

# Supporting Information

## Photocatalytic Reduction of Aromatic Azides to Amines using CdS and CdSe Nanoparticles

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### **I. Synthesis of cadmium sulfide and cadmium selenide nanoparticles**

*A. Materials:* Cadmium chloride ( $\text{CdCl}_2$ ), 2-aminoethanethiol hydrochloride (thiol-1), 2-(N,N-dimethylamino)ethanethiol hydrochloride (thiol-2) and 2-(N,N-diethylamino)ethanethiol hydrochloride (thiol-3) were obtained from Aldrich and were used without further purification. Sodium selenide metal-based ( $\text{Na}_2\text{Se}$ ) from Alfa Aesar was used without purification.

*B. Preparation of cadmium selenide nanoparticles (CdSe):* A sample of 400 ml of deionized water was brought to a boil. It was sparged continuously with argon while cooling to room temperature. To 150 ml of the boiled deionized water, 27.8 mg (0.152 mmol) of  $\text{CdCl}_2$  was added. Once all the powder was dissolved, 490 mg (3.5 mmol) of thiol-2 {400 mg (3.5 mmol) of thiol-1; 590 mg (3.5 mmol) of thiol-3} was added to the solution. The pH of the mixture was approximately 3.3 and there was no observable color to the solution. The pH was adjusted to 7.8 by dropwise addition of 1 M NaOH. In a separate flask, another solution was prepared by dissolving 12 mg (0.096 mmol) of  $\text{Na}_2\text{Se}$

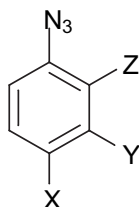
in 25 ml of boiled deionized water {9 mg (0.076 mmol) of thiol-1, or 15 mg (0.120 mmol) if thiol-3 is used}. The red solution solution was added immediately to the cadmium/thiol with vigorous swirling over two to three minutes. During addition, the color of the mixture gradually turned from colorless to yellowish-green (transparent) and the final pH was measured at 7.9. The growth of nanoparticles was monitored by measuring the absorbance over time.

*C. Preparation of cadmium sulfide nanoparticles (CdS):* The procedure was repeated as described previously for the CdSe particles. Typical amounts of reagents were as follows: 150 ml of boiled deionized water, 27.5 mg (0.15 mmol) of CdCl<sub>2</sub>, 398 mg (3.5 mmol) of thiol 1, 40 mg (0.096 mmol) of Na<sub>2</sub>S·9H<sub>2</sub>O in 25 ml of boiled deionized water. The growth of nanoparticles was monitored by measuring the absorbance over time.

## **II. Synthesis of Aromatic Azides**

*A. General.* NMR spectra were recorded on a Bruker ARX-400 spectrometer. A Hewlett Packard 8453 UV-Vis spectrophotometer was used to record UV-Vis spectra. IR spectra were acquired with a Perkin Elmer Paragon 100 FT-IR instrument. EI-HRMS was performed using a VG Autospec (Micromass: Beverly, MA) spectrometer.

*B. Materials.* Sodium azide (NaN<sub>3</sub>), sodium nitrite (NaNO<sub>2</sub>), and substituted anilines were obtained from Aldrich. Anhydrous magnesium sulfate (MgSO<sub>4</sub>) was obtained from Fisher Scientific. Hydrochloric acid 12 M was obtained from EM Science; Methanol-d<sub>4</sub> 99.8% (CD<sub>3</sub>OD) was obtained from Cambridge Isotope Laboratory. All materials were used as received. The aromatic azides synthesized for this work are listed in the table below.



**1**

Compound:	X	Y	Z
<b>1a</b>	NO <sub>2</sub>	H	H
<b>1b</b>	H	NO <sub>2</sub>	H
<b>1c</b>	H	H	NO <sub>2</sub>
<b>1d</b>	CO <sub>2</sub> H	H	H
<b>1e</b>	H	CO <sub>2</sub> H	H
<b>1f</b>	COMe	H	H
<b>1g</b>	H	OMe	H
<b>1h</b>	OMe	H	H
<b>1i</b>	Cl	H	H
<b>1j</b>	(CH <sub>3</sub> ) <sub>2</sub> OH	H	H
<b>1k</b>	MeO	NO <sub>2</sub>	H
<b>1l</b>	MeO	CO <sub>2</sub> Me	H

