

A Standard System of Characterization for Olefin Metathesis Catalysts

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1. Methods and Materials

1.1. Materials

Unless otherwise indicated, all compounds were purchased from Aldrich or Fisher. Allylbenzene, tridecane, and *cis*-1,4-diacetoxy-2-butene were distilled from anhydrous potassium carbonate prior to use. (Compounds can also be distilled and stored in degassed Schlenk flasks for extended periods of time.) Anhydrous dichloromethane (purchased from Fisher) was obtained via elution through a solvent column drying system.¹ 5-Hexenyl acetate (Aldrich) was distilled and stored in a sealed vial under Ar. Methyl acrylate (Aldrich, 99%) was used as received. Anthracene (Aldrich) was used as received. CD₂Cl₂ was purchased from Cambridge Isotope Laboratories and distilled from CaH₂ into a Schlenk tube and freeze/pump/thawed 3 times. *cis*, *cis*-1,5-Cyclooctadiene (Aldrich) was distilled immediately prior the polymerization reaction, as aged *cis*, *cis*-1,5-cyclooctadiene afforded inferior results.

1.2. Instrumentation

Gas chromatography data was obtained using an Agilent 6850 FID gas chromatograph equipped with a DB-Wax Polyethylene Glycol capillary column (J&W Scientific).

1.3. Stock Solution Preparation

A single stock solution can be prepared that contains enough catalyst for all three RCM reactions as well as the ROMP reaction. Inside a glovebox, a volumetric flask is charged with catalyst (0.016 mmol) and CD₂Cl₂ added to prepare 1.0 mL of stock solution (0.016 M).

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 518-1520.

2. Ring Closing Metathesis

2.1.RCM of Diethyldiallyl malonate (**8**)

An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.016 M, 50 μ L, 0.80 μ mol, 1.0 mol%) and CD₂Cl₂ (0.75 mL). The sample was equilibrated at 30 ° C in the NMR probe before **8** (19.3 μ L, 19.2 mg, 0.080 mmol, 0.1 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **9** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.61 (dt), with those in the product, δ 2.98 (s).

2.2.RCM of Diethylallylmethallyl malonate (**10**)

An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.016 M, 50 μ L, 0.80 μ mol, 1.0 mol%) and CD₂Cl₂ (0.75 mL). The sample was equilibrated at 30 ° C in the NMR probe before **10** (20.5 μ L, 20.4 mg, 0.080 mmol, 0.1 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **11** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.67 (s), 2.64 (dt), with those in the product, δ 2.93 (s), 2.88 (m).

2.3.RCM of Diethyldimethallyl malonate (**12**)

An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.016 M, 250 μ L, 4.0 μ mol, 5.0 mol%) and CD₂Cl₂ (0.55 mL). Olefin **12** (21.6 μ L, 21.5 mg, 0.080 mmol, 0.1 M) was added via syringe and the sample placed in an oil bath regulated at 30 °C. A ¹H NMR spectrum was taken after 4 d. The conversion to **13** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.71 (s), with those in the product, δ 2.89 (s).

2.4. Experimental Data

Figure S1. ^1H NMR spectrum of reaction mixture from eq 1.

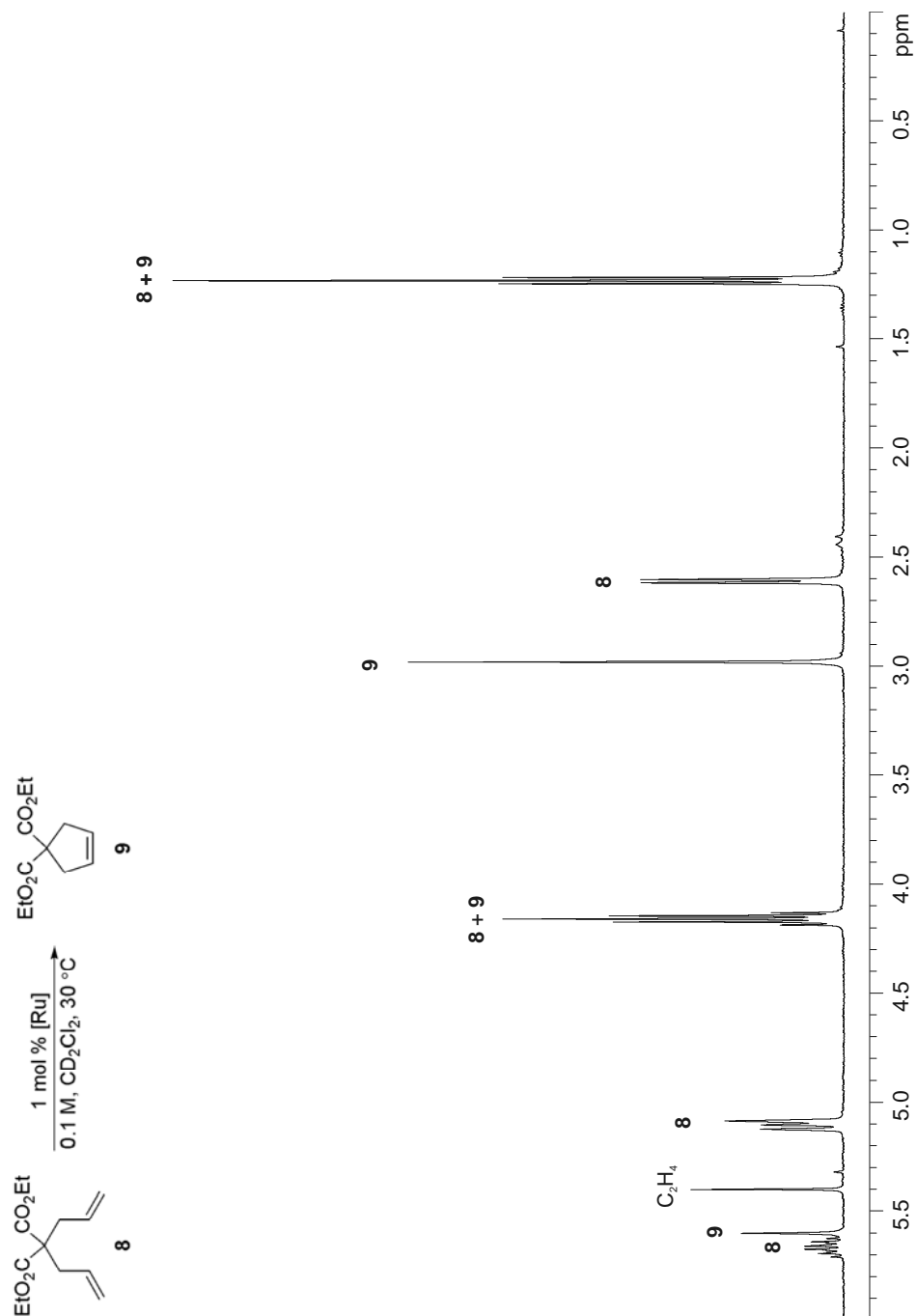


Table S1. Conversion to disubstituted olefin product **9** using **1**.

Time (min)	Conversion (%)
0.58	34.3
0.75	41.0
1.00	48.5
1.33	54.1
1.75	57.7
2.25	59.7
2.83	60.6
3.50	61.2
4.25	61.3
5.08	61.6
6.00	61.9
7.00	62.0
8.08	62.3
9.25	62.4
10.50	62.6
11.83	62.8
13.25	63.2
14.75	63.4
16.33	63.8
18.00	63.9
19.75	64.4
21.58	64.6
23.50	65.0
25.50	65.4
27.58	65.7
29.75	66.1
32.00	66.4
34.33	66.8
36.75	67.3
39.25	67.8
41.83	68.1
44.50	68.6
47.25	69.0
50.08	69.6
53.00	70.1
56.00	70.7
59.08	71.2
62.25	71.7
65.50	72.2
68.83	72.9
72.25	73.4
75.75	74.3

Table S2. Conversion to disubstituted olefin product **9** using **2**.

Time (min)	Conversion (%)
1.35	0.2
1.73	0.6
2.15	1.0
2.60	1.6
3.08	2.3
3.60	3.2
4.15	4.4
4.73	5.8
5.35	7.5
6.00	9.6
6.68	12.2
7.40	15.2
8.15	18.6
8.93	22.5
9.75	26.9
10.60	31.7
11.48	36.6
12.40	41.8
13.35	47.1
14.33	52.2
15.35	57.2
16.40	61.9
17.48	66.3
18.60	70.3
19.75	73.9
20.93	77.2
22.15	80.1
23.40	82.4
24.68	84.7
26.00	86.7
27.35	88.2
28.73	89.6
30.15	90.8
31.60	91.9
33.08	92.7
34.60	93.4
36.15	94.1
37.73	94.6
39.35	95.1
41.00	95.4
42.68	95.8
44.40	96.1
46.15	96.4
47.93	96.7

49.75	96.8
51.60	97.1
53.48	97.2
55.40	97.3
57.35	97.6
59.33	97.7
61.35	97.8
63.40	97.9
65.48	98.0
67.60	98.1
69.75	98.3
71.93	98.3
74.15	98.4
76.40	98.5

Table S3. Conversion to disubstituted olefin product **9** using **3**.

