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Photo-induced solvent-enabled catalyst-/additive-free selective C(α)–C(β) bond cleavage of β-O-4 ketone lignin model compounds at room temperature†

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In this work, an efficient catalyst-/additive-free selective C–C bond cleavage of β-O-4 ketone lignin model compounds was carried out to form the corresponding carboxylic acids and phenyl formates under the irradiation of light at room temperature in an air atmosphere, providing an efficient approach to the selective carbon–carbon bond cleavage reaction without using any photo catalysts. Results of mechanistic control experiments indicated that the *in situ* generation of radicals of dichloroethane (DCE) in the presence of visible light is essential to realize the selective C(α)–C(β) bond cleavage reaction.

Green foundation

1. We report an efficient catalyst-/additive-free selective C–C bond cleavage of β-O-4 ketone lignin model compounds to form the corresponding carboxylic acids and phenyl formates under the irradiation of light at room temperature in an air atmosphere. With this strategy, we were able to rapidly realize the efficient C–C bond cleavage of β-O-4 ketone lignin model compounds without using any transition-metal catalyst, photo-catalyst, external oxidant or chemical additive.

2. A variety of different substituted lignin model compounds underwent the current transformation to realize the challenging C–C bond cleavage at room temperature, indicating the feasibility of the strategy to be used in realistic lignin degradation and valorization.

3. In the future, efforts will be made to realize C–C bond cleavage in an aqueous system with a catalytic amount of DCE under sunlight irradiation, which would be a greener process.

Lignin has been regarded as a renewable resource for the production of value-added low-molecular-weight chemicals, as it is the most abundant natural polymer among the nonedible biomass.[1–10] In recent years, increasing attention has been paid to the development of a novel process for obtaining chemicals and fuels from the degradation of lignocellulosic biomass.[11–19] There are about 15–30 wt% of lignocellulose in lignin, comprising three different phenylpropanol subunits: sinapyl alcohol, ceniferyl alcohol and coumaryl alcohol.[2,20–23] Furthermore, the monomeric fragments are connected *via*

different linkages such as β-O-4, β-1, β-5, 4-O-5 and 5–5′. Among them, the most popular structure, ≈43%–65%, is the β-O-4 unit (Scheme 1A).[2] Realizing the selective cleavage of the β-O-4 unit with high yields under mild conditions is the major challenge for producing low-molecular-weight compounds from lignin.[24] Significant achievements have been made for the selective cleavage of C(β)–O bonds in lignin model compounds to form the corresponding phenols and ketones.[25–38]

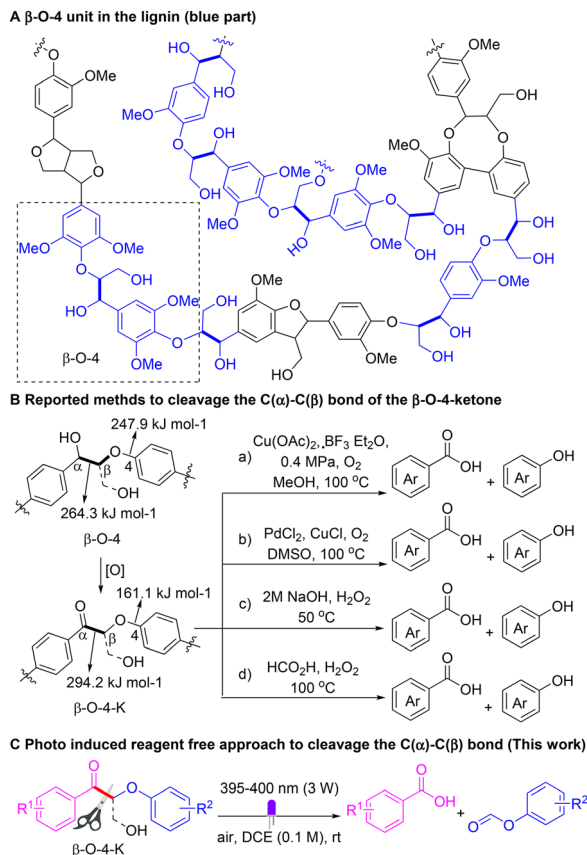Alternatively, the selective cleavage of the C(α)–C(β) bond of the β-O-4 linkage in lignin could also realize the production of the corresponding value-added chemicals from lignin in industries. However, owing to their stronger bond energies and non-polarity than those of the C–O bonds, the cleavage of C(α)–C(β) bonds in the lignin compounds is more difficult to be achieved.[39–43] Hanson, Baker and co-workers showed that the selective cleavage of C–O and C(α)–C(β) bonds in the β-O-4 linkage skeleton containing C(γ)–OH could be realized with vanadium catalysts, during which the β-O-4 ketone was the

