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Note

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Oxidative Deprotection of *p*-Methoxybenzyl Ethers via Metal-Free Photoredox Catalysis

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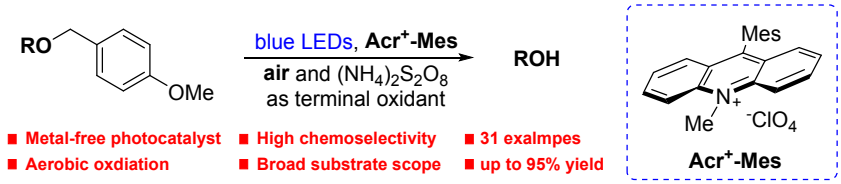
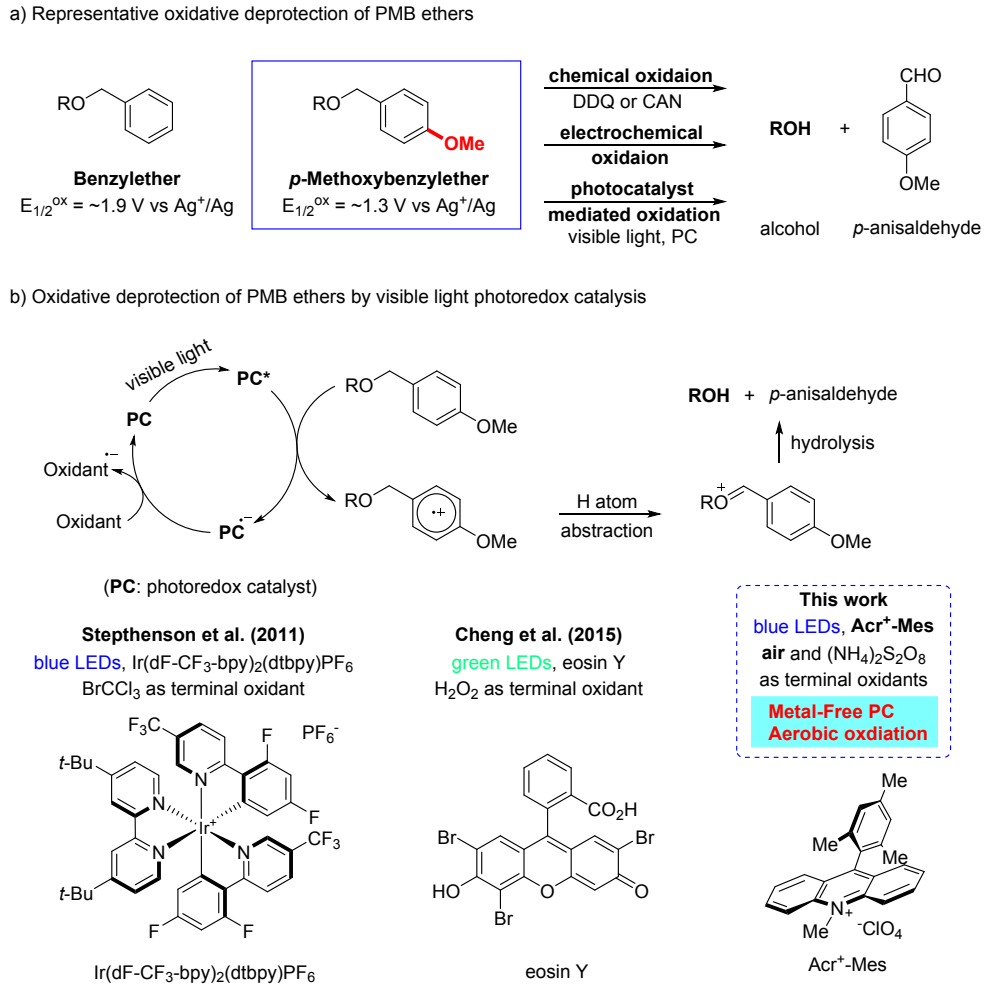
Abstract



An efficient and greener deprotection method for *p*-methoxybenzyl (PMB) ethers using a metal-free visible light photoredox catalyst and air and ammonium persulfate as the terminal oxidants is presented. Various functional groups and protecting groups were tolerated in the developed method to achieve good to excellent yields in short reaction times. Significantly, the developed method was compatible with PMB ethers derived from primary, secondary, and tertiary alcohols and a gram-scale reaction. Mechanistic studies support a proposed reaction mechanism that involves single electron oxidation of the PMB ether.

Protecting groups are used to achieve chemoselectivity in the multi-step synthesis of natural products, pharmaceuticals, and agrochemicals. Thus, numerous protecting groups that are easily introduced and removed and stable under the reaction conditions have been developed for chemoselective synthesis.[1] Benzyl ether is one of the widely used protecting groups for alcohols because it is readily introduced by Williamson ether synthesis, is removable by hydrogenolysis, and is stable under a variety of reaction conditions. However, benzyl ether cannot be used as protecting group for compounds possessing functional groups (e.g. alkene, alkyne, nitro, etc.) that are labile in reduction conditions. As an alternative, benzyl ether can be deprotected under strong oxidation conditions, but those conditions can be too harsh and cause side reactions in complex molecules.[2] In order to achieve oxidative deprotection, *p*-methoxybenzyl (PMB) ether has been developed because it has a lower oxidation potential[3] than benzyl ether, which can be easily cleaved by appropriate oxidation conditions.

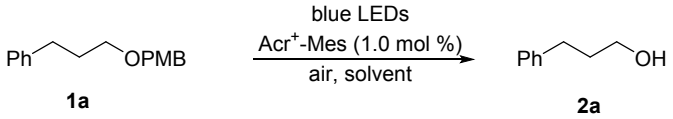
Scheme 1. Oxidative deprotection of *p*-methoxybenzyl (PMB) ethers



Representative oxidative deprotection of PMB ether is chemical oxidation,[4] electrochemical oxidation,[3b, 5] and recently developed photocatalyst mediated oxidation (Scheme 1a).[6] The chemical oxidative cleavage of PMB is usually carried out with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[4a, b] and ceric ammonium nitrate (CAN)[4c, d] as the oxidant. However, this method displays low atom-economy that it uses a stoichiometric amount of oxidant. As an alternative method to chemical oxidation, electrochemical oxidation for PMB deprotection has been studied as an environmentally friendly method with high atom economy. Despite the efficiency of electrochemical oxidation methods, electrochemical instruments are required in order to carry out the experiment.

Recently, many reactions that use photoredox catalysis with visible light have been developed for organic transformation because of their potential in green chemistry.[7] Single electron transfer (SET) by an excited photoredox catalyst is the main reaction pathway and produce odd-electron species. In particular, single electron oxidation pathways are useful for oxidizable compound (e.g. amines,[8] carboxylates,[9] arenes,[10] alkenes[11] and etc.[12]) to develop eco-friendly reactions. Electron-rich PMB ether can be oxidized by appropriate photoredox catalysts. Recently, two photoredox-catalyzed deprotection methods for PMB ether have been reported (Scheme 1b). In 2011, Stephenson and co-workers reported visible-light-photoredox-catalyzed deprotection of PMB ether using an iridium complex and $BrCCl_3$ as the terminal oxidant.[6a] Subsequently, Chen and co-workers developed a metal-free reaction using eosin Y as metal-free photocatalyst and H_2O_2 as the terminal oxidant.[6b] Although these methods are environmentally friendly reactions, it is still required that the deprotection method uses an inexpensive, metal-free catalyst with low catalyst loading and a greener terminal oxidant, and also has a short reaction time. Therefore, we envisioned the development of an efficient and greener deprotection method for PMB ether. A Fukuzumi acridinium salt (Acr^+-Mes)[13], which is an efficient and strong oxidant in photoredox catalysis, and molecular oxygen,[14] which is abundant, inexpensive, and greener, were considered as a metal-free photocatalyst and terminal oxidant.

