

# **Immobilization of a Boron Center-functionalized Scorpionate Ligand on Mesoporous Silica Supports for Heterogeneous Tp-based Catalysts**

Ayaka Nakamizu<sup>†</sup>, Takeshi Kasai<sup>†</sup>, Jun Nakazawa<sup>\*,†</sup>, Shiro Hikichi<sup>\*,†</sup>

<sup>†</sup>*Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University*

*3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan*

\*Corresponding authors

E-mail: hikichi@kanagawa-u.ac.jp (S. Hikichi), jnaka@kanagawa-u.ac.jp (J. Nakazawa)

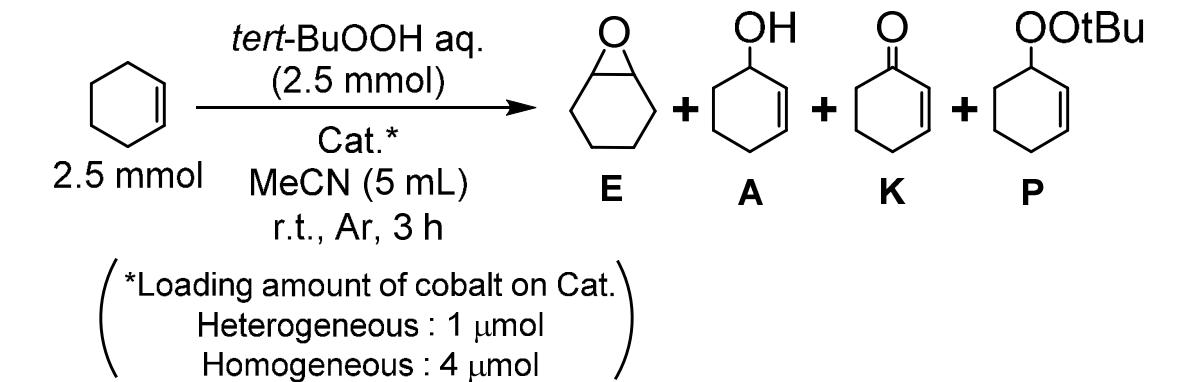
**Table S1.** Physicochemical properties of the supports.

	$x$ of $\text{SBA}^{\text{SH}}(x)$		$x$ of $\text{SBA}^{\text{COOH-L}}(x)$	
	<b>0.5</b>	<b>1.0</b>	<b>0.5</b>	<b>1.0</b>
BET surface area / $\text{m}^2 \cdot \text{g}^{-1}$	524	507	505	494
Pore volume / $\text{cm}^3 \cdot \text{g}^{-1}$	0.90	0.83	0.84	0.86
Average pore diameter / nm	5.86	5.55	5.60	5.79

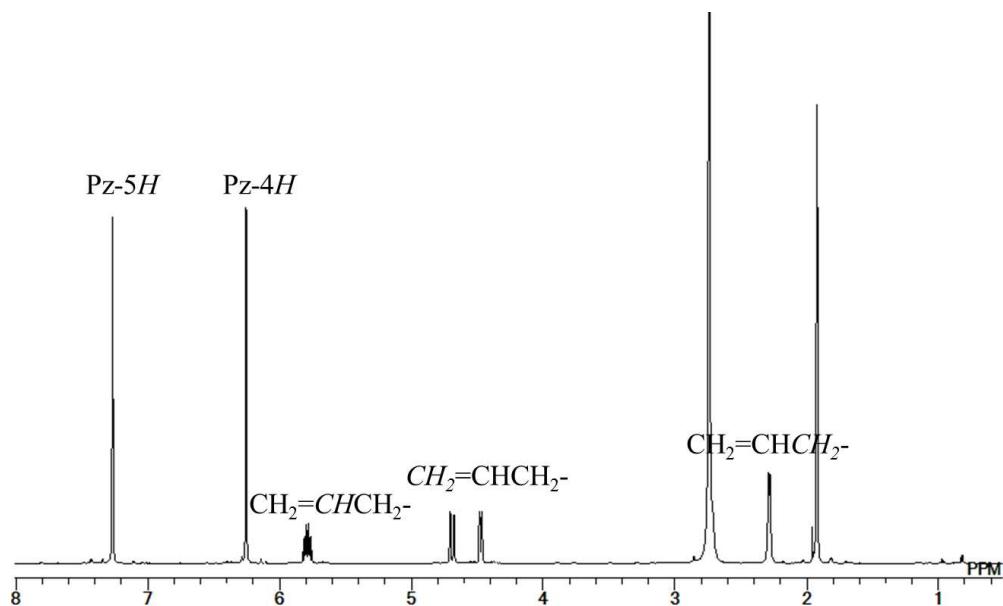
**Table S2.** Loading amounts of  $\text{Tp}^{\text{CF3}}$ , SH, and cobalt on the catalysts.

