

A Convenient Synthesis and Spectral Studies of Diamines

Derivatives

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Abstract

A new series of substituted anthranilic esters derivatives linked with a 1,3-dithiolane and benzyloximino moiety was synthesized using the simple esterification reaction and products were fully characterized. The isolated yields of these compounds range from 59 to 96%. 1,3-dithiolane ester and the benzyloxy substituted diamine derivatives are white solids and stable to air and moisture. The synthesized compounds can exhibit UV-vis absorption properties by their structures with an amine or amide group. It is observed that absorption maximum is excellent for 2,6-disubstituted benzyloxy esters which can be explained by electron transfer or conjugation is steric effect in ortho substitution from the amino group and the amide group.

Keywords: dithiolane; benzyloximates, diamines, supramolecular design, spectral studies

INTRODUCTION

In recent years, crystal engineering and construction of coordination networks with fascinating structural topologies have attracted great attention owing to their potential as functional materials.¹⁻² Concurrently, the development of multidimensional networks based primarily on linking metal centers with rigid bridging components, such as 4,4'-bipyridine has been initiated.³³

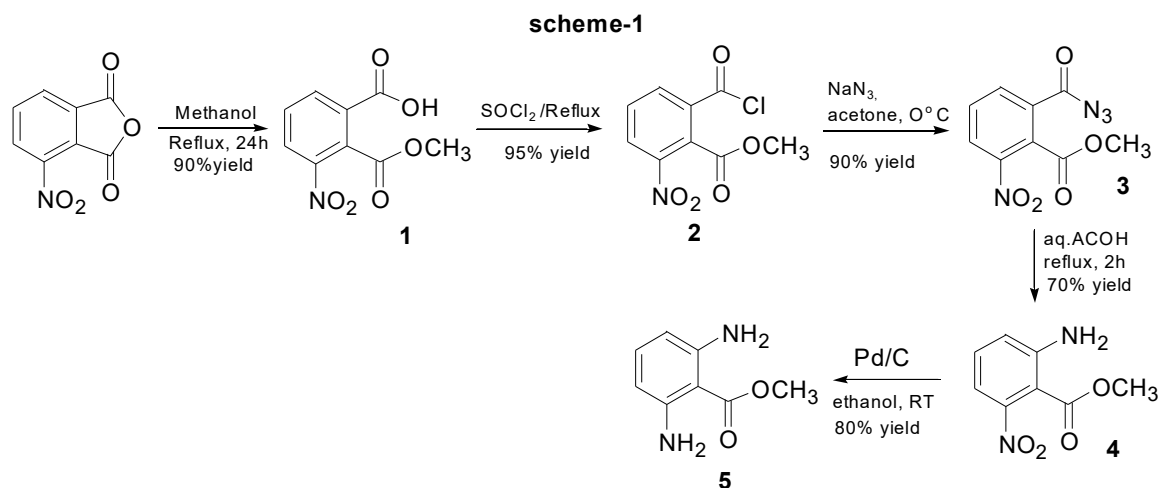
Since then chemiluminescence's of 3-aminophthalhydrazide was first investigated by Albrecht,⁴ the acyl hydrazides are growing interest in the development of luminescent materials due to their potential application in emissive devices.⁵ Moreover, the attractive and promising practical applications in many other areas have stimulated further investigations in light-emitting devices, nonlinear optics, and functional films,⁶ conjugated polymers,⁷ logic functions of molecular-scale,⁸ uranyl salts, saccharides, and aromatic organic molecular crystals which exhibit tribofluorescence or tribophosphorescence from the molecules comprising the crystal and/or nitrogen emission triboluminescence,⁹ azopolymers.¹⁰ Metal directed assembly have been used to generate luminescent materials¹¹ based on complexation of transition metal and multifunctional bridging ligands and is one of many useful strategies to design extended frameworks of various topology and dimensionality. Ligands with amino group of anthranilic acid derivative backbones may affect the properties of the resulting emissions by promoting the coupling of metal atoms through its emission systems. It has been of interest to use photoactive ligands as building blocks to generate supramolecular polymers. Some of these workers have been concerned with the influence of structural changes upon the chemiluminescent properties.¹²⁻¹³

PRESENT WORK

The luminescence is appreciably enhanced when the hydroxyl or amine groups are in the ortho position. The efficiency of chromogenic sensing is more remarkably affected by the chemical environment of the anthranilic acid derivatives, depending on the presence of a protecting free amino group or amide group. Taking into account these considerations, it is possible to optimize the uv-vis sensing of the molecules by structure modification. Keeping the above applications in mind, we have investigated the synthesis and characterization of a series of 2,6- and 2,3-diamino

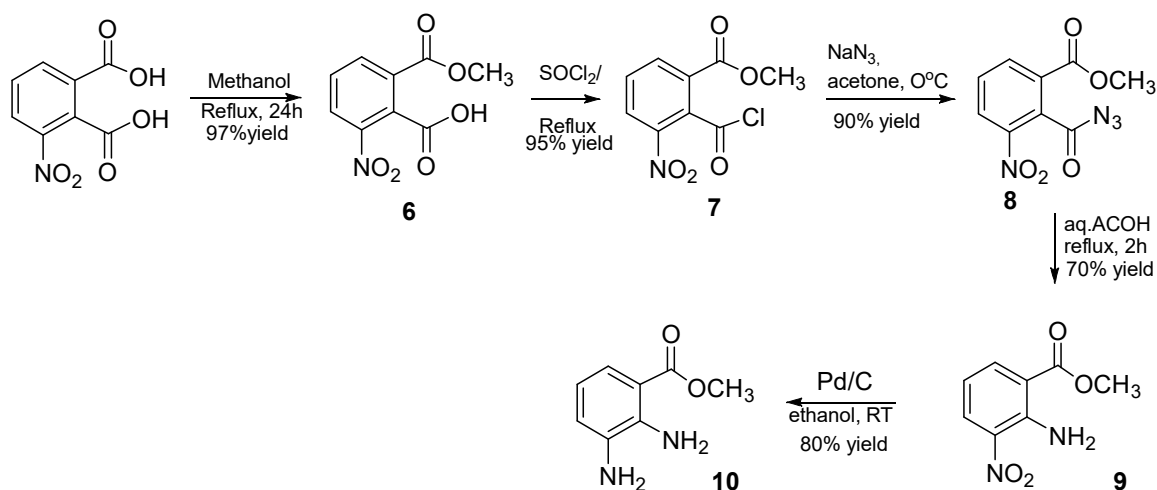
benzoic methyl esters derivatives with various electron-donor groups at the 2,6- or 2,3-positions. 3-nitrophthalic acid and its anhydrides was chosen as a starting material due to its ready availability and to the fact that it can be easily converted to diamine derivative **5** and **10**, a compound that can be selectively functionalized at the amino positions. The electron donor groups chosen for this study were pyridyl, 1,3-dithiolanyl, benzyloximate, and thiophenyl ether, all known for their Lewis basicity and ligating potential. This investigation reflects our ongoing interest in synthesizing new organic ligands for supramolecular design.¹⁴⁻²¹

The initial step is the functionalization described herein was the conversion of 3-nitrophthalic anhydride and 3-nitrophthalic acid to 2,6-diamino benzoic acid methyl ester (**5**) and 2,3-diamino benzoic acid methyl ester (**10**) respectively (scheme 1 and 2).



