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C_{70} Fullerene Catalyzed Photoinduced Aerobic Oxidation of Benzylamines to Imines and Aldehydes

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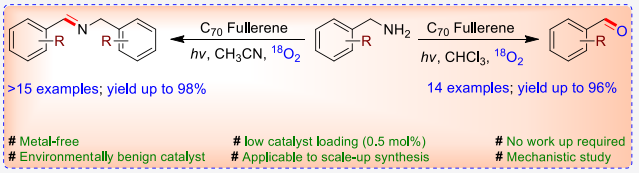
ABSTRACT: C_{70} fullerene catalyzed photoinduced oxidation of benzylic amines at ambient conditions has been explored here. The developed strategy's main feature includes the additive/oxidant-free conversion of benzylic amine to corresponding imine and aldehydes. The reaction manifests broad substrate scope with excellent function group leniency and is applicable up to the gram scale. Further, symmetrical secondary amines can also be synthesized from benzylic amine in a one-pot two-step process. Various experiments and density functional theory studies revealed that the current reaction involves the generation of reactive oxygen species, single electron transfer reaction, and benzyl radical formation as key steps under photocatalytic conditions.



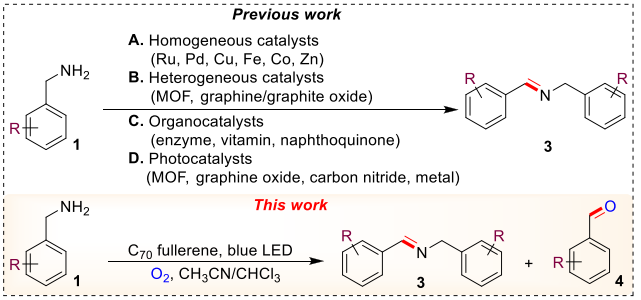
INTRODUCTION

Catalytic oxidation is always a fascinating and useful strategy in the field of organic synthesis.[1] Considering the increased environmental concern, researchers are continuously focusing on greener synthetic approaches. A wide variety of metal-based oxidants and organic oxidants such as H_2O_2, NaOCl, PhIO, and *t*-BuOOH have been used continuously;[2] however, most of these are associated with harsh reaction conditions, limited selectivity, and lower competence that bounded their practical applications. Consequently, in recent time, catalytic aerobic oxidations remain an eventual technique for producing valuable chemicals using O_2 as the solitary oxidant.[3] Recently, photocatalyzed emergence of reactive oxygen species (ROS) from O_2/air for chemical oxidation is being explored.[4]

Among the various chemical oxidations, the oxidative coupling of primary benzylic amines to imine derivatives received much consideration from chemists due to the prevalence of this building block in pharmaceuticals and fine chemicals.[5] Moreover, the conversion of benzylic amines to benzaldehydes via C−N bond cleavage also represents a paramount functional group transformation in organic synthesis.[6] Accordingly, researchers have developed different methods toward the oxidation of benzylamines to commensurate imines and benzaldehydes. Leading examples comprise metal/metal-free dehydrogenative coupling,[7] metal−organic framework (MOF) catalyzed oxidative coupling,[8] vitamin/enzymatic amine oxidation,[9] ionic liquid assisted oxidation,[10] naphthoquinone catalyzed aerobic dehydrogenation,[11] graphene oxide catalyzed coupling of amines to imines,[12] ball milling oxidation,[13] graphene/graphite oxide catalyzed oxidation,[12,14] and zinc dichromate catalyzed oxidative deamination (Scheme 1).[15]

Currently, photocatalysis is being explored as a greener approach in organic synthesis and is a handy tool for synthetic

Scheme 1. Oxidative Conversion of Primary Benzylic Amines to Imines



chemists. Hence, various research groups have developed photocatalytic methodologies to synthesize imines via oxidative coupling of primary benzylamines. Jiang and Lei's group independently reported MOF photocatalyzed oxidative coupling of benzylic amines,[8c,16] whereas similar transformation is reported by other groups using modified carbon-based photocatalytic systems such as silver-doped graphene oxide[17] and carbon nitride.[18] Metal-based photocatalytic oxidation of benzylic amines to imines or aldehydes is also disclosed.[19] However, these methods involve either a complex catalytic system or harsh reaction conditions, thus limiting their utility. Herein, we report pristine C_{70} fullerene

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catalyzed oxidation of primary benzylamines to corresponding imines and aldehydes in a state of metal/oxidant-free conditions. Fullerenes are known as exceptional photosensitizers for decades and exhibit prominent potential to produce ROS under aerobic conditions. Using this property, fullerenes were explored for secondary benzylamine oxidation to imines but only in an intramolecular fashion.[4b]

During our previous study on the photocatalytic conversion of phenyl boronic acid to corresponding phenols,[20] we perceived the hydrolysis of diisopropylethylamine to diisopropylamine (Figure 1). Building on this observation, we envisaged the benzylic C−N bond cleavage under photocatalytic conditions to form the analogous oxidized products.

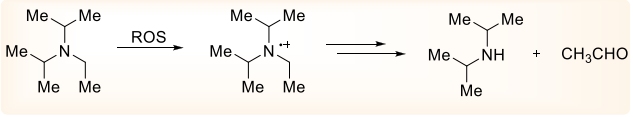
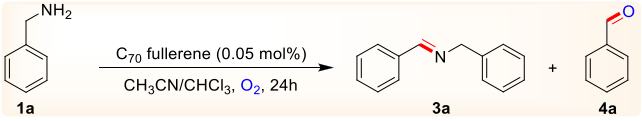


Figure 1. ROS-assisted photocatalytic cleavage of the C−N bond.

Initially, benzylamine, **1a** (0.1 mmol), was reacted with phenylboronic acid, **2a** (0.1 mmol), in the presence of C_{70} fullerene (0.05 mol %) in $CHCl_3$ (0.05 M) under blue light-emitting diode (LED) irradiation. Gas chromatography−mass spectrometry analysis of this reaction revealed the formation of benzaldehyde (**4a**) along with phenol. Formation of **4a** was observed even without **2a** (Table 1, entry 1), thus confirming

Table 1. Screening and Optimization of Conditions[a]



entry	variation from standard condition	3a yield (%)[b]	4a yield (%)[b]
1	none	**99 (98)**[c,d]	**60 (55)**[c,e]
2	C_{60} fullerene catalyst	24	22
3	white light instead of blue light	46	16
4	green light instead of blue light	traces	26
5	without catalyst	14	18
6	without light	traces	16
7	under Ar	12	traces
8	1,4-dioxane instead of CH_3CN	32	34
9	air instead of O_2	90	24
10	12 h instead of 24 h	64	
11	0.025 mol % of catalyst	84	
12	0.2 M CH_3CN	60	

