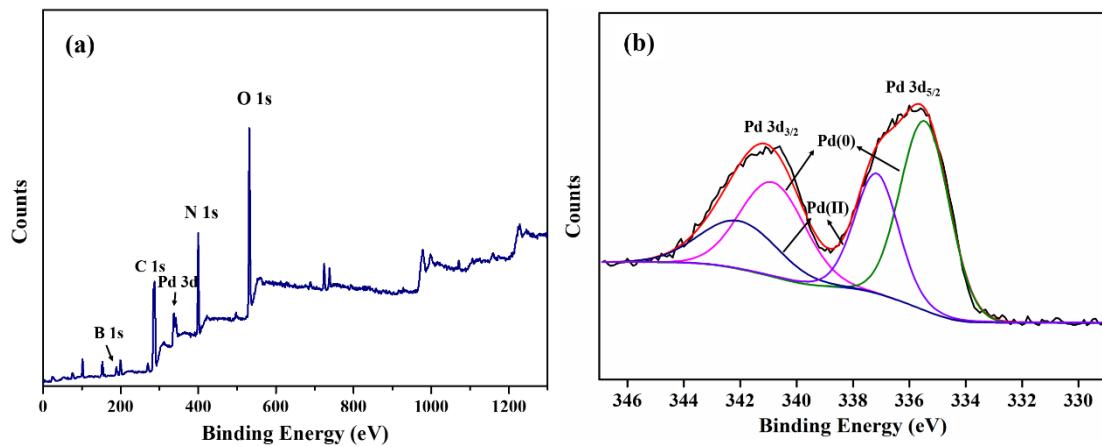
**Figure S5.** XRD results of CBn-BOFs and Au/CBn-BOFs.



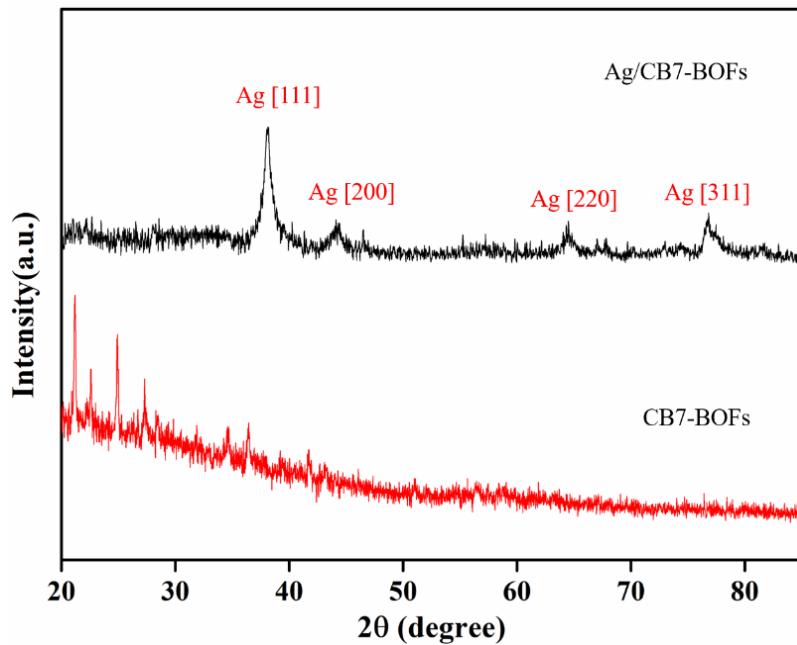
**Figure S6.** The survey XPS spectra (a) and high-resolution XPS Au 4f spectra (b) of Au-BOFs.



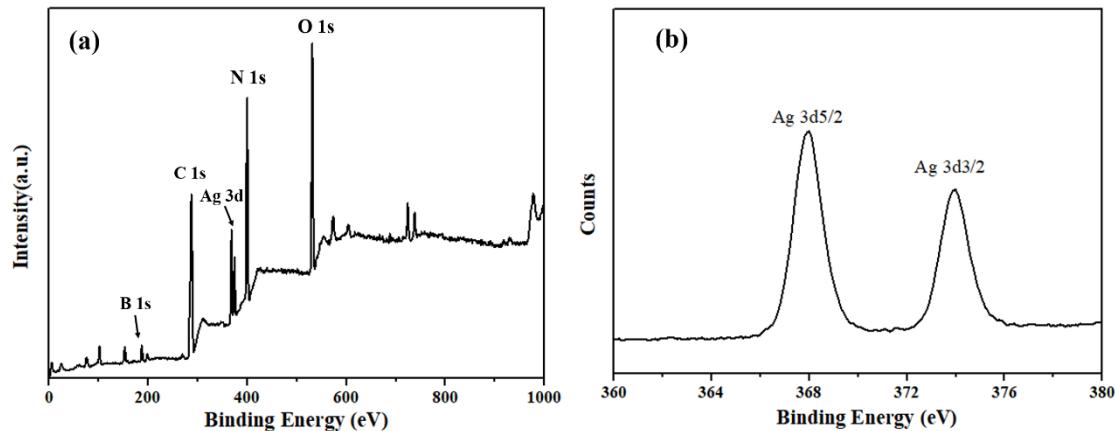
**Figure S7.** XRD results of CBn-BOFs and Pd/CBn-BOFs.



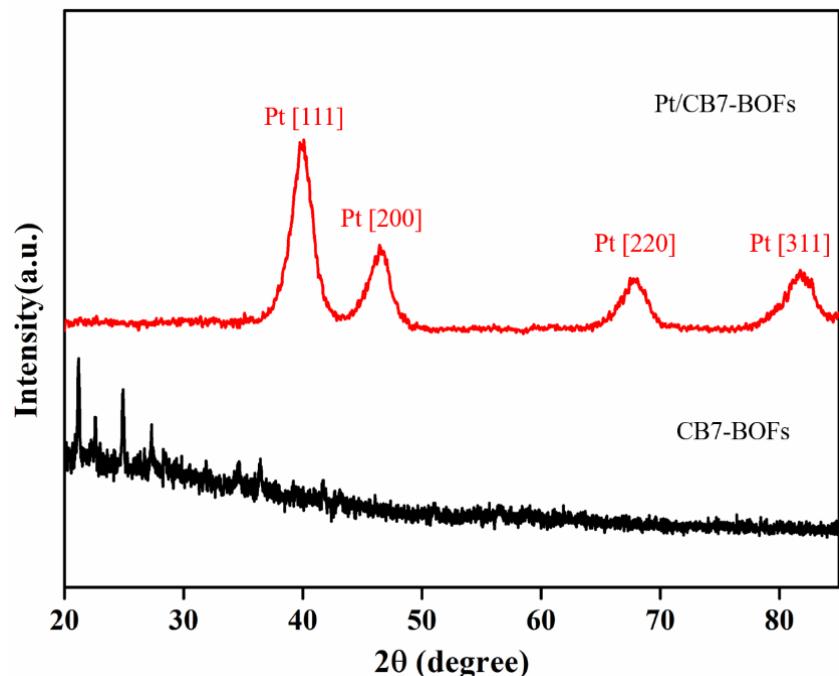
**Figure S8.** The survey XPS spectra (a) and high-resolution XPS Pd 3d spectra (b) of Pd-BOFs.