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†Electronic supplementary information (ESI) available: Details of experimental procedures, conditional screening table, characterization and NMR spectra. See DOI: https://doi.org/10.1039/d4gc05578k

Scheme 1 Representative β-O-4 unit in the lignin skeleton and different approaches to the selective C(α)–C(β) bond cleavage of the β-O-4 model compound.

reaction intermediate or the final product.[44] After the oxidation of β-O-4 alcohol to the corresponding ketone, the C(β)–O bond energy decreased from 247.9 to 161.1 kJ mol^{-1}. However, the C(α)–C(β) bond energy increased from 264.3 to 294.2 kJ mol^{-1}, making the C(α)–C(β) bond even harder to be cleaved (Scheme 1B).[14] Hence, previous studies on the selective cleavage of the C(α)–C(β) bond in β-O-4 lignin have often reported poor selectivity of aromatic aldehyde- or aromatic acid-derivative chemicals in low yields under harsh reaction conditions such as high temperature and/or high pressure.[45,46] For instance, the C(α)–C(β) bond in the lignin model could be cleaved to form aromatic aldehydes as the major products by the stoichiometric use of CuCl and TEMPO in pyridine at 100 °C for 40 h,[47] by stoichiometric use of TEMPO/2,6-lutidine in the catalysis of Cu(OTf) at 100 °C (52% yield, 40 h),[48] or by a catalytic VOSO$_4$/TEMPO system.[47,49,50] The corresponding aromatic acids could be formed by the catalytic amount of Cu(OAc)$_2$ under 0.4 MPa O$_2$ at 80 °C or alternatively via the Baller-Villager oxidation with H$_2$O$_2$ as the sole oxidant at 100 °C (Scheme 1B).[43,51–53]

Due to the mentioned importance and difficulty in realizing the selective cleavage of such a C–C bond in the β-O-4 ketone lignin model, we herein report photo-induced solvent-enabled

catalyst- and reagent-free highly selective aerobic C(α)–C(β) bond cleavage of β-O-4 ketones to form the corresponding aromatic acids and phenyl formates at room temperature in the air atmosphere, highlighting the generality with a variety of β-O-4 ketone lignin model skeletons (Scheme 1C).[54] During the process, dichloroethane (DCE)[15] was used as both the solvent and the promoter to realize the cleavage of the C–C bond under mild and robust conditions without the use of transition-metals or toxic oxidants.[55] Furthermore, in this friendly transformation, the β-O-4 ketone lignin skeletons containing C(γ)–OH, another type of model compound close to realistic lignin, were also successfully cleaved to form the corresponding acids and phenyl formates.

We commenced our research with the optimization of the reaction conditions. During the study of the project, 2-phenoxyacetophenone (**1aa**), a readily available substrate, was prepared and used as the lignin model compound to explore the best reaction condition. As shown in Table 1, many different solvents were screened, and there was trace or even no desired C(α)–C(β) bond cleaved product when toluene, MeCN, PhCl or DME was used as the solvent, but no products were observed in other solvents such as toluene, MeCN, PhCl, and DMSO (Table 1, entries 1–9). Further evaluation of the solvents showed that the corresponding benzoic acid **2a** and phenol formate **3a** could be isolated in moderate yields when the reaction was performed in dichloroethane (DCE) under 400–410 nm irradiation for 36 h. We found that the irradiation of light played a significant role in this reaction as photons in the ultraviolet and near-visible regions have moderate energy

