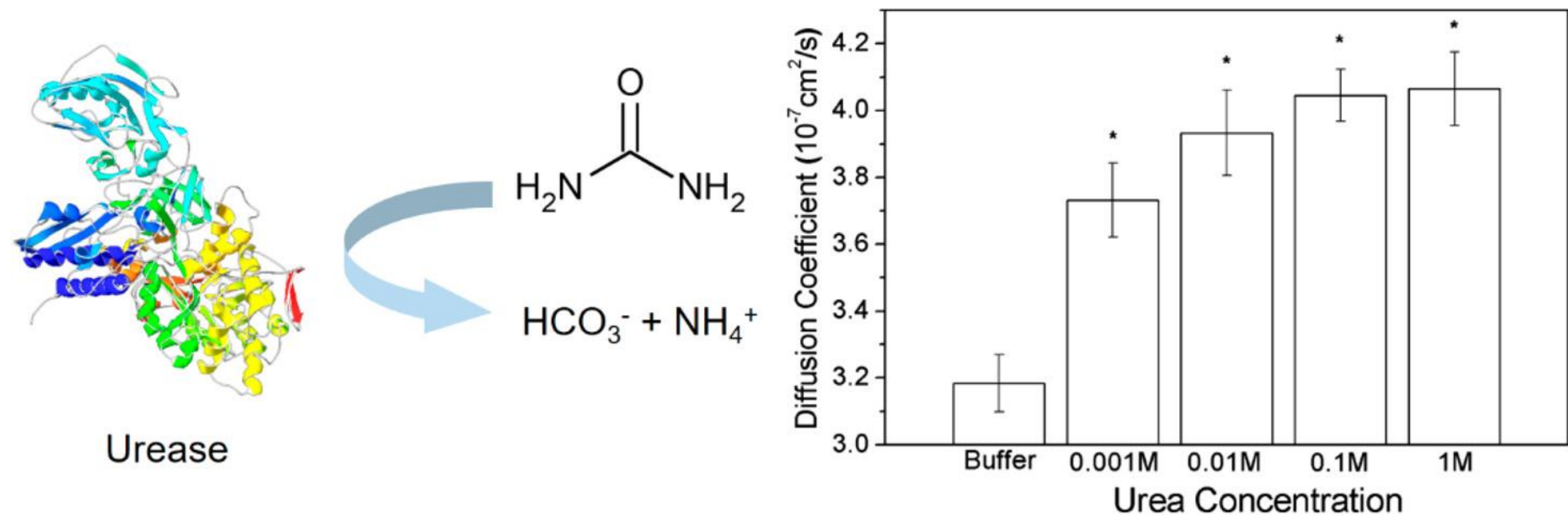


“Enhanced diffusion” of transition metal catalysts is caused by convection

T.S.C. MacDonald, W.S. Price, R.D. Astumian, J.E. Beves

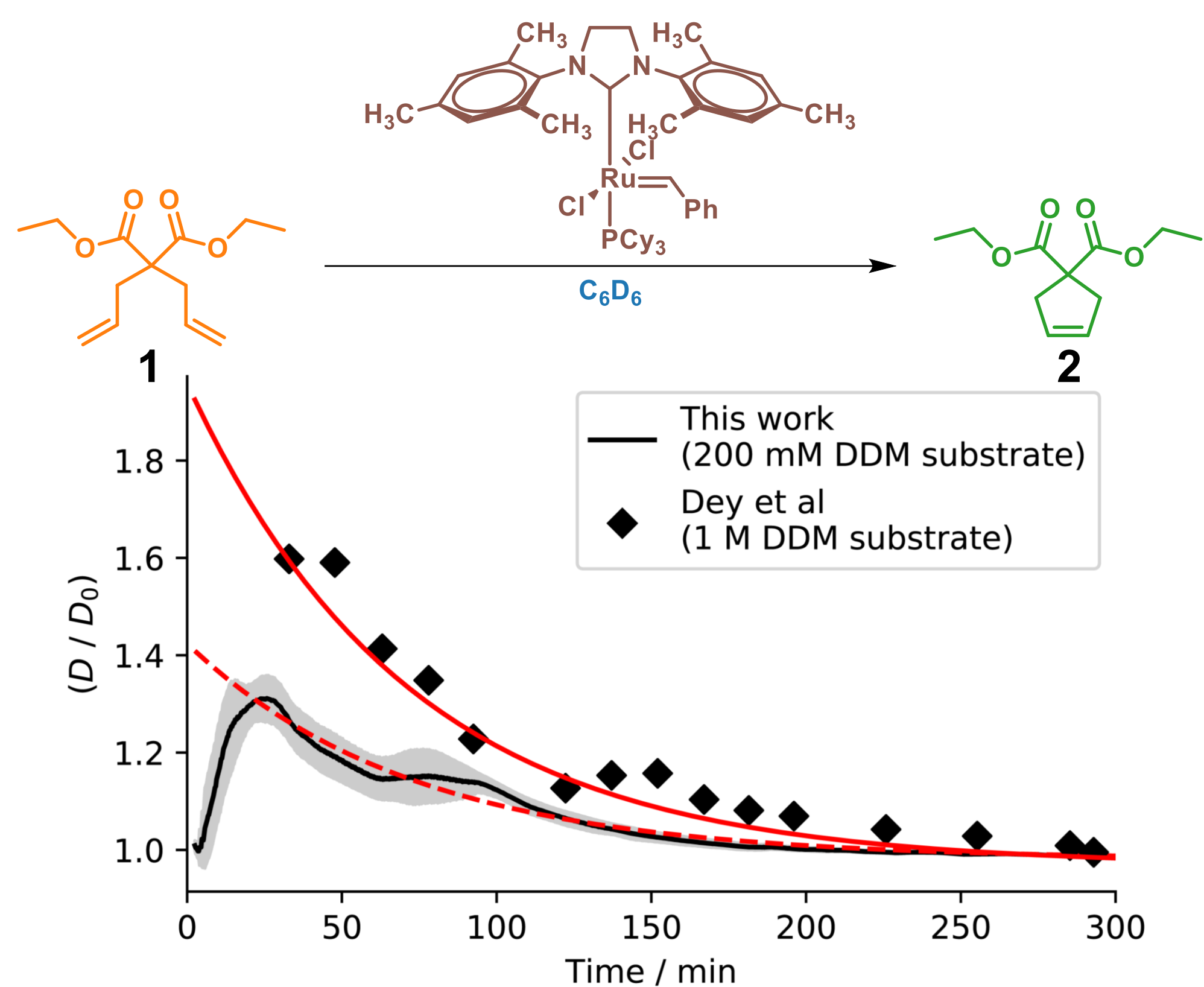
Driving translational motion at the nanoscale



Can molecules swim through solutions? Multiple recent publications report that enzymes such as urease are propelled by catalytic activity, leading to “enhanced diffusion” in the presence of substrate.^[1]

