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(54) Title: SYNTHESIS OF HEXAMETHYLENEDIAMINE AND ADIPIC ACID VIA HOMOCOUPLING OF ACRYLAMIDES

(57) Abstract: The present disclosure relates to a method of synthesising hexamethylenediamine and adipic acid. The method comprises homocoupling of acrylamide under conditions including using oxalic acid as a reductant and irradiating a reaction mixture comprising acrylamide with light from a light source to obtain an amide substrate, wherein the method further comprises a pathway 1 and a pathway 2 for forming hexamethylenediamine and adipic acid, respectively using the amide substrate.

SYNTHESIS OF HEXAMETHYLENEDIAMINE AND ADIPIC ACID VIA HOMOCOUPLING OF ACRYLAMIDES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore application No. 10202250766W filed 18 August 2022, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] The present disclosure generally relates to a method of synthesising hexamethylenediamine and adipic acid. In particular, the present disclosure relates to a method of synthesising hexamethylenediamine and adipic acid by homocoupling of acrylamides.

BACKGROUND

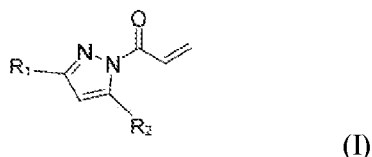
[0003] Hexamethylenediamine and adipic acid are used in the production of nylon, particularly nylon 66 which is synthesized by polycondensation of hexamethylenediamine and adipic acid. Nylon 66 is utilized in a variety of industries, including electronics, textiles, automotive and other industries. The increase in demand of nylon 66 from these industries in turn increases the demand for hexamethylenediamine and adipic acid.

[0004] One of the conventional methods for synthesising hexamethylenediamine involves energy-demanding electrocatalytic homocoupling of acrylonitrile. Other method includes homocoupling of acrylamides and acrylonitrile. These methods, however, use metals such as cobalt, ruthenium, etc. as catalysts in the homocoupling reactions, and metal zinc as the reductant. Some of these methods generate several by-products such as hydrogen, propionitrile, and oligomers. Further processes are often required for removing the by-products, and this increases the overall production costs.

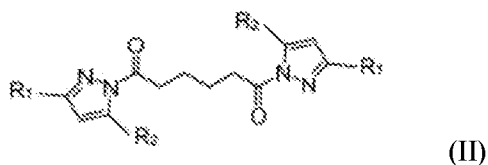
[0005] It is therefore desirable to provide a method of synthesising hexamethylenediamine and adipic acid which seeks to address at least one of the problems described hereinabove, or at least to provide an alternative.

SUMMARY

[0006] In one aspect, the present disclosure provides a method of synthesising hexamethylenediamine and adipic acid. The method comprises homocoupling of acrylamide represented by the general formula (I):



[0007] under conditions including using oxalic acid as a reductant and irradiating a reaction mixture comprising acrylamide with light from a light source to obtain an amide substrate represented by the general formula (II):



wherein R₁ and R₂ are each independently hydrogen, alkyl or aryl,

[0008] wherein the method further comprises a pathway 1 or a pathway 2 for forming hexamethylenediamine and adipic acid, respectively.

[0009] In one embodiment, the pathway 2 further comprises steps for forming adipamide.

DESCRIPTION

[0010] The following description sets forth exemplary methods, parameters, and the like. The embodiments are described in sufficient detail to enable those skilled in the art to practise

the invention. Other embodiments may be utilized, and structural and logical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0011] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0012] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0013] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance, e.g. within 10% of the specified value.

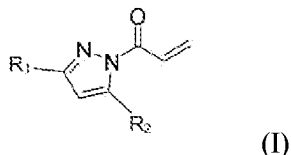
[0014] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0015] By “comprising” it is meant including, but not limited to, whatever follows the word “comprising”. Thus, use of the term “comprising” indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

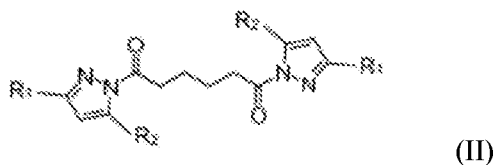
[0016] By “consisting of” is meant including, and limited to, whatever follows the phrase “consisting of”. Thus, the phrase “consisting of” indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0017] The present disclosure relates to a method of synthesising hexamethylenediamine and/or adipic acid via metal-free photocatalytic homocoupling of acrylamide, wherein oxalic

acid is used as a reductant. The method comprises homocoupling of acrylamide represented by the general formula (I):



under conditions including using oxalic acid as a reductant and irradiating a reaction mixture comprising acrylamide with light from a light source to obtain an amide substrate represented by the general formula (II):



wherein R_1 and R_2 are each independently hydrogen, alkyl or aryl; and

wherein the method further comprises a pathway 1 and/or a pathway 2.

