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(54) Title: TANDEM TRANSFER HYDROGENATION AND OLIGOMERIZATION FOR HYDROCARBON PRODUCTION

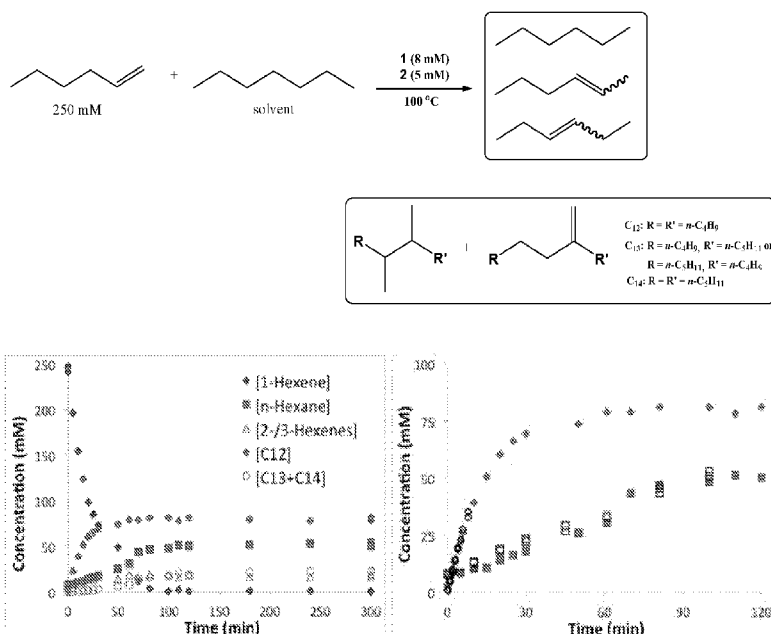


FIGURE 1



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TANDEM TRANSFER HYDROGENATION AND OLIGOMERIZATION FOR HYDROCARBON PRODUCTION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application serial number 61/753,768, filed on January 17, 2014, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The disclosure relates to hydrocarbon production by hydrogenation and oligomerization and, more particularly, to catalysis of alkanes and alkenes by a tandem transfer hydrogenation and oligomerization.

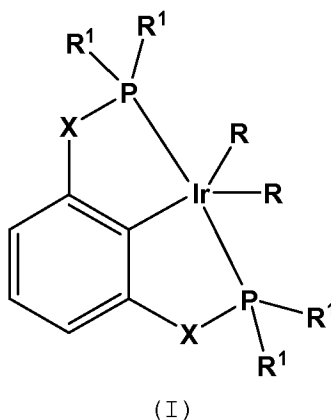
BACKGROUND

[0003] Light alkane gases (ethane, propane, butane) and low-boiling liquids (pentane, hexane, etc.) represent a considerable proportion of petroleum-derived hydrocarbons. These light alkanes are found in natural gas and petroleum reservoirs, and also generated as low-value byproducts of refinery processes such as catalytic cracking as well as in Fisher-Tropsch conversion of synthesis gas. The latter processes may also produce corresponding alkenes; streams containing substantial amounts of both alkane and alkene are commonly obtained. These light hydrocarbons have limited value as useful fuels, particularly in the transportation sector, which generally requires heavier hydrocarbons. As the cost of raw petrochemicals rises due to increased demand and an anticipated reduction in supply, and concern over carbon emissions leads to demands for increased energy efficiency, a method to convert these under-utilized light hydrocarbons into more valuable heavier products would greatly impact the production of chemical fuels.

SUMMARY

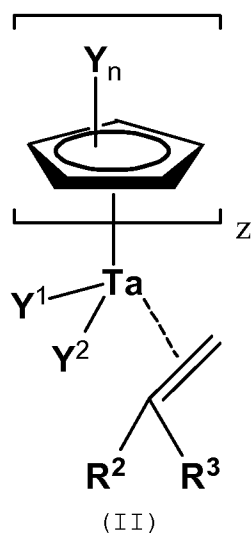
[0004] The disclosure provides methods and compositions to convert a mixture of hydrocarbons into a mixture of heavier hydrocarbons. In a simplified version, a mixture of an alkane and an alkene (which may or may not have the same carbon number) are coupled to give an overall increase of the average carbon number of the product components. This is accomplished through the action of

two catalysts that act concurrently. In one embodiment, a first catalyst ("hydrogenation catalyst") is a transfer hydrogenation catalyst. For example, a hydrogenation catalyst suitable for transfer hydrogenation includes, but is not limited to, soluble organometallic species containing a metal from group 9; these same species immobilized on a solid support such as silica or alumina; and platinum group metals dispersed on a suitable support. In one embodiment, a suitable hydrogenation catalyst comprises formula I:

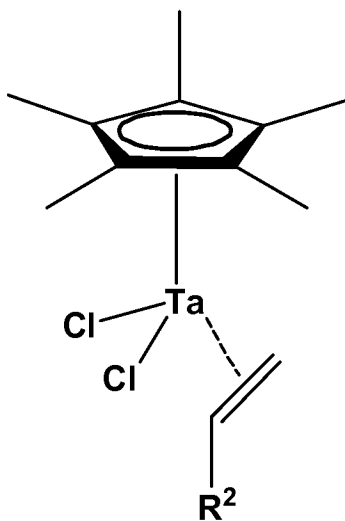


wherein, each R is independently H or a (C₁-C₃₀)hydrocarbyl radical; each R¹ is independently a (C₁-C₃₀)hydrocarbyl radical; and each X is independently an O or CH₂.

[0005] This hydrogenation catalyst serves to dehydrogenate the alkane reactants to alkenes, and to use the resulting H₂ to hydrogenate alkenes to alkanes. The alkenes may be sacrificial additives, or the products of the process itself. The second catalyst ("dimerization catalyst") effects alkene dimerization or oligomerization; dimers/oligomers can be a coupling of identical monomers ("homodimers/oligomers") or a coupling of similar, but not identical, monomers ("heterodimers/oligomers"). Exemplary dimerization catalysts include, but are not limited to, soluble organometallic species; supported versions of these same species; and zeolitic materials containing group 10 metal ions. In one embodiment, a suitable dimerization catalyst comprises Formula II:



wherein, Z is either 1 or 2; n is an integer from 1 to 5; each Y is independently selected from D, H, optionally substituted (C₁-C₆)alkyl, silane, and (C₁-C₄)alkylsilane; Y¹ is a H, D, halo, =S, =O, PMe₃, =C(H)(CMe₃); Y² is a H, D, halo, =S, =O, PMe₃, or absent; R² is a H, aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl; and R³ is a H, aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl. In another embodiment, the dimerization catalyst comprises the Formula II(a):

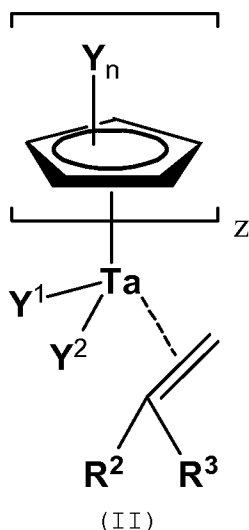


II (a)

wherein, R² is an aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl. This catalyst converts

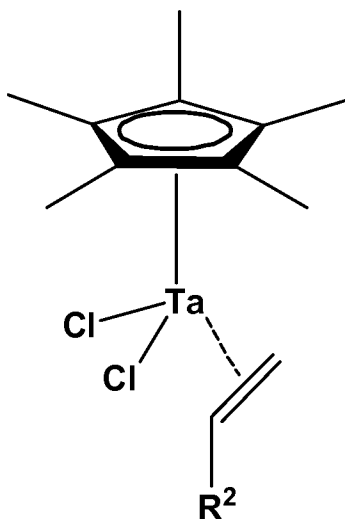
the C_n alkenes, present in the reactant mixture and/or formed by dehydrogenation catalysis, selectively into C_{2n} or higher alkenes.

[0006] In a particular embodiment, the disclosure provides a method of coupling an alkane with an alkene so as to form one or more higher molecular weight hydrocarbons, comprising: coupling an alkane (e.g., a straight chain (C_5 - C_{10})alkane) with an alkene (e.g., a straight chain (C_5 - C_{10})alkene) in the presence of catalysts comprising: (i) a hydrogen transfer catalyst and (ii) an alkene dimerization catalyst so as to generate one or more higher molecular weight hydrocarbons (e.g., alkanes or alkenes); wherein the hydrogen transfer catalyst is an iridium pincer complex catalyst and the alkene dimerization catalyst is tantalum catalyst, wherein the one or more higher molecular weight hydrocarbons comprise one or more carbon atoms from both the alkane and the alkene. In a further embodiment, both the hydrogen transfer catalyst and the dimerization catalyst are heterogeneous catalysts. In yet a further embodiment, the dimerization catalyst comprises a structure of Formula II:



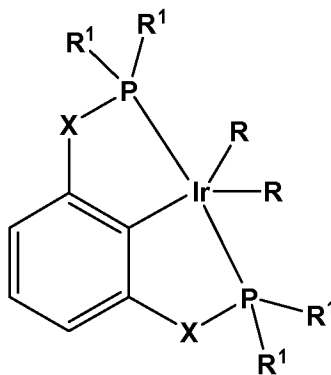
wherein, Z is either 1 or 2; n is an integer from 1 to 5; each Y is independently selected from D, H, optionally substituted (C_1 - C_6)alkyl, silane, and (C_1 - C_4)alkylsilane; Y^1 is a H, D, halo, =S, =O, PMe_3 , =C(H) (CMe_3); Y^2 is a H, D, halo, =S, =O, PMe_3 , or absent; R^2 is a H, aryl, optionally substituted (C_1 - C_{15})alkyl, or an optionally substituted (C_1 - C_{15})hetero-alkyl; and R^3 is a H, aryl, optionally substituted (C_1 - C_{15})alkyl, or an optionally substituted (C_1 -

C₁₅)hetero-alkyl. In another embodiment, the dimerization catalyst comprises a structure of Formula II(a):



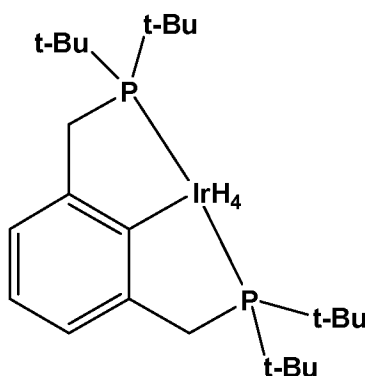
II (a)

wherein, R² is an aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl. In yet another embodiment, the hydrogen transfer catalyst comprises a structure of Formula I:



(I)

wherein, each R is independently H or a (C₁-C₃₀)hydrocarbyl radical; each R¹ is independently a (C₁-C₃₀)hydrocarbyl radical; and each X is independently an O or CH₂. In a further embodiment, the hydrogen transfer catalyst comprises a structure of Formula I(a):



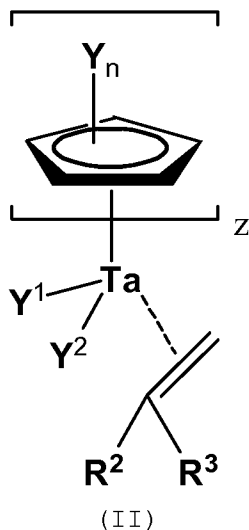
I (a) .

[0007] In a particular embodiment, for the methods disclosed herein, the hydrogen transfer catalyst is immobilized on a solid support, wherein the reaction is carried out in a solvent, and wherein the method further comprises the step of separating the free hydrogen transfer catalyst from the solvent.

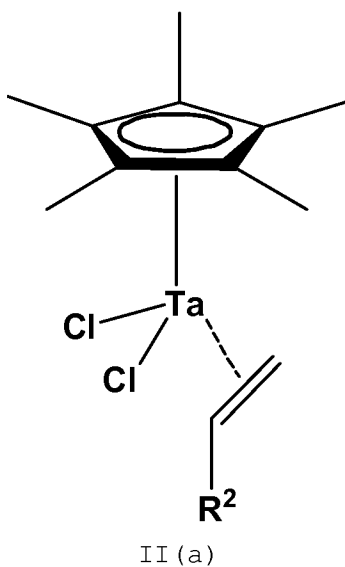
[0008] In a certain embodiment, for the methods disclosed herein, the hydrogen transfer catalyst is immobilized on a solid support, wherein the reaction is carried out in a solvent, and wherein the method further comprises the step of separating free hydrogen transfer catalyst from the solvent.

[0009] In a particular embodiment, the disclosure provides a method for coupling a first alkane with a second alkane to form one or more high molecular weight hydrocarbons, comprising: coupling a first alkane (e.g., a straight chain (C₅-C₁₀)alkane) with a second alkane (e.g., a straight chain (C₅-C₁₀)alkane) using a sacrificial hydrogen acceptor in the presence of catalysts comprising: (i) a hydrogen transfer catalyst and (ii) an alkene dimerization catalyst so as to generate one or more higher molecular weight hydrocarbons (e.g., alkanes or alkenes); wherein the hydrogen transfer catalyst is an iridium pincer complex catalyst and the alkene dimerization catalyst is tantalum catalyst, wherein the one or more higher molecular weight hydrocarbons comprise carbon atoms from the first alkane and the second alkane. In a further embodiment, the sacrificial hydrogen acceptor is styrene, tert-butylethylene or a combination thereof. In yet a further embodiment, the first alkane and the second alkane have the same structure. In an alternate embodiment, the first alkane and the second alkane do not have the same structure.

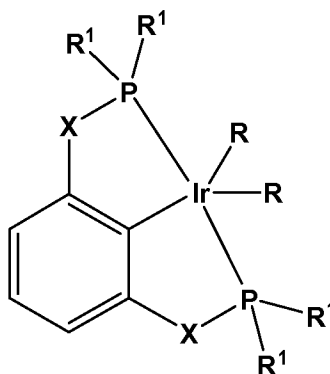
[0010] In a certain embodiment, for the methods disclosed herein, the hydrogen transfer catalyst and the dimerization catalyst are heterogeneous catalysts. In a further embodiment, the dimerization catalyst comprises a structure of Formula II:



wherein: Z is either 1 or 2; n is an integer from 1 to 5; each Y is independently selected from D, H, optionally substituted (C₁-C₆)alkyl, silane, and (C₁-C₄)alkylsilane; Y¹ is a H, D, halo, =S, =O, PMe₃, =C(H)(CMe₃); Y² is a H, D, halo, =S, =O, PMe₃, or absent; R² is a H, aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl; and R³ is a H, aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl. In another embodiment, the dimerization catalyst comprises a structure of Formula II(a):

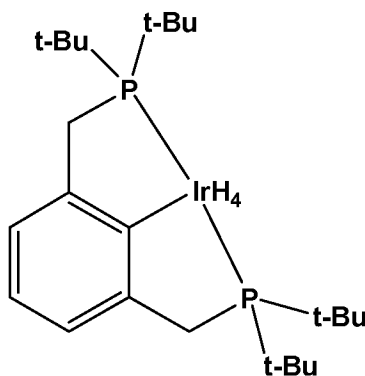


wherein, R^2 is a phenyl. In yet another embodiment, the hydrogen transfer catalyst comprises a structure of Formula I:



(I)

wherein, each R is independently H or a (C₁-C₃₀)hydrocarbyl radical; each R¹ is independently a (C₁-C₃₀)hydrocarbyl radical; and each X is independently an O or CH₂. In a further embodiment, the hydrogen transfer catalyst comprises a structure of Formula I(a):



I(a).

[0011] In a particular embodiment, for the methods disclosed herein the hydrogen transfer catalyst is immobilized on a solid support, wherein the reaction is carried out in a solvent system, and wherein the method further comprises the step of separating free hydrogen transfer catalyst from the solvent. In a further embodiment, the solvent system comprises the first alkane and/or the second alkane.

[0012] In another embodiment, for the methods disclosed herein, the method further comprises the step of hydrogenating or reducing the one or more higher molecular weight hydrocarbons made by the methods disclosed herein.

[0013] The disclosure further provides for a liquid hydrocarbon fuel comprising the one or more higher molecular weight hydrocarbons made by the methods disclosed herein.

[0014] The disclosure also provides for an apparatus for carrying out the methods of the disclosure, which comprises an inlet and an outlet; and a bed or column comprising a hydrogen transfer catalyst and a dimerization catalyst disclosed herein. In yet a further embodiment, for the bed or column comprising the catalysts: (i) the hydrogen transfer catalyst is immobilized on a solid support; and (ii) the dimerization catalyst is immobilized on a solid support.

BRIEF DESCRIPTION OF THE FIGURES

[0015] **Figure 1.** A time evolution plot of the tandem catalytic coupling of 1-hexene/*n*-heptane. Top: Reaction conditions and products observed ("1" denotes dimerization catalyst; "2" denotes hydrogenation catalysts). Bottom left: Time course plot for concentrations of all observed species. Bottom right: Expansion and simplification showing formation of C₁₂ (from 1-hexene dimerization) and *n*-hexane (from 1-hexene/*n*-heptane transfer hydrogenation). Points are from tandem reactions, while black hollow points represent several individual catalytic runs with either **1** (diamonds) or **2** (squares). These data indicate that the rates of the individual catalytic reactions are identical to the rates observed during tandem catalysis, and therefore the two catalysts operate independently.

[0016] **Figure 2.** A time evolution plot of the tandem catalytic coupling the dimerization of 1-hexene (240 mM) catalyzed by **1** (8 mM) at 100 °C (three runs).

[0017] **Figure 3.** Initial rate of formation of the major regioisomer from dimerization of 1-hexene (248-3996 mM) catalyzed by **1** (8 mM) at 100 °C (each line generated by linear regression of an overlay of at least three runs).

[0018] **Figure 4.** Top: Plot of initial rate (k_{obs}) for 1-hexene dimerization (blue points: major isomer; red points: minor isomer) catalyzed by **1** (8 mM) at 100 °C versus [1-hexene]₀ (248 mM-3996 mM; data from Table 1), indicating an approach to saturation. Bottom:

Corresponding double-reciprocal plot to calculate values for K_{eq} , k_1 , and k_2K_{eq}' according to equations 1-8.

[0019] **Figure 5.** *Left:* van't Hoff plot (80 °C-125 °C) for the equilibrium $Cp^*TaCl_2(1\text{-hexene}) (A) + 1\text{-hexene} \rightleftharpoons Cp^*TaCl_2(\text{metallacycle}) (B)$ governed by K_{eq} , with thermodynamic parameters. *Right:* Eyring plot (80 °C-125 °C) for the unimolecular decomposition of $Cp^*TaCl_2(\text{metallacycle}) (B)$ into C governed by k_1 , with activation parameters.

[0020] **FIGURE 6.** Rates of 1-hexene/*n*-decane transfer hydrogenation and 1-hexene isomerization catalyzed by **2** at 100 °C versus initial [1-hexene] (248-1010 mM). The data clearly show inverse order in 1-hexene for transfer hydrogenation, and positive order in 1-hexene for isomerization.

[0021] **Figure 7.** Plot of $\ln([styrene])$ versus time for the dimerization of styrene (250 mM) catalyzed by **1** (8 mM) at 100 °C through 4 half-lives (two runs, final 160 h data point not included in linear correlation).

[0022] **Figure 8.** Reaction progress for entry 7 (**Table 4**). Legend: blue ♦: styrene; red ■: ethylbenzene; green ▲: heptane dimers; purple ◇: co-dimers; orange ○: styrene dimer. Lines are drawn as visual guides only.

[0023] **Figure 9.** Comparison of transfer hydrogenation progress in the conversion of styrene (blue diamonds) to ethylbenzene (red squares) for catalysis with **2** only (hollow points, dashed lines) and with **1** and **2** in tandem (filled points, solid lines; values corrected for styrene converted to co-dimers and styrene dimers).

[0024] **Figure 10.** Linear correlation of response factors versus carbon number.

[0025] **Figure 11.** GC trace of the dimerization of 1-hexene to produce C_{12} dimers.

[0026] **Figure 12.** Time course plot of the dimerization of 1-hexene by **1** (overlay of three runs).

[0027] **Figure 13.** Initial rate of 1-hexene dimerization as a function of $[1\text{-hexene}]_0$ at 80 °C. *Top:* Rate vs.

[0028] **Figure 14.** Initial rate of 1-hexene dimerization as a function of $[1\text{-hexene}]_0$ at 80 °C. *Top:* Rate vs. concentration. *Bottom:* Double reciprocal plot.

[0029] **Figure 15.** Initial rate measurements for 1-hexene dimerization at 90 °C. *Top:* Major isomer product. *Bottom:* Minor isomer product.

[0030] **Figure 16.** Initial rate of 1-hexene dimerization as a function of [1-hexene]₀ at 90 °C. *Top:* Rate vs. concentration. *Bottom:* Double reciprocal plot.

[0031] **Figure 17.** Initial rate measurements for 1-hexene dimerization at 100 °C. *Top:* Major isomer product. *Bottom:* Minor isomer product.

[0032] **Figure 18.** Initial rate of 1-hexene dimerization as a function of [1-hexene]₀ at 100 °C. *Top:* Rate vs. concentration. *Bottom:* Double reciprocal plot.

[0033] **Figure 19.** Initial rate measurements for 1-hexene dimerization at 110 °C. *Top:* Major isomer product. *Bottom:* Minor isomer product.

[0034] **Figure 20.** Initial rate of 1-hexene dimerization as a function of [1-hexene]₀ at 110 °C. *Top:* Rate vs. concentration. *Bottom:* Double reciprocal plot.

[0035] **Figure 21.** Initial rate measurements for 1-hexene dimerization at 125 °C. *Top:* Major isomer product. *Bottom:* Minor isomer product.

[0036] **Figure 22.** Initial rate of 1-hexene dimerization as a function of [1-hexene]₀ at 125 °C. *Top:* Rate vs. concentration. *Bottom:* Double reciprocal plot.

[0037] **Figure 23.** Initial rate measurements for 1-hexene/*n*-decane transfer hydrogenation at 100 °C. *Top:* *n*-Hexane formation (hydrogenation). *Bottom:* 2-Hexenes formation (isomerization).

[0038] **Figure 24.** Initial rate measurements for 1-hexene/*n*-decane transfer hydrogenation at 125 °C. *Top:* *n*-Hexane formation (hydrogenation). *Bottom:* 2-Hexenes formation (isomerization).

[0039] **Figure 25.** Initial rate of 1-hexene hydrogenation and isomerization by **2** (5 mM) versus [1-hexene]₀. *Top:* 100 °C. *Bottom:* 125 °C.

[0040] **Figure 26.** GC trace of styrene (500 mM) dimerization by **1** (25 mM), 110 °C, 72 h.

[0041] **Figure 27.** Initial ¹H NMR spectrum of styrene (500 mM) dimerization by **1**.

[0042] **Figure 28.** ^1H NMR spectrum of styrene (500 mM) dimerization by **1** (25 mM), 110 °C, 72 h.

[0043] **Figure 29.** ^1H NMR spectrum of the dimerization of styrene with **1** ($t = 0$ h, initial).

[0044] **Figure 30.** ^1H NMR spectrum of the dimerization of styrene with **1** ($t = 42$ h, ~50%).

[0045] **Figure 31.** ^1H NMR spectrum of the dimerization of styrene with **1** ($t = 160$ h, final point).

[0046] **Figure 32.** Stack plot of ^1H NMR spectra (2.5-6.7 ppm) 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).

[0047] **Figure 33.** ^1H NMR spectrum of $\text{Cp}^*\text{TaCl}_2(\text{styrene})^3$ in C_6D_6 , establishing chemical shifts for comparison to catalytic runs.

[0048] **Figure 34.** 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.

[0049] **Figure 35.** Initial rates of styrene/1-heptene co-dimerization with **1**.

[0050] **Figure 36.** GC trace of the co-dimerization of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce co-dimers. The C_{14} products (1-heptene dimers) are assigned based upon the work of McLain *et al.* (*J. Am. Chem. Soc.* 102:5610 (1980)); the co-dimers are assigned based on GC/MS and comparison to authentic samples of three of the proposed compounds (*vide infra*). The styrene/1-nonane co-dimer (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 co-dimers. The 1-nonane is presumably generated from coupling 1-heptene and ethylene (from **1**).

[0051] **Figure 37.** GC/MS trace of the co-dimerization of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce co-dimers. Mass spectrum corresponds to indicated peak.

[0052] **Figure 38.** GC/MS trace of the co-dimerization of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce co-dimers. Mass spectrum corresponds to indicated peak.

[0053] **Figure 39.** GC/MS trace of the co-dimerization of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce co-dimers. Mass spectrum corresponds to indicated peak.

[0054] **Figure 40.** GC/MS trace of the co-dimerization of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce co-dimers. Mass spectrum corresponds to indicated peak.

[0055] **Figure 41.** GC/MS trace of the co-dimerization of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce co-dimers. Mass spectrum corresponds to indicated peak.

[0056] **Figure 42.** GC/MS trace of the co-dimerization of styrene (250 mM) and 1-heptene (250 mM) with **1** (25 mM) to produce co-dimers. Mass spectrum corresponds to indicated peak.

[0057] **Figure 43.** GC trace of the nickel-catalyzed co-dimerization 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 for this Ni-catalyst was similar to that presented by Ho *et al.* (*Angew. Chem. Int. Ed.* 49:9182 (2010)).

[0058] **Figure 44.** GC/MS trace of the nickel-catalyzed co-dimerization of styrene and 1-heptene. Mass spectrum corresponds to indicated peak.

[0059] **Figure 45.** GC/MS trace of the nickel-catalyzed co-dimerization of styrene and 1-heptene. Mass spectrum corresponds to indicated peak.

[0060] **Figure 46.** GC/MS trace of the nickel-catalyzed co-dimerization of styrene and 1-heptene. Mass spectrum corresponds to indicated peak.

[0061] **Figure 47.** *Top:* Reproduction of **FIG. 43** (bottom). *Middle:* Reproduction of **FIG. 36** (bottom). *Bottom:* GC trace of the co-injection of styrene/1-heptene co-dimerization 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 co-dimer peak at 10.29 min (middle trace) corresponds to the 2-phenyl-3-methylene-octane product.

[0062] **Figure 48.** Plots of reaction progress over time for Entry 7 in **Table 4**. *Top:* Overlay of both data sets. *Bottom:*

Expansion of product concentration range. Lines are drawn as visual guides.

[0063] **Figure 49.** Overlay of reaction progress for runs from Entry 7 in **Table 4** (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 co-dimers.

DETAILED DESCRIPTION

[0064] As used herein and in the appended claims, the singular forms "a," "and," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a catalyst" includes a plurality of such catalysts and reference to "the alkane" includes reference to one or more alkanes and so forth.

[0065] Also, the use of "or" means "and/or" unless stated otherwise. Similarly, "comprise," "comprises," "comprising" "include," "includes," "including," "have," "have," and "having" are interchangeable and not intended to be limiting.

[0066] It is to be further understood that where descriptions of various embodiments use the term "comprising," those skilled in the art would understand that in some specific instances, an embodiment can be alternatively described using language "consisting essentially of" or "consisting of."

[0067] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice of the disclosed methods and compositions, the exemplary methods, devices and materials are described herein.

[0068] As exploitation of traditional crude oil reserves becomes economically and geopolitically more volatile, and concern regarding CO₂ emissions from the current inefficient use of carbon-based energy carriers increases, many countries and industries are

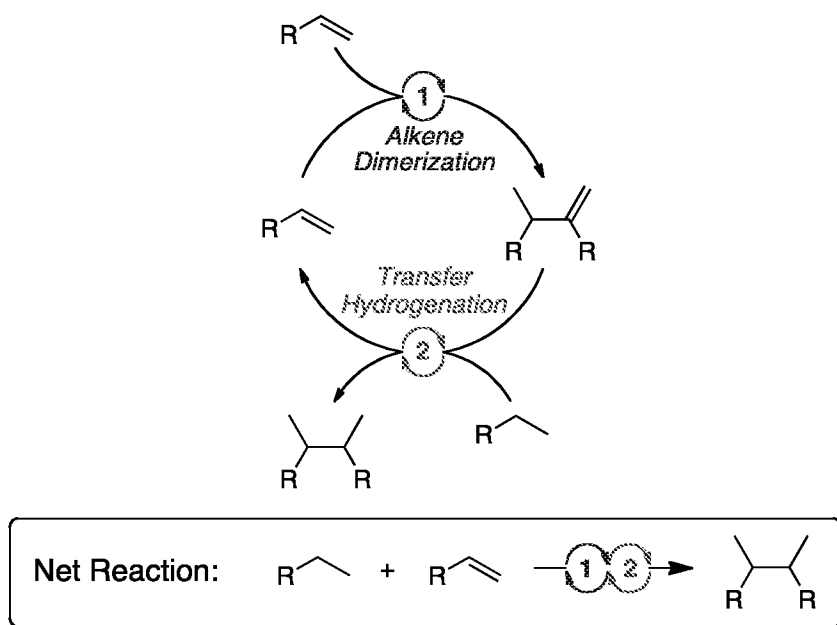
actively pursuing alternate fuel sources. These factors are driving the development of new technologies for fuel production from carbon sources such as bitumen and kerogen (so-called oilsands and shale oil), natural gas, and lignocellulosic biomass. In contrast to fuels derived from crude oil that are collected by fractional distillation, obtaining hydrocarbons in the desired weight range from these alternate carbon sources often requires extensive refining and synthetic manipulation, such as catalytic cracking and Fischer-Tropsch synthesis using syngas. In addition to the optimal fuel-range hydrocarbons (C_8 - C_{22}), lighter alkanes and alkenes are abundant by-products of these processes. Currently, these light hydrocarbons have little value as fuels due to their volatility and low volumetric energy density. This inherent inefficiency in fuel production will increase both the economic and environmental cost of continued exploitation of these emerging carbon sources.

[0069] In order to better utilize low carbon number energy carriers, these feedstocks need to be upgraded to higher molecular weight compounds, ideally in the diesel fuel-range (C_{10} - C_{22}). Such a process must necessarily perform chemistry on alkanes under relatively mild conditions: the entropic cost of coupling smaller carbon chains into larger ones means that high temperatures are potentially thermodynamically incompatible. One possible technology for achieving this goal is alkane metathesis. Alkane metathesis operates via combined alkane dehydrogenation and alkene metathesis using either two separate catalysts, or one catalyst capable of both transformations. In the ideal case, two C_n alkanes afford one C_{2n-2} alkane and one equivalent of ethane in an approximately thermoneutral reaction; however, alkane metathesis tends toward a statistical carbon number distribution of alkanes, with few examples that can achieve any selectivity for the desired C_{2n-2} product. While further catalyst development efforts may result in a viable process, alternative methods for upgrading light hydrocarbons are also needed.

[0070] The disclosure provides an approach toward light hydrocarbon upgrading based on a tandem alkane dehydrogenation and alkene dimerization. This method takes advantage of the mixed nature of many light by-product streams by incorporating both

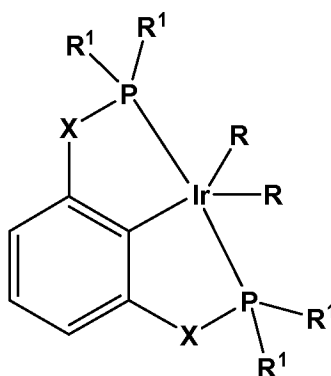
alkanes and alkenes as substrates. In an ideal system (shown for a linear alkane and 1-alkene in **Scheme I**), one catalyst would dimerize the alkene component of the mixed feedstock to a C_{2n} alkene. Subsequent transfer hydrogenation by a second catalyst would convert the alkane component to a 1-alkene, while hydrogenating the C_{2n} product to an alkane. The 1-alkene thus formed is then catalytically dimerized with a second equivalent of 1-alkene, and the cycle continues; the net reaction is coupling of alkane and alkene to higher alkane, with no by-products generated. Calculations indicate that such a reaction is thermodynamically favored below ~ 250 °C; therefore, catalysts for both dimerization and transfer hydrogenation must operate with appreciable rates at relatively mild temperatures.

Scheme I: Idealized Tandem Catalytic Approach toward Alkane / Alkene Upgrading



[0071] The disclosure demonstrates this process using a dual homogeneous catalytic system in which a dimerization catalyst (1) comprises a structure of Formula II effects alkene dimerization, and alkane/alkene transfer hydrogenation is carried out by a hydrogenation catalyst. These catalysts function in tandem to affect alkane/alkene coupling.