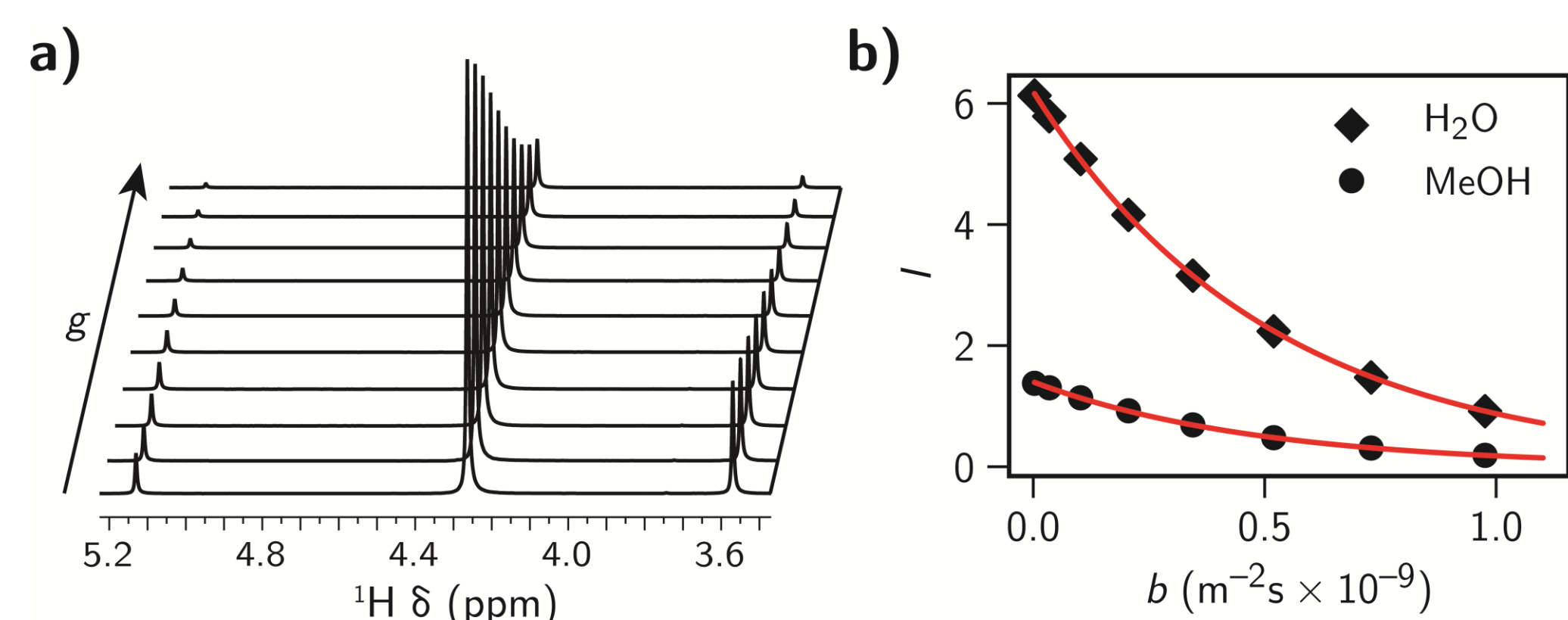
“Enhanced diffusion” of Grubbs’ catalyst

A single report of “enhanced diffusion” in a small molecular system found increased motion of Grubbs’ catalyst during ring-closing metathesis.^[2] The physical basis behind this behaviour remained unclear.



