Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Exploring Catalytic Activity of Lews-Acidic Uranyl(VI) Complexes in Nucleophilic Acyl Substitution of Acid Anhydrides

Koichiro Takao* and Shin Akashi

Laboratory for Advanced Nuclear Energy, Institute of Innovative Research, Tokyo Institute of Technology, 2-12-1 N1-32, O-okayama, Meguro-ku, 152-8550 Tokyo, Japan.

*To whom correspondence should be addressed. E-mail: ktakao@lane.iir.titech.ac.jp.

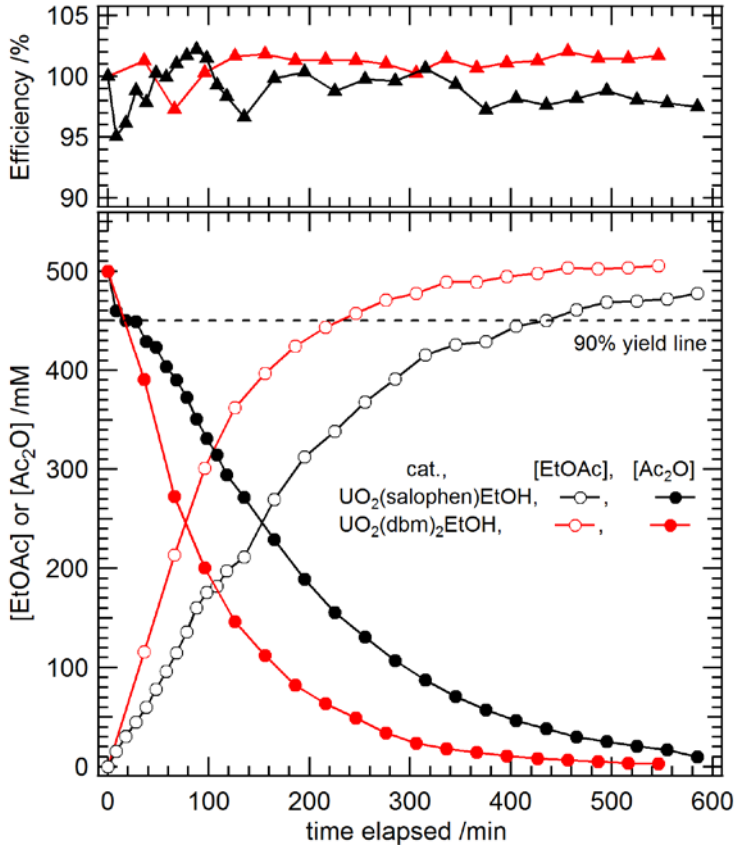

Figure S1. Progress and efficiency of acetylation of ethanol catalysed by UO_2(salophen)EtOH (**1**, 0.5 mol%, black) and $UO_2(dbm)_2$EtOH (**2**, 0.5 mol%, red) in $CDCl_3$ at 50°C. Concentrations of ethyl acetate (EtOAc) and acetic anhydride (Ac_2O) are denoted by open and solid circles, respectively.

