

Supporting Information

Room-Temperature Catalytic Oxidation of Alcohols with the Polyoxovanadate Salt $\text{Cs}_5(\text{V}_{14}\text{As}_8\text{O}_{42}\text{Cl})$

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General Material and Methods. All reagents were purchased from commercial sources and used without purification. Analytical gas chromatography (GC) was performed on an Agilent 7890A chromatograph equipped with an Agilent G4513A autosampler, a split mode capillary injection system, a flame ionization detector and an Agilent 19091J-413 column. GC analyses were carried out within the following parameters: inlet temperature: 250.0 °C; split injection with a 20:1 split ratio at 130 mL/min; injector sampling depth: 20 mm; column flow: 6.5 mL/min, constant pressure; carrier gas: helium; FID temperature: 300 °C; temperature program: 100 °C for 3 min, 50 °C/min ramp to 320 °C, hold for 3 min. GC yields were determined using tetraglyme as the internal standard. ^1H and ^{13}C NMR spectra were collected on a 300 MHz Bruker NMR spectrometer using CDCl_3 solvent. Chemical shifts are reported in parts per million (ppm) with spectra referenced to the residual solvent peak. An isolated sample of acetophenone (**5**) was characterized by ^1H and ^{13}C NMR and was in complete agreement with samples reported in literature.

The synthetic protocol and requisite reagents used in the preparation of $\text{Cs}_5(\text{V}_{14}\text{As}_8\text{O}_{42}\text{Cl})$ were reported previously.¹ The purity of the $\text{Cs}_5(\text{V}_{14}\text{As}_8\text{O}_{42}\text{Cl})$ catalyst prepared for our synthetic needs is seen in the X-ray powder diffraction (Figure S1). Overlay powder patterns for prepared batches 1 and 2 to the calculated powder pattern are a direct comparison.

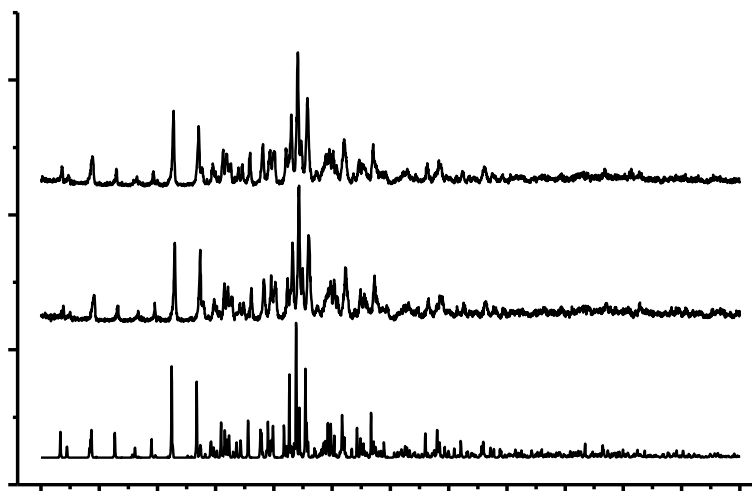


Figure S1. Powder X-ray Diffraction for the $\text{Cs}_5(\text{V}_{14}\text{As}_8\text{O}_{42}\text{Cl})$ catalyst with calculated pattern (bottom line) and observed patterns of batches 1 and 2 (middle and top lines, respectively).

Representative procedure for the catalytic oxidation of alcohols ran in triplicate. A 3 mL screw-capped vial was charged with 5.4 mg of $\text{Cs}_5(\text{V}_{14}\text{As}_8\text{O}_{42}\text{Cl})$ catalyst (0.002 mmol; 0.02 equiv.), 12.7 μL of 1-phenylethanol (0.1 mmol; 1.0 equiv.), and 400 μL of acetone as the solvent. To the stirring solution, 69 μL of 70% aqueous *tert*-butyl hydrogen peroxide (*t*BuOOH) (0.5 mmol; 5.0 equiv.) was added and allowed to stir for 12 hours at room temperature. After the 12h reaction time, the solution was transferred to a 1 mL volumetric flask and the internal standard tetraglyme (11 μL , 0.05 mmol) was added to the vial. The solution was diluted to 1 mL then the full volume of liquid was transferred to a screw-cap GC vial and analyzed by GC to determine the yield. Yields were calculated by means of product standard curves equating GC peak area to product concentration. Reported yields are triplicate averages with standard deviations.

Synthetic scale-up and isolation of acetophenone while regenerating the $\text{Cs}_5(\text{V}_{14}\text{As}_8\text{O}_{42}\text{Cl})$ catalyst. When probing the recyclability of the POV catalyst, the reaction was scaled to 1.0 mmol of 1-phenylethanol (121 μL ; 1.0 equiv.) using 54 mg of $\text{Cs}_5(\text{V}_{14}\text{As}_8\text{O}_{42}\text{Cl})$ catalyst (0.02 mol; 0.02 equiv.) in 4.0 mL of acetone. The catalyst was first impregnated on 100 mg of celite by uniform mixing of the solids before addition to the stirring solution described above. The co-oxidant *t*BuOOH (0.7 mL; 5.0 mmol; 5.0 equiv.) was introduced and the mixture was allowed to stir for 24 hours at room temperature. The magnetic stir bar was then removed and the heterogeneous solution was filtered through a fritted glass funnel and allowed to dry overnight. The remaining, clear liquid was concentrated *in vacuo* to approximately 5 mL before being diluted with 5 mL of water and quenched with saturated sodium meta-bisulfite. The aqueous mixture was extracted with ethyl acetate (3 x 15 mL), washed with saturated sodium bicarbonate (15 mL), and dried over anhydrous sodium sulfate. The collected aqueous layers were then back extracted with another 15 mL of ethyl acetate which was added to the drying organic layers. The organics were then filtered and concentrated *in vacuo*.

