

Supporting Information

Determination of Hydride Affinities of Various Aldehydes and Ketones in Acetonitrile

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SI-1. Experimental Section

S1. Materials

All reagents were of commercial quality from freshly opened containers or were purified before use. Reagent grade acetonitrile was refluxed over KMnO_4 and K_2CO_3 for several hours and was doubly distilled over P_2O_5 under argon before use. 4-acetylamino-2,2,6,6-tetramethyl-piperidine-1-oxoam-monium perchlorate (TEMPO^+) was prepared according to literature method.^{S1}

S2. Preparation of Hydrides of Aldehydes and ketones (XH^-)

Hydrides of aldehydes and ketones (XH^-) were prepared in situ from the reactions of the corresponding alcohols (XH_2) with 1.0–1.05 equivalents of KH in dry acetonitrile, which was identified by ^1H NMR spectrum (see Figures S1 and S2).

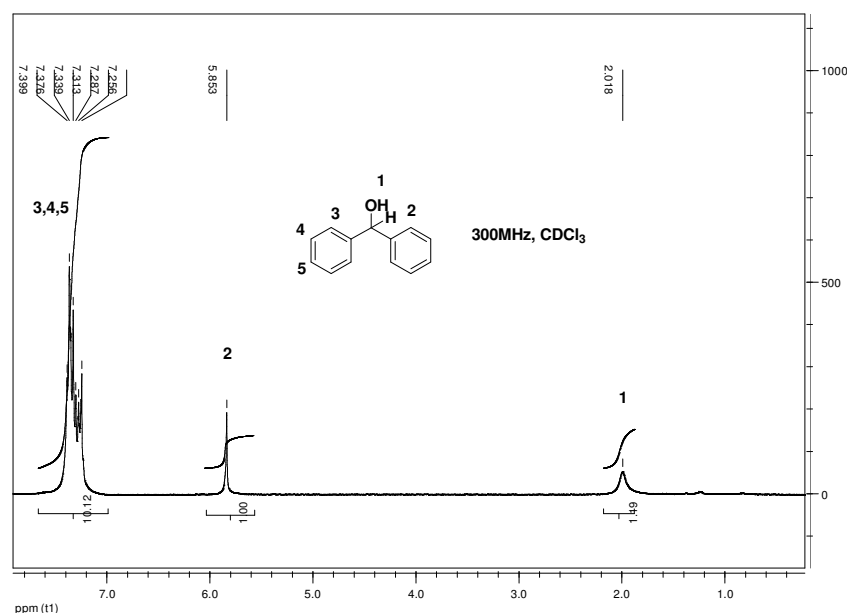


Figure S1. ^1H NMR spectrum of 16H_2 in CDCl_3 .

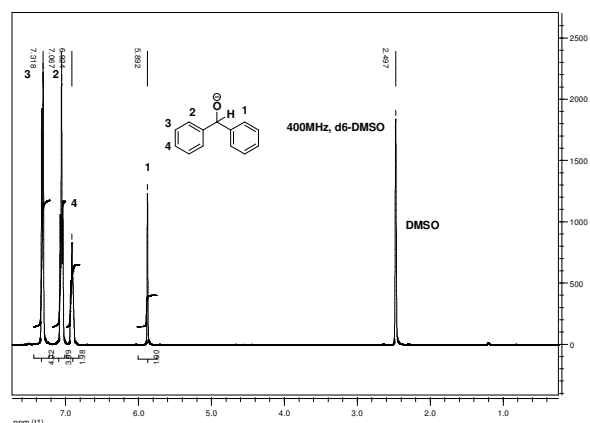


Figure S2. ^1H NMR spectrum of **16H** which was directly derived from **16** in DMSO by addition of KH.

S3. Product Analyses

The hydrides of aldehydes and ketones (**XH**[•]), such as **16H**[•] in acetonitrile was mixed with 0.5–1.0 equivalents of TEMPO⁺ in dry acetonitrile. The reaction mixtures were then stirred for 3 h at ambient temperature. Subsequently H₂O was added. The reaction mixture was then extracted with CH₂Cl₂. The combined organic layers were washed with H₂O and dried over Na₂SO₄. Evaporation of the solvent under reduced pressure yielded the crude products which were purified by chromatography (SiO₂, PE/EtOAc). The oxidation product of **16H**[•] was **16**, which was characterized by ^1H NMR (Figure S3) and IR (Figure S4), respectively.

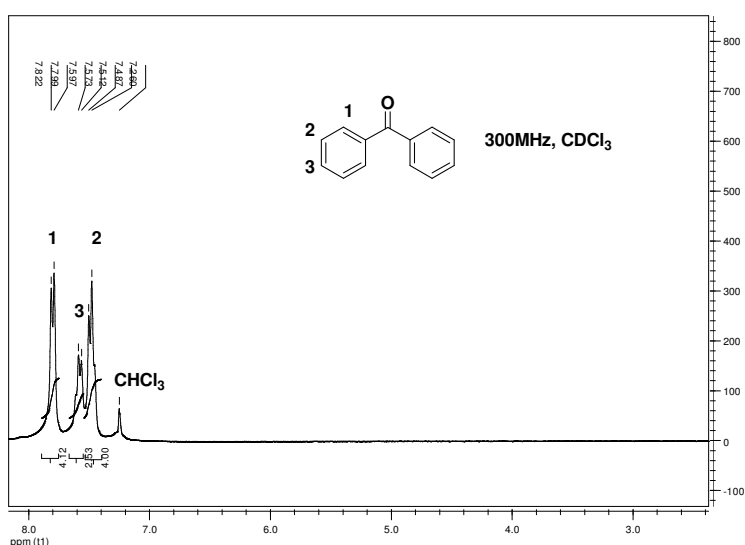


Figure S3. ^1H NMR spectrum of **16**, which was directly derived from the reaction of **16H**[•] and TEMPO⁺ in acetonitrile.

