

Scope and Mechanism of Homogeneous Ta/Ir Tandem Catalytic Alkane/Alkene Upgrading using Sacrificial Hydrogen Acceptors

David C. Leitch, Jay A. Labinger,* and John E. Bercaw*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California, 91125, United States

Supporting Information

Table of Contents

I: General Considerations.....	S2
Materials.....	S2
NMR Spectroscopy.....	S2
GC Analysis.....	S2
II: Mechanistic Analyses.....	S5
Procedure for Monitoring Dimerization of 1-Hexene over Five Half Lives.....	S5
Procedure for Determining Initial Rates of 1-Hexene Dimerization.....	S6
Alkene Dimerization Kinetic Data.....	S7
Kinetic Fitting using DynaFit.....	S18
Estimation of K_{eq} by ^1H NMR Spectroscopy.....	S21
Determining Initial Rates of 1-Hexene/ <i>n</i> -Decane Transfer Hydrogenation.....	S25
III: Full Table of Temperature/Concentration Effects on 1-Hexene/ <i>n</i> -Heptane Coupling.....	S29
IV: Styrene/ <i>n</i> -Heptane Coupling Reactions.....	S30
Procedure for Styrene Dimerization using 1	S30
Procedure for Monitoring Dimerization of Styrene over Four Half Lives.....	S32
Initial Rates of Styrene/1-Heptene Coupling using 1	S36
Procedure for Styrene/1-Heptene Coupling using 1	S37
Synthesis of Authentic Cross-Products.....	S44
Procedure for Styrene/ <i>n</i> -Heptane Coupling.....	S58
Full Table of Results for Styrene/ <i>n</i> -Heptane Coupling.....	S59
Procedure for Monitoring Styrene/ <i>n</i> -Heptane Coupling Reactions over Time.....	S60
Procedure for Monitoring Styrene/ <i>n</i> -Heptane Transfer Hydrogenation over Time.....	S62
V: References.....	S63

I: General Considerations

NOTE: Unless otherwise noted, all experiments were performed under an *argon* inert atmosphere using standard Schlenk line, high-vacuum line, or glovebox techniques. Transfer hydrogenation catalysis by many pincer-Ir complexes is known to be inhibited by N₂.¹

Materials:

Solvents for routine syntheses (pentane, toluene, diethyl ether, THF) were dried by passage through activated alumina, degassed under vacuum by several freeze-pump-thaw cycles, and stored over activated 4 Å molecular sieves under an inert atmosphere. *n*-Heptane for use in catalytic reactions (HPLC grade, >99%, Sigma-Aldrich) was pre-dried by stirring ~400 mL over CaH₂ (~10 g) for at least 48 hours. The solvent was then vacuum transferred onto “titanocene”² (~1 g) and stirred overnight; the solution remained black-green throughout. The *n*-heptane was collected from this titanocene solution by a final vacuum transfer and stored under an argon atmosphere. *n*-Decane for use in kinetics experiments (anhydrous, >99%, Sigma-Aldrich) was stored over activated 4 Å molecular sieves under an argon atmosphere, and aliquots were filtered through a small column of activated alumina immediately prior to use in making standard solutions. 1-Hexene and 1-heptene were distilled under argon from CaH₂ after stirring for several days, or vacuum-transferred from LiAlH₄ after sitting for several months. Styrene (>99.9%, 10-15 ppm 4-*tert*-butyl catechol as inhibitor, Sigma-Aldrich) was stored under an argon atmosphere at -35 °C, and filtered through a small column of alumina immediately prior to use in catalytic reactions in order to remove the inhibitor and trace water. Precatalysts **1**³ and **2**⁴ are known compounds, and were prepared according to published procedures.

NMR Spectroscopy:

Spectra were acquired on a Varian Mercury 300 MHz instrument at room temperature or elevated temperature with a relaxation delay time of 2 seconds. Spectra were processed in the following way using MestReNova: automatic baseline correction, automatic phase correction, exponential apodization along t1 of 1.00 Hz, and automatic linear correction applied to the integrals.

GC Analysis:

Gas chromatography was performed on an Agilent 6890N instrument using a flame ionization detector and a DB-1 capillary column (10 m length, 0.10 mm diameter, 0.40 μm film). Runs used the following program: hold at 35 °C for 2 minutes, ramp temperature at 2 °C min⁻¹ to 50 °C, hold at 50 °C for 2 minutes, ramp temperature at 100 °C min⁻¹ to 290 °C, hold at 290 °C for 5 minutes.

Response factors for linear hydrocarbons ranging from C₅ to C₁₈ versus adamantane were determined by the following procedure. Two standard samples were prepared containing known amounts of ten compounds (*n*-pentane, 1-hexene, *n*-heptane, *n*-octane, 1-dodecene, 1-tridecene, 1-tetradecene, 1-hexadecene, *n*-octadecane, and adamantane) dissolved in dichloromethane. Analysis of these two solutions by GC generated data used to calculate individual response factors for each compound versus adamantane using the following formula:

$$\text{Resp. factor} = ([\text{Area}_{\text{analyte}}] \times [\text{mmol}_{\text{adamantane}}]) / ([\text{Area}_{\text{adamantane}}] \times [\text{mmol}_{\text{analyte}}])$$

The following response factors were obtained:

	Run 1	Run 2
<i>n</i> -Pentane	0.3947	0.3979
1-Hexene	0.4970	0.5158
<i>n</i> -Heptane	0.6250	0.6320
<i>n</i> -Octane	0.7215	0.7364
1-Dodecene	1.1945	1.2061
1-Tridecene	1.3309	1.3274
1-Tetradecene	1.4134	1.3967
1-Hexadecene	1.6722	1.6639
<i>n</i> -Octadecane	1.8343	1.8544

These data were plotted versus carbon number, giving a linear correlation in the range analyzed (Figure S1).

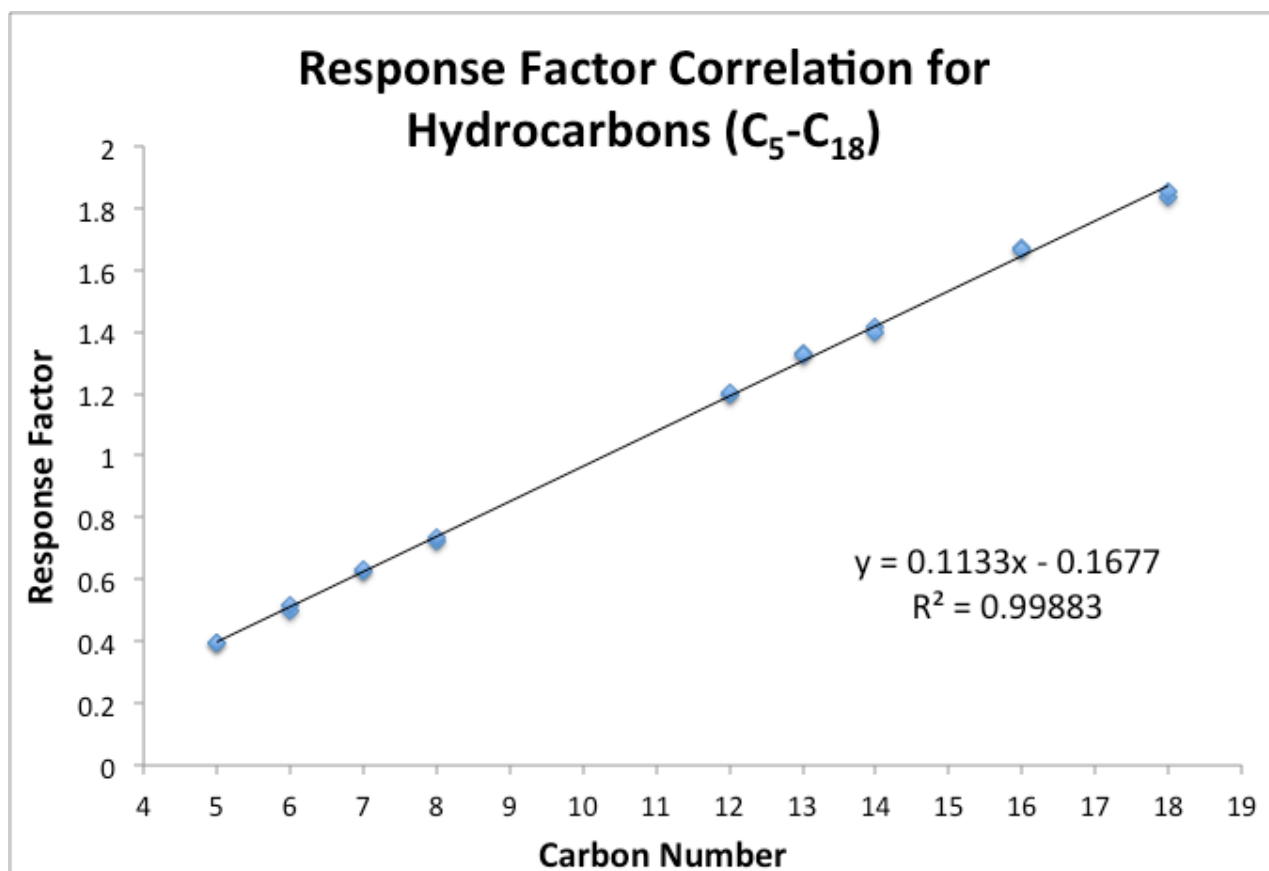


Figure S1: Linear correlation of response factors versus carbon number.

The equation of the line was used to determine response factors for all of the non-aromatic hydrocarbons analyzed (the branching in the C₁₂-C₁₄ dimers generated in catalytic reactions is assumed to have negligible effect on the response).

C ₆	0.5121
C ₁₂	1.1919
C ₁₃	1.3052
C ₁₄	1.4185

The response factor for styrene versus adamantane was determined independently from two separate runs, giving an average value of 0.8025. The response factor for the styrene dimer versus adamantane was taken as twice this value (1.605), and that of the styrene-heptane cross-products was assumed to be 1.5.

GC/MS analysis was performed on an HP Model 6890N instrument using an HP5-1 column (30 m length, 25 mm diameter, 0.40 μ m film) and an HP 5973 mass-selective EI detector.

II: Mechanistic Analysis

Procedure for Monitoring Dimerization of 1-Hexene over Five Half Lives (Figure 3, main text):

Precatalyst **1** (6.6 mg, 0.016 mmol) was dissolved in 2 mL of a standard solution of 1-hexene (240.8 mM) and adamantane (25.4 mM) in *n*-heptane in a 4 mL screw-top vial. The vial sealed with a Teflon-lined screw cap. The mixture was heated briefly with a heat gun to dissolve the precatalyst and ensure a homogeneous solution. The solution was then split into ten aliquots of 0.2 mL each in ten separate 4 mL vials containing stir bars. These vials were sealed and stirred at 100 °C in an aluminum block heater (except for one vial representing t_0). At specified time intervals, vials were removed from the heat block, immersed in a dry-ice/acetone bath to rapidly cool the contents, and then diluted with dichloromethane to quench the reaction. These solutions were passed through a short plug of silica gel into a GC autosampler vial, and analyzed by GC. This procedure was repeated three times to generate the time profile shown in Figure 3 (main text) and Figure S3.

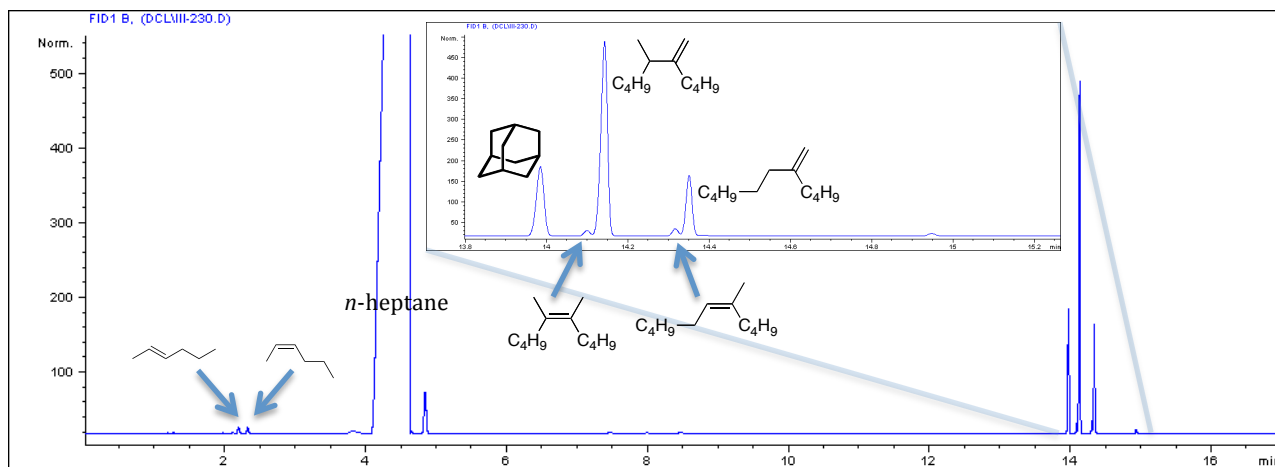


Figure S2: GC trace of the dimerization of 1-hexene to produce C₁₂ dimers.

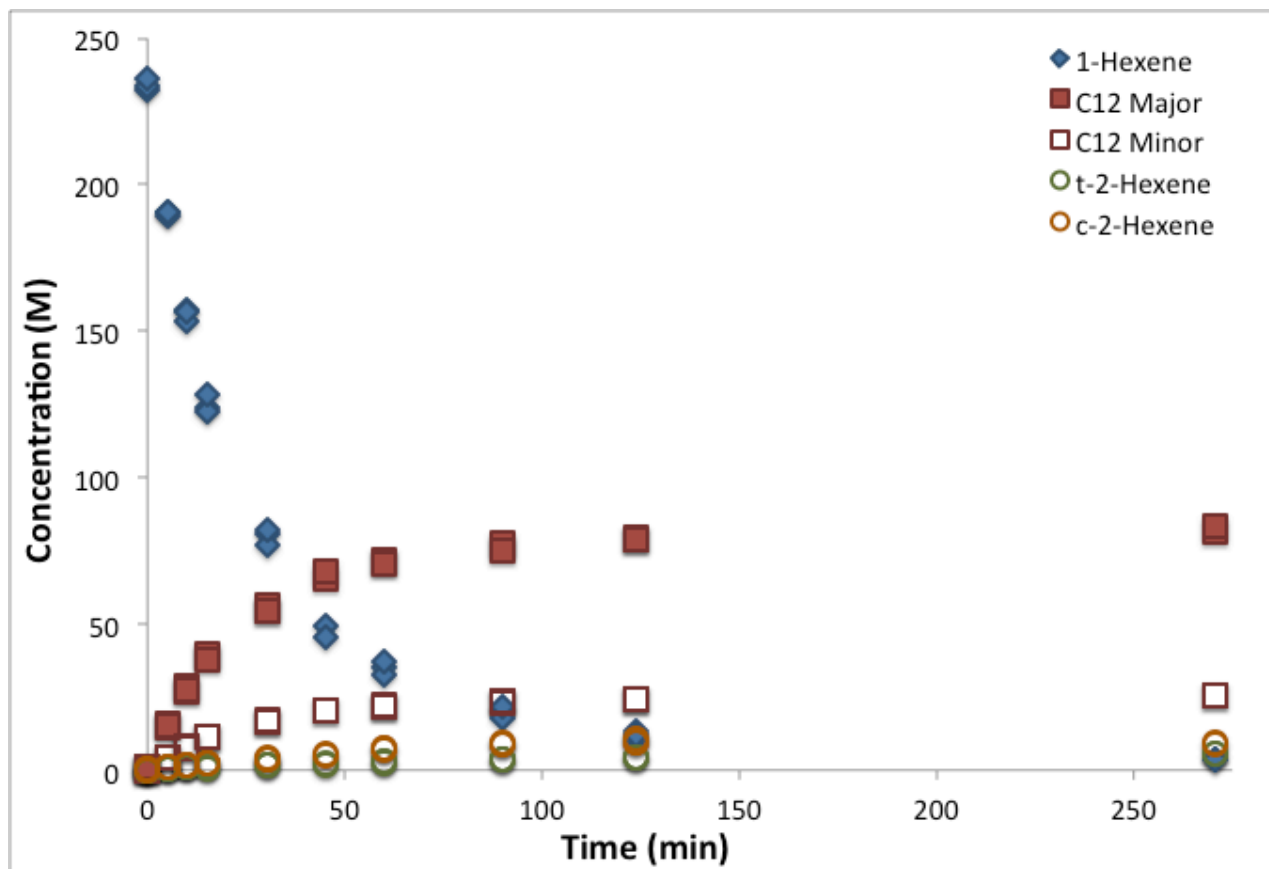


Figure S3. Time course plot of the dimerization of 1-hexene by **1** (overlay of three runs).

Procedure for Determining Initial Rates of 1-Hexene Dimerization

Precatalyst **1** (10.0 mg, 0.0240 mmol) was dissolved in 3 mL of a standard solution of 1-hexene (248, 252, 412, 699, 1010, 2000, or 4000 mM) and adamantane internal standard (~25 mM) in *n*-decane in a 4 mL screw-top vial. The vial was sealed with a Teflon-lined screw cap. The mixture was heated briefly with a heat gun and stirred vigorously to dissolve the precatalyst and ensure a homogeneous solution. The solution was then split into fifteen aliquots of 0.2 mL each in fifteen separate 4 mL vials containing stir bars. These vials were sealed and stirred at 80, 90, 100, 110, or 125 °C in an aluminum block heater. At specified time intervals, (1, 2, 3, or 4 minutes) vials were removed from the heat block, immersed in a dry-ice/acetone bath to rapidly cool the contents, and then diluted with dichloromethane to quench the reaction. These solutions were passed through a short plug of silica gel into a GC autosampler vial, and analyzed by GC.

Data for each time point was collected from 3 or 4 different vials, giving 12-15 data points for each initial rate determination. The concentrations of both major and minor product isomers were plotted versus time, and the k_{obs} values calculated by linear regression analysis (Table S1, Figures S4, S6, S8, S10, and S12). These data were used to generate double reciprocal plots for each product isomer at each temperature (Figures S5, S7, S9, S11, and S13). These plots were subject to linear regression analysis to generate slope/intercept values, which were used to calculate k_1 , K_{eq} , and k_2K_{eq} according to equations 2-9 in the main text.

Alkene Dimerization Kinetic Data

Table S1: Initial rate data (numbers in parentheses are standard errors determined from regression analysis).

Entry	Temp. (°C)	[1-Hexene] ₀ (mM)	<i>k</i> _{obs} Major (10 ⁻⁵ M s ⁻¹)	<i>k</i> _{obs} Minor (10 ⁻⁵ M s ⁻¹)
1	80	248	3.06(8)	0.73(3)
2	80	412	4.85(10)	1.19(3)
3	80	699	6.76(12)	1.59(4)
4	80	1010	7.28(25)	1.77(7)
5	80	2000	10.76(44)	2.54(13)
6	80	4000	12.42(55)	2.93(14)
7	90	248	4.35(10)	1.23(4)
8	90	412	7.52(15)	2.16(6)
9	90	699	10.21(21)	2.87(7)
10	90	1010	14.74(29)	4.10(8)
11	90	2000	18.58(58)	5.11(19)
12	90	4000	26.70(58)	7.44(17)
13	100	248	5.87(10)	1.85(4)
14	100	252	6.03(12)	2.00(5)
15	100	412	9.53(27)	2.98(10)
16	100	699	16.73(41)	5.56(15)
17	100	1010	21.37(52)	6.77(19)
18	100	2000	37.2(11)	12.24(38)
19	100	4000	42.9(14)	13.76(48)
20	110	248	6.66(18)	2.42(7)
21	110	412	10.75(22)	3.83(9)
22	110	699	18.22(35)	6.52(13)
23	110	1010	28.37(48)	10.17(19)
24	110	2000	41.7(13)	14.79(45)
25	110	4000	66.6(18)	23.78(71)
26	125	248	8.34(22)	3.62(11)
27	125	412	14.01(33)	6.08(14)
28	125	699	24.65(76)	10.84(32)
29	125	1010	33.4(16)	14.32(65)
30	125	2000	64.3(34)	28.3(16)
31	125	4000	102.1(64)	43.0(30)

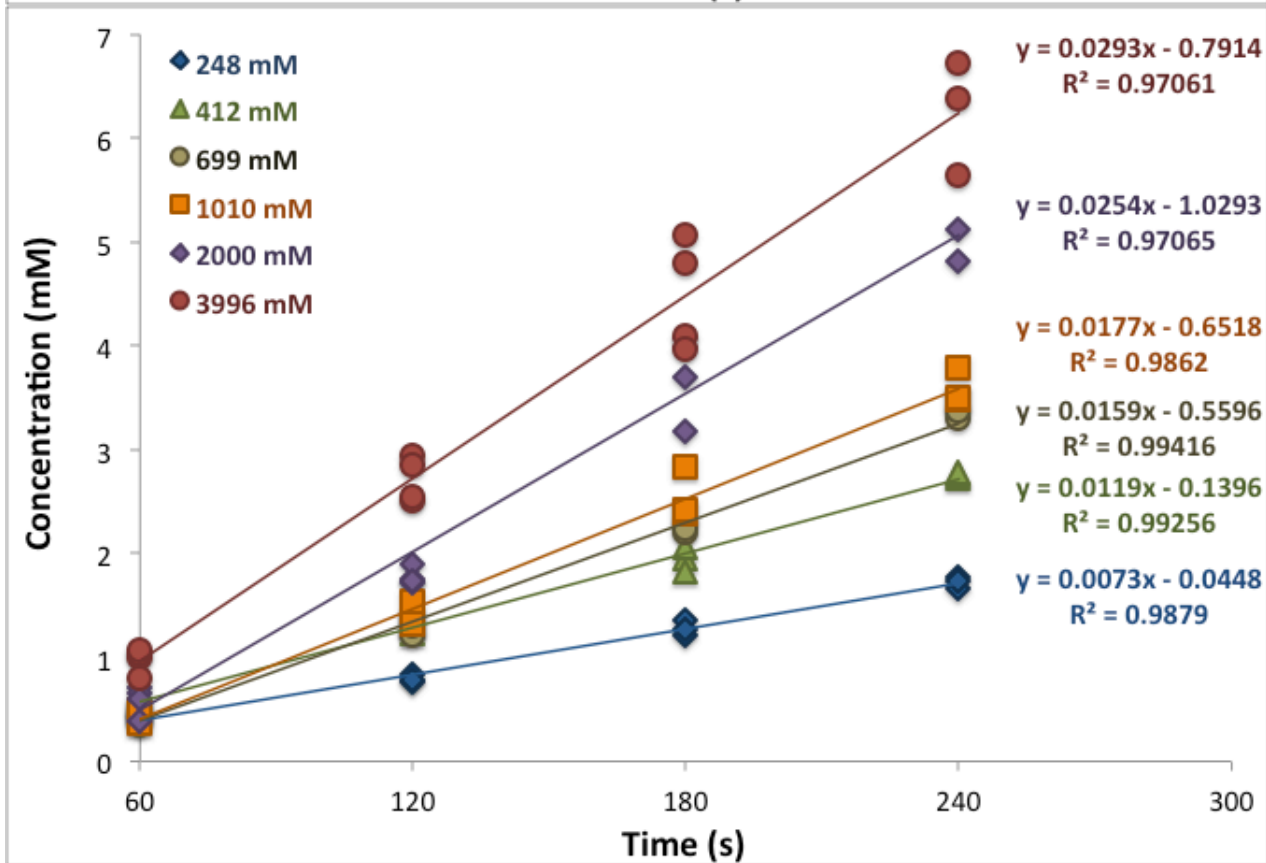
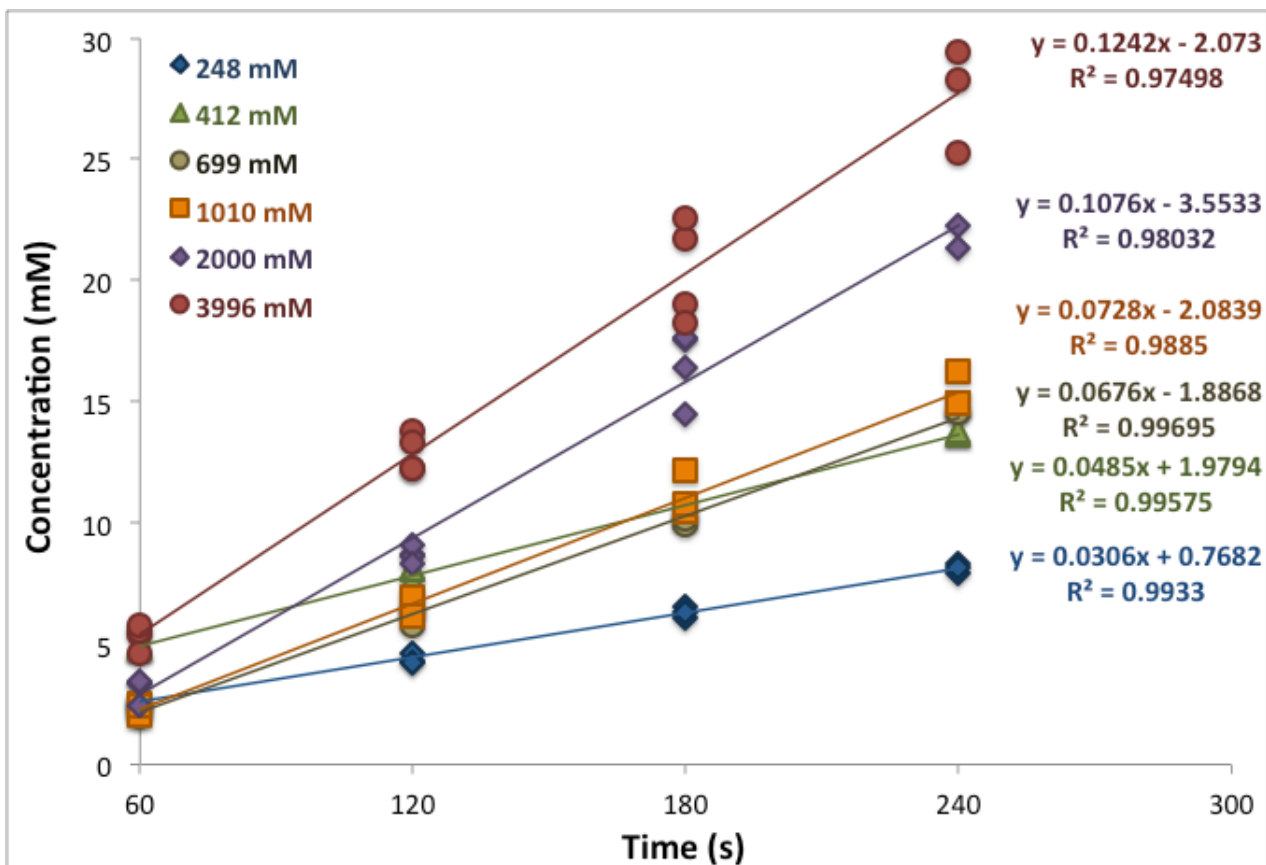


Figure S4. Initial rate measurements for 1-hexene dimerization at 80 °C. *Top:* Major isomer product. *Bottom:* Minor isomer product.

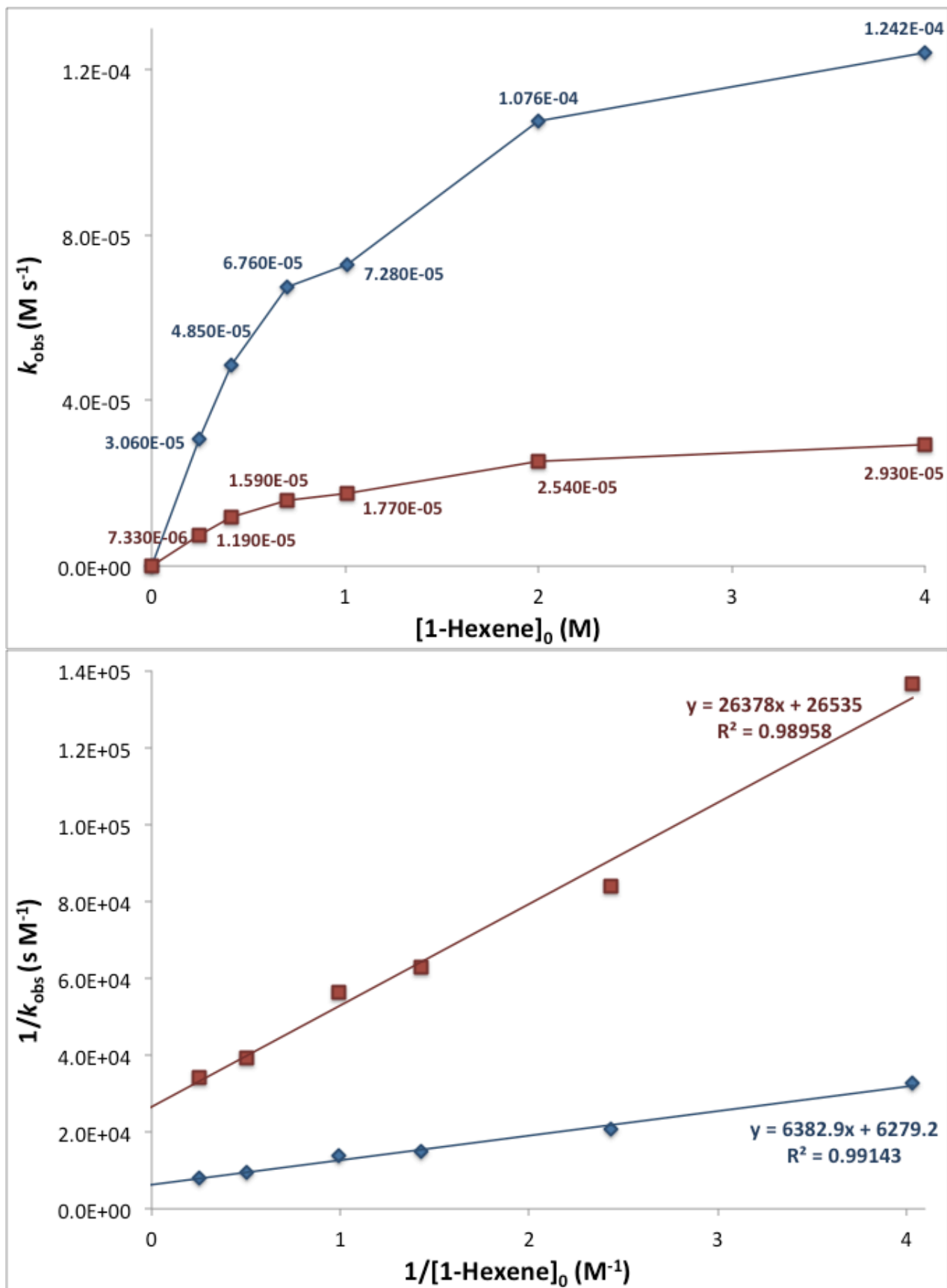


Figure S5. Initial rate of 1-hexene dimerization as a function of $[1-hexene]_0$ at 80 °C. *Top:* Rate vs. concentration. *Bottom:* Double reciprocal plot.

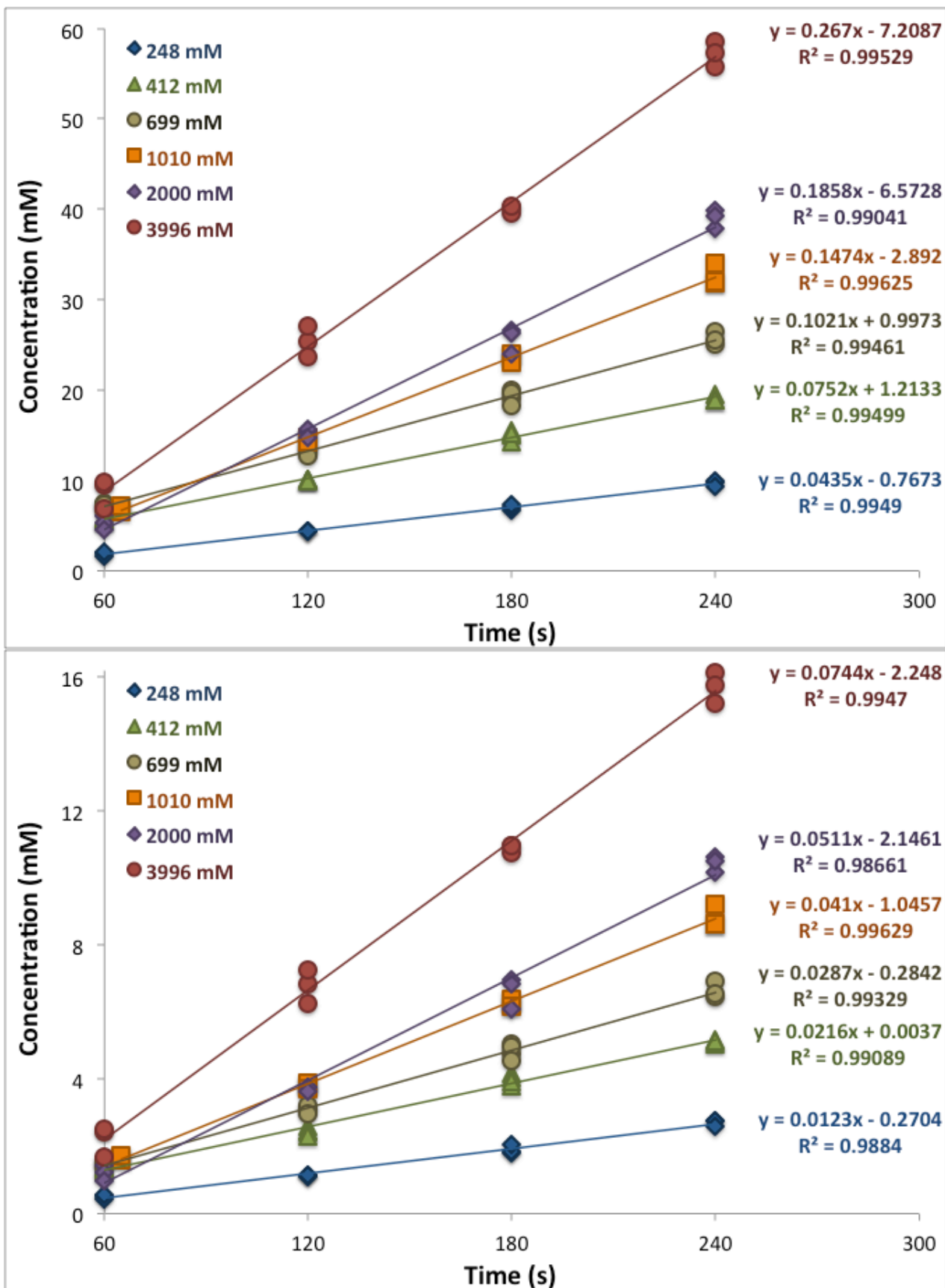


Figure S6. Initial rate measurements for 1-hexene dimerization at 90 °C. *Top:* Major isomer product. *Bottom:* Minor isomer product.