3-nitrophthalic anhydride under methanol reflux conditions gives mixture of **1** and **6** in ratio of 9:1 (by NMR) in 98% yield. The mixture on treatment with thionyl chloride under heating condition gives corresponding mixture of acid chlorides **2** and **7** from which the acyl azide **3** and **8** were prepared by treating with sodium azide in acetone in 90%. The mixture of acyl azides **3** and **8** under Curtius rearrangement followed by column chromatography purification gives two

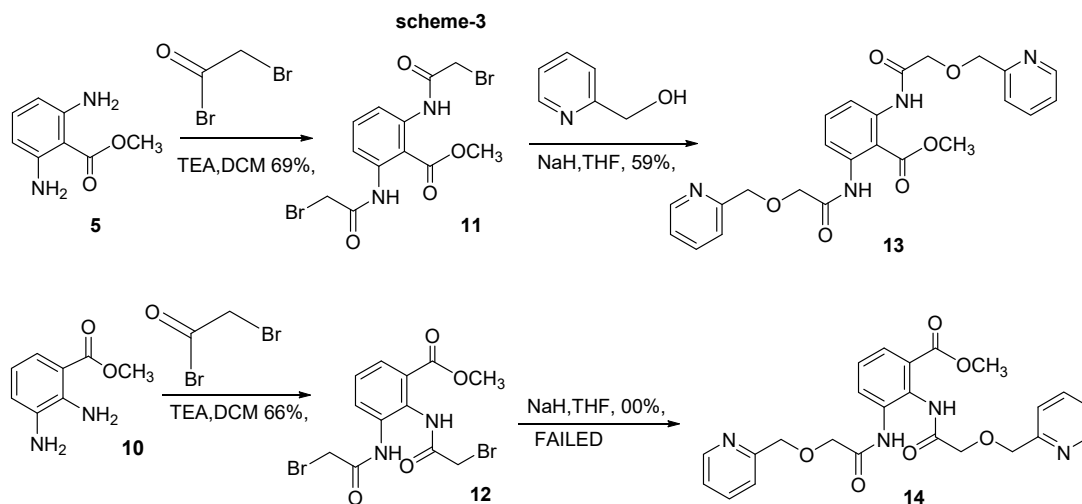
isolated product **4** and **9** in 70% and 5% respectively. The compound **4** under palladium charcoal treatment gives product **5** in 90% yields.



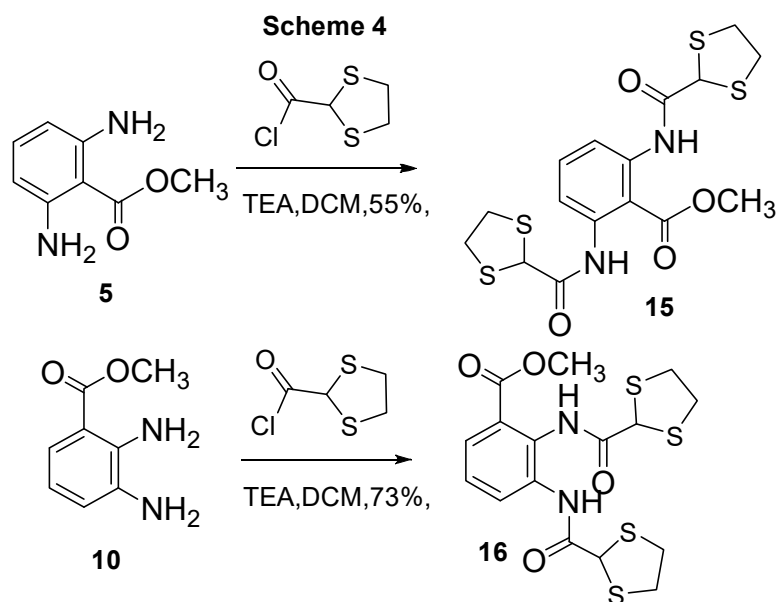
The compound **9** was independently prepared in four steps by regioselective esterification of 3-nitro phthalic acid, followed by its acid chloride **7** in 95% yield, which on acyl azide conversions **8** in 70% yield, followed by and Curties rearrangement. In these it is 100% regioselective conversion, no trace of its corresponding isomer was detected even in crude NMR. The compound **9** under reduction by using palladium charcoal condition gives the 2,3-diamino benzoic acid methyl ester **10** in 80% yield, and acetone protected diamine **16** (in 5%), is obtained as byproduct. The mechanism is unclear.

Derivatives **13-14** were each synthesized in straightforward two step procedures from **5** and **10** as summarized in Scheme 1. The diamines **5** and **10** on treatment with α -bromo acetyl chloride to give the bromo derivatives **11** and **12** in 69% and 66% yields, respectively. The bromo derivatives **11** under treatment with 2-pyridyl methanol gives the pyridyl derivative **13** as an oil in 59% yield after chromatographic purification. Attempts to prepare **14** by reaction of **12** with

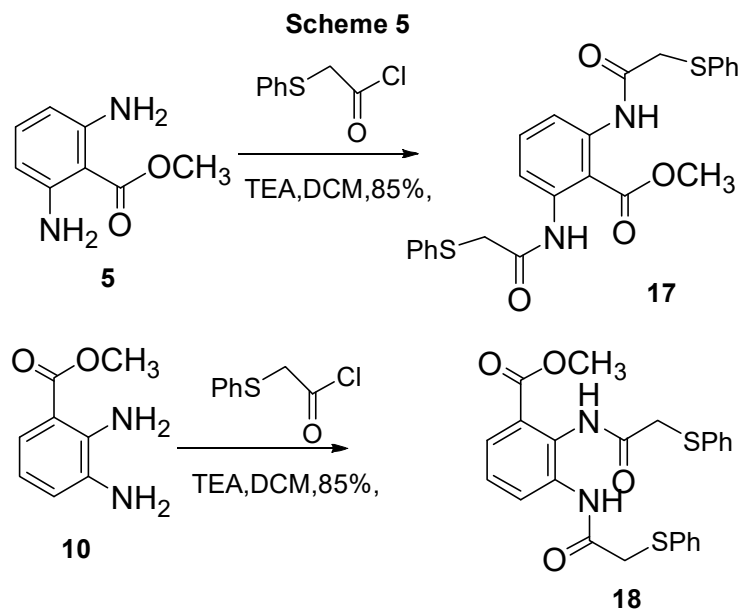
2-pyridyl methanol in the presence of triethylamine or NaH were unsuccessful and resulted in the isolation of pyridyl ester product with elimination of aromatic moiety (by nmr), it is understood that due to the steric hindrance, elimination of aromatic moiety might occur. (Scheme 3).



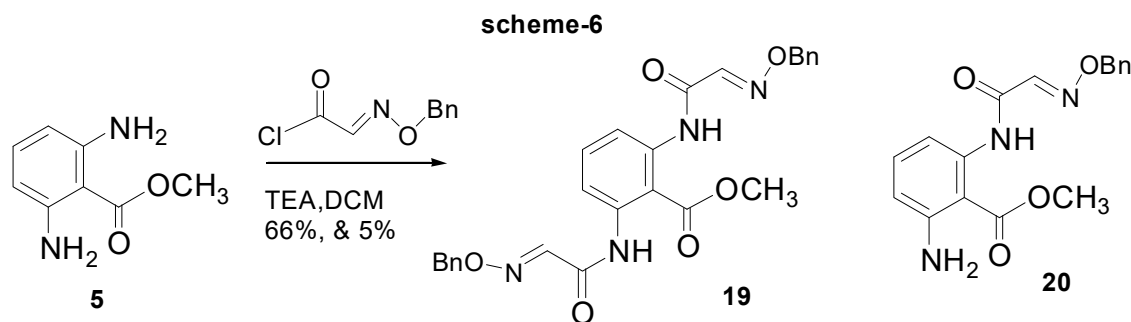
Reaction of **5** and **10** with 2.2 eq of 1,3-dithiolane-2-carbonyl chloride¹⁷ in the presence of triethylamine in THF led to the isolation of the *bis*(1,3-dithiolanyl) products **15** and **16** as white solids in 55% and 73% yield after purifications using column chromatography. The **16** structure is also confirmed by single crystal data. (Scheme 4).



In a similar procedure, compound **5** and **10** was reacted with 2.2 equivalents of α - thiophenyl acetyl chloride gives the corresponding esters **17** and **18** in 85% yields each. The compound **18** structure is also confirmed by single crystal data. (Scheme 5).

