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Heteropoly Acid Catalysts for the Synthesis of Fragrance Compounds from Biorenewables: The Alkoxylation of Monoterpenes

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The cesium salt of tungstophosphoric heteropoly acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40'}$ is an active and environmentally friendly solidacid catalyst for the liquid-phase alkoxylation of widespread monoterpenes, such as camphene, limonene, α -pinene, and β pinene. These reactions provide isobornyl or α -terpenyl ethers, useful as fragrances, in good to excellent yields. The reactions

Introduction

Monoterpenes are an abundant renewable feedstock for the pharmaceutical and flavor and fragrance industries.^[1–4] Major terpene sources are essential oils, natural resins, and byproducts of the pulp, paper, and citrus juice industries. The most widespread terpene hydrocarbons, considered as platform molecules in terpene chemistry,^[5] are limonene, α -pinene, and β -pinene. Limonene is extracted from citrus oils, whereas α and β -pinene are the main constituents of turpentine oils obtained from coniferous trees. The content of α -pinene can reach 85%, which depends on the oil source. Camphene is also available in nature from the essential oils of some plants but it is synthesized mostly from α -pinene in the liquid phase over acidic catalysts. Various useful terpenoid compounds are produced commercially by acid-catalyzed transformations of more abundant terpene precursors. Mineral acids are still used as catalysts in many of these processes, which generates a large amount of waste. The development of more efficient and environmentally friendly acid catalysts for the conversion of terpenes can contribute significantly to the valorization of biorenewable essential oils.

Heteropoly acids of the Keggin series (HPAs) are well known as promising acid catalysts for the green synthesis of many

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are equilibrium-controlled and occur with high catalyst turnover numbers (TONs) up to 1500–4200 without catalyst leaching. Heteropoly acid $H_3PW_{12}O_{40}$ also efficiently catalyzes the alkoxylation of these monoterpenes under homogeneous conditions with TONs up to 1500–11 300.

fine and specialty chemicals.^[6-8] As a result of their stronger acidity, HPAs usually show higher catalytic activities than conventional acid catalysts, such as mineral acids, zeolites, and ion-exchange resins, and cause less corrosion problems than mineral acids. HPAs are insoluble in nonpolar solvents and can be used as heterogeneous catalysts in such solvents. To create heterogeneous catalytic processes in polar media, in which HPAs are highly soluble, they can be substituted by their insoluble acidic salts. In particular, the Cs salt, Cs₂₅H₀₅PW₁₂O₄₀, which has strong Brønsted acid sites and a large surface area, has been used in a number of liquid-phase organic reactions as an efficient solid-acid catalyst.^[9-14] Previously, we have employed HPA catalysts for a variety of liquid-phase reactions of terpenic compounds, such as isomerization,^[13,15-18] hydration, and esterification,^[19-22] which includes the hydration and esterification of camphene, limonene, α -pinene, and β pinene.[19-21]

Through the acid-catalyzed addition of alcohols, camphene can be converted to isobornyl ethers, whereas limonene, α pinene, and β -pinene are converted to α -terpenyl ethers. These products possess strong characteristic woody or fruitberry aromas almost identical to the natural ones and have many applications in cosmetics, perfumes, and pharmaceutical formulations. Isobornyl ethers are also used for the production of synthetic camphor, the compound with more commercial applications than any other terpene.^[1] A number of solid-acid catalysts, such as zeolites,^[23-28] modified clay materials,^[29] sulfonated mesoporous silica,^[30] and poly(vinyl alcohol) with sulfonic acid groups,^[31] have been used for the alkoxylation of camphene, limonene, α -pinene, and β -pinene. Previously, HPAs have been reported as homogeneous catalysts for the alkoxylation of camphene.^[32] In addition, silica-occluded HPAs prepared by a sol-gel method have been reported as heterogeneous catalysts for the alkoxylation of camphene^[33] and α pinene.^[34] Silica-occluded HPAs are stable towards leaching in

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alcohol media. However, the reaction procedures are lengthy and require a high catalyst-to-substrate ratio.^[33,34] Therefore, the development of economically attractive and green catalysts for these reactions remains a challenge.

