

## ELECTRONIC SUPPLEMENTARY INFORMATION

### **Asymmetric benzoylation of hydrobenzoin by copper(II) bis(oxazoline) anchored onto ordered mesoporous silicas and their carbon replicas**

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#### **1. Preparation of SBA-15**

SBA-15 synthesis was based on the literature.<sup>1,2</sup> About 4.0 g of co-polymer (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> (Aldrich) was dissolved in a HCl (Panreac, 37%) solution. Then tetraethyl orthosilicate (TEOS) – (Sigma–Aldrich, 98%) was added to this solution with constant stirring. Obtained solution was stirred at 35 °C for 24 hours and subsequently heated at 100 °C for 24 hours, under static conditions. Afterwards, the solution was filtered and the filtrate was set aside for drying in air. Dried up filtrate was calcinated at 550 °C for 5 h with a ramp of 1 °C/min.

#### **2. Preparation of CMK-3**

The preparation of CMK-3 was based in previous works.<sup>1</sup> Briefly, solid sucrose was dissolved in a H<sub>2</sub>SO<sub>4</sub> (José Manuel Gomes dos Santos Lda, 95–97%) solution to which

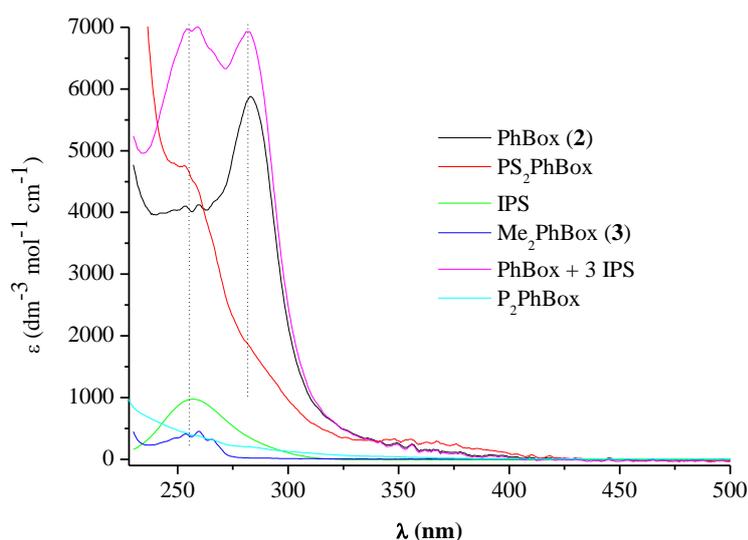
of SBA-15 sample was added to this under mixing. The as obtained paste was heated in an oven at 100 °C for 6 hours and subsequently at 160 °C for 6 hours. The resulted black powder was then mixed again with sucrose solution (in H<sub>2</sub>SO<sub>4</sub>) and reheated with a similar heating program. The obtained black powder was further carbonized, at 875 °C for 1 hour with a ramp of 10 °C/min, under vacuum. The silica template was then removed by treatment with HF (Sigma–Aldrich, ≥ 48%) acid followed by repeated washing with distilled water, (until neutral pH). The so obtained carbon (CMK-3) was then dried at 95 °C and stored in a dry place.