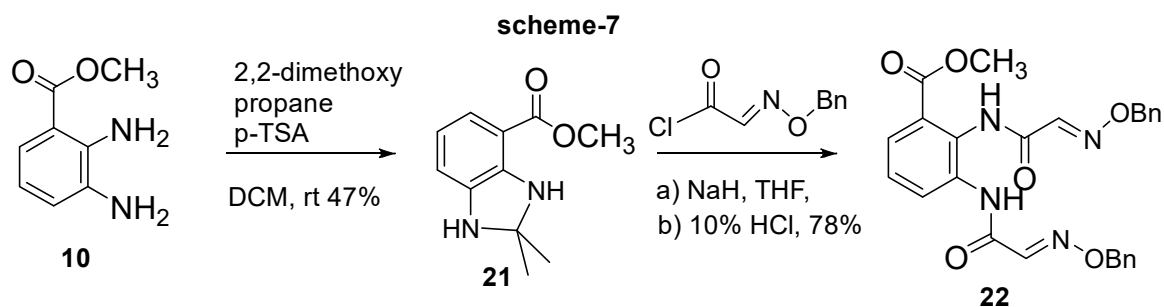


In a similar procedure, compound **5** was reacted with 2.2 equivalents of α -benzyloximino acid chloride²². After chromatographic separation, 2,6-bis-benzyloxy methylester **19** was isolated in 66% yield along with the 6-mono-benzyloxy methylester **20** in 5% yields. Both compounds were isolated as white solids. (Scheme 6).



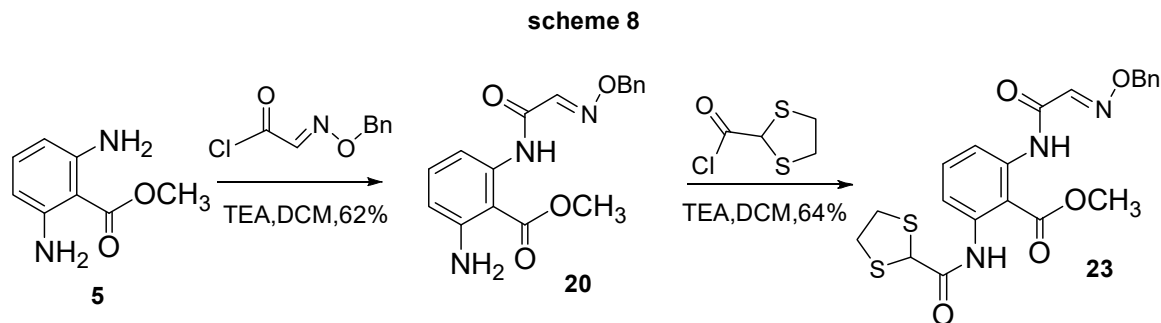
We also attempted to synthesize the 2,3-bis-benzyloxy methyl ester **22** from direct nucleophilic substitution reactions of diamine **10** with α -benzyloximino acid chloride in either of TEA or

pyridine and sodium hydride method. In both cases, our attempts were unsuccessful and resulted in either the isolation of starting materials or unidentified mixtures of products. But we were successful in synthesizing the **22** in two steps via acetonide protection (Scheme 7). Thus, reaction of **10** with 2,2-dimethoxy propane in presence catalytic amount of para toluene sulfonic acid gave **21** as residual oil in 47% yield after column chromatography purification, and reaction with α -benzyloximino acid chloride²² and workup with dil HCl gave **22** as white solid in 78% yield after chromatographic purification (Scheme 7).

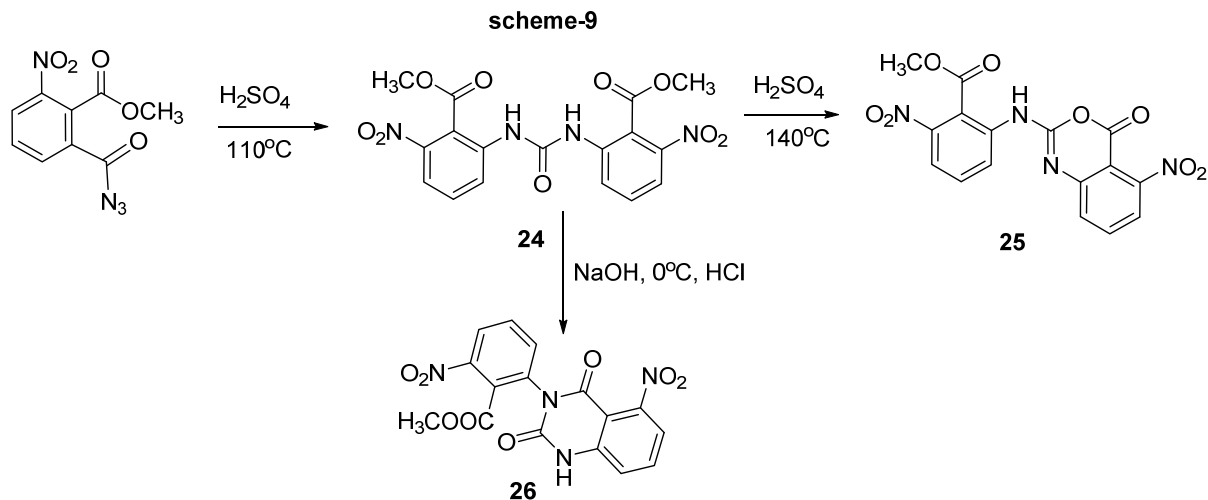


Different substitution at the 2- and 6-positions

As mentioned above, the synthesis of 2,6-bis-benzyloxy methylester **19** was accompanied by the isolation of the 6-mono-benzyloxy methyl ester **20**. Recognizing that 6-mono-benzyloxy methyl ester **20** could lead to derivatives with a different substituent at the 6-position, we sought to increase the yield of **20**. Accordingly, diamine **5** was reacted with 1.2 equivalents of α -benzyloximino acid chloride²². Column chromatographic purification resulted in the isolation of the desired 6-mono benzyloxy methyl ester **20** in 62% yield along with bis-benzyloxy methylester **19** in 15% yield. Subsequent reaction of **20** with 1,3-dithiolane-2-carbonyl chloride¹⁷ led to new ditopic derivative **23** as pale-yellow solid in 64% yield after column chromatographic purification (scheme 8).



It is worth to mentioned that the while doing the Curtius rearrangement on compound **3**, on heating at 110°C gives urea derivatives, which is common intermediate step for the synthesis of quinazoline derivatives which having biological properties²³⁻²⁴. Under acidic condition **24** gives benzo[d][1,3]oxazin-4-one²⁵ and in basic condition gives 2,4-quinazolindione derivatives²³ respectively (scheme-9).



All new compounds were isolated as air- and moisture-stable solids. All compounds were fully characterized using ¹H and ¹³C NMR spectroscopy and elemental analysis. The solubilities were excellent in common organic solvents, but **13** and **24** was soluble only in DMSO.

Preliminary experiments in which these compounds were mixed with various silver salts resulted in the formation of insoluble suspensions that could not be recrystallized for X-ray

crystallographic analysis. However, elemental analysis of the isolated suspensions confirms the presence of silver, suggesting that complexation reactions are indeed occurring.

OPTIC PROPERTIES

TABLE: UV-Vis Studies of compounds

entry	compound	λ	ϵ	λ	ϵ	λ	ϵ
1	5	206.52	20672.1875	249.95	12455.0434	348.52	5110.4080
2	10	194.23	12641.0729	232.87	17762.0000	348.87	4370.4688
3	13	192.31	25846.3190	236.29	16456.5333		
4	15	191.92	23265.5382	240.47	4003.2552	271.09	5111.8490
5	16	193.08	20814.8352	227.92	22114.2857		
6	17	191.92	21302.8571	238.57	17375.1429		
7	18	193.08	6515.9828	225.25	3893.0573		
8	19	192.69	109777.916	208.81	76122.4965	332.28	21387.4167
9	20	191.54	34272.9576	231.34	24875.3571	360.99	8007.1205
10	21	191.54	21627.6855	227.54	19688.2910		
11	22	191.92	29271.6667	258.65	7661.3333		
12	23	191.92	65453.3073	211.88	33804.6484		

The optical properties of compounds are of primary concern in chromogenic sensing and patterning. The solution-phase UV-vis absorption spectrum was recorded at room temperature in dilute chloroform solutions of about 10^{-5} M concentration. As shown in table, In the absorption spectra for all compounds shows around 192 nm band seems to be an inherent property of these compounds and is not due to impurities as was verified by thin layer chromatography and NMR

spectroscopy. The absorption maximum of **5** and **10** was remarkably blue shift shows at 348 nm each. But 2,6, disubstituted derivatives **15** and **19** shows absorption maximum at 271 and 332 nm respectively, the decrease of absorption maximum to 270 in case of **15** can be explained that it contains dithialone moiety, is responsible for it. Similarly, the compound **20** with a free amine group exhibited max at 360 nm, which is close to its parents compound **5** which having two free amines. Compound **19** compared with the absorption of corresponding its isomer compound **23** with the same chromophore showed a red-shifted absorption (no peaks and 443 nm, respectively), presumably due to extension of ineffective p-conjugation in ortho isomers.

