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Note

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# Stable TEMPO and ABNO Catalyst Solutions for User-Friendly (bpy)Cu/Nitroxyl-Catalyzed Aerobic Alcohol Oxidation

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**ABSTRACT**

Two solutions, one consisting of bpy/TEMPO/NMI and the other bpy/ABNO/NMI (bpy = 2,2'-bipyridyl; TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, ABNO = 9-azabicyclo[3.3.1]nonane *N*-oxyl; NMI = *N*-methylimidazole), in acetonitrile are shown to have good long-term stability (≥ 1 year) under refrigeration. The solutions may be combined in appropriate quantities with commercially available $[Cu(MeCN)_4]OTf$ to provide a convenient catalyst system for the aerobic oxidation of primary and secondary alcohols.

Alcohol oxidation is one of the most frequently used oxidation reactions in organic chemistry, and molecular oxygen is widely recognized as an ideal oxidant. Aerobic alcohol oxidations have been studied extensively,[1] but they are rarely used in preparative organic synthesis. Recent advances in Cu/nitroxyl catalyst systems,[1d,e,g,2-4] however, have led to aerobic alcohol oxidation methods that rival the scope, selectivity, and practicality of traditional oxidation protocols. These methods have emerged as some of the most versatile bench scale methods for aerobic alcohol oxidation.

In recent years, we have reported two highly practical catalyst systems for aerobic alcohol oxidation: (bpy)$Cu^{I}$/TEMPO/NMI[3] and ($^{MeO}$bpy)$Cu^{I}$/ABNO/NMI[4] (Figure 1). These Cu/nitroxyl-catalyzed aerobic alcohol oxidation methods exhibit a broad scope of benzylic, allylic, and aliphatic alcohols as well as high functional group tolerance. The first generation (bpy)$Cu^{I}$/TEMPO/NMI catalyst displays high chemoselectivity for unhindered primary alcohols over hindered primary alcohols and secondary alcohols. Mechanistic insights into this (bpy)$Cu^{I}$/TEMPO/NMI catalyst system[5] led to the development of a ($^{MeO}$bpy)$Cu^{I}$/ABNO/NMI catalyst system, which exhibits much faster rates for aliphatic alcohol oxidation and readily oxidizes secondary alcohols. Reactions with both catalyst systems typically can be performed in an open flask at room temperature, and the product often may be used in subsequent reactions without purification.[6]

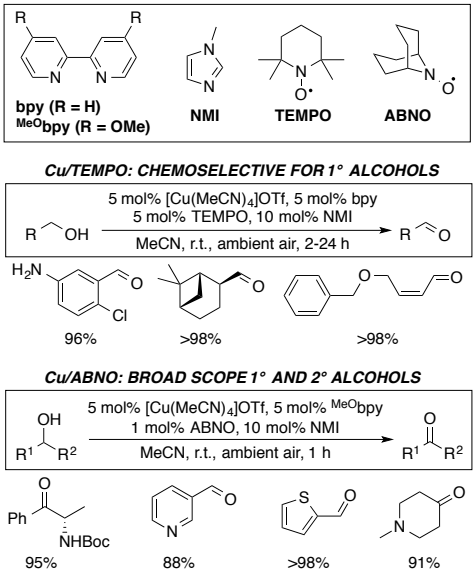



**Figure 1**. Cu/nitroxyl-catalyzed aerobic alcohol oxidation methods.[3,4]

In spite of the utility of these methods, their use can be somewhat cumbersome, especially for small-scale applications, because small quantities (sometimes submilligram) of the four different catalyst components must be independently weighed or dispensed into the reaction mixture. This feature can present a barrier to the use of the catalytic methods relative to easily dispensed stoichiometric reagents, such as chromium oxides or Dess-Martin periodinane. To address this issue, we sought to identify shelf-stable mixtures of the catalyst components that would improve the utility of the methods. Here, we show that solutions of bpy, nitroxyl, and NMI (nitroxyl = TEMPO or ABNO) are stable in acetonitrile solution for ≥ 1 year at 5 °C. This solution may be dispensed as a single catalyst component, together with solid $[Cu(MeCN)_4]OTf$, as a convenient means to perform air oxidation of diverse functionalized 1° and 2° alcohols.