Within our program aimed to add value to the natural ingredients of essential oils, we report the application of tungstophosphoric heteropoly acid $H_3PW_{12}O_{40}$ (HPW) and its acidic Cs salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) for the alkoxylation of camphene, limonene, α -pinene, and β -pinene.

Results and Discussion

The results of the alkoxylation of camphene (1a) by butan-1ol, ethanol, and methanol in the presence of HPW are presented in Table 1. The reactions occurred with 96–99% selectivity to the corresponding isobornyl ethers 1b, 1c, and 1d with only small amounts of isoborneol observed (Scheme 1). The reactions were not complicated by oligomerization and isomerization as often happens with terpenic compounds under acidic conditions. Blank reactions, without any catalyst added, showed virtually no conversion of camphene under the conditions used. The alkoxylation occurred with a remarkably high stereoselectivity without the formation of any borneol ethers, that is, *endo* isomers of 1b, 1c, and 1d.

The products **1 b**, **1 c**, and **1 d** were isolated by column chromatography and identified by GC–MS and NMR spectroscopy.

Table 1. Alkoxylation of 1 a catalyzed by HPW. ^[a]										
Run	HPW [µmol]	1 a [mmol]	T [°C]	t [h]	Conv. [%]	$TOF^{[b]}$ $[h^{-1}]$	TON ^[b]			
Butan	-1-ol									
1	8.3	4.0	80	7	76	65				
				13	91		450			
2	5.0	4.0	90	7	68	160	540			
3	5.0	4.0	100	7	76	280	610			
4	5.0	4.0	110	3	90	440				
				7	90		720			
5	5.0	6.0	110	3	86	660				
				7	90		1080			
6	5.0	8.0	110	3	87	880				
				7	90		1440			
Ethan	ol									
7	10.0	8.0	110	3	60	240				
				10	80					
				24	80		640			
8	10.0	32.0	110	3	40	480				
				10	65		2080			
Methanol										
9	10.0	16.0	90	3	40	240				
				7	77		1230			
10	5.0	8.0	100	3	59	720				
				10	86					
				24	86		1380			

[a] Reactions were performed in the specified alcohol as the solvent with the total volume of the reaction mixture of 5.0 mL in butan-1-ol (glass reactor) and 20 mL in methanol and ethanol (stainless-steel autoclave). The conversion and selectivity were determined by GC. Selectivity for ethers **1b-1d** was 96–99% in all runs. [b] TON in moles of substrate converted per mole of HPW. TOF is the initial turnover frequency (mol of the substrate converted per mol of HPW per hour).

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Scheme 1. Alkoxylation of 1 a.

The NOESY spectra revealed that in all these molecules hydrogen atoms H-2 give a NOE with hydrogen atoms H- 6_{axr} which shows their spatial proximity. This clearly indicates the *exo* configuration for ethers **1b**, **1c**, and **1d**, in which the alkoxy groups at C-2 and hydrogen atoms H- 6_{ax} are at the opposite sides of the six-membered ring (Scheme 1).

The butoxylation of camphene at 80 °C occurred with nearly 90% conversion to isobornyl butyl ether **1b** in 13 h (Table 1, run 1). At 110 °C, the same conversion to **1b** with excellent selectivity was reached in 3 h with no increase in conversion for the next 4 h (Table 1, run 4). This suggests that the reaction was equilibrium-controlled. With the same amount of catalyst, the reaction was equally efficient with increased substrate concentrations to give a 90% camphene conversion at almost 100% selectivity to **1b** (Table 1, runs 5 and 6). These results confirm that the incomplete conversion is because of equilibrium-control rather than catalyst deactivation. The reaction presented in run 6 (Table 1) corresponds to a turnover number (TON) of 1440 per mol of HPW. The time course for this reaction is shown in Figure 1.

The reaction with ethanol and methanol gave the corresponding isobornyl ethers 1c and 1d, which are also useful as fragrances. Under optimized conditions, ethers 1c and 1d were obtained in 80-85% yields, and these reactions were also equilibrium-controlled (Table 1, runs 7 and 10; Figure 1).



