

Upgrading Light Hydrocarbons via Tandem Catalysis: A Dual Homogeneous Ta and Ir System for Alkane / Alkene Coupling

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

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

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I: Experimental Procedures

General Considerations:

All experiments were performed under an argon inert atmosphere using standard Schlenk line, high-vacuum line, or glovebox techniques. 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”¹ (~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. 1-Hexene, 1-heptene, and neohexene (isoprene-free) were distilled under argon from CaH₂ after stirring for several days. Precatalysts **1**,² **2a**,³ **2b**,⁴ and **2c**⁵ are known compounds, and were prepared according to published procedures. Complexes **2b** and **2c** were purified by washing with pentane (3 x 5-10 mL for a 300 mg batch) and dried under vacuum prior to use in catalytic experiments; failure to do so resulted in substantial alkene isomerization immediately upon mixing the crude Ir compound with 1-hexene.⁶

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).

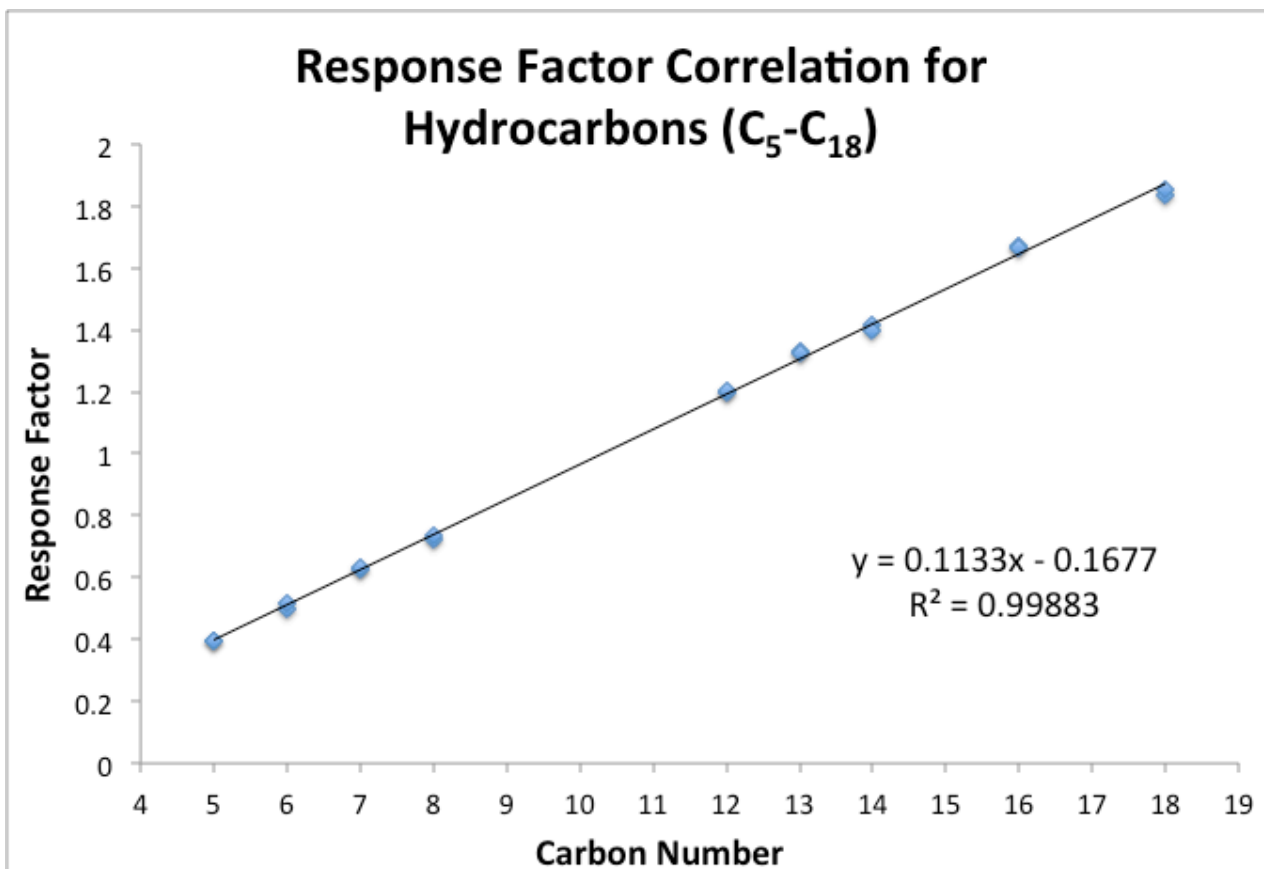


Figure S1: Linear correlation of response factors versus carbon number.

The equation of the line was used to determine response factors for all of the 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 neohexene versus adamantane was established to lie outside this correlation, and was determined independently from two separate runs. The response factors were 0.5982 (run 1) and 0.5853 (run 2) for an average value of 0.5853.

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

Dimerization of 1-Hexene using **1**:

Precatalyst **1** (6.6 mg, 0.016 mmol) and adamantane (internal standard, 9.6 mg, 0.070 mmol) were dissolved in 2 mL of *n*-heptane in a 4 mL screw-top vial containing a Teflon-coated stir bar. 1-Hexene (36.8 mg, 0.437 mmol) was added, and the vial sealed with a Teflon-lined screw cap. The vial was stirred at 100 °C in an aluminum block heater for 4 hours. After cooling to room temperature, the brown solution was passed through a short plug of silica gel into a GC autosampler vial. The mixture was analyzed by GC to determine the retention times of the C₁₂ dimers (Figure S2). The identities of the isomers produced by precatalyst **1** have been definitively established by Schrock and co-workers;⁷ therefore, all of the products here are assigned by analogy to this previous work.

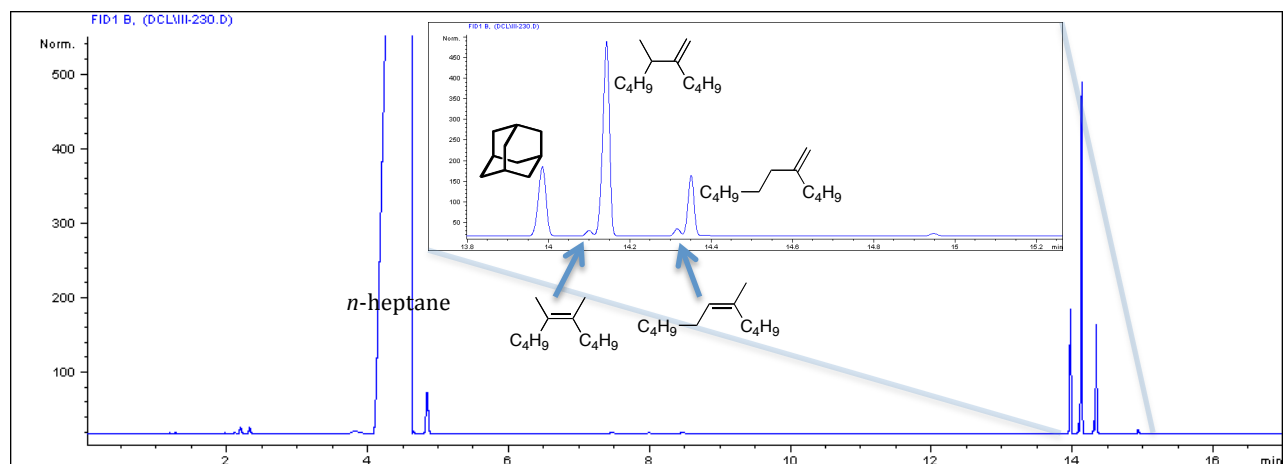


Figure S2: GC trace of the dimerization of 1-hexene to produce C₁₂ dimers.