C. *Synthetic procedure.*<sup>1</sup> To a 300-mL round-bottom flask, 20 mmol of the corresponding amine and 50 mL of 6 M HCl were added. The flask containing the reaction mixture was then placed in ice for at least 15 minutes with stirring. Two separate solutions were prepared of 21 mmol NaNO<sub>2</sub> in 10 mL of deionized water and 21 mmol NaN<sub>3</sub> in 10 mL of deionized water. The solutions were cooled in an ice bath. After 15 minutes, the NaNO<sub>2</sub> solution was added dropwise to the reaction mixture of the amine in HCl. The addition was done over 15 minutes, followed by 15 minutes of stirring in ice. The cooled NaN<sub>3</sub> solution was then added to this reaction mixture dropwise. The addition was finished within 15 minutes followed by another 15 minutes of stirring in ice. The reaction mixture was extracted three times with 50 mL portions of diethyl ether. The organic layer was washed with 50 mL 0.5M HCl, followed by 50 mL of brine, dried over NaSO<sub>4</sub>, filtered and evaporated under reduced pressure in a round-bottom flask. The isolated yields for the different aromatic azides averaged between 85-95 %. All the analytical for aromatic azides **1a-1j** was consistent with those reported in the literature.<sup>2</sup>

(1) Patai, S. *The Chemistry of the Azido Group*, John Wiley & Sons: New York. 1971; p. 57.

(2)4-Nitroazidobenzene **1a**: (a) Dyll, L. K. *Aust. J. Chem.*, **1975**, 28, 2147-59; (b) Liang T.

*J. Am. Chem. Soc.*, **1987**, 109, 7803-10 ; 3-Nitroazidobenzene **1b**: Liang T. *J. Am. Chem. Soc.*,

The analytical data for compounds **1k** and **1l**, which are new compounds, are listed below. Copies of the  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and FTIR spectra are included at the end of this document.

4-Methoxy-3-nitrophenylazide **1k**:  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  3.91 (s, 3 H), 7.27-7.30 (m, 2 H), 7.46-7.47 (m, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  55.9, 115.1, 115.2, 123.9, 132.6, 140.0, 149.6; IR (KBr,  $\text{cm}^{-1}$ ): 3116.8, 2116.2, 1527.7, 1347.5, 1273.7, 1183.5, 1015.5; HRMS calcd for  $\text{C}_7\text{H}_6\text{N}_4\text{O}_2$ : 194.0440, found 194.0441. m.p. 88.5-90.6°C.

Methyl 5-azido-2-methoxybenzoate **1l**:  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  3.91 (s, 6H), 6.96 (d, 1 H,  $J = 9$  Hz), 7.10 (dd, 1 H,  $J_1 = 9$  Hz,  $J_2 = 3$  Hz), 7.47 (d, 1 H, 3 Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  52.2, 56.3, 113.5, 121.1, 121.9, 123.7, 132.1, 156.3, 165.6. IR (KBr,  $\text{cm}^{-1}$ ): 3043.6, 2957.0, 2120.4, 1709.5, 1500.8, 1433.8, 1314.5, 1247.5, 1016.4; HRMS calcd for  $\text{C}_9\text{H}_9\text{N}_3\text{O}_3$ : 207.0644, found 207.0643. m.p. 41.5-44.4°C.

### III. The photocatalyzed reduction of aromatic azide to aromatic amine.

A. *Materials*: Sodium formate ( $\text{HCO}_2\text{Na}$ ) was obtained from Aldrich; 0.05 M potassium phosphate monobasic – sodium hydroxide pH 7.00 buffer (buffer) and magnesium sulfate anhydrous ( $\text{MgSO}_4$ ) were obtained from Fisher Scientific; Sodium hydroxide GR was obtained from EM Science; Methanol- $\text{d}_4$  99.8% ( $\text{CD}_3\text{OD}$ ) was obtained from Cambridge Isotope Laboratory. All materials were used directly without purification. All the aromatic azides used in the study were prepared by diazotization of

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**1987**, 109, 7803-10; 2-Nitroazidobenzene **1c**: Dyall, L. K. *Aust. J. Chem.*, **1975**, 28, 2147-59; 4-Azidobenzoic acid **1d**: Liu, Q. *Organic Letters*, **2003**, 5, 2571-72; 3-Azidobenzoic acid **1e**: Tisler, M., *Vestnik Slovenskega Kemijskega Drustva*, **1979**, 26, 163-71; 4-Acetyl-azidobenzene **1f**: Liu, Q. *Organic Letters*, **2003**, 5, 2571-72; 3-Azidoanisole **1g**: Nunno, L. D., *Tetrahedron*, **1986**, 42, 3913-20; 4-Azidoanisole **1h**: Nunno, L. D., *Tetrahedron*, **1986**, 42, 3913-20; 4-Azido-

commercially available aromatic amines with sodium nitrate/HCl followed by addition of sodium azide.

