A Photo-enzymatic cascade to transform racemic alcohols into enantiomerically pure amines

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Experimental section

Materials

Unless stated otherwise, the used chemicals were bought from Sigma Aldrich, Alfa Aesar, Fluka and used as received. The ω-transaminases were prepared by Tanja Knaus and Francesco Mutti and applied as received.

Expression of ω-transaminases

E. coli BL21 DE3 strain was used for the expression of *At*ωTA (ωTA from *Aspergillus terreus*, in pET21a, C-term His6-tag), *Bm*ωTA (ωTA from *Bacillus megaterium* SC6394, pET28b, N-term His6-tag), *Cv*ωTA (ωTA from *Chromobacterium violaceum* DSM 30191, pET28b, N-term His6-tag), *Pf*ωTA (ωTA from *Pseudomonas fluorescens*, pET21a, no tag) and *Vf*ωTA (ωTA from *Vibrio fluvialis*, pET28b,
N-term His6-tag). 800 mL of LB medium supplemented with the appropriate antibiotic (100 μg/mL ampicillin for pET21a and 50 μg/mL kanamycin for pET28b) were inoculated with 15 mL of an overnight culture harboring the desired vector with genes for the expression of the ωTAs. Cells were grown at 37 °C until an OD_{600} of 0.6-0.8 was reached and expression of proteins was induced by the addition of IPTG (0.5 mM). Cells were grown overnight at 25 °C and harvested by centrifugation (4 °C, 4500 rpm and 15 min). The pellets were resuspended in phosphate buffer (100 mM, pH 7.0) containing 0.5 mM PLP and lyophilized.

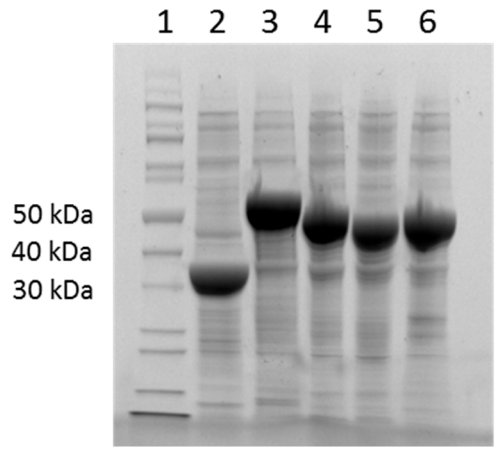


Figure S1: SDS-Page for the expression of the ωTAs. Lane 1: PageRuler™ Unstained Protein Ladder (ThermoFisher Scientific); lane 2: At-ωTA; lane 3: Bm-ωTA; lane 4: Cv-ωTA; lane 5: Pf-ωTA, lane 6: VfωTA

Measurements

Gas chromatography (GC)

The used systems are summarized in Table 1. The details of the analysis are summarized in the Analytics chapter.

Table S1: Used GC systems.

#	Machine	Column	Detector	Carrier gas
1	Shimadzu GC-2010 Plus	CP Wax 52CB (25 m × 0.25 mm × 1.2 μm)	FID	N_2
2	Shimadzu GC-2010 Plus	HYDRODEX β TBDAC (50 m × 0.25 mm × 0.25 μm)	FID	H_2
3	Shimadzu GC-2010	LIPODEX E (50 m × 0.25 mm × 0.25 μm)	FID	H_2
4	Shimadzu GC-2014	CP Sil 5 CB (50 m × 0.53 mm × 1.0 μm)	FID	N_2

5	Shimadzu GC-2010 Plus	Chirasil Dex CB (25 m × 0.32 mm × 0.25 μm	FID	H_2

Photocatalyst synthesis and characterization

Sodium anthraquinone-2-sulfonate (SAS)

SAS was bought from Sigma Aldrich (≥98% by HPLC) and used as received.

FT-IR spectrum

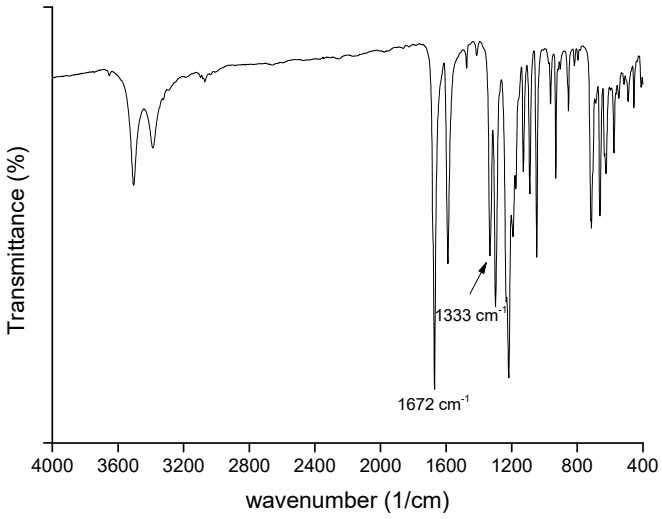


Figure S2: FT-IR spectrum of SAS. The characteristic stretching peaks of the ketone groups (1672 cm^{-1}) and the sulfonate group (1333 cm^{-1}) are visible.

Graphitic carbon nitride (g-C_3N_4)

Synthesis

10 g of urea (Riedel –de Haen; 99 %) was weighed into a ceramic crucible and covered with another one. The system was heated in a furnace (Carbolite CWF 1200 with a Eurotherm 2416 CG PID controller) according to the following program: from room temperature samples were heated up with 5 °C/min to 550 °C and kept at temperature for 4 h. Samples were cooled down with 10 °C/min to room temperature.

FT-IR spectrum

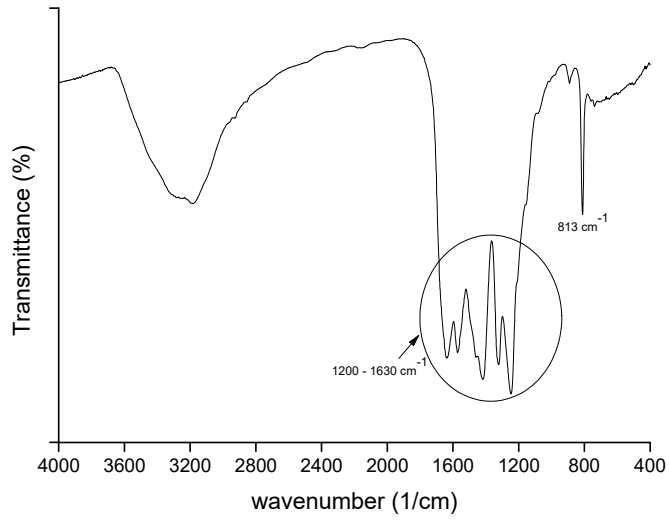


Figure S3: FT-IR spectrum of g-C_3N_4. The peak at 813 cm^{-1} is characteristic to the stretching mode of the s-triazine ring, while the peaks between 1200 and 1630 cm^{-1} are assigned to the stretching vibration modes of the C-N and C=N heterocycles [1].

XRD spectrum

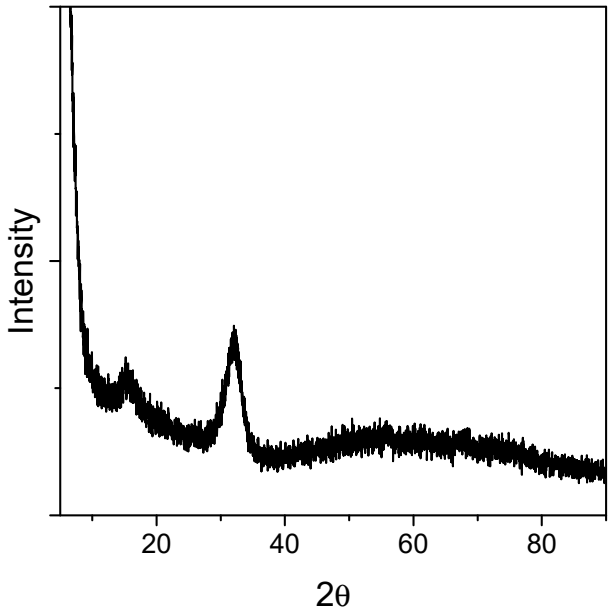


Figure S4: XRD spectrum of g-C_3N_4. The characteristic peak is visible at $2\Theta = 32$. Please note that there is a shift in the spectrum compared to the literature due to the used Co Kα radiation (1.789 Å) source [2] [1].

Graphitic carbon nitride doped with vanadium oxide (g-C_3N_4-VO)

Synthesis

10 g of urea (Riedel –de Haen; 99 %) was weighed into a ceramic crucible and covered with another one. The system was heated in a furnace (Carbolite CWF 1200 with a Eurotherm 2416 CG PID controller) according to the following program: from room temperature samples were heated up with 5 °C/min to 550 °C and kept at temperature for 4 h. Samples were cooled down with 10 °C/min to room temperature. Next, 0.1 g of the formed g-C_3N_4 was dispersed in 10 ml 50 % methanol-water mixture with 0.053 g (0.2 mmol) vanadyl(IV)acetylacetonate (Acros organics; >99 %). The system was stirred on a magnetic stirrer for 4 h. Eventually, the mixture was centrifuged and washed with 2*10 ml methanol. The sample was dried at 70 °C overnight.

FT-IR spectrum

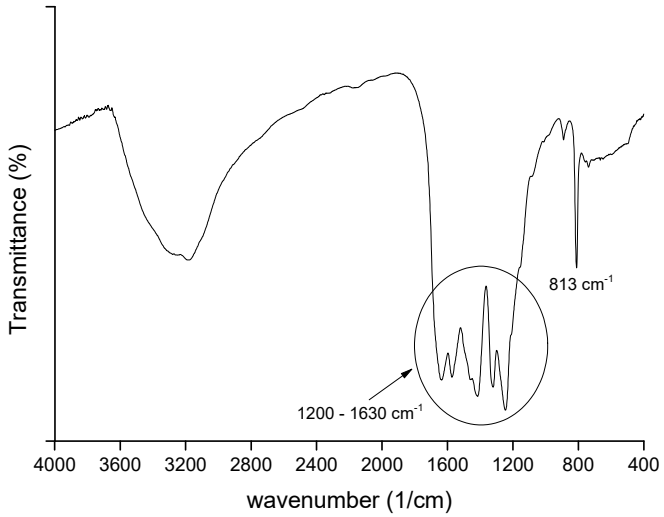


Figure S5: FT-IR spectrum of g-C_3N_4. The peaks at 813 cm^{-1} is characteristic to the stretching mode of the
s-triazine ring, while the peaks between 1200 and 1630 cm^{-1} are characteristic to the stretching vibration modes of the C-N and C=N heterocycles [1].

XRD spectrum

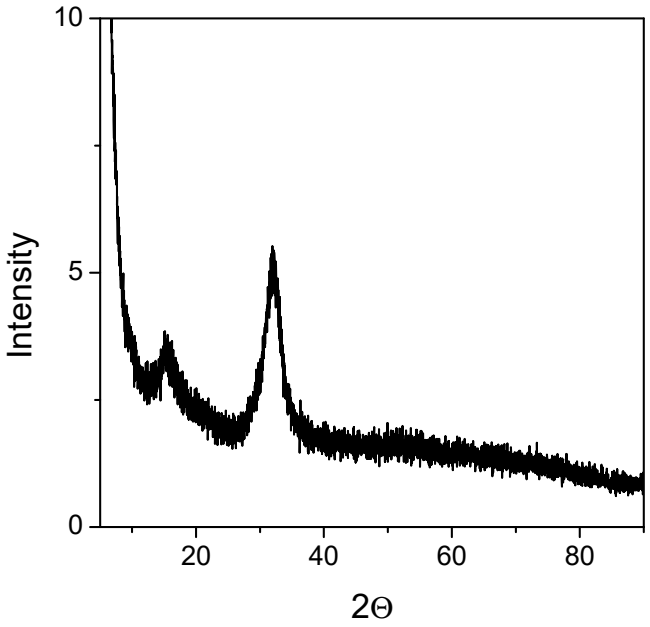


Figure S6: XRD spectrum of g-C_3N_4-VO. The characteristic peak is visible at 2Θ = 32. Please note that there is a shift in the spectrum compared to the literature due to the used Co Kα radiation (1.789 Å) source [3].

