

**Supplementary information**

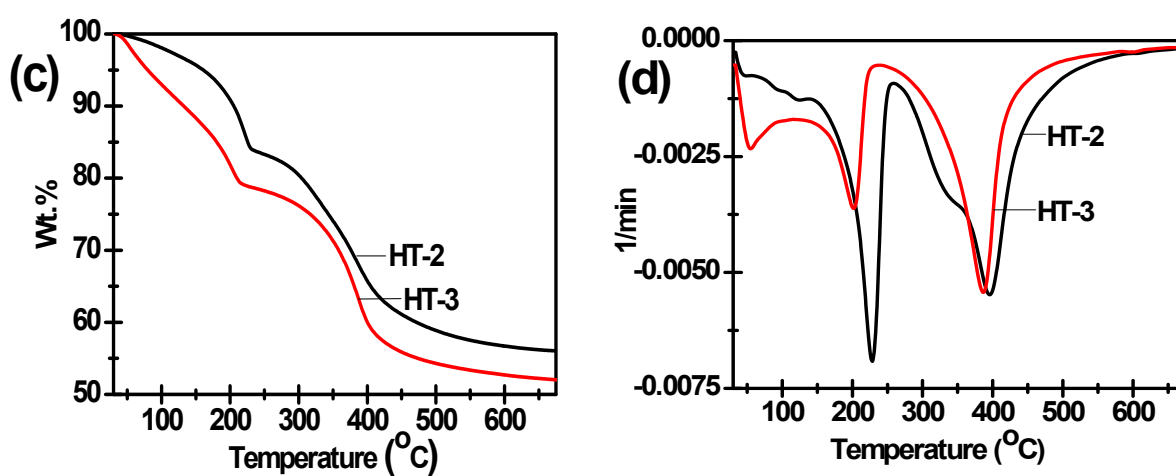
**Catalytic activity of Mg-Al hydrotalcites and derived mixed oxides for imination  
reactions *via* oxidative-dehydrogenation mechanism**

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The TGA-DTG profiles of the HTs (**Figure S1**) showed two step thermal decomposition on heating the samples from 30°C to 800°C. The decomposition below 300°C was due to the removal of physisorbed water and interlayer water molecules and the decomposition above 300°C was attributed to loss of hydroxyls of Brucite layer and interlayer carbonate and hydroxyl ions. However, the second step decomposition profile (above 300°C) of HT-2 sample was observed to be occurring in comparatively broader temperature range (300°C to 550°C) than that in HT-3.



