

## Electronic Supplementary Information

### **Additives boosting the performance of a tungsten imido-mediated ethylene dimerization systems for industrial application**

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## Experimental Procedures

All manipulations were carried under an atmosphere of dry nitrogen using standard Schlenk line techniques or in a nitrogen-filled glovebox (Saffron Scientific). All glassware was oven dried prior to use. Dry solvents were obtained from an Innovative Technologies SPS solvent purification system (passage over alumina) with the exception of chlorobenzene and 1,2-dimethoxyethane (dme), which were distilled under nitrogen from CaH<sub>2</sub> and sodium/benzophenone, respectively. All solvents were de-oxygenated prior to use by freeze-pump-thaw cycles, unless stated otherwise. Solvents for NMR spectroscopy (C<sub>6</sub>D<sub>6</sub>, d<sub>8</sub>-toluene, d<sub>5</sub>-chlorobenzene, CD<sub>2</sub>Cl<sub>2</sub>, CDCl<sub>3</sub>) were dried over CaH<sub>2</sub> prior to distillation and de-oxygenation, before being stored under nitrogen; these solvents were sourced from Apollo Scientific and Goss Scientific. Me<sub>3</sub>Al, EtAlCl<sub>2</sub>, Et<sub>4</sub>NCl, Oct<sub>4</sub>NBr, and Oct<sub>4</sub>NCl were purchased from Sigma-Aldrich and used as received. Triethylamine was purchased from Sigma-Aldrich, dried over KOH, distilled and degassed prior to use.

All NMR spectroscopy was carried out using 5 mm NMR tubes fitted with J. Young's taps. Solution-phase NMR spectra were collected on a Varian Mercury 400, Varian Inova 500, Varian VNMRS-700, Bruker Advance 400 or a Varian VNMRS-600 spectrometer at room temperature unless otherwise stated. All chemical shifts were referenced relative to residual solvent resonances (<sup>1</sup>H, <sup>13</sup>C).<sup>1</sup> Chemical shifts are reported in ppm and coupling constants in Hz.

All tungsten *bis*(imido) pro-catalysts were synthesized as reported previously by our group.<sup>2</sup>

Liquid phase sample GC-FID analyses were performed on an Agilent Technologies 6890N GC system equipped with a PONA column (50 m × 0.20 mm × 0.50 μm). Gas phase sample GC-FID analyses were performed using an Agilent Technologies 6890N GC system equipped a 250 μL sample loop and a GasPro column (30 m × 0.32 mm × 0.50 μm). Assignment of all products was made by comparison with authentic standards. Hydrogenative GC-FID analysis was performed using an Agilent Technologies 6890N GC System equipped an inlet liner packed with hydrogenating catalyst (Pt on Chromosorb W<sup>3</sup>) at 200 °C and PONA column (50 m × 0.20 mm × 0.50 μm).

## Catalysis Testing

Catalysis testing was performed in either:

- 1) a stainless steel 250 mL specified working volume (280 mL total volume) Buchi autoclave with Viton-ETP seals, equipped with a customised gas-entraining mechanical stirrer, internal cooling coil (tap water), fluidised jacket (connected to a Haake A28 refrigerated thermostatic bath with Haake SC 150 controller) and temperature and pressure monitoring. Dry, deoxygenated solvent was added *via* syringe from a bulb connected to a Schlenk line. Ethylene was added to the

reaction under pressure control using a regulator and supplied on demand to maintain reaction pressure *via* a Siemens MASSFLO MASS 2100 Coriolis mass flow meter, with a lower flow detection threshold of  $0.2 \text{ g min}^{-1}$ .

- 2) a stainless steel 1.2 L volume Premex autoclave with Kalrez and Viton-ETP seals, equipped with a customized gas-entraining mechanical stirrer, internal cooling coil (tap water) and fluidized jacket (connected to a Huber 405 W thermostatic bath). Ethylene was passed through moisture and oxygen-scrubbing columns. Dry, deoxygenated solvent was added *via* syringe from a bulb connected to a Schlenk line. Ethylene was added to the reaction under pressure control using a regulator and supplied on demand to maintain reaction pressure *via* a Siemens MASSFLO MASS 6000 Coriolis mass flow meter, with a lower flow detection threshold of  $0.2 \text{ g min}^{-1}$ .

### Catalysis Testing Protocol

Catalytic tests were performed in the following manner: the rigorously cleaned autoclave was heated ( $100 \text{ }^\circ\text{C}$ ) under vacuum for 30 mins, then cooled to reaction temperature and back-filled with ethylene (10 barg), which was then vented to 0 barg *via* a septa to purge the inlet valve. Solvent, an aliquot of pro-catalyst stock solution, and an aliquot of additive stock solution (where applicable) were then added *via* syringe. The autoclave was pressurised with ethylene to 10 barg and vented to 0 barg. In order to start the reaction an aliquot of  $\text{EtAlCl}_2$  activator solution was added, the autoclave rapidly pressurised and the pressure kept constant throughout the reaction by the continuous addition of ethylene, which was monitored *via* the flow meter. Heating and cooling were controlled to maintain a stable reaction temperature. Once ethylene uptake had fallen below the  $0.2 \text{ g min}^{-1}$  low flow detection threshold, or the autoclave was filled by product, the gas supply was closed, and the reactor cooled to  $-5 \text{ }^\circ\text{C}$ . The reactor was then carefully vented, with a portion of the vent gas being directly fed to a GC-FID instrument equipped with gas-sampling loop. The reactor contents were treated with  $1000 \mu\text{L}$  of nonane (GC internal standard) and stirred vigorously for 5 minutes. A sample of the organic phase was taken for liquid phase sample GC-FID analysis. Any solid formed was collected, washed with acetone, dried overnight and weighed. The analysis from the liquid phase and gas phase GC-FID analyses were then reconciled along with the mass of solid included, to create an overall analysis of the product slate. In order to fully assess the catalyst lifetimes (*i.e.* maximum productivities possible) all catalysis reactions were allowed to continue until either the reactor filled with product (known from the mass of ethylene added and the sudden drop in instantaneous ethylene uptake rate) or the instantaneous ethylene uptake fell below the lower detection threshold of  $0.2 \text{ g min}^{-1}$ . The activities quoted are the average for the entire reaction duration and are based upon the amount of product made, as measured by FID-GC analysis.

## Catalytic Test Reproducibility

The reproducibility of the catalyst test protocols described herein (and their associated data) have been rigorously assessed and reported by us previously.<sup>2</sup> This assessment involved conducting three catalytic reactions {20  $\mu\text{mol}$   $[\text{WCl}_2(\text{NDipp})_2(\text{dme})]$  (**1**) pro-catalyst; 300  $\mu\text{mol}$   $\text{EtAlCl}_2$  (15 eq to W); 74 mL PhCl (solvent); 70 °C; 45 barg  $\text{C}_2\text{H}_4$  pressure (46 bara); stirrer speed 1000 rpm; nonane standard (1.000 mL)} in order to assess the inherent experimental variability present during catalysis.<sup>2</sup> For TON and activity values the standard deviations expressed as a percentage of the mean values are typically < 8% and <6% of the values, respectively. For the  $\text{C}_4$  selectivities (wt%  $\text{C}_4$ , 1- $\text{C}_4$  in  $\text{C}_4$  and overall wt% 1- $\text{C}_4$ ) and wt% of  $\text{C}_6$ , the standard deviations expressed as a percentage of the mean values are typically < 2% of the value, suggesting a very small inherent experimental error in the liquid fraction selectivities measured.

## Exploring Tungsten Concentration and Reactor Volume Effects

Baseline catalytic dimerization performance of complexes **1-3**/ $\text{EtAlCl}_2$  was established prior to exploring the impact of modifiers as summarised in Table 1. Note, the productivity (TON) reported in Entry 1 (Table S2) is underestimated since catalysis had to be stopped as products had filled the reactor vessel to capacity. Consequently, catalysis was repeated at lower W loadings in order to explore the full ethylene dimerization potential of **1**, not limited by reactor size (Table S1, runs 2, 3). However, the resulting overall performance of **1**/ $\text{EtAlCl}_2$  at lower W loadings was significantly reduced. For example, although using 10 instead of 20  $\mu\text{mol}$  of W led to an improvement in productivity, this was accompanied by a halving of the activity (TOF), (*cf.* Table S1, runs 1 and 2) as well as a decrease in the amount of product formed (50.3 g vs 80.3 g).

Further reducing the W loading to 5  $\mu\text{mol}$  (Table S1, Entry 3) again resulted in a drop in productivity, albeit with a slight recovery in activity observed on between entries 2 and 3. The poor catalytic performance observed at W loadings below 20  $\mu\text{mol}$  has been attributed to the lower initial concentration of **1** (Table S1; entries 2 and 3). Indeed, repeating the experiment from run 2 in Table S1 with 50 mL of PhCl (minimum amount necessary for efficient stirring) instead of 74 mL, resulted in a catalysis run that filled the reactor to capacity (76.0 g of products), essentially doubled productivity and activity (*cf.* Table S1, Entries 2 and 4), and slightly increased selectivity from 67.4% to 71.9%.

## Catalysis Results Tables

**Table S1.** Catalytic performance of complexes **1-3** at 45 barg ethylene pressure and 70 °C under varying conditions.<sup>a</sup>

Entry	Pro-cat. ( $\mu\text{mol}$ )	Time, s	TON <sup>b</sup>	Activity <sup>c</sup>	Prod. mass, g	Polymer, %	C <sub>4</sub> , wt% (1-C <sub>4</sub> in C <sub>4</sub> , %)	Total 1-C <sub>4</sub> , wt%	C <sub>6</sub> , wt% (1-C <sub>6</sub> in C <sub>6</sub> , %)	Linear in C <sub>6</sub> , %	Methyl- pentenes, %	C <sub>8+</sub> , wt%
1 <sup>d</sup>	<b>1</b> (20)	45.1	134,340	178,680	75	0.0	73 (98)	71	26 (1)	6	94	2
2	<b>1</b> (10)	126.7	179,130	84,850	50	0.0	67 (98)	66	29 (2)	4	96	4
3	<b>1</b> (5)	23.8	45,195	113,780	8	0.0	69 (98)	68	27 (3)	6	94	4
4 <sup>e</sup>	<b>1</b> (10)	125.2	270,890	129,860	76	0.0	72 (98)	71	26 (2)	4	96	2
5 <sup>f,g</sup>	<b>1</b> (40)	136.1	443,070	195,280	497	0.0	69 (99)	68	30 (2)	5	95	1
6 <sup>d</sup>	<b>2</b> (20)	29.4	143,360	293,210	80	0.0	74 (98)	73	25 (2)	5	96	1
7 <sup>h</sup>	<b>2</b> (20)	25.5	140,170	329,660	79	0.0	76 (98)	75	23 (2)	5	95	1
8 <sup>f</sup>	<b>2</b> (40)	65	392,430	362,060	440	0.0	77 (99)	76	23 (2)	5	95	1
9 <sup>d</sup>	<b>3</b> (20)	21.2	141,610	409,410	80	0.0	82 (98)	80	18 (4)	5	95	1
10 <sup>h</sup>	<b>3</b> (20)	43.3	140,720	195,140	79.	0.1	83 (97)	80	16 (4)	5	95	2
11 <sup>f</sup>	<b>3</b> (40)	104.6	362,010	207,720	406	0.0	84 (98)	82	15 (5)	6	94	1

<sup>a</sup> Conditions: 15 eq. EtAlCl<sub>2</sub>; PhCl 74 mL; 70 °C; ethylene pressure (45 barg); stirrer speed 1000 rpm; nonane standard (1.000 mL); catalytic runs were performed until consumption of C<sub>2</sub>H<sub>4</sub> dropped below 0.2 g min<sup>-1</sup> or until the reactor was filled.; <sup>b</sup> TON (productivity) is reported in (mol C<sub>2</sub>H<sub>4</sub>)(mol W)<sup>-1</sup>. <sup>c</sup> Activity (TOF) is reported in (mol C<sub>2</sub>H<sub>4</sub>)(mol W)<sup>-1</sup> h<sup>-1</sup>. <sup>d</sup> Run taken from reference 2. <sup>e</sup> 50 mL PhCl were used. <sup>f</sup> Performed in a 1.2 L reactor with 148 mL PhCl and 2.000 mL nonane standard. <sup>g</sup> Reaction mixture reached intake holes and therefore the reported activity is underestimated. <sup>h</sup> 12.5 eq. of EtAlCl<sub>2</sub> were used.

