

Supporting Information for
Organo-photocatalytic C-H Bond Oxidation: An Operationally
Simple and Scalable Method to Prepare Ketones with Ambient Air

Ky V. Nguyen^{a*}, Van Thu Nguyen^a, Hieu Minh Tran^a, Phong V. Pham^{a*}

^a*Faculty of Chemistry, University of Science, Vietnam National University, Hanoi*

Phone: (+84) 963-398-889 (P. V. P.), (+84) 329-492-665 (K. V. N.)

E-mail: phvpham@hus.edu.vn

nvknguyen.hus@gmail.com

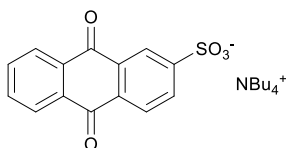
Table of Contents	Page
I. General Information	S1
II. Synthesis and Characterization of Catalysts	S2
III. Synthesis and Characterization of Alcohol Substrates	S4
IV. Synthesis and Characterization of Benzylic Substrates	S13
V. Synthesis and Characterization of Products from Oxidation of Alcohols	S17
VI. Synthesis and Characterization of Products from Benzylic Oxidation	S35
VII. Upscale Oxidations	S45
VIII. Mechanistic Investigation	S49
IX. References	S53
X. NMR Spectra	S54
I. General Information	

Commercial reagents were used without further purification unless otherwise indicated.

Acetone was purchased from Macron Fine Chemicals and used as received. Reactions under Argon atmosphere were performed with Schlenk apparatus. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator using an ice-water bath for volatile compounds. Chromatographic purification of products was accomplished by flash chromatography on silica gel according to the method of Still.¹ Thin-layer

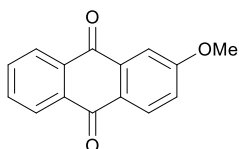
chromatography (TLC) was performed on Merk silica gel plates. Visualization of the developed chromatogram was performed by fluorescence quenching or potassium permanganate stains. ^1H , ^{13}C , and ^{19}F NMR spectra were recorded on a Bruker Advance-III 500 (500, 126, and 471 MHz) instrument at the Faculty of Chemistry, VNU University of Science or were recorded on a Bruker Advance Neo 600 (600, 151, 565 MHz) instrument at Vietnam Institute of Chemistry, Vietnam Academy of Science and Technology and are internally referenced to residual protic solvent signals (note: CDCl_3 referenced at δ 7.26 and 77.16 *ppm* respectively, DMSO-d_6 referenced at δ 2.50 and 39.52 *ppm* respectively, acetone- d_6 referenced at δ 2.05 and 29.84 *ppm* respectively). ^{13}C NMR spectra were recorded in JMOD mode which are the combination of ^{13}C and DEPT without losing quaternary ^{13}C signals. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, b = broad), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity, no special nomenclature is used for equivalent carbons. Data for ^{19}F NMR are reported in terms of chemical shift and multiplicity. 25 W 400-410 nm LEDs Lamps were purchased from Facai LED Zhaoming Co. Ltd. (website: <https://shop358870690.taobao.com/>).

II. Synthesis and Characterization of Catalysts



tetrabutylammonium anthraquinone-2-sulfonate (1a).

The title compound was prepared from an ion exchange reaction of sodium anthraquinone-2-sulfonate monohydrate and tetrabutylammonium chloride: To a 250 mL round-bottom flask was charged sodium anthraquinone-2-sulfonate monohydrate (2.437 g, 7.42 mmol), tetrabutylammonium chloride (1.876 g, 6.75 mmol), H₂O (12 mL), and CH₂Cl₂ (100 mL). The mixture was stirred at r.t. for 45 mins. The resultant mixture was filtered and layers were separated. The CH₂Cl₂ layer was washed with H₂O (100 mL x 2), dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation and later under high vacuum to afford the title compound as a yellow crystalline non-hygroscopic solid (3.325 g, 6.28 mmol, 93 %). ¹H NMR (500 MHz, CDCl₃) δ 8.79 (d, *J* = 1.7 Hz, 1H), 8.44 – 8.20 (m, 4H), 7.85 – 7.72 (m, 2H), 3.44 – 3.19 (m, 8H), 1.75 – 1.55 (m, 8H), 1.43 (h, *J* = 7.4 Hz, 8H), 0.98 (t, *J* = 7.4 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 182.90, 182.68, 153.11, 134.19, 134.16, 133.70, 133.60, 133.51, 133.38, 132.00, 127.45, 127.29, 127.25, 125.20, 58.80, 24.02, 19.77, 13.70.



2-methoxyanthraquinone (1b).

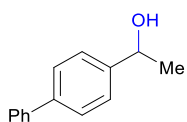
The title compound was prepared from the methylation of 2-hydroxyanthraquinone: To a 45-mL pressure-resistant tube was charged 2-hydroxyanthraquinone (1.000 g, 4.46 mmol), K₂CO₃ (0.998 g, 7.22 mmol), dimethyl sulfate (0.926 g, 7.34 mmol), and acetone (16 mL). The 45-mL pressure-resistant tube was sealed and heated in an oil bath in the dark at 65 °C for 2 days. Upon completion, the reaction mixture was concentrated by rotary evaporation. To the residue was added 100 mL H₂O. Extract the resultant mixture with CHCl₃ (80 mL

x 3). The CHCl_3 layers were combined, dried over Na_2SO_4 , and concentrated by rotary evaporation. The crude material was purified by silica column chromatography (hexane : $\text{CH}_2\text{Cl}_2 = 3:2$ to $1:1$ gradient elution) to afford the title compound as a yellow solid (0.966 g, 4.05 mmol, 91 %). ^1H NMR (500 MHz, CDCl_3) δ 8.38 – 8.14 (m, 3H), 7.86 – 7.64 (m, 3H), 7.35 – 7.14 (m, 1H), 3.98 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 183.37, 182.25, 164.49, 135.74, 134.28, 133.81, 133.78, 133.72, 129.88, 127.27, 121.29, 110.11, 56.09. Spectral properties are consistent with literature values.²

III. Synthesis and Characterization of Alcohol Substrates

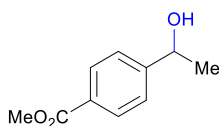
General Procedure A: Synthesis of Alcohols from Ketones

To a solution of ketones (0.15M, 1 equiv) in THF/ H_2O (4:1 v/v) solvent mixture at $0\text{ }^\circ\text{C}$ was added NaBH_4 (2 equiv) portion-wise over 15 mins. The mixture was stirred at $0\text{ }^\circ\text{C}$ for 15 mins, subsequently warmed to r.t. and stirred overnight. Upon completion, excess NaBH_4 was quenched by slow addition of 20 mL saturated NH_4Cl aqueous solution at $0\text{ }^\circ\text{C}$. To the resulting mixture, 80 mL water was added. The mixture was extracted with EtOAc (70 mL x 3). The organic layers were combined, dried over anhydrous Na_2SO_4 , filtered, and concentrated by rotary evaporation. The crude material was purified by filtration through a short column of silica gel rinsed with EtOAc or by flash column chromatography with silica gel as the stationary phase to yield the corresponding alcohols.



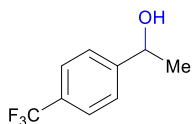
1-([1,1'-biphenyl]-4-yl)ethan-1-ol.

The title compound was prepared from the corresponding ketone (2.000 g, 10.19 mmol) following **General Procedure A**. The crude material was purified by filtration through a short column of 20 mL silica gel and rinsed by EtOAc to afford the title compound as a white solid (1.998 g, 10.08 mmol, 99 %). ¹H NMR (500 MHz, CDCl₃) δ 7.64 – 7.55 (m, 4H), 7.49 – 7.41 (m, 4H), 7.39 – 7.33 (m, 1H), 4.96 (q, *J* = 6.5 Hz, 1H), 1.95 (s, 1H), 1.55 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 144.95, 140.99, 140.58, 128.90, 127.40, 127.22, 125.99, 70.30, 25.28. Spectral properties are consistent with literature values.³



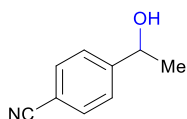
methyl 4-(1-hydroxyethyl)benzoate.

The title compound was prepared from the corresponding ketone (2.000 g, 11.22 mmol) following **General Procedure A**. The crude material was purified by silica column chromatography (hexanes : EtOAc = 5:1 to 2:1 gradient elution) to afford the title compound as a colorless liquid (1.920 g, 10.65 mmol, 95 %). ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 4.94 (q, *J* = 5.9 Hz, 1H), 3.89 (s, 3H), 2.19 (s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.11, 151.10, 129.96, 129.31, 125.41, 70.07, 52.18, 25.40. Spectral properties are consistent with literature values.⁴



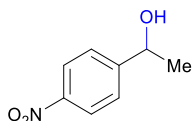
1-(4-(trifluoromethyl)phenyl)ethan-1-ol.

The title compound was prepared from the corresponding ketone (2.533 g, 13.46 mmol) following **General Procedure A**. The crude material was purified by filtration through a short column of 30 mL silica gel and rinsed by EtOAc to afford the title compound as a colorless liquid (2.400 g, 12.62 mmol, 94 %). ^1H NMR (500 MHz, CDCl_3) δ 7.59 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 4.94 (q, $J = 6.5$ Hz, 1H), 2.24 (s, 1H), 1.49 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 149.83, 129.75 (q, $J = 32.4$ Hz), 125.78, 125.56 (q, $J = 3.7$ Hz), 124.31 (q, $J = 272.4$ Hz), 69.93, 25.47. ^{19}F NMR (471 MHz, CDCl_3) δ -62.46. Spectral properties are consistent with literature values.⁵



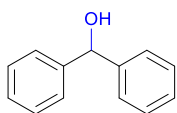
4-(1-hydroxyethyl)benzonitrile.

The title compound was prepared from the corresponding ketone (2.015 g, 13.88 mmol) following **General Procedure A**. The crude material was purified by silica column chromatography (hexanes : EtOAc = 2:1) to afford the title compound as a white solid (1.900 g, 12.91 mmol, 93 %). ^1H NMR (500 MHz, CDCl_3) δ 7.60 (d, $J = 8.3$ Hz, 2H), 7.47 (d, $J = 8.2$ Hz, 2H), 4.93 (qd, $J = 6.5, 3.4$ Hz, 1H), 2.37 (d, $J = 3.6$ Hz, 1H), 1.47 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.31, 132.41, 126.17, 118.97, 111.03, 69.67, 25.46. Spectral properties are consistent with literature values.⁶



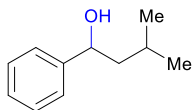
1-(4-nitrophenyl)ethan-1-ol.

The title compound was prepared from the corresponding ketone (2.000 g, 12.11 mmol) following **General Procedure A**. The crude material was purified by silica column chromatography (hexanes : EtOAc = 3:1) to afford the title compound as a yellow liquid (1.958 g, 11.71 mmol, 97%). ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 5.01 (qd, *J* = 6.4, 3.2 Hz, 1H), 2.25 (d, *J* = 3.7 Hz, 1H), 1.50 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.24, 147.28, 126.24, 123.86, 69.60, 25.60. Spectral properties are consistent with literature values.⁷



diphenylmethanol.

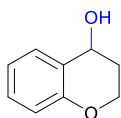
The title compound was prepared from the corresponding ketone (2.003 g, 10.99 mmol) following **General Procedure A**. The crude material was purified by silica column chromatography (hexanes : EtOAc = 5:1) to afford the title compound as a white solid (2.005 g, 10.88 mmol, 99 %). ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.32 (m, 8H), 7.32 – 7.26 (m, 2H), 5.83 (d, *J* = 3.5 Hz, 1H), 2.41 (b, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 143.92, 128.60, 127.67, 126.67, 76.34. Spectral properties are consistent with literature values.⁸



3-methyl-1-phenylbutan-1-ol.