*B. Photocatalysis Experiments:* In a Pyrex tube, 5 mg of the respective azide was dissolved in 0.5 ml of methanol, 4.5 ml of  $\text{HCO}_2\text{Na}$  (0.750 M in water, pH 7.0) and 5 ml of CdS/CdSe nanoparticle solution. This is the reaction mixture. In another tube, 5 mg of the same azide was dissolved in 5 ml of methanol and 5 ml of the corresponding aminethiol solution (thiol 1, 2 or 3 depending on which one is used as the capping agent for nanoparticle preparation). This is the control mixture. The reaction and the control were photolyzed simultaneously in a “black box”, with continuous stirring, for 15 minutes. An Oriel 1 kW Xe/Hg Lamp (Oriel Lamp) was employed as the radiation source. Two separate experiments were done with 400 nm and 420 nm cut-off filters. The mixture in each tube was extracted using the following protocol: The reaction mixture was transferred to a separatory funnel. The reaction tube was filled and rinsed with 15 ml of ethyl acetate, which was also transferred to the separatory funnel. The layers were separated after vigorous shaking and the ethyl acetate layer was saved. The aqueous layer was extracted two more times with 15 ml of ethyl acetate. The ethyl acetate layers were combined and washed with 5 ml of brine. The organic layer was dried using  $\text{MgSO}_4$ , filtered and evaporated under reduced pressure. The dried samples were re-dissolved in  $\text{CD}_3\text{OD}$  and analyzed by  $^1\text{H}$  NMR. Samples **1f**, **1g**, and **1i** were too volatile, which resulted in sample loss while preparing the samples for NMR and were analyzed by G.C instead. The NMR measurements were done on a Bruker ARX-400 spectrometer. A Hewlett-Packard HP-5890 series II gas chromatograph equipped with a flame ionization

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chlorobenzene **1i**: Dyll, L. K. *Aust. J. Chem.*, **1975**, 28, 2147-59; 2-(4-Azidophenyl)ethanol **1j**:

detector (FID) and a HP 3396 series II integrator was used to collect the G.C data. A Hewlett Packard HP-1 column (25m X 0.20 mm; 0.20  $\mu$ m film thickness) was used. A Hewlett Packard 8453 UV-VIS spectrophotometer was used to record UV-VIS spectra.

#### IV. Quantum yield measurements.

Quantum yields of the reaction were determined using Reinecke salt  $[\text{KCr}(\text{NH}_3)_2(\text{NCS})]$  actinometry<sup>3</sup> using Nessler's reagent to detect the presence of ammonium ions as reported by Wegner *et al.*<sup>4</sup> Nessler's reagent was prepared using the following procedure:<sup>5</sup> 3.5g of KI, and 5.0g of  $\text{HgI}_2$  were mixed in flask A, which contained 20 mL of deionized water. In flask B, 5.0 g of sodium hydroxide (NaOH) was dissolved in 25 mL of deionized water. The solutions were mixed and the total volume was adjusted to 50.0 mL using a volumetric flask. The solution was stored in a brown reagent bottle to avoid light, for one week. The solution was filtered before use.

A solution of ferric perchlorate (or FP) was made by mixing 0.1 M  $\text{FeNO}_3$  (2.43 g in 100 mL) and 0.1 M  $\text{HClO}_4$  (4.3 mL of a 70% stock) in a volumetric flask. The total volume of the solution is adjusted to 100.0 mL. This solution was used to detect the presence of ammonium and was also used to complex with free isothiocyanate ions, giving a characteristic  $\lambda_{\text{max}}$  close to 450 nm.

In a room with dim red light, 1.0 g (or 0.003 mol) of potassium reineckate (K-Rein) was recrystallized with 3 times excess of  $\text{KNO}_3$  (0.94 g, 0.009 mol) from the A-Rein with

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Brems, D. N., *Biochemistry*, **1979**, 18, 860-2 .

(3) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; 2nd ed.; Marcel Dekker, Inc.: New York, NY, 1993.

(4) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, 88, 394.

(5) Weast, R. C. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1979.

warm water at 40-50°C for 5 to 10 times. The crystals were filtered, and a portion of the salt was re-dissolved in water and tested with both Nessler's Reagent and FP solution. Both solutions turn brown when ammonium ions are present. Otherwise, the material is dried under reduced pressure overnight.

