SUPPLEMENTARY INFORMATION FOR

Ambient Condition Imine Formation from the Homocoupling of Benzylamine Using Copper Catalysis and Dialkylphosphite as a Substoichiometric Additive

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Methods

Effect of Copper Catalyst on Product Yields

0.150 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol) Cu(II) catalyst (0.0749 mmol, 5 mol %) and 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) in 2.0 mL of ethyl acetate solvent. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 24 hours. The reaction was monitored by NMR spectroscopy.

Effect of Solvent on Product Yields

0.150 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol), 0.0271 g of Cu(II) triflate (361.68 g mol^{-1}, 0.0749 mmol, 5 mol %) and 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) in 2.0 mL of solvent. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 24 hours. The reaction was monitored by NMR spectroscopy.

Optimisation Using Best Catalyst and Solvent

0.150 mL of diisopropyl phosphite (0.9970 g mL-1, 166.16 g mol-1, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL-1, 107.15 g mol-1, 1.46 mmol) with 0.0098 g (0.037 mmol, 2.5 mol%), 0.0196 g (0.0749 mmol, 5 mol%), or 0.0392 g (0.150 mmol, 10 mol%) of Cu(II) acetylacetonate (261.76 g mol-1) and 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol-1, 0.300 mmol) in 2.0 mL of ethyl acetate solvent. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 24 hours. The reaction was monitored by NMR spectroscopy.

Effect of amount of Catalyst Loading and amount of Phosphite Additive on Product Yields

0.0750 mL (0.0450 mmol, 31 mol%), 0.150 mL (0.900 mmol, 61 mol%), or 0.300 mL (1.80 mmol, 123 mol%) of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol) with 0.0134 g (0.0375 mmol, 2.5 mol%), 0.0271 g (0.0749 mmol, 5 mol %) or 0.0543 g (0.150 mmol, 10 mol%) of Cu(II) triflate (361.68 g mol^{-1}), and 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) in 2.0 mL of ethyl acetate solvent. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 24 hours. The reaction was monitored by NMR spectroscopy.

Effect of Additives on Product Yields

Additive (0.900 mmol, 61 mol%), or none, was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol),0.0271 g of Cu(II) triflate (361.68 g mol^{-1}, 0.0749 mmol, 5 mol %) and 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) in 2.0 mL of ethyl acetate solvent. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 24 hours. The reaction was monitored by NMR spectroscopy.

EPR Sample Preparation

At room temperature (24 °C) under air, 0.0271 g of Cu(II) triflate (361.68 g mol^{-1}, 0.0749 mmol, 5.0 mol %) was added to 2.0 mL of ethyl acetate. 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol), 0.150 mL diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %), both, or neither, were added to the reaction vessel and mixed before taking aliquots to fill a quartz flat cell for EPR analysis.

Effect of Both Cu(I) and Cu(II) on Product Yield

0.0319 g of Cu(OTf) (212.62 g mol^{-1}, 0.150 mmol, 5.7 mol %) was added to 1.0 mL of ethyl acetate solvent in the glove box. Separately in air, 0.290 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 2.66 mmol) was added to 1.0 mL of ethyl acetate solvent with 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol). 0.0543 g of $Cu(OTf)_2$ (361.68 g mol^{-1}, 0.150 mmol, 5.7 mol %), or none, was added to the reaction mixture. The Cu(OTf) in ethyl acetate was then taken from the glovebox and added to the mixture. 0.0125 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}) additive (0.0750 mmol, 2.8 mol %), or none, was added every 30 minutes for 6 hours for a total of twelve additions. The reaction vessel was left open, and the reaction mixture was stirred for a total of 24 hours. The reaction was monitored by NMR spectroscopy.

Effect of Oxygen Concentration on Product Yields

0.150 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.47 mmol), 0.0271 g of Cu(II) triflate (361.68 g mol^{-1}, 0.0749 mmol, 5 mol %) and 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) in 2.0 mL of ethyl acetate solvent. A lid was either screwed on the vial or left open with a water condenser attached, and the reaction mixture was stirred for 24 hours. Air-free was performed in a glovebox using degassed and dried solvents/reactants/additives. The reaction was monitored by NMR spectroscopy.

Effect of Copper Sequestering on Quantification

0.150 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mol) with 0.0271 g of Cu(II) triflate (361.68 g mol^{-1}), or 0.0196 g of Cu(II) acetylacetonate (261.76 g mol^{-1}) catalyst (0.0749 mmol, 5 mol%) in 2.0 mL of ethyl acetate. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 24 hours. 2 mL of ethyl acetate, 2 mL of deionized water and 0.0838 g ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA, 372.24 g mol^{-1}, 0.225 mmol, 15 mol %) were then added to the reaction mixture. The precipitate formed was decanted and the resultant liquid layers separated. 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) was added to the organic layer and 0.0218 g of the internal standard 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (218.32 g mol^{-1}, 0.0999 mmol) was added to the aqueous layer. The organic layer was evaporated before aliquots of layers were dissolved in deuterated DMSO and analysed by NMR spectroscopy.

Effect of Catalyst or Reactant Addition at 24 h

0.150 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol), 0.0196 g of Cu(II) acetylacetonate (261.76 g mol^{-1}, 0.0749 mmol, 5 mol%), and 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) in 2.0 mL of ethyl acetate. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for a total of 72 hours. At 24 hours, an additional equivalent amount of either Cu(II) acetylacetonate, diisopropyl phosphite, or benzylamine to that initially used was added to the reaction mixture. The reaction was monitored by NMR spectroscopy.

Effect of Base with Copper Sequestering

0.150 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol) and Cu(II) catalyst (0.0749 mmol, 5.0 mol %) in 2.0 mL of ethyl acetate solvent. 0.204 mL of triethylamine (0.726 g mL^{-1}, 101.19 g mol^{-1}) or 0.254 mL of diisopropylethylamine (0.742 g mL^{-1}, 129.24 g mol^{-1}) base (1.46 mmol, 100 mol%) was added to the mixture. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 24 hours 2 mL of ethyl acetate, 2 mL of deionized water and 0.0838 g ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA, 372.24 g mol^{-1}, 0.225 mmol, 15 mol %) was added to the reaction. The precipitate was decanted and the two liquid layers separated. 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) was added to the organic layer and 0.0218 g of the internal standard 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (218.32 g mol^{-1}, 0.0999 mmol) was added to the aqueous layer. The organic layer was evaporated before layers were analysed by NMR spectroscopy.

Effect of Ammonia Addition

0.150 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol), 0.0196 g of Cu(II) acetylacetonate (261.76 g mol^{-1}, 0.0749 mmol, 5 mol%) and 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) in 2.0 mL of ethyl acetate solvent. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 1 h. Ammonia was bubbled through the reaction mixture for 5 minutes and the condenser re-attached. The reaction was stirred for a total of 72 hours, and monitored by NMR spectroscopy.

Effect of 3Å Molecular Sieves

0.150 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol), 0.0196 g of Cu(II) acetylacetonate (261.76 g mol^{-1}, 0.0749 mmol, 5 mol%) and 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) in 2.0 mL of ethyl acetate solvent containing 0.300 g of 3Å molecular sieves. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 48 hours. The reaction was monitored by NMR spectroscopy.

Effect of Added Imine

0.150 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol), 0.0196 g of Cu(II) acetylacetonate (261.76 g mol^{-1}, 0.0749 mmol, 5 mol%) and 0.275 mL of n-benzylidenebenzylamine (1.047 g mL^{-1}, 195.26 g mol^{-1}, 1.47 mmol, 100 mol %) and 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) in 2.0 mL of ethyl acetate solvent. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 48 hours. The reaction was monitored by NMR spectroscopy.

Effect of Diisopropyl Phosphate

0.150 mL of diisopropyl phosphite (0.9970 g mL^{-1}, 166.16 g mol^{-1}, 0.900 mmol, 61 mol %) was added to a mixture of 0.160 mL of benzylamine (0.981 g mL^{-1}, 107.15 g mol^{-1}, 1.46 mmol), 0.0196 g of Cu(II) acetylacetonate (261.76 g mol^{-1}, 0.0749 mmol, 5 mol%), 0.0505 g of the internal standard 1,3,5-trimethoxybenzene (168.19 g mol^{-1}, 0.300 mmol) and 0.152 mL of diisopropyl phosphate (1.08 g mL^{-1}, 182.16 g mol^{-1}, 0.901 mmol, 62 mol %) in 2.0 mL of ethyl acetate solvent. A water condenser was placed over the reaction vessel, and the reaction mixture was stirred for 72 hours. The reaction was monitored by NMR spectroscopy.

^{1}H NMR Spectroscopy Assignments

(400 MHz, DMSO-d_6, 298 K, δ)
1, Benzylamine: 7.32-7.19 (m, 5H, Ar-H), 3.71 (s, 2H, PhCH$_2$), 1.92 (br s, 2H, NH$_2$)[1] – Aromatic peaks are broadened and shifted upon interactions with copper catalyst (**Figure S9, S7, S8, S9**).
2, Imine: 8.50 (s, 1H, N=CH), 7.80-7.77 (m, 2H, Ar-H), 7.47-7.25 (m, 8H, Ar-H), 4.77 (s, 2H, N-CH$_2$)[2] (**Figure S9, S7, S8, S9**).
3, Benzaldehyde: 10.02 (s, 1H, CHO), 7.91 (d, J = 7.2 Hz, 2H, Ar-H), 7.72 (t, J = 7.5 Hz, 1H, Ar-H), 7.61 (t, J = 7.6 Hz, 2H, Ar-H)[3] (**Figure S9**).
4, Diisopropyl phosphite: 6.82 (d, J = 686.9 Hz, 1H, PH), 4.59 (doublet of septets, J = 3.7 Hz, 2H, CH), 1.27 (d, J = 6.2 Hz, 12H, CH$_3$)[4] (**Figure S9, S7**).
5, Hypodiphosphate: 4.75-4.73 (m, 4H, CH), 1.30 (d, J = 6.2 Hz, 24H, CH$_3$)[5] (**Figure S10, S8**).
6, Phosphoramidate: 7.34-7.20 (m, 5H, Ar-H), 5.30 (m, 1H, NH), 4.39 (m, J = 6.3 Hz, OC*H*(CH$_3$)$_2$, 3.95 (dd, J = 4.4 Hz, 7.1 Hz, 2H, NCH$_2$), 1.21 (d, J = 6.1 Hz, 6H, OCH(C*H$_3$*)$_2$), 1.16 (d, J = 6.1 Hz, 6H, OCH(C*H$_3$*)$_2$)[6] (**Figure S10**).
7, Diisopropyl phosphate: 4.20 (m, 2H, CH), 1.13 (d, J = 6.2 Hz, 12H, CH$_3$)[4]; P-OH signal was not observed (**Figure S11**).
13, Dodecyl disulfide: 2.68 (t, J = 7.2 Hz, 4H, CH$_2$S)[7] – Other peaks were unidentified due to peak broadening or signal overlaps (**Figure S12**).

Yields of products and remaining reactants or additives were determined by the integrations relative to the methyl protons of the internal standard 1,3,5-trimethoxybenzene. **1** was determined by integrating aromatic peaks 7.32-7.19 ppm, **2** was determined by the methylene protons at 4.77 ppm, **3** by the formyl proton at 10.02 ppm, **4** by the methine protons at 4.59 ppm, **5** by the methine protons at 4.75-4.73 ppm, **6** by the methine protons at 4.39 ppm, **7** by the methine protons at 4.20 ppm, and **13** by the α-methylene protons at 2.68 ppm.

Calculations for moles of imine and oxygen in investigating the effect of oxygen

$$PV = nRT \qquad (1)$$[8]

$$n(air) = \frac{8.314\ J\ K^{-1}\ mol^{-1} \times 298.15\ K}{101325\ Pa \times 0.0000215719\ m^3} = 0.0008817\ mol \qquad (2)$$[8]

$$n(O_2) = 0.0008817\ mol \times 20.95\% = 0.185\ mmol \qquad (3)$$[9]

$$c = kP_{(O_2)} \qquad (4)$$

$$\rho_{(ethyl\ acetate\ @298\ K)} = 0.8945\ \frac{g}{cm^3} \times \frac{1\ kg}{1000\ g} \times \frac{1\ cm^3}{0.000001\ m^3} = 894.5\ \frac{kg}{m^3} \qquad (5)$$[10]

$$k_{(ethyl\ acetate\ @298\ K)} = 7.165\ \frac{mol}{kg\ bar} \times 894.5\ \frac{kg}{m^3} \times \frac{1\ bar}{100000\ Pa} = 0.06409\ \frac{mol}{m^3 \times Pa} \qquad (6)$$

$$P_{(O_2)} = 101325\ Pa \times 20.95\% = 21230\ Pa \qquad (7)$$[9]

$$c_{(O_2)} = 0.06409\ \frac{mol}{m^3 \times Pa} \times 21230\ Pa = 1361\ \frac{mol}{m^3} \qquad (8)$$[11]

$$n_{(O_2)} = 1361\ \frac{mol}{m^3} \times 0.00000216\ m^3 = 2.94\ mmol \qquad (9)$$

$$n(benzylamine) = 0.1600\ mL \times 0.981\ g\ mL^{-1} \div 107.15\ g\ mol^{-1} = 0.00146\ mol \qquad (10)$$

$$n(theoretical\ max.imine) = 0.000732\ mol \qquad (11)$$

$$n(imine) = 0.000732\ mol \times 15.6\% = 0.114\ mmol \qquad (12)$$

Volume of the headspace in a 20 mL scintillation vial reaction vessel was measured to be 2.15719×10^{-5} m^3. Using the ideal gas law the number of mols of O_2 available from air in the headspace was able to be calculated.[8] Standard pressure and room temperature were used in calculation. As O_2 is 20.95% by volume of air, moles of oxygen in the headspace were calculated to be 0.185 mmol.[9] By using Henry's Law, the amount of O_2 able to be dissolved in the reaction mixture solvent was also calculated. By using density and Henry's Law constant, the solubility of O_2 in ethyl acetate was calculated to be 1361 mol m^{-3}. Amount of ethyl acetate was measured to be 2.16×10^{-6} m^3, resulting in 2.94 mmol of O_2 able to be dissolved in the reaction mixture. In total, 3.054 mmol of O_2 was readily present.

