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DRAWINGS

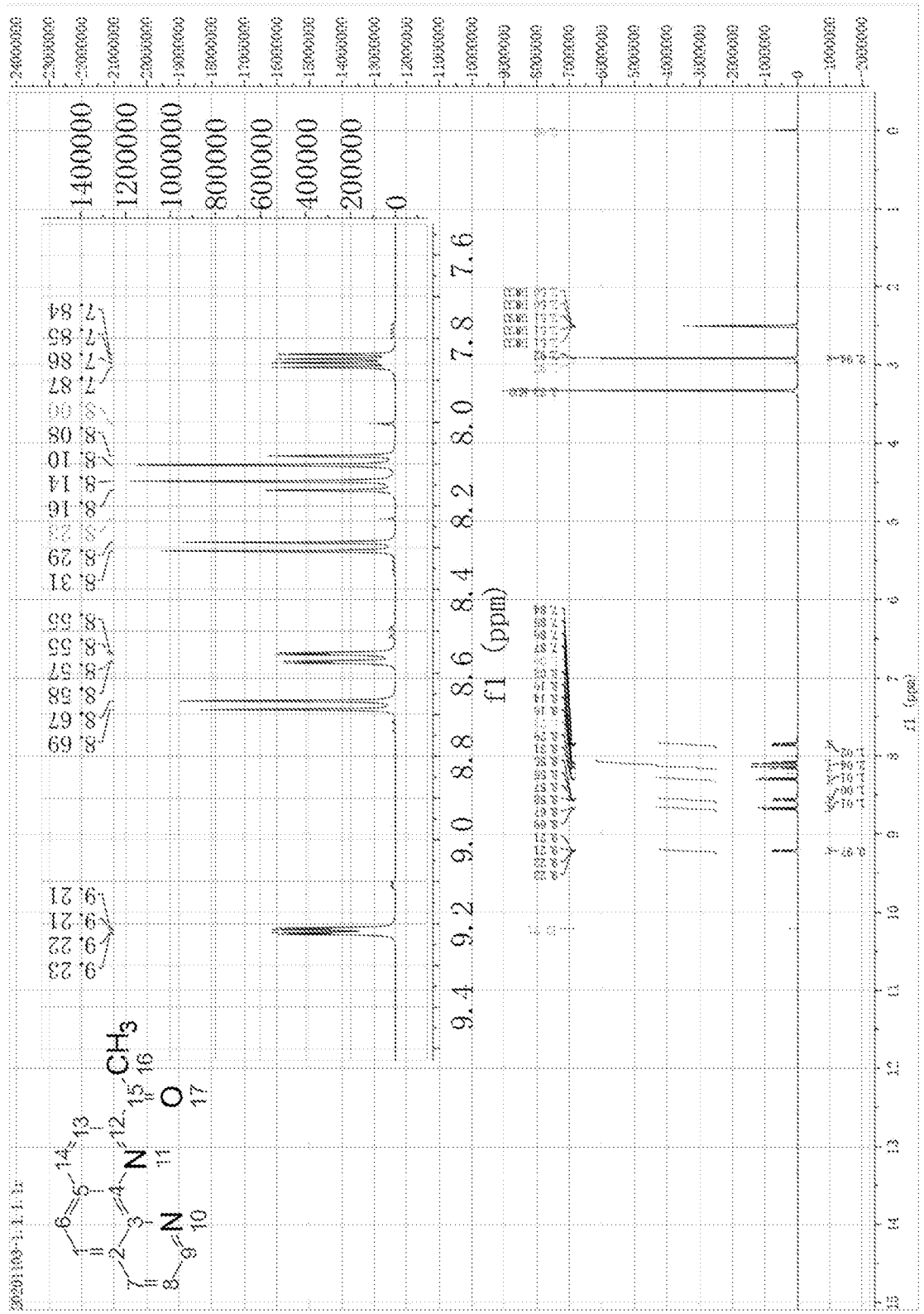


FIG. 1

PREPARATION METHOD FOR 2-ACETYL-1,10-PHENANTHROLINE

CROSS REFERENCE TO RELATED APPLICATION

[0001] This patent application claims the benefit and priority of Chinese Patent Application No. 202110175700.4 filed with the China National Intellectual Property Administration on 6 February, 2021 and entitled "PREPARATION METHOD FOR 2-ACETYL-1,10-PHENANTHROLINE", the disclosure of which is incorporated by reference herein in its entirety as part of the present application.

