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(71) Applicant: COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH [IN/IN]; Anusandhan Bhawan, 2 Rafi Marg, New Delhi 110 001 (IN).

(72) Inventors: **BORATE, Hanumant, Bapurao**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411 008 (IN). **GAIKWAD, Supriya, Hanumant**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411 008 (IN). **KUDALE, Ananda, Shahaji**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411 008 (IN). **CHAVAN, Subhash, Prataprao**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411 008 (IN). **PHARANDE, Shrikant, Ganpat**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411 008 (IN). **WAGH, Vitthal, Dattatraya**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411 008 (IN). **SAWANT, Vikram, Shahaji**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411 008 (IN).

(74) Agents: **TIWARI, Amrish** et al.; K & S Partners, Intellectual Property Attorneys, 109, Sector 44, Gurgaon, National Capital Region 122 003 (IN).

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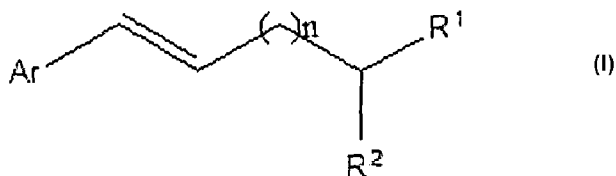
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(54) Title: SINGLE-STEP PROCESS FOR THE PREPARATION OF ARYL OLEFINS



(57) Abstract: The present invention relates to the single-step process for the synthesis of aryl olefin compounds of Formula (1) by reacting aryl aldehydes with alkyl aldehydes in presence of malononitrile and acid or base or salt, optionally in presence of solvent.

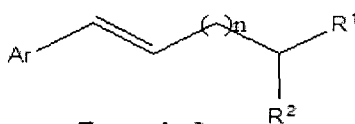


“SINGLE-STEP PROCESS FOR THE PREPARATION OF ARYL OLEFINS”

The following specification particularly describes the invention and the manner in which it is to be performed:

FIELD OF THE INVENTION:

The present invention relates to the single step process for the synthesis of aryl olefins of Formula 1.



Further the process for synthesis of compound of formula 1 comprises, reaction of aryl aldehyde with aliphatic aldehyde in presence of malononitrile and acid or base or salt, optionally in presence of solvent to afford aryl olefin compounds of formula 1 in good yield with trans selectivity.

BACKGROUND OF THE INVENTION:

Aryl olefins are useful intermediates in organic synthesis as well as medicinal chemistry. Further the aryl olefins were studied for various biological activities such as hypolipidemic and antiplatelet activities of aryl olefins particularly α -asarone is reported in *J. Med. Chem.*, 2000, 43 (20), pp 3671–3676 by Janusz Poplawski et al.; whereas anticonvulsant activity of aryl olefins is disclosed in Biological & Pharmaceutical Bulletin. 10/2012 by Qi-Xiong Chen et al. Various metal catalyzed processes for the synthesis of aryl olefins or alkenes are reported in the state of arts.

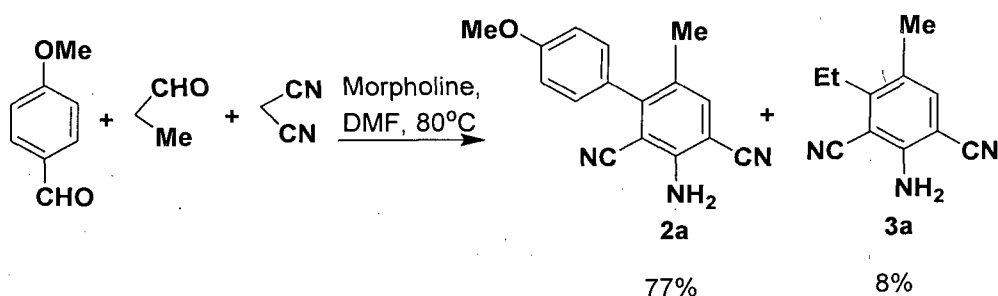
US4965361 (Edgar Kevin et al.) relates to the preparation of 4-substituted aryl olefins by contacting a 4-substituted aryl iodide with an olefin in an ester solvent in the presence of a catalyst system comprising a palladium compound and a Bronsted base.

US7282618 (David Milstein et al.) describes a method for the production of an aryl alkene, comprising reacting an arene with an olefin in the presence of a Ru or Os compound as catalyst, such that an aryl alkene is produced.

US3674884 (Ichiro Moritani et al.) discloses process for the preparation of aromatic hydrocarbon compounds containing monoethylenically unsaturated radicals, which comprises

reacting a monoethylenically unsaturated compound with an aromatic hydrocarbon compound in the presence of a palladium salt. Further cobalt (I)-catalyzed stereoselective olefination of alkylzinc reagents with aldehydes is reported by J.-X. Wang et al., in *SYNTHESIS*, 2003, 1506-1510.

- 5 A three-component, single-step method for the synthesis of 4-alkyl-3-aryl-2,6-dicyanoanilines involving reaction of alkyl aldehyde, malononitrile and aryl aldehyde in presence of morpholine is reported by H. B. Borate et al. in *Tetrahedron Lett.* 2011, 52, 5491–5493 (cf below Scheme 1).



Scheme 1.

- 10 Additionally, there are a number of methods reported to synthesize aryl olefin compounds which mainly include Wittig reaction (Mangold and Hanna in *J. Med Chem* 25, 630, 1982), (Tuntiwachwuttikul et al. in *Phytochemistry* 20, 1164, 1981); Grignard reaction followed by dehydration is reported by Sharma et al. in *Bull Chem Soc Jpn* 77, 2231, 2004; coupling of alkenyl alkyl ethers with aryl Grignard reagent by Xie and Wang in *Chem Eur J* 2011, 17, 4972. Suzuki cross-coupling and Suzuki–Miyaura cross coupling reported in (E. Peyroux, et al in *Eur. J. Org. Chem.* 1075 2004), (Zhang et al. in *SYNLETT* 2012, 23, 1221–1224) respectively.

- Further synthesis of aryl olefins is reported by isomerization of allyl benzenes (Alexander Canadian Journal of Chemistry 43, 3437, 1965; Mayer et al. *ChemCatChem* 3, 1567, 2011); and modified Julia olefination (Daniela Mirk, et al. *SYNLETT* 2006, No. 8, pp 1255–1259).

- Though these methods have their own advantages, some of these methods are accompanied by certain disadvantages such as requirement of bases like phenyllithium, catalysts which are either expensive or not easily available, preparation of intermediates like Grignard reagent or Wittig salts, less easily available starting materials like alkenyl- or arylboronic acids or 4-nitrophenyl sulfones etc. and some of the methods require multistep synthesis of starting materials. The main disadvantage of the known process pertains to poor yield and trans selectivity of aryl olefins.

Therefore the cost effective, simple and single-step process for synthesis of functionalized aryl olefins is needed.

However, there is no report in the art for the synthesis of aryl olefins by reacting aryl aldehydes with alkyl aldehydes in presence of malononitrile and an acid or a base or a salt in presence or absence of solvent.

The process of the current invention involves the reaction of easily available aldehydes as such to obtain the substituted olefins in single-step without any need of special catalyst so the efforts were made to increase the yield of aryl olefins with significant trans selectivity.

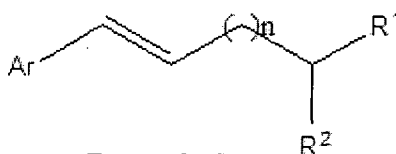
OBJECT OF THE INVENTION:

The main object of the present invention is to provide a process for the synthesis of aryl olefins of Formula 1 by reacting aryl aldehydes with alkyl aldehydes in presence of malononitrile and an acid or a base or a salt, optionally in presence of solvent.

Another object of the present invention is to provide novel aryl olefin compounds of Formula-1.

SUMMARY OF THE INVENTION:

Accordingly the present invention provides, a single-step process for the synthesis of aryl olefins of Formula 1, wherein the process comprising the step of reacting of aryl aldehydes with alkyl aldehydes, at temperature in between -10 to 150°C in presence of malononitrile and acid or base or salt,



Formula 1

wherein 'Ar' is selected from the group consisting of (un)substituted phenyl, naphthyl, anthracenyl or heteroaryl ring, substituted with (un)protected hydroxyl group, halogen selected from the group consisting of fluorine, chlorine, bromine and iodine, nitro or cyano group, linear or branched chain of 1 to 20 carbon atoms;

n=0-20 and;

'R¹' and 'R²' may be same or different and independently selected from the group consisting of hydrogen, alkyl group of linear or branched chain of 1 to 20 carbon atoms

optionally substituted with aryl group, alkoxy group -OR (wherein R= alkyl group with 1 to 4 carbon atoms), hydroxyl group, halogen selected from fluorine, chlorine, bromine and iodine, nitro or (un)substituted amino group.

In an embodiment of the present invention, the single-step process is optionally carried out in presence of organic solvent selected from the group consisting of acetonitrile, dimethyl formamide, 1,4-dioxane, ethanol, methanol, dimethyl sulfoxide, toluene or combinations thereof, preferably solvent is acetonitrile.

In still another embodiment of the present invention, the aryl aldehyde is selected from the group consisting of 3,4,5-trimethoxybenzaldehyde, anisaldehyde, 1-naphthaldehyde, thiophene-2-carboxaldehyde, 4-nitrobenzaldehyde, 4-cyanobenzaldehyde, 4-allyloxy benzaldehyde, 4-prop-2-yn-1-yloxybenzaldehyde, 4-(methoxybenzyloxy) benzaldehyde, anthracene-9-carboxaldehyde, 4-fluorobenzaldehyde, 2,4-dichlorobenzaldehyde, and 4-methoxybenzaldehyde.