**Table S2.** Effect of Et<sub>3</sub>N and Oct<sub>4</sub>NCl on the catalytic performance of complexes **1-3** at 45 barg ethylene pressure and 70 °C.<sup>a</sup>

Entry	Pro-cat. (μmol)	Modifier (eq.)	Time, s	TON <sup>b</sup>	Activity <sup>c</sup>	Prod. mass, g	Polymer, %	C <sub>4</sub> , wt% (1-C <sub>4</sub> in C <sub>4</sub> , %)	Total 1-C <sub>4</sub> , wt%	C <sub>6</sub> , wt% (1-C <sub>6</sub> in C <sub>6</sub> , %)	Linear in C <sub>6</sub> , %	Methyl-pentenes, %	C <sub>8+</sub> , wt%
1	1 (20)	Et <sub>3</sub> N (2)	32.1	144,230	269,420	81	0.0	80 (99)	79	20 (3)	9	91	1
2	1 (20)	Et <sub>3</sub> N (4)	23.6	143,430	366,350	81	0.0	82 (99)	81	17 (3)	8	92	1
3	1 (20)	Et <sub>3</sub> N (6)	23.8	144,280	364,240	81	0.0	87 (99)	86	13 (4)	23	77	1
4	1 (20)	Et <sub>3</sub> N (10)	55	101,920	111,140	57	0.0	91 (99)	91	9 (4)	6	94	<1
5	1 (20)	Oct <sub>4</sub> NCl (2)	18.2	143,450	473,460	81	0.0	79 (99)	78	20 (3)	6	94	1
6	1 (20)	Oct <sub>4</sub> NCl (4)	17.9	141,890	476,830	80	0.0	83 (99)	83	16 (3)	7	93	1
7	1 (20)	Oct <sub>4</sub> NCl (6)	17.9	140,440	471,420	79	0.0	87 (99)	87	13 (4)	8	92	<1
8	1 (20)	Oct <sub>4</sub> NCl (10)	19.4	35,690	110,660	20	0.0	93 (99)	93	7 (4)	8	92	<1
9	2 (20)	Et <sub>3</sub> N (4)	14.9	142,160	573,760	80	0.0	80 (99)	79	19 (3)	6	94	1
10	2 (20)	Oct <sub>4</sub> NCl (2)	14.8	141,180	573,970	79	0.0	79 (99)	78	20 (3)	6	94	1
11	3 (20)	Et <sub>3</sub> N (4)	46.3	15,060	19,530	9	0.0	93 (97)	90	6 (7)	8	92	<1
12	3 (20)	Oct <sub>4</sub> NCl (2)	34.3	141,530	247,810	79	0.0	86 (98)	85	13 (6)	7	93	<1
13 <sup>[d]</sup>	1 (40)	Oct <sub>4</sub> NCl (2)	37.8	367,710	584,180	413	0.0	84 (99)	84	15 (3)	6	94	<1
14 <sup>[d]</sup>	1 (20)	Oct <sub>4</sub> NCl (2)	61.6	707,570	689,560	397	0.0	84 (99)	83	16 (3)	6	94	<1
15 <sup>[d]</sup>	2 (20)	Oct <sub>4</sub> NCl (2)	88.5	675,340	457,690	379	0.0	82 (99)	82	1 (2)	5	95	<1

<sup>a</sup> Conditions: 15 eq. EtAlCl<sub>2</sub>; PhCl 74 mL; 70 °C; ethylene pressure (45 barg); stirrer speed 1000 rpm; nonane standard (1.000 mL); catalytic runs were performed until consumption of C<sub>2</sub>H<sub>4</sub> dropped below 0.2 g min<sup>-1</sup> or until the reactor was filled.; no polyethylene was detected. <sup>b</sup> TON (productivity) is reported in (mol C<sub>2</sub>H<sub>4</sub>)/(mol W)<sup>-1</sup>. <sup>c</sup> Activity (TOF) is reported in (mol C<sub>2</sub>H<sub>4</sub>)/(mol W)<sup>-1</sup> h<sup>-1</sup>. <sup>d</sup> Performed in a 1.2 L reactor with 148 mL PhCl and 2.000 mL nonane standard.

## Stoichiometric Reactions

### Reaction between $[\text{WCl}_2(\text{NDipp})_2(\text{dme})]$ (**1**) and $\text{EtAlCl}_2$

$\text{WCl}_2(\text{NDipp})_2(\text{dme})$  (**1**) (50 mg, 0.07 mmol) was dissolved in  $\text{C}_6\text{D}_6$  (0.8 mL). To this solution was added  $\text{EtAlCl}_2$  (53 mg, 0.42 mmol) and the reaction mixture was analysed immediately using  $^1\text{H}$  NMR spectroscopy. This showed that the reaction gave multiple products unassignable by  $^1\text{H}$  NMR spectroscopy, although ethane was detected at  $\delta$  0.79 ppm. Next, ethylene (0.17 mmol) was added to this  $\text{C}_6\text{D}_6$  solution. No reaction of ethylene occurred and no higher olefins were detected by  $^1\text{H}$  NMR spectroscopy.

### Reaction of $[\text{WMe}_2(\text{N}\{\text{Dipp}\}\text{AlMe}_2\{\mu\text{-Cl}\})(\text{NDipp})]$ (**4**) with $\text{Et}_3\text{N}$

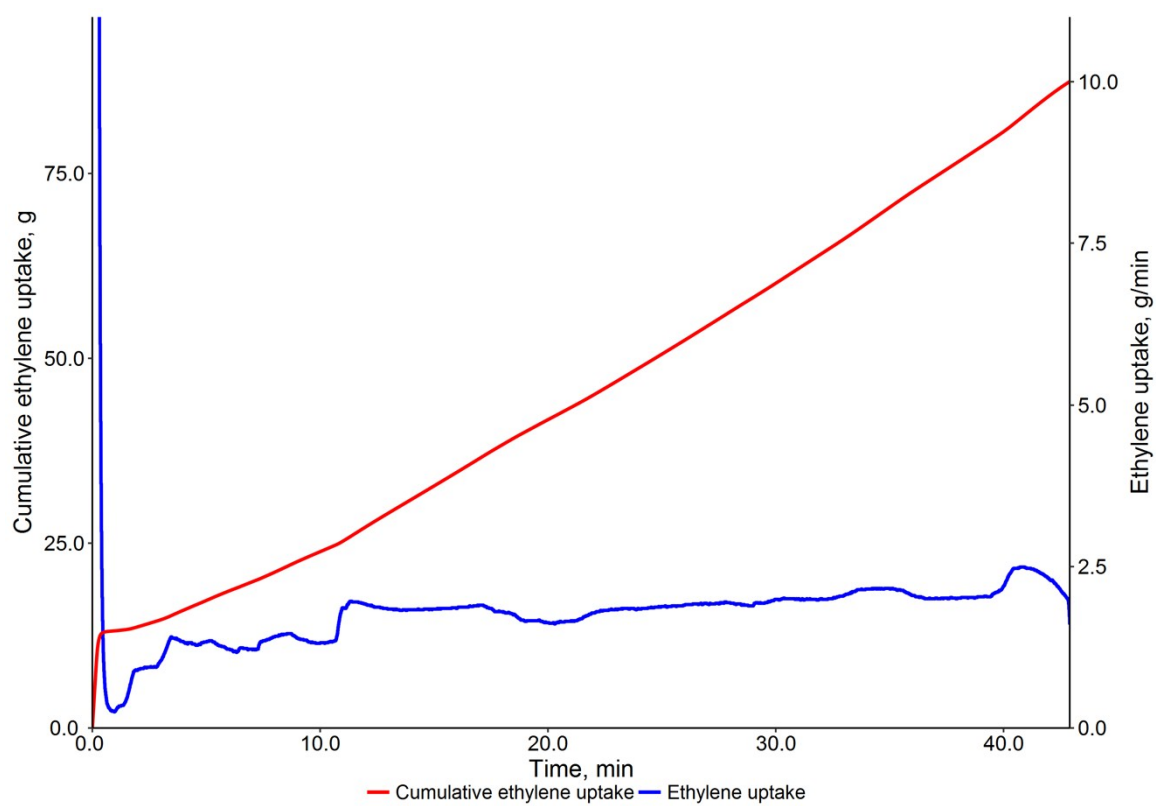
Complex **4** was formed *in situ* from reaction of **1** (50 mg, 0.07 mmol) with  $\text{Me}_3\text{Al}$  (25 mg, 0.34 mmol) in  $\text{C}_6\text{D}_6$  (0.8 mL) as indicated by  $^1\text{H}$  NMR spectroscopic analysis. Subsequent removal of volatile components *in vacuo*, give a tan brown solid. This material was then redissolved in  $\text{C}_6\text{D}_6$  (0.8 mL) containing  $\text{NEt}_3$  (8 mg, 0.08 mmol) and the reaction re-analysed using  $^1\text{H}$  NMR spectroscopy. The resulting spectrum was consistent with the *in situ* formation of  $[\text{W}(\text{NDipp})_2\text{Me}_2]$  by comparison to the  $^1\text{H}$  NMR spectrum previously reported for  $[\text{WMe}_2(\text{NDipp})_2]$ .<sup>4</sup> The  $^1\text{H}$  NMR spectrum also contained resonances attributable to aluminium adducts of both *dme* and  $\text{Et}_3\text{N}$ , formed as reaction by-products in this procedure.

### Reaction of $[\text{WMe}_2(\text{N}\{\text{Dipp}\}\text{AlMe}_2\{\mu\text{-Cl}\})(\text{NDipp})]$ (**4**) with $\text{Et}_4\text{NCl}$

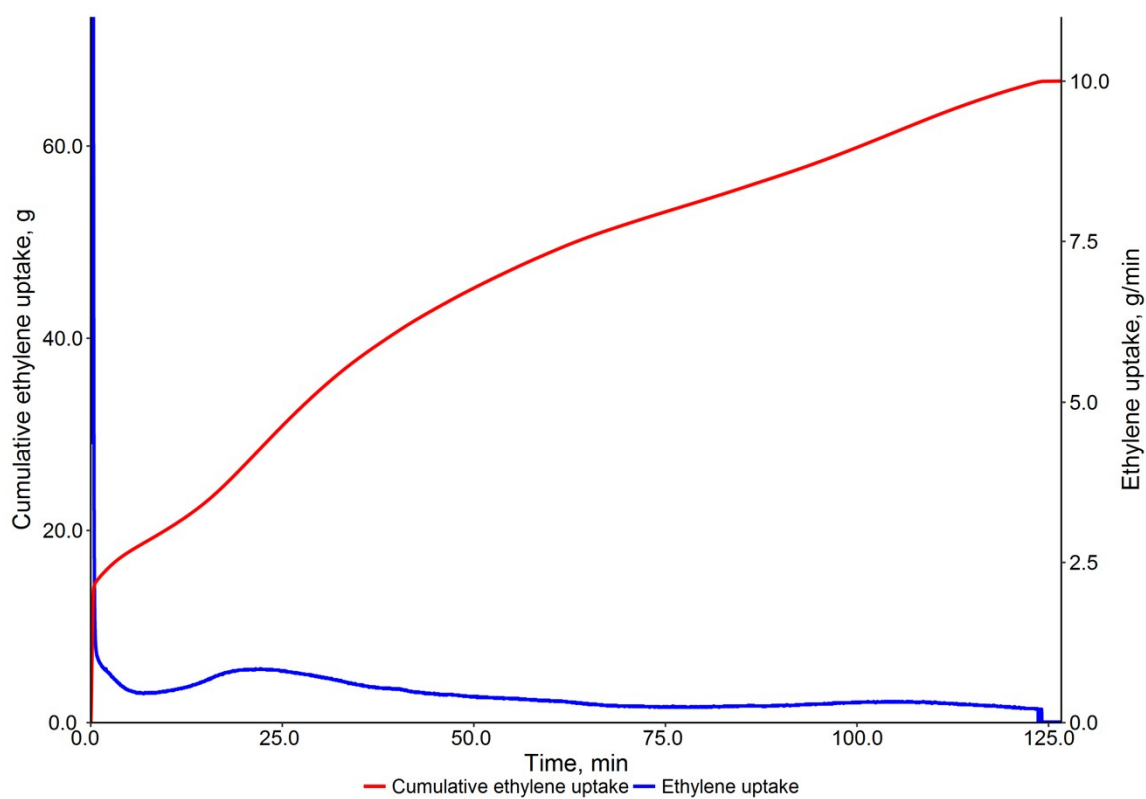
$[\text{WMe}_2(\text{N}\{\text{Dipp}\}\text{AlMe}_2\{\mu\text{-Cl}\})(\text{NDipp})]$  (**4**) (34 mg, 0.046 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.6 mL) followed by addition of  $[\text{Et}_4\text{N}]\text{Cl}$  (8.6 mg, 0.046 mmol). A colour change from yellow to red was observed due to formation of  $[\text{WMe}_2(\text{NDipp})_2]$  and  $[\text{Et}_4\text{N}][\text{Me}_2\text{AlCl}_2]$  as indicated by  $^1\text{H}$  NMR spectroscopic analysis.



