Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

SUPPORTING INFORMATION

Role of the gold-gold interaction in C-H activation of acetone

Mariarosa Anania, Lucie Jašíková, Juraj Jašík, and Jana Roithová*

*Correspondence to: roithova@natur.cuni.cz

Contents

Preparation of reaction mixtures

A) Solutions of gold complexes:

Gold chloride (L)AuCl (L= PMe_3, PPh_3) (5 µmol) was dissolved in dry THF (1 ml) and mixed with the solution of AgX (X = SbF_6, PF_6, OTf, NTf_2) (1.2 eq) in dry THF (1 ml). The reaction mixture was sonicated for 10 minutes and filtered through a PTFE filter (pore size 0.2 µm) to remove precipitated AgX.
Purchased gold complexes $[Au(L)(CH_3CN)]SbF_6$ (L = JohnPhos) and $[Au(L)(CH_3CN)]BF_4$ (L = IPr) were dissolved in THF (1 ml).
The stock solutions were stored for no longer than 2 days.

B) MS samples for labelling experiments:

The samples for measurements of labelling experiments were obtained by diluting a solution of (L)AuX or $[Au(JohnPhos)(CH_3CN)]SbF_6$ or $[Au(IPr)(CH_3CN)]BF_4$ (200 µL) with dry THF (600 µL). The solution was mixed with a 1:1 mixture of acetone and acetone-d_6. The specific percentage of water is then added.
The obtained solutions were immediately monitored by ESI-MS.

C) Preparation of reaction mixtures:

1) **$(PMe_3)Au(SbF_6)$**: The complex solution was prepared by dissolving 1.54 mg of $(PMe_3)Au(Cl)$ (5 µmol) in 1 ml of dry THF and 2.06 mg of $AgSbF_6$ (6 µmol) in 1 ml of dry THF. This two solution are then mixed in the same vial and put in ultrasonic bath for ten minutes in order to get a 2.5 mM solution of gold complex $[(PMe_3)Au]^+ [SbF_6]^-$ in 2 ml of THF. The white precipitate of AgCl which is obtained is then filtered away.
2) **$(PMe_3)Au(PF_6)$**: The complex solution was prepared by dissolving 1.54 mg of $[(PMe_3)Au(Cl)$ (5 µmol) in 1 ml of dry THF and 1.5 mg $AgPF_6$ (6 µmol) in 1 ml of dry THF. This two solution are then mixed in the same vial and put in ultrasonic bath for ten minutes in order to get a 2.5 mM solution of gold complex $[(PMe_3)Au]^+[PF_6]^-$ in 2 ml of THF. The white precipitate of AgCl which is obtained is then filtered away.
3) **$(PMe_3)Au(OTf)$**: The complex solution was prepared by dissolving 1.54 mg of $[(PMe_3)Au(Cl)$ (5 µmol) in 1 ml of dry THF and 1.28 mg AgOTf (6 µmol) in 1 ml of dry THF. This two solution are then mixed in the same vial and put in ultrasonic bath for ten minutes in order to get a 2.5 mM solution of gold complex $[(PMe_3)Au]^+[OTf]^-$ in 2 ml of THF. The white precipitate of AgCl which is obtained is then filtered away.
4) **$(PMe_3)Au(NTf_2)$**: The complex solution was prepared by dissolving 1.54 mg of $(PMe_3)Au(Cl)$ (5 µmol) in 1 ml of dry THF and 1.94 mg $AgNTf_2$ (6 µmol) in 1 ml of dry THF. This two solution are then mixed in the same vial and put in ultrasonic bath for ten minutes in order to get a 2.5 mM solution of gold complex $[(PMe_3)Au]^+[NTf_2]^-$ in 2 ml of THF. The white precipitate of AgCl which is obtained is then filtered away.
5) **$(PPh_3)Au(SbF_6)$**: The complex solution was prepared by dissolving 2.48 mg of $[(PPh_3)Au(Cl)]$ (5 µmol) in 1 ml of dry THF and 2.06 mg of $AgNTf_2$ (6 µmol) in 1 ml of dry THF. This two solution are then mixed in the same vial and put in ultrasonic bath for ten minutes in order to get a 2.5 mM solution of gold complex $[(PPh_3)Au]^+[SbF_6]^-$ in 2 ml of THF. The white precipitate of AgCl which is obtained is then filtered away.
6) **$(PPh_3)Au(NTf_2)$**: The complex solution was prepared by dissolving 2.48 mg of $[(PPh_3)Au(Cl)]$ (5 µmol) in 1 ml of dry THF and 1.94 mg of $AgNTf_2$ (6 µmol) in 1 ml of dry THF. This two solution are then mixed in the same vial and put in ultrasonic bath for ten minutes in order to get a 2.5 mM solution of gold complex $[(PPh_3)Au]^+[NTf_2]^-$ in 2 ml of THF. The white precipitate of AgCl which is obtained is then filtered away.
7) **$(JohnPhos)Au(CH_3CN)(SbF_6)$**: The complex solution was prepared by dissolving 1.93 mg of $[(JohnPhos)Au(SbF_6)$ (5 µmol) in 1 ml of dry THF. The solution is ready to be used as a stock solution.

8) **(IPr)Au(CH$_3$CN)(BF$_4$)**: The complex solution was prepared by dissolving 1.79 mg of [(IPr)Au(ACN)(BF$_4$) (5 µmol) in 1 ml of dry THF. The solution is ready to be used as a stock solution.

9) **(IPr)$_2$Au$_2$(OH)(BF$_4$)**: The complex solution was prepared by dissolving 3.158 mg of gold(I) complex [(IPr)$_2$ Au$_2$(OH)]$^+$ BF$_4^-$ (5 µmol) in 1 ml of dry THF.

10) **(IPr)Au(OTf)**: The complex solution was prepared by dissolving 3.08 mg of [(IPr)Au(Cl) (5 µmol) in 1 ml of dry dioxane and 1.28 mg AgOTf (6 µmol) in 1 ml of dry dioxane. This two solution are then mixed in the same vial and put in ultrasonic bath for ten minutes in order to get a 2.5 mM solution of gold complex [(IPr)Au]$^+$[OTf]$^-$ in 2 ml of THF. The white precipitate of AgCl which is obtained is then filtered away.

11) **(IPr)Au(NTf$_2$)**: The complex solution was prepared by dissolving 3.08 mg of [(IPr)Au(Cl) (5 µmol) in 1 ml of dry dioxane and 1.94 mg AgOTf (6 µmol) in 1 ml of dry dioxane. This two solution are then mixed in the same vial and put in ultrasonic bath for ten minutes in order to get a 2.5 mM solution of gold complex [(IPr)Au]$^+$[NTf$_2$]$^-$ in 2 ml of THF. The white precipitate of AgCl which is obtained is then filtered away.

Reaction of [Au(IPr)(OTf)] with cyclohexanone in dioxane/water solution.

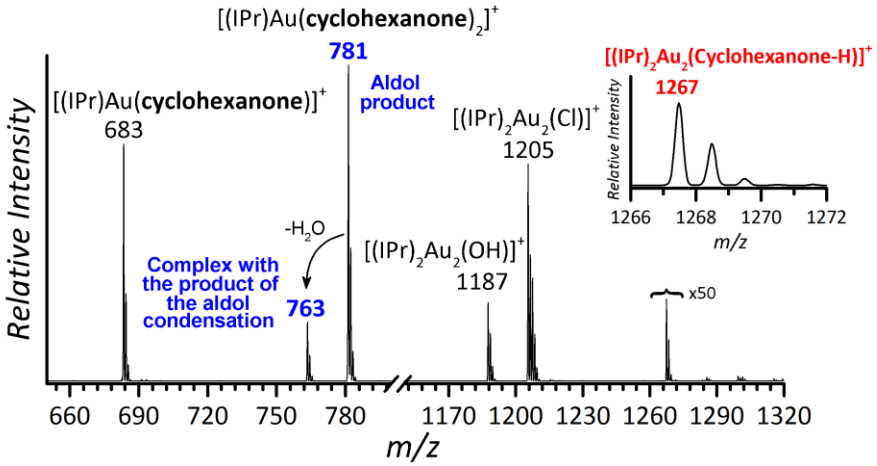

Figure S1: ESI-MS source spectrum of the [(IPr)Au(OTf)] (184 µg) complex in dry dioxane (0.1 ml) after the addition of cyclohexanone (0.1 mL) and 0.1 mL of H_2O.
The spectrum clearly shows formation of the digold kenonyl complex (m/z 1267). More importantly, it reveals aldol reaction (m/z 781) and subsequent water elimination (m/z 763).

IRPD, IRMPD and theoretical IR spectra for [Au(PMe₃)(SbF₆)]

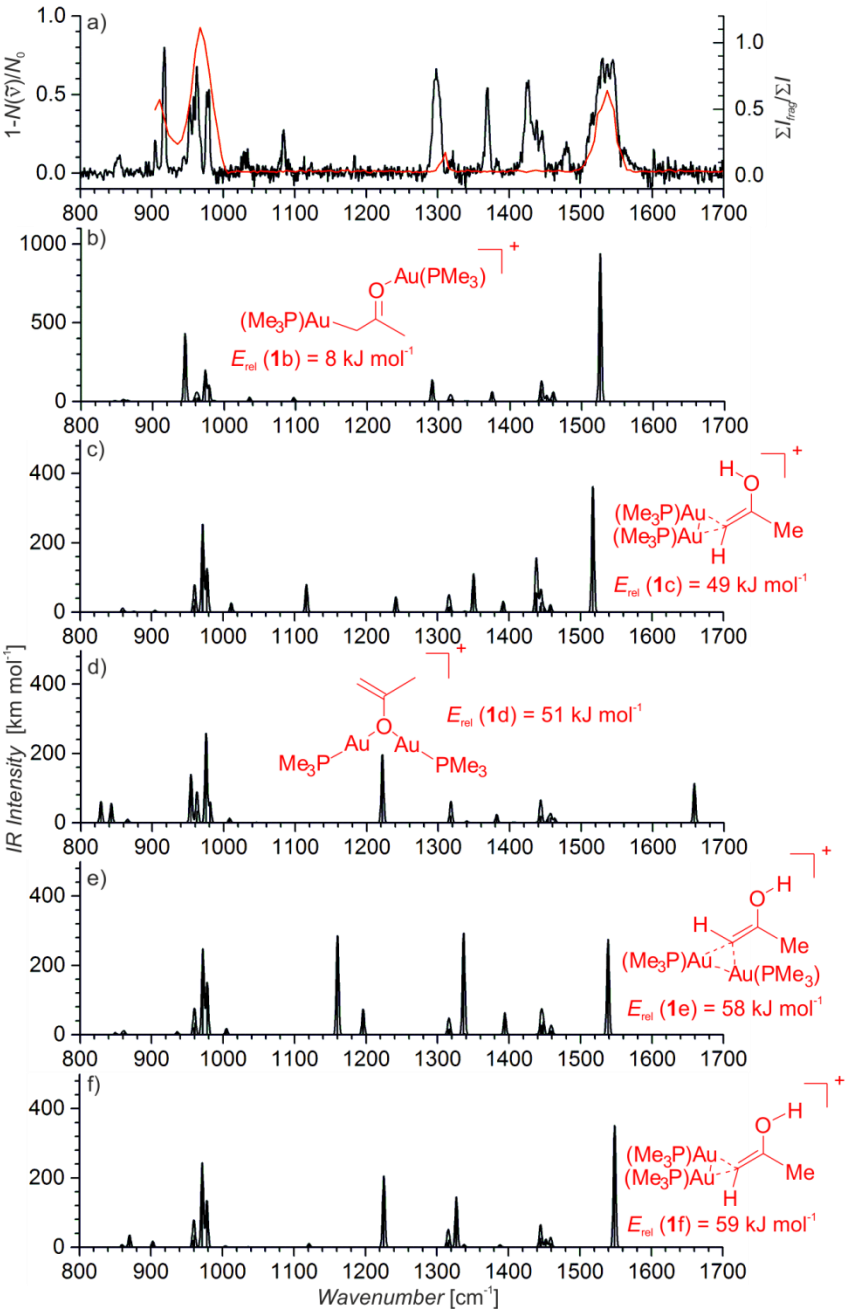

Figure S2: a) IRPD and IRMPD (an experiment from the CLIO facility in France) experimental spectra (black and red lines respectively) of the mass selected ion $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$ with m/z 603. Theoretical IR spectra (B3LYP-D3/6-311+G*(SDD:Au); scaling factor: 0.975) of different isomers of $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$ b) **1b**, c) **1c**, d) **1d**, e) **1e**, and f) **1f** .

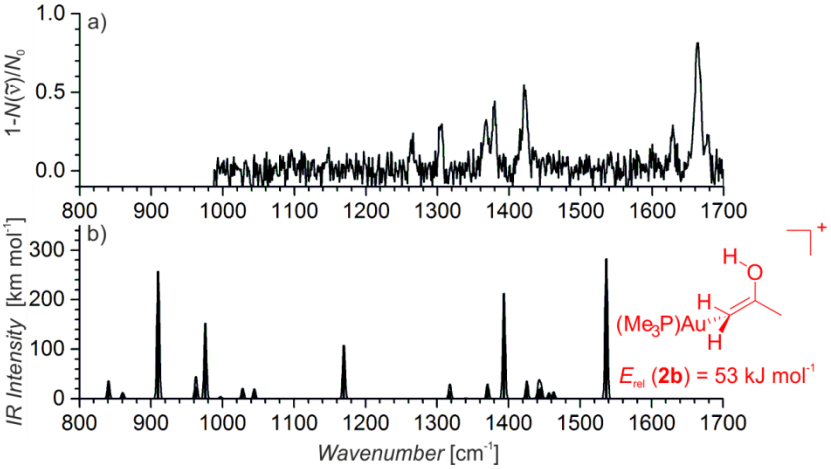

Figure S3: a) IRPD experimental spectrum of the mass selected ion $[(PMe_3)Au(CH_3COCH_3)]^+$ with m/z 331. b) Theoretical IR spectrum (B3LYP-D3/6-311+G*(SDD:Au); scaling factor: 0.975) of isomer **2b** of $[(PMe_3)Au(CH_3COCH_3)]^+$.

Kinetic Isotope Effect (KIE)

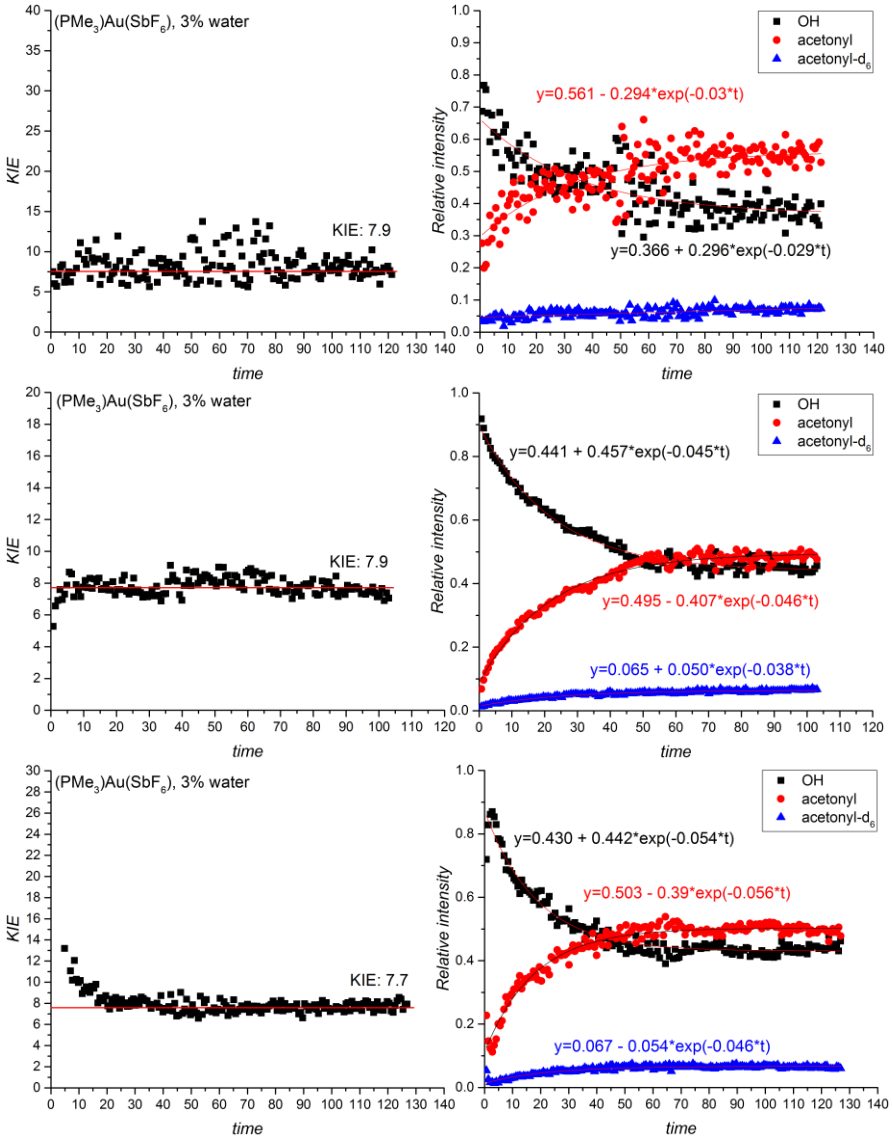

Figure S4: KIE as a function of time for the $(PMe_3)Au(SbF_6)$ complex after addition of 3% of water to the total volume of the solution. **OH**= $(PMe_3)_2Au_2(OH)$, **acetonyl**= $(PMe_3)_2Au_2(CH_2COCH_3)$, **acetonyl-d$_6$**= $(PMe_3)_2Au_2(CD_2COCD_3)$.

KIE: $(PMe_3)_2Au_2(CH_2COCH_3)/(PMe_3)_2Au_2(CD_2COCD_3)$.

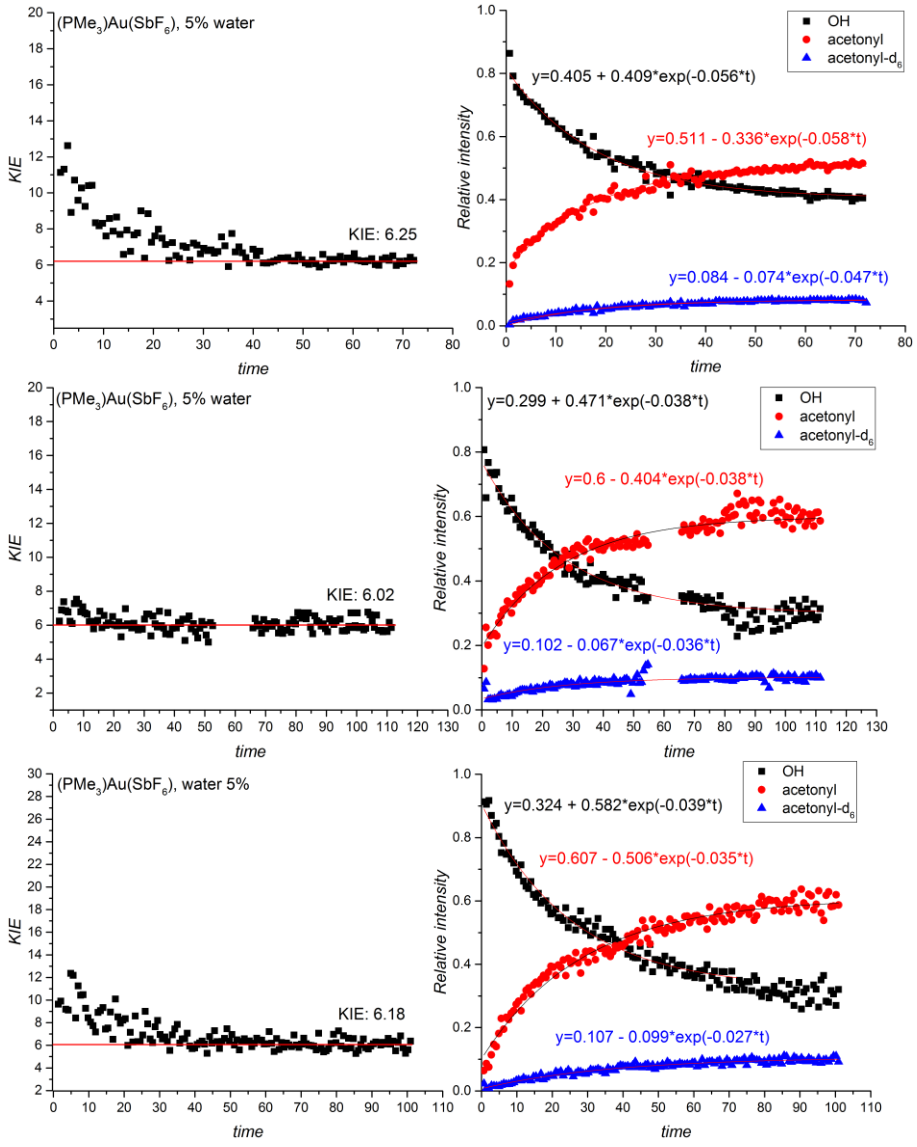

Figure S5: KIE as a function of time for the $(PMe_3)Au(SbF_6)$ complex after addition of 5% of water to the total volume of the solution. **OH**= $(PMe_3)_2Au_2(OH)$, **acetonyl**= $(PMe_3)_2Au_2(CH_2COCH_3)$, **acetonyl-$d_6$**= $PMe_3)_2Au_2(CD_2COCD_3)$.

KIE: $(PMe_3)_2Au_2(CH_2COCH_3)/(PMe_3)_2Au_2(CD_2COCD_3)$.

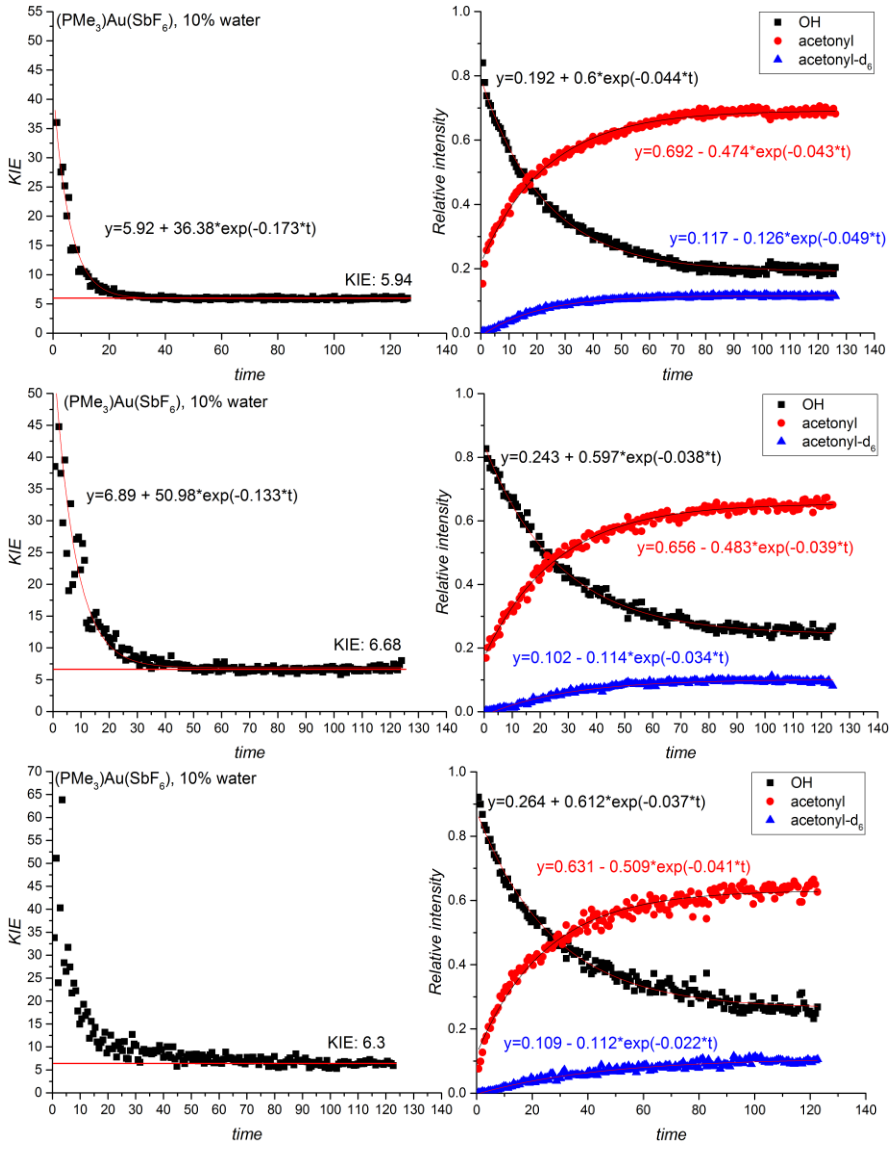

Figure S6: KIE as a function of time for the $(PMe_3)Au(SbF_6)$ complex after addition of 10% of water to the total volume of the solution. **OH**= $(PMe_3)_2Au_2(OH)$, **acetonyl**= $(PMe_3)_2Au_2(CH_2COCH_3)$, **acetonyl-$d_6$**= $(PMe_3)_2Au_2(CD_2COCD_3)$.

KIE: $(PMe_3)_2Au_2(CH_2COCH_3)/(PMe_3)_2Au_2(CD_2COCD_3)$.

