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Towards *ortho*-selective electrophilic substitution/addition to phenolates in anhydrous solvents

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ABSTRACT

Alkyl-substituted Li-phenolates with BnBr in water solution lead to a mixture of *o*- and *p*-Bn-substituted phenols together with a substantial amount of phenol Bn ether. In CPME, and especially in toluene with 1−2 equivalents of ether or alcohol additives, *ortho*-selective alkylation is achieved. In the case of *o,o,p*-tri- and *o,o*-di-substituted phenols dearomatization occurs affording *o*-Bn-substituted alkyl cyclohexadienones with yields up to 92% with an *o*/*p* ratio up to 90/1.

1. Introduction

Phenols are known electron-rich aromatic compounds with nucleophilicity at *C*- and *O*-nucleophilic sites, giving in the reaction with electrophiles both, *C*- and *O*-alkylated products. Phenolates are more reactive with increased reactivity towards electrophiles in *C*- and *O*-alkylation reactions [1]. With unsubstituted phenolates the electrophilic reactions proceed in a common way leading to the aromatic substitution and Williamson products [2]. With substituted phenolates the electrophilic addition reactions may lead to dearomatization, resulting in cyclic dienones [3]. These structures are of great synthetic interest being intermediates for the synthesis of various bioactive and natural products [4].

The dearomatization of phenols has been well studied using oxidative strategies with hypervalent iodine(III) [5] and with Rh and Ru catalysts under oxidative conditions [6]. However, simple electrophilic alkylation reactions have been almost neglected because of low *C*-/O-alkylation selectivity, with *O*-alkylation dominating [7]. Selective *O*-alkylations have been achieved by using quaternary ammonium salts [8] while selective mono-*p*- and *o*-alkylation has been achieved only in rare cases [9]. According to early studies by Kornblum et al., in strong hydrogen-bonding solvents such as water, phenol and fluorinated alcohols substantial amounts of C-alkylated products can form [10]. So, usually alkylations have been performed with Na- and K-phenolates in water solution affording alkylphenols and cyclohexadienones in moderate yields [11]. There are only a few examples of using, Li, Mg or Ti phenolates [12].

In the present study we tried to expand borders of electrophilic *C*-alkylation of phenolates and find ways for chemo- and regioselective substitution/addition in phenolates.

2. Results/discussion

In order to obtain comparable data, we started with the alkylation of various unsubstituted and substituted Li-phenolates with benzyl bromide (BnBr) in a water solution of LiOH. The obtained results are presented in Table 1.

Unsubstituted phenol (**1a**) shows moderate reactivity in aqueous LiOH solution, giving predominantly *O*-alkylated product (46%), and almost equally low amount of *o*- and *p*-substituted products. At used reaction conditions 28% of unreacted starting phenol **1a** was recovered after the reaction (Table 1, entry 1). Monosubstituted phenols show different activity and regioselectivity, depending on the substituents and their bulkiness. Introduction of an *ortho*-substituent, even not a bulky one, such as methyl, substantially reduces a relative amount of *O*-alkylated product. So, the amount of *O*-alkylation decreased from 46% for unsubstituted **1a** (Table 1, entry 1; **2a**) to 25% for *o*-Me phenol **1b** (Table 1, entry 2; **2b**) and to 16% for *tert*-butyl phenol **1d** (**2d**, Table 1, entry 4). Thus, *o*-Me phenol afforded mostly *C*-alkylation with *C*/*O*-alkylation ratio 1.7/1 (sum of **3b** + **3b'**+ **4b** to **2b**), while *o*/*p* ratio (**3b** + **3b'** to **4b**)

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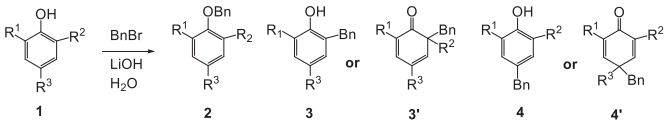
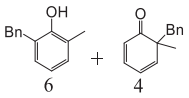
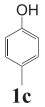
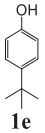
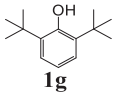
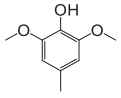
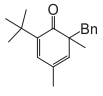
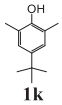
Table 1
Alkylation of phenols with benzyl bromide in aqueous LiOH solution[a].



Entry	Phenol No	Recovered 1 (%)	Yield of 2 (%)	Yield of *o*-product, %	Yield of *p*-product, %
				3	4
1	 **1a**	28	46	7	8
2	 **1b**	19	25	 6 + 4	32
3	 **1c**	32	35	13	–
4	 **1d**	41	16	 6	19
5	 **1e**	38	58	4	–
6	 **1f**	8	11	17	64
7	 **1g**	100	–	–	–
8	 **1h**	14	8	44	32
9	 **1i**	21	33	45	–
10	 **1j**	86	–	 6	–
11	 **1k**	51	14	27	5
12[b]	**1k**	19	15	44	4
13[c]	**1k**	51	15	28	4
14[d]	**1k**	37	21	32	5
15[e]	**1k**	71	9	17	1

[a] Reaction conditions: Phenol (1 mmol), BnBr (1.2 mmol), 1 M LiOH (1 mL), water (1 mL), room temperature, overnight; yields of isolated products are presented.
[b] No additional water added.
[c] NaOH as an alkali, no additional water added.
[d] 0.2 mL MeOH added. [e]No additional water added, 1 mL of CF_3CH_2OH added.

was 1/3.2 in favour to *p*-product. It is interesting to note that a quaternary *o*-substitution at Me group **3b'** was almost equal to that of substitution to a free *o*-position **3b** (4 and 6%, respectively).

Substituents in the *para*-position (Table 1, entries 3 and 5) did not support *C*-alkylation affording *O*-alkylation product predominantly with a **3c/2c** ratio of 1/2.7 for phenol **1c** and 1/14.5 for phenol **1e**.