Control reactions

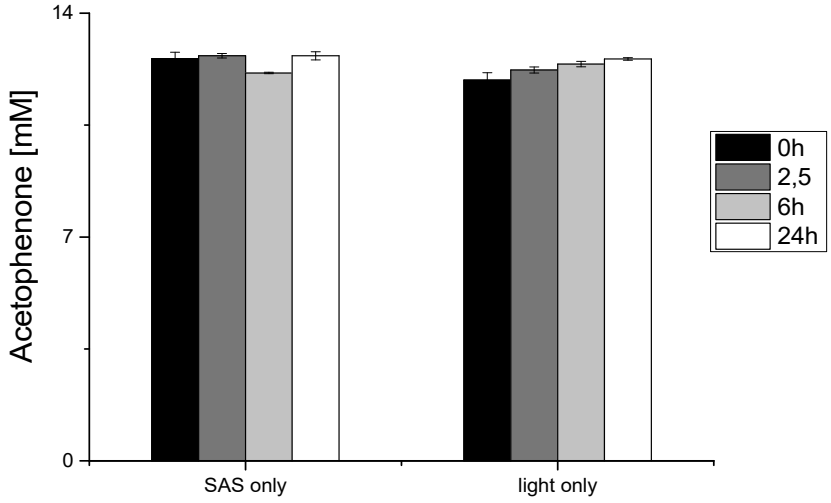


Figure S7: Effect of evaporation on the acetophenone concentration during the photo-oxidation of 1-phenylethanol. Reaction conditions: 1 ml MilliQ water with [Acetophenone] = 11 mM and [SAS] = 1.5 mM. Both reactions were incubated at 30 °C.

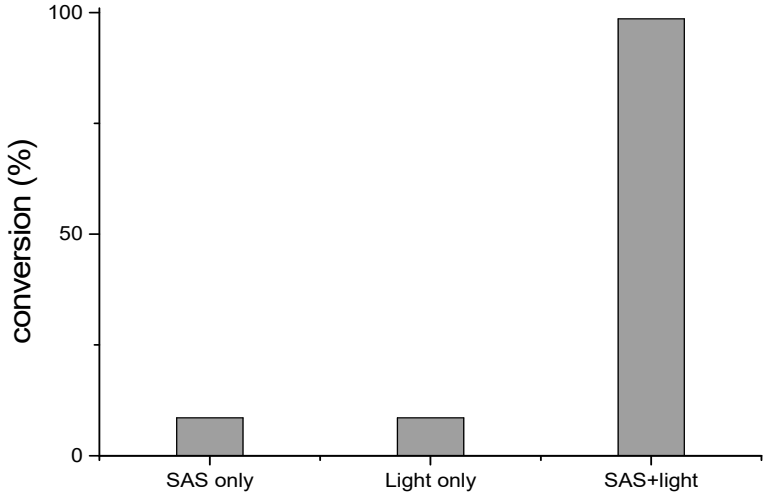


Figure S8: Control reaction of the photooxidation. Reaction conditions: 1 ml MilliQ water with [1-phenylethanol] = 15 mM, [SAS] = 1.5 mM. Reactions were incubated at 30 °C, irradiated with white light ($\lambda > 400$ nm) and stirred gently with a magnetic stirrer.

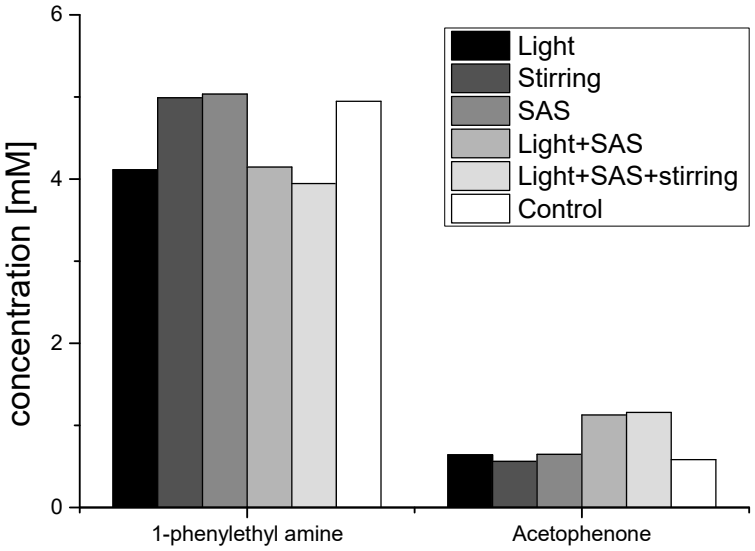


Figure S9: Effect of the circumstances of the photooxidation on the efficiency of the reductive amination. Reaction conditions: 1 ml pH 9 reaction mixture containing [NaPI] = 100 mM, [acetophenone] = 6 mM [SAS] = 0.75 mM, [IPRA] = 1 M, [PLP] = 1 mM, [crude cell extract overexpressed with *BM*ωTA enzyme] = 10 mg/ml. Samples were incubated at 30°C, irradiated with white light ($\lambda > 400$ nm) and stirred gently with a magnetic stirrer.

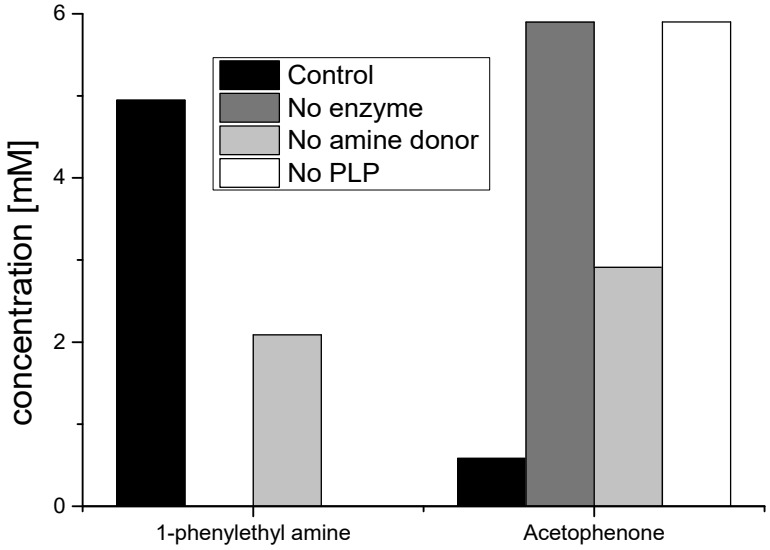


Figure S10: Control reaction of the reductive amination. Reaction conditions: 1 ml pH 9 reaction mixture containing [NaPI] = 100 mM, [acetophenone] = 6 mM, [SAS] = 0.75 mM, [IPRA] = 1 M, [PLP] = 1 mM, [crude cell extract overexpressed with *BM*ωTA enzyme] = 10 mg/ml. Samples were incubated at 30°C and shaken on a thermal shaker.

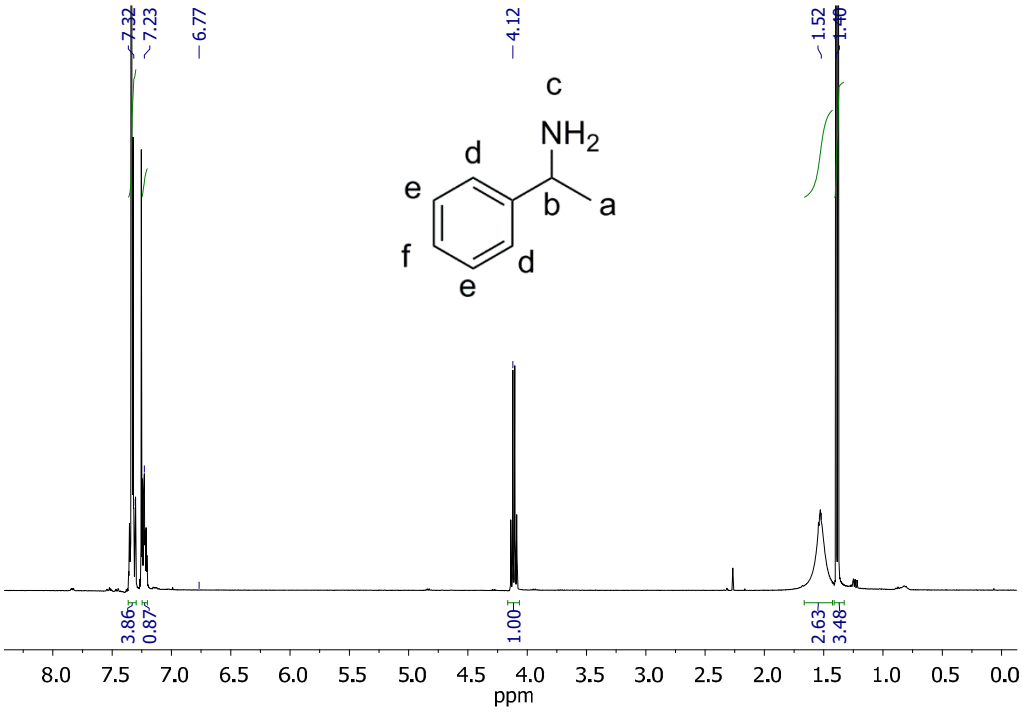


Figure S11: [1]H NMR spectrum of 1-phenylethyl amine. Protons: a = 1.16 ppm; b = 4.12 ppm; d & e = 7.32 ppm,
f = 7.23 ppm. Deuterated Ch_2Cl_2 was used as a solvent.

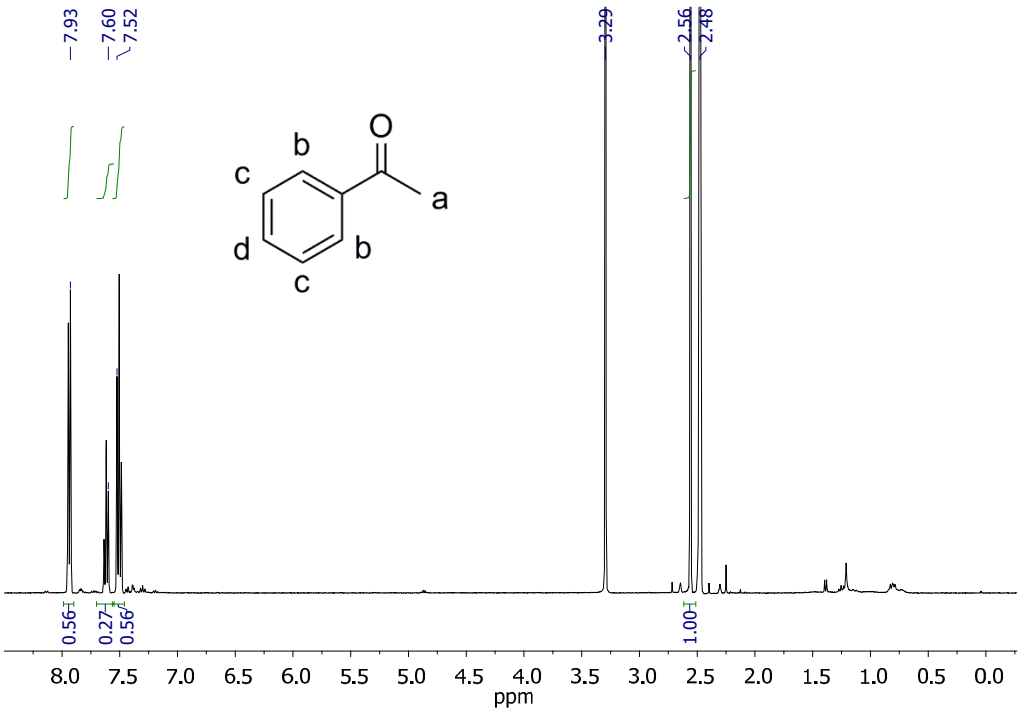


Figure S12: [1]H NMR spectrum of oxidation of 1-phenylethylamine. Protons: a = 2.48 ppm; b = 7.93 ppm; c = 7.52 ppm; d = 7.60 ppm. Deuterated DMSO was used as a solvent. Reaction conditions: 1 ml MilliQ water with [1-Phenylethyl amine] = 15 mM, [SAS] = 1.5 mM. The reaction was incubated at 30 °C, irradiated with white light ($\lambda > 400$ nm) and stirred gently with a magnetic stirrer.