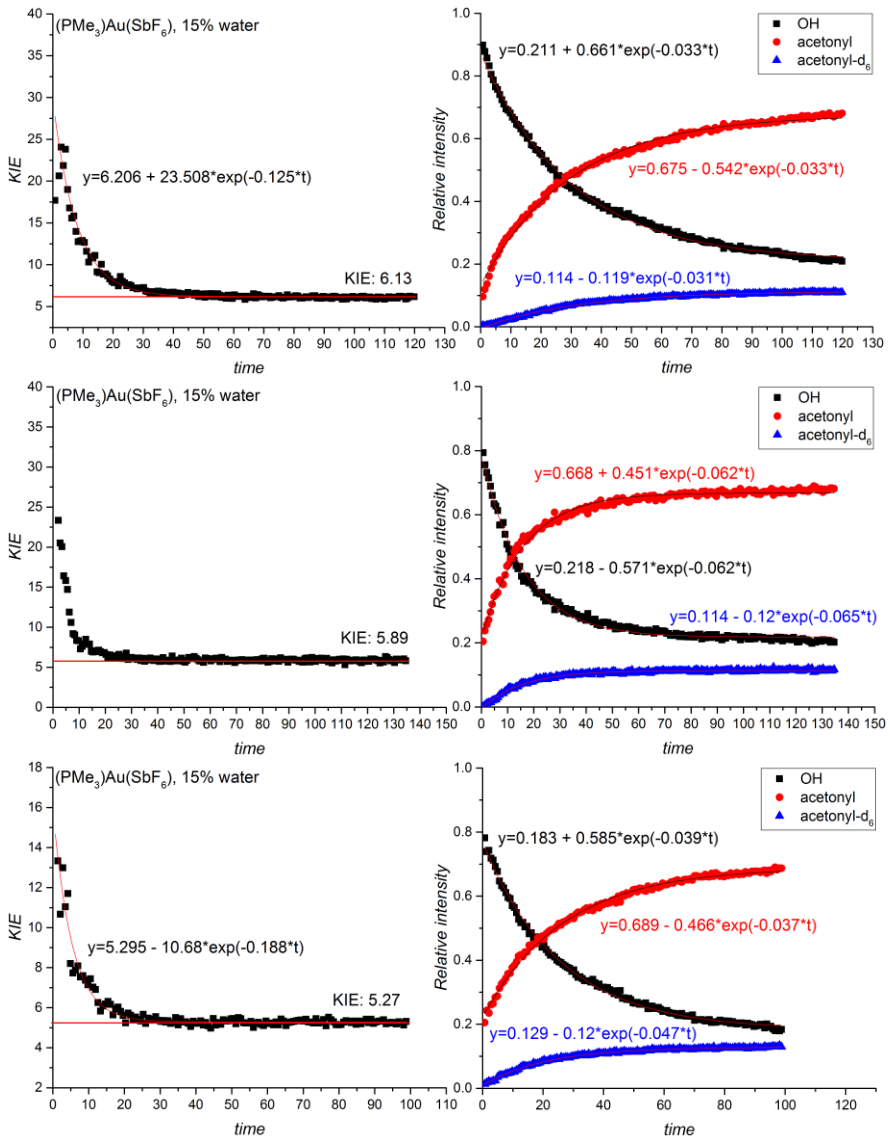

Figure S7: KIE as a function of time for the $(PMe_3)Au(SbF_6)$ complex after addition of 15% of water to the total volume of the solution. **OH**= $(PMe_3)_2Au_2(OH)$, **acetonyl**= $(PMe_3)_2Au_2(CH_2COCH_3)$, **acetonyl-$d_6$**= $(PMe_3)_2Au_2(CD_2COCD_3)$.

KIE: $(PMe_3)_2Au_2(CH_2COCH_3)/(PMe_3)_2Au_2(CD_2COCD_3)$.

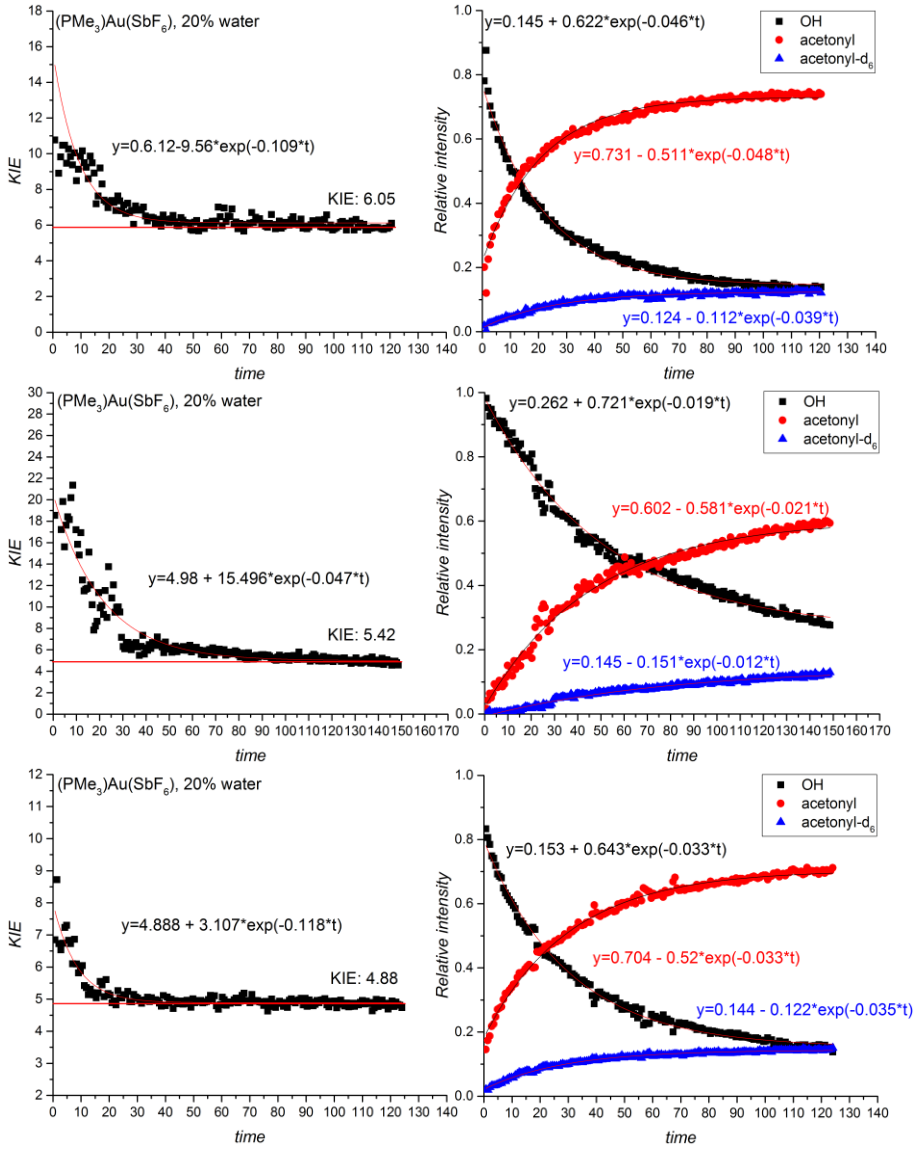

Figure S8: KIE as a function of time for the $(PMe_3)Au(SbF_6)$ complex after addition of 20% of water to the total volume of the solution. **OH**= $(PMe_3)_2Au_2(OH)$, **acetonyl**= $(PMe_3)_2Au_2(CH_2COCH_3)$, **acetonyl-d$_6$**= $(PMe_3)_2Au_2(CD_2COCD_3)$.

KIE: $(PMe_3)_2Au_2(CH_2COCH_3)/(PMe_3)_2Au_2(CD_2COCD_3)$.

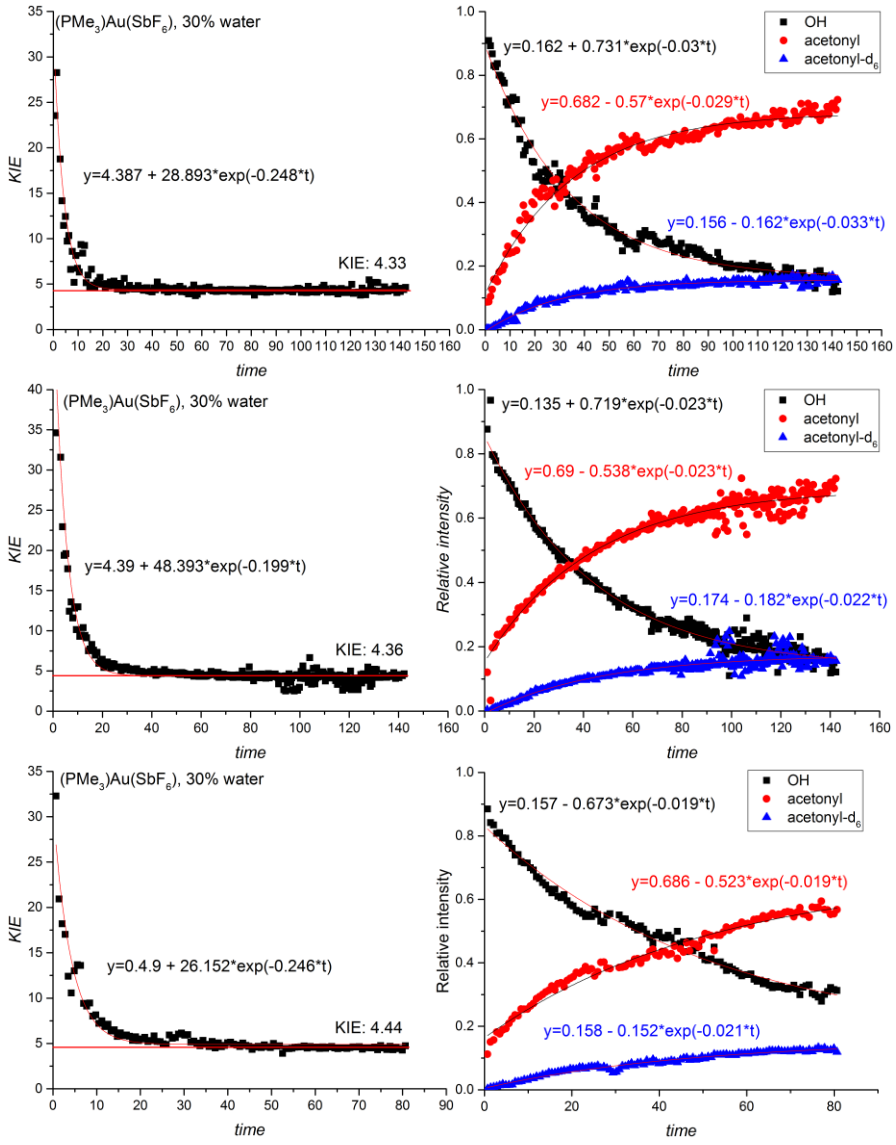

Figure S9: KIE as a function of time for the $(PMe_3)Au(SbF_6)$ complex after addition of 30% of water to the total volume of the solution. **OH**= $(PMe_3)_2Au_2(OH)$, **acetonyl**= $(PMe_3)_2Au_2(CH_2COCH_3)$, **acetonyl-$d_6$**= $(PMe_3)_2Au_2(CD_2COCD_3)$.

KIE: $(PMe_3)_2Au_2(CH_2COCH_3)/(PMe_3)_2Au_2(CD_2COCD_3)$.

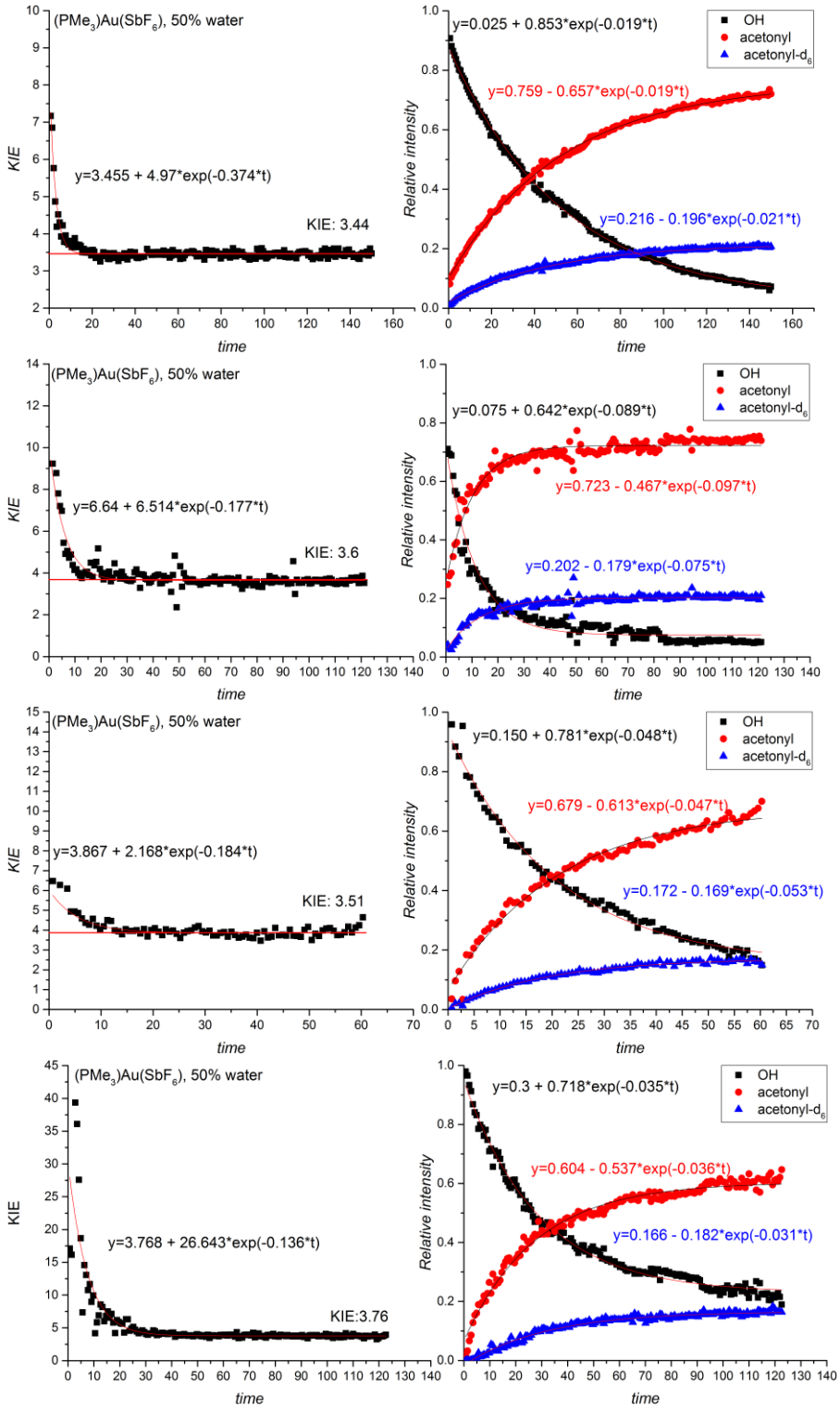

Figure S10: KIE as a function of time for the $(PMe_3)Au(SbF_6)$ complex after addition of 50% of water to the total volume of the solution. **OH**= $(PMe_3)_2Au_2(OH)$, **acetonyl**= $(PMe_3)_2Au_2(CH_2COCH_3)$, **acetonyl-d₆**= $(PMe_3)_2Au_2(CD_2COCD_3)$.

KIE: $(PMe_3)_2Au_2(CH_2COCH_3)/(PMe_3)_2Au_2(CD_2COCD_3)$.

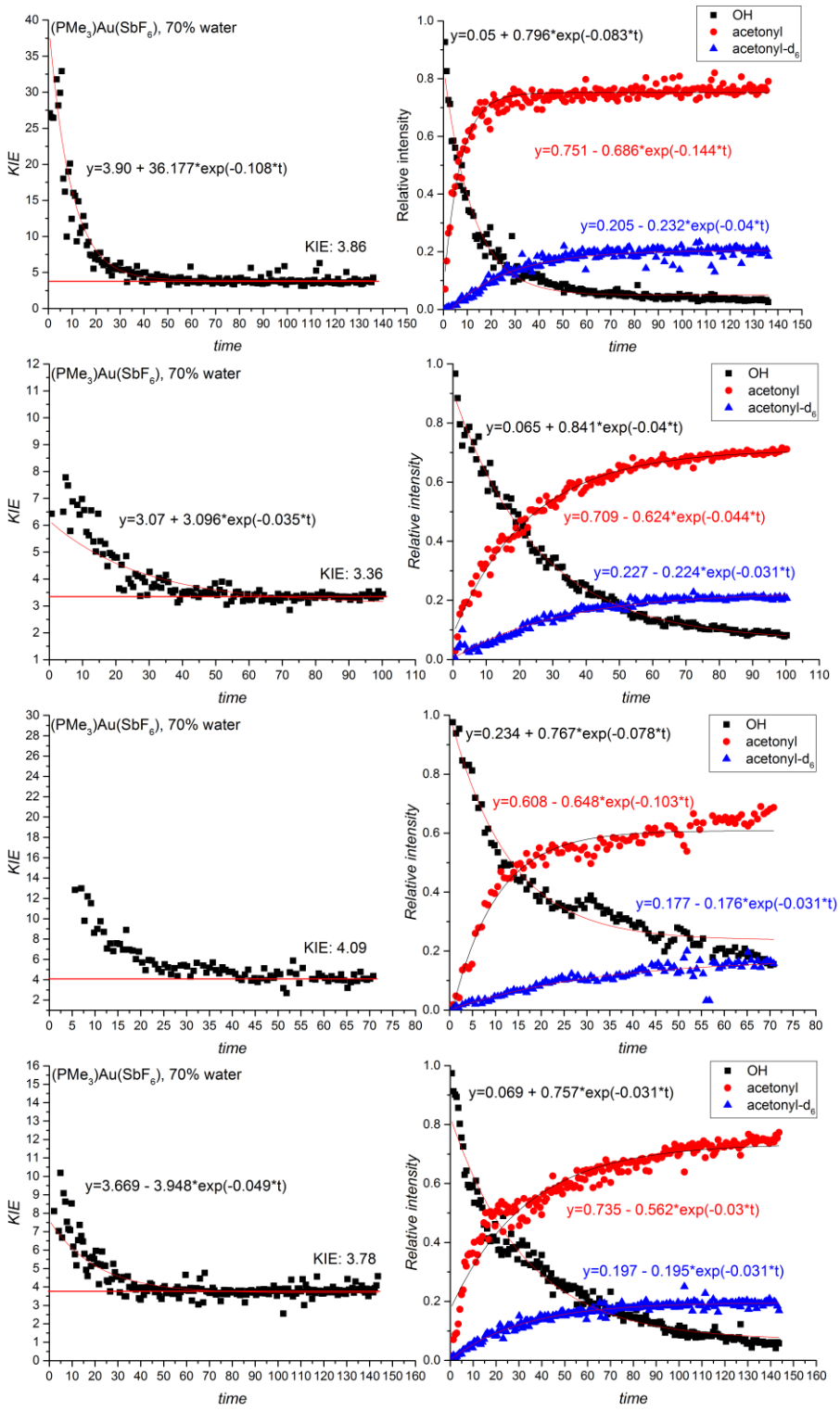

Figure S11: KIE as a function of time for the $(PMe_3)Au(SbF_6)$ complex after addition of 70% of water to the total volume of the solution. **OH**= $(PMe_3)_2Au_2(OH)$, **acetonyl**= $(PMe_3)_2Au_2(CH_2COCH_3)$, **acetonyl-d$_6$**= $(PMe_3)_2Au_2(CD_2COCD_3)$.

KIE: $(PMe_3)_2Au_2(CH_2COCH_3)/(PMe_3)_2Au_2(CD_2COCD_3)$

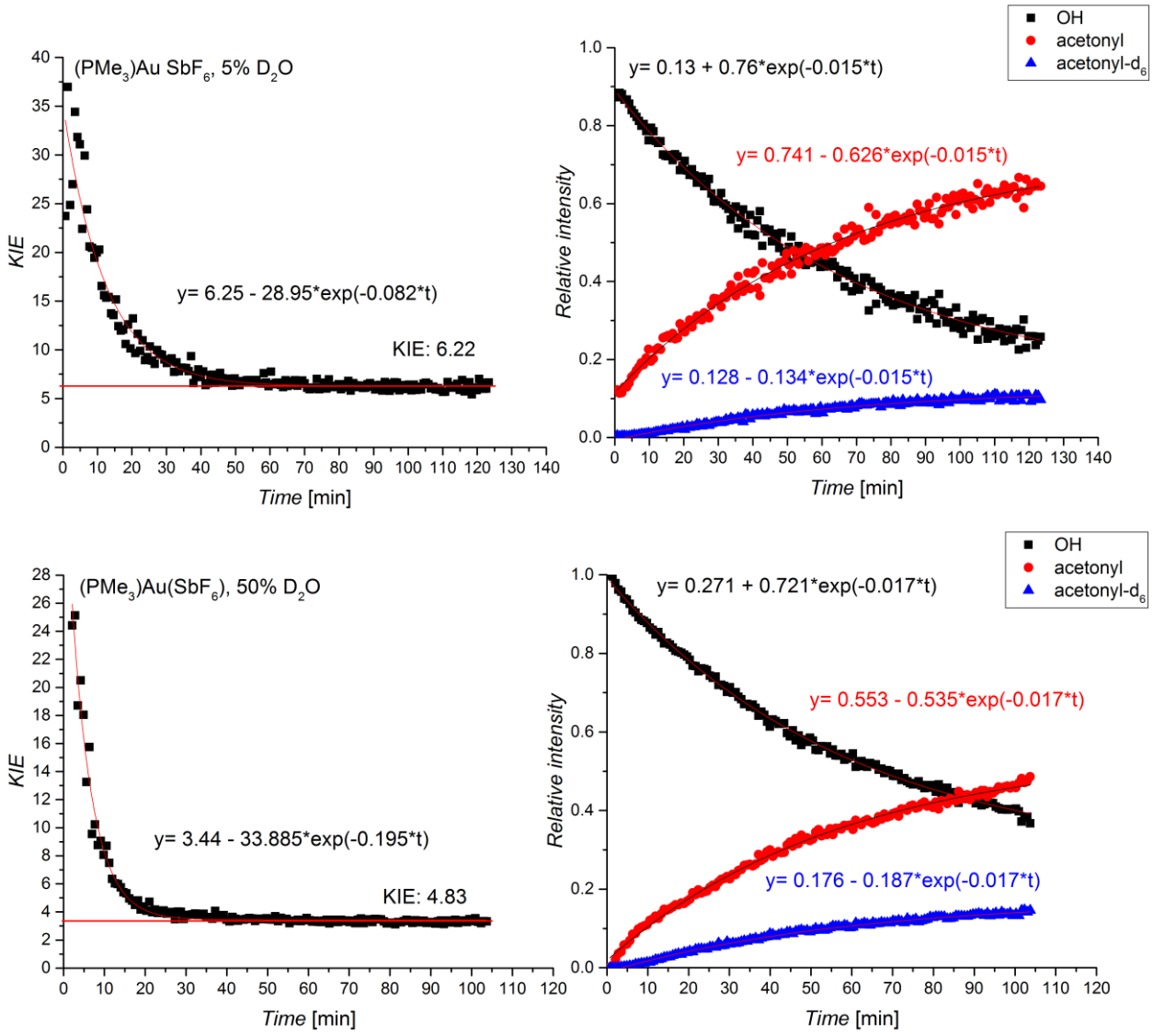

Figure S12: KIE as a function of time for the $(PMe_3)Au(SbF_6)$ complex after addition of 5% and 50% of D_2O to the total volume of the solution. **OH**= $(PMe_3)_2Au_2(OH)$, **acetonyl**= $(PMe_3)_2Au_2(CH_2COCH_3)$, **acetonyl-$d_6$**= $(PMe_3)_2Au_2(CD_2COCD_3)$.

KIE: $(PMe_3)_2Au_2(CH_2COCH_3)/(PMe_3)_2Au_2(CD_2COCD_3)$.