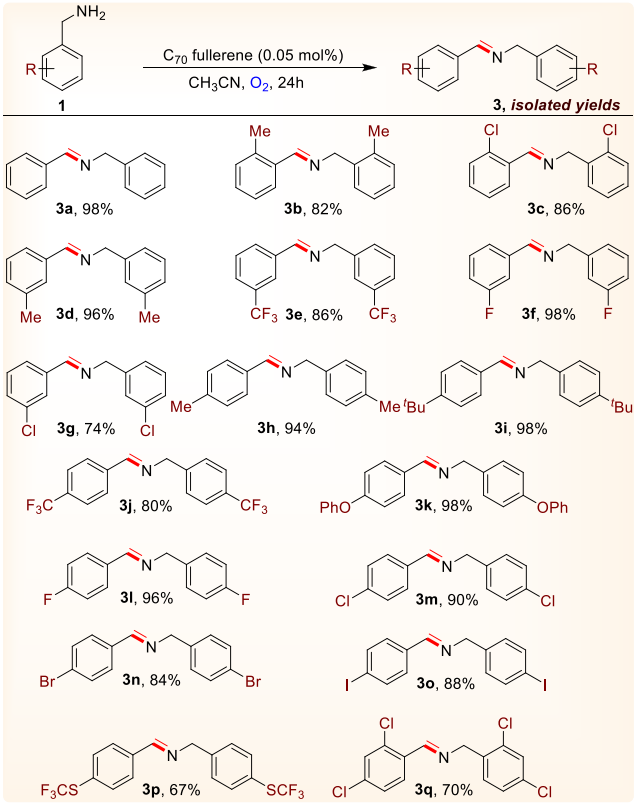
[a]Reagents and conditions: **1a** (0.2 mmol), C_{70} fullerene catalyst (0.05 mol %), CH_3CN (0.05 M), 34 W blue LED light, 24 h. [b]Yield determined by NMR analysis of crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard. [c]Isolated yield in parentheses. [d]Reaction solvent was CH_3CN. [e]Reaction solvent was $CHCl_3$.

the direct oxidation of benzylic amines to benzaldehyde. However, when the same reaction was carried out in MeCN as a solvent, we got (*E*)-*N*-benzylidene-1-phenylmethanamine **3a** as a major product in quantitative yield instead of **4a** (Table 1, entry 1). Further, any divergence from these reaction conditions has a detrimental effect on the yield of product **3a**. Changing the catalyst to C_{60} fullerene or changing the light source to white or green was inefficient for the current reaction (Table 1, entries 2−4). The reduction in the product yield with green or white light may be due to the absorption maxima of the C_{70} fullerene catalyst, which lies in the blue light region. Very low product emergence or no product was observed either in the absence of C_{70} catalyst or light irradiation, respectively, thus manifesting the developed strategy's photocatalytic disposition (Table 1, entries 5 and 6). Only 12% NMR yield of **3a** was observed, when the reaction was carried under argon atmosphere (Table 1, entry 7), thus indicating the crucial role of molecular oxygen in the course of the reaction.

Further, acetonitrile replacement with other solvents had a negative effect on product yield (Table 1, entry 8; see Supporting Information). The use of air instead of molecular oxygen was not adequate (Table 1, entry 9). Additionally, the reduction in reaction time, catalyst amount, and the amount of solvent was harmful to the reaction outcome (Table 1, entries 10−12).

Next, we explored the substrate scope by reacting various primary benzylic amines under the developed reaction condition (Table 2). Benzylamines with −Me and −Cl

Table 2. Substrate Scope of Benzylic Amines for the Synthesis of Corresponding Imines[a]



[a]Reagents and conditions: **1a** (0.2 mmol), C_{70} fullerene catalyst (0.05 mol %), CH_3CN (0.05 M), 34 W blue LED, 24 h.

substituent at the C-2 position resulted in oxidative imine products **3b** and **3c** in 82 and 86% yield, respectively. Benzylic amines with various functional groups at the C-3 position were successfully converted to corresponding imine product with good to plenteous yields (**3d−g**). Imines with methyl (**3d**) and trifluoromethyl (**3e**) substituents were obtained in 96 and 86% isolated yields, respectively. Similarly, −F- and −Cl-substituted benzylic amines resulted in 98 and 74% isolated yields of

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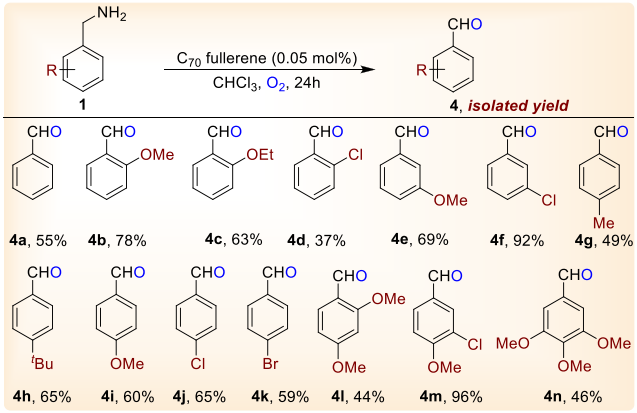
requisite products **3f** and **3g**, respectively. A variety of substituents were well-tolerated at the C-4 position of benzylic amines. Amines with alkyl substituents such as methyl and tertiary butyl led to the formation of imine products (**3h−i**) in 94−98% yield. 4-Trifluoromethyl benzylamine provided the corresponding imine **3j** in 80% isolated yield. We obtained a 98% isolated yield of 4-phenoxy-substituted imine **3k**. The halogen substituents at C-4 positions of primary benzylic amine were well-tolerated (**3l−o**). 4-Fluoro-, 4-chloro-, 4-bromo-, and 4-iodo-substituted amine generated products **3l−o** in 84−96% isolated yields.

A trifluoromethylthio substituent at the C-4 position was also well-tolerated under the current reaction condition, and as expected, product **3p** was obtained in 67% yield. 2,4-Dichlorobenzylamine also reacted successfully under the developed reaction condition (**3q**).

Further, photocatalytic oxidation of various benzylic amines to corresponding benzaldehyde was explored (Table 3).

Table 3. Substrate Scope of Benzylic Amines for the Synthesis of Corresponding Benzaldehydes[a]

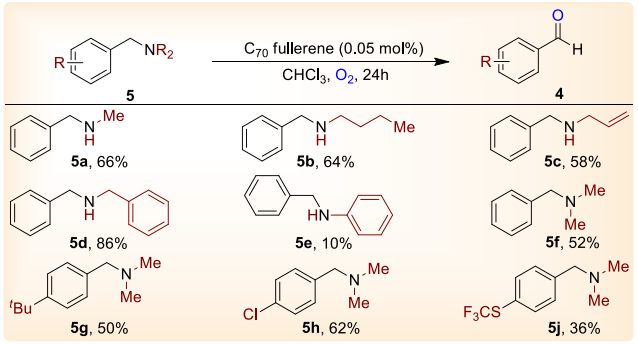


[a]Reagents and conditions: **1a** (0.2 mmol), C_{70} fullerene catalyst (0.05 mol %), $CHCl_3$ (0.05 M), 34 W blue LED, 24 h.