TECHNICAL FIELD

[0002] The present disclosure relates to the technical field of organic synthesis, in particular to a preparation method for 2-acetyl-1,10-phenanthroline.

BACKGROUND

[0003] At present, 2-acetyl-1,10-phenanthroline is mainly used in photoelectric materials, which is mainly prepared by removing bromine from 2-bromophenanthroline with butyl lithium at -78°C and reacting with *N*,*N*-dimethylacetamide. The raw materials used in the above preparation method are expensive, the synthesis conditions are too harsh, and the industrialisation advantage is not large. It had also been reported that 2-cyano-1,10-phenanthroline was synthesised first and then 2-acetyl-1,10-phenanthroline was synthesised, but trimethylsilyl cyanide with large toxicity and complex operation was used in the synthesis route.

SUMMARY

[0004] An objective of the present disclosure is to provide a preparation method for 2-acetyl-1,10-phenanthroline. The preparation method is simple in synthesis route, easy for industrial production, and green and eco-friendly in raw materials.

[0005] To achieve the above objective, the present disclosure provides the following technical solutions:

[0006] The present disclosure provides a preparation method for 2-acetyl-1,10-phenanthroline, including the following steps:

[0007] in a protective atmosphere, mixing 8-aminoquinoline, 3-acetylacrolein, an acid, and a solvent, and performing an addition reaction to obtain 4-oxo-3-(quinolin-8-ylamino)pentanal;

[0008] mixing the 4-oxo-3-(quinolin-8-ylamino)pentanal, a catalyst, and a first organic solvent, and performing a cyclisation reaction to obtain 2-acetyl-1,2-dihydrophenanthroline; and

[0009] mixing the 2-acetyl-1,2-dihydrophenanthroline, an oxidant, and a second organic solvent, and performing an oxidation reaction to obtain the 2-acetyl-1,10-phenanthroline.

[0010] Preferably, the 8-aminoquinoline and the 3-acetylacrolein may have a molar ratio of 1:(0.9-3.0).

[0011] Preferably, the acid may include an organic acid or an inorganic acid; and

[0012] the acid and the 8-aminoquinoline may have a mass ratio of 100:(60-145).

[0013] Preferably, the organic acid may be one or more selected from the group consisting of acetic acid, polyphosphoric acid, phosphorus oxychloride, trifluoroacetic acid (TFA), and trifluoromethanesulfonic acid (TFMSA); and

[0014] the inorganic acid may be one or more selected from the group consisting of hydrochloric acid, sulfuric acid, and vanadic acid.

[0015] Preferably, the addition reaction may be conducted at 50-65°C for 15-25 h.

[0016] Preferably, the catalyst may be one or more selected from the group consisting of polyphosphoric acid, vanadic acid, concentrated hydrochloric acid, sulfuric acid, TFMSA, and TFA; and

[0017] the concentrated hydrochloric acid may have a mass concentration of 30-36%.

[0018] Preferably, the 4-oxo-3-(quinolin-8-ylamino)pentanal and the catalyst may have a mass ratio of 1:(0.1-10).

[0019] Preferably, the cyclisation reaction may be conducted at 77-82°C for 15-25 h.

[0020] Preferably, the oxidant may be one selected from the group consisting of chloranil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), potassium permanganate, hydrogen peroxide, *t*-butyl hydroperoxide, and peracetic acid.

[0021] Preferably, the 2-acetyl-1,2-dihydrophenanthroline and the oxidant may have a mass ratio of (70-120):(35-200).

[0022] Preferably, the oxidation reaction may be performed at room temperature for 5-10 h.

[0023] Preferably, the oxidation reaction is followed by solid precipitation, a first filtration, beating, a second filtration, leaching, and drying sequentially.