**Figure S1.** (a) TGA and (b) DTG profiles of samples.

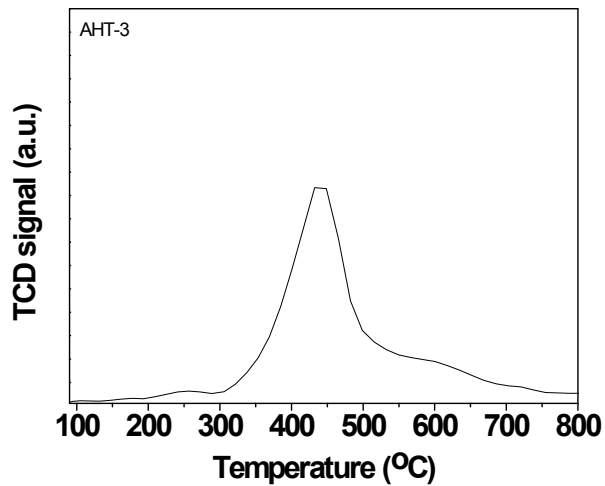
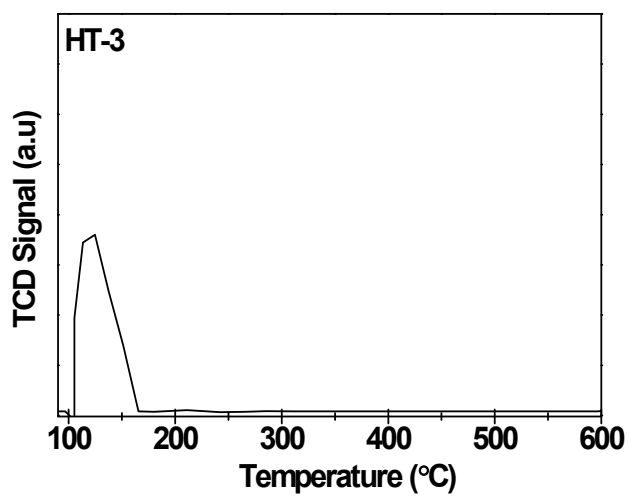
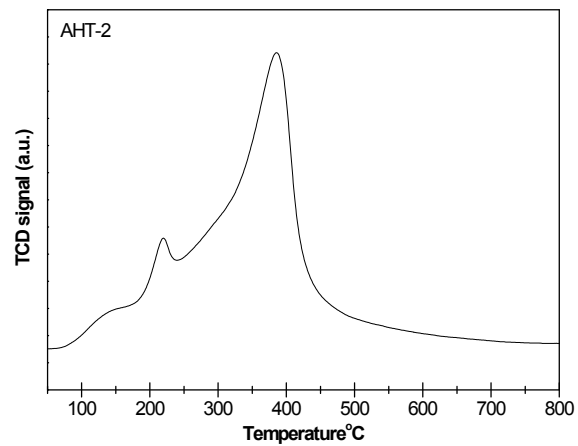
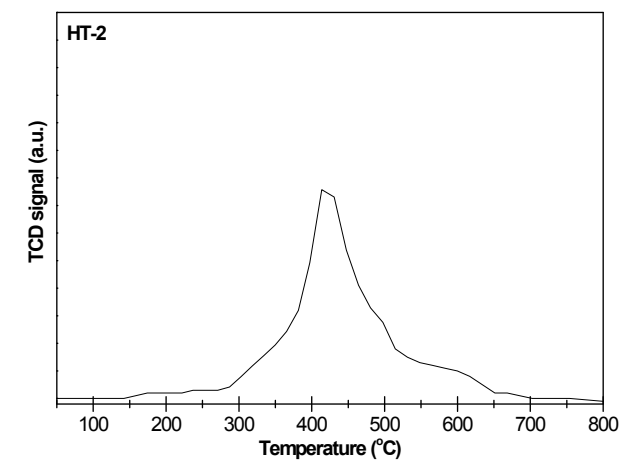
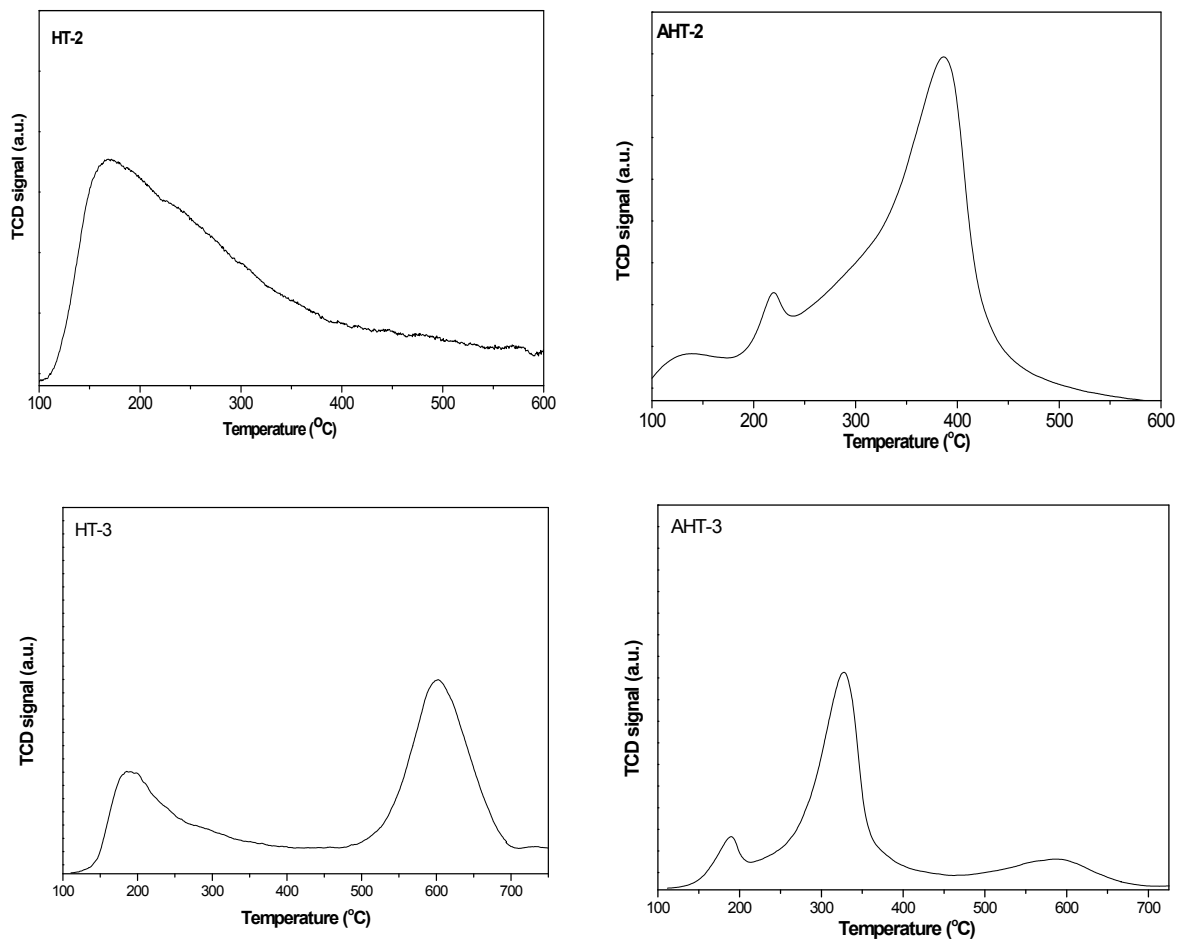