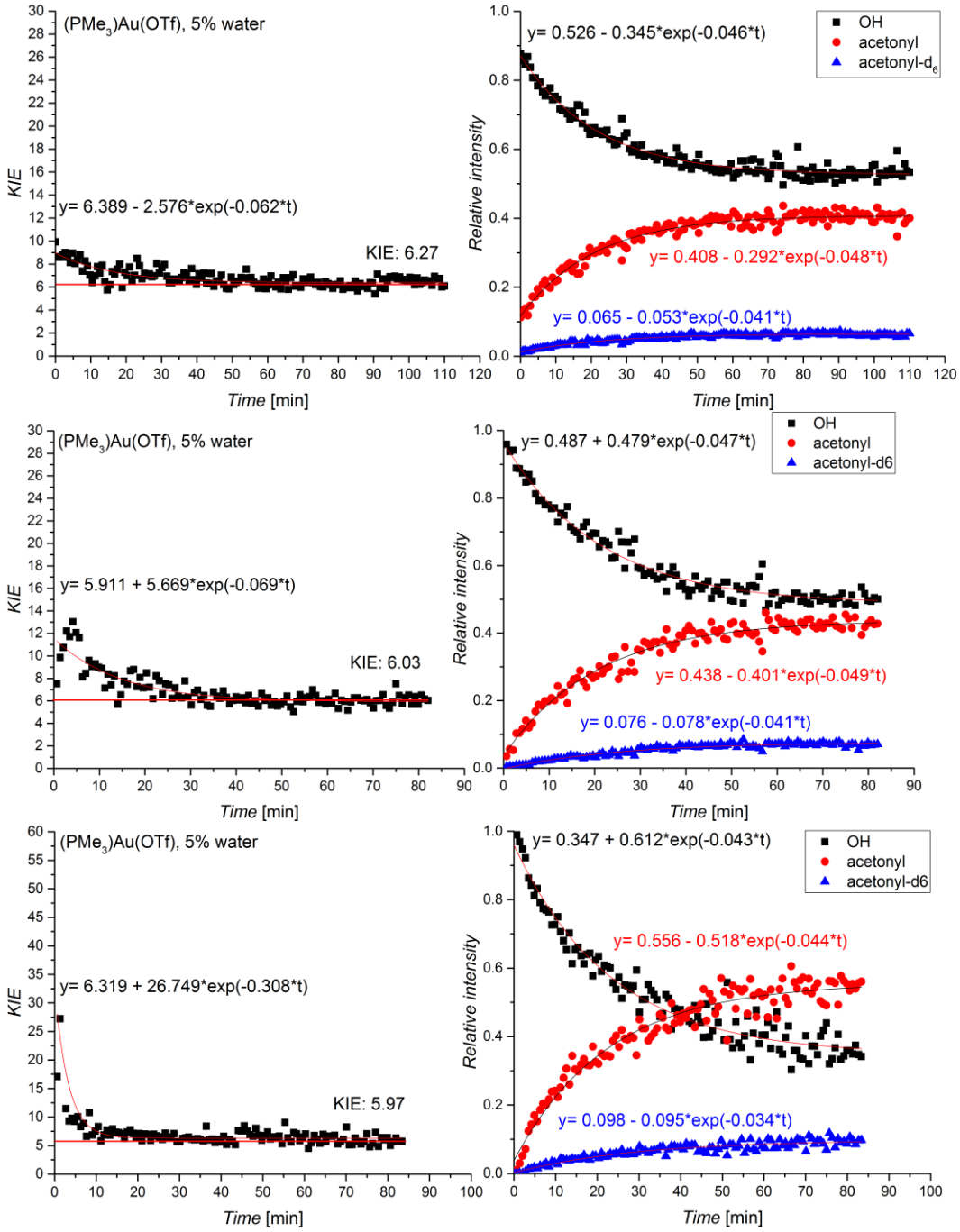

Figure S13. Relative intensity of selected ions $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$, $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$ and $[(PMe_3)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 5% of water to the reaction mixture of the $(PMe_3)Au(OTf)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

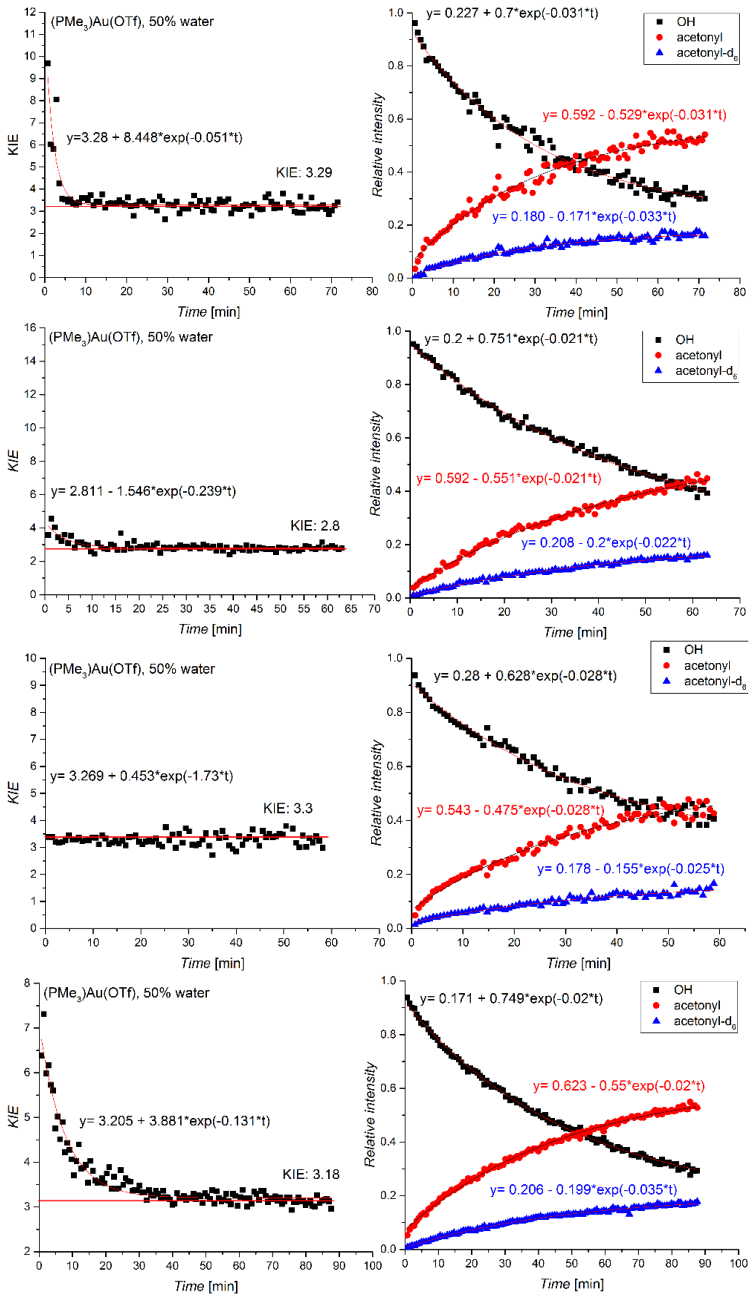

Figure S14. Relative intensity of selected ions $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$, $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$ and $[(PMe_3)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 50% of water to the reaction mixture of the $(PMe_3)Au(OTf)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

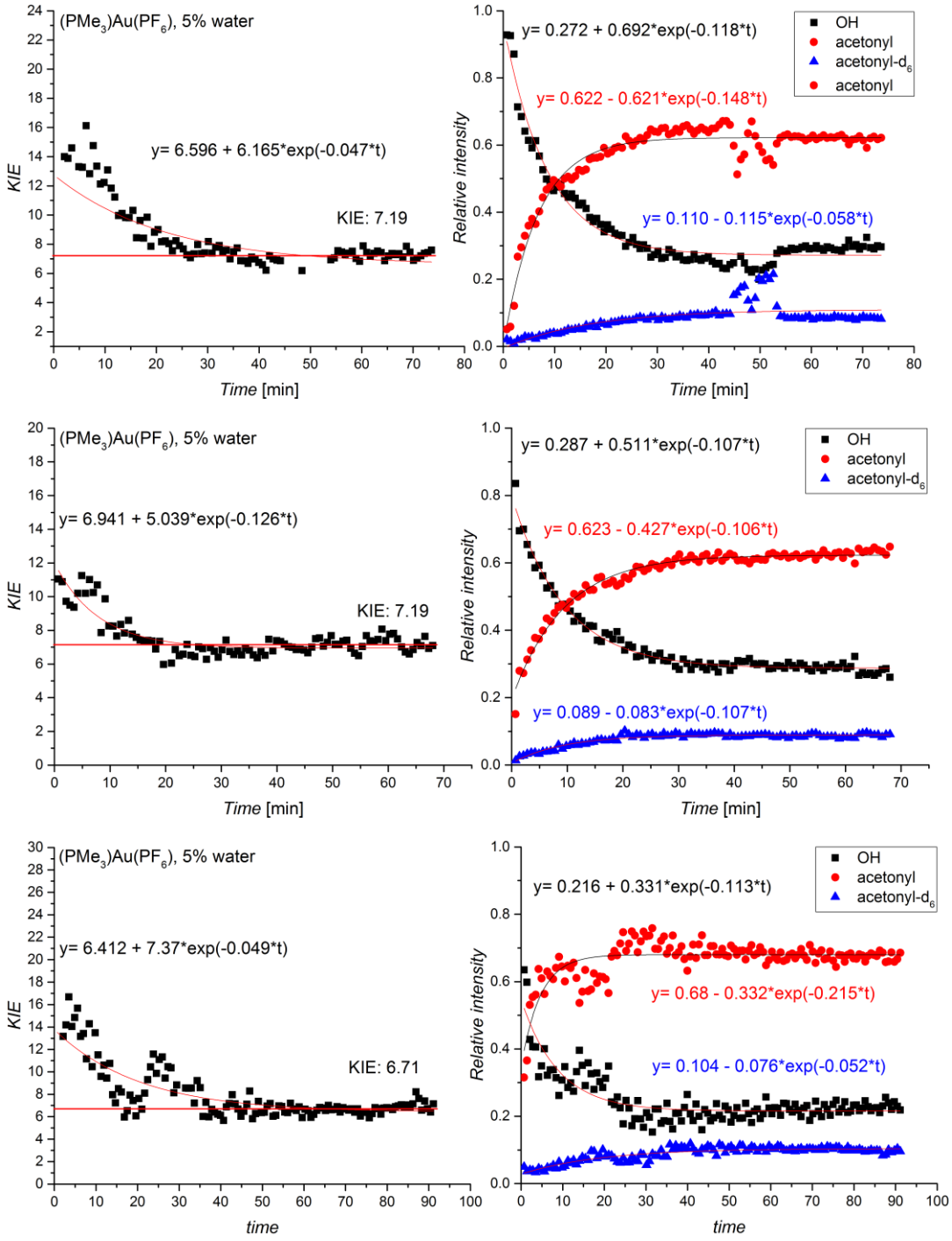

Figure S15. Relative intensity of selected ions $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$, $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$ and $[(PMe_3)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 5% of water to the reaction mixture of the $(PMe_3)Au(PF_6)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

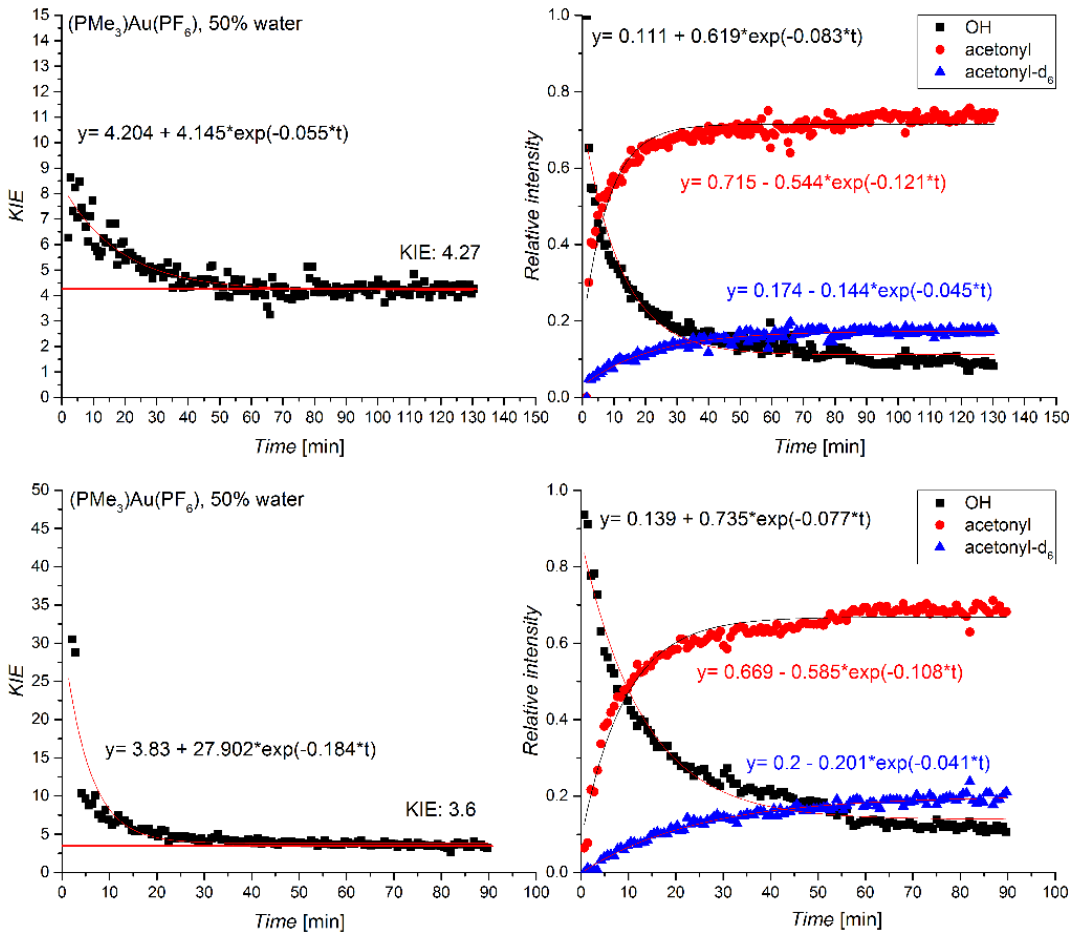

Figure S16. Relative intensity of selected ions $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$, $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$ and $[(PMe_3)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 50% of water to the reaction mixture of the $(PMe_3)Au(PF_6)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

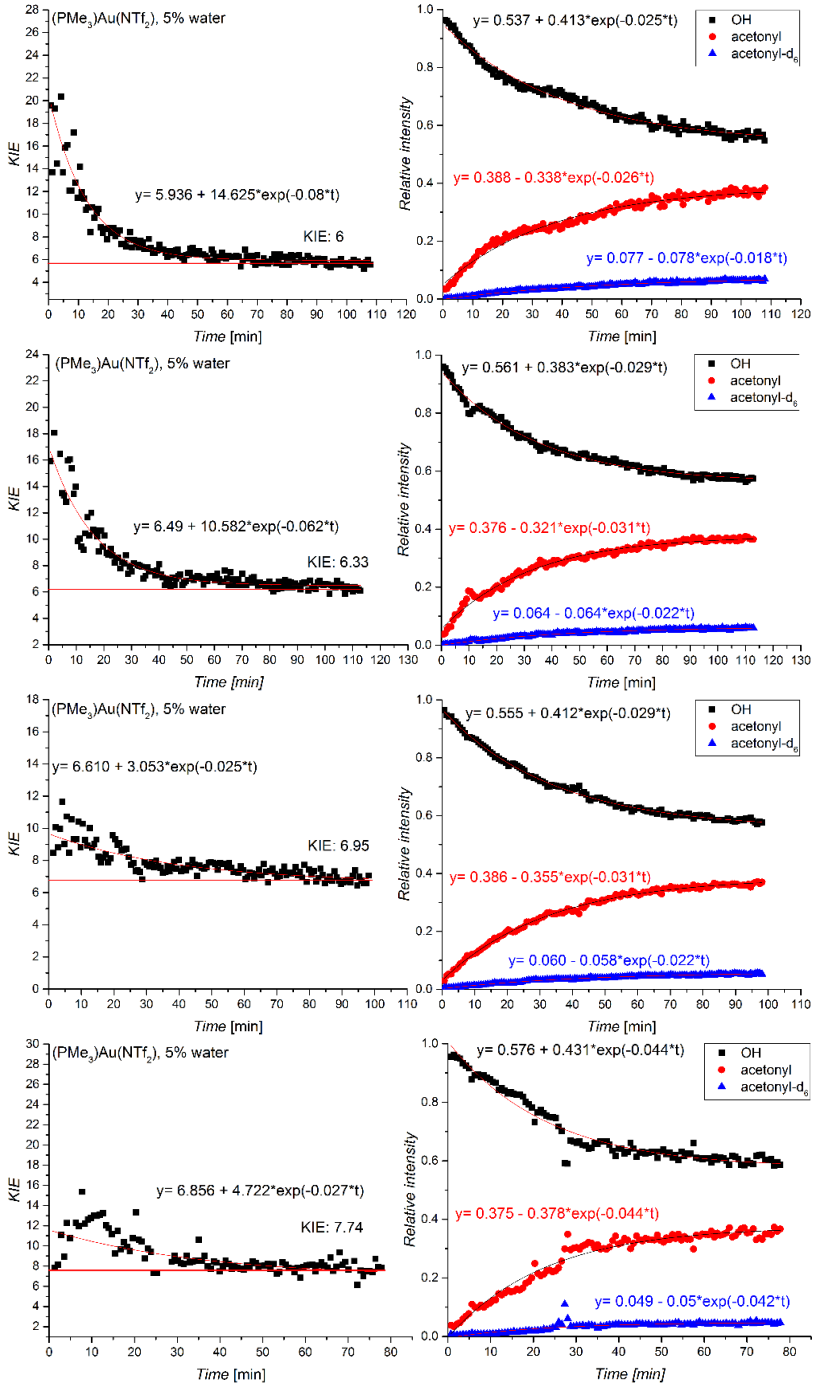

Figure S17. Relative intensity of selected ions $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$, $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$ and $[(PMe_3)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 5% of water to the reaction mixture of the $(PMe_3)Au(NTf_2)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

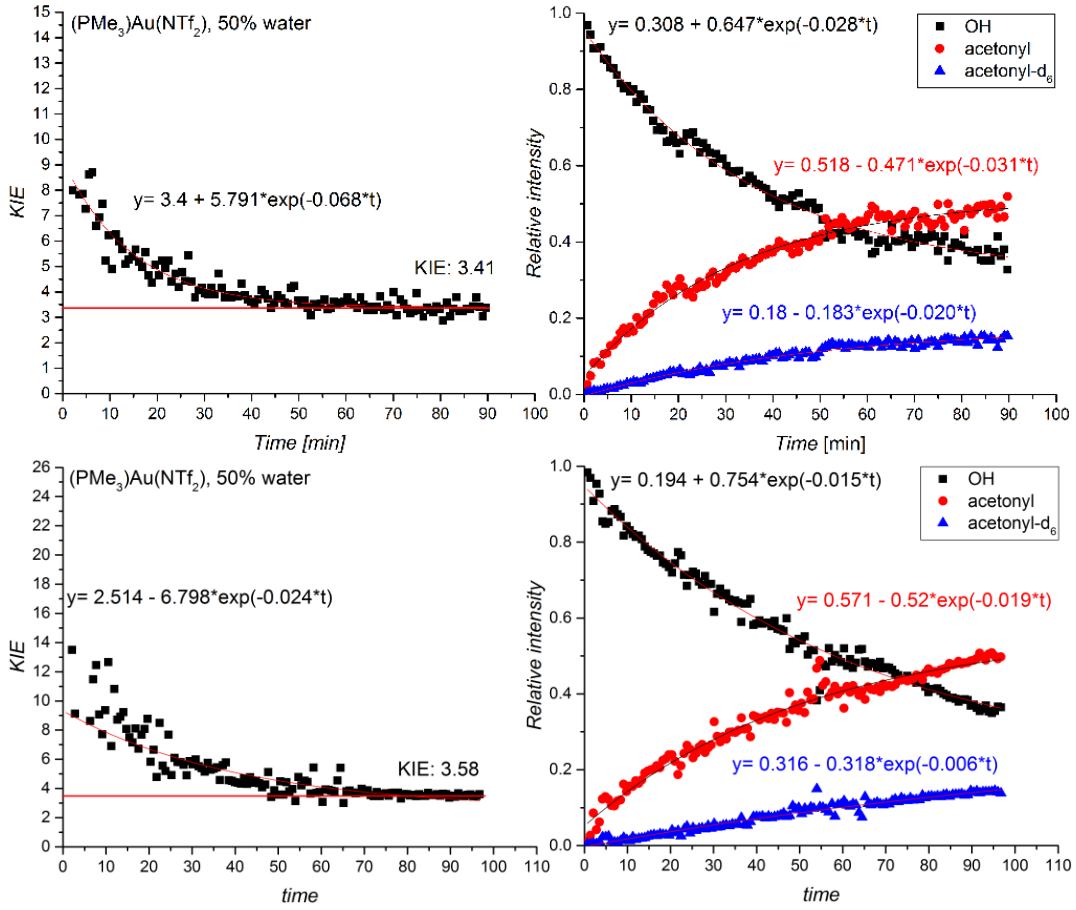

Figure S18. Relative intensity of selected ions ($(PMe_3)_2Au_2(CH_2COCH_3)$, $(PMe_3)_2Au_2(CD_2COCD_3)$ and $(PMe_3)_2Au_2(\mu$-OH)) as a function of time for the addition of 50% of water to the reaction mixture of the $(PMe_3)Au(NTf_2)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

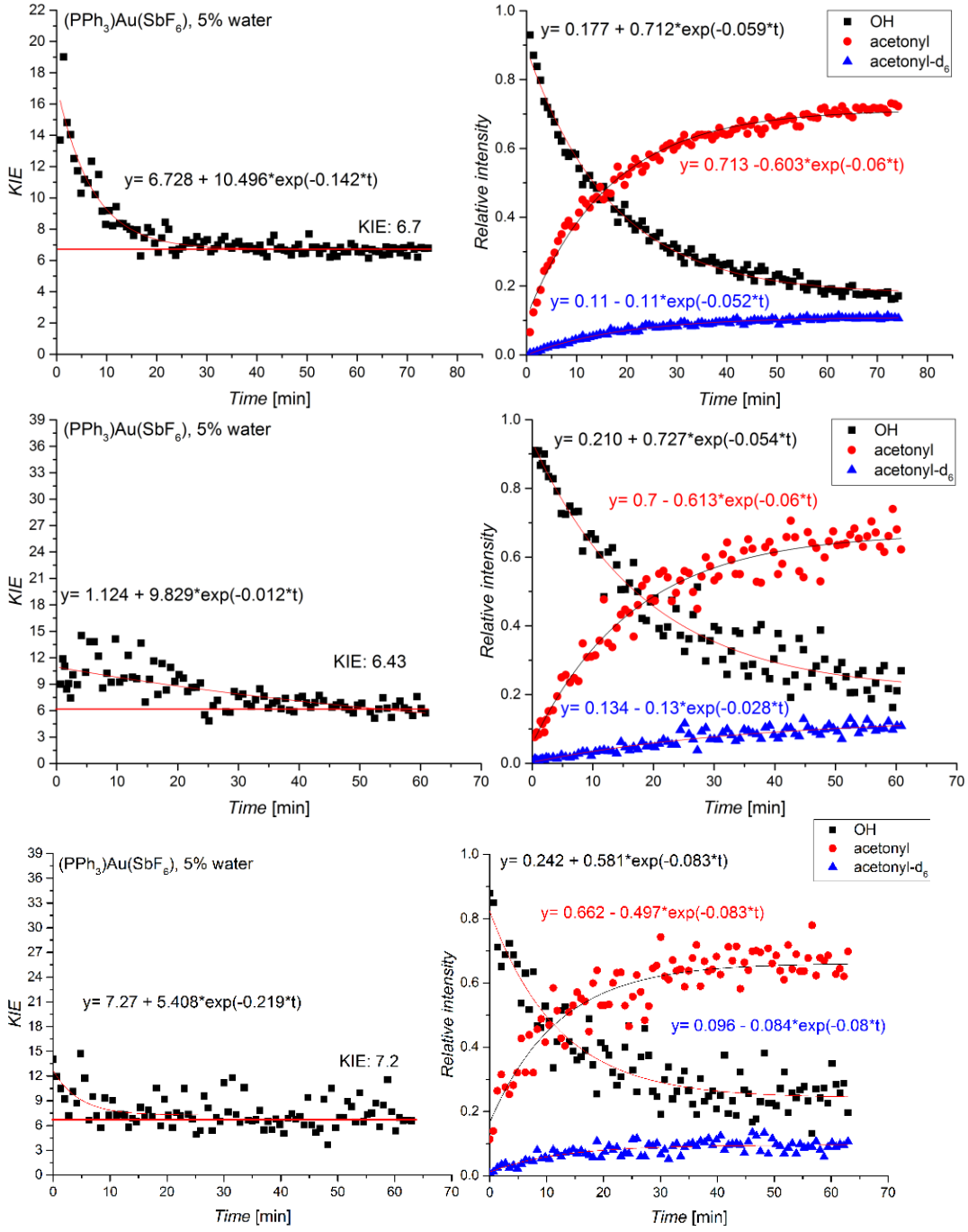

Figure S19. Relative intensity of selected ions $[(PPh_3)_2Au_2(CH_2COCH_3)]^+$, $[(PPh_3)_2Au_2(CD_2COCD_3)]^+$ and $[(PPh_3)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 5% of water to the reaction mixture of the $(PPh_3)Au(SbF_6)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