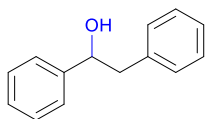
The title compound was prepared from the corresponding ketone (2.168 g, 13.36 mmol) following **General Procedure A**. The crude material was purified by silica column chromatography

(hexanes : EtOAc = 9:1) to afford the title compound as a colorless liquid (2.136 g, 13.00 mmol, 97 %). ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.16 (m, 5H), 4.75 – 4.57 (m, 1H), 1.84 (s, 1H), 1.90 – 1.75 (m, 1H), 1.72 – 1.56 (m, 2H), 1.51 – 1.38 (m, 1H), 0.95 – 0.82 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.36, 128.60, 127.62, 126.00, 72.92, 48.49, 24.94, 23.26, 22.39. Spectral properties are consistent with literature values.⁹



chroman-4-ol.

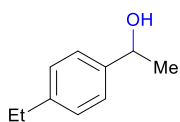
The title compound was prepared from the corresponding ketone (3.000 g, 20.25 mmol) following **General Procedure A**. The crude material was purified by filtration through a short column of 30 mL silica gel and rinsed by EtOAc to afford the title compound as a colorless liquid (3.005 g, 20.00 mmol, 99 %). ^1H NMR (500 MHz, CDCl_3) δ 7.30 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.20 (ddd, $J = 8.6, 7.3, 1.7$ Hz, 1H), 6.92 (td, $J = 7.4, 1.2$ Hz, 1H), 6.84 (dd, $J = 8.3, 1.2$ Hz, 1H), 4.76 (q, $J = 4.3$ Hz, 1H), 4.29 – 4.21 (m, 2H), 2.17 – 2.05 (m, 2H), 2.05 – 1.97 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.69, 129.82, 129.78, 124.43, 120.70, 117.18, 63.33, 62.04, 30.94. Spectral properties are consistent with literature values.¹⁰



1,2-diphenylethan-1-ol.

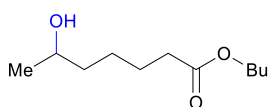
The title compound was prepared from the corresponding ketone (1.501 g, 7.65 mmol) following **General Procedure A**. The crude material was purified by filtration through a short column of

20 mL silica gel and rinsed by EtOAc to afford the title compound as a white solid (1.505 g, 7.59 mmol, 99 %). ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.13 (m, 10H), 4.87 (ddd, $J = 7.9, 4.8, 2.5$ Hz, 1H), 3.06 – 2.91 (m, 2H), 1.94 (b, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.95, 138.18, 129.65, 128.65, 128.55, 127.75, 126.76, 126.04, 75.48, 46.24. Spectral properties are consistent with literature values.¹¹



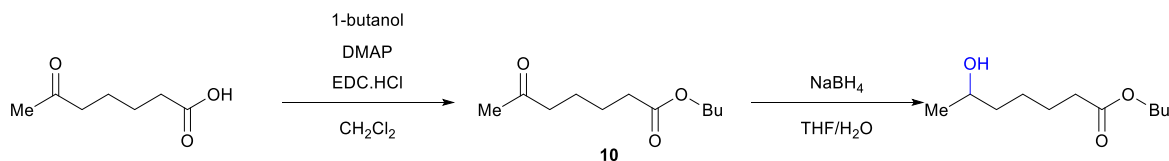
1-(4-ethylphenyl)ethan-1-ol.

The title compound was prepared from the corresponding ketone (2.500 g, 16.87 mmol) following **General Procedure A**. The crude material was purified by silica column chromatography (hexanes : EtOAc = 4:1) to afford the title compound as a colorless liquid (2.408 g, 16.03 mmol, 95 %). ^1H NMR (500 MHz, CDCl_3) δ 7.30 (d, $J = 8.2$ Hz, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 4.87 (q, $J = 6.5$ Hz, 1H), 2.65 (q, $J = 7.6$ Hz, 2H), 1.86 (s, 1H), 1.49 (d, $J = 6.5$ Hz, 3H), 1.24 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.70, 143.23, 128.11, 125.56, 70.40, 28.66, 25.15, 15.73.



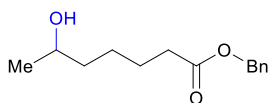
butyl 6-hydroxyheptanoate.

The title compound was prepared in a two-step synthesis.



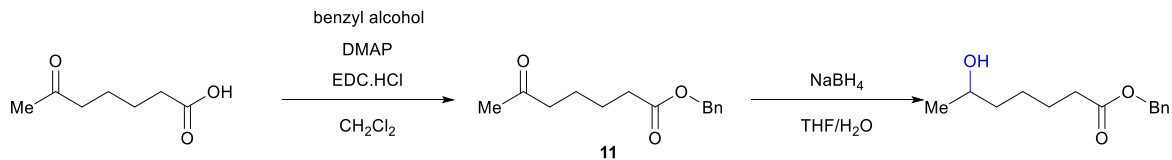
Step 1: To a solution of 6-oxoheptanoic acid (1.506 g, 10.45 mmol), DMAP (254 mg, 2.08 mmol), and 1-butanol (0.95 mL, 10.44 mmol) in CH₂Cl₂ (52 mL) under Argon, EDC.HCl (4.986 g, 26.00 mmol) was added at 0 °C. The mixture was then warmed to r.t. After stirring for 3.5 hrs, 40 mL CH₂Cl₂ was added. The resulting solution was washed with H₂O (100 mL x 3). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude material was purified by silica column chromatography (hexanes : EtOAc = 6:1) to afford **10** as a colorless liquid (1.742 g, 8.70 mmol, 83 %). ¹H NMR (500 MHz, CDCl₃) δ 4.04 (t, *J* = 6.7 Hz, 2H), 2.43 (t, *J* = 6.7 Hz, 2H), 2.28 (t, *J* = 7.0 Hz, 2H), 2.11 (s, 3H), 1.66 – 1.50 (m, 6H), 1.43 – 1.28 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 208.64, 173.60, 64.34, 43.36, 34.16, 30.77, 29.97, 24.52, 23.29, 19.23, 13.79. Spectral properties are consistent with literature values.¹²

Step 2: The reduction of **10** (1.500 g, 7.49 mmol) was accomplished following the **General Procedure A**. The crude material was purified by silica column chromatography (hexanes : EtOAc = 3:1) to afford the desired alcohol as a colorless liquid (1.324 g, 6.55 mmol, 87 %). ¹H NMR (500 MHz, CDCl₃) δ 4.05 (t, *J* = 6.7 Hz, 2H), 3.86 – 3.71 (m, 1H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.72 – 1.52 (m, 5H), 1.50 – 1.31 (m, 6H), 1.17 (d, *J* = 6.2 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 173.99, 67.95, 64.32, 38.98, 34.40, 30.81, 25.40, 25.01, 23.62, 19.26, 13.82.



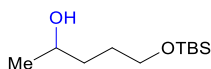
benzyl 6-hydroxyheptanoate.

The title compound was prepared in a two-step synthesis.



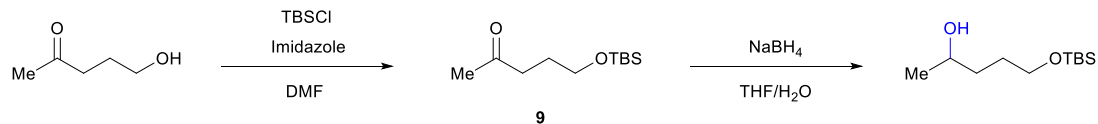
Step 1: To a solution of 6-oxoheptanoic acid (1.502 g, 10.42 mmol), DMAP (255 mg, 2.09 mmol), and benzyl alcohol (1.08 mL, 10.44 mmol) in CH₂Cl₂ (50 mL) under Argon, EDC.HCl (4.987 g, 26.01 mmol) was added at 0 °C. The mixture was then warmed to r.t. After stirring overnight, 50 mL CH₂Cl₂ was added. The resulting solution was washed with H₂O (100 mL x 3). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude material was purified by silica column chromatography (hexanes : EtOAc = 7:1 to 4:1 gradient elution) to afford **11** as a colorless liquid (2.152 g, 9.11 mmol, 87 %).

Step 2: The reduction of **11** (2.004 g, 8.55 mmol) was accomplished following the **General Procedure A**. The crude material was purified by silica column chromatography (hexanes : EtOAc = 4:1 to 2:1 to 1:1 gradient elution) to afford the desired alcohol as a colorless liquid (1.419 g, 6.00 mmol, 70 %). ¹H NMR (500 MHz, CDCl₃) δ 7.46 – 7.24 (m, 5H), 5.11 (s, 2H), 3.87 – 3.71 (m, 1H), 2.37 (t, *J* = 7.5 Hz, 2H), 1.73 – 1.60 (m, 2H), 1.52 – 1.28 (m, 5H), 1.17 (d, *J* = 6.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 173.66, 136.18, 128.67, 128.33, 67.93, 66.26, 38.95, 34.34, 25.36, 24.96, 23.62. Spectral properties are consistent with literature values.¹³



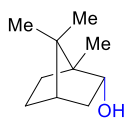
5-((tert-butyldimethylsilyloxy)pentan-2-ol.

The title compound was prepared in a two-step synthesis.



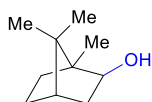
Step 1: To a solution of 4-hydroxypentan-2-one (2.019 g, 19.77 mmol) and imidazole (3.338 g, 49.03 mmol) in DMF (10 mL) under Argon at 0 °C, TBSCl (3.845 g, 25.51 mmol) was added in one portion. The mixture was stirred at 0 °C for 30 mins and warmed to r.t. After stirring overnight, 80 mL CH₂Cl₂ was added to the mixture. The resulting solution was washed thoroughly with H₂O (100 mL x 5). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude material was purified by silica column chromatography (hexanes : EtOAc = 20:1) to afford **9** as a colorless liquid (2.628 g, 12.14 mmol, 61 %). ¹H NMR (500 MHz, CDCl₃) δ 3.60 (t, *J* = 6.1 Hz, 2H), 2.49 (t, *J* = 7.3 Hz, 2H), 2.13 (s, 3H), 1.81 – 1.72 (m, 2H), 0.87 (s, 9H), 0.02 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 209.04, 62.24, 40.20, 30.07, 26.99, 26.04, 18.42, -5.26.

Step 2: The reduction of **9** (1.000 g, 4.62 mmol) was accomplished following the **General Procedure A**. The crude material was purified by silica column chromatography (hexanes : EtOAc = 5:1) to afford the desired alcohol as a colorless liquid (0.893 g, 4.09 mmol, 88 %). ¹H NMR (500 MHz, CDCl₃) δ 3.87 – 3.73 (m, 1H), 3.73 – 3.57 (m, 2H), 2.71 (d, *J* = 3.4 Hz, 1H), 1.69 – 1.54 (m, 3H), 1.53 – 1.41 (m, 1H), 1.18 (d, *J* = 6.3 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 67.86, 63.71, 36.84, 29.48, 26.05, 23.55, 18.45, -5.26, -5.27. HRMS *m/z*: calcd for [M+H]⁺ C₁₁H₂₇O₂Si⁺: 219.1775, found: 219.1772.



rac-borneol.