<u>Time (min)</u>	<u>Conversion (%)</u>
0.85	0.3
1.22	1.5
1.60	4.4
2.00	8.3
2.42	12.8
2.85	17.5
3.30	22.2
3.77	27.0
4.25	31.6
4.75	36.1
5.27	40.6
5.80	44.8
6.35	48.9
6.92	52.8
7.50	56.4
8.10	59.8
8.72	63.1
9.35	66.2
10.00	69.0
10.67	71.6
11.35	74.1
12.05	76.3
12.77	78.4
13.50	80.3
14.25	82.1
15.02	83.7
15.80	85.1
16.60	86.6
17.42	87.8

18.25	89.0
19.10	90.0
19.97	91.0
20.85	91.8
21.75	92.5
22.67	93.2
23.60	93.9
24.55	94.4
25.52	94.9
26.50	95.3
27.50	95.8
28.52	96.1
29.55	96.4
30.60	96.7
31.67	96.9
32.75	97.2
33.85	97.4
34.97	97.6
36.10	97.8
37.25	97.8
38.42	98.0
39.60	98.1
40.80	98.2
42.02	98.3

Table S4: Conversion to disubstituted olefin product **9** using **4**.

Time (min)	Conversion (%)
1.35	7.6
1.72	11.4
2.10	15.9
2.50	20.0
2.92	24.9
3.35	29.4
3.80	34.3
4.27	38.8
4.75	43.7
5.25	48.1
5.77	52.6
6.30	56.6
6.85	60.6
7.42	64.5
8.00	68.2
8.60	71.5
9.22	74.6
9.85	77.5
10.50	80.1

11.17	82.5
11.85	84.8
12.55	86.7
13.27	88.3
14.00	89.9
14.75	91.5
15.52	92.4
16.30	93.8
17.10	94.4
17.92	95.3
18.75	96.1
19.60	96.6
20.47	97.1
21.35	97.4
22.25	97.9
23.17	98.1
24.10	98.3
25.05	98.5
26.02	98.8
27.00	98.9
28.00	98.9
29.02	99.2
30.05	99.5
31.10	99.4
32.17	99.3
33.25	99.3
34.35	99.4
35.47	99.6
36.60	99.7
37.75	99.5
38.92	99.6
40.10	99.6
41.30	99.5
42.52	99.7
43.75	99.8
45.00	99.6
46.27	99.7
47.55	99.8
48.85	99.7
50.17	99.7
51.50	99.6
52.85	99.6

Table S5: Conversion to disubstituted olefin product **9** using **5**.

Time (min)	Conversion (%)
1.35	0.8
1.72	1.6
2.10	2.6
2.50	3.8
2.92	5.4
3.35	7.0
3.80	8.8
4.27	10.7
4.75	12.6
5.25	14.7
5.77	16.9
6.30	19.0
6.85	21.1
7.42	23.3
8.00	25.6
8.60	27.8
9.22	30.0
9.85	32.2
10.50	34.5
11.17	36.6
11.85	38.8
12.55	41.0
13.27	43.0
14.00	45.1
14.75	47.1
15.52	49.1
16.30	51.0
17.10	52.9
17.92	54.7
18.75	56.5
19.60	58.2
20.47	59.8
21.35	61.5
22.25	63.0
23.17	64.6
24.10	66.0
25.05	67.4
26.02	68.8
27.00	70.1
28.00	71.4
29.02	72.6
30.05	73.8
31.10	74.9
32.17	76.0

33.25	76.9
34.35	78.0
35.47	78.9
36.60	79.8
37.75	80.7
38.92	81.5
40.10	82.4
41.30	83.3
42.52	83.9
43.75	84.8
45.00	85.5
46.27	86.2
47.55	86.8
48.85	87.3
50.17	87.9
51.50	88.4
52.85	88.9
54.22	89.5
55.60	89.9
57.00	90.4
58.42	90.9
59.85	91.2
61.30	91.6
62.77	92.0
64.25	92.3
65.75	92.7
67.27	92.9
68.80	93.2
70.35	93.5
71.92	93.8
73.50	94.1
75.10	94.4
76.72	94.6
78.35	94.8
80.00	95.0
81.67	95.2
83.35	95.5
85.05	95.6
86.77	95.8

Table S6: Conversion to disubstituted olefin product **9** using **6**.

<u>Time (min)</u>	<u>Conversion (%)</u>
0.85	91.8
1.22	96.8
1.60	98.3
2.00	98.9

2.42	99.4
2.85	99.5
3.30	99.5
3.77	99.5
4.25	99.8
4.75	99.8
5.27	99.8
5.80	99.8
6.35	99.8
6.92	99.8

Table S7: Conversion to disubstituted olefin product **9** using **7**.

<u>Time (min)</u>	<u>Conversion (%)</u>
0.60	16.6
0.72	18.6
0.85	21.9
1.00	25.3
1.17	28.8
1.35	32.3
1.55	35.8
1.77	39.1
2.00	42.3
2.25	45.4
2.52	48.0
2.80	51.1
3.10	53.6
3.42	55.7
3.75	58.1
4.10	60.2
4.47	62.1
4.85	64.3
5.25	65.9
5.67	67.6
6.10	69.1
6.55	70.5
7.02	71.9
7.50	73.3
8.00	74.5
8.52	75.5
9.05	76.8
9.60	77.8
10.17	78.7
10.75	79.6
11.35	80.6
11.97	81.5
12.60	82.0

13.25	82.8
13.92	83.5
14.60	84.3
15.30	84.8
16.02	85.4
16.75	86.0
17.50	86.5
18.27	87.0
19.05	87.5
19.85	88.0
20.67	88.5
21.50	88.9
22.35	89.2
23.22	89.7
24.10	90.0
25.00	90.5
25.92	90.7
26.85	91.0
27.80	91.3
28.77	91.7
29.75	91.8
30.75	92.2
31.77	92.3
32.80	92.7
33.85	93.0
34.92	93.2
36.00	93.4
37.10	93.5
38.22	93.8
39.35	93.8
40.50	94.0
41.67	94.2
42.85	94.5
44.05	94.6
45.27	94.9
46.50	94.9
47.75	94.9
49.02	95.2
50.30	95.3
51.60	95.4
52.92	95.5
54.25	95.6

The plot shows $\ln[(100-\text{conversion in \%})/100 \times \text{concentration (0.1M)}]$ over time. The k_{obs} values can be obtained from the slope of the curve.

Figure S2. Log plots for **3**, **4**, and **7 (8→9)**.

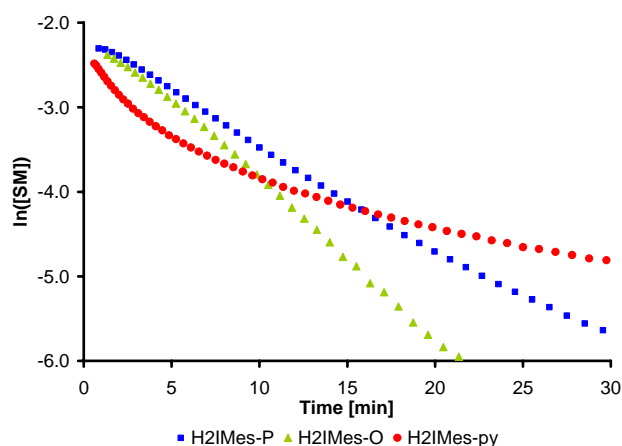


Figure S3. Log plots for **1**, **2**, and **5 (8→9)**.

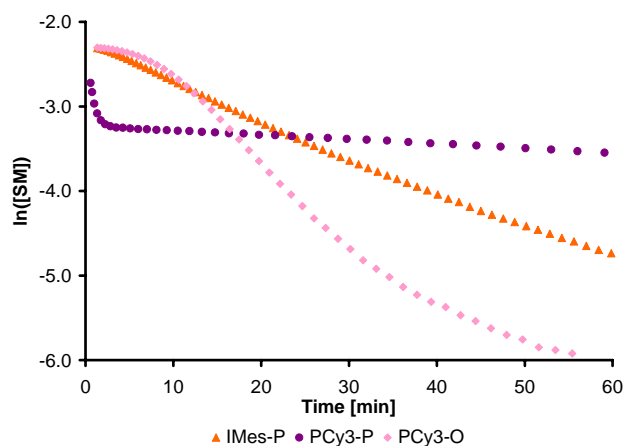


Table S8. k_{obs} values where appropriate (**8→9**).

Catalyst	k_{obs} [s^{-1}]
1	--
2	0.0016 after induction period (25-90%)
3	0.0022
4	0.0030
5	0.00075
6	>0.04
7	>0.0041 (first 50%)

Figure S4. ^1H NMR spectrum of reaction mixture from eq 2.

