Supporting Information For:

Solvent Effects on Grubbs' Pre-catalyst Initiation Rates

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Experimental

General

Pre-catalysts **1** and **2** and 1,3,5-trimethoxybenzene were purchased from Sigma-Aldrich and used as supplied. Ethyl vinyl ether was purchased from Alfa Aesar and distilled immediately before use. Benzene was purchased as anhydrous from Alfa Aesar. Chloroform was purchased from Sigma-Aldrich and dried by percolation through a column of activated alumina immediately before use. Dichloromethane and toluene were obtained from the in-house solvent purification system (Innovative Technologies PureSolv). 1,2-Difluorobenzene and hexafluorobenzene were purchased from Fluorochem and distilled from calcium hydride onto activated 4Å molecular sieves, under argon, then degassed with a stream of argon. Dimethyl carbonate, methyl *tert*-butyl ether and trifluorotoluene were purchased as anhydrous from Sigma-Aldrich. Benzene-d_6, chloroform-d and toluene-d_8 were purchased from Sigma-Aldrich and dried overnight on activated 4Å molecular sieves before use. Dichloromethane-d_2 was purchased from Goss Scientific and dried overnight on activated 4Å molecular sieves before use. All deuterated solvents were degassed by sparging with dry oxygen-free nitrogen or argon.

NMR spectra were recorded in-magnet at 298 K on a Bruker AV400 spectrometer (with BBFO-*z*-ATMA probe) or a Bruker AVII600 spectrometer (with TBI-*z* probe or BBO-*z*-ATMA probe). Both spectrometers have temperature control units.

UV/visible spectra were recorded using a Varian Cary 50 UV/visible spectrophotometer fitted with a peltier heated/cooled cell holder. All experiments were conducted at 298 K.

Measurement of Initiation Rates for Pre-catalyst

As per the method of Sanford *et al.* (*J. Am. Chem. Soc.*, 2001, **123**, 6543), a 0.5 mol L^{-1} solution of freshly distilled ethyl vinyl ether in the solvent under examination (plus 10% v/v chloroform-*d*, if deuterated solvent was unavailable) was added to the solid pre-catalyst which had been weighed into the NMR tube. If the solvent was deuterated, a known mass of 1,3,5-trimethoxybenzene was also present in the stock solution. The start time was noted, and ^{1}H NMR spectra were acquired periodically over the course of time; the receiver gain did not change between spectra.

In the case of deuterated solvents, the integrals of the internal standard and pre-catalyst were used to construct a concentration/time profile, which exhibited good first-order behaviour. A rate constant was obtained by plotting ln([**1**]) *versus* time.

In the case of non-deuterated solvents, the NMR spectrum window was amended to examine the ruthenium carbene region alone. The integral of the pre-catalyst signal *versus* time was used to construct a conversion/time profile; plotting the ln(integral) *versus* time yielded the first order rate constant.

Both the concentration (or integral) *versus* time and first order plots are presented below.

Measurement of Initiation Rates for Pre-catalyst 2

The method employed was the same as that published previously (Ashworth *et al.*, *Chem. Commun.*, 2011, **47**, 5428). Solutions of 0.1 mM **2** were prepared in cuvettes, from stock solutions prepared in volumetric glassware and manipulated using dry glass syringes. An appropriate quantity of a concentrated stock solution of ethyl vinyl ether was added to the solution of **2**, before the cuvette was shaken and the UV/vis spectra recorded periodically. A Guggenheim approach was used, in which $\ln[A(t) - A(t + \Delta t)]$ (absorbance at time t minus absorbance at time $t + \Delta t$, where $\Delta t = t_{1/2}$) was plotted *versus* time to yield a plot of slope $-kt$. First order rate constants were then plotted *versus* ethyl vinyl ether concentration to give second order rate constants.

First and second order rate constants are presented below.

