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Rhodium catalyzed selective hydroaminomethylation of biorenewable eugenol under aqueous biphasic condition

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ABSTRACT

This work reports a highly regioselective hydroaminomethylation of eugenol, anethole and estragole with piperidine in aqueous medium. This catalytic system was composed of rhodium complexes stabilized by trisulfonated triphenylphosphine (TPPTS) and of a native or chemically modified cyclodextrins. Various cyclodextrins such as α-cyclodextrins (α-CD), β-cyclodextrin (β-CD), γ-cyclodextrin (γ-CD), 2-hydroxy-propyl β-cyclodextrin (hp-β-CD) and RAndomly MEthylated β-cyclodextrin (RAME-β-CD) have been tested. The effect of different parameters such as syngas pressure, time, temperature, catalyst precursor/loading and the ratio of Metal/Ligand/Cyclodextrin were also investigated. The addition of cyclodextrins as a mass transfer agent remarkably increased the rate reaction and the selectivity of linear amines, specially in the case of RAME-β-CD. So, the Rh/TPPTS/RAME-β-CD as a catalyst exhibited high conversion (92%) and selectivity (79.2%) towards the linear amine as major product under mild conditions. Finally, the catalytic system was recycled up to five times without a significant loss in activity and selectivity.

1. Introduction

Amines are a class of valuable organic compounds for the pharmaceutical, agrochemical and fine chemical industries [1]. Hydroaminomethylation (HAM) reaction is a highly atom-economical, homogeneous industrial process for the synthesis of linear and branched amines from olefins, amines and syngas by the use of a single catalyst [2]. The HAM process is a triple sequential reaction involving hydroformylation of an alkene, condensation of the produced aldehyde with amine, and the hydrogenation of the resulting imine or enamine, which provides a highly efficient method to construct amines (Scheme 1) [3]. It has high attraction in industry as well as in academics, since it was discovered by Reppe in 1949 at BASF [4]. The several processes are available for the production of aliphatic amines consist of organic reactions like hydroamination, hydrocyanation of alkenes followed by reduction, nucleophilic substitution of alkyl halides, reductive amination of carbonyl compounds, *etc*. Despite these processes available, amine preparation often suffers from low generality, costly starting materials, side reactions and the necessity of protecting groups [5].

In general, the hydroaminomethylation reactions are carried out in a homogeneous catalytic system [6–9], which suffers from some shortcomings such as the difficulties of the catalyst recovery, catalyst separation from products, selectivity of desired product, to control the hydrogenation and isomerisation, *etc.* [10]. Probable solutions to these troubles consist of making the homogeneous catalyst into heterogeneous by anchoring the metal on support or by using two-phase catalytic system [11]. Beller and co-workers [12] reported the hydroaminomethylation of C5 olefins in aqueous-organic biphasic catalysis in 1999. The catalytic system was composed of iridium and rhodium complexes stabilized by trisulfonated triphenylphosphine (TPPTS: $P(m\text{-}C_6H_4SO_3Na)_3$) or sulfonated 2,2′-bis(diphenylphosphinomethyl)-1,1′-binaphthylene (BINAS). Addition of iridium complex was required to increase the catalytic activity and amine selectivity. Indeed, the rhodium catalysts are not sufficiently active for the hydrogenation of the imine at high phosphorus to rhodium ratio.

In 2004, Li group [13] reported the hydroaminomethylation of long chain olefins with poor water solubility in an aqueous-organic biphasic system using the water-soluble rhodium complex $RhCl(CO)(TPPTS)_2$ as catalyst in the presence of the cationic surfactant cetyltrimethylammonium bromide. The use of sulfonated 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl ligand (BISBIS) instead of TPPTS ligand significantly improved the amine selectivity (80% *vs.* 46% for the BISBIS and TPPTS, respectively) and linear/branched amines selectivities (l:b ratio: 83 *vs.* 15 for the BISBIS and TPPTS, respectively) [14].

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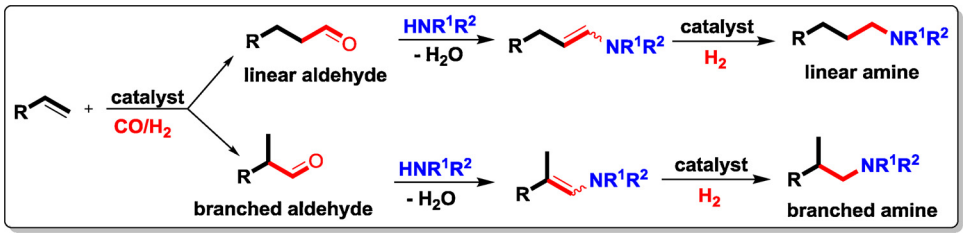


Scheme 1. The general hydroaminomethylation of olefins and amines.

Interestingly, A. Behr et al. have reported that the addition of inorganic and organic acids allowed the quantitative conversion of 1-octene with very high selectivity for the amines. For instance, the hydroaminomethylation of 1-octene with synthesis gas and di-*n*-butylamine gives rise to the desired amines in 96% yield in the presence of sulfuric acid [15].

Furthermore, Behr et al. [16] also achieved the hydroaminomethylation of 1-octene with morpholine in temperature-dependent solvent systems, in which reaction occurs in a single-phase at a higher temperature followed by splitting into two phases at a lower temperature. Wang and co-workers reported the biphasic hydroaminomethylation of long chain olefins in ionic liquids [17]. Although the catalyst could be easily separated by a simple phase separation, the catalyst recycling remained to be improved. Though the several practices have been explored for hydroaminomethylation of olefins in recent years [18], the synthesis of linear amines from internal and terminal natural olefins such as eugenol, anethole and estragole is always challenging. Such reactions are of industrially important because natural olefins such as eugenol, anethole and estragole are more cost-efficient and abundant in nature. These bio-renewable starting materials which are the derivatives of natural allyl benzenes were obtained from biomass, such as eugenol from cloves, anethole from basil and estragole from sweet basil *etc.* [19].