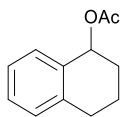
The title compound was purified by silica column chromatography (hexanes : EtOAc = 9:1) from a commercial mixture of rac-borneol and rac-isoborneol to afford the title compound as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 4.09 – 3.91 (m, 1H), 2.27 (dddd, $J = 13.3, 9.8, 4.8, 3.3$ Hz, 1H), 1.95 – 1.82 (m, 1H), 1.79 – 1.66 (m, 1H), 1.62 (t, $J = 4.7$ Hz, 1H), 1.51 – 1.42 (m, 1H), 1.30 – 1.18 (m, 2H), 0.93 (dd, $J = 13.4, 3.5$ Hz, 1H), 0.88 – 0.82 (m, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 77.51, 49.62, 48.16, 45.23, 39.16, 28.41, 26.05, 20.32, 18.81, 13.46.



rac-isoborneol.

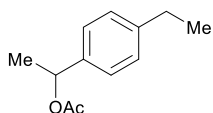
The title compound was purified by silica column chromatography (hexanes : EtOAc = 9:1) from a commercial mixture of rac-borneol and rac-isoborneol to afford the title compound as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 3.68 – 3.55 (m, 1H), 1.80 – 1.57 (m, 5H), 1.48 (td, $J = 11.7, 3.4$ Hz, 1H), 1.05 – 0.92 (m, 5H), 0.90 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 80.04, 49.08, 46.47, 45.16, 40.52, 34.05, 27.37, 20.61, 20.24, 11.44. Spectral properties are consistent with literature values.¹⁴

IV. Synthesis and Characterization of Benzylic Substrates



1,2,3,4-tetrahydronaphthalen-1-yl acetate.

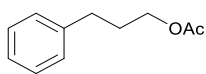
The title compound was prepared by acetylation of 1,2,3,4-tetrahydronaphthalen-1-ol: To a solution of 1,2,3,4-tetrahydronaphthalen-1-ol (1.487 g, 10.03 mmol), DMAP (122 mg, 1.00 mmol), and Et₃N (7.00 mL, 50.22 mmol) in CH₂Cl₂ (50 mL) under Argon, acetic anhydride (4.73 mL, 50.04 mmol) was added dropwise at 0 °C over 30 mins. The reaction mixture was then warmed to r.t. After stirring overnight, 50 mL CH₂Cl₂ was added. The resulting solution was washed with 100 mL saturated NaHCO₃ aqueous solution followed by washing with H₂O (100 mL x 2). The organic layer was separated, dried over anhydrous Na₂SO₄, and concentrated by rotary evaporation. The crude material was purified by silica column chromatography (hexanes : EtOAc = 30:1) to afford the title compound as a colorless liquid (1.772 g, 9.31 mmol, 93 %). ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.08 (m, 4H), 6.01 (t, *J* = 4.4 Hz, 1H), 2.95 – 2.82 (m, 1H), 2.82 – 2.68 (m, 1H), 2.09 (s, 3H), 2.04 – 1.93 (m, 3H), 1.89 – 1.78 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 170.93, 138.07, 134.68, 129.57, 129.22, 128.22, 126.21, 70.13, 29.21, 29.10, 21.63, 18.93. Spectral properties are consistent with literature values.¹⁵



1-(4-ethylphenyl)ethyl acetate.

The title compound was prepared by acetylation of 1-(4-ethylphenyl)ethan-1-ol: To a solution of 1-(4-ethylphenyl)ethan-1-ol (1.200 g, 7.99 mmol), DMAP (98 mg, 0.80 mmol), and Et₃N (5.57 mL, 40.00 mmol) in CH₂Cl₂ (40 mL) under Argon, acetic anhydride (3.80 mL, 40.20 mmol) was added dropwise at 0 °C over 30 mins. The reaction mixture was then warmed to r.t. After stirring overnight, 60 mL CH₂Cl₂ was added. The resulting solution was washed with

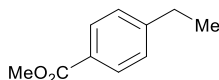
100 mL saturated NaHCO₃ aqueous solution followed by washing with H₂O (100 mL x 2). The organic layer was separated, dried over anhydrous Na₂SO₄, and concentrated by rotary evaporation. The crude material was purified by silica column chromatography (hexanes : EtOAc = 15:1) to afford the title compound as a colorless liquid (1.424 g, 7.41 mmol, 92 %). ¹H NMR (500 MHz, CDCl₃) δ 7.28 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.87 (q, *J* = 6.6 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.06 (s, 3H), 1.53 (d, *J* = 6.6 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 170.52, 144.10, 139.01, 128.10, 126.33, 72.37, 28.67, 22.20, 21.52, 15.62. Spectral properties are consistent with literature values.¹⁶



3-phenylpropyl acetate.

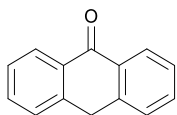
The title compound was prepared by acetylation of 3-phenylpropan-1-ol: To a solution of 3-phenylpropan-1-ol (1.364 g, 10.01 mmol), DMAP (122 mg, 1.00 mmol), and Et₃N (7.00 mL, 50.22 mmol) in CH₂Cl₂ (50 mL) under Argon, acetic anhydride (4.73 mL, 50.03 mmol) was added dropwise at 0 °C over 30 mins. The reaction mixture was then warmed to r.t. After stirring overnight, 50 mL CH₂Cl₂ was added. The resulting solution was washed with 100 mL saturated NaHCO₃ aqueous solution followed by washing with H₂O (100 mL x 2). The organic layer was separated, dried over anhydrous Na₂SO₄, and concentrated by rotary evaporation. The crude material was purified by silica column chromatography (hexanes : EtOAc = 10:1) to afford the title compound as a colorless liquid (1.601 g, 8.89 mmol, 89 %). ¹H NMR (600 MHz, CDCl₃) δ 7.35 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H), 4.10 (t, *J* = 6.6 Hz, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.06 (s, 3H), 2.01 – 1.93 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 171.25, 141.34,

128.57, 128.51, 126.14, 63.96, 32.32, 30.31, 21.07. Spectral properties are consistent with literature values.¹⁷



methyl 4-ethylbenzoate.

The title compound was synthesized from esterification of 4-ethylbenzoic acid with MeOH: To a solution of 4-ethylbenzoic acid (1.504 g, 10.01 mmol), DMAP (244 mg, 2.00 mmol), and MeOH (2.1 mL, 51.84 mmol) in CH₂Cl₂ (50 mL) under Argon, EDC.HCl (4.793 g, 25.00 mmol) was added at 0 °C. The mixture was then warmed to r.t. After stirring for overnight, 50 mL CH₂Cl₂ was added. The resulting solution was washed with H₂O (100 mL x 3). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude material was purified by silica column chromatography (hexanes : EtOAc = 20:1) to afford the product as a colorless liquid (1.447 g, 8.81 mmol, 88 %). ¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 167.32, 149.87, 129.84, 128.01, 127.81, 52.04, 29.08, 15.32. Spectral properties are consistent with literature values.¹⁴



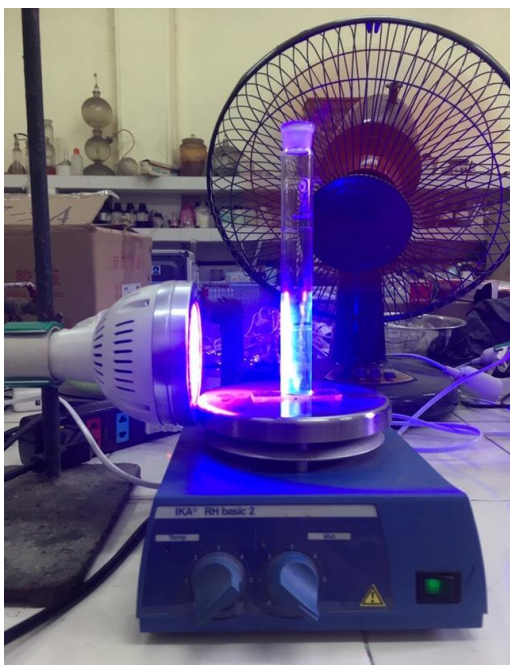
anthrone.

The title compound was prepared following a previously reported procedure for reduction of an anthraquinone derivative:² To a solution of anthraquinone (2.000 g, 9.61 mmol) in concentrated sulfuric acid (46 mL) was added copper (3.055 g, 48.07 mmol). The mixture was

stirred at 40 °C for 3 hrs. The reaction mixture was slowly poured on crushed ice (200 mL). The resulting mixture was extracted with EtOAc (100 mL x 3). The EtOAc layers were combined, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified by silica column chromatography (hexanes : EtOAc = 10:1 to 5:1 gradient elution) to afford the product as a slight yellow solid (0.713 g, 3.67 mmol, 38 %). ¹H NMR (500 MHz, CDCl₃) δ 8.36 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.59 (td, *J* = 7.4, 1.5 Hz, 2H), 7.52 – 7.33 (m, 4H), 4.35 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 184.39, 140.58, 132.86, 132.15, 128.58, 127.70, 127.13, 32.47. Spectral properties are consistent with literature values.¹⁸

V. Synthesis and Characterization of Oxidized Products from Alcohol Oxidation

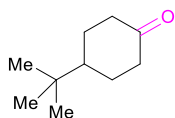
General Procedure B: Aerobic Photo-oxidation of Alcohols



Alcohol (1 equiv) was charged into 35-mL test tube along with a magnetic stir bar followed by the addition of 5 mL of Co(acac)₂ stock solution in acetone (0.01 equiv). Solid **1a** (0.05 equiv)

was added to the test tube. The dilution of the reaction mixture was accomplished by adding an appropriate amount of acetone. The reaction mixture was stirred vigorously open to air with fan cooling and irradiated with one 25W 400-410 nm LEDs Lamp, positioned about 6.5 cm away from the tube, until no starting material remained by TLC analysis. Upon reaction completion, the reaction mixture was concentrated by rotary evaporation and the crude material was purified by flash column chromatography with silica gel as the stationary phase to yield the desired product.

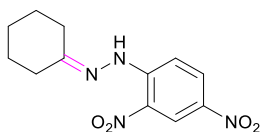
Modified procedure for volatile ketones: the photo-oxidation was accomplished in MeCN in place of acetone. Upon reaction completion (based on TLC analysis), the reaction mixture was subjected to treatment with H₂O (4 mL), HCl (0.5 mL, 6 M aq.), and 2,4-dinitrophenylhydrazine (1.03 eq). After stirring for 2 hrs, 40 mL H₂O was added, and the resultant mixture was extracted with CH₂Cl₂ (50 mL x 3). The CH₂Cl₂ layers were combined, dried over anhydrous Na₂SO₄, and concentrated by rotary evaporation. The residue was subjected to purification by flash column chromatography with silica gel as the stationary phase to yield the desired product.