Table 1. Optimization of the reaction conditions[a]



1a **2a**

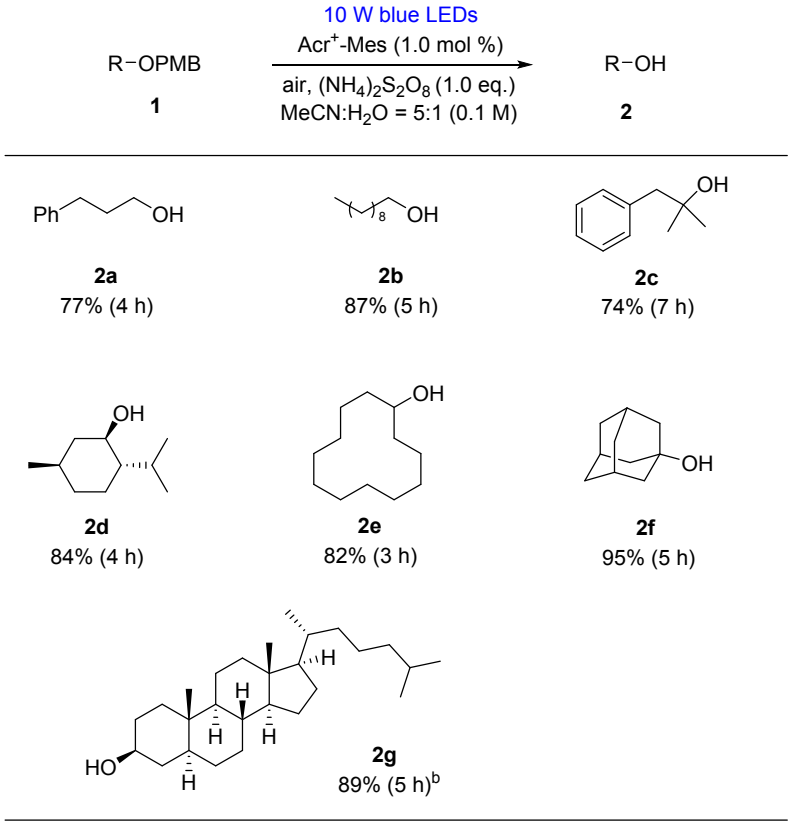
Entry	Solvent (0.1 M)	Additive (eq.)	Time (h)	Yield (%)[b]
1	MeOH/H_2O (5:1)	-	20	27
2	DCM/H_2O (5:1)	-	20	19
3	MeCN/H_2O (5:1)	-	20	33
4	THF/H_2O (5:1)	-	20	trace
5[c]	MeCN/H_2O (5:1)	-	20	27
6	MeCN/H_2O (5:1)	-	48	37
7[d]	MeCN/H_2O (5:1)	-	20	32
8	MeCN/H_2O (5:1)	$NaHSO_4$ (1.0)	20	33
9	MeCN/H_2O (5:1)	$K_2S_2O_8$ (1.0)	20	78
10	MeCN/H_2O (5:1)	$(NH_4)_2S_2O_8$ (1.0)	4	78 (77)[e]
11	MeCN/H_2O (5:1)	$(NH_4)_2S_2O_8$ (0.5)	20	64
12	MeCN/H_2O (5:1)	$(NH_4)_2S_2O_8$ (0.25)	20	47
13[f]	MeCN/H_2O (5:1)	$(NH_4)_2S_2O_8$ (1.0)	4	46
14[f]	MeCN/H_2O (5:1)	-	4	n.r.
15[g]	MeCN/H_2O (5:1)	$(NH_4)_2S_2O_8$ (1.0)	4	n.r.

[a]Reaction conditions: **1a** (0.25 mmol), Acr^+-Mes (1.0 mol %), solvent (0.1 M) with 10 W blue LEDs irradiation at room temperature under an air balloon. [b]Yield determined by HPLC (internal standard: benzophenone). [c]Under O_2 balloon. [d]Acr^+-Mes (5.0 mol %). [e]Isolated yield by flash column chromatography. [f]Under N_2 balloon. [g]In the absence of light source or photocatalyst. n.r. = no reaction.

In our initial study, Fukuzumi acridinium salt (Acr^+-Mes) and air were chosen as the metal-free photoredox catalyst and terminal oxidant because the Fukuzumi catalyst has enough oxidizing power ($E_{1/2}^{red}$ ($PC^*/PC^{\bullet-}$) = +2.06 V vs SCE in CH_3CN) for the oxidation of PMB ether and aerobic oxidation is a greener and inexpensive approach. The deprotection of **1a** was tested in various wet solvents using 1 mol % Acr^+-Mes with irradiation of 10 W blue LEDs under an air atmosphere for 20 h. Co-solvents of CH_3CN:H_2O (5:1) provide the best result of **2a**, with a 33% yield (Table 1, entry 3). Further optimization of reaction conditions, such as using oxygen as the terminal oxidant instead of air, increasing catalyst loading (5 mol %), and reacting for longer times (up to 48 h), were screened, keeping other parameters constant. Unfortunately, these changes did not significantly improve reaction yields (Table 1, entries 5-7). Next, we explored the additive effect (Table 1, entries 8-10). Ammonium persulfate ($(NH_4)_2S_2O_8$) significantly increased the yield to 78% (77% as an isolate yield) and reduced reaction time to 4 h (Table 1, entry 10). It has been reported that persulfate ($S_2O_8^{2-}$) is used as an oxidant in photocatalytic reactions and the reduced sulfate radical anion ($SO_4^{\bullet-}$) is a good hydrogen atom transfer (HAT) reagent.[15] Based on the literature, the synergistic effect of air and $(NH_4)_2S_2O_8$ accelerated both the catalytic cycle and the formation of oxocarbenium ion to improve the reaction rate and yield. The amount of $(NH_4)_2S_2O_8$ tested was 0.25-1.0 equivalents (Table 1, entries 10-12). 1.0 equivalent of

$(NH_4)_2S_2O_8$ gave the best results in reaction time and yield. When $(NH_4)_2S_2O_8$ was used as the sole oxidant, the yield decreased to 46%. This result shows that both air and $(NH_4)_2S_2O_8$ are essential to afford good yield. Control experiments showed that the photocatalyst (Acr^+-Mes), light source, and oxidant (air and $(NH_4)_2S_2O_8$) were essential for this reaction (Table 1, entries 14-15). After screening of the reaction conditions, we found the best result was achieved with 1.0 mol % of Fukuzumi acridinium salt (Acr^+-Mes) and 1.0 equivalent of $(NH_4)_2S_2O_8$ in CH_3CN:H_2O (5:1, 0.1 M) at room temperature and irradiating with 10 W blue LEDs under an air atmosphere to produce deprotected alcohol **2a** in 77% yield (Table 1, entry 10).

Table 2. Substrate scope of various PMB ethers[a]

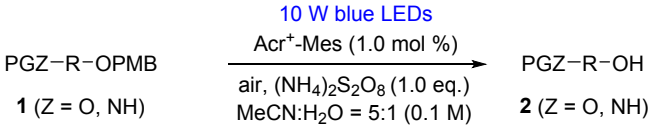


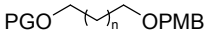
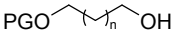
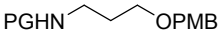
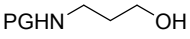
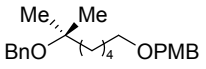
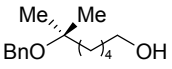
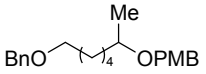
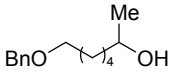
[a]Reaction conditions as given in Table 1, entry 10; reported yields are for isolated material. [b]Acr^+-Mes (5 mol %), CH_2Cl_2:H_2O (5:1). See Experimental section for details.

With the optimized conditions established, the scope and generality of the visible-light photoredox-catalyzed PMB deprotection (**1a-g**) were next investigated (Table 2). PMB ethers derived from primary, secondary, and tertiary alcohols were well deprotected in this method and gave the corresponding alcohols (**2a-g**) in good to excellent yields. Significantly, our developed method shows a shorter reaction time than previous photocatalytic deprotection methods for PMB ethers. The deprotection of PMB ethers were completed within 2-7 h. Additionally, the reaction showed good tolerance to aryl and chiral centers contained in PMB ethers (**1a, d** and **g**). Racemization of chiral PMB ethers (**1d, g**) did not occur in the developed conditions. Due to the low solubility of 5α-cholestan-3β-ol driven PMB ether

1g in CH_3CN, wet dichloromethane (CH_2Cl_2) was used as an alternative solvent system. However, this solvent system was less efficient than wet CH_3CN and required 5 mol % of photocatalyst.