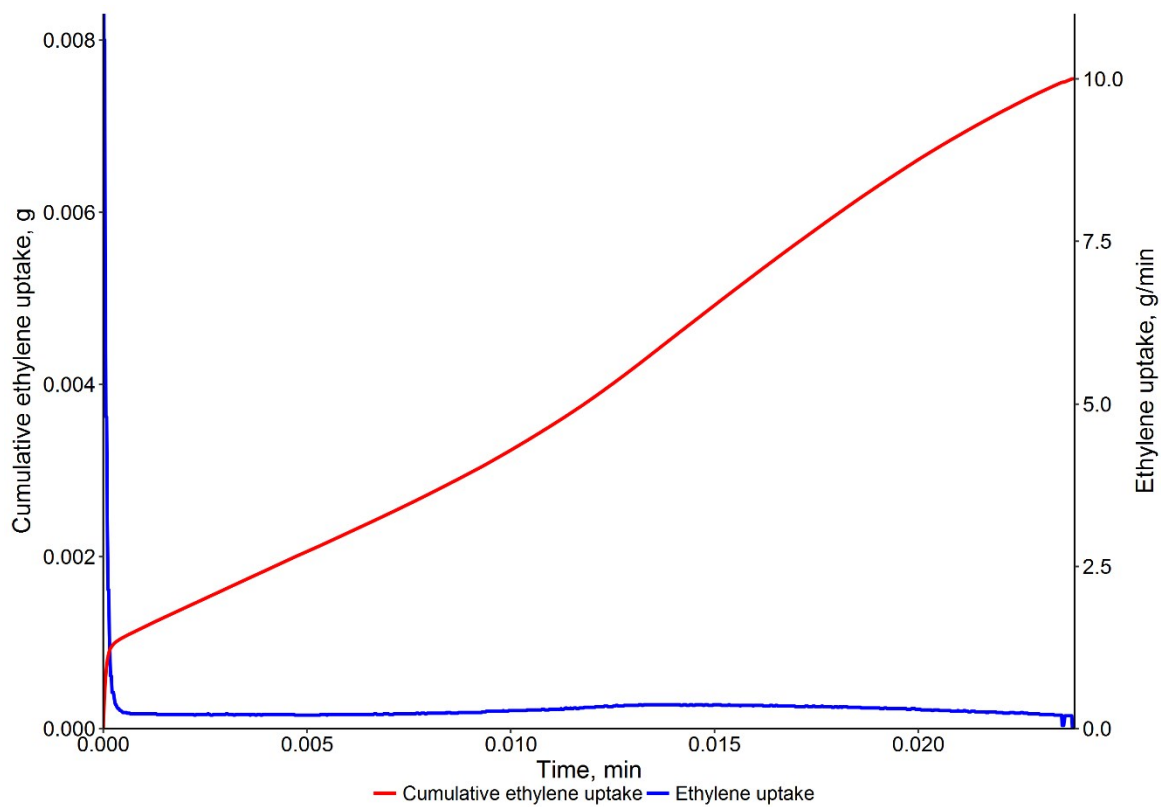
## Ethylene Uptake Traces for Catalytic Reactions



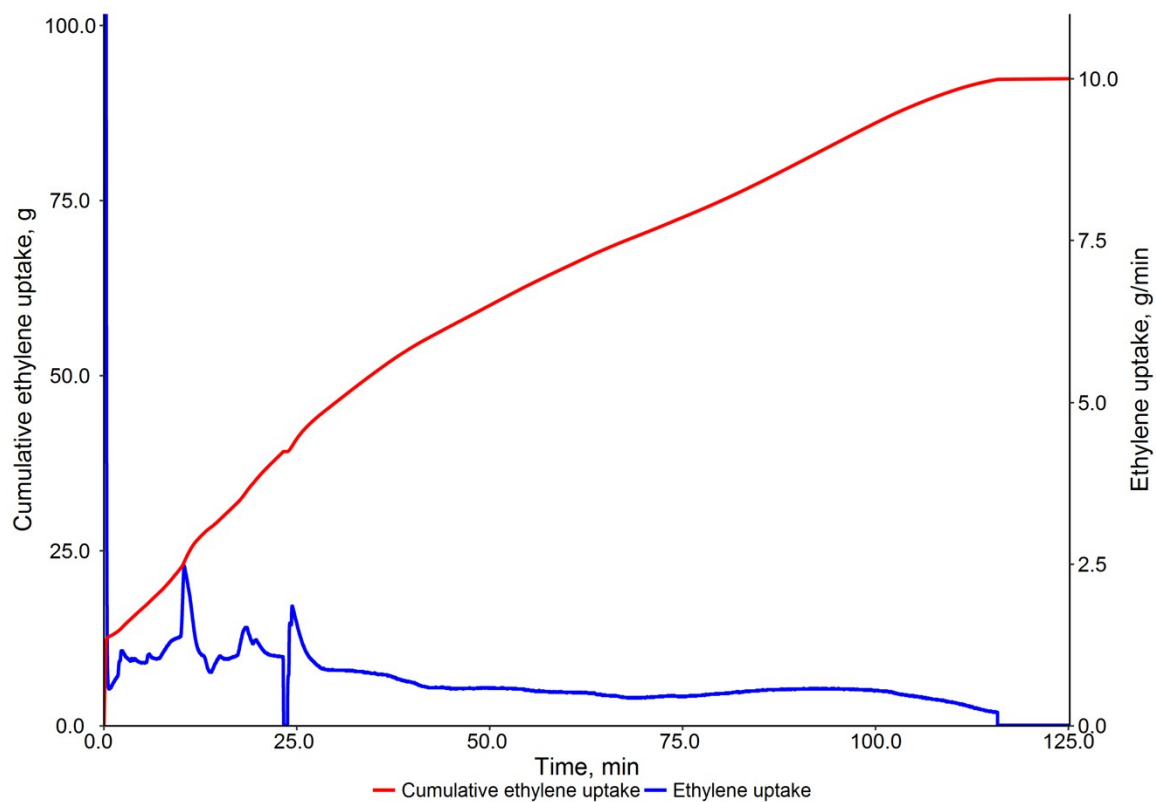
**Figure S1.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **1** and 15.0 eq.  $\text{EtAlCl}_2$  (Table 1 and Table S1, Entry 1).



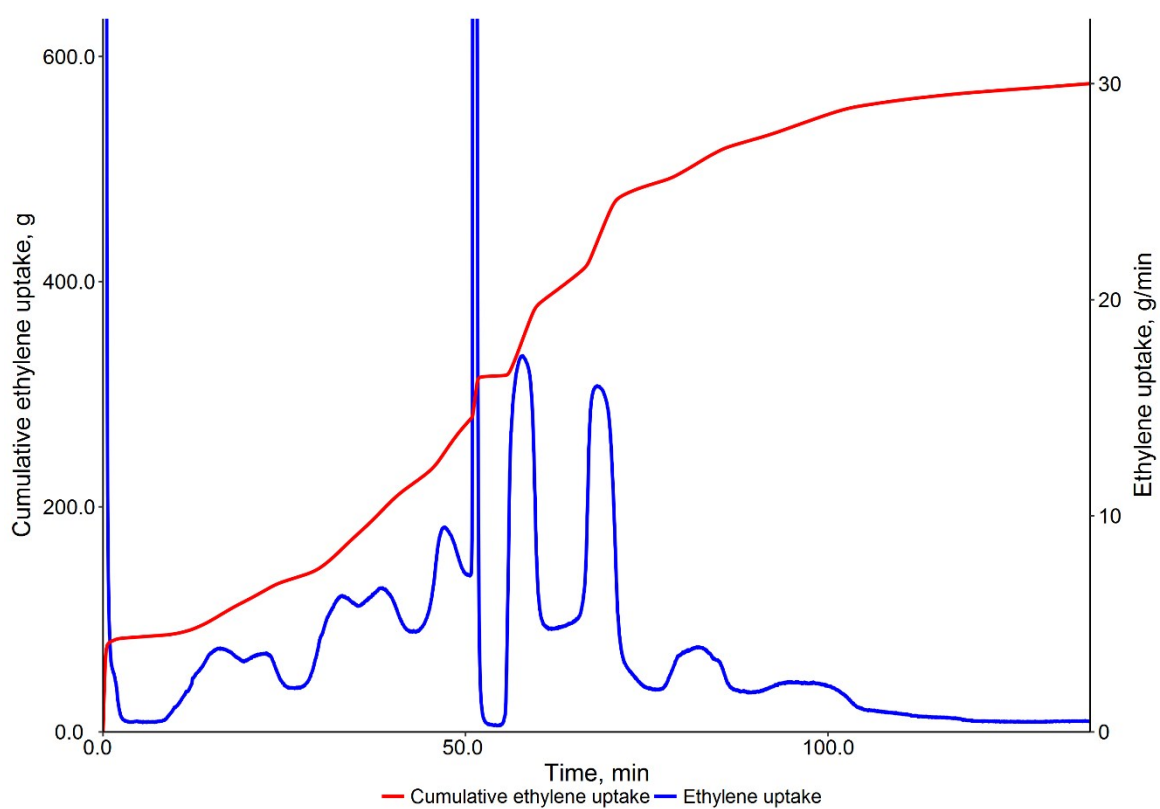
**Figure S2.** Ethylene uptake trace for catalysis with 10  $\mu\text{mol}$  of **1** and 15.0 eq.  $\text{EtAlCl}_2$  (Table S1, Entry 2).



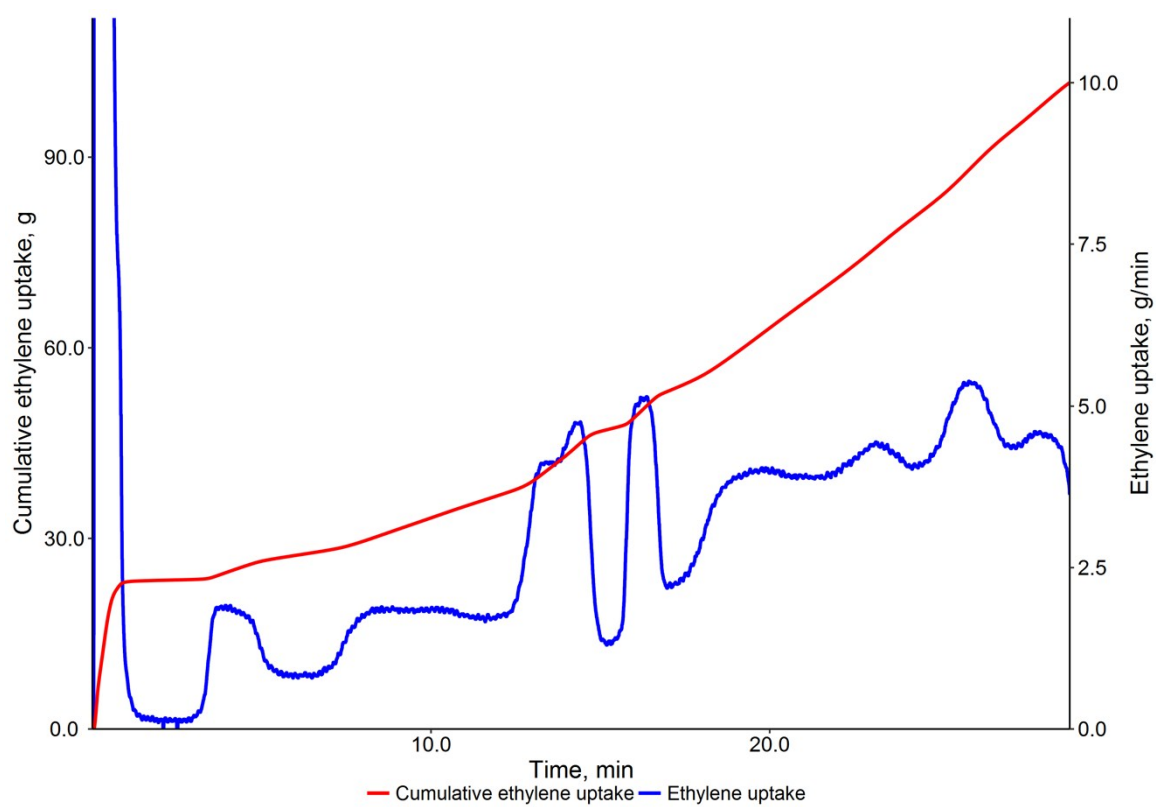
**Figure S3.** Ethylene uptake trace for catalysis with 5  $\mu\text{mol}$  of **1** and 15.0 eq.  $\text{EtAlCl}_2$  (Table S1, Entry 3).