Supporting Figures and Tables

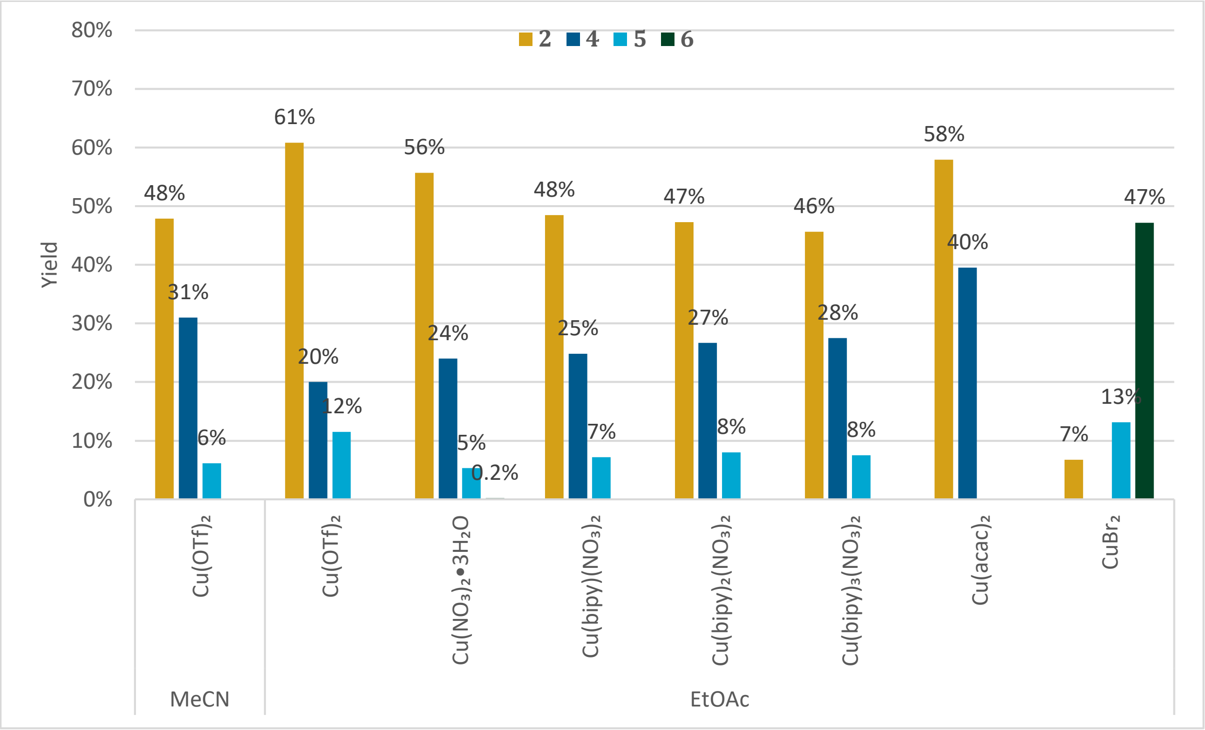

Figure S1. Product yields (imine (**2**), hypodiphosphate (**5**), phosphoramidate (**6**)) and remaining phosphite (**4**) for the oxidative homocoupling of amine (**1**) using copper catalysts and additive **4** in EtOAc or MeCN over 24 h (**Scheme 2**).

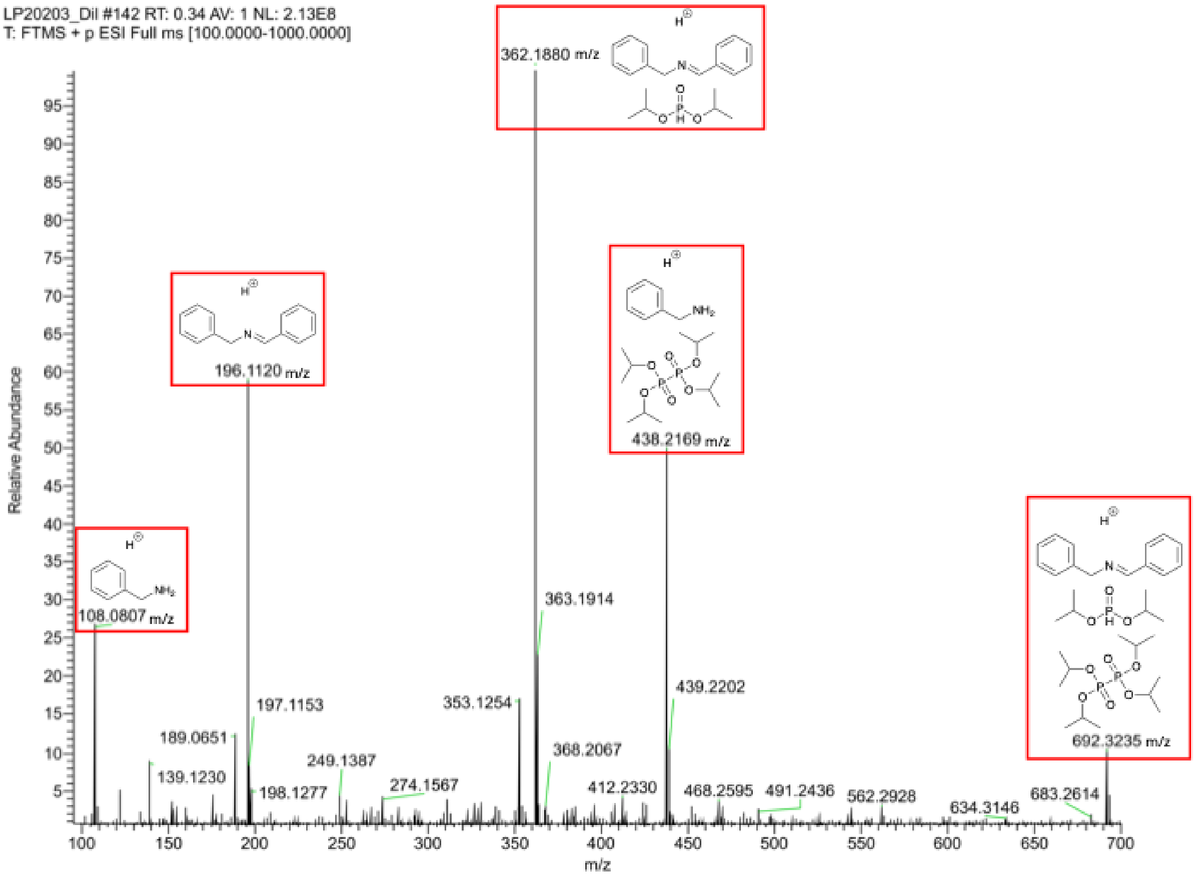

Figure S2. Electrospray ionisation mass-spectrometry positive spectrum of separated organic layer of oxidative homocoupling of amine (**1**) using Cu(OTf)₂ catalyst after sequestering with EDTA.

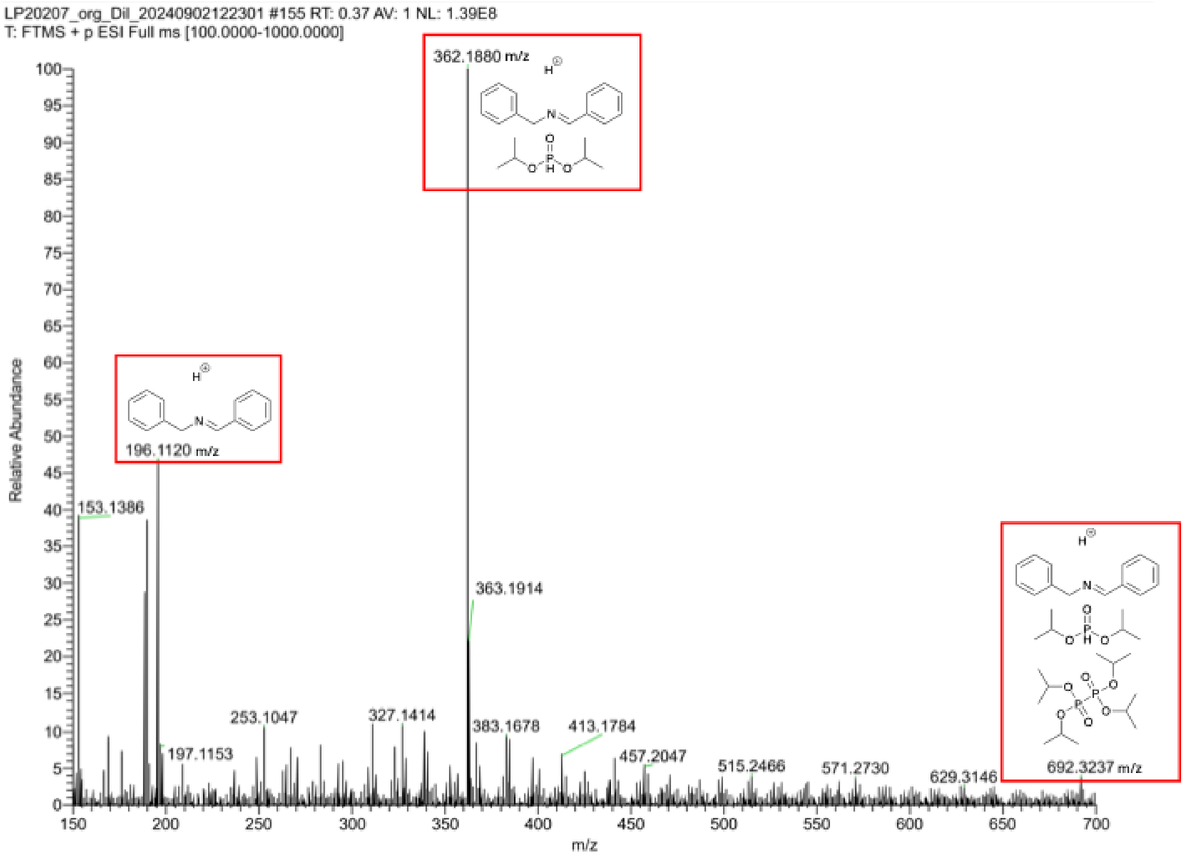

Figure S3. Electrospray ionisation mass-spectrometry positive spectrum of separated organic layer of oxidative homocoupling of amine (**1**) using Cu(acac)$_2$ catalyst after sequestering with EDTA (**Scheme 2**).

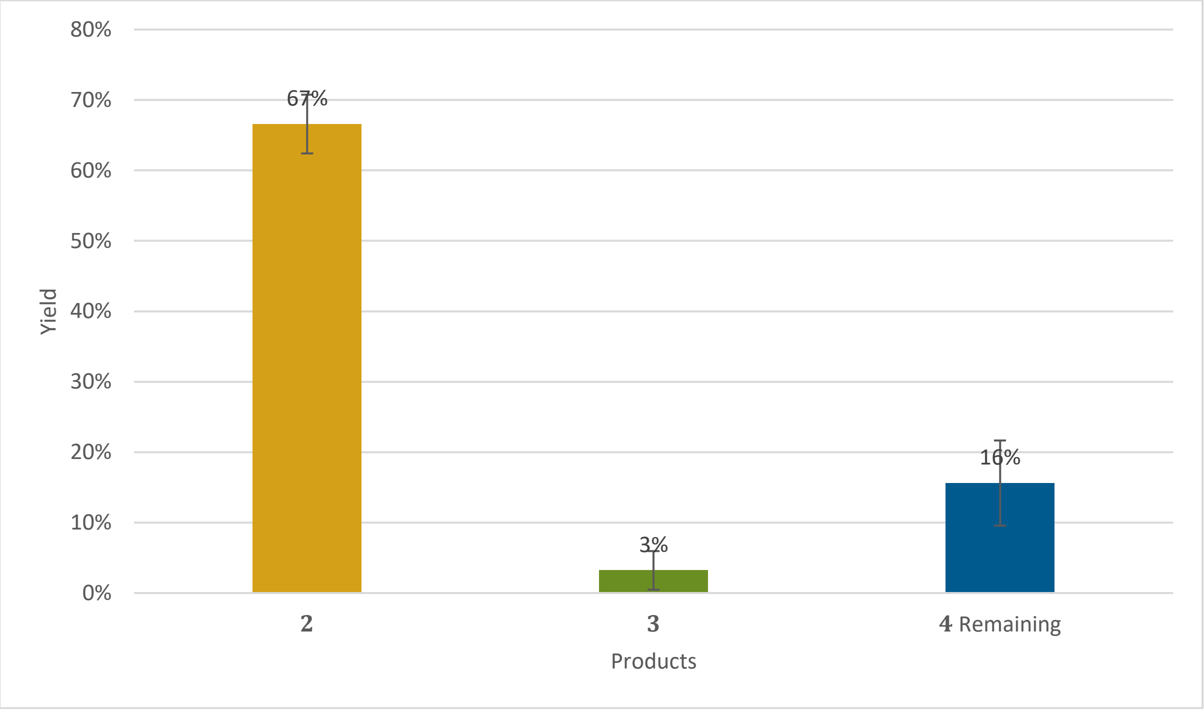

Figure S4. Yields of imine (**2**), aldehyde (**3**), and remaining phosphite (**4**) of triplicate reaction of oxidative homocoupling of amine (**1**) using optimized conditions with Cu(acac)$_2$ catalyst and additive **4** in EtOAc solvent for 96 h.

Table S1. Product yields and remaining phosphite (**4**) of triplicate reactions of oxidative homocoupling of amine (**1**) using optimized conditions with Cu(acac)$_2$ catalyst and additive **4** in EtOAc solvent for 96 h (**Scheme 2**).

	Single	Duplicate	Triplicate
2	68.4%	67.0%	64.3%
3	3.9%	4.1%	1.6%
4 Remaining	12.8%	18.8%	15.2%

Table S2. Average yields of imine (**2**), aldehyde (**3**), and average remaining phosphite (**4**) alongside margin of error (95% confidence interval) of triplicate reaction of oxidative homocoupling of amine (**1**) using optimized conditions with Cu(acac)$_2$ catalyst and additive **4** in EtOAc solvent for 96 h.

