2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)/tert-Butyl Nitrite/Oxygen: A Versatile Catalytic Oxidation System

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Abstract: A new catalytic oxidation system using catalytic amounts of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and *tert*-butyl nitrite with molecular oxygen serving as the environmentally benign, terminal oxidant has been developed. This aerobic catalytic system was established for the selective oxidation of non-sterically hindered benzylic alcohols and elec-

Introduction

Oxidation reactions play an important role in organic chemistry research and the organic chemical industry, and many oxidation methodologies and reagents have been developed to date.^[1] Although numerous stoichiometric inorganic oxidants have been traditionally employed in oxidation reactions, there are considerable drawbacks such as their high cost, toxicity, and serious environmental effluents. To meet the requirement for sustainable and environmentally benign processes, the use of molecular oxygen as the terminal oxidant in oxidation reactions has been received great attraction in recent years due to its remarkable advantages, including great abundance, lower cost, and generating water as the only by-product. However, the conflict between the triplet ground state of molecular oxygen and the singlet ground states of common organic compounds results in a difficulty for the application of molecular oxygen as the direct oxidant. This is also the reason that molecular oxygen possesses a high oxidative potential but exhibits unusual stability. Therefore, many efforts have been focusing on the activation and the application of molecular oxygen under mild condition.^[2]

tron-rich benzyl methyl ethers, and successfully extended to an application in the oxidative deprotection of PMB ethers to the alcohols in high selectivity.

Keywords: alcohols; deprotection; 2,3-dichloro-5,6dicyano-1,4-benzoquinone (DDQ); oxidation; oxygen

Previously, we had successfully developed an efficient aerobic oxidation of alcohols with a transition metal-free system, TEMPO/Br₂/NaNO₂.^[3] The key point of this aerobic oxidation is that NaNO₂ acted as the equivalent of NO/NO₂, which can efficiently activate molecular oxygen. With this concept, some aerobic alcohol oxidation systems have been developed and also extended to other reactions.^[4] Our later studies in this area were narrowly limited in the TEMPOcatalyzed selective oxidation of alcohols.^[5] We then wished to expand this transition metal-free system to other aerobic oxidations. Thus, some organic compounds with redox ability came to our sight, for example. 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). It is well known that DDQ is a powerful oxidant for a number of organic transformations.^[6] As the stoichiometric oxidant, it has been successfully applied in alcohol oxidation,^[7] protecting group remov-al,^[8] aromatization,^[9] benzylic acetoxylation,^[10] oxida-tive coupling,^[11] oxidative cyclization,^[12] biaryl construction,^[13] and many other reactions.

However, the use of stoichiometric DDQ may lead to purification difficulties because of the concomitant by-product 2,3-dichloro-5,6-dicyano-hydroquinone (DDHQ) and also resulted in cost concern. To avoid both these disadvantages, a combination of a catalytic

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amount of DDQ and a stoichiometric amount of a less-expensive co-oxidant is an interesting alternative. Chandrasekhar and co-workers reported that 4-methoxy- and 3,4-dimethoxybenzyl ethers could be deprotected with a catalytic amount of DDQ by oxidative recycling of the DDHQ with FeCl₃.^[14] Mn(OAc)₃ has also been developed as a mild oxidant for the regeneration of DDQ from HDDQ, and the combination of $Mn(OAc)_3$ (3 equiv.) and DDQ (0.1 equiv.) was successfully applied to the deprotection of p-methoxybenzyl ethers.^[15] Very recently, Floreancig and coworker described that a number of oxidation reactions including oxidative cyclization, deprotection and aromatization, can be effected by using catalytic DDO (0.15–0.2 equiv.) with a large excess of MnO_2 (up to 6 equiv.) serving as terminal oxidant.^[16] While this manuscript was being prepared, the chemoselective oxidation of alcohols employing catalytic quantities of DDQ as the oxidant and $Mn(OAc)_3$ as the cooxidant was described by Helquist et al.^[17] There is no doubt that using of a great amount of these inorganic oxidants did cut down the cost but did not change the waste problem which resulted in the serious purification problem and the environmental effluent. Thus, it would be ideal if molecular oxygen can serve as the terminal oxidant in DDO-mediated reactions. However, molecular oxygen cannot directly oxidize DDHO to DDQ under mild conditions.^[18] In other words, a redox compound should be employed as the bridge between molecular oxygen and the cycling DDHQ/ DDQ. With our previous TEMPO-catalyzed aerobic oxidation, we have clearly understood that NO is an effective reagent to activate molecular oxygen and tert-butyl nitrite (TBN) can served as an NO equivalent.^[5b,c] Thus we wished to establish a new protocol with the DDQ/TBN/ O_2 system for the oxidation as described in Scheme 1. Up to now, very limited examples of the DDQ-catalyzed aerobic oxidative dehydrogenation of dihydroarenes with an NO equivalent were reported.[19]