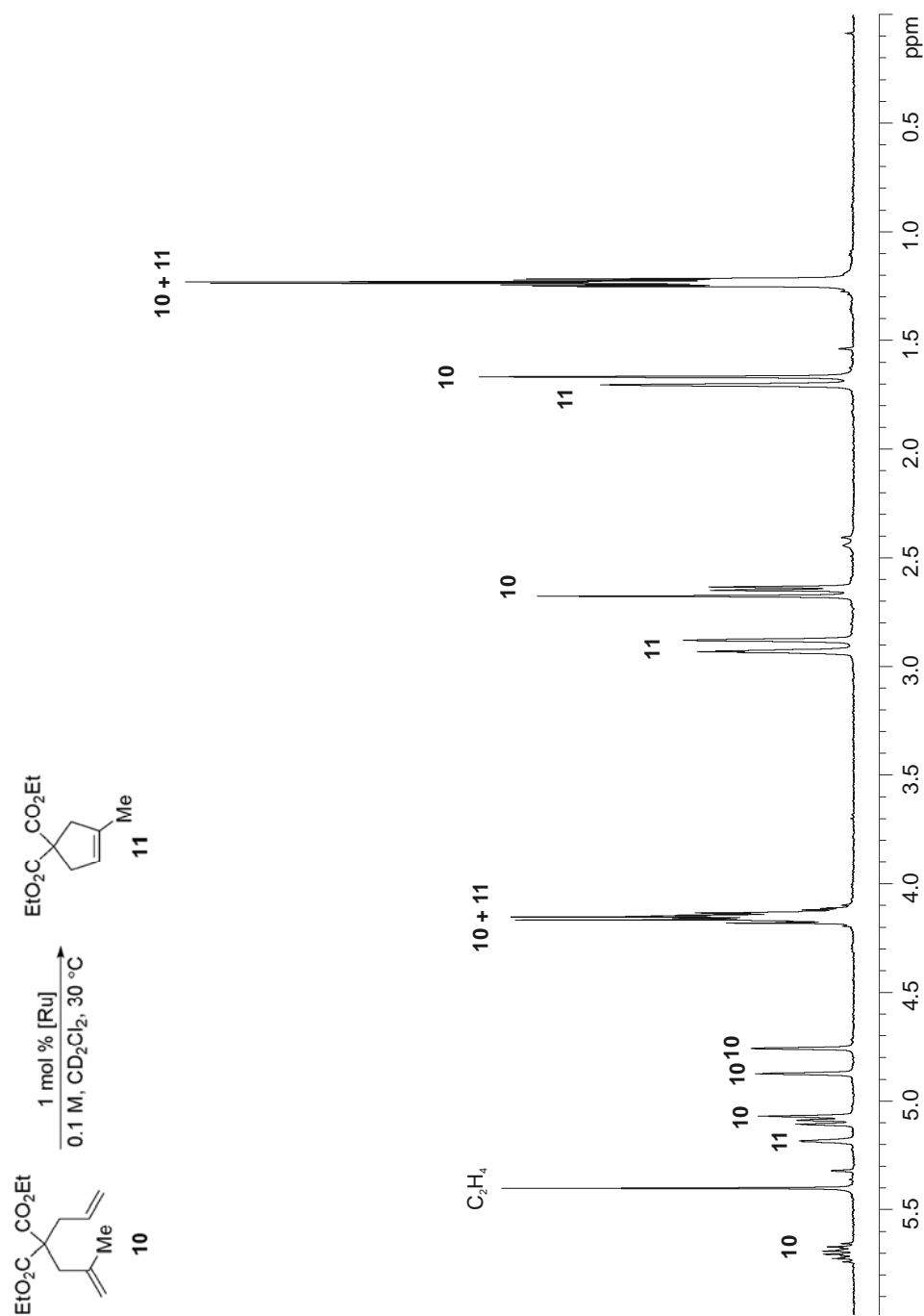


Table S9: Conversion to trisubstituted olefin product **11** using **1**.

Time (min)	Conversion (%)
1.35	6.5
1.75	8.7
2.20	11.0
2.70	12.7

3.25	14.1
3.85	15.1
4.50	16.0
5.20	16.7
5.95	17.1
6.75	17.4
7.60	17.6
8.50	17.9
9.45	17.9
10.45	18.1
11.50	18.0
12.60	18.2
13.75	18.1
14.95	18.3
16.20	18.3
17.50	18.6
18.85	18.5
20.25	18.7
21.70	18.7
23.20	18.7
24.75	18.8
26.35	18.8
28.00	18.9
29.70	19.2
31.45	19.2
33.25	19.4
35.10	19.4
37.00	19.5
38.95	19.7
40.95	19.7
43.00	19.9
45.10	20.0
47.25	20.2
49.45	20.3
51.70	20.2
54.00	20.5
56.35	20.7
58.75	20.9
61.20	21.0
63.70	21.3
66.25	21.3
68.85	21.6
71.50	21.8
74.20	22.0
76.95	22.3
79.75	22.6

82.60	22.7
85.50	23.1
88.45	23.3
91.45	23.6
94.50	23.9
97.60	24.3
100.75	24.6
103.95	24.8
107.20	25.3
110.50	25.7
113.85	26.0
117.25	26.4

Table S10: Conversion to trisubstituted olefin product **11** using **2**.

Time (min)	Conversion (%)
0.95	0.2
1.40	0.2
2.02	0.5
2.80	0.5
3.75	0.6
4.87	0.6
6.15	1.0
7.60	1.3
9.22	1.8
11.00	2.1
12.95	2.7
15.07	3.5
17.35	4.5
19.80	5.6
22.42	6.8
25.20	8.2
28.15	10.0
31.27	11.8
34.55	13.6
38.00	15.9
41.62	18.0
45.40	20.1
49.35	22.4
53.47	24.8
57.75	27.1
62.20	29.2
66.82	31.5
71.60	33.6
76.55	35.8
81.67	37.7
86.95	39.6

92.40	41.6
120.67	50.1
228.67	64.3
834.67	87.6

Table S11: Conversion to trisubstituted olefin product **11** using **3**.

Time (min)	Conversion (%)
1.35	2.4
1.73	5.1
2.15	8.1
2.60	11.5
3.08	14.7
3.60	18.4
4.15	21.8
4.73	25.4
5.35	29.1
6.00	32.8
6.68	36.6
7.40	40.3
8.15	43.9
8.93	47.4
9.75	50.9
10.60	54.2
11.48	57.4
12.40	60.4
13.35	63.4
14.33	65.9
15.35	68.4
16.40	70.7
17.48	73.0
18.60	75.1
19.75	77.0
20.93	78.8
22.15	80.4
23.40	82.0
24.68	83.5
26.00	84.8
27.35	86.1
28.73	87.2
30.15	88.3
31.60	89.4
33.08	90.4
34.60	91.2
36.15	92.1
37.73	92.9
39.35	93.5

41.00	94.1
42.68	94.6
44.40	95.1
46.15	95.5
47.93	95.8
49.75	96.1
51.60	96.6
53.48	97.0
55.40	97.1
57.35	97.5
59.33	97.7
61.35	98.0
63.40	98.0
65.48	98.2
67.60	98.3
69.75	98.6
71.93	98.7
74.15	98.8
76.40	99.0
78.68	99.0
81.00	99.2

Table S12: Conversion to trisubstituted olefin product **11** using **4**.

Time (min)	Conversion (%)
1.37	3.5
1.77	5.3
2.20	7.2
2.67	10.0
3.17	12.5
3.70	15.2
4.27	18.1
4.87	21.7
5.50	24.6
6.17	28.3
6.87	31.9
7.60	35.4
8.37	39.2
9.17	42.7
10.00	46.7
10.87	50.2
11.77	54.0
12.70	57.2
13.67	60.6
14.67	63.7
15.70	66.9
16.77	69.7

17.87	72.3
19.00	74.9
20.17	77.5
21.37	79.5
22.60	81.5
23.87	83.3
25.17	85.3
26.50	86.8
27.87	87.9
29.27	89.2
30.70	90.3
32.17	91.3
33.67	92.2
35.20	92.8
36.77	93.6
38.37	94.4
40.00	94.9
41.67	95.0
43.37	95.6
45.10	95.9
46.87	96.3
48.67	96.9
50.50	97.0
52.37	97.2
54.27	97.5
56.20	97.6
58.17	97.8
60.17	98.2
62.20	98.1

Table S13: Conversion to trisubstituted olefin product **11** using **5**.

Time (min)	Conversion (%)
1.37	0.0
1.77	0.7
2.20	1.6
2.67	2.8
3.17	4.2
3.70	5.6
4.27	7.5
4.87	9.2
5.50	11.0
6.17	13.1
6.87	15.0
7.60	17.0
8.37	19.2
9.17	21.3

10.00	23.5
10.87	25.7
11.77	27.8
12.70	30.1
13.67	32.2
14.67	34.3
15.70	36.5
16.77	38.4
17.87	40.6
19.00	42.5
20.17	44.4
21.37	46.2
22.60	48.1
23.87	49.9
25.17	51.6
26.50	53.3
27.87	54.9
29.27	56.4
30.70	57.9
32.17	59.3
33.67	60.8
35.20	62.2
36.77	63.5
38.37	64.7
40.00	65.9
41.67	67.1
43.37	68.2
45.10	69.3
46.87	70.4
48.67	71.5
50.50	72.6
52.37	73.7
54.27	74.7
56.20	75.9
58.17	76.9
60.17	77.6
62.20	78.5
64.27	79.3
66.37	80.1
68.50	80.8
70.67	81.5
72.87	82.2
75.10	83.0
77.37	83.6
79.67	84.2
82.00	84.7

84.37	85.2
86.77	85.8
89.20	86.3
91.67	86.9
94.17	87.3
96.70	87.7
99.27	88.2
101.87	88.7
104.50	89.1
107.17	89.5
109.87	90.0
112.60	90.3
115.37	90.6
118.17	91.0
121.00	91.4

Table S14: Conversion to trisubstituted olefin product **11** using **6**.