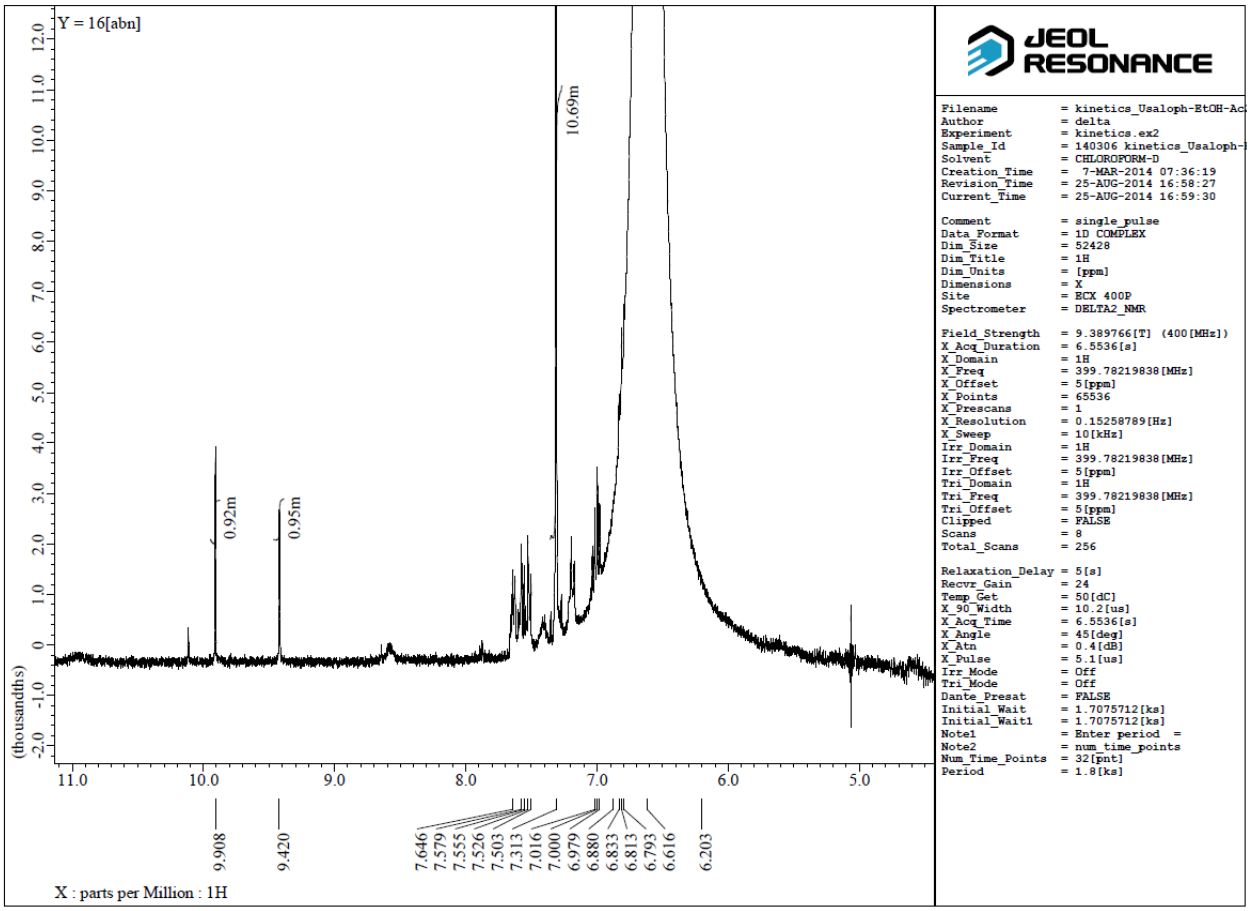

Figure S2. ^{1}H NMR spectrum of a $CDCl_3$ solution dissolving UO_2(salophen)EtOH (**1**, 2.4 mM), ethanol (1.00 M), acetic anhydride (0.50 M) 7 h passed from sample preparation. A signal at 9.42 ppm is attributable to UO_2(salophen)EtOH, while new signals at 10.12 (s), 9.91 (s), and 8.6 (bs) ppm grew up with the elapse of time during the catalytic acylation. The former two would be assigned to azomethine protons of some UO_2^{2+}-salophen^{2-} complexes different from either UO_2(salophen)EtOH (9.42 ppm) or $[UO_2(salophen)]_2$ (9.55-9.59 ppm). The broad singlet at 8.6 ppm is attributable to free *N*,*N*'-disalicylidene-*o*-phenylenediamine (H_2salophen). Assignments for other signals, 6.62 ppm (bs): $CH_3COO\underline{H}$ and Et$O\underline{H}$, 7.31 ppm (s): $C\underline{H}Cl_3$ (impurity of $CDCl_3$), 6.9-7.7 ppm (m): phenyl-$\underline{H}$ of salophen^{2-}.