In yet another embodiment of the present invention, the molar concentration of aryl aldehyde is in the range of 2-15 mmole.

In still another embodiment of the present invention, the alkyl aldehyde or aliphatic aldehyde is selected from the group consisting of propanal, hexanal, heptanal, octanal, dodecyl aldehyde.

In yet another embodiment of the present invention, the molar concentration of alkyl aldehyde is in the range of 2-20 mmole.

In still another embodiment of the present invention, the molar ratio of aryl aldehyde to alkyl aldehyde is in the range of 1:1.0 to 1:1.6.

In yet another embodiment of the present invention, the acid is selected from the group consisting of acetic acid, propionic acid, formic acid, p-toluenesulfonic acid, hydrochloric acid, proline, alanine.

In still another embodiment of the present invention, the base is selected from the group consisting of morpholine, triethyl amine, pyrrolidine, piperidine, pyridine, potassium carbonate, potassium hydroxide, sodium methoxide, and the salt is selected from the group consisting of ammonium acetate, ammonium formate.

In yet another embodiment of the present invention, the acid or base or salt is present either alone or combination thereof.

In still another embodiment of the present invention, the acid-base/salt combination is acetic acid and ammonium acetate.

In yet another embodiment of the present invention, the molar ratio of acid and base/salt combination used in the reaction is between 1:1 to 2:1.

In still another embodiment of the present invention, the molar concentration of malononitrile ranges from 3 to 40 mmole, preferably 5 to 35 mmole.

5 In yet another embodiment of the present invention, the aryl olefin compounds of Formula-1, are selected from the group consisting of;

(E)-1-methoxy-4-(prop-1-en-1-yl)benzene (**1-a**);

(E)-1-(hex-1-en-1-yl)-4-methoxybenzene (**1-b**);

(E)-1-(dodec-1-en-1-yl)-4-methoxybenzene (**1-c**);

10 (E)-1-(prop-1-en-1-yl)naphthalene (**1-d**);

(E)-2-(dodec-1-en-1-yl)thiophene (**1-e**);

(E)-1,2,3-trimethoxy-5-(prop-1-en-1-yl)benzene (**1-f**);

(E)-5-(hex-1-en-1-yl)-1,2,3-trimethoxybenzene(**1-g**);

(E)-5-(dodec-1-en-1-yl)-1,2,3-trimethoxybenzene (**1-h**);

15 (E)-1-nitro-4-(prop-1-en-1-yl) benzene (**1-i**);

(E)-1-(hex-1-en-1-yl)-4-nitrobenzene (**1-j**);

(E)-1-(dodec-1-en-1-yl)-4-nitrobenzene (**1-k**);

(E)-4-(prop-1-en-1-yl) benzonitrile (**1-l**);

(E)-4-(hex-1-en-1-yl) benzonitrile (**1-m**);

20 (E)-4-(dodec-1-en-1-yl) benzonitrile (**1-n**);

(E)-1-(allyloxy)-4-(prop-1-en-1-yl) benzene (**1-o**);

(E)-1-(prop-1-en-1-yl)-4-(prop-2-yn-1-yloxy) benzene (**1-p**);

(E)-1-methoxy-4-((4-(prop-1-en-1-yl)phenoxy)methyl) benzene (**1-q**);

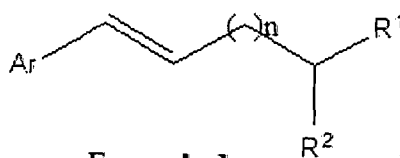
(E)-9-(prop-1-en-1-yl)anthracene (**1-r**);

25 (E)-4-fluoro-1-(hept-1-en-1-yl) benzene (**1-s**);

(E)-2,4-dichloro-1-(hept-1-en-1-yl)benzene (**1-t**);

(E)-4-(hept-1-en-1-yl)-1-methoxybenzene (**1-u**)

In still another embodiment of the present invention, novel aryl olefin compounds of formula-1, are selected from, the group consisting of



Formula 1

(*E*)-5-(dodec-1-en-1-yl)-1,2,3-trimethoxybenzene [1-h],

(*E*)-1-(dodec-1-en-1-yl)-4-nitrobenzene [1-k],

5 (*E*)-4-(dodec-1-en-1-yl)benzonitrile [1-n],

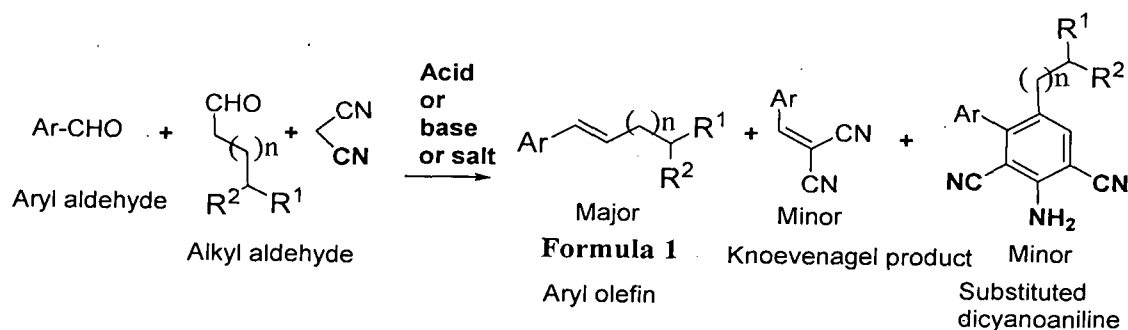
(*E*)-1-(prop-1-en-1-yl)-4-(prop-2-yn-1-yloxy)benzene [1-p] and

(*E*)-2,4-dichloro-1-(hept-1-en-1-yl)benzene [1-t].

DETAILED DESCRIPTION:

- 10 The present invention provides the single-step process for synthesis of aryl olefins of Formula 1, which comprises reacting aryl aldehydes with aliphatic/alkyl aldehydes at suitable temperature, in presence of malononitrile and acid or base or salt, optionally in presence of solvent, as depicted in Scheme 2.

Scheme 2.



- 15 wherein 'Ar' represents (un)substituted phenyl, naphthyl, anthracenyl or heteroaryl ring, substituted with (un)protected hydroxyl group, halogen selected from the group consisting of fluorine, chlorine, bromine and iodine, nitro or cyano group, linear or branched chain of 1 to 20 carbon atoms;
- $n=0-20$ and;
- 20 R^1 and R^2 may be same or different and independently selected from the group consisting of hydrogen alkyl group of linear or branched chain of 1 to 20 carbon atoms optionally substituted with aryl group, alkoxy group -OR (wherein R= alkyl group with 1 to 4 carbon atoms), hydroxyl group, halogen selected from fluorine, chlorine, bromine and iodine, nitro or (un)substituted amino group.

The aryl aldehyde is selected from the group consisting of 3,4,5-trimethoxybenzaldehyde, anisaldehyde, 1-naphthaldehyde, thiophene-2-carboxaldehyde, 4-nitrobenzaldehyde, 4-cyanobenzaldehyde, 4-allyloxybenzaldehyde, 4-prop-2-yn-1-yloxybenzaldehyde, 4-(methoxybenzyloxy) benzaldehyde, anthracene-9-carboxaldehyde, 4-fluorobenzaldehyde, 2,4-dichlorobenzaldehyde, and 4-methoxybenzaldehyde. The aryl aldehyde employed in the present invention is not limited to the aldehydes mentioned above.

Further the alkyl aldehyde or aliphatic aldehyde employed in the invention is selected from but not limited to propanal, hexanal, heptanal, octanal, dodecyl aldehyde. The molar ratio of aryl aldehyde to alkyl aldehyde is in the range of 1:1 to 1:2, preferably 1:1.1 to 1: 1.4.

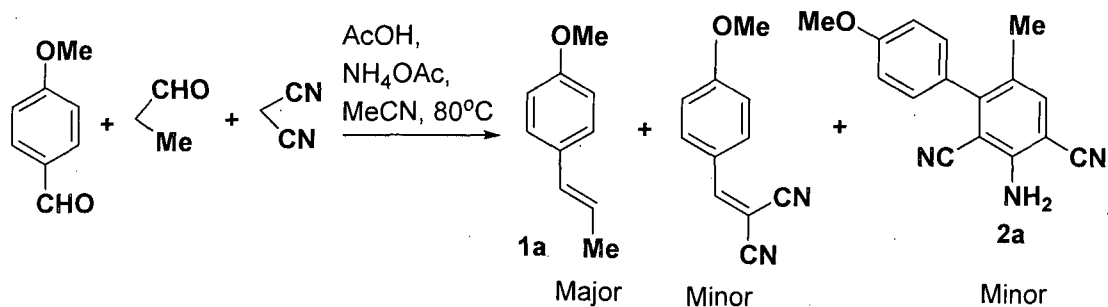
In another embodiment of the invention, the acid or base or salt used in the reaction is either alone or combinations thereof, where acid is selected from the group consisting of acetic acid, propionic acid, formic acid, p-toluenesulfonic acid, hydrochloric acid, proline, alanine, and base is selected from the group consisting of morpholine, triethyl amine, pyrrolidine, piperidine, pyridine, potassium carbonate, potassium hydroxide, sodium methoxide and salt is selected from the group consisting of ammonium acetate, ammonium formate or combinations thereof, preferably combination of acetic acid and ammonium acetate. Further the instant reaction is essentially carried out in presence of malononitrile. The molar ratio of aryl aldehyde to malononitrile is in the range of 1:2 to 1: 3 preferably 1:2.5. In optional embodiment of the invention, the solvent used in the reaction is selected from the group consisting of acetonitrile, dimethyl formamide, 1,4-dioxane, ethanol, methanol, dimethyl sulfoxide, toluene or combinations thereof, preferably solvent is acetonitrile. The use of solvent is optional, where the reaction can be carried out in absence of organic solvent by stirring the reaction mixture of reactants at suitable temperature (-10°C to 150°C) preferably 80°C but corresponding Knoevenagel product is obtained in substantial amount. The volume of solvent used depends on concentration of reactants.