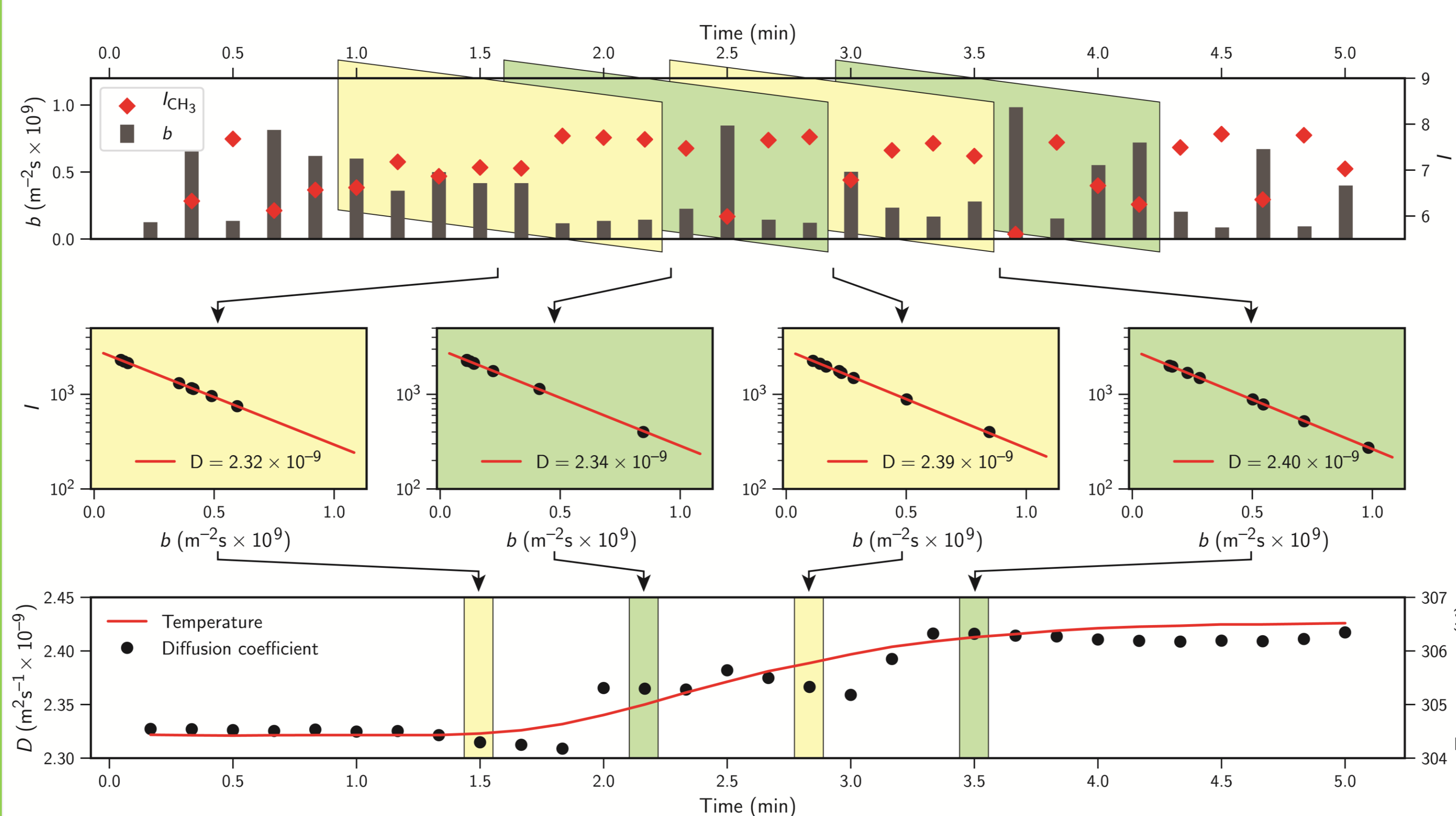
Enhanced diffusion of Grubbs’ catalyst during metathesis.^[2] Proposed models suggested a direct link between D and reaction rate (eg solid red line), but our time-resolved data^[4] (black line) tells a different story.

