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Regiospecific, one-pot, and pseudo-five-component synthesis of 6,6′-(arylmethylene)bis(2-(*tert*-butyl)4-methylphenol) antioxidants using highly sulfonated multi-walled carbon nanotubes under solvent-free conditions

Reza Fareghi-Alamdari, Mohsen Golestanzadeh, Farima Agend, and Negar Zekri

Abstract: This is the first report of an innovative, one-pot, pseudo-five-component, and solvent-free synthesis of 6,6′-(arylmethylene)bis(2-(*tert*-butyl)4-methylphenol) antioxidants from *p*-cresol, methyl *tert*-butyl ether, and aldehydes in the presence of sulfonated multi-walled carbon nanotubes (MWCNTs-SO$_3$H) as heterogeneous, robust, and reusable catalysts under solvent-free conditions. MWCNTs-SO$_3$H was prepared and characterized by some microscopic and spectroscopic techniques including scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, dispersibility in different solvent, and thermogravimetric analysis (one functionality every approximately five carbon atoms). The acidity of the catalyst was measured by acid–base titration (1.80 mmol g^{-1}). This reaction proceeds smoothly to give the products in good yields. The catalyst was reused several times without efficient loss of its activity for the preparation of 6,6′-(arylmethylene)bis(2-(*tert*-butyl)4-methylphenol) antioxidants. In addition, high yields of the products and solvent-free and nontoxicity of the catalyst are other worthwhile advantages of the present method.

Key words: one-pot, carbon nanotubes, solid catalyst, antioxidants, solvent-free.

Résumé : Dans ce rapport, on décrit pour la première fois une nouvelle réaction monotope, pseudo à cinq composants et sans solvant, de synthèse d'antioxydants de type 6,6′-(arylméthylène)bis(2-(*tert*-butyl)4-méthylphénol) à partir de *p*-crésol, d'oxyde de tert-butyle et de méthyle et d'aldéhydes en présence de nanotubes de carbone à parois multiples sulfonés (MWCNT-SO3H) comme catalyseurs hétérogènes, robustes et réutilisables dans des conditions sans solvant. Les MWCNT-SO$_3$H ont été préparés et caractérisés par des techniques microscopiques et spectroscopiques, y compris la microscopie électronique à balayage, la microscopie électronique de transmission, la spectroscopie infrarouge à transformée de Fourier, la spectroscopie Raman, la dispersibilité dans différents solvants et l'analyse thermogravimétrique (une valence fonctionnelle environ tous les cinq atomes de carbone). On a mesuré l'acidité du catalyseur par titrage acide-base (1,80 mmol g^{-1}). La réaction se déroule doucement et donne les produits avec un bon rendement. On a réutilisé le catalyseur plusieurs fois sans perte d'efficacité de son activité pour la préparation des antioxydants de type 6,6′-(arylméthylène)bis(2-(*tert*-butyl)4-méthylphénol). Les hauts rendements en produits, l'absence de solvant et la non-toxicité du catalyseur sont d'autres avantages intéressants de la méthode. [Traduit par la Rédaction]

Mots-clés : monotope, nanotubes de carbone, catalyseur solide, antioxydants, sans solvant.

Introduction

Phenol derivatives, especially *p*-cresol, are widely employed for the synthesis of pharmaceutical, herbicides, agrochemicals, dyes, and antioxidants.[1–5] 6,6′-(Arylmethylene)bis(2-(*tert*-butyl)4-methylphenol) antioxidants are an important class of organic compounds. These compounds are substances that play important roles in the prevention of oxidative damage caused by reactive oxygen species.[6,7] These compounds neutralize these types of oxygen by intercepting and interacting with reactive radicals. Several synthetic methods using homogeneous[8–12] and heterogeneous catalysts[13–24] have been developed for the preparation of antioxidants. However, in spite of their potential applications, many published papers report harsh conditions, poor yields, very long reaction times, use of an excessive amount of catalyst, toxic organic solvents, and nonreusable catalysts for successful reaction conditions. Therefore, development of an efficient, direct, and environmentally friendly method has recently attracted much interest in the synthesis of bisphenolic antioxidants. The

multicomponent reaction is one of the most attractive approaches to achieve this aim, which enables direct construction of the desired products having an increased structural complexity from a set of small and simple starting materials.[25]

Many industrial catalysts consist of metals or metal compounds supported on an appropriate support. It is well documented that the role of the support is not merely that of a carrier; it may actually contribute catalytic activity and it may react to some extent with other catalyst ingredients during the manufacturing process. The most important characteristics of a support are the chemical composition, surface area, stability, and mechanical properties. The potential of carbon as catalyst support has not yet been fully exploited, even although there has been a considerable volume of literature devoted to this field in the last 25 years.[26] Carbon is capable of forming many allotropes due to its valency. Well-known forms of carbon include diamond and graphite. In recent decades, many more allotropes and forms of carbon have been discovered such as fullerene, carbon nanotubes (CNTs), and

Published at www.nrcresearchpress.com/cjc on 13 June 2013.

Scheme 1. One-pot synthesis of antioxidants.
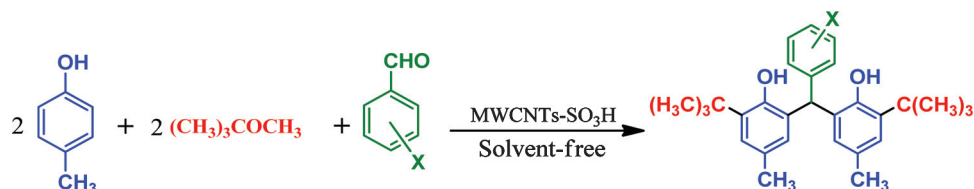
graphene. Some of the allotropes of carbon are widely used as support for the synthesis heterogeneous catalyst. Nevertheless, in spite of their potential applications, there are many disadvantages such as instability at high temperature and low specific surface area. On the other hand, carbon catalysts do not reuse at higher temperature in organic reactions and their structures destroy due to low mechanical and thermal properties. In addition, low specific surface area in carbon catalysts results in active sites in the catalyst being low. The superior properties of CNTs[27] and their wide ranges of potential applications in medicine,[28] electronic instruments, optical devices,[29] and catalytic applications[30] made them an important material in science and technology. Due to the high specific surface area of CNTs and mechanical and thermal stability, they are effective supports for the synthesis of solid acid catalysts. Sulfonated multi-walled CNTs (MWCNTs-SO$_3$H) are useful as a solid acid catalyst in organic transformations. In recent years, MWCNTs-SO$_3$H have been achieved by some reported methods.[31–35]

In continuation of our interest towards green methodologies and nanocatalyst,[36–40] we wish to disclose the regiospecific, one-pot, and pseudo-five-component synthesis of 6,6′-(arylmethylene) bis(2-(*tert*-butyl)4-methylphenol) antioxidants from *p*-cresol, methyl *tert*-butyl ether (MTBE), and aldehyde using MWCNTs-SO$_3$H in atomic economic and solvent-free conditions (Scheme 1).

