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Audrey Llevot, Etienne Grau, Stéphane Carlotti, Stéphane Grelier, Henri Cramail. Renewable (semi)aromatic polyesters from symmetrical vanillin-based dimers. *Polymer Chemistry*, 2015, 6 (33), pp.6058-6066. 10.1039/c5py00824g . hal-01366060

**HAL Id: hal-01366060**

**<https://hal.science/hal-01366060>**

Submitted on 27 Nov 2019

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# Renewable (semi)aromatic polyesters from symmetrical vanillin-based dimers

Audrey Llevot, Etienne Grau, Stéphane Carlotti, Stéphane Grelier and Henri Cramail

## Abstract

Two symmetrical biphenyl monomers derived from vanillin, a methylated divanillyl diol and a methylated dimethylvanillate dimer, were synthesized and employed as (co)monomers for the design of renewable (semi)aromatic polyesters. The reactivity in polytransesterification of these new monomers was investigated in bulk in the presence of various catalysts. The polytransesterification between methylated divanillyl diol and a series of bio-based diesters having different chemical structures led to amorphous thermoplastic polyesters with glass transition temperatures ranging from  $-5$  to  $139$  °C and thermal stability up to  $350$  °C.

## Introduction

Aromatic compounds constitute basic chemicals to manufacture everyday life items. Indeed, they play a key role in pharmaceuticals, perfumes, and dyestuff and polymer industries.<sup>1</sup> In polymeric backbones, aromatic units offer rigidity, hydrophobicity as well as fire resistance. For instance, aromatic polyesters, such as poly(ethyleneterephthalate)s (PET)s, have widespread commercial applications, especially in food packaging and textile field due to their good thermomechanical and barrier properties.<sup>2</sup>

In terms of sustainability, various studies have been recently carried out on the investigation of bio-based substitutes of aromatic petroleum-based compounds.<sup>3–6</sup> The main source of aromatic compounds, which can be found in Nature is lignin. However, despite extensive research studies, efficient recovering of aromatic products from lignin remains a challenge.<sup>7</sup> Nowadays, the only commercial process is the production of vanillin from lignosulfonates, formed as a by-product of the sulfite pulping industry.<sup>8,9</sup> Due to its carbonyl and phenolic groups, vanillin can be easily derivatized into interesting aromatic monomers.<sup>10,11</sup>

Pioneering work on the synthesis of polyesters from a vanillin derivative, *i.e.* vanillic acid, and exhibiting thermomechanical properties similar to those of PET was reported in 1955.<sup>12</sup> Vanillic acid was also used as a comonomer in the synthesis of a multitude of thermotropic polymers, which exhibit liquid crystal formation in the melt form. Due to their high order and aromatic structure, such polymers possess high mechanical strength at high temperature, extreme chemical resistance and inherent flame retardancy.<sup>13–23</sup> Recently, with the increasing interest on renewable resources, several bio-based polymers were produced from vanillin or its derivatives. For instance, Ma and coworkers copolymerized the diester obtained by the Williamson reaction of 1,4-dibromobutane and methylvanillate with vegetable oil-based polyols.<sup>24</sup> Meier and coworkers also reported the synthesis of 100% bio-based polymers from vanillin and vegetable oil derivatives by acyclic diene metathesis (ADMET) polymerization, thiol–ene addition and polycondensation.<sup>25</sup> Allais and coworkers synthesized bisphenols by chemo-enzymatic coupling of ferulic acid with different diols and polymerized these building blocks by polycondensation or ADMET polymerization.<sup>26–29</sup> Furthermore, Miller and coworkers used vanillin for the synthesis of renewable PET mimics.<sup>30,31</sup>

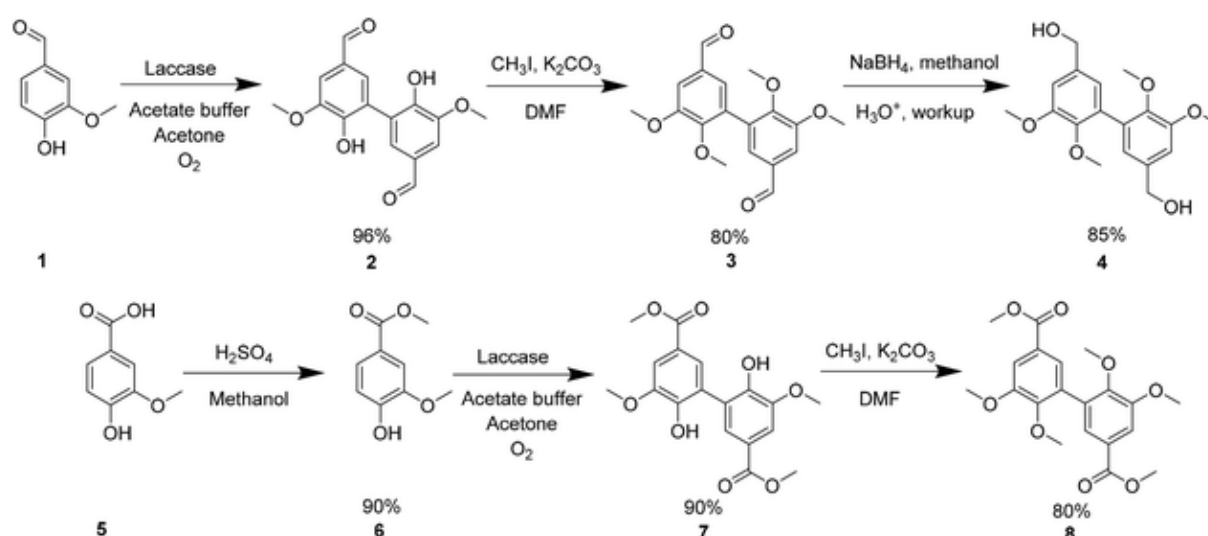
Divanillin was also employed as a building block for polymer synthesis. Razzaq and coworkers reported the synthesis of Schiff base polymers, exhibiting molar masses of around  $10000\text{ g mol}^{-1}$ , by the reaction of divanillin with alkyl diamines, as well as the synthesis of polyvanillin by reductive coupling of the aldehyde group of divanillin through electrochemical polymerization.<sup>32,33</sup> Divanillin was classically synthesized by oxidative phenol-coupling using iron(II) chloride ( $\text{FeCl}_3$ ) or iron(II) sulfate ( $\text{FeSO}_4$ ).<sup>34–39</sup> Nowadays, divanillin can be produced by enzymatic pathways. Several studies on the dimerization of vanillin employing horseradish peroxidase and hydrogen peroxide were reported.<sup>40–43</sup> The use of laccase as an enzyme catalyst for oxidative coupling also attracted attention because such approach avoids the use of hydrogen peroxide. Thus, Beifuss and colleagues employed laccase from *Trametes versicolor* to produce vanillidene derivative dimers with good yield and selectivity.<sup>44</sup> Also employing laccase from *Trametes versicolor* we recently developed an efficient enzymatic C–C coupling process – with a high yield and a high selectivity – yielding pure dimers of vanillin and some other phenol substrates.<sup>45</sup> Two of these symmetrical biphenyl monomers derived from vanillin, namely (i) a methylated divanillyl diol and (ii) a methylated dimethylvanillate dimer, have been tested in the present study as (co)monomers for the design of novel renewable (semi)aromatic polyesters. To this purpose, the

conditions of polycondensation have been optimized. Indeed, a series of polyesters were prepared by polytransesterification of methylated divanillyl diol with various diesters having different aliphatic or aromatic structures. The thermomechanical and thermal properties of the resulting bio-based thermoplastic polyesters were investigated.

## Results and discussion

### Synthesis of the monomers

The diol **4** and diester **8**, used as monomers in this study, were synthesized from vanillin, **1**, as a renewable resource (Scheme 1). On the one hand, vanillin was dimerized using a green process, employing a laccase from *Trametes versicolor* as the catalyst (see ESI, Fig. S1–S5†). The phenols of the obtained divanillin **2** were then methylated yielding methylated divanillin **3** (see ESI Fig. S6–S8†). Methylated divanillyl diol **4** was then prepared by the reduction of **3** (see ESI Fig. S9–S11†).<sup>45</sup>



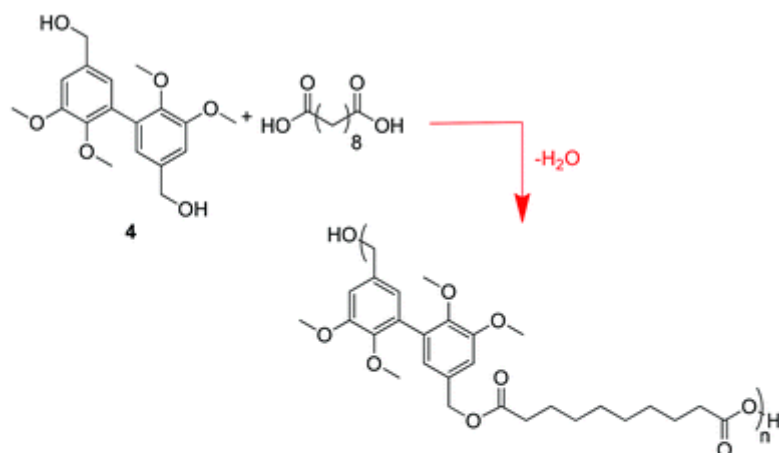
**Scheme 1** Synthesis of methylated divanillyl diol **4** and methylated dimethyl divanillate **8** from vanillin with their respective yields.

On the other hand, compound **5** is commercially available but can also be obtained by vanillin oxidation.<sup>46</sup> The carboxylic acid function of **5** was esterified into the methyl vanillate **6** (see ESI Fig. S12 and S13†). The latter was dimerized, employing the same enzymatic process as for the dimerization of vanillin, yielding the diester **7** (see the ESI, Fig. S14–S17†). Finally, the phenol groups of **7** were methylated yielding methylated dimethyl divanillate **8** (see ESI Fig. S18–S20†). The methylation of the phenol was performed before polymerization for two reasons: (i) the unprotected dimers were obtained as powders with lower degradation temperatures (around 200 °C) than the melting temperatures thus impeding their polymerization in bulk (melting temperatures of methylated dimers: around 30 °C) and, (ii) the methylation reaction prevents the phenolic moiety to get involved during the polymerization.

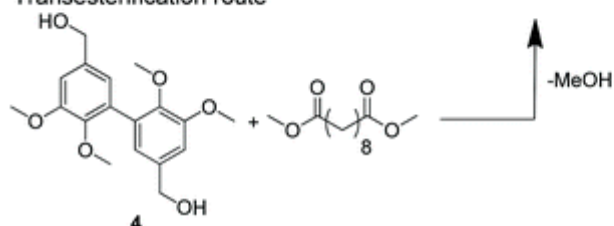
### Optimization of the bulk polymerization conditions

Polyesters can be produced either by an esterification reaction of diols and diacids or by a transesterification reaction between diols and diesters (Scheme 2). Preliminarily, the reaction of **4** with dimethylsebacate and sebacic acid was investigated to produce **P1** and **P1'**, respectively. Titanium butoxide,  $\text{Ti}(\text{OBu})_4$ , was employed as a catalyst at the concentration of 0.5 mol%, and the temperature of polymerization was set at 200 °C. **P1** and **P1'** were characterized by means of FTIR spectroscopy; the latter displays the same molecular structure (see Fig. S21†) but differs in terms of molar masses.

### Esterification route



### Transesterification route



**Scheme 2** Synthesis of polyester from vanillyl diol, **4**, and sebacic acid or dimethylsebacate.

Indeed, the molar masses of the resulting polyesters were determined by SEC analyses in DMF/DMSO 80/20 (w/w), using a PS calibration (Fig. S22<sup>†</sup>). **P1** exhibits a  $M_n$  of 65 000 g mol<sup>-1</sup> and a dispersity of 2.1 whereas **P1'** shows a  $M_n$  of 20 000 g mol<sup>-1</sup> and a dispersity of 1.7. While comparing the two routes, it appears that the transesterification method leads to polyesters with higher molar masses. This feature can be logically explained by the easier removal of methanol in comparison with water thus shifting more efficiently the reaction equilibrium towards the polymer. Consequently, all the polyesters described further in the study were synthesized by transesterification reaction.