Conclusions

We have prepared a series of new compounds containing dithiolane or benzyloxy oximate to aromatic rings bonded to substituted anthranilic acid core. The synthetic procedure is straightforward, and the products are obtained in good to excellent yields after chromatographic purification. Excellent solubility properties and the presence of electron donor groups in the modified anthranilic acid derivative described herein may be advantageous in applications such as anthranilic acid derivatives-metal conjugate synthesis, for example. The efficiency of chromogenic sensing is more remarkably affected by the chemical environment of the anthranilic acid derivatives, depending on the presence of a protecting amino group or amide group. Taking into account these considerations, it is possible to optimize the uv-vis sensing of the molecules by structure modification. All these compounds possess multiple sulfur atoms and are thus capable of binding in a multidentate fashion to soft transition metal ions. A reaction of these ligands with late transition metal ions is a current focus in our laboratory.

ACKNOWLEDGMENTS

The authors thank the National Science Foundation and the Welch Foundation for support of this work.

Declaration of Competing Interest The authors declare that they have no known competing financial interests

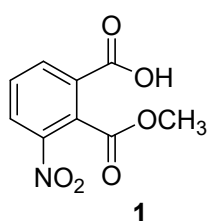
Data and materials availability: Requests for materials should be addressed to Sudershan Gondi (gondisr@gmail.com)

EXPERIMENTAL SECTION:

3-Nitrophthalic anhydride and 3-Nitrophthalic acid were obtained from Acros and Aldrich respectively. All other materials were reagent grade unless otherwise specified. All reactions were carried out in a dry nitrogen atmosphere. ¹H and ¹³C NMR spectra were obtained on a 400-MHz Bruker Avance NMR spectrometer. Infrared spectra were obtained on a Nicolet Magna-IR 560 spectrometer E.S.P. Elemental analyses were obtained with a CE Elantech Thermo-Finnigan Flash 1112 CHN elemental analyzer. Melting points were collected on a TA Instruments DSC 2010 Differential Scanning Calorimeter using a heating rate of 108°C/min and nitrogen as a purge gas. 2-Carbomethoxy-3-nitro-benzoic acid (1),²⁶ 2-carbomethoxy-3-nitro-benzoyl chloride (2),²⁷ 2-azidocarbonyl-6-nitro-benzoic acid methyl ester (3),²⁸ 2-amino-6-nitro-benzoic acid methyl ester (4),²⁹ 2,6-diamino benzoic acid methyl ester (5),³⁰ 2-Carbomethoxy-6-nitro-benzoic acid (6),³¹ 2-carbomethoxy-6-nitro-benzoyl chloride(7),³² 2-azidocarbonyl-3-nitro-benzoic acid methyl ester(8),³³ 2-amino-3-nitrobenzoic acid methyl ester (9),³⁰ 2,3-diamino

benzoic acid methyl ester (10),³⁴ were prepared with modified methods and spectral data is presented. α -Benzyloximino acid chloride²² and 1,3-dithiolane-2-carbonyl chloride¹⁶ were prepared as described previously.

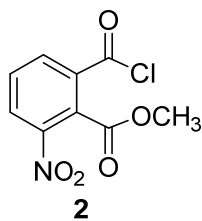
2-Carbomethoxy-3-nitro-benzoic acid²⁶ (1): This procedure is modified from an earlier



reported procedure.²⁶ 3-nitro-phthalic anhydride (30 g, 155 mmol) was refluxed in absolute methanol (320 mL) for 24 h. Thereafter methanol was distilled out to get the mixture of products **2** and **6** in 9.5:0.5 ratio (35.0 g, 99 %) as white solid, used in next reaction without purification. Mp 144.74°C. (lit

value Mp 152-153°C). ¹H-NMR (400 MHz, DMSO-d₆): δ 8.41-8.38 (d, 1H, $J = 8.2$ Hz), 8.32-8.30 (d, 1H, $J = 7.8$ Hz), 7.87-7.83 (t, 1H, $J = 8.0$ Hz), 3.87 (s, 3H, COOCH₃). ¹³C-NMR (100.6 MHz, DMSO-d₆): δ 166.2, 166.0, 146.9, 136.5, 132.1, 132.0, 130.2, 129.0, 53.9. IR (KBr): 3097, 2957, 1736, 1572, 1536, 1477, 1279 cm⁻¹.

2-Carbomethoxy-3-nitro-benzoyl chloride²⁷ (2): This procedure is modified from an earlier

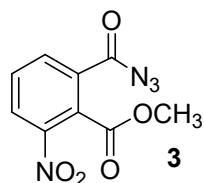


reported procedure²⁷. The reaction mixture **1** and **6** (30 g, 133 mmol) and thionyl chloride (29.2 mL, 47.6 g, 399 mmol) were heated at reflux for two hours, and the excess thionyl chloride removed by distillation under reduced pressure on rota evaporator to obtained the yellow residue. The residue was

evaporated in vacuum three times with 50 mL of dry toluene to remove all traces of thionyl chloride. The residue solidified upon cooling. Recrystallization from toluene gives 15.5 g of white crystals products **2** and **7** in (9.5:0.5 ratio) in 95% yield. Mp 72-74°C. (lit value Mp 78-79.5°C). ¹H-NMR (400 MHz, CDCl₃): δ 8.55-8.53 (d, 1H, $J = 7.9$ Hz), 8.45-8.43 (d, 1H, $J = 8.2$ Hz), 7.86-7.81 (t, 1H, $J = 8.2$ Hz), 3.98 (s, 3H, COOCH₃). ¹³C-NMR (100.6 MHz, CDCl₃): δ

166.2, 165.0, 145.6, 138.0, 133.6, 131.4, 130.8, 130.4, 54.2. IR (KBr): 3097, 2957, 1736, 1572, 1540, 1472, 1284 cm^{-1} .

2-Azidocarbonyl-6-nitro-benzoic acid methyl ester²⁸ (3): This procedure is modified from an earlier reported procedure.²⁸ To a solution of reaction mixture **2** and **7** (30 g,

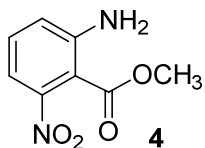


123 mmol) in 150 mL of dry acetone, pre-cooled to 0°C, was added (32.1 g, 494 mmol) of sodium azide. After 15 minutes of stirring, the reaction mixture was diluted by addition of water (100 mL) and stirred at same temperature for

1 h, during this time product solidified. Filter at pump, washed with water (100 mL) and hexane (100 mL) to obtained mixture of product **3** and **8** (in 9.5:0.5 ratio) as yellow solid. (29.3 g, 97%).

Mp 80-82°C which is used in next reaction without purification. ¹H-NMR (400 MHz, CDCl₃): δ 8.41-8.39 (d, 1H, $J = 8.2$ Hz), 8.31-8.29 (d, 1H, $J = 7.8$ Hz), 7.73-7.69 (t, 1H, $J = 8.0$ Hz), 4.02 (s, 3H, COOCH₃). ¹³C-NMR (100.6 MHz, CDCl₃): δ 169.9, 165.3, 146.4, 135.3, 130.8, 130.3, 130.0, 129.2, 53.5. IR (KBr): 3102, 2955, 2158, 1755, 1693, 1539, 1354, 1259 cm^{-1} .