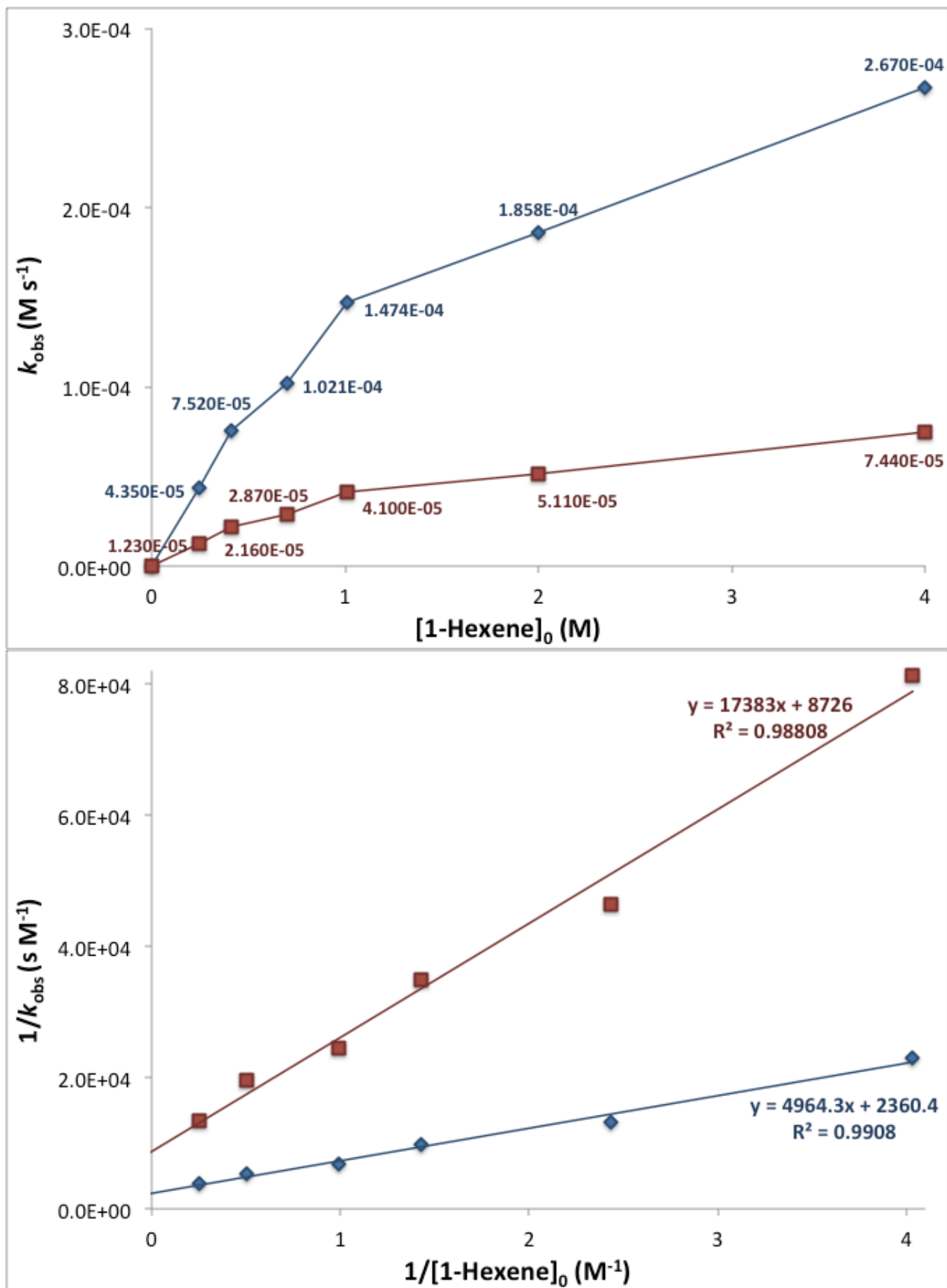


Figure S7. Initial rate of 1-hexene dimerization as a function of $[1-hexene]_0$ at 90 °C. *Top:* Rate vs. concentration. *Bottom:* Double reciprocal plot.

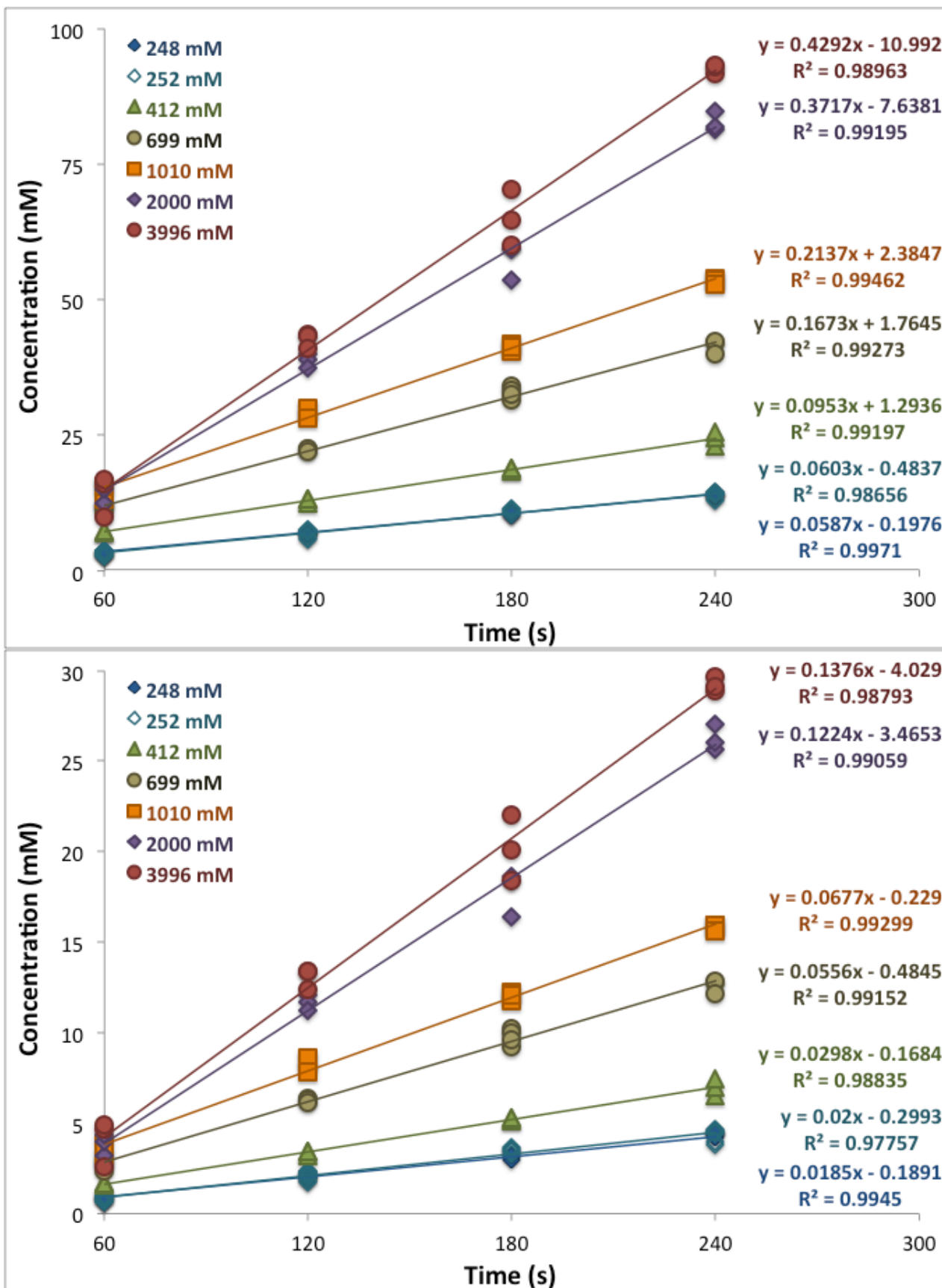


Figure S8. Initial rate measurements for 1-hexene dimerization at 100 °C. *Top:* Major isomer product. *Bottom:* Minor isomer product.

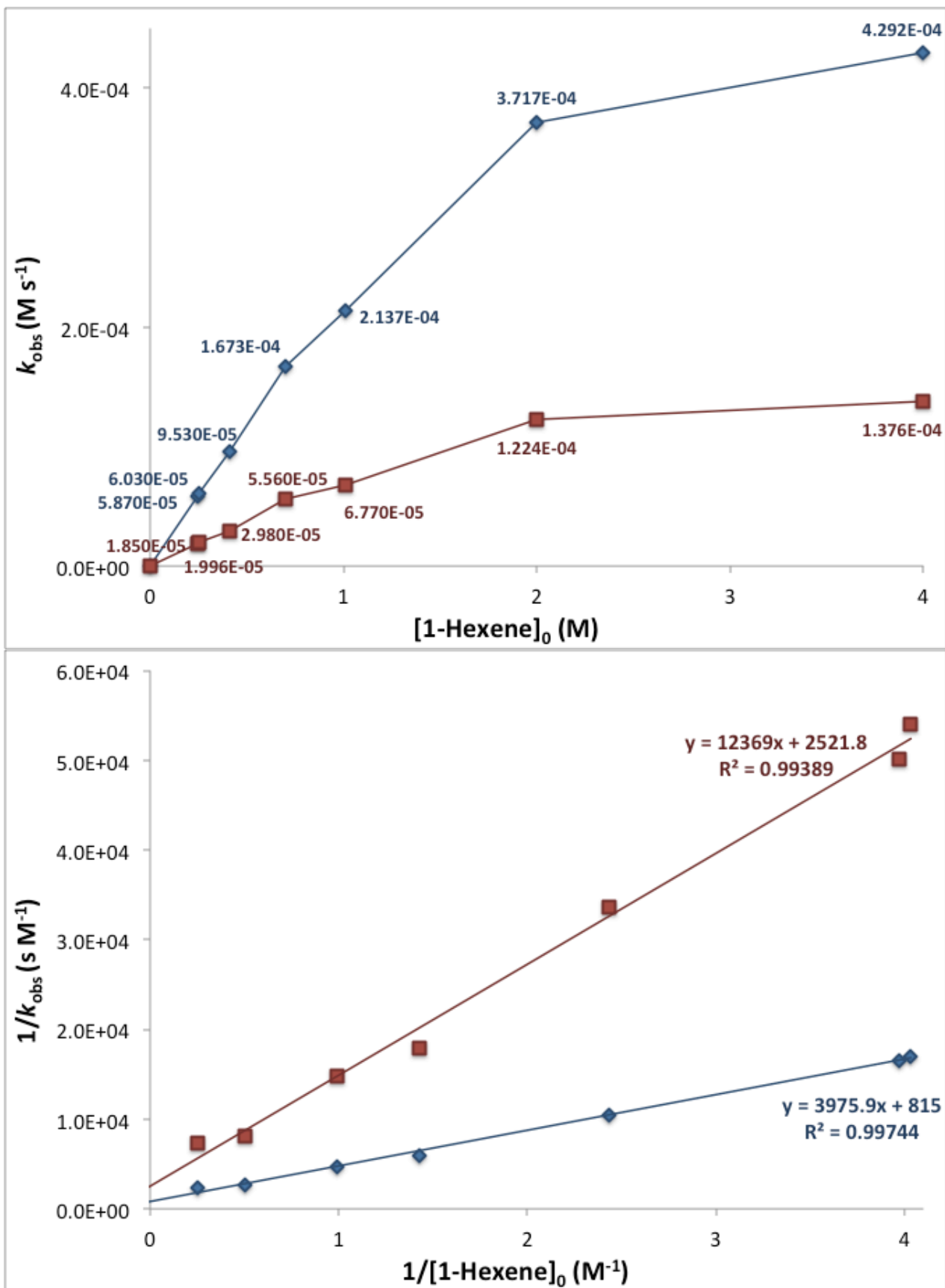


Figure S9. Initial rate of 1-hexene dimerization as a function of $[1\text{-hexene}]_0$ at 100 °C. *Top:* Rate vs. concentration. *Bottom:* Double reciprocal plot.

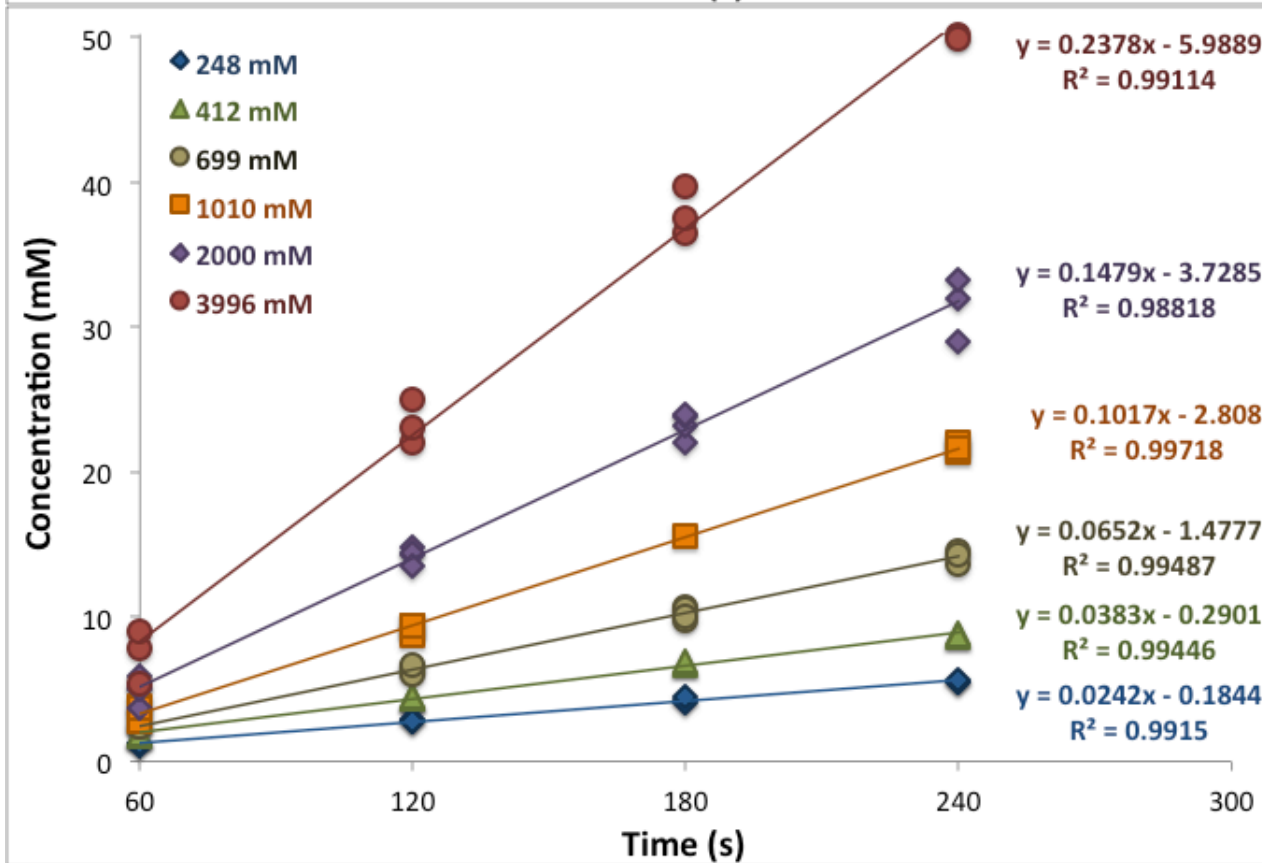
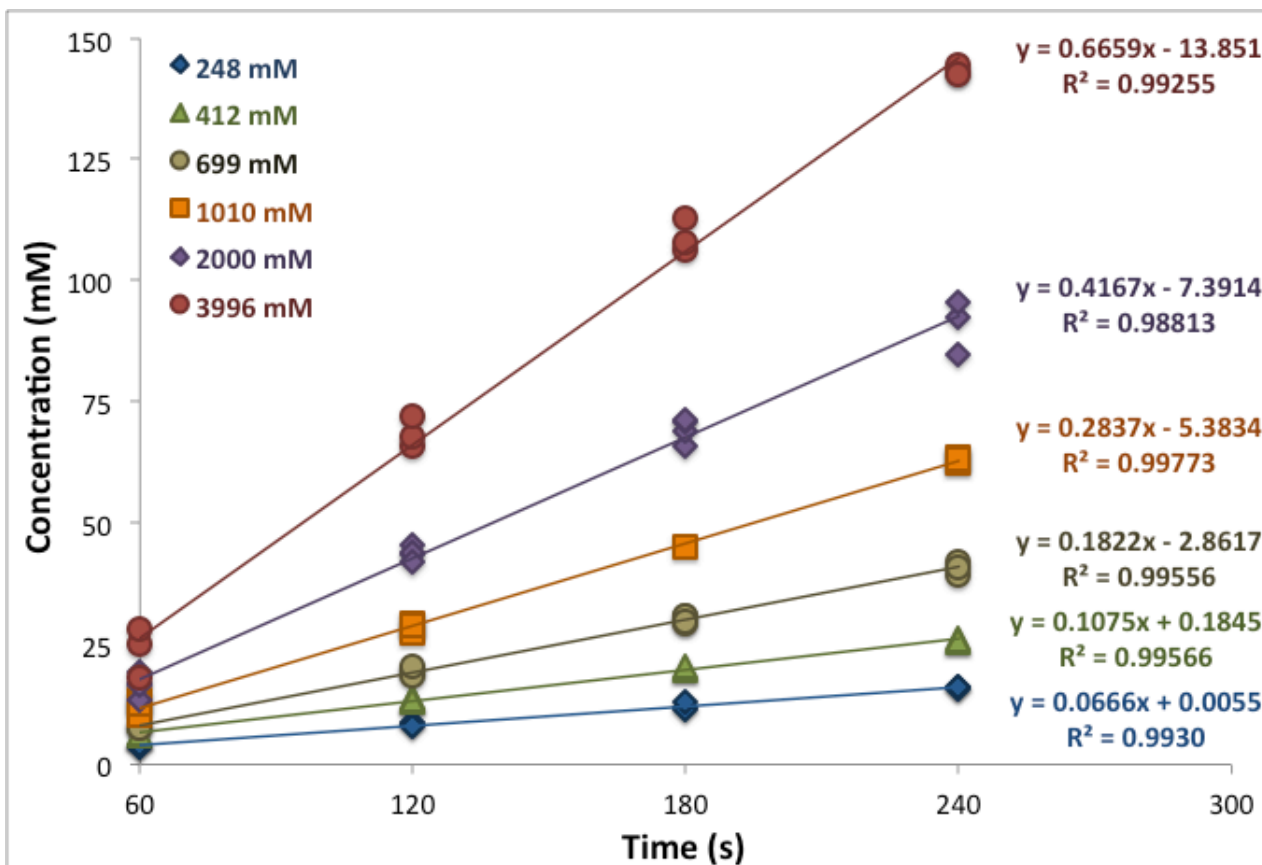


Figure S10. Initial rate measurements for 1-hexene dimerization at 110 °C. *Top:* Major isomer product. *Bottom:* Minor isomer product.

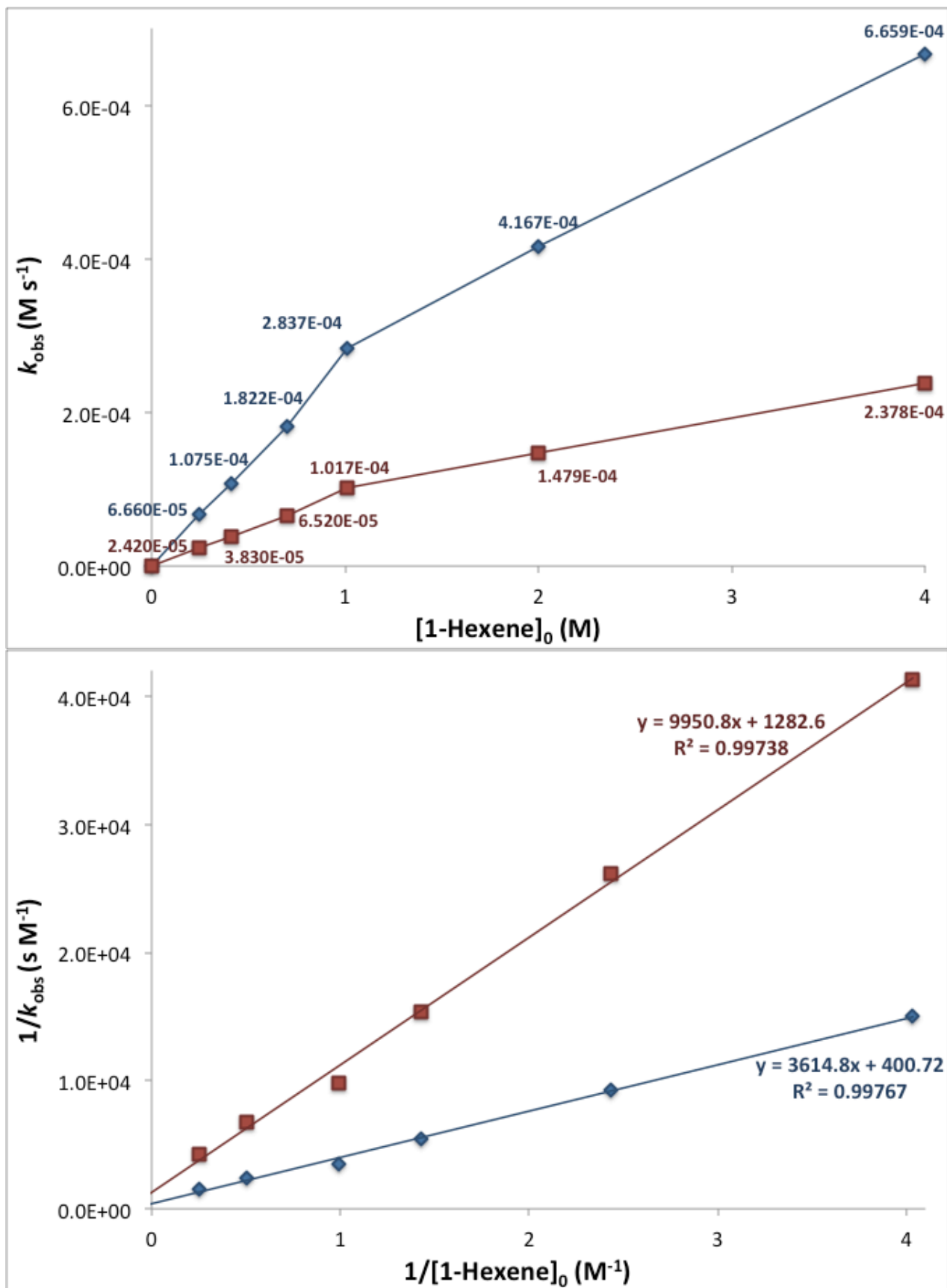


Figure S11. Initial rate of 1-hexene dimerization as a function of $[1-hexene]_0$ at 110 °C. *Top:* Rate vs. concentration. *Bottom:* Double reciprocal plot.

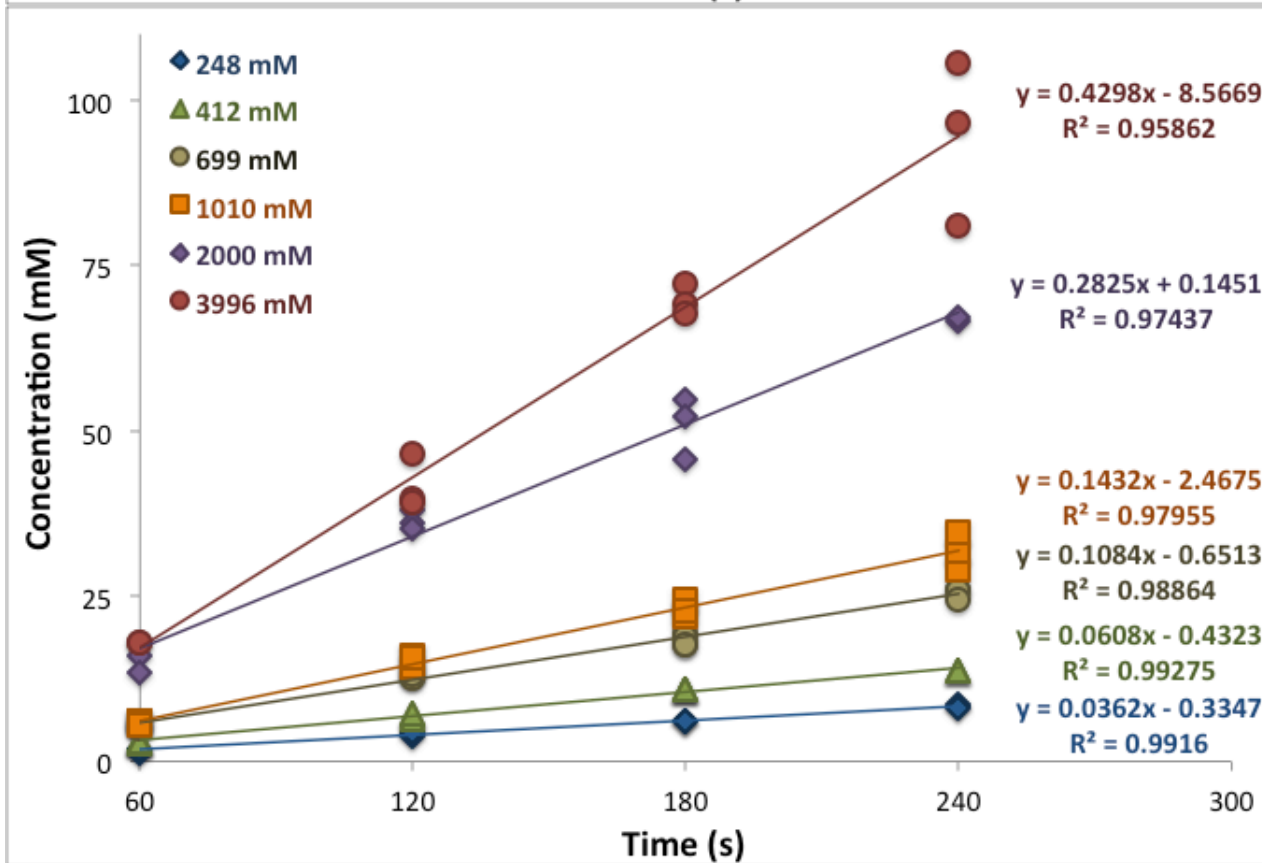
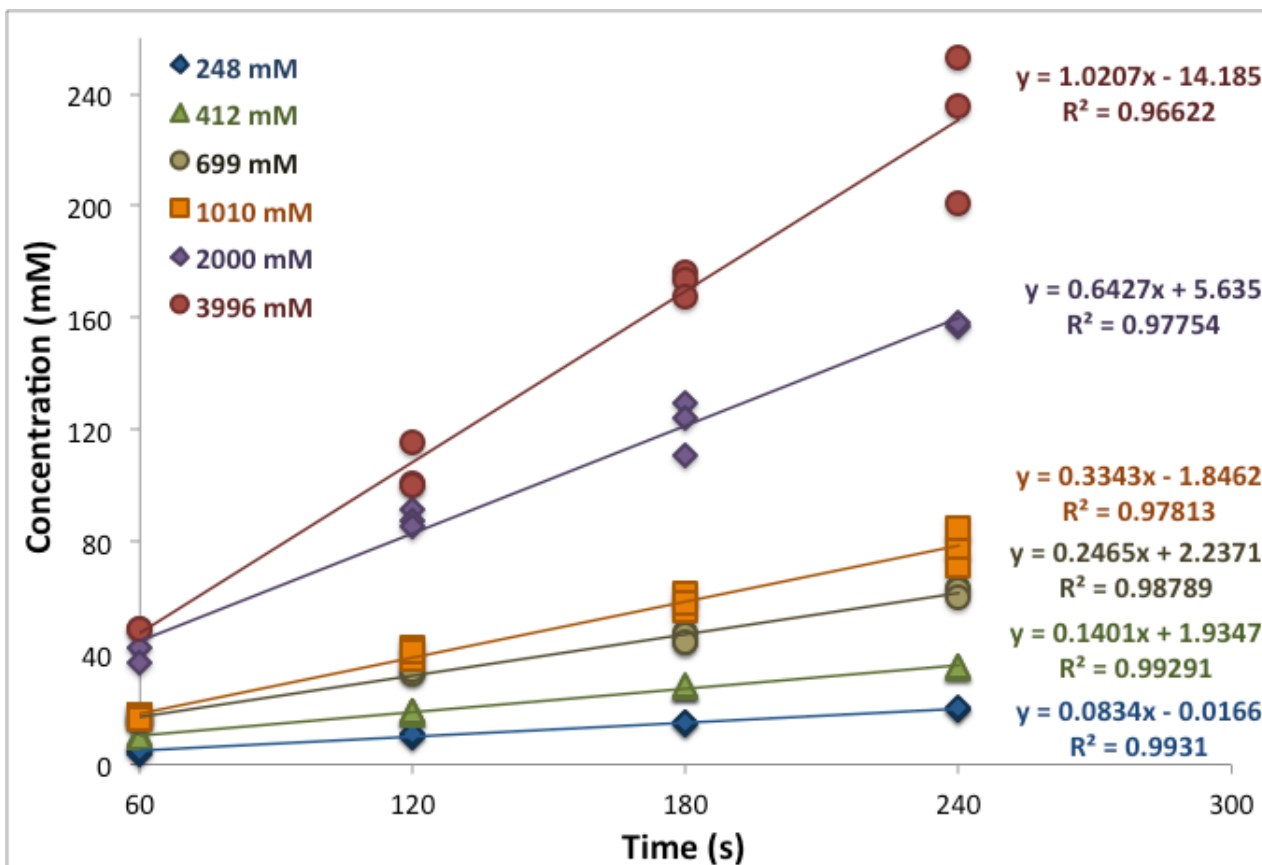


Figure S12. Initial rate measurements for 1-hexene dimerization at 125 °C. *Top:* Major isomer product. *Bottom:* Minor isomer product.

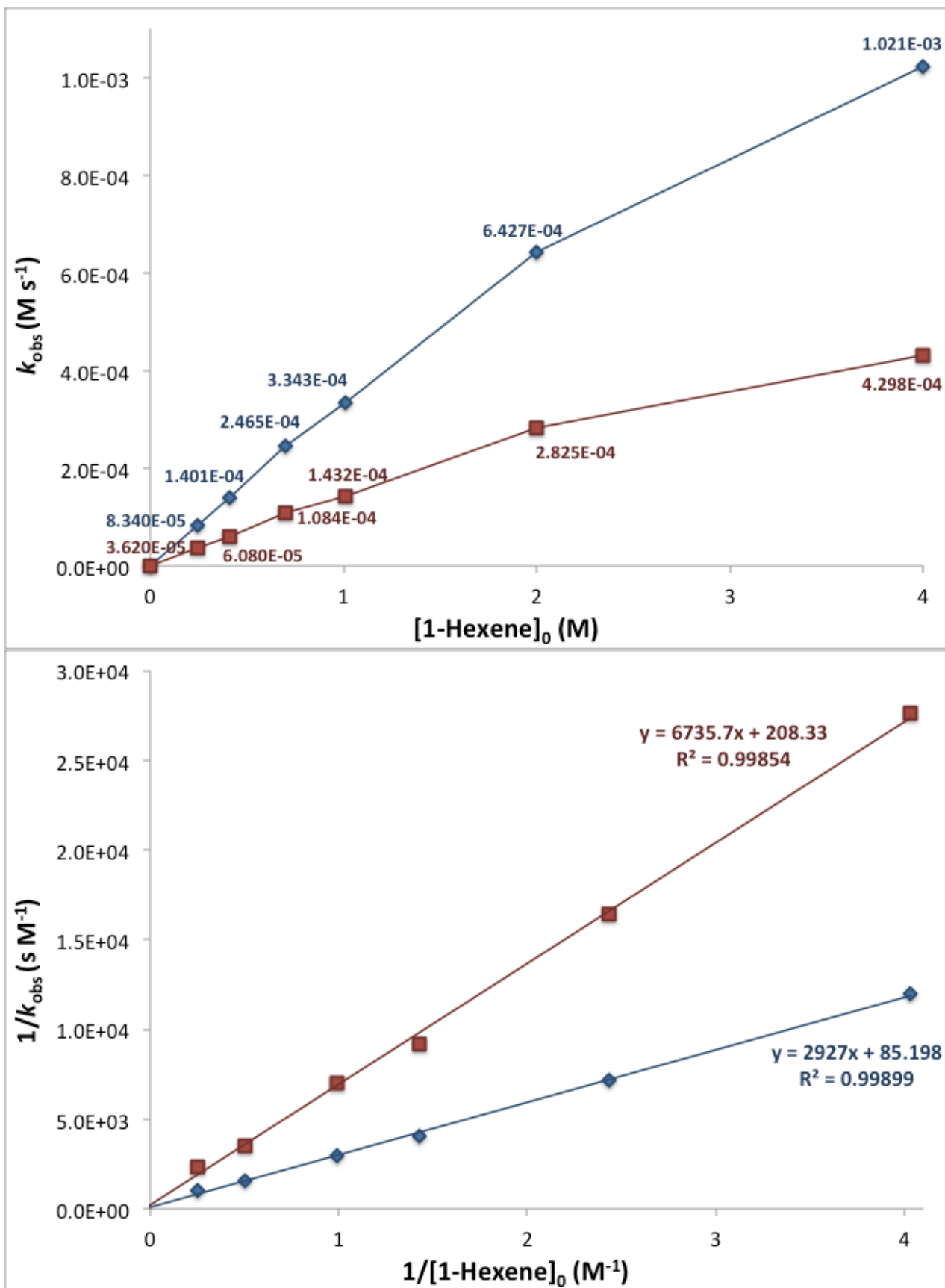
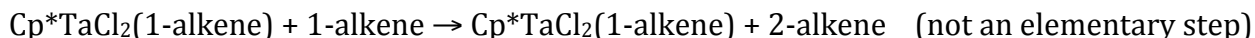


Figure S13. Initial rate of 1-hexene dimerization as a function of $[1-hexene]_0$ at 125 °C. *Top:* Rate vs. concentration. *Bottom:* Double reciprocal plot.