	Average	Standard Deviation	Standard Error	Margin of Error
2	66.6%	2.1%	1.2%	4.1%
3	3.2%	1.4%	0.8%	2.8%
4 Remaining	15.6%	3.0%	1.7%	6.0%

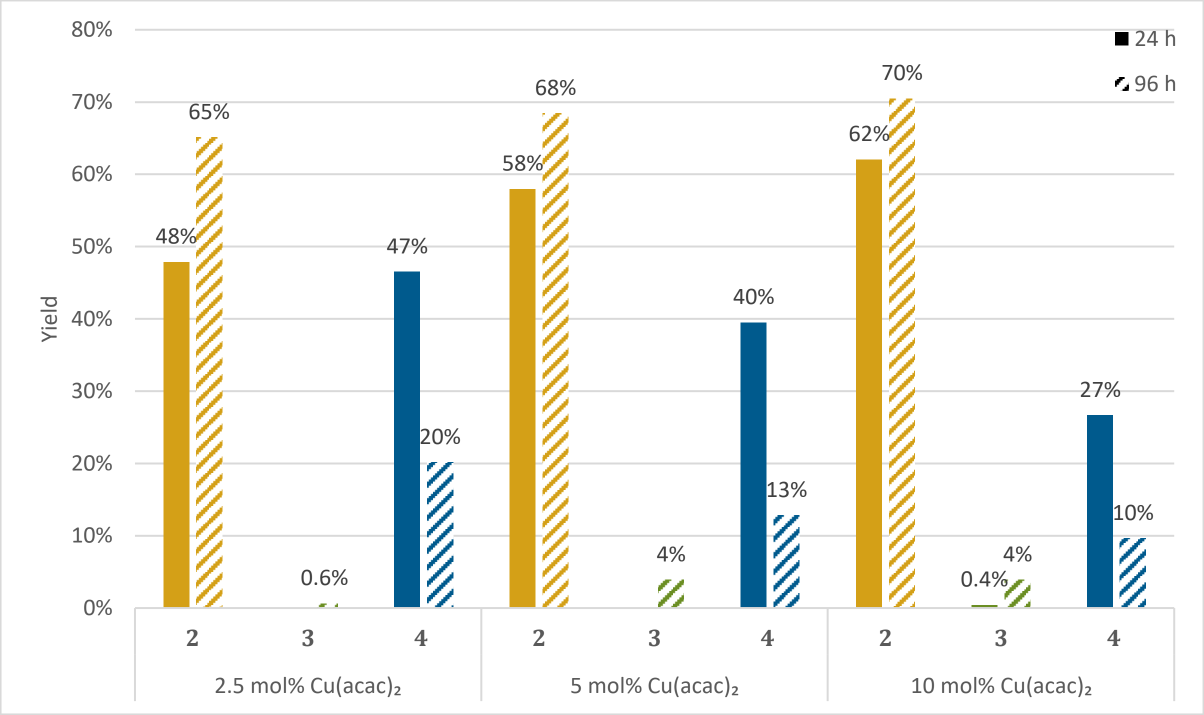

Figure S5. Yields of imine (**2**), aldehyde (**3**), and remaining phosphite (**4**) for the oxidative homocoupling of amine (**1**) using Cu(acac)$_2$ catalyst and additive **4** in EtOAc over 24 h (solid bars) and over 96 h (hashed bars).

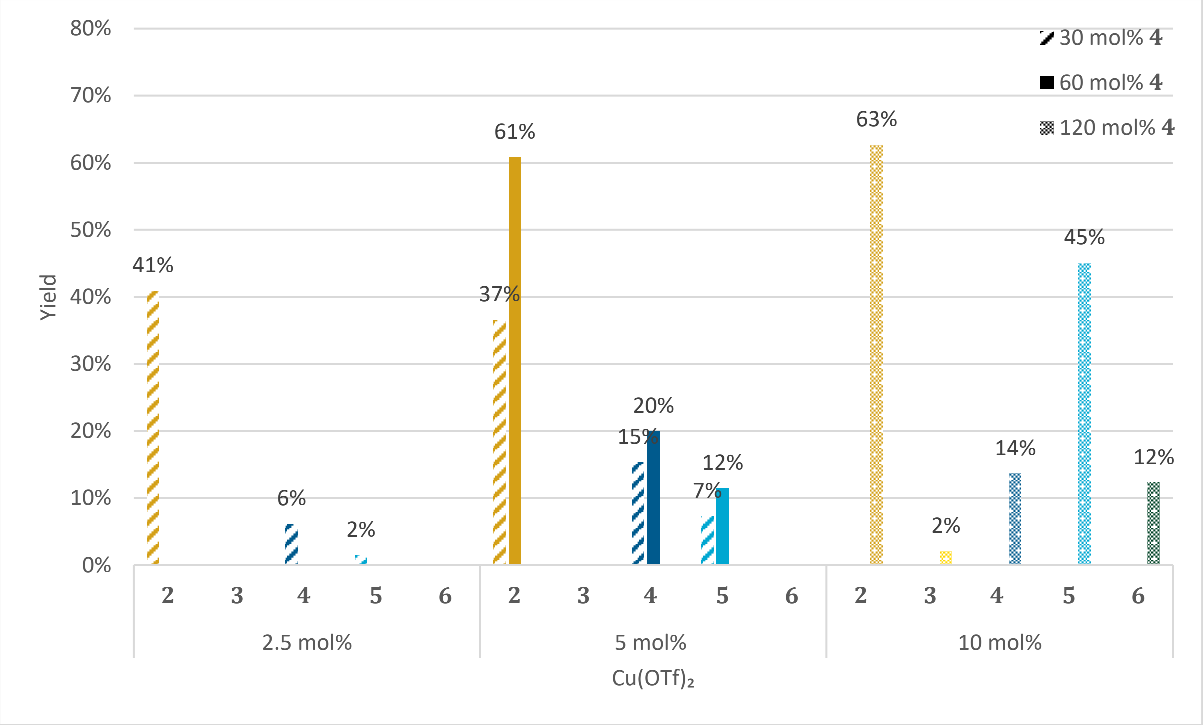

Figure S6. Product yields and remaining phosphite (**4**) for the oxidative homocoupling of amine (**1**) using Cu(OTf)$_2$ catalyst and additive **4** in EtOAc solvent at 24 h reaction time (**Scheme 2**).

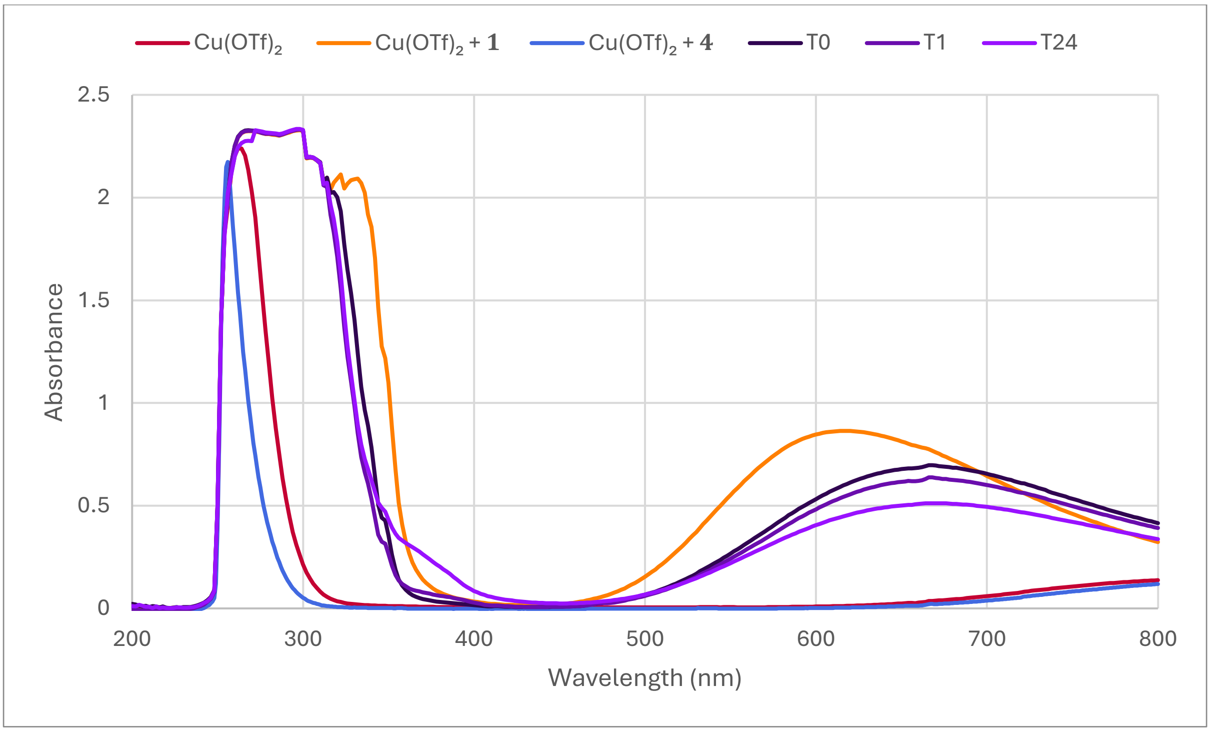

Figure S7. UV-Vis spectra of Cu(OTf)$_2$, Cu(OTf)$_2$ + amine (**1**), Cu(OTf)$_2$ + phosphite (**4**), and reaction mixtures at T0, T1, and T24, in EtOAc diluted 4-fold.

Table S3. λ_{max} of peaks observed in the UV-Vis spectra of $Cu(OTf)_2$ species and the corresponding molar extinction coefficients (**Figure S7**).

	Wavelength (nm)	Absorbance	Concentration (mol L⁻¹)	Molar extinction coefficient (L mol⁻¹ cm⁻¹)
$Cu(OTf)_2$	800	0.137	0.0087	16
$Cu(OTf)_2$ + **1**	616	0.864	0.0081	107
$Cu(OTf)_2$ + **4**	800	0.119	0.0081	15
T0	668	0.698	0.0076	92
T1	668	0.639	0.0076	84
T24	668	0.512	0.0076	67

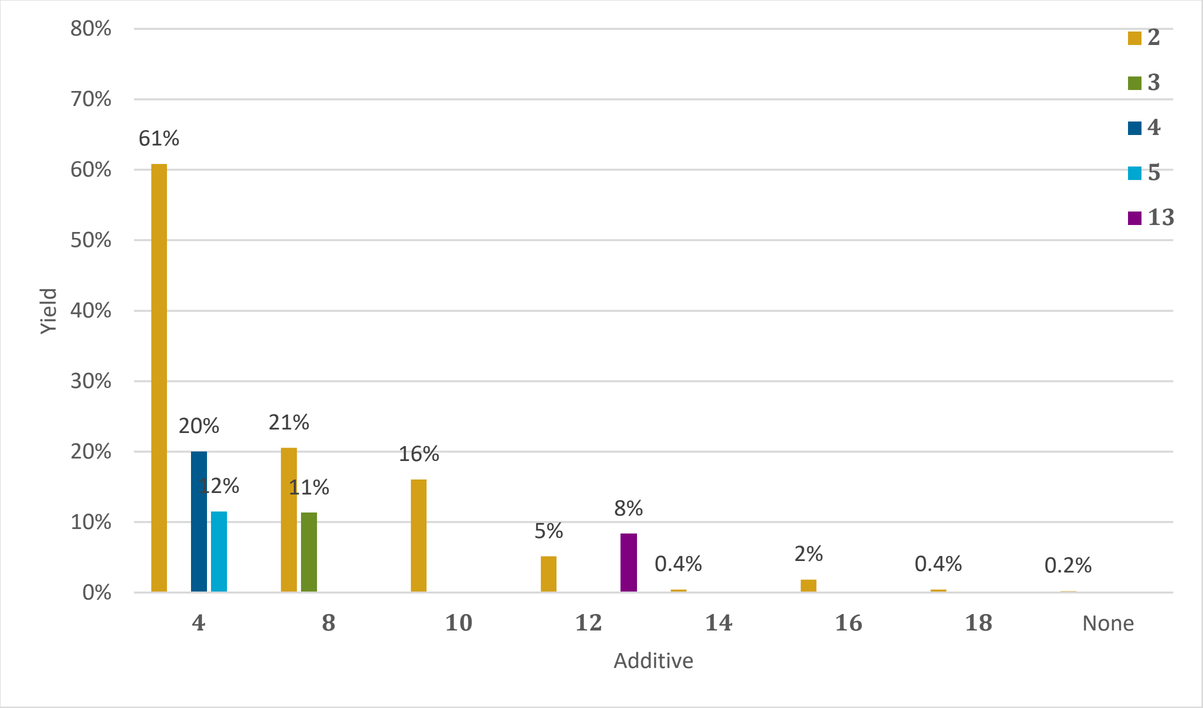

Figure S8. Product yields (imine (**2**), aldehyde (**3**), hypodiphosphate (**5**), disulfide (**13**)) and remaining phosphite (**4**) for the oxidative homocoupling of amine (**1**) using $Cu(OTf)_2$ catalyst with additives (ascorbic acid (**8**), glucose (**10**), thiol (**12**), phosphine (**14**), sodium iodide (**16**), sodium sulfite (**18**)) in EtOAc over 24 h (**Scheme 2**).

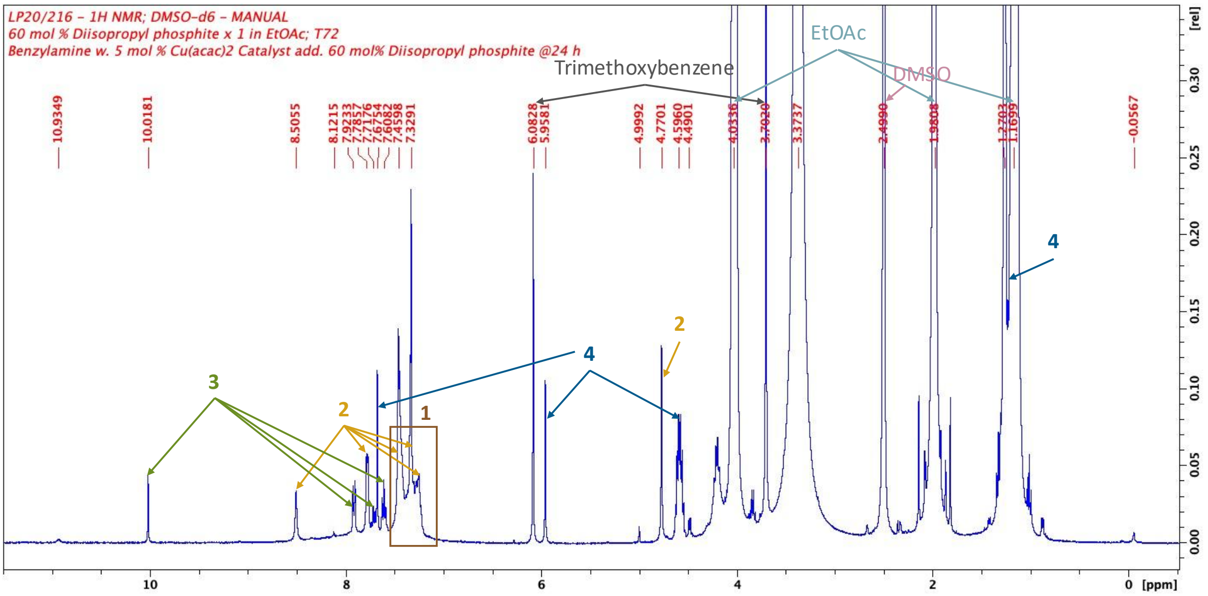

Figure S9. ^{1}H NMR spectrum of the oxidative homocoupling of amine (**1**) with Cu(acac)$_2$ catalyst and phosphite (**4**) additive in EtOAc solvent at 72 h with the addition of additive at 24 h (**Scheme 2**).

