Perfluorinated Sulfonate Resins as Reusable Heterogeneous Catalysts for the One-pot Synthesis of DiPhenolic Esters (DPEs)

RESEARCH ARTICLE

Perfluorinated Sulfonate Resins as Reusable Heterogeneous Catalysts for the One-pot Synthesis of DiPhenolic Esters (DPEs)

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Abstract: Levulinic acid, easily obtained from cellulose, represents a fundamental chemical platform for a number of valuable building blocks. Among them, diphenolic acid and its esters (DPA and DPE) are valid candidates to replace Bisphenol A in polycarbonate and epoxy resin production processes. In this study, we report a one-pot synthesis of alkyl DPEs in the presence of a heterogenous acid catalyst starting from levulinic acid, an alcohol and phenol as solvent-reagent. The most interesting member of the DPE family, the ethyl 4,4-bis(4-hydroxyphenyl)pentanoate, is selectively obtained in a good yield in the presence of a commercially available heterogeneous acid catalyst, the Aquivion, which can be reused for at least six times without any noticeable loss in activity.

Introduction

The depletion of petroleum reserves, environmental concerns associated with the use of fossil resources, and increasingly tense international political situation, have forced many industrial companies to focus their efforts on the exploitation and conversion of biomass into a wide variety of carbon sources as possible substitute of fossil feedstocks.[1] Currently, many organic compounds can be obtained from ligno-cellulosic biomass. In particular, levulinic acid (LA), obtained from cellulose through dehydration/hydration processes,[2] has been identified as one of the potential chemical platforms for a large family of high value-added materials and chemicals (Figure 1),[3] such as levulinic acid esters (LAEs), γ-valerolactone (GVL), methyltetrahydrofuran (MTHF), δ-amino levulinic acid (DALA), diphenolic acid and esters (DPA and DPEs). Levulinic acid esters (LAEs) have wide applications as plasticizers, herbicides, perfumery and diesel additives.[4] For instance, ethyl levulinate can be used as a 100% substitute of petroleum-based diesel in the existing diesel engines, as well as an oxygenate additive for biodiesel in order to improve the limitations related to its employment in cold regions.[5]

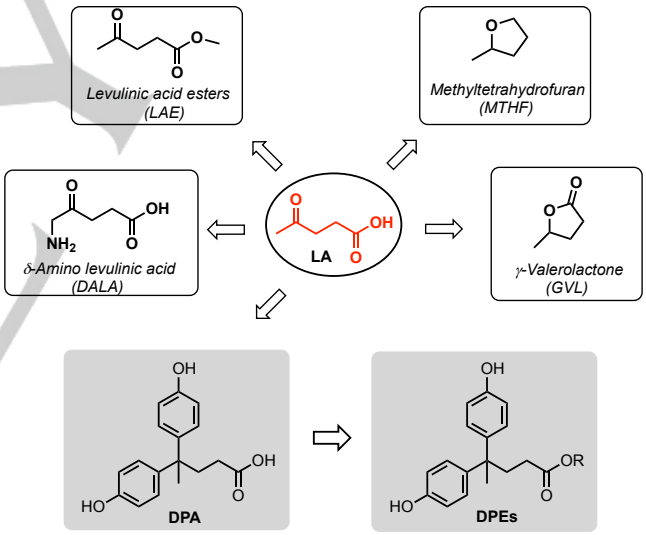
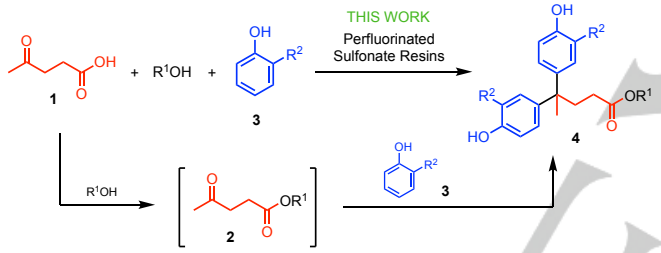


Figure 1. Selected chemicals obtained from LA.

