(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 December 2024 (12.12.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/254526 A1

(51) International Patent Classification:
C10G 47/02 (2006.01) *B01J 31/16* (2006.01)

(21) International Application Number:
PCT/US2024/033107

(22) International Filing Date:
07 June 2024 (07.06.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/472,212 09 June 2023 (09.06.2023) US

(71) Applicant: **THE REGENTS OF THE UNIVERSITY OF CALIFORNIA** [US/US]; 1111 Franklin Street, Twelfth Floor, Oakland, California 94607 (US).

(72) Inventors; and
(71) Applicants: **CONLEY, Matthew** [US/US]; 900 University Ave., Riverside, California 92521 (US). **SAMUDRALA, Kavyasripriya** [US/US]; 900 University Ave., Riverside, California 92521 (US).

(74) Agent: **NIU, Lin** et al.; Viksnins Harris Padys Malen LLP, 7900 International Drive, Suite 410, Bloomington, Minnesota 55425 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2024/254526 A1

(54) Title: CATALYSTS AND HYDROGENOLYSIS METHODS THEREOF

(57) Abstract: Certain embodiments of the invention provide a method of digesting polyolefin (e.g., polypropylene) using a catalyst described herein, such as hafnium-based cation compound supported on a Lewis acidic silica.

CATALYSTS AND HYDROGENOLYSIS METHODS THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority to United States Provisional Application Number 63/472,212 that was filed on June 9, 2023. The entire content of the application referenced above is hereby incorporated by reference herein.

GOVERNMENT FUNDING

This invention was made with government support under DE-SC0022203 awarded by the Department of Energy. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

Olefin polymerization reactions are the foundation of the plastics economy and produce millions of tons of highly versatile polyethylene or polypropylene products per year. Most polyolefins reach end-of-life as unrecyclable waste. New catalysts and methods for digesting waste plastic into smaller aliphatic fragments capable of further value-added processing are needed.

SUMMARY OF THE INVENTION

Certain embodiments of the invention provide a method of metabolizing a polymer (e.g., polyolefin) into fragments using a catalyst described herein.

Certain embodiments of the invention provide a compound described herein.

Certain embodiments of the invention provide a composition described herein. For example, in certain embodiments, the composition comprises a compound described herein and a support, wherein the compound is grafted on the support. In certain embodiments, the composition comprises:

a) Cp_2M^+R cation, wherein R is C_1-C_6 alkyl, M is Hf or Zr, and Cp is cyclopentadienyl ligand that is optionally substituted with one or more alkyl, wherein the two cyclopentadienyl ligands are optionally linked by a linker (e.g., $Si(CH_3)_2$, or $-(CH_2)_m-$ wherein m is 1, 2, or 3), and;

b) a support comprising aluminum and silica oxide.

Certain embodiments of the invention provide a catalyst compound or composition described herein.

Certain embodiments of the invention provide the use of a catalyst compound or composition described herein for metabolizing a polymer (e.g., polyolefin).

Certain embodiments of the invention provide a mixture described herein.

Certain embodiments of the invention provide a method described herein.

Certain embodiments of the invention provide a method of polymerizing olefin (e.g., propylene) into polymer using a catalyst described herein.

BRIEF DESCRIPTION OF THE FIGURES

Figures 1A-1C. Supported d^0 metal hydrides showing activity in C-C hydrogenolysis reactions. Zr–H supported on SiO_2/Al_2O_3 (Fig.1a). Ta–H supported on silica (Fig.1b). Ta–H^+ sites supported on sulfated aluminum oxide (Fig.1c).

Figures 2A-2B. Reaction of $Cp_2Hf(CH_3)_2$ and $\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2)$ to form $[Cp_2Hf–CH_3][\equiv SiOAl(OC(CF_3)_3)_2(CH_3)]$ (**1**), $Cp_2Hf(^{13}CH_3)(OSi\equiv)$ (**2**), and $[Cp_2Hf(OSi\equiv)][\equiv SiOAl(OC(CF_3)_3)_2(CH_3)]/\equiv Si–^{13}CH_3$ (**3**) (Fig.2a). $^{13}C\{^1H\}$ CPMAS NMR spectrum of the reaction products recorded at 10 kHz spinning speed (Fig.2b).

Figure 3. Quantitative $^{13}C\{^1H\}$ NMR spectra shown from 10 – 50 ppm for oils produced in hydrogenolysis reactions. End groups are highlighted for clarity.

Figure 4. Proposed steps explaining product selectivity in hydrogenolysis of iPP catalyzed by **1**.

Figure 5. An exemplary supported Ziegler-type organohafnium site metabolizes polypropylene.

Figures 6A-6B. Steps involved in a formal 3,1-insertion of propylene during polymerization reactions (Fig.6a). Regioirregular error formation under hydrogenolysis conditions (Fig.6b).

Figure 7. Exemplary schematic graph of certain catalyst composition.

Figure 8. FT-IR spectrum of $Cp_2HfMe_2/\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2)$.

Figure 9. 10kHz MAS ^1H NMR of $Cp_2HfMe_2/\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2)$ acquired at -20°C. Probe background signals are labeled with an "x," spinning sidebands are labeled with a *.

Figure 10. $^{27}Al\{^1H\}$ MAS NMR spectrum of $Cp_2HfMe_2/\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2)$ recorded at 10 kHz spinning speed.

Figure11. FT-IR spectrum of **2** wavenumbers (cm^{-1}).

Figure 12. ^1H NMR of **2** acquired at -20°C and 10 kHz spinning speed. Probe background signals are labeled with an "x," spinning sidebands are labeled with a *.

Figure 13. $^{13}C\{^1H\}$ CPMAS NMR of **2** acquired at -20°C at 10 kHz spinning speed. Spinning sidebands are labeled with a *.

Figure 14. Stacked plot of the $^{13}C\{^1H\}$ CPMAS NMR spectrum of

Cp_2HfMe_2/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$ (top) and **2** (bottom).

Figure 15. GC of the gas phase of iPP hydrogenolysis reactions with Cp_2HfMe_2/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$ under 1 atm H_2 (H_2:Hf ~ 100). The amounts gases are reported in the main text.

Figure 16. GC of the gas phase of iPP hydrogenolysis reactions with Cp_2HfMe_2/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$ under 1 atm D_2 (D_2:Hf ~ 100). The amounts gases generated in this reaction are essentially identical to those reported in the main text.

Figure 17. GC of the gas phase of iPP hydrogenolysis reactions with Cp_2HfMe_2/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$ under 1 atm H_2 (H_2:Hf ~ 1500). The amounts of gas evolved are 1.8 CH_4 Hf^{-1}, 0.4 C_2H_6 Hf^{-1}, 1.35 C_3H_6 Hf^{-1} and 9.9 C_4H_{10} Hf^{-1}, and 9.3 C_5H_{10} Hf^{-1}. The total yield of light gases are 11.5 % (23 mg) based on this data.

Figure 18. GC of the gas phase of iPP hydrogenolysis reactions with Cp_2ZrMe_2/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$ under 1 atm H_2 (H_2:Zr ~ 1500). The amounts of gas evolved are 1.1 CH_4 Hf^{-1}, 1.6 C_2H_6 Zr^{-1}, 1.0 C_3H_6 Zr^{-1} and 6.7 C_4H_{10} Zr^{-1}, and 4.9 C_5H_{10} Zr^{-1}. The total yield of light gases are 7 % (14 mg) based on this data.

Figure 19. Representative MALDI MS of the oils obtained from hydrogenolysis of iPP with H_2:Hf ~ 100.

Figure 20. Representative MALDI MS of the oils obtained from hydrogenolysis of iPP with D_2:Hf ~ 100.

Figure 21. Representative MALDI MS of the oils obtained from hydrogenolysis of iPP with H_2:Hf ~ 1500.

Figure 22. Representative MALDI MS of the oils obtained from hydrogenolysis of iPP under 2 atm H_2.

Figure 23. Representative MALDI MS of the oils obtained from hydrogenolysis of iPP under 5 atm H_2.

Figure 24. ^1H NMR spectra of extracted oils recorded in C_6D_6 at ambient temperature. The pressures in the figure correspond to the H_2 pressure used for the hydrogenolysis reaction.

Figure 25. ^2H NMR of extracted oil recorded in $CHCl_3$ at ambient temperature. The oil in this spectrum was generated at D_2:Hf ~ 100.

Figure 26. ^2H NMR spectrum of residual iPP after reaction with **1** and D_2. Signals for each C–D are given in the figure. The chemical shifts for $CH_3CH_2CD_2$=CDC(CH_3)P are from *J. Am. Chem. Soc.* **1998,** *120,* 2308-2321.

Figure 27. Quantitative $^{13}C\{^1H\}$ NMR spectrum of the residual polymer melt from the hydrogenolysis of iPP with Cp_2HfMe_2/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$ at 1atm, collected at 120°C in $C_2D_2Cl_4$.

Figure 28. ^{1}H NMR spectrum of the residual polymer melt from the hydrogenolysis of iPP with Cp_2HfMe_2/≡SiOAl(OC(CF$_3$)$_3$)$_2$(O(Si≡)$_2$) at 1atm, collected at 120°C in $C_2D_2Cl_4$.

Figure 29. An exemplary experimental setup.

Figure 30. GC data of oils produced with Cp_2HfMe_2/≡SiOAl(OC(CF$_3$)$_3$)$_2$(O(Si≡)$_2$) under the pressures given in the figure (bottom three chromatograms). The top chromatogram is a mixture of alkanes produced from alkane metathesis reactions of tetradecane with a different catalyst (see: Gao, J.; Zhu, L.; Conley, M. P. Cationic Tantalum Hydrides Catalyze Hydrogenolysis and Alkane Metathesis Reactions of Paraffins and Polyethylene. J. Am. Chem. Soc. 2023, 145, 4964-4968). The top chromatogram contains linear the C_n listed in the figure to show where linear alkanes appear with this method. Also apparent in this top chromatogram is the flat base line throughout the GC method, indicating the complexity of the oils produced in iPP hydrogenolysis reactions using this catalyst.

DETAILED DESCRIPTION

Certain embodiments of the invention provide a compound or composition described herein (e.g., for use to metabolize a polyolefin polymer).

In certain embodiments, the composition comprises:

a) $Cp_2M(R)_2$, or Cp_2M^+R cation, wherein R is C_1-C_6 alkyl, M is Hf or Zr, and Cp is cyclopentadienyl ligand that is optionally substituted with one or more alkyl, wherein the two cyclopentadienyl ligands are optionally linked by a linker (e.g., $Si(CH_3)_2$, or -$(CH_2)_m$- wherein m is 1, 2, or 3) and;

b) a support comprising aluminum and silica oxide.

In certain embodiments, the two cyclopentadienyl ligands are not linked by a linker.

In certain embodiments, the two cyclopentadienyl ligands are linked by a linker to form a tethered, *Ansa*-metallocene.

In certain embodiments, the linker has a molecular weight of from about 14 daltons to about 200 daltons. In certain embodiments, the linker has a molecular weight of from about 14 daltons to about 100 daltons. In certain embodiments, the linker has a molecular weight of from about 14 daltons to about 80 daltons.

In certain embodiments, the linker is a branched or unbranched, C_1-C_{12} hydrocarbon chain.

In certain embodiments, the linker is a branched or unbranched, C_2-C_6 hydrocarbon chain.

In certain embodiments, the linker is a branched or unbranched, C_1-C_3 hydrocarbon chain, such as -CH_2-, -$(CH_2)_2$-, or -$(CH_2)_3$-.

In certain embodiments, the linker is $Si(R_1)(R_2)$, wherein R_1 and R_2 are each independently C_1-C_6 alkyl, and the two cyclopentadienyl ligands are bonded to Si. In certain

embodiments, the linker is $Si(CH_3)_2$.

In certain embodiments, the composition comprises:

a) $Cp_2M(R)_2$, or Cp_2M^+R cation, wherein R is C_1-C_6 alkyl, M is Hf or Zr, and Cp is cyclopentadienyl ligand that is optionally substituted with one or more alkyl, and;

b) a support comprising aluminum and silica oxide.

In certain embodiments, the composition is a catalyst composition (e.g., for use to metabolize a polyolefin polymer).

In certain embodiments, the composition comprises:

a) Cp_2M^+R cation, wherein R is C_1-C_6 alkyl, M is Hf or Zr, and Cp is cyclopentadienyl ligand that is optionally substituted with one or more alkyl, and;

b) a support comprising aluminum and silica oxide.

In certain embodiments, the composition comprises:

a) $Cp_2M(R)_2$, or Cp_2M^+R cation, wherein R is C_1-C_6 alkyl, M is Hf or Zr, and Cp is cyclopentadienyl ligand, wherein the two cyclopentadienyl ligands are linked by a linker, and;

b) a support comprising aluminum and silica oxide.

In certain embodiments, the composition comprises:

a) $Cp_2M(R)_2$, or Cp_2M^+R cation, wherein R is C_1-C_6 alkyl, M is Hf or Zr, and Cp is cyclopentadienyl ligand, and;

b) a support comprising aluminum and silica oxide.

In certain embodiments, R is C_1-C_3 alkyl. In certain embodiments, R is $-CH_3$.

In certain embodiments, M is Hf.

In certain embodiments, M is Zr.

In certain embodiments, Cp is cyclopentadienyl.

In certain embodiments, Cp is cyclopentadienyl substituted with one or more alkyl. In certain embodiments, Cp is butylcyclopentadienyl. In certain embodiments, Cp is pentamethylcyclopentadienyl.

In certain embodiments, the support comprises aluminum on silica support or anion thereof having structure of R_a-$Al(OR_b)_2R_c$, wherein

R_a is silica oxide,

R_b is t-butyl substituted with one or more halo, and

R_c is silica oxide, or C_1-C_6 alkyl.

In certain embodiments, R_b is $-C(CF_3)_3$.

In certain embodiments, the support comprises aluminum anion on silica support having structure of R_a-$Al^-(OR_b)_2R_c$. In certain embodiments, R_c is C_1-C_6 alkyl. In certain embodiments, R_c is C_1-C_3 alkyl. In certain embodiments, R_c is -CH_3.

In certain embodiments, the aluminum on silica support has aluminum content of about 0.11 to 0.21 $mmol_{Al}$ g^{-1}. In certain embodiments, the aluminum on silica support has aluminum content of about 0.21 $mmol_{Al}$ g^{-1}.

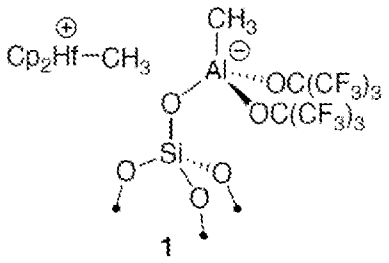
In certain embodiments, the composition has about 1:1 molar ratio between Al and M (e.g., Hf). In certain embodiments, the composition has Hf content of about 0.11 to 0.21 $mmol_{Hf}$ g^{-1}. In certain embodiments, the composition has Hf content of about 0.21 $mmol_{Hf}$ g^{-1}. In certain embodiments, the composition has Zr content of about 0.11 to 0.21 $mmol_{Zr}$ g^{-1}. In certain embodiments, the composition has Zr content of about 0.21 $mmol_{Zr}$ g^{-1}.

In certain embodiments, the composition comprises ion pair of Cp_2M^+R cation and aluminum anion on silica support having structure of R_a-$Al^-(OR_b)_2R_c$.

In certain embodiments, the support comprises [≡SiOAl$(OC(CF_3)_3)_2(CH_3)$].

In certain embodiments, the composition comprises [Cp_2Hf–CH_3][≡SiOAl$(OC(CF_3)_3)_2(CH_3)$].

In certain embodiments, the composition comprises ion pair of



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In certain embodiments, the composition comprises:

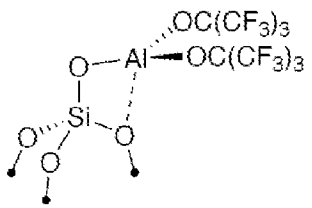
a) $Cp_2M(R)_2$, wherein R is C_1-C_6 alkyl, M is Hf or Zr, and Cp is cyclopentadienyl ligand, and;

b) a support comprising aluminum and silica oxide.

In certain embodiments, the support comprises ≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$.

In certain embodiments, the composition comprises Cp_2HfMe_2/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$.

In certain embodiments, the composition comprises

$Cp_2Hf(CH_3)_2$ and 

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Certain embodiments of the invention provide a method described herein.

Certain embodiments of the invention provide a method of metabolizing a polymer (e.g., polyolefin) into fragments, comprising contacting the polymer with a catalyst composition described herein (e.g., for catalyzing hydrogenolysis of iPP).

As used herein, the term "polyolefin" is a type of polymer with the general formula $(CH_2CHR)_n$ where R is H or alkyl. In certain embodiments, the polyolefin is polyethylene. In certain embodiments, the polyolefin is polypropylene.

In certain embodiments, the method further comprises heating. For example, in certain embodiments, heating the catalyst and/or polymer at a temperature where the polymer is melted. In certain embodiments, the catalyst and/or polymer is heated at a temperature of about 100°C to 300°C, 120°C to 280°C, 140°C to 260°C, 160°C to 240°C, or 180°C to 220°C. In certain embodiments, the temperature is about 120, 140, 160, 180, 200, 220, 240, 260, 280, or 300 °C. In certain embodiments, the temperature is about 200°C.

In certain embodiments, the method is conducted in the presence of H_2. Thus, in certain embodiments, H_2 is supplied. In certain embodiments, H_2 is supplied at about 1 to 5 atm. In certain embodiments, H_2 is supplied at about 1 atm. In certain embodiments, H_2 is supplied at about 2, 3, 4, or 5 atm. In certain embodiments, H_2 is supplied at about 2 to 5 atm. In certain embodiments, H_2 is supplied at about 2 to 4 atm. In certain embodiments, H_2 is supplied at about 2 to 3 atm. In certain embodiments, H_2 is supplied at about 2 to 4 atm. In certain embodiments, H_2 is supplied at about 3 to 5 atm. In certain embodiments, H_2 is supplied at about 1 to 4 atm. In certain embodiments, H_2 is supplied at about 1 to 3 atm. In certain embodiments, H_2 is supplied at about 1 to 2 atm.

In certain embodiments, the method is conducted for 1-48 or 6-24 hrs. In certain embodiments, the method is conducted for 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, or 36 hours. In certain embodiments, the method is conducted for at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36 hours, or longer.

In certain embodiments, H_2 is supplied for 1-48 hrs (e.g., 1-24 hrs, 2-20 hrs, 6-18 hrs,) or 6-24 hrs. In certain embodiments, H_2 is supplied for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, or 36 hours. In certain embodiments, H_2 is supplied for at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36 hours, or longer.

In certain embodiments, the method is conducted at a H_2:M (e.g., H_2:Hf or H_2:Zr) ratio of about 100-1500. In certain embodiments, the method is conducted at a H_2:M (e.g., H_2:Hf or H_2:Zr) ratio of about 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, or 1500.

In certain embodiments, the method is conducted in the absence of alkene (i.e., no alkene

is supplied).

In certain embodiments, the polymer (e.g., polypropylene) to be metabolized is a high molecular weight polymer. In certain embodiments, the polymer has molecular weight M_n >=10kDa. In certain embodiments, the polymer has molecular weight M_n > 10kDa, 11kDa, 12kDa, or 13kDa.