### 3. Preparation of SPSi and SPC in one step

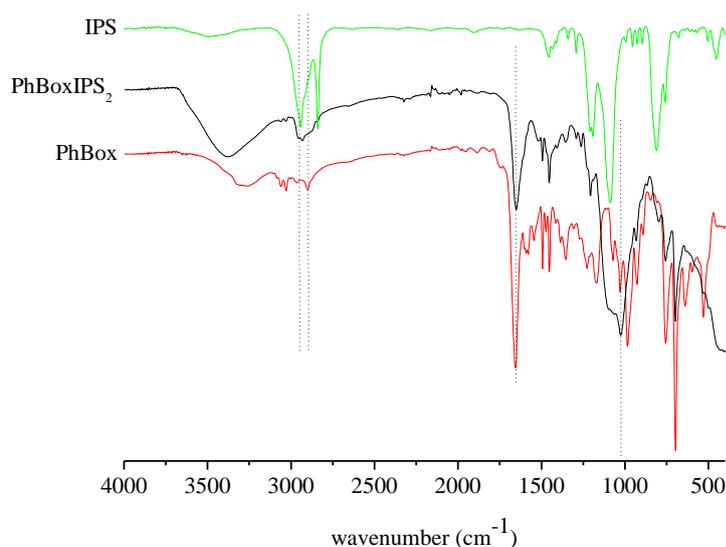
In this methodology a silica-carbon composite material is firstly formed. If heated, the composite will produce a silica material (SPSi) or, if carbonized, will produce the SPC carbon. The preparation of the porous silica SPSi and the corresponding carbon replica SPC was described in detail elsewhere.<sup>3</sup> In short, the co-polymer (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> (Aldrich) was dissolved in water and a 2M HCl (Panreac) solution was added under stirring. To the stirred mixture concentrated H<sub>2</sub>SO<sub>4</sub> (José Manuel Gomes dos Santos Lda, 95–97%), sucrose (Sigma–Aldrich, ≥99.5%), and tetraethylortosilicate (Sigma–Aldrich, 98%) were added. The solution was kept at 50 °C, and stirred for 24 hours, then it was aged hydrothermally in an autoclave at 100 °C for a further 24 hours. The obtained composite was dried in an oven at 100 °C and then in a furnace at 160 °C for 6 hours. When heated in air under static conditions at 550 °C for 6 hours, the synthesized composite generated silica sample (SPSi). The corresponding carbon sample (SPC) was formed via carbonization of the composite under a dry nitrogen flow at 900 °C for 12 hours, and then the silica being removed with a 40% HF (Sigma–Aldrich, ≥ 48%). The solid was finally filtered, washed with water and ethanol, and finally dried in at 70 °C.

#### 4. Preparation of HMS

HMS was made according to the literature.<sup>4</sup> A solution of 10.3 ml of 1-dodecylamine (Sigma-Aldrich) in 88.1 ml of ethanol (Panreac), and 88.5 ml of deionized water, was stirred for a few minutes. Then 37 ml of tetraethyl orthosilicate (TEOS) (Sigma-Aldrich) was added. The mixture was kept under stirring at room temperature for 24 hours. The white product was then filtered and washed with deionized water until the pH is neutral and then with ethanol. The final product was calcinated at 600 °C for 6 hours with a ramp of 1 °C/min.



