

Alkylation of Phenols with *tert*-Butanol Catalyzed by H-Form of Y Zeolites with a Hierarchical Porous Structure

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Abstract—*tert*-Butyl-substituted phenols have been synthesized via the reaction of phenol, *o*-, *m*-, and *p*-cresols with *tert*-butanol under the action of CBr₄-promoted Y-zeolites in the H-form with a hierarchical porous structure.

Keywords: phenol, *tert*-butanol, *tert*-butylphenols, 2,4-di-*tert*-butylphenol, cresol, zeolite HY

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The principal function of antioxidant additives to polymer materials is to decelerate the processes of (thermal) decomposition of polymers deteriorating the materials properties due to chains scission or cross-linking. The most efficient antioxidant stabilizers of polymers include shielded (substituted) phenols: *para-tert*-butylphenol, 2,6-di-*tert*-butyl-4-methylphenol (ionol, also known under the Agidol-1 trademark), 2-*tert*-butyl-4-methylphenol, 2-*tert*-butyl-5-methylphenol, and 2-isopropyl-5-methylphenol (thymol).

tert-Butylphenols are industrially produced via alkylation of phenol and its alkylated derivatives with isobutylene in the presence of sulfocationic resins. Despite high yield of the target product, this method suffers from serious drawbacks including relatively fast deactivation of the catalysts, high pressure, and side reaction of isobutylene polymerization leading to the formation of side products which should be separated off [1].

The interest to more environmentally friendly and cost-efficient catalytic processes of phenol, *o*-, *m*-, and *p*-cresols alkylation with alcohols in the presence of homogeneous and heterogeneous selective and active catalysts has recently emerged. Lewis acids (AlCl₃, FeCl₃, and ZnCl₂), Bronsted acids (H₃PO₄, H₂SO₄, HF, HClO₄), cationites, zeolites, mesoporous materials, sulfated zirconia, heteropoly acids, and ionic liquids have been used as catalysts of phenols and cresols alkylation. The drawbacks of the Bronsted acids are corrosion of the equipment and environmental pollution due to the

formation of toxic wastewater, whereas solid acids can be readily deactivated [2–4].

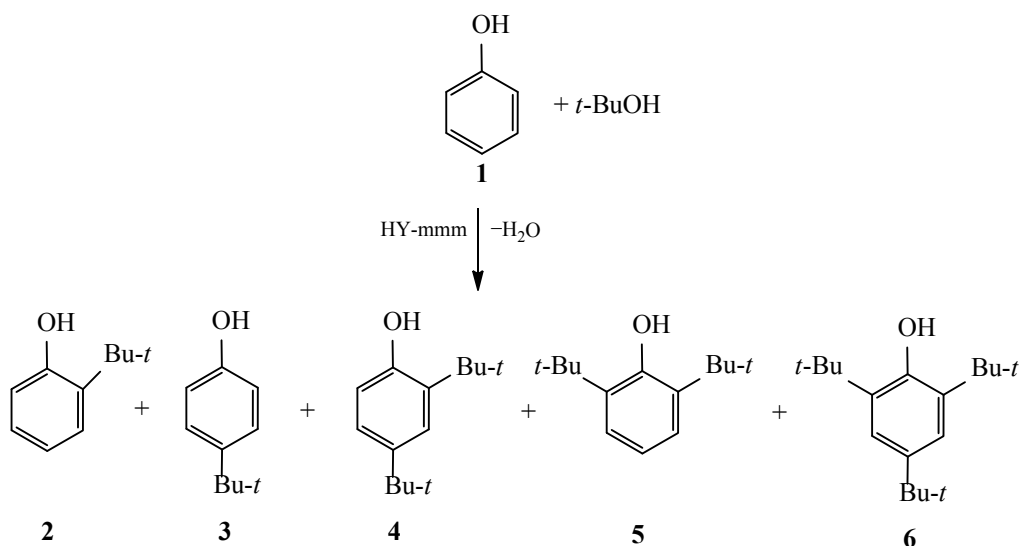
Special attention has been put to the development of acid catalysts based on structurally diverse zeolites recognized for facile separation of the reaction products, possibility to be used repeatedly, and elimination of corrosion issues [3, 5, 6]. MCM-22 zeolite is an efficient catalyst of the formation of *p-tert*-butylphenol via alkylation of phenol with *tert*-butanol [3]. The highest selectivity (81–91%) with respect to *p-tert*-butylphenol has been observed when using Beta zeolite in the H-form, yet phenol conversion has not exceeded 20% [1].