Results and discussion

Preparation of the catalyst

Synthesis of MWCNTs-SO$_3$H catalyst was achieved in two steps as described in Scheme 2. As can be seen, first the MWCNTs, which are commercially available, were converted to MWCNTs-COOH with HCl (37%) and HNO$_3$ (63%). This step was carried out to increase the reactivity and purity of MWCNTs and to remove amorphous carbon, fullerene, and catalyst particles such as iron, cobalt, and nickel. This step also introduced oxygen-containing groups, mainly carboxyl groups, on the MWCNTs.[41,42] After this step, H$_2$SO$_4$ (98%) was reacted with MWCNTs-COOH to afford the MWCNTs-SO$_3$H.

Characterization of MWCNTs-SO$_3$H

The prepared catalyst was characterized by scanning electronic microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, thermogravimetric analysis (TGA), dispersibility test in different organic solvents, and acid–base titration.

SEM and TEM

The SEM and TEM images of MWCNTs before and after the H$_2$SO$_4$ treatment are shown in Fig. 1. The SEM images (Figs. 1*a* and 1*b*) indicate that functional groups such as sulfonic acid have been attached to the MWCNTs. Compared with the pristine MWCNTs, the MWCNTs-SO$_3$H were covered by a layer of foreign matter, resulting in thickened MWCNTs bundles and a denser network of nanotubes. The TEM images (Figs. 1*c* and 1*d*) also show that the SO$_3$H group has been supported on the MWCNTs. Groups of sulfonic acids are the foreign matter and are marked by white arrows.

FT-IR characterization

The spectroscopic data confirmed that the functionalization of CNTs with sulfonic acids occurred. Figure 2 shows the FT-IR spectra of pristine MWCNTs, MWCNTs-COOH, and MWCNTs-SO$_3$H. FT-IR is mainly used to identify the presence or absence of functional groups in organic chemistry. The high symmetry presented on pristine MWCNTs generates very weak infrared signals due to the weak difference of charge states and very small induced electric dipole. The peak related to the C=C double bond at approximately 1500 cm^{-1} is not seen in the spectrum of pristine MWCNTs (Fig. 2*a*). The functionalization breaks the symmetry of CNTs, which enhances the generation of induced electric dipoles and signs as detected. An FT-IR spectrum of MWCNTs-COOH is shown in (Fig. 2*b*). This spectrum shows lines at about 1650–1700 cm^{-1}, which could be assigned to the C–O stretching mode of the COOH group. The broad band centered at about 3300 cm^{-1} is the contribution from the OH stretching mode of COOH groups.[43] The HNO$_3$:HCl oxidation process introduces not only carboxylic acid but also alcohol or ketone species.[44] A weak line at approximately 1150 cm^{-1} from the C–O stretching mode in alcohol species can be observed.[43] H$_2$SO$_4$ treatment also results in the appearance of peaks at about 1300 and 1120 cm^{-1}, which correspond to the SO$_2$ asymmetric and symmetric stretching modes, respectively. In addition, in the low-frequency part of the spectrum line at 550 cm^{-1} was assigned to the C–S stretching mode, suggesting the existence of covalent sulfonic acid groups (Fig. 2*c*).

Raman characterization

Raman spectroscopy is a technique frequently used to characterize CNTs.[45] In the region spectrum (1300–1600 cm^{-1}), two bands are observed showing the characteristic of CNTs. These bands point to the graphite band (G-band) and disorder and defects of the structure, named the D-band. The ratio between the intensity of the D-band and the G-band, the $I_{D/G}$ value, corresponds to a higher proportion of sp^3 carbon.[46] In the low-frequency part of the spectrum, there is a second region characteristic of CNTs; this region is named the radial breathing mode (RBM). The RBM Raman features (appearing between 150 and 250 cm^{-1} for MWCNTs within $1 < d_t < 3$ nm) correspond to the atomic vibration of the carbon atoms in the radial directions, as if the tube were breathing.[45,46] These features are very useful for characterizing nanotube diameter. Figure 3 shows the Raman spectra of MWCNTs, MWCNTs-COOH, and MWCNTs-SO$_3$H. As shown in Fig. 3*a*, the spectrum exhibits three peaks at about 1320, 1571, and 2660 cm^{-1}. The feature at 1571 cm^{-1} is identified with the tangential mode (G-band). The origin of the line at 1320 cm^{-1} is the D-band and its appearance has been tentatively assigned to a symmetry lowering effect, such as the presence of nanoparticles (synthesis of CNTs) and functional groups such as sulfonic acid on the side walls of MWCNTs. The line at 2660 cm^{-1} has been attributed to the overtone of the D-band (G′-band). We can calculate that the I_D/I_G values of MWCNTs, MWCNTs-COOH, and MWCNTs-SO$_3$H are 0.24, 0.37, and 0.84, respectively. This increasing value implies that strong damage to the side walls of CNTs is due to the functionalization. The existence of RBM in Fig. S3*c* (see Supplementary material section) indicated that MWCNTs are still in their tubular structure after treatment with H$_2$SO$_4$ and functionalization, although some

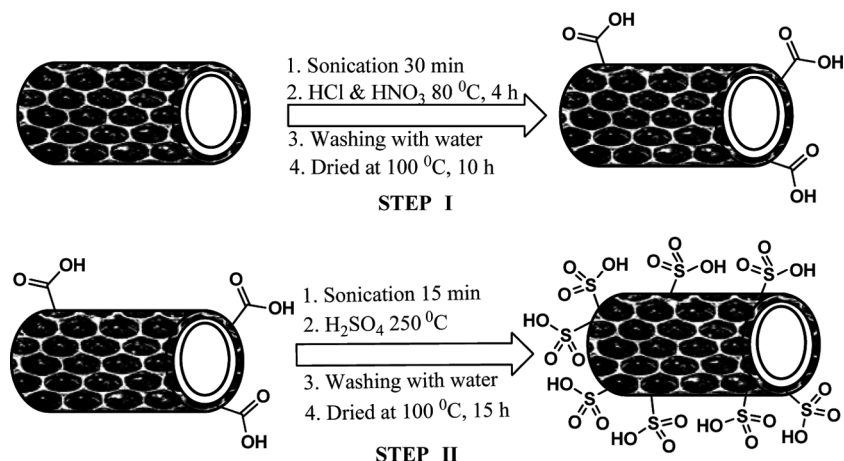**Scheme 2.** Synthetic route for preparation of the catalyst.