Of the *o*-disubstituted phenols **1f** and **1g**, only *o*-di-Me phenol **1f** reacted with BnBr, showing a good *C*/*O* selectivity (Table 1, entries 6 and 7). With *o*-di-Me phenol **1f** the *o*-addition reaction with dearomatization occurred, affording quaternary *o*-Bn-alkylated product **3f** in considerable yield (17%). The *para*-product was dominant with 64% yield. The yield of the *O*-alkylation product **2f** was only 11% which was only half of that for *o*-Me phenol **2b**.

The tri-Me-substituted phenol **1h** revealed a good reactivity but low regioselectivity affording dearomatized quaternary products **3h** (a chiral structure) and **4h** in 44% and 32% yield respectively. Also, with phenol **1h** a good ratio of *C*-and *O*-alkylation with only 8% of ether **2h** was observed. Trisubstituted *o*-dimethoxy-*p*-Me phenol **1i** also reacted smoothly, affording exclusively *ortho*-*C*-alkylation product **3i** in 45% yield, although together with 33% of the *O*-alkylation product **2i**.

The *t*-butyl group in the *ortho*-position (*o*-Me-*o*-*t*Bu-phenol **1j**) considerably reduced the reactivity, affording the addition to *ortho*-carbon at the Me group (ketone **3j**) only in 6% yield, while the initial phenol **1j** remained mostly unreacted (Table 1, entry 10). The trisubstituted *o*,*o*-diMe-*p*-*t*Bu-phenol **1k** was more reactive affording the *ortho*-addition product **3k** in 27% yield and surprisingly, also quaternary *p*-product **4k** in 5% yield (Table 1, entry 11). *O*-alkylation product ether **2k** was formed in 14% yield.

We observed that phenols with large *t*-Bu-substituents **1d, 1e**, **1j** and **1k** were less reactive, leaving a considerable amount of substrate unreacted (Table 1, entries 4, 5 and 10–15). 2,6-Di *t*-Bu phenol **1g** did not react at all (Table 1, entry 7). We believe that the low reactivity in the case of phenol **1k** in water solution was also caused by the low solubility of that Li-phenolate in alkaline water. So, we carried out some additional experiments with **1k** to clarify the matter.

First, we increased the concentration of Li-phenolate **1k** in the reaction mixture by reducing the water content (Table 1, entry 12). Only 19% of **1k** remained unreacted because of the increased solubility of phenolate. The sum of the alkylated products increased from 46% to 63% (calculated from Table 1, entries 11 and 12). Under these reaction conditions, the *o*/*p* ratio of alkylation increased considerably from 5.4/1 to 11/1. Also, the ratio of *C*/*O*-alkylation increased from 2.3/1 to 3.2/1.

Using NaOH instead of LiOH slightly improved the solubility of **1k** but resulted in low reactivity (51% of **1k** remained unreacted), and a low *C*/*O*-alkylation ratio (only 2.1/1). However, a good *o*/*p* ratio was observed (7/1; Table 1, entry 13).

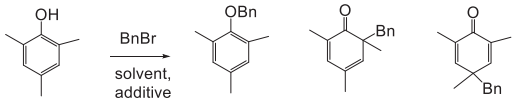
To further increase the homogeneity of the reaction medium, 0.2 mL MeOH (~10% from solvent) was added and the reaction was performed according to the usual conditions (footnote[d] in Table 1). We observed that MeOH had no positive effect on the *C*/*O*-alkylation, nor on the *o*/*p* ratio (Table 1, entry 14).

When fluorinated alcohol CF_3CH_2OH was used as an additive, the reaction selectivity changed. Thus, *ortho*-selectivity increased drastically to *o*/*p* > 17/1, together with moderate *C*/*O*-alkylation selectivity. However, the reactivity of phenol **1k** remained low, with 71% of the starting phenol **1k** recovered (Table 1, entry 15). The negative effect the additive was the reactivity of CF_3CH_2OH itself in the Williamson reaction towards BnBr consuming the reagent.

The main conclusion from the obtained results was that the reaction is very sensitive to phenol substitutes and the low solubility of some alkyl phenolates in water solution is a serious problem, causing low yield and selectivity. So, we turned to non-aqueous solutions using *n*-BuLi to generate the phenolate. Trimethyl phenol **1h** was selected as a model structure in the reaction with BnBr.

First, *n*-BuLi was used in hexane. To ensure the solubility of the

Table 2
Addition of BnBr to 2,4,6-trimethylphenol **1h** in non-aqueous conditions[a].



1h **2h** **3h** **4h**

Entry	n-BuLi (equiv)	Solvent	Additive (equiv)	Temperature (°C)	Yield, 3(%)			
					1 h	2 h	3 h	4 h
1[b]	1	CPME	–	r.t.	85	0.2	5	
2[b]	2	CPME	–	r.t.	51	1	13	1
3[b]	2.2	CPME	–	50	27	2	44	1
4[b]	2.2	CPME	–	80		10	84	2
5	2.2	toluene	–	80	57	1	38	3
6	2.2	toluene	CPME; 1	80	19	2	71	3
7	1.1	toluene	CPME; 2	80	25	3	66	2
8	2.2	toluene	CPME; 2	80	9	3	79	3
9	2.2	toluene	CPME; 4	80	45	2	43	1
10	2.2	toluene	MTBE; 1	80	33	2	62	2
11	2.2	toluene	anisole; 2	80	21	1	63	3
12	1.1	toluene	*t*-BuOH; 1	80	–	15	83	1
13	2.2	toluene	(R)-*s*-BuOH; 1	80	–	8	90	1
14	1.3	toluene	(R)-*s*-BuOH; 0.2	80	15	4	63	2
15	2.2	toluene	*n*-BuOH; 1	80	7	3	87	2
16	2.2	toluene	*L*-Menthol; 1	80	–	5	82	12
17	2.2	toluene	*i*-PrOH; 1	60	–	5	92	2
18	2.2	toluene	MeOH; 1	60	10	1	86	2

[a] Conditions: 1 mmol phenol **1h**, solvent, n-BuLi, additive, overnight at given temperatures.
[b] Hexane changed to CPME after *n*-BuLi was added to phenol; yields are determined by ^{1}H NMR analysis of the crude reaction mixture.

phenolates in the reaction medium hexane was replaced by cyclopentyl methyl ether (CPME) which was used earlier in the case of naphthols [13].