Results and Discussion

With our familiar TEMPO/TBN/O₂ system in the alcohol oxidation, we explored the possibility that the DDQ/TBN/O₂ system can be applied to the oxidation of alcohols. After detailed exploration of the reaction conditions with benzyl alcohol as the substrate, we concluded that 5 mol% of DDQ and 5 mol% TBN in 1,2-dichloroethane were suitable for the aerobic oxidation.^[20] With the optimized reaction conditions, the results of DDQ/TBN-catalyzed aerobic oxidation of selected benzylic alcohols and their heteroaromatic analogues are summarized in Table 1. As can be seen from Table 1, benzylic alcohols 1a-1c, 1e-1f were fully converted into their corresponding benzaldehydes in high selectivity (entries 1-3, 5 and 6). However, sterically hindered 2-methylbenzyl alcohol (1d) could not achieve a high conversion even upon elongating the reaction time (entry 4). For heteroaromatic analogues, 2-furfurylmethanol (1g) and 2-thiophenemethanol (1h), this catalytic oxidation system can also afford clean aldehyde products (entries 7 and 8). 4-Methylthiobenzyl alcohol (1i), which possesses two easily oxidizable functional groups, could be selectively converted into 4-methylthiobenzaldehyde (2i) without any observable sulfur oxidation (entry 9). For some secondary benzylic alcohols, α -phenylethanols (1j-1m) could also be smoothly oxidized into their corresponding acetophenones (2j-2m) in high selectivity (entries 10-13). When 1,2-diphenylethane-1,2diol (10) was used as the substrate, it could be converted to benzoin in 95% isolated yield and no C-C bond cleavage was observed (entry 14). Surprisingly, 3-pyridinemethanol, which was a representative substrate in our previous TEMPO-catalyzed aerobic oxidation systems, could not be oxidized in this catalytic oxidation system.^[21] When an aliphatic alcohol, such as 1-octanol, was used as the substrate, no oxidation product was observed after a reaction time of 24 h.^[21]

Although we have successfully developed this DDQ/TBN catalytic system and applied it in the



Scheme 1. Proposed DDQ-mediated aerobic oxidation reactions.

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				2/TBN/O ₂ H ₂ Cl, 80 °C			
Entry	Substrate		Product		<i>t</i> [h]	Conversion [%]	Selectectivity [%] ^[b]
1	ОН	1 a	СНО	2a	5	99	> 99
2	OH	1b	СНО	2b	3	100	>99
3	ОН	1c	СНО	2c	3	100	98
4	ОН	1d	СНО	2d	4	47	98
5	O-CO-OH	1e	о- Сно	2e	6	100	>99
6 ^[c]	CI	1f	сі—	2f	6	100	98
7	CH ₂ OH	1g	СНО	2g	3	100	>99
8	CH ₂ OH	1h	СНО	2h	3	100	>99
9	S-C-OH	1i	_SСНО	2i	2	100	>99
10 ^[c]	OH	1j	$\mathbf{A} = \mathbf{A}$	2ј	12	98	> 99
11		1k	\sim	2k	6	99	>99
12 ^[c]	CI	11	ci	21	12	98	97
13	р-С ОН	1m		2m	6	100	>99
14	OH	1n		2n	8	100	> 99
15 ^[c]	OH OH OH	10	O OH	20	15	100	(95)

[a]	All reactions were carried out with 10 mmol of substrate in 10 mL of ClCH ₂ CH ₂ Cl, DDQ (5 mol%), TBN (5 mol%), O ₂
	(0.2 MPa), 80 °C. The conversion and selectivity were determined by GC with area normalization.

