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FULL PAPER

Heteropoly acid catalysts for the synthesis of fragrance compounds from bio-renewables: acetylation of nopol and terpenic alcohols

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Abstract. Cesium salt of tungstophosphoric heteropoly acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, is an active and environmentally friendly heterogeneous catalyst for the liquid-phase acetylation of nopol and several biomass-derived terpenic alcohols (i.e., α-terpineol, nerol, geraniol, linalool, menthol, isoborneol, perillyl alcohol, carveol, isopulegol, carvacrol and nerolidol) with acetic anhydride. The resulting flavor and fragrance acetic esters, which are widely used in perfumery, household and food products, are obtained in good to excellent yields. The reactions occur at room temperature with low catalyst loadings without substantial catalyst leaching and can be performed with stoichiometric amounts of acetylating agent in solvent free systems.

Keywords: Acetylation; Acid catalysis; Biomass-based feedstock; Polyoxometalates; Terpenes

Introduction

Terpenic esters are widely used as ingredients and raw materials in flavor and fragrance industry.[1–4] Although many of these compounds are natural products found in essential oil of various plants, their high commercial demand often is not satisfied by natural sources. For this reason, various commercial terpenic esters are produced synthetically from more abundant natural precursors, e.g., terpenic alcohols.[4] Terpenic alcohols themselves have many direct industrial applications as fragrance and flavor ingredients; however, their esters often posses olfactory or other characteristics that are more important for practical purposes. For example, linalool and geraniol are among the most important components in flavor and fragrance industries. These monoterpenic alcohols are commonly used in non-food applications, whereas linalyl acetate and geranyl acetate are particularly appreciated as food additives due to low toxicity, high stability and special flavors.[5,6]

Terpenic acetates can be produced by acid-catalyzed esterification of alcohols with acetic acid, alkyl acetates or acetic anhydride.[4] A number of acidic catalysts, such as $CoCl_2$,[7] zeolites,[8] trimethylsilyl trifluoromethanesulfonate,[9] $Ce(OTf)_3$[10] and $NbCl_5$[11] have been reported for the acetylation of terpenic alcohols. A valuable alternative for these reactions could be heteropoly acids (HPAs), which are well known as environmentally attractive acid catalysts for the synthesis of special chemicals.[12-15] Due to their strong acidity, the HPAs of the Keggin series are usually more active than conventional acid catalysts, such as mineral acids and zeolites, and therefore can be used in low concentrations thus avoiding waste problems.

It is important for the development of heterogeneous processes in polar media, where HPAs are readily soluble, that HPAs can be substituted by their insoluble acidic salts. In particular, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ possessing strong Brønsted acidity, large surface area and high water tolerance has been widely used as a solid acid catalyst in various heterogeneous processes, including those in aqueous and other polar media.[16-21] The use of water-soluble cobalt, aluminum or ammonium salts of HPAs as catalysts has been previously reported for the acetylation of monoterpenic alcohols such as menthol[22-25] and geraniol.[26]

Nopol acetate is also a fragrant and flavor compound with a fresh-fruity-woody odor widely used in cosmetics, shampoos, soaps, household and food products such as bakery, soft and alcoholic drinks, ice creams and candies. Nopol acetate is produced by the acetylation of nopol, which is synthesized by Prins condensation of paraformaldehyde with β-pinene, one of the most widespread terpenic hydrocarbons available from turpentine oils.[4,27,28]

Within our program aimed at adding value to natural ingredients of essential oils, we report now the application of tungstophosphoric heteropoly acid

1

$H_3PW_{12}O_{40}$ (HPW) and its acidic Cs salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) for the acetylation of nopol and a series of terpenic alcohols, i.e., geraniol, nerol, perillyl alcohol, carveol, isopulegol, menthol, isoborneol, carvacrol, α-terpineol, linalool, and nerolidol. The acetates obtained in these reactions have many applications in cosmetics, perfumes and pharmaceutical formulations and also as food additives. To our knowledge, no attempt to use CsPW as the catalyst for the esterification of terpenic alcohols has been made so far.