γ-Valerolactone (GVL) is a natural, non-toxic and biodegradable chemical utilized as a food supplement, green solvent and fuel additive.[6] Furthermore, GVL can be easily transformed into various derivatives such as 1,4-pentandiol or linear and branched alkanes.[7] Methyltetrahydrofuran (MTHF) is considered one of the most promising biofuels and gasoline additives owing to its low solubility in water and high energy density.[8] Moreover, MTHF is employed as a greener alternative to THF, and by some criteria displays even better performance and utility if compared to it.[9] δ-Amino levulinic acid (DALA), a naturally occurring substance present in plant and animal cells, is found to be active as herbicide[10] insecticide[11] and in the treatment of cancer as well.[12]

Diphenolic acid and esters (DPA and DPEs), due to their chemical properties, are nowadays considered valid candidates to replace Bisphenol A, the main raw material used in the manufacture of polycarbonates and epoxy resins,[13] which in turn are useful intermediates for lubricating oil additives, surfactants, plasticizers and paint formulations.[14] The replacement of Bisphenol A has become an urgent need given its well-known mutagenic and carcinogenic effects on living organisms.[15] Traditionally, the synthesis of DPA can be efficiently performed starting from LA and using strong mineral acids, such as HCl and H_2SO_4.[16] More recently, composite materials, such as $H_3PW_{12}O_4$/SBA-15[17] and Cs substituted heteropolyacids of Dawson type[18] provided DPA in good yield. Ionic liquids were also successfully employed.[19] In most cases, however, the recovery and the potential reuse of these catalytic systems is a non-trivial issue. In this regard, the development of new, operationally simple and sustainable catalytic methods for the synthesis of DPA and DPEs is still of high relevance.

Driven by our ongoing interest in developing catalytic environmentally friendly methodologies for the synthesis of industrially significant compounds,[20] we here describe a new heterogeneous protocol that allows the one-pot production of DPEs starting from levulinic acid (**1**), an alcohol (low excess), and a phenol derivative **3** used both as reagent and solvent (Scheme 1).

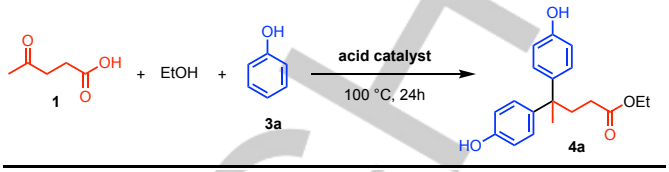


Scheme 1. Perfluorinated Sulfonate Resins as catalysts for the synthesis of DPEs from LA (*This work*).

Results and Discussion

Recently, we have developed a simple method for the synthesis of levulinic acid esters through a catalytic esterification of LA that allowed to minimize the molar excess of the corresponding alcohol.[21] A highly efficient process was achieved by designing hybrid heterogeneous catalysts in which a sulfonic acid is supported over silica. On the basis of these results, we decided to investigate the best reaction conditions for the one-pot synthesis of ethyl 4,4-bis(4-hydroxyphenyl)pentanoate **4a** starting from LA (**1**), phenol (**3a**) and ethanol (Table 1). Homogeneous (sulfuric and *para*-toluenesulfonic acids) and heterogeneous catalysts (commercial acid alumina, Amberlite IR-120, Aquivion PW66S, Nafion, $PhSO_3H$@SiO_2 and Aquivion@SiO_2) were tested (Table 1).[22] The reactions were carried out in a Schlenk tube by mixing levulinic acid **1** (4 mmol), ethanol (5 mmol), phenol **3a** as solvent-reagent (20 mmol) and the catalyst (3 mol% of acid sites) under inert atmosphere (N_2). The resulting mixtures were heated at 100 °C for 24 hours and then analyzed by gas-chromatography (GC). A complete consumption of the starting LA was observed in all the conducted experiments due to its complete esterification with ethanol. Target product **4a** was formed together with its isomer, ethyl 4-(2-hydroxyphenyl)-4-(4-hydroxyphenyl)pentanoate, usually present in the reaction mixture in 10:1 ratio. The structure of compound **4a** was unambiguously confirmed by SC-XRD (Figure 2, see the SI for details).

Table 1. Screening of homogeneous and heterogeneous catalysts.