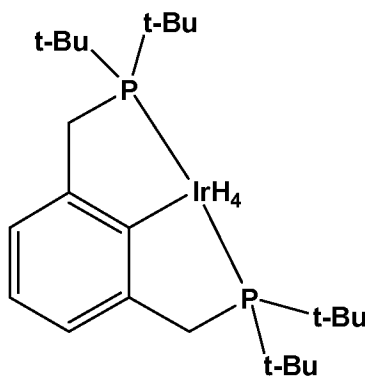
[0072] In a particular embodiment, hydrogen transfer catalyst (2) comprises a structure of Formula I:



(I)

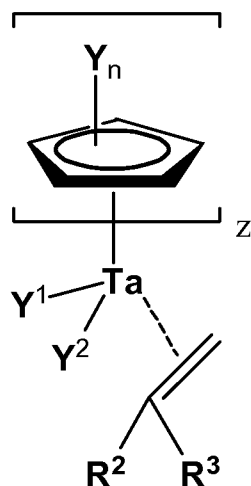
wherein, each R is independently H or a (C₁-C₃₀)hydrocarbyl radical; each R¹ is independently a (C₁-C₃₀)hydrocarbyl radical; and each X is independently an O or CH₂.

[0073] In a further embodiment, hydrogen transfer catalyst (2) comprises a structure of Formula I(a):



I(a).

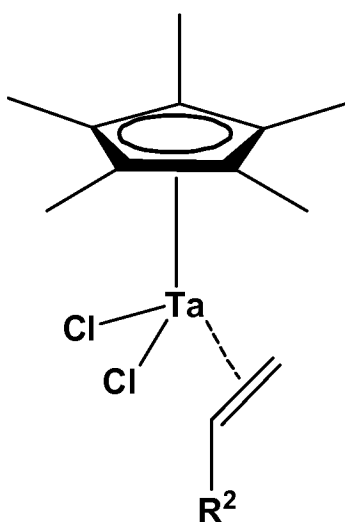
[0074] In a particular embodiment, dimerization catalyst (1) comprises a structure of Formula II:



Formula II

wherein, Z is either 1 or 2; n is an integer from 1 to 5; each Y is independently selected from D, H, optionally substituted (C₁-C₆)alkyl, silane, and (C₁-C₄)alkylsilane; Y¹ is a H, D, halo, =S, =O, PMe₃, =C(H)(CMe₃); Y² is a H, D, halo, =S, =O, PMe₃, or absent; R² is a H, aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl; and R³ is a H, aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl.

[0075] In another embodiment, dimerization catalyst (1) comprises a structure of Formula II(a):

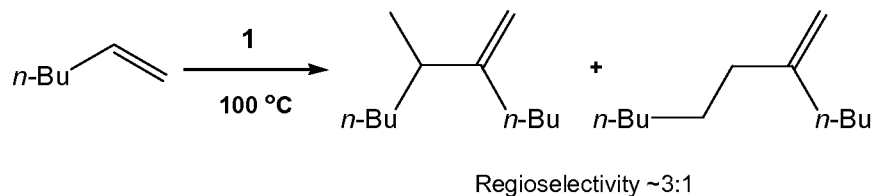


II(a)

wherein, R² is an aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl.

[0076] Ta-based alkene dimerization catalyst having the general Formula II were used in the Examples presented herein.

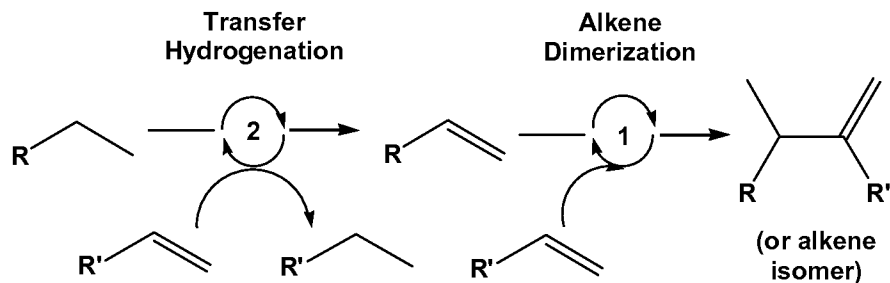
Cp*TaX₂(alkene) complexes are reported to be "indefinitely active" for the selective dimerization of 1-alkenes to two regioisomers at temperatures up to 100 °C (see **Scheme II** below); they are inert to internal alkenes and the product 1,1-disubstituted alkenes. In addition, no co-catalyst or activator is required.



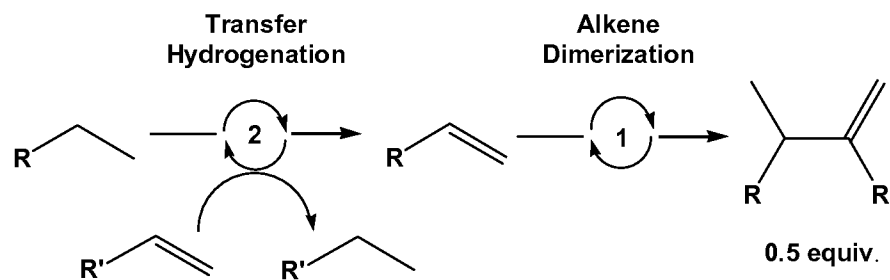
Scheme II

[0077] As described above, the disclosure provides a dual homogeneous catalytic system for alkane/alkene coupling based on an early/late transition metal dichotomy: alkene dimerization is effected by a dimerization catalyst (1) comprising the structure of Formula II or Formula II(a), while transfer hydrogenation is performed by a hydrogen transfer catalyst (2) comprising the structure of Formula I or Formula I(a). This system is capable of coupling, for example, 1-hexene and *n*-heptane with a high degree of catalyst cooperativity. This system operates by a sacrificial H₂ acceptor pathway, in which the alkene substrate, and not the C_{2n} product, acts as the hydrogen acceptor (**Scheme III**). Thus, for every equivalent of alkane upgraded, one equivalent of a different alkane is generated as a byproduct. An additional feature of this system is that in most cases the alkene substrate can also function as a coupling partner: for example, in 1-hexene/*n*-heptane mixtures, competitive homodimerization of 1-hexene generates a substantial amount of C₁₂, along with C₁₃ resulting from the coupling of 1-hexene and 1-heptene (generated *via* transfer hydrogenation).

Alkene as Coupling Partner and H₂ acceptor



Alkene as Sacrificial H₂ acceptor



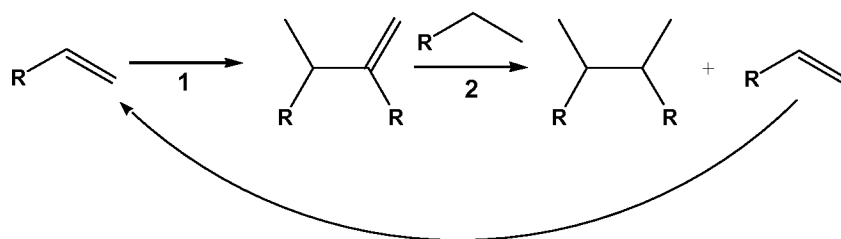
Scheme III

[0078] Both catalysts operate independently, with no mutual inhibition or decomposition over the course of the reaction (see **FIG. 1**). For example, kinetic studies reveal that 1-hexene dimerization catalyzed by the dimerization catalyst of Formula II exhibits positive order (<1) dependence on [1-hexene], with an approach to saturation at high concentrations; additionally, the dimerization rate increases very little with temperature. In stark contrast, the rate of 1-hexene/*n*-heptane transfer using the hydrogenation catalyst of Formula I has inverse order dependence on [1-hexene], and increases substantially with temperature. These opposing kinetic features lead to an imbalance in the relative rates of these two processes as either the concentration of 1-hexene is raised, or the reaction temperature is raised. In an effort to identify other alkene/alkane combinations that are amenable to tandem catalysis, the use of styrene has been studied as a sacrificial hydrogen acceptor for alkane dimerization. By attenuating the ratio of the two catalysts, a high degree of selectivity ($>26:1$) for tandem catalysis in this styrene/alkane system can be realized.

[0079] The disclosure also provides a in-depth kinetic study of the dimerization of 1-hexene catalyzed by dimerization catalyst **1** (see, **Scheme I - III**) at elevated temperatures and low initial substrate concentrations. The catalyst of Formula II (e.g., $\text{Cp}^*\text{TaCl}_2(\text{alkene})$ complexes) undergo rapid decomposition at 100°C in the absence of added alkene. Thus, catalyst decomposition at these elevated temperatures should be especially problematic at low concentrations of 1-alkene, since these conditions would favor $\text{Cp}^*\text{TaCl}_2(\text{alkene})$ as the catalyst resting state. It is surprising, then, that the tandem catalytic alkane/alkene coupling operates at exactly this set of conditions with no apparent catalyst decomposition, even over >30 hours with 1-alkene added slowly via syringe pump (see Examples, below).

[0080] Thus, an aspect of the disclosure is that the transfer hydrogenation/dimerization occurs in a single-stage tandem process. In one particular version the C_n alkene reactant is dimerized by dimerization catalyst **1** (comprising a structure of Formula II or II(a)) to generate a new C_{2n} alkene product. This C_{2n} alkene is

converted to the C_{2n} alkane by transfer hydrogenation with hydrogenation transfer catalyst **2** (comprising a structure of Formula I or I(a)); the source of hydrogen in this case is the C_n alkane reactant. This generates a C_n alkene, which will undergo dimerization with dimerization catalyst **1** having the structure of Formula II or II(a), producing more C_{2n} alkane. This process would continue until all of the alkene equivalents are consumed and converted to the C_{2n} alkane. For simplicity **Scheme IV** shows a single isomer of the product, but a different isomer or a mixture of two or more might result preferentially, depending on the choice of dimerization catalyst **1**.



Scheme IV

[0081] This tandem process can also be applied to a number of alternate transformations, such as combining transfer hydrogenation with oligomerization, such that the reaction of one molecule of C_n alkane with x molecules of C_n alkene would result in a $C_{(x+1)n}$ alkane. It may also be possible to effect conversion of two (or more) molecules of C_n alkane to higher alkanes, either by carrying out the reaction in the presence of a sacrificial hydrogen acceptor, such as an alkene that cannot undergo oligomerization or another species; or by devising conditions such that the H_2 liberated during transfer dehydrogenation can be separated from reactant and products.

[0082] In order for this tandem process to occur, the two catalysts are present in the same reactor, and retain their activity under the reaction conditions needed to effect both transformations. This is accomplished by careful choice of the two catalysts such that mutual or individual deactivation does not occur. For example, in a batch reaction, both catalysts are dissolved and/or suspended in the reaction medium containing or consisting of the alkane/alkene mixture. In a flow reactor, the

two catalysts would be supported on the same solid, or two solid catalysts would be intimately mixed, and the alkane/alkene reactants passed over this dual catalyst as either a gas or liquid.

[0083] The specific examples below have been successfully carried out, demonstrating the feasibility of the disclosed process. The disclosure thus, provides a homogeneous dual Ta/Ir catalyst system can affect both selective coupling of alkane/alkene mixtures and dimerization of alkanes to branched alkene products with a high degree of cooperation. Additional modification can include modifying the Ir catalyst and/or by selecting a different dimerization catalyst to produce less branched alkene isomers; these latter products may be more desirable from a fuels standpoint as well.

EXAMPLE 1

[0084] **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, tetrahydrofuran (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.

[0085] **NMR Spectroscopy:** Spectra were acquired on a Varian Mercury 300 MHz instrument 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.

[0086] **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 $^{\circ}\text{C}$ for 2 minutes, ramp temperature at 2 $^{\circ}\text{C min}^{-1}$ to 50 $^{\circ}\text{C}$, hold at 50 $^{\circ}\text{C}$ for 2 minutes, ramp temperature at 100 $^{\circ}\text{C min}^{-1}$ to 290 $^{\circ}\text{C}$, hold at 290 $^{\circ}\text{C}$ for 5 minutes.

[0087] Response factors for linear hydrocarbons ranging from C_5 to C_{18} 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 (See **FIG. 10**).

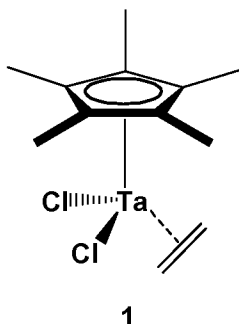
[0088] The equation of the line was used to determine response factors for all of the hydrocarbons analyzed (the branching in the C_{12} - C_{14} dimers generated in catalytic reactions is assumed to have negligible effect on the response).

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.

[0089] 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.

[0090] **Dimerization of 1-Hexene using dimerization catalyst:**



Dimerization catalyst **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 **FIG. 2**.

[0091] **Procedure for Determining Initial Rates of 1-Hexene**

Dimerization. Dimerization catalyst **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 3996 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.

[0092] 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 1**, **FIGs. 13, 15, 17, 19, and 21**). These data were used to generate double reciprocal plots for each product isomer at each temperature (see **FIGs. 14, 16, 18, 20, and 22**). 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 1-8.

$$\text{Rate} = \frac{k_1 K_{\text{eq}} [1 - \text{Hexene}] [Ta]_0}{1 + K_{\text{eq}} [1 - \text{Hexene}]} \quad (1)$$

$$\text{Rate}^{-1} = \frac{1}{k_1 K_{\text{eq}} [Ta]_0} [1 - \text{Hexene}]^{-1} + \frac{1}{k_1 [Ta]_0} \quad (2)$$

$$k_1 = \frac{1}{b [Ta]_0} \quad (3)$$

$$K_{\text{eq}} = \frac{b}{m} \quad (4)$$

$$\text{Rate} = \frac{k_2 K_{\text{eq}}' [1 - \text{Hexene}] [Ta]_0}{1 + K_{\text{eq}} [1 - \text{Hexene}]} \quad (5)$$

$$\text{Rate}^{-1} = \frac{1}{k_2 K_{\text{eq}}' [Ta]_0} [1 - \text{Hexene}]^{-1} + \frac{K_{\text{eq}}}{k_2 K_{\text{eq}}' [Ta]_0} \quad (6)$$

$$k_2 K_{\text{eq}}' = \frac{1}{m [Ta]_0} \quad (7)$$

$$K_{\text{eq}} = \frac{b}{m} \quad (8)$$

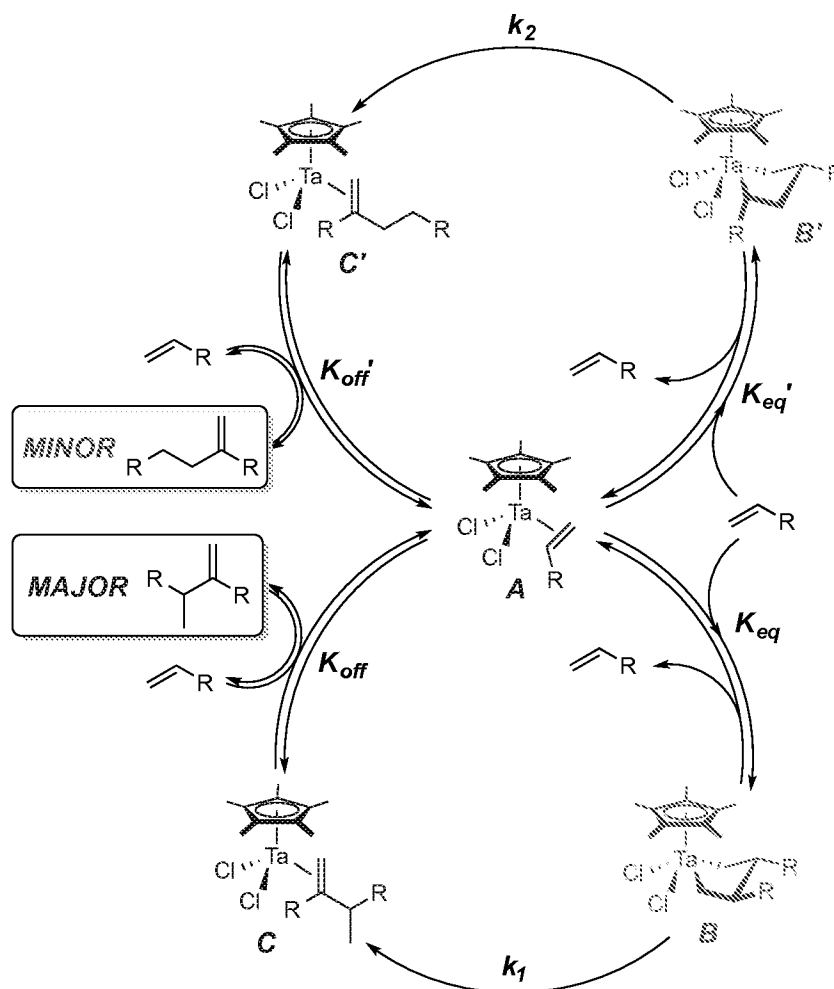
TABLE 1: Initial Rate Data (numbers in parentheses are standard error determined from regression analysis)

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	3996	12.42 (55)	2.93 (14)
6	90	248	4.35 (10)	1.23 (4)
7	90	412	7.52 (15)	2.16 (6)
8	90	699	10.21 (21)	2.87 (7)
9	90	1010	14.74 (29)	4.10 (8)
10	90	2000	18.58 (58)	5.11 (19)
11	90	3996	26.70 (58)	7.44 (17)
12	100	248	5.87 (10)	1.85 (4)
13	100	252	6.03 (12)	2.00 (5)
14	100	412	9.53 (27)	2.98 (10)
15	100	699	16.73 (41)	5.56 (15)
16	100	1010	21.37 (52)	6.77 (19)
17	100	2000	37.2 (11)	12.24 (38)
18	100	3996	42.9 (14)	13.76 (48)
19	110	248	6.66 (18)	2.42 (7)
20	110	412	10.75 (22)	3.83 (9)
21	110	699	18.22 (35)	6.52 (13)
22	110	1010	28.37 (48)	10.17 (19)
23	110	2000	41.7 (13)	14.79 (45)
24	110	3996	66.6 (18)	23.78 (71)
25	125	248	8.34 (22)	3.62 (11)
26	125	412	14.01 (33)	6.08 (14)
27	125	699	24.65 (76)	10.84 (32)
28	125	1010	33.4 (16)	14.32 (65)
29	125	2000	64.3 (34)	28.3 (16)
30	125	3996	102.1 (64)	43.0 (30)

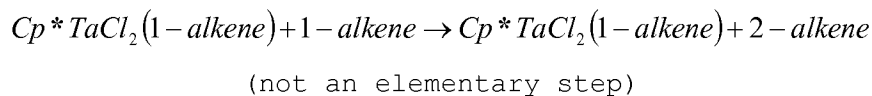
[0093] Kinetic Fitting using DynaFit. The full time course data represented in **FIG. 2** was fitted according to the mechanistic model from **Scheme V**, as well as terms for alkene isomerization to *cis*- and *trans*-2-hexene, using the freeware kinetics program DynaFit. Values for the rate and equilibrium constants *k*₁, *K*_{eq}, and *k*₂*K*_{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 ($K_{off} = K_{off}' = 1, 2.5, 5, 10,$ and 15) and the quality of the fit determined by inspection.

Scheme V: Postulated Catalytic Cycles for the Dimerization of 1-Alkenes into Two Regioisomers Catalyzed by 1



[0094] 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. Second order rate constants for alkene isomerization were determined by fitting according to the equation:



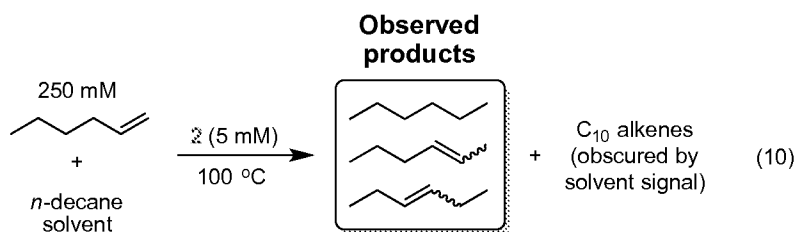
[0095] These values are $3.6(2) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $1.8(2) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for the formation of *cis*- and *trans*-2-hexene respectively. Presumably this isomerization occurs via a π -allylic-type mechanism, since the major catalyst resting state is the $[Ta](1-alkene)$ complex, rather than an insertion/ β -hydride elimination mechanism;

however, due to the low degree of isomerization observed, the mechanism of this side-reaction was not experimentally tested.

[0096] Procedure for Determining Initial Rates of 1-Hexene/*n*-Decane Transfer Hydrogenation. Hydrogen transfer catalyst **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.

[0097] 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 (See **FIG. 23** and **FIG. 24**). These rate data were then plotted versus $[1\text{-hexene}]_0$ (see **FIG. 25**).

[0098] Heating a solution of 1-hexene (248 mM) and hydrogen transfer catalyst **2** (5 mM) in *n*-decane leads to the generation of several products that can be analyzed by GC (**Scheme VI**).



Scheme VI

[0099] In the C₆ fraction, *n*-hexane (from transfer hydrogenation) and internal hexenes (from alkene isomerization) are observed. C₁₀ alkenes are also observed (including 1-decene), but accurate quantification of these species is not reliable due to overlap with the large signal for *n*-decane solvent. Therefore, the

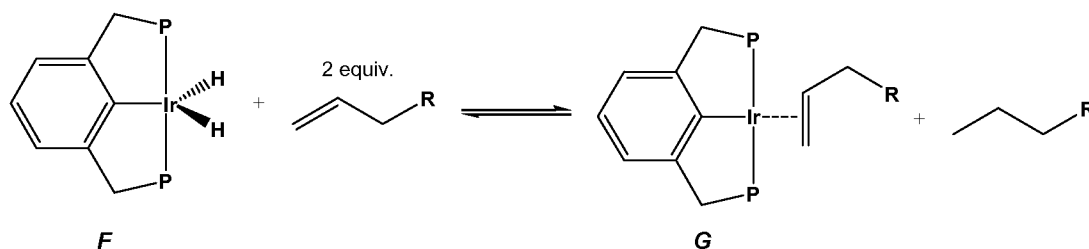
formation of *n*-hexane and internal hexenes has been monitored to generate initial rate data for transfer hydrogenation and alkene isomerization respectively (Table 2).

Table 2. Initial Rate Data for 1-Hexene/*n*-Decane Transfer Hydrogenation and 1-Hexene Isomerization Catalyzed by 2.

Entry	[1-Hexene] ₀ (mM)	Temp. (°C)	<i>k</i> _{obs} (hydrog) (10 ⁻⁵ M s ⁻¹) ^a	<i>k</i> _{obs} (isom) (10 ⁻⁵ M s ⁻¹) ^a
1	248	100	1.26 (5)	1.00 (4)
2	412	100	0.753 (38)	1.53 (5)
3	699	100	0.572 (20)	2.31 (7)
4	1010	100	0.387 (10)	2.79 (6)
5	248	125	12.4 (4)	4.73 (20)
6	412	125	8.85 (23)	6.30 (16)
7	1010	125	2.88 (14)	11.8 (5)

^aNumbers in parenthesis are standard error from regression analysis.

[00100] Analysis of the initial rates of transfer hydrogenation and isomerization versus [1-hexene]₀ reveals that transfer hydrogenation is inverse order in [1-hexene] from 248-1010 mM, whereas isomerization is positive order in [1-hexene], exhibiting saturation behavior (see **FIG. 6**). The inverse dependence on [1-hexene] is consistent with previous work on cyclooctane/*tert*-butylethylene (TBE) transfer hydrogenation catalyzed by hydrogen transfer catalyst **2**: the rate is first order in [TBE] at low concentrations (where the Ir dihydride **F** is the major resting state), and inverse order at higher concentrations. While inhibition by TBE is due to reversible oxidative addition/reductive elimination of a vinyl C-H bond, linear alpha olefins (LAOs, such as 1-hexene) inhibit catalysis by competitive formation of the 1-alkene complex **G**. Indeed, **G** (where the alkene is 1-octene) is reportedly a major resting state in TBE/*n*-octane transfer hydrogenation. Thus, at higher [1-hexene], the equilibrium in **Scheme VII** would be shifted toward **G**, which is not on the transfer hydrogenation cycle.



Scheme VII

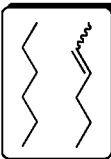
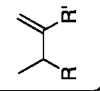
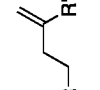
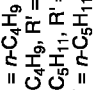
[00101] This shift in equilibrium between resting states is also consistent with the observation that the transfer hydrogenation rate is affected dramatically by temperature, increasing nearly 10-fold from 100-125 °C (see **Table 2**, entries 1 and 5). The equilibrium in **Scheme VII** is a 3-into-2 reaction, which means that the reverse direction is entropically favored; thus, an increase in temperature would shift the equilibrium toward **F**, which is an on-cycle intermediate for transfer hydrogenation. Furthermore, since **G** is also an active catalyst for alkene isomerization, this shift should decrease the rate of isomerization relative to transfer hydrogenation. This is exactly the case, where with an initial [1-hexene] of 248 mM, $k_{\text{obs}}(\text{hydrog})/k_{\text{obs}}(\text{isom})$ is 1.26 at 100 °C and 2.62 at 125 °C. Of course, temperature effects on the other steps of both catalytic cycles will influence these rates as well.

[00102] Notably, the determination that isomerization is positive order in [1-hexene] (from initial rate data) is in contrast to the zero order dependence previously reported for alkene isomerization catalyzed by hydrogen transfer catalyst **2** (observation over 5 half-lives with initial [1-alkene] = 100 mM). This reaction proceeds by a π -allylic mechanism that has a unimolecular turnover-limiting step and thus should be zero order in [1-alkene]; however, the positive order dependence observed here can be explained in terms of the equilibrium between resting states in **Scheme VII**. As the concentration of 1-hexene is increased, the steady state concentration of **G** will increase, leading to a higher rate of alkene isomerization. Thus, increasing [1-hexene] not only inhibits transfer hydrogenation, it also favors the undesirable alkene isomerization pathway. The trend toward saturation in the rate of 1-hexene isomerization shown in **FIG. 6** is entirely consistent with a unimolecular turnover-limiting step in the π -allylic isomerization catalytic cycle.

[00103] **Implications for Tandem Catalytic Alkane/Alkene Coupling.** The diametrically opposed kinetic trends in alkene dimerization catalyzed by dimerization catalyst **1** and transfer hydrogenation catalyzed by hydrogen transfer catalyst **2** is a major

factor in the homogeneous tandem catalytic coupling of 1-hexene and *n*-heptane. As for many other one-pot dual catalyst processes, the optimal conditions for the individual catalysts do not necessarily translate into the optimal conditions for the pair. While dimerization catalyst **1** operates most efficiently at lower temperatures and high substrate loading, hydrogen transfer catalyst **2** works best at high temperatures and low substrate loading. Thus, in order to best match the rates of the two individual reactions, tandem catalysis is effective at a moderate temperature (100 °C) and an alkene concentration that is as low as possible. In terms of simple batch reactions, the initial optimization led to a 1-hexene loading of ~250 mM (see **TABLE 3**, entry 1).

TABLE 3. Temperature and Concentration Effects on 1-Hexene/*n*-Heptane Coupling by 1 and 2.

Observed products																																																																																																							
 +  solvent 1 and 2^b 5 hours  Observed products  +  R'  R' C₁₂: R = R' = <i>n</i>-C₄H₉ C₁₃: R = <i>n</i>-C₄H₉, R' = <i>n</i>-C₅H₁₁ or R = <i>n</i>-C₅H₁₁, R' = <i>n</i>-C₄H₉ C₁₄: R = R' = <i>n</i>-C₅H₁₁ <tr><th>Entry</th><th>[1-Hexene]₀ (mM)</th><th>[1]/[2] (mM)</th><th>Temp. (°C)</th><th><i>n</i>- Hexane (mM)^a</th><th>C₁₂ (mM)^a</th><th>C₁₃ / C₁₄ (mM)^a</th><th>TON for 1^b</th><th>TON for 2^b</th><th>Coop. (%)</th></tr><tr><td>1</td><td>250</td><td>8 / 5</td><td>100</td><td>52</td><td>81</td><td>13 / 10</td><td>13 (3)</td><td>10 (6)</td><td>63</td></tr><tr><td>2</td><td>500</td><td>8 / 5</td><td>100</td><td>88</td><td>193</td><td>15 / 10</td><td>27 (3)</td><td>18 (7)</td><td>40</td></tr><tr><td>3</td><td>1000</td><td>8 / 5</td><td>100</td><td>87</td><td>432</td><td>18 / 10</td><td>58 (4)</td><td>17 (8)</td><td>45</td></tr><tr><td>4</td><td>250</td><td>8 / 5</td><td>125</td><td>106</td><td>58</td><td>15 / 13</td><td>11 (4)</td><td>21 (8)</td><td>39</td></tr><tr><td>5</td><td>500</td><td>8 / 5</td><td>125</td><td>140</td><td>162</td><td>24 / 14</td><td>25 (5)</td><td>28 (10)</td><td>37</td></tr><tr><td>6</td><td>1000</td><td>8 / 5</td><td>125</td><td>161</td><td>386</td><td>32 / 14</td><td>54 (6)</td><td>32 (12)</td><td>38</td></tr><tr><td>7</td><td>250</td><td>8 / 5</td><td>150</td><td>147</td><td>39</td><td>12 / 12</td><td>8 (3)</td><td>29 (7)</td><td>24</td></tr><tr><td>8</td><td>500</td><td>8 / 5</td><td>150</td><td>216</td><td>128</td><td>26 / 15</td><td>21 (5)</td><td>43 (11)</td><td>27</td></tr><tr><td>9</td><td>1000</td><td>8 / 5</td><td>150</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>				Entry	[1-Hexene] ₀ (mM)	[1]/[2] (mM)	Temp. (°C)	<i>n</i> - Hexane (mM) ^a	C ₁₂ (mM) ^a	C ₁₃ / C ₁₄ (mM) ^a	TON for 1 ^b	TON for 2 ^b	Coop. (%)	1	250	8 / 5	100	52	81	13 / 10	13 (3)	10 (6)	63	2	500	8 / 5	100	88	193	15 / 10	27 (3)	18 (7)	40	3	1000	8 / 5	100	87	432	18 / 10	58 (4)	17 (8)	45	4	250	8 / 5	125	106	58	15 / 13	11 (4)	21 (8)	39	5	500	8 / 5	125	140	162	24 / 14	25 (5)	28 (10)	37	6	1000	8 / 5	125	161	386	32 / 14	54 (6)	32 (12)	38	7	250	8 / 5	150	147	39	12 / 12	8 (3)	29 (7)	24	8	500	8 / 5	150	216	128	26 / 15	21 (5)	43 (11)	27	9	1000	8 / 5	150						
Entry	[1-Hexene] ₀ (mM)	[1]/[2] (mM)	Temp. (°C)	<i>n</i> - Hexane (mM) ^a	C ₁₂ (mM) ^a	C ₁₃ / C ₁₄ (mM) ^a	TON for 1 ^b	TON for 2 ^b	Coop. (%)																																																																																														
1	250	8 / 5	100	52	81	13 / 10	13 (3)	10 (6)	63																																																																																														
2	500	8 / 5	100	88	193	15 / 10	27 (3)	18 (7)	40																																																																																														
3	1000	8 / 5	100	87	432	18 / 10	58 (4)	17 (8)	45																																																																																														
4	250	8 / 5	125	106	58	15 / 13	11 (4)	21 (8)	39																																																																																														
5	500	8 / 5	125	140	162	24 / 14	25 (5)	28 (10)	37																																																																																														
6	1000	8 / 5	125	161	386	32 / 14	54 (6)	32 (12)	38																																																																																														
7	250	8 / 5	150	147	39	12 / 12	8 (3)	29 (7)	24																																																																																														
8	500	8 / 5	150	216	128	26 / 15	21 (5)	43 (11)	27																																																																																														
9	1000	8 / 5	150																																																																																																				

^aDetermined by GC/FID using adamantane as an internal std., avg. of at least 2 runs.

^bTONs in parentheses are for production of C₁₃ + C₁₄.

