

Electronic Supplementary Information for

Catalytic Behavior of Cu(I)/L/TEMPO System for Aerobic Oxidation of Alcohols – A Kinetic and Predictive Model

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1. General Information

All reagents were purchased from Aldrich, handled as obtained.

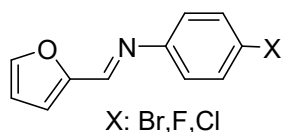
^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer and the chemical shifts are reported in parts per million (δ) relative to TMS (0 ppm). The peak patterns are indicated as follows: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; m = multiplet. J -coupling values are reported in Hertz (Hz).

GC-MS analyses were performed on Varian Technologies 2200 GC/MS using an Agilent DB-WAX (30 m, 0.25 mm, 0.25 μm) column. The oxidation products were identified with GC-MS by comparison with commercial samples. Yield determinations were determined with GC-MS using calibration curves with 1,2-dichlorobenzene as an internal standard.

UV-Visible absorption measurements were performed on Agilent Technologies Cary 60 instruments.

2. Ligands characterization

Ligands 1–3 (L1–3)



A mixture of Pyrrole-2-carboxaldehyde (1 eq., 0.761 g) and 4-halogenated aniline (1 eq.) were added in a 50 ml round bottom flask with dry methanol and 3Å molecular sieves, the reaction was stirred at RT for half hour. Later the crude was filtered and recrystallized to obtain the product. ^1H NMR and ^{13}C NMR was recorded from the crude product in d -chloroform.

N -(4-bromophenyl)-1-(furan-2-yl)methanimine (L1), L2 and L3 spectra were compared to the published spectra.^{1,2}

N -(4-bromophenyl)-1-(furan-2-yl)methanimine (L1)

^1H NMR (CDCl_3 , 500 MHz): δ 8.24 (s, 1H, N=CH), δ 7.67 (1 H, ar-H), δ 7.19 (2H, ar-H), δ 7.05 (2H, ar-H), δ 6.93 (1H, ar-H), δ 6.53 (1H, ar-H)

Ligand 2: *N*-(4-fluorophenyl)-1-(furan-2-yl)methanimine (L2)

¹H NMR

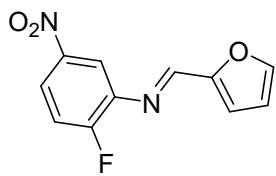
¹H NMR (CDCl₃, 500 MHz): δ 8.24 (s, 1H, N=CH), δ 7.67 (1 H, ar-H), δ 7.19 (2H, ar-H), δ 7.05 (2H, ar-H), δ 6.93 (1H, ar-H), δ 6.53 (1H, ar-H)

Ligand 3: *N*-(4-chlorophenyl)-1-(furan-2-yl)methanimine (L3)

¹H NMR (CDCl₃, 500 MHz): δ 8.24 (s, 1H, N=CH), δ 7.67 (1 H, ar-H), δ 7.19 (2H, ar-H), δ 7.05 (2H, ar-H), δ 6.93 (1H, ar-H), δ 6.63 (1H, ar-H)

Ligand 4: *N*-(2-fluoro-4-nitrophenyl)-1-(furan-2-yl)methanimine (L4)

The crude product was recrystallized and later stored afterwards in a freezer under argon. ¹H NMR and ¹³C NMR was recorded from the crude product in *d*-chloroform. Spectra was compared to previously published spectra.¹



¹H NMR

¹H NMR (CDCl₃, 500 MHz): δ 8.26 (s, 1H, N=CH), δ 10.27 (1 H, NH), δ 7.21 (2H, ar-H), δ 7.07 (2H, ar-H), δ 6.82 (1H, ar-H), δ 6.71 (1H, ar-H), δ 6.30 (1H, ar-H)

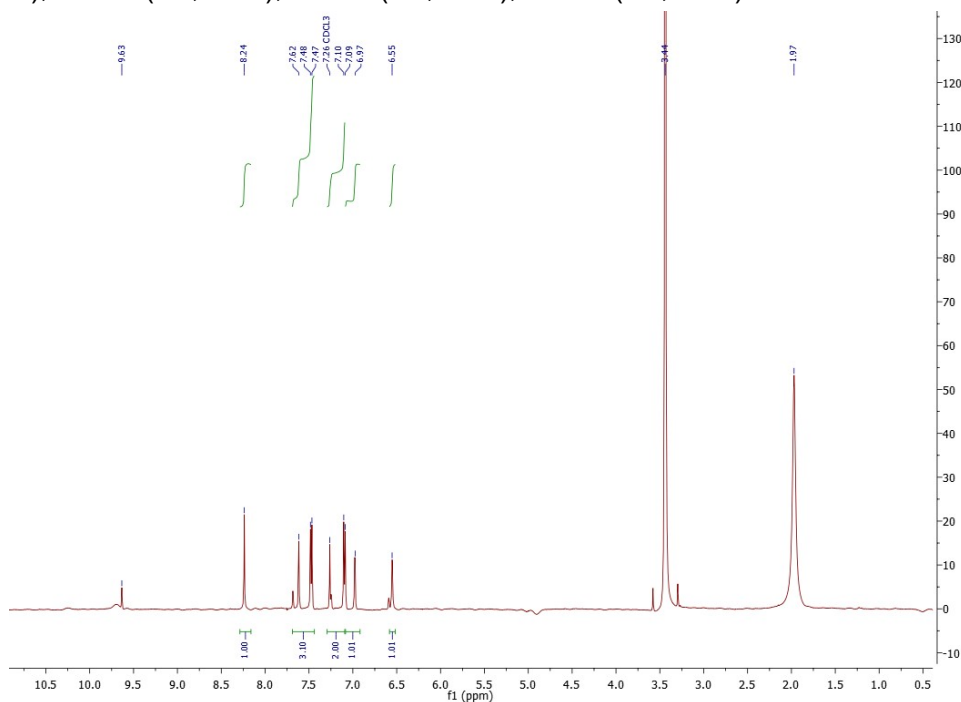
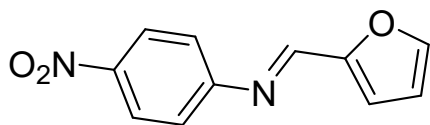


Fig. S1

Ligand 5: N-(4-fluorophenyl)-1-(furan-2-yl)methanimine (L5)

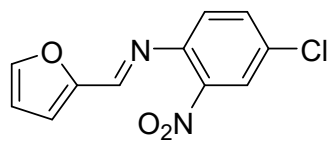


Furfural (1 eq., 0.83 ml) and 4-fluoroaniline (1 eq., 0.95 ml) were mixed in a 50 ml round bottom flask without solvent and was stirred at RT for 15 minutes. Stored afterwards in a freezer under argon. ^1H NMR and ^{13}C NMR was recorded from the crude product in *d*-chloroform.