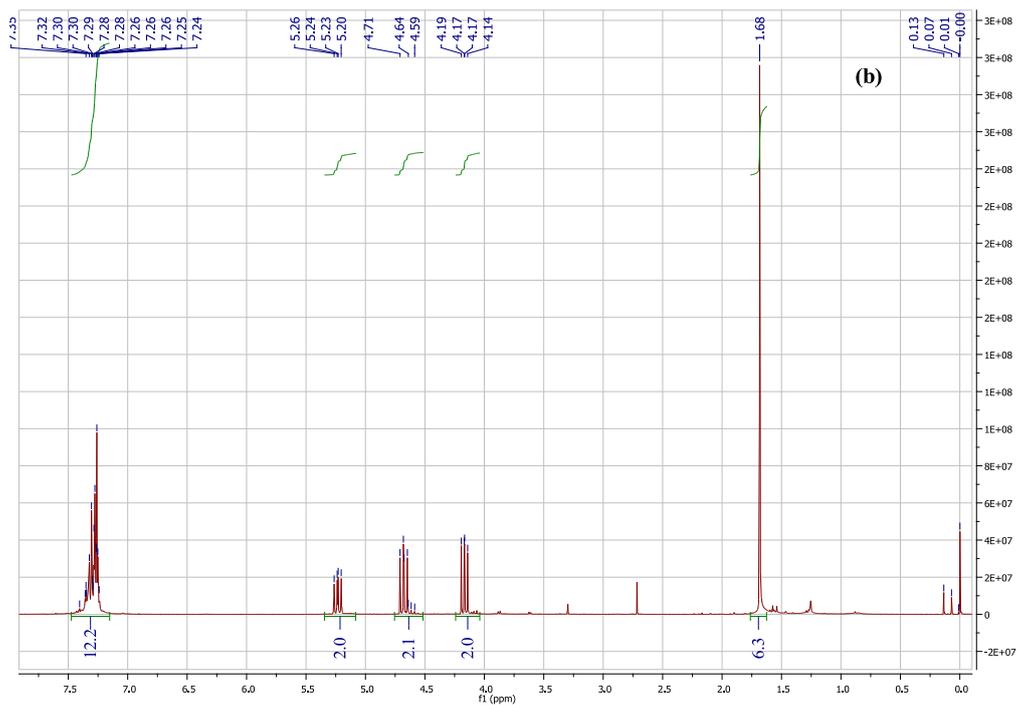
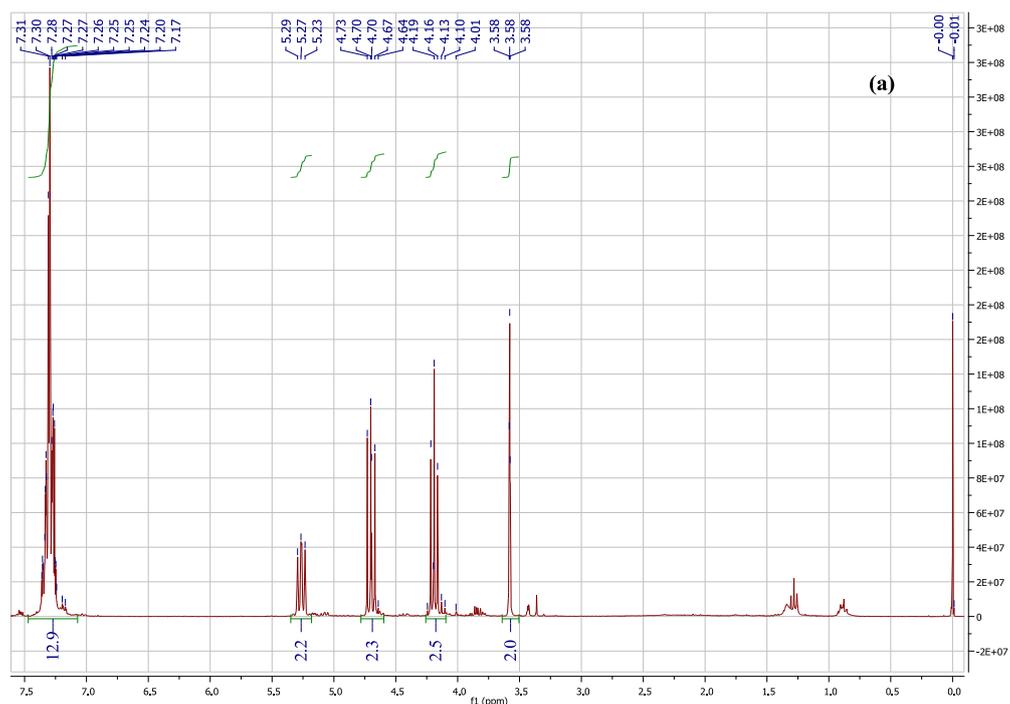
**Fig. S1** UV-visible spectra of the bis(oxazoline) ligands **2** (black) and **3** (dark blue), 3-iodopropyltrimethoxysilane (IPS, green), the trimethoxypropylsilane functionalized ligand **2** (PS<sub>2</sub>PhBox, red) prior to the addition of copper(II) triflate in Scheme 2 (at the end of the synthesis procedure (i) in 2.3), the sum of spectra of **2** with 3 times that of IPS (pink) and the dipropyl functionalized ligand **2** (cyan).

