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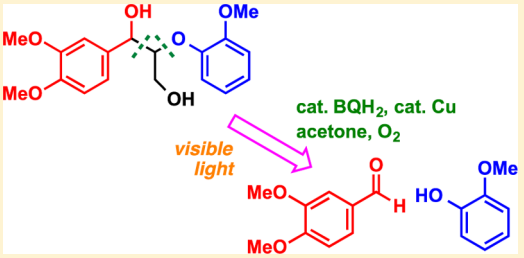
Solar Photochemical Oxidation of Alcohols using Catalytic Hydroquinone and Copper Nanoparticles under Oxygen: Oxidative Cleavage of Lignin Models

Lorna J. Mitchell and Christopher J. Moody*

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.

Supporting Information

ABSTRACT: Alcohols are converted into to their corresponding carbonyl compounds using catalytic amounts of 1,4-hydroquinone with a copper nanoparticle electron transfer mediator with oxygen as the terminal oxidant in acetone as solvent under visible light irradiation. These conditions employing biorenewable hydroquinone as reagent were developed from initial experiments using stoichiometric amounts of 1,4-benzoquinone as oxidant. A range of benzylic and aliphatic primary and secondary alcohols are oxidized, affording the corresponding aldehydes or ketones in moderate to excellent yields. The methodology is also applicable to the oxidative degradation of lignin model compounds that undergo C−C bond cleavage to give simple aromatic compounds.

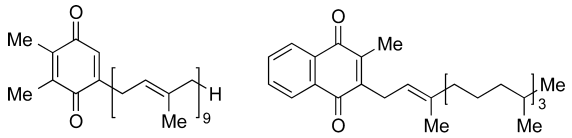


INTRODUCTION

Oxidation is at the core of many processes in chemistry and biology. For example, the oxidation of alcohols to carbonyl compounds is one of the most important transformations in chemical synthesis.[1−4] One complex alcohol-containing substrate that has recently received particular attention is the biopolymer lignin, owing to its potential as a renewable feedstock.[5−7] Lignin contains a highly functionalized network of alkyl aryl ether monomers, most commonly linked by a β-O-4 bond, with each unit featuring a primary aliphatic alcohol and a secondary benzylic alcohol as key structural motifs. The chemoselective oxidation of the benzylic alcohols contained within lignin facilitates oxidative fragmentation,[8−14] enabling access to valuable, low-molecular-weight, aromatic compounds such as vanillin.[15,16]

While numerous methods for the oxidation of alcohols are well-established, many of these, such as the stoichiometric use of high-valent metal salts,[2,3] pose problems in terms of cost and toxicity. In an era driven by the need for sustainable and environmentally benign processes for chemical synthesis, the use of such reagents with their low atom economy and waste stream production is undesirable. Consequently, efforts have been made to use metals in catalytic amounts,[17−21] organo-oxidants such as DMSO- or TEMPO-based protocols, or hypervalent iodine reagents[2,3,22] to effect the oxidation of alcohols. One class of organo-oxidants well-known for their remarkable oxidizing ability are the quinones.[23] Indeed, quinones are commonly employed in natural redox processes (Figure 1), with both plastoquinone and phylloquinone acting as electron acceptors in the light-dependent reactions of photosynthesis.

In chemical synthesis, however, the use of high-potential quinones such as 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is more common. Indeed, DDQ is a useful organo-oxidant for a range of transformations in organic chemistry.[24,25] Inspired by Nature's use of lower potential quinones under photochemical conditions, we sought to use simpler (and cheaper) quinones such as 1,4-benzoquinone (BQ) itself in oxidation reactions,[26] with the eventual aim of establishing a catalytic method. We now report a new protocol for the oxidation of alcohols that, following initial experiments using stoichiometric amounts of BQ, employs catalytic amounts of BQ, formed in situ by oxidation of 1,4-hydroquinone, copper nanoparticles as the electron transfer mediator (ETM), and oxygen as the terminal oxidant under visible light (solar) irradiation.



plastoquinone phylloquinone

Figure 1. Naturally occurring quinones that participate in redox processes.

RESULTS AND DISCUSSION

Although the photochemical hydrogen abstraction properties of quinones have long been known and the reactions have been subject to extensive mechanistic and kinetic studies,[27,28] they remain largely unexplored in chemical synthesis. This is

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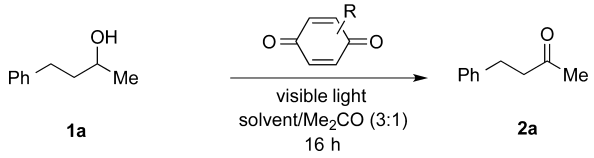
notwithstanding the fact that one of the earliest examples of solar photochemistry involved the oxidation of ethanol with BQ.[29] Initially, we set about developing BQ as a mild and efficient stoichiometric oxidant of alcohols. As a test reaction, the oxidation of 4-phenylbutan-2-ol (**1a**) was considered in the presence of various substituted 1,4-benzoquinones and solvents using a sunlight-mimicking lamp, a commonly employed light source in commercial greenhouses (Table 1). Trifluorotoluene (TFT), a less hazardous and more

Table 1. Oxidation of 4-Phenylbutan-2-ol with Various Quinones under Visible Light Irradiation[a]



1a **2a**

Entry	R	Redox (mV)[b]	Solvent	Atmosphere	Conversion (%)
1	2-Cl	734	TFT	air	21
2	2,3,5,6-Cl	755	TFT	air	5
3	2-Me	693	TFT	air	44
4	2,6-OMe	612	TFT	air	0
5	H	711	TFT	air	50
6	H		Me_2CO	air	41
7	H		Me_2CO	O_2	48
8	H		Me_2CO	Ar	37
9	none		Me_2CO	O_2	0

[a]All reactions were carried out on 0.33 mmol scale at a 0.08 M concentration in sealed 15 mL Pyrex tubes, using 1.1 equiv of the benzoquinone. The visible light source was a 400 W HQI-T metal halide lamp. Conversions were measured by ^{1}H NMR integration and calculated as a ratio of starting material to product. [b]Quinone redox potentials obtained from ref 31.

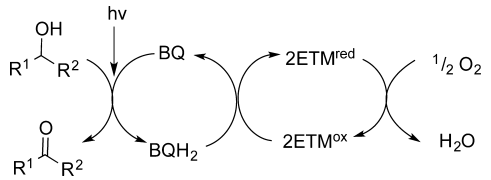
acceptable alternative to aromatic solvents commonly employed in such photochemical hydrogen abstraction reactions,[30] was selected as the initial solvent with acetone as the cosolvent for improved solubility. While the use of electron-poor and electron-rich quinone oxidants proved disappointing (entries 1, 2 and 4), a promising result was achieved with the use of 2-methylbenzoquinone (entry 3). However, the use of *p*-benzoquinone itself (entry 5) proved to be optimal, with moderate conversion being achieved. Further optimization, by variation of the solvent, showed that acetone could be employed as the sole solvent with little impact on the reaction outcome (entry 6), while variation of concentration (0.01−1.0 M) established that 0.08 M was optimal (data not shown). While this result was slightly improved by irradiation under an oxygen atmosphere (entry 7), the reaction still proceeded in the absence of oxygen (entry 8). No reaction was observed in the absence of benzoquinone (entry 9). At the end of the irradiation period, both benzoquinone and hydroquinone were observed to be present in the reaction mixture by NMR spectroscopic analysis.

The optimized conditions were then appied to a broad range of alcohols to examine the substrate scope (Table 2). While the methodology tolerates a range of primary and secondary benzylic alcohols (entries 2−5 and 6−12), the level of success is dependent on the degree of activation of the substrate toward H abstraction. Excellent conversions were obtained with the highly activated 4-methoxybenzyl alcohol (entry 2) and bis-benzylic alcohols (entries 10 and 11), while lower conversions and yields were achieved with electron-poor substrates, such as those possessing 4-halo or 4-trifluoromethyl functionalities (entries 4, 5, 8, and 9). The reaction was also successful on a range of allylic alcohols (entries 13−15). Moderate conversions were also achieved with unactivated secondary alcohols (entries 1 and 16−18), but initial attempts to oxidize primary aliphatic alcohols were unsuccessful. In several cases (entries 3, 6, 9, 15, and 18) isolated yields were significantly less than the observed conversions due to losses on workup.