[0024] Preferably, the solid precipitation is to precipitate a solid by adding water or a saturated aqueous solution of sodium bicarbonate in a product system obtained after the oxidation reaction is completed; and

[0025] the water or the saturated aqueous solution of sodium bicarbonate and the second organic solvent may have a volume ratio of 30:13 or 30:15.

[0026] Preferably, the beating is to mix a filter cake obtained by the first filtration with toluene and beat at a temperature of 70°C for 30 min.

[0027] The present disclosure provides a preparation method for 2-acetyl-1,10-phenanthroline, including the following steps: in a protective atmosphere, mixing 8-aminoquinoline, 3-acetylacrolein, an acid, and a solvent, and performing an addition reaction to obtain 4-oxo-3-(quinolin-8-ylamino)pentanal; mixing the 4-oxo-3-(quinolin-8-ylamino)pentanal, a catalyst, and a first organic solvent, and performing a cyclisation reaction to obtain 2-acetyl-1,2-dihydrophenanthroline; and mixing the 2-acetyl-1,2-dihydrophenanthroline, an oxidant, and a second organic solvent, and performing an oxidation reaction to obtain the 2-acetyl-1,10-phenanthroline. The preparation method is simple in synthesis route, mild in reaction conditions, easy for industrial production, and green and eco-friendly in raw material preparation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] FIG. 1 is a nuclear magnetic resonance (NMR) spectrum of 2-acetyl-1,10-phenanthroline prepared in Example 1.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0029] The present disclosure provides a preparation method for 2-acetyl-1,10-phenanthroline, including the following steps:

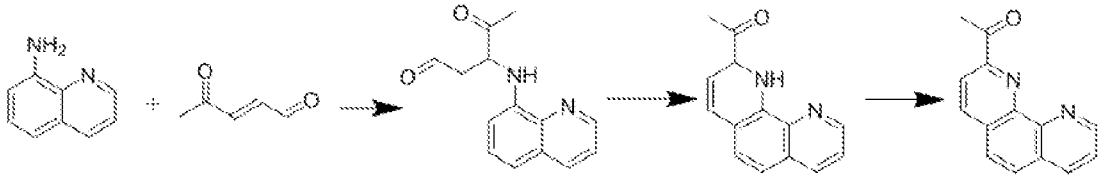
[0030] in a protective atmosphere, mixing 8-aminoquinoline, 3-acetylacrolein, an acid, and a solvent, and performing an addition reaction to obtain 4-oxo-3-(quinolin-8-ylamino)pentanal;

[0031] mixing the 4-oxo-3-(quinolin-8-ylamino)pentanal, a catalyst, and a first organic solvent, and performing a cyclisation reaction to obtain 2-acetyl-1,2-dihydrophenanthroline; and

[0032] mixing the 2-acetyl-1,2-dihydrophenanthroline, an oxidant, and a second organic solvent, and performing an oxidation reaction to obtain the 2-acetyl-1,10-phenanthroline.

[0033] In the present disclosure, unless otherwise specified, all raw materials for preparation are commercially available products well known to those skilled in the art.

[0034] In the present disclosure, a preparation process of the 2-acetyl-1,10-phenanthroline is preferably as shown in formula I:

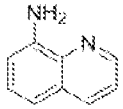
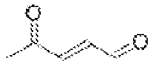
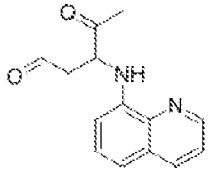


[0035]

formula I.

[0036] In a protective atmosphere, 8-aminoquinoline, 3-acetylacrolein, an acid, and a solvent are mixed and subjected to an addition reaction to obtain 4-oxo-3-(quinolin-8-ylamino)pentanal. The protective atmosphere is not particularly limited in the present disclosure, as long as a non-oxygen

atmosphere well known to those skilled in the art may be used. In an example of the present disclosure, the protective atmosphere is specifically a nitrogen atmosphere.