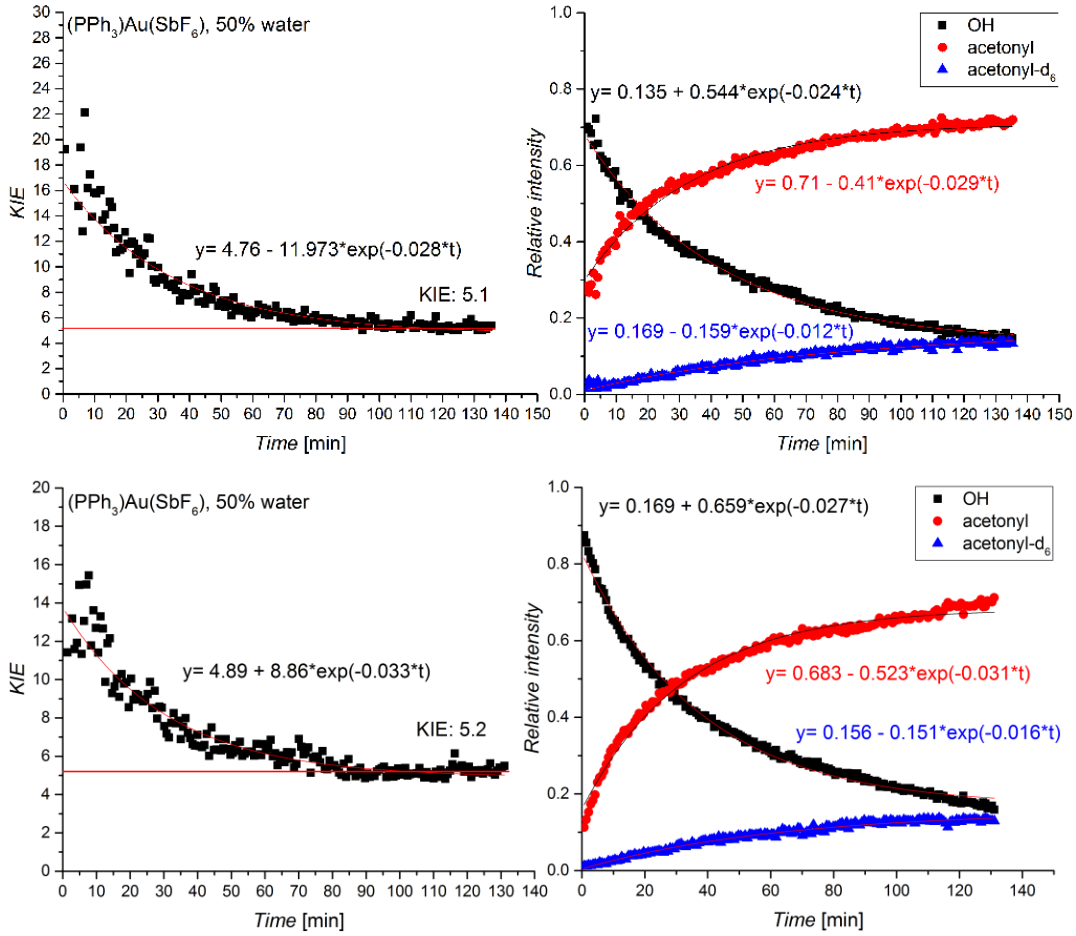

Figure S20. Relative intensity of selected ions $[(PPh_3)_2Au_2(CH_2COCH_3)]^+$, $[(PPh_3)_2Au_2(CD_2COCD_3)]^+$ and $[(PPh_3)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 50% of water to the reaction mixture of the $(PPh_3)Au(SbF_6)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

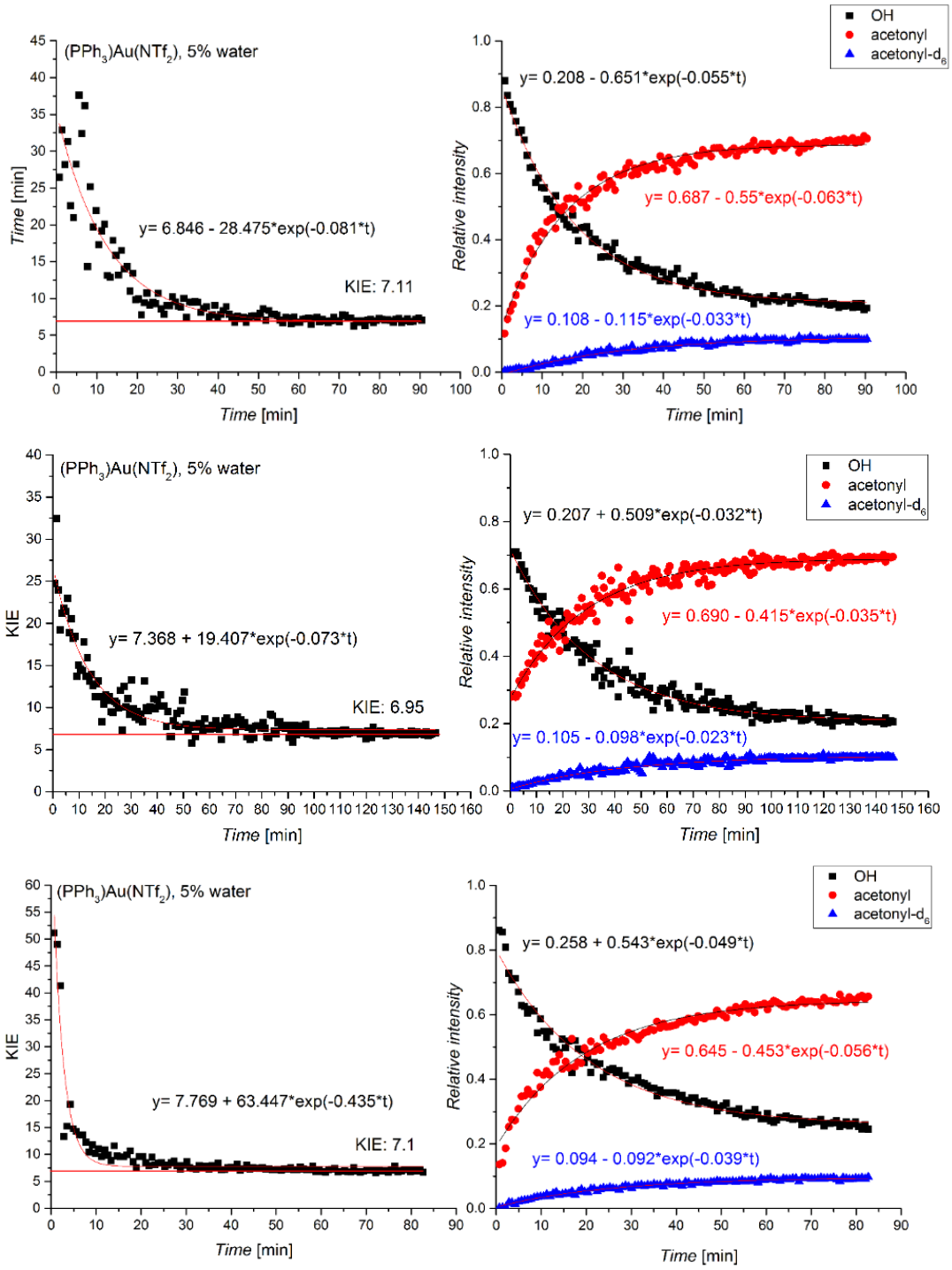

Figure S21. Relative intensity of selected ions $[(PPh_3)_2Au_2(CH_2COCH_3)]^+$, $[(PPh_3)_2Au_2(CD_2COCD_3)]^+$ and $[(PPh_3)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 5% of water to the reaction mixture of the $(PPh_3)Au(NTf_2)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

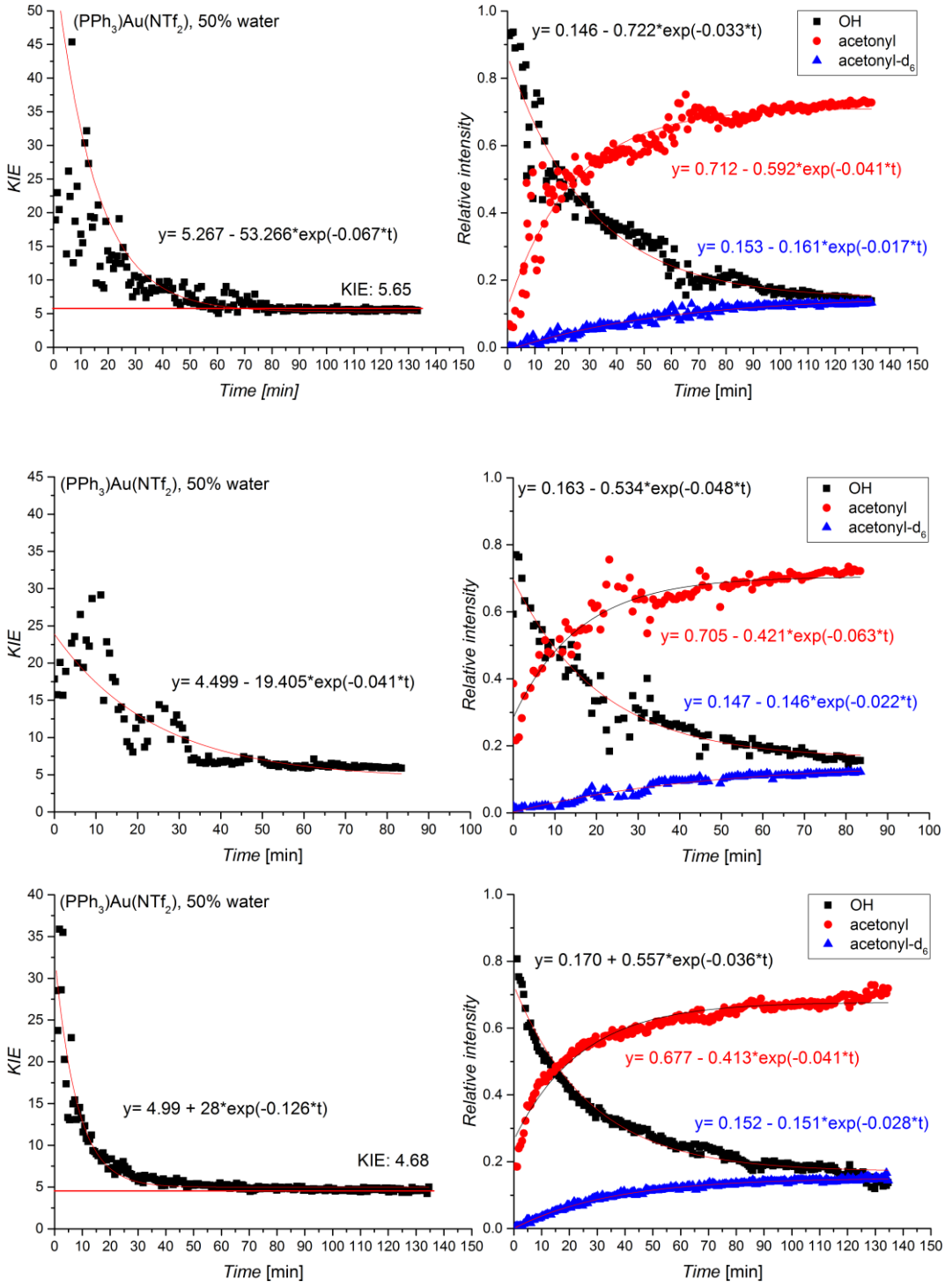

Figure S22. Relative intensity of selected ions $[(PPh_3)_2Au_2(CH_2COCH_3)]^+$, $[(PPh_3)_2Au_2(CD_2COCD_3)]^+$ and $[(PPh_3)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 50% of water to the reaction mixture of the $(PPh_3)Au(NTf_2)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

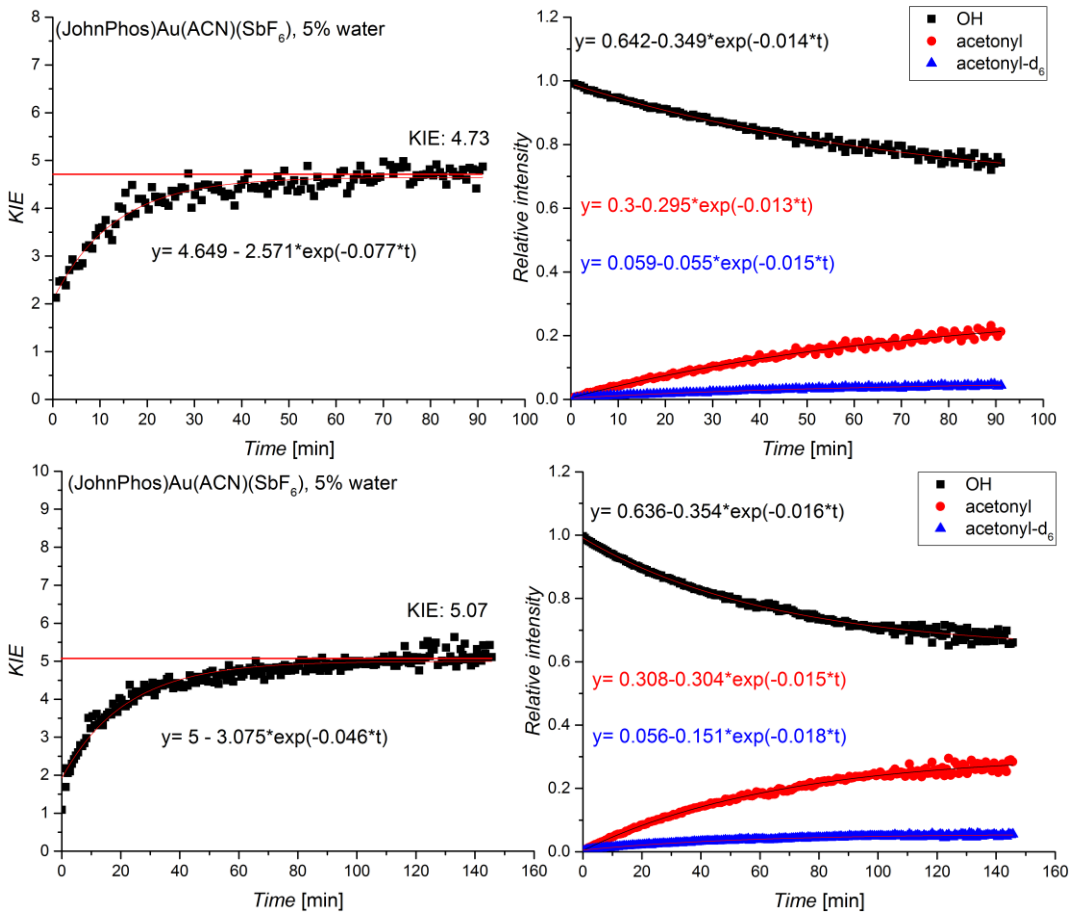

Figure S23. Relative intensity of selected ions $[(JohnPhos)_2Au_2(CH_2COCH_3)]^+$, $[(JohnPhos)_2Au_2(CD_2COCD_3)]^+$ and $[(JohnPhos)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 5% of water to the reaction mixture of the (JohnPhos)Au(ACN)(SbF_6) complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

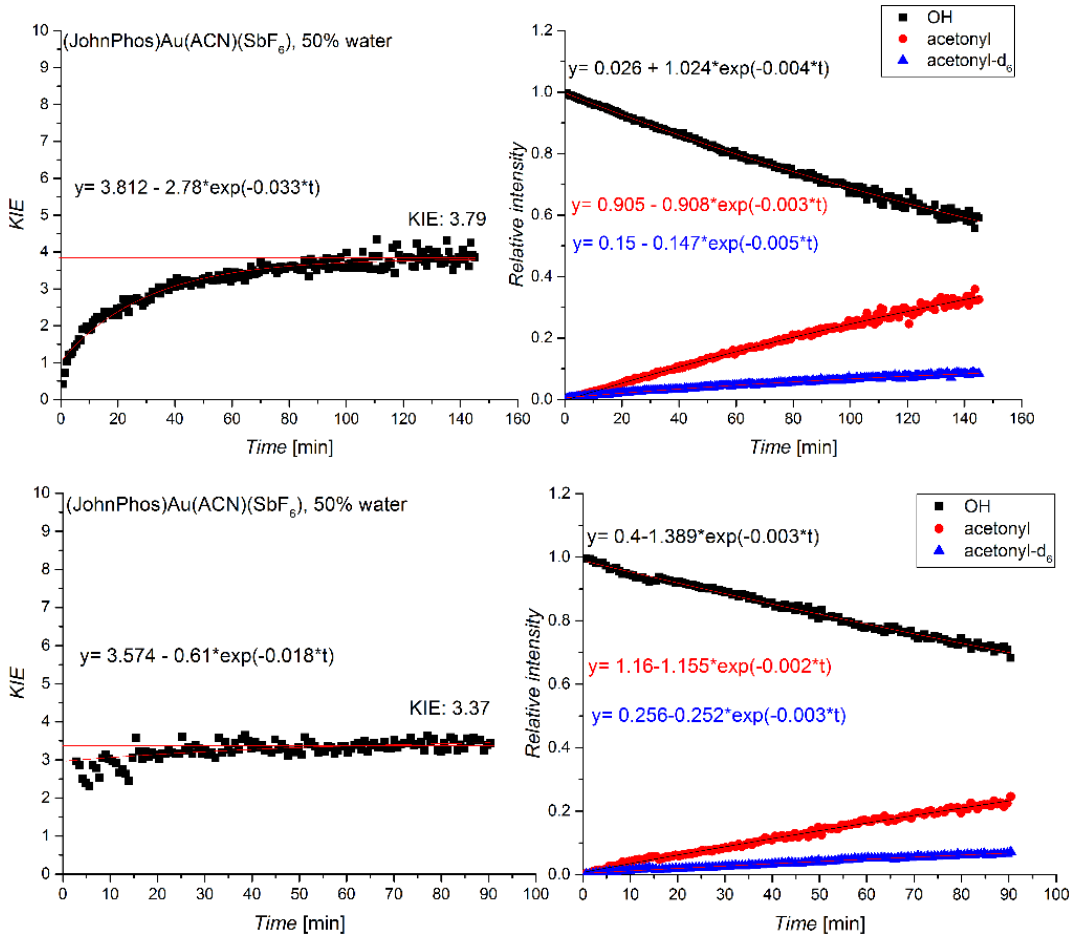

Figure S24. Relative intensity of selected ions $[(JohnPhos)_2Au_2(CH_2COCH_3)]^+$, $[(JohnPhos)_2Au_2(CD_2COCD_3)]^+$ and $[(JohnPhos)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 50% of water to the reaction mixture of the (JohnPhos)Au(ACN)(SbF_6) complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

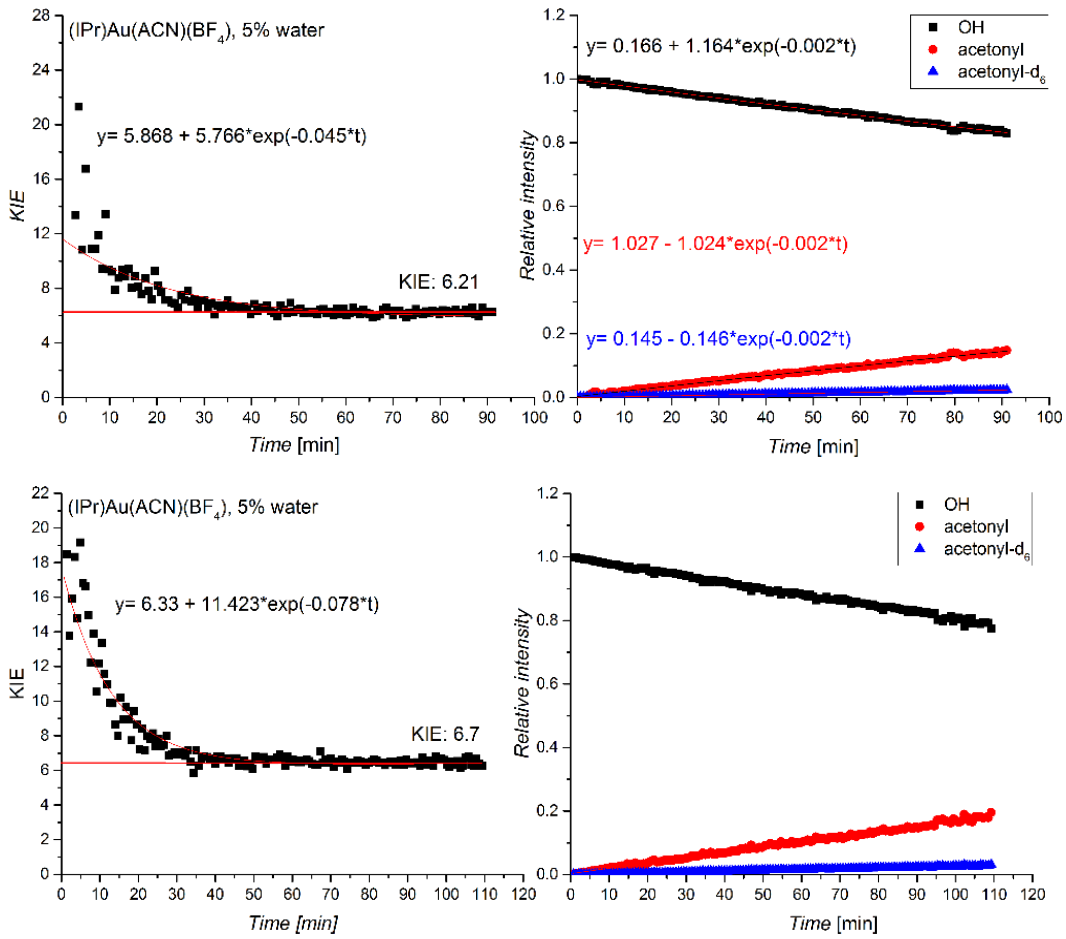

Figure S25. Relative intensity of selected ions $[(IPr)_2Au_2(CH_2COCH_3)]^+$, $[(IPr)_2Au_2(CD_2COCD_3)]^+$ and $[(IPr)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 5% of water to the reaction mixture of the $(IPr)Au(ACN)(BF_4)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

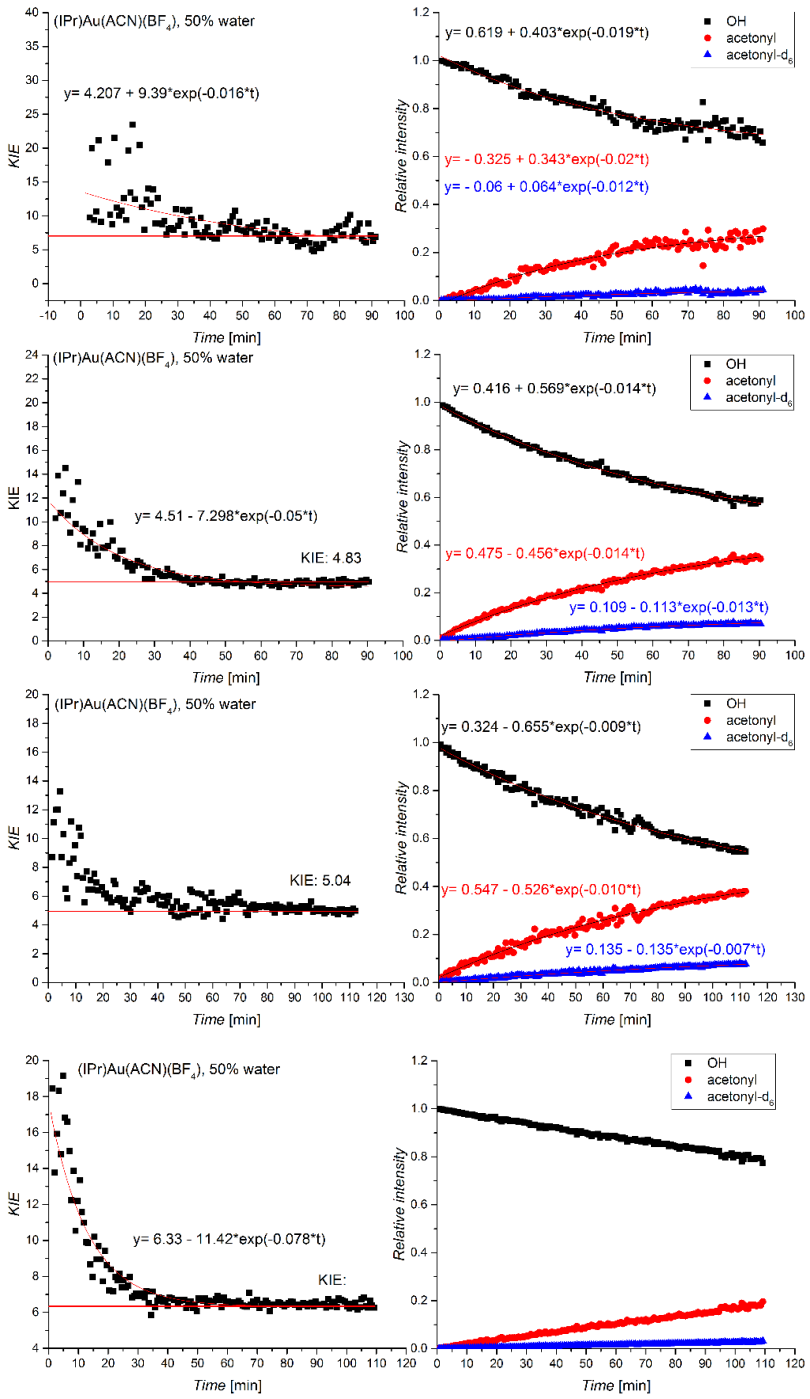

Figure S26. Relative intensity of selected ions $[(IPr)_2Au_2(CH_2COCH_3)]^+$, $[(IPr)_2Au_2(CD_2COCD_3)]^+$ and $[(IPr)_2Au_2(\mu\text{-}OH)]^+$ as a function of time for the addition of 50% of water to the reaction mixture of the $(IPr)Au(ACN)(BF_4)$ complex. The sum of the signal intensities of the labelled and the unlabelled ions and the diaurated hydroxide was normalized to 1.