Dimerization of 1-Heptene using **1**:

As for the dimerization of 1-hexene with the following reagents: **1** (6.6 mg, 0.016 mmol), adamantane (14.9 mg, 0.109 mmol), 1-heptene (40.0 mg, 0.407 mmol), and *n*-heptane (2 mL). This reaction was also analyzed by GC to determine the retention times of the C₁₄ dimers (Figure S3).

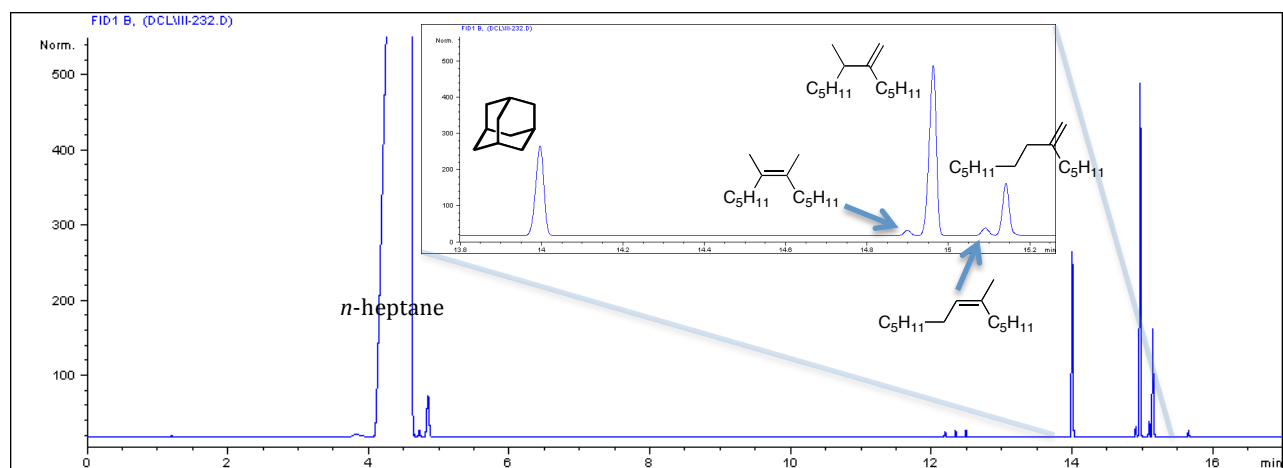


Figure S3: GC trace of the dimerization of 1-heptene to produce C₁₄ dimers.

Co-dimerization of 1-Hexene / 1-Heptene using **1**:

Precatalyst **1** (6.6 mg, 0.016 mmol) and adamantane (internal standard, 9.6 mg, 0.070 mmol) were dissolved in 2 mL of *n*-heptane in a 4 mL screw-top vial containing a Teflon-coated stir bar. 1-Hexene (22.1 mg, 0.263 mmol) and 1-heptene (24.9 mg, 0.254 mmol) were added, and the vial sealed with a Teflon-lined screw cap. The vial was stirred at 100 °C in an aluminum block heater for 4 hours. After cooling to room temperature, the brown solution was passed through a short plug of silica gel into a GC autosampler vial. The mixture was analyzed by GC to determine the retention times of the C₁₃ cross-dimers between 1-hexene and 1-heptene (Figure S4).

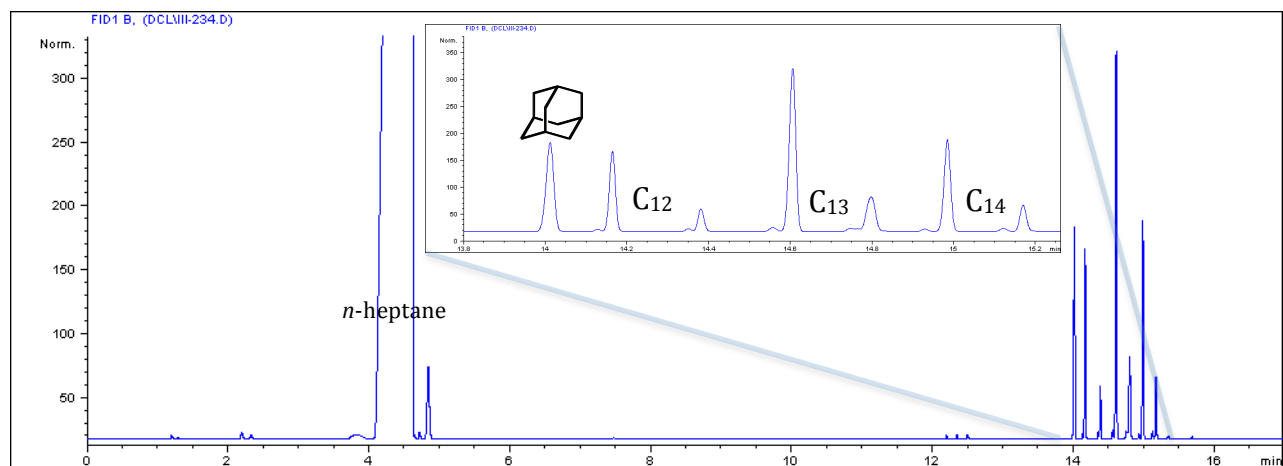


Figure S4: GC trace of the co-dimerization of 1-hexene and 1-heptene to produce C₁₂/C₁₃/C₁₄ dimers.

Attempted Tandem Catalysis with **1** and **2a**:

The following is a representative example. **1** (15.0 mg, 0.0361 mmol), **2a** (12.8 mg, 0.0207 mmol), and adamantane (33.2 mg, 0.244 mmol) were dissolved in 2 mL of *n*-heptane in a 5 mL glass reaction tube (Kontes-valve) containing a Teflon-coated stir bar. 1-Hexene (218.9 mg, 2.60 mmol) was added, and the tube sealed with a Teflon-plug. The mixture was stirred at 125 °C in an oil bath for 24 hours. After cooling to room temperature, the brown solution was diluted with dichloromethane and passed through a short plug of silica gel into a GC autosampler vial. The mixture was analyzed by GC, indicating >98% conversion. The major products were *n*-hexane (113.2 mM, 8.7%) and the C₁₂ dimers (583.6 mM, 89.8%). No C₁₃ or C₁₄ products were observed (Figure S5).