In addition, several of the reactions (entries 2, 10, 11, and 16) were successfully carried out in sunlight on the windowsill of the laboratory (ca. 150 h, latitude 52° 56′ N, 32 m above sea level). However, in most cases, prolonged irradiation times were required and/or low conversions were obtained, thus highlighting the limitations of using sunlight in regions of higher latitude and the need for a "sun-mimicking" light source.

However, there are potential problems with the use of BQ as an oxidant from safety aspects. The compound is toxic and is itself normally prepared by oxidation reactions of phenol, aniline, or diisopropylbenzene. On the other hand, 1,4-hydroquinone (BQH_2) is less toxic,[32] and can be obtained from biorenewable materials such as quinic acid or by hydrolysis of the BQH_2 glycoside arbutin. Hence, we set out to develop a photochemical oxidation protocol based on the use of catalytic amounts of BQH_2 that could be reoxidized in situ to the active oxidant BQ, employing oxygen as the terminal oxidant. However, since BQH_2 cannot be oxidized directly by molecular oxygen under neutral reaction conditions,[33] an ETM is required to facilitate the process (Scheme 1).

Scheme 1. Schematic BQ−BQH_2 Redox Cycle with an Electron Transfer Mediator (ETM)



We began by considering the photochemical oxidation of 4-methoxybenzyl alcohol (**1b**), a good substrate under the stoichiometric reaction conditions, in the presence of various ETMs (Table 3). Following preliminary experiments with iron and cobalt salts (entries 1−3), which proved unsuccessful, we focused on the use of copper salts as ETMs.[34] Use of copper(II) chloride dihydrate (entry 4) resulted in no reaction being observed, while the use of copper(II) acetate resulted in a disappointing conversion into the aldehyde (entry 5). However, the use of the copper nanoparticle ETM

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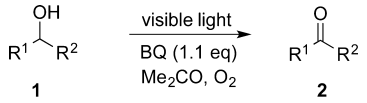
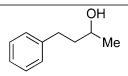
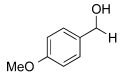
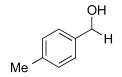
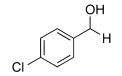
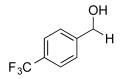
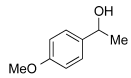
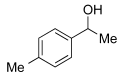
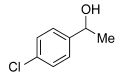
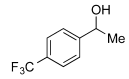
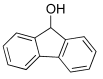
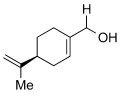
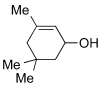
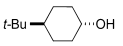
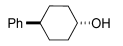
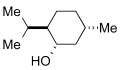
Table 2. Photochemical Oxidation of Primary and Secondary Alcohols[a]



Entry	Starting Material		Time/h	Conversion/%	Yield/%
1		**1a**	16	48	36
2		**1b**	14	72 71 (sunlight)[b]	55
3		**1c**	16	44	19
4		**1d**	16	47	36
5		**1e**	16	34	25
6		**1f**	7	74	43
7		**1g**	15	55	48
8		**1h**	20	53[c]	49
9		**1i**	30	42	29
10		**1j**	14	60 36 (sunlight)[b]	55
11		**1k**	16	84 43 (sunlight)[b]	80
12		**1l**	16	64	40
13		**1m**	17	44	42[d]
14		**1n**	16	64	50[d]
15		**1o**	16	80	54
16		**1p**	6	46 59 (sunlight)[b]	35
17		**1q**	16	46	32
18		**1r**	16	50[e]	25[e]

[a]The visible light source was a 400 W HQI-T metal halide lamp, unless otherwise stated. Conversions were measured by ^{1}H NMR integration and calculated as a ratio of starting material to product. [b]After ca. 150 h irradiation in sunlight on the windowsill of the laboratory. [c]Carried out using 2 equiv of BQ. [d]Yield calculated by GC analysis. [e]Reaction was carried out in trifluorotoluene/acetone (3/1).

4 (Cu/AlO(OH), 3.7 % Cu by ICP analysis), easily prepared from readily available materials in a simple single-step procedure,[35,36] and characterized by XPS (see the Supporting Information), proved more promising (entry 6), although some of the corresponding benzoic acid **3** was also formed. The catalyst contains copper nanoparticles entrapped in an aluminum oxyhydroxide support and is proposed to function as an ETM through the Cu(I)/Cu(II) redox couple. Pleasingly, the catalytic loadings of BQH_2 could be decreased to 10 mol % with 2 mol % of ETM **4** with little impact on the reaction (entry 7). Longer irradiation times resulted in an overall excellent conversion to the corresponding aldehyde **2b** and acid **3** (entry 8). In the absence of **4** (entry 9), no conversion into **2b** was observed, showing that the presence of copper was required as an ETM for the initial oxidation of BQH_2 to BQ. Likewise, in the absence of BQH_2 (entry 10), ETM **4** alone was incapable of effecting the oxidation. Although the reaction proceeds in air, it is much slower than that under oxygen; no reaction occurs under argon. Finally, it was established that the oxidations were indeed light mediated; no reaction occurred in the dark.

We then appied the optimized conditions (10 mol % of BQH_2, 2 mol % of **4**) to a range of primary and secondary alcohols to examine the scope of the oxidation (Table 4). Primary and secondary benzylic alcohols, including those containing electron-withdrawing substituents, were found to give moderate to excellent yields, with 1-(4-chlorophenyl)-ethanone (entry 5) and benzophenone (entry 6) affording yields of 70% and 90%, respectively. Furthermore, in the case of benzophenone, the catalytic loadings of BQH_2 could be reduced to 5 mol %, with minimal impact on the isolated yield (70%). When primary benzylic alcohols were employed as substrates (entries 2 and 3), formation of the corresponding carboxylic acids, 4-methoxybenzoic acid and 4-chlorobenzoic acid, was also observed. This process does not require BQH_2 or ETM **4** and occurs when solutions of 4-methoxybenzaldehyde and 4-chlorobenzaldehyde are irradiated under the reaction conditions. In the case of 4-methoxybenzyl alcohol (entry 2) the reaction could be taken to completion (100% conversion into the acid) after 66 h of irradiation, whereas conversions of greater than 85% could not be achieved for 4-chlorobenzoic acid (entry 3).

Unactivated secondary alcohols, such as 4-phenylbutan-2-ol, 4-*tert*-butylcyclohexanol, and 4-phenylcyclohexanol (entries 1, 9, and 10) were also good substrates, although increased loading of BQH_2 and prolonged irradiation times were required for the oxidation of 4-phenylbutan-2-ol (entry 1). In a majority of cases, comparable or superior yields were

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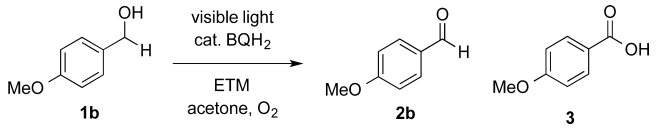
Table 3. Optimization of the Oxidation of 4-Methoxybenzyl Alcohol using Catalytic Amounts of BQH_2[a]



Entry	BQH_2/mol%	ETM	ETM/mol%	Time/h	Conversion into **2b**/%	Conversion into **3**/%
1	20	Salcomine	2	6	0	0
2	20	Co(TPP)	2	6	0	0
3	20	Fe^{III}(EDTA)	2	6	0	0
4	20	$CuCl_2$•$2H_2O$	2	6	0	0
5	20	$Cu(OAc)_2$	2	6	10	0
6	20	**4**	2	6	23	5
7	10	**4**	2	6	22	7
8	10	**4**	2	16	52	23
9	10	-	-	16	0	0
10	0	**4**	2	16	0	0

[a]The visible light source was a 400 W HQI-T metal halide lamp. Conversions were measured by ^{1}H NMR spectroscopy and calculated as a ratio of starting material to product; Salcomine = *N*,*N*′-bis(salicylidene)ethylenediaminocobalt(II); Co(TPP) = (5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine)cobalt(II); ETM **4** = [Cu/AlO(OH)] = Cu nanoparticles entrappd on aluminum oxyhydroxide (3.7% Cu by ICP analysis).

achieved using catalytic amounts of BQH_2 plus ETM in comparison to those with the use of stoichiometric amounts of BQ as oxidant. The reactions could also be carried out in sunlight (entries 2, 6, and 9), but in all cases, low conversions were observed over the 8 h irradiation period.