Initiation Rates for G2

Concentration /time data are represented by circles; a first-order treatment is represented by triangles.
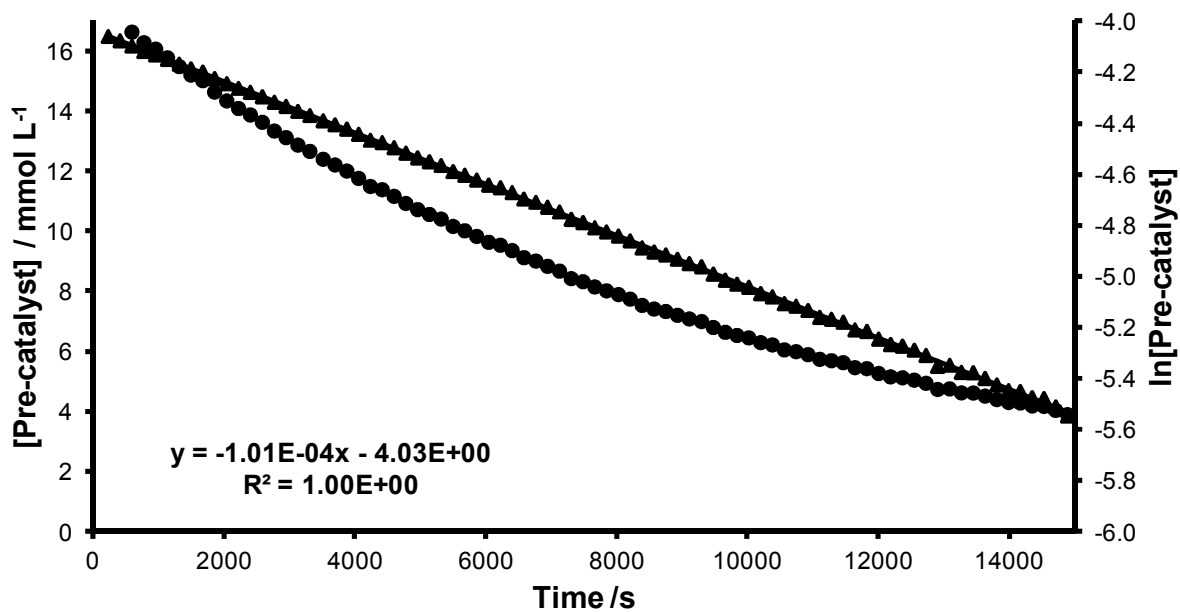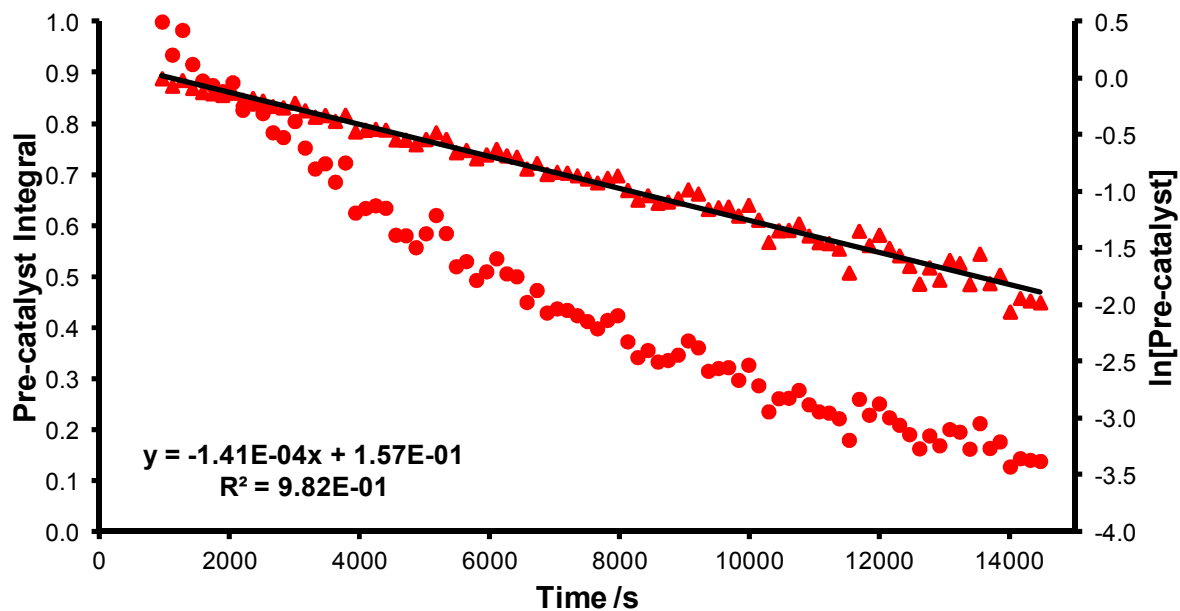