Benzylic amine with a methoxy and ethoxy substituent at the C-2 position converted to corresponding carbonyl products (**4b,c**) in 63−78% yields. Chloro-substituted benzylamine at the C-2 position gave only 37% isolated yield of oxidized carbonyl product **4d**. Photocatalytic oxidation of primary benzylic amine having methoxy and chloro substituents at the C-3 position furnished the corresponding benzaldehydes (**4e,f**) in 69−92% yield. Benzylic amines comprising alkyl substituents such as methyl and tertiary butyl at the C-4 position were also well-tolerated under the developed conditions and provided the expected products **4g,h** in good yield. Similarly, we isolated 4-methoxybenzaldehyde (**4i**) in 60% yield. Halogen-substituted benzylic amines such as 4-chloro and 4-bromo afforded the desired products **4j** and **4k** in good yield. Di- and trisubstituted benzylic amines were also found to be compatible, and 2,4-dimethoxybenzaldehyde (**4l**) was isolated in 44% yield, whereas 3,4,5-trimethoxybenzaldehyde (**4n**) was obtained in 46% isolated yield. Furthermore, 3-chloro-4-methoxybenzylamine gave 96% isolated yield of expected product **4m**.

After the successful oxidation of primary benzylic amines to corresponding benzaldehydes, we explored the oxidation of a few secondary and tertiary benzylic amines to corresponding carbonyl products (Table 4). *N*-Methyl, *N*-butylbenzylamines, and *N*-allylbenzylamine (**5a−c**) brought forth the benzaldehyde formation in good yields. Dibenzylamine (**5d**) also displayed good reactivity under the devised conditions and rendered the carbonyl product in excellent yield. Conversely, *N*-phenylbenzylamine (**5e**) bestowed only 10% yield of oxidized product, which might be attributed to the involvement of the nitrogen lone pair in resonance with the benzene ring, making it less readily available for donation.

Table 4. Scope of Secondary and Tertiary Benzylic Amines[a,b]

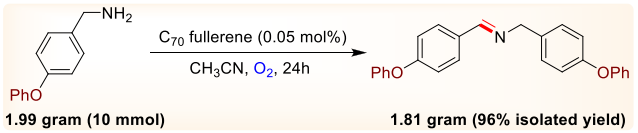


[a]Reagents and conditions: **1a** (0.2 mmol), C_{70} fullerene catalyst (0.05 mol %), $CHCl_3$ (0.05 M), 34 W blue LED, 24 h. [b]Percentage NMR yields only.

Alternatively, *N,N*-dimethylbenzylamine (**5f**) dispensed the anticipated benzaldehyde in good yield. Tertiary benzylic amines with substituents such as 4-*tert*-butyl (**5g**) and 4-chloro (**5h**) led to the formation of corresponding benzaldehydes in 50 and 62% NMR yield, respectively. Likewise *N,N*-dimethyl-1-(4-((trifluoromethyl)thio)phenyl)methanamine (**5j**) furnished the expected benzaldehyde in 36% NMR yield (Table 4).

Also, we endeavored the scale-up synthesis with 4-phenoxybenzylamine (Scheme 2) and successfully isolated 1.81 g of the imine product while attempting the reaction at 10 mmol scales.

Scheme 2. Gram-Scale Synthesis of Imine



Furthermore, we brought in a one-pot two-step conversion of benzylic primary amine to symmetrical secondary amine (Scheme 3). Here, we used a combination of polyethylene glycol and $NaBH_4$ for the reduction of oxidized dimer product.[21]

Quenching experiments with 1,4-diazabicyclo[2.2.2]octane (DABCO), benzoquinone and 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO) resulted in diminished or extremely low product yield, endorsing the ubiquity of radical species (ROS) in the course of the present reaction (Scheme 4).[22]

In addition, we performed the oxidation of benzylamine to analogous aldehyde in the presence of $^{18}O_2$ (Scheme 5). Liquid chromatograph−mass spectrometry (LC-MS) analysis

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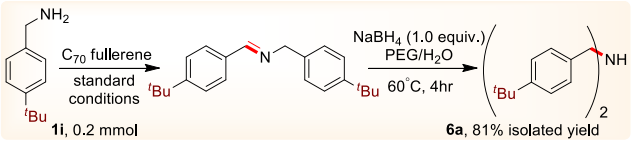
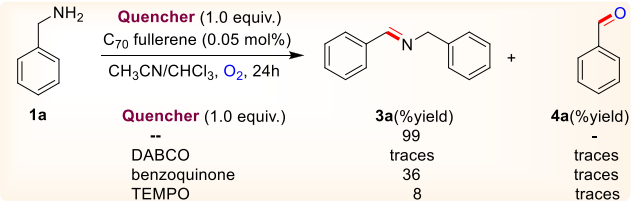
Scheme 3. One-Pot Two-Step Synthesis of Symmetrical Secondary Amines

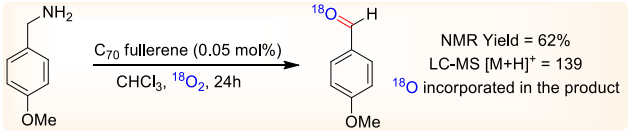


Scheme 4. ROS Quenching Experiments



of the crude reaction mixture evinced the incorporation of ^{18}O in the oxidation product (corresponding benzaldehyde).

Scheme 5. ^{18}O-Labeling Experiment



As the reaction proceeds through the free radical mechanism, we disproved the possibility of a chain reaction mechanism through light on−off experiments (Figure 2). There was no increase in the yield of the product when the light was turned off, thus insinuating the cessation of the reaction in that interval of time.

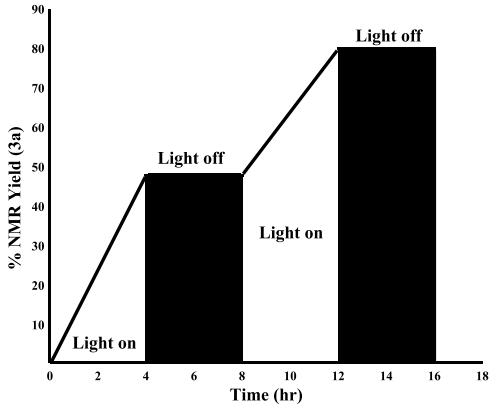


Figure 2. Disproved radical chain reactions through light on−off experiments.