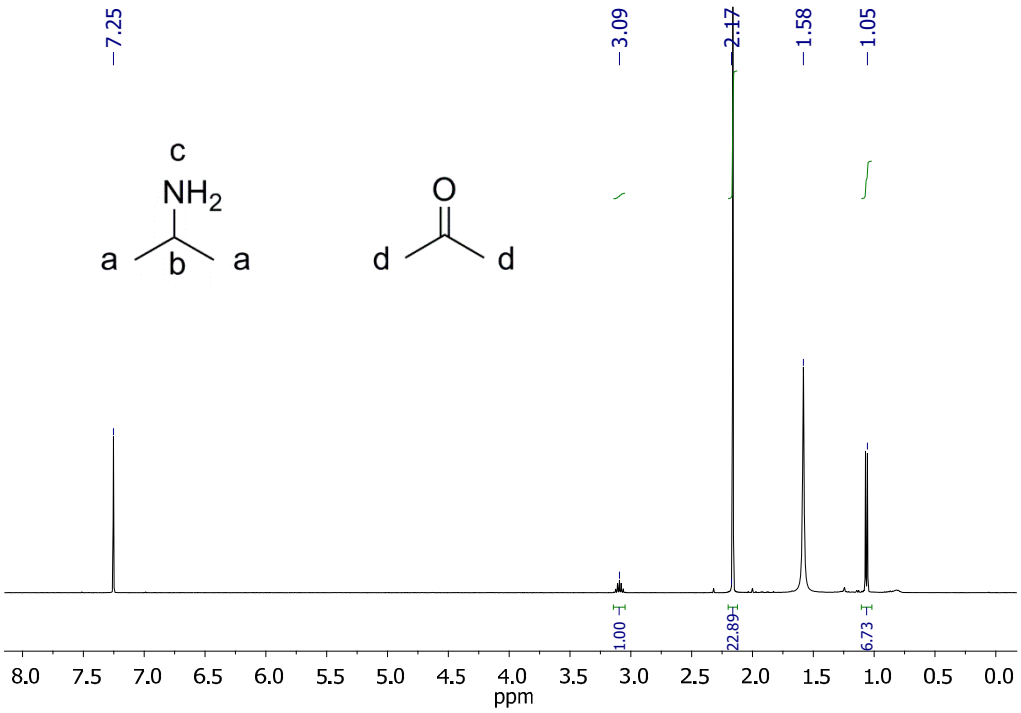


Figure S13: ^{1}H NMR spectrum of oxidation of isopropylamine. Protons: a = 1.05 ppm; b = 3.09 ppm; c = 1.58 ppm; d = 2.17 ppm. Reaction conditions: 1 ml reaction mixture containing [isopropylamine] = 1 M,
[NaPI] = 100 mM and [SAS] = 1.5 mM. The reaction was incubated at 30 °C, irradiated with white light ($\lambda > 400$ nm) and stirred gently with a magnetic stirrer.

Optimization of the individual reaction steps

Photooxidation

Sodium anthraquinone-2-sulfonate (SAS)

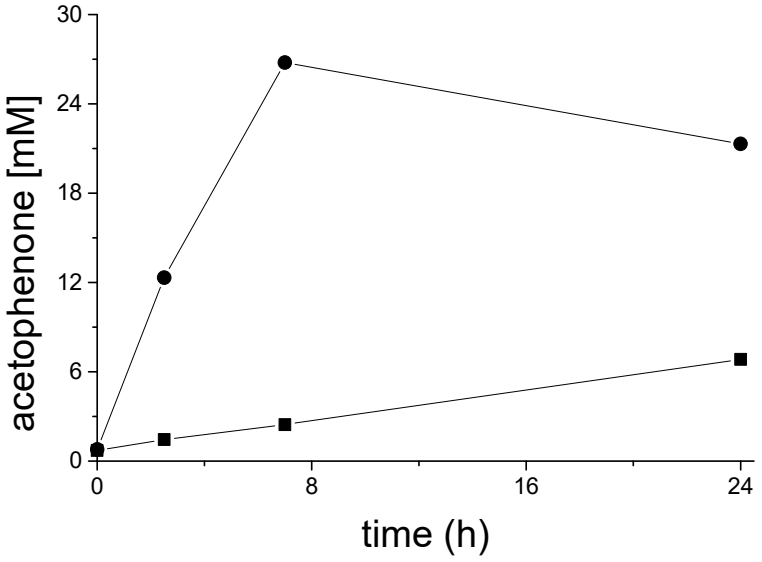


Figure S14: Effect of light intensity on the photocatalytic activity of SAS. Commercial white light bulb 205W (■) and white LED (●) were compared. Reaction conditions: 1 ml MilliQ water with [1-phenylethanol] = 25 mM and [SAS] = 1.5 mM. Reactions were run at 30 °C under atmospheric conditions and stirred with a magnetic stirrer.

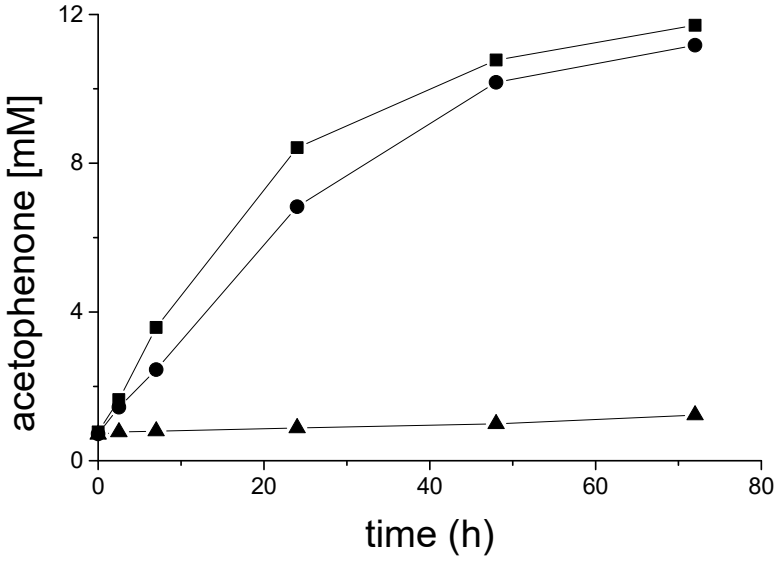


Figure S5: Effect of light composition on the photocatalytic activity of SAS. Blue LED (■), white LED (●) and red LED (▲) were investigated. Reaction conditions: 1 ml MilliQ water with [1-phenylethanol] = 25 mM and

[SAS] = 1.5 mM. Reactions were run at 30 °C under atmospheric conditions and stirred with a magnetic stirrer.

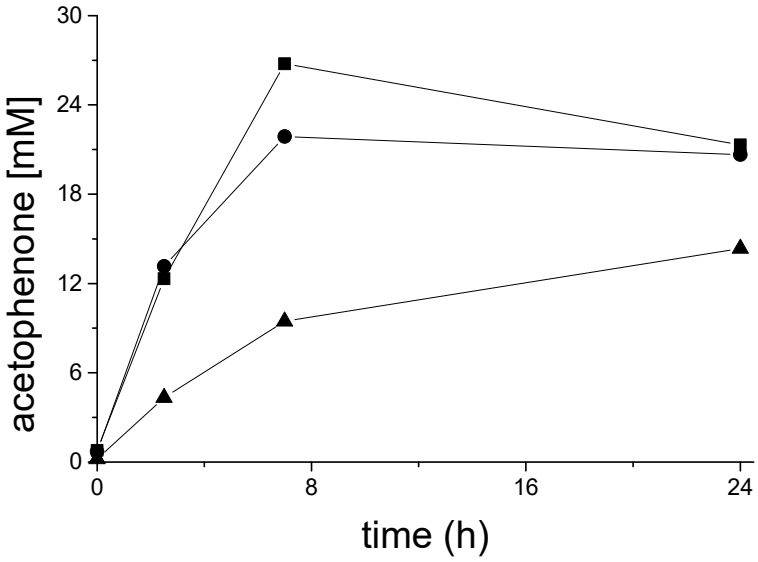


Figure S16: Effect of the reaction atmosphere on the photocatalytic activity of SAS. Air (■), oxygen (●) and nitrogen (▲) atmospheres were investigated. Reaction conditions: 1 ml MilliQ water with [1-phenylethanol] = 25 mM and [SAS] = 1.5 mM. Reactions were run at 30 °C and stirred with a magnetic stirrer.

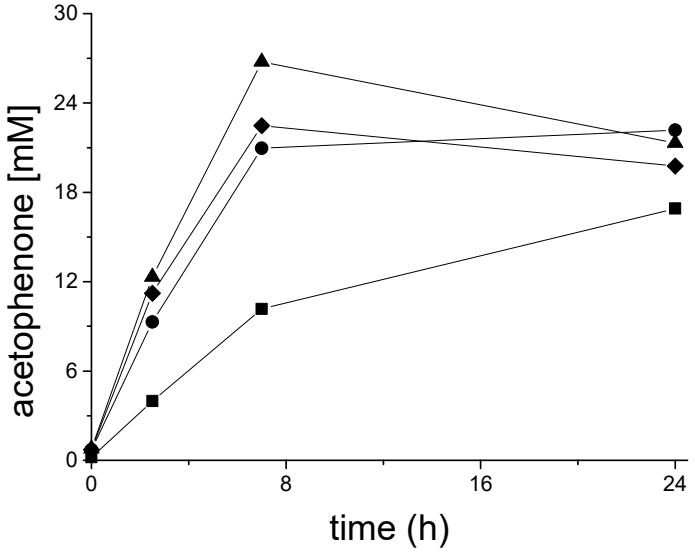


Figure S17: Effect of the amount of photocatalyst on the photocatalytic activity of SAS. 0.38 mM (■), 0.75 mM (●), 1.5 mM (▲) and 2.25 mM (◆) concentrations were investigated. Reaction conditions: 1 ml MilliQ water with [1-phenylethanol] = 25 mM. Reactions were run at 30 °C and stirred with a magnetic stirrer.

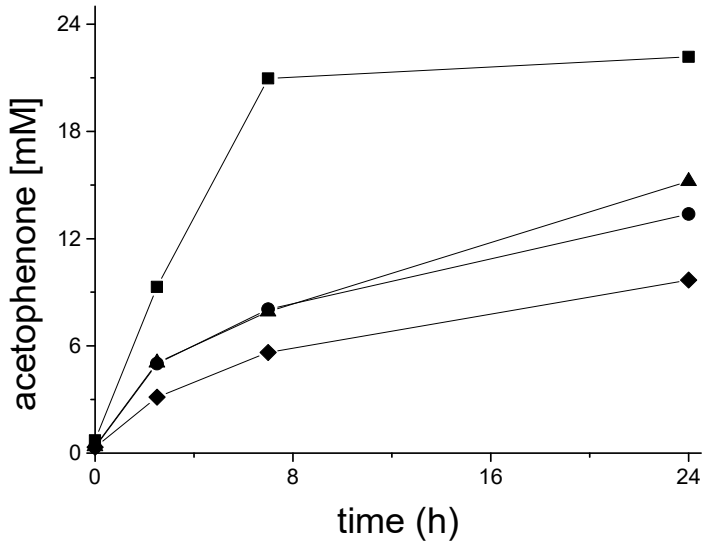


Figure S18: Effect of pH on the photocatalytic activity of SAS. pH 8.5 (●), pH 9.2 (▲), pH 10.2 (◆) and MilliQ water (■) were examined. Reaction conditions: MilliQ: 1 ml MilliQ water with [1-phenylethanol] = 25 mM and [SAS] = 1.5 mM. Varied pH: 1 ml reaction mixture containing [NaPI] = 100 mM, [isopropylamine] = 1 M, [1-phenylethanol] = 25 mM and [SAS] = 0.75 mM. Reactions were run at 30 °C and stirred with a magnetic stirrer.