Results and Discussion

The results on the acetylation of nopol (**1a**, Scheme 1) with acetic acid and acetic anhydride catalyzed by CsPW and HPW in various solvents are presented in Table 1. All the reactions were performed at room temperature under air. With CsPW in dichloroethane solution at an acetic acid/nopol molar ratio of 3:1, a 50% conversion of nopol was observed in 1 h with the formation of several unidentified products, but no trace of nopyl acetate (Table 1, run 1). The use of acetic anhydride as the acetylating agent was more efficient: the desired nopyl acetate was obtained in 52% selectivity at a complete nopol conversion (Table 1, run 2). In addition, acetic anhydride can enhance the reaction by removing the by-product

water: $Ac_2O + H_2O \rightarrow 2\ HOAc$. Attempts to improve the reaction selectivity by decreasing the CsPW catalyst amount gave no better results (Table 1, run 3). On the other hand, increasing the concentration of acetic anhydride allowed the efficient transformation of nopol to nopyl acetate with 90% selectivity at a nearly complete nopol conversion (Table 1, run 4 vs. run 3). In a blank reaction without catalyst added, the conversion of nopol was negligible under similar conditions (Table 1, run 5).
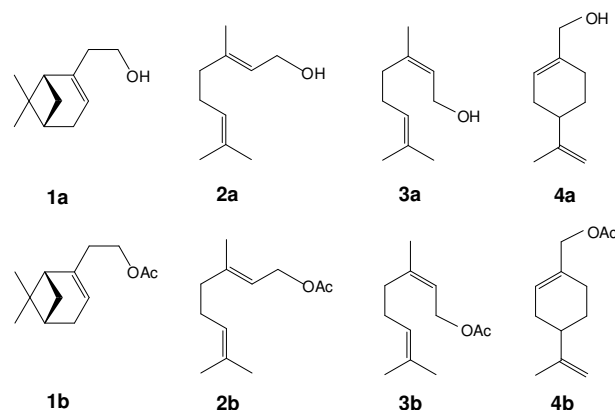
Scheme 1. Structures of alcoholic substrates **1a**–**4a** and corresponding products **1b**–**4b**.

Table 1. Acetylation of nopol (**1a**) catalyzed by CsPW and HPW[a]

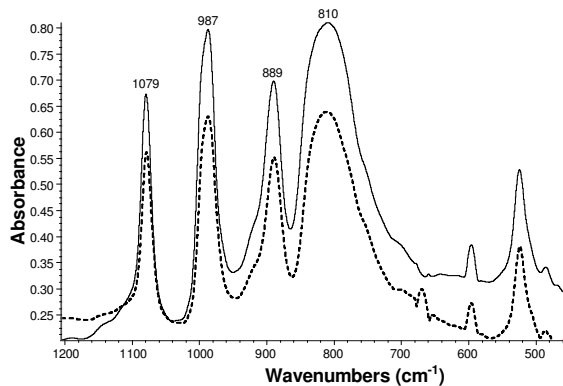| Run	Solvent	Catalyst (µmol)	HOAc (mmol)	Ac$_2$O (mmol)	Time (h)	Conversion (%)	Selectivity for **1b** (%)	TON[b]
1	dichloroethane	CsPW (9.0)	2.25	none	1.0	50	<1	42
2	dichloroethane	CsPW (9.0)	none	2.25	1.0	100	52	83
3	dichloroethane	CsPW (4.5)	none	2.25	1.0	100	51	170
4	dichloroethane	CsPW (4.5)	none	6.00	1.5	95	90	160
5	dichloroethane	none	none	2.25	1.5	2	-	-
6	acetic acid	none	solvent	none	4.0	5	-	-
7	acetic acid	CsPW (3.0)	solvent	none	4.0	72	8	180
8	acetic acid	CsPW (9.0)	solvent	none	4.0	100	6	83
9	acetic acid	HPW (1.5)	solvent	none	1.0	86	-	430
10	acetic anhydride	HPW (1.5)	none	solvent	0.25	100	100	500
11	acetic anhydride	CsPW (4.5)	none	solvent	0.25	100	100	170
12	acetic anhydride	none	none	solvent	1.0	9	25	-
13[c]	acetic anhydride	supernatant	none	solvent	1.0	9	27	-
14	acetic acid	CsPW (4.5)	solvent	4.00	1.5	95	60	160
15	acetic acid	CsPW (4.5)	solvent	6.00	1.5	100	100	170
16[d]	acetic acid	CsPW (4.5)	solvent	6.00	4.0	90	94	700

[a] Conditions: nopol (0.15M; 0.75 mmol), solvent (5 mL), room temperature; conversion and selectivity were determined by GC. [b] TON in moles of nopol converted per mole of CsPW or HPW. [c] After run 11, the catalyst was removed, the solution was recharged with fresh substrate (0.75 mmol) and the reaction was allowed to proceed further. [d] Nopol - 3.5 mmol (0.7 M).