We assume that the reactions proceed by initial oxidation of BQH_2 to BQ and that the alcohol oxidation proceeds via hydrogen abstraction by the photoexcited triplet quinone.[27,28] In support of this, it was found that benzylic alcohols with a more easily abstracted hydrogen were oxidized more quickly than aliphatic alcohols. Thus, 4-methoxyphenylethanol and 4-chlorobenzyl alcohol were oxidized faster than 4-phenylbutan-2-ol and 4-*tert*-butylcyclohexanol (see the Supporting Information). Also, when the oxidation of 4-methoxybenzyl alcohol (**1b**) was carried out in the presence of butylated hydroxytoluene (BHT), no reaction was observed.

Finally, we applied the procedure to a range of secondary benzylic alcohols contained within lignin model compounds to determine its appicability and selectivity. A number of lignin model substrates have been reported, including both 1,2-diols and *β*-O-4 linked aryl ethers, and their chemoselective oxidation has attracted considerable attention recently,[5] owing to the potential of lignin as a biorenewable source of aromatic compounds. A number of oxidative degradation methods have been reported, including TEMPO-based oxidants,[10,13] and enzyme,[11] cobalt,[9] and vanadium catalyzed procedures,[8] in addition to SET processes under UV irradiation.[12,17−19] To our surprise, the application of our photochemical oxidative conditions did not simply result in selective oxidation of the benzylic alcohol but also in oxidative cleavage of the C−C bond, leading to a range of aromatic products (Table 5).[37]

In the case of 1,2-diols **5a**,**b**, the formation of both ketones **6a**,**b** and photochemically cleaved benzaldehydes **2b** and **7**, respectively, was observed. The other fragment of oxidative cleavage, which was anticipated to be formaldehyde, was not isolated or characterized. In these cases, TFT was employed as solvent, with acetone as a cosolvent for improved solubility. The use of acetone as the sole solvent, although more environmentally benign,[38] proved problematic due to formation of the corresponding acetonide of the 1,2-diol substrate. Interestingly, the rate of the photochemical cleavage appears to be strongly influenced by the electron-donating ability of the aryl ring system, with more electron rich 1,2-diols (entry 2) requiring longer irradiation times.

When lignin model aryl ethers **5c−g** were subjected to the oxidation conditions, the formation of both the corresponding benzaldehyde (**2b** or **7**) and phenol **8** was observed (Table 5, entries 3, 5, and 7). In the case of **5c** (entry 3), ketone **5d** (3%) was also formed, which was not itself oxidatively cleaved (entry 4). As it has been previously shown that the chemoselective oxidation of benzylic alcohols related to **5c** weakens the C−O bond of the *β*-O-4 linkage by appoximately 58 kJ mol^{-1},[39] thus facilitating the cleavage process, such a result seemed surprising. However, the use of ketone **5f** (entry 6), formed by the oxidation of alcohol **5e** (entry 5), also gave no reaction. Improved yields could be achieved by the use of stoichiometric BQ (entries 1 and 5), and several reactions were successfully demonstrated in sunlight (entries 2, 3, and 5), though poor conversions were achieved. Control reactions were carried out in darkness and without any hydroquinone, with no reaction being observed.

Despite the modest conversions, the present method has advantages in that it directly cleaves the lignin model compounds into simple aromatic fragments. Many of the

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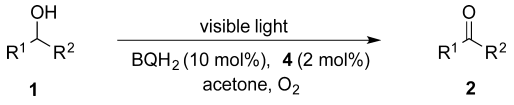
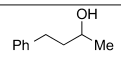
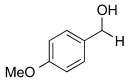
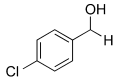
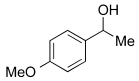
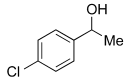
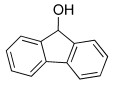
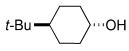
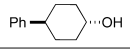
Table 4. Oxidation of Alcohols using Hydroquinone/Copper Nanoparticle System in Visible Light[a]

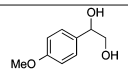
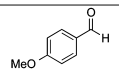
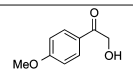
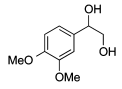
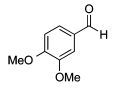
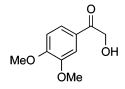
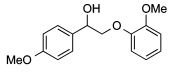
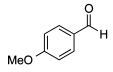
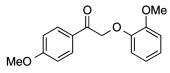
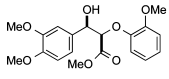
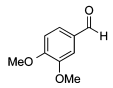
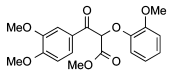
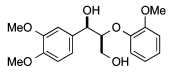
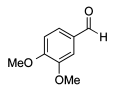


Entry		Alcohol	Time /h	Conversion /%	Yield /%
1[b]	**1a**		120	50	30
			16	52	42
2	**1b**			23 (acid) 19 (sunlight)[c] 5 (acid)[c]	16 (acid)
			66	100 (acid)	41 (acid)
3[b]	**1d**		72	15 85 (acid)	15 56 (acid)
4	**1f**		65	75	37
5	**1h**		65	100	70
6	**1j**		14	90 [72][d] 17 (sunlight)[c]	90 [70][d]
7	**1k**		15	78	61
8	**1l**		14	60	40
9	**1p**		16	49 16 (sunlight)[c]	32
10	**1q**		65	52	32

[a]Conversions were measured by ^{1}H NMR spectroscopy and calculated as a ratio of starting material to product. The visible light source was a 400 W HQI-T metal halide lamp, unless otherwise stated. [b]20 mol % BQH_2 and 1.4 mol % **4** were used. [c]Conversion obtained after 8 h irradiation in sunlight. [d]Carried out using 5 mol % of HQ and 0.5 mol % of **4**.

recently reported methods, while selectively oxidizing the benzylic alcohol in lignin models, require a second separate oxidative step to cleave the C−C bond.[10,13] The fact that both alcohol oxidation and C−C bond cleavage in the lignin models are observed suggests that two competing reaction pathways are operating (Scheme 2). Presumably alcohol oxidation occurs by the accepted mechanism of initial hydrogen abstraction from the α-C−H bond by the photochemically excited triplet quinone (^{3}BQ) to give a C-centered radical that can undergo a further hydrogen abstraction from the O−H bond to afford the ketone product and hydroquinone (Scheme 2A). On the other hand, the C−C cleavage reaction is most probably initiated by hydrogen abstraction from the O−H bond to form an alkoxy radical that undergoes C−C homolytic fragmentation to the aldehyde and a new alkyl radical (Scheme 2B). The C−C cleavage

Table 5. Photochemical Oxidative Cleavage of Lignin Models[a]

Entry	Substrate	Method	Time/h	Products and Yields/%	
1					
	5a			**2b**	**6a**
		stoich	16	47	14
		cat	16	22	6
2					
	5b			**7**	**6b**
		stoich	88	15	16
		cat	120	28	10
				1 (sunlight)[b]	
3					
	5c			**2b**	**8**
		stoich	42	20	16
		cat	40	22	12
				7 (sunlight)[b]	
4					
		stoich	18	no reaction	
	5d				
5[c]					
	5e			**7**	**8**
		stoich	88	23	10
		cat	66	7	7
				3 (sunlight)[b]	
6[c]					
		stoich	19	no reaction	
	5f				
7					
	5g			**7**	**8**
		stoich	66	17	8
		cat	66	18	4

[a]Conditions: (stoichiometric) BQ (110 mol %), TFT/acetone (3/1), O_2 atmosphere, $h\nu$; (catalytic) BQH_2 (10 mol %), Cu/AlO(OH) (2 mol %), TFT/acetone (3/1), O_2 atmosphere, $h\nu$. The visible light source was a 400 W HQI-T metal halide lamp, unless otherwise stated. [b]Conversion obtained after 8 h irradiation in sunlight. [c]Acetone as solvent.