Furthermore, in addition to the anticipated dimerized imine, we also presume the formation of other side products such as H_2O_2 and NH_3 in the reaction. The addition of concentrated HCl drops into the reaction vial after completion of the reaction led to the formation of dense white fumes, confirming ammonia formation. A standard spectrophotometric method was used to detect *in situ* generated H_2O_2. Appearance of two absorption maxima at 510 and 551 nm (Figure 3) substantiated the presence of H_2O_2 in the reaction.[23]

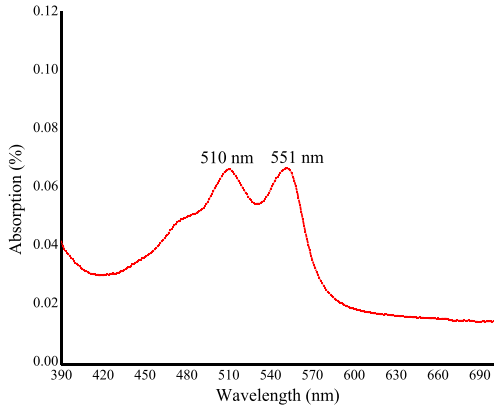
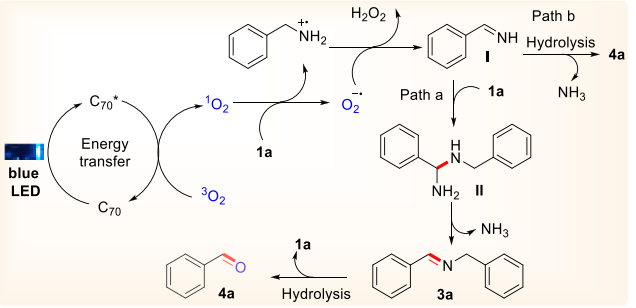


Figure 3. UV−visible absorption spectra for the detection of H_2O_2.

Based on these experiments, we propose that the current reaction involves the generation of $^1O_2$ from $^3O_2$ via energy transfer from photoactivated C_{70} fullerene (Scheme 6). $^1O_2$

Scheme 6. Proposed Mechanism for the Photocatalytic Oxidation of Benzylic Amine to Imine and Aldehyde



then undergoes single electron transfer with **1a** to form $O_2^{\bullet-}$ and amine radical cation. The two products thus generated undergo hydrogen transfer to generate imine **I** and H_2O_2. Further, pathway **a** involves the nucleophilic addition of **1a** and intermediate **I** to give **II**, which then gives the product **3a** with the elimination of NH_3. Additionally, **3a** may undergo hydrolysis to give **4a** (see Supporting Information). Pathway **b** involves the direct hydrolysis of **I** to give benzaldehyde **4a**. Moreover, we observed exclusively imine product **3** while using CH_3CN solvent, whereas aldehyde **4** as the major product with $CHCl_3$ solvent. This selectivity of product due to solvent might be attributed to the acidic/basic nature of solvent being used for the synthesis of these compounds. Chloroform being weakly acidic in nature may favor the hydrolysis of imine **I** to **4a**, whereas acetonitrile being weakly basic in nature, may be endorsing the nucleophilic addition reaction among **1a** and **I**, thus yielding product **3a** (Supporting Information, Figure S6).

Further, the formation of intermediate **I** from an imine radical cation may occur through two possible intermediates, **A** or **B** (Figure 4), as proposed by Jiang's group.[8c] Here, we performed density functional theory (DFT) energy calculations of these possible intermediates of the reaction at B3LYP/6-31G level. As shown in the energy profile diagram, benzyl-free-radical **B**'s energy is lower than that of amine-free-radical **A**. The energy difference between the two was 19.44 kcal/mol, thus indicating **I**'s formation from an amine radical cation through benzylic radical intermediate **B** (Supporting Information, Table S3).

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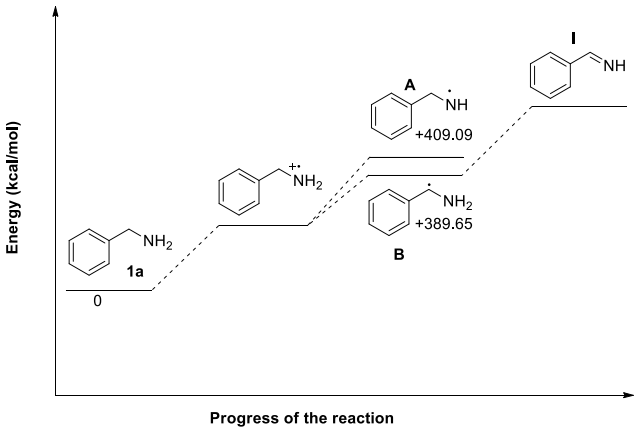

Figure 4. DFT energy profile diagram for reaction intermediates.

We also calculated the green metrics parameters for the developed oxidative reaction.[24] We found imine synthesis more endorsing in terms of atom economy (91%) and atom efficiency (89.3) compared to that of benzaldehyde synthesis (49% atom economy and 27.2 atom efficiency). Oxidation to imine was carbon efficient (98%), as well, compared to that of oxidation to benzaldehyde (55% carbon efficiency). Moreover, we also computed other green metrics parameters, *viz*. reaction mass efficiency, optimum efficiency, mass intensity, process mass intensity and e-factor, and solvent intensity, for both oxidation reactions (Supporting Information, Table S2).

In summary, we uncovered photoinduced synthesis of imines and aldehydes using a pristine C_{70} fullerene catalyst via oxygenous oxidation of primary benzylamines. The solvent plays a vital role in deciding the outcome of the reaction as MeCN leads to the formation of imines, whereas $CHCl_3$ leads to aldehydes, thus stipulating the endorsement of basic solvent to imine.

EXPERIMENTAL SECTION

Unless otherwise stated, all reactions were carried out under an oxygen atmosphere in screw cap reaction vials. All solvents were bought from Sigma-Aldrich in sure-seal bottles and used as such. Chemicals were bought from Sigma-Aldrich, Alfa-Aesar, and TCI. For column chromatography, silica gel (230−400 mesh) from Merck was used. A gradient elution using *n*-hexane and ethyl acetate was used based on Merck aluminum TLC sheets (silica gel $60F_{254}$). The melting points were recorded on a Barnstead Electrothermal 9100 instrument. All isolated compounds were characterized by ^{1}H NMR, $^{13}C\{^1H\}$ NMR, and LC-MS. In addition, all of the compounds were further characterized by high-resolution mass spectrometry (HRMS). Mass spectra were recorded on Water Q-ToF-Micro Micromass instrument. Copies of ^{1}H and $^{13}C\{^1H\}$ NMR are included in the NMR (Supporting Information). Nuclear magnetic resonance spectra were recorded either on a Bruker Avance 600 or 300 MHz instrument. All ^{1}H NMR experiments are reported in units of parts per million (ppm) and were measured relative to the signals for residual chloroform (7.26), acetone (2.05), pyridine (7.22), and methanol (3.31) in the deuterated solvents. All ^{13}C NMR spectra were reported in ppm relative to deuterated chloroform (77.16), acetone (29.84), pyridine (135.91), and methanol (49.00), and all were obtained with ^{1}H decoupling. Optimization studies were done by ^{1}H NMR, and NMR yield was calculated using tetrachloroethane as an internal standard.