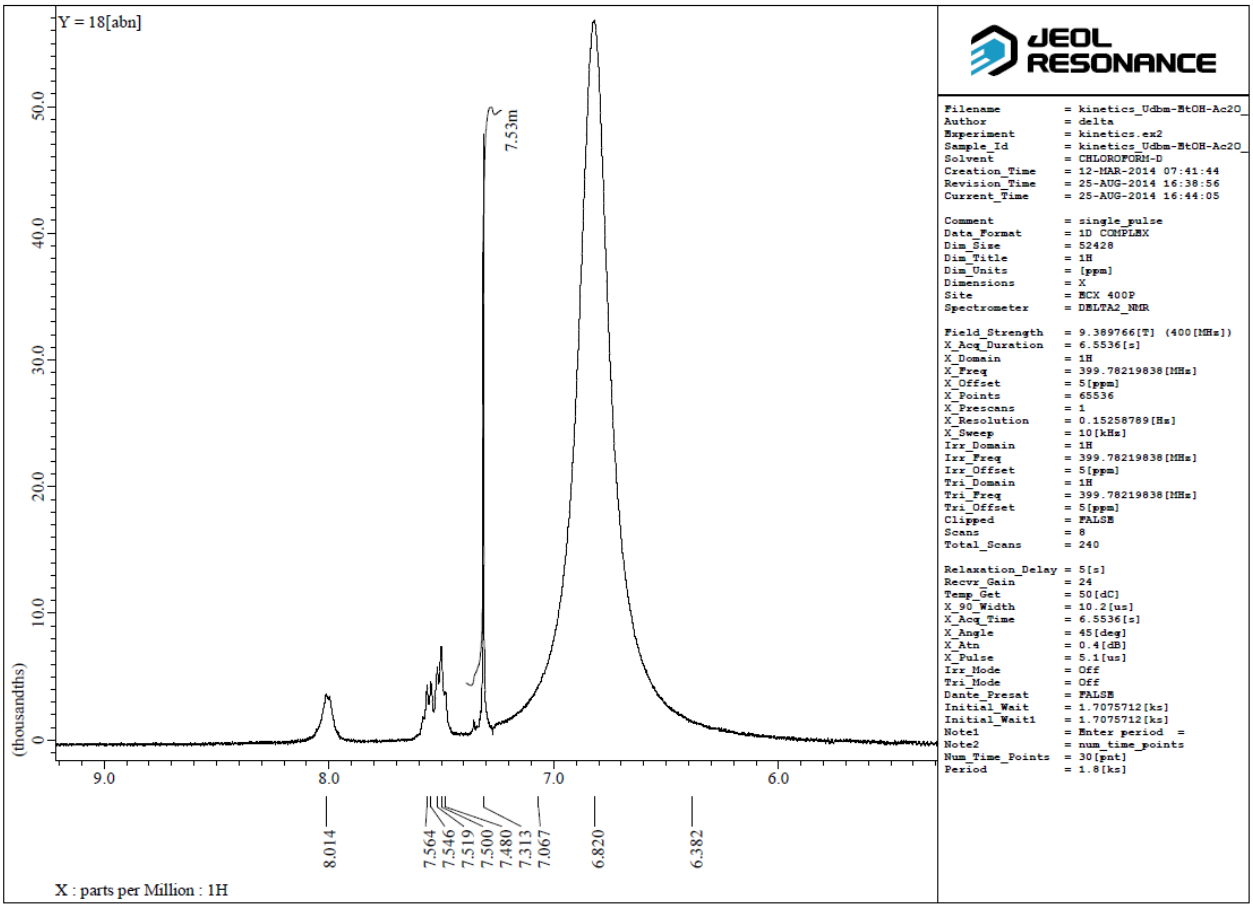

Figure S3. ^{1}H NMR spectrum of a $CDCl_3$ solution dissolving $UO_2(dbm)_2EtOH$ (**2**, 2.8 mM), ethanol (1.00 M), acetic anhydride (0.50 M) 4 h later than sample preparation. A signal at 8.01 ppm of *o*-H in dbm^- indicates that the dbm^- ligand dissociated from UO_2^{2+}, and protonated to form a free dibenzoylmethane (Hdbm). Assignments for other signals, 6.82 ppm (bs): CH_3COOH and EtOH, 7.31 ppm (s): $CHCl_3$ (impurity of $CDCl_3$), 7.48-7.56 ppm (m): *m*- and *p*-H of Hdbm.