Silica gel column chromatography (20% ethyl acetate/hexanes) returned the desired product.

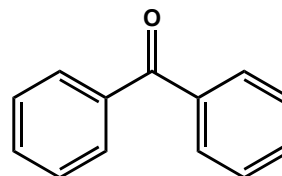
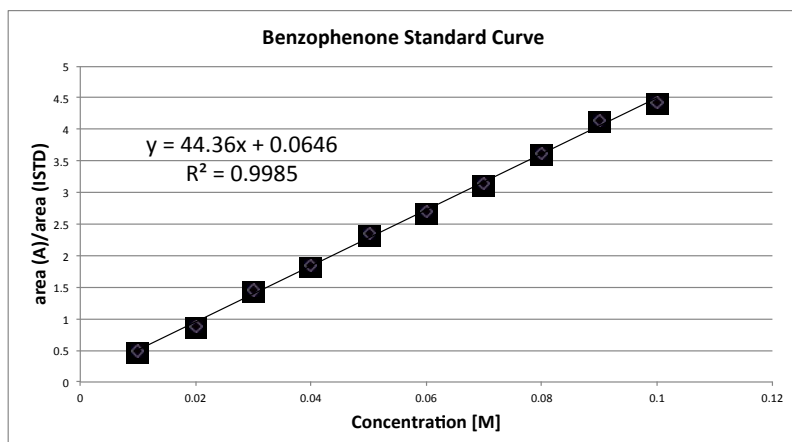
¹H and ¹³C NMR Characterization of Acetophenone, 5²: ¹H NMR (300 MHz, CDCl₃): δ 7.97-7.93 (dt, 2H, *J* = 1.5, 6.9), 7.55-7.47 (tt, 1H, *J* = 1.2, 7.2), 7.45 (t, 2H, *J* = 7.8) 2.59 (s, 3H); ¹³C NMR (90 MHz, CDCl₃): δ 198.1, 137.1, 133.1, 128.6, 128.3, 26.6



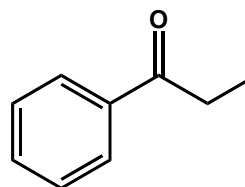
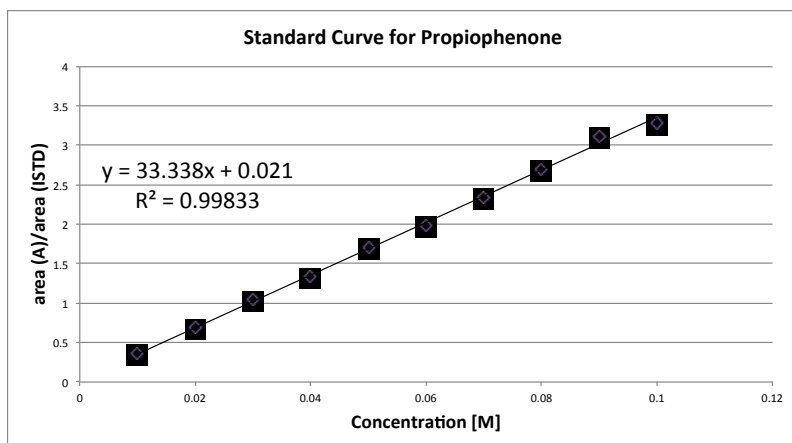
Standard Curves for ketone products; 5-22, 24-25, 27-28, 30-31, 33-35.

Acetophenone, **5**: See citation 3.

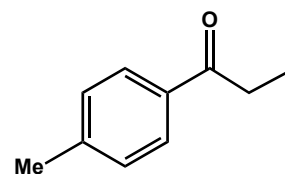
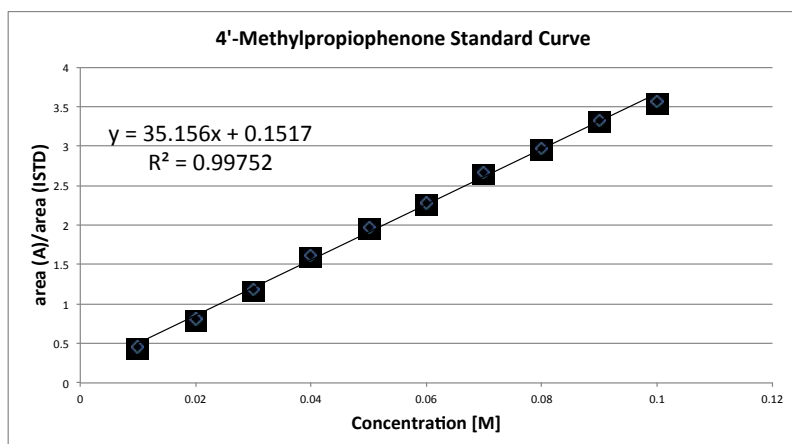
Benzophenone, **6**.