Table 1 Optimization of the reaction conditions^a

Entry	Light source	Solvent	Yield^b
1	400–410 nm	Toluene	Trace
2	400–410 nm	MeCN	Trace
3	400–410 nm	PhCl	Trace
4	400–410 nm	DMSO	ND
5	400–410 nm	DMA	ND
6	400–410 nm	DME	Trace
7	400–410 nm	NMP	ND
8	400–410 nm	EtOAc	ND
9	400–410 nm	Dioxane	ND
10	400–410 nm	DCE	2a: 70%; 3a: 59%
11	Blue LED	DCE	2a: 25%; 3a: 15%
12	**395–400 nm**	**DCE**	**2a: 72%; 3a: 61%**
13	390–395 nm	DCE	2a: 71%; 3a: 60%
14	380–385 nm	DCE	2a: 65%; 3a: 51%
15	365 nm	DCE	Trace
16	Yellow LED	DCE	ND
17	Green LED	DCE	ND
18	White LED	DCE	ND
19	—	DCE	ND

^{a} Unless otherwise noted, the reaction was performed with **1aa** (0.05 mmol) in a solvent (0.5 mL, 0.1 M) under the irradiation of indicated light. ^{b} Yields refer to the isolated products.

and can trigger specific electronic transitions in organic molecules; in particular, for the n → π transition, the corresponding wavelengths appear in the near-ultraviolet region or even the visible region. Indeed, further screening of different light sources showed that the C(α)–C(β) bond cleavage has been achieved with full conversion with near-visible light under the irradiation of 395–400 nm light for 36 h. In contrast, there was almost no desired C(α)–C(β) cleaved products when irradiated under other ultraviolet light (365 nm, 380–385 nm) or yellow, green, white LED light, indicating the specificity of the current transformation (Table 1, entries 10–18). Control experiment results indicated that there was not any product detected when the reaction was performed under darkness. Therefore, the irradiation of substrate **1aa** in DCE at 395–400 nm light was identified as the optimized condition, and 72% yield of the benzoic acid **2a** and 61% yield of phenyl formate **3a** were obtained individually with full conversion of **1aa**.

