Supplementary Information

SI-1: Analysis of perdeuterated acrolein

The quantitative evaluation of the NMR spectra was carried out by integration the H-(for the degree of labeling, $\eta(D)$) or D-signal (for purity, α) of the allylic group. The integrated signal (I) is proportional to the amount of substance of the hydrogen or deuterium.

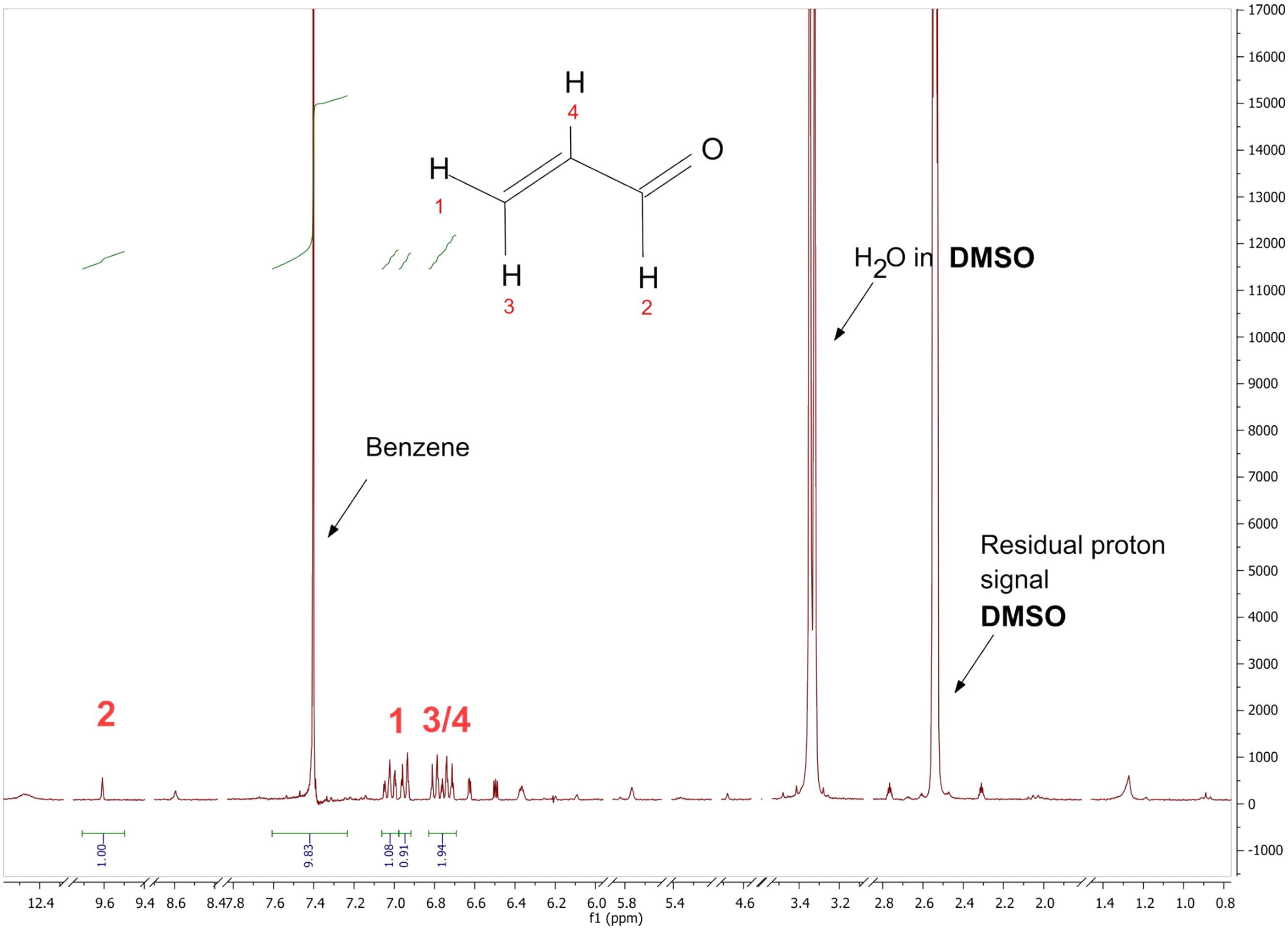
$$\eta(D) = \frac{m(ACR-D_4)}{m(sample)} = 1 - \frac{m(ACR)}{m(sample)} = 1 - \frac{n(ACR)\cdot M(ACR)}{m(sample)} = 1 - \frac{\frac{I(ACR)}{I(benzene)}\cdot 6\cdot n(benzene)\cdot M(ACR)}{m(sample)}$$

$$\eta(D) = 1 - \frac{\frac{I(ACR)}{I(benzene)}\cdot 6\cdot \frac{m(benzene)}{M(benzene)}\cdot M(ACR)}{m(sample)}$$

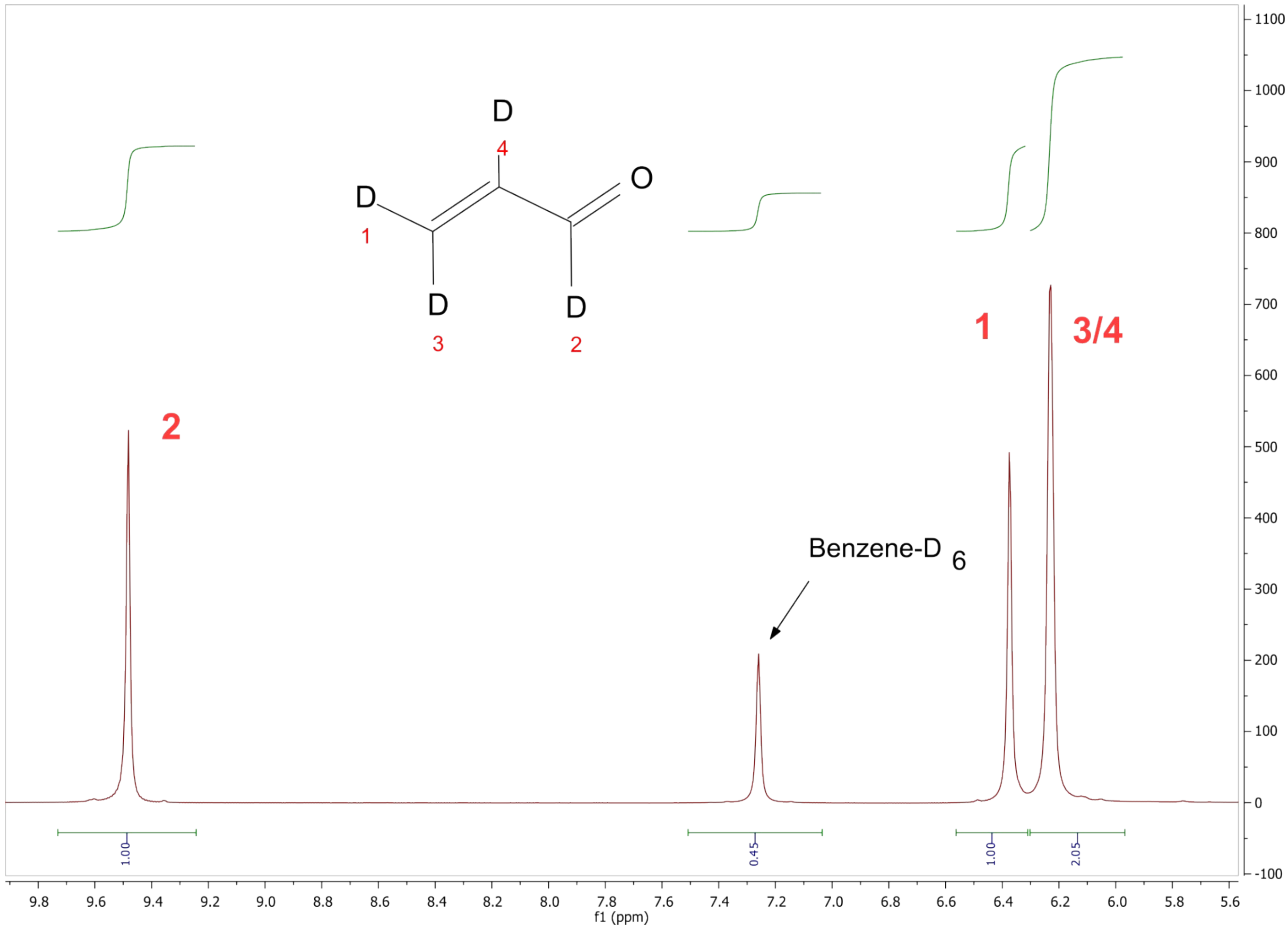
$$\alpha = \frac{m(ACR-D_4)}{m(sample)} = \frac{n(ACR-D_4)\cdot M(ACR-D_4)}{m(sample)} = \frac{\frac{I(ACR-D_4)}{I(benzene-D_6)}\cdot 6\cdot n(benzene-D_6)\cdot M(ACR-D_4)}{m(sample)}$$

$$\alpha = \frac{\frac{I(ACR-D_4)}{I(benzene-D_6)}\cdot 6\cdot \frac{m(benzene-D_6)}{M(benzene-D_6)}\cdot M(ACR-D_4)}{m(sample)}$$

The degree of deuteration is determined to 99.5 % and the purity to 95.8 %, where the main impurity is D_2O.

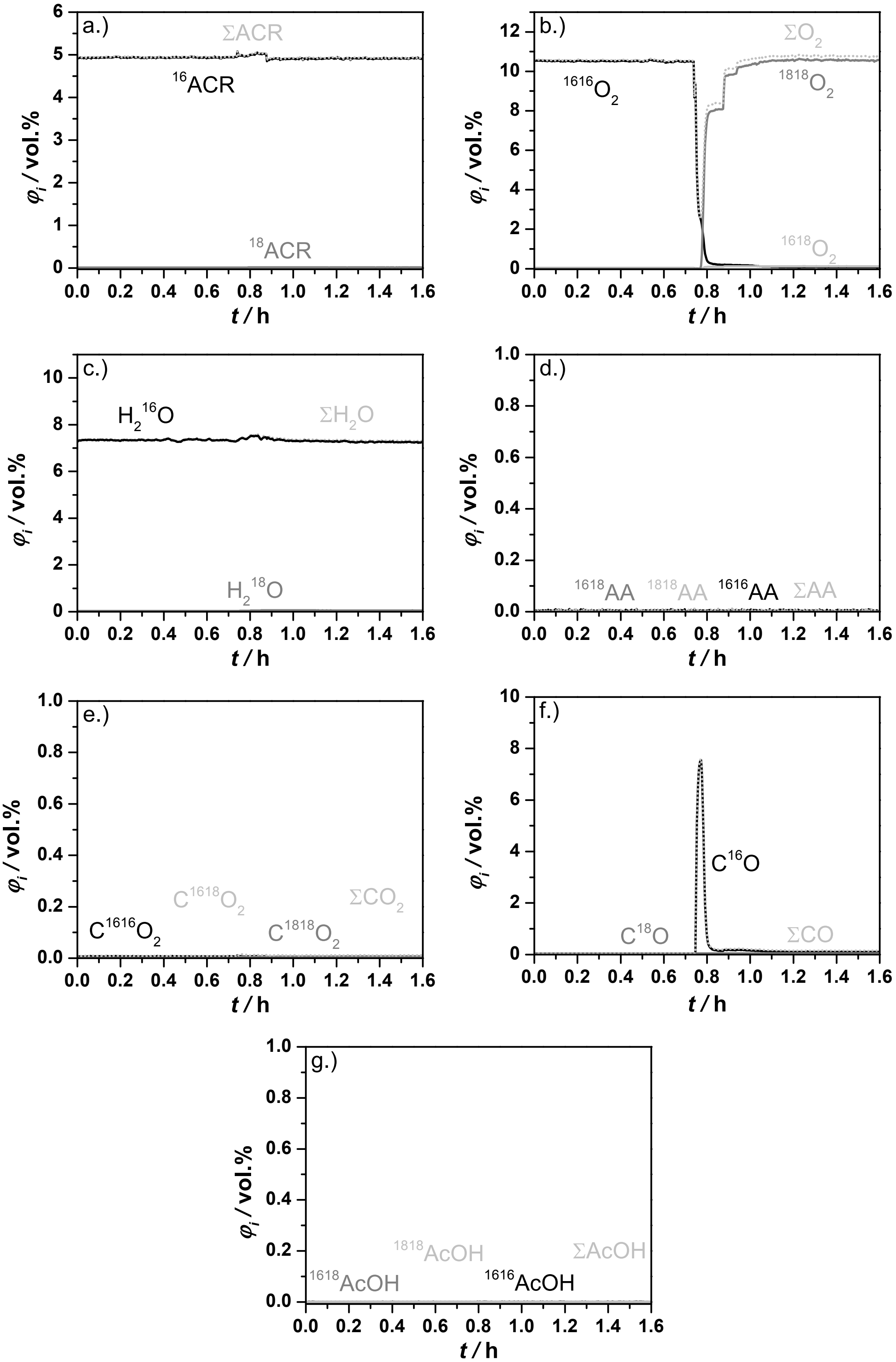


SI-Fig. 1: Quantitative ^{1}H-NMR, with 0.163 mg benzene as internal standard and DMSO-D_6 as solvent. 14.2 mg of the ACR-D_4 sample was used.