[00104] Raising the substrate loading to 500 or 1000 mM merely results in the production of more C₁₂ homodimer, with little additional tandem catalysis observed (see entries 2 and 3 of **Table 3**); this is due to the positive order dependence on [1-hexene] for dimerization catalyst **1**, and the inverse order dependence on [1-hexene] for hydrogen transfer catalyst **2**. Conversely, raising the temperature to 125 °C or 150 °C dramatically reduces catalyst cooperativity (entries 4 and 7 of **Table 3**), due to the much stronger temperature dependence exhibited by hydrogen transfer catalyst **2** relative to dimerization catalyst **1**.

[00105] While increasing [1-hexene] or temperature results in a rate imbalance between the two catalysts, it is possible that increasing *both* of these variables would have complementary effects, allowing a higher degree of tandem catalysis at increased substrate loading

[00106] **Procedure for Styrene Dimerization using Dimerization Catalyst 1.** Dimerization Catalyst **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 (see **FIG. 27**), 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 (about 72 h, see **FIG. 28**). 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 product 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 regioisomer (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%.

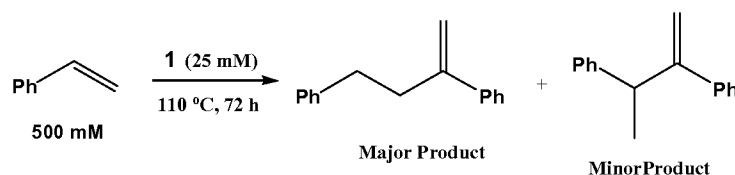
NMR yields:

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%)

[00107] 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 (see **FIG. 26**). The yield of both major and minor styrene dimers was determined to be 81% (major) and 2% (minor).

[00108] Heating a 500 mM solution of styrene in C₆D₆ with 25 mM dimerization catalyst **1** to 110 °C does in fact lead to dimerization, albeit slowly ($t_{1/2}$ ~14 h, see **Scheme VIII**). By ¹H NMR spectroscopy and GC analysis, there is one major product of this reaction, the "head-to-tail" dimer formed. Interestingly, there is a complete switch in regioselectivity from reactions with LAOs; the "tail-to-tail" product in styrene dimerization is formed.



Scheme VIII

[00109] Procedure for Monitoring Dimerization of Styrene over Four Half Lives. Dimerization catalyst **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,

wherein $[Styrene]_0 = 0.255 \text{ M}$; I = area of vinylic signal @ 5.6 ppm; and I_0 = initial area of vinylic signal @ 5.6 ppm:

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

The dimerization of Styrene was evaluated by ^1H NMR over various time points (see **FIGs. 29-32**).

[00110] Initial Rates of Styrene/1-Heptene Co-Dimerization using Dimerization Catalyst 1. Dimerization catalyst **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 dimerization catalyst **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.

[00111] 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 co-dimers (all isomers combined) were plotted versus time, and the k_{obs} values calculated by linear regression analysis (see **FIG. 35**). 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 $[1\text{-heptene}]_0/[styrene]_0$), giving an initial rate ratio of 4.05:1 for 1-heptene dimerization versus styrene/1-heptene co-dimerization. Styrene dimers were not observed under these conditions.

[00112] Procedure for Co-Dimerization of Styrene/1-Heptene using Dimerization Catalyst 1. Dimerization catalyst **1** (20.4 mg,

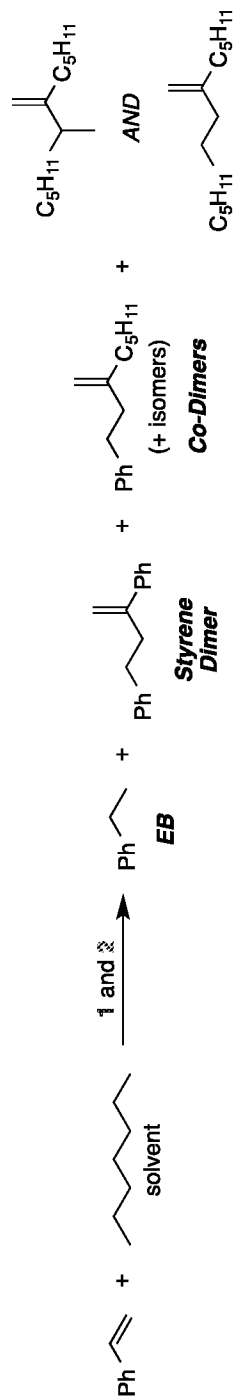
0.050 mmol), styrene (52.1 mg, 0.500 mmol), 1-heptene (49.0 mg, 0.499 mmol), and adamantane (internal standard, 10.2 mg, 0.075 mmol) were dissolved in 2 mL of *n*-heptane in a 4 mL screw-top vial containing a Teflon-coated stir bar. The vial was sealed with a Teflon-lined screw cap and the contents stirred 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 (see **FIGs. 36-42**).

[00113] Synthesis of Authentic Co-Dimers: (1-Methyl-2-methylene-octyl)-benzene was prepared by Ni-catalyzed coupling of 1-heptene and styrene according to Ho *et al.*, *Angew. Chem. Int. Ed.* 49:9182 (2010). 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 (see **FIGs. 43-46**). The regiochemistry of the major co-dimer was definitively established by Ho *et al.*, as well as the regiochemistry of styrene homodimerization. This co-dimer solution was co-injected with the co-dimer mixture generated by dimerization catalyst 1 (see **FIG. 47**).

[00114] Procedure for Monitoring Styrene/*n*-Heptane Coupling Reactions over Time: Dimerization catalyst **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.

[00115] 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 (see **FIG. 48**). The effects of the cooperativity in Styrene/n-Heptane Coupling by dimerization catalyst **1** and hydrogen transfer catalyst **2** is presented in **Table 4**.

Table 4. Evaluation of Catalyst Cooperativity in Styrene/*n*-Heptane Coupling by 1 and 2.

Entry	[Styrene] ₀ (mM)	[1]/[2] (mM)	Time (h)	Temp. (°C)	% Conv.	EB (mM) ^a	Styrene Dimer (mM) ^a	Co- Dimers (mM) ^a	Heptane Dimers (mM) ^a	TON for 1 ^b	TON for 2 ^b	Coop . (%)
1	250	8 / 5	18	100	62	70	23	23	11	7 (4)	14 (9)	63
2	250	8 / 5	48	100	75	71	35	28	12	9 (5)	14 (10)	72
3	250	5 / 8	18	100	78	132	11	27	26	13 (11)	17 (10)	60
4	250	5 / 10	18	100	89	162	8	26	35	14 (12)	16 (10)	60
5	250	10 / 10	18	100	99	163	17	31	42	9 (7)	16 (11)	70
6	250	10 / 15	18	100	99	192	6	24	46	8 (7)	13 (8)	60
7	250	8 / 15	18	100	99	202	4	20	44	8 (8)	13 (7)	53
8	1000	10 / 15	72	100	67	99	229	42	4	27 (5)	7 (3)	50
9	250	10 / 15	18	125	99	215	2	15	38	5 (5)	14 (6)	42
10	250	10 / 15	18	150	>99	209	2	14	36	5 (5)	14 (6)	41

^aDetermined by GC/FID using adamantane as an internal std., avg. of at least 2 runs.

BTONS in parentheses are for production of co-dimers + heptane dimers.

[00116] Procedure for Monitoring Styrene/*n*-Heptane

Transfer Hydrogenation over Time: Hydrogen transfer catalyst **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.

[00117] 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 (see **FIG. 49**).

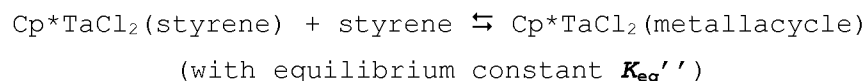
[00118] Results of Styrene Dimerization and Styrene/1-Heptene Co-Dimerization Catalyzed by Dimerization Catalyst 1. In the catalytic coupling of 1-hexene/*n*-heptane, competitive homodimerization of 1-hexene is prevalent; even with slow addition of 1-hexene by syringe pump, the C_{12} fraction represents ~50% of the higher molecular weight products. In an effort to minimize this side reaction, TBE was initially examined as a possible sacrificial hydrogen acceptor that would not be incorporated into the dimerization catalytic cycle, enabling the catalytic dimerization of alkanes.

[00119] While modest yield was achieved with TBE, poor conversion and suspected catalyst decomposition led to the consideration other hydrogen acceptors. Styrene is an attractive alternative, since competitive alkene isomerization would be avoided. Furthermore, the ethylbenzene generated during transfer hydrogenation could, in principle, be regenerated by

dehydrogenation (steam cracking), which is practiced industrially on a large scale to synthesize styrene monomer.

[00120] In previously reported studies, the stoichiometric and catalytic alkene dimerization by dimerization catalyst **1** and related complexes was not reported for the dimerization of styrenes. While the $\text{Cp}^*\text{TaCl}_2(\text{styrene})$ complex was prepared and characterized, attempts to observe metallacycles derived from two styrene units, or styrene and an aliphatic alkene, were unsuccessful. These observations (or rather lack thereof) were encouraging in the context of tandem catalysis, as competitive dimerization of the hydrogen acceptor (*i.e.* styrene) should be minimized.

[00121] Monitoring the dimerization of styrene under conditions analogous to tandem catalysis (250 mM styrene, 8 mM dimerization catalyst **1**, 100 °C) reveals strict exponential decay of styrene up to ~3.5 half-lives, with $t_{1/2} = 40$ h (see **FIG. 7**); deviation from linearity at high conversion is likely due to product inhibition, as observed for 1-hexene dimerization. This first order dependence on [styrene] is consistent with a mechanism analogous to the top catalytic cycle in **Scheme V**, where the equilibrium of:

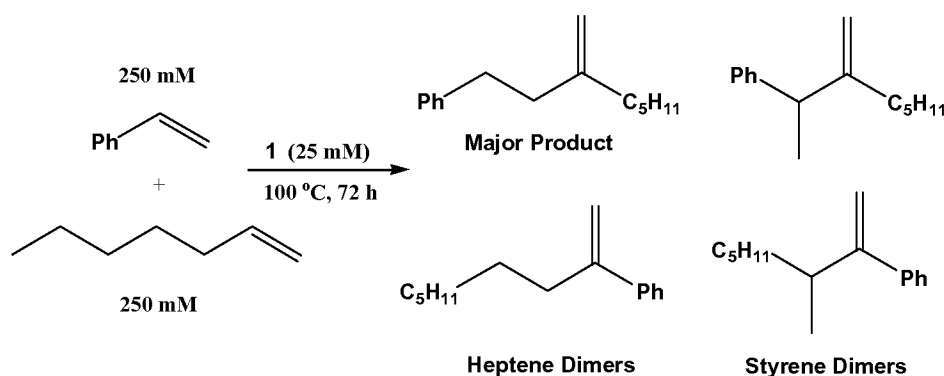


heavily favors reactants, which is in accord with the inability to observe metallacycles derived from styrenes. The observed first order rate constant $k_{\text{obs}} = K_{\text{eq}}'' k_3 [\text{Ta}]_0$, and therefore $K_{\text{eq}}'' k_3 = 6.00(6) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (where k_3 is the rate constant for the unimolecular decomposition of the styrene metallacycle, analogous to k_2 in **Scheme V**). Comparing $K_{\text{eq}}'' k_3$ to the corresponding values for 1-hexene dimerization to the major and minor isomers gives a ratio of 53:17:1 ($K_{\text{eq}} k_1 : K_{\text{eq}}' k_2 : K_{\text{eq}}'' k_3$); thus 1-hexene dimerization is ~70x faster than styrene dimerization.

[00122] The markedly slower dimerization of styrene relative to 1-hexene means that styrene should be useful as a sacrificial hydrogen acceptor in tandem catalysis; however, co-dimerization of styrene and the alkane is another likely product. In order to determine the relative rates of LAO dimerization relative to styrene/LAO coupling, a mixture of styrene (313 mM) and

1-heptene (258 mM) was dimerized with dimerization catalyst **1**. Under initial rate conditions, 1-heptene dimerization is 4x faster than 1-heptene/styrene co-dimerization. Notably, under these conditions 1-heptene dimerization is 2.8 x slower than 1-hexene dimerization in the absence of styrene. Clearly, the presence of styrene inhibits LAO dimerization, probably because $\text{Cp}^*\text{TaCl}_2(\text{styrene})$ is a significant resting state, which could be a complicating factor in achieving a high degree of tandem catalysis.

[00123] Analysis of the GC traces of these initial rate experiments indicated that there are multiple styrene/1-heptene co-dimer products. Running a 1-heptene/styrene co-dimerization to completion gives 1-heptene dimers, co-dimers, and styrene dimer. By GC, there appear to be three or four co-dimers (one peak has a consistent shoulder), with one major species. If both "tail-to-tail" and "head-to-tail" regioisomers are considered, there are four possible products (**Scheme IX**).



Scheme IX

[00124] Other embodiments, combinations and modifications of the compositions and methods presented herein will occur readily to those of ordinary skill in the art in view of these teachings. Therefore, the compositions and methods are to be limited only by the following claims, which include all such embodiments and modifications when viewed in conjunction with the above specification and accompanying drawings.

CLAIMS

1. A method of coupling an alkane with an alkene so as to form one or more higher molecular weight hydrocarbons, comprising:

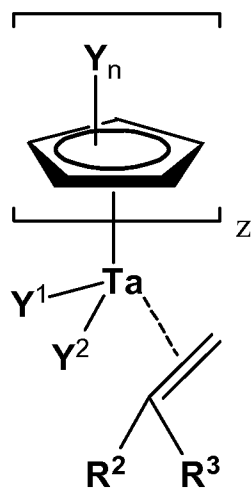
coupling an alkane with an alkene in the presence of catalysts comprising: (i) a hydrogen transfer catalyst and (ii) an alkene dimerization catalyst so as to generate one or more higher molecular weight hydrocarbons;

wherein the hydrogen transfer catalyst is an iridium pincer complex catalyst and the alkene dimerization catalyst is tantalum catalyst,

wherein the one or more higher molecular weight hydrocarbons comprise one or more carbon atoms from both the alkane and the alkene.

2. The method of claim 1, wherein both the hydrogen transfer catalyst and the dimerization catalyst are heterogeneous catalysts.

3. The method of claim 1 or claim 2, wherein the dimerization catalyst comprises a structure of Formula II:



(II)

wherein,

Z is either 1 or 2;

n is an integer from 1 to 5;

each Y is independently selected from D, H, optionally substituted (C₁-C₆)alkyl, silane, and (C₁-C₄)alkylsilane;

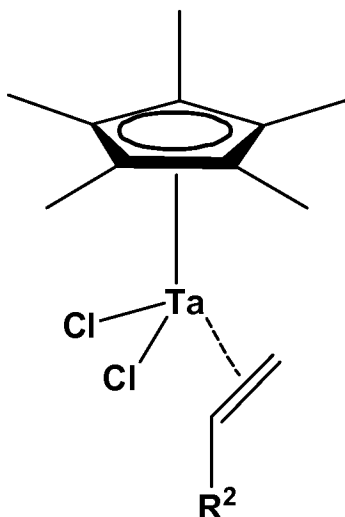
Y¹ is a H, D, halo, =S, =O, PMe₃, =C(H)(CMe₃);

Y² is a H, D, halo, =S, =O, PMe₃, or absent;

R² is a H, aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl; and

R³ is a H, aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl.

4. The method of claim 3, wherein the dimerization catalyst comprises a structure of Formula II(a):

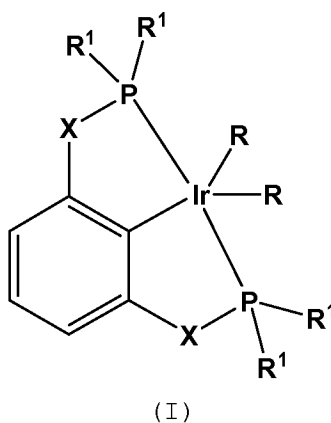


II(a)

wherein,

R² is an aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl.

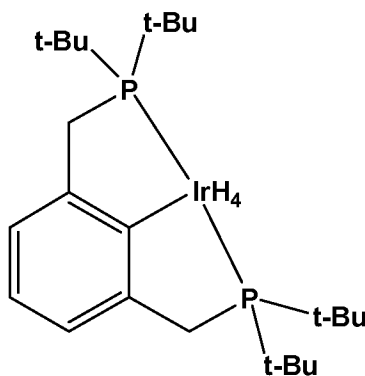
5. The method of any one of claims 1 to 4, wherein the hydrogen transfer catalyst comprises a structure of Formula I:



wherein,

each R is independently H or a (C₁-C₃₀)hydrocarbonyl radical;
 each R¹ is independently a (C₁-C₃₀)hydrocarbonyl radical; and
 each X is independently an O or CH₂.

6. The method of claim 5, wherein the hydrogen transfer catalyst comprises a structure of Formula I(a):



I(a).

7. The method of any one of claims 1 to 6, wherein the hydrogen transfer catalyst is immobilized on a solid support, wherein the reaction is carried out in a solvent, and wherein the method further comprises the step of separating free hydrogen transfer catalyst from the solvent.

8. The method of any one of claims 1 to 7, wherein the alkane is a straight chain (C₅-C₁₀)alkane.

9. The method of any one of claims 1 to 8, wherein the alkene is a straight chain (C₅-C₁₀)alkene.

10. A method for coupling a first alkane with a second alkane to form one or more high molecular weight hydrocarbons, comprising:

coupling a first alkane with a second alkane using a sacrificial hydrogen acceptor in the presence of catalysts comprising: (i) a hydrogen transfer catalyst and (ii) an alkene dimerization catalyst so as to generate one or more higher molecular weight hydrocarbons;

wherein the hydrogen transfer catalyst is an iridium pincer complex catalyst and the alkene dimerization catalyst is tantalum catalyst,

wherein the one or more higher molecular weight hydrocarbons comprise carbon atoms from the first alkane and the second alkane.

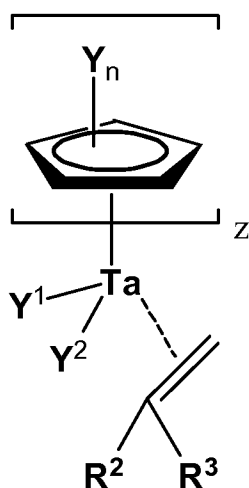
11. The method of claim 10, wherein the sacrificial hydrogen acceptor is styrene, tert-butylethylene or a combination thereof.

12. The method of claim 10 or claim 11, wherein the first alkane and the second alkane have the same structure.

13. The method of claim 10 or claim 11, wherein the first alkane and the second alkane do not have the same structure.

14. The method of any one of claims 10 to 13, wherein both the hydrogen transfer catalyst and the dimerization catalyst are heterogeneous catalysts.

15. The method of any one of claims 10 to 14, wherein the dimerization catalyst comprises a structure of Formula II:



(II)

wherein:

Z is either 1 or 2;

n is an integer from 1 to 5;

each Y is independently selected from D, H, optionally substituted (C₁-C₆)alkyl, silane, and (C₁-C₄)alkylsilane;

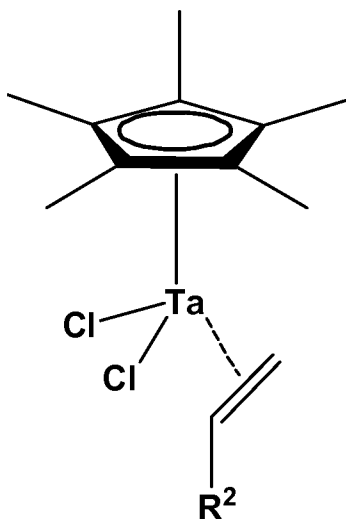
Y¹ is a H, D, halo, =S, =O, PMe₃, =C(H)(CMe₃)

Y² is a H, D, halo, =S, =O, PMe₃, or absent;

R² is a H, aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl; and

R³ is a H, aryl, optionally substituted (C₁-C₁₅)alkyl, or an optionally substituted (C₁-C₁₅)hetero-alkyl.

16. The method of claim 15, wherein the dimerization catalyst comprises a structure of Formula II(a):

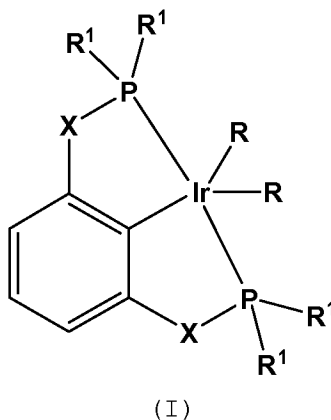


II (a)

wherein,

R² is a phenyl.

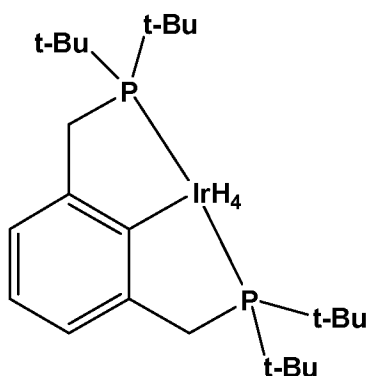
17. The method of any one of claims 10 to 16, wherein the hydrogen transfer catalyst comprises a structure of Formula I:



wherein,

each R is independently H or a (C₁-C₃₀)hydrocarbyl radical;
 each R¹ is independently a (C₁-C₃₀)hydrocarbyl radical; and
 each X is independently an O or CH₂.

18. The method of claim 17, wherein the hydrogen transfer catalyst comprises a structure of Formula I(a):



I (a) .

19. The method of any one of claims 10 to 18, wherein the hydrogen transfer catalyst is immobilized on a solid support, wherein the reaction is carried out in a solvent system, and wherein the method further comprises the step of separating free hydrogen transfer catalyst from the solvent system.

20. The method of claim 19, wherein the solvent system comprises the first alkane and/or the second alkane.

21. The method of any one of claims 10 to 20, wherein the first alkane and the second alkane are straight chain (C₅-C₁₀)alkanes.

22. The method of any one of claims 1 to 21, wherein the method further comprises hydrogenating or reducing the one or more higher molecular weight hydrocarbons.

23. The method of any one of claims 1 to 21, wherein the one or more higher molecular weight hydrocarbons are alkanes.

24. A liquid hydrocarbon fuel comprising the one or more higher molecular weight hydrocarbons made by the methods of any one of claims 1 to 23.

25. An apparatus for carrying out the method of any one of claims 1 to 22, comprising
an inlet and an outlet; and

a bed or column comprising the hydrogen transfer catalyst and the dimerization catalyst.

26. The apparatus of claim 25, wherein: (i) the hydrogen transfer catalyst is immobilized on a solid support; and (ii) the dimerization catalyst is immobilized on a solid support.

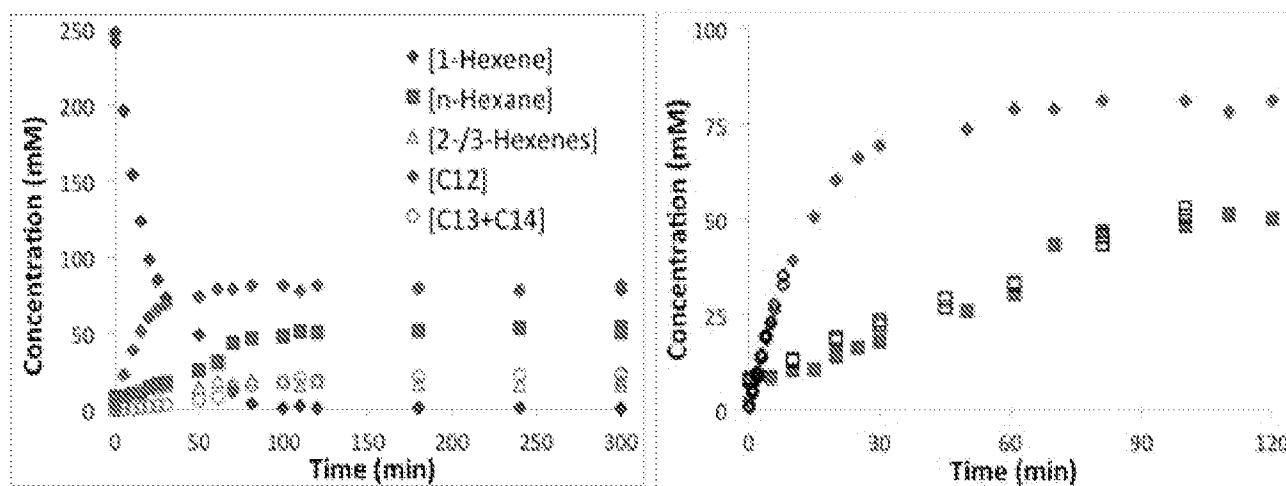
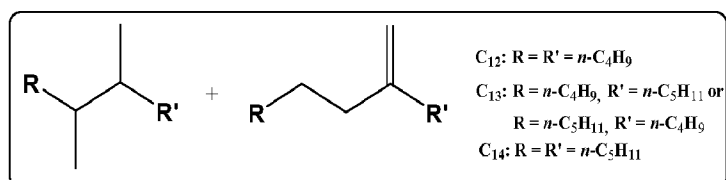
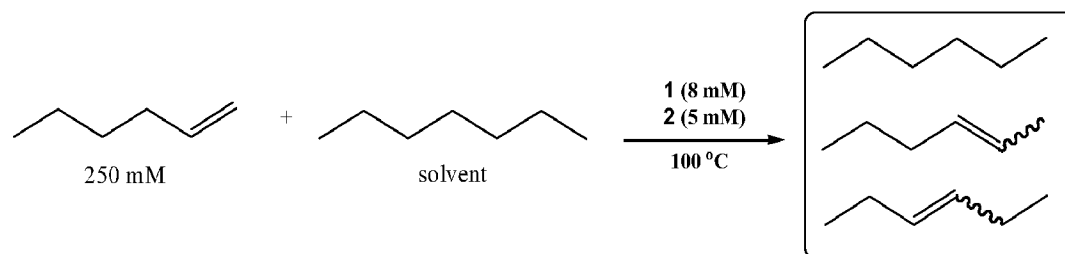


