

## Supporting Information

### **Entropic Electrolytes for Anodic Cycloadditions of Unactivated Alkene Nucleophiles**

**Yasushi Imada,<sup>1</sup> Yusuke Yamaguchi,<sup>1</sup> Naoki Shida,<sup>1</sup> Yohei Okada,<sup>2</sup> Kazuhiro Chiba\*<sup>1</sup>**

<sup>1</sup>Department of Applied Biological Science, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan

<sup>2</sup>Department of Chemical Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

Tel: (+81)-42-367-5667

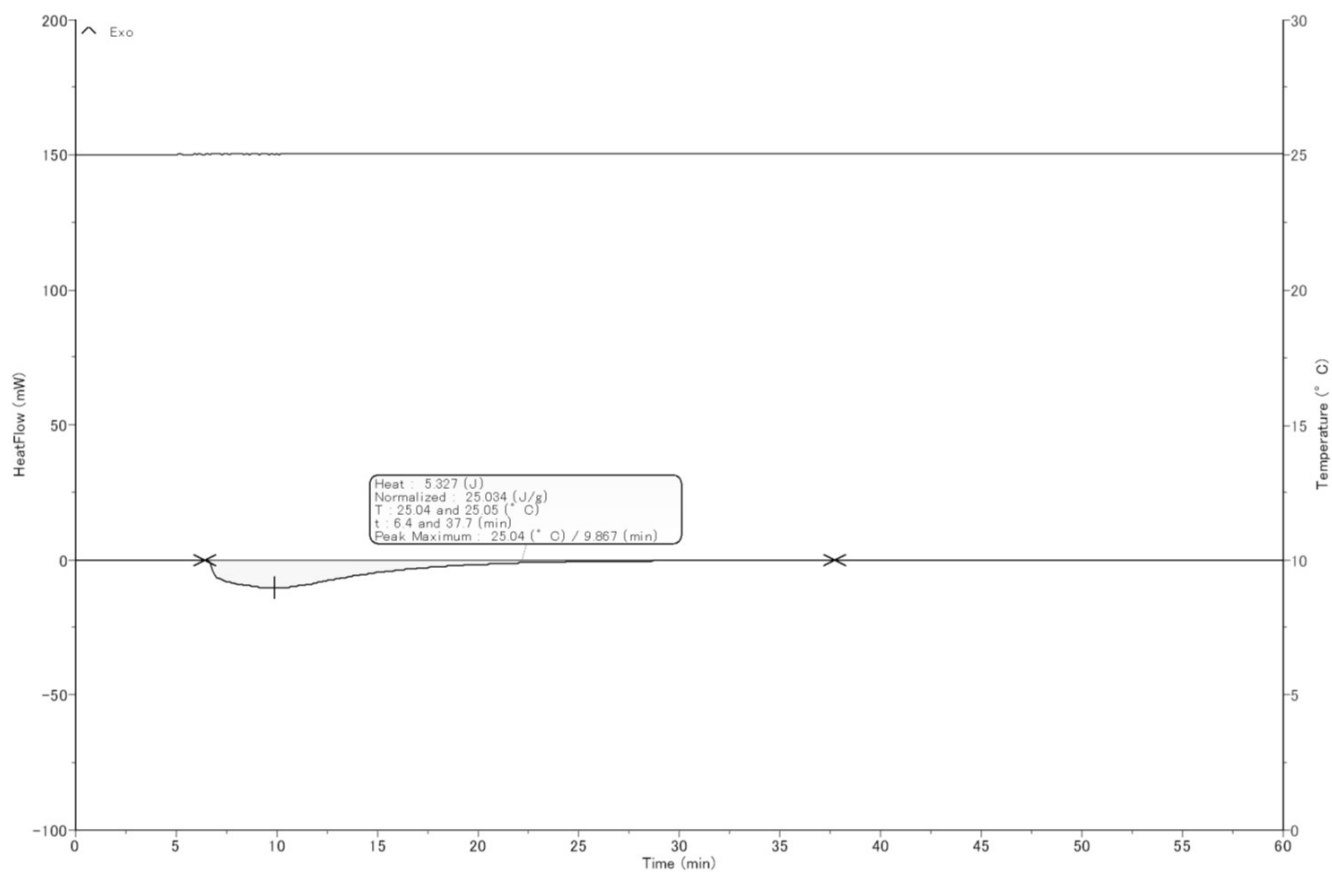
Fax: (+81)-42-367-5667

E-mail: [chiba@cc.tuat.ac.jp](mailto:chiba@cc.tuat.ac.jp)