This study aimed to elaborate a novel efficient method to prepare *tert*-butylphenols via the interaction of phenol and cresols with *tert*-butanol in the presence of a heterogeneous catalyst: granular zeolite Y in the H-form exhibiting high degree of crystallinity (95%) and hierarchical (micro-, meso-, and macroporous) structure (HY-mmm) [7] or ultrastable zeolite (USY-mmm) obtained via high-temperature steam treatment (100% water vapor, 540°C, 3 h) of ammonium form of Y-mmm zeolite, in order to exchange the Na⁺ cations with NH₄⁺ ones 0.72 [8].

A series of experiments revealed that HY-mmm zeolite with degree of crystallinity 0.94 catalyzed alkylation of phenol **1** with *tert*-butanol. The reaction occurred at 150–175°C during 2–6 h and led to the formation of isomeric *tert*-butylphenols **2–6** (Scheme 1).

The major products of the reaction were *ortho*- (**2**), *para*- (**3**), and 2,4-di-*tert*-butylphenols (**4**). For example,

Scheme 1.



phenol conversion at 175°C after 6 h was 54%, the ratio of products **2** : **3** : **4** being 1.2 : 1 : 1.

We further attempted to increase the phenol conversion via addition of promoters enhancing acidic properties of HY-mmm zeolite. It is known that mere treatment of zeolites with solutions of strong acids does not lead to noticeable increase in their acidity; moreover, acids can deteriorate the crystal structure of zeolite. On the other hand, the exchange of hydroxide anions in the zeolite structure with halide ones has increased the acidity due to strong inductive effect of halide ions [9–11]. In view of that, we attempted incorporation of halides in the HY-

mmm zeolite via the treatment with hydrochloric and hydrobromic acids. The result was negative, since the reaction was performed at 150–175°C, and HCl (HBr) were almost completely evaporated off under the process conditions.

Since water is a side product of phenol alkylation with *tert*-butanol, we decided to use halide derivatives of methane (CHCl_3 , CCl_4 , CHBr_3 , and CBr_4) as the source of chloride and bromide: those compounds could be hydrolyzed and gradually release HCl or HBr. The experiments revealed that CCl_4 , CHBr_3 , and CBr_4 indeed promoted HY-mmm zeolite, the effect being the strongest

Table 1. Yield of *tert*-butylphenols **2–6** depending on the reagents concentration and temperature in the presence of HY-mmm zeolite (5 wt %)^a

CHlg ₄	[Phenol] : [<i>t</i> -BuOH] : [CHlg ₄]	<i>T</i> , °C	Phenol conversion, %	Yield of the products, %				
				2	3	4	5	6
–	100 : 200 : 0	150	37	14	15	8	0	0
CBr_4	100 : 200 : 10	"	92	20	9	39	10	14
–	100 : 200 : 0	175	54	20	17	17	0	0
CBr_4	100 : 200 : 5	"	94	9	33	49	3	
CHBr_3	100 : 200 : 10	"	64	21	21	22	1	1
CCl_4	"	"	72	21	17	23	4	7
CBr_4	"	"	100	4	39	52	0	5
CBr_4	100 : 400 : 10	"	100	6	65	29	0	0

^a Duration of the reaction 6 h.