Time (min)	Conversion (%)
0.60	66.5
0.72	71.1
0.85	76.0
1.00	79.9
1.17	82.9
1.35	85.1
1.55	87.2
1.77	88.6
2.00	89.7
2.25	90.8
2.52	91.6
2.80	92.1
3.10	92.9
3.42	93.3
3.75	93.9
4.10	93.9
4.47	94.3
4.85	94.7
5.25	94.7
5.67	95.0
6.10	95.3
6.55	95.4
7.02	95.4
7.50	95.3
8.00	95.7
8.52	95.4
9.05	95.8
9.60	95.7

10.17	95.9
10.75	95.9
11.35	95.7
11.97	96.0
12.60	95.7
13.25	95.8
13.92	95.8
14.60	95.8
15.30	95.8
16.02	96.0
16.75	95.8
17.50	95.8
18.27	95.8
19.05	95.8
19.85	96.1
20.67	96.0
21.50	96.2
22.35	96.2
23.22	96.1
24.10	95.9
25.00	96.2

Table S15: Conversion to trisubstituted olefin product **11** using **7**.

Time (min)	Conversion (%)
0.67	11.3
0.87	13.7
1.10	16.2
1.37	19.2
1.67	21.7
2.00	24.1
2.37	26.4
2.77	28.7
3.20	31.1
3.67	32.7
4.17	34.6
4.70	36.5
5.27	38.0
5.87	39.7
6.50	41.2
7.17	43.2
7.87	44.4
8.60	45.9
9.37	47.1
10.17	48.6
11.00	50.1
11.87	51.0

12.77	52.1
13.70	53.7
14.67	54.8
15.67	55.8
16.70	57.0
17.77	58.0
18.87	59.1
20.00	60.3
21.17	61.3
22.37	62.4
23.60	63.6
24.87	64.5
26.17	65.7
27.50	66.5
28.87	67.5
30.27	68.4
31.70	69.3
33.17	70.2
34.67	71.0
36.20	71.8
37.77	72.6
39.37	73.0
41.00	73.6
42.67	74.1
44.37	74.7
46.10	75.5
47.87	75.5
49.67	76.1
51.50	76.8
53.37	77.2
55.27	77.3
57.20	78.3
59.17	78.2
61.17	78.5
63.20	78.9
65.27	79.1
67.37	79.4
69.50	79.2

Figure S5. Log plots for **3**, **4**, and **6** (**10**→**11**).

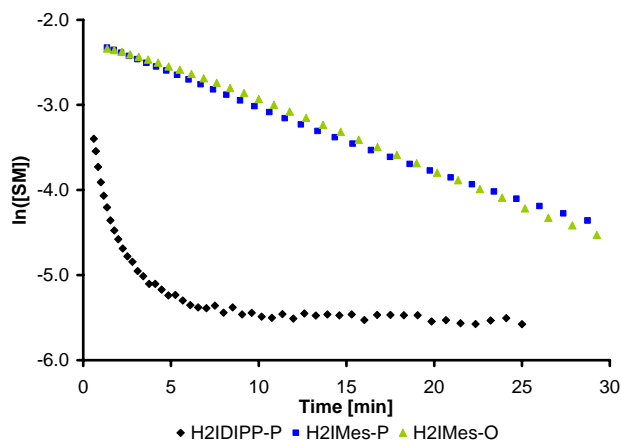


Figure S6. Log plots for **1**, **2**, **5** and **7** (**10**→**11**).

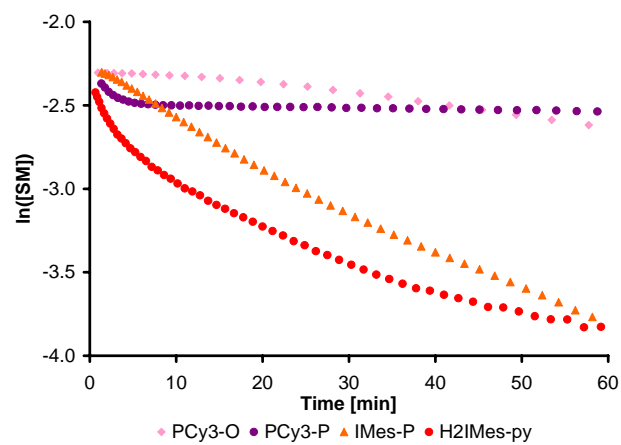
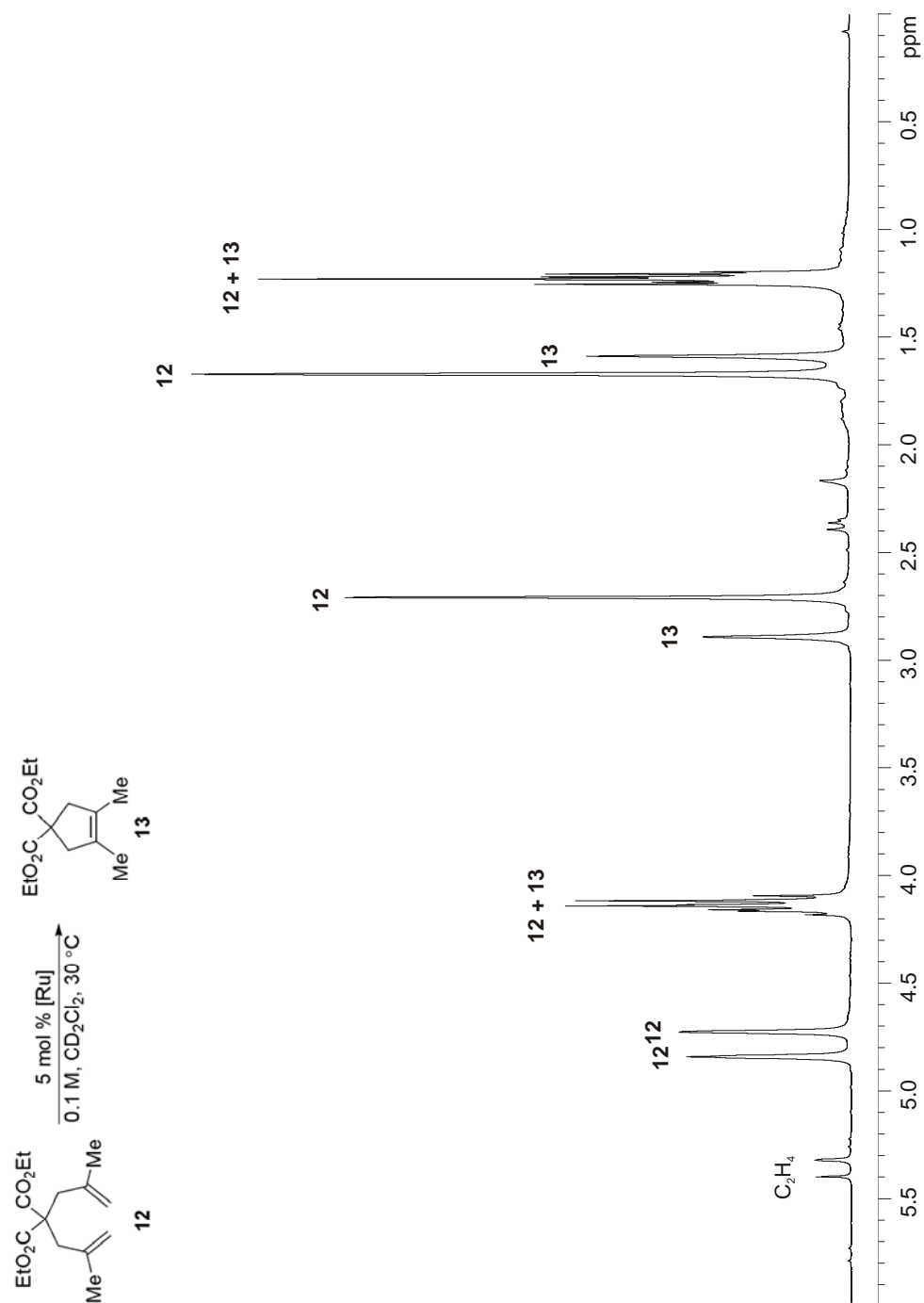


Table S16. k_{obs} values where appropriate (**10**→**11**).

Catalyst	k_{obs} [s^{-1}]
1	--
2	0.00011 after induction period (25-90%)
3	0.0012
4	0.0012
5	0.00038 (some slowing)
6	>0.01
7	>0.0018 (first 25%)

Figure S7. ^1H NMR spectrum of reaction mixture from eq 2.

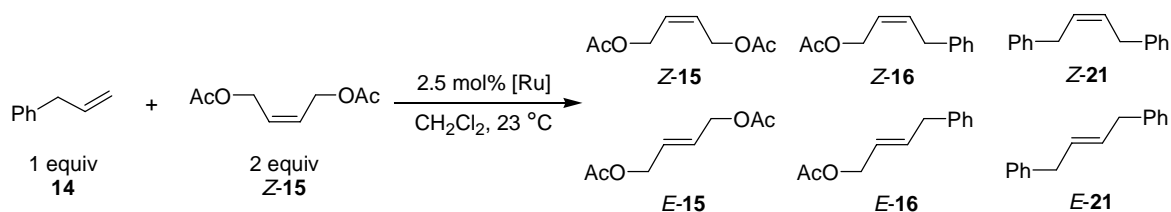


3. Cross Metathesis

3.1. Cross metathesis of allylbenzene with *cis*-1,4-diacetoxy-2-butene

Allylbenzene (1.00 mL, 7.55 mmol) and tridecane (0.920 mL, 3.77 mmol) were combined in a flame-dried, 1-dram vial under an atmosphere of argon. The mixture was stirred before taking a t_0 timepoint. Reactions were run with 51 μL of this solution in lieu of adding the allylbenzene and tridecane separately.