In certain embodiments, the metabolized end products comprise volatile gas (e.g., light gas such as methane, ethane, propane, butane, or pentane) and non-volatile oil (e.g., alkane compounds such as C_9-C_{24} alkane compound, or oil that is extractable by dichloromethane).

In certain embodiments, about 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, 11%, 12%, 13%, 14%, or 15% (weight %) of the polyolefin polymer (e.g., polypropylene) to be metabolized is converted to volatile gas end products.

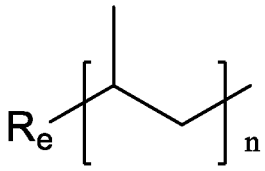
In certain embodiments, at least 20%, 25%, 30%, 40%, 50%, 60%, 70%, or 80% (weight %) of the polyolefin polymer (e.g., polypropylene) to be metabolized is converted to non-volatile end products. In certain embodiments, at least 60%, 70%, or 80% (weight %) of the polymer to be metabolized is converted to non-volatile end products (alkane oil).

In certain embodiments, about 30-90%, 50-85%, or 60-85% (weight %) of the polymer to be metabolized is converted to non-volatile end products.

In certain embodiments, the metabolized end products comprise atactic oil (e.g., atactic polypropylene polymer fragment or oligomer).

In certain embodiments, the metabolized end products comprise polymer (e.g., polypropylene) that has lower molecular weight M_n as compared to the original polymer prior to metabolism. For example, in certain embodiments, the metabolized end products comprise polymer that has molecular weight M_n <=1200Da. In certain embodiments, the metabolized end products comprise polymer that has molecular weight M_n <1200, 1100, 1000, 900, 800, 700, 600, 500, 400, or 300Da. In certain embodiments, the metabolized end products comprise polymer that has molecular weight M_n of about 290-1200Da or 510-1200Da. In certain embodiments, the metabolized end products comprise polymer that has molecular weight M_n of about 200-1200Da, 220-1200Da, 240-1200Da, 350-1200Da, 390-1200Da, 200-600Da, or 200-500Da, or 300-600Da. In certain embodiments, the metabolized end products comprise polymer that has molecular weight M_n of about 200, 220, 240, 260, 280, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, or 1200 Da.

In certain embodiments, the metabolized end product comprise end product (e.g., polypropylene) of Formula I



(Formula I)

wherein n is >=1, and the polypropylene of formula I is terminated with end group R_e that is ethyl, propyl, or butyl.

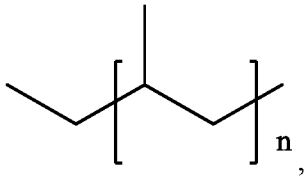
In certain embodiments, n is in the range of about 5-30, 7-28, or 12-26.

In certain embodiments, n is in the range of about 3-12, 3-8, 4-7, or 4-6.

In certain embodiments, n is in the range of about 1-30, 1-19, 1-18, 2-20, 2-19, or 2-18.

In certain embodiments, n is in the range of about 1-10, 1-9, 1-8, 1-7, 1-6, 1-5, 2-10, 2-9, 2-8, 2-7, 2-6, or 2-5.

In certain embodiments, the metabolized end product comprises



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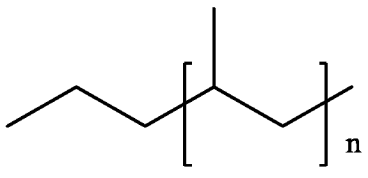

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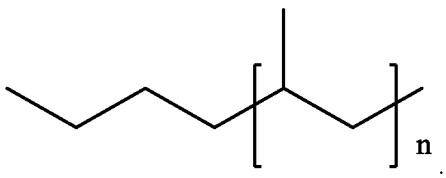

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Certain embodiments of the invention provide a method of polymerizing olefin (e.g., propylene) into polymer using a catalyst described herein.

In certain embodiments, the method comprises contacting propylene with a catalyst composition described herein.

Certain Definition

The term "alkyl", by itself or as part of another substituent, means, unless otherwise stated, a straight or branched chain hydrocarbon radical, having the number of carbon atoms designated (i.e., C_{1-8} means one to eight carbons). Examples include (C_1-C_8)alkyl, (C_2-C_8)alkyl, (C_1-C_6)alkyl, (C_2-C_6)alkyl, (C_1-C_3)alkyl, and (C_3-C_6)alkyl. Examples of alkyl groups include methyl, ethyl, n-propyl, iso-propyl, n-butyl, t-butyl, iso-butyl, sec-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, and higher homologs and isomers.

The term "halo" or "halogen" refers to bromo, chloro, fluoro or iodo. In some embodiments, halogen refers to chloro or fluoro. In some embodiments, halogen refers to fluoro.

Certain embodiments of the invention are provided as follows:

Embodiment 1. A catalyst composition comprising:

Cp_2M^+R cation, wherein R is C_1-C_6 alkyl, M is Hf or Zr, and Cp is cyclopentadienyl ligand, and;

a support comprising aluminum and silica oxide.

Embodiment 2. The catalyst composition of Embodiment 1, wherein R is $-CH_3$.

Embodiment 3. The catalyst composition of Embodiment 1, wherein the support comprises aluminum on silica support or anion thereof having structure of R_a-$Al(OR_b)_2R_c$, wherein

R_a is silica oxide,

R_b is t-butyl substituted with one or more halo, and

R_c is silica oxide, or C_1-C_6 alkyl.

Embodiment 4. The catalyst composition of any one of Embodiments 1-3, wherein M is Hf.

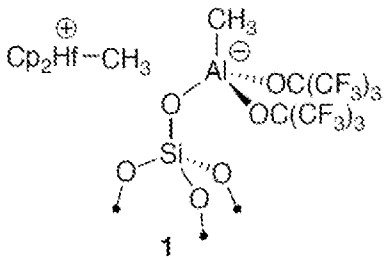
Embodiment 5. The catalyst composition of any one of Embodiments 1-3, wherein M is Zr.

Embodiment 6. The catalyst composition of any one of Embodiments 1-5, wherein R_b is $-C(CF_3)_3$.

Embodiment 7. The catalyst composition of any one of claims 1-6, wherein the aluminum on silica support has aluminum content of about 0.21 $mmol_{Al}\ g^{-1}$.

Embodiment 8. The catalyst composition of Embodiment 1, wherein the support comprises aluminum anion on silica support having structure of R_a-$Al^-(OR_b)_2CH_3$.

Embodiment 9. The catalyst composition of Embodiment 1, comprising cation-anion pair of



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Embodiment 10. A method of metabolizing a polymer into fragments, comprising contacting the polymer with a catalyst composition of any one of Embodiments 1-9.

Embodiment 11. The method of Embodiment 10, further comprising heating (e.g., heating the catalyst composition and/or the polymer at 200°C).

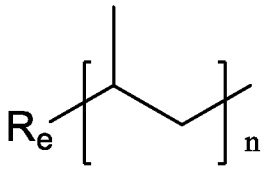
Embodiment 12. The method of any one of Embodiments 10-11, wherein H_2 is supplied.

Embodiment 13. The method of Embodiment 12, wherein H_2 is supplied at about 1 atm.

Embodiment 14. The method of Embodiment 12, wherein H_2 is supplied at about 2-5 atm.

Embodiment 15. The method of any one of Embodiments 10-14, wherein the polymer is polypropylene (e.g., polypropylene with molecular weight M_n >=10kDa).

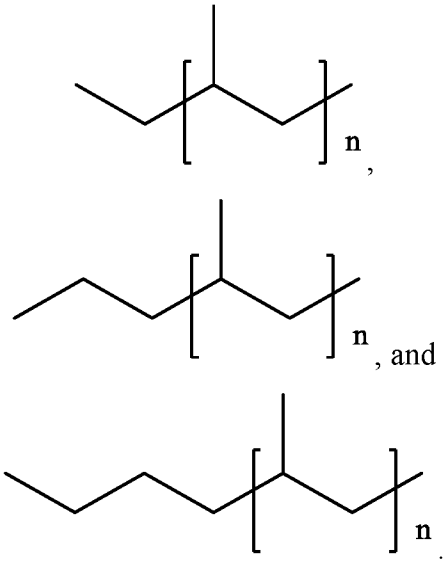
Embodiment 16. The method of any one of Embodiments 10-15, wherein the metabolized end product comprise polypropylene of Formula I



(Formula I)

wherein n is >=1 (e.g., n is in the range of about 5-30), and the polypropylene of formula I is terminated with end group R_e that is ethyl, propyl, or butyl.

Embodiment 17. The method of Embodiment 16, wherein the metabolized end product comprise



Embodiment 18. The method of any one of Embodiments 10-17, wherein the metabolized end products comprise polypropylene that has molecular weight M_n <=1200Da.

Embodiment 19. The method of any one of Embodiments 10-18, wherein no alkene is supplied.

Embodiment 20. A method of polymerizing olefin, comprising contacting olefin (e.g., propylene) with a catalyst composition of any one of Embodiments 1-9.

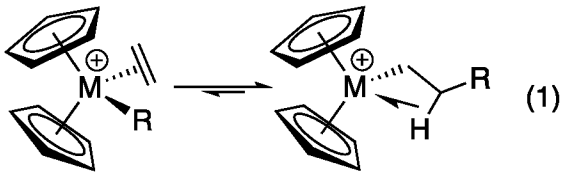
Certain embodiments of the invention will be illustrated in the following non-limiting Example.

Example 1 *A Supported Ziegler-Type Organohafnium Site Metabolizes Polypropylene.*

$Cp_2Hf(CH_3)_2$ reacts with silica containing strong aluminum Lewis acid sites to form $[Cp_2Hf–^{13}CH_3]$ cations paired to aluminate anions. Solid-state NMR characterization shows that

this reaction also forms neutral organohafnium and hafnium sites lacking methyl groups, but control experiments show that these species are unreactive in catalytic reactions. [$Cp_2Hf–^{13}CH_3$] cations on this support react with isotatic polypropylene (iPP, M_n = 13.3 kDa; $Đ$ = 2.4; mmmm = 94 %; ~110 C_3H_6/Hf) in the presence of H_2 to form oils with moderate molecular weights (M_n = 290 - 1200 Da) in good yields. The aliphatic oils show characteristic $^{13}C\{^1H\}$ NMR properties consistent with complete loss of diastereoselectivity and formation of regioirregular errors under 1 atm H_2. Regioirregular errors are less common in hydrogenolysis reactions run under higher H_2 pressures, but these conditions also favor formation of light gases. These results show that a typical Ziegler-Natta type active site is compatible in a common reaction used to digest waste plastic into smaller aliphatic fragments capable of further value-added processing.

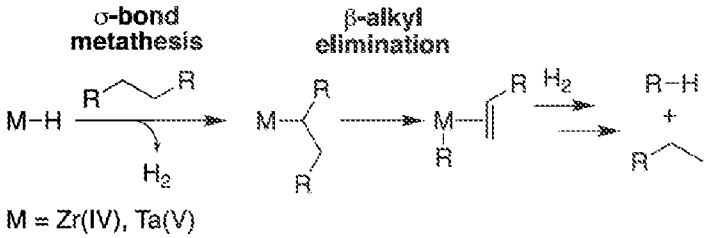
In Ziegler-Natta olefin polymerization reactions the key step that grows polymer chains is insertion of the olefin into a M–R^+ (R = H, alkyl). This reaction is very favorable. DFT calculations give DG_{rxn} ~ 21 kcal mol^{-1} with very small activation barriers for ethylene insertion in typical $Cp_2M–R^+$ (M = Ti, Zr, Hf),[1] to form stable and often observable β-H agostic intermediates, eq 1.[2] Though energetically favorable, this reaction could also be described as an equilibrium between $Cp_2M–CH_2CH_2R^+$ and $Cp_2MR(olefin)^+$ (M = Ti, Zr, Hf) because competitive β-alkyl elimination can occur during polymerization reactions, particularly those involving propylene.[3]



(1)

M = Ti, Zr, Hf

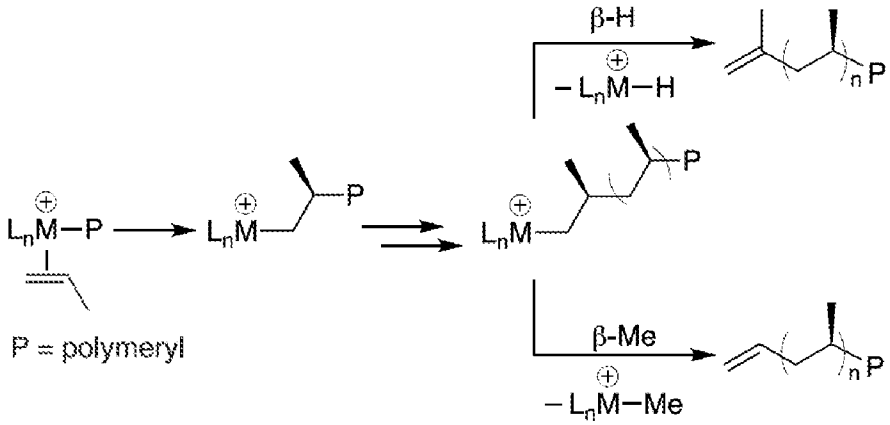
Indeed, β-alkyl elimination has emerged as an important step in efforts to achieve a circular polyolefin economy because intercepting the $MR(olefin)^+$ intermediate with H_2 forms alkanes and provides a driving force for the reaction. The low molecular weight alkanes formed in this reaction are easier to process to monomer than the parent polyolefin. These reactions are usually catalyzed by the heterogeneous "single-site" d^0 metal hydrides shown in Figure 1.[4] The well-defined catalysts activate a C–H bond in the polymer by σ-bond metathesis and β-alkyl eliminate to form MR(olefin) intermediates that are hydrogenated under the reaction conditions. The classic alkane or polymer hydrogenolysis catalyst is the Zr–H supported on SiO_2/Al_2O_3.[5] This catalyst also mediates C-C bond cleavage in polymers in the presence of AlR_3.[6] Ta–H supported on silica hydrogenate or metathesize C–C bonds in low molecular weight alkanes.[7] Related Ta–H^+ sites supported on sulfated aluminum oxide are more active in these reactions, and catalyze hydrogenolysis of high density polyethylene (HDPE)[8] and isotactic polypropylene (iPP).[9]



Scheme A. Key steps in C–C hydrogenolysis.

Our hypothesis is that cationic organometallics used as olefin polymerization catalysts could engage in the reactions shown in scheme A. Modern olefin polymerization catalysts contain a Group IV metallocene or postmetallocene precatalyst that is activated to form $L_nM–R^+$ (M = Ti, Zr, Hf; R = H, alkyl) that coordinate and insert olefins to grow the polymer chain. These steps are shown in scheme B for the formation of isotactic polypropylene (iPP) through the common 1,2-insertion of propylene into $L_nM–R^+$.

Chain transfer releases the polymer from the metal to regenerate catalytically active $L_nM–R^+$. In the absence of alkylaluminum, the most common chain transfer pathways are β-H elimination to generate $LnM–H^+$ and iPP with vinylidene end groups or β-Me elimination to generate $L_nM–Me^+$ and iPP with vinyl end groups. The outcome of this reaction depends on sterics. $Cp_2Hf–CH_3^+$ terminates propylene polymerization by β-H elimination, but bulkier $Cp^*_2Hf–CH_3^+$ favors chain termination by β-methyl elimination.



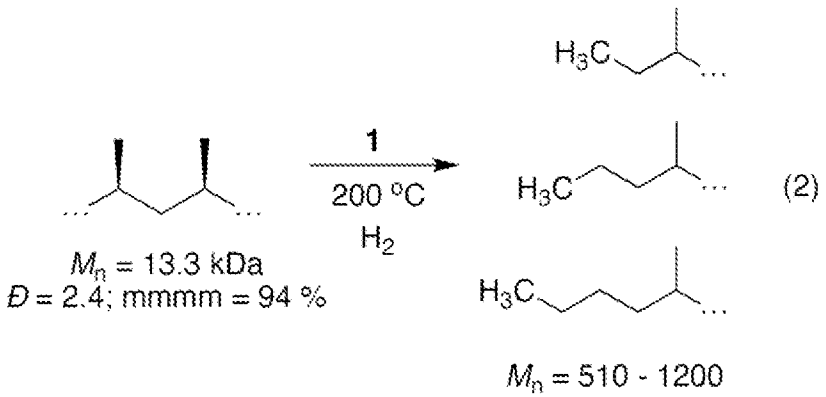
Scheme B. Abbreviated key steps in iPP synthesis.

The β-Me elimination shown in scheme B is a signature of β-alkyl elimination required for C–C hydrogenolysis shown in scheme A. Cationic hafnocenes generated in solution can engage in σ-bond metathesis reactions, analogous to the d^0 metal hydrides shown in Figure 1. Because the reaction(s) in eq 1 are related by the principle of microscopic reversibility, similar cationic organometallic complexes may show activity in reactions that digest polyolefins in the presence of H_2. In many respects, catalysts of this type are more desirable than those shown in Figure 1. $Cp_2M–R^+$ form readily in solution[10] or on solid supports in common industrial

compositions used in olefin polymerization reactions.[11] This Example describes formation of $Cp_2Hf–CH_3^+$ sites on a weakly coordinating oxide[12] that catalyze hydrogenolysis of iPP.

Silica functionalized with $Al(OC(CF_3)_3)(PhF)$[13] forms $\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2)$, which contains 0.21 $mmol_{Al}\ g^{-1}$ and residual unreacted ≡SiOH.[14] $Cp_2Hf(^{13}CH_3)_2$ reacts with this Lewis acidic silica support to form the mixture of species shown in Figure 2a (0.21 $mmol_{Hf}\ g^{-1}$). The $^{13}C\{^1H\}$ cross polarization magic angle spinning (CPMAS) NMR spectrum of this material is shown in Figure 2b and contains signals at 38 ($Hf–^{13}CH_3^+$), 24 ($Hf–^{13}CH_3$), 2 ($Si–^{13}CH_3$), and -11 ppm ($Al–^{13}CH_3$), respectively. The reactivity shown in Figure 2a can be rationalized by the following chemical steps. $[Cp_2Hf–^{13}CH_3][\equiv SiOAl(OC(CF_3)_3)_2(CH_3)]$ (**1**) forms by methide abstraction from $Cp_2Hf(^{13}CH_3)_2$ by the strong aluminum Lewis acid sites, analogous to reactions of $B(C_6F_5)_3$ with d^0 organometallics in solution.[15] Residual –OH sites present on the support react with $Cp_2Hf(^{13}CH_3)_2$ to form CH_4 (0.07 ± 0.01 $mmol_{CH4}\ g^{-1}$) and $Cp_2Hf(^{13}CH_3)(OSi\equiv)$ (**2**). This result indicates that ~30% of the Lewis sites in $\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2)$ do not react with $Cp_2Hf(^{13}CH_3)_2$. **3** forms when $Hf–Me^+$ in **1** reacts with nearby siloxane bridge to generate $[Cp_2Hf(OSi\equiv)][\equiv SiOAl(OC(CF_3)_3)_2(CH_3)]$ and $\equiv Si–^{13}CH_3$, which is also observed when $Cp_2Zr–CH_3^+$ fragments are generated on silica.[16]

The catalytic properties of $Cp_2Hf(CH_3)_2/\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2)$ in a melt of iPP (M_n = 13.3 kDa; $Đ$ = 2.4; mmmm = 94 %; ~110 C_3H_6/Hf) with H_2 are given in Table 1 and Table 1a. These reactions form a complex mixture of saturated alkane products lacking any measurable diastereocontrol, eq 2. Similar to previous studies,[9] high temperature $^{13}C\{^1H\}$ NMR analysis of the recovered unreacted polymer maintains high mmmm purity. Control experiments with **2**, independently prepared from the reaction of $Cp_2Hf(^{13}CH_3)_2$ with SiO_2 partially dehydroxylated at 700 °C (see the SI), under identical conditions shows no appreciable reactivity with iPP, implicating **1** as the catalytically active site in $Cp_2Hf(CH_3)_2/\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2$.