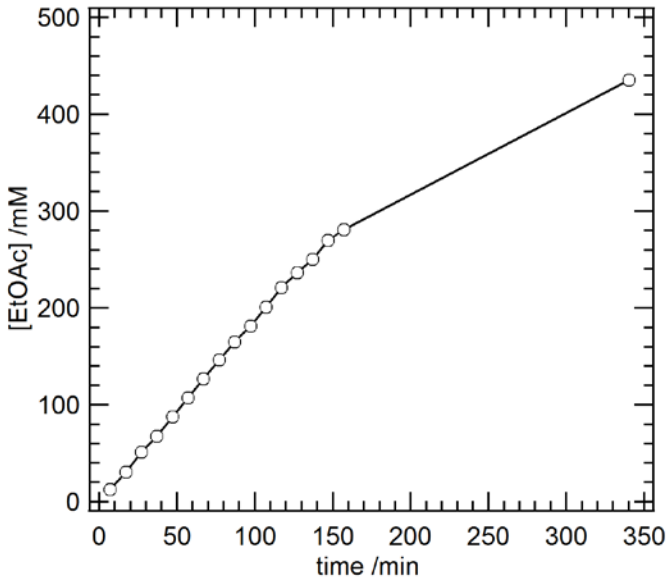

Figure S4. Progress of acetylation of ethanol catalysed by $[UO_2(DMF)_5]^{2+}$ (**3**, 2.3 mol%) in CD_3CN. Initial concentration; ethanol: 0.50 M, acetic anhydride: 0.50 M.

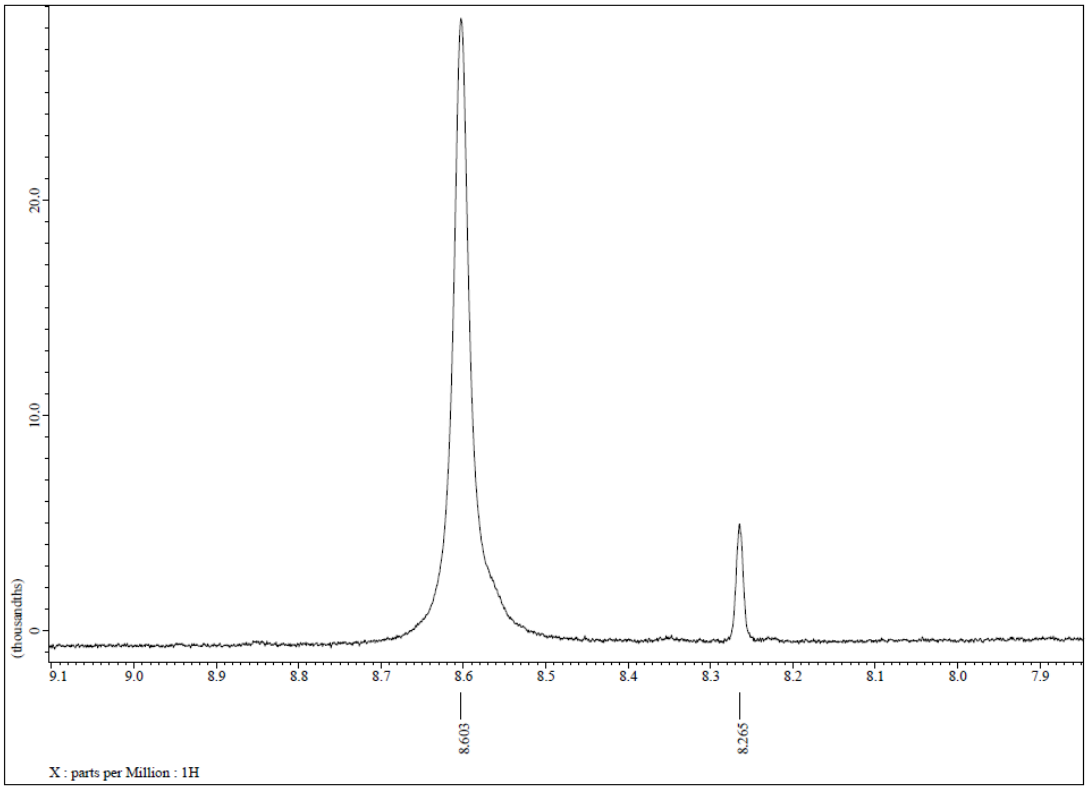

Figure S5. ^1H NMR spectrum of the CD_3CN solution of Fig. S4 at 6 h.

