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ADMET polymerization of bio-based biphenyl compounds

A. Llevot, E. Grau, S. Carlotti, S. Grelier and H. Cramail

Abstract

Four biphenyl monomers derived from vanillin or eugenol were synthesized and polymerized by the ADMET methodology. The biphenyl compounds were produced by enzymatic dimerization of 2-methoxy-4-methylphenol, methyl vanillate, vanillin and eugenol. Further chemical modifications of the obtained dimers such as transesterification, Wittig reaction or allylation led to α,ω -dienes. The reactivity of these bio-based monomers towards ADMET polymerization employing several catalysts was investigated. Only oligomers were obtained when the diallylated compound was employed. The polymers based on dieugenol and the bis-unsaturated diester exhibit good thermal stability and T_g at 17 and 54 °C, respectively. Polymerization of the divinyl compound obtained by the Wittig reaction of divanillin showed a reasonable molar mass of 30 000 g mol⁻¹, a high T_g at around 160 °C and thermostability with a 5% weight loss occurring at 380 °C.

Introduction

Due to important environmental concerns and petrol depletion, the chemical industry is currently considering the use of renewable building blocks for the synthesis of polymers.¹⁻⁹ In particular, the substitution of fossil aromatic compounds derived from benzene is a topic of current interest.¹⁰⁻¹² Lignin, the second most abundant renewable biopolymer after cellulose and a source of phenolic compounds after depolymerisation, is considered as the most interesting substitute.¹³⁻¹⁹

Acyclic diene metathesis (ADMET) polymerization is a step-growth polymerisation driven by the release of a condensate, usually ethylene. ADMET is typically performed on α,ω -dienes to produce well-defined polymers with unsaturated backbones. This methodology revealed to be an efficient polymerization method.^{20,21} Indeed, due to the tolerance of the catalysts towards a wide range of substrates, a multitude of bio-based (bis)unsaturated molecules have been polymerized by the ADMET methodology in recent years.²²⁻²⁶

In particular, the polymerization and copolymerization of lignin derivatives by ADMET have been reported. Meier and coworkers prepared and polymerized bis-unsaturated esters from ferulic acid²⁷ and vanillin.^{27,28} The α,ω -diene derived from ferulic acid was obtained by reaction with allyl bromide, which led simultaneously to the formation of the allyl ester from the carboxylic acid and allyl ether on the phenol moiety.²⁷ On the other hand, the vanillyl phenol moiety was etherified by reaction with allyl bromide and subsequently esterified with methyl undecenoate, in a 1 : 1 molar ratio or with dimethyl adipate, a bio-based compound, in a 2 : 1 molar ratio, leading to α,ω -dienes.²⁸ Allais and coworkers produced bisphenols by enzymatic transesterification of ethyl dihydroferulate with isosorbide, 1,3-propanediol and 1,4-butanediol.²⁹ Etherification of the bisphenols with bromoalkene led to α,ω -dienes.³⁰

Eugenol, a naturally occurring unsaturated compound extracted from clove oil, was also polymerized by the ADMET methodology.³¹ The α,ω -dienes were prepared by linking two molecules of eugenol with an alkyl chain, a carbonate or a diethylene glycol moiety.

All these α,ω -dienes were polymerized by ADMET leading to polymers exhibiting a T_g between -31 and 18 °C depending on the monomer and comonomer employed.

Symmetrical biphenyl monomers can also be obtained by oxidative phenolic coupling catalyzed by an enzyme such as horseradish peroxidase or laccase.³²⁻³⁶ In previous work, we have investigated the enzymatic coupling of several phenolic compounds potentially derived from lignin. Employing a laccase from *Trametes versicolor*, we developed a process to selectively synthesize vanillin-based biphenyl compounds in large quantities and high yields.³⁷ Semi-aromatic polyesters based on this biphenyl platform were also prepared.^{37,38}

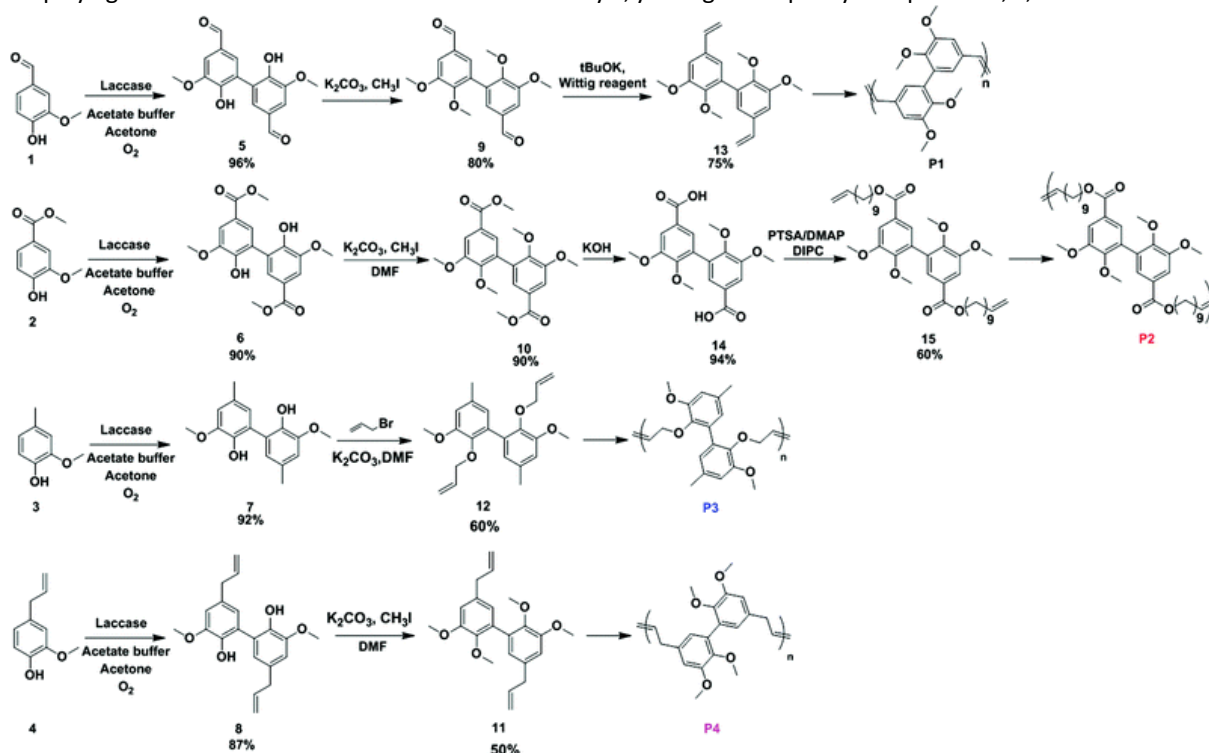
In this paper, we report the synthesis and ADMET polymerization of bis-unsaturated bio-based biphenyl compounds. First, phenolic compounds, derived from vanillin and eugenol, were dimerized *via* oxidative phenolic coupling catalyzed by laccase. The obtained biphenyl compounds were then chemically modified to yield α,ω -dienes. ADMET

polymerization of these unsaturated monomers was performed by employing several catalysts. The structures and thermo-mechanical properties of the resulting polymers were investigated.

Results and discussion

Monomer synthesis

Vanillin **1**, methyl vanillate **2**, 2-methoxy-4-methylphenol **3** and eugenol **4** were used as starting materials for the synthesis of building blocks (Scheme 1). Phenols **2** and **3** can be obtained respectively by oxidative esterification and by hydrogenation of a lignin derivative, vanillin.^{39,40} The four bio-based phenols were dimerized using a green process, employing a laccase from *Trametes versicolor* as the catalyst, yielding the bisphenyl compounds **5**, **6**, **7** and **8**.³⁷



Scheme 1 Synthesis and polymerization of α,ω -dienes from vanillin **1**, methyl vanillate **2**, 2-methoxy-4-methylphenol **3** and eugenol **4**.

The phenols of the dimers **5**, **6** and **8** were then methylated yielding methylated divanillin **9**, methylated diester **10** and methylated dieugenol **11**. The phenols of **7** were allylated, yielding the bis-unsaturated monomer **12**. A Wittig reaction was performed on methylated divanillin **9**, employing methyltriposponium iodide as the Wittig reagent, yielding the divinyl compound **13**. The last bis-unsaturated compound was prepared from methylated diester **10**. Diester **10** was hydrolyzed into the diacid **14** and subsequently esterified with undecenol, a bio-based compound, yielding the α,ω -dienes **15**. The ^1H and ^{13}C NMR spectra of all the molecules are displayed in the ESI (see Fig. S1–S26†).

Polymer synthesis

The α,ω -dienes **15**, **13**, **12** and **11** were polymerized by acyclic diene metathesis (ADMET) polymerization resulting in **P1**, **P2**, **P3** and **P4**, respectively (Scheme 1). Due to the incompatibility between the high melting temperature of the monomers (over 80 °C) and the thermal stability of the catalyst, the polymerizations were performed in the solvent. Polarclean was selected as the solvent for its high boiling point, its compatibility with the Grubbs catalyst and its sustainability.^{23,26} Thus, the polymerizations were performed employing the Grubbs catalyst (2 mol%) in the Polarclean solvent at a concentration of 0.22 mol L⁻¹, under vacuum, at 80 °C, for 18 h.

The first step of this study focuses on the reactivity of the α,ω -diene to ruthenium-based olefin metathesis catalysts. The catalyst efficiency depends on the functional groups of the diene to be polymerized and other factors like the melting point or solubility of the monomers.²⁰ In order to select the catalyst which leads to the polymer with the highest molar mass, each monomer was polymerized employing 2 mol% of Grubbs 1st (G1), Grubbs 2nd (G2), Hoveyda–Grubbs 1st (HG1) and Hoveyda–Grubbs 2nd (HG2) generation catalysts (Fig. S27[†]) at 80 °C under dynamic vacuum. It has been reported in the literature that olefin isomerization (double bond migration) can be observed in ADMET polymerization when employing G2 and HG2 catalysts. However, such an isomerization can be limited by using quinone-type compounds.^{41,42} Thus, when G2 and HG2 were used, 5 mol% of 1,4-benzoquinone was added to limit isomerization in the cases of monomers **11**, **12** and **15**. The polymers were purified by reprecipitation in cold methanol, yielding a white solid. The polymer molar masses with respect to the catalyst used are summarized in Table 1. The SEC profiles of the highest molar masses of **P1**, **P2**, **P3** and **P4** employing HG2, G1, HG1 and HG2 respectively are shown in the ESI (Fig. S28[†]). **P1** and **P4** synthesized from divinyl, **13**, and methylated dieugenol, **11**, respectively, exhibited the highest molar mass whereas the polymerization of **12** leads to oligomers (**P3**). More details about the polymer structures were extracted from ¹H NMR analyses (Fig. 1–4). **13** exhibits a conjugation between the double bond and the aromatic ring. The synthesis of low molar mass poly(*p*-phenylenevinylene)-type polymers by ADMET in the presence of a molybdenum carbene complex has already been reported.^{43,44} High molar mass, defect-free, all-*trans* poly(*p*-phenylenevinylene)s can be prepared employing ruthenium-based catalysts, G2 and HG2.^{45,46} In the present study, only G2 and HG2 catalysts led to polymers and the highest molar mass, 29 000 g mol⁻¹, was achieved employing the HG2 catalyst. The ¹H NMR spectrum of the polymer synthesized employing the HG2 catalyst is displayed in Fig. 1. The decrease of the signals at 6.68, 5.701 and 5.22 ppm attributed to the terminal double bonds on the ¹H NMR spectrum of **P1** also indicates the successful polymerization. The integration of these signals characteristic of the chain-end moieties enables the calculation of a molar mass of 33 000 g mol⁻¹, in agreement with the SEC analyses. The spectrum also shows signals of the methoxy protons at 3.94 and 3.63 ppm, signals of the aromatic protons at 7.06 ppm and signals of the methylene protons at 7.00 ppm. Such analysis proves the all-*trans* configuration of the vinylene bonds. Indeed, no signal is detected at 6.65 ppm, which is the value of *cis*-vinylene bonding signals reported in the literature.⁴⁴

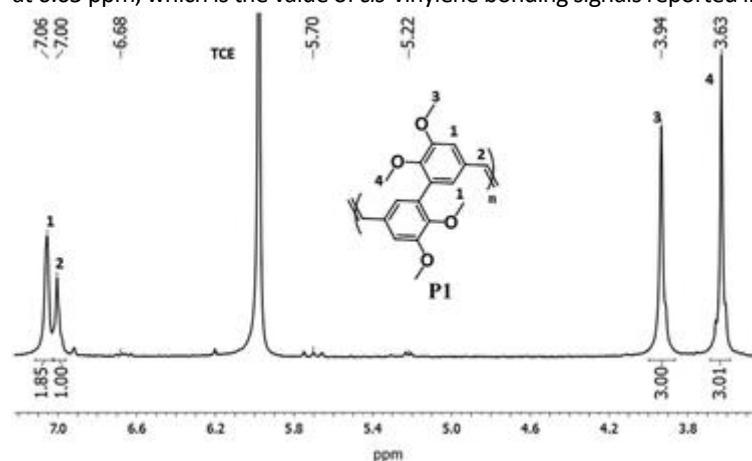


Fig. 1 ¹H NMR spectrum of **P1** in TCE, at room temperature.

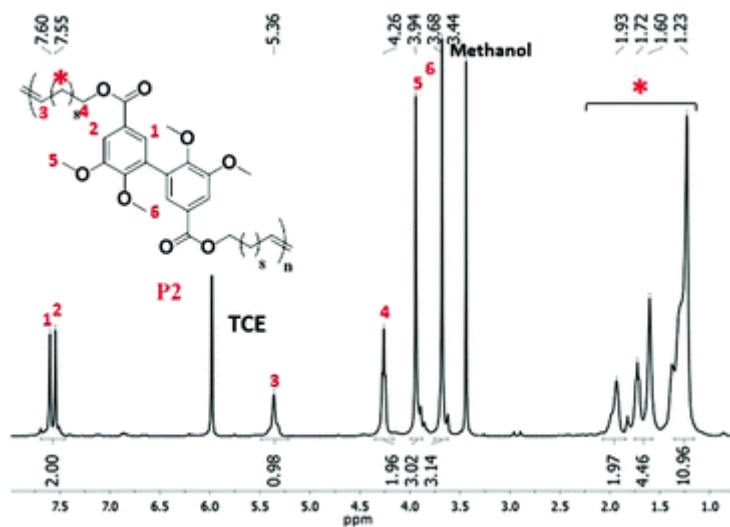


Fig. 2 ^1H NMR spectrum of **P2** in TCE, at room temperature.