In another embodiment of the invention, the reaction mixture is stirred at -10 °C to 150 °C preferably 70°- 80 °C or subjected to microwave irradiation.

In yet another preferred embodiment of the invention, the process leads to synthesis of trans isomers or (E) isomers of compounds of Formula 1. The aryl olefins obtained by the instant process have trans selectivity and cis isomer is undetectable.

A preferred embodiment of the process of the invention is depicted herein in Scheme 3.

Scheme 3.



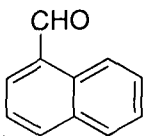
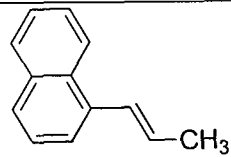
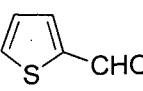
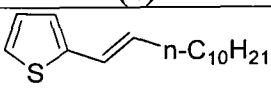
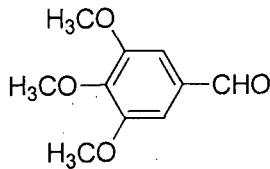
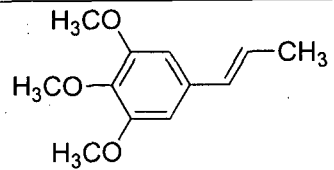
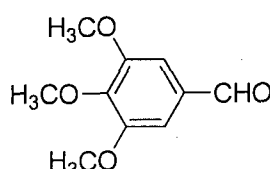
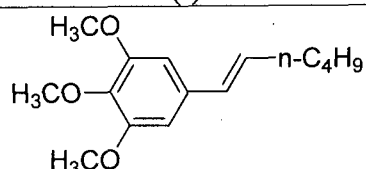
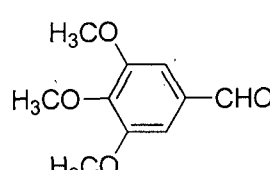
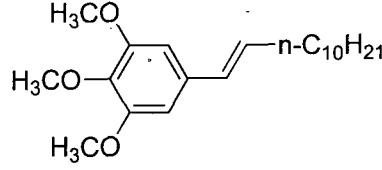
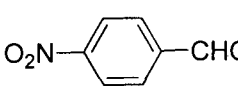
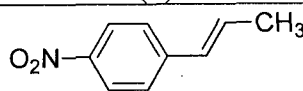
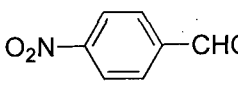
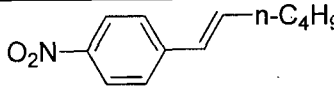
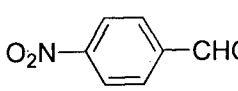
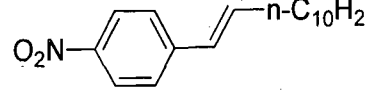
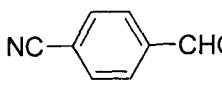
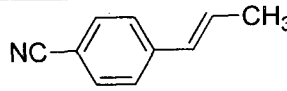
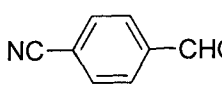
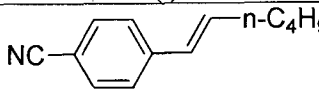
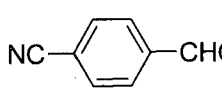
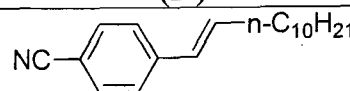
According to the Scheme 3, mixture of anisaldehyde and propionaldehyde in suitable ratio (1:1.1 to 1:1.4) and malononitrile is added to organic solvent preferably acetonitrile (10-50 ml), followed by the addition of acetic acid and then ammonium acetate. The reaction mixture is stirred at 70-80 °C for 8 h, subsequently allowed to cool at room temperature, filtered and the filtrate is concentrated on rotavapor. Further extracted in presence of aqueous and organic phase, the organic layer is concentrated and purified by column chromatography to get the desired product of formula 1. It is found that in the absence of ammonium acetate, only the corresponding Knoevenagel product is formed and the olefinic product is not obtained. Ammonium acetate can be replaced with ammonium formate, while acetic acid can be replaced with proline or alanine affording similar yields.

In another embodiment, the invention provides library of novel aryl olefin compounds of Formula 1, prepared by the novel process of the invention.

Table 1 enlists the compounds prepared by the novel process of the invention and the yields of the products.

Table 1. Synthesis of olefins

Entry	Aromatic Aldehyde	Aliphatic Aldehyde	Product (1)	Yield ^a %
1		CH ₃ CH ₂ CHO		A:49
2		CH ₃ (CH ₂) ₄ CHO		A:46
3		CH ₃ (CH ₂) ₁₀ CHO		A:38

4		$\text{CH}_3\text{CH}_2\text{CHO}$	 (d)	A:51
5		$\text{CH}_3(\text{CH}_2)_{10}\text{CHO}$	 (e)	A:39
6		$\text{CH}_3\text{CH}_2\text{CHO}$	 (f)	A:33
7		$\text{CH}_3(\text{CH}_2)_4\text{CHO}$	 (g)	A:60 B:57 C:58
8		$\text{CH}_3(\text{CH}_2)_{10}\text{CHO}$	 (h)	A:51
9		$\text{CH}_3\text{CH}_2\text{CHO}$	 (i)	A:22
10		$\text{CH}_3(\text{CH}_2)_4\text{CHO}$	 (j)	A: 37 B: 48
11		$\text{CH}_3(\text{CH}_2)_{10}\text{CHO}$	 (k)	A:52
12		$\text{CH}_3\text{CH}_2\text{CHO}$	 (l)	A:24
13		$\text{CH}_3(\text{CH}_2)_4\text{CHO}$	 (m)	A:56
14		$\text{CH}_3(\text{CH}_2)_{10}\text{CHO}$	 (n)	A:31

15		$\text{CH}_3\text{CH}_2\text{CHO}$		A:39
16		$\text{CH}_3\text{CH}_2\text{CHO}$		A:38
17		$\text{CH}_3\text{CH}_2\text{CHO}$		A:42
18		$\text{CH}_3\text{CH}_2\text{CHO}$		A:18
19		$\text{CH}_3(\text{CH}_2)_5\text{CHO}$		A:23
20		$\text{CH}_3(\text{CH}_2)_5\text{CHO}$		A:21
21		$\text{CH}_3(\text{CH}_2)_5\text{CHO}$		A:20

^aAcid-base-salt used: A—Acetic acid, ammonium acetate; B—Alanine, ammonium acetate; C—Proline, ammonium acetate. The yields are given for the isolated desired products. In addition, the corresponding Knoevenagel products and dicyanoanilines were isolated in minor amounts in varying yields.

According to Table 1, the aryl olefins of Formula-1, synthesized by instant process are namely;

- (E)-1-methoxy-4-(prop-1-en-1-yl)benzene (1-a)
- (E)-1-(hex-1-en-1-yl)-4-methoxybenzene (1-b)
- (E)-1-(dodec-1-en-1-yl)-4-methoxybenzene (1-c)

- iv. (E)-1-(prop-1-en-1-yl)naphthalene (**1-d**)
- v. (E)-2-(dodec-1-en-1-yl)thiophene (**1-e**)
- vi. (E)-1,2,3-trimethoxy-5-(prop-1-en-1-yl)benzene (**1-f**)
- vii. (E)-5-(hex-1-en-1-yl)-1,2,3-trimethoxybenzene (**1-g**)
- 5 viii. (E)-5-(dodec-1-en-1-yl)-1,2,3-trimethoxybenzene (**1-h**)
- ix. (E)-1-nitro-4-(prop-1-en-1-yl) benzene (**1-i**)
- x. (E)-1-(hex-1-en-1-yl)-4-nitrobenzene (**1-j**)
- xi. (E)-1-(dodec-1-en-1-yl)-4-nitrobenzene (**1-k**)
- xii. (E)-4-(prop-1-en-1-yl) benzonitrile (**1-l**)
- 10 xiii. (E)-4-(hex-1-en-1-yl) benzonitrile (**1-m**)
- xiv. (E)-4-(dodec-1-en-1-yl) benzonitrile (**1-n**)
- xv. (E)-1-(allyloxy)-4-(prop-1-en-1-yl) benzene (**1-o**)
- xvi. (E)-1-(prop-1-en-1-yl)-4-(prop-2-yn-1-yloxy) benzene (**1-p**)
- xvii. (E)-1-methoxy-4-((4-(prop-1-en-1-yl)phenoxy)methyl)benzene (**1-q**)
- 15 xviii. (E)-9-(prop-1-en-1-yl)anthracene (**1-r**)
- xix. (E)-4-fluoro-1-(hept-1-en-1-yl) benzene (**1-s**)
- xx. (E)-2,4-dichloro-1-(hept-1-en-1-yl)benzene (**1-t**)
- xxi. (E)-4-(hept-1-en-1-yl)-1-methoxybenzene (**1-u**)

20 In another preferred embodiment, the process of the invention led to novel aryl olefin compounds of formula-1 selected from, but not limited to (*E*)-5-(dodec-1-en-1-yl)-1,2,3-trimethoxybenzene [**1-h**], (*E*)-1-(dodec-1-en-1-yl)-4-nitrobenzene [**1-k**], (*E*)-4-(dodec-1-en-1-yl)benzonitrile [**1-n**], (*E*)-1-(prop-1-en-1-yl)-4-(prop-2-yn-1-yloxy)benzene [**1-p**] and (*E*)-2,4-dichloro-1-(hept-1-en-1-yl)benzene [**1-t**].