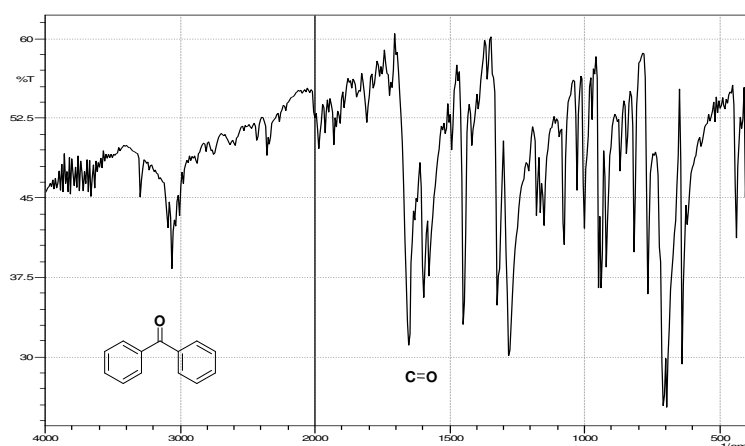


Figure S4. IR spectrum of **16**, which was derived from the reaction of **16H⁻** and TEMPO⁺ in acetonitrile.

S4. Reaction Tracer Experiment

The hydride transfer from **13H⁻** to TEMPO⁺ in acetonitrile was monitored by using UV-vis absorption spectra (see Figure S5). The result showed that **13H⁻** was completely changed into **13** when slightly excess TEMPO⁺ was added into the **13H⁻** solution.

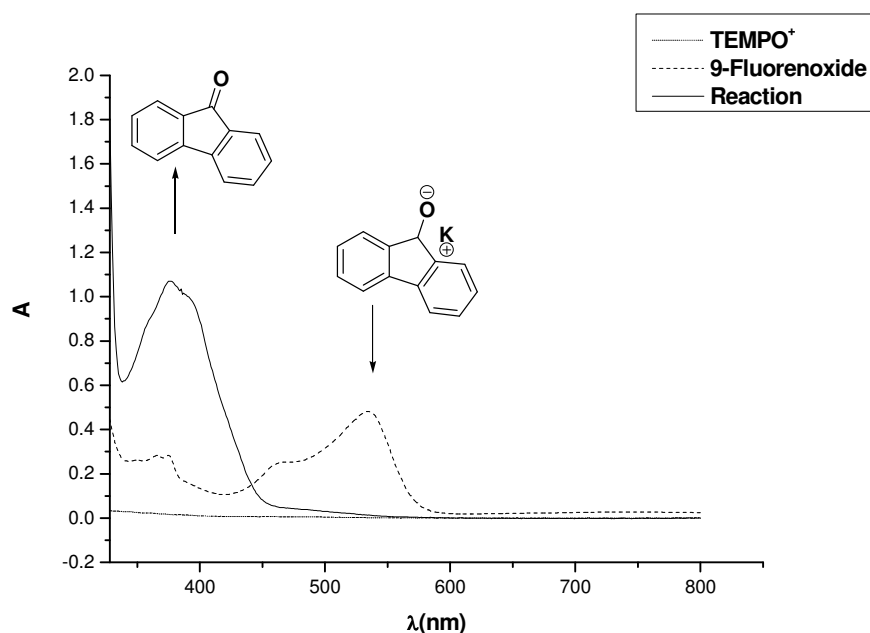


Figure S5. UV-Vis spectrum of the reaction mixture of **13H⁻** and TEMPO⁺ in acetonitrile after 5 minutes when the two reactants were mixed (full line). The dot line is the UV-Vis spectrum of TEMPO⁺ in acetonitrile. The dash line is the UV-Vis spectrum of **13H⁻** in acetonitrile.

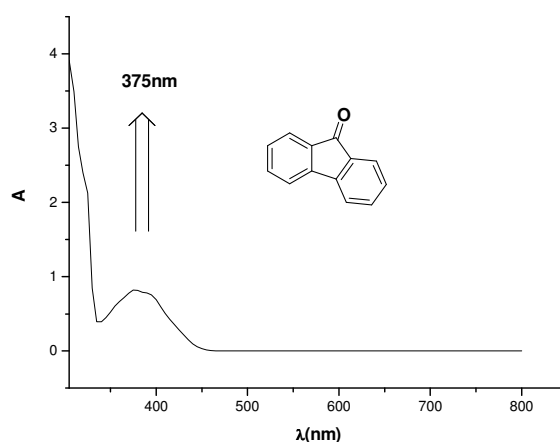


Figure S6. UV-Vis spectrum of pure **13** in acetonitrile.