Table 3. Selective deprotection of PMB ethers for various protecting groups[a]



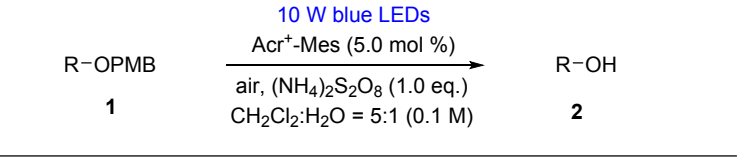
Entry	Sbustate	Product	Time (h)	Yield (%)
				
1	**1h** (PG = Bn, n = 3)	**2h**	2	70
2	**1i** (PG = Ac, n = 3)	**2i**	3	89
3	**1j** (PG = Bz, n = 4)	**2j**	2	74
4	**1k** (PG = Piv, n = 4)	**2k**	4	84
5[b]	**1l** (PG = THP, n = 4)	**2l**	2	70
6[b]	**1m**(PG = TBS, n = 3)	**2m**	2	72
7[b]	**1n** (PG = TBDPS, n = 3)	**2n**	5	86
				
8	**1o** (PG = Boc)	**2o**	4	73
9	**1p** (PG = Bz)	**2p**	4	95
				
10	**1q**	**2q**	3	58 21 (diol)
				
11	**1r**	**2r**	4 (2.5)[b]	76 (85)[b]

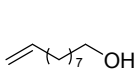
[a]Reaction conditions as given in Table 1, entry 10; reported yields are for isolated material. [b]Acr^+-Mes (5 mol %), CH_2Cl_2:H_2O (5:1). See Experimental section for details.

Next, we examined the possibility of orthogonal deprotection of other protection groups for alcohols and amines (Table 3). The PMB ethers possessing benzyl (Bn) ether, which is labile to oxidative cleavage, were selectively deprotected by the optimized reaction conditions (Table 2, entry 1). Various types of ester protecting groups such as acetyl (Ac), benzoyl (Bz) and pivaloyl (Piv) showed excellent tolerance to photoredox-catalyzed oxidative deprotection (Table 3, entries 2-4). The PMB ethers that contained acid labile protecting groups, such as *t*-butyldimethylsilyl (TBS), *t*-butyldiphenylsilyl (TBDPS), and tetrahydropyranyl (THP) ether, were deprotected in low yield (Table 2, entries 5-7) because the reaction solution was acidified by HSO_4^- that was formed from $(NH_4)_2S_2O_8$ in

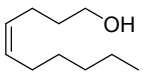
the photoredox catalysis. In order to neutralize the acidic solution, we tried the addition of weak bases or buffer solutions. However, deprotection of the PMB ethers was less efficient in the neutralized conditions. Eventually, we found tolerable reaction conditions for acid labile protecting groups. We changed the solvent to wet CH_2Cl_2, which does not mix well with water, to lower the acidity of the reaction solution (CH_3CN is miscible in water, whereas CH_2Cl_2 is less soluble in water (13.8 g/100 mL (20 °C)).[16] In addition, amine protecting groups such as *t*-butyloxycarbonyl (Boc) and benzoyl (Bz) exhibited excellent stability to oxidative deprotection conditions (Table 3, entries 8-9). Next, we investigated selective deprotection of PMB ether possessing Bn ethers in the same compounds. Various types of PMB ethers were selectively deprotected in the presence of various types of Bn ethers (e.g., primary to primary, primary to tertiary, secondary to primary) (Table 3, entries 1, 10-11).

Table 4. Selective deprotection of PMB ethers for various functional groups[a]

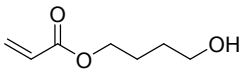




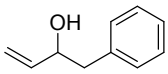
2s
80% (2 h)



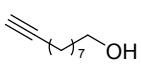
2t
73% (3 h)



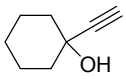
2u
45% (3 h)



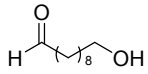
2v
71% (5 h)



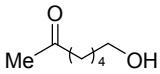
2w
78% (2 h)



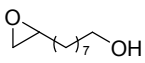
2x
88% (3 h)



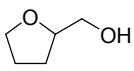
2y
76% (3 h)



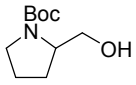
2z
81% (3.5 h)
80% (3 h)[b]



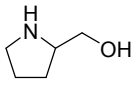
2aa
82% (3 h)



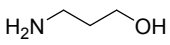
2ab
65% (3.5 h)



2ac
85% (3 h)



2ad
70% (3 h)[c]

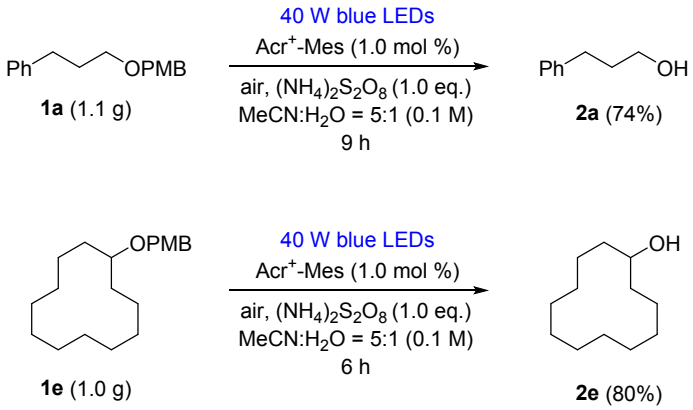


2ae
73% (3 h)[c]

[a]Reaction conditions: **1** (0.25 mmol), Acr^+-Mes (5.0 mol %), $(NH_4)_2S_2O_8$ (1 eq.), CH_2CH_2/H_2O (5:1, 0.1 M) with 10 W blue LEDs irradiation at room temperature under an air balloon, reported yields are for isolated material. [b]Acr^+-Mes (1 mol %), MeCN:H_2O (5:1). [c]Yield determined by ^1H NMR (internal standard: DMF). See Experimental section for details.

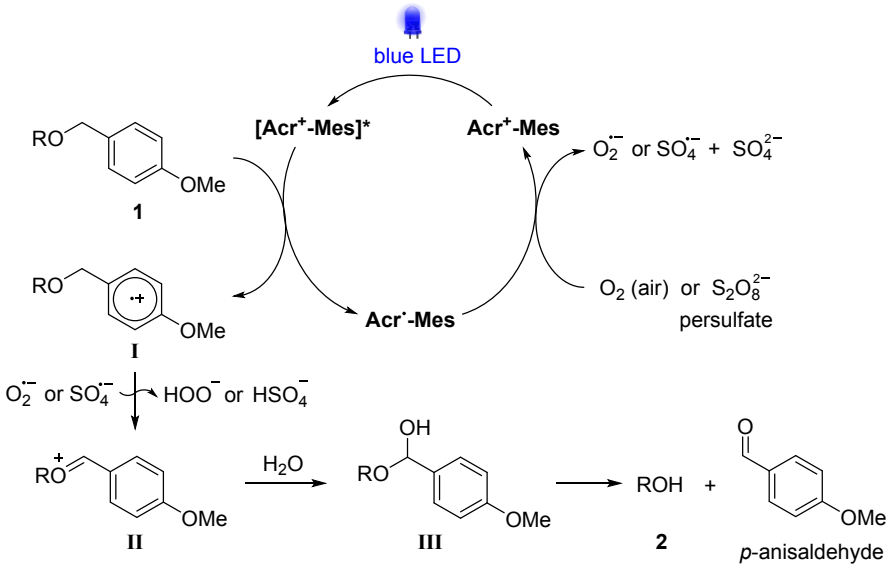
Next, we examined selective deprotection of PMB ethers **1** for various functional groups (Table 4). Under the developed reaction conditions, PMB ethers (**1s-ae)** containing various functional groups such as akenes, alkynes, carbonyl gorups, heterocycles and amines were deprotected to afford the corresponding alcohols (**2s-ae**) in 45-88% yields. Remarkably, reactive functional groups in acidic conditions such as internal, α,β-unsaturated, and allylic alkenes (**1t-v**) and epoxide (**1aa**) showed moderate to good tolerance, providing the corresponding alcohols (**2t-v, aa)** in 45-82% yields. And free primary, secodary amines contained PMB ethers (**1ad-ae**) also worked well, providing the corresponding products in good yields. The developed reaction shows good to excellent tolerance to various functional groups and protecting groups.

Scheme 2. Gram scale reaction



In addition, to develop a useful method in organic synthesis, gram-scale reaction conditions were established by increasing the intensity of the light source (40 W). Visible-light photoredox-catalyzed oxidative deprotection of PMB ethers (**1a**, **e)** provided the deprotected corresponding alcohols (**2a**, **e)** in 74% and 80% yields using modified reaction conditions for the gram scale (Scheme 2).