Support	Loadings on the Cat. / $\text{mmol} \cdot \text{g}^{-1}$			Co/Tp <sup>CF3</sup> on the Cat.
	$\text{Tp}^{\text{CF3}}$ Density of $\text{Tp}^{\text{CF3}}$ / molecule $\cdot \text{nm}^{-2}$	SH	Co	
$\text{SBA}^{\text{SH}}(0.5)$	—	0.052	Not detected 0.13	—
$\text{SBA}^{\text{SH-Tp}}(0.5)$	0.051 (0.061)	0.001	0.055 0.038	1.08 0.74
$\text{SBA}^{\text{SAc-Tp}}(0.5)$	0.051 (0.061)	(none)	0.042 0.065	0.82 1.27
$\text{SBA}^{\text{SH}}(1.0)$	—	0.097	0.0004 0.23	—
$\text{SBA}^{\text{SH-Tp}}(1.0)$	0.065 (0.079)	0.032	0.10 0.12	1.54 1.85
$\text{SBA}^{\text{SAc-Tp}}(1.0)$	0.065 (0.079)	(none)	0.063 0.082	0.97 1.26

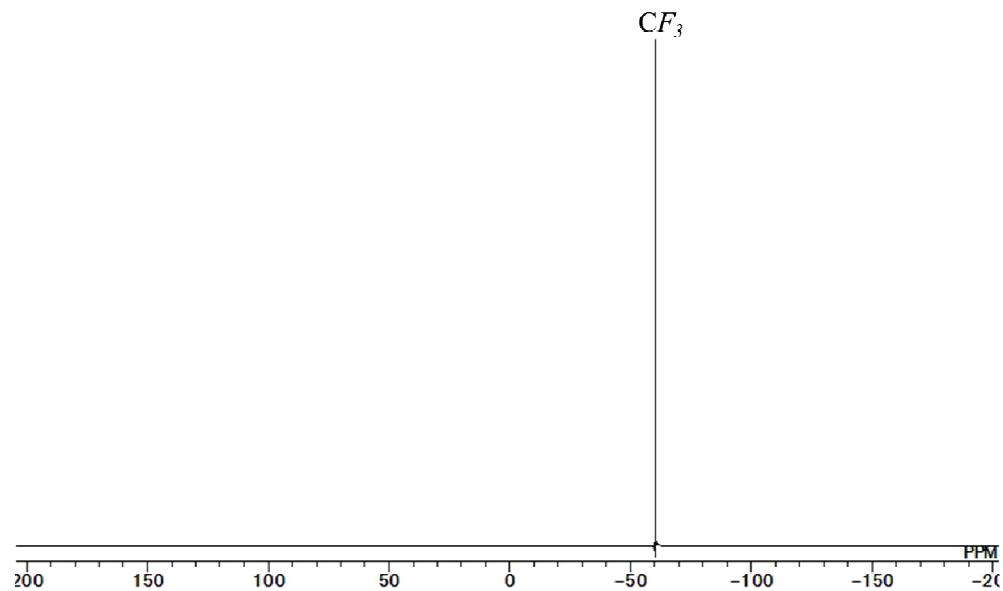
**Table S3.** Products yields and TONs of the immobilized catalysts on the oxidation of cyclohexene with *tert*-BuOOH.