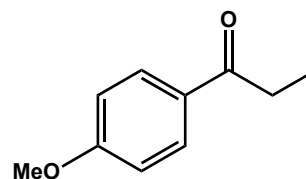
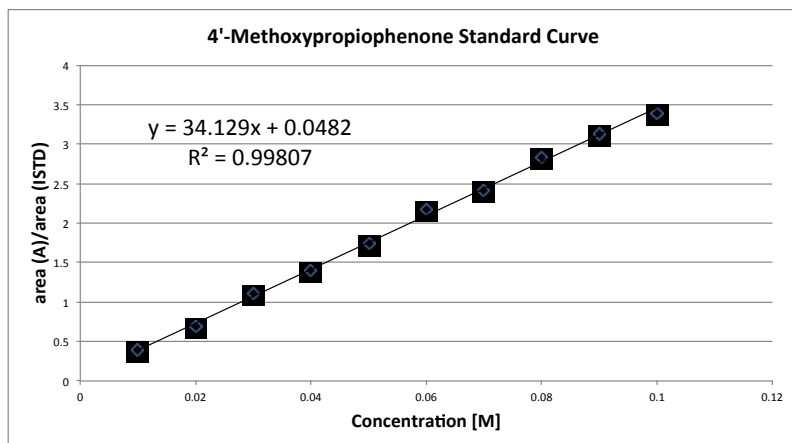
Propiophenone, **7**.



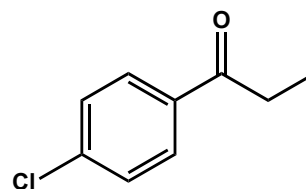
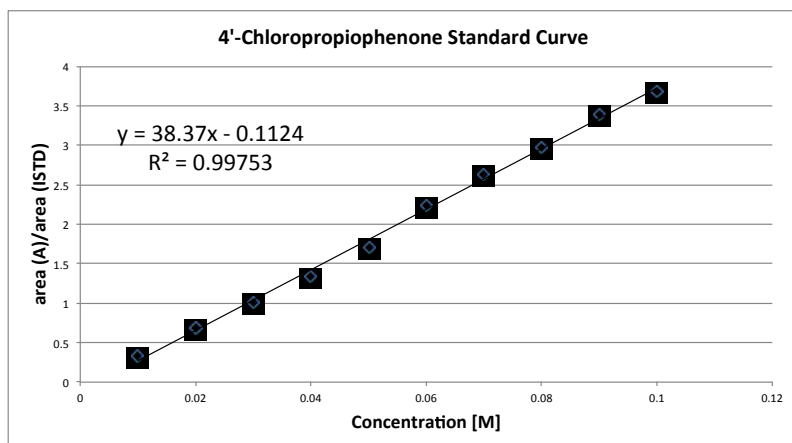
4'-Methylpropiophenone, 8.



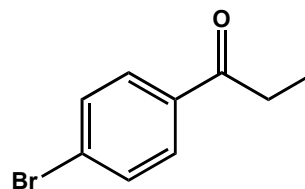
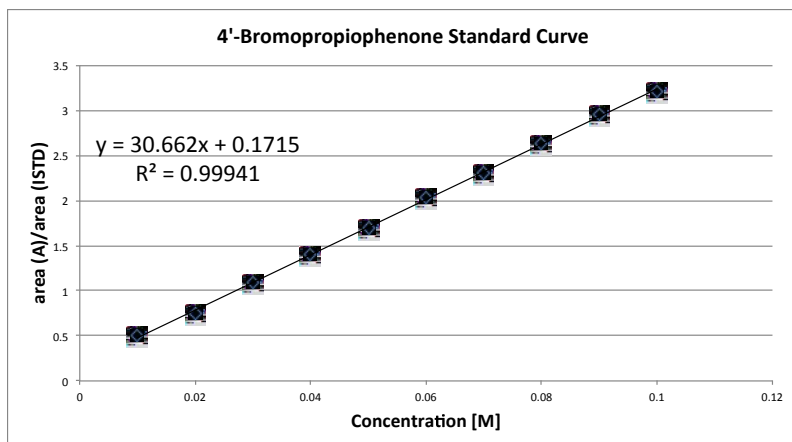
4'-Methoxypropiophenone, 9.