Entry[a]	Catalyst[b]	Yield[c] (%) **4a**	Sel.[d] (%) **4a**
1	-	0	-
2	H_2SO_4	51	79
3	TsOH	14	88
4	Amberlite IR-120	< 5	93
5	Al_2O_3 acid	< 5	92
6	$PhSO_3H$@SiO_2	8	68
7	Nafion	36	81
8	**Aquivion PW66S**	**71**	**84**
9	Aquivion@SiO_2	49	82

[a] Reaction conditions: **1** (4 mmol), **3a** (20 mmol), ethanol (5 mmol), catalyst, 100 °C, 24 h. [b] 3% acid sites with respect to **1**. [c] By GC (Gas Chromatography), upon calibration with an authentic sample and using dodecane as internal standard. [d] Measured as **4a** yield/**2a** conversion ratio.

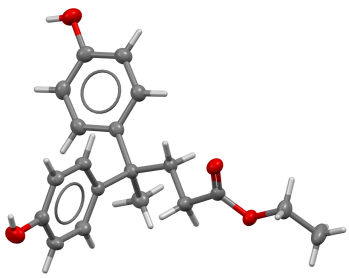


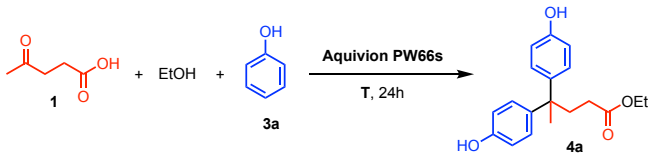
Figure 2. X-ray structures (ORTEP) for compound **4a**. Asymmetric unit. Colour code C=grey, O=red, H=white; All non-hydrogen atoms are reported in ellipsoid style while H atoms are reported in capped stick for the sake of clarity.

The presence of an acid catalyst was crucial for the reaction (Table 1, entry 1). Homogeneous catalysts, such as sulfuric acid and *para*-toluenesulfonic acid (Table 1, entry 2 and 3) afforded **4a** in 51 and 14% yield, respectively. Both provided a good selectivity but were unable to fully convert the ethyl ester of LA (**2a**) into the desired product **4a**. Heterogeneous catalysts, such as commercial Amberlite and acid alumina (Table 1, entries 4 and 5) afforded the product in lower yields (<5%), and a similar result was observed utilizing $PhSO_3H$@SiO_2 (Table 1, entry 6, 8% yield). To our delight, a breakthrough under heterogeneous catalysis was achieved when fluorinated sulfonic acids, Nafion and Aquivion, were employed. In particular, Nafion led to 36% of **4a** (Table 1, entry 7), while Aquivion PW66s (powder form) afforded the desired product in 71% yield (Table 1, entries 8). A less

satisfactory result was observed by using Aquivion@SiO_2, that allowed to obtain 49% yield of **4a** (Table 1, entry 9). The structure of these two perfluorinated polymeric resins features a linear backbone which contains short branches terminating with sulfonic acid groups.[20b] Their acidity is comparable (H_0 = -12), however, Aquivion has a higher loading of acid sites per kilogram of powder (1.5 *vs* 0.8 mol -SO_3H/kg). Moreover, Aquivion shows a glass transition temperature of 140 °C, higher than Nafion (~ 100 °C), and due to its shorter chain, has a higher degree of crystallinity. Consequently, Aquivion can be used at higher temperatures, exhibiting better mechanical properties and reduced solvent swelling. All the above-mentioned reasons can account for the better results obtained with Aquivion.

With these preliminary data in our hands, we decided to further optimize the reaction conditions using unsupported Aquivion (Aquivion PW66s) as catalyst. The influence of the reaction temperature and the amount of the catalyst were specifically evaluated (Table 2).

Table 2. Influence of the reaction temperature and catalyst amount.



Entry[a]	T (°C)	Catalyst amount[b]	Yield[c] (%) **4a**	Sel.[d] (%) **4a**
1	60	3 mol%	traces	-
2	80	3 mol%	36	92
3	100	3 mol%	71	84
4	120	3 mol%	51	67
5	100	1 mol%	29	75
6	**100**	**5 mol%**	**78**	**87**
7	100	7 mol%	74	86

[a] Reaction conditions: see Table 1, entry 8. [b] with respect to LA. [c] by GC, upon calibration with an authentic sample and using dodecane as internal standard. [d] measured as **4a** yield/**2a** conversion ratio.