S5. Isothermal Titration Calorimetry (ITC)

The titration experiments were performed on a CSC4200 isothermal titration calorimeter in acetonitrile at 298 K. The performance of the calorimeter was checked by measuring the standard heat of neutralization of an aqueous solution of sodium hydroxide with a standard aqueous HCl solution. Data points were collected every 2 s. The heat of reaction was determined following 10 automatic injections from a 250 μL injection syringe containing a standard solution into the reaction cell (1.30 mL) containing 1 mL of other concentrated reactant. Injection volumes (10 μL) were delivered in 0.5 s time intervals with 500 s between every two injections.

Ref:

S1. Bobbitt, J. M. *J. Org. Chem.* **1998**, *63*, 9367.

SI-2. Some Representative ITC Spectra (Figures S7-S27)

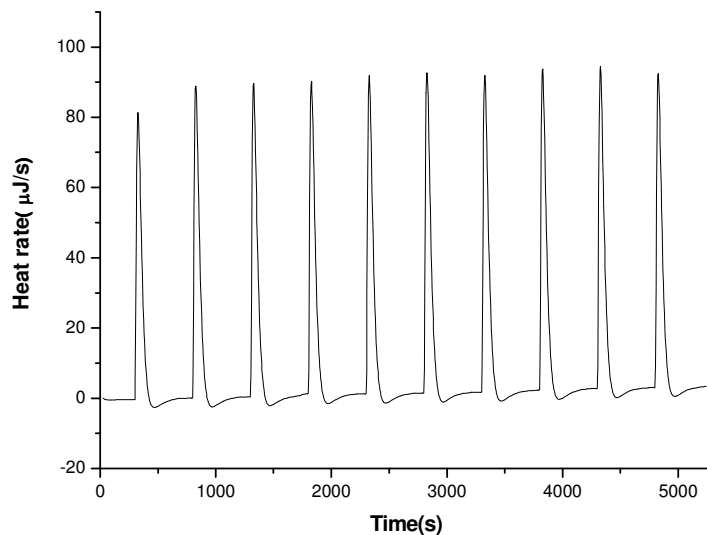


Figure S7. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion 1H^- with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO^+) in acetonitrile at 298 K. Titration was conducted by adding 10 μl of TEMPO^+ (1.89 mM) every 500 s into the acetonitrile containing the 1H^- (ca. 20.0 mM), which was obtained in situ from the reactions of the corresponding alcohol (1H_2) with KH. The reaction heat was obtained by integration of each peak except the first one.

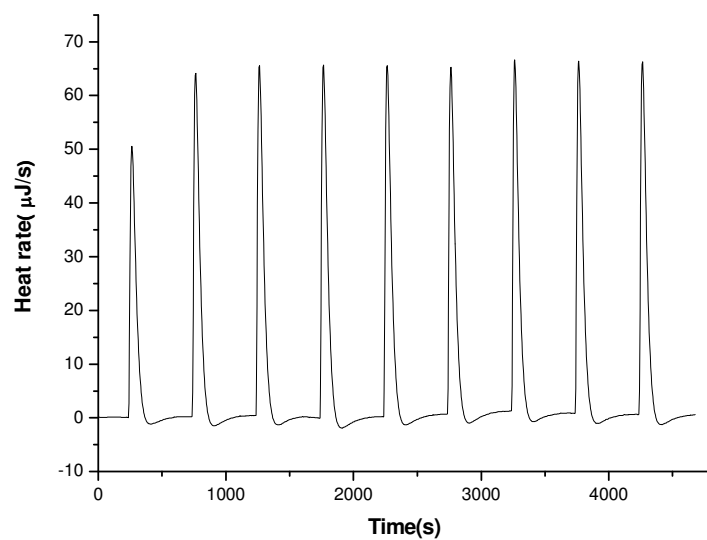


Figure S8. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion 2H^- with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO^+) in acetonitrile at 298 K. Titration was conducted by adding 10 μl of TEMPO^+ (1.29 mM) every 500 s into the acetonitrile containing the 2H^- (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (2H_2) with KH. The reaction heat was obtained by integration of each peak except the first one.

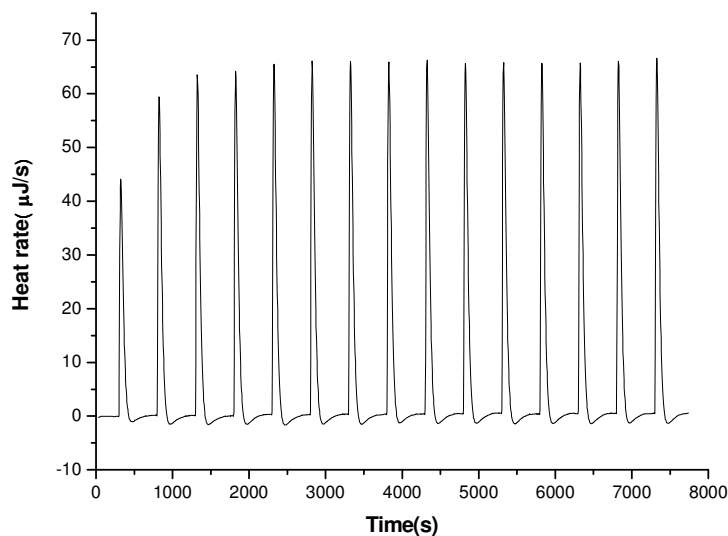


Figure S9. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion 3H^- with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO^+) in acetonitrile at 298 K. Titration was conducted by adding $10\ \mu\text{l}$ of TEMPO^+ (1.28 mM) every 500 s into the acetonitrile containing the 3H^- (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (3H_2) with KH. The reaction heat was obtained by integration of each peak except the first two.