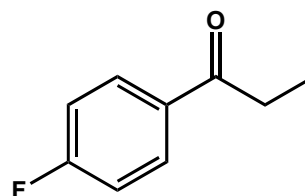
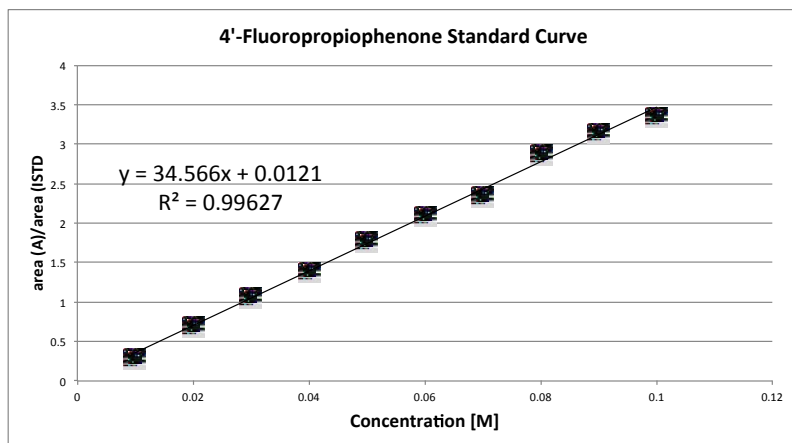
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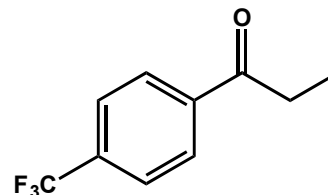
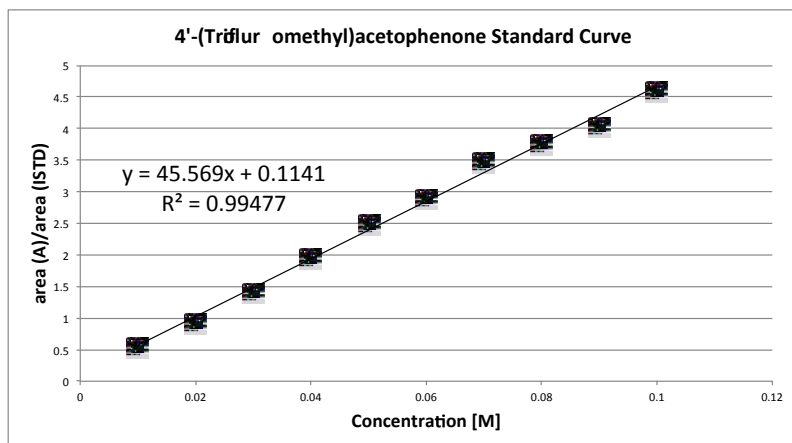
4'-Bromopropiophenone, 11.



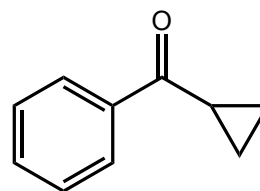
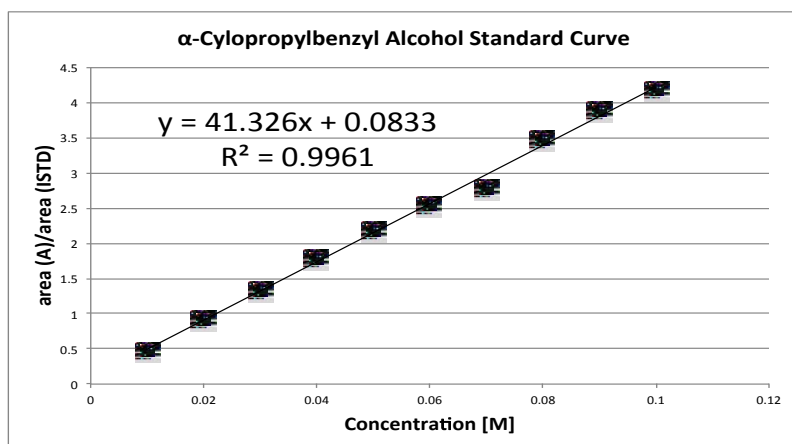
4'-Fluoropropiophenone, 12.



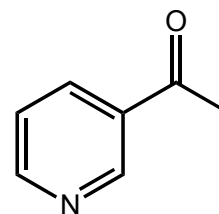
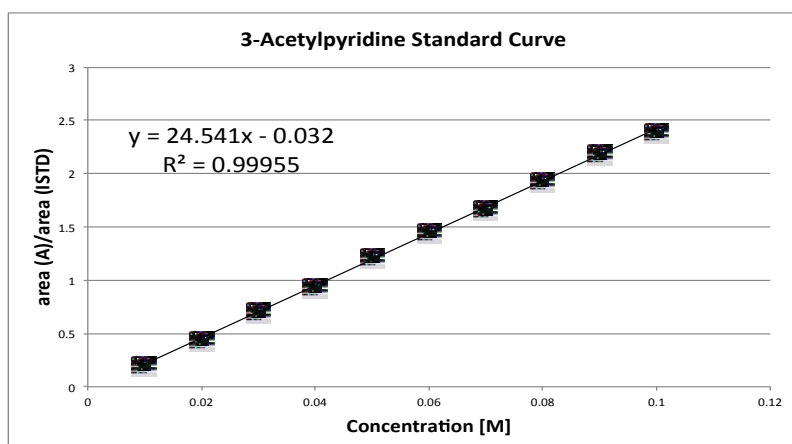
4'-(Trifluoromethyl)acetophenone, 13.



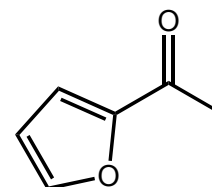
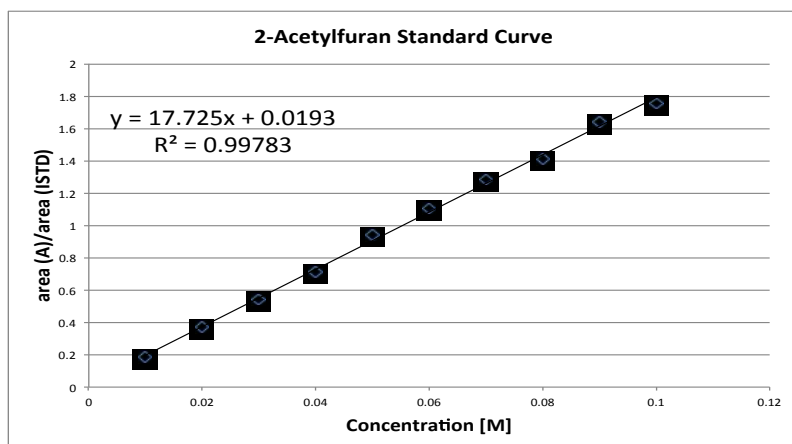
α -Cylopropylbenzyl Alcohol, 14.