Table 2. Yield of *tert*-butylphenols **2–7** depending on the reagents concentration and temperature in the presence of HY-mmm zeolite (5 wt %) promoted with CBr₄^a

Catalyst	[Phenol] : [<i>t</i> -BuOH] : [CHlg ₄]	Phenol conversion, %	Yield of the products, %					
			2	3	4	5	6	7
HY-mmm	100 : 200 : 10	100	4	39	52	0	5	0
HY-mmm ^b	100 : 200 : 10	95	3	26	53	0	10	3
HY-mmm ^c	100 : 200 : 10	100	3	44	50	0	1	2
HY-mmm ^c	100 : 200 : 0	76	23	11	29	6	7	0

^a Reaction conditions: 175°C, 6 h.

^b Repeated use of the catalyst (the second cycle).

^c Repeated use of the catalyst (the third cycle).

in the case of CBr₄ which was most readily hydrolyzed under the reaction conditions (Table 1).

To confirm the hydrolysis of CBr₄, we performed mercurimetry titration of the reaction mixture after the experiment. The content of HBr after 4 h was 70 mg/mL.

HY-mmm zeolite promoted with CBr₄ could be used repeatedly: it practically retained its activity in three cycles of the process (Table 2). Besides compounds **2–6**, trace amounts of isomeric *tert*-butyl derivatives **7** were detected in the mixture.

At the next stage of the study, we investigated the catalytic activity of USY-mmm zeolite (prepared via high-temperature steam treatment of NH₄Ymmm zeolite) in the reaction of phenols alkylation with *tert*-butanol. It has been earlier found that such treatment leads to partial dealumination of the zeolite crystal lattice. As a result, the concentration of the acidic sites was decreased, whereas the volume of meso- and macropores was increased (at the expense of decrease in the volume of the micropores), therefore, the yields of bulky 4-*tert*-butylphenol **3** and 2,4-di-*tert*-butylphenol **4** were increased. For example, the interaction of phenol with Bu^tOH in the presence of 5 wt % of USY-mmm {175°C, 6 h, [phenol] : [*t*-BuOH] : [CBr₄] molar ratio 100 : 200 : (0–10)} led to predominant formation of 2,4-di-*tert*-butylphenol **4** (Table 3). That trend was preserved for the reactions of *o*-, *m*-, and *p*-cresols **8–10** with *t*-BuOH catalyzed by 5 wt % of USY-mmm zeolite promoted with CBr₄ (175°C, 6 h). The increase in temperature to 280°C led to the loss of reaction selectivity and gave a mixture of isomers (Scheme 2).

An analogous reaction of phenols (in particular, *m*-cresol) in the presence of micro-, macro-, and mesoporous HY-mmm zeolite (5 wt %) with 2-propanol gave two products: 2-isopropyl-5-methylphenol **18** (yield 25–32%)

and 2,4-diisopropyl-5-methylphenol **19** (yield 33–48%). The reaction occurred at higher temperature (220–250°C).

Primary alcohols, in particular *n*-PrOH, also gave the C-alkylated products (a mixture of *o*- and *p*-propylphenols and 2,4-dipropylphenol) upon the interaction with phenol in the presence of HY-mmm (220°C, 6 h), but the O-alkylation product was also formed (49% of propyl phenyl ether at [PhOH] : [*n*-PrOH] : [CBr₄] : [HY-mmm] = 100 : 200 : 10 : 1). HY-mmm zeolite (5 wt %) catalyzed the C- and O-alkylation of *o*-, *m*-, and *p*-cresols with *n*-PrOH as well.

