

## Supporting Information

### Terminal and Internal Olefin Epoxidation with Cobalt(II) as the Catalyst: Evidence for an Active Oxidant $\text{Co}^{\text{II}}$ -Acylperoxo Species

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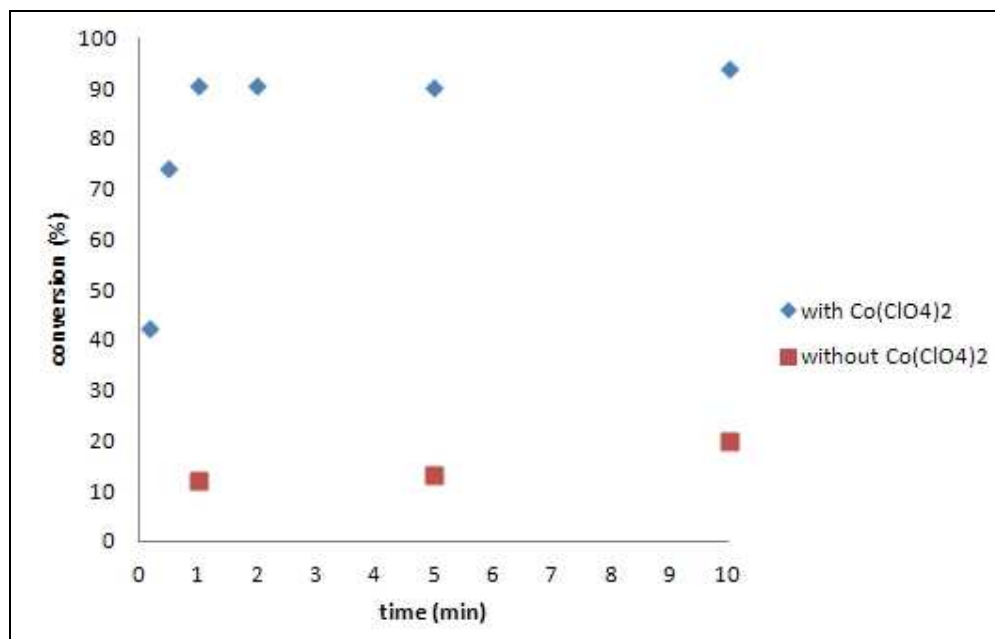
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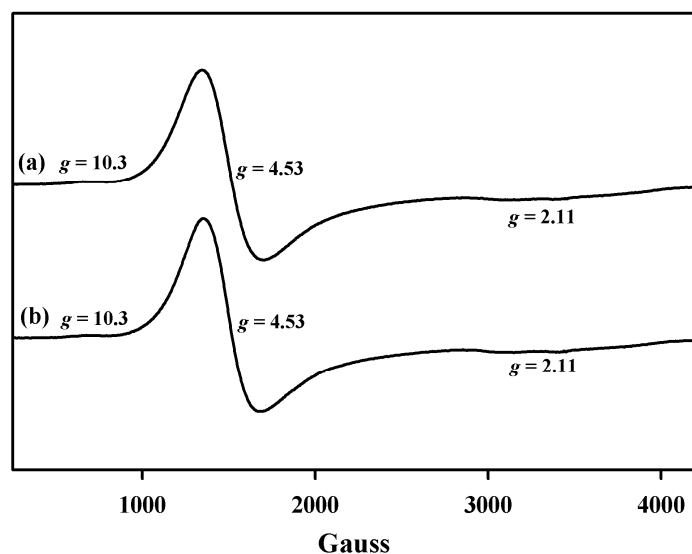
**Table S1.** Percentage of  $^{18}\text{O}$ -incorporated from  $\text{H}_2^{18}\text{O}$  into cyclohexene oxide formed during cyclohexene oxidation by MCPBA and cobalt(II) perchlorate<sup>[a]</sup>

Entry	Amount of cyclohexene (M)	Amount of MCPBA (M)	Amount of $\text{H}_2^{18}\text{O}$ (M)	$^{18}\text{O}$ in cyclohexene oxide (%)
1	0.02	0.01	0.556	0
2	0.02	0.01	1.111	0
3	0.02	0.01	2.222	0
4	0.01	0.01	2.222	0