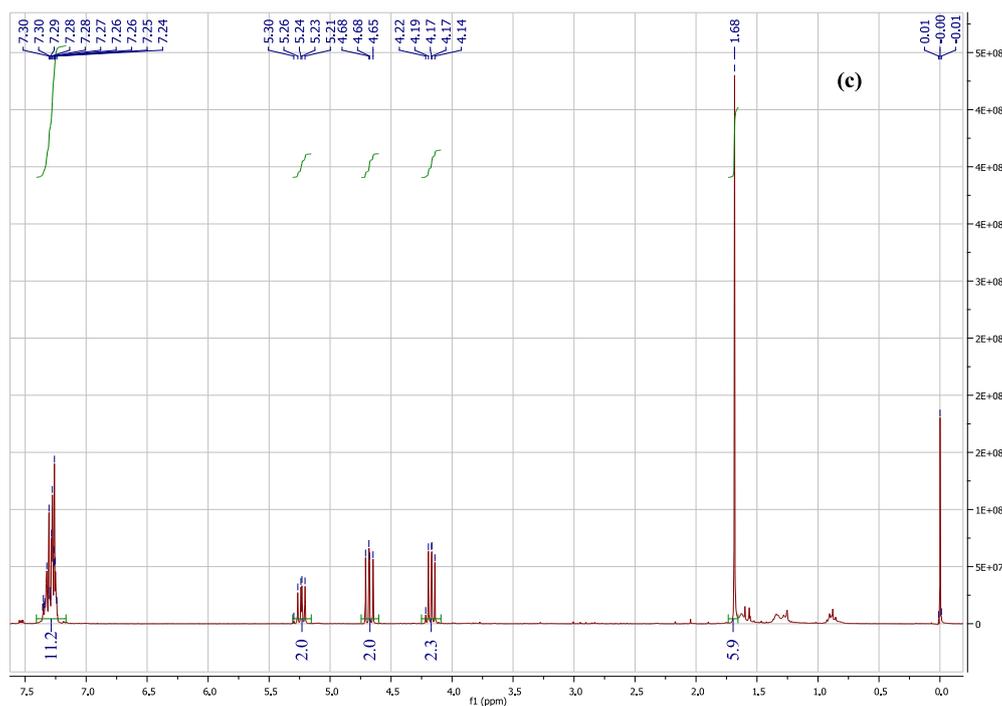


**Fig. S2** FTIR spectra of the bis(oxazoline) ligand **2** (red), 3-iodopropyltrimetoxysilane (IPS, green), the propylsilane functionalized ligand **2** (PhBoxPS<sub>2</sub>, black) prior to the addition of copper(II) triflate in Scheme 2.

### 5. Functionalization of **2** with iodomethane (synthesis of ligand **3**)

Typically, 0.23 mmol of **2** in 8 ml of dry tetrahydrofuran were reacted with 0.68 mmol of butyl lithium (1.6 M in hexane), under inert atmosphere. Then the reaction was cooled with liquid nitrogen, before dropwise addition of 0.68 mmol of iodomethane during 30 minutes.<sup>5</sup> After stirring for 3 days at room temperature, under inert atmosphere, the solvent was evaporated and the product was purified by silica gel column chromatography using dichloromethane/ethyl acetate 30:70 as eluent. The product was isolated in 53% yield and as can be seen in Fig. S3 presented a <sup>1</sup>H NMR spectrum similar to the commercial bis(oxazoline) **3**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ/ppm: 7.33-7.25 (m, 10 H), 5.26-5.21 (m, 2 H), 4.71-4.65 (m, 2 H), 4.19-4.14 (m, 2 H), 1.69 (s, 6 H).





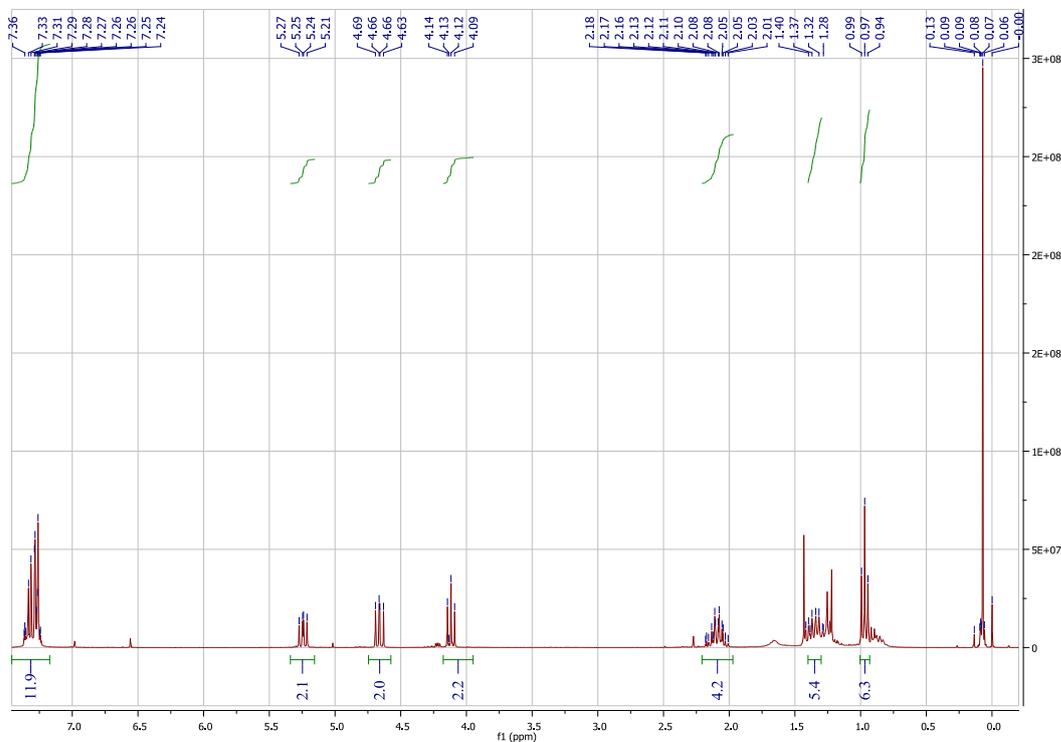
**Fig. S3**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of the (a) original ligand **2**, (b) synthesized bis(oxazoline) ligand **3** and (c) the commercial one.