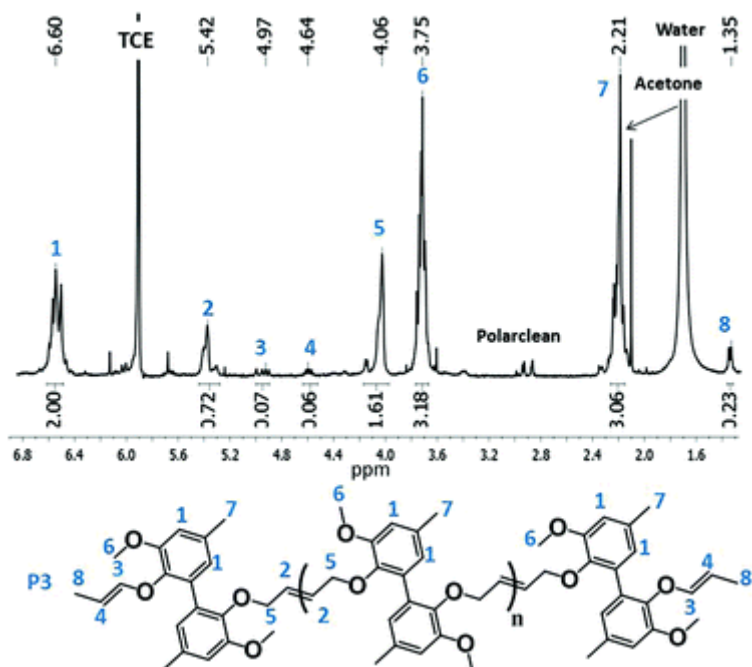


Fig. 3 ^1H NMR spectrum of **P3** in TCE, at room temperature.

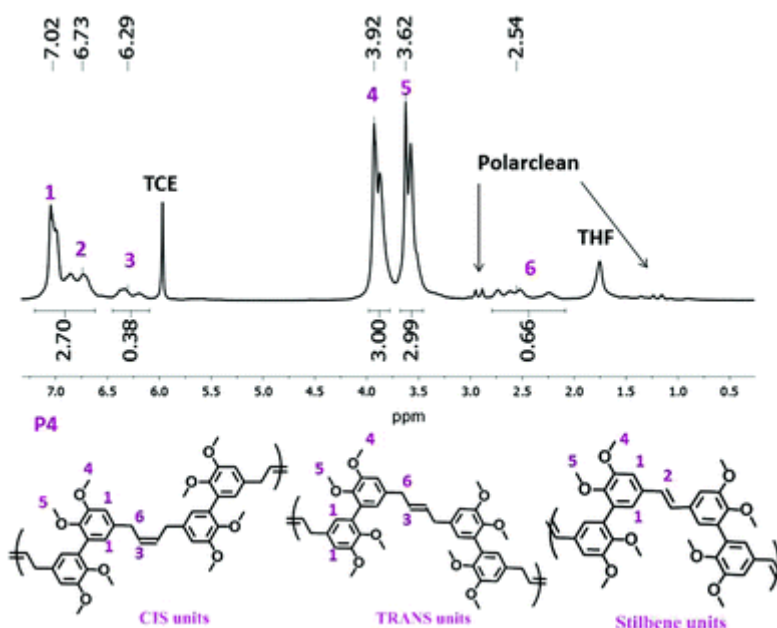


Fig. 4 ^1H NMR spectrum of **P4** in TCE, at room temperature.

Table 1 Properties of polymers **P1**, **P2**, **P3** and **P4** synthesized by ADMET of biphenyl compounds

Monomers	Polymer	Catalyst	M_n^a (g mol $^{-1}$)	D^a
13	P1	G1	/	/
		HG1	/	/
		G2	16 000	1.4
		HG2	29 000	1.7
15	P2	G1	11 000	1.6
		HG1	7000	1.6
		G2	/	/
		HG2	10 000	1.6
12	P3	G1	/	/
		HG1	7000	1.1
		G2	/	/
		HG2	/	/
11	P4	G1	/	/
		HG1	6000	1.3
		G2	28 000	1.7
		HG2	40 000	1.7

^a Determined by SEC in DMF, PS calibration, / no precipitation.

Dimer **15** possesses an aliphatic chain of 10 carbons between the aromatic ring and the terminal double bond. Polymers prepared from **15** employing G1, HG1 and HG2 catalysts were recovered as precipitates in cold methanol (Table 1). The highest molar masses of 11 000 g mol $^{-1}$ were achieved employing G1 and HG2 catalysts. The ^1H NMR spectrum of **P2** shows signals of the methoxy protons at 3.92 and 3.66 ppm, signals of the aromatic protons at 7.53 ppm and signals of the aliphatic chain between 1.00 and 2.00 ppm (Fig. 2).

The disappearance of the signals at 5.00 and 4.35 ppm attributed to the terminal double bonds and the appearance of a signal at 5.34 ppm assigned to internal double bonds indicate the success of polymerization.

Dimer **12** contains a heteroatom at the β -position of the terminal double bond. It is well-known that heteroatoms can be included in ADMET polymerization if sufficient "spacing" separates the active olefin site and the functional group containing the heteroatom itself.⁴⁷ The polymer prepared from **12** employing the HG1 catalyst was recovered as a precipitate in cold methanol (Table 1). **P3** exhibited the lowest molar mass of the study, 7000 g mol⁻¹. The ¹H NMR spectrum of **P3** shows the signal characteristic of aromatic, methoxy and methyl protons, respectively at 6.60, 3.75, and 2.21 ppm (Fig. 3).

The signals at 5.42 and 4.06 ppm are assigned to internal double bonds and methylene at the α -position of the ether moiety. The integration of the signal at 4.06 ppm, lower than 2.00, indicates the occurrence of isomerization. In addition, a doublet at 1.35 ppm can be attributed to the methyl group at the γ -position of the ether moiety. These vinyl ether moieties are not reactive towards ADMET polymerization and can act as chain stoppers.⁴⁷ These chain ends allowed us to calculate the degree of polymerization of **13**. This value is a little lower than the value of 20 determined by SEC analyses. Thus, only oligomers were synthesized by the ADMET polymerization of **13**, probably due to the complexation of the non-bonded electrons of the heteroatom with the metal center.

The ADMET polymerization of dieugenol **8** employing G1, HG1, G2 and HG2 catalysts did not lead to the formation of polymers. The phenolic moieties might deactivate the Grubbs catalysts. Thus, the polymerization was performed on methylated dieugenol, **11**. The polymers prepared from **11** employing HG1, G2, and HG2 catalysts were recovered as precipitates in cold methanol (Table 1). The highest molar mass of 40 000 g mol⁻¹ was achieved in the presence of the HG2 catalyst. The ¹H NMR spectrum of **11** showed 3 broad signals between 6.40 and 7.20 ppm. The signals at 7.02 ppm and 6.29 ppm were attributed to the aromatic ring and to the internal double bonds at the β -position of the aromatic ring (Fig. 4).³¹ However, the signal at 6.73 ppm is characteristic of the *trans* configuration of the vinylene bonds into stilbenes. The integration of the signal at 2.54 ppm, commonly assigned to benzyl protons was 0.66 instead of 2. These two observations suggested the isomerization of eugenol into isoeugenol. This isomerization commonly occurs in eugenol metathesis due to the thermodynamic stability of the resulting styrene derivative and the kinetically faster subsequent metathesis to stilbene oligomers. In our case, 60% of the units were stilbene derivatives. The duplication of the methoxy signals could be attributed to the presence of both kinds of units.⁴⁸

Thermal and thermomechanical characterization

The thermomechanical properties of the ADMET-based polymers were analyzed by DSC, TGA, and DMA (Table 2). DSC analyses revealed the amorphous character of the polymers (Fig. S32[†]). Depending on their structures, the polymers present a glass transition temperature ranging from 4 to 157 °C. As expected, the reduction of the number of atoms between the aromatic ring and the terminal double bond of the monomer resulted in a T_g increase. Indeed, **P2** exhibits the lowest T_g due to its C12 aliphatic chain. The presence of oxygen atoms in the **P3** backbone leads to a lower T_g (17 °C) in comparison with **P4** (54 °C). The T_g of **P1** seems to be at 157 °C but is difficult to detect by DSC due to the rigidity of the conjugated polymer. In order to confirm this value and to investigate the thermomechanical properties of **P1**, DMA analyses were performed (Fig. 5). The end of the glassy state was revealed by the decrease of the storage modulus E' at 140 °C. The rubbery state was reached when E' stops decreasing at 250 °C. The transition between the two states was spread on 110 °C due to its rigid conjugated structure. The maximum $\tan \delta$ was measured at 208 °C. The T_g of **P1** was 100 °C higher than the T_g of **P4** although the structures of **13** and **11** differ by only one carbon between the aromatic ring and the double bond. The high T_g of **P1** may be explained by its conjugated backbone and its all-*trans* structure, whereas the T_g of **P4** is lower due to its ill-defined structure (isomerizations) and *cis-trans* configurations.

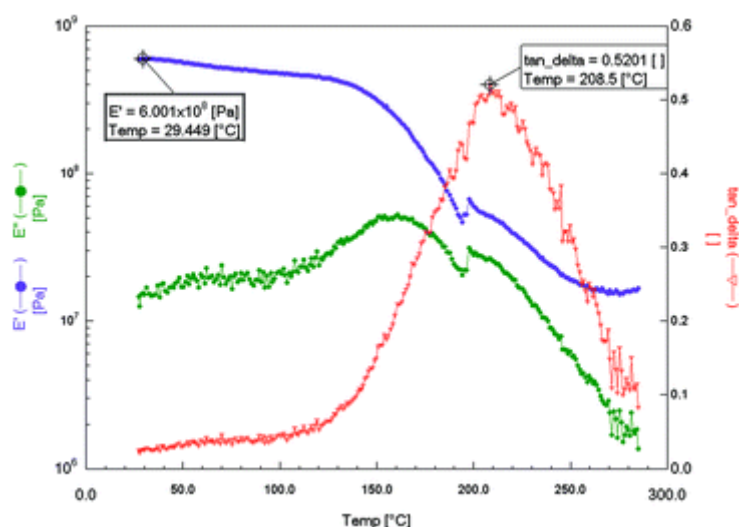


Fig. 5 DMA analysis of diviny ADMET polymer, **P1**, using the 3-point bending test at 1 Hz from 20 to 300 °C at 10 K min⁻¹.

Table 2 Thermomechanical properties of polymers **P11**, **P12**, **P13** and **P14** synthesized by ADMET

Monomer	Polymer	Catalyst	T_g^a (°C)	$T_{d5\%}^b$ (°C)
13	P1	HG2	156	380
15	P2	HG2	4	310
12	P3	HG1	17	250
11	P4	HG2	54	330

a Determined by DSC second heating cycle. b Determined by TGA in air; temperature of 5% degradation.

The thermal stability of the polymers was evaluated by TGA in air (Fig. S33†). 5 wt% loss of **P3** appeared at 250 °C, due to its oligomeric structure. The thermal robustness of **P1**, **P2** and **P4** is high; the latter exhibits 5 wt% loss at temperatures between 310 and 380 °C.

Conclusions

Four α,ω -dienes were synthesized from bio-based biphenyl compounds derived from vanillin and eugenol. Their reactivity towards ADMET polymerization was investigated. A screening of Grubbs catalysts allowed us to synthesize three families of polymers with reasonable molar masses between 11 000 and 40 000 g mol⁻¹. Only oligomers were obtained when the diallylated compound was employed probably because the heteroatom close to the terminal double bond reduces the activity of the Grubbs catalyst. Methylated dieugenol and the bis-unsaturated diesters derived from methyl vanillate and undecenol exhibit good thermal stability and T_g at 17 and 54 °C, respectively. The polymerization of diviny compounds obtained by the Wittig reaction of divanillin led to a polymer with a high T_g at around 160 °C and thermostability with a 5% weight loss occurring at 380 °C.

Experimental

Material

Laccase from *Trametes versicolor*, iodomethane (99%), eugenol (99%), sodium acetate (99%), acetic acid (99.7%), *N,N'*-diisopropylcarbodiimide (DIPC 99%), *p*-toluenesulfonic acid monohydrate (PTSA 99%), 4-(dimethylamino)pyridine (DMAP 99%), allyl bromide (99%), potassium *tert*-butoxide (98%), benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Grubbs 1st generation metathesis catalyst (97%)), dichloro(*o*-

isopropoxyphenylmethylene)(tricyclohexylphosphine)ruthenium(II) (Hoveyda Grubbs 1st generation metathesis catalyst), benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (Grubbs 2nd generation metathesis catalyst), and (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)ruthenium (Hoveyda Grubbs 2nd generation metathesis catalyst (97%)) were purchased from Sigma Aldrich. Potassium carbonate (99%) was supplied by Prolabo. Vanillin (99%), methyl vanillate (99%) and 2-methoxy-4-methylphenol (98%) were purchased from Alfa Aesar. Polarclean (methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate) was supplied by Solvay. 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 a deuterated solvent (DMSO or tetrachloroethylene – TCE). Size exclusion chromatography (SEC) analyses were performed in DMF (80 °C) on a PL-GPC 50 plus integrated SEC from Polymer Laboratories – Varian with a series of three columns from PLgel (PLgel 5 µm Guard (guard column 7.5 mm ID × 5.0 cm L); PLgel 5 µm MIXED-D (7.5 mm ID × 30.0 cm L) and PLgel 5 µm MIXED-D (7.5 mm ID × 30.0 cm L)). The elution of the filtered samples was monitored using simultaneous refractive indices 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 0 °C to 220 °C at a rate of 10 °C min⁻¹. Consecutive cooling and a second heating run were also performed at 10 °C min⁻¹. The glass transition temperatures and melting points were calculated from the second heating run. Thermogravimetric analyses (TGA) were performed on a TGA-Q50 system from TA Instruments at a heating rate of 10 °C min⁻¹ under a nitrogen or an air atmosphere as mentioned in the manuscript, DMA RSA 3 (TA Instruments). The sample's temperature was modulated from -80 °C to 250 °C, depending on the sample at a heating rate of 5 °C min⁻¹. The measurements were performed in a 3-point bending mode at a frequency of 1 Hz, the initial static force varying between 0.1 and 0.5 N and a strain sweep of 0.1%.

