A Mild Dehydroformylation using Base-Metal Catalysis

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Supplementary Materials

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General Methods.

Reactions were run under an atmosphere of argon, with magnetic stirring. Molecular sieves were activated by flame-drying under reduced pressure, and were maintained by storage in an oven at 110 °C. All NMR spectra were taken using Bruker 500 (500 MHz) magnets, in CD₃CN or CDCl₃, as noted, and are referenced to residual solvent shifts at δ 1.94 ppm and δ 7.26 ppm respectively. When stated, CD₃CN was degassed using the usual freeze-pump-thaw method. Other solvents were purified using the method of Grubbs.¹ Norbornenecarboxaldehyde was obtained from Oakwood Chemicals. Benzyl bromide was obtained from EMD Millipore through VWR International. All other chemicals were obtained from Sigma-Aldrich. All chemicals were used as received unless otherwise noted. Borosilicate vials (17 x 60 mm, 8 mL) were obtained from Fischer Scientific and were oven dried >12 hours before use. Reactions were irradiated with near UV light using an Exo-Terra 26W Reptile UVB 150 compact fluorescent bulb. UV-Vis measurements were acquired using an Agilent 8453 UV-Visible Spectroscopy System. Mass spectrum data was taken on an Agilent 6220 Accurate-Mass Time-of-Flight LC/MS. Hydrogen gas and carbon monoxide production was confirmed via headspace gas analysis using a Hewlett-Packard 6890 GC with an agilent CP7536 column and a thermal conductivity detector with column head pressure of 60 psi, oven temperature of 70 °C, injection temperature of 250 °C, and a detector temperature of 250 °C.

Wavelength of Irradiation

The spectral output of the Exo-Terra Reptile 150 lamp can be found online at:

http://www.exo-terra.com/en/products/reptile_uvb150.php

Importantly, the lamp has significant output in the near-UV region (300-400 nm) needed for tetrabutylammonium decatungstate (TBADT) photocatalysis.

Transmittance of Reaction Glassware.

All photoreactions were carried out in Fisherbrand 03-339-21D 8 mL vials as described in the procedure. These vials are made from code 7800 pharmaceutical glass, a type 1 class B borosilicate glass of a thickness of \sim 1 mm. The glass transmits \sim 80% of incident 325 nm light and over 90% for 360 nm and greater. As decatungstate excitation occurs above 325 nm, we are confident that sufficient luminous flux at the necessary wavelength occurs to efficiently excite the TBADT. While cobaloximes are known to undergo some photochemistry in the same frequency regime, it appears that this reactivity is of less significance (vide infra). A transmittance graph for code 7800 pharmaceutical glass is provided by Corning online:

http://csmedia2.corning.com/LifeSciences//media/pdf/Description_of_%20Code_7800.pdf

Catalyst Synthesis and Purity Analysis.

TBADT. *Tetrabutylammonium decatungstate* was synthesized according to the literature method.² Purity was analyzed by UV-Vis spectroscopy and determined by comparing the absorbance of the 323 nm peak to the published extinction coefficient (ε_{323} =1.35x10⁴ M⁻¹ cm⁻¹).² Catalyst purity ranged from 74-93%. The reaction was shown to be insensitive to this purity range of the photocatalyst.

COPC. *Cobaloxime pyridine chloride* was synthesized according to the literature method.³ Catalyst identity was confirmed by comparison of ¹H NMR spectrum to literature spectra.

COBF. *Cobaloxime boron fluoride* was synthesized according to the literature method ⁴ and was also obtained from Strem (CAS: 26220-72-4).

Substrate Purification and Synthesis.

General alkylation procedure

$$\begin{array}{c} R_{1} & \overbrace{R^{2}}^{1.1 \text{ equiv. KO'Bu}} \\ R_{2}^{1} & \overbrace{THF, r.t., Ar, 16 h}^{1.1 \text{ equiv. R}^{3}-X} \\ S1 & S2 \end{array}$$

To a 0 °C solution of aldehyde (3 mmol, 1 equiv.) in dry THF (15 ml) under argon was added $KO^{t}Bu$ (3.3 mmol, 1.1 equiv.) followed by methyl iodide (3.3 mmol, 1.1 equiv.). The solution was stirred at room temperature overnight. The reaction was then diluted with water, extracted with ethyl acetate, washed with brine and dried with Na₂SO₄. Solvent was removed under reduced pressure to yield the desired product.

For substrates where the direct purification of **S2** following the general alkylation procedure was impractical, a reduction was first carried out to enable separation followed by a Swern oxidation, described below.