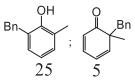
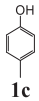
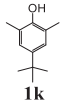
The obtained results are presented in Table 2 (entries 1–4). By using 1 equivalent of *n*-BuLi at room temperature the reaction was very slow, resulting predominantly in quaternary *ortho*-product **3h** in 5% yield, with 85% of unreacted substrate **1h** left. A higher yield of the addition product **3h** was obtained with 2 equivalents of *n*-BuLi (Table 2, entry 2). Higher temperature substantially increased the yield of the product **3h**, from 13% at r.t., to 44% at 50 °C, and finally, to 84% at 80 °C. The increase in temperature slightly reduced the *C*/*O*-alkylation selectivity from 20/1 at 50 °C to 8.4/1 at 80 °C. Still, the *C*/*O*-selectivity was acceptable. The *o*/*p* selectivity remained excellent at all temperatures (*o*/*p* ratio at 80 °C > 40/1) (Table 2, entries 2–4).

In order to simplify the experimental procedure and avoid solvent change, toluene as a solvent was introduced together with the use of *n*-BuLi solution in toluene. The first attempt in neat toluene affording good *C*/*O*-alkylation selectivity but moderate reactivity encouraged us to continue in this direction. (Table 2, No 5). To improve the solubility of the Li-phenolate in the reaction medium, different additives to the toluene were tested. First, CMPE, which was a good solvent for alkylation was used as a toluene additive. With 1 equivalent of CMPE to phenolate, an almost selective *ortho*-addition reaction was observed with high *C*/*O*-alkylation ratio (35/1), and with only 19% of the starting compound **1h** recovered (Table 2, entry 6). To find the optimal amount of the additive, experiments with 2 and 4 equivalents of CMPE were performed. The best result was achieved by using 2.2 equivalents of *n*-BuLi in toluene with 2 equivalents of CPME additive, after the overnight reaction at 80 °C, with only 9% of substrate **1h** unreacted and with 79% of *ortho*-benzyl dearomatized product **3h** formed. The ether **2h** and *para*-addition product **4h** were observed in minor amounts (Table 2, entry 8). The reaction was quite sensitive to the reagents' ratio: reducing the amount of *n*-BuLi to 1.1 equivalents in respect to phenol caused a considerable drop in both, reactivity and selectivity; increasing the amount of CPME additive to 4 equivalents reduced the reactivity of phenolate and increasing the amount of unreacted **1h** to 45% (Table 2, entry 9).

We also checked the effect of methyl *tert*-butyl ether (MTBE) and anisole additives to the alkylation. We found that they both also acted as selective catalysts in the electrophilic addition of BnBr to phenolate, being slightly less active than CPME (Table 2, entries 10 and 11).

To our surprise, different alcohol additives also had a positive effect on BnBr addition to Li-phenolate in toluene. All of the used alcohols, primary, secondary and tertiary butanols in 1 equivalent quantity, revealed similar high activity and selectivity to the reaction, affording *ortho*-addition product in >80% yield. Of them, *n*-BuOH was the most selective and *s*-BuOH the most active (Table 2,

Table 3
Electrophilic reaction of various phenolates in non-aqueous conditions [a].

Entry	Phenol	*n*-BuLi (eq)	BnBr (eq)	2 (%)	3 (%)	4 (%)	5 (%)
1	 **1a**	2	2	5	39	2	 5
2[b]	**1a**	1.2	2	10	52	3	8
3[b]	 **1b**	1.5	2	4	 25 5	3	–
4	 **1c**	1.5	2	2	50	–	 5
5	 **1j**	2.2	1.2	1	20	–	–
6[c]	**1f**	2.2	1.2	27	56	1	
7	 **1h**	2.2	1.2	3	79	3	–
8	 **1i**	2.2	1.2	42	–	–	–
9	 **1j**	2.2	1.2	–	 35	–	–
10	 **1k**	2.2	1.2	3	45	–	–

[a] Conditions: CPME 2 eq, temperature 80 °C; yields of isolated compounds are presented.
[b] temperature 90 °C.
[c] Reaction conditions: CPME as that for Table 2, entry 4.

entries 12–15). The chiral ligands (*R*)-*sec*-butanol and *L*-menthol both afforded chiral quaternary addition product **3h** in high yields (90 and 88% respectively; Table 2, entries 13, 16). However, to our disappointment, these were in a racemic form. Even methanol and isopropanol in 1 equivalent amounts revealed high activity and selectivity as catalysts in a phenolate alkylation reaction (Table 2, entries 17 and 18).

With 2 equivalents of *n*-BuLi, the phenol **1h** turned to Li-phenolate anion with one equivalent of *n*-BuLi, and the second equivalent turned the alcohol additive to an alcoholate. The alcoholates catalyse the selective electrophilic *C*-addition on BnBr to the phenolate.

We re-investigated the electrophilic substitution/additions of BnBr to various phenolates in non-aqueous conditions with CPME additive. The obtained results are presented in Table 3. The reaction conditions for individual phenolates were not optimized.

As expected, less substituted phenol derivatives revealed lower reactivity. So, to overcome this, more BnBr was added to those phenols.

The unsubstituted phenol **1a**, which in a LiOH solution with BnBr led to only 7% of *ortho*-substitution and mainly the *O*-alkylation with formation of **2a** in 46% yield (Table 1, entry 1), in a non-aqueous medium resulted mainly in *ortho*-substitution product **3a** in 39% yield at 80 °C, and in 52% yield at 90 °C, with the formation of ether **2a** in ~10%. The regioselectivity of the substitution was also satisfactory, with *p*- and *o*,*o*-disubstitution products observed only in ~10% yield in total (Table 3, entries 1 and 2).

