Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Direct observation of Ru-alkylidene forming into ethylene in ring-closing metathesis from hyperpolarized ^{1}H NMR

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1. Dynamic nuclear polarization

For hyperpolarization, a mixture of pure diethyl diallylmalonate (DEDAM) and 30 mM 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO; Sigma-Aldrich, St. Louis, MO) in isooctane was prepared at a volume ratio of 1:1. Isooctane is a solvent, which forms an amorphous glass when frozen. Aliquots of 20 μL of this mixture were hyperpolarized on ^{1}H in a HyperSense DNP polarizer (Oxford Instruments, Abingdon, U.K.) by irradiating 94.005 GHz microwaves with 100 mW power for 15 min at a temperature of 1.4 K. The hyperpolarized sample was rapidly dissolved with 4 mL of dry toluene, which was preheated to 145 °C, and then transferred into an NMR tube located in the NMR magnet by an injection system using pressurized argon gas.[1] The tubing used for injection was purged with argon gas before each experiment. For the metathesis reactions, 50 μL of 11.3 mM dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine)ruthenium(II) (3rd generation Grubbs catalyst, G3 catalyst; Sigma-Aldrich) in toluene was pre-loaded in the NMR tube under dry argon atmosphere in a glovebox. The final sample concentrations after the dissolution were estimated to be 35 mM DADEM and 1.5 mM catalyst before the reaction occurred based on the volume of injected sample (~ 380 μL) and the sample recovery (~ 32 %) after the dissolution.

2. NMR spectroscopy

The hyperpolarized ^{1}H NMR spectra were acquired on a Bruker 400 MHz NMR spectrometer equipped with a broadband probe containing three pulsed field gradients (Bruker Biospin, Billerica, MA) at a temperature of 298 K. NMR measurements were triggered after the injection of hyperpolarized DEDAM into the NMR tube for 560 ms and a stabilization time of 400 ms. The time-resolved ^{1}H NMR spectra shown in Figure 1 were measured using the pulse sequence (trigger – [shaped 90° – Gz]$_{\times 3}$ – [Gz – αx – acquire]$_{\times 64}$). The pulse sequence started with three EBURP2 shaped 90º pulses, each for 10 ms, to suppress the hyperpolarized isooctane signals, followed by a randomized pulsed field gradient, Gz (35.5 G/cm, 2 ms). A small flip angle pulse with flip angle α = 16.5° and pulse strength $\gamma B_1/(2\pi)$ = 22.1 kHz was applied for NMR detection. The pulsed field gradient was applied before this pulse to remove the residual coherence from the previous scan.

The pulse sequence designed for the selective saturation experiments was implemented with the saturation pulse scheme during acquisition using the programmatic syntax for homonuclear decoupling (HD), as described in Figure S1a. The saturation pulses were applied with a field strength of $\gamma B_1/(2\pi)$= 26.5 Hz and at 10 % duty cycle. The cycle time for the series of saturation pulses was approximately 22 μs (Figure S1b). The transmitter frequency was set to the resonance frequency targeted for the selective saturation. This frequency was chosen as the frequency of the observed intermediate in on-resonance experiments, and at an equal frequency difference to product peaks (= 5,631 Hz), but at the opposite end of the spectrum in off-resonance experiments. The solvent signals were saturated using the aforementioned EBUPR2 pulses before the first scan. A total of 64 spectra were acquired by applying a series of small flip angle (α = 15°) pulses. Each scan was composed of 12,818 data points, collected for 400 ms. All NMR spectra were calibrated to the chemical shift of methyl protons of toluene at 2.11 ppm.

A non-hyperpolarized NMR spectrum of styrene in toluene (Figures 2b) was acquired by saturating the toluene resonance with continuous radio-frequency irradiation, followed by a 90° pulse for signal detection.