Graphitic carbon nitride

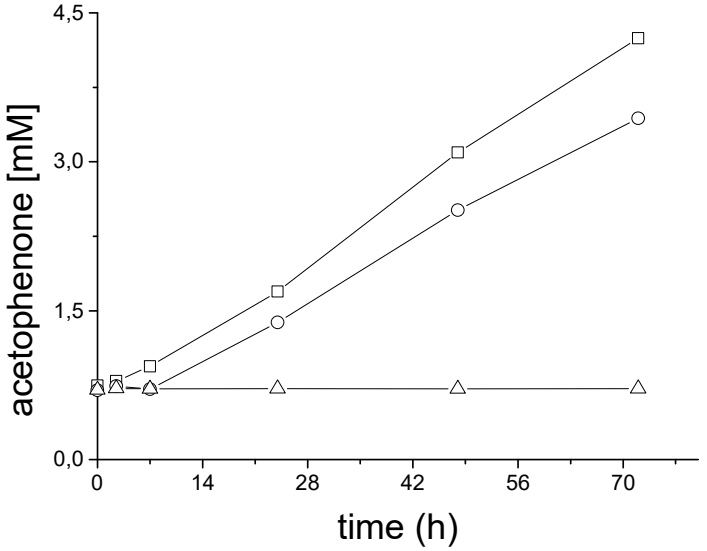


Figure S19: Effect of light composition on the photocatalytic activity of g-C_3N_4. Blue LED (□), white LED (○) and red LED (△) were investigated. Reaction conditions: 1 ml MilliQ water with [1-phenylethanol] = 25 mM and [g-C_3N_4] = 10 mg/ml. Reactions were run at 30 °C and stirred with a magnetic stirrer.

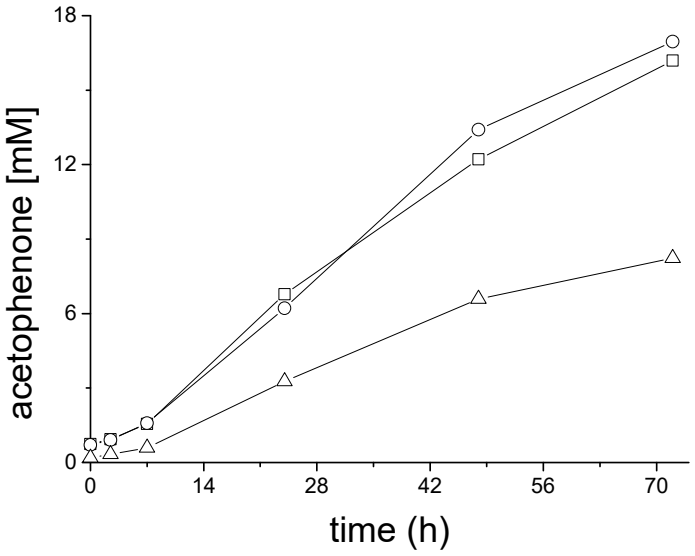


Figure S20: Effect of the reaction atmosphere on the photocatalytic activity of g-C_3N_4. Air (□), oxygen (○) and nitrogen (△) were investigated. Reaction conditions: 1 ml MilliQ water with [1-phenylethanol] = 25 mM and [g-C_3N_4] = 10 mg/ml. Reactions were run at 30 °C and stirred with a magnetic stirrer.

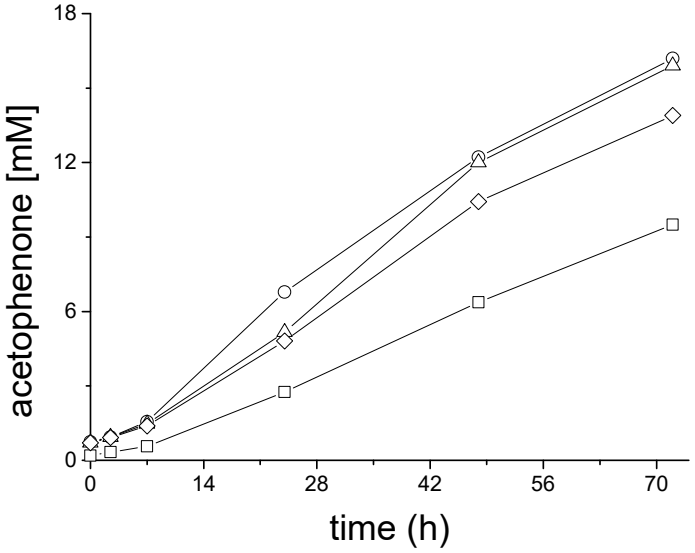


Figure S21: Effect of the photocatalyst amount on the photocatalytic activity of g-C_3N_4. 5 mg/ml (□), 10 mg/ml (○), 15 mg/ml (△) and 30 mg/ml (◇) concentrations were investigated. Reaction conditions: 1 ml MilliQ water with [1-phenylethanol] = 25 mM. Reactions were run at 30 °C under and stirred with a magnetic stirrer.

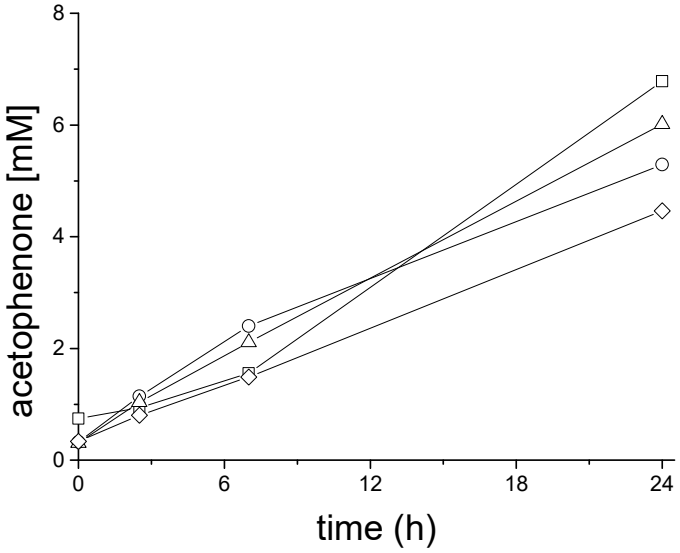


Figure S22: Effect of the pH on the photocatalytic activity of g-C_3N_4. pH 8.5 (○), pH 9.2 (△) pH 10.2 mM (◇) and MilliQ water (□). were examined. Reaction conditions: MilliQ: 1 ml MilliQ water with [1-phenylethanol] = 25 mM and [g-C_3N_4] = 10 mg/ml. Varied pH: 1 ml reaction mixture containing [NaPI] = 100 mM, [isopropylamine] = 1 M, [1-phenylethanol] = 25 mM and [g-C_3N_4] = 10 mg/ml. Reactions were run at 30 °C and stirred with a magnetic stirrer.

Reductive amination

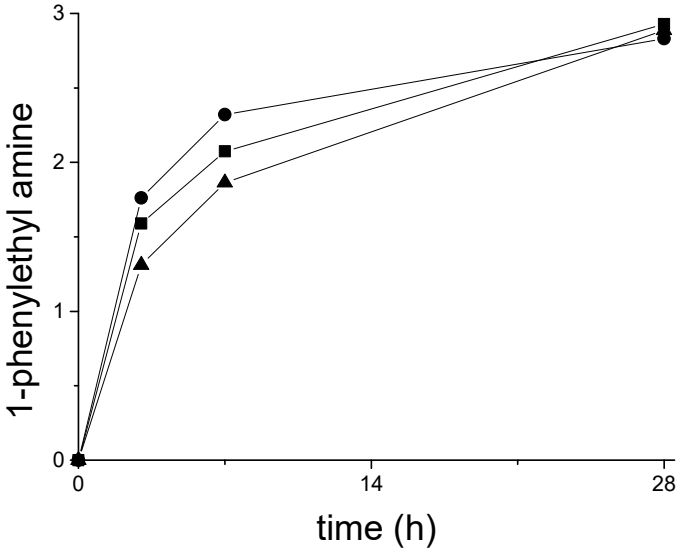


Figure S23: Effect of the enzyme concentration on the yield of the reductive amination: 5 mg/ml (●) 10 mg/ml (■) 15 mg/ml (▲) *AT*ωTA concentrations were examined. Reaction conditions: 1 ml pH 9.1 reaction mixture containing [NaPI] = 100 mM [isopropylamine] = 1 M, [acetophenone] = 4.5 mM and [PLP] = 1 mM. Samples were incubated at 30 °C and shaken on a shaking plate.

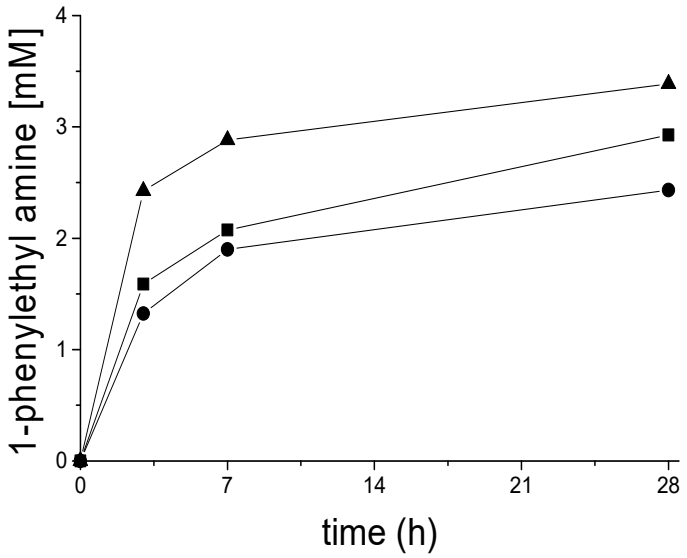


Figure S24: Effect of the amine donor concentration on the conversion of the reductive amination. 0.5 M (●)
1 M (■) and 2 M (▲) isoproylamine concentrations were examined. Reaction conditions: 1 ml pH 9 reaction mixture containing [NaPI] = 100 mM, [acetophenone] = 4.5 mM, [*AT*ωTA] = 10 mg/ml and [PLP] = 1 mM. Samples were incubated at 30 °C and shaken on a shaking plate.

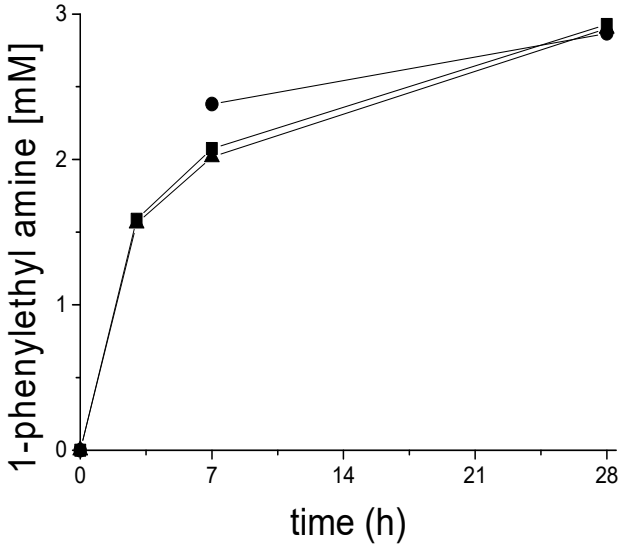


Figure S25: Effect of the cofactor concentration on the yield of the reductive amination. 0.5 mM (●) 1 mM (■) and 2 mM (▲) PLP concentrations were examined. Reaction conditions: 1 ml pH 9 reaction mixture containing [NaPI] = 100 mM, [isopropylamine] = 1 M, [acetophenone] = 4.5 mM and [*AT*ωTA] = 10 mg/ml. Samples were incubated at 30 °C and shaken on a shaking plate.

pH dependency of the used ω-transaminases

From aspergillus terreus (*AT*ωTA)

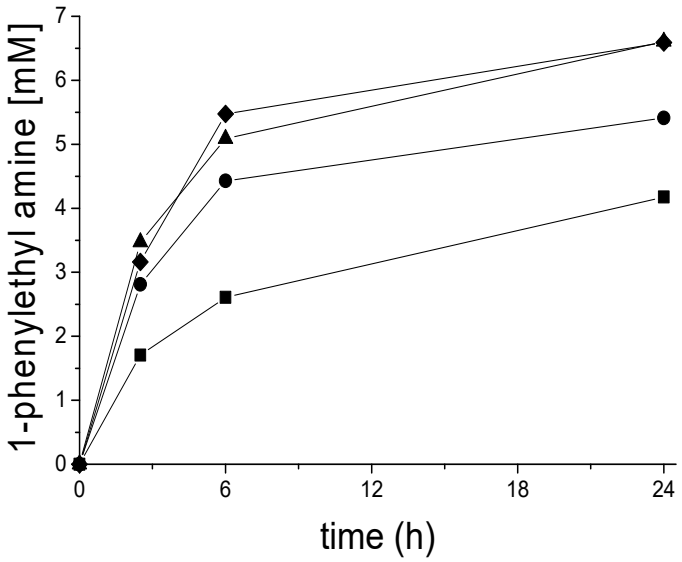


Figure S26: pH dependency of *AT*ω-TA. pH 8 (■), pH 8.5 (●) pH 9.2 (▲) and pH 10.2 (◆) were examined.
Reaction conditions: 1 ml reaction mixture containing [NaPI] = 100 mM, [acetophenone] = 4.5 mM, [isopropylamine] = 1M, [*AT*ωTA] = 10 mg/ml and [PLP] = 1 mM. Samples were incubated at 30 °C and shaken on a shaking plate.

