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(54) **Title**: PREPARATION OF ALKYLAROMATIC COMPOUNDS

(57) **Abstract**: Described herein are methods useful for preparing alkylaromatics.

PREPARATION OF ALKYLAROMATIC COMPOUNDS

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of priority of U.S. Provisional application serial No. 62/173,778, filed June 10, 2015, which application is herein incorporated by reference.

STATEMENT OF GOVERNMENT SUPPORT

This invention was made with government support under CHE-0650456 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND

p-Xylene is an extremely important chemical building block and is used in a variety of applications, but particularly as a starting material for the ubiquitous polymer polyethylene terephthalate or "polyester" (Köpnick, H., et al., 2000. Polyesters. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA, 2002). Accordingly, there is a need to develop new or less expensive ways to prepare xylene (e.g., p-xylene) or methods to prepare p-xylene from alternative starting materials.

SUMMARY OF CERTAIN EMBODIMENTS OF THE INVENTION

Compounds including butenes can be utilized as a starting material to synthesize *p*-xylene through the intermediate 3-methyleneheptane or 3-methylheptane. Accordingly, one embodiment provides a method of preparing p-xylene, comprising converting 3-methyleneheptane or 3-methylheptane to *p*-xylene. Since 3-methyleneheptane (also known as 2-ethyl-1-hexene or 2-butyl-1-butene) is readily accessible from dimerization of butenes (e.g., 1-butene, 2-butene and mixtures thereof), this represents a route to *p*-xylene from butenes. Since butenes can be readily prepared from ethylene, the methods described herein represent a route to p-xylene from ethylene. Butenes are also accessible from a variety of sources including the cracking of petroleum and the dehydrogenation of butane.

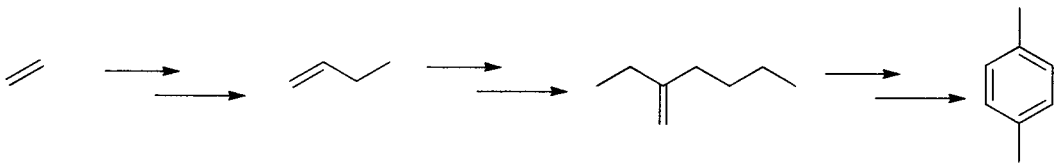
One embodiment provides a method of preparing *p*-xylene, comprising converting 3-methyleneheptane to *p*-xylene. One embodiment provides a method of preparing *p*-xylene, comprising converting 3-methylheptane to *p*-xylene. Accordingly, one embodiment provides a method of preparing p-xylene, comprising converting 3-methyleneheptane or 3-methylheptane or a mixture thereof to *p*-xylene. One embodiment provides a method of preparing p-xylene, comprising converting 1-butene to *p*-xylene. One embodiment provides a

method of preparing p-xylene, comprising converting 2-butene to *p*-xylene. One embodiment provides a method of preparing p-xylene, comprising converting 1-butene or 2-butene or a mixture thereof to *p*-xylene.

DETAILED DESCRIPTION

It has been discovered that ethylene, via butenes, can be utilized as a starting material to synthesize *p*-xylene through the intermediate 3-methyleneheptane or 3-methylheptane. This is especially important as ethylene is quite inexpensive due to the abundance of ethane precursor from shale gas. Alternatively, butenes from any other sources can be utilized as starting material. For example, this process could be easily integrated within existing industrial plants using Fluidized Catalytic Cracking (FCC) which produces butenes. This process is also important as in some embodiments it selectively (e.g., in greater ratio) produces p-xylene over other products (e.g., ethyl benzene, *o*-xylene and dimers) including other regioisomers of xylene (e.g., *o*-xylene). In one embodiment *o*-xylene is produced by the process described herein. *O*-xylene obtained by the process described herein can be converted to *p*-xylene by a conventional *p*-xylene unit. In one embodiment ethylbenzene is produced by the process described herein. Ethylbenzene obtained by the processes described herein can be converted to styrene. The conversion of ethylene to p-xylene is illustrated in Scheme I.

