Supplementary information

C(sp³)–H bond activation by carboxylate-adduct of osmium tetroxide (OsO₄)

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Fig. S1 (a) UV-vis spectral changes observed in the titration of OsO₄ (0.5 mM) by Bu₄NOBz in acetonitrile at 30 °C. Inset: Plot of ΔAbs at 390 nm against [Bu₄NOBz]. (b) Plot of $(A-A_0)/(A_{\infty}-A)$ against [Bu₄NOBz]₀ – α [OsO₄]₀.



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



Fig. S3 Cyclic voltammograms of (a) OsO_4 , (b) 1^{OAc} and (c) 1^{OBz} in CH₃CN containing 0.1 M of Bu₄NPF₆ 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 OsO₄ by Bu₄NOAc at 70 °C. Inset: Δ Abs at 390 nm. (b) Plot of $(A-A_0)(A_{\infty}-A)$ against [Bu₄NOAc]₀ – α [OsO₄]₀ according to eq (1). $K_{\rm f}^{\rm OAc} = 1.3 \times 10^3 \,{\rm M}^{-1}$ at 70 °C in CH₃CN

Fig. S5 UV-vis spectrum of the authentic sample of [PPh4][Os^{VII}O4] in CH₃CN.

Fig. S6 ESI-MS of the resultant solution after the reaction of 1^{OAc} 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]₀ = 0.5 mM, [Bu4NOBz]₀ = 20 mM) observed upon addition of xanthene (5.0 mM) in CH₃CN at 70 °C under N₂ atmosphere. (b) The time course of the growth of Os^{VII} 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 OsO₄ by Bu₄NOBz at 70 °C. Inset: Δ Abs at 390 nm. (b) Plot of $(A-A_0)(A_{\infty}-A)$ against [Bu₄NOBz]₀ – α [OsO₄]₀ according to equation (1). $K_f^{OBz} = 1.0 \times 10^3 \text{ M}^{-1}$ at 70 °C in CH₃CN

Fig. S9. (a) UV-vis spectral change of 1^{OAc} ([OsO₄]₀ = 1.0 mM, [NBu₄OAc]₀ = 20 mM) upon addition of xanthene- d_2 (40 mM) in CH₃CN at 70 °C under N₂ atmosphere. (b) The time course of the growth of Os^{VII} 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} ([OsO₄]₀ = 1.0 mM, [Bu₄NOAc]₀ = 20 mM) upon addition of 9,10-dihydroanthracene (10 mM) in CH₃CN at 70 °C under N₂ atmosphere. (b) The time course of the growth of Os^{VII} 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} ([OsO₄]₀ = 1.0 mM, [Bu₄NOAc]₀ = 20 mM) upon addition of fluorene (50 mM) in CH₃CN at 70 °C under N₂ atmosphere. (b) The time course of the growth of Os^{VII} 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} ([OsO₄]₀ = 1.0 mM, [Bu₄NOAc]₀ = 20 mM) upon addition of tetralin (250 mM) in CH₃CN at 70 °C under N₂ atmosphere. (b) The time course of the growth of Os^{VII} 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.