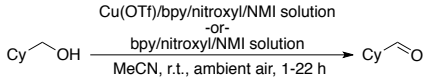
We initially targeted a solid catalyst mixture containing all catalyst components needed for alcohol oxidation. In this case, NMI would be replaced by a solid alternative; however, all

combinations of the solid components, $[Cu(MeCN)_4]OTf$, bpy, and nitroxyl, led to decomposition and poor catalyst activity as a result of deleterious interactions between the components in the solid state.

We then elected test solutions of the catalytic reagents in acetonitrile, the preferred reaction solvent. The electron-rich bpy derivative, $^{MeO}$bpy, was shown to have among the best activity for the Cu/ABNO catalyst system,[4] but this bpy derivative is sparingly soluble in MeCN and ligand precipitation was observed from solutions stored in a refrigerator. Thus, we chose to test bpy as a ligand for both of the alcohol oxidation solutions (i.e., with TEMPO and ABNO). Oxidation of cyclohexanemethanol was used to assess catalyst performance because aliphatic alcohols are less reactive than allylic and benzylic alcohols and, therefore, would provide a sensitive assay of catalyst stability (Table 1). Solutions of $[Cu(MeCN)_4]OTf$, bpy, nitroxyl, and NMI (0.05-0.2 M in $[Cu(MeCN)_4]OTf$ and bpy) under air or $N_2$ were unstable on the basis of their loss of activity for cyclohexanemethanol oxidation after being stored at 5 °C for a 1–2 month period (Table 1, entries 1, 3, 5, 7). This problem was solved by removing $[Cu(MeCN)_4]OTf$. Solutions of bpy, nitroxyl, and NMI in acetonitrile (0.2 M bpy/0.2 M TEMPO/0.4 M NMI or 0.2 M bpy/0.04 M ABNO/0.4 M NMI) were stable over the same periods (Table 1, entries 2, 4, 6, 8). Full activity for cyclohexanemethanol oxidation was observed when this catalyst solution was combined with solid $[Cu(MeCN)_4]OTf$. The most reliable catalyst activity and stability was observed when bpy/nitroxyl/NMI solutions were stored in a refrigerator (5 °C), and minimal differences in activity were observed from solutions prepared under air or $N_2$ (cf. entries 2 vs 4 and 6 vs 8). Very good activity was also observed over a two-month period with bpy/nitroxyl/NMI solutions stored under air at room temperature (22 °C) (entries 9 and 10). Solid $[Cu(MeCN)_4]OTf$ has indefinite stability when stored under $N_2$ in a dry environment, but

can be stored at room temperature (22 °C) on a lab shelf for at least six months without appreciable activity loss.

**Table 1.** Stability Testing of Catalyst Solutions.[a]




| entry | storage atmosphere | $[Cu(MeCN)_4]OTf$? | nitroxyl | % yield (1 month) | % yield (2 month) |
|---|---|---|---|---|---|
| 1 | $N_2$ | yes | TEMPO | 73 | 63 |
| 2 | $N_2$ | no | TEMPO | 97 | 98 |
| 3 | air | yes | TEMPO | 81 | 83 |
| 4 | air | no | TEMPO | 98 | 95 |
| 5 | $N_2$ | yes | ABNO | 83 | 71 |
| 6 | $N_2$ | no | ABNO | 99 | 94 |
| 7 | air | yes | ABNO | 79 | 77 |
| 8 | air | no | ABNO | 98 | 94 |
| 9[b] | air | no | TEMPO | 98 | 100 |
| 10[b] | air | no | ABNO | 97 | 92 |

[a] GC yields vs internal standard. Catalyst solutions stored in a refrigerator at 5 °C when not in use. Reactions were performed on a 0.2 mmol scale in 2 mL of MeCN. [b] Catalyst solutions stored at 22 °C when not in use.

