

Developing Fluorescent Aminoazobenzene Metal-Organic Frameworks



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Abstract

Azobenzene is a functional component used in a wide array of photoresponsive molecules, chelators, and molecular machines. Azobenzene compounds are easily modifiable and cheap to prepare, which present many opportunities for preparation of new materials. Derivatives of aminoazobenzene, named AzoAMpBE and AzoAMpBA, have been developed synthetically for use in design of various fluorescent or photoactive metal-organic frameworks. Encapsulating this Azobenzene moiety in a metal-organic framework yields the possibility for applications in photo-induced molecular release, molecular sensing, and more.

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Executive Summary

Azobenzene (AB) is a functional component used in a wide array of molecules, chelators, and molecular machines ^[1-3]. These functions work by taking advantage of the photoisomerization of AB in the presence of UV light. When in one form of AB, either trans or cis, the functional application is switched one way, and when irradiated with light the AB group will undergo isomerization and the function of the whole molecule will change due to a conformational change, like an on-off switch. When isomerization of the AB is hindered, such as with introducing hydrogen bond donors and acceptors ^[6], the fluorescence emission of the AB can still be analyzed.

For this project, derivatives of aminoazobenzene, named AzoAMpBE and AzoAMpBA, were developed synthetically, and characterized by ¹H NMR, ¹³C NMR, FR-IR, ESI-MS, and single x-ray diffraction. The development of these aminoazobenzene derivatives was for design of various fluorescent or photoactive metal-organic frameworks. AzoAMpBE was synthesized by reductive amination of DAAB and the benzaldehyde. The DAAB amines form imine bonds with the aldehyde carbonyl carbon, and with introduction of the reducing agent NaBH(OAc)₃, the imine is reduced to an amine.

The goal of this project was to develop fluorescent aminoazobenzene metal-organic frameworks, consisting of synthesized aminoazobenzene ligands coordinated around metal cores, constructing 3-D rigid scaffolds. These scaffolds, due to rigidifying the photoisomerizable azobenzene moiety, have the capacity for absorbance and emission of light, and thus providing fluorescence. Achieved in the span of this project was the thorough and consistent synthetic procedure for developing a workable ligand, AzoAMpBE, for construction of metal-organic frameworks.

Once the synthesis of the AzoAMpBA MOFs is complete, then the spectroscopic analysis follows. Fluorescence spectroscopy of the Azo MOFs will give results of quantum yield, absorbance, and emission and answer the viability of AzoAMpBA as a fluorescent ligand in a MOF. Success in strong fluorescence ultimately leads to applications in fluorescent materials, and molecular solid-state sensing.

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1. Introduction

Azobenzene (AB) is a functional component used in a wide array of molecules, chelators, and molecular machines ^[1-3]. These functions work by taking advantage of the photoisomerization of AB in the presence of UV light. When in one form of AB, either trans or cis, the functional application is switched one way, and when irradiated with light the AB group will undergo isomerization and the function of the whole molecule will change due to a conformational change, like an on-off switch. When isomerization of the AB is hindered, such as with introducing hydrogen bond donors and acceptors ^[6], the fluorescence emission of the AB can still be analyzed. AB compounds are easily modifiable and cheap to prepare, which present many opportunities for preparation of new materials with different properties.

For this project, derivatives of aminoazobenzene, named AzoAMpBE and AzoAMpBA, were developed synthetically, and characterized by ¹H NMR, ¹³C NMR, FR-IR, ESI-MS, and single x-ray diffraction. The development of these aminoazobenzene derivatives was for design of various fluorescent or photoactive metal-organic frameworks. When the AB ligands are locked in a metal-organic framework, AB isomerization does not occur, but fluorescence and emission can be analyzed. The Burdette research group has synthesized other aminoazobenzene MOFs with different levels of absorbance and emission, and using many different aminoazobenzene derivatives.

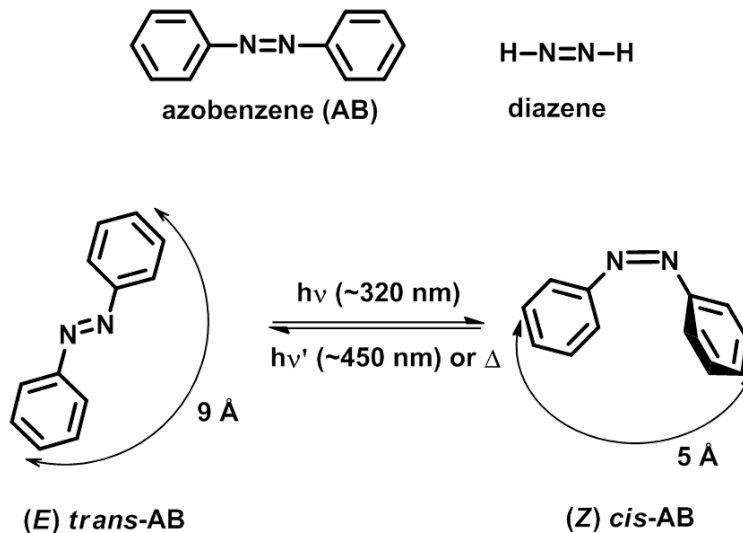
This project is an exploration of an aminoazobenzene derived ligand for use in pillared paddle-wheel, as well as MOF-5 metal-organic frameworks. Encapsulating this AB moiety in a metal-organic framework yields the possibility for applications in photo-induced molecular release, molecular sensing, and more.

2. Background

In this chapter, the science of azobenzene will be discussed, as well as its utility in various fields of research. Metal-organic frameworks will be introduced, and the different framework structures which can result, in particular the pillared paddle-wheel and MOF-5 will be discussed.

2.1 Azobenzene

The azobenzene molecule consists of a nitrogen-nitrogen double bond in the center each bonded also to a benzene ring. Azobenzene derivatives in the presence of light will undergo photoisomerization from a stable *trans* form into a less stable *cis* form, and in the absence of light return to *trans*.



Scheme 1. Azobenzene Photoisomerization.

2.2 Metal-Organic Frameworks

Synthesizing crystalline, solid state materials with various different functionalities, dimensions, and all this with the same precision practiced in organic synthesis proves to be an outstanding challenge^[4]. The assembly and synthesis of metal-organic frameworks (MOFs) facilitates the need to assemble this solid in a single step^[5]. Synthesis of a MOF consists of the metal ion of choice, the desired organic ligands (linkers), solvent to dissolve the entire mixture, and all heated 80-120°C.

2.2.1 Pillared Paddle-wheel

Mixed-ligand metal-organic frameworks provide an interesting and functional structure, called a pillared paddle-wheel [4]. In a pillared paddle-wheel MOF, one linker forms the paddles and the other linker forms the pillars connecting the paddles in 3-D space. The versatility of the synthesis of a mixed-ligand MOF allows for construction of a framework with different functionalities and dimensions [4].

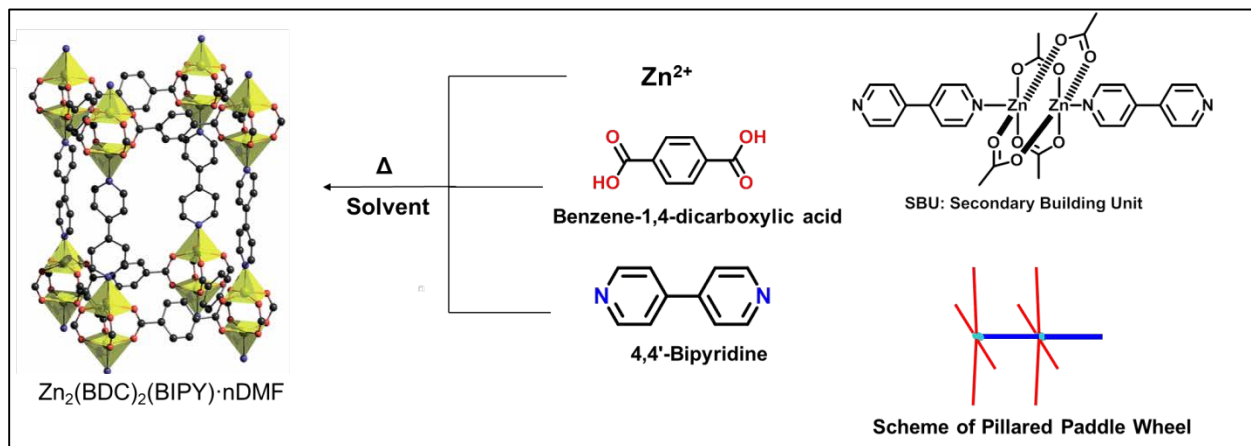


Figure 1. Pillared Paddle-Wheel Metal-Organic Framework [4].

2.2.2 MOF-5

Construction of the MOF-5 structure comes from a more simple scheme than the pillared paddle-wheel MOF. The MOF-5 variety uses one exclusive linker which coordinates with the desired metal. The desired metal, in the cases of this report, is often Zn. This Zn metal in a MOF-5 exists as Zn-O-C clusters when the MOF begins forming, where 4 Zn metals are clustered around oxygen, and then two Zn atoms at a time are coordinated by the organic linkers. These octahedral clusters result in an overall cubic framework. These MOFs maintain their scaffold when evacuated of their guest solvent, and can uptake gases [6].