Scheme 3. Proposed mechanism



Additional experiments were carried out to gain insight into the reaction mechanism. In a Stern-Volmer luminescence quenching experiment, the excited state of the photoredox catalyst was quenched by PMB ether **1**. This result showed that SET occurred between PMB ether **1** and the excited photocatalyst. Additionally, the photoredox catalyzed oxidative cleavage of PMB ether was suppressed by the addition of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as a radical trapping reagent. This result indicated that the reaction involves a radical process. On the basis of our observations and reports in the literature,[6, 14b, 15b, c] a plausible mechanism for photoredox-catalyst-mediated oxidative cleavage of PMB ether has been depicted in Scheme 3. The Fukuzumi acridinium (Acr^+-Mes) is excited by blue LED irradiation into its excited state ([Acr^+-Mes]*). The excited photocatalyst oxidizes PMB ether **1** to cation radical **I** by SET, along with reduced the photocatalyst ($Acr^•$-Mes). The photoredox catalytic cycle is completed via a SET oxidation of $Acr^•$-Mes in the presence of a terminal oxidant (air or persulfate), with the production of a superoxide radical anion ($O_2^{•−}$) or sulfate radical anion ($SO_4^{•−}$). An oxocarbenium ion **II** is afforded by hydrogen atom abstraction of the PMB ether cation radical **I** by the superoxide radical anion ($O_2^{•−}$) or the sulfate radical anion ($SO_4^{•−}$). Finally, hydrolysis of oxocarbenium ion **II** produces deprotected alcohol **2** and *p*-anisaldehyde as a by-product through the hemiacetal intermediate **III**.

Conclusion

In conclusion, we have developed an efficient and greener deprotection method for PMB ethers using a metal-free visible light photoredox catalyst and air and ammonium persulfate as the terminal oxidants. The PMB ethers derived from primary, secondary, and tertiary alcohols were well deprotected in this method and gave corresponding alcohols in good to excellent yields. The deprotection method tolerated a variety of functional groups and protecting groups. In addition, the reaction conditions for selective and gram-scale deprotection were established. We proposed a reaction mechanism, supported by mechanistic studies, that involved single electron oxidation of PMB ether.

Experimental section

General Experimental Information.

Acetonitrile and dichloromethane were purchased from Sigma-Aldrich and air saturated by bubbling of air for 30 minutes. Pressure tubes (13 x 100 mm, PYREXPLUS, and 50 mL flask, purchased from Chem Glass) were used for reaction. All commercial reagents were used directly without further purification. The progress of reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F_{254}), and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plate into a *p*-anisaldehyde solution (5.6 mL of *p*-anisaldehyde, 2.3 mL acetic acid and 3.0 mL of concentrated sulfuric acid in 200 mL of ethanol. Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60) using Hexanes-EtOAc (v/v) or DCM-MeOH (v/v). High-resolution mass spectra (EI) were obtained on a Jeol JMS 700 HRMS at the Korea Basic Science Center (KBSI), Daegu, Korea. Accurate masses are reported for the molecular ion $[M^+]$ or $[M+H]^+$. Nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR) were recorded with a Bruker 300 or 400 MHz spectrometer. Chemical shift values were recorded as parts per million relatives to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz. The following abbreviations are used: m (multiplet), s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. Absorption spectra of the photocatalysts and emission spectra of the visible light sources were measured on a Varian Carry 100, Horiba Fluoromax-4P spectrophotometer. HPLC data were obtained on Agilent infinity 1200 series.

General procedure for Deprotection of PMB ethers 1.

To a re-sealable pressure tube (13 x 100 mm) with a tiny magnetic stir bar was charged with PMB ether **1** (0.25 mmol, 1.0 equiv), ammonium persulfate (57 mg, 1.0 equiv) and 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes) (1.0 mg, 0.0025 mmol, 1.0 mol %). Then, a mixture of air saturated solvents (2.5 mL, 0.1 M for **1**) of acetonitrile/water in a ratio of 5:1 was added. The reaction mixture was irradiating with 2 x 5W blue LEDs at room temperature (20 ~ 30 ^{o}C) under an air balloon using customized reactor. After the reaction was completed (monitored by TLC analysis), the mixture was poured into saturated aqueous $NaHCO_3$ (20 mL). The mixture was extracted with ethyl acetate (three times), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography with ethyl acetate/hexanes or DCM/methanol as the eluent to give the corresponding alcohol **2**.

3-Phenyl propan-1-ol (2a).[6b] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **2a** was obtained as a colorless liquid (26.4 mg, 77% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H), 3.68 (t, J = 6.4 Hz, 2H), 2.71 (t, J = 8.7, 6.7 Hz, 2H), 1.98 – 1.81 (m, 2H), 1.37 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9, 128.6, 128.5, 126.0, 62.4, 34.4, 32.2.

Decan-1-ol (2b).[17] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **2b** was obtained as a colorless liquid (34.5 mg, 87% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.6 Hz, 2H), 1.62 – 1.50 (m, 2H), 1.44 (s, 1H), 1.37 – 1.20 (m, 14H), 0.86 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 62.9, 32.8, 32.0, 29.7, 29.7, 29.6, 29.4, 25.9, 22.8, 14.2.

2-Methyl-1-phenylpropan-2-ol (2c).[6b] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **2c** was obtained as a colorless liquid (27.8 mg, 74% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.19 (m, 5H), 2.77 (s, 2H), 1.23 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9, 130.6, 128.3, 126.6, 70.9, 49.8, 29.3.

L-Menthol (2d).[6a] Following the general procedure using 1% ethyl acetate in dchloromethane as eluant, **2d** was obtained as a white solid (33 mg, 84% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.41 (ddd, *J* = 10.8, 9.9, 4.3 Hz, 1H), 2.17 (heptd, *J* = 7.0, 2.8 Hz, 1H), 2.03 – 1.89 (m, 1H), 1.73 – 1.54 (m, 2H), 1.53 – 1.30 (m, 2H), 1.19 – 1.04 (m, 1H), 1.07 – 0.82 (m, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 71.7, 50.3, 45.2, 34.7, 31.8, 26.0, 23.3, 22.4, 21.2, 16.2.

Cyclododecanol (2e).[18] Following the general procedure using 1% ethyl acetate in dchloromethane as eluant, **2e** was obtained as a white solid (37.8 mg, 82% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (tt, *J* = 7.3, 3.6 Hz, 1H), 1.75 – 1.57 (m, 2H), 1.46 – 1.28 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.3, 32.6, 24.3, 23.9, 23.5, 23.4, 21.1.

Adamantan-1-ol (2f).[6b] Following the general procedure using 1% ethyl acetate in dichloromethane as eluant, **2f** was obtained as a white solid (36.2 mg, 95% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.23 – 2.05 (m, 3H), 1.71 (d, *J* = 2.9 Hz, 6H), 1.66 – 1.58 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 68.3, 45.4, 36.2, 30.8.

5-α-Cholestan-3β-ol (2g).[19] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **2g** was obtained as a white solid (86.5 mg, 89% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59 (tt, *J* = 10.6, 4.8 Hz, 1H), 1.96 (dt, *J* = 12.5, 3.4 Hz, 1H), 1.85 – 0.94 (m, 30H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 1.4 Hz, 3H), 0.85 (d, *J* = 1.4 Hz, 3H), 0.80 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 71.5, 56.6, 56.4, 54.5, 45.0, 42.7, 40.2, 39.6, 38.3, 37.1, 36.3, 35.9, 35.6, 35.6, 32.2, 31.7, 28.9, 28.4, 28.1, 24.4, 24.0, 23.0, 22.7, 21.4, 18.8, 12.5, 12.2.

5-(Benzyloxy)pentan-1-ol (2h).[20] Following the general procedure using 7% ethyl acetate in hexanes as eluant, **2h** was obtained as a colorless liquid (34 mg, 70% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 4.51 (s, 2H), 3.65 (t, *J* = 6.4 Hz, 2H), 3.49 (t, *J* = 6.4 Hz, 2H), 1.72 – 1.59 (m, 4H), 1.51 – 1.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 128.4, 127.8, 127.6, 73.0, 70.4, 62.7, 32.5, 29.5, 22.5.

5-Hydroxypentyl acetate (2i).[20] Following the general procedure using 10% ethyl acetate in hexanes as eluant, **2i** was obtained as a colorless liquid (32.5 mg, 89% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07 (t, *J* = 6.6 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.05 (s, 3H), 1.74 – 1.59 (m, 4H), 1.51 – 1.35 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 64.6, 62.8, 32.4, 28.5, 22.4, 21.2.

6-Hydroxyhexyl benzoate (2j).[20] Following the general procedure using 7% ethyl acetate in hexanes as eluant, **2j** was obtained as a colorless liquid (41.2 mg, 74% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 – 7.97 (m, 2H), 7.62 – 7.50 (m, 1H), 7.49 – 7.38 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 3.65 (t, *J* = 6.5 Hz, 2H), 1.86 – 1.71 (m, 2H), 1.66 – 1.37 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 133.0, 130.5, 129.6, 128.5, 65.1, 62.9, 32.7, 28.8, 26.0, 25.5.