Further study was directed to substitute dichloroethane for greener solvents. In the absence of acid catalysts, nopol was stable in acetic acid solutions, whereas both solid CsPW and dissolved HPW promoted a relatively fast nopol conversion

(Table 1, runs 6–9). However, these reactions were unselective towards the desired nopyl acetate. On the other hand, in neat acetic anhydride containing only 0.2 mol% of dissolved HPW or 0.6 mol% of solid CsPW, nopol was converted into nopyl acetate in a

2

virtually quantitative yield, with both reactions being complete within 15 min at room temperature (Table 1, runs 10 and 11). In the absence of the catalyst, only 9% of nopol was consumed in 1 h, and the selectivity to nopyl acetate was only 25% (Table 1, run 12 vs. runs 10 and 11).

Although CsPW is insoluble in acetic acid and acetic anhydride, the possible contribution of homogeneous catalysis has been checked by special experiments: after run 11, the CsPW catalyst was removed by centrifugation, the solution was recharged with fresh substrate (0.75 mmol) and the reaction was allowed to proceed further. The results obtained were compatible with those of the blank reaction: 9% conversion of nopol in 1 h with 24% selectivity to nopyl acetate (Table 1, run 13 vs. run 12). Moreover, the UV spectrum of the supernatant (Fig S1) obtained by the centrifugation of CsPW from the CsPW/Ac$_2$O mixture similar to that used in run 11 exhibited a weak absorption band near 285 nm characteristic of the Keggin-type PW$_{12}$O$_{40}$$^{3-}$ ions,[17] which corresponded to less than 2% leaching of CsPW. The results show that the reaction occurs essentially by heterogeneous catalysis, and homogeneous catalysis does not play significant role in our system. The characterization of fresh versus spent catalysts did not reveal any significant change in the catalyst texture, nor did it show any structural alteration of CsPW, as expected for such mild reaction conditions. Both fresh and spent CsPW catalyst samples exhibited the well-known FTIR spectrum with strong bands of stretching vibrations at 1079 (P-O), 987 (terminal W=O group), 889 and 810 cm^{-1} (edge- and corner-sharing W-O-W groups) characteristic of the Keggin structure[29] (Fig. 1).


**Figure 1.** FTIR spectra of the CsPW catalyst: fresh (solid line) and spent (dash).

The process can also be performed in solutions of acetic acid, which is cheaper than acetic anhydride; however, the presence of acetic anhydride in over-stoiquiometric amounts with respect to nopol was required to ensure high selectivity for nopyl acetate (Table 1, runs 14–16). Thus, in run 16 with 1.7 equivalent of acetic anhydride, the reaction reached 90% conversion in 4 h to give nopyl acetate in 94%

selectivity. These results correspond to a turnover number (TON) of 700 per mol of the total amount of CsPW. Considering that a part of acid sites may be located in the bulk of the CsPW phase and hence not accessible to the substrate the real efficiency of the surface active sites could be even higher. The density of surface proton sites in CsPW can be estimated from the cross-sectional area of the PW$_{12}$O$_{40}$$^{3-}$ anion (144 Å^2) and the surface area of CsPW (111 m^{2}g^{-1}, Experimental Section).[30] This gives a proton site density of 6.5 $\times$ 10^{-5}mol(H$^+$)/g(CsPW) or 0.21 mol(H$^+$)/mol(CsPW) and a TON value of 3300 per surface proton site of CsPW.