[0018] The pathway 1 comprises mixing the amide substrate of formula (II) with benzylamine in a first solvent at a first elevated temperature to obtain a dibenzyladipamide substrate after cooling the mixture to room temperature; mixing the dibenzyladipamide substrate with borane-tetrahydrofuran in a second solvent; quenching the reaction with a quenching reagent; extracting dibenzylamine and drying the extracted dibenzylamine; and mixing the dibenzylamine with a first acid and a third solvent in the presence of a catalyst at a second elevated temperature under a hydrogen gas atmosphere to form a 1,6-diamine, wherein the 1,6-diamine is hexamethylenediamine.

[0019] In some embodiments, the amide substrate is mixed with the benzylamine at the first elevated temperature ranging from 45°C to 55°C. The dibenzyladipamide substrate precipitates as solid after the mixture is cooled to room temperature, and pyrazole is recovered from the

mixture and purified before it is recycled for use to produce the acrylamide of general formula (I).

[0020] In some embodiments, the reaction mixture comprising the dibenzyladipamide substrate and the borane-tetrahydrofuran in the second solvent is subjected to refluxing for a duration ranging from 13 to 17 hours.

[0021] In some embodiments, hydrochloric acid is used as the quenching reagent. One skilled in the art will appreciate that other suitable quenching reagents may be used without departing from the scope of the present disclosure.

[0022] The pH of the reaction mixture comprising the dibenzyladipamide substrate and the borane-tetrahydrofuran may be adjusted before extraction of dibenzylidiamine takes place. In various embodiments, the pH is 13 to 15, and in one embodiment, the pH is 14.

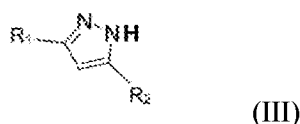
[0023] In some embodiments, the dibenzylidiamine is mixed with the first acid and the third solvent in the presence of palladium on active carbon as the catalyst, at a second elevated temperature ranging from 65°C to 75°C. The mixture is heated for a duration ranging from 14 to 18 hours. This step is carried out under a hydrogen gas atmosphere. The mixture is filtered after it is cooled to room temperature and the filtrate is dried to provide the pure 1,6-diamine, which is hexamethylenediamine, with a yield of 80% to 85%. In various embodiments, the first acid is hydrochloric acid. One skilled in the art will appreciate that other suitable acids may be used without departing from the scope of the present disclosure.

[0024] The pathway 2 comprises the steps for producing adipic acid. The steps include mixing the amide substrate with an aqueous sodium hydroxide in a fourth solvent to obtain an aqueous phase; and adding a second acid into the aqueous phase to adjust the pH value and extracting 1,6-diacid, wherein the 1-6-diacid is adipic acid, with a yield of 85% to 90%.

[0025] In some embodiments, the aqueous phase comprises adipic acid and pyrazole. The pyrazole is extracted from the aqueous phase and recycled for use to produce acrylamide of

general formula (I). The pH of the remaining aqueous phase is adjusted before the aqueous phase is subjected to evaporation to form a solid. The adipic acid is extracted from the solid to obtain a yield of 85% to 90%. In various embodiments, the second acid is hydrochloric acid. One skilled in the art will appreciate that other suitable acids may be used without departing from the scope of the present disclosure.

[0026] In some embodiments, the acrylamide represented by the general formula (I) is prepared by mixing a pyrazole represented by the general formula (III):



wherein R₁ and R₂ are each independently hydrogen, alkyl or aryl, with triethylamine in a fifth solvent at a temperature of 0°C to obtain a second reaction mixture; and adding an acryloyl chloride to the reaction mixture. The reaction mixture is quenched, and the acrylamide of general formula (I) is extracted from the reaction mixture.