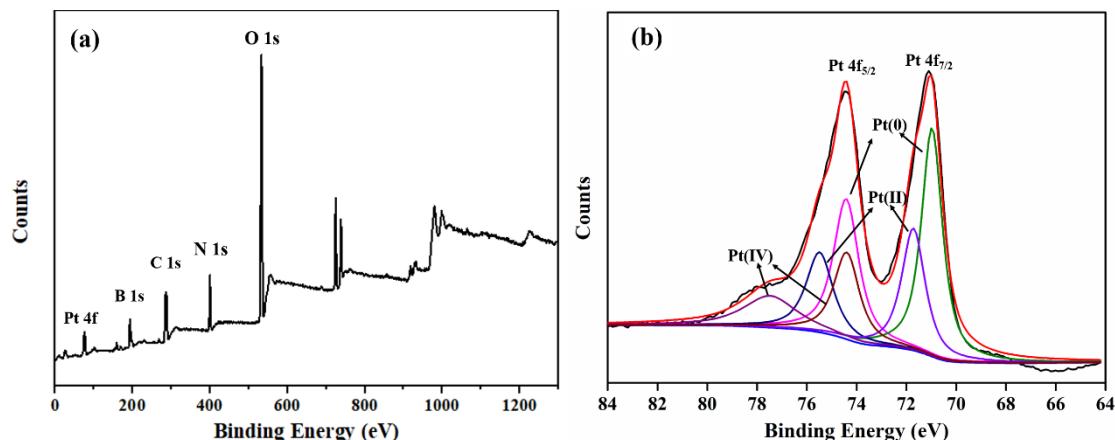
**Figure S9. XRD results of Ag/ BOFs.**



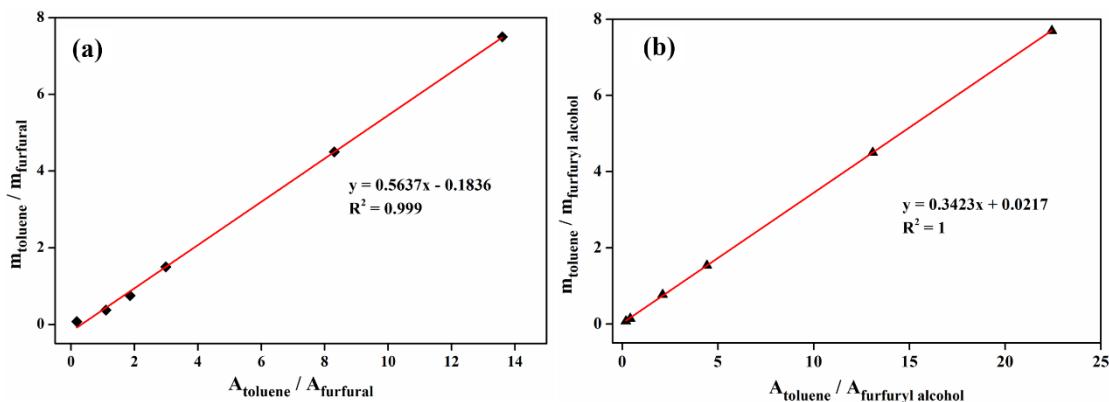
**Figure S10. The survey XPS spectra (a) and high-resolution XPS Ag 3d spectra (b) of Ag/BOFs.**



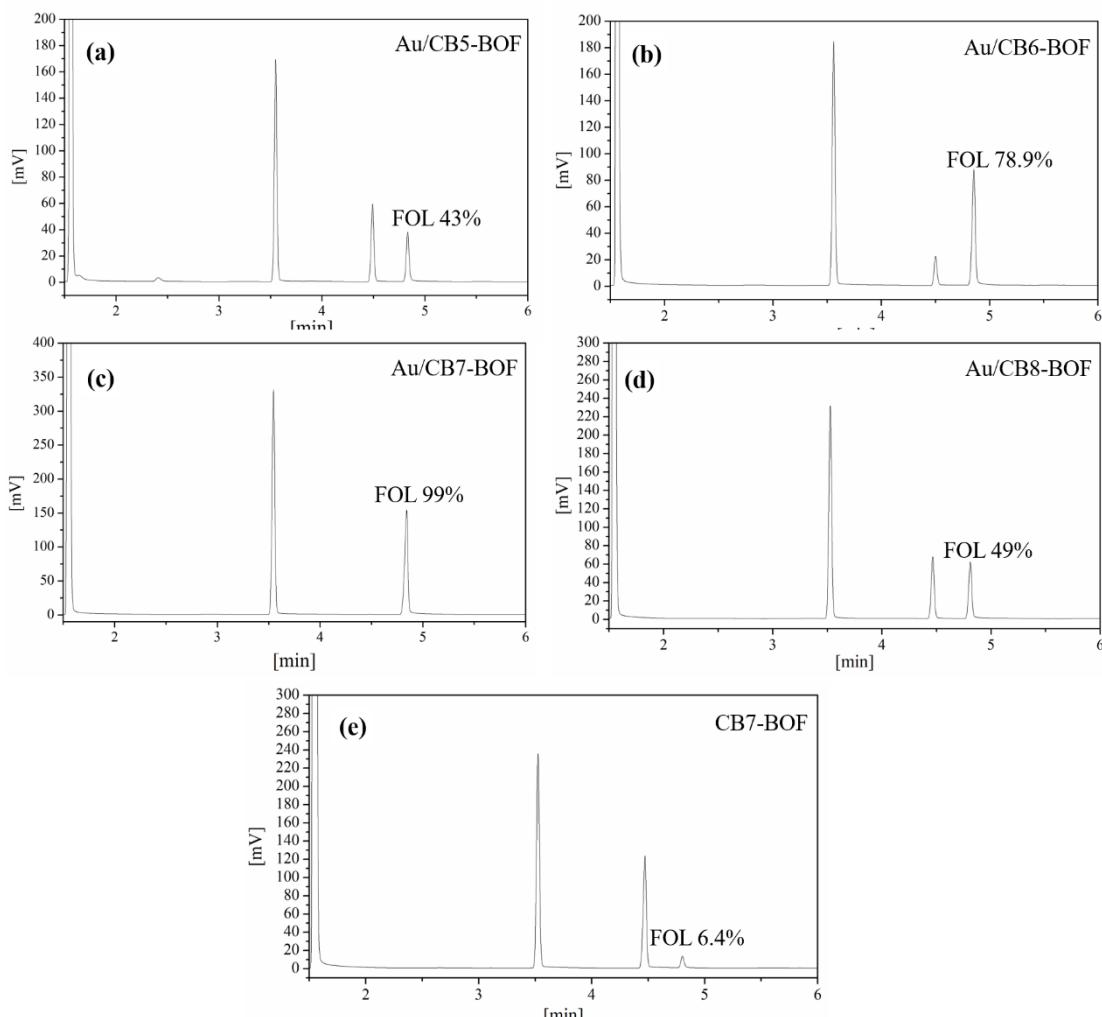
**Figure S11.** XRD results of Pt/ BOFs.



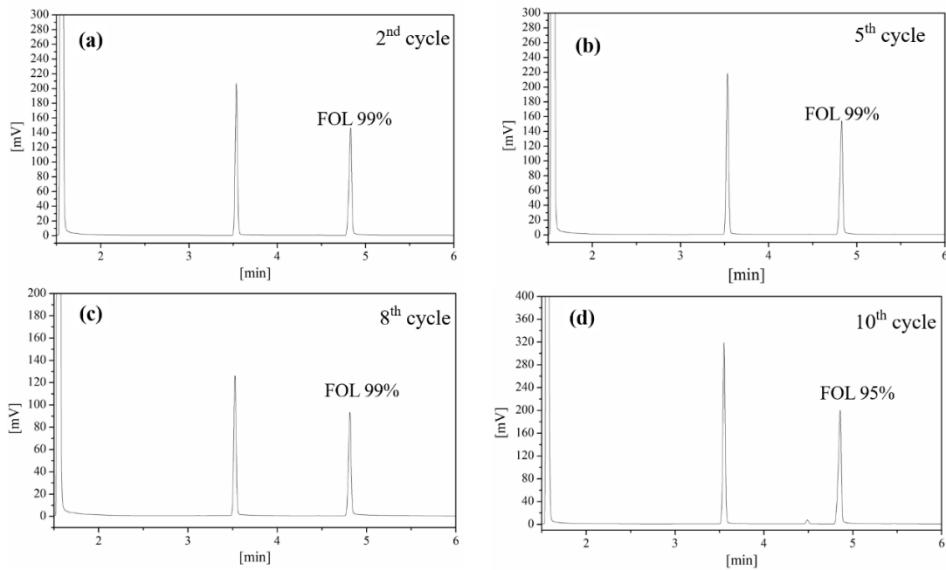
**Figure S12.** The survey XPS spectra (a) and high-resolution XPS Pt 4f spectra (b) of Pt/BOFs.