## 6. Functionalization of **2** with 1-iodopropane

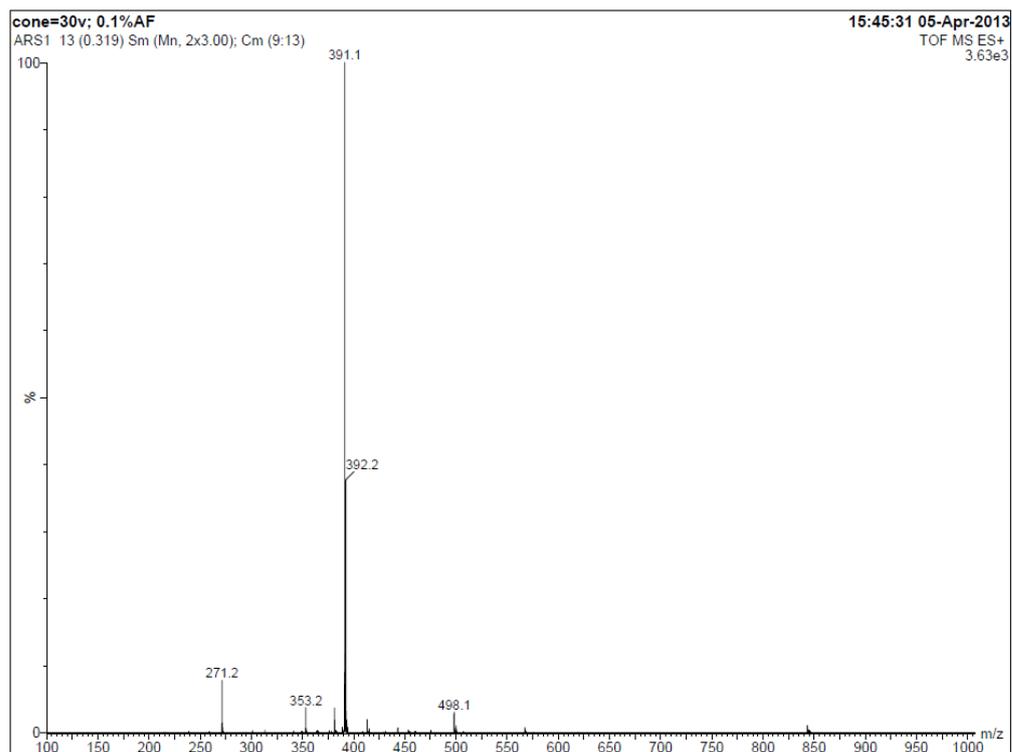
Typically, 0.11 mmol of **2** in 5 ml of dry tetrahydrofuran were reacted with 0.32 mmol of butyl lithium (1.6 M in hexane), under inert atmosphere. Then the reaction was cooled with liquid nitrogen, before dropwise addition of 0.31 mmol of 1-iodopropane during 30 minutes.<sup>5</sup> After stirring for 3 days at room temperature, under inert atmosphere, the solvent was evaporated and the product was purified by silica gel column chromatography using dichloromethane/ethyl acetate 30:70 as eluent. The product was isolated in 85% yield as white oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta/\text{ppm}$ : 7.36-7.24 (m, 10 H), 5.27-5.21 (m, 2 H), 4.69-4.63 (m, 2 H), 4.14-4.09 (t, 2 H), 2.18-2.01 (m, 4 H), 1.32-1.40 (m, 4 H), 0.99-0.94 (t, 6 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta/\text{ppm}$ : 169.1, 142.4, 128.7, 127.5, 126.7, 75.0, 69.6, 46.2, 35.0, 17.4, 14.4. ESI-HRMS,

m/z: calculated ( $C_{25}H_{31}N_2O_2^+$ ) 391.23800, experimental 391.23794; FTIR,  $\nu/cm^{-1}$ : 2960 m, 2932 m, 2874 m (propyl C-H stretching), 1653 s (C=N stretching).