^1H NMR

^1H NMR (CDCl_3 , 500 MHz): δ 8.24 (s, 1H, N=CH), δ 7.67 (1 H, -ar-H), δ 7.19 (2H, ar-H), δ 7.05 (2H, ar-H), δ 6.93 (1H, ar-H), δ 6.53 (1H, ar-H)

Ligand 6: 1-(furan-2-yl)-N-(3-chloro-2-nitrophenyl)methanimine (L6)



^1H NMR and ^{13}C NMR was recorded from the crude product in *d*-dmso

^1H NMR (CDCl_3 , 500 MHz): δ 8.5 (s, 1H, HC=N), 8.27 (s, 1H, N=CH), δ 7.61 (1H, ar-H), δ 7.26 (1H, ar-H), δ 6.96 (1H, ar-H), δ 6.79 (3H, ar-H), δ 6.54 (1H, ar-H), δ 3.81 (3H, methoxy CH_3)

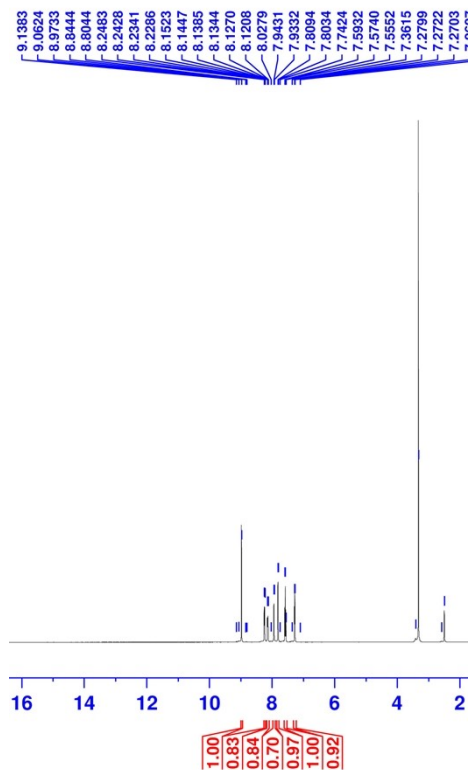
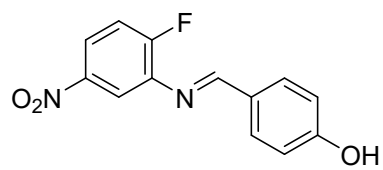


Fig. S2

Ligand 7: 2-fluoro-4-nitrophenyl-(N-hydroxyphenyl)methanimine (L7)



^1H NMR was recorded from the crude product in *d*-chloroform.

^1H NMR (CDCl_3 , 500 MHz): δ 9.8 (s, 1H, OH), δ 8.4 (s, 1H, HC=N), δ 7.82 (1H, furan-H), δ 7.62 (1H, ar-H), δ 7.22 (4H, ar-H), δ 6.98 (1H, ar-H), δ 6.56 (1H, ar-H).

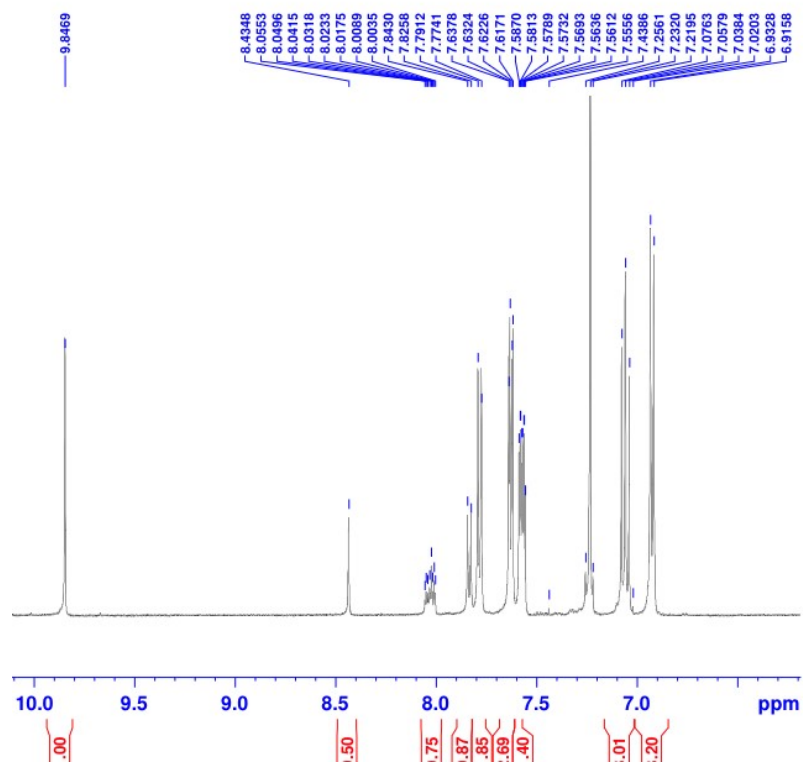
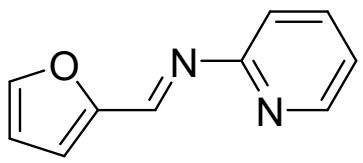


Fig. S3

Ligand 8: 1-(furan-2-yl)-N-(pyridin-2-yl)methanimine (L8)



^1H NMR and ^{13}C NMR was recorded from the crude product in *dms*o

^1H NMR

^1H NMR (CDCl_3 , 500 MHz): δ 8.52 (s, 1H, N=CH), δ 7.96 (1H, ar-H), δ 7.84 (1H, ar-H), δ 7.58(2H, ar-H), δ 7.11 (1H, ar-H), δ 6.99 (1H, ar-H), δ 6.93 (1H, ar-H), δ 6.63 (1H, ar-H)