Experimental procedure

General procedure for dimerization: synthesis of dimers 5 to 8

A solution of phenol substrate (**5–8**) (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 O₂ 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 from the solution and the product was dried overnight at 80 °C under vacuum.

*Divanillin***5**: yield: 96%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 9.85 (s, CHO), 7.50 (s, 2H, Ar), 4.00 (s, OCH₃).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): δ 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 (OCH₃).

*Dimethyl divanillate***6**: yield: 90%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 9.60 (s, 2H, HO), 7.46 (s, 4H, Ar), 3.90 (s, 6H, OCH₃), 3.80 (s, 6H, OCH₃ ester).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): δ 166.04 (OCH₃ 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 (OCH₃), 51.75 (OCH₃ ester).

*2-Methoxy-4-methyl phenol dimer***7**: yield: 92%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 6.73 (s, 2H, Ar), 6.53 (s, 2H, Ar), 3.79 (s, 6H, OCH₃), 2.23 (s, 6H, CH₃).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): 147.52 (Ar-C), 140.99 (Ar-C), 126.92 (Ar-C), 125.68 (Ar-C), 123.04 (Ar-C), 111.61 (Ar-C), 55.85 (OCH₃), 20.65 (CH₃).

*Dieugenol***8**: yield: 87%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 6.74 (s, 2H, Ar), 6.52 (s, 2H, Ar), 5.94 (q, 2H, CH-CH₂), 5.03 (d, 4H, CH-CH₂), 3.79 (s, OCH₃), 3.27 (d, 2H, CH₂).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): δ 147.80 (Ar-C), 141.62 (Ar-C), 138.38 (v H-CH₂), 129.57 (Ar-C), 125.67 (Ar-C), 122.62 (Ar-C), 115.28 (CH-vH₂), 105.56 (Ar-C), 55.64 (OCH₃), 39.19 (CH₂).

General procedure for phenol methylation of 5, 6 and 8: synthesis of methylated divanillin 9 and methylated dimethyl vanillate 10 and methylated dieugenol 11

Bisphenol **5**, **6** or **8** (26 mmol) was dissolved in DMF (120 mL). Potassium carbonate (15.2 g, 110 mmol) was added before the 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***9**: yield: 80%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 9.94 (s, CHO), 7.58 (s, 2H, Ar), 7.55 (s, 2H, Ar), 3.95 (s, OCH₃), 3.68 (s, OCH₃).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): δ 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 (OCH₃), 55.93 (OCH₃).

*Methylated dimethyl divanillate***10**: yield: 80%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 7.59 (s, 2H, Ar), 7.41 (s, 2H, Ar), 3.92 (s, OCH₃), 3.84 (s, OCH₃), 3.62 (s, OCH₃).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): δ 165.63 (OCH₃ 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 (OCH₃), 55.7.

*Methylated dieugenol***11**: yield: 50%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 6.93 (s, 2H, Ar), 6.61 (s, 2H, Ar), 6.03 (q, 2H, CH-CH₂), 5.13 (d, 4H, CH-CH₂), 3.89 (s, OCH₃), 3.56 (s, OCH₃), 3.42 (d, 2H, CH₂).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): δ 152.02 (Ar-C), 144.15 (Ar-C), 137.53 (vH-CH₂), 134.73 (Ar-C), 132.29 (Ar-C), 122.19 (Ar-C), 115.77 (CH-vH₂), 112.15 (Ar-C), 59.80 (OCH₃), 55.44 (OCH₃), 39.29 (CH₂).

Allylation of 2-methoxy-4-methylphenol dimer 7: synthesis of 12

Bisphenol compound **7** (8 g, 26 mmol) was dissolved in acetone (120 mL). Potassium carbonate (15.2 g, 110 mmol) was added before the slow addition of allyl bromide (13.5 mL, 158 mmol). After 15 h of stirring at 80 °C, the mixture was filtered, the solvent was evaporated and the resulting solid was dried under vacuum. Yield: 60%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 6.84 (s, 2H, Ar), 6.55 (s, 2H, Ar), 5.70 (m, 2H, CH-CH₂), 4.99 (dd, 4H, CH-CH₂), 4.21 (d, 4H, OCH₂), 3.80 (s, 6H, OCH₃), 2.26 (s, 6H, CH₃).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): 151.98 (Ar-C), 142.92 (Ar-C), 134.95 (H-CH₂), 132.30 (Ar-C), 132.17 (Ar-C), 123.03 (Ar-C), 116.43 (CH-H₂), 112.67 (Ar-C), 73.21 (CH₂), 55.36 (OCH₃), 20.78 (CH₃).

Wittig reaction on methylated divanillin 9: synthesis of divinyl compound 13

Triphenylphosphine (3 g, 11.4 mmol) was dissolved in toluene (30 mL). Iodomethane (0.7 mL, 11.4 mmol) was added dropwise. The mixture was stirred to reflux at 120 °C under nitrogen flow. Methyltriposponium iodide precipitated and was filtered off and dried under vacuum.

To a solution of methyltriposponium iodide (8.8 g, 22 mmol) in dry THF (36 mL), potassium *tert*-butoxide (2.7 g, 24 mmol) was added at 0 °C. After 1 h of stirring at room temperature under nitrogen, methylated divanillin **9** (3.2 g, 10 mmol) was added. The mixture was stirred at 35 °C for 24 h. The solution was diluted with dichloromethane (75 mL), washed with water and 2 times with brine. The solvent of the organic phase was evaporated. The remaining reactants were eliminated by silica column purification using dichloromethane/cyclohexane 50/50. Yield: 75%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 7.17 (s, 2H, Ar), 6.83 (s, 2H, Ar), 6.70 (q, 2H, CH-CH₂), 5.77 (d, 2H, CH-CH₂), 5.19 (d, 2H, CH-CH₂), 3.87 (s, OCH₃), 3.53 (s, OCH₃).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): δ 152.34 (Ar-C), 145.84 (Ar-C), 136.25 (H-CH₂), 132.66 (Ar-C), 132.01 (Ar-C), 120.82 (CH-H₂), 113.30 (Ar-C), 109.25 (Ar-C), 59.94 (OCH₃), 55.53 (OCH₃).

Hydrolysis of diester 10: synthesis of diacid 14

Diester **10** (7 mmol, 2.7 g) was dissolved in methanol (10 mL). Potassium hydroxide (45 mmol, 2.5 g) was added and the solution was warmed to reflux for 9 h. The reaction was stopped with water (2.5 mL). The remaining diester was extracted with diethyl ether. The aqueous phase was acidified with HCl and the diacid precipitated. Yield: 94%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 7.63 (s, 2H, Ar), 7.42 (s, 2H, Ar), 3.96 (s, OCH₃), 3.64 (s, OCH₃).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): δ 166.72 (COOH), 152.21 (Ar-C), 149.91 (Ar-C), 131.06 (Ar-C), 123.86 (Ar-C), 112.88 (Ar-C), 59.89 (Ar-C), 55.84 (OCH₃), 55.86 (OCH₃).

Esterification of diacid **14** with undecenol: synthesis of bis-unsaturated diester **15**

Diacid **15** (8 mmol, 3 g) was dissolved in CH₂Cl₂ (80 ml) under stirring. Subsequently *p*-toluene sulfonic acid/4-dimethylaminopyridine catalyst in a molar ratio of 1/1.2 was added. The flask was placed in an ice bath and subsequently an excess of undecenol (4.8 mL, 24 mmol) was added to the solution. Finally, *N,N'*-diisopropylcarbodiimide (DIPC, 7.2 ml 46 mol) was added dropwise under stirring. The reaction was left under stirring for 72 hours at room temperature. Afterwards the solution was washed three times with water, dried and the solvent was removed under reduced pressure. The product was a yellow brown viscous liquid. The acylurea formed was eliminated by filtration after dissolution of the product in toluene. The remaining reactants were eliminated by silica column purification using dichloromethane. Yield: 60%.

¹H NMR (400 MHz, CDCl₃, δ (ppm)): δ 7.37 (s, 2H, Ar), 7.58 (s, 2H, Ar), 4.92 (m, 3H, CH-CH₂), 4.25 (t, 2H, CH₂-COO), 3.92 (s, OCH₃), 3.62 (s, OCH₃), 1.97 (m, 3H, -CH₂-), 1.67 (m, 2H, -CH₂-), 1.23 (m, 13H, -CH₂-).

¹³C NMR (400 MHz, CDCl₃, δ (ppm)): δ 164.84 (COO), 152.12 (Ar-C), 150.30 (Ar-C), 138.56 (CC), 131.26 (Ar-C), 125.08 (Ar-C), 123.50 (Ar-C), 114.34 (CC), 112.55 (Ar-C), 64.59 (OCH₂), 60.23 (OCH₃), 56.06 (OCH₃), 25.40–32.99 (CH₂).

ADMET polymerization: synthesis of **P1**, **P2**, **P3** and **P4**

α,ω-Dienes (0.22 mmol) were dissolved in Polarclean (1 mL). The Grubbs catalyst (2 mol%) was added to the flask. When needed, 1,4-benzoquinone (5 mol%) was added to limit isomerization. The flask was heated at 80 °C under vacuum for 18 h. Then 1 mL of ethyl vinyl ether was introduced into the flask to quench the reaction. The final polymer was dissolved into 1 mL of THF and reprecipitated in cold methanol.

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Supporting Information

ADMET polymerization of bio-based biphenyl compounds

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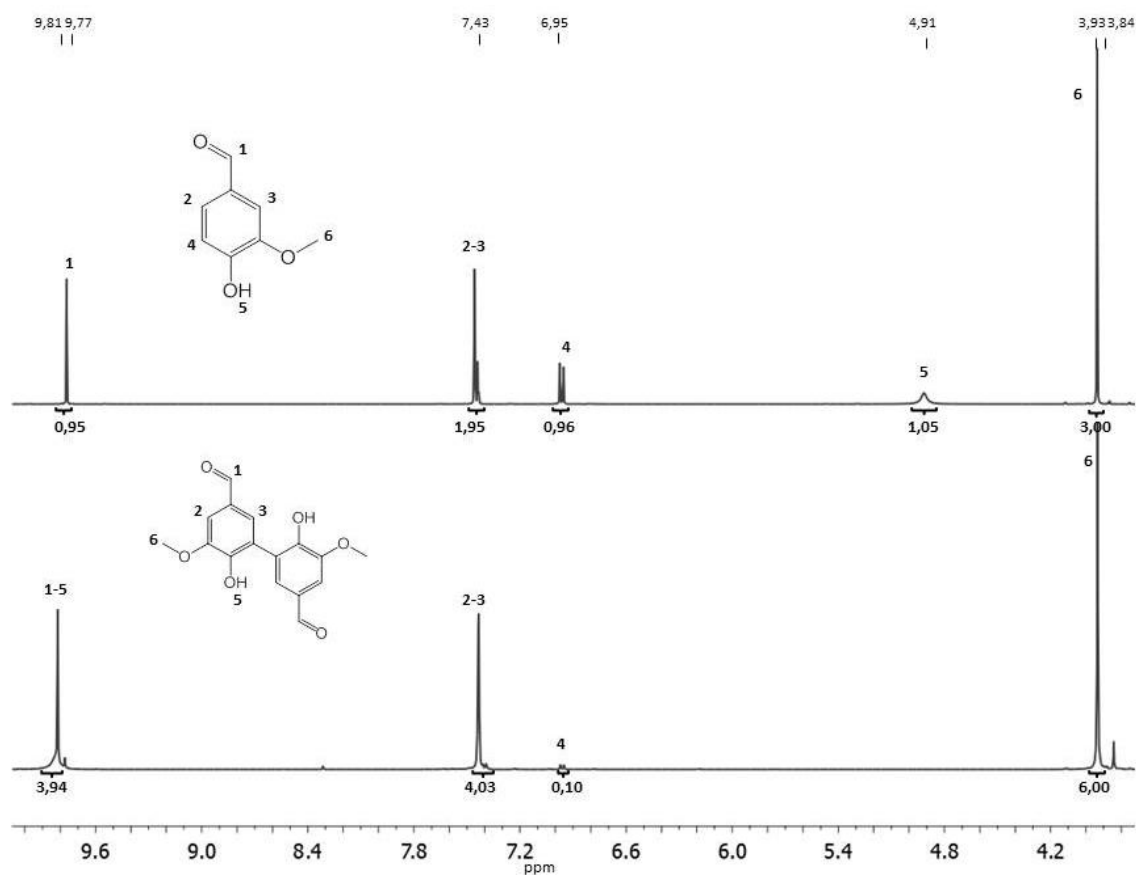


Figure S 1: ^1H NMR spectra of vanillin 1 (top) and divanillin 5 (bottom) in DMSO at room temperature