25 In yet another embodiment, the obtained compounds of formula-1 are characterized by spectral techniques such as IR, ¹³C NMR spectroscopy, ¹H NMR spectroscopy, High-resolution mass spectrometry HRMS as exemplified herein.

Further the aryl olefins of Formula-1 are useful as intermediates for the synthesis of active and new molecules.

In another embodiment, the present invention provides a pharmaceutical composition comprising aryl olefins of formula-1 or its pharmaceutically acceptable salts, along with pharmaceutically acceptable excipients or carriers, to decrease platelet aggregation or for the treatment of hyperlipidemias. Further the composition may be formulated into preparations like solid, semi-solid, liquid or gaseous forms, such as tablets, capsules, powders, granules, ointments, syrup, solutions, injections, gels and microspheres etc. The dosage forms can also be prepared as sustained, controlled, modified and immediate dosage forms.

In another embodiment, the present invention relates to administering 'an effective amount' of the 'composition of invention' to the subject suffering from cardiovascular disease. Accordingly, compound of the invention and pharmaceutical compositions containing them may be administered using any amount, any form of pharmaceutical composition via any route of administration effective for treating the disease. Typical routes of administering such pharmaceutical compositions include, without limitation, oral, topical, transdermal, inhalation, parenteral, sublingual, buccal, rectal, vaginal, and intranasal.

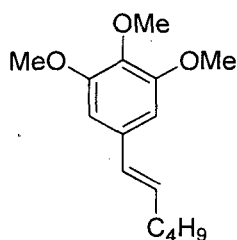
The excipients or carriers are selected from the group such as diluents, disintegrants, crosslinked polymers, binders, glidants, surfactants, sweeteners, lubricants, coatings layer.

EXAMPLES

The following examples are given by way of illustrating the present invention and should not be construed to limit the scope of the present invention:

Example 1:

Preparation of (E)-5-(hex-1-en-1-yl)-1,2,3-trimethoxybenzene: (1-g)



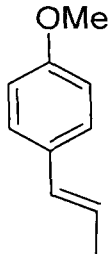
To a mixture of 3,4,5-trimethoxybenzaldehyde (0.784 g, 0.004 mol), hexanal (0.5 g, 0.005 mol) and malononitrile (0.66 g, 0.01 mol), was added 30 ml of acetonitrile followed by the addition of glacial acetic acid (0.42 ml 0.0075 mol). The reaction mixture was stirred for 10 min and then ammonium acetate (0.385 g, 0.005 mol) was added. The reaction was stirred at

80 °C for 8 h. The mixture was then allowed to come to room temperature, filtered through Whatmann filter paper and the filtrate was concentrated on rotavapor. The residual oil was then partitioned between water and ethyl acetate and the organic extract was dried over sodium sulfate, concentrated and purified over silica gel using ethyl acetate - pet ether (3% ethyl acetate in pet ether) as an eluent to give (E)-5-(hex-1-en-1-yl)-1,2,3-trimethoxybenzene as a colourless liquid (0.6 g, 60%); **IR** (chloroform): 810, 925, 1377, 1506, 1582, 1651, 2929, 2989 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3): δ 0.93 (t, $J = 7\text{Hz}$, 3H), 1.30-1.56 (m, 4H), 2.27 (q, $J = 7\text{Hz}$, 2H), 3.84 (s, 3H), 3.88 (s, 6H), 6.14 (dt, $J = 16, 7\text{ Hz}$, 1H), 6.32 (d, $J = 16\text{ Hz}$, 1H), 6.58 (s, 2H); **^{13}C NMR** (50 MHz, CDCl_3): δ 13.7, 22.0, 31.3, 32.4, 55.7 (2C), 60.6, 102.6 (2C), 129.4, 130.5, 133.5, 136.9, 153.0 (2C); **HRMS** (ESI) m/z calcd for $[\text{C}_{15}\text{H}_{22}\text{O}_3 + \text{Na}]^+$: 273.1461, found 273.1462; $[\text{C}_{15}\text{H}_{22}\text{O}_3 + \text{H}]^+$: 251.1642, found 251.1642.

The following compounds were prepared by using the procedure given for the preparation of (E)-5-(hex-1-en-1-yl)-1,2,3-trimethoxybenzene (**1g**) described in Example 1.

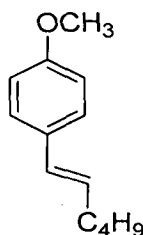
Example 2:

15 (E)-1-Methoxy-4-(prop-1-en-1-yl) benzene (1-a)



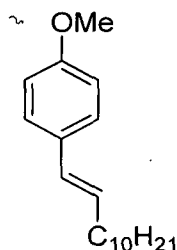
This compound was prepared from anisaldehyde and propionaldehyde following the procedure similar to the one described in Example 1.

Colorless liquid; **Yield**: 49 %; **IR** (Neat): 1036, 1175, 1282, 1509, 1608, 2835, 2957, 3023 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3): δ 1.89 (d, $J = 6\text{ Hz}$, 3H), 3.82 (s, 3H), 6.12 (dq, $J = 16, 6\text{ Hz}$, 1H), 6.38 (d, $J = 16\text{ Hz}$, 1H), 6.86 (d, $J = 8\text{ Hz}$, 2H), 7.29 (d, $J = 8\text{ Hz}$, 2H); **^{13}C NMR** (50 MHz, CDCl_3): δ 18.3, 55.0, 113.7 (2C), 123.2, 126.7 (2C), 130.2, 130.6, 158.4.

Example 3:**(*E*)-1-(Hex-1-en-1-yl)-4-methoxybenzene (1-b)**

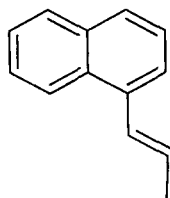
This compound was prepared from anisaldehyde and hexyl aldehyde following the procedure similar to the one described in Example 1.

Colorless liquid; **Yield:** 46%; **IR** (chloroform): 1037, 1174, 1248, 1509, 1608, 2929, 2957, 3016 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3): δ 0.98 (t, $J = 8$ Hz, 3H), 1.34-1.53 (m, 4H), 2.24 (q, $J = 8$ Hz, 2H), 3.85 (s, 3H), 6.13 (dt, $J = 16, 7$ Hz, 1H), 6.38 (d, $J = 16$ Hz, 1H), 6.88 (d, $J = 8$ Hz, 2H), 7.33 (d, $J = 8$ Hz, 2H); **^{13}C NMR** (50 MHz, CDCl_3): δ 13.9, 22.2, 31.6, 32.6, 55.1, 113.8 (2C), 126.9 (2C), 128.9 (2C), 130.7, 158.5.

Example 4:**(*E*)-1-(Dodec-1-en-1-yl)-4-methoxybenzene (1-c)**

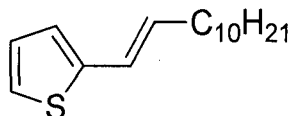
This compound was prepared from anisaldehyde and dodecyl aldehyde following the procedure similar to the one described in Example 1.

White low melting solid, **Yield:** 38%; **IR** (chloroform): 784, 837, 1034, 1250, 1465, 1577, 1608, 2851, 2950 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3): δ 0.90 (t, $J = 6$ Hz, 3H), 1.20-1.55 (m, 16H), 2.19 (q, $J = 6$ Hz, 2H), 3.81 (s, 3H), 6.09 (dt, $J = 16, 6$ Hz, 1H), 6.34 (d, $J = 16$ Hz, 1H), 6.85 (d, $J = 8$ Hz, 2H), 7.29 (d, $J = 8$ Hz, 2H); **^{13}C NMR** (50 MHz, CDCl_3): δ 14.1, 22.6, 29.2, 29.3, 29.5 (2C), 29.6 (2C), 31.9, 33.0, 55.1, 113.8 (2C), 126.9 (2C), 128.9 (2C), 130.7, 158.5.

Example 5:**(E)-1-(Prop-1-en-1-yl) naphthalene (1-d)**

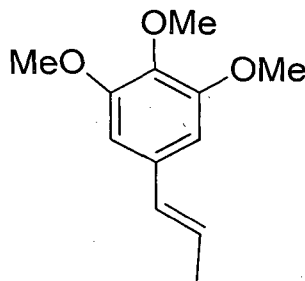
This compound was prepared from 1-naphthaldehyde and propionaldehyde following the procedure similar to the one described in Example 1.

Colorless liquid; **Yield:** 51%; **IR** (chloroform): 1508, 1590, 3016 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3) : δ 2.04 (dd, $J = 6, 2$ Hz, 3H), 6.29 (dq, $J = 16, 6$ Hz, 1H), 7.17 (dd, $J = 16, 2$ Hz, 1H), 7.41-7.61 (m, 4H), 7.75-7.91 (m, 2H), 8.14-8.22 (m, 1H); **^{13}C NMR** (50 MHz, CDCl_3): δ 18.9, 123.4, 123.9, 125.5, 125.6, 125.7, 127.1, 128.1, 128.3, 128.8, 131.0, 133.5, 135.6.