(2)

Available data suggest that a $Hf–CH_3^+$ is the catalytically active site in $Cp_2Hf(CH_3)_2/\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2$. Native $\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2)$ sluggishly

converts iPP to extractable oils in the presence of 1 atm H_2 (15% yield), suggesting that unreactive Lewis sites play a minimal role in the catalytic chemistry involving **1**. Reacting $Cp_2Hf(CH_3)_2/{\equiv}SiOAl(OC(CF_3)_3)_2(O(Si{\equiv})_2$ with H_2 at 150 °C for 12 h in the absence of iPP forms methane (0.09 mmol g^{-1}), and the FTIR of this material contains a broad signal at 1650 cm^{-1} tentatively assigned to a hafnium hydride. This reactivity pattern is expected from extensive precedent in the homogeneous and heterogeneous literature showing that M–R species react with H_2 to form M–H and RH. Under identical conditions, independently synthesized **2** forms only 0.001 $mmol_{CH4}$ g^{-1}. In addition, **2** does not react with iPP under hydrogenolysis conditions to form extractable oils nor incorporate deuterium into residual iPP in the presence of D_2.

After 24 h at 200 °C under 1 atm H_2, **1** forms an oil in 62 % yield after extraction of the mixture with dichloromethane, Entry 1. Analysis of the gas phase before extraction of the oil shows that only ~2 % of the polymer is converted to light gases form in this reaction (1.5 CH_4 Hf^{-1}, 0.01 C_2H_6 Hf^{-1}, 0.11 C_3H_6 Hf^{-1} and 1.1 C_4H_{10} Hf^{-1}, 1.2 C_5H_{10} Hf^{-1}). Increasing H_2:Hf ratio to ~1500 results in near complete conversion of iPP to oil (83 %) with a slight increase in light gas formation (12 %), Entry 2. The zirconium derivative of **1**[14] is also active in this reaction but produces less oil (38 %) and light gas (7 %) than hafnium, Entry 3. A closed Parr reactor charged with 5 or 10 atm H_2 also results in a good yield of oils with minimal volatile gas formation (Table 1a. Entries 4 and 5). Pressures higher than 1 atm (at 2 or 5 atm) with H_2 supplied on demand, conditions that prevent recovery of volatile gases, results in lower mass balance and lower yields of extracted oils (Table 1, Entries 4 – 5), suggesting that oils are converted to gases faster than iPP is converted to oils, similar to that observed for supported metal hydrides. The ^1H NMR data for the extracted oils is largely uninformative, but these spectra contain signals for internal olefins. The intensity of these signals range from ~1:50 to ~1:2000 olefin:C_3H_6 unit, depending on the conditions (see the SI).

Table 1. Catalytic activity of 1 in PP hydrogenolysis.[a]

Entry	*Pressure (atm)*	*% Yield*[b]	*% Mass Bal*[c]	*M_n*[d] *(g/mol)*
1	1[e]	62	>99	390
2	1[f]	95	>99	290
3[g]	1[f]	45	>99	350

4	2	29[h]	76	1100
5	5	20[h]	74	1200

[a] Reactions run with 200 mg iPP and 200 mg $Cp_2Hf(CH_3)_2$/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$ (0.042 mmol Hf) at 200 °C for 24 h at the pressure given in the table. [b] $(mg_{product})/(mg_{iPP})$ including light gases. [c] $(mg_{product} + mg_{solid})/(mg_{iPP} + mg_{cat})$. [d] Determined from quantitative $^{13}C\{^1H\}$ NMR of extracted oils. [e] H_2:Hf ~ 100. [f] H_2:Hf (or Zr) ~ 1500. [g] Zr derivative of **1**, reported in ref 14. [h] Excludes light gases.

Table 1a. Catalytic activity of 1 in PP hydrogenolysis.[a]

Entry	Pressure (atm)	Yield C_1-C_5 (%)	Yield Oil[b] (%)	M_n[c] (g/mol)
1	1[d]	2	62	390
2	1[e]	12	83	290
3[f]	1[e]	7	38	350
4	5	4	62	220
5	10	8	88	240
6	2[g]	n.d.	29	1100
7	5[g]	n.d.	20	1200

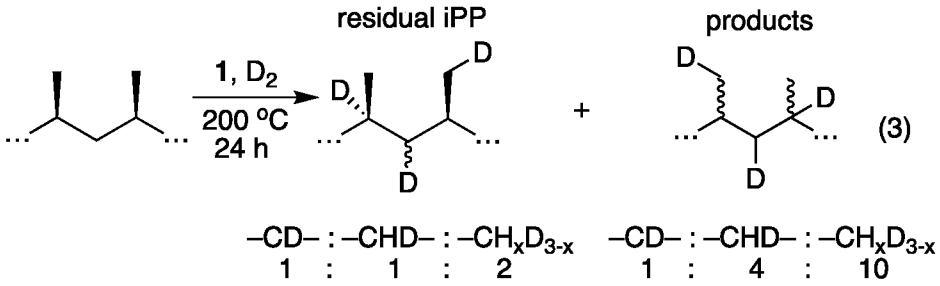
[a] Reactions run with 200 mg iPP and 200 mg $Cp_2Hf(CH_3)_2$/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$ (0.042 mmol Hf) at 200 °C for 24 h at the pressure given in the table. [b] $(mg_{oil})/(mg_{iPP})$. [c] Determined from quantitative $^{13}C\{^1H\}$ NMR of extracted oils. [d] H_2:Hf ~ 100. [e]H_2:Hf (or Zr) ~ 1500. [f]Zr derivative of **1**, reported in ref 14. [g] Performed with H_2 fed to the reactor on demand. N.d. = not determined.

Quantitative $^{13}C\{^1H\}$ NMR spectra of the oils in C_6D_6 are shown in Figure 3. All $^{13}C\{^1H\}$ NMR spectra contain signals for ethyl, propyl, and/or butyl end groups. Integration of the end groups relative to the rest of the $^{13}C\{^1H\}$ NMR signals gives the M_n of the oils reported in Table 1 and Table 1a. The matrix assisted laser desorption ionization (MALDI) mass spectrum of extracted oil from Entry 1 contains a broad molecular weight distribution of products centered at m/z of 538 (~10 C_3H_6 units *Ag^+) that is close to M_n obtained from integration of $^{13}C\{^1H\}$ NMR signals. The MALDI MS of oils generated at 2 or 5 atm H_2 pressure also contain signals near the M_n shown in Table 1 and Table 1a, but also suffer from significant fragmentation.

At 1 atm H_2 pressure signals that are characteristic of regioirregular errors encountered in polypropylene synthesis,[17] or copolymerization reactions of ethylene and propylene,[18] are present in these spectra. Oils obtained from reactions performed at higher H_2 pressures contain similar complexities in the $^{13}C\{^1H\}$ NMR spectra, but the intensities of signals for "errors" are

suppressed. These results indicate that some degree of chain-straightening occurs during hydrogenolysis with **1**, and this process is dependent on H_2 pressure.

Reactions of iPP with **1** and D_2 (1 atm, D_2:Hf ~ 100) at 200 °C also result in formation of oils and small amounts of light gas in similar yields as those performed with H_2. The ^2H NMR spectrum of unreacted iPP at 120 °C in $C_2D_2Cl_4$ contains signals for –CD–, –CHD–, and $–CH_xD_{3-x}$ in a ~1:1:2 ratio, eq 3. This spectrum also contains a signals for $CH_3CH_2CD_2CD=C(CH_3)P$ (P = polymeryl). The oils formed in this reaction also contain deuterium at all possible positions (–CD–:–CHD–:$–CH_xD_{3-x}$ ~ 1:4:10).



The proposed key steps in iPP hydrogenolysis mediated by **1** are shown in Figure 4 and account for the end groups obtained in hydrogenolysis of iPP. Hf–H^+, formed from the reaction of **1** with H_2, undergoes σ-bond metathesis with a primary or secondary C–H bond in iPP to form Hf–R^+. Cationic Hf–H^+ generated in solution may engage in σ-bond metathesis reactions with silanes.[19] β-Alkyl elimination forms Hf(R)(olefin)$^+$ intermediates that are hydrogenated by H_2. The exact sequence of steps to form initially isotactic alkanes from Hf(R)(olefin)$^+$ is not clear at this time, but probably involves olefin dissociation to facilitate hydrogenolysis of Hf–R^+ by a σ-bond metathesis reaction prior to olefin hydrogenation. This process forms propyl (observed) and isopropyl (not observed) end groups. Deuterium incorporation into recovered iPP suggests that the σ-bond metathesis reactions shown in Figure 4 are reversible and accounts for the −CHD– and $–CD_xH_{3-x}$ in recovered iPP and atactic oils.

The steps involved in loss of diastereoselectivity and incorporation of regioirregular "errors" are also shown in Figure 4. The atactic oils must lose diastereoselectivity. Epimerization can occur by reversible β-H elimination and unselective olefin insertion through a 3° Hf–R intermediate,[20] or HfH(olefin)$^+$ could also undergo non-dissociative alkene flipping[21] followed by unselective olefin reinsertion. Deuterium incorporation into the product alkanes is consistent with either process. These steps also account for the incorporation of deuterium into tertiary positions of residual iPP, though reinsertion must be stereoselective because high mmmm purity of unreacted polymer is observed in solution NMR. Residual Lewis acidic

aluminum in $Cp_2Hf(CH_3)_2/{\equiv}SiOAl(OC(CF_3)_3)_2(O(Si{\equiv})_2)$ could also promote isomerization reactions, resulting in loss of tacticity. Why the oils are atactic and the recovered iPP maintains high isotacticity is currently unclear but could imply that unreacted iPP chains are the dominant species in the recovered polymer.

The atactic oils also incorporate regioirregular "errors" into the chain. The quantitative $^{13}C\{^1H\}$ NMR data of extracted oils in Figure 3 indicate that regioirregular errors occur throughout the alkyl chain and not solely at chain ends. In propylene polymerization reactions the regioirregular errors, formally 3,1 insertion products, generally arise from 2,1-insertion of propylene to form a 2° M–R that b-H eliminates and reinserts to form a 1° M–R, Figure 6a.[17] This pathway is not plausible under hydrogenolysis conditions. Instead, C–H bond activation by $Hf–H^+$ generates a $Hf–R^+$ that b-alkyl eliminates, and 2,1-reinsertion gives the chain-straightened product after hydrogenolysis, Figure 6b. Reactions from a terminal isopropyl position generate the butyl end group. If the chain-straightened intermediate β-alkyl eliminates, the ethyl end group forms after hydrogenation.

Until this Example 1 the most common catalysts for hydrogenolysis of polyolefins were the supported d^0 metal hydrides shown in Figure 1 or supported noble metal nanoparticles.[22] Comparisons between these disparate classes of catalysts are difficult, but **1** does appear to offer some advantage. **1** selectively produces long chain hydrocarbons and avoids significant formation of light gases at low H_2 pressure for prolonged reaction times. We suspect that the selectivity rests on the moderate activity of **1** in the reactions shown in Figure 4. For example, under essentially identical reaction conditions $Ta–H^+$ sites supported on sulfated aluminum oxide convert the same iPP to shorter liquid hydrocarbon fragments and more light gas, indicating that $Ta–H^+$ facilitates more chain cleavage events than **1**.

In the seminal review by Veige and co-workers countless examples show that β-alkyl elimination reactions are correlated with sterically bulky ligand environments.[3] Indeed, sterically open $Cp_2Hf–CH_3^+$ catalyzes polymerization of propylene to exclusively form vinylidene end groups, indicating that only β-hydride elimination occurs during chain-transfer. In contrast, propylene polymerization reactions catalyzed by sterically bulky $Cp^*_2Hf–CH_3^+$ that favor chain termination by b-methyl elimination.[23] That $Cp_2Hf–CH_3^+$ in **1** can β-alkyl eliminate in the absence of olefin is surprising, and may be general in sterically open metallocenium ions.

Metallocene catalysts that polymerize olefins have been overlooked as catalysts for degradation of fully saturated polyolefin plastics.[24] The reactivity of **1**, and inactivity of **2**, in iPP hydrogenolysis shows the important role of forming an organometallic ion-pair in this reaction.

Many industrially relevant catalysts for olefin polymerization contain mixtures of metallocene, aluminum alkyl (or methaluminoxane), and an oxide support; and these mixtures may self-assemble to form ion-pairs similar to the Hf–H^+ derived from **1**.[11] A potential implication of the results shown here is that the portfolio of catalysts available for olefin polymerization reactions may also catalyze reactions that degrade the polymers these catalysts produce.

The entire content of Kavyasripriya Samudrala et al., *J. Am. Chem. Soc*. 2023, 145, 45, 24447–24451 (titled "A Supported Ziegler-Type Organohafnium Site Metabolizes Polypropylene") is incorporated by reference herein.

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Supporting Information:

General Considerations

All manipulations were performed under an inert atmosphere of dinitrogen or argon using standard Schlenk or glovebox techniques. C_6D_6 was purchased from Cambridge Isotope Laboratories, dried over sodium/benzophenone, degassed by three successive freeze-pump-thaw cycles, distilled under vacuum, and stored in an inert atmosphere glovebox. $C_2D_2Cl_4$ was purchased from Cambridge Isotope Laboratories and used as received. Pentane was dried by passing through a J.C. Meyer solvent system containing two activated alumina columns, stored over sodium/benzophenone, degassed, and distilled under vacuum. Hydrogen (UHP grade) was purchased from Airgas and was passed through oxygen/water trap (CRS, ZPure H_2O/O_2) immediately before use. Isotactic polypropylene (M_n =13.3 kDa) was purchased from Sigma-Aldrich and used without further purification. Deuterium was purchased from CIL and was dried/ deoxygenated using activated 4Å molecular sieves and regenerated BASF Cu catalyst. $\equiv SiOAl(OC(CF_3)_3)_2(O(Si\equiv)_2)$ was prepared as previously described.[1] Cp_2HfMe_2 and $Cp_2Hf(^{13}CH_3)_2$ were prepared as reported.[2] FTIR spectra were recorded in transmission mode as pressed pellets using a Bruker Alpha IR spectrometer in an argon-filled glovebox. Elemental analysis of Al and Hf were carried out by digesting solid samples in 2% nitric acid for 12 hours at room temperature and measuring samples at the University of California, Riverside Environmental Sciences Research Laboratory (ESRL) on a Perkin-Elmer Optima 7300DV ICP-OES.

Solution NMR data (^1H, ^2H, and $^{13}C\{^1H\}$) was acquired at 14.1T on an Avance Bruker 600 MHz NMR spectrometer. ^1H and ^{13}C NMR spectra were referenced to the residual proton signal from the NMR solvent. Quantitative $^{13}C\{^1H\}$ NMR experiments were acquired using an inverse-gated decoupling pulse sequence using a 90° pulse of 9.0 μs, a relaxation time of 5 s and an acquisition time of 2 s. Samples for this measurement were prepared at 10% weight solution of polymers in 0.05 M $Cr(acac)_3$ dissolved in 1,1,2,2-tetrachloroethane-d_2 solution at 120 °C. Analogous procedures were used to analyze oils in C_6D_6 solution at ambient temperature. Solid state NMR spectra were recorded under magic angle spinning at 14.1 T using Bruker NEO600 spectrometer. All solid-state NMR samples were packed in 4 mm zirconia rotors and sealed with

a Kel-F cap in an argon filled glovebox.

Matrix assisted laser desorption ionization (MALDI) mass spectrometry were recorded on an AB-SCIEX 5800 MALDI TOF/TOF mass spectrometer. Samples were prepared by dissolving extracted oil (5 mg) in THF (5 mL). Prior to spotting on the sample plate, an aliquot of this solution (0.1 mL) was mixed with a saturated solution of $AgNO_3$ in MeCN (0.1 mL). ~ 0.5 μL of the solution was placed on the sample plate, followed by 0.5 μL of the matrix solution (2,5 dihydroxybenzoic acid (DHB) solution prepared in a 3:2 (*v*:*v*) mixture of tetrahydrofuran and methanol at a 10 mg/mL concentration). The solvents were removed by gently heating the stainless-steel sample plate under air.

Synthesis of Cp_2HfMe_2/≡SiOAl(OC(CF_3)$_3$)$_2$(O(Si≡)$_2$): ≡SiOAl(OC(CF_3)$_3$)$_2$(O(Si≡)$_2$) (0.500 g, 0.11 $mmol_{Al}$ g^{-1}) and Cp_2HfMe_2 (1 eq, 0.11 mmol, 0.037 g) were transferred to one arm of a double-Schlenk flask inside an argon-filled glovebox. The flask was removed from the glovebox, connected to a high vacuum line, and evacuated for 5 min. Pentane (~8 mL) was condensed onto the solids under vacuum at 77 K. The mixture was warmed to room temperature and stirred gently for 40 minutes. The clear, colorless solution was then filtered away from the solids to the other side of the double-Schlenk. The arm of the double-Schlenk containing the functionalized silica was cooled to 77K, causing the pentane on the other side of the flask to condense onto the solids. The mixture was warmed to 25˚C, stirred for 5 min, and filtered back to the other side of the double Schlenk. This procedure was repeated two more times to wash the functionalized silica of unreacted Cp_2HfMe_2. The volatiles were distilled into a separate large volume Schlenk flask (2 L) fitted with a Teflon-tap cooled to 77K under vacuum. Warming the flask to room temperature places all solvent and any CH_4 formed in this reaction into the gas phase. Analysis of the gas phase by GC-FID shows 0.07 ± 0.001 $mmol_{CH4}$ g^{-1} released during the grafting. The double-Schleck flask was dried under diffusion pump vacuum for 45 minutes. Cp_2HfMe_2/≡SiOAl(OC(CF_3)$_3$)$_2$(O(Si≡)$_2$) is a white solid. This material was stored in an Ar glovebox freezer at -20˚C. An identical procedure was used to prepare ^{13}C labeled $Cp_2Hf(^{13}CH_3)_2$/≡SiOAl(OC(CF_3)$_3$)$_2$(O(Si≡)$_2$). The white solid was stored in an Ar glovebox freezer at -20˚C. Digestion of this material in 2% nitric acid for 12 hours at room temperature gives 0.21 $mmol_{Hf}$ g^{-1} by ICP-EOS analysis. FT-IR: νC-H = 3120 and 2924 (C-H from Cp2HfMe) cm^{-1}. ^1H MAS NMR (10 kHz, -20 °C): d 5.7 ppm (Cp), 0.2 ppm (Hf-Me/Al-Me) ; $^{13}C\{^1H\}$ CPMAS NMR (10 kHz, -20 °C): d 112 (Cp), 38 (Hf-Me^+), 24 (Hf-Me), 2 Si-Me, -11 (Al-Me^-) ppm.