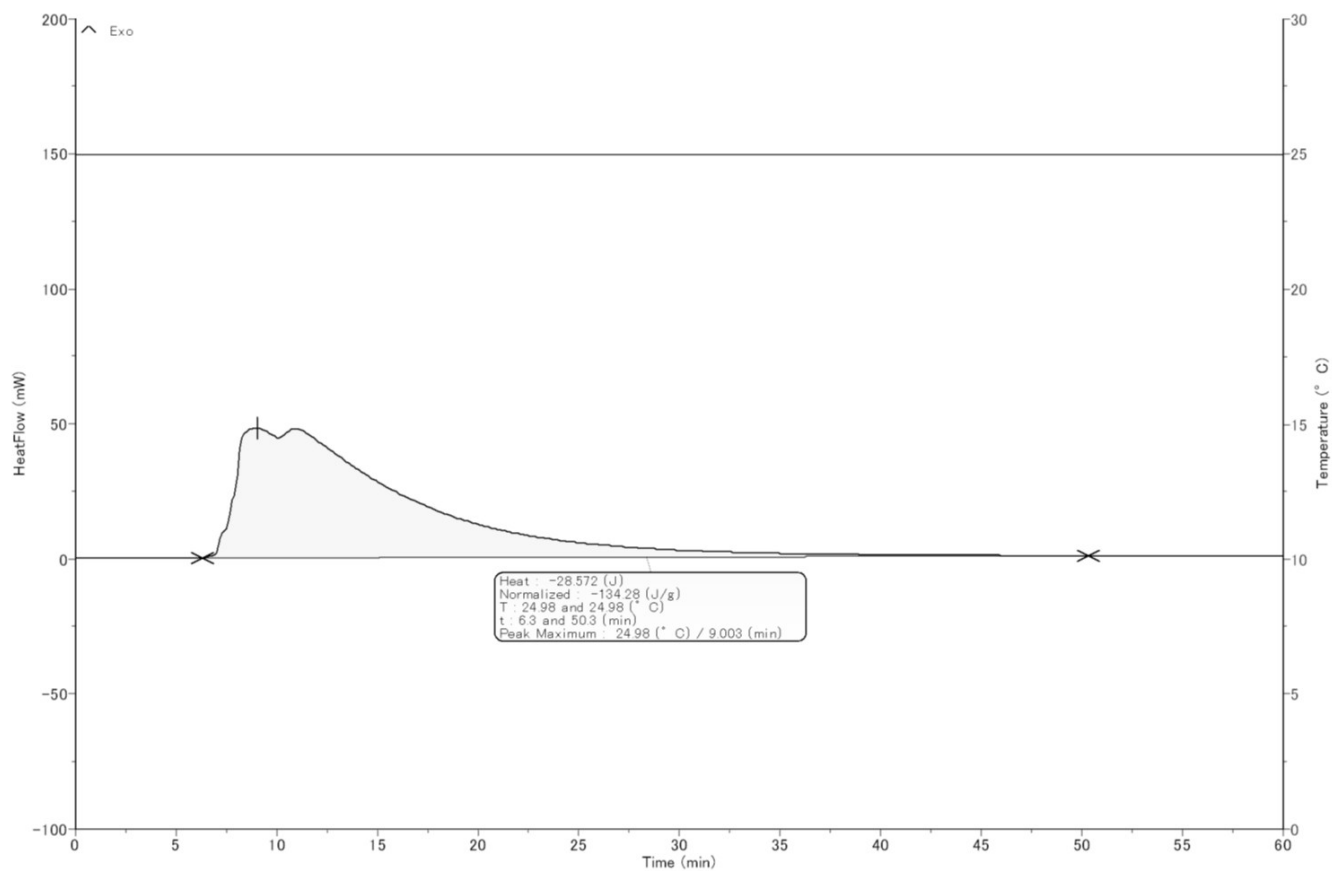
#### Table of Contents

- 1. Additional Figures and Scheme    p 2**
- 2. General Remarks    p 9**
- 3. Synthesis and Characterization Data    p 9**
- 4. Calorimetric Studies    p 12**
- 5. Copies of <sup>1</sup>H and <sup>13</sup>C NMR Spectra    p 13**