General reduction procedure

$$\begin{array}{c} R^{1} \stackrel{R^{3} \stackrel{O}{\longrightarrow}}_{R^{2}} H \\ \end{array} \xrightarrow{1.3 \text{ equiv. NaBH}_{4}}_{THF, r.t., Ar, 13 h} \\ S2 \\ \end{array} \xrightarrow{R^{2} \stackrel{OH}{\longrightarrow}}_{R^{2}} R^{2} \\ \end{array}$$

Following the general alkylation procedure, the resulting crude oil **S2** was dissolved in THF (0.2 M) under argon and sodium borohydride (1.3 equiv.) was added. The solution was stirred for 13 hours under argon at room temperature and quenched with methanol. Solvent was removed and the alcohol was purified by column chromatography. The product alcohol (**int**) was then carried on to the general oxidation procedure or used for the dehydroxymethylation reaction (see substrate **15**)

General oxidation procedure



Alcohol **int** was oxidized according to a literature procedure.¹⁰ Oxalyl chloride (2 equiv.) was dissolved in dry DCM (1.2 M) and cooled to -78 °C. Dimethyl sulfoxide (3.5 equiv.) was added and the solution was stirred for 10 minutes. A solution of the above alcohol (0.19 g, 1 equiv.) in dry DCM (2.5 M) was added and the solution was stirred for 30 minutes under argon. Anhydrous triethylamine (5 equiv.) was then added and the resulting slurry was stirred for 10 minutes, warmed to 0 °C, and stirred for 5 minutes. The reaction was quenched with 1N aqueous HCl, and extracted with ether. The organic layers were combined, washed with brine, and stirred over Na₂SO₄ for 30 minutes. Solvent was removed and the oil was redissolved in ether and filtered through celite. Solvent was removed, and the resulting oil was flushed through a short silica plug with hexanes/ethyl acetate to furnish **S2**.

2,2-Dimethyl-3-(3,4-methylenedioxyphenyl)-propanal (2a)



2-methyl-3-(3,4-methylenedioxyphenyl)-propanal (3 mmol, 1 equiv.) was alkylated with methyl iodide (0.21 ml, 3.3 mmol) using the general alkylation procedure to yield a yellow oil. The aldehyde was determined to be suitably pure by ¹H NMR and was used without further purification (0.61 g, 2.94 mmol, 98% yield). ¹H NMR (500 MHz, CD₃CN) δ 9.55 (s, 1H), 6.74 (d, J = 7.9 Hz, 1H), 6.63 (d, J = 1.7 Hz, 1H), 6.58 (dd, J = 7.9, 1.8 Hz, 1H), 5.91 (s, 2H), 2.71 (s, 2H), 0.99 (s, 6H). ¹³C NMR (126 MHz, CD₃CN) δ 207.01, 148.27, 147.12, 132.16, 124.14, 111.31, 108.66, 102.10, 47.83, 43.22, 21.52. Mass calculated for C₁₂H₁₄O₃: 206.09429, found 206.0944.

2,2-Dimethyl-3-phenyl-propanal (3a)



Freshly distilled isobutyraldehyde (0.27 ml, 3 mmol) was alkylated with benzyl bromide (0.39 ml, 3.3 mmol) according to the general alkylation procedure. Due to observed instability, the aldehyde was isolated as a 9:1 mixture of desired 3a to benzyl bromide and used without further purification in 91% yield (2.7 mmol). Product identity was confirmed by comparison to literature spectra.⁵

4-(2,2-dimethyl-3-oxopropyl)benzonitrile (4a)



Freshly distilled isobutyraldehyde (0.27 ml, 3 mmol) was alkylated with α -bromide-p-tolunitrile (0.590 g, 3 mmol) according to the alkylation-reduction-oxidation procedure. Reduction of crude aldehyde **4a** on 3 mmol scale followed by column chromatography (9:1, then 1:1 hexanes:ethyl acetate), yielded pure alcohol **4-int** as a colorless oil (0.233 g, 1.23 mmol, 41% yield over two steps). ¹H NMR (CDCl₃) δ 7.57 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 3.28 (d, J = 5.6 Hz, 2H), 2.65 (s, 2H), 1.42 (t, J = 5.6 Hz, 1H), 0.88 (s, 6H). ¹³C NMR (CDCl₃) δ 144.85, 131.76, 131.38, 119.29, 109.99, 70.67, 44.58, 36.78, 24.08. Mass calculated for C₁₂H₁₅NO: 189.11536, found 189.11547.

4-int was oxidized according to the general oxidation procedure on a 1 mmol scale to provide **4a** as a light yellow oil (0.161 g, 0.858 mmol, 86% yield). 1H NMR (CDCl₃) δ 9.55 (s, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 2.84 (s, 2H), 1.06 (s, 6H). 13C NMR (CDCl₃) δ 204.97, 142.96, 132.08, 131.19, 118.95, 110.72, 47.08, 42.95, 21.67. Mass calculated for C₁₂H₁₃NO: 187.09971, found 187.09932.

methyl 4-(2,2-dimethyl-3-oxopropyl)benzoate (5a)



Freshly distilled isobutyraldehyde (0.27 ml, 3 mmol) was alkylated with methyl 4-(bromomethyl)benzoate (0.690 g, 3 mmol) according to the alkylation-reduction-oxidation procedure. Reduction of crude aldehyde **5a** on a 3 mmol scale followed by column chromatography (9:1, then 1:1 hexanes:ethyl acetate), yielded pure alcohol **5-int** as a colorless oil (0.128 g, 0.574 mmol, 17% yield over two steps). ¹H NMR (CDCl₃) δ 7.94 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 3.91 (s, 3H), 3.30 (d, J = 5.4 Hz, 2H), 2.64 (s, 2H), 1.41 (t, J = 5.7 Hz, 1H), 0.88 (s, 6H). ¹³C NMR (CDCl₃) δ 167.37, 144.63, 130.67, 129.27, 128.08, 71.02, 52.16, 44.60, 36.73, 24.11. Mass calculated for C₁₃H₁₈O₃: 222.12559, found 222.12566.