General Reaction Procedure:



To a flame-dried 1-dram vial, 5.0 μmol of catalyst was added. The vial was purged with argon (~5 min), and then 1.0 mL of anhydrous dichloromethane was added. *cis*-1,4-Diacetoxy-2-butene (64 μL , 0.40 mmol) and the allylbenzene/tridecane mixture (51 μL ; 0.20 mmol 14 + 0.10 mmol tridecane) were then added via syringe. The reaction was allowed to stir at 23 °C. Aliquots were taken at the specified time periods.

Samples for GC analysis were obtained by adding ca. 30- μL reaction aliquot to 500 μL of a 3M solution of ethyl vinyl ether in dichloromethane.² The sample was shaken, allowed to stand for 5 min, and then analyzed via GC. All reactions were performed in duplicate to confirm reproducibility.

Data Analysis. To obtain accurate conversion data, GC response factors were obtained for all starting materials and products (ethylene excluded). Tridecane was used as the internal standard. To determine conversion factors, 0.025 M stock solutions were prepared of each compound. These solutions were then used for the preparation of various 10-mL solutions at different

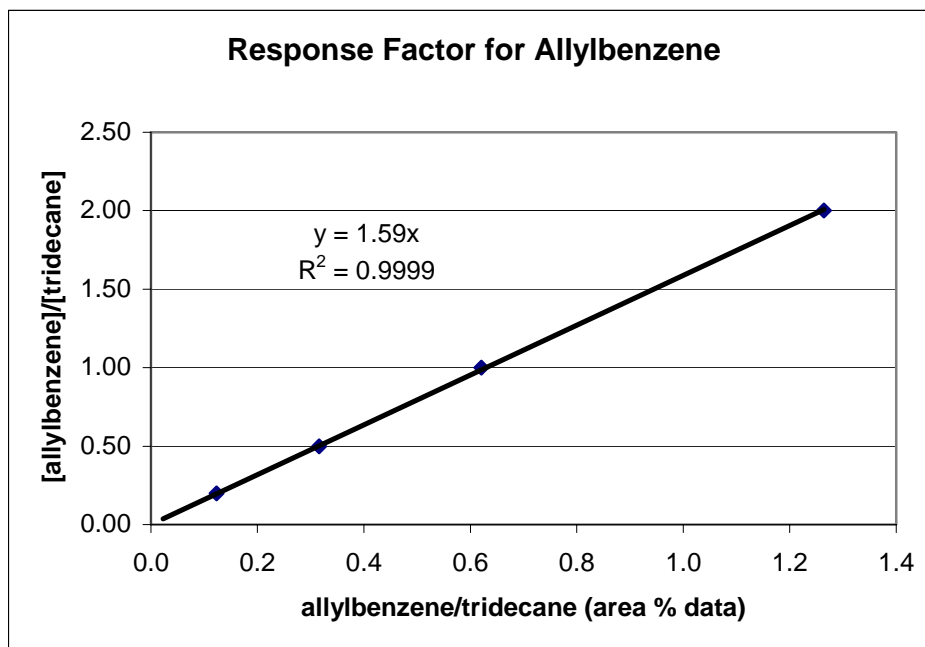
² Ethyl vinyl ether functions as an effective catalyst quencher, as the corresponding Fischer carbene complex is inactive for CM. See: Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153-2164.

[olefin]/[tridecane] ratios. For example, to obtain the GC response factor for allylbenzene (**14**), the following solutions were prepared and analyzed via GC:

Table S17: Determination of the conversion factor of allylbenzene vs. tridecane.

[allylbenzene]/[tridecane]	allylbenzene [%]	tridecane [%]	allylbenzene/tridecane (exp)
2.00	55.83	44.17	1.26
1.00	38.30	61.70	0.62
0.50	24.02	75.98	0.32
0.20	10.96	89.04	0.12

The ratio of the area percent data was plotted against to the molar ratio of each solution. The corresponding response factor for allylbenzene (1.59 ± 0.01) was determined by fitting the data to a linear trendline ($y = mx$):



The response factors for the *E* and *Z* stereoisomers of 1,4-diacetoxy-2-butene (**15**), cross-product **16**, and 1,4-diphenyl-2-butene (**21**) were analogously obtained. Molar ratios were confirmed via ^1H NMR spectroscopy (CDCl_3 ; Varian Mercury 300 MHz NMR spectrometer). The GC response factor and retention time data for each compound are listed below:

Table S18: Response factors.

compound	response factor	retention time (min)
tridecane	--	11.34
allylbenzene	1.59	10.78
Z-15	2.48	18.04
E-15	2.48	18.62
Z-16	1.27	21.15
E-16	1.27	21.37
Z-21	0.91	24.20
E-21	0.91	23.95

**Note: response factors and retention times are instrument dependent; values may vary on alternate machines.*

Instrument conditions. Inlet temperature: 250 °C; detector temperature: 250 °C; hydrogen flow: 32 mL/min; air flow: 400 mL/min; constant col + makeup flow: 30 mL/min.

GC Method. 50 °C for 5 minutes, followed by a temperature increase of 10 °C/min to 240 °C and a subsequent isothermal period at 240 °C for 5 minutes (total run time = 29 minutes).

GC data for each timepoint were analyzed according to the following model spreadsheets:

Table S19: Example for calculation of compound concentrations

timepoint at t = x min

Compound	GC Peak Area%	ratio (compound/tridecane)	ratio * convfactor	[compound] (M)
tridecane	A			0.09
14	B	B/A	1.59(B/A)	0.09[1.59(B/A)]
<i>cis</i> - 15	C	C/A	2.48(C/A)	0.09[2.48(C/A)]
<i>trans</i> - 15	D	D/A	2.48(D/A)	0.09[2.48(D/A)]
<i>cis</i> - 16	E	E/A	1.27(E/A)	0.09[1.27(E/A)]
<i>trans</i> - 16	F	F/A	1.27(F/A)	0.09[1.27(F/A)]
<i>cis</i> - 22	G	G/A	0.91(G/A)	0.09[0.91(G/A)]
<i>trans</i> - 22	H	H/A	0.91(H/A)	0.09[0.91(H/A)]

For example, in the CM of **14** with **15** using catalyst **3**, the following data were obtained:

t₀ timepoint

Compound	GC Peak Area%	ratio (olefin/tridecane)	ratio * convfactor	[compound] (M)
tridecane	43.76			0.09
14	56.24	1.29	2.04	0.18

timepoint at 4 min

Compound	GC Peak Area%	ratio (compound/tridecane)	ratio * convfactor	[compound] (M)
tridecane	26.73			0.090
14	14.92	0.56	0.89	0.079
<i>cis</i> - 15	17.29	0.65	1.60	0.144
<i>trans</i> - 15	16.02	0.60	1.49	0.133
<i>cis</i> - 16	4.41	0.17	0.21	0.019
<i>trans</i> - 16	19.05	0.71	0.90	0.081
<i>cis</i> - 22	0.16	0.01	0.01	0.0005
<i>trans</i> - 22	0.53	0.02	0.02	0.0016

<i>cis:trans</i> 15	1.1
% conv of 14 to 16	55
<i>trans:cis</i> 16	4.3
% conv of 14 to 21	1
<i>trans:cis</i> 21	3.2

E/Z ratios were calculated directly from the molarity data for each compound; conversions were determined via comparison of the molarity data at each timepoint to the starting concentration of **14**.

3.2. Experimental Data.

Figure S8. Sample GC chromatogram from eq 4.