2-Amino-6-nitro-benzoic acid methyl ester²⁹ (4): This procedure is modified from an earlier reported procedure.²⁹ Dissolved reaction mixture **3** and **8** (14.3 g, 57.2 mmol)

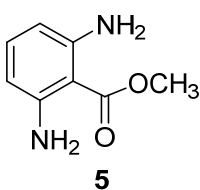


in aqueous glacial acetic acid 60mL/20mL) and heated at 80°C until no more nitrogen gas evolved (2 h). Poured the reaction mixture into crushed ice (100

g) and stirred for 30 minutes to precipitate the product. Filtered and washed well with water (250 mL). The solid residue was taken up in ethyl acetate (100 mL), washed with water (100 mL), brine solution (100 mL), dried over anhydrous MgSO₄ and filter. All volatiles were removed, and the residue was purified using column chromatography (70:30 EtOAc:hex) to give **4** as yellow solid (7.85 g, 70%). Mp 109.13°C. (lit value Mp 108-110°C). ¹H-NMR (400 MHz, CDCl₃): δ 7.19-7.15 (t, 1H, $J = 7.9$ Hz), 6.92-6.90 (d, 1H, $J = 7.8$ Hz), 6.80-6.78 (d, 1H, $J = 8.4$

Hz), 5.26 (br-s, 2H, NH₂), 3.73 (s, 3H, COOCH₃). ¹³C-NMR (100.6 MHz, CDCl₃): δ 165.9, 151.4, 148.8, 131.8, 120.4, 112.2, 106.8, 52.5. IR (KBr): 3492, 3385, 3103, 2955, 1716, 1624, 1514, 1344, 1285, 836 cm⁻¹. Elemental Analysis: Calcd for C₈H₈N₂O₄: C, 48.98; H, 4.11, N, 14.28. Found: C, 49.32; H, 4.01; N, 14.29. And eluted with (20:80 EtOAc:hex) to give product **9** as yellow solid (0.2 g, 5%). Mp 97.28°C. (lit value Mp 95-97°C).

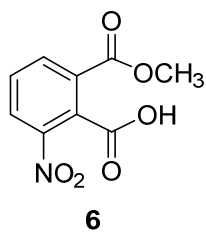
2, 6-Diamino benzoic acid methyl ester³⁰ (5): This procedure is modified from an earlier reported procedure.³⁰ To a solution of 2-amino-6-nitro-benzoic acid methyl



ester (**4**) (1.0 g, 5.1 mmol) in 80 mL of methanol, 50 mg of 10% palladium carbon was added. The reaction mixture stirred under hydrogen atmosphere until the starting material disappeared (18 h). After completion of reaction,

filter through celite pad and wash with additional methanol (50 mL). The filtrate on concentration, the residue was purified by column chromatography (40:60 EtOAc:hex) to give **5** as brown solid (0.76 g, 90%). Mp 81.61°C. (lit value Mp 80-82°C). ¹H-NMR (400 MHz, CDCl₃): δ 6.98-6.94 (t, 1H, *J* = 8.0 Hz), 5.97-5.95 (d, 2H, *J* = 8.0 Hz), 3.91 (s, 3H, COOCH₃). ¹³C-NMR (100.6 MHz, CDCl₃): δ 169.1, 151.2, 133.9, 104.6, 97.6, 51.2. IR (KBr): 3481, 3364, 2946, 1664, 1576, 1458, 1347, 805 cm⁻¹. Elemental Analysis: Calcd for C₈H₁₀N₂O₂: C, 57.82; H, 6.07; N, 16.86. Found: C, 58.19; H, 6.18; N, 16.72.

2-Carbomethoxy-6-nitro-benzoic acid³¹ (6): This procedure is modified from an earlier reported procedure.³¹ 3-nitro-phthalic acid (3.4 g, 21.3 mmol) was refluxed in

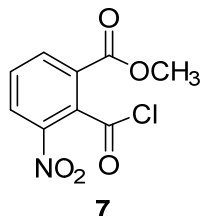


absolute methanol (50 mL) for 16 h. Concentrated the volatile to obtained pure **6** as white solid. (4.6 g, 97%), Mp 155-157°C. (lit value Mp 155-157°C). ¹H-NMR (400 MHz, DMSO-d₆): δ 8.30-8.28 (d, 1H, *J* = 7.5 Hz). 8.19-8.17 (d,

1H, *J* = 7.2 Hz), 7.80-7.78 (d, 1H, *J* = 7.7 Hz), 3.82 (s, 3H, COOCH₃). ¹³C-NMR (100.6 MHz,

DMSO-d₆): δ 166.5, 165.5, 147.3, 135.6, 131.6, 131.3, 130.7, 128.8, 53.8. IR (KBr): 3089, 2960, 2664, 1732, 1532, 1350, 1278 cm⁻¹.

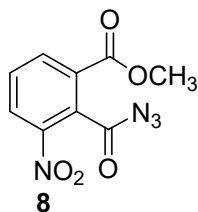
2-Carbomethoxy-6-nitro-benzoyl chloride³² (**7**): This procedure is modified from an earlier reported procedure.³² In the same manner described for **2** and **6**,



2-carbomethoxy-3-nitro benzoic acid (**6**) (4.5 g, 20.0 mmol) and thionyl chloride (4.4 mL, 7.13 g, 60.0 mmol) to give **7** as yellow crystals. (4.60 g, 96%). Mp 93-95°C. (lit value Mp 97-99°C). ¹H-NMR (400 MHz, CDCl₃): δ 8.40-8.38 (d, 1H, *J* = 8.4 Hz), 8.39-8.35 (d, 1H, *J* = 8.6 Hz), 7.75-7.71 (t, 1H, *J* = 8.0 Hz), 3.93 (s, 3H, COOCH₃).

¹³C-NMR (100.6 MHz, CDCl₃): δ 164.6, 163.3, 144.2, 136.2, 133.6, 131.3, 128.7, 128.3, 53.4. IR (KBr): 3089, 2961, 980, 754, 1803, 1728, 1545, 1344, 1287 cm⁻¹. Elemental Analysis: Calcd: C, 44.37; H, 2.48; N, 5.75. Found: C, 44.89; H, 2.46; N, 5.79.

2-Azidocarbonyl-3-nitro-benzoic acid methyl ester³³ (**8**): To a solution of 2-carbomethoxy-6-nitro-benzoyl chloride (**7**) (4.5 g, 18.0 mmol) in 150 mL of dry acetone, pre-

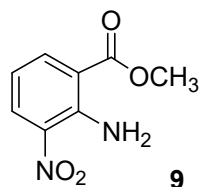


cooled to 0°C, was added (4.81 g, 70.0 mmol) of sodium azide. After 15 minutes of stirring, the reaction mixture was diluted by addition of water and stirred at same temperature for 1 h during this time product solidified. Filtered

at pump, dissolve the residue solid in dichloromethane (100 mL). The organic layer was washed with water (100 mL), saturated sodium bicarbonate solution (100 mL), brine solution (100 mL) and dried over MgSO₄. After filtration, evaporation and purification through column chromatography (20:80 EtOAc:hex) gave **8** as yellow solid (4.30 g, 94%). Mp 88-90°C. ¹H-NMR (400 MHz, CDCl₃): δ 8.31-8.29 (d, 1H, *J* = 8.2 Hz), 8.17-8.15 (d, 1H, *J* = 6.9 Hz), 6.59-6.55 (t, 1H, *J* = 8.0 Hz), 3.84 (s, 3H, COOCH₃). ¹³C-NMR (100.6 MHz, CDCl₃): δ 167.3, 147.1,

139.2, 133.1, 132.1, 114.3, 113.8, 52.2. IR (KBr): 3085, 2956, 2271, 2176, 3451, 3332, 1728, 1701, 1618, 1570, 1241, 1110 cm^{-1} .

2-Amino-3-nitro-benzoic acid methyl ester²⁹ (**9**): In the same manner described for 2-amino-6-



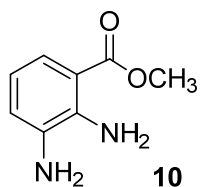
nitro-benzoic acid methyl ester (**4**), 2-azidocarbonyl-3-nitro-benzoic acid methyl ester (**8**) (4.0 g, 16.0 mmol) was treated aqueous glacial acetic acid.