Figure S1. Benzene-d_6

Figure S2. 1,2-Difluorobenzene/Chloroform-d (90/10 *v/v*)
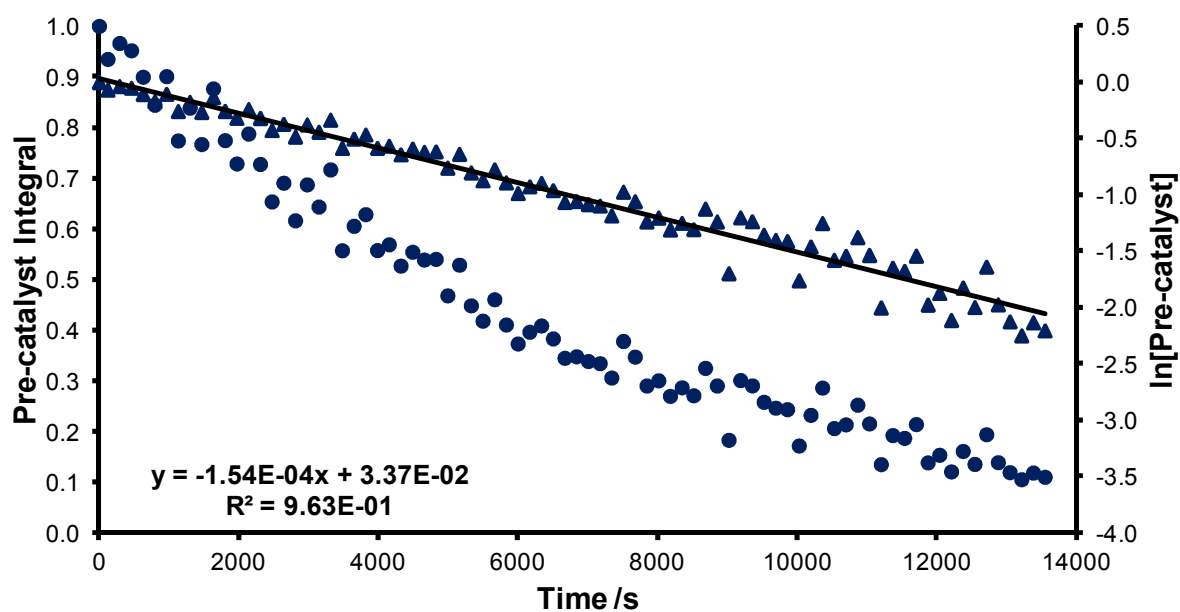
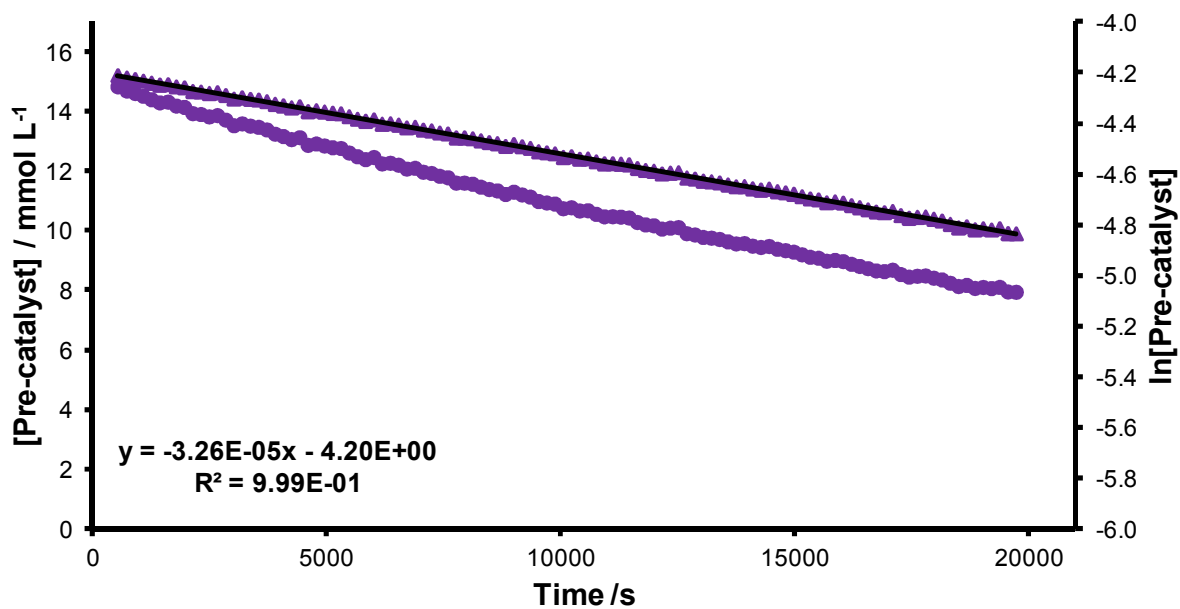**Figure S3.** Dimethyl carbonate/Chloroform-*d* (90/10 *v/v*)