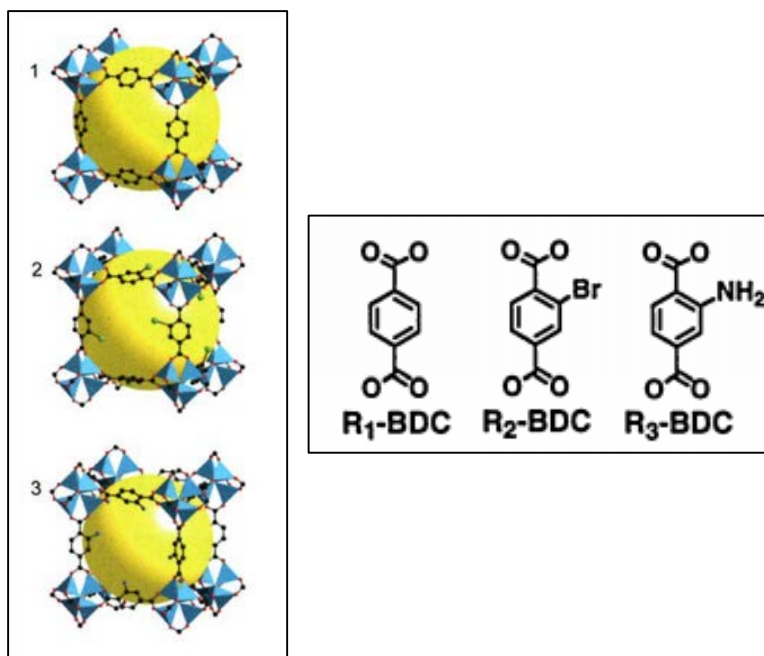


Figure 2. MOF-5 Metal-Organic Framework ^[7]. Derivatives of benzenedicarboxylic acid.

2.2.3 Azobenzene in a MOF

As mentioned before, azobenzene undergoes a photoisomerization under UV radiation, resulting in a switch from stable *trans* to less stable *cis*. In a MOF, the organic linkers and metals are rigid and coordinated in a solid state scaffold. An azobenzene in a MOF would be locked in the configuration which formed during synthesis, because of this expected locking, one would expect that UV radiation would not cause the MOF to photoisomerize. Recently, studies have shown that some chromophores which show no emission in dilute solutions can be turned on through aggregation, even in the case of a MOF scaffold ^[8]. Rigidifying fluorescent ligands into MOFs has the advantage of allowing for locked special conformations which can produce different fluorescence and absorption energies, as well as increasing the quantum yield by decreasing self-quenching in regular molecular aggregate ^[9].

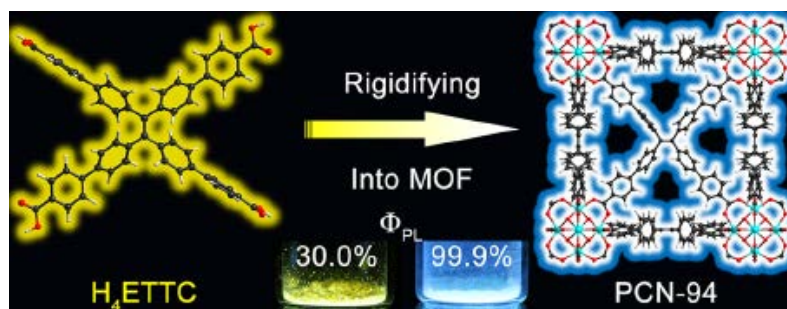


Figure 3. Rigidifying H4ETTC in a MOF to Improve Fluorescence^[9].

3. Methodology

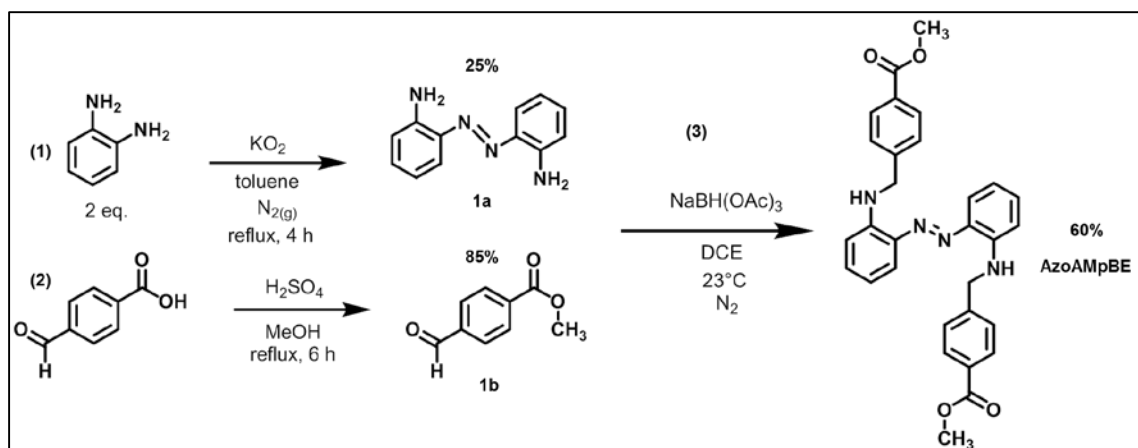
AzoAMpBE was synthesized in a multi-step process. Characterization of AzoAMpBE includes ¹H NMR, ¹³C NMR, FT-IR, and ESI-MS. X-ray diffraction was used to determine the crystal structure of AzoAMpBE.

3.1 General synthetic procedures

All materials were obtained in their highest pure form available from Fisher, Acros Organic or Alfa Aesar and used without further purification. Solvents were purged with argon and dried using a Seca Solvent Purification System. ¹H and ¹³C NMR were recorded using a 500 MHz Bruker-Biospin NMR instrument, and chemical shifts are reported in ppm on the δ scale relative to tetramethylsilane (TMS). FT-IR spectra were recorded using Bruker Optics Vertex 70 with MIR source as neat crystalline powdered samples and Spectrum 100 Version 10.4.2 (PerkinElmer) fitted with diamond ATR as oils.

3.2 AzoAMpBE Multi-step Synthesis

o-Phenylenediamine is refluxed under dry conditions and purified on a silica column, yielding diaminoazobenzene (DAAB). 4-carboxybenzaldehyde is esterified under acidic conditions, yielding methyl-4-carboxybenzaldehyde. DAAB and methyl-4-carboxybenzaldehyde are combined through reductive amination using NaBH(OAc)₃ under dry conditions for 48 hours, purified on an alumina column, and ultimately yielding AzoAMpBE. AzoAMpBE was recrystallized using slow evaporation to produce X-ray diffracting quality crystals.



Scheme 2: Multi-step synthesis of AzoAMpBE.

3.2.1 2,2'-Diaminoazobenzene (DAAB)

o-Phenylenediamine (1.063 g, 9.8 mmol) was dissolved in dried toluene (40 mL). The solution was stirred with the aid of low heat. KO_2 (2.85g, 40 mmol) was added to the solution. The reaction mixture was stirred for 4 hours at 85°C under N_2 gas. The mixture was then left stirring overnight at 23°C under N_2 . The reaction was then quenched by adding DI water (50 mL). The organic layer was extracted with EtOAc (3 x 100 mL) and dried over anhydrous Na_2SO_4 . Solvent removal under reduced pressure yielded a reddish-brown solid requiring further purification. Column chromatography on silica with DCM as a mobile phase, followed by solvent removal under reduced pressure yielded **1a** as a red solid. (0.277 g, 26% yield); ^1H NMR (500MHz, CDCl_3) δ 7.68 (d, 2H), 7.19 (d, 2H), 6.79 (t, 4H), 5.0-6.0 (s, broad, 4H).