FIGURE 1

2 / 42

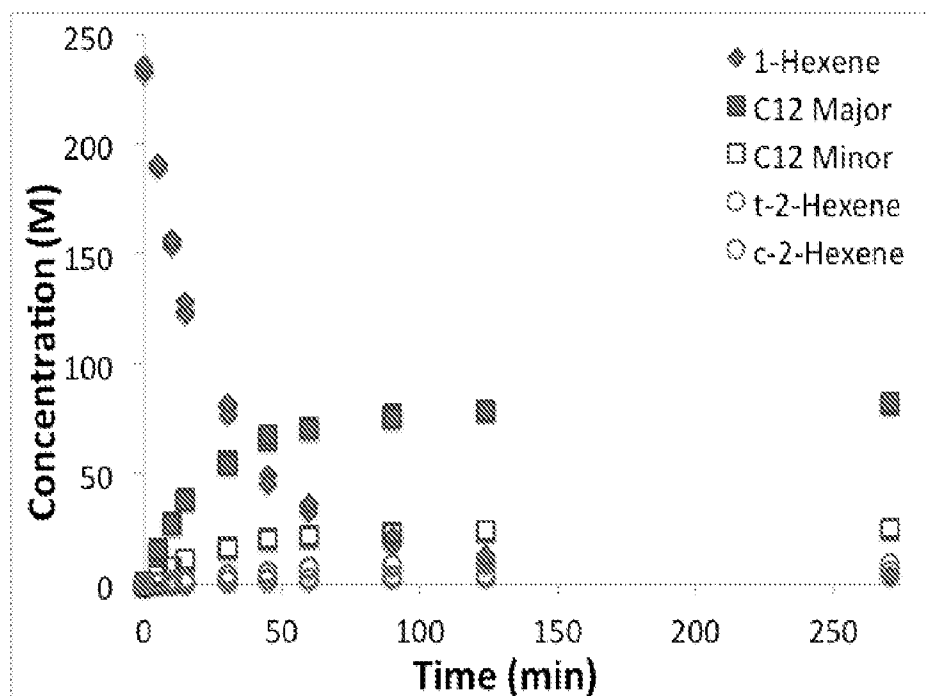


FIGURE 2

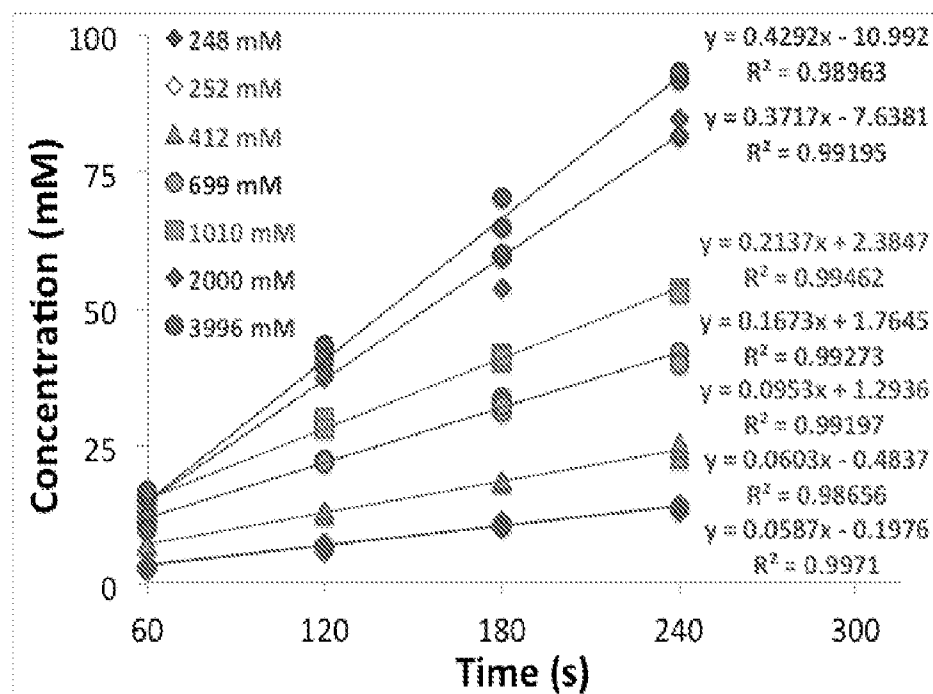


FIGURE 3

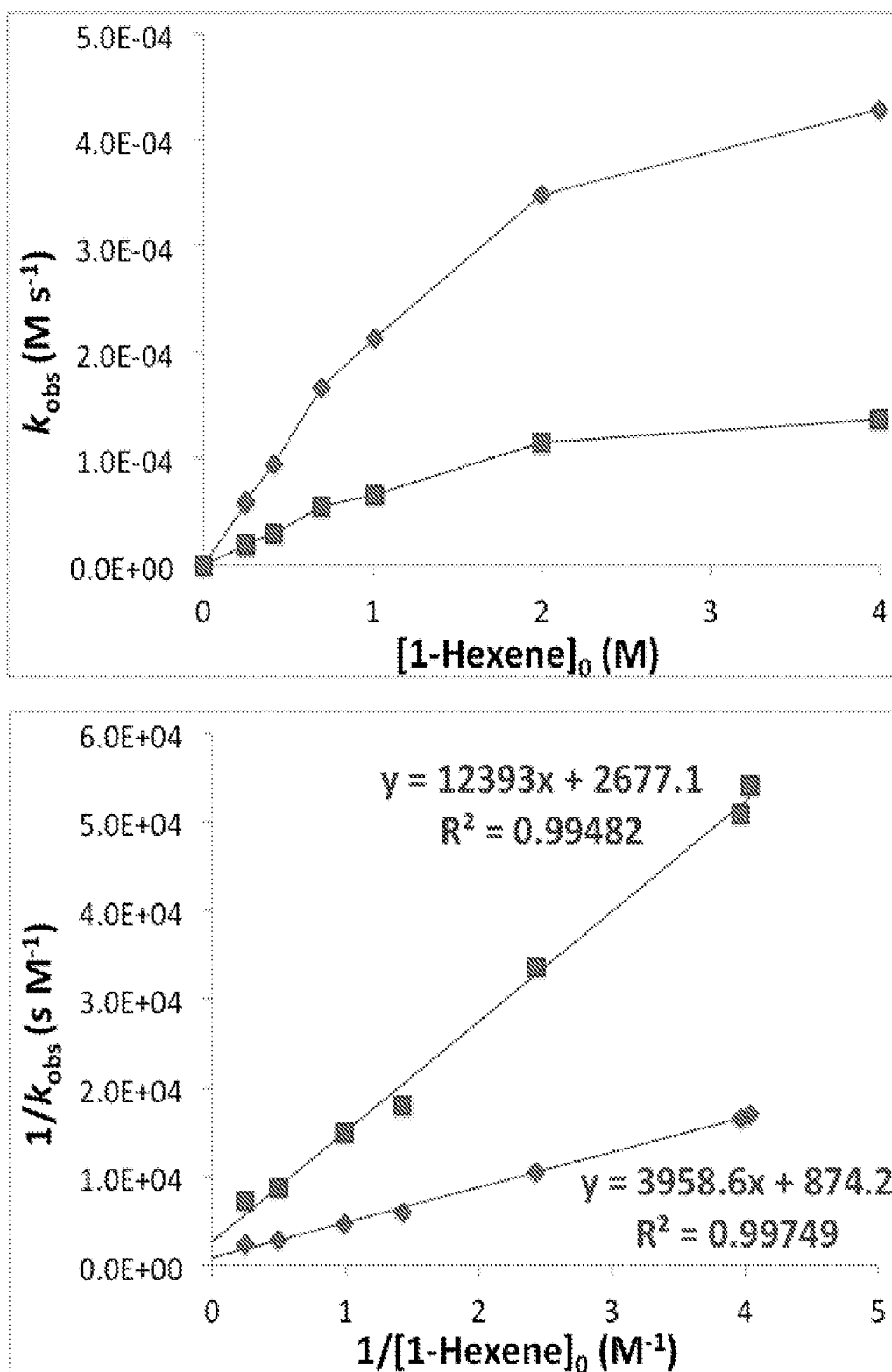


FIGURE 4

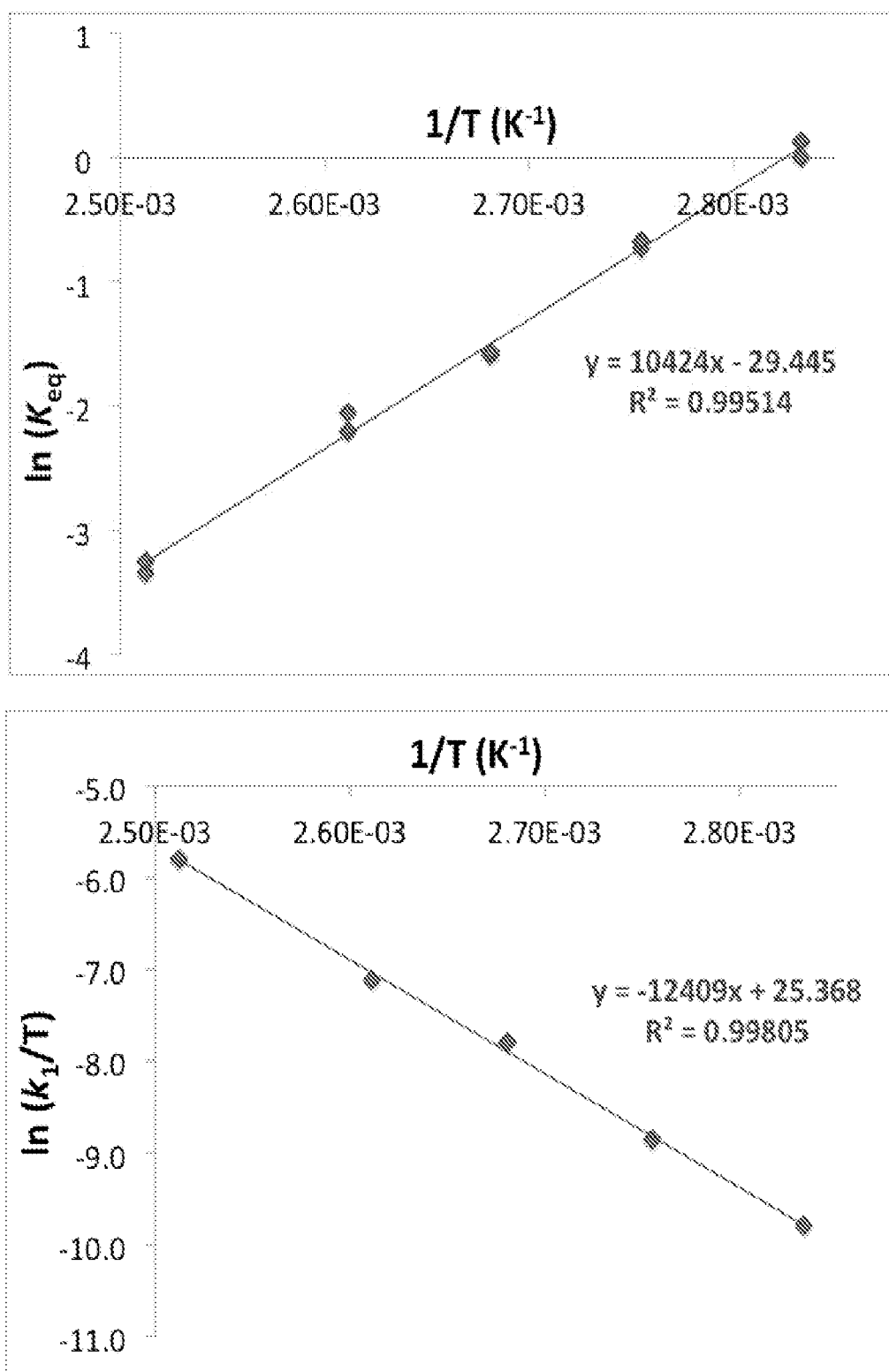


FIGURE 5

5 / 42

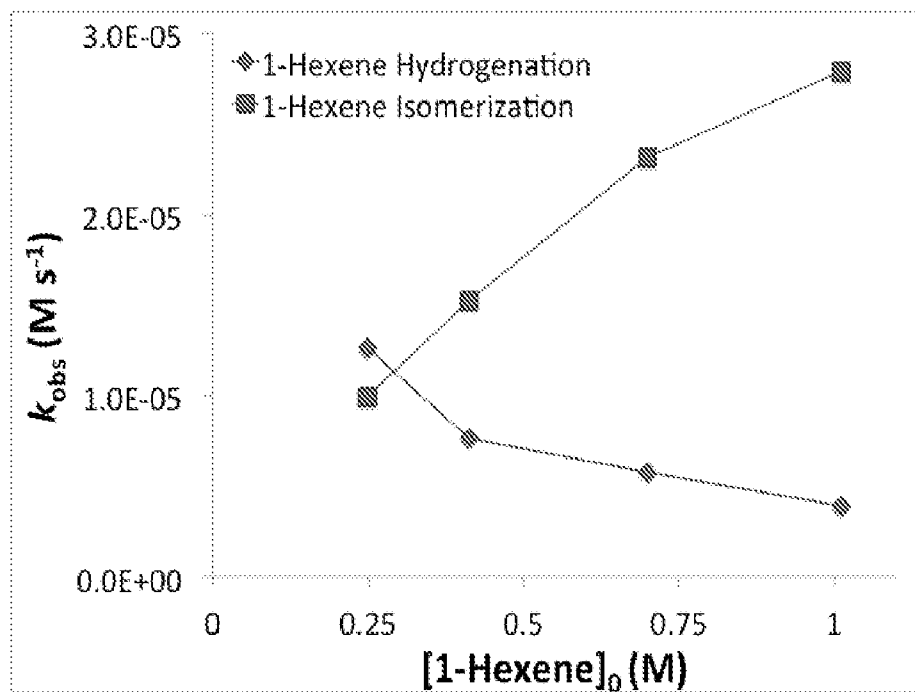


FIGURE 6

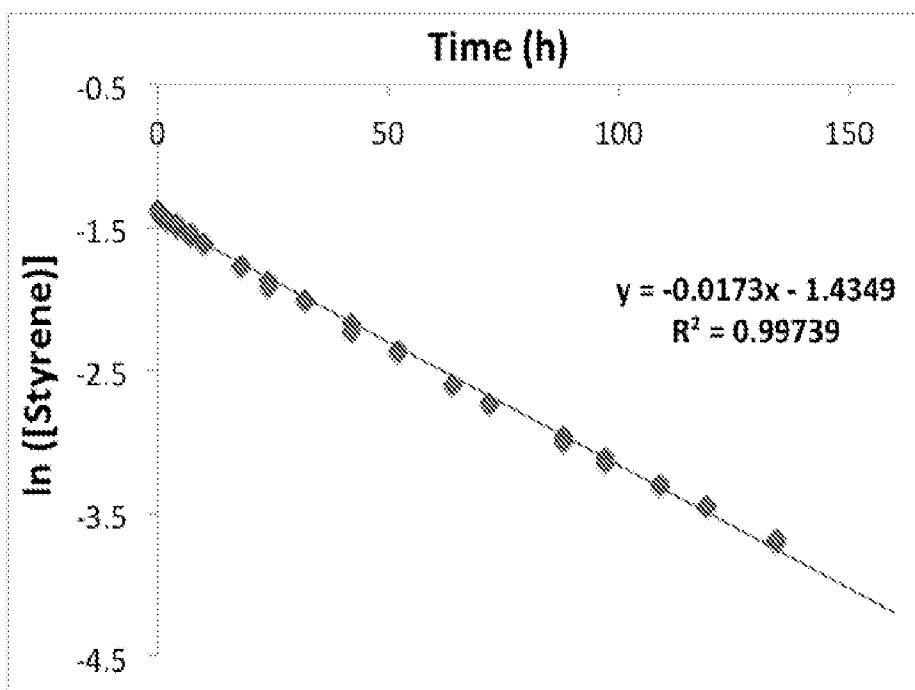


FIGURE 7

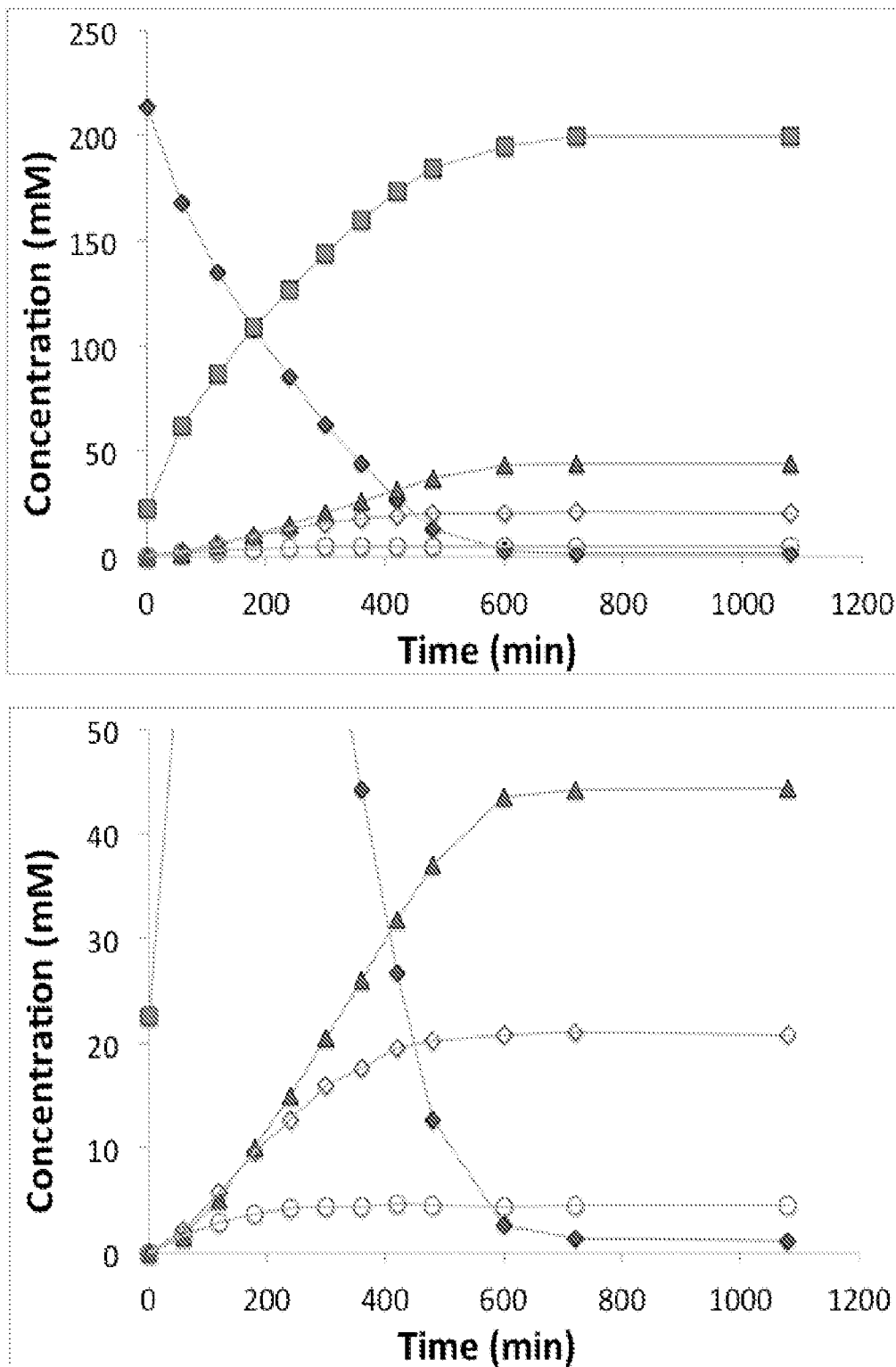


FIGURE 8

7 / 42

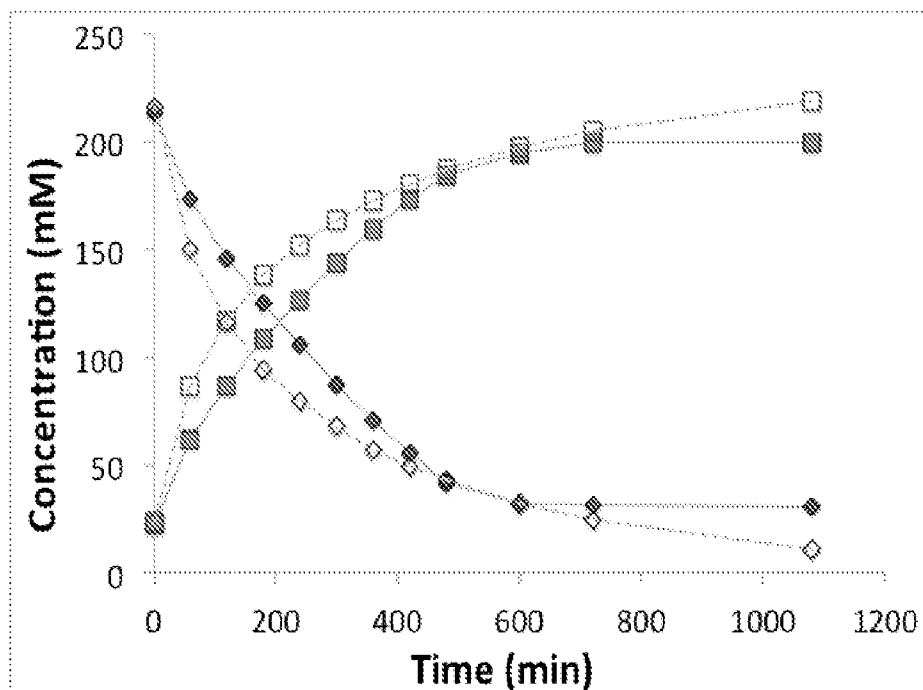


FIGURE 9

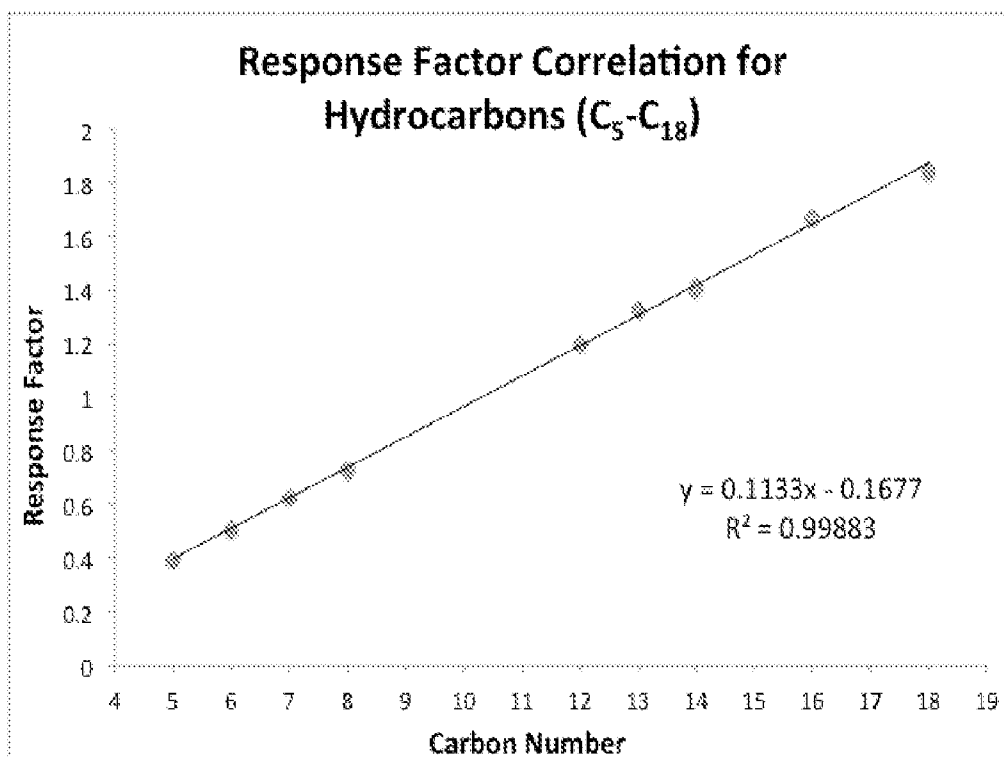


FIGURE 10

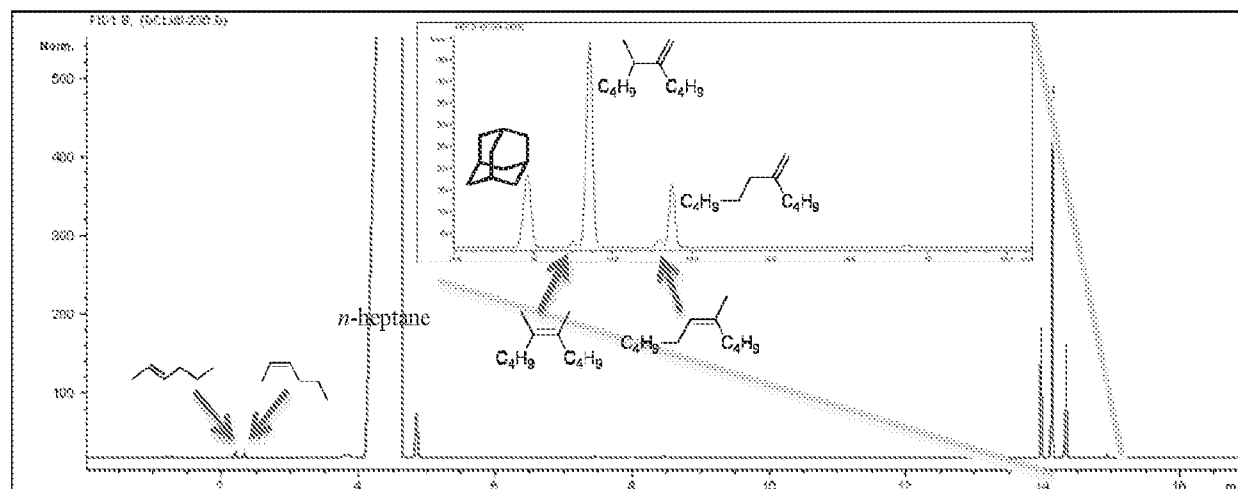


FIGURE 11

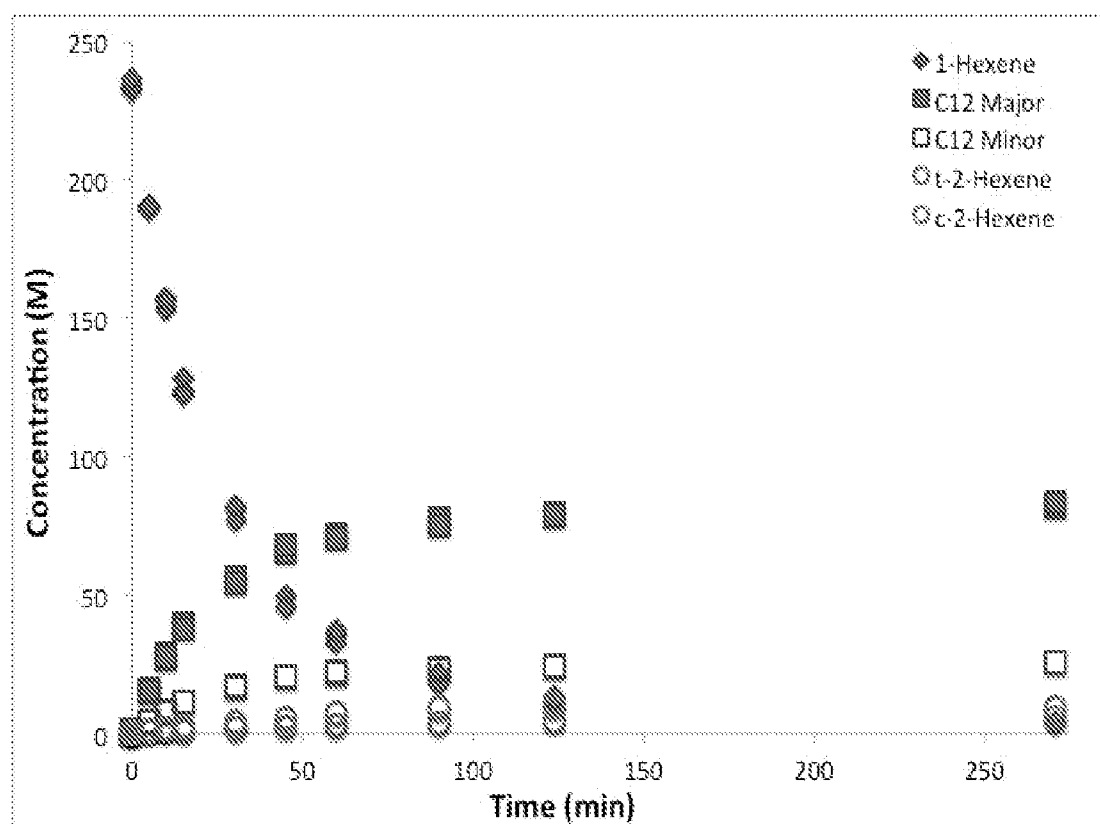


FIGURE 12

9 / 42

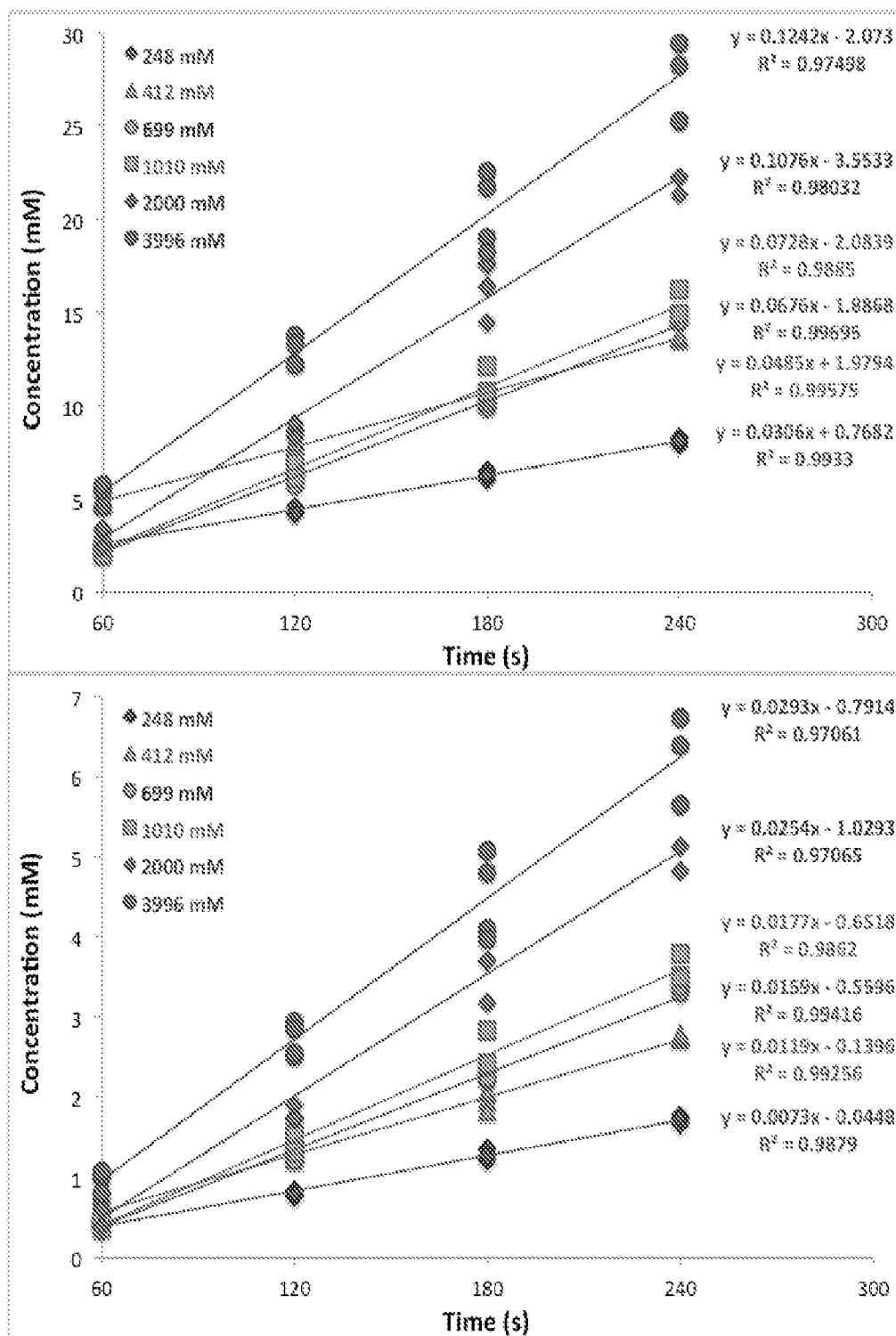


FIGURE 13

10 / 42

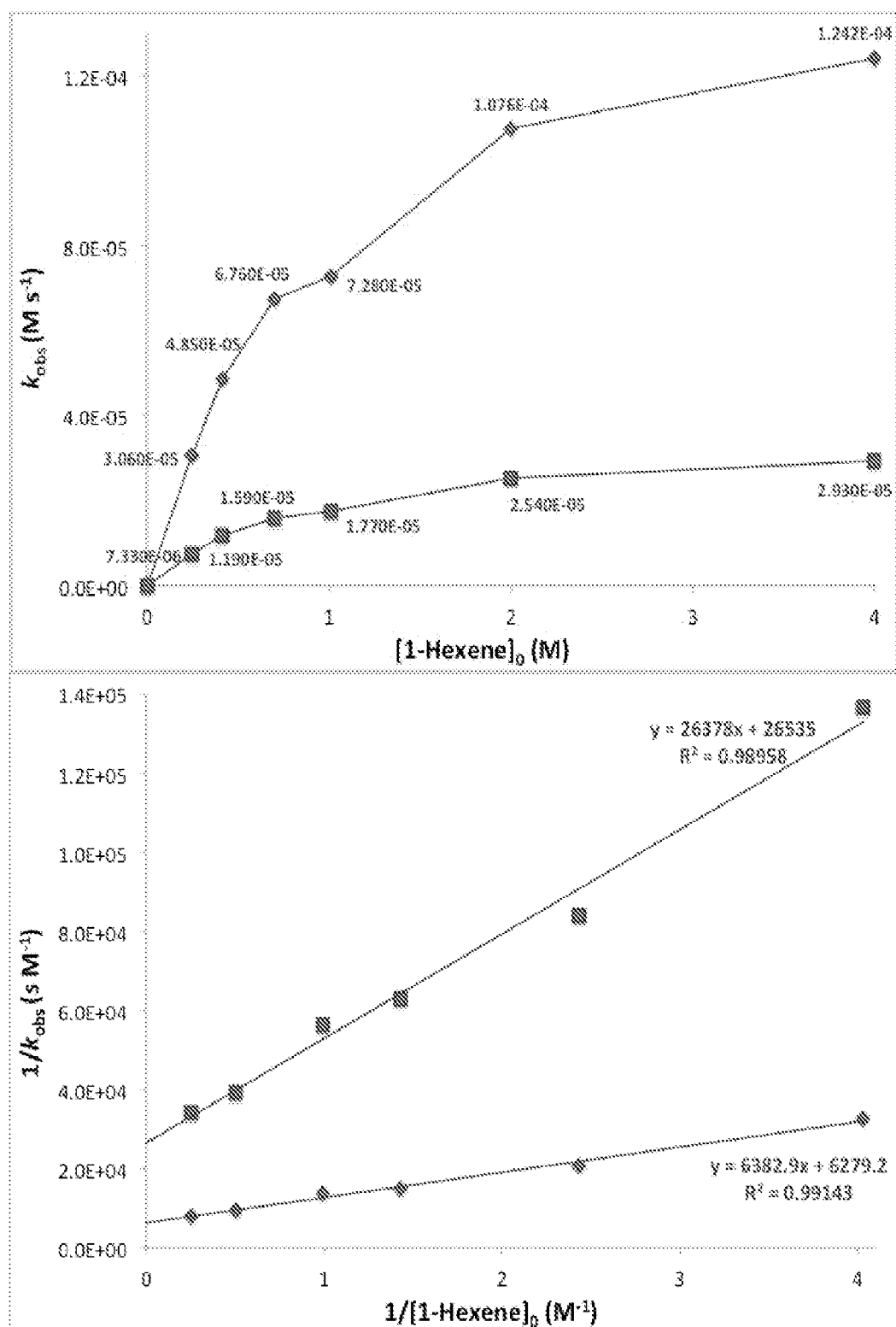


FIGURE 14

11 / 42

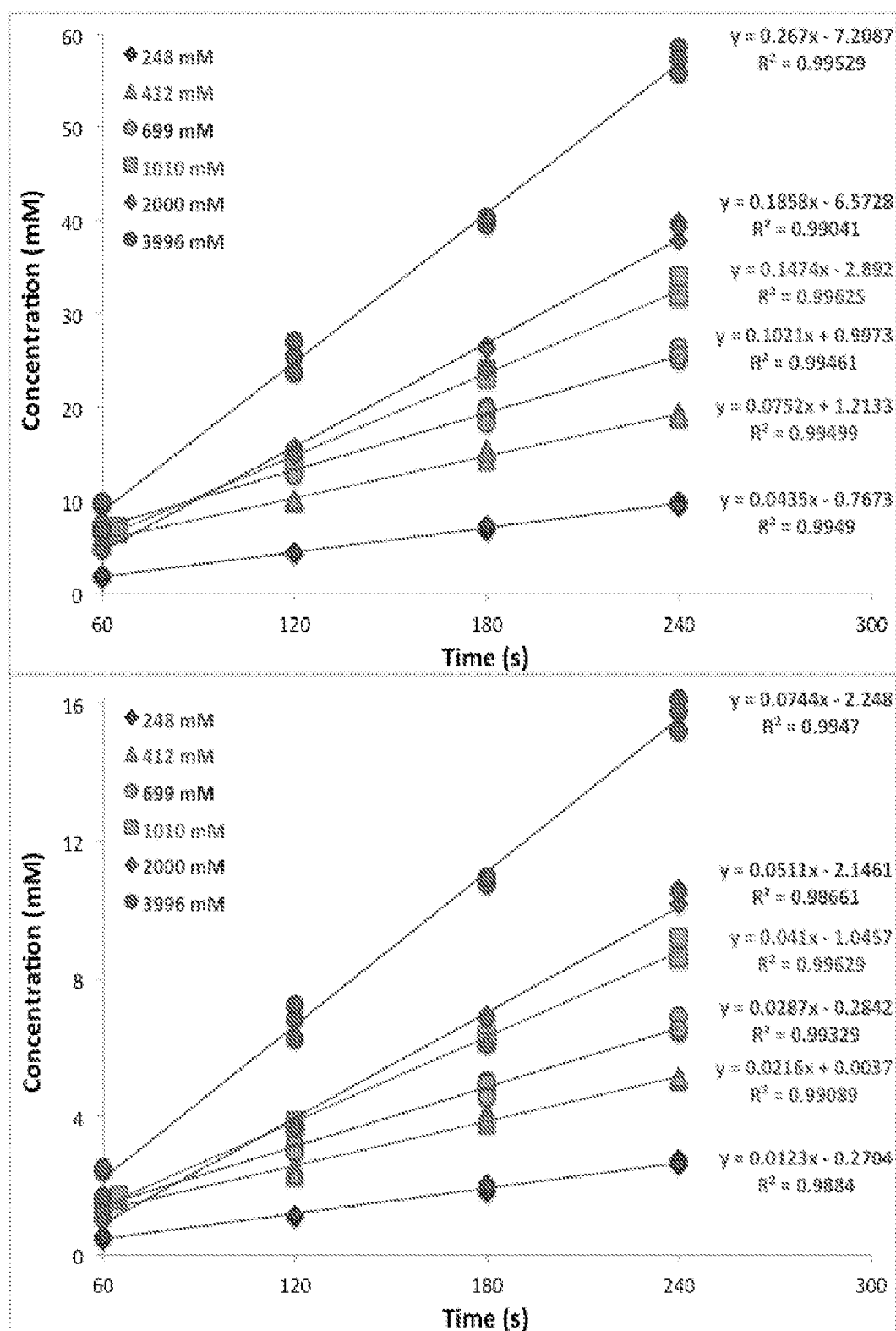


FIGURE 15

12 / 42

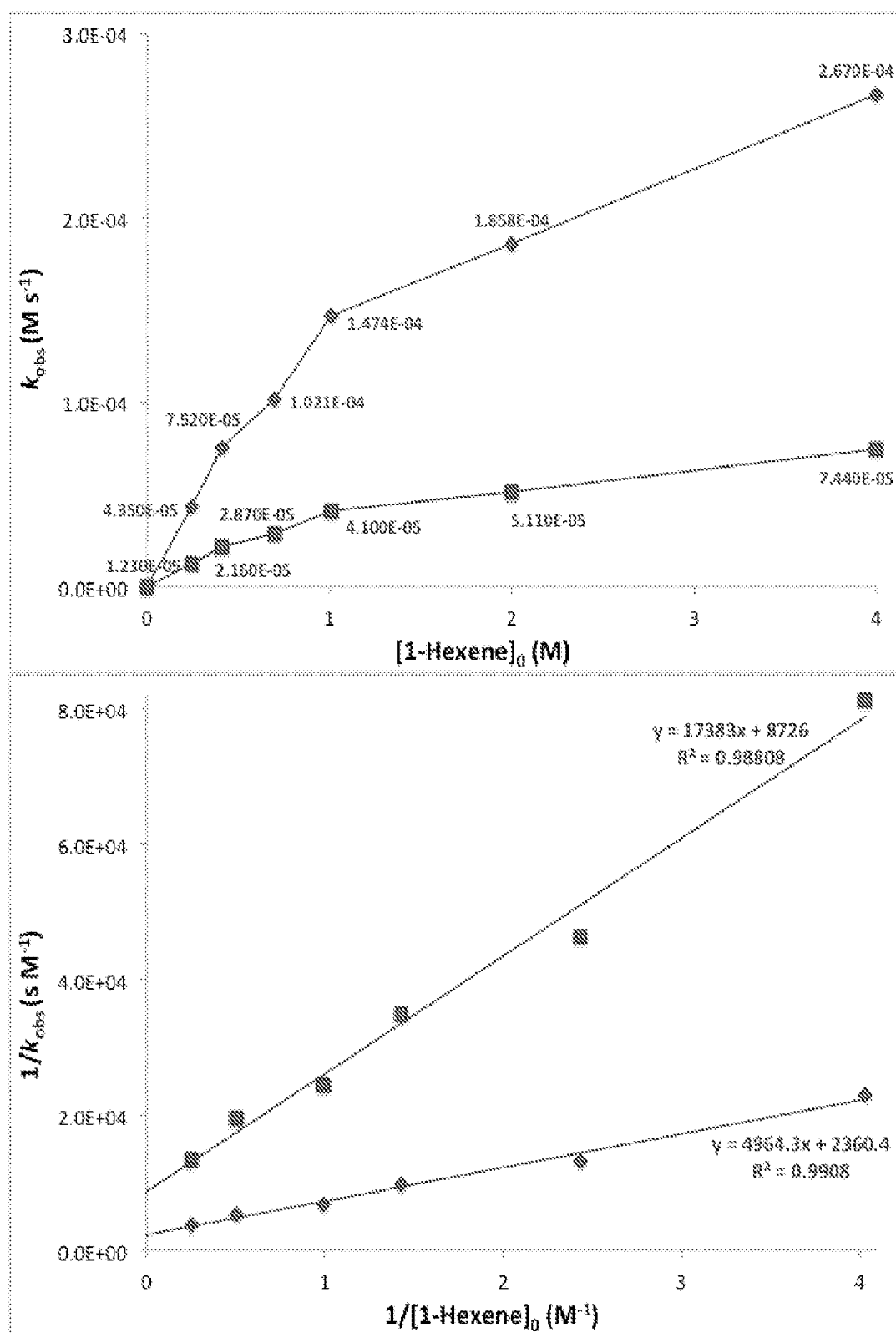


FIGURE 16

13 / 42

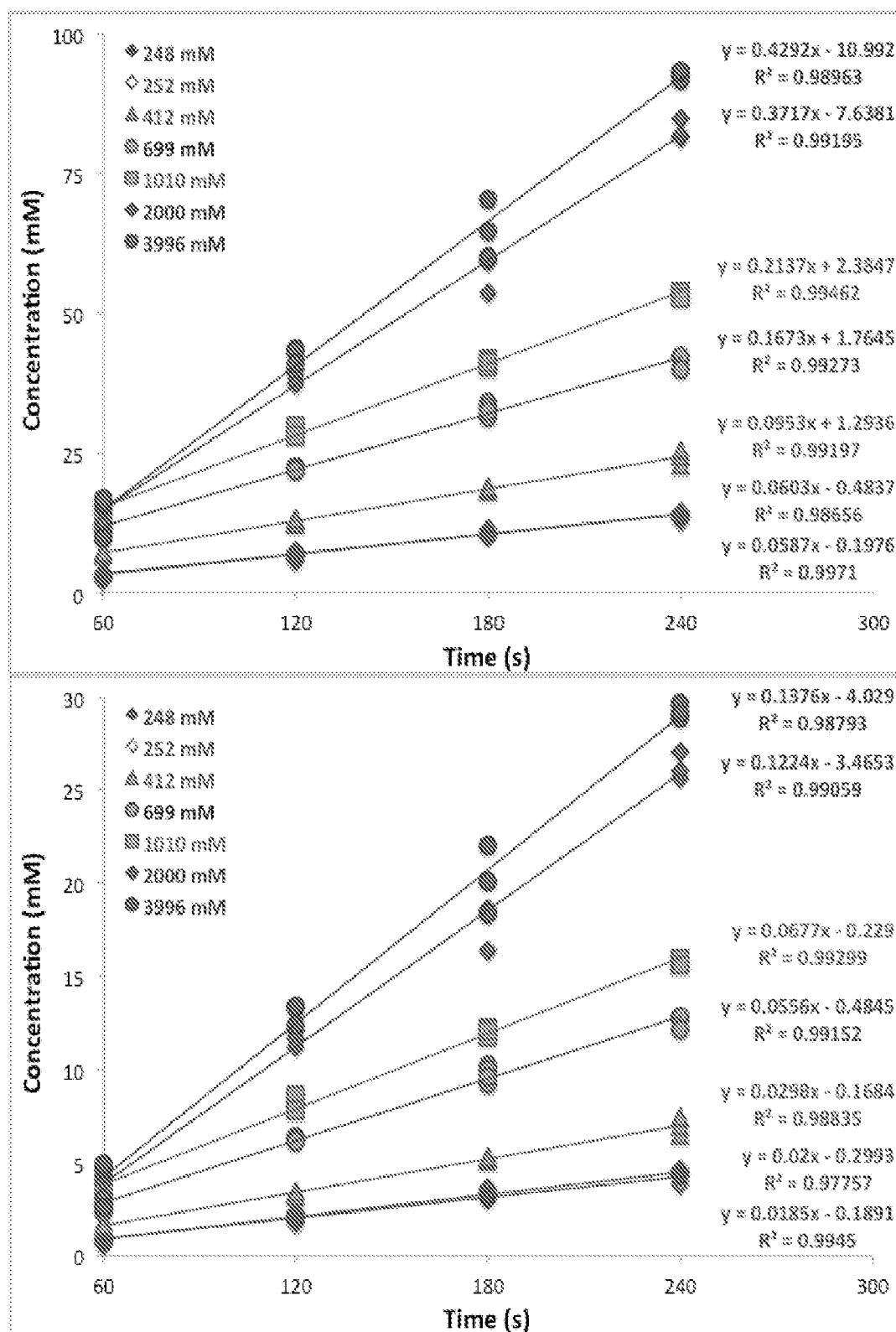


FIGURE 17

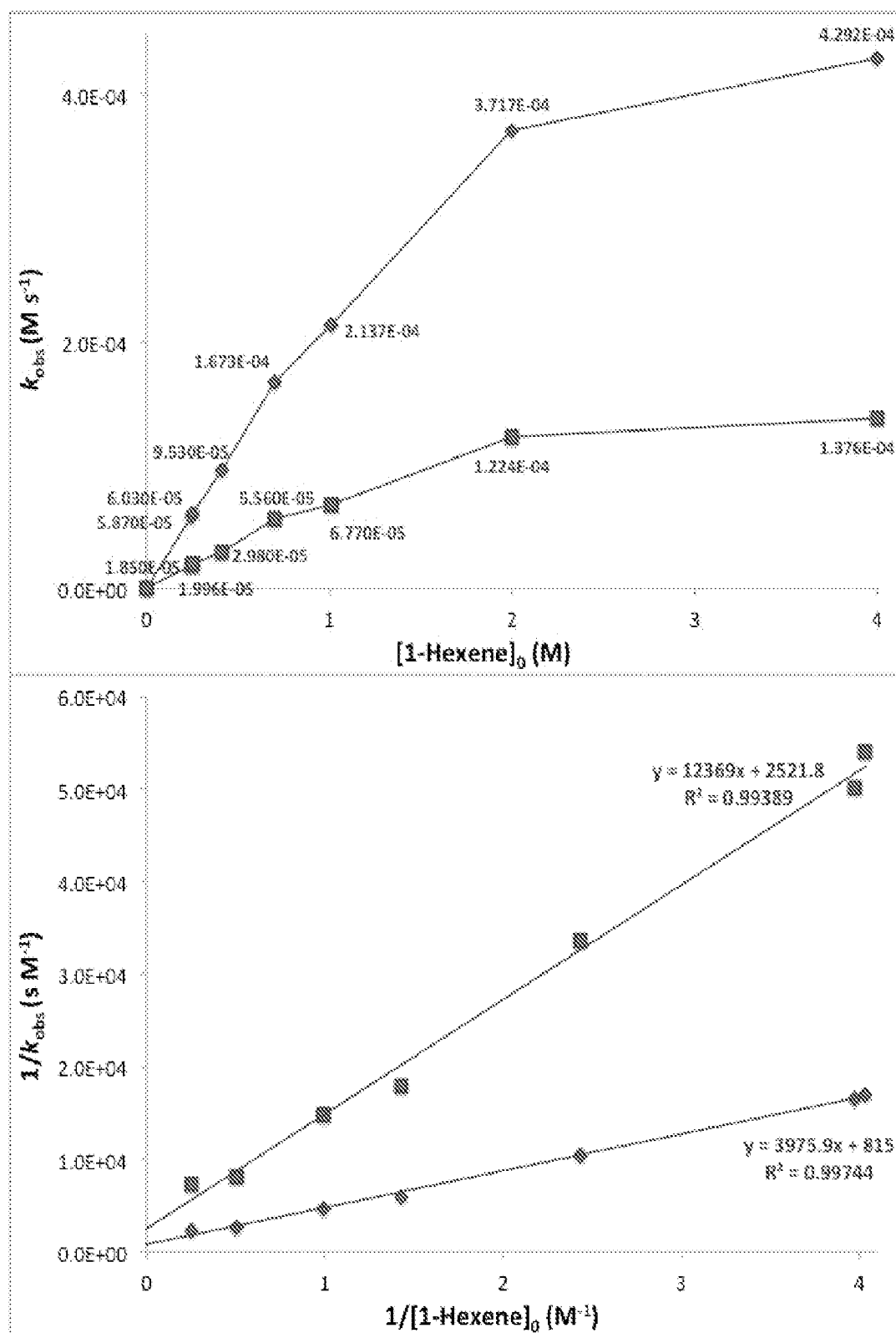


FIGURE 18