Time-resolved diffusion NMR



Diffusion coefficients can be measured by gradient NMR experiments, where signal intensities decrease as a function of gradient strength (above). Typical experiments performed on static samples can measure a diffusion coefficient within 5 – 20 minutes.

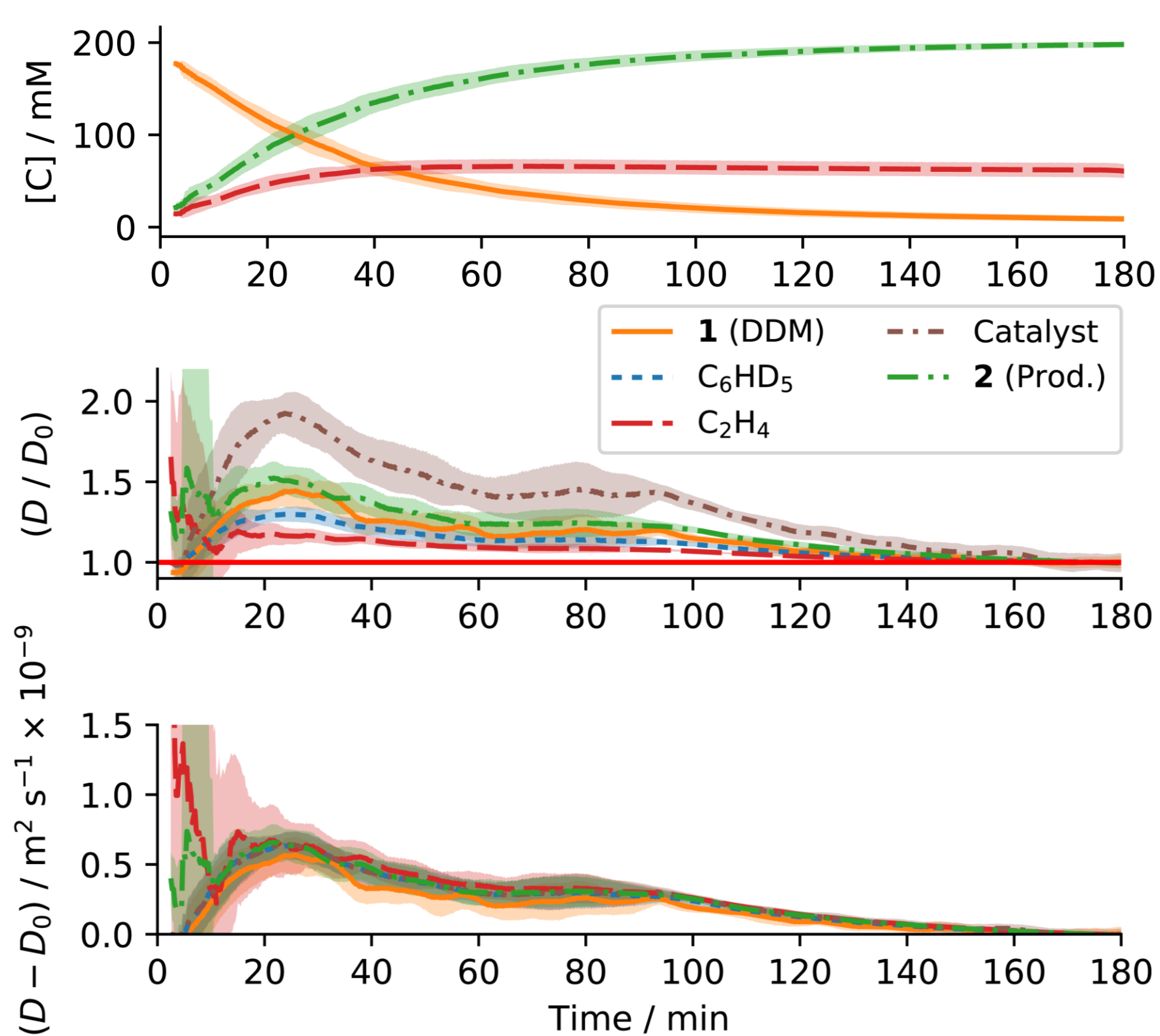
We have recently developed techniques to obtain time resolved data from diffusion NMR experiments.^[3]