4-(tert-butyl)cyclohexan-1-one (2)

The title compound was prepared according to the **General Procedure B** from a commercial mixture of cis- and trans-4-(tert-butyl)cyclohexan-1-ol (312.5 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01

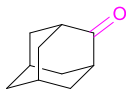
equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 50 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 7:1) to afford the product as a white solid (279.4 mg, 1.81 mmol, 91 %). ¹H NMR (500 MHz, CDCl₃) δ 2.44 – 2.35 (m, 2H), 2.35 – 2.25 (m, 2H), 2.13 – 2.03 (m, 2H), 1.53 – 1.38 (m, 3H), 0.91 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 212.72, 46.85, 41.45, 32.60, 27.74, 27.73. Spectral properties are consistent with literature values.¹⁹



cyclohexanone-(2,4-dinitrophenylhydrazone) (3)

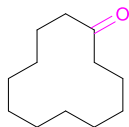
The title compound prepared according to the *modified procedure for volatile ketones* from cyclohexanol (200.3 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in MeCN (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL MeCN, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 60 mins. Upon completion, the reaction mixture was subjected to treatment with H₂O (4 mL), HCl (0.5 mL, 6 M aq.), and 2,4-dinitrophenylhydrazine (408.2 mg, 2.06 mmol, 1.03 eq). After stirring for 2 hrs, 40 mL H₂O was added, and the resultant mixture was extracted with CH₂Cl₂ (50 mL x 3). The CH₂Cl₂ layers were combined, dried over anhydrous Na₂SO₄, and concentrated by rotary evaporation. The residue was subjected to purification by silica column chromatography (hexanes : CH₂Cl₂ = 1:1 to 1:2 gradient elution) to afford the product as an orange solid (490.8 mg, 1.76 mmol, 88 %). ¹H NMR (500 MHz, CDCl₃) δ 11.19

(s, 1H), 9.11 (d, $J = 2.6$ Hz, 1H), 8.27 (dd, $J = 9.6, 2.6$ Hz, 1H), 7.96 (d, $J = 9.6$ Hz, 1H), 2.56 – 2.37 (m, 4H), 1.87 – 1.64 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 161.59, 145.47, 137.59, 130.07, 128.93, 123.75, 116.38, 35.72, 27.35, 27.17, 26.13, 25.62. Spectral properties are consistent with literature values.²⁰



2-adamantanone (4)

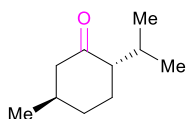
The title compound was prepared according to the **General Procedure B** from 2-adamantanol (304.5 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL $\text{Co}(\text{acac})_2$ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 15 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 45 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 7:1) to afford the product as a white solid (229.2 mg, 1.53 mmol, 76 %). ^1H NMR (500 MHz, CDCl_3) δ 2.54 (s, 2H), 2.18 – 1.81 (m, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 218.60, 47.12, 39.40, 36.44, 27.59. Spectral properties are consistent with literature values.²⁰



cyclododecanone (5)

The title compound was prepared according to the **General Procedure B** from cyclododecanol (184.3 mg, 1 mmol), **1a** (26.5 mg, 0.05 mmol, 0.05 equiv), 2.5 mL $\text{Co}(\text{acac})_2$ stock solution in

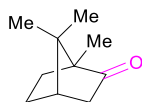
acetone (2.6 mg in 2.5 mL, 0.01 mmol, 0.01 equiv). The mixture was diluted with 7.5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 60 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 10:1) to afford the product as a white solid (145.9 mg, 0.80 mmol, 80 %). ^1H NMR (500 MHz, CDCl_3) δ 2.50 – 2.40 (m, 4H), 1.75 – 1.67 (m, 4H), 1.35 – 1.20 (m, 14H). ^{13}C NMR (126 MHz, CDCl_3) δ 213.06, 40.52, 24.89, 24.75, 24.37, 22.70, 22.49. Spectral properties are consistent with literature values.¹³



(-)-menthone (6)

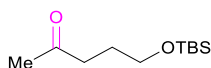
The title compound was prepared according to the **General Procedure B** from (-)-menthol (312.5 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL $\text{Co}(\text{acac})_2$ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 15 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 120 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 30:1) to afford the product as a colorless liquid (217.4 mg, 1.41 mmol, 70 %). ^1H NMR (500 MHz, CDCl_3) δ 2.34 (ddd, $J = 13.0, 4.0, 2.2$ Hz, 1H), 2.19 – 1.77 (m, 6H), 1.45 – 1.25 (m, 2H), 1.00 (d, $J = 6.3$ Hz, 3H), 0.90 (d, $J = 6.8$ Hz, 3H), 0.84 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 212.58,

56.04, 51.01, 35.60, 34.07, 28.00, 26.03, 22.42, 21.35, 18.83. Spectral properties are consistent with literature values.²⁰



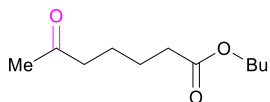
rac-camphor (7 & 8)

The title compound was prepared according to the **General Procedure B** from either rac-borneol or rac-isoborneol (308.5 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 40 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 10:1) to afford the title compound. The catalytic oxidation of rac-borneol afforded a white solid (278.0 mg, 1.83 mmol, 91 %) and the catalytic oxidation of rac-isoborneol afforded a white solid (281.2 mg, 1.85 mmol, 92 %). The two mentioned products have similar spectral properties. ¹H NMR (500 MHz, CDCl₃) δ 2.34 (db, *J* = 18.2 Hz, 1H), 2.07 (t, *J* = 4.5 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.83 (d, *J* = 18.2 Hz, 1H), 1.67 (td, *J* = 12.7, 3.7 Hz, 1H), 1.45 – 1.26 (m, 2H), 0.94 (s, 3H), 0.90 (s, 3H), 0.82 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 219.81, 57.84, 46.92, 43.44, 43.19, 30.05, 27.19, 19.91, 19.28, 9.38. Spectral properties are consistent with literature values.¹⁹



5-((tert-butyl dimethylsilyl)oxy)pentan-2-one (9)

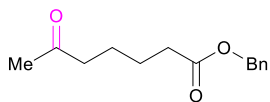
The title compound prepared according to the **General Procedure B** from 5-((tert-butyltrimethylsilyl)oxy)pentan-2-ol (218.4 mg, 1 mmol), **1a** (26.5 mg, 0.05 mmol, 0.05 equiv), 2.5 mL Co(acac)₂ stock solution in acetone (2.6 mg in 2.5 mL, 0.01 mmol, 0.01 equiv). The mixture was diluted with 7.5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 3 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 20:1) to afford the product as a colorless liquid (115.2 mg, 0.53 mmol, 53 %). ¹H NMR (500 MHz, CDCl₃) δ 3.60 (t, *J* = 6.1 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.14 (s, 3H), 1.87 – 1.73 (m, 2H), 0.88 (s, 9H), 0.03 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 209.09, 62.26, 40.22, 30.09, 27.01, 26.05, 18.44, -5.25.



butyl 6-oxoheptanoate (10)

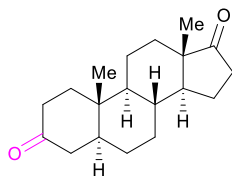
The title compound prepared according to the **General Procedure B** from butyl 6-hydroxyheptanoate (202.3 mg, 1 mmol), **1a** (26.5 mg, 0.05 mmol, 0.05 equiv), 2.5 mL Co(acac)₂ stock solution in acetone (2.6 mg in 2.5 mL, 0.01 mmol, 0.01 equiv). The mixture was diluted with 7.5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 90 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 6:1) to afford the product as a colorless liquid (191.6 mg, 0.95 mmol, 95 %). ¹H NMR (500 MHz, CDCl₃) δ 4.04 (t, *J* = 6.7 Hz, 2H), 2.43 (t, *J* = 6.7 Hz, 2H), 2.28 (t, *J* = 7.0 Hz, 2H), 2.11 (s, 3H), 1.66 – 1.50 (m, 6H), 1.43 – 1.28 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 208.64,

173.60, 64.34, 43.36, 34.16, 30.77, 29.97, 24.52, 23.29, 19.23, 13.79. Spectral properties are consistent with literature values.¹²



benzyl 6-oxoheptanoate (11)

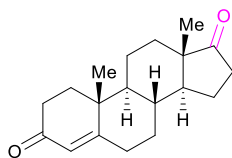
The title compound prepared according to the **General Procedure B** from benzyl 6-hydroxyheptanoate (236.3 mg, 1 mmol), **1a** (26.5 mg, 0.05 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (2.6 mg in 5 mL, 0.01 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 120 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 6:1) to afford the product as a colorless liquid (183.4 mg, 0.78 mmol, 78 %). ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.29 (m, 5H), 5.11 (s, 2H), 2.43 (t, *J* = 6.9 Hz, 2H), 2.37 (t, *J* = 7.0 Hz, 2H), 2.11 (s, 3H), 1.69 – 1.54 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 208.62, 173.32, 136.11, 128.68, 128.66, 128.34, 66.32, 43.33, 34.14, 29.98, 24.47, 23.27. Spectral properties are consistent with literature values.¹³



5 α -Androstane-3,17-dione (12)

The title compound prepared according to the **General Procedure B** from trans-androsterone (580.9 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 10 mL acetone,

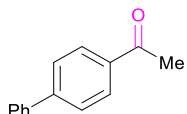
stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 45 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 3:1) to afford the product as a white solid (513.4 mg, 1.78 mmol, 89 %). ^1H NMR (500 MHz, CDCl_3) δ 2.49 – 2.32 (m, 2H), 2.31 – 2.20 (m, 2H), 2.14 – 1.97 (m, 3H), 1.97 – 1.87 (m, 1H), 1.85 – 1.75 (m, 2H), 1.72 – 1.64 (m, 1H), 1.63 – 1.44 (m, 3H), 1.43 – 1.18 (m, 6H), 1.06 – 0.93 (m, 4H), 0.86 (s, 3H), 0.82 – 0.72 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 220.97, 211.64, 53.98, 51.32, 47.81, 46.69, 44.67, 38.53, 38.16, 35.90, 35.05, 31.58, 30.62, 28.71, 21.87, 20.80, 13.90, 11.55. Spectral properties are consistent with literature values.¹⁹



androst-4-ene-3,17-dione (13)

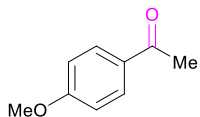
The title compound prepared according to a modified version of the **General Procedure B** from testosterone (288.4 mg, 1 mmol), **1a** (26.5 mg, 0.05 mmol, 0.05 equiv), 3 mL $\text{Co}(\text{acac})_2$ stock solution in acetone (7.7 mg in 3 mL, 0.03 mmol, 0.03 equiv). The mixture was diluted with 7 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 105 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 2:1) to afford the product as a white solid (228.1 mg, 0.80 mmol, 80 %). ^1H NMR (500 MHz, CDCl_3) δ 5.72 (s, 1H), 2.51 – 2.23 (m, 5H), 2.13 – 1.91 (m, 4H), 1.87 – 1.81 (m, 1H), 1.76 – 1.61 (m, 3H), 1.54 (tt, $J = 12.5, 9.1$ Hz, 1H), 1.43 (qd, $J = 13.3, 4.1$ Hz, 1H), 1.32 – 1.21 (m, 2H), 1.19 (s, 3H), 1.09 (dtd,

$J = 13.6, 11.8, 4.3$ Hz, 1H), 0.96 (ddd, $J = 12.4, 10.6, 4.1$ Hz, 1H), 0.89 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 220.39, 199.32, 170.37, 124.21, 53.89, 50.92, 47.57, 38.71, 35.81, 35.77, 35.22, 33.98, 32.63, 31.36, 30.83, 21.81, 20.39, 17.45, 13.78. Spectral properties are consistent with literature values.⁸



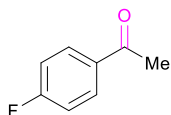
4-acetylbiphenyl (14)

The title compound was prepared according to the **General Procedure B** from 1-([1,1'-biphenyl]-4-yl)ethan-1-ol (396.6 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL $\text{Co}(\text{acac})_2$ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 60 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 4:1) to afford the product as a white solid (392.0 mg, 1.99 mmol, 99 %). ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.63 (d, $J = 7.0$ Hz, 2H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.41 (t, $J = 7.4$ Hz, 1H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.87, 145.91, 140.01, 135.99, 129.09, 129.05, 128.36, 127.40, 127.35, 26.79. Spectral properties are consistent with literature values.⁷



4'-methoxyacetophenone (15)