Synthesis of $Cp_2Hf(^{13}CH_3)$(OSi≡) (2): Silica partially dehydroxylated at 700 °C ($SiO_{2\text{-}700}$, 0.500 g, 0.13 mmol -OH) and Cp_2HfMe_2 (1 eq, 0.13 mmol, 0.044 g) were transferred to one arm of a

double-Schlenk flask inside an argon-filled glovebox. The flask was removed from the glovebox, connected to a high vacuum line, and evacuated for 5 min. Pentane (~ 8 mL) was condensed onto the solids under vacuum at 77 K. The mixture was warmed to room temperature and stirred gently for 40 minutes. The clear, colorless solution was then filtered away from the solids to the other side of the double-Schlenk. The arm of the double Schlenk containing the functionalized silica was cooled to 77K, causing the pentane on the other side of the flask to condense onto the solids. The mixture was warmed to 25°C, stirred for 5 min, and filtered back to the other side of the double Schlenk. This procedure was repeated two more times to wash the functionalized silica of unreacted Cp_2HfMe_2. The volatiles were distilled into a separate large volume Schlenk flask (2 L) fitted with a Teflon-tap cooled to 77K under vacuum. Warming the flask to room temperature places all solvent and any CH_4 formed in this reaction into the gas phase. Analysis of the gas phase by GC-FID shows 0.25 $mmol_{CH4}$ g^{-1} released during the grafting. The double-Schleck flask was dried under diffusion pump vacuum for 45 minutes. The white solid was stored in an Ar glovebox freezer at -20°C. FT-IR: νC-H = 3115 and 2915 (C-H from Cp2HfMe) cm^{-1}. ^1H MAS NMR (10 kHz, -20 °C): d 5.5 (CpH), 0.18 (Hf–CH_3); $^{13}C\{^1H\}$ CPMAS NMR (10 kHz, -20 °C): d 110 (Cp), 23 (Hf-Me) ppm.

Procedure for the hydrogenolysis of iPP with Cp_2HfMe_2/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$.

At 1 atm:

In an argon-filled glovebox, a 100mL Schlenk flask fitted with a Teflon-tap was loaded with 200 mg iPP and 200 mg $Cp_2Hf(CH_3)_2$/≡SiOAl$(OC(CF_3)_3)_2(O(Si≡)_2)$ (0.042 mmol Hf). The flask was removed from the glovebox, connected to a high vacuum line, and evacuated for 5 min. The flask was filled with 1atm of H_2 (4.16 mmol), sealed, disconnected from the line, and heated at 200 °C for 24h. Volatiles were sampled directly from the flask and analyzed by GC FID. Following analysis of volatile gases, the flask was opened to ambient atmosphere to proceed with the extraction of oils and remaining solids. Dichloromethane (~10 mL) was added to the flask at room temperature, and the solution was decanted from the residual polymer melt and spent catalyst mixture. This was repeated two more times. The combined dichloromethane extract was concentrated by heating gently to remove the solvent.

An identical procedure was used for reactions of iPP with D_2, except purified D_2 was used in place of H_2. An essentially identical procedure was used in experiments with H_2:Hf(Zr) ~ 1500, but a 1.5L glass bottle as shown below was used. The polymer and the catalyst were placed in the nub on the bottom of the flask and heated under 1 atm H2 (Figure S22).

At 5 or 10atm Pressure in a Parr Reactor:

A 100 mL glass reaction liner was charged with 200 mg of $Cp_2Hf(CH_3)_2$/≡ $SiOAl(OC(CF_3)_3)_2(O(Si≡)_2)$ and 200 mg iPP in an argon filled glovebox. The reactor was sealed and pressurized with desired pressure of hydrogen (passed through a CRS ZPure O_2/H_2O filter) on demand and heated at 300 °C for 24h. The higher temperature is necessary because the thermocouple is not measuring temperature in the glass sleave. Control experiments showed that 300 °C is required to melt iPP; 200 °C to 250 °C was not hot enough to melt the polymer. After the reaction, the reactor was cooled to ambient temperature and the volatile gases were transferred into a 2L flask. Gas samples were aliquoted to determine volatile gas yields. CH_2Cl_2 (10 mL) was added to each glass liner under ambient atmosphere, and the solution was decanted from the remaining solid. This procedure was repeated three more times. The combined CH_2Cl_2 extract was concentrated by heating gently to remove the solvent and yields were calculated by weighing the amount of oil isolated.

At elevated pressures (At 2 or 5atm Pressure fed on Demand in a Parallel High Pressure Reactor):

Hydrogenolysis of iPP reactions at elevated H_2 pressures on demand were performed in a Biotage Endeavor parallel reactor in a N_2 filled glovebox. A 15 mL glass reaction liner was charged with 200 mg of $Cp_2Hf(CH_3)_2$/≡$SiOAl(OC(CF_3)_3)_2(O(Si≡)_2)$ and 200 mg iPP. The reactor was sealed and pressurized with desired pressure of hydrogen on demand and heated at 200 °C for 24h. After the reaction the reactor was vented with N_2 and cooled to ambient temperature inside the glovebox. The glass liners were removed from the glovebox, and were weighed to determine mass balance, which was calculated as $(mg_{product} + mg_{solid})/(mg_{iPP} + mg_{cat})$. CH_2Cl_2 (10 mL) was added to each glass liner under ambient atmosphere, and the solution was decanted from the remaining solid. This procedure was repeated three more times. The combined CH_2Cl_2 extract was concentrated by heating gently to remove the solvent and yields were calculated by weighing the amount of oil isolated.

iPP degradation reactions using ≡$SiOAl(OC(CF_3)_3)_2(O(Si≡)_2)$.

In an argon-filled glovebox, a 100mL Schlenk flask fitted with a Teflon-tap was loaded with 200 mg iPP and 200 mg ≡$SiOAl(OC(CF_3)_3)_2(O(Si≡)_2)$ (0.044 mmol Al). The flask was removed from the glovebox, connected to a high vacuum line, and evacuated for 5 min. The flask was filled with 1atm of H2 (4.16 mmol), sealed, disconnected from the line, and heated at 200 °C for 24h. Volatiles were sampled directly from the flask and analyzed by GC FID. Following

analysis of volatile gases, the flask was opened to ambient atmosphere to proceed with the extraction of oils and remaining solids. Dichloromethane (~10 mL) was added to the flask at room temperature, and the solution was decanted from the residual polymer melt and spent catalyst mixture. This was repeated two more times. The combined dichloromethane extract was concentrated by heating gently to remove the solvent. The yield of oil from this reaction was 30 mg (15 % from initial iPP mass).

Table S1. Integral values obtained from ^{1}H NMR data shown in Figure 24.

Conditions	Olefin:C_3H_6
1 atm (~100:1 H_2:Hf)	1:294
1 atm (~1500:1 H_2:Hf)	1:54
1 atm (~1500:1 H_2:Zr)	1:58
5 atm Parr	1:200
10 atm Parr	1:82
2 atm	1:1768
5 atm	1:533

Table S2. Integral values obtained from quantitative $^{13}C\{^{1}H\}$ NMR data shown in Figure 3.

	Sum of Integrals for end groups	Sum of Integrals for all other carbons	Ratio of end group integral to C_3H_6 units	Calculated M_n[a] (g/mol)
1atm (H_2:Hf ~ 100)	1.46	35	8.1	388
1atm (H_2:Hf ~ 1500)	4.19	72.1	5.7	290
1atm (H_2:Zr ~ 1500)	3.74	79.3	7.06	347
5atm (Parr)	1	14.00	4.67	238
10atm (Parr)	1	12.84	4.28	221
2atm	7.5	572	25.4	1136
5atm	4.62	355.73	25.6	1146

[a] – All M_n values also include a propyl end group in the molecular weight.

References in Supporting Information of Example 1:

(1) Samudrala, K. K.; Huynh, W.; Dorn, R. W.; Rossini, A. J.; Conley, M. P. Formation of a Strong Heterogeneous Aluminum Lewis Acid on Silica. *Angew. Chemie - Int. Ed.* **2022**, *61* (40). https://doi.org/10.1002/anie.202205745.

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All publications, patents, and patent documents are incorporated by reference herein, as though individually incorporated by reference. The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope of the invention.

CLAIMS

What is claimed is:

1. A catalyst composition comprising:

Cp_2M^+R cation, wherein R is C_1-C_6 alkyl, M is Hf or Zr, and Cp is cyclopentadienyl ligand that is optionally substituted with one or more alkyl, wherein the two cyclopentadienyl ligands are optionally linked by a linker (e.g., $Si(CH_3)_2$, or $-(CH_2)_m-$, wherein m is 1, 2, or 3), and

a support comprising aluminum and silica oxide.

2. The catalyst composition of claim 1, wherein Cp is cyclopentadienyl ligand.

3. The catalyst composition of any one of claims 1-2, wherein R is $-CH_3$.

4. The catalyst composition of any one of claims 1-3, wherein the support comprises aluminum on silica support, or anion thereof, having structure of R_a-$Al(OR_b)_2R_c$, wherein

R_a is silica oxide,

R_b is t-butyl substituted with one or more halo, and

R_c is silica oxide, or C_1-C_6 alkyl (e.g., methyl).

5. The catalyst composition of any one of claims 1-4, wherein M is Hf.

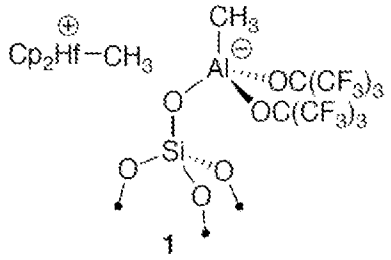
6. The catalyst composition of any one of claims 1-4, wherein M is Zr.

7. The catalyst composition of any one of claims 1-6, wherein R_b is $-C(CF_3)_3$.

8. The catalyst composition of any one of claims 1-7, wherein the aluminum on silica support has aluminum content of about 0.21 $mmol_{Al}\ g^{-1}$.

9. The catalyst composition of any one of claims 1-8, wherein the support comprises aluminum anion on silica having structure of R_a-$Al^-(OR_b)_2CH_3$.

10. The catalyst composition of any one of claims 1-9, comprising cation-anion pair of



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11. The catalyst composition of any one of claims 1-10, wherein M and Al has a molar ratio of about 1:1.

12. The catalyst composition of any one of claims 1-5, and 7-11, comprising Hf content of about 0.21 $mmol_{Hf}\ g^{-1}$.

13. A method of metabolizing a polyolefin polymer, comprising contacting the polyolefin polymer with a catalyst composition of any one of claims 1-12.

14. The method of claim 13, further comprising heating the catalyst composition and/or the polyolefin polymer.

15. The method of claim 14, wherein the catalyst composition and/or the polyolefin polymer are heated at about 100-300°C.

16. The method of any one of claims 13-15, wherein H_2 is supplied.

17. The method of claim 16, wherein H_2 is supplied at about 1 atm.

18. The method of claim 16, wherein H_2 is supplied at about 2-5 atm.

19. The method of any one of claims 13-18, wherein H_2 is supplied for at least 2 hours.

20. The method of any one of claims 13-19, wherein the polyolefin polymer is polypropylene (e.g., polypropylene with molecular weight M_n >=10kDa).

21. The method of any one of claims 13-20, wherein the metabolized end products comprise alkane compound that has molecular weight M_n <=1200Da.

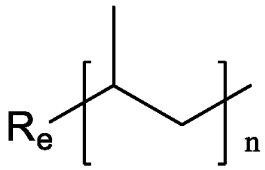
22. The method of any one of claims 13-21, wherein the metabolized end products comprise alkane compound that has molecular weight M_n of about 200 to 1200Da.

23. The method of any one of claims 13-21, wherein the metabolized end products comprise alkane compound that has molecular weight M_n of about 290 to 1200Da.

24. The method of any one of claims 13-23, wherein at least 60% of the polyolefin is metabolized to end products of non-volatile alkane compound.

25. The method of any one of claims 13-24, wherein at least 80% of the polyolefin is metabolized to end products of non-volatile alkane compound.

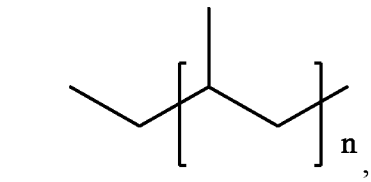
26. The method of any one of claims 13-25, wherein the metabolized end products comprise polypropylene of Formula I



(Formula I)

wherein n is >=1 (e.g., n is in the range of about 5-30), and the polypropylene of formula I is terminated with end group R_e that is ethyl, propyl, or butyl.

27. The method of claim 26, wherein the metabolized end product comprise



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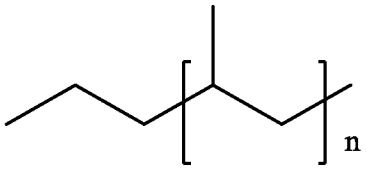

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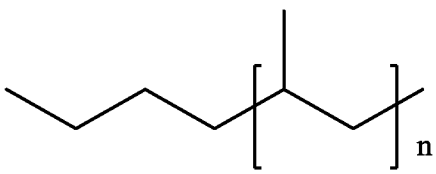

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28. The method of any one of claims 13-27, wherein no alkene is supplied.