^[b] Value in parentheses is isolated yield.

^[c] DDQ (10 mol%), TBN (10 mol%).

aerobic oxidations of the benzylic alcohols, it is obvious that this catalytic system could not compare with our previously developed TEMPO/TBN system, either in terms of substrate scope or catalyst loading. However, DDQ possesses a broad oxidative capability that TEMPO cannot compete with as described before. Because the DDQ-catalyzed aerobic oxidation showed a significantly different oxidative ability between benzylic alcohols and aliphatic alcohols, we reasoned that this catalyst combination can be applied

Table 2. DDQ/TBN-catalyzed	aerobic oxidation of	f benzyl methyl	ethers.[a]
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$R_{\underline{l}}^{\underline{l}} \xrightarrow{O} BDQ^{I} \overset{BNO_2}{\longrightarrow} R_{\underline{l}}^{\underline{l}} \xrightarrow{O} O$								
			3 2 or		2 or 4	4		
Entry	Substrate		Product		<i>t</i> [h]	Conversion [%]	Selectivity [%]	
1	0	3 a	СНО	2a	3	99	98	
2	0	3b	СНО	2b	1	100	>99	
3	0	3c	СНО	2c	1.5	100	>99	
4	0	3d	0	2d	2	90	98	
5		3e	~ <u>o</u> ~~o	2e	1.5	100	>99	
6	CI	3f	CI O	2f	3.5	88	98	
7	CI	3g	CI	4 a	3.5	32	95	
8	O ₂ N O	3h	O ₂ N O	4b	3.5	11	82	
9 ^[b]		3i		4c	4	100	>99	

[a] Reaction conditions: substrate (8 mmol), EGDE (10 mL), O₂ (0.2 MPa), 140 °C. The conversion and selectivity were determined by GC with area normalization.

^[b] DDQ (5 mol%), TBN (5 mol%), 120 °C.

to the oxidation of benzyl ethers. With our primarily optimized reaction condition,^[20] the DDQ/TBN/O₂ system was applied in the oxidation of benzyl methyl ethers to the corresponding benzaldehydes in ethylene glycol diethyl ether (EGDE), and the results are listed in Table 2. From Table 2, we can see that those electron-donating and non-sterically hindered benzylic methyl ethers can obtain high conversions with high selectivities (entries 2, 3 and 5), while the electron-donating but sterically hindered **3d** and weakly electron-deficient but non-sterically hindered 3f afforded reasonable conversions in high selectivities (entries 4 and 6). The weakly electron-deficient and sterically hindered 3g and the strong electron-deficient 3h only achieved low conversions (entries 7 and 8). On the contrary, the oxidation of the strong electron-donating substrate, 3,4-dimethoxybenzyl methyl ether (3i) was completed at under 120°C even when reducing DDQ and TBN to 5 mol% (entry 9).

Indeed, the transformation of benzyl methyl ethers to benzaldehydes by DDQ/TBN/O2 greatly inspired us to explore the potential of DDQ-catalyzed aerobic oxidative deprotection. Considering that the oxidation of 3,4-dimethoxybenzyl methyl ether (3i) could be carried out under a lower temperature with less catalyst, we would like to choose *para*-methoxybenzyl methyl ether (3e) as the substrate to further optimize the oxidation condition because PMB (para-methoxybenzyl group) is the more commonly used alcohol protecting group in the type of benzyl series.^[22] After carefully optimizing the reaction conditions, it was found that 5 mol% of DDQ, 5 mol% of TBN in EGDE under 0.2 MPa of oxygen at 120°C could complete the oxidation of para-methoxybenzyl methyl ether in 4 h (Table 3).