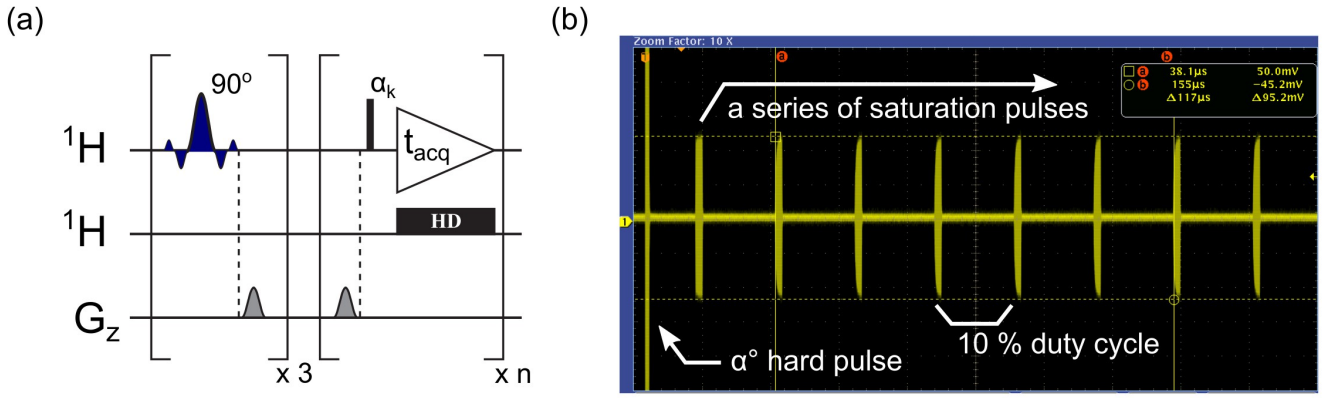

Figure S1. (a) Selective saturation pulse sequence used for acquiring time-resolved pseudo 2D ^{1}H NMR spectra implemented with HD syntax. (b) Oscilloscope measurement of the attenuated radio-frequency pulse voltage from the HD scheme.