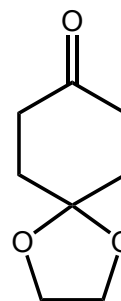
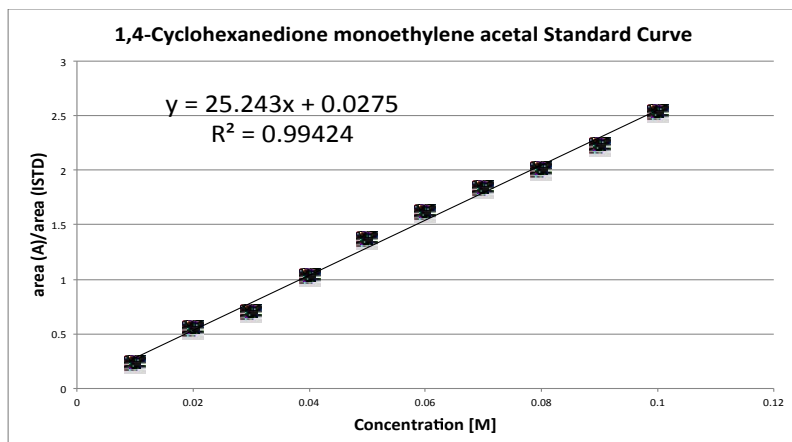
3-Acetylpyridine, 15.



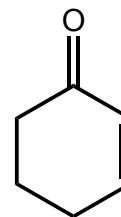
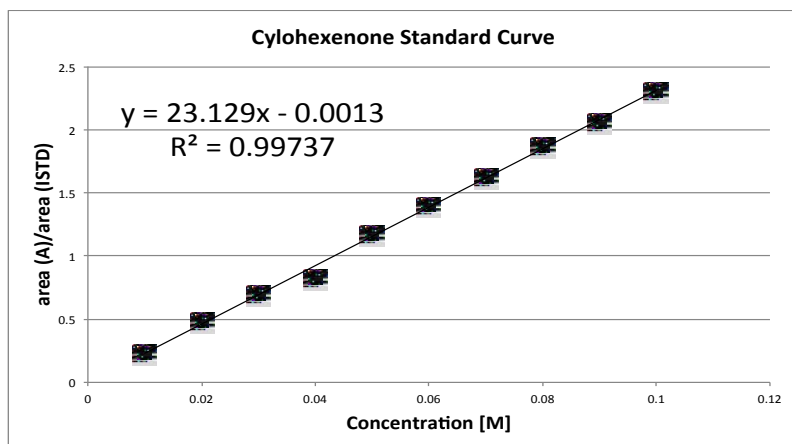
2-Acetylfuran, 16.



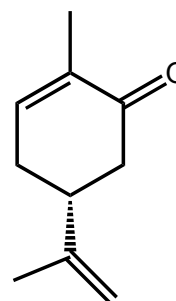
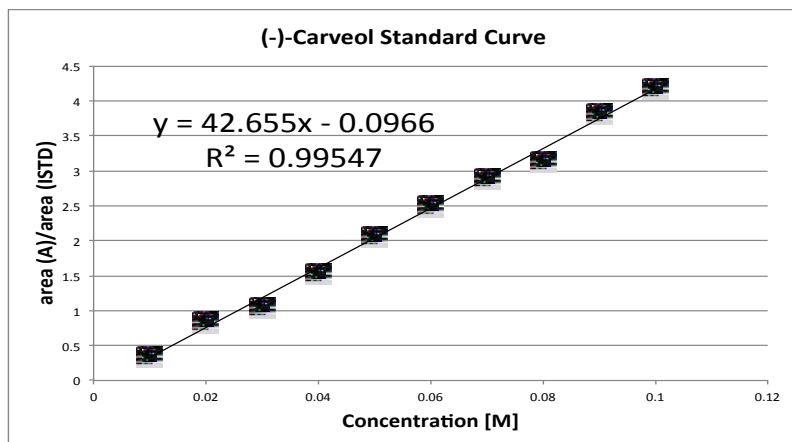
1,4-Cyclohexanedione monoethylene acetal, 17.



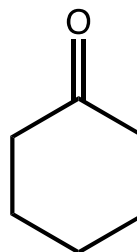
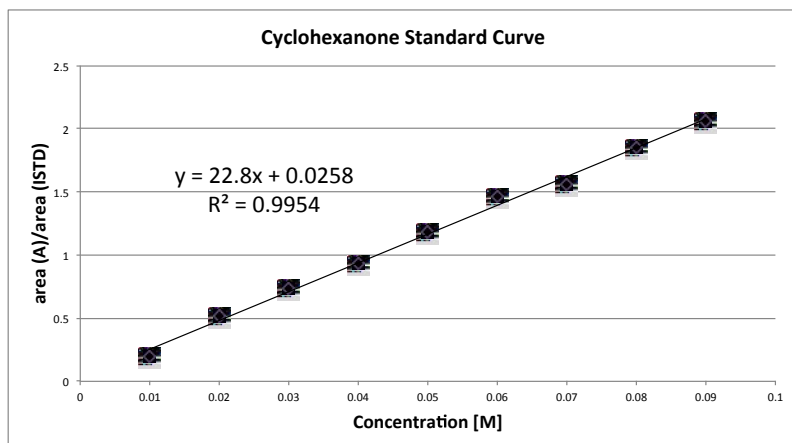
Cyclohexenone, 18.