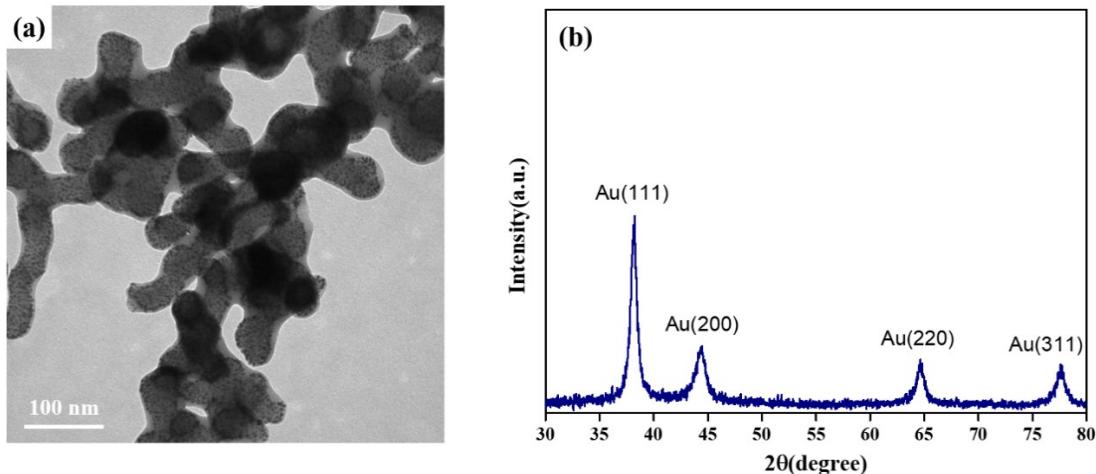
**Figure S13. The GC standard curves of (a) toluene and FAL, (b) toluene and FOL. A represented the integral value in the GC spectrum.**



**Figure S14. The GC spectrum of the conversion of FAL to FOL treated with various a) b) c) d) Au/BOFs and e) BOFs catalysts.**



**Figure S15.** The GC spectrum of the recycling tests of FAL to FOL treated with Au/CB7-BOFs catalysts.

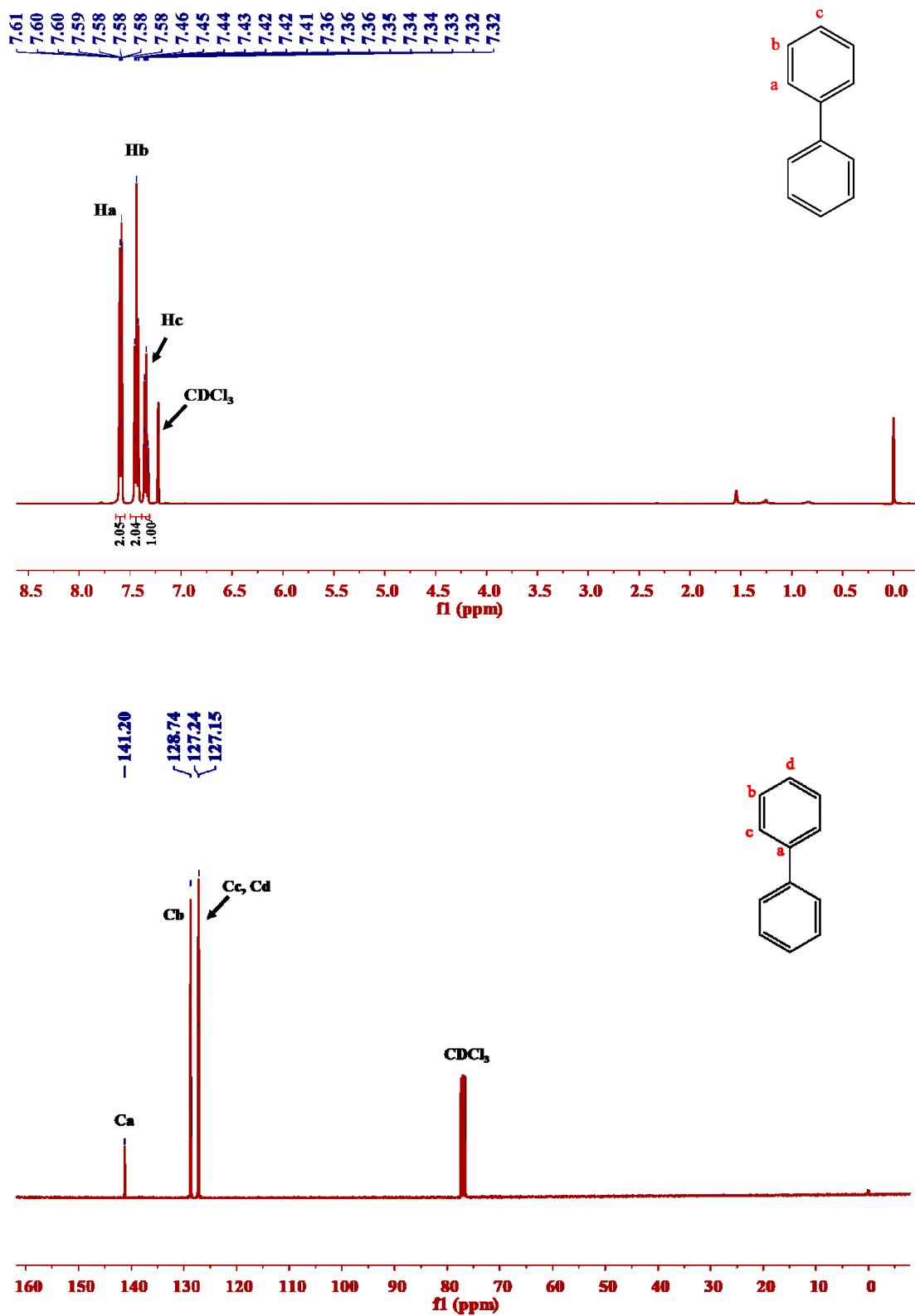


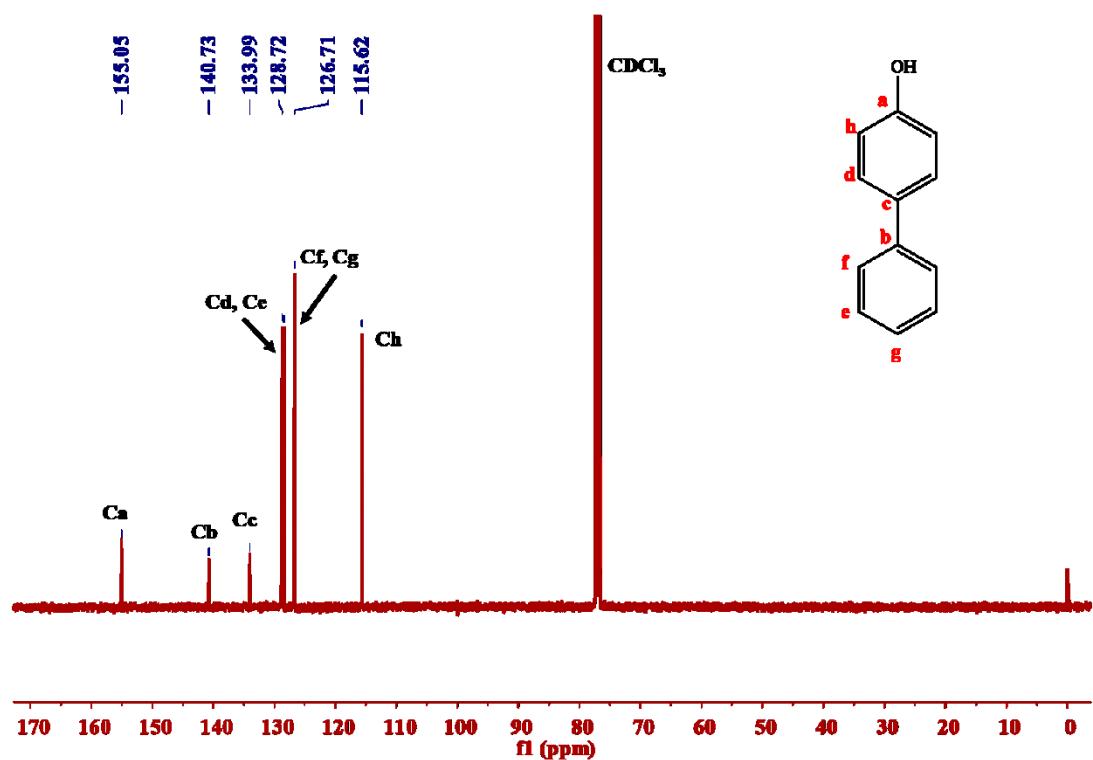
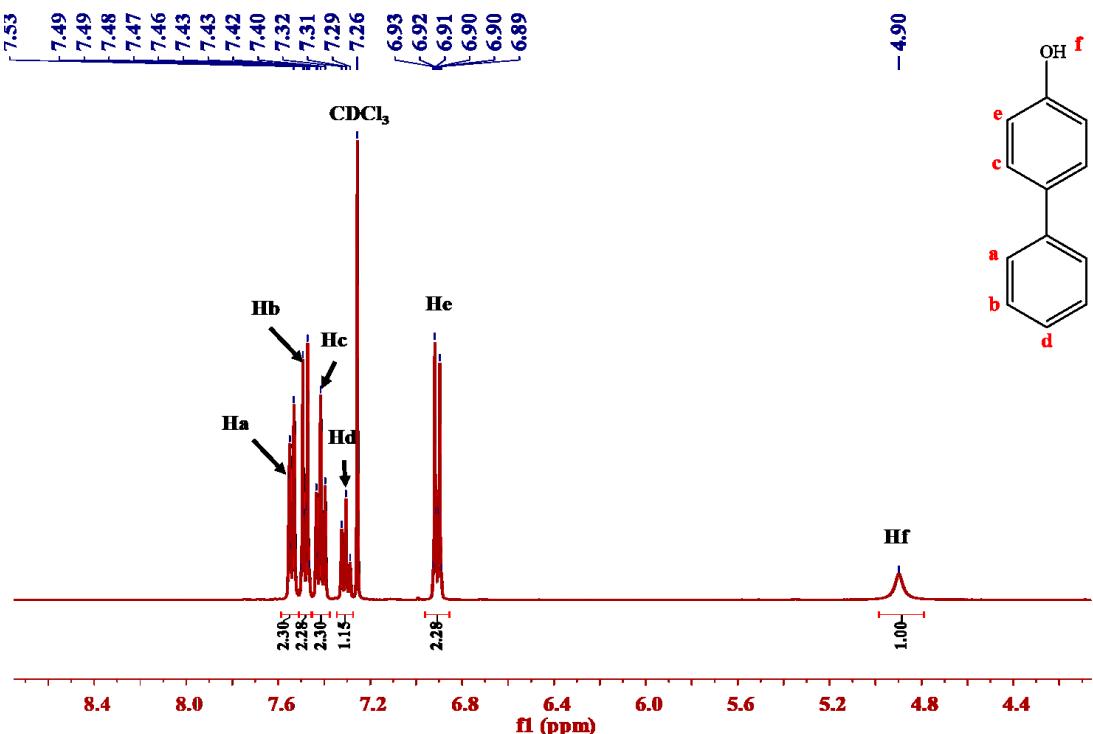
**Figure S16.** The TEM image (a) and powder XRD pattern (b) of the Au/CB7-BOFs catalysts after 15<sup>th</sup> round of catalysis.