Alcohol **5-int** was oxidized according to the general oxidation procedure on a 0.57 mmol scale to provide **5a** as a light yellow oil (0.122 g, 0.556 mmol, 97% yield). ¹H NMR (CDCl₃) δ 9.57 (s, 1H), 7.94 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 3.90 (s, 3H), 2.83 (s, 2H), 1.05 (s, 6H). ¹³C NMR (CDCl₃) δ 205.48, 167.12, 142.62, 130.44, 129.58, 128.68, 52.23, 47.06, 43.06, 21.60. Mass calculated for C₁₃H₁₆O₃: 220.10994, found 220.1089.

2-(4-chlorophenoxy)-2-methylpropanal (6a)



Lithium aluminum hydride (1M in THF, 1.1 ml, 1.1 mmol) was dissolved in dry THF (5 ml) under argon. The solution was cooled to 0 °C, and (4-chlorophenoxy)isobutyric acid (clofibric acid; 0.235 g, 1.1 mmol) dissolved in dry THF (1.25 ml) was added dropwise. The resultant solution was warmed to room temperature, and stirred overnight. The reaction was then cooled to 0 °C, and 0.05 ml H₂O, 0.05 ml 1N aq. NaOH, and 0.15 ml of H₂O were added. The solution was warmed to room temperature, and MgSO₄ was added. The slurry was stirred for 2 hours, and then diluted with ether and filtered through celite. Solvent was removed under reduced pressure. The alcohol **6-int** was purified by column chromatography (1:1 hexanes:ethyl acetate) yielding a colorless oil (0.138 g, 68% yield). ¹H NMR (CDCl₃) δ 7.24 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.58 (d, J = 6.4 Hz, 2H), 2.12 (t, J = 6.5 Hz, 1H), 1.26 (s, 6H). ¹³C NMR (CDCl₃) δ 153.30, 129.27, 129.22, 125.35, 81.26, 70.34, 23.13. Compound could not be visualized by high resolution mass spectrometry.

Alcohol **6-int** was oxidized according to the general oxidation procedure on a 0.7 mmol scale to furnish **6a** as a colorless oil (0.057 g, 42% yield). ¹H NMR (CDCl₃) δ 9.81 (s, 1H), 7.22 (d, J = 8.9 Hz, 1H), 6.80 (d, J = 8.9 Hz, 1H), 1.41 (s, 4H). ¹³C NMR (CDCl₃) δ 202.97, 153.78, 129.57, 128.24, 121.46, 83.67, 21.90. Compound could not be visualized by high resolution mass spectrometry.

1-Methyl-1-cyclohexanecarboxaldehyde (7a)



Synthesized using a known modification of the general alkylation procedure.⁶ To a 0 °C solution of freshly distilled cyclohexanecarboxaldehyde (0.36 ml, 1 mmol, 1 equiv.) in dry dichloromethane (15 ml) under argon was added KO^tBu (0.44 g, 3.9 mmol, 3.9 equiv.) followed by methyl iodide (0.19 ml, 3 mmol, 3 equiv.). The solution was stirred at room temperature overnight. The reaction was then diluted with water, extracted with dichloromethane, washed with brine and dried with Na₂SO₄. Solvent was removed under modest reduced pressure and isolated as a 3:2 solution of **4a** in dichloromethane due to high volatility of the product in 72% yield. Product identity was confirmed by comparison to literature spectra.⁶

2-Methyl-bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (4:1 mixture of regioisomers 9a)



Synthesized according to the method described by Mellor and Webb.⁷ A solution of freshly cracked cyclopentadiene (1 ml, 12.2 mmol) and methacrolein (1.1 ml, 13.4 mmol) in dry benzene (16 ml) under argon was heated to reflux overnight. Solvent was removed under reduced pressure and the resulting mixture was purified by column chromatography (4:1 hexanes:ethyl acetate) as described by Loh et. al. ⁸ to yield 2-methyl-norbornene-2-carboxaldehyde (0.65 g, 4.8 mmol, 40% yield) as a colorless oil. Product identity was confirmed by comparison to the spectral assignments of Loh et. al.⁸ Product was obtained as a 4:1 mixture of *exo:endo* isomers, in accordance with the report of Mellor and Webb.⁷

2-methyl-3-phenylpropanal (11a)