Column chromatographic purification (20:80 EtOAc:hex) gave **9** as yellow solid. (2.8 g, 89%). Mp 94-96°C. (lit value Mp 95-97°C). ¹H-NMR (400 MHz, CDCl₃): δ 8.30-8.28 (d, 1H, $J = 8.4$ Hz), 8.16-8.14 (d, 1H, $J = 7.7$ Hz), 6.59-6.55 (t, 1H, $J = 8.2$ Hz), 3.84 (s, 3H, COOCH₃).

¹³C-NMR (100.6 MHz, CDCl₃): δ 167.4, 147.2, 139.3, 133.2, 132.2, 114.4, 113.9, 52.2. IR (KBr): 3453, 3318, 3102, 2964, 1701, 1619, 1515, 1254, 883 cm^{-1} .

Elemental Analysis: Calcd for C₈H₈N₂O₄: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.09; H, 4.02; N, 14.22.

2, 3-Diamino benzoic acid methyl ester³⁴ (**10**): In the same manner described for 2, 6-diamino



benzoic acid methyl ester (**5**), the 2-amino-3-nitro-benzoic acid methyl ester (**9**)

(2.0 g, 10.0 mmol) was treated with 100 mg of 10% palladium over charcoal in 80 mL of methanol. Column chromatographic purification (30:70 EtOAc:hex)

gave **10** as brown solid. (1.55 g, 91%). Mp 64.24°C. (lit value Mp 63-64°C). ¹H-NMR (400

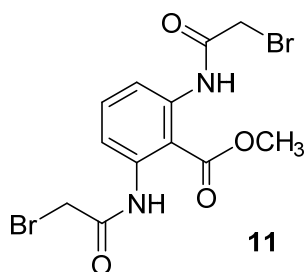
MHz, CDCl₃): δ 7.49-7.47 (d, 1H, $J = 8.1$ Hz), 6.83-6.81 (d, 1H, $J = 7.5$ Hz), 6.61-6.57 (t, 1H, $J = 7.7$ Hz), 4.43 (br-s, 4H, NH₂), 3.91 (s, 3H, COOCH₃).

¹³C-NMR (100.6 MHz, CDCl₃): δ 168.8, 140.9, 134.1, 122.3, 120.4, 116.5, 111.6, 51.4. IR (KBr): 3428, 3368, 1701, 1693, 1560, 1473, 1287, 2947, 854 cm^{-1} .

Elemental Analysis: Calcd for C₈H₁₀N₂O₂: C, 57.82; H, 6.07; N, 16.86.

Found: C, 57.85; H, 6.01; N, 16.75. and eluted with (20:80 EtOAc:hex) to give corresponding acetone **16** as residual oil (70 mg, 5%).

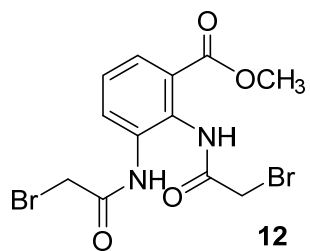
2,6-Bis-(2-bromo-acetylamino)-benzoic acid methyl ester (11): Dissolved 2,6-bis-amino-



benzoic acid methyl ester (**5**) (1.0 g, 6.0 mmol) in dichloromethane (40 mL) and cooled in a water/ice bath. Triethylamine (1.85 mL, 1.33 g, 13.2 mmol) was then added, and the resulting suspension was stirred for 15 min. A solution of bromo-acetyl bromide (2.67 g, 13.2 mol) in dichloromethane (15 mL) was added dropwise over a period of 15 min,

and the resulting mixture was allowed to warm to room temperature and stirred for 6 h. The reaction mixture was quenched by the addition of aqueous solution of HCl (50 mL). The aqueous solution was extracted with dichloromethane (100 mL), and the organic layer was washed with water (100 mL), saturated sodium bicarbonate solution (100 mL), water again (100 mL), and brine (100 mL) dried over anhydrous MgSO₄ and filtered. Removal of volatiles and the residue was purified using column chromatography (SiO₂, 15:85 EtOAc:hex) to give **11** as white solid. (1.70 g, 69%). Mp 150.59°C. ¹H-NMR (400 MHz, CDCl₃): δ 10.6 (br-s, 2H, NH), 8.20-8.18 (d, 2H, *J* = 8.4 Hz), 7.56-7.52 (t, 1H, *J* = 8.4 Hz), 4.11 (s, 3H, COOCH₃), 4.06 (s, 4H, CH₂Br). ¹³C-NMR (100.6 MHz, CDCl₃): δ 166.9, 164.1, 138.6, 133.7, 118.0, 108.8, 53.4, 29.7. IR (KBr): 3309, 3263, 3036, 2960, 1713, 1676, 1525, 1467, 1260 cm⁻¹. Elemental Analysis: Calcd for C₁₂H₁₂Br₂N₂O₄: C, 35.32; H, 2.96; N, 6.87. Found: C, 35.17; H, 3.01; N, 6.68.

2,3-Bis[(-Bromo-acetyl)-amino]-benzoic acid methyl ester (12): In the manner described

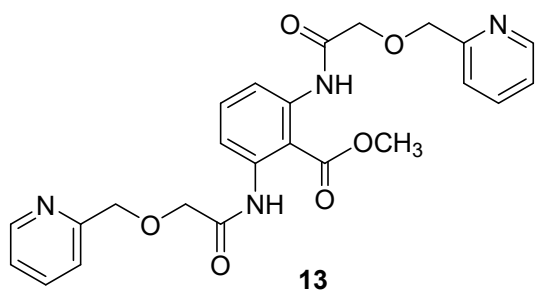


above, 2,3-bis-amino-benzoic acid methyl ester (**10**) (1.0 g, 6.0 mmol) was treated with bromo-acetyl bromide (2.67 g, 13.2 mmol) in presence of 1.85 ml, (1.33 g, 13.2 mmol) of triethylamine at 0°C in 40 mL of dichloromethane. Column chromatography (20:80 EtOAc:hex) to give

12 as white solid (1.6 g, 65%). Mp 164.18°C. ¹H-NMR (400 MHz, CDCl₃): δ 10.72 (br-s, 1H,

NH), 9.09 (br-s, 1H, NH), 7.95-7.93 (d, 2H, $J = 7.8$ Hz), 7.42-7.38 (t, 1H, $J = 8.0$ Hz), 4.12 (s, 2H, CH₂Br), 4.01 (s, 2H, CH₂Br), 3.97 (s, 3H, COOCH₃). ¹³C-NMR (100.6 MHz, CDCl₃): δ 167.7, 166.5, 165.2, 132.3, 132.0, 131.5, 129.1, 126.7, 123.0, 53.2, 29.6, 28.9. IR (KBr): 3448, 3269, 3008, 2952, 1720, 1666, 1546, 1295. Elemental Analysis: Calcd for C₁₂H₁₂Br₂N₂O₄: C, 35.32; H, 2.96; N, 6.87. Found: C, 35.80; H, 3.14; N, 6.96.

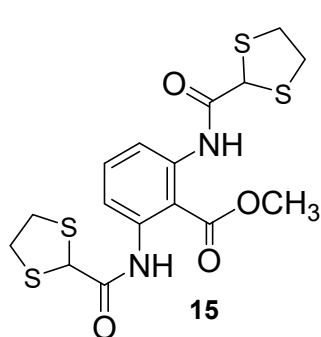
2,6-Bis-[2-(pyridin-2-ylmethoxy)-acetyl-amino]-benzoic acid methyl ester (13): Pyridine



methylalcohol (588 mg, 5.4 mmol) was dissolved in THF (10 mL) and cooled in an ice bath. Sodium hydride (130 mg, 5.4 mmol) was added, and the mixture was stirred 15 minutes. **11** (1.0 g, 2.4 mmol) was added portion wise over a period of 15 minutes.