[0037] In the present disclosure, a structural formula of the 8-aminoquinoline is  , and the 8-aminoquinoline is preferably a commercially available product. A structural formula of the 3-acetylacrolein is  ; a structural formula of the 4-oxo-3-(quinolin-8-ylamino)pentanal is  .

[0038] In the present disclosure, the acid may preferably include an organic acid or an inorganic acid; the organic acid may be one or more selected from the group consisting of hydrochloric acid, sulfuric acid, and vanadic acid; in the present disclosure, if the inorganic acid includes the hydrochloric acid, the hydrochloric acid may preferably be mixed in the form of a solution, and the hydrochloric acid may preferably have a mass concentration of 30-36%; if the inorganic acid includes the sulfuric acid and/or the vanadic acid, both the sulfuric acid and the vanadic acid may preferably be pure products of the sulfuric acid or the vanadic acid. The organic acid may preferably include one or more selected from the group consisting of acetic acid, polyphosphoric acid, phosphorus oxychloride, TFA, and TFMSA. The acid functions as a catalyst to promote the occurrence of the addition reaction.

[0039] In the present disclosure, the solvent includes water and an alcohol organic solvent; the alcohol organic solvent may be more preferably methanol. The present disclosure has no special limitation on a ratio of the water to the alcohol organic solvent, as long as the water and the alcohol organic solvent may be mixed in any ratio. In a specific example of the present disclosure, the alcohol organic solvent is methanol, and the water and the alcohol organic solvent have a volume ratio of 3:4 and 1:2. In the present disclosure, a mixed solvent consisting of the water and the alcohol organic solvent may be used to prevent 3-acetylacrolein polymerisation, and ensure system uniformity, thereby further improving a product yield.

[0040] In the present disclosure, the 8-aminoquinoline and the 3-acetylacrolein may preferably have a molar ratio of 1:(0.9-3.0), and more preferably 1:(1.5-2.5); and the acid and the 8-aminoquinoline may preferably have a mass ratio of 100:(60-145), and more preferably 100:(70-75). In the present disclosure, a mass of the 8-aminoquinoline and a volume of the solvent may preferably have a ratio of 1 g: (3-20) mL, and more preferably 1 g: (4-7) mL.

[0041] The present disclosure has no special limitation on the mixing, as long as a procedure well known to those skilled in the art may be used.

[0042] In the present disclosure, the addition reaction may preferably be conducted at 50-65°C, and more preferably 55-60°C; the addition reaction may preferably last for 15-25 h, and more preferably 18-23 h.

[0043] During the addition reaction, it is preferable to determine whether the addition reaction is finished by detecting whether the 8-aminoquinoline is consumed or not by thin layer chromatography (TLC).

[0044] After the addition reaction is completed, the present disclosure further preferably includes filtration; the present disclosure has no special limitation on the filtration, as long as a procedure well known to those skilled in the art may be used.

[0045] In the present disclosure, after the 4-oxo-3-(quinolin-8-ylamino)pentanal is obtained, the 4-oxo-3-(quinolin-8-ylamino)pentanal is mixed with the catalyst and the first organic solvent, and the cyclisation reaction is performed to obtain the 2-acetyl-1,2-dihydrophenanthroline.

[0046] In the present disclosure, the catalyst may preferably be one or more selected from the group consisting of polyphosphoric acid, vanadic acid, concentrated hydrochloric acid, sulfuric acid, TFMSA, and TFA; the concentrated hydrochloric acid may preferably have a mass concentration of 30-36%; if the catalyst is at least two of the foregoing provided specific substances, the present disclosure has no special limitation on a proportion of the foregoing specific substances, and these specific substances may be mixed in any proportion. In a specific example of the present disclosure, the catalyst is the polyphosphoric acid and the vanadic acid; the polyphosphoric acid and the vanadic acid specifically have a mass ratio of 45:1.

[0047] In the present disclosure, the first organic solvent may preferably be one or more selected from the group consisting of ethyl acetate, methyl *tert*-butyl ether, toluene, chloroalkanes, and polyphosphoric acid; when the first organic solvent is at least two of the foregoing provided specific substances, the present disclosure has no special limitation on a proportion of the foregoing specific substances, and these specific substances may be mixed in any proportion. In a specific example of the present disclosure, the first organic solvent is the ethyl acetate.