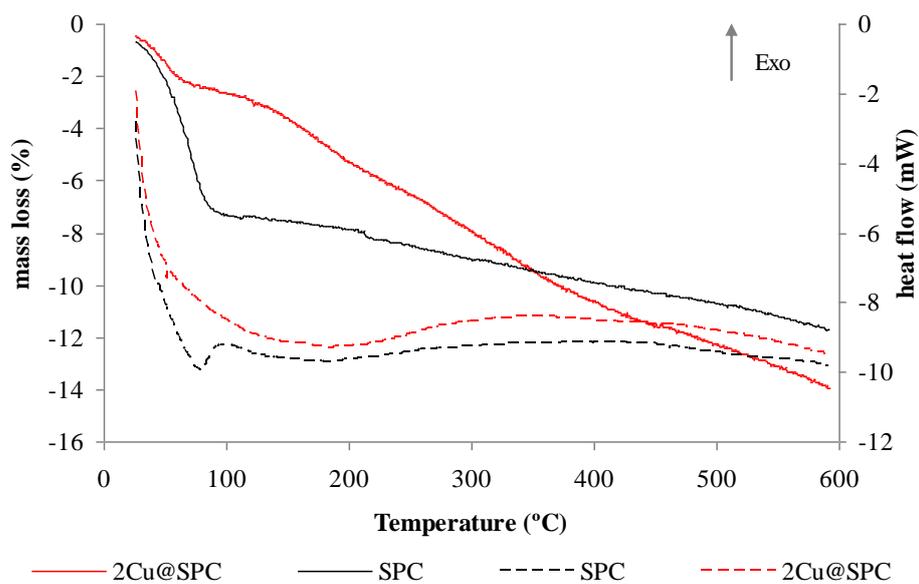
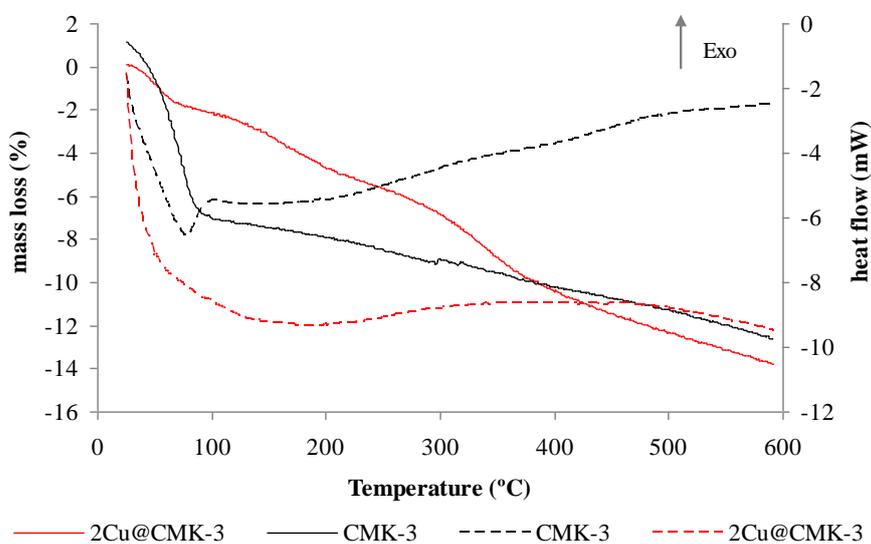
(a)



(b)



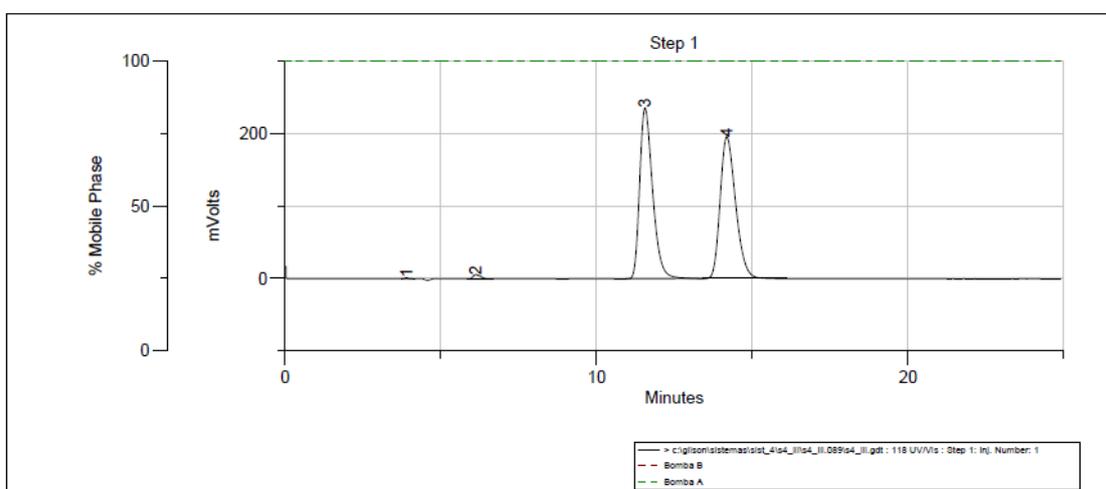
**Fig. S4**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of the synthesized di-propylated ligand **2** (a) and ESI mass spectra (b).