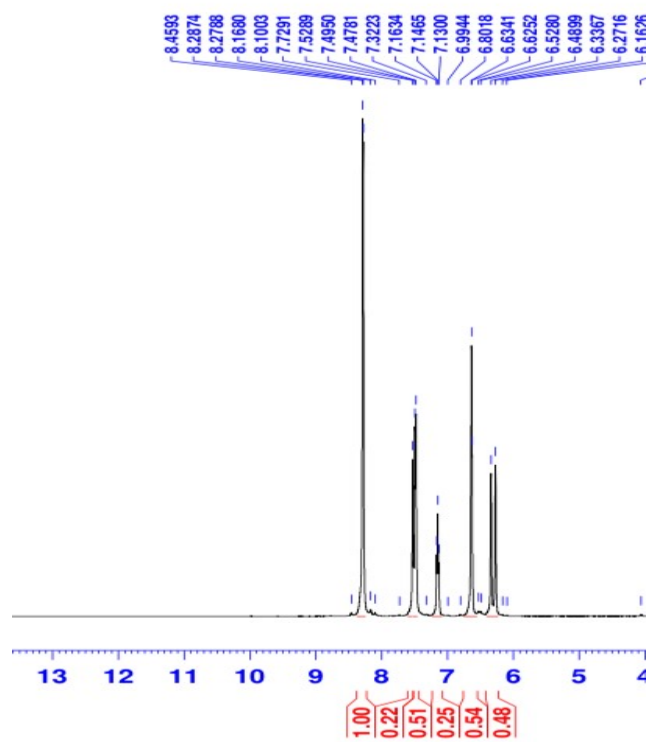
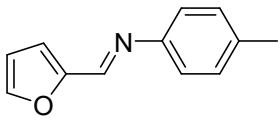


Fig. S4

Ligand 9: 1-Furan-2-yl)-N-p-tolyl) methanimine (L9)



^1H NMR was recorded from the crude product in *d*-chloroform.

^1H NMR (CDCl_3 , 500 MHz): δ 8.45(s,1H, HC=N), 8.24 (d, 3H, ar-H), δ 7.62 (1H, Furan-H), δ 7.1 (4H, ar-H), δ 6.4(2H, furan-H), δ 6.1 (1H, furan-H), 2.3 (s,1H,ar-CH₃)

3. Kinetic measurements:

Our initial mechanistic studies focused on probing mechanistic differences between 2 ligands (L2 and L4) on the reaction rate in combination with the other reaction parameters (TEMPO, NMI, Alcohol, Copper salts Figure 13-15). First, reaction time-course plots, showing the concentrations of aldehyde, Cu^I, Cu^{II}, TEMPO, determined by GC spectroscopy during the oxidation of PhCH₂OH and 1-Octanol are shown in Figure 6-10.

In the oxidation of BOH2 the formation of benzaldehyde exhibits a linear time course, similar results obtained from aliphatic alcohols however with slow reaction rate. this observation indicate that the catalyst oxidation has the only effect on turnover rate with more reactive benzylic alcohols substrate, while with less reactive aliphatic substrates shows both substrate and catalyst oxidations contribution into the turnover rate.

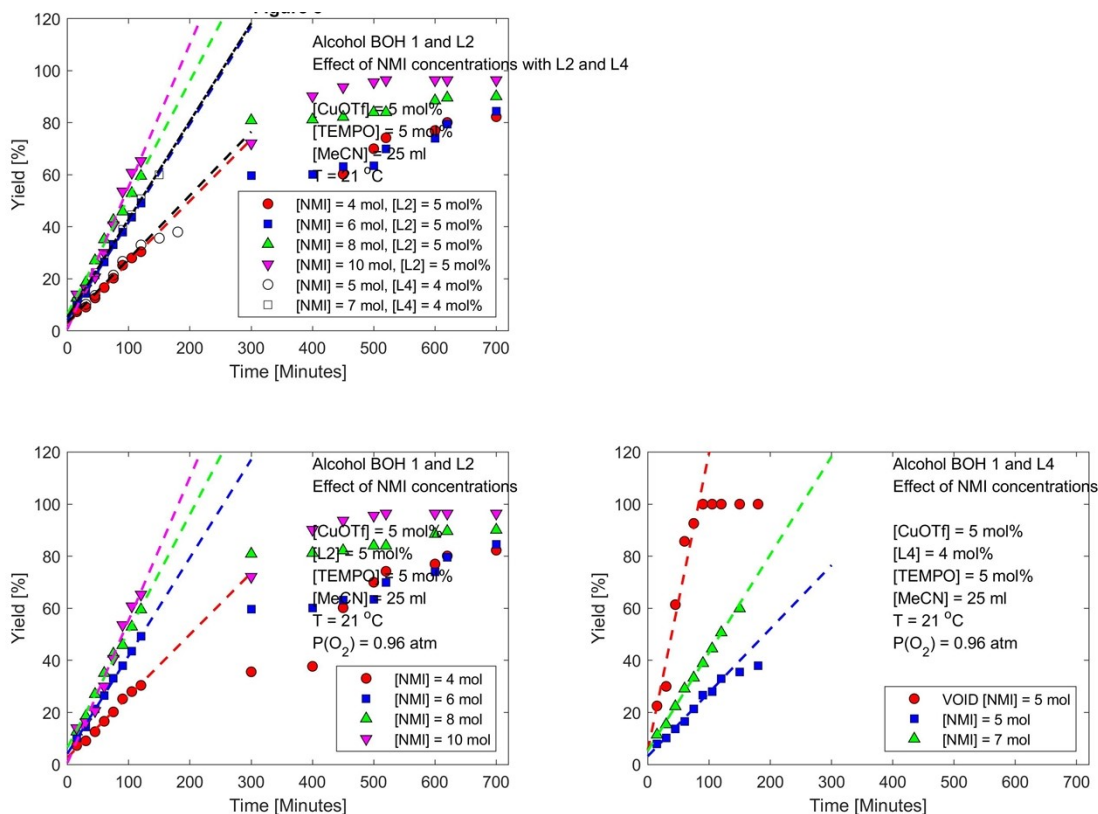
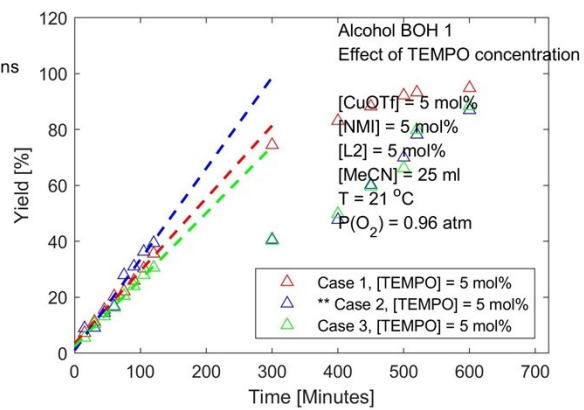
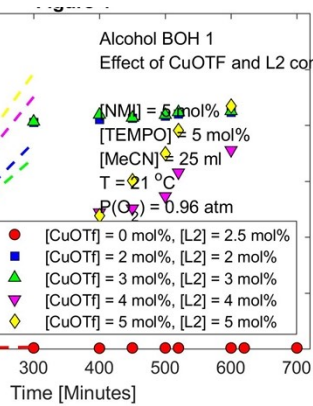
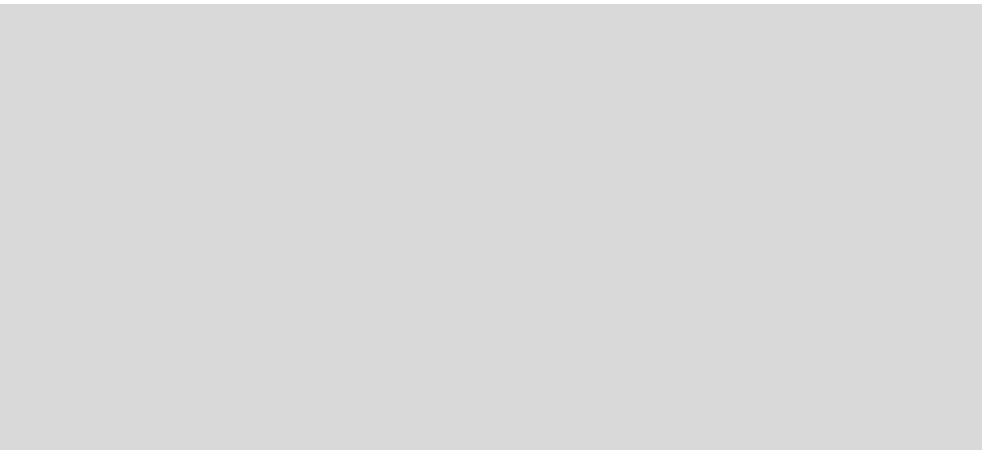