General Procedure for Synthesis of Imines from Corresponding Primary Benzylic Amines (3). To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar was added 168 μL of C_{70} solution (1 mg/2 mL in toluene) (0.05 mol %) and dried over a rotary evaporator. To this were added primary benzylic amine (21.9 μL, 0.2 mmol) and acetonitrile (4 mL). The reaction vial was closed with the screw cap, purged with oxygen, and kept for vigorous stirring under blue LED light at room temperature for 24 h. After completion, the reaction mixture was dried over a rotary evaporator and purified by column chromatography using silica gel (60−120 mesh size) as the stationary phase and *n*-hexane/EtOAc as the eluent. Also, triethylamine (5%) was added to the eluent to avoid any kind of degradation of the imine product.

General Procedure for Synthesis of Benzaldehydes (4) from Corresponding Benzylic Amines. To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar was added 168 μL of C_{70} solution (1 mg/2 mL in toluene) (0.05 mol %) and dried over a rotary evaporator. To this were added primary benzylic amine (21.9 μL, 0.2 mmol) and chloroform (4 mL). The reaction vial was closed with a screw cap, purged with oxygen, and kept for vigorous stirring under blue LED light at room temperature for 24 h. After completion, the reaction mixture was dried over a rotary evaporator and purified by flash chromatography using silica gel (230−400 mesh size) as the stationary phase and *n*-hexane/EtOAc as the eluent.

Characterization Data. *(E)-N-Benzylidene-1-phenylmethanamine (Table 2, entry **3a**):* Yellow liquid (19.1 mg, 98%); isolated from column chromatography (5% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.42 (s, 1H), 7.82−7.83 (m, 2H), 7.43−7.46 (m, 3H), 7.38−7.39 (m, 4H), 7.28−7.32 (m, 1H), 4.86 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 162.1, 139.4, 136.3, 130.9, 128.7, 128.6, 128.4, 128.1, 127.1, 65.1; HRMS (EI) *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{14}N$ 196.1121; found 196.1125.

*(E)-N-(2-Methylbenzylidene)-1-(o-tolyl)methanamine (Table 2, entry **3b**):* Yellow liquid (18.3 mg, 82%); isolated from column chromatography (3% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.72 (s, 1H), 7.98 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.35 (m, 2H), 7.29 (m, 1H), 7.24 (m, 4H), 4.88 (s, 2H), 2.56 (s, 3H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 160.7, 137.8, 137.7, 136.2, 134.4, 130.9, 130.4, 130.2, 128.4, 127.8, 127.2, 126.3, 126.2, 63.4, 19.5, 19.4; HRMS (EI) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{18}N$ 224.1434; found 224.1430.

*(E)-N-(2-Chlorobenzylidene)-1-(2-chlorophenyl)methanamine (Table 2, entry **3c**):* Yellow liquid (22.6 mg, 86%); isolated from column chromatography (10% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.88 (s, 1H), 8.13 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.43−7.44 (m, 1H), 7.39−7.40 (m, 2H), 7.35−7.37 (m, 1H), 7.30−7.32 (m, 1H), 7.25−7.28 (m, 1H), 7.21−7.24 (m, 1H), 4.96 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 159.9, 137.0, 135.5, 133.6, 133.3, 131.9, 130.0, 129.8, 129.5, 128.6, 128.5, 127.2, 127.1, 62.3; HRMS (EI) *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{12}Cl_2N$ 264.0341; found 264.0346.

*(E)-N-(3-Methylbenzylidene)-1-(m-tolyl)methanamine (Table 2, entry **3d**):* Yellow liquid (21.4 mg, 96%); isolated from column chromatography (5% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.39 (s, 1H), 7.69 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.33−7.35 (m, 1H), 7.28 (m, 2H), 7.18 (m, 2H), 7.11 (d, *J* = 7.2 Hz, 1H), 4.82 (s, 2H), 2.42 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 162.2, 139.3, 138.4, 138.2, 136.2, 131.7, 128.9, 128.58, 128.56, 128.5, 126.0, 125.2, 65.2, 21.5, 21.4; HRMS (EI) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{18}N$ 224.1434; found 224.1434.

*(E)-N-(3-(Trifluoromethyl)benzylidene)-1-(3-(trifluoromethyl)-phenyl)methanamine (Table 2, entry **3e**):* Yellow liquid (28.4 mg, 86%); isolated from column chromatography (5% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.47 (s, 1H), 8.08 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.62 (s, 1H), 7.55−7.58 (m, 3H), 7.49 (t, *J* = 7.8 Hz, 1H), 4.89 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 161.1, 140.0, 136.7, 131.6, 131.5, 131.39 (q, J_{C-F} = 33.0 Hz), 130.98 (q, J_{C-F} = 31.5 Hz), 129.4, 129.2, 127.6 (q, J_{C-F} = 3.0 Hz), 125.2 (q, J_{C-F} = 4.5 Hz), 124.8 (q, J_{C-F} = 3.0 Hz), 124.3 (q, J_{C-F} = 271.5 Hz), 124.2 (q, J_{C-F} = 4.5 Hz), 124.0 (d, J_{C-F} = 271.5 Hz), 64.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ −62.53, −62.73; HRMS (EI) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{12}F_6N$ 332.0868; found 332.0871.