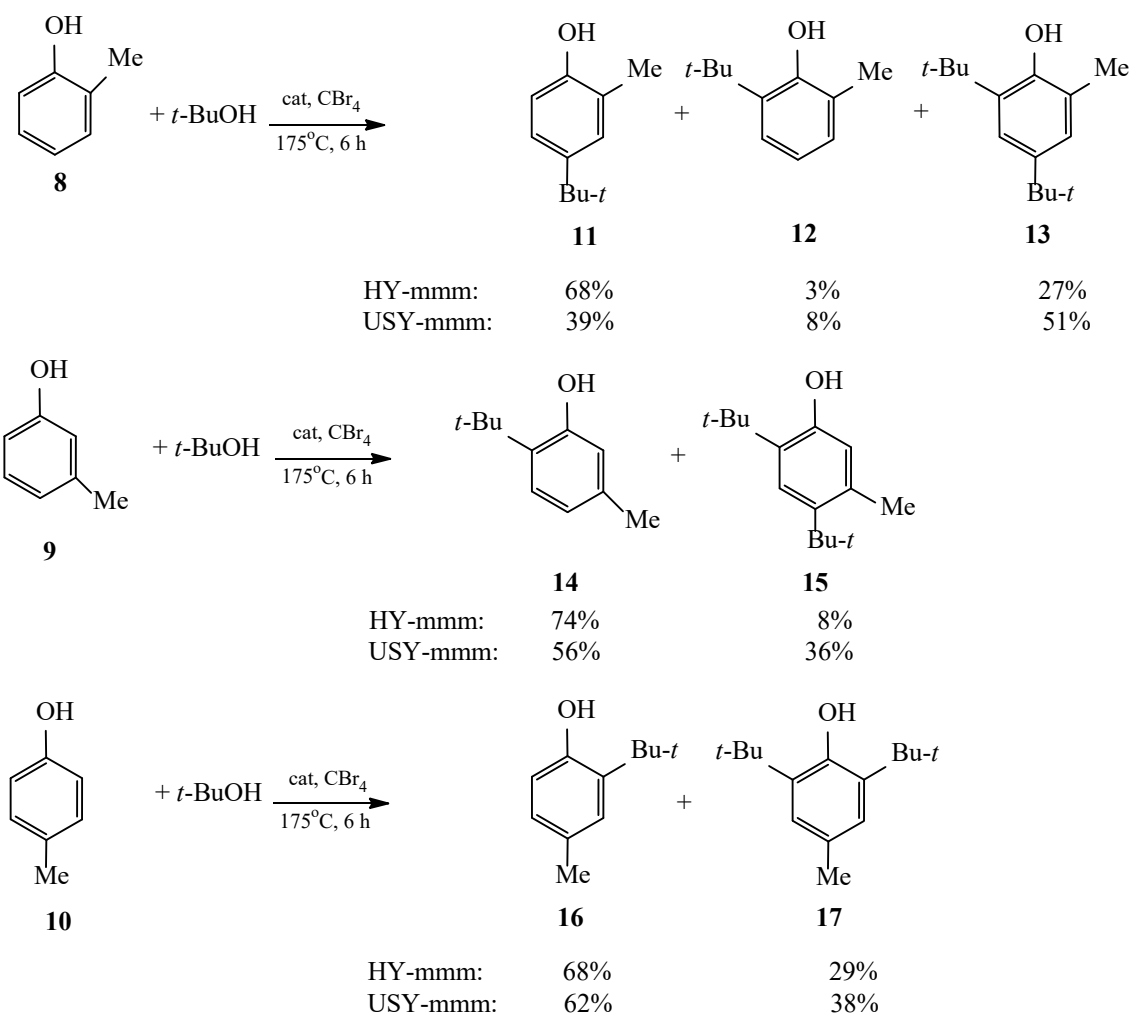
In summary, we found that HY-mmm and USY-mmm zeolites promoted with CBr₄ were efficient catalysts of alkylation of phenol as well as *m*- and *p*-cresols ring with *tert*-butanol.