6-Hydroxyhexyl pivalate (2k).[6a] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **2k** was obtained as a colorless liquid (42.5 mg, 84% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.01 (t, *J* = 6.5 Hz, 2H), 3.59 (t, *J* = 6.5 Hz, 2H), 1.99 (s, 1H), 1.66 – 1.47 (m, 4H), 1.43 – 1.26 (m, 4H), 1.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 64.4, 62.7, 38.8, 32.6, 28.6, 27.2, 25.8, 25.4.

6-((Tetrahydro-2H-pyran-2-yl)oxy)hexan-1-ol (2l).[6a] Following the general procedure using 15% ethyl acetate in

hexanes as eluant, **2l** was obtained as a colorless liquid (35.4 mg, 70% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.57 (dd, *J* = 4.5, 2.7 Hz, 1H), 3.93 – 3.81 (m, 1H), 3.74 (dt, *J* = 9.6, 6.8 Hz, 1H), 3.64 (t, *J* = 6.6 Hz, 2H), 3.55 – 3.45 (m, 1H), 3.39 (dt, *J* = 9.6, 6.5 Hz, 1H), 1.90 – 1.77 (m, 1H), 1.73 (dt, *J* = 12.5, 2.7 Hz, 1H), 1.67 – 1.48 (m, 8H), 1.44 – 1.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 98.9, 77.6, 77.2, 76.7, 67.6, 62.8, 62.5, 32.7, 30.8, 29.7, 26.1, 25.6, 25.5, 19.7.

5-((Tert-butyldimethylsilyl)oxy)pentan-1-ol (2m).[6a] Following the general procedure using 10% ethyl acetate in hexanes as eluant, **2m** was obtained as a colorless liquid (39.3 mg, 72% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 – 3.55 (m, 4H), 1.68 (s, 1H), 1.63 – 1.48 (m, 4H), 1.45 – 1.33 (m, 2H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.3, 63.0, 32.6, 32.6, 26.1, 22.1, 18.5, -5.2.

6-((Tert-butyldiphenylsilyl)oxy)hexan-1-ol (2n).[6b] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **2n** was obtained as a colorless liquid (74 mg, 83% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 4H), 7.46 – 7.32 (m, 6H), 3.72 – 3.56 (m, 4H), 1.65 – 1.35 (m, 9H), 1.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7, 134.1, 129.6, 127.7, 63.9, 62.9, 32.5, 32.4, 27.0, 22.1, 19.3.

Tert-butyl (3-hydroxypropyl)carbamate (2o).[20] Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2o** was obtained as a colorless liquid (32 mg, 73% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.78 (s, 1H), 3.65 (t, *J* = 5.7 Hz, 2H), 3.28 (q, *J* = 6.3 Hz, 2H), 1.65 (p, *J* = 5.8 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 79.8, 59.3, 36.9, 33.1, 28.5.

N-(3-Hydroxypropyl)benzamide (2p).[21] Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2p** was obtained as a colorless liquid (42.5 mg, 95% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 2H), 7.53 – 7.45 (m, 1H), 7.44 – 7.36 (m, 2H), 6.96 (s, 1H), 3.70 (d, 2H), 3.60 (q, *J* = 6.1 Hz, 2H), 2.74 (s, 1H), 1.78 (tt, *J* = 6.1, 4.9, 1.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 134.2, 131.7, 128.7, 127.0, 59.9, 37.3, 32.1.

6-(Benzyloxy)-6-methylheptan-1-ol (2q).[22] Following the general procedure using 10% ethyl acetate in hexanes as eluant, **2q** was obtained as a colorless liquid (34.3 mg, 58% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 4H), 4.41 (s, 2H), 3.65 (t, *J* = 6.6 Hz, 2H), 1.65 – 1.52 (m, 4H), 1.48 – 1.34 (m, 4H), 1.24 (s, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 128.4, 127.4, 127.2, 75.3, 63.8, 63.2, 40.6, 32.9, 26.4, 25.8, 23.9.

7-(Benzyloxy)heptan-2-ol (2r).[23] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **2r** was obtained as a colorless liquid (42.3 mg, 76% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 5H), 4.50 (s, 2H), 3.88 – 3.69 (m, 1H), 3.47 (t, *J* = 6.6 Hz, 2H), 1.72 – 1.56 (m, 2H), 1.50 – 1.30 (m, 6H), 1.18 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 128.5, 127.8, 127.6, 73.0, 70.4, 68.2, 39.4, 29.8, 26.3, 25.7, 23.6.

9-Decen-1-ol (2s).[24] Following the general procedure using 1% ethyl acetate in dichloromethane as eluant, **2s** was obtained as a colorless liquid (31.5 mg, 80% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.09 – 4.83 (m, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 2.16 – 1.92 (m, 2H), 1.70 (s, 1H), 1.63 – 1.48 (m, 2H), 1.43 – 1.24 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3, 114.3, 63.1, 33.9, 32.9, 29.6, 29.5, 29.2, 29.0, 25.8.

(Z)-dec-4-en-1-ol(2t).[25] Following the general procedure using 1% ethyl acetate in dichloromethane as eluant, **2t** was obtained as a colorless liquid (28.5 mg, 73% yield); ^{1}H NMR (300 MHz, $CDCl_3$) 5.46 – 5.29 (m, 2H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.18 – 2.07 (m, 2H), 2.02 (m, *J* = 6.0, 2.4 Hz, 2H), 1.63 (q, *J* = 7.9, 6.7 Hz, 2H), 1.43 (br s, 1H), 1.41 – 1.20 (m, 6H), 0.94 – 0.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.0, 128.9, 62.8, 32.8, 31.6, 29.5, 27.3, 23.7, 22.7, 14.2.

4-Hydroxybutyl acrylate (2u).[26] Following the general procedure using 3% ethyl acetate in dichloromethane as eluant, **2u** was obtained as a colorless liquid (16.2 mg, 45% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.39 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.10 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.81 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.18 (t, *J* = 6.4 Hz, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 1.79 – 1.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 130.8, 128.6, 64.5, 62.4, 29.2, 25.2.

1-Phenylbut-3-en-2-ol (2v).[27] Following the general procedure using 1% ethyl acetate in dichloromethane as eluant, **2v** was obtained as a colorless liquid (26.3 mg, 62% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 5H), 5.94 (ddd, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.32 – 5.08 (m, 2H), 4.42 – 4.30 (m, 1H), 2.94 – 2.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 137.7, 129.6, 128.5, 126.6, 115.0, 73.7, 43.8.

Dec-9-yn-1-ol (2w).[28] Following the general procedure using 1% ethyl acetate in dichloromethane as eluant, **2w** was obtained as a colorless liquid (30 mg, 78% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.55 (t, *J* = 6.7 Hz, 2H), 2.26 (s, 1H), 2.12 (td, *J* = 7.0, 2.7 Hz, 2H), 1.90 (t, *J* = 2.7 Hz, 1H), 1.56 – 1.39 (m, 4H), 1.40 – 1.15 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 84.7, 68.1, 62.7, 32.7, 29.3, 29.0, 28.6, 28.4, 25.7, 18.3.

1-Ehynylcyclohexan-1-ol (2x).[6b] Following the general procedure using 1% ethyl acetate in dichloromethane as eluant, **2x** was obtained as a white solid (27.3 mg, 88% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 1H), 1.95 – 1.84 (m, 3H), 1.76 – 1.47 (m, 6H), 1.36 – 1.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 87.8, 72.2, 68.7, 39.9, 25.2, 23.3.

10-Hydroxydecanal (2y).[29] Following the general procedure using 1% methanol in dichloromethane as eluant, **2y** was obtained as a white solid (32.7 mg, 76% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.8 Hz, 1H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.42 (td, *J* = 7.3, 1.8 Hz, 2H), 1.69 – 1.49 (m, 6H), 1.42 – 1.26 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.1, 63.1, 44.0, 32.9, 29.4, 29.3, 29.2, 25.8, 22.2.

7-Hydroxyheptan-2-one (2z).[30] Following the general procedure using 1% methanol in dichloromethane as eluant, **2z** was obtained as a colorless liquid (26.4 mg, 81% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.61 (t, *J* = 6.5 Hz, 2H), 2.42 (t, *J* = 7.3 Hz, 2H), 2.11 (s, 3H), 1.68 – 1.44 (m, 3H), 1.42 – 1.26 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.5, 62.6, 43.7, 32.5, 30.0, 25.3, 23.5.