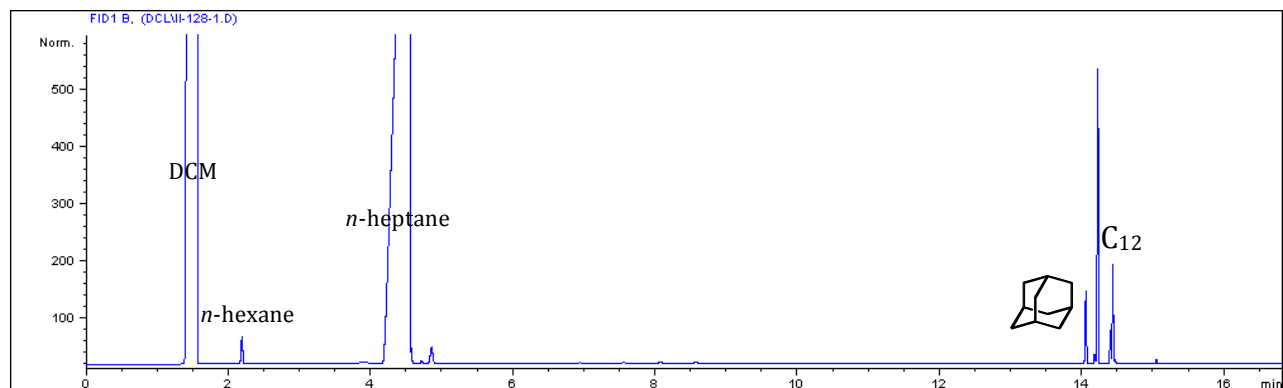


Figure S5: GC trace of attempted 1-hexene / *n*-heptane dimerization with **1** and **2a**.

General Procedure for Reactions from Table 1:

The following is a representative example (entry 1, Table 1, main text). **1** (6.6 mg, 0.016 mmol) and **2b** (5.9 mg, 0.010 mmol) were dissolved in 1 mL of a standard solution of 1-hexene (250 mM) and adamantane (24.8 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 stirred at 125 °C in an aluminum block heater for 5 hours. After cooling to room temperature, the brown solution was diluted with *n*-heptane and passed through a short plug of silica gel into a GC autosampler vial. The mixture was analyzed by GC, indicating >99% conversion. The C₁₃ and C₁₄ dimers are clearly observed in this case (Figure S6, compare to Figure S4).

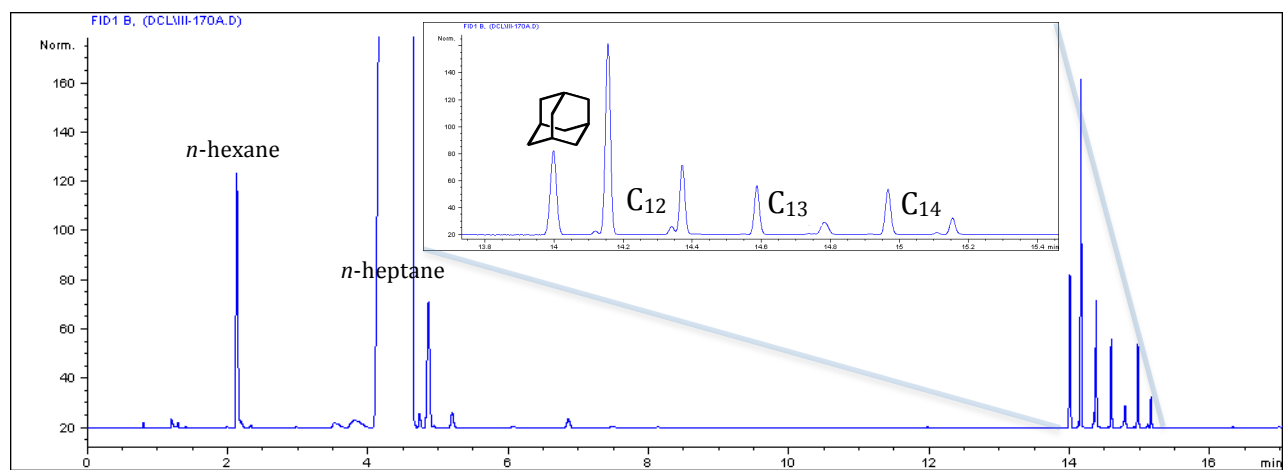


Figure S6: GC trace for reaction from entry 1a, Table S1.

Expanded Results for 1-Hexene / *n*-Heptane Dimerization

Table S1. Results for standard batch reactions (Table 1, main text, entries 1-6)

Observed products

$C_{12}: R = R' = n-C_4H_9$
 $C_{13}: R = n-C_4H_9, R' = n-C_5H_{11} \text{ or } R = n-C_5H_{11}, R' = n-C_4H_9$
 $C_{14}: R = R' = n-C_5H_{11}$

Entry	[1-Hexene] ₀ mM ^a (Final Conc.)	[1]/[2b] mM	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 2b ^c	Coop. (%) ^d
1a	250 (0.7)	16 / 10	125	113.7 (46.2)	3.2 (1.3) / 1.6 (0.7)	56.5 (46.0)	13.7 (11.1) / 12.4 (10.1)	245.9	5 (2)	11 (4)	33.9
1b	250 (0.6)	16 / 10	125	110.5 (45.2)	3.0 (1.2) / 1.3 (0.5)	57.6 (47.1)	14.0 (11.5) / 12.7 (10.4)	244.7	5 (2)	11 (4)	35.7
2a	250 (0.8)	8 / 5	125	108.4 (43.2)	7.4 (2.9) / 3.4 (1.4)	57.7 (46.0)	15.4 (12.3) / 13.0 (10.3)	250.9	11 (4)	22 (8)	38.2
2b	250 (0.7)	8 / 5	125	103.3 (41.5)	8.0 (3.2) / 3.5 (1.4)	59.1 (47.5)	15.2 (12.2) / 13.0 (10.4)	248.7	11 (4)	21 (8)	39.9
3a	250 (0.4)	8 / 5	100	50.2 (20.5)	11.3 (4.6) / 8.0 (3.3)	81.3 (66.3)	12.6 (10.3) / 9.6 (7.8)	245.2	13 (3)	10 (6)	63.5
3b	250 (0.7)	8 / 5	100	54.7 (22.6)	11.0 (4.5) / 5.0 (2.1)	78.6 (64.9)	13.8 (11.4) / 10.0 (8.2)	242.5	13 (3)	11 (7)	61.7
3c	250 (0.9)	8 / 5	100	51.9 (21.2)	10.8 (4.4) / 4.8 (2.0)	81.7 (66.9)	12.6 (10.3) / 9.9 (8.1)	244.4	13 (3)	10 (6)	62.4
4a	250 (0.7)	5 / 5	100	76.4 (30.5)	6.1 (2.4) / 3.2 (1.3)	75.5 (60.3)	13.0 (10.4) / 9.4 (7.5)	250.5	20 (4)	15 (6)	41.7
4b	250 (0.6)	5 / 5	100	78.7 (31.4)	6.9 (2.8) / 3.5 (1.4)	73.8 (58.9)	13.1 (10.5) / 9.3 (7.4)	250.3	19 (4)	16 (6)	40.2
5a	250 (0.3)	12 / 5	100	52.8 (22.3)	3.3 (1.4) / 2.2 (0.9)	84.5 (71.5)	8.8 (7.4) / 7.8 (6.6)	236.4	8 (1)	11 (5)	46.3
5b	250 (0.4)	12 / 5	100	53.3 (22.4)	3.0 (1.3) / 2.0 (0.8)	85.0 (71.5)	9.2 (7.7) / 8.1 (6.9)	237.8	9 (1)	11 (5)	47.8
6a	1000 (3.4)	8 / 5	100	86.3 (8.6)	17.4 (1.7) / 9.6 (1.0)	432.8 (86.5)	18.7 (3.7) / 10.2 (2.0)	1000.9	58 (4)	17 (8)	45.3
6b	1000 (3.4)	8 / 5	100	87.2 (8.7)	18.5 (1.8) / 10.0 (1.0)	431.1 (86.2)	18.8 (3.8) / 10.2 (2.0)	1002.0	58 (4)	17 (8)	45.0