Scheme 1



As indicated in Scheme 1, ethylene can be dimerized to form 1-butene (Köpnick, H., et al., 2000. Polyesters. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA; Al-Sa'doun, A. W. Applied Catalysis A: General, 1993; 105 (1), 1-40., Al-Jarallah, A. M et al., Catal. Today, 1992, 14 (1), 1-121.) 1-Butene can then be dimerized to 3-methyleneheptane (Zhang, W. Li, et al., Catalysis Letters, 2000, 64, 147-150; Karinen, R. S., et al., J. Mol. Catal. A: Chem, 2000, 152, 253). Similarly, 2-butene can also be dimerized to form 3-methyleneheptane as the major product (Goddard, R. E., et al., Dimerization of olefins. GB 824002, November 25, 1959; Ziegler, K., et al., 2-Ethyl-1-hexene. DE 945390, July 5, 1956; Endler, H., et al., Dimerizing monoolefins. FR 1380349, November 27, 1964).

As shown herein, 3-methyleneheptane (or 3-methylheptane) can be dehydroaromatized to give *p*-xylene.

Reagents that facilitate dehydroaromatization (e.g., catalysts).

The dehydroaromatization reactions described herein (e.g., reactions for preparing *p*-xylene) are generally conducted in the presence of a reagent to facilitate (e.g., catalyze) the reaction. In one embodiment the dehydroaromatization reaction is conducted in the presence of a catalyst. The catalyst can be any reagent that is used to convert the starting material used in the dehydroaromatization reaction to a product (e.g., p-xylene). In one embodiment the catalyst is used in a sub-stoichiometric amount when compared to starting material. In one embodiment the catalyst is a metal catalyst. In one embodiment the catalyst is a transition metal catalyst (the catalyst comprises a transition metal). In one embodiment the catalyst is an iridium catalyst (the catalyst comprises iridium).

There are many pincer catalysts and other potential catalysts that may be useful for the methods described herein. (van Koten et al., J. Mol. Catal. A: Chem. 146, 317-323 (1999); The Chemistry of Pincer Compounds; Morales-Morales, D.; Jensen, C., Eds.; Elsevier: Amsterdam, 2007). The US patent application 2013/0123552 A1 and the PCT application WO2012/061272 also describe catalysts including pincer catalysts. The content of each of these documents, and in particular the catalysts describer therein are hereby incorporated by reference. Accordingly, in one embodiment the catalyst is a pincer-ligated metal catalyst e.g., complex). In one embodiment the catalyst is a pincer-ligated transition metal catalyst. In one embodiment the catalyst is a pincer-ligated iridium catalyst. In one embodiment the catalyst is a pincer-ligated iridium complex. In one embodiment the catalyst comprises a pincer-ligated iridium complex. In one embodiment the catalyst comprises a pincer-ligated iridium complex in solution. Many such pincer complexes, however, are also well known to be effective dehydrogenation catalysts when supported on solid surfaces as well as in solution (Huang, Z. et al., Adv. Synth. Catal. 351, 188-206 (2009); Huang, Z. et al., Adv. Synth. Catal. 352, 125-135 (2010)) which document is hereby incorporated by reference in its entirety. In one embodiment the catalyst precursor is (^{iPr4}PCOP)Ir(H)(Cl) or (^{iPr4}PCOP)Ir(H)(Cl). In one embodiment the catalyst precursor comprises (^{iPr4}PCOP)Ir(H)(Cl) or (^{iPr4}PCOP)Ir(H)(Cl) and base. Other metal catalysts may be used including other derivatives of the (^{iPr}PCP)Ir and (^{iPr4}PCOP)Ir groups and other pincer-ligated iridium complexes.

In one embodiment the metal catalyst further comprises additional atoms associated (e.g., bonded, coordinated) with the metal. The additional atoms can be for example ligands

that are associated with the metal. In one embodiment the catalyst is a soluble catalyst such as a soluble metal catalyst. In one embodiment the catalyst is a homogeneous catalyst (e.g., a soluble metal catalyst). Heterogeneous catalysts are also known to perform dehydroaromatization reactions similar to homogeneous catalysts (Smiešková, A., et al., *Applied Catalysis A: General* **2004**, *268*, 235). In one embodiment the catalyst is a heterogeneous catalyst. In one embodiment the catalyst is an insoluble catalyst (e.g., partially or completely insoluble). In one embodiment the catalyst is supported on a solid surface. It is to be understood that the term "catalyst(s)" as used herein includes all forms of the catalyst including pre-catalyst forms of a catalyst which provide the corresponding active form of the catalyst (e.g., an active catalyst).

Hydrogen acceptors.