In further studies, we applied this procedure for the acetylation of natural terpenic alcohols aiming to obtain terpenic acetates, valuable ingredients in the flavor and fragrance industry. The structures of substrates and the corresponding acetates are presented in Schemes 1, 2 and 3. The reactions were performed at room temperature in acetic anhydride with 0.2–0.6 mol% of solid CsPW as the catalyst. With most alcohols, the reaction conditions were varied to achieve better yields of esters. The results are presented in Table 2.
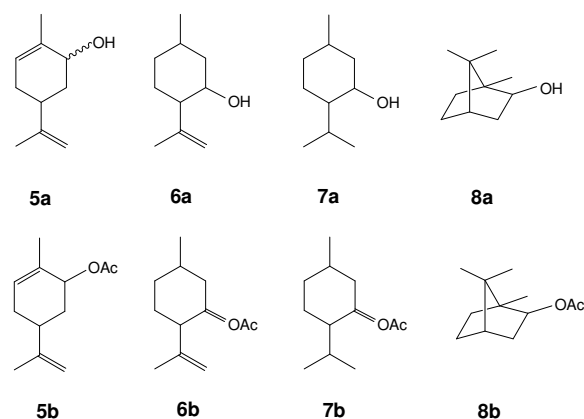
Scheme 2. Structures of alcoholic substrates **5a**–**8a** and corresponding products **5b**–**8b**.
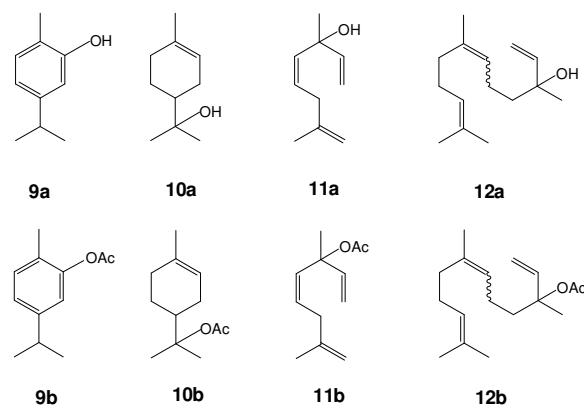
Scheme 3. Structures of alcoholic substrates **9a**–**12a** and corresponding products **9b**–**12b**.

Table 2. Acetylation of terpenic alcohols with Ac_2O catalyzed by CsPW[a]

Run	Substrate	Substrate (mmol)	Time (h)	Conversion (%)	Product	Selectivity (%)	TON[b]
1	geraniol (**2a**)	0.75	0.5	91	**2b**	100	
			1.0	100		100	170
2	nerol (**3a**)	0.75	0.5	100	**3b**	98	170
3	perillyl alcohol (**4a**)	0.75	0.25	100	**4b**	100	170
4	perillyl alcohol (**4a**)	2.25	0.5	100	**4b**	100	500
5	carveol (**5a**)	2.25	0.5	90	**5b**	100	
			1.0	100		100	500
6	isopulegol (**6a**)	2.25	0.5	35	**6b**	100	
			4.0	100		100	500
7	menthol (**7a**)	2.25	0.5	100	**7b**	100	500
8	isoborneol (**8a**)	2.25	0.5	100	**8b**	100	500
9	carvacrol (**9a**)	2.25	0.5	100	**9b**	100	500
10	α-terpineol (**10a**)	0.75	0.5	100	**10b**	90	170
11[c]	linalool (**11 a**)	0.75	0.5	60	**11b**	56	
			5.0	90		57	295
12	nerolidol (**12a**)	2.25	0.5	24	**12b**	60	300
			4.0	60		65	

[a] Conditions: CsPW (4.5 μmol), acetic anhydride (5 mL), room temperature; conversion and selectivity were determined by GC. [b] TON in moles of nopol converted per mole of CsPW. [c] CsPW - 2.3 μmol, among the products were detected **10b** (10%) and **2b** (4%).

Geraniol (**2a**) and nerol (**3a**), monoterpenic primary allylic alcohols available from many essential oils such as geranium, neroli and rose oils, were rapidly and almost quantitatively transformed into the corresponding acetates (Table 2, runs 1 and 2). Geranyl acetate (**2b**) and neryl acetate (**3b**) are important aroma compounds with sweet fruity-flowery odors widely used in perfumery, cosmetics and food industry.[4,6]

The acetylation of another monoterpenic primary allylic alcohol, perillyl alcohol (**4a**), also occurred smoothly to give perillyl acetate (**4b**) in excellent yields. Perillyl acetate is a fragrant compound with a spicy herbal odor suggestive of spearmint used in perfume and flavor compositions, e.g., in spice and condiment flavor blends[31] (Table 2, runs 3 and 4).