3.2.2 Methyl-4-carboxybenzaldehyde

4-Carboxybenzaldehyde (1.00 g, 6.6 mmol) was dissolved in MeOH (25 mL). H_2SO_4 (5 mL) was added to the mixture dropwise. The reaction mixture was refluxed for 6 hours. Excess solvent was removed under reduced pressure, and leftover solvent mixture was neutralized with saturated NaHCO_3 . The organic layer was extracted with DCM (3 x 20 mL), dried over anhydrous Na_2SO_4 , and solvent was removed under reduced pressure yielding a yellowish-white crystalline product **1b**. (0.9084 g, 82% yield); ^1H NMR (500MHz, CDCl_3) δ 10.11 (s, 1H), 8.20 (d, $J=8.4$ Hz, 2H), 7.96 (d, $J=8.6$ Hz, 2H), 3.97 (s, 3H)

3.2.3 *AzoAMpBE*

DAAB (1.00 g, 4.71 mmol) was dissolved in dry DCE (90 mL). Methyl-4-carboxybenzaldehyde (2.30 g, 14. mmol) was added to the reaction mixture, and both reactants were left to stir for 1 h, allowing for the imine formation. NaBH(OAc)₃ (3.00 g, 14.1 mmol) was introduced and quickly yielded a dark brown mixture. The reaction mixture was stirred under N_{2(g)} for 48 h. Mixture was quenched with H₂O (1 mL), extracted with DCM (3 x 50 mL), dried over anhydrous Na₂SO₄, and solvent was removed under reduced pressure. The crude solid was further purified using column chromatography on alumina with diethyl ether as a mobile phase. The final product yielded was a reddish-orange solid, AzoAMpBE. (1.40 g, 60% yield); ¹H NMR (500MHz, CDCl₃) δ 8.47 (t, J=5.4 Hz, 2H), 8.00 (d, J=8.4 Hz, 4H), 7.61 (d of d, J=7.9 Hz, J=1.5 Hz, 2H), 7.43 (d, J=8.5 Hz, 4H), 7.17 (t, J=7.8 Hz, 2H), 6.76 (t, J=7.6 Hz, 2H), 6.66 (d of d, J=8.4 Hz, J=0.95 Hz, 2H), 4.53 (d, J=5.7 Hz, 4H), 3.90 (s, 6H). ¹³C NMR (500 MHz, CDCl₃) δ 166.8, 131.7, 130.0, 129.3, 127.2, 52.1, 47.4. FT-IR (neat, cm⁻¹) 3481.4, 3354.6, 3235.7, 3016.0, 2952.9, 2879.8, 2837.9, 1712.1, 1603.8, 1561.2, 1499.2, 1272.3, 1113.5, 1019.8, 760.6, 743.9. LC-MS (+ESI) (C₃₀H₂₈N₄O₄) observed m/z = 509.2.

4. Results and Discussion

The synthesis AzoAMpBE, and full resolution of its crystal structure, gives insight into the potential MOFs to synthesize with these dicarboxylate ligands.

4.1 AzoAMpBE Organic Linker

The final synthesis fully achieved was the synthesis of AzoAMpBE, which will ultimately result in a MOF linker, thus introducing the azobenzene moiety into the MOF.

4.1.1 *Synthesis of AzoAMpBE*

AzoAMpBE was synthesized by reductive amination of DAAB and the benzaldehyde. The DAAB amines form imine bonds with the aldehyde carbonyl carbon, and with introduction of the reducing agent NaBH(OAc)₃, the imine is reduced to an amine. Reductive amination is an

efficient an accessible reaction which can produce many DAAB derivatives with different groups bonded via the symmetrical amines.

4.1.2 X-Ray Crystallography

Single AzoAMpBE crystals were grown and placed on the Bruker Kappa Apex II single crystal x-ray. The red-orange, rhombic plate crystals were packed in a monoclinic space group and with an alternating planar packing. Figure 4 shows the crystal structure with atoms placed in idealized locations with the H-atoms omitted. The crystal structure parameters, as well as a full crystal structure are in found in Appendix A.

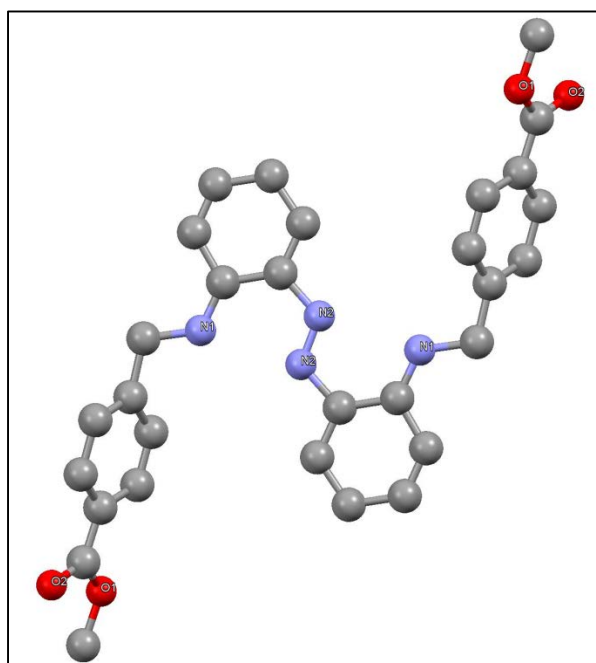
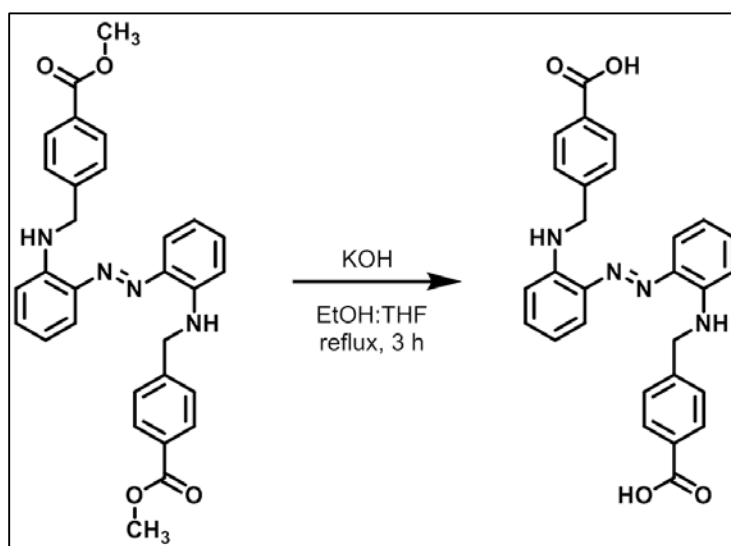


Figure 4. AzoAMpBE Crystal Structure. Atoms are placed in idealized locations. H-atoms omitted.

4.2 Synthesis of AzoAMpBA

Synthesis of AzoAMpBA was a rather elusive synthesis. Saponification of the benzoic ester groups into benzoic acid, in a largely conjugated system, requires stronger conditions than a normal hydrolysis, and multiple conditions were attempted (KOH in MeOH, KOH in MeOH reflux, KOH in EtOH reflux, LiOH in MeOH, LiOH in MeOH reflux). When the reaction mixture was examined via TLC, a distinct product was formed in a majority of the reactions,

however through extraction and separation, insoluble products were lost. Extraction of the organic layer proved to be difficult with the AzoAMpBA due to the polar groups of acids and secondary amines. Final NMR of suspected product yielded crude results where aromatic, aliphatic, and amine hydrogens could be parsed out, but the methyl ester group was not found. This result meant that the ester was indeed hydrolyzed, however the rest of the NMR was nearly unperceivable. NMR could only be performed in DMSO for the resulting hydrolysis products, as solubility in less polar organic solvents was low. ESI-MS however, gave a much more clear result for the AzoAMpBA product. ESI-MS concludes with an m/z of 481.2 ($C_{28}H_{24}N_4O_4$).

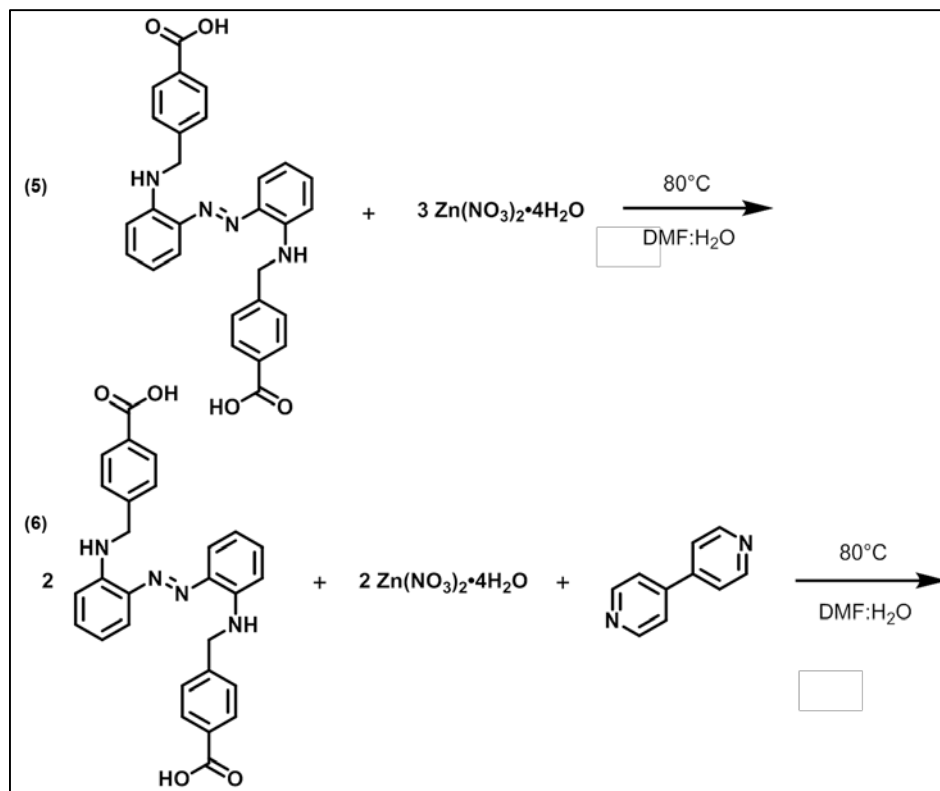


Scheme 3. Saponification of AzoAMpBE.