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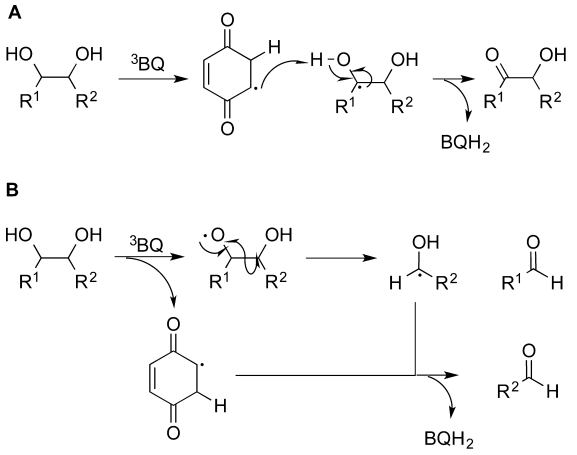
Scheme 2. Proposed Mechanistic Cleavage Pathways



reactions of β-hydroxy-alkoxy radicals into two carbonyl compounds is a known radical process.[40,41]

In summary, we have developed a new catalytic photochemical oxidation protocol for the oxidation of alcohols into their corresponding carbonyl compounds in moderate to excellent yields. The protocol offers a photochemical alternative to current procedures and can be successfully carried out in sunlight or using a "sun-mimicking" light source. In addition, we have expanded the methodology to include a range of 1,2-diols and β-O-4 linked aryl ethers contained within lignin model compounds, with a photochemical cleavage process being observed, allowing for access to high-value, low-molecular-weight aromatic compounds.

EXPERIMENTAL SECTION

For general experimental details, see the Supporting Information. For NMR spectra, δ values are in ppm and J values in Hz.

Preparation of the Catalyst [Cu/AlO(OH)] (4).[36] The reaction was carried out according to the procedure of Kim et al.,[36] with minor modifications. To a suspension of copper(II) chloride dehydrate (100 mg, 0.575 mmol), aluminum *sec*-butoxide (2.27 g, 9.2 mmol), Pluronic P123 (1.00 g) ($EO_{20}PO_{70}EO_{20}$ (EO = ethylene oxide, PO = propylene oxide)) was added ethanol (3 mL), and the reaction mixture was heated to 160 °C for 3 h. To the resulting colorless suspension was added water (20 mL), and the resulting blue gel was washed with successive portions of acetone (6 × 20 mL) to give a pale green solid, which was dried at 120 °C for 2 h. The catalyst **4** (521 mg) was used in successive steps without further purification. The catalyst was characterized by ICP-MS analysis (3.7% w/w Cu) and XPS. For full characterization details, see the Supporting Information.

Preparation of Alcohols and Lignin Models. *trans-4-Phenylcyclohexan-1-ol (**1q**).* To a solution of 4-phenylcyclohexan-1-one (436 mg, 2.52 mmol) in methanol (15 mL) was added sodium borohydride (113 mg, 3 mmol), and the reaction mixture was stirred at ambient temperature. After 16 h, the reaction mixture was concentrated in vacuo and the residue was dissolved in dichloromethane (50 mL), washed with water (2 × 50 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (light petroleum → 4/1 light petroleum/ethyl acetate) to afford the *title compound* **1q** (252 mg, 58%) as a fine colorless solid: mp 117−121 °C (lit.[42] mp 120−121 °C); δ_H (400 MHz; $CDCl_3$) 7.35−7.20 (5 H, m, ArH), 3.76−3.69 (1 H, m, CH), 2.54 (1 H, tt, J 11.8, 3.3, CH), 2.16−2.12 (2 H, m, CH), 2.00−1.95 (2 H, m, CH), 1.70−1.42 (4 H, m, CH); δ_C (100 MHz; $CDCl_3$) 146.5 (C), 128.3 (CH), 126.8 (CH), 126.1 (CH), 70.6 (CH), 43.3 (CH), 35.9 (CH_2), 32.4 (CH_2). Data are consistent with those previously reported.[42,43]

*1-(4-Methoxyphenyl)ethane-1,2-diol (**5a**).* To a stirred solution of 4-methoxystyrene (1.10 g, 8.2 mmol) and 4-methylmorpholine *N*-oxide hydrate (1.66 g, 12.3 mmol) in acetone/water (4/1, 100 mL) was added osmium tetroxide (2.5% in 2-methyl-2-propanol; 0.83 mL, 0.08 mmol), and the reaction mixture was stirred at ambient temperature. After 16 h, the reaction mixture was quenched with saturated sodium sulfite solution (50 mL) and stirred at ambient temperature for 2 h. The product was extracted with ethyl acetate (2 × 100 mL), and the combined organic layers were washed with further saturated sodium sulfite solution (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (50% light petroleum/50% ethyl acetate) to afford the *title compound* **5a** (956 mg, 70%) as a colorless solid: mp 78−80 °C (lit.[44] mp 78−89 °C); δ_H (400 MHz; $CDCl_3$) 7.27 (2 H, d, J 8.7, ArH), 6.90 (2 H, d, J 8.7, ArH), 4.75 (1 H, dd, J 8.1, 3.5, CH), 3.81 (3 H, s, Me), 3.71−3.61 (2 H, m, CH_2); δ_C (100 MHz; $CDCl_3$) 159.3 (C), 132.6 (C), 127.3 (CH), 113.9 (CH), 74.3 (CH), 68.0 (CH_2), 55.2 (CH_3). Data are consistent with those previously reported.[45]

*1-(3,4-Dimethoxyphenyl)ethane-1,2-diol (**5b**).* To a stirred solution of 3,4-dimethoxystyrene (1.64 g, 10 mmol) and 4-methylmorpholine *N*-oxide hydrate (2.03 g, 15 mmol) in acetone/water (4/1, 125 mL) was added osmium tetroxide (2.5% in 2-methyl-2-propanol; 1.01 mL, 0.1 mmol), and the reaction mixture was stirred at ambient temperature. After 16 h, the reaction mixture was quenched with saturated sodium sulfite solution (50 mL) and stirred at ambient temperature for 30 min. The product was extracted with ethyl acetate (2 × 100 mL), and the combined organic layers were washed with further saturated sodium sulfite solution (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (50% light petroleum/50% ethyl acetate to 100% ethyl acetate) to afford the *title compound* **5b** (1.87 g, 94%) as a colorless solid: mp 80−82 °C (lit.[46] mp 83 °C); δ_H (400 MHz; $CDCl_3$) 6.93−6.84 (3 H, m, ArH), 4.78 (1 H, dd, J 8.0, 3.6, CH), 3.90 (3 H, s, CH_3), 3.88 (3 H, s, CH_3), 3.76−3.65 (2 H, m, CH_2); δ_C (100 MHz; $CDCl_3$) 149.1 (C), 148.8 (C), 133.1 (C), 118.4 (CH), 111.1 (CH), 109.2 (CH), 74.4 (CH), 68.1 (CH_2), 55.93 (CH_3), 55.88 (CH_3). Data are consistent with those previously reported.[10,46]

*2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**5d**).* To 2-methoxyphenol (3.72 g, 30 mmol) and potassium carbonate (8.30 g, 60 mmol) in acetone (40 mL) was added 2-bromo-4-methoxyacetophenone (4.00 g, 17.4 mmol), and the reaction mixture was stirred at ambient temperature for 3 days. The reaction mixture was concentrated in vacuo, and the residue was recrystallized from ethanol to afford 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**5d**; 3.79 g, 80%) as a microcrystalline brown solid: mp 78−80 °C; δ_H (400 MHz; $CDCl_3$) 8.00 (2 H, d, J 8.8, ArH), 7.00−6.83 (6 H, m, ArH), 5.27 (2 H, s, CH_2), 3.86 (3 H, s, CH_3), 3.85 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 193.0 (C), 163.8 (C), 149.6 (C), 147.5 (C), 130.3 (CH), 127.5 (C), 122.2 (CH), 120.7 (CH), 114.6 (CH), 113.8 (CH), 112.1 (CH), 71.8 (CH_2), 55.8 (CH_3), 55.3 (CH_3). Data are consistent with those previously reported.[13]