Figure S2. NH<sub>2</sub> TPD profiles of samples.



**Figure S3.** CO<sub>2</sub> TPD profiles of samples.

### Adsorption behavior of HTs and AHTs for **1a** and **1b**

To measure the amount of adsorption of **1a** and **1b** on HTs and AHTs at room temperature, the samples (25 mg; activated at 110°C for 1h) were treated with the solutions of **1a** and **1b** in cyclohexane (3.0 mM, 25 mL) separately in the closed reaction tubes under stirring for 3 h. The solid samples were separated by filtration, which were washed with acetonitrile (2 X 10 mL) to remove physisorbed molecules and dried at 110°C for 4 h, and then analyzed by TGA. The amount of adsorbed **1a** and **1b** on HTs and AHTs were calculated from TGA results using following equation:<sup>1</sup>

$$W = (W_2 - W_1) / FW$$

Where,

$W_1$  = weight loss (mg/g) of pristine sample in the range of 50°C to 500 °C,

$W_2$  = weight loss (mg/g) of sample after adsorption in the range of 50°C to 500 °C,

FW = molecular weight of adsorbate (**1a/ 1b**)

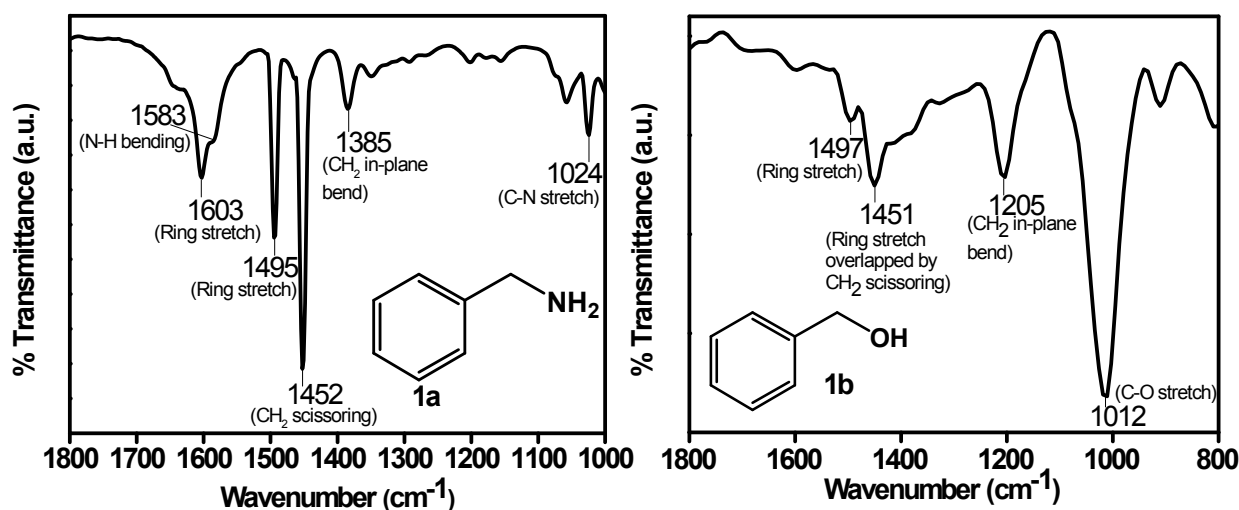
**Table S1.** Amount of **1a** and **1b** adsorbed in HTs and AHTs.