29. The use of a catalyst composition of any one of claims 1-12 for metabolizing a polyolefin polymer.

FIGURES 1A-1C

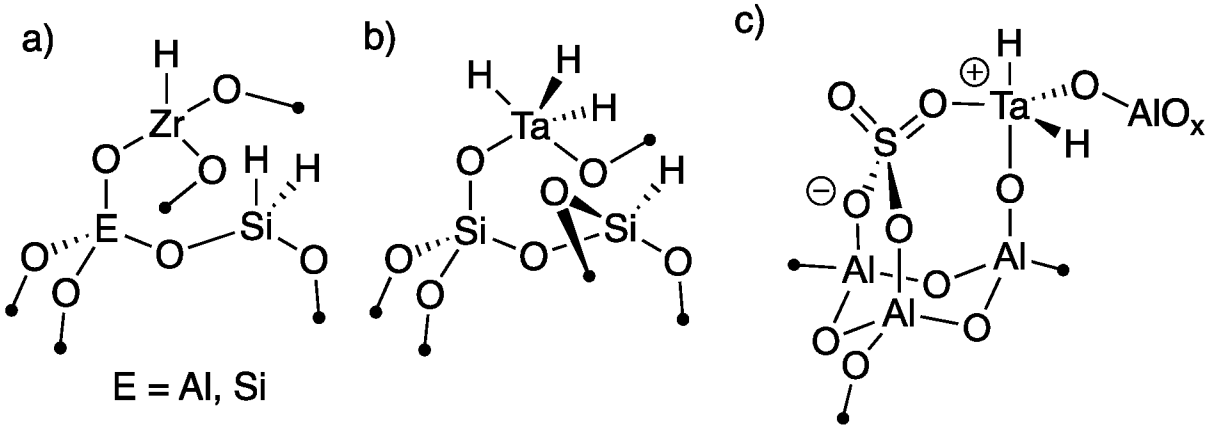


FIGURE 2A

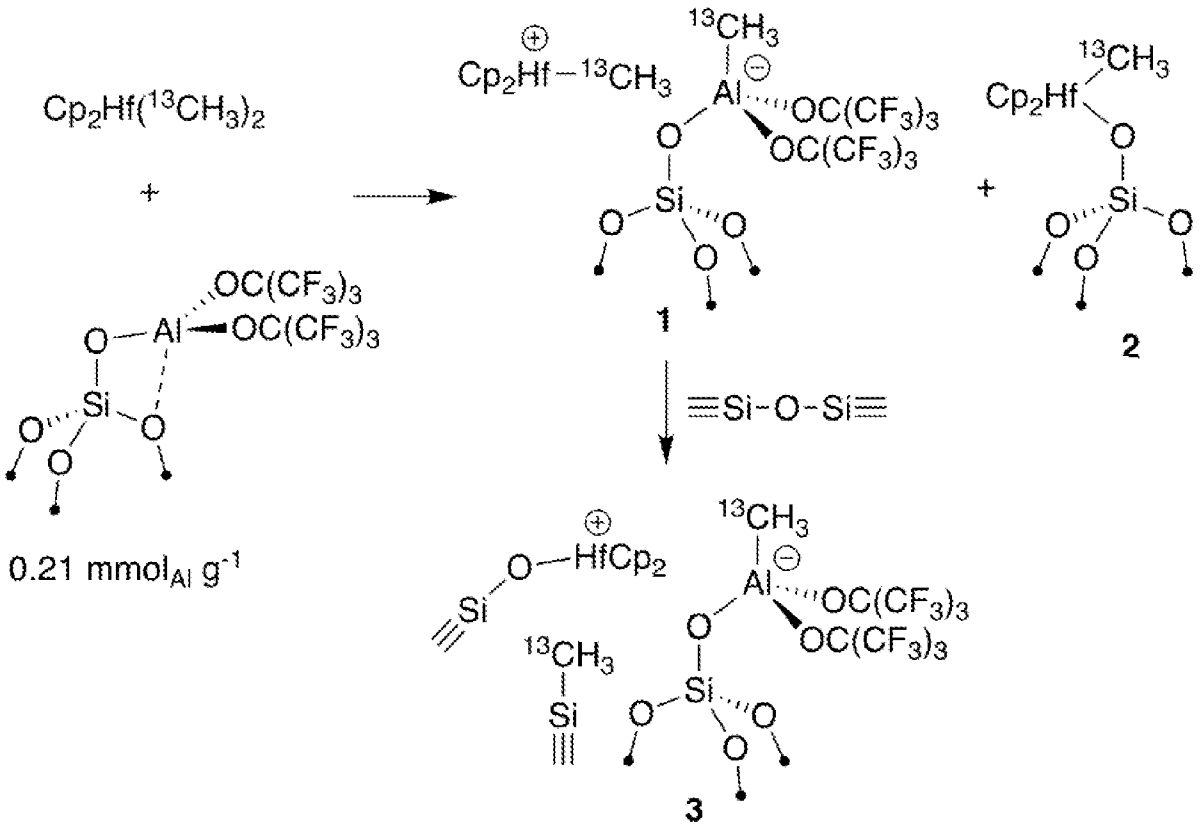


FIGURE 2B

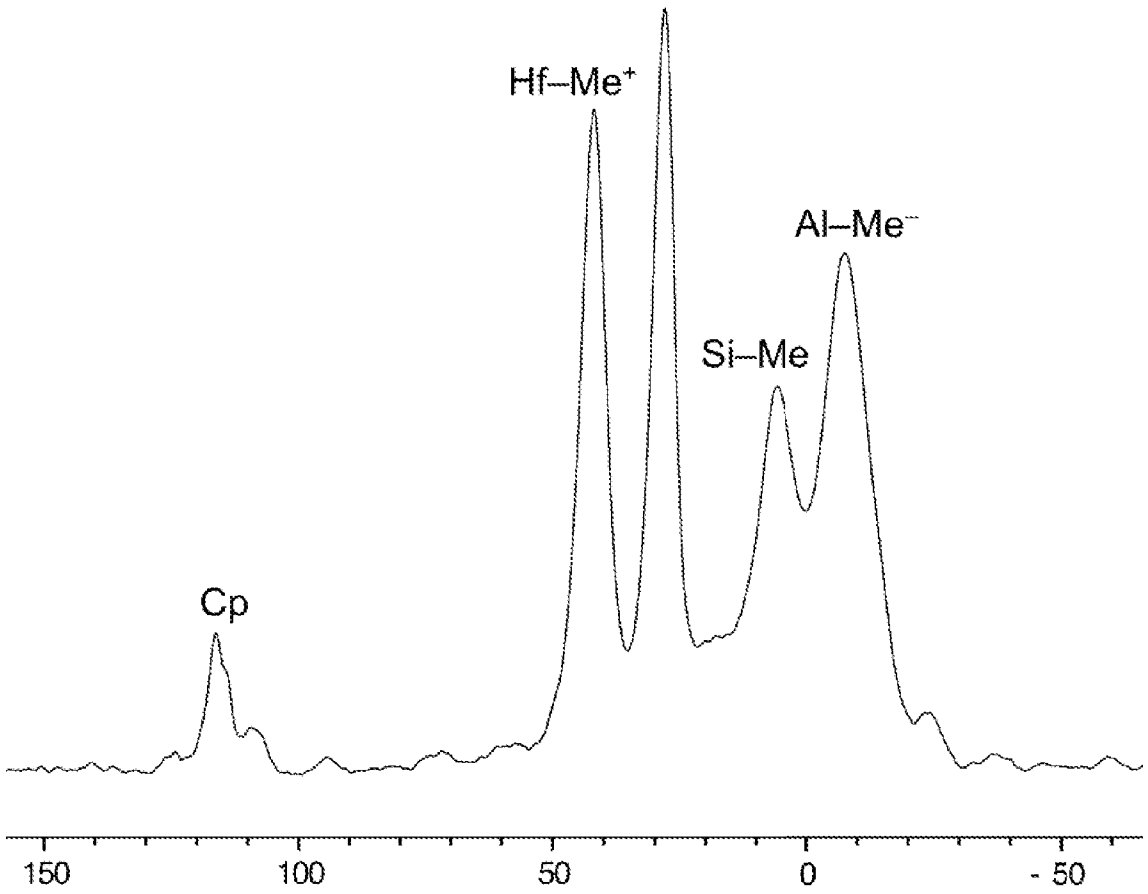


FIGURE 3

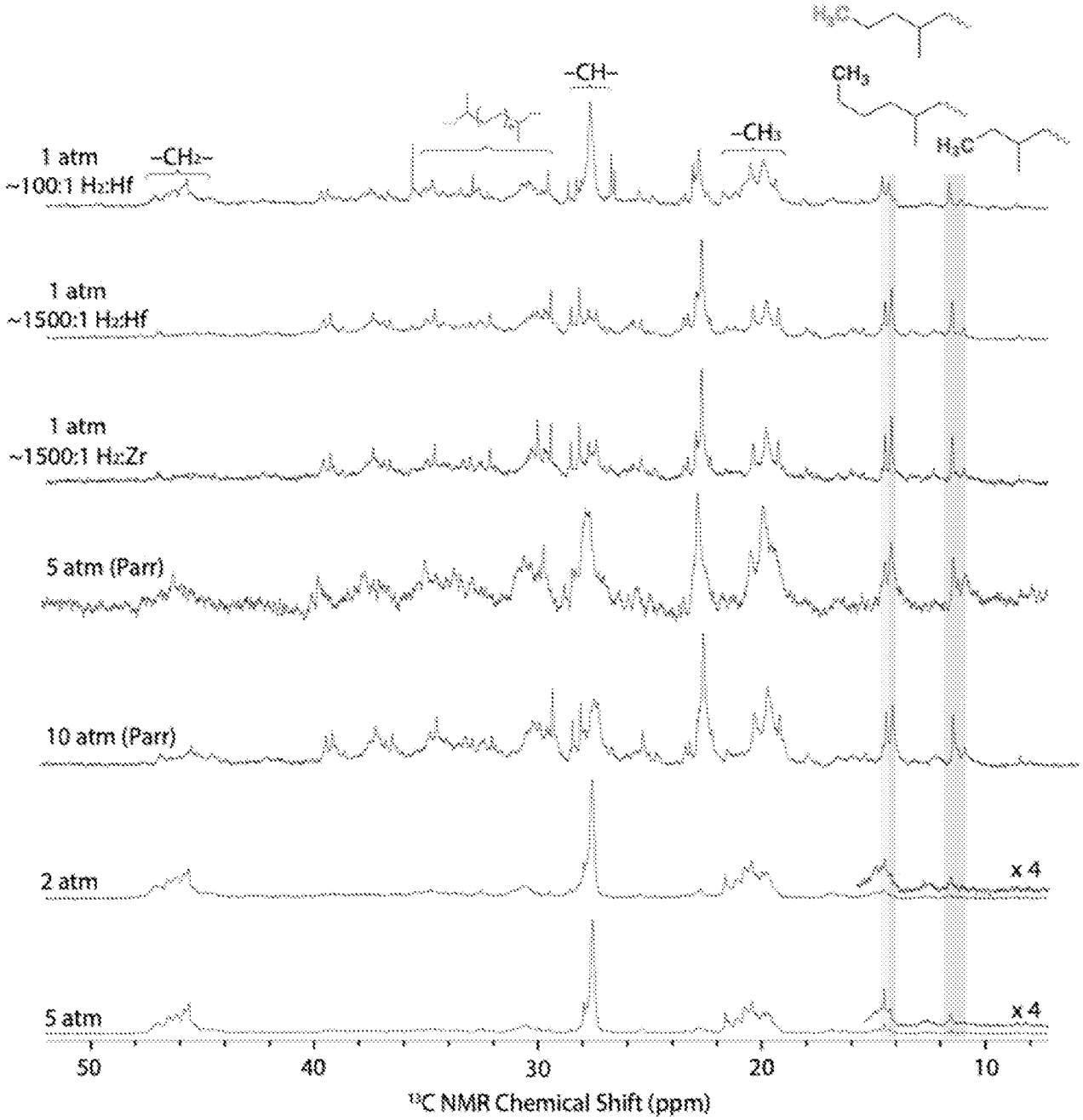

~CH~
~CH3
1 atm
~100:1 H2:Hf
~CH2~
1 atm
~1500:1 H2:Hf
1 atm
~1500:1 H2:Zr
5 atm (Parr)
10 atm (Parr)
2 atm
x 4
5 atm
x 4
50
40
30
20
10
13C NMR Chemical Shift (ppm)

FIGURE 4

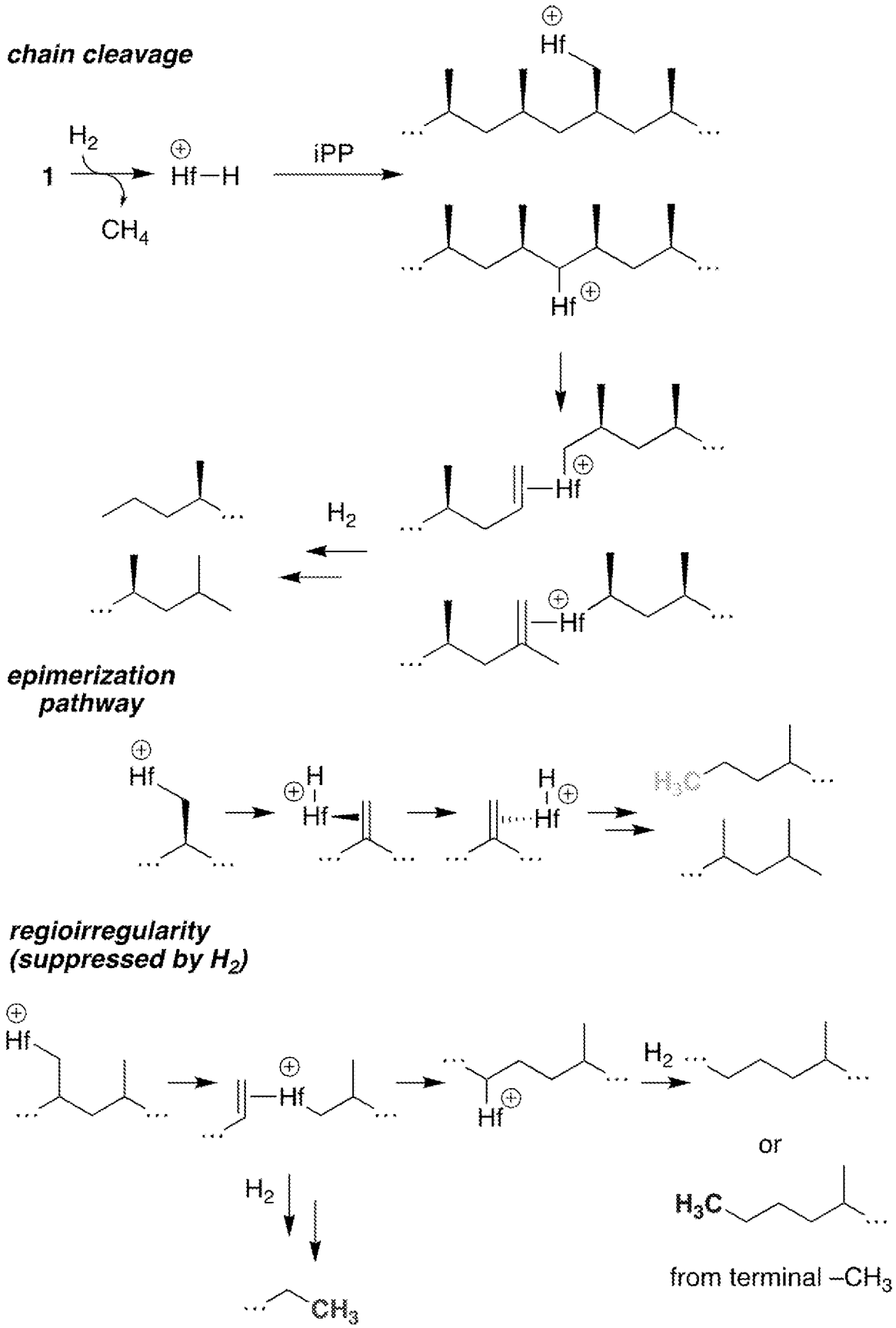
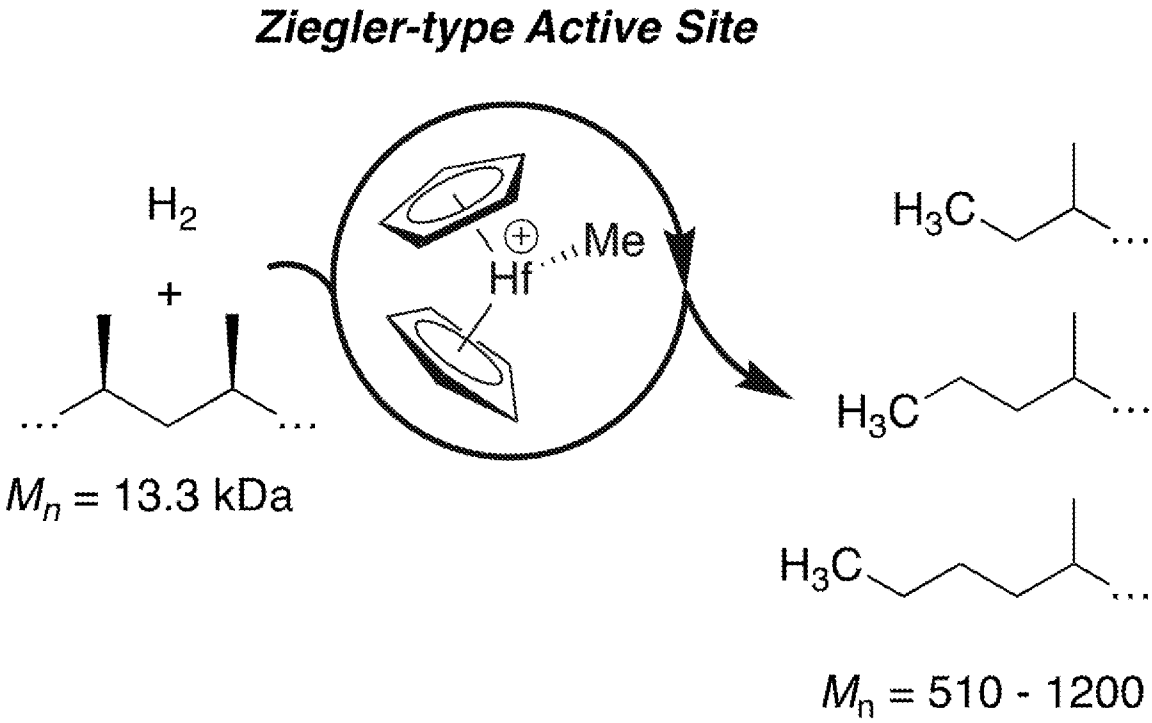

chain cleavage
1
H2
CH4
Hf—H
iPP
Hf
H2
epimerization pathway
regioirregularity (suppressed by H2)
or
H3C
from terminal –CH3
CH3