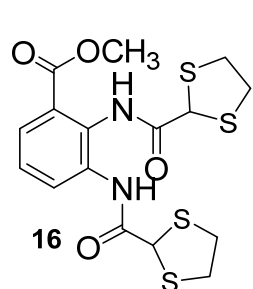
The reaction mixture was stirred at room temperature for 24 h. The THF was removed using a rotary evaporator and the residue was quenched by the addition of water (100 mL). The aqueous solution was extracted with ethyl acetate (100 mL), and the organic layer was washed with water (100 mL), saturated sodium bicarbonate solution (100 mL), water (100 mL), and brine (100 mL), and then dried over anhydrous MgSO₄. After filtration and concentration of the filtrate, the residue was purified by column chromatography (20:80 EtOAc:hex) to give **13** as residual oil (0.67 g, 59%). ¹H-NMR (400 MHz, CDCl₃): δ 10.7 (br-s, 2H, NH), 8.53-8.52 (d, 2H, $J = 3.4$ Hz), 8.20-8.18 (d, 2H, $J = 8.3$ Hz), 7.69-7.65 (t, 1H, $J = 7.6$ Hz), 7.48-7.41 (m, 3H), 7.19-7.17 (t, 2H, $J = 2.7$ Hz), 4.73 (s, 4H), 4.16 (s, 4H), 3.61 (s, 3H, COOCH₃). ¹³C-NMR (100.6 MHz, CDCl₃): δ 167.9, 167.0, 156.7, 149.4, 138.6, 136.8, 133.7, 122.9, 121.8, 117.5, 108.9, 74.5, 70.7, 52.3. IR (KBr): 3361, 2967, 1694, 1585, 1469 cm⁻¹

2,6-Bis-([(1,3]dithiolane-2-carbonyl)-amino]-benzoic acid methyl ester (**15**):



2,6-Bis-amino-benzoic acid methyl ester (**5**) (0.5 g, 3.0 mmol) was dissolved in dichloromethane (20 mL) and cooled in an ice bath. Triethylamine (1.67 mL, 1.21 g, 12.0 mmol) was added and the solution was stirred for 15 minutes. 1,3-dithiolane-2-carbonyl chloride¹⁶ (1.22 g, 7.2 mmol) was dissolved in dichloromethane (5 mL) and the solution was added dropwise over a period of 15 minutes. The reaction mixture was stirred in the ice bath for 1h and stirred at room temperature overnight, and reaction mixture was quenched with aqueous solution of HCl and extracted with dichloromethane (50 mL X 2), and the organic layer was washed with water (100 mL), saturated sodium bicarbonate solution (100 mL), water (100 mL), brine (100 mL), dried over anhydrous MgSO₄ and filtered. All volatiles were removed and the residue was purified using column chromatography (20:80 EtOAc:hex) to give **15** as white solid (0.4 g, 55%). Mp 152-154°C. ¹H-NMR (400 MHz, CDCl₃): δ 10.74 (s, 2H, NH), 8.14-8.12 (d, 2H, *J* = 8.3 Hz), 7.52-7.48 (t, 1H, *J* = 8.3 Hz), 5.01 (s, 2H), 4.05 (s, 3H), 3.44-3.35 (m, 8H). ¹³C-NMR (100.6 MHz, CDCl₃): δ 168.5, 167.1, 138.7, 133.6, 118.0, 109.4, 54.7, 53.1, 39.2. IR (KBr): 3292, 1695, 1678, 1584, 1466, 1273, 1074, 805 cm⁻¹. Elemental Analysis: Calcd for C₁₆H₁₈N₂O₄S₄: C, 44.63; H, 4.21; N, 6.51. Found: C, 44.91; H, 3.92; N, 6.47.

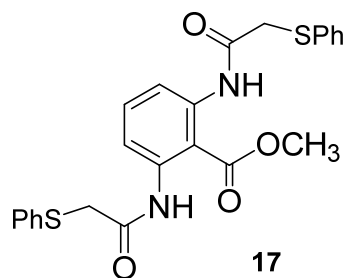
2,3-Bis-([(1,3]dithiolane-2-carbonyl)-amino]-benzoic acid methyl ester (**16**):



In the manner described above, 2,3-bis-amino-benzoic acid methyl ester (**10**) (0.5 g, 3.0 mmol) was treated with 1,3-dithiolane-2-carbonyl chloride¹⁶ (1.22 g, 7.2 mmol) in presence of 1.67 mL, (1.21 g, 12 mmol) of triethylamine at 0°C in 20 mL of dichloromethane. Column chromatography (30:70 EtOAc:hex)

to give **16** as white crystalline solid (0.95 g, 73%). Mp 92-94°C. ¹H-NMR (400 MHz, CDCl₃): δ 10.79 (s, 1H, NH), 9.03 (s, 1H, NH), 7.90-7.88 (d, 1H, *J* = 8.0 Hz), 7.80-7.78 (d, 1H, *J* = 7.8 Hz), 7.29-7.25 (t, 1H, *J* = 8.0 Hz), 5.00 (s, 1H), 4.89 (s, 1H), 3.86 (s, 3H), 3.44-3.40 (m, 4H), 3.32-3.26 (m, 4H). ¹³C-NMR (100.6 MHz, CDCl₃): δ 170.1, 169.5, 167.2, 132.3, 131.4, 130.9, 128.2, 126.1, 122.9, 54.1, 54.0, 52.7, 39.4, 39.3, IR (KBr): 3237, 2926, 1718, 1676, 1646, 1508, 1301, 1142, 758 cm⁻¹. Elemental Analysis: Calcd for C₁₆H₁₈N₂O₄S₄: C, 44.63; H, 4.21; N, 6.51. Found: C, 44.68; H, 4.18; N, 6.38. Structure was confirmed by single crystals data.

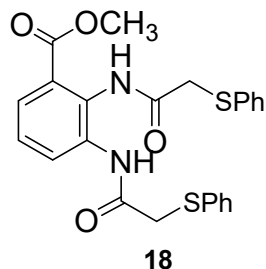
2,6-Bis-(2-phenylsulfanyl-acetylamino)-benzoic acid methyl ester (17): In the manner



described above, 2,6-bis-amino-benzoic acid methyl ester (**5**) (0.25 g, 1.5 mmol) was treated with thiophenyl acetyl chloride (0.618 g, 3.3 mmol) in presence of 480 mg (6.0 mmol) of pyridine at 0°C in 20 mL of dichloromethane. Column chromatography (30:70 EtOAc:hex) to give **17** as white crystalline solid (0.6 g, 85%). Mp

120-122°C. ¹H-NMR (400 MHz, CDCl₃): δ 10.79 (s, 2H, NH), 8.16-8.14 (d, 2H, *J* = 8.3 Hz), 7.51-7.47 (t, 1H, *J* = 8.3 Hz), 7.32-7.28 (m, 8H), 7.24-7.22 (m, 2H), 3.79 (s, 4H), 3.76 (s, 3H). ¹³C-NMR (100.6 MHz, CDCl₃): δ 166.8, 166.7, 138.5, 134.4, 133.4, 129.3, 128.2, 126.8, 117.9, 109.5, 52.9, 38.9. IR (KBr): 3338, 3290, 2950, 1714, 1685, 1583, 1218, 1116, 735 cm⁻¹. Elemental Analysis: Calcd for C₂₄H₂₂N₂O₄S₂: C, 61.78; H, 4.75; N, 6.00. Found: C, 61.91; H, 4.47; N, 5.96. Structure was confirmed by by single crystals data.