EXPERIMENTAL

¹H and ¹³C NMR spectra were recorded using a Bruker Avance-400 spectrometer (400.13 and 100.62 MHz, respectively) in CDCl₃. Mass spectra were recorded using a Shimadzu GCMS-QP2010Plus chromatomass spectrometer (capillary column SPB-5 30 m × 0.25 mm, helium as carrier gas, temperature program 40 to 300°C at 8 deg/min, evaporator temperature 280°C, ionization chamber temperature 200°C, ionization energy 70 eV). Chromatographic analysis was performed using Shimadzu GC-9A and GC-2014 instruments [column 2 m × 3 mm, stationary phase: SE-30 silicon (5%) on Chromaton N-AW-HMDS, temperature program 50 to 270°C at 8 deg/min, helium as carrier gas (47 mL/min)].

Commercially available starting compounds (phenol, *o*-, *m*-, and *p*-cresols, *tert*-butanol, 2-propanol, CBr₄, CHBr₃, CHCl₃, and CCl₄) and catalysts (HY-mmm and USY-mmm) were used.

Scheme 2.



General procedure of the synthesis. The reactions were performed in a glass ampoule ($V = 12$ mL) put in a stainless steel microautoclave ($V = 17$ mL). The ampoule was charged with 5 wt % of the catalyst (with respect to ArOH), 100 mmol of phenol or cresol, 200 mmol of the alcohol, and 10 mmol of CBr_4 (CHBr_3 , CHCl_3 , CCl_4)

Table 3. Yield of *tert*-butylphenols under different conditions in the presence of USY-mmm (5 wt %)^a

[Phenol] : [<i>t</i> -BuOH] : [CHlg_4]	Phenol conversion, %	Yield of the products, %					
		2	3	4	5	6	7
100 : 200 : 0	9	5	4	0	0	0	0
100 : 200 : 5	95	8	41	44	0	2	0
100 : 200 : 10	100	0	24	67	0	9	0
100 : 200 : 20	100	2	39	55	0	5	1
100 : 200 : 10	100 ^b	3	38	49	0	3	7
100 : 400 : 10	94	16	6	34	13	25	0

^a Reaction conditions: 175°C, 6 h.

^b 175°C, 8 h.

under argon. The sealed ampoule was put in the autoclave which was closed and heated at 150–250°C during 6–8 h at stirring. After cooling the reactor to ~20°C, the ampoule was opened, the reaction mass was neutralized with 10% aqueous solution of Na₂CO₃, and the organic layer was extracted with methylene chloride and filtered. After removal of the solvent, the residue was separated via chromatography (eluting with a 3 : 1 *n*-hexane–benzene mixture on a column with *l* = 21 cm, *d* = 1.2 cm).

Structure of the obtained alkylphenols **2–6**, **11–19** was confirmed by means of NMR spectroscopy, mass spectrometry, and comparison with reference samples and data. Compounds **2–6**, **11–19** were identified using combined samples obtained in 3–6 experiments.

2-tert-Butylphenol (2). Yield 23%. ¹H NMR spectrum, δ, ppm: 1.38 s [9H, C(CH₃)₃], 4.75 s (1H, OH), 6.50–7.40 m (4H, C^{3,4,5,6}H). ¹³C NMR spectrum, δ_C, ppm: 29.60 [C(CH₃)₃], 34.38 [C(CH₃)₃], 116.52 (C⁶), 120.45 (C⁴), 126.78 (C⁵), 126.80 (C³), 153.90 (C¹). Mass spectrum, *m/z* (*I*_{rel.}, %): 150 (25) [M]⁺, 135 (100), 115 (85), 107 (100), 91 (20), 77 (15), 65 (10).

4-tert-Butylphenol (3). Yield 65%. ¹H NMR spectrum, δ, ppm: 1.37 s [9H, C(CH₃)₃], 5.32 s (1H, OH), 6.88 d (2H, C^{2,6}H, *J* = 8.0 Hz), 7.32 d (2H, C^{3,5}H, *J* = 8.0 Hz). ¹³C NMR spectrum, δ_C, ppm: 31.62 [C(CH₃)₃], 34.11 [C(CH₃)₃], 115.01 (C^{2,6}), 126.48 (C^{3,5}), 143.41 (C⁴), 153.23 (C¹). Mass spectrum, *m/z* (*I*_{rel.}, %): 150 (25) [M]⁺, 135 (100), 119 (4), 107 (49), 95 (18), 77 (10), 65 (7), 51 (4), 41 (14).