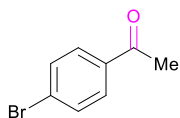
The title compound was prepared according to the **General Procedure B** from 1-(4-methoxyphenyl)ethan-1-ol (304.4 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 45 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 6:1) to afford the product as a white solid (289.0 mg, 1.92 mmol, 96 %). ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H), 2.55 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.89, 163.61, 130.71, 130.48, 113.80, 55.58, 26.46. Spectral properties are consistent with literature values.⁷



4'-fluoroacetophenone (16)

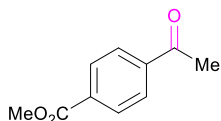
The title compound was prepared according to the **General Procedure B** from 1-(4-fluorophenyl)ethan-1-ol (280.3 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 40 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 4:1) to afford the product as a colorless liquid (261.3 mg, 1.89 mmol, 94 %). ¹H NMR (500 MHz, CDCl₃) δ 8.07 – 7.89 (m, 2H), 7.19 – 7.03 (m, 2H), 2.58 (s, 3H). ¹³C NMR (126

MHz, CDCl₃) δ 196.61, 165.89 (d, $J = 255.2$ Hz), 133.72 (d, $J = 3.0$ Hz), 131.07 (d, $J = 9.4$ Hz), 115.77 (d, $J = 21.9$ Hz), 26.65. ¹⁹F NMR (471 MHz, CDCl₃) δ -105.34. Spectral properties are consistent with literature values.²¹



4'-bromoacetophenone (17)

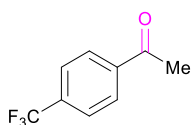
The title compound was prepared according to the **General Procedure B** from 1-(4-bromophenyl)ethan-1-ol (201.1 mg, 1 mmol), **1a** (26.5 mg, 0.05 mmol, 0.05 equiv), 2.5 mL Co(acac)₂ stock solution in acetone (2.6 mg in 2.5 mL, 0.01 mmol, 0.01 equiv). The mixture was diluted with 7.5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 60 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 8:1) to afford the product as a white solid (184.0 mg, 0.92 mmol, 92 %). ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, $J = 8.6$ Hz, 2H), 7.59 (d, $J = 8.6$ Hz, 2H), 2.57 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.10, 135.95, 132.00, 129.95, 128.41, 26.64. Spectral properties are consistent with literature values.⁷



methyl 4-acetylbenzoate (18)

The title compound was prepared according to the **General Procedure B** from methyl 4-(1-hydroxyethyl)benzoate (360.4 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL

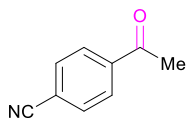
Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 50 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 4:1) to afford the product as a white solid (351.0 mg, 1.97 mmol, 98 %). ¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 3H), 2.63 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.64, 166.34, 140.36, 134.03, 129.95, 128.33, 52.58, 26.99. Spectral properties are consistent with literature values.²²



4'-(trifluoromethyl)acetophenone (19)

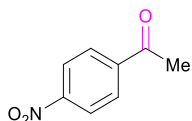
The title compound was prepared according to the **General Procedure B** from 1-(4-(trifluoromethyl)phenyl)ethan-1-ol (380.3 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 45 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 6:1) to afford the product as a colorless liquid (357.6 mg, 1.90 mmol, 95 %). ¹H NMR (500 MHz, CDCl₃) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 2.63 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.09, 139.81, 134.51 (q, *J* = 32.7 Hz), 128.74, 125.79 (q, *J* = 3.8 Hz),

123.73 (q, $J = 273.2$ Hz), 26.87. ^{19}F NMR (471 MHz, CDCl_3) δ -63.16. Spectral properties are consistent with literature values.²³



4-acetylbenzotrile (20)

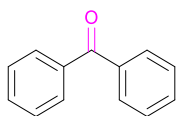
The title compound was prepared according to the **General Procedure B** from 4-(1-hydroxyethyl)benzotrile (294.4 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL $\text{Co}(\text{acac})_2$ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 45 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 5:1) to afford the product as a white solid (284.8 mg, 1.96 mmol, 98 %). ^1H NMR (500 MHz, CDCl_3) δ 8.03 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 196.64, 140.04, 132.63, 128.81, 118.03, 116.52, 26.87. Spectral properties are consistent with literature values.²⁴



4-nitroacetophenone (21)

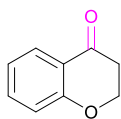
The title compound was prepared according to the **General Procedure B** from 1-(4-nitrophenyl)ethan-1-ol (167.2 mg, 1 mmol), **1a** (26.5 mg, 0.05 mmol, 0.05 equiv), 2.5 mL $\text{Co}(\text{acac})_2$ stock solution in acetone (2.6 mg in 2.5 mL, 0.01 mmol, 0.01 equiv). The mixture

was diluted with 7.5 mL acetone, stirred open to air, and irradiated with two 25-W 400-410 nm LEDs Lamps with fan cooling for 8 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 10:1) to afford the product as a yellow solid (159.5 mg, 0.96 mmol, 96 %). ¹H NMR (500 MHz, CDCl₃) δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.9 Hz, 2H), 2.67 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.43, 150.50, 141.51, 129.44, 123.99, 27.11. Spectral properties are consistent with literature values.⁷



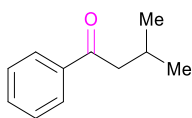
benzophenone (22)

The title compound was prepared according to the **General Procedure B** from diphenylmethanol (368.5 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 40 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 7:1) to afford the product as a colorless liquid (362.9 mg, 1.99 mmol, 99 %). ¹H NMR (500 MHz, CDCl₃) δ 7.85 – 7.75 (m, 4H), 7.62 – 7.55 (m, 2H), 7.53 – 7.43 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 196.87, 137.71, 132.53, 130.16, 128.39. Spectral properties are consistent with literature values.⁸



4-chromanone (23)

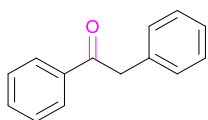
The title compound was prepared according to the **General Procedure B** from 4-chromanol (300.4 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 45 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 7:1) to afford the product as a slight yellow liquid (286.7 mg, 1.93 mmol, 96 %). ¹H NMR (500 MHz, CDCl₃) δ 7.89 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.46 (ddd, *J* = 8.6, 7.2, 1.8 Hz, 1H), 7.01 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 6.96 (dd, *J* = 8.4, 1.1 Hz, 1H), 4.62 – 4.44 (m, 2H), 2.87 – 2.74 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 191.92, 161.96, 136.07, 127.23, 121.47, 117.98, 67.11, 37.88. Spectral properties are consistent with literature values.⁸



isovalerophenone (24)

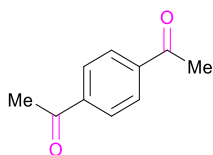
The title compound was prepared according to the **General Procedure B** from 3-methyl-1-phenylbutan-1-ol (328.5 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp

with fan cooling for 90 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 30:1) to afford the product as a colorless liquid (301.1 mg, 1.86 mmol, 93 %). ^1H NMR (500 MHz, CDCl_3) δ 7.99 – 7.89 (m, 2H), 7.58 – 7.50 (m, 1H), 7.50 – 7.41 (m, 2H), 2.83 (d, $J = 6.9$ Hz, 2H), 2.30 (n, $J = 6.7$ Hz, 1H), 0.99 (d, $J = 6.7$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 200.39, 137.53, 132.96, 128.65, 128.21, 47.63, 25.28, 22.88. Spectral properties are consistent with literature values.²⁵



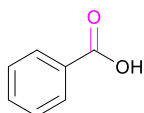
2-phenylacetophenone (25)

The title compound was prepared according to the **General Procedure B** from 1,2-diphenylethan-1-ol (396.6 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL $\text{Co}(\text{acac})_2$ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 15 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 90 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 10:1) to afford the product as a slight yellow solid (282.4 mg, 1.44 mmol, 72 %). ^1H NMR (500 MHz, CDCl_3) δ 8.05 – 7.95 (m, 2H), 7.58 – 7.50 (m, 1H), 7.48 – 7.41 (m, 2H), 7.35 – 7.28 (m, 2H), 7.28 – 7.20 (m, 3H), 4.27 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.78, 136.74, 134.67, 133.30, 129.60, 128.81, 128.78, 128.75, 127.03, 45.64. Spectral properties are consistent with literature values.²⁶



1,4-diacetylbenzene (26)

The title compound was prepared according to the **General Procedure B** from 1-(4-ethylphenyl)ethan-1-ol (150.2 mg, 1 mmol), **1a** (26.5 mg, 0.05 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (2.6 mg in 5 mL, 0.01 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 12 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 5:1) to afford the product as a white solid (133.9 mg, 0.82 mmol, 82 %). ¹H NMR (500 MHz, CDCl₃) δ 8.02 (s, 4H), 2.64 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 197.59, 140.30, 128.62, 27.01. Spectral properties are consistent with literature values.²⁴

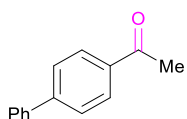


benzoic acid (27)

The title compound was prepared according to the **General Procedure B** from benzyl alcohol (216.3 mg, 2 mmol), **1a** (53.0 mg, 0.1 mmol, 0.05 equiv), 5 mL Co(acac)₂ stock solution in acetone (5.1 mg in 5 mL, 0.02 mmol, 0.01 equiv). The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 9 hrs. The reaction mixture was concentrated by rotary evaporation and the residue was dissolved in 50 mL NaHCO₃ 5 % aqueous solution. The resultant mixture was washed with

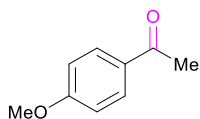
CH₂Cl₂ (30 mL x 2). The aqueous layer was acidified by concentrated HCl to pH 2 and extracted with EtOAc (50 mL x 3). The EtOAc layers were combined, dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation to afford the title compound as a slight yellow solid (171.0 mg, 1.40 mmol, 70 %). ¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 172.45, 133.98, 130.37, 129.45, 128.64. Spectral properties are consistent with literature values.²⁷

VI. Synthesis and Characterization of Oxidized Products from Benzylic Oxidation



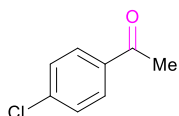
4-acetylbiphenyl (28)

The title compound was prepared from a mixture of 4-ethylbiphenyl (364.5 mg, 2 mmol) and **1a** (53.0 mg, 0.1 mmol, 0.05 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 4 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 10:1) to afford the product as a white solid (316.2 mg, 1.61 mmol, 80 %). ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 2.64 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.88, 145.90, 139.99, 135.98, 129.08, 129.03, 128.36, 127.39, 127.34, 26.78. Spectral properties are consistent with literature values.⁷



4'-methoxyacetophenone (29)

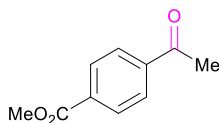
The title compound was prepared from a mixture of 4-ethylanisole (136.2 mg, 1 mmol) and **1a** (26.5 mg, 0.05 mmol, 0.05 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 4 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 8:1) to afford the product as a slight yellow solid (154.8 mg, 1.03 mmol, quant.). ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.55 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.95, 163.62, 130.73, 130.48, 113.81, 55.60, 26.48. Spectral properties are consistent with literature values.⁷



4'-chloroacetophenone (30)

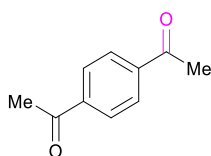
The title compound was prepared from a mixture of 1-chloro-4-ethylbenzene (140.8 mg, 1 mmol) and **1a** (26.5 mg, 0.05 mmol, 0.05 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 5.5 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 15:1) to afford the product as a colorless liquid (111.7 mg, 0.72 mmol, 72 %). ¹H NMR (500 MHz, CDCl₃) δ 7.89 (d, *J* = 8.6

Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 196.99, 139.71, 135.56, 129.86, 129.03, 26.70. Spectral properties are consistent with literature values.²⁸



methyl 4-acetylbenzoate (31)