Several polymerization reactions of methylated divanillyl diol **4** with dimethylsebacate were carried out employing different catalysts: triazabicyclodecene (TBD), titanium butoxide (Ti(OBu)<sub>4</sub>), zinc acetate (Zn(OAc)<sub>2</sub>), and dibutyltin oxide (DBTO). Molar masses of the resulting polyesters were compared with respect to the catalyst used (Table 1).

**Table 1** Synthesis of polyesters from methylated divanillyl diol, **4**, and methyl sebacate in the presence of different catalysts

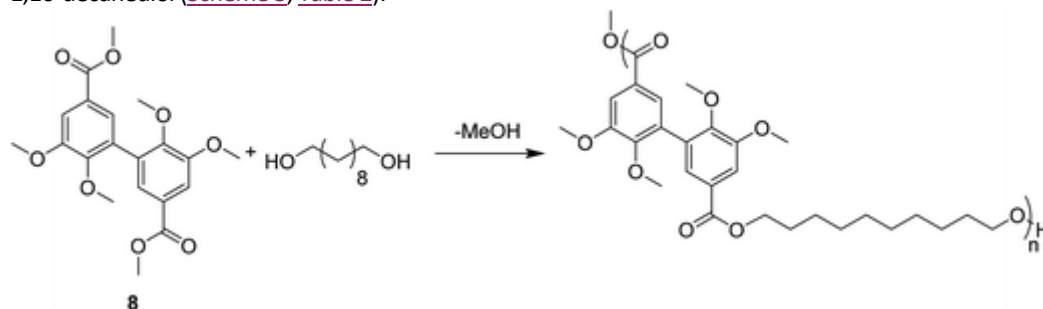
Catalyst/conc.	Polymerization temperature (°C)	$M_n^a$ (kg mol <sup>-1</sup> )	$\bar{D}^a$
TBD/10 mol%	120	33	1.6
Ti(OBu) <sub>4</sub> /0.5 mol%	200	65	2.1
Ti(OBu) <sub>4</sub> /2 mol%	200	30	2.0
Zn(OAc) <sub>2</sub> /2 mol%	200	43	1.8
DBTO/2 mol%	200	44	1.9

<sup>a</sup> Determined by SEC in DMF/DMSO 80/20.

Employing organocatalysts such as TBD generally requires higher catalyst loadings (10 mol%) in comparison with the transition metal-based catalysts (2 mol%) and lower polymerization temperature (120 °C) to avoid degradation/sublimation of the catalyst. In addition, a polyester sample was prepared with 0.5 mol% of Ti(OBu)<sub>4</sub>, in order to investigate the influence of the catalyst concentration on the polymerization. It was observed that polyester molar masses decrease with the loading of Ti(OBu)<sub>4</sub>. This reverse effect on the polymerization has already been observed in other studies reported in the literature, for titanium alkoxide in general.<sup>47,48</sup> Zn(OAc)<sub>2</sub> and DBTO presented lower catalytic activities, but the molar masses of the resulting polyesters remained high, at around 45 000 g mol<sup>-1</sup> and the

dispersity close to 2.0. TBD exhibited the lowest catalytic activity and produced polyesters with molar masses of 35 000 g mol<sup>-1</sup> and a dispersity of 1.6.

A similar study on the catalyst effect was conducted for the polymerization of methylated methyl vanillate **8** with 1,10-decanediol (Scheme 3, Table 2).



**Scheme 3** Synthesis of polyester from methylated dimethyl divanillate, **8**, and 1,10-decanediol.

**Table 2** Synthesis of polyesters from methylated dimethyl divanillate, **8**, and 1,10-decanediol in the presence of different catalysts

Catalyst/conc.	Polymerization temperature (°C)	$M_n^a$ (kg mol <sup>-1</sup> )	$\bar{D}^a$
TBD/10 mol%	120	3	1.2
Ti(OBu) <sub>4</sub> /0.5 mol%	200	20	1.8
Ti(OBu) <sub>4</sub> /2 mol%	200	11	1.3
Zn(OAc) <sub>2</sub> /2 mol%	200	3	1.1
DBTO/2 mol%	200	12	1.6

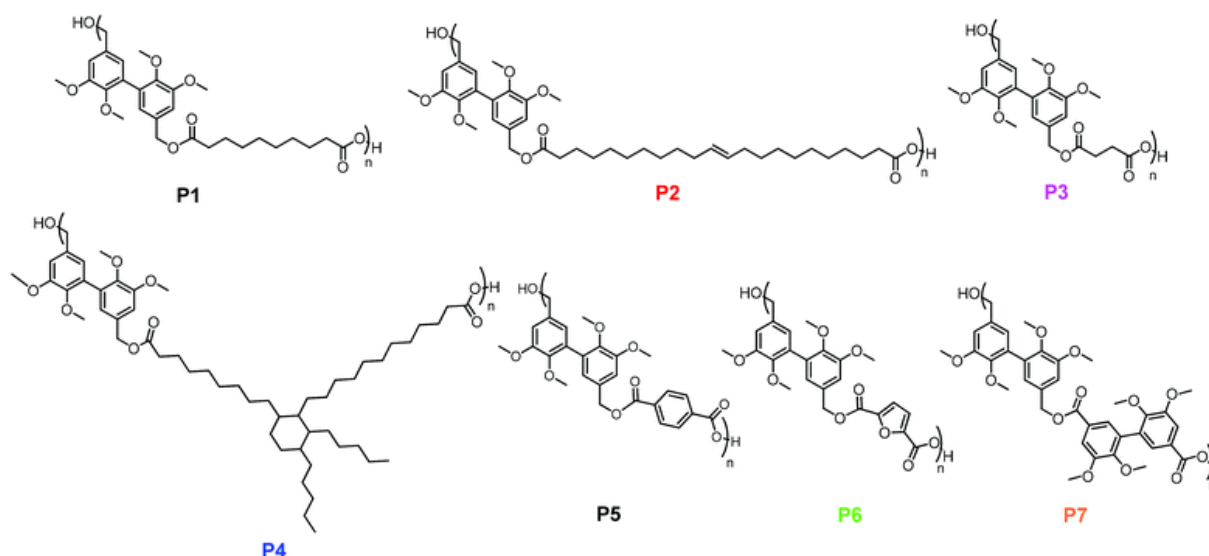
<sup>a</sup> Determined by SEC in DMF/DMSO 80/20.

In such a case, a low catalytic activity of TBD and Zn(OAc)<sub>2</sub> was observed. Indeed, polyesters with a molar mass of 3000 g mol<sup>-1</sup> and a dispersity in the range of 1.1 to 1.2 were obtained. As previously, the polymerization with 0.5 mol% of Ti(OBu)<sub>4</sub> afforded the highest molar mass, 20 000 g mol<sup>-1</sup>, with a dispersity of 1.8.

The polyesters synthesized by polytransesterification of methylated dimethyl divanillate, **8**, with 1,10-decanediol exhibited lower molar masses than the polyesters prepared by polytransesterification of methylated divanillyl diol, **4**, with dimethylsebacate. This feature shows that methylated dimethyl divanillate, **8**, is less reactive toward polycondensation than the divanillyl diol, **4**. Indeed, the first reaction involves an aromatic ester and an aliphatic primary alcohol, whereas the second one involves an aliphatic ester and a benzyl alcohol. Aromatic esters are stabilized due to electronic effects, which lead to a decrease of reactivity in comparison with aliphatic esters. Moreover, **4** and **8** show different steric hindrances. Indeed, the ester moiety of **4** is closer to the aromatic ring than the benzyl alcohol group of **8**; it is thus more hindered and logically less reactive.

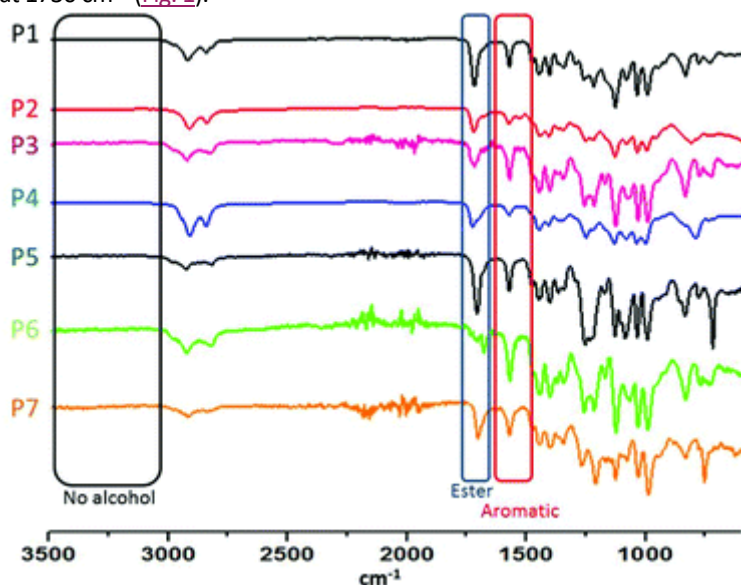
### Synthesis and characterization of (semi)-aromatic polyesters

A series of polyesters were thus synthesized in the bulk based on methylated divanillyl diol, **4**, and several diesters with aromatic, aliphatic or cycloaliphatic structures using as the catalyst Ti(OBu)<sub>4</sub> (0.5 mol%), in order to produce polymeric materials with a wide range of thermo-mechanical properties (Scheme 4). The copolymerization of **4** with dimethylsebacate, dimethylsuccinate and dimethyl-11-docosenoate produced polyesters **P1**, **P2** and **P3** with alternating aromatic and aliphatic sequences, the latter having different chain lengths. **P4** was synthesized by copolymerization of **4** with Pripol 1009 (a fatty acid dimer from Croda), named Pripol in the following. The copolymerization of **4** with dimethyl terephthalate and with its common bio-based substitute, 2,5-furandimethylester, led to the aromatic polyesters **P5** and **P6**, respectively. Finally, an aromatic polyester, 100% derived from vanillin, **P7**, was prepared by the polytransesterification of methylated divanillyl diol **4** and methylated dimethyl vanillate dimer **8**.



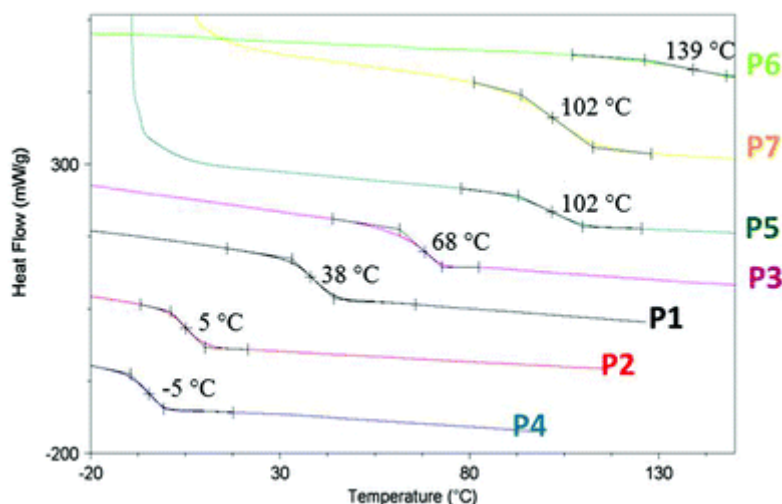
**Scheme 4** Structures of polyesters synthesized from methylated divanillyl diol **4** and diesters with different structures in the presence of  $\text{Ti}(\text{OBu})_4$ , 0.5 mol%.

Except for **P1** that was characterized above, all the polyesters (**P2–P7**) were not soluble in any solvent impeding their characterization through NMR spectroscopy and SEC analysis. Thus, the chemical structure of these polyesters was determined by FTIR analyses. FTIR revealed the success of the transesterification reaction, *i.e.* full conversion, by: (i) the disappearance of a broad peak between 3000 and 3500  $\text{cm}^{-1}$ , characteristic for the hydroxyl stretching, whereas the typical C-C stretching vibration of the aromatic ring was found at 1583  $\text{cm}^{-1}$ , and (ii) the presence of the C-O ester linkage at 1730  $\text{cm}^{-1}$  (Fig. 1).