Among the successful catalyst solutions in Table 1, the solutions under air in a refrigerator (entries 4 and 8) offer a convenient storage option and should minimize catalyst decomposition over time, so we proceeded with further testing of these mixtures. A solution concentration of 0.2 M in bpy, 0.04-0.2 M in nitroxyl, and 0.4 M in NMI was selected for long-term testing because these concentrations allow for convenient dispensing of the catalyst into a reaction vessel via syringe. For example, 250 $\mu$L of catalyst solution is required for a 1 mmol reaction, and 2.5 mL of catalyst solution is required for a 10 mmol reaction. These solutions were stored at 5 °C for six months and tested in the oxidation of a collection of alcohols bearing

diverse functional groups (Figure 2). The reactions proceeded with essentially the same efficiency as reported previously using freshly prepared catalysts (Figure 2).[3,4] As observed previously, various halides, ethers, amines, and heterocycles are well tolerated, a *cis*-allylic alcohol is oxidized without significant isomerization, and a Boc-protected aminoalcohol is oxidized without racemization.

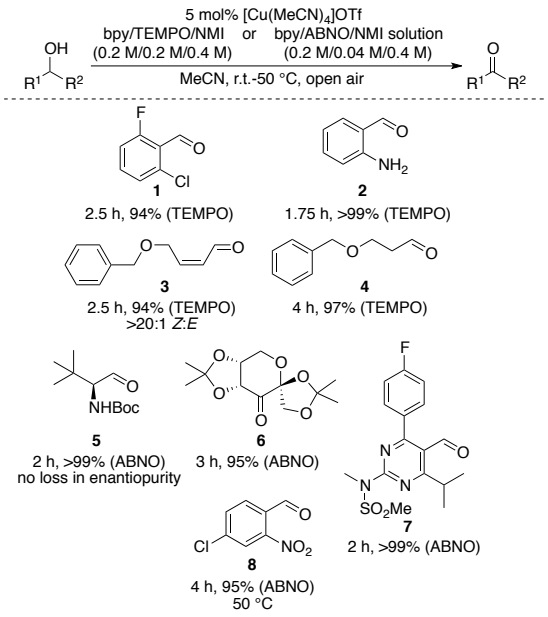



**Figure 2.** Isolated product yields from oxidation of functionalized alcohols with $[Cu(MeCN)_4]OTf$ in combination of bpy/TEMPO/NMI or bpy/ABNO/NMI catalyst solutions stored for six months under air at 5 °C.

These bpy/ABNO/NMI and bpy/TEMPO/NMI solutions were then tested over a one-year period for the oxidation of cyclohexanemethanol to gauge catalyst stability (Figure 3). Time-course data were acquired, rather than just analysis of the final yield, in order to increase the sensitivity of the assay. ABNO and TEMPO solutions afforded >92% cyclohexanecarboxaldehyde within 2 h (ABNO, Figure 3A) or 24 h (TEMPO, Figure 3B) when

the reactions were performed open to air at room temperature, and no loss of catalyst activity was observed during the one-year trial.