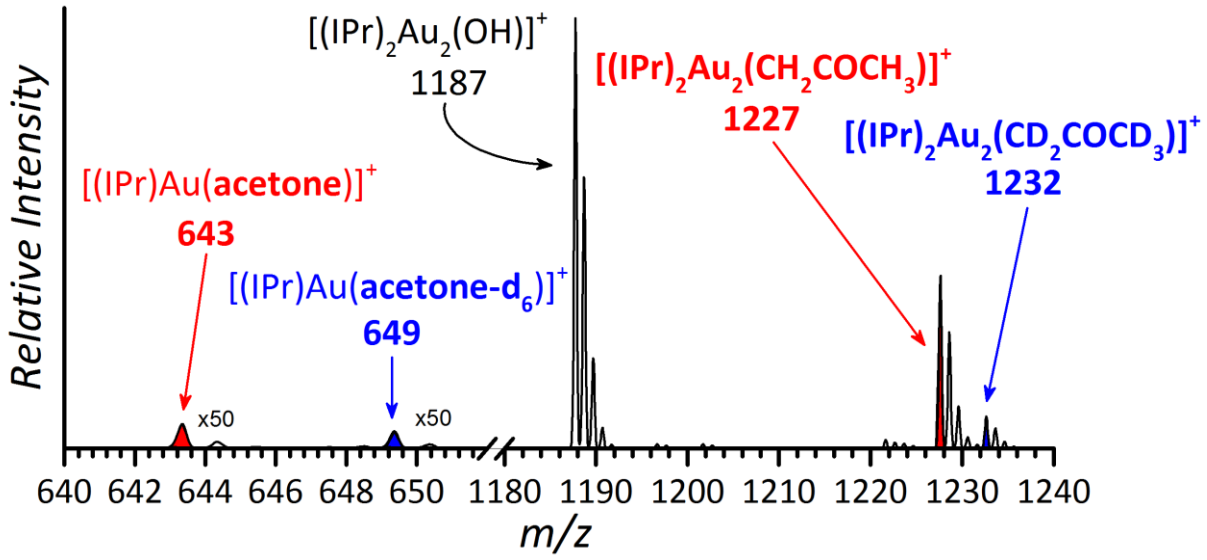

Figure S27. The ESI-MS source spectrum of the $[(IPr)_2Au_2(OH)BF_4]$ (637 µg) complex in dry dioxane (0.2 ml), dry acetone (0.7 ml) and dry acetone-d_6 (0.7 ml).

Formation of gold acetonyl complexes in time

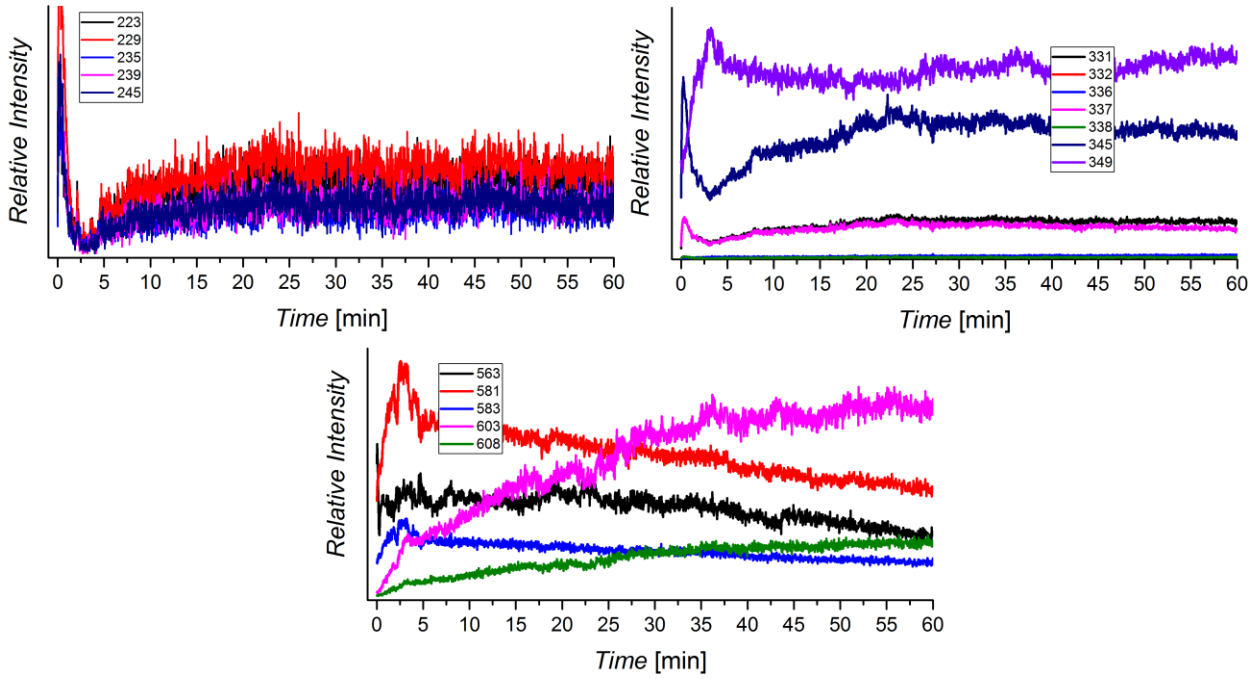

Figure S28. Experiment: [$(PMe_3)AuSbF_6$] (77 µg) was dissolved in THF (0.8 ml) and of H_2O (0.56 ml) and left to react overnight. Then, 0.8 ml of a 1:1 solution of CH_3COCH_3 and CD_3COCD_3 was added to the solution, and the solution was immediately monitored by ESI-MS. The sum of the signal intensities of the ions was normalized to TIC.

[($^{107}Ag(CH_3COCH_3)_2$]$^+$ (***m/z* 223**), [$^{107}Ag(CH_3COCH_3)(CD_3COCD_3)$]$^+$ (***m/z* 229**), [$^{107}Ag(CD_3COCD_3)_2$]$^+$ (***m/z* 235**), [$^{107}Ag(CH_3COCH_3)(THF)$]$^+$ (***m/z* 239**), [$^{109}Ag(CD_3COCD_3)(THF)$]$^+$ (***m/z* 245)**, [$(PMe_3)Au(CH_3COCH_3)$]$^+$ (***m/z* 331**), [$(PMe_3)Au(CH_2COCH_3)$]D^+ (***m/z* 332**), [$(PMe_3)Au(CD_2COCD_3)$]H^+ (***m/z* 336**), [$(PMe_3)Au(CD_3COCD_3)$]$^+$ (***m/z* 337**), [$(PMe_3)Au(CD_2COCD_3)$]D^+ (***m/z* 338**), [$(PMe_3)Au(THF)$]$^+$ (***m/z* 345**), [$(PMe_3)_2Au$]$^+$ (***m/z* 349**), [$(PMe_3)_2Au_2(OH)$]$^+$ (***m/z* 563**), [$(PMe_3)_2Au_2(Cl)$]$^+$ (***m/z* 581**), [$(PMe_3)_2Au_2(^{37}Cl)$]$^+$ (***m/z* 583**), [$(PMe_3)_2Au_2(CH_2COCH_3)$]$^+$ (***m/z* 603**), [$(PMe_3)_2Au_2(CD_2COCD_3)$]$^+$ (***m/z* 608**).

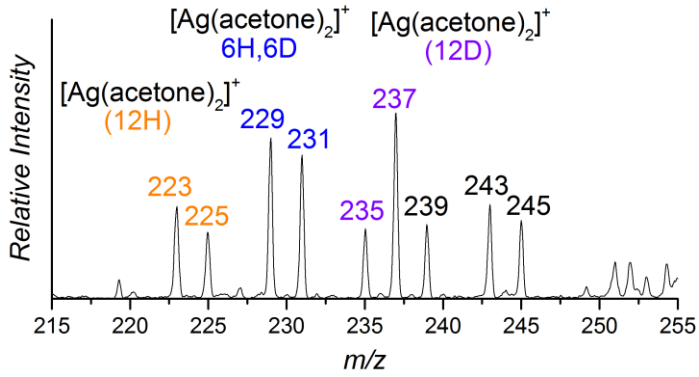

Figure S29. ESI-MS spectrum of the experiment, in which [$(PMe_3)AuSbF_6$] (77 µg) was dissolved in THF (0.8 ml) and H_2O (0.56 ml) and left to react for 15 hours. Then, a 1:1 mixture of CH_3COCH_3 and CD_3COCD_3 (0.8 ml) was added and the solution was immediately monitored by ESI-MS.

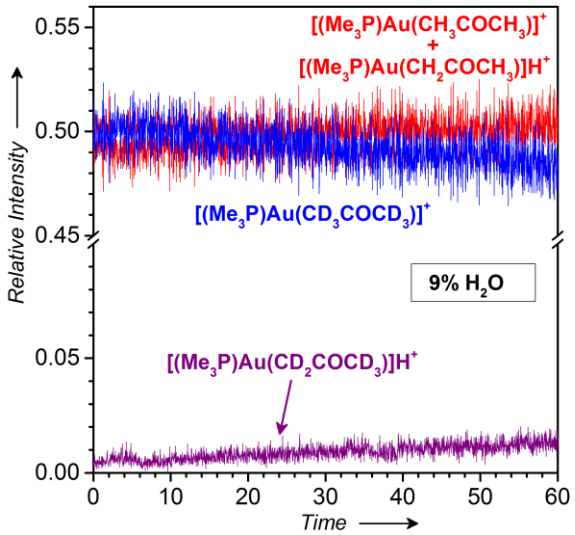

Figure S30. Results of the experiment, in which [(PMe₃)AuSbF₆] (77 µg) was dissolved in THF (0.8 ml), of H_2O 0.08 ml (9% v/v) and left to react for 15 hours. Then, a 1:1 mixture of CH_3COCH_3 and CD_3COCD_3 (0.8 ml) was added and the solution was immediately monitored by ESI-MS. The figure shows the time evolution of the relative concentration of $[(PMe_3)Au(CD_3COCD_3)]^+$ (m/z 337) with respect to the sum of both gold acetone complexes $[(PMe_3)Au(CH_3COCH_3)]^+$ and $[(PMe_3)Au(CD_2COCD_3)]D^+$. The purple lines show the evolution of the $[(PMe_3)Au(CD_2COCD_3)]H^+$ species (m/z 337).

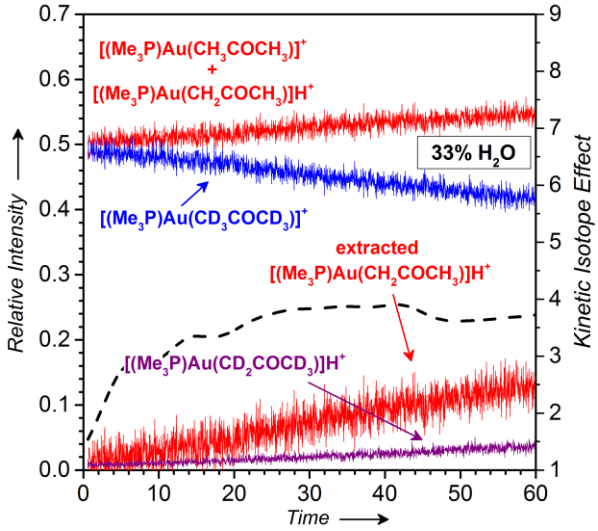

Figure S31. Results of the experiment, in which [(PMe₃)AuSbF₆] (77 µg) was dissolved in THF (0.8 ml), 0.4 ml of H_2O (33% v/v) and left to react for 15 hours. Then, a 1:1 mixture of CH_3COCH_3 and CD_3COCD_3 (0.8 ml) was added and the solution was immediately monitored by ESI-MS. The figure shows the time evolution of the relative concentration of $[(PMe_3)Au(CD_3COCD_3)]^+$ (m/z 337) with respect to the sum of both gold acetone complexes $[(PMe_3)Au(CH_3COCH_3)]^+$ and $[(PMe_3)Au(CD_2COCD_3)]D^+$. The purple lines show the evolution of the $[(PMe_3)Au(CD_2COCD_3)]H^+$ species (m/z 337).

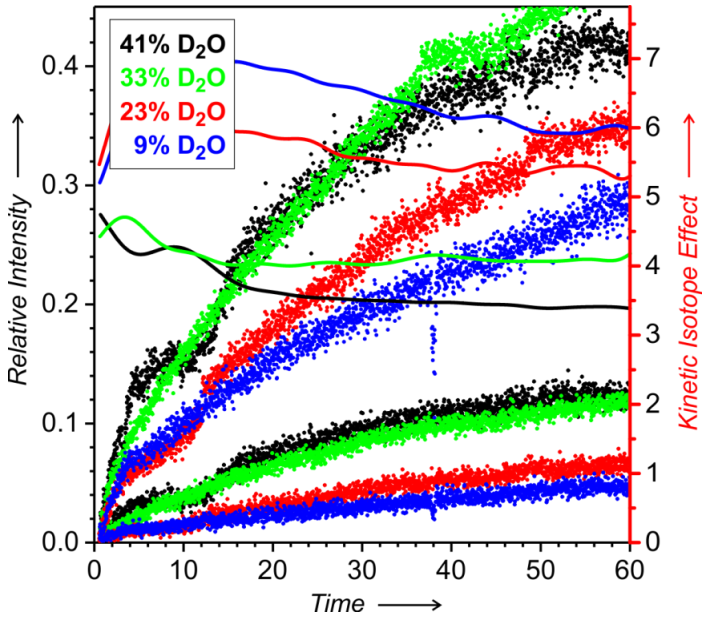

Figure S32. Time evolution of the relative concentrations $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$ (*m/z* 603, the upper curves) and $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$ (*m/z* 608, the lower curves) with respect to the sum of all diaurated complexes ($[(PMe_3)_2Au_2OH]^+$, $[(PMe_3)_2Au_2Cl]^+$, $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$ and $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$) in solution with D_2O. The right-hand axis refers to the kinetic isotope effect for the formation of digold acetonyls and the smoothed out ratio of $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$ and $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$ is shown as lines. Experiment: $[(PMe_3)AuSbF_6]$ (77 µg) was dissolved in THF (0.8 ml) and D_2O (80 – 9 % v/v in blue, 240 – 23% v/v in red, 400 – 33% v/v in green, and 560 – 41% v/v in black µL and left to react for 15 hours. Then, a 1:1 mixture of CH_3COCH_3 and CD_3COCD_3 (0.8 ml) was added and the solution was immediately monitored by ESI-MS.

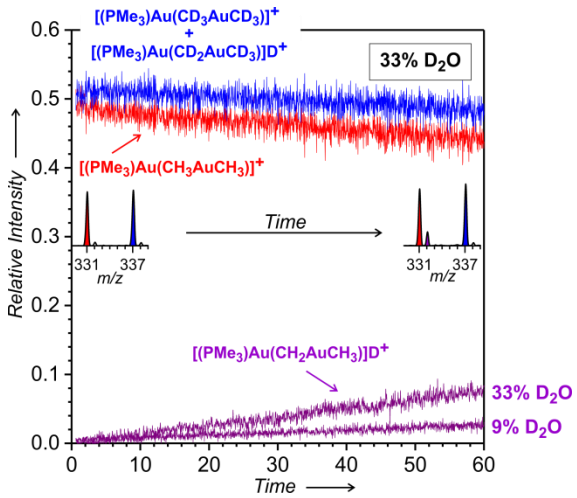

Figure S33: Results of the experiment, in which $[(PMe_3)AuSbF_6]$ (77 µg) was dissolved in THF (0.8 ml), 0.56 ml of D_2O (33% v/v) and left to react for 15 hours. Then, a 1:1 mixture of CD_3COCD_3 and CH_3COCH_3 (0.8 ml) was added and the solution was immediately monitored by ESI-MS. Time evolution of the relative concentration of $[(PMe_3)Au(CH_3COCH_3)]^+$ (m/z 331) with respect to the sum of both gold acetone complexes $[(PMe_3)Au(CD_3COCD_3)]^+$ and $[(PMe_3)Au(CD_2COCD_3)]D^+$. The purple lines show the evolution of the $[(PMe_3)Au(CH_3COCH_3)]D^+$ species (m/z 332).

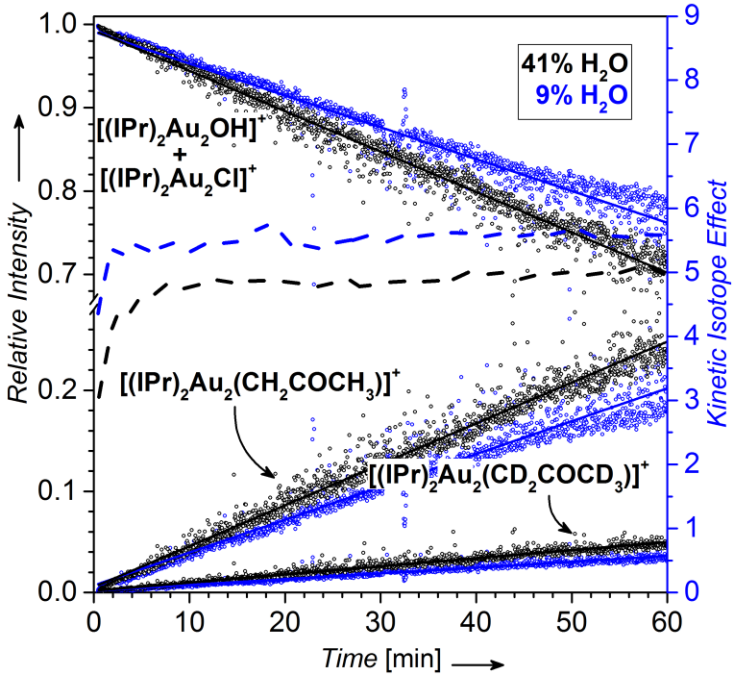

Figure S34. Results of the experiment, in which [(IPr)AuBF$_4$] (358 µg) was dissolved in dioxane (0.2 ml) and 0.14 ml or 0.02 ml of H_2O (41 % v/v or 9 % v/v, respectively) and left to react for 15 hours. Then, a 1:1 mixture of CH_3COCH_3 and CD_3COCD_3 (1.4 ml) was added and the solution was immediately monitored by ESI-MS. Time evolution of the relative concentrations of $[(IPr)_2Au_2OH]^+$ together with $[(IPr)_2Au_2Cl]^+$ (*m/z* 1187 + *m/z* 1205 + *m/z* 1207), $[(IPr)_2Au_2(CH_2COCH_3)]^+$ (*m/z* 1227) and $[(IPr)_2Au_2(CD_2COCD_3)]^+$ (*m/z* 1232) with respect to the sum of all these diaurated complexes in solution with H_2O (41 % v/v in black and 9% v/v in blue; the lines serve to guide the eyes). The right-hand axis refers to the kinetic isotope effect for the formation of digold acetonyls and the smoothed out ratio of $[(IPr)_2Au_2(CH_2COCH_3)]^+$ and $[(IPr)_2Au_2(CD_2COCD_3)]^+$ is shown as dashed lines.

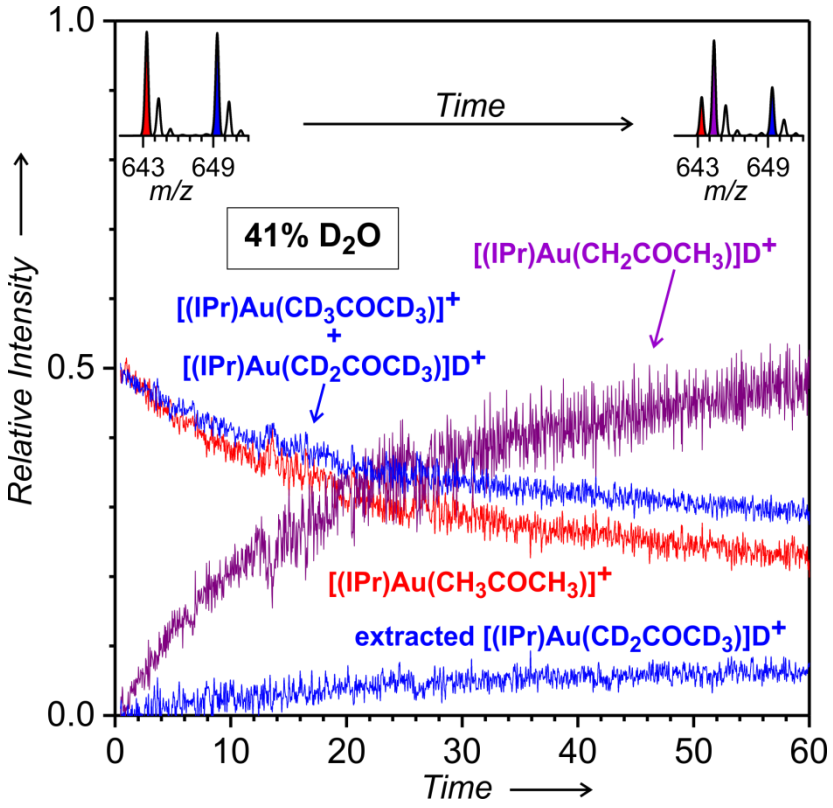

Figure S35: Results of the experiment, in which [(IPr)AuBF$_4$] (358 µg) was dissolved in dioxane (0.2 ml), 41% of D_2O (0.14 ml) and left to react for 15 hours. Then, a 1:1 mixture of CH_3COCH_3 and CD_3COCD_3 (1.4 ml) was added and the solution was immediately monitored by ESI-MS. Time evolution of the relative concentration of $[(IPr)Au(CH_3COCH_3)]^+$ (m/z 643) with respect to the sum of both gold acetone complexes $[(IPr)Au(CD_3COCD_3)]^+$ and $[(IPr)Au(CD_2COCD_3)]D^+$. The purple lines show the evolution of the $[(IPr)Au(CH_2COCH_3)]D^+$ species.

C-H activation

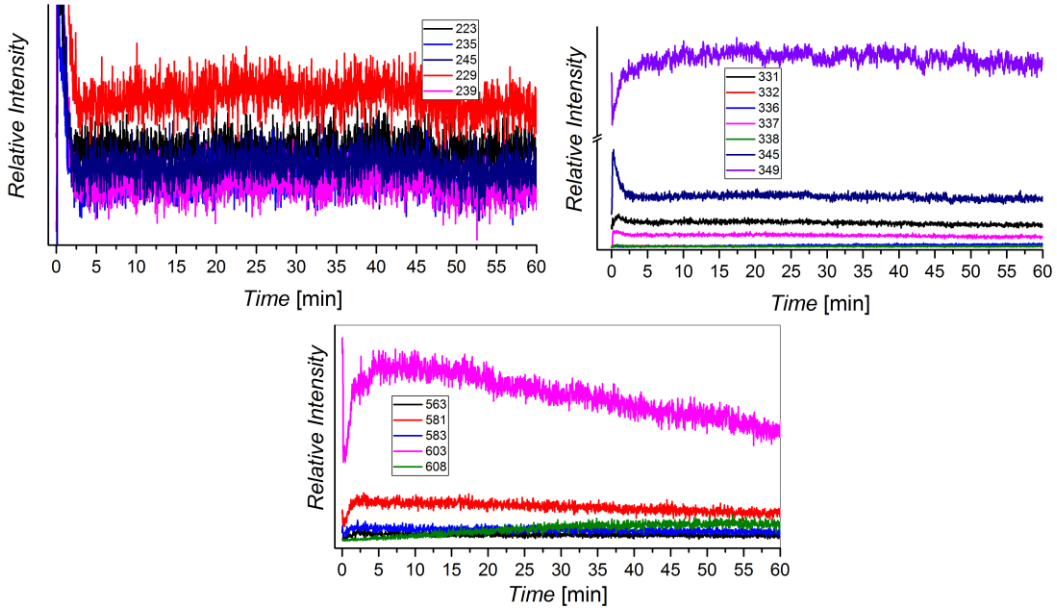

Figure S36. Results of the experiment, in which a final solution was prepared by addition of 0.4 ml of CD_3COCD_3 to an overnight reaction mixture of [$(PMe_3)AuSbF_6$] (77 µg) in THF (0.8 ml), H_2O (0.6 ml) and CH_3COCH_3 (0.4 ml). Then the solution was immediately monitored by ESI-MS. The sum of the signal intensities of the ion was normalized to TIC.

$[(^{107}Ag(CH_3COCH_3)_2]^+$ (***m/z* 223**), $[^{107}Ag(CH_3COCH_3)(CD_3COCD_3)]^+$ (***m/z* 229**), $[^{107}Ag(CD_3COCD_3)_2]^+$ (***m/z* 235**), $[^{107}Ag(CH_3COCH_3)(THF)]^+$ (***m/z* 239**), $[^{109}Ag(CD_3COCD_3)(THF)]^+$ (***m/z* 245)**, $([(PMe_3)Au(CH_3COCH_3)]^+$ (***m/z* 331**), $[(PMe_3)Au(CH_2COCH_3)]D^+$ (***m/z* 332**), $[(PMe_3)Au(CD_2COCD_3)]H^+$ (***m/z* 336**), $[(PMe_3)Au(CD_3COCD_3)]^+$ (***m/z* 337**), $[(PMe_3)Au(CD_2COCD_3)]D^+$ (***m/z* 338**), $[(PMe_3)Au(THF)]^+$ (***m/z* 345**), $[(PMe_3)_2Au]^+$ (***m/z* 349**), $[(PMe_3)_2Au_2(OH)]^+$ (***m/z* 563**), $[(PMe_3)_2Au_2(Cl)]^+$ (***m/z* 581**), $[(PMe_3)_2Au_2(^{37}Cl)]^+$ (***m/z* 583**), $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$ (***m/z* 603**), $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$ (***m/z* 608**).