Results depicted in Table 2 show that decreasing the reaction temperature was detrimental to the reaction (Table 2, entries 1 and 2 in comparison with entry 3). This is likely due to the high thermal barrier of this transformation. A similar outcome was obtained when the temperature was increased from 100 to 120 °C (Table 2, entry 4). As expected, when the catalyst loading was reduced to 1 mol% a lower yield of **4a** was observed (Table 2, entry 5), whereas an increase in both yield and selectivity (from 71% to 78% and from 84% to 87%, respectively) was achieved when the reaction was carried out in the presence of 5 mol% of Aquivion PW66S (Table 2, entry 6, based on the content of -SO_3H groups). No further improvements were attained by further increase in the catalyst amount up to 7 mol% (Table 2, entry 7).

The progress of the yield of **4a** in function of the reaction time has been then investigated (Figure 3). The yield of product **4a** raises quickly in the first five hours and then reaches a plateau after around ten hours. Remarkably, the rate of the reaction is compatible with a possible exploitation on a large scale. In addition, in order to evaluate the efficiency of the process, the Process Mass Intensity (PMI, the percentage of the total input mass incorporated into the product), was calculated (PMI = 2.69) for the experiment conducted under the optimized reaction conditions.[23]

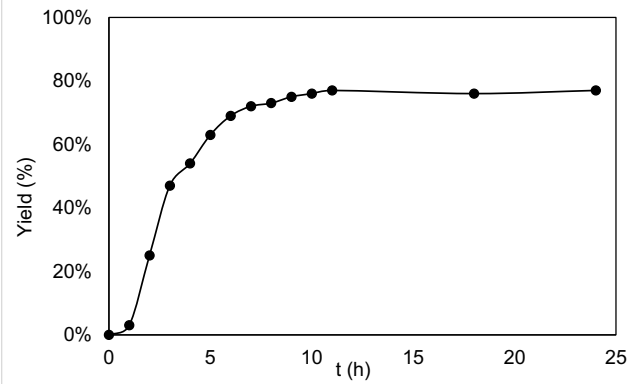


Figure 3. Reaction trend as a function of time.

The formation of compound **4a** is likely the result of the combination of two sequential processes, namely the esterification of LA and the Friedel-Crafts reactions, both promoted by acid catalysts.[24] In order to confirm this hypothesis, the model reaction was carried out by using Aquivion pre-treated with NaOH in order to neutralize all the acidic sites. In this case, the starting phenol was fully recovered after heating the reaction mixture at 100 °C for 5 h, confirming the crucial role of the sulfonic acid groups of the catalyst for the Friedel-Crafts step. Only traces of ethyl ester of levulinic acid were detected, suggesting a possible autocatalytic effect of levulinic acid in the esterification process.

We then ensured that the catalyst acts as a real heterogeneous species by performing a filtration test, the so called "Sheldon test".[25] By adding Aquivion to the reaction and filtering it off before the heating, we did not observe the formation of **4a**, proving that leaching of active species did not occur (see the SI for details).

The recyclability of the catalyst was then evaluated (Table 3). Upon performing the model experiment, the catalyst was recovered by filtration, washed with ethyl acetate (20 ml), dried and reused in the subsequent run. Results shown in Table 3 indicate that the catalyst can be recycled at least six times without any significant loss in its activity. In addition, the FT-IR performed on the starting catalyst did not show any remarkable difference when compared to those registered for the recovered catalyst after the fifth run (see Figures S1 and S2 in the SI).

Table 3. Catalyst recycling tests.

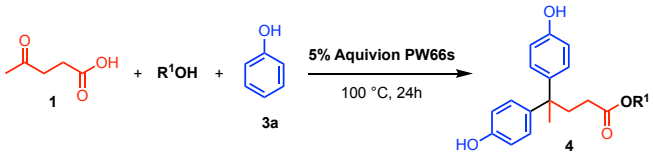
Catalytic run[a]	Yield[b] (%) **4a**	Catalytic run[a]	Yield[b] (%) **4a**
1	78	4	76
2	78	5	75
3	77	6	76