Figure 1. Alkoxylation of camphene catalyzed by HPW in various solvents: butan-1-ol (▲), ethanol (■), and methanol (●). The kinetic curves correspond to runs 6, 7, and 10 in Table 1, respectively. Reaction conditions are given in Table 1.

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Table 2. Alkoxylation of 1 a catalyzed by CsPW. ^[a]											
Run	CsPW [µmol]	1 a [mmol]	Т [°С]	Conv. [%]	TOF ^(b) [h ⁻¹]	TON ^[b]					
Butan-	Butan-1-ol										
1	7.5	8.0	80	26	50	280					
2	7.5	8.0	90	59	140	630					
3	7.5	8.0	100	77	210	820					
4 ^[c]	7.5	8.0	110	85	370	910					
5	9.0	8.0	110	86	480	760					
6	6.0	8.0	110	82	530	1090					
7	4.5	8.0	110	84	750	1490					
Ethano	1										
8	9.0	32.0	125	50	710						
				61 ^[d]		2170					
Methar	nol										
9	9.0	32.0	125	41	550						
				44 ^[d]		1560					

[a] Reactions were performed for 7 h in the specified alcohol as the solvents with the total volume of the reaction mixture of 5.0 mL in butan-1ol (glass reactor) and 20 mL in methanol and ethanol (stainless-steel autoclave). The conversion and selectivity were determined by GC. Selectivity for ethers **1b-1d** was 96–99% in all runs. [b] TON in moles of substrate converted per mole of CsPW. TOF is the initial turnover frequency (mol of the substrate converted per mol of CsPW per hour). [c] After run 4, the catalyst was removed, the solution was recharged with fresh substrate (8 mmol), and the reaction was allowed to proceed further, and no further conversion was observed thereupon. [d] 24 h reaction time.

The reactions presented in Table 1 are catalyzed homogeneously by the dissolved HPW. The use of solid catalysts based on HPW in alcohol solvents was not possible because of HPW leaching. To overcome this problem, we tested the insoluble CsPW salt as the catalyst for the alkoxylation of camphene. This allowed the truly heterogeneous synthesis of isobornyl ethers in alcohol solvents. Representative results are given in Table 2. The reaction in butan-1-ol at 80 °C in the presence of small amounts of CsPW ($\approx 0.1 \text{ mol }\%$) reached a rather moderate conversion of 26% in 7 h; however, isobornyl ether **1b** was the only product observed (Table 2, run 1). At higher temperatures (Table 2, runs 2–4), the reactions were also highly selective to ether **1b**, and they were much faster. At 110 °C, the reaction was complete in 7 h to give an 85% conversion.

To verify the catalyst stability, we performed runs with different catalyst amounts (Table 2, runs 4-7, Figure 2). With the same amount of substrate, the reaction was equally efficient with approximately 0.05 mol% of CsPW to give 84% camphene conversion in 7 h (Table 1, run 7). These results indicate the equilibrium-control of the reaction and also show the high-performance stability of the CsPW catalyst, which gave a TON value up to approximately 1500 per mol of CsPW. If we consider that some acid sites may be located in the bulk of the solid phase and hence not accessible to the substrate, the real efficiency of the surface active sites could be even higher. The reaction rate depended only slightly on the catalyst amount (Figure 2), so that the initial turnover frequencies (TOF, mol of the substrate converted per mol of CsPW per hour) were higher in the reaction with smaller catalyst amounts (Table 2, run 7 vs. run 5).



Figure 2. Alkoxylation of camphene catalyzed by 9.0 (**a**), 7.5 (**o**), 6.0 (**a**), or 4.5 (**v**) μ mol CsPW in butan-1-ol (8 mmol of camphene, 5 mL of solvent, 110 °C).

The CsPW catalyst was also effective for the methoxylation and ethoxylation of camphene to give the corresponding ethers. Under optimized conditions, isobornyl ethers **1 c** and **1 d** were obtained with virtually 100% selectivity at nearly equilibrium conversions and high TONs (Table 2, runs 8 and 9). Runs performed at lower substrate concentrations resulted in lower conversions over the same time. Importantly, CsPW operated heterogeneously in these reactions without leaching. Although CsPW is insoluble in alcohols, the possibility of leaching and any contribution of homogeneous reactions were verified in special experiments. After reaction, the catalyst was separated by centrifugation, and the filtrate was recharged with fresh camphene and allowed to react (Table 2, run 4). No further reaction was observed after catalyst removal, which implies the lack of any significant leaching.