8-(Oxiran-2-yl)octan-1-ol (2aa).[31] Following the general procedure using 1% methanol in dichloromethane as eluant, **2aa** was obtained as a colorless liquid (35.3 mg, 82% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.64 (t, *J* = 6.6 Hz, 2H), 2.92 (ddd, *J* = 5.3, 2.8 Hz, 1H), 2.80 – 2.71 (m, 1H), 2.48 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.66 – 1.23 (m, 14H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.1, 52.6, 47.3, 32.9, 32.6, 29.6, 29.5, 29.4, 26.1, 25.8.

(Tetrahydrofuran-2-yl)methanol (2ab).[32] Following the general procedure using 1% methanol in dichloromethane as eluant, **2ab** was obtained as a colorless liquid (17.5 mg, 62% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.09 – 3.89 (m, 1H), 3.89 – 3.66 (m, 1H), 3.69 – 3.53 (m, 1H), 3.45 (dd, *J* = 11.6, 6.1 Hz, 1H), 2.80 (br s, 1H), 1.99 – 1.72 (m, 3H), 1.70 – 1.46 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 79.6, 68.3, 64.9, 27.2, 26.0.

Tert-butyl 2-(hydroxymethyl)pyrrolidine-1-carboxylate (2ac).[32] Following the general procedure using 1% methanol in dichloromethane as eluant, **2ac** was obtained as a colorless liquid (43 mg, 85% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.94 (br s, 1H), 3.67 – 3.52 (m, 2H), 3.52 – 3.37 (m, 1H), 3.37 – 3.23 (m, 1H), 2.09 – 1.91 (m, 1H), 1.92 – 1.65 (m, 2H), 1.65 – 1.49 (m, 1H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 80.4, 67.9, 60.3, 47.7, 28.9, 28.6, 24.2.

Pyrrolidin-2-ylmethanol (2ad).[33] Following the general procedure, the yield was determined by ^{1}H NMR (DMF as internal standard); ^{1}H NMR (300 MHz, D_2O) δ 3.76 – 3.66 (m, 1H), 3.64 – 3.43 (m, 2H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.03 – 1.76 (m, 3H), 1.65 – 1.47 (m, 1H).

3-Aminopropan-1-ol (2ae).[34] Following the general procedure, the yield was determined by ^{1}H NMR (DMF as internal standard); ^{1}H NMR (300 MHz, D_2O) δ 3.65 (t, *J* = 6.1 Hz, 2H), 3.04 (t, *J* = 7.4 Hz, 2H), 1.84 (p, *J* = 6.4 Hz, 2H).

Procedure for the gram scale synthesis of 2a.

An oven-dried 100 mL round bottomed flask containing a magnetic stir bar was charged with **1a** (1.1g, 4.29 mmol), $(NH_4)_2S_2O_8$ (979 mg, 1.0 equiv) and Acr^+-Mes (17.6 mg, 1.0 mol %) under air atmosphere. Then, a mixture of solvents (43 mL, 0.1 M for **1a**) of acetonitrile/water in a ratio of 5:1 was added to that round bottomed flask. The resultant mixture was irradiating with Kessil 40 W blue LEDs under constant stirring condition at room temperature for 9 h. After finish reaction, the mixture was poured into saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate (three times), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the corresponding alcohol product **2a** (435 mg, 74%).

Procedure for the gram scale synthesis of 2e.

An oven-dried 100 mL round bottomed flask containing a magnetic stir bar was charged with **1e** (1.0g, 3.28 mmol), $(NH_4)_2S_2O_8$ (749 mg, 1.0 equiv) and Acr^+-Mes (13.5 mg, 1.0 mol %) under air atmosphere. Then, a mixture of solvents (43 mL, 0.1 M for **1a**) of acetonitrile/water in a ratio of 5:1 was added to that round bottomed flask. The resultant mixture was irradiating with Kessil 40 W blue LEDs under constant stirring condition at room temperature for 6 h. After finish reaction, the mixture was poured into saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate (three times), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the corresponding alcohol product **2e** (484 mg, 80%).

General procedure A for the synthesis of *p*-methoxybenzyl ethers (1a-ac)

A flame dried round bottom flask equipped with a magnetic stir bar was charged with alcohol, dry THF 0.2 M and cooled to 0 ^oC. The mixture was added NaH (60% dispersion in mineral oil) (2 eq.) and stirred at room temperature for 30 minutes. PMBCl 1.2 eq. and TBAI 0.1 eq. were added to reaction mixture. After the reaction was completed (monitored by TLC analysis), the mixture was poured into H_2O and ethyl acetate. The mixture was extracted with ethyl acetate (three times), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography with ethyl acetate/hexanes as the eluent to give the corresponding PMB ether **1**.

1-Methoxy-4-((3-phenylpropoxy)methyl)benzene (1a).[6b] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1a** was obtained as a colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.13 (m, 7H), 6.88 (d, 2H), 4.44 (s, 2H), 3.81 (s, 3H), 3.46 (t, J = 6.4 Hz, 2H), 2.70 (t, 2H), 2.01 – 1.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 142.2, 130.8, 129.4, 128.6, 128.4, 125.9, 113.9, 72.7, 69.3, 55.4, 32.5, 31.5.

1-((Decyloxy)methyl)-4-methoxybenzene (1b).[17] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1b** was obtained as a colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 2H), 6.87 (d, 2H), 4.42 (s, 2H), 3.80 (s, 3H), 3.43 (t, J = 6.7 Hz, 2H), 1.67 – 1.45 (m, 4H), 1.25 (s, 12H), 0.87 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 130.9, 129.4, 113.9, 72.6, 70.4, 55.4, 32.0, 29.9, 29.8, 29.7, 29.6, 29.5, 26.4, 22.8, 14.3.

1-Methoxy-4-(((2-Methyl-1-phenylpropan-2-yl)oxy)methyl)benzene (1c).[6b] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1g** was obtained as a colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 7H), 6.93 – 6.85 (m, 2H), 4.47 (s, 2H), 3.81 (s, 3H), 2.88 (s, 2H), 1.24 (s, 6H);^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 138.6, 132.0, 130.8, 128.8, 127.9, 126.2, 113.8, 75.9, 63.6, 55.4, 47.4, 25.4.

1-((((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)methyl)-4-methoxybenzene (1d).[6a] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1d** was obtained as a colorless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, 2H), 6.86 (d, 2H), 4.58 (d, J = 11.1 Hz, 1H), 4.33 (d, J = 11.1 Hz, 1H), 3.80 (s, 3H), 3.14 (td, J = 10.6, 4.1 Hz, 1H), 2.35 – 2.13 (m, 2H), 1.70 – 1.61 (m, 2H), 1.40 – 1.21 (m, 2H), 1.04 – 0.77 (m, 9H), 0.69 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 131.4, 129.5, 113.8, 78.5, 70.2, 55.4, 48.4, 40.5, 34.7, 31.7, 25.6, 23.4, 22.5, 21.2, 16.2.

((4-Methoxybenzyl)oxy)cyclododecane (1e).[35] Following the general procedure using 5% ethyl acetate in hexanes as

eluant, **1e** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, 2H), 6.87 (d, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.58 – 3.43 (m, 1H), 1.74 – 1.46 (m, 4H), 1.43 – 1.21 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 131.5, 129.4, 113.8, 76.0, 70.0, 55.4, 29.0, 24.7, 24.3, 23.4, 23.2, 20.9.

(3s,5s,7s)-1-((4-Methoxybenzyl)oxy)adamantane (1f).[6b] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1f** was obtained as a white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, 2H), 6.87 (d, 2H), 4.44 (s, 2H), 3.79 (s, 3H), 2.24 – 2.07 (m, 2H), 1.85 (d, 6H), 1.69 – 1.50 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 132.3, 129.1, 113.8, 72.7, 62.1, 55.4, 41.9, 36.6, 30.7.

(3S,5S,8R,9S,10S,13R,14S,17R)-3-((4-Methoxybenzyl)oxy)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene (1g).[36] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1g** was obtained as a white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 2H), 6.94 – 6.83 (m, 2H), 4.50 (s, 2H), 3.82 (s, 3H), 3.42 – 3.23 (m, 1H), 2.08 – 0.96 (m, 30H), 0.92 (d, J = 6.5 Hz, 3H), 0.90 (d, J = 1.4 Hz, 3H), 0.88 (d, J = 1.4 Hz, 3H), 0.82 (s, 4H), 0.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 131.4, 129.3, 113.9, 77.9, 69.5, 56.6, 56.4, 55.4, 54.6, 45.0, 42.7, 40.2, 39.7, 37.2, 36.3, 35.9, 35.6, 35.0, 32.3, 29.0, 28.4, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.4, 18.8, 12.4, 12.2.