1. Sonication 30 min
2. HCl & HNO$_3$ 80 ^{0}C, 4 h
3. Washing with water
4. Dried at 100 ^{0}C, 10 h

STEP I

1. Sonication 15 min
2. H$_2$SO$_4$ 250 ^{0}C
3. Washing with water
4. Dried at 100 ^{0}C, 15 h

STEP II

Fig. 1. SEM images of (*a*) MWCNTs (normal magnification) and (*b*) MWCNTs-SO$_3$H (high magnification). TEM images of (*c*) MWCNTs and (*d*) MWCNTs-SO$_3$H.
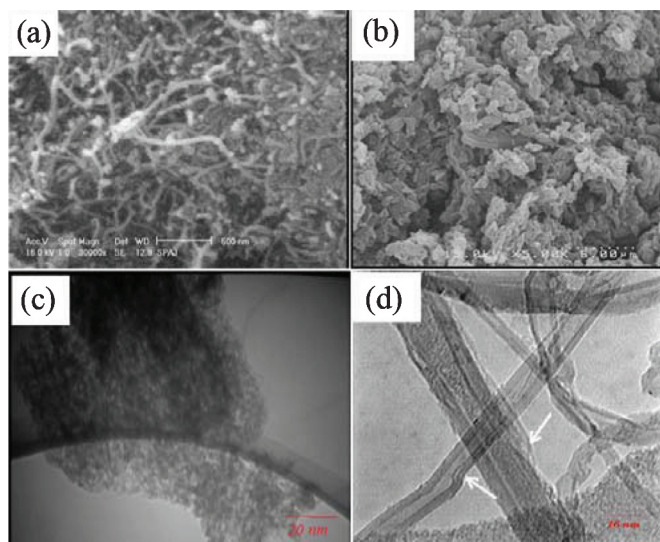

Fig. 2. FT-IR spectra of (*a*) MWCNTs, (*b*) MWCNTs-COOH, and (*c*) MWCNTs-SO$_3$H.
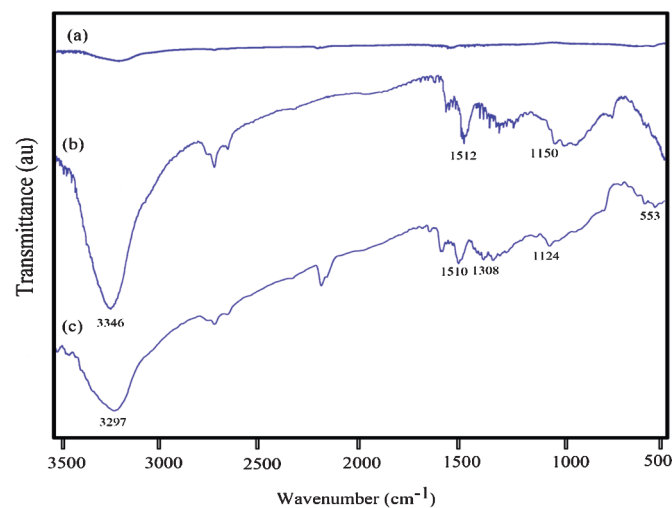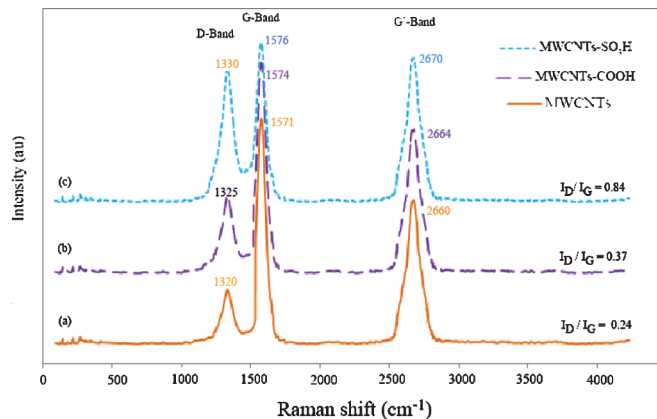

Fig. 3. Raman spectra of (*a*) MWCNTs, (*b*) MWCNTs-COOH, and (*c*) MWCNTs-SO$_3$H.

MWCNTs were probably damaged by strong oxidation. Results obtained by Raman spectroscopy showed good agreement with results of FT-IR spectroscopy.

TGA

TGA thermograms were used to determine the amount of sulfonic acid groups on the MWCNTs. We know that the weight loss between 100 and 200 °C is entirely due to the presence of amorphous carbon, water, metals, and so on.[47] Also, weight loss between 200 and 600 °C is completely due to functional groups on MWCNTs. It is possible that these functional groups are –OH, –COOH, and SO$_3$H groups. As shown in Fig. 4, the attached SO$_3$H groups decomposed at ~200 °C, while the MWCNTs remained stable up to ~600 °C, at which temperature oxidation started. Accordingly, these results indicate that about 49 wt% can be ascribed to the covalency of sulfonic acid groups. In Fig. 4*a*, we calculated that the weight loss was COOH groups (18% weight loss). Therefore, taking into account that the covalent SO$_3$H measurements indicated one functionality every approximately five carbon atoms. Results obtained by TGA showed good agreement with results of FT-IR and Raman spectroscopy.

Dispersibility of the catalyst in different solvents

The dispersibility of MWCNTs was significantly enhanced by functionalization. Figure 5 shows the dispersed states of MWCNTs, MWCNTs-COOH, and MWCNTs-SO$_3$H samples in various organic solvents used in this work. The MWCNTs-SO$_3$H (50 mg) dispersed well and formed uniform dispersion in 20 mL of organic solvents (son-

Fig. 4. Thermograms of (*a*) MWCNTs-COOH and (*b*) MWCNTs-SO$_3$H.
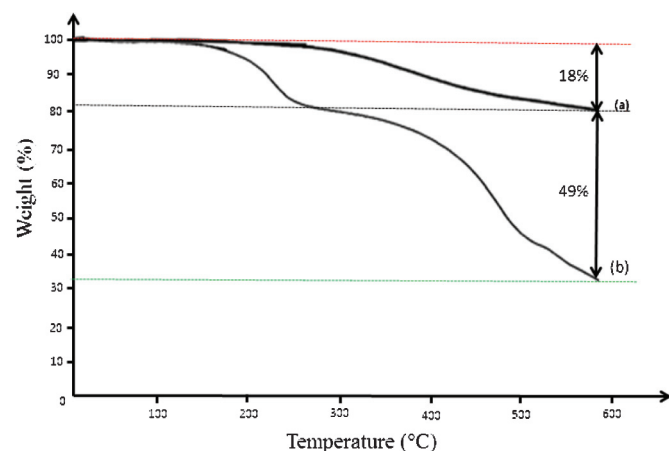
Fig. 5. Dispersibility of CNTs: (A) MWCNTs (CH$_3$NO$_2$), (B) MWCNTs-COOH (CH$_3$NO$_2$), (C) MWCNTs-SO$_3$H (*n*-hexane), (D) MWCNTs-SO$_3$H (H$_2$O), (E) MWCNTs-SO$_3$H (CH$_3$CN), and (F) MWCNTs-SO$_3$H (CH$_3$NO$_2$).

ication method). These dispersions were stable in nitromethane, acetonitrile, and water, respectively, after 100 days. Comparison of dispersion analysis images indicates that the suspension stability of the pristine MWCNTs was poor, as they easily sedimented. This sedimentation could be due to the agglomeration of nanotubes and lack of hydrogen bonding. Thus, the sulfonation process can be used as an effective method to obtain dispersive MWCNTs for a variety of applications, e.g., composites and catalysts. In addition, the highly sulfonated surfaces of MWCNTs act as a proton carrier; therefore, they can be used as solid acid catalysts in organic synthesis.