To explore the substrate scope, we applied this newly developed method to the oxidative deprotection of a variety of PMB ethers, and the results are summarized in Table 4. PMB ethers of primary and

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Table 3. Optimization of aerobic oxidation of p-methoxybenzyl methyl ether.^[a]



Entry	DDQ [mol%]	TBN [mol%]	<i>Т</i> [°С]	<i>t</i> [h]	Conversion [%]	Selectivity [%]
1	10	10	140	1.5	100	>99
2	5	5	140	2	100	>99
3	5	5	120	2	58	>99
4	5	5	120	3	92	>99
5	5	5	120	4	100	>99
6	3	3	120	4	43	>99
7	3	5	120	4	74	98
8	5	3	120	4	72	>99
9	5	5	100	4	56	>99

^[a] *Reaction conditions: para*-methoxybenzyl methyl ether (8 mmol), EGDE (10 mL), O_2 (0.2 MPa), temperature (oil bath). The conversion and selectivity were determined by GC with area normalization.

secondary alcohols 5a-5f underwent a facile and complete deprotection of the PMB group to furnish the corresponding alcohols 6a-6f in high selectivities (entries 1-6). To test the tolerance of this newly developed aerobic oxidative deprotection with DDQ/TBN catalytic system, one hydroxy group of 1,6-hexanediol was protected with PMB and the other one was converted to other protecting groups [Me (5g), Ac (5h), Bz (5i), MOM (5j)], and these different bifunctional ethers were also submitted to the oxidative deprotection reactions (entries 7–10). As can be seen, not only the stable methyl ether (5g), but also the base-sensitive groups Ac (5h) and Bz (5i), proceeded through an efficient PMB removal to afford 6g, 6h and 6i (entries 7-9). The isolated yield of 6i was 93%. Substrate 5j with an acid-sensitive MOM group could also be converted to the deprotection product 6j in 98% selectivity (entry 10). It should be noted that prolonging of oxidative deprotection of 5j would result in a drop of the reaction selectivity, and we observed some removal of MOM group in a by-product which was probably caused by the weak acidity of the reaction system. Similarly, substrate 51, bearing two acid-sensitive isopropylidene groups as well as a glycosidic ring, can achieve a satisfactory result by increasing the catalyst loading and cutting down the reaction time (entry 12). Further study showed that the oxidative deprotection can endure the Boc group (entry 13). 8-Hydroxy-2-chloro-5,6,7,8-tetrahydroquinoline (60), an intermediate for synthesis of chiral pyridine-phosphite ligands,^[23] could also be obtained from its PMB ether 50 in 90% yield (entry 15).

Conclusions

In conclusion, we have developed a new catalytic oxidation system using catalytic amounts of DDQ and TBN with molecular oxygen serving as the environmentally benign terminal oxidant. The catalytic oxidation system was established from the aerobic oxidation of non-sterically hindered benzylic alcohols and applied in the oxidative deprotection of PMB ethers. Under the optimal reaction conditions, a variety of PMB ethers can be deprotected in high conversions to their corresponding alcohols with high selectivities. This aerobic oxidative deprotection can tolerate a broad range of other protecting groups under the reaction conditions.

Experimental Section

General Remarks

Gas chromatography (GC) analyses were conducted on an Agilent GC6890N system with a flame ionization detector (FID) and an FFAP capillary column. Conversions and selectivities were determined by area normalization. ¹H NMR and ¹³C NMR spectra were carried out on a Bruker Avance III (500 MHz) spectrometer. $CDCl_3$ and $DMSO-d_6$ were used as the solvent with tetramethylsilane (TMS) as the internal standard. GC-MS was performed on Finnigan Trace GC Ultra-Finnigan Trace DSQ instrument. Low- and highresolution mass spectra were recorded in the ESI mode on an Agilent 6210 LC/TOF mass spectrometer. All solvents and chemicals were used as received from commercial suppliers, unless otherwise noted. 1,2-Diphenylethane-1,2-diol was reduced from benzoin with NaBH₄. Benzyl methyl ethers (3a-3i) were synthesized from the corresponding benzyl alcohols and dimethyl sulfate. PMB ethers (5a-5f, 5k-5o) were obtained from corresponding alcohols and 4methoxybenzyl chloride. Bifunctional PMB ethers (5g-5j) were synthesized as follows: (i) one hydroxy group of 1,6hexanediol was protected as PMB ether with 4-methoxybenzyl chloride to give 6-(4-methoxybenzyloxy)hexan-1-ol; (ii) the hydroxy group of 6-(4-methoxybenzyloxy)hexan-1-ol was protected by other alcohol protecting groups (Me, Ac, Bz, MOM) to obtain 5g–5j.