Example 6:**(E)-2-(Dodec-1-en-1-yl) thiophene (1-e)**

This compound was prepared from thiophene-2-carboxaldehyde and dodecyl aldehyde following the procedure similar to the one described in Example 1.

Colorless liquid; **Yield:** 39%; **IR** (chloroform): 1464, 1687, 2853, 2924, 3070 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3) : δ 0.89 (t, $J = 6$ Hz, 3H), 1.17-1.54 (m, 16H), 2.17 (q, $J = 7$ Hz, 2H), 6.07 (dt, $J = 16, 7$ Hz, 1H), 6.51 (d, $J = 16$ Hz, 1H), 6.83-6.97 (m, 2H), 7.08 (d, $J = 6$ Hz, 1H); **^{13}C NMR** (50 MHz, CDCl_3): δ 14.1, 22.7, 29.2 (2C), 29.3, 29.5, 29.6 (2C), 31.9, 32.8, 122.9 (2C), 124.0, 127.1, 131.1, 143.1.

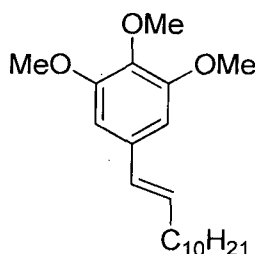
Example 7:**(E)-1,2,3-Trimethoxy-5-(prop-1-en-1-yl) benzene (1-f)**

This compound was prepared from 3,4,5-trimethoxybenzaldehyde and propionaldehyde following the procedure similar to the one described in Example 1.

Colorless liquid; **Yield:** 33%; **IR** (neat): 1010, 1126, 1238, 1273, 1506, 1582 1692, 2838, 2938 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3): δ 1.87 (d, $J = 6$ Hz, 3H), 3.83 (s, 3H), 3.86 (s, 6H), 6.13 (dq, $J = 16, 6$ Hz, 1H), 6.33 (d, $J = 16$ Hz, 1H), 6.55 (s, 2H). **^{13}C NMR** (50 MHz, CDCl_3): δ 18.0, 55.6 (2C), 60.5, 102.4 (2C), 124.8, 130.6, 133.4, 136.7, 152.9 (2C).

Example 8:

(E)-5-(Dodec-1-en-1-yl)-1,2,3-trimethoxybenzene (1-h)

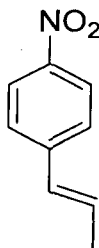


This compound was prepared from 3,4,5-trimethoxybenzaldehyde and dodecyl aldehyde following the procedure similar to the one described in Example 1.

Colorless liquid; **Yield:** 51%; **IR** (chloroform): 1130, 1215, 1326, 1464, 1583, 2855, 2928, 3019 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3): δ 0.89 (t, $J = 7$ Hz, 3H), 1.20-1.52 (m, 16H), 2.20 (q, 7 Hz, 2H), 3.84 (s, 3H), 3.88 (s, 6H), 6.14 (dt, $J = 16, 7$ Hz, 1H), 6.32 (d, 16 Hz, 1H), 6.58 (s, 2H).

Example 9:

(E)-1-Nitro-4-(prop-1-en-1-yl) benzene (1-i)



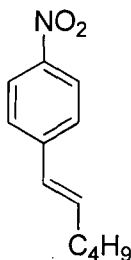
This compound was prepared from 4-nitrobenzaldehyde and propionaldehyde following the procedure similar to the one described in Example 1.

Yellow solid; **Yield:** 22%; **IR** (chloroform): 1047, 1243, 1346, 1520, 1596, 1655, 2985, 3024 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3): δ 1.85-2.05 (m, 3H), 6.36-6.58 (m, 2H), 7.44 (d, $J = 8$ Hz,

2H), 8.16 (d, $J = 8\text{Hz}$, 2H); ^{13}C NMR (50 MHz, CDCl_3): δ 18.5, 123.7 (2C), 126.0 (2C), 129.2, 131.1, 144.2, 146.1.

Example 10:

(E)-1-(Hex-1-en-1-yl)-4-nitrobenzene (1-j)



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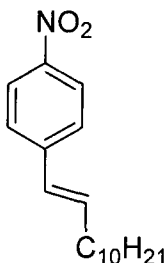
This compound was prepared from 4-nitrobenzaldehyde and hexyl aldehyde following the procedure similar to the one described in Example 1.

Yellowish semisolid; **Yield:** 37%; **IR** (chloroform): 1339, 1512, 1597, 2928 cm^{-1} . ^1H NMR (200 MHz, CDCl_3): δ 0.94 (t, $J = 6\text{Hz}$, 3H), 1.30-1.55 (m, 4H), 2.20-2.34 (m, 2H), 6.40-6.48 (m, 2H), 7.45 (d, $J = 8\text{Hz}$, 2H), 8.15 (d, $J = 8\text{Hz}$, 2H). ^{13}C NMR (50 MHz, CDCl_3): δ 13.7, 22.1, 30.9, 32.7, 123.7 (2C), 126.1 (2C), 127.8, 136.5, 144.3, 146.1.

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Example 11:

(E)-1-(Dodec-1-en-1-yl)-4-nitrobenzene (1-k)

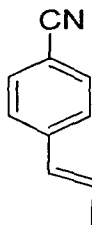


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This compound was prepared from 4-nitrobenzaldehyde and dodecyl aldehyde following the procedure similar to the one described in Example 1.

Pale yellow low melting solid; **Yield:** 52 %; **IR** (chloroform): 967, 1109, 1342, 1465, 1518, 1597, 1649, 2854, 2925 cm^{-1} . ^1H NMR (200 MHz, CDCl_3): δ 0.88 (t, $J = 6\text{Hz}$, 3H), 1.24-1.40 (m, 16H), 2.21-2.32 (m, 2H), 6.42-6.48 (m, 2H), 7.46 (d, $J = 8\text{Hz}$, 2H), 8.16 (d, $J = 8\text{Hz}$, 2H). ^{13}C NMR: (50 MHz, CDCl_3): δ 14.0, 22.6, 28.9, 29.1, 29.2, 29.4, 29.5 (2C), 31.8, 33.1, 123.8 (2C), 126.2 (2C), 127.9, 136.6, 144.3, 146.2.

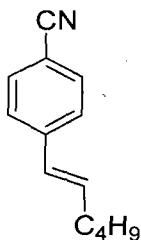
20

Example 12:**(E)-4-(Prop-1-en-1-yl) benzonitrile (1-l)**

This compound was prepared from 4-cyanobenzaldehyde and propionaldehyde following the procedure similar to the one described in Example 1.

Colorless liquid; **Yield:** 24%; **IR** (chloroform): 966, 1445, 1501, 1604, 1652, 2224, 2853, 2965, 3026 cm^{-1} .

^1H NMR (200 MHz, CDCl_3): δ 1.93 (d, $J = 5\text{Hz}$, 3H), 6.29-6.51 (m, 2H), 7.39 (d, $J = 8\text{Hz}$, 2H), 7.57 (d, $J = 8\text{Hz}$, 2H); **^{13}C NMR** (50 MHz, CDCl_3): δ 18.4, 109.6, 118.9, 126.0 (2C), 129.5, 130.0, 132.1 (2C), 142.1.

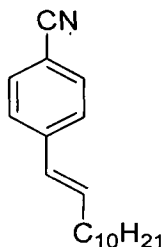
Example 13:**(E)-4-(Hex-1-en-1-yl) benzonitrile (1-m)**

This compound was prepared from 4-cyanobenzaldehyde and hexyl aldehyde following the procedure similar to the one described in Example 1.

Colorless liquid; **Yield:** 56%;

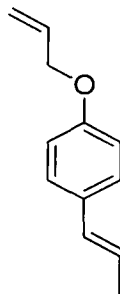
IR (Chloroform): 968, 1503, 1605, 1650, 2225, 2859, 2958 cm^{-1} .

^1H NMR (200MHz, CDCl_3): δ 0.93 (t, $J = 6\text{Hz}$, 3H), 1.25-1.54 (m, 4H), 2.19-2.32 (m, 2H), 6.29-6.48(m, 2H), 7.41(d, $J = 8\text{Hz}$, 2H), 7.57(d, $J = 8\text{Hz}$, 2H). **^{13}C NMR** (50 MHz, CDCl_3): δ 13.7, 22.1, 31.0, 32.6, 109.7, 119.0, 126.2 (2C), 128.2, 132.1 (2C), 135.4, 142.3.

Example 14:**(E)-4-(Dodec-1-en-1-yl) benzonitrile (1-n)**

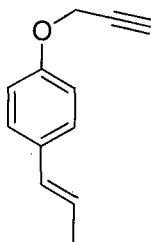
- 5 This compound was prepared from 4-cyanobenzaldehyde and dodecyl aldehyde following the procedure similar to the one described in Example 1.

Low melting solid; **Yield:** 31%; **IR** (chloroform): 758, 1520, 1605, 2227, 2855, 2928, 3020 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3): δ 0.88 (t, $J = 6\text{Hz}$, 3H), 1.19-1.55 (m, 16H), 2.18-2.30 (m, 2H), 6.29-6.48 (m, 2H), 7.41 (d, $J = 8\text{Hz}$, 2H), 7.57 (d, $J = 8\text{Hz}$, 2H); **^{13}C NMR** (50 MHz, CDCl_3): δ 14.0, 22.6, 28.9, 29.1, 29.2, 29.4, 29.5 (2C), 31.8, 33.0, 109.8, 119.1, 126.2 (2C), 128.3, 132.2 (2C), 135.5, 142.3.