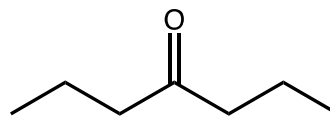
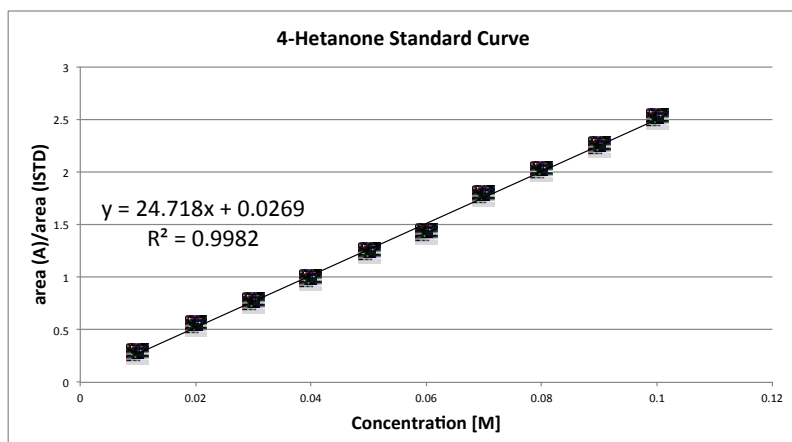
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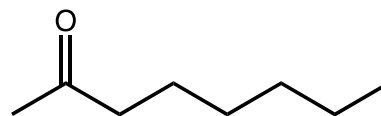
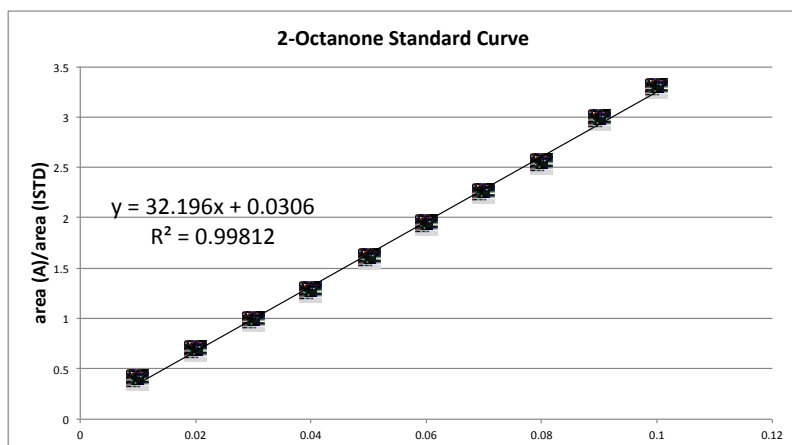
Cyclohexanone, 20.



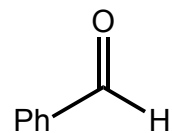
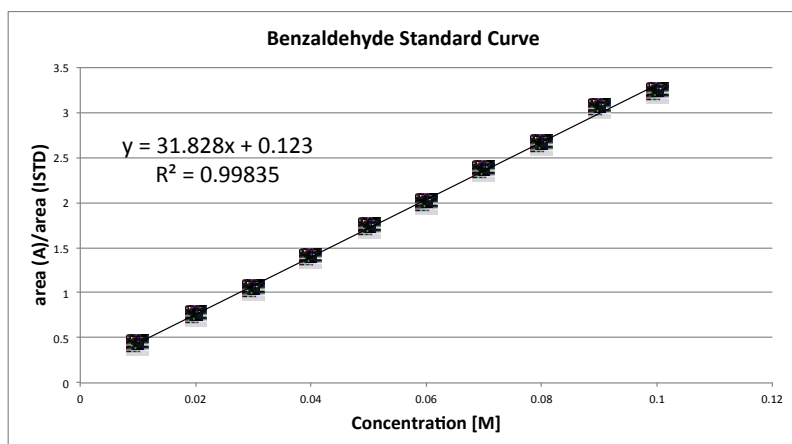
4-Heptanone, 21.



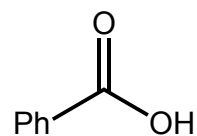
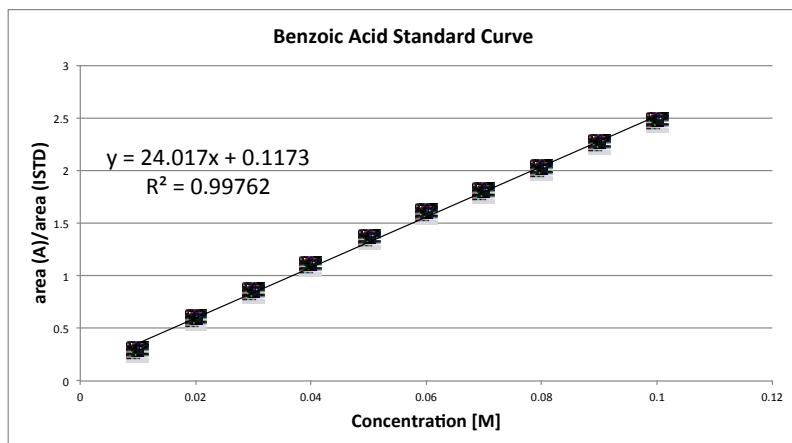
2-Octanone, 22.