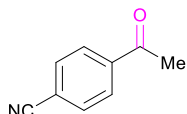
The title compound was prepared from a mixture of methyl 4-ethylbenzoate (164.2 mg, 1 mmol) and **1a** (106.0 mg, 0.2 mmol, 0.20 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 12 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 10:1 to 5:1 gradient elution) to afford the product as a white solid (137.2 mg, 0.76 mmol, 76 %). ^1H NMR (600 MHz, CDCl_3) δ 8.11 (d, $J = 8.6$ Hz, 2H), 7.99 (d, $J = 8.5$ Hz, 2H), 3.94 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 197.61, 166.33, 140.39, 134.04, 129.95, 128.32, 52.56, 26.96. Spectral properties are consistent with literature values.²²



1,4-diacetylbenzene (32)

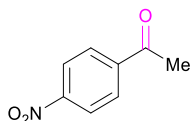
The title compound was prepared from a mixture of 4'-ethylacetophenone (148.2 mg, 1 mmol) and **1a** (106.0 mg, 0.2 mmol, 0.20 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 10 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified

by silica column chromatography (hexanes : EtOAc = 5:1) to afford the product as a white solid (145.2 mg, 0.89 mmol, 89 %). ^1H NMR (500 MHz, CDCl_3) δ 8.02 (s, 4H), 2.64 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.62, 140.30, 128.62, 27.02. Spectral properties are consistent with literature values.²⁴



4-acetylnitrile (33)

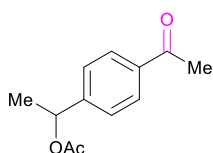
The title compound was prepared from a mixture of 4-ethylbenzonitrile (131.2 mg, 1 mmol) and **1a** (53.0 mg, 0.1 mmol, 0.10 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 12 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 7:1 to 6:1 gradient elution) to afford the product as a white solid (82.8 mg, 0.57 mmol, 57 %). ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 196.68, 140.05, 132.66, 128.83, 118.05, 116.55, 26.90. Spectral properties are consistent with literature values.²⁴



4'-nitroacetophenone (34)

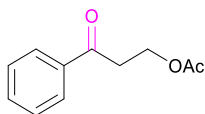
The title compound was prepared from a mixture of 1-ethyl-4-nitrobenzene (151.2 mg, 1 mmol) and **1a** (106.0 mg, 0.2 mmol, 0.20 equiv) in 10 mL acetone. The mixture was stirred

open to air and irradiated with two 25-W 400-410 nm LEDs Lamps with fan cooling for 24 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc =10:1) to afford the product as a yellow solid (112.2 mg, 0.68 mmol, 68 %). ¹H NMR (500 MHz, CDCl₃) δ 8.31 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 8.7 Hz, 2H), 2.68 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.44, 150.51, 141.51, 129.45, 124.01, 27.14. Spectral properties are consistent with literature values.⁷



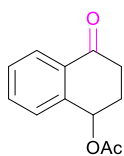
1-(4-acetylphenyl)ethyl acetate (35)

The title compound was prepared from a mixture of 1-(4-ethylphenyl)ethyl acetate (192.3 mg, 1 mmol) and **1a** (53.0 mg, 0.1 mmol, 0.10 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 4 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 7:1) to afford the product as a colorless liquid (172.1 mg, 0.83 mmol, 83 %). ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 5.89 (q, *J* = 6.7 Hz, 1H), 2.59 (s, 3H), 2.09 (s, 3H), 1.53 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.76, 170.32, 147.11, 136.72, 128.78, 126.22, 71.89, 26.76, 22.34, 21.37.



3-oxo-3-phenylpropyl acetate (36)

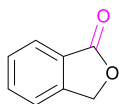
The title compound was prepared from a mixture of 3-phenylpropyl acetate (178.2 mg, 1 mmol) and **1a** (53.0 mg, 0.1 mmol, 0.10 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 4 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 6:1) to afford the product as a white solid (108.3 mg, 0.56 mmol, 56 %). ¹H NMR (600 MHz, CDCl₃) δ 8.00 – 7.91 (m, 2H), 7.62 – 7.53 (m, 1H), 7.51 – 7.42 (m, 2H), 4.51 (t, *J* = 6.4 Hz, 2H), 3.31 (t, *J* = 6.4 Hz, 2H), 2.02 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 197.11, 171.10, 136.76, 133.51, 128.81, 128.19, 59.80, 37.49, 21.00. Spectral properties are consistent with literature values.²⁹



4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate (37)

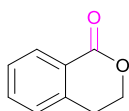
The title compound was prepared from a mixture of **1,2,3,4-tetrahydronaphthalen-1-yl acetate** (190.2 mg, 1 mmol) and **1a** (53.0 mg, 0.1 mmol, 0.10 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 4 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 10:1 to 7:1 gradient elution) to afford the product as a slight yellow liquid (178.2 mg, 0.87 mmol, 87 %). ¹H NMR (500 MHz, CDCl₃) δ 8.11 – 8.01 (m, 1H), 7.62 – 7.53 (m, 1H), 7.51 – 7.39 (m, 2H), 6.13 (dd, *J* = 6.4, 3.7 Hz, 1H), 3.00 – 2.87 (m, 1H), 2.76 – 2.63 (m, 1H), 2.45 – 2.36 (m, 1H), 2.36 – 2.26 (m, 1H), 2.12 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.00, 170.63, 140.82,

134.08, 132.13, 129.19, 128.49, 127.34, 69.21, 34.51, 28.60, 21.36. Spectral properties are consistent with literature values.³⁰



phthalide (38)

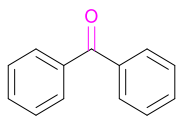
The title compound was prepared from a mixture of phthalan (120.1 mg, 1 mmol) and **1b** (11.9 mg, 0.05 mmol, 0.05 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 2 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 5:1) to afford the product as a yellow solid (111.1 mg, 0.83 mmol, 83 %). ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.58 – 7.46 (m, 2H), 5.32 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 171.25, 146.65, 134.15, 129.17, 125.90, 125.85, 122.23, 69.79. Spectral properties are consistent with literature values.³¹



isochroman-1-one (39)

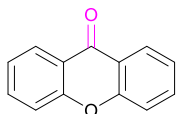
The title compound was prepared from a mixture of isochroman (134.2 mg, 1 mmol) and **1b** (11.9 mg, 0.05 mmol, 0.05 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 90 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 4:1) to afford the product as a yellow liquid

(102.2 mg, 0.69 mmol, 69 %). ^1H NMR (500 MHz, CDCl_3) δ 8.10 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.54 (td, $J = 7.5, 1.4$ Hz, 1H), 7.40 (td, $J = 7.6, 1.1$ Hz, 1H), 7.26 (d, $J = 7.7$ Hz, 1H), 4.54 (t, $J = 6.0$ Hz, 2H), 3.06 (t, $J = 6.0$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.29, 139.68, 133.81, 130.57, 127.84, 127.36, 125.46, 67.45, 27.97. Spectral properties are consistent with literature values.³²



diphenylmethane (40)

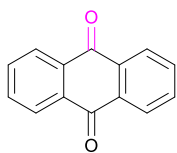
The title compound was prepared from a mixture of diphenylmethane (336.5 mg, 2 mmol) and **1a** (53.0 mg, 0.1 mmol, 0.05 equiv) in 20 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 6 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 20:1) to afford the product as a colorless liquid (308.0 mg, 1.69 mmol, 84 %). ^1H NMR (500 MHz, CDCl_3) δ 7.85 – 7.76 (m, 4H), 7.62 – 7.56 (m, 2H), 7.53 – 7.45 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 196.89, 137.73, 132.54, 130.19, 128.40. Spectral properties are consistent with literature values.⁸



xanthone (41)

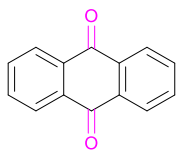
The title compound was prepared from a mixture of xanthene (182.2 mg, 1 mmol) and **1a** (26.5 mg, 0.05 mmol, 0.05 equiv) in 10 mL acetone. The mixture was stirred open to air and

irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 5 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : EtOAc = 10:1) to afford the product as a white solid (173.2 mg, 0.88 mmol, 88 %). ¹H NMR (500 MHz, CDCl₃) δ 8.34 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.72 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 2H), 7.49 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.38 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 177.36, 156.32, 134.95, 126.87, 124.04, 121.99, 118.11. Spectral properties are consistent with literature values.⁷



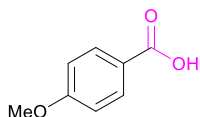
anthraquinone (42)

The title compound was prepared from a mixture of anthrone (194.2 mg, 1 mmol) and **1a** (53.0 mg, 0.1 mmol, 0.10 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 60 mins. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : CH₂Cl₂ = 1:2) to afford the product as a yellow solid (101.0 mg, 0.49 mmol, 49 %). ¹H NMR (500 MHz, CDCl₃) δ 8.54 – 8.12 (m, 4H), 8.02 – 7.58 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 183.32, 134.28, 133.67, 127.39. Spectral properties are consistent with literature values.²⁸



anthraquinone (43)

The title compound was prepared from a mixture of 9,10-dihydroanthracene (180.3 mg, 1 mmol) and **1a** (26.5 mg, 0.05 mmol, 0.05 equiv) in 10 mL acetone. The mixture was stirred open to air and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 4.5 hrs. The reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column chromatography (hexanes : CH₂Cl₂ = 1:2) to afford the product as a yellow solid (134.0 mg, 0.64 mmol, 64 %). ¹H NMR (600 MHz, CDCl₃) δ 8.40 – 8.23 (m, 4H), 7.89 – 7.71 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 183.31, 134.27, 133.71, 127.39. Spectral properties are consistent with literature values.²⁸

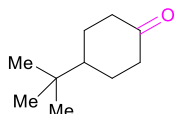


4-methoxybenzoic acid (44)

The title compound was prepared from a mixture of 4-methylanisole (244.3 mg, 2 mmol), **1a** (106 mg, 0.2 mmol, 0.10 equiv) in 10 mL acetone. The mixture was diluted with 5 mL acetone, stirred open to air, and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 9 hrs. The reaction mixture was concentrated by rotary evaporation and the residue was dissolved in 50 mL NaHCO₃ 5 % aqueous solution. The resultant mixture was washed with CH₂Cl₂ (30 mL x 2). The aqueous layer was acidified by concentrated HCl to pH 2 and extracted with EtOAc (50 mL x 3). The EtOAc layers were combined, dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation to afford the title compound as a slight yellow solid (171.0 mg, 1.40 mmol, 70 %). ¹H NMR (600 MHz, DMSO) δ 7.89 (d, *J* =

8.9 Hz, 2H), 7.01 (d, $J = 8.8$ Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 166.98, 162.83, 131.32, 122.98, 113.79, 55.41. Spectral properties are consistent with literature values.³³

VII. Upscale Oxidations



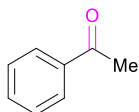
4-tert-butylcyclohexanone.