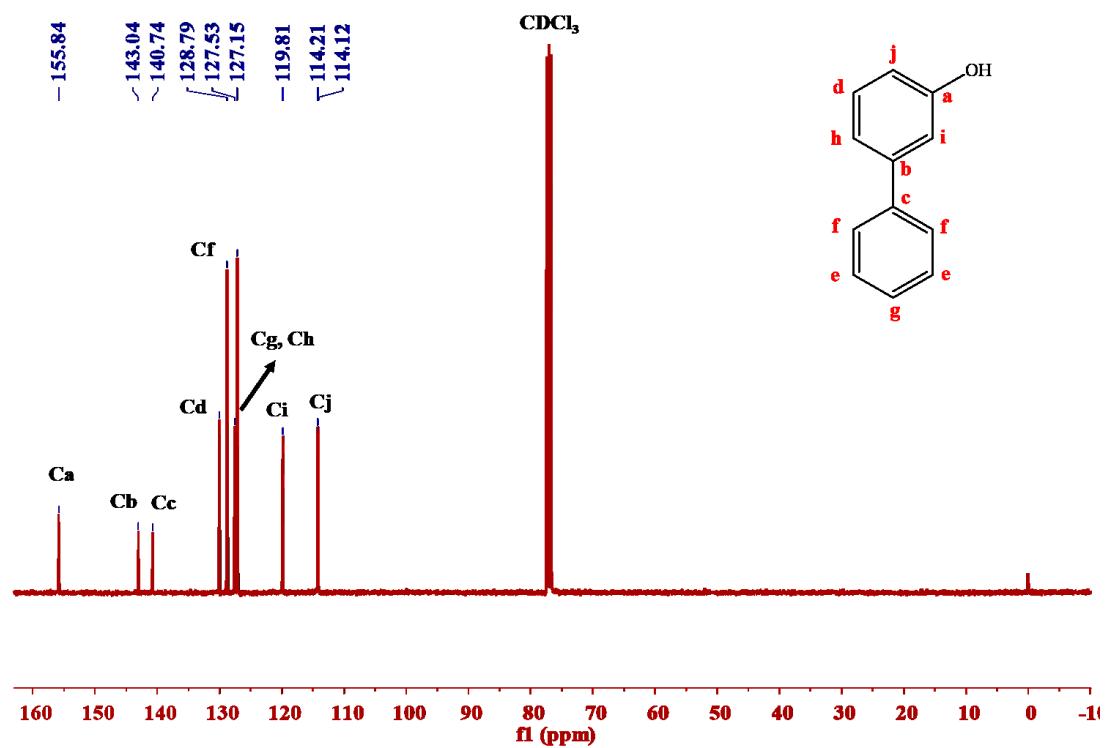
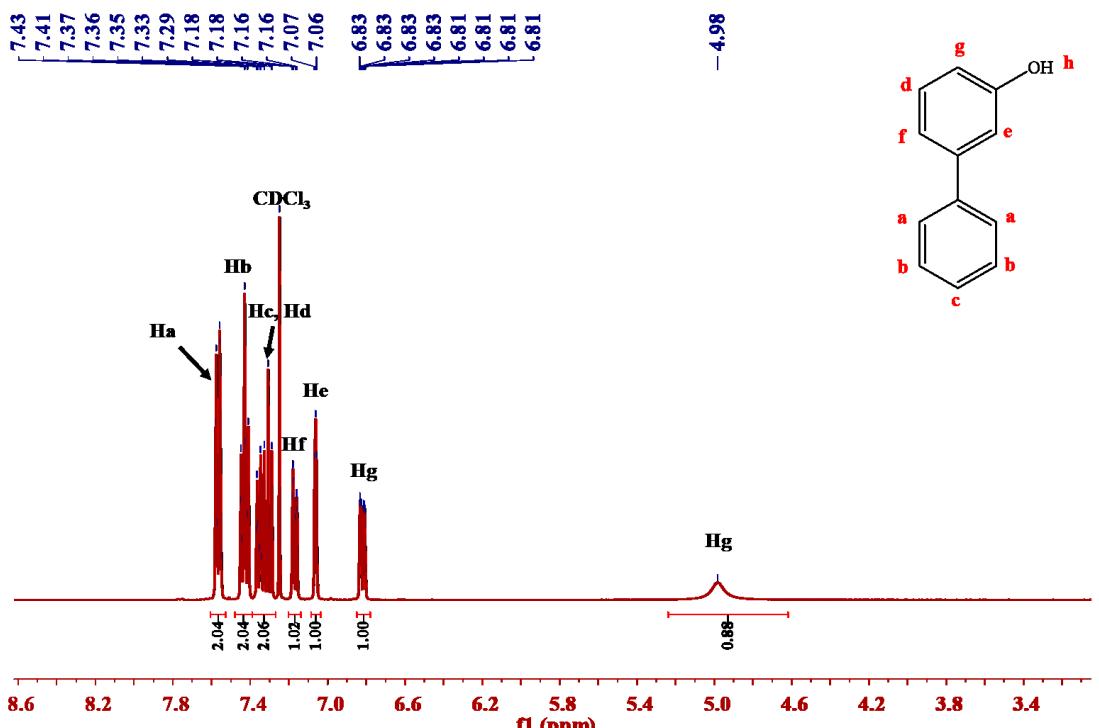
**Table S1.** Comparison of the catalytic performances of Au/BOFs catalyst with already reported catalysts towards the selective reduction of FAL with FOL.