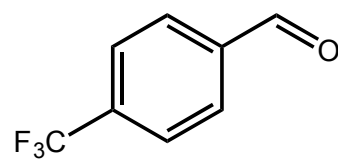
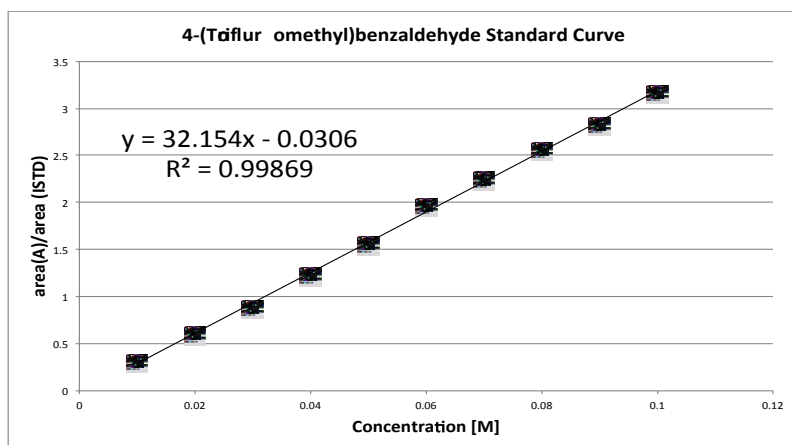
Benzaldehyde, 24.



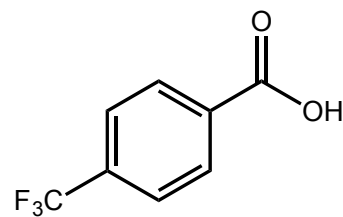
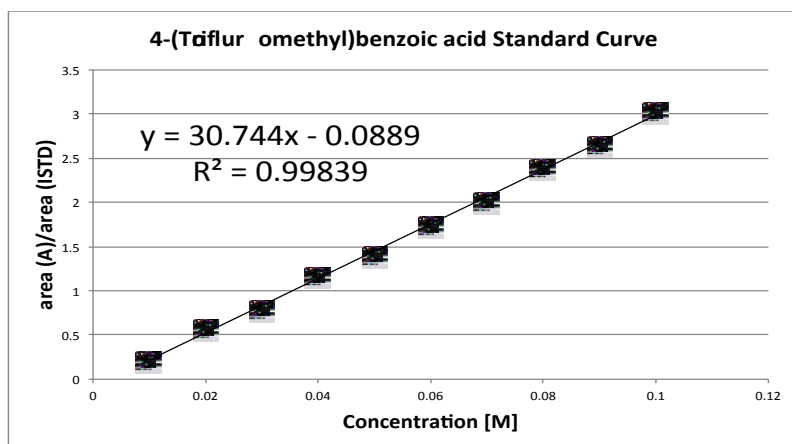
Benzoic Acid, 25.



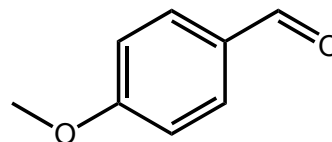
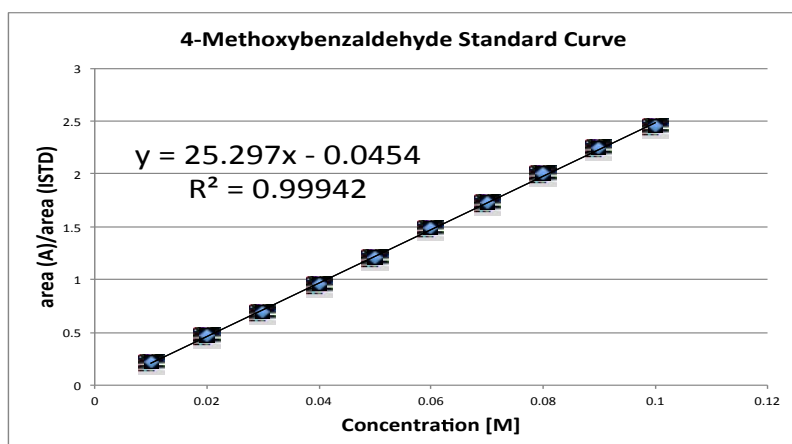
4-(Trifluoromethyl)benzaldehyde, 27.



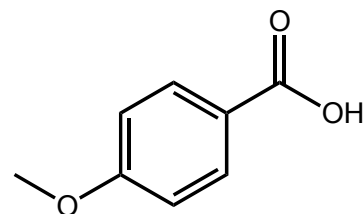
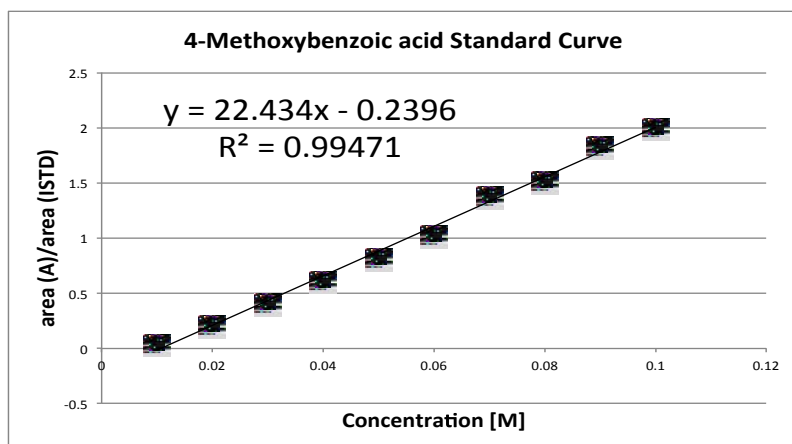
4-(Trifluoromethyl)benzoic acid, **28**.