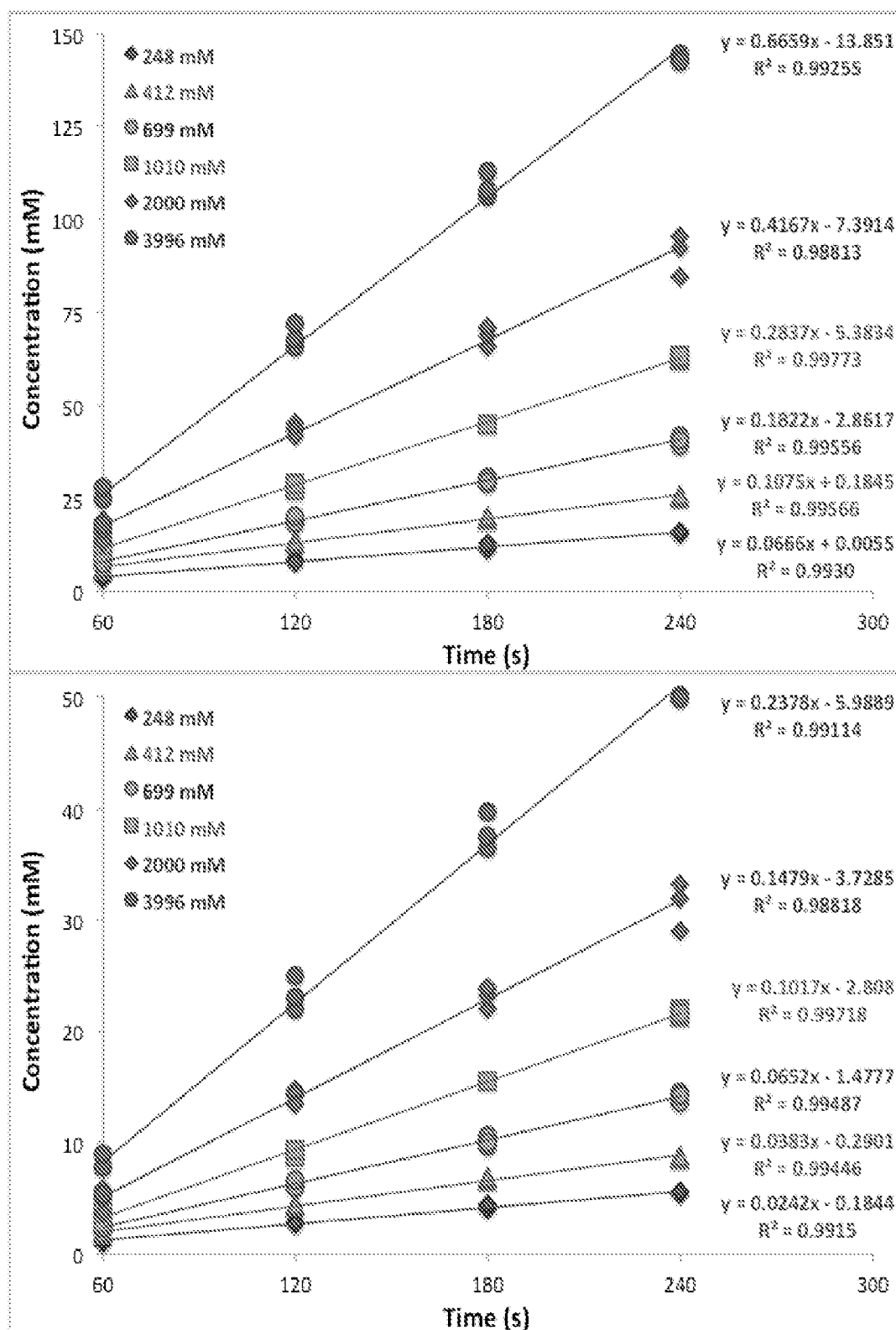


FIGURE 19

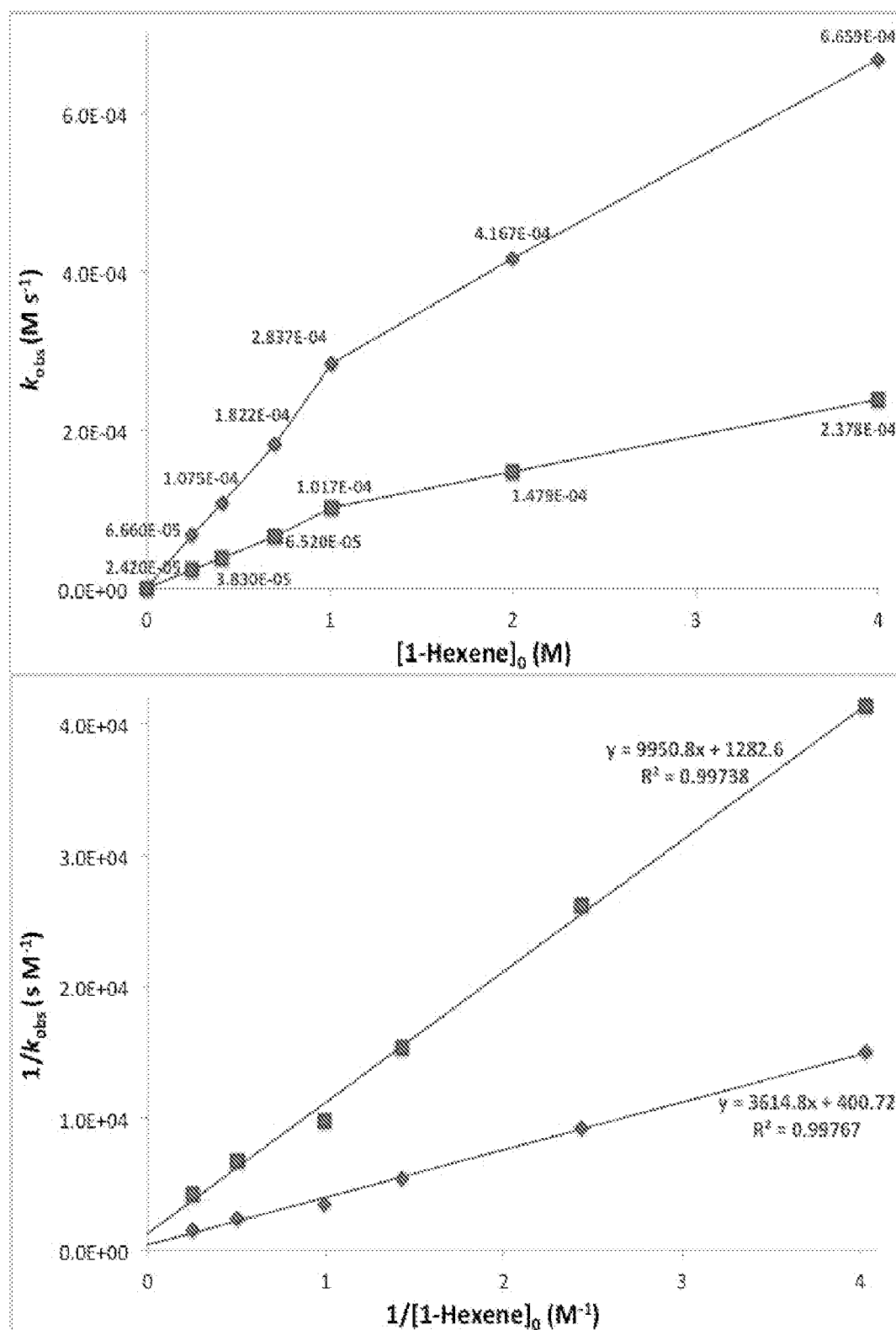


FIGURE 20

17 / 42

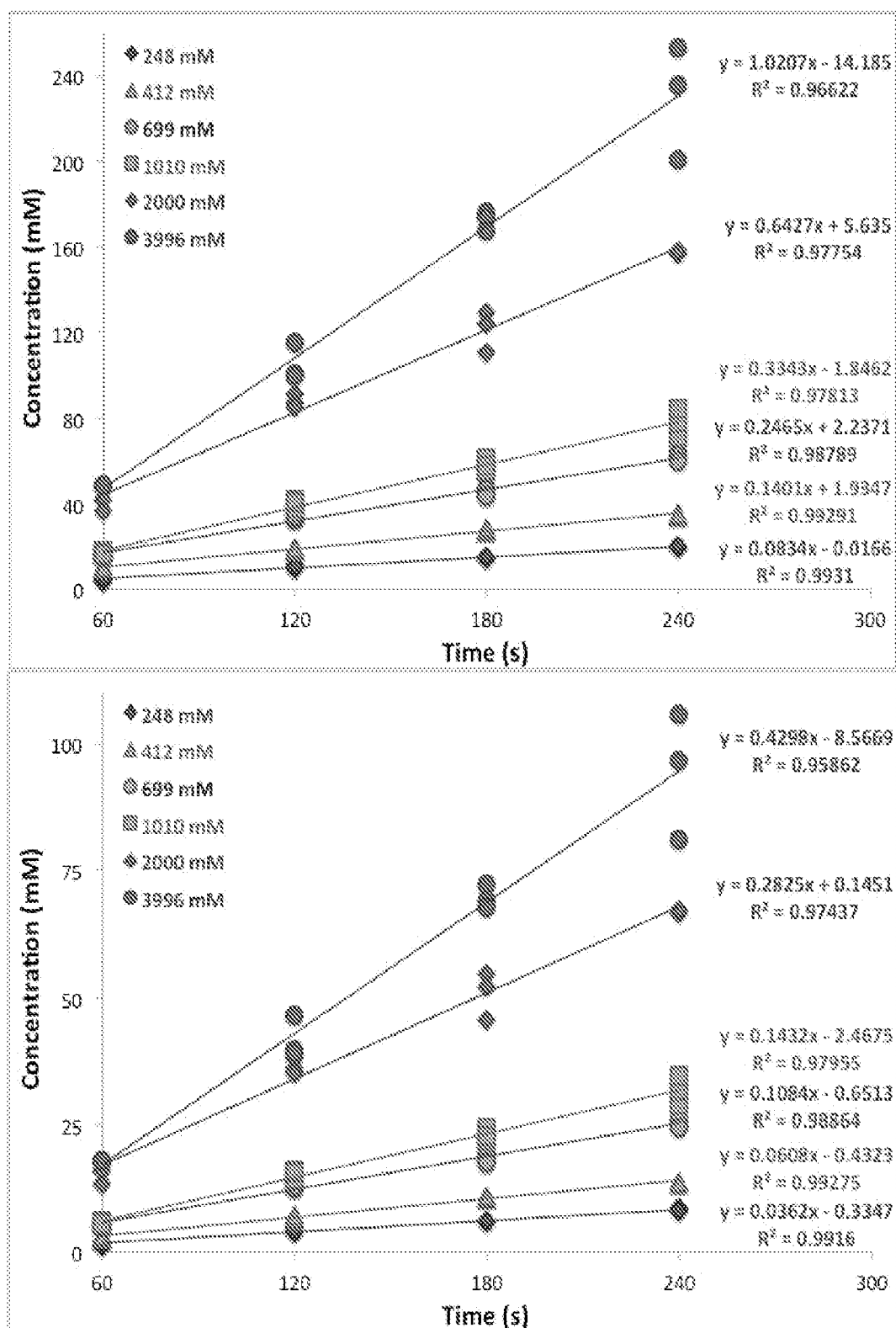


FIGURE 21

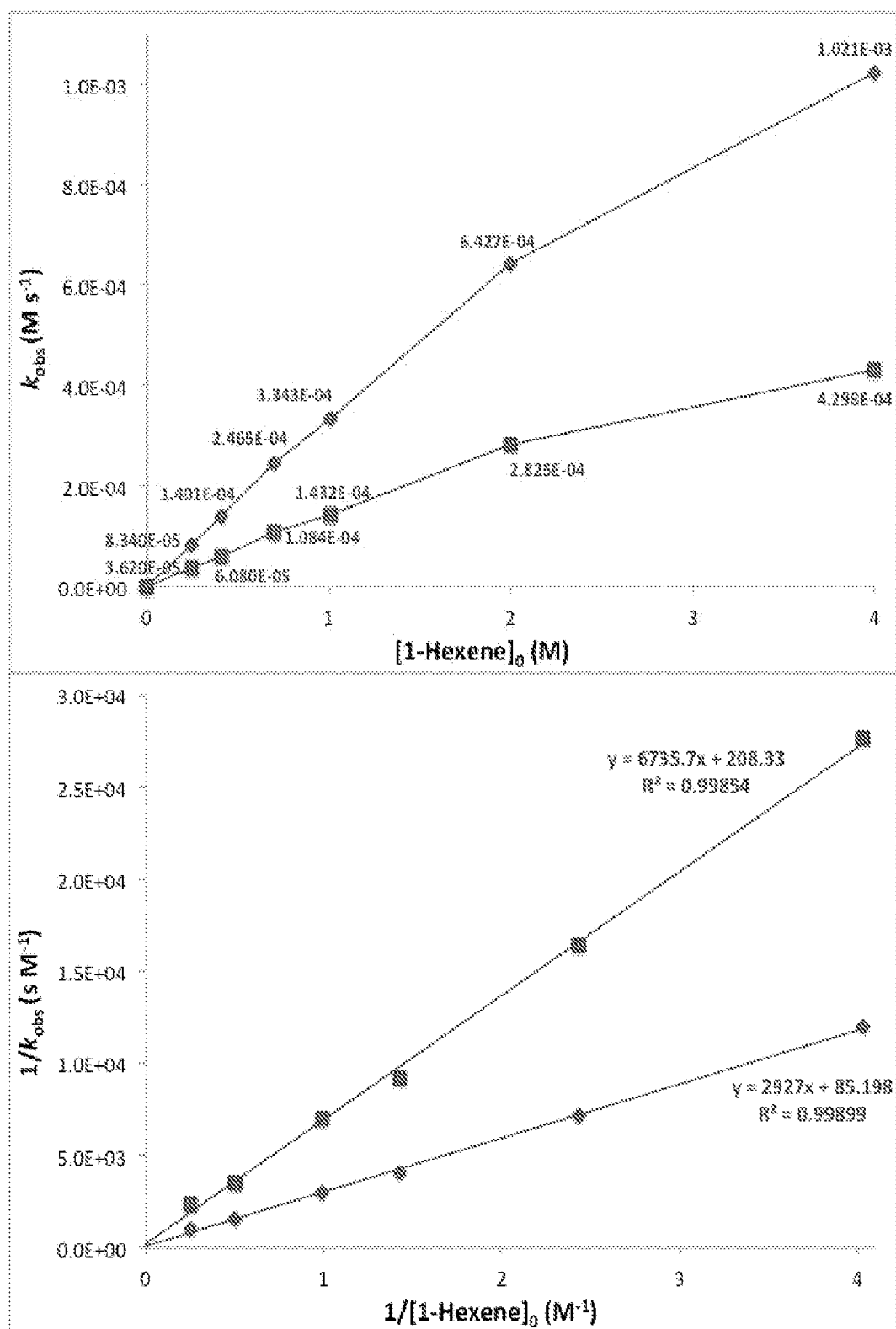


FIGURE 22

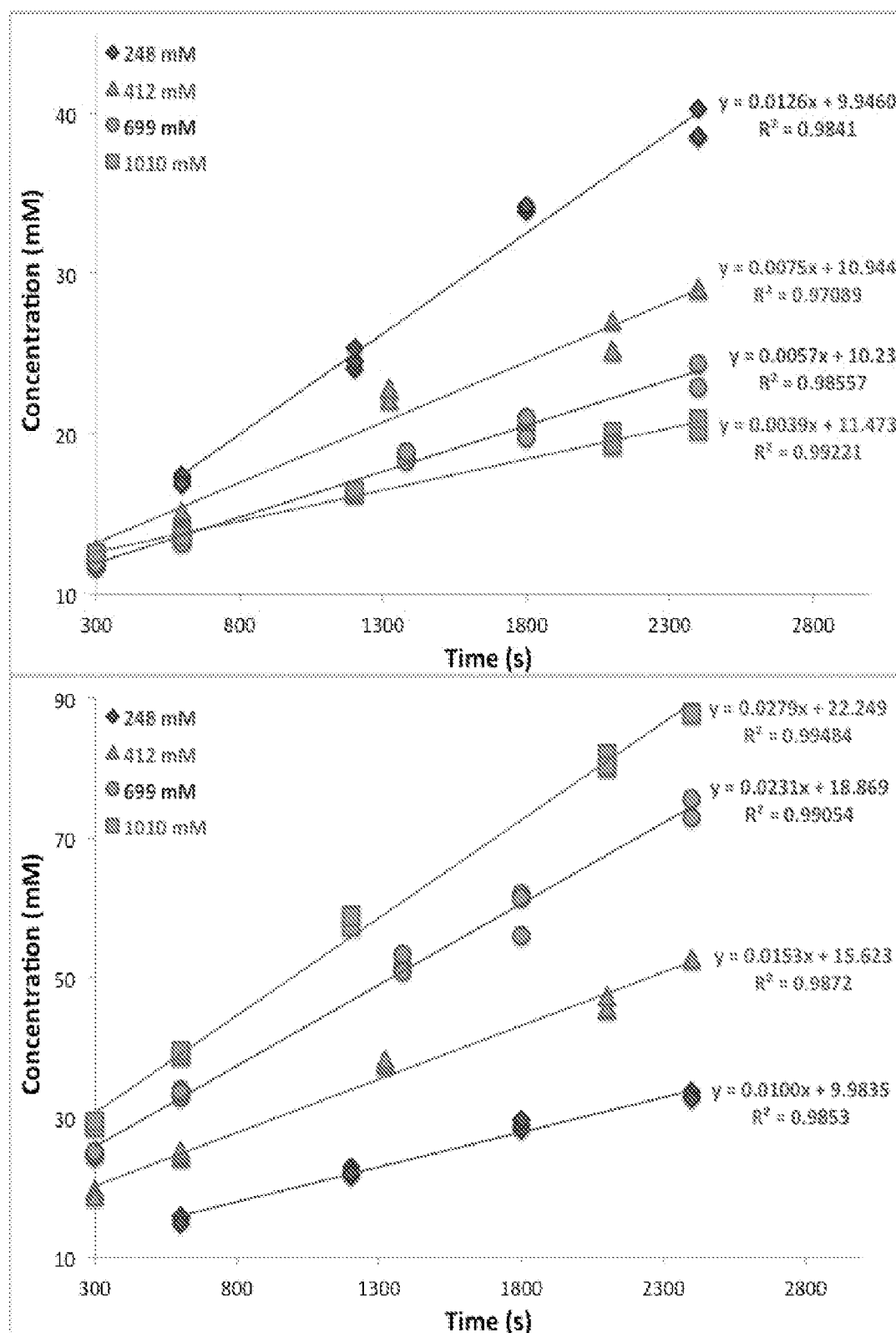


FIGURE 23

20 / 42

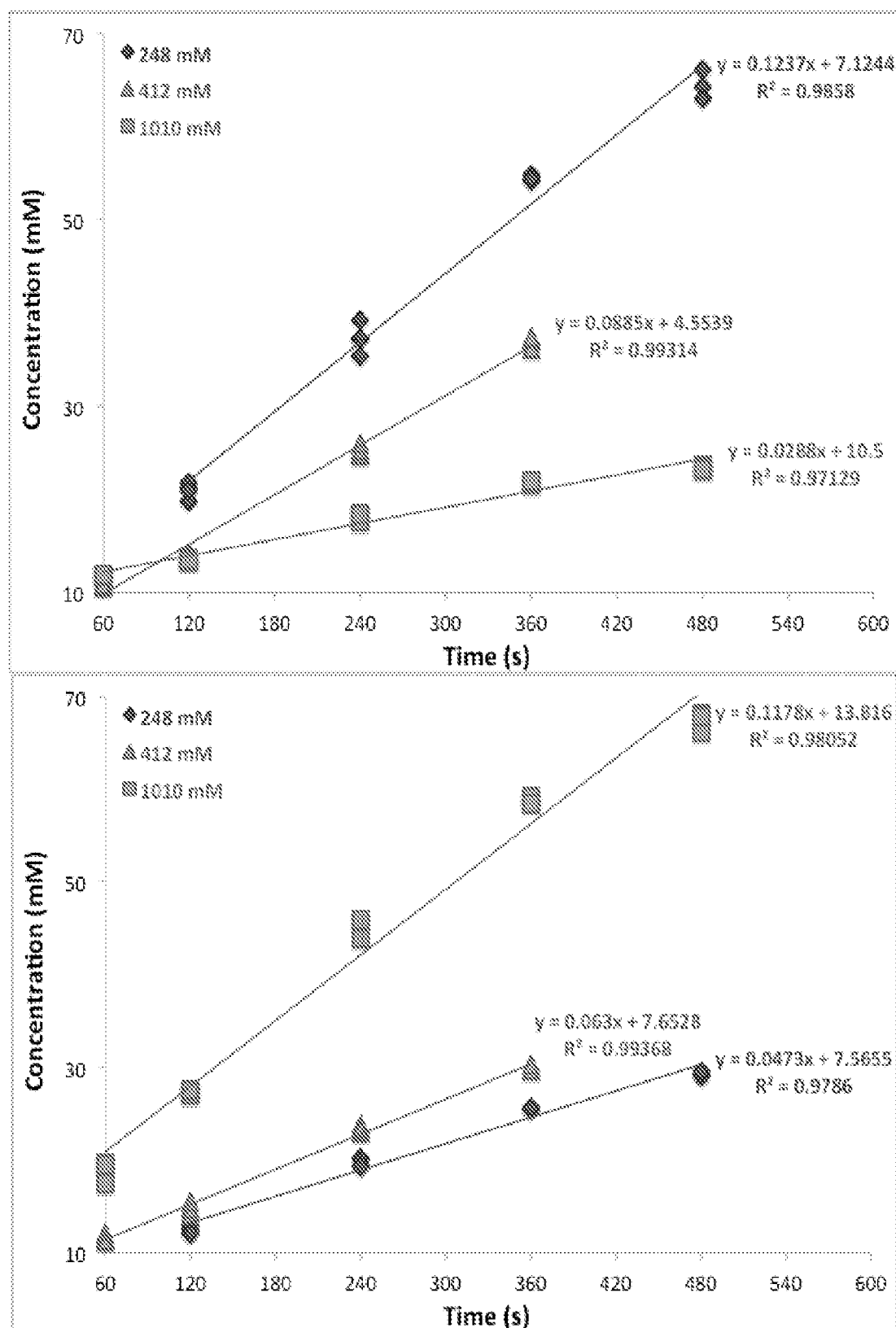


FIGURE 24

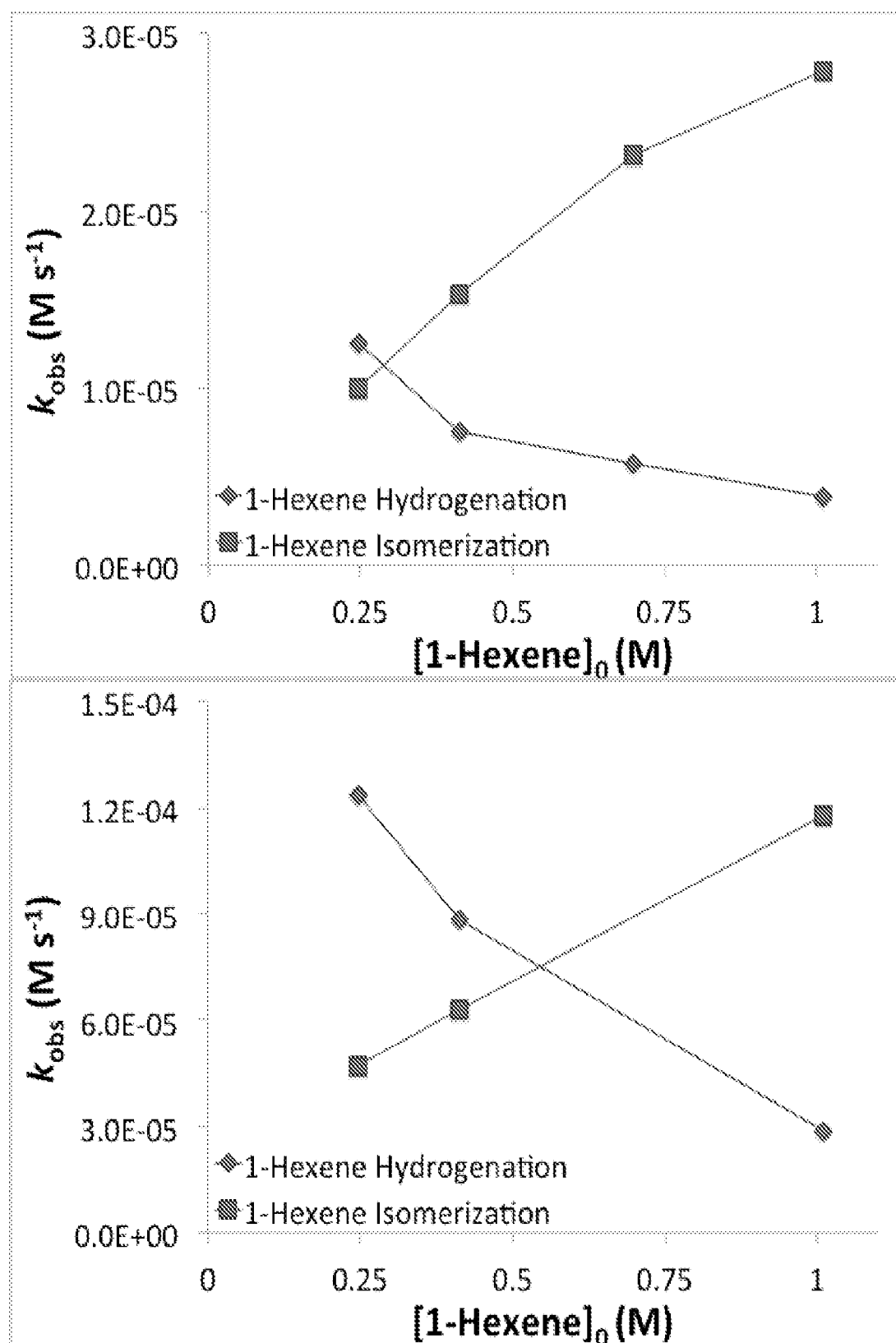


FIGURE 25

22 / 42

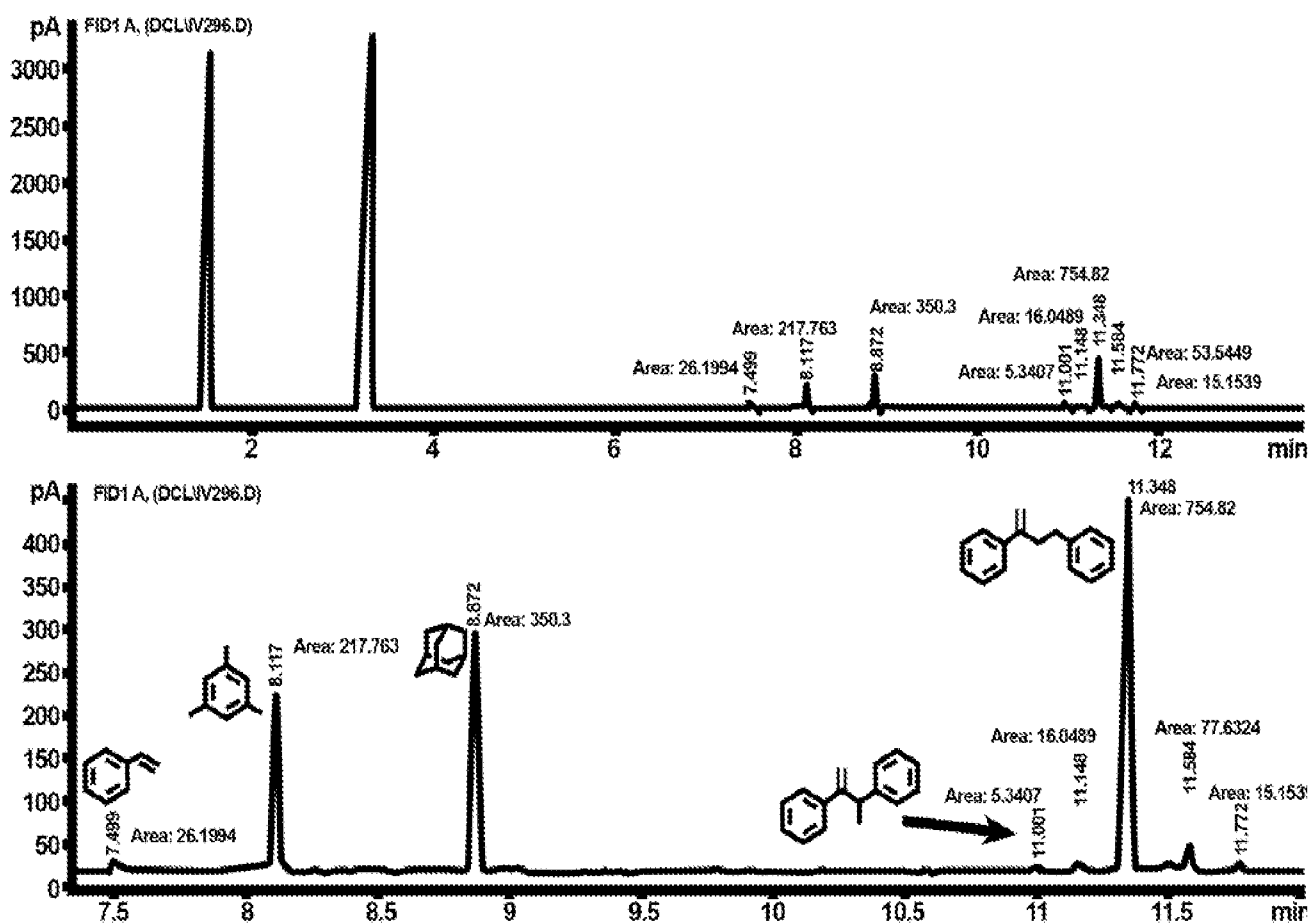


FIGURE 26

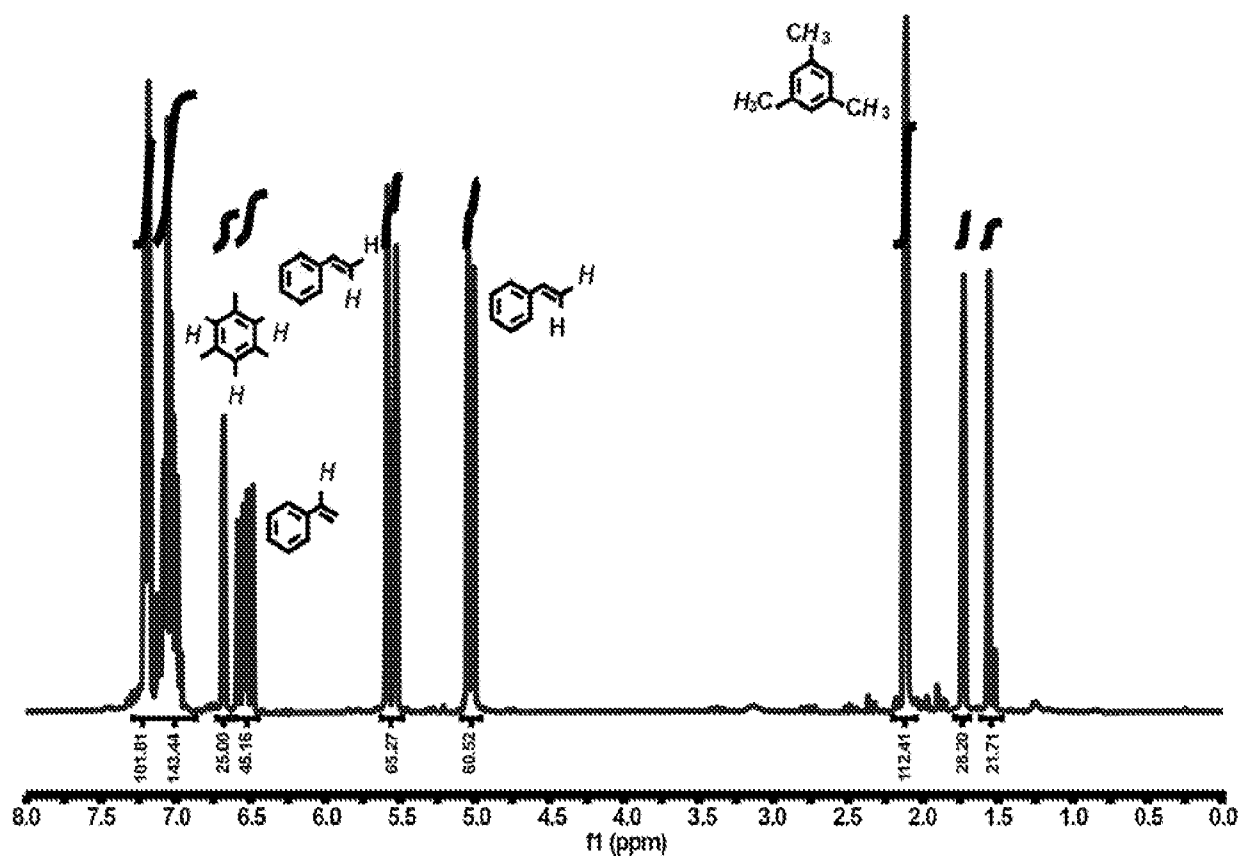


FIGURE 27

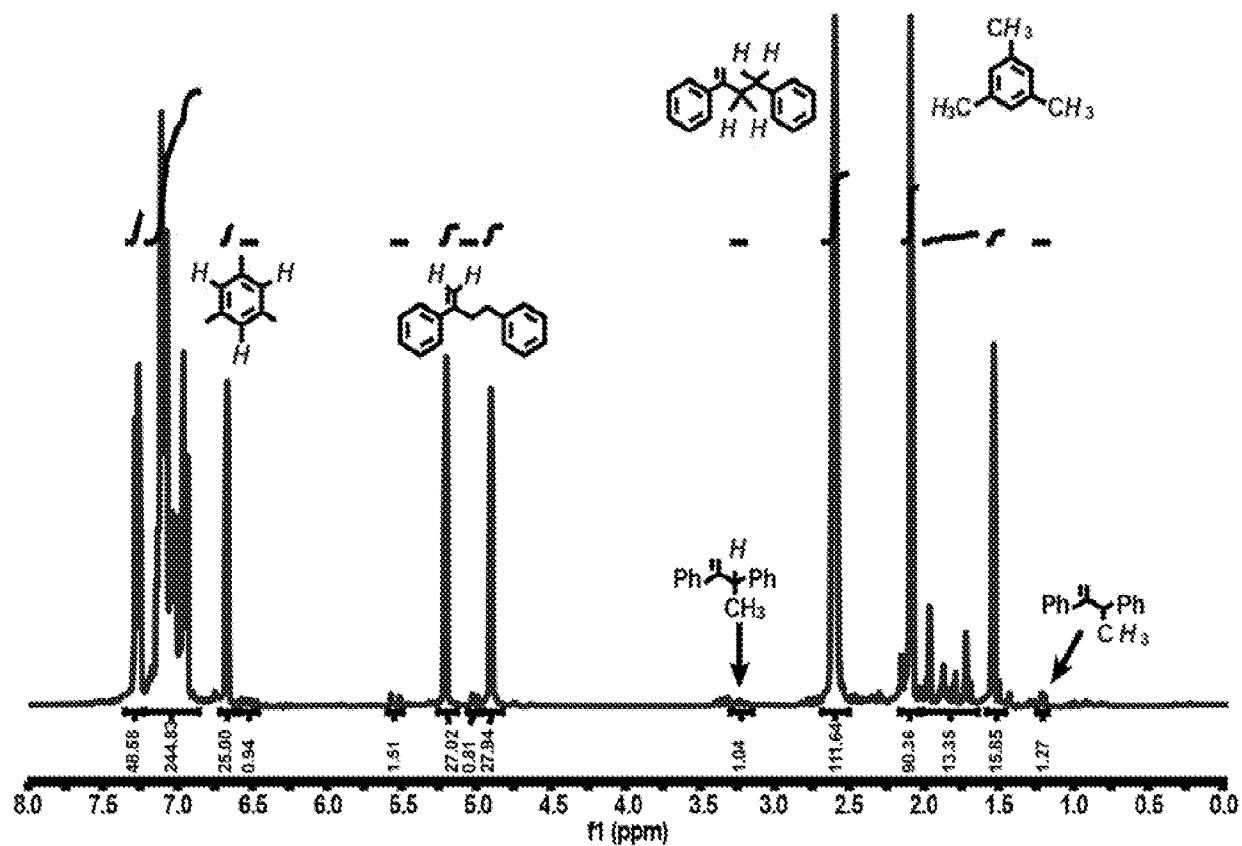


FIGURE 28

24 / 42

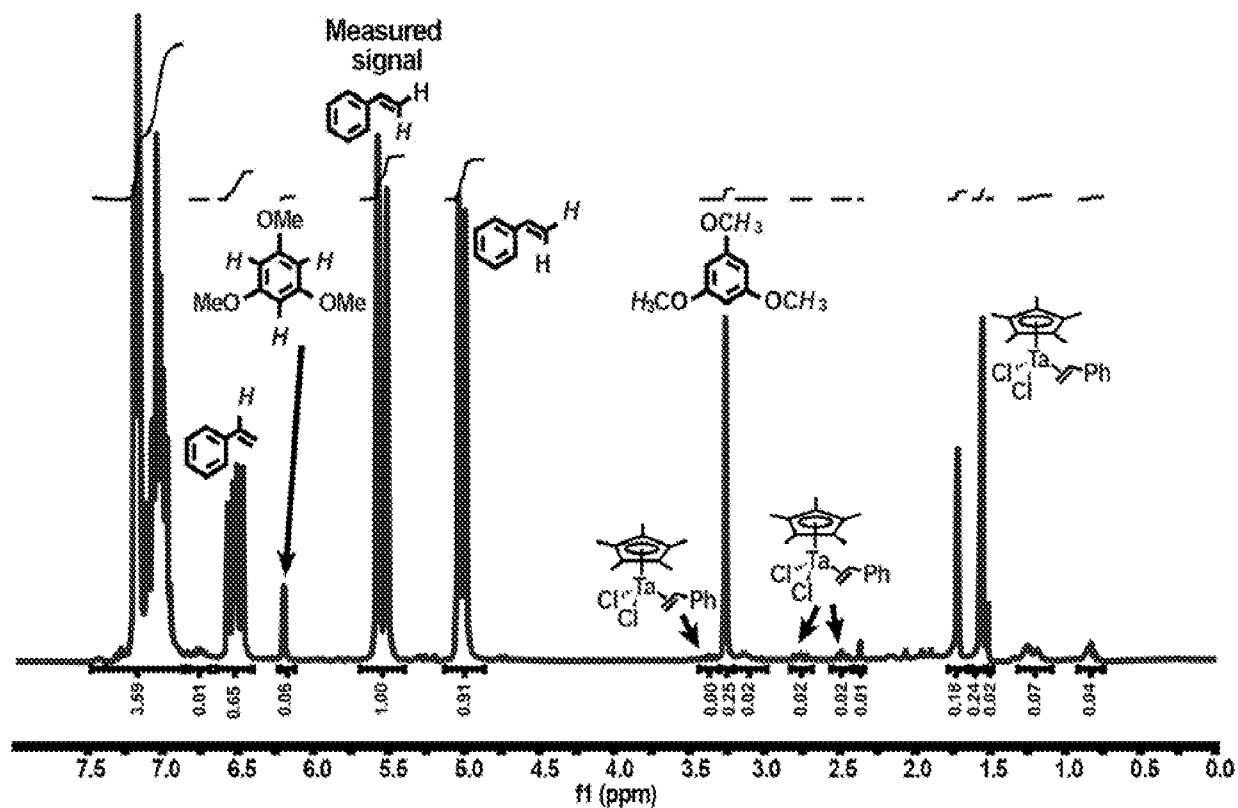


FIGURE 29

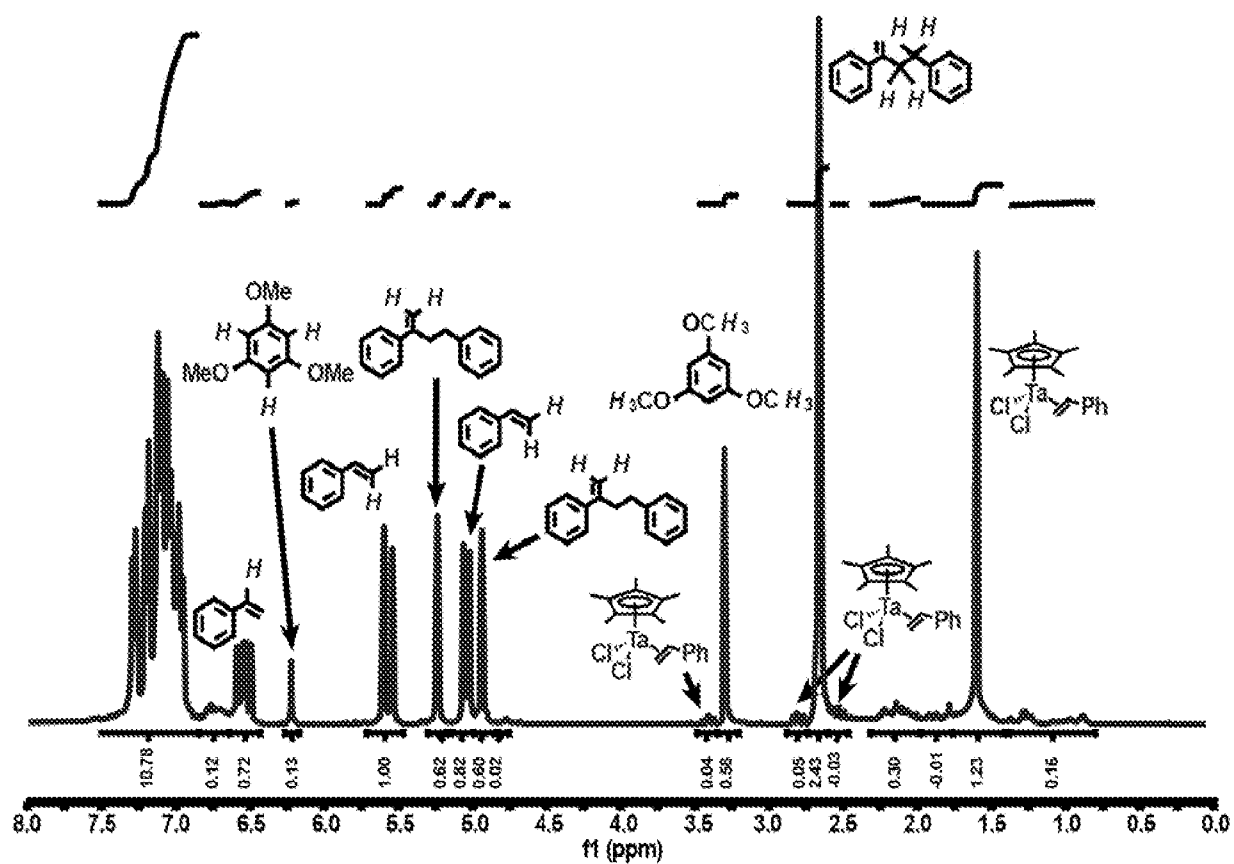


FIGURE 30

25 / 42

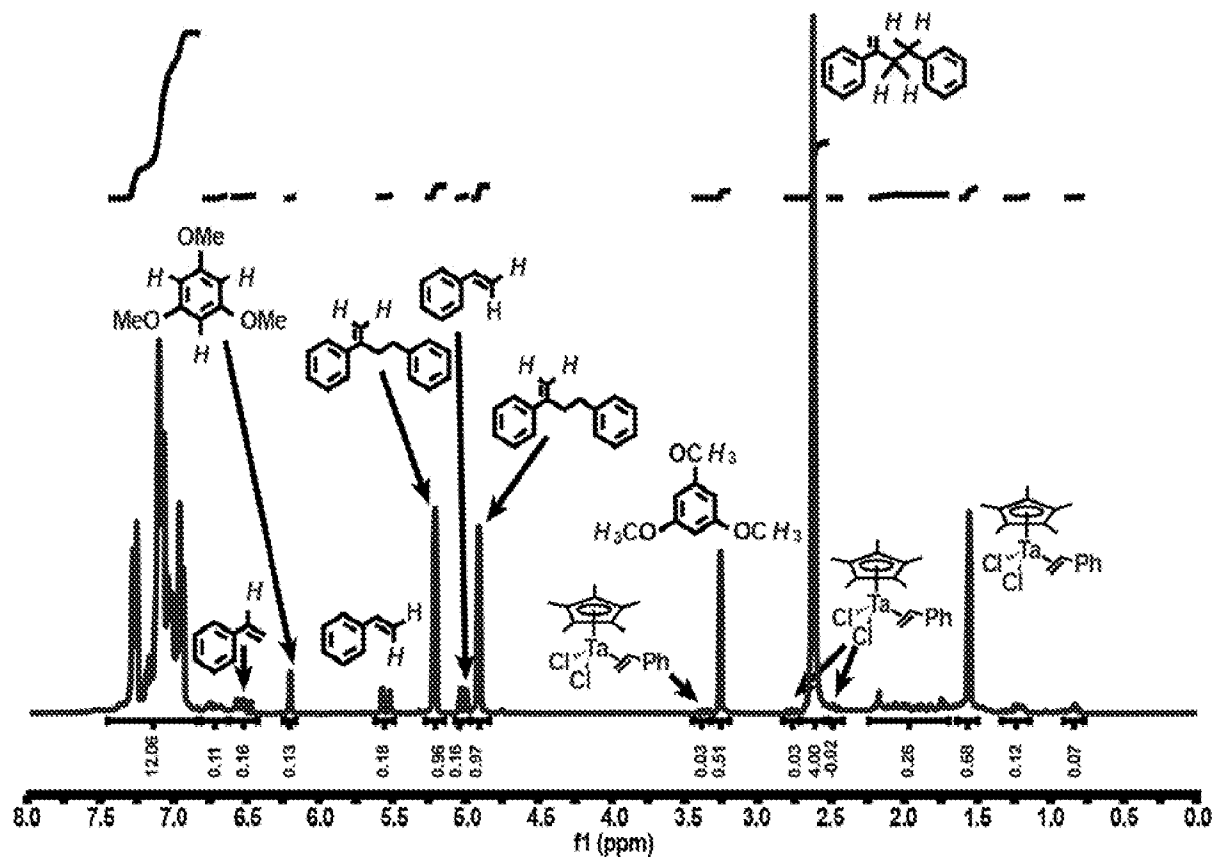


FIGURE 31

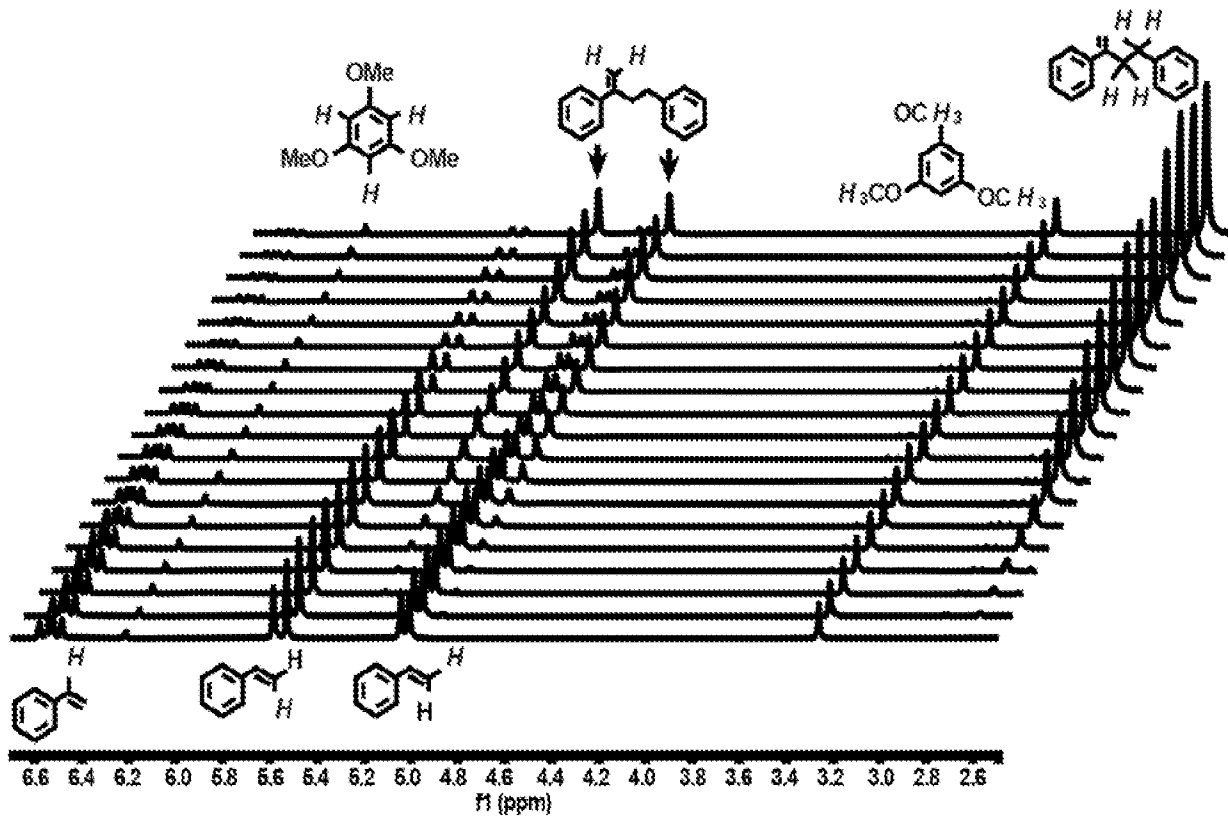


FIGURE 32

26 / 42

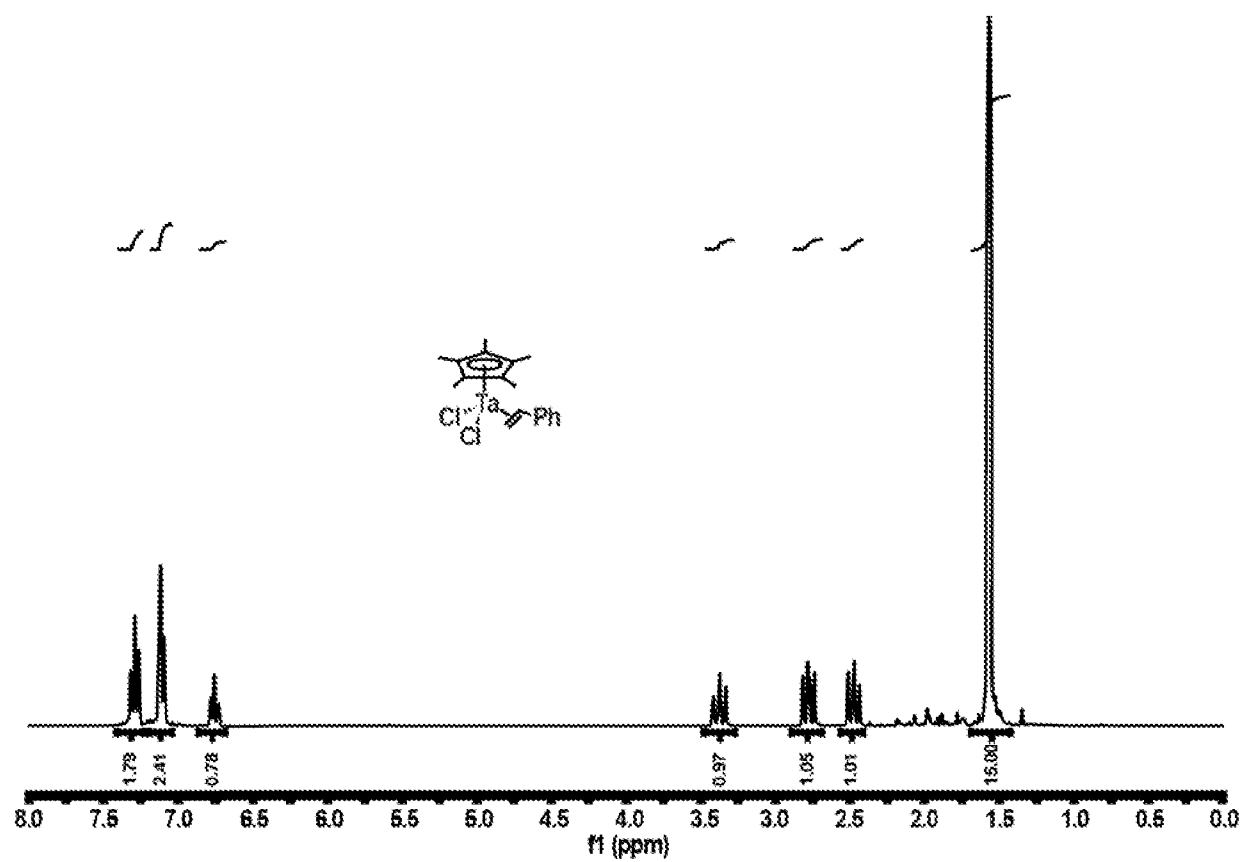


FIGURE 33

27 / 42

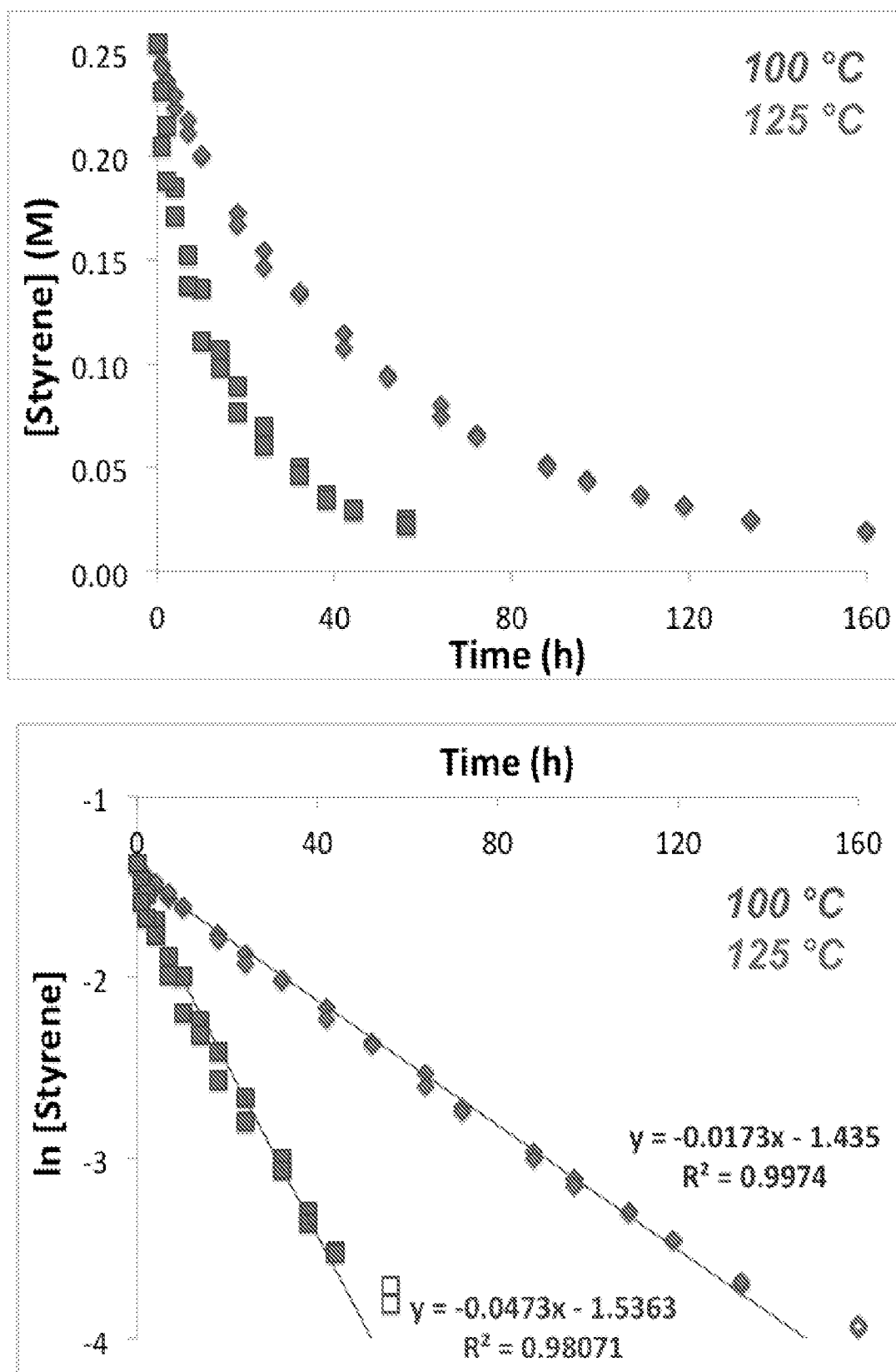


FIGURE 34

28 / 42

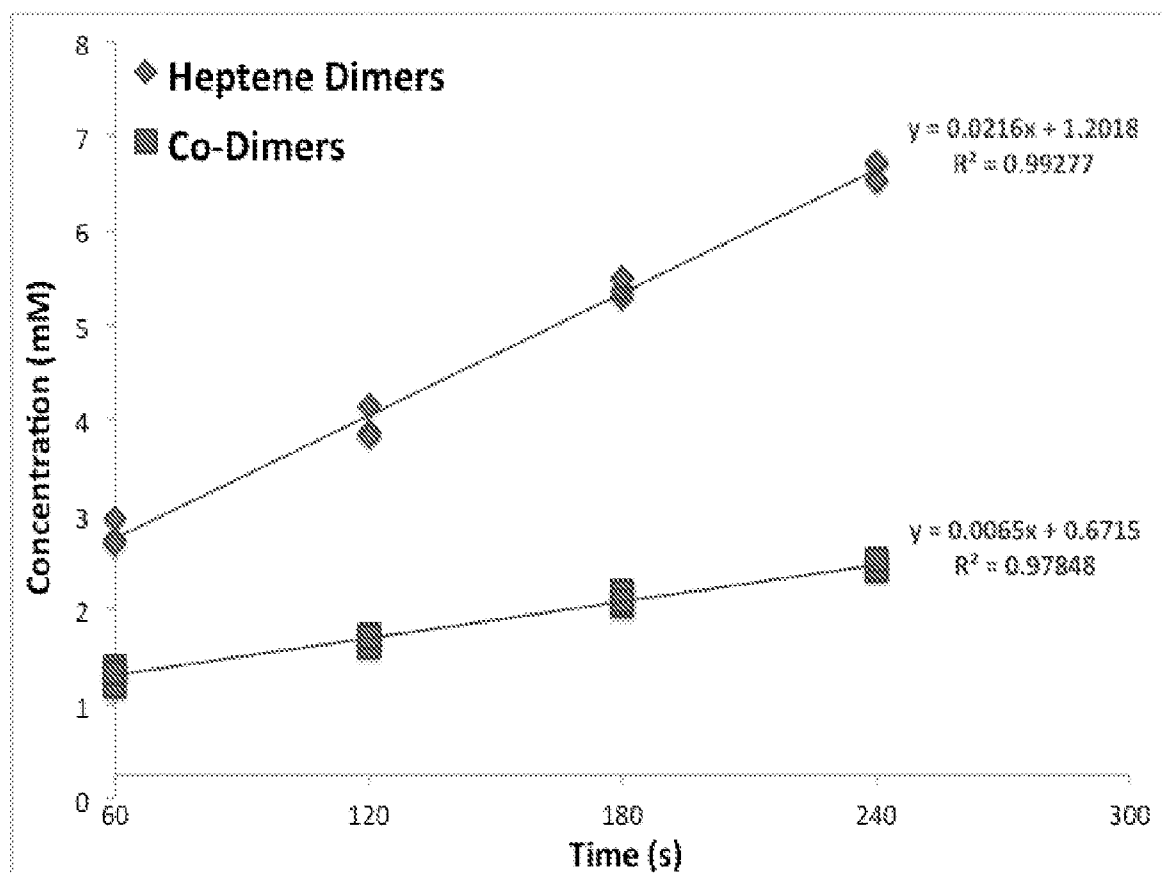


FIGURE 35