As a continuation of our research on the catalytic valorization of biomass to value-added products [20], we hereby report the aqueous biphasic hydroaminomethylation of eugenol into linear amines using Rh/TPPTS as catalytic system and cyclodextrins (CDs) as mass transfer promoters (Scheme 2). Chemically modified CDs are cyclic oligosaccharides composed of (α-1,4) -linked α-D-glucopyranose units which is obtained from the enzymatic conversion of starch [21]. These compounds allowed to achieve the catalytic functionalisation of numerous substrate in an aqueous organic two-phase system with high reaction rates, while avoiding the formation of an emulsion and the partition of the catalyst between the organic and aqueous phases. This outstanding result was attributed to the formation of inclusion complexes at the aqueous/organic interface [22]. The main objective of this work is to investigate the effect of the various cyclodextrins such as α-cyclodextrin (α-CD), *β*-cyclodextrin (*β*-CD), γ-cyclodextrin (γ-CD), hydroxyl propyl *β*-cyclodextrin (hp-*β*-CD) and RAndomly MEthylated *β*-cyclodextrin (RAME-*β*-CD) on the rate and selectivities of hydroaminomethylation of eugenol.

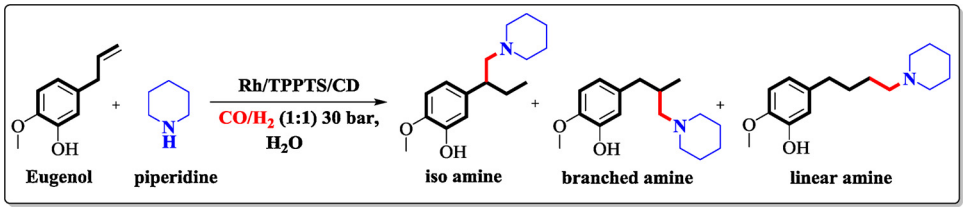
2. Experimental

2.1. General methods and reagents

All the reaction experiments were carried out under the nitrogen atmosphere. Chemicals and reagents were procured from Sigma Aldrich, Alfa Aesar, Spectrochem Pvt. Ltd., India with a purity grade of 99% and higher which are used as received. Distilled deionized water was used as solvent in all experiments. A syngas containing mixture of hydrogen (49.9%) and carbon monoxide (49.9%) were purchased from Rakhangi Gas Service, Mumbai. All experiments were performed in a 100 mL autoclave. The reaction process was monitored by gas chromatography on Perkin Elmer Clarus 400 GC equipped with flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 µm). GC–MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness 0.25 µm df) (column flow 2 10 mL min^{-1}, 80–240 °C at 10°/min rise).

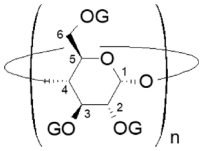
2.2. Typical experimental procedure for aqueous biphasic hydroaminomethylation of eugenol and recycling of the catalyst (Rh/TPPTS/CD)

In a 100 mL volume of high pressure reactor, eugenol (1 mmol), piperidine (1 mmol), [Rh(acac)$(CO)_2$] (0.0015 mmol), TPPTS (0.0075 mmol), RAME-*β*-CD (0.015 mmol) and deionised distilled water (10 mL) were added. Then reactor was closed, flushed three times with syngas and pressurized with 30 bar syngas pressure heated to 80 °C for 8 h. After the completion of the reaction, the reactor was cooled down to room temperature, remaining syngas was vented carefully and the reactor was opened. The organic layer containing product from aqueous layer was separated by a simple separation technique using separatory funnel. The reactor vessel was thoroughly washed with ethyl acetate (3 × 5 mL) to remove traces of the product. Then reaction mixture and catalytic system was separated by separatory funnel. The organic layer containing product was passed through dry Na_2SO_4 to remove traces of water (moisture) if present and it is subjected to GC and GC–MS analysis. The recovery and recycling of the catalytic system were carried out under inert condition that is in nitrogen atmosphere. Aqueous solution containing metal, ligand and cyclodextrin was collected and used as it is for next recycle experiment. The Rh/TPPTS/CDs as biphasic catalytic system was easily recycled up to five consecutive cycles without loosing its catalytic activity and selectivity.



Scheme 2. Aqueous biphasic selective hydroaminomethylation of naturally occurring eugenol and piperidine using Rh/TPPTS/CD as greener and reusable catalytic system.
[a]**Reaction Conditions:** eugenol (1 mmol), piperidine (1 mmol), Rhacac$(CO)_2$ (0.002 mmol), TPPTS (0.008 mmol), CD (0.02 mmol), CO/H_2 (30 bar), Distilled water (10 mL), 80 °C, 8 h.
[b]Determined by GC and GC–MS.

Table 1
Chemical structure and characteristic of the cyclodextrin derivatives.



G:H or R

Entry	Abbreviation	n	Substituent R	Carbons bearing the OR group	Number of R groups per CD	Molecular weight ($g\,mol^{-1}$)
1	α-CD	6	(−)	(−)	0	972
2	β-CD	7	(−)	(−)	0	1134
3	γ-CD	8	(−)	(−)	0	1297
4	RAME-α-CD	6	CH_3	2, 3 and 6	10.8	1127
5	RAME-β-CD	7	CH_3	2, 3 and 6	12.6	1314
6	HP-β-CD	7	CH_2-CHOH-CH_3	2, 3 and 6	5.6	1460

3. Results and discussion

3.1. Selective hydroaminomethylation of eugenol and piperidine using Rh/TPPTS/CD as reusable catalyst under aqueous biphasic condition

Aqueous biphasic hydroaminomethylation of eugenol (**1a**) and piperidine (**1a***) converted into linear amine *i.e.* 2-methoxy-5-(4-(piperidin-1-yl)butyl)phenol (**4a**) was chosen as model reaction. The reaction was conducted under aqueous media with $Rhacac(CO)_2$ as a catalyst precursor, TPPTS as water soluble phosphine ligand and cyclodextrin as mass transfer promoter. The reaction experiments was carried out under the nitrogen atmosphere.