Photolysis was carried out in the same pyrex tubes that were used to carry out the photocatalytic reductions. A tube containing 10 mL of an aqueous K-Rein solution at an absorbance of about 0.80 between 390nm and 410 nm, which corresponded to roughly 27.5 mg of salt in 10 mL,  $V_1$ , deionized water (approximately 0.008 M), was placed into the blackbox. The photocatalytic reduction of 4-azidobenzoic acid using CdSe nanoparticles was performed alongside. A bandgap filter, between 390 and 410 nm, was placed between the window of the blackbox and the Oriel Xe/Hg 6253 Lamp. The mixture was kept stirring during the 30 minutes-long photolysis. A tube containing 10 mL of the same solution was placed away from light for 30 minutes simultaneously. This was the blank.

Immediately upon completing the photolysis, 5.0 mL of the solution ( $V_2$ ) was diluted 5 folds with deionized water (a new total volume,  $V_3$ , of 25 mL). 1.0 mL of this solution was mixed with 1.0 mL of FP solution. The absorbance of the mixture at 450 nm was recorded. This entire procedure was repeated at least 3 times for the same sample and the entire photolysis was repeated 3 times. The net absorbance of each trial corresponded to the difference of sample absorbance and blank absorbance at 450 nm. The quantum yield of the photocatalytic reduction was calculated for the conversion of aromatic azide to aromatic amines determined by  $^1\text{H-NMR}$ .