Our further study indicated that this established reaction condition could be applied to a variety of substituted lignin model compounds, as shown in Scheme 2. Many different substituted 2-phenoxyacetophenones bearing a variety of functional groups on the phenol rings were well tolerated, and delivered the corresponding C(α)–C(β) bond-cleaved products in moderate to good yields. For instance, the substrates containing a methoxy group on different positions of the phenoxy part could be well tolerated and afford the desired benzoic acid in good yields and substituted phenyl formates in relative low yields. When the MeO-substitution was switched to other electron-donating groups like methyl or *tert*-butyl, it could deliver the corresponding C(α)–C(β) bond-cleaved products in higher yields. To our delight, when the substitutions were changed to a bromo- or chloro-group on the different positions of the phenoxy part, the corresponding aromatic formates could be afforded in moderate yields (Scheme 2, entries 6–8). Encouraged by these results, more lignin model compounds were synthesized and subjected to the established mild photo-induced aerobic C(α)–C(β) bond cleavage reactions. When the substitution was methoxy group at different positions on the acetophenone part, the desired substituted aromatic acids were isolated in good yields together with the corresponding phenyl formates in moderate yields. Similar results could be obtained when a chloro-substituted β-O-4 ketone model was applied under the standard reaction condition. Furthermore, the substrate **1fa**, containing two methoxy groups on the acetophenone part, could also produce the corresponding veratric acid (**2f**) in 45% yield together with the phenyl formate **3a** in 30% yield.
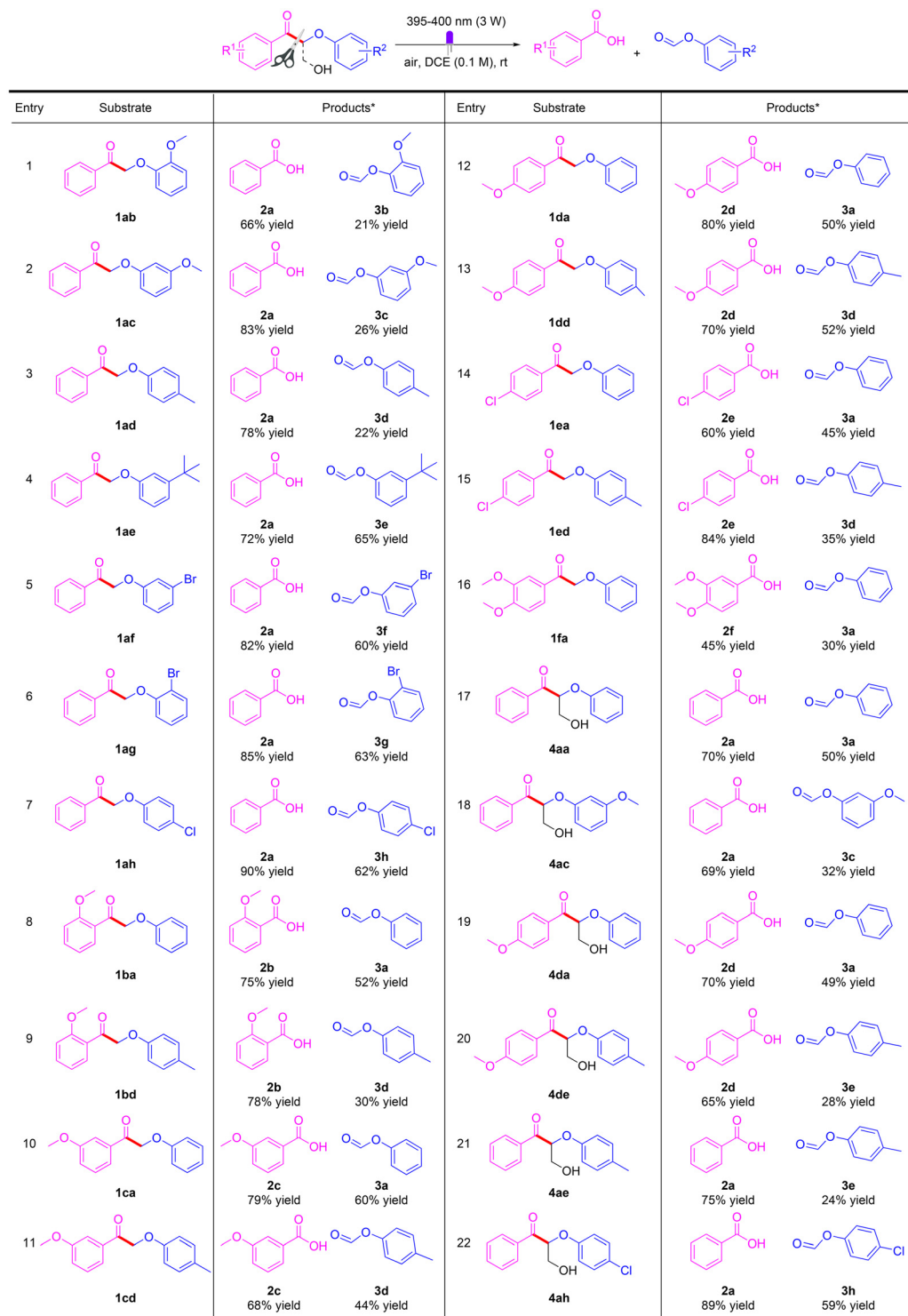
Compared to the 2-phenoxyacetophenone skeleton, the lignin model compounds containing a C(γ)–OH moiety usually need harsher conditions such as higher temperatures and stronger oxidative systems to realize the selective C(α)–C(β) bond cleavage as the C(γ)–OH side chain made this chemical bond more resistant to the oxidative conditions. Inspired by these promising results, the β-O-4 ketones with C(γ)–OH were prepared and applied to the DCE-enabled photo-induced selective C(α)–C(β) bond cleavage process. To our delight, the C(α)–

C(β) bond in such skeleton (**4aa**) could be efficiently cleaved to form the corresponding benzoic acid **2a** and the phenyl formate **3a**. Therefore, more substituted β-O-4 ketones with C(γ)–OH were prepared and investigated under the standard condition. With methoxy substitutions either on the phenoxy part or on the acetophenone part, the corresponding β-O-4 ketones were converted to the desired aromatic acids and phenyl formates in moderate to good yields. Further scope showed that *para*-methyl or chloro group on the phenoxy part could also be well tolerated and undergo the photo-induced aerobic oxidative C(α)–C(β) bond cleavage to produce the corresponding benzoic acids and substituted phenyl formates in moderate to good yields, indicating the broad scope of the current methodology (Scheme 2, entries 17–22).