Acidity of the MWCNTs-SO$_3$H

The density of SO$_3$H groups on the MWCNTs was determined by acid–base titration. The acid–base titration showed that the amount of SO$_3$H attached to MWCNTs is 1.80 mmol g^{-1}.

Catalytic activity

The prepared catalyst was used for the synthesis of 6,6′-(arylmethylene)bis(2-(*tert*-butyl)4-methylphenol) antioxidants. First, the reaction parameters were optimized in the reaction of *p*-cresol (**1**), (MTBE) (**2**), and 4-nitrobenzaldehyde (**3a**) in the presence of MWCNTs-SO$_3$H as the model reaction. The results have been summarized in Table 1. To choose the solvent, the model reaction was performed in different solvents such as *n*-hexane, CHCl$_3$, CH$_3$CN, and CH$_3$NO$_2$ and also under solvent-free conditions (Table 1, entries 1–5). As this table shows, entry 5 gave the best result. Thus, a solvent-free condition was chosen as the reaction medium. Also, an increase in temperature of the reaction (70 to 110 °C) led to decreased 2,6-di*tert*-butyl-*p*-cresol (2,6-DTBC) (Table 1, entries 5–9). 2,6-DTBC is an unfavorable product and it prevents the formation of the desired products (6,6′-(arylmethylene)bis

(2-(*tert*-butyl)4-methylphenol) antioxidants). The model reaction was studied with different molar ratios of *p*-cresol:MTBE: 4-nitrobenzaldehyde and the best results were obtained with the molar ratios of 3:4.5:1, respectively (Table 1, entry 11). To optimize the amount of the catalyst, the model reaction was carried out in the presence of different amounts of the catalyst (Table 1, entries 13–15). The best result was obtained with 25 mg of the catalyst. Furthermore, we examined the type of alkylating agent in this reaction. We observed that *tert*-BuOH reduces yield of the reaction and increases unfavorable product (Table 1, entries 16–18).

To generalize the optimum conditions, different derivatives of 6,6′-(arylmethylene)bis(2-(*tert*-butyl)4-methylphenol) were prepared from the one-pot reaction mixture of *p*-cresol, MTBE, and the appropriate aldehyde (**3a–3m**) in the presence of a catalytic amount of MWCNTs-SO$_3$H (25 mg) under solvent-free conditions. The results have been summarized in Table 2. As shown in Table 2, aromatic aldehydes with electron-withdrawing groups (Table 2, entries 1–6) accelerate the reaction compared with the electron-donating groups (Table 2, entries 8–12).

The suggested mechanism in Scheme 3 seems to be reasonable for the one-pot, pseudo-five-component reaction of *p*-cresol, MTBE, and aldehyde catalyzed by MWCNTs-SO$_3$H under solvent-free conditions. The reaction proceeds via two catalytic cycles and a series of protonic shifts from MWCNTs-SO$_3$H to the substances. In the first catalytic cycle, MTBE is first activated by protonation with MWCNTs-SO$_3$H to give **I**. Nucleophilic attack of *p*-cresol on **I** affords **II**, which is subsequently converted to 2-*tert*-butyl-*p*-cresol (2-TBC) and releases MWCNTs-SO$_3$H. After the first catalytic cycle, the aldehyde is first activated by MWCNTs-SO$_3$H to give **III**. Nucleophilic attack of 2-TBC on **III** affords **IV** and **V**, which in turn are activated by MWCNTs-SO$_3$H to give **VI**. Nucleophilic attack of a second molecule of 2-TBC (produced from the first catalytic cycle) on **VI** gives **VII**, which is subsequently converted to the desired product and releases MWCNTs-SO$_3$H for the next catalytic cycle.

### The reusability and stability of the catalyst

For practical applications of heterogeneous catalysts, the lifetime of the MWCNTs-SO$_3$H and its level of reusability are very important features. The homogeneous acidic catalyst cannot recover even one time, in contrast with the MWCNTs-SO$_3$H catalyst, which can be filtered and reused several times without significant loss of its activity. The reusability of MWCNTs-SO$_3$H was investigated in the multiple sequential reaction of *p*-cresol, MTBE, and 4-chloro-3-nitrobenzaldehyde (**3c**). The catalyst was consecutively reused for eight runs without signifigant loss of its activity (Fig. 6). At the end of each reaction, the catalyst was isolated by filtration, washed exhaustively with chloroform and ethanol, and dried at 100 °C for 24 h before being used with fresh materials. The catalyst can be reused for eight runs without any treatment in its catalytic activity.

A comparison study with SWCNTs-SO$_3$H as catalyst

The catalytic properties of highly sulfonated multiwalled and single-walled CNTs were compared for the synthesis of 6,6′-((4-chloro-3-nitrophenyl)methylene)bis(2-(*tert*-butyl)-*p*-cresol). We observed that there is no high significant difference between these two types of catalysts.

Conclusions

In conclusion, in this work, a heterogeneous and stable MWCNTs-SO$_3$H was prepared and characterized by SEM, TEM, FT-IR spectroscopy, Raman spectroscopy, and TGA. The total surface acidity of SO$_3$H groups on the MWCNTs was 1.80 mmol g^{-1}. MWCNTs-SO$_3$H relative to other sulfonated allotropes of carbon is more stable at high temperature and high acidity because of the high specific surface area. For the first time, we disclosed a highly efficient regiospecific, one-pot, and pseudo-five-component approach for the