**Fig. 1** FTIR spectra of polyesters synthesized from methylated divanillyl diol **4** with different diesters, **P1** to **P7**.

The thermomechanical properties of the so-formed polyesters were determined by DSC, TGA and DMA. DSC traces did not show any melting transition between  $-70$  and  $200\text{ }^{\circ}\text{C}$  (Fig. 2). The polyesters displayed a glass transition temperature ranging from  $-5$  to  $139\text{ }^{\circ}\text{C}$ , influenced by the structure of the co-monomer.

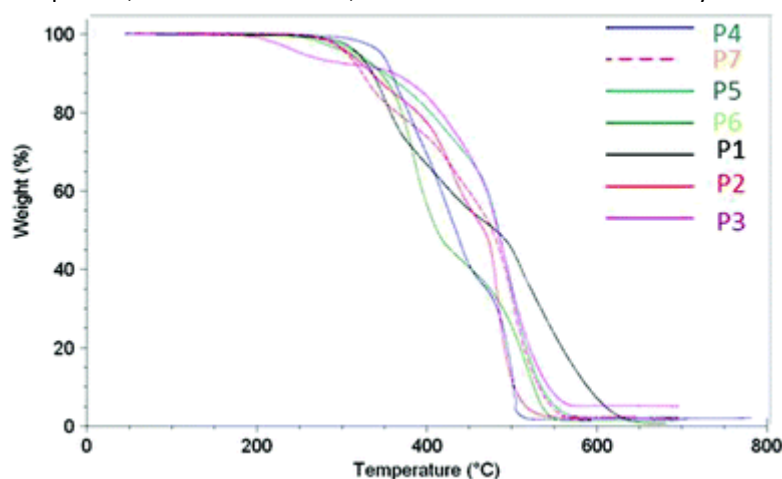


**Fig. 2** DSC traces (second heating cycle) of polyesters synthesized from methylated divanillyl diol **4** and different methyl diesters, **P1** to **P7**.

The absence of crystallinity of the polyesters so-formed is in agreement with the studies of Miller and coworkers who showed the influence of methoxy groups attached to the aromatic ring. Indeed, the authors showed that polyacetals synthesized from vanillin derivatives are semi-crystalline while polyacetals from syringaldehyde are amorphous.<sup>49</sup> Indeed, the presence of two methoxy groups attached to the aromatic rings induces a higher free volume. This special disposition hinders the mobility and packing of the polymer chains, resulting in amorphous polymers.

The  $T_g$  value depends on the molar mass and backbone flexibility of the polymer and also of the free volume. As expected, **P4**, which contains a ring with aliphatic dangling chains in the polymer backbone, exhibits the lowest glass transition temperature. The aromatic polyesters **P5**, **P6** and **P7**, exhibit the highest  $T_g$  of over 100 °C due to the inherent rigidity of the aromatic structures. In contrast, aliphatic chains give flexibility to the resulting polymers. Thus, the  $T_g$  of the semi-aromatic polymers **P2**, **P1** and **P3** ranged from 5 to 68 °C. Varying the aliphatic co-monomer structure allowed us to tailor the  $T_g$  of the resulting polyesters. In general, shorter aliphatic chains led to a polymer with higher  $T_g$ . Indeed, **P3** synthesized from the C4 diester exhibits a  $T_g$  higher than the one of **P2** synthesized from the C22 diester.  $T_g$  of **P5**, synthesized by copolymerization of methylated divanillyl diol, **4**, with dimethylterephthalate, and **P7**, synthesized by copolymerization of methylated divanillyl diol, **4**, with methylated dimethyl divanillate, **8**, are identical. Finally **P6**, synthesized by copolymerization of methylated divanillyl diol and 2,5-furandimethylester displays a remarkably high  $T_g$  of 139 °C. It is worth mentioning that differences in the  $T_g$  values of **P5**, **P6** and **P7** can also be attributed to differences in their molar masses.

TGA experiments were performed under air (Fig. 3). All the copolymers presented a 5 wt% degradation temperature of over 300 °C except for **P3** for which 5% weight loss occurred at 270 °C, a phenomenon that may be explained by the presence of residual impurities. **P4**, obtained by copolymerization of divanillyl diol and Pripol, surprisingly exhibited at 347 °C, the highest 5% degradation temperature (Table 3). Such a high degradation temperature may be explained by a cross-linked structure due to the presence of some trimers in the Pripol precursor. As a conclusion, all these biphenyl compounds, derived from vanillin, are excellent candidates for the synthesis of polyesters with high thermal stability.





**Fig. 3** TGA thermogram (under air atmosphere) of polyesters synthesized from methylated divanillyl diol **4** and different methyl diesters.

**Table 3** Thermo-mechanical properties of polyesters from methylated divanillyl diol, **4**, and different methyldiesters

Polyester	$T_g^a$ (°C)	$T_{d5\%}^b$ (°C)	$T_\alpha^c$ (°C)	$E'$ (GPa)
<b>P1</b>	38	319	42	8.1
<b>P2</b>	5	308	13	2.0
<b>P3</b>	68	270	72	5.1
<b>P4</b>	−5	347	8	0.1
<b>P5</b>	102	310	—	2.0
<b>P6</b>	139	342	—	1.4
<b>P7</b>	102	305	—	1.3

a Determined by DSC second heating cycle. b Temperature of 5% degradation determined by DMA. c Determined by DMA 3 point-bending mode.

The thermo-mechanical properties of the polyesters were also investigated by dynamical mechanical analyses (DMA) (see ESI, Fig. S23<sup>†</sup>), performed on bar samples in a 3-point bending mode (Table 3). In agreement with DSC data, the decrease of the storage modulus was observed first for **P4**, then for the semi-aromatic polyesters **P2**, **P1** and **P3** and finally for the aromatic polyesters **P6**, **P5** and **P7**. The storage modulus in the glassy state ( $E'$ ) of the semi-aromatic polyesters increases when the length of the aliphatic chain decreases, *i.e.* **P4** < **P2** < **P1**. **P3** and **P1** exhibit similar high storage modulus, in the range of 5–8 GPa. Unfortunately, the shape and thickness of the barrels could not be well-defined, impeding in most cases a precise measurement of the elastic modulus and  $T_\alpha$  value.

## Conclusion

In conclusion, novel bio-based (semi)aromatic polyesters from original symmetrical vanillin-based dimers were synthesized. The experimental polymerization conditions were optimized in the bulk by polycondensation of the methylated divanillyl diol/dimethylsebacate system. Titanium butoxide at a loading of 0.5 mol% was proven to produce the polyesters with the highest molar masses of up to 65 000 g mol<sup>−1</sup>, that exhibit a  $T_g$  of 38 °C, a storage modulus of 8.1 GPa and a  $T_{d5\%}$  of 319 °C. The same conditions were applied to the polymerization of methylated divanillyl diol with a series of bio-sourced diesters. Varying the structure of the diester allowed us to tailor the thermomechanical properties of the resulting polyesters, that all exhibit an amorphous morphology with a  $T_g$  ranging from −5 to 139 °C. The thermal stability of such (semi)aromatic polyesters is high with a 5% weight loss temperature over 300 °C. Such a new family of symmetrical aromatic monomers from vanillin clearly opens new perspectives in the challenging field of bio-based polymers. In addition, greener routes to phenol methylation are still to be investigated together with the design of polyesters bringing free phenol functions, the latter giving additional properties to such materials.

## Experimental section

### Material

2,5-Furandicarboxylic acid (98.0%), 1,10-diaminodecane, and dimethylsebacate (97.0%) were supplied by TCI Europe. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), zinc acetate (99.999%), sodium acetate (99%), acetic acid (99.7%), laccase from *Trametes versicolor*, sulphuric acid (95%), iodomethane (99%), dibutyltin oxide (98%), succinic acid (99%), dimethyl succinate (98%), and dimethyl terephthalate (98%) were purchased from Sigma Aldrich. Titanium butoxide (99%) was bought from Fisher. Pripol was supplied by Croda. Sodium borohydride (98%) and vanillic acid (98%) were bought from Alfa Aesar. Potassium carbonate (99%) and terephthalic acid (98%) were supplied by Prolabo. All products and solvents (reagent grade) were used as received, unless mentioned explicitly.



## Instrumentations

All NMR experiments were performed at 298 K on a Bruker Avance 400 spectrometer operating at 400 MHz, in DMSO. Infrared spectra were obtained on a Thermo Scientific Nicolet iS10 spectrometer using the attenuated total reflection (ATR) mode. HPLC was performed using a Spectra system instrument fitted with a Phenomenex Luna 5 $\mu$  C18100A column and compounds were detected with a Sedere Sedex 85 LT ELSD detector at 40 °C ( $G = 4$ , filter OFF). These analyses were performed in acetonitrile at a flow rate of 1 mL min<sup>-1</sup>. The spectra were acquired using 16 scans. Size exclusion chromatography (SEC) analyses were performed in DMSO/DMF (20/80) (80 °C) on a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian with a series of three columns from PLgel (PLgel 5  $\mu$ m Guard (guard column 7.5 mm ID  $\times$  5.0 cm  $L$ ); PLgel 5  $\mu$ m MIXED-D (7.5 mm ID  $\times$  30.0 cm  $L$ ) and PLgel 5  $\mu$ m MIXED-D (7.5 mm ID  $\times$  30.0 cm  $L$ )). The elution of the filtered samples was monitored using simultaneous refractive index and UV detection. The elution times were converted to molar mass using a calibration curve based on low dispersity ( $M_w/M_n$ ) polystyrene (PS) standards. Differential Scanning Calorimetry (DSC) measurements were performed on DSC Q100 (TA Instruments). The sample was heated from -70 °C to 200 °C at a rate of 10 °C min<sup>-1</sup>. Consecutive cooling and second heating run were also performed at 10 °C min<sup>-1</sup>. The glass transition temperatures were calculated from the second heating run, the reported temperature is the value at the midpoint. Thermogravimetric analyses (TGA) were performed on a TGA-Q50 system from TA Instruments at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen or an air atmosphere as mentioned in the manuscript; DMA RSA 3 (TA Instruments). The sample temperature was modulated from -80 °C to 220 °C, depending on the sample at a heating rate of 5 °C min<sup>-1</sup>. The measurements were performed in a 3-point bending mode at a frequency of 1 Hz, an initial static force varying between 0.1 and 0.5 N and a strain sweep of 0.1%.

## Experimental procedure

### Synthesis of methylvanillate (6)

Vanillic acid (5) (15.0 g, 0.09 mol) was dissolved in methanol (75 mL). Sulfuric acid (2.1 mL) was added and the mixture was stirred and warmed to reflux for 8 h. After the evaporation of methanol, the solid was dissolved in ethylacetate (60 mL), washed with a NaHCO<sub>3</sub> solution (30 mL), water (twice) and brine (once). The organic phase was evaporated under reduced pressure. Yield: 90%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)):  $\delta$  7.45 (m, 2H, Ar), 6.88 (d, 1H, Ar), 3.81 (s, 3H, OCH<sub>3</sub>), 3.79 (s, 3H, OCH<sub>3</sub> ester).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)):  $\delta$  166.03 (OCH<sub>3</sub> ester), 151.22 (Ar-C), 147.20 (Ar-C), 123.38 (Ar-C), 120.30 (Ar-C), 115.13 (Ar-C), 112.42 (Ar-C), 55.27 (OCH<sub>3</sub>), 51.60 (OCH<sub>3</sub> ester).

### General procedure for dimerization: synthesis of divanillin (2) and dimethyl divanillate (7)

A solution of phenol (1) or (6) (1.5 g) in acetone (20 mL) was added to NaOAc buffer (180 mL, 0.1 M, pH 5.0). The solution was saturated in O<sub>2</sub> for 5 min. Laccase from *Trametes versicolor* (20 U, 12.4 mg) was added and the reaction was stirred at room temperature for 24 h. The precipitate was filtered off the solution and the product was dried overnight at 80 °C under vacuum.

