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Photo-on-Demand Synthesis of Vilsmeier Reagents with Chloroform and Their Applications to One-Pot Organic Syntheses

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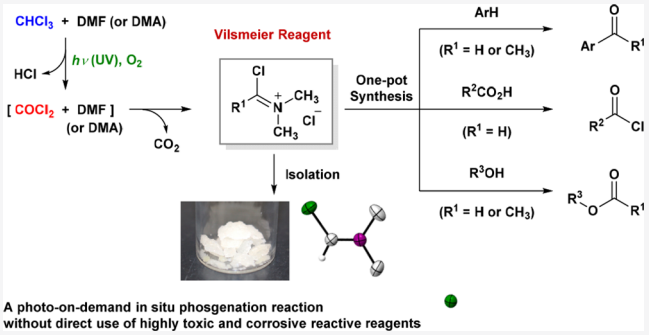
ABSTRACT: The Vilsmeier reagent (VR), first reported a century ago, is a versatile reagent in a variety of organic reactions. It is used extensively in formylation reactions. However, the synthesis of VR generally requires highly toxic and corrosive reagents such as $POCl_3$, $SOCl_2$, or $COCl_2$. In this study, we found that VR is readily obtained from a $CHCl_3$ solution containing *N*,*N*-dimethylformamide or *N*,*N*-dimethylacetamide upon photoirradiation under O_2 bubbling. The corresponding Vilsmeier reagents were obtained in high yields with the generation of gaseous HCl and CO_2 as byproducts to allow their isolations as crystalline solid products amenable to analysis by X-ray crystallography. With the advantage of using $CHCl_3$, which bifunctionally serves as a reactant and a solvent, this photo-on-demand VR synthesis is available for one-pot syntheses of aldehydes, acid chlorides, formates, ketones, esters, and amides.



A photo-on-demand in situ phosgenation reaction without direct use of highly toxic and corrosive reactive reagents

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INTRODUCTION

The Vilsmeier reagent (VR), an iminium salt, is used in a variety of organic syntheses, especially in formylation reactions.[1−3] The typical synthetic protocol for VR is the reaction of *N*,*N*-dimethylformamide (DMF) with phosphorus oxychloride ($POCl_3$) (Scheme 1, reaction **I**).[3,4] The produced VR is known to be in equilibrium between VR**1a** and VR**1b** due to intramolecular conversion of the anions. VR**1a** possess higher reactivity than most of the other Vilsmeier reagents (VRs) reported. However, $POCl_3$ has high toxicity and a corrosive nature. Furthermore, phosphorus-containing byproducts formed after the reaction contaminate the product and are known to be environmental pollutants.[3,5] Phosgene ($COCl_2$) is also available for synthesizing VR instead of $POCl_3$ (Scheme 1, reaction **II**). It reacts with DMF to give VR**2**·CO_2, which irreversibly decarbonates to form VR**2**.[3,6] In contrast to VR**1** prepared in reaction (**I**), there are fewer byproducts generated in its synthetic applications. However, since $COCl_2$ is a gas at room temperature and has high toxicity, organic synthesis with $COCl_2$ requires careful handling with special safety equipment.[7] For this reason, $COCl_2$ is produced through on-demand synthetic methods generally with CO and Cl_2 as raw materials.[8] In an alternative method to synthesize VR**2**, DMF is reacted with $SOCl_2$ to give VR**2**·SO_2, which is in equilibrium with VR**2** and SO_2 (Scheme 1, reaction **III**).[3,9] $SOCl_2$ also has high toxicity and corrosive properties, and SO_2 gas generated in the reaction is an environmental air pollutant.[10] These three synthetic methods have been used widely in both academic and industrial laboratories with few modifications. In addition to these reactions, as an innovative method without using hazardous reagents, Kimura and coworkers reported VR**2** synthesis with DMF and phthaloyl dichloride (OPC).[11] The reaction provides VR**2**, precipitated as a white solid in the sample solution, together with phthalic anhydride (PA) as a co-product. PA can be reconverted to OPC through reaction with 4-chlorobenzotrichloride in the presence of a $ZnCl_2$ catalyst. This method can produce VR**2** with higher quality compared with previous methods. However, VR**2**, which is very unstable in air, must be isolated from the sample solution when using it as a reagent for subsequent reactions. This background motivated us to develop a novel artificially controllable on-demand synthesis method for VR**2** and its derivatives with high quality and efficiency by simple procedures using as few chemicals as possible.

We previously reported a photo-on-demand synthesis of phosgene from chloroform and successfully applied the reaction to a variety of organic reactions.[12] We then developed in situ photo-on-demand synthesis of chloroformate with a

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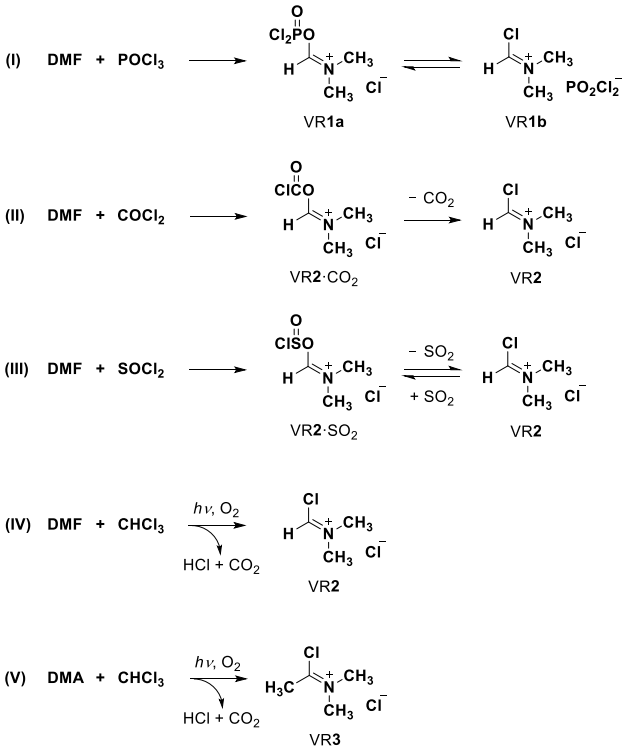
Scheme 1. Reactions of Synthesizing Vilsmeier Reagents



mixed solution of chloroform and an aliphatic alcohol without any other reagents. This allowed the one-pot chemical conversion of the resulting chloroformate to carbonates and carbamates.[13] In this system, chloroform served bifunctionally as both a solvent and a reactant. The reactions were conducted in solution with simple and easy procedures using only UV irradiation under O_2 bubbling. As a further extension of the reactions, we herein report a photo-on-demand in situ synthesis of Vilsmeier reagents (Scheme 1, reactions **IV** and **V**) with chloroform, and their applications to one-pot syntheses of a variety of organic compounds, such as aldehydes, acid chlorides, formates, ketones, esters, and amides.[14]

RESULTS AND DISCUSSION

A low-pressure mercury lamp, which generally has low electric power consumption, mainly generates UV light with wavelengths of 184.9 and 253.7 nm, which covers electronic absorption bands of $CHCl_3$ from $\sigma-\sigma^*$ and/or $n-\sigma^*$ transitions.[13,15] The lamp (20 W, ø24 mm × 120 mm), whose illuminances at 185 and 254 nm are 2.0−2.8 and 5.6−8.1 mW/cm^2, respectively, at a distance of 5 mm from the lamp, was inserted into the reaction solution via a quartz glass jacket (ø28 mm) fixed in the center of a cylindrical flask (ø42 mm).[12,13] Photochemical reactions were conducted with this reaction apparatus with vigorous stirring of the sample solution at 10−50 °C under a steady flow of O_2 (7−35 mL/min) bubbled through 20 mL (250 mmol) of $CHCl_3$ containing 5−50 mmol of DMF or DMA with or without a reaction substrate. The reactions were carried out in a closed system, but the unreacted photo-decomposed gas from the system was trapped outside with water containing a base such as $NaHCO_3$.

Initially, we demonstrated VR synthesis upon photo-irradiation of a $CHCl_3$ solution containing DMF at 30 °C. The reaction was monitored by ^{1}H NMR spectroscopy with $CDCl_3$ as the solvent. DMF peaks at δ = 2.97 and 2.88 ppm, and 8.02 ppm, corresponding to the *N*-methyl groups and the formyl group, respectively, decreased and new broad singlets at δ = 3.97 and 10.56 ppm increased (Figure 1). These two new

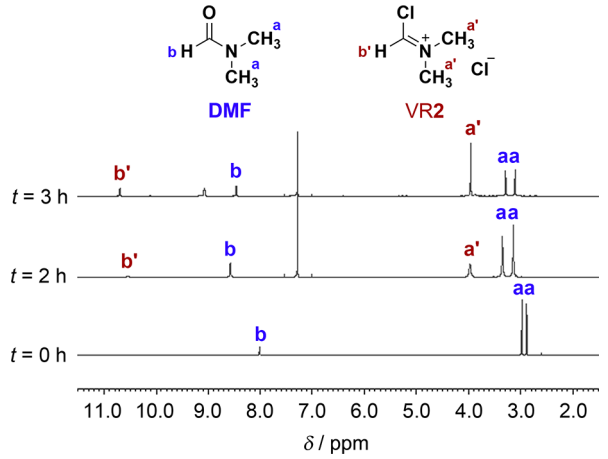


Figure 1. Time-course changes of DMF (20 mmol) in $CHCl_3$ (20 mL) upon photo-irradiation with a low-pressure mercury lamp under O_2 bubbling at 30 °C monitored by ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$). The $CDCl_3$ solutions for the measurement were prepared by collecting the sample solution at 0, 2, and 3 h.

peaks were consistent with those of VR**2** reported previously.[9a,11a,16] DMF may be converted to VR**2** by the following mechanism: $CHCl_3$ brings about C−Cl bond breaking under exposure to the UV light to generate $Cl^•$ and $^•CHCl_2$. They initiate radical chain reactions with other $CHCl_3$ molecules and O_2 to produce $COCl_2$ and HCl,[12] and then the generated $COCl_2$ immediately reacts in situ with DMF to give VR**2**·CO_2. The eliminated Cl^- then attacks the iminium cation to give VR**2** through elimination of CO_2.

