Supporting Information for

An Interchangeable Homogeneous⇔Heterogeneous Catalyst System for Furfural Upgrading

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Materials and Methods. All oxygen- and moisture-sensitive manipulations were carried out in a nitrogen-filled glovebox or under nitrogen atmosphere using standard Schlenk techniques. HPLC-grade organic solvents were sparged extensively with nitrogen during filling of the solvent reservoir and then dried by passage through activated alumina (for CH_2Cl_2) followed by passage through Q-5-supported copper catalyst (for toluene and hexanes) stainless steel columns. Tetrahydrofuran (THF) was refluxed over metallic sodium/potassium alloy with benzophenone and distilled under nitrogen atmosphere before use. Acetonitrile and *n*-pentane were distilled over calcium hydride. Furfural (Alfa Aesar) was vacuum-distilled over calcium hydride prior to use. Triethylamine (Et_3N, Alfa Aesar) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich) were dried with activated molecular sieves. NaH (60% dispersion in mineral oil, Aldrich) was washed with dry hexanes to prepare oil-free NaH prior to use. Cloisite Na^+ montmorillonite (MMT), with a cation exchange capacity (CEC) of 92.6 mequiv/100 g, was purchased from Southern Clay Products, Inc., Gonzales, TX. MMT was dried at 70 ^oC under vacuum overnight prior to use. Benzimidazole (Acros Organics), dodecyl bromide (Acros Organics), 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride ([TM]Cl, Alfa Aesar), methyl iodide (Aldrich), $NaHCO_3$ (EMD Chemicals Inc.), KO^tBu (Acros Organics), and 5-hydroxymethylfurfural (HMF, Acros Organics) were used as received.

^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. Highresolution mass spectrometry (HRMS) data were collected on an Agilent 6220 Accurate time-of-flight LC/MS spectrometer. Fourier transform infrared (FT-IR) spectroscopy was performed on a Thermoscientific (Nicolet iS50) FT-IR spectrometer equipped with a diamond attenuated total reflectance (ATR) at room temperature in the range of 550–4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10 ^{o}C/min from 20 ^{o}C to 900 ^{o}C using TA Q-series Q50, TA Instruments. X-ray diffraction (XRD) analyses, employed to determine the basal spacing of MMT samples, were performed on a Scintag X-2 Powder X-Ray Diffractometer using Cu Kα (λ = 0.154 nm) radiation and a Peltier detector on the diffracted beam side. The XRD measurements were conducted at a step size of 0.01^{o} with 5 seconds per step in the 2θ range of 1^{o}–10^{o}.

Synthesis of 1-Dodecyl-3-methyl Benzimidazolium Bromide [^{1,12}BI]Br. To a 250 mL three-necked round-bottom flask equipped with a stir bar and a condenser was charged with benzimidazole (5.00 g, 42.3 mmol) and oil-free NaH (1.02 g, 42.3 mmol). While stirring at 0 ^{o}C under a nitrogen atmosphere, dry THF (30 mL) was slowly added into the flask. The mixture was stirred at room temperature for 30 min after which it was cooled to 0 ^{o}C again and methyl iodide (6.00 g, 42.3 mmol) was added dropwise. The mixture was stirred at 0 ^{o}C for 1 h and then at room temperature for another 2 h. Then dry dichloromethane (30 mL) was added to the mixture to extract the organic product. After filtering through a pad of Celite, the solvents of the filtrate were removed under reduced pressure, and the obtained 3-methylbenzimidazole as an off-white solid was used directly for the next step without any further purification.

To the above resulting 3-methylbenzimidazole was added dodecyl bromide (15.8 g, 63.5 mmol) and dry acetonitrile (30 mL), and the mixture was stirred under reflux under a nitrogen atmosphere for 48 h. Then the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was washed with *n*-pentane, and [^{1,12}BI]Br was isolated as an off-white solid (15.2 g, yield: 94%). The ^{1}H and ^{13}C NMR spectra of [^{1,12}BI]Br are shown in Figures S1 and S2, respectively.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, J = 7.2 Hz, 3H, CH_3), 1.10–1.50 (m, 18H, $NCH_2CH_2(CH_2)_9CH_3$), 2.04 (m, 2H, NCH_2CH_2), 4.30 (s, 3H, N-CH_3), 4.56 (t, J = 7.6 Hz, 2H, NCH_2), 7.69 (m, 4H, Ar-*H*), 11.37 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.87, 22.40, 26.34, 28.81, 29.04, 29.12, 29.24, 29.31, 31.62, 33.84, 47.56, 112.80, 127.12, 130.86, 131.81, 142.35 ppm. HRMS calculated for $C_{20}H_{33}N_2^+$ [M]$^+$: m/z = 301.2644, found: 301.2638.