#### Divanillin (2): yield: 96%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)):  $\delta$  9.85 (s, CHO), 7.50 (s, 2H, Ar), 4.00 (s, OCH<sub>3</sub>).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)):  $\delta$  191.04 (CHO), 150.70 (Ar-C), 147.95 (Ar-C), 128.30 (Ar-C), 127.69 (Ar-C), 124.52 (Ar-C), 109.10 (Ar-C), 55.88 (OCH<sub>3</sub>).

#### Dimethyl divanillate (7): yield: 90%, $T_d = 200$ °C, no $T_m$

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)):  $\delta$  9.60 (s, 2H, HO), 7.46 (s, 4H, Ar), 3.90 (s, 6H, OCH<sub>3</sub>), 3.80 (s, 6H, OCH<sub>3</sub> ester).

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  166.04 ( $\text{OCH}_3$  ester), 148.60 (Ar–C), 147.27 (Ar–C), 125.25 (Ar–C), 123.93 (Ar–C), 119.21 (Ar–C), 110.89 (Ar–C), 55.97 ( $\text{OCH}_3$ ), 51.75 ( $\text{OCH}_3$  ester).

#### General procedure for phenol methylation of (2) and (7): synthesis of methylated divanillin (3) and methylated dimethyl vanillate (8)

Bisphenol (2) or (7) (7.9 g of (2) or 9.4 g of (7), 26 mmol) was dissolved in DMF (120 mL). Potassium carbonate (15.2 g, 110 mmol) was added before a slow addition of iodomethane (9.6 mL, 158 mmol). After 15 h of stirring at 80 °C, the mixture was filtered and the resulting solution was poured into cold water. The methylated compound which precipitated was filtered off and dried under vacuum.

##### Methylated divanillin (3): yield: 80%

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  9.94 (s, CHO), 7.58 (s, 2H, Ar), 7.55 (s, 2H, Ar), 3.95 (s,  $\text{OCH}_3$ ), 3.68 (s,  $\text{OCH}_3$ ).

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  191.83 (CHO), 152.80 (Ar–C), 151.21 (Ar–C), 131.90 (Ar–C), 131.58 (Ar–C), 125.96 (Ar–C), 111.14 (Ar–C), 60.47 ( $\text{OCH}_3$ ), 55.93 ( $\text{OCH}_3$ ).

##### Methylated dimethyl divanillate (8): yield: 80%, $T_d = 215\text{ °C}$ , $T_m = 33\text{ °C}$

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  7.59 (s, 2H, Ar), 7.41 (s, 2H, Ar), 3.92 (s,  $\text{OCH}_3$ ), 3.84 (s,  $\text{OCH}_3$ ), 3.62 (s,  $\text{OCH}_3$ ).

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  165.63 ( $\text{OCH}_3$  ester), 152.16 (Ar–C), 149.95 (Ar–C), 131.19 (Ar–C), 124.44 (Ar–C), 123.81 (Ar–C), 112.43 (Ar–C), 60.38 ( $\text{OCH}_3$ ), 55.7.

#### Synthesis of methylated divanillyl diol (4)

Methylated divanillin (3) (6.6 g, 20 mmol) was dissolved in ethanol (100 mL). The flask was placed in an ice bath and sodium borohydride (3.6 g, 100 mmol) was added slowly. Then the mixture was stirred at room temperature for 30 min. Water (45 mL) was added to stop the reaction and the solution was acidified with HCl to pH 7 and warmed for 5 min at 50 °C. The solvent was evaporated; the resulting solid was solubilized in dichloromethane and washed 3 times with water. Yield: 85%.  $T_d = 230\text{ °C}$ ,  $T_m = 26\text{ °C}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  6.99 (s, 2H, Ar), 6.67 (s, 2H, Ar), 5.15 (t, 2H, OH), 4.47 (d, 4H,  $\text{CH}_2\text{OH}$ ), 3.83 (s,  $\text{OCH}_3$ ), 3.51 (s,  $\text{OCH}_3$ ).

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  151.93 (Ar–C), 144.86 (Ar–C), 137.52 (Ar–C), 132.14 (Ar–C), 120.27 (Ar–C), 110.20 (Ar–C), 62.69 ( $\text{CH}_2\text{OH}$ ), 59.83 ( $\text{OCH}_3$ ), 55.53 ( $\text{OCH}_3$ ).

#### Polyester synthesis

Methylated divanillyl diol (1 equivalent) and diacid or diester (1 equivalent) were solubilized and stirred in a minimum amount of THF. THF was then evaporated yielding a homogeneous mixture. The mixture was stirred at 160 °C for 2 h under nitrogen flow and then at 200 °C under vacuum for 6 h in the presence of 2 mol% of the catalyst (titanium butoxide, zinc acetate or dibutyltin oxide) or in the presence of 0.5 mol% of titanium butoxide or stirred at 120 °C for 24 h in the presence of 10 mol% of TBD.

#### Acknowledgements

The authors thank Emmanuel Ibarboure and Gerard Dimier for the DMA analyses and ANR-10-EQPX-16 XYLOFOREST. This study was financially supported by the University of Bordeaux-1, IPB and CNRS.

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## Supporting Information

# Renewable (semi)aromatic polyesters from symmetrical vanillin-based dimers

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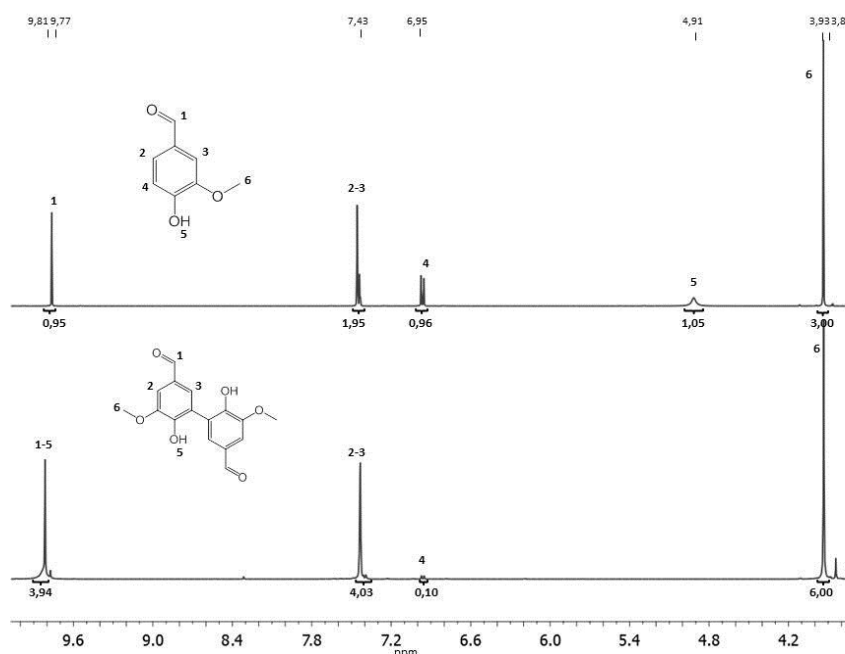
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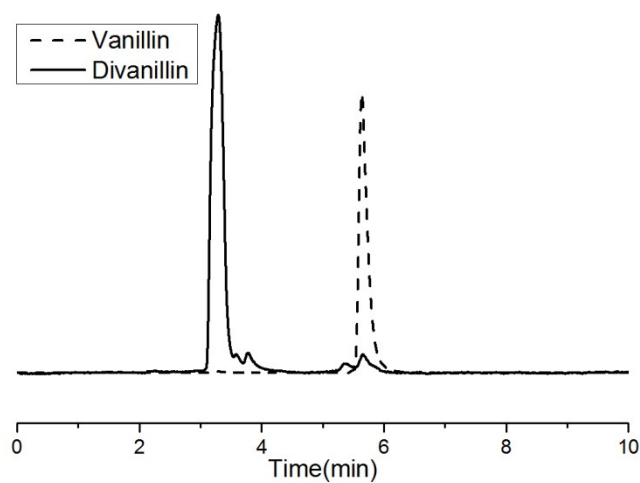
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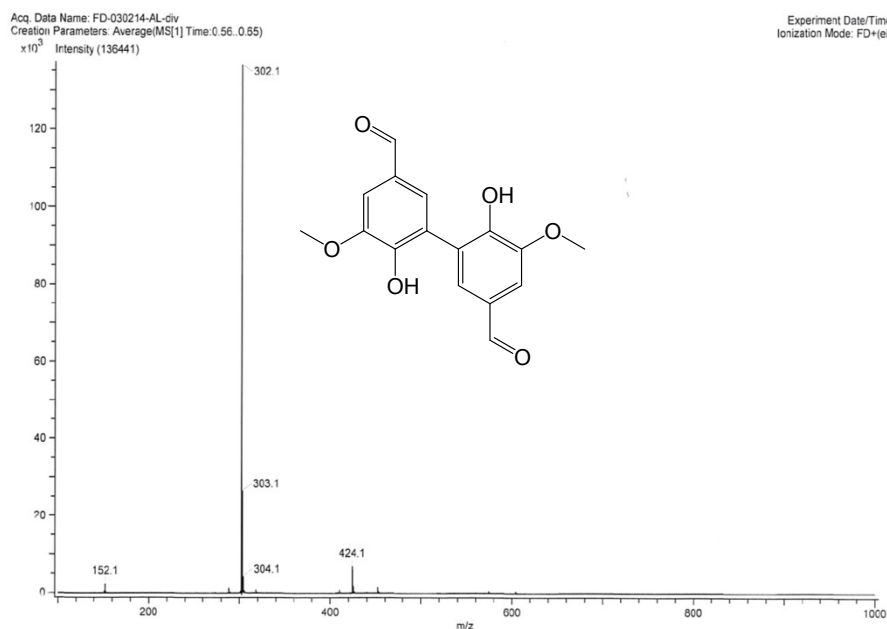
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**Figure S 1:  $^1\text{H}$  NMR spectra of vanillin 1 (top) and divanillin 2 (bottom) in DMSO at room temperature**



**Figure S 2: HPLC profile of Vanillin 1 (dashed line) and Divanillin 2 (straight line), using a C18 grafted silica column in acetonitrile with a UV detector**



**Figure S 3: Mass spectrum of divanillin 2 ionized by electronic impact, direct introduction**



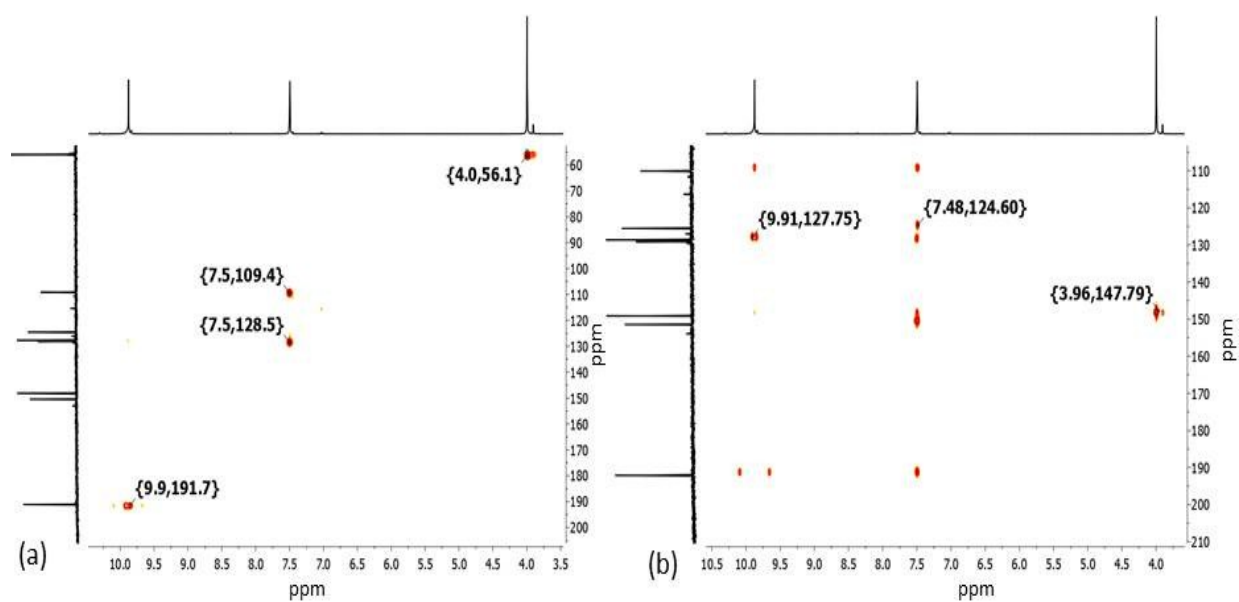


Figure S 4: HSQC (a) and HMBC (b) spectra of divanillin in DMSO, at room temperature.