From Bacillus megaterium (*BM*ωTA)

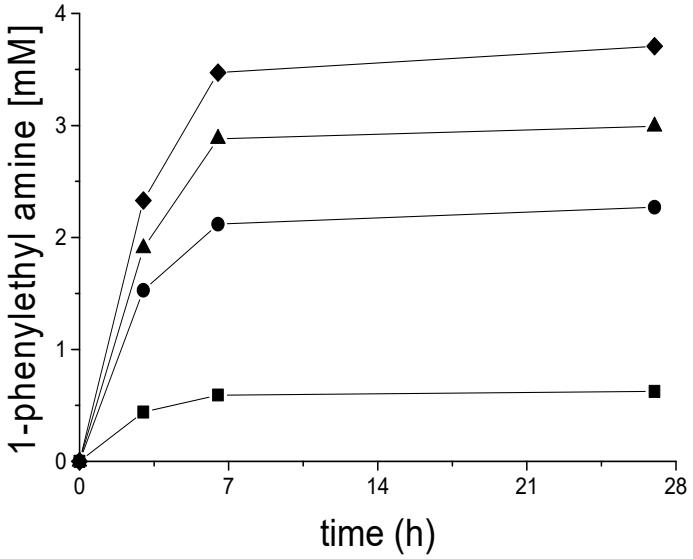


Figure S27: pH dependency of *BM*ωTA. pH 7 (■), pH 8 (●) pH 8.5 (▲) and pH 9.1 (◆) were examined.
Reaction conditions: 1 ml reaction mixture containing [NaPI] = 100 mM, [acetophenone] = 4.5 mM,

[isopropylamine] = 1M, [*BM*ωTA] = 10 mg/ml and [PLP] = 1 mM. Samples were incubated at 30 °C and shaken on a shaking plate.

From Vibrio fluvialis (*VF*ωTA)

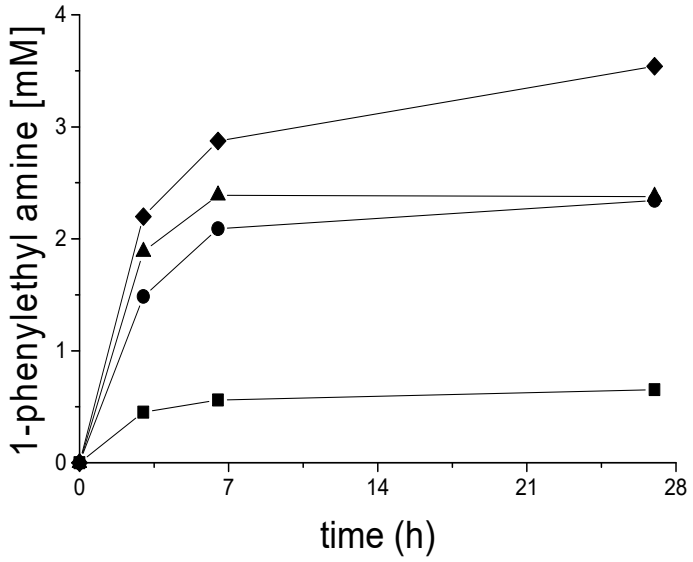


Figure S28: pH dependency of *VF*ωTA. pH 8 (■), pH 8.5 (●) pH 9.2 (▲) and pH 10.2 (◆) were examined.
Reaction conditions: 1 ml reaction mixture containing [NaPI] = 100 mM, [acetophenone] = 4.5 mM, [isopropylamine] = 1M, [*VF*ωTA] = 10 mg/ml and [PLP] = 1 mM. Samples were incubated at 30 °C and shaken on a shaking plate.

From Pseudomonas fluorescens (*PF*ωTA)

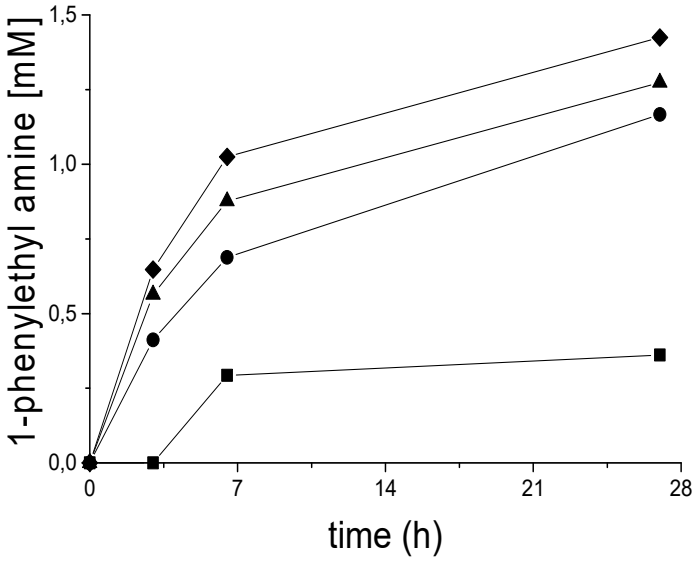


Figure S29: pH dependency of *PF*ωTA. pH 7 (■), pH 8 (●) pH 8.5 (▲) and pH 9 (◆) were examined. Reaction conditions: 1 ml reaction mixture containing [NaPI] = 100 mM, [acetophenone] = 4.5 mM, [isopropylamine] = 1 M, [*PF*ωTA] = 10 mg/ml and [PLP] = 1 mM. Samples were incubated at 30 °C and shaken on a shaking plate.

From Chromobacterium violaceum (*CV*ωTA)

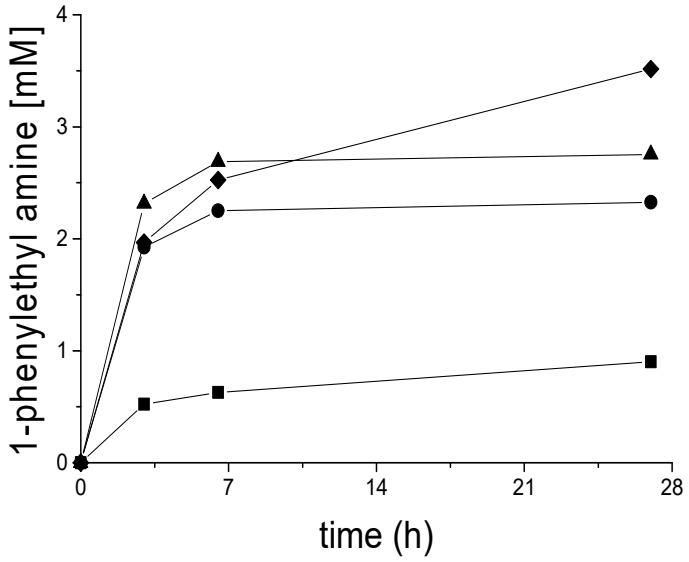
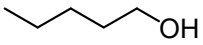
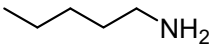


Figure S30: pH dependency of *CV*ωTA. pH 7 (■), pH 8 (●) pH 8.5 (▲) and pH 9 (◆) were examined. Reaction conditions: 1 ml reaction mixture containing [NaPI] = 100 mM, [acetophenone] = 4.5 mM, [isopropylamine] = 1M, [*CV*ωTA] = 10 mg/ml and [PLP] = 1 mM. Samples were incubated at 30 °C and shaken on a shaking plate

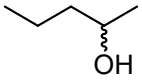
Analytics



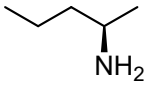
1a



1b



2a



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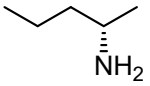

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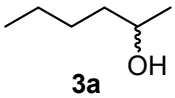
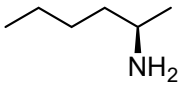


3a



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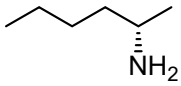

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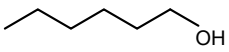

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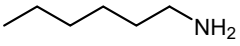
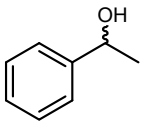


4b



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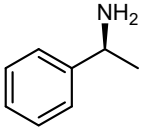
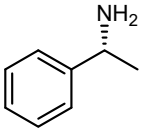
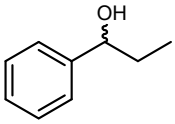


(***S***)-**5b**



(***R***)-**5b**



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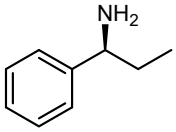

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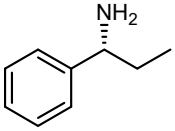
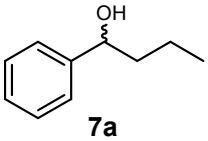


(***R***)-**6b**



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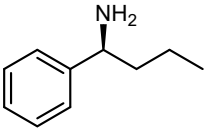

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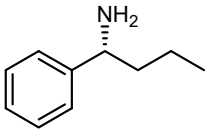

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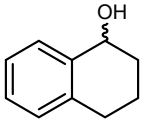

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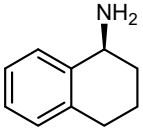

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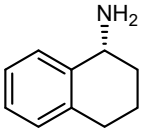
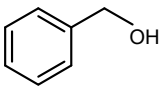
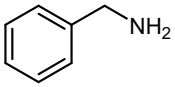


(***R***)-**8b**



9a



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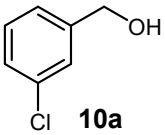

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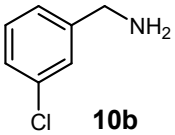

10b

Conversion determination of the alcohol oxidation

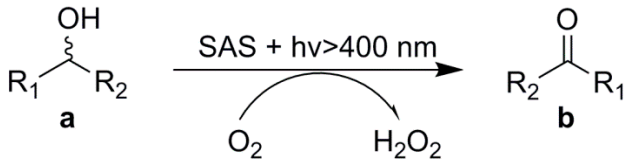

Table S2: Details of GC analysis of the alcohol oxidation.

Substrate	Used GC system	Retention time [min]	Temperature profile
1a	System 1	n-pentanol 6.39 pentanal 3.22 dodecane 5.62	100 °C hold 4 min, 25 °C /min to 135 °C hold 1.5 min, 30 °C /min to 245 °C hold 2 min.
2a	System 1	2-pentanol 4.65 2-pentanone 3.19 dodecane 6.20	100 °C hold 5 min, 25 °C /min to 110 °C hold 1.5 min, 30 °C /min to 245 °C hold 2 min.
3a	System 1	n-hexanol 6.03 hexanal 3.11 dodecane 4.03	110 °C hold 2.5 min, 20 °C /min to 120 °C hold 1.5 min, 30 °C /min to 150 °C hold 1 min, 30 °C /min to 245 °C hold 2 min.

4a	System 1	2-hexanol 5.16 2-hexanone 3.72 dodecane 4.88	110 °C hold 3 min, 15 °C /min to 120 °C hold 2 min, 30 °C /min to 240 °C hold 2 min.
5a	System 1	1-phenylethanol 8.98 acetophenone 7.49 1-octanol 6.00	130 °C hold 3 min, 30 °C /min to 200 °C hold 3.9 min, 30 °C /min to 240 °C hold 1 min.
6a	System 1	1-phenylpropanol 10.12 propiophenone 8.91 dodecane 3.55	150 °C hold 3 min, 25 °C /min to 160 °C hold 1 min, 25 °C /min to 235 °C hold 3 min.
7a	System 1	1-phenylbutanol 11.16 butyrophenone 9.63 dodecane 3.55	150 °C hold 3 min, 25 °C /min to 160 °C hold 1 min, 25 °C /min to 235 °C hold 4 min, 30 °C /min to 245 °C hold 2 min.
8a	System 1	1,2,3,4-tetrahydro-1-naphthol 16.36 α-Tetralone 15.06 Dodecane 3.55	150 °C hold 3 min, 25 °C /min to 160 °C hold 1 min, 15 °C /min to 240 °C hold 8 min, 30 °C /min to 250°C hold 2 min.
9a	System 1	Benzyl alcohol 8.37 Benzaldehyde 5.62 1-octanol 5.24	150 °C hold 2.2 min, 25 °C /min to 210 °C hold 1.2 min, 25 °C /min to 230 °C hold 2.3 min, 25 °C /min to 240 °C hold 0.8 min.
10a	System 1	3-chlorobenzyl alcohol 14.53 3-chlorobenzaldehyde 8.97 dodecane 2.78	150 °C hold 3 min, 25 °C /min to 160 °C hold 1 min, 15 °C /min to 225 °C hold 1 min, 25 °C /min to 240 °C hold 5 min, 25 °C /min to 245 °C hold 1 min.

