Oxidation of anisoles to *p*-benzoquinone monoketals catalyzed by a ruthenium complex of 1,4,7-trimethyl-1,4,7-triazacyclononane with *tert*-butyl hydroperoxide[1]

Wai-Hung Cheung, Wing-Ping Yip, Wing-Yiu Yu, and Chi-Ming Che

Abstract: A protocol based on $[Ru^{III}(Me_3tacn)(CF_3CO_2)_2(H_2O)]CF_3CO_2$ (**1**, Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) as catalyst and *tert*-butyl hydroperoxide (TBHP) as oxidant was developed for oxidation of anisoles to *p*-benzoquinone monoketals. This reaction can be formally considered as regioselective aromatic C-H oxidation. With 2-methoxyanisole as substrate, 3,4-dimethoxy-4-*tert*-butoxy-2,5-cyclohexadienone can be obtained in up to 82% yield based on 84% substrate conversion.

Key words: oxidation, quinones, *tert*-butyl hydroperoxide, ruthenium catalyst.

Résumé : Un protocole basé sur l'utilisation du $[Ru^{III}(Me_3tacn)(CF_3CO_2)_2(H_2O)]CF_3CO_2$ (**1**, Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) comme catalyseur et de l'hydroperoxyde de *tert*-butyle comme oxydant a été élaboré pour l'oxydation des anisoles menant à la formation de monocétals de *p*-benzoquinone. On peut considérer formellement cette réaction comme une oxydation C-H aromatique régiosélective. Avec le 2-méthoxyanisole comme substrat, on obtient la 3,4-diméthoxy-4-*tert*-butoxycyclohexa-2,5-diénone avec un rendement pouvant atteindre 82 %, en se basant sur un taux de conversion du substrat de 84 %.

Mots clés : oxydation, quinones, hydroperoxyde de *tert*-butyle, catalyseur de ruthénium.

[Traduit par la Rédaction]

Introduction

p-Benzoquinones constitute a key structural element in many biologically interesting natural products such as neolignans and anthraquinone antibiotics (1, 2). Stoichiometric oxidation of substituted phenols by oxidants such as ammonium cerium(IV) nitrate (3) and thallium(III) nitrate (4) represents a common approach for quinone synthesis. Similarly, quinone monoketal, which is a valuable class of synthetic intermediates, can be readily obtained through oxidation of *para*-methoxy phenols by either electrochemical (5) or chemical oxidation using hypervalent iodine reagents (6). In view of growing environmental concern, there is an upsurge of interest in developing environmentally friendly and operationally safe catalytic protocols for hydrocarbon oxidations using more tractable oxidants such as molecular oxygen, aqueous hydrogen peroxide, and *tert*-butyl hydroperoxide (TBHP) (7). However, metal-catalyzed phenol oxidations by alkyl hydroperoxides are known to give poor product selectivity because of coupling of the phenoxy radicals (8). Recently, selective oxidation of phenols by TBHP has been achieved by Murahashi et al. (9) using $Ru(PPh_3)_3Cl_2$ as catalyst, and 4-(*tert*-butyldioxy)-4-alkyl-2,5-cyclohexadienones were produced in good yields.

It is well documented that ruthenium complexes are versatile catalysts for oxidative functionalization of C=C and C—H bonds (10). Extensive studies have shown that oxo-ruthenium complexes of chelating tertiary amines are powerful oxidants for alkenes, alkynes, and alkanes (11). We previously reported the preparation and X-ray structure characterization (12*c*) of $[Ru^{III}(Me_3tacn)(CF_3CO_2)_2(H_2O)]CF_3CO_2$ (**1**, Fig. 1), which is a robust catalyst (12) for homogeneous and heterogeneous oxidation of alcohols and alkenes using TBHP as the terminal oxidant; aldehydes and (or) ketones and epoxides can be obtained in excellent yields with product turnovers >6000. As part of our continuous effort to develop

Received 9 December 2004. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 13 May 2005.