In general, Vilsmeier reagents, especially VR**2**, are extremely moisture sensitive and readily react with water to regenerate DMF and HCl. Even after isolating VR**2** in the purification process, DMF is still detected when analyzing VR**2** spectroscopically such as by NMR spectroscopy (see the Supporting Information (SI)).[11a] For this reason, in order to estimate the true yield of VR**2** in the photoreaction, we demonstrated its one-pot conversion to an aldehyde through reaction with *N*-methylpyrrole, having high reactivity. The yield of VR**2** could then be estimated from the yield of the product by ^{1}H NMR spectroscopy. For example, a mixture of 2- and 3-formyl-1-methylpyrroles **1a** was quantitatively obtained with respect to the amount of DMF through the one-pot reaction with equivalent amounts (20 mmol) of DMF and *N*-methylpyrrole in $CHCl_3$ (20 mL, 250 mmol). On the other hand, the total consumption of $CHCl_3$, including its vaporization, was estimated to be 43% (107 mmol) by ^{1}H NMR analysis after the reaction for 3 h at 30 °C.

With this procedure, it was revealed that the yield of VR**2** was highly dependent on reaction conditions such as temperature, flow rate of oxygen gas, DMF concentration, and light intensity of the UV lamp. Figure 2a shows that the formation of VR**2** is accelerated upon elevating the temperature. However, the reaction profiles with respect to time are nonlinear, which may result from acceleration of the reaction upon decreasing the reactant DMF. It can be expected that DMF more efficiently hindered the oxidative photo-decom-

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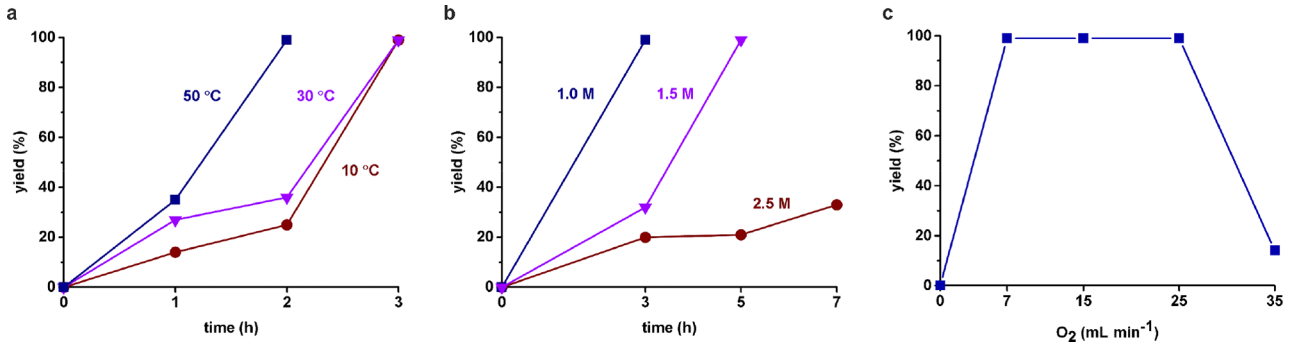

Figure 2. Plots of the yields of VR**2** formed upon photo-irradiation of $CHCl_3$ solutions containing DMF at variable (a) temperature ([DMF] = 1.0 M, O_2 flow: 25 mL·min^{-1}), (b) concentration of DMF (30 °C, O_2 flow: 25 mL·min^{-1}), and (c) flow rate of O_2 gas ([DMF] = 1.0 M, 3 h, 30 °C).

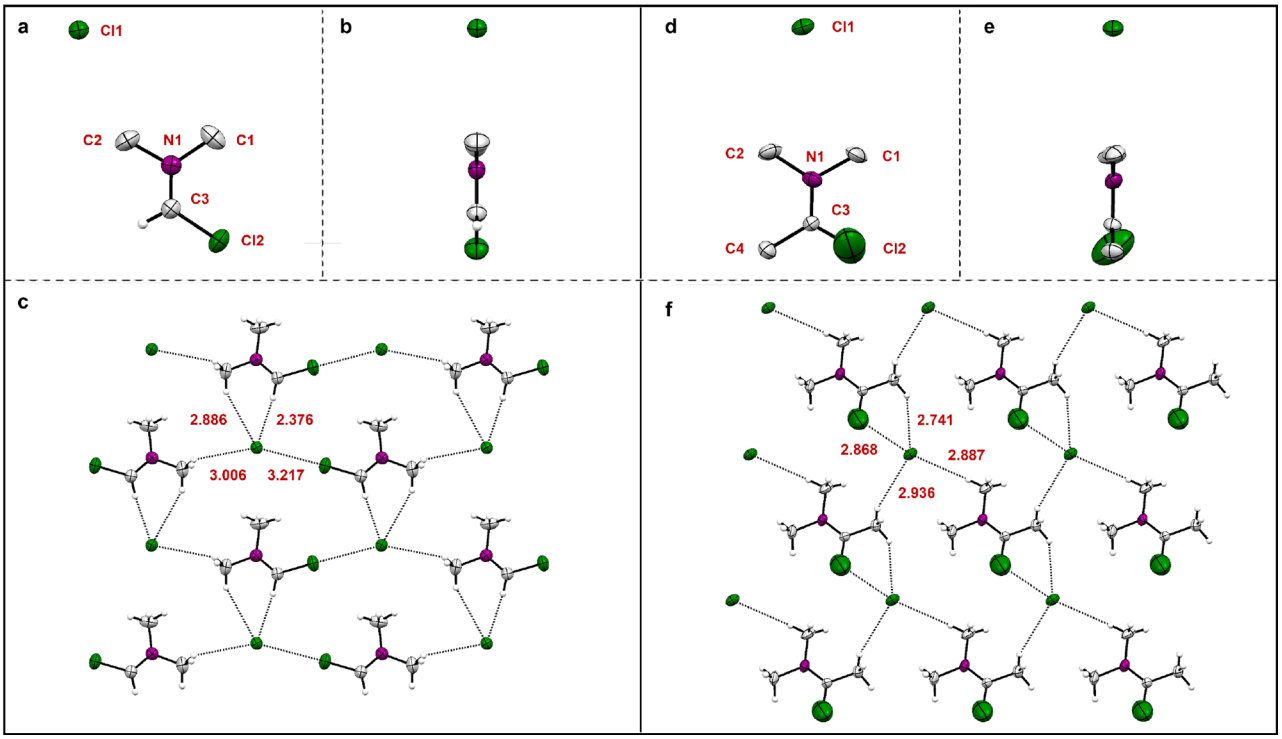

Figure 3. Single-crystal X-ray structures of VR**2** and VR**3**. (a, d) Top views, (b, e) side views, and (c, f) the crystal packing structures viewed from the crystallographic axis *b*. Color code: gray, C; purple, N; green, Cl; white, H.

position of $CHCl_3$ than the produced VR**2**. This is supported by the fact that the rate of the reaction is clearly faster with a lower concentration of DMF in the $CHCl_3$ solution (Figure 2b). As expected, the reaction could be accelerated by continuous injection of DMF with a syringe pump to keep the DMF concentration low, but it increased the vaporization of $COCl_2$ generated from $CHCl_3$. Although further investigation is necessary to elucidate the possible inhibition mechanism, it may result from the larger absorbance of 184.9 nm UV light by DMF than by VR**2**, and/or from DMF acting as a radical scavenger. Hence, the reaction is also dependent on the extent of oxidative photo-decomposition of $CHCl_3$, which can be controlled by the flow rate of oxygen. Although no reaction occurred without O_2, relatively high conversions of DMF to VR**2** were observed by slow bubbling (7−25 mL·min^{-1}) of O_2 gas to the sample solution. In contrast, the conversion was dramatically decreased by fast bubbling of O_2 gas (35 mL·min^{-1}), which may help to evaporate the generated $COCl_2$ from the system before its reaction with DMF (Figure 2c).

Photo-on-demand VR synthesis was also possible with *N*,*N*-dimethylacetamide (DMA) (Scheme 1, reaction **V**). Using similar conditions to those for the synthesis of VR**2**, VR**3**, which has a methyl group on the iminium carbon, was successfully obtained with quantitative conversion and isolated in 66% yield as a white crystalline solid. In contrast to the case of VR**2**, which could be stored for only a couple of days even in a closed bottle at low temperature, the obtained VR**3** was relatively stable under air and could be stored for several months under the same conditions as VR**2** in a closed bottle at low temperature. This stability most likely originated from the attached methyl group that may allow hyperconjugation with the C═N$^+$ group as well as steric protection of the iminium carbon.