Typical Procedure for the Oxidation of Alcohols (Table 1, entry 15)

To a teflon-lined 316L stainless steel autoclave (300 mL) was added 2.14 g of 1,2-diphenylethane-1,2-diol (10, 10 mmol), 227 mg of DDQ (1 mmol, 10 mol%), 58 μ L of TBN (51 mg, 0.5 mmol, 5 mol%), and 10 mL of 1,2-dichloro-ethane. Then the autoclave was closed and charged oxygen to 0.2 MPa. The autoclave was put into an oil bath that was preheated to 80 °C. The autoclave was taken out of the heating bath after a reaction time of 15 h, cooled to room temperature, and carefully depressurized. The sample from the reaction mixture was diluted with CH₂Cl₂ and the conversion and selectivity were detected by GC without any purification. The GC result showed that the reaction was com-

Table 4. Oxidative deprotection of PMB ethers.^[a]

			ROPMB <u>DDQ/TBN/O2</u> EGDE, 120 ° 5	Ċ	ROH 6		
Entry	Substrate		Product		<i>t</i> [h]	Conversion [%]	Selectivity [%] ^[b]
1	CH ₃ (CH ₂) ₇ OPMB	5a	CH ₃ (CH ₂) ₇ OH	6a	2	100	>99
2	ОРМВ	5b	OH	6b	2	100	>99
3	ОРМВ	5c	ОН	6c	1.5	100	>99
4	ОРМВ	5d	ОН	6d	1.5	100	>99
5		5e	OH OH	6e	2	100	>99
6	ОРМВ	5f	С	6f	1.5	100	>99
7 8 9 10 11	MeO(CH ₂) ₆ OPMB AcO(CH ₂) ₆ OPMB BzO(CH ₂) ₆ OPMB MOMO(CH ₂) ₆ OPMB PMBO(CH ₂) ₆ OPMB	5g 5h 5i 5j 5k	MeO(CH ₂) ₆ OH AcO(CH ₂) ₆ OH BzO(CH ₂) ₆ OH MOMO(CH ₂) ₆ OH HO(CH ₂) ₆ OH	6g 6h 6i 6j 6k	2 1.5 1.5 1.5 2	100 100 100 100 100	> 99 > 99 > 99 (93) 98 > 99
12 ^[c]		51		61	0.5	100	(84)
13		5m	OH N. Boc	6m	2	100	>99 (93)
14	ОРМВ	5n	ОН	6n	1.5	100	>99
15		50		60	1	100	97 (90)

^[a] *Reaction conditions: para*-methoxybenzyl methyl ether (8 mmol), EGDE (10 mL), O₂ (0.2 MPa), temperature (oil bath). The conversion and selectivity were determined by GC with area normalization.

^[b] Values in parentheses are isolated yields.

^[c] DDQ (12 mol%), TBN (12 mol%).

pleted. Then the mixture was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel to afford benzoin (**2o**) as a white solid; yield: 2.02 g (95%). ¹H NMR (CDCl₃): δ = 5.95 (s, 1H), 7.26–7.35 (m, 5H), 7.38–7.41 (m, 2H), 7.50–7.53 (m, 1H), 7.91–7.92 (2H).

Typical Procedure for the Deprotection of PMB Ethers (Table 4, entry 9)

Caution! Potentially a peroxide could be formed in the reaction when EGDE was used as the solvent in the O_2/NO_x system!