*(E)-N-(3-Fluorobenzylidene)-1-(3-fluorophenyl)methanamine (Table 2, entry **3f**):* Yellow liquid (22.6 mg, 98%); isolated from

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column chromatography (3% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.36 (d, J = 1.2 Hz, 1H), 7.54−7.56 (m, 1H), 7.51−7.53 (m, 1H), 7.38−7.41 (m, 1H), 7.29−7.33 (m, 1H), 7.11−7.16 (m, 2H), 7.05−7.07 (m, 1H), 6.96 (td, J = 8.4, 2.4 Hz, 1H), 4.81 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 163.1 (d, J_{C-F} = 244.5 Hz), 163.1 (d, J_{C-F} = 244.5 Hz), 161.2 (d, J_{C-F} = 3.0 Hz), 141.7 (d, J_{C-F} = 7.5 Hz), 138.3 (d, J_{C-F} = 7.5 Hz), 130.3 (d, J_{C-F} = 9.0 Hz), 130.1 (d, J_{C-F} = 7.5 Hz), 124.5 (d, J_{C-F} = 3.0 Hz), 124.5 (d, J_{C-F} = 3.0 Hz), 118.0 (d, J_{C-F} = 21.0 Hz), 114.9 (d, J_{C-F} = 21.0 Hz), 114.4 (d, J_{C-F} = 21.0 Hz), 114.0 (d, J_{C-F} = 21.0 Hz), 64.3 (d, J_{C-F} = 3.0 Hz); HRMS (EI) m/z [M + H]$^+$ calcd for $C_{14}H_{12}F_2N$ 232.0932; found 232.0935.

*(E)-N-(3-Chlorobenzylidene)-1-(3-chlorophenyl)methanamine (Table 2, entry **3g**):* Yellow liquid (19.5 mg, 74%); isolated from column chromatography (10% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.33 (s, 1H), 7.82 (t, J = 1.8 Hz, 1H), 7.63 (dd, J = 7.8, 1.2 Hz, 1H), 7.41 (ddd, J = 7.8, 2.4, 1.2 Hz, 1H), 7.34−7.37 (m, 2H), 7.28−7.30 (m, 1H), 7.22−7.27 (m, 2H), 4.79 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.0, 141.1, 137.7, 134.9, 134.5, 131.0, 130.0, 129.9, 128.1, 128.0, 127.4, 126.8, 126.1, 64.4; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{14}H_{12}Cl_2N$ 264.0341; found 264.0346.

*(E)-N-(4-Methylbenzylidene)-1-(p-tolyl)methanamine (Table 2, entry **3h**):* Yellow solid (21.0 mg, 94%); mp = 73−75 °C; isolated from column chromatography (5% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.35 (s, 1H), 7.67 (d, J = 7.8 Hz, 2H), 7.22−7.23 (m, 4H), 7.16 (d, J = 7.8 Hz, 2H), 4.78 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.8, 141.1, 136.6, 136.5, 133.7, 129.4, 129.3, 128.4, 128.1, 64.9, 21.6, 21.2; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{16}H_{18}N$ 224.1434; found 224.1432.

*(E)-N-(4-(tert-Butyl)benzylidene)-1-(4-(tert-butyl)phenyl)-methanamine (Table 2, entry **3i**):* Yellow solid (30 mg, 98%); meting point: 56−58 °C; isolated from column chromatography (5% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.42 (s, 1H), 7.77−7.80 (m, 2H), 7.48−7.50 (m, 2H), 7.41−7.43 (m, 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.84 (s, 2H), 1.39 (s, 9H), 1.37 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.8, 154.2, 149.8, 136.5, 133.6, 128.2, 127.8, 125.6, 125.5, 64.9, 35.0, 34.5, 31.5, 31.3; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{22}H_{30}N$ 308.2373; found 308.2376.

*(E)-N-(4-(Trifluoromethyl)benzylidene)-1-(4-(trifluoromethyl)-phenyl)methanamine (Table 2, entry **3j**):* Yellow liquid (26.5 mg, 80%); isolated from column chromatography (5% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.47 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 4.90 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.3, 143.1(d, J_{C-F} = 2.8 Hz), 139.1, 132.7 (q, J_{C-F} = 33.0 Hz), 129.5 (d, J_{C-F} = 33.0 Hz), 128.7, 128.3, 125.8 (q, J_{C-F} = 3.0 Hz), 125.6 (q, J_{C-F} = 3.0 Hz), 124.4 (d, J_{C-F} = 270.0 Hz), 124.0 (d, J_{C-F} = 271.5 Hz), 64.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ −62.42, −62.81; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{16}H_{12}F_6N$ 332.0868; found 332.0870.

*(E)-N-(4-Phenoxybenzylidene)-1-(4-phenoxyphenyl)-methanamine (Table 2, entry **3k**):* White solid (37.1 mg, 98%); mp = 96−97 °C; isolated from column chromatography (10% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.37 (s, 1H), 7.77 (dd, J = 10.8, 2.4 Hz 2H), 7.37−7.40 (m, 2H), 7.32−7.35 (m, 4H), 7.16−7.18 (m, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.05−7.07 (m, 3H), 7.01−7.04 (m, 5H), 4.80 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.1, 159.9, 157.6, 156.5, 156.2, 134.5, 131.2, 130.04, 130.02, 129.8, 129.5, 124.1, 123.2, 119.7, 119.2, 118.8, 118.4, 64.6; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{26}H_{22}NO_2$ 380.1645; found 380.1651.

*(E)-N-(4-Fluorobenzylidene)-1-(4-fluorophenyl)methanamine (Table 2, entry **3l**):* Yellow liquid (22.2 mg, 96%); isolated from column chromatography (5% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.35 (s, 1H), 7.76−7.78 (m, 2H), 7.30 (dd, J = 8.4, 6.0 Hz, 2H), 7.09−7.12 (m, 2H), 7.02−7.05 (m, 2H), 4.77 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.6 (d, J_{C-F} = 249 Hz), 162.1 (d, J_{C-F} = 243 Hz), 160.7, 135.1 (d, J_{C-F} = 3.0 Hz), 132.5 (d, J_{C-F} = 3.0 Hz), 130.3 (d, J_{C-F} = 9.0 Hz), 129.6 (d, J_{C-F} = 9.0 Hz), 115.9 (d, J_{C-F} = 21.0 Hz) 115.5 (d, J_{C-F} = 21.0 Hz), 64.3; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{14}H_{12}F_2N$ 232.0932; found 232.0935.

*(E)-N-(4-Chlorobenzylidene)-1-(4-chlorophenyl)methanamine (Table 2, entry **3m**):* Yellow solid (23.7 mg, 90%); mp = 62−63 °C; isolated from column chromatography (15% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.34 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 4.77 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.0, 137.8, 137.1, 134.6, 133.0, 129.6, 129.4, 129.1, 128.8, 64.3; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{14}H_{12}Cl_2N$ 264.0341; found 264.0346.

*(E)-N-(4-Bromobenzylidene)-1-(4-bromophenyl)methanamine (Table 2, entry **3n**):* White solid (29.6, 84%); mp = 96−98 °C; isolated from column chromatography (10% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.33 (s, 1H), 7.63−7.65 (m, 2H), 7.54−7.57 (m, 2H), 7.46−7.48 (m, 2H), 7.21 (d, J = 8.4 Hz, 2H), 4.75 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.2, 138.2, 134.9, 132.0, 131.7, 129.81, 129.76, 125.5, 121.1, 64.4; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{14}H_{12}Br_2N$ 351.9331; found 351.9337.