[0027] In some embodiments, the reaction is quenched using a quenching reagent. In one embodiment, the quenching reagent is ammonium chloride. One skilled in the art will appreciate that other suitable quenching reagents may be used without departing from the scope of the present disclosure.

[0028] In some embodiments, the acryloyl chloride is added slowly into the reaction mixture. The reaction is an exothermic reaction and adding the acryloyl chloride slowly into the reaction mixture helps to control the temperature to near 0°C.

[0029] In some embodiments, the conditions for homocoupling of the acrylamide comprises mixing the acrylamide of general formula (I) with an oxalic acid, 1,3,3-tetramethylguanidine and 1,3-dicyano-2,4,5,6-tetrakis(diphenylamino)-benzene in a sixth solvent to form a third reaction mixture; irradiating the third reaction mixture with light from a light source; quenching the reaction; and extracting the amide substrate.

[0030] In some embodiments, the light source contains blue light with a wavelength of 400 to 490 nm. Examples of such light source include, but are not limited to, blue LED, white LED and compact fluorescent lamps.

[0031] In some embodiments, the reaction is quenched using ammonium chloride. One skilled in the art will appreciate that other suitable quenching reagent may be used without departing from the scope of the present disclosure.

[0032] In another embodiment, the pathway 2 further comprises mixing a second batch of amide substrate with an aqueous ammonium hydroxide in a seventh solvent to form a solid phase and a second aqueous phase, wherein the solid phase is collected by filtration to obtain adipamide. In some embodiments, pyrazole is extracted from the filtrate and recycled for use to produce the acrylamide of general formula (I).

[0033] In some embodiments, the pyrazole is 3,5-dimethylpyrazole when R_1 and R_2 in general formula (III) are both CH_3 .

[0034] In some embodiments, the acrylamide is 1-(3,5-dimethyl-1H-pyrazol-1-yl)prop-2-en-1-one.

[0035] In some embodiments, the the amide substrate is 1,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)hexane-1,6-dione.

[0036] In some embodiments, the dibenzyladipamide substrate is N1, N6-dibenzyladipamide.

[0037] In some embodiments, the dibenzyl diamine is N1, N6-dibenzylhexane-1,6-diamine.

[0038] The solvents used in the various steps may be any solvents suitable for dissolving the compounds used in that step. In various embodiments, the solvents include, but are not limited to, dichloromethane, dimethylformamide (DMF), chloroform, tetrahydrofuran (THF), water/THF and ethanol.

[0039] In the present disclosure, the amide substrate is formed from photocatalytic homocoupling of acrylamide utilizing oxalic acid as the reductant. The amide substrate is transformed into adipamide and adipic acid in excellent yield by simple aminolysis and hydrolysis. Hexamethylenediamine is obtained with several steps of transformations from the amide substrate.

[0040] The synthesis of the present disclosure offers several advantages. The advantages include metal-free photocatalytic homocoupling of acrylamide, use of oxalic acid as a cheap reductant, and recyclable pyrazole.

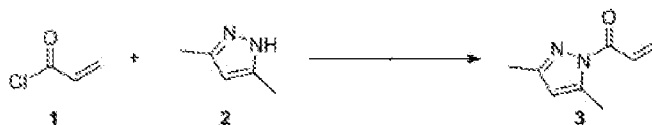
[0041] The method of the present disclosure utilizes oxalic acid as a reductant which can be prepared from biomass. This eliminates the use of energy-demanding electrocatalysis. The method employs an environmental-friendly metal-free photocatalysis in the homocoupling process and this eliminates the use of metal catalysts in the reaction processes for producing hexamethylenediamine and adipic acid. The method displays an excellent selectivity. The pyrazole produced during the various processes can be recycled for use in producing the acrylamide for the homocoupling process.

[0042] To facilitate a better understanding of the present disclosure, the following examples of specific embodiments are given. In no way should the following examples be read to limit or define the entire scope of the disclosure. One skilled in the art will recognize that the examples set out below are not an exhaustive list of the embodiments of this disclosure.