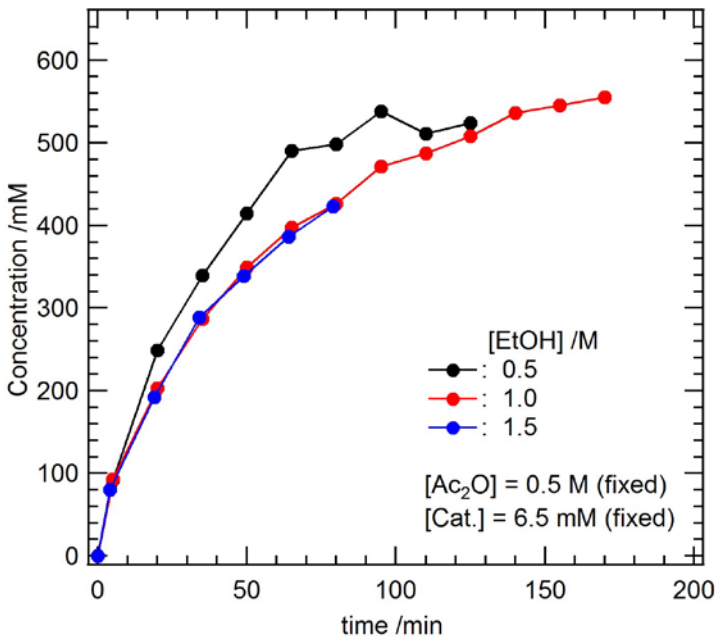

Figure S6. Progress of acetylation of ethanol catalysed by $UO_2(OPPh_3)_4^{2+}$ (**4**, 1.3 mol%) in CD_2Cl_2 at different ethanol concentrations.

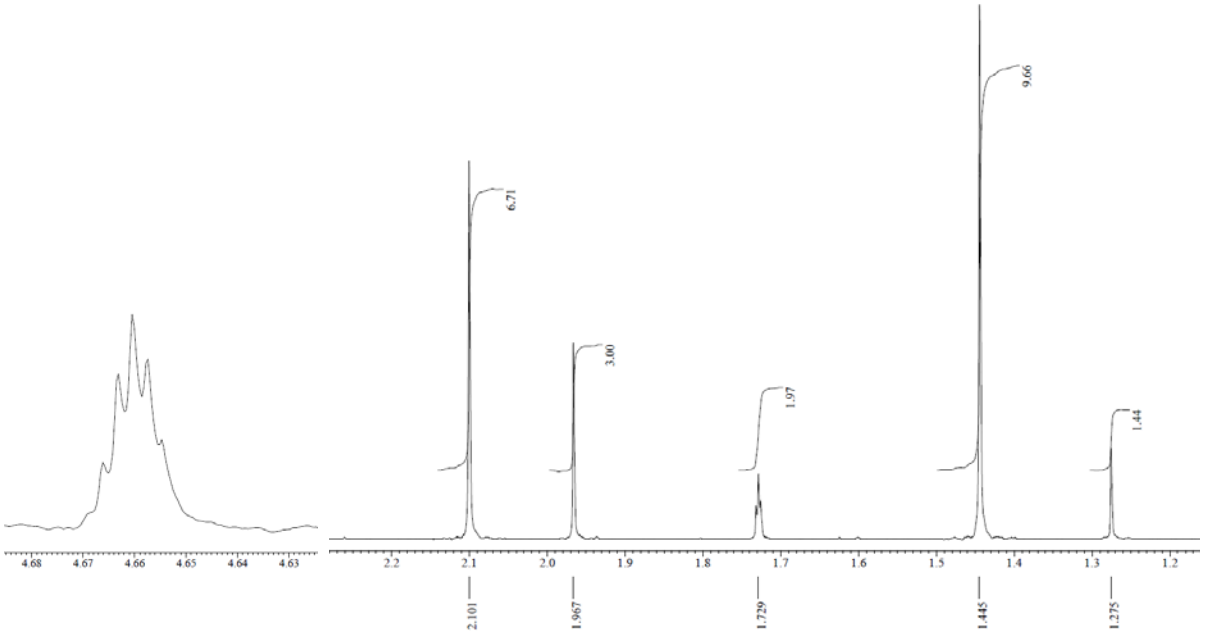

Fig. S7. ^{1}H NMR spectrum of entry 4 in Table 2 (solvent: $CDCl_3$). Singlet signals at 1.97 and 1.45 ppm are attributable to *tert*-butyl acetate. Singlets at 1.28 and 2.10 ppm arise from $(\underline{H_3}C)_3COH$ and $C\underline{H_3}COOH$, respectively. A triplet at 1.73 ppm is coupled with a septet at 4.66 ppm (J_{HH} = 1.2 Hz), and both are assigned to isobutene, $H_2C{=}C(CH_3)_2$, the *E*1 product of *tert*-butyl alcohol.