^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. 19 in the main text.

Procedure for Monitoring Reactions over Time:

1 (6.6 mg, 0.016 mmol) and **2b** (5.9 mg, 0.010 mmol) were dissolved in 2 mL of a standard solution of 1-hexene (250 mM) and adamantane (24.8 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 briefly with a heat gun to dissolve the precatalysts 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. Concentrations were plotted versus time (Figure S7).

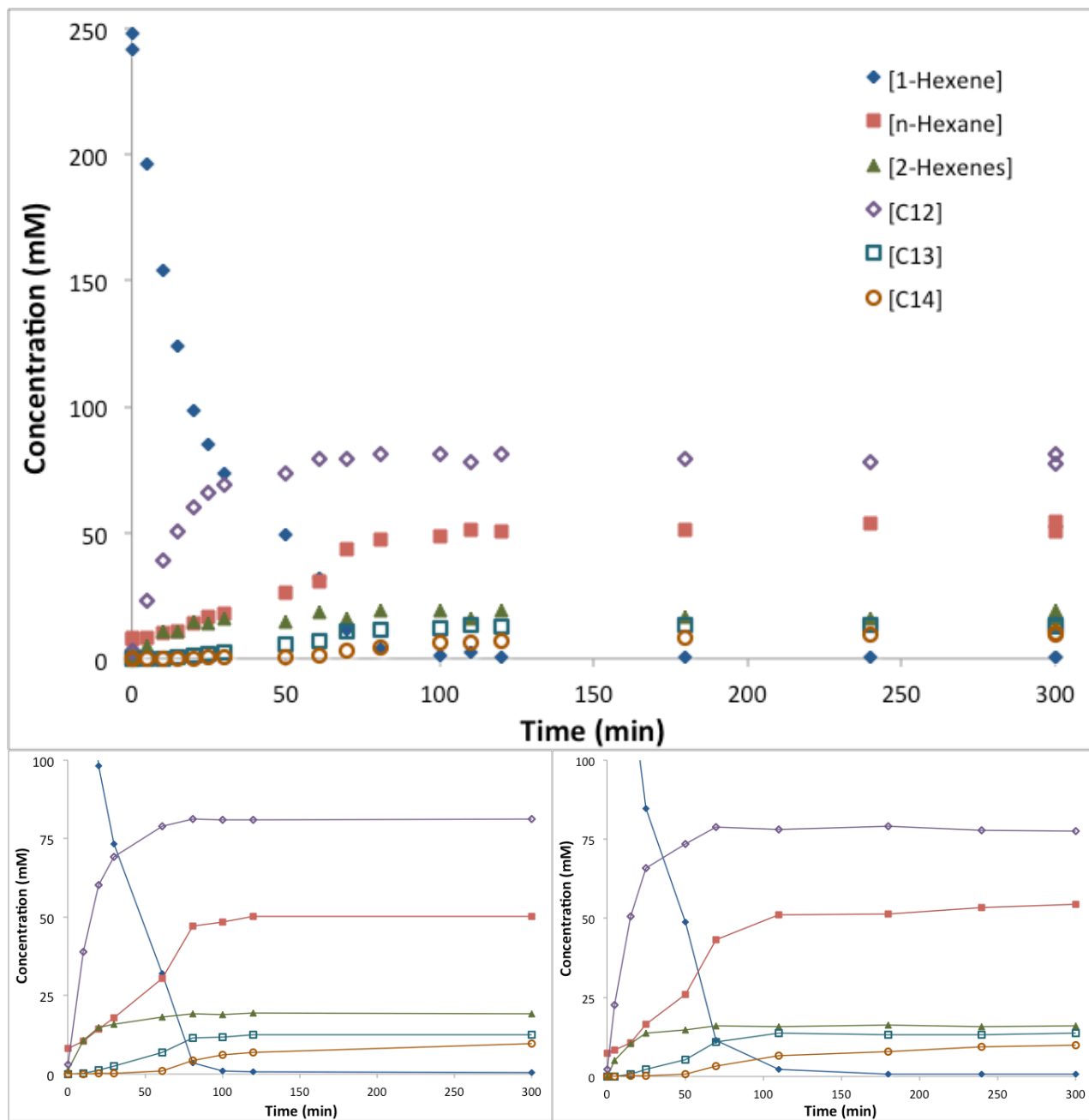


Figure S7: Plots of reaction progress over time for entries 3a and 3b in Table S1. **Top:** Overlay of both data sets. **Bottom left:** Expansion of product concentration range for entry 3a. **Bottom Right:** Expansion of product concentration range for entry 3b. Lines are drawn as visual guides.

Procedure for Monitoring Individual Reactions with **1** or **2b** over Time:

1 (6.6 mg, 0.016 mmol) or **2b** (5.9 mg, 0.010 mmol) was dissolved in 2 mL of a standard solution of 1-hexene (250 mM) and adamantane (24.8 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. For reactions involving **1**, the mixture was heated briefly with a heat gun to dissolve the precatalyst and ensure a homogeneous solution. The solution was then split into aliquots (5 aliquots for reactions with catalyst **1**, 8 for reactions with catalyst **2b**) in 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. Concentrations were plotted versus time (Figure S8). Runs were repeated in triplicate (catalyst **1**) or duplicate (catalyst **2b**).