Since the photochemical reactions of DMF and DMA with $CHCl_3$ allowed formation of VR**2** and VR**3**, respectively, without notable byproducts, we could successfully obtain

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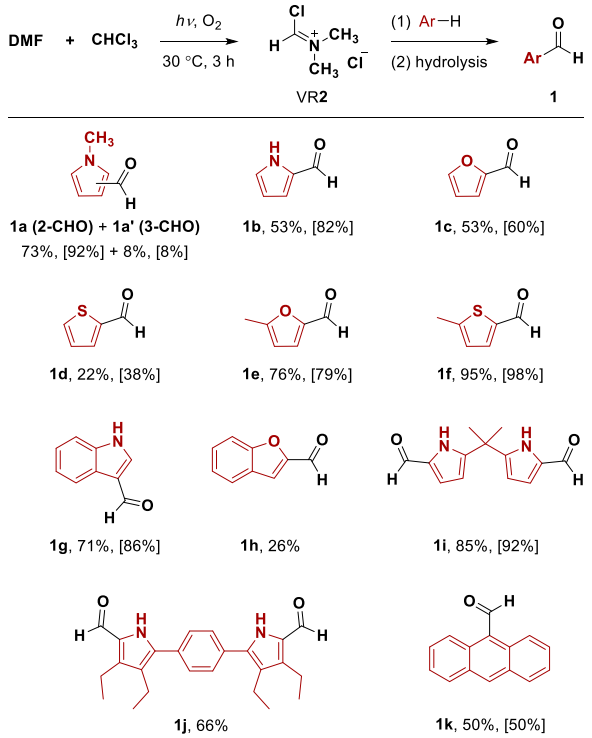
single crystals amenable to analysis by X-ray crystallography (Figure 3). To the best of our knowledge, this is the first example of the crystallographic analysis of VR. The X-ray crystallographic analysis showed that VR**2** adopts a planar conformation with a bond length of the iminium group (C3−N1) of 1.266 Å (Figure 3a,b). The length observed is almost the same as that (1.273 Å) for diethylmethyleneiminium chloride ($H_2C{=}NEt_2^+Cl^-$) reported previously.[17] The iminium cation is separated from the counter Cl^- ion by the *N*−methyl groups (C1−N1 and C2−N1 = 1.461 and 1.470 Å, respectively). In the crystal packing structure shown in Figure 3c, counter Cl^- ions are surrounded by multiple C−H groups (bond lengths = 2.376−3.006 Å), in which the observed CH−Cl^- interactions are stronger at the acidic hydrogen attached on the iminium-carbon bearing Cl group. Furthermore, Cl^- ions are situated in the 2D network structure of the iminium ions with Cl−Cl distances of 3.217 Å, indicating halogen bonding.[18] Similar structural features are observed in the crystal structure of VR**3**, having a methyl group on the iminium-carbon. It also has a planar structure with a $C{=}N^+$ distance of 1.286 Å (Figure 3d,e). The slightly longer bond length than that of VR**2** may be ascribed to the steric repulsion between the methyl groups (C2 and C4) and/or hyperconjugation between the methyl and iminium groups. In the crystal packing structure, counter Cl^- ions are also surrounded by multiple C−H groups with distances of 2.741−2.936 Å, which are shorter than those observed in VR**2** (Figure 3f). The halogen bonding between Cl^- and iminium-Cl with a distance of 2.868 Å also supports formation of a 2D-network structure.

The photo-on-demand in situ synthesis of VR with $CHCl_3$, which plays dual roles as reagent and solvent, has a strong advantage for utilization in one-pot organic syntheses. We initially attempted one-pot formylation reactions of aromatic compounds by extended applications of the reaction with *N*-methylpyrrole as described above (Scheme 2). In a plausible reaction mechanism, VR reacts with the aromatic compound to form an iminium salt that displaces the iminium-Cl group. Its subsequent hydrolysis provides the corresponding formyl-substituted compounds. As a general experimental procedure, VR**2** was prepared through the photo-on-demand phosgenation reaction of DMF (20 mmol) in $CHCl_3$ (250 mmol, 20 mL) at 30 °C. After elevating the temperature to remove possible remaining reactive species such as $COCl_2$ and HCl, the aromatic substrate (1.8−10.0 mmol) was added to the sample solution. After the reaction at 0−100 °C for 0.5−20.0 h, the product was hydrolyzed with base-containing water to give the formyl compound. For example, five-membered heterocyclic compounds, 1*H*-pyrrole, furan, and thiophene provided 2-formyl products in 82, 60, and 38% NMR yields, respectively (**1b**−**1d**). Substitution with an electron-donating CH_3 group on the heterocyclic compounds increased the product yields, likely due to the acceleration of the electrophilic substitution reaction with VR (cf. **1a** and **1b**, **1c** and **1e**, and **1d** and **1f**). Indole with its larger aromatic structure also allowed formylation at the 3-position in 86% yield, but benzofuran provided the 2-formyl product in relatively low yield (**1g** and **1h**, respectively). Since VR**2** efficiently reacted with 1*H*-pyrrole, we next carried out one-pot formylation reactions of bispyrroles, which are utilized for fabricating functional supramolecular architectures and macrocyclic rings.[19] Bispyrrole derivatives, including an aliphatic and an aromatic bridge, both provided the corresponding bisformyl products in high yields (**1i** and **1j**). Anthracene, having a larger

Scheme 2. One-Pot Synthesis of Aldehydes with VR2 Prepared upon Photo-irradiation of a $CHCl_3$ Solution Containing DMF[a,b]



[a]Reaction procedures and conditions: (i) A mixture solution of $CHCl_3$ (20 mL) and DMF (20 mmol) under bubbling with O_2 (25 $mL{\cdot}min^{-1}$) was exposed to UV light with a 20 W low-pressure mercury lamp. (ii) Ar−H (1.8−10.0 mmol) was added to the sample solution slowly at 0 °C and then stirred at 0−100 °C for 0.5−20.0 h. (iii) The sample was hydrolyzed slowly with saturated Na_2CO_3 aq. (30 mL) at 0 °C. [b]Yields in brackets were determined by ^1H NMR using 1,2-dichloroethane as an internal standard.

π-conjugation structure without a heteroatom, also reacted with VR**2** to give the 9-formylation product in 50% yield (**1k**).

Using a similar procedure to the above formylation reactions, VR**3** was prepared through the photo-on-demand phosgenation reaction of DMA (20 mmol) in $CHCl_3$ (250 mmol, 20 mL) at 30 °C. However, its reactivity was clearly lower than that of VR**2**, probably due to the effects of the methyl group substituted on the iminium-carbon as described above. After the workup process, an aromatic substrate (5−10 mmol) was added to the sample solution and stirred for a relatively long time. One-pot syntheses of ketones were achieved (Scheme 3), but the yields of the products were lower than in the formylation with VR**2**, likely due to the lower reactivity of VR**3**. For example, pyrrole provided the 2-acetyl product (**2a**) in 28% yield, but *N*-methylpyrrole improved the combined yield of the 2- and 3-acetyl products to >99% (**2b**). Although no reactions were observed with either furan or thiophene, 2-methylfuran reacted with VR**3** to give the corresponding ketone (**2c**) in 48% yield after reaction at room temperature for 144 h.

VR**2** and VR**3** were available for the one-pot syntheses of formates and esters, respectively (Scheme 4). It is known that VR reacts with an alcohol to form an iminium salt through substitution of the iminium-Cl group, and its subsequent hydrolysis allows formation of the corresponding formate and

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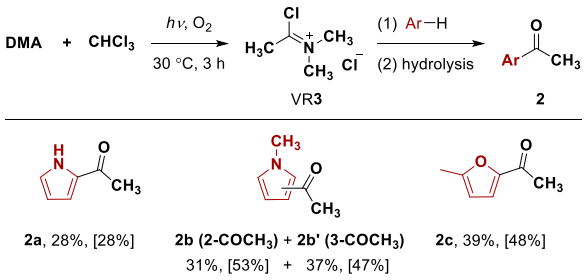
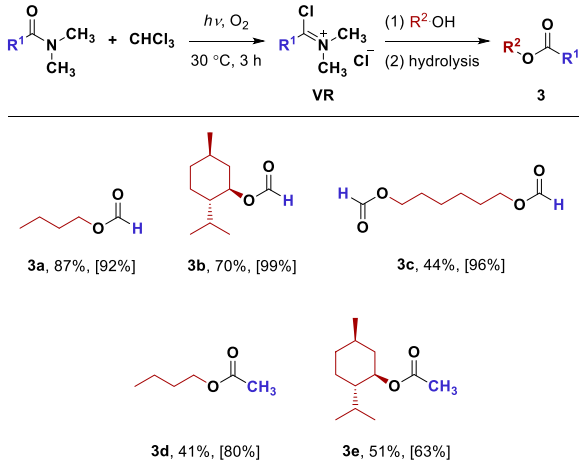
Scheme 3. One-Pot Synthesis of Ketones with VR3 Prepared upon Photo-irradiation of a $CHCl_3$ Solution Containing DMA[a,b]



[a]Reaction procedures and conditions: (i) A mixture solution of $CHCl_3$ (20 mL) and DMA (20 mmol) under bubbling with O_2 (25 mL·min^{-1}) was exposed to UV light with a 20 W low-pressure mercury lamp. (ii) Ar−H (10.0 mmol for **2a**, and 5.0 mmol for **2b** and **2c**) was added to the sample solution at 0 °C and stirred at r.t. for 21−156 h. (iii) The sample solution was hydrolyzed with saturated Na_2CO_3 aq. (30 mL for **2a**) or 3 M NaOH aq. (30 mL for **2b** and **2c**) at 0 °C. [b]Yields in brackets were determined by ^{1}H NMR using *n*-hexane or 1,2-dichloroethane as internal standards.