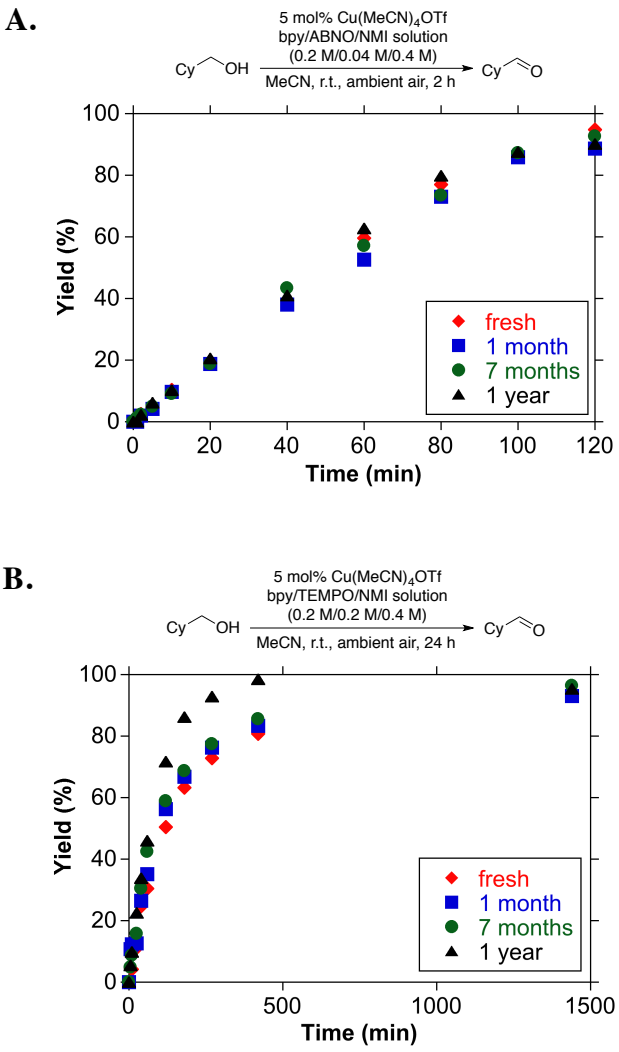



**Figure 3.** Time course of cyclohexanemethanol oxidation with $[Cu(MeCN)_4]OTf$ and bpy/nitroxyl/NMI solutions stored under air at 5 °C over a one-year period.

A typical protocol for use of these catalyst solutions is as follows. For a 1 mmol reaction, a 25 mL round bottom flask is equipped with a stir bar and charged with alcohol (1 mmol), $[Cu(MeCN)_4]OTf$ (19 mg), and MeCN (10 mL). The bpy/nitroxyl/NMI solution (250 $\mu$L; 0.2 M

bpy/0.2 M TEMPO/0.4 M NMI or 0.2 M bpy/0.04 M ABNO/0.4 M NMI) is added, which results in a red-brown solution. The reaction is stirred rapidly at room temperature open to air.[7] The reaction may be monitored by TLC, and upon completion (often accompanied by a color change to green or blue), the crude reaction mixture is purified via aqueous extraction or flash chromatography to afford the desired carbonyl compound.

The catalyst solutions described here are now commercially available through Sigma-Aldrich.[8]

## CONCLUSION

Shelf-stable solutions of several catalyst components have been developed for the Cu/TEMPO- and Cu/ABNO-based alcohol oxidation catalysts that are capable of operating efficiently at room temperature with air as the oxidant. These solutions should make these methods more convenient for bench-scale applications of aerobic alcohol oxidation. In short, these bpy/$[Cu(MeCN)_4]$OTf/nitroxyl/NMI catalysts represent a compelling alternative to traditional stoichiometric oxidants for alcohol oxidation.

## EXPERIMENTAL SECTION

### General Considerations.

$^1$H and $^{13}C\{^1H\}$ NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts (δ) are given in parts per million and are referenced to the residual solvent signal (all $^{13}$C NMR spectra) or tetramethylsilane (all $^1$H NMR spectra in $CDCl_3$). All coupling constants are reported in Hz. GC analyses were performed using a DB-Wax column installed on a GC with FID. Silica gel plugs used 40-63 μm (230-400 mesh) 60 Å silica gel.

All commercial reagents were purchased and used as received unless otherwise noted. $[Cu(MeCN)_4]$OTf is commercially available, but can be prepared according to literature procedure.[9] 1,2:4,5-di-*O*-isopropylidene-β-D-(-)-fructopyranose was prepared according to literature procedure.[10] $CH_3CN$ was taken from a solvent system which passes the solvent through a column of activated molecular sieves, but no precautions to exclude air or water from the

solvent or reaction mixtures were taken. Reaction mixtures were monitored by GC or TLC using a UV lamp or $KMnO_4$ stain to visualize the plate.

**General Method for Screening Catalyst Combinations.**

*Preparation of Catalyst Mixtures*

**Testing of solid catalyst mixtures.**

$[Cu(MeCN)_4]OTf$, 2,2'-bipyridine, and TEMPO were each separately ground to a fine powder with a pestle in a ceramic mortar. The finely ground powders of $[Cu(MeCN)_4]OTf$ (0.6 mmol), bpy (0.6 mmol), and TEMPO (0.6 mmol) were then dispensed into a glass vial and shaken for 20 s to form a homogeneous mixture. The vial was closed with a Teflon cap and stored at 22 °C, 5 °C, or -20 °C for 1 week. All combinations of the three components resulted in a sticky black solid and were not tested for activity.

**For catalyst solutions**:

Under air:

2,2'-Bipyridine (0.6 mmol), nitroxyl (TEMPO: 0.6 mmol, ABNO: 0.12 mmol), NMI (1.2 mmol), and $[Cu(MeCN)_4]OTf$ (0.6 mmol) were added to a glass vial, then MeCN (3 mL) was added. The glass vial was sealed with a Teflon cap, and the solutions were stored at 22 °C, 5 °C, or -20 °C. For copper-free solutions, $[Cu(MeCN)_4]OTf$ was omitted.