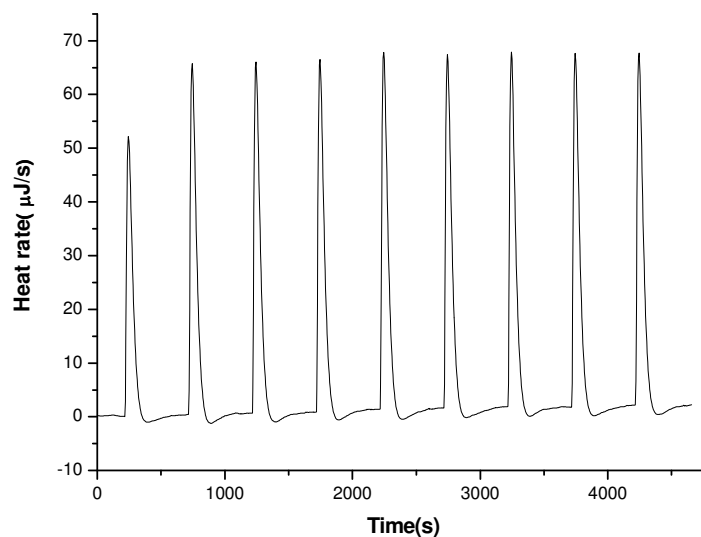


Figure S10. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion 4H^- with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO^+) in acetonitrile at 298 K. Titration was conducted by adding $10\ \mu\text{l}$ of TEMPO^+ (1.23 mM) every 500 s into the acetonitrile containing the 4H^- (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (4H_2) with KH. The reaction heat was obtained by integration of each peak except the first one.

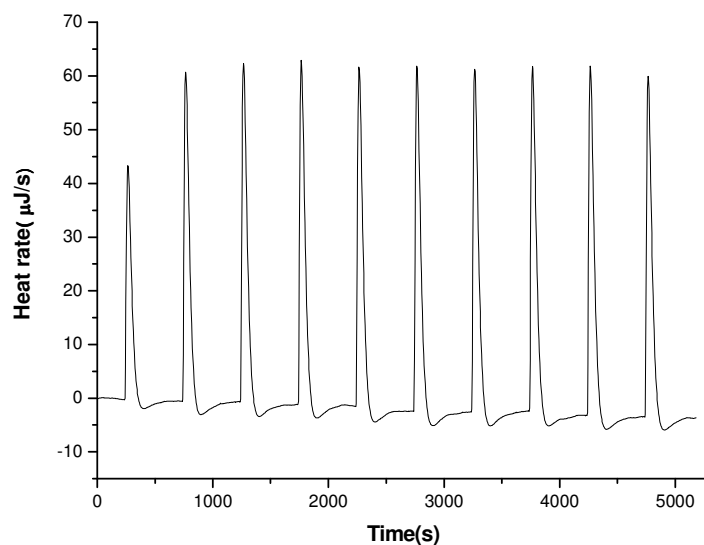


Figure S11. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **5H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.47 mM) every 500 s into the acetonitrile containing the **5H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**5H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

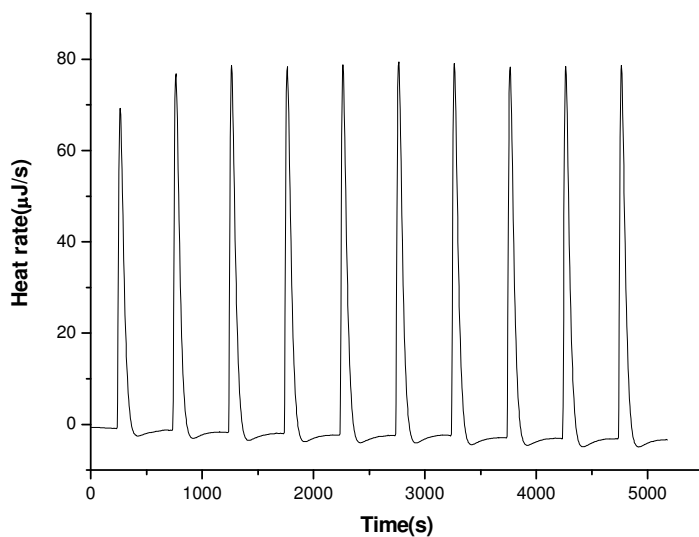


Figure S12. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **6H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.75 mM) every 500 s into the acetonitrile containing the **6H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**6H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

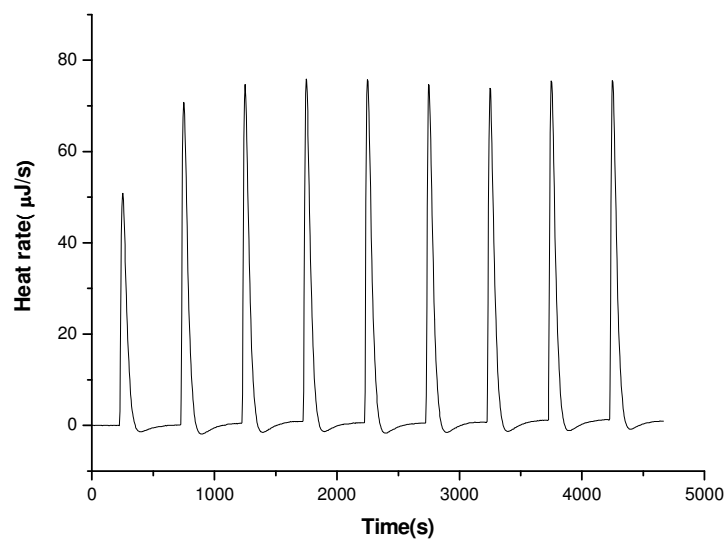


Figure S13. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **7H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.29 mM) every 500 s into the acetonitrile containing the **7H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**7H₂**) with KH. The reaction heat was obtained by integration of each peak except the first two.