Figure S4. Hexafluorobenzene/Chloroform-*d* (90/10 *v/v*)
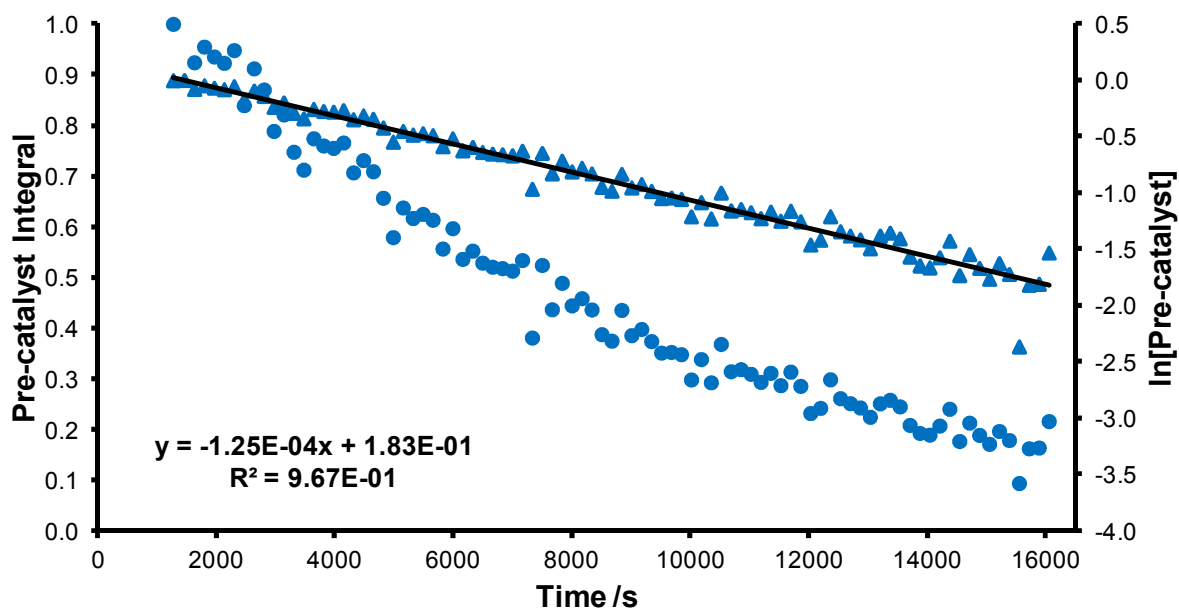
Figure S5. Methyl *tert*-butyl ether/Chloroform-*d* (90/10 *v/v*)