The alkoxylation of limonene (2 a), α -pinene (3 a), and β pinene (4 a) in solutions of butan-1-ol that contained dissolved HPW resulted in the formation of the same product: α -terpenyl butyl ether (2 b; Scheme 2, Table 3). A possible mechanism of



Scheme 2. Alkoxylation of 2a, 3a, and 4a.

Table 3. Alkoxylation of 2 a, 3 a, and 3 a catalyzed by HPW. ^[a]												
Run	HPW [µmol]	Substrate [mmol]	<i>Т</i> [°С]	t [h]	Conv. [%]	Selec Isomerization	tivity 2 b	/ [%] Additio Others	n Total	TOF ^[b] [h ⁻¹]	TON ^[b]	
1	6.6	2 a (8.0)	80	7	60	15	76	9	85	300	730	
2	6.6	2 a (8.0)	90	7	75	17	67	16	83	730	910	
3	6.6	2 a (8.0)	100	2	71	52	36	12	48	n.d.	860	
4	10.0	2 a (8.0)	80	7	80	22	57	21	78	200	640	
5	1.7	3 a (4.0)	80	9	85	37	46	17	63	500	2000	
6	1.6	3 a (4.0)	100	2	96	60	23	17	40	n.d.	2260	
7	1.7	3 a (4.0)	70	7	71	40	42	18	60	250	1670	
8	0.7	3 a (4.0)	70	7	26	32	50	18	68	470	1490	
9	1.7	4a (4.0)	40	7	47	15	70	15	85	175	1110	
10	1.7	4a (4.0)	60	5	86	36	44	21	65	500	2020	
11	0.7	4 a (4.0)	80	2	99	37	47	16	63	n.d.	5660	
12	0.7	4 a (8.0)	80	2	99	38	42	20	62	n.d.	11 320	

ture was 5.0 mL in a glass reactor. The conversion and selectivity were determined by GC; n.d. = not determined. [b] TON in moles of substrate converted per mole of HPW. TOF is the initial turnover frequency (mol of the substrate converted per mol of HPW per hour).

this reaction is shown in Scheme 3. The protonation of α - and β -pinene gives carbenium ion **A**, which isomerizes to α -terpen-

yl carbenium ion (B). This ion can also form directly from limonene by protonation of its exocyclic double bond (Scheme 3). The nucleophilic attack of alcohol on **B** gives product **2b**. The alkoxylation of limonene, α -pinene, and β -pinene is more complicated than the alkoxylation of camphene because of the isomerization of these substrates. As a result, numerous minor alkoxylation products were formed in these reactions along with α -terpenyl ether. The nature of the minor products was suggested based on their GC retention times and mass spectra. Under optimized conditions, ether 2b was obtained with 70-75% selectivity from limonene and 40–50% selectivity from α - and β pinene. Blank reactions, without any catalyst added, showed virtually no conversion of limonene, α pinene, and β -pinene under the conditions used.



Scheme 3. Schematic representation of acid-catalyzed alkoxylation of 2a, 3a, and 4a.

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CsPW can also be used in these reactions as heterogeneous catalyst to give α -terpenyl butyl ether **2b** with yields comparable to those obtained in the homogeneous reaction (Table 4).

Conclusions

Heteropoly acid $H_3PW_{12}O_{40}$ and its acidic Cs salt, Cs_{2.5}H_{0.5}PW₁₂O₄₀, are efficient catalysts for the liquidphase alkoxylation of camphene, limonene, α -pinene, and β -pinene. These reactions provide effective routes for the synthesis of isobornyl and α -terpenyl ethers, important fragrances that possess a strong characteristic aroma, from renewable biomass-based substrates. The reaction yield is equilibrium-controlled, the selectivity of which is virtually 100% for isobornyl ethers and up to 70–75% for the α -terpenyl ether. As it is insoluble in the reaction mixtures, the Cs salt acts as a truly heterogeneous and environmentally friendly catalyst, which can be recycled easily.