Moreover, to explore the possible reaction mechanism, a series of control experiments were conducted, as shown in Scheme 3. First of all, when a radical scavenger, 2,6-di-*tert*-butylhydroxytoluene (BHT) or 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), was added to the aerobic oxidation reaction, the transformation was greatly inhibited and trace amounts of the C(α)–C(β) bond cleavage products were detected, indicating that the radical species might be generated in the aerobic process (Scheme 3a). Second, the reaction did not occur when performed in a N_2 atmosphere, showing that the air is the sole oxidant in the transformation (Scheme 3b). Third, when the reaction was carried out either in the presence of extra chloro sources such as TBACl in MeCN (Scheme 3c) or in other chloro-containing solvents such as chloroform or chlorobenzene, the reaction could work but resulted in relatively low yields, indicating the essential role of the chloro radical in the reaction. It is worth mentioning that the reaction does not work in the absence of light at room temperature or even under heating at 100 °C, showing that the light irradiation is essential for the reaction (Scheme 3d). In order to confirm that oxygen in the air acts as the sole oxidant, $^{18}O_2$ was used instead of air, and the corresponding ^{18}O-labeled benzoic acid and phenyl formate were detected by HRMS, which clearly indicated that O_2 in the air participated in the transformation (Scheme 3e). Both chloroacetic acid **6** and benzoyl chloride were detected by GC-MS in the crude reaction mixture, further supporting the reaction mechanism (Scheme S1†).

Furthermore, a light on/off experiment was conducted, and in Fig. 1A, we can see that light plays an essential role in the photo-induced C(α)–C(β) bond cleavage reaction, as the reaction has been absolutely suppressed when the light is turned off. Furthermore, electron paramagnetic resonance (EPR) measurement was conducted as shown in Fig. 1B. The strong signal indicates that $^1O_2$ was generated during the irradiation of light, which plays a significant role in the C(α)–C(β) bond cleavage process of the lignin model compound.

Based on the above-mentioned experimental results, a possible mechanism was proposed, as shown in Scheme 4. Under the light irradiation, the reactive oxygen species $^1O_2$ was generated and further a hydrogen radical from the DCE solvent was obtained to form radical species **H** and $HO_2^•$. The dichloroethane radical species **H** was further converted into chloroa-
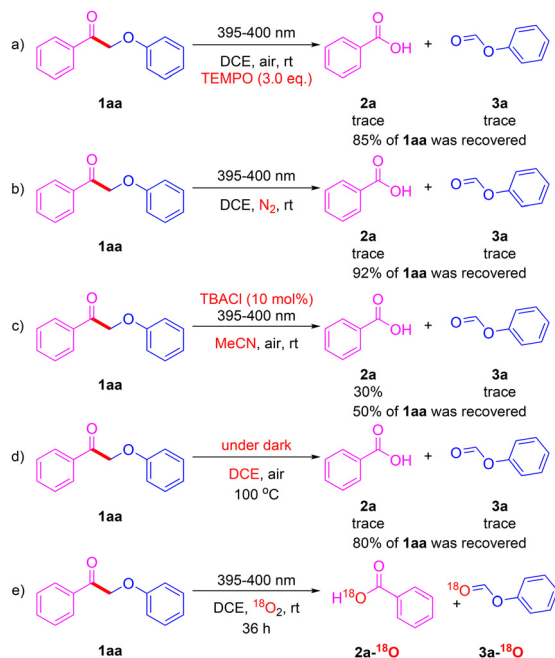
Scheme 2 Scope of β-O-4 ketone model compounds bearing different substitutions.

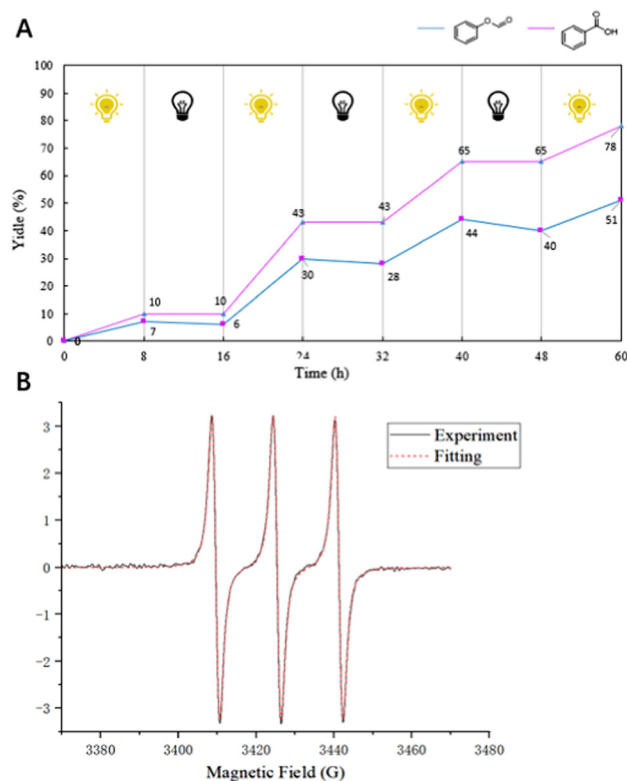cetic acid **6** and Cl⁻, which could form the Cl• radical under light irradiation. The hydrogen radical on the β-position of lignin model compound **1aa** was obtained to form the β-C radical species **A** by HO₂• generated under the light irradiation, which further reacted with oxygen (O₂) to produce alkdioxyl