Freshly distilled diisopropyl amine (0.77 ml, 5.5 mmol, 1.1 equiv.) was dissolved in dry THF (10 ml) under argon. The solution was cooled to 0 °C and ⁿButyl lithium (2.5M in hexanes, 2 ml, 5 mmol, 1 equiv.) was added. The solution was cooled to -78 °C and methyl propionate (480 μ L, 5.0 mmol, 1 equiv.) was added dropwise. The solution was stirred for 5 minutes and benzyl bromide (0.89 ml, 7.5 mmol, 1.5 equiv.) was added. The solution was warmed to room temperature and stirred overnight. The reaction was cooled to 0 °C and quenched with sat. aqueous NH₄Cl. The solution was extracted with ethyl acetate, and the organic layers were combined, washed with brine, and dried over Na₂SO₄. Solvent was removed, and the compound was purified by column chromatography (97:3 hexanes:ethyl acetate), yielding the pure alkylated intermediate **11-int-1** as a colorless oil (0.359 g, 2.0 mmol, 40% yield). Product identity was confirmed by comparison to literature spectra.¹¹

The ester alkylation product **11-int-1** (0.589 g, 3.3 mmol, 1 equiv.) was added dropwise to a 0 °C solution of lithium aluminum hydride in dry THF (0.18M in THF, 20 mL, 3.6 mmol, 1.1 equiv.) which was then allowed to warm to room temperature overnight. The reaction was then cooled to 0 °C, and 0.12 ml H₂O, 0.12 ml 1N aq. NaOH was added followed by 0.35 ml of H₂O. The resultant solution was warmed to room temperature, and MgSO₄ was added. The slurry was stirred

overnight, and then filtered through celite and washed with ether. The filtrate was washed with water and brine, and dried over Na_2SO_4 . Solvent was removed under reduced pressure. The alcohol was purified by column chromatography (4:1 hexanes:ethyl acetate, R_f =0.26) yielding alcohol **11**-int-2 as a colorless oil (0.403 g, 81% yield). Product identity was confirmed by comparison to literature spectra.¹²

Alcohol **11-int-2** was oxidized according to the general oxidation procedure on a 1.51 mmol scale to furnish aldehyde **11a** as a light yellow oil (0.082 g, 0.56 mmol, 37% yield). Product identity was confirmed by comparison to literature spectra.¹³

2,2-Dimethyl-3-phenylpropanol (15)



Aldehyde **3a** was reduced according to the general reduction procedure on a 2.7 mmol scale to furnish alcohol **15** as a colorless oil (0.083 g, 0.50 mmol, 17% yield). Alcohol identity was confirmed by comparison to literature spectra.⁹

Determination of In-Situ Purity and Concentration

For those substances that were found to be unstable to or too volatile for rigorous purification (**3a** and **4a**), the mixture isolated from the substrate preparation was added to the reaction instead. Multiple attempts were made to further purify these substrates with no success. The impurities were identified and quantified via ¹H NMR analysis and were used to determine a molar ratio of the mixture components which was then used to calculate an effective molecular mass of the product. This effective molar mass was then used to determine the mass of crude substrate to add to the dehydroformylation reaction. In both cases, the dehydroformylation reaction tolerated the minor impurities.

Exploration of Reaction Conditions

Control studies and optimization were performed with 2,2-Dimethyl-3-(3,4methylenedioxyphenyl)-propanal (2a). For the entries in table 1, a known amount of Aldehyde 2a was added to a flame-dried 2-dram vial equipped with a stir-bar. The vial was evacuated and refilled with Argon. TBADT, COPC and/or molecular sieves (10 mg) could then be added and the vial sealed with a screw cap equipped with a silicone septum. Under argon pressure, degassed CD₃CN (1 mL) and *ca*. 4 drops (roughly 21 mg) of methyl acetate were added to the vial. The reaction was then sparged with argon for 10 minutes. An initial aliquot for calibration (see "determination of *in situ* yields" below) was removed via syringe, and the reaction was sealed with parafilm and irradiated by the above-mentioned UV-compact fluorescent bulb ~3 cm away. The reaction was maintained at 31 °C (see below) by directing a steady stream of compressed air on the reaction flask. Reaction progress was monitored by ¹H NMR spectra of subsequent aliquots. Molecular sieve loading is presented in weight/volume, (i.e. 10% wt/v is 100 mg in 1 mL).

Conditions were varied to increase both rate and yield of olefin, meaning instances of high olefin yield and slower rate were not actively pursued. It was found that decreasing either catalyst loading was detrimental to yield; however, the low solubility of TBADT in acetonitrile limited potential catalyst loading. Nevertheless, the reaction was found to be largely insensitive to changes in concentration, so increases in effective catalyst loading were accompanied by analogous decreases in substrate concentration. The related cobaloxime catalyst, cobaloxime boron fluoride (COBF), gave comparable activity to COPC. Additionally, it was found that both 4 Å molecular sieves and degassed acetonitrile (entries in the following table were run without degassed solvent except where noted) were beneficial for the reaction rate, yield, and heightened product ratio. If molecular sieves were not used, side products were observed, including what was assigned to be heliotropin (piperonal), the benzylic aldehyde of the starting material.