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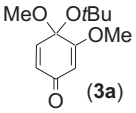
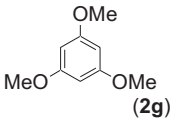
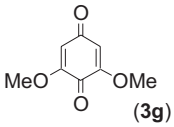
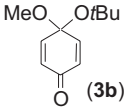
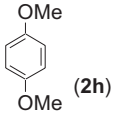
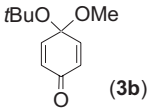
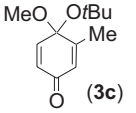
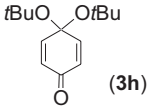
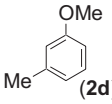
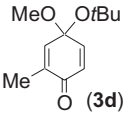
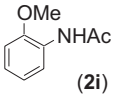
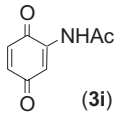
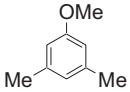
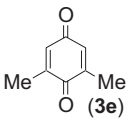
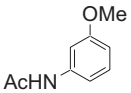
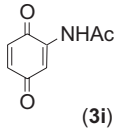
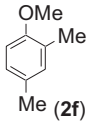
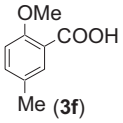
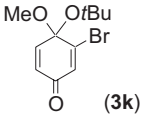
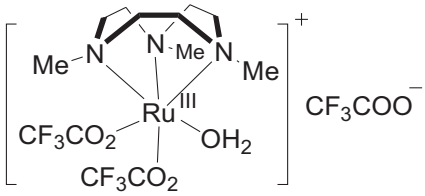
 doi: 10.1139/V05-060

Table 1. Ruthenium-catalyzed TBHP oxidation of anisoles.

Entry	Substrate	Conversion[a] (%)	Product	Yield[b] (%)	Entry	Substrate	Conversion[a] (%)	Product	Yield[b] (%)
1	 (**2a**)	46	 (**3a**)	48	7	 (**2g**)	100	 (**3g**)	76
2	 (**2b**)	84	 (**3b**)	53	8	 (**2h**)	99	 (**3b**)	32
3	 (**2c**)	100	 (**3c**)	57				 (**3h**)	19
4	 (**2d**)	95	 (**3d**)	41	9	 (**2i**)	32	 (**3i**)	12
5	 (**2e**)	100	 (**3e**)	15	10	 (**2j**)	56	 (**3i**)	20
6	 (**2f**)	45	 (**3f**)	89	11	 (**2k**)	29	 (**3k**)	15

Note: Reaction conditions (protocol I): 1:anisole:TBHP = 1:100:230, CH_2Cl_2 (5 mL), room temperature for 14 h.
[a]Substrate conversions were determined by GLC analysis.
[b]Isolated yields.

Fig. 1. Molecular structure of $[Ru^{III}(Me_3tacn)(CF_3CO_2)_2(H_2O)]$-$CF_3CO_2$.



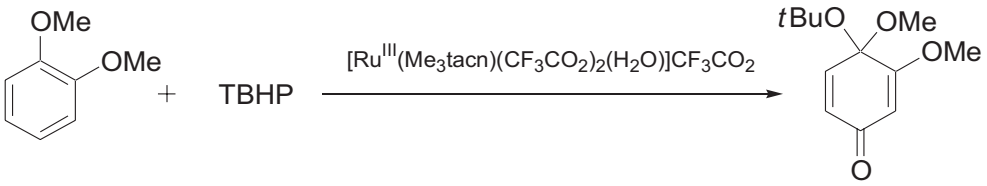
structurally characterized ruthenium complexes for organic catalysis, we are attracted to a recent work by Hirobe and co-workers (13), which states that $[Ru^{II}(Por)(CO)]$ (Por = porphyrinato) can effect catalytic oxidation of anisoles by 2,6-dichloropyridine *N*-oxide to give *p*-benzoquinones as the major product. The transformation was proposed to occur via oxidation of an aromatic C—H bond as a principal step (13). In this work we report that complex **1** can catalyze anisole to *p*-benzoquinone monoketals with up to 90% yield using TBHP as the oxidant. Results obtained under various reaction conditions (e.g., solvent systems, temperature) and with use of various substrates will be discussed.

Results and discussion

At the outset, treatment of 2-methoxyanisole (**2a**, 1 mmol) with TBHP (2.3 mmol) in the presence of $[Ru^{III}(Me_3tacn)(CF_3CO_2)_2(H_2O)]CF_3CO_2$ (**1**, 1 mol%) in CH_2Cl_2 at ambient temperature for 14 h produced 3,4-dimethoxy-4-*tert*-butoxy-2,5-cyclohexadienone (**3a**) in 48% isolated yield based on 46% anisole consumption (Table 1, entry1). Other oxidants such as *m*-chloroperoxybenzoic acid, hydrogen peroxide – urea adduct, Oxone®, chloramine-T, TEMPO, and 2,6-dichloropyridine *N*-oxide have been tested for their ability to oxidize **2a**. Under our reaction conditions (i.e., **1**:**2a**:oxidant = 1:100:230 in CH_2Cl_2), formation of **3a** was not detected, and the starting anisole (>90%) was recovered. According to Murahashi et al. (9), $Ru(PPh_3)_3Cl_2$ and $RuCl_3{\cdot}H_2O$ were reported to be effective catalysts for selective phenol oxidation by TBHP to give 4-(*tert*-butyldioxy)-4-alkyl-2,5-cyclohexanedienone. In this work, when $Ru(PPh_3)_3Cl_2$ and $RuCl_3{\cdot}H_2O$ were employed as catalysts for the oxidation of **2a** using THBP as oxidant, no effective consumption of the starting anisole was observed without product **3a** being detected.

