

Supporting Information

Expanding the Catalytic Activity of Nucleophilic N-Heterocyclic Carbenes For Transesterification Reactions

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General Experimental Procedures. THF was dried by refluxing over sodium and distilled prior to use. 1,3-(2,4,6-trimethylphenyl)imidazolium chloride, 1,3-(2,4,6-trimethylphenyl)imidazolium chloride, 1,3-Bis-(2,6-diisopropylphenyl)imidazolium chloride, and 1,3-Dimethyl imidazolium iodide were prepared according to literature procedures.¹ 1-Ethyl-3-methyl-1-H-imidazolium chloride was purchased from Aldrich and used without further purification. ¹H-NMR spectra were recorded in either CDCl₃ or acetone-d₆ with a Bruker Avance 400 (400 MHz) spectrometer with the solvent proton signal as an internal standard. ¹³C-NMR spectra were recorded at 100 MHz on a Bruker Avance 400 spectrometer with the solvent carbon signal as internal standard. Gel permeation chromatography (GPC) or size exclusion chromatography (SEC) were carried out on a Waters chromatography connected to a Waters 410 differential refractometer. Polystyrene samples of known molecular weight were used as calibration standards. Four 5 μm Waters columns (300 x 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10⁵, 10⁶) were used with THF as a solvent.

General Procedure for Transesterifications with Methyl Benzoate. The transesterifications were carried out under an inert atmosphere in a dry box. Solvents and reagents were dried and degassed prior to use. The carbene catalysts were generated *in situ* by adding potassium *tert*-butoxide to the imidazolium salts (0.8 eq. potassium *tert*-butoxide/1 eq. imidazolium salt) in THF (2 mL). The reaction was allowed to proceed for one hour and then filtered. Methyl benzoate was reacted with ethanol, isopropanol and *tert*-butanol (20 eq.) in the presence of three different carbenes as transesterification catalysts at room temperature for 12 h. Gas chromatography, GC/MS and ¹H NMR spectrometry were used to analyze the reaction products.

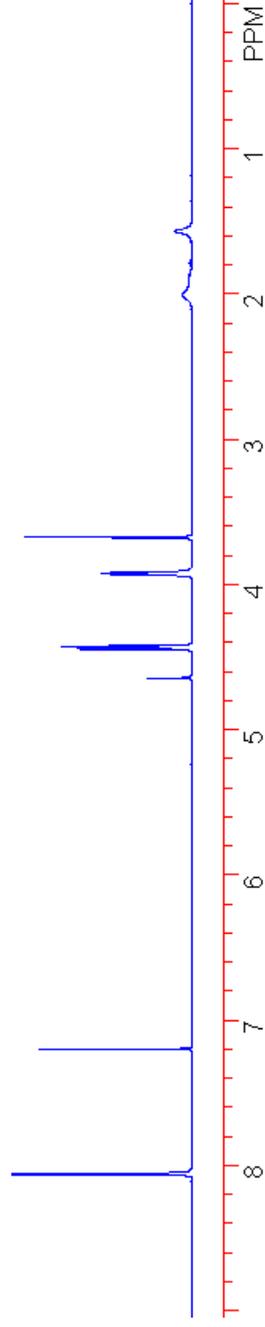
General Procedure for Polycondensation Polymerization Reactions. In a dry box carbene catalysts were generated *in-situ* by adding potassium *tert*-butoxide to the imidazolium salts (0.8 eq. potassium *tert*-butoxide/1 eq. carbene salt) in THF (2 mL). The reaction was allowed to proceed for one hour and then filtered. The catalyst solution was placed in a round bottom flask equipped with a stirbar. An appropriate AB monomer was then added to the round bottom flask. The flask was then equipped with a vacuum adapter and placed on a vacuum line. The reaction flask was evacuated and then heated to 60 °C. After 30 min the reaction was noticeably viscous. After 24 h the reaction was then quenched with a drop of water. The polymer was then dissolved in THF and then precipitated from cold methanol.