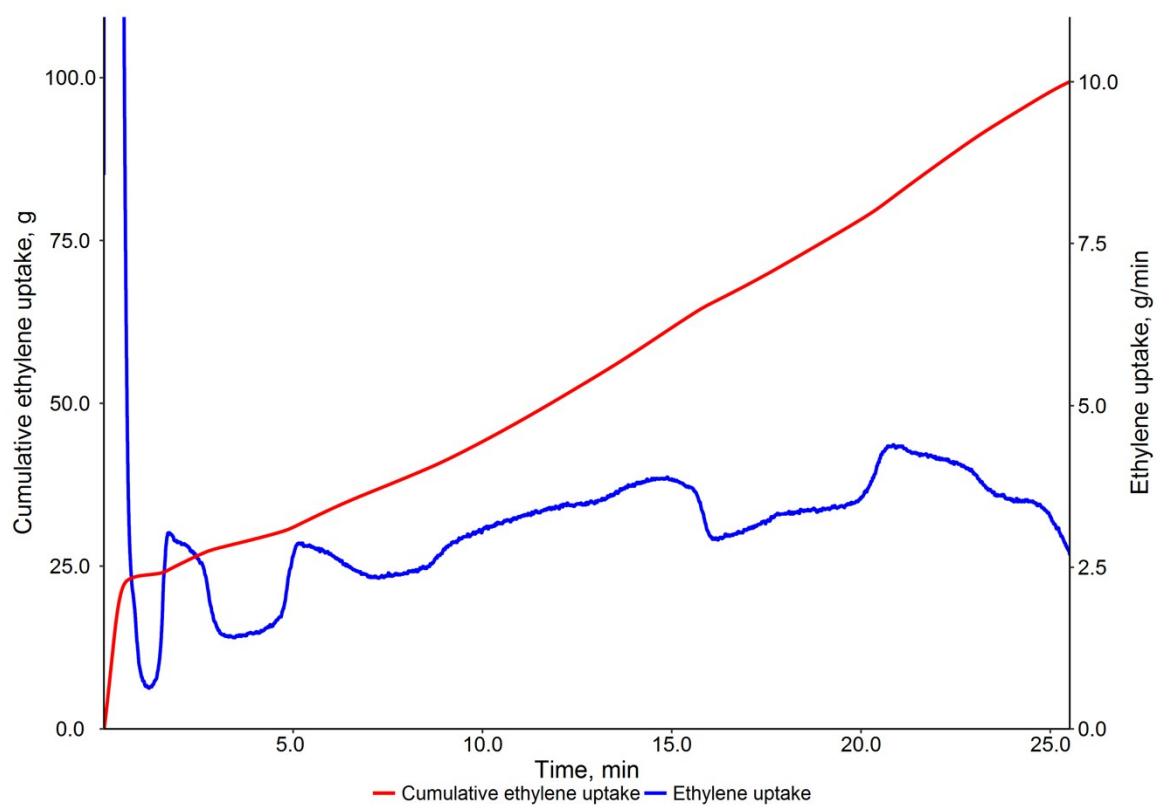
**Figure S4.** Ethylene uptake trace for catalysis with 10  $\mu\text{mol}$  of **1** and 15.0 eq.  $\text{EtAlCl}_2$  at 50.0 mL PhCl (Table S1, Entry 4).



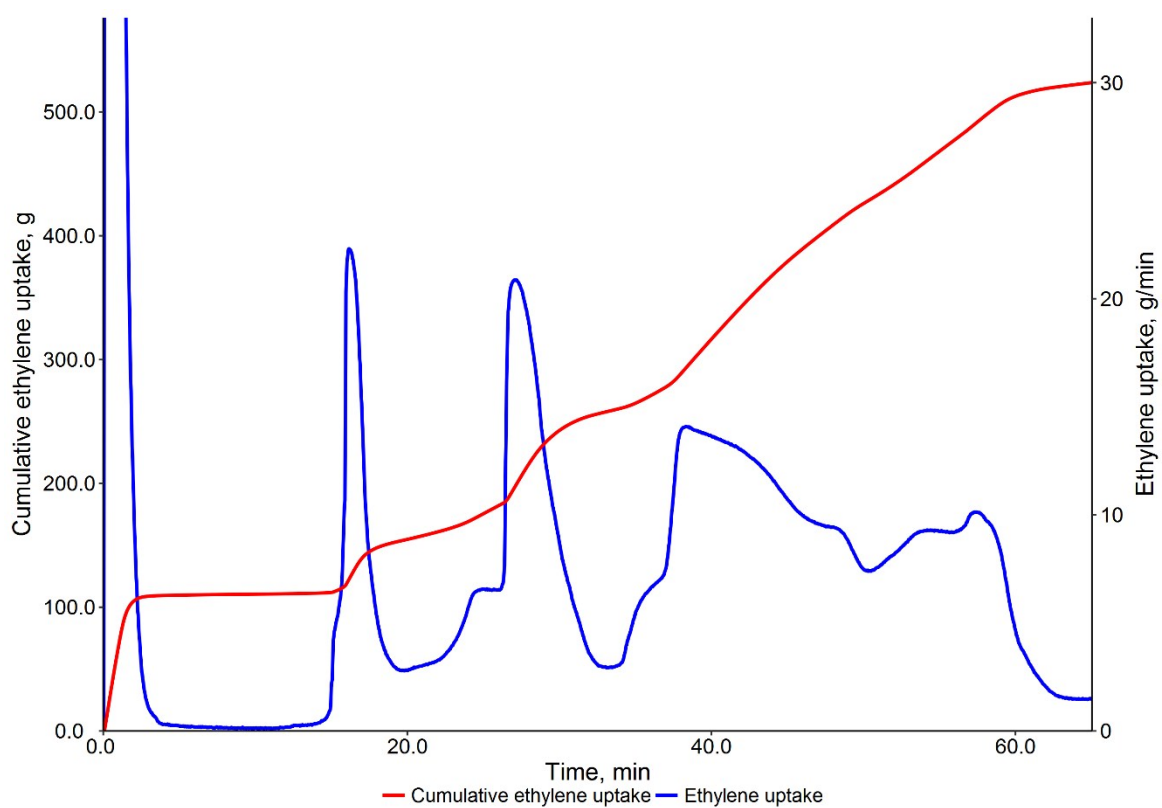
**Figure S5.** Ethylene uptake trace for catalysis with 40  $\mu\text{mol}$  of **1** and 15.0 eq.  $\text{EtAlCl}_2$  in a 1.2 L reactor (Table 1, Entry 2 and Table S1, Entry 5).



**Figure S6.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **2** and 15.0 eq.  $\text{EtAlCl}_2$  (Table 1, Entry 3 and Table S1, Entry 6).

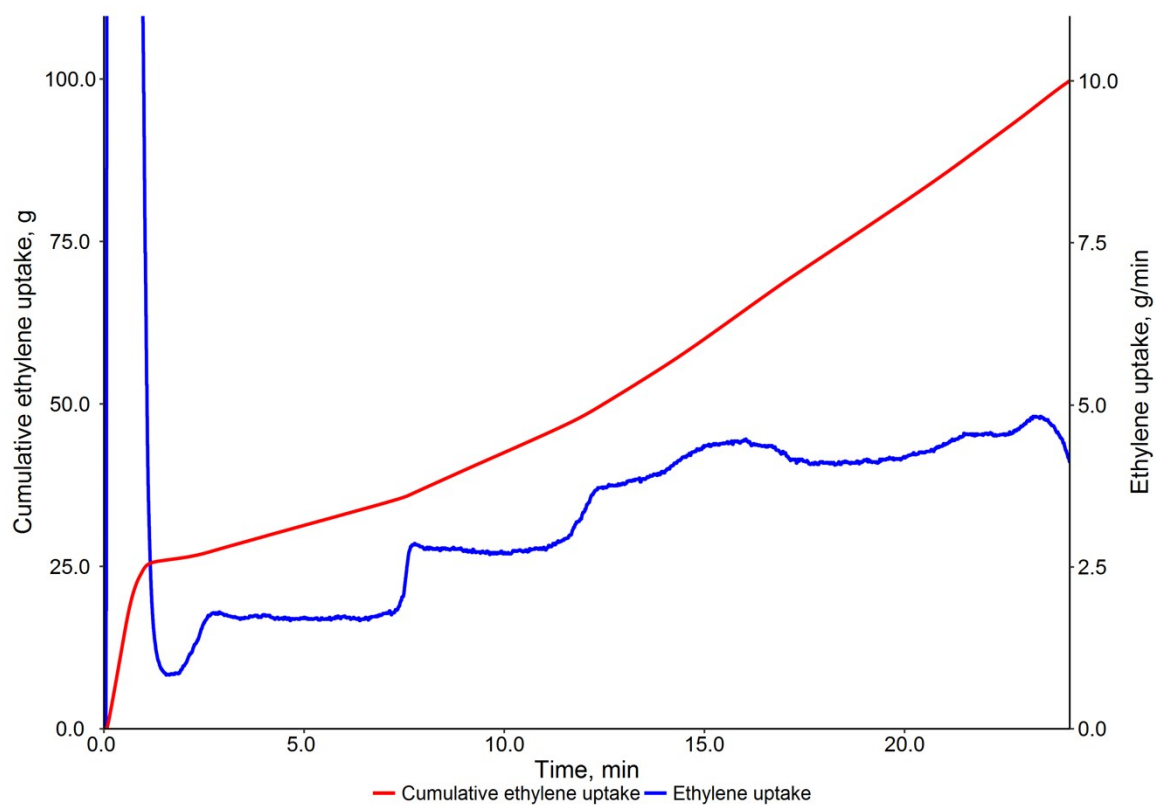


**Figure S7.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **2** and 12.5 eq.  $\text{EtAlCl}_2$  (Table S1, Entry 7).

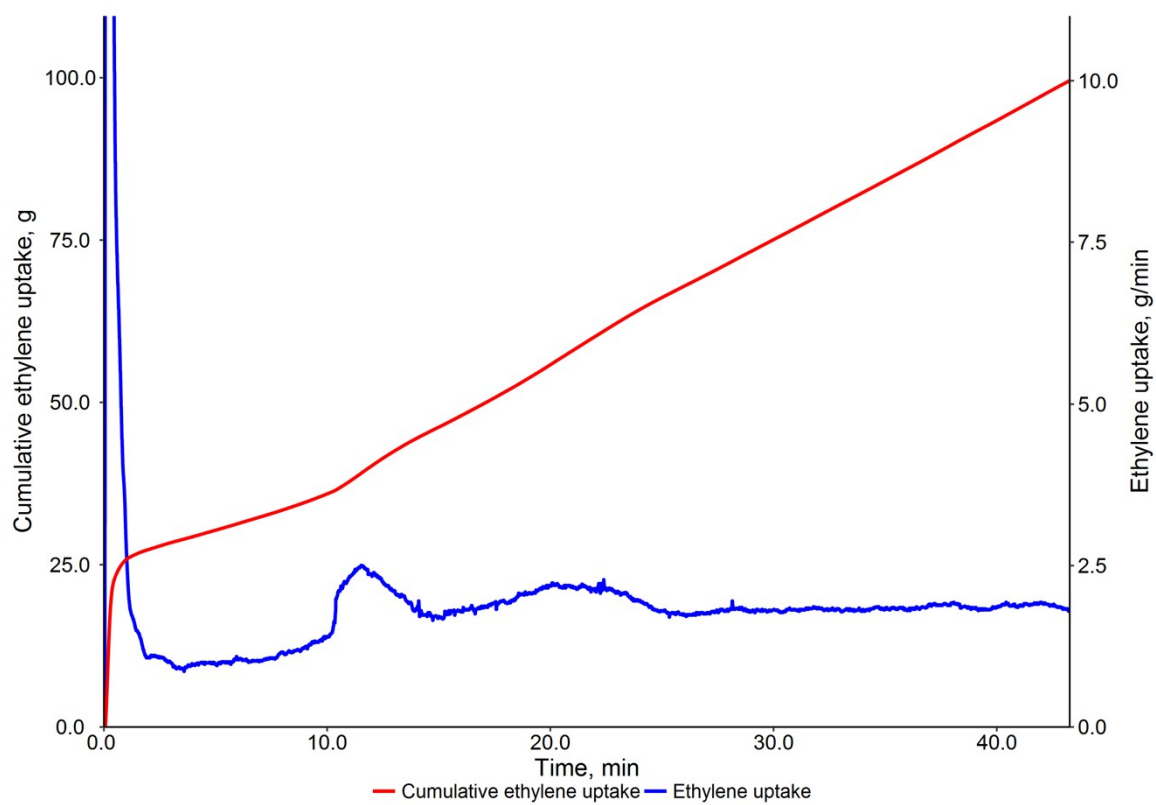


**Figure S8.** Ethylene uptake trace for catalysis with 40  $\mu\text{mol}$  of **2** and 15.0 eq.  $\text{EtAlCl}_2$  in a 1.2 L reactor (Table 1, Entry 4 and Table S1, Entry 8).