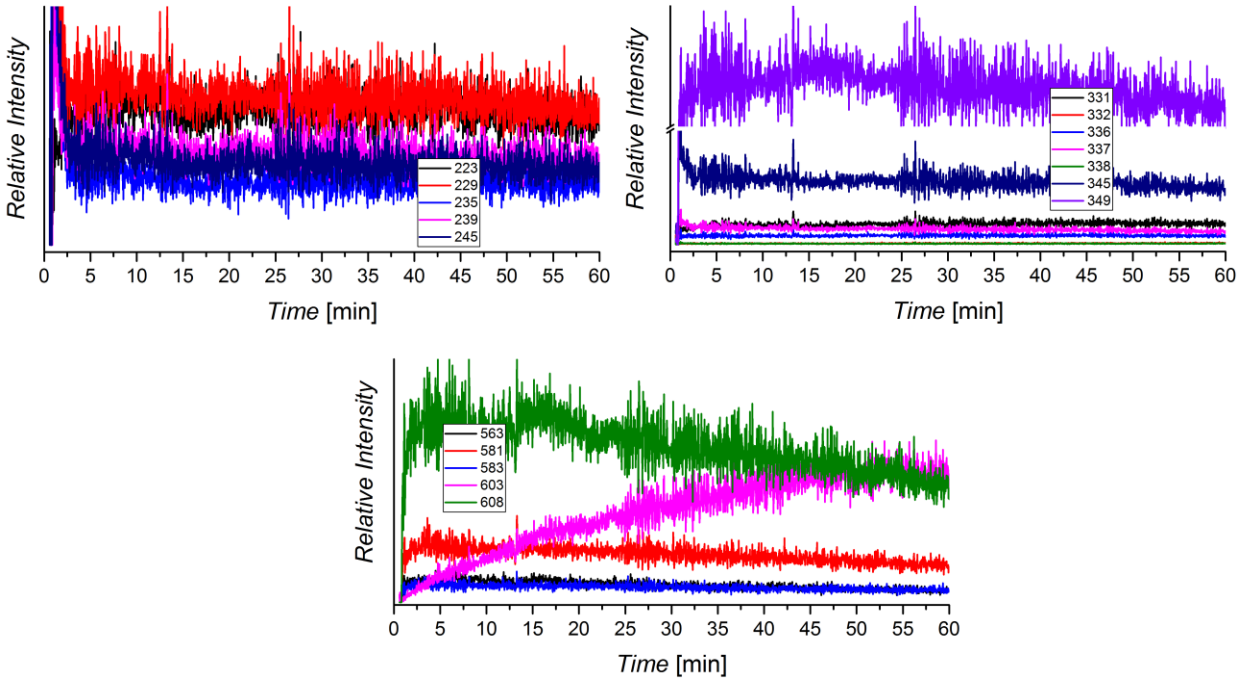

Figure S37. Results of the experiment, in which a final solution was prepared by addition of 0.4 ml of CH_3COCH_3 to an overnight reaction mixture of [$(PMe_3)AuSbF_6$] (77 µg) in THF (0.8 ml), H_2O (0.6 ml) and CD_3COCD_3 (0.4 ml). Then the solution was immediately monitored by ESI-MS. The sum of the signal intensities of the ions was normalized to TIC.

[$(^{107}Ag(CH_3COCH_3)_2]^+$ (***m/z* 223**), [$^{107}Ag(CH_3COCH_3)(CD_3COCD_3)]^+$ (***m/z* 229**), [$^{107}Ag(CD_3COCD_3)_2]^+$ (***m/z* 235**), [$^{107}Ag(CH_3COCH_3)(THF)]^+$ (***m/z* 239**), [$^{109}Ag(CD_3COCD_3)(THF)]^+$ (***m/z* 245)**, ([$(PMe_3)Au(CH_3COCH_3)]^+$ (***m/z* 331**), [$(PMe_3)Au(CH_2COCH_3)]D^+$ (***m/z* 332**), [$(PMe_3)Au(CD_2COCD_3)]H^+$ (***m/z* 336**), [$(PMe_3)Au(CD_3COCD_3)]^+$ (***m/z* 337**), [$(PMe_3)Au(CD_2COCD_3)]D^+$ (***m/z* 338**), [$(PMe_3)Au(THF)]^+$ (***m/z* 345**), [$(PMe_3)_2Au]^+$ (***m/z* 349**), [$(PMe_3)_2Au_2(OH)]^+$ (***m/z* 563**), [$(PMe_3)_2Au_2(Cl)]^+$ (***m/z* 581**), [$(PMe_3)_2Au_2(^{37}Cl)]^+$ (***m/z* 583**), [$(PMe_3)_2Au_2(CH_2COCH_3)]^+$ (***m/z* 603**), [$(PMe_3)_2Au_2(CD_2COCD_3)]^+$ (***m/z* 608**).

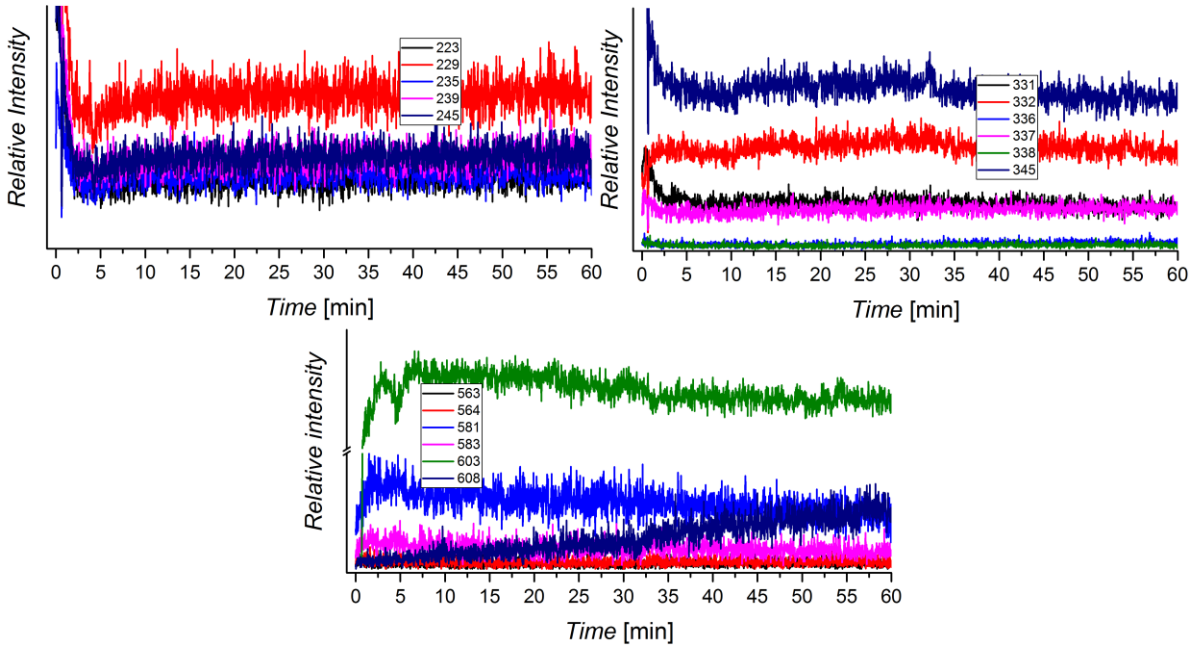

Figure S38. Results of the experiment, in which a final solution was prepared by addition of 0.4 ml of CH_3COCH_3 to an overnight reaction mixture of $[(PMe_3)AuSbF_6]$ (77 µg) in THF (0.8 ml), D_2O (0.6 ml) and CD_3COCD_3 (0.4 ml). Then the solution was immediately monitored by ESI-MS. The sum of the signal intensities of the ions was normalized to TIC.

$[(^{107}Ag(CH_3COCH_3)_2]^+$ (***m/z* 223**), $[^{107}Ag(CH_3COCH_3)(CD_3COCD_3)]^+$ (***m/z* 229**), $[^{107}Ag(CD_3COCD_3)_2]^+$ (***m/z* 235**), $[^{107}Ag(CH_3COCH_3)(THF)]^+$ (***m/z* 239**), $[^{109}Ag(CD_3COCD_3)(THF)]^+$ (***m/z* 245)**, $([(PMe_3)Au(CH_3COCH_3)]^+$ (***m/z* 331**), $[(PMe_3)Au(CH_2COCH_3)]D^+$ (***m/z* 332**), $[(PMe_3)Au(CD_2COCD_3)]H^+$ (***m/z* 336**), $[(PMe_3)Au(CD_3COCD_3)]^+$ (***m/z* 337**), $[(PMe_3)Au(CD_2COCD_3)]D^+$ (***m/z* 338**), $[(PMe_3)Au(THF)]^+$ (***m/z* 345**), $[(PMe_3)_2Au]^+$ (***m/z* 349**), $[(PMe_3)_2Au_2(OH)]^+$ (***m/z* 563**), $[(PMe_3)_2Au_2(Cl)]^+$ (***m/z* 581**), $[(PMe_3)_2Au_2(^{37}Cl)]^+$ (***m/z* 583**), $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$ (***m/z* 603**), $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$ (***m/z* 608**).

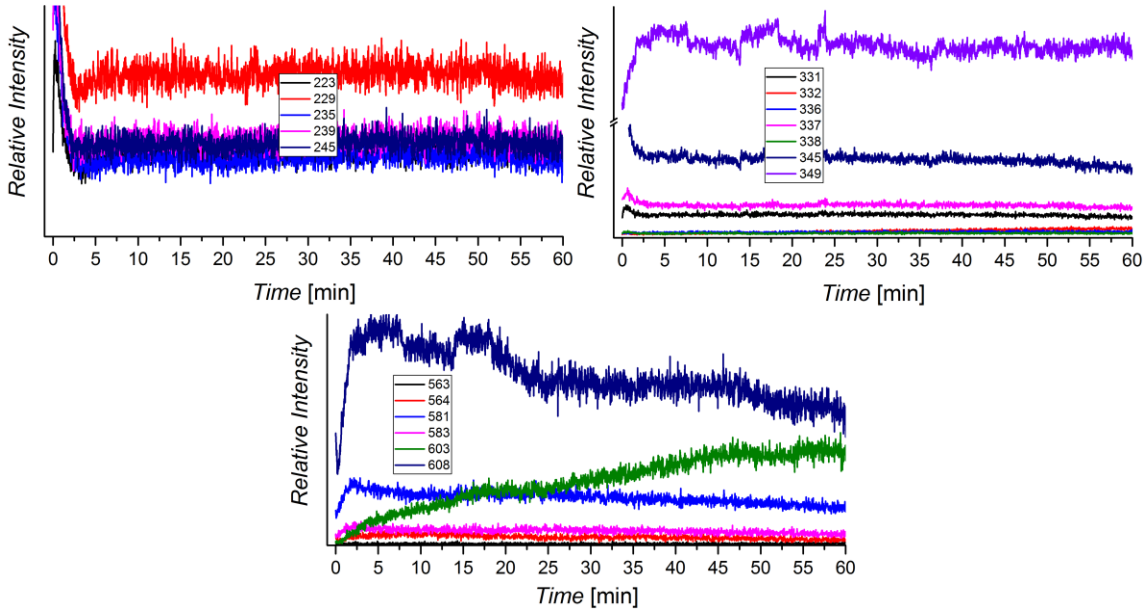

Figure S39. Results of the experiment, in which a final solution was prepared by addition of 0.4 ml of CD_3COCD_3 to an overnight reaction mixture of [$(PMe_3)AuSbF_6$] (77 µg) in THF (0.8 ml), D_2O (0.6 ml) and CH_3COCH_3 (0.4 ml). Then the solution was immediately monitored by ESI-MS. The sum of the signal intensities of the ions was normalized to TIC.

$[(^{107}Ag(CH_3COCH_3)_2]^+$ (***m/z* 223**), $[^{107}Ag(CH_3COCH_3)(CD_3COCD_3)]^+$ (***m/z* 229**), $[^{107}Ag(CD_3COCD_3)_2]^+$ (***m/z* 235**), $[^{107}Ag(CH_3COCH_3)(THF)]^+$ (***m/z* 239**), $[^{109}Ag(CD_3COCD_3)(THF)]^+$ (***m/z* 245)**, $([(PMe_3)Au(CH_3COCH_3)]^+$ (***m/z* 331**), $[(PMe_3)Au(CH_2COCH_3)]D^+$ (***m/z* 332**), $[(PMe_3)Au(CD_2COCD_3)]H^+$ (***m/z* 336**), $[(PMe_3)Au(CD_3COCD_3)]^+$ (***m/z* 337**), $[(PMe_3)Au(CD_2COCD_3)]D^+$ (***m/z* 338**), $[(PMe_3)Au(THF)]^+$ (***m/z* 345**), $[(PMe_3)_2Au]^+$ (***m/z* 349**), $[(PMe_3)_2Au_2(OH)]^+$ (***m/z* 563**), $[(PMe_3)_2Au_2(Cl)]^+$ (***m/z* 581**), $[(PMe_3)_2Au_2(^{37}Cl)]^+$ (***m/z* 583**), $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$ (***m/z* 603**), $[(PMe_3)_2Au_2(CD_2COCD_3)]^+$ (***m/z* 608**).

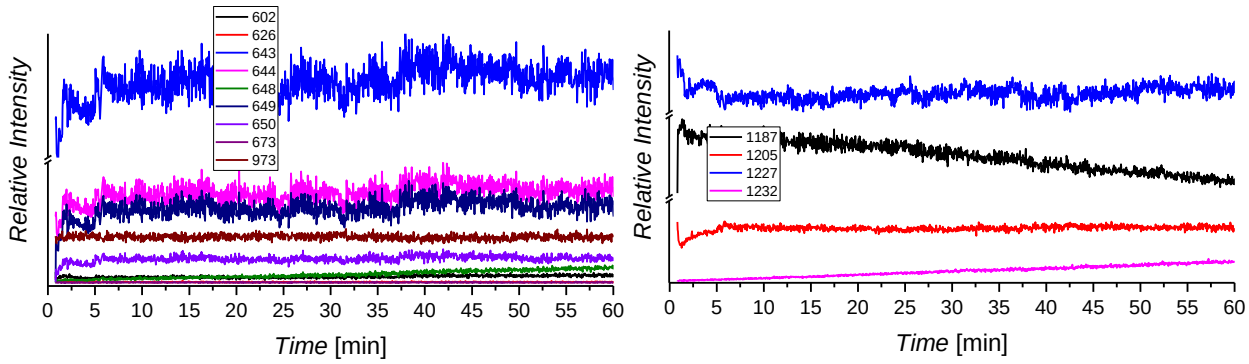

Figure S40. Results of the experiment, in which a final solution was prepared by addition of 0.7 ml of CD_3COCD_3 to an overnight reaction mixture of [(IPr)$AuBF_4$] (358 µg) in dioxane (0.2 ml), H_2O (0.45 ml) and CH_3COCH_3 (0.7 ml). Then the solution was immediately monitored by ESI-MS. The sum of the signal intensities of the ions was normalized to TIC.

([(IPr)Au(H_2O)]$^+$ (***m/z* 602**), [(IPr)Au(CH_3CN)]$^+$ (***m/z* 626**), [(IPr)Au(CH_3COCH_3)]$^+$ (***m/z* 643**), [(IPr)Au(CH_3COCH_3)]$^+$ (***m/z* 644**), [(IPr)Au(CD_2COCH_3)]H^+ (***m/z* 648**), [(IPr)Au(CD_3COCD_3)]$^+$ (***m/z* 649**), [(IPr)Au($^{13}CH_3COCH_3$)]$^+$ (***m/z* 650**), [(IPr)$_2$Au(CH_3COCH_3)]$^+$ (***m/z* 973**), [(IPr)$_2$Au$_2$(OH)]$^+$ (***m/z* 1187**), [(IPr)$_2$Au$_2$(Cl)]$^+$ (***m/z* 1205**), [(IPr)$_2$Au$_2$(CH_2COCH_3)]$^+$ (***m/z* 1227**), [(IPr)$_2$Au$_2$(CD_2COCD_3)]$^+$ (***m/z* 1232**).

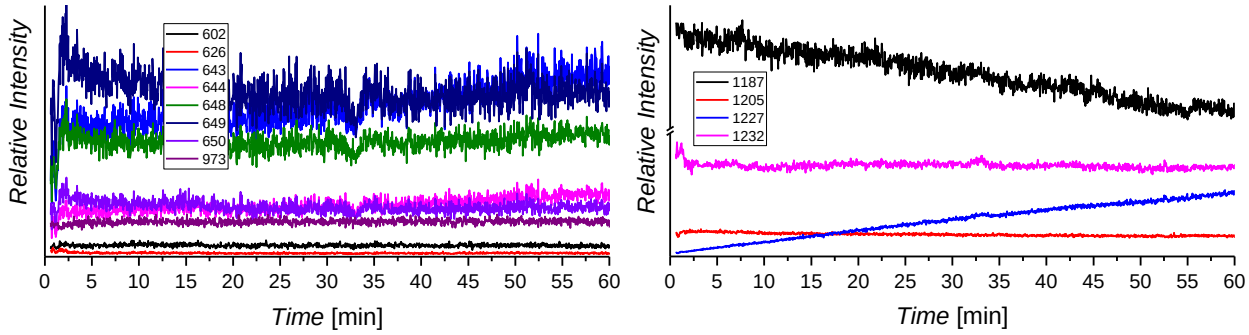

Figure S41. Results of the experiment, in which a final solution was prepared by addition of 0.7 ml of CH_3COCH_3 to an overnight reaction mixture of [(IPr)$AuBF_4$] (358 µg) in dioxane (0.2 ml), H_2O (0.45 ml) and CD_3COCD_3 (0.7 ml). Then the solution was immediately monitored by ESI-MS. The sum of the signal intensities of the ions was normalized to TIC.

([(IPr)Au(H_2O)]$^+$ (***m/z* 602**), [(IPr)Au(CH_3CN)]$^+$ (***m/z* 626**), [(IPr)Au(CH_3COCH_3)]$^+$ (***m/z* 643**), [(IPr)Au(CH_3COCH_3)]$^+$ (***m/z* 644**), [(IPr)Au(CD_2COCH_3)]H^+ (***m/z* 648**), [(IPr)Au(CD_3COCD_3)]$^+$ (***m/z* 649**), [(IPr)Au($^{13}CH_3COCH_3$)]$^+$ (***m/z* 650**), [(IPr)$_2$Au(CH_3COCH_3)]$^+$ (***m/z* 973**), [(IPr)$_2$Au$_2$(OH)]$^+$ (***m/z* 1187**), [(IPr)$_2$Au$_2$(Cl)]$^+$ (***m/z* 1205**), [(IPr)$_2$Au$_2$(CH_2COCH_3)]$^+$ (***m/z* 1227**), [(IPr)$_2$Au$_2$(CD_2COCD_3)]$^+$ (***m/z* 1232**).

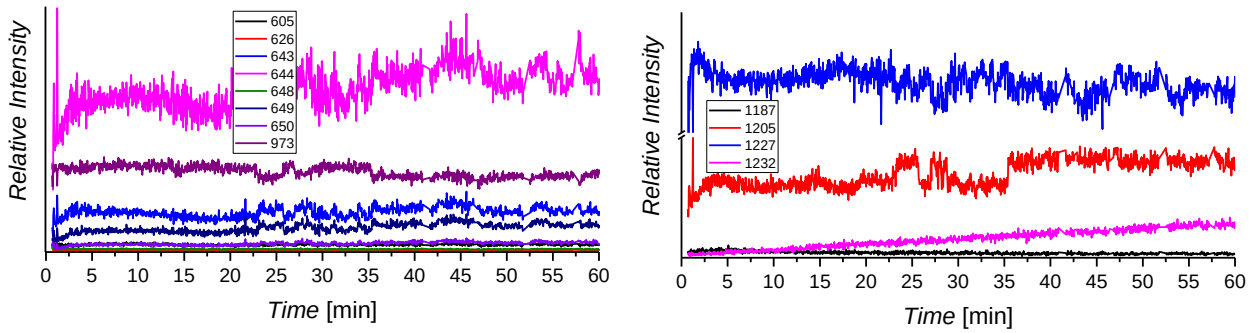

Figure S42. Results of the experiment, in which a final solution was prepared by addition of 0.7 ml of CD_3COCD_3 to an overnight reaction mixture of [(IPr)$AuBF_4$] (358 µg) in dioxane (0.2 ml), D_2O (0.45 ml) and CH_3COCH_3 (0.7 ml). Then the solution was immediately monitored by ESI-MS. The sum of the signal intensities of the ions was normalized to TIC.

$([(IPr)Au(H_2O)]^+$ (***m/z* 602**), $[(IPr)Au(CH_3CN)]^+$ (***m/z* 626**), $[(IPr)Au(CH_3COCH_3)]^+$ (***m/z* 643**), $[(IPr)Au(CH_3COCH_3)]^+$ (***m/z* 644**), $[(IPr)Au(CD_2COCH_3)]H^+$ (***m/z* 648**), $[(IPr)Au(CD_3COCD_3)]^+$ (***m/z* 649**), $[(IPr)Au(^{13}CH_3COCH_3)]^+$ (***m/z* 650**), $[(IPr)_2Au(CH_3COCH_3)]^+$ (***m/z* 973**), $[(IPr)_2Au_2(OH)]^+$ (***m/z* 1187**), $[(IPr)_2Au_2(Cl)]^+$ (***m/z* 1205**), $[(IPr)_2Au_2(CH_2COCH_3)]^+$ (***m/z* 1227**), $[(IPr)_2Au_2(CD_2COCD_3)]^+$ (***m/z* 1232**).

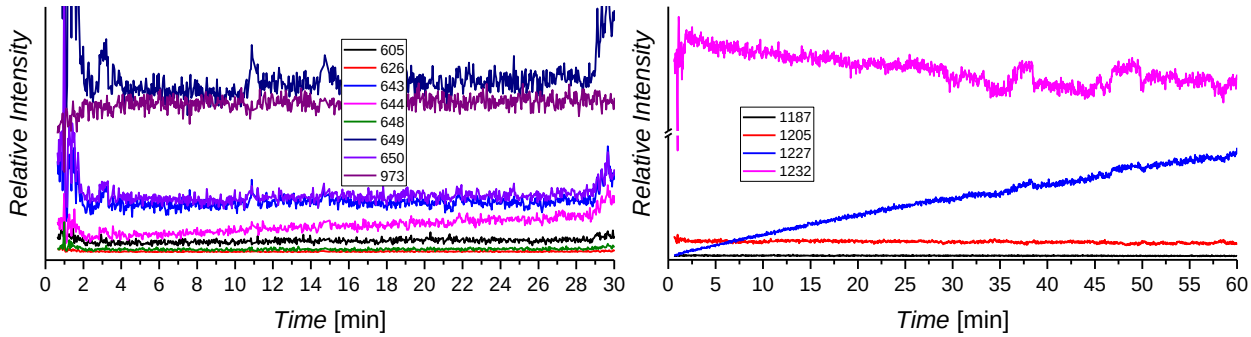

Figure S43. Results of the experiment, in which a final solution was prepared by addition of 0.7 ml of CH_3COCH_3 to an overnight reaction mixture of [(IPr)$AuBF_4$] (358 µg) in dioxane (0.2 ml), D_2O (0.45 ml) and CD_3COCD_3 (0.7 ml). Then the solution was immediately monitored by ESI-MS. The sum of the signal intensities of the ions was normalized to TIC.

$([(IPr)Au(H_2O)]^+$ (***m/z* 602**), $[(IPr)Au(CH_3CN)]^+$ (***m/z* 626**), $[(IPr)Au(CH_3COCH_3)]^+$ (***m/z* 643**), $[(IPr)Au(CH_3COCH_3)]^+$ (***m/z* 644**), $[(IPr)Au(CD_2COCH_3)]H^+$ (***m/z* 648**), $[(IPr)Au(CD_3COCD_3)]^+$ (***m/z* 649**), $[(IPr)Au(^{13}CH_3COCH_3)]^+$ (***m/z* 650**), $[(IPr)_2Au(CH_3COCH_3)]^+$ (***m/z* 973**), $[(IPr)_2Au_2(OH)]^+$ (***m/z* 1187**), $[(IPr)_2Au_2(Cl)]^+$ (***m/z* 1205**), $[(IPr)_2Au_2(CH_2COCH_3)]^+$ (***m/z* 1227**), $[(IPr)_2Au_2(CD_2COCD_3)]^+$ (***m/z* 1232**).

ESI-MS source and CID spectra

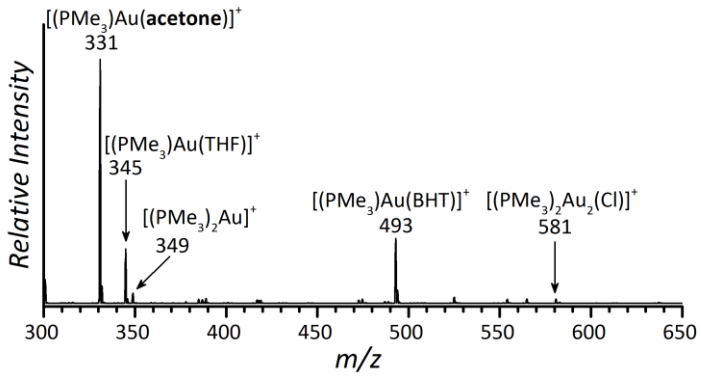

Figure S44. The ESI-MS source spectrum of [(PMe₃)Au(SbF₆)] (77 µg) complex in dry THF (0.8 ml) and acetone (0.4 ml).