Hydrogen acceptors are compounds that facilitate the dehydroaromatization reactions described herein by facilitating the removal of hydrogen formed during the reaction. Hydrogen acceptors used herein include *t*-butylethylene (TBE). It is known that pincer-ligated iridium complexes can be used to effect alkane dehydrogenation and dehydroaromatization using many hydrogen acceptors other than TBE (Zhang, W., et al., *Catalysis Letters*, **2000**, *64*, 147-150). Accordingly, other hydrogen acceptors may be useful in the dehydroaromatization reactions described herein.

Acceptorless Systems (dehydroaromatization reactions in the absence of a hydrogen acceptor).

Dehydrogenation can be effected by catalysts without the use of any sacrificial acceptor ("acceptorless dehydrogenation") (Choi, J.; et al., Chem. Rev. 2011, 111, 1761-1779; Liu, F.; et al., Chem. Commun. 1999, 655-656). Accordingly, "acceptorless" systems (systems without a hydrogen acceptor in which hydrogen is released) may be useful in the dehydroaromatization methods described herein. Other methods to remove hydrogen which are not based on acceptors may be used and may involve refluxing or a physical method (e.g., bubbling inert gas through the system) to remove hydrogen. Hydrogen sponges (materials or molecules that absorb hydrogen reversibly) or hydrogen-permeable membranes (e.g., palladium) may also be used. Possible hydrogen sponges include MOF's (metal-organic-frameworks), Rosi et al., Science 300, 1127-1129 (2003)), palladium metal or metal alloys, (Sakamoto et al., Ber. Bunsen-Ges. Phys. Chem. Chem. Phys. 99, 807-820 (1995)), crystalline pincer complexes. (Huang et al., Nature 465, 598-601 (2010). These or other such

materials may be recycled after absorbing hydrogen. Hydrogen-permeable membranes are known in the art. (Paglieri et al., Purif. Methods 31, 1-169 (2002); Dittmeyer et al., J. Mol. Catal. A-Chem. 173, 135-184 (2001)).

Co-catalysts

Co-catalysts may also be used in the methods provided herein. In particular, co-catalysts for dehydroaromatization reactions may be used. Addition of a cyclization co-catalyst may promote the overall reaction rates and/or yields; for example, it is known that Lewis acid catalysts may be used to catalyze electrocyclization reactions. (Kagan et al., Chemical Reviews 92, 1007-1019 (1992); Okuhara, Chemical Reviews 102, 3641-3665 (2002)).

It is to be understood that the embodiments described below are non-limiting and that two or more embodiments may be combined.

One embodiment provides a method of preparing *p*-xylene, comprising converting 3-methyleneheptane or 3-methylheptane to *p*-xylene. One embodiment provides a method of preparing *p*-xylene, comprising converting 3-methyleneheptane to *p*-xylene. One embodiment provides a method of preparing *p*-xylene, comprising converting 3-methylheptane to *p*-xylene. One embodiment provides a method of preparing *p*-xylene, comprising converting 3-methyleneheptane or 3-methylheptane or a mixture thereof to *p*-xylene.

One embodiment provides a method of preparing *p*-xylene, comprising converting 1-butene or 2-butene to *p*-xylene. One embodiment provides a method of preparing *p*-xylene, comprising converting 1-butene or 2-butene or a mixture thereof to *p*-xylene. One embodiment provides a method of preparing *p*-xylene, comprising converting 1-butene to *p*-xylene. One embodiment provides a method of preparing *p*-xylene, comprising converting 2-butene to *p*-xylene. In one embodiment the method is characterized in that the conversion comprises the use of a catalyst. In one embodiment the method is characterized in that the 1-butene or 2-butene is first converted to an intermediate compound (e.g., 3-methyleneheptane) which intermediate is contacted with a catalyst. In one embodiment the method is characterized in that the 1-butene is first converted to an intermediate compound (e.g., 3-methyleneheptane) which intermediate is contacted with a catalyst. In one embodiment the method is characterized in that the 2-butene is first converted to an intermediate compound (e.g., 3-methyleneheptane) which intermediate is contacted with a catalyst. In one embodiment the method is characterized in that the 1-butene or 2-butene or a mixture thereof

is first converted to an intermediate compound (e.g., 3-methyleneheptane or 3methylheptane or a mixture thereof) which intermediate is contacted with a catalyst.

One embodiment provides a method of preparing *p*-xylene, comprising converting ethylene to *p*-xylene. In one embodiment the method is characterized in that the conversion comprises the use of a catalyst. In one embodiment the method is characterized in that the ethylene is first converted to an intermediate compound (e.g., 3-methyleneheptane) which intermediate is contacted with a catalyst.