[0048] In the present disclosure, the 4-oxo-3-(quinolin-8-ylamino)pentanal and the catalyst may preferably have a mass ratio of 1:(0.1-10), and more preferably 1:(0.3-1). In the present disclosure, a mass of the 4-oxo-3-(quinolin-8-ylamino)pentanal and a volume of the first organic solvent may preferably have a ratio of 1 g: (3-20) mL, more preferably 1 g: (3-5) mL.

[0049] The present disclosure has no special limitation on the mixing, as long as a procedure well known to those skilled in the art may be used.

[0050] In the present disclosure, the cyclisation reaction may preferably be conducted at 77-82°C, and more preferably 80°C; the cyclisation reaction may preferably last for 15-25 h, and more preferably 18-22 h. The cyclisation reaction may preferably be conducted under reflux conditions.

[0051] During the cyclisation reaction, it is preferable to determine whether the cyclisation reaction is finished by detecting whether the 3-acetylacrolein is consumed or not by TLC.

[0052] After the cyclisation reaction is completed, the present disclosure may further preferably include solvent recovery and a process of steaming with acetic acid in sequence; the solvent recovery may preferably be in the form of vacuum distillation; and the process of steaming with acetic acid may preferably be the vacuum distillation. If the catalyst includes the polyphosphoric acid or the first organic solvent includes the polyphosphoric acid, before the solvent recovery, it may be preferable to include washing the polyphosphoric acid with a lye. The present disclosure has no special limitation on the type of the lye, as long as the type well known to those skilled in the art may be used.

[0053] In the present disclosure, after the 2-acetyl-1,2-dihydrophenanthroline is obtained, the 2-acetyl-1,2-dihydrophenanthroline is mixed with the oxidant and the second organic solvent, and the oxidation reaction is performed to obtain the 2-acetyl-1,10-phenanthroline.

[0054] In the present disclosure, the oxidant may preferably be one selected from the group consisting of chloranil, DDQ, potassium permanganate, hydrogen peroxide, *t*-butyl hydroperoxide, and peracetic acid, and more preferably one selected from the group consisting of the chloranil and the peracetic acid; if the catalyst is the peracetic acid, the peracetic acid may preferably be added in the form of a solution; and the peracetic acid may preferably have a mass concentration of 35%.

[0055] In the present disclosure, the second organic solvent may preferably be one selected from the group consisting of acetic acid, dichloromethane, chloroform, dichloroethane, toluene, and ether solvents, and more preferably the acetic acid.

[0056] In the present disclosure, the 2-acetyl-1,2-dihydrophenanthroline and the oxidant may preferably have a mass ratio of (70-120):(35-200), more preferably (100-110):(38-180), and most preferably 109:175 or 75:38.5.

[0057] In the present disclosure, a mass of the 2-acetyl-1,2-dihydrophenanthroline and a volume of the second organic solvent may preferably have a ratio of 1 g: (3-15) mL, more preferably 1 g: (4-7) mL, and most preferably 1 g: 5.96 mL.

[0058] The present disclosure has no special limitation on the mixing, as long as a procedure well known to those skilled in the art may be used. In an example of the present disclosure, the mixing is to dissolve the 2-acetyl-1,2-dihydrophenanthroline in the second organic solvent and add the oxidant.

[0059] In the present disclosure, the oxidation reaction may preferably be conducted at room temperature; the oxidation reaction may preferably last for 5-10 h, and more preferably 6-8 h. In the present disclosure, the oxidation reaction may preferably be conducted under stirring. The present disclosure has no special limitation on a rotational speed of the stirring, as long as a rotational speed well known to those skilled in the art may be used.