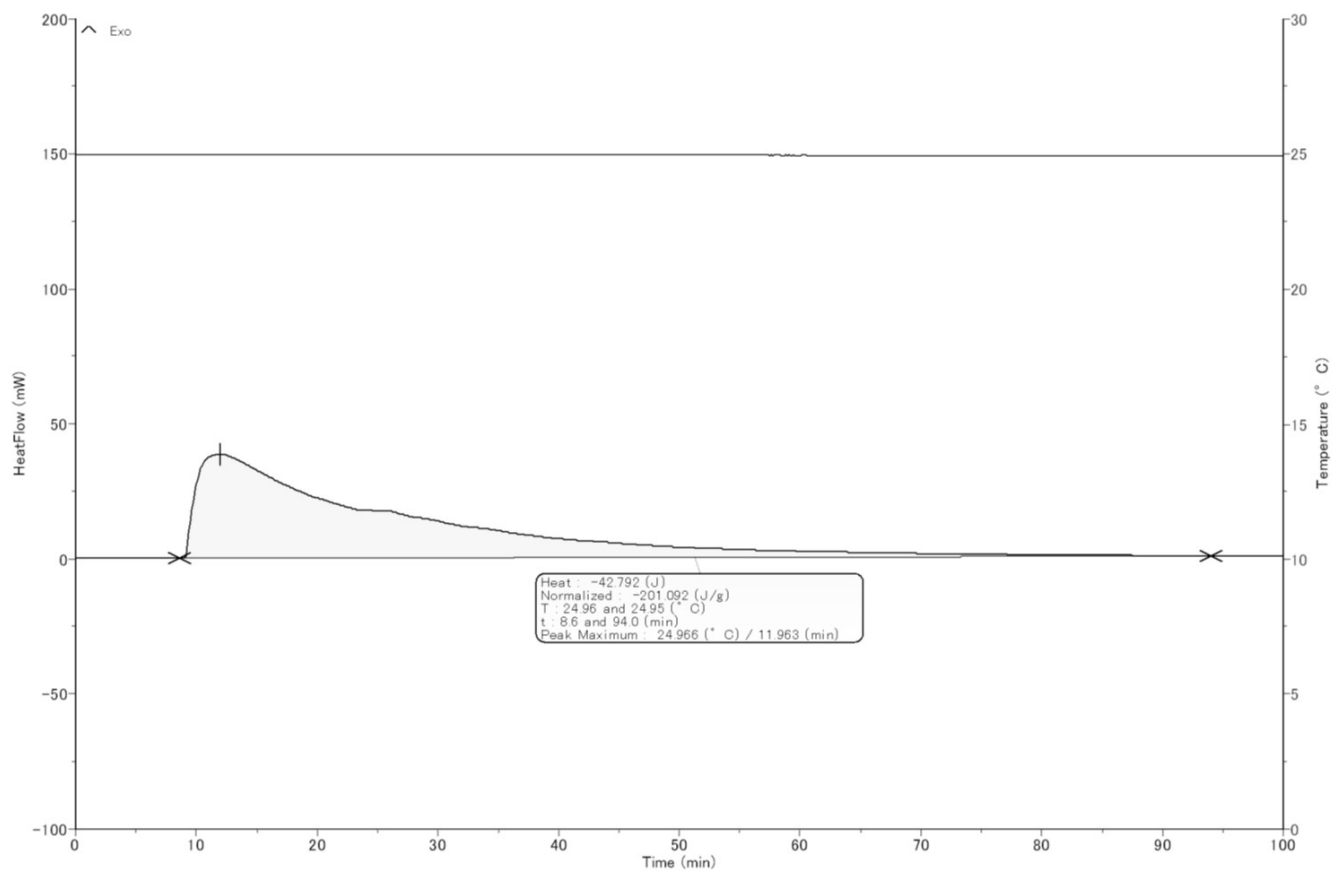
## 1. Additional Figures and Scheme



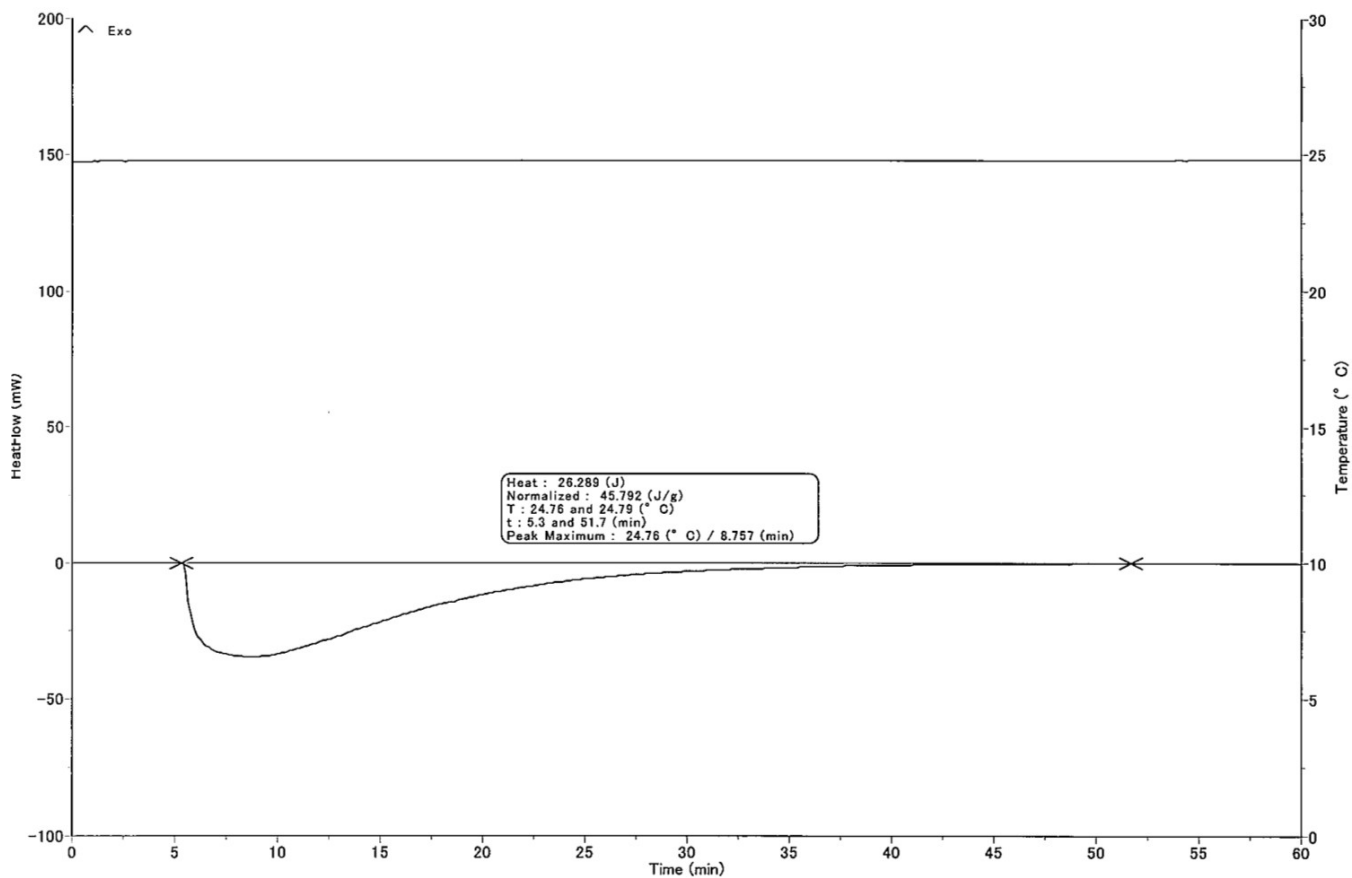
**Figure S1.** Calorimetric Study of  $\text{LiClO}_4$  in  $\text{MeNO}_2$ .