Equation on figure:

$$y = -1.25\text{E-}04x + 1.83\text{E-}01$$
$$R^2 = 9.67\text{E-}01$$

Figure S6. Toluene-*d*$_8$

Equation on figure:

$$y = -9.24\text{E-}05x - 4.10\text{E+}00$$
$$R^2 = 1.00\text{E+}00$$
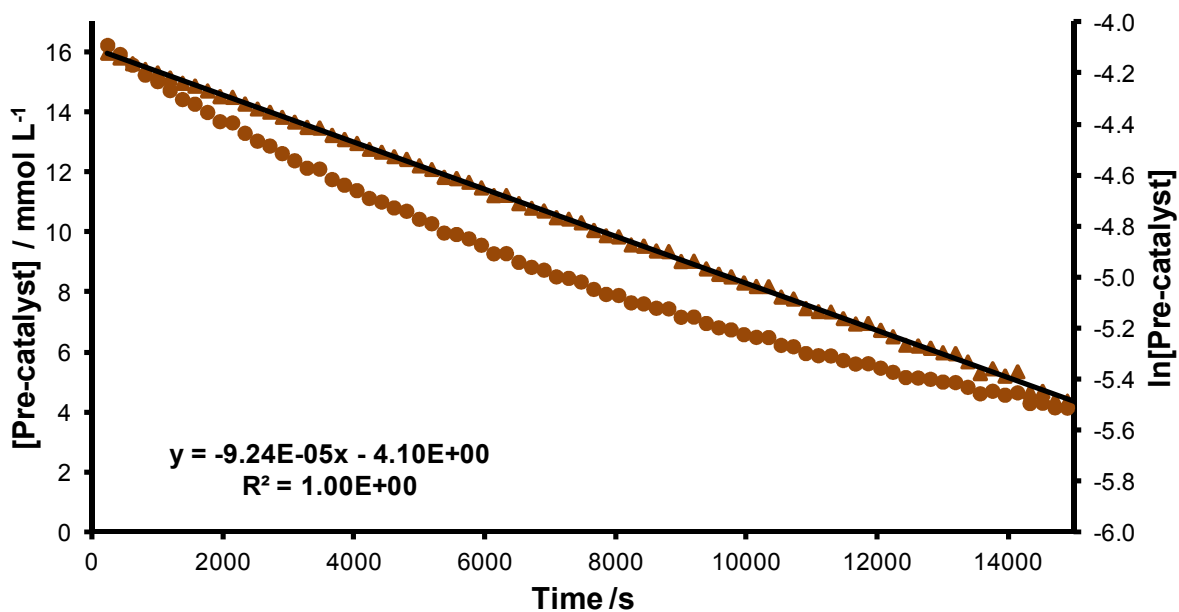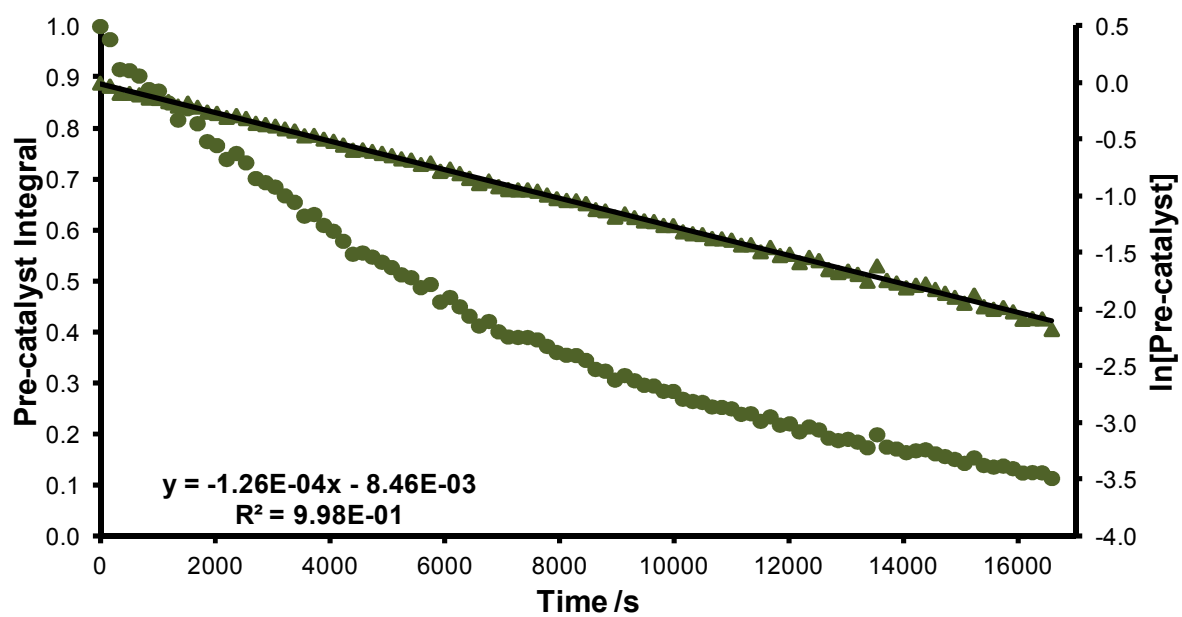
Figure S7. Trifluorotoluene/Chloroform-*d* (90/10 *v/v*)