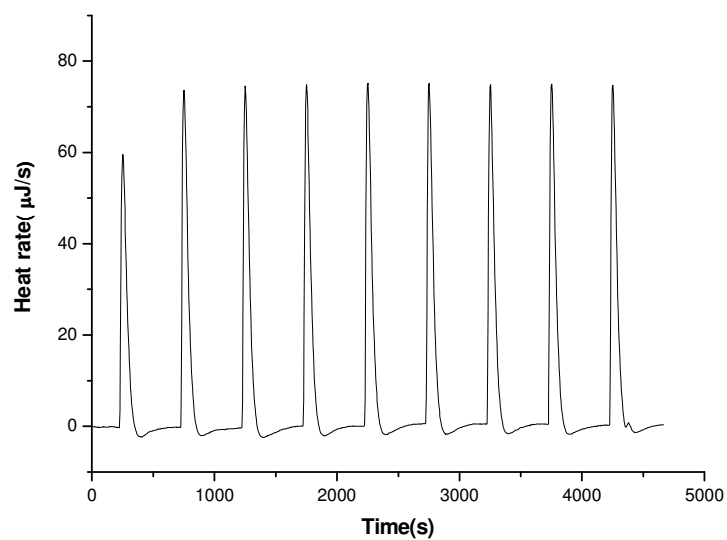


Figure S14. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **8H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.27 mM) every 500 s into the acetonitrile containing the **8H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**8H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

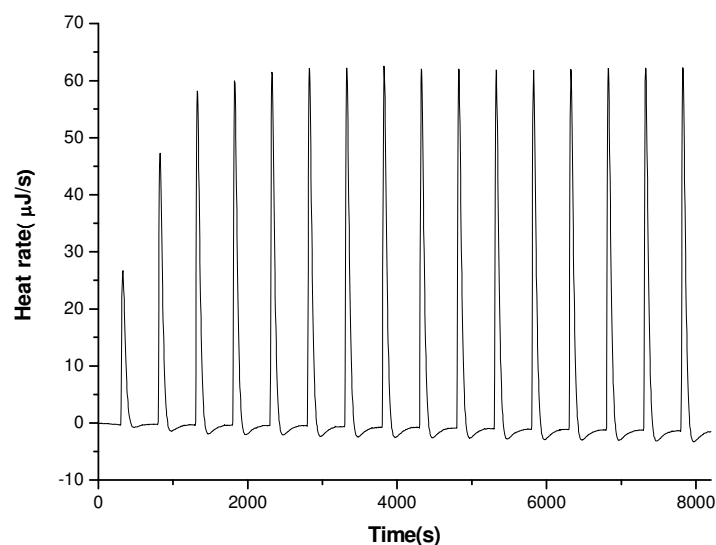


Figure S15. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **9H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.25 mM) every 500 s into the acetonitrile containing the **9H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**9H₂**) with KH. The reaction heat was obtained by integration of each peak except the first three.

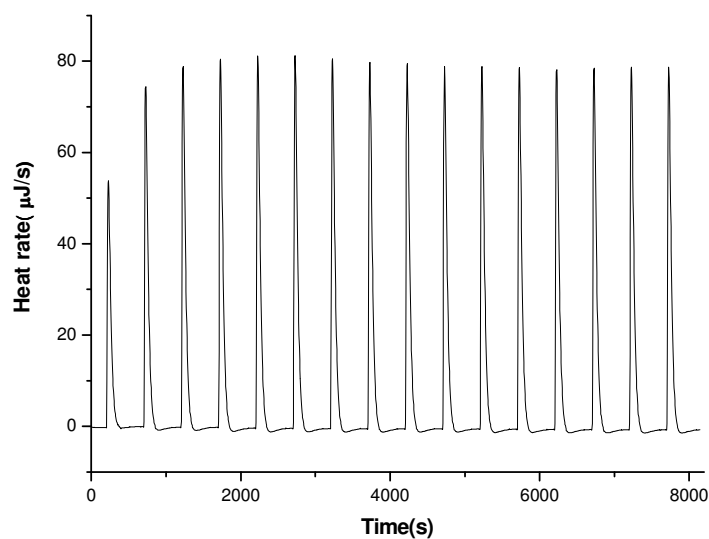


Figure S16. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **10H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.64 mM) every 500 s into the acetonitrile containing the **10H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**10H₂**) with KH. The reaction heat was obtained by integration of each peak except the first two.