Scheme 4. One-Pot Synthesis of Formates and Esters with VR2 or VR3 Prepared upon Photo-irradiation of a $CHCl_3$ Solution Containing DMF or DMA, Respectively[a,b]

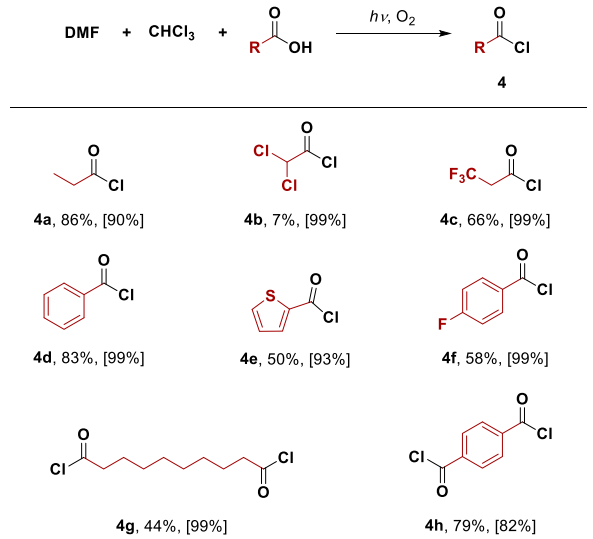


[a]Reaction procedures and conditions: (i) A mixture solution of $CHCl_3$ (20 mL) and DMF or DMA (20 mmol) under bubbling with O_2 (25 mL·min^{-1}) was exposed to UV light with a 20 W low-pressure mercury lamp. (ii) R^2OH (5.0−10.0 mmol) without pyridine for **3a**−**3c** or with pyridine (6 mmol for **3d**, and 20 mmol for **3e**) was added to the sample solution at 0 °C and stirred at 10−50 °C for 1.0 h. (iii) The sample solution was hydrolyzed with saturated Na_2CO_3 aq. (30 mL for **3a**−**3c**) or 3 M NaOH aq. (30 mL for **3d**−**3e**) at 0 °C. [b]Yields in brackets were determined by ^{1}H NMR using 1,2-dichloroethane as an internal standard.

ester. As a general procedure, these products were synthesized with one-pot addition of an alcohol (5−10 mmol) to the VR**2** or VR**3**, prepared through the photo-irradiation of a $CHCl_3$ (20 mL) solution containing DMF or DMA (20 mmol) under O_2 bubbling at 30 °C. In the reaction with VR**3**, whose reactivity is lower than that of VR**2**, 1.2−4.0 equiv amounts of organic base such as pyridine were also added to the sample solution as a catalyst. With a solution containing VR**2**, 1-BuOH was successfully converted to *n*-butyl formate in 92% yield (**3a**). A similar reaction proceeded with (−)-menthol, a secondary alcohol, to give (−)-menthyl formate quantitatively (**3b**). 1,6-Hexanediol provided the corresponding bisformate in 96% yield (**3c**). On the other hand, with a $CHCl_3$ solution containing VR**3**, 1-BuOH and (−)-menthol were converted to butyl acetate and (−)-menthyl acetate in 80% and 63% yields, respectively (**3d** and **3e**).

Next, we attempted a photo-on-demand catalytic synthesis of acyl chlorides, which are key building blocks to synthesize esters and amides (Scheme 5). It is known that carboxylic acids

Scheme 5. Photo-on-Demand in Situ Synthesis of Acyl Chlorides with $CHCl_3$ Solutions Containing Carboxylic Acids[a,b]



[a]Reaction procedures and conditions: A mixture solution of $CHCl_3$ (20 mL), DMF (5−20 mmol), and carboxylic acid (10 mmol) under bubbling with O_2 (25 mL·min^{-1}) was exposed to UV light with a 20 W low-pressure mercury lamp at 30 °C for 3.0−6.0 h. [b]Yields in brackets were determined by ^{1}H NMR using 1,2-dichloroethane as an internal standard.

convert to the corresponding acyl chlorides through reaction with phosgene in the presence of DMF. Here, we expected that the oxidative photochemical conversion of $CHCl_3$ to $COCl_2$ would allow an in situ photo-on-demand synthesis of the acyl chloride with a $CHCl_3$ solution containing a carboxylic acid and catalytic amounts of DMF. As a general procedure, the photo-on-demand synthesis was carried out through photo-irradiation of a $CHCl_3$ (250 mmol, 20 mL) solution containing a carboxylic acid and a 0.5 equiv amount of DMF at 30 °C under O_2 bubbling. Propanoic acid, an aliphatic carboxylic acid, provided propionyl chloride (**4a**) in 90% NMR yield (86% isolated yield). Dichloroacetic acid and 3,3,3-trifluoropropionic acid, having higher acidity (lower nucleophilicity), also resulted in formation of the corresponding acyl chlorides in quantitative yields (**4b** and **4c**). Efficient conversions were observed with aromatic carboxylic acids such as benzoic acid and 2-thiophenecarboxylic acid (**4d** and **4e**). 4-Fluorobenzoic acid, having an electron-withdrawing F group (**4f**), also provided the corresponding acid chloride in quantitative yield. This reaction was also available for substrates having multiple carboxyl groups such as sebacic acid and terephthalic acids, whose acyl chlorides are utilized for fabricating polyamides and polyesters. They provided the corresponding

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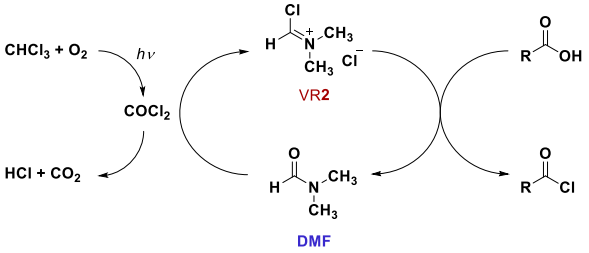
acyl chlorides in quantitative and 82% yields, respectively (**4g** and **4h**).

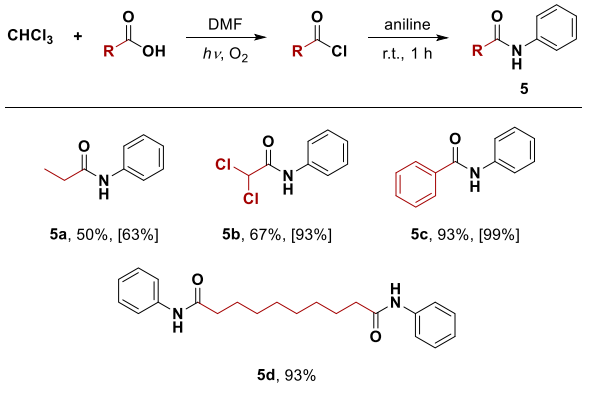
A possible reaction mechanism for the photo-on-demand synthesis of the acyl chlorides is shown in Scheme 6. $COCl_2$ generated through oxidative photo-decomposition of $CHCl_3$ reacts with DMF to give VR**2** with elimination of HCl and CO_2. The generated VR**2** then reacts with the carboxylic acid to form an iminium salt that substitutes the iminium-Cl group. Subsequent nucleophilic substitution of the eliminated Cl^- with the carbonyl group provides the corresponding acyl chloride with regeneration of DMF. In support of this proposed mechanism, we demonstrated the reaction of benzoic acid with a smaller amount of DMF (0.1 equiv). The reaction proceeded to give the acyl chloride quantitatively but was clearly decelerated compared to the case using 0.5 equiv of DMF, indicating that DMF acts as a catalyst in this reaction.

Scheme 6. Chemical Flow Scheme of the in Situ Conversion of a Carboxylic Acid to Acyl Chloride in $CHCl_3$ under Exposure to UV Light



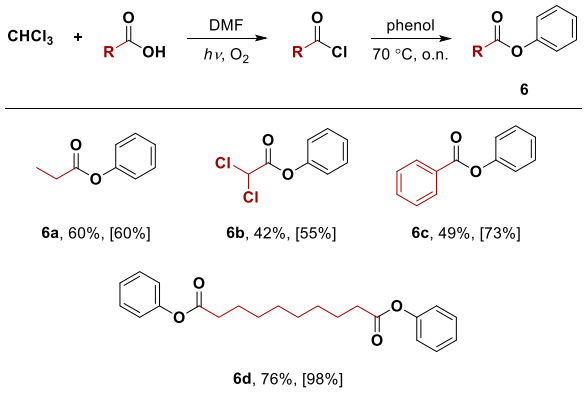
With the advantage of the photo-on-demand synthesis of acyl chlorides with a $CHCl_3$ solution containing a catalytic amount of DMF, the sample solution was further applied to the one-pot synthesis of amides and esters (Schemes 7 and 8, respectively). When 2.0−5.0 equiv amounts of aniline or phenol were added directly to the as-prepared sample solution containing the acyl chloride, the corresponding amides and esters were obtained in high yields. However, the yields of most of the esters were lower than those of the corresponding amides. This may be due to the different reactivities of aniline and phenol. Thermal decomposition and/or vaporization of the acyl chlorides may occur under reflux conditions for the longer reaction times required for synthesizing esters. Benzoic acid and sebacic acid having relatively high boiling points provided the corresponding esters in 73% and 98% yields, respectively.

Scheme 7. One-Pot Synthesis of Amides with Acyl Chlorides Prepared upon Photo-irradiation of $CHCl_3$ Solutions Containing Carboxylic Acids[a,b]



[a]Reaction procedures and conditions: (i) A mixture solution of $CHCl_3$ (20 mL), DMF (5−10 mmol), and carboxylic acid (10 mmol) under bubbling with O_2 (25 mL·min^{-1}) was exposed to UV light with a 20 W low-pressure mercury lamp at 30 °C for 3.0−4.5 h. (ii) Aniline (50 mmol) was added to the sample solution at 0 °C and stirred at r.t. for 1 h. [b]Yields in brackets were determined by ^{1}H NMR using 1,2-dichloroethane as an internal standard.