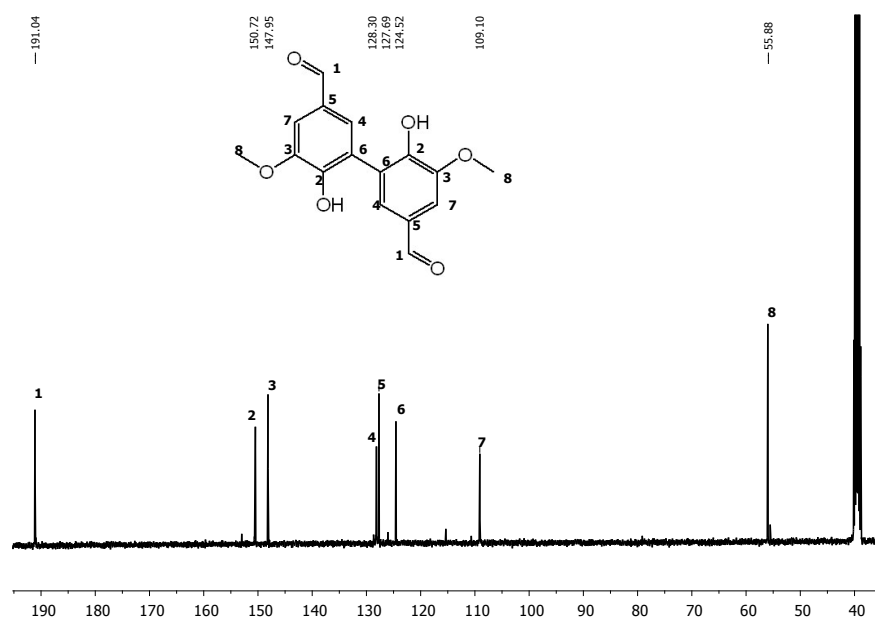


Figure S 5:  $^{13}\text{C}$  NMR spectrum of Divanillin 2 in DMSO

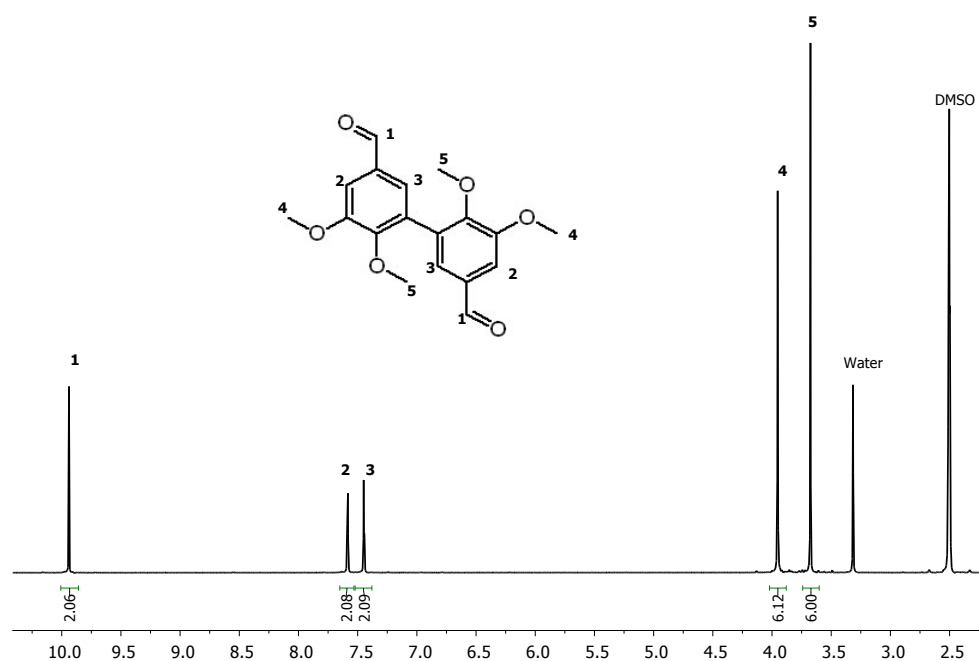


Figure S 6:  $^1\text{H}$  NMR spectrum of methylated divanillin 3 in DMSO

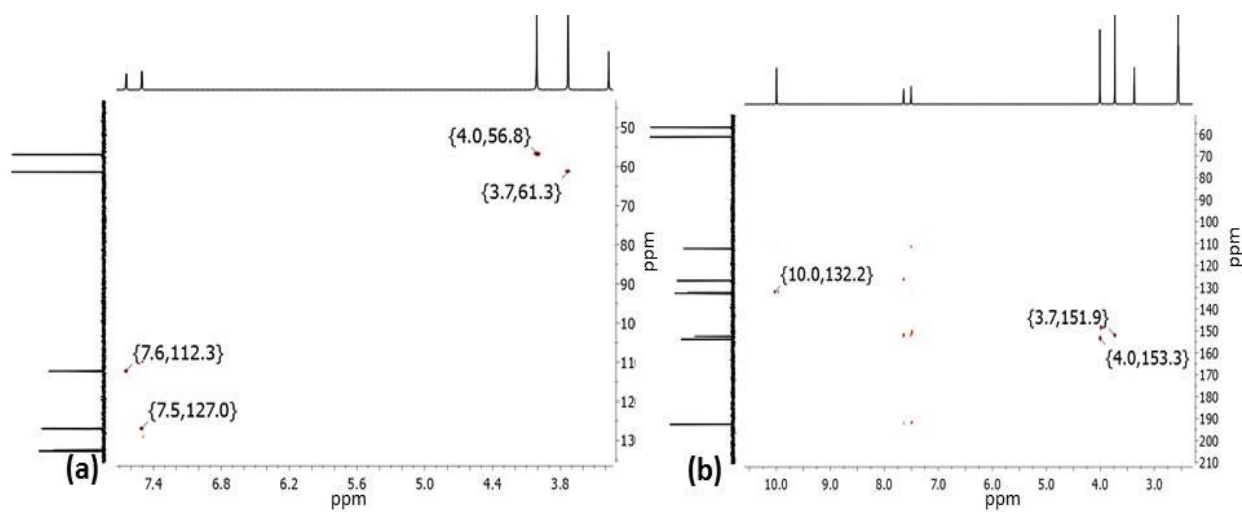


Figure S 7: HSQC (a) and HMBC (b) spectra of methylated divanillin 3 in DMSO, at room temperature.