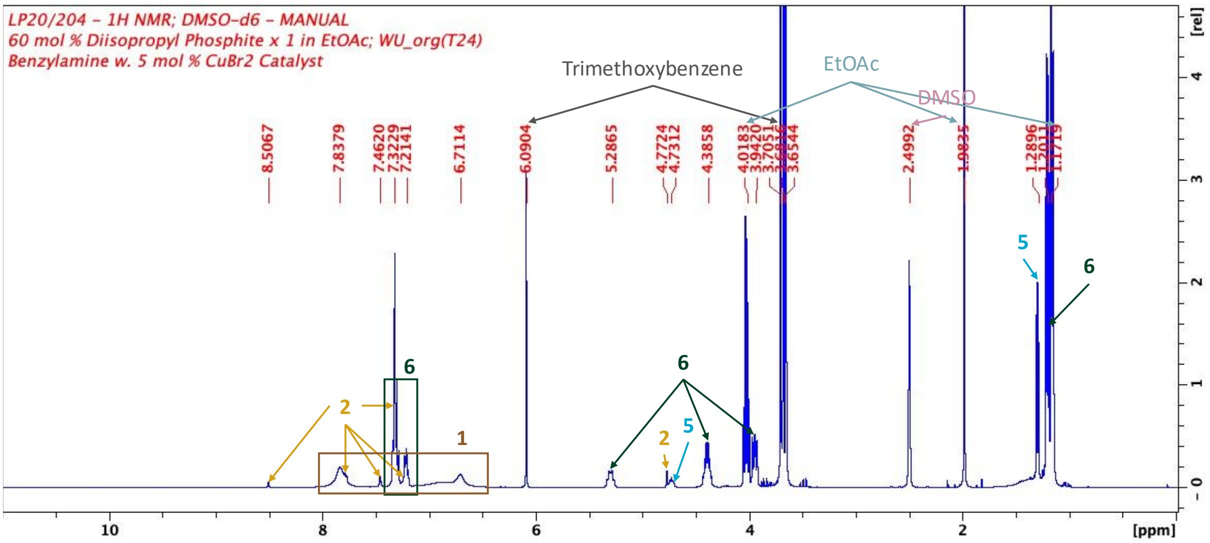

Figure S10. ^{1}H NMR spectrum of the oxidative homocoupling of amine (**1**) with CuBr$_2$ catalyst and phosphite (**4**) additive in EtOAc solvent at 24 h.

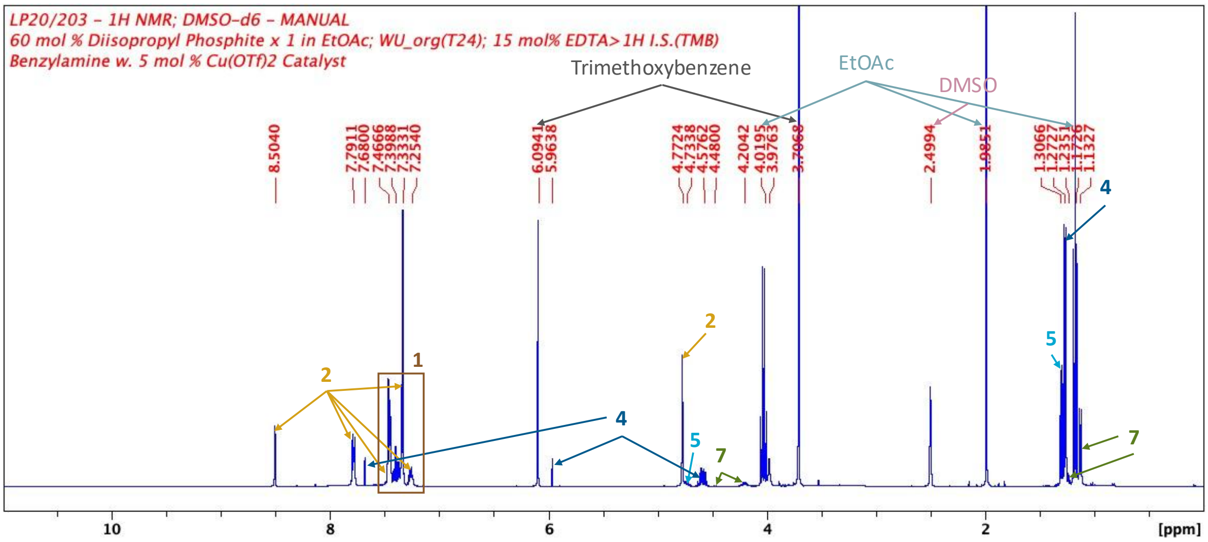

Figure S11. ^{1}H NMR spectrum of the oxidative homocoupling of amine (**1**) with Cu(OTf)$_2$ catalyst and phosphite (**4**) additive in EtOAc solvent, with copper sequestering by EDTA at 24 h (organic layer) (**Scheme 2**).

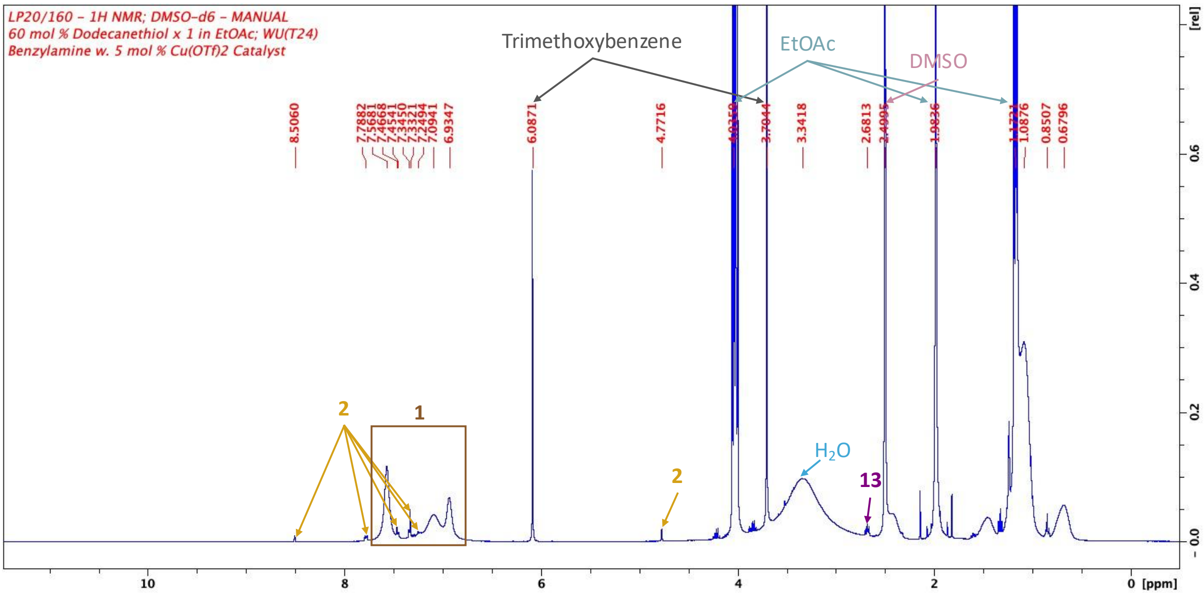

Figure S12. ^{1}H NMR spectrum of the oxidative homocoupling of amine (**1**) with Cu(OTf)$_2$ catalyst and thiol (**12**) additive in EtOAc solvent.

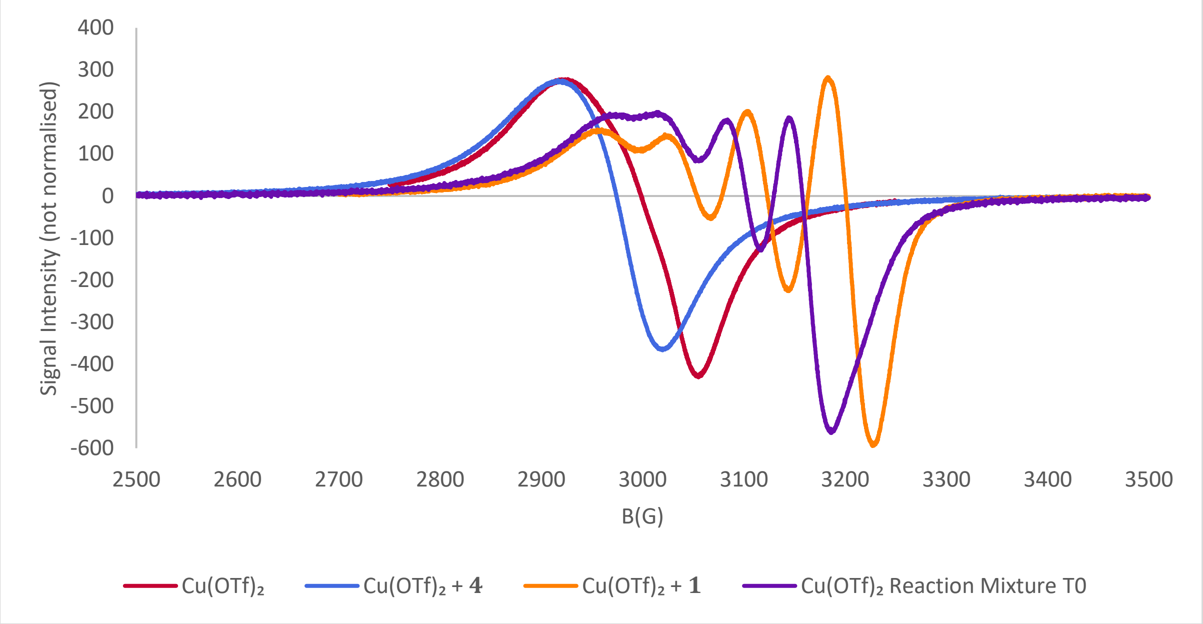

Figure S13. Overlapping electron paramagnetic resonance spectra of samples containing only $Cu(OTf)_2$ (amplitude = 8) (red), $Cu(OTf)_2$ with phosphite (**4**) additive (amplitude = 8) (blue), $Cu(OTf)_2$ with amine (**1**) (amplitude = 8) (orange), and $Cu(OTf)_2$ with both (amplitude = 20) (purple), in EtOAc (**Scheme 2**).

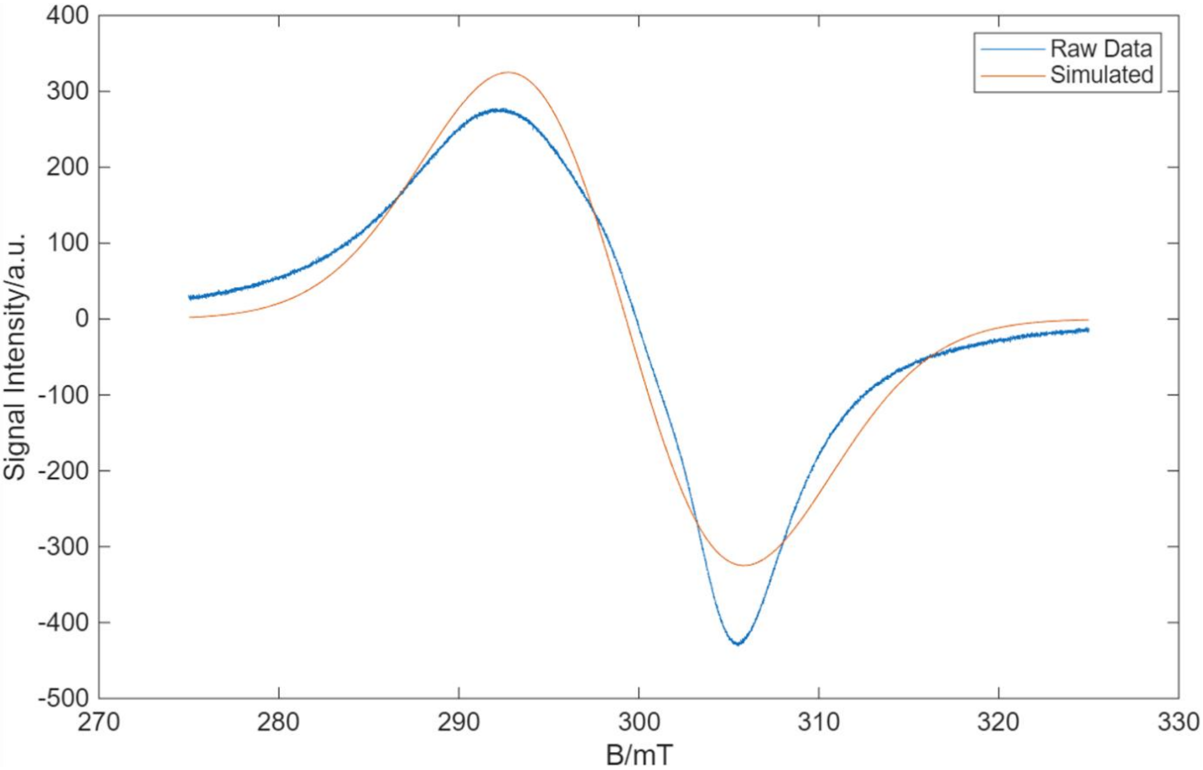

Figure S14. Simulated and experimental EPR spectra of $Cu(OTf)_2$; $g^1 = 2.174$.