*(E)-N-(4-Iodobenzylidene)-1-(4-iodophenyl)methanamine (Table 2, entry **3o**):* White solid (93.3 mg, 88%); mp = 146−148 °C; isolated from column chromatography (15% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.30 (s, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 4.73 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.3, 138.9, 138.0, 137.7, 135.5, 130.1, 129.9, 97.7, 92.5, 64.4; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{14}H_{12}I_2N$ 447.9054; found 447.9058.

*(E)-N-(4-((Trifluoromethyl)thio)benzylidene)-1-(4-((trifluoromethyl)thio)phenyl)methanamine (Table 2, entry **3p**):* Yellow solid (26.5 mg, 67%); mp = 42−43 °C; isolated from column chromatography (15% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.44 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 4.87 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.3, 142.4, 138.2, 136.7, 136.4, 129.8 (q, J = 306 Hz), 129.6 (q, J = 306 Hz), 129.2, 129.0, 127.4 (d, J = 3.0 Hz), 123.0 (d, J = 1.5 Hz), 64.5; ^{19}F NMR (565 MHz, chloroform-*d*) δ −42.25, −42.86; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{16}H_{12}F_6NS_2$ 396.0310; found: 396.0315.

*(E)-N-(2,4-Dichlorobenzylidene)-1-(2,4-dichlorophenyl)-methanamine (Table 2, entry **3q**):* Yellow solid (23.3 mg, 70%); mp = 68−69 °C; isolated from column chromatography (15% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.80 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.42 (dd, J = 4.8, 1.8 Hz, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.29 (dd, J = 8.4, 1.8 Hz, 1H), 7.25 (dd, J = 8.4, 2.4 Hz, 1H), 4.88 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 159.0, 137.5, 136.0, 135.4, 134.1, 133.6, 131.7, 130.6, 129.8, 129.5, 129.3, 127.7, 127.4, 61.7; HRMS (EI) m/z [M + H]$^+$ calcd for $C_{14}H_{10}Cl_4N$ 331.9562; found 331.9565.

*Benzaldehyde (Table 3, entry **4a**):*[25] Colorless liquid (11.5 mg, 55%); isolated from column chromatography (5% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 10.01 (s, 1H), 7.86−7.88 (m, 2H), 7.60−7.63 (m, 1H), 7.52 (t, J = 7.8 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 192.5, 136.5, 134.6, 129.8, 129.1.

*2-Methoxybenzaldehyde (Table 3, entry **4b**):*[25] Yellow liquid (21.2 mg, 78%); isolated from column chromatography (5% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 10.47 (s, 1H), 7.82 (dd, J = 7.8, 1.2 Hz, 1H), 7.53−7.56 (m, 1H), 7.01−7.03 (m, 1H), 6.98 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 190.0, 161.9, 136.1, 128.7, 124.9, 120.8, 111.7, 55.7.

*2-Ethoxybenzaldehyde (Table 3, entry **4c**):*[26] Yellow liquid (18.9 mg, 63%); isolated from column chromatography (5% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 10.50 (s, 1H), 7.81 (dd, J = 7.8, 1.8 Hz, 1H), 7.50−7.52 (m, 1H), 6.98−7.00 (m, 1H), 6.96 (d, J = 8.4 Hz, 1H), 4.12−4.17 (m, 2H), 1.45−1.48 (m, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 190.0, 161.5, 136.0, 128.3, 125.0, 120.6, 112.6, 64.2, 14.7.

*2-Chlorobenzaldehyde (Table 3, entry **4d**):*[27] Yellow solid (10.4 mg, 37%); mp = 131−133 °C; isolated from column chromatography (10% EtOAc/*n*-hexane); ^{1}H NMR (600 MHz, chloroform-*d*) δ 10.48 (s, 1H), 7.92 (dd, J = 7.8, 1.8 Hz, 1H), 7.51−7.54 (m, 1H), 7.45 (m,

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1H), 7.37−7.40 (m, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 189.9, 138.1, 135.3, 132.6, 130.7, 129.5, 127.4.

*3-Methoxybenzaldehyde (Table 3, entry **4e**):*[25] Yellow liquid (18.8 mg, 69%); isolated from column chromatography (10% EtOAc/*n*-hexane); ^1H NMR (600 MHz, chloroform-*d*) δ 9.97 (s, 1H), 7.43−7.46 (m, 2H), 7.38−7.39 (m, 1H), 7.16−7.18 (m, 1H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 192.3, 160.2, 137.9, 130.2, 123.7, 121.7, 112.1, 55.6.

*3-Chlorobenzaldehyde (Table 3, entry **4f**):*[28] White solid (25.9 mg, 92%), mp = 136−139 °C; isolated from column chromatography (10% EtOAc/*n*-hexane); ^1H NMR (600 MHz, chloroform-*d*) δ 9.95 (s, 1H), 7.82 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.56−7.58 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 190.9, 137.9, 135.5, 134.4, 130.5, 129.3, 128.1.

*4-Methylbenzaldehyde (Table 3, entry **4g**):*[25] Yellow liquid (11.8 mg, 49%); isolated from column chromatography (5% EtOAc/*n*-hexane); ^1H NMR (600 MHz, chloroform-*d*) δ 9.96 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 192.1, 145.7, 134.3, 130.0, 129.8, 22.0.

*4-(tert-Butyl)benzaldehyde (Table 3, entry **4h**):*[27] White solid (21 mg, 65%);mp = 147−149 °C; isolated from column chromatography (5% EtOAc/*n*-hexane); ^1H NMR (600 MHz, chloroform-*d*) δ 9.97 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 1.34 (s, 9H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 192.1, 158.5, 134.2, 129.8, 126.1, 35.4, 31.1.

*4-Methoxybenzaldehyde (Table 3, entry **4i**):*[25] Yellow liquid (16.3 mg, 60%); isolated from column chromatography (10% EtOAc/*n*-hexane); ^1H NMR (600 MHz, chloroform-*d*) δ 9.88 (s, 1H), 7.84 (dd, *J* = 10.8, 2.4 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 191.0, 164.7, 132.1, 130.0, 114.4, 55.7.

*4-Chlorobenzaldehyde (Table 3, entry **4j**):*[28] White solid (18.3 mg, 65%); mp = 175−177 °C; isolated from column chromatography (5% EtOAc/*n*-hexane); ^1H NMR (600 MHz, chloroform-*d*) δ 9.96 (s, 1H), 7.79−7.81 (m, 2H), 7.49 (d, *J* = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 190.9, 141.0, 134.8, 131.0, 129.5.