Sample	Amount of adsorption of <b>1a</b> (mmol/g)	Amount of adsorption of <b>1b</b> (mmol/g)
HT-2	0.1	0.3
HT-3	0.3	0.6
AHT-2	0.8	0.7
AHT-3	2.3	1.3

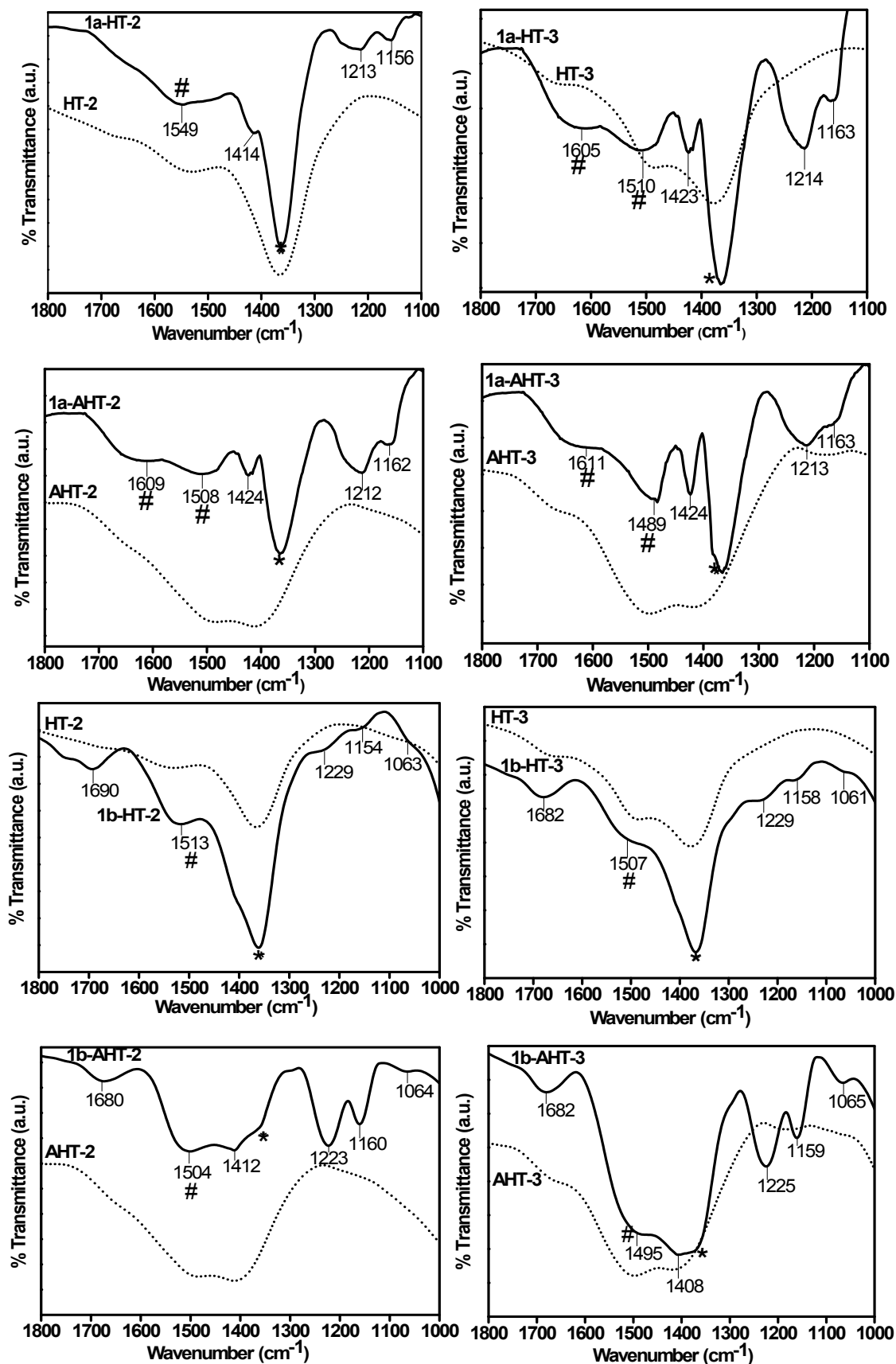
## Characterization of surface adsorbed species of **1a** & **1b** on HTs and AHTs by FTIR analysis