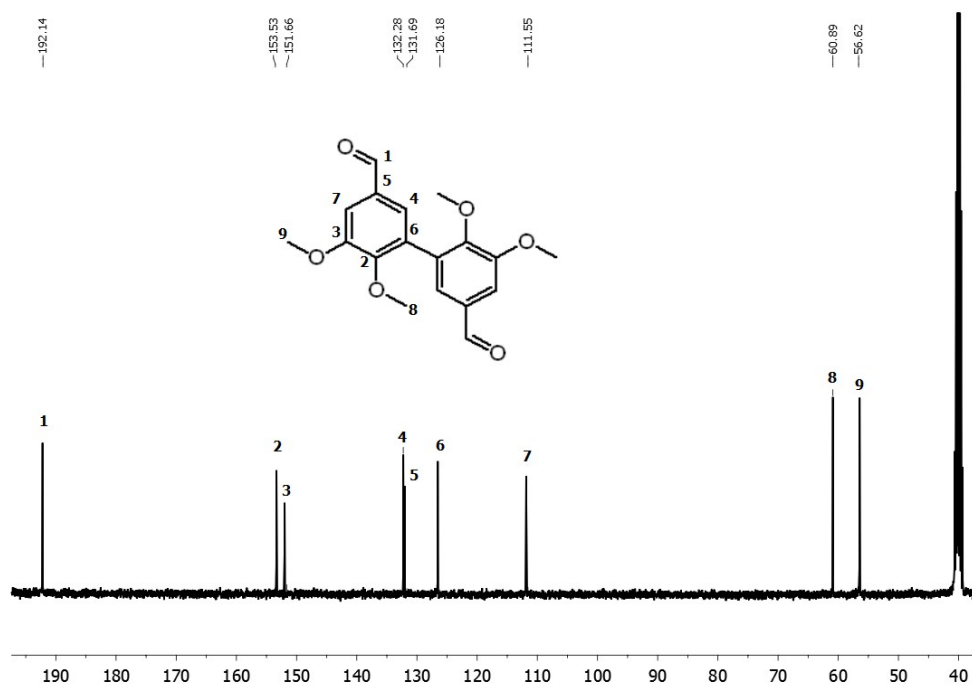


Figure S 8:  $^{13}\text{C}$  NMR spectrum of methylated divanillin 3 in DMSO

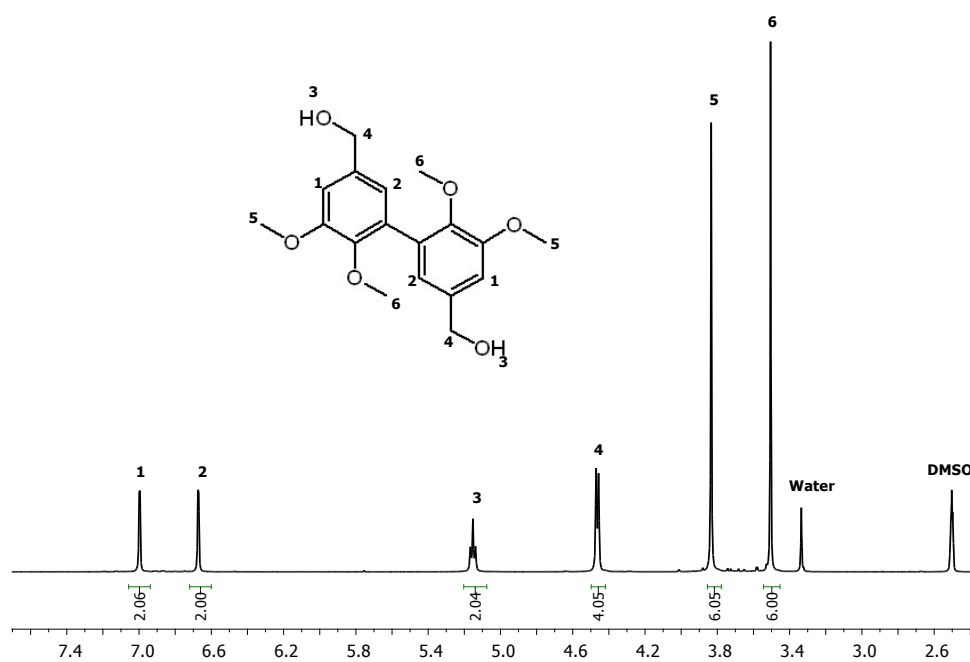


Figure S 9:  $^1\text{H}$  NMR spectrum of methylated divanillyl diol 4 in DMSO

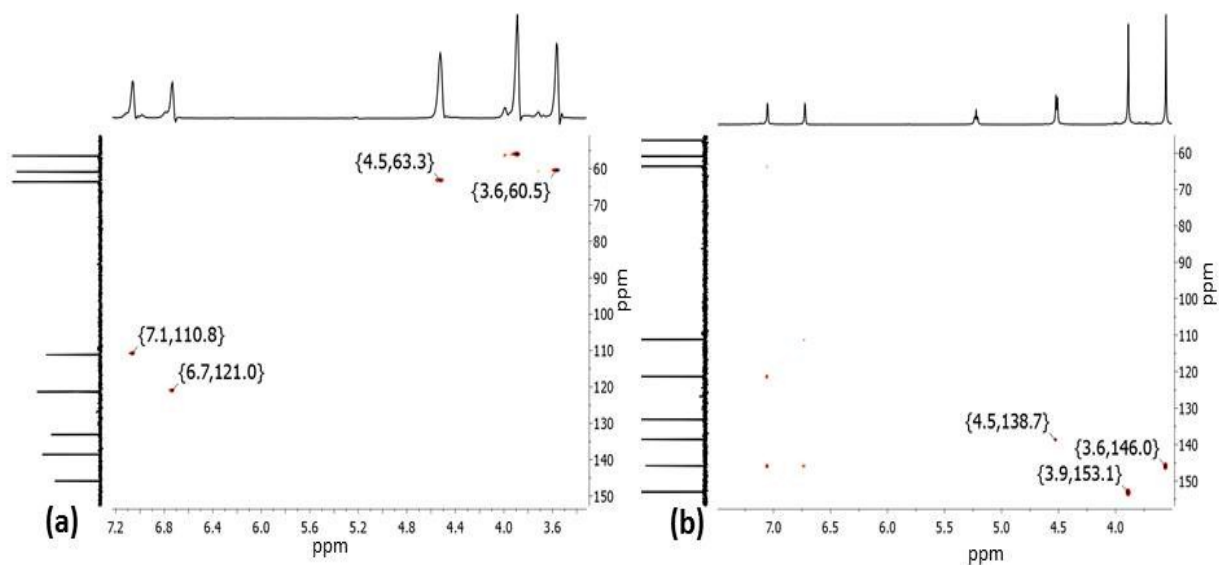


Figure S 10: HSQC (a) and HMBC (b) spectra of methylated diol 4 in DMSO.

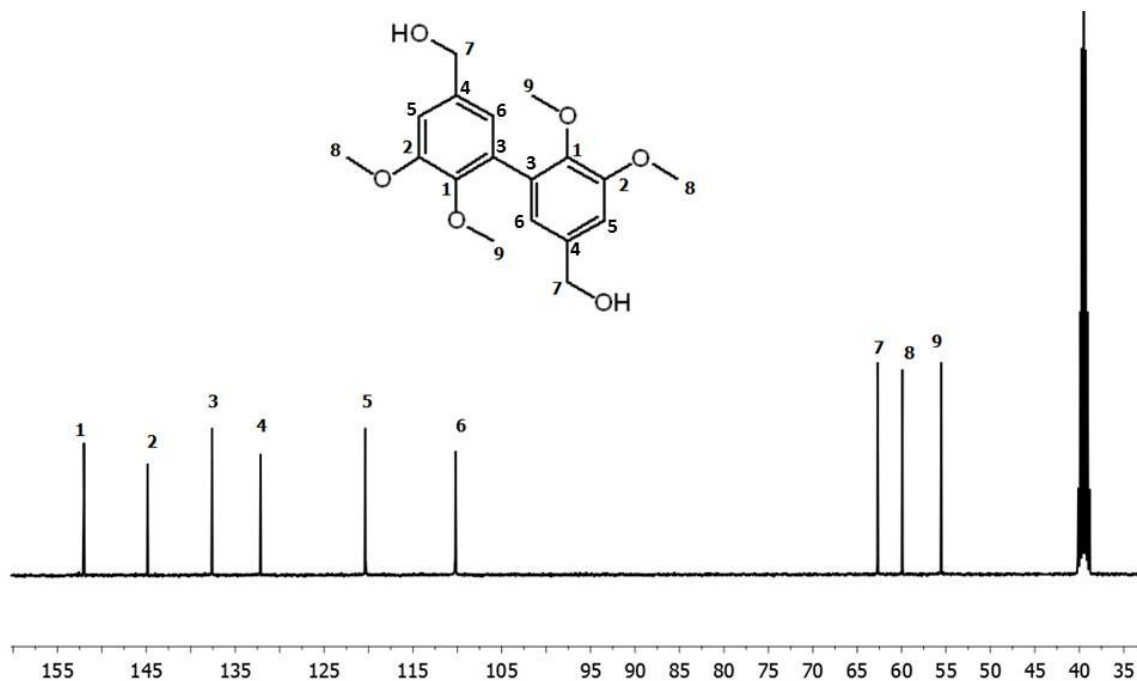


Figure S 11:  $^{13}\text{C}$  NMR spectrum of methylated divanillyl diol 4 in DMSO

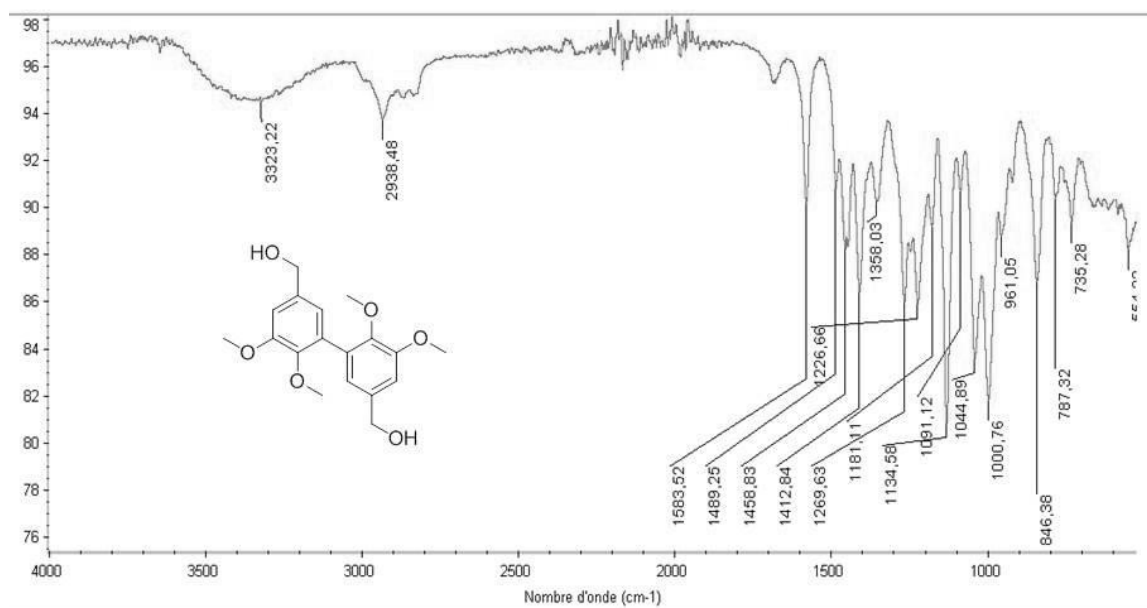


Figure S 12: FTIR spectrum of methylated divanillyl diol 4

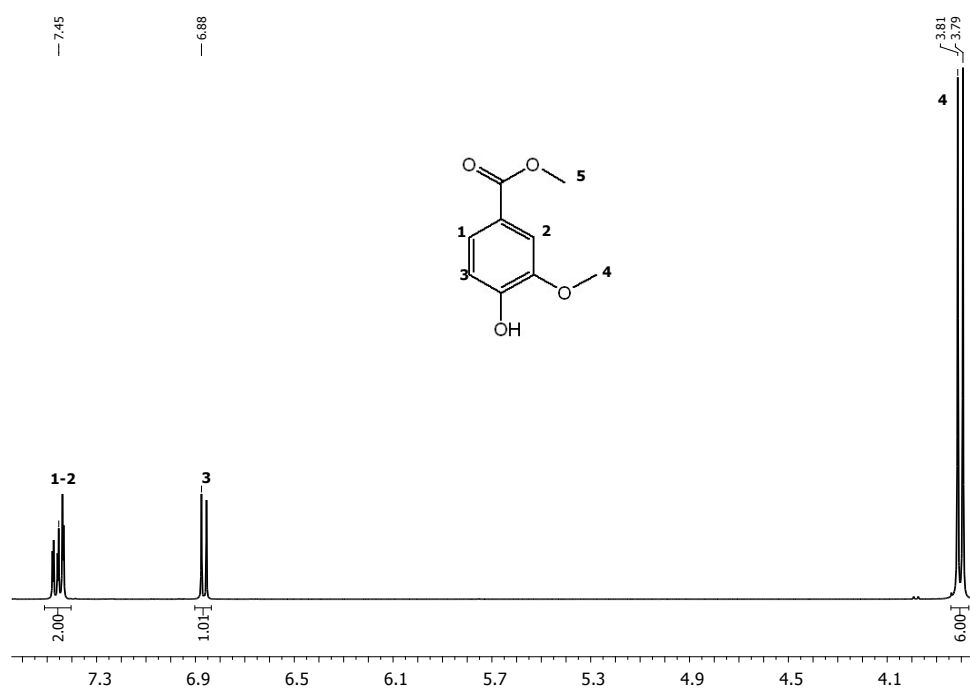


Figure S 13: <sup>1</sup>H NMR spectrum of methyl vanillate 6 in DMSO, at room temperature.

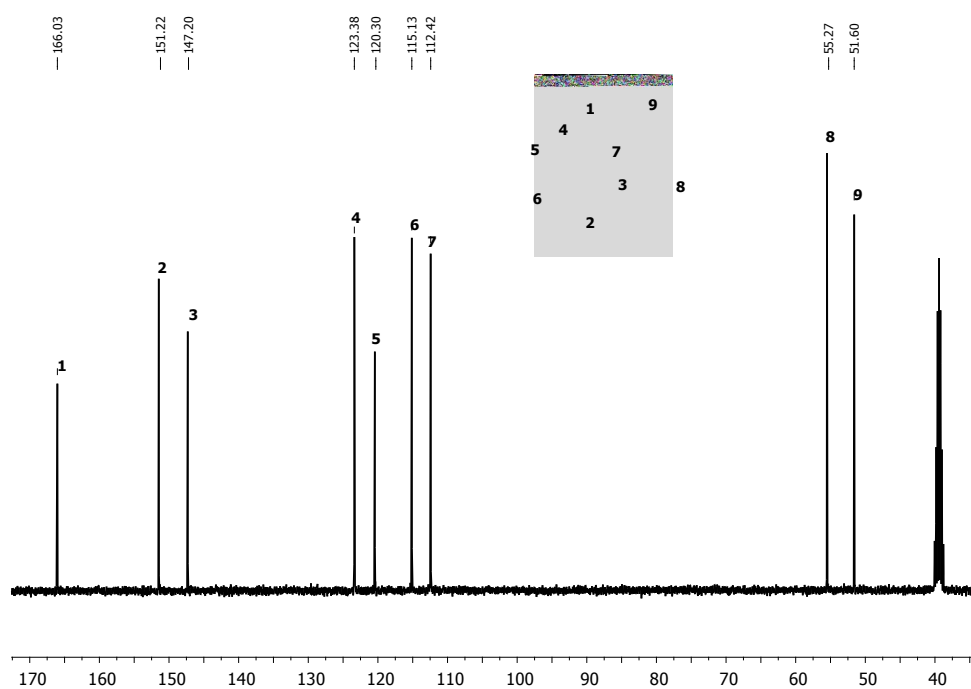


Figure S 14:  $^{13}\text{C}$  NMR spectrum of methyl vanillate 6 in DMSO, at room temperature.