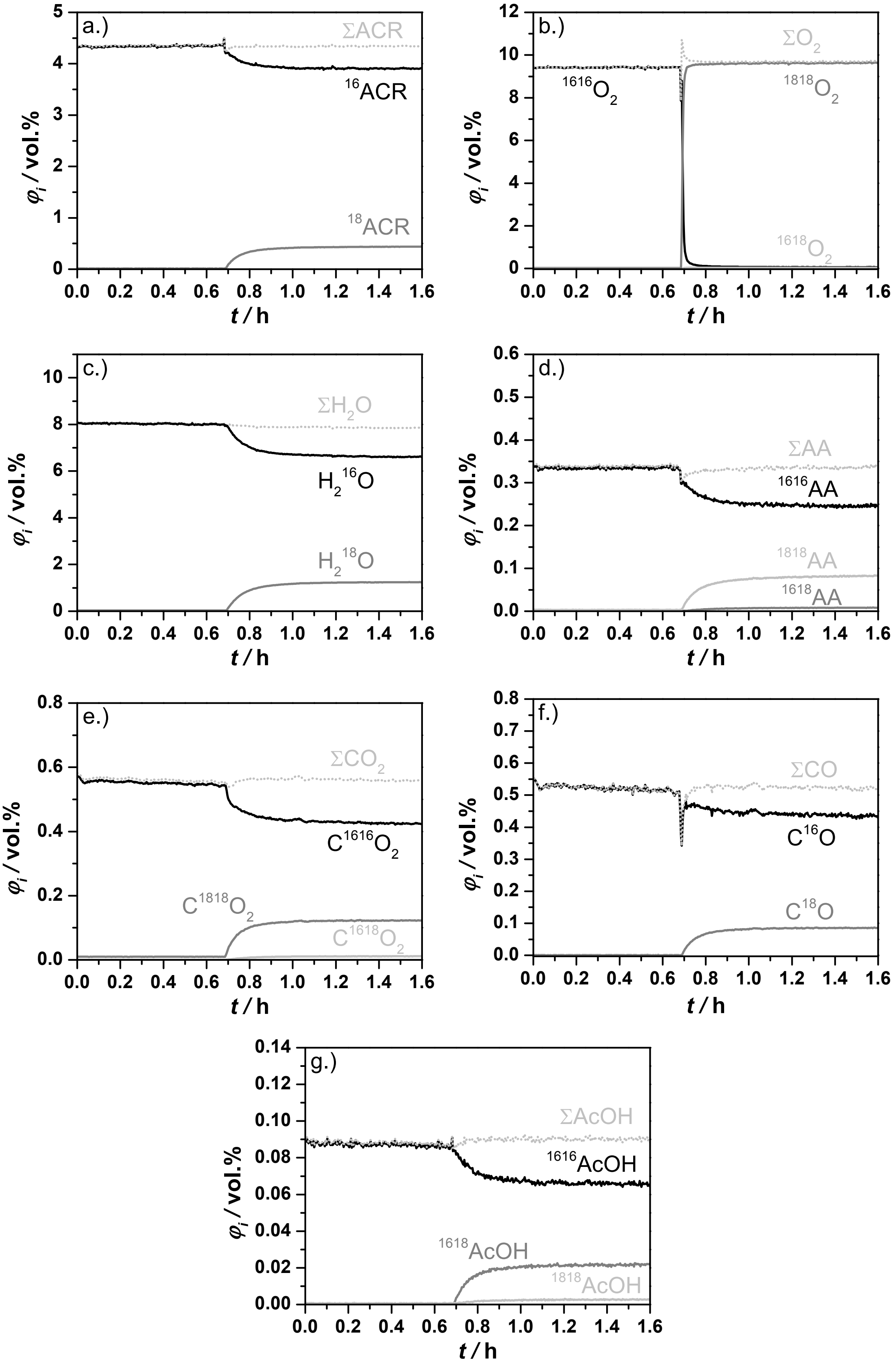


SI-Fig. 2: Quantitative D-NMR, with 40.4 mg benzene as internal standard in mass (no solvent). 402.9 mg of the ACR-D_4 sample was used.

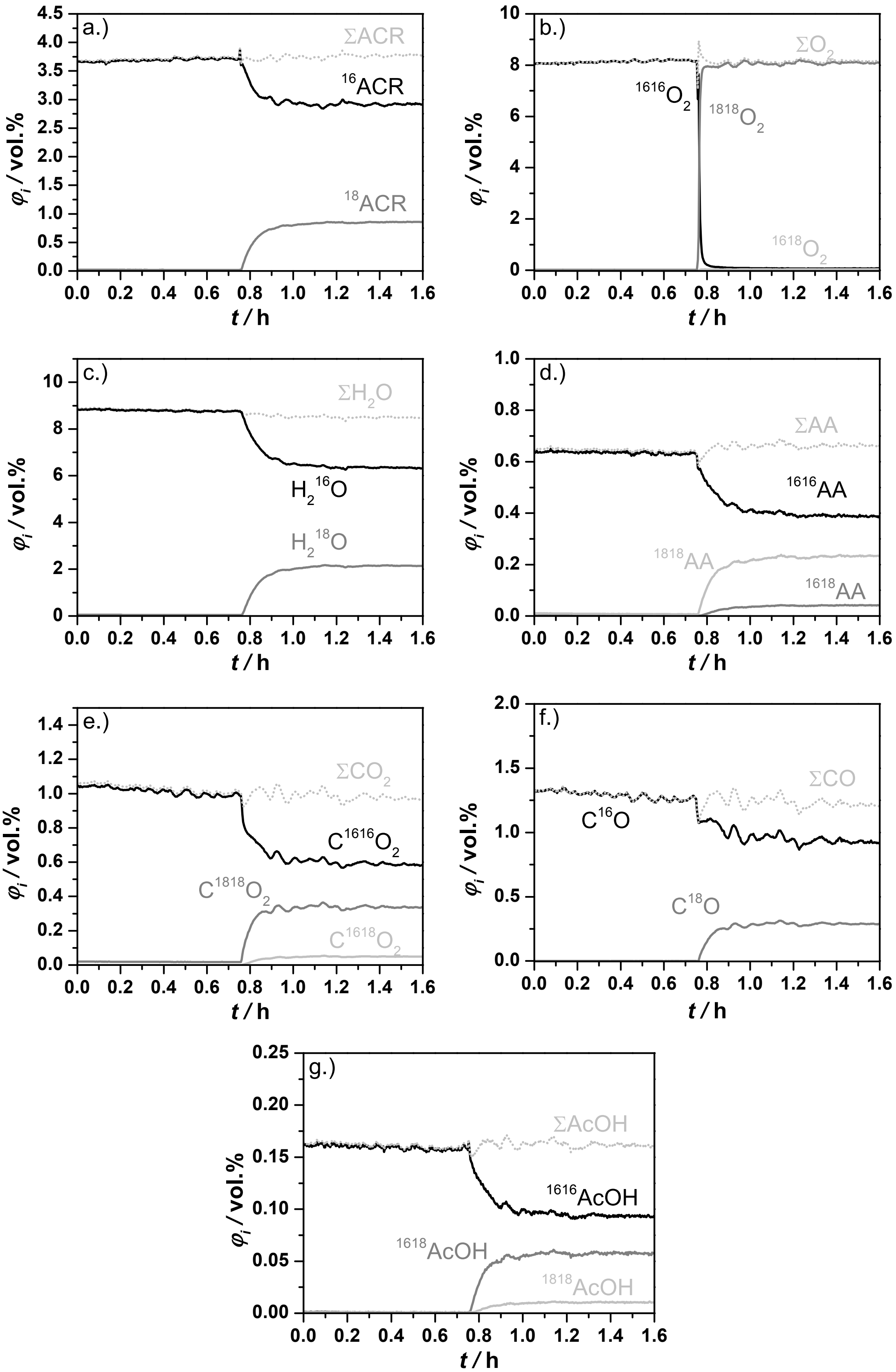
SI-2: $^{18}O_2$-SSITKA



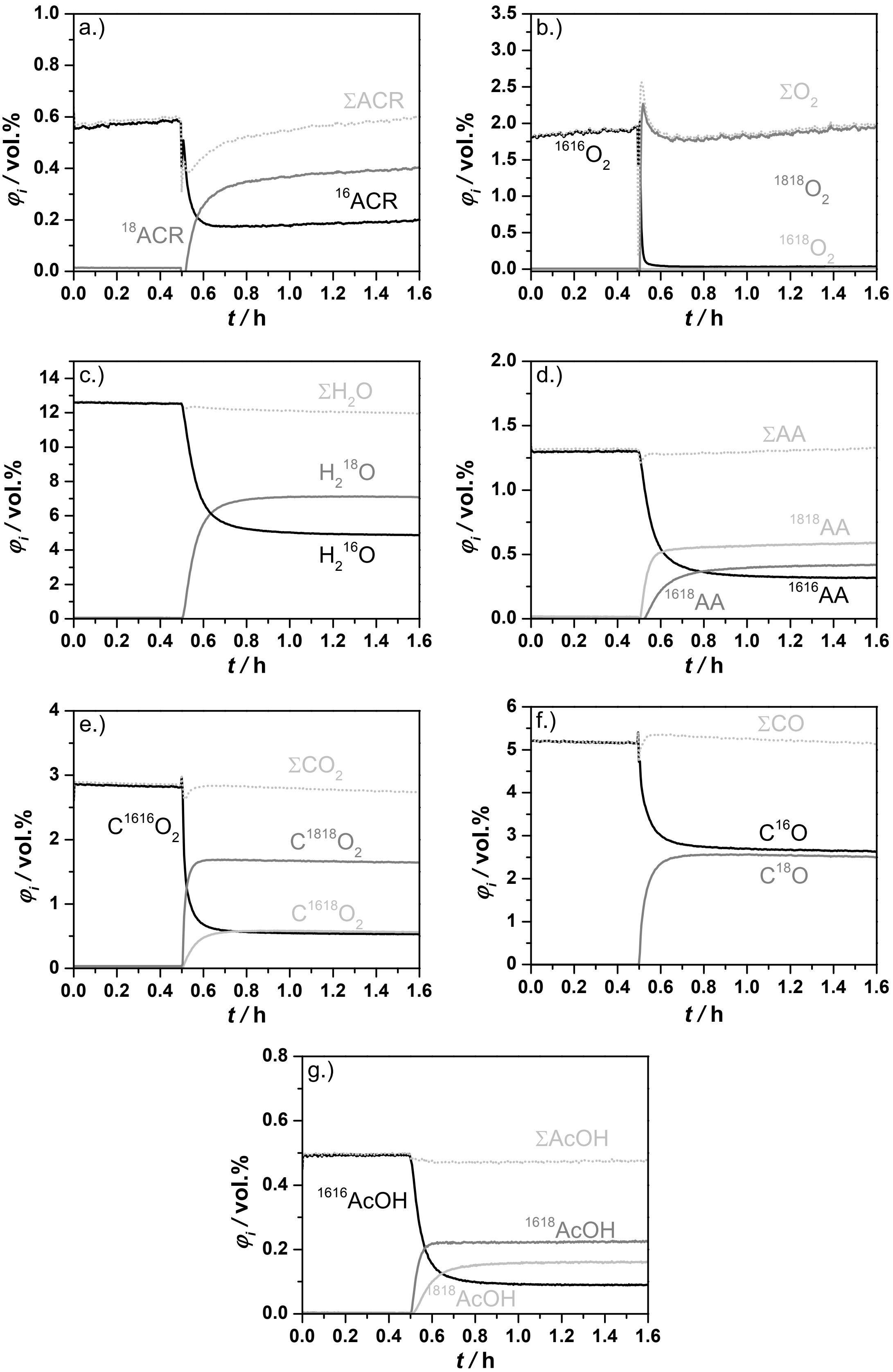
SI-Fig. 3: Response of ACR (a), O_2 (b), H_2O (c), AA (d), CO_2 (e), CO (f) and AcOH (g) during a $^{18}O_2$-SSITKA (5.0 vol.% ACR, 10 vol.% O_2/$^{18}O_2$, 7.5 vol.% H_2O, balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ · 1.4 H_2O, 20 mL min^{-1} (STP), 150 °C).



SI-Fig. 4: Response of ACR (a), O_2 (b), H_2O (c), AA (d), CO_2 (e), CO (f) and AcOH (g) during a $^{18}O_2$-SSITKA (5.0 vol.% ACR, 10 vol.% O_2/$^{18}O_2$, 7.5 vol.% H_2O, balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ · 1.4 H_2O, 20 mL min^{-1} (STP), 300 °C).