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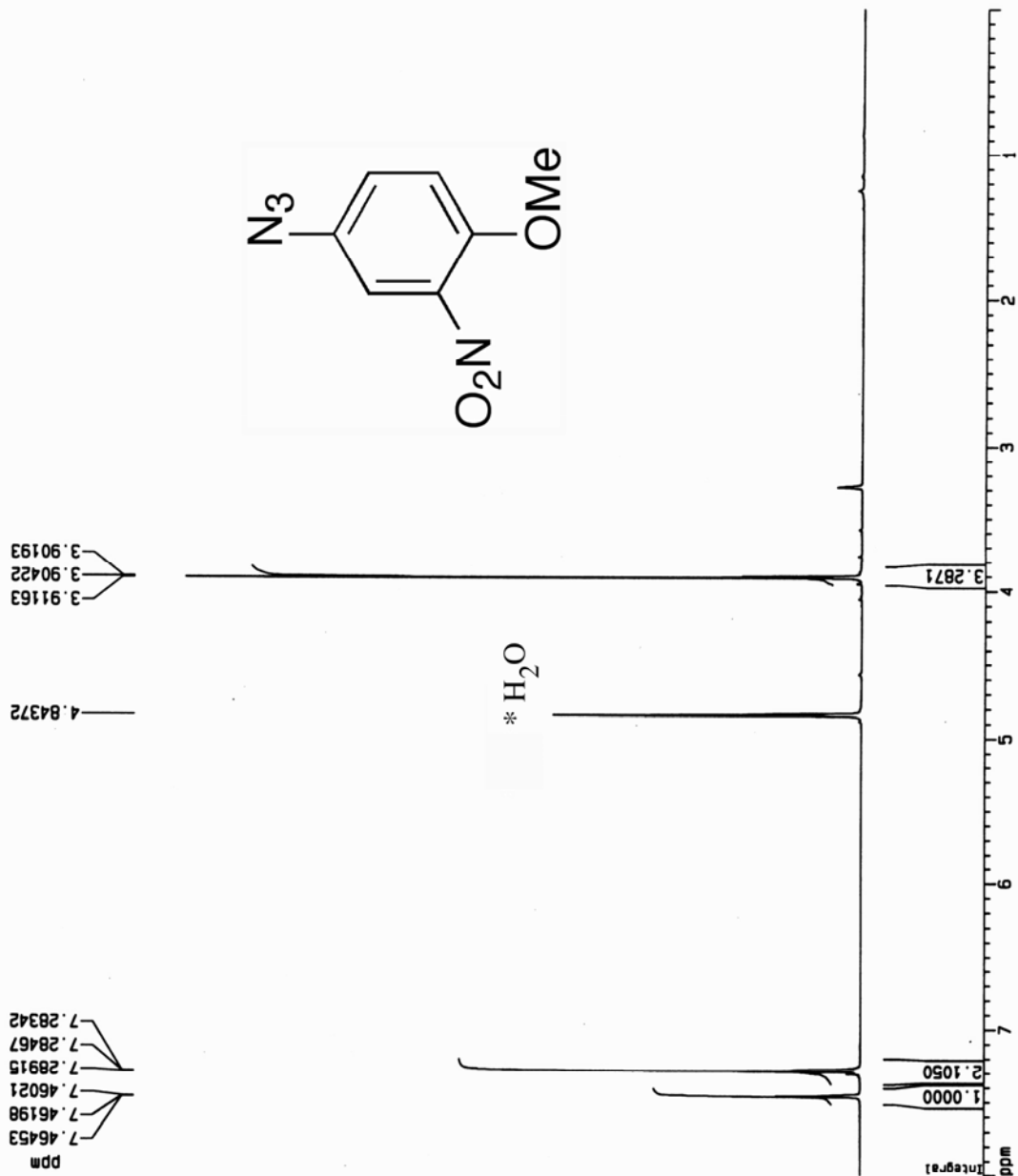
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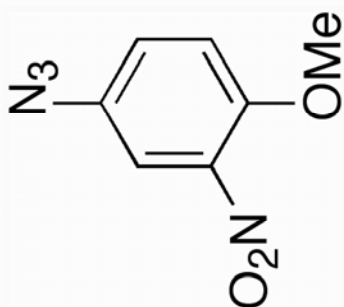