radical species **B**. In the pathway I process, the alkdioxyl radical species **B** could possibly undergo intramolecular radical addition to the carbonyl group to form the dioxetane oxygen radical species **C**, which was further decomposed to form the phenyl formate **3a** and benzyl oxygen radical **D** via
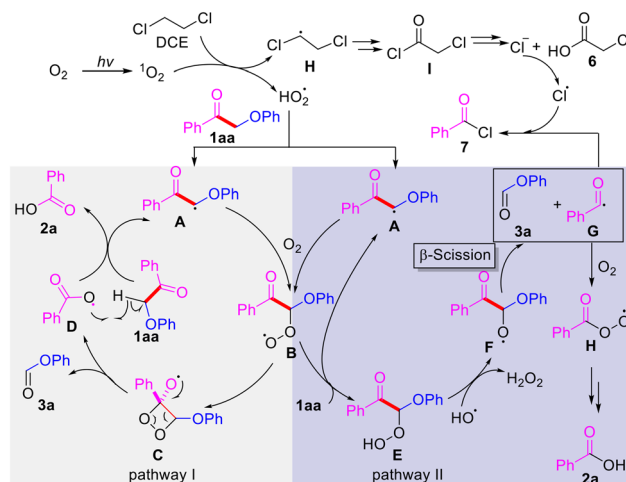
Scheme 3 Control experiments to study the possible mechanism.

Fig. 1 (A) Light on/off experiment. (B) Electron paramagnetic resonance (EPR) spectra. After irradiation at 395–400 nm for 12 h, TEMP was added, and the EPR reaction was conducted.

the strain release process. The resulting benzyl oxygen radical species **D** abstracts a H atom from another β-O-4 ketone substrate **1aa** to form the benzoic acid **2a** and the carbon radical

Scheme 4 Possible mechanism of the photo-induced reagent-free selective C(α)–C(β) bond cleavage reaction.

intermediate **A** that undergo the next catalytic cycle. In pathway II, the alkdioxyl radical species **B** could directly abstract a H radical from substrate **1aa** to form intermediate **E**, which is unstable and hence decomposed to form oxygen radical **F**, which further undergo the β-scission to form the phenyl formate **3a** and benzoyl radical **G**, which was further oxidized to form benzoic acid. Otherwise, it could also couple with a Cl radical to form benzoyl chloride **7**, a trace amount of which was detected and confirmed by GC-MS.

Conclusions

In summary, a photo-induced catalyst- and additive-free aerobic oxidative C(α)–C(β) bond cleavage reaction at room temperature has been developed. In this protocol, a wide range of β-O-4 ketone lignin model compounds with different substitutions including MeO-, Me-, *t*-Butyl-, Cl- and Br-groups either on phenoxyl part or benzoyl part could be well tolerated, and afford the corresponding benzoyl acids and phenyl formates in moderate to good yields under the irradiation of near-visible light (395–400 nm) without the participation of any transition-metal catalysts or toxic oxidants. Nevertheless, this reaction could also be applied to the β-O-4 ketone models with the C(γ)–OH group, providing guidance for the degradation of realistic lignin in nature. Further studies on the deep understanding of the reaction mechanism and the application to the natural lignin polymers are still ongoing and will be demonstrated in due course.

Data availability

This is to certify that the data supporting this article have been included as part of the ESI,† and all relevant data are within the manuscript and its additional file.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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