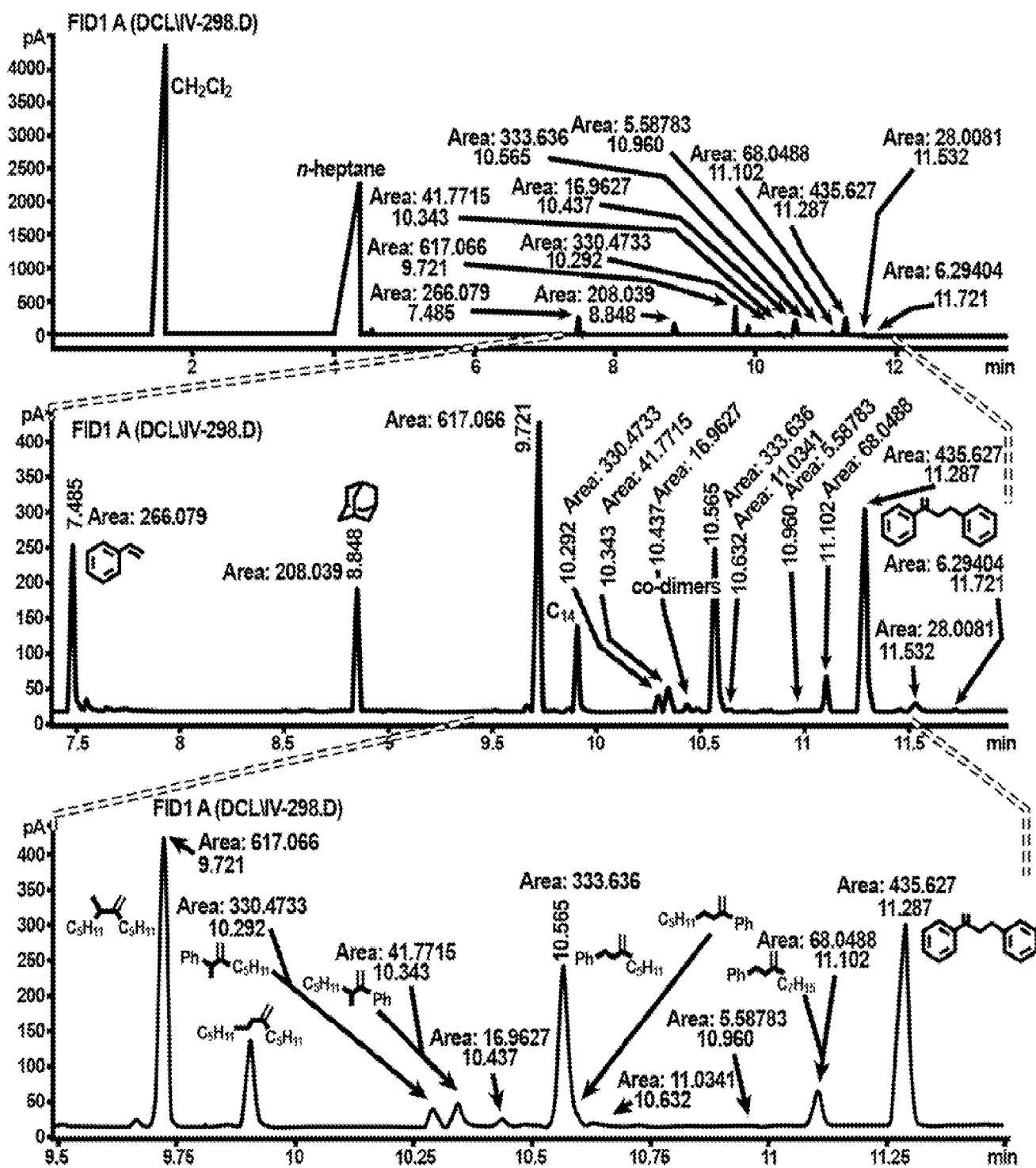


FIGURE 36

30 / 42

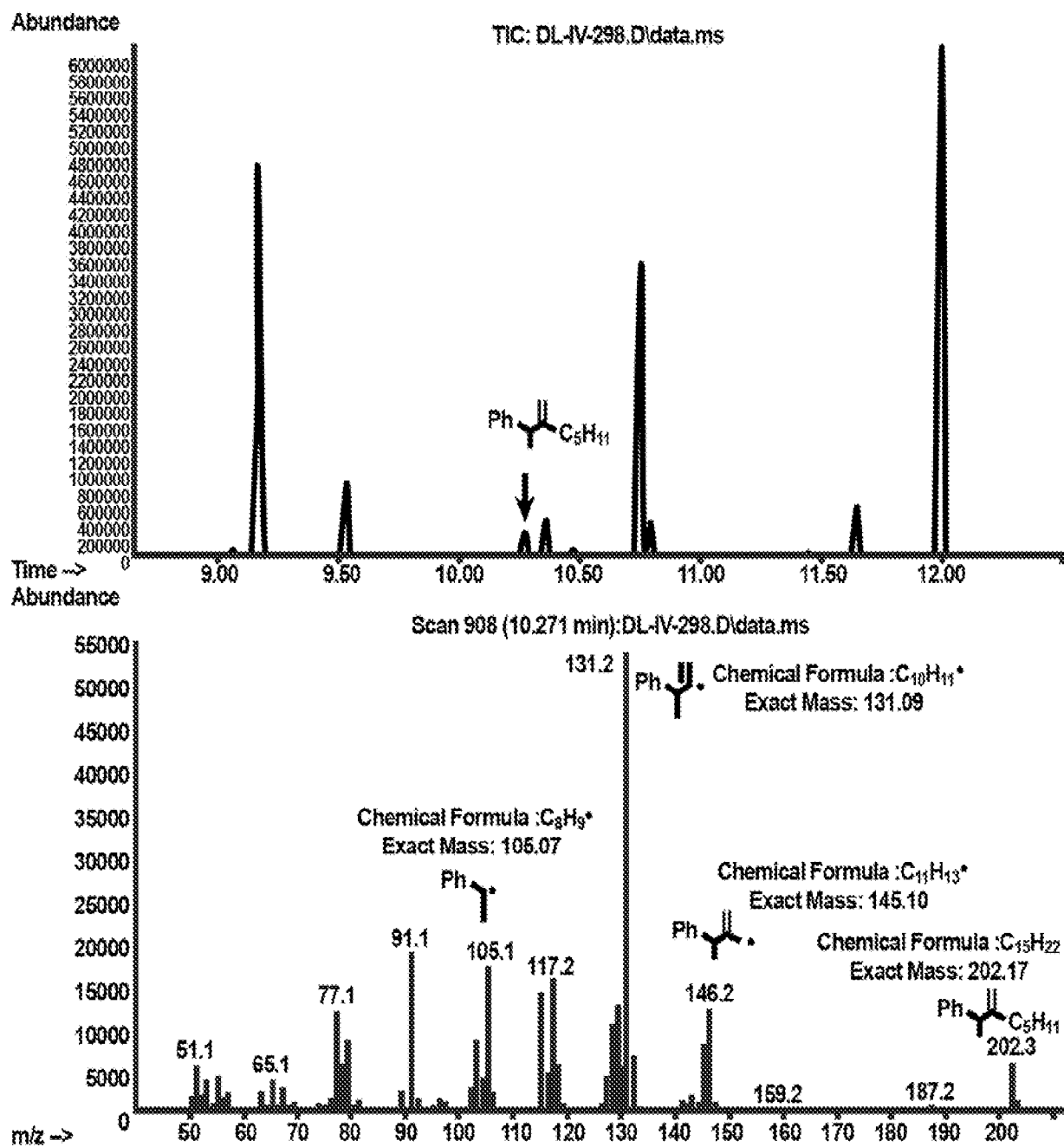


FIGURE 37

31 / 42

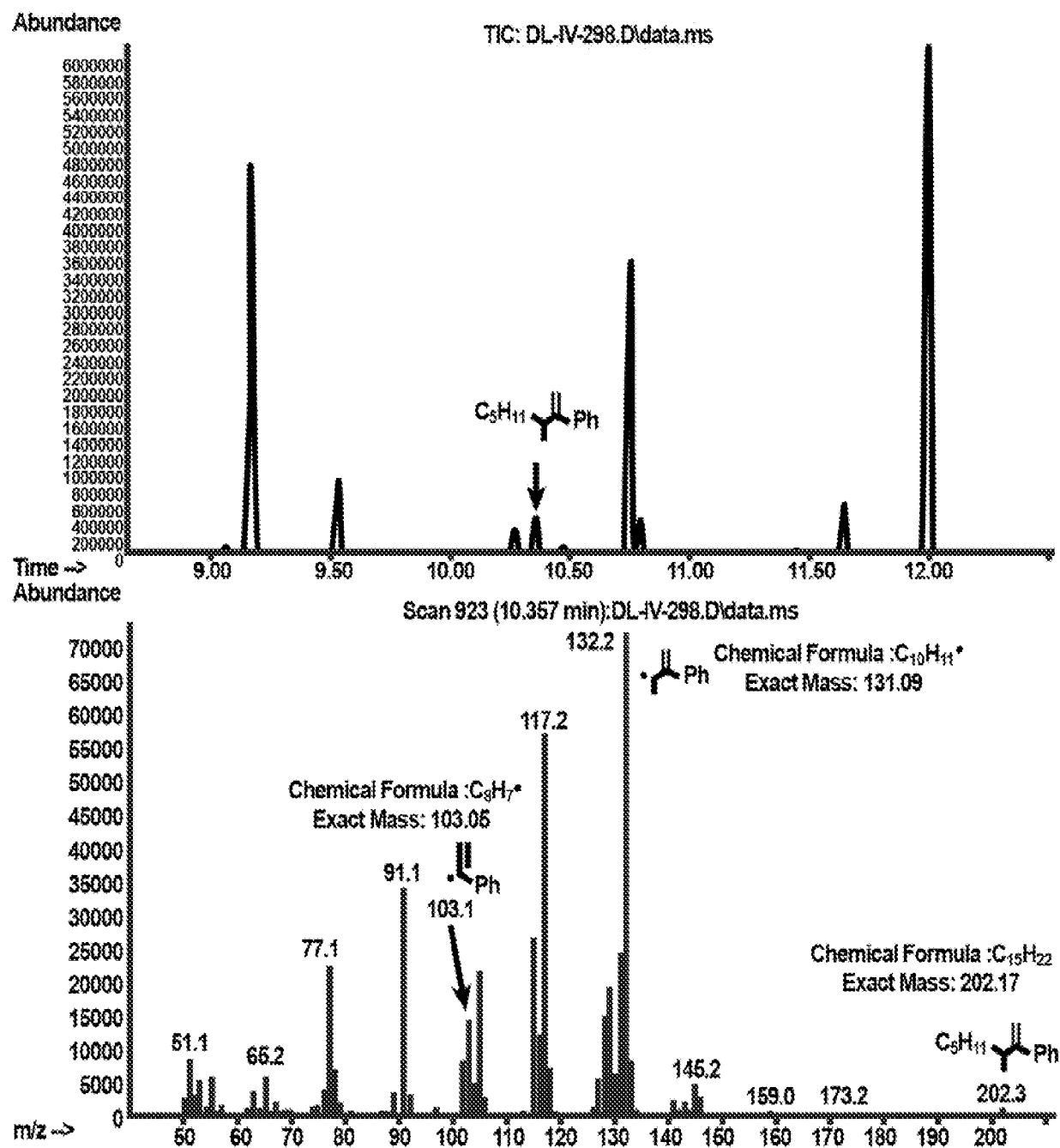


FIGURE 38

32 / 42

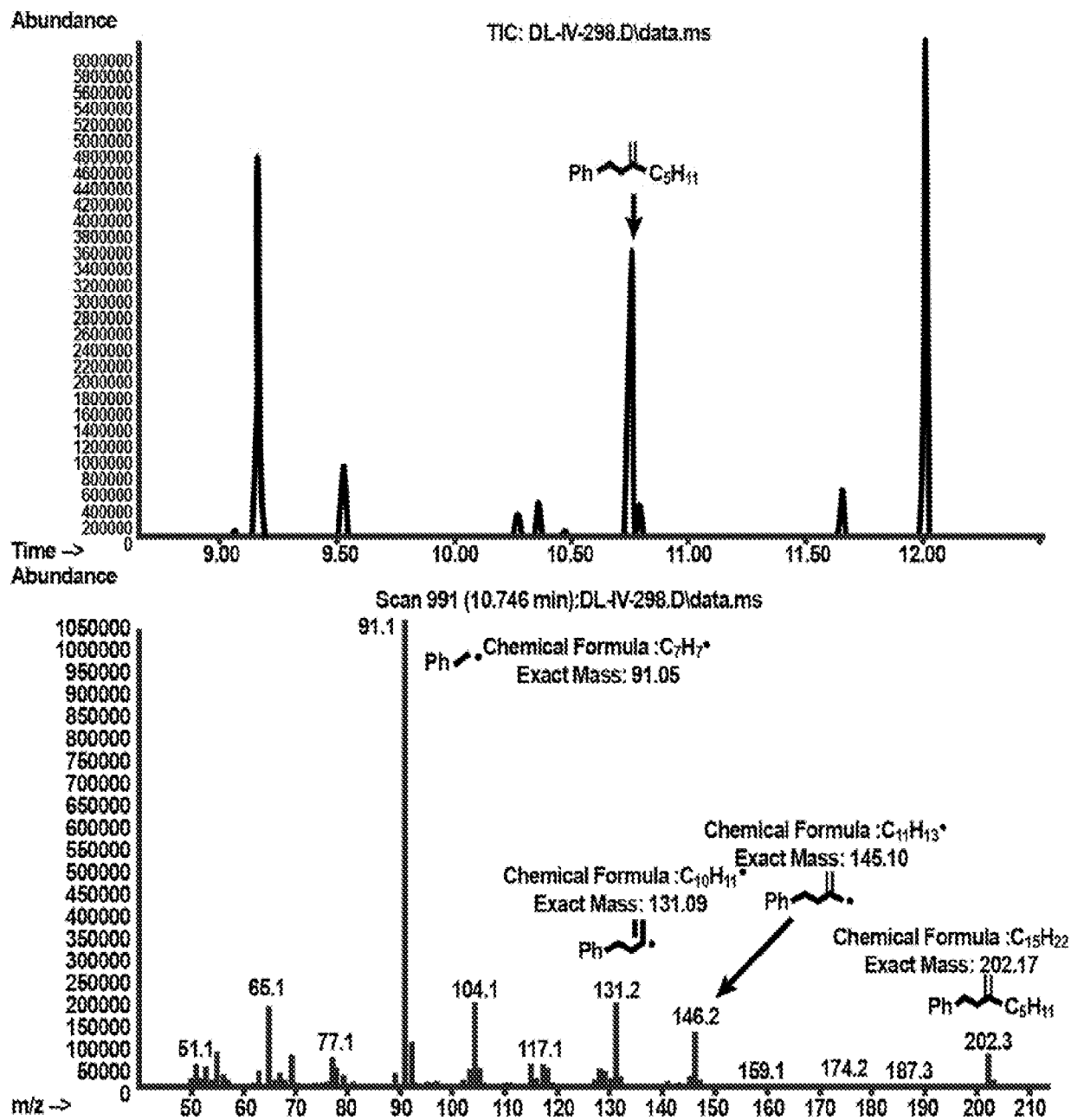


FIGURE 39

33 / 42

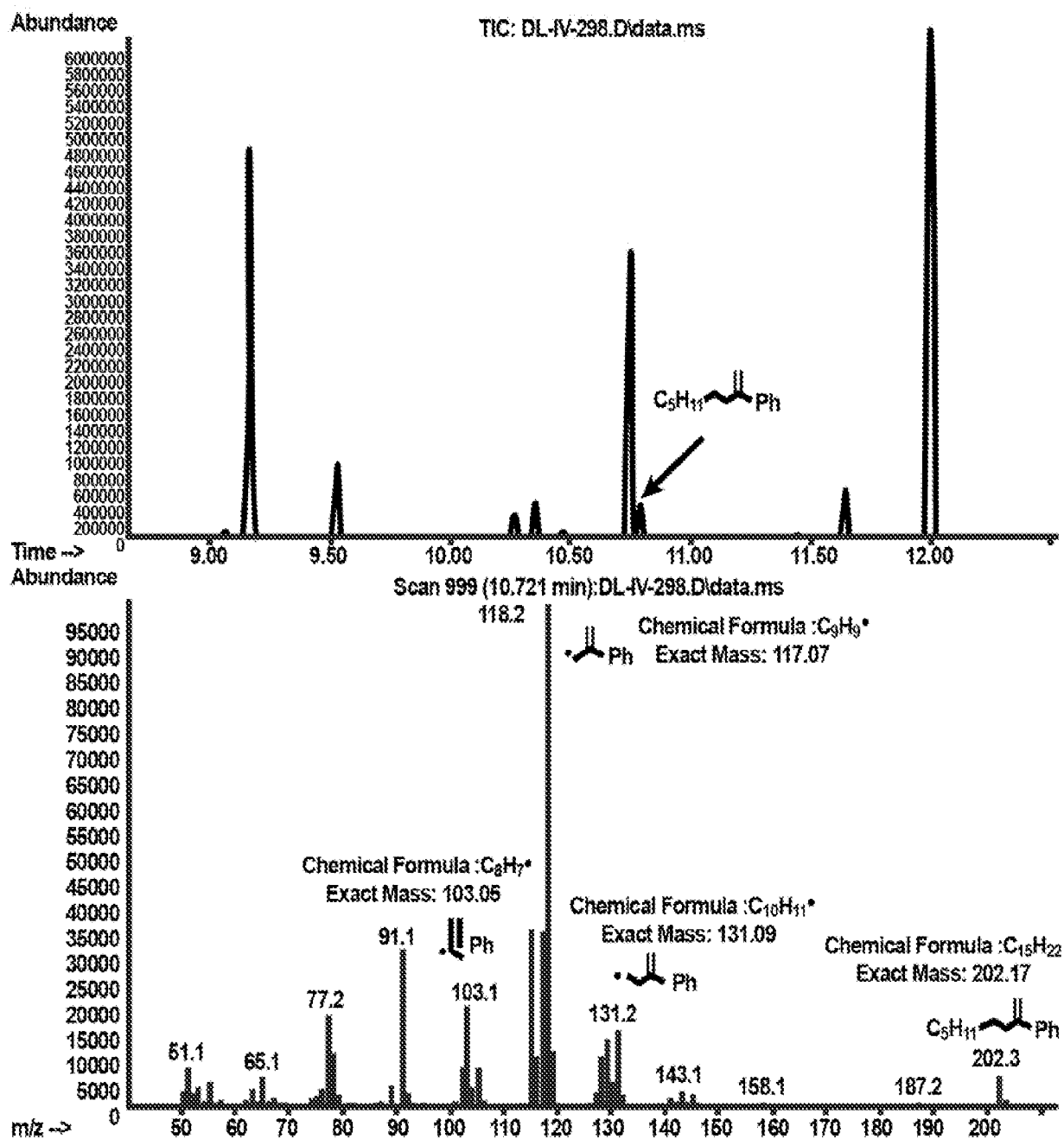


FIGURE 40

34 / 42

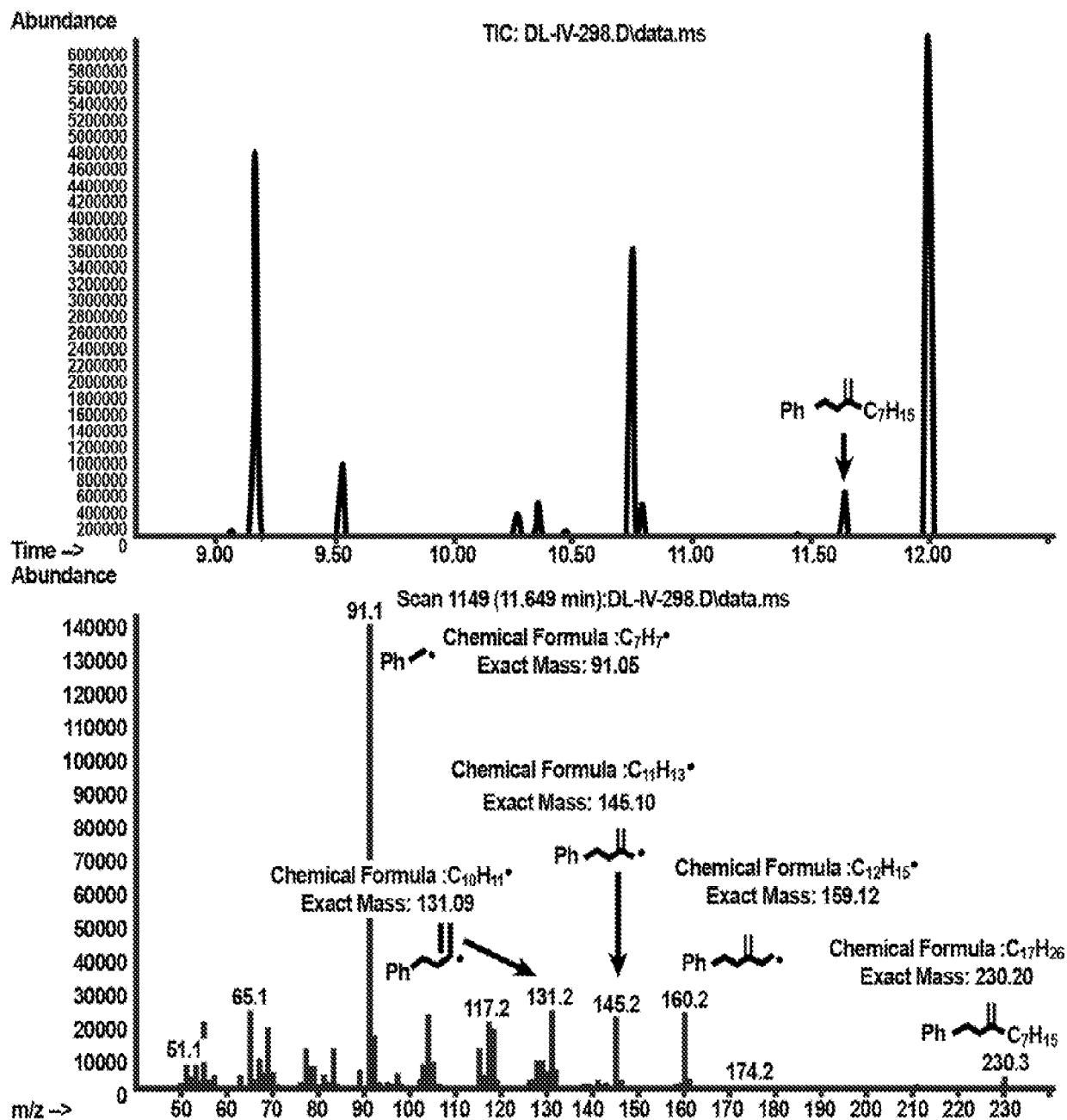


FIGURE 41

35 / 42

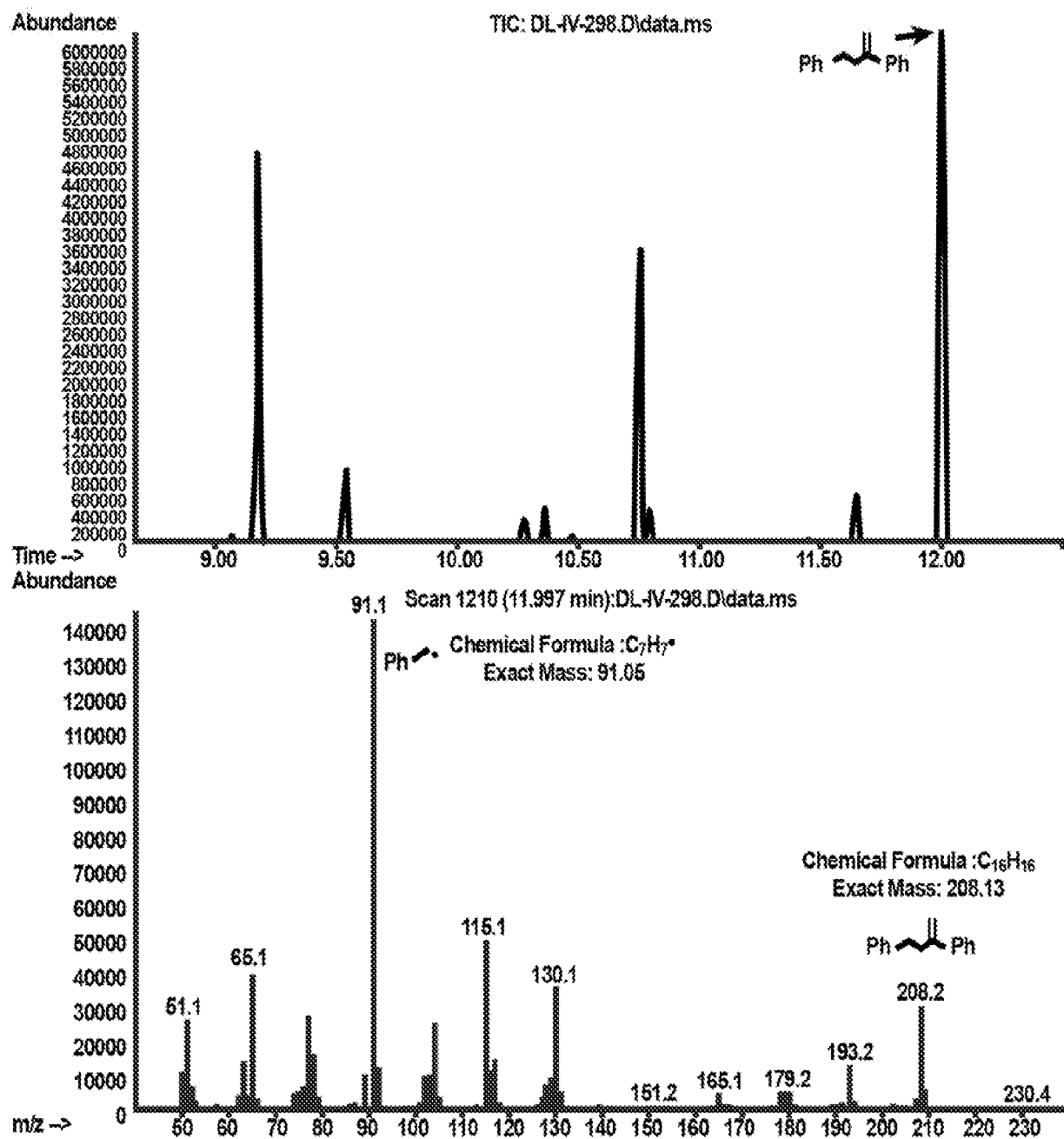


FIGURE 42

36 / 42

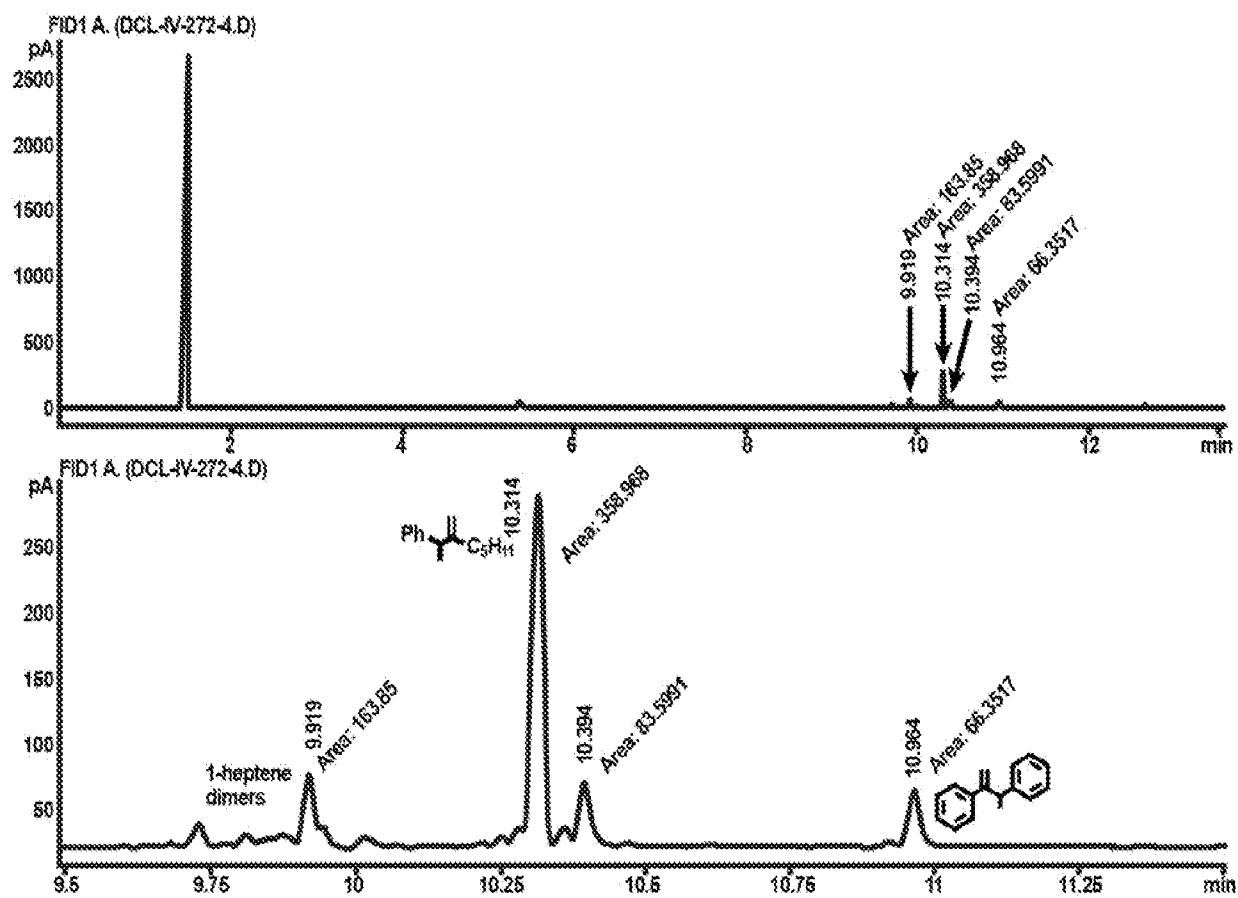


FIGURE 43

37 / 42

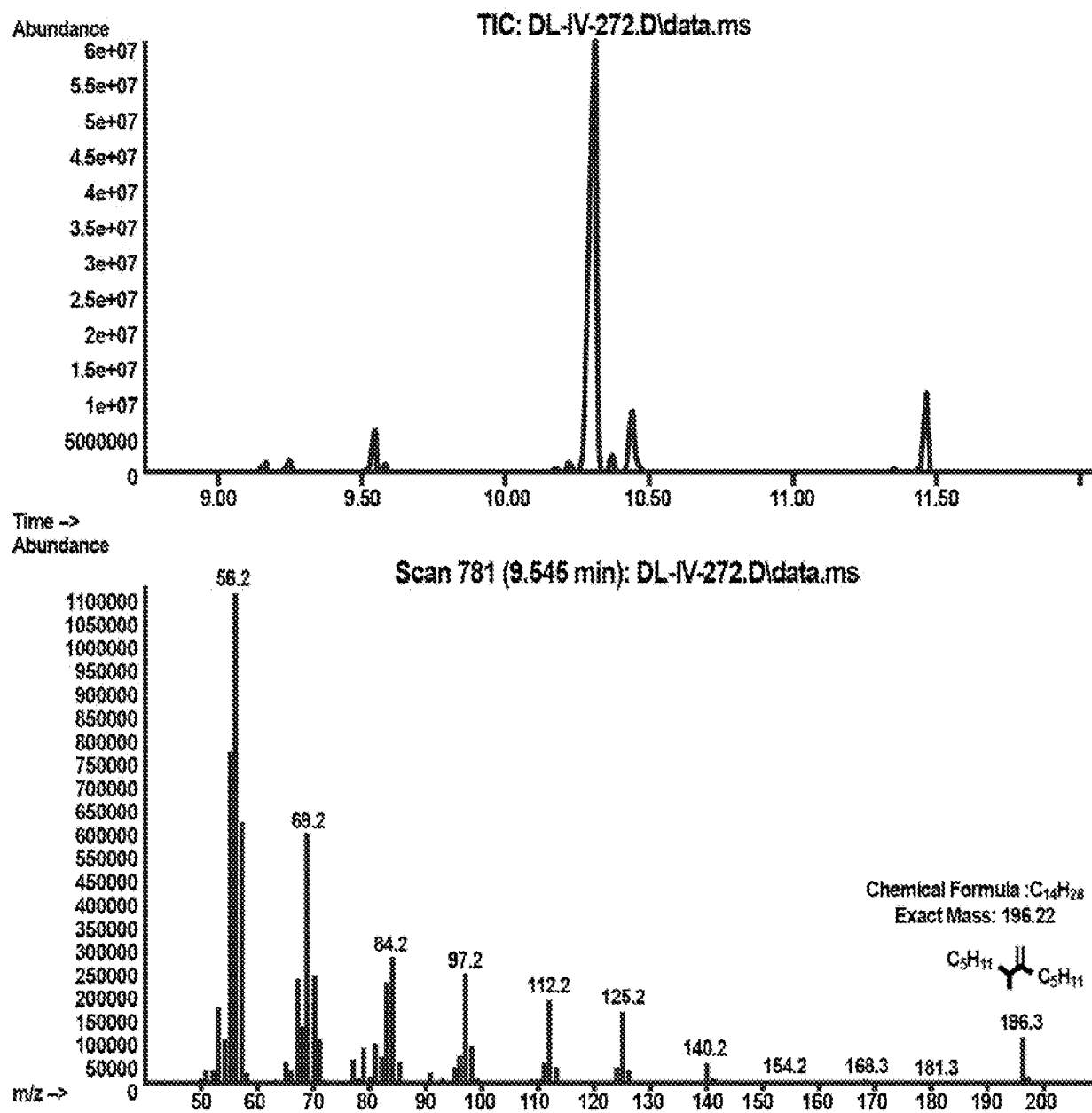


FIGURE 44

38 / 42

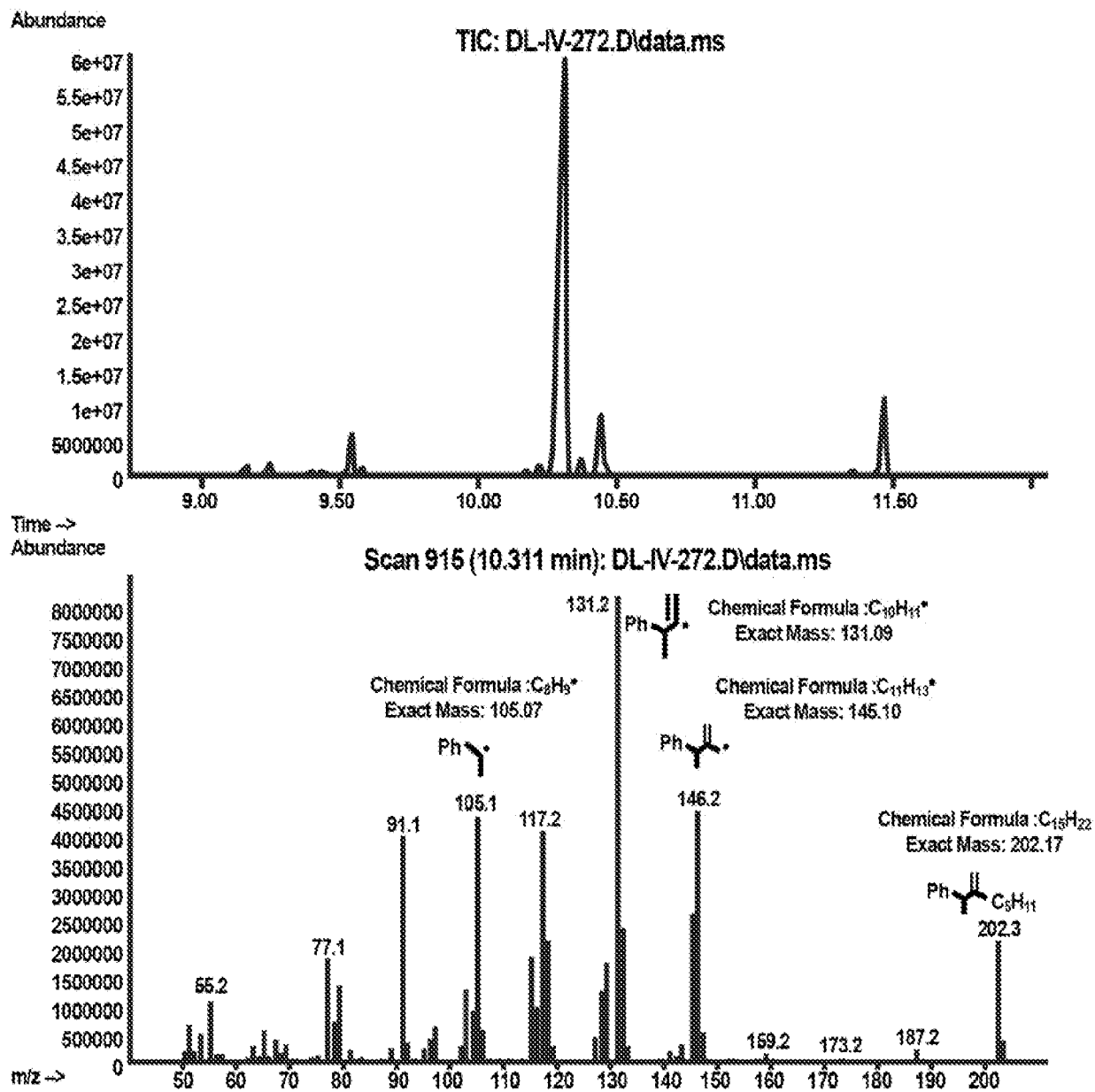


FIGURE 45

39 / 42

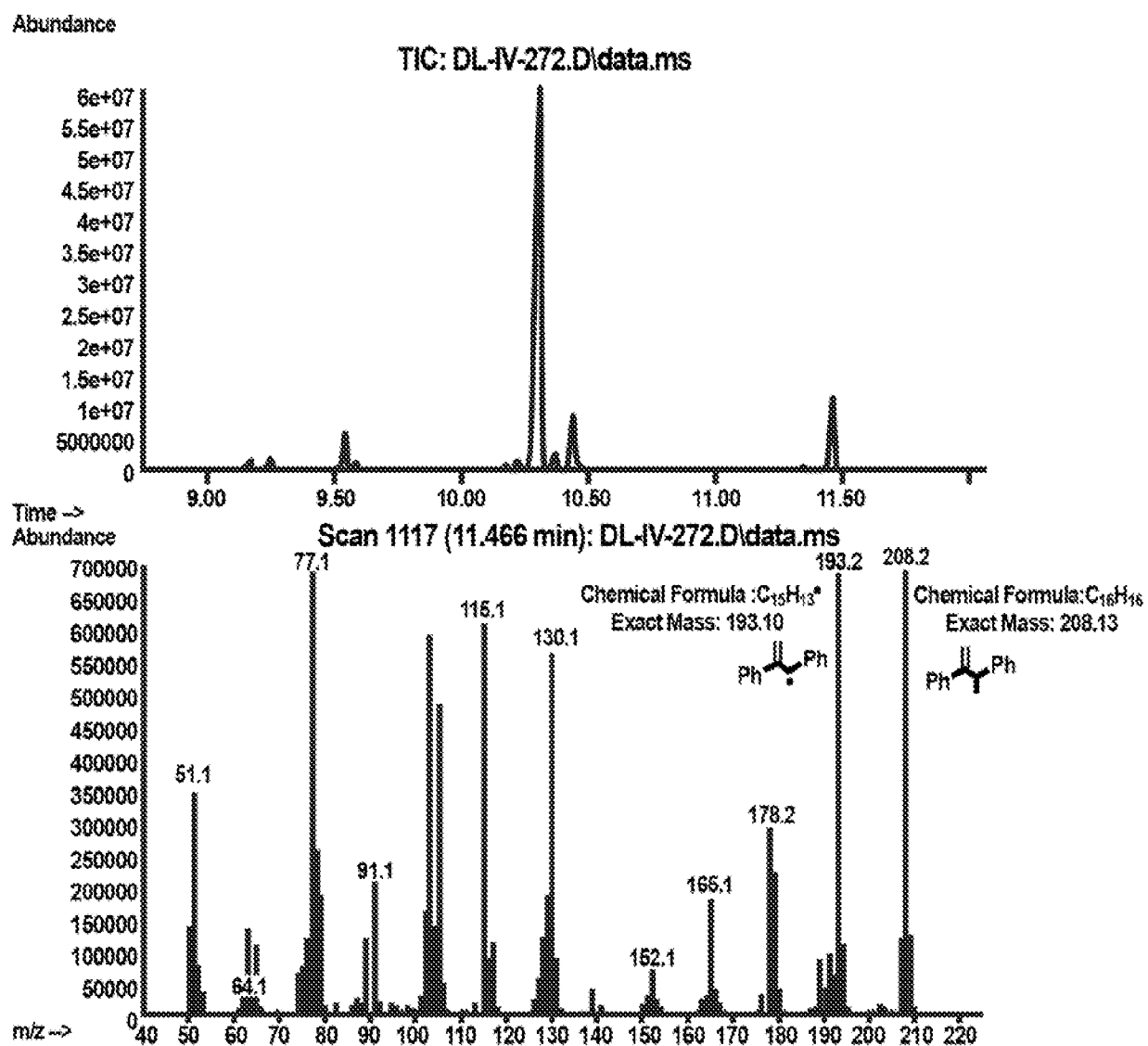


FIGURE 46

40 / 42

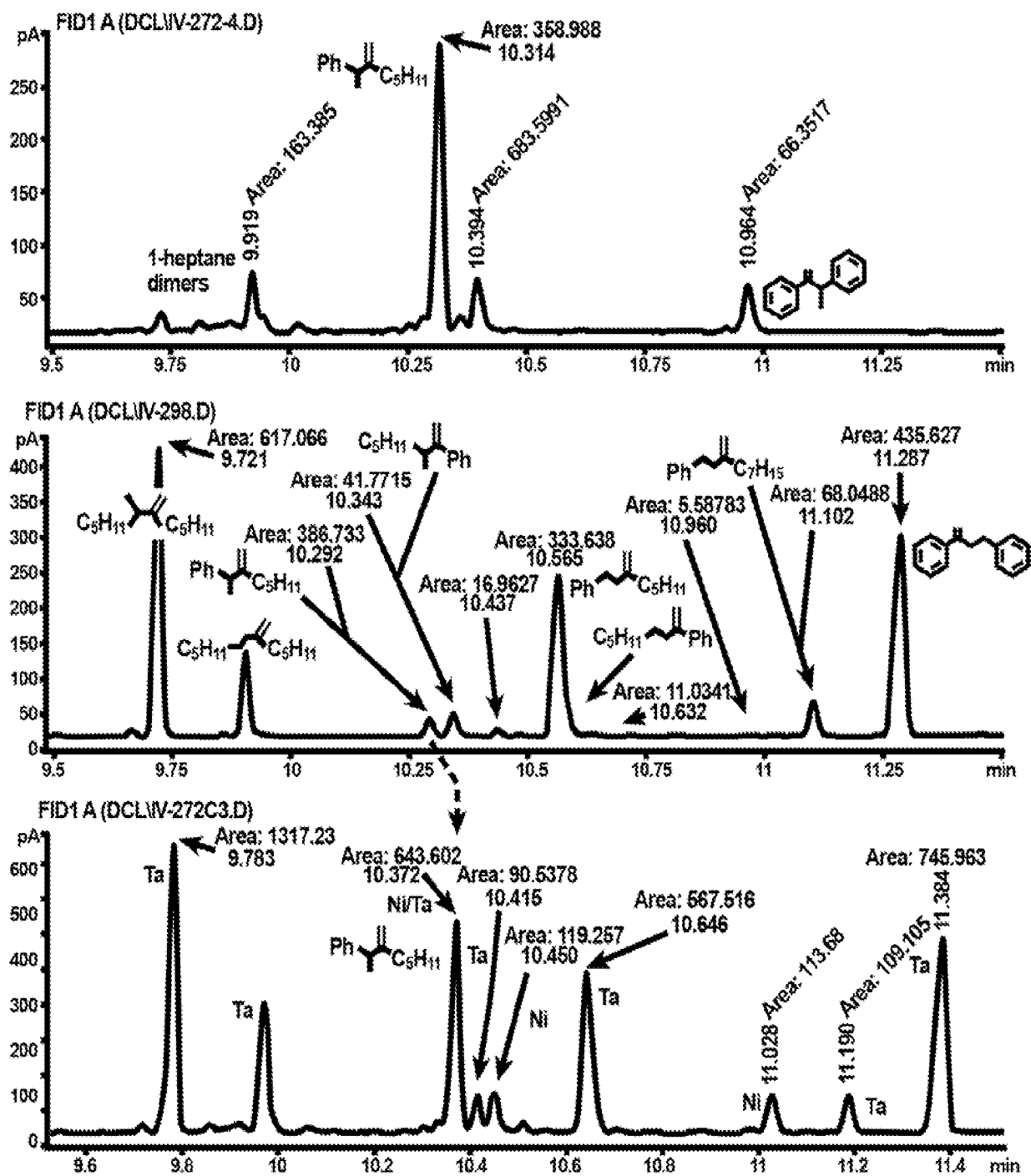


FIGURE 47

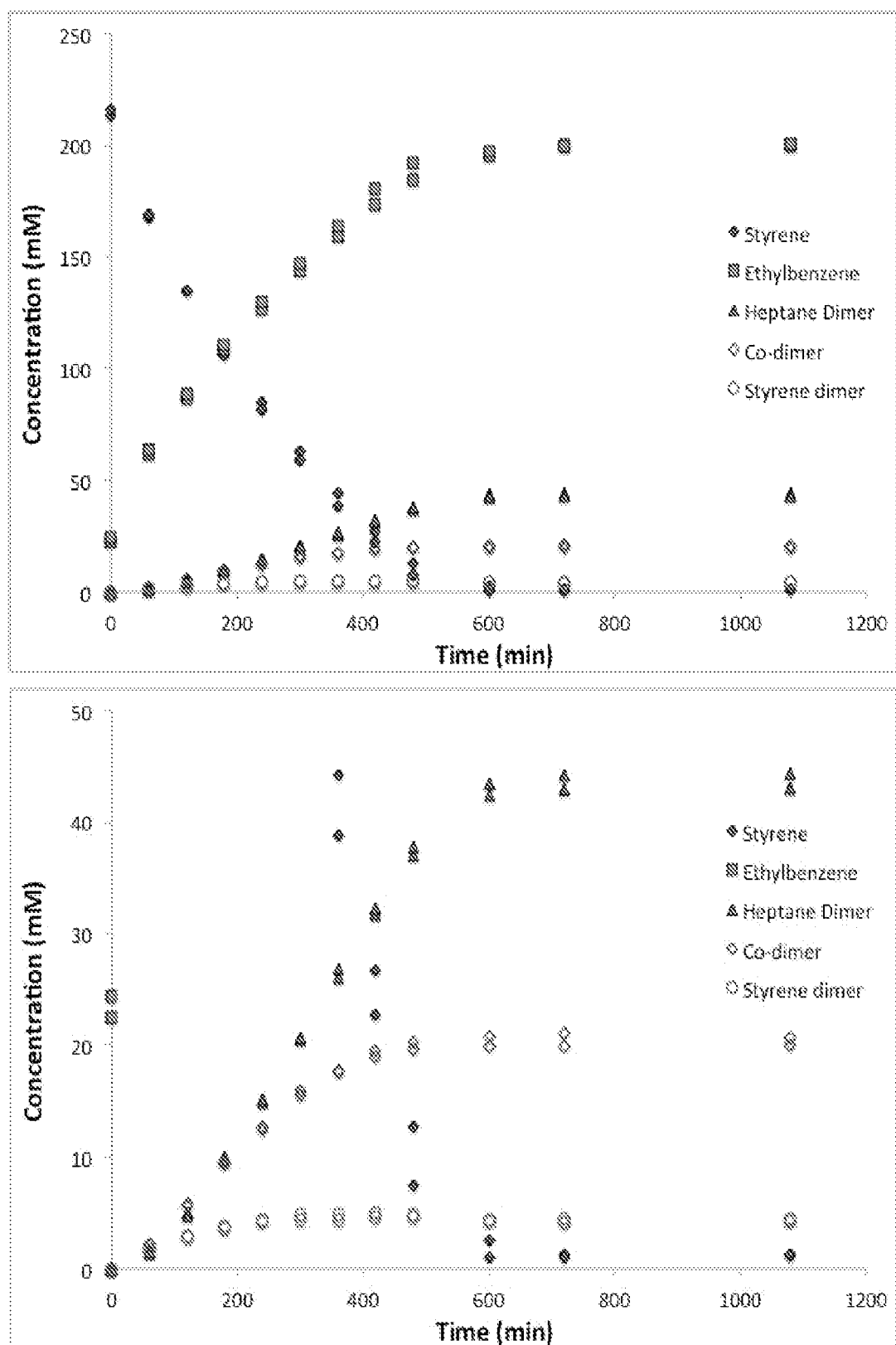


FIGURE 48

42 / 42

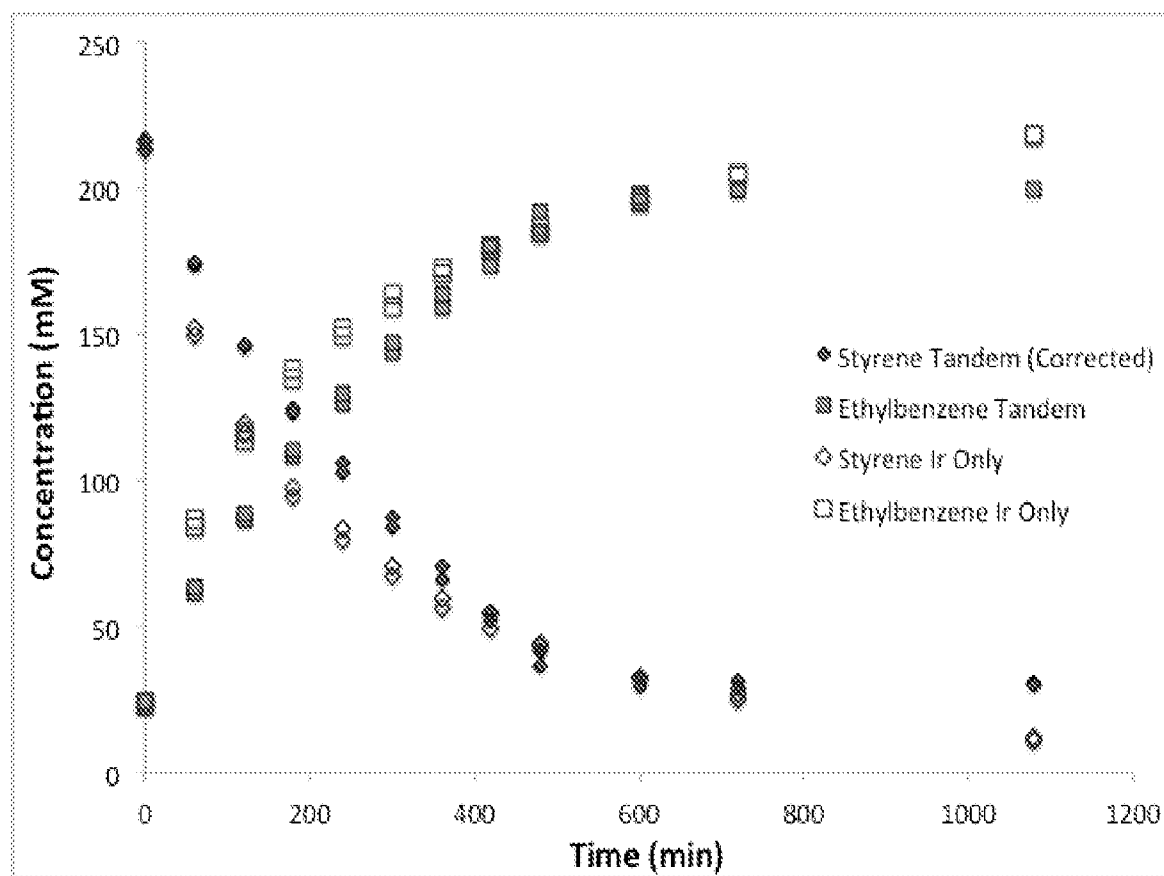


FIGURE 49