The *o*-Me phenol **1b** resulted in 25% of the *ortho*-substitution product **3b** at 90 °C. It is interesting to note that the yield of the quaternary *ortho*-addition product **3b'** was higher than that of the *para*-substitution product **4b** (5 vs 3%; Table 3, entry 3). This was different from that observed in water solution, where the *para*-substitution product **4b** together with *O*-alkylation product **2b**, dominated (Table 1, entry 2).

p-Me phenol **1c** afforded almost exclusively the *ortho*-substituted product **3c** with a small amount of ether **2c.** No quantity of the quaternary *para*-product **4c** was observed. (Table 3, entry 4).

Disubstituted 2,6-diMe-phenol **1f** which reacts quite smoothly in water solution affording mainly *para*-product **4f** in 64% yield (Table 1, entry 6), in the non-aqueous conditions afforded only quaternary *ortho*-product **3f** in 20% yield, with only a very small amount of ether **2f** (Table 3, entry 5). At the same time, in CPME the **3f** was formed in 56% yield, with a substantial amount of ether **2f** (27%; Table 3, entry 6).

Comparing the benzylation of Li-phenolate of 2,4,6-tri-Me phenol **1h** in a non-aqueous environment and in a water solution, we observed almost exclusive *ortho*-addition affording quaternary dearomatized **3h** in good yield (79%; Table 3, entry 7), while in water-LiOH solution *ortho*- and *para*-addition products were formed in almost equal amounts, in 44% and 32%, respectively (Table 1, entry 8). A remarkable difference in reactivities was also observed for 2,6-dimehoxy-4-mehyl phenol **1i**: in the LiOH water solution the *ortho*-product **3i** in 45% yield was formed, together with ether **2i** in 33% yield, while in the toluene solution with a CPME additive only ether **2i** was observed in a 42% yield, without any traces of other products (Table 3, entry 8). Phenol **1j** with a bulky *t*-Bu group in *ortho*-position almost failed to react in an alkali water solution because of solubility problems. In non-aqueous conditions, **1j** afforded mainly the quaternary *ortho*-product with Bn addition to Me-carbon **3j** in 35% yield, with only a trace amount of *p*-quaternary product **4j** (Table 3, entry 9). When the bulky *t*-Bu group was in *para*-position, the *ortho*-addition occurred in both media. In water solution the solubility of the substrate was a problem, and the yield was only 27% (Table 1, entry 11), while in the toluene solution the *ortho*-addition product **3k** was formed in 45% yield (Table 3, entry 10). In both cases the formation of ether was insignificant.

3. Conclusion

The alkylation of phenolates in non-aqueous conditions offers mainly *C*-alkylation, with the *C*/*O*-alkylation ratio usually >10/1. The *C*-alkylation is *ortho*-selective in up to 92% yield. Even in the case of unsubstituted phenol **1** the yield of *o*-Bn-phenol exceeded 50%. In the case of *o*,*o*,*p*-tri- and *o*,*o*-substituted phenols dearomatization occurs affording *o*-Bn-substituted alkyl cyclohexadienones with yields up to 92%, with an *o*/*p* ratio up to 90/1. The method is sensitive to phenol structure, therefore, optimal conditions separately for every phenolate may be needed. The substitution reaction is catalysed by ethers and by alcohols. The possibility of introducing asymmetric induction to the dearomatization reaction is currently under study.

4. Experimental section

^{1}H and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker Avance USLA 400 spectrometer. Deuterated solvent peaks were used as references. 2D FT methods were used for the full assignment of ^{1}H and ^{13}C chemical shifts. High-resolution mass spectra were recorded with an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS spectrometer by using AJ-ESI ionization. IR spectra were recorded on a Bruker PMA 50 spectrometer. Precoated Merck silica gel 60 F_{254} plates were used for TLC. Column chromatography was performed with 40–63 μm silica gel. The measured melting points obtained on a Boëtius (Nagema) instrument and are uncorrected. All reactions sensitive to oxygen or moisture were conducted under argon atmosphere in oven-dried glassware. Purchased chemicals and solvents were used as received. The petroleum ether fraction b.p. 40–60 °C was used. The yields of isolated compounds are presented; in Table 2 the yields were determined from ^{1}H NMR analysis of the crude mixture.

4.1. General procedure A (GPA) for the dearomatization reaction in aqueous conditions

To an aqueous solution of 1 M LiOH (1 mL) on an ice bath phenol (1 mmol) was added and the mixture stirred for 15 min. Then water (1 mL) and BnBr (1.2 mmol) was added, the reaction mixture warmed up to room temperature and stirred overnight. To the reaction mixture water (5 mL) was added, pH adjusted to ~7 and the mixture was extracted with EtOAc. The combined organic layers were washed with brine and dried with phase separator or on $MgSO_4$ and filtered if necessary. Then solvent was removed with rotary evaporator and the products were obtained after flash chromatography on silica gel (petroleum ether/EtOAc).

4.2. General procedure B (GPB) for the dearomatization reaction in non-aqueous conditions

To solution of phenol (1 mmol) in a solvent under argon atmosphere n-BuLi (2.7 M in toluene; 0.82 mL; 2.2 mmol) was added dropwise. After addition of the additives BnBr (1.2 mmol) was applied. The reaction mixture was warmed up to 80 °C and stirred at this temperature overnight. After cooling water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were washed with brine and dried with phase separator or on $MgSO_4$. The crude product solution was filtered if necessary, and then solvent was removed with rotary evaporator. The products were separated by flash chromatography on silica gel (petroleum ether/EtOAc).

4.3. General procedure C (GPC) for the dearomatization reaction in non-aqueous conditions

Phenol (1 mmol) was dissolved in hexane (3 mL) and n-BuLi (2.5 M in toluene; 0.88 mL; 2.2 mmol) was added dropwise under argon atmosphere and stirred for 15 min. Then hexane was removed with argon flow and CPME (1 mL) was added. To the obtained clear solution BnBr (1.2 mmol) was added, the reaction mixture warmed up to 80 °C and stirred overnight at this temperature. After cooling water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were washed with brine and dried with phase separator or on $MgSO_4$. The crude solution was filtered if necessary and the solvent was removed with rotary evaporator. The products were separated by flash chromatography on silica gel (petroleum ether/EtOAc).