Scheme 8. One-Pot Synthesis of Esters with Acyl Chlorides Prepared upon Photo-irradiation of $CHCl_3$ Solutions Containing Carboxylic Acids[a,b]



[a]Reaction procedures and conditions: (i) A mixture solution of $CHCl_3$ (20 mL), DMF (5−10 mmol), and carboxylic acid (10 mmol) under bubbling with O_2 (25 mL·min^{-1}) was exposed to UV light with a 20 W low-pressure mercury lamp at 30 °C for 3.0−4.5 h. (ii) Phenol (20 mmol) was added to the sample solution at 0 °C and stirred at 70 °C for overnight. [b]Yields in brackets were determined by ^{1}H NMR using 1,2-dichloroethane as an internal standard.

CONCLUSION

In this study, we have developed a novel in situ photo-on-demand synthesis of VRs with a $CHCl_3$ solution containing DMF or DMA. This procedure enables the synthesis of VRs easily as well as safely without highly toxic corrosive reagents such as $POCl_3$, $SOCl_2$, and $COCl_2$. The reaction generates a $CHCl_3$ solution containing VR without notable byproducts simply by photo-irradiation under O_2 bubbling. These solutions enabled the one-pot syntheses of aldehydes, acid chlorides, formates, ketones, esters, and amides. This photochemical reaction provides enormous advantages in terms of efficiency, safety, cost, and environmental impact and is expected to create much innovation in a variety of organic syntheses in both academia and industry.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. 5,5′-Dimethyldipyrromethane and 1,4-bis(3,4-diethyl-1*H*-pyrrol-2-yl)benzene were synthesized according to the literature methods.[19a,c,20,21] For column chromatography, Wakogel (60N, particle size 38−100 μm, silica gel, irregular) was used. Heating of the sample solutions, if necessary, were performed with a water bath (≲50 °C) or an aluminum block bath (>50 °C). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. Fourier transform infrared spectroscopy (FT-IR) was recorded on a JASCO FT/IR 4200. Fourier transform mass spectrometry (FT-MS) was performed on a Thermo Fisher Scientific LTQ Orbitrap. The single-crystal X-ray diffraction data of single crystals were collected on

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a Bruker APEX II Ultra CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The data were collected at 193 or 173 K, and the structures were resolved by direct methods and refined by full-matrix least-squares on F^2 (SHELXL97). Single crystals of VR**2** and VR**3** were prepared by sublimation crystallization with a glass tube oven (SIBATA SCIENTIFIC TECHNOLOGY, Model GTO-1000) at 80 and 50 °C, respectively, under full vacuum with an oil rotary vacuum pump.

General Procedure for the One-Pot Synthesis of Aldehydes. A cylindrical flask (ø42 mm × 120 mm) equipped with a low-pressure mercury lamp (SEN Light Co., UVL20PH-6, 20 W, ø24 × 120 mm) was charged with a 20 mL of $CHCl_3$ solution containing 20 mmol of *N*,*N*-dimethylformamide (DMF). The solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. An aromatic substrate was added to the sample solution, and the mixture was stirred for 0.5−20 h with or without heating of the sample solution. The resulting sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. The corresponding aldehyde was obtained through silica gel column chromatography or washing with an appropriate solvent.

General Procedure for the One-Pot Synthesis of Ketones. A cylindrical flask equipped with a low-pressure mercury lamp was charged with a 20 mL of $CHCl_3$ solution containing 20 mmol of *N*,*N*-dimethylacetamide (DMA). The solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h to generate a yellow solid. $CHCl_3$ (8 mL) was added to dissolve the precipitates. An aromatic substrate was then added to the sample solution, and the mixture was stirred for 21−156 h at room temperature. The resulting sample solution was neutralized with an alkaline aqueous solution and extracted with CH_2Cl_2 (20 mL × 3) or ethyl acetate (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. The corresponding ketone was obtained through silica gel column chromatography.

General Procedure for the One-Pot Synthesis of Formates. A cylindrical flask equipped with a low-pressure mercury lamp was charged with a 20 mL of $CHCl_3$ solution containing 20 mmol of DMF. The solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. An aliphatic alcohol was then added to the sample solution, and the mixture was stirred at room temperature for 1 h. The resulting sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. The corresponding formate was isolated through distillation.

General Procedure for the One-Pot Synthesis of Esters. A cylindrical flask equipped with a low-pressure mercury lamp was charged with a 20 mL of $CHCl_3$ solution containing 20 mmol of DMA. The solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h to generate a yellow solid. $CHCl_3$ (8 mL) was added to dissolve the precipitates. A mixture of alcohol and pyridine was then added to the sample solution and stirred at 10−50 °C for 1 h. The resulting sample solution was neutralized with a NaOH aqueous solution (3 M, 30 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. The corresponding ester was obtained through silica gel column chromatography.

General Procedure for the in Situ Synthesis of Acid Chlorides. A cylindrical flask equipped with a low-pressure mercury lamp was charged with a 20 mL of $CHCl_3$ solution containing 5−20 mmol of DMF and 10 mmol of carboxylic acid. The solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3−6 h. The lamp was turned off, and the sample solution was stirred at 30−50 °C for 2 h. The corresponding acid chloride was isolated through distillation.

General Procedure for the One-Pot Synthesis of *N*-Phenyl Amides. A cylindrical flask equipped with a low-pressure mercury lamp was charged with a 20 mL of $CHCl_3$ solution containing 5−10 mmol of DMF and 10 mmol of carboxylic acid. The solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3.0−4.5 h. The lamp was turned off, and the sample solution was stirred at 30−50 °C for 2 h. Aniline (50 mmol) was then added slowly, and the sample solution was stirred at room temperature for 1 h. The corresponding amide was obtained through silica gel column chromatography or washing with an appropriate solvent.

General Procedure for the One-Pot Synthesis of Phenyl Ester. A cylindrical flask equipped with a low-pressure mercury lamp was charged with a 20 mL of $CHCl_3$ solution containing 5−10 mmol of DMF and 10 mmol of carboxylic acid. The solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3.0−4.5 h. The lamp was turned off, and the sample solution was stirred at 30−50 °C for 2 h. Phenol (20 mmol) disssolved in 2 mL of $CHCl_3$ was then added slowly and refluxed for overnight. The sample solution was evaporated to dryness and washed with hot water (>65 °C, 30 mL × 7). The corresponding ester was obtained through silica gel column chromatography, recrystallization, or washing with an appropriate solvent.

*N,N-Dimethylchloroformiminium Chloride (VR**2**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. Vacuum distillation of the resulting sample with a glass tube oven provided VR**2** as a white crystalline solid in 69% yield (1.76 g, 13.9 mmol). ^{1}H NMR spectrum is in agreement with that reported in the literature.[9a,11a,16] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 3.96 (s, 6H), 10.95 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 166.1, 46.3.

*1-Chloro-N,N-dimethylethaniminium Chloride (VR**3**).* Chloroform (20 mL, 250 mmol) and DMA (1.85 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. Vacuum distillation of the resulting sample with a glass tube oven provided VR**3** as a white crystalline solid in 66% yield (1.86 g, 13.2 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 3.26 (s, 6H), 2.65 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 175.0, 38.7, 18.5.

*2-Formyl-1-methylpyrrole (**1a**) and 3-Formyl-1-methylpyrrole (**1a′**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. *N*-Methylpyrrole (0.89 mL, 10 mmol) was then added slowly at 0 °C. The sample solution was stirred while gradually elevating the temperature, and then, refluxed for 1 h. The sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^{1}H NMR spectroscopy revealed that the residue contains **1a** and **1a′** in 92% and 8% yields, respectively. It was then subjected to silica gel column chromatography (ethyl acetate/CH_2Cl_2, v/v = 1:10) to afford **1a** and **1a′** as yellow liquids in 73% yield (0.80 g, 7.3 mmol) and 8% yield (0.09 g, 0.8 mmol), respectively. Their ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[22] **1a**: ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.55 (s, 1H), 6.91 (dd, J = 4.0, 1.6 Hz, 1H), 6.88 (brs, 1H), 6.22 (dd, J = 4.0, 2.4 Hz, 1H), 3.96 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 179.6, 132.1, 132.0, 124.1, 109.5, 36.5. **1a′**: ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.73 (s, 1H), 7.24 (t, J = 1.6 Hz, 1H), 6.64−6.62 (m, 2H), 3.72 (s, 3H).

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$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 185.3, 129.8, 126.7, 124.4, 108.6, 36.7.

*1H-Pyrrole-2-carbaldehyde (**1b**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. 1*H*-Pyrrole (0.74 mL, 10 mmol) was added slowly at 0 °C. The sample solution was stirred while gradually elevating the temperature, and then, refluxed for 1 h. The sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains **1b** in 82% yield. It was then subjected to silica gel column chromatography (ethyl acetate/CH_2Cl_2, v/v = 1:10) to afford **1b** as a yellow liquid in 53% yield (0.51 g, 5.3 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[23] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.54 (s, 1H), 7.14−7.12 (m, 1H), 7.00−6.98 (m, 1H), 6.37−6.35 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 179.5, 132.8, 127.1, 122.0, 111.3.