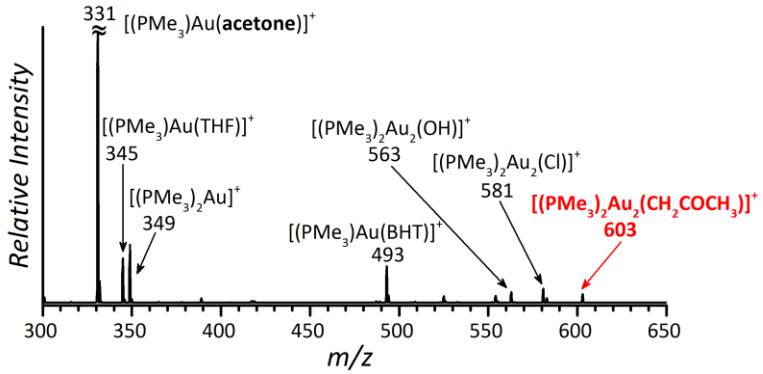

Figure S45. The ESI-MS source spectrum of [(PMe₃)Au(SbF₆)] (77 µg) complex in dry THF (0.8 ml) and acetone (0.4 ml), upon water (0.4 ml) addition.

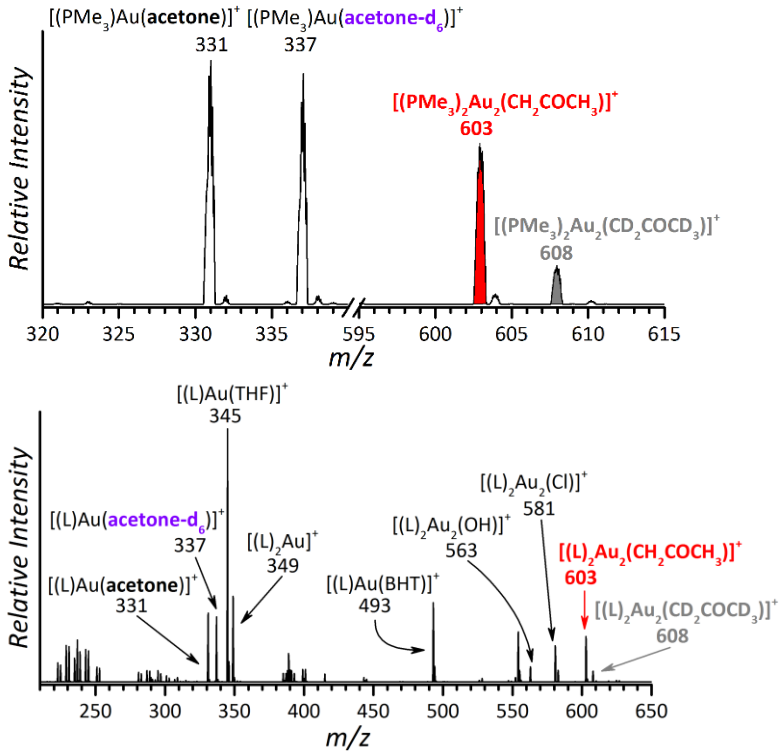

Figure S46. The ESI-MS source spectrum of [(PMe₃)Au(SbF₆)] (77 µg) complex in THF (0.8 ml), acetone (0.4 ml) and acetone-d_6 (0.4 ml), upon water (0.8 ml) addition. (L= PMe₃)

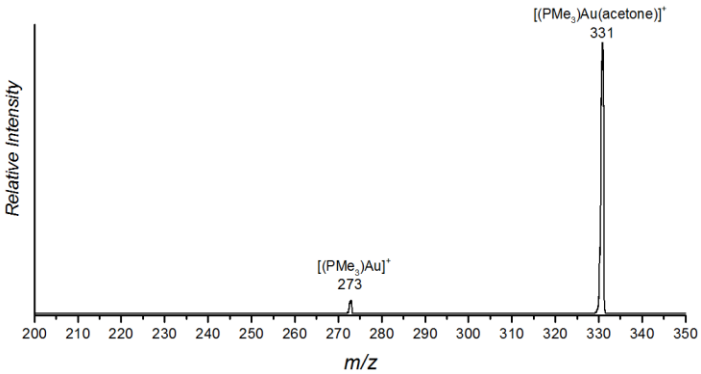

Figure S47: CID (Collision Induced Dissociation) experiment for the mass selected [(PMe₃)Au(acetone)]⁺ ion with m/z 331. The main fragmentation channel leads to the loss of acetone.

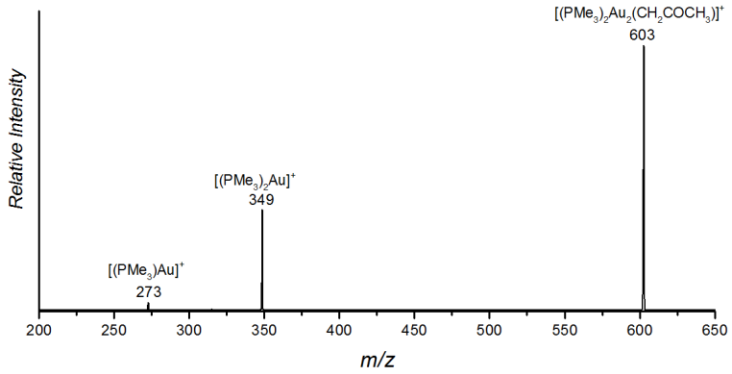

Figure S48: CID (Collision Induced Dissociation) experiment for the mass selected $[(PMe_3)_2Au_2(CH_2COCH_3)]^+$ ion with m/z 603. The main fragmentation channels is the loss of neutral $Au(CH_2COCH_3)$.

IRPD spectrum for [Au(IPr)(BF_4)]

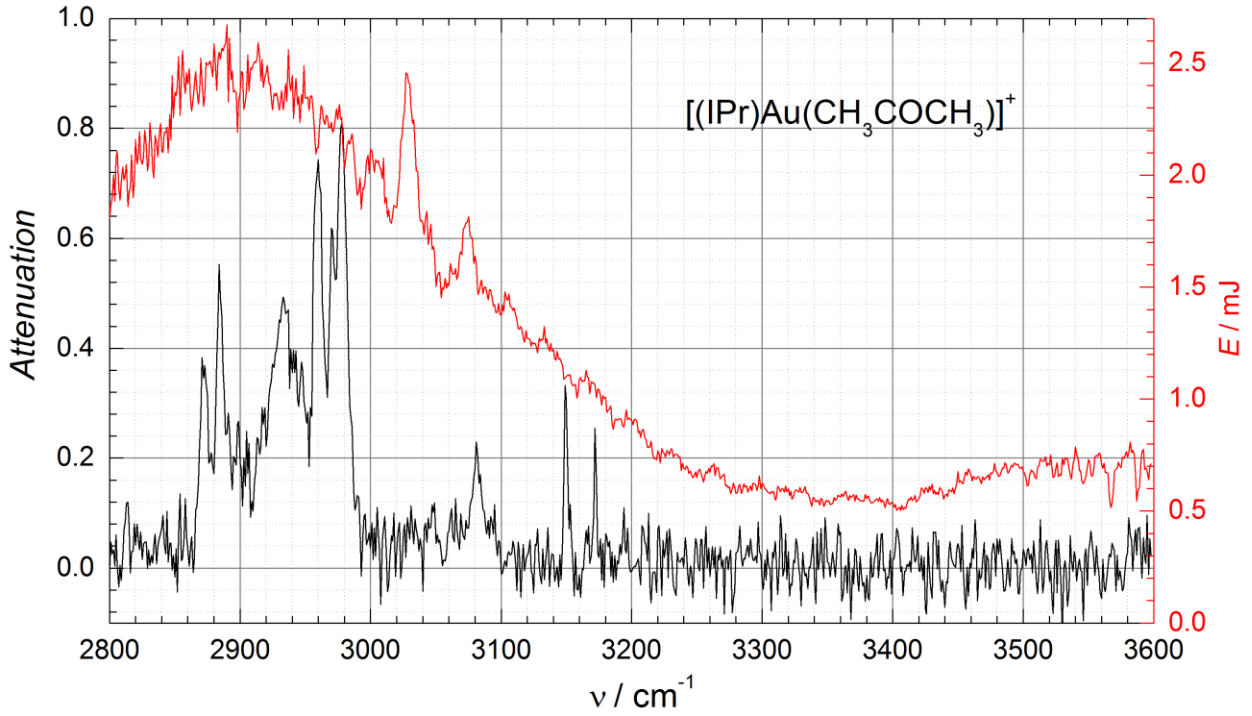

Figure 49: IRPD spectrum (in black) of the mass selected ion $[(IPr)Au(CH_3COCH_3)]^+$ with m/z 643 and the power of the OPO/OPA is in red.

Computational results

Table S1. Geometries and energetics for the stationary points on the potential energy surface shown in Figure 9 of the main document. The structures were optimized at the M06-D3/6-311+G*(SDD:Au) + SMD (water) level of theory.

A	TT1.log Low frequencies --- -5.3789 -0.0012 -0.0012 -0.0011 10.2867 16.2408 Low frequencies --- 29.3364 33.1439 40.8786 Zero-point correction= 0.328056 (Hartree/Particle) Thermal correction to Energy= 0.354632 Thermal correction to Enthalpy= 0.355576 Thermal correction to Gibbs Free Energy= 0.268380 Sum of electronic and zero-point Energies= -1462.117529 Sum of electronic and thermal Energies= -1462.090952 Sum of electronic and thermal Enthalpies= -1462.090008 Sum of electronic and thermal Free Energies= -1462.177204 C,0,1.5959369042,-2.5388430028,-0.4231908803 P,0,2.4493859503,-0.9445709425,-0.5487412296 Au,0,1.188515906,0.8014901682,0.2276594539 Au,0,-1.8228314463,1.3458263612,0.1756722729 O,0,-0.0902121776,2.4166902996,0.8667680309 C,0,4.0351261932,-1.2016322643,0.2891050707 C,0,2.8676005037,-0.7990772574,-2.3066095783 O,0,5.0352429967,1.8187130612,-1.0159037748 C,0,4.1786053506,2.5319767112,-0.5157638673 C,0,3.2328130581,3.327821082,-1.3500034999 C,0,4.0403341232,2.6660554376,0.9652690657 P,0,-3.6003170127,0.1633550691,-0.6462378873 C,0,-4.7487617532,-0.4532498776,0.6123333155 C,0,-3.0769275183,-1.3173373493,-1.5516137192 C,0,-4.6506536438,1.0681156501,-1.8132790991 H,0,2.2248205555,-3.3314126204,-0.8448847585 H,0,1.3798447463,-2.7689764682,0.623931465 H,0,0.6518498255,-2.4963509438,-0.9746637017 H,0,-5.542076971,-1.0369850118,0.1312635261 H,0,-4.2165951072,-1.089500836,1.3251259774 H,0,-5.1963618021,0.3840271041,1.1550295742 H,0,3.5284756803,3.330623818,-2.4016069626 H,0,2.2310314412,2.8829937532,-1.2582959126 H,0,3.1499738494,4.3538986851,-0.9742349517 H,0,4.4850538394,1.813586352,1.4859933842 H,0,4.5737295348,3.575554069,1.2742838004 H,0,3.4066943432,0.1346298284,-2.4905810309 H,0,3.4944922896,-1.6451014426,-2.6111394165 H,0,1.9505252929,-0.7962729976,-2.9030552574 H,0,4.6998050884,-0.3528051848,0.1019233712 H,0,3.8811043318,-1.3017923109,1.3672690161 H,0,4.5052534758,-2.1153253029,-0.0931391809 H,0,-2.4116152725,-1.0379770621,-2.3738197409 H,0,-2.5354918237,-1.9898140038,-0.8793594459 H,0,-3.9522748098,-1.8389254565,-1.9557659651 H,0,-4.0604956576,1.3936875764,-2.6744768868 H,0,-5.4620246411,0.4164382668,-2.1574540915

	H,0,-5.0782743664,1.949468359,-1.3273387451 H,0,-0.1106932248,2.3874515716,1.8306631691 H,0,2.993875948,2.7917291114,1.2636210905
B	TT_2.log Low frequencies --- -9.3718 -0.0009 -0.0007 0.0004 9.6969 18.1289 Low frequencies --- 37.5633 46.7835 50.6424 Zero-point correction= 0.327880 (Hartree/Particle) Thermal correction to Energy= 0.354346 Thermal correction to Enthalpy= 0.355290 Thermal correction to Gibbs Free Energy= 0.270158 Sum of electronic and zero-point Energies= -1462.114649 Sum of electronic and thermal Energies= -1462.088183 Sum of electronic and thermal Enthalpies= -1462.087238 Sum of electronic and thermal Free Energies= -1462.172370 C,0,3.2984904349,-0.9404771502,1.6196457699 P,0,2.7005347035,-1.0239975125,-0.0878083911 Au,0,1.2364545528,0.6636918073,-0.6134138394 O,0,-0.1034431844,2.306960957,-1.2413568186 C,0,-0.8161402844,2.9873944706,-0.4971092001 C,0,-0.6990422206,2.9391055796,0.9773302713 C,0,4.1995560917,-1.0629381796,-1.1032701833 C,0,1.983568536,-2.6805822951,-0.2425405481 Au,0,-0.9735491036,-0.6178821509,1.1959753678 P,0,-2.1467916784,-1.075653648,-0.7292365152 C,0,-1.1742831066,-1.8812282097,-2.0317096524 O,0,0.0870974547,-0.2235920961,2.961609265 C,0,-1.8521636166,3.869889012,-1.0820472416 C,0,-2.8660469605,0.36679343,-1.5669984934 C,0,-3.5596361709,-2.1837632301,-0.4745352525 H,0,4.0105245434,-1.7546563548,1.7978144491 H,0,3.7933361962,0.0184061121,1.7967052891 H,0,2.4577745252,-1.036711098,2.3124009919 H,0,-1.7907386601,-2.0104324962,-2.9289258244 H,0,-0.3054206214,-1.2592564017,-2.2767257703 H,0,-0.8297773991,-2.8626238964,-1.6930990704 H,0,-2.7978957485,3.7510102445,-0.5414568667 H,0,-1.5464581231,4.9138902352,-0.9347046703 H,0,-1.9920747805,3.6813488274,-2.1478796432 H,0,0.3138579006,2.6616923839,1.2844043185 H,0,-1.010427253,3.879208328,1.4404693576 H,0,1.7162704184,-2.8817011578,-1.2838899392 H,0,2.7158101435,-3.4255347252,0.0899310841 H,0,1.085034503,-2.7516936064,0.380486968 H,0,3.9350384155,-1.1793000686,-2.1579804677 H,0,4.7573200618,-0.1301693237,-0.9810187779 H,0,4.8325618419,-1.9031743346,-0.7951356821 H,0,-3.4184981743,0.9884026431,-0.8561933643 H,0,-2.0743832831,0.9625906172,-2.0299300973 H,0,-3.5500109714,0.0241907071,-2.3521216198 H,0,-4.2754694949,-1.7255444451,0.2141937771 H,0,-4.0579178127,-2.3822830698,-1.4305766038 H,0,-3.2184174296,-3.1293279452,-0.0430258684 H,0,-0.5489064745,-0.2791807261,3.6829634416 H,0,-1.3824827708,2.1504107667,1.3329570507
C	TT_3.log

	Low frequencies --- -22.3903 -13.5170 -0.0009 0.0008 0.0012 10.8798 Low frequencies --- 29.4003 37.4171 47.3057 Zero-point correction= 0.328356 (Hartree/Particle) Thermal correction to Energy= 0.354569 Thermal correction to Enthalpy= 0.355514 Thermal correction to Gibbs Free Energy= 0.270276 Sum of electronic and zero-point Energies= -1462.099518 Sum of electronic and thermal Energies= -1462.073305 Sum of electronic and thermal Enthalpies= -1462.072360 Sum of electronic and thermal Free Energies= -1462.157598 C,0,0.558539764,-0.3958065306,0.2137758746 P,0,0.3011746882,-0.1594751959,1.9937864855 Au,0,2.2650766946,0.0300918125,3.1607910881 O,0,4.1473435715,0.1769809069,4.1700402407 C,0,4.91859321,1.2170251061,3.9309726784 C,0,4.4942354763,2.4298246831,3.4924448682 C,0,-0.7556959546,1.3103962607,2.0901211527 C,0,-0.7803931237,-1.5276573925,2.4869670553 Au,0,4.2372316177,-0.5871988171,0.8478649169 P,0,4.1998782509,-2.8419953522,1.222492562 C,0,2.5878252322,-3.6243943235,0.9572449034 O,0,4.2942057566,1.6047549608,0.6115891589 C,0,6.37270826,0.9401609227,4.1590673353 C,0,4.6115985075,-3.2405343761,2.9415793406 C,0,5.3595280593,-3.8145497903,0.2285396717 H,0,-0.4107934817,-0.4274668795,-0.2976044571 H,0,1.1496715206,0.4327679456,-0.1887366991 H,0,1.0932270699,-1.3319054366,0.0256327044 H,0,1.8310896164,-3.1429904645,1.5854609509 H,0,2.2892822776,-3.5366970944,-0.0911754084 H,0,2.6550090878,-4.6851035888,1.2248918151 H,0,7.0016499731,1.8177651637,3.9864524286 H,0,6.5378522972,0.5864707744,5.1838357708 H,0,6.703406373,0.134047485,3.4902054387 H,0,3.4287666072,2.6378440355,3.3840229895 H,0,5.1917201993,3.2564656099,3.3845362401 H,0,-1.0837868909,-1.4058841149,3.5306347082 H,0,-1.6737280496,-1.5382601592,1.8518423499 H,0,-0.2551764936,-2.4819996056,2.3851902661 H,0,-1.0320509762,1.5091541008,3.1292079432 H,0,-0.2191266662,2.1792866046,1.6979536313 H,0,-1.6645003306,1.1504274909,1.4985133699 H,0,5.5955441534,-2.837882385,3.1990057746 H,0,3.8657273284,-2.8080042973,3.6155357215 H,0,4.6224762765,-4.32938055,3.0697071023 H,0,6.3825085175,-3.4709915798,0.4054799111 H,0,5.2802090555,-4.8728845966,0.5026274473 H,0,5.1290608126,-3.6993966608,-0.8342703228 H,0,5.0764278967,1.8555756441,0.1030220214 H,0,4.4371077147,1.9389246656,1.5309969353
D	TT_final.log Low frequencies --- -2.2232 0.0006 0.0011 0.0012 11.0027 22.8741 Low frequencies --- 40.8566 42.6058 51.9501

	Zero-point correction= 0.328919 (Hartree/Particle) Thermal correction to Energy= 0.355312 Thermal correction to Enthalpy= 0.356257 Thermal correction to Gibbs Free Energy= 0.271753 Sum of electronic and zero-point Energies= -1462.116318 Sum of electronic and thermal Energies= -1462.089924 Sum of electronic and thermal Enthalpies= -1462.088980 Sum of electronic and thermal Free Energies= -1462.173484 C,0,-0.1922438165,-0.1317238251,-0.052234546 P,0,-0.1179677238,-0.0861441105,1.756858617 C,0,1.6540920363,-0.0427097101,2.1345863116 Au,0,-1.2629364241,1.6699879843,2.6798377146 Au,0,0.4993353732,2.7420527725,5.1831253632 P,0,1.4827557148,0.9243087428,6.3055686158 C,0,0.7191672748,-0.6857565505,5.9474286572 C,0,-0.6835023878,-1.7202070335,2.2928572548 O,0,-2.4076740605,3.2796309826,3.625674045 C,0,-1.7687894701,4.138944015,4.3101066099 C,0,-2.5496530282,4.8710929245,5.3500399763 C,0,-0.3885041388,4.4257247163,4.1325915973 C,0,1.4236599121,1.0424666559,8.1160798639 C,0,3.2421057431,0.6599730582,5.9435843407 H,0,0.4036510039,-0.9721570571,-0.4263884161 H,0,-1.2281213565,-0.2504301942,-0.3817222214 H,0,0.2031176916,0.8014770834,-0.464405286 H,0,1.9092315536,0.1660628377,8.5607315478 H,0,1.9409771304,1.9466054952,8.449702569 H,0,0.3853654191,1.0890212924,8.4573096288 H,0,-1.9033112956,5.3417198944,6.0948752354 H,0,-3.1295072352,5.6625192596,4.8580640907 H,0,-3.2628829853,4.204333862,5.8430250008 H,0,-0.0284223215,4.2766282337,3.1101172348 H,0,-0.0423421134,5.3519583167,4.5935943723 H,0,1.811133065,-0.0455660785,3.216830125 H,0,2.1491342211,-0.9161711024,1.6947375827 H,0,2.0979190243,0.8681181833,1.7220152601 H,0,-0.6507245305,-1.7943114604,3.3838115925 H,0,-1.7138983607,-1.8804574737,1.9628629571 H,0,-0.0408673481,-2.4937978544,1.857086526 H,0,3.3847765298,0.5007865991,4.8703511346 H,0,3.8215948482,1.5374813028,6.2450797091 H,0,3.6095241196,-0.2171164218,6.48913658 H,0,0.8874616921,-0.9530247111,4.8996541742 H,0,1.1647908351,-1.4583674427,6.5850791363 H,0,-0.3581099404,-0.6428443858,6.1321938233 O,0,1.212707628,3.4065791347,0.9226589583 H,0,0.3274992256,3.0185457362,0.9784639278 H,0,1.614934847,3.2268166956,1.7815383761
TS**B/C**	TS_5.log Low frequencies ----1502.2715 -18.7825 -16.0158 0.0002 0.0012 0.0012 Low frequencies --- 18.6336 37.0910 42.6323 Zero-point correction= 0.322769 (Hartree/Particle) Thermal correction to Energy= 0.348425 Thermal correction to Enthalpy= 0.349370 Thermal correction to Gibbs Free Energy= 0.265653

	Sum of electronic and zero-point Energies= -1462.094912 Sum of electronic and thermal Energies= -1462.069255 Sum of electronic and thermal Enthalpies= -1462.068311 Sum of electronic and thermal Free Energies= -1462.15202 C,0,-1.9048226329,-1.8385441777,-1.8429689227 P,0,-2.711747848,-0.9665625348,-0.4738114398 C,0,-3.3733055005,-2.2773367334,0.5871107788 Au,0,-1.3015761172,0.5169903621,0.5543604393 Au,0,1.3755476276,-0.0893901512,-0.87752605 O,0,0.906518869,1.5259245775,-2.1981308991 C,0,-4.1689186528,-0.1960043927,-1.2261637723 O,0,0.095948968,1.9212277711,1.4670612252 C,0,0.6209742963,2.843020705,0.7645797005 C,0,1.9434500375,3.3404130627,1.2477653004 C,0,0.0885728979,3.3145240414,-0.4502134272 P,0,1.8565386176,-1.6744545538,0.7082123916 C,0,3.1308424199,-2.8941794524,0.293831473 C,0,0.4343516998,-2.6635986641,1.2448618936 C,0,2.4464514678,-0.8971489339,2.2385329981 H,0,-2.6207117516,-2.5176727242,-2.3204433054 H,0,-1.5431664299,-1.1179130571,-2.5827815703 H,0,-1.0539213416,-2.4172207537,-1.4709971104 H,0,-0.356198366,-1.9957052101,1.6065057772 H,0,0.0473089775,-3.2590872344,0.4129603541 H,0,0.7413516912,-3.3362723452,2.0544468858 H,0,1.8426779591,3.7321294832,2.2661042517 H,0,2.6424643016,2.4957201651,1.3024816326 H,0,2.3661064266,4.1167806373,0.6065012544 H,0,-0.9822084909,3.140032857,-0.5912549481 H,0,0.4439377128,4.2882602338,-0.7883532135 H,0,-3.9563522322,-1.8394454925,1.4020281875 H,0,-4.0190732708,-2.9368064083,-0.004191797 H,0,-2.555917288,-2.8651270535,1.0154698597 H,0,-4.7707731498,0.2990658676,-0.4591078455 H,0,-3.854301648,0.5514389485,-1.9601852425 H,0,-4.7764117966,-0.959062957,-1.7261555523 H,0,3.3651465398,-0.3354106174,2.0465233062 H,0,1.6854882329,-0.2100971327,2.6223299077 H,0,2.647423184,-1.6662862765,2.9937466531 H,0,4.0715607036,-2.3881903911,0.0593021294 H,0,3.2842760181,-3.5672635551,1.1450381078 H,0,2.8200775336,-3.4780792025,-0.5770305608 H,0,1.7232491483,1.8148062139,-2.6233881699 H,0,0.5854401862,2.4358570792,-1.360723681
TS**C/D**	c p 1 pc2 c 2 cp3 1 cpc3 c 2 cp4 3 cpc4 1 dih4 0 au 2 aup5 3 aupc5 4 dih5 0 o 5 oau6 2 oaup6 3 dih6 0 c 6 co7 5 coau7 2 dih7 0 c 7 cc8 6 cco8 5 dih8 0 au 5 auau9 2 auaup9 1 dih9 0 p 9 pau10 5 pauau10 2 dih10 0 c 10 cp11 9 cpau11 5 dih11 0 o 9 oau12 5 oauau12 2 dih12 0 c 7 cc13 6 cco13 5 dih13 0

	c 10 cp14 9 cpau14 5 dih14 0 c 10 cp15 9 cpau15 5 dih15 0 h 1 hc16 2 hcp16 4 dih16 0 h 1 hc17 2 hcp17 4 dih17 0 h 1 hc18 2 hcp18 4 dih18 0 h 15 hc19 10 hcp19 9 dih19 0 h 15 hc20 10 hcp20 9 dih20 0 h 15 hc21 10 hcp21 9 dih21 0 h 13 hc22 7 hcc22 6 dih22 0 h 13 hc23 7 hcc23 6 dih23 0 h 13 hc24 7 hcc24 6 dih24 0 h 8 hc25 7 hcc25 6 dih25 0 h 8 hc26 7 hcc26 6 dih26 0 h 4 hc27 2 hcp27 1 dih27 0 h 4 hc28 2 hcp28 1 dih28 0 h 4 hc29 2 hcp29 1 dih29 0 h 3 hc30 2 hcp30 1 dih30 0 h 3 hc31 2 hcp31 1 dih31 0 h 3 hc32 2 hcp32 1 dih32 0 h 11 hc33 10 hcp33 9 dih33 0 h 11 hc34 10 hcp34 9 dih34 0 h 11 hc35 10 hcp35 9 dih35 0 h 14 hc36 10 hcp36 9 dih36 0 h 14 hc37 10 hcp37 9 dih37 0 h 14 hc38 10 hcp38 9 dih38 0 h 12 ho39 9 hoau39 5 dih39 0 h 12 ho40 9 hoau40 5 dih40 0 Variables: pc2 1.81408 cp3 1.81282 cpc3 104.069 cp4 1.81356 cpc4 104.358 dih4 -109.173 aup5 2.2946 aupc5 115.288 dih5 -127.04 oau6 2.14934 oaup6 177.44 dih6 167.433 co7 1.3131 coau7 117.478 dih7 99.555 cc8 1.36469 cco8 125.026 dih8 23.221 auau9 3.13864 auaup9 99.345 dih9 -6.781 pau10 2.30615 pauau10 89.972 dih10 -90.115 cp11 1.8145 cpau11 112.333 dih11 -78.788 oau12 2.34156 oauau12 99.151 dih12 69.195

	cc13 1.49741 cco13 114.119 dih13 -156.794 cp14 1.81371 cpau14 117.008 dih14 160.479 cp15 1.81541 cpau15 114.021 dih15 38.556 hc16 1.09627 hcp16 109.496 dih16 52.154 hc17 1.09413 hcp17 109.796 dih17 171.926 hc18 1.09469 hcp18 110.473 dih18 -68.115 hc19 1.0961 hcp19 109.339 dih19 -54.335 hc20 1.09415 hcp20 110.341 dih20 65.697 hc21 1.09658 hcp21 109.491 dih21 -174.266 hc22 1.09348 hcc22 112.342 dih22 176.519 hc23 1.09716 hcc23 109.868 dih23 -62.815 hc24 1.09666 hcc24 110.653 dih24 54.676 hc25 1.09036 hcc25 119.856 dih25 11.071 hc26 1.08704 hcc26 120.416 dih26 175.752 hc27 1.09358 hcp27 110.161 dih27 -178.079 hc28 1.09626 hcp28 109.527 dih28 -58.051 hc29 1.09401 hcp29 110.216 dih29 61.987 hc30 1.09382 hcp30 110.097 dih30 173.132 hc31 1.09361 hcp31 110.134 dih31 -67.045 hc32 1.0962

	hcp32 109.539 dih32 53.173 hc33 1.09391 hcp33 110.111 dih33 -59.999 hc34 1.09484 hcp34 109.712 dih34 59.792 hc35 1.09628 hcp35 109.746 dih35 179.742 hc36 1.09364 hcp36 110.155 dih36 58.276 hc37 1.0966 hcp37 109.732 dih37 178.51 hc38 1.09383 hcp38 109.87 dih38 -61.348 ho39 0.96537 hoau39 108.913 dih39 -140.998 ho40 0.96601 hoau40 108.405 dih40 103.768

Table S2. Geometries and energetics for the calculated structures used for comparison of theoretical IR spectra with the helium tagging IRPD spectra. The structures were optimized at the B3LYP-D3/6-311+G*(SDD:Au) level of theory.