Example 15:**(E)-1-(Allyloxy)-4-(prop-1-en-1-yl) benzene (1-o)**

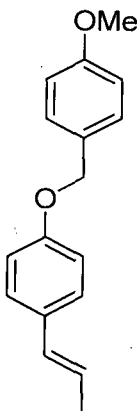
- 15 This compound was prepared from 4-allyloxybenzaldehyde and propionaldehyde following the procedure similar to the one described in Example 1.

Colorless low melting solid; **Yield:** 39 %; **IR** (chloroform): 787, 1022, 1176, 1283, 1509, 1574, 1605, 1649, 2851, 2959, 3021, 3087 cm^{-1} . **^1H NMR** (200 MHz, CDCl_3): δ 1.90 (d, $J = 6\text{Hz}$, 3H), 4.57 (d, $J = 6\text{Hz}$, 2H), 5.27-5.53 (m, 2H), 5.99-6.24 (m, 2H), 6.39 (d, $J = 17\text{Hz}$, 1H), 6.89 (d, $J = 8\text{Hz}$, 2H), 7.29 (d, $J = 8\text{Hz}$, 2H); **^{13}C NMR** (50 MHz, CDCl_3): δ 18.3, 68.5, 114.5 (2C), 117.3, 123.2, 126.7 (2C), 130.2, 130.7, 133.2, 157.4.

Example 16:**(*E*)-1-(Prop-1-en-1-yl)-4-(prop-2-yn-1-yloxy) benzene (1-p)**

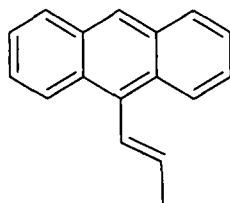
This compound was prepared from 4-prop-2-yn-1-yloxybenzaldehyde and propionaldehyde following the procedure similar to the one described in Example 1.

White solid, **Yield:** 38%, **IR** (chloroform): 1023, 1279, 1508, 1604, 2131, 2923, 3273 cm^{-1}
 ^1H NMR (400 MHz, CDCl_3): δ 1.86 (d, $J = 6$ Hz, 3H), 2.53 (s, 1H), 4.69 (s, 2H), 6.09 -6.15 (m, 1H), 6.36 (d, $J = 16$ Hz, 1H), 6.90 (d, $J = 8$ Hz, 2H), 7.28 (d, $J = 8$ Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3): δ 18.31, 55.7, 75.4, 78.5, 114.8 (2C), 123.9, 126.7 (2C), 130.1, 131.6, 156.3.

Example 17:**(*E*)-1-Methoxy-4-((4-(prop-1-en-1-yl) phenoxy) methyl) benzene (1-q)**

This compound was prepared from 4-(methoxybenzyloxy) benzaldehyde and propionaldehyde following the procedure similar to the one described in Example 1.

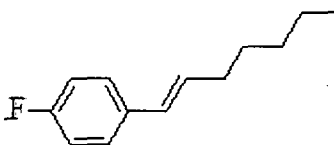
White solid; **Yield:** 42%; **^1H NMR** (200 MHz, CDCl_3): δ 1.87 (dd, $J = 6, 2$ Hz, 3H), 3.83 (s, 3H), 4.99 (s, 2H), 6.10 (dq, $J = 16, 6$ Hz, 1H), 6.35 (dd, $J = 16, 2$ Hz, 1H), 6.90 (d, $J = 10$ Hz, 2H), 6.93 (d, $J = 10$ Hz, 2H), 7.26 (d, $J = 10$ Hz, 2H), 7.36 (d, $J = 10$ Hz, 2H); **C^{13} NMR** (50 MHz, CDCl_3): δ 18.3, 55.1, 69.7, 113.9 (2C), 114.8 (2C), 123.4, 126.8 (2C), 128.9, 129.1 (2C), 130.2, 130.8, 157.7, 159.3.

Example 18:**(*E*)-9-(Prop-1-en-1-yl) anthracene (1-r)**

This compound was prepared from anthracene-9-carboxaldehyde and propionaldehyde following the procedure similar to the one described in Example 1.

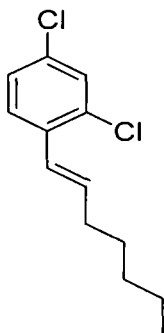
Colorless liquid; **Yield:** 18%; **IR** (chloroform): 1655, 2846, 2922, 3043 cm^{-1} .

^1H NMR (200 MHz, CDCl_3): δ 2.18 (d, $J = 6$ Hz, 3H), 6.06 (dq, $J = 16$, 6 Hz, 1H), 7.16 (d, $J = 16$ Hz, 1H), 7.42-7.52 (m, 4H), 7.98-8.05 (m, 2H), 8.31-8.45 (m, 3H).

Example 19:**(*E*)-4-Fluoro-1-(hept-1-en-1-yl) benzene (1-s)**

This compound was prepared from 4-fluorobenzaldehyde and heptaldehyde following the procedure similar to the one described in Example 1.

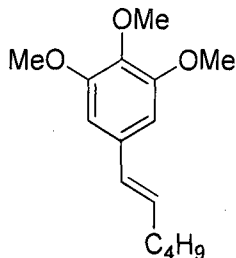
Yield: 23%; **^1H NMR** (200 MHz, CDCl_3): δ 0.93 (t, $J = 6$ Hz, 3H), 1.25-1.53 (m, 6 H), 2.15-2.27 (m, 2 H), 6.15 (dt, $J = 16$, 6 Hz, 1H), 6.36 (d, $J = 16$ Hz, 1H), 6.93-7.06 (m, 2H), 7.27-7.37 (m, 2H).

Example 20:**(*E*)-2,4-Dichloro-1-(hept-1-en-1-yl)benzene (1-t)**

This compound was prepared from 2,4-dichlorobenzaldehyde and heptaldehyde following the procedure similar to the one described in Example 1.

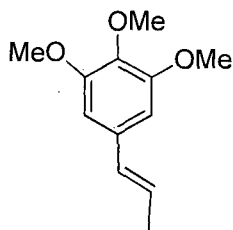
Colorless liquid; **Yield:** 21%; **IR** (neat): 965, 1470, 1586 1649, 2855, 2926, 2961, 3038 cm^{-1} ; **^1H NMR** (200 MHz, CDCl_3): δ 0.92 (t, J = 6 Hz, 3H), 1.27-1.58 (m, 6 H), 2.21-2.32 (m, 2 H), 6.21 (dt, J = 16, 6 Hz, 1H), 6.69 (d, J = 16 Hz, 1H), 7.18 (dd, J = 8, 2 Hz, 1H), 7.35 (d, J = 2 Hz, 1H), 7.43 (dd, J = 8, 2 Hz, 1H); **^{13}C NMR** (50 MHz, CDCl_3): δ 14.0, 22.5, 28.8, 31.4, 33.1, 124.9, 126.9, 127.2, 129.1, 132.5, 132.9, 134.5, 134.6.

Example 21: Preparation of (*E*)-5-(hex-1-en-1-yl)-1,2,3-trimethoxybenzene (1-g)



To a mixture of 3,4,5-trimethoxybenzaldehyde (1.56 g, 0.008 mole), hexanal (1.0 g, 0.01 mole) and malononitrile (1.32 g, 0.02 mole), was added 50 ml of dioxan followed by the addition of glacial acetic acid (1.15 ml 0.02 mole). The reaction mixture was stirred for 10 min and then ammonium acetate (0.77 g, 0.01 mole) was added. The reaction was stirred at 75 $^{\circ}\text{C}$ for 14 h. The mixture was then diluted with water (100 ml) and extracted with ethyl acetate (3 x 50 ml). The combined organic layer was dried over sodium sulphate and concentrated on rotavapor and purified over silica using ethyl acetate-pet ether (3 % ethyl acetate in pet ether) as an eluent to give (*E*)-5-(hex-1-en-1-yl)-1,2,3-trimethoxybenzene as a colourless liquid (0.468 g, 22%).

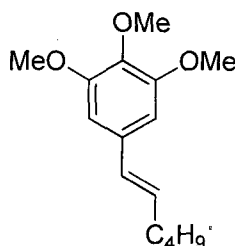
Example 22: Preparation of (*E*)-1,2,3-trimethoxy-5-(prop-1-en-1-yl)benzene (1-f)



A mixture of 3,4,5-trimethoxybenzaldehyde (1.34 g, 0.0069 mole), propionaldehyde (0.61 ml, 0.5 g, 0.0086 mol), malononitrile (1.13 g, 0.017 mole), acetonitrile (20 ml), ammonium formate (0.54 g, 0.0086 mol) and acetic acid (0.77 g, .012 mol) was stirred at 75 $^{\circ}\text{C}$ for 10 hr. It was then concentrated on rotavapor, diluted with water (50 ml), ethyl acetate (100 ml) was added and the shaken well. It was then filtered through Whatmann filter paper and the filtrate

was taken in separating funnel to separate the layers. The organic layer was concentrated and purified by column chromatography to get the product (355 mg, 25%).