**Fig. S5** Thermo analysis curves for carbon based samples. Solid lines for thermogravimetric data (TG) and broken lines for Differential Scanning Calorimetry data.

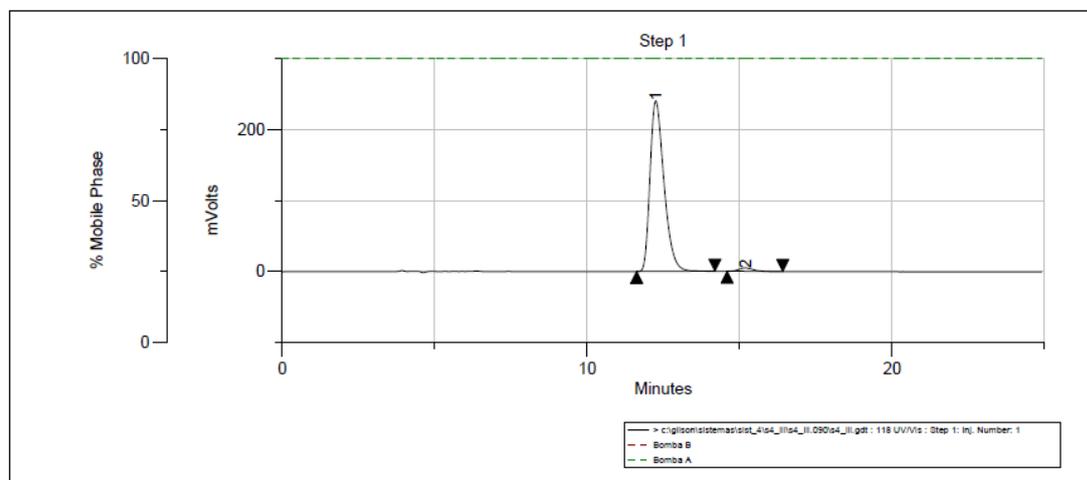
## 7. Synthesis of racemic benzoic acid 2-hydroxy-1,2-diphenyl-ethyl ester(5)

To 0.48 mmol (*R,R*)-1,2-diphenyl-1,2-ethanediol, 0.48 mmol (*S,S*)-1,2-diphenyl-1,2-ethanediol, 1.00 mmol DIPEA (170  $\mu$ l) and 0.05 mmol of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 5.00 ml of dichloromethane 0.50 mmol of benzoyl chloride (58  $\mu$ l) was added.<sup>6,7</sup> The reaction was stirred for 2 hours and the solution was evaporated under reduced pressure and the racemic monobenzoylated product (**5**) was purified by column chromatography using *n*-hexane/ethyl acetate 3:1 as eluent. Yield: 0.1139 g (68%);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ /ppm: 8.13-8.10 (m, 2 H), 7.62-7.56 (m, 1 H), 7.50-7.44 (m, 2 H), 7.26-7.17 (m, 10 H), 6.11 (d,  $J=7.3$  Hz, 1 H), 5.09 (dd,  $J=7.3$  Hz,  $J=2.2$  Hz, 1 H), 2.65 (d,  $J=2.9$  Hz, 1 H). FTIR,  $\text{cm}^{-1}$ : 3480, 1695, 1277, 1117, 711; HPLC: ChiralcelOD column, *n*-hexane/isopropanol 9:1, detection wavelength: 254 nm, flow rate: 1 ml/min,  $t_r$  (*R*) = 12 min and  $t_r$  (*S*) = 15 min.