4.2.1 Proposed Synthesis of AzoAMpBA MOF

The proposed syntheses of AzoAMpBA MOFs in Scheme 3 follow the usually stoichiometries for MOF-5 and pillared paddle-wheel, respectively. AzoAMpBA, as well as 3 equivalents of Zn in solvent and heated to varying temperatures (80°C and higher) will produce a MOF-5 coordinate with the 4 Zn metal core surrounded by carboxylic acid groups. 2 equivalents of AzoAMpBA, 2 equivalents of Zn, and 1 equivalent of 4,4'-bipyridine will produce a pillared paddle-wheel structure, with 4,4'-bipy bridging the AzoAMpBA paddles in the MOF.

Adjustment to the solvent system, as well as to the reaction temperature will facilitate the growth of single MOF crystals for x-ray crystallography.



Scheme 4: Syntheses of AzoAMpBA MOFs. Synthesis (5) results in the MOF-5 configuration where only acids coordinate with the Zn core. Synthesis (6) results in a pillared paddle-wheel, with 4,4'-bipyridine aiding formation of the configuration.

5. Conclusions and Future Directions

The goal of this project was to develop fluorescent aminoazobenzene metal-organic frameworks, consisting of synthesized aminoazobenzene ligands coordinated around metal cores, constructing 3-D rigid scaffolds. These scaffolds, due to rigidifying the photoisomerizable azobenzene moiety, have the capacity for absorbance and emission of light, and thus providing fluorescence. Achieved in the span of this project was the thorough and consistent synthetic procedure for developing a workable ligand, AzoAMpBE, for construction of metal-organic frameworks, and listed below are some steps before the characterization and investigation of the AzoAMpBA metal-organic frameworks proposed.

The first step which was almost complete was the purification of AzoAMpBA after synthesis. The synthesis proved successful by ^1H NMR and ESI-MS, however attaining a usable quantity of AzoAMpBA is difficult with the current purification procedure. By considering other purification methods, such as a simple column or recrystallization, a workable amount of AzoAMpBA could be isolated for use in the MOF synthesis.

The second step would be performing the proposed MOF syntheses for MOF-5 and pillared paddle-wheel. These MOF syntheses could prove difficult as well and so preparation of different solvent systems and temperature runs, as well as some patience, will yield a crystal with sufficient crystallographic quality. Once the synthesis of these MOFs is complete, then the spectroscopic analysis follows. Fluorescence spectroscopy of the Azo MOFs will give results of quantum yield, absorbance, and emission and answer the viability of AzoAMpBA as a fluorescent ligand in a MOF. Success in strong fluorescence ultimately leads to applications in fluorescent materials, and molecular solid-state sensing.

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7. Supplementary Information

7.1 AzoAMpBE Crystal Parameters

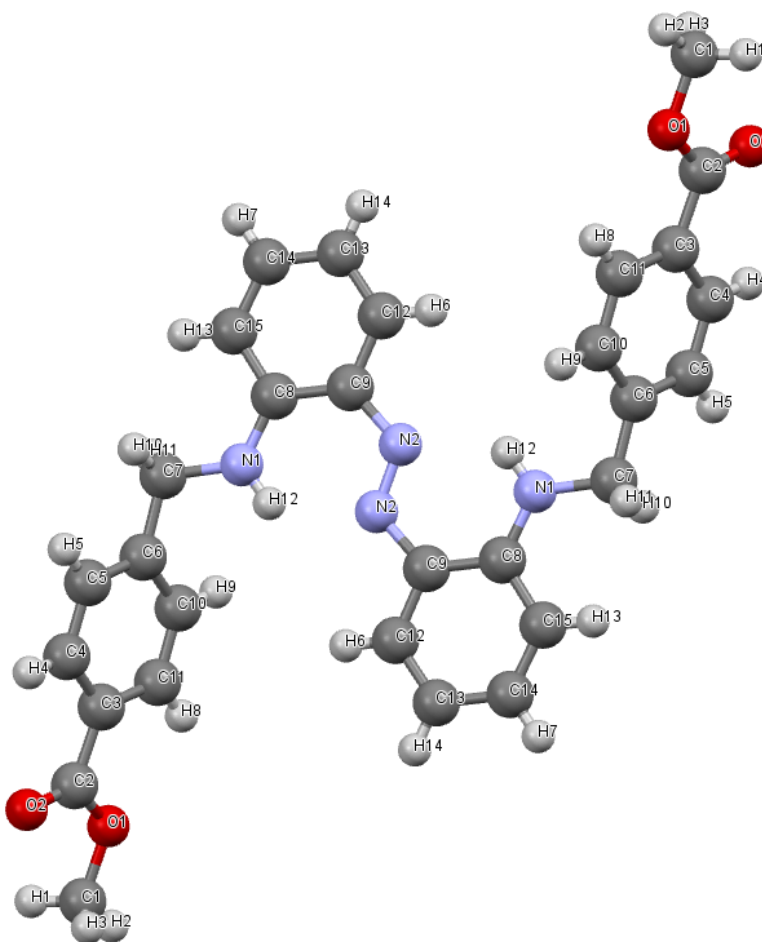


Figure S1. Complete Labeling of AzoAMpBE. Hydrogen atoms are placed at idealized positions.

Table S1: Crystallographic parameters for AzoAMpBE

formula	C₃₀H₂₈N₄O₄
formula wt (M_r)	508.56
Crystal system, space group	Monoclinic, P-2
a, Å	13.0965
b, Å	13.3909
c, Å	7.5594
α, °	90
β, °	98.858
γ, °	90
V, Å³	1309.91
Z	4
ρ_{calcd} (g cm⁻³)	1.289
absorp. coeff. μ (mm⁻¹)	0.087
temp, K	296
total no. data	14571
no. unique data	3597
obs. Data	2554
R, %	0.046
wR2, %	0.157
no. of parameters	173
max/min peaks, e/Å	0.23, -0.21
^a Observation criterion: $I > 2\sigma(I)$. ^b $R = \sum F_o - F_c / \sum F_o$ ^c $wR2 = [\sum (w (F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$	

Table S2: AzoAMpBE fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O1	0.94466 (8)	0.41304 (9)	0.35499 (17)	0.0654 (3)
O2	0.97715 (10)	0.25345 (10)	0.42296 (19)	0.0820 (4)
N1	0.48448 (8)	0.37183 (8)	0.71289 (14)	0.0392 (3)
H12	0.5337	0.4108	0.7588	0.047*
N2	0.45545 (7)	0.49884 (7)	1.02410 (12)	0.0345 (2)
C1	1.04258 (14)	0.42058 (17)	0.2922 (3)	0.0808 (6)
H2	1.0532	0.4882	0.2567	0.121*
H1	1.0430	0.3770	0.1915	0.121*
H3	1.0969	0.4016	0.3864	0.121*
C2	0.92053 (11)	0.32411 (12)	0.41496 (19)	0.0515 (4)
C3	0.81477 (10)	0.32267 (10)	0.46342 (16)	0.0426 (3)
C4	0.77553 (11)	0.23295 (11)	0.51353 (18)	0.0472 (3)
H4	0.8164	0.1759	0.5217	0.057*
C5	0.67623 (11)	0.22774 (10)	0.55143 (17)	0.0445 (3)
H5	0.6509	0.1670	0.5858	0.053*
C6	0.61338 (10)	0.31132 (9)	0.53925 (15)	0.0392 (3)
C7	0.50371 (11)	0.30332 (11)	0.57413 (18)	0.0469 (3)
H11	0.4569	0.3179	0.4649	0.056*
H10	0.4905	0.2356	0.6100	0.056*
C8	0.39223 (9)	0.37792 (8)	0.77478 (15)	0.0334 (3)
C9	0.37977 (9)	0.43901 (8)	0.92346 (16)	0.0339 (3)
C10	0.65323 (11)	0.40152 (10)	0.49042 (19)	0.0464 (3)
H9	0.6123	0.4586	0.4831	0.056*
C11	0.75292 (11)	0.40749 (10)	0.4525 (2)	0.0470 (3)
H8	0.7787	0.4683	0.4197	0.056*
C12	0.28323 (10)	0.44296 (10)	0.98157 (19)	0.0428 (3)
H6	0.2753	0.4830	1.0791	0.051*
C13	0.20006 (10)	0.38931 (11)	0.8984 (2)	0.0492 (3)
H14	0.1365	0.3932	0.9384	0.059*
C14	0.21237 (10)	0.32954 (10)	0.7546 (2)	0.0495 (3)
H7	0.1564	0.2929	0.6978	0.059*
C15	0.30580 (10)	0.32320 (9)	0.69353 (18)	0.0431 (3)
H13	0.3120	0.2820	0.5967	0.052*