Table 1. Optimizing the reaction conditions.
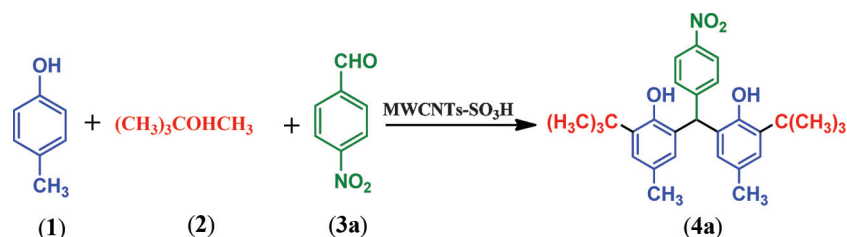
Entry	Catalyst (mg)	Alkylating agent (mmol)	Solvent	T (°C)	Time (h)	2,6-DTBC (%)[a]	Yield (%)[b]
1	30	MTBE (6)	n-Hexane	Reflux	8	33	25
2	30	MTBE (6)	CHCl$_3$	Reflux	8	21	35
3	30	MTBE (6)	CH$_3$CN	Reflux	8	15	40
4	30	MTBE (6)	CH$_3$NO$_2$	Reflux	8	15	40
5	30	MTBE (6)	Solvent-free	70	7	12	50
6	30	MTBE (6)	Solvent-free	80	6.5	10	55
7	30	MTBE (6)	Solvent-free	90	5	7	60
8	30	MTBE (6)	Solvent-free	100	4	5	75
9	30	MTBE (6)	Solvent-free	110	4	5	75
10	30	MTBE (7.5)	Solvent-free	100	4	5	80
11	30	MTBE (9)	Solvent-free	100	4	0	95
12	30	MTBE (10.5)	Solvent-free	100	4	8	80
13	25	MTBE (9)	Solvent-free	100	4	0	95
14	20	MTBE (9)	Solvent-free	100	5	0	75
15	0	MTBE (9)	Solvent-free	100	72		
16	25	$tert$-BuOH (6)	Solvent-free	100	5	18	75
17	25	$tert$-BuOH (7.5)	Solvent-free	100	5	14	70
18	25	$tert$-BuOH (9)	Solvent-free	100	5	17	65

Note: General reaction conditions: p-cresol (**1**) (6 mmol), 4-nitrobenzaldehyde (**3a**) (2 mmol), and solvent (2 mL).
[a]Yields analyzed by GC.
[b]Isolated yields.

synthesis of 6,6′-(arylmethylene)bis(2-(*tert*-butyl)4-methylphenol) antioxidants from *p*-cresol, MTBE, and aldehyde catalyzed by MWCNTs-SO$_3$H under solvent-free and atomic economic conditions. In addition, relatively short reaction times, high yields of the products, solvent-free, and nontoxicity of the catalyst are other worthwhile advantages of this work.

Experimental

Materials and apparatus

The chemicals used in this work were purchased from Fluka and Merck chemical companies. The MWCNTs used in this study (L = 20–30 μm, D = 20–40 nm) were purchased from the Research Institute of Petroleum Industry (Iran). Melting points were determined using a melting point IA 8103 apparatus. FT-IR spectra were obtained with KBr pellets in the range of 400–4000 cm^{-1} with a Nicolet-860 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in DMSO-(d_6) solvent on a Brucker-Avance 500 MHz spectrometer using TMS as an internal standard. Mass spectra were recorded on a Micromass Platform II spectrometer from, EI mode at 70 eV. The Raman spectra were recorded with an Almega Thermo Nicolet Dispersive Raman spectrometer excited at 532 nm. TGA was performed on a mettle TA 4000 instrument at a heating rate of 10 K min^{-1}. SEM images of MWCNTs were taken on a Philips XL30 SEM instrument. TEM images were recorded with a JEOL-JEM 2010 microscope. The thermal analyses (carbon, hydrogen, and nitrogen) were obtained with a Carlo ERBA model EA 1108 analyzer.

Preparation of the MWCNTs-SO$_3$H

In a typical experiment, MWCNTs (1 g) and 100 mL of deionized water were added to a well becher and sonicated for 30 min. After the sonication, the solvent was removed under reduced pressure and the obtained MWCNTs were transferred to another flask con-

taining 25 mL of HCl (37%) and 25 mL of HNO$_3$ (63%) and stirred at 80 °C for 4 h under a nitrogen atmosphere. Then the solution was filtered under reduced pressure and the obtained materials were first washed thoroughly with deionized water and then dried at 100 °C for 10 h. In this step, the MWCNTs-COOH were obtained. After the first step, the MWCNTs-COOH (1 g) and 50 mL of deionized water were sonicated for 15 min. Then the water was filtered and 40 mL of H$_2$SO$_4$ (98%) was added to the setup at 250–270 °C (H$_2$SO$_4$ boils at 335 °C) for 20 h under a nitrogen atmosphere. After cooling the solution to room temperature, the liquid was filtered and washed completely with deionized water several times. The solid obtained materials were dried at 100 °C for 15 h. After this step, the MWCNTs-SO$_3$H were obtained and used in the synthesis of 6,6′-(arylmethylene)bis(2-(*tert*-butyl)4-methylphenol) antioxidants as a catalyst. These steps are described in Scheme 2.

General procedure for the synthesis of bisphenolic antioxidants catalyzed by MWCNTs-SO$_3$H

In a 10 mL round-bottom flask equipped with a magnetic bar and condenser, a mixture of *p*-cresol (6 mmol), MTBE (9 mmol), and MWCNTs-SO$_3$H (25 mg) was heated at 100 °C under solvent-free conditions. The progress of the reaction was monitored by TLC (*n*-hexane–EtOAc, 10:2). After preparation of 2-TBC, aldehyde (2 mmol) was added to the setup and the reaction mixture was stirred at 100 °C under solvent-free conditions. After completion of the reaction, 15 mL of acetone was added. The catalyst was filtered by simple filtration. The liquid was recovered by evaporation on a rotary evaporator. Then the solid material was washed with *n*-hexane (5 mL) and water successively to afford the pure product. The pure product was kept in an oven at 80 °C for 24 h.

Regeneration of the MWCNTs-SO$_3$H

The used catalyst was washed exhaustively with CHCl$_3$ and EtOH and it dried at 100 °C for 24 h before using with fresh substances.

Table 2. Synthesis of 6,6′-(arylmethylene)bis(2-(*tert*-butyl)4-methylphenol) antioxidants.
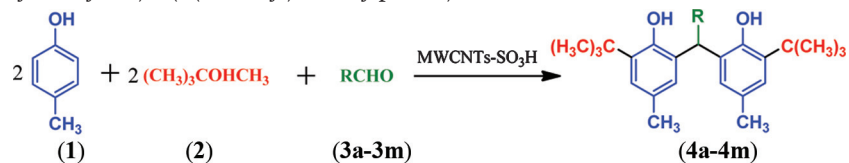
Entry	Aldehyde	Product	Yield (%)[a]	Time (h)	mp (°C)	Turnover frequency (h⁻¹)
1	(3a)	(4a)	95	4	217–219	10.6
2	(3b)	(4b)	95	4.2	174–176	10.1
3	(3c)	(4c)	100	3.5	201–203	12.7
4	(3d)	(4d)	95	4	203–205	10.6
5	(3e)	(4e)	95	3.7	193–195	11.4