Monoterpenic secondary alcohols carveol (**5a**), isopulegol (**6a**) and menthol (**7a**), all natural compounds having a *p*-menthane skeleton, can be found in various essential oils like peppermint and cornmint oils.[3,4] Isopulegol and menthol are produced industrially on a large scale from myrcene or thymol.[4] The acetylation of these alcohols with acetic anhydride in the presence of only 0.2 mol% of CsPW resulted in the corresponding acetates in practically quantitative yields (Table 2, runs 5, 6 and 7). Acetates **5b**, **6b** and **7b** are also fragrant compounds with many applications in household perfumery and essential oil compositions; menthyl acetate, in particular, is used in peppermint flavours.[4]

Isobornyl acetate (**8b**) was obtained in a virtually quantitative yield from isoborneol (**8a**), also a secondary monoterpenic alcohol (Table 2, run 8). Most of the reactions presented in Table 2 show high TONs (up to 500) illustrating high stability of the CsPW catalyst. Isobornyl acetate has a pleasant, pine-needle odor and is largely used for perfuming soaps, bath products and air fresheners.[4] It is noteworthy that no trace of borneol acetate, the *endo*-isomer of **8b**, was observed, which indicates high reaction stereoselectivity.

Our procedure was also successfully applied to tertiary terpenic achohols. Carvacrol (**9a**) and α-terpineol (**10a**), natural monoterpenic alcohols with a *p*-menthane skeleton, rapidly reacted with acetic anhydride in the presence of CsPW to give the corresponding acetates with excellent selectivities (Table 2, runs 9 and 10). α-Terpenyl acetate **10b** is largely used in perfumery for lavender and bergamot compositions due to its fresh specific odor, stability and low price.[4]

The esterification of tertialy allylic alcohols, linalool (**11a**) and nerolidol (**12a**), was more difficult due to their isomerization under the reaction conditions (Table 2, runs 11 and 12). Linalool is found in the essential oils of several plants, such as Brazilian rosewood and Chinese Ho leaf oils, and also produced industrially from α-pinene. Linalool is a key building block for the synthesis of various vitamins and fragrances, in particular, linalyl acetate, which is extensively used in food applications, differently from linalool itself.[5] Nerolidol is also available from essential oils of various plants and flowers, which may contain up to 50–90% of this sesquiterpenoid with

a delicate sweet floral and woody odor. The use of nerolidol can be significantly extended by its esterification. The reactions of linalool and nerolidol with acetic anhydride in the presence of CsPW presented in Table 2 (runs 11 and 12) gave acetates **11b** and **12b** with nearly 60% selectivities; however, the reaction conditions have not been fully optimized yet. Several isomeric acetates, such as α-terpenyl acetate **10b** and geranyl acetate **2b** in the case of linalool, were also detected in significant amounts.
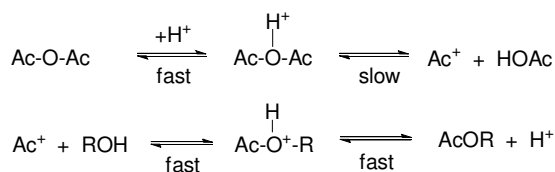
Table 3. Acetylation of terpenic alcohols with Ac$_2$O catalyzed by CsPW[a]

Run	Substrate	Substrate (mmol)	Ac$_2$O (mmol)	Time (h)	Conversion (%)	Selectivity for ester (%)
1	nopol (**1a**)	10	10	1.0	100	100 (**1b**)
2	geraniol (**2a**)	10	10	1.5	100	96 (**2b**)
3	carvacrol (**9a**)	10	10	1.0	100	100 (**9b**)
4	α-terpineol (**10a**)	10	10	1.5	98	90 (**10b**)
5	menthol (**7a**)	10	50	1.0	100	100 (**7b**)
6	isoborneol (**8a**)	10	50	1.5	100	100 (**8b**)

[a] Catalyst: CsPW (10 µmol), room temperature; conversion and selectivity were determined by GC.

