Electronic Supporting Information

Thermodynamic and molecular origin of interfacial rate enhancements and endo-selectivities of a Diels-Alder reaction

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1. Solubility measurements using $^1$H NMR spectroscopy:
2. GC parameters: The Detailed GC Method:

Column make: CP SIL 5CB

Column length: 15m

Internal diameter: 0.25 mm

Film thickness: 0.25-micron

Flow rate: 0.8 ml/min of nitrogen

Column oven temperature: 280°C

Injector temperature: 250°C

Detector temperature: 280°C

Total run time 16.77 min (Hold at 70°C for 5 min., ramp at 4°C, then maintain at 180°C for 0 min, ramp at 79°C and then maintain at 280°C for 5 min.)

Internal Standard (IS): Chlorobenzene in acetone (2% V/V). Calibration of GC method has been done with the product concentrations using the solutions of pure product in acetone. The amount of product formed at time (t) was calculated by measuring the relative peak area with respect to time.
3. $^1$H NMR and $^{13}$C NMR spectra of CPMA product:

(a) $^1$H NMR spectrum of CPMA product using CDCl$_3$ as solvent at 200 MHz

(b) $^{13}$C NMR spectrum of CPMA product with D$_2$O capillary at 200 MHz
4. $^1$H NMR and $^{13}$C NMR spectra of ionic liquids:

(a) $^1$H NMR spectrum of $[C_2C_1im][ClO_4]$ with D$_2$O capillary at 200 MHz

(b) $^{13}$C NMR spectrum of $[C_2C_1im][ClO_4]$ with D$_2$O capillary at 200 MHz
(c) $^1$H NMR spectrum of [C$_4$C$_1$im][ClO$_4$] with D$_2$O capillary at 200 MHz

(d) $^{13}$C NMR spectrum of [C$_4$C$_1$im][ClO$_4$] with D$_2$O capillary at 200 MHz
(e) $^1$H NMR spectrum of $[C_6C_{1}\text{im}][\text{ClO}_4]$ in DMSO-$d_6$ as solvent at 200 MHz

(f) $^{13}$C NMR spectrum of $[C_6C_{1}\text{im}][\text{ClO}_4]$ in DMSO-$d_6$ as solvent at 200 MHz
(g) $^1$H NMR spectrum of [C$_8$C$_1$im][ClO$_4$] in DMSO-D$_6$ as solvent at 200 MHz

(h) $^{13}$C NMR spectrum of [C$_8$C$_1$im][ClO$_4$] in DMSO-D$_6$ as solvent at 200 MHz
(i) $^1$H NMR spectrum of $[\text{C}_{10}\text{C}1\text{im}][\text{ClO}_4]$ in DMSO-$D_6$ as solvent at 200 MHz

(j) $^{13}$C NMR spectrum of $[\text{C}_{10}\text{C}1\text{im}][\text{ClO}_4]$ in DMSO-$D_6$ as solvent at 200 MHz