The catalytic oxidation of other anisole derivatives has been examined by employing the following reaction condi-

Table 2. Effect of various experimental parameters on the catalytic oxidation of 2-methoxyanisole.



Entry	Loading (%)	TBHP (equiv.)	Temp (°C)	Time (h)	Solvent	Yield[a] (%)	Conversion[b] (%)
1	1.0	2.3	24	14	CH_2Cl_2	48	46
2	1.0	2.3	24	14	*n*-hexane	68	9
3	1.0	2.3	24	14	*t*-BuOH	N/A	<1
4	1.0	2.3	24	14	MeOH	N/A	<1
5	1.0	2.3	24	14	1,2-DCE[c]	50	45
6	1.0	7.0	24	14	1,2-DCE	60	49
7	5.0	2.3	24	14	1,2-DCE	49	57
8	0.5	2.3	24	14	1,2-DCE	78	28
9	1.0	7.0	80	14	1,2-DCE	86	62
10	1.0	7.0	24	14	1,2-DCE	66	45
11	1.0	14.0	80	14	1,2-DCE	93	62
12[d]	1.0	3.5/3.5	80	4	MeOH/*t*-BuOH/1,2-DCE	84	82

[a]Isolated yield.
[b]The percentage of conversion was determined by GLC analysis.
[c]1,2-DCE = 1,2-dichloroethane.
[d]A dissolved mixture of complex **1** (1 mol%) in MeOH:*t*-BuOH with TBHP (3.5 mmol) was added slowly by a syringe pump (0.5 mL min^{-1}) to a solution of **2a** (1 mmol) with TBHP (3.5 mmol) in 1,2-DCE at 80 °C for 2 h. The reaction mixture was further stirred for 2 h, followed by a general work-up procedure.

tions (protocol I): **1** (1 mol%), TBHP (2.3 equiv.), and CH_2Cl_2 at room temperature. Unsubstituted anisole **2b** reacted with TBHP to afford quinone monoketal **3b** in 53% yield based on 84% conversion (Table 1, entry 2). Likewise, *ortho*- and *meta*-substituted methyl anisoles (**2c** and **2d**) were converted to their corresponding ketals in 57% and 41% yields, respectively (entries 3 and 4) under the Ru-catalyzed conditions. Yet the analogous reaction of 3,5-dimethylanisole gave quinone **3e** in 15% yield despite complete substrate conversion (entry 5). Analysis of the crude reaction mixture by ^{1}H NMR failed to identify any defined products other than **3e**. Interestingly, when 2,4-dimethylanisole (**2f**) was employed as substrate, the **1**-catalyzed TBHP reaction furnished benzoic acid **3f** as the only identifiable product in 89% yield (entry 6), presumably via benzylic C-H oxidation. Based on these findings, the **1**-catalyzed oxidation of anisoles to quinone monoketal could be regarded as a formal regioselective oxidation of the aromatic C—H bond *para* to the methoxy group.

Adopting protocol I, oxidaton of other functionalized anisoles was also explored. For example, the oxidation of 1,3,5-trimethoxybenzene was found to give dimethoxyquinone **3g** in 76% yield, without any ketal product (Table 1, entry 7). Notably, effective oxidation of 1,4-dimethoxybenzene, which does not bear any available aromatic C—H bonds, was observed under the "**1** + TBHP" conditions, and a mixture of monoketals **3b** (32%) and **3h** (19%) was obtained (entry 8).