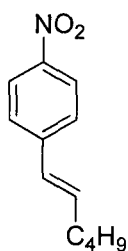
Example 23: Preparation of (*E*)-5-(hex-1-en-1-yl)-1,2,3-trimethoxybenzene (1-g)



- 5 To a mixture of 3,4,5-trimethoxybenzaldehyde (0.470 g, 2.4 mmol), hexanal (0.3 g, 3 mmol) and malononitrile (0.396 g, 6 mmol), was added 10 ml of acetonitrile followed by the addition of L-proline (0.517 g, 4.5 mmol). The reaction mixture was stirred for 10 min and then ammonium acetate (0.231 g, 3 mmol) was added. The reaction was stirred at 80 °C for 8 h. The mixture was then allowed to come to room temperature, filtered through Whatman
10 filter paper and the filtrate was concentrated on rotavapor. The residual oil was then partitioned between water and ethyl acetate and the organic extract was dried over sodium sulfate, concentrated and purified over silica gel using ethyl acetate: pet ether (3% ethyl acetate in pet ether) as an eluent to give (*E*)-5-(hex-1-en-1-yl)-1,2,3-trimethoxybenzene as a colourless liquid (0.350 g, 58%).

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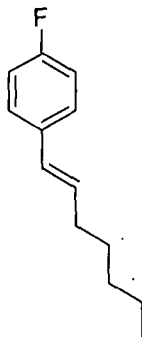
Example 24: Preparation of (*E*)-1-(hex-1-en-1-yl)-4-nitrobenzene (1-j)



- To a mixture of 4-nitrobenzaldehyde (0.362 g, 2.4 mmol), hexanal (0.3 g, 3 mmol) and
20 malononitrile (0.396 g, 6 mmol), was added 10 ml of acetonitrile followed by the addition of β-alanine (0.667 g, 7.5 mmol). The reaction mixture was stirred for 10 min and then ammonium acetate (0.392 g, 5.1 mmol) was added. The reaction was stirred at 80 °C for 8 h. The mixture was then allowed to come to room temperature, filtered through Whatman filter
25 paper and the filtrate was concentrated on rotavapor. The residual oil was then partitioned between water and ethyl acetate and the organic extract was dried over sodium sulfate, concentrated and purified over silica gel using ethyl acetate : pet ether (3% ethyl acetate in

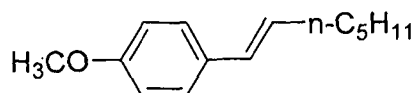
pet ether) as an eluent to give (*E*)-1-(hex-1-enyl)-4-nitrobenzene as a colourless liquid (0.238 g, 48%).

Example 25: Preparation of (*E*)-4-Fluoro-1-(hept-1-en-1-yl)benzene (1-s)

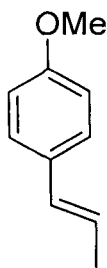


5 To a mixture of 4-fluorobenzaldehyde (0.870 g, 7 mmol), heptanal (1 g, 8.7 mmol) and malononitrile (1.157 g, 17.5 mmol), acetic acid (0.789 g, 13 mmol) was added. The reaction mixture was stirred for 10 min and then ammonium acetate (0.675 g, 8.7 mmol) was added. The reaction was stirred at 80°C for 12 h. The mixture was then allowed to come to room temperature and diluted with ethyl acetate, then filtered through Whatman filter paper and the
10 filtrate was extracted with water and the organic extract was dried over sodium sulfate, concentrated and purified over silica gel using ethyl acetate: pet ether (3% ethyl acetate in pet ether) as an eluent to give (*E*)-1-fluoro-4-(hept-1-enyl) benzene as a colourless liquid (0.310 g, 23%).

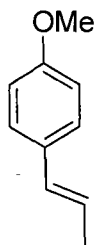
Example 26: (*E*)-4-(Hept-1-en-1-yl)-1-methoxybenzene (1-u)



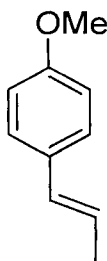
15 To a mixture of 4-methoxybenzaldehyde (0.286 g, 2.1 mmol), heptanal (0.300 g, 2.6 mmol) and malononitrile (0.347 g, 5.2 mmol), was added 15 ml of dimethylformamide followed by the addition of glacial acetic acid (0.22 ml, 3.9 mmol). The reaction mixture was stirred for 10 minutes and then ammonium acetate (0.202 g, 2.6 mmol) was added. The reaction mixture
20 was stirred at 80 °C for 8 h. The reaction was then allowed to come to room temperature, filtered through Whatman filter paper and the filtrate was concentrated on rotavapor. The residual oil was partitioned between water and ethyl acetate and the organic extract was dried over sodium sulphate, concentrated and purified over silica gel using ethyl acetate–pet ether (3 % ethyl acetate in pet ether) as an eluent to give (*E*)-4-(hept-1-en-1-yl)-1-methoxybenzene
25 as yellowish liquid (0.087 g, 20%).

Example 27: Preparation of (E)-1-methoxy-4-(prop-1-en-1-yl) benzene (1-a)

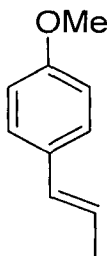
To a mixture of 4-methoxybenzaldehyde (1.87 g, 13 mmol), propanal (1 g, 17 mmol) and malononitrile (2.27 g, 34 mmol), was added 25 ml of ethanol followed by the addition of glacial acetic acid (1.4 ml, 25 mmol). The reaction mixture was stirred for 10 min and then ammonium acetate (1.32 g, 17 mmol) was added. The reaction mixture was stirred at 80 °C for 8 h. The mixture was then allowed to come to room temperature, filtered through Whatman filter paper and the filtrate was concentrated on rotavapor. The residual oil was partitioned between water and ethyl acetate and the organic extract was dried over sodium sulphate, concentrated and purified over silica gel using ethyl acetate-pet ether (3 % ethyl acetate in pet ether) as an eluent to give (E)-1-methoxy-4-(prop-1-en-1-yl) benzene as colourless liquid (0.095 g, 10%).

Example 28: Preparation of (E)-1-methoxy-4-(prop-1-en-1-yl)benzene (1-a)

To a mixture of 4-methoxybenzaldehyde (0.563 g, 4.14 mmol), propanal (0.3 g, 5.17 mmol) and malononitrile (0.682 g, 10.34 mmol), was added 10 ml of *N,N*-dimethylformamide followed by the addition of formic acid (0.356 g, 7.76 mmol). The reaction mixture was stirred for 10 min and then ammonium acetate (0.398 g, 5.17 mmol) was added. The reaction was stirred at 80 °C for 8 h. The mixture was then allowed to come to room temperature, filtered through Whatman filter paper and the filtrate was concentrated on rotavapor. The residual oil was then partitioned between water and ethyl acetate and the organic extract was dried over sodium sulfate, concentrated and purified over silica gel using ethyl acetate: pet ether (3% ethyl acetate in pet ether) as an eluent to give (E)-1-methoxy-4-(prop-1-en-1-yl)benzene as a colourless liquid (0.170 g, 24%).

Example 29: Preparation of (*E*)-1-methoxy-4-(prop-1-en-1-yl) benzene (1-a)

To a mixture of 4-methoxybenzaldehyde (0.563 g, 4 mmol), propanal (0.3 g, 5 mmol) and malononitrile (0.682 g, 10 mmol), was added 10 ml of *N,N*-dimethylformamide followed by the addition of propanoic acid (0.574 g, 7.76 mmol). The reaction mixture was stirred for 10 min and then ammonium acetate (0.398 g, 5.17 mmol) was added. The reaction was stirred at 80 °C for 8 h. The mixture was then allowed to come to room temperature, filtered through Whatman filter paper and the filtrate was concentrated on rotavapor. The residual oil was then partitioned between water and ethyl acetate and the organic extract was dried over sodium sulfate, concentrated and purified over silica gel using ethyl acetate: pet ether (3% ethyl acetate in pet ether) as an eluent to give (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene as a colourless liquid (0.133 g, 21%).

Example 30: Preparation of (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene (1-a)

To a mixture of 4-methoxybenzaldehyde (0.937 g, 6.8 mmol), propanal (0.500 g, 8 mmol) and malononitrile (1.13 g, 17 mmol), was added 15 ml of dimethylformamide. The reaction mixture was stirred for 10 min and then morpholine (0.748 g, 8.6 mmol) was added. The reaction mixture was kept in microwave for 10 minutes. The mixture was then filtered through Whatman filter paper and the filtrate was concentrated on rotavapor. The residual oil was partitioned between water and ethyl acetate and the organic extract was dried over sodium sulphate, concentrated and purified over silica gel using ethyl acetate-pet ether (3 % ethyl acetate in pet ether) as an eluent to give (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene as colourless liquid (0.220 g, 21%).

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as
5 illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

ADVANTAGES OF INVENTION:

- 10 The process of the invention yields aryl olefins of Formula-1 that can serve as intermediates for many other compounds having biological activity.

The present invention does not use inert atmosphere, dry solvents, and cryogenic conditions. In the instant process the hazardous chemicals and strong bases are avoided and the easily available starting materials lead to aryl olefins in single step with a variety of substituent with
15 good yield and trans selectivity. Additionally the desired aryl olefins can be easily separated from other products formed.

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'R¹' and 'R²' may be same or different and independently selected from the group consisting of hydrogen alkyl group of linear or branched chain of 1 to 20 carbon atoms optionally substituted with aryl group, alkoxy group -OR (wherein R= alkyl group with 1 to 4 carbon atoms), hydroxyl group, halogen selected from fluorine, chlorine, bromine and iodine, nitro or (un)substituted amino group.