1-(((5-(Benzyloxy)pentyl)oxy)methyl)-4-methoxybenzene (1h).[20] Following the general procedure using 8% ethyl acetate in hexanes as eluant, **1h** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, CDCl3) δ 7.38 – 7.28 (m, 5H), 7.25 (d, J = 8.6 Hz, 2H), 6.87 (d, 2H), 4.49 (s, 2H), 4.42 (s, 2H), 3.80 (s, 3H), 3.45 (dt, J = 8.3, 6.6 Hz, 4H), 1.62 (tt, J = 6.6, 3.3 Hz, 4H), 1.51 – 1.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 138.8, 130.9, 129.4, 128.5, 127.8, 127.6, 113.9, 73.0, 72.7, 70.5, 70.1, 55.4, 29.7, 23.0.

5-((4-Methoxybenzyl)oxy)pentyl acetate (1i).[20] Following the general procedure using 7% ethyl acetate in hexanes as eluant, **1i** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, 2H), 6.87 (d, 2H), 4.43 (s, 2H), 4.05 (t, J = 6.6 Hz, 2H), 3.80 (s, 3H), 3.44 (t, J = 6.4 Hz, 2H), 2.04 (s, 3H), 1.70 – 1.60 (m, 4H), 1.51 – 1.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 159.2, 130.7, 129.4, 113.9, 72.7, 69.9, 64.6, 55.4, 29.5, 28.5, 22.8, 21.1.

6-((4-Methoxybenzyl)oxy)hexyl benzoate (1j).[20] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1j** was obtained as a slightly yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 – 8.13 (m, 1H), 8.08 – 8.01 (m, 2H), 7.48 – 7.39 (m, 2H), 7.31 – 7.22 (m, 2H), 6.94 – 6.81 (m, 2H), 4.43 (s, 2H), 4.31 (t, J = 6.6 Hz, 2H), 3.80 (s, 3H), 3.45 (t, J = 6.5 Hz, 2H), 1.76 (d, J = 7.0 Hz, 2H), 1.63 (t, J = 6.7 Hz, 2H), 1.51 – 1.38 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 132.9, 130.7, 130.6, 129.7, 129.4, 129.0, 128.5, 113.9, 72.7, 70.1, 65.2, 55.4, 29.8, 28.8, 26.1.

6-((4-Methoxybenzyl)oxy)hexyl pivalate (1k).[6a] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1k** was obtained as a slightly yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.20 (dd, 2H), 6.93 – 6.82 (dd, 2H), 4.43 (s, 2H), 4.04 (t, J = 6.6 Hz, 2H), 3.80 (s, 3H), 3.43 (t, J = 6.5 Hz, 2H), 1.62 (m, J = 4.5 Hz, 4H), 1.41 – 1.32 (m, 4H), 1.19 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 159.2, 130.8, 129.4, 113.9, 72.7, 70.1, 64.5, 55.4, 38.8, 29.8, 28.7, 27.3, 26.0, 25.9.

2-((6-((4-Methoxybenzyl)oxy)hexyl)oxy)tetrahydro-2H-pyran (1l).[6a] Following the general procedure using 10% ethyl acetate in hexanes as eluant, **1l** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 2H), 6.91 – 6.84 (m, 2H), 4.56 (t, J = 4.6, 2.7 Hz, 1H), 4.43 (s, 2H), 3.91 – 3.82 (m, 1H), 3.80 (s, 3H), 3.78 – 3.67 (m, 1H), 3.55 – 3.46 (m, 1H), 3.43 (t, J = 6.6 Hz, 2H), 3.40 – 3.32 (m, 1H), 1.88 – 1.64 (m, 3H), 1.64 – 1.45 (m, 7H), 1.43 – 1.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 130.9, 129.3, 113.8, 99.0, 72.6, 70.2, 67.7, 62.5, 55.4, 30.9, 29.8, 26.2, 26.2, 25.6, 19.8.

Tert-butyl((5-((4-methoxybenzyl)oxy)pentyl)oxy)dimethylsilane (1m).[6a] Following the general procedure using 6% ethyl acetate in hexanes as eluant, **1m** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 2H), 6.91 – 6.84 (m, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.60 (t, J = 6.5 Hz, 2H), 3.44 (t, J = 6.6 Hz, 2H), 1.68 – 1.49

(m, 4H), 1.49 – 1.33 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 130.9, 129.3, 113.9, 72.7, 70.2, 63.3, 55.4, 32.8, 29.7, 26.1, 22.6, 18.5, -5.1.

Tert-butyl((6-((4-methoxybenzyl)oxy)hexyl)oxy)diphenylsilane (1n).[6b] Following the general procedure using 7% ethyl acetate in hexanes as eluant, **1n** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.62 (m, 4H), 7.50 – 7.34 (m, 6H), 7.28 (d, *J* = 6.3 Hz, 2H), 6.89 (d, *J* = 9.1, 2.5 Hz, 2H), 4.44 (s, 2H), 3.82 (s, 3H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 1.68 – 1.53 (m, 6H), 1.52 – 1.37 (m, 2H), 1.06 (d, *J* = 2.7 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 135.7, 134.2, 130.9, 129.6, 129.3, 127.7, 113.9, 72.6, 70.2, 64.0, 55.4, 32.5, 29.6, 27.0, 22.6, 19.4.

Tert-butyl (3-((4-methoxybenzyl)oxy)propyl)carbamate (1o).[20] Following the general procedure using 10% ethyl acetate in hexanes as eluant, **1o** was obtained as a slightly yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (dd, 2H), 6.88 (dd, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.51 (t, *J* = 5.9 Hz, 2H), 3.23 (tt, *J* = 6.2 Hz, 2H), 1.77 (tt, *J* = 6.2 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 156.1, 130.5, 129.4, 113.9, 79.0, 72.8, 68.5, 55.4, 38.8, 29.8, 28.5.

N-(3-((4-Methoxybenzyl)oxy)propyl)benzamide (1p). Following the general procedure using 8% ethyl acetate in hexanes as eluant, **1p** was obtained as a slightly yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.53 (m, 2H), 7.52 – 7.37 (m, 1H), 7.36 – 7.23 (m, 4H), 7.11 (s, 1H), 6.99 – 6.75 (m, 2H), 4.48 (s, 2H), 3.83 (s, 3H), 3.72 (t, *J* = 5.5 Hz, 2H), 3.67 – 3.52 (m, 2H), 1.94 (p, *J* = 5.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 159.5, 134.5, 131.2, 130.2, 129.8, 128.4, 126.9, 114.0, 73.3, 70.3, 55.4, 39.5, 28.8; HRMS m/z (EI): calcd. For $C_{18}H_{21}NO_3$ (M^+) 299.1521, found 299.1524.

1-(((6-(Benzyloxy)-6-methylheptyl)oxy)methyl)-4-methoxybenzene (1q). Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1q** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.19 (m, 7H), 6.92 – 6.84 (m, 2H), 4.44 (s, 2H), 4.42 (s, 2H), 3.80 (s, 3H), 3.45 (t, *J* = 6.6, 3.5 Hz, 2H), 1.70 – 1.53 (m, 4H), 1.44 – 1.36 (m, 4H), 1.25 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 140.0, 130.9, 129.3, 128.4, 127.4, 127.2, 113.8, 75.3, 72.6, 70.2, 63.7, 55.4, 40.5, 29.9, 26.9, 25.8, 23.9; HRMS m/z (EI): calcd. For $C_{23}H_{32}O_3$ (M^+) 356.2351, found 356.2347.

1-(((7-(Benzyloxy)heptan-2-yl)oxy)methyl)-4-methoxybenzene (1r). Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1r** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 7H), 6.91 – 6.83 (m, 2H), 4.55 – 4.34 (m, 4H), 3.80 (s, 3H), 3.54 – 3.40 (m, 3H), 1.69 – 1.51 (m, 4H), 1.39 (tdd, *J* = 8.9, 5.4, 3.1 Hz, 5H), 1.17 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 138.8, 131.3, 129.3, 128.5, 127.7, 127.6, 113.8, 74.6, 73.0, 70.5, 70.0, 55.4, 36.7, 29.9, 26.4, 25.5, 19.8; HRMS m/z (EI): calcd. For $C_{22}H_{30}O_3$ (M^+) 342.2195, found 356.2197.

1-((Dec-9-en-1-yloxy)methyl)-4-methoxybenzene (1s).[37] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1s** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 6.3, 2.7 Hz, 2H), 6.88 (d, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05 – 4.87 (m, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.43 (t, *J* = 6.6 Hz, 2H), 2.10 – 1.97 (m, 2H), 1.58 (dd, *J* = 11.7, 4.8 Hz, 2H), 1.44 – 1.21 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 139.4, 130.9, 129.4, 114.3, 113.9, 77.6, 77.2, 76.7, 72.6, 70.3, 55.4, 33.9, 29.9, 29.6, 29.2, 29.0, 26.3.