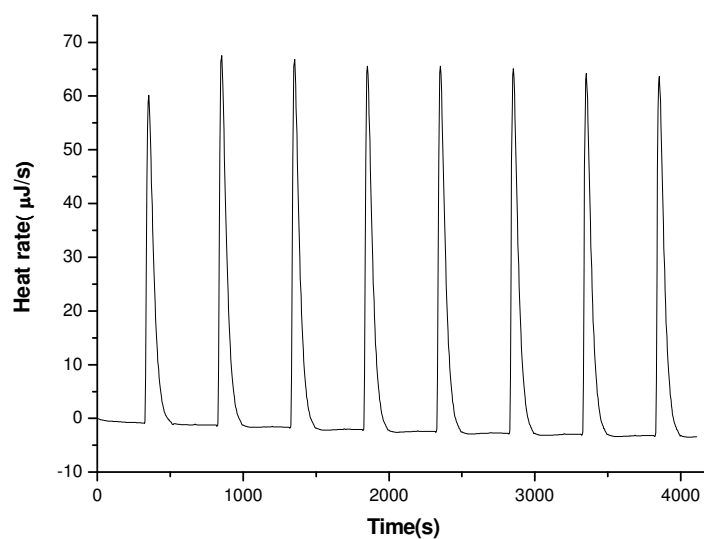


Figure S17. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **11H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.65 mM) every 500 s into the acetonitrile containing the **11H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**11H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

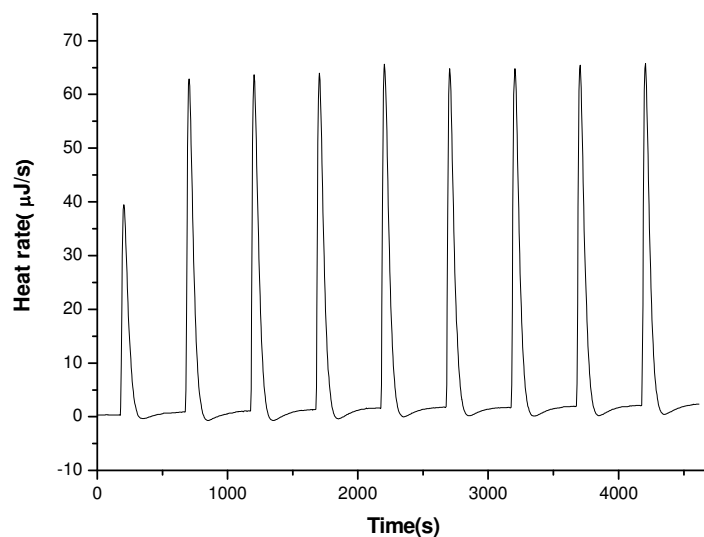


Figure S18. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **12H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.25 mM) every 500 s into the acetonitrile containing the **12H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**12H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

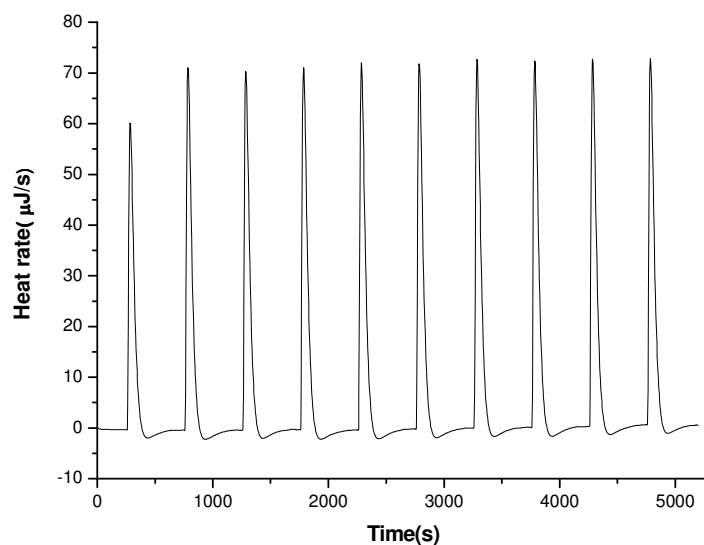


Figure S19. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **13H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μl of TEMPO⁺ (1.78 mM) every 500 s into the acetonitrile containing the **13H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**13H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

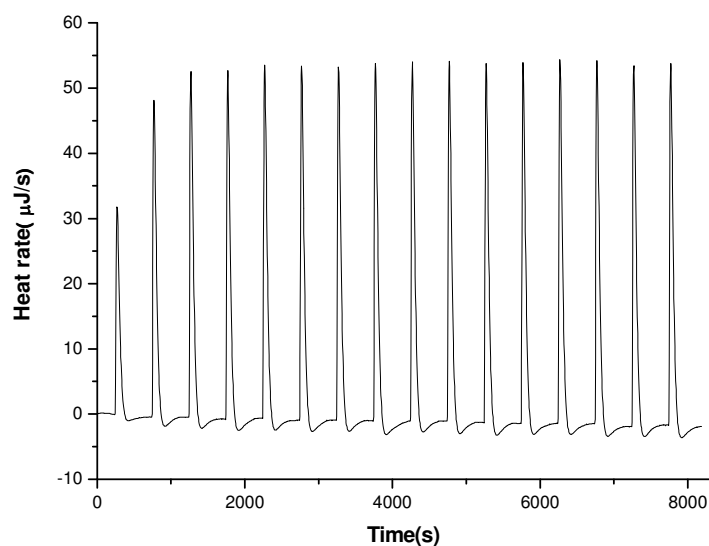


Figure S20. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **14H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μl of TEMPO⁺ (1.38 mM) every 500 s into the acetonitrile containing the **14H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**14H₂**) with KH. The reaction heat was obtained by integration of each peak except the first two.