Table 2 (*continued*).
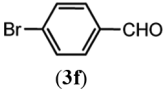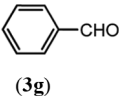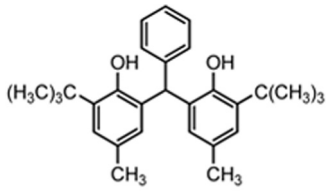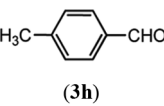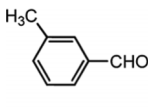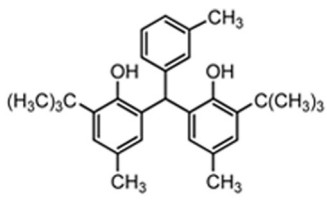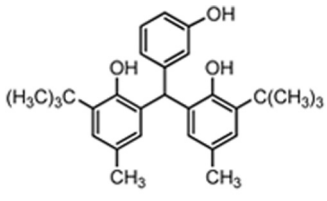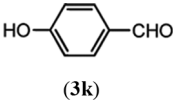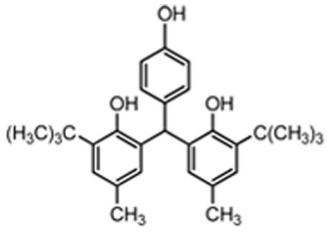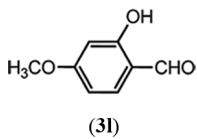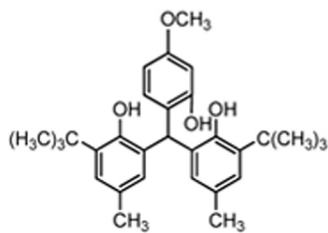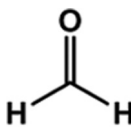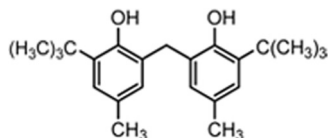
Entry	Aldehyde	Product	Yield (%)[a]	Time (h)	mp (°C)	Turnover frequency (h⁻¹)
6	(3f)	(4f)	92	4.5	210–212	9.1
7	(3g)	(4g)	90	4.7	176–178	8.5
8	(3h)	(4h)	87	5.5	195–197	7.0
9	(3i)	(4i)	88	5.2	166–168	7.5
10	(3j)	(4j)	88	4.7	196–198	8.3
11	(3k)	(4k)	Trace	24		

Table 2 (*concluded*).

Entry	Aldehyde	Product	Yield (%)[a]	Time (h)	mp (°C)	Turnover frequency (h⁻¹)
12	(3l)	(4l)	Trace	24		
13	(3m)	(4m)	100	2.5	129–131	26.7

Note: General reaction conditions: *p*-cresol (**1**) (6 mmol), MTBE (**2**) (9 mmol), aldehyde (**3a–3l**) (2 mmol), solvent-free, 100 °C, catalyst (25 mg). For entry 13: formaline (**3m**) (3 mmol). For entries 11 and 12, the starting materials were recovered from the reaction mixtures.

[a]Isolated yields.

Scheme 3. Proposed reaction mechanism.
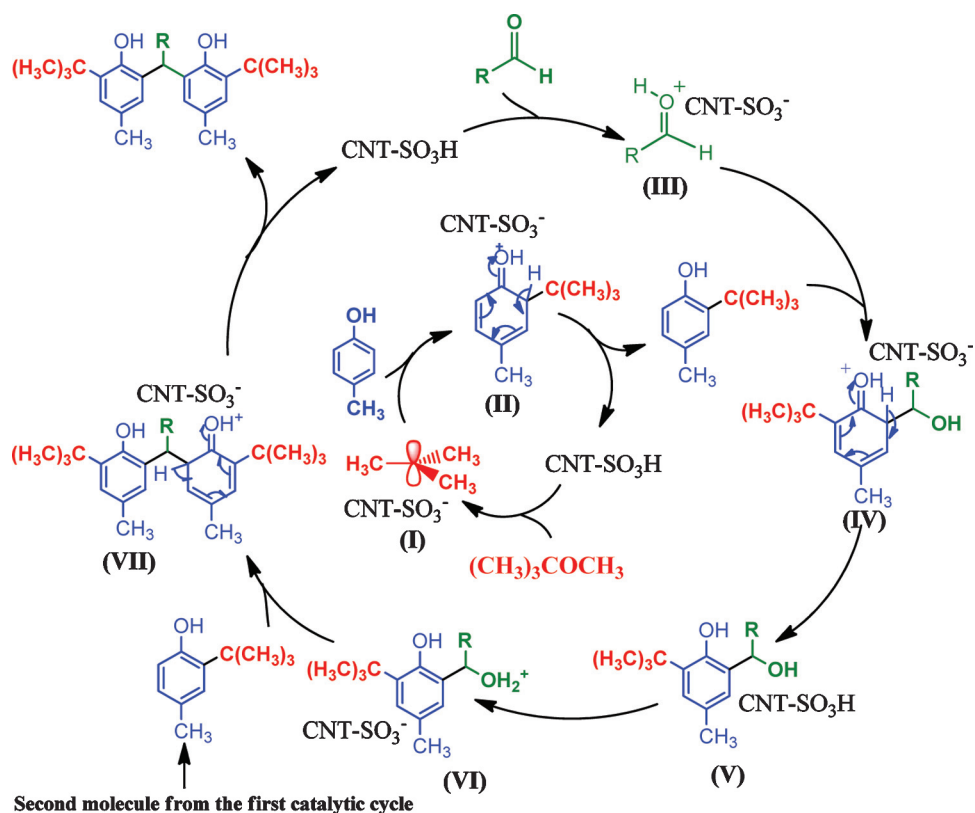
Spectroscopic and physical data

6,6′-((4-Nitrophenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (*Table 2*, compound 4a)

mp 217–219 °C. IR (KBr) ν (cm⁻¹): 3608, 3507, 2955, 1600, 1515, 1447, 1347, 1230, 1118, 884. ¹H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.39 (18H, s, *tert*-butyl), 2.08 (6H, s, CH₃), 6.24 (1H, s, Ar₃CH), 6.30 (2H, s, OH), 6.93 (2H, s, 3-H TBMP), 7.16 (2H, d, *J* = 8 Hz, 2,6-H aldehyde), 7.64 (2H, s, 5-H TBMP), 8.12 (2H, d, *J* = 8 Hz, 3,5-H aldehyde). ¹³C NMR (125 MHz, DMSO-d_6) δ (ppm): 20.82, 29.82, 34.39, 38.65, 38.93, 39.21, 39.48, 40.04, 40.32, 43.27, 123.09, 125.91, 127.8, 130.67, 137.92, 145.79,

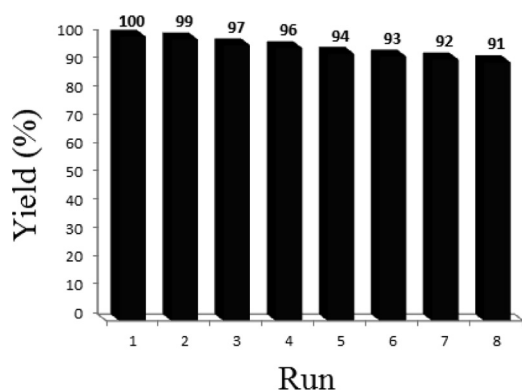150.65, 152.38. MS: *m/z* = 461.26 (M⁺). Anal. calcd. for C₂₉H₃₅NO₄: C 75.46, H 7.64, N 3.03%; found: C 75.62, H 7.39, N, 2.95%.