Under $N_2$:

2,2'-Bipyridine (0.6 mmol), nitroxyl (TEMPO: 0.6 mmol, ABNO: 0.12 mmol), NMI (1.2 mmol), and $[Cu(MeCN)_4]OTf$ (0.6 mmol) were added to a flame-dried glass vial. The vial was sealed with a rubber septum and purged with $N_2$ for 30 min. At this point, anhydrous and degassed MeCN (3 mL) was added via syringe, and the solutions were stored at 22 °C, 5 °C, or -20 °C. For copper-free solutions, $[Cu(MeCN)_4]OTf$ was omitted.

*General Procedure for Evaluation of Catalyst Solution Activity*

Cyclohexanemethanol (25 µL, 0.2 mmol. 1 equiv) was added to a 13x100 mm test tube with 5x3 mm stirbar. Solid $[Cu(MeCN)_4]OTf$ (3.8 mg, 0.01 mmol, 0.05 equiv) was added if the catalyst solution employed lacked $[Cu(MeCN)_4]OTf$. The material was dissolved in MeCN (2 mL), then bpy/nitroxyl/NMI or $(bpy)Cu^{I}$/nitroxyl/NMI catalyst solution (50 µL, 0.01 mmol bpy, 0.01 mmol TEMPO or 0.002 mmol ABNO, 0.02 mmol NMI; 0.05 equiv bpy, 0.05 equiv TEMPO or 0.01 equiv ABNO, 0.1 equiv NMI) was added via syringe. The resulting red-brown solution was stirred rapidly open to air and monitored by TLC until no further conversion was observed. Internal standard (trimethyl(phenyl)silane, 0.1 mmol) was then added, and the reaction was diluted with EtOAc (1 mL) and filtered through a pipet $SiO_2$ plug. The plug was flushed with EtOAc (2 mL), and filtrate was taken up for GC analysis.

**Representative Procedure for the Aerobic Oxidation of Alcohols.**

Neat substrate (1 mmol) and solid $[Cu(MeCN)_4]OTf$ (18.8 mg, 0.05 mmol, 0.05 equiv) were added to a 25 mL round-bottom flask with an oval (0.625 x 0.25 in) stirbar. MeCN (10 mL) and bpy/TEMPO/NMI or bpy/ABNO/NMI solution (250 µL) were then added, and the dark red/brown solution was stirred rapidly (ca. 950 RPM) open to air at room temperature until no starting material remained by TLC analysis. Reaction completion is often accompanied by a

change in color to blue or green. Preliminary experiments indicate that stir rate impacts the rate of reaction for reactions with ABNO. The order of addition of reaction components does not affect product yield.

The concentration of the reaction may be adjusted depending on the type of substrate:
For primary aliphatic alcohols, substrate concentration should be ≤0.1 M in MeCN
For primary benzylic, allylic, and propargylic alcohols and all secondary alcohols, substrate concentration can be increased to 0.2 M in MeCN without loss of reactivity.

Larger scale reactions should be performed in an appropriately sized round bottom flask:
10 mmol reactions should be performed with 50-100 mL MeCN in a 250 mL round bottom flask.
50 mmol reactions should be performed with 250-500 mL MeCN in a 1-2 L round bottom flask.
Large scale reactions should be concentrated in vacuo to ~10% of the original volume prior to performing purification as described below.

*Purification Method A*: for most products
Upon completion by TLC, the reaction was diluted (10 mL) with an appropriate organic solvent (e.g. EtOAc, $Et_2O$, pentane, $CH_2Cl_2$) and filtered through a $SiO_2$ plug. The plug was rinsed with additional solvent (80 mL), and the filtrate was concentrated in vacuo to yield the product carbonyl compound. Residual nitroxyl (<1 mol%) is observed by GC analysis, and can be removed by $SiO_2$ column chromatography.