In one embodiment the 3-methyleneheptane or 3-methylheptane is contacted with a catalyst.

In one embodiment the catalyst is a metal catalyst.

In one embodiment the catalyst is a transition metal catalyst.

In one embodiment the catalyst is an iridium catalyst.

In one embodiment the catalyst is a pincer-ligated catalyst.

In one embodiment the catalyst is a homogeneous catalyst (e.g., the catalyst is uniformly mixed in the reaction media such as being soluble in the reaction media).

In one embodiment the catalyst is a heterogeneous catalyst (e.g., the catalyst is not uniformly mixed in the reaction media such as being insoluble (such as partially or completely) in the reaction media).

In one embodiment the catalyst is (^{iPr4}PCOP)Ir or (^{iPr4}PCP)Ir.

In one embodiment the catalysts (^{iPr4}PCOP)Ir and (^{iPr4}PCP)Ir are derived from the corresponding catalyst precursors (^{iPr4}PCOP)Ir(H)(Cl) and (^{iPr4}PCP)Ir(C_2H_4).

In one embodiment the step of contacting 3-methyleneheptane or 3-methylheptane with the catalyst is performed in the presence of an H-acceptor.

In one embodiment the H-acceptor is *t*-butylethylene (TBE).

In one embodiment the conversion is performed above 170 °C.

In one embodiment the conversion is performed at about 200 °C.

In one embodiment the conversion is performed in a solvent.

In one embodiment the solvent is an aromatic hydrocarbon solvent.

In one embodiment the solvent is mesitylene.

In one embodiment the 3-methyleneheptane or 3-methylheptane is less than or about 0.50 M in the solvent.

One embodiment provides a composition comprising 3-methyleneheptane or 3-methylheptane or a mixture thereof and a catalyst.

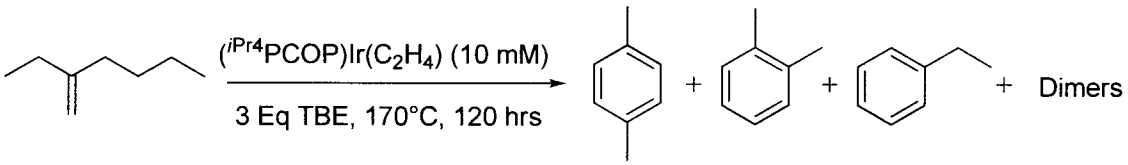
One embodiment provides a composition comprising 1-butene or 2-butene or a mixture thereof and a catalyst.

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

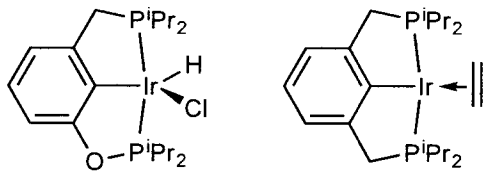
Example 1. Dehydroaromatization of 3-methyleneheptane.

The dehydroaromatization of 3-methyleneheptane yields multiple products. The products include *p*-xylene, *o*-xylene, ethylbenzene, and a variety of unidentified compounds including dimers due to Diels-Alder reactions. Scheme 2 shows the conditions of a representative test reaction using *tert*-butyl ethylene (TBE) as a hydrogen acceptor. Scheme 3 shows the catalyst precursors used in the dehydroaromatization reaction. Table 1 shows the concentration of the products after dehydroaromatization and percent conversion for reactions with varying conditions.

Scheme 2



Scheme 3



(^{iPr4}PCOP)Ir(H)(Cl) (^{iPr4}PCP)Ir(C_2H_4)