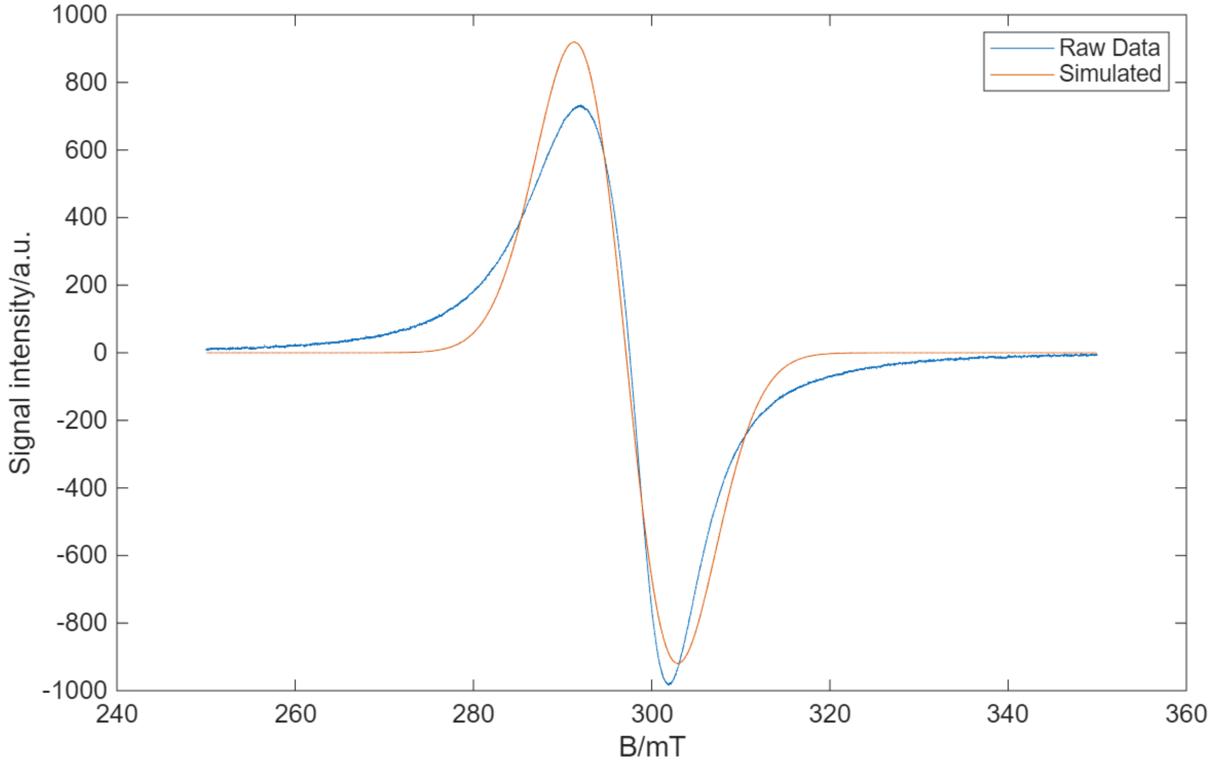

Figure S15. Simulated and experimental EPR spectra of $Cu(OTf)_2$ with phosphite (**4**); $g^1 = 2.190$ (**Scheme 2**).

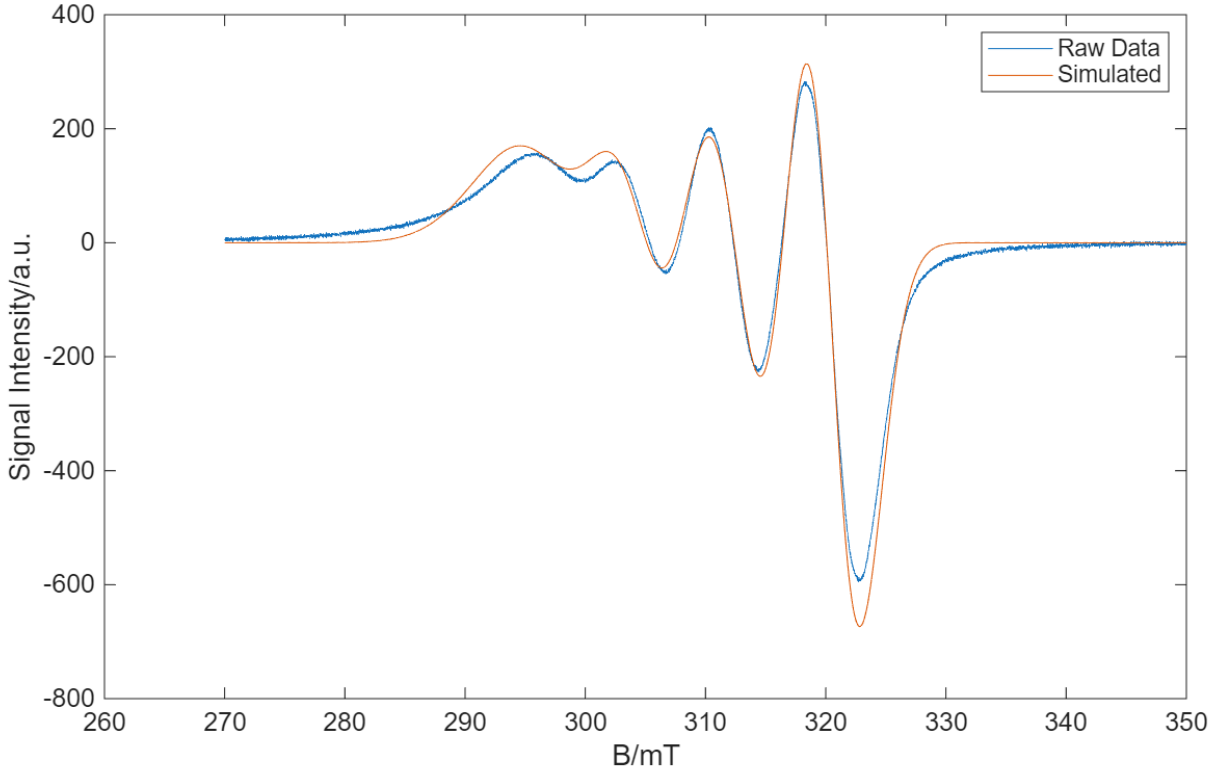

Figure S16. Simulated and experimental EPR spectra of $Cu(OTf)_2$ with amine (**1**); $g^1 = 2.174$, $g^2 = 2.131$, $g^3 = 2.081$, $g^4 = 2.031$.

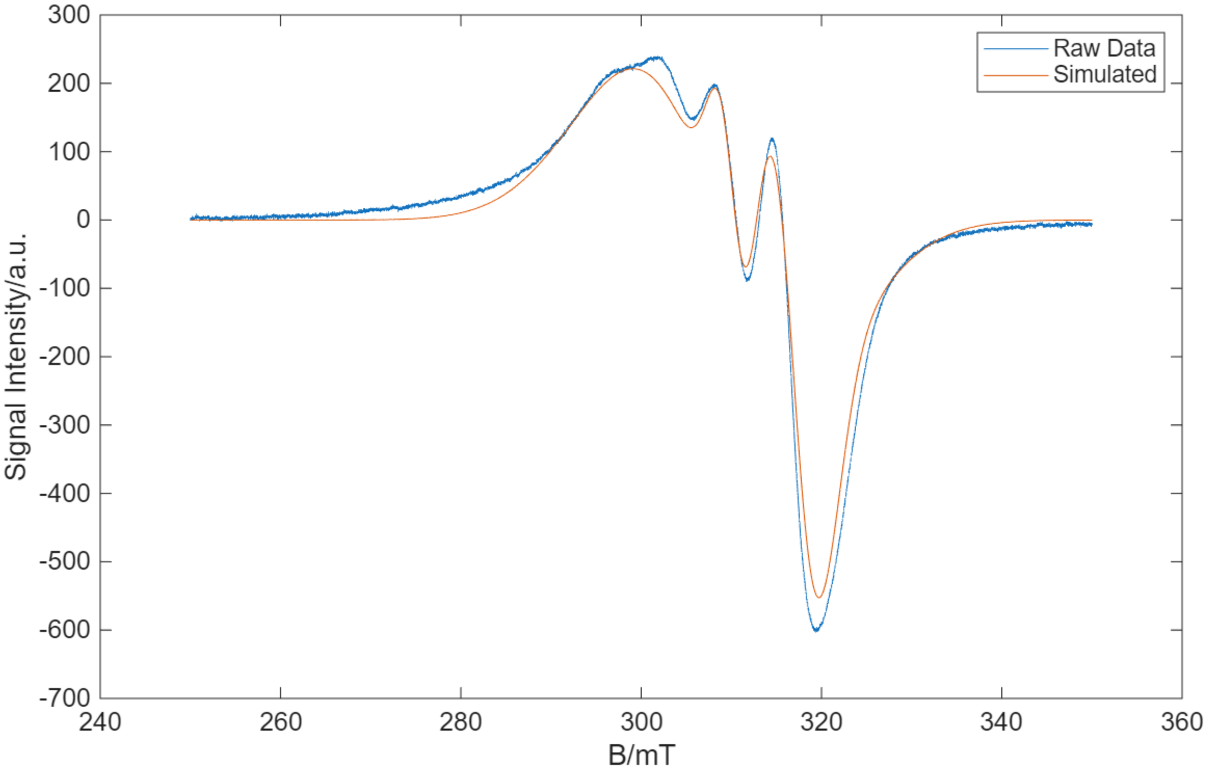

Figure S17. Simulated and experimental EPR spectra of reaction mixture, Cu(OTf)$_2$ with phosphite (**4**) and amine (**1**); $g^1 = 2.110$, $g^2 = 2.097$, $g^3 = 2.054$ (**Scheme 2**).

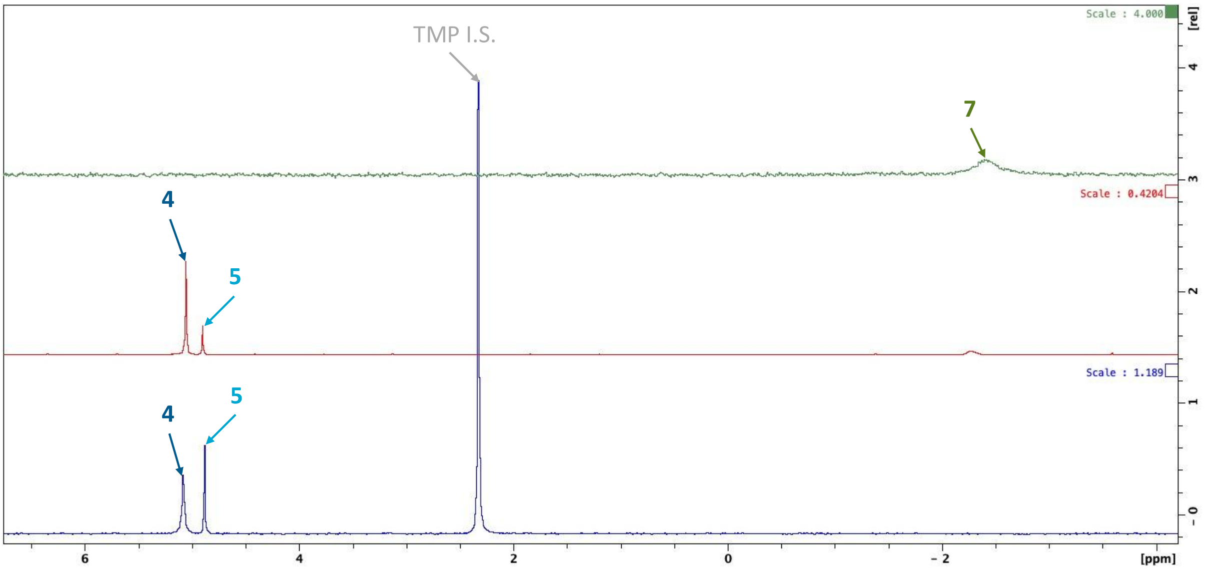

Figure S18. $^{31}P\{^1H\}$ NMR spectra of oxidative homocoupling of amine (**1**) using Cu(OTf)$_2$ catalyst in sequestering conditions (aqueous layer, green) (organic layer, red) and without sequestering (blue) (TMP I.S.: trimethyl phosphate internal standard).

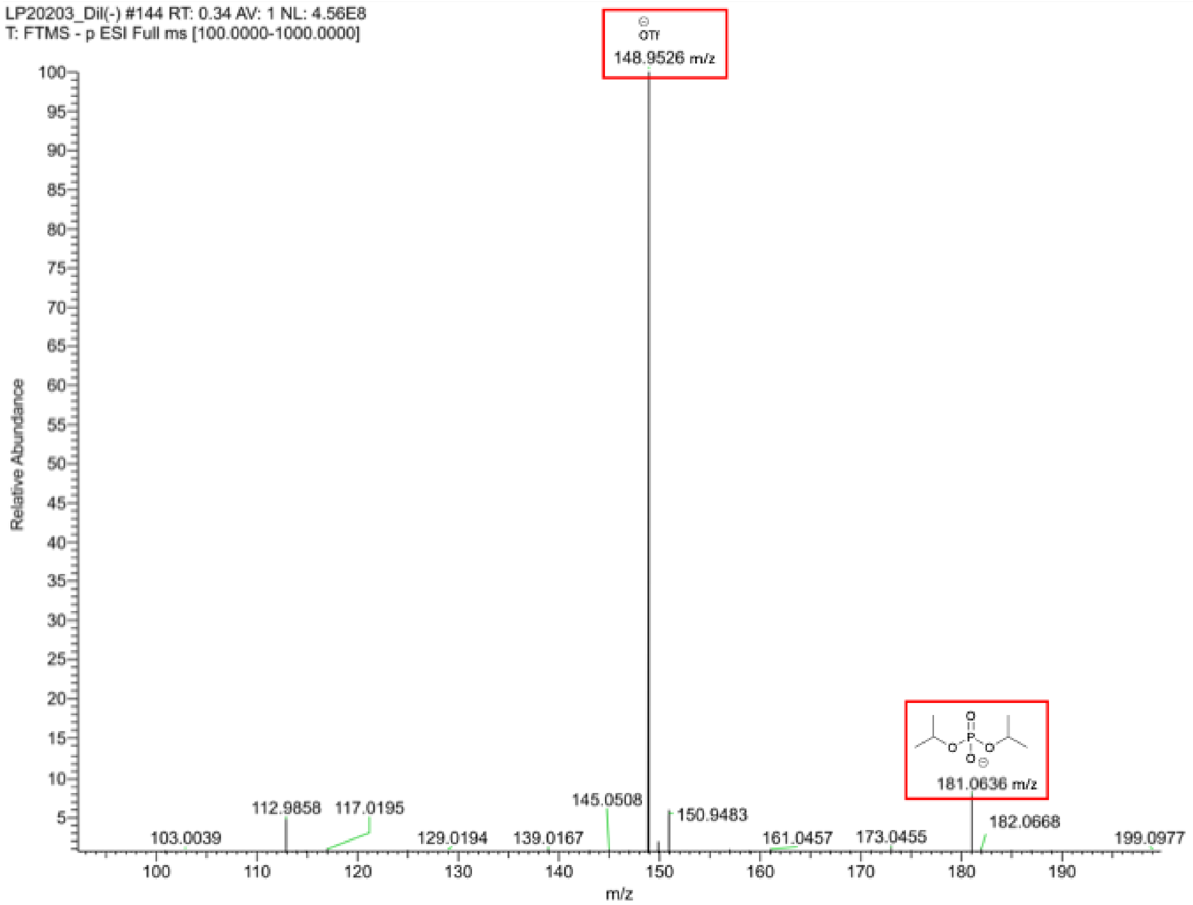

Figure S19. Electrospray ionisation mass-spectrometry negative spectrum of separated organic layer of oxidative homocoupling of amine (**1**) using Cu(OTf)$_2$ catalyst after sequestering with EDTA (**Scheme 2**).