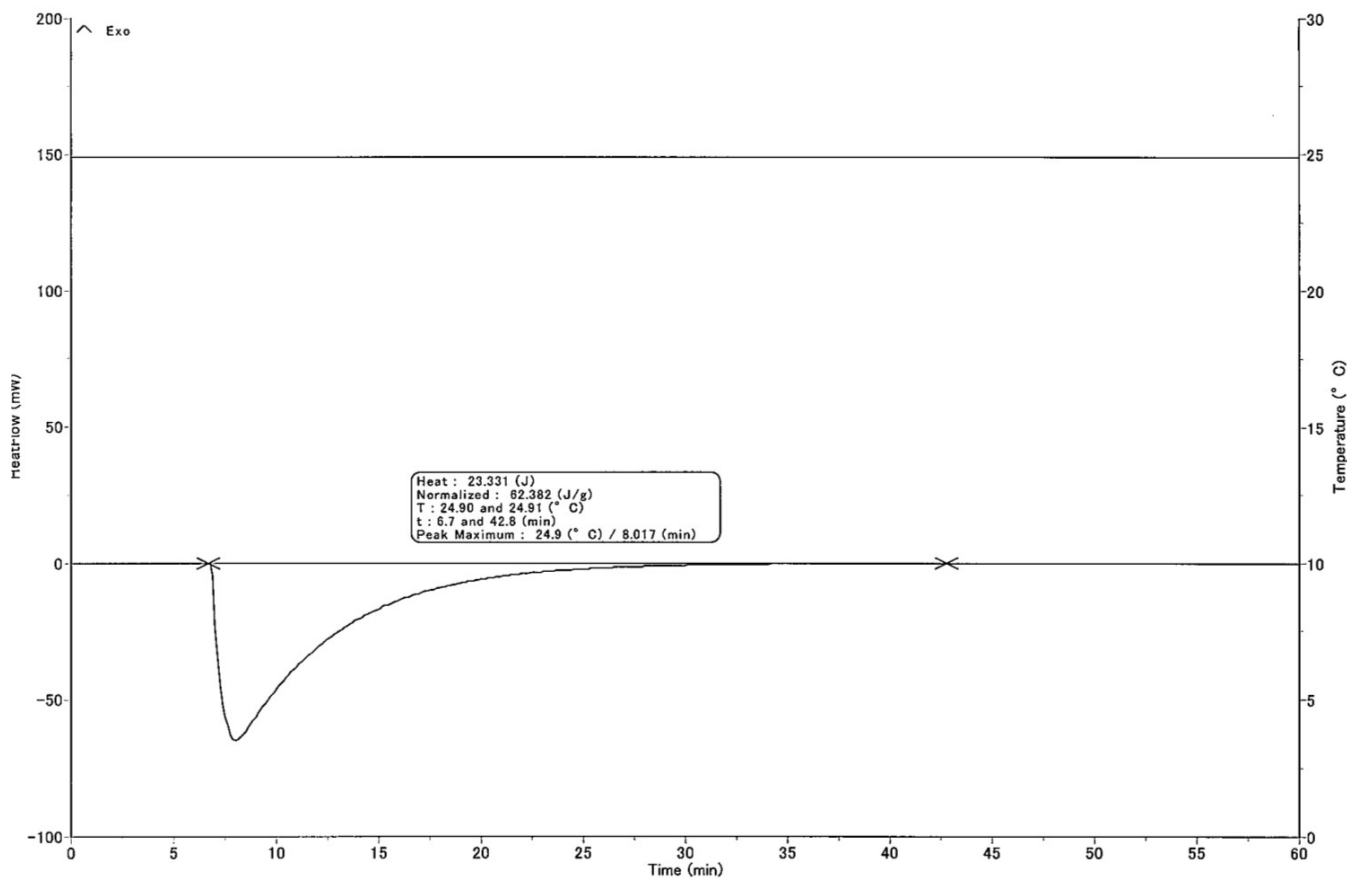
**Figure S2.** Calorimetric Study of  $\text{LiClO}_4$  in MeCN.