Table 1: Concentrations of Products after Dehydroaromatization and Conversions

Conditions (10 mM catalyst)	**Ethylbenzene/mM (% yield)**	***o*-Xylene/mM (% yield)**	***p*-Xylene/mM (% yield)**	**Dimers/mM (% yield)**
(^{iPr4}PCOP)Ir(H)(Cl) at 170 °C 1.8 M 3-methyleneheptane 5.45 M TBE 30 mM NaOtBu, 120 hours	40 (2 %)	130 (7 %)	680 (38 %)	400 (44 %)
(^{iPr4}PCOP)Ir(H)(Cl) at 200 °C 1.8 M 3-methyleneheptane 5.45 M TBE 30 mM NaOtBu, 120 hours	100 (6 %)	130 (7 %)	910 (51 %)	300 (33 %)
(^{iPr4}PCP)Ir(C_2H_4) at 170 °C 1.8 M 3-methyleneheptane 5.45 M TBE 20 mM NaOtBu, 120 hours	25 (1 %)	160 (9 %)	850 (47 %)	325 (36 %)
(^{iPr4}PCOP)Ir(HCl) at 170 °C 0.36 M 3-methyleneheptane 1.09 M TBE 30 mM NaOtBu, 120 hours Reaction diluted 80 % in mesitylene	15 (4 %)	40 (11 %)	200 (55 %)	45 (25 %)
(^{iPr4}PCP)Ir(HCl) at 200 °C 0.24 M 3-methyleneheptane 1.09 M TBE 30 mM NaOtBu, 120 hours Reaction diluted 80 % in mesitylene	15 (7 %)	30 (11 %)	140 (53 %)	25 (18 %)
(^{iPr4}PCOP)Ir(HCl) at 200 °C 0.25 M 3-methyleneheptane 1.09 M TBE 30 mM NaOtBu, 120 hours Reaction diluted 80 % in mesitylene	20 (7 %)	30 (11 %)	165 (60 %)	30 (20 %)

Entry 1 shows yields from a typical dehydroaromatization reaction, entry 2 shows good yields due to increased temperature, entry 3 shows that the (^{iPr4}PCP)Ir(C_2H_4)catalyst works very well for this reaction, entry 4 shows that dilution with mesitylene gives good yields of *p*-xylene while lowering dimer formation, entry 5 shows the lowest amount of dimers formed and entry 6 shows the best yield of *p*-xylene.

All publications cited herein are incorporated herein by reference. While in this application certain embodiments of invention have been described, and many details have been set forth for purposes of illustration, it will be apparent to those skilled in the art that certain of the details described herein may be varied without departing from the basic principles of the invention.

The use of the terms "a" and "an" and "the" and similar terms in the context of describing embodiments of invention are to be construed to cover both the singular and the

plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (*i.e.*, meaning "including, but not limited to") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. In addition to the order detailed herein, the methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, "such as") provided herein, is intended merely to better illuminate embodiments of invention and does not pose a limitation on the scope of the invention unless otherwise specifically recited in the claims. No language in the specification should be construed as indicating that any non-claimed element as essential to the practice of the invention.

CLAIMS

What is claimed is:

1. A method of preparing *p*-xylene, comprising converting 3-methyleneheptane or 3-methylheptane to *p*-xylene.

2. The method of claim 1 comprising converting 3-methyleneheptane to *p*-xylene.

3. The method of claim 1 or claim 2, wherein the 3-methyleneheptane or 3-methylheptane is contacted with a catalyst.

4. The method of claim 3, wherein the catalyst is a metal catalyst.

5. The method of claim 3, wherein the catalyst is a transition metal catalyst.

6. The method of claim 3, wherein the catalyst is an iridium catalyst.

7. The method of claim 3, wherein the catalyst is a pincer-ligated catalyst.

8. The method of claim 3, wherein the catalyst is a homogeneous catalyst.

9. The method of claim 3, wherein the catalyst is a heterogeneous catalyst.

10. The method of claim 3, wherein the catalyst is (^{iPr4}PCOP)Ir or (^{iPr4}PCP)Ir.

11. The method of claim 10, wherein the catalysts (^{iPr4}PCOP)Ir and (^{iPr4}PCP)Ir are derived from the corresponding catalyst precursors (^{iPr4}PCOP)Ir(H)(Cl) and (^{iPr4}PCP)Ir(C_2H_4).

12. The method of any one of claims 3-11, wherein the step of contacting 3-methyleneheptane or 3-methylheptane with the catalyst is performed in the presence of an H-acceptor.

13. The method of claim 12, wherein the H-acceptor is *t*-butylethylene (TBE).

14. The method of any one of claims 1-13, wherein the conversion is performed above 170 °C.

15. The method of any one of claims 1-13, wherein the conversion is performed at about 200 °C.

16. The method of any one of claims 1-15, wherein the conversion is performed in a solvent.

17. The method of any one of claims 1-15, wherein the solvent is an aromatic hydrocarbon.

18. The method of any one of claims 1-15, wherein the solvent is mesitylene.

19. The method of any one of claims 16-18, wherein the 3-methyleneheptane or 3-methylheptane is less than or about 0.50 M in the solvent.