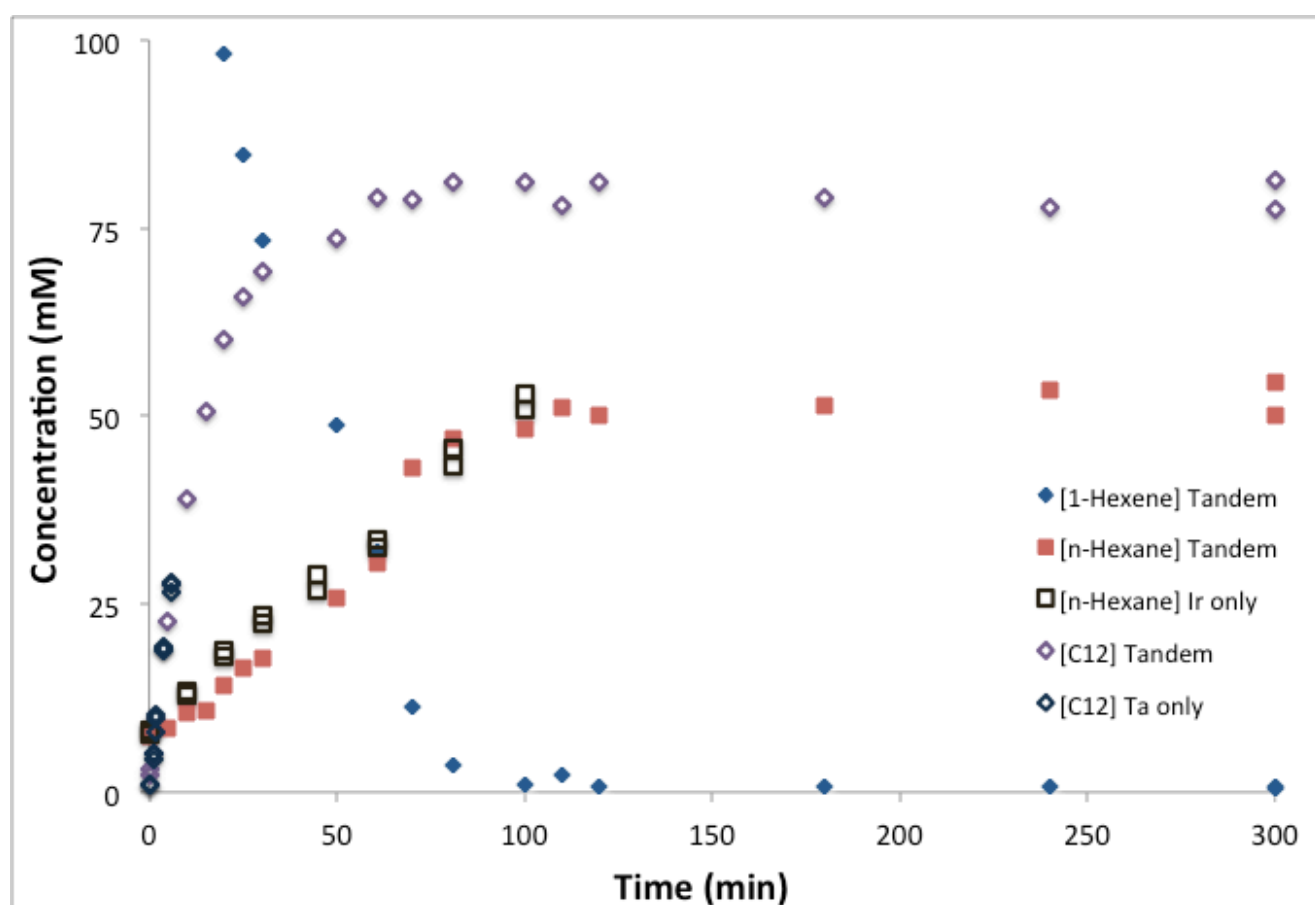


Figure S8: Overlay of reaction progress for tandem catalytic reaction from entries 3a and 3b in Table S1, initial rate for 1-hexene dimerization to C_{12} catalyzed by **1** (3 runs), and *n*-hexane formed by 1-hexene/*n*-heptane transfer hydrogenation catalyzed by **2b** (2 runs). These data clearly show that the catalytic rates exhibited by **1** and **2b** are unchanged under the tandem catalysis conditions, and hence the two catalysts do not undergo mutual inhibition / deactivation.

([1-Hexene] for individual runs, [C_{13}] and [C_{14}] for tandem runs, and [2-hexenes] for all runs not shown for clarity).

Procedure for Syringe-Pump Addition:

1 (6.6 mg, 0.016 mmol), **2b** (5.9 mg, 0.010 mmol) and adamantane (14.5 mg, 0.106 mmol) were dissolved in 2 mL of *n*-heptane in a 10 mL round-bottom flask containing a Teflon-coated stir bar. Three drops of 1-hexene were added. The flask was connected to a reflux condenser with Apiezon H-grease and fixed with rubber bands. A 90° adapter with 14/20 and 24/40 joints and a Kontes Teflon-plug was attached to the top of the condenser with H-grease and fixed with rubber bands. With the plug sealed, the apparatus was removed from the glovebox and connected to an argon line. With a strong flow of argon (mercury bubbler), the Teflon plug was replaced with a rubber septum that was fixed with copper wire. After this, the apparatus was subject to a constant, slow stream of argon and vented through an oil bubbler to prevent overpressure. A gastight Hamilton syringe (500 μ L) with a long (~30 cm) needle was filled with 300 μ L 1-hexene (~200 mg, ~2.38 mmol) in the glovebox. With the needle-tip inside a rubber stopper, the syringe was removed from the glovebox and quickly inserted into the septum at the top of the reflux condenser. The flask was lowered into an oil bath at 120 °C. The needle was threaded through the reflux condenser such that the tip was at the reflux level. The syringe was placed inside a syringe-pump and set to deliver the 1-hexene at ~12.5 μ L h⁻¹ (~50 mM 1-hexene h⁻¹), corresponding to ~24 h addition time, while the reaction was run for a total of 32 hours (run 1) or 36 hours (run 2). After completion, the flask was cooled to room temperature, the brown solution passed through a short plug of silica gel into a GC autosampler vial, and the contents analyzed by GC. The results of two separate runs are given in Table S2.

Table S2. Results for slow addition protocol (Table 1, main text, entry 7)

1200 mM added over 24 h

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

Run	[1-Hexene] ₀ mM ^a (Final Conc.)	<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 2b ^c	Coop. (%) ^d
1	~1200 (32.4)	270.6 (22.5)	28.8 (2.4) / 21.0 (1.8)	302.2 (50.4)	179.6 (29.9) / 59.1 (9.9)	1136.8	68 (30)	54 (60)	110.1
2	~1200 (83.8)	206.7 (17.2)	24.1 (2.0) / 18.5 (1.5)	283.5 (47.2)	182.2 (30.4) / 59.1 (9.9)	1082.1	66 (30)	41 (60)	145.4
1'	~1200 (32.4)	333.8 ^e (27.8)	28.8 (2.4) / 21.0 (1.8)	302.2 (50.4)	179.6 (29.9) / 59.1 (9.9)	1200	68 (30)	67 (60)	89.2
2'	~1200 (83.8)	324.6 ^e (27.0)	24.1 (2.0) / 18.5 (1.5)	283.5 (47.2)	182.2 (30.4) / 59.1 (9.9)	1200	66 (30)	65 (60)	92.6

^aDetermined from total amount of 1-hexene added. ^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. 19 in the main text. ^eCorrected values, see discussion below.