Fig. S6. NMI concentration effect on L2 and L4 system on BOH.





Fig, S7. Cu concentration, TEMPO effect on BOH1.

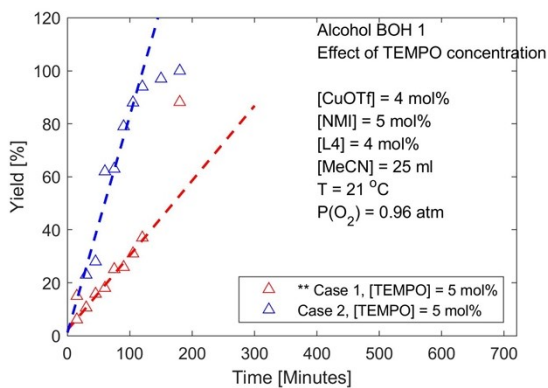
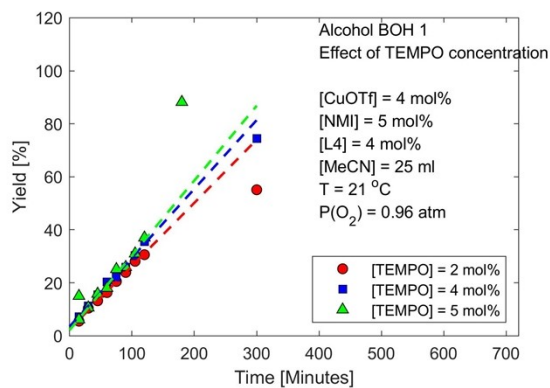
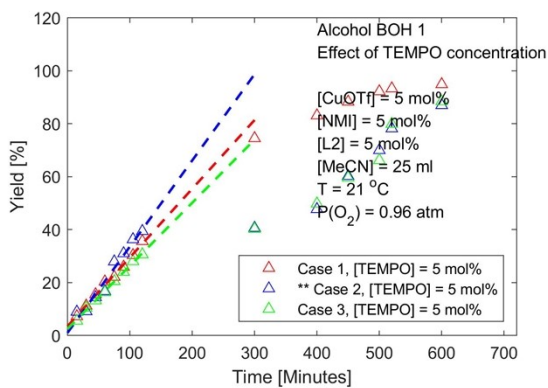
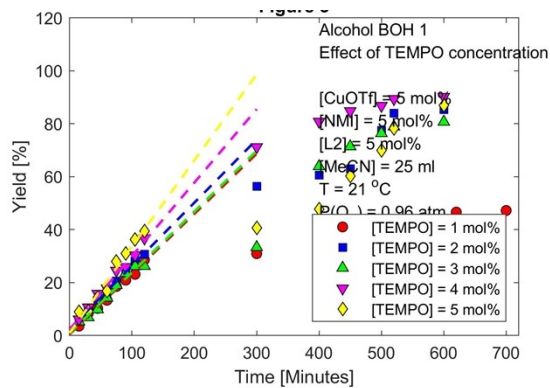


Fig. S8. the Tempo effect on the reaction conversion,

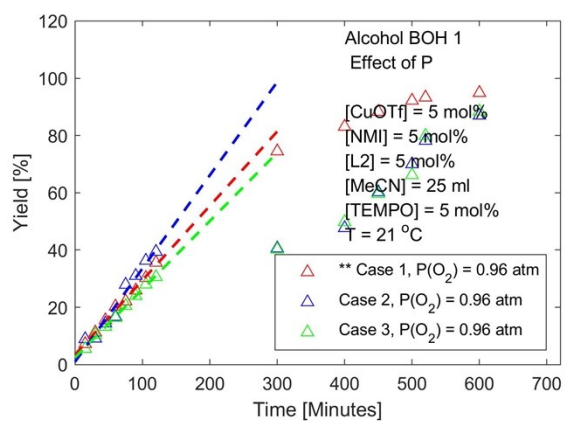
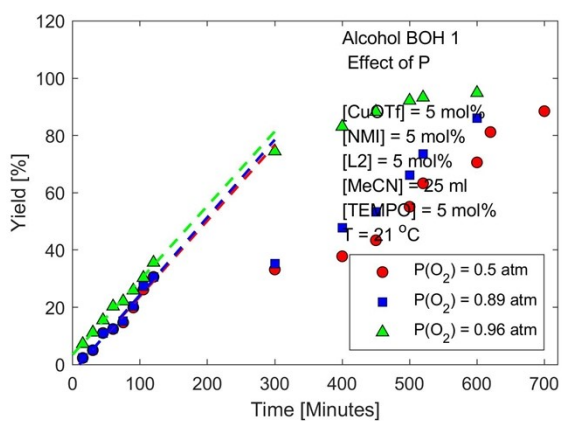
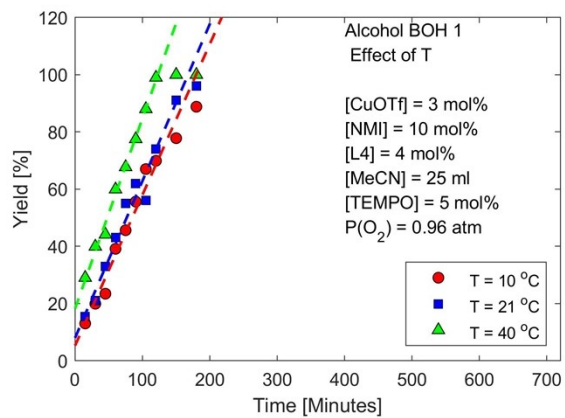
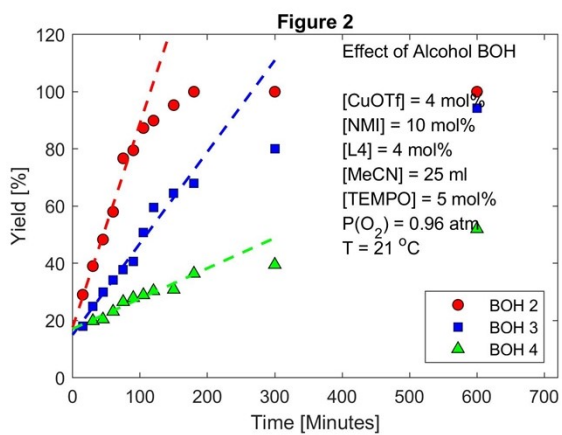