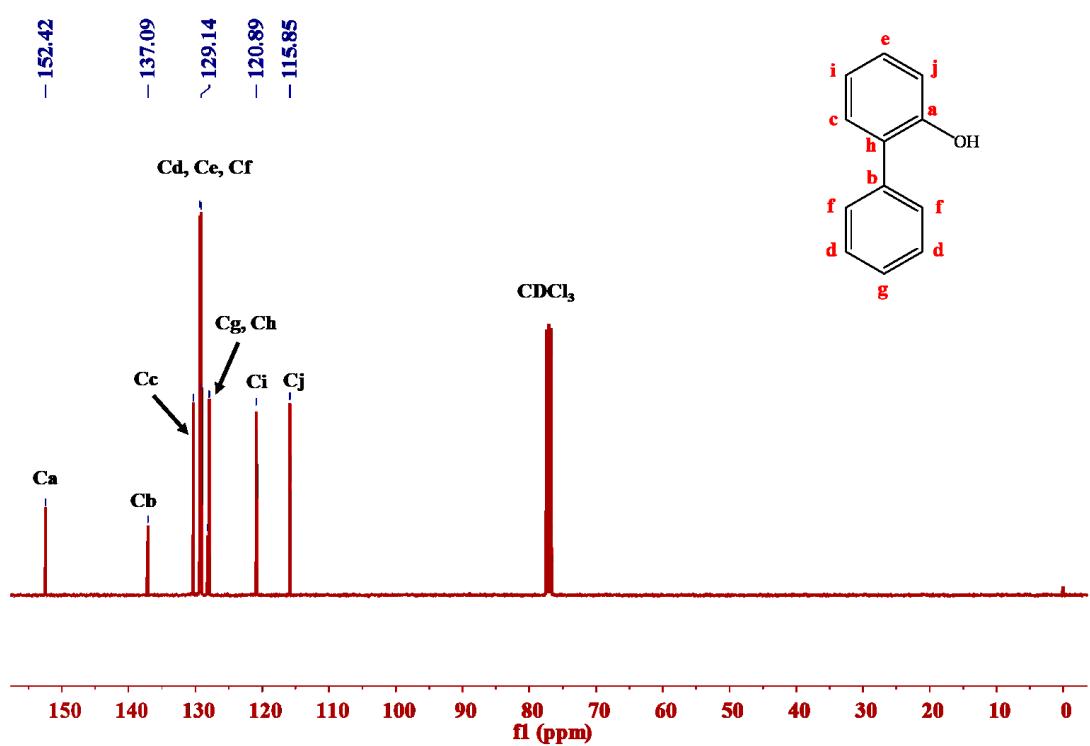
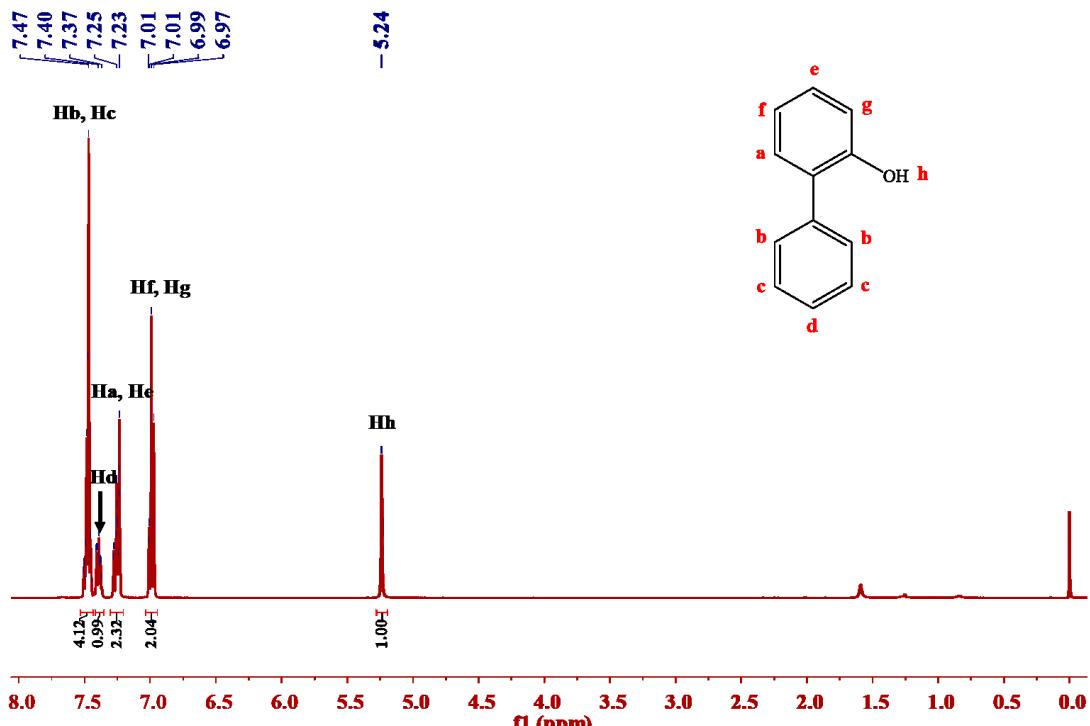
catalyst	solvent	H <sub>2</sub> pressure (bar)	temperature (°C)	time (h)	FOL yield (%)	Publication date
Ru(acac) <sub>3</sub>	/	30	120	9	98.1	2018 <sup>[1]</sup>
Cu/AC-SO <sub>3</sub> H	2-propanol	4	100	3	47.3	2017 <sup>[2]</sup>
SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -APG	/	1	170	0.33	93.1	2017 <sup>[3]</sup>
Pt-NPs@SiO <sub>2</sub>	heptane	40	80	4	87	2017 <sup>[4]</sup>
LaCu <sub>0.67</sub> Si <sub>1.33</sub>	methanol	30	120	3	99	2017 <sup>[5]</sup>
Ru-NNS	2-propanol	30	80	1	99	2017 <sup>[6]</sup>
m-PhPZr	iPrOH	1	120	2	99	2017 <sup>[7]</sup>
Co-Ru/C	2-propanol	1	150	4	100	2016 <sup>[8]</sup>
Fe-Ru NPs@SILP	/	20	120	18	99	2016 <sup>[9]</sup>
Ir@CN	H <sub>2</sub> O/HCOOH	1	100	18	99	2015 <sup>[10]</sup>
<b>Au/BOFs</b>	<b>2-propanol</b>	<b>1</b>	<b>45</b>	<b>1</b>	<b>99</b>	<b>This work</b>

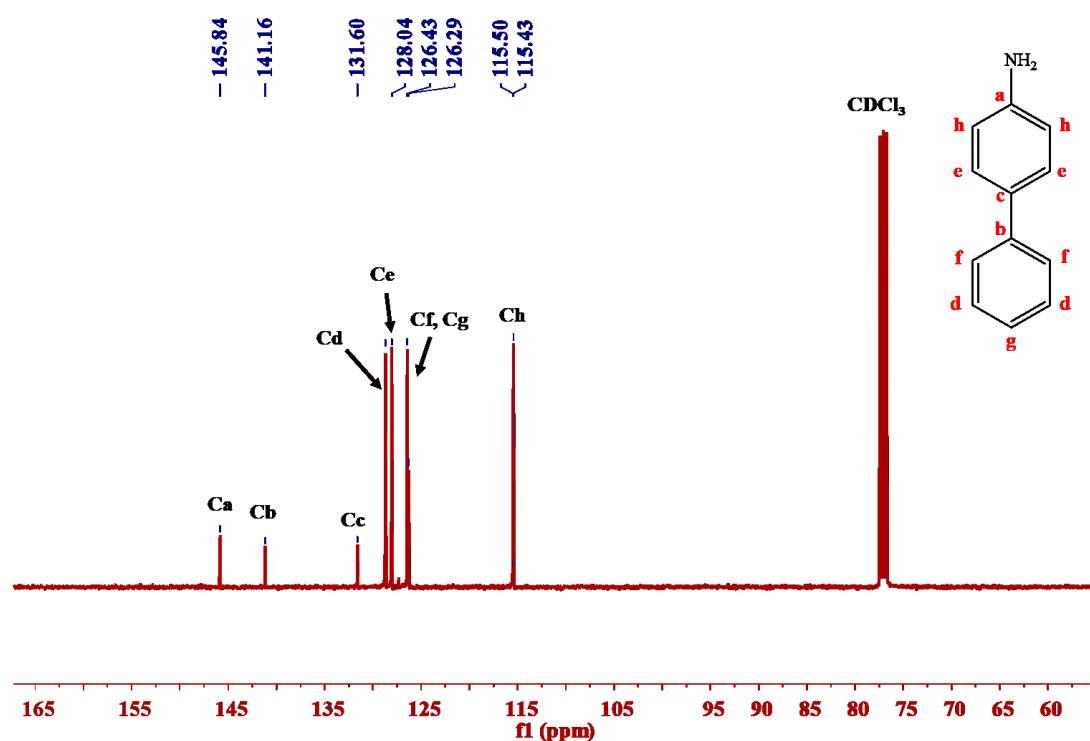
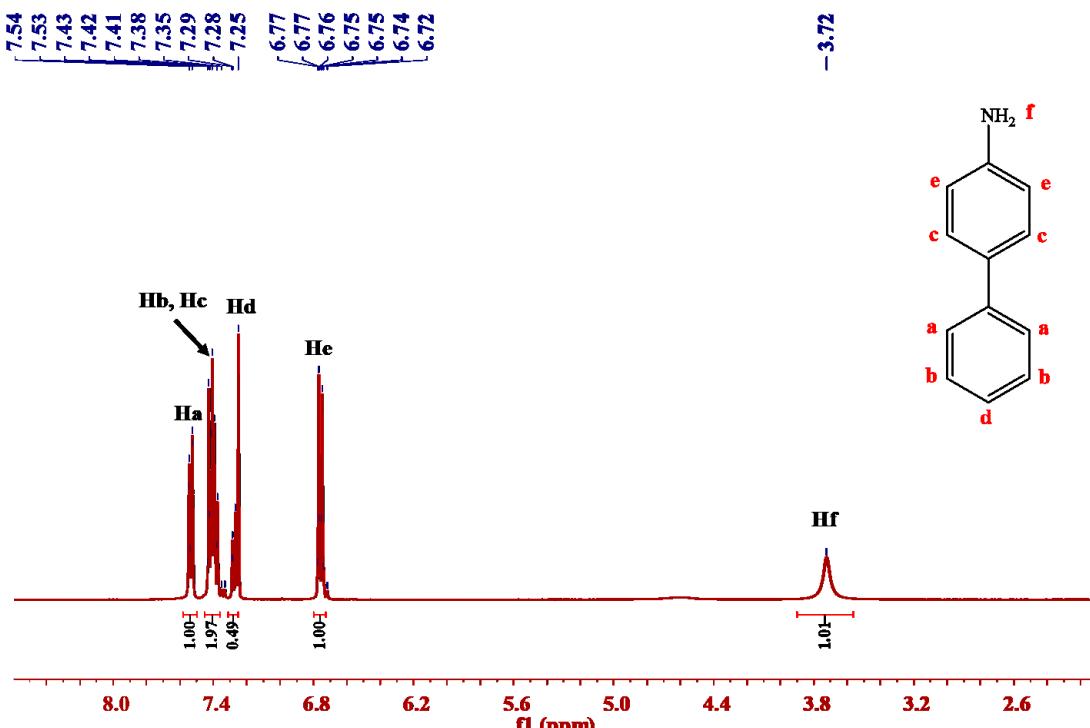
<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for the products listed in Table 2 of the main text