2,4-Di-tert-butylphenol (4). Yield 52%. ¹H NMR spectrum, δ, ppm: 1.61 s [9H, *ortho*-C(CH₃)₃], 1.49 s [9H, *para*-C(CH₃)₃], 5.35 s (1H, OH), 6.75 d (1H, C⁶H, *J* = 8.0 Hz), 7.25 d (1H, C⁵H, *J* = 8.0 Hz), 7.51 s (1H, C³H). ¹³C NMR spectrum, δ_C, ppm: 29.91 [*ortho*-C(CH₃)₃], 31.72 [*para*-C(CH₃)₃], 34.44 [*ortho*-C(CH₃)₃], 34.93 [*para*-C(CH₃)₃], 116.26 (C⁶), 123.71 (C⁵), 124.20 (C³), 135.51 (C²), 143.05 (C⁴), 152.05 (C¹). Mass spectrum, *m/z* (*I*_{rel.}, %): 206 (33) [M]⁺, 191 (100), 175 (4), 161 (3), 147 (2), 115 (3), 91 (4), 74 (3), 57 (25), 41(10).

2,6-Di-tert-butylphenol (5). Yield 13%. ¹H NMR spectrum, δ, ppm: 1.54 s [18H, C(CH₃)₃], 4.85 br. s (1H, OH), 6.75 t (1H, C⁴H, *J* = 8.0 Hz), 7.20 d (2H, C^{3,5}H, *J* = 8.0 Hz). ¹³C NMR spectrum, δ_C, ppm: 30.20 [C(CH₃)₃], 34.85 [C(CH₃)₃], 120.10 (C⁴), 124.30 (C^{3,5}), 137.17 (C^{2,6}), 153.95 (C¹). Mass spectrum, *m/z* (*I*_{rel.}, %): 206 (25) [M]⁺, 191 (100), 175 (5), 163 (15), 131 (10), 115 (10).

2,4,6-Tri-tert-butylphenol (6). Yield 25%. ¹H NMR spectrum, δ, ppm: 1.30 s [18H, *ortho*-C(CH₃)₃], 1.46 s [9H, *para*-C(CH₃)₃], 5.02 s (1H, OH), 7.25 s (2H, C^{3,5}H). ¹³C NMR spectrum, δ_C, ppm: 30.20 [*ortho*-C(CH₃)₃], 32.10 [*para*-C(CH₃)₃], 32.84 [*para*-C(CH₃)₃], 35.15 [*ortho*-C(CH₃)₃], 142.10 (C⁴), 122.30 (C^{3,5}), 138.97 (C^{2,6}), 152.56 (C¹). Mass spectrum, *m/z* (*I*_{rel.}, %): 262 (20) [M]⁺, 247 (100), 205 (5), 128 (5), 116 (5), 91 (5), 57 (30).

4-tert-Butyl-*o*-cresol (11). Yield 68%. ¹H NMR spectrum, δ, ppm: 1.39 s [9H, C(CH₃)₃], 2.33 s (3H, CH₃), 4.78 s (1H, OH), 7.23 s (1H, C³H), 7.18 d (1H, C⁵H, *J* = 8.0 Hz), 6.79 d (1H, C⁶H, *J* = 8.0 Hz). ¹³C NMR spectrum, δ_C, ppm: 16.17 (CH₃), 31.66 [C(CH₃)₃], 34.04 [C(CH₃)₃], 114.57 (C⁶), 123.18 (C²), 123.82 (C⁵), 128.06 (C³), 142.32 (C⁴), 150.39 (C¹). Mass spectrum, *m/z* (*I*_{rel.}, %): 164 (47) [M]⁺, 149 (100), 121 (20), 109 (10), 91 (15), 77 (10).