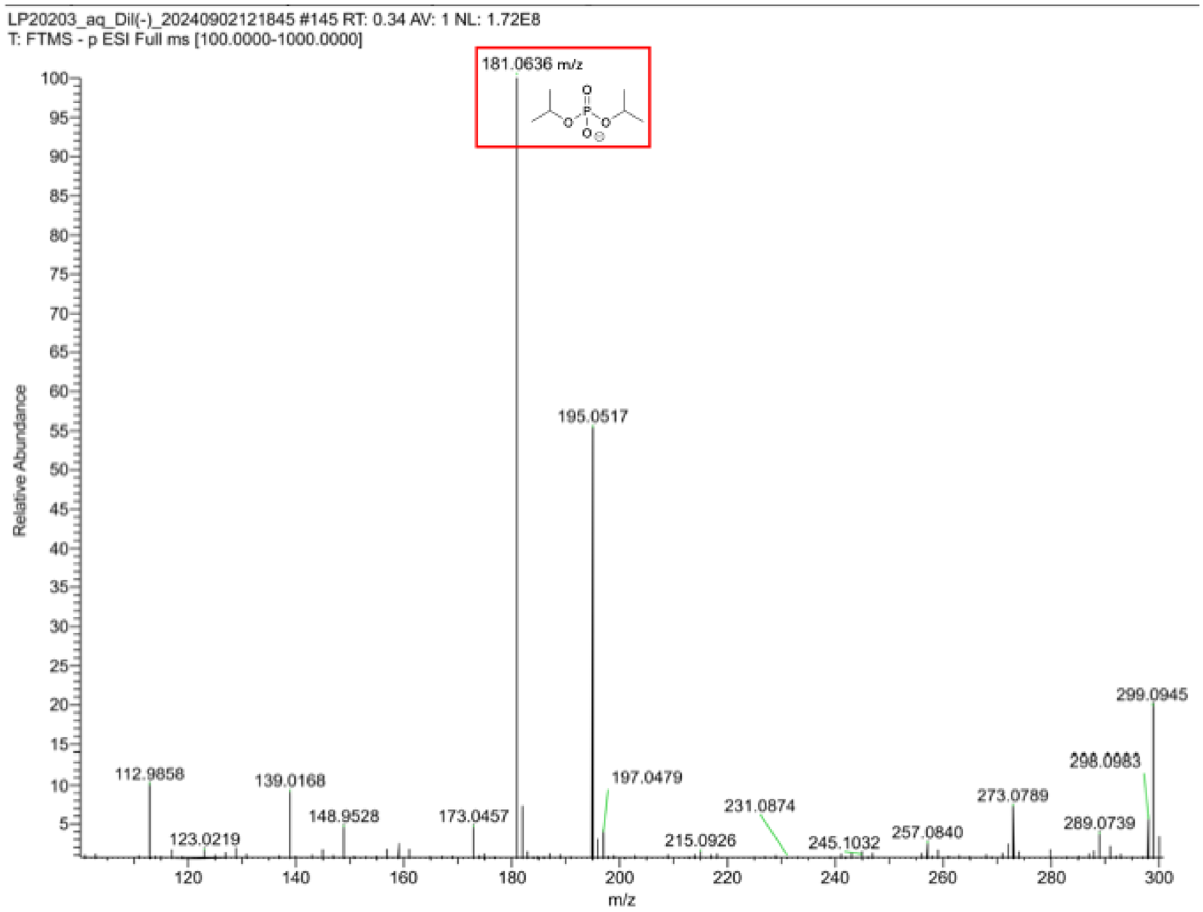

Figure S20. Electrospray ionisation mass-spectrometry negative spectrum of separated aqueous layer of oxidative homocoupling of amine (**1**) using Cu(OTf)$_2$ catalyst after sequestering with EDTA (**Scheme 2**).

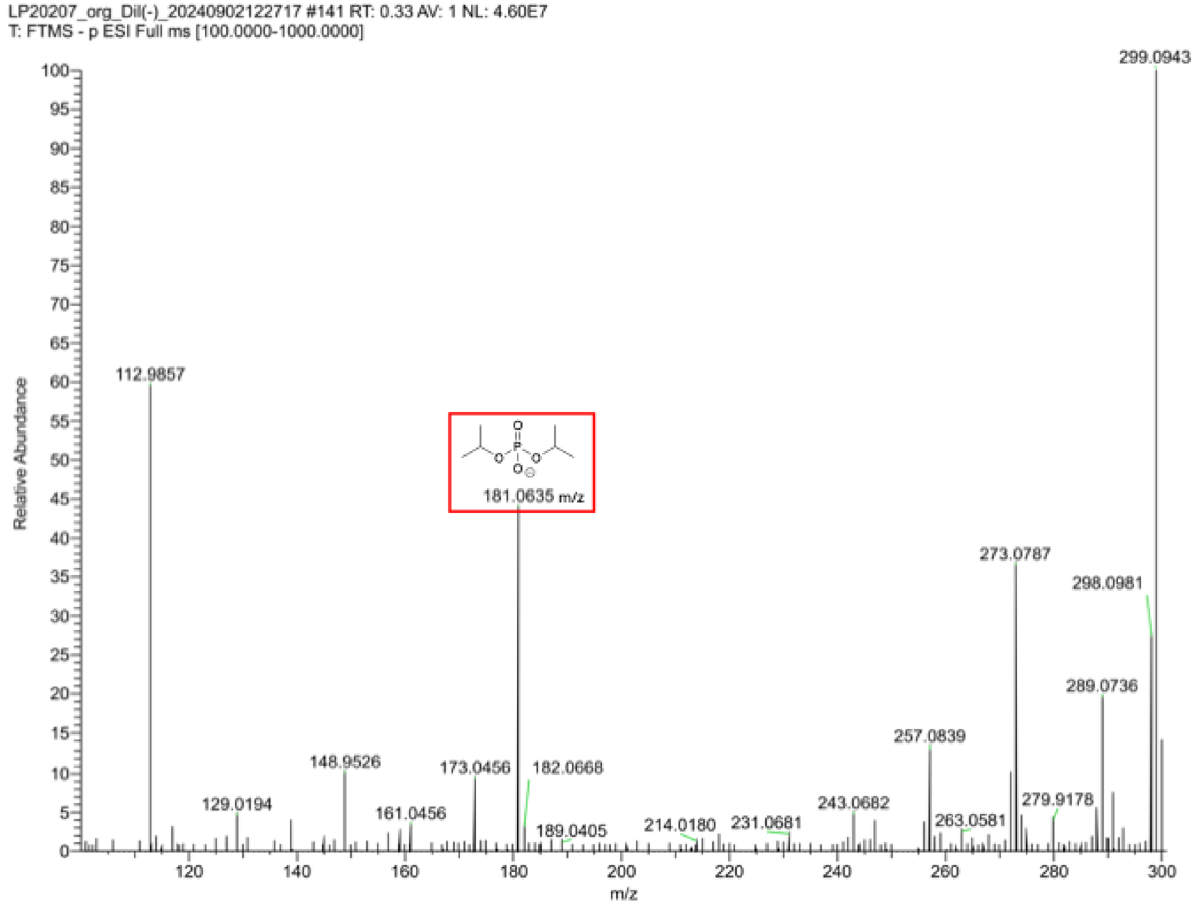

Figure S21. Electrospray ionisation mass-spectrometry negative spectrum of separated organic layer of oxidative homocoupling of amine (**1**) using Cu(acac)$_2$ catalyst after sequestering with EDTA (**Scheme 2**).

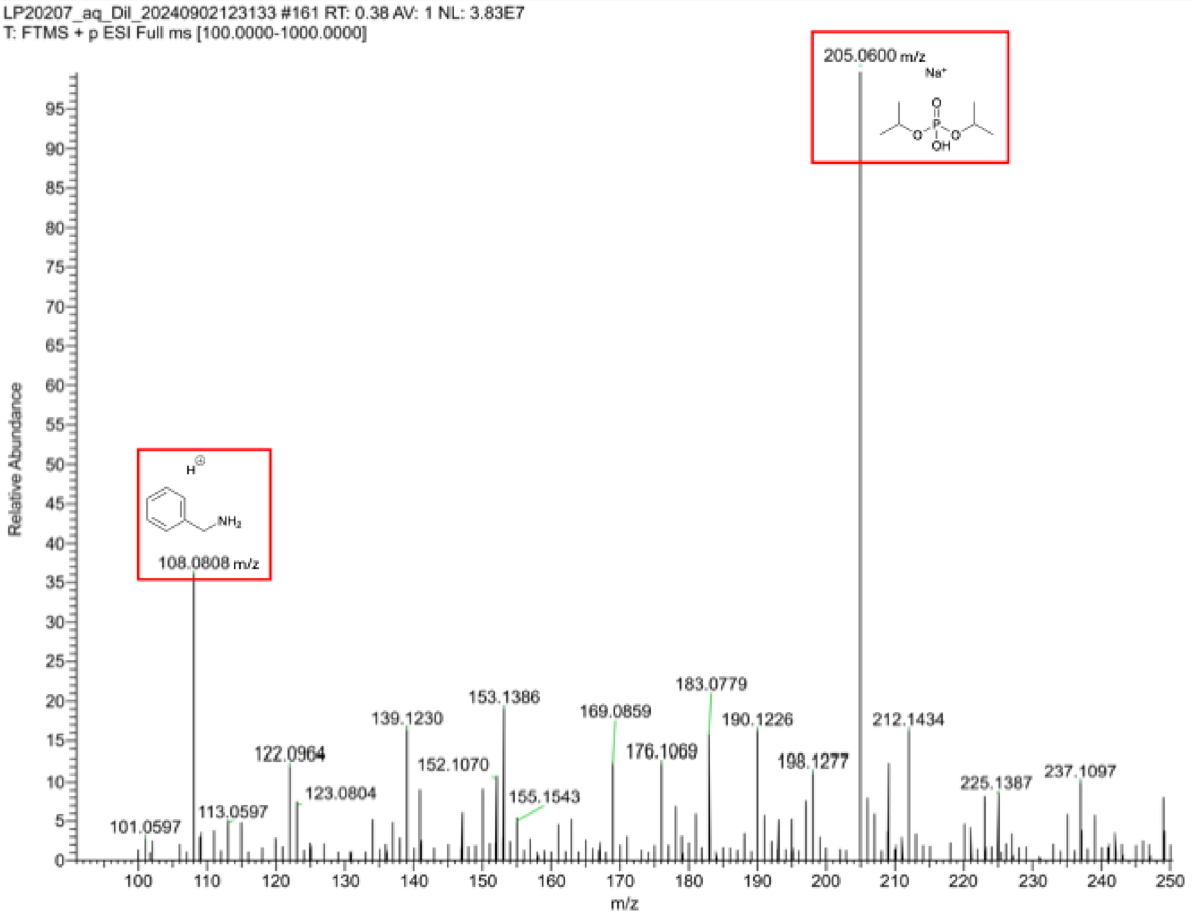

Figure S22. Electrospray ionisation mass-spectrometry positive spectrum of separated aqueous layer of oxidative homocoupling of amine (**1**) using Cu(acac)$_2$ catalyst after sequestering with EDTA (**Scheme 2**).