Recently, Nicolaou et al. (14) reported a facile synthesis of aminoquinones by oxidation of anilides with hypervalent iodine reagents (Dess–Martin periodinane, DMP); aminoquinones have been shown to be valuable synthetic intermediates for polycycle constructions. In this work, we have studied the reactions of 2- and 3-methoxyanilides (**2i** and **2j**) with TBHP by employing protocol I, and the product *ortho*-aminoquinone **3i** was formed in merely 12%–20% yield (Table 1, entries 9–10). Oxidation of 2-bromoanisole also met with limited success, and the product **3k** was isolated in only 15% yield based on 29% substrate conversion (entry 11).

Having found a protocol for anisole oxidation by TBHP, we examined the effect of various experimental parameters on the efficiency of the transformation. Using **2a** as substrate, the **1**-catalyzed anisole oxidation was found to be sensitive to the solvent used. For instance, with hexane as solvent and under the reaction conditions **1**:**2a**:TBHP = 1:100:230 at room temperature for 14 h, a higher yield (68%) of **3a** was obtained, albeit with 9% conversion (Table 2, entry 2). Poor substrate conversion could be explained by the insolubility of the catalyst in hexane. Our previous results showed that **1** dissolves in alcoholic solvents such as MeOH and *t*-BuOH, leading to the formation of an alkoxyruthenium complex (12*c*). In this work, the ruthenium catalyst was found to be inactive when MeOH or *t*-BuOH was used as the solvent, and negligible substrate conversion was observed (entries 3 and 4). Compared to the case when CH_2Cl_2 was the solvent, other halogenated solvents, such as 1,2-dichloroethane, gave similar results (ca. 50% yield; 45% conversion) under identical experimental conditions (entry 5). Increasing the TBHP amount to 7.0 equiv. produced moderate improvement in product yields (60%) and substrate conversion (49%) for the **1**-catalyzed oxidation of **2a** (entry 6).

At higher catalyst loading (5.0 mol%), little improvement in the substrate conversion (57%) and product yield (49%) was observed for the **1**-catalyzed TBHP oxidation of **2a** (en-

Table 3. Catalytic oxidation of selected anisoles using protocol II.

Entry	Substrate	Product	Yield (%)[a]	Conversion (%)[b]
1	**2a**	**3a**	84	82
2	**2k**	**3k**	49	54
3	**2i**	**3i**	39	31
4	**2c**	**3c**	49	75
5	**2d**	**3d**	33	76

Note: Reaction conditions: a mixture of complex **1** (1.0 mol%) and TBHP (3.5 mmol) dissolved with MeOH-*t*-BuOH (1:1 by volume) was added slowly through a syringe pump (0.5 mL min^{-1}) over 2 h at 80 °C to a solution of the substrate (1 mmol) with TBHP (3.5 mmol). The reaction mixture was stirred for a further 2 h and quenched with sodium thiosulphate (100 mg).

[a]Isolated yield based on conversion.

[b]Conversions were determined by GLC analysis.

try 7, compare results in entry 1). However, reducing the catalyst loading to 0.5 mol% led to a higher product yield of 78% for the catalytic oxidation in spite of a 28% substrate conversion (entry 8). This finding suggests that higher catalyst loading may favor TBHP decomposition; however, the possibility of catalyst deactivation under the reaction conditions cannot be excluded.

Interestingly, when the catalytic oxidation was conducted at 80 °C (**1**:**2a**:TBHP = 1:100:700), the product ketal was obtained in 86% yield based on 62% anisole consumption (entry 9). At room temperature, the identical transformation resulted in only 45% substrate conversion and 66% yield for the formation of **3a**. Up to 93% yield of **3a** was attained when 14 equiv. TBHP was employed, though the substrate conversion remained at 62% (entry 11).

Based on the above studies, halogenated solvents are the solvents of choice for the **1**-catalyzed anisole oxidation, and an elevated temperature seems to produce high product yield and substrate conversion. While the amount of the TBHP has a moderate effect on the catalytic oxidation, low catalyst loading was found to favor high product yield. Taking these results into consideration, a modified catalytic procedure (protocol II) was developed (see experimental section for details). Complex **1** was first dissolved in an MeOH:*t*-BuOH mixture (1:1 by volume) and TBHP (3.5 equiv.). The homogenous mixture was added slowly through a syringe pump (0.5 mL min^{-1}) to a 1,2-dichloroethane solution containing **2a** (1 mmol) and TBHP (3.5 equiv.) at 80 °C. After 4 h of reaction, monoketal **3a** was obtained in 84% yield with 82% substrate conversion (entry 12). By employing protocol II and 2-bromoanisole (**2k**) as substrate, the Ru-catalyzed oxidation afforded **3k** in 49% yield based on 54% conversion (Table 3, entry 2). This result is a significant improvement when compared with the results using protocol I (yield 29%, conversion 15%; see Table 1, entry 11). As noted earlier, oxidation of 2-methoxyanilide **2i** using protocol I afforded quinone **3i** in 12% yield based on 32% conversion (Table 1, entry 9). However, when protocol II was adopted for the same reaction, a better yield of 39% for the formation of **3i** was observed, albeit with 31% conversion (Table 3, entry 3). Using protocol II, oxidation of methyl anisoles **2c** and **2d** by TBHP produced the corresponding ketals in 49% (**3c**) and 33% (**3d**) yields (Table 3, entries 4 and 5). These findings are comparable to those obtained by employing protocol I (Table 1, entries 3 and 4).