4.4. Characterisation of compounds

4.4.1. Benzyloxybenzene (**2a**)

Following GPA gave **2a** (84 mg, 46%) after purification as a white solid; mp 36–37 °C; IR (KBr) ν_{max}: 3035, 2907 2867 1599, 1586, 1498, 1468, 1455, 1378, 1300, 1247, 1171, 1079, 1030, 1013, 991, 916, 858, 745, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–7.44 (m, 2H), 7.44–7.37 (m, 2H), 7.37–7.28 (m, 3H), 7.03–6.96 (m, 3H), 5.09 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 137.2, 129.6, 128.7, 128.1, 127.6, 121.1, 115.0, 70.0; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{13}H_{12}O$ 207.0780, found 207.0776.

4.4.2. 2-Benzylphenol (**3a**)

Following GPB product **3a** (96 mg, 52%) was obtained as a colourless oil; IR (neat) ν_{max}: 3535, 3028, 2920, 1593, 1494, 1454, 1329, 1213, 1169, 1094, 1040, 936, 851, 754, 731, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.27 (m. 2H), 7.23–7.18 (m, 3H), 7.14–7.10 (m, 2H), 6.89 (td, J = 1.21, 7.49 Hz, 1H), 6.77 (d, J = 8.27 Hz, 1H), 4.66 (s, 1H), 3.99 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.8, 140.0, 131.2, 128.81, 128.76, 128.0, 127.1, 126.5, 121.1, 115.8, 36.5; HRMS (ESI): *m/z* $[M-H]^-$ calculated for $C_{13}H_{12}O$ 183.0815, found 183.0816.

4.4.3. 4-Benzylphenol (**4a**)

Following GPA **1p** (15 mg, 8%) was obtained after purification as a white solid; mp 77–79 °C; IR (KBr) ν_{max}: 3223, 3021, 1600, 1511, 1493, 1454, 1379, 1243, 1175, 1102, 843, 785, 731, 698, 595 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.25 (m, 2H), 7.26–7.15 (m, 3H), 7.11–7.03 (m, 2H), 6.80–6.72 (m, 2H), 4.66 (s, 1H), 3.93 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 141.6, 133.6, 130.2, 129.0, 128.6, 126.1, 115.4, 41.1; HRMS (ESI): *m/z* $[M-H]^-$ calculated for $C_{13}H_{12}O$ 183.0815, found 183.0818.

4.4.4. 2,6-Dibenzylphenol (**5a**)

Following GPB **5a** (21 mg, 8%) as a white solid was obtained; mp 28–29 °C; IR (KBr) ν_{max}: 3559, 3062, 3027, 2924, 1602, 1494, 1452, 1252, 1186, 1079, 1030, 840, 735, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.27 (m. 4H), 7.22–7.19 (m, 6H), 7.03 (d, J = 7.52 Hz, 2H), 6.85 (dd, J = 7.15, 7.89 Hz, 1H), 4.60 (s, 1H), 3.97 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.3, 139.8, 129.5, 128.82, 128.77, 127.3, 126.6, 120.8, 36.8; HRMS (ESI): *m/z* $[M-H]^-$ calculated for $C_{20}H_{18}O$: 273.1285, found 273.1300.

4.4.5. 1-(Benzyloxy)-2-methylbenzene (**2b**)

Following GPA **2b** (49 mg, 25%) after purification as a colourless oil was obtained; IR (neat) ν_{max}: 3031, 2927, 1602, 1495, 1454, 1380, 1312, 1289, 1243, 1191, 1122, 1051, 1026, 855, 750, 713, 696, 624, 441 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50–7.45 (m, 2H), 7.43–7.38 (m, 2H), 7.37–7.30 (m, 1H), 7.21–7.15 (m, 2H), 6.90 (d, J = 7.7 Hz, 2H), 5.10 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 137.7, 130.9, 128.6, 127.9, 127.2, 126.9, 120.7, 111.6, 70.0, 16.6; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{14}H_{14}O$ 221.0937, found 221.0927.

4.4.6. 2-Benzyl-6-methylphenol (**3b**)

Following GPB **3b** (50 mg, 25%) as a white solid was obtained; mp 46–47 °C; IR (KBr) ν_{max}: 3565, 3026, 2920, 1594, 1494, 1470, 1453, 1324, 1263, 1197, 1084, 1030, 946, 833, 767,734, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m. 2H), 7.23–7.18 (m, 3H), 7.02 (d, J = 7.60 Hz, 1H), 6.98 (d, J = 7.28 Hz, 1H), 6.80 (t, J = 7.48 Hz, 1H), 4.60 (s, 1H), 3.98 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.3, 139.9, 129.4, 128.81, 128.78, 126.55, 126.49, 123.9, 120.5, 36.8, 16.0; HRMS (ESI): *m/z* $[M+H]^+[-H_2O]$ calculated for $C_{14}H_{14}O$ 181.1012, found 181.1008.

4.4.7. 6-Benzyl-6-methylcyclohexa-2,4-dien-1-one (**3b'**)

Following GPA **3b'** (8 mg, 4%) after purification as a green oil was obtained; IR (neat) ν_{max}: 3030, 2925, 2854, 1721, 1662, 1631, 1559, 1495, 1453, 1417, 1379, 1141, 761, 705, 496 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (td, J = 5.1, 2.4 Hz, 3H), 7.05 (dd, J = 7.5, 2.0 Hz, 2H), 6.86 (ddd, J = 9.8, 5.8, 1.8 Hz, 1H), 6.35 (ddd, J = 9.4, 1.8, 0.9 Hz, 1H), 6.14 (ddd, J = 9.5, 5.8, 0.9 Hz, 1H), 5.95 (dt, J = 9.7, 0.9 Hz, 1H), 3.22 (d, J = 13.2 Hz, 1H), 2.75 (d, J = 13.2 Hz, 1H), 1.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5, 147.3, 141.8, 137.1, 130.0, 128.0, 126.7, 126.1, 120.6, 52.7, 46.2, 24.8; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{14}H_{14}O$ 221.0937, found 221.0925.