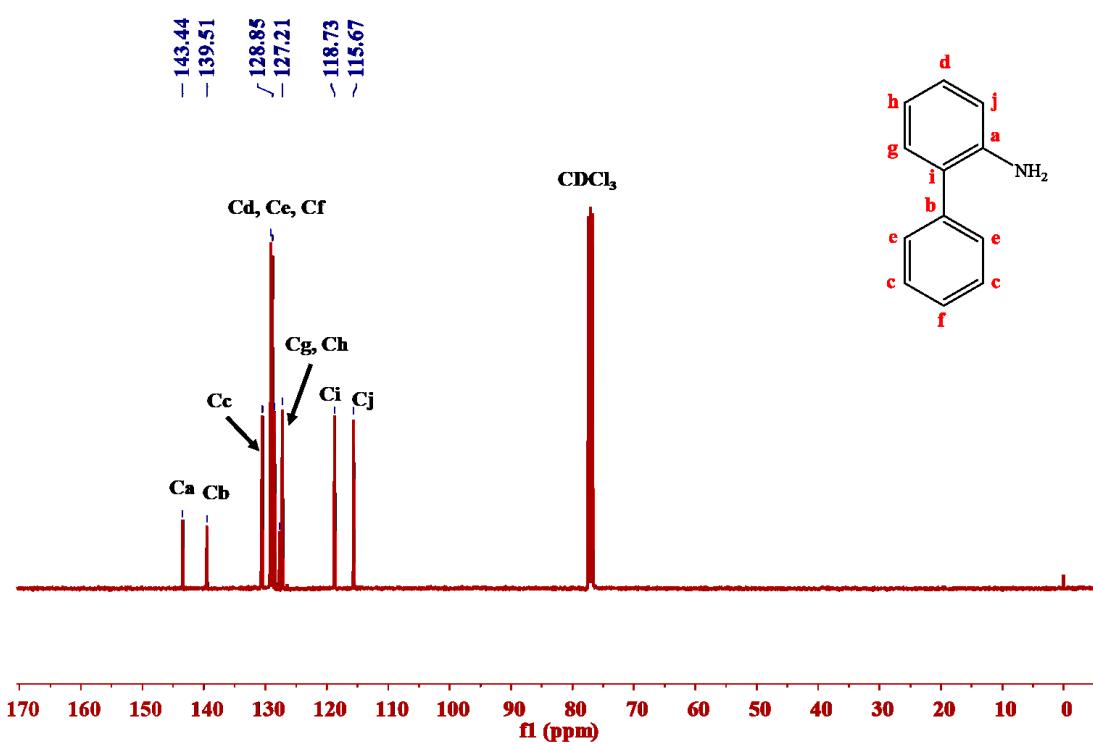
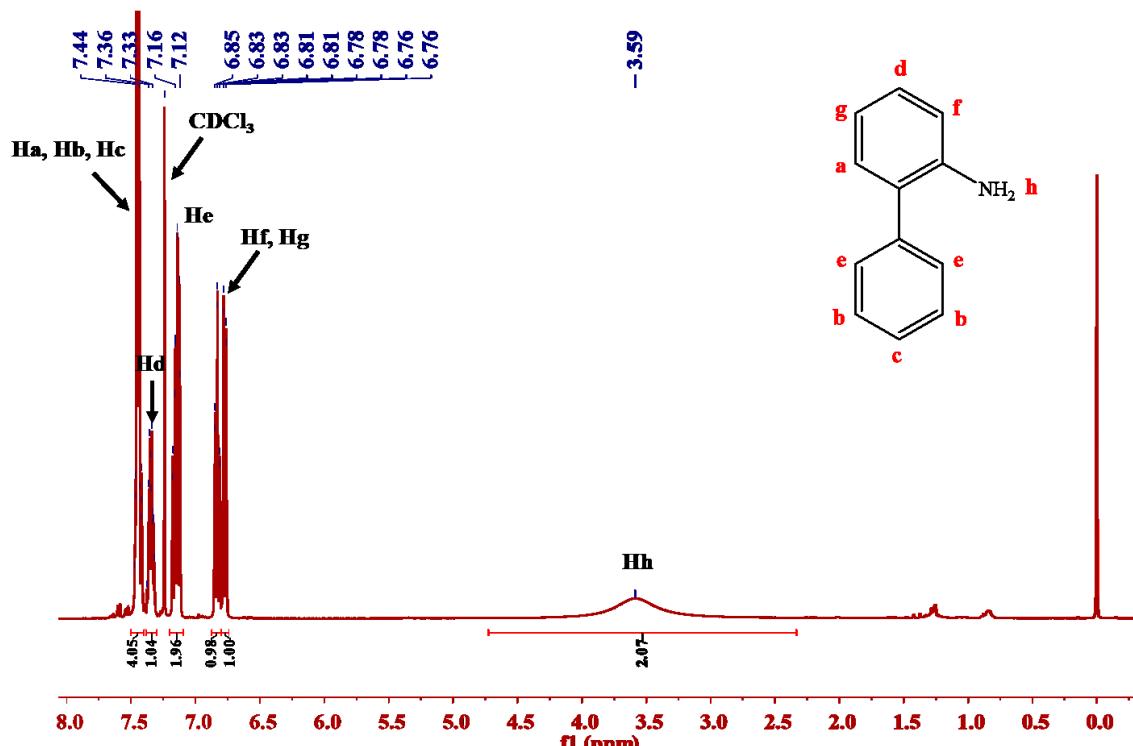