FIGURE 5



FIGURES 6A-6B

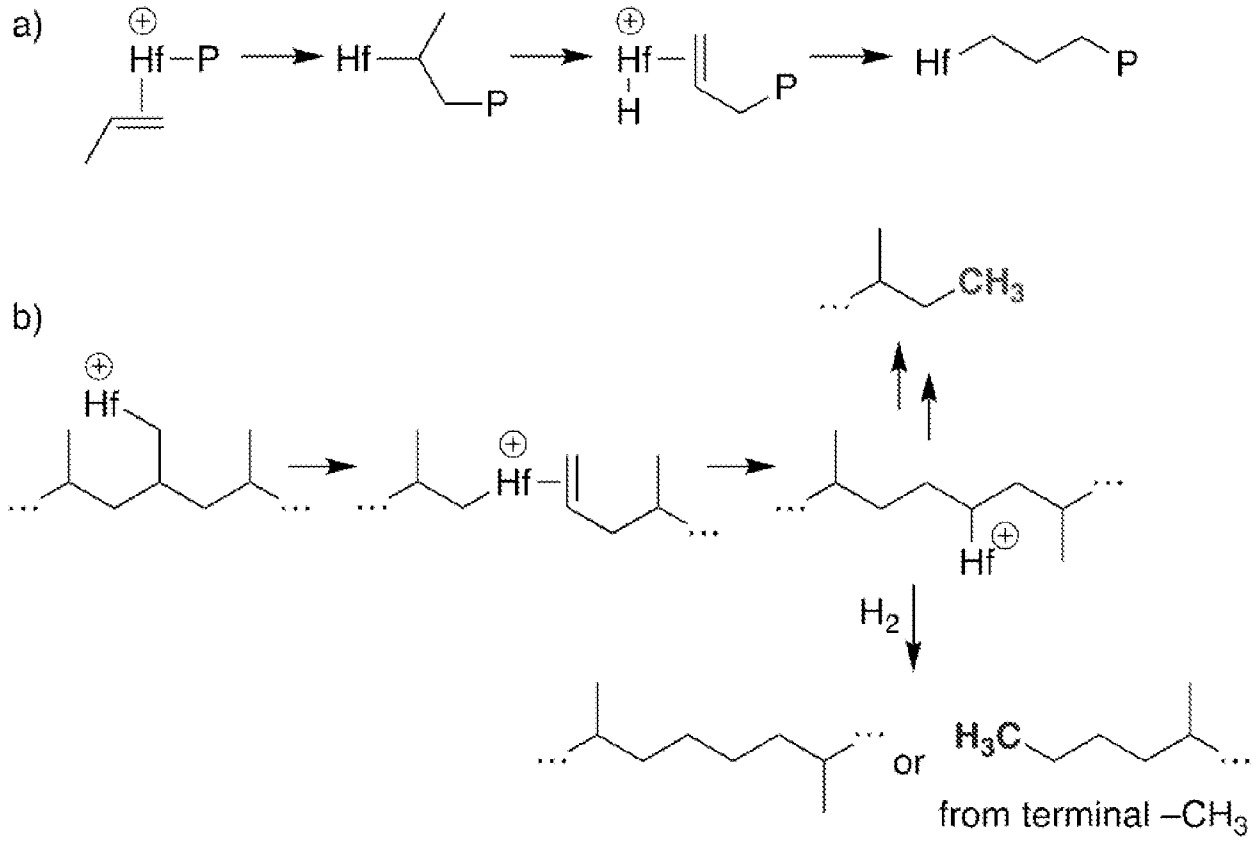


FIGURE 7

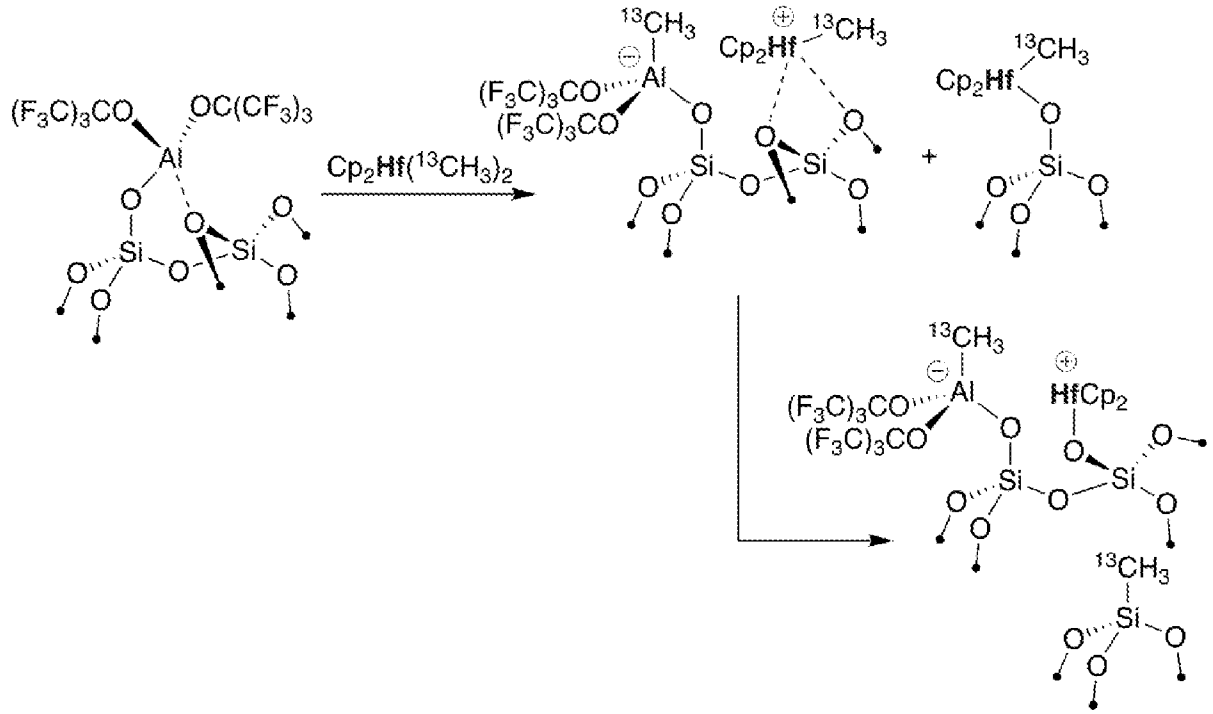


FIGURE 8

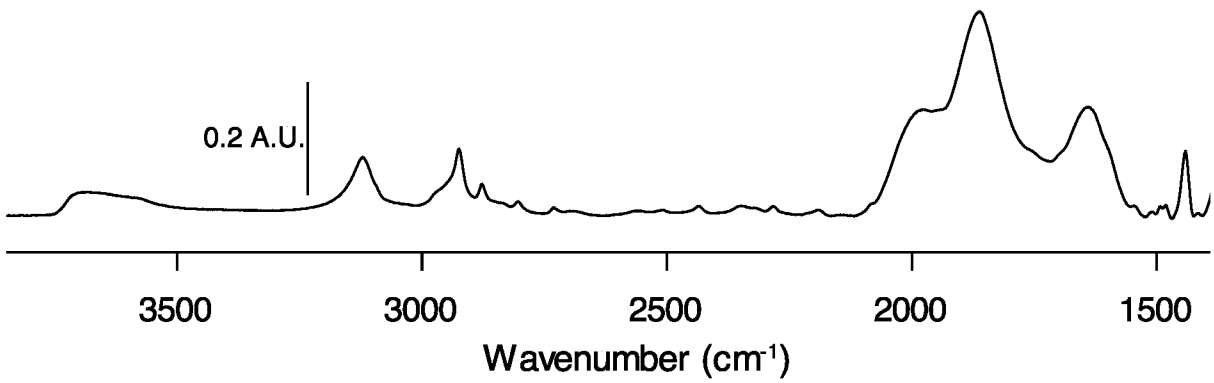


FIGURE 9

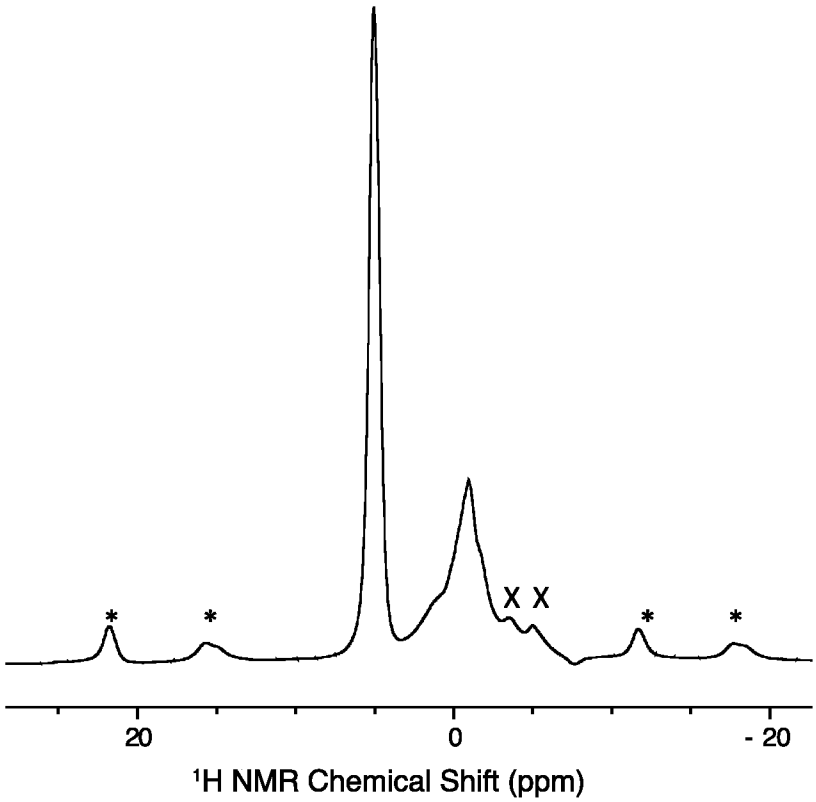


FIGURE 10

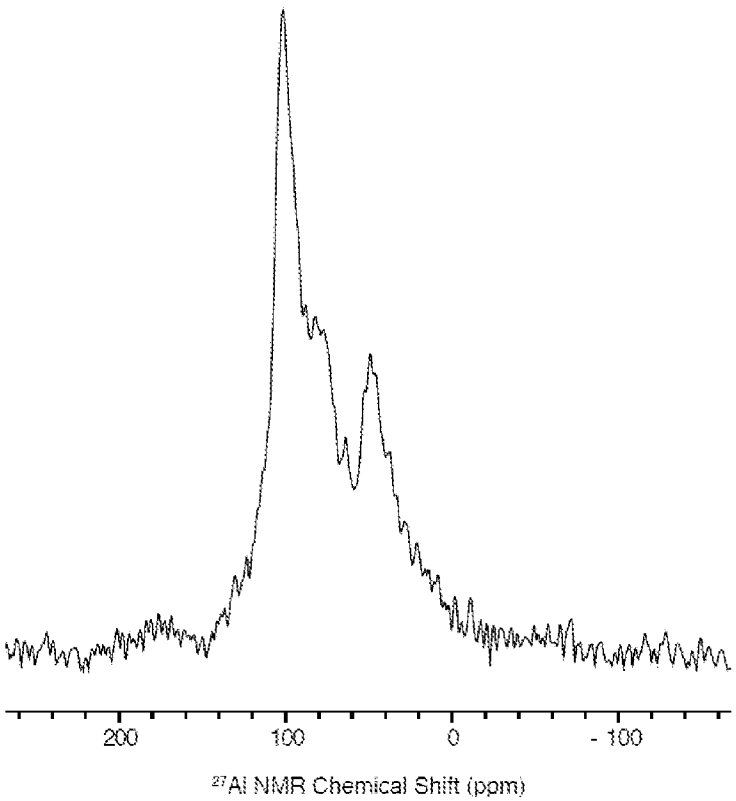


FIGURE 11

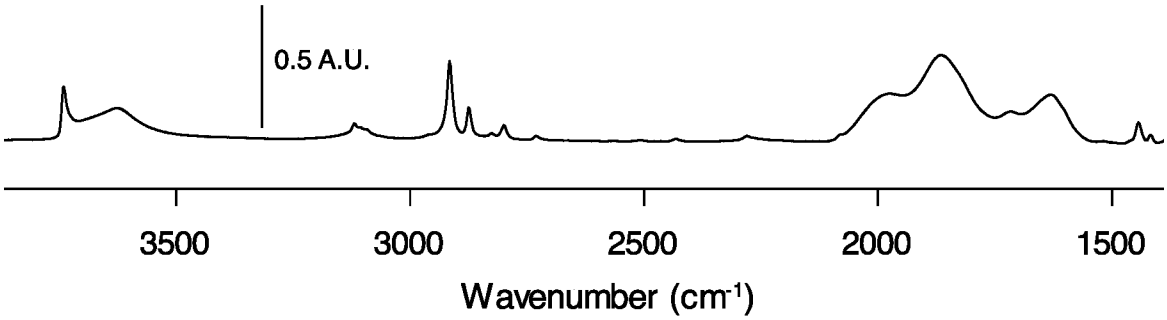


FIGURE 12

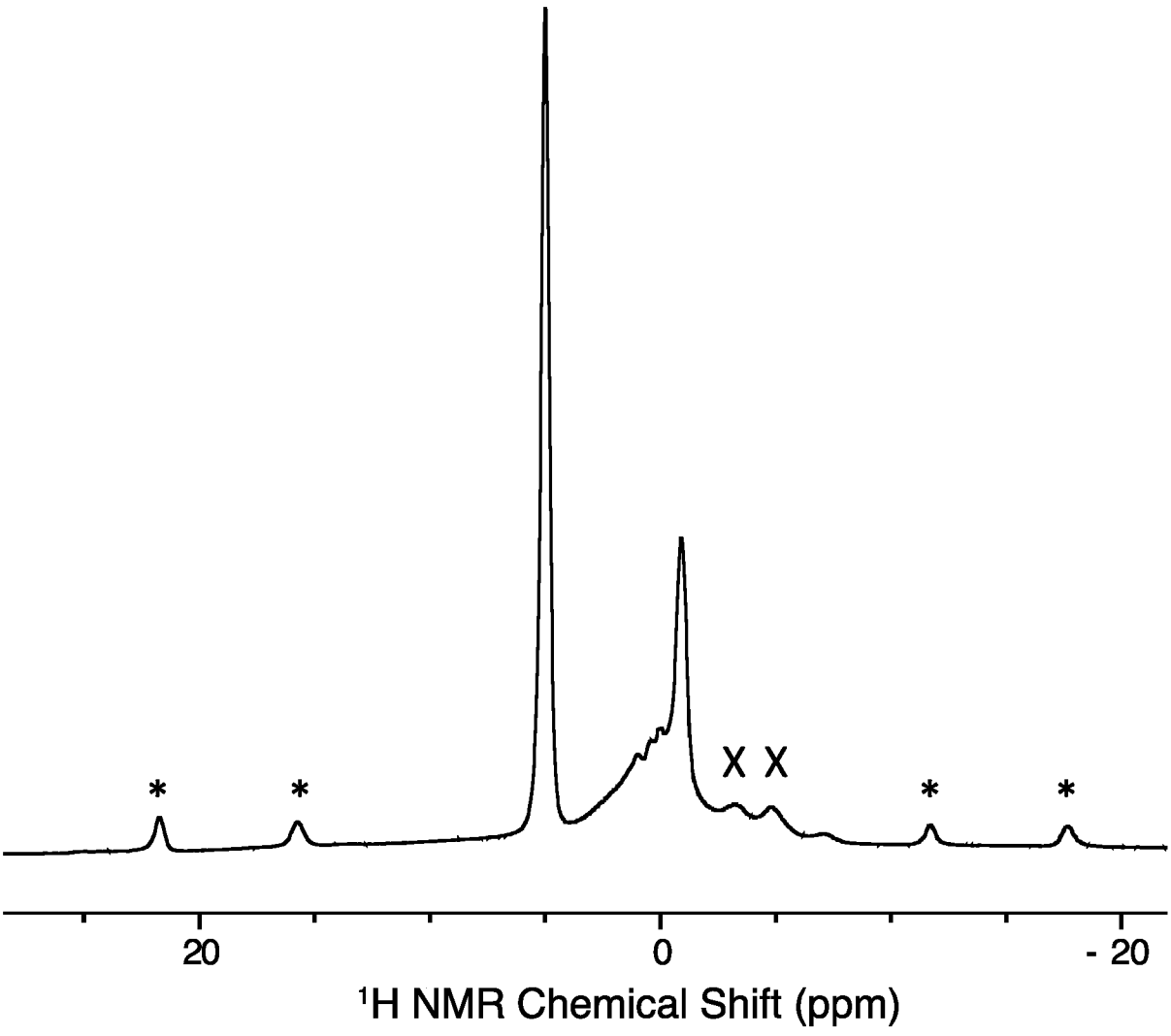


FIGURE 13

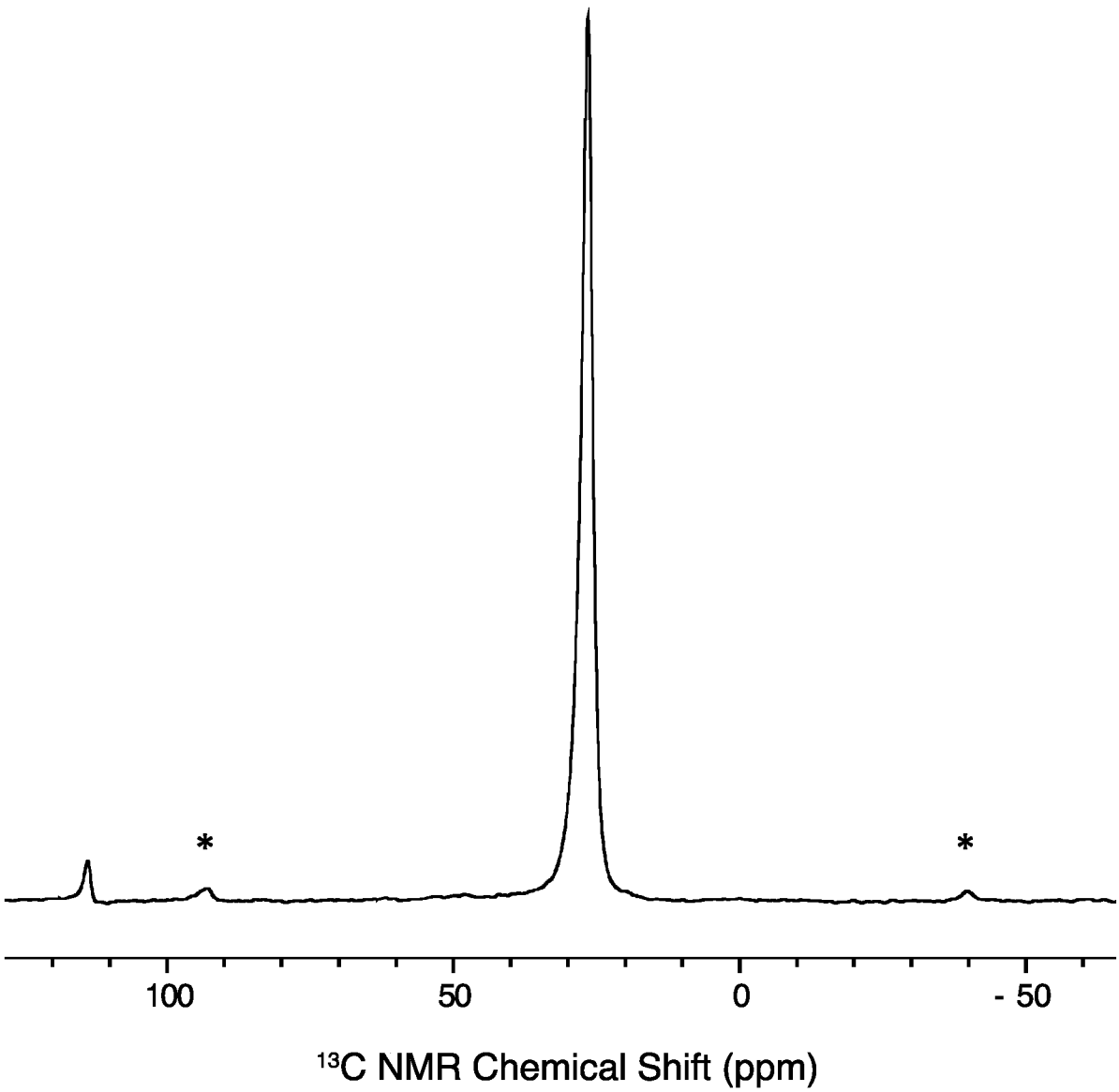


FIGURE 14

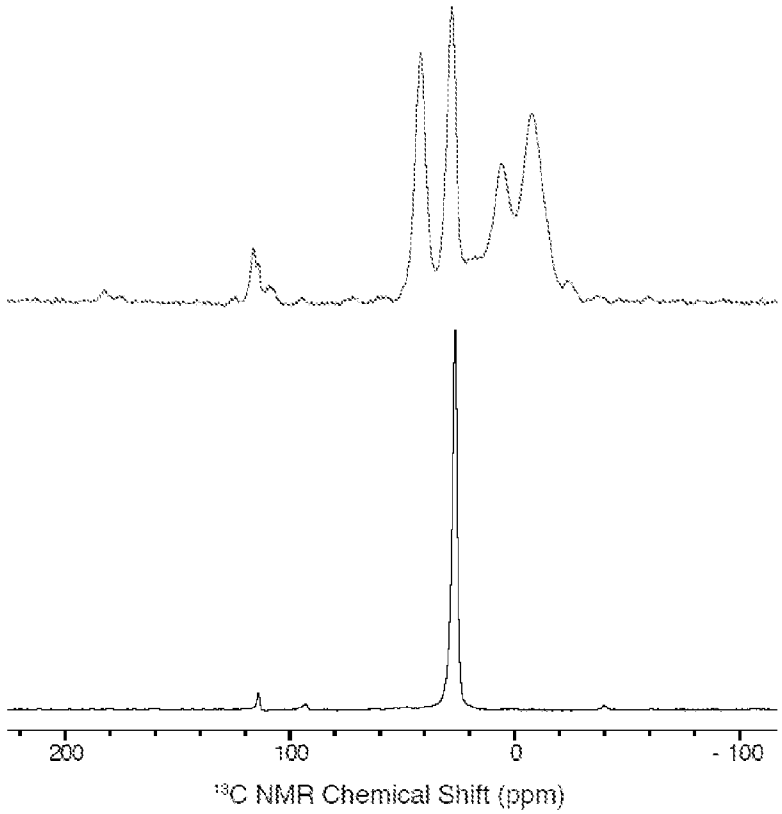


FIGURE 15

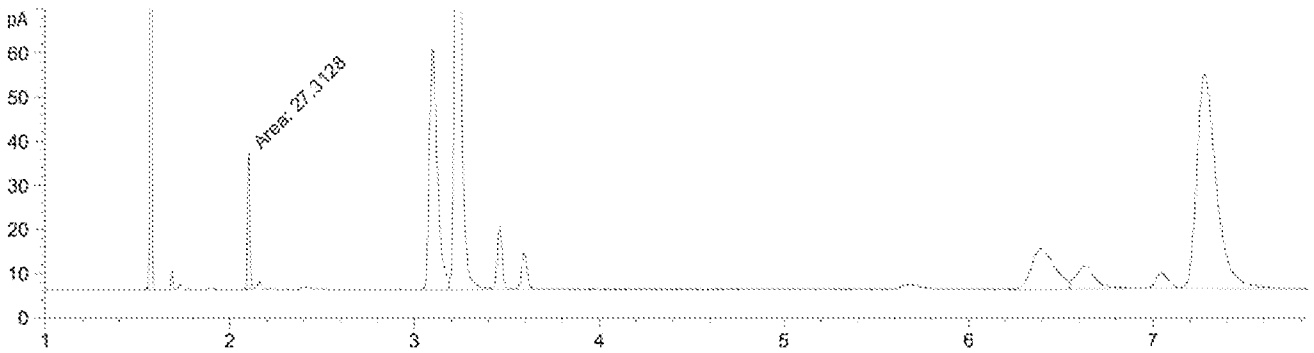


FIGURE 16