Kinetic Fitting using DynaFit

The full time course data represented in Figure 3 (main text) and Figure S3 was fitted according to the mechanistic model from Scheme 2 (main text), as well as terms for alkene isomerization to *cis*- and *trans*-2-hexene, using the freeware kinetics program DynaFit.⁵ Values for the rate and equilibrium constants k_1 , K_{eq} , and k_2K_{eq} determined at 100 °C were used. All equilibria were assumed to be rapid. The values of K_{off} and K_{off}' were set at different values ($K_{off} = K_{off}' = 1, 2.5, 5, 10, \text{ and } 15$) and the quality of the fit determined by inspection (see Figures S14-18). Clearly, intermediate values of $K_{off} \cong K_{off}' \cong 2.5-5$ gave the best correlation. Refining K_{off} and K_{off}' gave values of 4.4(6) and 2.8(9) respectively (Figure S19). Second order rate constants for alkene isomerization were determined by fitting according to the equation:



These values are $3.6(2) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $1.8(2) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for the formation of *cis*- and *trans*-2-hexene respectively. Presumably this isomerization occurs via a π -allylic-type mechanism,⁶ since the major catalyst resting state is the [Ta](1-alkene) complex, rather than an insertion/ β -hydride elimination mechanism;⁶ however, due to the low degree of isomerization observed, the mechanism of this side-reaction was not experimentally tested.

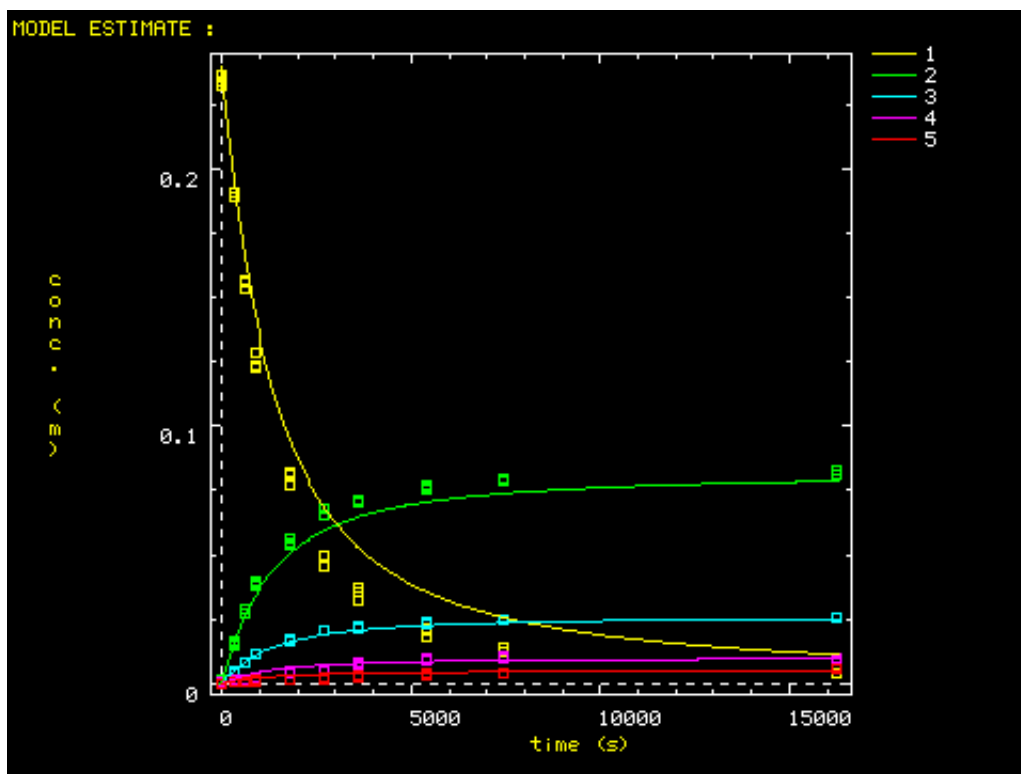


Figure S14. Data fit for dimerization of 1-hexene by **1** with $K_{off} = K_{off}' = 1$ (data from Fig. S3).
Legend: 1 (yellow): 1-hexene; 2 (green): C₁₂ major; 3 (blue): C₁₂ minor; 4 (pink): *cis*-2-hexene; 5 (red): *trans*-2-hexene.

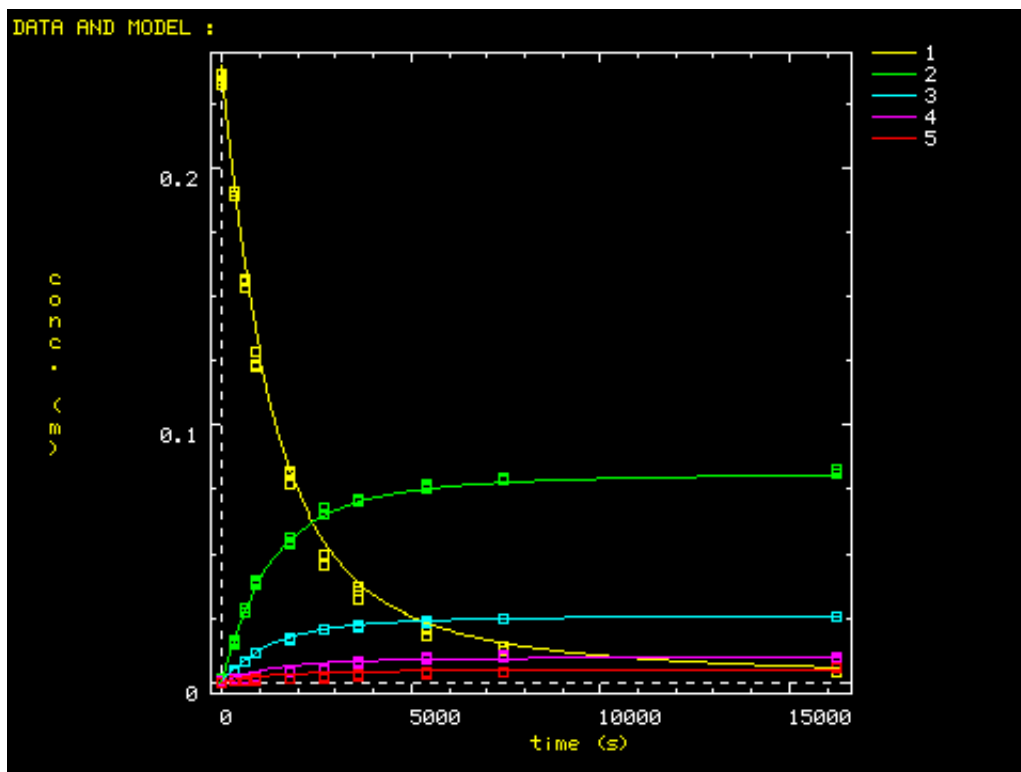


Figure S15. Data fit for dimerization of 1-hexene by **1** with $K_{\text{off}} = K_{\text{off}}' = 2.5$ (data from Fig. S3). *Legend:* 1 (yellow): 1-hexene; 2 (green): C₁₂ major; 3 (blue): C₁₂ minor; 4 (pink): *cis*-2-hexene; 5 (red): *trans*-2-hexene.

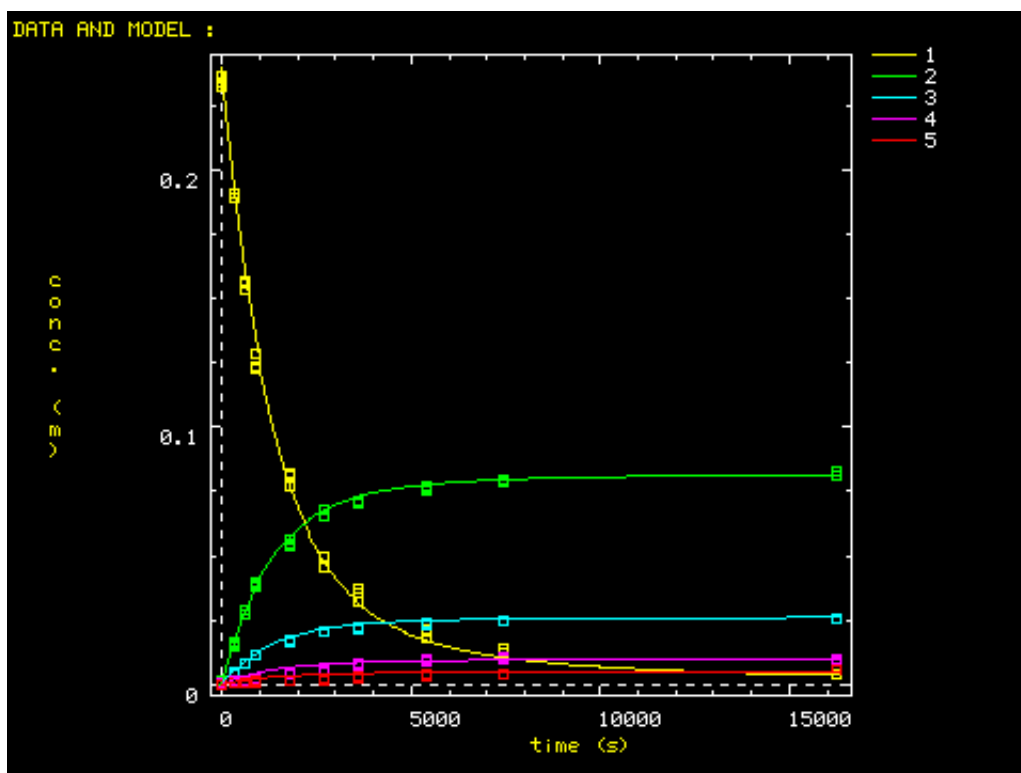


Figure S16. Data fit for dimerization of 1-hexene by **1** with $K_{\text{off}} = K_{\text{off}}' = 5$ (data from Fig. S3). *Legend:* 1 (yellow): 1-hexene; 2 (green): C₁₂ major; 3 (blue): C₁₂ minor; 4 (pink): *cis*-2-hexene; 5 (red): *trans*-2-hexene.

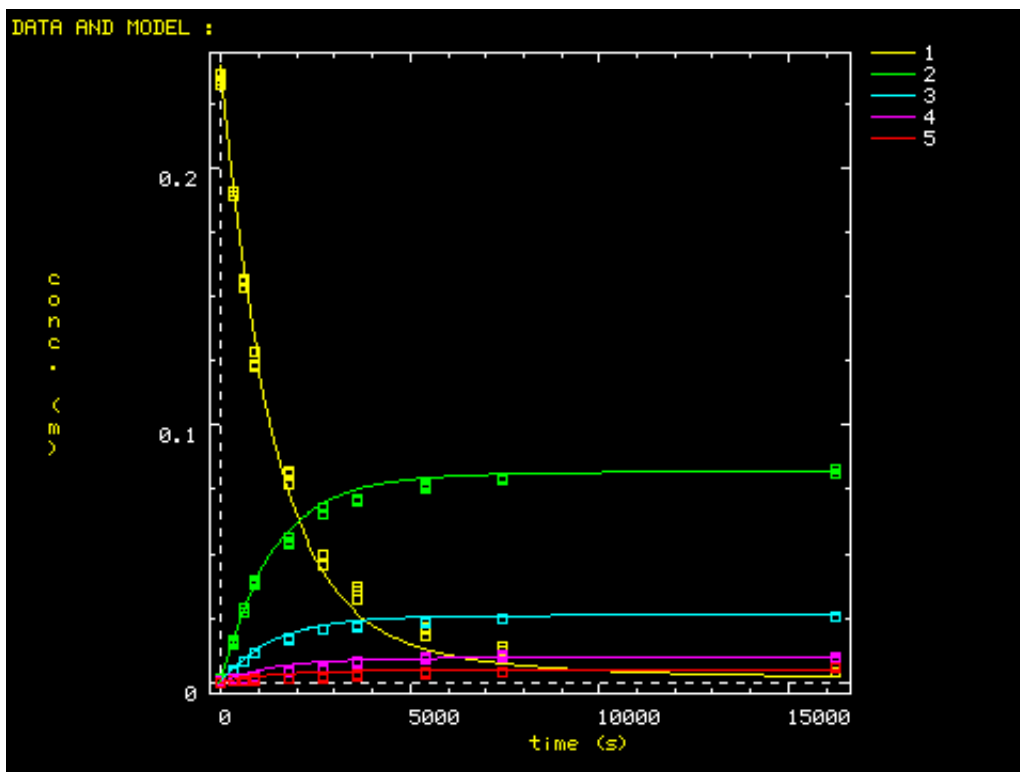


Figure S17. Data fit for dimerization of 1-hexene by **1** with $K_{\text{off}} = K_{\text{off}'} = 10$ (data from Fig. S3).
Legend: 1 (yellow): 1-hexene; 2 (green): C₁₂ major; 3 (blue): C₁₂ minor; 4 (pink): *cis*-2-hexene; 5 (red): *trans*-2-hexene.

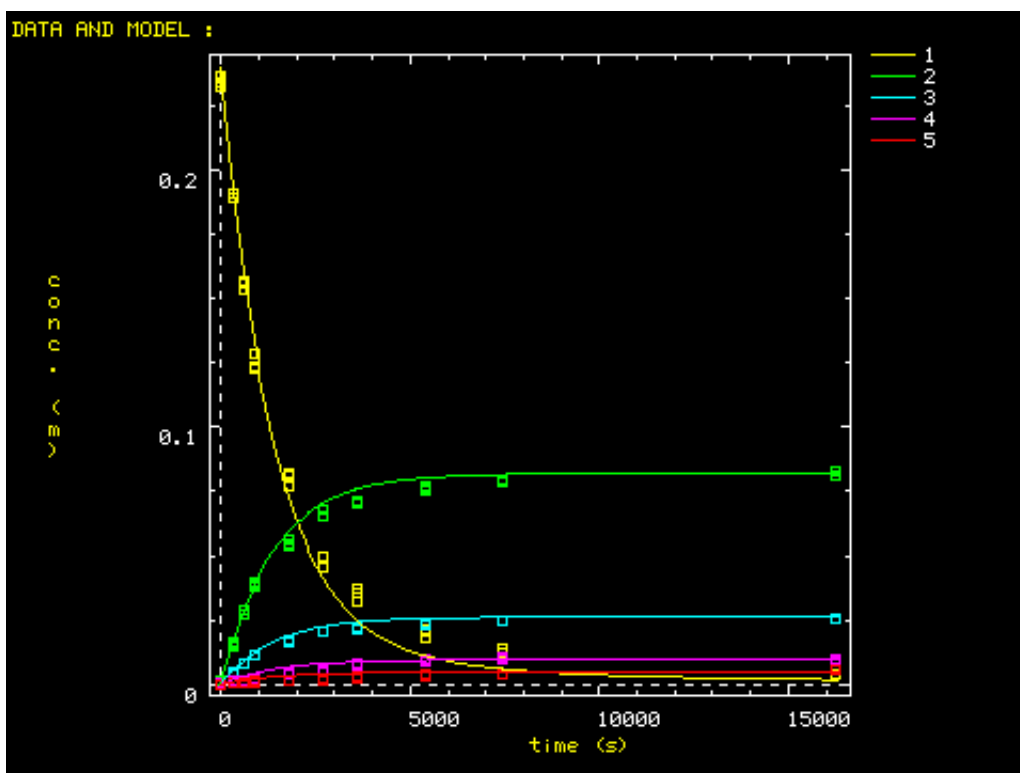


Figure S18. Data fit for dimerization of 1-hexene by **1** with $K_{\text{off}} = K_{\text{off}'} = 15$ (data from Fig. S3).
Legend: 1 (yellow): 1-hexene; 2 (green): C₁₂ major; 3 (blue): C₁₂ minor; 4 (pink): *cis*-2-hexene; 5 (red): *trans*-2-hexene.

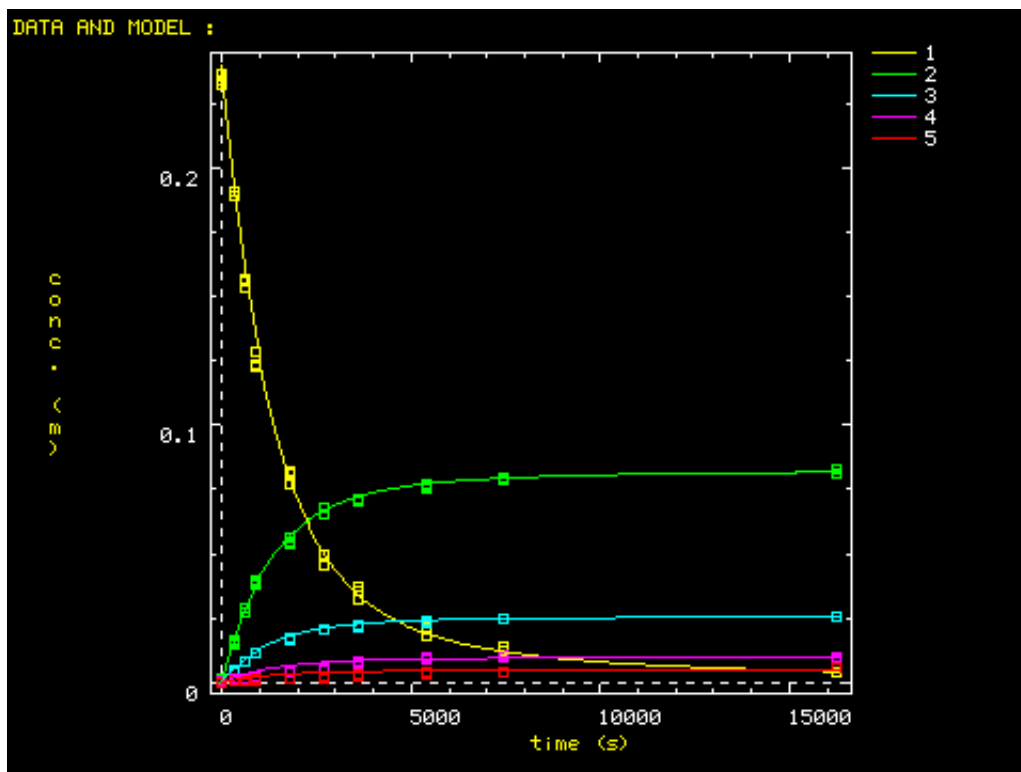


Figure S19. Data fit for dimerization of 1-hexene by **1** with K_{off} and $K_{\text{off}'}$ refined to 4.4(6) and 2.8(9) respectively (data from Fig. S3). *Legend:* **1** (yellow): 1-hexene; **2** (green): C₁₂ major; **3** (blue): C₁₂ minor; **4** (pink): *cis*-2-hexene; **5** (red): *trans*-2-hexene.

Estimation of K_{eq} by ¹H NMR Spectroscopy

The equilibrium between Cp*TaCl₂(1-hexene) and Cp*TaCl₂(metallacycle) was observed by variable temperature ¹H NMR spectroscopy (300 MHz, C₆D₆). Standard solutions of precatalyst **2** (solution **A**: 41.3 mg, 0.0995 mmol; solution **B**: 41.8 mg, 0.101 mmol) and 1-hexene (solution **A**: 170.1 mg, 2.02 mmol; solution **B**: 343.3 mg, 4.08 mmol) in C₆D₆ (2.00 mL total solution volume) were prepared and split into four aliquots of ~0.5 mL each. These aliquots were transferred to J. Young NMR tubes.

Concentrations: Solution **A**: [Ta] = 49.8 mmol; [1-hexene] = 1.01 M

Solution **B**: [Ta] = 50.5 mmol; [1-hexene] = 2.04 M

The singlet corresponding to the methyl protons of the Cp* ligand are diagnostic for Cp*TaCl₂(alkene) (~1.6-1.7 ppm) and Cp*TaCl₂(metallacycle) (~1.8-1.9 ppm) based on reference spectra for precatalyst **1** (alkene complex, 1.58 ppm, 22 °C) and **1** treated with a large excess of 1-hexene (metallacycle, 1.81 ppm, 22 °C).

Spectra of the **1**/1-hexene mixtures were acquired at 72, 82, and 93 °C (calibrated using neat ethylene glycol standard). Because the amount of 1-hexene bound to Ta is negligible relative to the total amount of 1-hexene, K_{eq} can be estimated by the following equation:

$$K_{\text{eq}} = \text{Area}(\text{metallacycle}) / \text{Area}(\text{alkene complex}) / [\text{1-hexene}]$$

Unfortunately, at these temperatures catalysis is rapid enough that the concentration of 1-hexene changes during the course of temperature equilibration and sample shimming. As a result, the observed concentration of 1-hexene was estimated by determining the % conversion of 1-hexene to C₁₂ product from the peak areas of the signals for the =CH₂ groups.

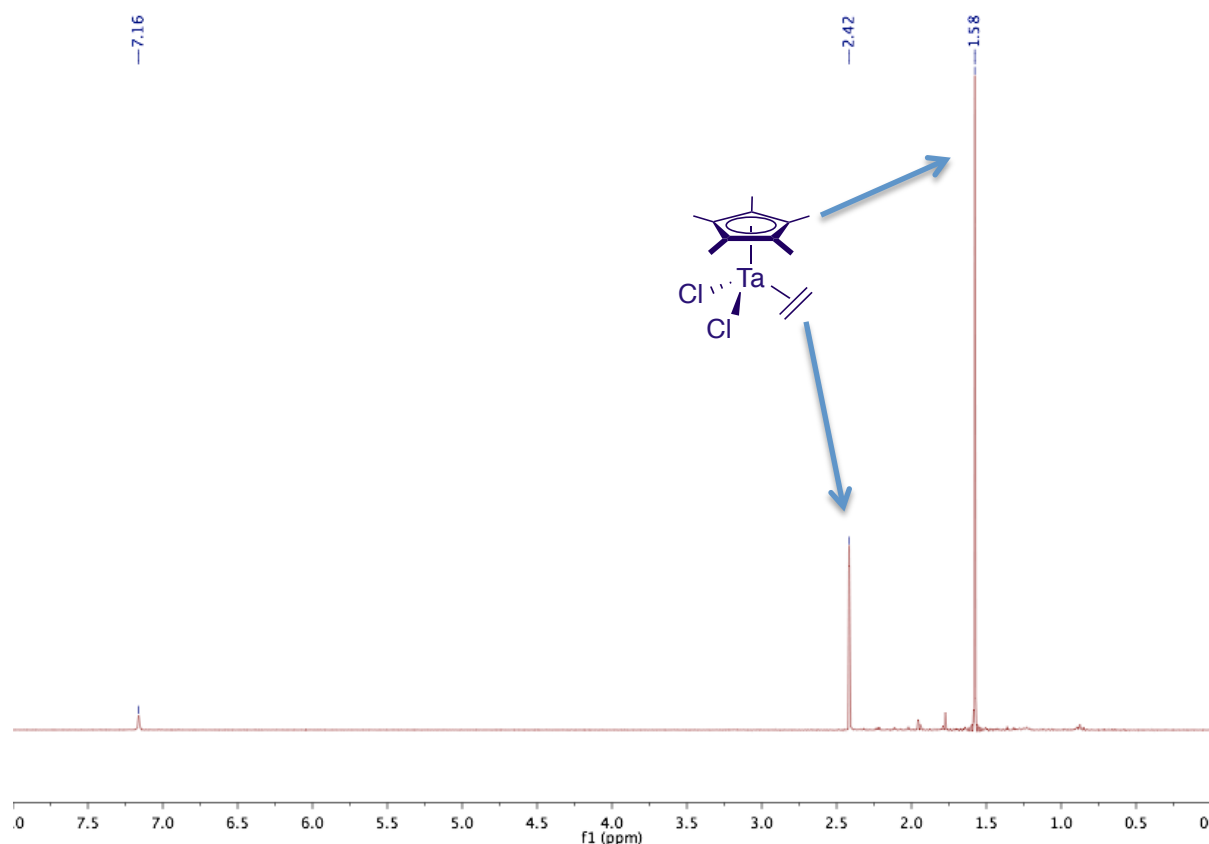
Table S2: K_{eq} data obtained by VT NMR spectroscopy

Entry	Temp. (°C) ^a	[1-Hexene] (M) ^b	$A_{metallacycle}/A_{alkene\ complex}$	K_{eq} (M ⁻¹)
1	72	1.96 (2.04)	5.26	2.68
2	72	1.92 (2.04)	4.55	2.37
3	72	0.94 (1.02)	2.27	2.43
4	72	0.92 (1.02)	2.00	2.19
5	82	1.83 (2.04)	1.85	1.01
6	82	1.69 (2.04)	1.59	0.94
7	82	1.61 (2.04)	1.41	0.88
8	82	0.78 (1.02)	0.68	0.88
9	93	1.57 (2.04)	0.82	0.52
10	93	1.38 (2.04)	0.58	0.42
11	93	0.81 (1.02)	0.47	0.58
12	93	0.74 (1.02)	0.35	0.47

^a +/- 1°C. ^bNumbers in parentheses are [1-hexene]₀

Averaging the obtained data gives estimated K_{eq} values of 2.4(3) (72 °C), 0.93(8) (82 °C), and 0.50(8) (93 °C); these are in excellent agreement with the values obtained at 80 °C (1.00) and 90 °C (0.49) from the kinetic data described in the main text.

Representative ¹H NMR spectra:

**Figure S20.** ¹H NMR spectrum of precatalyst **1** at 22 °C.

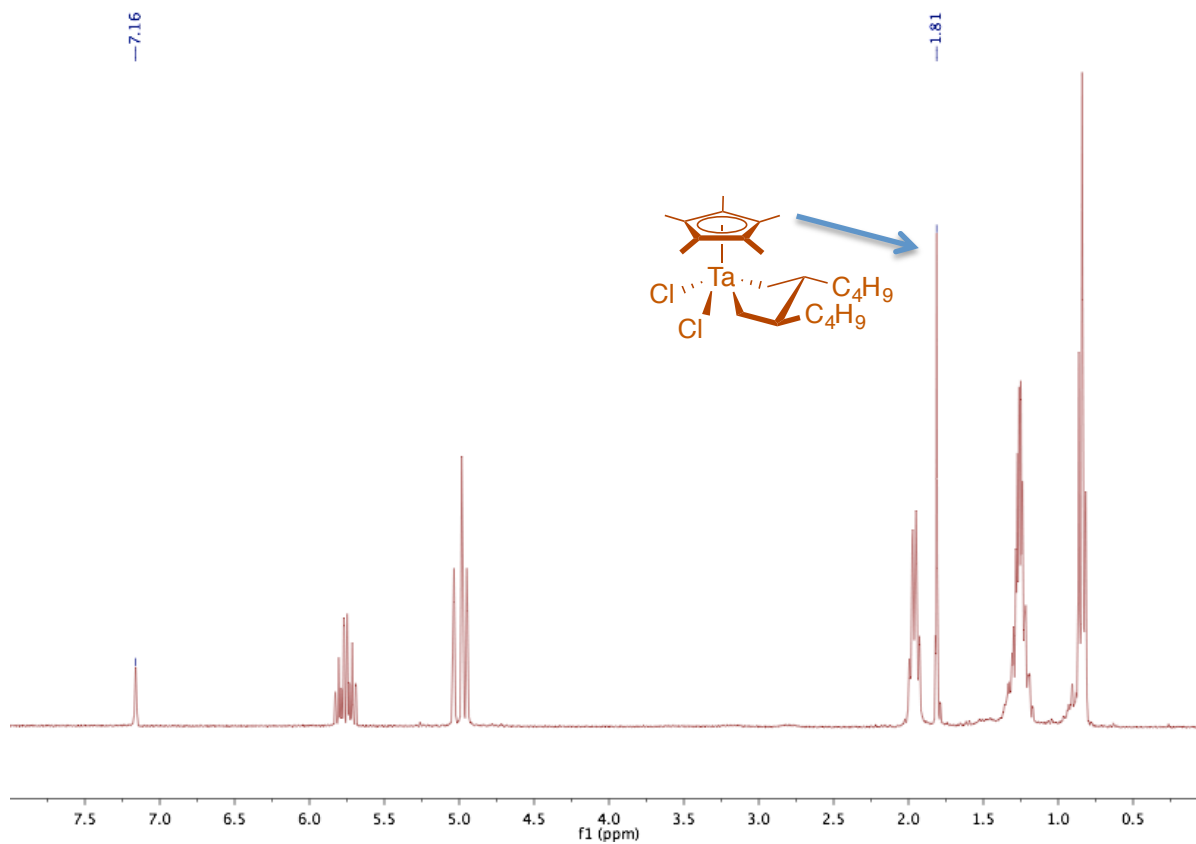


Figure S21. ^1H NMR spectrum of precatalyst **1** + excess 1-hexene at 22 °C.

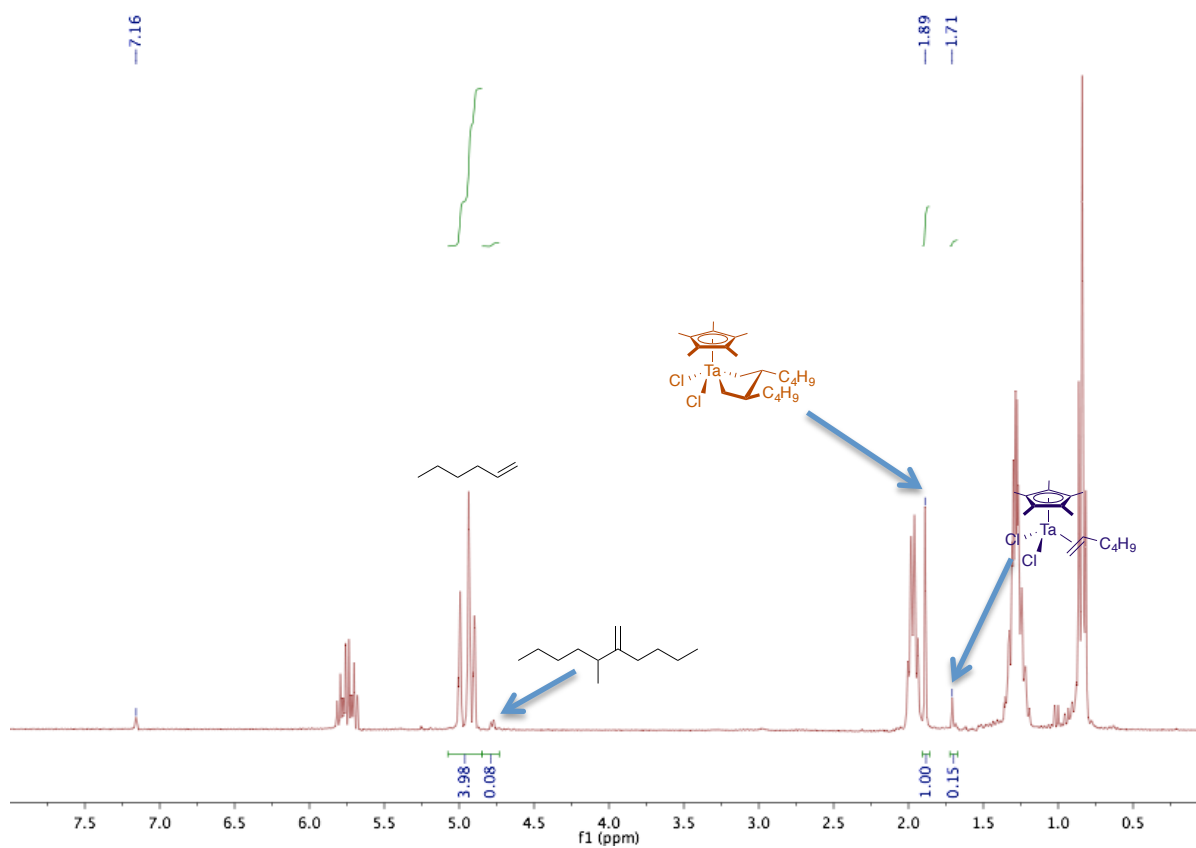


Figure S22. ^1H NMR spectrum of precatalyst **1** + excess 1-hexene (2.04 M initial) at 72 °C.

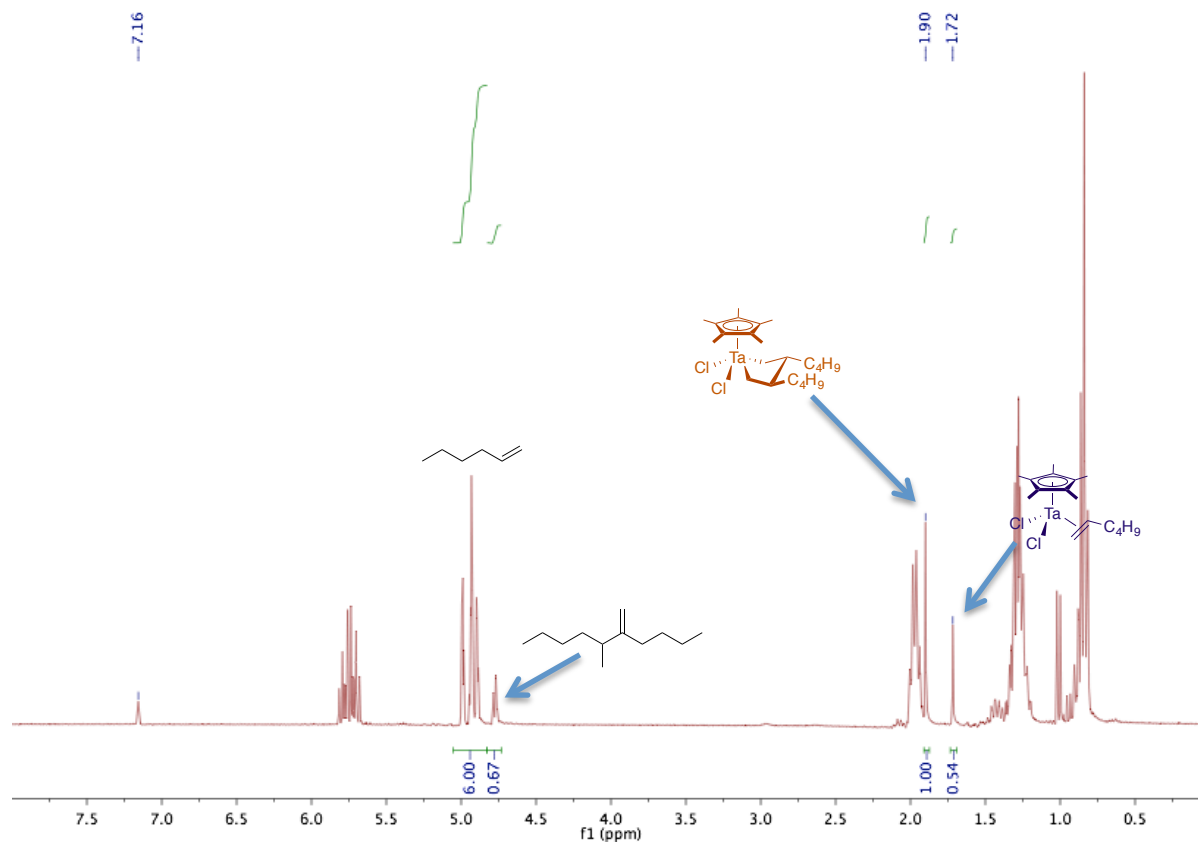


Figure S23. ^1H NMR spectrum of precatalyst **1** + excess 1-hexene (2.04 M initial) at 82 °C.