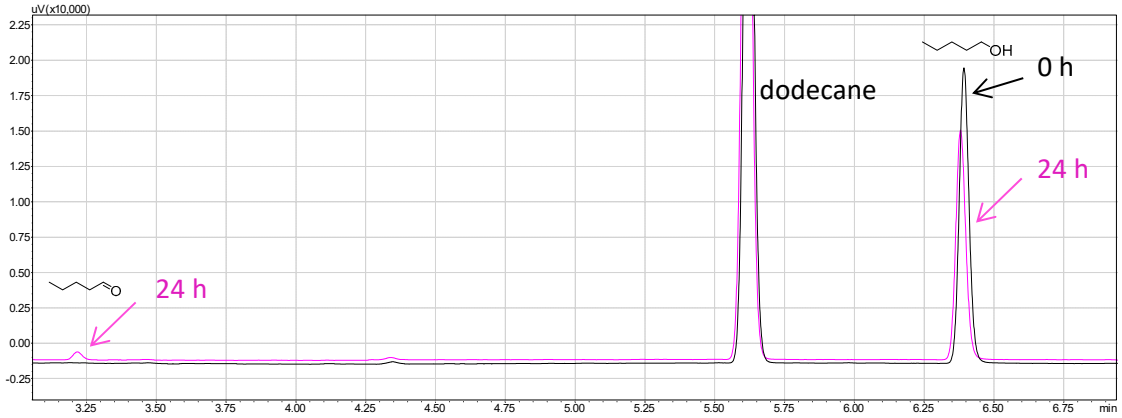

Figure S31: Representative GC chromatogram of SAS catalyzed photooxidation of 1-pentanol. Samples were diluted two times with ethyl acetate.

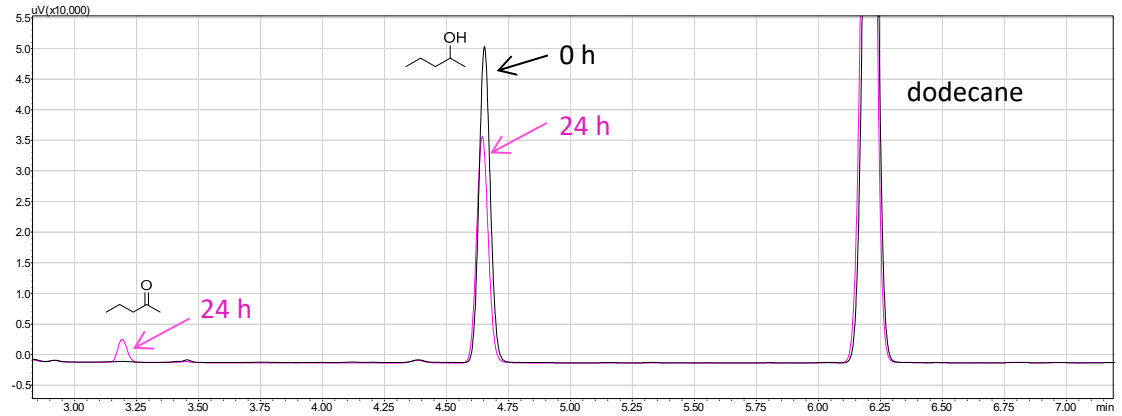

Figure S32: Representative GC chromatogram of SAS catalyzed photooxidation of 2-pentanol. Samples were diluted two times with ethyl acetate.

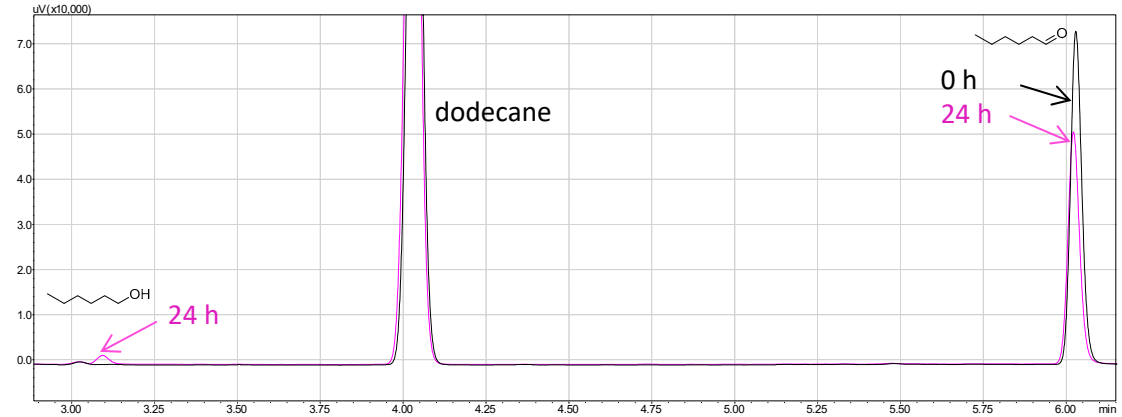

Figure S33: Representative GC chromatogram of SAS catalyzed photooxidation of 1-hexanol. Samples were diluted two times with ethyl acetate.

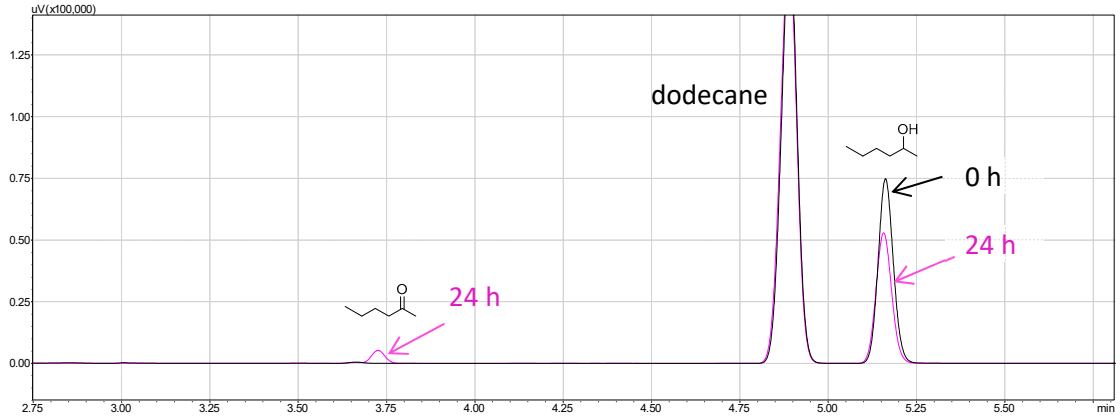

Figure S34: Representative GC chromatogram of SAS catalyzed photooxidation of 2-hexanol. Samples were diluted two times with ethyl acetate.

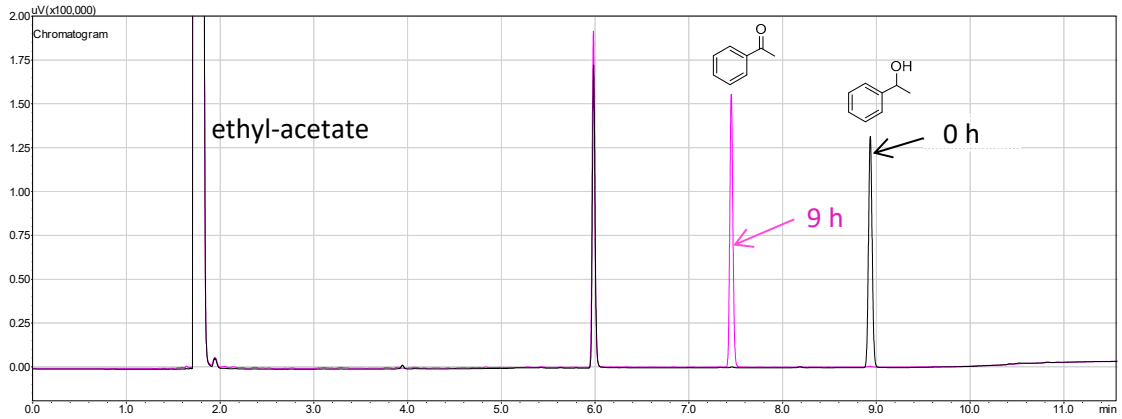

Figure S35: Representative GC chromatogram of SAS catalyzed photooxidation of 1-phenylethanol. Samples were diluted two times with ethyl acetate.

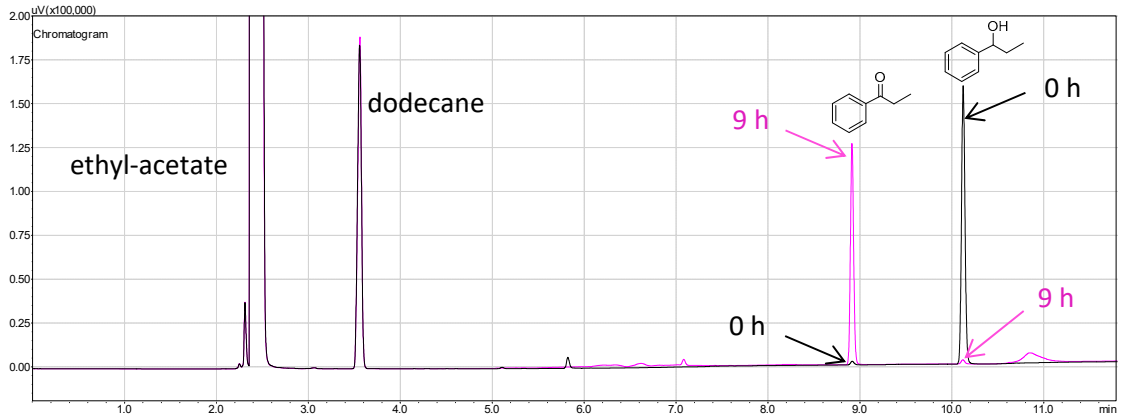

Figure S36: Representative GC chromatogram of SAS catalyzed photooxidation of 1-phenylpropanol. Samples were diluted two times with ethyl acetate.

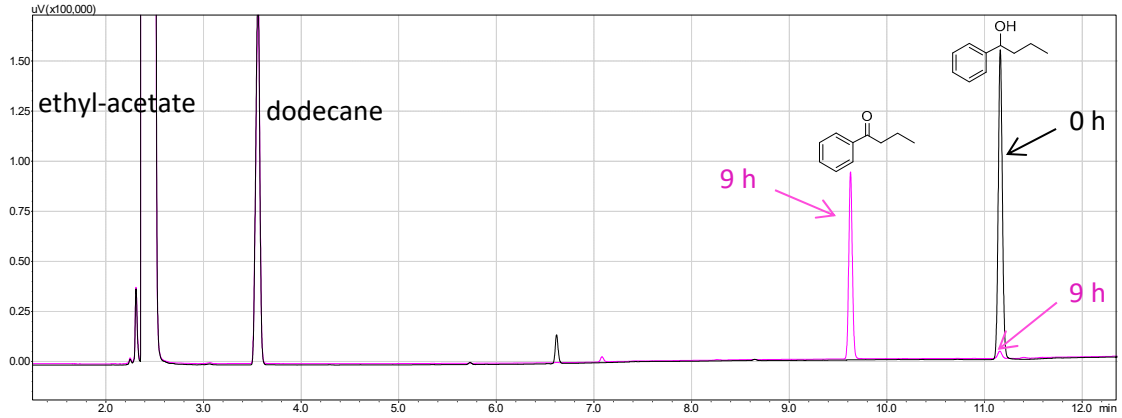

Figure S37: Representative GC chromatogram of SAS catalyzed photooxidation of 1-phenylbutanol. Samples were diluted two times with ethyl acetate.