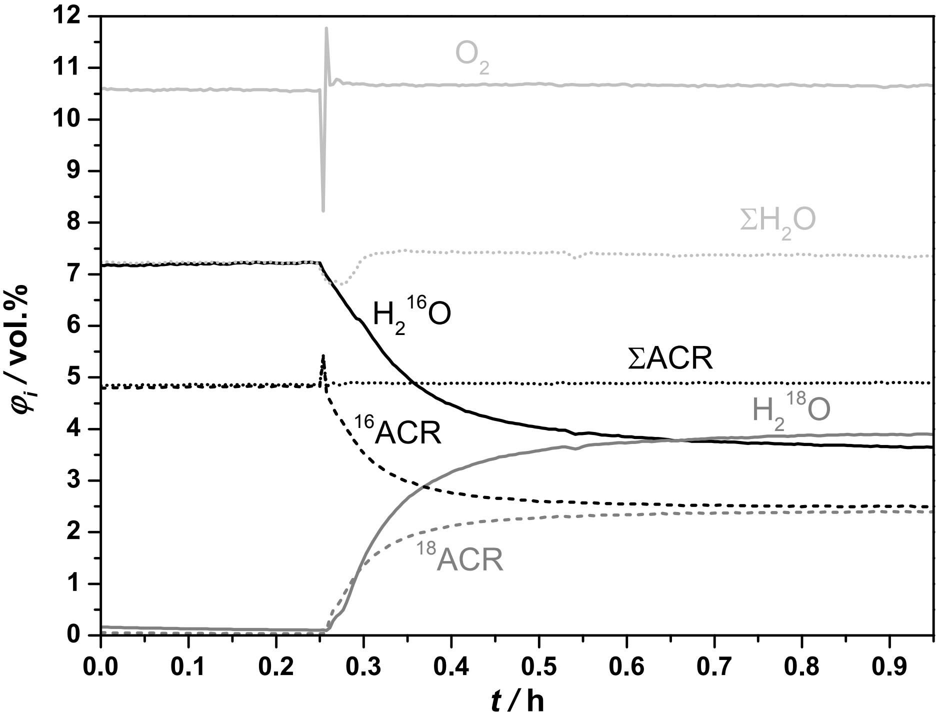


SI-Fig. 5: Response of ACR (a), O_2 (b), H_2O (c), AA (d), CO_2 (e), CO (f) and AcOH (g) during a $^{18}O_2$-SSITKA (5.0 vol.% ACR, 10 vol.% $O_2/^{18}O_2$, 7.5 vol.% H_2O, balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40} \cdot 1.4\ H_2O$, 20 mL min^{-1} (STP), 320 °C).

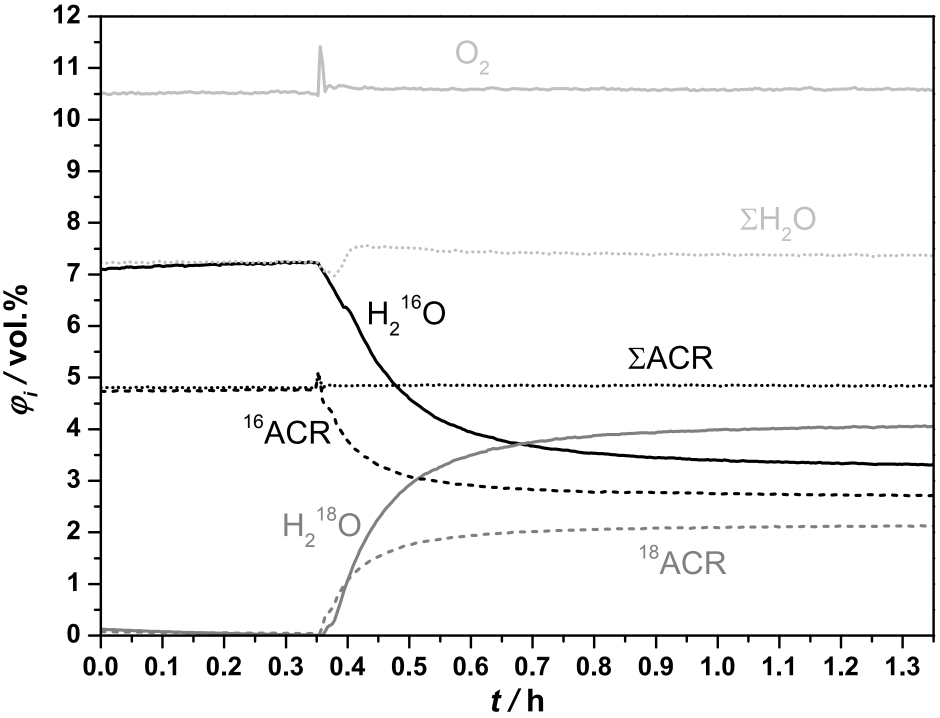


SI-Fig. 6: Response of ACR (a), O_2 (b), H_2O (c), AA (d), CO_2 (e), CO (f) and AcOH (g) during a $^{18}O_2$-SSITKA (5.0 vol.% ACR, 10 vol.% O_2/$^{18}O_2$, 7.5 vol.% H_2O, balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40} \cdot 1.4\ H_2O$, 20 mL min^{-1} (STP), 360 °C).

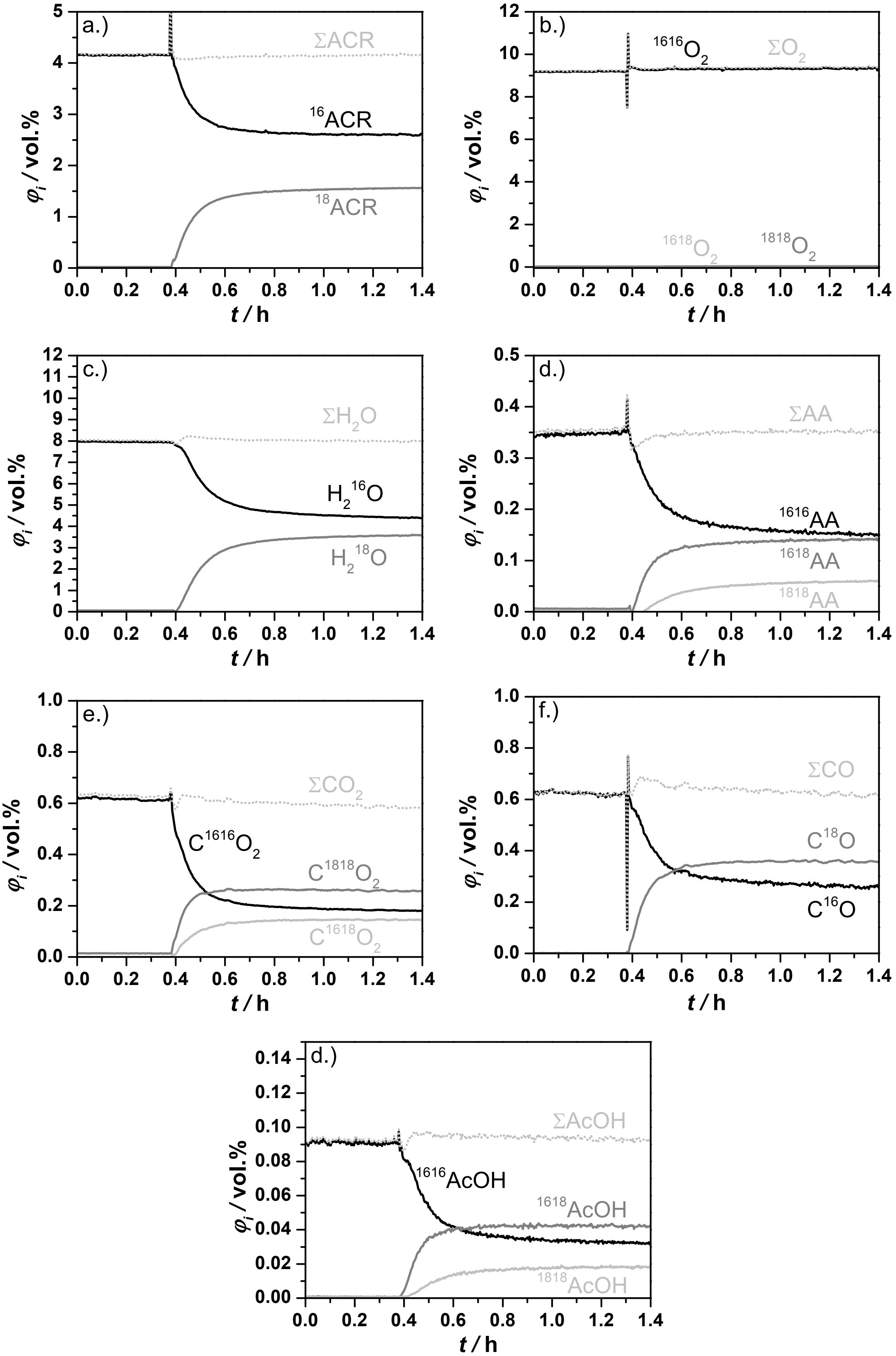
SI-3: $H_2{}^{18}O$-SSITKA



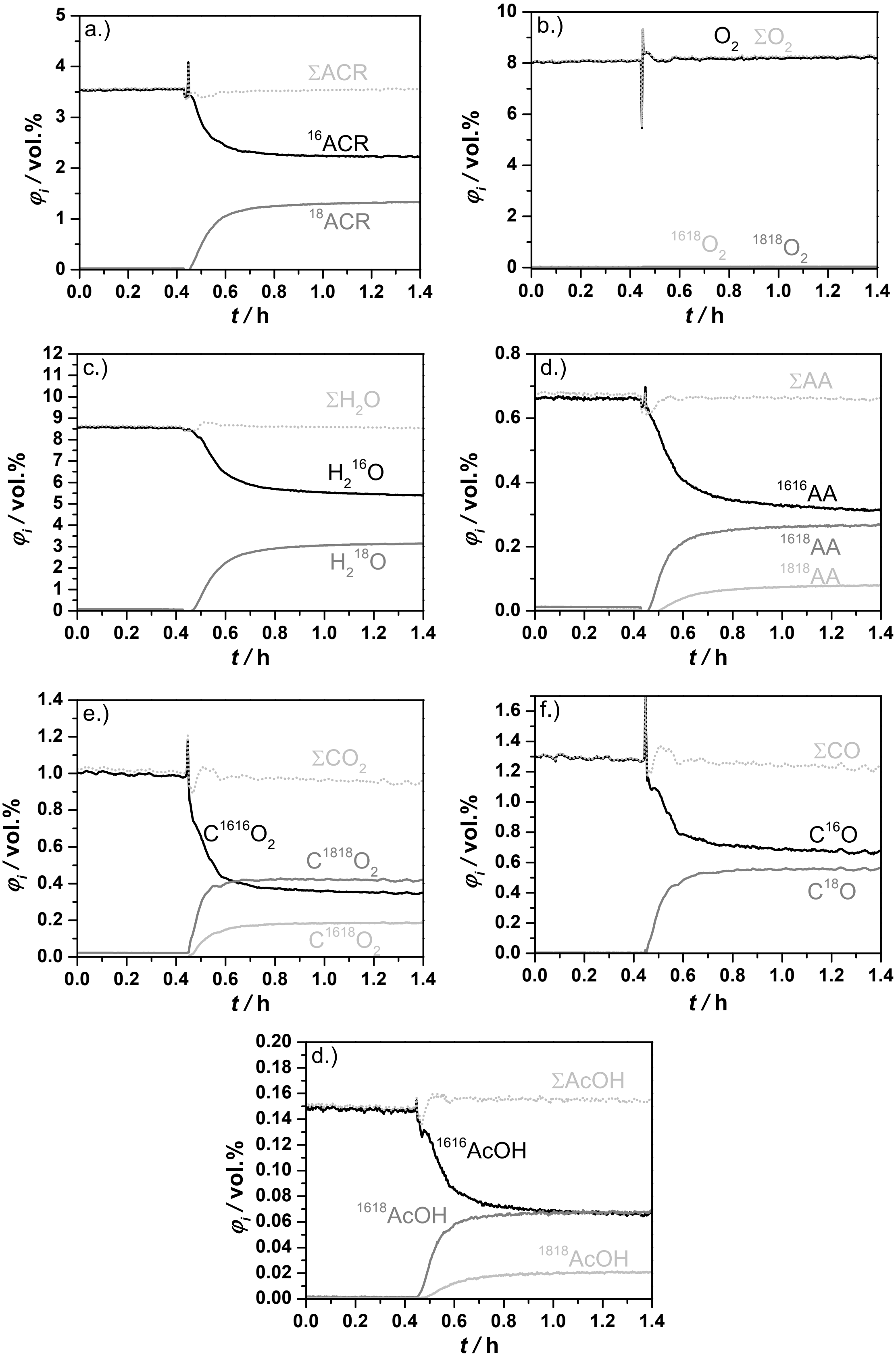
SI-Fig. 7: Response of ACR, O_2 and H_2O during a $H_2{}^{18}O$-SSITKA (5.0 vol.% ACR, 10 vol.% O_2, 7.5 vol.% $H_2{}^{16}O/H_2{}^{18}O$, balance: He, 50 mg $Mo_8V_2W_{0.5}O_x$, 20 mL min^{-1} (STP), 200 °C (no ACR conversion)).