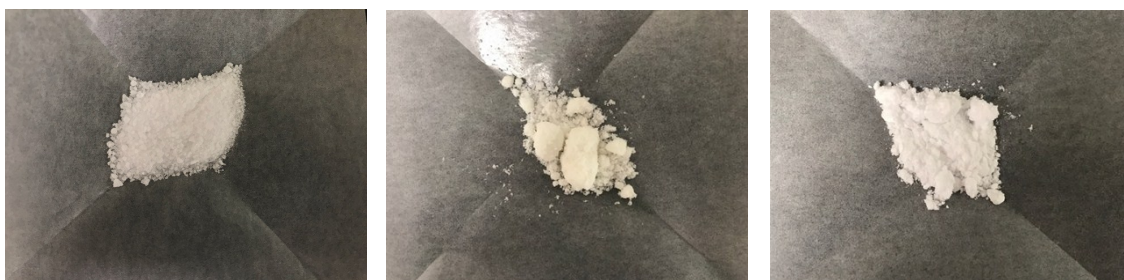
**Figure S3.** Calorimetric Study of  $\text{LiClO}_4$  in MeOH.



**Figure S4.** Calorimetric Study of LiFSI in MeNO<sub>2</sub>.



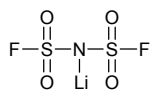
**Figure S5.** Calorimetric Study of LiTFSI in MeNO<sub>2</sub>.



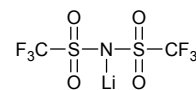
LiClO<sub>4</sub>



LiFSI

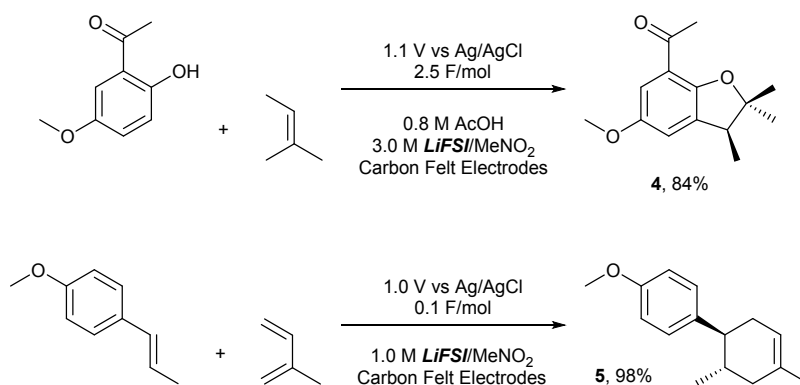


LiTFSI



**Figure S6.** Pictures of the Li<sup>+</sup>-Based Electrolytes.

### Scheme S1. Anodic Cycloadditions in LiFSI/MeNO<sub>2</sub> Electrolyte Solution.



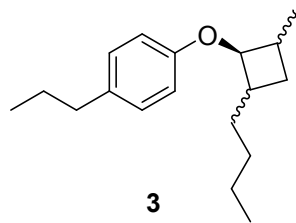
## 2. General Remarks

All reagents and solvents were purchased from commercial sources and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates, with detection by UV absorption (254 nm) and by heating the plates after dipping them in a solution of 12 molybdo(VI) phosphoric acid n-hydrate in 95% ethanol. Silica gel (particle size 40–50  $\mu\text{m}$ ) was used for column chromatography. <sup>1</sup>H NMR spectra were collected on 600 or 400 MHz NMR spectrometers using the deuterated solvent as an internal deuterium reference. Chemical shift data are given in  $\delta$  units calibrated with residual protic solvent. The multiplicity of a signal is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet. <sup>13</sup>C NMR spectra were collected on 150 or 100 MHz spectrometers with proton decoupling using the deuterated solvent as an internal carbon reference. Chemical shift data are given in  $\delta$  units calibrated with residual solvent. All cyclic voltammograms were recorded at 2 mM of substrate using a glassy carbon working electrode, platinum counter electrode, and Ag/AgCl reference electrode in 0.1 M LiClO<sub>4</sub>/MeNO<sub>2</sub> at 100 mV/s.