3.2. Influence of various modified cyclodextrins and their concentration on the hydroaminomethylation of eugenol (1a) and piperidine (1a)*

The properties and chemical environment of native cyclodextrins (α-CD, β-CD and γ-CD) and modified cyclodextrins (RAME-α-CD, RAME-β-CD and hp-β-CD) were shown in Table 1. Cyclodextrins are the cyclic oligosaccharides with a hydrophilic outer surface and a lipophilic central cavity. The α-CD, β-CD and γ-CD contains 6, 7 and 8 (α-1,4) linked α-D-glucopyranose units, respectively. The RAME-α-CD and RAME-β-CD were a mixture of CDs partially *O*-methylated with statistically 11.8 OH and 12.6 groups modified per CD, respectively. The OH groups in C-6 position are fully methylated whereas those in C-2 and C-3 positions are partially methylated (Table 1, entries 4 and 5). The hp-β-CD is a mixture of β-CDs partially *O*-hydroxypropylated with statistically 5.6 OH groups modified per CD. The OH groups can be in C-2, C-3 or C-6 positions (Table 1, entry 6).

Primarily, we have studied an influence of various cyclodextrins with their concentration on the hydroaminomethylation of eugenol (**1a**) and piperidine (**1a***) to the synthesis of **4a** as shown in Table 2. The first reaction was carried out in absence of cyclodextrins *i.e.* the Rh/TPPTS/H_2O used as a catalytic system which afforded 67% conversion with 62% selectivity of total amines (**2a** + **3a** + **4a**) and 31% selectivity towards **4a** within the amines (Table 2, entry 1). We tested the α-CD at various concentrations of 0.030 mmol, 0.061 mmol and 0.102 mmol (Table 2, entries 2–4) for the hydroaminomethylation of **1a**, out of these three concentrations 0.061 mmol of α-CD provides 84% conversion of **1a** and 75% selectivity of total amines with 49.5% selectivity of **4a** within the amines (Table 2, entry 3). A 92% conversion was observed with 75% selectivity of total amines and 60% selectivity towards **4a** for 0.052 mmol concentration of β-CD (Table 2, entry 6). As compared to the α-CD and γ-CD, superior results were obtained with 0.026 mmol and 0.088 mmol concentration of β-CD used (Table 2, entries 5–7). Lower selectivity of total amines and low selectivity towards **4a** was found using α-CD (Table 2, entries 2–4) and γ-CD (Table 2, entries 8–10) rather than the use of β-CD at the same reaction conditions. From these results, it is indicated that the size of CDs cavity played a key role to handle the catalytic activity and selectivity.

Furthermore, modified CDs such as RAME-α-CD, RAME-β-CD and hp-β-CD were also evaluated. At 0.053 mmol concentration of RAME-α-CD provides 85% conversion of **1a** and 70% selectivity of total amines with 43.4% selectivity towards **4a** within the amines (Table 2, entry 12). The RAME-α-CD provides better conversion, but the selectivity was observed to be less as compared to the RAME-β-CD and hp-β-CD (Table 2, entries 11–13). Then the RAME-β-CD showed the best results at 0.0252 mmol concentration afforded high conversion (100%) of **1a,** high selectivity of total amines (87%) and the selectivity (73.95%) of **4a** within amines (Table 2, entry 15). If we increase the concentration of RAME-β-CD from 0.010 mmol to 0.040 mmol then it was found that the conversion increases from 94% to 99%. The selectivity of total amines and selectivity of linear amine initially increases and then decreases at last (Table 2, entries 14–16). A high activity likely attributed to be the surface-active properties of RAME-β-CD and the selectivity towards **4a** could be due to the steric hinderance of randomly methyl groups present in the RAME-β-CD. Finally, the hp-β-CD was also demonstrated finer results for the conversion of **1a** and the selectivity towards **4a** (Table 2, entries 17–19). A high conversion up to 85% and better selectivity of total amines to 86% with moderate selectivity (59.34%) towards **4a** within amines was observed using 0.041 mmol concentration of hp-β-CD (Table 2, entry 18).

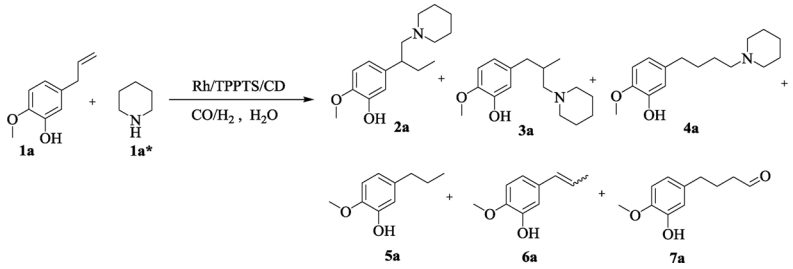
These results indicate that the presence of CD allows in every case to enhance the selectivity of linear amines. This selectivity increase can be explained by the inclusion of the substrate inside the cavity of cyclodextrins. Definitely, the CD can transitorily accommodate the substrate into its cavity restricting its conformational flexibility and masking a part of the allyl group while exposing distal position of the allyl group to Rh catalytic species. This result is noteworthy given the well-known ability of CD to interact with TPPTS to form phosphane low-coordinated species which are expected to be less regioselective in the hydroaminomethylation reaction (Scheme 3) [23–25].

3.3. Optimization of various reaction parameters for the hydroaminomethylation of eugenol (1a) and piperidine (1a)*

The various parameters such as the effect of syngas (CO/H_2) pressure, time, temperature, catalyst screening and loading were studied for the regio-selective hydroaminomethylation of eugenol (**1a)** and piperidine (**1a***). These results are summarized in Tables 3 and 4. Similarly the effect of metal to ligand to CDs ratio were screened and results are shown in Fig. 1.

Effect of syngas pressure plays a crucial role in the hydroaminomethylation reaction using aqueous biphsic Rh/TPPTS/CDs. Use of 40 bar pressure, conversion was found almost complete but the lower selectivity (49.2%) towards the linear amine (**4a)** within amines was observed (Table 3, entry 1). Then 30 bar syngas pressure was found as optimum pressure, which offered high conversion (99%) of **1a** and better selectivity (67.86%) towards **4a** (Table 3, entry 2). Next, we decreased syngas pressure up to 20 bar then conversion diminished to 94% and the selectivity towards **4a** up to 58.8% with trace amount (10%) of other products (**5a** + **6a** + **7a**) was observed (Table 3, entry 3). Moreover, we also studied the relative concentration ratio of carbon monoxide (CO) and hydrogen (H_2) gas by varying the ratio of $CO:H_2$ such as 1:2 for 45 bar, 1:2 for 30 bar and 1:3 for 32 bar (Table 3, entries 4–6). At 1:2 or 1:3 ratio of $CO:H_2$, good selectivity were obtained though the results obtained indicate that the high conversion and selectivity were achieved at 1:1 ratio of $CO:H_2$. We examine the 1:2 ratio of $CO:H_2$ at 45 bar syngas pressure, 92% conversion and 39.44% selectivity towards **4a** with less amount 24% of other products (**5a** + **6a** + **7a**) was detected (Table 3, entry 4). Then we reduced the pressure to 30 bar at same ratio of $CO:H_2$, slightly increase in the