3. Characterization of selective saturation pulses

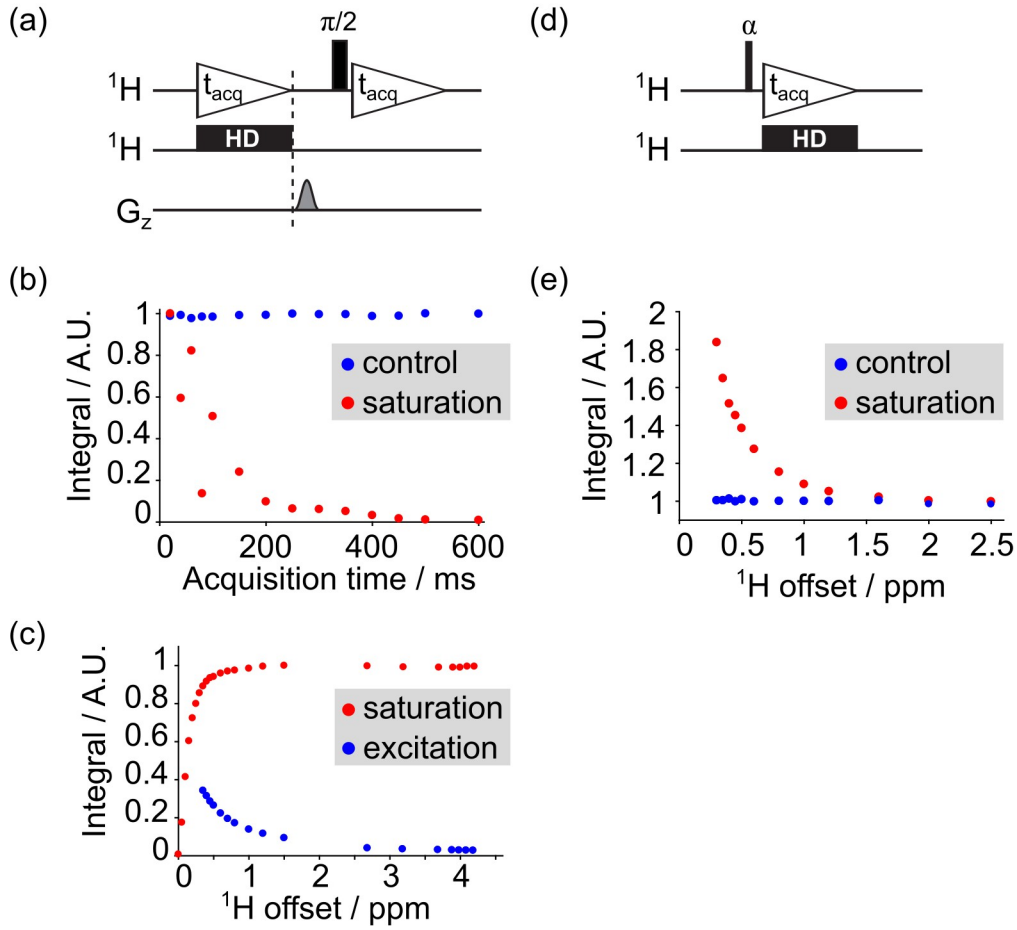

Figure S2. (a) Pulse sequence used for measuring time-dependent saturation and saturation width. (b) Resulting profile of time-dependent saturation as a function of acquisition time. (c) Saturation and excitation profiles of selective saturation obtained using 400 ms saturation time. (d) Pulse sequence used for measuring the combined pulse effect caused by a small flip angle (α°) hard pulse and saturation pulses. (e) Resulting profile for the combined pulse effect with 400 ms saturation time. The sample was toluene in all measurements.

The capability of the selective saturation scheme to saturate the target spin during acquisition was investigated. First, the time-dependent saturation effect was assessed by varying the acquisition time, using the pulse sequence in Figure S2a. Various acquisition times between 20 – 600 ms were tested on

the methyl protons of toluene as target spins. For control experiments, the experiments were repeated with zero power for the saturation pulses. The resulting signal intensities from the on-resonance and control experiments are indicated by red and blue circles, respectively, in Figure S2b. It can be seen that less than 10 % of the signal remained when the acquisition time was 200 ms, and that less than 3 % of the signal intensity remained when the acquisition time was 400 ms.

Next, the saturation width was examined by applying the saturation pulses to the methyl protons with several different offsets, having 400 ms of acquisition time. The same pulse sequence was used, which allows acquiring two free induction decays (FID) from a single measurement; one from the saturation block and the other obtained immediately after a 90° pulse. It is apparent from the first FIDs that the nuclear spins can be excited by the saturation pulses. The signal intensities were normalized to the signal intensity obtained from a single 90° pulse excitation. When the offset was greater than 1.5 ppm with respect to the frequency of the target signal, less than 10 % of the signal remained (blue circles in Figure S2c). A narrow saturation width was observed from the second FIDs (red circles in Figure S2c). More than 98 % of the signal was obtained with an offset of 1 ppm. The full width at half maximum of the saturation profile was approximately 0.25 ppm (= 100 Hz). The combined effect from a 15° pulse followed by the selective saturation pulses was examined using the pulse sequence shown in Figure S2d. This sequence is the same as the one used for selective saturation experiments with hyperpolarized spins (Figure S1a), without a loop for acquiring a series of scans. The measurements were carried out at several different offsets with and without the saturation pulse power. As shown in Figure S2e, the signal intensities were higher than those measured from the control experiments, when the offset was less than 2 ppm. This observation indicates that the spins were further excited by the saturation pulses, presumably because the hard excitation pulse was not a full 90° pulse. This effect subsided as the offset increased, and became negligible when the offset was larger than 2 ppm.

4. Initial buildup of signals from reaction products

The initial buildup of signals of Ru-alkylidene as well as the reaction products including styrene, cyclopentene*, and ethylene is shown in Figure S3a. These signals are from the hyperpolarized ^{1}H NMR experiment shown in Figure 1b. The signals were processed by applying a linear baseline correction, except for styrene, where a polynomial baseline correction was applied. It can be seen from the signal integrals that cyclopentene and ethylene signals build up more slowly than styrene or Ru-alkylidene (Figure S3b). Considering that the doublet signal from styrene corresponds to a single proton *cis* to the phenyl ring, the signal for Ru-alkylidene, likely comprising two protons, also shows a slower buildup than that for styrene.