Table S1. Exploration of conditions for the dehydroformylation of 2,2-Dimethyl-3-(3,4-methylenedioxyphenyl)-propanal (2a).

0		cat. TBAD cat. COPC		\sim		\sim			
$\langle D_{3}CN, Ar, 31 °C, hv \rangle$									
2a				2b	2c				
Entry	[SM] (Mol/L)	TBADT (mol%)	[Co] (mol%)	M.S. (%wt/v)	Time (hours)	% conversion	Olefin % yield ^a	2b:2c	
1	0.67	0	0	1	96	17	trace	-	
2	0.67	2	0	1	96	34	0	-	
3	0.67	0	2	1	96	5	trace	-	
4	0.67 ^b	2	2	1	96	No reaction	-	-	
5	0.67	2	2	-	96	39	14	1.2:1	
					60	26	7	1.3:1	
6	0.67	2	2 ^c	-	96	32	trace	-	
7	0.67	2	2	1	96	23	17	1.9:1	
8	0.67	2	2 ^c	1	96	27	15	1.9:1	
9	0.67	1	1	1	96	15	14	1.8:1	
10	0.67	2	1	1	96	42	20	1.3:1	
11	0.67	1	2	1	96	20	16	1.2:1	
12	0.33	2	2	1	48	36	18	1.7:1	
13	0.33	4	4	1	96	67	0	-	
14	0.33	4	4	10	48	48	20	1.9:1	
					72	62	28	1.6:1	
15	0.133	10	10	10	72	81	0	-	
16	0.67 ^d	2	2	1	96	38	24	1.6:1	
17	0.33 ^d	4	4	10	96	46	31	1.6:1	
18	0.33 ^d	4	4 ^c	10	48	44	18	2.8:1	
					96	60	22	2.2:1	

^a Raw yield. ^bNo light. ^cCOBF used as cobalt catalyst. ^d Performed using degassed acetonitrile.

Determination of In-Situ Yields

An initial t = 0 aliquot (100 µL) of the reaction mixture is diluted to 500 µL using CD₃CN and aerated via vigorous shaking. Integration of the characteristic ¹H NMR substrate peak for each aldehyde (specific peaks noted in the section "Reaction Details and Structure Analysis of Olefin Products" below) followed by normalization to the correct number of protons allows for the integration of the well resolved methyl acetate O–CH₃ peak (δ 3.59) to serve as the calibrated standard. Following the specified irradiation time, additional aliquots may be removed and prepared using the above procedure to acquire a spectrum. The O–CH₃ peak of the standard is then integrated to the same value as measured in the t=0 and the starting material and product (specific peaks also noted below) integrations serve to afford conversion and yield respectively.

As mentioned in our previous report, the high reactivity of TBADT precludes the use of many common internal standards as these can serve as competitive substrates for the initial hydrogen atom transfer (HAT) reaction. Methyl acetate was chosen due to the very low reactivity of hydrogen atoms alpha to ketones and ester carbonyls under TBADT photocatalysis.¹⁴

Determination of Reaction Temperature

Although the reported dehydroformylation reactions were run without heating, significant heat from the lamp necessitated cooling via a steady stream of air over the reaction vessels. The temperature of the air around the reaction vessels was consistently found to be 33 °C over the course of multiple days. Penetrating the Teflon septum of a reaction vessel and inserting a thermometer found that the internal temperature ranged from 30-31 °C, also across multiple days.

General procedure for base-metal catalyzed dehydroformylation of aldehydes



Aldehyde **S3** (0.33 mmol) was added to a flame-dried 2-dram vial equipped with a stir-bar. The vial was evacuated and refilled with Argon. TBADT (44 mg, 0.013 mmol, 4 mol%), COPC (5.3 mg, 0.013 mmol, 4 mol%), and molecular sieves (100 mg) were added and the vial was sealed with a screw cap equipped with a silicone septum. Under argon pressure, degassed CD₃CN (1 mL) and *ca.* 4 drops (roughly 21 mg) of methyl acetate were added to the vial. The reaction was then sparged with argon for 10 minutes. An initial aliquot for calibration (see below) was removed via syringe, and the reaction was sealed with parafilm and irradiated by the above-mentioned UV-compact fluorescent bulb ~3 cm away. The reaction was maintained at 31 °C (see below) by directing a steady stream of compressed air on the reaction flask. Reaction progress was monitored by ¹H NMR spectra of subsequent aliquots.

Identification of evolved gases was performed by withdrawing an aliquot of the headspace via a gastight syringe and injecting it on a GC/TCD instrument equipped with a molecular sieve column.

All reactions were run with a 4 mol% catalyst loading of TBADT and COPC, 10% w/v 4 Å molecular sieves, and at 0.33 M starting material as described above.