Initiation Rates for GH2

Table S1.

Non-Aromatic							
Chloroform		Dichloromethane		Dimethyl Carbonate		Methyl *tert*-Butyl Ether	
[EVE] / mol L^{-1}	k_{obs} /s^{-1}	[EVE] / mol L^{-1}	k_{obs} /s^{-1}	[EVE] / mol L^{-1}	k_{obs} /s^{-1}	[EVE] / mol L^{-1}	k_{obs} /s^{-1}
0.02493	0.000584	0.02493	0.000637	0.02610	0.001069	0.02668	0.001842
0.02511	0.000581	0.02500	0.000646	0.02707	0.001152	0.02540	0.001737
0.02483	0.000591	0.02483	0.000657	0.02541	0.001057	0.02729	0.001842
0.04956	0.001174	0.04956	0.001323	0.04930	0.002048	0.04798	0.003223
0.04990	0.001142	0.04999	0.001331	0.05112	0.002200	0.05039	0.003403
0.04935	0.001178	0.04968	0.001300	0.04800	0.002041	0.05154	0.003333
0.09988	0.002327	0.09988	0.002667	0.10065	0.004186	0.10288	0.006488
0.10058	0.002287	0.10076	0.002694	0.10437	0.004469	0.09795	0.006346
0.09946	0.002358	0.10013	0.002652	0.09799	0.004120	0.10522	0.006549
0.19810	0.004609	0.09946	0.002645	0.19706	0.008072	0.20143	0.011131
0.19949	0.004440	0.19810	0.005215	0.20434	0.008529	0.19178	0.011589
0.19727	0.004617	0.19983	0.005255	0.19185	0.007516	0.20601	0.011751
0.29469	0.007008	0.19859	0.005206	0.29314	0.011097	0.29965	0.015141
0.29676	0.006812	0.19727	0.005255	0.30398	0.011918	0.28530	0.016028
0.29346	0.007082	0.29542	0.007651	0.28540	0.010269	0.30646	0.016481
		0.29346	0.007696				

Table S2.