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/011992**A. CLASSIFICATION OF SUBJECT MATTER****C07C 7/20(2006.01)i, C07C 15/107(2006.01)i, B01J 31/22(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C 7/20; H01M 8/04; C07C 6/08; C07C 2/76; C07C 2/00; C07F 9/00; C07C 3/21; C07C 15/107; B01J 31/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: hydrocarbon production, hydrogenation, oligomerization, catalysis, alkane, alkene, tandem transfer hydrogenation and oligomerization

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2007-0060781 A1 (ALAN GOLDMAN et al.) 15 March 2007 See abstract; paragraphs [0035], [0044], [0052]; and claim 1.	1-4, 10-13
Y	US 04197419 A (SCHROCK, RICHARD R.) 08 April 1980 See abstract; claims 2, 8, 14 and 20.	1-4, 10-13
A	US 2010-0028735 A1 (BASSET JEAN MARIE et al.) 04 February 2010 See abstract.	1-4, 10-13
A	US 2011-0071331 A1 (BASSET JEAN-MARIE et al.) 24 March 2011 See abstract.	1-4, 10-13
A	US 2005-0272966 A1 (JEAN-MARIE BASSET et al.) 08 December 2005 See abstract.	1-4, 10-13
PX	DAVID C. LEITCH et al., 'Upgrading Light Hydrocarbons via Tandem Catalysis: A Dual Homogeneous Ta/Ir System for Alkane/Alkene Coupling', J. Am. Chem. Soc., 25 JUNE 2013, Vol.135, pp. 10302-10305 See abstract; and Scheme 1.	1-4, 10-13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 May 2014 (15.05.2014)

Date of mailing of the international search report

15 May 2014 (15.05.2014)

Name and mailing address of the ISA/KR

International Application Division
Korean Intellectual Property Office
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Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

KIM, Jong Ho

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2014/011992**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 6, 16, 18, 20, 26
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 6, 16, 18, 20, 26 are unsearchable because they are worded in reference to multiple dependent claims.
3. ☒ Claims Nos.: 5, 7-9, 14, 15, 17-19, 21-25
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/011992

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