Tabl	Table 4. Alkoxylation of 2 a, 3 a, and 3 a catalyzed by CsPW. ^[a]												
Run	CsPW [µmol]	Substrate [mmol]	<i>Т</i> [°С]	t [h]	Conv. [%]	Selec Isomerization	tivit 2 b	y [%] Additio Others	n Total	TOF ^[b] [h ⁻¹]	TON ^[b]		
1	7.5	2 a (4.0)	80	7	75	13	73	14	87	133	400		
2	7.5	2 a (8.0)	80	7	75	17	67	16	83	210	800		
3	1.5	3 a (4.0)	100	7	78	60	30	10	40	590	2080		
4	1.5	3 a (8.0)	80	24	85	30	52	18	70	220	2270		
5	1.5	3 a (8.0)	70	24	80	40	44	16	60	213	4270		
6	1.5	4 a (4.0)	80	5	93	58	30	12	42	1050	2480		
7	1.5	4 a (4.0)	60	7	60	42	37	21	58	530	1600		

[a] Reactions were performed in butan-1-ol, and the total volume of the reaction mixture was 5.0 mL in a glass reactor. The conversion and selectivity were determined by GC. [b] TON in moles of substrate converted per mole of CsPW. TOF is the initial turnover frequency (mol of the substrate converted per mol of CsPW per hour).

Experimental Section

All chemicals were purchased from commercial sources and used as received, unless otherwise stated. Camphene (1 a), *R*-(+)-limonene (2 a), (-)- α -pinene (3 a), (-)- β -pinene (4 a), and H₃PW₁₂O₄₀ hydrate were from Aldrich.

³¹P magic-angle spinning (MAS) NMR spectra were recorded at RT and a 4 kHz spinning rate by using a Bruker Avance DSX 400 NMR spectrometer using 85% H_3PO_4 as a reference. Powder XRD patterns of the catalysts were obtained by using a Rigaku Geigerflex-3034 diffractometer with CuK_a radiation. The textural characteristics were determined from N₂ physisorption measured by using a Micromeritics ASAP 2010 instrument at 77 K. The W and P content was determined by inductively coupled plasma atomic emission spectroscopy by using a Spectro Ciros CCD spectrometer.

The acidic heteropoly salt CsPW was prepared according to the literature $\mathsf{procedure}^{\scriptscriptstyle[35]}$ by the dropwise addition of the required

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amount of an aqueous solution of cesium carbonate (0.47 μ) to an aqueous solution of HPW (0.75 μ) at RT with stirring. The precipitate obtained was aged in an aqueous mixture for 48 h at RT and dried by using a rotary evaporator at 45 °C/3 kPa and an oven at 150 °C/0.1 kPa for 1.5 h. CsPW thus prepared had a surface area of 111 m²g⁻¹, a pore volume of 0.07 cm³g⁻¹, and a pore diameter of 24 Å. The acid strength of CsPW was characterized calorimetrically using ammonia and pyridine adsorption as discussed previously.^[36]

The reactions were performed in a 10 mL glass reactor equipped with a magnetic stirrer and a condenser or in a homemade 100 mL stainless-steel reactor with a magnetic stirrer. The latter reactor was used in the runs performed at a higher temperature than the solvent boiling point. In a typical run, a mixture (5.0 mL in the glass reactor or 20.0 mL in the stainless-steel rector) of the substrate (4.0-32.0 mmol, 0.4-1.6 M), dodecane or undecane (2.0-8.0 mmol, 0.4 m, GC internal standards), and the catalyst [HPW (2-30 mg, 0.7-10.0 µmol) or CsPW (5-30 mg, 1.5-9.0 µmol)] in alcohol solvent was stirred intensely under air at a specified temperature (40-125 °C). The reactions were followed by GC by using a Shimadzu 17 instrument fitted with a Carbowax 20м capillary column and a flame ionization detector. After the appropriate reaction time, the stirring was stopped, the catalyst settled quickly, and 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. Turnover frequencies (TOF) were measured by GC at low conversions (up to 20-40%) by taking aliquots at short reaction times (usually within the first 30-60 min).