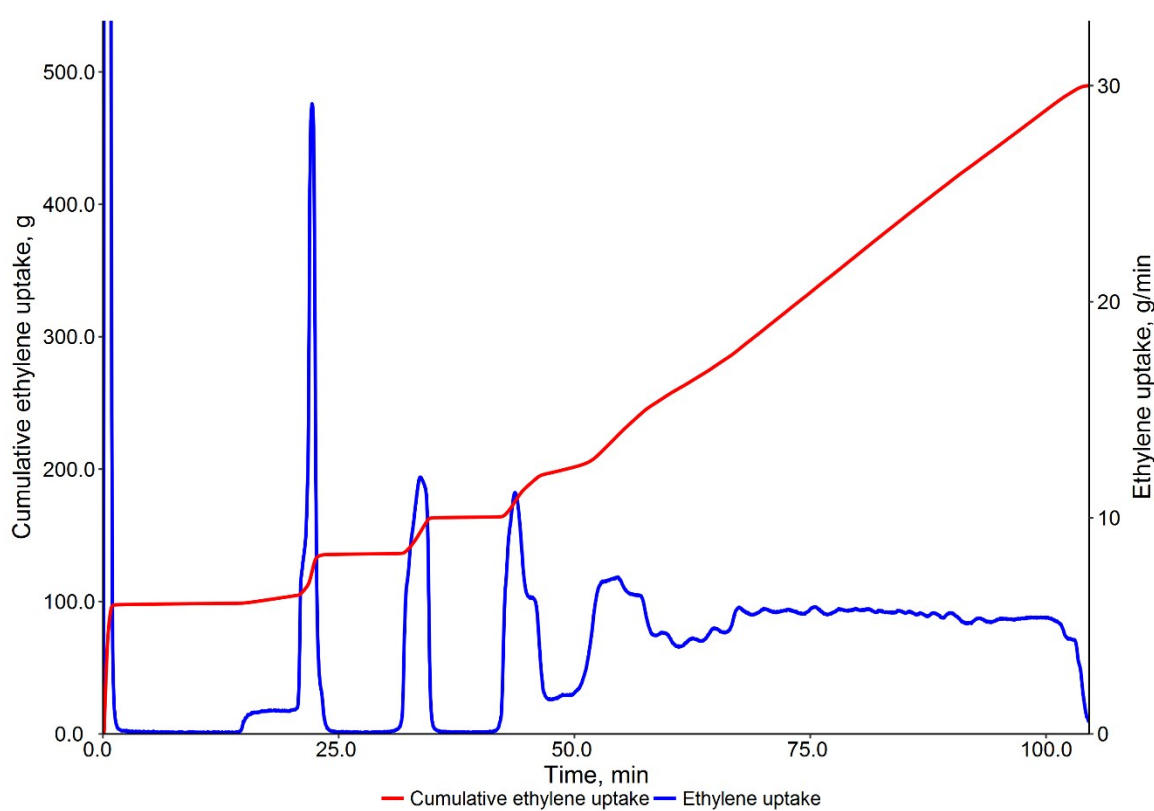




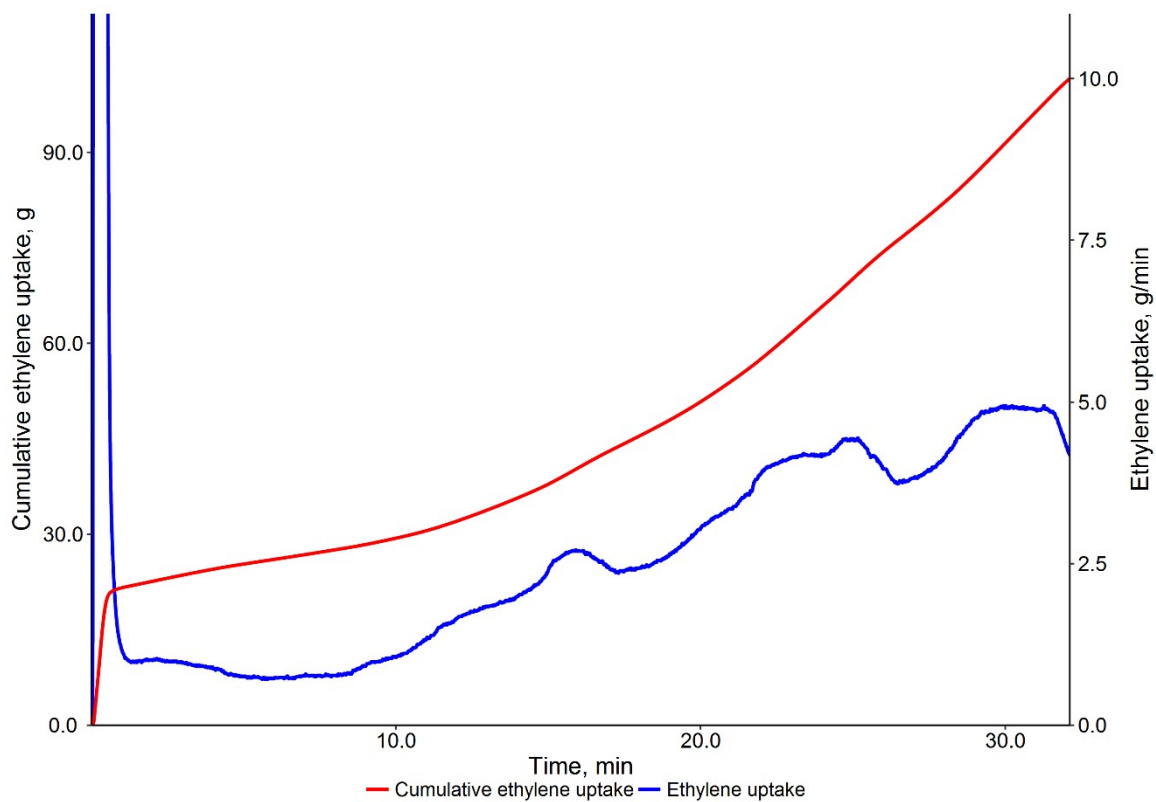
**Figure S9.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **3** and 15.0 eq.  $\text{EtAlCl}_2$  (Table 1, Entry 5 and Table S1, Entry 9).



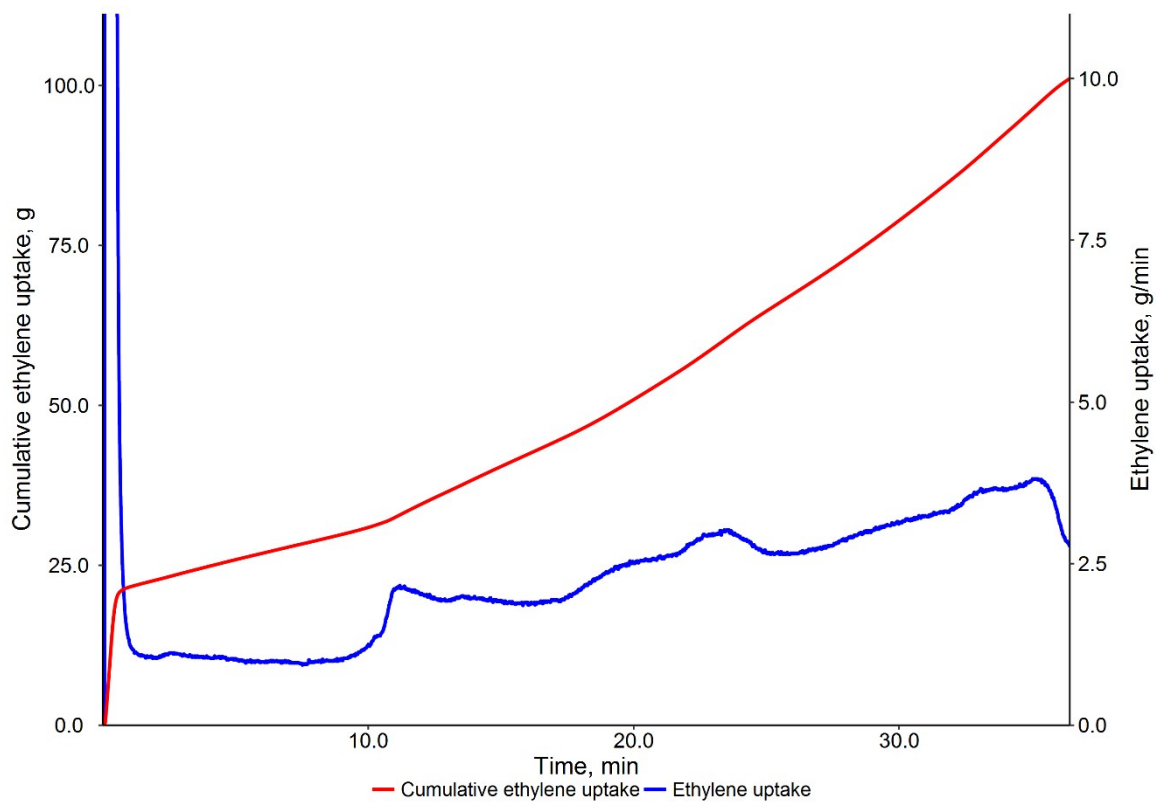
**Figure S10.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **3** and 12.5 eq.  $\text{EtAlCl}_2$  (Table S1, Entry 10).



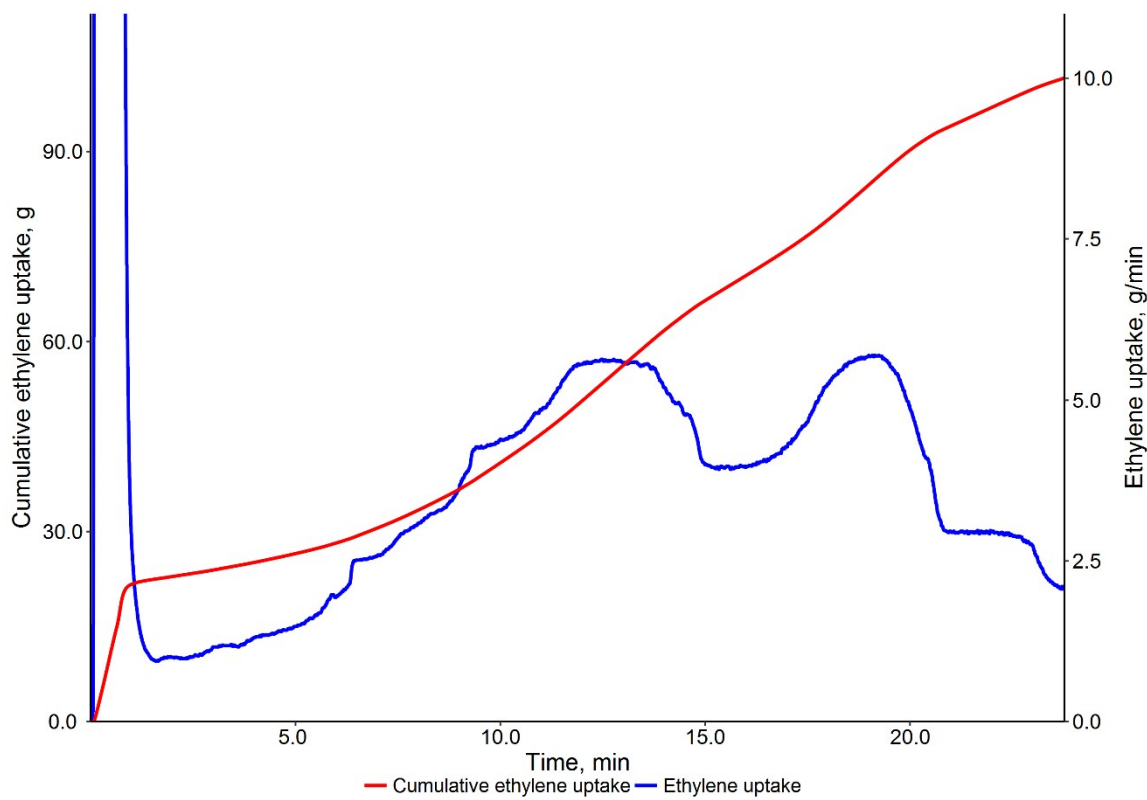
**Figure S11.** Ethylene uptake trace for catalysis with 40  $\mu\text{mol}$  of **3** and 15.0 eq.  $\text{EtAlCl}_2$  in a 1.2 L reactor (Table 1, Entry 6 and Table S1, Entry 11).