By FTIR study of the **1a** and **1b** adsorbed samples (viz. 1a-HT-2, 1a-HT-3, 1a-AHT-2, 1a-AHT-3, 1b-HT-2, 1b-HT-3, 1b-AHT-2 and 1b-AHT-3), we found that the benzylic hydrogen atoms ( $-\text{CH}_2-$ ) of the adsorbed **1a** and **1b** species were significantly influenced after their adsorption (on basic sites). The characteristic IR bands for neat **1a** and **1b** in the region of 1800-1000  $\text{cm}^{-1}$  are shown in their FTIR spectra (**Figure S4**).<sup>2</sup> From 1465  $\text{cm}^{-1}$  to 1150  $\text{cm}^{-1}$  is the region for H-C-H vibrations (scissoring and in-plane) of  $-\text{CH}_2-$ .<sup>2</sup> The  $\text{CH}_2$  scissoring for neat **1a** and **1b** were at 1452  $\text{cm}^{-1}$  and 1451  $\text{cm}^{-1}$ , respectively. In FTIR spectra of **1a** and **1b** adsorbed samples (**Figure S5**), a band observed in the range of 1425-1400  $\text{cm}^{-1}$  can be assigned to the shifted  $\text{CH}_2$  scissoring to lower frequency for adsorbed **1a** and **1b** species indicating the weakened/ polarized C-H bonds of  $-\text{CH}_2-$ . This band is merged with carbonate's band in FTIR spectra of **1b** adsorbed on HTs. The  $\text{CH}_2$  in-plane bending for neat **1a** and **1b** are at 1385  $\text{cm}^{-1}$  and 1205  $\text{cm}^{-1}$ , respectively. Two closely located bands at  $\sim 1212$ -1225  $\text{cm}^{-1}$  and at  $\sim 1154$ -1163  $\text{cm}^{-1}$  in FTIR spectra of **1a** and **1b** adsorbed samples can be assigned to in-plane and out of plane  $\text{CH}_2$  bending, respectively, for adsorbed species. The gas phase IR spectra of formaldehyde exhibits similar bands for  $\text{CH}_2$  rocking (in-plane) and wagging (out of plane) at 1250  $\text{cm}^{-1}$  and 1165  $\text{cm}^{-1}$ , respectively.<sup>3</sup> Usually, the intensity of the H-C-H scissoring is weaker than H-C-H in-plane and out of plane vibrations.<sup>2</sup> The intense peaks for H-C-H in-plane and out of plane vibrations as compared to H-C-H scissoring (for most of samples) indicates the weakening of C-H bonds of  $-\text{CH}_2-$ . Furthermore, the C-N and C-O stretching bands (1024  $\text{cm}^{-1}$  and 1012  $\text{cm}^{-1}$ , respectively) were not observed in the spectra of **1a** and **1b** adsorbed samples, respectively. The FTIR spectra of **1b** adsorbed samples exhibit a band centered at  $\sim 1680$ -1690  $\text{cm}^{-1}$ , which can be assigned to a C-O bond with partial double bond character. The absence of C-N stretching band also indicates partial