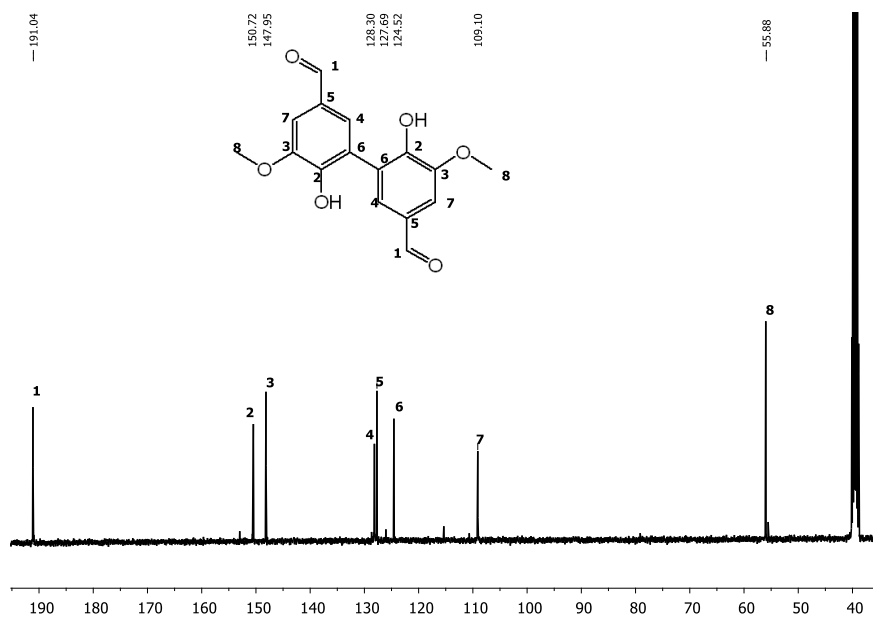


Figure S 2: ^{13}C NMR spectrum of Divanillin 5 in DMSO

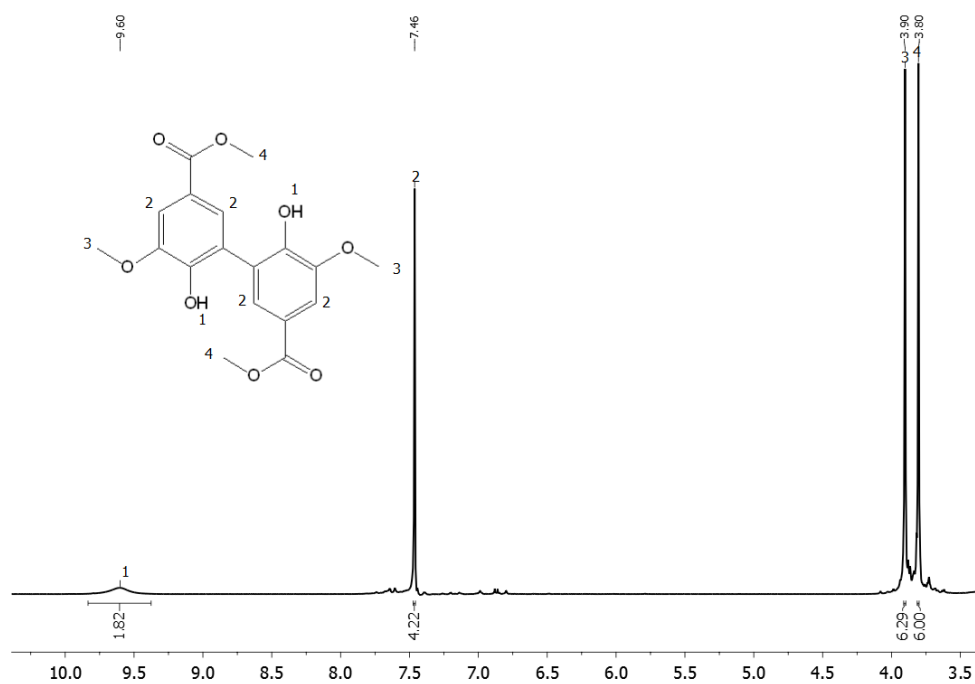


Figure S 3: ^1H NMR spectrum of dimethyl divanillate 6 in DMSO

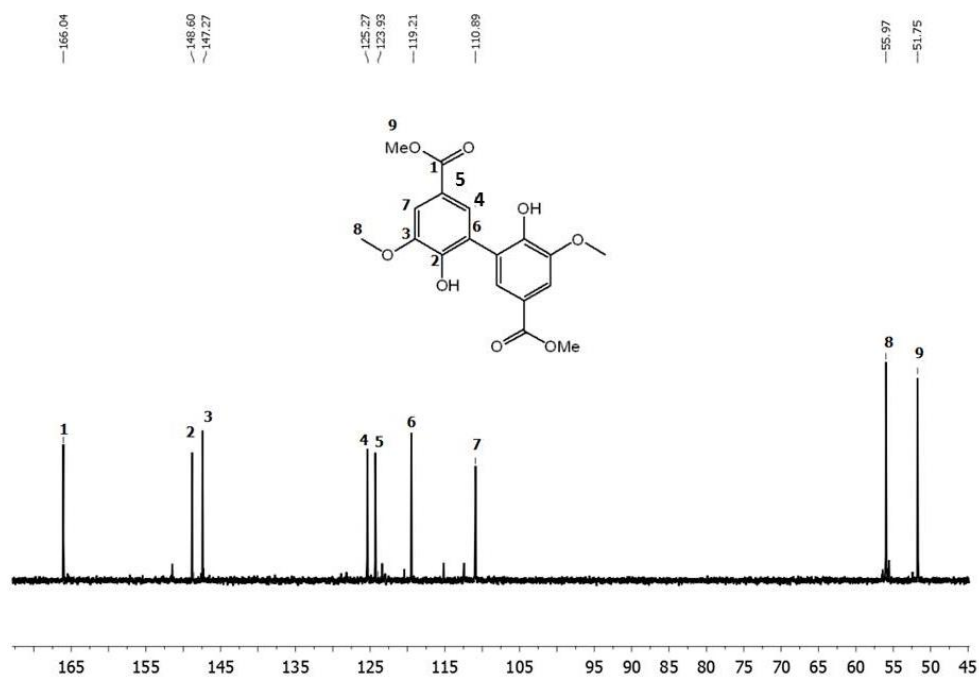


Figure S 4: ¹³C NMR spectrum of dimethyl divanillate 6 in DMSO

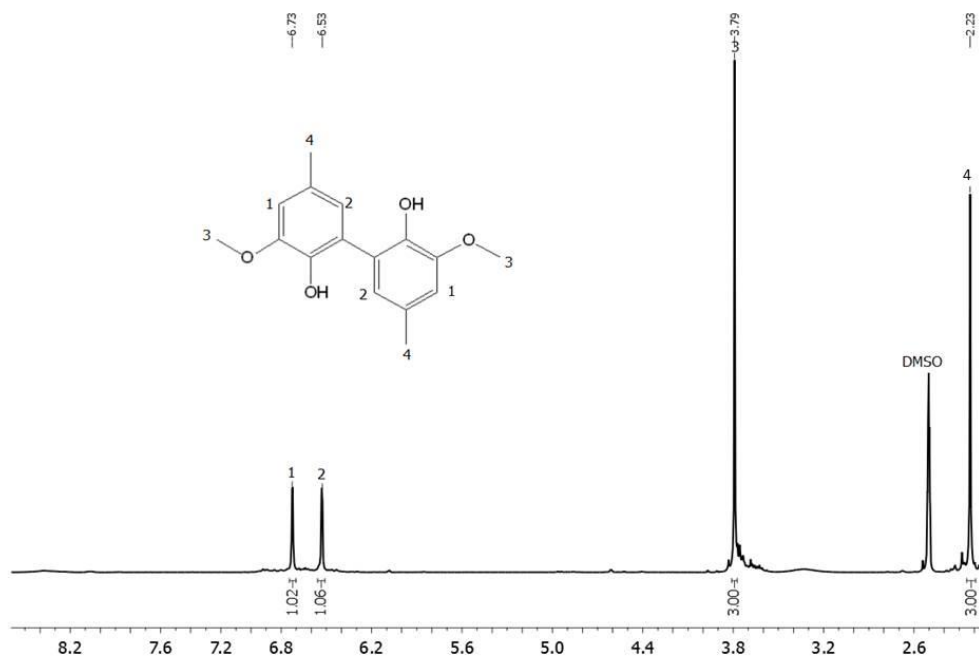


Figure S 5: ¹H NMR spectrum of 2-methoxy-4-methylphenol dimer 7 in DMSO

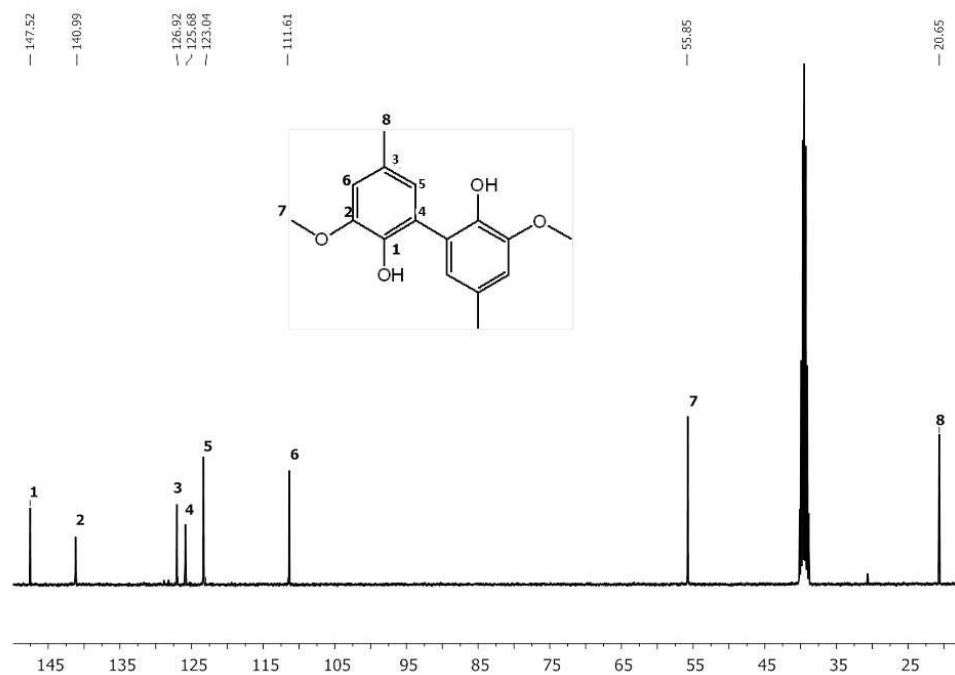


Figure S 6: ^{13}C NMR spectrum of 2-methoxy-4-methylphenol dimer 7 in DMSO

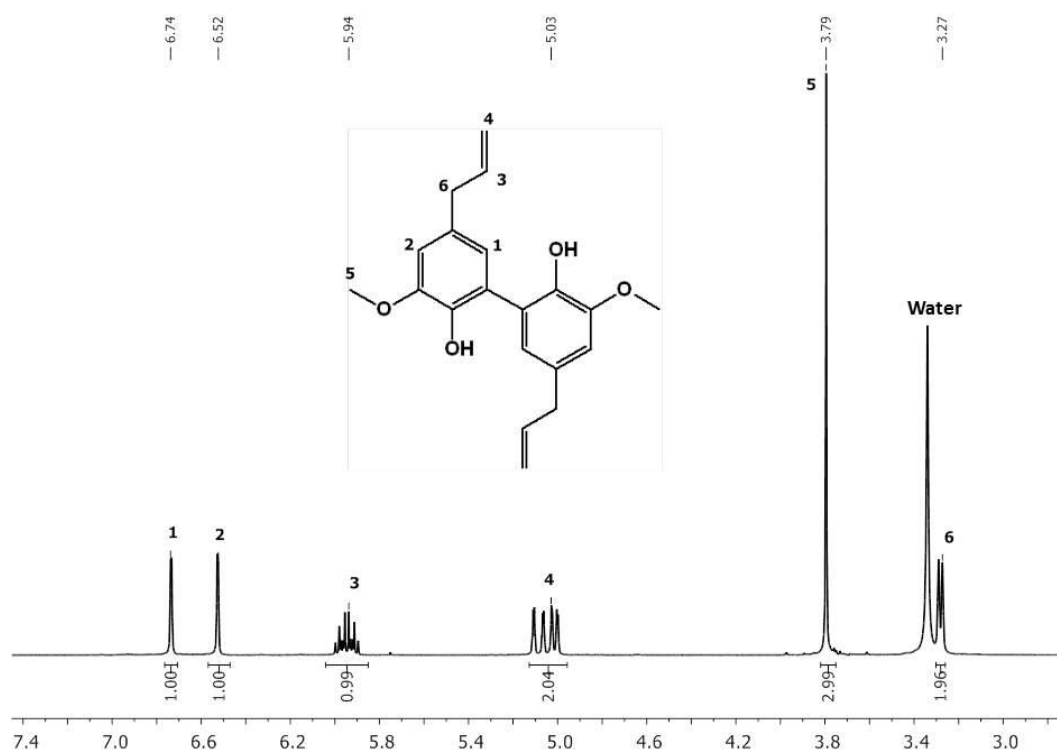


Figure S 7: ^1H NMR spectrum of Dieugenol 8 in DMSO

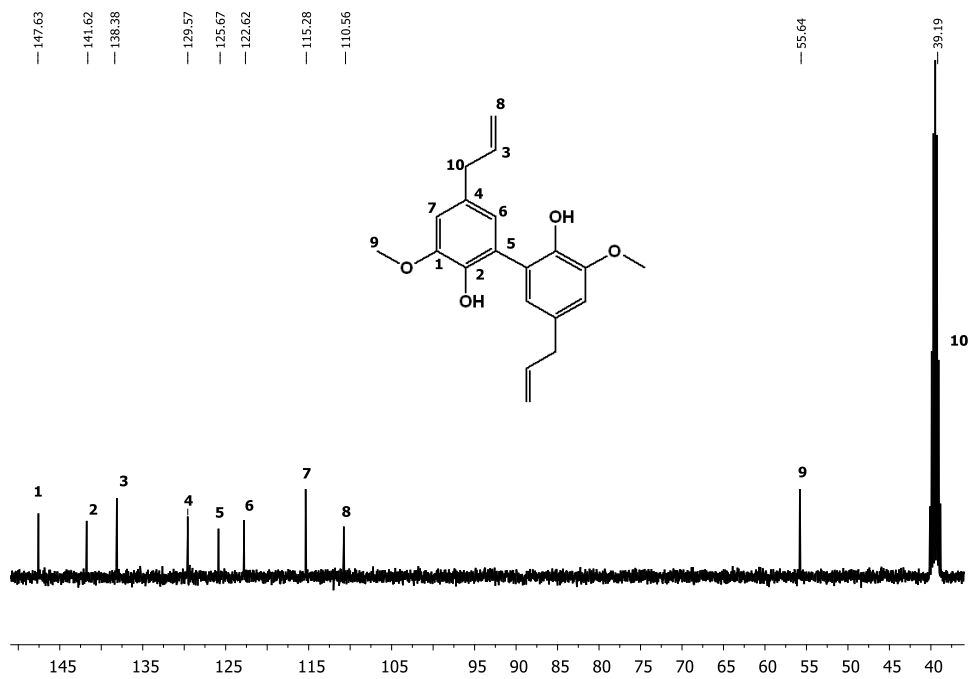