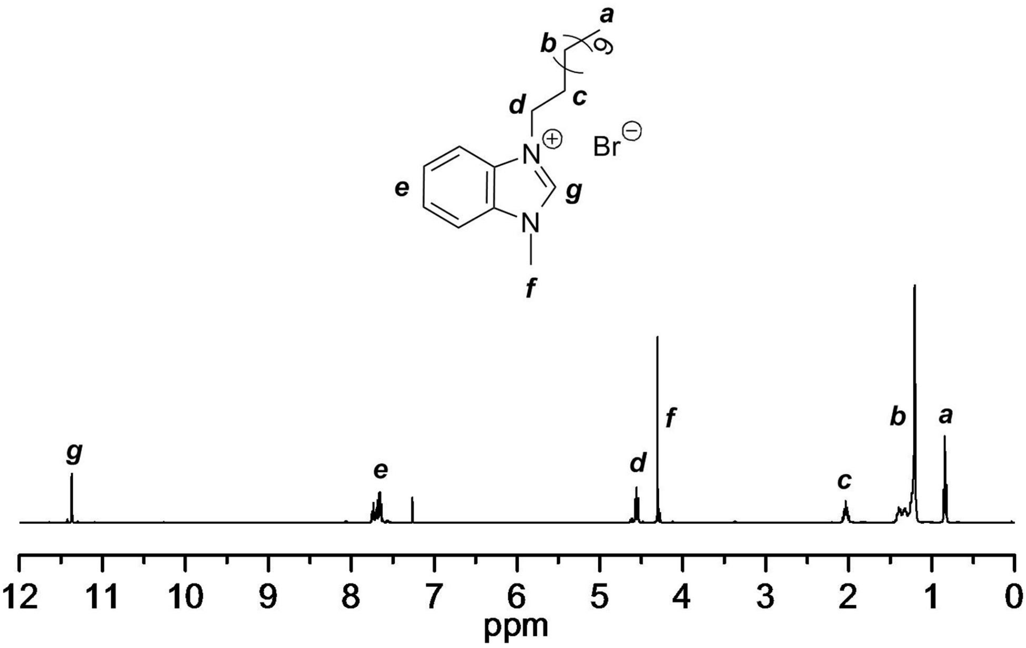

Figure S1. ^{1}H NMR spectrum of 1-dodecyl-3-methyl benzimidazolium bromide [^{1,12}BI]Br in $CDCl_3$.