100-mmol reaction



To a 1-L round bottom flask was charged a magnetic stir bar, sodium anthraquinone-2-sulfonate monohydrate (1.641 g, 5 mmol, 0.05 equiv), tetrabutylammonium chloride (1.389 g, 5 mmol, 0.05 equiv), and 250 mL acetone. The mixture was stirred vigorously for 30 mins. To the resultant mixture was added 4-tert-butylcyclohexanol (15.627 g, 100 mmol, 1 equiv) followed by the addition of solid $\text{Co}(\text{acac})_2$ (257.2 mg, 1 mmol, 0.01 equiv) and 250 mL acetone. The reaction mixture was stirred open to air and irradiated with four 25-W 400-410 nm LEDs Lamps with fan cooling for 3 hrs and 15 mins. The internal temperature of the mixture over the course of reaction was 44 °C. Upon completion, the reaction mixture was concentrated by rotary evaporation and the crude material was purified by silica column

chromatography (hexanes : EtOAc = 8:1) to afford the product as a white solid (14.735 g, 95.5 mmol, 95 %). ^1H NMR (500 MHz, CDCl_3) δ 2.45 – 2.36 (m, 2H), 2.36 – 2.26 (m, 2H), 2.13 – 2.04 (m, 2H), 1.54 – 1.39 (m, 3H), 0.92 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 212.78, 46.86, 41.47, 32.61, 27.75, 27.74. Spectral properties are consistent with literature values.¹⁹



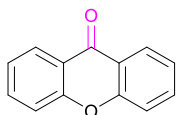
acetophenone.

500-mmol reaction



To a 2-L round bottom flask was charged a magnetic stir bar, sodium anthraquinone-2-sulfonate monohydrate (3.283 g, 10 mmol, 0.02 equiv), tetrabutylammonium chloride (2.779 g, 10 mmol, 0.02 equiv), and 500 mL acetone. The mixture was stirred vigorously for 45 mins. To the resultant mixture was added 1-phenylethanol (61.080 g, 500 mmol, 1 equiv) followed by the addition of solid $\text{Co}(\text{acac})_2$ (514.3 mg, 2 mmol, 0.004 equiv) and 500 mL acetone. The reaction mixture was stirred open to air and irradiated with four 25-W 400-410 nm LEDs Lamps with fan cooling for 11 hrs. The internal temperature of the mixture over the course of reaction was 40 °C. Upon completion, the reaction mixture was concentrated by rotary evaporation. To the residue was added 40 mL CH_2Cl_2 and 2 mL concentrated HCl. The

resultant mixture was stirred at r.t. for 30 mins, filtered through a short column of 60 mL silica gel, rinsed by CH₂Cl₂, and collected in fractions. The last fractions containing the desired product co-eluted with a blue impurity, and was washed twice with mixtures of 1 mL concentrated HCl in 100 mL H₂O, dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The total product was combined into two different big fractions, one is a slight yellow liquid and one is a brown liquid. The combined mass was 58.889 g, 490.1 mmol, 98 %. The two fractions had similar NMR data. ¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, *J* = 7.0 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 6.6 Hz, 2H), 2.60 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 198.26, 137.30, 133.21, 128.69, 128.43, 26.70. Spectral properties are consistent with literature values.³⁴



Xanthone.

10-mmol reaction

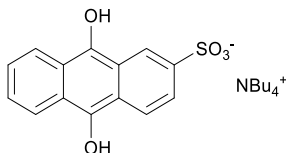


To a 500-mL round bottom flask was charged magnetic stir bar, sodium anthraquinone-2-sulfonate monohydrate (164.1 mg, 0.5 mmol, 0.05 equiv), tetrabutylammonium chloride (139.0 mg, 0.5 mmol, 0.05 equiv), and 50 mL acetone. The mixture was stirred vigorously for

30 mins. To the resultant mixture was added xanthene (1.822 g, 10 mmol, 1 equiv) and 50 mL acetone. The mixture was stirred open to air and irradiated with two 25-W 400-410 nm LEDs Lamps with fan cooling for 2 hrs. The internal temperature of the reaction mixture was 34 °C. Upon completion, the reaction mixture was concentrated by rotary evaporation and the crude material was purified by filtration through a short column of 30 mL silica gel and rinsed by CH₂Cl₂ to afford the desired product as a slight yellow solid (1.783 g, 9.09 mmol, 91 %). ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 7.9 Hz, 2H), 7.78 – 7.68 (m, 2H), 7.54 – 7.46 (m, 2H), 7.43 – 7.35 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 177.36, 156.31, 134.95, 126.87, 124.04, 121.99, 118.11. Spectral properties are consistent with literature values.⁷

VIII. Mechanistic Investigation

A. Isolation and Characterization of **1a** in Its Reduced State



tetrabutylammonium anthrahydroquinone-2-sulfonate (**1c**)

In an Ar-filled glove bag, to a 12-mL tube was charged **1a** (211.9 mg, 0.40 mmol, 1 equiv), cyclooctanol (76.9 mg, 0.60 mmol, 1.5 equiv), and 6 mL acetone. The 12-mL tube was capped, sealed by electric tape, and taken out of the Ar-filled glove bag. The reaction mixture in the 12-mL tube was stirred and irradiated with one 25-W 400-410 nm LEDs Lamp with fan cooling for 16 hrs. Upon irradiation, a yellow precipitate appeared.



Before irradiation



Reaction Setup



After 16-hr irradiation

The resultant mixture in the 12-mL tube was taken back to an Ar-filled glove bag and the yellow precipitate was filtered, rinsed thoroughly with acetone, and placed under high vacuum for 1 hr. The yellow precipitate was dissolved in DMSO-d₆ for NMR analysis. ¹H

NMR (500 MHz, DMSO) δ 9.57 (s, 1H), 9.48 (s, 1H), 8.63 (d, $J = 1.6$ Hz, 1H), 8.36 – 8.29 (m, 2H), 8.26 (d, $J = 9.1$ Hz, 1H), 7.58 (dd, $J = 9.1, 1.6$ Hz, 1H), 7.48 – 7.34 (m, 2H), 3.17 – 3.08 (m, 8H), 1.59 – 1.49 (m, 8H), 1.28 (h, $J = 7.4$ Hz, 8H), 0.91 (t, $J = 7.3$ Hz, 12H). ^{13}C NMR (126 MHz, DMSO) δ 143.15, 142.14, 140.99, 124.25, 124.12, 122.66, 122.65, 122.29, 122.24, 121.43, 121.29, 120.24, 119.92, 119.31, 57.65, 23.17, 19.31, 13.62.

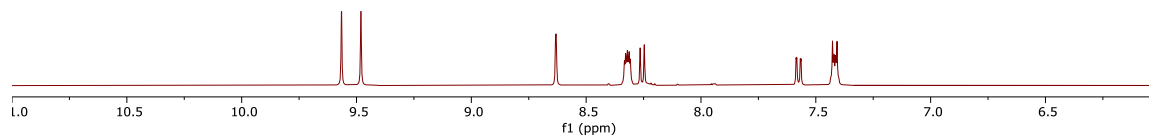
Because of low solubility of **1c** in acetone (image above), attempts to obtain clean spectra of **1c** without concomitant signals of **1a** in acetone- d_6 have been unsuccessful.

B. Fidelity of aerobic oxidation of **1c**

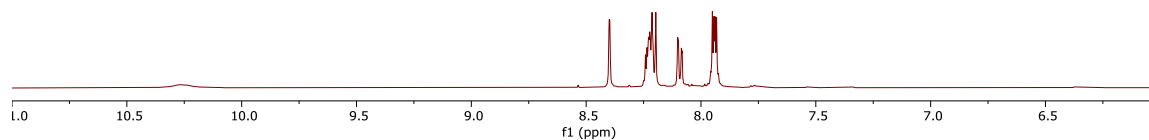
The recycling of **1a** from aerobic oxidation of **1c** was studied by NMR analysis.

In DMSO

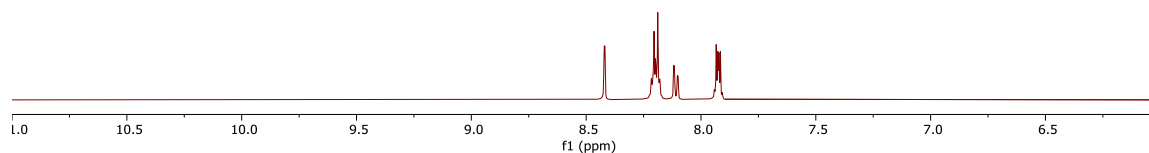
^1H NMR of **1c** in DMSO- d_6



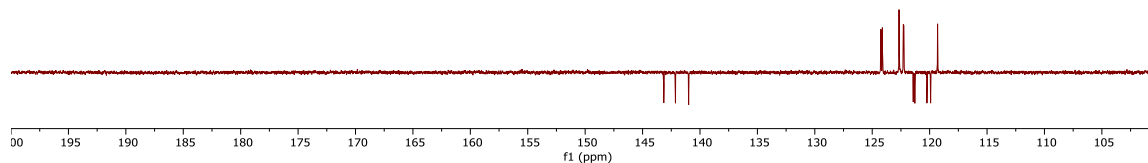
^1H NMR of **1c** upon exposure to air in DMSO- d_6