6,6′-((3-Nitrophenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (*Table 2*, compound 4b)

mp 174–176 °C. IR (KBr) ν (cm⁻¹): 3542, 3477, 3004, 2956, 2915, 1530, 1441, 1344, 1175, 696. ¹H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.39 (18H, s, *tert*-butyl), 2.14 (6H, s, CH₃), 6.25 (1H, s, Ar₃CH), 6.30 (2H, s, OH), 6.94 (2H, s, 3-H TBMP), 7.35 (1H, d, *J* = 7.3 Hz, 5-H aldehyde), 7.55 (1H, t, *J* = 7.3 Hz, 6-H aldehyde), 7.65 (2H, s, 5-H

Fig. 6. Reusability of the catalyst in the synthesis of 6,6′-((4-chloro-3-nitrophenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (**4c**).

δ (ppm): 1.33 (18H, s, *tert*-butyl), 2.08 (6H, s, CH$_3$), 6.04 (1H, s, Ar$_3$CH), 6.30 (2H, s, OH), 6.85 (2H, d, *J* = 8.34 Hz, 2,6-H aldehyde), 6.90 (2H, s, 3-H TBMP), 7.42 (2H, d, *J* = 8.32 Hz, 3,5-H aldehyde), 7.55 (2H, s, 5-H TBMP). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 20.86, 29.84, 34.39, 38.66, 38.94, 39.21, 39.49, 39.77, 40.05, 40.32, 42.60, 119.00, 125.67, 127.64, 127.69, 130.78, 130.99, 131.18, 137.58, 143.18, 150.57. MS: *m/z* = 494.18 (M$^+$), 496.18 (M$^+$ + 2). Anal. calcd. for C$_{29}$H$_{35}$BrO$_2$: C 70.30, H 7.12%; found: C 70.15, H 7.30%.

6,6′-(Phenylmethylene)bis(2-(tert-butyl)4-methylphenol) (Table 2, compound 4g)

mp 176–178 °C. IR (KBr) ν (cm^{-1}): 3562, 3495, 3001, 2930, 1870, 1443, 1215, 873, 645. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.33 (18H, s, *tert*-butyl), 2.07 (6H, s, CH$_3$), 6.06 (1H, s, Ar$_3$CH), 6.33 (2H, s, OH), 6.89 (2H, s, 3-H TBMP), 6.92 (2H, d, *J* = 6.2 Hz, 3,5-H aldehyde), 7.17 (1H, t, *J* = 7.00 Hz, 4-H aldehyde), 7.24 (2H, d, 3,5-H aldehyde), 7.53 (2H, s, 5-H TBMP). ^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm): 20.88, 29.93, 34.38, 38.65, 38.93, 39.21, 39.49, 39.77, 40.05, 40.32, 42.99, 125.47, 125.87, 127.41, 127.83, 127.90, 128.99, 131.29, 137.34, 143.46, 150.62. MS: *m/z* = 416.27 (M$^+$). Anal. calcd. for C$_{29}$H$_{36}$O$_2$: C 83.61, H 8.71%; found: C 83.44, H 8.66%.

6,6′-(p-Tolylmethylene)bis(2-(tert-butyl)4-methylphenol) (Table 2, compound 4h)

mp 195–197 °C. IR (KBr) ν (cm^{-1}): 3542, 3514, 2948, 2916, 1470, 1141, 1320, 1178, 847, 760, 666. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.33 (18 H, s, *tert*-butyl), 2.07 (6H, s, CH$_3$), 2.25 (3H, s, CH$_3$-aldehyde), 5.99 (1H, s, Ar$_3$CH), 6.33 (2H, s, OH), 6.80 (2H, d, *J* = 7.82 Hz, 3,5-H aldehyde), 6.88 (2H, s, 3-H TBMP), 7.04 (2H, d, *J* = 7.82 Hz, 2,6-H aldehyde), 7.48 (2H, s, 5-H TBMP). ^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm): 20.57, 20.90, 29.83, 34.38, 38.66, 38.94, 39.22, 39.49, 39.77, 40.05, 40.33, 42.59, 125.44, 127.41, 127.78, 128.57, 128.88, 131.39, 134.77, 137.26, 140.30, 150.52. MS: *m/z* = 430.32 (M$^+$). Anal. calcd. for C$_{30}$H$_{38}$O$_2$: C 83.67, H 8.89%; found: C 83.64, H 8.96%.

6,6′-(m-Tolylmethylene)bis(2-(tert-butyl)4-methylphenol) (Table 2, compound 4i)

mp 166–168 °C. IR (KBr) ν (cm^{-1}): 3552, 3524, 2948, 2906, 1466, 1141, 1318, 1168, 847, 760, 656. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.33 (18H, s, *tert*-butyl), 2.07 (6H, s, CH$_3$), 2.16 (3H, s, CH$_3$-aldehyde), 6.01 (1H, s, Ar$_3$CH), 6.34 (2H, s, OH), 6.65 (1H, d, *J* = 7.95 Hz, 6-H aldehyde), 6.90 (2H, s, 3-H TBMP), 6.98 (1H, t, *J* = 7.60 Hz, 5-H aldehyde), 7.48 (2H, s, 5-H TBMP). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 20.89, 21.06, 29.35, 29.83, 34.07, 34.38, 38.65, 38.93, 39.21, 39.49, 39.77, 40.04, 40.32, 42.95, 125.46, 126.05, 126.66, 126.80, 127.40, 127.77, 127.86, 129.70, 131.28, 136.82, 137.29, 143.38, 150.55, 153.44. MS: *m/z* = 430.14 (M$^+$). Anal. calcd. for C$_{30}$H$_{38}$O$_2$: C 83.67, H 8.89%; found: C 83.74, H 8.86%.