Diffusion NMR data with a time resolution of minutes obtained by moving-frame processing of a continuous dataset.

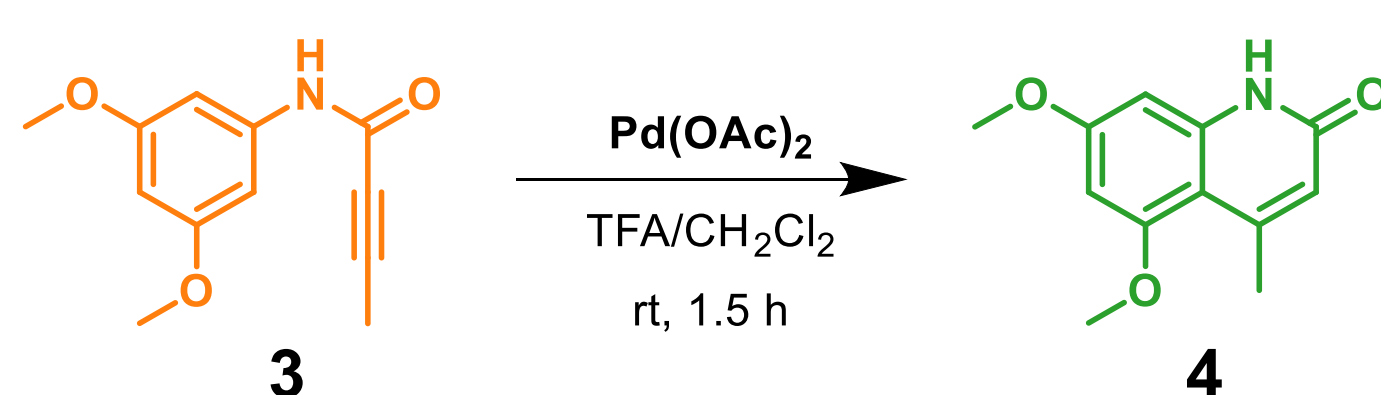
Grubbs metathesis

Diffusion NMR measurements during Grubbs metathesis found a large relative increase in D , as reported, but all species showed the same absolute increase. This implies bulk flow.