*Furan-2-carbaldehyde (**1c**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. Furan (0.73 mL, 10 mmol) was then added slowly at 0 °C, and the sample solution was stirred at room temperature for 2.5 h. The sample solution was then neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains **1c** in 60% yield. It was then subjected to silica gel column chromatography (CH_2Cl_2) to afford **1c** as a light yellow liquid in 53% yield (0.51 g, 5.3 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[24] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.68 (s, 1H), 7.71−7.70 (m, 1H), 7.27 (dd, J = 3.2, 0.8 Hz, 1H), 6.62 (dd, J = 3.2, 1.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 177.9, 153.0, 148.1, 121.0, 112.6.

*Thiophene-2-carbaldehyde (**1d**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. Thiophene (0.79 mL, 10 mmol) was added slowly at 0 °C. The sample solution was stirred while gradually elevating the temperature, and then, refluxed for 6 h. The sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains **1d** in 38% yield. It was then subjected to silica gel column chromatography (CH_2Cl_2) to afford **1d** as a light yellow liquid in 22% yield (0.25 g, 2.2 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[25] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.95 (s, 1H), 7.80−7.77 (m, 2H), 7.24 (dd, J = 4.8, 3.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 183.1, 144.0, 136.4, 135.2, 128.3.

*5-Methyl-2-furaldehyde (**1e**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. 2-Methylfuran (0.90 mL, 10 mmol) was then added slowly and stirred for 1 h at 0 °C. The sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains **1e** in 79% yield. It was then subjected to silica gel column chromatography (CH_2Cl_2) to afford **1e** as a yellow liquid in 76% yield (0.84 g, 7.6 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[26] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.52 (s, 1H), 7.17 (d, J = 3.6 Hz, 1H), 6.24 (dd, J = 3.6, 0.8 Hz, 1H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 176.9, 159.8, 151.9, 123.9, 109.5, 14.1.

*5-Methylthiophene-2-carboxaldehyde (**1f**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. 2-Methylthiophene (0.97 mL, 10 mmol) was added slowly at 0 °C. The sample solution was stirred while gradually elevating the temperature, and then, refluxed for 0.5 h. The sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains **1f** in 98% yield. It was then subjected to silica gel column chromatography (*n*-hexane/CH_2Cl_2, v/v = 1:10) to afford **1f** as a light yellow liquid in 95% yield (1.2 g, 9.5 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[27] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.81 (s, 1H), 7.60 (d, J = 4.0 Hz, 1H), 6.90−6.88 (m, 1H), 2.58 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 182.7, 151.7, 142.0, 137.4, 127.1, 16.2.

*1H-Indole-3-carbaldehyde (**1g**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. 1*H*-Indole (1.17 g, 10 mmol) dissolved in 1 mL of DMF was added slowly at 0 °C and stirred at room temperature for 18 h. The sample solution was then neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4. ^1H NMR spectroscopy revealed that the resulting sample solution contains **1g** in 86% yield. It was then evaporated to leave a brown solid. The residue was washed with CH_2Cl_2 to give **1g** as a light pink solid in 71% yield (1.03 g, 7.1 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[28] ^1H NMR (400 MHz, DMSO-d_6, 293 K): δ 12.16 (brs, 1H), 9.96 (s, 1H), 8.30 (s, 1H), 8.13 (d, J = 6.8 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.30−7.21 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 293 K): δ 184.9, 138.4, 137.0, 124.0, 123.4, 122.0, 120.7, 118.1, 112.3.

*2-Benzofuran-carboxaldehyde (**1h**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. 2,3-Benzofuran (1.08 mL, 10 mmol) dissolved in 10 mL of DMF was added slowly at 0 °C, and then, the temperature was gradually elevated to 100 °C. The sample solution was stirred at 100 °C for 20 h. It was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was subjected to silica gel column chromatography (*n*-hexane/CH_2Cl_2, v/v = 1:2) to afford **1h** as a yellow liquid in 26% yield (0.39 g, 2.6 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[29] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.89 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 1.2 Hz, 1H), 7.56−7. 51 (m, 1H), 7.38−7.34 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 179.8, 156.3, 152.7, 129.2, 126.7, 124.2, 123.7, 117.8, 112.7.

*5,5′-(Propane-2,2-diyl)bis(1H-pyrrole-2-carbaldehyde) (**1i**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. 5,5′-Dimethyldipyrromethane (0.44 g, 2.5 mmol) dissolved in 5 mL of $CHCl_3$ was added slowly at 0 °C. The sample solution was stirred while gradually elevating the temperature, and then, refluxed for 1 h. The sample solution was

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neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains **1i** in 92% yield. It was then subjected to silica gel column chromatography (ethyl acetate/CH_2Cl_2, v/v = 1:5) to afford **1i** as a yellowish white solid in 85% yield (0.49 g, 2.1 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[30] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 10.25 (brs, 2H), 9.32 (s, 2H), 6.89 (dd, J = 3.6, 2.4 Hz, 2H), 6.24 (dd, J = 4.0, 2.8 Hz, 2H), 1.75 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 179.3, 147.9, 132.6, 122.6, 108.3, 36.3, 28.3.

*5,5′-(1,4-Phenylene)bis(3,4-diethyl-1H-pyrrole-2-carbaldehyde) (**1j**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. 1,4-Bis(3,4-diethyl-1*H*-pyrrol-2-yl)benzene (580 mg, 1.8 mmol) dissolved in 20 mL of $CHCl_3$ was added slowly at 0 °C. The sample solution was stirred while gradually elevating the temperature, and then, refluxed for 0.5 h. The sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was recrystallized by CH_2Cl_2/MeOH and dried under vacuum to give **1j** as a light yellow solid in 66% yield (450 mg, 1.2 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[31] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.66 (s, 2H), 9.18 (brs, 2H), 7.58 (s, 4H), 2.84 (q, J = 7.6 Hz, 4H), 2.68 (q, J = 7.6 Hz, 4H), 1.31 (t, J = 7.6 Hz, 6H), 1.21 (t, J = 7.6 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 177.2, 138.8, 135.7, 131.6, 128.7, 127.7, 125.0, 17.7, 17.3, 17.1, 15.9.

*Anthracene-9-carbaldehyde (**1k**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. Anthracene (0.98 g, 5 mmol) dissolved in 30 mL of $CHCl_3$ was added slowly at 0 °C. The sample solution was stirred while gradually elevating the temperature, and then, refluxed for 16 h. The sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains **1k** in 50% yield. It was then subjected to silica gel column chromatography (*n*-hexane/CH_2Cl_2, v/v = 1:1) to afford **1k** as a yellow solid in 50% yield (0.51 g, 2.5 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[32] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 11.55 (s, 1H), 9.02 (dd, J = 9.2, 0.8 Hz, 2H), 8.73 (s, 1H), 8.10 (d, J = 8.4 Hz, 2H), 7.70−7.68 (m, 2H), 7.59−7.55 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 193.0, 135.2, 132.1, 131.1, 129.3, 129.1, 125.7, 124.7, 123.5.

*2-Acetyl Pyrrole (**2a**).* Chloroform (20 mL, 250 mmol) and DMA (1.85 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h to generate a yellow solid. Then, $CHCl_3$ (8 mL) was added to dissolve the precipitates. 1*H*-Pyrrole (0.74 mL, 10 mmol) was added slowly at 0 °C, and then, stirred at room temperature for 21 h. The sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with ethyl acetate (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains **2a** in 28% yield. It was then subjected to silica gel column chromatography (ethyl acetate/CH_2Cl_2, v/v = 1:10) to afford **2a** as a colorless crystal in 28% yield (0.30 g, 2.8 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[33] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.26 (brs, 1H), 7.02 (td, J = 2.4, 1.2 Hz, 1H), 6.92−6.90 (m, 1H), 6.30−6.27 (m, 1H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 188.1, 132.2, 124.7, 116.8, 110.6, 25.4.

*2-Acetyl-1-methylpyrrole (**2b**) and 3-Acetyl-1-methylpyrrole (**2b′**).* Chloroform (20 mL, 250 mmol) and DMA (1.85 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h to generate a yellow solid. Then, $CHCl_3$ (8 mL) was added to dissolve the precipitates. *N*-Methylpyrrole (0.45 mL, 5 mmol) was added slowly at 0 °C, and then, stirred at room temperature for 156 h. The sample solution was then neutralized with a NaOH aqueous solution (3 M, 30 mL) at 0 °C and extracted with ethyl acetate (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains **2b** and **2b′** in 53% and 47% yields, respectively. It was then subjected to silica gel column chromatography (ethyl acetate/CH_2Cl_2, v/v = 15:100) to afford **2b** and **2b′** as yellow liquids in 31% yield (0.19 g, 1.5 mmol) and 37% yield (0.23 g, 1.9 mmol), respectively. Their ^1H and ^{13}C NMR spectra are in agreement with those recorded in the Sigma-Aldrich FT-NMR Library (ver. 4.0.10). **2b**: ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 6.95 (dd, J = 4.4, 2.0 Hz, 1H), 6.79 (t, J = 2.0 Hz, 1H), 6.13 (dd, J = 4.0, 2.4 Hz, 1H), 3.94 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ 188.6, 130.9, 119.7, 107.9, 37.6, 27.1. **2b′**: ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.23 (t, J = 1.6 Hz, 1H), 6.58 (d, J = 2.0 Hz, 2H), 3.69 (s, 3H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 193.5, 126.8, 126.1, 123.3, 109.5, 36.6, 27.0.