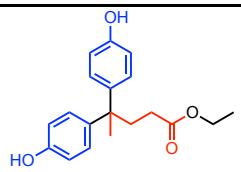
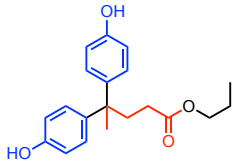
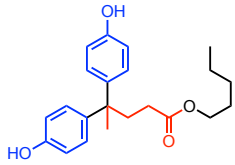
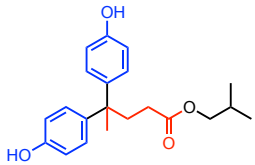
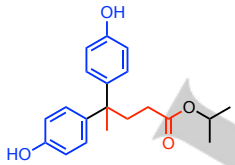
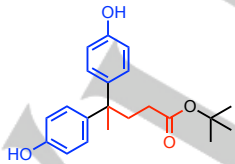
[a] Reaction conditions: see Table 2, entry 6, under heating for 10 hours. [b] by GC, upon calibration with an authentic sample and using dodecane as internal standard.

These results highlight the potential interest of this protocol, which allows to prepare DPE in a single step, by a sequential catalytic process, and efficiently recycle the solid catalyst in a simple and practical manner.

The applicability of the reaction to other alcohols (Table 4) and phenols (Table 5) was then explored.

Table 4. Aquivion PW66S-catalyzed synthesis of DPEs: effect of alcohol (R^1OH).

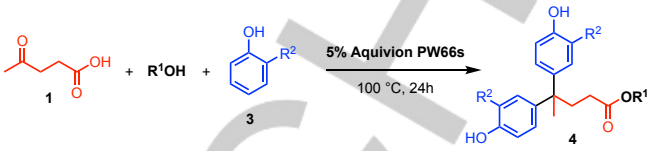


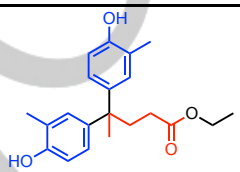
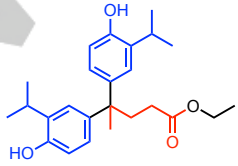
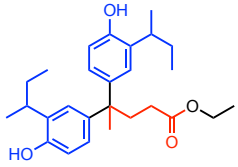
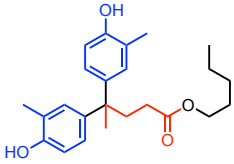
Entry[a]	R^1OH	Product	Yield[b] (%) **4**	Sel.[c] (%) **4**
1	ethanol		**4a**, 78	87
2	*n*-propanol		**4b**, 65	85
3	*n*-pentanol		**4c**, 54	83
4	*iso*-butanol		**4d**, 44	86
5	*iso*-propanol		**4e**, 15	85
6	*tert*-butanol		**4f**, -	-

[a] Reaction conditions: see Table 2, entry 6, heating for 24 hours. [b] by GC, upon calibration with an authentic sample and using dodecane as internal standard. [c] measured as **4** yield/**2** conversion ratio.

In detail, we tested four primary alcohols (ethanol, propanol, *iso*-butanol and pentanol), a secondary alcohol (*iso*-propanol) and a tertiary one (*tert*-butanol). Data reported in Table 4 suggest that the reaction output is negatively impacted by the steric hindrance of the alcohol. Indeed, the best yield was achieved employing ethanol (Table 4, entry 1, **4a**, 78%). Other primary alcohols still provided the desired product, although in lower yields (Table 4, entries 2-4, **4b-d**, 44-65%). The lowest yield was observed using *iso*-butanol (Table 4, entry 4), which features the most hindered hydroxy group of the series. Not surprisingly, a poor yield was observed when the reaction was carried out with the secondary *iso*-propyl alcohol (Table 4, entry 5, **4e**, 15%), whereas no reaction was observed with *tert*-butanol (Table 4, entry 6).

Table 5. Aquivion PW66S-catalyzed synthesis of DPEs from various phenols **3**.



Entry[a]	R^1	R^2	Product	Yield[b] (%) **4**	Sel.[c] (%) **4**
1	C_2H_5	CH_3		**4g**, 65	85
2	C_2H_5	*i*-C_3H_7		**4h**, 45	89
3	C_2H_5	*s*-C_4H_9		**4i**, 55	83
4	C_5H_{11}	CH_3		**4j**, 47	83

[a] Reaction conditions: see Table 2, entry 6, heating for 24 hours. [b] by GC, upon calibration with an authentic sample and using dodecane as internal standard. [c] measured as **4** yield/**2** conversion ratio.