1a	Ac_vicAu2_a.log Low frequencies --- -10.2622 -5.7938 -0.0016 -0.0015 -0.0010 4.6865 Low frequencies --- 17.5840 21.0821 24.7129 Zero-point correction= 0.305835 (Hartree/Particle) Thermal correction to Energy= 0.330142 Thermal correction to Enthalpy= 0.331086 Thermal correction to Gibbs Free Energy= 0.246576 Sum of electronic and zero-point Energies= -1386.139746 Sum of electronic and thermal Energies= -1386.115440 Sum of electronic and thermal Enthalpies= -1386.114495 Sum of electronic and thermal Free Energies= -1386.199005 C,0,-1.5794719191,-0.5911120762,-0.0575535581 O,0,-1.8761441338,-0.8476907576,1.1455715663 C,0,-0.3197996271,-0.0296457937,-0.4715909785 C,0,-2.6370048262,-0.9089194645,-1.0769973427 Au,0,1.0007442179,-1.730785051,-0.5176177114 H,0,2.554618238,-5.8206539961,-1.470541242 C,0,2.9652934085,-4.1842361272,1.0590367107 C,0,4.0702953402,-3.1781061529,-1.4240394504 C,0,1.8230459717,-5.0090016961,-1.4698884509 P,0,2.4813579896,-3.5438455922,-0.5902375004

	Au,0,-0.5294220071,-0.7799726894,2.7766284028 P,0,0.8532091239,-0.7561073153,4.5863541822 C,0,2.4570334318,-1.5761304528,4.2639513554 C,0,1.2807804164,0.9316544896,5.1437620046 C,0,0.168250492,-1.5929953116,6.0599750612 H,0,3.881850471,-2.8696082454,-2.4534072422 H,0,4.7172450164,-4.0585823349,-1.4282483225 H,0,4.5807149644,-2.3610561408,-0.9118954665 H,0,3.4528399696,-3.3942031886,1.6322380055 H,0,2.0758474679,-4.5098529146,1.6008035242 H,0,3.6516531483,-5.028603963,0.9610778708 H,0,1.5843673824,-4.743196574,-2.500730562 H,0,0.9079078172,-5.352283106,-0.985046097 H,0,2.2896271827,-2.6242634775,4.0124908631 H,0,3.1019253561,-1.5172816728,5.1436648867 H,0,2.9520012179,-1.089968911,3.4220787352 H,0,1.7699116945,1.4771419396,4.335635912 H,0,0.3730698208,1.4693515353,5.4208458318 H,0,1.9497948646,0.8899052771,6.006539065 H,0,0.8815536066,-1.5513653703,6.8865303587 H,0,-0.0531263176,-2.6354997632,5.8276871604 H,0,-0.7589318006,-1.1046552218,6.3628964461 H,0,-0.3323235763,0.4115058187,-1.4673708635 H,0,-2.2071585652,-1.0984506753,-2.0609137775 H,0,-3.2401922712,-1.7572258044,-0.7545285888 H,0,-3.3001967841,-0.0411193989,-1.1634527353 H,0,0.1155208153,0.6447951492,0.2682671823
1b	Ac_vicAu2_b.log Low frequencies --- -0.9640 -0.0017 -0.0016 0.0010 3.0678 8.9078 Low frequencies --- 13.9729 15.0821 22.7241 Zero-point correction= 0.306015 (Hartree/Particle) Thermal correction to Energy= 0.330260 Thermal correction to Enthalpy= 0.331204 Thermal correction to Gibbs Free Energy= 0.246159 Sum of electronic and zero-point Energies= -1386.136698 Sum of electronic and thermal Energies= -1386.112453 Sum of electronic and thermal Enthalpies= -1386.111509 Sum of electronic and thermal Free Energies= -1386.196554 C,0,-0.1192432291,0.3072383951,-0.014223764 P,0,-0.0389572484,0.2132886889,1.8137193073 C,0,1.7527522001,0.1783668031,2.1950348241 Au,0,-1.2217002529,1.8982795199,2.92807087 C,0,-2.3895195383,3.3468713905,4.0258918622 C,0,-1.9530105518,4.6075602529,3.5087045876 C,0,-0.7163436417,5.2708529039,4.0605429419 O,0,-2.599074648,5.1735489692,2.5763312065 Au,0,-2.2615103943,7.005626816,1.5966759311 P,0,-2.0342161673,8.9884595973,0.4949971214 C,0,-3.5907044653,9.5770392943,-0.2622213262 C,0,-0.6255825997,-1.4752868154,2.2130815815 C,0,-1.4776223147,10.352852932,1.5771054494 C,0,-0.8222951631,8.9328639856,-0.8728658387 H,0,2.2472133082,-0.6352817043,1.6587934454 H,0,-0.5356990756,-1.6532528925,3.2856614535 H,0,-0.0391168313,-2.2244245509,1.6757439543

	H,0,-1.6759782861,-1.578143605,1.9366926878 H,0,-1.1581921388,0.2470654164,-0.3417175525 H,0,0.2924696314,1.2586935516,-0.3540875378 H,0,0.4466941762,-0.5098476662,-0.4681513088 H,0,1.8984359051,0.0390544265,3.2672645736 H,0,2.2112945028,1.1257656661,1.9077914232 H,0,-2.1970120625,10.5029106934,2.3831773472 H,0,-1.3839479566,11.2781515913,1.0038083838 H,0,-0.511241815,10.1060844926,2.0187168719 H,0,0.1596669818,8.6550084656,-0.4876391876 H,0,-1.1280986774,8.1881459233,-1.6088178561 H,0,-0.7535809709,9.9091642647,-1.3585153109 H,0,-3.4259934791,10.5272161125,-0.7758798041 H,0,-4.349548955,9.713291595,0.5093840761 H,0,-3.9569062338,8.8406910887,-0.9787601358 H,0,-2.1127011027,3.1697771863,5.0651325482 H,0,-0.2034871973,4.653581213,4.7967069713 H,0,-0.0260564731,5.5062457242,3.2460469563 H,0,-1.0043867409,6.2177466468,4.5278940835 H,0,-3.4339761575,3.1248052248,3.8121444088
1c	Ac_gemAu2.log Low frequencies --- -5.1170 -0.0016 -0.0013 -0.0006 5.2292 10.4035 Low frequencies --- 13.1970 15.8705 23.6205 Zero-point correction= 0.306233 (Hartree/Particle) Thermal correction to Energy= 0.330885 Thermal correction to Enthalpy= 0.331829 Thermal correction to Gibbs Free Energy= 0.245657 Sum of electronic and zero-point Energies= -1386.121260 Sum of electronic and thermal Energies= -1386.096609 Sum of electronic and thermal Enthalpies= -1386.095665 Sum of electronic and thermal Free Energies= -1386.181836 Au,0,1.5495822403,0.2351027817,-0.1662549717 Au,0,-1.550287542,0.2357305319,-0.1641332428 C,0,-0.0003448306,1.6763161247,-0.5597055669 P,0,3.3612342591,-1.2120002825,0.1350886282 P,0,-3.3602582135,-1.2131913806,0.1361530328 C,0,-3.0406313589,-2.6047949484,1.2837817577 C,0,-4.8593902463,-0.3999299634,0.8033583871 C,0,-3.9185264258,-2.0108219036,-1.4151573898 C,0,3.4107271822,-2.0290856543,1.7738784502 C,0,3.4184962071,-2.5889889419,-1.0712032615 C,0,4.9917351301,-0.3932781743,-0.0201095959 H,0,-4.2168384578,-1.2486249025,-2.1366223152 H,0,-4.7666487355,-2.6725169241,-1.2244430751 H,0,-3.1030165493,-2.5912727754,-1.8487916404 H,0,-2.2058784305,-3.2030167728,0.9152171423 H,0,-2.7784122188,-2.2186115604,2.2697801636 H,0,-3.9239948373,-3.2417417934,1.3744725767 H,0,-5.6750878755,-1.1195387641,0.9056373711 H,0,-5.1729234513,0.4020028055,0.1333860662 H,0,-4.6434263477,0.0355472911,1.7800993387 H,0,2.5155275066,-3.1952937735,-0.98437675 H,0,4.2921348725,-3.2207205341,-0.8935904158 H,0,3.4675570343,-2.1907773285,-2.0855011631 H,0,5.089078389,0.053591156,-1.0104421846

	H,0,5.0788748938,0.4002932158,0.7229738827 H,0,5.8004744434,-1.1123754058,0.128189808 H,0,4.2795339455,-2.6870961246,1.849734003 H,0,2.5037514923,-2.6170772183,1.9229960299 H,0,3.4656698835,-1.2763975276,2.5615362859 H,0,-0.0010305697,1.9501007485,-1.6143888413 C,0,0.0007447207,2.7811556231,0.2715195658 O,0,0.0017820521,2.7016715008,1.6068780499 C,0,0.0010339382,4.205053583,-0.1773937113 H,0,0.0002217497,4.2886656605,-1.2619260346 H,0,-0.875828017,4.7181727582,0.2278165232 H,0,0.8790659585,4.7173226503,0.2266315285 H,0,0.0010274457,1.7722802564,1.8852761026
1d	Ac_OdiAu_a.log Low frequencies --- -9.2500 -5.9645 -2.1026 -0.0013 -0.0012 -0.0010 Low frequencies --- 10.7836 13.0896 16.2743 Zero-point correction= 0.305449 (Hartree/Particle) Thermal correction to Energy= 0.329954 Thermal correction to Enthalpy= 0.330898 Thermal correction to Gibbs Free Energy= 0.244410 Sum of electronic and zero-point Energies= -1386.120601 Sum of electronic and thermal Energies= -1386.096096 Sum of electronic and thermal Enthalpies= -1386.095152 Sum of electronic and thermal Free Energies= -1386.181640 C,0,4.3085071212,-1.5275576504,-1.6332980999 P,0,3.7583125378,-0.9998026826,0.0288729649 Au,0,1.8081095784,0.1691370764,0.0101048291 O,0,-0.0078125942,1.2573442811,0.0431939023 Au,0,-1.806681622,0.1462274424,-0.0008134095 P,0,-3.7269252487,-1.07475587,-0.0419572014 C,0,-3.6162162459,-2.5947527013,-1.0525624025 C,0,5.1537256874,-0.0402280062,0.7167899526 C,0,3.6900598961,-2.5336684548,1.0223190062 C,0,-0.0010218044,2.6412344476,-0.0752385503 C,0,-0.9965232576,3.3238863343,0.8143565213 C,0,0.8404504271,3.2685732212,-0.8971295922 C,0,-4.2708293254,-1.6336784716,1.6120521027 C,0,-5.1437002294,-0.1439325077,-0.7255035996 H,0,3.4446058017,-2.2923208999,2.0571591931 H,0,4.6531697061,-3.0484736137,0.9935297634 H,0,2.9173711502,-3.1952591764,0.6289576505 H,0,3.5565138124,-2.1766988786,-2.0841355043 H,0,4.438765784,-0.6547317778,-2.2746253225 H,0,5.2553316582,-2.0685968936,-1.5675939432 H,0,6.0702630006,-0.6344952567,0.69438535 H,0,4.9355953081,0.2453379619,1.7465429392 H,0,5.3015068604,0.8682937453,0.1316208037 H,0,-3.5022999514,-2.2636540783,2.0620993264 H,0,-5.201020076,-2.201403142,1.5359632953 H,0,-4.4301853727,-0.7700763216,2.259003642 H,0,-5.3236102144,0.7477854983,-0.1236329908 H,0,-4.9245978924,0.1678621051,-1.7475326434 H,0,-6.0426131229,-0.7649008942,-0.7232405077 H,0,-4.5681153953,-3.1308139762,-1.0351010212 H,0,-2.8327574755,-3.2449830892,-0.6613191967

	H,0,-3.3697320229,-2.3372975401,-2.0833810301 H,0,-2.0215652877,3.0496362584,0.5382434344 H,0,-0.8480209287,3.0217089014,1.8550624246 H,0,-0.9101689454,4.408341516,0.7475518188 H,0,1.5242025867,2.7224407492,-1.5375530897 H,0,0.8605497943,4.3489378816,-0.9490811471
1e	Ac_gemAu2_c.log Low frequencies --- -5.9025 -3.6603 0.0004 0.0006 0.0009 3.2859 Low frequencies --- 10.3657 11.9710 23.8170 Zero-point correction= 0.306190 (Hartree/Particle) Thermal correction to Energy= 0.330737 Thermal correction to Enthalpy= 0.331681 Thermal correction to Gibbs Free Energy= 0.245642 Sum of electronic and zero-point Energies= -1386.117888 Sum of electronic and thermal Energies= -1386.093341 Sum of electronic and thermal Enthalpies= -1386.092397 Sum of electronic and thermal Free Energies= -1386.178436 C,0,-0.0021905943,-0.0190758362,-0.0088906727 Au,0,-0.0032176982,-0.0392459188,2.1297094137 Au,0,2.1358339743,-0.0388096736,0.0271623882 P,0,4.5326788456,0.0943468583,-0.1759931016 P,0,-0.2534112153,0.0909074062,4.5224184178 C,0,-2.0368777014,0.016356819,5.097240208 C,0,0.5985709332,-1.2739261351,5.4865803353 C,0,0.4073264426,1.6755781354,5.2764493581 C,0,5.5004471814,-0.6611948019,1.2420744248 C,0,5.1751097259,1.8521542878,-0.2933804892 C,0,5.2186656613,-0.7503694955,-1.7031991731 C,0,-0.6147254374,-1.0988478766,-0.633839577 O,0,-1.5606260363,-0.809363438,-1.5959123949 C,0,-0.3670391799,-2.5693458876,-0.3839809915 H,0,4.7345492048,2.34597764,-1.1642866778 H,0,6.2661898467,1.8514799435,-0.3914721604 H,0,4.8921942676,2.4086897792,0.6047473724 H,0,5.2383451564,-0.1550711422,2.1757514018 H,0,5.2504741244,-1.7222422061,1.333520936 H,0,6.5765516709,-0.5577450472,1.0643652946 H,0,6.305772203,-0.6235444141,-1.7500962951 H,0,4.7650605177,-0.3138737474,-2.5976540473 H,0,4.9804362622,-1.817602123,-1.673608174 H,0,1.4799864827,1.7584398785,5.0789470204 H,0,0.2365781337,1.6801114364,6.3585855374 H,0,-0.0997376037,2.534398057,4.8273240703 H,0,-2.6002400857,0.8421094889,4.6532310271 H,0,-2.4875975782,-0.9273472141,4.7768296663 H,0,-2.0864002266,0.0893711913,6.1891757105 H,0,0.4282535148,-1.1412374864,6.560640256 H,0,1.6735538374,-1.2515608105,5.2854058511 H,0,0.202670765,-2.24536279,5.1763406696 H,0,-0.3722742215,0.9407770658,-0.3842267594 H,0,0.3920556351,-2.7090880071,0.3864875024 H,0,-1.2921488198,-3.0669580341,-0.0593368659 H,0,-0.0275991605,-3.065435336,-1.3045877227 H,0,-1.9706467965,-1.5969350725,-2.0141630359
1f	Ac_gemAu2_b.log

	Low frequencies --- -2.6862 0.0003 0.0006 0.0015 4.9081 7.9801 Low frequencies --- 12.9601 15.2028 26.0234 Zero-point correction= 0.305913 (Hartree/Particle) Thermal correction to Energy= 0.330622 Thermal correction to Enthalpy= 0.331566 Thermal correction to Gibbs Free Energy= 0.245642 Sum of electronic and zero-point Energies= -1386.117512 Sum of electronic and thermal Energies= -1386.092803 Sum of electronic and thermal Enthalpies= -1386.091859 Sum of electronic and thermal Free Energies= -1386.177783 C,0,-2.9081488129,-2.5704552742,1.3676085348 P,0,-3.2646477952,-1.2462635352,0.1521117921 C,0,-3.7733210883,-2.138858114,-1.3640933264 Au,0,-1.5019358961,0.2428012093,-0.1799842873 C,0,-0.0005996151,1.7331008649,-0.6042262133 C,0,0.0021980378,2.8103187047,0.2453701063 C,0,-0.0000511652,4.2467473375,-0.1858015528 Au,0,1.5025296611,0.2418464246,-0.1881153626 P,0,3.2676701442,-1.2457028243,0.1395279616 C,0,4.9265159519,-0.4729083839,0.0648149666 C,0,3.2315505182,-2.0986027622,1.760487927 C,0,3.3390371296,-2.5991622174,-1.0928431221 C,0,-4.8043083221,-0.465946536,0.7648498187 O,0,0.0061670985,2.6045494686,1.5796802768 H,0,-4.0879137111,-1.4243471121,-2.1262317584 H,0,-4.5999372771,-2.8211350515,-1.1520458333 H,0,-2.9308398267,-2.70918258,-1.7580650523 H,0,-2.0497971716,-3.1548629451,1.0329762089 H,0,-2.6658938954,-2.1282656201,2.3351597193 H,0,-3.7693447933,-3.2330989971,1.4823667224 H,0,-5.5921035173,-1.2124175624,0.891708734 H,0,-5.1413172225,0.2916283759,0.0557839316 H,0,-4.6167196328,0.0212157085,1.7228317447 H,0,2.4147319675,-3.1776950124,-1.0610225452 H,0,4.1835347765,-3.262022406,-0.889543993 H,0,3.4467204005,-2.1812705758,-2.0948379382 H,0,5.0736431313,-0.0075079952,-0.9109705186 H,0,5.0094303288,0.3014288787,0.8288608306 H,0,5.7081600711,-1.2190896147,0.22640573 H,0,4.0814181088,-2.7780700893,1.8598314167 H,0,2.3055585224,-2.6672006455,1.8581211318 H,0,3.2667488436,-1.3627777776,2.5652083062 H,0,-0.00349825,2.0256533346,-1.6528562954 H,0,-0.0026771424,4.3437131304,-1.2694089732 H,0,-0.8827116026,4.7625322241,0.2086193074 H,0,0.8832196497,4.7647299432,0.2045556448 H,0,0.0079881197,3.4382714794,2.0679640725
2a	AuAcetone.log\ Low frequencies --- -12.1723 -4.3393 -0.0015 -0.0010 0.0016 7.8828 Low frequencies --- 18.4298 41.8366 42.4478 Zero-point correction= 0.200705 (Hartree/Particle) Thermal correction to Energy= 0.215842 Thermal correction to Enthalpy= 0.216786 Thermal correction to Gibbs Free Energy= 0.155361

	Sum of electronic and zero-point Energies= -789.814526 Sum of electronic and thermal Energies= -789.799389 Sum of electronic and thermal Enthalpies= -789.798445 Sum of electronic and thermal Free Energies= -789.859870 C,0,0.0421257506,0.0767488842,-0.0198878796 P,0,0.0281537107,0.0437741085,1.8057971291 C,0,1.7797740977,0.0144374327,2.3208595263 C,0,-0.6257103758,1.6647513837,2.3341306695 Au,0,-1.1664275656,-1.7027842547,2.6641799967 O,0,-2.2438244359,-3.3232921229,3.6057766001 C,0,-3.0463183232,-4.170795803,3.1954723414 C,0,-3.4693343544,-4.2535370757,1.7626345624 C,0,-3.610411623,-5.1567056479,4.1670335259 H,0,0.4811393947,-0.8439231799,-0.4061688397 H,0,0.6287292162,0.9281519066,-0.37295444 H,0,-0.9764972334,0.163490999,-0.4000802084 H,0,-1.6572851493,1.7782548514,1.9987072654 H,0,-0.6044919439,1.7379064318,3.4221673319 H,0,-0.0200926798,2.4687632828,1.9092944179 H,0,2.3077409949,0.8713179437,1.895651866 H,0,2.2546022124,-0.9053043377,1.9770640321 H,0,1.8492603264,0.0551369324,3.4085485361 H,0,-3.2315480451,-3.3397882071,1.2177455456 H,0,-2.9348879857,-5.0894276869,1.2952482691 H,0,-4.5347241384,-4.4788644781,1.6777696189 H,0,-3.0601571523,-5.1417186836,5.1057538436 H,0,-4.6565370316,-4.8918832861,4.3628042245 H,0,-3.6206137188,-6.1632714859,3.7407282785
2b	Au_enol_1.log Low frequencies --- -7.0519 -4.5348 -0.0005 -0.0002 0.0014 5.0207 Low frequencies --- 15.3260 45.1480 55.4015 Zero-point correction= 0.201888 (Hartree/Particle) Thermal correction to Energy= 0.216457 Thermal correction to Enthalpy= 0.217401 Thermal correction to Gibbs Free Energy= 0.157455 Sum of electronic and zero-point Energies= -789.793703 Sum of electronic and thermal Energies= -789.779135 Sum of electronic and thermal Enthalpies= -789.778191 Sum of electronic and thermal Free Energies= -789.838136 C,0,0.0789471426,-0.0084880419,0.0088081995 P,0,-0.0201710013,-0.0430863124,1.8338918007 Au,0,2.079206396,-0.0768243479,2.855408247 C,0,4.1404974026,0.0287773985,3.6753045388 C,0,3.9744119559,-0.9709513236,4.6325029861 C,0,3.4632663574,-0.7410682985,6.012521793 C,0,-1.0215463803,1.4145961962,2.2968610477 C,0,-1.053882889,-1.4951925015,2.2419269631 O,0,4.2740585819,-2.2404705242,4.4147314751 H,0,-2.0208882454,-1.4213368862,1.7386048465 H,0,-1.1845836509,1.428911291,3.3753519454 H,0,-1.9890953109,1.3820648173,1.7903975086 H,0,-0.5012755262,2.330348076,2.0129179478 H,0,0.6240946198,0.8777626476,-0.3187848846 H,0,0.6057678772,-0.8922729948,-0.3535618644

	H,0,-0.9245220726,0.0104637964,-0.4228263848 H,0,-1.2166481749,-1.5461603724,3.3193082722 H,0,-0.5548853952,-2.4111039107,1.9227003936 H,0,4.1828606704,1.0495048805,4.0450830809 H,0,3.0864259925,0.2714448425,6.1405804302 H,0,2.6829851087,-1.4647809271,6.2558095625 H,0,4.2855665312,-0.9085276553,6.7156869457 H,0,4.791074929,-0.1756280317,2.8257381776 H,0,4.6673410287,-2.3884313625,3.5407893413