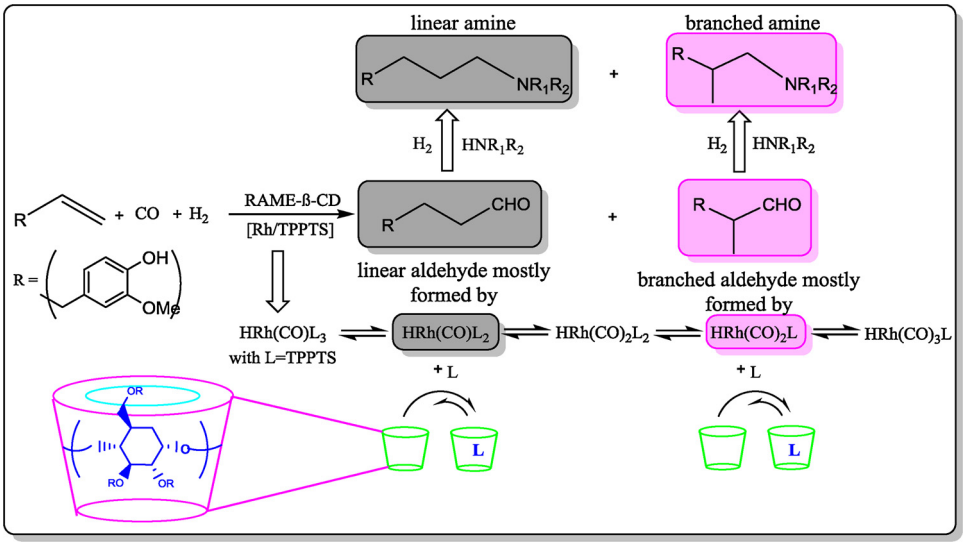
Table 2
An influence of different cyclodextrins (CDs) and its concentration on the aqueous biphasic hydroaminomethylation of eugenol (1a) and piperidine (1a*).[a]



Entry	CDs	Conc. of CDs (mmol)	Conv.* (%)[b]	Total selectivity of amines (%)[b]	Selectivity within amines (**2a**/**3a**/**4a**) (%)[c]	Other products (%)[b]		
						5a	**6a**	**7a**
1[d]	–	–	67	62	12.4/18.6/31	09	09	20
2	α-CD	0.030	82	68	9.52/16.32/42.16	08	10	14
3	α-CD	0.061	84	75	9/16.5/49.5	07	09	09
4	α-CD	0.102	83	70	7/18.2/16.8	08	12	10
5	β-CD	0.026	88	70	7/10.5/52.5	08	12	10
6	β-CD	0.052	92	75	4.5/10.5/60	10	10	05
7	β-CD	0.088	91	72	7.2/12.96/51.84	08	12	08
8	γ-CD	0.025	69	62	6.2/12.4/43.4	14	12	12
9	γ-CD	0.050	79	66	6.6/10.56/48.84	10	14	10
10	γ-CD	0.083	77	68	9.52/12.24/46.24	10	13	09
11	RAME-α-CD	0.028	80	68	14.28/8.16/45.56	09	08	15
12	RAME-α-CD	0.055	85	70	12.6/14/43.4	10	10	10
13	RAME-α-CD	0.090	84	69	10.35/13.8/44.85	11	10	10
14	RAME-β-CD	0.010	94	85	6.8/10.2/68	03	04	08
15	**RAME-β-CD**	**0.020**	**100**	**87**	**3.48/9.57/73.95**	**04**	**03**	**06**
16	RAME-β-CD	0.040	99	86	8.6/9.46/67.94	05	06	03
17	hp-β-CD	0.020	80	85	12.75/17/55.25	03	05	07
18	hp-β-CD	0.040	85	86	9.46/17.2/59.34	03	03	08
19	hp-β-CD	0.068	90	84	15.12/16.8/52.08	03	04	09

[a] **Reaction Conditions**: **1a** (1 mmol), **1a*** (1 mmol), [Rhacac$(CO)_2$] (0.002 mmol), TPPTS (0.008 mmol), CO/H_2 (30 bar), Distilled water (10 mL), 80 °C, 24 h.
[b] Determined by GC and GC–MS.
[c] Percentage ratio of amines by considering total amine as 100%.
[d] Rh/TPPTS/H_2O as catalyst. **CDs** = Cyclodextrins, **RAME** = RAndomly MEthylated, **hp** = hydroxy propyl.
* Conversion on the basis of **1a**, [**5a** = Hydrogenation, **6a** = Isomerization, **7a** = Aldehydes].

selectivity (40.92) towards **4a** and decrease the selectivity of **5a** and **6a** (Table 3, entry 5). Afterwards, we scrutinized 1:3 ratio of $CO:H_2$ for 32 bar, selectivity of expected product (**4a**) decreased to 30.6%, but the selectivity of other products (**5a** + **6a** + **7a**) increased up to 45% (Table 3, entry 6). Thus, 30 bar pressure of $CO:H_2$ with 1:1 ratio was selected as optimum pressure for the hydroaminomethylation reaction of eugenol (**1a**) and it was used for further optimization of various reaction parameters.



Scheme 3. Plausible reaction mechanism for the selective hydroaminomethylation of eugenol using Rh/TPPTS with RAME-*β*-CD as greener and reusable catalytic system.