Figure S 8: ¹³C NMR spectrum of Dieugenol 8 in DMSO

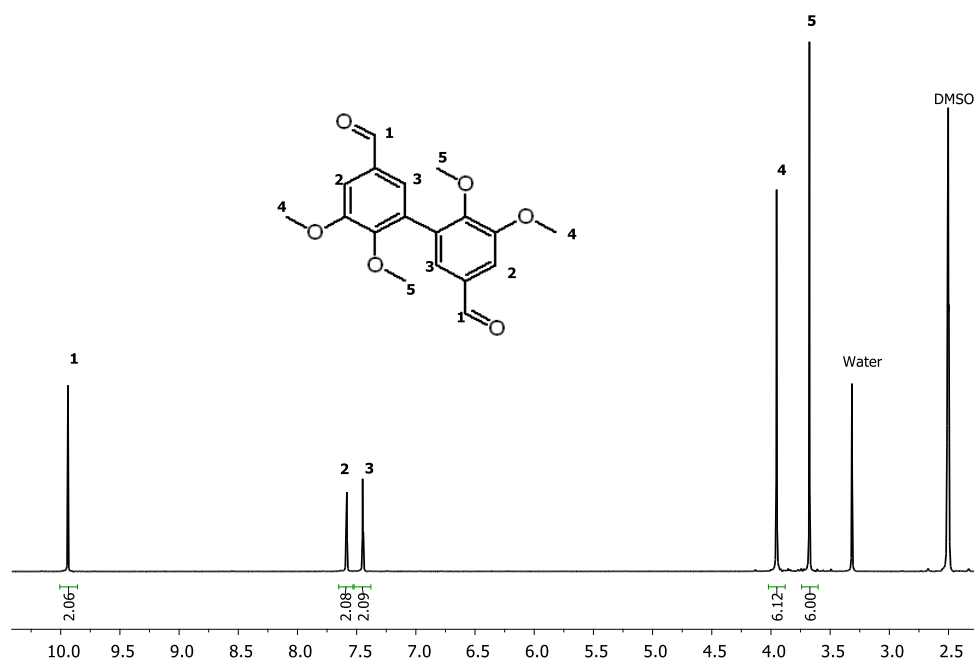


Figure S 9: ¹H NMR spectrum of methylated divanillin 9 in DMSO

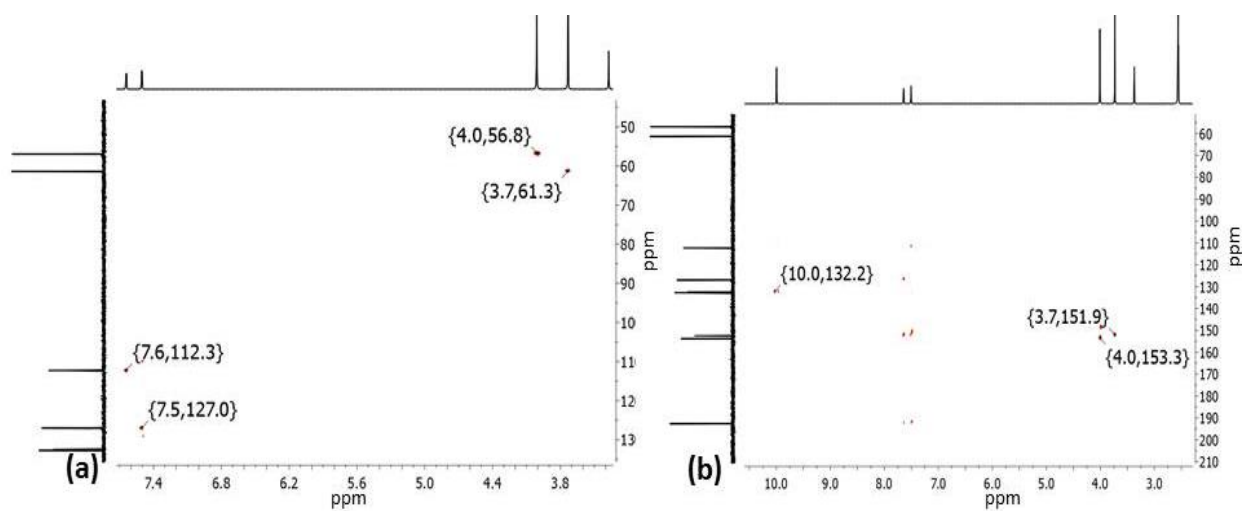


Figure S 10: HSQC (a) and HMBC (b) spectra of methylated divanillin 9 in DMSO, at room temperature.

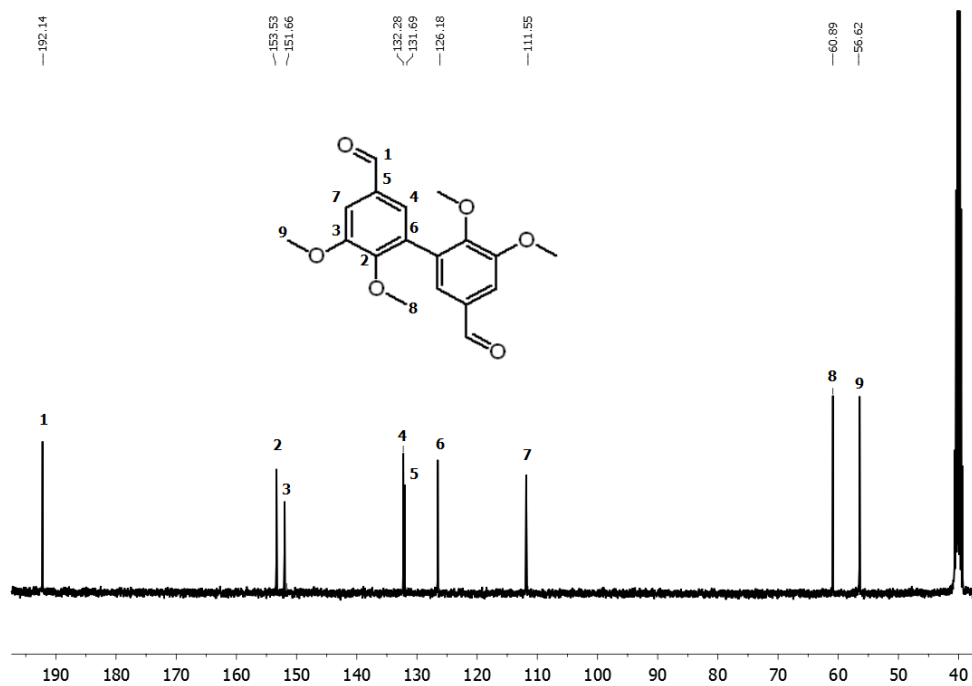


Figure S 11: ^{13}C NMR spectrum of methylated divanillin 9 in DMSO

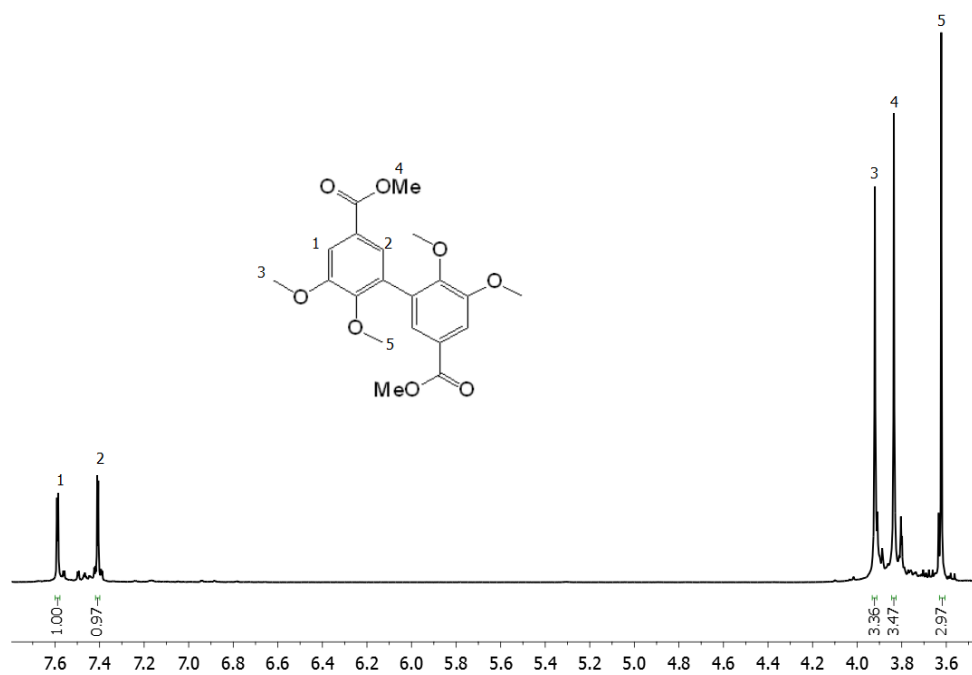


Figure S 12: ^1H NMR spectrum of methylated dimethyl divanillate 10 in DMSO

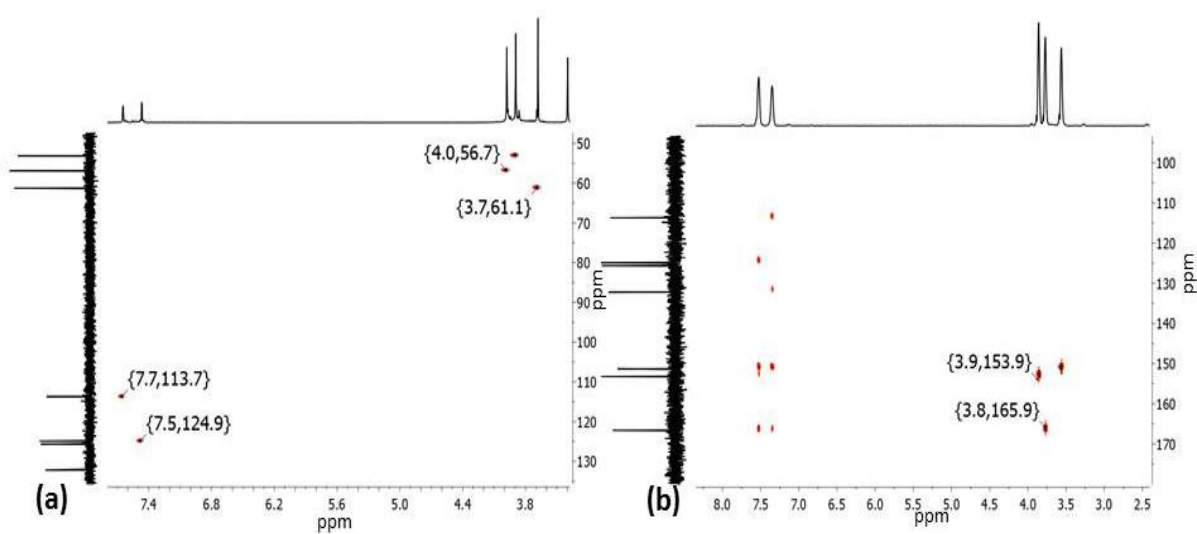


Figure S 13: HSQC (a) and HMBC (b) spectra of methylated diester 10 in DMSO.