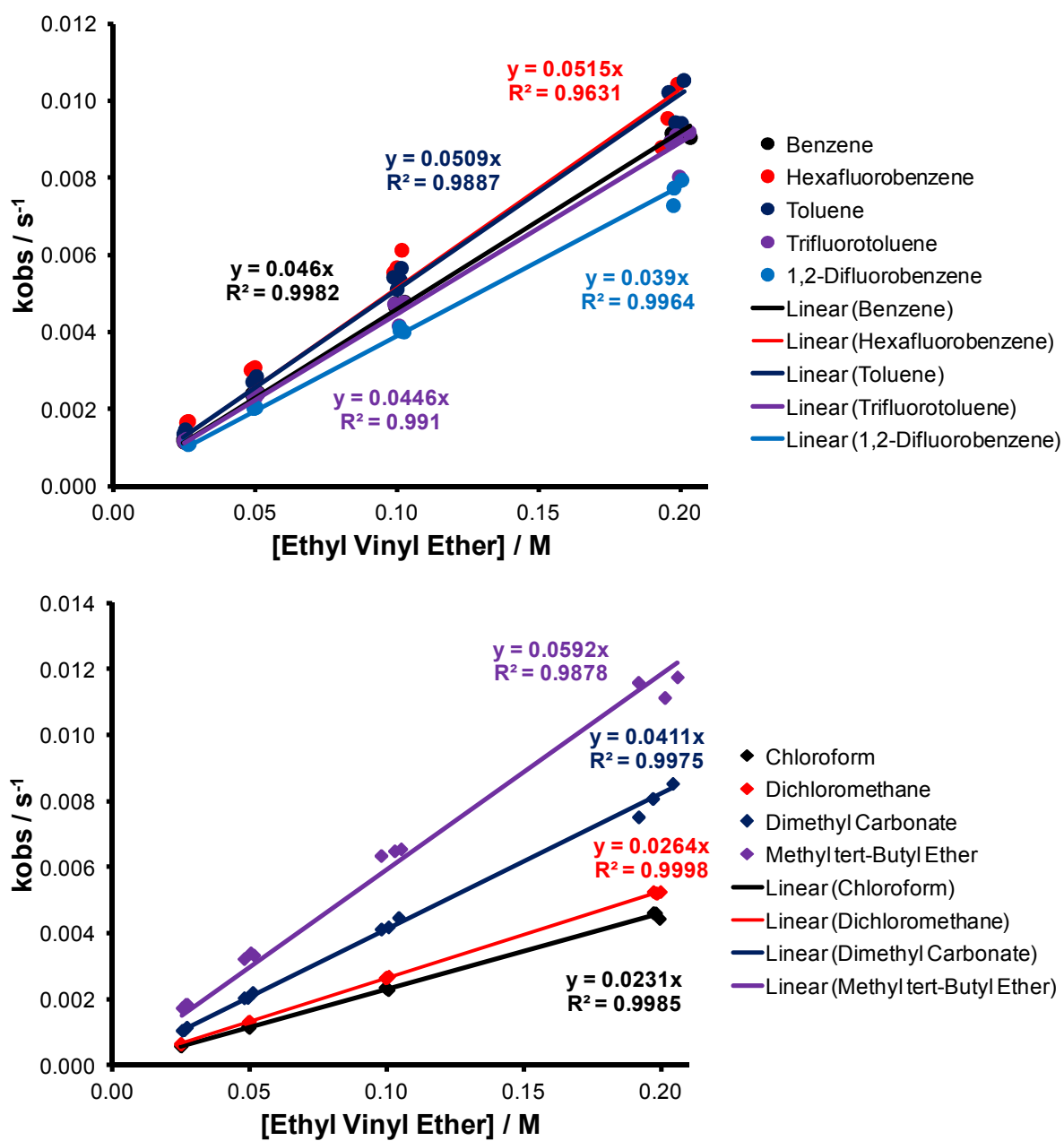| Aromatic									
Benzene		1,2-Difluorobenzene		Hexafluorobenzene		Toluene		Trifluorotoluene	
[EVE] / mol L^{-1}	k_{obs} /s^{-1}	[EVE] / mol L^{-1}	k_{obs} /s^{-1}	[EVE] / mol L^{-1}	k_{obs} /s^{-1}	[EVE] / mol L^{-1}	k_{obs} /s^{-1}	[EVE] / mol L^{-1}	k_{obs} /s^{-1}
0.02480	0.001145	0.026160	0.001083	0.02590	0.001675	0.02522	0.001467	0.02513	0.001151
0.02454	0.001203	0.026560	0.001096	0.02561	0.001649	0.02496	0.001367	0.02499	0.001147
0.02562	0.001135	0.026190	0.001098	0.02636	0.001684	0.02466	0.001358	0.02556	0.001221
0.04930	0.002315	0.049420	0.002020	0.04892	0.003045	0.02533	0.001432	0.02473	0.001181
0.04878	0.002394	0.050160	0.002043	0.04838	0.003014	0.05013	0.002797	0.04994	0.002307
0.05091	0.002422	0.049470	0.002028	0.04978	0.003082	0.04961	0.002668	0.04966	0.002306
0.09936	0.004670	0.100900	0.004124	0.09987	0.005671	0.04900	0.002708	0.05081	0.002405
0.09932	0.004743	0.102420	0.004004	0.09877	0.005546	0.05034	0.002846	0.04916	0.002376
0.10261	0.004779	0.101000	0.004033	0.10164	0.006126	0.10104	0.005352	0.10065	0.004163
0.19706	0.009011	0.197540	0.007284	0.19553	0.009545	0.09999	0.005111	0.10009	0.004631
0.19699	0.009158	0.200530	0.007945	0.19338	0.008792	0.09876	0.005421	0.10240	0.004767
0.20351	0.009049	0.197750	0.007737	0.19900	0.010434	0.10146	0.005657	0.09908	0.004728
0.29315	0.012682					0.20039	0.009418	0.19963	0.008026
0.29005	0.012513					0.19831	0.009437	0.19852	0.009099
0.30274	0.012751					0.19588	0.010221	0.20309	0.009189
						0.20122	0.010533	0.19651	0.008930
						0.29139	0.014641	0.30212	0.013080
						0.29934	0.014657	0.29232	0.012779