double bond character in C–N bond, which will be in the imine’s C=N stretching region ( $\sim 1600\text{ cm}^{-1}$ ) and possibly merged with the broad band for ring stretching and N–H bending. Thus, FTIR study shows that the adsorbed species of **1a** and **1b** have partially double bonded C–N and C–O bonds, respectively, and polarized benzylic C–H bonds as  $\text{C}^{\delta+}\text{--H}^{\delta-}$  as shown in **Scheme 4c & 4d**. The adsorbed species of **1a** and **1b** are possible to be produced by partial deprotonation of their functional groups ( $\text{--NH}_2$  and  $\text{--OH}$ , respectively) by catalyst’s basic sites.



**Figure S4.** FTIR spectra of **1a** and **1b** (neat).

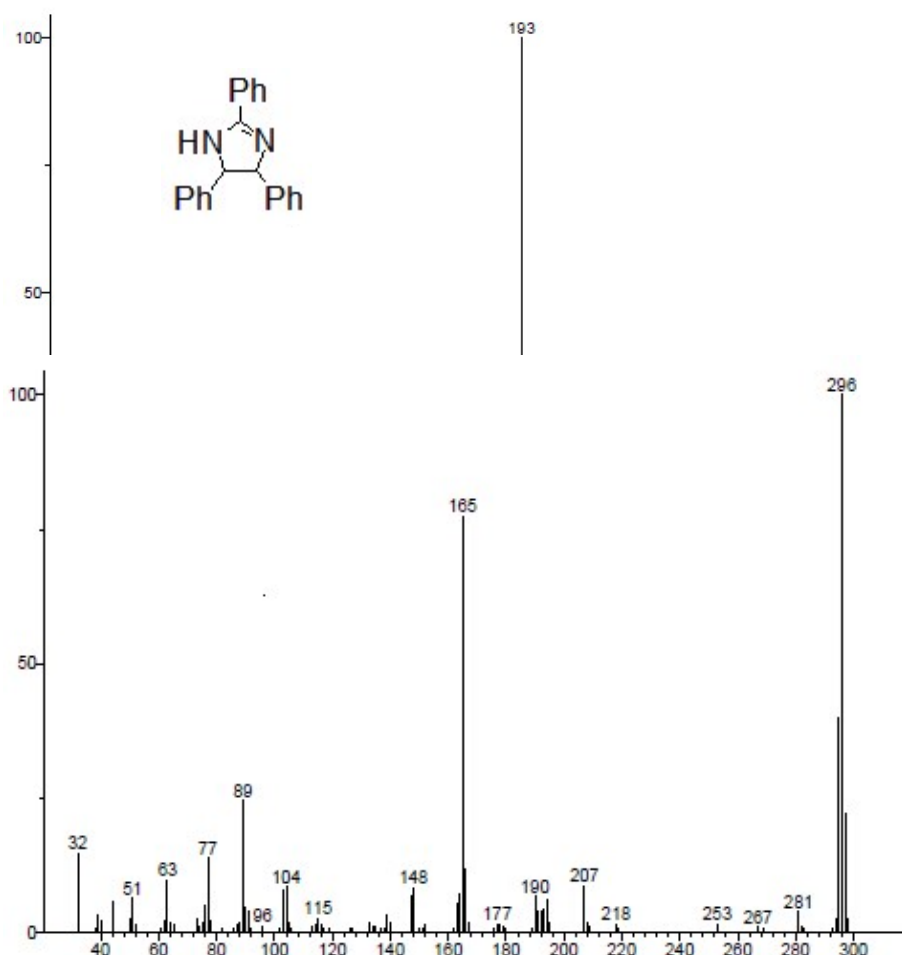
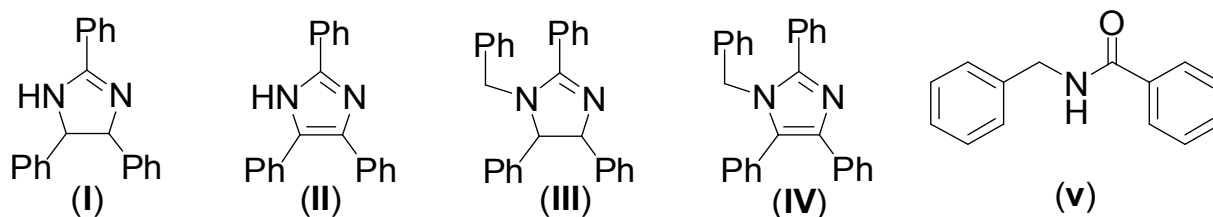