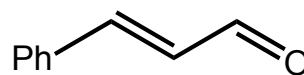
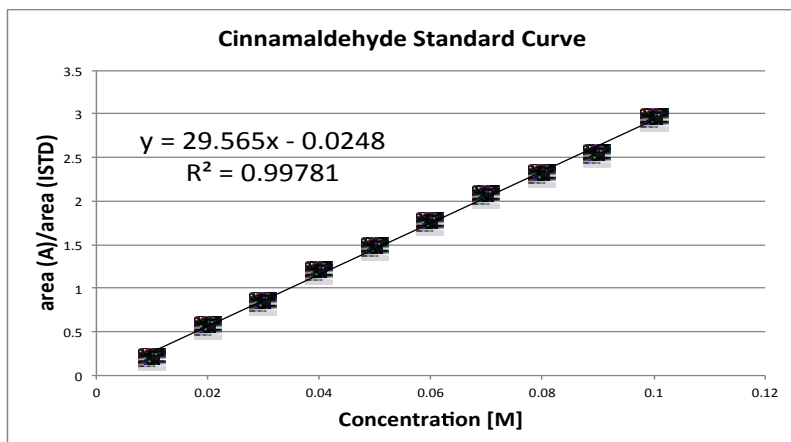
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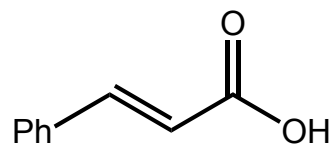
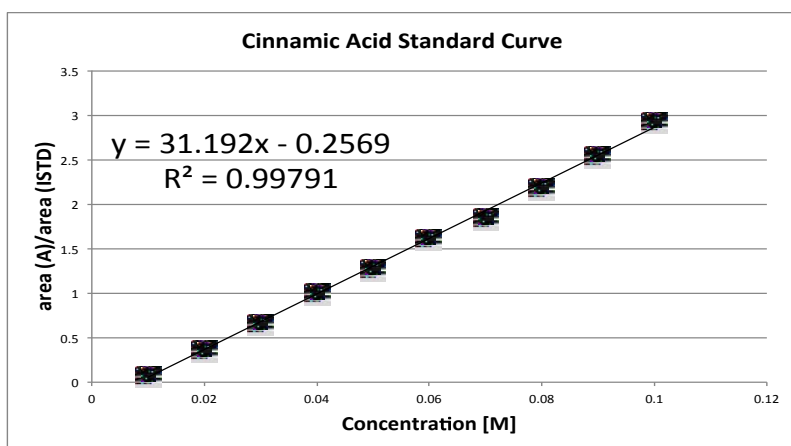
4-Methoxybenzoic acid, **32**.



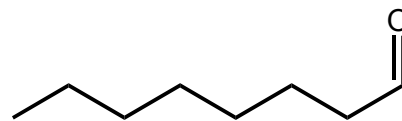
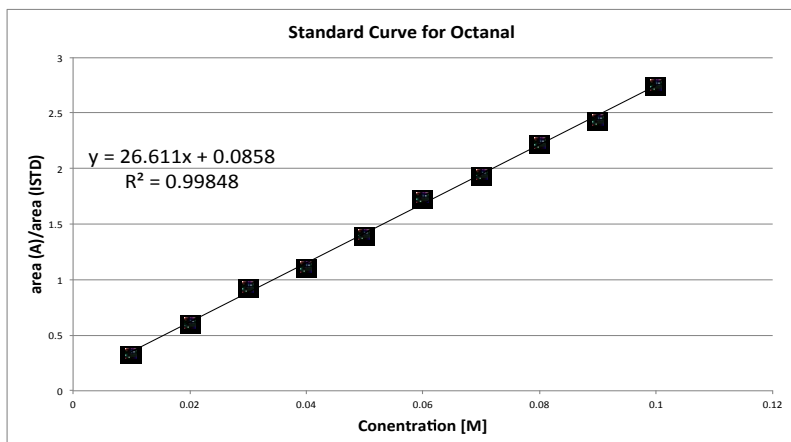
Cinnamaldehyde, **33**.



Cinnamic Acid, **34**.



Octanal, **35**.



References:

1. Queen, W.; West, J. P.; Hwu, S., -J.; Tran, T. T.; Halasyamani, P. S.; and VanDerveer, D. *Chem. Commun.* 2012, **48**, 1665-1667.
2. Kamijo, S.; Tao, K.; Takao, G.; Tonoda, H. and Murafuji, T. *Org. Lett.* 2015, **17**, 3326-3329.
3. Drew, E. T.; Yang, Y.; Russo, J. A.; Campbell, M. L.; Rackley, S. A.; Hudson, J.; Schmucki, P. and Whitehead, D. C. *Catal. Sci. Technol.* 2013, **3**, 2610-2613.