*2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol (**5c**).* To a stirred solution of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-ethan-1-one (**5d**; 1.63 g, 6 mmol) in THF/water (3/1, 60 mL) was added sodium borohydride (908 mg, 24 mmol), and the reaction mixture was stirred at ambient temperature. After 1 h, hydrochloric acid (1 M; 20 mL) was added and the reaction mixture was stirred for a further 10 min. Ethyl acetate (50 mL) was then added, and the phases were separated. The organic layer was washed with further hydrochloric acid (1 M; 2 × 20 mL) and water (20 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The *title compound* **5c** (165 mg, 100%), was isolated as a yellow oil which did not require further purification and was used directly in the next step: δ_H (400 MHz; $CDCl_3$) 7.37 (2 H, d, J 8.6, ArH), 7.05−6.85 (6 H, m, ArH), 5.07 (1 H, dd, J 9.6, 2.9, CH), 4.16 (1 H, dd, J 9.6, 2.9, CH), 3.98 (1 H, t, J 9.6, CH), 3.89 (3 H, s, CH_3), 3.82 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 159.4 (C), 150.1 (C), 148.0 (C), 131.6 (C), 127.5 (CH), 122.4 (CH), 121.0 (CH), 115.9 (CH), 113.9 (CH), 112.0

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(CH), 76.2 (CH_2), 71.9 (CH), 55.8 (CH_3), 55.3 (CH_3). Data are consistent with those previously reported.[13]

*erythro-Methyl 3-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate (**5e**).* To a stirred solution of 2-methoxyphenol (12.4 g, 100 mmol) in acetone (160 mL) were added K_2CO_3 (23.0 g, 150 mmol) and methyl bromoacetate (13.9 mL, 150 mmol), and the reaction mixture was stirred at ambient temperature. After 16 h, the reaction mixture was filtered and concentrated in vacuo to afford the methyl 2-(2-methoxyphenoxy)-acetate (24.8 g, 100%) as a colorless oil, which did not require further purification and was used directly in the next step: δ_H (400 MHz; $CDCl_3$) 6.97 (1 H, app td, *J* 7.0, 1.9, ArH), 6.91−6.82 (3 H, m, ArH), 4.68 (2 H, s, CH_2), 3.86 (3 H, s, CH_3), 3.77 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 169.4 (C), 149.6 (C), 147.1 (C), 122.5 (CH), 120.6 (CH), 114.4 (CH), 112.0 (CH), 66.4 (CH_2), 55.7 (CH_3), 52.0 (CH_3). Data are consistent with those previously reported.[47] A solution of diisopropylamine (5 mL, 36 mmol) in THF (40 mL) was cooled to 0 °C, and *n*-BuLi (16.5 mL, 33 mmol, 2 M in hexanes) was added dropwise. The resulting solution was stirred at 0 °C for 30 min and cooled to −78 °C, a solution of methyl 2-(2-methoxyphenoxy)acetate (5.88 g, 30 mmol) in THF (40 mL) was added dropwise, and the resulting solution was stirred at −78 °C. After 15 min, a solution of 2,3-dimethoxybenzaldehyde (5.48 g, 33 mmol) in THF (20 mL) was added and the reaction mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched with saturated ammonium chloride solution (100 mL) and warmed to ambient temperature to give a two-phase mixture. The phases were separated, and the aqueous layer was back-extracted with ethyl acetate (2 × 100 mL). The combined organics were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was recrystallized from ethyl acetate to afford the *title compound* **5e** (1.78 g, 16%) as a single diastereomer and as a colorless solid: mp 109−111 °C (found M + Na^+ *m*/*z* 385.1242, calcd for $C_{19}H_{22}O_7Na^+$ 385.1258); ν_{max} ($CHCl_3$)/cm^{-1} 3480, 1750, 1518, 1258, 1028; δ_H (400 MHz; $CDCl_3$) 7.06−6.98 (3 H, m, ArH), 6.92−6.84 (4 H, m, ArH), 5.15 (1 H, app t, *J* 5.2, CH), 4.76 (1 H, d, *J* 5.2, CH), 3.89 (6 H, m, CH_3), 3.86 (3 H, s, CH_3), 3.70 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 169.8 (C), 150.4 (C), 148.72 (C), 148.65 (C), 147.1 (C), 131.7 (C), 123.9 (CH), 121.0 (CH), 119.1 (CH), 118.6 (CH), 112.2 (CH), 110.6 (CH), 110.0 (CH), 83.8 (CH), 73.8 (CH), 55.8 (CH_3), 55.8 (CH_3), 55.7 (CH_3), 52.0 (CH_3); *m*/*z* 385 (M + Na^+, 100%).

*Methyl 3-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-3-oxopropanoate (**5f**).* To a stirred solution of DMP (1.27 g, 3 mmol) in CH_2Cl_2 (4 mL) at 0 °C was added *erythro*-methyl 3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate (**5e**; 0.724 mg, 2 mmol), and the reaction mixture was stirred and warmed to ambient temperature over 16 h. The reaction mixture was quenched with sodium hydroxide solution (1 M; 100 mL), the product was extracted with ethyl acetate (3 × 50 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (19/1 light petroleum/ethyl acetate to 4/1 light petroleum/ethyl acetate) to afford the *title compound* **5f** (189 mg, 26%) as a yellow oil (found M + H^+, 361.1269, calcd for $C_{19}H_{21}O_7^+$ 361.1282); ν_{max} ($CHCl_3$)/cm^{-1} 3011, 1757, 1597, 1516, 1343; δ_H (400 MHz; $CDCl_3$) 7.90 (1 H, dd, *J* 8.5, 2.1, ArH), 7.70 (1 H, d, *J* 2.1, ArH), 7.05−6.97 (2 H, m, ArH), 6.92−6.90 (2 H, m, ArH), 6.86−6.82 (1 H, m, ArH), 5.79 (1 H, s, CH), 3.96 (3 H, s, CH_3), 3.93 (3 H, s, CH_3), 3.82 (3 H, s, CH_3), 3.81 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 190.0 (C), 167.6 (C), 154.1 (C), 150.4 (C), 148.9 (C), 146.1 (C), 127.2 (C), 124.9 (CH), 124.1 (CH), 120.9 (CH), 118.7 (CH), 112.6 (CH), 111.6 (CH), 110.1 (CH), 82.8 (CH), 56.1 (CH_3), 55.9 (CH_3), 55.8 (CH_3), 52.9 (CH_3); *m*/*z* 361 (M + H^+, 100%).

*erythro-1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol (**5g**).* To a stirred solution of *erythro*-methyl 3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate (**5e**; 500 mg, 1.38 mmol) in THF/water (3/1, 20 mL) was added sodium borohydride (261 mg, 6.9 mmol), and the reaction mixture was stirred at ambient temperature for 2 h. Further sodium borohydride (3 × 261 mg, 20.7 mmol) was added portionwise after 2, 3, and 4 h. The reaction mixture was quenched with water (20 mL), and the phases were separated. The aqueous layer was back-extracted with ethyl acetate (2 × 20 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated in vacuo to afford the *title compound* **5g** (440 mg, 95%) as a colorless gum which did not require further purification and was used directly in the next step: δ_H (400 MHz; $CDCl_3$) 7.07 (1 H, app t. d, *J* 7.1, 1.9, ArH), 7.00−6.90 (5 H, m, ArH), 6.85 (1 H, m, ArH), 5.00 (1 H, d, *J* 4.6, CH), 4.19−4.15 (1 H, m, CH), 3.95 (1 H, m, CH), 3.89 (3 H, s, CH_3), 3.88 (3 H, s, CH_3), 3.88 (3 H, s, CH_3), 3.69−3.66 (1 H, m, CH); δ_C (100 MHz; $CDCl_3$) 151.6 (C), 149.0 (C), 148.5 (C), 146.9 (C), 132.5 (C), 124.2 (CH), 121.6 (CH), 121.0 (CH), 118.4 (CH), 112.1 (CH), 110.0 (CH), 109.2 (CH), 87.4 (CH), 72.7 (CH), 60.7 (CH_2), 55.9 (CH_3). Data are consistent with those previously reported for the *erythro* diastereomer.[48]

Photochemical Alcohol Oxidation and Lignin Model Degradation. *Method A.* To a stirred solution of the alcohol (1 mmol) in acetone (12.5 mL) was added *p*-benzoquinone (1.1 equiv 119 mg), and the reaction mixture was vacuum-evacuated, refilled with oxygen five times, stirred, and irradiated for the time specified (see Table 2) under an oxygen balloon. The reaction mixture was then concentrated in vacuo, and the residue was taken up into ethyl acetate or ether (50 mL), washed with sodium dithionite solution (1 M; 2 × 20 mL) and saturated sodium carbonate solution (4 × 10 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified using flash chromatography on silica gel (99/1 light petroleum/ethyl acetate) to afford the final product.