Fig. S9. various parameters effect on L2 and L4 system on BOH.

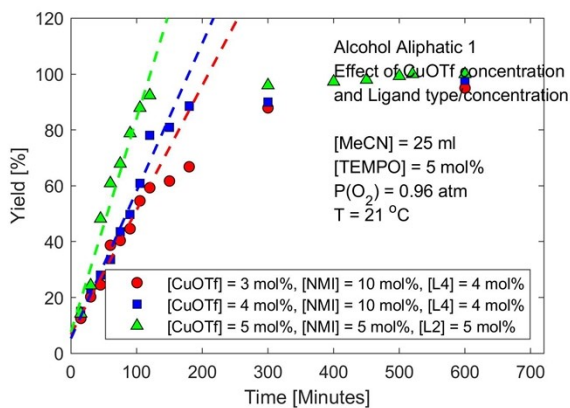
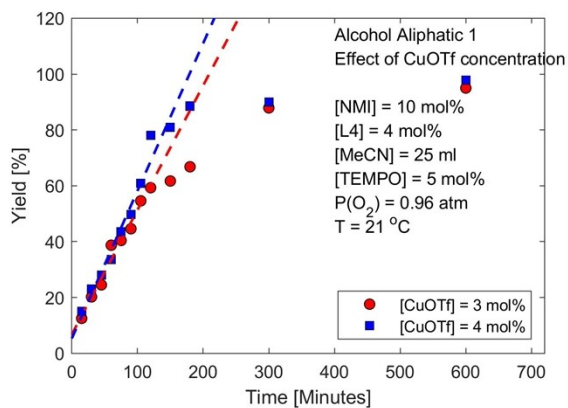
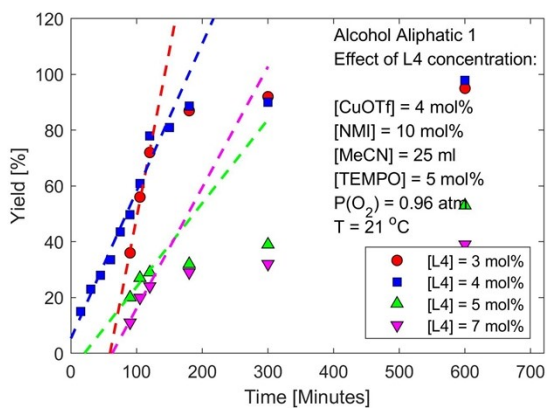
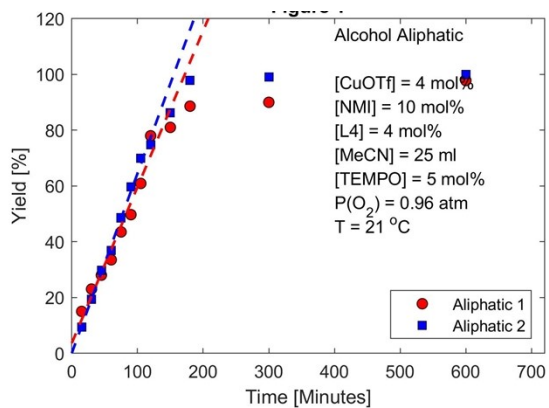


Fig. S10. Time course data for the oxidation of aliphatic (1-Octanol, 2-octene-ol), benzyl alcohols (BOH2 benzyl alcohol, BOH3 cinnamyl alcohol, BOH4 diphenylmethanol based in the Ligand amount.

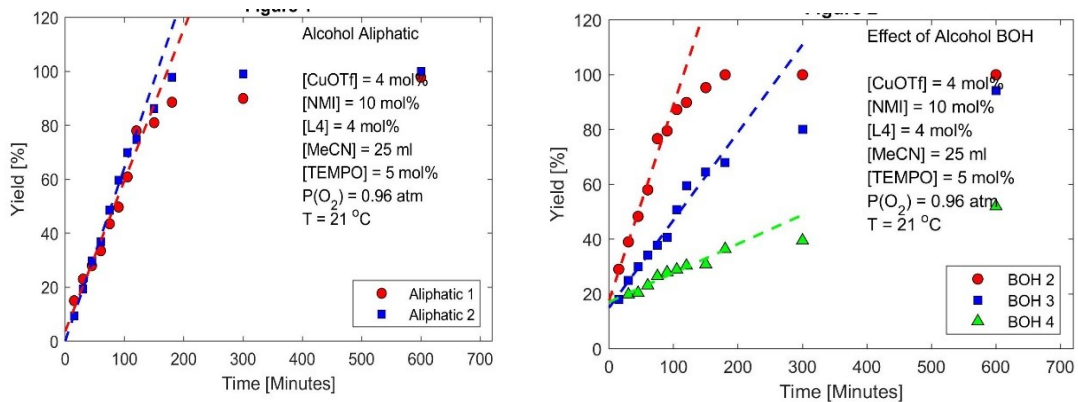


Fig. S11. Time course data for the oxidation of aliphatic (1-Octanol, 2-octene-ol), benzyl alcohols (BOH2 benzyl alcohol, BOH3 cinnamyl alcohol, BOH4 diphenylmethanol).