As analyzed, these two runs are deficient in *n*-hexane, presumably due to evaporation during the prolonged reflux. This gives apparent cooperativity percentages that are over 100%, and a C₆ mass balance below the anticipated value of ~1200 mM (runs 1 and 2 in Table S2). As “acceptorless” dehydrogenation of *n*-heptane is extremely unlikely under these conditions, we have estimated the total amount of *n*-hexane generated based on the expected C₆ mass balance of 1200 mM (runs 1' and 2' in Table S2). Thus, the “missing” *n*-hexane is 63.2 mM in run 1 and 117.9 mM in run 2. Applying this correction gives TONs for catalyst **2b** and cooperativity values that are in excellent agreement between the two runs.

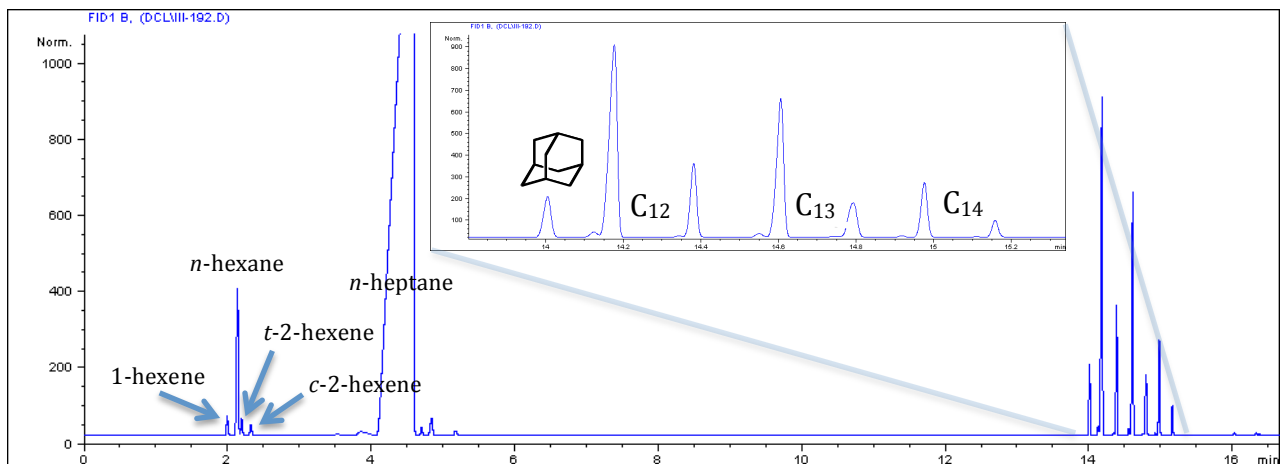


Figure S9: GC trace for reaction from run 1, Table S2.

Procedure for Catalytic Dimerization of *n*-Heptane:

1 (6.6 mg, 0.016 mmol), **2c** (2.1 mg, 0.0039 mmol) were dissolved in 2 mL of a standard solution of neohexene (252 mM) and adamantane (34.7 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 stirred at 100 °C in an aluminum block heater for 18 hours. After cooling to room temperature, the brown solution was passed through a short plug of silica gel into a GC autosampler vial. The mixture was analyzed by GC, indicating ~50% conversion (Table S3). Longer reaction times give similar results, indicating catalyst decomposition.

Table S3. Results for catalytic *n*-heptane dimerization (Eq. 4, main text)

Observed products

252.1 mM
t-Bu
+

solvent

1 (8 mM)
2c (2 mM)

→

100 °C
18 h

t-Bu + *t*-Bu

TBE TBA

C₁₃

+ alkene isomers

C₁₄

R = *n*-C₅H₁₁

Run	Final [TBE] mM	[TBA] mM	% Conv.	C ₁₃ mM (%)	C ₁₄ mM (%)	TON 1 ^a	TON 2c ^a	Coop. (%) ^b
1	133.2	109.1	45	1.9 (1.6)	20.6 (16.9)	(3)	55 (22)	39.5
2	107.0	124.8	53	1.5 (1.3)	21.4 (18.3)	(3)	62 (22)	35.5

^aTONs in parentheses are for production of C₁₃/C₁₄. ^bSee Ref. 19 in the main text.

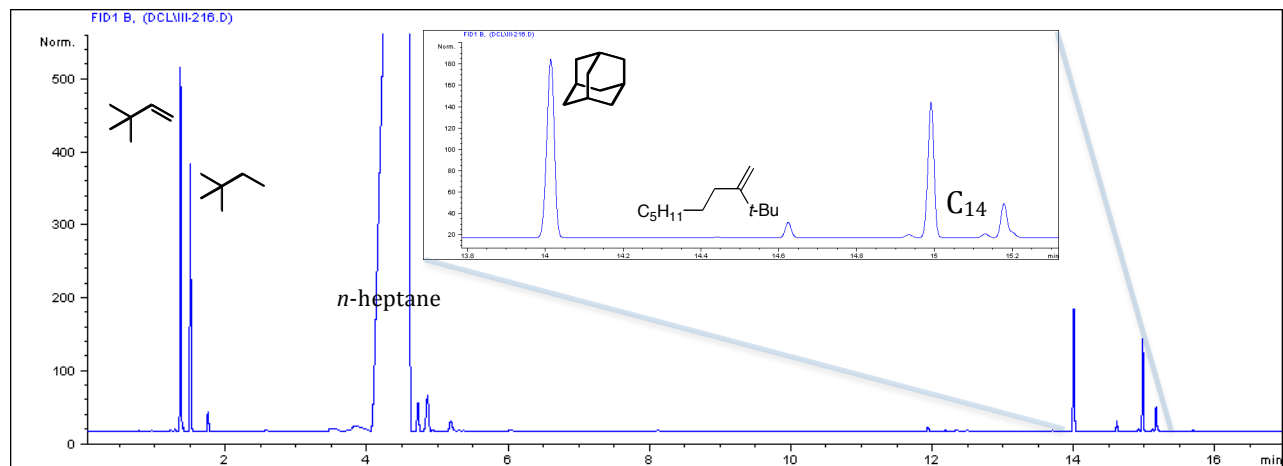


Figure S10: GC trace for catalytic *n*-heptane dimerization (run 1, Table S3).