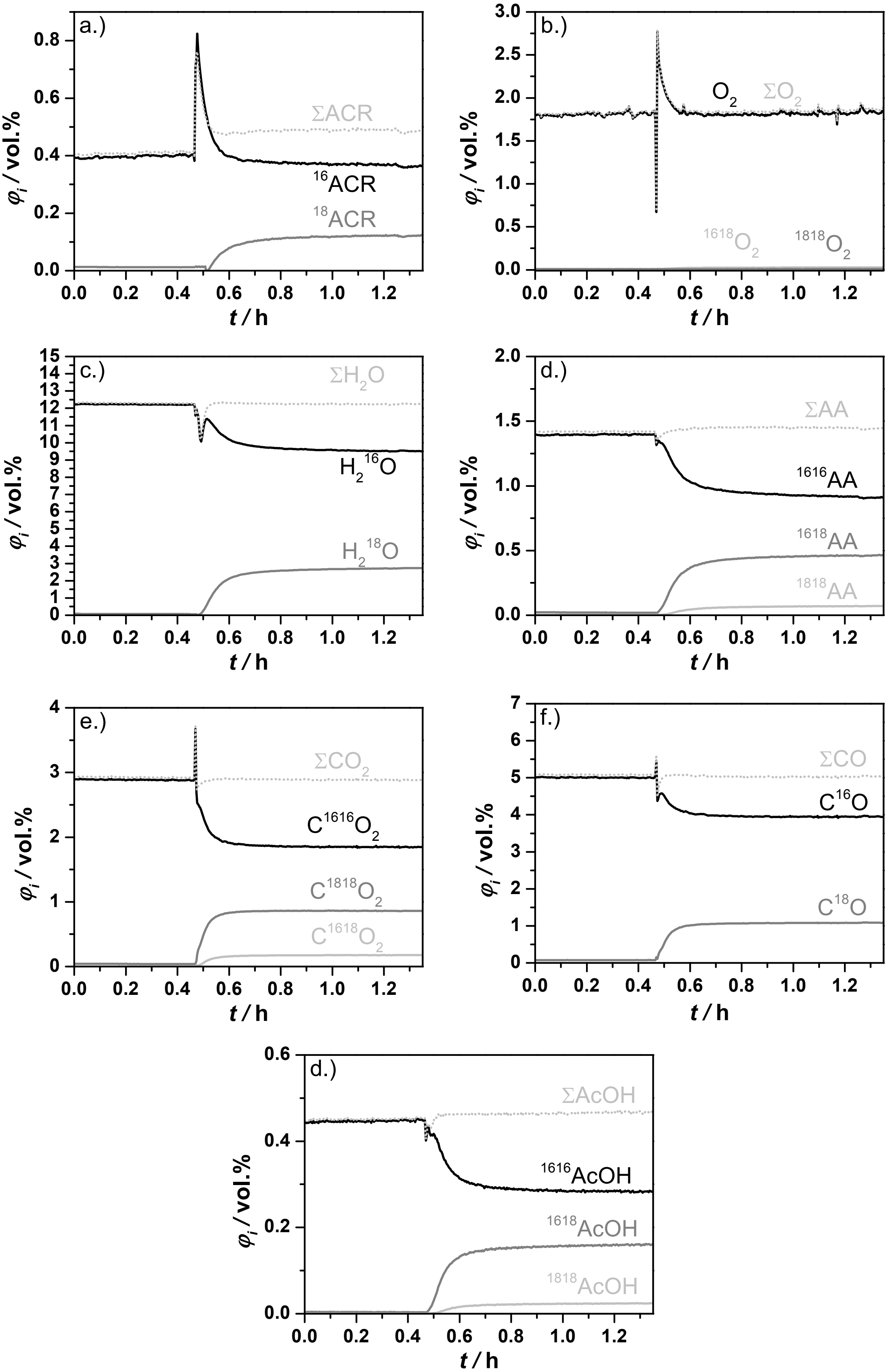
SI-Fig. 8: Response of ACR, O_2 and H_2O during a $H_2{}^{18}O$-SSITKA (5.0 vol.% ACR, 10 vol.% O_2, 7.5 vol.% $H_2{}^{16}O/H_2{}^{18}O$, balance: He, 50 mg $Mo_8V_2W_{0.5}O_x$, 20 mL min^{-1} (STP), 250 °C (very low ACR conversion, see SI-5)).



SI-Fig. 9: Response of ACR (a), O_2 (b), H_2O (c), AA (d), CO_2 (e), CO (f) and AcOH (g) during a $H_2{}^{18}O$-SSITKA (5.0 vol.% ACR, 10 vol.% O_2, 7.5 vol.% $H_2{}^{16}O/H_2{}^{18}O$, balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40} \cdot 1.4\ H_2O$, 20 mL min^{-1} (STP), 300 °C).

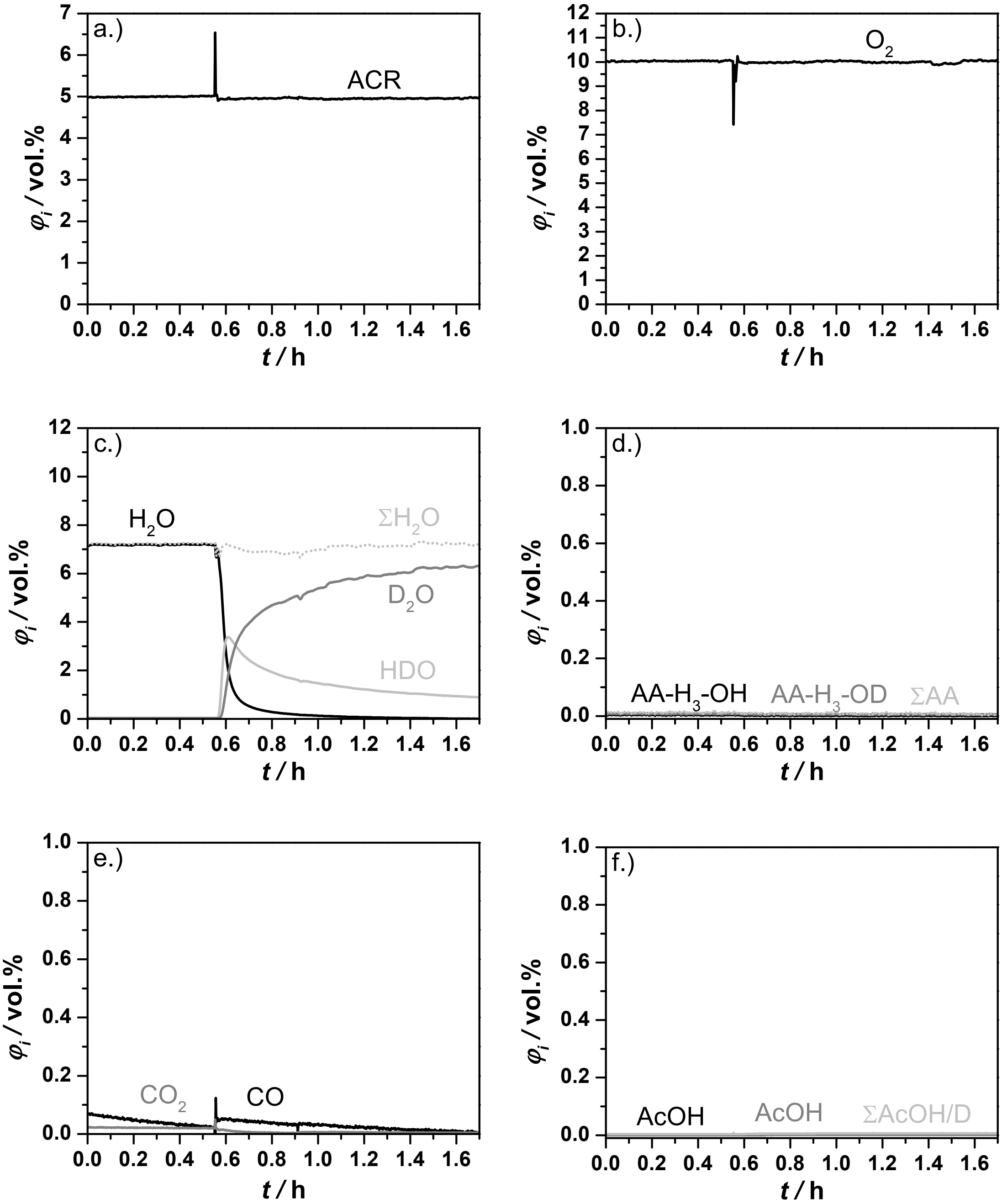


SI-Fig. 10: Response of ACR (a), O_2 (b), H_2O (c), AA (d), CO_2 (e), CO (f) and AcOH (g) during a $H_2{}^{18}O$-SSITKA (5.0 vol.% ACR, 10 vol.% O_2, 7.5 vol.% $H_2{}^{16}O/H_2{}^{18}O$, balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40} \cdot 1.4\ H_2O$, 20 mL min^{-1} (STP), 320 °C).

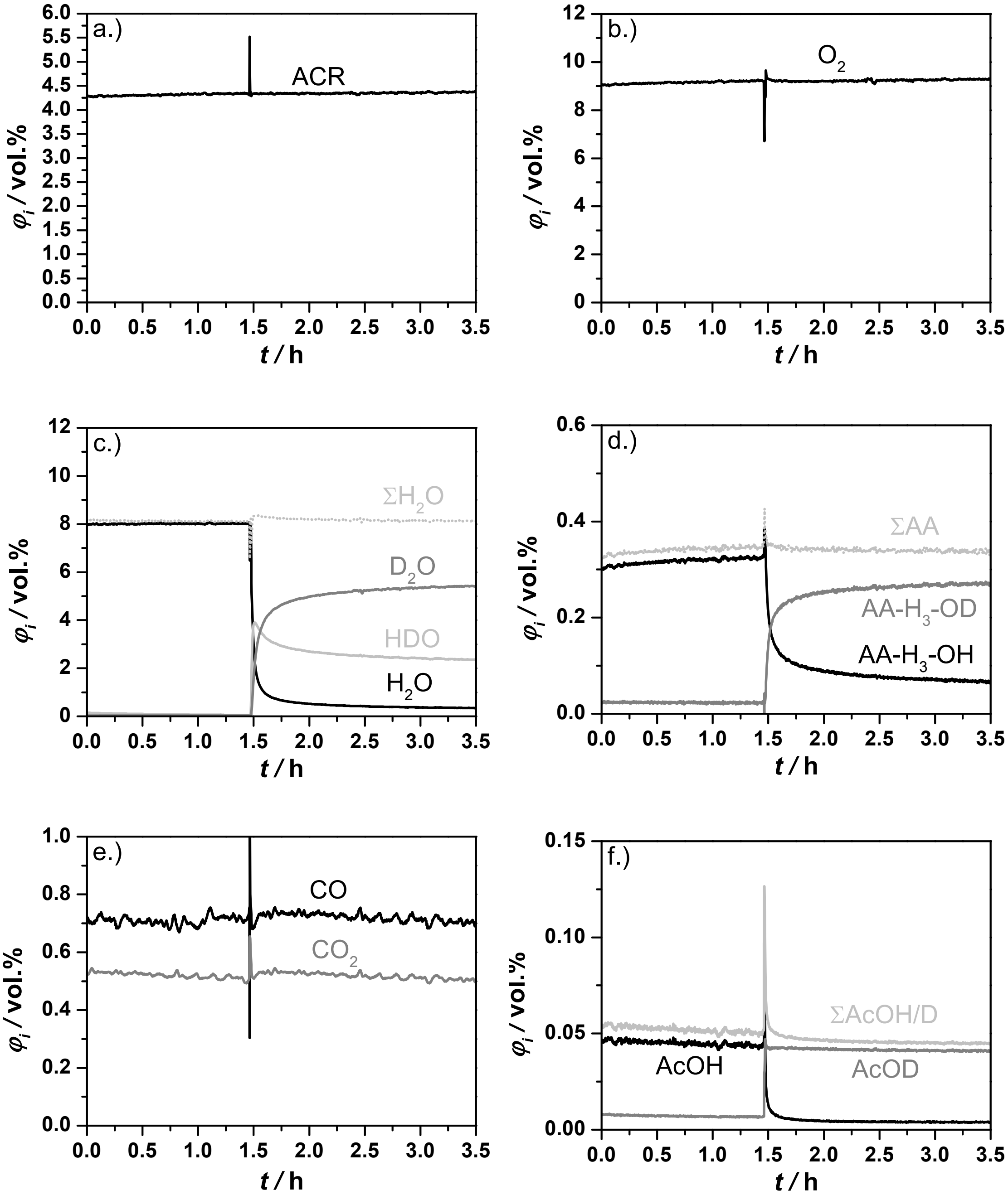


SI-Fig. 11: Response of ACR (a), O2 (b), H2O (c), AA (d), CO2 (e), CO (f) and AcOH (g) during a H218O-SSITKA (5.0 vol.% ACR, 10 vol.% O2, 7.5 vol.% H216O/H218O, balance: He, 100 mg Cs2H2Mo11VPO40 · 1.4 H2O, 20 mL min-1 (STP), 360 °C).