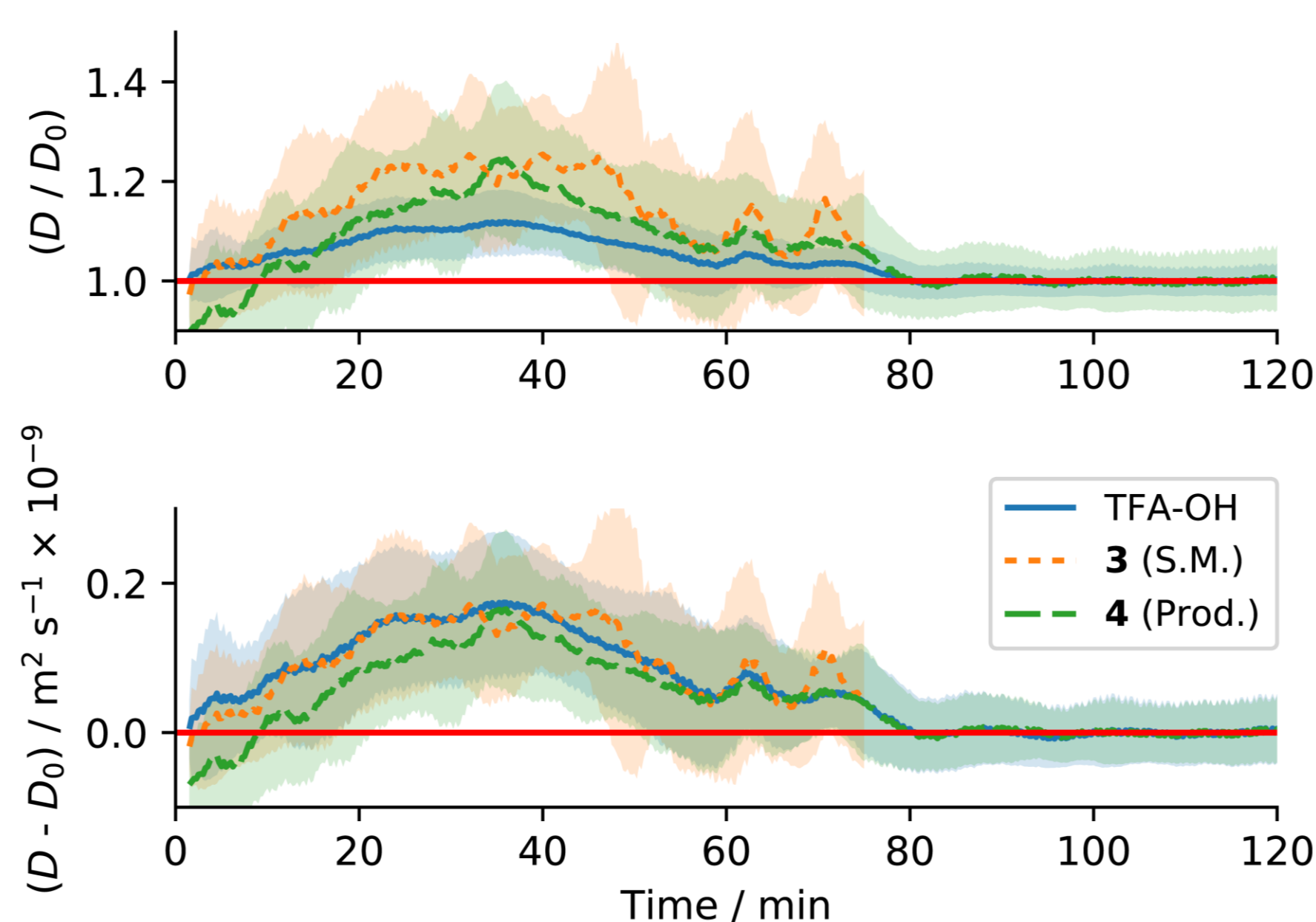


Time-resolved diffusion measurements of species involved in Grubbs metathesis. The active catalyst has a higher relative increase in measured diffusion (middle plot), but this appears coincidental as all species see the same absolute increase (bottom plot).