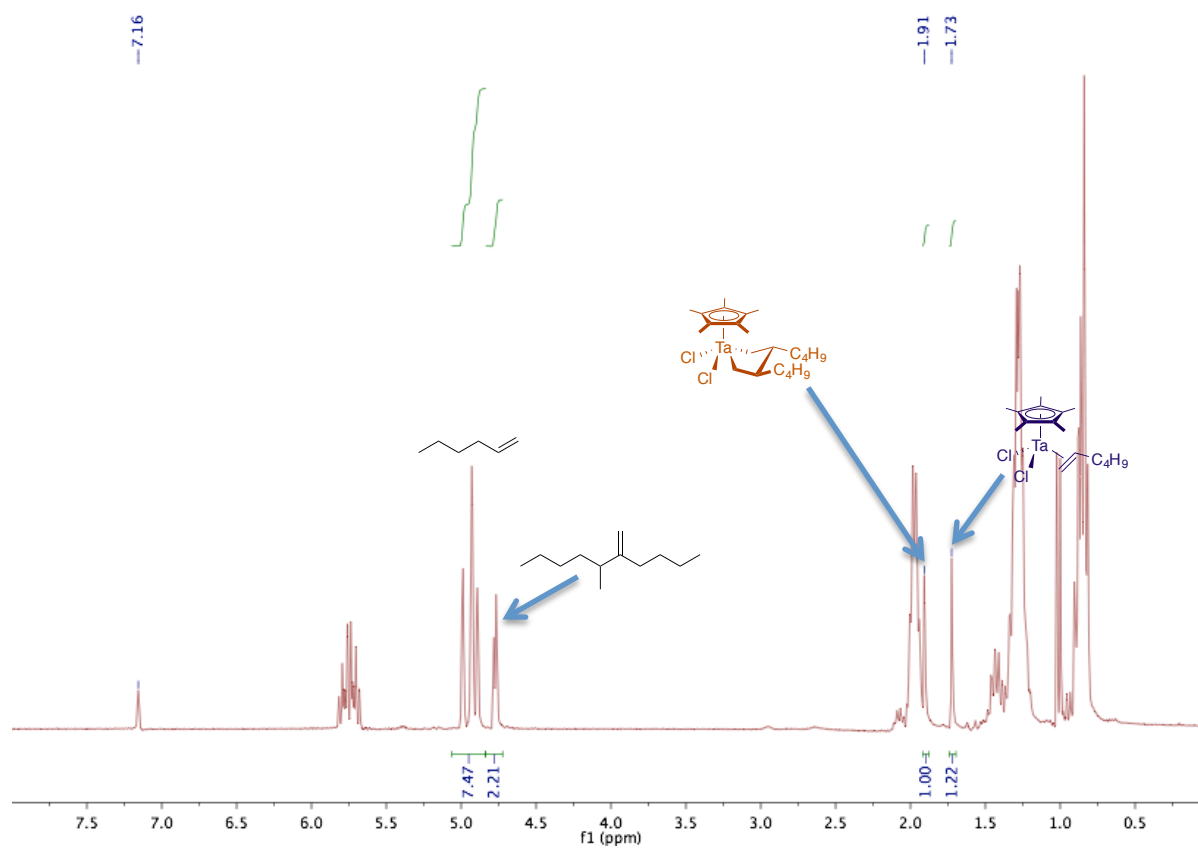


Figure S24. ^1H NMR spectrum of precatalyst **1** + excess 1-hexene (2.04 M initial) at 93 °C.

Procedure for Determining Initial Rates of 1-Hexene/*n*-Decane Transfer Hydrogenation

Precatalyst **2** (8.8 mg, 0.0150 mmol) was dissolved in 3 mL of a standard solution of 1-hexene (248, 412, 699, or 1010 mM) and adamantane internal standard (~25 mM) in *n*-decane in a 4 mL screw-top vial. The solution was stirred to dissolve the precatalyst and ensure a homogeneous solution. The solution was then split into fifteen aliquots of 0.2 mL each in fifteen separate 4 mL vials containing stir bars. These vials were sealed and stirred at either 100 or 125 °C in an aluminum block heater. At specified time intervals, (10, 20, 30, or 40 minutes) vials were removed from the heat block, immersed in a dry-ice/acetone bath to rapidly cool the contents, and then diluted with dichloromethane to quench the reaction. These solutions were passed through a short plug of silica gel into a GC autosampler vial, and analyzed by GC.

Data for each time point was collected from 3 or 4 different vials, giving 12-15 data points for each initial rate determination. The concentrations of *n*-hexane and the 2-hexenes (combined) were plotted versus time, and the k_{obs} values calculated by linear regression analysis (Figures S25-S26). These rate data were then plotted versus $[1\text{-hexene}]_0$ (Figure S27).

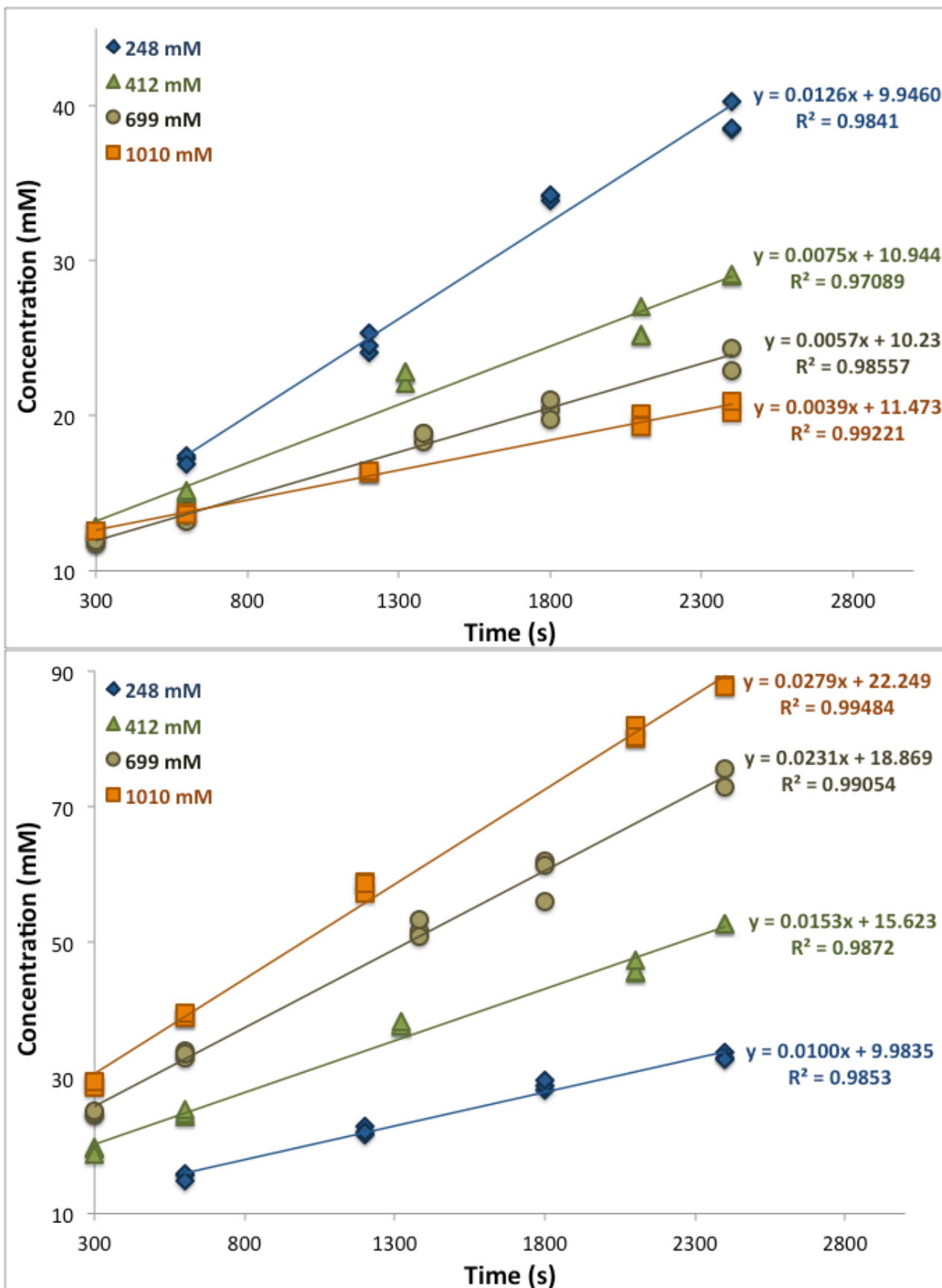


Figure S25. Initial rate measurements for 1-hexene/*n*-decane transfer hydrogenation at 100 °C. *Top:* *n*-Hexane formation (hydrogenation). *Bottom:* 2-Hexenes formation (isomerization).

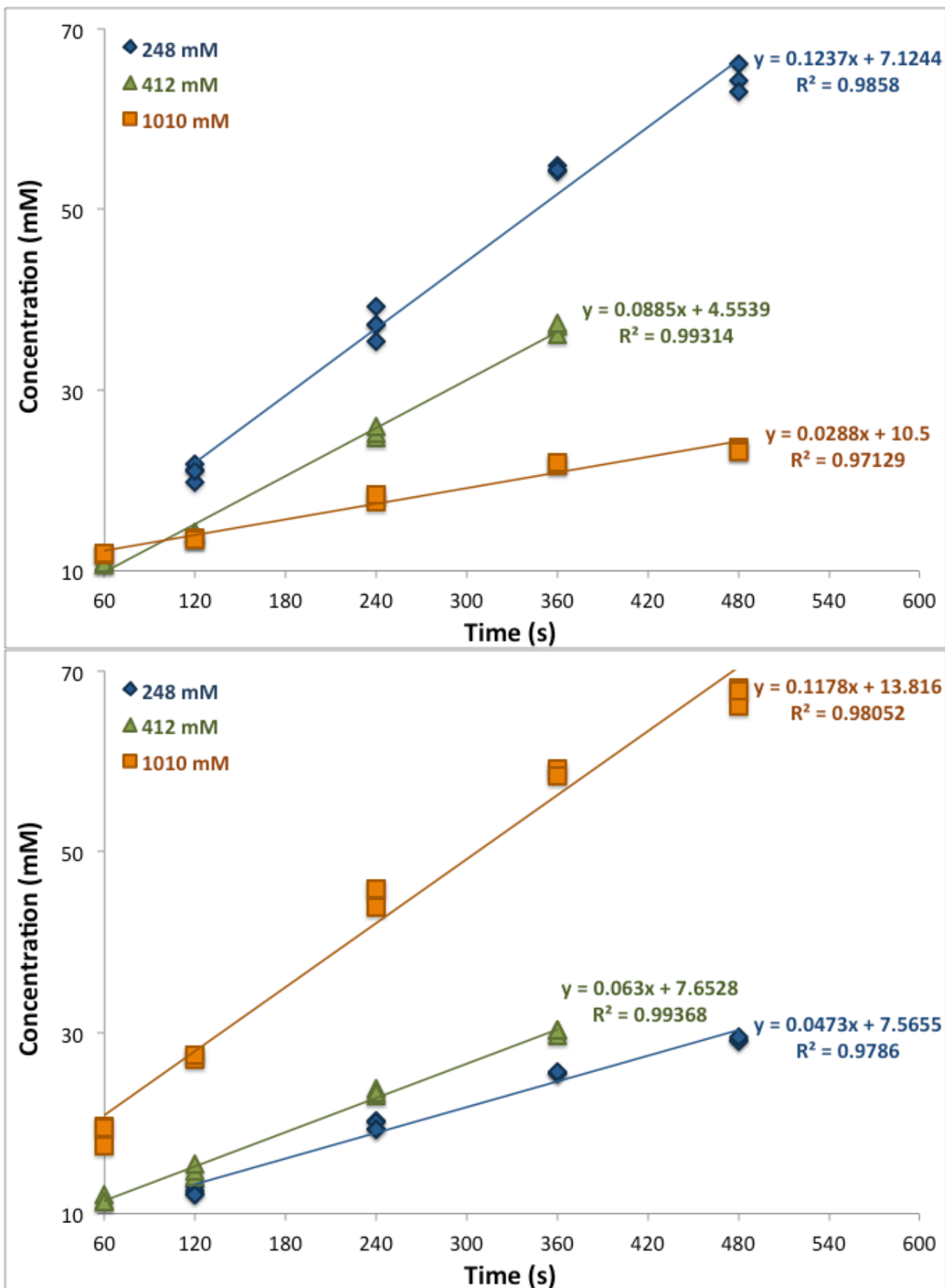


Figure S26. Initial rate measurements for 1-hexene/*n*-decane transfer hydrogenation at 125 °C. *Top:* *n*-Hexane formation (hydrogenation). *Bottom:* 2-Hexenes formation (isomerization).

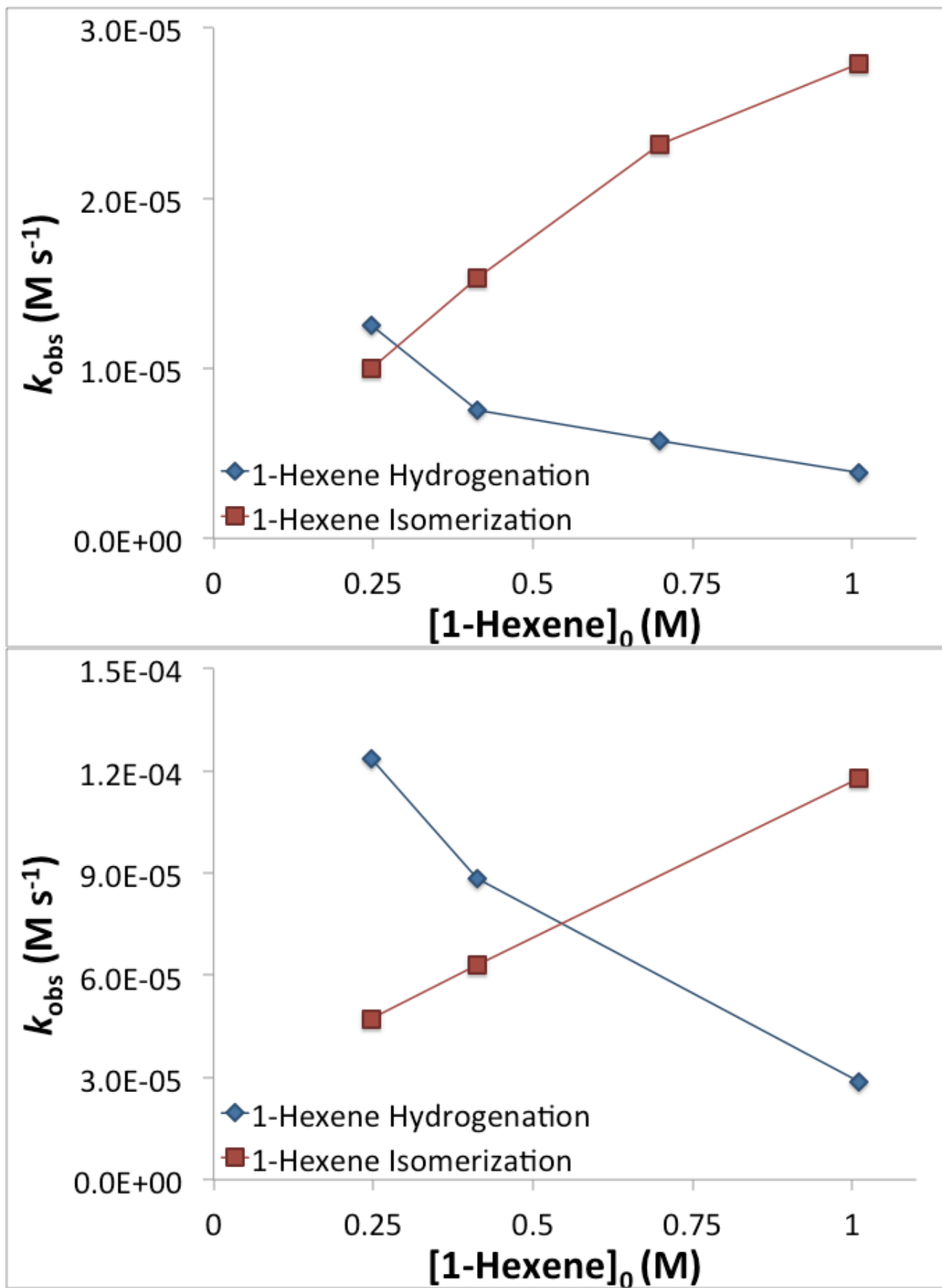


Figure S27. Initial rate of 1-hexene hydrogenation and isomerization by **2** (5 mM) versus $[1\text{-hexene}]_0$. *Top:* 100 °C. *Bottom:* 125 °C.

III: Full Table of Temperature/Concentration Effects on 1-Hexene/*n*-Heptane Coupling

Table S3. Expanded version of Table 4 (main text)

Observed products

C_{12} : R = R' = *n*-C₄H₉
 C_{13} : R = *n*-C₄H₉, R' = *n*-C₅H₁₁ or
R = *n*-C₅H₁₁, R' = *n*-C₄H₉
 C_{14} : R = R' = *n*-C₅H₁₁

Entry	[1-Hexene] ₀ mM ^a (Final Conc.)	Temp. °C	<i>n</i> -Hexane mM (%)	<i>t</i> -2-Hexene + <i>c</i> -2-Hexene mM (%)	C ₁₂ mM (%)	C ₁₃ / C ₁₄ mM (%)	C ₆ Mass Balance mM ^b	TON 1 ^c	TON 2 ^c	Coop. (%) ^d
1a	250 (0.4)	100	50.2 (20.5)	19.3 (7.7)	81.3 (66.3)	12.6 (10.3) / 9.6 (7.8)	245.2	13 (3)	10 (6)	63.5
1b	250 (0.7)	100	54.7 (22.6)	16.0 (6.4)	78.6 (64.9)	13.8 (11.4) / 10.0 (8.2)	242.5	13 (3)	11 (7)	61.7
1c	250 (0.9)	100	51.9 (21.2)	15.6 (6.2)	81.7 (66.9)	12.6 (10.3) / 9.9 (8.1)	244.4	13 (3)	10 (6)	62.4
2a	500 (~0)	100	88.2 (17.7)	11.0 (2.2)	192.7 (77.2)	14.5 (5.8) / 10.7 (4.3)	499.0	27 (3)	18 (7)	40.7
2b	500 (~0)	100	87.1 (17.4)	11.1 (2.2)	193.7 (77.4)	14.8 (5.9) / 9.7 (3.9)	500.3	27 (3)	17 (7)	39.4
3a	1000 (3.4)	100	86.3 (8.6)	27.0 (2.7)	432.8 (86.5)	18.7 (3.7) / 10.2 (2.0)	1000.9	58 (4)	17 (8)	45.3
3b	1000 (3.4)	100	87.2 (8.7)	28.5 (2.8)	431.1 (86.2)	18.8 (3.8) / 10.2 (2.0)	1002.0	58 (4)	17 (8)	45.0
4a	250 (0.8)	125	108.4 (43.2)	10.8 (4.3)	57.7 (46.0)	15.4 (12.3) / 13.0 (10.3)	250.9	11 (4)	22 (8)	38.2
4b	250 (0.7)	125	103.3 (41.5)	11.5 (4.6)	59.1 (47.5)	15.2 (12.2) / 13.0 (10.4)	248.7	11 (4)	21 (8)	39.9
5a	500 (0.8)	125	145.0 (28.6)	18.1 (3.6)	160.1 (63.1)	23.9 (9.4) / 14.4 (5.7)	507.3	25 (5)	29 (11)	36.4
5b	500 (0.7)	125	135.4 (26.9)	17.3 (3.4)	163.8 (65.0)	23.3 (9.3) / 14.1 (5.6)	503.6	25 (5)	27 (10)	38.1
6a	960 (~0)	125	157.3 (16.5)	38.5 (4.0)	362.7 (76.1)	32.0 (6.7) / 14.8 (3.1)	953.2	51 (6)	31 (12)	39.1
6b	1040 (~0)	125	164.5 (15.6)	40.0 (3.8)	408.6 (77.5)	32.2 (6.1) / 13.4 (2.5)	1054.0	57 (6)	33 (12)	35.9
7a ^e	250 (0.6)	150	145.6 (58.8)	14.6 (5.9)	37.4 (30.2)	11.9 (9.6) / 11.7 (9.5)	247.4	8 (3)	29 (7)	24.3
7b ^e	250 (~0)	150	147.3 (57.9)	15.1 (14.8)	40.3 (31.7)	11.3 (8.9) / 12.4 (9.8)	254.3	8 (3)	29 (7)	24.5
8a ^e	500 (~0)	150	198.6 (39.6)	42.0 (8.4)	118.2 (47.2)	24.3 (9.7) / 14.2 (5.6)	501.4	20 (5)	40 (11)	26.5
8b ^e	500 (2.3)	150	193.6 (38.8)	36.0 (7.2)	122.4 (49.1)	21.9 (8.8) / 13.6 (5.5)	498.6	20 (4)	39 (10)	25.4
9 ^{e,f}	1000 (6.2)	150	295.6 (29.7)	97.8 (9.8)	276.2 (55.6)	41.8 (8.4) / 15.2 (3.1)	993.7	42 (7)	59 (14)	24.4

^aDetermined from concentration of standard solution. ^b[1-hexene] + [*n*-hexane] + [*t*-2-hexene] + [*c*-2-hexene] + 2[C₁₂] + [C₁₃]
^cTONs in parentheses are for production of C₁₃/C₁₄. ^dSee Ref. 17 in the main text. ^eReactions performed in thick-walled glass pressure tubes with screw-down Teflon plugs sealed with an O-ring. The tubes were immersed in a 150 °C oil bath up to the bottom of the plug. ^fRepeat attempts of this reaction resulted in O-ring seal failure and evaporation of the contents; therefore, only one run was performed.

IV: Styrene/*n*-Heptane Coupling Reactions

Procedure for Styrene Dimerization using **1** (Equation 12, main text)

Precatalyst **1** (10.4 mg, 0.025 mmol), styrene (53.5 mg, 0.514 mmol), and mesitylene (internal standard, 10.8 mg, 0.0898 mmol) were dissolved in C₆D₆ (1 mL). This solution was then transferred into two J. Young NMR tubes. Initial ¹H NMR spectra were recorded (Figure S29), and then the tubes were heated to 110 °C in an oil bath. After set time intervals, the tubes were removed from the oil baths and new spectra acquired, until ~95% conversion was reached (72 h, Figure S30). NMR yields were determined in the following manner: The area of the signal for the three aromatic protons of the mesitylene internal standard (~6.75 ppm) was set at 25.00. The areas of the peaks for the two terminal alkene protons of styrene were determined in the initial spectra, as well as the areas of the two peaks for the vinylidene protons of the major product⁷ at 72 hours. The ratios of these values were determined, giving four measurements of the yield. These values were averaged for each run, and then these two values were averaged again to give a final NMR yield of ~88%. The peaks for the minor regioisomer⁸ (d, 3H, 1.23 ppm, CH₃; m, 1H, 3.25 ppm, -CH(CH₃)Ph) were also integrated in the 72 h spectra, giving an average NMR yield of ~2%.

NMR yields: Run 1: 82.8%; 89.3%; 85.6%; 92.3%. Average: 87.5% (Minor isomer: 2.3%)
Run 2: 84.4%; 86.3%; 90.9%; 92.9%. Average: 88.6% (Minor isomer: 2.3%)

Once NMR yields were established, the two samples were combined and diluted with dichloromethane to a total volume of ~4 mL. Adamantane (16.2 mg, GC standard) was added, and the mixture analyzed by GC (Figure S28). The yield of both major and minor styrene dimers was determined to be 81% (major) and 2% (minor).

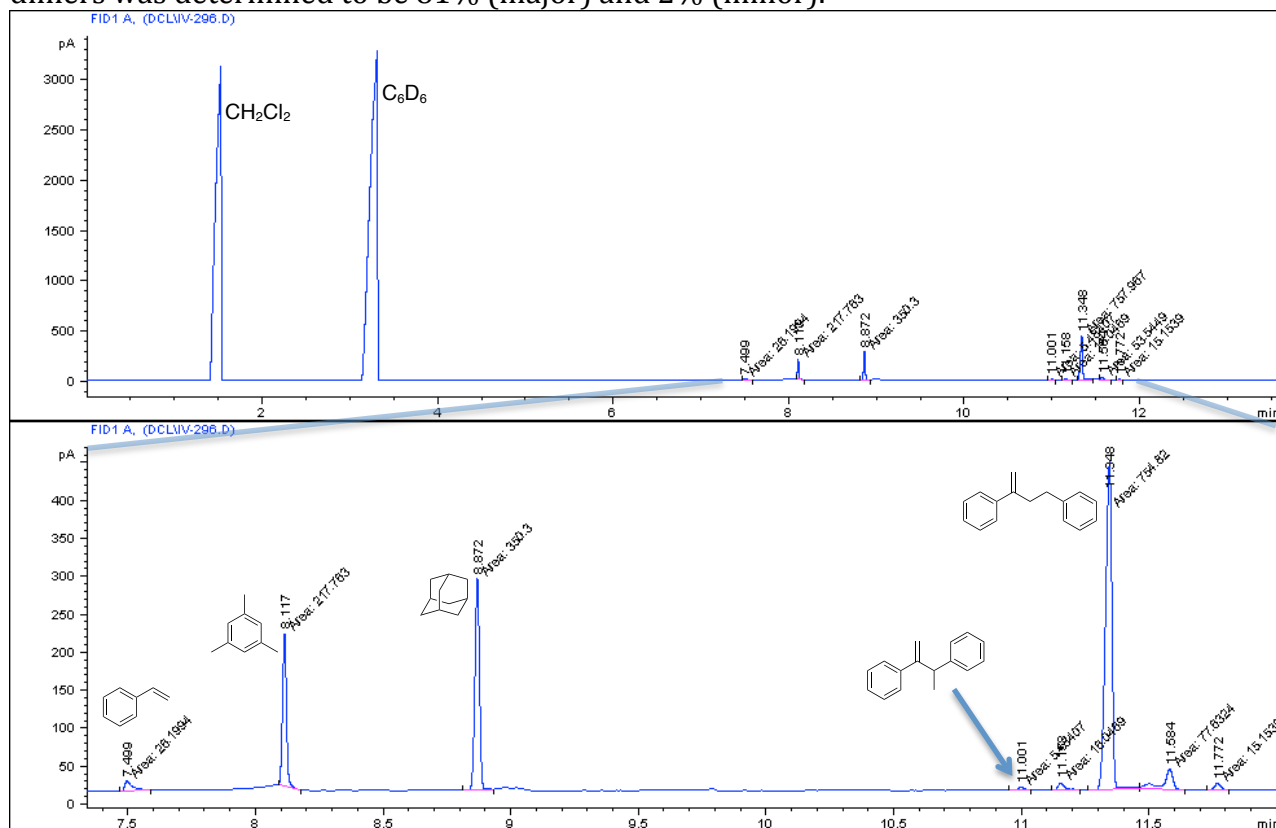


Figure S28: GC trace of styrene (500 mM) dimerization by **1** (25 mM), 110 °C, 72 h.

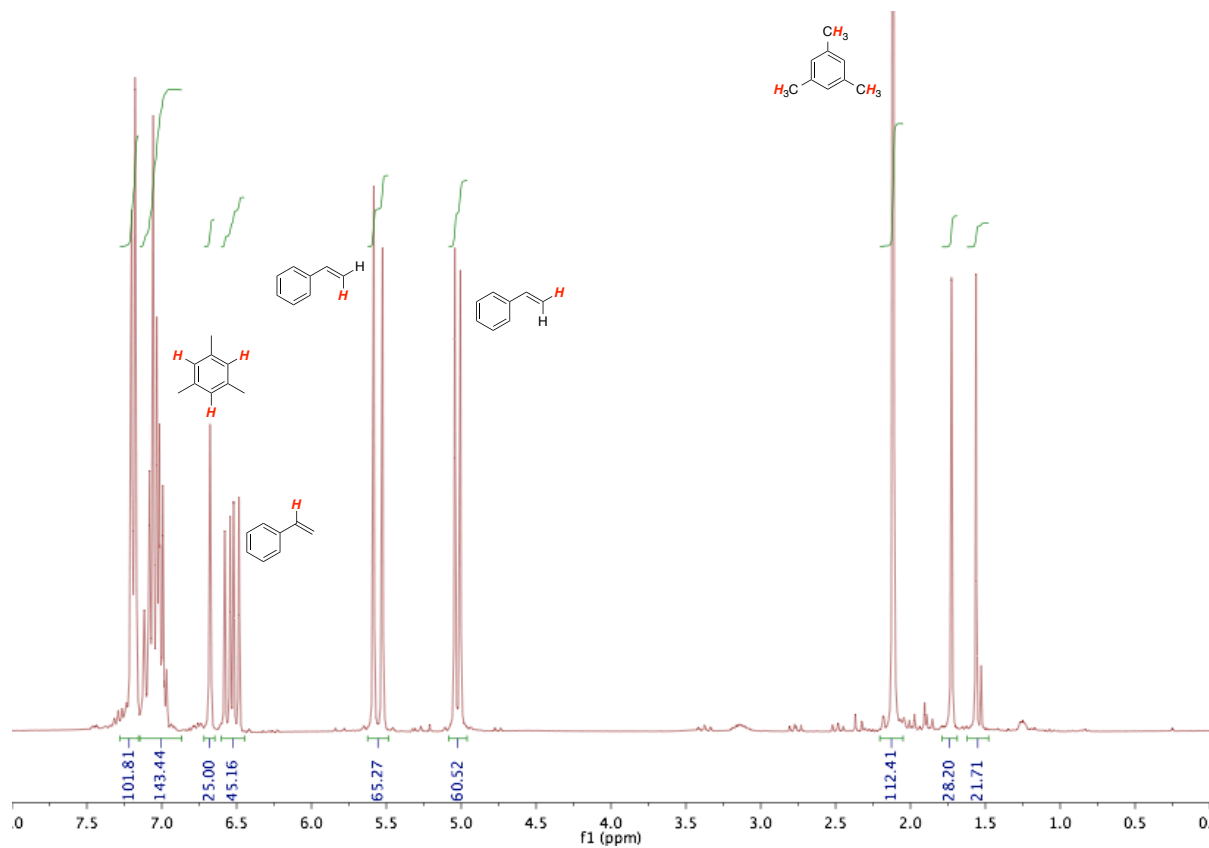


Figure S29 Initial ¹H NMR spectrum of styrene (500 mM) dimerization by **1** (300 MHz, C₆D₆)

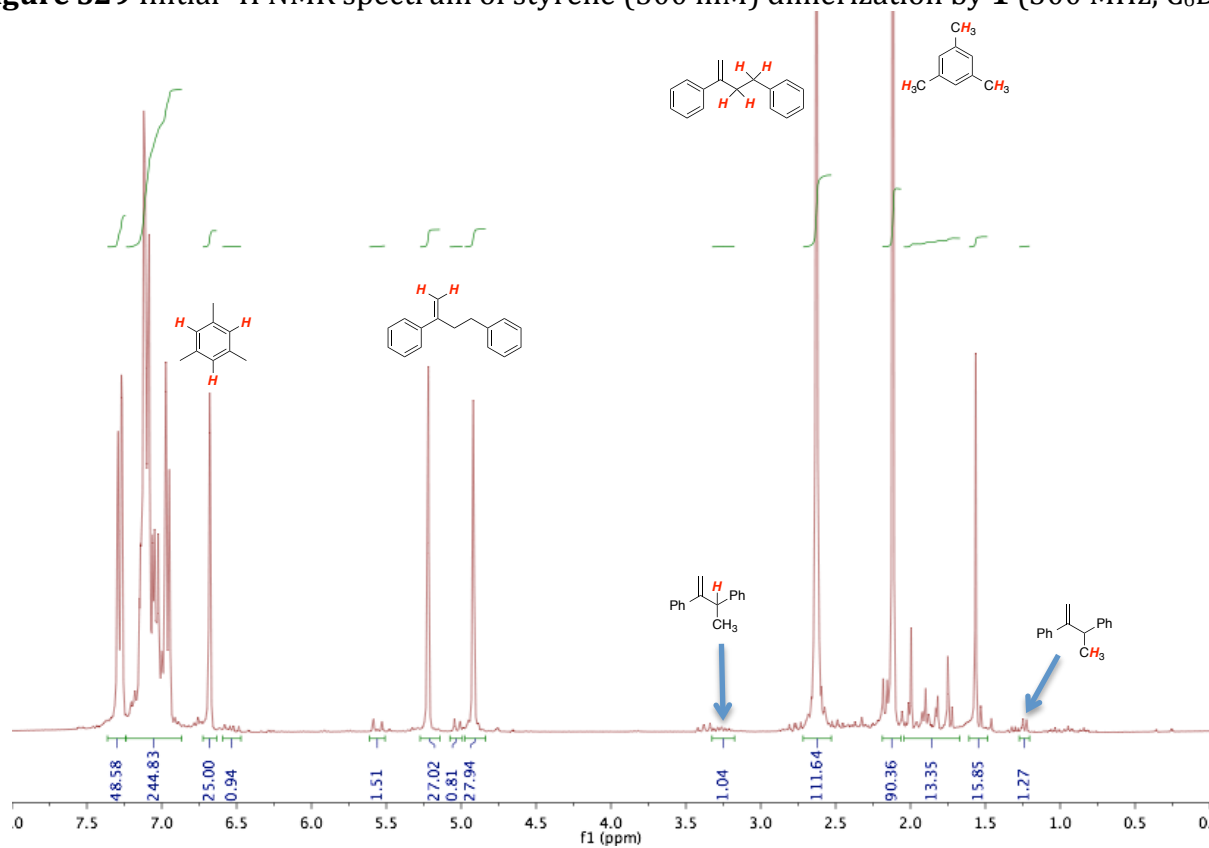


Figure S30. ¹H NMR spectrum of styrene (500 mM) dimerization by **1** (25 mM), 110 °C, 72 h (300 MHz, C₆D₆).