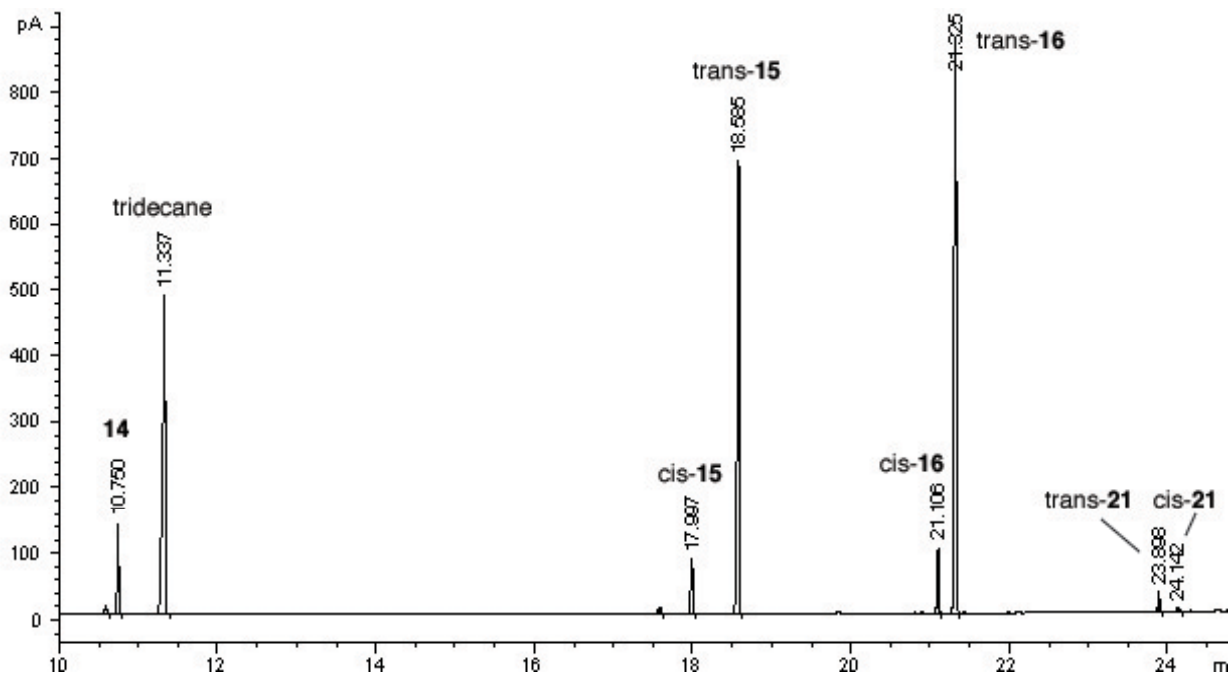


Table S20. CM of **14** with **15** using catalyst **1**.

time (min)	2	5	10	15	30	45	60	90	120	180	240	480
<i>Z:E</i> of 15	32.2	31.1	28.8	26.1	19.2	14.1	10.6	6.7	4.6	2.7	1.8	0.80
% conv of 14 to 16	2	4	8	11	18	25	31	39	46	54	59	66
<i>E:Z</i> of 16	4.7	4.5	4.3	4.2	4.0	3.9	3.8	3.8	3.9	4.1	4.3	5.0
% conv of 14 to 21	2	3	5	7	10	12	13	15	16	16	14	12
<i>E:Z</i> of 21	1.1	1.1	1.2	1.2	1.4	1.5	1.5	1.8	1.8	2.1	2.0	2.4

Table S21. CM of **14** with **15** using catalyst **2**.

time (min)	5	10	15	20	30	45	60	90	120	240
<i>Z:E</i> of 15	31.4	28.6	25.8	23.5	20.0	16.2	13.6	10.3	8.3	5.0
% conv of 14 to 16	3	7	11	13	17	21	25	30	34	43
<i>E:Z</i> of 16	4.7	4.4	4.3	4.2	4.1	4.0	3.9	3.9	3.8	3.9
% conv of 14 to 21	4	6	8	8	10	10	13	14	15	14
<i>E:Z</i> of 21	2.3	1.8	1.9	1.4	1.5	1.4	1.7	1.7	1.9	1.6

Table 22. CM of **14** with **15** using catalyst **3**.

time (min)	2	4	6	8	10	12	15	30
<i>Z:E</i> of 15	3.7	1.1	0.44	0.23	0.14	0.11	0.08	0.07
% conv of 14 to 16	24	55	70	76	78	79	79	79
<i>E:Z</i> of 16	3.2	4.3	5.7	7.0	8.2	9.0	9.7	10.1
% conv of 14 to 21		1	2	2	3	3	3	4
<i>E:Z</i> of 21		3.2	3.7	4.2	4.6	4.9	5.2	5.5

Table S23. CM of **14** with **15** using catalyst **4**.

time (min)	1	2	5	7.5	10	15	20	30
<i>Z:E</i> of 15	0.34	0.13	0.07	0.07	0.07	0.07	0.07	0.07
% conv of 14 to 16	70	75	75	74	73	72	72	72
<i>E:Z</i> of 16	6.2	8.4	10.0	10.1	10.1	10.1	10.0	10.1
% conv of 14 to 21	2	4	6	4	4	5	5	5
<i>E:Z</i> of 21	3.6	4.4	4.9	5.3	5.6	5.9	5.8	5.9

Table S24. CM of **14** with **15** using catalyst **5**.

time (min)	10	15	20	45	60	90	120	150	255	330	1376
<i>Z:E</i> of 15	12.6	9.8	7.9	3.4	2.4	1.3	0.75	0.47	0.15	0.11	0.07
% conv of 14 to 16	4	6	9	20	28	39	49	59	71	75	84
<i>E:Z</i> of 16	2.7	3.2	3.5	4.1	4.4	4.9	5.5	6.0	7.7	7.9	8.9
% conv of 14 to 21										2	3
<i>E:Z</i> of 21										2.5	4.2

Table S25. CM of **14** with **15** using catalyst **6**.

time (min)	2	5	10	15	30
<i>Z:E</i> of 15	0.08	0.07	0.07	0.07	0.07
% conv of 14 to 16	75	73	73	73	74
<i>E:Z</i> of 16	9.0	8.8	8.9	9.1	9.2
% conv of 14 to 21	5	6	6	6	6
<i>E:Z</i> of 21	5.1	5.3	5.4	5.6	5.7

Table S26. CM of **14** with **15** using catalyst **7**.

time (min)	1	2	3	4	6	8	10	12	15	20	30
<i>Z:E</i> of 15	4.8	2.4	1.5	1.0	0.53	0.33	0.22	0.17	0.12	0.09	0.08
% conv of 14 to 16	23	38	49	56	66	71	74	75	77	76	76
<i>E:Z</i> of 16	3.1	3.5	3.9	4.4	5.4	6.4	7.2	7.9	8.6	9.4	9.9
% conv of 14 to 21				0.9	1.3	1.6	1.9	2.1	2.4	2.8	3.1
<i>E:Z</i> of 21				3.3	3.5	3.8	4.0	4.2	4.5	4.8	4.9

3.3. Cross metathesis of methyl acrylate and 5-hexenyl acetate

5-Hexenyl acetate (88 mg, 100 μ L, 0.62 mmol) and methyl acrylate (54 mg, 56 μ L, 0.62 mmol) were added to a solution of anthracene (15–20 mg) in 1.55 mL CD_2Cl_2 in a 10 mL round-bottomed flask under argon topped with a reflux condenser. An aliquot of 100 μ L was removed from the solution and was diluted with CD_2Cl_2 in an NMR tube (this is the $t = 0$ point). The reaction solution was heated to 35 $^\circ\text{C}$ and catalyst (0.015 mmol, 2.5 mol % after removal of 100 μ L aliquot) was added in one portion. Aliquots (50–100 μ L) were removed from the reaction solution at the desired times, diluted with CD_2Cl_2 in an NMR tube, and cooled to -78 $^\circ\text{C}$ until the NMR spectrum was taken. Attempts to perform this reaction in an NMR tube or in a sealed flask resulted in incomplete conversions due to ethylene build-up.

All conversions were determined relative to the anthracene internal standard. The anthracene multiplet at 7.48 ppm was given an integration of 1.00 in the spectrum at each time point. The multiplet at 4.98 ppm (2H; $\text{C}=\text{CH}_2$ of 5-hexenyl acetate) and the doublet of doublets at 6.37 ppm (1H; $J = 17.3, 1.7$ Hz; *cis*- $\text{C}=\text{CHH}$ of methyl acrylate) were used as peaks to monitor the disappearance of the starting materials. Product formation was determined two ways: (1) the disappearance of methyl acrylate; (2) the integration of the doublet of triplets at 6.93 ppm (1H; $J = 15.7, 7.2$ Hz; $\text{C}=\text{CHR}$) divided by the sum of the integrations of the peaks at 6.37 ppm and 6.93 ppm. Typically the difference between these two methods was no greater than 5%.

Characterization of **19**:

^1H NMR (300 MHz, CDCl_3) δ : 6.93 (1H, dt, $J = 15.7, 7.2$ Hz), 5.81 (1H, dt, $J = 15.7, 1.4$ Hz), 4.04 (2H, t, $J = 6.3$ Hz), 3.70 (3H, s), 2.22 (2H, dq, $J = 7.2, 1.4$ Hz), 2.02 (3H, s), 1.59–1.66 (2H, m), 1.48–1.56 (2H, m).

^{13}C NMR (75 MHz, CDCl_3) δ : 171.3, 167.2, 148.9, 121.5, 64.2, 51.6, 31.8, 28.2, 24.6, 21.1.

Figure S9. ¹H NMR spectrum of reaction mixture from eq 5.