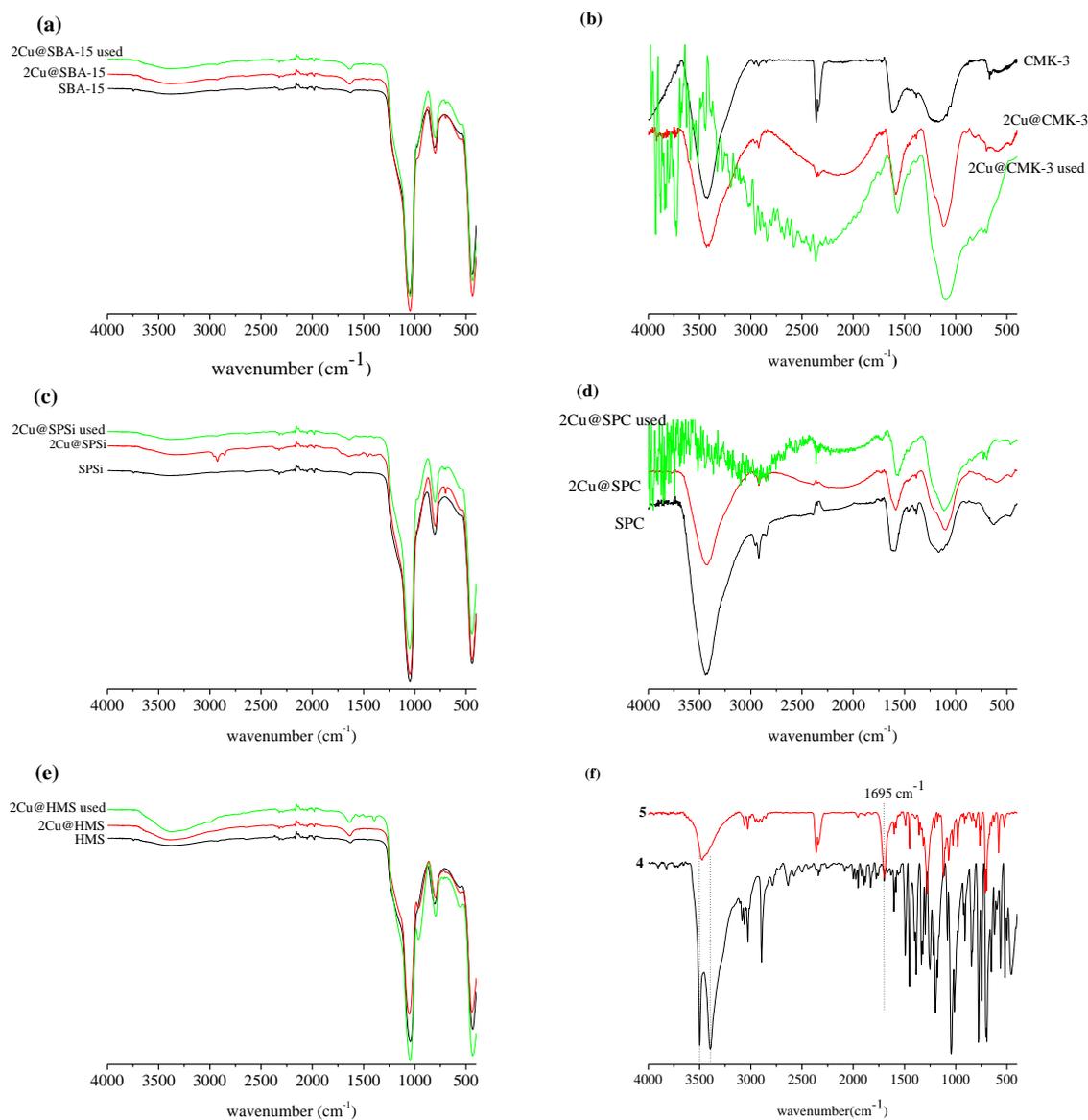
	Inj. Number	Peak Name	R. Time	Area	Sample Descrip.					
1	1.00	1	3.89	20970.42	Step 1					
2	1.00	2	6.12	166460.84	Step 1					
3	1.00	3	11.55	11436456.00	Step 1					
4	1.00	4	14.18	11316825.00	Step 1					

**Fig. S6** HPLC chromatogram of racemic benzoic acid 2-hydroxy-1,2-diphenyl-ethyl ester(**5**), prepared using 5% mol  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .



	Inj. Number	Peak Name	R. Time	Area	Sample Descrip.				
1	1.00	*1	12.25	12815401.00	Step 1				
2	1.00	2	15.18	284844.91	Step 1				

**Fig. S7** HPLC chromatogram of enantioenriched benzoic acid 2-hydroxy-1,2-diphenylethyl ester(**5**), prepared using 5% mol (***R,R***-**3**+CuCl<sub>2</sub>.2H<sub>2</sub>O.



**Fig. S8** FTIR spectra (ATR silicas and KBr pellets carbon materials) of the heterogeneous catalysts before and after kinetic resolution of hydrobenzoin: (a) SBA-15, (b) CMK-3, (c) SPSi, (d) SPC and (e) HMS materials and (f) reagents (**4** - Scheme 3) and product (**5**- Scheme 3).

## References

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