Procedure for Monitoring Dimerization of Styrene over Four Half Lives (Figure 8, main text):

Precatalyst **1** (6.6 mg, 0.016 mmol), styrene (53.0 mg, 0.509 mmol), and 1,3,5-trimethoxybenzene (internal standard, 1.6 mg) were dissolved in C₆D₆ (2 mL). This solution was then split evenly into four J. Young NMR tubes. Initial ¹H NMR spectra were recorded, and then the tubes were heated to either 100 °C (two tubes) or 125 °C (two tubes) in an oil bath. After set time intervals, the tubes were removed from the oil baths and new spectra acquired, until ~4 half lives had passed. The three aromatic protons of the 1,3,5-trimethoxybenzene internal standard (~6.25 ppm) were integrated versus the terminal vinylic proton of styrene that is *cis* relative to the phenyl group (~5.6 ppm), with the former area set at 25.00. The concentration of styrene at each time point was determined by the following formula:

$$[\text{Styrene}] = [\text{Styrene}]_0 \times (I/I_0)$$

$$[\text{Styrene}]_0 = 0.255 \text{ M}$$

$$I = \text{area of vinylic signal @ 5.6 ppm}$$

$$I_0 = \text{initial area of vinylic signal @ 5.6 ppm}$$

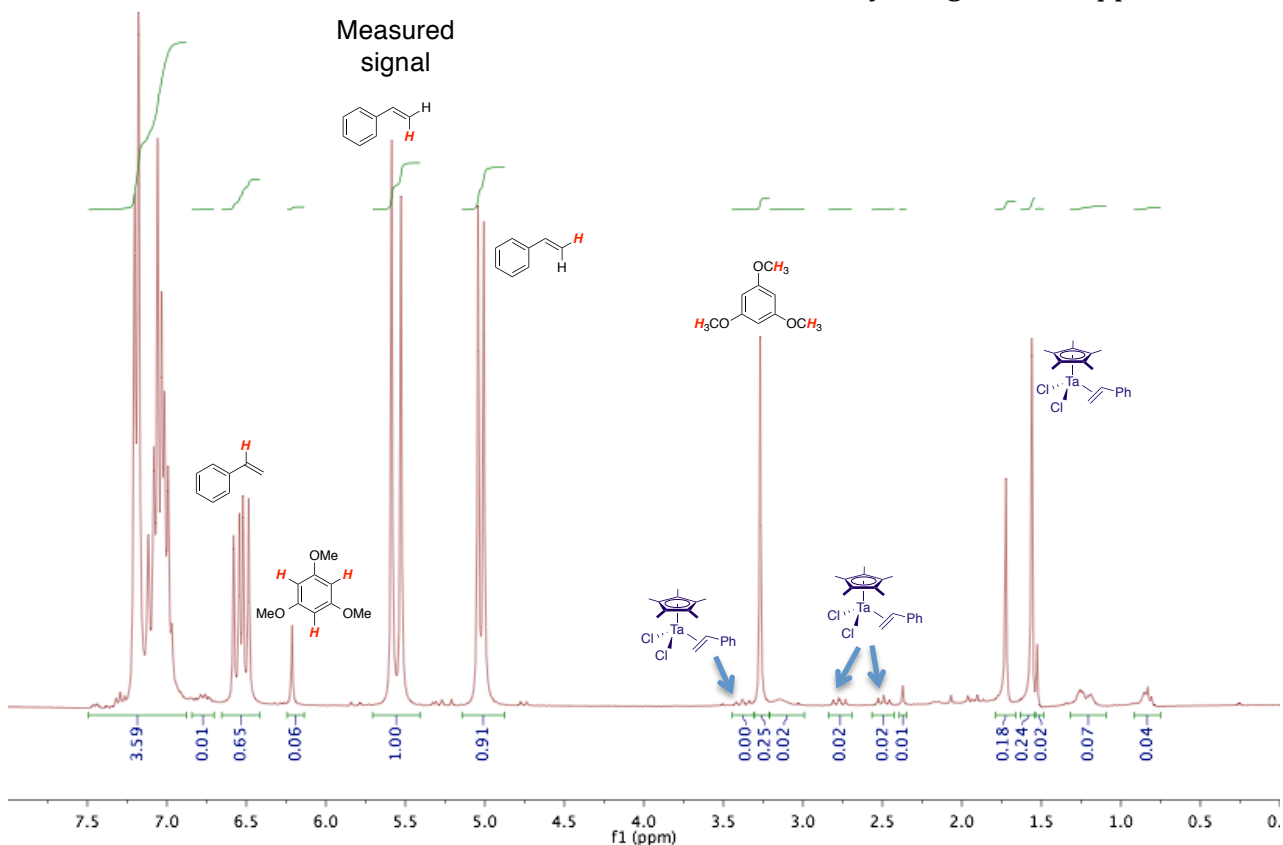


Figure S31: ¹H NMR spectrum of the dimerization of styrene with **1** (t = 0 h, initial, 300 MHz, C₆D₆).

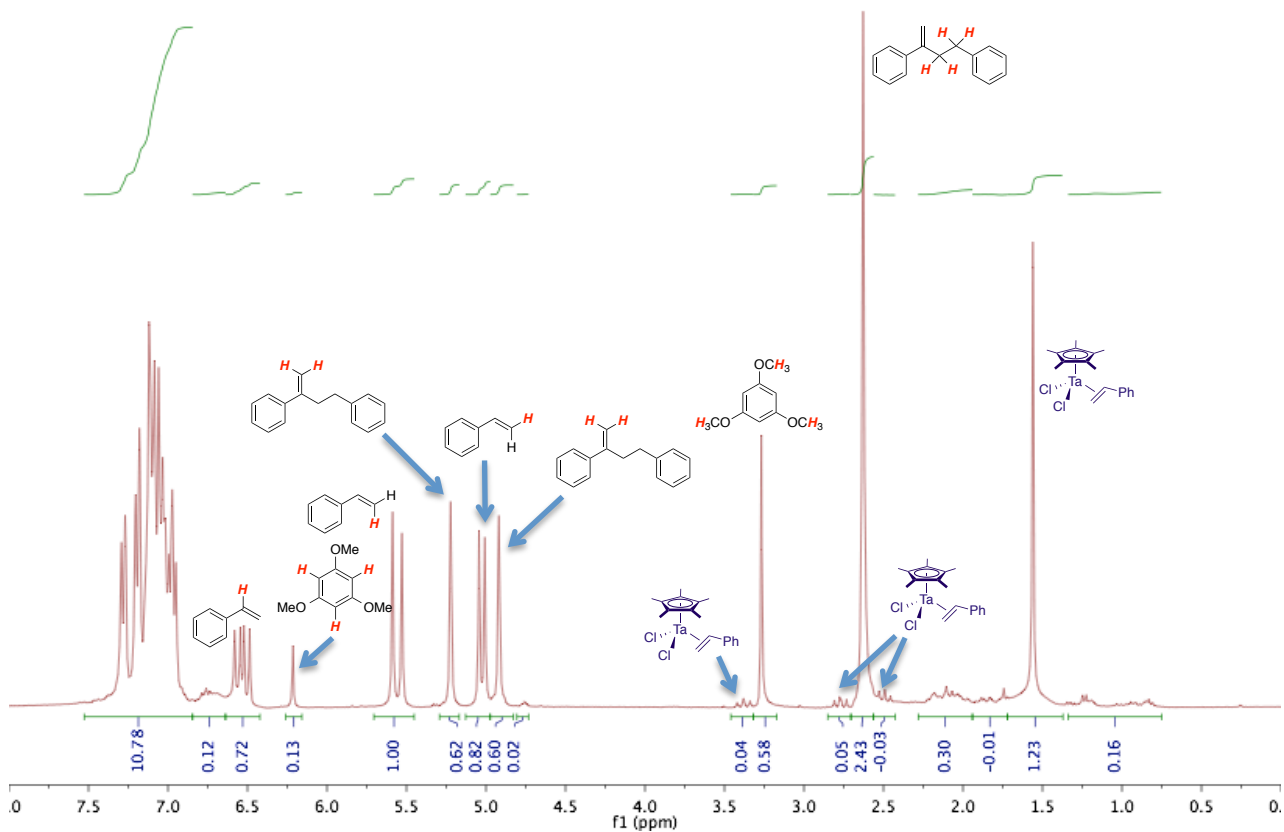


Figure S32: ^1H NMR spectrum of the dimerization of styrene with **1** ($t = 42$ h, ~50%, 300 MHz, C_6D_6).

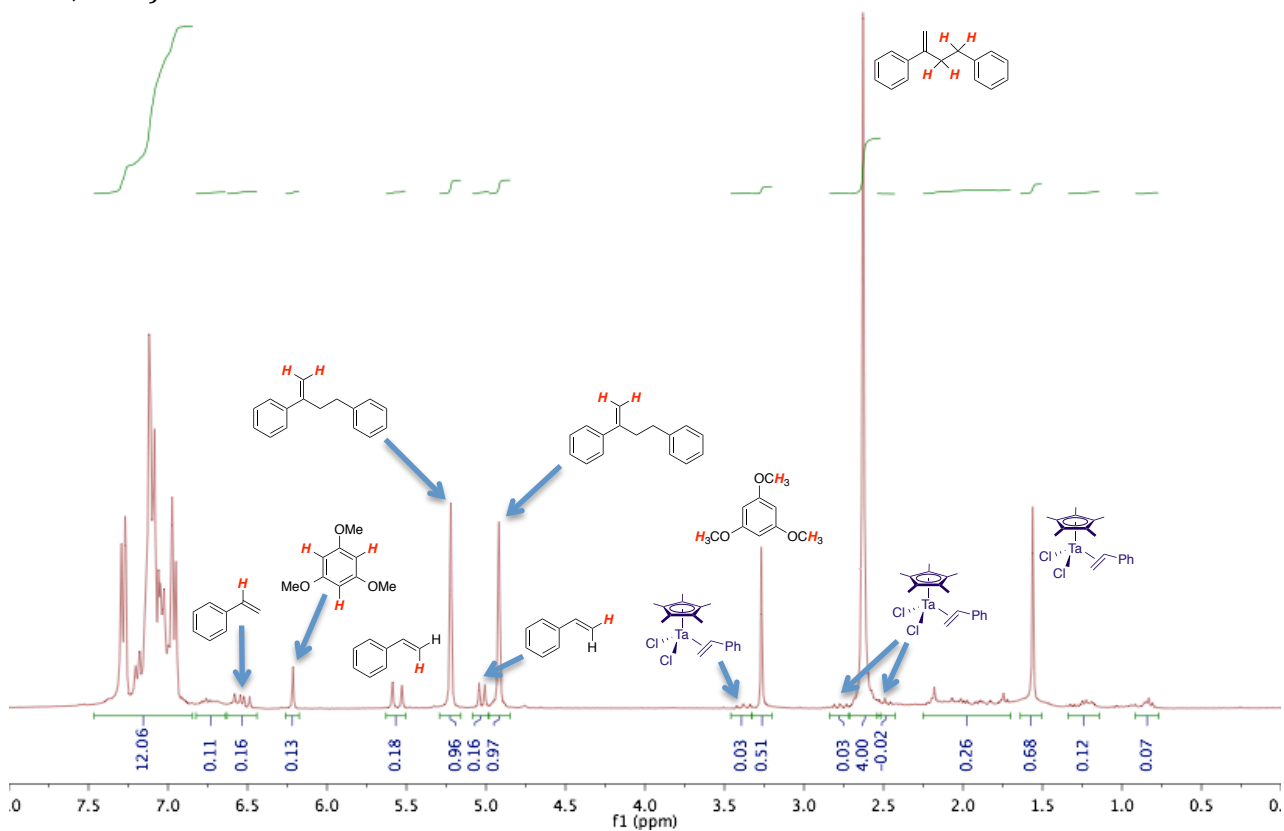


Figure S33: ^1H NMR spectrum of the dimerization of styrene with **1** ($t = 160$ h, final point, 300 MHz, C_6D_6).

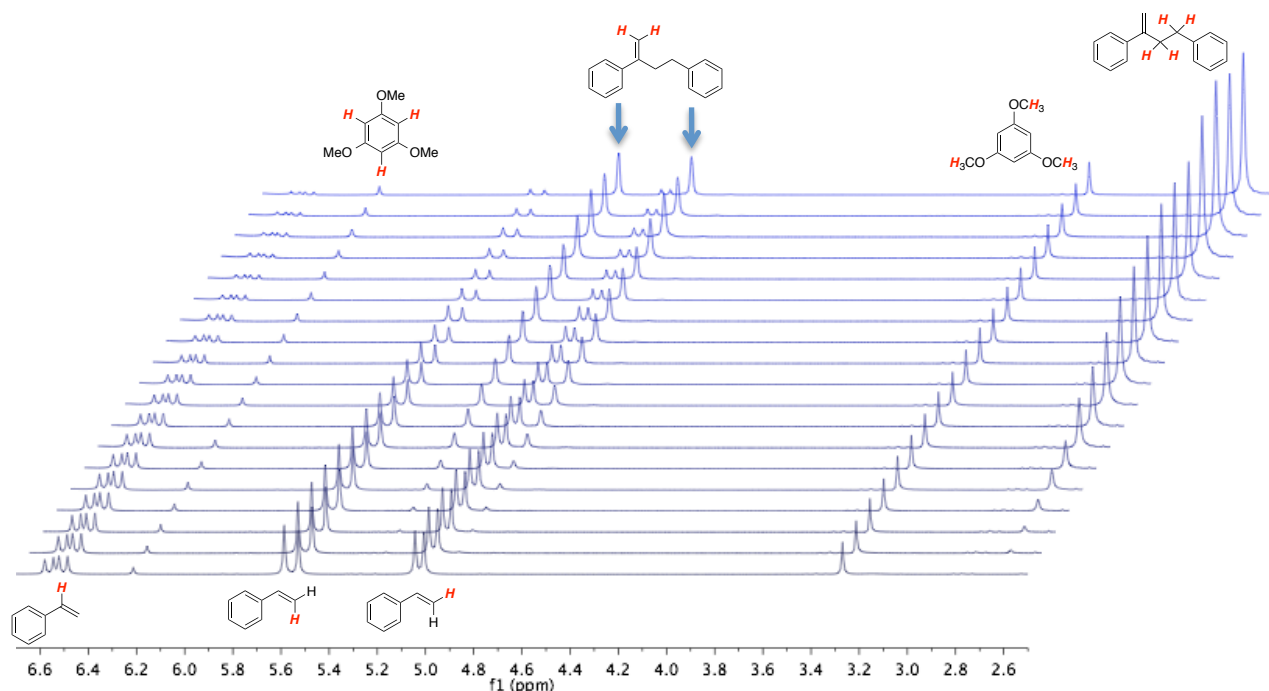


Figure S34: Stack plot of ^1H NMR spectra (2.5-6.7 ppm, 300 MHz, C_6D_6) for styrene dimerization catalyzed by **1** at 100 °C. Nineteen spectra were taken at the following time points: 0, 1, 2, 4, 7, 10, 18, 24, 32, 42, 52, 64, 72, 88, 97, 109, 119, 134, and 160 hours ($t = 0$ h at bottom).

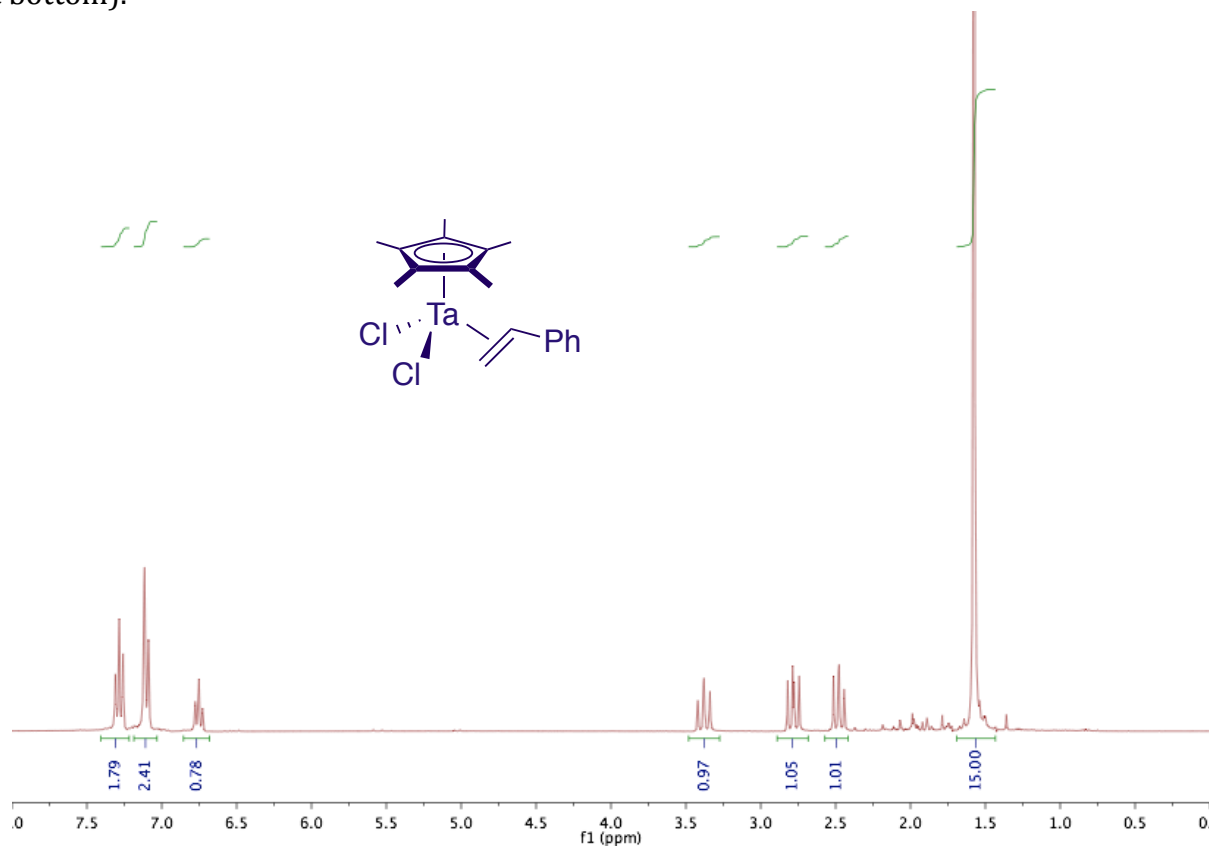


Figure S35: ^1H NMR spectrum of $\text{Cp}^*\text{TaCl}_2(\text{styrene})_3$ in C_6D_6 (300 MHz, room temp.), establishing chemical shifts for comparison to catalytic runs.

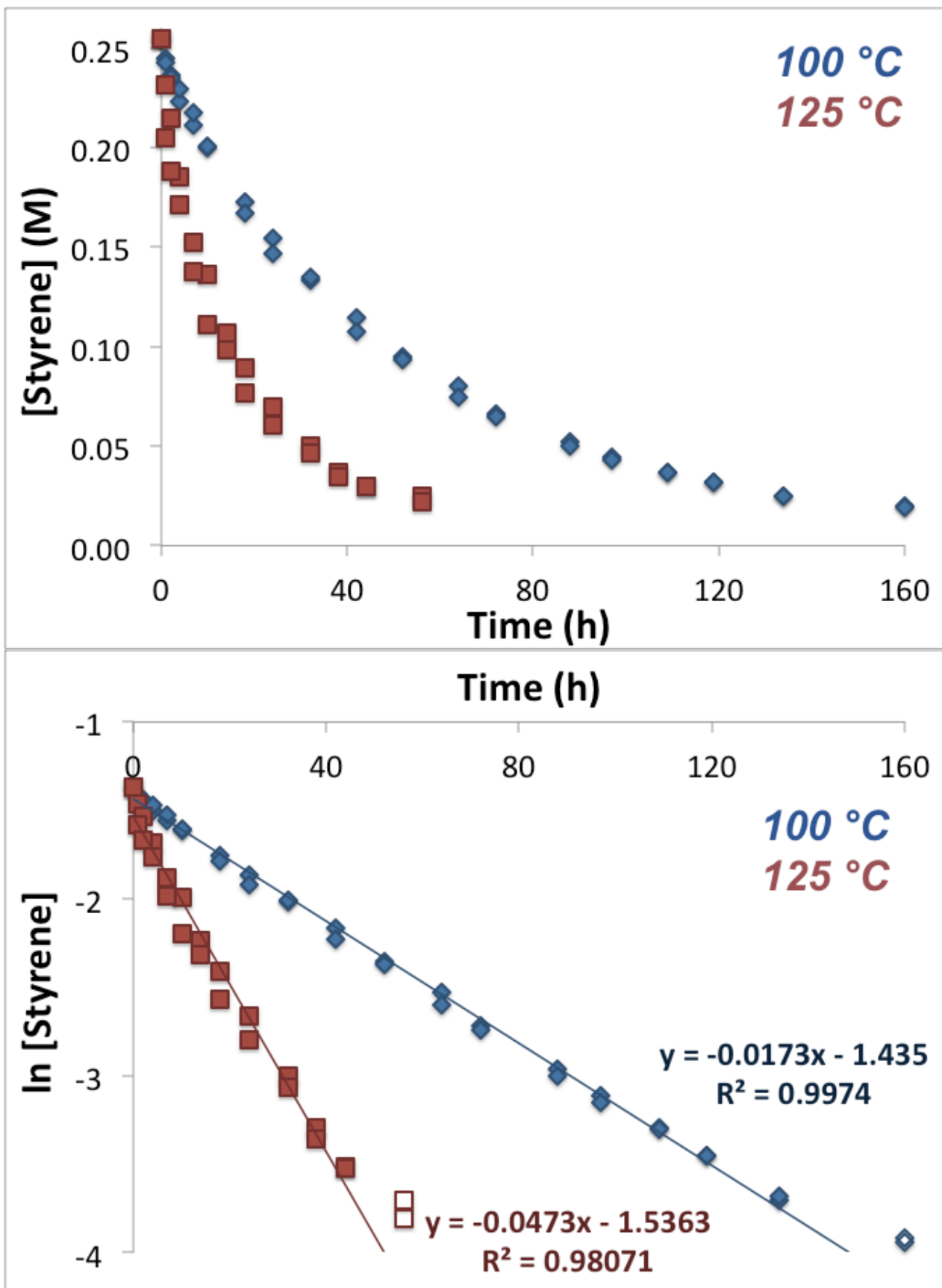


Figure S36. Consumption of styrene during dimerization catalyzed by **1** at 100 °C and 125 °C monitored by 1H NMR spectroscopy (two runs). *Top*: Conc. plot. *Bottom*: \ln plot.

Initial Rates of Styrene/1-Heptene Coupling using 1:

Precatalyst **1** (10.1 mg, 0.0243 mmol), styrene (97.7 mg, 0.938 mmol), 1-heptene (76.0 mg, 0.774 mmol), and adamantane (internal standard, 12.0 mg, 0.088 mmol) were dissolved in 2.8 mL of *n*-decane in a 4 mL screw-top vial containing a Teflon-coated stir bar. The vial was sealed with a Teflon-lined screw cap and the contents stirred vigorously to ensure complete dissolution of **1**. The solution was then split into fifteen aliquots of 0.2 mL each in fifteen separate 4 mL vials containing stir bars. These vials were sealed and stirred at 100 °C in an aluminum block heater. At specified time intervals, (1, 2, 3, or 4 minutes) vials were removed from the heat block, immersed in a dry-ice/acetone bath to rapidly cool the contents, and then diluted with dichloromethane to quench the reaction. These solutions were passed through a short plug of silica gel into a GC autosampler vial, and analyzed by GC.

Data for each time point was collected from 3 different vials, giving 12 data points for each initial rate determination. The concentrations of the 1-heptene dimers (both regioisomers combined), and the cross-products (all isomers combined) were plotted versus time, and the k_{obs} values calculated by linear regression analysis (Figure S37). In order to normalize for the different concentrations of 1-heptene and styrene used, the initial rate for styrene dimerization was multiplied by a factor of 0.825 (the ratio of $[\text{1-heptene}]_0/[\text{styrene}]_0$), giving an initial rate ratio of 4.05:1 for 1-heptene dimerization versus styrene/1-heptene coupling. Styrene dimers were not observed under these conditions.

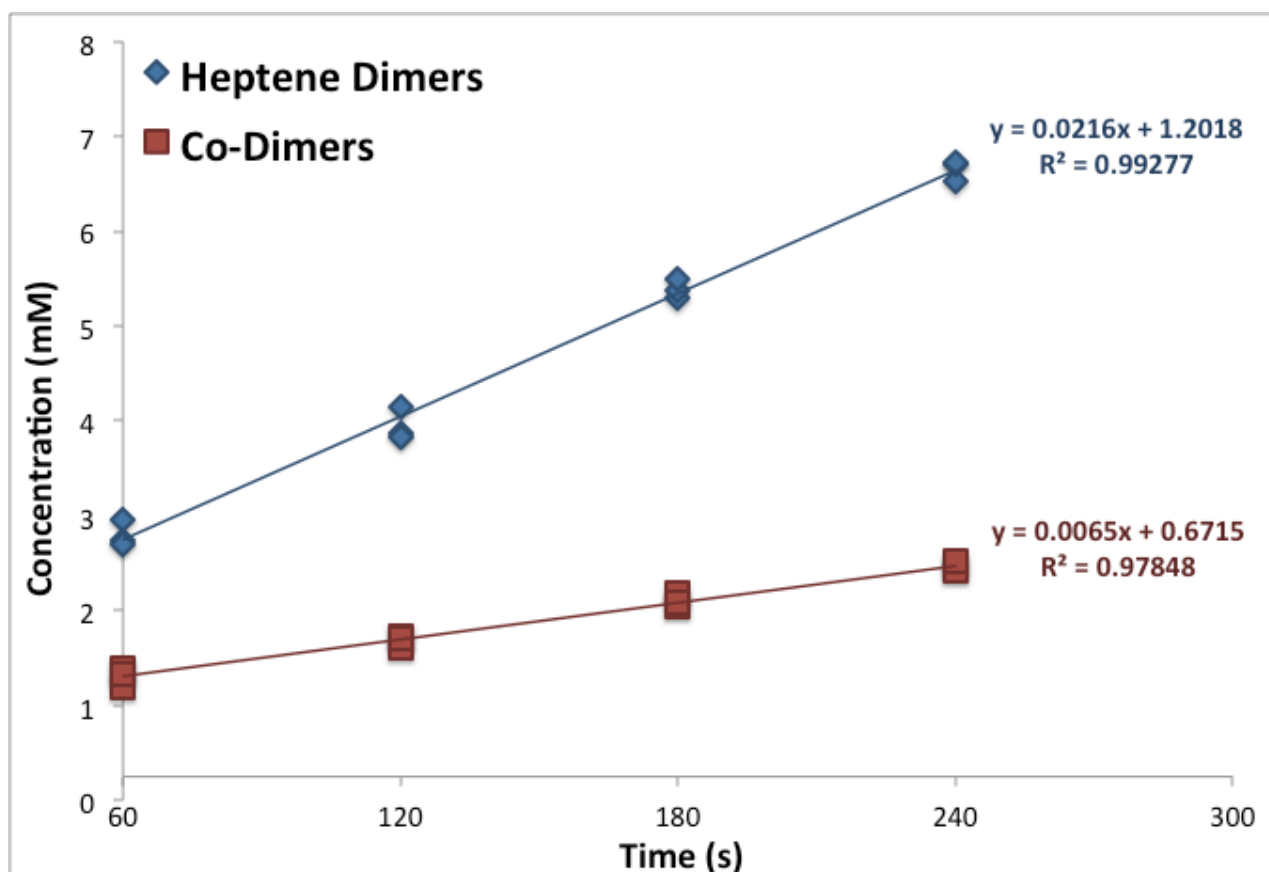


Figure S37. Initial rates of styrene/1-heptene coupling with **1**.

Procedure for Styrene/1-Heptene Coupling using **1** (Equation 13, main text):

Precatalyst **1** (20.4 mg, 0.050 mmol), styrene (52.1 mg, 0.500 mmol), 1-heptene (49.0 mg, 0.499 mmol), and adamantane (internal standard, 10.2 mg, 0.075 mmol) were dissolved in 2 mL of *n*-heptane in a 4 mL screw-top vial containing a Teflon-coated stir bar. The vial was sealed with a Teflon-lined screw cap and the contents stirred at 100 °C in an aluminum block heater. After 18 hours, the vial was removed, and the contents diluted with dichloromethane to a total volume of ~4 mL. This solution was passed through a short plug of silica gel before analysis by GC and GC/MS (Figures S38 and S39-S44).

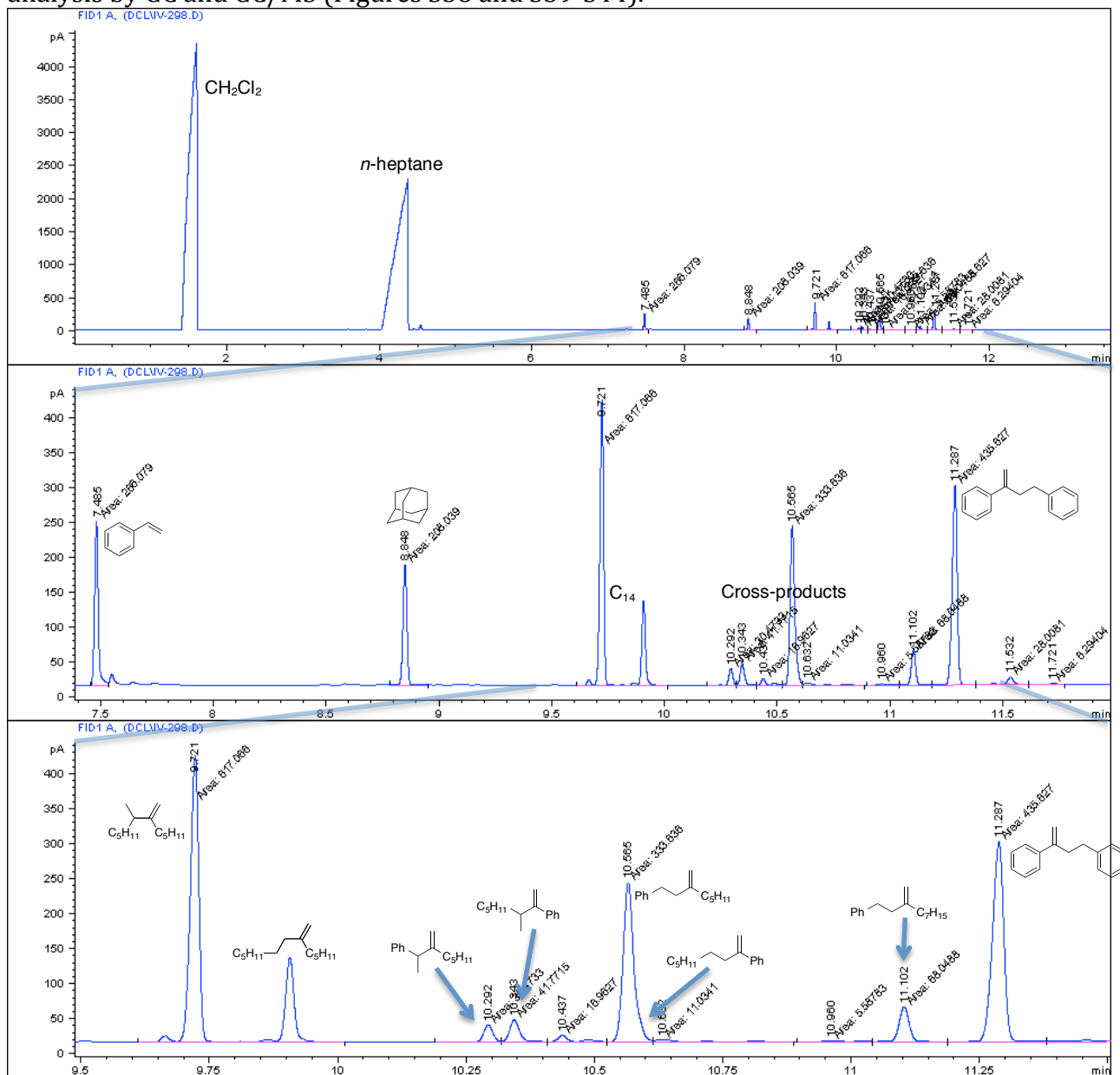


Figure S38: GC trace of the coupling of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce cross-products. The C₁₄ products (1-heptene dimers) are assigned based on previous work;⁹ the cross-products are assigned based on GC/MS and comparison to authentic samples of three of the proposed compounds (*vide infra*). The styrene/1-nonane cross-product (peak at 11.102 min) is assigned based on GC/MS, and its regiochemistry by analogy to the major isomer of the styrene/1-heptene cross-products. The 1-nonane is presumably generated from coupling 1-heptene and ethylene (from **1**).

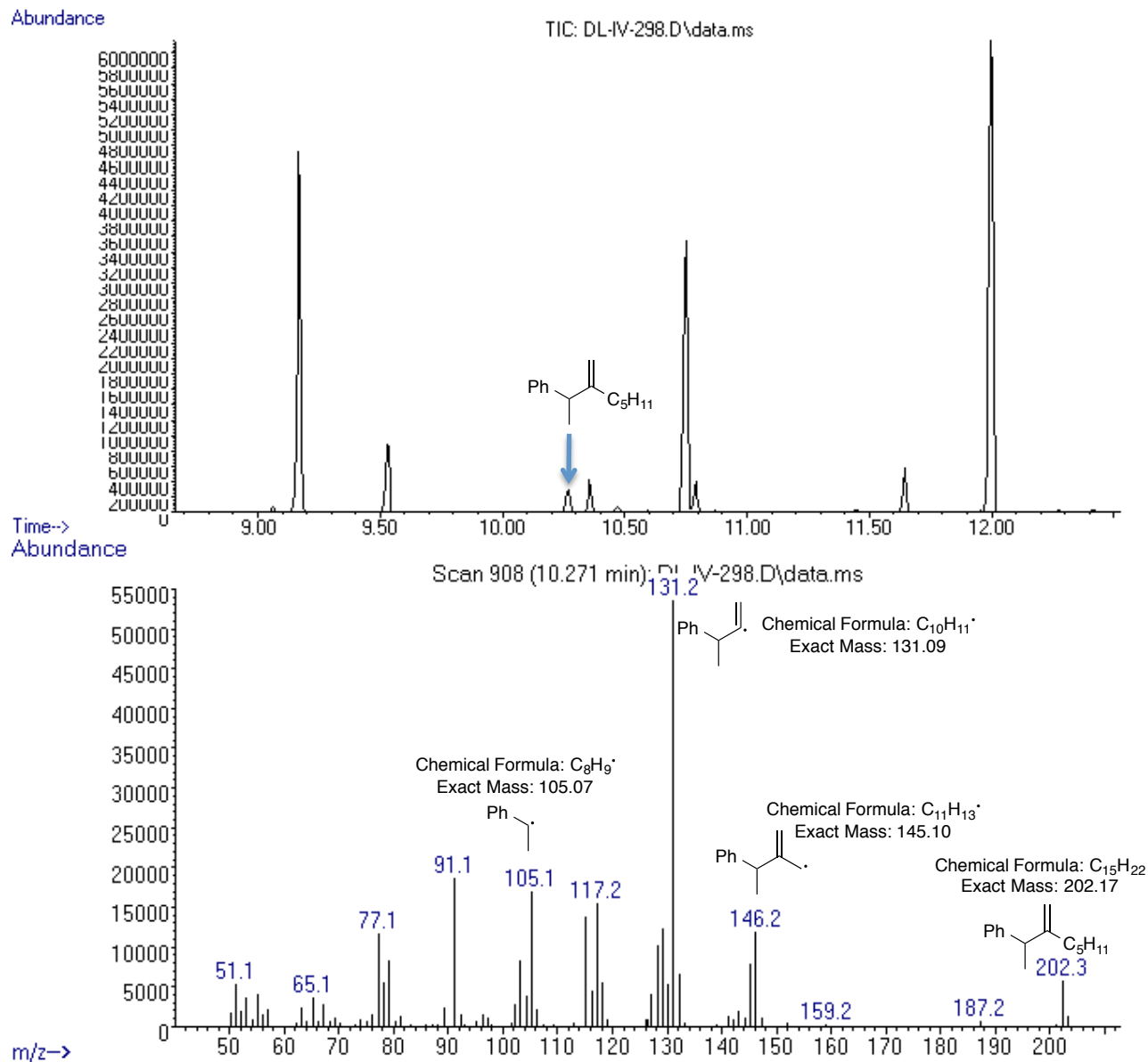


Figure S39: GC/MS trace of the coupling of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce cross-products. Mass spectrum corresponds to indicated peak.