Method B. To a stirred solution of the alcohol (1 mmol) in acetone (12.5 mL) were added hydroquinone (11 mg, 10 mol %) and [Cu/AlO(OH)] (3.7% Cu by ICP analysis; 34 mg, 2 mol %), and the reaction mixture was vacuum evacuated, refilled with oxygen five times, stirred, and irradiated for the time specified (see Table 4) under an oxygen balloon. The reaction mixture was then concentrated in vacuo, and the workup procedure and purification as in method A were followed.

Method C. To a stirred solution of the alcohol (1 mmol) in acetone (12.5 mL) was added *p*-benzoquinone (118 mg, 1.1 equiv), and the reaction mixture was vacuum evacuated, refilled with oxygen five times, stirred, and irradiated for the time specified (see Table 5) under an oxygen balloon. The reaction mixture was then concentrated in vacuo, and the residue was taken up into ethyl acetate or ether (50 mL), washed with sodium dithionite solution (1 M; 2 × 20 mL) and sodium hydroxide (1 M; 4 × 10 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The aqueous layers were placed to one side. The residue was purified using flash chromatography on silica gel (99/1 light petroleum/ethyl acetate to 4/1 light petroleum/ethyl acetate) to afford the aldehyde. The aqueous layers were then acidified to pH 1−2 with hydrochloric acid (1 M), extracted with ethyl acetate (2 × 50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified using flash chromatography on silica gel (9/1 light petroleum/ethyl acetate to 4/1 light petroleum/ethyl acetate) to afford 2-methoxyphenol.

Method D. To a stirred solution of the alcohol (1 mmol) in acetone (12.5 mL) were added hydroquinone (11 mg, 10 mol %) and [Cu/AlO(OH)] (3.7% Cu by ICP analysis; 34 mg, 2 mol %), and the reaction mixture was vacuum evacuated, refilled with oxygen five times, stirred, and irradiated for the time specified (see Table 5) under an oxygen balloon. The reaction mixture was then concentrated in vacuo, and the workup procedure and purification as in method C was followed.

*4-Phenylbutan-2-one (**2a**) (Table 2, Entry 1; Table 4, Entry 1).* Compound **2a** was isolated as a colorless oil: yield 53 mg (36%, method A); 44 mg (30%, method B, using 20 mol % BQH_2 and 1.4 mol % **4**); ν_{max} ($CHCl_3$)/cm^{-1} 3011, 1715, 1361, 1163; δ_H (400 MHz; $CDCl_3$) 7.34−7.29 (2 H, m, ArH), 7.25−7.20 (3 H, m, ArH), 2.94 (2 H, t, *J* 7.5, CH_2), 2.79 (2 H, t, *J* 7.5, CH_2), 2.17 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 207.8 (C), 140.9 (C), 128.4 (CH),

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128.2 (CH), 126.1 (CH), 45.1 (CH_2), 30.0 (CH_3), 29.7 (CH_2). Data are consistent with those previously reported.[49]

*4-Methoxybenzaldehyde (**2b**) (Table 2, Entry 2; Table 4, Entry 2).* Compound **2b** was obtained as a colorless oil: yield 75 mg (55%, method A); 57 mg (42%, method B); ν_{max} ($CHCl_3$)/cm^{-1} 3011, 1697, 1600, 1512, 1315, 1239, 1029; δ_H (400 MHz; $CDCl_3$) 9.90 (1 H, s, CH), 7.86 (2 H, d, *J* 8.8, ArH), 7.02 (2 H, d, *J* 8.8, ArH), 3.91 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 190.8 (CH), 164.6 (C), 132.0 (CH), 130.0 (C), 114.3 (CH), 55.6 (CH_3). Data are consistent with those previously reported.[50] In addition, 4-methoxybenzoic acid **3** was isolated as a colorless solid: yield 25 mg, (16%, method B); mp 178−179 °C (lit.[51] mp 182−183 °C); ν_{max} ($CHCl_3$)/cm^{-1} 3051, 1686, 1605, 1259, 1182; δ_H (400 MHz; MeOD) 7.99 (2 H, d, *J* 8.9, ArH), 6.99 (2 H, d, *J* 8.9, ArH), 3.87 (3 H, s, CH_3); δ_C (100 MHz; MeOD) 169.9 (C), 165.2 (C), 133.0 (CH), 124.1 (C), 114.8 (CH), 56.1 (CH_3). Data are consistent with those previously reported.[52]

*4-Methylbenzaldehyde (**2c**) (Table 2, Entry 3).* Compound **2c** was isolated as a colorless oil: yield 23 mg (19%, method A); ν_{max} ($CHCl_3$)/cm^{-1} 3011, 2740, 1703, 1688, 1606, 1169, 909; δ_H (400 MHz; $CDCl_3$) 9.97 (1 H, s, CH), 7.78 (2 H, d, *J* 8.2, ArH), 7.34 (2 H, d, *J* 8.2, ArH), 2.45 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 192.0 (CH), 145.5 (C), 134.2 (C), 129.8 (CH), 129.7 (CH), 21.8 (CH_3). Data are consistent with those previously reported.[53]

*4-Chlorobenzaldehyde (**2d**) (Table 2, Entry 4; Table 4, Entry 3).* Compound **2d** was isolated as a pale yellow oil: yield 51 mg (36%, method A); 21 mg (15%, method B, using 20 mol % BQH_2 and 1.4 mol % **4**); ν_{max} ($CHCl_3$)/cm^{-1} 1736, 1596, 1422, 1239, 1094, 836; δ_H (400 MHz; $CDCl_3$) 9.99 (1 H, s, CH), 7.84 (2 H, d, *J* 8.5, ArH), 7.53 (2 H, d, *J* 8.5, ArH); δ_C (100 MHz; $CDCl_3$) 190.8 (CH), 141.0 (C), 134.7 (C), 130.9 (CH), 129.5 (CH). Data are consistent with those previously reported.[50] In addition, 4-chlorobenzoic acid was isolated as a colorless solid: yield 88 mg, (56%, method B); mp 238−241 °C (lit.[54] mp 238−239 °C); ν_{max} ($CHCl_3$)/cm^{-1} 3633, 3468, 3010, 2681, 1698, 1117; δ_H (400 MHz; MeOD) 8.01 (2 H, d, *J* 8.5, ArH), 7.49 (2 H, d, *J* 8.5, ArH); δ_C (100 MHz; MeOD) 168.9 (C), 140.4 (C), 132.5 (CH), 130.9 (C), 129.9 (CH). Data are consistent with those previously reported.[52]

*4-(Trifluoromethyl)benzaldehyde (**2e**) (Table 2, Entry 5).* Compound **2e** was isolated as a pale yellow oil: yield 43 mg (25%; method A); ν_{max} ($CHCl_3$)/cm^{-1} 2837, 1710, 1325, 1175, 1138, 1106, 836; δ_H (400 MHz; $CDCl_3$) 10.11 (1 H, s, CH), 8.01 (2 H, d, *J* 8.3, ArH), 7.81 (2 H, d, *J* 8.3, ArH); δ_C (100 MHz; $CDCl_3$) 191.0 (CH), 138.7 (C), 135.6 (C, d, J_{FC} 32), 129.9 (CH), 126.1 (CH, q, J_{FC} 3.8), 123.4 (C, d, J_{FC} 273). Data are consistent with those previously reported.[55]

*1-(4-Methoxyphenyl)ethan-1-one (**2f**) (Table 2, Entry 6; Table 4, Entry 4).* Compound **2f** was isolated as a pale yellow solid: yield 65 mg (43%, method A); 55 mg (37%, method B); mp 31−33 °C (lit.[56] mp 30−31 °C); ν_{max} ($CHCl_3$)/cm^{-1} 2964, 1614, 1589, 1508, 1466, 1288, 1180, 1037; δ_H (400 MHz; $CDCl_3$) 7.94 (2 H, d, *J* 9.0, ArH), 6.94 (2 H, d, *J* 9.0, ArH), 3.87 (3 H, s, CH_3), 2.56 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 196.8 (C), 163.5 (C), 130.6 (CH), 130.3 (C), 113.7 (CH), 55.4 (CH_3), 26.3 (CH_3). Data are consistent with those previously reported.[56,57]