EXAMPLES

Example 1 – Synthesis of acrylamide

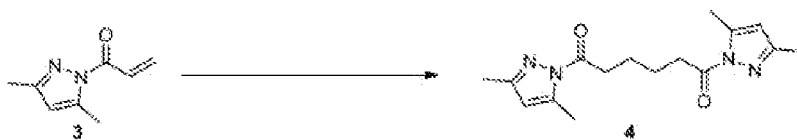
1-(3,5-dimethyl-1H-pyrazol-1-yl)prop-2-en-1-one



[0043] A flask was charged with 3,5-dimethylpyrazole (2), triethylamine (1.5 equiv.), and dichloromethane (0.1 M). The mixture was stirred at 0°C in an ice-water bath, and then acryloyl chloride (1) (1.1 equiv.) was slowly added to the reaction mixture. The ice bath was then removed and stirred for 30 min, while the temperature was naturally warmed to room temperature. The reaction was quenched by adding aqueous ammonium chloride, and the target acrylamide compound, was extracted by ethyl acetate. Pure product of acrylamide (3), 1-(3,5-dimethyl-1H-pyrazol-1-yl)prop-2-en-1-one was obtained by silica gel column chromatography with about 86% yield.

Example 2 – Synthesis of amide substrate

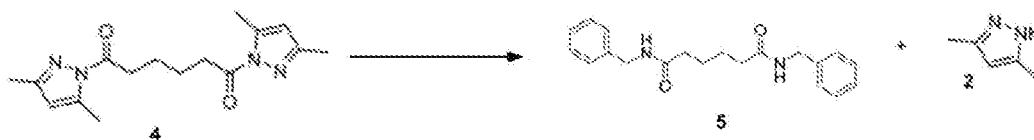
1,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)hexane-1,6-dione



[0044] A flask was charged with acrylamide compound (3), oxalic acid (1.1 equiv.), 1,1,3,3-tetramethylguanidine (TMG, 1.1 equiv.), 1,3-dicyano-2,4,5,6-tetrakis(diphenylamino)-benzene (4DPAIPN, 0.01 equiv.), and dimethylformamide (DMF) (0.1 M). The atmosphere was exchanged by applying vacuum and backfilling with argon. The resulting mixture was stirred at room temperature and irradiated under blue LED lamps. After 12 hours, the reaction was quenched by aqueous ammonium chloride solution, and extracted by ethyl acetate. The organic phase was dried under vacuum. The target compound, amide substrate (4) with formula 1,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)hexane-1,6-dione was isolated in about 55% yield by silica gel column chromatography (hexane/EA).

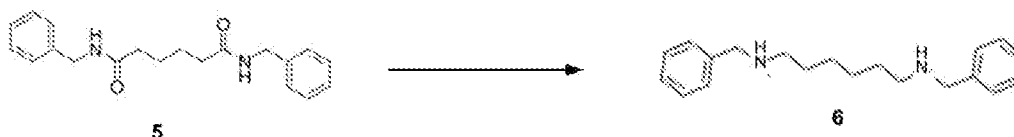
Example 3 - Synthesis of hexamethylenediamine

[0045] (Step 3-1) Synthesis of N1, N6-dibenzyladipamide



[0046] A flask was charged with amide substrate (4) (1 equiv.), benzylamine (2.1 equiv.), and chloroform (0.05 M). The mixture was stirred and heated to 50°C for 12 hours. The target compound (5) (N1, N6-dibenzyladipamide) was precipitated as solid after cooling to room temperature. N1, N6-dibenzyladipamide (5) was collected by filtration and washed by hexane/dichloromethane with 98% yield. Pyrazole (2) was recycled from the filtrate and purified by silica gel column chromatography with about 87% yield.

[0047] (Step 3-2) Synthesis of N1, N6-dibenzylhexane-1,6-diamine



[0048] A flask was charged with N1, N6-dibenzyladipamide (5) (1 equiv.) and connected to a condenser. The atmosphere was exchanged by applying vacuum and backfilling with argon. Then tetrahydrofuran (THF) (0.05 M) and borane-tetrahydrofuran (BH₃·THF) solution (9 equiv., 0.9 M in THF) was injected into the reaction system via syringe. The reaction mixture was stirred and refluxed for 15 hours. After cooling down to room temperature, aqueous hydrochloric acid solution (1.2 equiv. 6 M) was added carefully to quench the exceeded borane. Water (0.05 M) was added into the solution and stirred for 10 min. Then 10% aqueous sodium hydroxide was added until pH reached 14. The mixture was extracted by diethyl ether and dried under vacuum. The compound (6), N1, N6-dibenzylhexane-1,6-diamine was purified by silica gel chromatography (CH₂Cl₂/MeOH). The yield was determined by crude NMR with dibromomethane as the internal standard (93%).