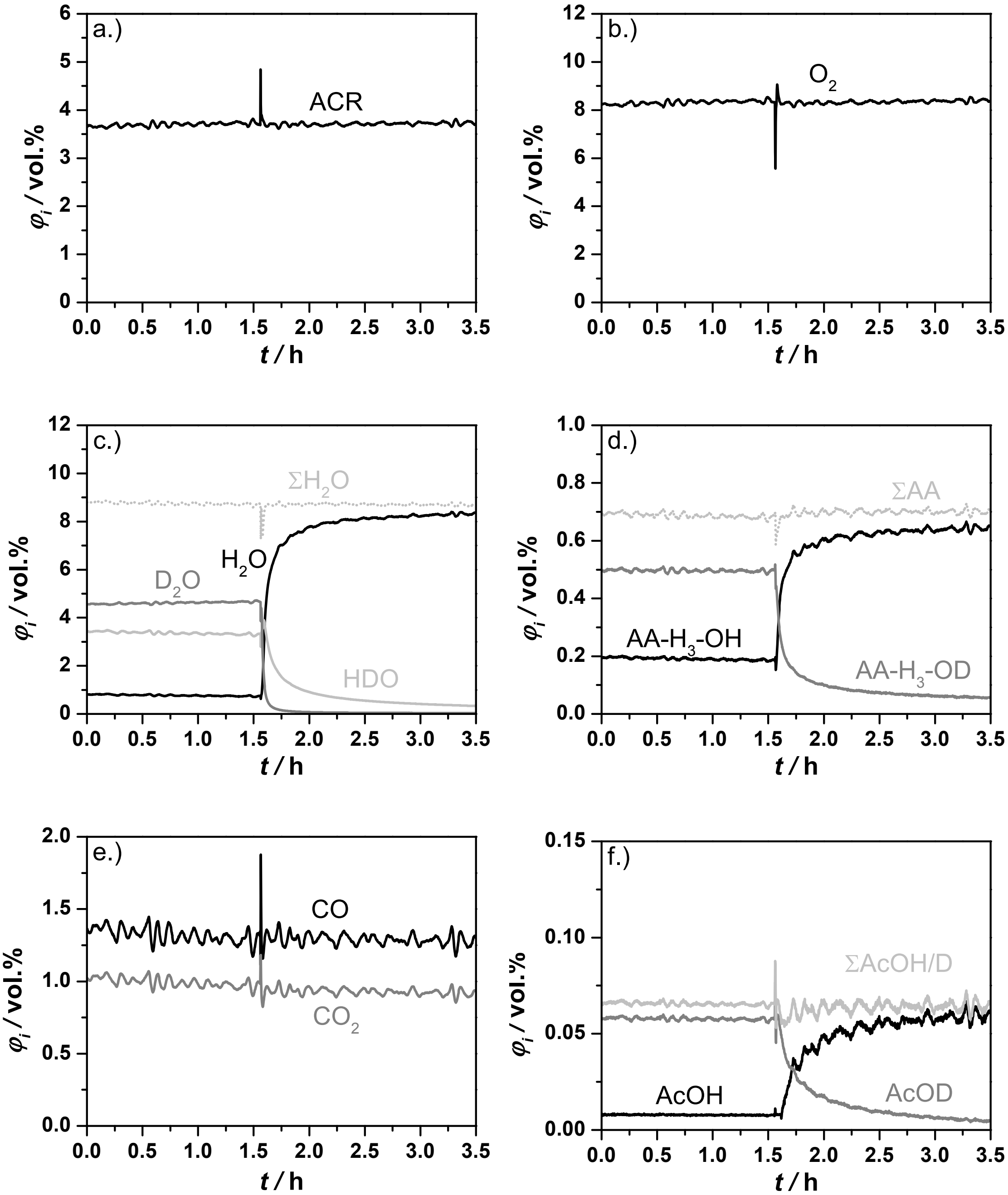
SI-4: D_2O-SSITKA



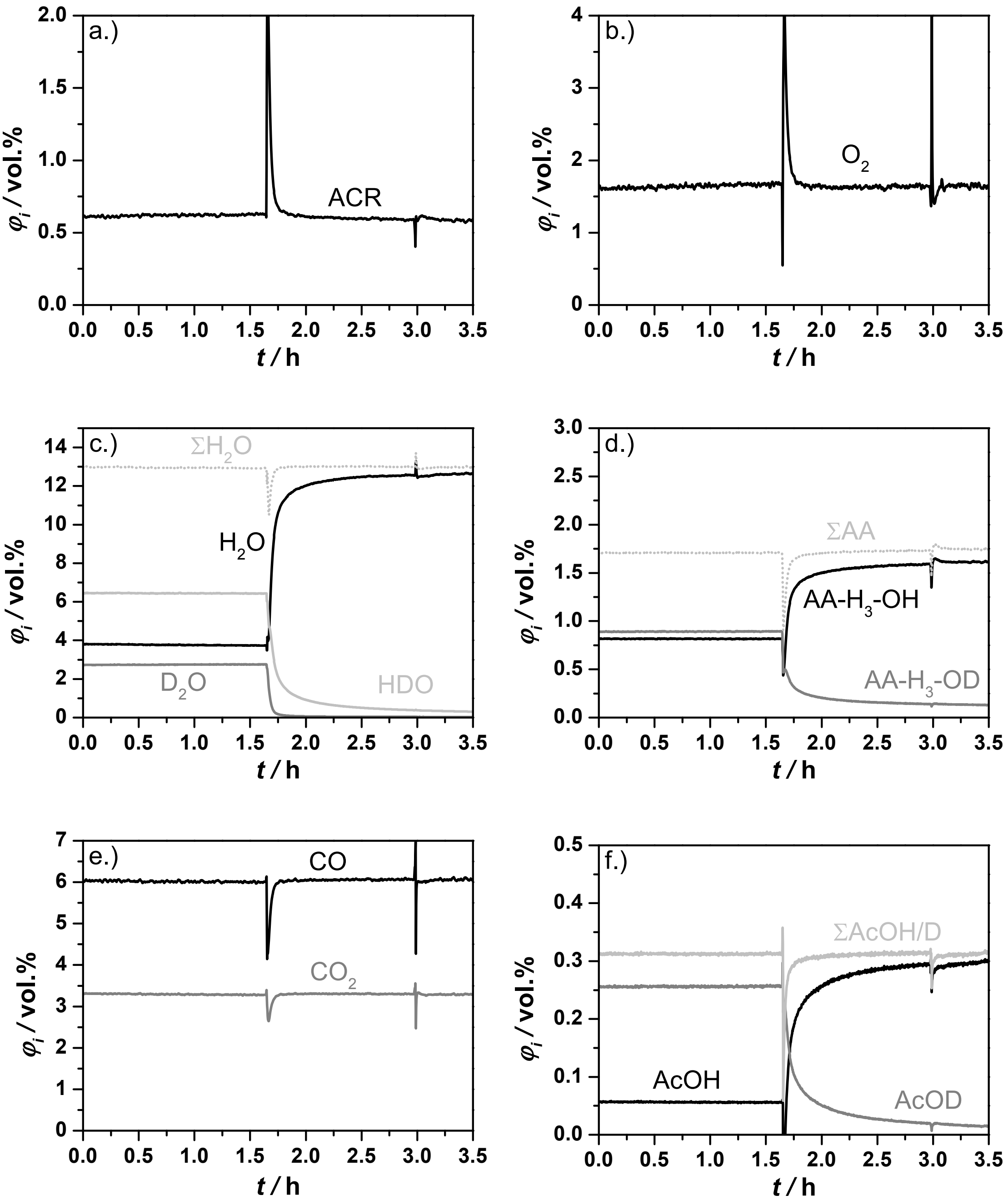
SI-Fig. 12: Response of ACR (a), O_2 (b), H_2O (c), AA (d), CO2, CO (e) and AcOH (d) during a D_2O-SSITKA (5.0 vol.% ACR, 10 vol.% O_2, 7.5 vol.% H_2O/D_2O, balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ · 1.4 H_2O, 20 mL min^{-1} (STP), 150 °C). See Fig 18 for the designation of the detected components.



SI-Fig. 13: Response of ACR (a), O_2 (b), H_2O (c), AA (d), CO2, CO (e) and AcOH (d) during a D_2O-SSITKA (5.0 vol.% ACR, 10 vol.% O_2, 7.5 vol.% H_2O/D_2O, balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}\cdot 1.4\ H_2O$, 20 mL min^{-1} (STP), 300 °C). See Fig 18 for the designation of the detected components.

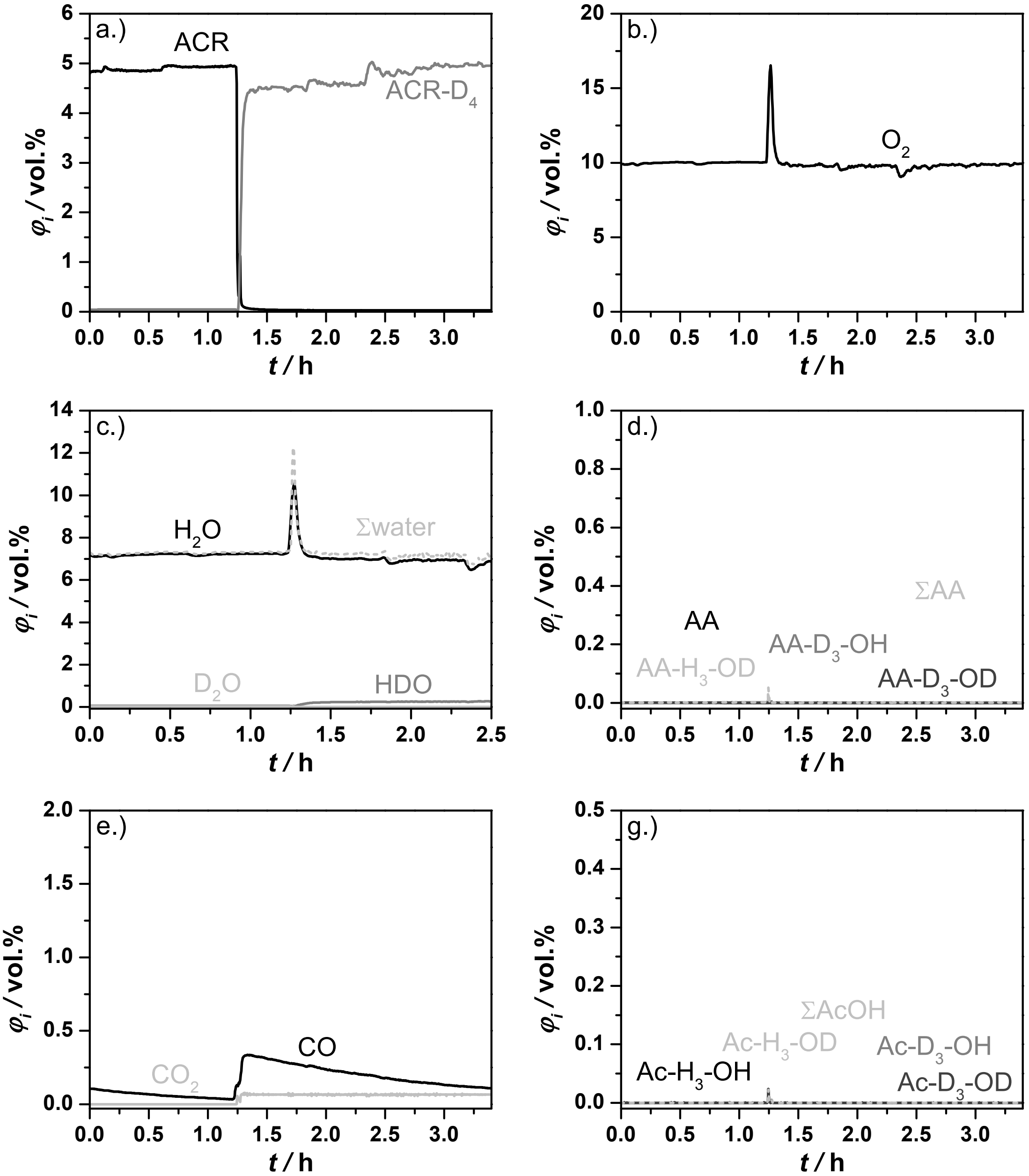


SI-Fig. 14: Response of ACR (a), O_2 (b), H_2O (c), AA (d), CO2, CO (e) and AcOH (d) during a D_2O-SSITKA (5.0 vol.% ACR, 10 vol.% O_2, 7.5 vol.% H_2O/D_2O, balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ · 1.4 H_2O, 20 mL min^{-1} (STP), 320 °C). Here D_2O is stepwise replaced by H_2O. See Fig 18 for the designation of the detected components.