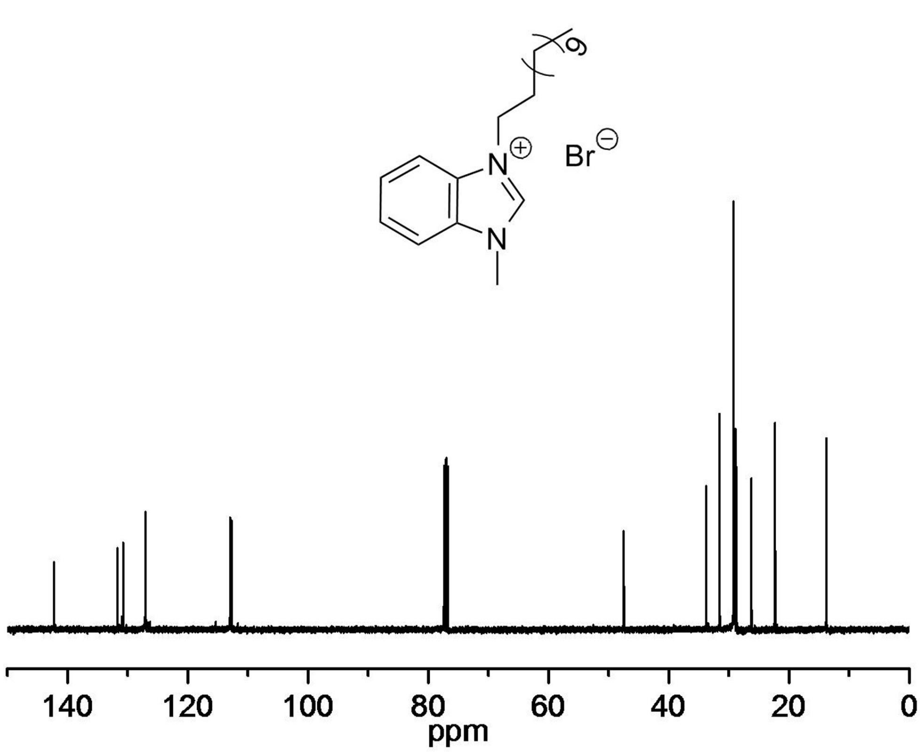

Figure S2. ^{13}C NMR spectrum of 1-dodecyl-3-methyl benzimidazolium bromide [^{1,12}BI]Br in $CDCl_3$.

Synthesis of 1,3-Didodecyl Benzimidazolium Bromide [^{12,12}BI]Br. To a 250 mL three-necked round-bottom flask equipped with a stir bar and a condenser was charged with benzimidazole (5.00 g, 42.3 mmol), $NaHCO_3$ (3.56 g, 42.3 mmol), dodecyl bromide (31.6 g, 127 mmol), and acetonitrile (30 mL). The mixture was stirred under reflux for 72 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, and dichloromethane (50 mL) was added to the mixture to extract the organic product. After filtering through a pad of Celite, the volatiles of the filtrate were removed under reduced pressure. The residue was washed with *n*-pentane, and [^{12,12}BI]Br was isolated as an off-white solid (21.1 g, yield: 93%). The ^{1}H and ^{13}C NMR spectra of [^{12,12}BI]Br are shown in Figures S3 and S4, respectively.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, J = 7.2 Hz, 6H, CH_3), 1.10–1.50 (m, 36H, $NCH_2CH_2(CH_2)_9CH_3$), 2.05 (m, 4H, NCH_2CH_2), 4.62 (t, J = 7.6 Hz, 4H, NCH_2), 7.67 (m, 4H, Ar-H), 11.59 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.13, 22.69, 26.59, 29.08, 29.33, 29.41, 29.52, 29.58, 29.60, 31.91, 47.74, 113.17, 127.18, 131.33, 142.75 ppm. HRMS calculated for $C_{31}H_{55}N_2^+$ [M]$^+$: *m*/*z* = 455.4365, found: 455.4360.