*1-(4-Tolyl)ethan-1-one (**2g**) (Table 2, Entry 7).* Compound **2g** was isolated as a pale yellow oil: yield 65 mg (48%, method A); ν_{max} ($CHCl_3$)/cm^{-1} 3011, 1678, 1574, 1270; δ_H (400 MHz; $CDCl_3$) 7.88 (2 H, d, *J* 8.1, ArH), 7.28 (2 H, d, *J* 8.1, ArH), 2.60 (3 H, s, Me), 2.43 (3 H, s, Me); δ_C (100 MHz; $CDCl_3$) 197.8 (C), 143.9 (C), 134.7 (C), 129.2 (CH), 128.4 (CH), 26.5 (CH_3), 21.6 (CH_3). Data are consistent with those previously reported.[58]

*1-(4-Chlorophenyl)ethan-1-one (**2h**) (Table 2, Entry 8; Table 4, Entry 5).* Compound **2h** was isolated as a pale yellow oil: yield 75 mg (49%, method A, using 2 equiv of BQ); 109 mg (70%, method B); ν_{max} ($CHCl_3$)/cm^{-1} 1684, 1591, 1359, 1262, 1096, 833; δ_H (400 MHz; $CDCl_3$) 7.90 (2 H, d, *J* 8.6, ArH), 7.44 (2 H, d, *J* 8.6, ArH), 2.59 (3 H, s, Me); δ_C (100 MHz; $CDCl_3$) 196.8 (C), 139.6 (C), 135.4 (C), 129.7 (CH), 128.9 (CH), 26.5 (CH_3). Data are consistent with those previously reported.[59]

*1-(4-(Trifluoromethyl)phenyl)ethan-1-one (**2i**) (Table 2, Entry 9).* Compound **2i** was isolated as a colorless oil: yield 54 mg (29%, method A); ν_{max} ($CHCl_3$)/cm^{-1} 1580, 1312, 1265, 1174, 1137; δ_H (400 MHz; $CDCl_3$) 8.08 (2 H, d, *J* 8.2, ArH), 7.75 (2 H, d, *J* 8.2, ArH), 2.66 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 196.9 (C), 139.7 (C), 134.5 (t, J_{FC} 33, C), 128.6 (CH), 125.6 (q, J_{FC} 3.7, CH), 123.6 (d, J_{FC} 272, C), 26.7 (CH_3). Data are consistent with those previously reported.[60]

*Benzophenone (**2j**) (Table 2, Entry 10; Table 4, Entry 6).* Compound **2j** was isolated as a colorless oil: yield 109 mg (55%, method A); 164 mg (90%, method B); ν_{max} ($CHCl_3$)/cm^{-1} 3065, 1658, 1600, 1448, 1319, 1280, 910; δ_H (400 MHz; $CDCl_3$) 7.82 (4 H, dd, *J* 8.4, 1.7, ArH), 7.60 (2 H, tt, *J* 7.3, 1.7, ArH), 7.49 (4 H, app br t, *J* 7.8, ArH); δ_C (100 MHz; $CDCl_3$) 196.7 (C), 137.6 (C), 132.4 (CH), 130.0 (CH), 128.2 (CH). Data are consistent with those previously reported.[50]

*Fluorenone (**2k**) (Table 2, Entry 11; Table 4, Entry 7).* Compound **2k** was isolated as a brght yellow solid: yield 152 mg (80%, method A); 110 mg (61%, method B); mp 80−83 °C (lit.[61] mp 80−82 °C); ν_{max} ($CHCl_3$)/cm^{-1} 3070, 1715, 1612, 1454, 1327, 918; δ_H (400 MHz; $CDCl_3$) 7.67 (2 H, dt, *J* 7.3, 1.3, CH), 7.53−7.47 (4 H, m, CH), 7.30 (2 H, td, *J* 7.3, 1.3, CH); δ_C (100 MHz; $CDCl_3$) 193.9 (C), 144.4 (C), 134.6 (CH), 134.1 (C), 129.0 (CH), 124.3 (CH), 120.3 (CH). Data are consistent with those previously reported.[61,62]

*2,3-Dihydro-1H-inden-1-one (**2l**) (Table 2, Entry 12; Table 4, Entry 8).* Compound **2l** was isolated as a pale yellow oil: yield 53 mg (40%, method A); 53 mg (40%, method B); ν_{max} ($CHCl_3$)/cm^{-1} 3011, 1711, 1611, 1473, 1280, 909; δ_H (400 MHz; $CDCl_3$) 7.75 (1 H, app br d, *J* 7.7, ArH), 7.58 (1 H, td, *J* 7.2, 1.0, ArH), 7.47 (1 H, dt, *J* 7.7, 1.0, ArH), 7.36 (1 H, td, *J* 7.2, 1.0, ArH), 3.14 (2 H, t, *J* 5.6, CH_2), 2.69−2.66 (2 H, m, CH_2); δ_C (100 MHz; $CDCl_3$) 207.0 (C), 155.1 (C), 137.0 (C), 134.5 (CH), 127.2 (CH), 126.6 (CH), 123.6 (CH), 36.1 (CH_2), 25.7 (CH_2). Data are consistent with those previously reported.[63]

*(S)-Perillaldehyde (**2m**) (Table 2, Entry 13).* Compound **2m** was isolated as a colorless oil: yield 42% by GC, method A; $[\alpha]$ = = −73.5° (*c* 0.285, EtOH); ν_{max} ($CHCl_3$)/cm^{-1} 3007, 1710, 1418, 1360, 1240, 1090; δ_H (400 MHz; $CDCl_3$) 9.44 (1 H, s, CH), 6.84−6.83 (1 H, m, CH), 4.79 (1 H, s, CH), 4.74 (1 H, s, CH), 2.55−2.42 (2 H, m, 2 × CH), 2.30−2.00 (3 H, m, 3 × CH), 2.00−1.85 (1 H, m, CH), 1.77 (3 H, s, CH_3), 1.55−1.40 (1 H, m, CH); δ_C (100 MHz; $CDCl_3$) 193.9 (CH), 150.7 (CH), 148.3 (C), 141.2 (C), 109.6 (CH_2), 40.7 (CH), 31.7 (CH_2), 26.3 (CH_2), 21.5 (CH_2), 20.7 (CH_3). Data are consistent with those previously reported.[53,64]

*Cyclohex-2-en-1-one (**2n**) (Table 2, Entry 14).* Compound **2n** was isolated as a colorless oil: yield 50% by GC, method A; ν_{max} ($CHCl_3$)/cm^{-1} 3011, 1670, 1389, 909; δ_H (400 MHz; $CDCl_3$) 6.99 (1 H, td, *J* 10.1, 4.0, CH), 6.02 (1 H, td, *J* 10.1, 1.9, CH), 2.43 (2 H, t, *J* 6.2, CH_2), 2.37−2.33 (2 H, m, CH_2), 2.02 (2 H, pent, *J* 6.2, CH_2); δ_C (100 MHz; $CDCl_3$) 199.7 (C), 150.6 (CH), 129.9 (CH), 38.1 (CH_2), 25.6 (CH_2), 22.7 (CH_2). Data are consistent with those previously reported.[65]

*3,5,5-Trimethylcyclohex-2-en-1-one (**2o**) (Table 2, Entry 15).* Compound **2o** was isolated as a colorless oil: yield 75 mg (54%, method A); ν_{max} ($CHCl_3$)/cm^{-1} 2960, 1668, 1467, 1380, 1247, 1034; δ_H (400 MHz; $CDCl_3$) 5.91 (1 H, q, *J* 1.4, CH), 2.23 (2 H, s, CH_2), 2.19 (2 H, s, CH_2), 1.97 (3 H, s, CH_3), 1.00 (6 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 200.0 (C), 160.4 (C), 125.5 (CH), 50.8 (CH_2), 45.3 (CH_2), 33.6 (C), 28.3 (CH_3), 24.6 (CH_3). Data are consistent with those previously reported.[66]