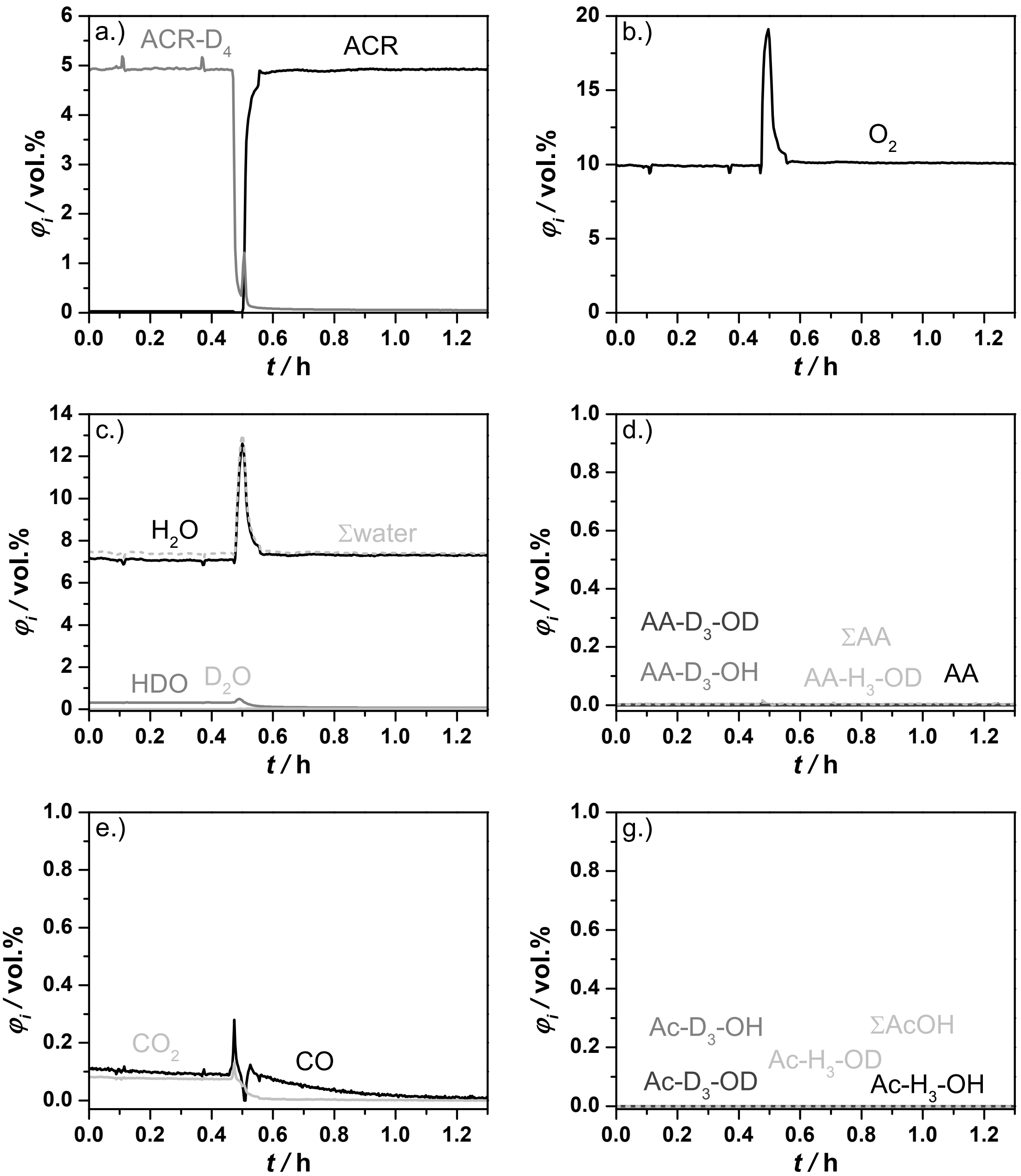


SI-Fig. 15: Response of ACR (a), O_2 (b), H_2O (c), AA (d), CO2, CO (e) and AcOH (d) during a D_2O-SSITKA (5.0 vol.% ACR, 10 vol.% O_2, 7.5 vol.% H_2O/D_2O, balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40} \cdot 1.4\ H_2O$, 20 mL min^{-1} (STP), 360 °C). Here D_2O is stepwise replaced by H_2O. See Fig 18 for the designation of the detected components.

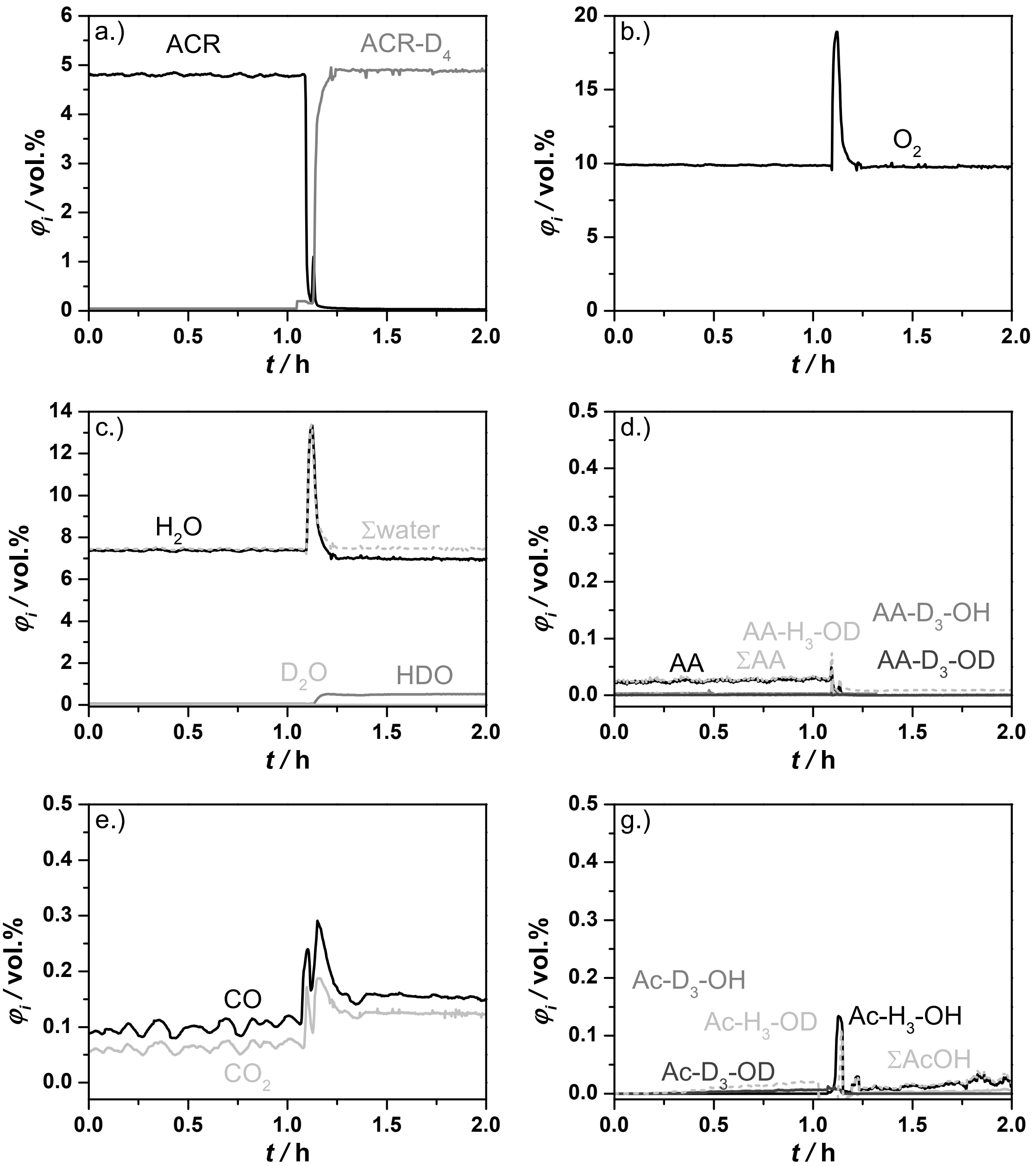
SI-5: Isotopic exchange of ACR by ACR-D_4



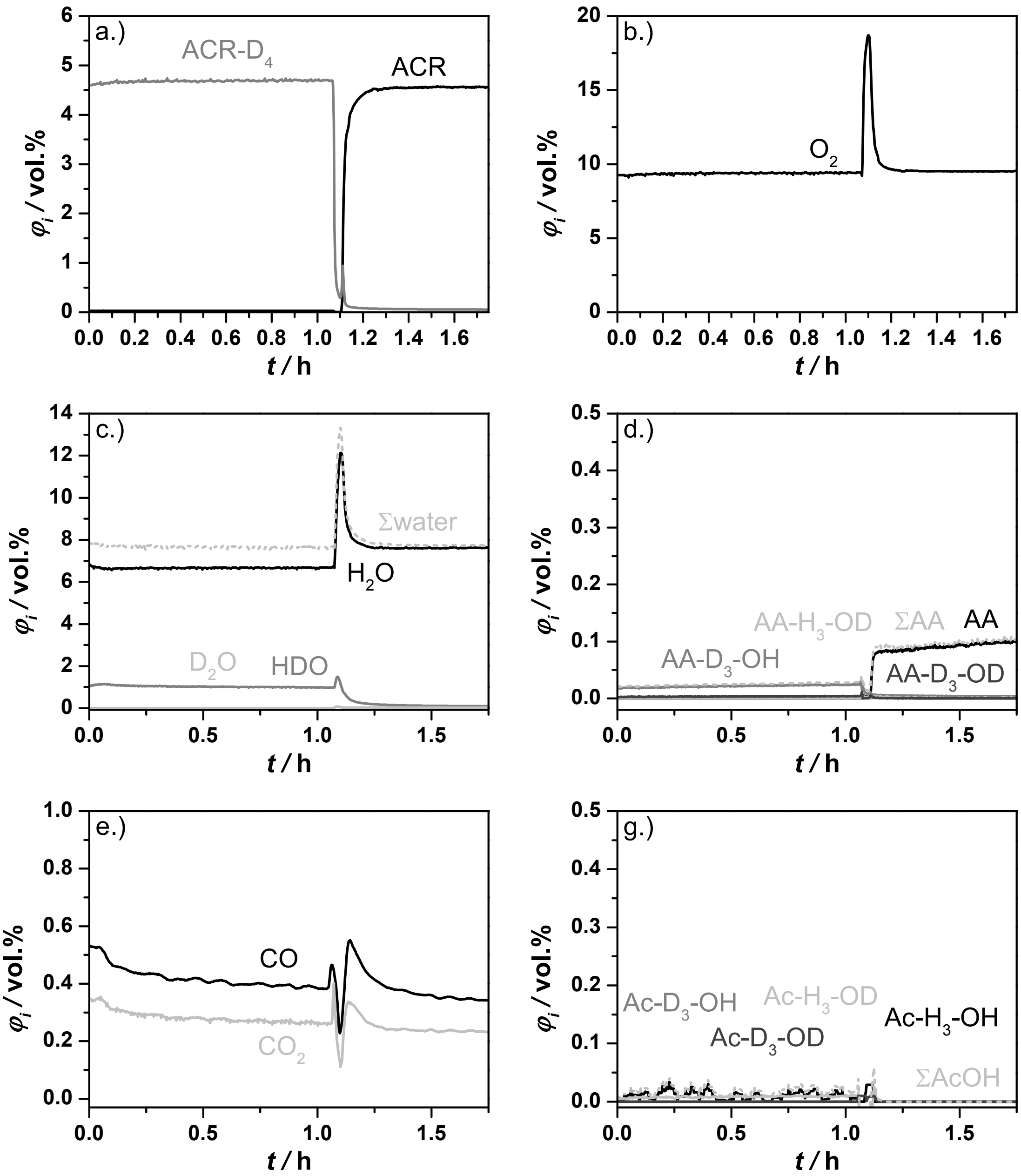
SI-Fig. 16: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR by ACR-D_4 in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40} \cdot 1.4\ H_2O$, 20 mL min^{-1} (STP), 150 °C). The high amounts of detected CO are an experimentell artefact, due to residual air (N_2 and CO have the same atomic mass (28 u) resulting in wrongly detected CO if N_2 is present) in the apparatus.



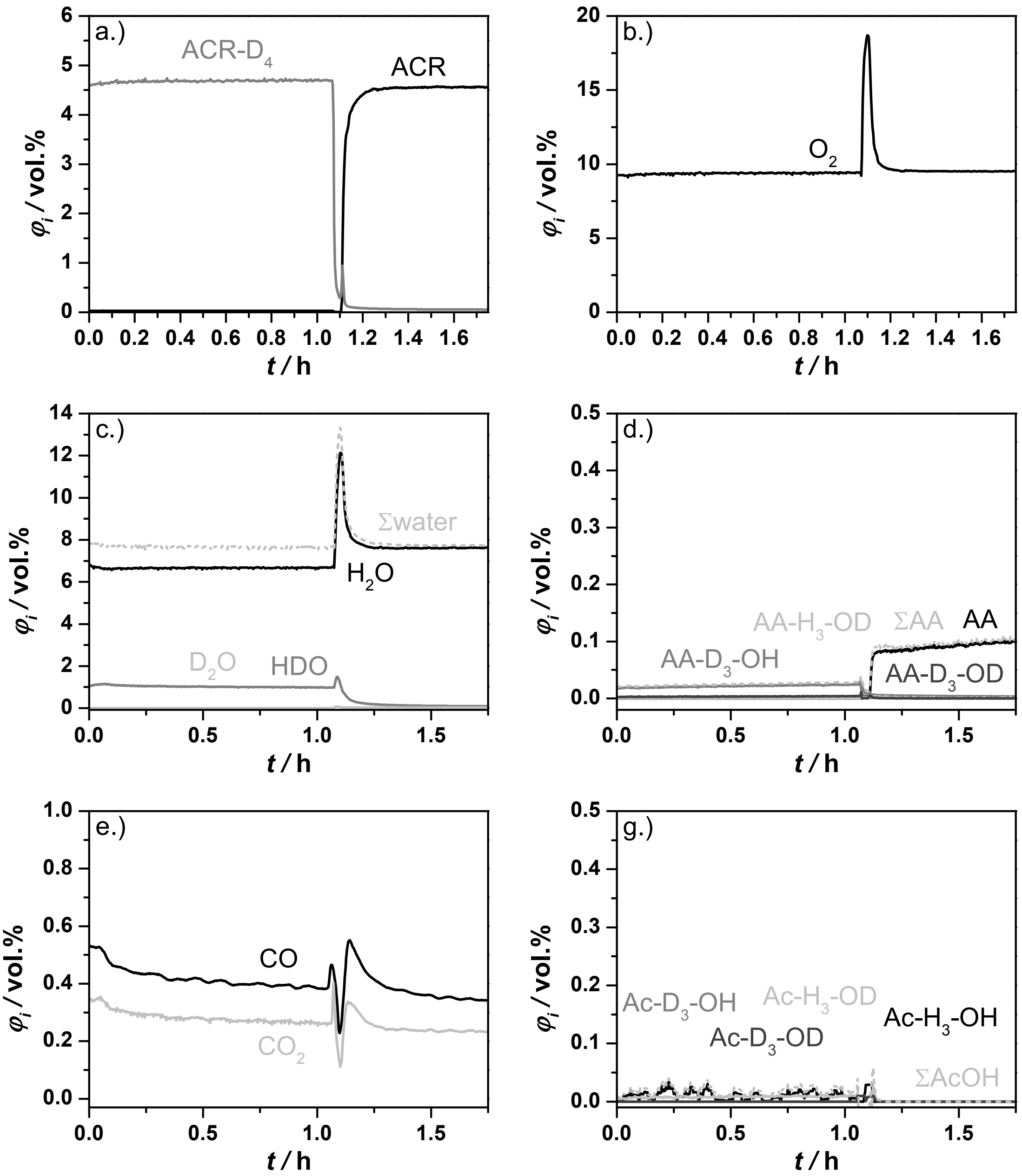
SI-Fig. 17: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR-D_4 by ACR in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ · 1.4 H_2O, 20 mL min^{-1} (STP), 200 °C). The high amounts of detected CO are an experimentell artefact, due to residual air (N_2 and CO have the same atomic mass (28 u) resulting in wrongly detected CO if N_2 is present) in the apparatus.