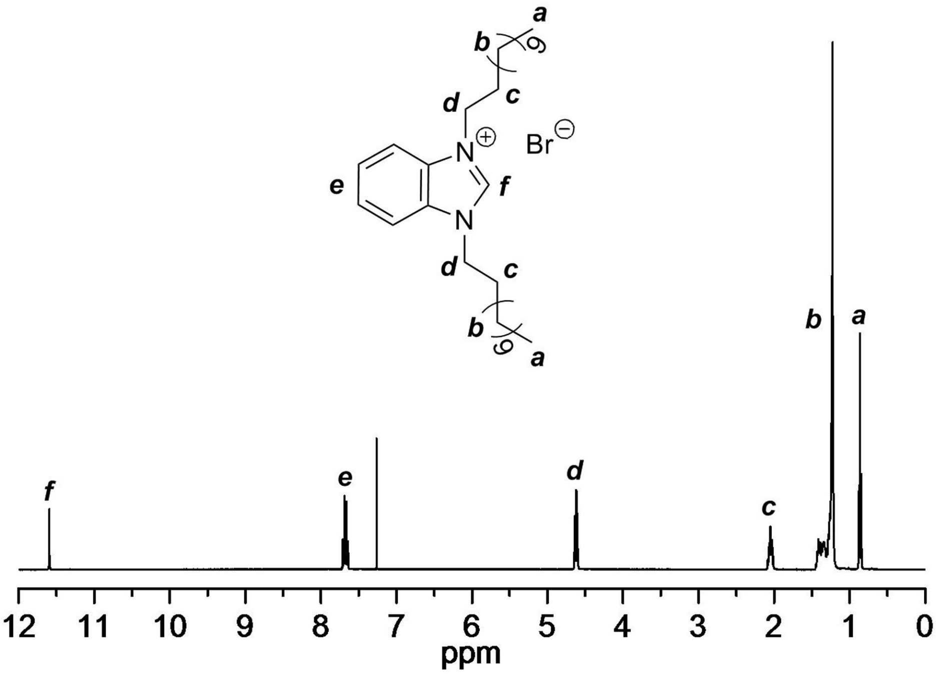

Figure S3. ^{1}H NMR spectrum of 1,3-didodecyl benzimidazolium bromide [^{12,12}BI]Br in CDCl$_3$.

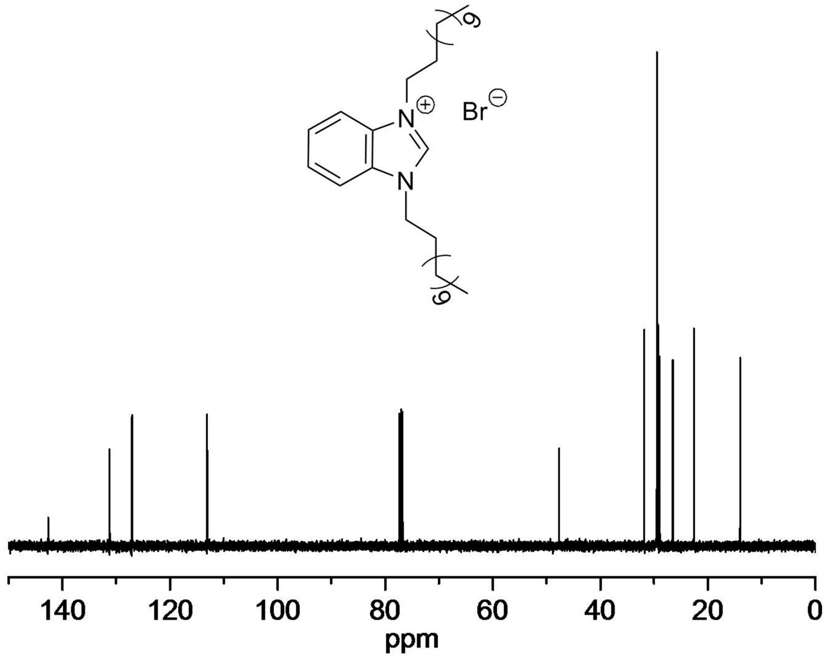

Figure S4. ^{13}C NMR spectrum of 1,3-didodecyl benzimidazolium bromide [^{12,12}BI]Br in CDCl$_3$.

Preparation of MMT Supported Thiazolium {$[TM]^+$/MMT} and Benzimidazolium {$[BI]^+$/MMT} Precatalysts. MMT (10 g, 92.6 mequiv/100 g cation exchange capacity), an azolium salt {13.89 mmol: [TM]Cl, 3.75 g; [^{1,12}BI]Br, 5.30 g; [^{12,12}BI]Br, 7.44 g}, and methanol (200 mL) were loaded into a 500 mL round bottom flask. The mixture was stirred vigorously at room temperature overnight. Then the precipitate was filtered, washed with methanol, and dried at 70 °C under vacuum for 24 h.