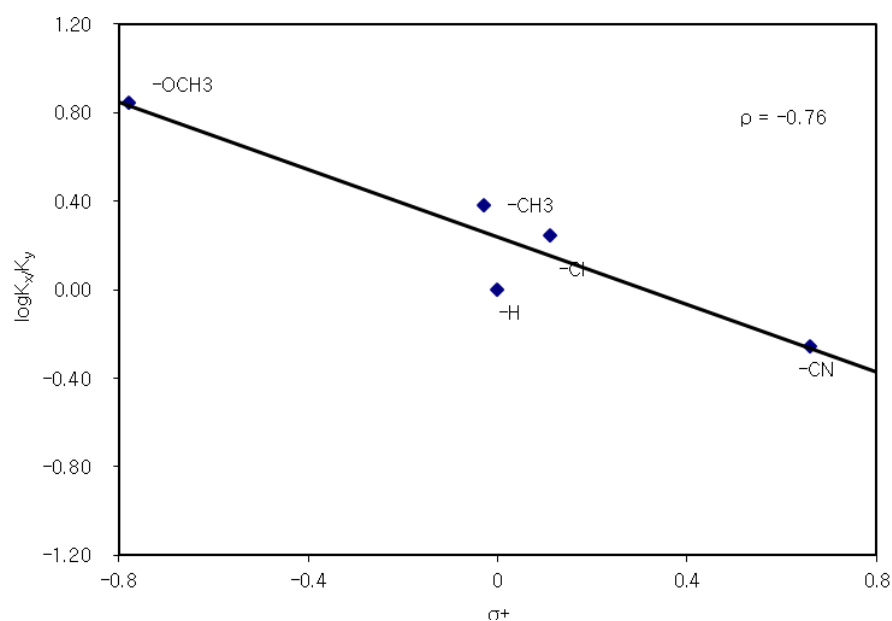
[a] Reaction conditions: cyclohexene (0.01-0.02 mmol), catalyst ( $1.0 \times 10^{-3}$  mmol), MCPBA (0.01 mmol), solvent (1 mL, anhydrous  $\text{CH}_3\text{CN}$ ).



**Figure S1.** Epoxidation reaction of cyclohexene (35 mM) by MCPBA (50 mM) in the absence and the presence of Co(ClO<sub>4</sub>)<sub>2</sub> (1 mM) in CH<sub>3</sub>CN (1 mL) at room temperature.



**Figure S2.** X-band EPR spectra of (a)  $\text{Co}(\text{ClO}_4)_2$  (1 mM) and (b) the reaction solution that was frozen 5 s and 1 min, respectively, after  $\text{Co}(\text{ClO}_4)_2$  (1 mM) was mixed with MCPBA (1.2 or 50 mM) at  $-40^\circ\text{C}$  in MeCN. The same EPR spectra were obtained for the reaction solutions prepared at room temperature. X-band EPR spectra were taken at 5 K using a X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Low temperatures were achieved and controlled with an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. The experimental parameters for EPR spectra were as follows: Microwave frequency = 9.646 GHz, microwave power = 1 mW, modulation amplitude = 10 G, gain =  $5 \times 10^3$ , time constant = 40.96 ms, conversion time = 81.00 ms.



**Figure S3.** Hammett plot for relative reactivities of styrene to *para*-substituted styrenes by MCPBA. To a mixture of styrene (0.03 mmol) and *para*(X)-substituted styrene (0.03 mmol, X = -OCH<sub>3</sub>, -CH<sub>3</sub>, -Cl, and -CN) in CH<sub>3</sub>CN (1 mL) was added MCPBA (0.05 mmol). The mixture was stirred for 10 min at room temperature. The amounts of styrenes before and after reactions were determined by GC. The relative reactivities were determined using the following equation:  $k_x/k_y = \log(X_f/X_i)/\log(Y_f/Y_i)$  where  $X_i$  and  $X_f$  are the initial and final concentrations of substituted styrenes and  $Y_i$  and  $Y_f$  are the initial and final concentrations of styrene.