Bis(2-hydroxyethyl) terephthalate (BHET) synthesis. In a glove box, a vial was charged with 1,3 Bi-phenyl imidazolium chloride salt (35 mg, 0.13 mmol) and *tert*-butoxide (11 mg, 0.09 mmol). THF (2 mL) was added to the vial and the reaction mixture was stirred for 20 min. Dimethyl terephthalate (1.1 g, 5.6 mmol) and dry ethylene glycol (920 mg, 14.8 mmol) was mixed in 10 mL of THF. The catalyst solution was filtered into ester/ethylene glycol solution and stirred for 30 min. The THF and residual ethylene glycol was removed under reduced pressure. A cream colored solid (1.2 g, 83%) was isolated. The ¹H, ¹³C NMR, and GC/MS spectra were identical to a commercially available sample of BHET.

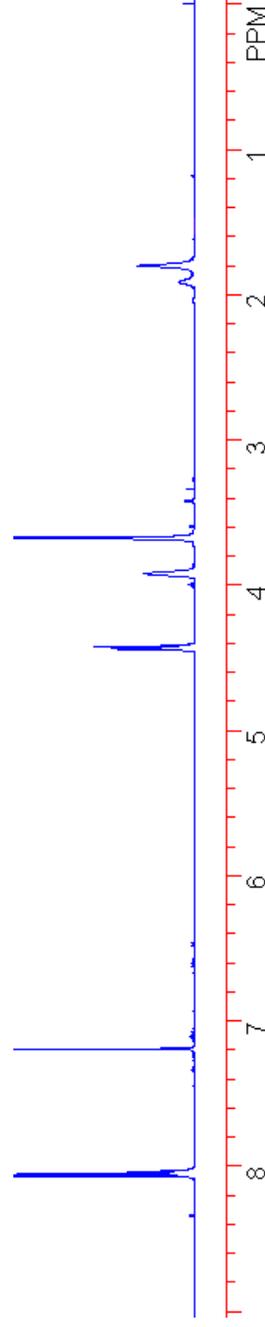
Polyethyleneterephthalate (PET) synthesis. In a glove box, a round bottom flask was charged with 1,3 Bi-phenyl imidazolium chloride salt (**5**, see reference 10 in main text) (37 mg, 0.146 mmol) and *tert*-butoxide (9.2 mg, 0.08 mmol). THF (2 mL) was added to the vial and the reaction mixture was stirred for 20 min. Bis(2-hydroxyethyl) terephthalate (BHET) (550 mg, 2.1 mmol) was added to the catalyst mixture. The round bottom flask was equipped with a vacuum adapter and placed under reduced pressure. After the THF had completely evaporated, the flask was heated to 250 °C which resulted in the immediate melting of the reactants. The reaction was allowed to stir under vacuum for 1.5 h. The flask was cooled to yield a solid cream colored product (450 mg). ¹H, ¹³C NMR and melting point were identical to a commercially available sample of PET.

¹ Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523..

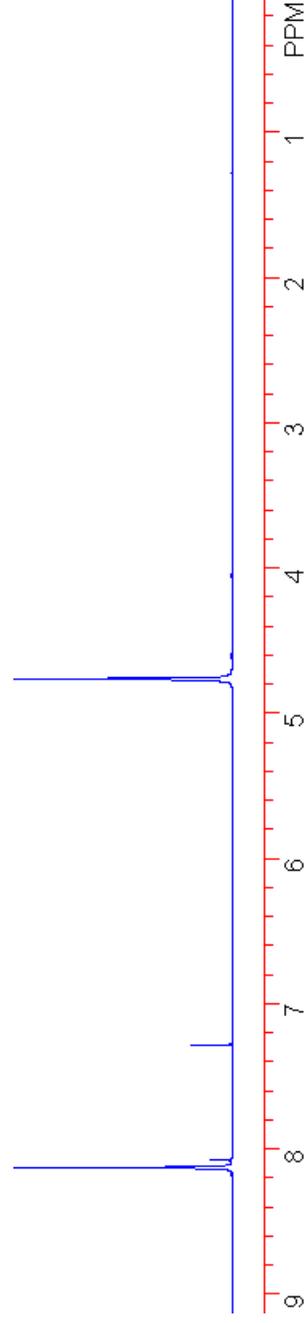
^1H NMR Spectrum of Commercially Available BHET



^1H NMR Spectrum Synthesized BHET



^1H NMR Spectrum of Commercially Available PET



^1H NMR Spectrum of Synthesized PET