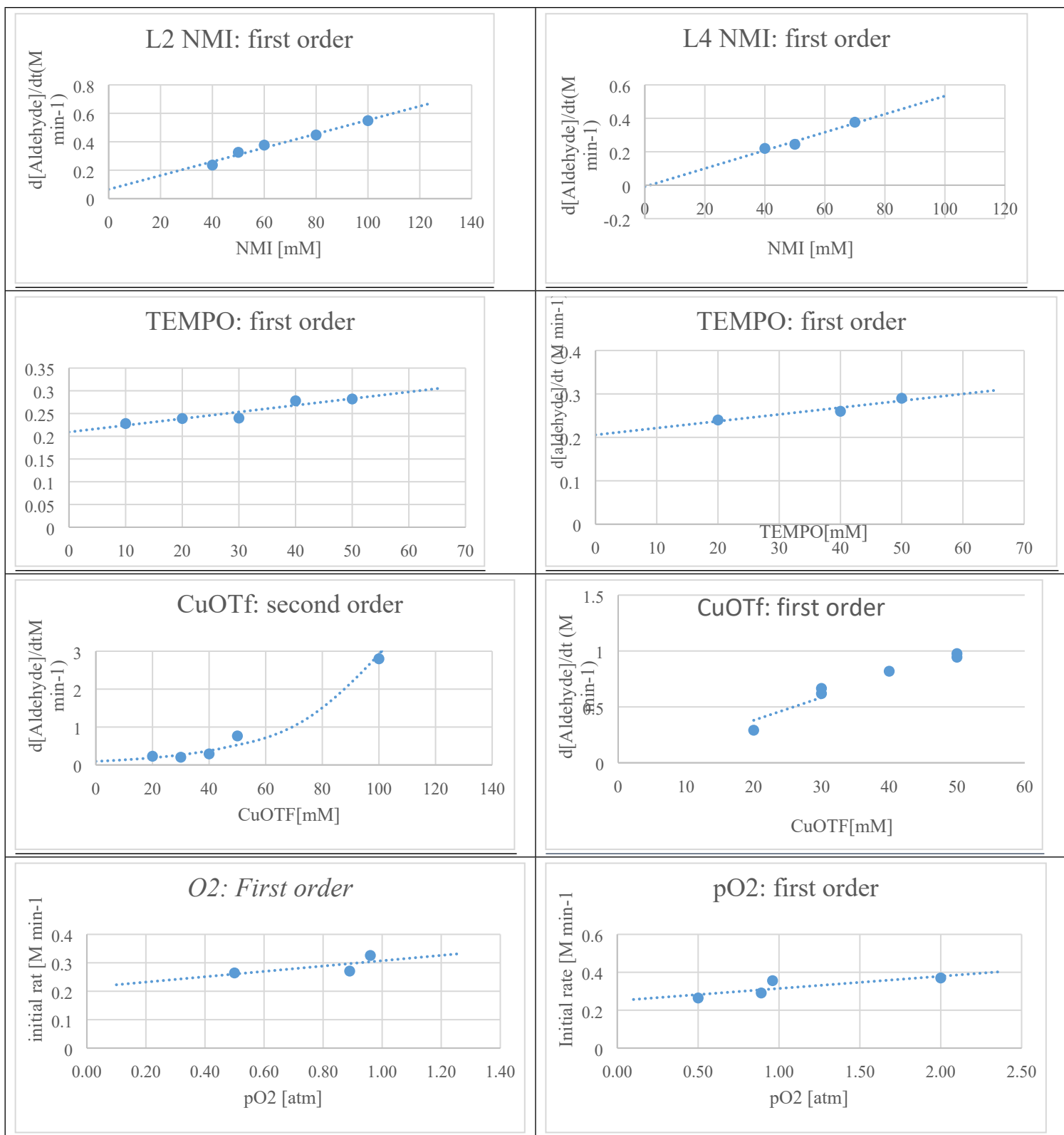


Fig. S12. The kinetic data from oxidation of PhCH₂OH by L2Cu(OTf)/TEMPO assigns the following parameters (A)Base (B) TEMPO (C) Copper (D) O₂ pressure (F) Ligand(L2) and L4

4. Predictive model

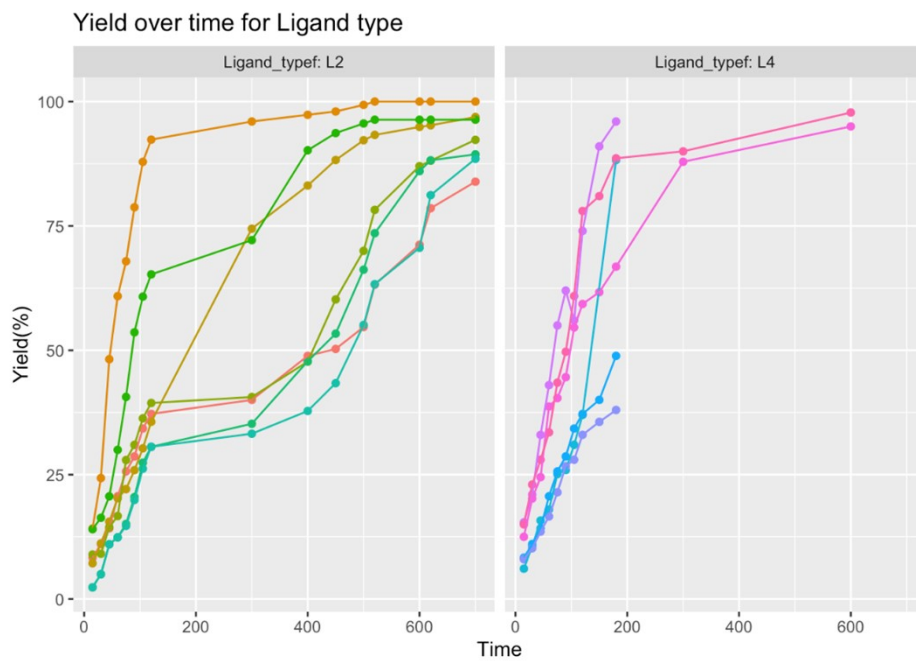


Fig. S13: Yield over time for Ligand Type (L2 and L4)