Table 3
The study of various reaction parameters for an aqueous biphasic hydroaminomethylation of eugenol (1a) and piperidine (1a*).[a]

Entry	Pressure in bar (CO:H_2)	Time (h)	Temp. (°C)	Conv.* (%)[b]	Total selectivity of amines (%)[b]	**2a**/**3a**/**4a** (%)[c]	Other products (%)[b]		
							5a	**6a**	**7a**
Effect of syngas pressure									
1	40 (1:1)	12	80	100	82	13.12/19.68/49.2	03	06	09
2	30 (1:1)	12	80	99	87	8.7/10.44/67.86	03	04	05
3	20 (1:1)	12	80	94	84	11.76/13.44/58.8	03	03	04
4	45 (1:2)	12	80	92	68	9.52/19.04/39.44	14	06	04
5	30 (1:2)	12	80	90	66	7.92/17.16/40.92	10	05	09
6	32 (1:3)	12	80	96	51	7.65/12.75/30.6	20	12	13
Effect of time									
7	30 (1:1)	24	80	100	87	3.48/9.57/73.95	04	03	06
8	30 (1:1)	20	80	99	76	6.08/9.12/60.8	12	06	05
9	30 (1:1)	16	80	99	81	6.48/8.1/66.42	10	04	04
10	30 (1:1)	8	80	92	88	2.64/6.16/79.2	02	01	01
11	30 (1:1)	6	80	90	77	5.39/11.55/60.06	05	03	05
Effect of temperature									
12	30 (1:1)	8	110	100	77	7.7/15.4/59.29	12	06	05
13	30 (1:1)	8	90	99	83	6.64/9.96/66.4	08	03	05
14	30 (1:1)	8	70	89	76	7.6/13.68/54.72	05	05	03
15	30 (1:1)	8	50	72	58	8.7/11.6/37.7	04	08	02

[a] **Reaction Conditions: 1a** (1 mmol), **1a*** (1 mmol), $Rhacac(CO)_2$ (0.002 mmol), TPPTS (0.008 mmol), RAME-β-CD (0.020 mmol), Distilled water (10 mL), 800 rpm.
[b] Confirmed by GC and GC–MS analysis.
[c] Percentage ratio of amines by considering total amine as 100%.
* Conversion on the basis of **1a**, [**5a** = Hydrogenation, **6a** = Isomerization, **7a** = Aldehydes].

Furthermore, we checked the effect of time within the period from 24 h to 6 h (Table 3, entries 7–11). At first, we studied the reaction performance at 24 h by keeping the constant pressure (30 bar) and temperature (80 °C), 100% conversion of **1a** and 73.95% selectivity towards **4a** was observed (Table 3, entry 7). If we reduce reaction time from 24 h to 20 h and again from 20 h to 16 h, then conversion was almost the same but the selectivity towards **4a** slightly decreased from 73.95% to 60.8% and then slightly increase from 60.8% to 66.42% respectively (Table 3, entries 8 and 9). Furthermore, we reduce reaction time to 8 h the results showed high conversion (92%) and high selectivity of total amines (88%) with excellent selectivity (79.2%) towards **4a** within the amines (Table 3, entry 10). The reaction time 6 h was not favourable reaction time to get the best results because it provides the 90% conversion of **1a** with 60.06% selectivity towards **4a** within amines (Table 3, entry 11). Later, we look at the temperature study from 110 °C to 50 °C to optimize the most favourable temperature for an aqueous biphasic hydroaminomethylation of eugenol (**1a**) and piperidine (**1a***) (Table 3, entries 12–15). At the high temperature of 110 °C complete conversion was observed, but the selectivity towards **4a** was slightly reduced to 59.29% and the selectivity of branched amines (**2a** and **3a**) increased up to 23.1% (Table 3, entry 12). By reducing temperature to 90 °C, conversion does not affect but increase in selectivity towards **4a** up to 66.4% (Table 3, entry 13). Best results were obtained at 80 °C of reaction temperature providing 98% conversion of **1a** with 79.2% selectivity of **4a** (Table 3, entry 10). At the temperature of 70 °C, both the conversion (89%) and selectivity of **4a** (54.72%) slightly decreased (Table 3, entry 14). At the end, for 50 °C of reaction temperature, 72% conversion of **1a** and 37.7% selectivity towards **4a** was observed (Table 3, entry 15). Therefore, we keep constant 80 °C as optimum temperature for hydroaminomethylation reaction, it was used for further metallic precursors, loading study, metal-ligand-CD ratio study, substrate study and recyclability study.

Table 4
The study of some metallic precursors on aqueous biphasic hydroaminomethylation (HAM) of eugenol (**1a**) and piperidine (**1a***).[a]

Entry	Metallic precursors	Conc. (mmol)	Conv.* (%)[b]	Selectivity of total Amines (%)[b]	**2a:3a:4a** (%)[c]
1	No catalyst	00	00	00	00:00:00
2	$PdCl_2(PPh_3)_2$	0.035	30	00	00:00:00
3	$Pd(OAc)_2$	0.044	28	00	00:00:00
4	$RuCl_3$	0.048	59	58	5.8/11.6/40.6
5	$Ru_3(CO)_{12}$	0.012	78	62	6.2/11.16/44.64
6	$RhCl_3$	0.020	68	65	9.75/13/42.25
7	$Rh(acac)(CO)_2$	0.001	90	82	4.92/11.48/65.6
8	$Rh(acac)(CO)_2$	0.002	94	85	4.25/8.5/72.25
9	$[Rh(COD)Cl]_2$	0.003	92	87	8.7/9.57/68.73
10	$Rh(COD)_2BF_4$	0.003	87	84	10.08/16.8/57.12
11	$Rh_2(OAc)_4$	0.002	89	89	8.9/16.02/64.08
12[d]	$Co_2(CO)_8$	0.025	52	48	7.68/13.44/26.88
13[e]	$CoCl_2{\cdot}6H_2O$	0.050	49	44	7.04/14.08/22.88

[a]**Reaction Conditions**: **1a** (1 mmol), **1a*** (1 mmol), TPPTS (0.008 mmol), RAME-β-CD (0.02 mmol), CO/H_2 (30 bar), Distilled water (10 mL), 800 rpm, 80 °C, 8 h.
[b]Confirmed by GC and GC–MS analysis.
[d] and [e] 45 bar, 100 °C, 24 h.
[c]Percentage ratio of amines by considering total amine as 100%.
* Conversion on the basis of **1a**.