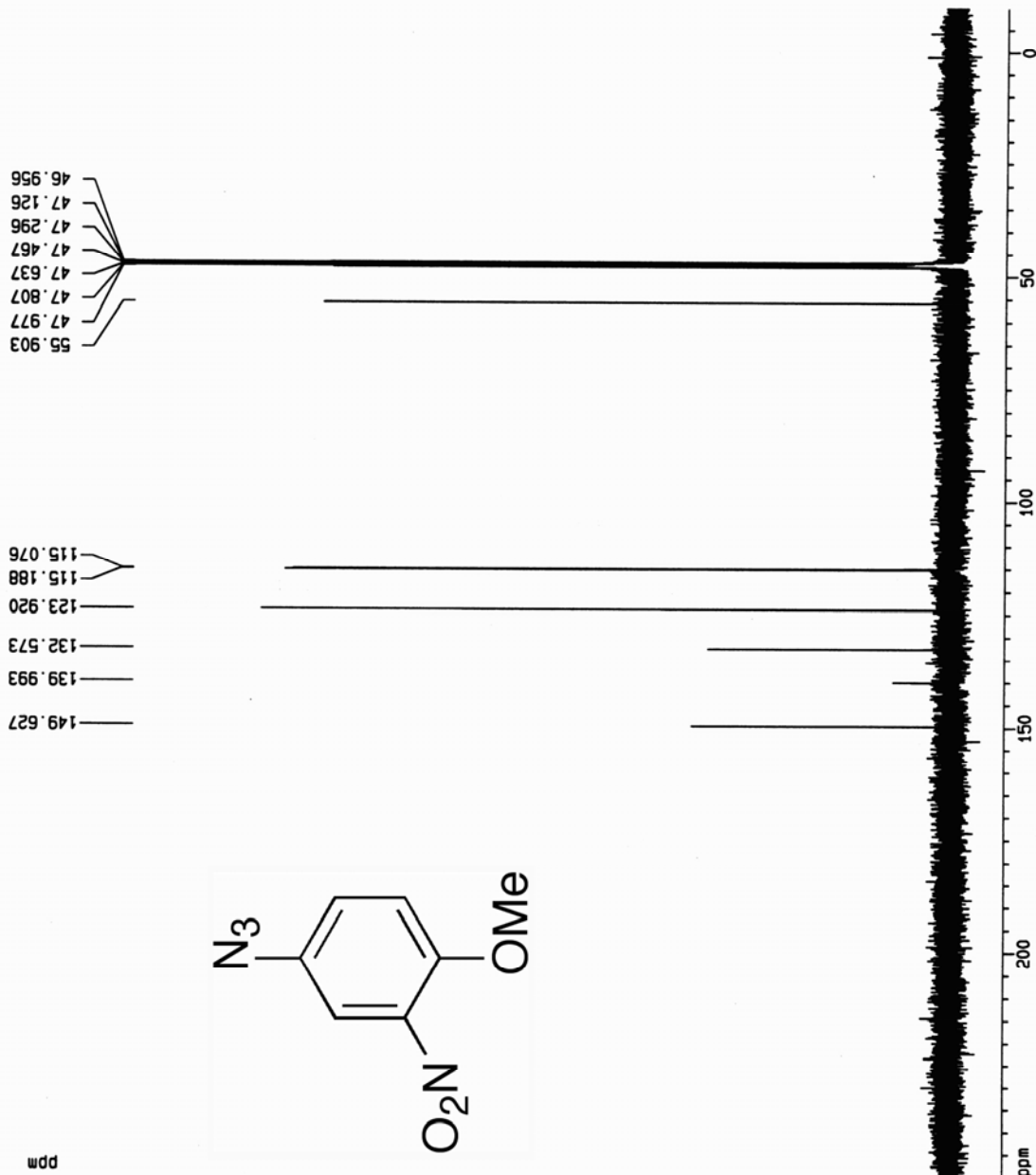
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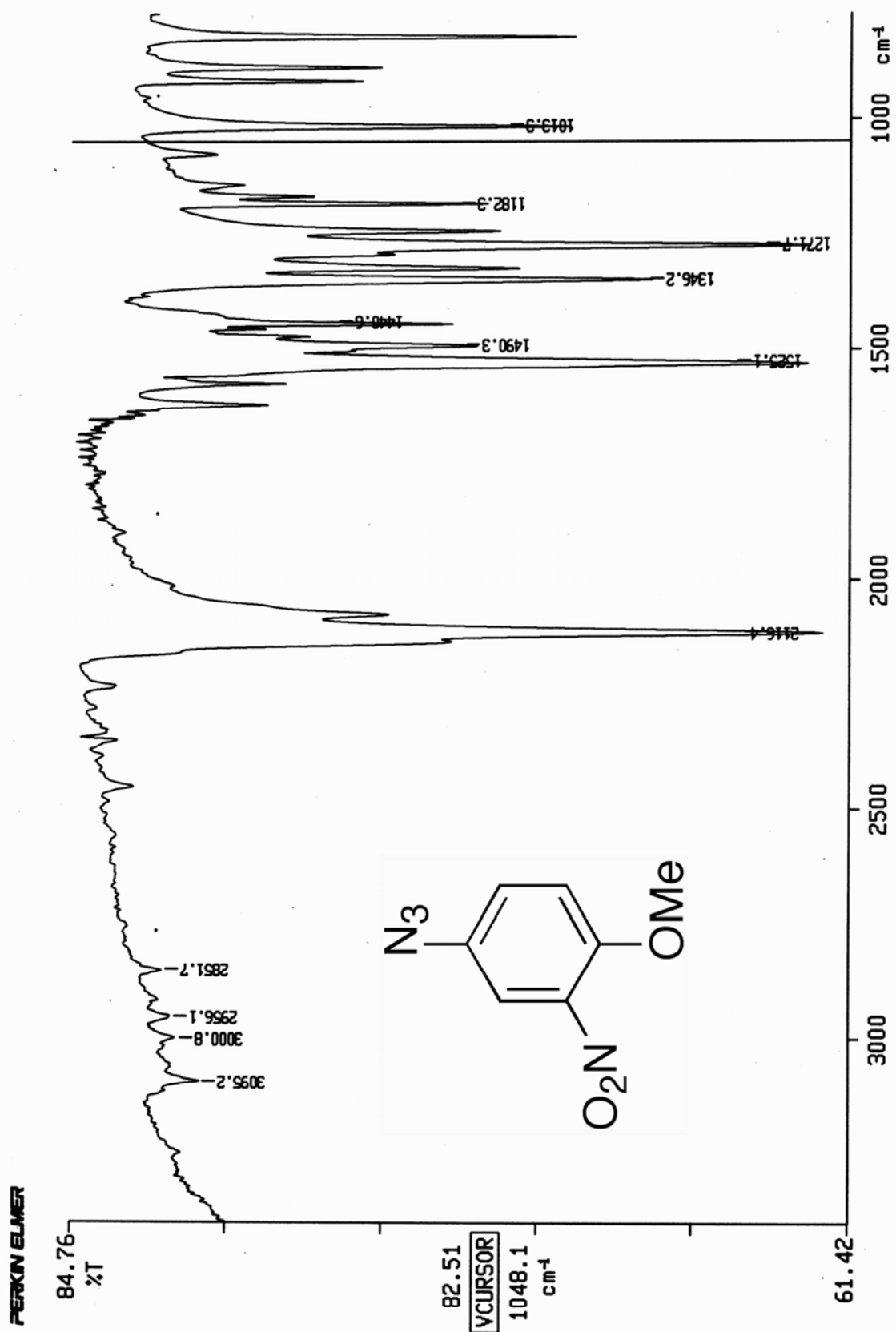
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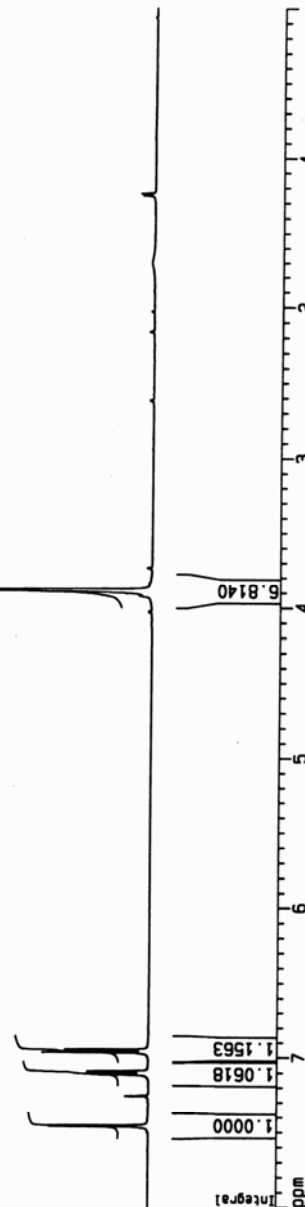