4.4.8. 4-Benzyl-2-methylphenol (**4b**)

Following GPA **4b** (63 mg, 32%) as a yellow oil was obtained after purification; IR (neat) ν_{max}: 3418, 3026, 2921, 1602, 1507, 1494, 1453, 1327, 1260, 1204, 1115, 1074, 1030, 781, 724, 698, 621, 524, 443 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.25 (m, 2H), 7.25–7.16 (m, 3H), 6.96 (d, J = 2.1 Hz, 1H), 6.91 (dd, J = 8.1, 2.2 Hz, 1H), 6.70 (d, J = 8.1 Hz, 1H), 4.60 (s, 1H), 3.89 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 141.8, 133.5, 131.7, 128.9, 128.6, 127.6, 126.1, 123.8, 115.0, 41.2, 15.9; HRMS (ESI): *m/z* $[M-H]^-$ calculated for $C_{14}H_{14}O$ 197.0972, found 197.0973.

4.4.9. 1-(Benzyloxy)-4-methylbenzene (**2c**)

Following GPA **2c** (89 mg, 45%) as a white solid was obtained after purification; mp 33–35 °C; IR (KBr) ν_{max}: 3032, 2922, 1613, 1585, 1511, 1454, 1381, 1291, 1239, 1175, 1110, 1026, 861, 817, 734, 696, 604, 512 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.3 Hz, 2H), 7.46 (t, J = 7.3 Hz, 2H), 7.40 (d, J = 7.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 5.11 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 137.4, 130.2, 130.0, 128.6, 128.0, 127.6, 114.8, 70.1, 20.6; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{14}H_{14}O$ 221.0937, found 221.0931.

4.4.10. 2-Benzyl-4-methylphenol (**3c**)

Following GPB **3c** (99 mg, 50%) as a colourless oil was obtained; IR (neat) ν_{max}: 3536, 3026, 2922, 2859, 1602, 1506, 1495, 1325, 1259, 1188, 1104, 1030, 935, 812, 751, 728, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29–7.25 (m. 2H), 7.22–7.17 (m, 3H), 6.91–6.89 (m, 2H), 6.65 (d, J = 8.26 Hz, 1H), 4.60 (s, 1H), 3.94 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.6, 140.2, 131.7, 130.3, 128.78, 128.75, 128.3, 126.8, 126.4, 115.7, 36.5, 20.7; HRMS (ESI): *m/z* $[M-H]^-$ calculated for $C_{14}H_{14}O$: 197.0972, found 197.0978.

4.4.11. 2,6-Dibenzyl-4-methylphenol (**5c**)

Following GPB gave product **5c** (14 mg, 5%) as a colourless oil; IR (neat) ν_{max}: 3556, 3026, 2920, 1602, 1494, 1479, 1245, 1198, 1075, 1030, 863, 731, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m. 4H), 7.21–7.18 (m, 6H), 6.84 (s, 2H), 4.42 (s, 1H), 3.93 (s, 4H),

2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.0, 140.0, 130.0, 129.9, 128.8, 128.7, 127.1, 126.5, 36.8, 20.7; HRMS (ESI): *m/z* $[M-H]^-$ calculated for $C_{21}H_{20}O$ 287.1441, found 287.1459.

*4.4.12. 1-(Benzyloxy)-2-(tert-butyl)-benzene (**2d**)*

Following GPA **2d** (39 mg, 16%) as a colourless oil was obtained after purification; IR (neat) ν_{max}: 2961, 1744, 1608, 1513, 1455, 1364, 1295, 1244, 1182, 1025, 828, 735, 697, 553 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.3 Hz, 2H), 7.46–7.40 (m, 2H), 7.40–7.33 (m, 2H), 7.21 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.00–6.92 (m, 2H), 5.16 (s, 2H), 1.46 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 138.5, 137.6, 128.7, 127.8, 127.4, 127.2, 126.9, 120.7, 112.6, 70.2, 35.0, 30.0; HRMS (ESI): *m/z* $[M+H]^+$ calculated for $C_{17}H_{20}O$ 241.1587, found 241.1576.

*4.4.13. 2-Benzyl-6-(tert-butyl)-phenol (**3d**)*

Following GPA **3d** (15 mg, 6%) after purification as a green oil was obtained; IR (neat) ν_{max}: 3560, 3062, 3028, 2958, 1603, 1494, 1437, 1391, 1361, 1247, 1206, 1134, 1088, 1029, 887, 844, 797, 776, 747, 699, 532, 458 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.2 Hz, 2H), 7.29–7.25 (m, 1H), 7.23 (d, *J* = 7.7 Hz, 3H), 7.03 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 4.77 (s, 1H), 4.01 (s, 2H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 139.0, 136.8, 129.1, 129.0, 128.7, 127.0, 126.8, 125.8, 120.3, 37.3, 34.7, 30.0; HRMS (ESI): *m/z* $[M-H]^-$ calculated for $C_{17}H_{20}O$ 239.1441, found 239.1448.

*4.4.14. 4-Benzyl-2-(tert-butyl)-phenol (**4d**)*

Following GPA **4d** (46 mg, 19%) as a brown oil was obtained after purification; IR (neat) ν_{max}: cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.27 (m, 2H), 7.24–7.18 (m, 3H), 7.13 (d, *J* = 2.2 Hz, 1H), 6.86 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 4.71 (s, 1H), 3.93 (s, 2H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 141.8, 136.1, 133.1, 129.0, 128.5, 127.9, 127.3, 126.0, 116.7, 41.5, 34.6, 29.7; HRMS (ESI): *m/z* $[M-H]^-$ calculated for $C_{17}H_{20}O$ 239.1441, found 239.1443.

*4.4.15. 1-(Benzyloxy)-4-(tert-butyl)-benzene (**2e**)*

Following GPA **2e** (139 mg, 58%) as a white solid was obtained after purification; mp 61–63 °C; IR (KBr) ν_{max}: 2952, 2931, 2866, 1608, 1514, 1454, 1363, 1299, 1243, 1187, 1125, 914, 837, 811, 750, 701, 555, 514 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2H), 7.43–7.37 (m, 2H), 7.36–7.29 (m, 3H), 6.99–6.89 (m, 2H), 5.06 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 143.7, 137.4, 128.7, 128.0, 127.6, 126.4, 114.4, 70.2, 34.2, 31.7; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{17}H_{20}O$ 263.1406, found 263.1393.