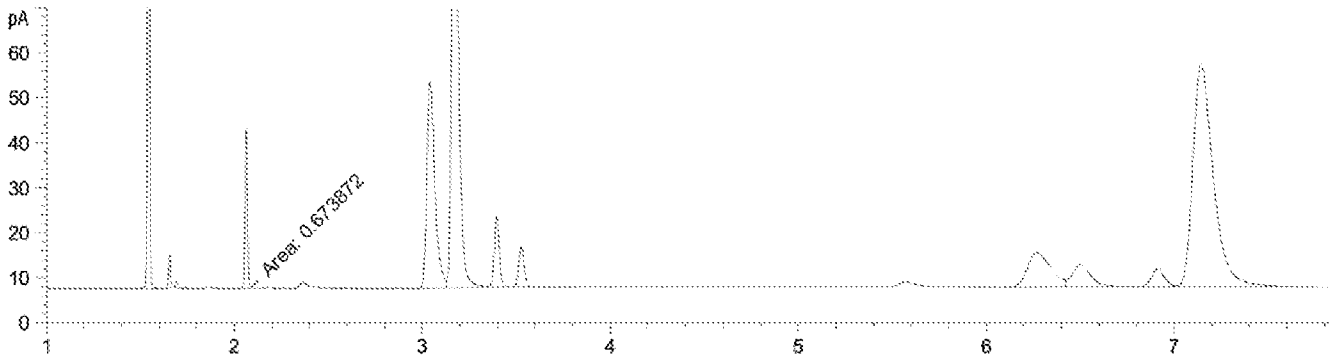


FIGURE 17

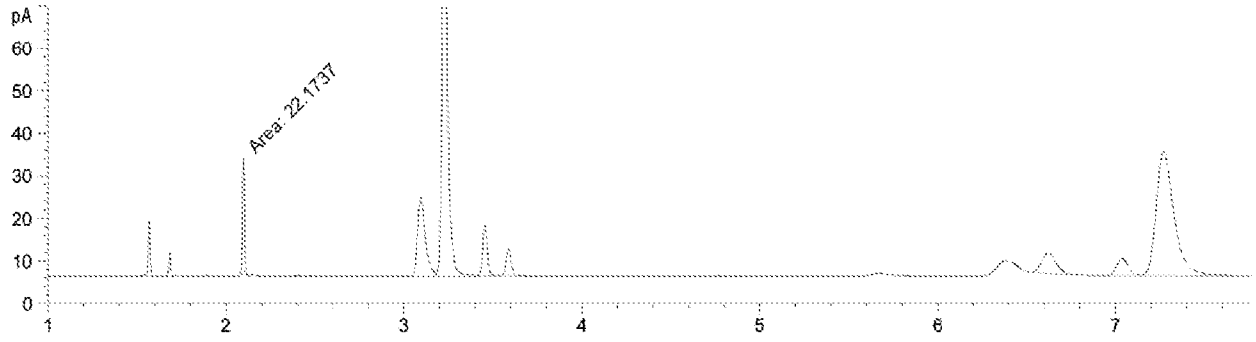


FIGURE 18

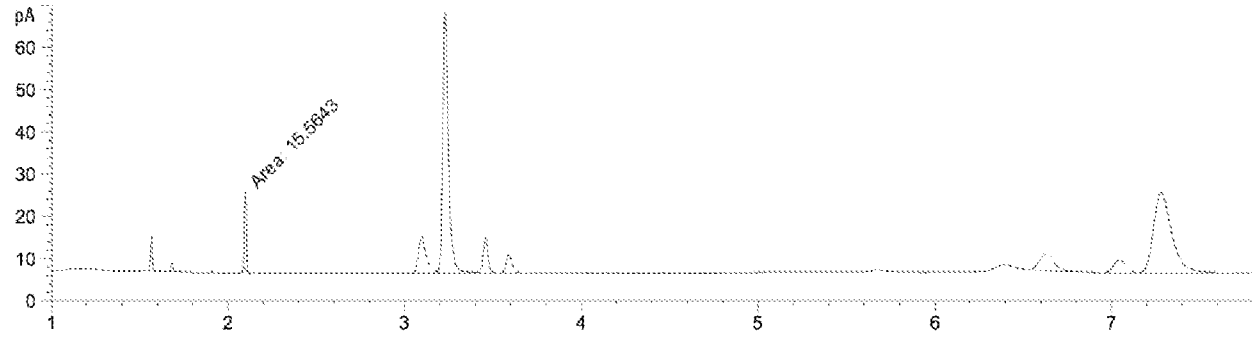


FIGURE 19

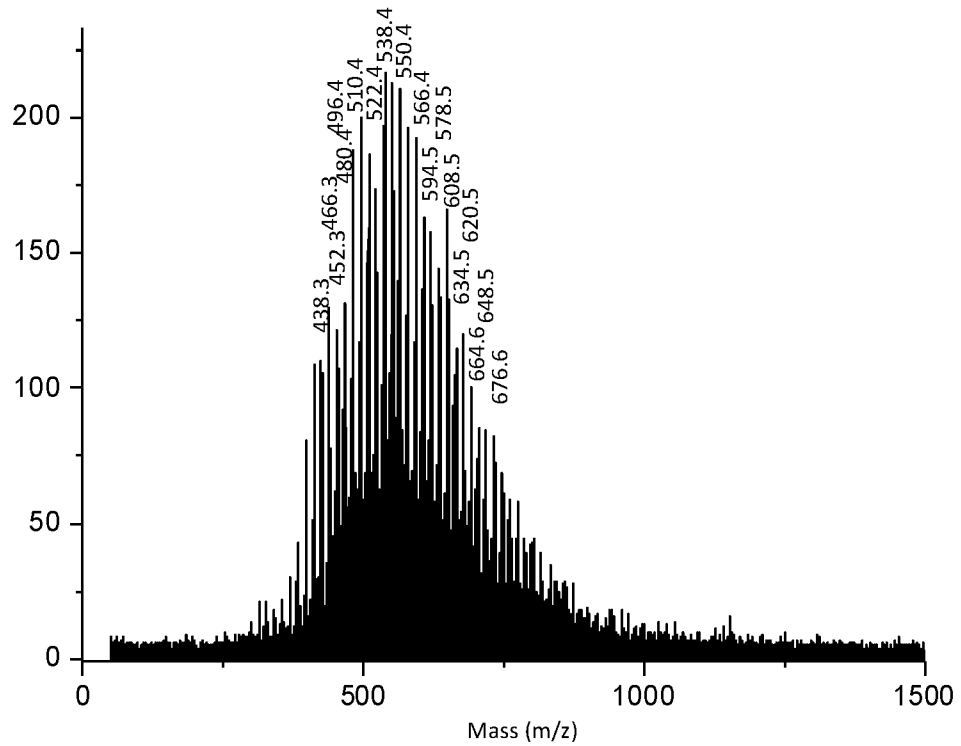


FIGURE 20

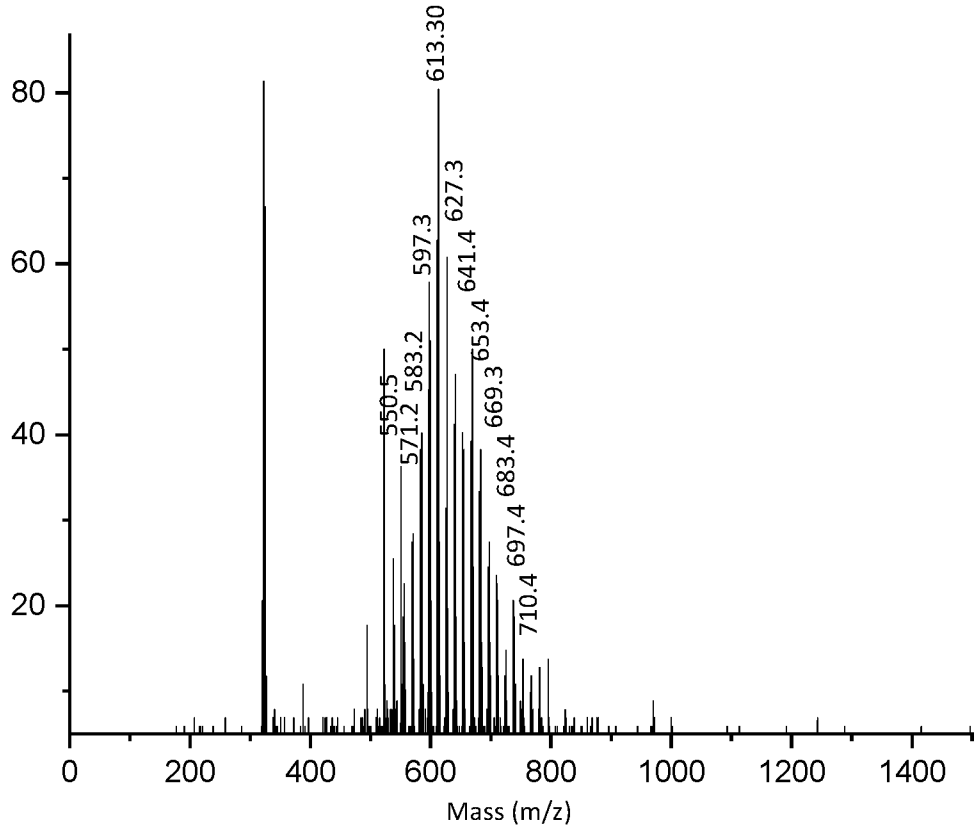


FIGURE 21

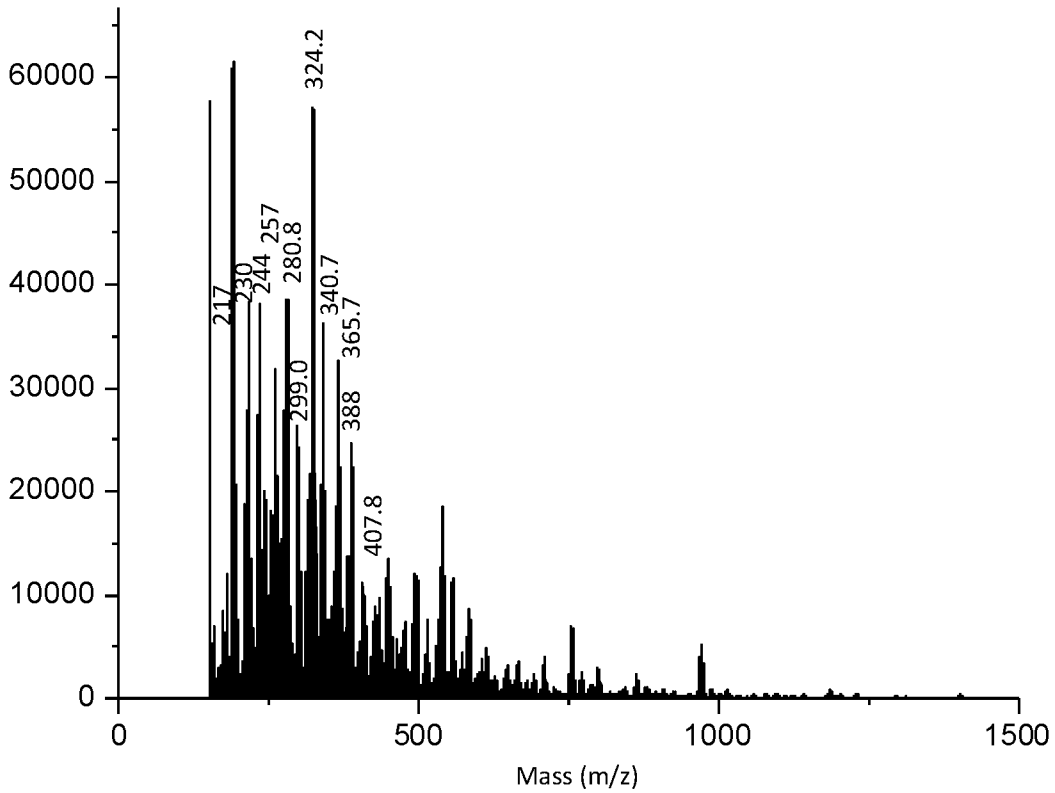


FIGURE 22

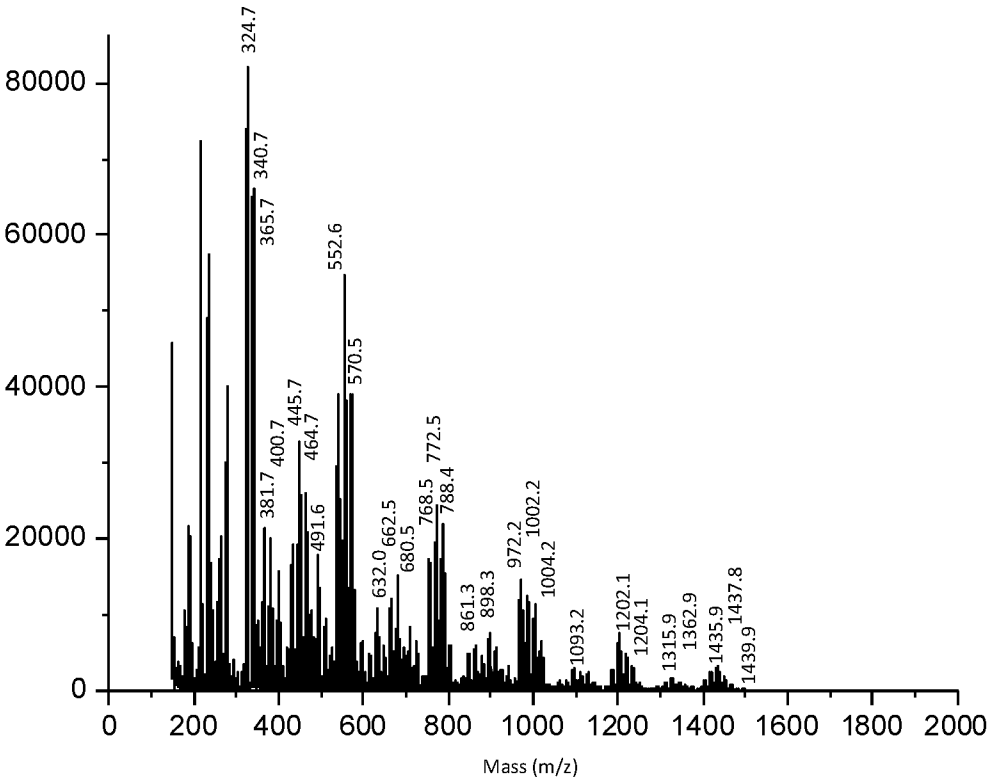


FIGURE 23

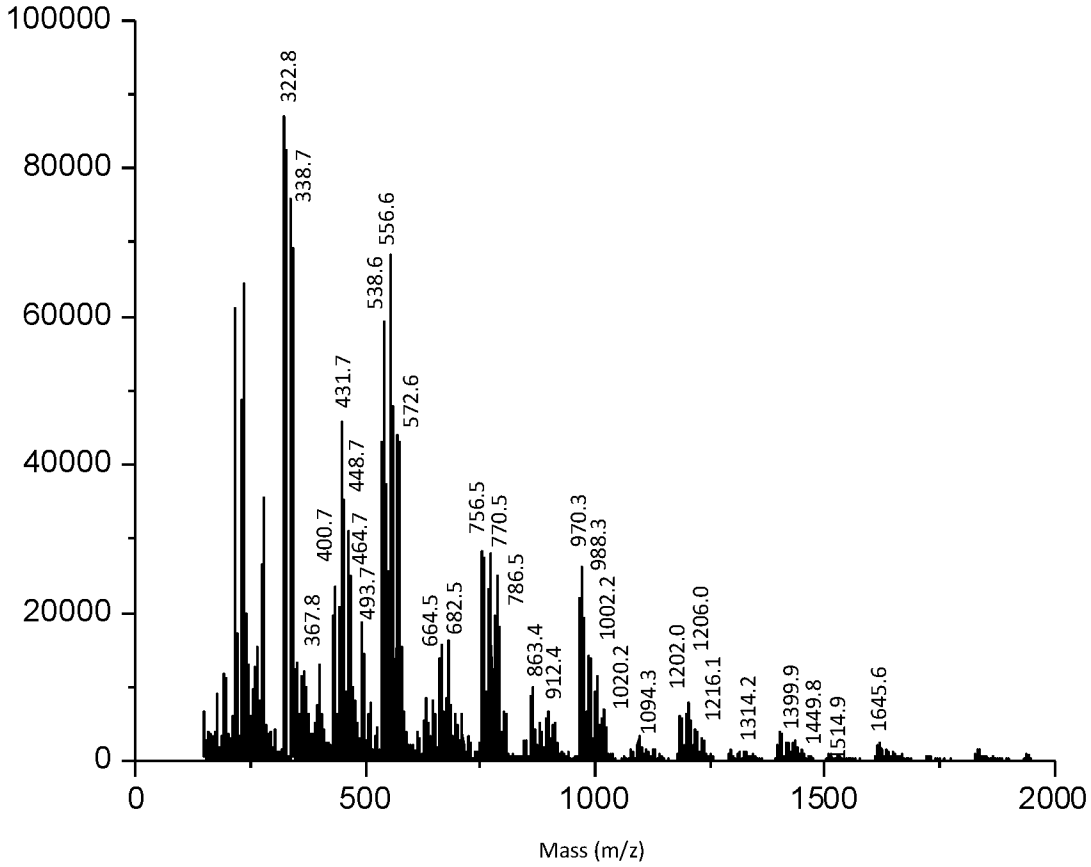


FIGURE 24

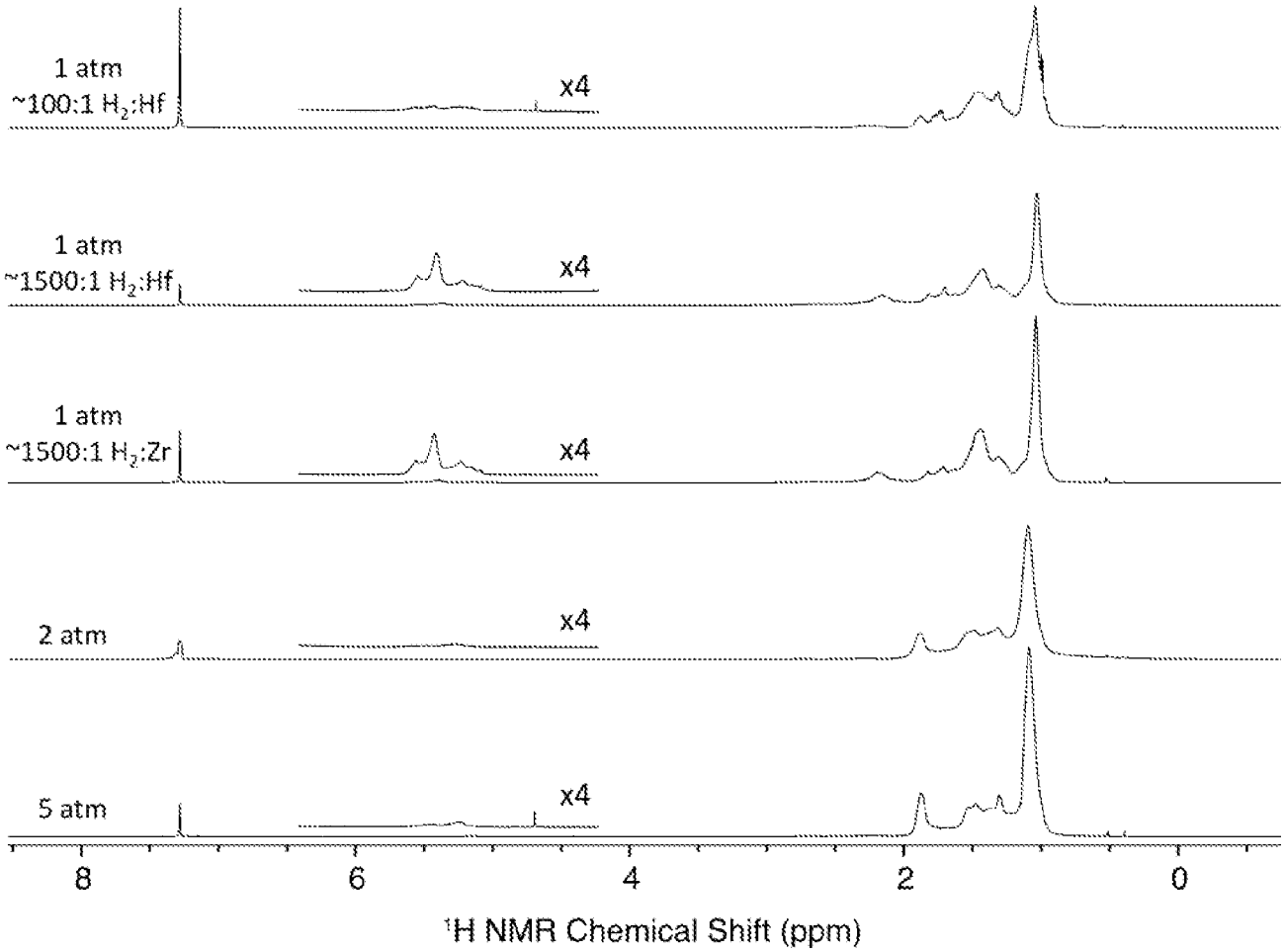

1 atm
~100:1 H2:Hf
x4
1 atm
~1500:1 H2:Hf
x4
1 atm
~1500:1 H2:Zr
x4
2 atm
x4
5 atm
x4
8
6
4
2
0
1H NMR Chemical Shift (ppm)