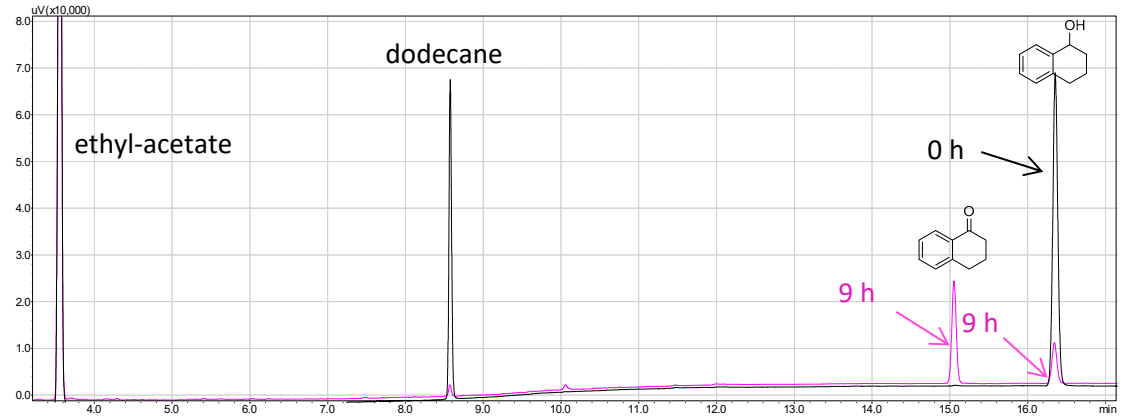

Figure S38: Representative GC chromatogram of SAS catalyzed photooxidation of 1,2,3,4-tetrahydro-1-naphtol. Samples were diluted two times with ethyl acetate.

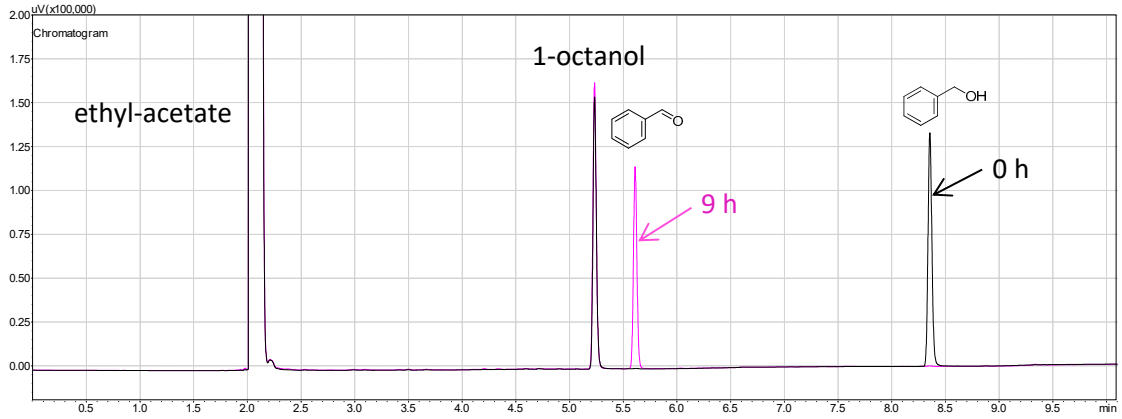

Figure S39: Representative GC chromatogram of SAS catalyzed photooxidation of benzyl alcohol. Samples were diluted two times with ethyl acetate.

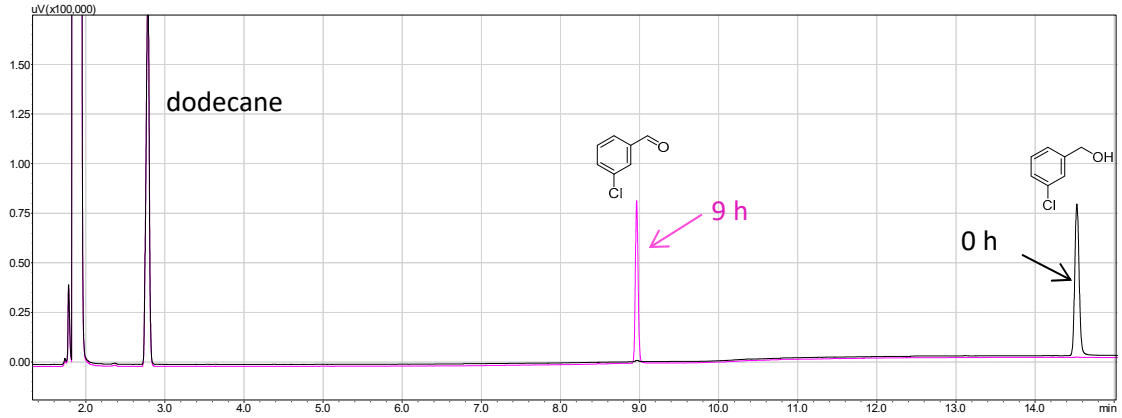

Figure S40: Representative GC chromatogram of SAS catalyzed photooxidation of 3-chlorobenzyl alcohol. Samples were diluted two times with ethyl acetate.

Conversion and enantiomeric access determination of the reductive amination

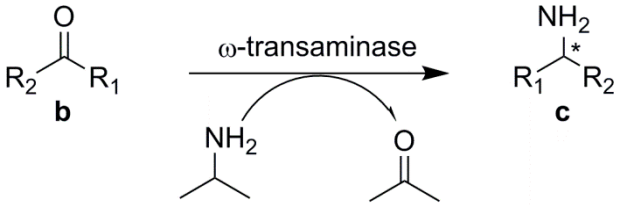

Table S3: Details of GC analysis of the reductive amination.

Substrate	Used GC system	Retention time [min]	Temperature profile
1b	System 2	n-pentylamine 13.71 dodecane 7.85	110 °C hold 3.5 min, 20 °C /min to 115 °C hold 2 min, 20 °C /min to 140 °C hold 2 min, 20 °C /min to 215 °C hold 1 min, 25 °C /min to 235 °C hold 1 min

2b	System 3	2-pentanone 4.00 *(S)*- 2-aminopentane 10.77 *(R)*- 2-aminopentane 10.93 dodecane 8.86	80 °C hold 5 min, 25 °C /min to 150 °C hold 1.5 min, 25 °C /min to 175 °C hold 1 min, 25 °C /min to 215 °C hold 1 min.
3b	System 4	hexanal 8.91 1-aminohexane 7.33 dodecane 6.40	90 °C hold 3 min, 30 °C /min to 105 °C hold 1 min, 30 °C /min to 140 °C hold 2 min, 30 °C /min to 150 °C hold 2 min, 30 °C /min to 265 °C hold 2 min, 30 °C /min to 325 °C hold 2 min.
4b	System 5	2-hexanone 3.20 *(S)*- 2-aminohexane 9.20 dodecane 8.54	90 °C hold 3 min, 20 °C /min to 100 °C hold 2 min, 20 °C /min to 150 °C hold 2 min, 25 °C /min to 225 °C hold 2 min.
5b	System 2	acetophenone 6.76 *(R)*- 1-phenylethyl amine 16.14 *(S)*- 1-phenylethyl amine 16.29 dodecane 5.42	130 °C hold 3 min, 10 °C /min to 140 °C hold 4.5 min, 15 °C /min to 210 °C hold 5 min, 25 °C /min to 235 °C hold 2 min.
6b	System 5	propiophenone 4.82 *(S)*- 1-phenylpropyl amine 9.50 *(R)*- 1-phenylpropyl amine 9.62 dodecane 4.10	130 °C hold 3 min, 15 °C /min to 140 °C hold 2 min, 20 °C /min to 190 °C hold 2 min, 25 °C /min to 225 °C hold 3 min.
7b	System 5	butyrophenone 9.63 *(S)*- 1-phenylbutyl amine 9.50 *(R)*- 1-phenylbutyl amine 9.62 dodecane 3.55	130 °C hold 3 min, 25 °C /min to 140 °C hold 1 min, 15 °C /min to 155 °C hold 2 min, 25 °C /min to 200 °C hold 4.5 min, 25 °C /min to 215 °C hold 1 min.
8b	System 5	α-Tetralone 8.17	120 °C hold 3 min, 20 °C /min to 150 °C hold 1 min, 20 °C /min to

		(S)- 1,2,3,4-Tetrahydro-1-naphthylamine 12.29 *(R)*- 1,2,3,4-Tetrahydro-1-naphthylamine 12.49 Dodecane 4.75	180 °C hold 2 min, 20 °C /min to 220 °C hold 1.75 min 25 °C /min to 225 °C hold 3 min.
9b	System 4	Benzaldehyde 1.91 Benzyl amine 7.99 dodecane 4.42	120 °C hold 5 min, 20 °C /min to 170 °C hold 2 min, 20 °C /min to 200 °C hold 1 min, 30 °C /min to 305 °C hold 1 min.
10b	System 4	3-chlorobenzaldehyde 4.56 3-chlorobenzyl amine 11.00 dodecane 5.49	100 °C hold 3 min, 30 °C /min to 130 °C hold 3 min, 30 °C /min to 155 °C hold 1 min, 30 °C /min to 215 °C hold 1 min, 30 °C /min to 270 °C hold 1 min, 30 °C /min to 325 °C hold 2 min,

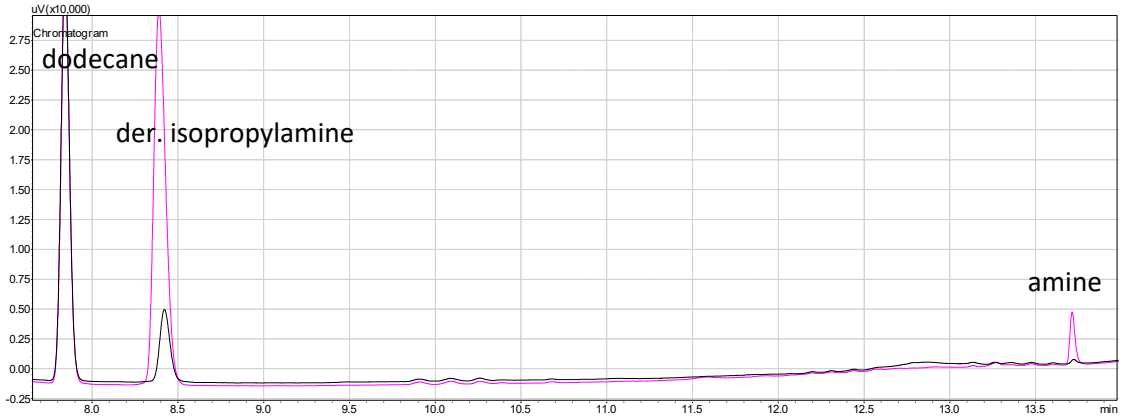

Figure S41: Representative GC chromatogram of derivatized n-pentylamine

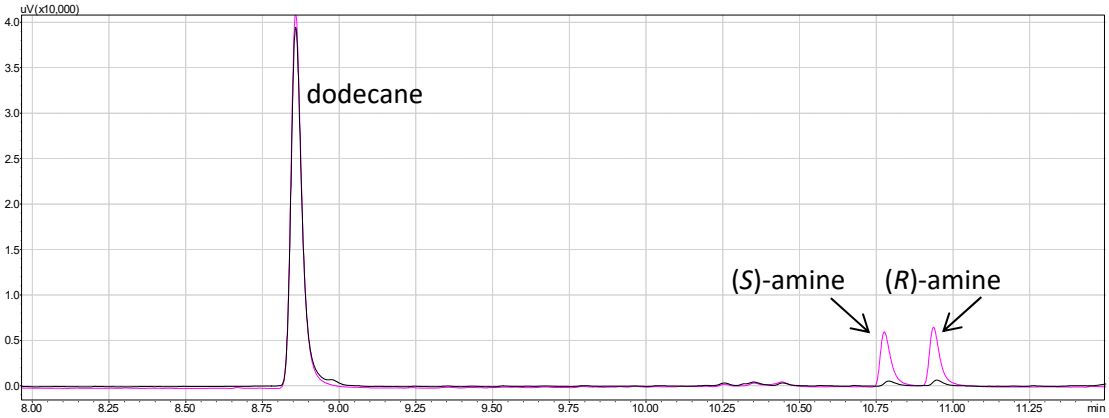

Figure S42: Representative GC chromatogram of derivatized 2-aminopentane.