Table S3: AzoAMpBE atomic displacement parameters (\AA^2).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0510 (6)	0.0709 (8)	0.0802 (8)	-0.0042 (5)	0.0287 (6)	-0.0071 (6)
O2	0.0550 (7)	0.0911 (10)	0.1024 (10)	0.0295 (6)	0.0194 (7)	0.0152 (8)
N1	0.0353 (5)	0.0417 (6)	0.0410 (6)	-0.0053 (4)	0.0075 (4)	-0.0133 (4)
N2	0.0329 (5)	0.0313 (5)	0.0398 (5)	0.0000 (4)	0.0073 (4)	-0.0048 (4)
C1	0.0539 (10)	0.1035 (15)	0.0924 (14)	-0.0138 (9)	0.0347 (10)	-0.0138 (11)
C2	0.0430 (7)	0.0666 (10)	0.0442 (7)	0.0064 (6)	0.0044 (6)	-0.0046 (6)
C3	0.0416 (7)	0.0514 (8)	0.0345 (6)	0.0053 (5)	0.0046 (5)	-0.0021 (5)
C4	0.0510 (8)	0.0448 (7)	0.0442 (7)	0.0115 (6)	0.0026 (6)	0.0019 (5)
C5	0.0546 (8)	0.0388 (7)	0.0398 (7)	-0.0024 (5)	0.0065 (6)	0.0004 (5)
C6	0.0453 (7)	0.0426 (7)	0.0308 (6)	-0.0030 (5)	0.0090 (5)	-0.0074 (5)
C7	0.0484 (7)	0.0502 (8)	0.0440 (7)	-0.0113 (6)	0.0136 (5)	-0.0166 (6)
C8	0.0335 (6)	0.0312 (6)	0.0349 (6)	-0.0021 (4)	0.0037 (4)	0.0015 (4)
C9	0.0322 (6)	0.0306 (5)	0.0392 (6)	-0.0001 (4)	0.0059 (4)	0.0008 (4)
C10	0.0486 (8)	0.0388 (7)	0.0545 (8)	0.0060 (5)	0.0162 (6)	-0.0007 (6)
C11	0.0495 (8)	0.0418 (7)	0.0525 (8)	0.0002 (5)	0.0171 (6)	0.0024 (6)
C12	0.0382 (7)	0.0443 (7)	0.0480 (7)	0.0006 (5)	0.0134 (5)	-0.0006 (5)
C13	0.0323 (6)	0.0567 (8)	0.0603 (9)	-0.0049 (5)	0.0124 (6)	0.0076 (7)
C14	0.0376 (7)	0.0513 (8)	0.0572 (8)	-0.0130 (6)	-0.0003 (6)	0.0047 (6)
C15	0.0426 (7)	0.0418 (7)	0.0434 (7)	-0.0090 (5)	0.0022 (5)	-0.0036 (5)

Table S4: Geometric parameters (\AA , $^\circ$).

O1—C2	1.3296 (19)	C6—C10	1.3881 (18)
O1—C1	1.4379 (18)	C6—C7	1.5035 (17)
O2—C2	1.1979 (18)	C7—H11	0.9700
N1—C8	1.3635 (14)	C7—H10	0.9700
N1—C7	1.4445 (16)	C8—C15	1.4076 (16)

N1—H12	0.8600	C8—C9	1.4197 (16)
N2—N2ⁱ	1.2752 (18)	C9—C12	1.4019 (16)
N2—C9	1.4039 (15)	C10—C11	1.3813 (19)
C1—H2	0.9600	C10—H9	0.9300
C1—H1	0.9600	C11—H8	0.9300
C1—H3	0.9600	C12—C13	1.3738 (19)
C2—C3	1.4863 (19)	C12—H6	0.9300
C3—C4	1.382 (2)	C13—C14	1.379 (2)
C3—C11	1.3902 (19)	C13—H14	0.9300
C4—C5	1.3758 (19)	C14—C15	1.3752 (18)
C4—H4	0.9300	C14—H7	0.9300
C5—C6	1.3840 (19)	C15—H13	0.9300
C5—H5	0.9300		
C2—O1—C1	116.51 (13)	C6—C7—H11	109.4
C8—N1—C7	123.36 (10)	N1—C7—H10	109.4
C8—N1—H12	118.3	C6—C7—H10	109.4
C7—N1—H12	118.3	H11—C7—H10	108.0
N2ⁱ—N2—C9	117.37 (11)	N1—C8—C15	120.97 (11)
O1—C1—H2	109.5	N1—C8—C9	121.47 (10)
O1—C1—H1	109.5	C15—C8—C9	117.56 (11)
H2—C1—H1	109.5	C12—C9—N2	113.84 (10)
O1—C1—H3	109.5	C12—C9—C8	119.27 (11)
H2—C1—H3	109.5	N2—C9—C8	126.89 (10)
H1—C1—H3	109.5	C11—C10—C6	120.77 (12)
O2—C2—O1	123.15 (15)	C11—C10—H9	119.6
O2—C2—C3	124.78 (15)	C6—C10—H9	119.6
O1—C2—C3	112.04 (12)	C10—C11—C3	120.08 (12)
C4—C3—C11	119.24 (13)	C10—C11—H8	120.0
C4—C3—C2	118.60 (12)	C3—C11—H8	120.0
C11—C3—C2	122.10 (13)	C13—C12—C9	121.78 (12)
C5—C4—C3	120.29 (12)	C13—C12—H6	119.1
C5—C4—H4	119.9	C9—C12—H6	119.1
C3—C4—H4	119.9	C12—C13—C14	118.92 (12)

C4—C5—C6	121.11 (12)	C12—C13—H14	120.5
C4—C5—H5	119.4	C14—C13—H14	120.5
C6—C5—H5	119.4	C15—C14—C13	121.22 (12)
C5—C6—C10	118.51 (12)	C15—C14—H7	119.4
C5—C6—C7	120.35 (12)	C13—C14—H7	119.4
C10—C6—C7	121.13 (12)	C14—C15—C8	121.25 (12)
N1—C7—C6	111.11 (10)	C14—C15—H13	119.4
N1—C7—H11	109.4	C8—C15—H13	119.4
C1—O1—C2—O2	2.2 (2)	N2ⁱ—N2—C9—C8	1.8 (2)
C1—O1—C2—C3	-175.66 (13)	N1—C8—C9—C12	179.79 (11)
O2—C2—C3—C4	-3.3 (2)	C15—C8—C9—C12	-0.50 (16)
O1—C2—C3—C4	174.58 (13)	N1—C8—C9—N2	-0.11 (18)
O2—C2—C3—C11	179.50 (15)	C15—C8—C9—N2	179.60 (11)
O1—C2—C3—C11	-2.64 (19)	C5—C6—C10—C11	0.8 (2)
C11—C3—C4—C5	0.3 (2)	C7—C6—C10—C11	-177.73 (11)
C2—C3—C4—C5	-177.03 (11)	C6—C10—C11—C3	-0.1 (2)
C3—C4—C5—C6	0.5 (2)	C4—C3—C11—C10	-0.4 (2)
C4—C5—C6—C10	-1.00 (19)	C2—C3—C11—C10	176.78 (12)
C4—C5—C6—C7	177.58 (11)	N2—C9—C12—C13	179.85 (12)
C8—N1—C7—C6	-177.95 (11)	C8—C9—C12—C13	-0.06 (19)
C5—C6—C7—N1	124.13 (13)	C9—C12—C13C14	0.4 (2)
C10—C6—C7—N1	-57.34 (16)	C12—13—C14—C1	-0.2 (2)
C7—N1—C8—C15	-6.13 (18)	C13—C14—C15—C8	-0.4 (2)
C7—N1—C8—C9	173.56 (12)	N1—C8—C15—C14	-179.56 (11)
N2ⁱ—N2—C9—C12	-178.12 (12)	C9—C8—C15—C14	0.73 (18)