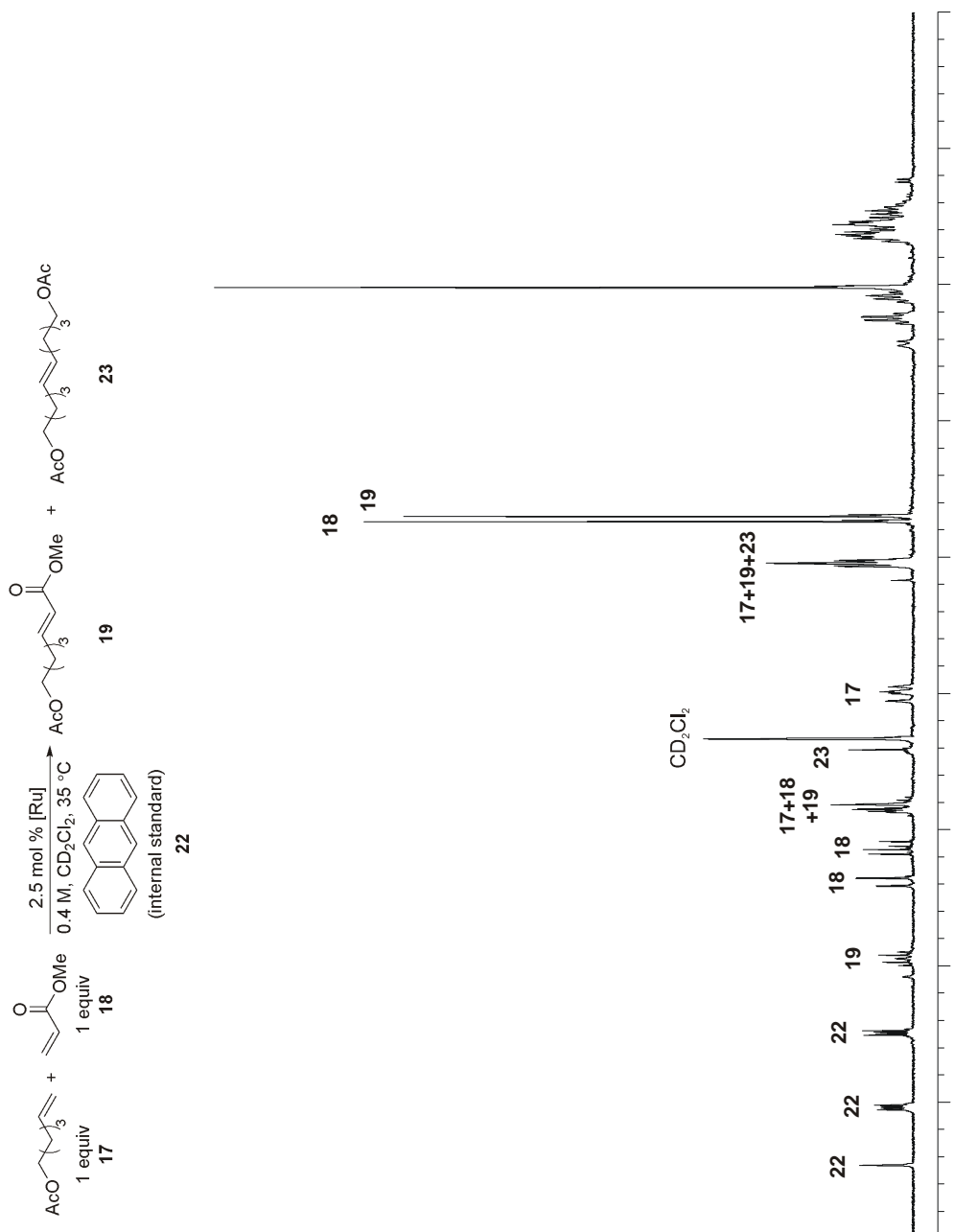


Table S27. Conversion to heterocoupled product **19** using **1**.

time (min)	% hexenyl acetate consumed	% acrylate consumed	% product formed
0	0	0	0
3	35	10	0
5	44	10	0
10	55	9	4
15	62	8	4
20	68	13	6
45	82	15	6
70	87	15	8
460	91	17	10

Table S28. Conversion to heterocoupled product **19** using **2**.

time (min)	% hexenyl acetate consumed	% acrylate consumed	% product formed
0	0	0	0
3	16	6	0
5	26	3	0
10	36	8	0
15	43	8	0
20	48	6	2
45	63	8	3
70	73	9	3
495	91	19	9

Table S29. Conversion to heterocoupled product **19** using **3**.

time (min)	% hexenyl acetate consumed	% acrylate consumed	% product formed
0	0	0	0
3	25	21	21
5	33	29	29
10	66	56	56
15	75	70	70
20	84	71	71
45	96	85	85
70	97	90	90
120	99	98	98
240	98	96	96

Table S30. Conversion to heterocoupled product **19** using **4**.

time (min)	% hexenyl acetate consumed	% acrylate consumed	% product formed
0	0	0	0
3	58	54	54
5	69	62	62
10	76	68	68
15	77	72	72
20	86	78	78
45	95	92	91
70	99	90	90
160	99	92	92
465	99	96	96

Table S31. Conversion to heterocoupled product **19** using **5**.

time (min)	% hexenyl acetate consumed	% acrylate consumed	% product formed
0	0	0	0
3	2	0	0
5	10	8	3
10	8	5	5
15	15	12	9
20	18	16	15
45	41	33	33
70	60	48	48
130	81	70	70
195	89	81	81
460	95	91	91

Table S32. Conversion to heterocoupled product **19** using **6**.

time (min)	% hexenyl acetate consumed	% acrylate consumed	% product formed
0	0	0	0
1	51	30	28
3	61	38	38
5	69	58	56
7.5	76	68	67
10	81	74	73
15	85	81	81
20	88	85	85
45	96	94	94
70	96	93	93

110	98	91	91
320	97	93	93

Table S33. Conversion to heterocoupled product **19** using **7**.

time (min)	% hexenyl acetate consumed	% acrylate consumed	% product formed
0	0	0	0
0.5	19	10	10
1	24	18	16
2	36	27	24
3	42	33	30
4	45	36	35
5	49	38	37
7.5	51	39	38
10	53	42	40
15	56	44	41
495	67	55	54

4. ROMP of 1,5-cyclooctadiene (**20**)

An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.016 M, 25 μ L, 0.40 μ mol, 0.1 mol%) and CD₂Cl₂ (0.775 mL). The sample was equilibrated at 30 ° C in the NMR probe before **20** (49.1 μ L, 43.3 mg, 0.40 mmol, 0.5 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **poly(20)** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.36 (m), with those in the product, δ 2.09 (br m), 2.04 (br m).

Figure S10. ^1H NMR spectrum of reaction mixture from eq 6.

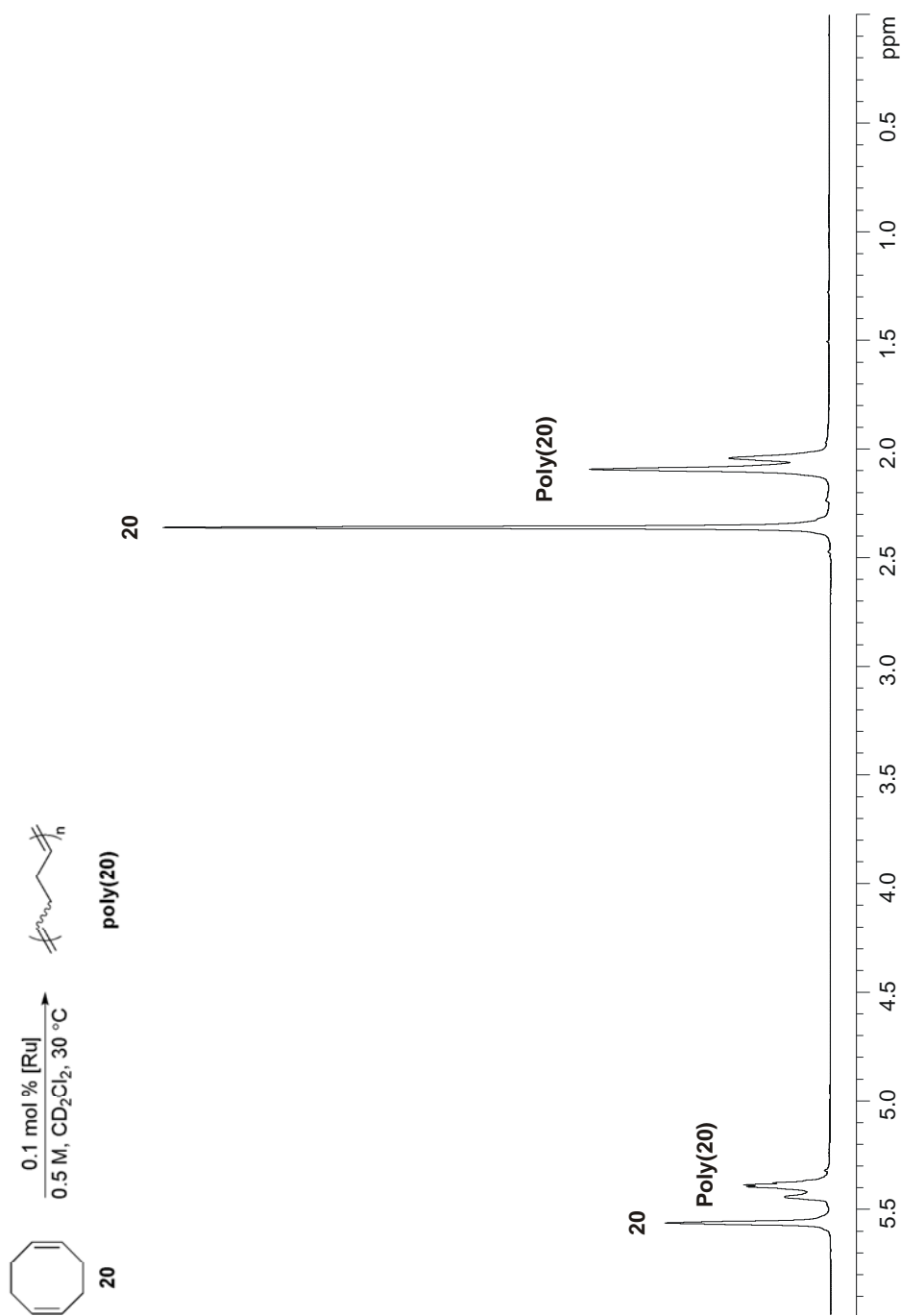


Table S34: Conversion to polymer product poly(**20**) using **1**.