FIGURE 25

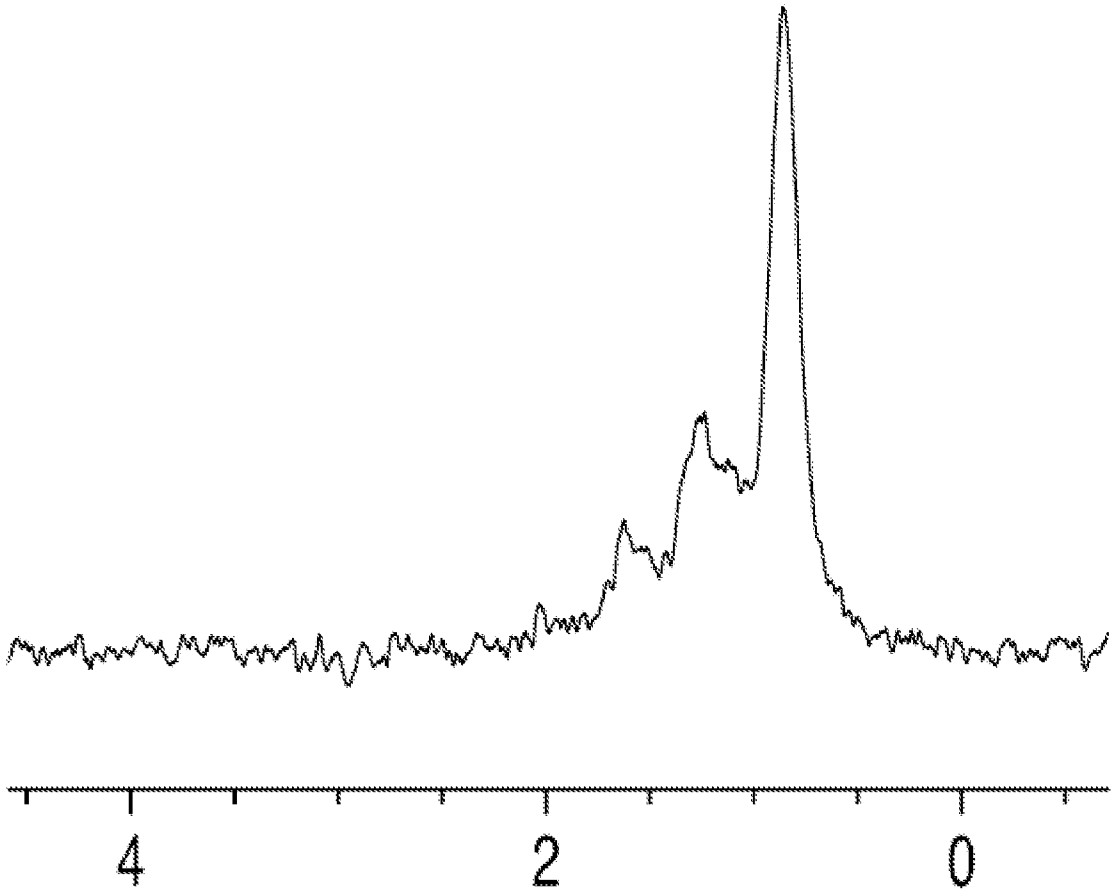


FIGURE 26

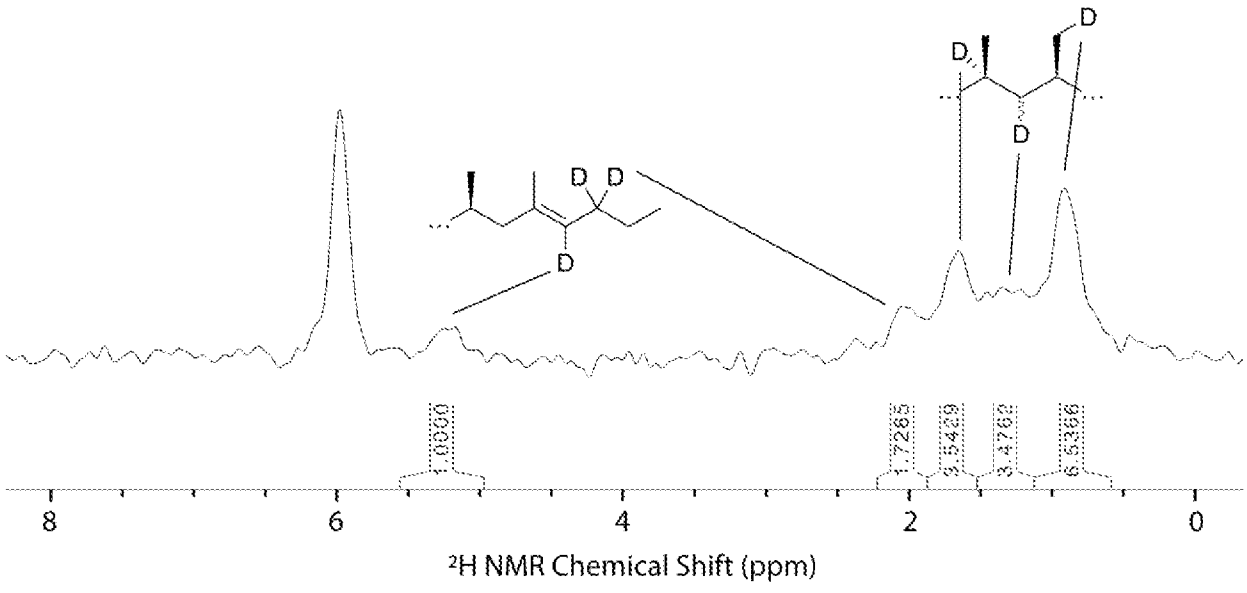


FIGURE 27

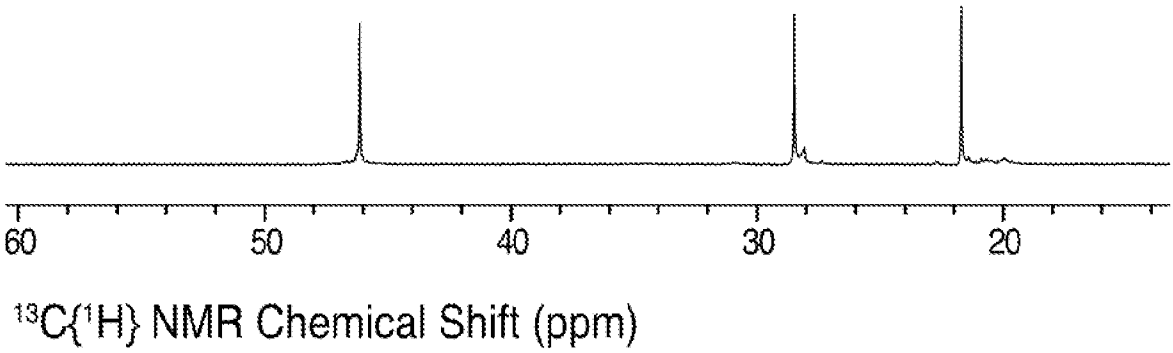


FIGURE 28

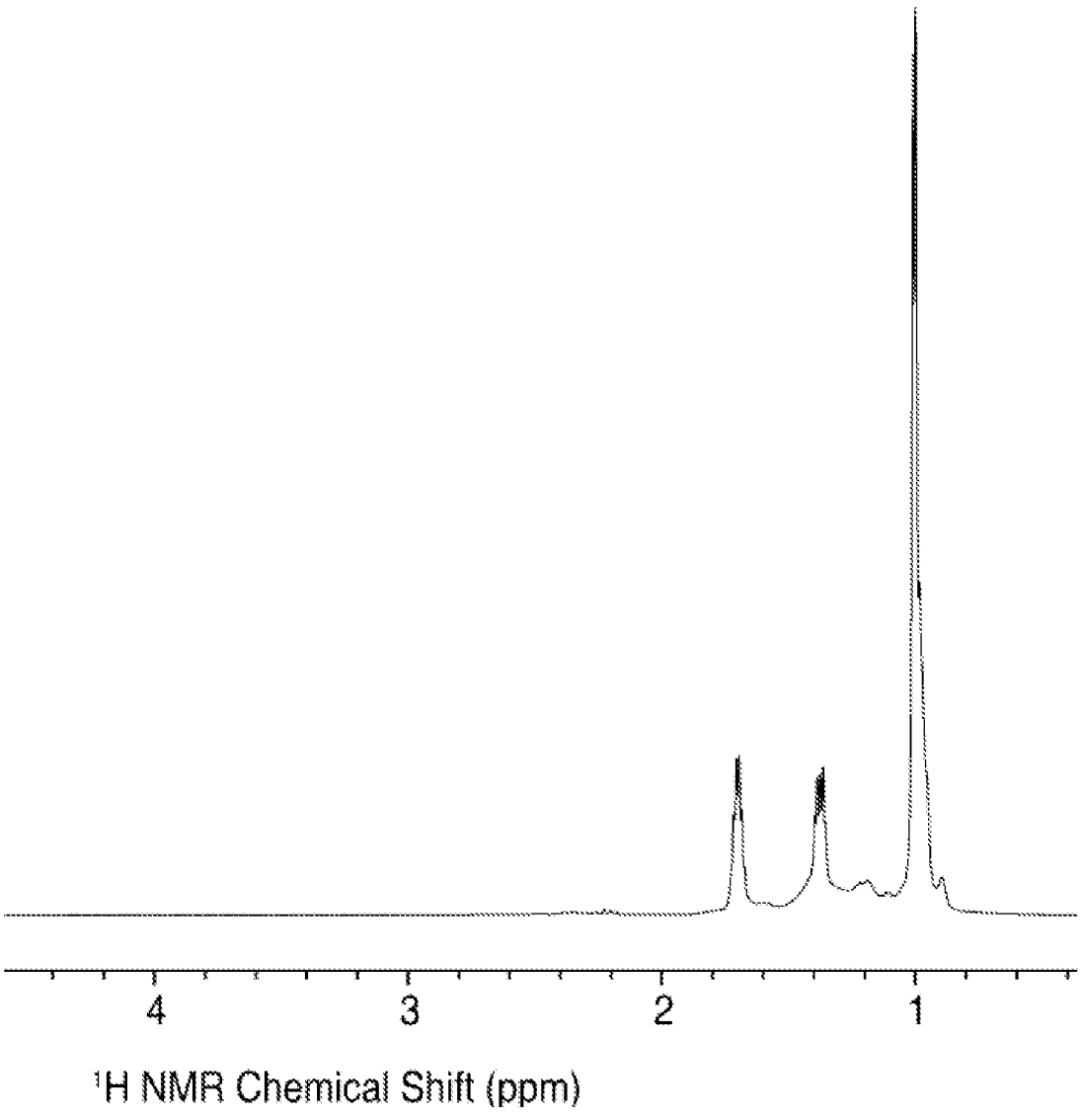


FIGURE 29

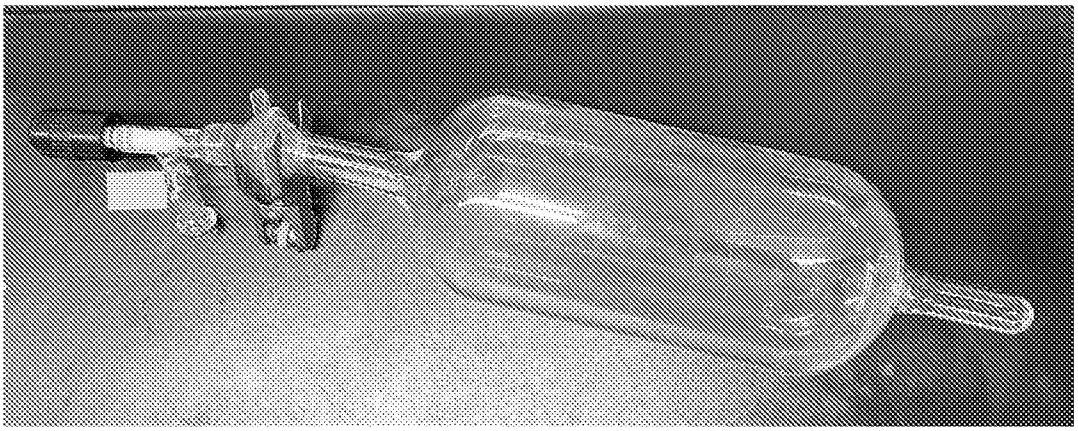
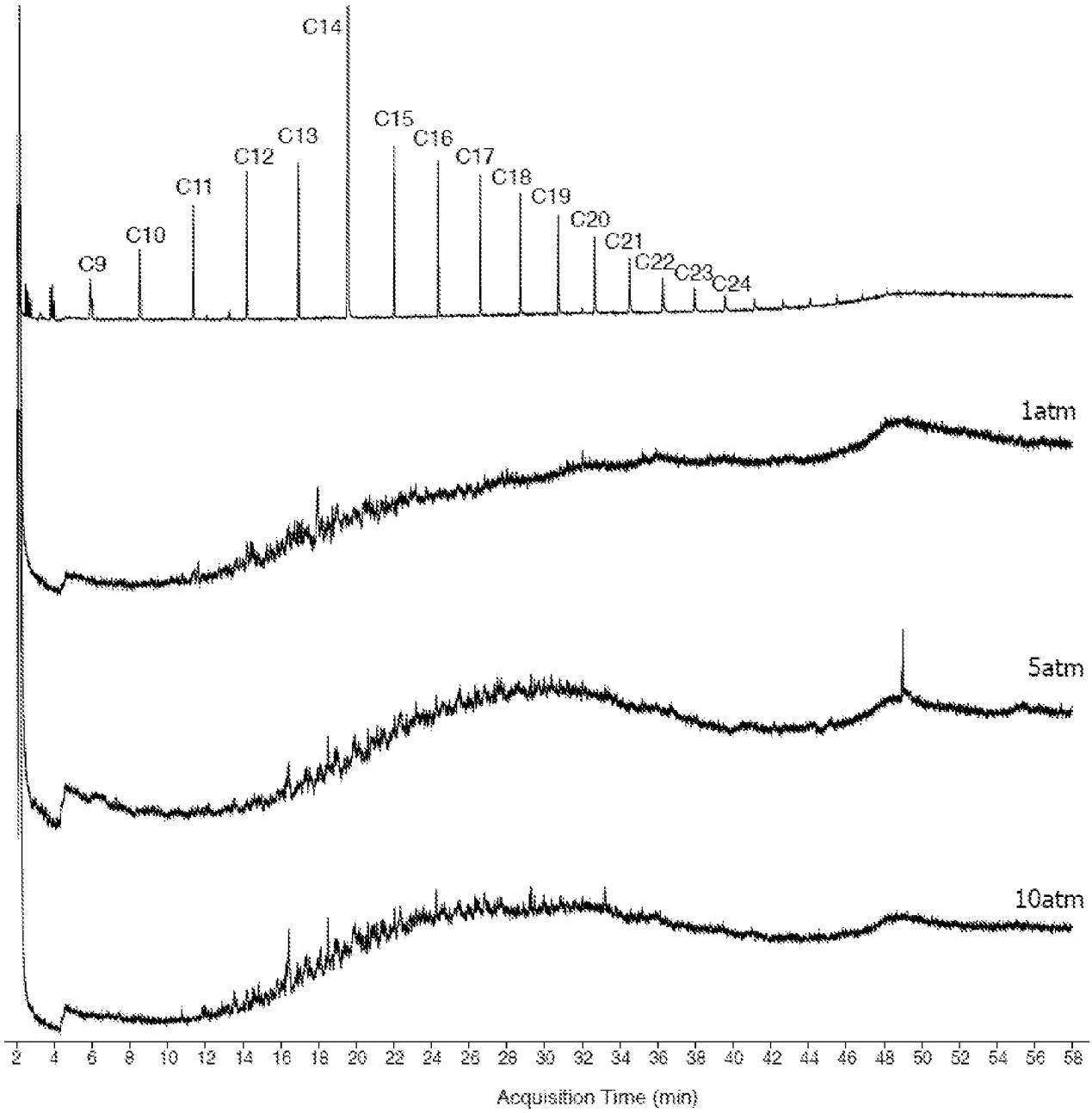


FIGURE 30


C14
C15
C16
C13
C12
C17
C11
C18
C19
C10
C20
C21
C9
C22
C23
C24
1atm
5atm
10atm
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58
Acquisition Time (min)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 24/33107

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. C08F 4/42, C08F 4/64, C08F 4/659, C07F 5/06 (2024.01)
ADD. C08F 4/02 (2024.01)

CPC - INV. C08F 4/42, C08F 4/64, C08F 4/65925, C07F 5/06, C08F 4/65916
ADD. C08F 4/02, C08F 4/65922

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)
See Search History document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2018/0022843 A1 (ExxonMobil Chemical Patents Inc.) 25 January 2018 (25.01.2018) entire document especially para [0018], [0063], [0064]	1-3
A	US 2013/0059990 A1 (Kaji et al.) 07 March 2013 (07.03.2013) entire document	1-3
A	US 2008/0282970 A1 (Heys et al.) 20 November 2008 (20.11.2008) entire document	1-3
A	US 2021/0302835 A1 (Fujifilm Corporation) 30 September 2021 (30.09.2021) entire document	1-3

☐ 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
"D" document cited by the applicant in the international application
"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	Date of mailing of the international search report
23 July 2024 (23.07.2024)	AUG 20 2024
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 24/33107

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.:
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:

3. ☒ Claims Nos.: 4-29
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 additional fees, this Authority did not invite payment of 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.