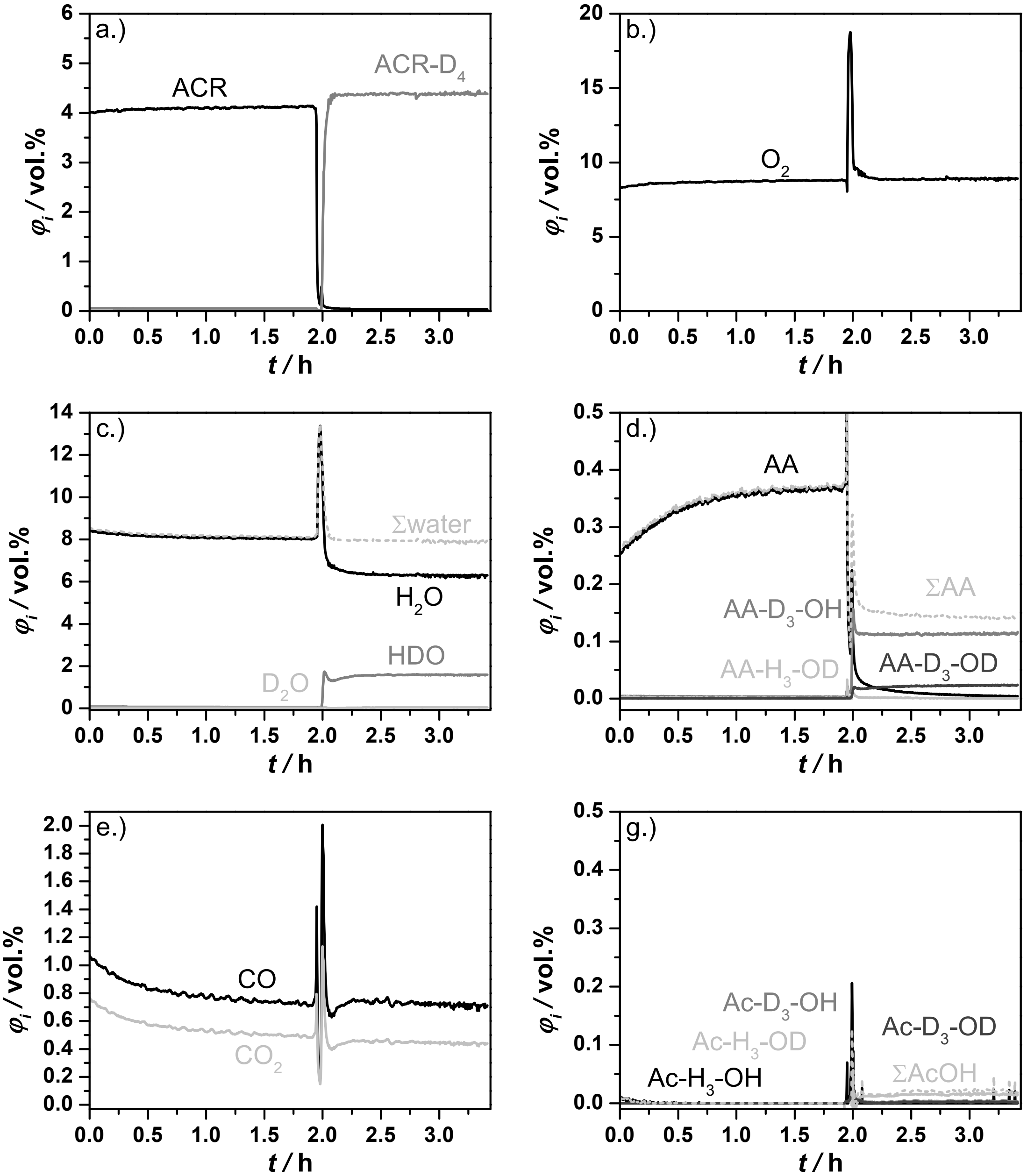
SI-Fig. 18: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR-D_4 by ACR in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ · 1.4 H_2O, 20 mL min^{-1} (STP), 250 °C).



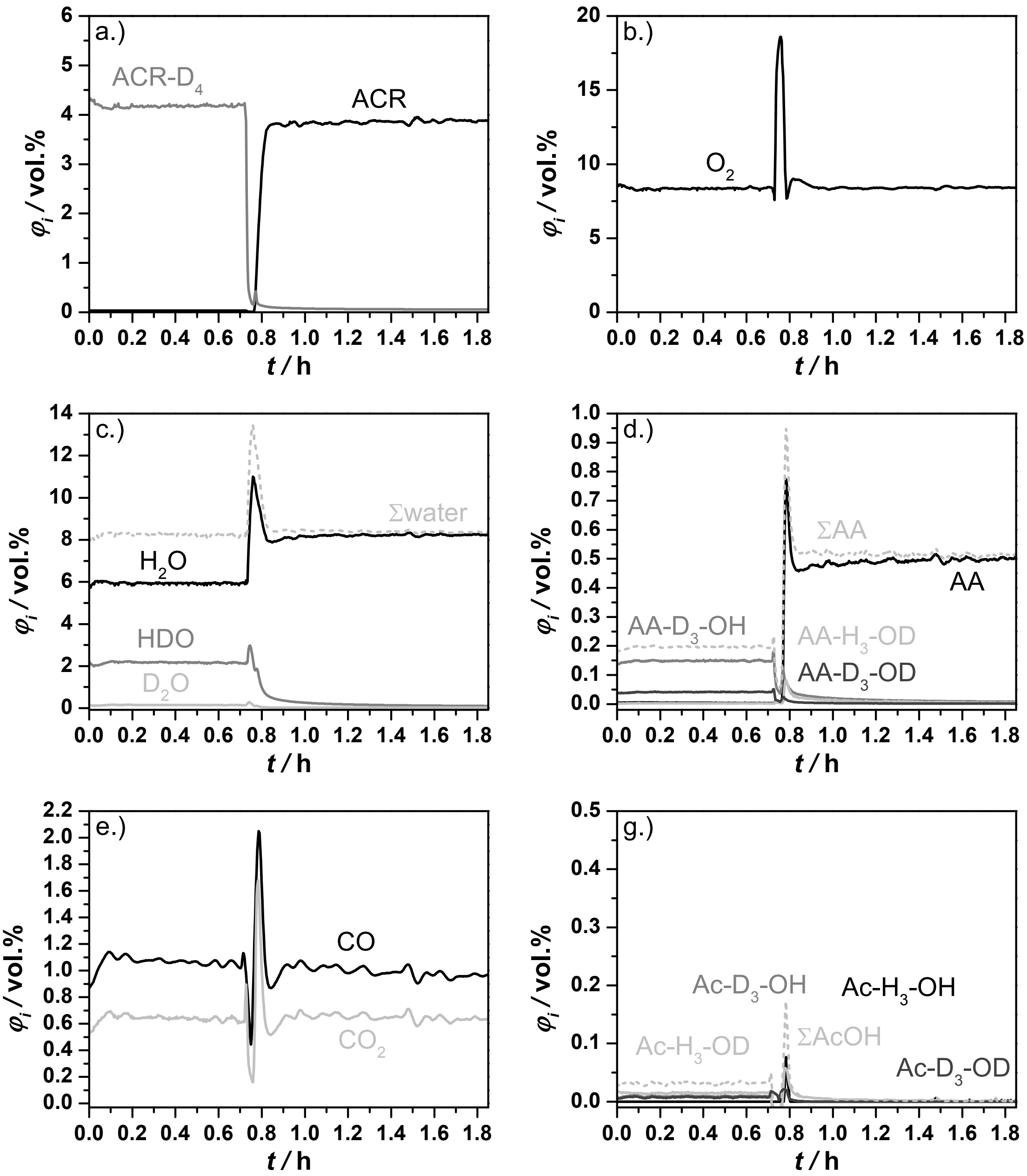
SI-Fig. 19: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR-D_4 by ACR in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ $\cdot$ 1.4 H_2O, 20 mL min^{-1} (STP), 275 °C).



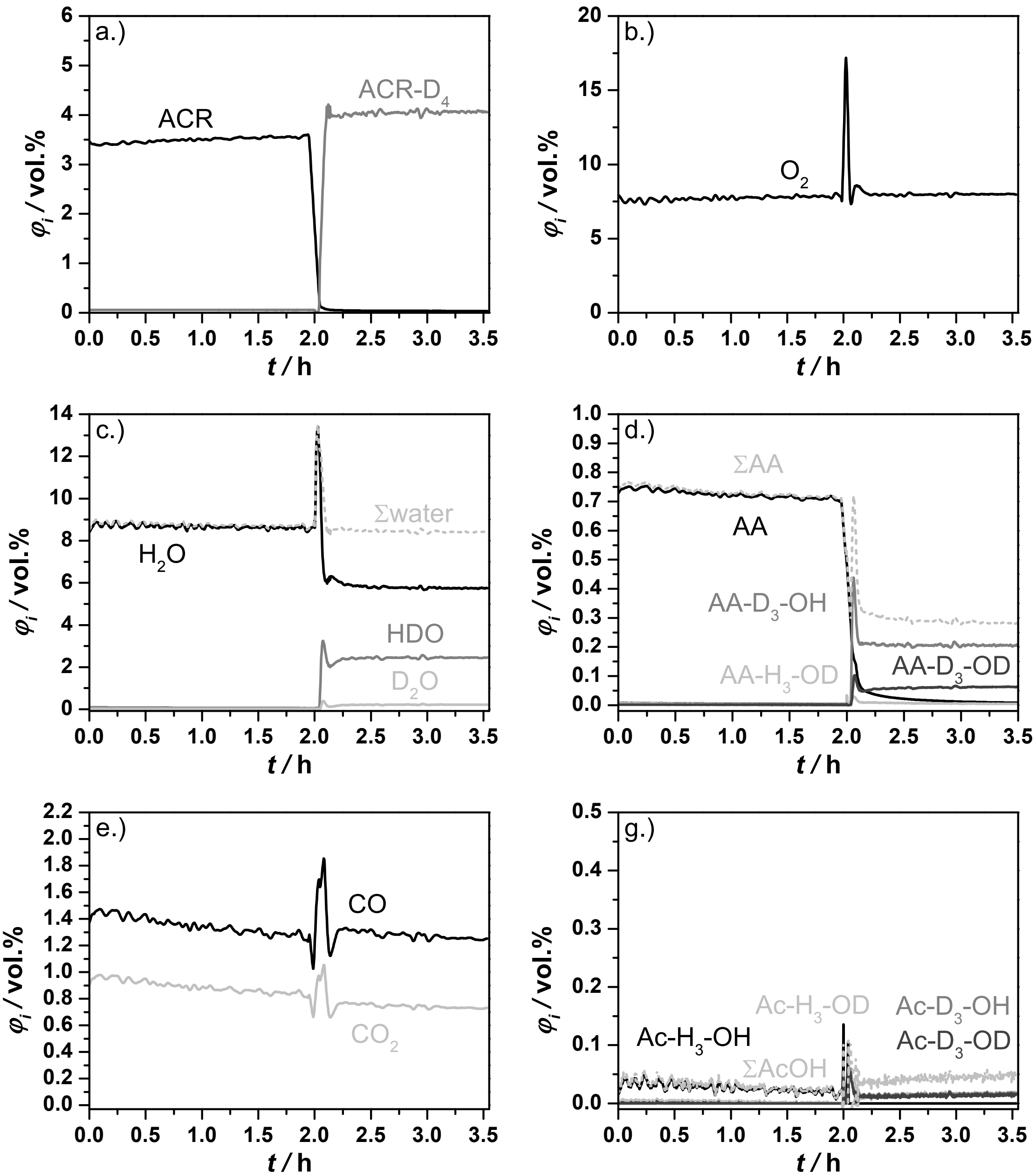
SI-Fig. 20: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR-D_4 by ACR in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40} \cdot 1.4\ H_2O$, 20 mL min^{-1} (STP), 300 °C).



