## **Supplementary information**

## C(sp<sup>3</sup>)–H bond activation by carboxylate-adduct of osmium tetroxide (OsO<sub>4</sub>)

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	Contents	Page
Fig. S1:	(a) UV-vis spectral changes observed in the titration of $OsO_4$ by $Bu_4NOBz$ at 30 °C.	S3
	(b) Plot of $(A-A_0)/(A_{\infty}-A)$ against $[Bu_4NOBz]_0 - \alpha[OsO_4]_0$ .	
<b>Fig. S2</b> :	FT–IR spectra of $1^{OAc}$ and $1^{OBz}$ .	S4
<b>Fig. S3</b> :	Cyclic voltammograms of (a) $OsO_4$ , (b) $1^{OAc}$ and (c) $1^{OBz}$ in $CH_3CN$ .	S5
Fig. S4:	(a)UV-vis spectral changes observed in the titration of OsO4 by Bu4NOAc at 70 $^{\circ}\mathrm{C}.$	S6
	(b) Plot of $(A-A_0)/(A_{\infty}-A)$ against $[Bu_4NOBz]_0 - \alpha[OsO_4]_0$ .	
<b>Fig. S5</b> :	UV-vis spectrum of the authentic sample of $[Ph_4P][Os^{VII}O_4]$ in CH <sub>3</sub> CN.	S6
<b>Fig. S6</b> :	ESI–MS after the reaction of $1^{OAc}$ with xanthene.	S7
Table S1:	Oxidation of xanthene by $OsO_4$ , $1^{OAc}$ and $1^{OBz}$ .	<b>S</b> 7
Fig. S7:	(a) UV-vis spectral changes upon addition of xanthene to $1^{OBz}$ .	S8
	(b) Time course of the growth of Os species monitored at 694 nm.	
	(c) The plot of $k_{obs}$ against [xanthene].	
<b>Fig. S8</b> :	(a) UV-vis spectral changes observed in the titration of $OsO_4$ by $Bu_4NOBz$ at 70 °C.	S9
	(b) Plot of $(A-A_0)/(A_{\infty}-A)$ against $[Bu_4NOBz]_0 - \alpha[OsO_4]_0$ .	
Fig. S9:	(a) UV-vis spectral changes upon addition of xanthene- $d_2$ to $1^{OAc}$ .	S10
	(b) Time course of the growth of Os species monitored at 694 nm.	
	(c) The plot of $k_{obs}$ against [xanthene- $d_2$ ].	
Fig. S10:	(a) UV-vis spectral changes upon addition of [9,10-dihydroanthracene] to 1 <sup>OAc</sup> .	S11
	<ul><li>(b) Time course of the growth of Os species monitored at 694 nm.</li><li>(c) The plot of k<sub>obs</sub> against [9,10-dihydroanthracene].</li></ul>	
<b>Fig. S11</b> :	<ul> <li>(a) UV-vis spectral changes observed upon addition of fluorene to 1<sup>OAc</sup>.</li> <li>(b) Time course of the growth of Os species monitored at 694 nm.</li> <li>(c) The plot of k<sub>obs</sub> against [fluorene].</li> </ul>	S12
Fig. S12:	<ul> <li>(a) UV-vis spectral changes observed upon addition of tetralin to 1<sup>OAc</sup>.</li> <li>(b) Time course of the growth of Os species monitored at 694 nm.</li> <li>(c) The plot of k<sub>obs</sub> against [tetralin].</li> </ul>	S13
Fig. S13:	The plot of $k_{obs}$ against the concentration of the substrates.	S13
<b>Fig. S14</b> :	3D structures during the oxidation of xanthene by 1 <sup>OAc</sup> .	S14
Fig. S15:	Energy plots of relaxed scan calculations as a function of C–O distance.	S15
Scheme S1	: A possible reaction scheme for the generation of Os <sup>VII</sup> products.	S15



**Fig. S1** (a) UV-vis spectral changes observed in the titration of OsO<sub>4</sub> (0.5 mM) by Bu<sub>4</sub>NOBz in acetonitrile at 30 °C. Inset: Plot of  $\Delta Abs$  at 390 nm against [Bu<sub>4</sub>NOBz]. (b) Plot of  $(A-A_0)/(A_{\infty}-A)$  against [Bu<sub>4</sub>NOBz]<sub>0</sub> –  $\alpha$ [OsO<sub>4</sub>]<sub>0</sub>.



**Fig. S2** FT-IR spectra of  $1^{OAc}$  (red) and  $1^{OBz}$  (blue) in a range from (a) 800 to 1000 cm<sup>-1</sup> and (b) 500 to 4000 cm<sup>-1</sup>.



**Fig. S3** Cyclic voltammograms of (a)  $OsO_4$ , (b)  $1^{OAc}$  and (c)  $1^{OBz}$  in CH<sub>3</sub>CN containing 0.1 M of Bu<sub>4</sub>NPF<sub>6</sub> as the electrolyte at 25 °C. Conditions:  $[OsO_4]_0 = 1.0$  mM,  $[Bu_4NOAc] = 10$  mM,  $[Bu_4NOBz] = 10$  mM, Scan rate = 100 mV/sec.