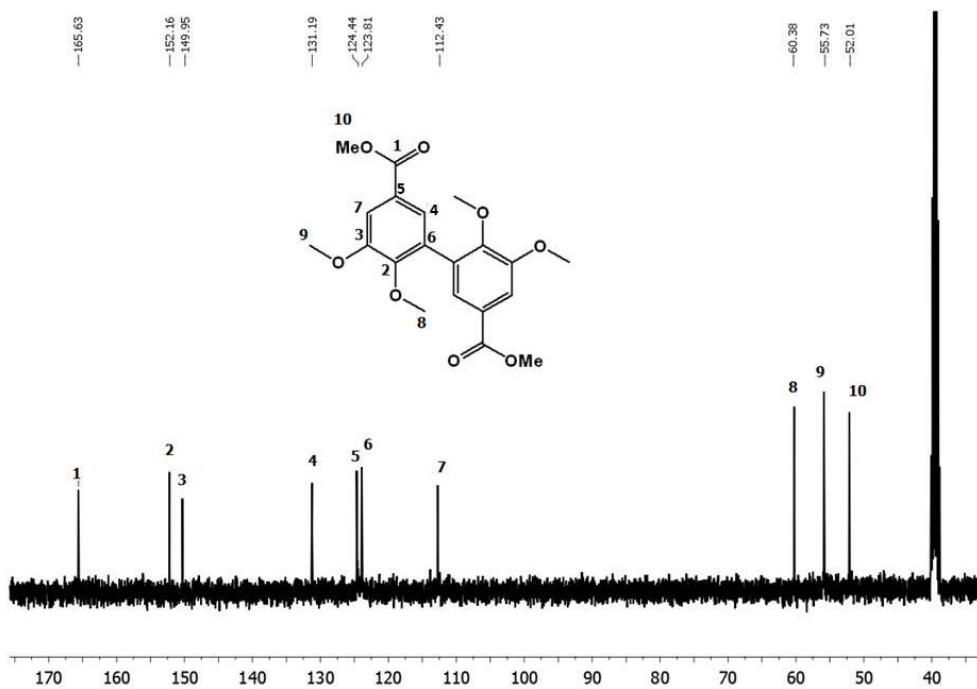


Figure S 14: ^{13}C NMR spectrum of methylated dimethyl divanillate 10 in DMSO

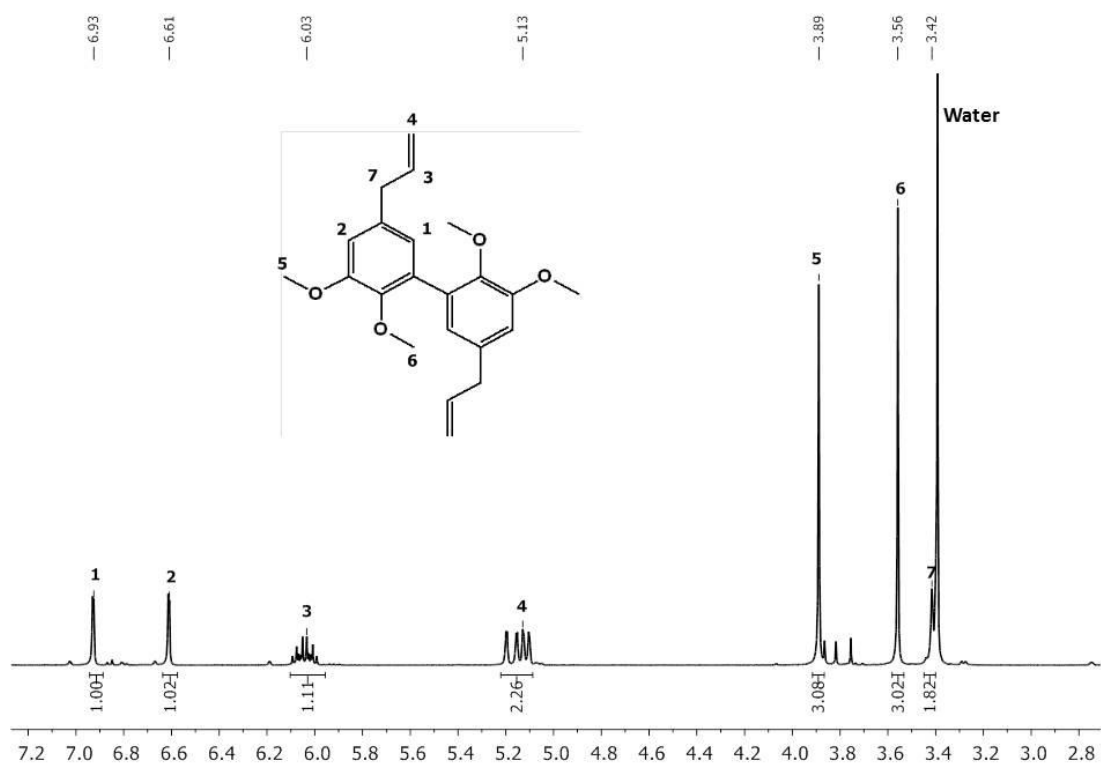


Figure S 15: ^1H NMR of methylated dieugenol 11 in DMSO

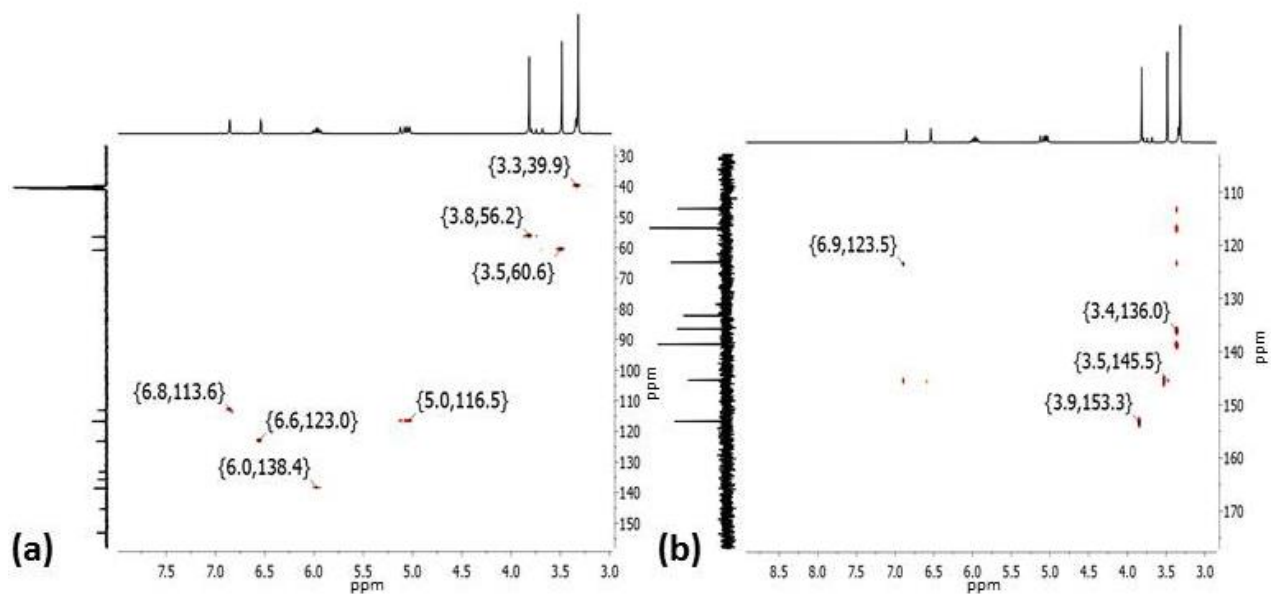


Figure S 16: HSQC (a) and HMBC (b) spectra of methylated dieugenol 11 in DMSO.