**Figure S5.** FTIR spectra of pristine, and **1a** & **1b** adsorbed samples [\*: $\text{O}-\text{C}-\text{O}$  symmetric stretching of carbonate; #: ring stretching and  $\text{N}-\text{H}/\text{O}-\text{H}$  bendings of adsorbed **1a/1b**, and  $\text{O}-\text{C}-\text{O}$  asymmetric stretching of carbonate ions].

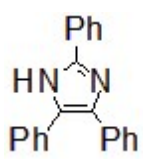


## Characterization of by-products formed in imination of **1a** with **2**

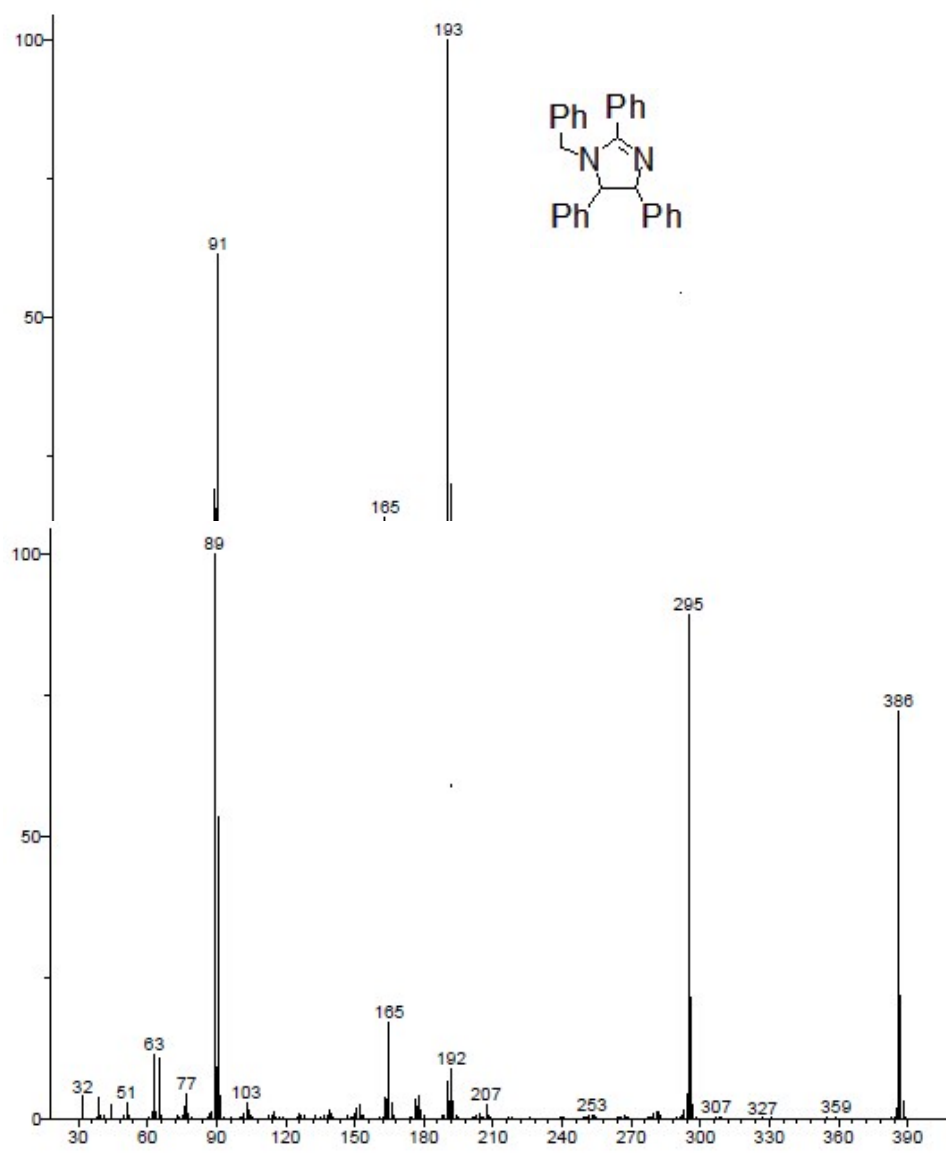
The by-products (**I-IV**) shown below were identified by mass spectroscopy and were expected to be formed from self-imine product (**4**; by its reactions with **1a**). This was confirmed by carrying out an equimolar reaction of **4** and **1a** in presence of AHT-3 and air, at 180°C for 12 h, which gave complete conversion of **4** into the products, similar to those obtained as by-products in the imination reaction of **1a** and **2**. The significant amount of by-products formed with more basic catalysts HT-3 and AHT-3 in aerobic reactions clearly indicates that these by-products are formed by base catalyzed reactions of **4** and **1a**. Furthermore, the formation of by-products in only aerobic reactions shows that they are produced by oxidative reactions.