*Purification Method B*: for racemizeable products
Upon completion by TLC, the reaction was diluted with $H_2O$ (50 mL) and the product was extracted with an appropriate organic solvent (e.g. EtOAc, $Et_2O$, pentane, $CH_2Cl_2$, 3x50 mL). The organic layers were combined, washed with brine (100 mL), and dried over $MgSO_4$. The solvent was removed in vacuo to yield the product carbonyl compound. Residual nitroxyl (<1 mol%) is observed by GC analysis, and can be removed by $SiO_2$ column chromatography.

*Purification Method C*: for volatile products
Upon completion by TLC, the reaction was diluted with $H_2O$ (50 mL) and the product was extracted with an appropriate low-boiling organic solvent (e.g. $Et_2O$ or pentane, 3x50 mL). The organic layers were combined, washed with brine (100 mL), and dried over $MgSO_4$. The solvent was removed in vacuo at 0 °C (rotary evaporation in an ice bath) to yield the product carbonyl compound.

**Product Characterization.**

**2-chloro-6-fluorobenzaldehyde (1)**

The product was purified according to *Method A* (EtOAc eluent), and was isolated as a yellow solid (151 mg, 94%). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.49 (td, $J$ = 8.2, 5.7 Hz, 1H), 7.30 – 7.28 (m, 1H), 7.13 – 7.08 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 187.0 (d, $J_{C–F}$ = 2.0 Hz), 163.4 (d, $J_{C–F}$ = 265.6 Hz), 137.2 (d, $J_{C–F}$ = 4.0 Hz), 135.3 (d, $J_{C–F}$ = 11.0 Hz), 126.9 (d, $J_{C–F}$ = 4.0 Hz), 121.9 (d, $J_{C–F}$ = 10.1 Hz), 115.8 (d, $J_{C–F}$ = 20.2). Spectral properties are consistent with literature values.[11]

**2-aminobenzaldehyde (2)**

The product was purified according to *Method A* ($Et_2O$ eluent), and was isolated as a yellow oil (121 mg, >99%). $^1$H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 7.48 (dd, $J$ = 7.8, 1.5 Hz, 1H), 7.40 – 7.21 (m, 1H), 6.74 (t, $J$ = 7.8 Hz, 1H), 6.65 (d, $J$ = 8.3 Hz, 1H), 6.11 (s, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 194.0, 149.8, 135.7, 135.2, 118.8, 116.3, 116.0. Spectral properties are consistent with literature values.[12]

**(Z)-4-benzyloxy-but-2-enal (3)**

The reaction was performed in a flask covered with black electrical tape in a fume hood with hood lights turned off. It is unnecessary to turn auxiliary laboratory lights off during the reaction. Upon completion by TLC analysis, the product was purified according to *Method A* (EtOAc eluent) with fume hood lights off. Rotary evaporation was performed in normal lab lighting. The product was isolated as a pink oil (165 mg, 94%) and was stored in a glass vial covered with black electrical tape. >20:1 *Z*:*E* by $^1$H NMR spectroscopy. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.05 (d, $J$ = 6.8 Hz, 1H), 7.34 (m, 5H), 6.64 (dt, $J$ = 11.2, 5.6 Hz, 1H), 6.06 (ddt, $J$ = 11.2, 6.8, 2.0 Hz, 1H), 4.59 (s, 2H), 4.53 (dd, $J$ = 5.6, 2.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 191.6, 147.7, 137.5, 129.9, 128.8, 128.2, 128.0, 73.3, 67.2.
Spectral properties are consistent with literature values.[13]

**3-benzyloxy-propionaldehyde (4)**

The product was purified according to *Method A* ($Et_2O$ eluent), and was isolated as a pink oil (159 mg, 97%). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.80 (q, $J$ = 1.5 Hz, 1H), 7.88 – 6.35 (m, 5H), 4.54 (s, 2H), 3.82 (td, $J$ = 6.1, 1.3 Hz, 2H), 2.70 (t, $J$ = 6.1 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 201.3, 137.9, 128.6, 127.9, 127.8, 73.4, 64.0, 44.0. Spectral properties are consistent with literature values.[14]