7.2 DAAB Characterization Data

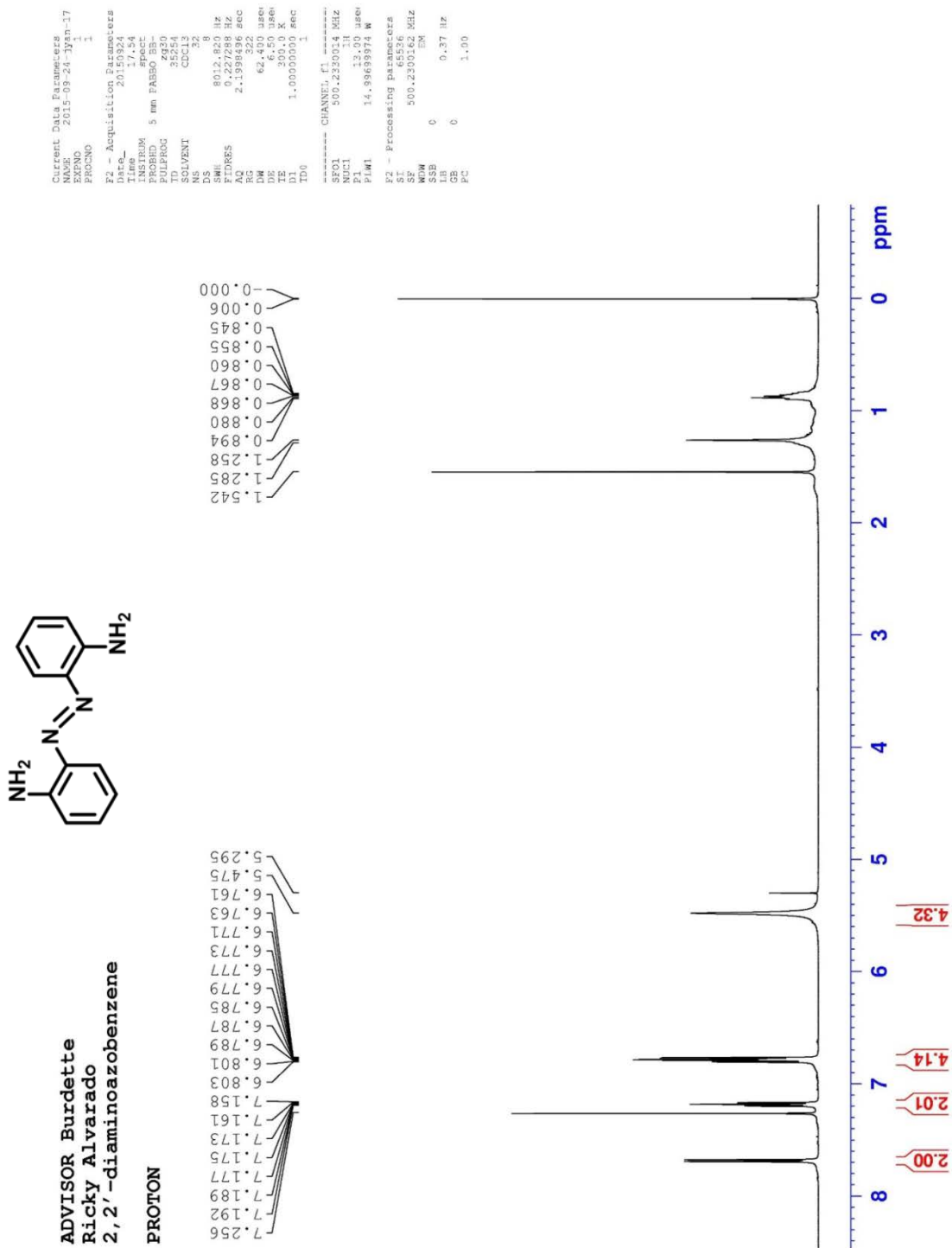


Figure S2. ¹H NMR of DAAB

7.3 Methyl-4-carboxybenzaldehyde Characterization Data

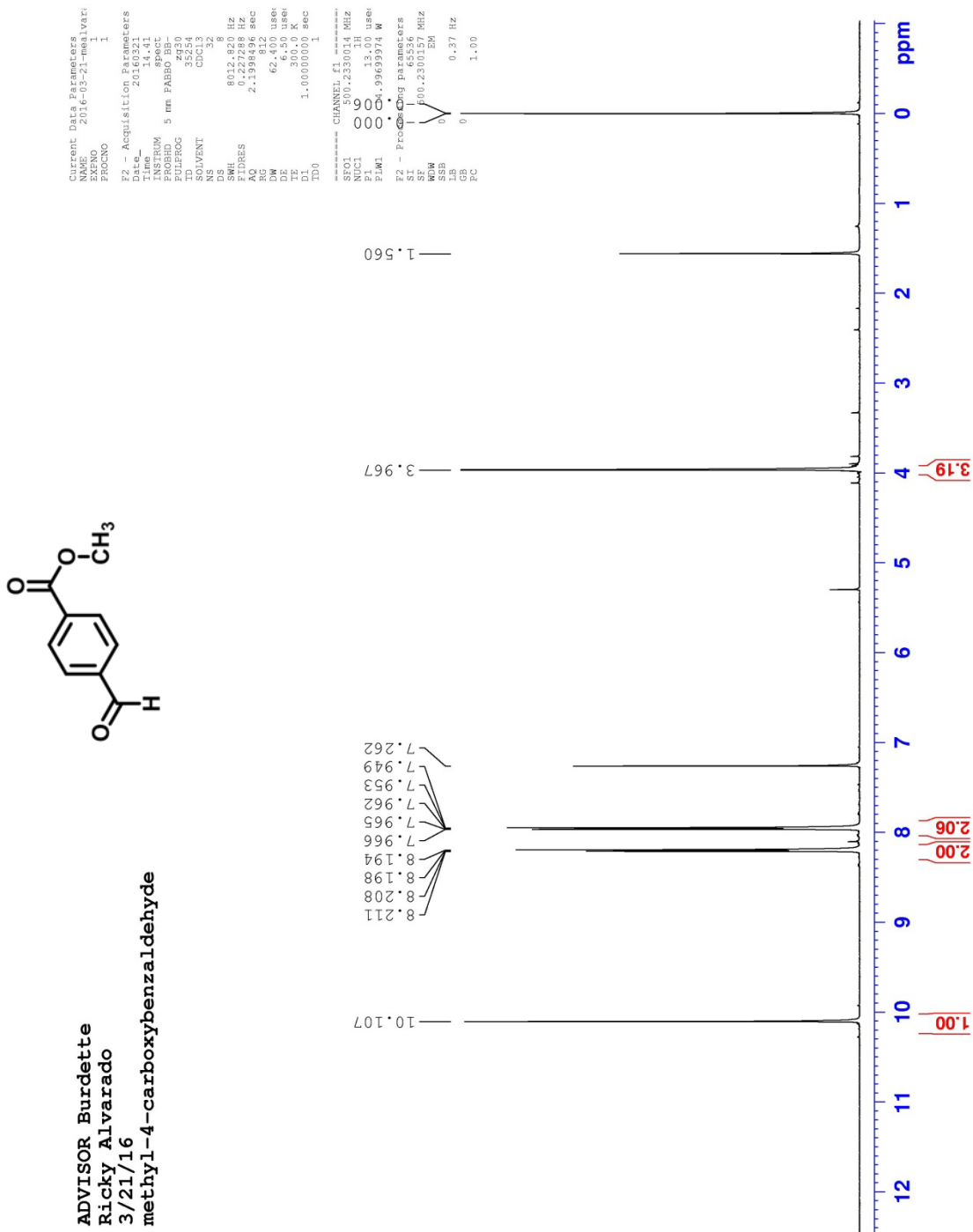


Figure S3. ¹H NMR of Methyl-4-carboxybenzaldehyde

7.4 AzoAMpBE Characterization Data

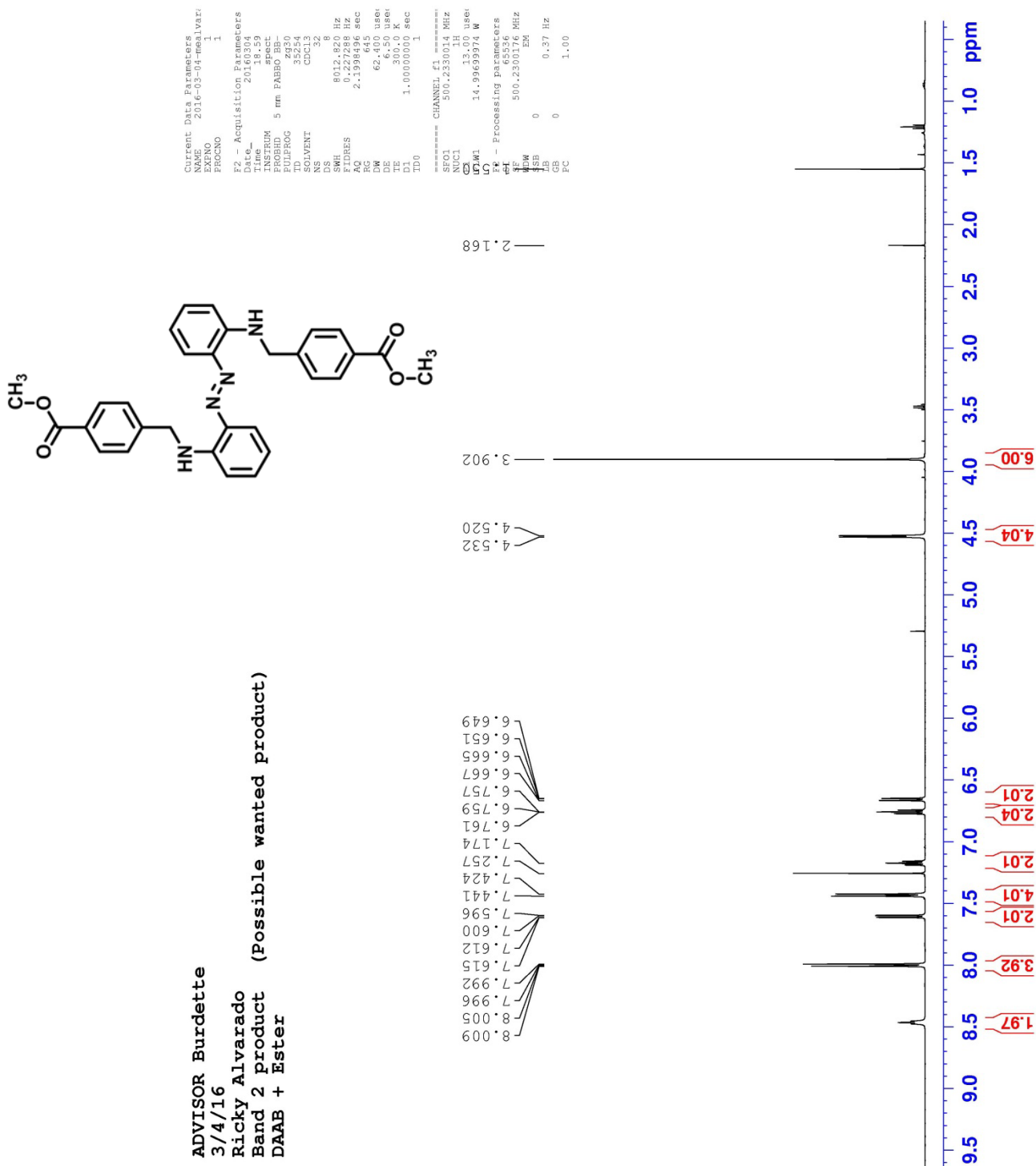


Figure S4. ¹H NMR of AzoAMpBE

**ADVISOR Burdette
AzoAMpBE**

CARBON

Current Data Parameters
NAME: 2016 04 27 ResulVerado
EXPNO: 1
PROCNO: 1

F2 - Acquisition Parameters
Date_UTC: 2016 04 27
Time: 23:15:18

INSTRUM: spect
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ZULPOC
PULPROG: zgpg30
SOLVENT: CDCl3
NS: 1024
DS: 4
SWH: 97500.000 Hz
FIDRES: 0.833087 Hz
AQ: 0.6092467 sec
RG: 327.500
DM: 13.332 usec
DC: 6.50 usec
DE: 0.500000 Hz
TE: 300.2 K
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D11: 0.2500000 sec
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D16: 0.2500000 sec
D17: 0.2500000 sec
D18: 0.2500000 sec
D19: 0.2500000 sec
D20: 0.2500000 sec

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P1: 9.10 usec
PL1: 0.00 dB
PC1: 39.99399940 W

===== CHANNEL f2 =====
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P2: 9.10 usec
PL2: 0.00 dB
PC2: 39.99399940 W

===== CHANNEL f3 =====
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===== CHANNEL f5 =====
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PC7: 39.99399940 W

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===== CHANNEL f9 =====
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PC9: 39.99399940 W

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P10: 9.10 usec