A similar operating procedure was used for the deprotection of 6-(benzyloxy)hexyl benzoate (5i). A mixture of 2.5 g of **5i** (8 mmol)), 90.8 mg of DDQ (0.4 mmol, 5 mol%), 46 µL of TBN (41 mg, 0.4 mmol, 5 mol%), 10 mL of EGDE, and 0.2 MPa of oxygen were heated to 120 °C for 1.5 h. After the vessel had been cooled and carefully depressurized, the conversion and selectivity were detected by GC. The reaction mixture was directly purified by chromatography on silica gel, and 6-hydroxyhexyl benzoate (**6i**) was obtained as a pale yellow liquid; yield: 1.65 g (93%). ¹H NMR (CDCl₃): δ =1.44–1.48 (m, 4H), 1.59–1.62 (m, 2H), 1.77– 1.80 (m, 3H), 3.65 (t, *J*=6.5 Hz, 2H), 4.32 (t, *J*=6.5 Hz, 2H), 7.45 (t, *J*=7.5 Hz, 2H), 7.55 (t, *J*=7.5 Hz, 1H), 8.04 (d, *J*=7.0 Hz, 2H).

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References

- a) J. E. Bäckvall, Modern Oxidation Methods, VCH-Wiley, Weinheim, 2004, pp 83–118; b) M. Hundlucky, Oxidation in Organic Chemistry, American Chemical Society, Washington, DC, 1990; c) S. Caron, R. W. Dugger, S. G. Ruggeri, J. A. Ragan, D. H. B. Ripin, Chem. Rev. 2006, 106, 2943–2989.
- [2] For some reviews, see: a) S. S. Stahl, Science 2005, 309, 1824–1826; b) D. Lenoir, Angew. Chem. 2006, 118, 3280–3284; Angew. Chem. Int. Ed. 2006, 45, 3206–3210; c) M. S. Sigman, D. R. Jensen, Acc. Chem. Res. 2006, 39, 221–229; d) J. Piera, J.-E. Backvall, Angew. Chem. 2008, 120, 3558–3576; Angew. Chem. Int. Ed. 2008, 47, 3506–3523; e) T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 2005, 105, 2329–2363.
- [3] R. H. Liu, X. M. Liang, C. Y. Dong, X. Q. Hu, J. Am. Chem. Soc. 2004, 126, 4112–4113.
- [4] a) R. Z. Mu, Z. Q. Liu, Z. J. Yang, Z. G. Liu, L. M. Wu, Z. L. Liu, Adv. Synth. Catal. 2005, 347, 1333–1336;
 b) C. I. Herrerias, T. Y. Zhang, C. J. Li, Tetrahedron Lett. 2006, 47, 13–17; c) B. Karimi, A. Biglari, J. H. Clark, V. Budarin, Angew. Chem. 2007, 119, 7348–7351; Angew. Chem. Int. Ed. 2007, 46, 7210–7213; d) Z. J. An, X. L. Pan, X. M. Liu, X. W. Han, X. H. Bao, J. Am. Chem. Soc. 2006, 128, 16028–16029.
- [5] a) R. H. Liu, C. Y. Dong, X. M. Liang, X. J. Wang, X. Q. Hu, J. Org. Chem. 2005, 70, 729–731; b) Y. Xie, W. M. Mo, D. Xu, Z. L. Shen, N. Sun, B. X. Hu, X. Q. Hu, J. Org. Chem. 2007, 72, 4288–4291; c) X. J. He, Z. L. Shen, W. M. Mo, N. Sun, B. X. Hu, X. Q. Hu, Adv. Synth. Catal. 2009, 351, 89–92.
- [6] For reviews, see: a) D. Walker, J. D. Hiebert, *Chem. Rev.* 1967, 67, 153–195; b) S. B. Bharate, *Synlett* 2006, 496–497.
- [7] Some examples of alcohol oxidation, see: a) K. Peng, F. X. Chen, X. G. She, C. H. Yang, Y. X. Cui, X. F. Pan, *Tetrahedron Lett.* 2005, 46, 1217–1220; b) H. D. Becker, A. Bjork, E. Adler, J. Org. Chem. 1980, 45, 1596–1600; c) K. Mori, K. Koseki, *Tetrahedron* 1988, 44, 6013– 6020; d) B. A. McKittrick, B. Ganem, J. Org. Chem. 1985, 50, 5897–5898.
- [8] Some examples of protecting group removal, see: a) Y. Oikawa, T. Tanaka, K. Horita, T. Yoshioka, O. Yonemitsu, *Tetrahedron Lett.* **1984**, 25, 5393–5396; b) J. S. Yadav, S. Chaadrasekhar, G. Sumithra, R. Kache, *Tetrahedron Lett.* **1996**, 37, 6603–6606; c) G. V. M. Sharma, Rakesh, *Tetrahedron Lett.* **2001**, 42, 5571–5573; d) J. M. Vatele, *Tetrahedron* **2002**, 58, 5689–5698; e) K. Jarowicki, P. Kocienski, J. Chem. Soc. Perkin Trans. 1 **2001**, 2109–2135; f) K. W. Maurer, R. W. Armstrong, J. Org. Chem. **1996**, 61, 3106–3116; g) M. A. Rahim, S. Matsumura, K. Toshima, *Tetrahedron Lett.* **2005**, 46, 7307–7309.