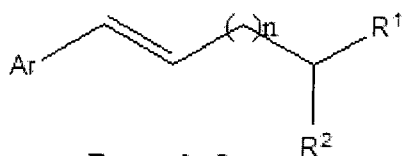
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5. The single-step process according to claim 1, wherein the alkyl aldehyde or aliphatic aldehyde is selected from the group consisting of propanal, hexanal, heptanal, octanal, dodecyl aldehyde.
6. The single-step process according to claim 1, wherein the molar concentration of alkyl aldehyde is in the range of 2-20 mmole.
7. The single-step process according to claim 1, wherein the molar ratio of aryl aldehyde to alkyl aldehyde is in the range of 1:1.0 to 1:1.6.
8. The single-step process according to claim 1, wherein the acid is selected from the group consisting of acetic acid, propionic acid, formic acid, p-toluenesulfonic acid, hydrochloric acid, proline, alanine.
9. The single-step process according to claim 1, wherein the base is selected from the group consisting of morpholine, triethyl amine, pyrrolidine, piperidine, pyridine, potassium carbonate, potassium hydroxide, sodium methoxide, and the salt is selected from the group consisting of ammonium acetate, ammonium formate.
10. The single-step process according to claim 1, wherein the acid or base or salt is present either alone or combination thereof.
11. The single-step process according to claim 10, wherein the acid-base/salt combination is acetic acid and ammonium acetate.
12. The single-step process according to claim 10, wherein the molar ratio of acid and base/salt combination used in the reaction is between 1:1 to 2:1.
13. The single-step process according to claim 1, wherein the molar concentration of malononitrile ranges from 3 to 40 mmole, preferably 5 to 35 mmole.
14. The single-step process according to claim 1, wherein the aryl olefin compounds of Formula-1, are selected from the group consisting of;
 - (E)-1-methoxy-4-(prop-1-en-1-yl)benzene (**1-a**);
 - (E)-1-(hex-1-en-1-yl)-4-methoxybenzene (**1-b**);
 - (E)-1-(dodec-1-en-1-yl)-4-methoxybenzene (**1-c**);
 - (E)-1-(prop-1-en-1-yl)naphthalene (**1-d**);
 - (E)-2-(dodec-1-en-1-yl)thiophene (**1-e**);
 - (E)-1,2,3-trimethoxy-5-(prop-1-en-1-yl)benzene (**1-f**);
 - (E)-5-(hex-1-en-1-yl)-1,2,3-trimethoxybenzene (**1-g**);
 - (E)-5-(dodec-1-en-1-yl)-1,2,3-trimethoxybenzene (**1-h**);
 - (E)-1-nitro-4-(prop-1-en-1-yl) benzene (**1-i**);

- (E)-1-(hex-1-en-1-yl)-4-nitrobenzene (**1-j**);
 (E)-1-(dodec-1-en-1-yl)-4-nitrobenzene (**1-k**);
 (E)-4-(prop-1-en-1-yl) benzonitrile (**1-l**);
 (E)-4-(hex-1-en-1-yl) benzonitrile (**1-m**);
 5 (E)-4-(dodec-1-en-1-yl) benzonitrile (**1-n**);
 (E)-1-(allyloxy)-4-(prop-1-en-1-yl) benzene (**1-o**);
 (E)-1-(prop-1-en-1-yl)-4-(prop-2-yn-1-yloxy) benzene (**1-p**);
 (E)-1-methoxy-4-((4-(prop-1-en-1-yl)phenoxy)methyl) benzene (**1-q**);
 (E)-9-(prop-1-en-1-yl)anthracene (**1-r**);
 10 (E)-4-fluoro-1-(hept-1-en-1-yl) benzene (**1-s**);
 (E)-2,4-dichloro-1-(hept-1-en-1-yl)benzene (**1-t**);
 (E)-4-(hept-1-en-1-yl)-1-methoxybenzene (**1-u**)

15. Novel aryl olefin compounds of formula-1, are selected from, the group consisting of



Formula 1

- (E)-5-(dodec-1-en-1-yl)-1,2,3-trimethoxybenzene [**1-h**],
 (E)-1-(dodec-1-en-1-yl)-4-nitrobenzene [**1-k**],
 (E)-4-(dodec-1-en-1-yl)benzonitrile [**1-n**],
 20 (E)-1-(prop-1-en-1-yl)-4-(prop-2-yn-1-yloxy)benzene [**1-p**] and
 (E)-2,4-dichloro-1-(hept-1-en-1-yl)benzene [**1-t**].

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2013/000688

A. CLASSIFICATION OF SUBJECT MATTER INV. C07B37/00 C07C255/50 C07C41/18 C07C201/12 C07C205/06 C07C43/215 C07C253/30 C07C1/207 C07C15/60 C07D333/08 C07C17/263 C07C25/08											
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) C07B C07C C07D 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) EPO-Internal, WPI Data											
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>SANGMESHWER P SAWARGAVE ET AL: "One-step synthesis of 4-alkyl-3-aryl-2,6-dicyanoanilines and their use in the synthesis of highly functionalized 2,3,5,6,7- and 2,3,4,5,7-substituted indoles", TETRAHEDRON LETTERS, PERGAMON, GB, vol. 52, no. 42, 10 August 2011 (2011-08-10), pages 5491-5493, XP028293801, ISSN: 0040-4039, DOI: 10.1016/J.TETLET.2011.08.064 [retrieved on 2011-08-18] cited in the application</td> <td>1-10,13,14</td> </tr> <tr> <td>A</td> <td>Scheme 1; page 5491, column 2 - page 5492, column 2; table 1 reference 9; page 5493 -/-</td> <td>11,12,15</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	SANGMESHWER P SAWARGAVE ET AL: "One-step synthesis of 4-alkyl-3-aryl-2,6-dicyanoanilines and their use in the synthesis of highly functionalized 2,3,5,6,7- and 2,3,4,5,7-substituted indoles", TETRAHEDRON LETTERS, PERGAMON, GB, vol. 52, no. 42, 10 August 2011 (2011-08-10), pages 5491-5493, XP028293801, ISSN: 0040-4039, DOI: 10.1016/J.TETLET.2011.08.064 [retrieved on 2011-08-18] cited in the application	1-10,13,14	A	Scheme 1; page 5491, column 2 - page 5492, column 2; table 1 reference 9; page 5493 -/-	11,12,15
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
X	SANGMESHWER P SAWARGAVE ET AL: "One-step synthesis of 4-alkyl-3-aryl-2,6-dicyanoanilines and their use in the synthesis of highly functionalized 2,3,5,6,7- and 2,3,4,5,7-substituted indoles", TETRAHEDRON LETTERS, PERGAMON, GB, vol. 52, no. 42, 10 August 2011 (2011-08-10), pages 5491-5493, XP028293801, ISSN: 0040-4039, DOI: 10.1016/J.TETLET.2011.08.064 [retrieved on 2011-08-18] cited in the application	1-10,13,14									
A	Scheme 1; page 5491, column 2 - page 5492, column 2; table 1 reference 9; page 5493 -/-	11,12,15									
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.											
* Special categories of cited documents : <table border="0"> <tr> <td> "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 </td> <td> "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 </td> </tr> </table>			"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							
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Date of the actual completion of the international search		Date of mailing of the international search report									
27 February 2014		06/03/2014									
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Patteux, Claudine									

INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2013/000688

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	----- FELIPE GÁNDARA ET AL: "Two-Dimensional Hybrid Germanium Zeotype Formed by Selective Coordination of the trans -1,2-Diaminocyclohexane Isomer to the Ge Atom: Heterogeneous Acid-Base Bifunctional Catalyst", INORGANIC CHEMISTRY, vol. 47, no. 15, 1 August 2008 (2008-08-01), pages 6791-6795, XP055104207, ISSN: 0020-1669, DOI: 10.1021/ic8004097 page 6794, column 2 - page 6795, column 2 -----	11,12,15
A	B. GREEN ET AL: "Unusual Knoevenagel condensations of 16a-substituted-16-methylene-17-keto-steroids", TETRAHEDRON, vol. 32, no. 24, 1 January 1976 (1976-01-01), pages 2997-3001, XP055104545, ISSN: 0040-4020, DOI: 10.1016/0040-4020(76)80158-5 the whole document -----	11,12,15
T	HANUMANT B. BORATE ET AL: "One-step method for the synthesis of aryl olefins from aryl aldehydes and aliphatic aldehydes", TETRAHEDRON LETTERS, vol. 54, no. 12, 1 March 2013 (2013-03-01), pages 1528-1530, XP055103874, ISSN: 0040-4039, DOI: 10.1016/j.tetlet.2013.01.008 the whole document -----	1-15
X	JANUSZ POPLAWSKI ET AL: "Synthesis and Hypolipidemic and Antiplatelet Activities of [alpha]-Asarone Isomers in Humans (in Vitro), Mice (in Vivo), and Rats (in Vivo)", JOURNAL OF MEDICINAL CHEMISTRY, vol. 43, no. 20, 1 October 2000 (2000-10-01), pages 3671-3676, XP055104555, ISSN: 0022-2623, DOI: 10.1021/jm000905n cited in the application compound 3 page 3673, column 2; tables 1,3 ----- -/--	15

INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2013/000688

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LIU J-T ET AL: "One-pot synthesis of trans-beta-alkylstyrenes", TETRAHEDRON LETTERS, PERGAMON, GB, vol. 42, no. 35, 27 August 2001 (2001-08-27), pages 6147-6150, XP004298202, ISSN: 0040-4039, DOI: 10.1016/S0040-4039(01)01185-6 the whole document -----	1-15