[0060] After the oxidation reaction is completed, the present disclosure further preferably include solid precipitation, a first filtration, beating, a second filtration, leaching, and drying sequentially; in the present disclosure, the solid precipitation may preferably be to precipitate a solid by adding water or a saturated aqueous solution of sodium bicarbonate in a product system obtained after the oxidation reaction is completed. The water or the saturated aqueous solution of sodium bicarbonate and the second organic solvent may preferably have a volume ratio of 30:13 or 30:15. The present disclosure has no special limitation on the procedure of the first filtration and the second filtration, as long as a procedure well known to those skilled in the art may be used. In the present disclosure, the beating may preferably be to mix a filter cake obtained by the first filtration with toluene and beat at a temperature of 70°C for 30 min; the toluene and acetic acid may preferably have a volume ratio of 20:13. A leaching agent used in the leaching may preferably be isopropyl ether; the drying may preferably be oven drying; the present disclosure has no special limitation on the drying, as long as a procedure well known to those skilled in the art may be used.

[0061] The preparation method of the 2-acetyl-1,10-phenanthroline provided by the present disclosure will be described in detail below in conjunction with the examples, but they cannot be construed as a limitation to the protection scope of the present disclosure.

[0062] Example 1

[0063] 72 g (0.499 mol) of 8-aminoquinoline, 85 g (0.867 mol) of 3-acetylacrolein, 150 g of water, 100 g of acetic acid, and 200 mL of methanol were mixed, heated to 60°C in a nitrogen atmosphere, subjected to addition reaction for 18 h, and filtered to obtain 118 g of 4-oxo-3-(quinolin-8-ylamino)pentanal.

[0064] After dissolving the 4-oxo-3-(quinolin-8-ylamino)pentanal in 400 mL of ethyl acetate, 45 g of polyphosphoric acid and 1 g of vanadic acid were added, heated to a reflux state (77°C), and reacted for 20 h; polyphosphoric acid was washed away with lye, the solvent was recovered under reduced pressure, followed by steaming with acetic acid to obtain 109 g of 2-acetyl-1,2-dihydrophenanthroline.

[0065] After dissolving the 2-acetyl-1,2-dihydrophenanthroline in 650 mL of acetic acid, 175 g of chloranil was added and stirred at room temperature for 6 h, and 1,500 mL of water was added for solid precipitation; the solid was filtered, beaten with 1,000 mL of toluene at 70°C for 30 min,

cooled to 5°C, filtered, leached with isopropyl ether, and dried to obtain 87 g of 2-acetyl-1,10-phenanthroline, with a total yield of 78.3% and a purity of 98.8%.

[0066] The 2-acetyl-1,10-phenanthroline was subjected to NMR spectrometry. The results are shown in FIG. 1: ^{1}H NMR spectral interpretation data were as follows: ^{1}H NMR (400 MHz, DMSO-d_6) δ9.22 (dd, J = 4.3, 1.8 Hz, 1H), 8.68 (d, J = 8.3 Hz, 1H), 8.56 (dd, J = 8.1, 1.8 Hz, 1H), 8.30 (d, J = 8.3 Hz, 1H), 8.19-8.06 (m, 2H), 7.85 (dd, J = 8.1, 4.3 Hz, 1H), and 2.92 (s, 3H).

[0067] Example 2

[0068] 72 g (0.499 mol) of 8-aminoquinoline, 65 g (0.66 mol) of 3-acetylacrolein, 100 g of water, 50 g of 30wt% hydrochloric acid, and 200 mL of methanol were mixed, heated to 65°C in a nitrogen atmosphere, subjected to addition reaction for 18 h, and filtered to obtain 92 g of 4-oxo-3-(quinolin-8-ylamino)pentanal.

[0069] After dissolving the 4-oxo-3-(quinolin-8-ylamino)pentanal in 450 mL of ethyl acetate, 50 g of polyphosphoric acid was added, heated to a reflux state (77°C), and reacted for 20 h; polyphosphoric acid was washed away with lye, the solvent was recovered under reduced pressure, followed by steaming with acetic acid to obtain 70 g of 2-acetyl-1,2-dihydrophenanthroline.