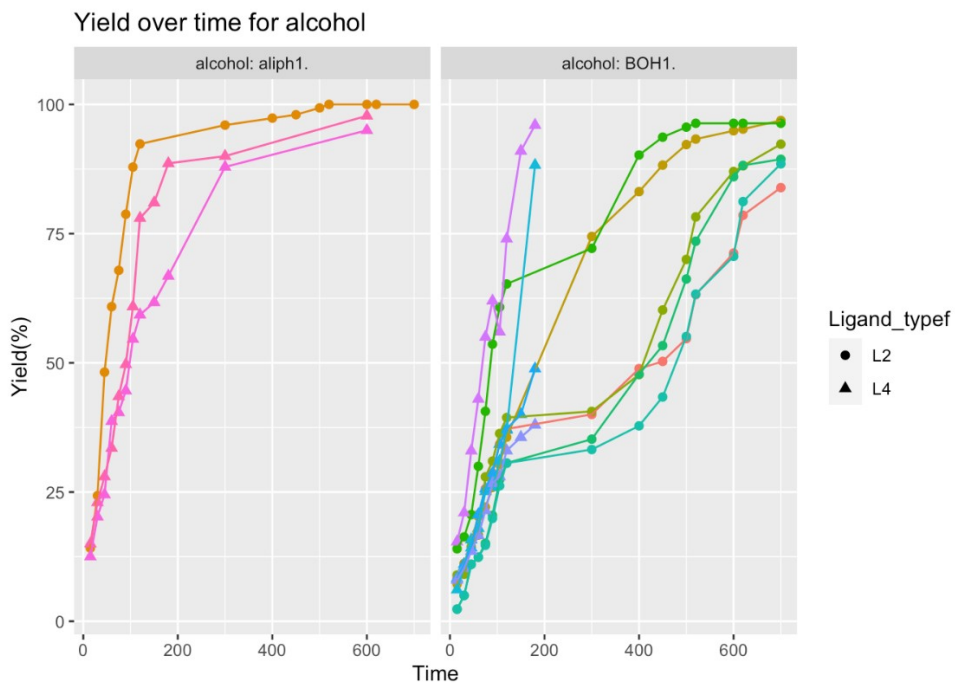


Fig. S14: Yield over time for Alcohol (Aliph1. and BOH1.) by Ligand Type (L2 or L4)

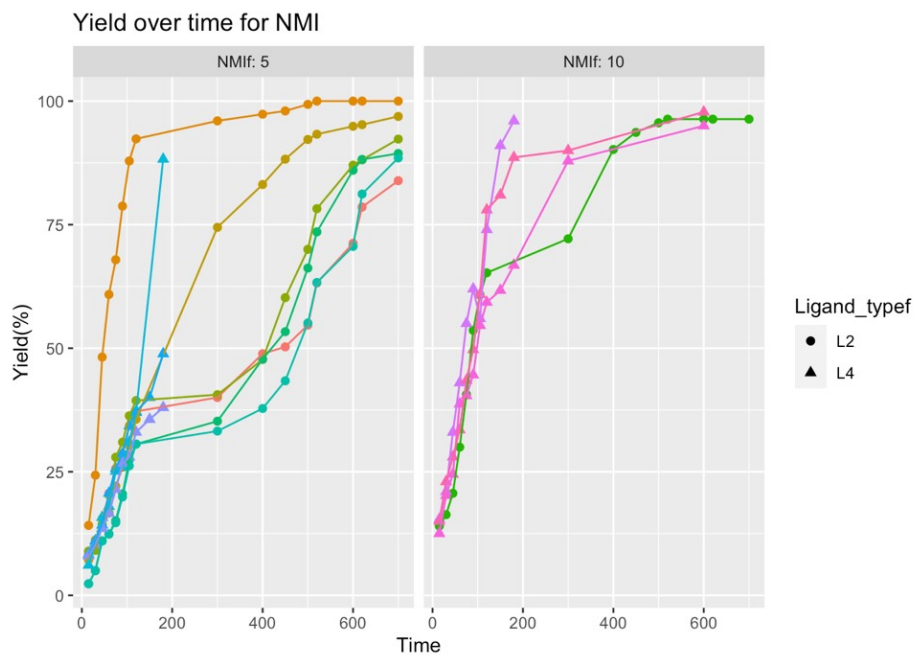


Fig. S15: Yield over time for NMI (5 and 10) by Ligand Type (L2 or L4)

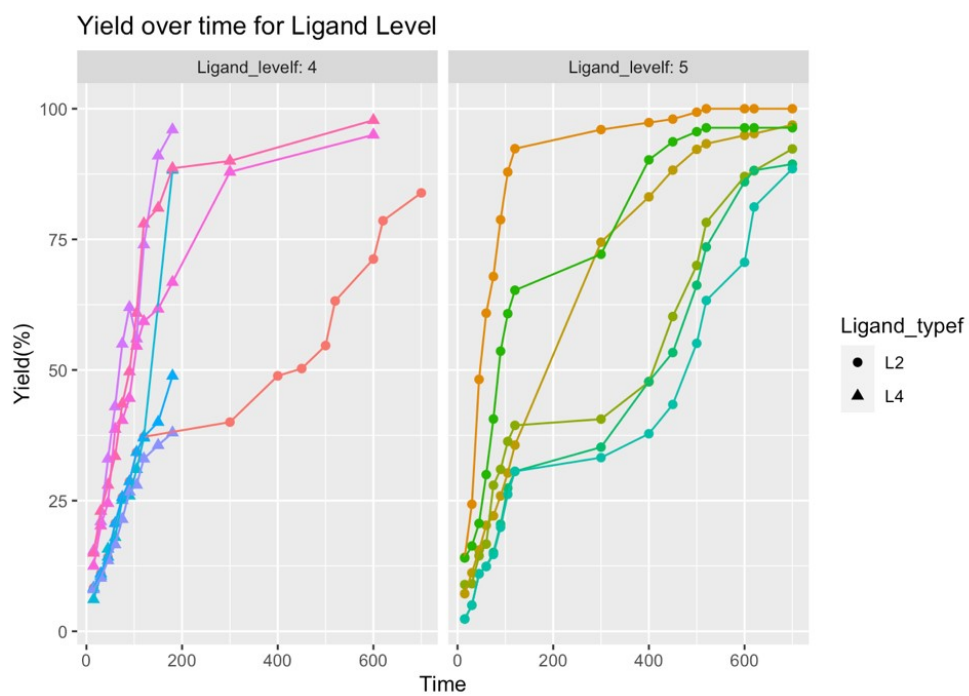


Fig. S16: Yield over time for Ligand Level (4 and 5) by Ligand Type (L2 or L4)