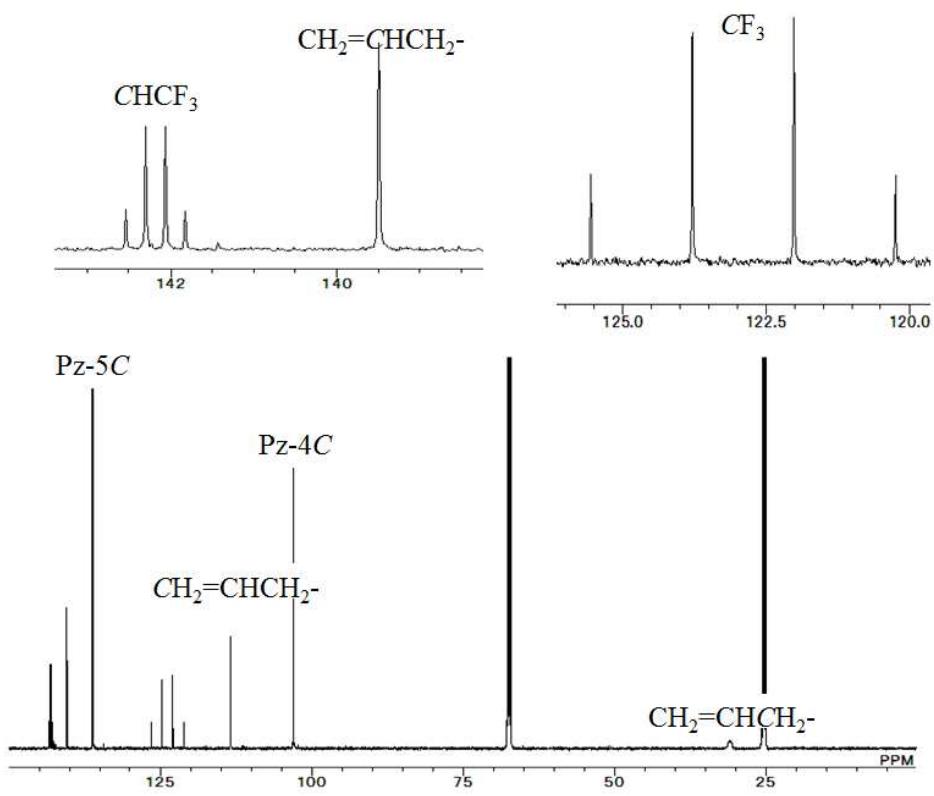
Source of Co	Support	Amounts of products / $\mu\text{mol}$				TON
		E	A	K	P	
None	None	0.48	1	1.42	3.87	—
	None (genuine salt : homogeneous)	0.67	5.11	4.97	16.51	8.1
	None (Complex <b>1</b> : homogeneous)	3.64	3.27	11.90	21.83	12.5
$\text{CoBr}_2$	<b>SBA</b> <sup>SH-TpCF<sub>3</sub></sup> (0.5)	3.55	5.05	18.36	23.41	68.8
	<b>SBA</b> <sup>SAc-TpCF<sub>3</sub></sup> (0.5)	2.32	9.12	26.44	31.63	95.4
	<b>SBA</b> <sup>SH-TpCF<sub>3</sub></sup> (1.0)	6.72	1.43	4.33	14.97	31.8
	<b>SBA</b> <sup>SAc-TpCF<sub>3</sub></sup> (1.0)	7.07	4.17	25.49	24.55	87.6
	None (genuine salt : homogeneous)	1.41	2.79	11.13	49.32	18.9
$\text{Co(OAc)}_2$	<b>SBA</b> <sup>SH</sup> (0.5)	11.71	3.84	23.01	24.47	84.7
	<b>SBA</b> <sup>SH-TpCF<sub>3</sub></sup> (0.5)	4.00	10.27	16.64	28.72	64.5
	<b>SBA</b> <sup>SAc-TpCF<sub>3</sub></sup> (0.5)	4.03	13.46	30.45	39.05	117.9
	<b>SBA</b> <sup>SH-TpCF<sub>3</sub></sup> (1.0)	13.84	4.53	23.92	23.92	91.6
	<b>SBA</b> <sup>SAc-TpCF<sub>3</sub></sup> (1.0)	6.06	4.12	17.38	22.45	65.8