Noteworthy, if the reaction is carried out in one-pot/two steps mode, by firstly reacting the levulinic acid with phenol for 12 h and then adding *iso*-propanol, a slightly higher yield of 21% can be achieved. In all cases the selectivity values towards the desired products **4** remain well above 80%.

Concerning the best results achieved using ethanol, we speculate that, probably, its higher polarity with respect to all the other alcohols utilized, can justify the observed behaviour. This might indeed favour the stabilization of the ionic intermediates of the Friedel-Crafts reactions, thus increasing the overall yield of the sequential reaction.

Finally, other *ortho*-substituted phenols were subjected to the reaction with LA and ethanol (or pentanol) under the optimised conditions (Table 5). Acceptable to good yields were achieved by using activated phenols (R^1 = 2-Me, 2-*iso*-Pr, 2-*sec*-Bu) while, as expected, no reaction occurred when deactivated phenols (R^1 = 2-Cl, 2-NO_2) were employed. Surprisingly, the reaction carried out with catechol resulted in the complete recovery of the aromatic reagent.

Conclusion

A new protocol for the one-pot synthesis of diphenolic acid esters (DPEs) making use of a commercial heterogeneous catalyst has been disclosed. The process features the use of alcohol in small molar excess, and phenol as solvent-reagent. The catalyst, easily recovered by filtration, can be recycled at least six times without significant loss in activity. The combination of low catalyst loadings and a reduced molar excess of the reagents ensures the practical viability of this approach, which affords value-added chemicals through the derivatization of renewable-sourced building blocks. The present methodology allows to minimize the consumption of chemicals and the formation of wastes (PMI = 2.69), suggesting its potential for future developments.

Experimental Section

General remarks

All reactions were carried out under nitrogen atmosphere employing standard Schlenk techniques and magnetic stirring. All starting materials were commercial products used as received. NMR spectra were recorded at room temperature on Bruker Avance 400, operating at 400 MHz in deuterated chloroform, using the solvent residual signals as internal standards (7.26 and 77.00 ppm respectively for ^{1}H and ^{13}C). Chemical shifts (δ) and coupling constants (J) are given in ppm and in Hz, respectively. SCXRD analysis was performed on single crystal samples **4a** on a Bruker D8 Venture diffractometer equipped with a kappa goniometer and an Oxford cryostream. Low temperature data collections were performed under nitrogen flux. Microfocused CuKα radiation (λ = 1.541846 Å) was used; Lorentz polarization and absorption correction were applied. Data were reprocessed using APEX v3 software. Structures were solved by direct methods using SHELXT[26] and refined by full-matrix least-squares on all F^2 using SHELXL[27] implemented in Olex2.15[28]. Anisotropic displacement parameters were refined except for hydrogen atoms. Table SX reports crystal data collection and refinement results. ORTEP diagrams are reported in Supporting Information. CCDC 2174267 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

General procedure for one-pot condensation and esterification of levulinic acid to form DPEs

In a glass Schlenk tube, levulinic acid (4 mmol), alcohol (5 mmol), phenol (20 mmol), and Aquivion PW66s (5% acid sites) are added together at room temperature under nitrogen atmosphere. The sealed Schlenk tube is then placed in an oil bath pre-heated at 100 °C and kept under stirring for 24 h. Inert atmosphere is maintained by using a balloon filled with nitrogen. After cooling to room temperature, the catalyst is filtered and washed with ethyl acetate (20 mL). The organic solution is dried over Na_2SO_4, filtered and then concentrated under reduced pressure. The resulting crude was then analyzed by GC-MS and finally purified by flash column chromatography over silica gel using a mixture of hexane/ethyl acetate 9:10 as eluent.

Ethyl 4,4-bis(4-hydroxyphenyl) pentanoate **4a**: pale yellow solid (980 mg, yield 78%); m.p 126.5-127.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 – 7.04 (m, 4H), 6.76 – 6.73 (m, J = 6.73 Hz, 4H), 4.11 (q, J = 7.1 Hz, 2H), 2.40 (m, 2H), 2.23 – 2.03 (m, 2H), 1.57 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 153.6 (2C), 141.1 (2C), 128.4 (4C), 115.1 (4C), 60.9, 44.5, 36.6, 30.4, 27.7, 14.1. EI-MS [M+H$^+$] calcd 315.16, found 315.00.