**Fig. S4** (a) UV-vis spectral changes observed in the titration of OsO<sub>4</sub> by Bu<sub>4</sub>NOAc at 70 °C. Inset:  $\Delta$ Abs at 390 nm. (b) Plot of  $(A-A_0)(A_{\infty}-A)$  against [Bu<sub>4</sub>NOAc]<sub>0</sub> –  $\alpha$ [OsO<sub>4</sub>]<sub>0</sub> according to eq (1).  $K_{\rm f}^{\rm OAc} = 1.3 \times 10^3 \,{\rm M}^{-1}$  at 70 °C in CH<sub>3</sub>CN



Fig. S5 UV-vis spectrum of the authentic sample of [PPh4][Os<sup>VII</sup>O4] in CH<sub>3</sub>CN.



Fig. S6 ESI-MS of the resultant solution after the reaction of 1<sup>OAc</sup> with xanthene.

Table S1. Oxidation of xanthene by  $OsO_4$ ,  $1^{OAc}$  and  $1^{OBz}$  in  $CH_3CN$ .





**Fig. S7** UV-vis spectral change of  $1^{OBz}$  ([OsO4]<sub>0</sub> = 0.5 mM, [Bu4NOBz]<sub>0</sub> = 20 mM) observed upon addition of xanthene (5.0 mM) in CH<sub>3</sub>CN at 70 °C under N<sub>2</sub> atmosphere. (b) The time course of the growth of Os<sup>VII</sup> species monitored at 694 nm ([xanthene] = 5.0 mM). Inset: Plot of ln( $A_{\infty} - A_t$ ) against the reaction time. (c) Plot of  $k_{obs}$  against [xanthene].



**Fig. S8** (a) UV-vis spectral changes observed in the titration of OsO<sub>4</sub> by Bu<sub>4</sub>NOBz at 70 °C. Inset:  $\Delta$ Abs at 390 nm. (b) Plot of  $(A-A_0)(A_{\infty}-A)$  against [Bu<sub>4</sub>NOBz]<sub>0</sub> –  $\alpha$ [OsO<sub>4</sub>]<sub>0</sub> according to equation (1).  $K_f^{OBz} = 1.0 \times 10^3 \text{ M}^{-1}$  at 70 °C in CH<sub>3</sub>CN



**Fig. S9.** (a) UV-vis spectral change of  $1^{OAc}$  ([OsO<sub>4</sub>]<sub>0</sub> = 1.0 mM, [NBu<sub>4</sub>OAc]<sub>0</sub> = 20 mM) upon addition of xanthene- $d_2$  (40 mM) in CH<sub>3</sub>CN at 70 °C under N<sub>2</sub> atmosphere. (b) The time course of the growth of Os<sup>VII</sup> species monitored at 694 nm ([xanthene- $d_2$ ] = 40 mM). Inset: Plot of ln( $A_{\infty} - A_t$ ) against the reaction time. (c) The plot of  $k_{obs}$  against [xanthene- $d_2$ ].



**Fig. S10** (a) UV-vis spectral change of  $1^{OAc}$  ([OsO<sub>4</sub>]<sub>0</sub> = 1.0 mM, [Bu<sub>4</sub>NOAc]<sub>0</sub> = 20 mM) upon addition of 9,10-dihydroanthracene (10 mM) in CH<sub>3</sub>CN at 70 °C under N<sub>2</sub> atmosphere. (b) The time course of the growth of Os<sup>VII</sup> species monitored at 694 nm ([9,10-dihydroanthracene] = 10 mM). Inset: Plot of  $\ln(A_{\infty} - A_{t})$  against the reaction time. (c) The plot of  $k_{obs}$  against [9,10-dihydroanthracene].



**Fig. S11** (a) UV-vis spectral change of  $1^{OAc}$  ([OsO<sub>4</sub>]<sub>0</sub> = 1.0 mM, [Bu<sub>4</sub>NOAc]<sub>0</sub> = 20 mM) upon addition of fluorene (50 mM) in CH<sub>3</sub>CN at 70 °C under N<sub>2</sub> atmosphere. (b) The time course of the growth of Os<sup>VII</sup> species monitored at 694 nm ([fluorene] = 50 mM). Inset: Plot of ln( $A_{\infty} - A_t$ ) against the reaction time. (c) The plot of  $k_{obs}$  against [fluorene].



**Fig. S12** (a) UV-vis spectral change of  $1^{OAc}$  ([OsO<sub>4</sub>]<sub>0</sub> = 1.0 mM, [Bu<sub>4</sub>NOAc]<sub>0</sub> = 20 mM) upon addition of tetralin (250 mM) in CH<sub>3</sub>CN at 70 °C under N<sub>2</sub> atmosphere. (b) The time course of the growth of Os<sup>VII</sup> species monitored at 694 nm ([tetralin] = 250 mM). Inset: Plot of ln( $A_{\infty} - A_t$ ) against the reaction time. (c) The plot of  $k_{obs}$  against [tetralin].



**Fig. S13** The plot of  $k_{obs}$  against the concentration of the substrates.



**Fig. S14** DFT-calculated 3D-structures of (a) reactant complex, (b) the transition state, (c) intermediate A and substrate radical and (d) product **B**.



Fig S15. Energy plots of relaxed scan calculations as a function of C–O distance.



Scheme S1. A possible mechanism for the generation of  $Os^{VII}$  products.