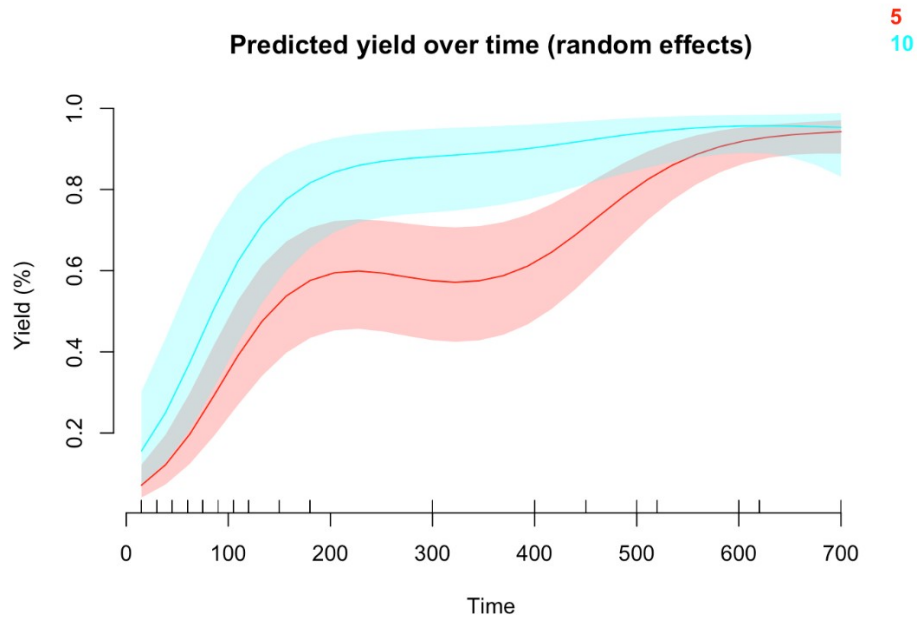


Fig. S17. Predicted yield over time for NMI (5 and 10) using GAM results

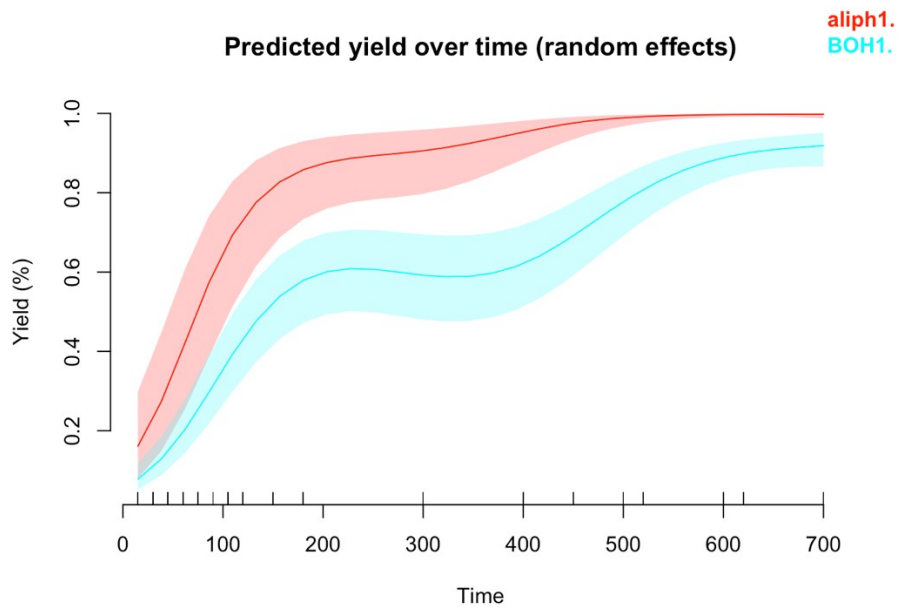


Fig. S18: Predicted yield over time for Alcohol (Aliph1. And BOH1) using GAM results

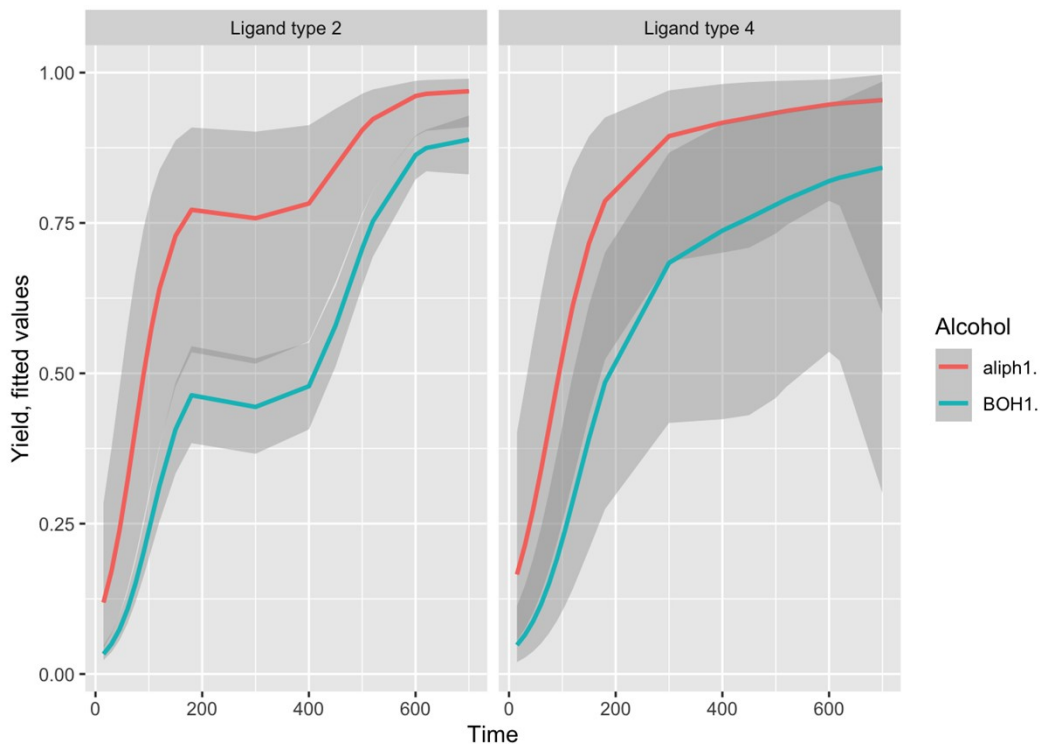


Fig. S19: Predicted yield over time for Ligand Type by Alcohol (Aliph1 or BOH1)

References:

1. I. Iovel, L. Golomba, J. Popelis, S. Grinberga, E. Lukevics, Synthesis and hydrosilylation of furan and thiophene N- methylenefluoroanilines in the presence of Pd (I) complex, Chem. Heterocycl. 41 (2005) 1112–1118.
2. E. Lagerspets, K. Lagerblom, E. Heliövaara, O-M Hiltunen, K. Moslova, M. Nieger, T. Repo. Schiff base Cu(I) catalyst for aerobic oxidation of primary alcohols