6-tert-Butyl-*o*-cresol (12). Yield 8%. ¹H NMR spectrum, δ, ppm: 1.59 s [9H, C(CH₃)₃], 2.35 s (3H, CH₃), 4.95 s (1H, OH), 6.80–7.10 m (3H, C^{3,4,5}H). ¹³C NMR spectrum, δ_C, ppm: 15.98 (CH₃), 29.78 [C(CH₃)₃], 32.30 [C(CH₃)₃], 120.03 (C⁴), 122.45 (C²), 124.14 (C⁵), 128.43 (C³), 135.46 (C⁶), 152.45 (C¹). Mass spectrum, *m/z* (*I*_{rel.}, %): 164 (30) [M]⁺, 149 (100), 121 (75), 91 (20), 77 (15).

4,6-Di-tert-butyl-*o*-cresol (13). Yield 51%. ¹H NMR spectrum, δ, ppm: 1.40 s [9H, *para*-C(CH₃)₃], 1.53 s [(9H, *ortho*-C(CH₃)₃], 2.34 s (3H, CH₃), 4.90 s (1H, OH), 7.11 s (1H, C³H), 7.40 s (1H, C⁵H). ¹³C NMR spectrum, δ_C, ppm: 16.36 (CH₃), 29.95 [*ortho*-C(CH₃)₃], 31.73 [*para*-C(CH₃)₃], 34.27 [*para*-C(CH₃)₃], 34.82 [*ortho*-C(CH₃)₃], 122.08 (C⁵), 122.38 (C²), 125.43 (C³), 134.86 (C⁶), 143.42 (C⁴), 150.39 (C¹). Mass spectrum, *m/z* (*I*_{rel.}, %): 220 (20) [M]⁺, 205 (100), 189 (5), 161 (3), 149 (3), 121 (3), 115 (3).

6-tert-Butyl-*m*-cresol (14). Yield 74%. ¹H NMR spectrum, δ, ppm: 1.50 s [9H, C(CH₃)₃], 2.35 s (3H, CH₃), 5.07 s (1H, OH), 6.56 s (1H, C²H), 6.70–6.88 m (1H, C⁴H), 7.18–7.30 s (1H, C⁵H). ¹³C NMR spectrum, δ_C, ppm: 20.63 (CH₃), 29.77 [C(CH₃)₃], 34.27 [C(CH₃)₃], 117.46 (C²), 121.23 (C⁴), 126.98 (C⁵), 133.27 (C⁶), 136.96 (C³), 154.15 (C¹). Mass spectrum, *m/z* (*I*_{rel.}, %): 164 (35) [M]⁺, 149 (100), 133 (2), 121 (63), 115 (9), 91 (19), 77 (10), 65 (3), 51 (4), 41(7).

4,6-Di-tert-butyl-*m*-cresol (15). Yield 36%. ¹H NMR spectrum, δ, ppm: 1.44 s [9H, *para*-C(CH₃)₃], 1.45 s [9H, *ortho*-C(CH₃)₃], 2.58 s (3H, CH₃), 4.97 s (1H, OH), 6.56 s (1H, C²H), 7.45 s (1H, C⁵H). ¹³C NMR spectrum, δ_C, ppm: 20.63 (CH₃), 31.12 [*ortho*-C(CH₃)₃], 31.30 [*para*-C(CH₃)₃], 34.67 [*ortho*-C(CH₃)₃], 35.66 [*para*-C(CH₃)₃],

120.83 (C²), 125.26 (C⁵), 132.54 (C³), 134.84 (C⁶), 139.64 (C⁴), 151.79 (C¹). Mass spectrum, m/z (I_{rel} , %): 220 (23) [M]⁺, 205 (100), 177 (4), 149 (1), 121 (4), 91 (3), 81 (4), 57 (24), 41(7).