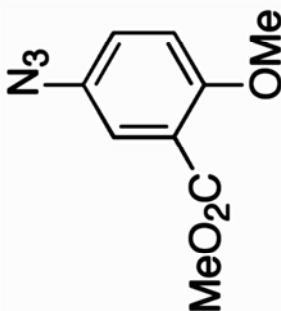
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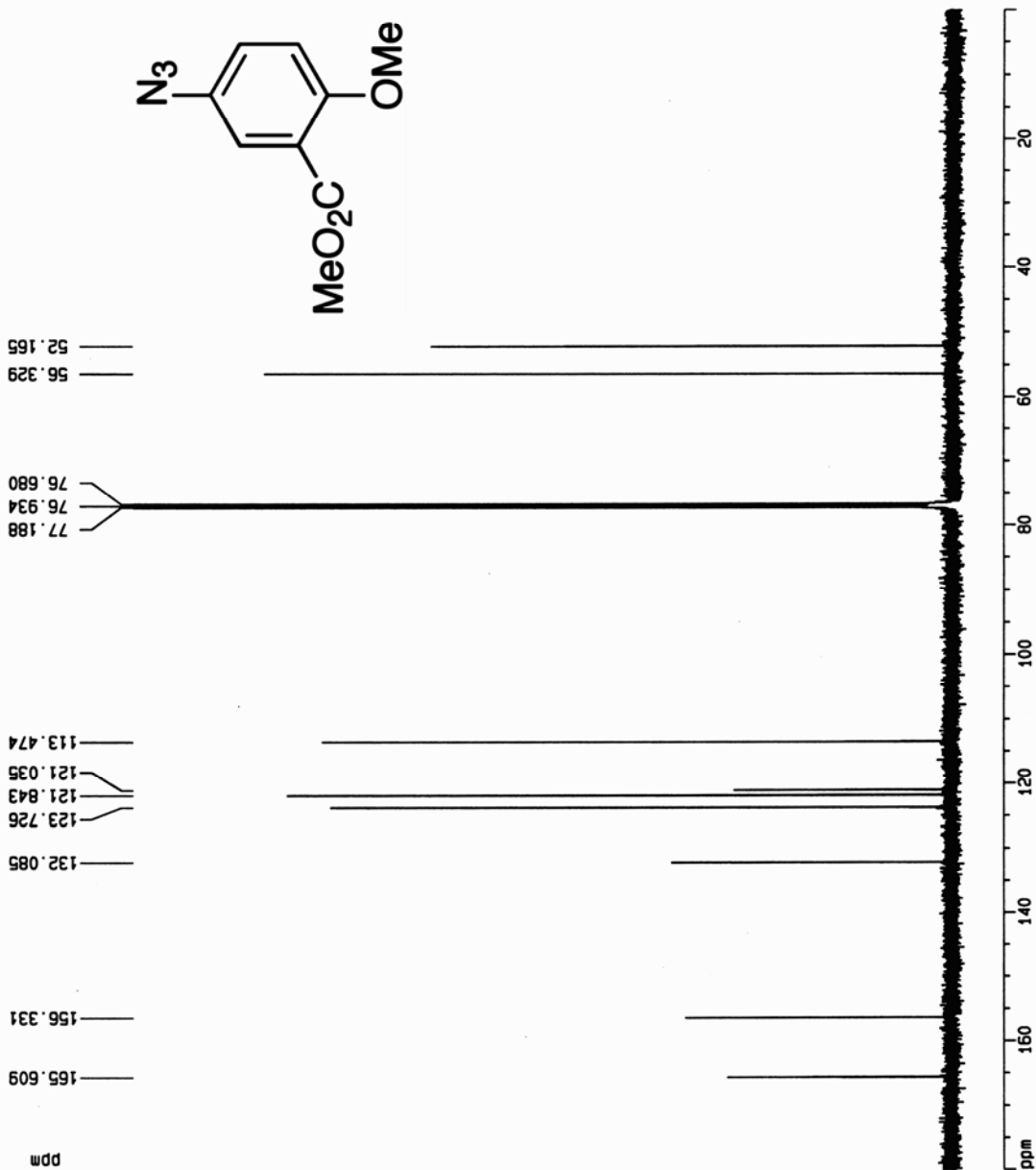
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