*2-Acetyl-5-methyl Furan (**2c**).* Chloroform (20 mL, 250 mmol) and DMA (1.85 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h to generate a yellow solid. Then, $CHCl_3$ (8 mL) was added to dissolve the precipitates. 2-Methylfuran (0.45 mL, 5 mmol) was added slowly at 0 °C, and then, stirred at room temperature for 144 h. The sample solution was neutralized with a NaOH aqueous solution (3 M, 30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains **2c** in 48% yield. It was then subjected to silica gel column chromatography (ethyl acetate/CH_2Cl_2, v/v = 1:20) to afford **2c** as a yellow oil in 39% yield (0.24 g, 3.9 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[34] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.10 (d, J = 3.6 Hz, 1H), 6.16 (dd, J = 3.6, 0.8 Hz, 1H), 2.43 (s, 3H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 186.1, 157.9, 151.5, 119.5, 109.0, 25.7, 14.1.

*Butyl Formate (**3a**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. 1-Butanol (0.93 mL, 10 mmol) was added slowly at 0 °C, and then, stirred at room temperature for 1 h. The sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^1H NMR spectroscopy revealed that the residue contains butyl formate (**3a**) in 92% yield. Atmospheric distillation of the residue afforded **3a** as a colorless liquid in 87% yield (0.89 g, 8.7 mmol). ^1H and ^{13}C NMR spectra are in agreement with those recorded in the Sigma-Aldrich FT-NMR Library (ver. 4.0.10). ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.06 (s, 1H), 4.17 (t, J = 7.6 Hz, 2H), 1.69−1.62 (m, 2H), 1.45−1.36 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 161.2, 63.8, 30.5, 19.0, 13.6.

*(−)-Menthyl Formate (**3b**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25

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mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. (−)-Menthol (1.56 g, 10 mmol) dissolved in 2 mL of $CHCl_3$ was added slowly at 0 °C, and then, stirred at room temperature for 1 h. The sample solution was neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^{1}H NMR spectroscopy revealed that the residue contains **3b** in 99% yield. Vacuum distillation of the residue afforded **3b** as a colorless liquid in 70% yield (1.28 g, 7.0 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[35] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.08 (s, 1H), 4.81 (td, J = 10.8, 4.0 Hz, 1H), 2.04−1.99 (m, 1H), 1.96−1.85 (m, 1H), 1.73−0.81 (m, 7H), 0.93 (d, J = 5.2 Hz, 3H), 0.91 (d, J = 6.0 Hz, 3H), 0.78 (d, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 160.9, 74.2, 46.8, 40.9, 34.1, 31.4, 26.0, 23.2, 22.0, 20.8, 16.1.

*Hexane-1,6-diyl Diformate (**3c**).* Chloroform (20 mL, 250 mmol) and DMF (1.56 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. 1,6-Hexanediol (0.59 g, 5 mmol) dissolved in 15 mL of $CHCl_3$ was added slowly at 0 °C, and then, stirred at room temperature for 1 h. The sample solution was then neutralized with a saturated Na_2CO_3 aqueous solution (30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^{1}H NMR spectroscopy revealed that the residue contains **3c** in 96% yield. Vacuum distillation of the residue afforded **3c** as a colorless liquid in 44% yield (0.38 g, 2.2 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.06 (s, 1H), 4.17 (t, J = 6.4 Hz, 4H), 1.73−1.64 (m, 4H), 1.45−1.38 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 161.1, 63.8, 28.4, 25.5. IR (ATR) ν (cm^{-1}): 2938, 2863, 1716, 1160. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{14}O_4Na$ 197.0784; Found: 197.0783.

*n-Butyl Acetate (**3d**).* Chloroform (20 mL, 250 mmol) and DMA (1.85 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h to generate a yellow solid. Then, $CHCl_3$ (8 mL) was added to dissolve the precipitates. A mixture of 1-butanol (0.46 mL, 5 mmol) and pyridine (0.48 mL, 6 mmol) was added slowly at 0 °C, and then, stirred at 10 °C for 1 h. The sample solution was neutralized with a NaOH aqueous solution (3 M, 30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^{1}H NMR spectroscopy revealed that the residue contains **3d** in 80% yield. It was then subjected to silica gel column chromatography (CH_2Cl_2) to afford **3d** as a colorless liquid in 41% yield (0.24 g, 2.0 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those recorded in the Sigma-Aldrich FT-NMR Library (ver. 4.0.10). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 4.07 (t, J = 6.8 Hz, 2H), 2.05 (s, 3H), 1.65−1.55 (m, 2H), 1.43−1.34 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 171.3, 64.4, 30.7, 21.0, 19.1, 13.7.

*(−)-Menthyl Acetate (**3e**).* Chloroform (20 mL, 250 mmol) and DMA (1.85 mL, 20 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h to generate a yellow solid. Then, $CHCl_3$ (8 mL) was added to dissolve the precipitates. A 2 mL of $CHCl_3$ solution containing (−)-menthol (0.78 g, 5 mmol) and pyridine (1.6 mL, 20 mmol) was added slowly at 0 °C, and then, stirred at 50 °C for 1 h. The sample solution was neutralized with a NaOH aqueous solution (3 M, 30 mL) at 0 °C and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^{1}H NMR spectroscopy revealed that the residue contains **3e** in 63% yield. It was then subjected to silica gel column chromatography (*n*-hexane/CH_2Cl_2, v/v = 5:1) to afford **3e** as a colorless liquid in 51% yield (0.58 g, 2.5 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[36] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 4.68 (td, J = 10.8, 4.4 Hz, 1H), 2.04 (s, 3H), 2.02−1.96 (m, 1H), 1.92−1.81 (m, 1H), 1.71−0.81 (m, 7H), 0.91 (d, J = 2.0 Hz, 3H), 0.89 (d, J = 2.8 Hz, 3H), 0.77 (d, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 170.7, 74.2, 47.0, 40.9, 34.3, 31.4, 26.3, 23.5, 22.0, 21.4, 20.7, 16.4.

*Propionyl Chloride (**4a**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and propionic acid (0.67 mL, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 30 °C for 2 h. ^{1}H NMR spectroscopy revealed that the resulting sample solution contains **4a** in 90% yield. Atmospheric distillation of the sample solution afforded **4a** as a colorless liquid in 86% yield (0.80 g, 8.6 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those recorded in the Sigma-Aldrich FT-NMR Library (ver. 4.0.10). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 2.96 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 174.7, 40.9, 9.5.

*2,2-Dichloroacetyl Chloride (**4b**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and 2,2-dichloroacetic acid (0.82 mL, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3.5 h. The lamp was turned off, and the sample solution was stirred at 30 °C for 2 h. ^{1}H NMR spectroscopy revealed that the resulting sample solution contains **4b** in 99% yield. Atmospheric distillation of the sample solution afforded **4b** as a colorless liquid in 7% yield (0.11 g, 0.7 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those recorded in the Spectral Database for Organic Compounds (SDBS).[37] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 6.12 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 165.5, 70.1.

*3,3,3-Trifluoropropanoyl Chloride (**4c**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and 3,3,3-trifluoropropanoic acid (0.88 mL, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 30 °C for 2 h. ^{1}H NMR spectroscopy revealed that the resulting sample solution contains **4c** in 99% yield. Atmospheric distillation of the sample solution afforded **4c** as a colorless liquid in 66% yield (0.96 g, 6.6 mmol). ^{1}H and ^{19}F NMR spectra are in agreement with those reported in the literature.[38] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 3.77 (q, J = 9.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 164.2, 123.0 (C−F, $^1J_{C-F}$ = 275.6 Hz), 120.2 (C−F, $^1J_{C-F}$ = 275.6 Hz), 50.3(C−F, $^2J_{C-F}$ = 31.3 Hz), 50.0 (C−F, $^2J_{C-F}$ = 31.3 Hz), 49.6 (C−F, $^2J_{C-F}$ = 31.3 Hz), 49.3 (C−F, $^2J_{C-F}$ = 31.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ −64.15, −64.12, −64.10.

*Benzyl Chloride (**4d**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and benzoic acid (1.28 g, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. ^{1}H NMR spectroscopy revealed that the resulting sample solution contains **4d** in 99% yield. Vacuum distillation of the sample solution afforded **4d** as a colorless liquid in 83% yield (1.17 g, 8.3 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[39] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.14 (dd, J = 8.4, 1.2 Hz, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 168.4, 135.3, 133.3, 131.4, 129.0.

*2-Thiophenecarbonyl Chloride (**4e**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and 2-thiophenecarboxylic acid (1.28 g, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. ^{1}H NMR spectroscopy revealed that the resulting sample solution contains **4e** in 93% yield. Vacuum distillation of the sample solution afforded **4e** as

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a colorless liquid in 50% yield (0.73 g, 5 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those recorded in the Spectral Database for Organic Compounds (SDBS).[40] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.99 (dd, J = 4.0, 1.2 Hz, 1H), 7.84 (dd, J = 5.2, 1.6 Hz, 1H), 7.21 (dd, J = 4.8, 4.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 159.7, 138.0, 137.7, 137.4, 128.7.

*4-Fluorobenzoyl Chloride (**4f**).* Chloroform (30 mL, 250 mmol), DMF (0.78 mL, 10 mmol), and 4-fluorobenzoic acid (1.4 g, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3.5 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. ^{1}H NMR spectroscopy revealed that the resulting sample solution contains **4f** in 99% yield. Vacuum distillation of the sample solution afforded **4f** as a colorless liquid in 58% yield (0.92 g, 5.8 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[39] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.19−8.14 (m, 2H), 7.22−7.17 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 168.4 (C−F, $^1J_{C-F}$ = 256.6 Hz), 167.0, 165.9 (C−F, $^1J_{C-F}$ = 256.6 Hz), 134.3 (C−F, $^3J_{C-F}$ = 10.2 Hz), 134.2 (C−F, $^3J_{C-F}$ = 10.2 Hz), 129.6 (C−F, $^4J_{C-F}$ = 2.9 Hz), 129.5 (C−F, $^4J_{C-F}$ = 2.9 Hz), 116.5 (C−F, $^2J_{C-F}$ = 21.9 Hz), 116.2 (C−F, $^2J_{C-F}$ = 21.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ −100.82, −100.80, −100.79, −100.78, −100.77, −100.76, −100.74.