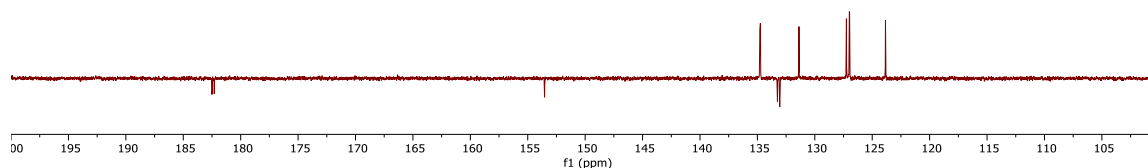
^1H NMR of **1a** in DMSO- d_6



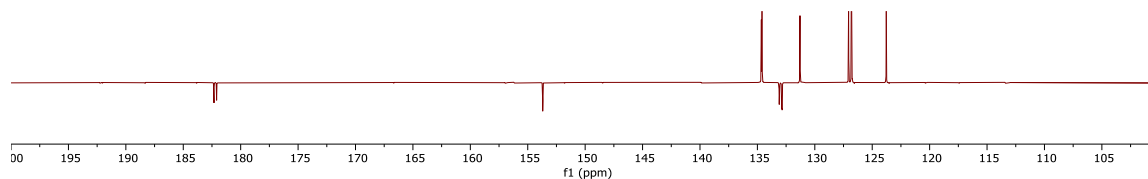
^{13}C NMR of **1c** in DMSO- d_6



^{13}C NMR of **1c** upon exposure to air in DMSO- d_6



^{13}C NMR of **1a** in DMSO- d_6



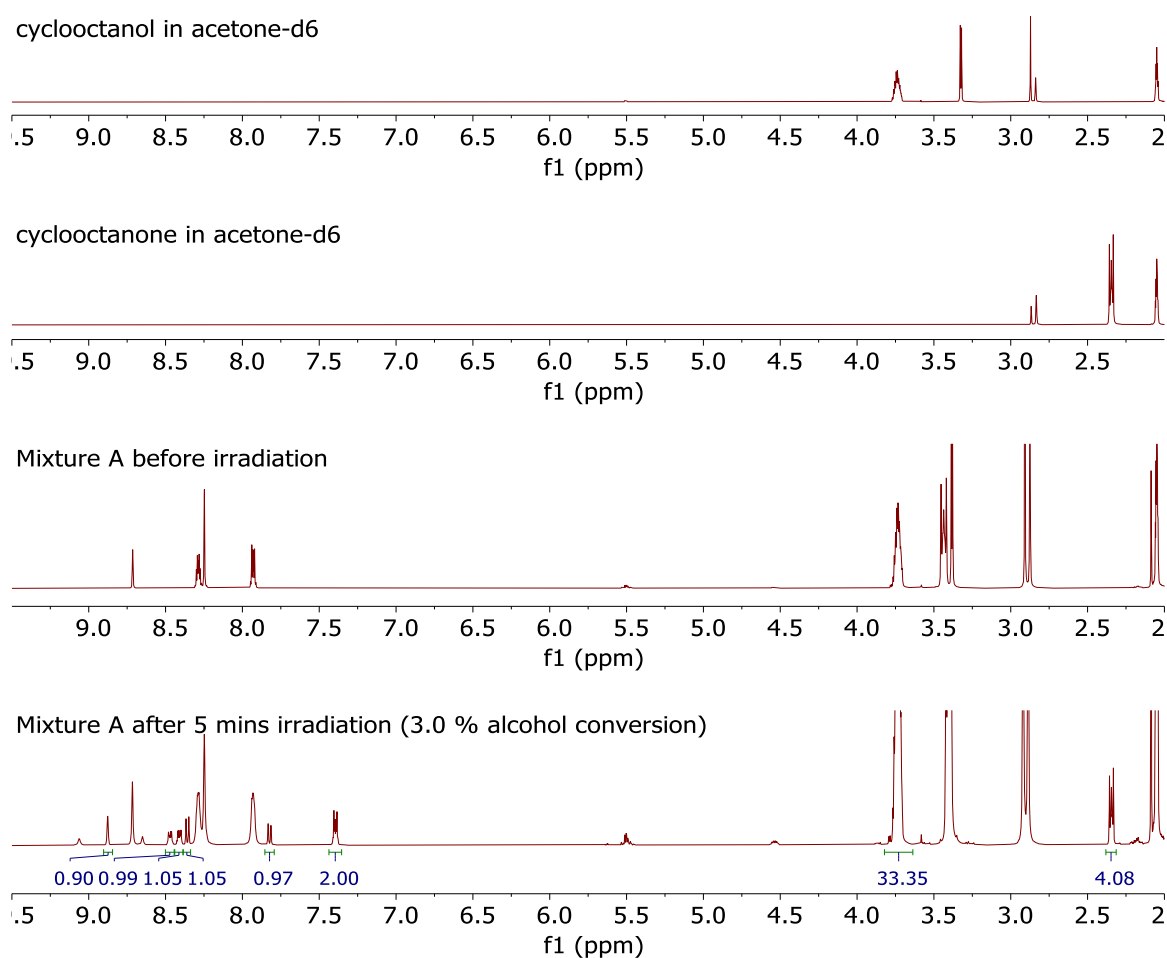
C. Determination of reaction stoichiometry between **1a** and alcohols

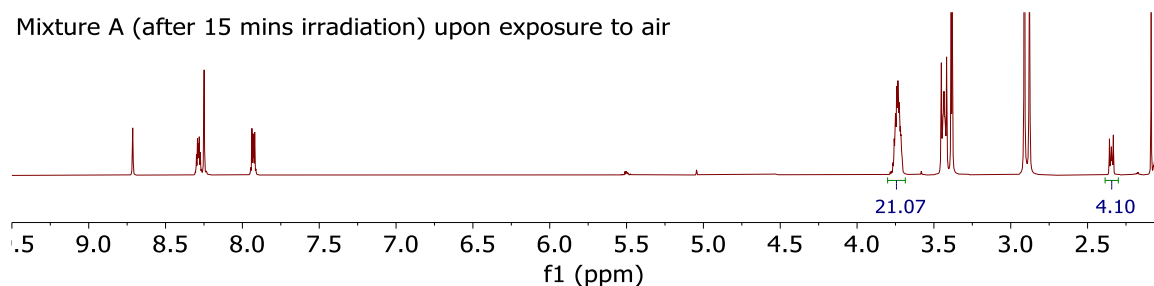
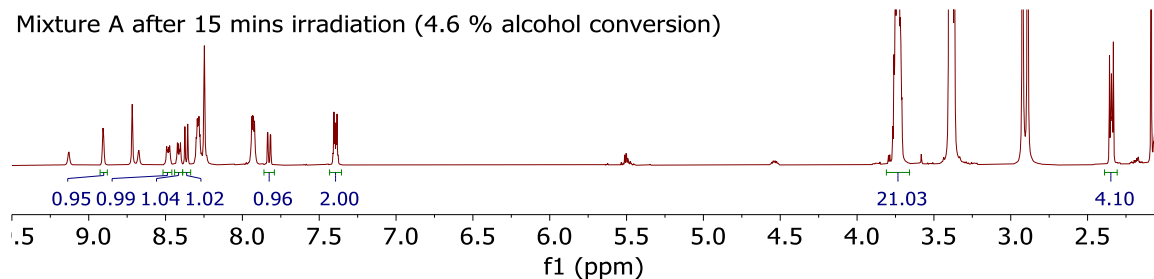
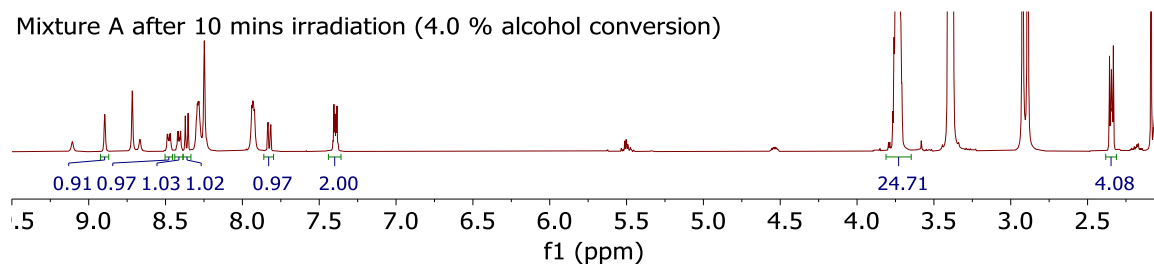
In an Ar-filled glove bag, a mixture of **1a**, cyclooctanol, and acetone- d_6 were prepared in a NMR tube.

Mixture A: **1a** (8.6 mg, 0.016 mmol, 0.1 equiv) and cyclooctanol (20.4 mg, 0.16 mmol, 1 equiv) in 0.8 mL acetone- d_6 .

The NMR tube was capped, sealed with electric tape, taken out of the Ar-filled glove bag, and irradiated with one 25-W 400-410 nm LEDs Lamp, positioned 10 cm way from the NMR tube, with fan cooling. NMR data were recorded before irradiation and at 5, 10, 15 mins of irradiation. Based on the ratio of intensity of signals at $\delta = 2.34$ ppm (cyclooctanone) and $\delta = 7.40$ ppm (**1c**), the reaction stoichiometry between **1a** and alcohol was determined to be 1:1, and the plausibility of a direct chemical reaction (a putative transfer of 2 Hydrogen atoms from

alcohol to **1a**) between the excited state of **1a** and alcohol in the absence of O₂ was established. In addition, the exact 1:1 ratio of **1c** and cyclooctanone formed over the course of the reaction and the absence of signals of isopropanol ruled out the plausibility of oxidation of **1c** by acetone (or a ketone in general). A comparison of ¹H NMR data in aromatic region of 15-min-irradiated mixture A upon exposure to air and ¹H NMR data of **1a** in acetone-d₆ confirmed the high fidelity of aerobic oxidation of **1c** in acetone.





IX. References

1. W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **14**, 2923-2925.
2. D. Pijper, R. A. van Delden, A. Meetsman and B. L. Feringa, *J. Am. Chem. Soc.*, 2005, **127**, 17612-17613.
3. C. Wang, Q. Luo, H. Sun, X. Guo and Z. Xi, *J. Am. Chem. Soc.*, 2007, **129**, 3094-3095.
4. R. J. Rahaim and R. E. Maleczka, *Org. Lett.*, 2011, **13**, 584-587.
5. F. Jiang, D. Bézier, J. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2011, **353**, 239-244.
6. B. Martín-Matute, M. Edin, K. Bogár, F. B. Kaynak and J. Backvall, *J. Am. Chem. Soc.*, 2005, **127**, 8817-8825.
7. N. F. Nikitas, D. L. Tzaras, I. Triandafillidi and C. G. Kokotos, *Green Chem.*, 2020, **22**, 471-477.
8. W. Schilling, D. Riemer, Y. Zhang, N. Hatami and S. Das, *ACS Catal.*, 2018, **8**, 5425-5430.
9. P. He, Y. Lu, C. Dong and Q. Hu, *Org. Lett.*, 2007, **9**, 343-346.
10. A. P. Dieskau, J. Begouin and B. Plietker, *Eur. J. Org. Chem.*, 2011, **27**, 5291-5296.

11. G. Y. Fang, O. A. Wallner, N. B. Blasio, X. Ginesta, J. N. Harvey and V. K. Aggarwal, *J. Am. Chem. Soc.*, 2007, **129**, 14632-14639.
12. S. Biswas, S. Maiti and U. Jana, *Eur. J. Org. Chem.*, 2010, **15**, 2861-2866.
13. H. Fuse, H. Mitsunuma and M. Kanai, *J. Am. Chem. Soc.*, 2020, **142**, 4493-4499
14. R. J. Rahaim, R. E. Maleczka, *Org. Lett.*, 2011, **13**, 584-587.
15. S. Magens, M. Ertelt, A. Jatsch and B. Plietker, *Org. Lett.*, 2008, **10**, 53-56.
16. H. Baba, K. Moriyama and H. Togo, *Tetrahedron Lett.*, 2011, **52**, 4303-4307.
17. A. Sakakura, K. Kawajiri, T. Ohkubo, Y. Kosugi and K. Ishihara, *J. Am. Chem. Soc.*, 2007, **129**, 14775-14779.
18. C. Jin, L. Zhang and W. Su, *Synlett*, 2011, **10**, 1435-1438.
19. W. Zhang, K. L. Carpenter and S. Lin, *Angew. Chem. Int. Ed.*, 2020, **59**, 409-417.
20. J. E. Steves and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 15742-15745.
21. P. Tang and T. Ritter, *Tetrahedron*, 2011, **67**, 4449-4454.
22. S. Liu, N. Berry, N. Thomson, A. Pettman, Z. Hyder, J. Mo and J. Xiao, *J. Org. Chem.*, 2006, **71**, 7467-7470.
23. H. Morimoto, T. Tsubogo, N. D. Litvinas and J. F. Hartwig, *Angew. Chem. Int. Ed.*, 2011, **50**, 3793-3798.
24. J. Mo, L. Xu and J. Xiao, *J. Am. Chem. Soc.*, 2005, **127**, 751-760.
25. C. F. Malosh and J. M. Ready, *J. Am. Chem. Soc.*, 2004, **126**, 10240-10241.
26. A. Takemiya and J. F. Hartwig, *J. Am. Chem. Soc.*, 2006, **128**, 14800-14801.
27. A. C. Bonaparte, M. P. Betush, B. M. Panseri, D. J. Mastarone, R. K. Murphy and S. S. Murphree, *Org. Lett.*, 2011, **13**, 1447-1449.
28. J. A. Marko, A. Durgham, S. L. Bretz and W. Liu, *Chem. Commun.*, 2019, **55**, 937-940.
29. J. W. Wrigglesworth, B. Cox, G. C. Lloyd-Jones and K. I. Booker-Milburn, *Org. Lett.*, 2011, **13**, 5326-5329.
30. T. Dohi, N. Takenaga, A. Goto, H. Fujioka and Y. Kita, *J. Org. Chem.*, 2008, **73**, 7365-7368.
31. X. Xie and S. S. Stahl, *J. Am. Chem. Soc.*, 2015, **137**, 3767-3770.
32. J. M. Hoover and S. S. Stahl, *J. Am. Chem. Soc.*, 2011, **133**, 16901-16910.
33. J. Takaya, S. Tadami, K. Ukai and N. Iwasawa, *Org. Lett.*, 2008, **10**, 2697-2700.
34. C. Bai, A. Li, X. Yao, H. Liu and Y. Li, *Green Chem.*, 2016, **18**, 1061-1069.

X. NMR Spectra