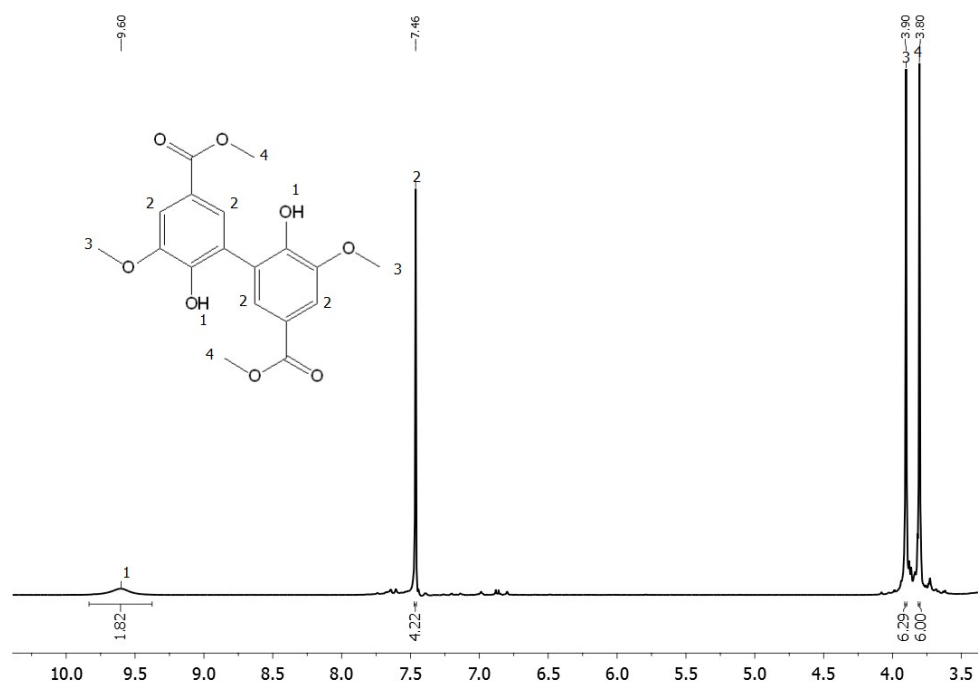


Figure S 15:  $^1\text{H}$  NMR spectrum of dimethyl divanillate 7 in DMSO

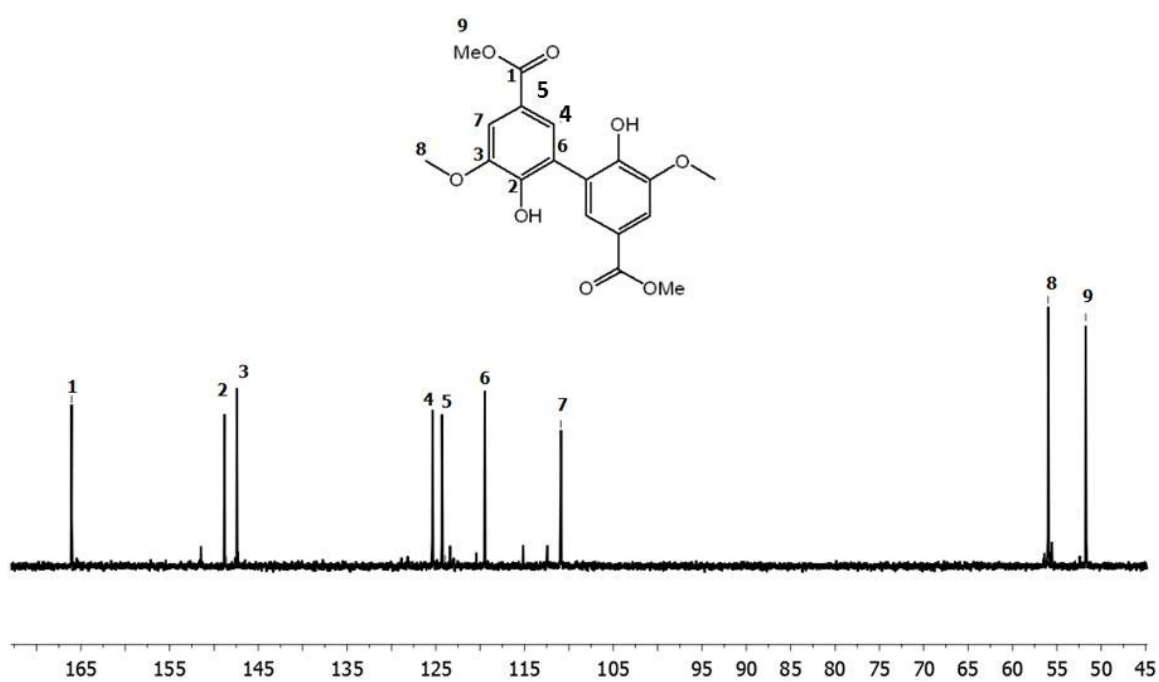


Figure S 16:  $^{13}\text{C}$  NMR spectrum of dimethyl divanillate 7 in DMSO



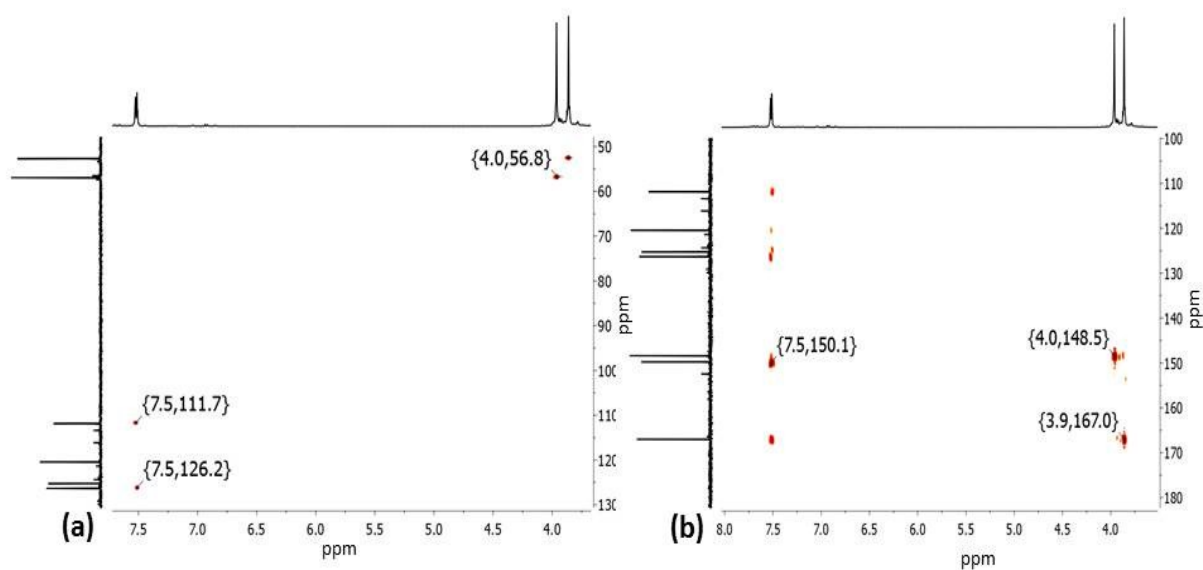


Figure S 17: HSQC (a) and HMBC (b) spectra of methyl vanillate dimer 7 in DMSO, at room temperature.

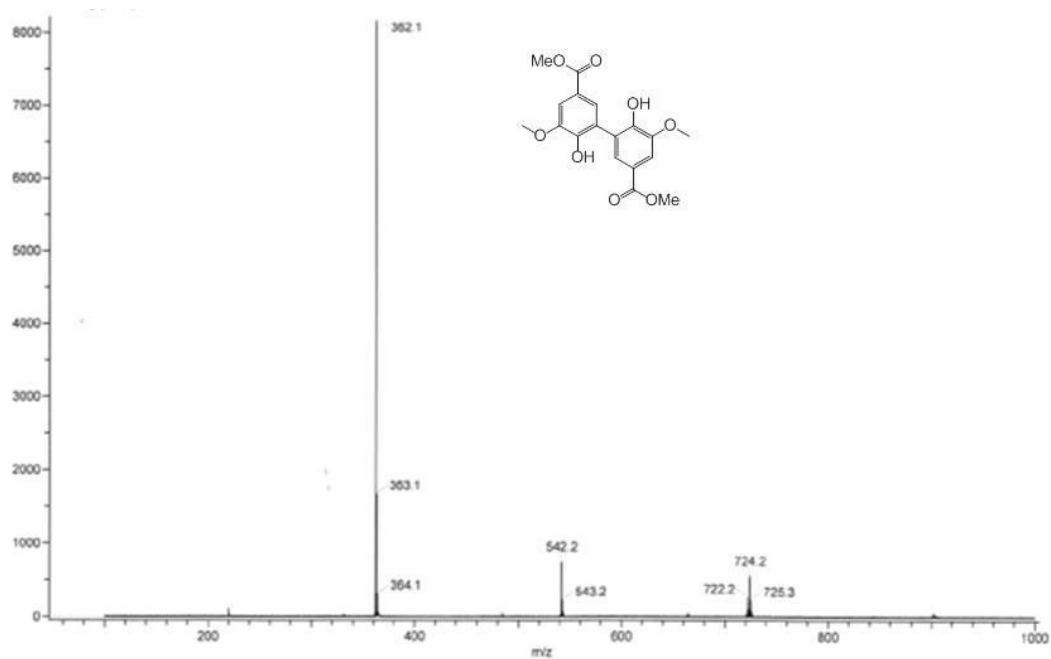


Figure S 18: Mass spectrum of dimethyl divanillate 7 ionized by electronic impact, direct introduction

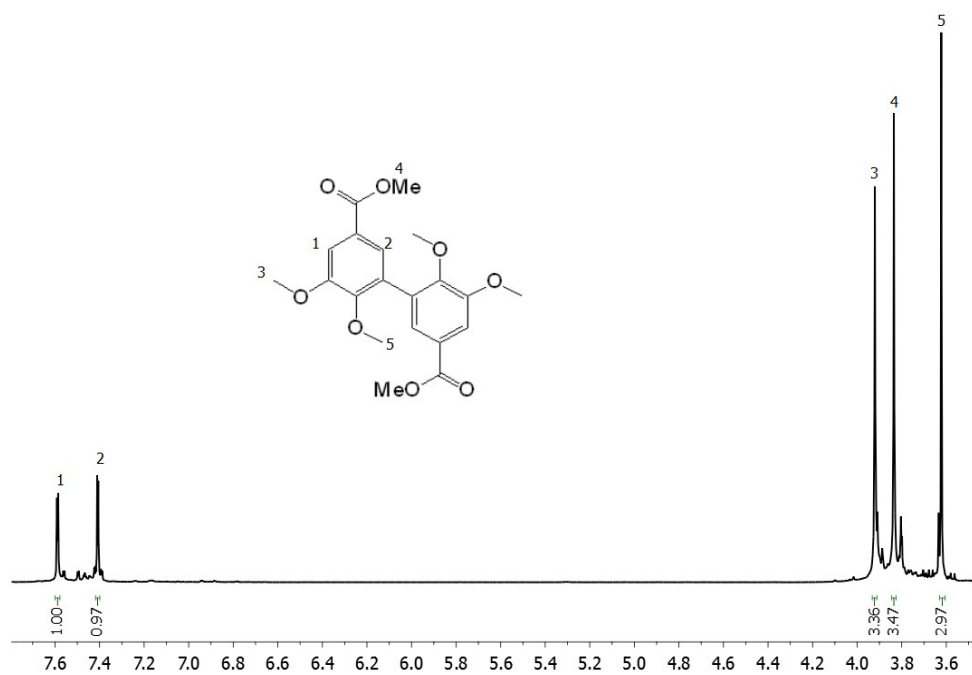


Figure S 19:  $^1\text{H}$  NMR spectrum of methylated dimethyl divanillate 8 in DMSO

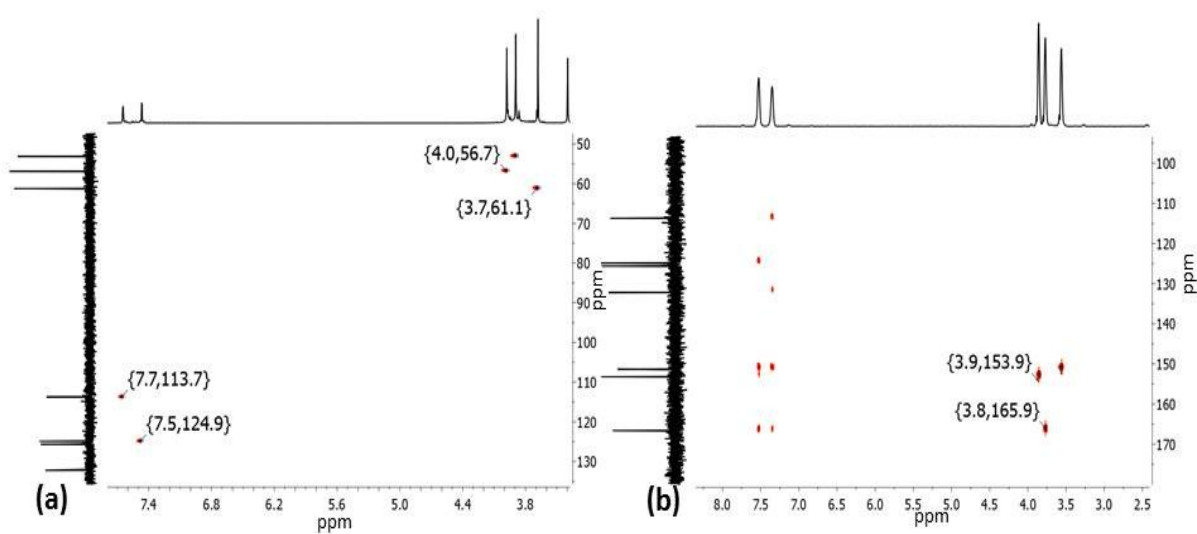


Figure S 20: HSQC (a) and HMBC (b) spectra of methylated diester 8 in DMSO.