Propyl 4,4-bis(4-hydroxyphenyl) pentanoate **4b**: pale yellow solid (853 mg, yield 65%); m.p. 100-101.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (m, 4H), 6.76 (m, 4H), 6.18 (s, 2H), 4.01 (t, J = 6.7 Hz, 2H), 2.43 – 2.38 (m, 2H), 2.17 – 2.12 (m, 2H), 1.65 – 1.54 (m, 5H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 153.6 (2C), 141.0 (2C), 128.9 (4C), 115.0 (4C), 66.6, 44.4, 36.6, 30.4, 27.6, 21.9, 10.4. EI-MS [M+H$^+$] calcd 329.18, found: 329.00.

Pentyl 4,4-bis(4-hydroxyphenyl) pentanoate **4c**: colorless oil (770 mg, yield 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (m, 4H), 6.74 (m, 4H), 5.51 (s, 2H), 4.06 – 4.03 (t, 6.7 Hz, 2H), 2.43 (m, 2H), 2.18 – 2.05 (m, 2H), 1.63 – 1.59 (m, 5H), 1.33 (m, 4H), 0.91 (t, J = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 153.7 (2C), 140.9 (2C), 128.4 (4C), 115.1 (4C), 65.3, 44.4, 36.6, 30.5, 28.2, 28.0, 27.1, 22.1, 14.0. EI-MS [M+H$^+$] calcd 358.21, found 356.20.

Isobutanyl 4,4-bis(4-hydroxyphenyl) pentanoate **4d**: yellow solid (602 mg, yield 44%); m.p. 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 – 6.74 (m, 4H), 6.76– 6.74 (m, 4H), 3.84 (d, J = 6.7 Hz, 2H), 2.44 – 2.40 (m, 2H), 2.17 – 2.13 (m, 2H), 1.94 – 1.88 (m, 1H), 1.57 (s, 3H), 0.92 (d, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 153.6 (2C), 141.1 (2C), 128.4 (4C), 114.9 (4C), 70.8, 44.5, 36.6, 30.3, 27.7, 27.7, 19.1 (2C). EI-MS [M+H$^+$] calcd 343.19, found 343.18.

Isopropyl 4,4-bis(4-hydroxyphenyl) pentanoate **4e**: colorless oil (197 mg, yield 15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (m, 4H), 6.76 (m, 4H), 5.02 – 4.96 (m, 1H), 2.40 (m, 2H), 2.12 – 2.08 (m, 2H), 1.57 (s, 3H), 1.22 (d, J = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 153.6 (2C), 141.1 (2C), 128.4 (4C), 114.9 (4C), 68.0, 44.5, 36.6, 30.7, 27.7, 21.8 (2C). EI-MS [M+H$^+$] calcd 329.18, found 329.17.

Ethyl 4,4- bis(4-hydroxy-3-methylphenyl)pentanoate **4g**: yellow solid (890 mg, yield 65%); m.p. 140.1 – 142.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, J = 2.4 Hz, 2H), 6.87 (dd, J = 8.3, 2.4 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 2.42 (dd, J = 6.7, 4.7 Hz, 2H), 2.21 (s, 6H), 2.19 – 2.11 (m, 2H), 1.55 (s, 3H), 1.27 – 1.22 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 151.9 (2C), 141.0 (2C), 129.9 (2C), 125.7 (2C), 123.6 (2C), 114.5 (2C), 60.9, 44.3, 36.6, 30.5, 27.7, 16.2 (2C), 14.1. EI-MS [M+H$^+$] calcd 343.19, found 343.18.