[0049] (Step 3-3) Synthesis of hexamethylenediamine



[0050] A flask was charged with N1, N6-dibenzylhexane-1,6-diamine (6) (1 equiv.), 10% w/w palladium on active carbon (10% w/w), aqueous hydrochloric acid solution (3 equiv.), and ethanol (0.05 M). The atmosphere was exchanged by hydrogen (1 atm). The mixture was stirred and heated to 70°C for 16 hours. After cooling to room temperature, the mixture was filtered through a diatomite pad and the filtrate was dried under vacuum to provide the target pure product, hexamethylenediamine (7). The yield was determined by crude NMR with dibromomethane as the internal standard (82%).

Example 4 - Synthesis of adipamide



[0051] A flask was charged with amide substrate (4) (1 equiv.) and aqueous ammonium hydroxide (22-25%) / THF (1:1, 0.05 M). The mixture was stirred at room temperature for 12 hours. The target compound (8), adipamide was precipitated as solid and collected by filtration with about 91% yield. Pyrazole (2) was recycled from the filtrate and purified by silica gel column chromatography with about 72% yield.

Example 5 - Synthesis of adipic acid



[0052] A flask was charged with amide substrate (4) (1 equiv.), sodium hydroxide (5 equiv.),

and water/THF (1:1, 0.05 M). The mixture was stirred at room temperature for 12 hours. Pyrazole (2) was extracted from the mixture by diethyl ether and purified by silica gel column chromatography with about 81% yield. The remaining aqueous phase was acidified by aqueous hydrochloric acid solution until pH reached 1. Water was evaporated under vacuum, and target compound (9), adipic acid was extracted from the remaining solids by methanol with 87% yield.

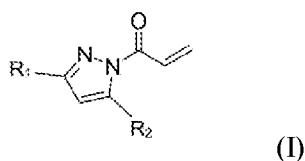
[0053] As demonstrated hereinabove, hexamethylenediamine, adipamide and adipic acid can be synthesised from amide substrate in excellent yield by simple aminolysis and hydrolysis.

[0054] Although embodiments of the invention have been shown and described, the invention is not limited to the described embodiments. Instead, it would be appreciated by those skilled in the art that various modifications and variations can be made to the embodiments of the invention without departing from the scope of the invention, the scope of which is set forth in the following claims.

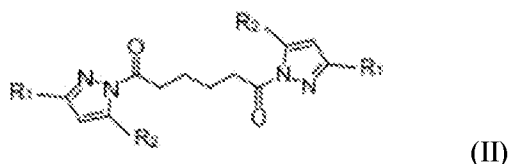
Claims

1. A method of synthesising hexamethylenediamine and/or adipic acid, the method comprising:

homocoupling of acrylamide represented by the general formula (I):



under conditions including using oxalic acid as a reductant and irradiating a reaction mixture comprising acrylamide with light from a light source to obtain an amide substrate represented by the general formula (II):



wherein R₁ and R₂ are each independently hydrogen, alkyl or aryl,

wherein the method further comprises a pathway 1 and/or a pathway 2,

wherein the pathway 1 comprises:

mixing the amide substrate with benzylamine in a first solvent at a first elevated temperature to obtain a dibenzyladipamide substrate after cooling the mixture to room temperature;

mixing the dibenzyladipamide substrate with borane-tetrahydrofuran in a second solvent;

quenching reaction with a quenching reagent;

extracting dibenzylamine and drying the extracted dibenzylamine; and

mixing the dibenzyl diamine with a first acid and a third solvent in the presence of a catalyst at a second elevated temperature under a hydrogen gas atmosphere to form hexamethylenediamine;

wherein the pathway 2 comprises:

mixing the amide substrate with an aqueous sodium hydroxide in a fourth solvent to obtain a first aqueous phase;

adding a second acid into the first aqueous phase to adjust the pH value; and

extracting adipic acid to obtain a yield of 85% to 90%.