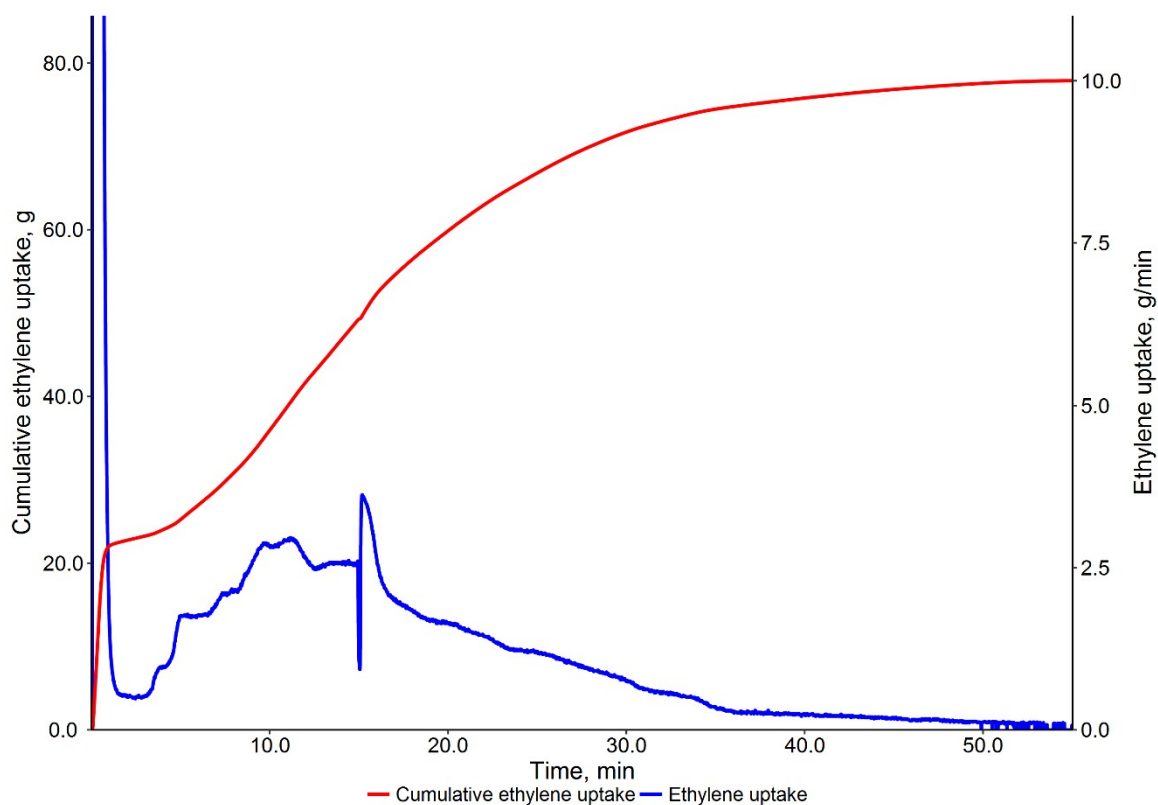
**Figure S10.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **1** combined with 2 eq.  $\text{Et}_3\text{N}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 1).



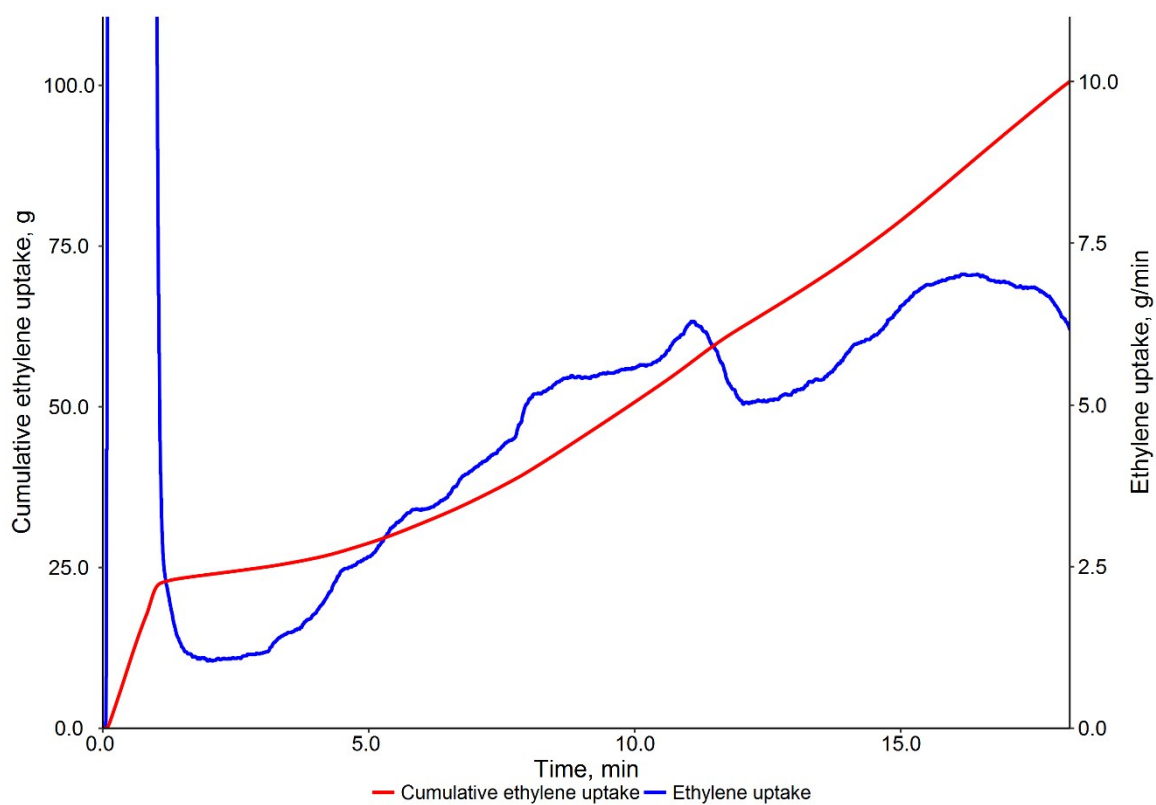
**Figure S11.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **1** combined with 4 eq.  $\text{Et}_3\text{N}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 2).



**Figure S12.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **1** combined with 6 eq.  $\text{Et}_3\text{N}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 3).

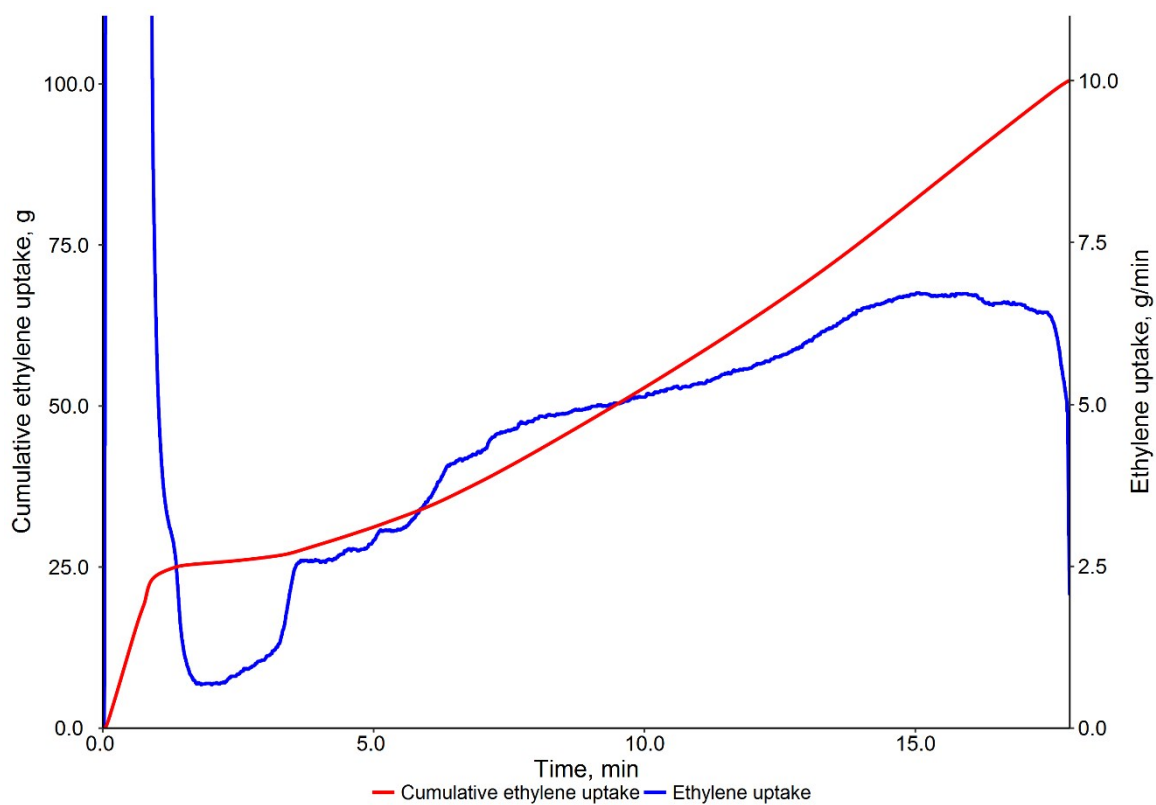


**Figure S13.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **1** combined with 10 eq.  $\text{Et}_3\text{N}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 4).

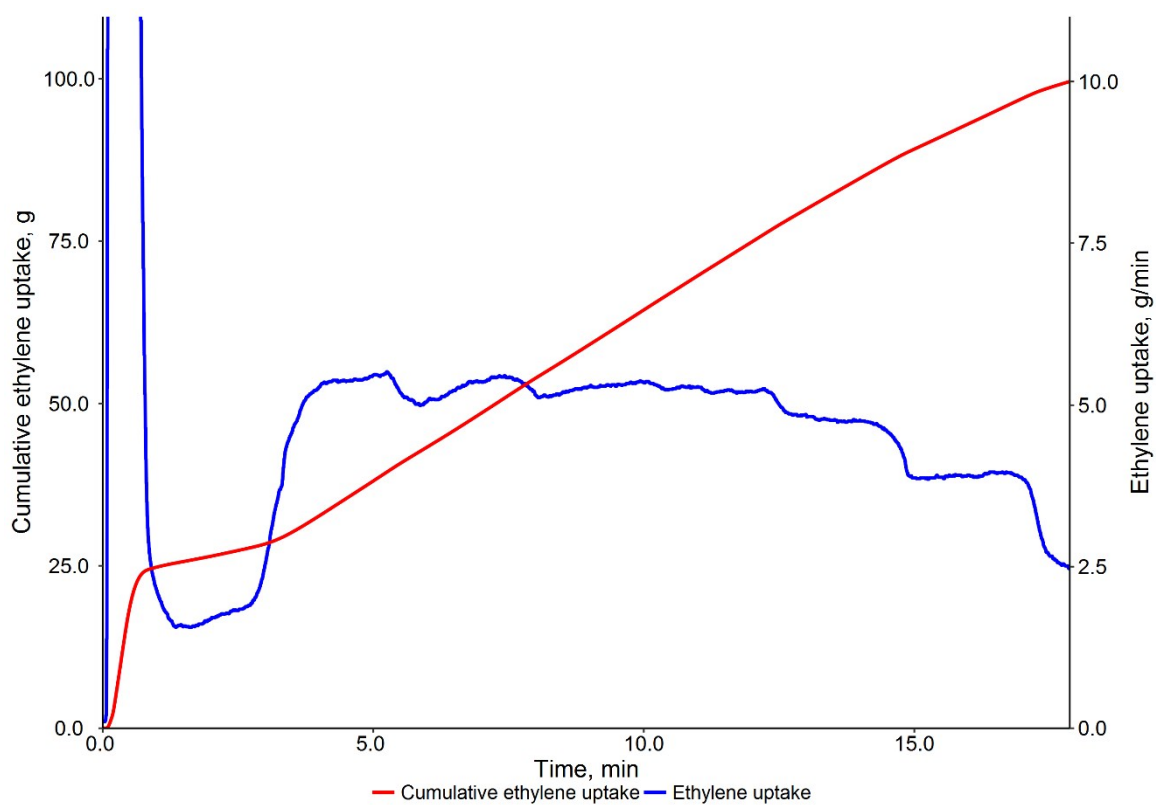


**Figure S14.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **1** combined with 2 eq.  $\text{Oct}_4\text{NCl}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 5).