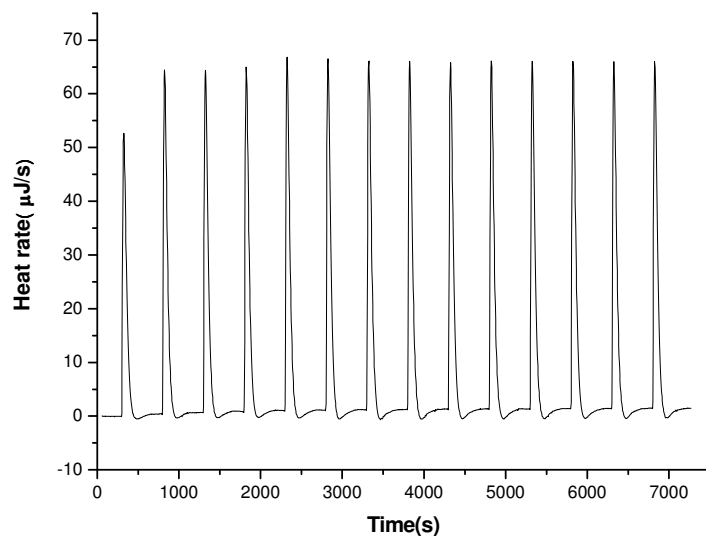


Figure S21. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **15H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.57 mM) every 500 s into the acetonitrile containing the **15H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**15H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

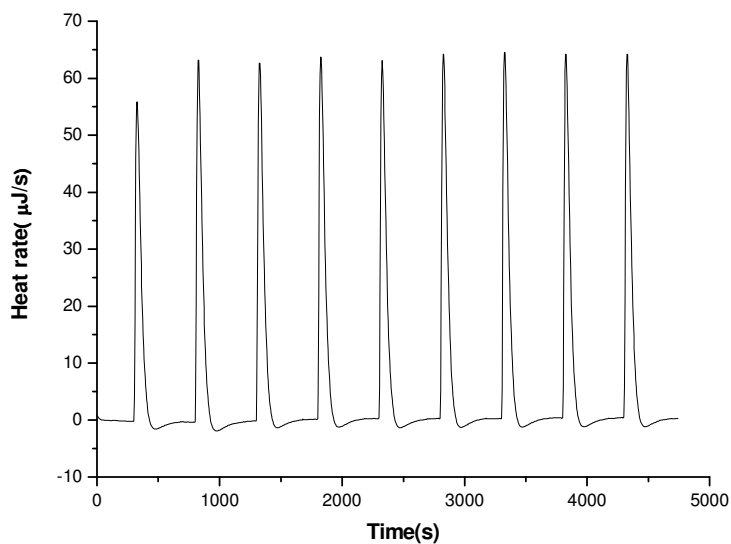


Figure S22. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **16H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.27 mM) every 500 s into the acetonitrile containing the **16H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**16H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

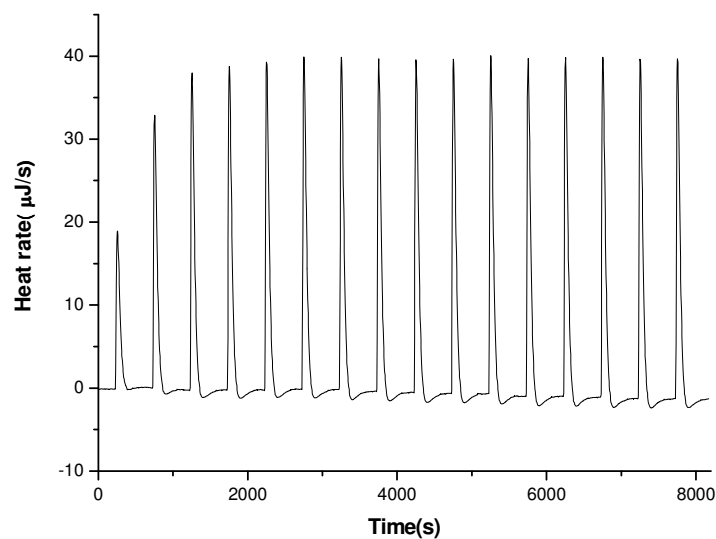


Figure S23. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **17H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.20 mM) every 500 s into the acetonitrile containing the **17H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**17H₂**) with KH. The reaction heat was obtained by integration of each peak except the first two.