20. A method of preparing p-xylene, comprising converting 1-butene or 2-butene or a mixture thereof to *p*-xylene.

21. The method claim 20 characterized in that conversion comprises the use of a catalyst.

22. The method claim 21 characterized in that the 1-butene is first converted to an intermediate compound which intermediate is contacted with a catalyst.

23. The method of claim 21, wherein the catalyst is a metal catalyst.

24. The method of claim 21, wherein the catalyst is a transition metal catalyst.

25. The method of claim 21, wherein the catalyst is an iridium catalyst.

26. The method of claim 21, wherein the catalyst is a pincer-ligated catalyst.

27. The method of claim 21, wherein the catalyst is a homogenous catalyst.

28. The method of claim 21, wherein the catalyst is a heterogeneous catalyst.

29. The method of claim 21, wherein the catalyst is any species containing the unit (^{iPr4}PCOP)Ir or (^{iPr4}PCP)Ir or other pincer-ligated iridium species.

30. The method of claim 29, wherein the catalysts (^{iPr4}PCOP)Ir and (^{iPr4}PCP)Ir are derived from the corresponding catalyst precursors (^{iPr4}PCOP)Ir(H)(Cl) and (^{iPr4}PCP)Ir(C_2H_4).

31. The method of any one of claims 1-30, wherein the *p*-xylene is obtained in greater than 5% yield.

32. The method of any one of claims 1-30, wherein the *p*-xylene is obtained in greater than 10% yield.

33. The method of any one of claims 1-30, wherein the *p*-xylene is obtained in greater than 30% yield.

34. The method of any one of claims 1-30, wherein the *p*-xylene is obtained in greater than 50% yield.

35. The method of any one of claims 1-30, wherein the *p*-xylene is obtained in greater than 70% yield.

36. The method of any one of claims 1-30, wherein the *p*-xylene is obtained in greater than 90% yield.

37. The method of any one of claims 1-36, wherein the *p*-xylene is isolated from other compounds.

38. The method of any one of claims 1-36, wherein the *p*-xylene is separated from other compounds.

39. The method of any one of claims 1-38, wherein the *p*-xylene is purified.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/036690

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C07C 2/42; C07C 2/46; C07C 5/52; C07C 5/54; C07C 15/08 (2016.01)
CPC - C07C 2/42; C07C 2/46; C07C 5/52; C07C 5/54; C07C 15/08; C07C 2531/24 (2016.08)
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)
IPC - C07C 2/42; C07C 2/46; C07C 5/52; C07C 5/54; C07C 15/08
CPC - C07C 2/42; C07C 2/46; C07C 5/52; C07C 5/54; C07C 15/08; C07C 2531/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 585/2; 585/3; 585/254; 585/303; 585/414; 585/418; 585/419; IPC - C07C 2/42; C07C 2/46; C07C 5/52; C07C 5/54; C07C 15/08; CPC - C07C 2/42; C07C 2/46; C07C 5/52; C07C 5/54; C07C 15/08; C07C 2531/24 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Patents, Google, STN, PubChem, SureChem
Search terms used: p-xylene, 3-methylheptane, 3-methyleneheptane, 1-butene, 2-butene, aromatic, dehydroaromatization, cyclization

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/0158111 A1 (JOHNSON et al) 12 August 2004 (12.08.2004) entire document	1, 3-6, 9
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Y		7, 8, 10, 11
X	US 2011/0172475 A1 (PETERS et al) 14 July 2011 (14.07.2011) entire document	20-25
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Y		26-30
Y	US 2013/0123552 A1 (GOLDMAN et al) 16 May 2013 (16.05.2013) entire document	7, 8, 10, 11, 26-30
A	AHUJA et al. Catalytic dehydroaromatization of n-alkanes by pincer-ligated iridium complexes. Nature Chemistry, Vol. 3, 167-171; 19 December 2010. [retrieved on 01.08.2016]. Retrieved from the Internet. <URL: https://rucore.libraries.rutgers.edu/rutgers-lib/49330/>. entire document	1-11, 20-30
A	US 5,304,694 A (DESSAU et al) 19 April 1994 (19.04.1994) entire document	1-11, 20-30
A	US 2014/0017744 A1 (PRAKASH et al) 16 January 2014 (16.01.2014) entire document	1-11, 20-30

☐ 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	Date of mailing of the international search report
05 August 2016	07 SEP 2016

Name and mailing address of the ISA/	Authorized officer
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/036690

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.: 12-19, 31-39
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.