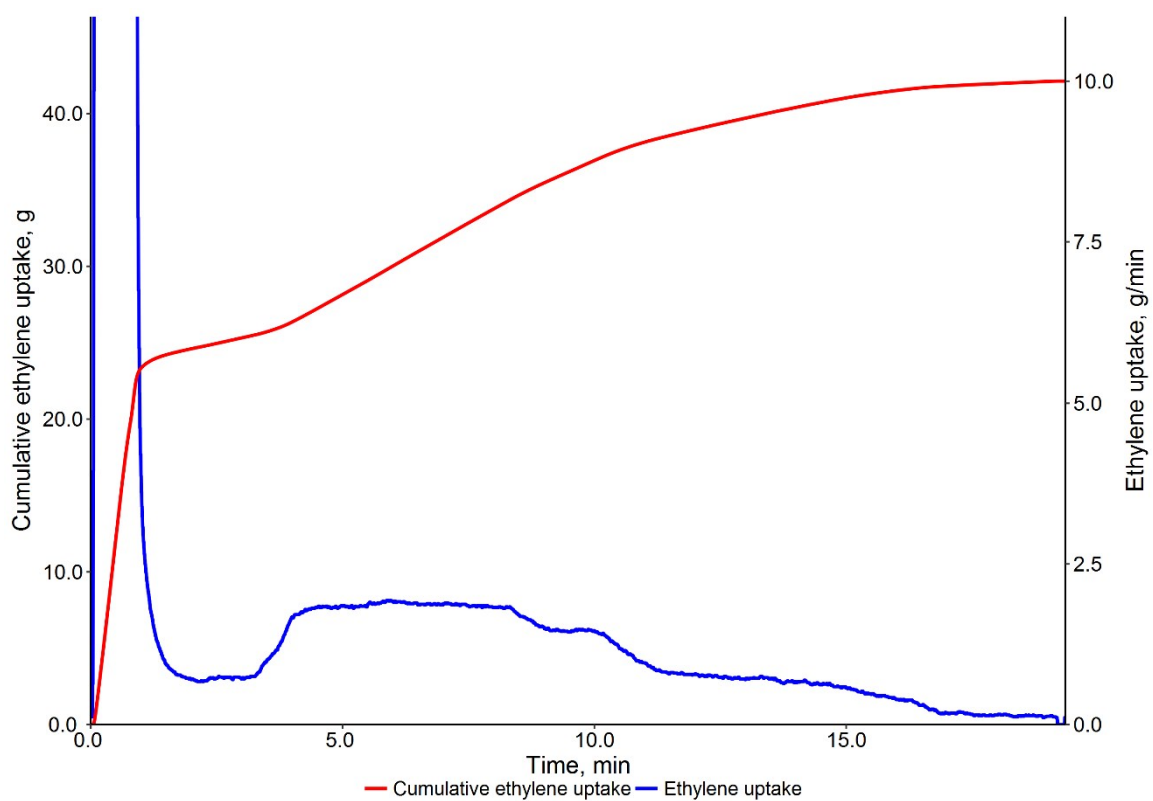




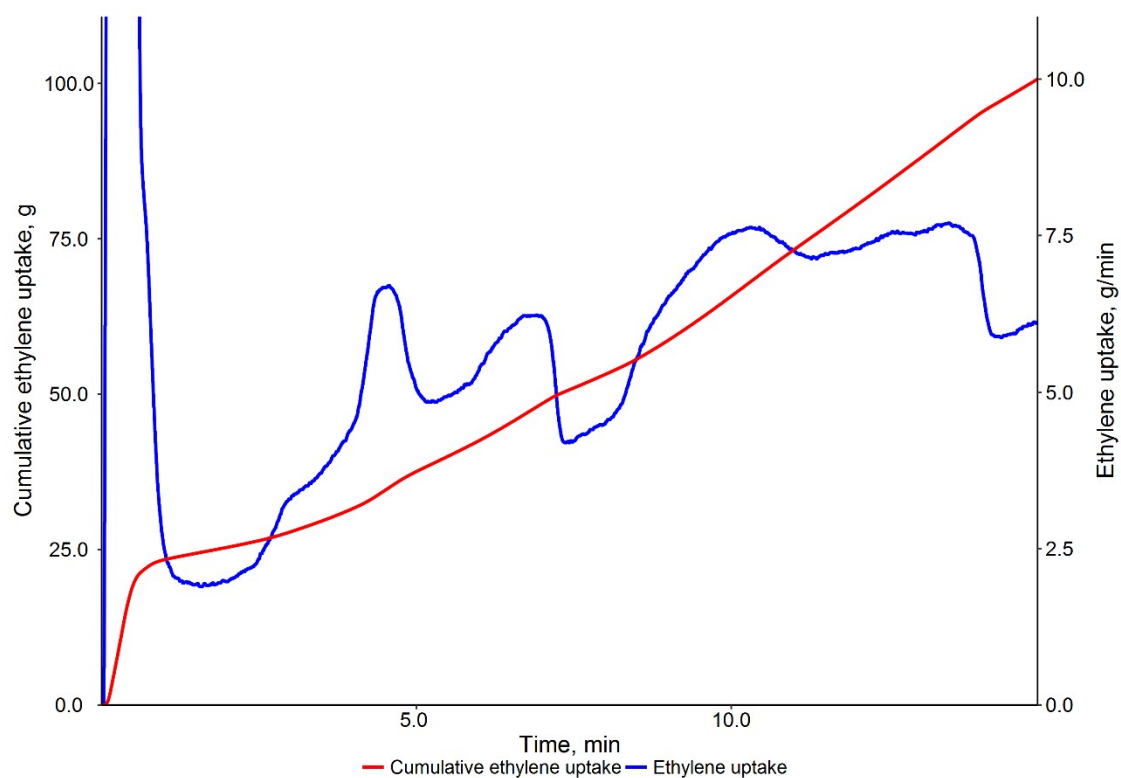
**Figure S15.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **1** combined with 4 eq.  $\text{Oct}_4\text{NCl}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 6).



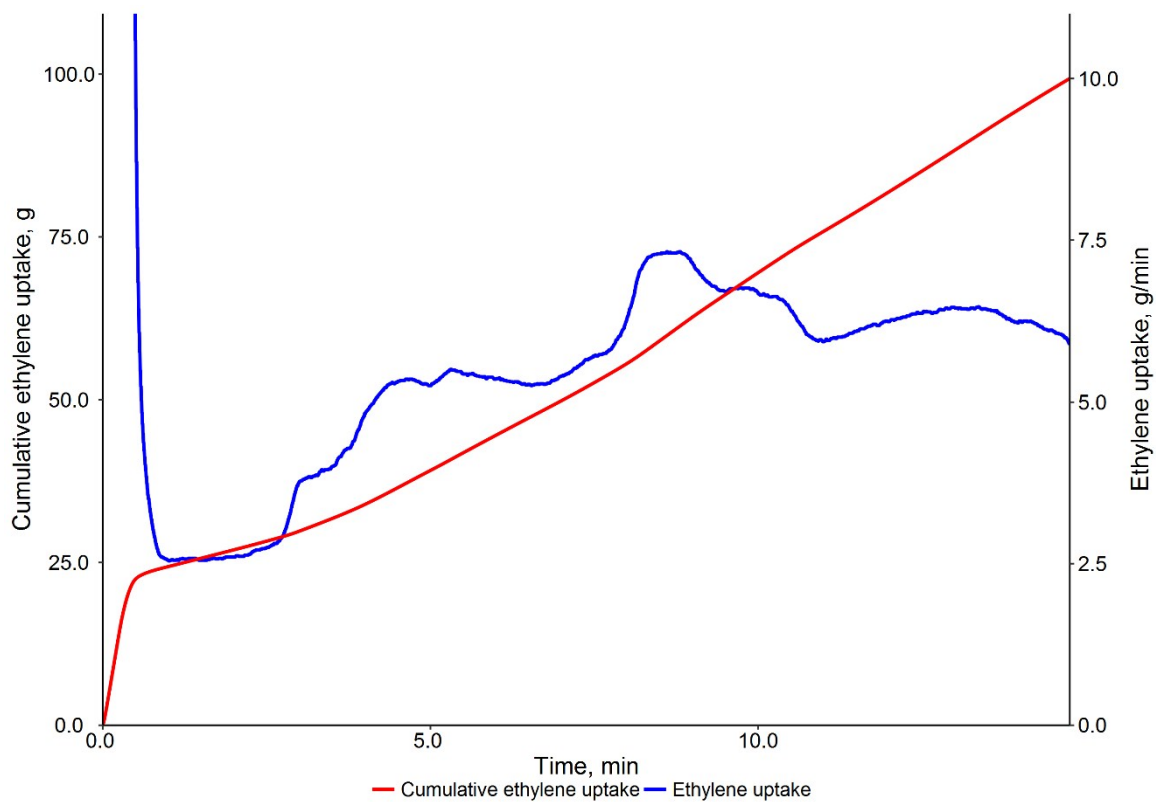
**Figure S16.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **1** combined with 6 eq.  $\text{Oct}_4\text{NCl}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 7).



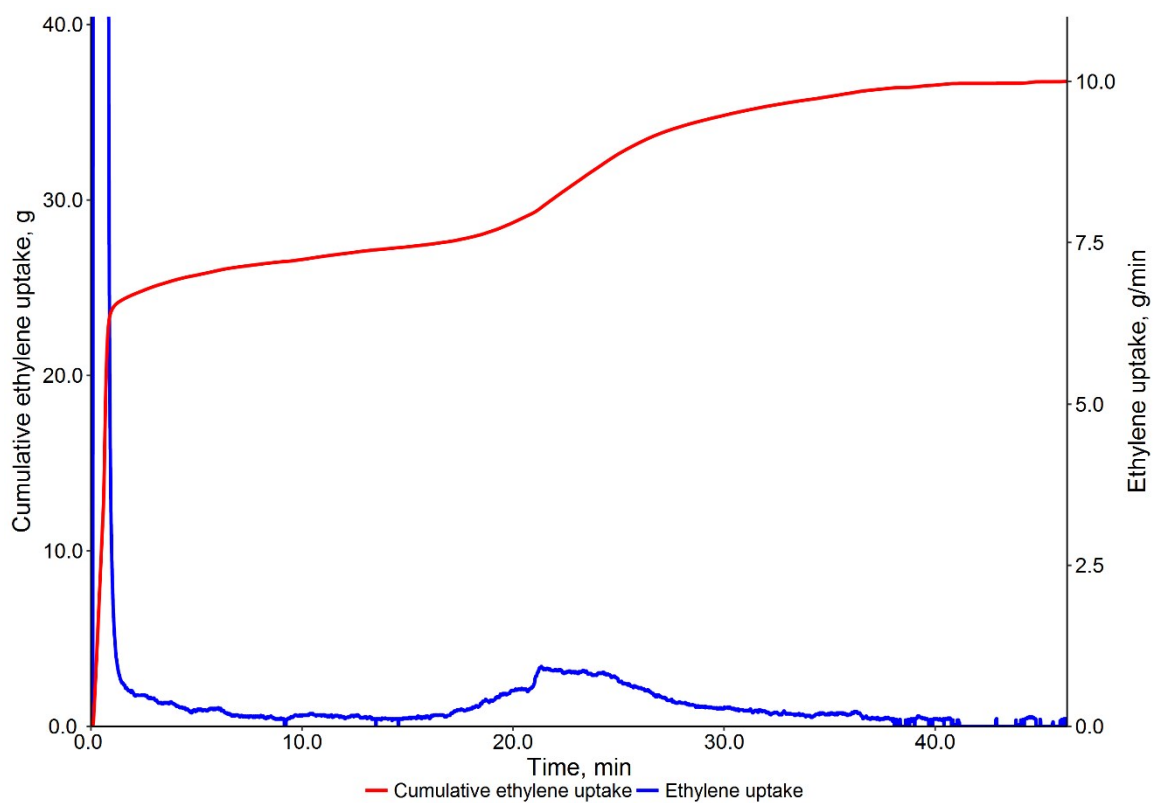
**Figure S17.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **1** combined with 10 eq.  $\text{Oct}_4\text{NCl}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 8).