*Sebacoyl Chloride (**4g**).* Chloroform (20 mL, 250 mmol), DMF (0.78 mL, 10 mmol), and sebacic acid (2.02 g, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 4.5 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. ^{1}H NMR spectroscopy revealed that the resulting sample solution contains **4g** in 99% yield. Vacuum distillation of the sample solution afforded **4g** as a colorless liquid in 44% yield (1.05 g, 4.4 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those recorded in the Spectral Database for Organic Compounds (SDBS).[41] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 2.89 (t, J = 7.6 Hz, 4H), 1.74−1.67 (m, 4H), 1.37−1.30 (m, 8H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 173.8, 47.0, 28.8, 28.3, 25.0.

*Terephthaloyl Dichloride (**4h**).* Chloroform (30 mL, 250 mmol), DMF (1.56 mL, 20 mmol), and terephthalic acid (1.66 g, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 6 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. ^{1}H NMR spectroscopy revealed that the resulting sample solution contains **4h** in 82% yield. Vacuum distillation of the sample solution afforded **4h** as a colorless liquid in 79% yield (1.60 g, 7.9 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[42] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.26 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 167.5, 138.3, 131.4.

*N-Phenylpropionamide (**5a**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and propionic acid (0.67 mL, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 30 °C for 2 h. Aniline (4.6 mL, 50 mmol) was added slowly at 0 °C, and then, stirred at room temperature for 1 h. The sample solution was washed with water (30 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^{1}H NMR spectroscopy revealed that the residue contains **5a** in 63% yield. It was then subjected to silica gel column chromatography (*n*-hexane/CH_2Cl_2, v/v = 1:2) to afford **5a** as a yellow solid in 50% yield (0.75 g, 5.0 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[43] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.52 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.10 (t, J = 7.2 Hz, 1H), 2.43 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 171.9, 137.9, 129.0, 124.2, 119.7, 30.8, 9.7.

*2,2-Dichloro-N-phenylacetamide (**5b**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and 2,2-dichloroacetic acid (0.82 mL, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3.5 h. The lamp was turned off, and the sample solution was stirred at 30 °C for 2 h. Aniline (4.6 mL, 50 mmol) was added slowly at 0 °C, and then, stirred at room temperature for 1 h. The sample solution was washed with water (30 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. ^{1}H NMR spectroscopy revealed that the residue contains **5b** in 93% yield. It was then subjected to silica gel column chromatography (CH_2Cl_2) to afford **5b** as a yellow solid in 67% yield (1.36 g, 6.7 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[44] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.09 (brs, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 6.04 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 161.7, 136.2, 129.2, 125.7, 120.2, 66.9.

*N-Phenylbenzamide (**5c**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and benzoic acid (1.28 g, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. Aniline (4.6 mL, 50 mmol) was added slowly at 0 °C, and then, stirred at room temperature for 1 h. The sample solution was washed with water (30 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4. ^{1}H NMR spectroscopy revealed that the sample solution contains **5c** in 99% yield. It was then evaporated to leave an orange solid. The residue was washed with a 20:1 mixture solution of *n*-hexane and CH_2Cl_2 to afford **5c** as a yellow solid in 93% yield (1.84 g, 9.3 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those recorded in the Sigma-Aldrich FT-NMR Library (ver. 4.0.10). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.89 (d, J = 7.2 Hz, 2H), 7.79 (brs, 1H), 7.66 (d, J = 7.6 Hz, 2H), 7.58−7.49 (m, 3H), 7.39 (t, J = 7.2 Hz, 2H), 7.16 (t, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K): δ 165.7, 137.9, 135.0, 131.9, 129.1, 128.8, 127.0, 124.6, 120.2.

*N^1,N^{10}-Diphenyldecanediamide (**5d**).* Chloroform (20 mL, 250 mmol), DMF (0.78 mL, 10 mmol), and sebacic acid (2.02 g, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 4.5 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. Aniline (4.6 mL, 50 mmol) was added slowly at 0 °C and stirred at room temperature for 1 h to give a precipitate. It was then collected through filtration and washed with methanol to give **5d** as a white solid in 93% yield (3.29 g, 9.3 mmol). mp 199−202 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 293 K): δ 9.83 (brs, 2H), 7.59 (d, J = 7.6 Hz, 4H), 7.27 (t, J = 7.2 Hz, 4H), 7.01 (t, J = 7.6 Hz, 2H), 2.86 (t, J = 7.2 Hz, 4H), 1.60−1.57 (m, 4H), 1.30 (m, 8H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 293 K): δ 171.1, 139.2, 128.5, 122.8, 118.9, 36.3, 28.6, 28.6, 25.0. IR (ATR) ν (cm^{-1}): 3310, 2928, 2851, 1655, 1597, 1534, 1442, 755, 712, 687. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{28}N_2O_2$ 353.2224; Found: 353.2216.

*Phenyl Propionate (**6a**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and propionic acid (0.67 mL, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 30 °C for 2 h. Phenol (1.88 g, 20 mmol) disssolved in 2 mL of $CHCl_3$ was added slowly at 0 °C, and then, refluxed for overnight. ^{1}H NMR spectroscopy revealed that the sample solution contains **6a** in 60% yield. It was then evaporated to dryness and washed with hot water (>65 °C, 30 mL × 7). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was subjected to silica gel column chromatography (CH_2Cl_2) to afford **6a** as a colorless liquid in 60% yield (0.91 g, 6.0 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those recorded in the Spectral Database for Organic Compounds (SDBS).[45] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.37 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.62 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.6 Hz,

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3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 172.9, 150.8, 129.4, 125.7, 121.5, 27.8, 9.1.

*Phenyl 2,2-Dichloroacetate (**6b**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and 2,2-dichloroacetic acid (0.82 mL, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3.5 h. The lamp was turned off, and the sample solution was stirred at 30 °C for 2 h. Phenol (1.88 g, 20 mmol) disssolved in 2 mL of $CHCl_3$ was added slowly at 0 °C, and then, refluxed for overnight. ^1H NMR spectroscopy revealed that the sample solution contains **6b** in 55% yield. It was then evaporated to dryness and washed with hot water (>65 °C, 30 mL × 7). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was subjected to silica gel column chromatography (*n*-hexane/CH_2Cl_2, v/v = 1:1) to afford **6b** as a crystalline white solid in 42% yield. ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[44] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.43 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.16 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 163.0, 150.1, 129.7, 126.8, 120.7, 64.2.

*Phenyl Benzoate (**6c**).* Chloroform (20 mL, 250 mmol), DMF (0.4 mL, 5 mmol), and benzoic acid (1.28 g, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 3 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. Phenol (1.88 g, 20 mmol) disssolved in 2 mL of $CHCl_3$ was added slowly at 0 °C, and then, refluxed for overnight. ^1H NMR spectroscopy revealed that the sample solution contains **6c** in 73% yield. It was then evaporated to dryness and washed with hot water (>65 °C, 30 mL × 7) to leave a yellow solid. It was further recrystallized with methanol/CH_2Cl_2 to afford **6c** as a colorless crystal in 49% yield (0.97 g, 4.9 mmol). ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[46] ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.22 (d, J = 8.4 Hz, 2H), 7.64 (tt, J = 7.2, 1.6 Hz, 1H), 7.52 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 165.2, 151.0, 133.6, 130.2, 129.6, 129.5, 128.6, 125.9, 121.7.

*Diphenyl Sebacate (**6d**).* Chloroform (20 mL, 250 mmol), DMF (0.78 mL, 10 mmol), and sebacic acid (2.02 g, 10 mmol) were mixed in a cylindrical flask. The sample solution was vigorously stirred upon bubbling with O_2 (25 mL/min) under exposure to the light at 30 °C for 4.5 h. The lamp was turned off, and the sample solution was stirred at 50 °C for 2 h. Phenol (1.88 g, 20 mmol) disssolved in 2 mL of $CHCl_3$ was added slowly at 0 °C, and then, refluxed for overnight. ^1H NMR spectroscopy revealed that the sample solution contains **6d** in 98% yield. It was then evaporated to dryness and washed with hot water (>65 °C, 30 mL × 7) to leave a yellow solid. It was further washed with methanol to afford **6d** as a white solid in 76% yield (2.68 g, 7.6 mmol). mp 63−66 °C. ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.37 (t, J = 8.0 Hz, 4H), 7.22 (t, J = 7.2 Hz, 2H), 7.08 (d, J = 8.0 Hz, 4H), 2.56 (t, J = 7.2 Hz, 4H), 1.80−1.72 (m, 4H), 1.45−1.40 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 172.3, 150.7, 129.4, 125.7, 121.6, 34.4, 29.1, 29.0, 24.9. IR (ATR) ν (cm^{-1}): 2930, 2852, 1743, 1590, 1483, 1360, 1288, 1194, 1130, 763, 711, 689. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{27}O_4$ 355.1904; Found: 355.1904.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00334.

Crystallographic data; ^1H, ^{13}C, and ^{19}F NMR spectra (PDF)

Accession Codes

CCDC 2054184 and 2054219 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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