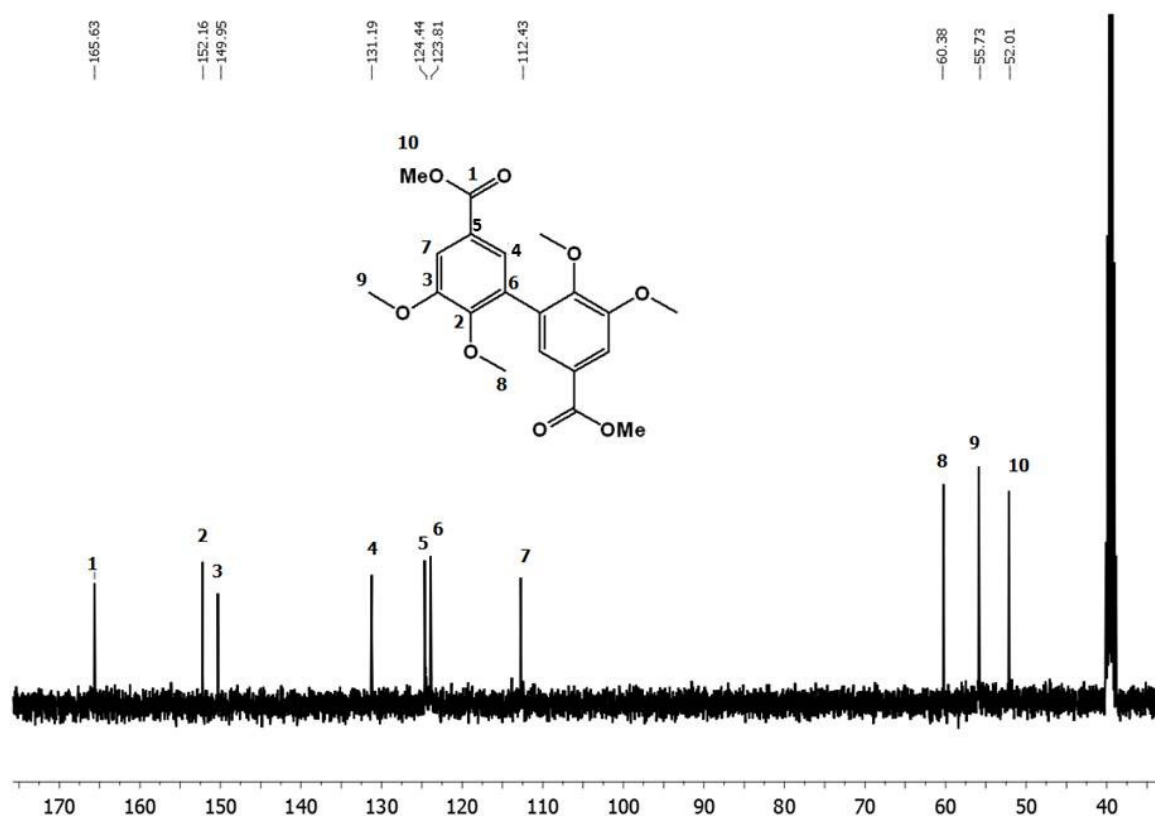


Figure S 21: <sup>13</sup>C NMR spectrum of methylated dimethyl divanillate 8 in DMSO

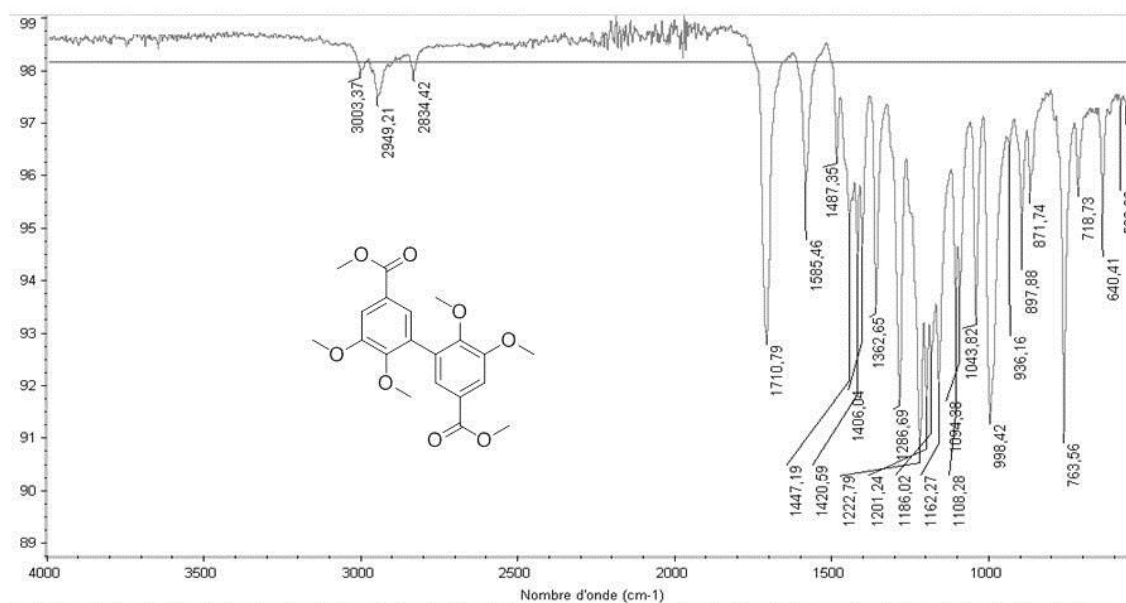


Figure S 22: FTIR spectrum of methylated dimethyl divanillate 8

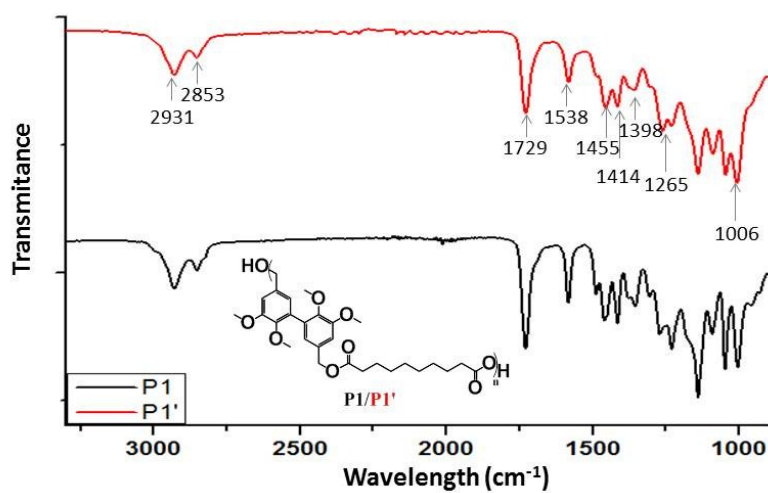


Figure S 23: FTIR spectra of methylated divanillyl diol/dimethylsebacate polyester, P1, and of divanillyl diol/sebacid acid polyester, P1'

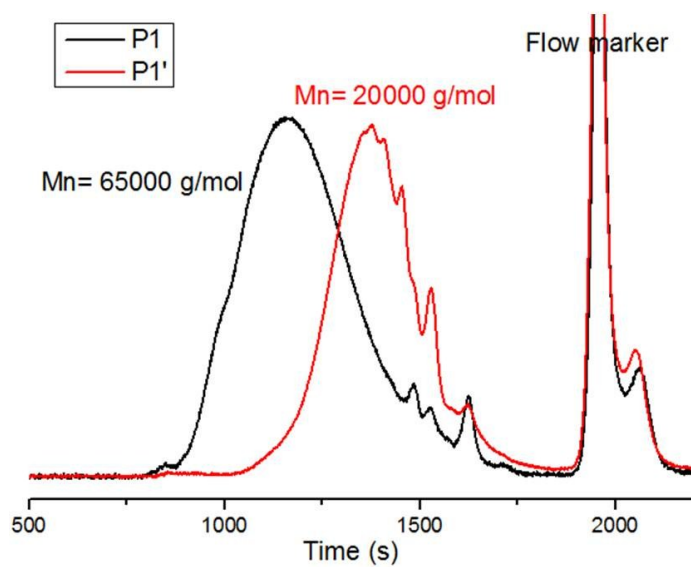
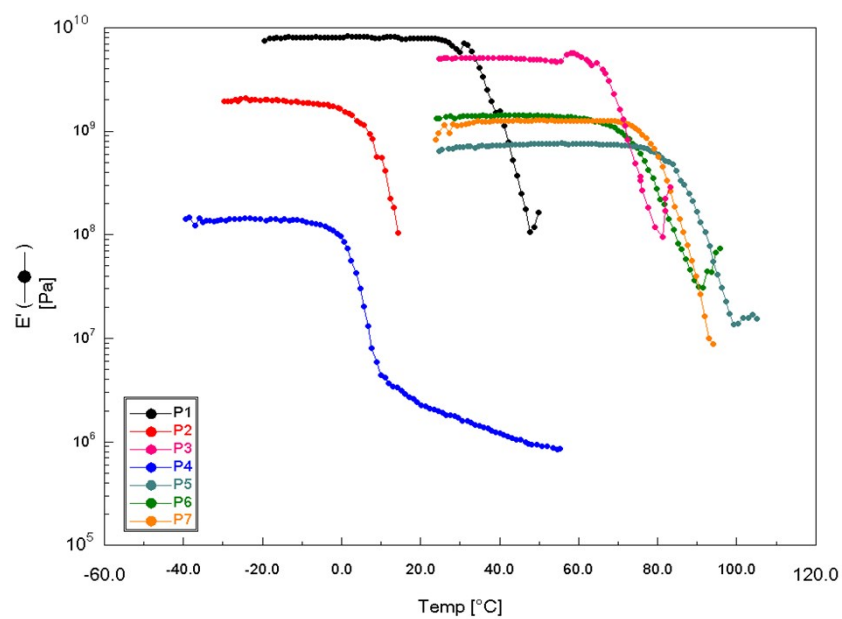


Figure S 24: SEC traces of methylated divanillyl diol/dimethylsebacate polymer P1 and divanillyl diol/sebacid acid polymer P1' in DMSO/DMF 20/80.



**Figure S 25: DMA analysis of the copolymers synthesized from divanillyl diol 4, using 3-point bending test at 1 Hz from -40 to 120 °C at 10 K/min.**