Reaction of peroxides with $[Ru^{III}(N_4)(H_2O)_2]^{3+}$ (N_4 = macrocyclic amine ligand) is known to generate oxo-ruthenium complexes (15, 16). To gain insight about the plausible reactive intermediates responsible for the **1**-catalyzed anisole oxidation by TBHP, we performed a stoichiometric reaction of a structurally defined oxo-ruthenium complex — $[Ru^{VI}(Me_3tacn)(CF_3CO_2)O_2](ClO_4)$ — with 2-methoxyanisole (**2a**). When **2a** (10 mmol) was treated with $[Ru^{VI}(Me_3tacn)(CF_3CO_2)O_2](ClO_4)$ (0.5 mmol) in degassed aqueous *tert*-butanol [*t*-BuOH:H_2O = 6:3 (by volume)] at room temperature for 16 h under an inert atmosphere, 2-methoxy-*p*-benzoquinone (**3l**) was isolated in 81% yield. The dioxoruthenium(VI) complex was reduced to $[Ru^{III}_2(Me_3tacn)(CF_3CO_2)_2(O)](ClO_4)$ in 76% yield. This finding appears to be consistent with the results reported by Hirobe and co-workers (13) that reactive oxo-ruthenium complex is an active intermediate for anisole oxidation.

Experimental section

Materials

All the solvents were distilled and dried before used. All the common laboratory reagents were used as received. $[Ru^{III}(Me_3tacn)(CF_3CO_2)_2(H_2O)]CF_3CO_2$ (**1**) was synthesized using a literature procedure (12*c*). *tert*-Butyl hydroperoxide was obtained commercially as a 70% aqueous solution, and the oxidant was pretreated according to a procedure described by Sharpless and Verhoeven (17) using 1,2-dichloroethane. The TBHP oxidant concentration was standardized by ^1H NMR (5.38 mol L^{-1} in 1,2-dichloroethane) prior to use (17).

General procedure for the catalytic oxidation of anisoles

Protocol I

A mixture of anisole (1 mmol), TBHP in 1,2-dichloroethane (0.65 mL, 2.3 equiv.), and **1** (6.3 mg, 1.0 mol%) was stirred in CH_2Cl_2 (5 mL) at room temperature for 14 h. The reaction was quenched by the addition of sodium thiosulphate (100 mg), and the mixture was analyzed by GLC to determine the substrate consumption. To isolate the reaction products, the solvent was removed by rotary evaporation, and the residue was purified by flash column chromatography using 1% ethyl acetate in *n*-hexane as eluant.

Protocol II

A mixture of complex **1** (10.6 mg, 1.6 mol%, MeOH-*t*-BuOH, 1:1 by volume, 2 mL) and TBHP (3.5 equiv.) was

added dropwise (0.5 mL min^{-1}) to a solution of 1,2-dichloroethane (2 mL) containing anisole (1 mmol) and TBHP (3.5 equiv.) at 80 °C over 2 h. The reaction mixture was stirred for an additional 2 h. The reaction was quenched by adding sodium thiosulphate (100 mg), and the substrate consumption was determined by GLC analysis. After removal of solvent by rotary evaporation, the residue was purified by flash column chromatography using 0.5%–1% ethyl acetate in *n*-hexane as eluant.

3,4-Dimethoxy-4-*tert*-butoxy-2,5-cyclohexadienone (3a)

TLC: R_f = 0.5 (30% ethyl acetate in *n*-hexane). IR (neat KBr, υ cm^{-1}): 1670, 1634, 1607. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 6.92 (d, *J* = 10.3 Hz, 1H), 6.25 (dd, *J* = 10.3, 1.7 Hz, 1H), 5.59 (d, *J* = 1.7 Hz, 1H), 3.80 (s, 3H), 3.42 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 187.89, 169.89, 141.68, 131.41, 104.99, 98.22, 83.14, 57.71, 53.86, 26.72. EI (%): 153 ([M – O-*t*-Bu], 100). HRMS (EI) calcd. for [M – O-*t*-Bu]$^+$: 153.1552; found: 153.1554 ($C_8H_9O_3$).