## 3. Synthesis and Characterization Data



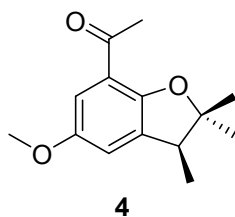
*1-(2-butyl-4-methylcyclobutoxy)-4-propylbenzene (3)<sup>1</sup>, diastereomixture*



To a solution of respective supporting electrolyte (10.0 mmol) in nitromethane (10 mL) stirred at r.t. was added 1-(prop-1-en-1-yloxy)-4-propylbenzene (**1**) (18.5  $\mu$ L, 0.1 mmol) and 1-hexene (**2**) (250  $\mu$ L, 2.0 mmol). The resulting reaction mixture was electrolyzed at r.t. using carbon felt electrodes (2 cm x 2 cm) in an undivided cell with stirring at a constant potential of 1.2 V vs. Ag/AgCl. After completion (1.0 F/mol, also monitored by TLC), the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  and washed with brine. The organic layer was dried over  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. Yields were determined by  $^1\text{H}$  NMR analysis using benzaldehyde as an internal standard.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.05 (2H, m), 6.82 (0.4H, d,  $J = 8.0$  Hz), 6.75 (1.6H, m), 4.71 (0.15H, t,  $J = 7.2$  Hz), 4.19 (0.5H, t,  $J = 7.2$  Hz), 4.17 (0.15H,  $J = 7.2$  Hz), 3.86 (0.2H, t,  $J = 7.2$  Hz), 2.73-2.64 (0.65H, m), 2.60 (0.65H, sept,  $J = 7.2$  Hz), 2.51 (2H, t,  $J = 7.2$  Hz), 2.25-2.13 (0.5H, m), 2.10 (0.2H, q,  $J = 9.5$  Hz), 1.80-1.69 (0.15H, m), 1.69- (3.65H, m), 1.54-1.34 (2H, m), 1.33-1.18 (4H, m), 1.16 (0.6H, d,  $J = 7.2$  Hz), 1.15 (0.45H, d,  $J = 7.2$  Hz) 1.05 (0.45H, d,  $J = 7.2$  Hz), 1.03 (1.5H, d,  $J = 7.2$  Hz), 0.92 (3H, t,  $J = 7.2$  Hz), 0.89-0.82 (3H, m), 0.80 (0.2H, q,  $J = 9.5$  Hz);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.6, 157.0, 156.7, 156.6, 135.1, 134.7, 134.4, 129.4, 129.4, 129.3, 115.9, 114.9, 114.7, 114.6, 84.1, 79.6, 78.3, 75.9, 41.3, 41.0, 38.7, 38.5, 37.4, 36.3, 36.2, 34.6, 34.4, 33.6, 32.8, 31.7, 30.0, 29.7, 29.7, 29.7, 27.9, 27.7, 27.4, 27.2, 25.0, 23.0, 22.9, 22.9, 22.9, 19.9, 19.3, 15.9, 14.4, 14.3, 14.3, 14.3, 14.0.