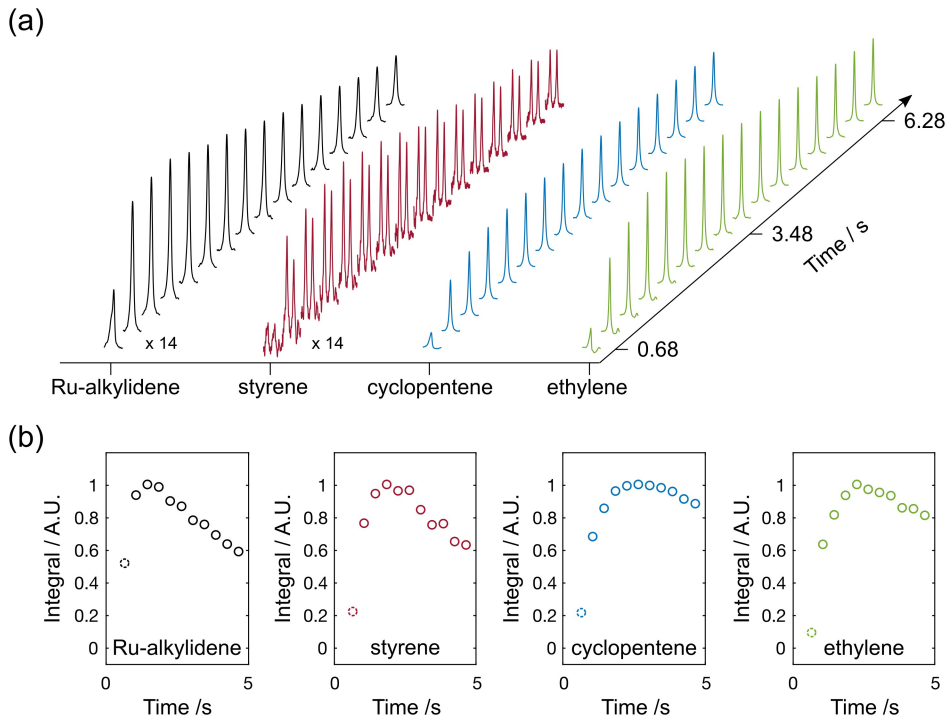

Figure S3 (a) Time-resolved ^{1}H NMR signals of reaction products from the RCM reaction. The data was acquired with an interscan delay of 400 ms. (b) Signal integrals of reaction products from the spectra shown in Figure S3a. The maximum signal integral in each plot was scaled to unit intensity. The first data points are shown with dotted circle, indicating less accuracy due to a broader line width and low signal intensity.

* diethyl 3-cyclopentene-1,1-dicarboxylate

5. Dependence of Ru-alkylidene chemical shifts on 3-bromopyridine concentration

In order to characterize possible chemical exchange behavior of 3-bromopyridine ligands, the dependence of Ru-alkylidene chemical shift on 3-bromopyridine was measured. The sample solutions were prepared as described in Section 1, except that 3-bromopyridine (**py**) was added to the catalyst solutions at a ratio of 1:1.5, 3, 5, and 10 to the concentration of G3 catalyst. The procedure for acquiring the ^{1}H hyperpolarized NMR spectra was the same as described in Section 2. Figure S3 displays the ^{1}H NMR signals of Ru-alkylidene obtained from the RCM reactions, which took place in the absence and the presence of additional **py**. At higher **py** loading, the chemical shift of this species moved to farther downfield.

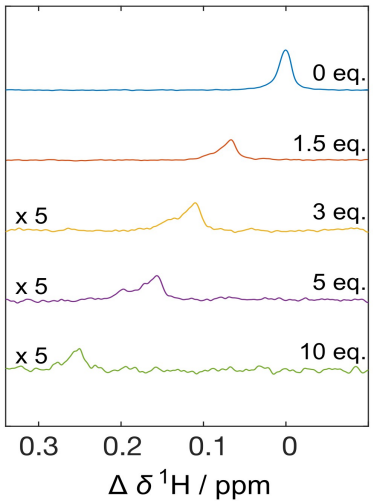

Figure S4. The hyperpolarized ^{1}H NMR spectra showing the chemical shift changes of observable Ru-alkylidene complex, obtained from the third scans of a series of spectra from the RCM reaction with varying **py** concentrations. The equivalents of the added **py** in each spectrum are indicated in the figure. The chemical shifts are referenced to the CH_3 proton of toluene, and shown as the change from the value in the reaction without any added **py**.

References

1 S. Bowen and C. Hilty, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5766-5770.