2. The method according to claim 1, wherein the acrylamide represented by the general formula (I) is prepared by:

mixing pyrazole with triethylamine in a fifth solvent at a temperature of 0°C to obtain a second reaction mixture and adding an acryloyl chloride to the second reaction mixture; and

quenching the reaction and extracting the acrylamide of general formula (I) from the second reaction mixture.

3. The method according to claim 1 or 2, wherein the conditions for homocoupling of the acrylamide comprises:

mixing the acrylamide of general formula (I) with the oxalic acid, 1,3,3-tetramethylguanidine and 1,3-dicyano-2,4,5,6-tetrakis(diphenylamino)-benzene in a sixth solvent to form a third reaction mixture;

irradiating the third reaction mixture with light from the light source; and

quenching the reaction and extracting the amide substrate.

4. The method according to claim 1, wherein the pathway 2 further comprises:

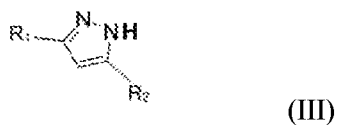
mixing a second batch of amide substrate with an aqueous ammonium hydroxide in a seventh solvent to form a solid phase and a second aqueous phase, wherein the solid phase is collected by filtration to obtain adipamide.

5. The method according to claim 1, further comprising extracting pyrazole from the first aqueous phase.

6. The method according to claim 4, further comprising extracting pyrazole from the second aqueous phase.

7. The method according to any one of the preceding claims, wherein the solvent is selected from the group consisting of dichloromethane, dimethylformamide (DMF), chloroform, tetrahydrofuran (THF), water/THF and ethanol.

8. The method according to claim 2, wherein the pyrazole is represented by the general formula (III):



wherein R₁ and R₂ are each independently hydrogen, alkyl or aryl.

9. The method according to claim 8, wherein the pyrazole is 3,5-dimethylpyrazole.

10. The method according to claim 2 or 8, wherein the acrylamide is 1-(3,5-dimethyl-1H-pyrazol-1-yl)prop-2-en-1-one.

11. The method according to claim 3, wherein the amide substrate is 1,6-bis(3,5-dimethyl-1H-pyrazol-1-yl) hexane-1,6-dione.
12. The method according to claim 1, wherein the dibenzyladipamide substrate is N1, N6-dibenzyladipamide.
13. The method according to claim 1, wherein the dibenzylamine is N1, N6-dibenzylhexane-1,6-diamine.
14. The method according to claim 3, wherein the light source contains blue light with a wavelength of 400 to 490 nm.
15. The method according to claim 1, wherein the acid is hydrochloric acid and the catalyst is palladium on active carbon.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2023/050558

A. CLASSIFICATION OF SUBJECT MATTER

C07C 2/74 (2006.01) C07C 231/08 (2006.01) C07C 231/14 (2006.01) C07C 209/50 (2006.01) C07C 51/06 (2006.01)

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

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

CAS REGISTRY, CAPLUS, Medline, BIOSIS, EMBASE: Structure search based on formula II, homocoupling of acrylamide, preparation of hexamethylenediamine, adipic acid, adipamide and like terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
D,A	BLANCO, D.E. ET AL., Optimizing organic electrosynthesis through controlled voltage dosing and artificial intelligence. <i>Proceedings of the National Academy of Sciences</i> , 21 August 2019, Vol. 116, No. 36, pages 17683-17689 [Retrieved on 2023-11-03] <DOI: 10.1073/PNAS.1909985116> Whole document	1-15
D,A	WANG, C.C. ET AL., Cobalt-catalyzed dimerization of alkenes. <i>Tetrahedron Letters</i> , 2 August 2004, Vol. 45, No. 32, pages 6203-6206 [Retrieved on 2023-11-03] <DOI: 10.1016/J.TETLET.2004.04.085> Whole document	1-15
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☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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PCT/SG2023/050558

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WU, Z. ET AL., Photocatalytic coupling of electron-deficient alkenes using oxalic acid as a traceless linchpin. <i>Chem</i> , 13 April 2023, Vol. 9, No. 4, pages 978-988 [Retrieved on 2023-11-03] <DOI: 10.1016/J.CHEMPR.2022.12.013> Figure 3, compound 4ap, section (B)(2); Figure 4, section (C)	1-15