[0070] After dissolving the 2-acetyl-1,2-dihydrophenanthroline in 750 mL of acetic acid, 110 g of 35wt% peracetic acid was added dropwise and stirred at room temperature for 6 h; the resulting solution was stirred with 1,500 mL of water and left to stand for layering; the toluene layer was washed with water, heated to 70°C, beaten for 30 min, cooled to 5°C, filtered, leached with isopropyl ether, and dried to obtain 61 g of 2-acetyl-1,10-phenanthroline, with a purity of 98.1%.

[0071] The 2-acetyl-1,10-phenanthroline was subjected to NMR spectrometry. The result was similar to that of Example 1.

[0072] The foregoing descriptions are merely preferred implementations of the present disclosure. It should be noted that several improvements and modifications can be made by a person of ordinary skill in the art without departing from the principles of the present disclosure, and these improvements and modifications should be deemed as falling within the protection scope of the present disclosure.

WHAT IS CLAIMED IS:

1. A preparation method for 2-acetyl-1,10-phenanthroline, comprising the following steps:

in a protective atmosphere, mixing 8-aminoquinoline, 3-acetylacrolein, an acid, and a solvent, and performing an addition reaction to obtain 4-oxo-3-(quinolin-8-ylamino)pentanal;

mixing the 4-oxo-3-(quinolin-8-ylamino)pentanal, a catalyst, and a first organic solvent, and performing a cyclisation reaction to obtain 2-acetyl-1,2-dihydrophenanthroline; and

mixing the 2-acetyl-1,2-dihydrophenanthroline, an oxidant, and a second organic solvent, and performing an oxidation reaction to obtain the 2-acetyl-1,10-phenanthroline.

2. The preparation method according to claim 1, wherein the 8-aminoquinoline and the 3-acetylacrolein have a molar ratio of 1:(0.9-3.0).

3. The preparation method according to claim 1, wherein the acid comprises an organic acid or an inorganic acid; and

the acid and the 8-aminoquinoline have a mass ratio of 100:(60-145).

4. The preparation method according to claim 3, wherein the organic acid is one or more selected from the group consisting of acetic acid, polyphosphoric acid, phosphorus oxychloride, trifluoroacetic acid (TFA), and trifluoromethanesulfonic acid (TFMSA); and

the inorganic acid is one or more selected from the group consisting of hydrochloric acid, sulfuric acid, and vanadic acid.

5. The preparation method according to any one of claims 1 to 4, wherein the addition reaction is conducted at 50-65°C for 15-25 h.

6. The preparation method according to claim 1, wherein the catalyst is one or more selected from the group consisting of polyphosphoric acid, vanadic acid, concentrated hydrochloric acid, sulfuric acid, TFMSA, and TFA; and

the concentrated hydrochloric acid has a mass concentration of 30-36%.

7. The preparation method according to claim 1 or 6, wherein the 4-oxo-3-(quinolin-8-ylamino)pentanal and the catalyst have a mass ratio of 1:(0.1-10).

8. The preparation method according to claim 7, wherein the cyclisation reaction is conducted

at 77-82°C for 15-25 h.

9. The preparation method according to claim 1, wherein the oxidant is one selected from the group consisting of chloranil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), potassium permanganate, hydrogen peroxide, t-butyl hydroperoxide, and peracetic acid.

10. The preparation method according to claim 1 or 9, wherein the 2-acetyl-1,2-dihydrophenanthroline and the oxidant have a mass ratio of (70-120):(35-200).

11. The preparation method according to claim 10, wherein the oxidation reaction is conducted at room temperature for 5-10 h.

12. The preparation method according to claim 1, wherein the oxidation reaction is followed by solid precipitation, a first filtration, beating, a second filtration, leaching, and drying sequentially.

13. The preparation method according to claim 12, wherein the solid precipitation is to precipitate a solid by adding water or a saturated aqueous solution of sodium bicarbonate in a product system obtained after the oxidation reaction is completed; and

the water or the saturated aqueous solution of sodium bicarbonate and the second organic solvent have a volume ratio of 30:13 or 30:15.

14. The preparation method according to claim 12, wherein the beating is to mix a filter cake obtained by the first filtration with toluene and beat at a temperature of 70°C for 30 min.