GC/MS Characterization of C₁₃ Product:

In order to confirm the proposed structure of the neohexene/*n*-heptane heterodimer (C₁₃), the reaction mixture was analyzed by GC/MS (Figure S9). The trace gives a similar pattern to the GC analysis carried out with the FID (Figure S8). The peak at 8.38 min, corresponding to the C₁₃ product, has a molecular ion of $m/z = 182.6$ (calc. for C₁₃H₂₆: 182.20). Furthermore, diagnostic fragments are observed. The base peak corresponds to a *t*-BuC=CH₂ fragment ($m/z = 83.1$ found, 83.09 calc.), confirming the presence of the C₆ neohexene coupling partner.

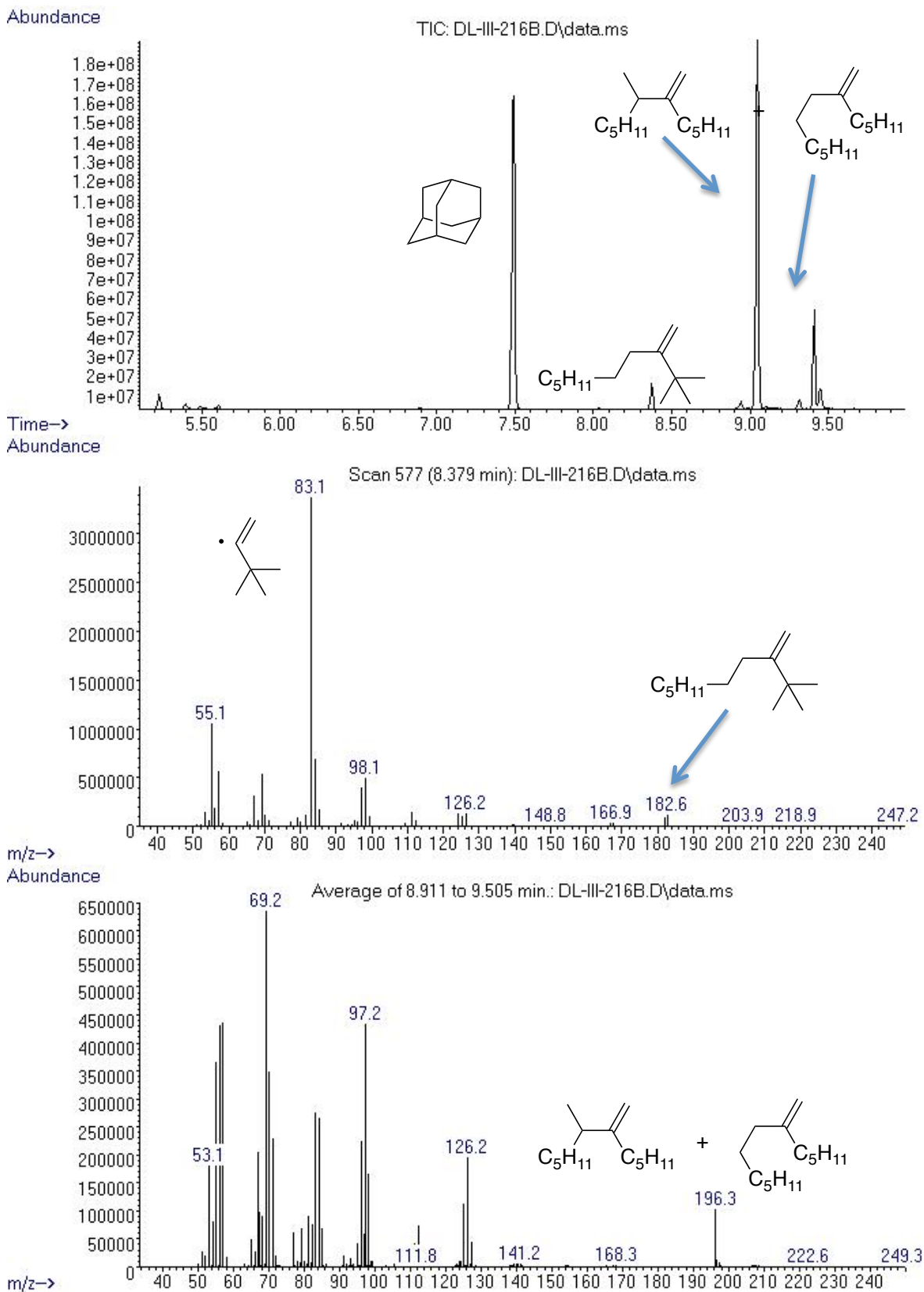


Figure S11: GC/MS analysis of catalytic *n*-heptane dimerization (Eq. 4, main text). **Top:** GC trace, indicating products. **Middle:** MS for peak corresponding to C₁₃ product with diagnostic fragment indicated. **Bottom:** Average MS for C₁₄ region.

The regioisomer shown for the C_{13} product is proposed based on steric arguments in the tantallacyclopentane intermediate (Figure S10).

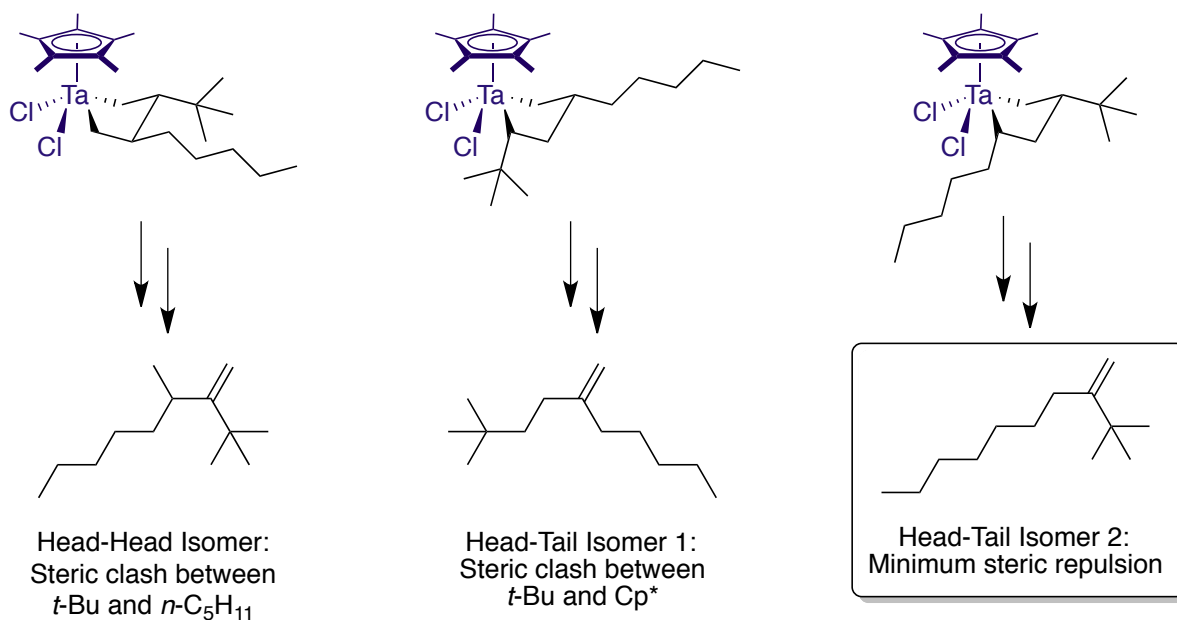


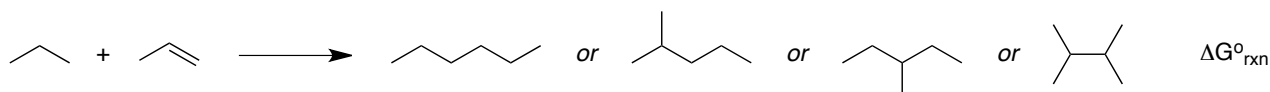
Figure S12: Steric rationale for the proposed regiochemistry of the C_{13} neoheptene / n -heptane dimer.