*4-Bromobenzaldehyde (Table 3, entry **4k**):*[27] White solid (21.8 mg, 59%); mp = 150−152 °C; isolated from column chromatography (5% EtOAc/*n*-hexane); ^1H NMR (600 MHz, chloroform-*d*) δ 9.96 (s, 1H), 7.73 (dd, *J* = 6.6 Hz, *J* = 1.8 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 191.2, 135.2, 132.5, 131.1, 129.9.

*2,4-Dimethoxybenzaldehyde (Table 3, entry **4l**):*[26] White solid (14.6 mg, 44%), mp = 65−67 °C; isolated from column chromatography (10% EtOAc/*n*-hexane); ^1H NMR (600 MHz, chloroform-*d*) δ 10.27 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 6.52−6.54 (m, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 188.5, 166.3, 163.7, 130.8, 119.1, 105.8, 98.0, 55.7, 55.7.

*2-Chloro-4-methoxybenzaldehyde (Table 3, entry **4m**):*[29] White solid (32.7 mg, 96%), mp = 48−50 °C; isolated from column chromatography (10% EtOAc/*n*-hexane); ^1H NMR (600 MHz, chloroform-*d*) δ 9.81 (s, 1H), 7.86 (d, *J* = 2.4 Hz, 1H), 7.73 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 189.8, 159.8, 131.1, 130.7, 130.3, 123.7, 111.7, 56.6.

*3,4,5-Trimethoxybenzaldehyde (Table 3, entry **4n**):*[26] White solid (18.0 mg, 46%); mp = 65−66 °C; isolated from column chromatography (10% EtOAc/*n*-hexane); ^1H NMR (600 MHz, chloroform-*d*) δ 9.84 (s, 1H), 7.11 (s, 2H), 3.92 (s, 3H), 3.91 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.2, 153.7, 143.6, 131.8, 106.8, 61.1, 56.3.

*Bis(4-(tert-butyl)benzyl)amine (Scheme 3, **6a**).*[29] To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar was added 168 μL of C_{70} solution (1 mg/2 mL in toluene) (0.05 mol %) and dried over rotary evaporator. To this were added primary benzylic amine (21.9 μL, 0.2 mmol) and acetonitrile (4 mL). The reaction vial was closed with a screw cap, purged with oxygen, and kept for vigorous stirring under blue LED light at room temperature for 24 h. After completion, the reaction mixture was dried over a rotary evaporator and 2.0 equiv of distilled water was added along with 0.5 mL of PEG (polyethylene glycol) 400. The reaction mixture was then stirred for 10 min. Next, 0.5 equiv of $NaBH_4$ was then added slowly, and the reaction mixture was heated to 60 °C for 4 h using an oil bath.[29] After completion, the reaction mixture was washed with 30 mL of distilled water (3 × 10 mL) and extracted with ethyl acetate. The organic layer was then subjected to column chromatography using hexane/ethyl acetate (85:15) as an eluent to get the pure form of the desired product: white solid (50.0 mg, 81%); mp = 142−144 °C, ^1H NMR (600 MHz, chloroform-*d*) δ 7.36 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 3.82 (s, 1H), 1.30 (s, 4H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 150.86, 144.63, 128.69, 125.70, 51.17, 34.67, 31.45.

Reactive Oxygen Species Quenching Experiments. To the oven-dried screw cap reaction vials charged with a spin vane magnetic stir-bar was added 84 μL of C_{70} solution (1 mg/2 mL in toluene) (0.05 mol %) in two different vials and dried over a rotary evaporator. To this werd added primary benzylic amine (10.9 μL, 0.1 mmol) and acetonitrile (2 mL). Then to this standard reaction were added separately ROS quenchers (DABCO, benzoquinone). The reaction vials were closed with screw caps, purged with oxygen, and kept for vigorous stirring under blue LED light at room temperature for 24 h. After completion, the reactions were dried over a rotary evaporator, and crude reactions were analyzed with the help of NMR using tetrachloroethane as an internal standard.

Radical Quenching Experiments. To the oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar was added 84 μL of C_{70} solution (1 mg/2 mL in toluene) (0.05 mol %) in vial and dried over a rotary evaporator. To this were added primary benzylic amine (10.9 μL, 0.1 mmol) and acetonitrile (2 mL). Then to this standard reaction was added a radical quencher (2,2,6,6-tetramethylpiperidin-1-yl)oxyl. The reaction vial was closed with a screw cap, purged with oxygen, and kept for vigorous stirring under blue LED light at room temperature for 24 h. After completion, the reaction was dried over a rotary evaporator, and the crude reaction was analyzed with the help of NMR using tetrachloroethane as an internal standard.

^{18}O-Labeling Experiment. To the oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar was added 84 μL of C_{70} solution (1 mg/2 mL in toluene) (0.05 mol %) in vial and dried over a rotary evaporator. To this were added primary benzylic amine (13.1 μL, 0.1 mmol) and chloroform (2 mL). The reaction vial was closed with a screw cap, purged with ^{18}O, and kept for vigorous stirring under blue LED light at room temperature for 24 h. After completion, the crude reaction was analyzed by LC-MS.

Light On−Off Experiments. To the four oven-dried screw cap reaction vials charged with a spin vane magnetic stir-bar was added 84 μL of C_{70} solution (1 mg/2 mL in toluene) (0.05 mol %) in each vial and dried over rotary evaporator. To this were added primary benzylic amine **1a** (10.9 μL, 0.1 mmol) and acetonitrile (2 mL). The reaction vials were closed with a screw cap, purged with oxygen, and kept for vigorous stirring under blue LED light at room temperature. First, the reactions were irradiated for 4 h; the LED light was turned off, and the NMR yield of one reaction was calculated. Second, the reaction was analyzed after 8 h, and light was then turned on. Further, again, the light was turned off after 12 h, and third reaction was analyzed with NMR after 12 h and the fourth one after 16 h.

Detection of Hydrogen Peroxide (H_2O_2). To the oven-dried screw cap reaction vials charged with a spin vane magnetic stir-bar was added 84 μL of C_{70} solution (1 mg/2 mL in toluene) (0.05 mol %) in vial and dried over a rotary evaporator. To this were added primary benzylic amine (10.9 μL, 0.1 mmol) and acetonitrile (2 mL). The reaction vial was closed with a screw cap, purged with oxygen, and kept for vigorous stirring under blue LED light at room temperature for 24 h. After completion, the reaction mixture was added to 20 mL of water and then extracted three times with 30 mL of ethyl acetate (10 × 3). The aqueous layer was then used for the determination of H_2O_2 by following the standard procedure reported by Bader et al.[23]

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00297.

Experimental set up, optimization detail, spectral data (PDF)

FAIR data, including the primary NMR FID files, for compounds **3a−3q**, **4a−4n**, and **6a** (ZIP)

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Notes

The authors declare no competing financial interest.

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