6,6′-((3-Hydroxyphenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (Table 2, compound 4j)

mp 196–198 °C. IR (KBr) ν (cm^{-1}): 3544, 3497, 3001, 2957, 2914, 1599, 1444, 1254, 1176, 868, 766, 466. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.28 (18H, s, *tert*-butyl), 2.09 (6H, s, CH$_3$), 5.91 (1H, s, Ar$_3$CH), 6.35 (2H, s, OH), 6.35 (2H, d, *J* = 7.65 Hz, 2,6-H aldehyde), 6.56 (1H, d, *J* = 7.25 Hz, 6-H aldehyde), 6.89 (2H, s, 3-H TBMP), 7.03 (1H, t, *J* = 7.76 Hz, 5-H aldehyde), 7.49 (2H, s, 5-H TBMP), 9.16 (1H, s, OH aldehyde). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 20.92, 29.85, 34.40, 38.63, 38.91, 39.19, 39.47, 39.75, 40.03, 40.30, 42.84, 113.06, 116.15, 119.83, 125.46, 127.44, 127.86, 128.80, 131.30, 137.31, 144.86, 150.52, 152.02. MS: *m/z* = 432.23 (M$^+$). Anal. calcd. for C$_{29}$H$_{36}$O$_3$: C 80.52, H 8.39%; found: C 80.74, H 8.26%.

6,6′-Methylenebis(2-(tert-butyl)4-methylphenol) (Table 2, compound 4m)

mp 129–131 °C. IR (KBr) ν (cm^{-1}): 3533, 3490, 3004, 2957, 2904, 1599, 1444, 1214, 1176, 868, 766, 466. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.30 (18H, s, *tert*-butyl), 2.11 (6H, s, CH$_3$), 5.84 (2H, s, Ar$_2$CH$_2$),

TBMP), 7.72 (1H, s, 2-H aldehyde), 8.06 (1H, d, *J* = 7.3 Hz, 4-H aldehyde). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 20.85, 29.82, 34.40, 38.65, 38.93, 39.20, 39.48, 39.76, 40.04, 40.32, 42.94, 121.60, 123.18, 125.90, 127.76, 127.91, 129.32, 130.77, 135.76, 137.96, 146.43, 147.60, 150.66. MS: *m/z* = 461.54 (M$^+$). Anal. calcd. for C$_{29}$H$_{35}$NO$_4$: C 75.46, H 7.64, N 3.03%; found: C 75.55, H 7.69, N 3.00%.

6,6′-((4-Chloro-3-nitrophenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (Table 2, compound 4c)

mp 201–203 °C. IR (KBr) ν (cm^{-1}): 3564, 3522, 3000, 2951, 2914, 1530, 1470, 1364, 1185, 1155, 1051, 842, 766, 664, 482. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.34 (18H, s, *tert*-butyl), 2.09 (6H, s, CH$_3$), 6.20 (1H, s, Ar$_3$CH), 6.30 (2H, s, OH), 6.94 (2H, s, 3-H TBMP), 7.17 (1H, d, *J* = 7.9 Hz, 6-H aldehyde), 7.52 (1H, s, 5-H aldehyde), 7.63 (1H, d, *J* = 1.3 Hz, 2-H aldehyde), 7.64 (2H, s, 5-H TBMP). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 20.84, 29.83, 34.41, 38.66, 38,94, 39.22, 39.49, 39.77, 40.05, 40.33, 42.63, 122.49, 125.62, 126.01, 127.71, 128.03, 130.56, 131.10, 134.36, 138.12, 145.53, 147.14, 150.65. MS: *m/z* = 495.22 (M$^+$), 497.28 (M$^+$ + 2). Anal. calcd. for C$_{29}$H$_{34}$ClNO$_4$: C 70.22, H 6.91, N 2.82%; found: C 70.55, H 7.09, N 2.85%.

6,6′-((4-Chlorophenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (Table 2, compound 4d)

mp 203–205 °C. IR (KBr) ν (cm^{-1}): 3564, 3517, 2993, 2913, 2861, 1441, 1410, 1174, 1090,1015, 873, 762. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.38 (18H, s, *tert*-butyl), 2.08 (6H, s, CH$_3$), 6.06 (1H, s, Ar$_3$CH), 6.30 (2H, s, OH), 6.90 (2H, s, 3-H TBMP), 6.92 (2H, d, *J* = 7.4 Hz, 2,6-H aldehyde), 7.29 (2H, d, *J* = 7.4 Hz, 3,5-H aldehyde), 7.54 (2H, s, 5-H TBMP). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 20.85, 29.83, 34.38, 38.65, 38.93, 39.21, 39.49, 39.77, 40.04, 40.32, 42.54, 125.66, 127.63, 127.68, 127.86, 130.49, 130.76, 131.04, 137.57, 142.71, 150.58. MS: *m/z* = 450.23 (M$^+$), 452.03 (M$^+$ + 2). Anal. calcd. for C$_{29}$H$_{35}$ClO$_2$: C 77.22, H 7.82%; found: C 77.55, H 7.59%.

6,6′-((2-Chlorophenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (Table 2, compound 4e)

mp 193–195 °C. IR (KBr) ν (cm^{-1}): 3577, 3515, 3000, 2962, 2914, 2866, 1440, 1360, 1182, 1045, 869, 757, 663. ^{1}H NMR (500 MHz, DMSO-d_6) δ(ppm): 1.32 (18H, s, *tert*-butyl), 2.16 (6H, s, CH$_3$), 6.23 (1H, s, Ar$_3$CH), 6.20 (2H, s, OH), 6.61 (1H, t, *J* = 6.9 Hz, 4-H aldehyde), 6.92 (2H, s, 3-H TBMP), 7.20 (2H, m, 5,6-H aldehyde), 7.39 (1H, d, *J* = 7.08 Hz, 3-H aldehyde), 7.46 (2H, s, 5-H TBMP). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 20.91, 29.78, 34.38, 38.64, 38.92, 39.20, 39.48, 39.76, 40.04, 40.32, 41.06, 125.79, 127.46, 129.83, 137.53, 150.79. MS: *m/z* = 450.87 (M$^+$), 452.29 (M$^+$ + 2). Anal. calcd. for C$_{29}$H$_{35}$ClO$_2$: C 77.22, H 7.82%; found: C 77.15, H 7.80%.

6,6′-((4-Bromophenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (Table 2, compound 4f)

mp 210–212 °C. IR (KBr) ν (cm^{-1}): 3560, 3517, 3026, 2944, 2862, 1441, 1251, 1216, 1175, 1010, 873, 825, 424. ^{1}H NMR (500 MHz, DMSO-d_6)

6.33 (2H, s, OH), 6.89 (2H, s, 3-H TBMP), 7.49 (2H, s, 5-H TBMP). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 20.63, 29.94, 32.07, 34.20, 126.33, 126.61, 128.61, 129.69, 136.23, 150.00. MS: m/z = 340.24 (M$^+$). Anal. calcd. for $C_{23}H_{32}O_2$: C 81.13, H 9.47%; found: C 81.64, H 9.54%.

Supplementary material

Supplementary material is available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0160.

Acknowledgements

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