In reactions with CsPW, to control catalyst leaching and the possibility of a homogeneous reaction, the CsPW catalyst was removed by centrifugation of the reaction mixture at the reaction temperature, the supernatant was added to a fresh portion of substrate, if necessary, and allowed to react on. The absence of a further reaction in such experiments indicated the absence of active component leaching.

Ethers **1 b**, **1 c**, **1 d**, and **2 b** were separated by column chromatography (silica gel 60) using mixtures of hexane and CH_2CI_2 as eluents and identified by GC–MS and ¹H and ¹³C NMR spectroscopy. The ¹H and ¹³C NMR signals were assigned by using 2D techniques. NMR spectra were recorded in CDCI₃ by using a Bruker 400 MHz spectrometer with Me₄Si as an internal standard. Mass spectra were obtained by using a Shimadzu QP2010-PLUS instrument that operated at 70 eV.

Isoborneol butyl ether (**1b**): MS (70 eV, El): *m/z* (%): 210 (8) [*M*]⁺, 195 (1.5) [*M*-CH₃]⁺, 136 (15) [*M*-C₄H₇OH]⁺, 121 (39), 110 (14), 108 (31), 101 (13), 95 (100), 93 (27), 81 (12), 69 (10), 67 (15), 57 (16), 55 (15); ¹H NMR (400 MHz, CDCI₃, 25 °C, Me₄Si): $\delta = 0.70$, (s, 3H; C⁸H₃), 0.78 (s, 3H; C¹⁰H₃), 0.80 (t, ³*J*=7.2 Hz, 3H; C¹⁴H₃), 0.89 (s, 3H; C⁹H₃), 0.80-0.90 (m, 2H; C⁵HH and C⁶H_{ax}H), 1.20-1.30 (m, 2H; C¹³H₂), 1.30-1.40 (m, 3H; C¹²H₂ and C⁶HH_{eq}), 1.40-1.50 (m, 1H; C³HH), 1.50-1.60 (m, 2H; C⁴H and C⁵HH), 1.55-1.65 (m, 1H; C³HH), 3.05 (dd, ³*J*=3.6 Hz, ³*J*=7.6 Hz, 1H; C²H), 3.14 (dt, ²*J*=9.2 Hz, ³*J*=6.4 Hz, 1H; C¹¹HH), 3.14 ppm (dt, ²*J*=9.2 Hz, ³*J*=6.4 Hz, 1H; C¹¹HH); ¹³C NMR (100 MHz, CDCI₃, 25 °C, Me₄Si): $\delta = 11.81$ (C¹⁰), 13.93 (C¹⁴), 19.55 (C¹³), 20.16 (C⁸), 20.27 (C⁹), 27.36 (C⁵), 32.28 (C¹²), 34.55 (C⁶), 38.67 (C³), 45.13 (C⁴), 46.36 (C⁷), 49.14 (C¹), 68.83 (C¹¹), 86.92 ppm (C²).

Isoborneol ethyl ether (**1 c**): MS (70 eV, El): m/z (%): 182 (5) $[M]^+$, 167 (2) $[M-CH_3]^+$, 136 (10) $[M-C_2H_5OH]^+$, 121 (22), 110 (14), 108 (13), 96 (10), 95 (100), 93 (19), 73 (12), 71 (12), 67 (13), 55 (10);