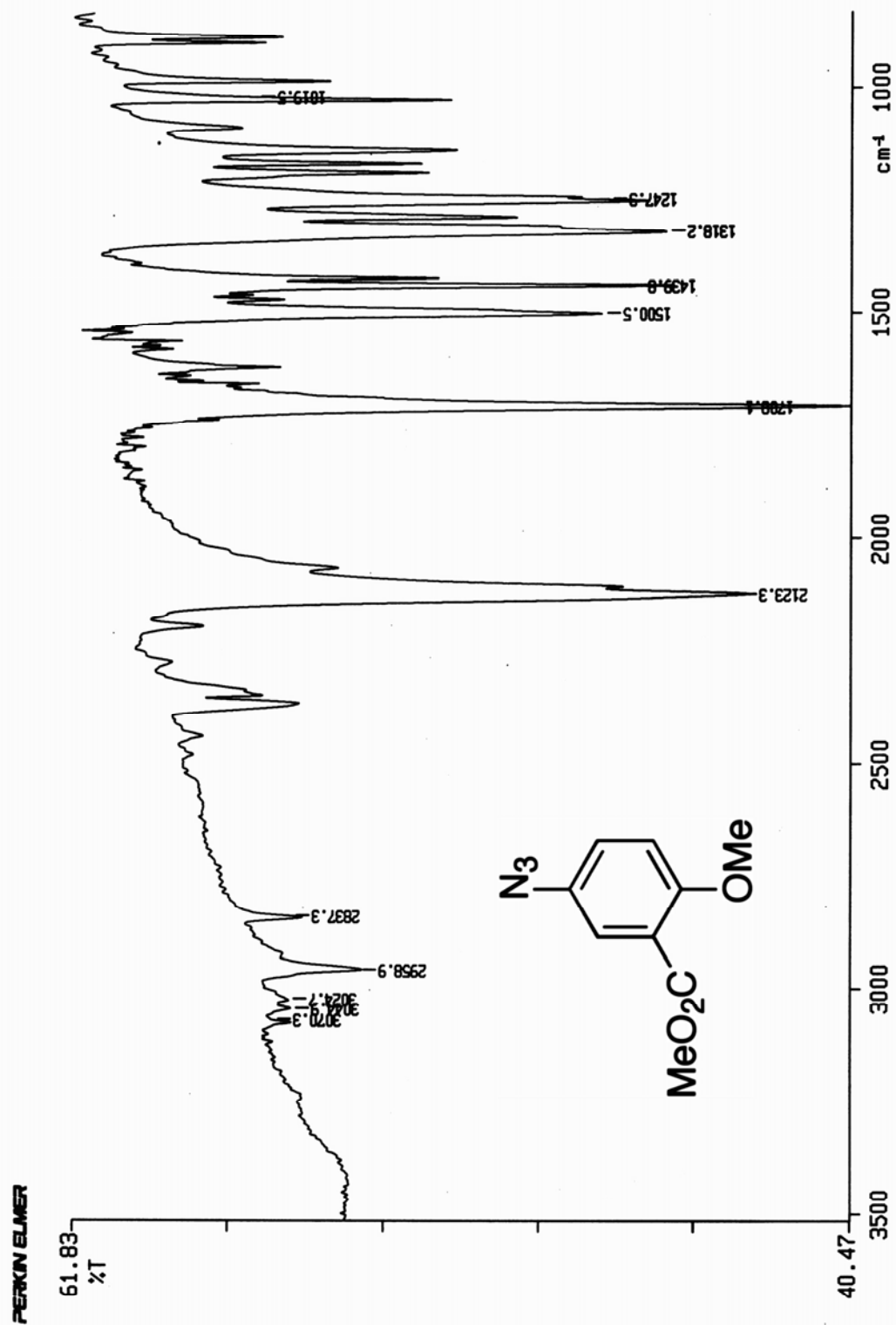
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03/10/08 09:16 CHEMISTRY  
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