*4.4.16. 2-Benzyl-4-(tert-butyl)-phenol (**3e**)*

Following GPA **3e** (10 mg, 4%) after purification as a white solid was obtained; mp 48–50 °C; IR (KBr) ν_{max}: 3346, 2962, 1637, 1551, 1509, 1469, 1429, 1385, 1365, 1318, 1270, 1220, 1175, 1124, 1093, 1031, 953, 816, 770, 730, 698, 605 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.36 (m, 2H), 7.36–7.28 (m, 3H), 7.28–7.21 (m, 2H), 6.86–6.77 (m, 1H), 4.63 (s, 1H), 4.10 (s, 2H), 1.39 (d, *J* = 0.5 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 143.8, 140.2, 128.8, 128.7, 128.2, 126.4, 126.2, 124.7, 115.4, 37.0, 34.2, 31.7; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{17}H_{20}O$ 263.1406, found 263.1402.

*4.4.17. 2-(Benzyloxy)-1,3-dimethylbenzene (**2f**)*

Following GPA **2f** (23 mg, 11%) after purification as a colorless oil was obtained; IR (neat) ν_{max}: 3031, 2922. 2860, 1591, 1496, 1476, 1454, 1373, 1263, 1198, 1091, 1013, 915, 859, 769, 734, 698, 562, 462 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 2H), 7.48–7.36 (m, 3H), 7.11–7.04 (m, 2H), 6.99 (dd, *J* = 8.2, 6.6 Hz, 1H), 4.85 (s, 2H), 2.35 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 137.9, 131.3, 129.0, 128.7, 128.1, 127.9, 124.1, 74.0, 16.5; HRMS (ESI): *m/z* $[M+H]^+$ calculated for $C_{15}H_{16}O$ 213.1274, found 213.1262.

*4.4.18. 6-Benzyl-2,6-dimethylcyclohexa-2,4-dien-1-one (**3f**)*

Following GPB **3f** (119 mg, 56%) as a green viscous oil was obtained after purification; IR (neat) ν_{max}: 3029, 2974, 2922, 1715, 1677, 1655, 1639, 1582, 1495, 1452, 1376, 1072, 1019, 738, 702, 512 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.2 Hz, 3H), 7.02 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.63 (dt, *J* = 6.0, 1.6 Hz, 1H), 6.22 (ddd, *J* = 9.5, 1.8, 0.9 Hz, 1H), 6.05 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.17 (d, *J* = 13.0 Hz, 1H), 2.74 (d, *J* = 13.0 Hz, 1H), 1.79 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 144.6, 138.2, 137.2, 133.3, 129.8, 127.8, 126.5, 120.6, 52.0, 46.7, 24.9, 15.5; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{15}H_{16}O$ 235.1093, found 235.1086.

*4.4.19. 4-Benzyl-2,6-dimethylphenol (**4f**)*

Following GPA **4f** (136 mg, 64%) as a yellow solid was obtained after purification; mp 62–64 °C; IR (KBr) ν_{max}: 3395, 3026, 2915, 1603, 1490, 1452, 1385, 1348, 1303, 1212, 1147, 1030, 960, 879, 780, 726, 695, 657, 589, 494, 449 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.25 (m, 2H), 7.21 (ddt, *J* = 7.4, 3.0, 1.8 Hz, 3H), 6.83 (s, 2H), 4.52 (s, 1H), 3.87 (s, 2H), 2.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 141.9, 132.9, 129.2, 128.9, 128.5, 126.0, 123.1, 41.2, 16.0; HRMS (ESI): *m/z* $[M-H]^-$ calculated for $C_{15}H_{16}O$ 211.1128, found 211.1124.

*4.4.20. 2-(Benzyloxy)-1,3,5-trimethylbenzene (**2h**)*

Following GPB **2h** (22 mg (10%) as a colorless oil was obtained after purification; IR (neat) ν_{max}: 2920, 1483, 1454, 1373, 1307, 1213, 1147, 1020, 857, 727, 696, 573 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.51 (m, 2H), 7.48–7.42 (m, 2H), 7.42–7.36 (m, 1H), 6.90 (s, 2H), 4.84 (s, 2H), 2.33 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 137.9, 133.4, 130.8, 129.6, 128.6, 128.0, 127.9, 74.2, 20.8, 16.4; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{16}H_{18}O$ 249.1250, found 249.1253.

*4.4.21. 6-Benzyl-2,4,6-trimethylcyclohexa-2,4-dien-1-one (**3h**)*

Following GPB **3h** (190 mg, 84%) as a white solid was obtained after purification; mp 43–45 °C; IR (KBr) ν_{max}: 3449, 3060, 3027, 2977, 2918, 2862, 1667, 1638, 1585, 1495, 1449, 1383, 1237, 1190, 1074, 1018, 983, 949, 855, 772, 746, 703, 603, 565, 503, 424 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.09 (m, 3H), 7.00 (dd, *J* = 7.5, 2.1 Hz, 2H), 6.46 (dq, *J* = 2.8, 1.5 Hz, 1H), 5.87 (s, 1H), 3.08 (d, *J* = 12.8 Hz, 1H), 2.70 (d, *J* = 12.9 Hz, 1H), 1.82 (d, *J* = 1.6 Hz, 3H), 1.76 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7, 142.5, 138.9, 137.4, 132.8, 129.9, 128.0, 127.6, 126.4, 51.1, 47.2, 25.0, 21.2, 15.4; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{16}H_{18}O$ 249.1250, found 249.1250.