Typical Procedures for Furfural Self-coupling Reaction Catalyzed by $[BI]^+$/MMT + NaH. Furfural (0.192 g, 2.00 mmol), THF (3 mL), a $[BI]^+$/MMT (0.20 mmol, 10 mol% relative to furfural), and oil-free NaH (0.20 mmol, 10 mol% relative to furfural) were loaded into a 20 mL glass reactor in a glovebox. The reaction mixture was stirred at room temperature for 6 h. For the recycling experiments, after the reaction, 37% HCl (18 μL, 0.214 mmol) was added to the reactor to quench the reaction. The *in situ* formed carbene was converted back into the $[BI]^+$ salt by reacting with HCl. Then the vial was charged with 3 mL of methanol. The mixture was stirred at room temperature overnight to exchange the $[BI]^+$ salt back into the interlayers of MMT. Then the solid was filtered, washed with methanol, and dried at 70 °C overnight under vacuum. The recycled $[BI]^+$/MMT was reused to catalyze the furfural self-coupling reaction under the same conditions. The control experiments catalyzed by MMT and [^{12,12}BI]Br + NaH, respectively, were conducted under the same conditions. The experimental results are summarized in Table 1. For isolation of the furoin product, furfural (1.0 g, 10.4 mmol), THF (15 mL), [^{12,12}BI]$^+$/MMT (1.892 g, 1.04 mmol [^{12,12}BI]$^+$, 10 mol% relative to furfural), and oil-free NaH (25.0 mg, 1.04 mmol, 10 mol%) were loaded into a 50 mL round-bottom flask in the glovebox. The reaction mixture was stirred at room temperature for 6 h. The reaction was quenched with 37% HCl (88 μL, 1.047 mmol). Then the solid catalyst was filtered and washed with

THF. The solvent of the filtrate was removed under reduced pressure, and the residue was washed with 2 mL of toluene. Furoin (0.952 g, 95.2% isolated yield) was obtained as a yellow powder after vacuum drying. The ^{1}H NMR spectrum of furoin is shown in Figure S5. ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.19 (br s, 1 H, CHO*H*), 5.80 (s, 1H, C*H*OH), 6.35, 6.40, 6.54, 7.25, 7.37, 7.61 (m, 6 H, furan ring H).

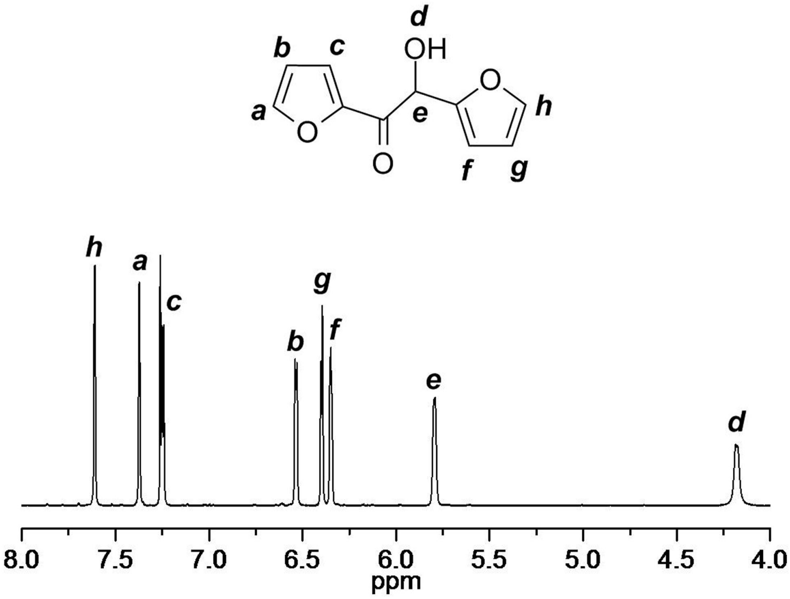

Figure S5. ^{1}H NMR spectrum of furoin in CDCl$_3$.

Model Reaction of [^{12,12}BI]$^+$/MMT Reacting with NaH in THF. [^{12,12}BI]$^+$/MMT (0.20 mmol), oil-free NaH (0.20 mmol), and THF (3 mL) were loaded into a 20 mL glass reactor in a glovebox. The reaction mixture was stirred at room temperature for 6 h. Then the solid was filtered, washed with THF, and dried at 70 °C overnight under vacuum. The TGA curve of the recovered MMT-supported catalyst after reacting with NaH is shown in Figure S6.