**Boc-L-*tert*-leucinal (5)**

The product was purified according to *Method B* (EtOAc organic layer), and was isolated as a white solid (195 mg, 97%). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 5.15 (s, 1H), 4.18 (d, $J$ = 8.7 Hz, 1H), 1.45 (s, 9H), 1.05 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 201.4, 156.3, 80.2, 67.8, 35.9, 28.6, 27.1. >99% ee based on HPLC analysis. Analysis of % ee is shown in the HPLC traces of (*S*)-2-((Boc)amino)-3,3-dimethylbutyl-4-nitrobenzoate (see Supporting Information). (*S*)-2-((Boc)amino)-3,3-dimethylbutyl-4-nitrobenzoate was synthesized according to literature procedure.[4] Spectral properties are consistent with literature values.[4]

**1,2:4,5-Di-*O*-isopropylidene-β-D-*erythro*-2,3-hexodiulo-2,6-pyranose (6)**

The product was purified according to *Method A* (EtOAc eluent), and was isolated as a white crystalline solid (246 mg, 95%). $^1$H NMR (400 MHz, $CDCl_3$) δ 4.73 (d, $J$ = 5.6 Hz, 1H), 4.62 (d, $J$ = 9.5 Hz, 1H), 4.55 (ddd, $J$ = 5.6, 2.2, 1.0 Hz, 1H), 4.39 (dd, $J$ = 13.5, 2.2 Hz, 1H), 4.12 (d, $J$ = 13.5 Hz, 1H), 4.00 (d, $J$ = 9.5 Hz, 1H), 1.55 (s, 3H), 1.47 (s, 3H), 1.40 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.3, 114.2, 111.0, 104.5, 78.3, 76.2, 70.3, 60.4, 27.5, 26.9, 26.41, 26.36. Spectral properties are consistent with commercially available product.

***N*-[4-(4-Fluorophenyl)-5-formyl-6-isopropylpyrimidin-2-yl]-*N*-methylmethanesulfonamide (7)**

The product was purified according to *Method A* ($CH_2Cl_2$ eluent), and was isolated as a white solid (351 mg, >99%). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.68 – 7.58 (m, 2H), 7.26 – 7.19 (m, 2H), 4.01 (hept, $J$ = 6.7 Hz, 1H), 3.64 (s, 3H), 3.55 (s, 3H), 1.32 (d, $J$ = 6.7 Hz, 6H). $^{13}$C

NMR (101 MHz, $CDCl_3$) δ 190.9, 179.4, 170.2, 164.8 (d, $J_{C–F}$ = 253.5 Hz), 159.2, 133.0 (d, $J_{C–F}$ = 9.1 Hz), 132.5 (d, $J_{C–F}$ = 3.0 Hz), 119.9, 116.4 (d, $J_{C–F}$ = 21.0 Hz), 42.9, 33.5, 32.4, 22.1. Spectral properties are consistent with literature values.[15]

**4-Chloro-2-nitrobenzaldehyde (8)**
The product was purified according to *Method A* (EtOAc eluent), and was isolated as a light yellow solid (175 mg, 95%). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.39 (d, $J$ = 0.7 Hz, 1H), 8.11 (d, $J$ = 2.0 Hz, 1H), 7.95 (d, $J$ = 8.3 Hz, 1H), 7.77 (ddd, $J$ = 8.3, 2.0, 0.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 187.2, 150.1, 140.6, 134.5, 131.3, 129.6, 125.1. Spectral properties are consistent with literature values.[16]

## ASSOCIATED CONTENT

**Supporting Information**. Spectral data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

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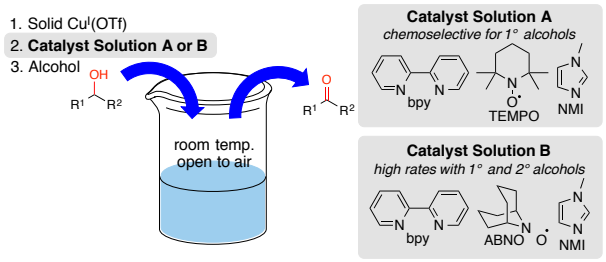
## TOC GRAPHIC


1. Solid Cu$^{I}$(OTf)
2. Catalyst Solution A or B
3. Alcohol
OH
R1 R2
room temp.
open to air
O
R1 R2
Catalyst Solution A
chemoselective for 1° alcohols
bpy
TEMPO
NMI
Catalyst Solution B
high rates with 1° and 2° alcohols
bpy
ABNO
NMI