4-*tert*-Butoxy-4-methoxy-2,5-cyclohexadienone (3b)

TLC: R_f = 0.6 (20% ethyl acetate in *n*-hexane as developing solvent). IR (neat KBr, υ cm^{-1}): 1644. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 6.94 (d, *J* = 10.3 Hz, 2H), 6.26 (d, *J* = 10.3 Hz, 2H), 3.45 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 185.13, 141.39, 129.59, 95.47, 81.11, 50.75, 26.29. EI (%): 123 ([M – O-*t*-Bu], 100). HRMS (EI) calcd. for [M – O-*t*-Bu]$^+$: 123.0447; found: 123.0446 ($C_7H_7O_2$).

3-Methyl-4-*tert*-butoxy-4-methoxy-2,5-cyclohexadienone (3c)

TLC: R_f = 0.6 (30% ethyl acetate in *n*-hexane as developing solvent). IR (neat KBr, υ cm^{-1}): 1678. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.14 (d, *J* = 10.4 Hz, 1H), 6.32 (d, *J* = 10.4 Hz, 1H), 6.16 (m, 1H), 3.26 (s, 3H), 2.00 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 185.48, 153.85, 143.57, 130.69, 129.52, 98.02, 81.74, 52.04, 26.72, 17.56. EI (%): 137 ([M – O-*t*-Bu], 100). HRMS (EI) calcd. for [M – O-*t*-Bu]$^+$: 137.0598; found 137.0603 ($C_8H_9O_2$).

2-Methyl-4-*tert*-butoxy-4-methoxy-2,5-cyclohexadienone (3d)

TLC: R_f = 0.6 (30% ethyl acetate in *n*-hexane as developing solvent). IR (neat KBr, υ cm^{-1}): 1651. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 6.94 (dd, *J* = 10.3 Hz, 1H), 6.67 (m, 1H), 6.24 (d, *J* = 10.3 Hz, 1H), 3.44 (s, 3H), 1.93 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 186.20, 141.91, 137.28, 136.64, 129.86, 96.43, 81.35, 51.12, 26.74, 16.00. EI (%): 137 ([M – O-*t*-Bu], 100). HRMS (EI) calcd. for [M – O-*t*-Bu]$^+$: 137.0598; found: 137.0603 ($C_8H_9O_2$).

4,4-Di-*tert*-butoxy-2,5-cyclohexadienone (3h)

TLC: R_f = 0.7 (20% ethyl acetate in *n*-hexane as developing solvent), colorless crystal. IR (neat KBr, υ cm^{-1}): 1644. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.02 (d, *J* = 10.4 Hz, 2H), 6.25 (d, *J* = 10.4 Hz, 2H), 1.26 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 185.81, 140.33, 129.67, 99.05, 81.77, 26.72. EI (%): 123 ([M – O-*t*-Bu], 100). HRMS (EI) calcd. for [M – O-*t*-Bu]$^+$: 123.0447; found: 123.0448 ($C_7H_7O_2$).

3-Bromo-4-*tert*-butoxy-4-methoxy-2,5-cyclohexadienone (3k)

TLC: R_f = 0.6 (30% ethyl acetate in *n*-hexane as developing solvent). IR (neat KBr, υ cm^{-1}): 1674. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.20 (d, *J* = 10.3 Hz, 1H), 6.82 (d, *J* = 1.9 Hz, 1H), 6.40 (dd, *J* = 10.3, 1.9 Hz, 1H), 3.35 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 182.83, 143.50, 143.24, 134.98, 129.86, 96.34, 82.00, 52.07, 26.38. EI (%): 203 ([M – O-*t*-Bu], 47), 201 ([M – O-*t*-Bu], 100). HRMS (EI) calcd. for [M – O-*t*-Bu]$^+$: 200.9550; found: 200.9551 ($C_7H_6BrO_2$).

Acknowledgments

This work is supported by the Areas of Excellence Scheme (AoE/P–10/01) established under the University Grants Committee (HKSAR, China), The University of Hong Kong (University Development Fund), and the Hong Kong Research Grants Council (HKU7384/02P).

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