The acetylation of alcohols can also be performed under solvent-free conditions using near-stoichiometric amounts of acetic anhydride and only 0.1 mol% of CsPW catalyst with excellent yields of desired acetates. Representative examples are shown in Table 3. The reactions of nopol, geraniol, carvacrol and α-terpineol proceeded selectively with 1 equivalent of acetic anhydride and were complete at room temperature in 1–1.5 h (runs 1–4). In the case of menthol and isoborneol, larger amounts of acetic anhydride (5 equivalents) were required to dissolve the alcohols, which are solid under ambient conditions, to give menthyl and isobornyl acetate in excellent yields (runs 5 and 6).

The mechanism of acid-catalyzed alcohol acetylation with acetic anhydride can be represented by Scheme 4.[32] It involves protonation of acetic anhydride followed by formation of the acetyl cation, which attacks an alcohol molecule to give the ester after proton elimination. Acetic acid present in the system may also act as an acetylating agent, but appears to be much less efficient than the acetic anhydride (Table 1).

heterogeneous catalyst for the liquid-phase acetylation of nopol and several renewable biomass-based terpenic alcohols with acetic anhydride. In most cases, the acetylations are not complicated by oligomerization and isomerization, as often happens with terpenic compounds under acidic conditions. These reactions occur at room temperature with low catalyst loadings and can be performed solvent-free with stoichiometric amounts of acetic anhydride providing excellent yields of flavor and fragrance acetic acid esters, which have many applications in cosmetic, perfume, pharmaceutical, household and food products.

Experimental Section

Scheme 4. Mechanistic scheme of the acetylation of alcohols with acetic anhydride.

Conclusion

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$, easily prepared from the commercial tungstophosphoric heteropoly acid, is a highly active and environmentally friendly

thus confirming the identity of the HPW and CsPW catalyst samples used. UV spectra were recorded on a UV-VIS spectrophotometer Shimadzu UV-2600.

The acidic heteropoly salt CsPW was prepared according to the method described previously[33] by adding dropwise the required amount of the aqueous solution of cesium carbonate (0.47 M) to the aqueous solution of HPW (0.75 M) with stirring at room temperature. The precipitate obtained was aged in an aqueous mixture for 48 h at room temperature and dried in a rotary evaporator at 45 °C/3 kPa and after that in an oven at 150 °C/0.1 kPa for 1.5 h. CsPW had a surface area of 111 m^2g^{-1}, pore volume of 0.07 cm^3g^{-1}, and pore diameter of 24 Å. The acid strength of CsPW was characterized calorimetrically using ammonia and pyridine adsorption; its proton sites were found somewhat weaker than those in the bulk HPW but stronger than in zeolites.[29]

The reactions were carried out in a 10 mL glass reactor equipped with a magnetic stirrer and a condenser. In a typical run, a mixture (3.0–5.0 mL) of the substrate (0.75–10.0 mmol), dodecane or undecane (0.5–1.0 mmol GC internal standards) and the catalyst (HPW (5 mg, 1.5 µmol) or CsPW (10–30 mg, 3.0–10.0 µmol), acetic anhydride or acetic acid and a solvent (if any) was intensely stirred under air at room temperature. The reactions were followed by gas chromatography (GC) using a Shimadzu 17 instrument fitted with a Carbowax 20 M capillary column and a flame ionization detector. After an appropriate reaction time, the stirring was stopped and after quick catalyst settling down aliquots were taken and analyzed by CG. The mass balance and the product selectivity and yield were determined using dodecane or undecane as internal standards. Any difference in the mass balance was attributed to the formation of oligomers, which were unobservable by GC. The products were identified by GC-MS by comparison with authentic compounds. Mass spectra were obtained on a Shimadzu QP2010-PLUS instrument operating at 70 eV.

In order to control catalyst leaching and the possibility of a homogeneous reaction, the CsPW catalyst was removed from the reaction mixture by centrifugation then a fresh portion of substrate was added to the supernatant and the reaction was allowed to proceed.

Acknowledgements

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FULL PAPER

Heteropoly acid catalysts for the synthesis of
fragrance compounds from bio-renewables:
acetylation of nopol and terpenic alcohols

RSC Advances **Year**, *Volume*, Page – Page

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8