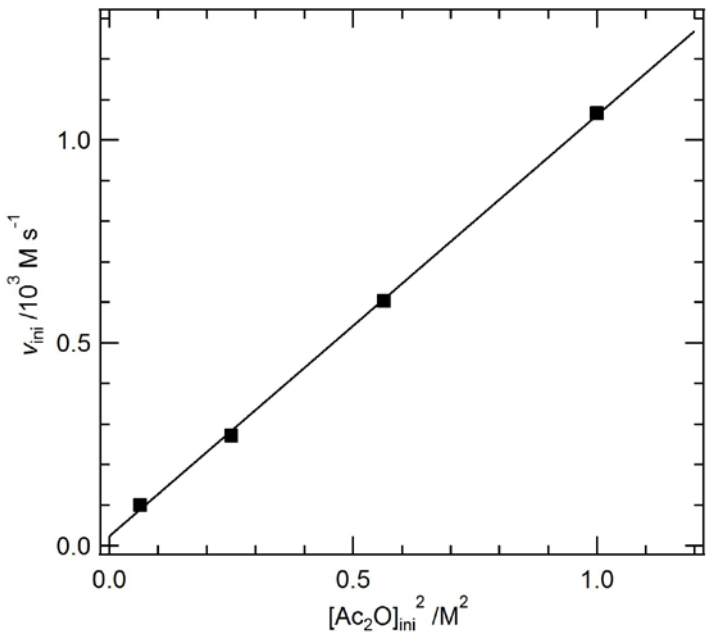

Figure S8. Plot of initial rate (v_{ini}) against $[Ac_2O]_{ini}^2$ in the acetylation of $Ph(CH_2)_2OH$ catalyzed by **4** in CD_2Cl_2 at 22°C (Figure 3a).

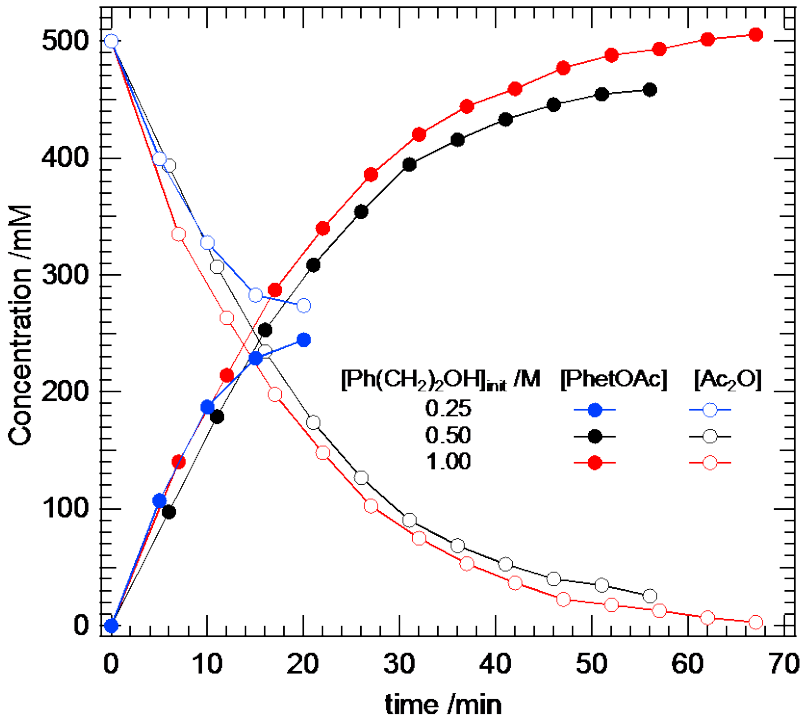

Figure S9. Progress of acetylation of phenethyl alcohol catalyzed by $[UO_2(OPPh_3)_4]^{2+}$ (**4**) in CD_2Cl_2 at 22°C. Initial condition: 0.25-1.00 M phenethyl alcohol + 0.50 M acetic anhydride + 6.5 mM **4**.