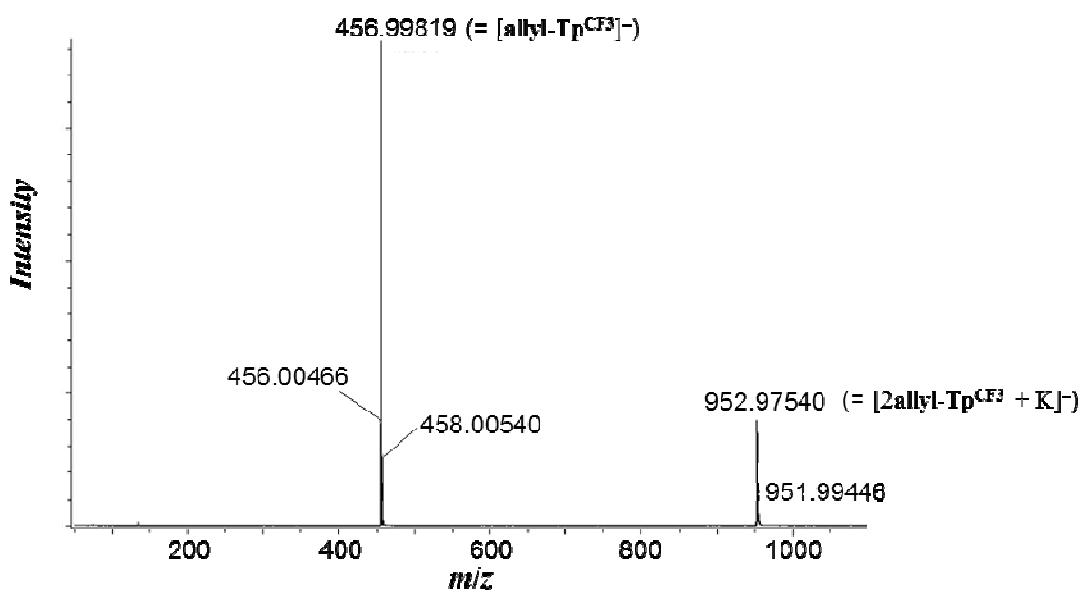
**Figure S1.**  $^1\text{H}$  NMR spectrum of  $[\text{K}(\text{allyl}-\text{Tp}^{\text{CF}_3})]$  ( $\text{C}_3\text{D}_6\text{O}$ , r.t.)



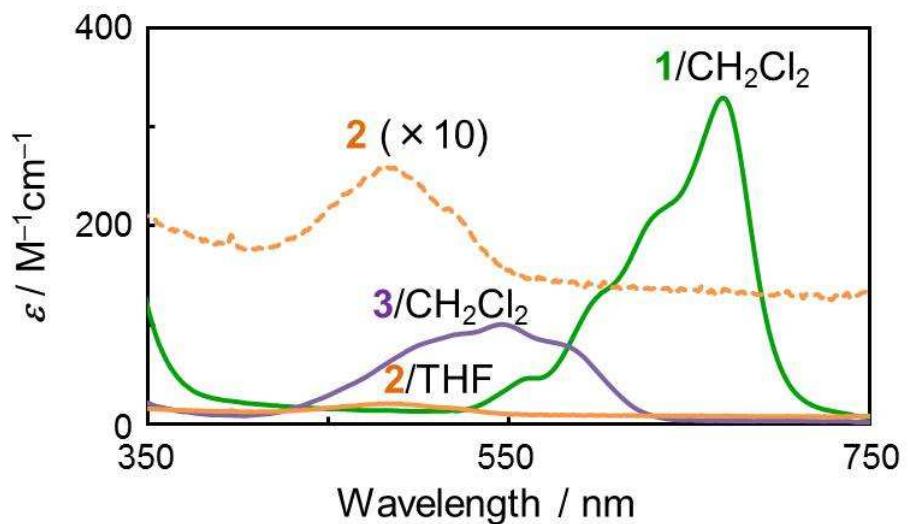
**Figure S2.**  $^{19}\text{F}$  NMR spectrum of  $[\text{K}(\text{allyl}-\text{Tp}^{\text{CF}_3})]$  ( $\text{C}_3\text{D}_6\text{O}$ , r.t.)