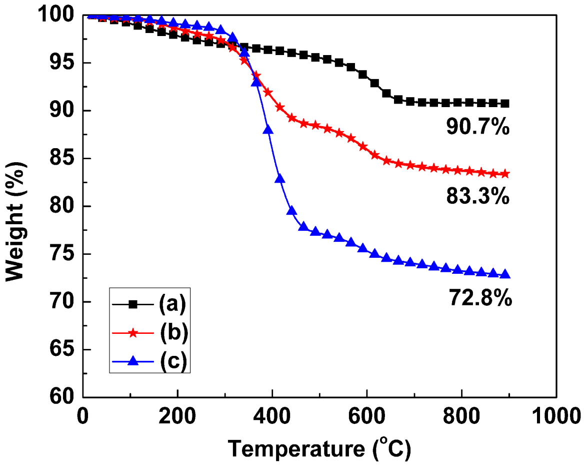

Figure S6. TGA curves of MMT (a), recovered MMT-supported catalyst after reaction with NaH (b), and recovered [^{12,12}BI]$^+$/MMT after the first catalytic cycle (c). The [^{12,12}BI]$^+$ content in the recycled precatalyst was calculated to be 413.6 μmol/g.

Model Reaction of [^{1,12}BI]$^+$/MMT with NaH in THF. [^{1,12}BI]$^+$/MMT (0.20 mmol), oil-free NaH (0.20 mmol), and THF (3 mL) were loaded into a 20 mL glass reactor in a glovebox. The reaction mixture was stirred at RT for 6 h. Then the solid was filtered, washed with THF, and the filtrate was concentrated in the glovebox. The ^{1}H NMR spectrum of the residue is shown in Figure S7.

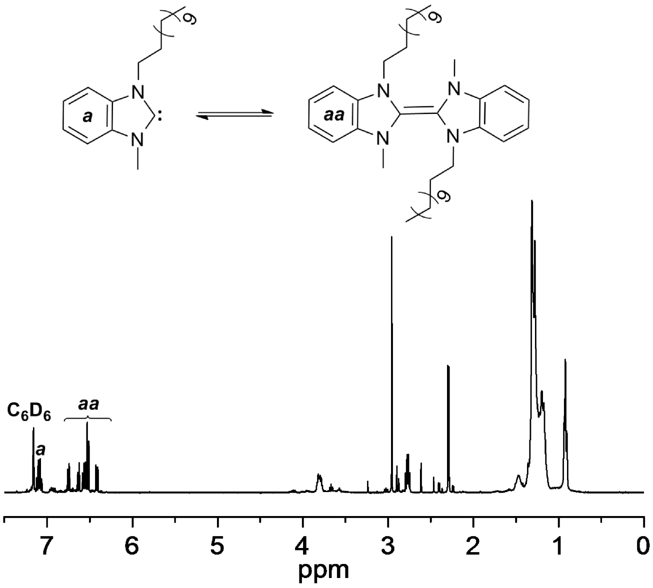

Figure S7. ^{1}H NMR spectrum of the Wanzlick equilibrium of the NHC catalyst derived from [^{1,12}BI]$^+$/MMT + NaH in C_6D_6.

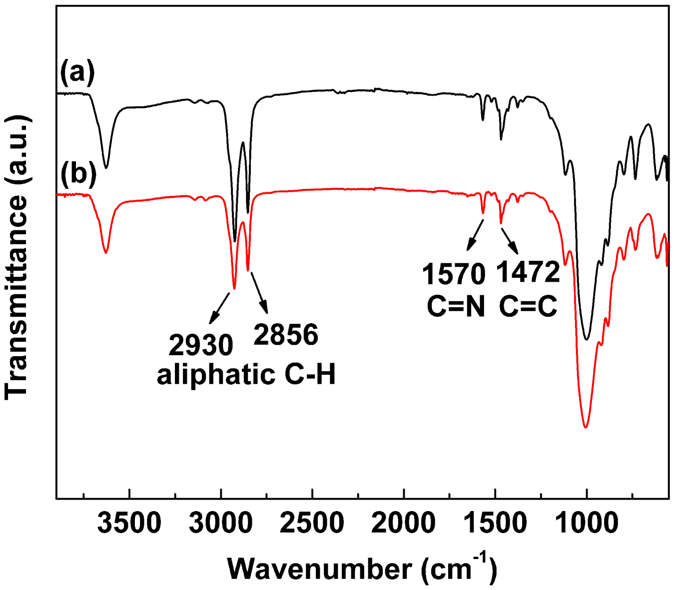

Figure S8. FT-IR spectra of MMT (a) and recovered [^{12,12}BI]$^+$/MMT after the first catalytic cycle (b).