¹H NMR (400 MHz, CDCl₃, 25 °C, Me₄Si): δ = 0.78, (s, 3 H; C⁸H₃), 0.88 (s, 3 H; C¹⁰H₃), 0.97 (s, 3 H; C⁹H₃), 0.92–1.02 (m, 2 H; C⁵HH and C⁶H_{ax}H), 1.13 (t, ³*J* = 7.0 Hz, 3 H; C¹²H₃), 1.40–1.50 (m, 1 H; C⁶HH_{eq}), 1.55–1.60 (m, 1 H; C³HH), 1.65–1.70 (m, 2 H; C⁴H and C⁵HH), 1.70–1.75 (m, 1 H; C³HH), 3.17 (dd, ³*J* = 3.6 Hz, ³*J* = 7.6 Hz, 1 H; C²H), 3.31 (dq, ²*J* = 9.6 Hz, ³*J* = 7.0 Hz, 1 H; C¹¹HH), 3.46 ppm (dq, ²*J* = 9.6 Hz, ³*J* = 7.0 Hz, 1 H; C¹¹HH), ¹³C NMR (100 MHz, CDCl₃, 25 °C, Me₄Si): δ = 11.51 (C¹⁰), 15.29 (C¹²), 19.96 (C⁹), 20.03 (C⁸), 27.04 (C⁵), 34.28 (C⁶), 38.54 (C³), 45.75 (C⁴), 46.09 (C⁷), 48.75 (C¹), 64.10 (C¹¹), 86.48 ppm (C²).

Isoborneol methyl ether (**1** d): MS (70 eV, EI): m/z (%): 168 (2) $[M]^+$, 153 (3) $[M-CH_3]^+$, 136 (11) $[M-C_4H_7OH]^+$, 121 (19), 110 (18), 108 (13), 95 (100), 93 (16), 67 (11), 55 (11); ¹H NMR (400 MHz, CDCI₃, 25 °C, Me₄Si): $\delta = 0.80$, (s, 3 H; C⁸H₃), 0.89 (s, 3 H; C¹⁰H₃), 0.96 (s, 3 H; C⁹H₃), 0.97–1.03 (m, 2 H; C⁵HH and C⁶H_{ax}H), 1.42–1.52 (m, 1 H; C⁶HH_{eq}), 1.52–1.58 (m, 1 H; C³HH), 1.62–1.70 (m, 2 H; C⁴H and C⁵HH), 1.70–1.75 (m, 1 H; C³HH), 3.11 (dd, ³J = 6.0 Hz, ³J = 9.0 Hz, 1 H; C²H), 3.23 ppm (s, 3 H; C¹¹H₃); ¹³C NMR (100 MHz, CDCI₃, 25 °C, Me₄Si): $\delta =$ 11.91 (C¹⁰), 20.35 (C⁸), 20.40 (C⁹), 27.50 (C⁵), 34.80 (C⁶), 38.02 (C³), 45.08 (C⁴), 46.57 (C⁷), 49.30 (C¹), 56.66 (C¹¹), 89.10 ppm (C²).

α-Terpenyl butyl ether (**2b**): MS (70 eV, EI): *m/z* (%): 195 (0.3) [*M*-CH₃]⁺, 136 (19) [*M*-C₄H₇OH] ⁺, 121 (26), 115 (24), 93 (27), 81 (9), 79 (9), 68 (11), 67 (13), 59 (100); ¹H NMR (400 MHz, CDCl₃, 25 °C, Me₄Si): δ = 0.85 (t, ³*J* = 4.4 Hz, 3H; C¹⁴H₃), 1.02 (s, 3H; C⁹H₃), 1.03 (s, 3 H; C¹⁰H₃), 1.15-1.20 (m, 1H; C⁵HH), 1.25-1.35 (m, 2H; C¹³H₂), 1.38-1.45 (m, 2H; C¹²H₂), 1.57 (s, 3H; C⁷H₃), 1.55-1.60 (m, 1H; C⁴H), 1.70-1.80 (m, 2H; C³HH and C⁵HH), 1.85-1.95 (m, 3H; C³HH and C⁶H₂), 3.24 (t, ³*J* = 3.6 Hz, 2H; C¹¹H₂), 5.31 ppm (brs, 1H; C²H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, Me₄Si): δ = 14.00 (C¹⁴), 19.80 (C¹³), 22.52 (C¹⁰), 22.66 (C⁹), 22.87 (C⁷), 23.95 (C⁵), 26.84 (C³), 31.13 (C⁶), 32.77 (C¹²), 41.99 (C⁴), 60.26 (C¹¹), 76.08 (C⁸), 121.00 (C²), 133.88 ppm (C¹).

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Heteropoly Acid Catalysts for the Synthesis of Fragrance Compounds from Biorenewables: The Alkoxylation of Monoterpenes