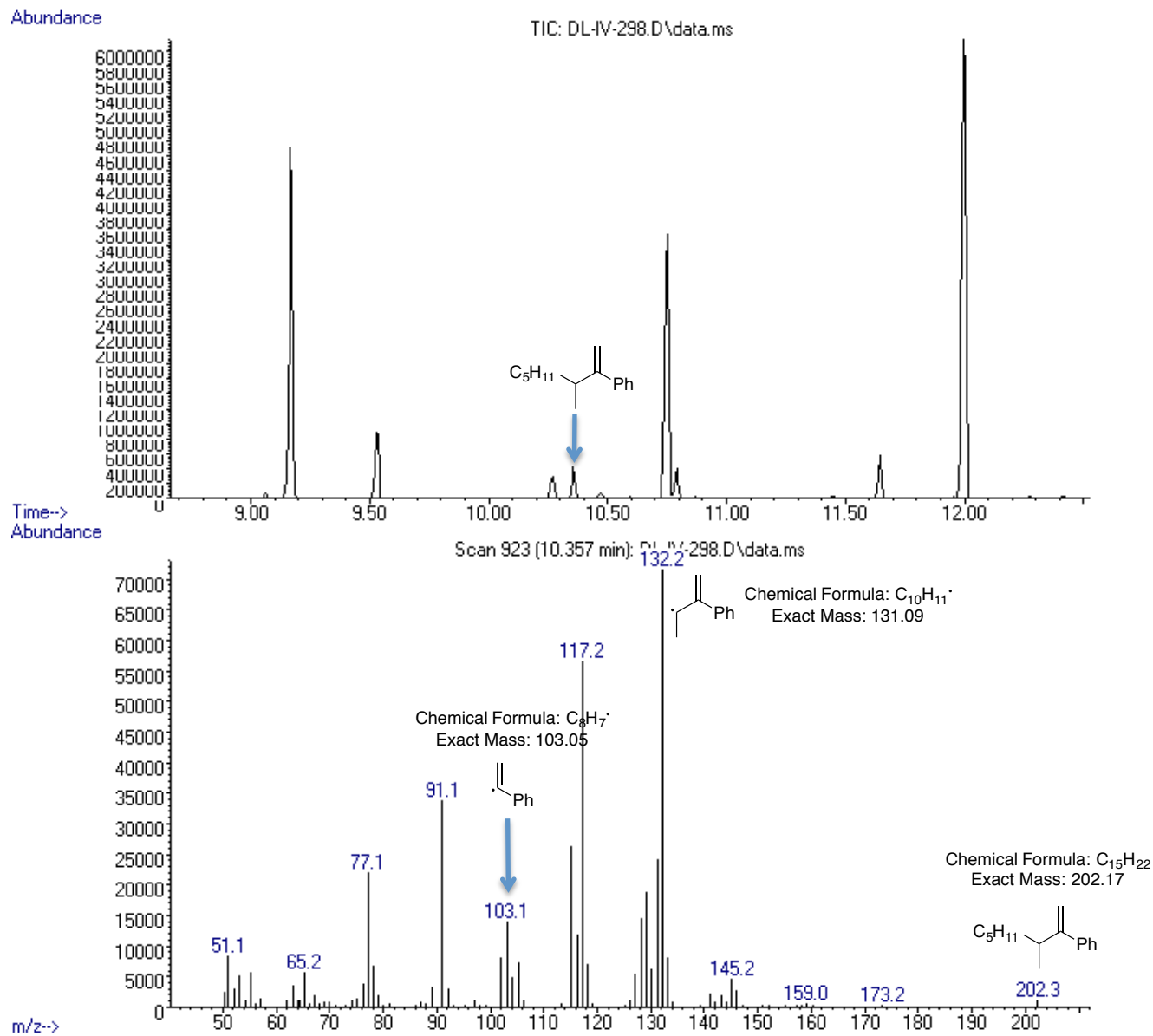


Figure S40: GC/MS trace of the coupling of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce cross-products. Mass spectrum corresponds to indicated peak.

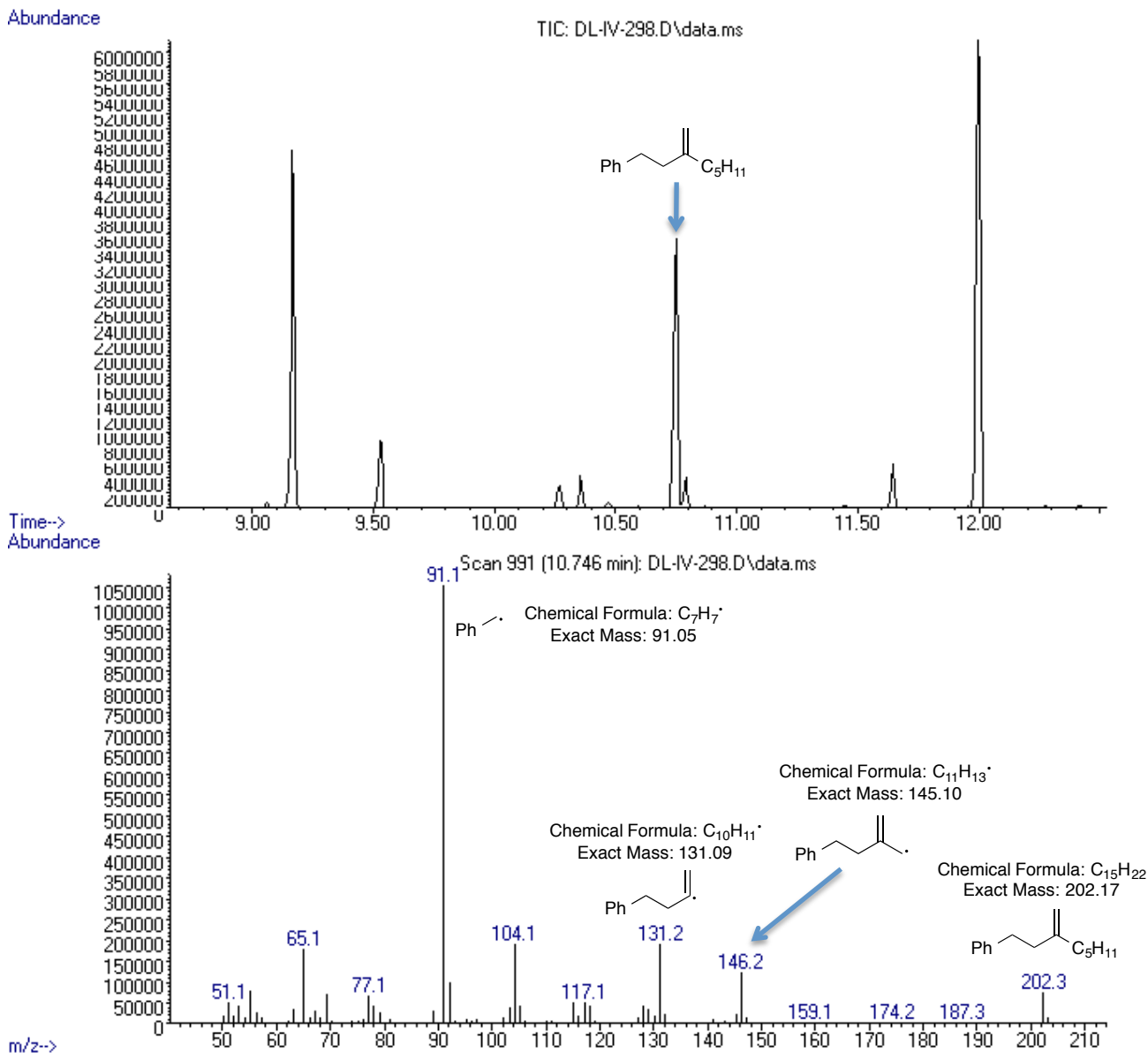


Figure S41: GC/MS trace of the coupling of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce cross-products. Mass spectrum corresponds to indicated peak.

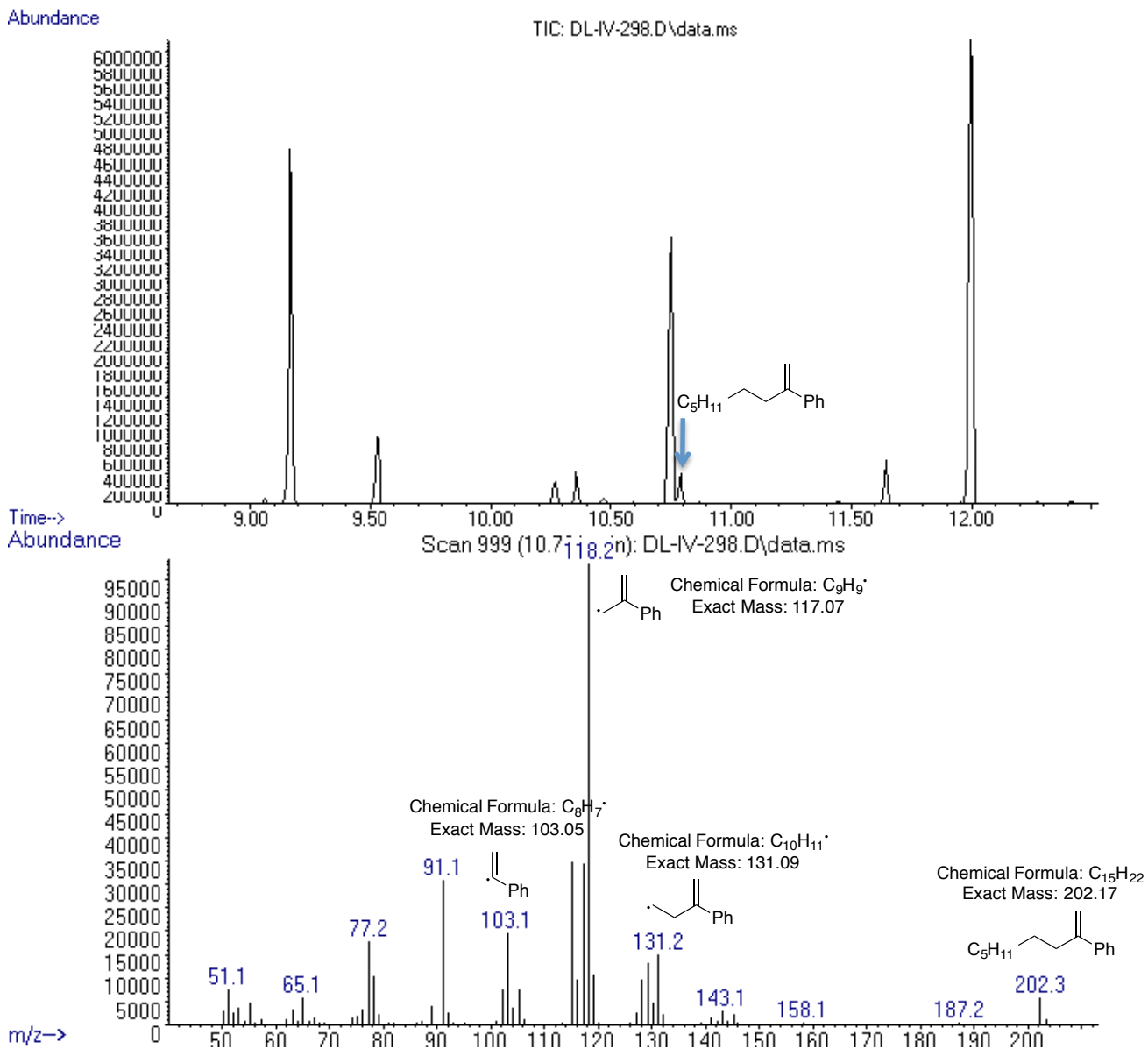


Figure S42: GC/MS trace of the coupling of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce cross-products. Mass spectrum corresponds to indicated peak.

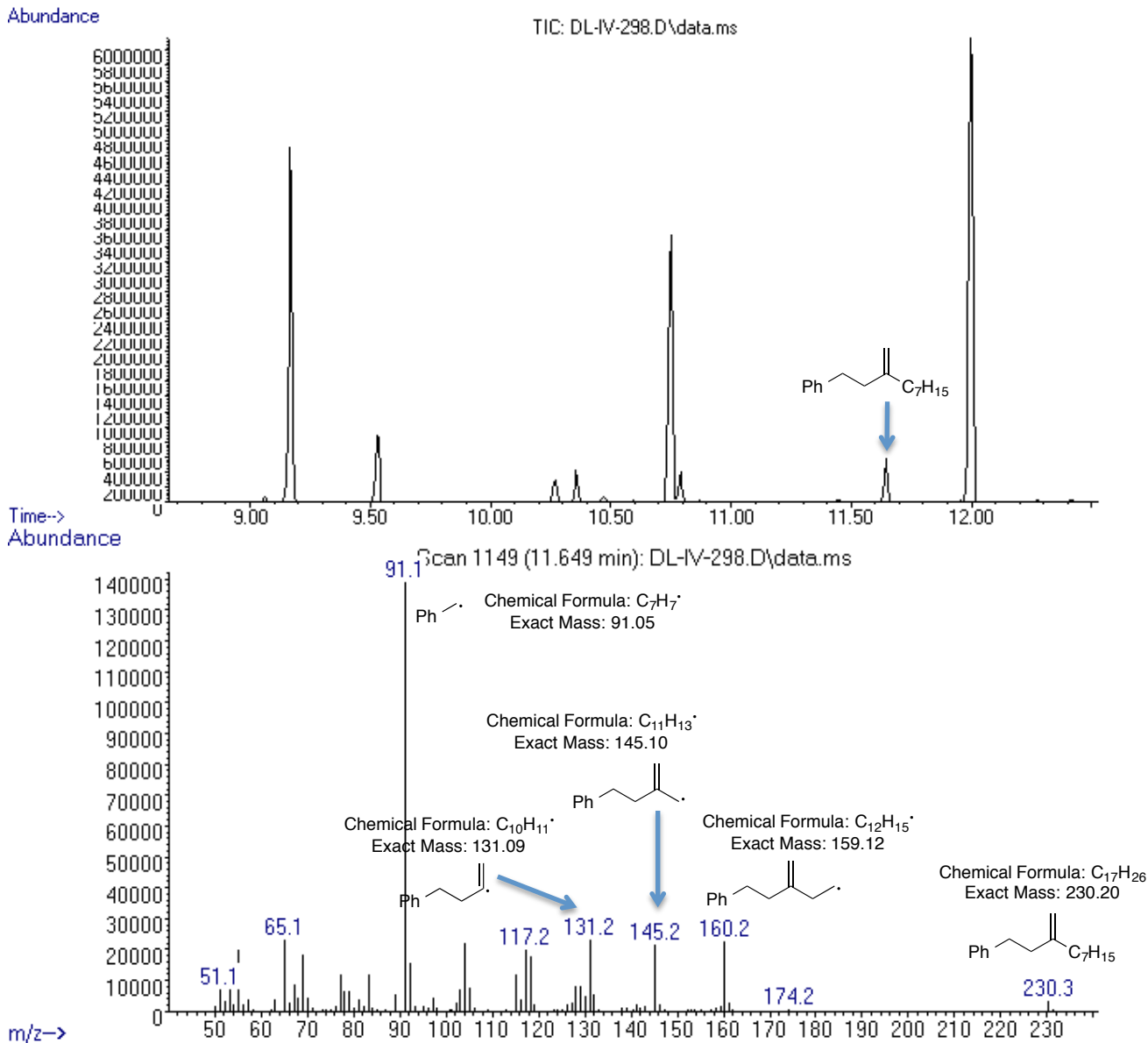


Figure S43: GC/MS trace of the coupling of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce cross-products. Mass spectrum corresponds to indicated peak.

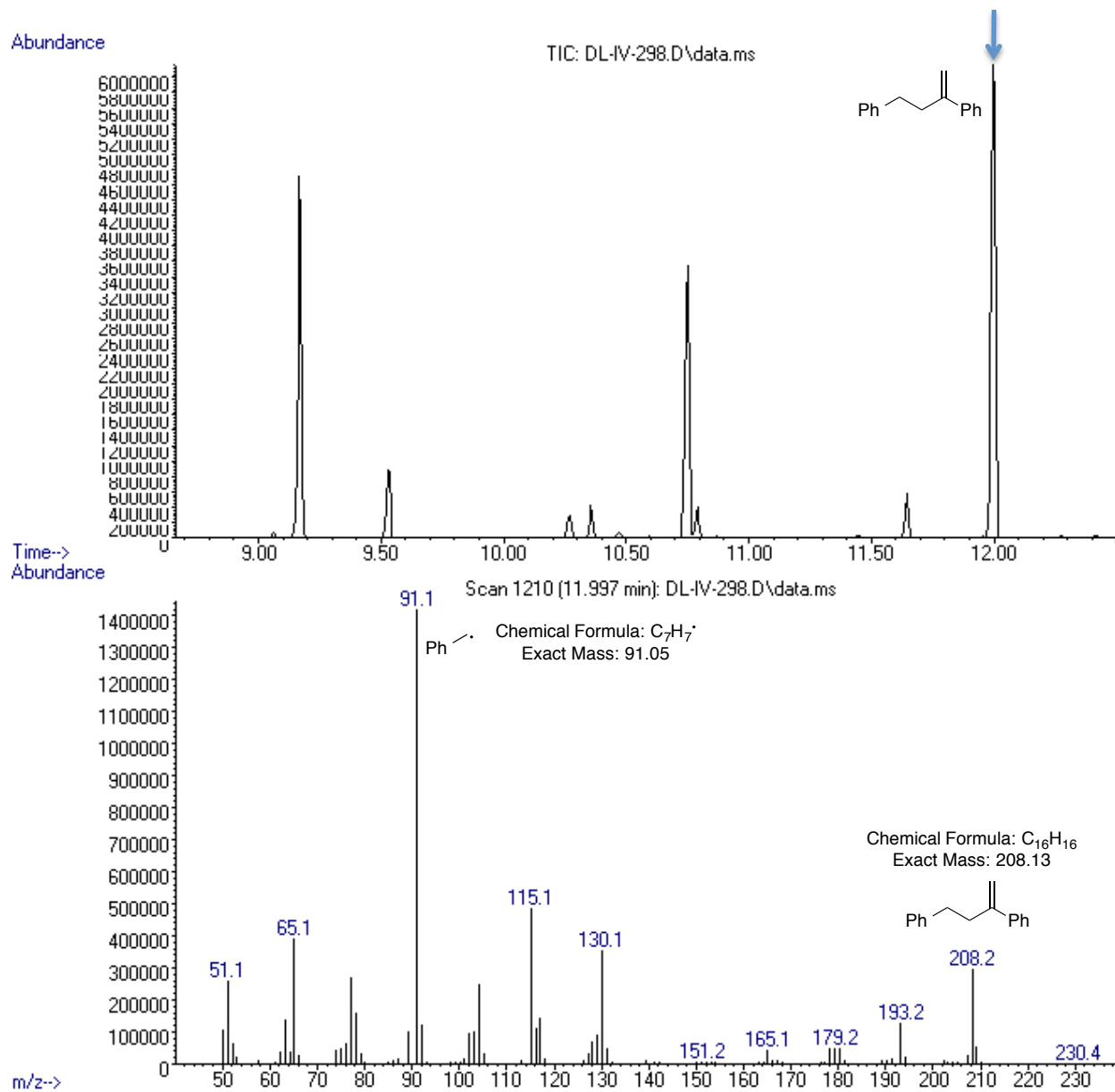
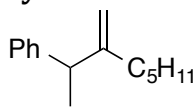


Figure S44: GC/MS trace of the coupling of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce cross-products. Mass spectrum corresponds to indicated peak.

Synthesis of Authentic Cross-Products:



This compound was prepared by Ni-catalyzed coupling of 1-heptene and styrene according to a published procedure.⁸ Briefly: Under an N₂ atmosphere, Ni[COD]₂ (27.5 mg, 0.10 mmol) and 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (IPr, 38.9 mg, 0.10 mmol) were dissolved in toluene (4 mL) in a reaction tube and stirred for ~1 hour. An aliquot of 1-heptene (~28 μL) was added, followed by the addition of triethylamine (60.7 mg, 0.60 mmol), *p*-anisaldehyde (13.6 mg, 0.10 mmol), and TESOTf (52.9 mg, 0.20 mmol). The solution was stirred for ~15 minutes. Finally, styrene (208.3 mg, 2.00 mmol) and 1-heptene (589.1 mg, 6.00 mmol) were added, and the solution was stirred for ~24 hours at room temperature under N₂. The contents were then exposed to air and diluted with hexanes (~10 mL). The mixture was filtered through a short silica plug, followed by elution of the solid with 20% EtOAc in hexanes (~25 mL). The solvent was evaporated, and the residue dissolved in dichloromethane. The product solution was analyzed by GC and GC/MS (Figures S45 and S46-S48). The regiochemistry of the major cross-product was definitively established by the original authors, as was the regiochemistry of styrene homodimerization.⁸ This cross-product solution was co-injected with the cross-product mixture generated by **1** (Figure S49).

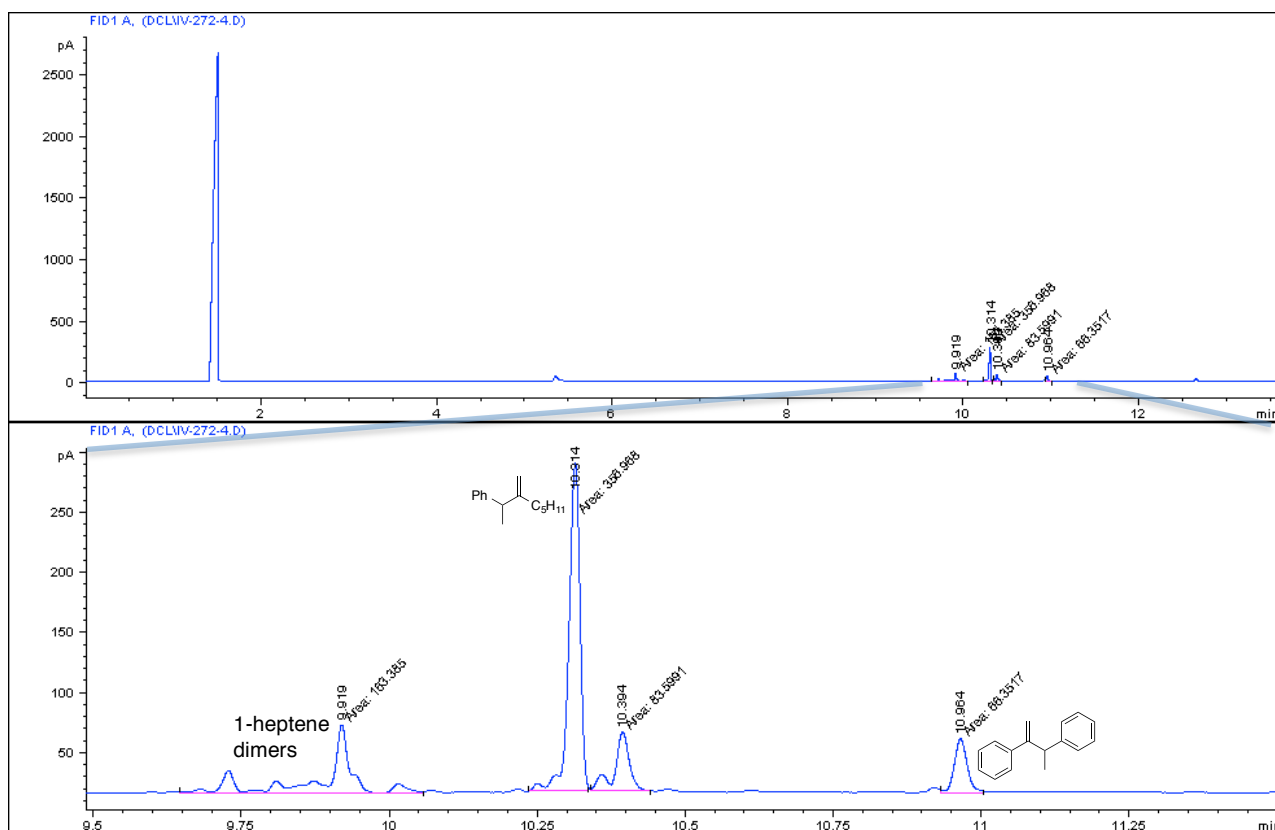
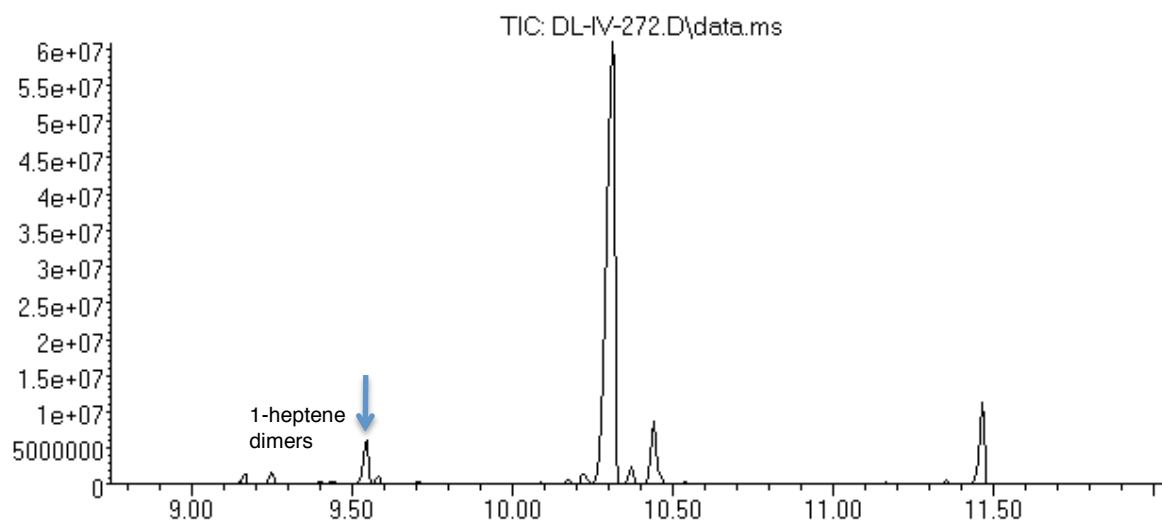


Figure S45: GC trace of the nickel-catalyzed coupling of styrene and 1-heptene to generate the major product shown. The 1-heptene dimers and styrene dimer are assigned based on GC/MS (*vide infra*). The regiochemistry of the styrene dimer was established previously for this Ni-catalyst.⁸

Abundance



Abundance

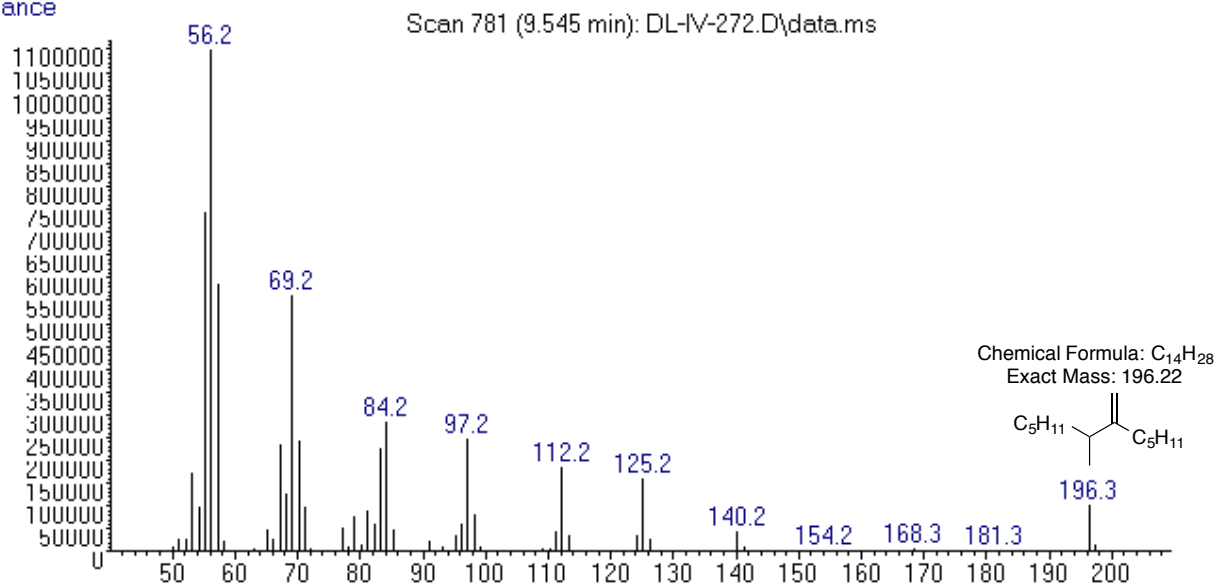
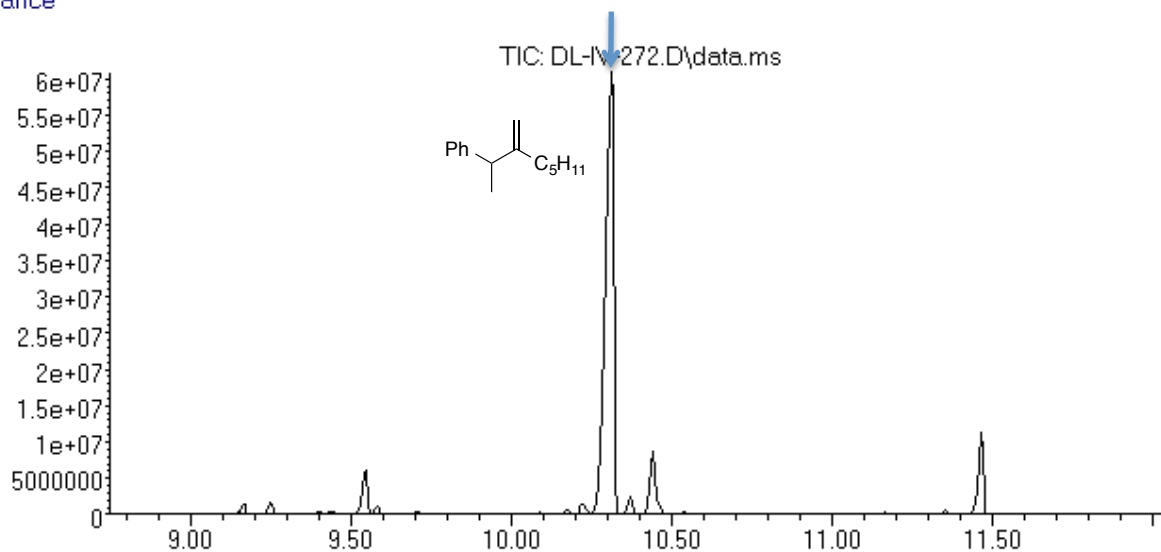


Figure S46: GC/MS trace of the nickel-catalyzed coupling of styrene and 1-heptene. Mass spectrum corresponds to indicated peak.

Abundance



Abundance

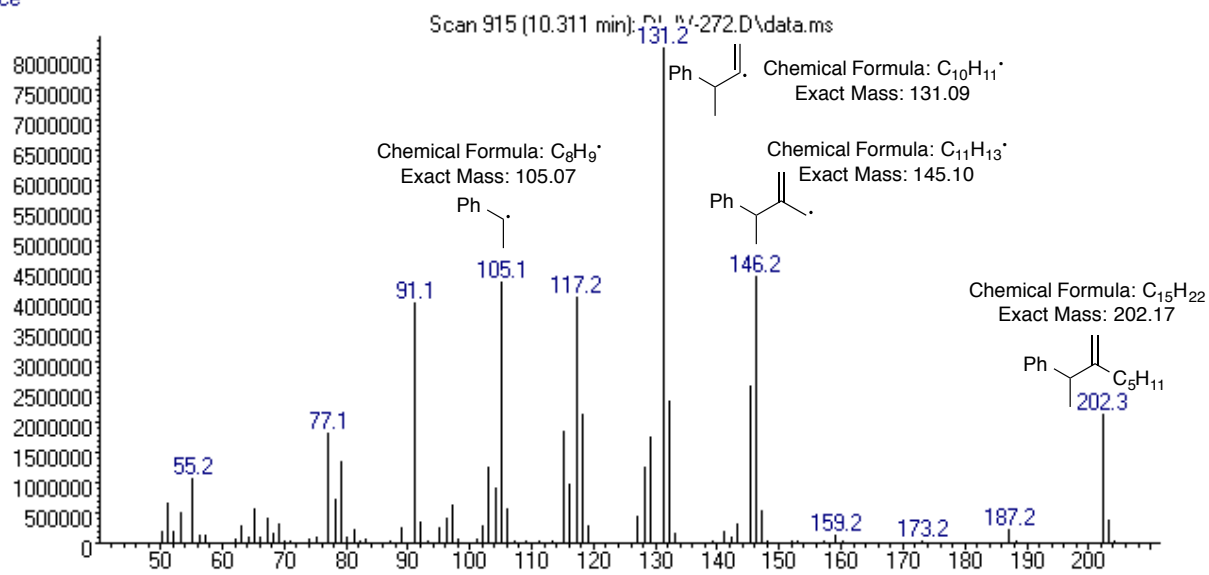
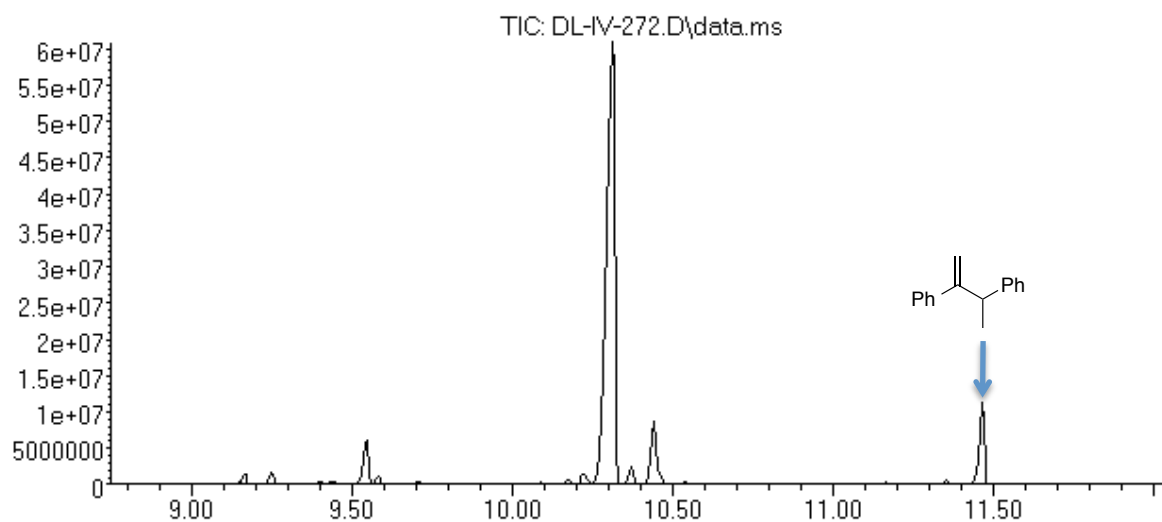


Figure S47: GC/MS trace of the nickel-catalyzed coupling of styrene and 1-heptene. Mass spectrum corresponds to indicated peak. Compare fragmentation pattern to that in Figure S39.