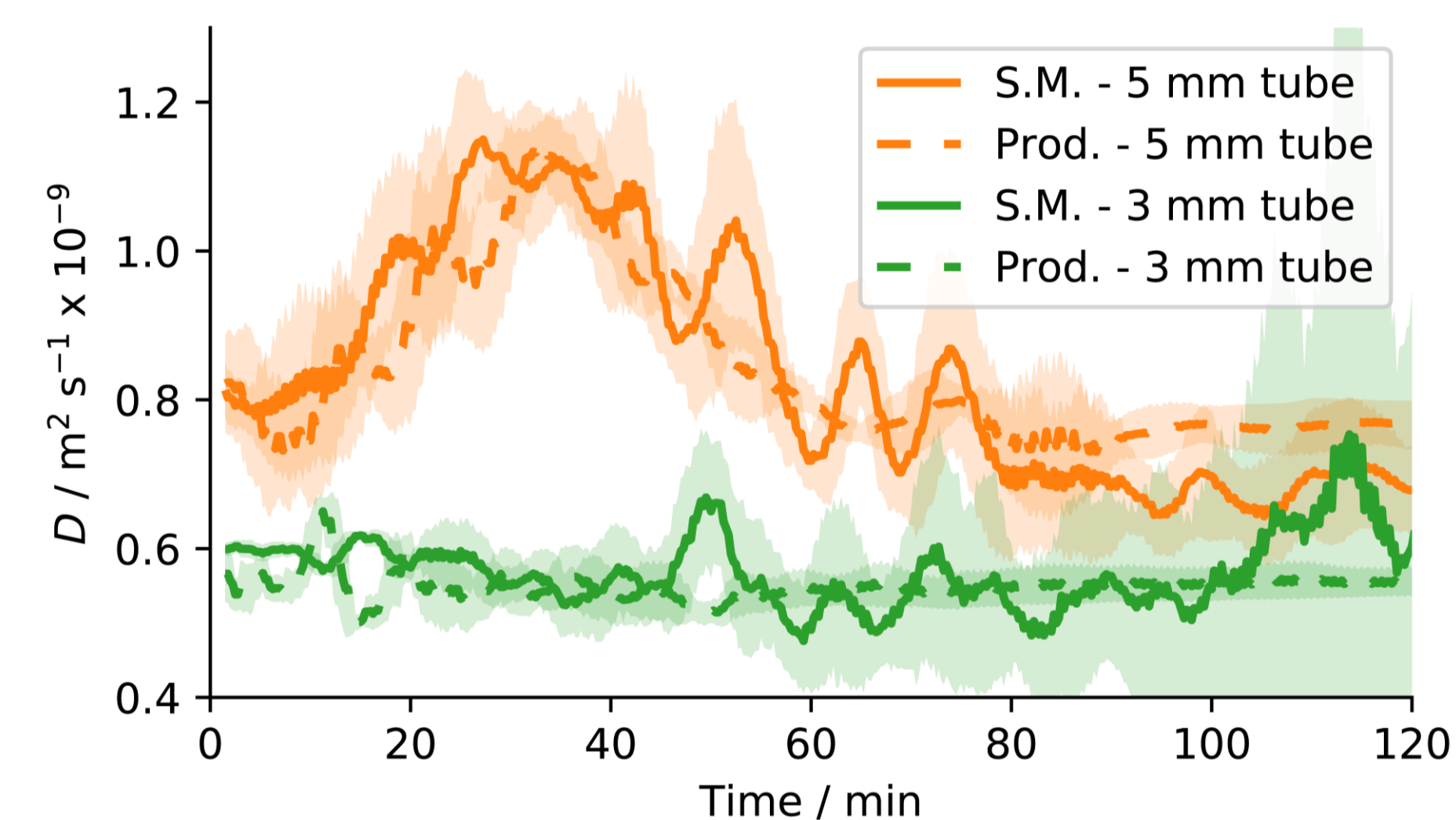
Palladium-catalysed cyclisation



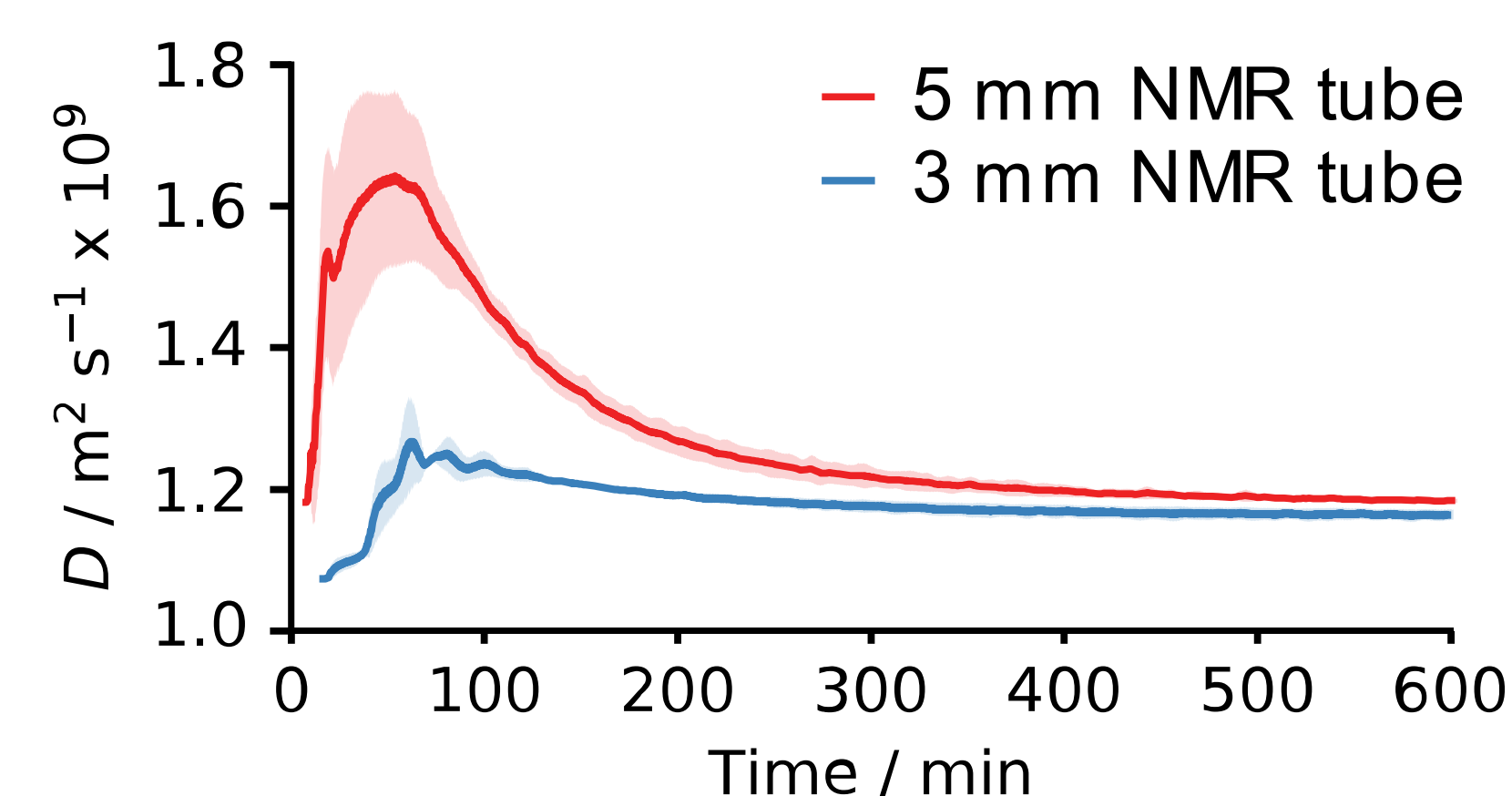
Was ‘enhanced diffusion’ a result of C_2H_4 gas generated during metathesis? A Pd-catalysed unimolecular reaction also showed a transient increase in measured D but again the change seemed absolute rather than relative.



...was this just convection?



As a bulk phenomenon, convection (but not diffusion) is influenced by sample geometry. Repeating the reactions in narrow 3 mm NMR tubes eliminated (Pd-catalysed reaction, above) or sharply reduced (Grubbs RCM, below) the increase in measured D . “Enhanced diffusion” under these conditions appears to be an artefact.



[1] X. Zhao, K. Gentile, F. Mohajerani, A. Sen, *Acc. Chem. Res.* **2018**, *51*, 2373 – 2381

[2] K.K. Dey, F.Y. Pong, J. Brefke, R. Pavlick, E. Hatzakis, C. Pacheco, A. Sen, *Angew. Chem. Int. Ed.* **2015**, *55*, 1113 – 1117

[3] T.S.C. MacDonald, W.S. Price, J.E. Beves, *ChemPhysChem* **2019**, *20*, 926 – 930

[4] T.S.C. MacDonald, W.S. Price, R.D. Astumian, J.E. Beves, *Angew. Chem. Int. Ed.* **2019**, *58*, 18864-18867