Figure S8.

Solvents PCA Data

While a number of solvents were tested here, several classes of solvents are not well tolerated by metathesis pre-catalysts (e.g. alcohols) and so were not assessed. Ballistreri *et al.* have published solvent data and used principal components analysis (PCA) to yield a plot in which solvents which are located in the same area of space have similar properties. Highlighting the solvents tested here on such a plot (see **Figure S11** in the supporting information) reveals that only a relatively small experimental space is accessible.[16] Some areas of experimental space are difficult to access due to incompatible functional groups, such as alcohols.[17-19]

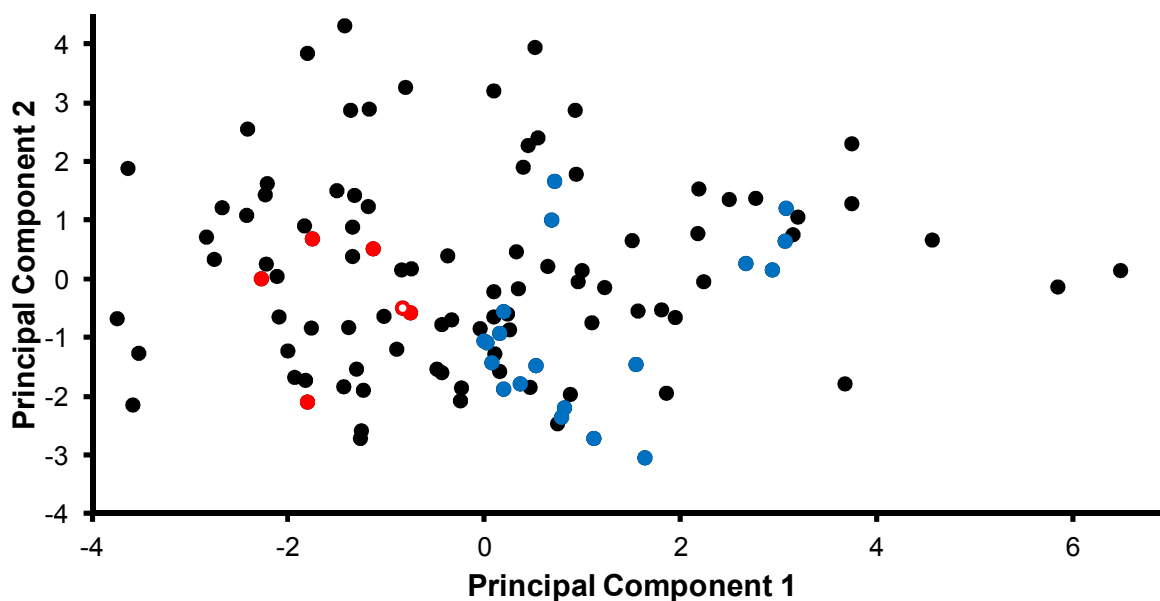Data taken from reference 22 in the manuscript (*ARKIVOC* **2002**, *xi*, 54).

Figure S9. Solvent PCA scores plot, in which solvents close together share similar properties, with the solvents used in this study highlighted in red and alcoholic solvents highlighted in blue; diethyl carbonate (open point) is used in place of dimethyl carbonate, while data for trifluorotoluene, hexafluorobenzene and 1,2-difluorobenzene are not available.