*4-tert-Butylcyclohexan-1-one (**2p**) (Table 2, Entry 16; Table 4, Entry 9).* Compound **2p** was isolated as a colorless solid: yield 54 mg (35%, method A), 50 mg (32%, method B, cocatalyst added in 2 portions at 0 and 3 h); mp 44−46 °C (lit.[67] mp 44−47 °C); ν_{max} ($CHCl_3$)/cm^{-1} 2963, 1711, 1368; δ_H (400 MHz; $CDCl_3$) 2.43−2.29 (4 H, m, CH), 2.11−2.07 (2 H, m, CH), 1.55−1.43 (3 H, m, CH), 0.92 (9 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 212.6 (C), 46.7 (CH), 41.3 (CH_2), 32.5 (C), 27.6 (CH_2 and CH_3). Data are consistent with those previously reported.[67−69]

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*4-Phenylcyclohexan-1-one (**2q**) (Table 2, Entry 17; Table 4, Entry 10).* Compound **2q** was isolated as a colorless solid: yield 55 mg (32%, method A); 55 mg (32%, method B); mp 75−77 °C (lit.[70] mp 75−77 °C); ν_{max} ($CHCl_3$)/cm^{-1} 3066, 2942, 1713, 1164; δ_H (400 MHz; $CDCl_3$) 7.36−7.22 (5 H, m, ArH), 3.04 (1 H, tt, *J* 12.2, 3.4, CH), 2.58−2.51 (4 H, m, CH), 2.28−2.21 (2 H, m, CH), 2.02−1.91 (2 H, m, CH); δ_C (100 MHz; $CDCl_3$) 211.1 (C), 144.7 (C), 128.6 (CH), 126.6 (CH), 126.5 (CH), 42.7 (CH), 41.3 (CH_2), 33.9 (CH_2). Data are consistent with those previously reported.[69]

*(+)-Menthone (**2r**) (Table 2, Entry 18).* Compound **2r** was isolated as a colorless oil: yield 29 mg (25%, method A, using TFT/acetone (3/1) as solvent); [α] = +11.6° (*c* 0.91, EtOH); ν_{max} ($CHCl_3$)/cm^{-1} 3005, 1702, 1456, 1384, 1111, 909; δ_H (400 MHz; $CDCl_3$) 2.37 (1 H, ddd, *J* 13.0, 3.7, 2.0, CH), 2.18−1.84 (6 H, m, CH), 1.44−1.33 (2 H, m, CH), 1.02 (3 H, d, *J* 6.3, CH_3), 0.93 (3 H, d, *J* 6.8, CH_3), 0.87 (3 H, d, *J* 6.8, CH_3); δ_C (100 MHz; $CDCl_3$) 212.3 (C), 55.9 (CH), 50.8 (CH_2), 35.4 (CH), 33.9 (CH_2), 27.8 (CH), 25.8 (CH_2), 22.2 (CH_3), 21.1 (CH_3), 18.7 (CH_3). Data are consistent with those previously reported.[70,71]

Photochemical Cleavage of 1-(4-Methoxyphenyl)ethane-1,2-diol (5a) (Table 5, Entry 1). The reaction was carried out using trifluorotoluene/acetone (3/1) as solvent, and purification was undertaken by flash chromatography on silica gel (99/1 to 4/1 light petroleum/ethyl acetate). 4-Methoxybenzaldehyde (**2b**) was isolated as a colorless oil: yield 65 mg (47%, method A); 30 mg (22%, method B). 2-Hydroxy-1-(4-methoxyphenyl)ethan-1-one (**6a**) was isolated as a colorless solid: yield 24 mg (14%, method A); 10 mg (6%, method B); mp 100−105 °C (lit.[72] mp 104−107 °C); ν_{max} ($CHCl_3$)/cm^{-1} 3470, 1710, 1602, 1264, 909; δ_H (400 MHz; $CDCl_3$) 7.92 (2 H, d, *J* 8.9, ArH), 6.99 (2 H, d, *J* 8.9, ArH), 4.83 (2 H, s, CH_2), 3.90 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 196.7 (C), 164.4 (C), 130.0 (CH), 126.3 (C), 114.1 (CH), 65.0 (CH_2), 55.5 (CH_3). Data are consistent with those previously reported.[72]

Photochemical Cleavage of 1-(3,4-Dimethoxyphenyl)-ethane-1,2-diol (5b) (Table 5, Entry 2). The reaction was carried out using trifluorotoluene/acetone (3/1) as solvent, and purification was undertaken by flash chromatography on silica gel (99/1 to 4/1 light petroleum/ethyl acetate). 3,4-Dimethoxybenzaldehyde (**7**) was isolated as a colorless oil: yield 24 mg (15%, method A); 47 mg (28%, method B); ν_{max} ($CHCl_3$)/cm^{-1} 1684, 1516, 1271, 1136, 1024; δ_H (400 MHz; $CDCl_3$) 9.86 (1 H, s, CH), 7.47 (1 H, dd, *J* 8.2, 1.8, ArH), 7.42 (1 H, d, *J* 1.8, ArH), 6.99 (1 H, d, *J* 8.2, ArH), 3.97 (3 H, s, CH_3), 3.95 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 190.9 (CH), 154.5 (C), 149.6 (C), 130.1 (C), 126.9 (CH), 110.4 (CH), 108.9 (CH), 56.2 (CH_3), 56.0 (CH_3). Data are consistent with those previously reported.[73] 2-Hydroxy-1-(3,4-dimethoxyphenyl)ethan-1-one (**6b**) was isolated as a yellow solid: yield 31 mg (16%, method A); 19 mg (10%, method B); mp 82−86 °C; (lit.[74] mp 86−87 °C); ν_{max} ($CHCl_3$)/cm^{-1} 3478, 1676, 1518, 1339, 1095; δ_H (400 MHz; $CDCl_3$) 7.51−7.48 (2 H, m, ArH), 6.91 (1 H, d, *J* 8.0, ArH), 4.84 (2 H, d, *J* 4.5, CH_2), 3.96 (3 H, s, CH_3), 3.95 (3 H, s, CH_3), 3.55 (1 H, t, *J* 4.6, OH); δ_C (100 MHz; $CDCl_3$) 196.8 (C), 154.2 (C), 149.4 (C), 126.5 (C), 122.2 (CH), 110.3 (CH), 109.8 (CH), 64.9 (CH_2), 56.1 (CH_3), 56.0 (CH_3). Data are consistent with those previously reported.[10]

Photochemical Cleavage of 2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol (5c) (Table 5, Entry 3). 4-Methoxybenzaldehyde (**2b**) was isolated as a colorless oil: yield 28 mg (20%, method C); 30 mg (22%, method D). 2-Methoxyphenol (**8**) was isolated as a colorless oil: yield 20 mg (16%, method C), 15 mg (12%, method D); δ_H (400 MHz; $CDCl_3$) 6.97−6.88 (4 H, m, ArH), 5.69 (1 H, s, OH), 3.91 (3 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 146.6 (C), 145.7 (C), 121.5 (CH), 120.2 (CH), 114.6 (CH), 110.8 (CH), 55.9 (CH_3). Data are consistent with those previously reported.[75]

Photochemical Cleavage of *erythro*-Methyl 3-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate (5e) (Table 5, Entry 5). 3,4-Dimethoxybenzaldehyde (**7**) was isolated as a colorless oil: yield 39 mg (23%, method C); 11 mg (7%, method D). 2-Methoxyphenol (**8**) was isolated as a colorless oil: yield 13 mg (10%, method C); 9 mg (7%, method D).

Photochemical Cleavage of *erythro*-1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (5g) (Table 5, Entry 7). The reaction was carried out using trifluorotoluene/acetone (3/1) as solvent. 3,4-Dimethoxybenzaldehyde (**7**) was isolated as a colorless oil: yield 29 mg (17%, method C); 20 mg (18%, method D). 2-Methoxyphenol (**8**) was isolated as a colorless oil: yield 11 mg (8%, method C); 5 mg (4%, method D).

■ ASSOCIATED CONTENT

Supporting Information

Text and figures giving XPS characterization data for the Cu nanoparticle catalyst, details of competition experiments, and ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for C.J.M.: c.j.moody@nottingham.ac.uk.

Notes

The authors declare no competing financial interest.

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