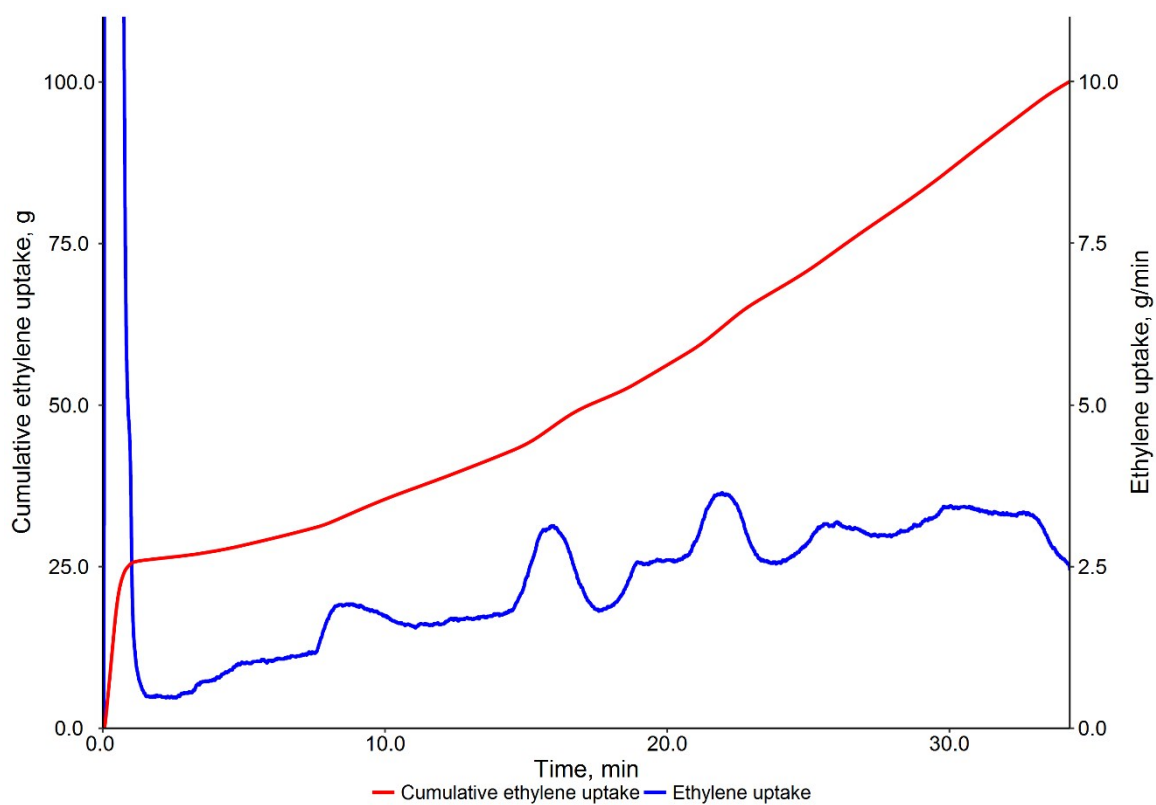
**Figure S18.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **2** combined with 4 eq.  $\text{Et}_3\text{N}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 9).



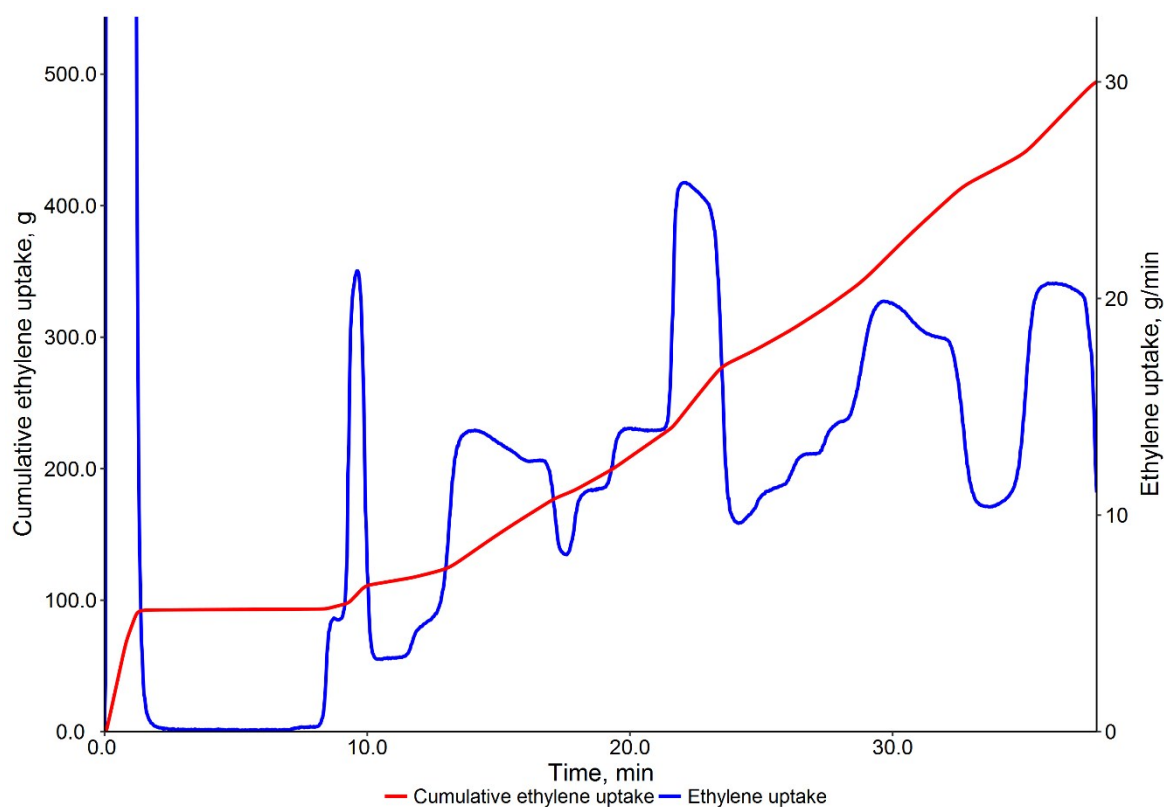
**Figure S19.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **2** combined with 2 eq.  $\text{Oct}_4\text{NCl}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 10).



**Figure S20.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **3** combined with 4 eq.  $\text{Et}_3\text{N}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 11).

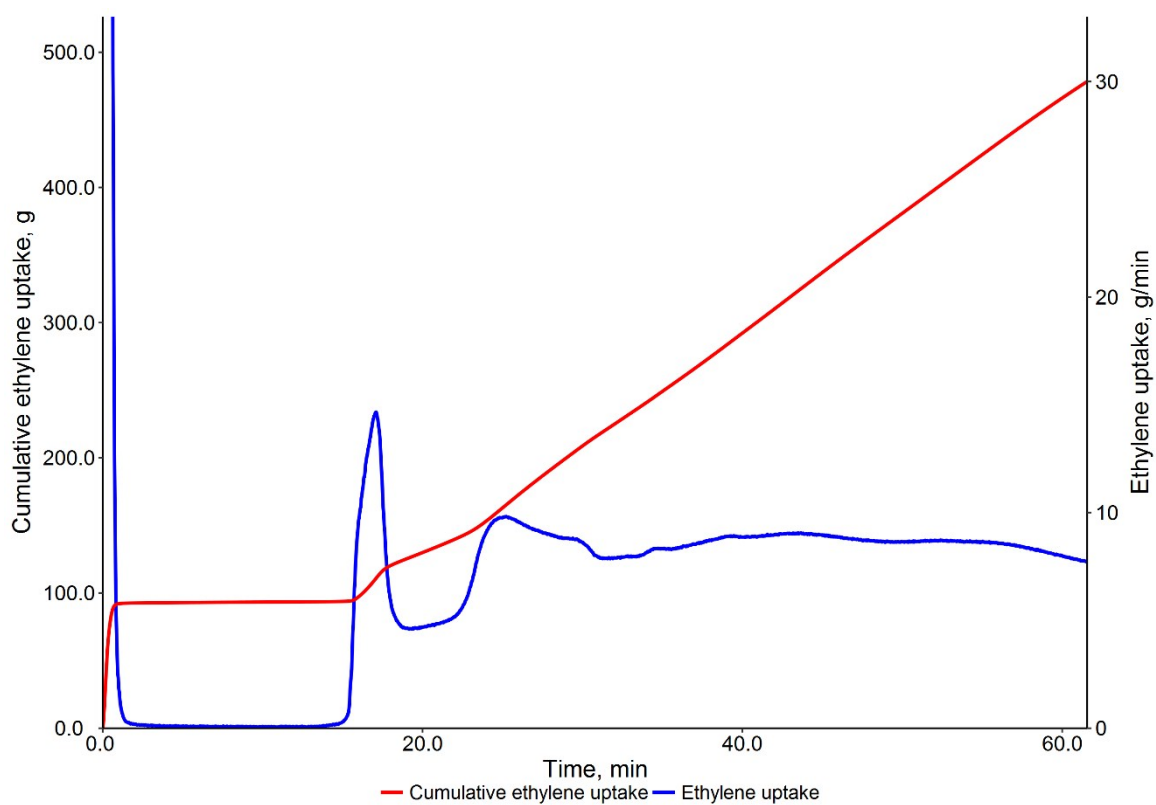


**Figure S21.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **3** combined with 2 eq.  $\text{Oct}_4\text{NCl}$  and 15.0 eq.  $\text{EtAlCl}_2$  (Table 2 and Table S2, Entry 12).

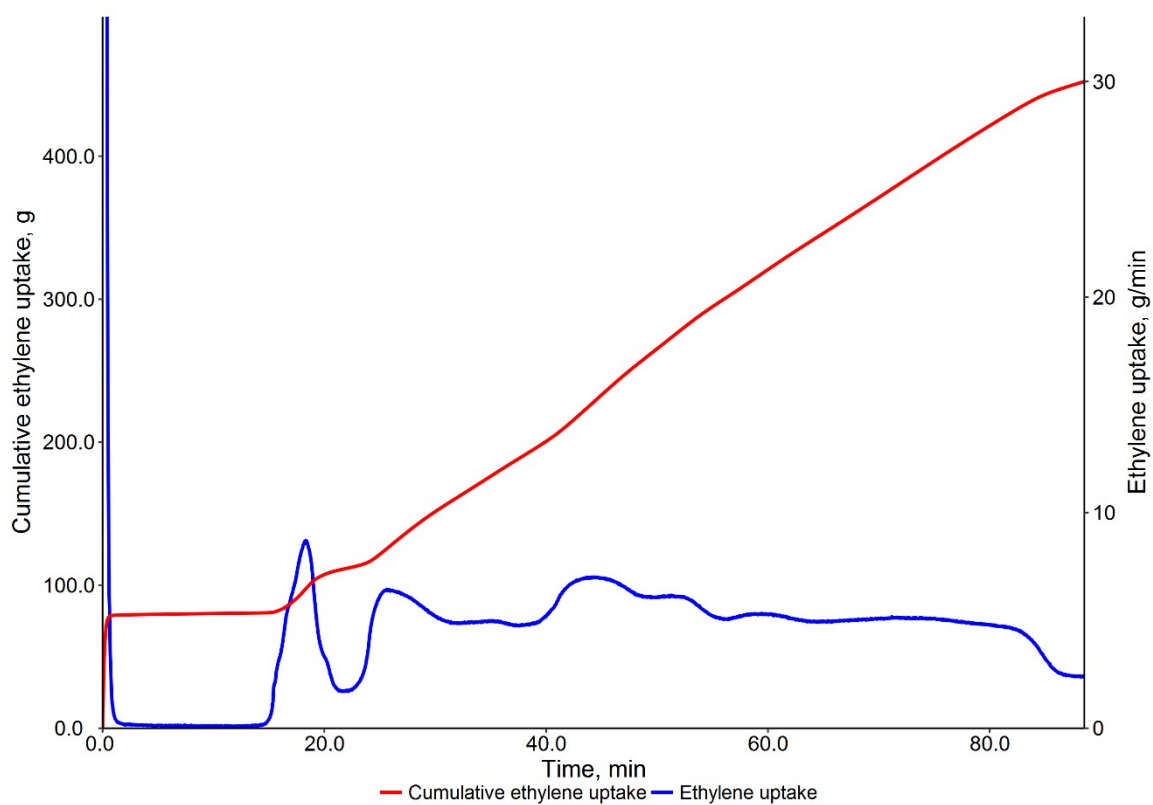


**Figure S22.** Ethylene uptake trace for catalysis with 40  $\mu\text{mol}$  of **1** combined with 2 eq.  $\text{Oct}_4\text{NCl}$  and 15.0 eq.  $\text{EtAlCl}_2$  in a 1.2 L reactor (Table 2 and Table S2, Entry 13).





**Figure S23.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **1** combined with 2 eq.  $\text{Oct}_4\text{NCl}$  and 15.0 eq.  $\text{EtAlCl}_2$  in a 1.2 L reactor (Table 2 and Table S2, Entry 14).



**Figure S24.** Ethylene uptake trace for catalysis with 20  $\mu\text{mol}$  of **2** combined with 2 eq.  $\text{Oct}_4\text{NCl}$  and 15.0 eq.  $\text{EtAlCl}_2$  in a 1.2 L reactor (Table 2 and Table S2, Entry 15).

## References

- 1 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.
- 2 A. M. Messinis, A. S. Batsanov, W. R. H. Wright, J. A. K. Howard, M. J. Hanton and P. W. Dyer, *ACS Catal.*, 2018, **8**, 11249–11263.
- 3 T. E. Kuzmenko, A. L. Samusenko, V. P. Uralets and R. V. Golovnya, *J. High Resolut. Chromatogr.*, 1979, **2**, 43–44.
- 4 W. R. H. Wright, A. S. Batsanov, J. A. K. Howard, R. P. Tooze, M. J. Hanton and P. W. Dyer, *Dalton Trans.*, 2010, **39**, 7038–7045.