Abundance



Time→
Abundance

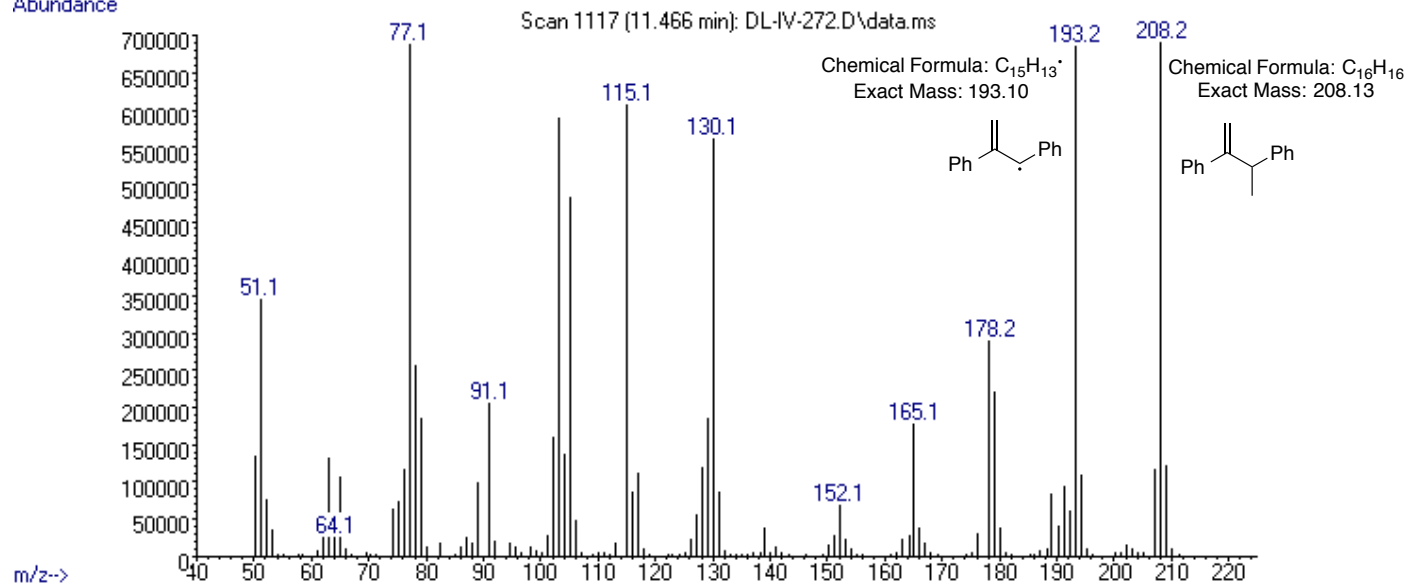


Figure S48: GC/MS trace of the nickel-catalyzed coupling of styrene and 1-heptene. Mass spectrum corresponds to indicated peak.

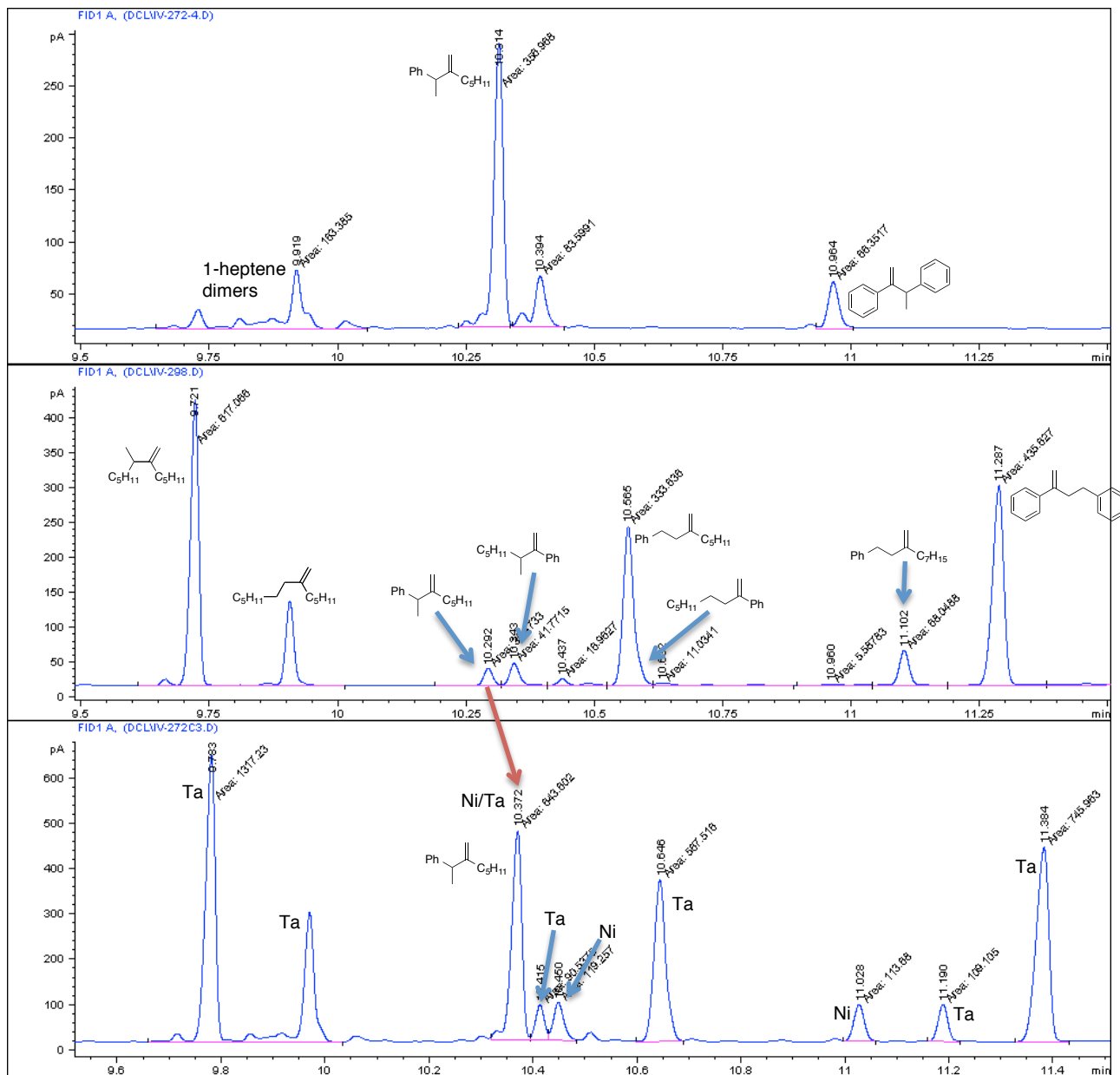
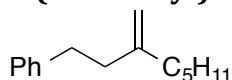


Figure S49: *Top:* Reproduction of Figure S45 (bottom). *Middle:* Reproduction of Figure S38 (bottom). *Bottom:* GC trace of the co-injection of styrene/1-heptene coupling reactions effected by **1** and the *in situ* generated Ni-catalyst. The peaks marked with “Ta” are from the tantalum-catalyzed reaction, and those marked with “Ni” are from the nickel-catalyzed reaction. The red arrow highlights that the cross-product peak at 10.29 min (middle trace) corresponds to the 2-phenyl-3-methylene-octane product.

2-(Phenethyl)-hex-1-ene



This compound was prepared from 1-phenyl-octan-3-one¹⁰ *via* Wittig olefination. Briefly, methyltriphenylphosphonium bromide (2.62 g, 7.34 mmol) was added as a solid portionwise over a period of ~1 hour to a stirring solution of *n*-butyllithium (7.34 mmol) in hexanes/diethyl ether (4.6/10 mL). 1-Phenyl-octan-3-one (1.50 g, 10.0 mmol) in diethyl ether (10 mL) was added *via* syringe. The mixture was heated to reflux for ~3 hours, and then stirred at room temperature overnight. The suspension was filtered, and the solid washed with diethyl ether. The organic phase was washed with water, and then dried over Na₂SO₄. The solvent was removed. The resulting residue was extracted with hexanes and filtered to remove the remaining triphenylphosphine oxide. The crude alkene was purified by flash chromatography on silica gel with hexanes as the eluent. The solvent was removed to give 0.82 g (55% yield) of 2-(phenethyl)-hex-1-ene. ¹H NMR (300 MHz, CDCl₃) δ 7.35 (2H, m, 2x Ar-H), 7.26 (3H, m, 3x Ar-H), 4.83 (2H, s, C=CH₂), 2.82 (2H, m, -CH₂-), 2.39 (2H, m, -CH₂-), 2.13 (2H, m, -CH₂-), 1.52 (2H, m, -CH₂-), 1.37 (4H, m, -CH₂-), 0.93 (3H, t, *J* = 6 Hz, -CH₃). ¹³C NMR (300 MHz, CDCl₃) δ 149.5, 142.4, 128.4, 128.3, 125.8, 109.05, 37.9, 36.4, 34.5, 31.7, 27.6, 22.7, 14.1. MS (EI) 202.3 (M⁺).

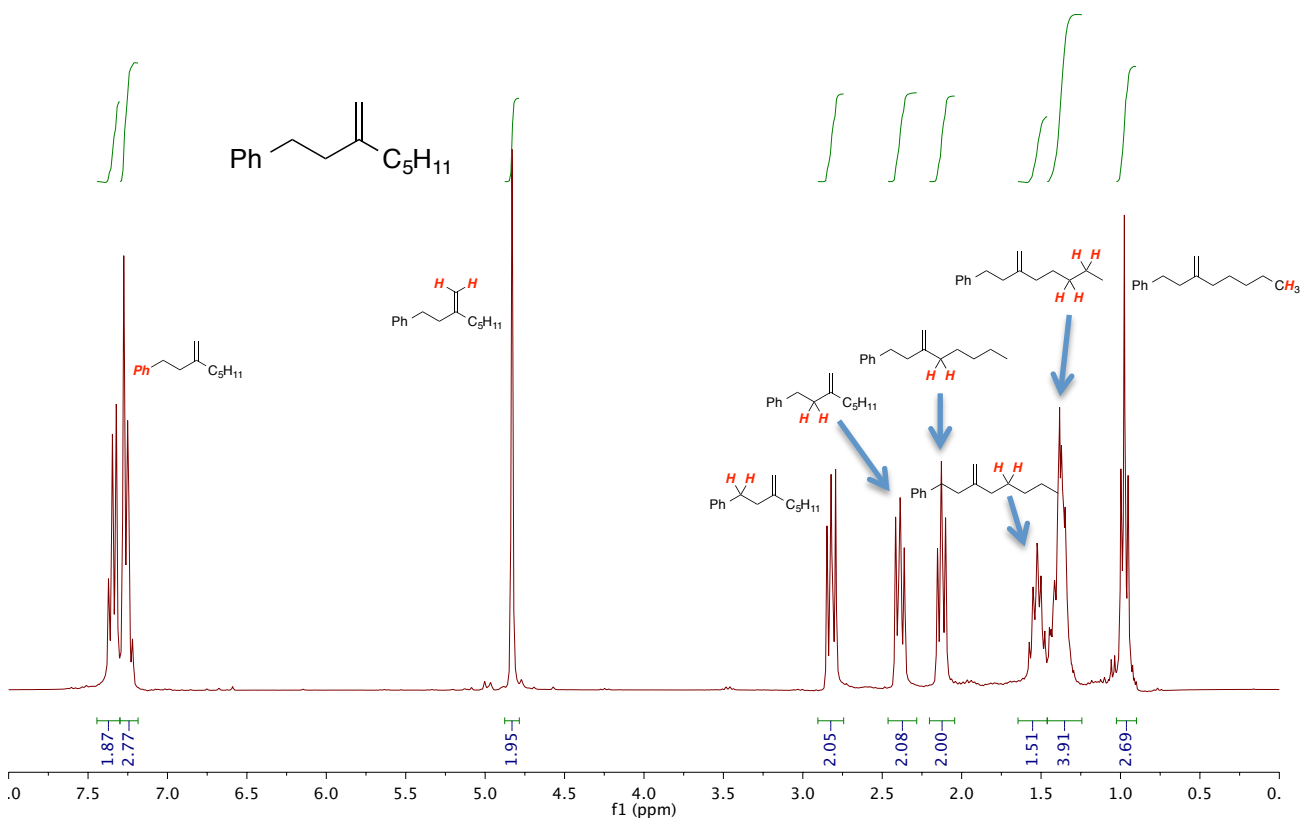


Figure S50: ¹H NMR spectrum of 2-(phenethyl)-hex-1-ene (300 MHz, CDCl₃).

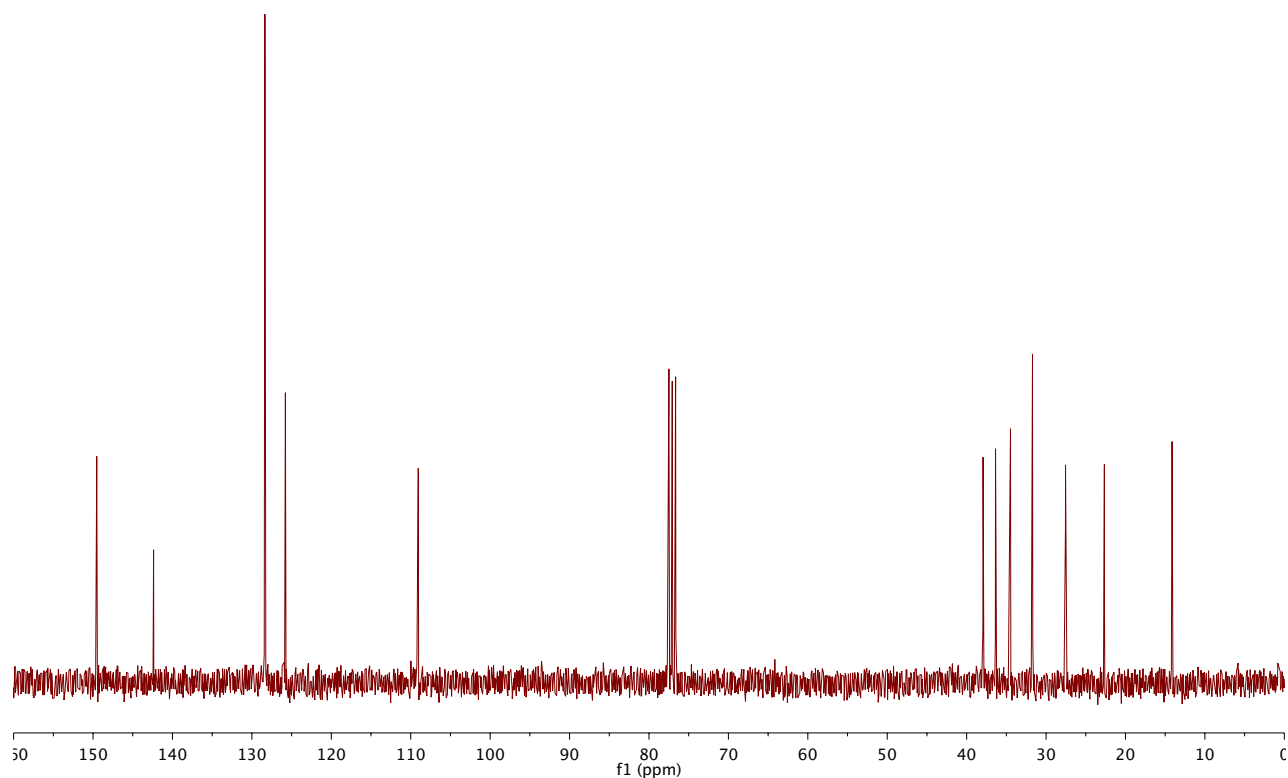


Figure S51: ^{13}C NMR spectrum of 2-(phenethyl)-hex-1-ene (300 MHz, CDCl_3).

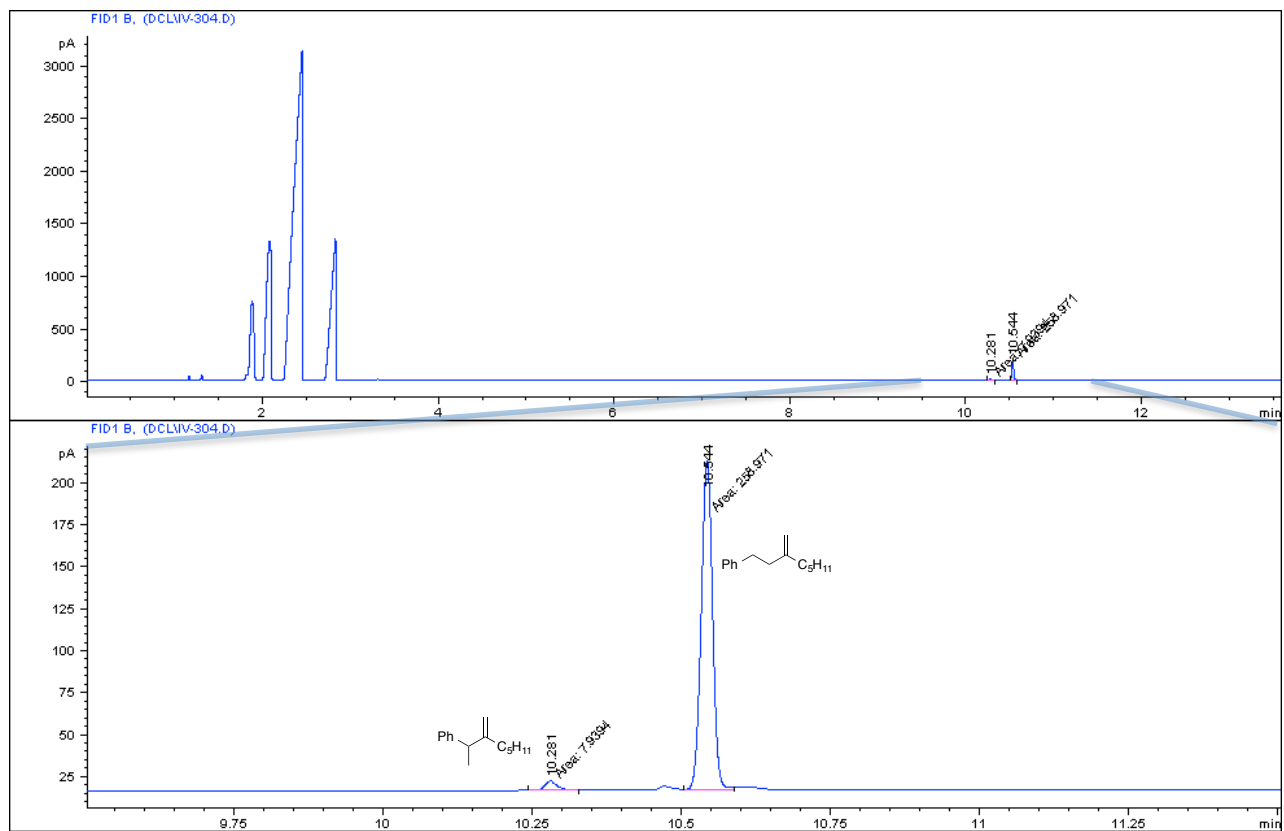


Figure S52: GC trace of 2-(phenethyl)-hex-1-ene.

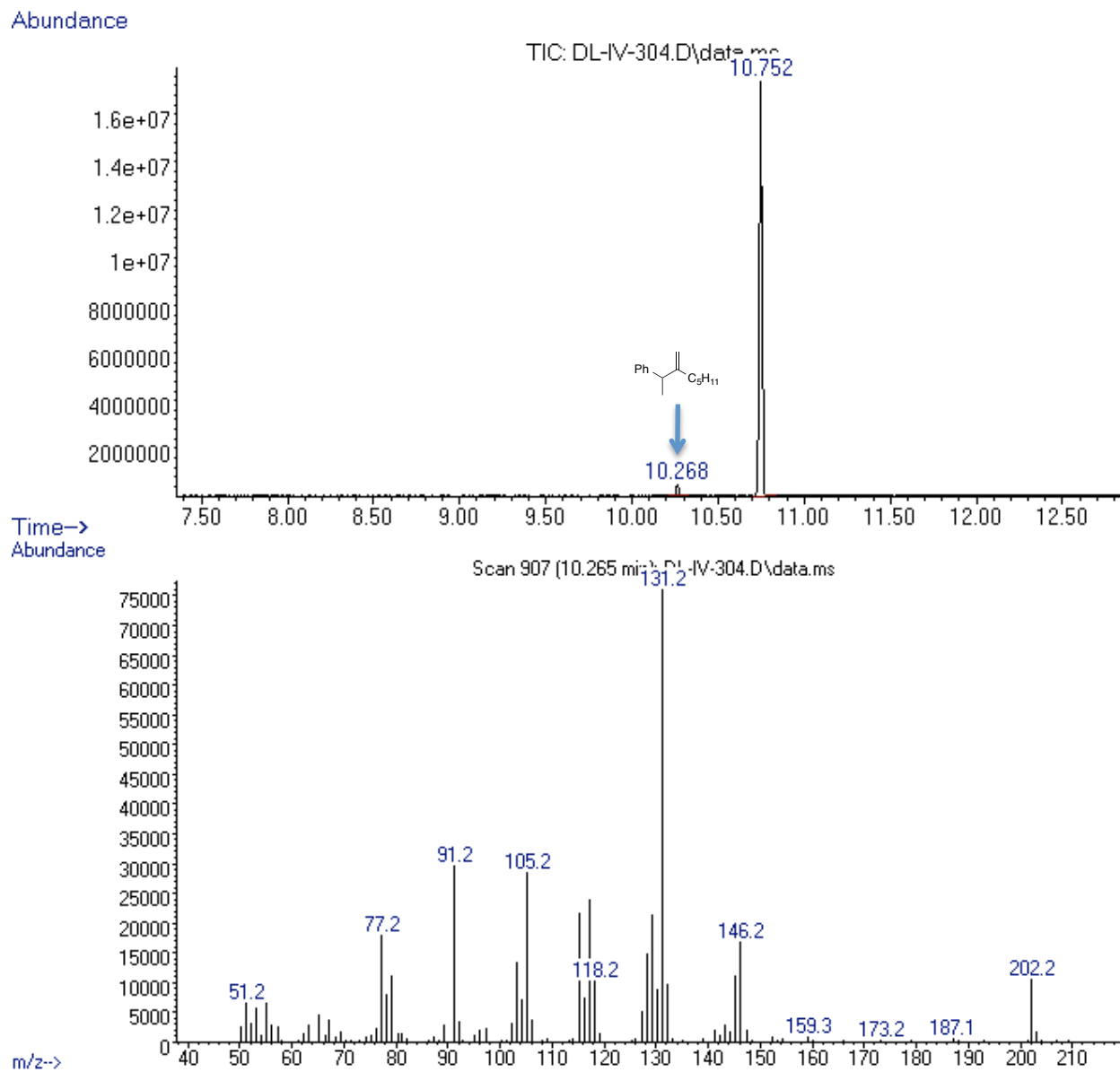


Figure S53: GC/MS trace of 2-(phenethyl)-hex-1-ene (MS for indicated peak). Compare to fragmentation pattern in Figures S39 and S47.

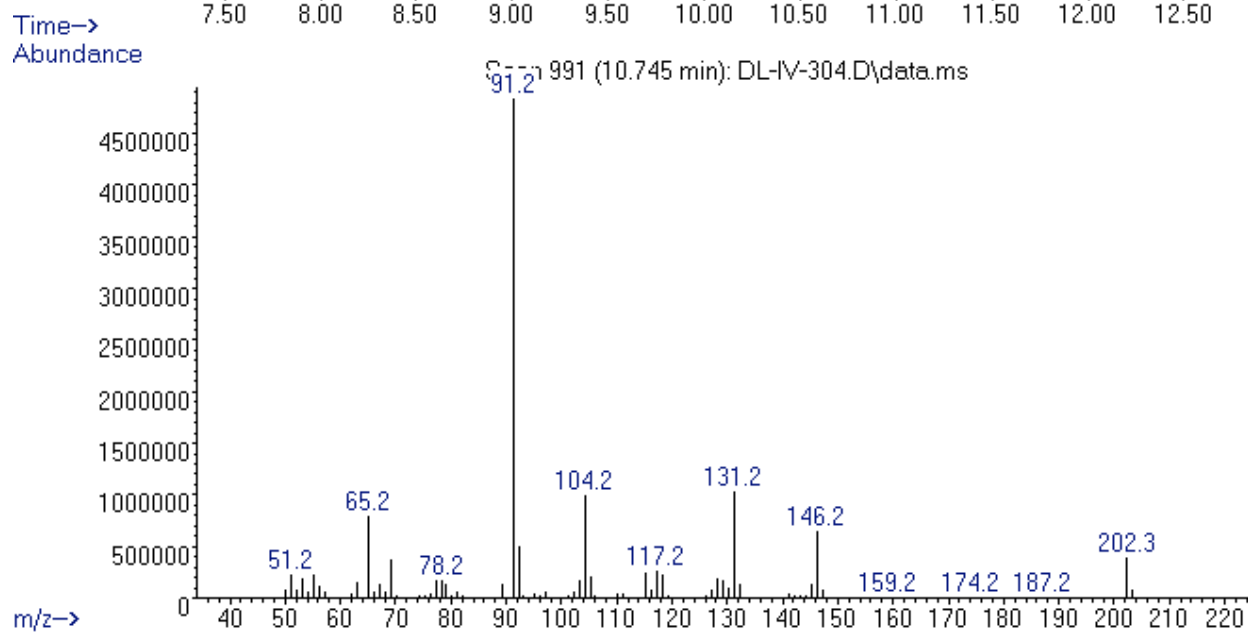
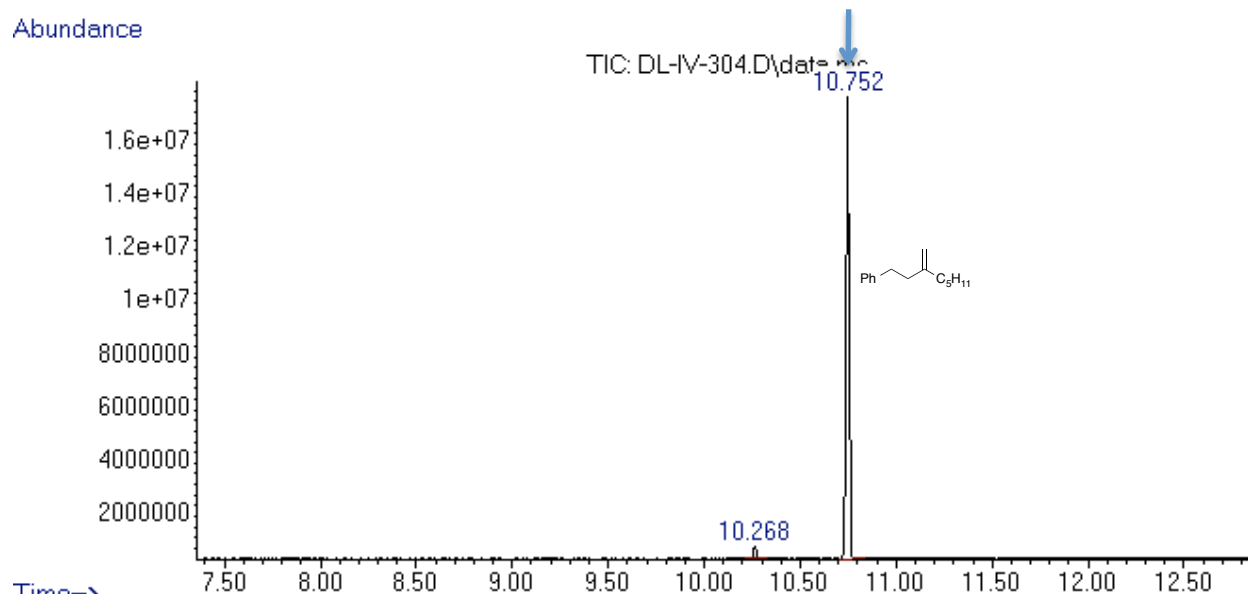


Figure S54: GC/MS trace of 2-(phenethyl)-hex-1-ene (MS for indicated peak). Compare to fragmentation pattern in Figure S41.

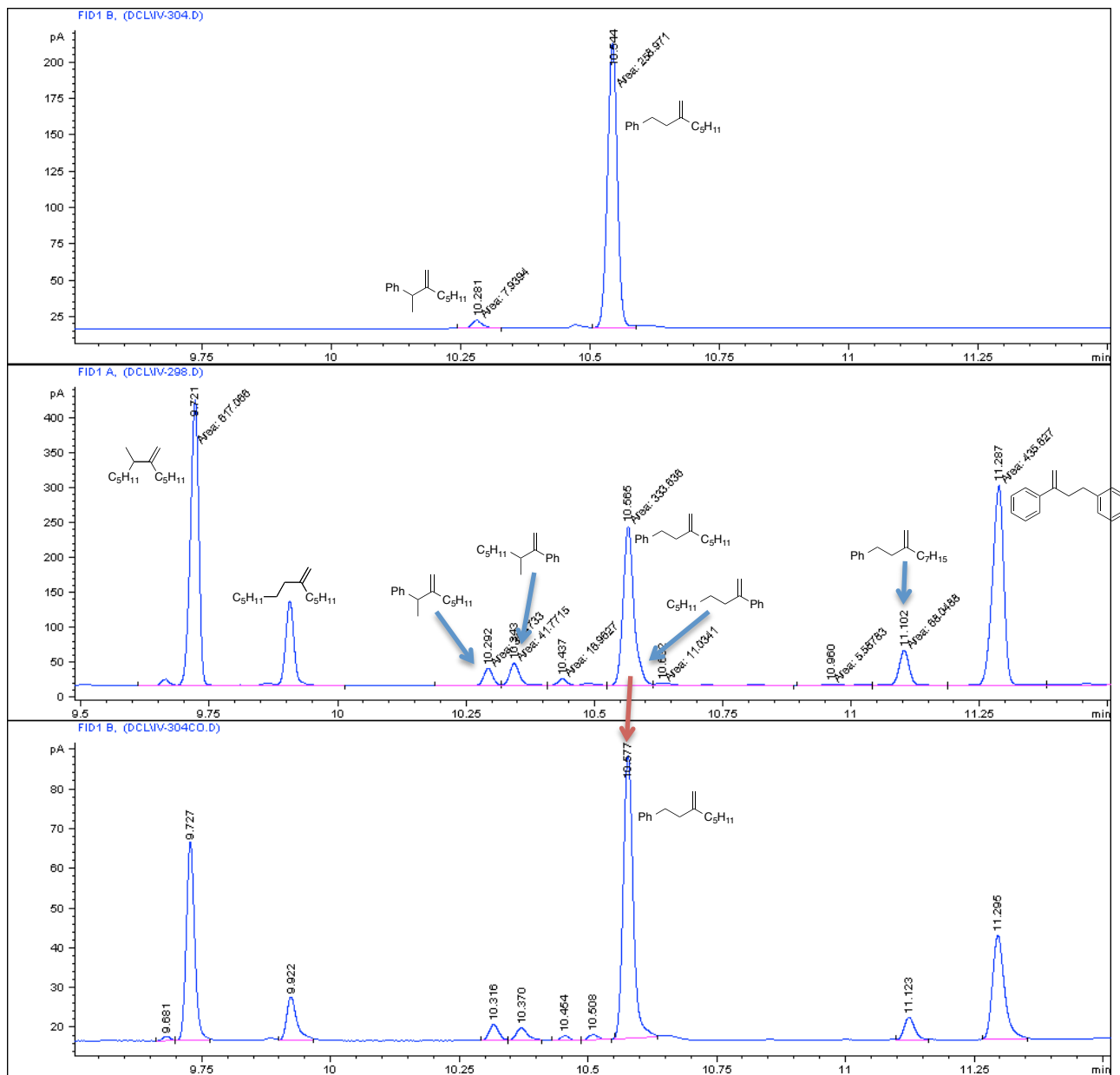
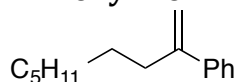


Figure S55: *Top:* Reproduction of Figure S52 (bottom). *Middle:* Reproduction of Figure S38 (bottom). *Bottom:* GC trace of the co-injection of styrene/1-heptene coupling effected by **1** and authentic 2-(phenethyl)-hex-1-ene. The increase in intensity of the peak at ~10.57 min clearly shows that the major product of styrene/1-heptene coupling effected by **1** is 2-(phenethyl)-hex-1-ene.

2-Phenyl-non-1-ene



This known compound was prepared from octanophenone (Sigma-Aldrich) *via* Wittig olefination according to a literature procedure.¹¹ Briefly, methyltriphenylphosphonium bromide (3.57 g, 10.0 mmol) was added as a solid portionwise over a period of ~1 hour to a stirring solution of *n*-butyllithium (10.0 mmol) in hexanes/diethyl ether (6.25/10 mL). Octanophenone (2.04 g, 2.20 mL, 10.0 mmol) in diethyl ether (10 mL) was added *via* cannula. The mixture was heated to reflux for ~3 hours, and then stirred at room temperature overnight. The suspension was filtered, and the solid washed with diethyl ether. The organic phase was washed with water, and then dried over Na₂SO₄. The solvent was removed. The resulting residue was extracted with hexanes and filtered through a short plug of silica gel to remove the remaining triphenylphosphine oxide. The solvent was removed, and the crude product was purified by flash chromatography on silica gel with hexanes eluent to give 1.10 g (54% yield) of the desired alkene.