2,2-Dimethyl-3-(3,4-methylenedioxyphenyl)-propanal (2a)



Dehydroformylation of 2,2-Dimethyl-3-(3,4-methylenedioxyphenyl)-propanal **2a** produced a mixture of 5-(2-methylallyl)benzo[d][1,3]dioxole (**2b**) and 5-(2-methylprop-1-en-1-yl)benzo[d][1,3]dioxole (**2c**) in 19% and 12% respective yields after 96 h of irradiation. The products were identified by Nuclear Overhauser Effect (NOE) NMR spectroscopy and Heteronuclear Single Quantum Correlation (HSQC) NMR Spectroscopy and comparison to a known spectrum of **2b**. Attempts to extract the material from the reaction mixture by preparatory TLC were unsuccessful.

2,2-Dimethyl-3-phenyl-propanal (3a)



Dehydroformylation of 2,2-dimethyl-3-phenylpropanal (**3a**) produced a mixture of 3-phenyl-2methyl-1-propene (**3b**) and 3-phenyl-2-methyl-2-propene (**3c**) in 61% and 12% respective yields after 72 h of irradiation. Disappearance of starting **3a** was monitored by the benzylic CH₂ (δ 2.80). Identity of products was confirmed by comparison to literature spectra; appearance of **3b** was monitored by the terminal olefin CH₂ (δ 4.79 and 4.73) as well as the lone CH₃ (δ 3.33)¹⁵ and appearance of **3c** was monitored by the two distinct CH₃ peaks (δ 1.89 and 1.85).¹⁶ Due to instability during attempted chromatographic purifications, the starting material contained 13% benzyl bromide, which was tolerated by the reaction. 4-(2,2-dimethyl-3-oxopropyl)benzonitrile (4a)



Dehydroformylation of 4-(2,2-dimethyl-3-oxopropyl)benzonitrile (4a) produced a mixture of terminal alkene 4b and internal alkene 4c in 65% and 13% respective yields in addition to trace alkane product. Disappearance of starting 4a was monitored by the benzylic CH₂ (δ 2.87). Appearance of terminal olefin 4b was monitored by terminal CH₂ (δ 4.85 and 4.73) and benzylic CH₂ (δ 3.41). Appearance of internal olefin isomer 4c was monitored by vinyl CH (δ 6.32). After 72 hours of irradiation, Furthermore, these products were able to be isolated via dilution with ether, and flushing through celite with ether. Removal of solvent permitted purification via column chromatography (9:1 hexanes:diethyl ether, R_f=0.41) to furnish the products as a *4.25:1:trace* mixture of 4b/4c/alkane (0.0201g, 40% yield, colorless oil). Product contained trace alkane product, identifiable from the doublets at δ 2.53 and 0.90. Product identity was confirmed by comparison to literature spectra.^{22, 23}

methyl 4-(2,2-dimethyl-3-oxopropyl)benzoate (5a)



Dehydroformylation of produced terminal alkene 5b in 59% yield, internal alkene 5c in 9% yield, and the respective alkane in trace yield after 72 h of irradiation. Disappearance of starting material was monitored by the benzylic CH₂ (δ 2.87). Appearance of terminal olefin was monitored by terminal CH₂ (δ 4.83 and 4.74) and benzylic CH₂ (δ 3.40). Appearance of internal olefin isomer was monitored by vinyl CH (δ 6.34). Furthermore, these products were able to be isolated via dilution with ether, and flushing through celite with ether. Removal of solvent permitted purification via iterative column chromatography (9:1 Hexanes:diethyl ether, R_f=0.47; then 95:5 Hexanes:diethyl ether, R_f=0.26) to furnish the products as an inseparable 7:1:trace mixture of **5b/5c/alkane** in 41% combined yield (0.0273 g, 0.135 mmol, 41% yield of olefins, colorless oil). Product identity was confirmed by comparison to literature spectra.²⁴

2-(4-chlorophenoxy)-2-methylpropanal (6a)



Dehydroformylation of 2-(4-chlorophenoxy)-2-methylpropanal (6a) produced a 1:1 mixture of enol hydrolysis products 4-chlorophenol 6b and acetone 6c in 63% yield after 96 h of irradiation. Disappearance of starting 6a was monitored by an aromatic CH (δ 6.89). Appearance of p-chlorophenol 6b was monitored by the appearance of the two aromatic CH (δ 7.19 and 6.79). Appearance of acetone 6c was monitored by the two CH₃ (δ 2.09). Product identitie were confirmed by comparison to literature spectra.²⁵

1-Methyl-1-cyclohexanecarboxaldehyde (7a)



Dehydroformylation of 1-methyl-1-cyclohexanecarboxaldehyde (7a) produced a mixture of methylene cyclohexane (7b) and 1-methylcyclohexene (7c) in 21% and 17% respective yields after 48 h of irradiation. Disappearance of starting 7a was monitored by aldehyde CHO at δ 9.41. Identity of the products was confirmed by comparison to literature spectra; appearance of 7b was monitored by CH₂ singlet (δ 4.57)¹⁷ and appearance of 7c was monitored by broad CH singlet (δ 5.38).¹⁸ Due to volatility, the substrate used contained 36% dichloromethane, which was tolerated by the reaction.