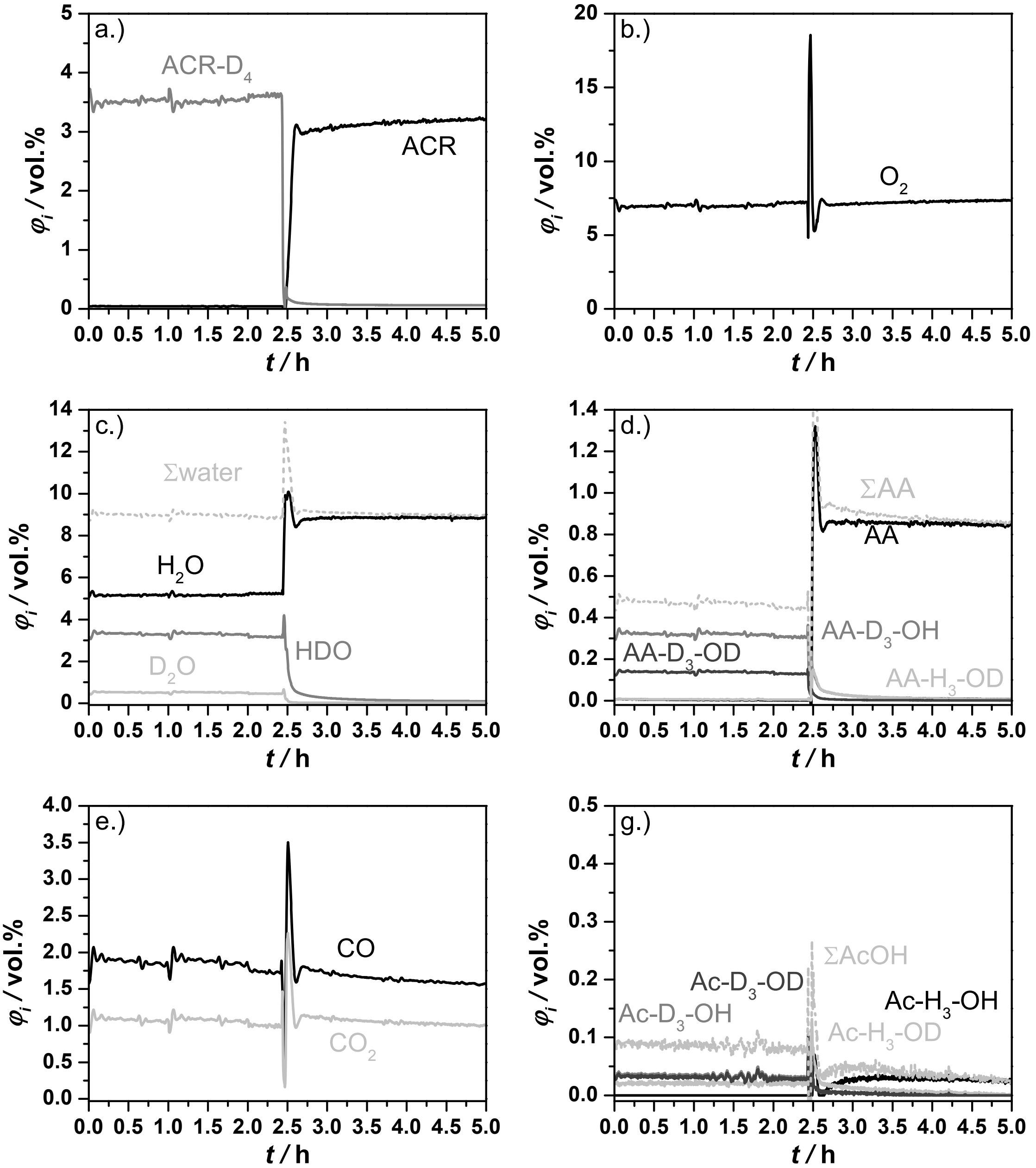
SI-Fig. 21: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR-D_4 by ACR in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ · 1.4 H_2O, 20 mL min^{-1} (STP), 300 °C).



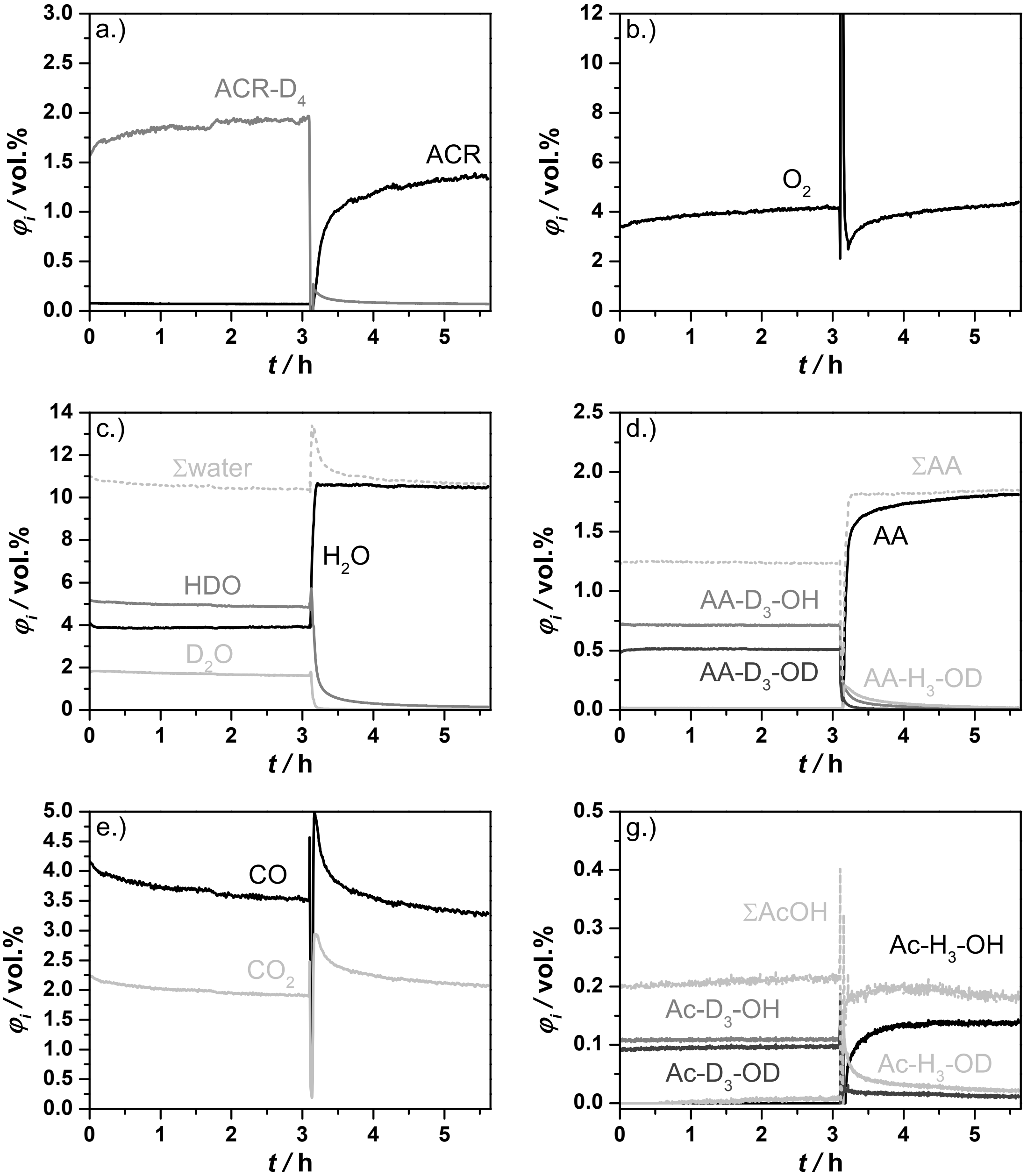
SI-Fig. 22: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR-D_4 by ACR in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40} \cdot 1.4\ H_2O$, 20 mL min^{-1} (STP), 310 °C).



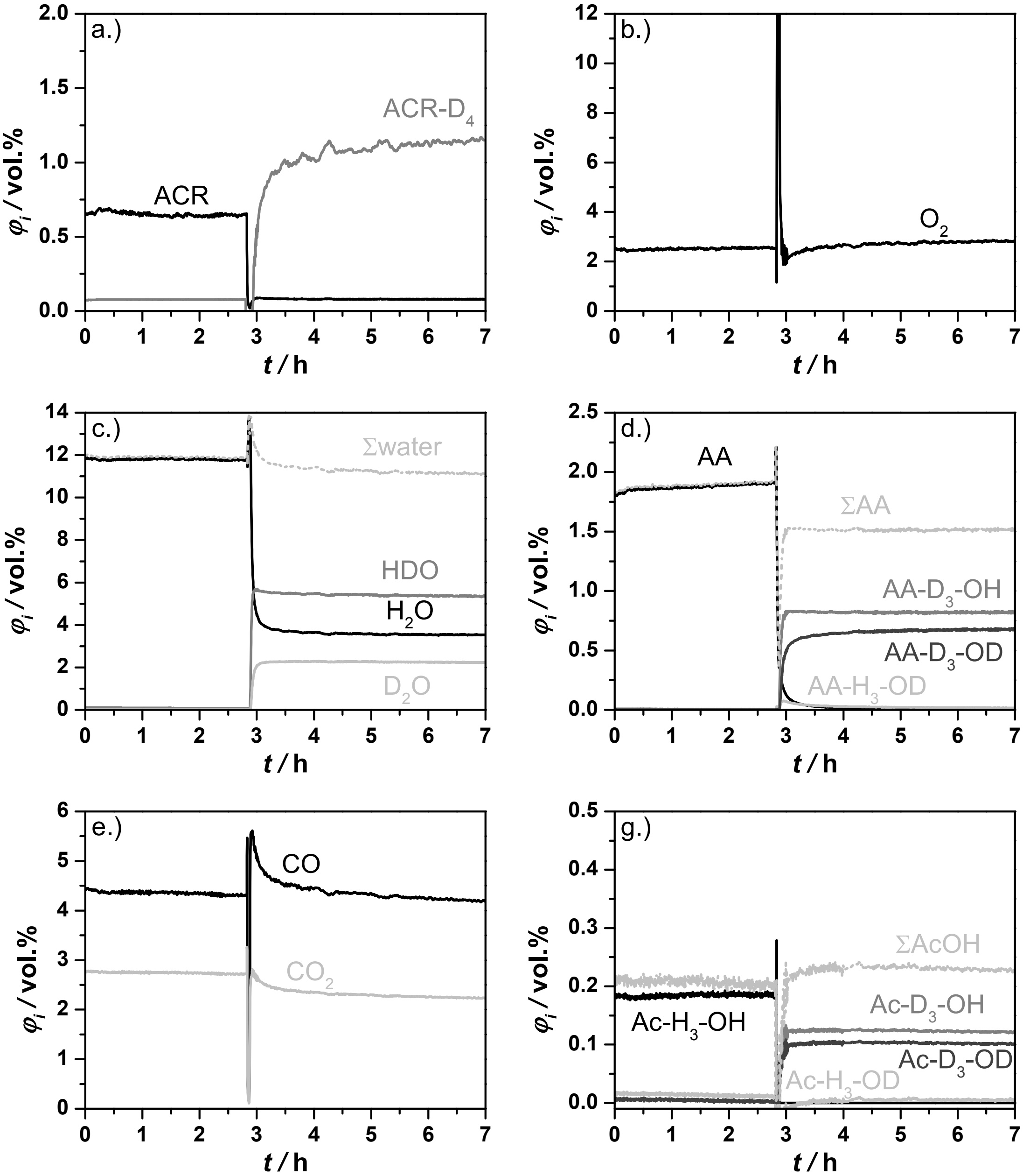
SI-Fig. 23: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR-D_4 by ACR in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ · 1.4 H_2O, 20 mL min^{-1} (STP), 320 °C).



SI-Fig. 24: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR-D_4 by ACR in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40} \cdot 1.4\ H_2O$, 20 mL min^{-1} (STP), 330 °C).



SI-Fig. 25: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR-D_4 by ACR in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ · 1.4 H_2O, 20 mL min^{-1} (STP), 350 °C).



SI-Fig. 26: Transient response of ACR (a), O_2 (b), H_2O (c), AA (d), CO, CO_2 (e) and AcOH (g) as well as their isotopologues during the stepwise exchange of ACR-D_4 by ACR in the feed gas (5 vol.% ACR/ACR-D_4, 10 vol.% O_2, 7.5 vo.% H_2O balance: He, 100 mg $Cs_2H_2Mo_{11}VPO_{40}$ · 1.4 H_2O, 20 mL min^{-1} (STP), 360 °C).