Ethyl 4,4-bis(4-hydroxy-3-isopropylphenyl)pentanoate **4h**: colourless oil (716 mg, yield 45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, J = 2.4 Hz, 2H), 6.89 (dd, J = 8.3, 2.4 Hz, 2H), 6.66 (d, J = 8.3 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.26 – 3.14 (m, 2H), 2.48 – 2.34 (m, 2H), 2.24 – 2.08 (m, 2H), 1.59 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.21 (dd, J = 6.9, 1.5 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 150.7 (2C), 141.1 (2C), 133.7 (2C), 125.5 (2C), 114.7 (2C), 60.5, 45.0, 36.9, 30.6, 28.1, 27.3, 22.6 (4C), 14.2. EI-MS [M+H$^+$] calcd 399.55, found 399.25.

Ethyl 4,4-bis(3-(sec-butyl)-4-hydroxyphenyl)pentanoate **4i**: yellow oil (938 mg, yield 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 – 6.92 (m, 2H), 6.91 – 6.87 (m, 2H), 6.67 (d, J = 12.4 Hz, 2H), 4.11 (d, J = 7.1 Hz, 2H), 2.92 (qd, J = 6.9, 2.3 Hz, 2H), 2.45 – 2.35 (m, 2H), 2.17 – 2.08 (m, 2H), 1.58 (s, 3H), 1.56 – 1.52 (m, 4H), 1.24 (t, J = 7.1 Hz, 3H), 1.18 (dd, J = 7.0, 1.6 Hz, 6H), 0.82 (tdd, J = 7.4, 3.2, 1.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 151.1 (2C), 141.0 (2C), 132.5 (2C), 126.4 (2C), 125.1 (2C), 114.7 (2C), 60.6, 44.9, 36.9, 34.1 (2C), 30.6, 29.7 (2C), 28.0, 20.5 (2C), 14.2, 12.1 (2C). EI-MS [M+H$^+$] calcd 427.28, found 427.28.

Pentyl 4,4- bis(4-hydroxy-3-methylphenyl)pentanoate **4j**:colorless oil (722 mg, yield 47%); 1H NMR (400 MHz, CDCl3) δ 6.98 – 6.93 (m, 2H), 6.89 (dd, J = 8.3, 2.5 Hz, 2H), 6.68 (d, J = 8.3 Hz, 2H), 4.05 (t, J = 6.8 Hz, 2H), 2.45 – 2.36 (m, 2H), 2.21 (s, 6H), 2.17 – 2.08 (m, 2H), 1.65 – 1.59 (m, 2H), 1.56 (s, 3H), 1.42 – 1.27 (m, 4H), 0.97 – 0.86 (m, 3H).13C NMR (101 MHz, CDCl3) δ 174.8, 151.8 (2C), 141.1 (2C), 129.8 (2C), 125.8 (2C), 123.2

(2C), 114.4 (2C), 64.8, 44.3, 36.6, 30.4, 28.3, 28.1, 27.7, 22.3, 16.1 (2C), 14.0. EI-MS [M+H+] calcd 385.24, found 385.23.

Acknowledgements

We wish to thank the MIUR (Progetto Competitivo 2020 CMPT200224) and the UniPR for the financial support and CIM (Interdepartmental Measurements Centre) for NMR facilities. The Laboratorio di Strutturistica "M. Nardelli" of the University of Parma and Chiesi Farmaceutici SpA are thanked for the X-ray diffraction data collection. We warmly thank Dr. Claudio Oldani (Solvay) for a gift of Aquivion samples.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Levulinic acid • Heterogeneous catalysis • Sulfonic resins • Diphenolic acid esters • One-pot procedure

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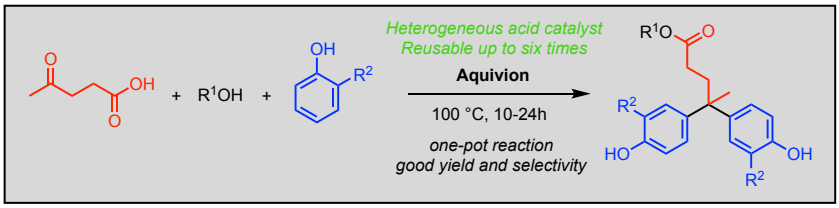
Entry for the Table of Contents



The synthesis of DPE, a valid candidate to replace bisphenol A, has been accomplished in good yield (78%) and selectivity (87%) by using Aquivion, a recyclable perfluorinated polymeric resins. The two step reaction, successfully applied to other alcohols and phenols, is carried out following a one-pot procedure and using phenols as solvent-reagent.