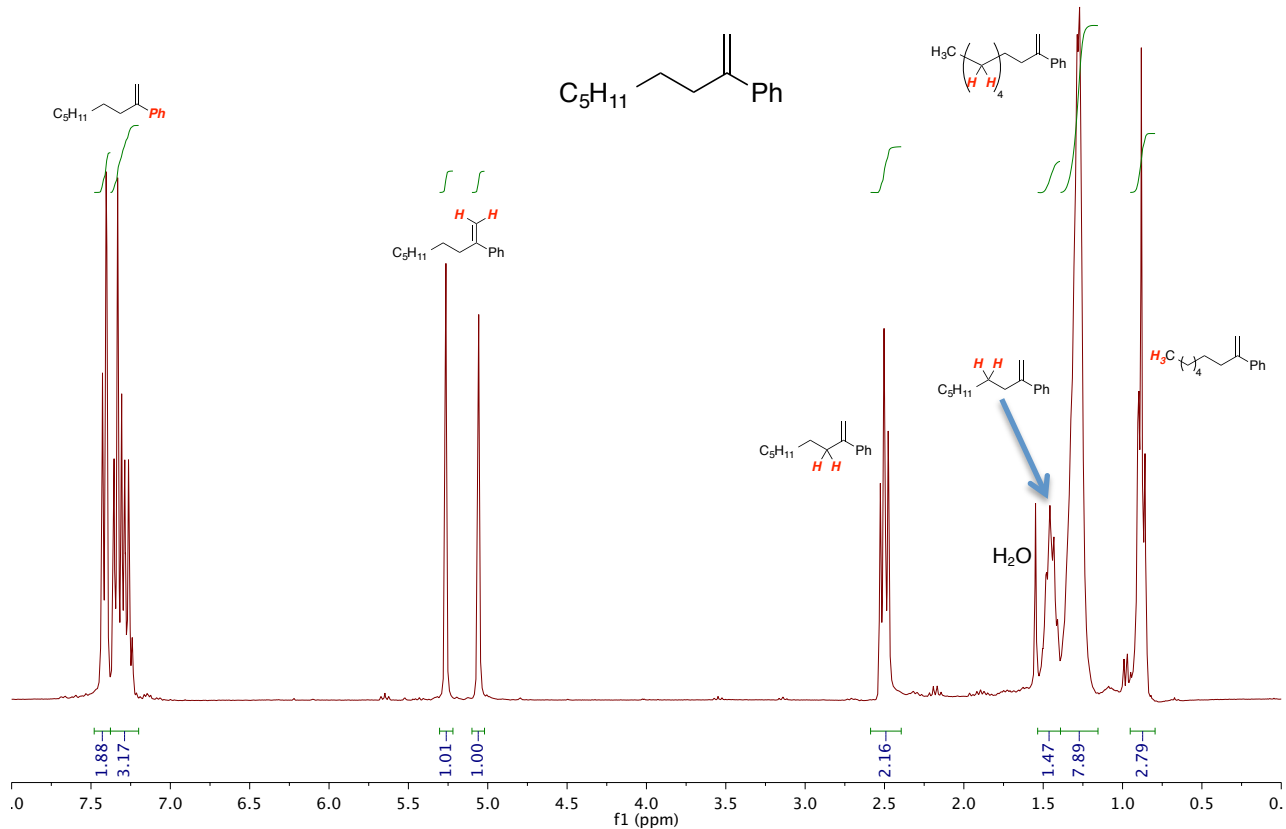


Figure S56: ¹H NMR spectrum of 2-phenyl-non-1-ene (300 MHz, CDCl₃).

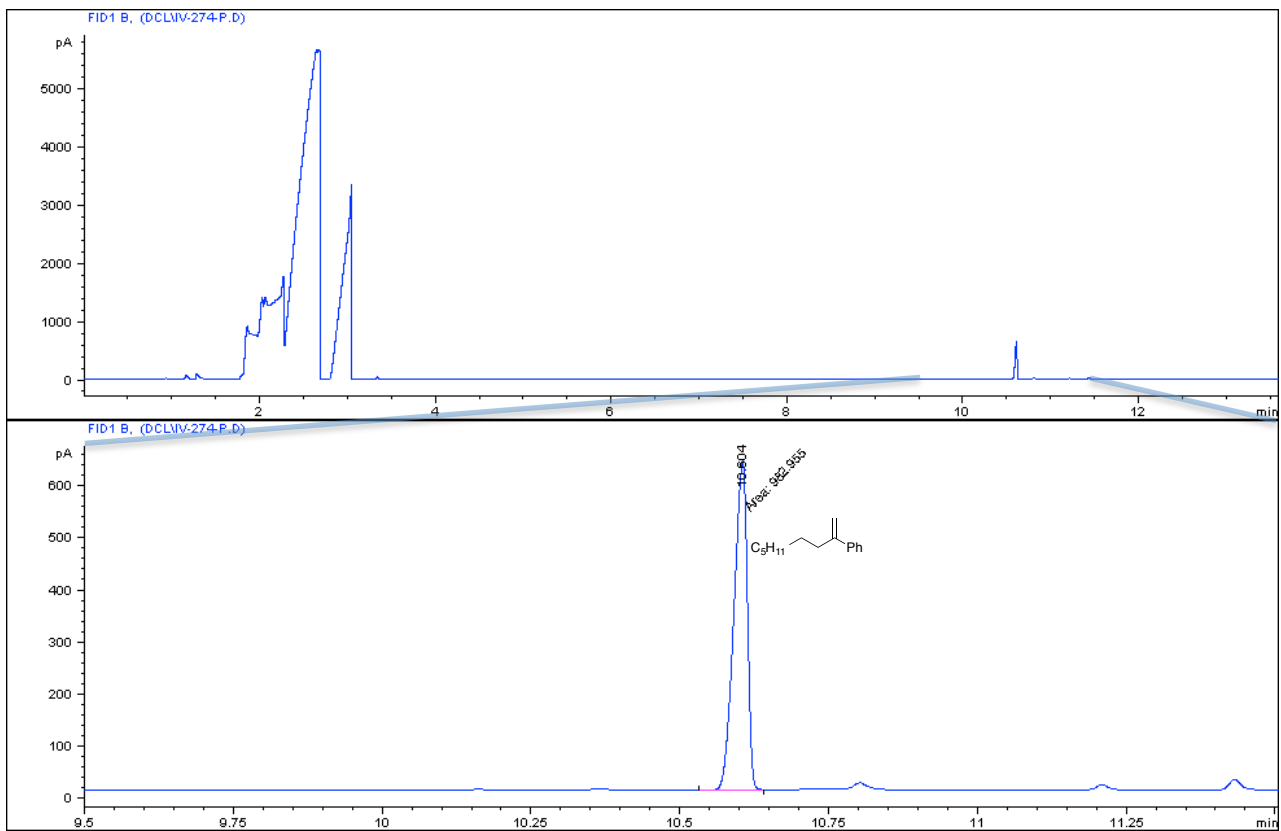


Figure S57: GC trace of 2-phenyl-non-1-ene.

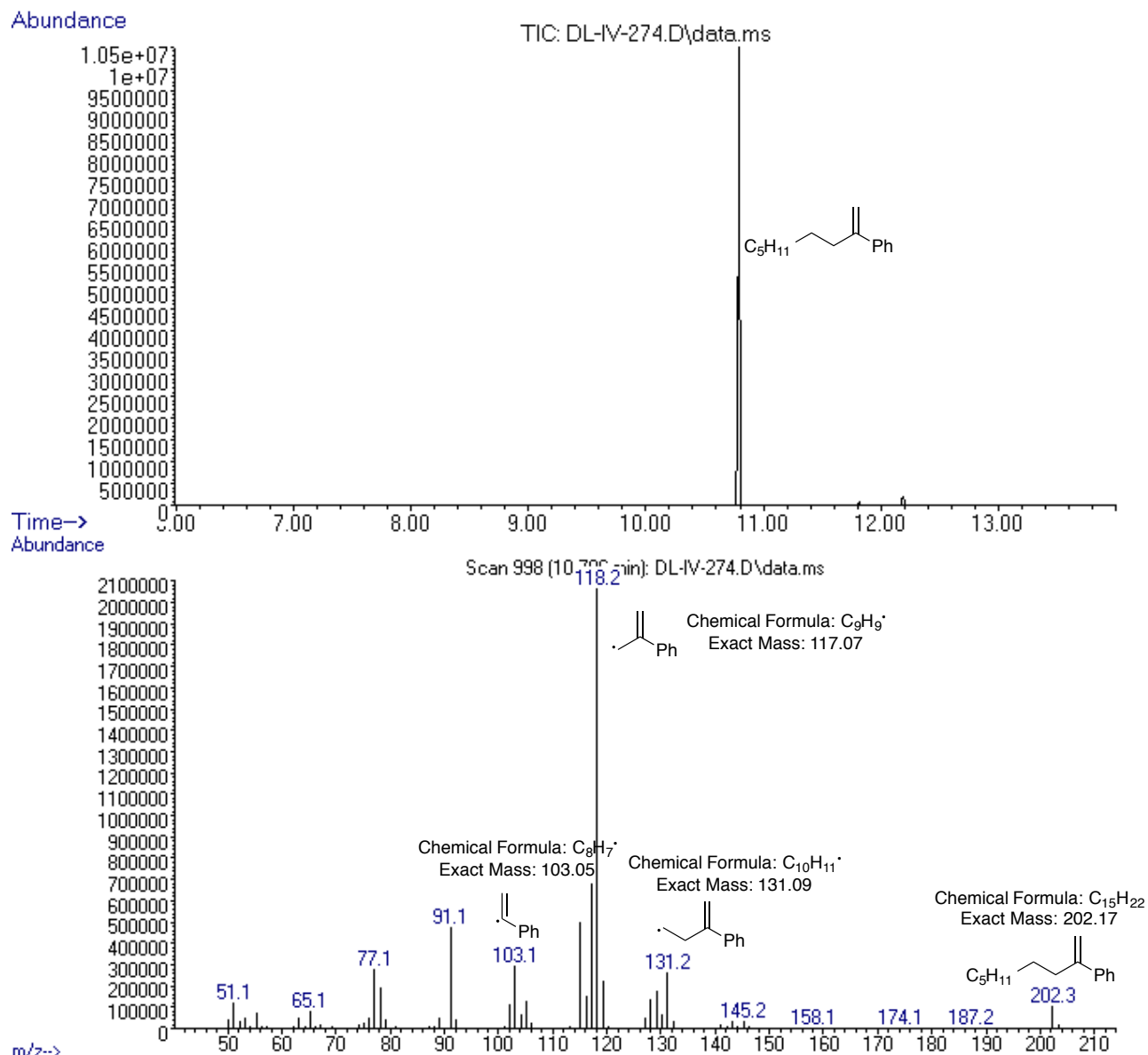


Figure S58: GC/MS trace of 2-phenyl-non-1-ene. Compare fragmentation pattern to that in Figure S42.

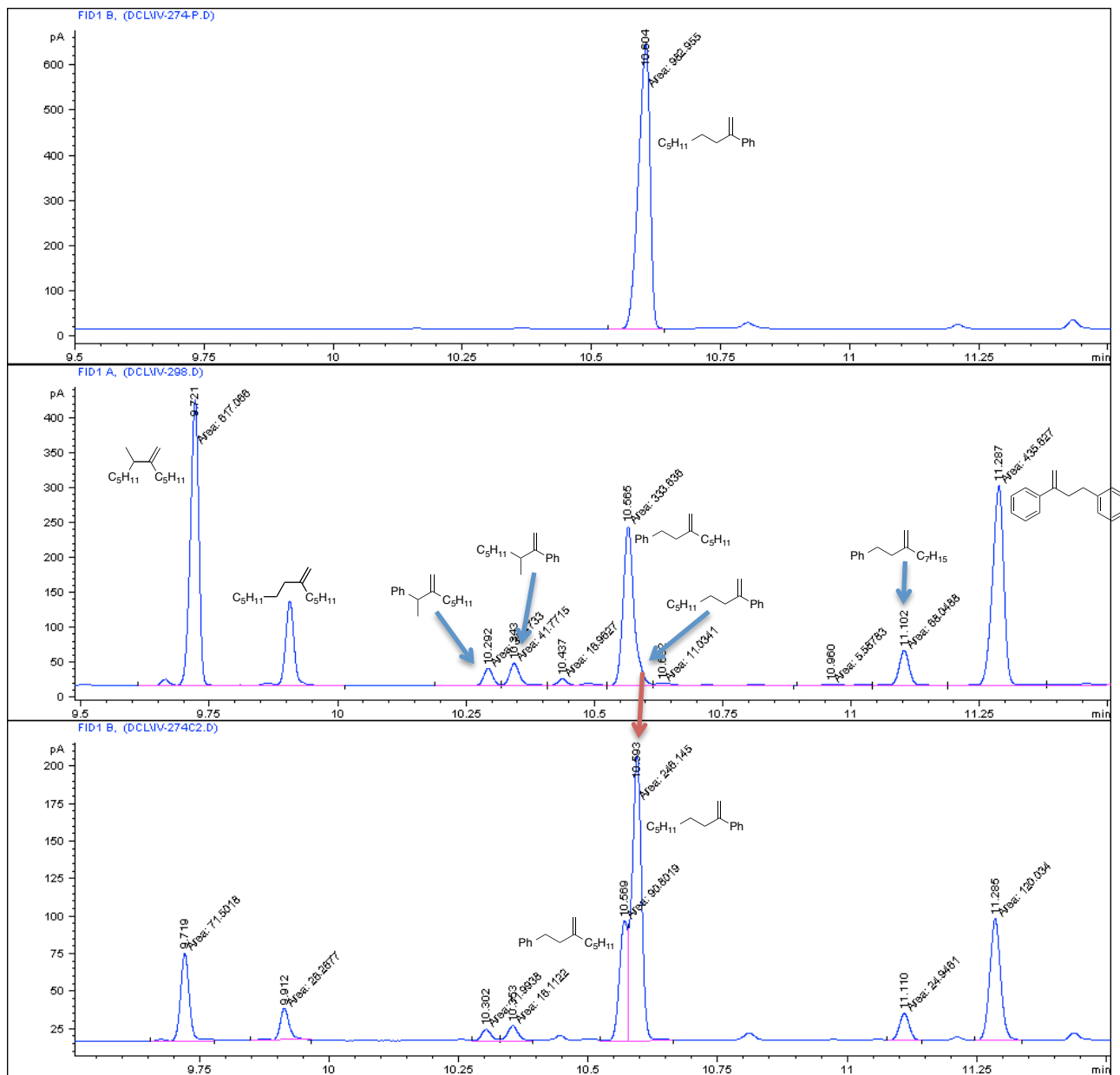


Figure S59: *Top:* Reproduction of Figure S57 (bottom). *Middle:* Reproduction of Figure S38 (bottom). *Bottom:* GC trace of the co-injection of styrene/1-heptene coupling effected by **1** and authentic 2-phenyl-non-1-ene. The doubling of the peak at ~10.57 min clearly shows that the major product of styrene/1-heptene coupling effected by **1** is not 2-phenyl-non-1-ene.

Procedure for Styrene/*n*-Heptane Coupling

NOTE: This is a representative procedure, corresponding to Entry 7a in Table S3 (*vide infra*). **1** (3.3 mg, 0.0080 mmol) and **2** (8.8 mg, 0.015 mmol) were dissolved in 1 mL of a standard solution of styrene (250 mM) and adamantane (25.3 mM) in *n*-heptane in a 4 mL screw top vial containing a Teflon-coated stir bar. The vial was sealed with a Teflon-lined screw cap. The mixture was heated with stirring at 100 °C in an aluminum block heater for 18 hours. Upon completion, the vial was removed from the heat block, cooled to room temperature, and then diluted with dichloromethane. This solution was passed through a short plug of silica gel into a GC autosampler vial, and analyzed by GC (Figure S46).

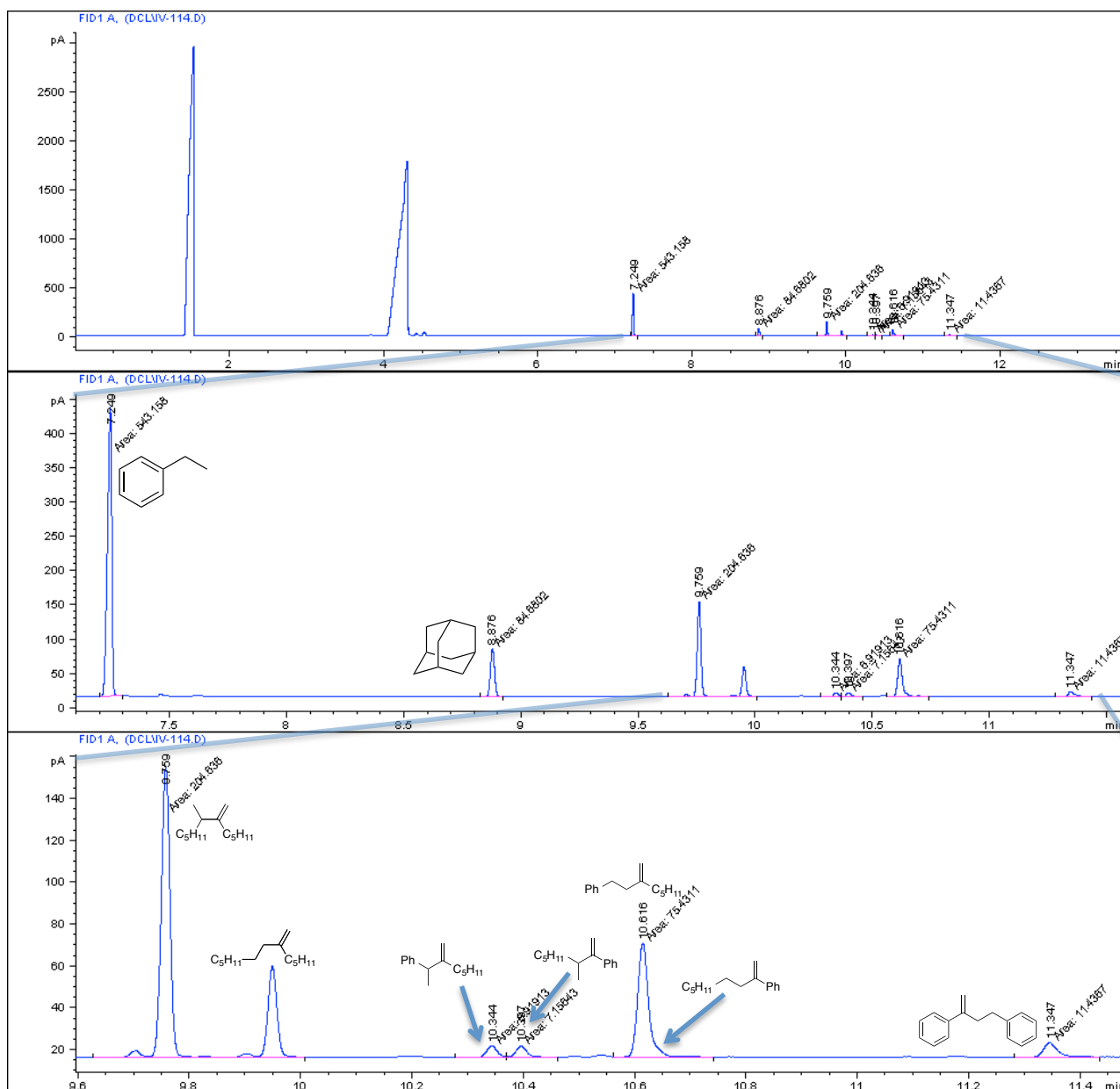
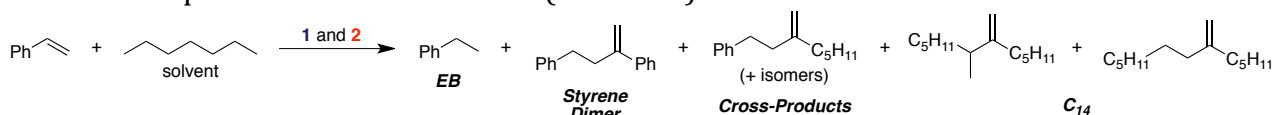


Figure S60. GC trace of styrene/*n*-heptane coupling, corresponding to Entry 7a, Table S4.

Full Table of Results for Styrene/*n*-Heptane Coupling

Table S4. Expanded version of Table 5 (main text)



Entry	[Styrene] ₀ mM ^a (Final Conc.)	[1]/[2] mM	Time h	Temp. °C	% Conv.	EB mM (%)	Styrene Dimer mM (%)	Cross- products mM (%)	C ₁₄ mM (%)	TON 1 ^b	TON 2 ^b	Coop. % ^c
1z	250 (91.2)	8/5	18	100	60.7	71.1 (28.4)	23.1 (18.5)	23.3 (18.7)	10.8 (8.6)	7 (4)	14 (9)	63.1
1b	250 (95.0)	8/5	18	100	58.8	65.6 (26.2)	23.9 (19.1)	22.1 (17.7)	9.2 (7.4)	7 (4)	13 (8)	61.8
1c	250 (77.1)	8/5	18	100	65.1	74.0 (29.6)	22.8 (18.2)	23.9 (19.1)	11.7 (9.4)	7 (4)	15 (9)	63.9
2a	250 (50.9)	8/5	48	100	77.2	74.8 (29.9)	34.3 (27.4)	28.7 (23.0)	12.8 (10.2)	9 (5)	15 (11)	72.6
2b	250 (62.9)	8/5	48	100	72.4	66.3 (26.5)	36.0 (28.8)	26.9 (21.5)	10.3 (8.2)	9 (5)	13 (9)	71.6
3a	250 (42.5)	5/8	18	100	81.4	138.3 (55.3)	10.6 (8.4)	27.1 (21.6)	28.4 (22.8)	13 (11)	17 (10)	60.7
3b	250 (56.9)	5/8	18	100	75.3	126.2 (50.5)	10.5 (8.4)	26.2 (21.0)	24.1 (19.3)	12 (10)	16 (9)	58.9
4a	250 (26.0)	5/10	18	100	88.6	161.6 (64.6)	7.8 (6.2)	25.9 (20.8)	34.6 (27.7)	14 (12)	16 (10)	58.9
4b	250 (25.9)	5/10	18	100	88.7	161.7 (64.7)	8.1 (6.5)	26.4 (21.1)	35.7 (28.6)	14 (12)	16 (10)	60.5
5a	250 (2.2)	10/10	18	100	99.0	164.4 (65.8)	15.6 (12.5)	31.7 (25.3)	41.1 (32.9)	9 (7)	16 (11)	69.3
5b	250 (2.6)	10/10	18	100	98.9	162.0 (64.8)	17.4 (13.9)	30.0 (24.0)	42.2 (33.8)	9 (7)	16 (11)	70.6
6a	250 (2.7)	10/15	18	100	98.8	192.0 (76.8)	5.8 (4.7)	22.8 (18.2)	45.3 (36.3)	7 (7)	13 (8)	59.1
6b	250 (2.8)	10/15	18	100	98.8	191.8 (76.7)	6.6 (5.3)	24.2 (19.4)	45.8 (36.6)	8 (7)	13 (8)	60.4
7a	250 (1.8)	8/15	18	100	99.2	203.5 (81.4)	2.2 (1.7)	18.0 (14.4)	43.5 (34.8)	8 (8)	14 (7)	51.6
7b	250 (1.1)	8/15	18	100	99.5	199.5 (79.8)	4.5 (3.6)	20.7 (16.6)	44.3 (35.4)	9 (8)	13 (7)	54.8
7c	250 (1.2)	8/15	18	100	99.5	200.5 (80.2)	4.3 (3.4)	20.1 (16.1)	43.0 (34.4)	8 (8)	13 (7)	53.0
8a	1000 (317.0)	10/15	72	100	63.6	100.3 (10.3)	206.1 (41.2)	42.5 (8.5)	3.8 (0.8)	25 (5)	7 (3)	49.9
8b	1000 (273.9)	10/15	72	100	70.1	97.0 (9.7)	252.2 (50.4)	41.8 (8.4)	3.4 (0.7)	30 (5)	6 (3)	50.1
9a	250 (2.5)	10/15	18	125	99.0	217.9 (87.2)	1.9 (1.5)	14.4 (11.5)	38.0 (30.4)	5 (5)	15 (6)	41.4
9b	250 (2.8)	10/15	18	125	98.9	211.6 (84.6)	2.3 (1.8)	14.9 (11.9)	38.2 (30.5)	6 (5)	14 (6)	43.1
10a	250 (~0)	10/15	18	150 ^d	>99	205.5 (82.2)	2.2 (1.7)	15.3 (12.3)	35.6 (28.5)	5 (5)	14 (6)	42.1
10b	250 (~0)	10/15	18	150 ^d	>99	212.2 (84.9)	1.9 (1.5)	13.2 (10.6)	35.4 (28.3)	5 (5)	14 (6)	39.6

^aDetermined from concentration of standard solution. ^bTONs in parentheses are for production of tandem products. ^cSee Ref. 17 in the main text. ^dReactions performed in thick-walled glass pressure tubes with screw-down Teflon plugs sealed with an O-ring. The tubes were immersed in a 150 °C oil bath up to the bottom of the plug.

Procedure for Monitoring Styrene/*n*-Heptane Coupling Reactions over Time:

NOTE: This procedure was performed in duplicate.

1 (6.6 mg, 0.016 mmol) and **2** (17.7 mg, 0.030 mmol) were dissolved in 2 mL of a standard solution of styrene (250 mM) and adamantane (25.3 mM) in *n*-heptane in a 4 mL screw top vial containing a Teflon-coated stir bar. The vial was sealed with a Teflon-lined screw cap. The mixture was heated to 100 °C for ~30 seconds in an aluminum block heater inside an argon-filled glovebox to dissolve the precatalysts and ensure a homogeneous solution, and then immediately cooled to -35 °C in the freezer. An aliquot (~0.1 mL, representing t_0) was removed and placed into a GC autosampler vial; this aliquot was then diluted with dichloromethane to a total volume of ~1 mL before analysis by GC.

The reaction mixture was heated to 100 °C in the aluminum block heater, and at specified times (1, 2, 3, 4, 5, 6, 7, 8, 10, 12, and 18 hours) the vial was removed and cooled to -35 °C in the freezer before taking an aliquot for analysis by GC. The concentrations of all major species were then plotted versus time to give time course profiles of the tandem reaction (Figure S61).

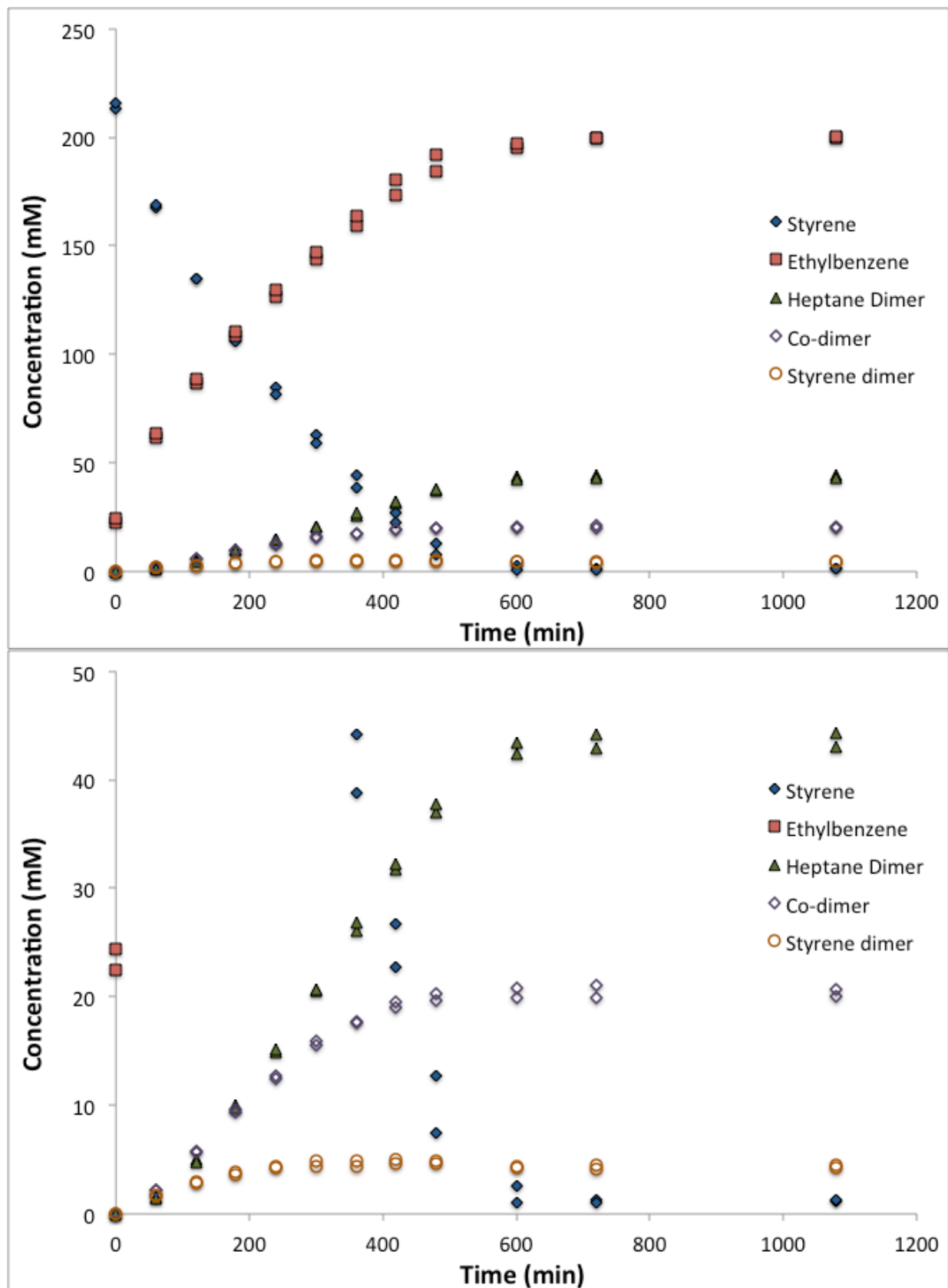


Figure S61: Plots of reaction progress over time for entries 7b and 7c in Table S4. *Top:* Overlay of both data sets. *Bottom:* Expansion of product concentration range. Lines are drawn as visual guides.

Procedure for Monitoring Styrene/*n*-Heptane Transfer Hydrogenation over Time:

NOTE: This procedure was performed in duplicate.

2 (17.7 mg, 0.030 mmol) was dissolved in 2 mL of a standard solution of styrene (250 mM) and adamantane (25.3 mM) in *n*-heptane in a 4 mL screw top vial containing a Teflon-coated stir bar. The vial was sealed with a Teflon-lined screw cap. The mixture was heated to 100 °C for ~30 seconds in an aluminum block heater inside an argon-filled glovebox to dissolve the precatalysts and ensure a homogeneous solution, and then immediately cooled to -35 °C in the freezer. An aliquot (~0.1 mL, representing t_0) was removed and placed into a GC autosampler vial; this aliquot was then diluted with dichloromethane to a total volume of ~1 mL before analysis by GC.

The reaction mixture was heated to 100 °C in the aluminum block heater, and at specified times (1, 2, 3, 4, 5, 6, 7, 8, 10, 12, and 18 hours) the vial was removed and cooled to -35 °C in the freezer before taking an aliquot for analysis by GC. The concentrations of styrene and ethylbenzene were then plotted versus time to give time course profiles of the transfer hydrogenation reaction. These data were overlaid on the styrene/ethylbenzene concentrations from the tandem reaction (Figure S62).

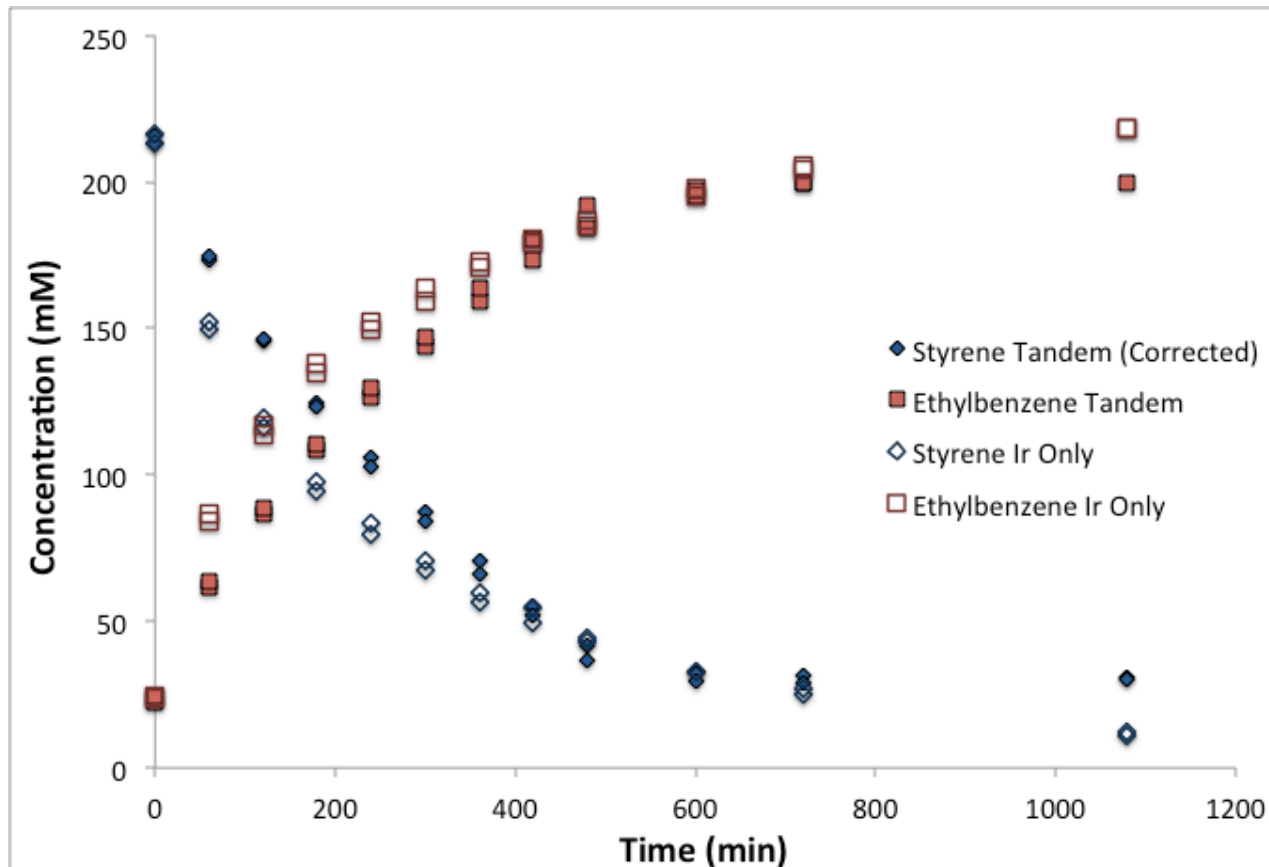


Figure S62: Overlay of reaction progress for runs from Entries 7b and 7c in Table S3 (filled points), and styrene/*n*-heptane transfer hydrogenation catalyzed by only **2** (hollow points). Only styrene and ethylbenzene concentrations are shown for clarity. The styrene concentration for the tandem reactions was corrected by compensating for the amount of styrene consumed in dimerization reactions to form either styrene dimers or styrene/*n*-heptane cross-products.

V: References

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