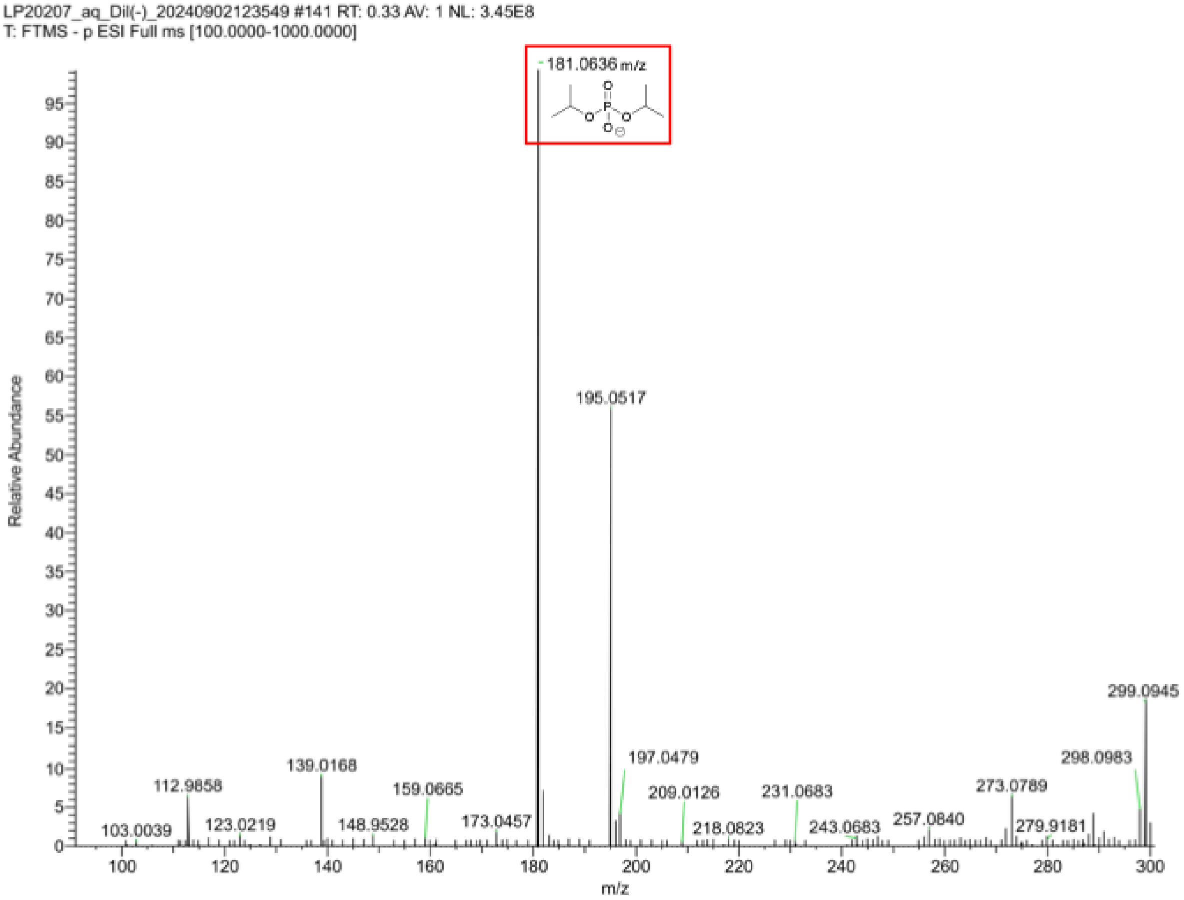

Figure S23. Electrospray ionisation mass-spectrometry negative spectrum of separated aqueous layer of oxidative homocoupling of amine (**1**) using Cu(acac)$_2$ catalyst after sequestering with EDTA (**Scheme 2**).

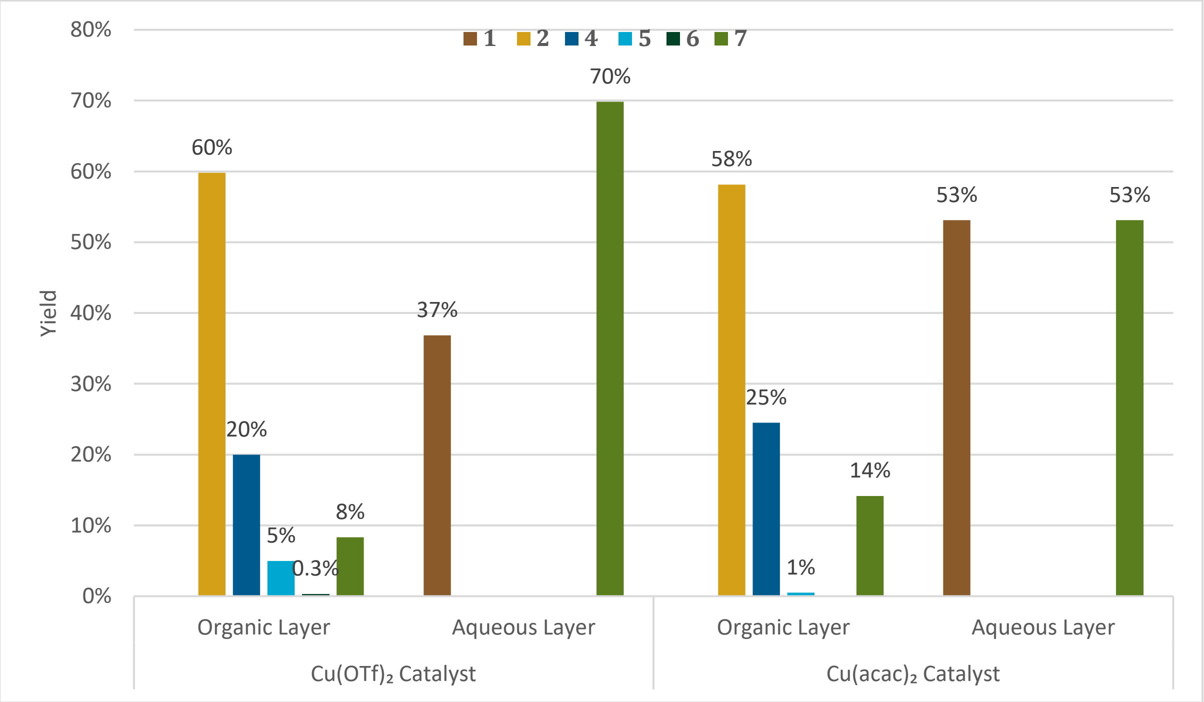

Figure S24. Product yields, remaining amine (**1**), and residual phosphite (**4**) for the oxidative homocoupling of **1** using Cu(II) catalyst and additive **4** in EtOAc over 24 h, after copper sequestration by EDTA.

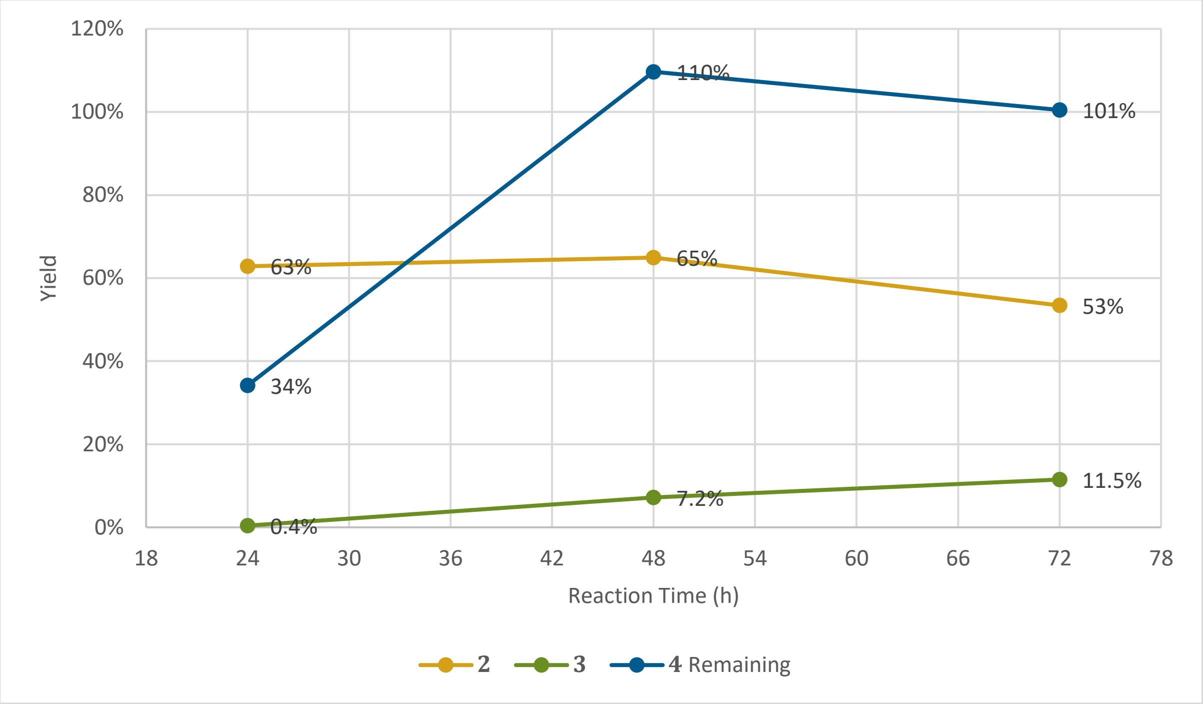

Figure S25. Product yields and remaining phosphite (**4**) when doubling **4** at 24 h in reaction using Cu(acac)$_2$ catalyst and additive **4** in EtOAc for the oxidative homocoupling of amine (**1**) (**Scheme 2**).

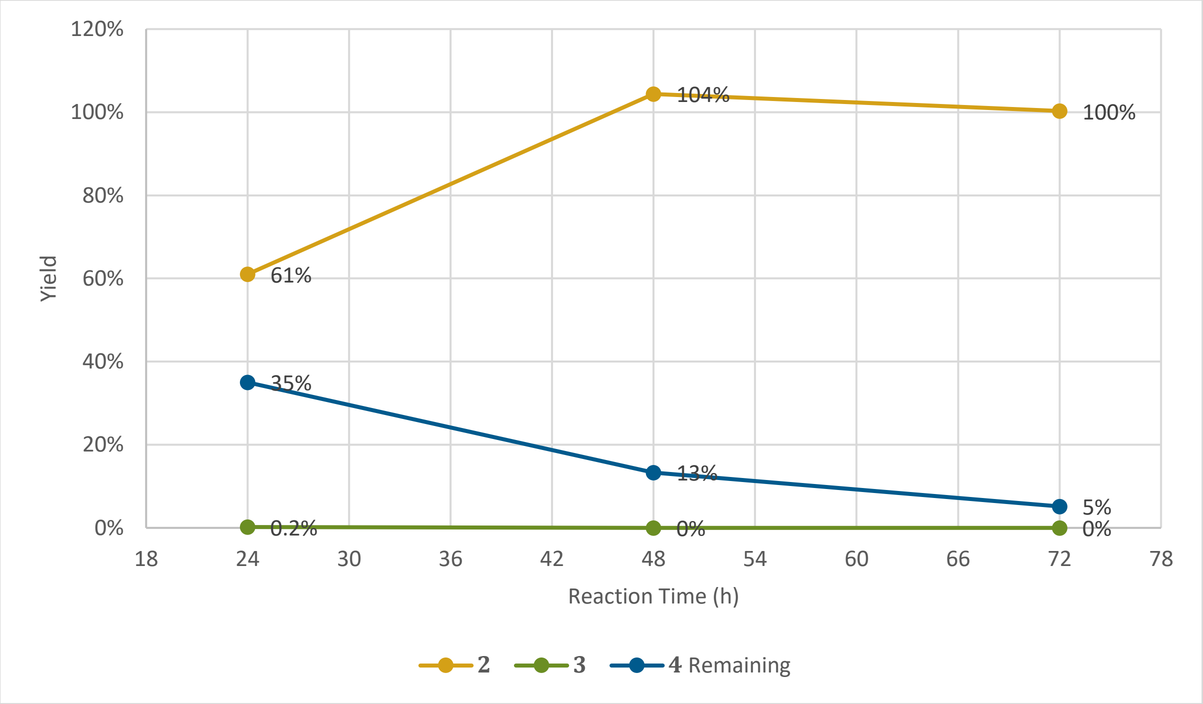

Figure S26. Product yields and remaining phosphite (**4**) when doubling amine (**1**) at 24 h in reaction using Cu(acac)$_2$ catalyst and additive **4** in EtOAc for the oxidative homocoupling of **1**.

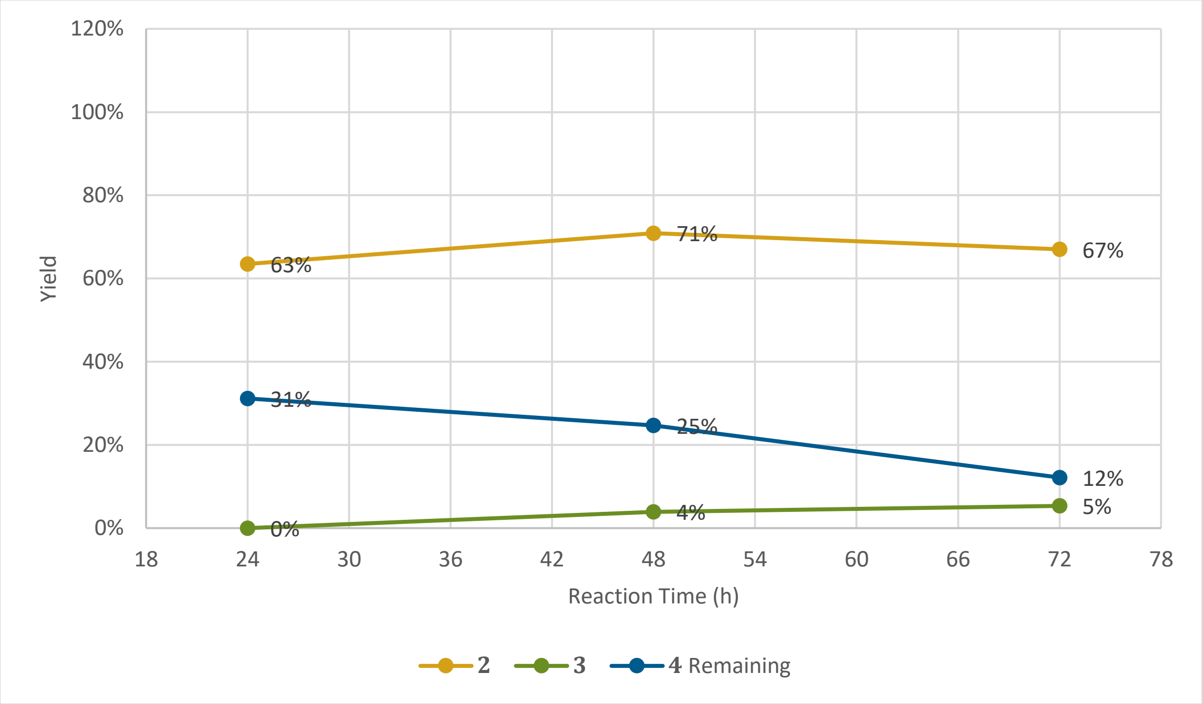

Figure S27. Product yields and remaining phosphite (**4**) when doubling Cu catalyst at 24 h in reaction using Cu(acac)$_2$ catalyst and additive **4** in EtOAc for the oxidative homocoupling of amine (**1**) (**Scheme 2**).