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===== CHANNEL f11 =====
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PC11: 39.99399940 W

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PC14: 39.99399940 W

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===== CHANNEL f16 =====
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PL16: 0.00 dB
PC16: 39.99399940 W

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===== CHANNEL f18 =====
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P36: 9.10 usec
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PC36: 39.99399940 W

===== CHANNEL f37 =====
NUC37: 13C
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PC37: 39.99399940 W

===== CHANNEL f38 =====
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P38: 9.10 usec
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PC38: 39.99399940 W

===== CHANNEL f39 =====
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P39: 9.10 usec
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PC39: 39.99399940 W

===== CHANNEL f40 =====
NUC40: 13C
P40: 9.10 usec
PL40: 0.00 dB
PC40: 39.99399940 W

===== CHANNEL f41 =====
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P41: 9.10 usec
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PC41: 39.99399940 W

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P43: 9.10 usec
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===== CHANNEL f44 =====
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===== CHANNEL f45 =====
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P45: 9.10 usec
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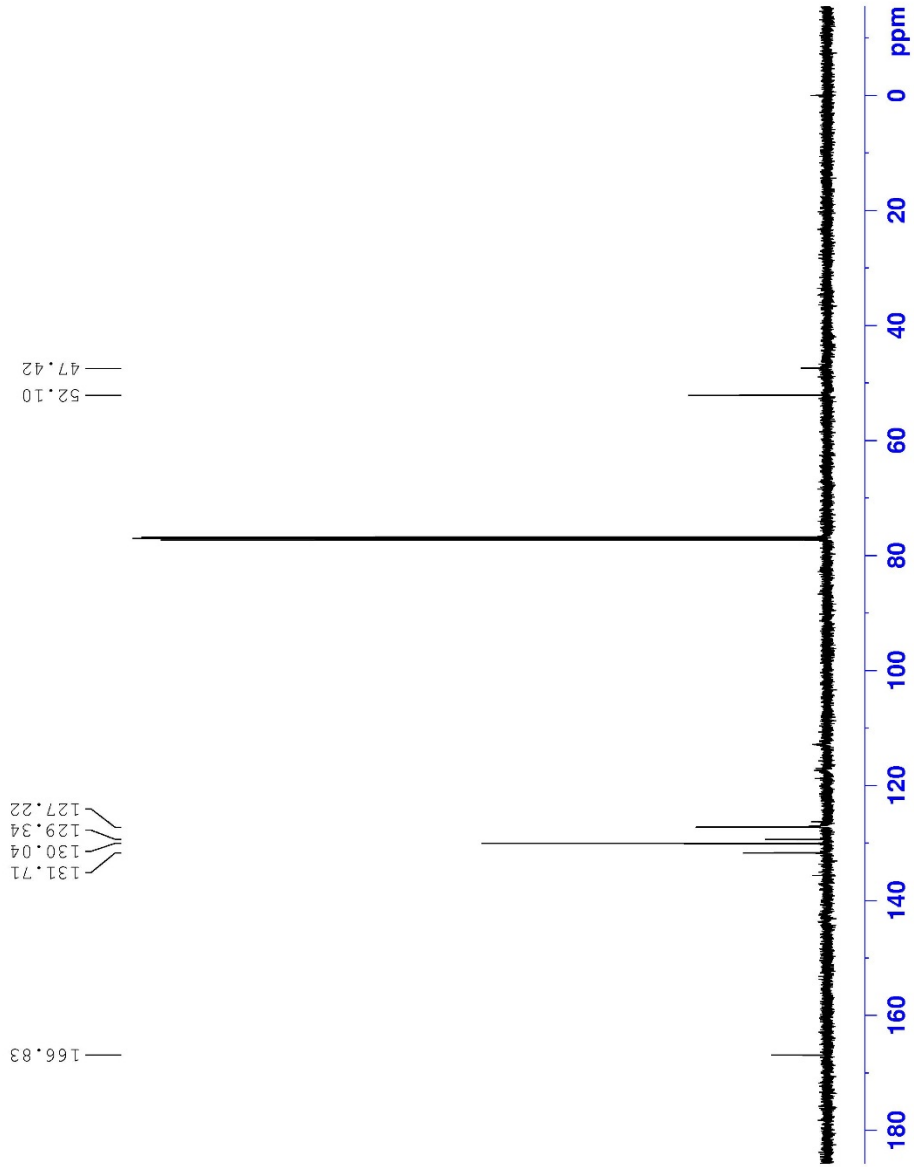