- [9] Some examples of aromatization, see: a) T. Ohmura, K. Masuda, I. Takase, M. Suginome, J. Am. Chem. Soc. 2009, 131, 16624-16625; b) J. Sun, E. Y. Xia, L. L. Zhang, C. G. Yan, Eur. J. Org. Chem. 2009, 5247-5254; c) J. R. Manning, H. M. L. Davies, J. Am. Chem. Soc. 2008, 130, 8602-8603; d) G. Hilt, M. Danz, Synthesis 2008, 2257-2263; e) L. X. Alvarez, B. Bessieres, J. Ein-Horn, Synthesis 2008, 1376-1380; f) P. Haldar, G. Barman, J. K. Ray, Tetrahedron 2007, 63, 3049-3056; g) D. Pla, A. Marchal, C. A. Olsen, F. Albericio, M. Alvarez, J. Org. Chem. 2005, 70, 8231-8234; h) P. Ploypradith, T. Petchmanee, P. Sahakitpichan, N. D. Litvinas, S. Ruchirawat, J. Org. Chem. 2006, 71, 9440-9448; i) R. P. Wurz, A. B. Charette, Org. Lett. 2005, 7, 2313-2316; j) M. Shimizu, A. Takahashi, S. Kawai, Org. Lett. 2006, 8, 3585-3587; k) E. Bellur, I. Freifeld, P. Langer, Tetrahedron Lett. 2005, 46, 2185-2187.
- [10] Some examples of benzylic acetoxyation, see: a) M. Bouquet, A. Guy, M. Lemaire, J. P. Guette, Synth. Commun. 1985, 15, 1153–1157; b) R. E. Lehr, P. L. Kole, K. D. Tschappat, Tetrahedron Lett. 1986, 27, 1649–1652; c) E. Marcantoni, M. Petrini, R. Profeta, Tetrahedron Lett. 2004, 45, 2133–2136; d) S. Aubry, S. Pellet-Rostaing, M. Lemaire, Eur. J. Org. Chem. 2007, 5212–5225.
- [11] For a review of oxidative coupling, see: a) C. J. Li, Acc. Chem. Res. 2009, 42, 335–344. For some examples, see: b) B. P. Ying, B. G. Trogden, D. T. Kohlman, S. X. Liang, Y. C. Xu, Org. Lett. 2004, 6, 1523–1526; c) Y. H. Zhang, C. J. Li, J. Am. Chem. Soc. 2006, 128, 4242– 4243; d) D. P. Cheng, W. L. Bao, Adv. Synth. Catal. 2008, 350, 1263–1266; e) D. P. Cheng, W. L. Bao, J. Org. Chem. 2008, 73, 6881–6883; f) G. L. V. Damu, J. J. P. Selvam, C. V. Rao, Y. Venkateswarlu, Tetrahedron Lett. 2009, 50, 6154–6158; g) Y. Li, W. L. Bao, Adv. Synth. Catal. 2009, 351, 865–868; h) J. Jin, Y. Li, Z. J. Wang, W. X. Qian, W. L. Bao, Eur. J. Org. Chem. 2010, 1235– 1238; i) D. Ramesh, U. Ramulu, S. Rajaram, P. Prabhakar, Y. Venkateswarlu, Tetrahedron Lett. 2010, 51, 4898–4903.
- [12] Some examples of oxidative cyclization, see: a) L. Liu, P. E. Floreancig, Org. Lett. 2009, 11, 3152–3155;
 b) W. Y. Tu, P. E. Floreancig, Angew. Chem. 2009, 121, 4637–4641; Angew. Chem. Int. Ed. 2009, 48, 4567–4571;
 c) J. J. V. Eynde, F. Delfosse, P. Lor, Y. V. Haverbeke, Tetrahedron 1995, 51, 5813–5818;
 d) J. Chang, K. Zhao, S. Pan, Tetrahedron Lett. 2002, 43, 951–954.
- [13] For biaryl construction, see: L. Zhai, R. Shukla, R. Rathore, Org. Lett. 2009, 11, 3474–3477.
- [14] S. Chandrasekhar, G. Sumithra, J. S. Yadav, *Tetrahedron Lett.* **1996**, *37*, 1645–1646.
- [15] G. V. M. Sharma, B. Lavanya, A. K. Mahalingam, P. R. Krishna, *Tetrahedron Lett.* **2000**, *41*, 10323–10326.
- [16] L. Liu, P. E. Floreancig, Org. Lett. 2010, 12, 4686–4689.
- [17] C. C. Cosner, P. J. Cabrera, K. M. Byrd, A. M. A. Thomas, P. Helquist, Org. Lett. 2011, 13, 2071–2073.
- [18] Some other quinones can be regenerated by molecular oxygen in the presence of catalysts, some representative examples: a) H. Miyamura, M. Shiramizu, R. Matsubara, S. Kobayashi, Angew. Chem. 2008, 120, 8213–8215; Angew. Chem. Int. Ed. 2008, 47, 8093–8095; b) H. Miyamura, K. Kaehata, S. Kobayashi, Chem. Commun. 2010, 46, 8052–8054; c) J. Piera, K. Narhi, J. Bäckvall,