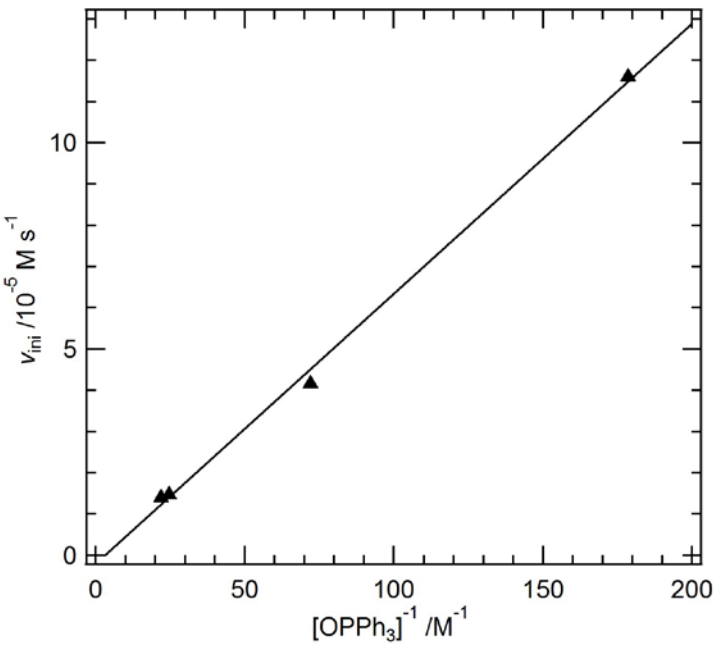

Figure S10. Plot of initial rate (v_{ini}) against $[OPPh_3]_{free}^{-1}$ in the acetylation of $Ph(CH_2)_2OH$ catalyzed by **4** in CD_2Cl_2 at 22°C (Figure 3b).

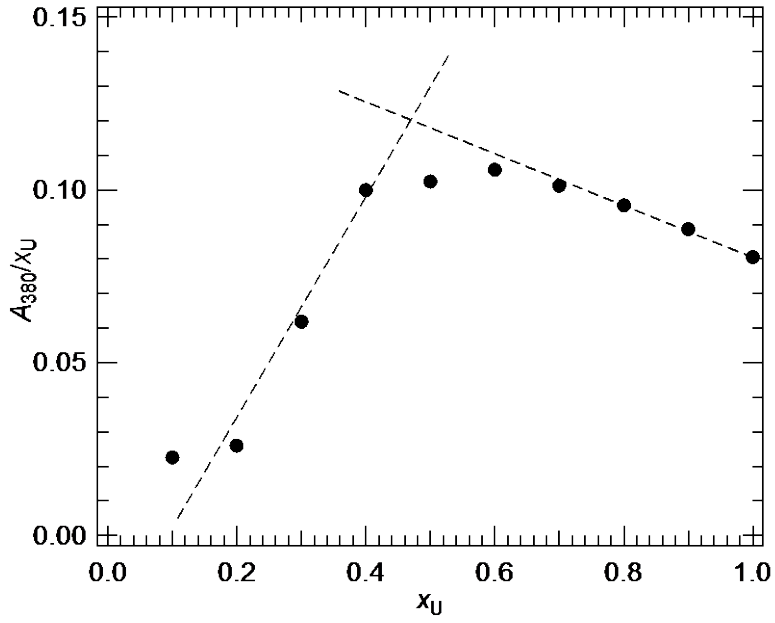

Figure S11. Job's plot for complexation between complex **4** and Ac_2O (total concentration: 4.81 mM) in CH_2Cl_2 at 25°C.

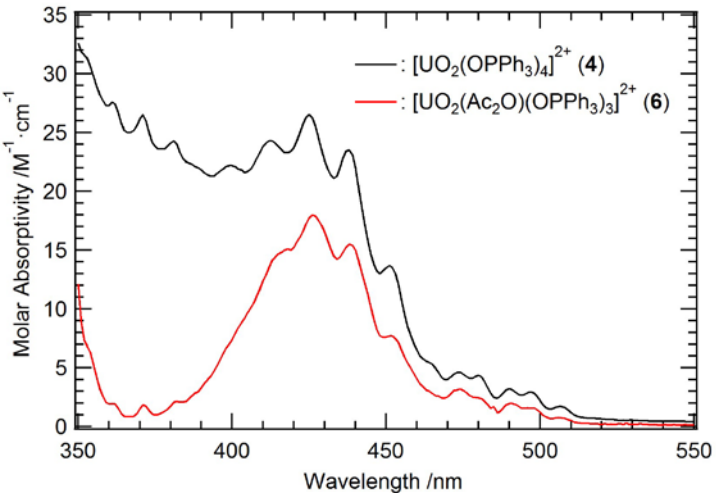

Figure S12. Molar absorption spectra of $[UO_2(OPPh_3)_4]^{2+}$ (**4**) and $[UO_2(Ac_2O)(OPPh_3)_3]^{2+}$ (**6**) resulted from equilibrium analysis using HypSpec.