Time (min)	Conversion (%)
1.37	1.9
1.77	2.6
2.20	3.0
2.67	3.5
3.17	3.9
3.70	4.3
4.27	4.9
4.87	5.3
5.50	5.9
6.17	6.5
6.87	6.9
7.60	7.7
8.37	8.3
9.17	8.7
10.00	9.5
10.87	9.9
11.77	10.5
12.70	11.3
13.67	11.8
14.67	12.4
15.70	13.1
16.77	13.7
17.87	14.4
19.00	15.0
20.17	15.6
21.37	16.3
22.60	17.0
23.87	17.6
25.17	18.4
26.50	19.1
27.87	19.7
29.27	20.3
30.70	20.9
32.17	21.6
33.67	22.3
35.20	22.8
36.77	23.7
38.37	24.2
40.00	24.9
41.67	25.5
43.37	26.2
45.10	26.7
46.87	27.5
48.67	28.0

50.50	28.3
52.37	29.7
54.27	29.6
56.20	30.2
58.17	31.1
60.17	31.8
62.20	32.5
64.27	32.9
66.37	33.8
68.50	34.2
70.67	34.6
72.87	35.3
75.10	35.8
77.37	36.3
79.67	37.0
82.00	37.7
84.37	38.2
86.77	38.8
89.20	39.0
91.67	39.7

Table S35: Conversion to polymer product poly(**20**) using **2**.

Time (min)	Conversion (%)
1.37	1.4
1.77	1.7
2.20	1.4
2.67	1.6
3.17	1.4
3.70	1.4
4.27	1.7
4.87	1.7
5.50	1.7
6.17	1.4
6.87	1.7
7.60	1.1
8.37	1.3
9.17	1.5
10.00	1.4
10.87	1.5
11.77	1.1
12.70	1.3
13.67	1.3
14.67	1.6
15.70	1.2
16.77	1.9
17.87	1.4

19.00	2.1
20.17	1.8
21.37	1.7
22.60	1.8
23.87	1.9
25.17	1.8
26.50	1.9
27.87	2.0
29.27	1.9
30.70	1.7
32.17	2.0
33.67	2.4
35.20	2.3
36.77	2.2
38.37	2.7
40.00	2.0
41.67	2.7
43.37	2.5
45.10	2.6
46.87	2.5
48.67	2.6
50.50	2.6
52.37	2.7
54.27	2.6
56.20	2.9
58.17	3.2
60.17	3.0
62.20	3.1
64.27	3.6
66.37	3.2
68.50	3.0
70.67	3.6
72.87	3.5
75.10	3.7
77.37	4.0
79.67	3.6
82.00	3.9
84.37	3.7
86.77	3.8
89.20	4.1
91.67	4.2
94.17	4.4
96.70	4.4
99.27	4.4
101.87	4.4
104.50	4.8

107.17	5.0
109.87	4.8

Table S36: Conversion to polymer product poly(**20**) using **3**.

Time (min)	Conversion (%)
0.60	17.9
0.72	28.3
0.85	38.0
1.00	47.2
1.17	55.8
1.35	64.2
1.55	71.5
1.77	77.3
2.00	82.0
2.25	86.0
2.52	89.1
2.80	91.7
3.10	93.6
3.42	94.9
3.75	96.3
4.10	97.2
4.47	97.6
4.85	98.1
5.25	98.3
5.67	98.5
6.10	99.2
6.55	99.1
7.02	99.2
7.50	99.5
8.00	99.3
8.52	99.4
9.05	99.4
9.60	99.6
10.17	99.5
10.75	99.4

Table S37: Conversion to polymer product poly(**20**) using **4**.

Time (min)	Conversion (%)
0.60	21.7
0.72	32.5
0.85	43.6
1.00	55.3
1.17	65.7
1.35	73.8
1.55	80.3

1.77	85.1
2.00	88.9
2.25	91.9
2.52	94.0
2.80	95.3
3.10	96.8
3.42	97.8
3.75	98.2
4.10	98.9
4.47	99.2
4.85	99.5
5.25	99.4
5.67	99.9
6.10	99.8
6.55	99.7
7.02	99.8
7.50	99.9
8.00	100.1
8.52	100.1
9.05	99.9
9.60	100.0
10.17	99.9
10.75	100.0

Table S38: Conversion to polymer product poly(**20**) using **5**.

Time (min)	Conversion (%)
1.37	0.6
1.77	0.8
2.20	0.8
2.67	0.8
3.17	0.8
3.70	0.8
4.27	1.0
4.87	1.2
5.50	1.3
6.17	1.7
6.87	2.3
7.60	2.8
8.37	4.0
9.17	5.5
10.00	7.6
10.87	10.2
11.77	13.3
12.70	17.1
13.67	20.9
14.67	25.1

15.70	29.6
16.77	33.9
17.87	38.3
19.00	42.5
20.17	46.7
21.37	50.8
22.60	54.6
23.87	58.4
25.17	61.8
26.50	65.2
27.87	68.4
29.27	71.3
30.70	73.6
32.17	76.4
33.67	78.6
35.20	80.7
36.77	82.8
38.37	84.7
40.00	86.2
41.67	87.8
43.37	89.1
45.10	90.4
46.87	91.6
48.67	92.6
50.50	93.6
52.37	94.4
54.27	95.1
56.20	95.7
58.17	96.2
60.17	96.8
62.20	97.3
64.27	97.6
66.37	98.1
68.50	98.2
70.67	98.5
72.87	98.6
75.10	98.8
77.37	99.0
79.67	99.1
82.00	99.2

Table S39: Conversion to polymer product poly(**20**) using **6**.

Time (min)	Conversion (%)
0.60	77.8
0.72	86.3
0.85	89.8

1.00	91.8
1.17	93.5
1.35	95.1
1.55	96.1
1.77	97.0
2.00	97.6
2.25	98.1
2.52	98.5
2.80	98.7
3.10	98.8
3.42	98.9
3.75	99.3
4.10	99.4
4.47	99.6
4.85	99.9
5.25	99.8
5.67	99.6

Table S40: Conversion to polymer product poly(**20**) using **7**.

Time (min)	Conversion (%)
0.60	99.2
0.71	99.2
0.83	99.5
0.95	99.2
1.08	99.9
1.23	99.7
1.38	100.0
1.53	99.9
1.70	99.3
1.88	99.5
2.06	99.9
2.25	99.9
2.45	99.9
2.66	99.5
2.88	99.9
3.10	99.9
3.33	99.9
3.58	99.4
3.83	99.8

Figure S11. Log plots for **3**, **4**, and **6** (**20**→poly(**20**)).

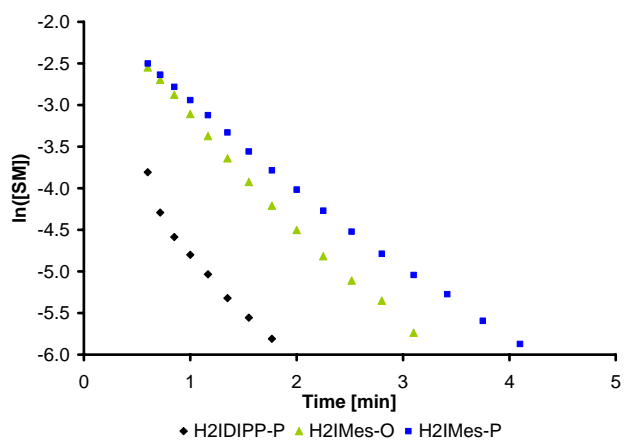


Figure S12. Log plots for **1**, **2**, and **5** (**20**→poly(**20**)).

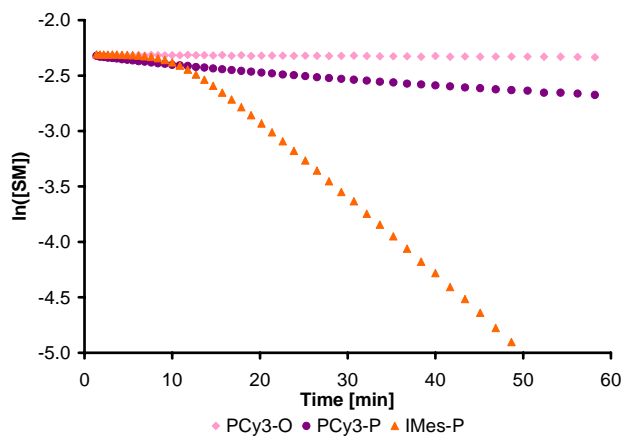


Table S41. k_{obs} values where appropriate (**20**→poly(**20**)).

Catalyst	k_{obs} [s^{-1}]
1	--
2	--
3	0.016
4	0.020
5	0.0012
6	--
7	--(99.5% in <36s)