Adv. Synth. Catal. 2011, 353, 3031-3038

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Angew. Chem. 2006, 118, 7068–7071; Angew. Chem. Int. Ed. 2006, 45, 6914–6917.

- [19] a) W. Zhang, H. Ma, L. P. Zhou, Z. Q. Sun, Z. T. Du, H. Miao, J. Xu, *Molecules* 2008, 13, 3245–3245; b) W. Zhang, H. Ma, L. P. Zhou, H. Miao, J. Xu, *Chin. J. Catal.* 2009, 30, 86–88.
- [20] See the Supporting Information.
- [21] The result was not listed in the Table 1.
- [22] Recent examples of benzyl-type ethers as alcohol protecting groups: a) S. F. Tlais, H. Lam, S. E. House, G.

Dudley, J. Org. Chem. 2009, 74, 1876–1885; b) R. Mezaache, Y. A. Dembele, Y. Bikard, J.-M. Weibel, A. Blanc, P. Pale, *Tetrahedron Lett.* 2009, 50, 7322–7326; c) M. Ramanathan, D.-R. Hou, *Tetrahedron Lett.* 2010, 51, 6143–6145.

[23] Y. J. Xie, H. M. Huang, W. M. Mo, X. Q. Fan, Z. Q. Shen, Z. L. Shen, N. Sun, B. X. Hu, X. Q. Hu, *Tetrahedron: Asymmetry* **2009**, 20,1425–1432.