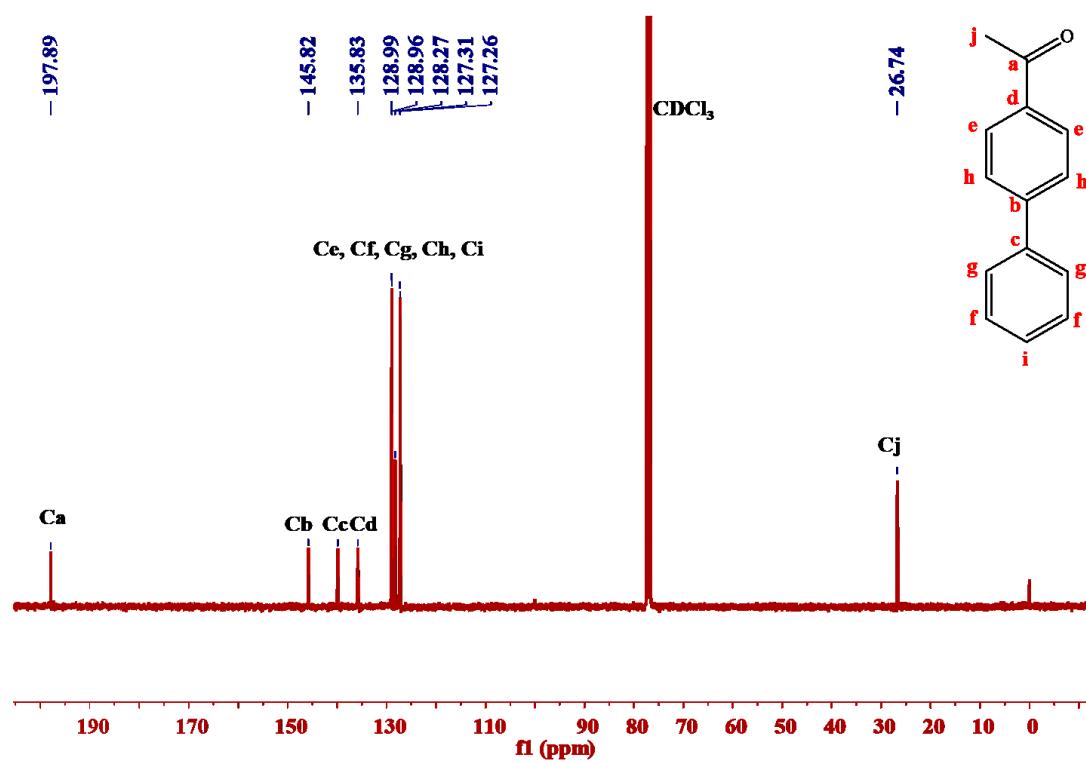
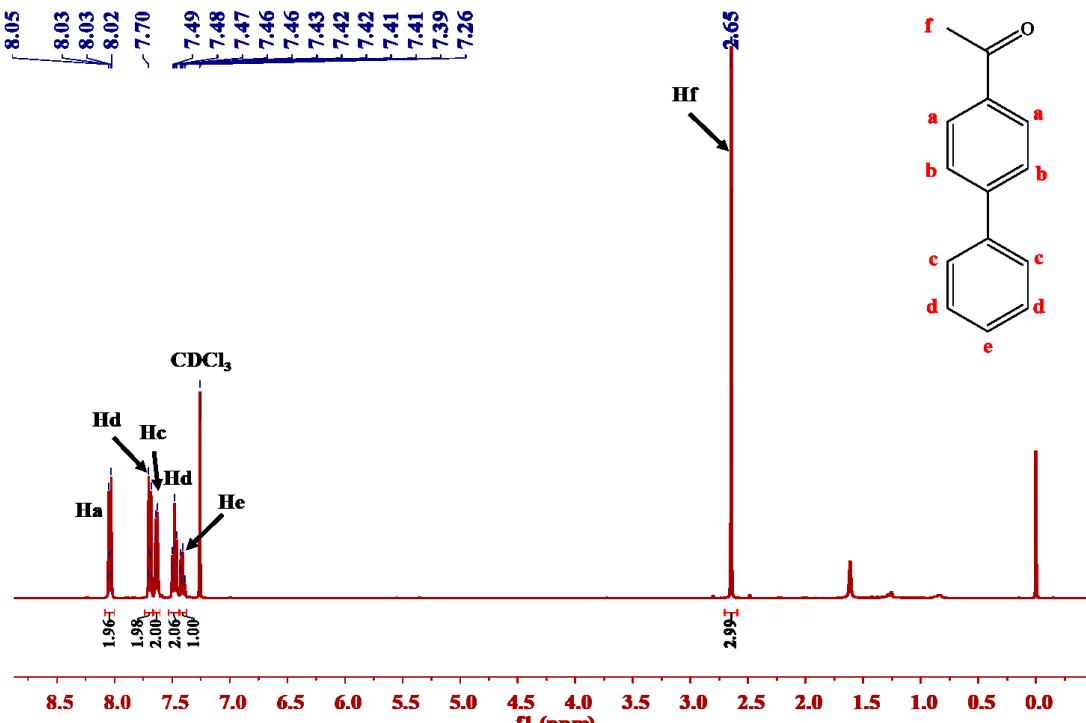


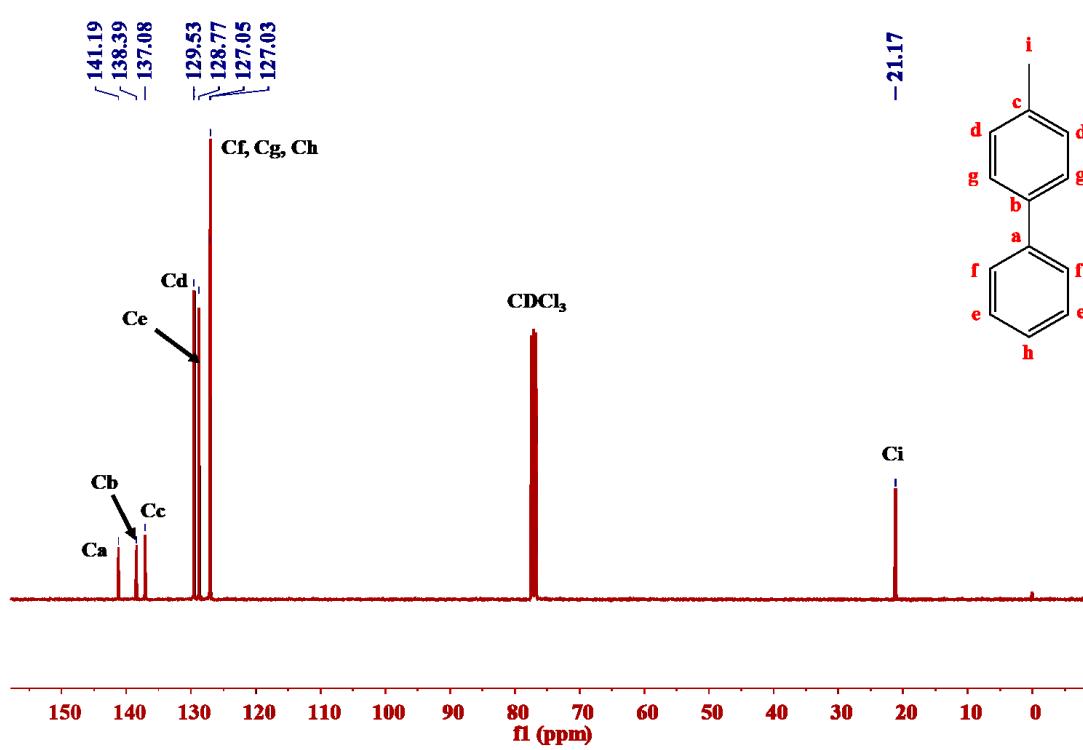
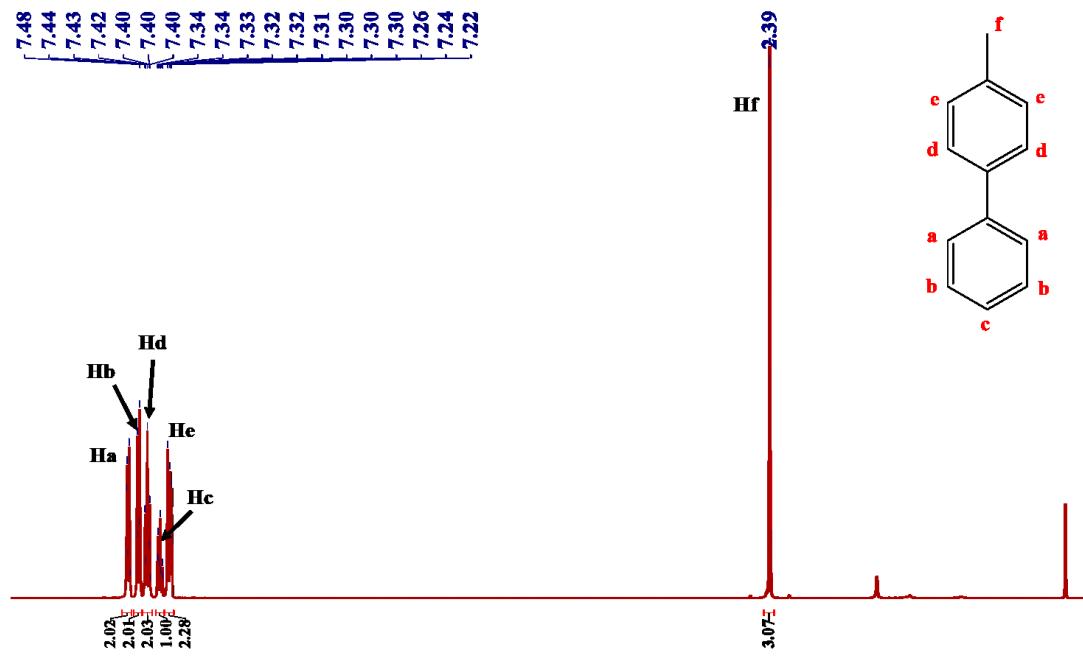