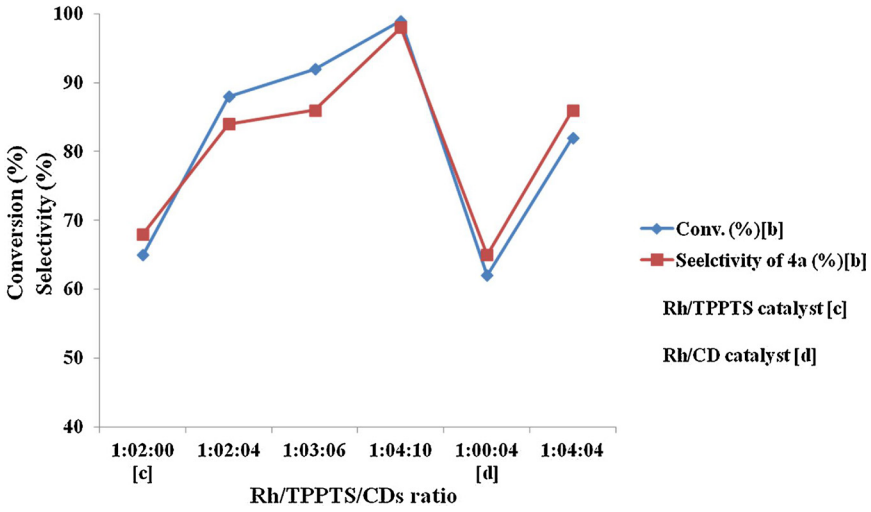


Fig. 1. Rh/TPPTS/CD ratio study for biphasic hydroaminomethylation of eugenol and piperidine.
[a]**Reaction Conditions**: eugenol (1 mmol), piperidine (1 mmol), $Rhacac(CO)_2$ (0.002 mmol), CO/H_2 (30 bar), Distilled Water (10 mL), 80 °C, 8 h. [b]Confirmed by GC and GC–MS analysis. [c]Rh/TPPTS as catalyst. [d]Rh/CDs as a catalyst.

3.4. Effect of metallic precursors and loading for selective hydroaminomethylation of eugenol(1a) and piperidine(1a)*

As expected, no activity was observed in the absence of catalyst confirming that the the catalyst is one and only sensible for the reaction (Table 4, entry 1). The catalyst $PdCl_2(PPh_3)_2$ provided low conversion (30%), for this conversion hydrogenation (18%) and isomerisation (12%) products are obtained (Table 4, entry 2) and the catalyst Pd $(OAc)_2$ provided the low conversion (28%), only hydrogenation (19%) and isomerisation (9%) products were obtained (Table 4, entry 3). Ruthenium metal precursors such as $RuCl_3$ and $Ru_3(CO)_{12}$ gave rise to moderate conversions 59% and 78% with selectivity towards **4a** 40.6% and 44.64%, respectively (Table 4, entries 4 and 5). Rhodium metal precursors led to more active catalysts than other metals for this reaction. The results obtained with some important rhodium precursors such as rhodium (III) chloride [$RhCl_3$], acetylacetonato dicarbonyl rhodium (I) [$Rhacac(CO)_2$]; chloro(1,5-cyclooctadiene)rhodium(I) dimer [$Rh(COD)Cl]_2$; Bis(1,5-cyclooctadiene) rhodium(I) tetrafluoroborate [$Rh(COD)_2$] [BF_4] and rhodium(II) acetate dimer [$Rh_2(OAc)_4$] were presented in Table 4, entries 6–11. From all of above rhodium precursors, $Rhacac(CO)_2$ was found to be most active precursor for hydroaminomethylation of **1a** and **1a***. A high conversion of **1a** up to 94% and better selectivity of **4a** up to 77.25% were obtained (Table 4, entry 8). We also checked the cobalt metal precursors such as dicobalt octacarbonyl [$Co_2(CO)_8$] and cobalt (II) chloride hexahydrate $CoCl_2{\cdot}6H_2O$. Even at high pressure (45 bar), high temperature (100 °C) and long reaction time (24 h), moderate conversion and lower selectivity were observed (Table 4, entries 12 and 13).

3.5. Influence of Rh/TPPTS/CDs ratio on hydroaminomethylation of eugenol(1a) and piperidine(1a)*

Influence of ratio of Rh/TPPTS/CDs as a catalyst on the conversion of **1a** and selectivity of **4a** as shown in Fig. 1. The different ratios were used as 1:2:0, 1:2:4, 1:3:6, 1:4:10, 1:0:4 and 1:4:4 with respect to Rh:TPPTS:CDs for the better conversion and selectivity of **4a**. The Rh/TPPTS was used as catalyst with 1:2 ratio, which afforded moderate 65% conversion and 68% selectivity of linear amine **4a** (Fig. 1). Addition of RAME-*β*-CD to the Rh/TPPTS catalyst the notably increase in the 88% conversion and 84% % selectivity of **4a**. As the 1:3:6 ratio of Rh/TPPTS/RAME-*β*-CD provided 92% conversion and 86% selectivity of **4a** as shown in Fig. 1.

A ratio of Rh/TPPTS/CDs as 1:4:10 was observed to be optimum ratio which furnished high conversion of 99% and excellent selectivity towards **4a** up to 98%. In absence of TPPTS, with 1:4 ratio of Rh/RAME-*β*-CD as a catalyst furnished moderate conversion up to 62%, but selectivity of **4a** fall down to 56%. It was noticed that the catalytic system was in organic phase due to absence of water soluble TPPTS ligand. The catalyst Rh/TPPTS/CDs with 1:4:4 ratio delivered good conversion (82%) of **1a** and 86% selectivity towards **4a**. It was observed from the influence of Rh/TPPTS/CD ratio, the whole catalytic system (Rh/TPPTS/RAME-*β*-CD) with the ratio of 1:4:10 is solely responsible for 99% conversion and excellent selectivity (98%) towards **4a** in an aqueous biphasic hydroaminomethylation of **1a** [Fig. 1].