Pivalaldehyde (8a)



Dehydroformylation of pivalaldehyde (**8a**) produced isobutylene (**8b**) in 58% yield after 48 h of irradiation and was performed in a J-Young tube. The t=0 aliquot was taken, and the reaction was run as usual in the tube without stirring. Disappearance of starting **8a** was monitored by the *tert*-butyl CH₃ peak (δ 1.04). Identity of isobutylene **8b** was confirmed by comparison to literature spectra; appearance of isobutylene was monitored by the olefin CH₂ (δ 4.66).¹⁹ Additionally, hydrogen formation was confirmed by the H₂ peak at δ 4.57.

2-Methyl-bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (9a)



Dehydroformylation of 4:1 *endo:exo* mixture **9a** produced 5-methylene-2-norbornene (**9b**) in 47% yield after 48 h of irradiation. The olefin CH peak of the major *exo* isomer of **9a** at δ 6.30 was calibrated to 0.80 H, to accommodate the 4:1 *exo:endo* ratio. Disappearance of starting **9a** was monitored by this peak, and the ratio of isomers was confirmed to remain unchanged by the ratio of the aldehyde peaks (δ 9.66 and δ 9.37). Identity of 5-methylene-2-norbornene **9b** was confirmed by comparison to literature spectra; appearance was monitored by the olefinic CH₂ peak (δ 4.68 and δ 4.97).²⁰ The absence of 2-methyl-norbornadiene was confirmed by the lack of peaks in the δ 3.50-3.20 region (reported as the protons at the C1 and C4 positions).²¹

2-Methyl-3-(3,4-methylenedioxyphenyl)-propanal (10a)



Dehydroformylation of 2-methyl-3-(3,4-methylenedioxyphenyl)-propanal (**10a**) produced 3-(3,4-methylenedioxyphenyl)-1-propene (**10c**) in 6% yield in addition to trace 1-(3,4-methylenedioxyphenyl)-propene (**10b**) after 96 h of irradiation. Disappearance of starting **10a** was monitored by the benzylic CH₂ and the α -CH (δ 2.99, 2.65, 2.57). Product identities were confirmed by comparison to known spectra; appearance of terminal olefin (safrole) **10b** was monitored by the olefin protons at δ 5.08-5.01, and the CH₃ at δ 3.29 while internal olefin (isosafrole) **10c** appearance was monitored by the CH₃ doublet at δ 1.81-1.82.²⁶

2-methyl-3-phenylpropanal (11a)



Dehydroformylation of 2-methyl-3-phenylpropanal **11a** produced 3-phenylpropene **11b** in 7% yield in addition to trans-1-phenylpropene **11c** in 7% yield after 96 h of irradiation. Disappearance of starting **11a** was monitored by one of the benzylic CH₂ hydrogens (δ 2.62, dd, 1H). Appearance of terminal olefin was monitored by the appearance of the benzylic CH₂ (δ 3.39) and the vinyl CH (δ 5.99). Appearance of internal olefin was monitored by the vinyl peaks (δ 6.43 and 6.30) and the methyl CH₃ (δ 1.86). Product identity was confirmed by comparison to literature spectra.^{9, 10}

Cyclohexanecarboxaldehyde (12a)



Dehydroformylation of cyclohexanecarboxaldehyde **12a** produced trace cyclohexene (**12b**) after 24 h of irradiation with almost complete consumption of **12a**. The consumption of starting compound **12a** was monitored by the multiplet peaks at δ 1.87, 1.71, 1.62. Trace cyclohexene **12b** was assigned to a doublet at δ 5.68. Significant white precipitate accumulated throughout the reaction with concomitant loss of solution mass balance is tentatively assigned to formation of a polymeric product.

1-Octanal (13a)



Subjecting 1-octanal (13a) to the dehydroformylation conditions for 72 h led to the production of no products assignable to dehydroformylation. Starting material disappearance was monitored by the aldehyde peak (δ 9.69). No olefin peaks were observed that could be assigned to material aside from those arising from catalyst decomposition.

Bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (14a)



Subjecting bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (14a) to the dehydroformylation conditions for 48 h hours led to the production of no products assignable to dehydroformylation. The consumption of starting compound 14a was monitored by the aldehyde peaks at δ 9.74 and 9.41. No olefin peaks were observed aside from those arising from catalyst decomposition.

Dehydroxymethylation of 2,2-Dimethyl-3-phenylpropanol (15)



The dehydroxymethylation reaction used identical conditions to the dehydroformylation reaction described above. Dehydroxymethylation of 2,2-dimethyl-3-phenylpropanol (15) produced a mixture of 2,2-dimethyl-3-phenylpropanal (3a), 3-phenyl-2-methyl-1-propene (3b), and 3-phenyl-2-methyl-2-propene (3c) in 8%, 32%, and 5% respective yields after 72 h of irradiation. The

consumption of starting compound 11 was monitored by the benzylic peak at δ 2.56. Aldehyde product (**3a**) formation was monitored by the benzylic CH₂ at δ 2.80 and olefin products were confirmed and monitored as described above for compound **3a**, save that the benzylic peak at δ 6.29 was used for quantitation instead of the obscured δ 1.89 and 1.85 peaks.