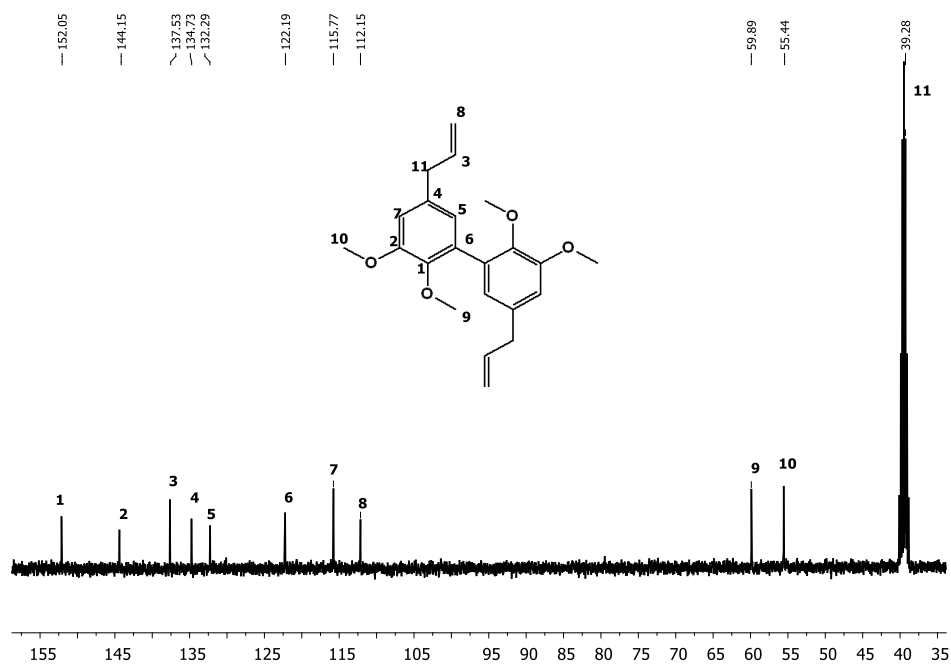


Figure S 17: ^{13}C NMR of methylated dieugenol 11 in DMSO

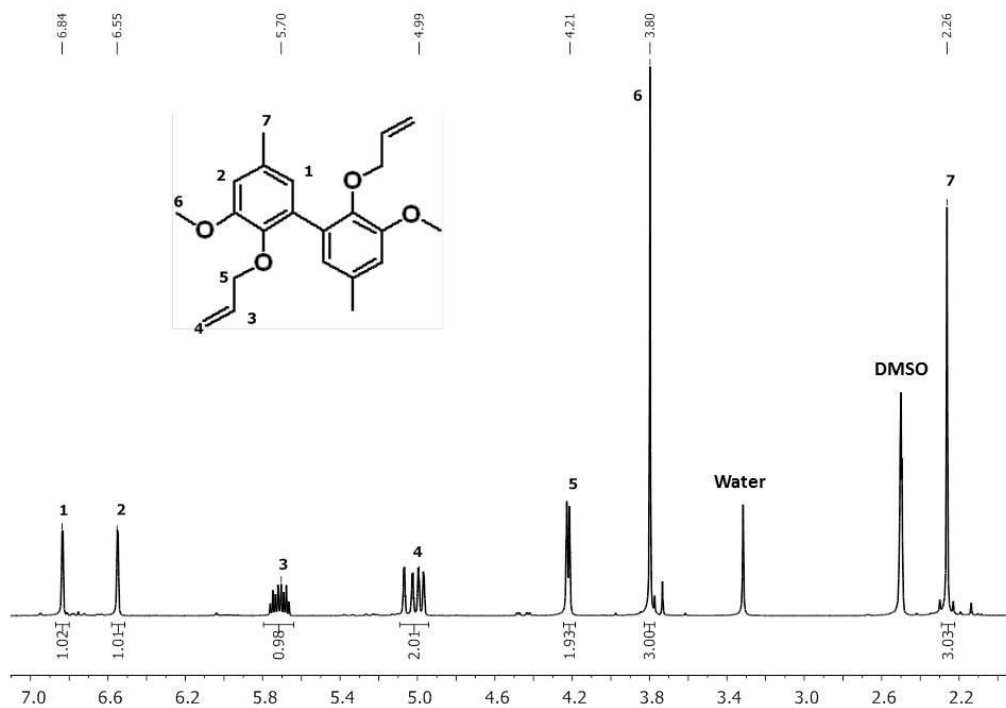


Figure S 18: ¹H NMR of allylated 2-methoxy-4-methylphenol 12 dimer in DMSO

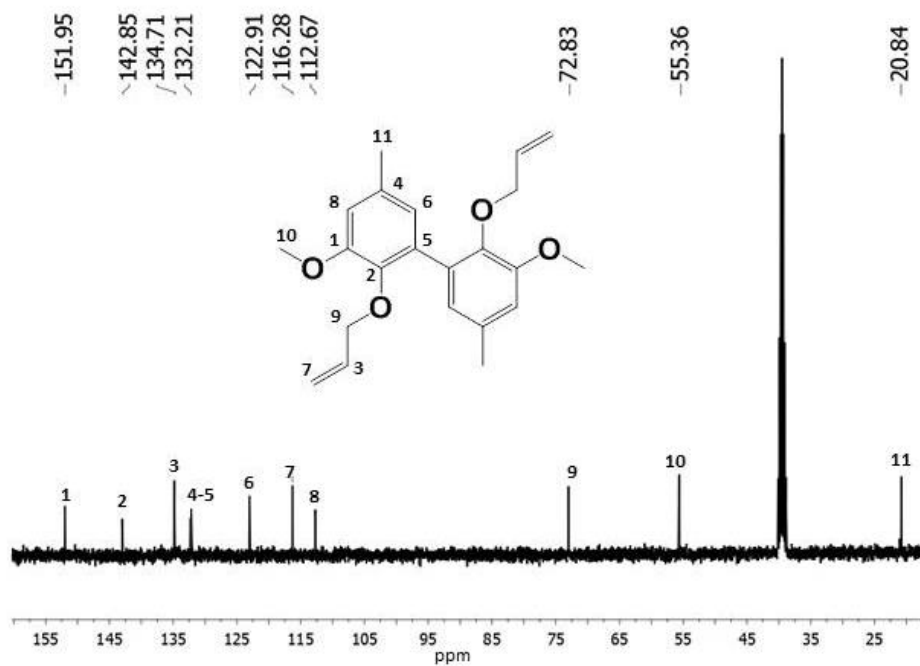


Figure S 19: ¹³C NMR of allylated 2-methoxy-4-methylphenol dimer 12 in DMSO

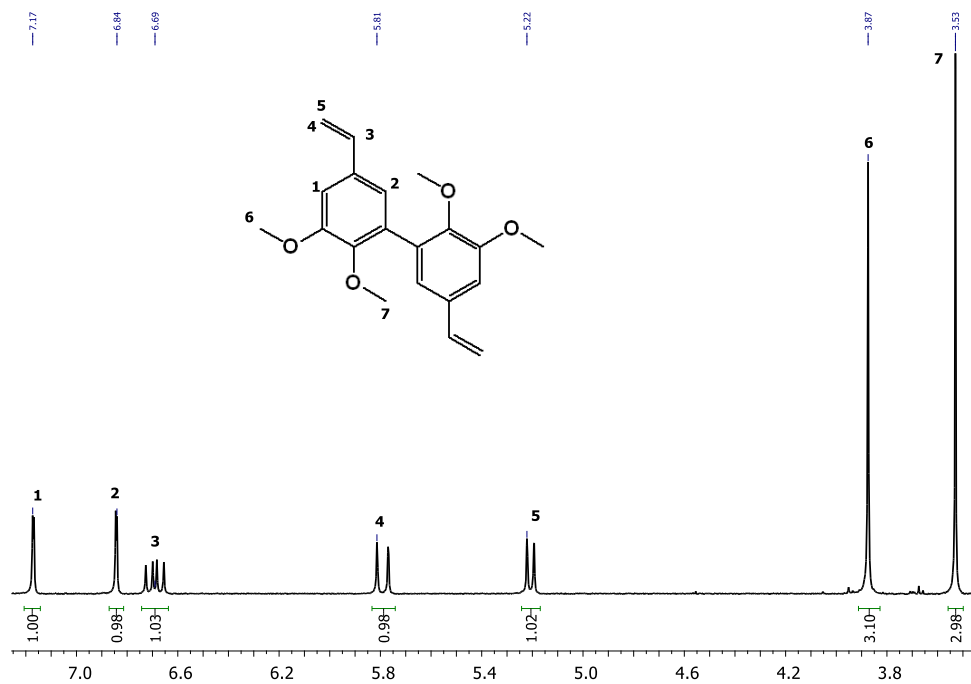


Figure S 20: ¹H NMR spectrum of divinyl 13 in DMSO

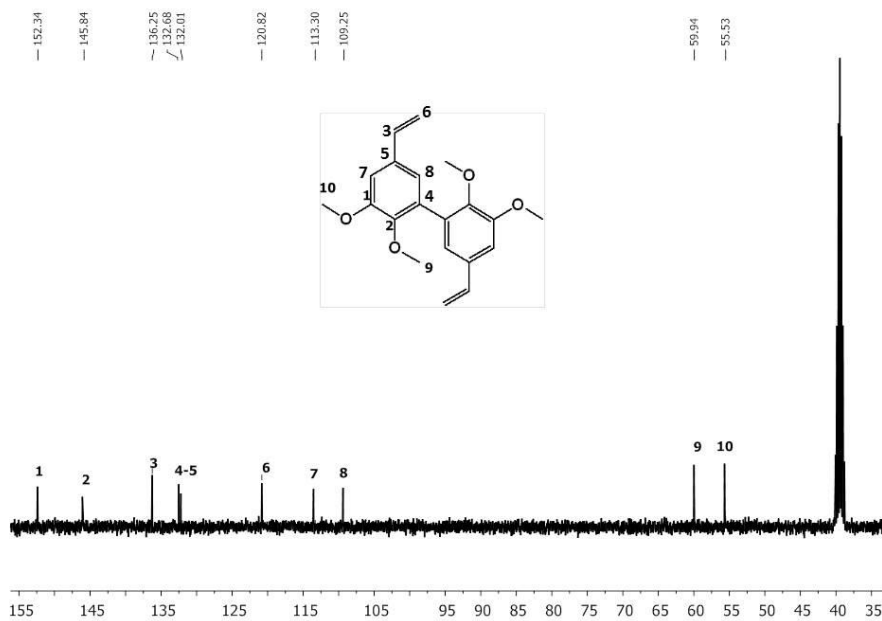


Figure S 21: ¹³C NMR of methylated divinyl 13 in DMSO

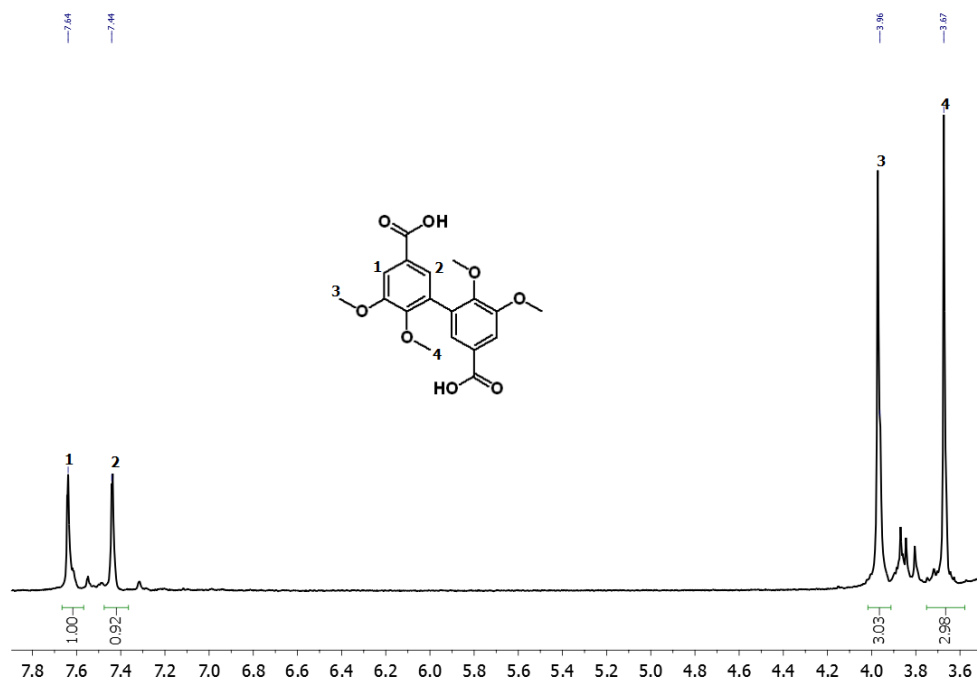


Figure S 22: ^1H NMR spectrum of methylated divanillic diacid 14 in DMSO

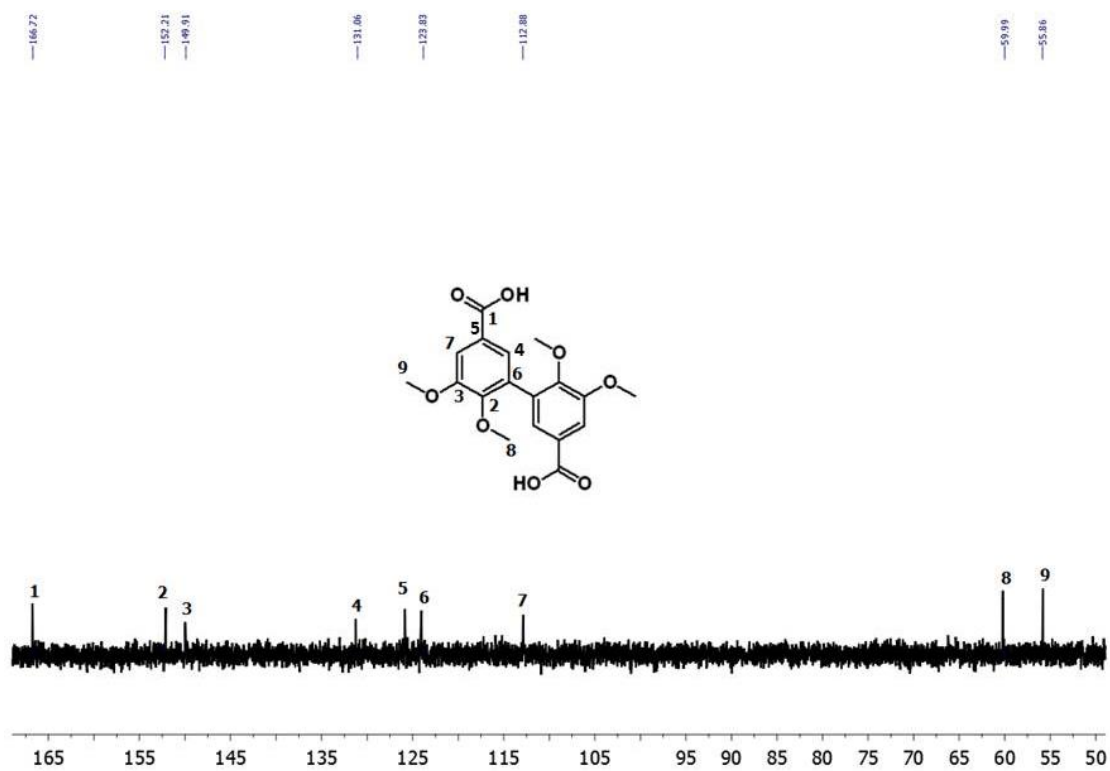


Figure S 23: ^{13}C NMR spectrum of methylated divanillic diacid 14 in DMSO

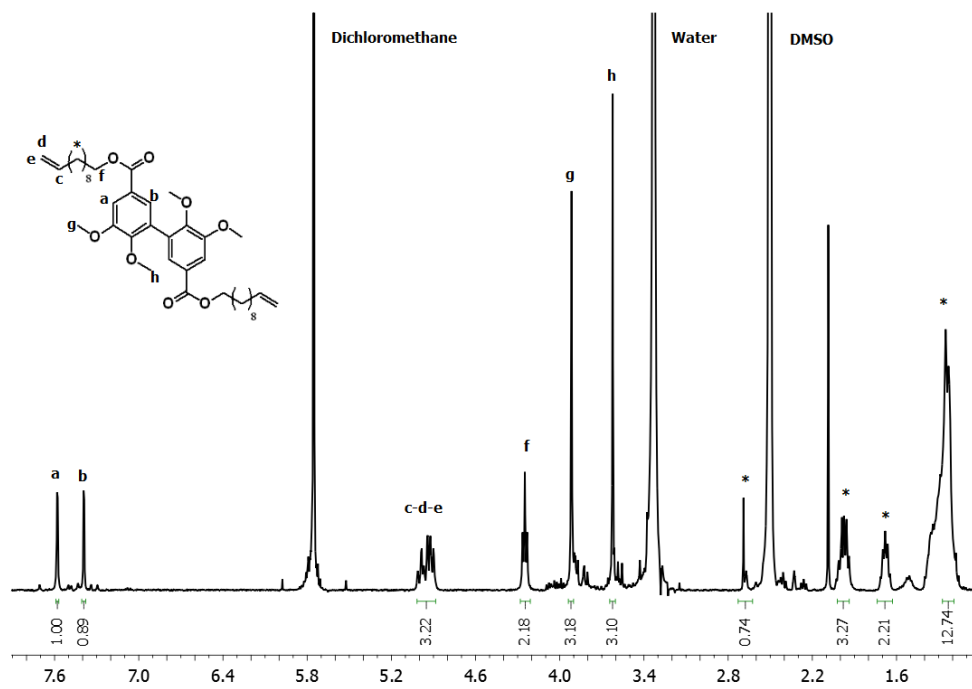


Figure S 24: ¹H NMR spectrum of bisunsaturated diester 15 in DMSO

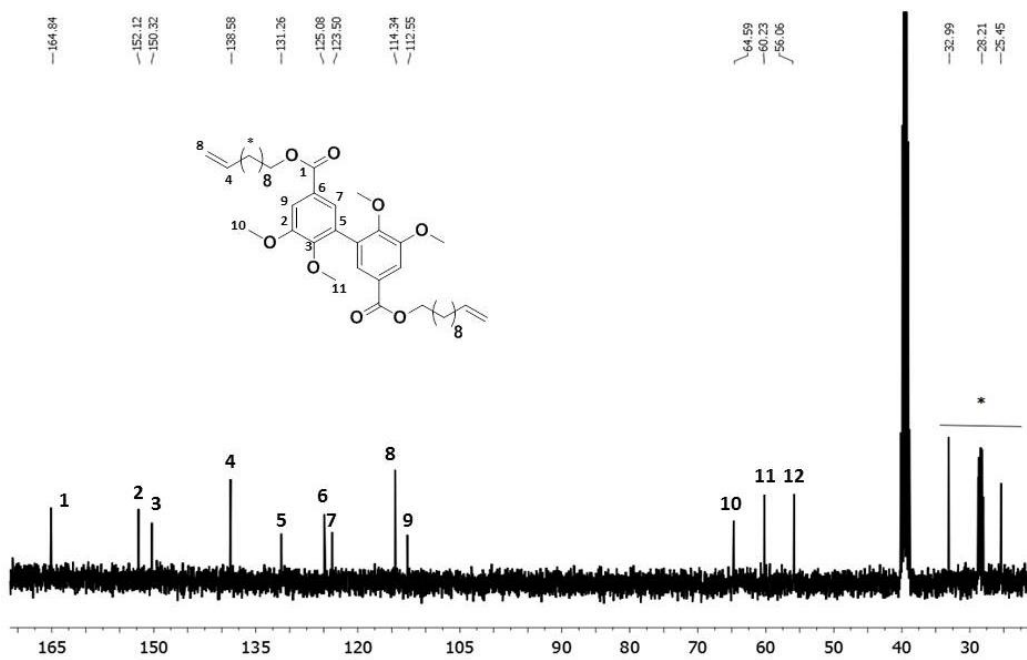


Figure S 25: ¹³C NMR spectrum of bisunsaturated diester 15 in DMSO

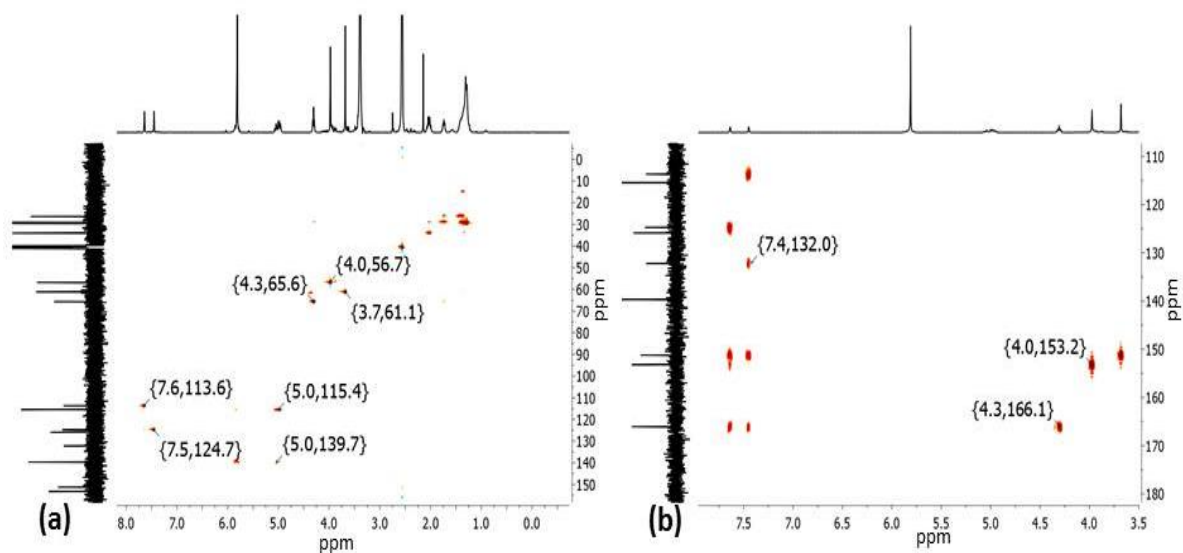


Figure S 26: HSQC (a) and HMBC (b) spectra of bis-unsaturated diester 15 in DMSO, at room temperature

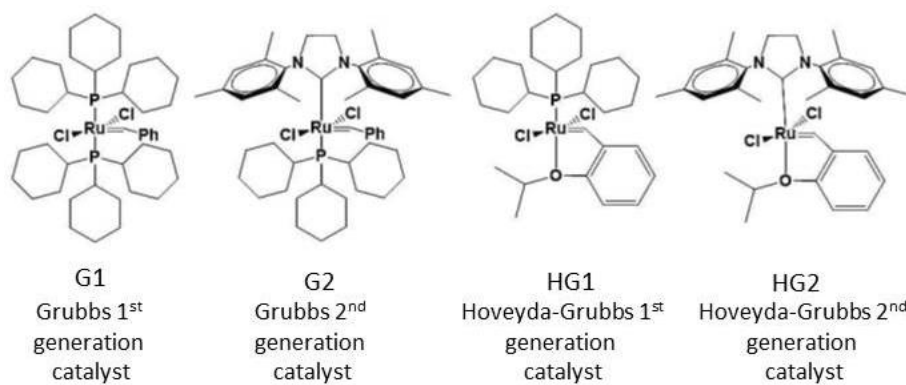


Figure S 27: Chemical structures of the first and second generation ruthenium metathesis catalysts.

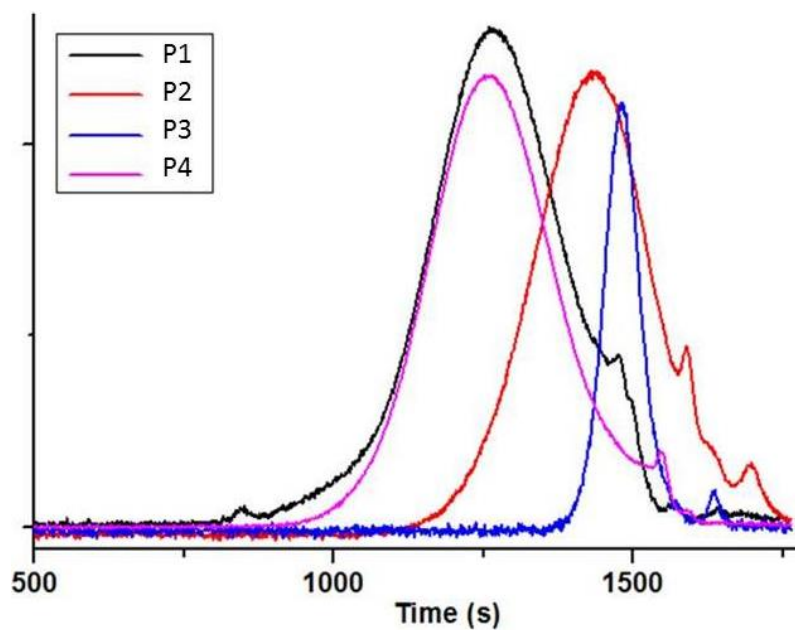


Figure S 28: SEC profiles of P1, P2, P3 and P4 synthesized by ADMET polymerization of unsaturated biphenyls, in DMF using PS calibration.