2-*tert*-Butyl-*p*-cresol (16). Yield 68%. ¹H NMR spectrum, δ , ppm: 1.54 s [9H, C(CH₃)₃], 2.37 s (3H, CH₃), 4.76 s (1H, OH), 6.63 d (1H, C⁶H, $J = 8.0$ Hz), 6.96 d (1H, C⁵H, $J = 8.0$ Hz), 7.17 s (1H, C³H). ¹³C NMR spectrum, δ_C , ppm: 20.88 (CH₃), 29.71 [C(CH₃)₃], 34.32 [C(CH₃)₃], 116.49 (C⁶), 127.28 (C³), 127.81 (C⁵), 129.51 (C⁴), 135.91 (C²), 152.06 (C¹). Mass spectrum, m/z (I_{rel} , %): 164 (52) [M]⁺, 149 (100), 121 (87), 91 (22), 77 (14), 51 (5), 41 (7).

2,6-Di-*tert*-butyl-*p*-cresol (17). Yield 38%. ¹H NMR spectrum, δ , ppm: 1.51 s [18H, C(CH₃)₃], 2.38 s (3H, CH₃), 4.90 s (1H, OH), 7.10 s (1H, C^{3,5}H). ¹³C NMR spectrum, δ_C , ppm: 21.28 (CH₃), 30.42 [C(CH₃)₃], 34.51 [C(CH₃)₃], 125.62 (C^{3,5}), 128.36 (C⁴), 135.91 (C^{2,6}), 151.63 (C¹). Mass spectrum, m/z (I_{rel} , %): 220 (52) [M]⁺, 205 (100), 177 (13), 161 (5), 145 (14), 115 (6), 105 (12), 81 (8), 57 (28), 41 (11).

6-Isopropyl-*m*-cresol (18). Yield 32%. ¹H NMR spectrum, δ , ppm: 1.27 d [6H, CH(CH₃)₂, $J = 8.0$ Hz], 3.31–3.41 m [1H, CH(CH₃)₂], 2.31 s (3H, CH₃), 4.98 s (1H, OH), 6.62 s (1H, C²H), 6.19 d (1H, C⁴H, $J = 8.0$ Hz), 7.14 d (1H, C⁵H, $J = 8.0$ Hz). ¹³C NMR spectrum, δ_C , ppm: 20.68 (CH₃), 22.72 [CH(CH₃)₂], 26.71 [CH(CH₃)₂], 116.09 (C²), 120.80 (C⁴), 126.71 (C⁵), 131.4 (C⁶), 136.63 (C³), 152.54 (C¹). Mass spectrum m/z (I_{rel} , %): 150 (40) [M]⁺, 135 (100), 115 (24), 91 (100), 77 (8), 65 (6), 41 (3).

4,6-Diisopropyl-*m*-cresol (19). Yield 48%. ¹H NMR spectrum, δ , ppm: 1.21 d [6H, *para*-CH(CH₃)₂, $J = 8.0$ Hz], 1.31 d [(6H, *ortho*-CH(CH₃)₂, $J = 8.0$ Hz], 3.07–3.14 m [6H, *para*-CH(CH₃)₂], 3.19–3.25 m [6H, *ortho*-CH(CH₃)₂], 2.29 s (3H, CH₃), 4.83 s (1H, OH), 6.59 s (1H, C²H), 7.11 s (1H, C⁵H). ¹³C NMR spectrum, δ_C , ppm: 18.75 (CH₃), 22.78 [*ortho*-CH(CH₃)₂], 23.51 [*para*-CH(CH₃)₂], 27.15 [*ortho*-CH(CH₃)₂], 28.89 [*para*-CH(CH₃)₂], 117.09 (C²), 122.74 (C⁵), 131.81 (C³), 133.46 (C⁶), 139.21 (C⁴), 150.16 (C¹). Mass spectrum, m/z (I_{rel} , %): 192 (30) [M]⁺, 177 (100), 149 (4), 135 (20), 121 (5), 91 (11), 77 (4), 65 (2), 43(8).

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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