General Reaction Observations for Dehydroformylation Reaction

As all reactions were run and monitored in acetonitrile, conversions and yields are based on NMR integrations with methyl acetate as an internal standard, and all peaks given are in reference to the residual solvent signal in CD₃CN. Upon irradiation, in most cases, the solution changed from a light orange color to green, and then blue, which is in-line with previous reports using TBADT.^{14, 27} In some cases the reaction would instead change to a deep red color, and on the timescale of hours oscillate between shades of red and green. No correlation was observed between this unusual color and increased or decreased reaction efficiency. If syringe needles were not appropriately sparged with argon before removing aliquots, the blue solution would rapidly turn green or, eventually, red or yellow. Subsequent irradiation would return the blue color (**Fig. S1-S6**). Occasionally, olefin peaks were observed at δ 5.27 ppm and δ 5.18 ppm. These occurred across multiple reactions and were often visible only in small quantity. These can be attributed to tetrabutylammonium counter ion decomposition as discussed in the previous work of our lab and others.^{27, 28}



Figure S1. Representative reaction before irradiation.



Figure S2. Representative reaction after several hours of irradiation.



Figure S3. Representative reaction after further irradiation.



Figure S4. Representative reaction quenched by air.



Figure S5. Representative reaction with blue color returned by subsequent irradiation.



Figure S6. Representative reaction after being removed from irradiation and stirring.



Identification of dehydroformylation products of Substrate 2a

Figure S7. The NOE (top) and HSQC (bottom) correlations for **2b** (left) and **2c** (right). The shifts given are in ppm, and for the top are the associated proton shifts, and for the bottom are the associated carbon shifts.

NOE data was first used to confirm the protons assignments. For **2b**, the terminal olefin peaks at δ 4.72 and δ 4.78 were found to correlate with peaks at δ 3.24 and δ 1.66 respectively. The former was assigned to be the benzylic methylene, and the latter was assigned the allylic methyl. For 2-methyl-isosafrole, of the two distinct allylic CH₃, only one (δ 1.87) was found to correlate with another peak, at δ 6.18, which was assigned to the benzylic, vinyl methine. HSQC was then used to support these assignments. For **2b**, both olefinic protons correlated with a peak at δ 111.57, and the benzylic methylene correlates with a peak at δ 44.13. For 2-methyl-isosafrole, the two allylic methyl groups at δ 1.87 and δ 1.82 correlates to carbon peaks at δ 26.44 and δ 19.48 respectively. The methine correlates to a carbon peak at δ 124.86. The assignments for **2b** were well in line with reported peaks, which supports our assignment for these two molecules (¹H reported as δ 4.82, 4.76, 3.14 and 1.69 ppm in CDCl₃ at 300 MHz. Found δ 4.78, 4.72, 3.24 and 1.66 ppm in CD₃CN at 500 MHz. ¹³C reported as δ 111.7 and 44.3 ppm in CDCl₃ at 300 MHz. Found δ 111.57 and 44.13 ppm in CD₃CN at 500 MHz.



Figure S8. The NOE correlation spectrum of the crude mixture of 2a, 2b, and 2c.



Figure S9. The HSQC spectrum for the crude mixture of 2a, 2b, and 2c.

Disappearance of starting 2,2-Dimethyl-3-(3,4-methylenedioxyphenyl)-propanal **2a** was monitored by the benzylic CH₂ (δ 2.71). Appearance of 2-methyl-safrole **2b** was confirmed and monitored by the CH₂ on the olefin (δ 4.78 and 4.72), as well as the lone CH₃ (δ 3.24). Appearance of 2-methyl-isosafrole **2c** was confirmed and monitored by the two distinct CH₃ peaks (δ 1.86 and 1.82).



Figure S10. A representative NMR spectrum of the dehydroformylation of 2a. The bottom is before reaction, the top after.

NMR spectra for new compounds



Figure S12. ¹³C NMR APT experiment of 2a.



Figure S13. ¹H NMR of 4-int.



Figure S14. ¹³C NMR APT experiment of 4-int.



Figure S15. ¹H NMR of 4a.



Figure S16. ¹³C NMR APT experiment of 4a.



Figure S17. ¹H NMR of 5-int.



Figure S18. ¹³C NMR APT experiment of 5-int.



Figure S19. ¹H NMR of 5a.



Figure S20. ¹³C NMR APT experiment of 5a.



Figure S21. ¹H NMR of 6-int.



Figure S22. ¹³C NMR APT experiment of 6-int.



Figure S23. ¹H NMR of 6a.



Figure S24. ¹³C NMR APT experiment of 6a.

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