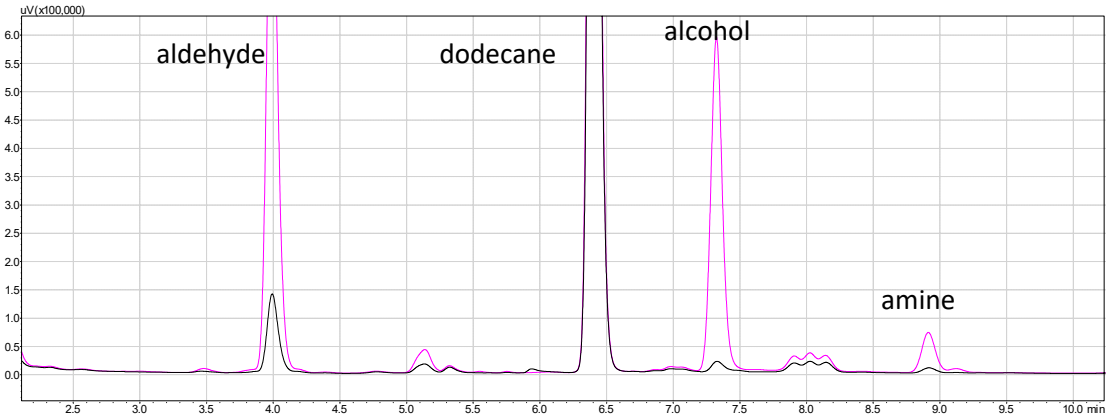

Figure S43: Representative GC chromatogram of derivatized 1-hexanol, hexanal and 1-hexylamine mixture.

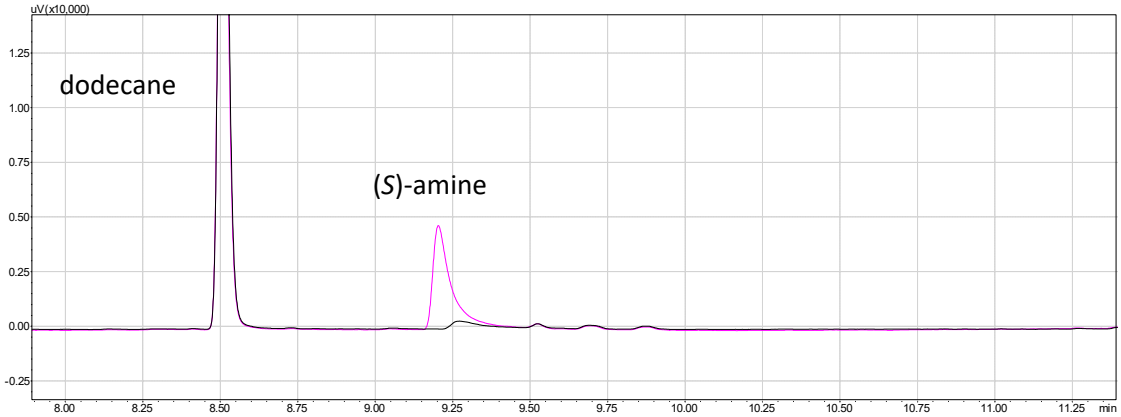

Figure S44: Representative GC chromatogram of derivatized 2-aminohexane.

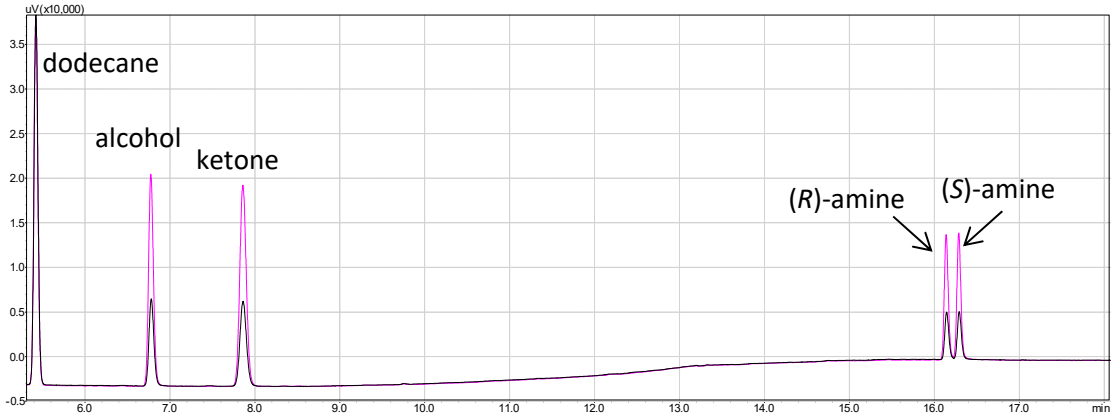

Figure S45: Representative GC chromatogram of derivatized 1-phenylethanol, acetophenone and 1-phenylethyl amine.

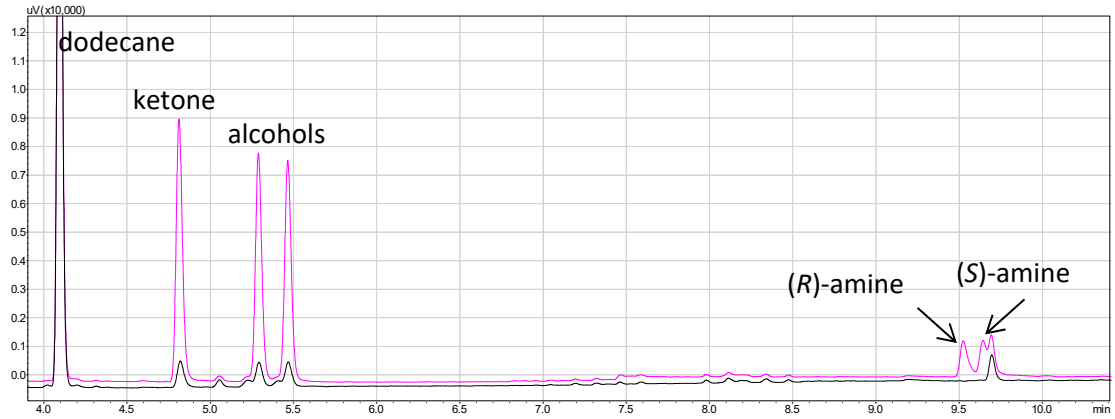

Figure S46: Representative GC chromatogram of derivatized 1-phenylpropanol, propiophenone (*R*) and (*S*)
1-phenylpropyl amine.

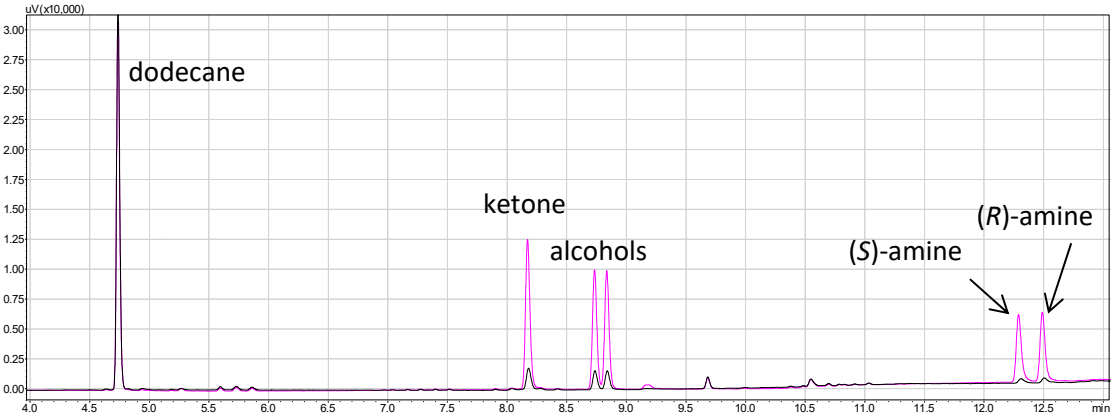

Figure S47: Representative GC chromatogram of derivatized 1,2,3,4-tetrahydro-1-naphthol, α-tetralone, (*R*) and (*S*) 1,2,3,4-tetrahydro-1-naphthylamine.

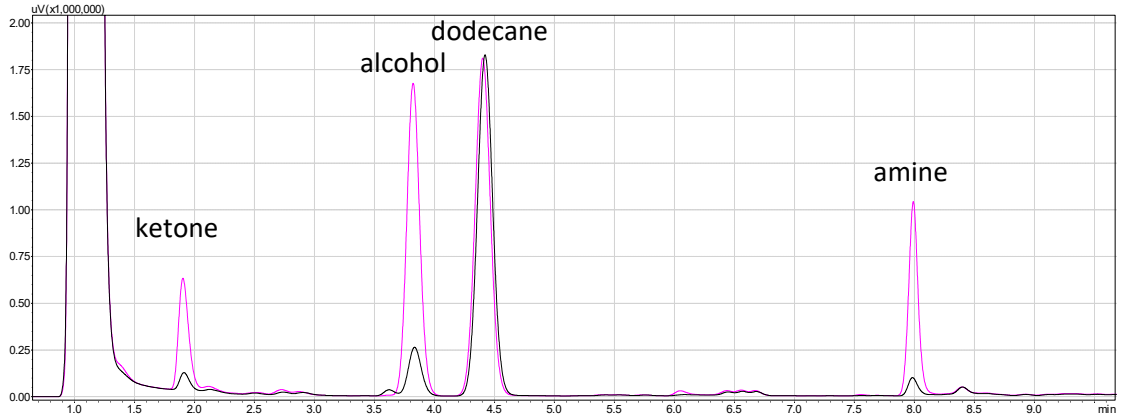

Figure S48: Representative GC chromatogram of derivatized benzyl alcohol, benzaldehyde, benzyl amine.

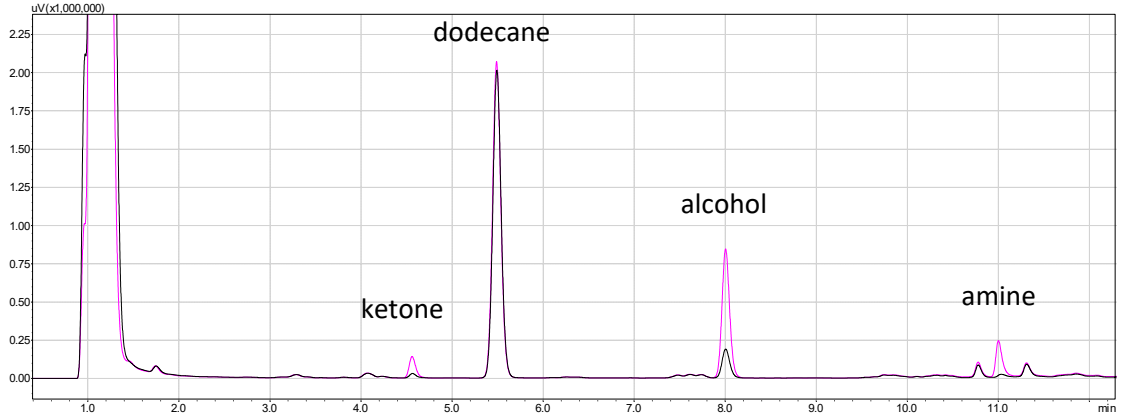

Figure S49: Representative GC chromatogram of derivatized 3-chlorobenzyl alcohol, 3-chlorobenzaldehyde,
3-chlorobenzyl amine.

References

1. Xu, H.; Yan, J.; She, X.; Xu, L.; Xia, J.; Xu, Y.; Song, Y.; Huang, L.; Li, H. Graphene-analogue carbon nitride: Novel exfoliation synthesis and its application in photocatalysis and photoelectrochemical selective detection of trace amount of cu 2+. *Nanoscale* **2014**, *6*, 1406-1415.
2. Zhang, W.; Bariotaki, A.; Smonou, I.; Hollmann, F. Visible-light-driven photooxidation of alcohols using surface-doped graphitic carbon nitride. *Green Chemistry* **2017**, *19*, 2096-2100.
3. Verma, S.; Baig, R.N.; Nadagouda, M.N.; Varma, R.S. Selective oxidation of alcohols using photoactive vo@ g-c3n4. *ACS Sustainable Chemistry & Engineering* **2016**, *4*, 1094-1098.