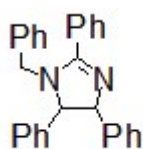
Mass spectrum of **I**

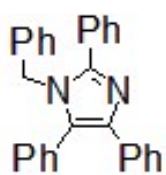


Mass spectrum of **II**

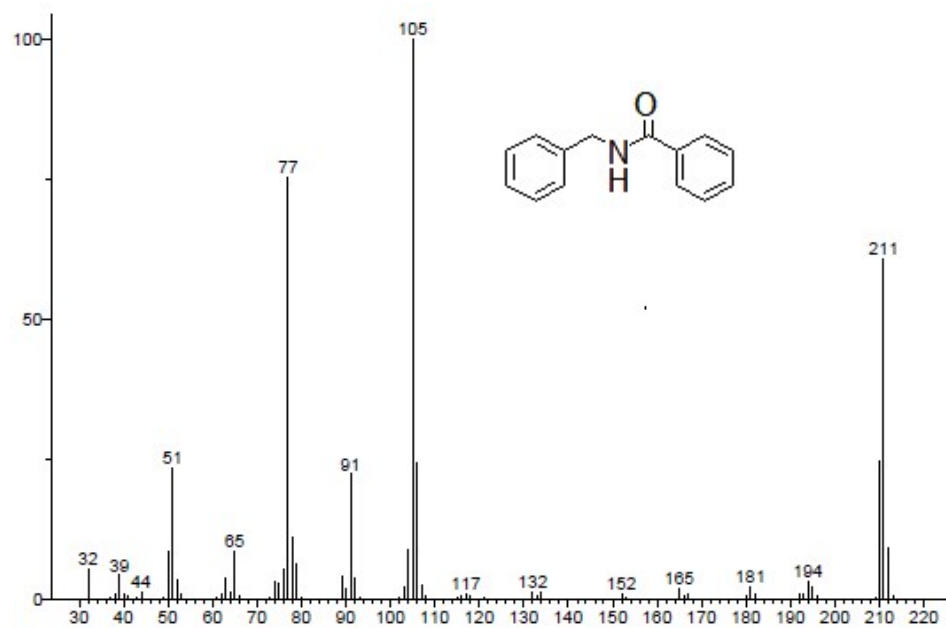


Mass spectrum of **III**





Mass spectrum of **IV**



Mass spectrum of **V**

## References

- [1] D.O. Bennardi, G.P. Romanelli, J.C. Autino, L.R. Pizzio, *Catal. Commun.*, **10**, 2009, 576.
- [2] R.M. Silverstein, G.C. Bassler, T.C. Morrill, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons Inc., Hoboken, NJ, 1991.
- [3] Chemistry LibreTexts,  
[https://chem.libretexts.org/Bookshelves/Organic\\_Chemistry/Map%3A\\_Organic\\_Chemistry\\_\(Wade\)/11%3A\\_Infrared\\_Spectroscopy\\_and\\_Mass\\_Spectrometry/11.02%3A\\_The\\_Infrared\\_Region](https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map%3A_Organic_Chemistry_(Wade)/11%3A_Infrared_Spectroscopy_and_Mass_Spectrometry/11.02%3A_The_Infrared_Region) (accessed October 2019).