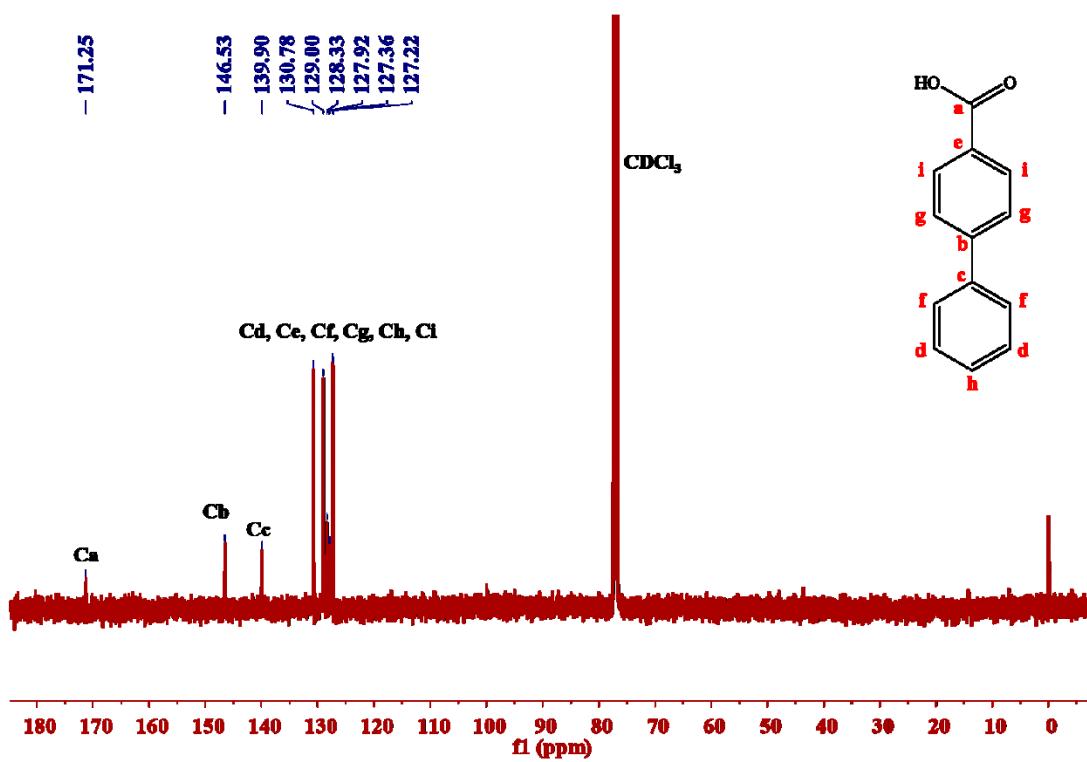
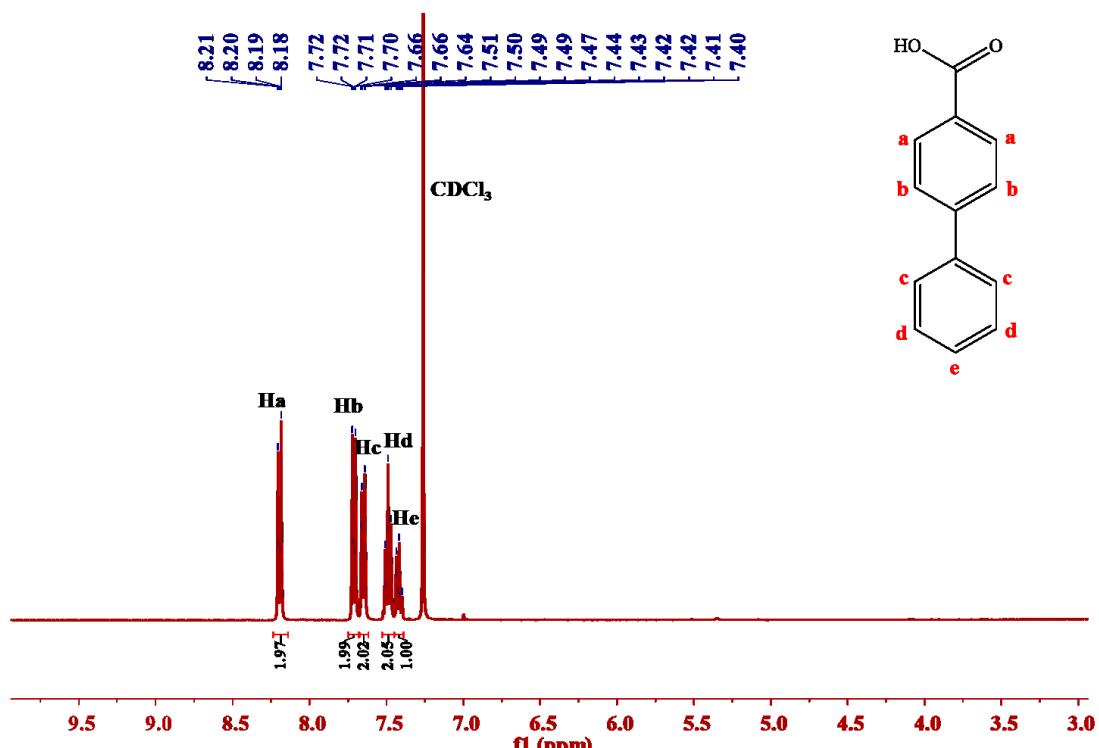












## References

- [1] F. Christie, A. Zanotti-Gerosa, and D. Grainger, *ChemCatChem*, 2018, **10**, 1012–1018.
- [2] W. B. Gong, C. Chen, Y. Zhang, H. J. Zhou, G. Z. Wang and Huijun Zhao, *ACS Sustainable Chem. Eng.*, 2017, **5**, 2172–2180.
- [3] Y. C. He, Y. Ding, C. L. Ma, J. H. Di, C. X. Jiang and A. T. Li, *Green Chem.*, 2017, **19**, 3844–3850.
- [4] J. Llop Castelbou, K. C. Szeto, W. Barakat, N. Merle, C. Godard, M. Taoufik and C. Claver, *Chem. Commun.*, 2017, **53**, 3261–3264.
- [5] T. N. Ye, Ya. F. Lu, J. Li, T. Nakao, H. S. Yang, T. Tada, M. Kitano and H. Hosono, *J. Am. Chem. Soc.*, 2017, **139**, 17089–17097.
- [6] P. Puylaert, J. Medlock, W. Bonrath, L. Lefort, S. Hinze and J. G. de Vries, *Chem. Eur. J.*, 2017, **23**, 8473 – 8481.
- [7] H. Li, Z. Fang, J. He and S. Yang, *ChemSusChem*, 2017, **10**, 681–686.
- [8] Z. Gao, L. Yang, G. L. Fan and Feng Li, *ChemCatChem*, 2016, **8**, 3769–3779.
- [9] K. L. Luska, A. Bordet, S. Tricard, I. Sinev, W.g Grünert, B. Chaudret and W. Leitner, *ACS Catal.*, 2016, **6**, 3719–3726.
- [10] Z. Wang, L. Huang, L. F. Geng, R. Z. Chen, W. H. Xing, Y. Wang, J. Huang, *Catal Lett.*, 2015, **145**, 1008–1013.