*4.4.22. 4-Benzyl-2,4,6-trimethylcyclohexa-2,5-dien-1-one (**4h**)*

Following GPA **4h** (73 mg, 32%) as a colourless oil was obtained after purification; IR (neat) ν_{max}: 3028, 2963, 2923, 1669, 1635, 1495, 1452, 1400, 1374, 1217, 1039, 1015, 916, 776, 740, 702, 478 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.16 (m, 3H), 7.09–6.96 (m, 2H), 6.59 (s, 2H), 2.79 (s, 2H), 1.83 (s, 6H), 1.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3, 150.5, 136.7, 134.2, 130.2, 127.9, 126.8, 47.3, 41.7, 25.3, 16.2; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{16}H_{18}O$ 249.1250, found 249.1251.

*4.4.23. 2-(Benzyloxy)-1,3-dimethoxy-5-methylbenzene (**2i**)*

Following GPA **2i** (85 mg, 33%) as a yellow oil was obtained after purification; IR (neat) ν_{max}: 2938, 1591, 1505, 1464, 1415, 1374, 1332, 1238, 1129, 1011, 969, 914, 814, 734, 698, 585, 528 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.44 (m, 2H), 7.42–7.27 (m, 3H), 6.39 (s,

2H), 4.98 (s, 2H), 3.81 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 138.1, 134.9, 133.8, 128.6, 128.2, 127.8, 106.2, 75.2, 56.2, 22.0; HRMS (ESI): *m/z* $[M+H]^+$ calculated for $C_{16}H_{18}O_3$ 259.1329, found 259.1325.

4.4.24. 6-Benzyl-2,6-dimethoxy-4-methylcyclohexa-2,4-dien-1-one (**3i**)

Following GPA **3i** (117 mg, 45%) as a yellow oil was obtained after purification; IR (neat) ν_{max}: 2927, 1684, 1659, 1584, 1496, 1454, 1376, 1342, 1248, 1111, 1083, 1033, 953, 817, 771, 746, 701, 526 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.13 (m, 3H), 7.09 (dq, *J* = 4.5, 3.3, 2.5 Hz, 2H), 5.62–5.47 (m, 2H), 3.54 (s, 3H), 3.13 (s, 3H), 2.93 (q, *J* = 12.6 Hz, 2H), 1.90 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 151.5, 134.6, 132.5, 130.6, 128.0, 127.6, 126.9, 115.1, 84.6, 55.4, 54.0, 47.2, 22.1; HRMS (ESI): *m/z* $[M+H]^+$ calculated for $C_{16}H_{18}O_3$ 259.1329, found 259.1320.

4.4.25. 6-Benzyl-2-(tert-butyl)-4,6-dimethylcyclohexa-2,4-dien-1-one (**3j**)

Following GPC **3j** (94 mg, 35%) as a yellow solid was obtained after purification; mp 82–85 °C; IR (KBr) ν_{max}: 3026, 2949, 2917, 2866, 1640, 1576, 1492, 1450, 1364, 1266, 1201, 1072, 1030, 921, 842, 792, 748, 701, 601, 571, 521, 432 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.10 (m, 3H), 7.07–6.98 (m, 2H), 6.50 (d, *J* = 2.3 Hz, 1H), 5.88 (dd, *J* = 2.3, 1.5 Hz, 1H), 3.13 (d, *J* = 13.0 Hz, 1H), 2.67 (d, *J* = 12.9 Hz, 1H), 1.86 (d, *J* = 1.5 Hz, 3H), 1.18 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 143.4, 140.0, 139.2, 137.6, 130.1, 127.8, 127.7, 126.3, 52.0, 46.7, 34.2, 29.3, 25.1, 22.0; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{19}H_{24}O$ 291.1719, found 291.1720.

4.4.26. 2-(Benzyloxy)-5-(tert-butyl)-1,3-dimethylbenzene (**2k**)

Following GPA **2k** (37 mg, 14%) as a yellow oil was obtained after purification; IR (neat) ν_{max}: 3032, 2962, 2867, 1486, 1455, 1363, 1310, 1243, 1196, 1123, 1020, 911, 872, 754, 726, 695, 645 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.50 (m, 2H), 7.48–7.40 (m, 2H), 7.40–7.33 (m, 1H), 7.07 (s, 2H), 4.83 (s, 2H), 2.35 (s, 6H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 146.7, 138.1, 130.3, 128.6, 128.0, 127.8, 125.9, 74.0, 34.3, 31.7, 16.8; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{19}H_{24}O$ 291.1719, found 291.1721.

4.4.27. 6-Benzyl-4-(tert-butyl)-2,6-dimethylcyclohexa-2,4-dien-1-one (**3k**)

Following GPB **3k** (120 mg, 45%) as a yellow oil was obtained after purification; IR (neat) ν_{max}: 3029, 2964, 2869, 1644, 1585, 1494, 1451, 1364, 1264, 1019, 852, 773, 745, 700, 616, 522 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.07 (m, 3H), 7.02–6.92 (m, 2H), 6.70 (dq, *J* = 2.8, 1.4 Hz, 1H), 5.90 (dd, *J* = 2.4, 0.8 Hz, 1H), 3.12 (d, *J* = 12.7 Hz, 1H), 2.70 (d, *J* = 12.8 Hz, 1H), 1.78 (dd, *J* = 1.4, 0.6 Hz, 3H), 1.24 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 140.1, 139.5, 137.2, 135.3, 132.7, 129.8, 127.5, 126.4, 50.5, 47.8, 33.9, 29.0, 24.9, 15.8; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{19}H_{24}O$ 291.1719, found 291.1718.

4.4.28. 4-Benzyl-4-(tert-butyl)-2,6-dimethylcyclohexa-2,5-dien-1-one (**4k**)

Following GPA a mixture of **4k** (14 mg, 5%) and **11** (11 mg, 6%) as a yellow oil was obtained after purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17–7.04 (m, 3H), 6.96–6.85 (m, 2H), 6.79 (s, 2H), 3.00 (s, 2H), 1.78 (s, 6H), 1.09 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.0, 148.1, 137.3, 136.5, 129.9, 127.3, 126.4, 51.4, 40.2, 38.0, 26.7, 16.2; HRMS (ESI): *m/z* $[M+Na]^+$ calculated for $C_{19}H_{24}O$ 291.1719, found 291.1721.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.131935.

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