Figure S5. ^{13}C NMR of AzoAMpBE

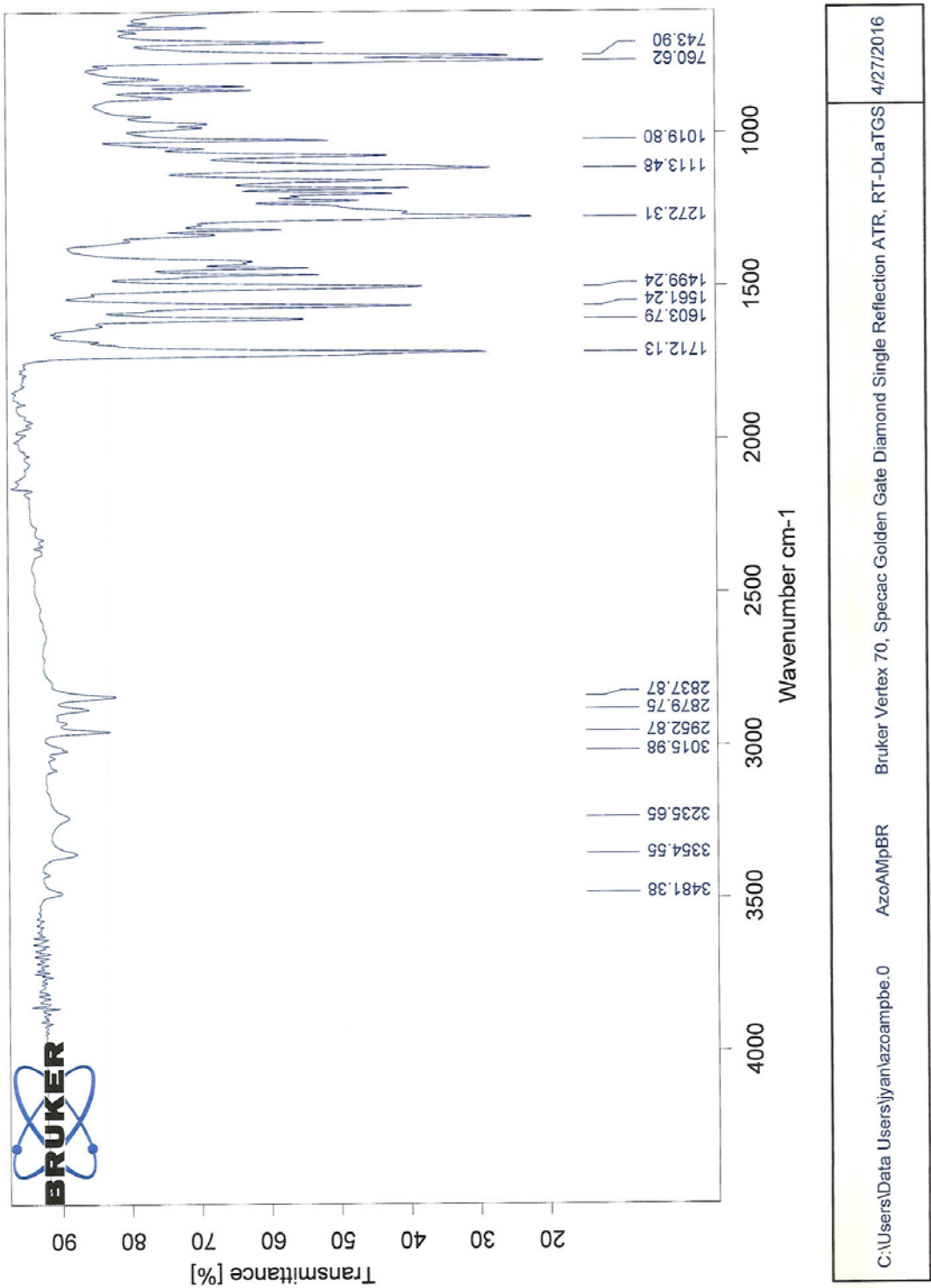


Figure S6. FT-IR of AzoAMpBE

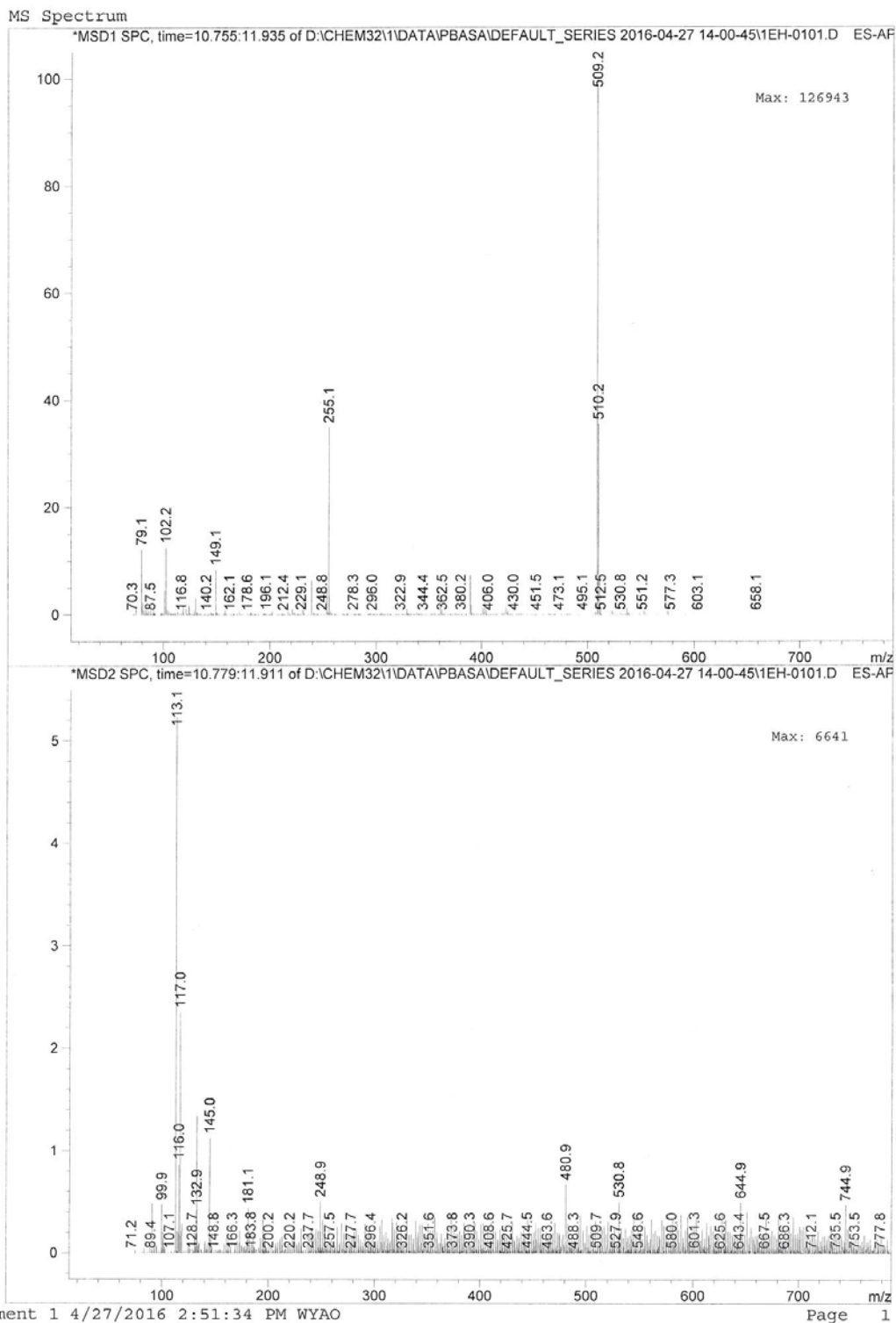


Figure S7. ESI-MS of AzoAMpBE

7.5 AzoAMpBA Characterization Data

Print of window 80: MS Spectrum

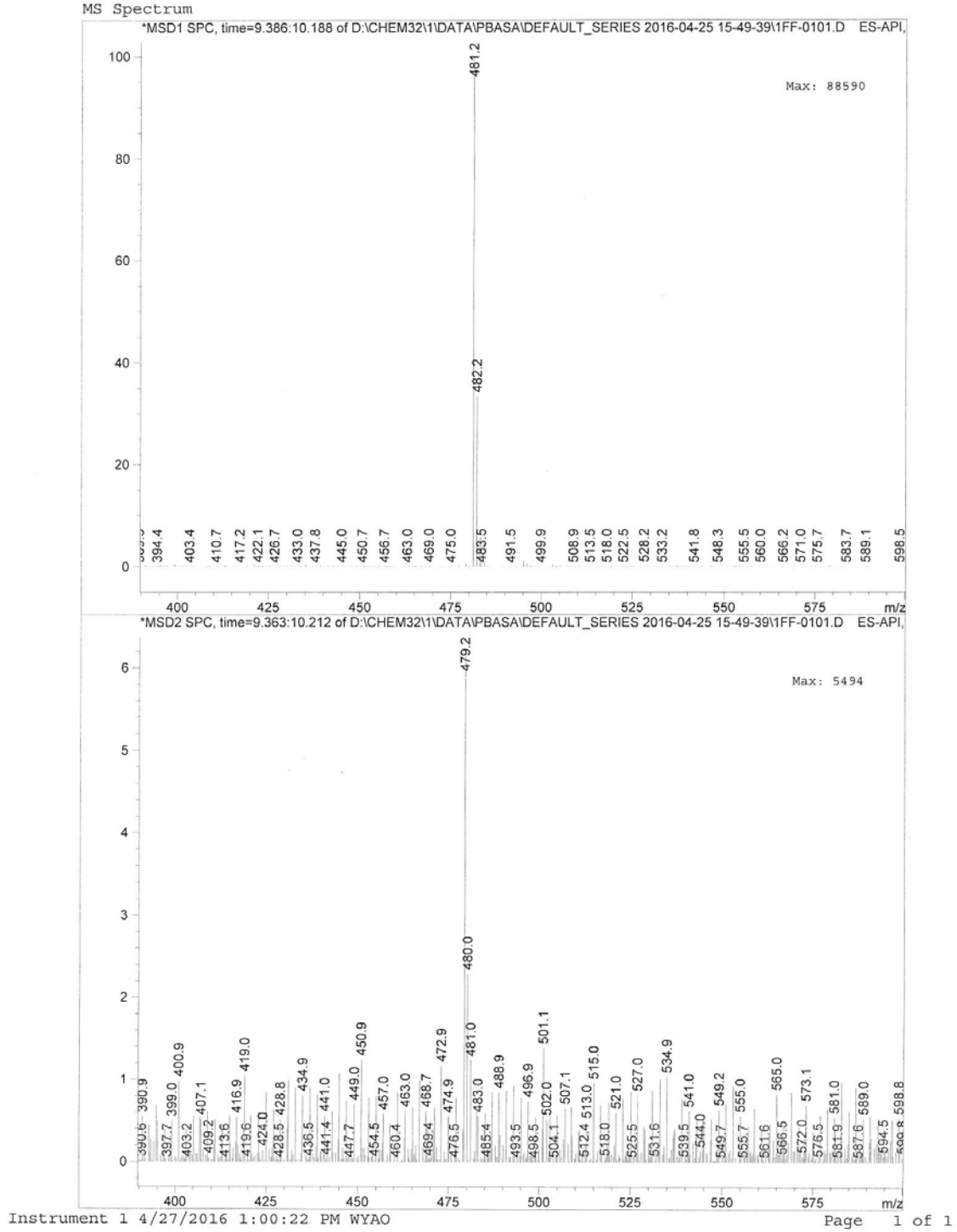


Figure S8. ESI-MS of AzoAMpBA