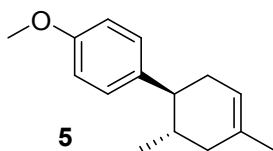
*1-(5-methoxy-2,2,3-trimethyl-2,3-dihydrobenzofuran-7-yl)ethan-1-one (4)*<sup>2</sup>



To a solution of lithium bis(fluorosulfonyl)imide (5.61 g, 30.0 mmol) or lithium bis(trifluoromethane)sulfonamide (7.46 g, 26.0 mmol: *Note that LiTFSI was almost saturated at this concentration*) in nitromethane (10 mL) and acetic acid (457.96  $\mu$ L, 8.0 mmol) stirred at r.t. was added 2-hydroxy-5-methoxyacetophenone (8.31 mg, 0.05 mmol) and 2-methyl-2-butene (52.88  $\mu$ L, 0.5 mmol). The resulting reaction mixture was electrolyzed at r.t. using carbon felt electrodes (2 cm x 2 cm) in an undivided cell with stirring at a constant potential of 1.1 V vs. Ag/AgCl. After completion (2.5 F/mol, also monitored by TLC), the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  and washed with  $\text{NaHCO}_3$  aq. The organic layer was dried over  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. Yields were determined by  $^1\text{H}$  NMR analysis using benzaldehyde as an internal standard.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.16 (1H, d,  $J = 2.2$  Hz), 6.87 (1H, q,  $J = 1.4$  Hz), 3.79 (3H, s), 3.13 (1H, q,  $J = 7.2$  Hz), 2.61 (3H, s), 1.51 (3H, s), 1.30 (3H, s), 1.23 (3H, d,  $J = 7.5$  Hz);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  197.2, 153.7, 153.7, 137.2, 120.0, 118.2, 108.6, 91.2, 56.0, 45.3, 31.4, 28.1, 22.2, 14.6.

*4'-methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (5)*<sup>3</sup>



To a solution of lithium bis(fluorosulfonyl)imide (1.87 g, 10.0 mmol) or lithium bis(trifluoromethane)sulfonamide (2.87 g, 10.0 mmol) in nitromethane (10 mL) stirred at r.t. was added *trans*-anethole (150  $\mu$ L, 1.0 mmol) and isoprane (303  $\mu$ L, 3.0 mmol). The resulting reaction mixture was electrolyzed at r.t. using carbon felt electrodes (2 cm x 2 cm) in an undivided cell with stirring at a constant potential of 1.0 V vs. Ag/AgCl. After completion (0.1 F/mol, also monitored by TLC), the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with brine. The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. Yields were determined by <sup>1</sup>H NMR analysis using benzaldehyde as an internal standard.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$  7.07 (2H, d,  $J$  = 8.6 Hz), 6.83 (2H, d,  $J$  = 8.3 Hz), 5.44 (1H, br. s), 3.78 (3H, s), 2.29 (1H, m), 2.23-2.10 (2H, m), 2.07 (1H, dd,  $J$  = 17.4, 5.0 Hz), 1.93-1.84 (1H, m), 1.83-1.76 (1H, m), 1.68 (3H, s), 0.70 (3H, d,  $J$  = 6.2 Hz); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  157.9, 138.3, 133.9, 128.6, 121.0, 113.8, 55.3, 47.1, 39.9, 35.4, 34.1, 23.5, 20.4.

(1) Okada, Y.; Chiba, K. *Electrochim. Acta* **2010**, *55*, 4112–4119.

(2) Kim, S.; Hirose, K.; Uematsu, J.; Mikami, Y.; Chiba, K. *Chem. Eur. J.* **2012**, *18*, 6284–6288.

(3) Okada, Y.; Yamaguchi, Y.; Ozaki, A.; Chiba, K. *Chem. Sci.* **2016**, *7*, 6387–6393.

#### 4. Calorimetric Studies

All calorimetric studies were carried out using reversal mixing vessel. The two chambers of the reversal mixing vessel are separated by a tilting lid. The samples (liquid-liquid or liquid-solid) are separately introduced into the vessel outside of the calorimeter. In order to obtain a complete separation of the chambers, a mercury seal on the lid can be used. If the vapor pressures of the samples are low, the mercury

seal is not required. After the introduction of the vessels into the calorimeter, the thermal equilibrium is to be achieved in order to have the two separated components at the same temperature. Then, mixing is performed by reversing the calorimeter. If the samples mix easily, only a few rotations of the calorimeter are necessary. In the case of difficult mixing, the reversing mechanism can be maintained during the whole test.