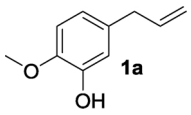
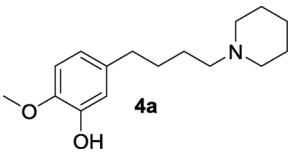
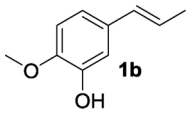
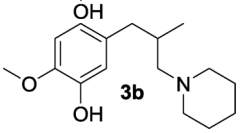
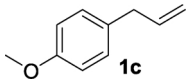
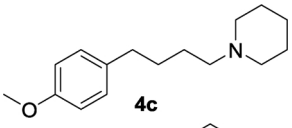
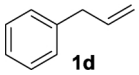
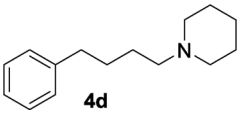
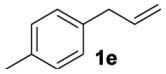
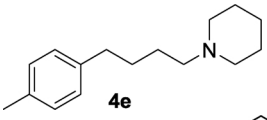
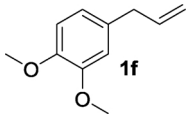
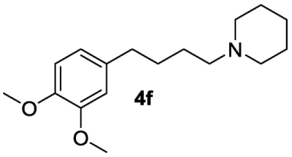
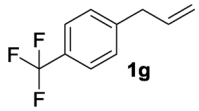
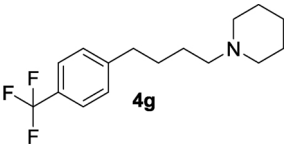
3.6. Substrate-olefins study of hydroaminomethylation of various olefins and piperidine

The standard optimized reaction parameters were applied for the substrate scope. We screened various derivatives of allyl benzenes bearing electron-donating groups (−Me, −OMe), simple allyl benzene and bearing electron withdrawing groups (−OH, $-CF_3$) were reacted with piperidine and smoothly transfered to the expected linear amines. Eugenol (**1a**) provides high selectivity (85%) of total amines with excellent selectivity (72.25%) towards linear amine **4a** (Table 5, entry 1). Anethole (**1b**) as internal olefin also provided 91% conversion along with 81% selectivity of total amines, but 46.98% selectivity was observed towards the branched amine (**3b**) as a chief product (Table 5, entry 2). Estragole (**1c**) containing electron donating −OMe group at para position of allyl benzene, furnished 87% selectivity of total amines with 73.95% selectivity towards the linear amine (**4c**) (Table 5, entry 3). Afterwards, a simple allyl benzene provided 88% selectivity of total amines with 69.52% selectivity towards the linear amine **4d** (Table 5, entry 4). The electron donating groups such as −Me (**1e**) and −OMe (**1f**) also furnished high selectivity of total amines 90% and 84% with higher selectivity 72% towards **4e,** 65.52% towards **4f** respectively (Table 5, entries 5 and 6). At last, allyl benzene containing electron withdrawing group ($-CF_3$) delivered 76% selectivity of total amines with faintly lower selectivity (51.68%) towards linear amine **4g** (Table 5, entry 7).

3.7. Substrate-amines study for selective hydroaminomethylation of eugenol under aqueous biphasic catalysis

We investigated the reactivity of various primary and secondary amines using eugenol as substrate for the hydroaminomethylation reaction under aqueous biphasic condition as shown in Table 6. Initially, we used cyclohexyl amine ($\mathbf{A_1}$), 76% selectivity of total amines with 53.2% selectivity of linear amine $\mathbf{4A_1}$ was achieved (Table 6, entry 1). The reaction of cyclopentyl amine ($\mathbf{A_2}$) reacted with eugenol (**1a**) resulted into 66.4% selectivity of $\mathbf{4A_2}$ was achieved (Table 6, entry 2). Dicyclohexyl amine ($\mathbf{A_3}$) also furnished good selectivity of total amines

Table 5
Substrates-olefins study for aqueous biphasic hydroaminomethylation of natural olefins with piperidine (**1a***).[a]

Entry	Substrates (Olefins)	Major Product (**4a–4g**)	Conv.* (%)[b]	Selectivity of total amine (%)[b]	**2a–2g/3a–3g/4a–4g** (%)[c]
1	 **1a**	 **4a**	92	88	2.64/6.16/79.2
2[d]	 **1b**	 **3b**	91	81	22.68/46.98/11.34
3	 **1c**	 **4c**	96	87	5.22/7.83/73.95
4	 **1d**	 **4d**	98	88	8.8/9.68/69.52
5	 **1e**	 **4e**	98	90	7.2/10.8/72
6	 **1f**	 **4f**	90	84	8.4/10.08/65.52
7	 **1g**	 **4g**	86	76	9.12/15.2/51.68

[a] **Reaction Conditions**: Olefin (1 mmol), **1a*** (1 mmol), $Rhacac(CO)_2$ (0.002 mmol), TPPTS (0.008 mmol), RAME-β-CD (0.02 mmol), CO/H_2 (30 bar), Distilled water (10 mL), 80 °C, 8 h.
[b] Confirmed by GC and GC–MS analysis.
[c] Percentage ratio of amines by considering as total amine as 100%.
[d] 90 °C, 12 h, 40 bar.
* Conversion on the basis of **1a–1g**.

and better selectivity of $\mathbf{4A_3}$ (Table 6, entry 3). Higher selectivity of total amines and excellent selectivity of $\mathbf{4A_4}$ and $\mathbf{4A_5}$ were achieved with cyclic secondary amines like piperidine ($\mathbf{A_4}$) and morpholine ($\mathbf{A_5}$) respectively (Table 6, entries 4 and 5). Acyclic aliphatic amines such as di-*iso*-propylamine ($\mathbf{A_6}$), diallylamine ($\mathbf{A_7}$) and diethylamine ($\mathbf{A_8}$) also undergoes this transformation easily with high selectivity of linear amines ($\mathbf{4A_6}$, $\mathbf{4A_7}$ and $\mathbf{4A_8}$) (Table 6, entries 6–8). In case of diallyl amine ($\mathbf{A_7}$) the product was obtained with increase in molecular weight by 4 than the expected product. This was observed due to the reduction of both double bonds present in diallyl amine (Table 6, entry 8). The reaction was not proceed in case of substrates like aq. NH_3 and aq. methyl amine.