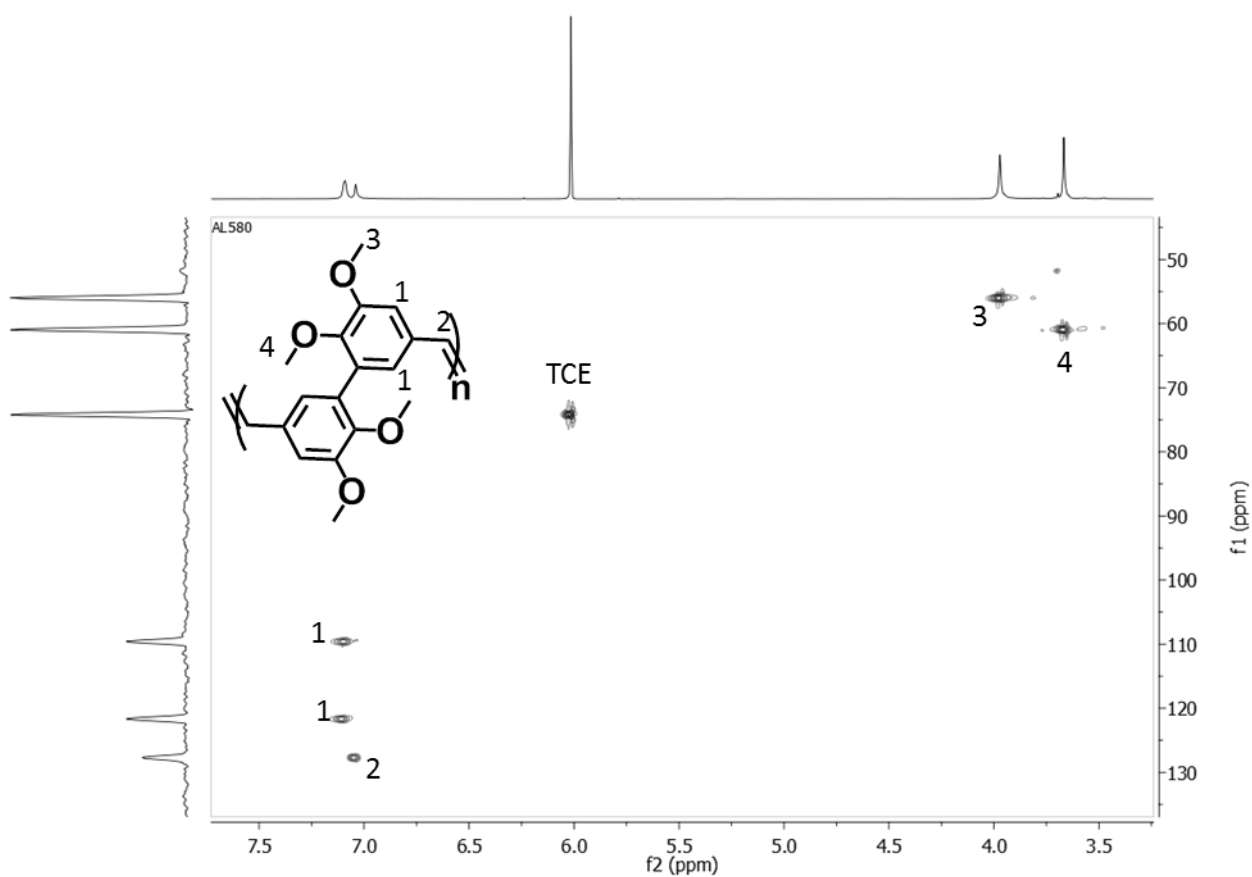


Figure S 29: HSQC spectrum of P1 in TCE, at room temperature.

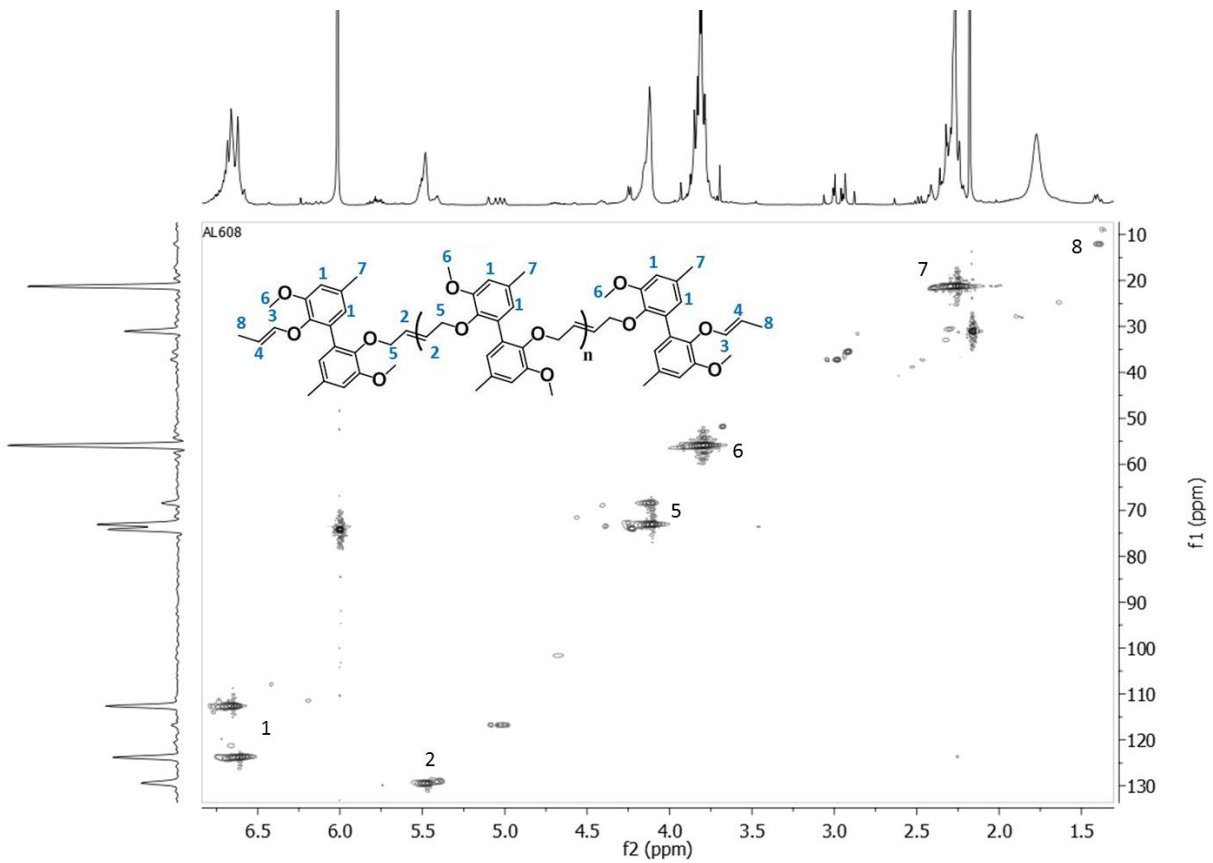


Figure S 30: HSQC spectrum of P3 in TCE, at room temperature.

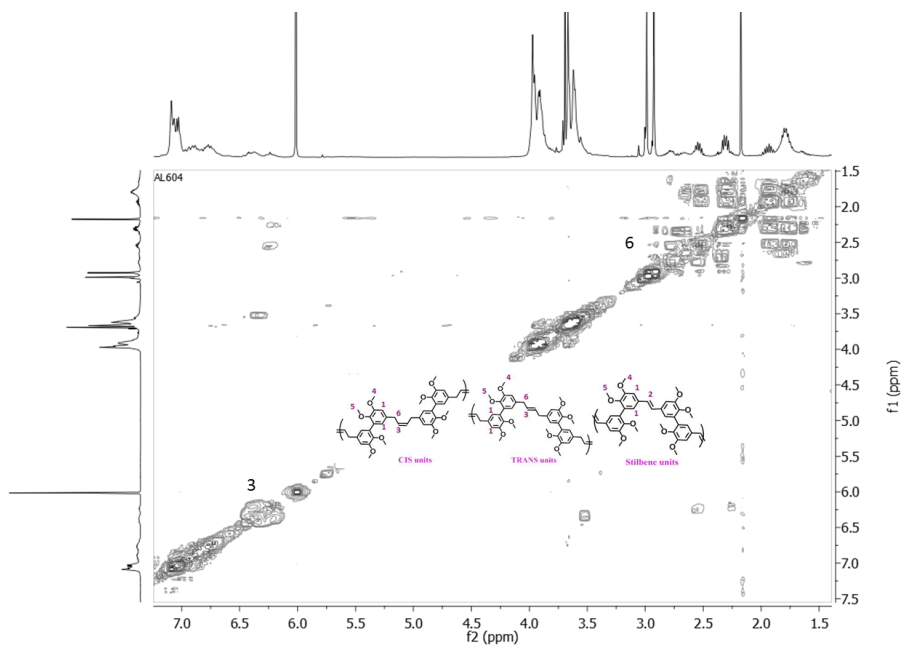


Figure S 31: COSY spectrum of P4 in TCE, at room temperature.

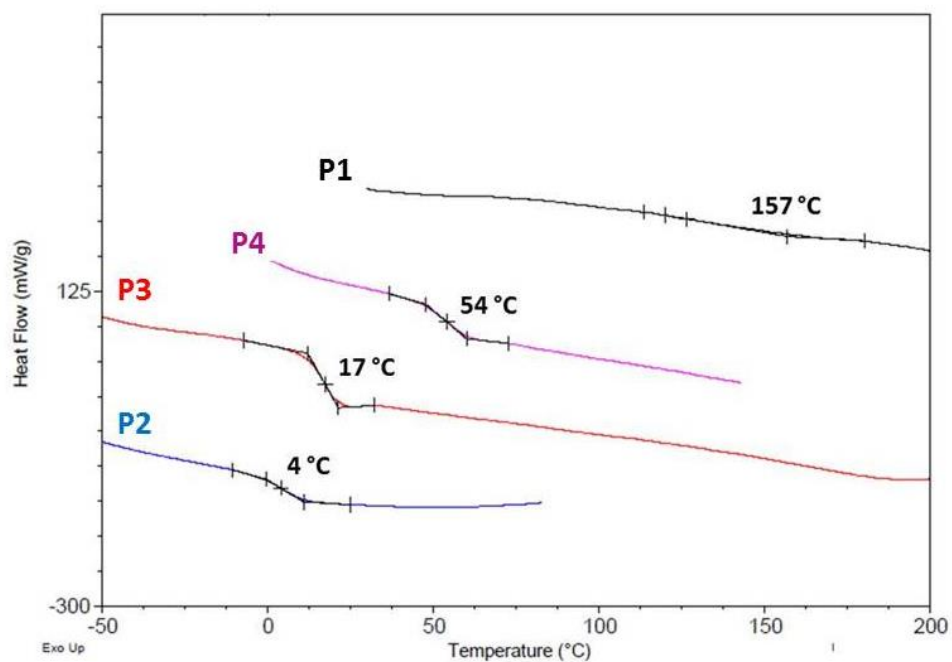


Figure S 32: DSC analyses of P1, P2, P3 and P4, second heating cycle.

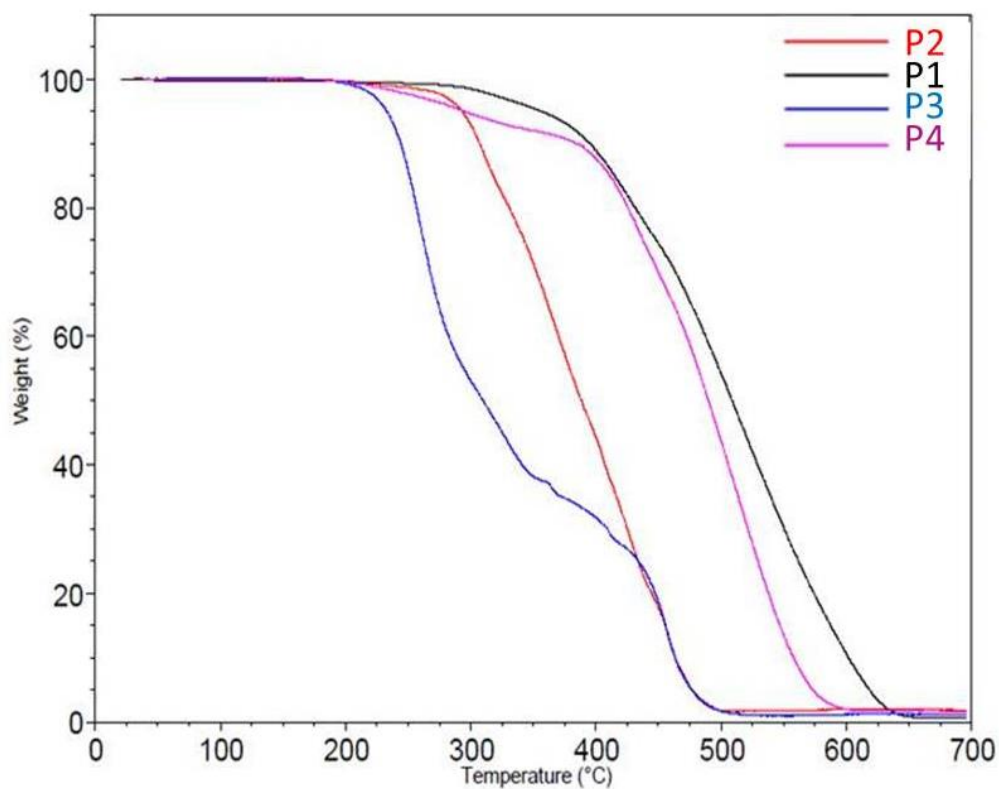


Figure S 33: TGA analyses under air of ADMET polymers, P1, P2, P3 and P4.