II: Thermodynamic Analysis

Table S4. Gibbs energies of formation for propane, propene, and C₆ alkanes in the gas phase (1 atm). Data obtained from ref. 8.

Temp. K (°C)	Propane	Propene	$\Delta_f G^\circ_m$			
			Hexane	2-Methylpentane	3-Methylpentane	2,3-Dimethylbutane
0 (-273.15)	-82.4	34.7	-130.5	-135.3	-132.5	-134.8
200 (-73.15)	-49.5	49.1	-52.8	-58.8	-56.6	-57.1
298.15 (25)	-24.3	62.2	0.2	-5.1	-3.2	-2.0
300 (26.15)	-23.8	62.5	1.2	-4.1	-2.1	-1.0
400 (126.15)	4.2	77.4	58.9	54.4	56.2	59.0
500 (226.15)	33.7	93.5	119.0	115.2	116.9	-
600 (326.15)	64.1	110.3	180.5	177.5	179.2	185.3
700 (426.15)	95.2	127.6	243.1	241.2	242.4	250.2

Table S5. Calculated free energies of reaction for propane/propene coupling.


 $\Delta G^\circ_{\text{rxn}}$

Temp. K (°C)	$\Delta G^\circ_{\text{rxn}}$			
	Hexane	2-Methylpentane	3-Methylpentane	2,3-Dimethylbutane
0 (-273.15)	-82.8	-87.6	-84.8	-87.1
200 (-73.15)	-52.4	-58.4	-56.2	-56.7
298.15 (25)	-37.7	-43	-41.1	-39.9
300 (26.15)	-37.5	-42.8	-40.8	-39.7
400 (126.15)	-22.7	-27.2	-25.4	-22.6
500 (226.15)	-8.2	-12	-10.3	-
600 (326.15)	6.1	3.1	4.8	10.9
700 (426.15)	20.3	18.4	19.6	27.4

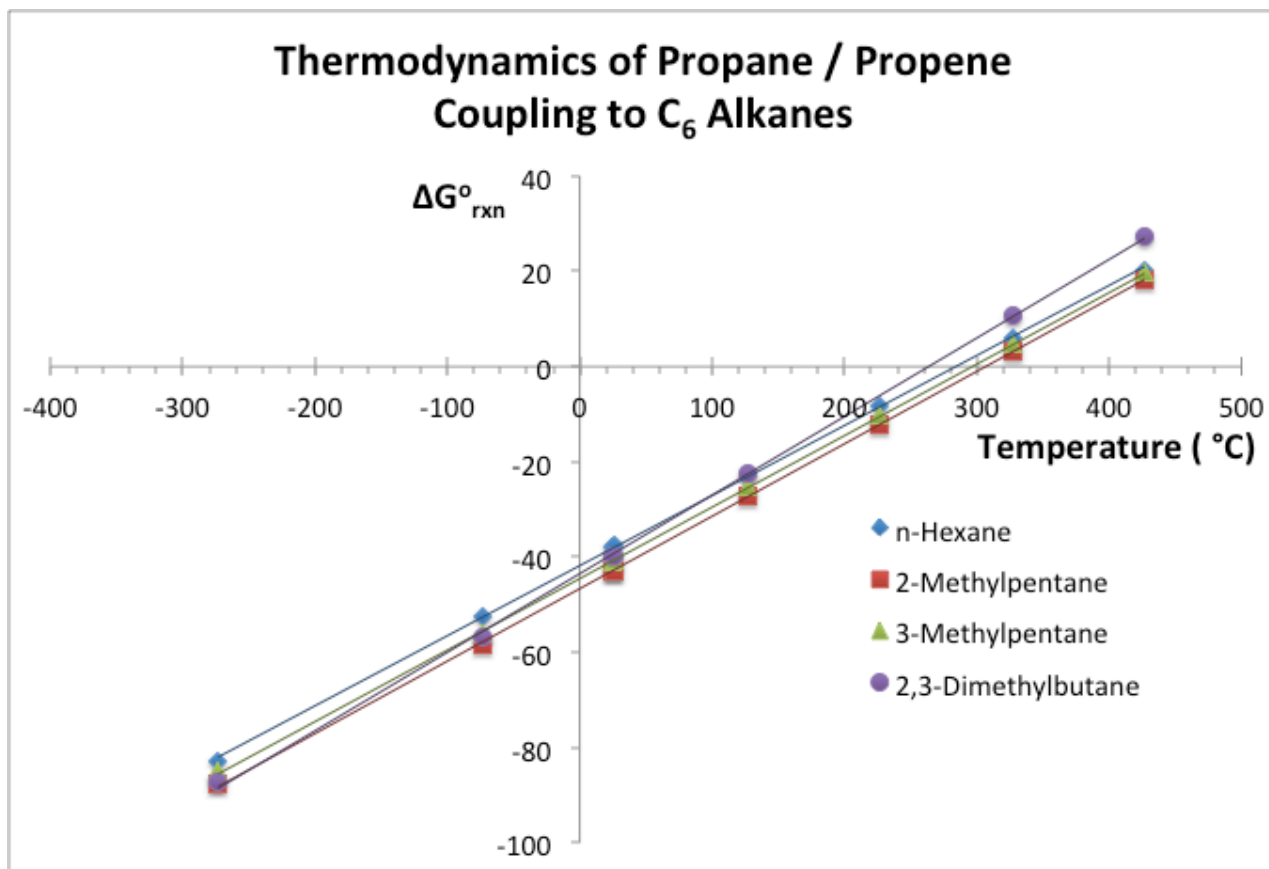


Figure S13: Plots of $\Delta G^\circ_{\text{rxn}}$ for propane / propene coupling to generate four C₆ alkane isomers. The linear correlations cross the x-axis between ~ 260 °C for 2,3-dimethylbutane, and ~ 310 °C for 2-methylpentane; thus, these reactions can be expected to be spontaneous below 250 °C.

III: References

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