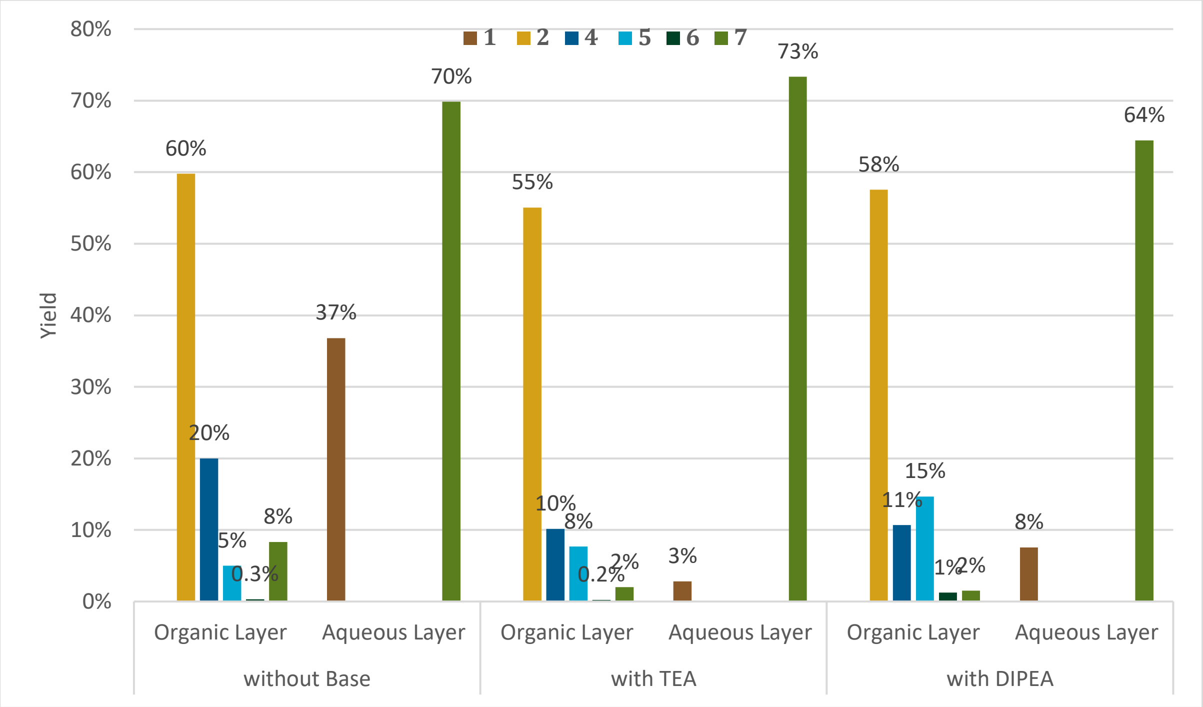

Figure S28. Product yields (imine (**2**), hypodiphosphate (**5**), phosphoramidate (**6**), phosphate (**7**)), remaining amine (**1**), and residual phosphite (**4**) for the oxidative homocoupling of **1** using Cu(OTf)$_2$ catalyst and additive **4** in EtOAc over 24 h, comparing the reactions with and without bases, all quantified following copper sequestration by EDTA.

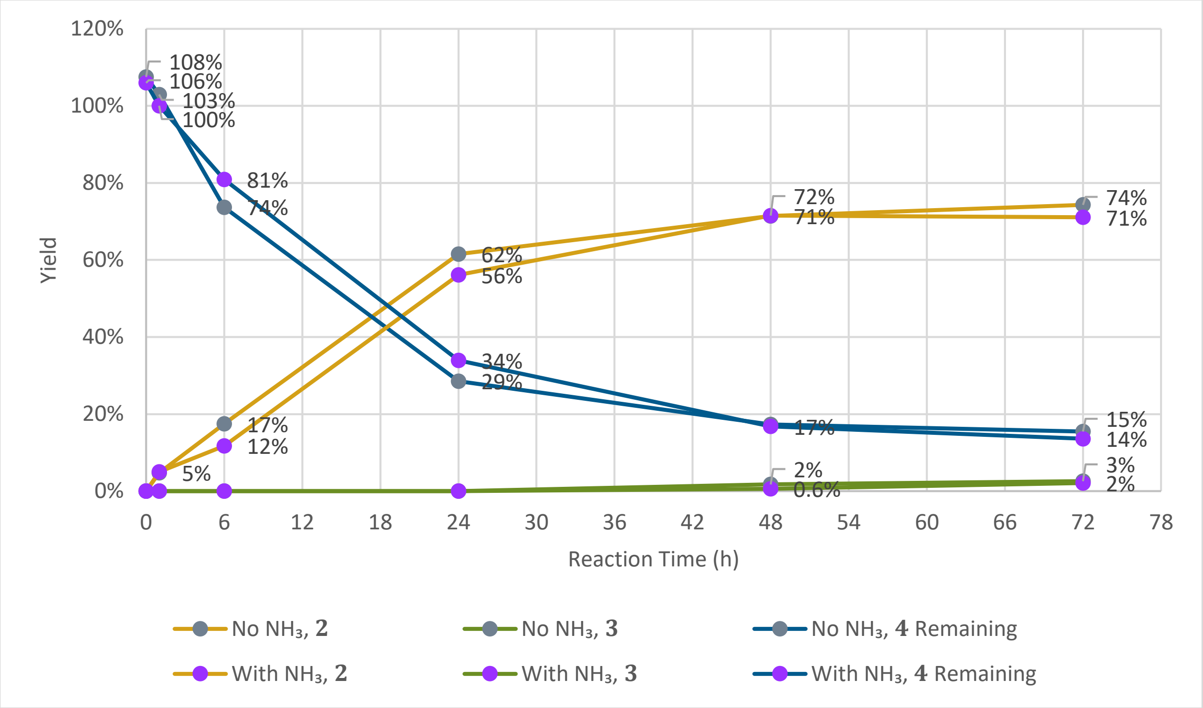

Figure S29. Product yields and remaining phosphite (**4**) for the oxidative homocoupling of amine (**1**) using Cu(acac)$_2$ catalyst with additive **4** in EtOAc over time points 0, 1, 6, 24, 48, and 72 hours, with and without bubbling NH$_3$ at 1 hour time point (**Scheme 2**).

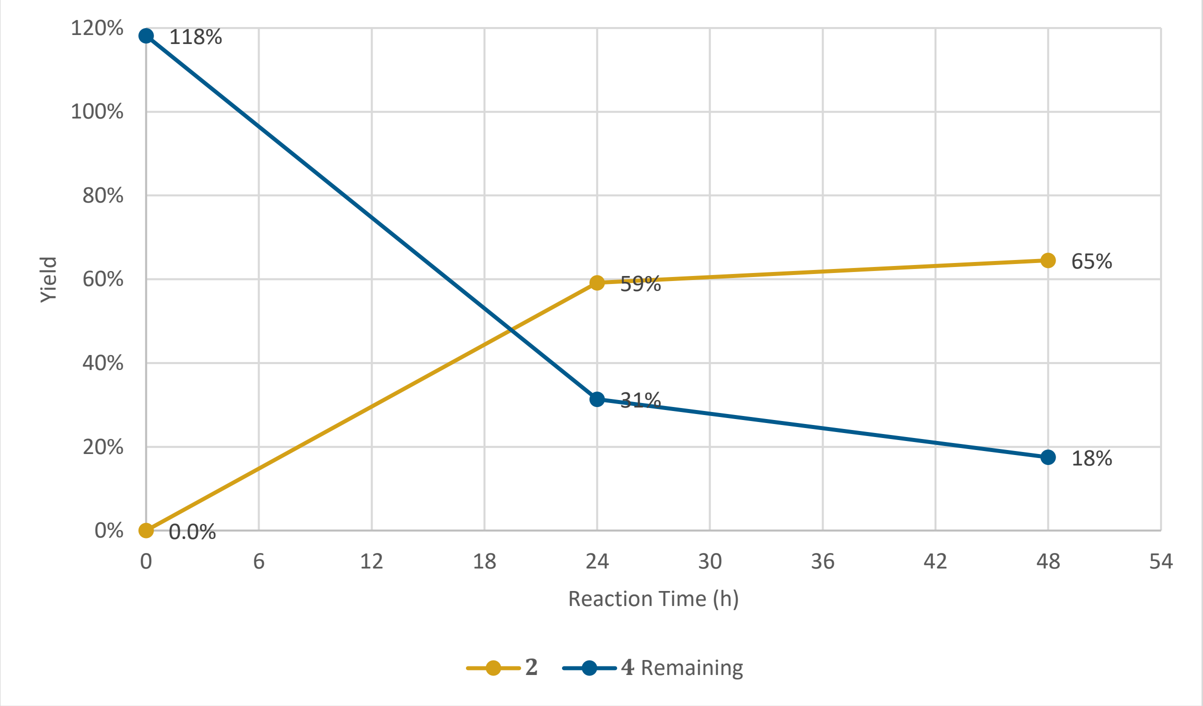

Figure S30. Product yield and remaining phosphite (**4**) in the presence of 3Å molecular sieves using Cu(acac)$_2$ catalyst with additive **4** in EtOAc for the oxidative homocoupling of amine (**1**).

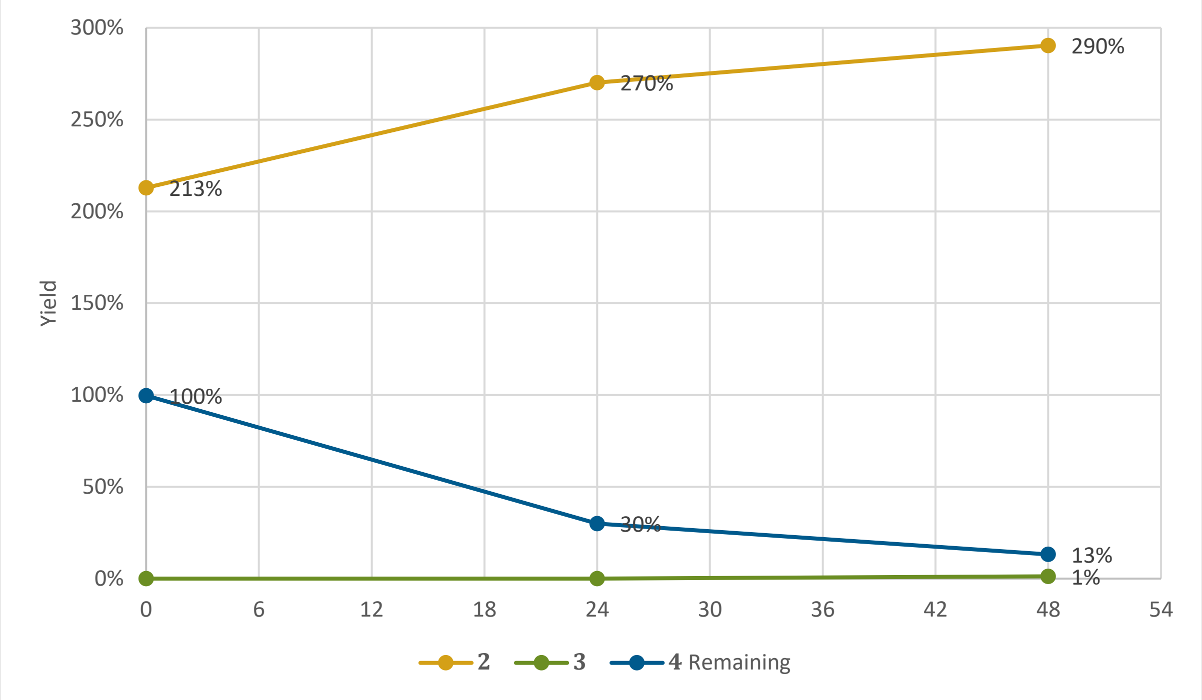

Figure S31. Imine (**2**) yield and remaining phosphite (**4**) using Cu(acac)$_2$ catalyst with additive **4** and **2** used as an additive in EtOAc for the oxidative homocoupling of amine (**1**) (**Scheme 2**).

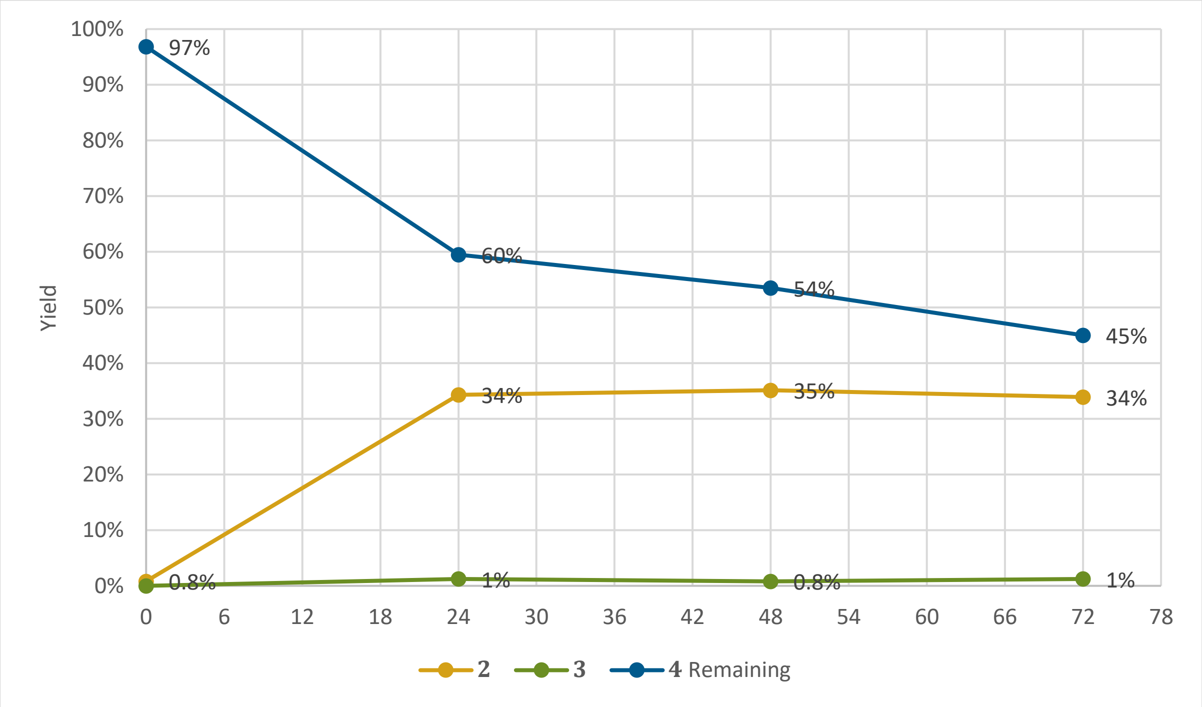

Figure S32. Product yields and remaining phosphite (**4**) using Cu(acac)$_2$ catalyst with additive **4** and preloaded phosphate (**7**) in EtOAc for the oxidative homocoupling of amine (**1**).

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