(Z)-1-((dec-4-en-1-yloxy)methyl)-4-methoxybenzene (1t). Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1t** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 2H), 6.92 – 6.82 (m, 2H), 5.46 – 5.26 (m, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.17 – 1.96 (m, 4H), 1.73 – 1.60 (m, 2H), 1.41 – 1.21 (m, 6H), 0.88 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 130.9, 130.7, 129.4, 129.1, 113.8, 72.7, 69.7, 55.4, 31.7, 29.9, 29.5, 27.3, 24.0, 22.7, 14.2.

4-((4-methoxybenzyl)oxy)butyl acrylate (1u).[26] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1u** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 2H), 6.92 – 6.80 (m, 2H),

6.39 (dd, J = 17.3, 1.6 Hz, 1H), 6.11 (dd, J = 17.3, 10.4 Hz, 1H), 5.81 (dd, J = 10.4, 1.5 Hz, 1H), 4.43 (s, 2H), 4.17 (t, J = 6.3 Hz, 2H), 3.80 (s, 4H), 3.48 (t, J = 6.1 Hz, 2H), 1.83 – 1.63 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 159.3, 130.7, 129.6, 129.4, 128.7, 113.9, 72.7, 69.6, 64.5, 55.4, 26.4, 25.7.

1-methoxy-4-(((1-phenylbut-3-en-2-yl)oxy)methyl)benzene (1v).[38] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1v** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.17 (m, 5H), 7.15 – 7.04 (m, 2H), 6.87 – 6.77 (m, 2H), 5.77 (ddd, J = 17.1, 10.4, 7.5 Hz, 1H), 5.28 – 5.08 (m, 2H), 4.50 (d, J = 11.5 Hz, 1H), 4.25 (d, J = 11.6 Hz, 1H), 3.94 (q, J = 7.5, 5.8, 0.9 Hz, 1H), 3.79 (s, 3H), 3.03 – 2.72 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 138.5, 138.5, 130.8, 129.8, 129.3, 128.2, 126.2, 117.4, 113.8, 81.2, 70.0, 55.4, 42.4.

1-((dec-9-yn-1-yloxy)methyl)-4-methoxybenzene (1w).[28] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1w** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 2H), 6.97 – 6.81 (m, 2H), 4.45 (s, 2H), 3.83 (s, 3H), 3.45 (t, J = 6.6 Hz, 2H), 2.20 (td, J = 7.1, 2.6 Hz, 2H), 1.96 (t, J = 2.6 Hz, 1H), 1.70 – 1.24 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 130.9, 129.4, 113.9, 84.9, 72.7, 70.3, 68.2, 55.4, 29.9, 29.5, 29.2, 28.8, 28.6, 26.3, 18.5.

1-(((1-ethynylcyclohexyl)oxy)methyl)-4-methoxybenzene (1x).[6b] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1x** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 6.91 – 6.84 (m, 2H), 4.58 (s, 2H), 3.80 (s, 3H), 2.52 (s, 1H), 2.02 – 1.90 (m, 2H), 1.77 – 1.59 (m, 5H), 1.54 – 1.23 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 131.3, 129.4, 113.8, 85.6, 73.9, 65.3, 55.4, 37.3, 25.5, 22.8.

10-((4-methoxybenzyl)oxy)decanal (1y).[29] Following the general procedure using 8% ethyl acetate in hexanes as eluant, **1y** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.75 (t, J = 1.9 Hz, 1H), 7.36 – 7.18 (m, 2H), 6.95 – 6.81 (m, 2H), 4.42 (s, 2H), 3.80 (s, 3H), 3.42 (t, J = 6.6 Hz, 2H), 2.41 (td, J = 7.3, 1.9 Hz, 2H), 1.70 – 1.51 (m, 4H), 1.46 – 1.19 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.1, 159.2, 130.9, 129.4, 113.9, 72.7, 70.3, 55.4, 44.0, 29.9, 29.4, 29.4, 29.2, 26.3, 22.2.

7-((4-methoxybenzyl)oxy)heptan-2-one (1z).[39] Following the general procedure using 9% ethyl acetate in hexanes as eluant, **1z** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 6.90 – 6.84 (m, 2H), 4.42 (s, 2H), 3.80 (s, 3H), 3.43 (t, J = 6.5 Hz, 2H), 2.42 (t, J = 7.4 Hz, 2H), 2.13 (s, J = 0.5 Hz, 3H), 1.65 – 1.52 (m, 4H), 1.42 – 1.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.3, 159.2, 130.8, 129.4, 113.9, 72.7, 70.0, 55.4, 43.8, 30.0, 29.7, 25.9, 23.7.

2-(8-((4-methoxybenzyl)oxy)octyl)oxirane (1aa).[40] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1aa** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 2H), 6.91 – 6.82 (m, 2H), 4.42 (s, 2H), 3.80 (s, 3H), 3.43 (t, J = 6.6 Hz, 2H), 2.96 – 2.83 (m, 1H), 2.81 – 2.69 (m, 1H), 2.51 – 2.39 (m, 1H), 1.68 – 1.24 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 130.8, 129.3, 113.7, 72.5, 70.2, 55.3, 52.5, 47.2, 32.5, 29.8, 29.5, 29.4, 26.2, 26.0.

2-(((4-methoxybenzyl)oxy)methyl)tetrahydrofuran (1ab).[32] Following the general procedure using 5% ethyl acetate in hexanes as eluant, **1ab** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 6.91 – 6.84 (m, 2H), 4.58 – 4.43 (m, 2H), 4.13 – 4.01 (m, 1H), 3.94 – 3.84 (m, 1H), 3.80 (s, 2H), 3.78 – 3.72 (m, 1H), 3.44 (d, J = 5.3 Hz, 2H), 2.01 – 1.80 (m, 3H), 1.70 – 1.51 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 130.9, 129.3, 113.8, 72.6, 70.3, 55.4, 52.5, 47.3, 26.3, 26.1.

tert-butyl 2-(((4-methoxybenzyl)oxy)methyl)pyrrolidine-1-carboxylate (1ac).[32] Following the general procedure using 8% ethyl acetate in hexanes as eluant, **1ac** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$; 2 rotamers) δ 7.27 (m, J = 9.2, 2.7 Hz, 2H), 6.90 (m, J = 9.8, 3.5 Hz, 2H), 4.48 (s, J = 3.9 Hz, 2H), 4.13 – 3.87 (m, 1H), 3.82 (s, J = 3.8 Hz, 3H), 3.71 – 3.50 (m, 1H), 3.34 (s, 3H), 2.10 – 1.71 (m, 4H), 1.31 (s, 9H).

General procedure B for the synthesis of *p*-methoxybenzyl ethers (1ad-ae)

A round bottom flask equipped with a magnetic stir bar was charged with **1** (1 mmol) in MeOH (0.5 M). The mixture was added $TsOH{\cdot}H_2O$ (1 equiv.) and stirred at 40 °C for 3h. After the reaction was completed (monitored by TLC analysis), the mixture was poured into diethyl ether (10 mL) and 1N HCl (10 mL). The mixture was extracted with water (three times). Then the aqueous phase was neutralized using 1N NaOH (pH = 10~11). Aqueous layer was then extracted with ethyl acetate (three times), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was no further purification to give the corresponding PMB ether **1.**

2-(((4-methoxybenzyl)oxy)methyl)pyrrolidine (1ad).[41] Following the general procedure, **1ad** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 2H), 6.89 – 6.82 (m, 2H), 4.46 (s, 2H), 3.80 (s, 3H), 3.53 – 3.34 (m, 3H), 3.13 – 2.85 (m, 2H), 1.91 – 1.69 (m, 3H), 1.57 – 1.41 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 130.4, 129.5, 113.9, 73.0, 72.0, 58.2, 55.4, 46.3, 27.7, 24.9.

3-((4-methoxybenzyl)oxy)propan-1-amine (1ae).[42] Following the general procedure, **1ae** was obtained as a colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 2H), 6.91 – 6.83 (m, 2H), 4.42 (s, 2H), 3.80 (s, 3H), 3.52 (t, J = 6.2 Hz, 2H), 3.29 (t, J = 7.0 Hz, 2H), 1.99 – 1.89 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 130.8, 129.4, 113.9, 72.7, 68.2, 55.4, 48.3, 31.1.

Supporting Information

Photophysical measurements and mechanism studies; experimental procedures; spectroscopic data for deprotected alcohols (^{1}H NMR, ^{13}C NMR), including images of NMR spectra.

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