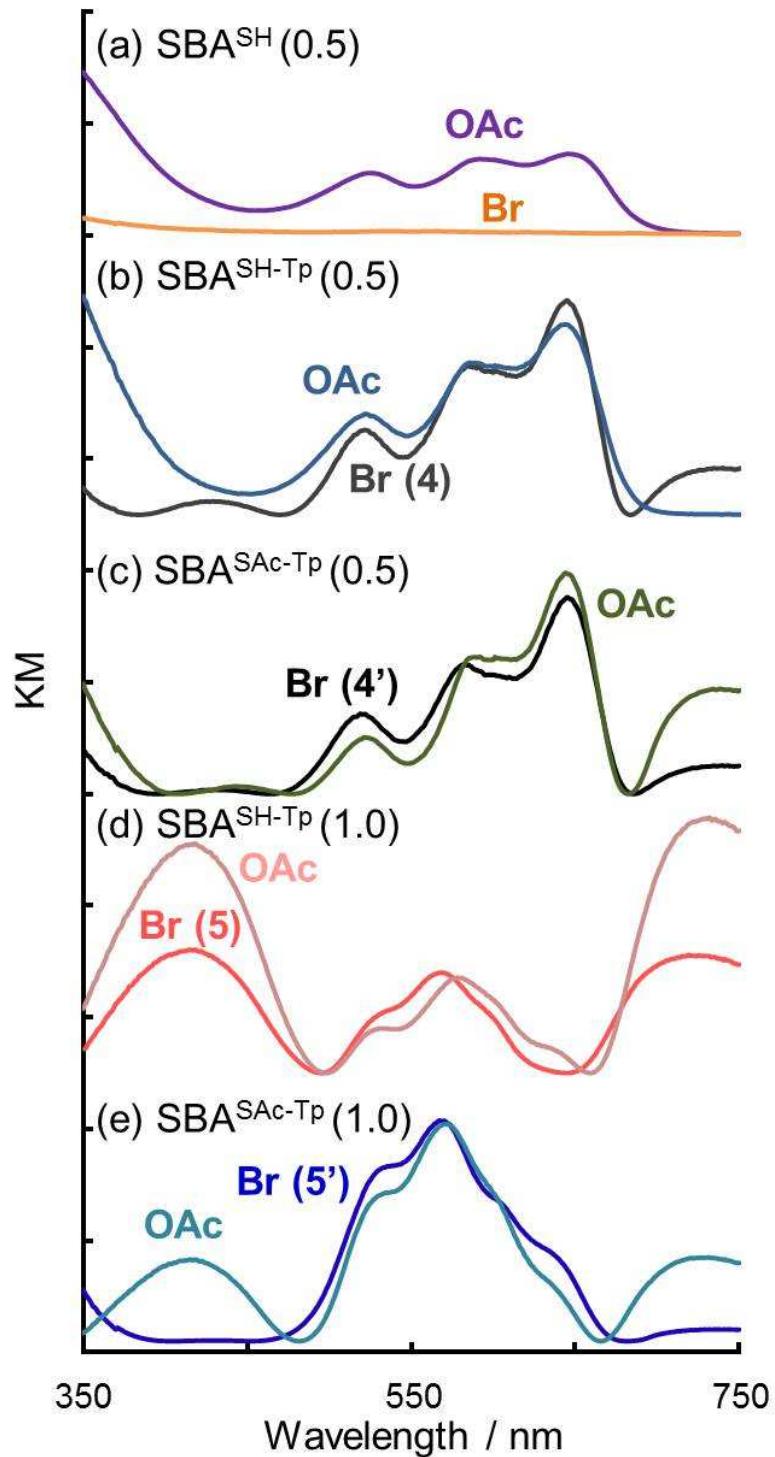
**Figure S3.**  $^{13}\text{C}$  NMR spectrum of  $[\text{K}(\text{allyl}-\text{Tp}^{\text{CF3}})]$  ( $\text{THF}-d_8$ , r.t.)



**Figure S4.** ESI-MS spectrum of  $[\text{K}(\text{allyl}-\text{Tp}^{\text{CF3}})]$  (anion mode)



**Figure S5.** UV-vis spectra of solutions of the complexes **1**, **2**, and **3**.



**Figure S6.** Diffuse reflectance UV-vis spectra of the immobilized cobalt species derived from  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$  (indicated as “Br”) and  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (as “OAc”) on the each supports.