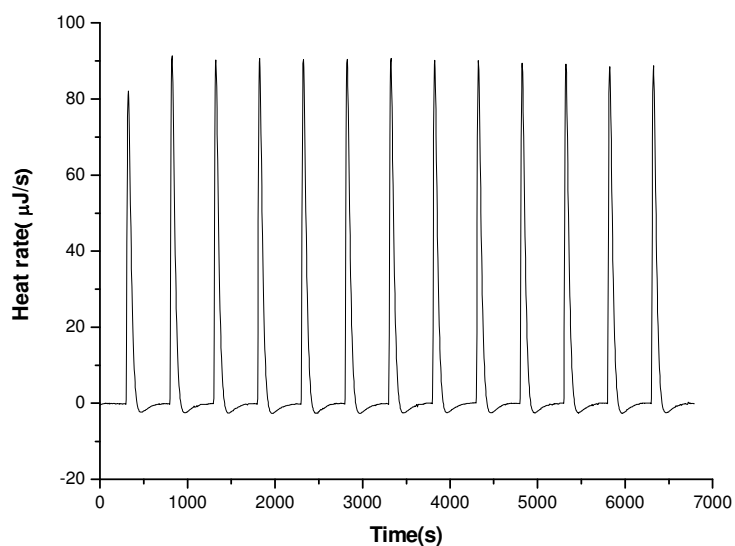


Figure S24. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **18H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.76 mM) every 500 s into the acetonitrile containing the **18H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**18H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

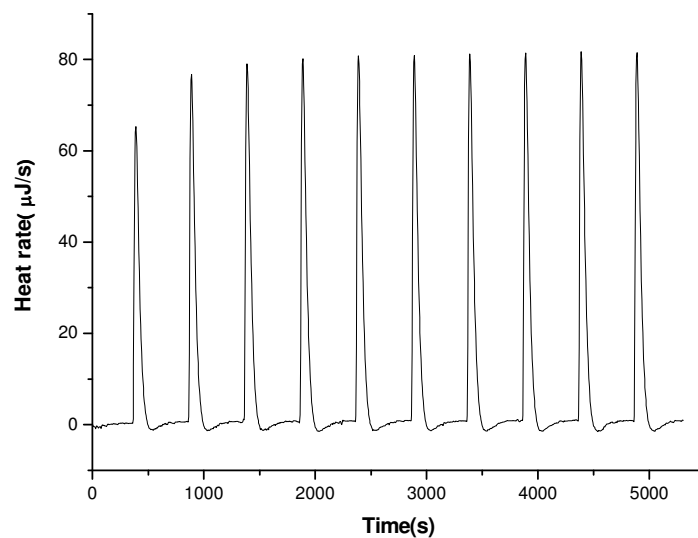


Figure S25. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **19H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.61 mM) every 500 s into the acetonitrile containing the **19H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**19H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

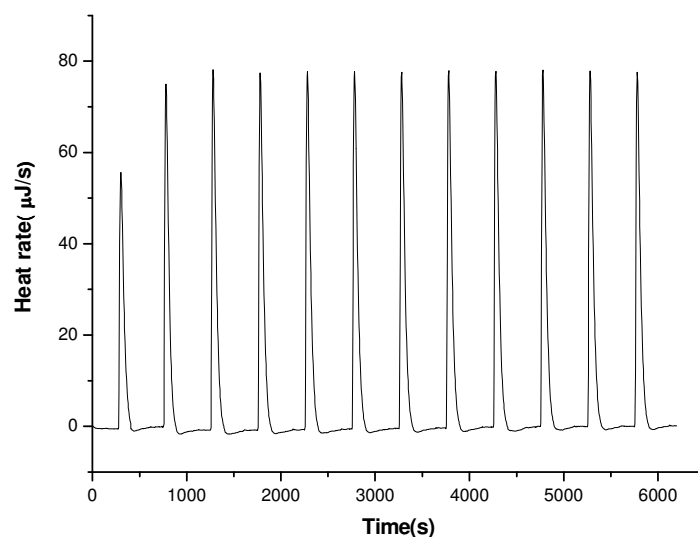


Figure S26. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **20H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.78 mM) every 500 s into the acetonitrile containing the **20H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**20H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.

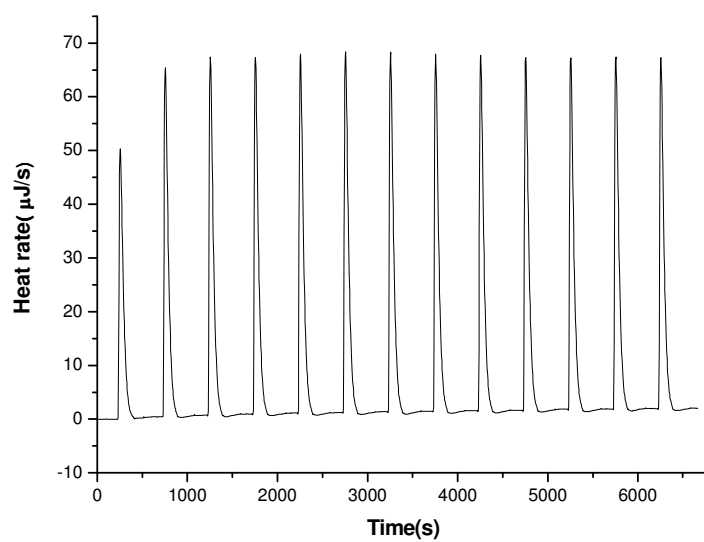


Figure S27. Isothermal titration calorimetry (ITC) for the reaction heat of alkoxide anion **21H⁻** with 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate (TEMPO⁺) in acetonitrile at 298 K. Titration was conducted by adding 10 μ l of TEMPO⁺ (1.53 mM) every 500 s into the acetonitrile containing the **21H⁻** (ca. 20.0 mM), which was obtained in situ from the reaction of the corresponding alcohol (**21H₂**) with KH. The reaction heat was obtained by integration of each peak except the first one.