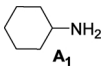
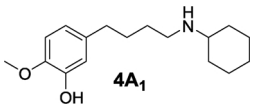
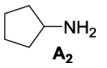
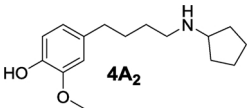
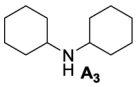
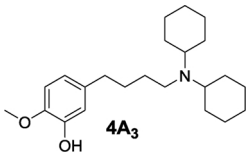
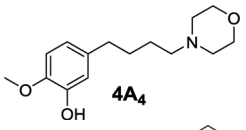
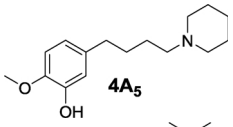
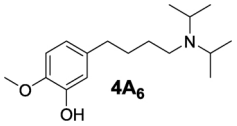
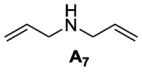
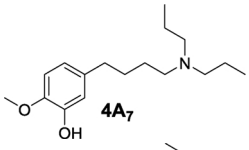
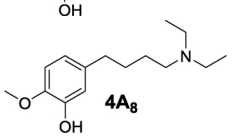
4. Catalyst reusability

The reusability of Rh/TPPTS/CDs catalyst is a significant feature to ensure the efficiency of catalytic system. We checked the reusability of Rh/TPPTS/CDs catalyst for an aqueous biphasic hydroaminomethylation of naturally occurring olefins such as eugenol, anethole and estragole. The experiments of recovery of catalysts was performed under the inert condition using nitrogen atmosphere. The catalytic system was found to be reused for five consecutive cycles with an excellent catalytic activity and selectivity towards the formation of desired product **4a** (Fig. 2). The leaching of rhodium metal was investigated after the 1st and 5th recycle run by ICP-AES analysis and observed below detected level (≈0.1 ppm) of rhodium in solution which revealed that negligible leaching of rhodium metal into the solution.

5. Conclusion

In summary, we report a novel strategy for selective hydroaminomethylation of biomass derived eugenol, anethole and estragole. We have described the effect of various cyclodextrins for the aqueous biphasic hydroaminomethylation of natural olefins using Rh/TPPTS/CDs as an efficient, recyclable and greener protocol. The various cyclodextrins such as α-CD, *β*-CD, γ-CD, RAME-α-CD, RAME-*β*-CD and hp-*β*-CD were efficiently screened for aqueous biphasic hydroaminomethylation of eugenol. A RAME-*β*-CD from other cyclodextrins provided the greatest conversion and selectivity towards the linear amines. Due to hydrophobic internal cavity of RAME-*β*-CD, the benzene ring may be directed towards fixation into the cavity of cyclodextrin. The terminal double bond of allyl group remains at outerside of cavity may makes the favourable path for the linear amines as major product instead of isomerisation and branched amines. The natural olefins like

Table 6
Substrates-amines study for aqueous biphasic hydroaminomethylation of eugenol (**1a**).[a]

Entry	Substrates (Amines)	Major Product ($4A_1$–$4A_8$)	Conv.* (%)[b]	Selectivity of total amine (%)[b]	$2A_1$–$2A_8$:$3A_1$–$3A_8$:$4A_1$–$4A_8$ (%)[c]
1	 A_1	 $4A_1$	92	76	9.12/13.68/53.2
2	 A_2	 $4A_2$	87	80	7.2/6.4/66.4
3	 A_3	 $4A_3$	86	78	6.24/9.36/62.4
4	 A_4	 $4A_4$	92	88	2.64/6.16/79.2
5	 A_5	 $4A_5$	94	86	5.16/8.6/72.24
6	 A_6	 $4A_6$	90	81	6.48/8.1/66.42
7	 A_7	 $4A_7$	92	82	11.48/11.48/59.04
8	 A_8	 $4A_8$	89	83	8.3/8.3/66.4

[a] **Reaction Conditions**: **1a** (1 mmol), amine (1 mmol), $Rhacac(CO)_2$ (0.002 mmol), TPPTS (0.008 mmol), RAME-β-CD (0.02 mmol), CO/H_2 (30 bar), Distilled water (10 mL), 80 °C, 8 h.
[b] Confirmed by GC and GC–MS analysis.
[c] Percentage ratio of amines by considering total amine as 100%.
* Conversion on the basis of **1a**.

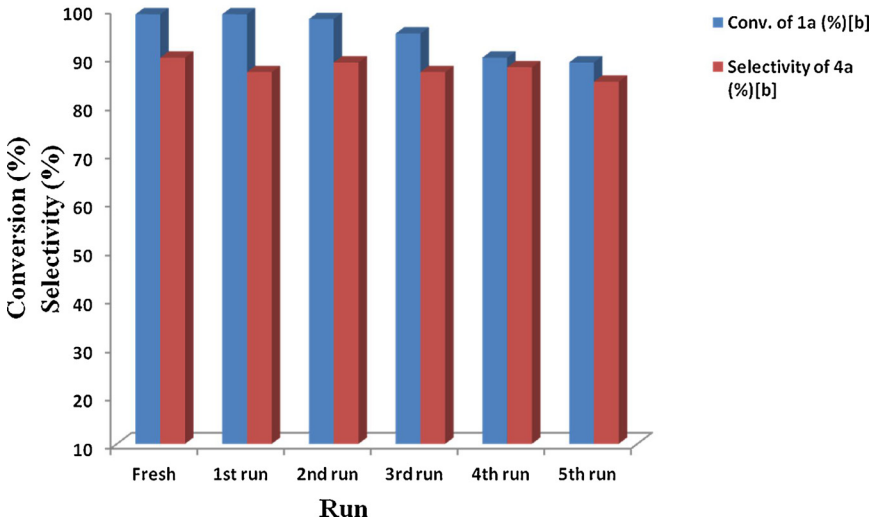


Fig. 2. Recyclability study of biphasic selective hydroaminomethylation of eugenol and piperidine [a].
[a]**Reaction Conditions**: eugenol (1 mmol), piperidine (1 mmol), $Rhacac(CO)_2$ (0.002 mmol), TPPTS (0.008 mmol), RAME-β-CD (0.020 mmol), CO/H_2 (30 bar), Distilled Water (10 mL), 800 rpm. [b]Confirmed by GC and GC–MS analysis.

eugenol, anethole and estragole were smoothly converted selectively to the linear amines with moderate to excellent yields. The derivatives of eugenol containing various electron withdrawing and donating groups were also be capably employed in hydroaminomethylation reaction providing greater selectivity towards linear amines as major products. This protocol furnished a simple and easy access for linear amines which will be very profitable in agrochemical and pharmaceutical industry. Also, the catalyst is recycled up to five consecutive cycles with an excellent catalytic activity and selectivity towards linear amines.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2018.04.005.

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