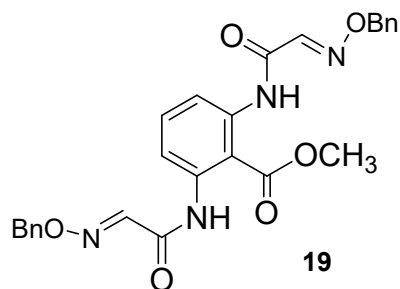
2,3-Bis-(2-phenylsulfanyl-acetylamino)-benzoic acid methyl ester (18): In the manner



described above, 2,3-bis-amino-benzoic acid methyl ester (**10**) (0.25 g, 1.5 mmol) was treated with thiophenyl acetyl chloride (0.618 g, 3.3 mmol) in presence of 480 mg (6.0 mmol) of pyridine at 0°C in 20 mL of

dichloromethane. Column chromatography (30:70 EtOAc:hex) to give **18** as white solid (0.58 g, 85%). Mp 100-102°C. ¹H-NMR (400 MHz, CDCl₃): δ 10.76 (s, 1H, NH), 9.40 (s, 1H, NH), 7.85-7.79 (m, 2H), 7.36-7.20 (m, 11H), 3.77 (s, 3H), 3.69 (s, 2H), 3.53 (s, 2H). ¹³C-NMR (100.6 MHz, CDCl₃): δ 168.8, 167.1, 167.0, 135.1, 134.7, 132.0, 131.7, 131.1, 129.2, 129.1, 128.4, 128.2, 126.7, 126.5, 125.9, 123.0, 52.5, 38.2, 38.0. IR (KBr): 3276, 3239, 3056, 2957, 1706, 1670, 1495, 1306, 1151, 787 cm⁻¹. Elemental Analysis: Calcd for C₂₄H₂₂N₂O₄S₂: C, 61.78; H, 4.75; N, 6.00. Found: C, 61.90; H, 4.77; N, 5.90.

2,6-Bis-(2-benzyloxyimino-acetylamino)-benzoic acid methyl ester (19): 2,6-Bis-amino-

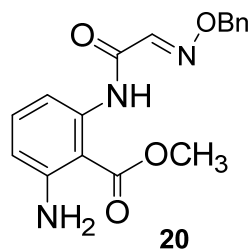


benzoic acid methyl ester (**5**) (0.25 g, 1.5 mmol) was dissolved in dichloromethane (20 mL) and cooled in an ice bath. Triethylamine (365 mg, 3.6 mmol) was added, and the solution was stirred for 15 minutes. α-benzyloximino acid chloride³⁰ (650 mg, 3.2 mmol) was dissolved in dichloromethane (5 mL)

and the solution was added dropwise over a period of 15 minutes. The reaction mixture was stirred in the ice bath for 1 h and stirred at room temperature overnight, and reaction mixture was quenched with aqueous solution of HCl and extracted with dichloromethane (50 mL X 2), and the organic layer was washed with water (100 mL), saturated sodium bicarbonate solution (100 mL), water (100 mL), brine (100 mL), dried over anhydrous MgSO₄ and filtered. All volatiles were removed and the residue was purified using column chromatography (15:85 EtOAc:hex) to give **19** as white solid. (0.4 g, 55%). Mp 108-110°C. ¹H-NMR (400 MHz, CDCl₃): δ 10.87 (s, 2H, NH), 8.30-8.28 (d, 2H, *J* = 8.4 Hz), 7.59 (s, 2H), 7.54-7.50 (t, 1H, *J* = 8.3 Hz), 7.46-7.38 (m, 10H), 5.31 (s, 4H), 3.85 (s, 3H). ¹³C-NMR (100.6 MHz, CDCl₃): δ 167.4, 160.2, 144.5, 139.3, 136.6, 134.3, 129.0, 128.9, 128.8, 117.8, 108.4, 78.1, 53.0. IR (KBr): 3357, 3031, 2952, 1695,

1676, 1585, 1500, 1407, 1270, 916 cm^{-1} . Elemental Analysis: Calcd for $\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_6$: C, 63.93; H, 4.95; N, 11.48. Found: C, 64.02; H, 4.94; N, 11.32 and eluted with (20:80 EtOAc:hex) to give **20** as white solid (90 mg, 18%). Mp 90-92°C.

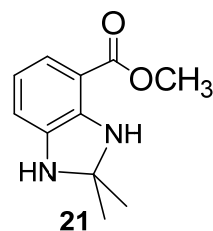
2-Amino-6-(2-benzyloxyimino-acetyl-amino)-benzoic acid methyl ester (20): In the manner



described above, 2,6-bis-amino-benzoic acid methyl ester (**5**) (0.25 g, 1.5 mmol) was treated with α -benzyloximino acid chloride³⁰ (326 mg, 1.6 mmol) in presence of 0.25 mL, (190 mg, 1.8 mmol) of triethylamine at 0°C in 20 mL of dichloromethane. Column chromatography (20:80 EtOAc:hex)

to give **20** as white solid (0.3 g, 62%). Mp 90-92°C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 11.21 (br-s, 1H, NH), 7.82-7.80 (d, 1H, $J = 8.2$ Hz), 7.46 (s, 1H), 7.33-7.23 (m, 5H), 7.08-7.06 (t, 1H, $J = 8.2$ Hz), 6.31-6.29 (d, 1H, $J = 8.2$ Hz), 5.42 (br-s, 2H, NH_2), 5.18 (s, 2H), 3.75 (s, 3H). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3): δ 168.1, 159.6, 150.7, 144.5, 139.6, 136.2, 133.9, 128.4, 128.3, 128.2, 112.6, 109.6, 100.9, 77.4, 51.7. IR (KBr): 3456, 3317, 3023, 1683, 1618, 1543, 1462, 1234, 922 cm^{-1} . Elemental Analysis: Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_4$: C, 62.38; H, 5.23; N, 12.84. Found: C, 62.65; H, 5.75; N, 12.89. and eluted with (15:85 EtOAc:hex) to give diester product **19** as white solid (40 mg, 5%). Mp 108-110°C.

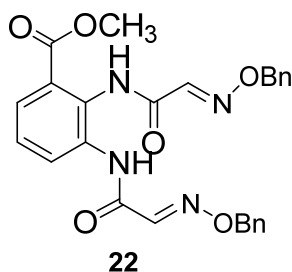
2,2-Dimethyl-2,3-dihydro-1H-benzimidazole-4-carboxylic acid methyl ester (21):



2,3-Bis-amino-benzoic acid methyl ester (**10**) (0.5 g, 3.0 mmol) and 2,2'-dimethoxypropane (5.0 mL) was stirred in presence of catalytic amount (100 mg) of para-toulenesulfonic acid at room temperature for 16 h. Reaction mixture on concentrated gives the residue, which on dilution with dichloromethane (100 mL). Separate the organic layer and wash with saturated sodium bicarbonate solution (100 mL), water (100 mL), and brine solution (100 mL) and dried over

MgSO₄ (5.0 g) and filter. Concentrate the filtrate and the residue on column chromatography (20:80 EtOAc:hex) to give **22** as residual oil (0.3 g, 47%). ¹H-NMR (400 MHz, CDCl₃): δ 7.00-6.98 (d, 1H, *J* = 7.2 Hz), 6.36-6.33 (t, 2H, *J* = 7.5 Hz), 5.93 (br-s, 1H, NH), 3.86 (br-s, 1H, NH), 3.73 (s, 3H, COOCH₃). ¹³C-NMR (100.6 MHz, CDCl₃): δ 167.9, 143.3, 139.6, 118.8, 116.6, 110.2, 106.3, 79.0, 51.1, 30.0. IR (KBr): 3372, 2975, 1687, 1573, 1485, 1257 cm⁻¹.

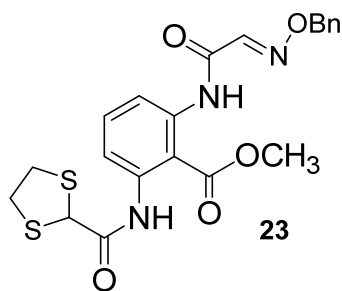
2,3-Bis-(2-benzyloxyimino-acetylamino)-benzoic acid methyl ester (22): The compound **22**,



(0.5 g, 2.4 mmol) was dissolved in THF (10 mL) and cooled in an ice bath. Sodium hydride (138 mg, 5.7 mmol) was added and the mixture was stirred 15 minutes. α-benzyloximino acid chloride³⁰ solution (1.04 g, 5.2 mmol) in dry THF (10 mL) was added to the reaction mixture and stirred at room temperature for 24 h. The THF was removed and

the residue was quenched by the addition of 10% aqueous HCl (100 mL) and stir for 3 h. The aqueous solution was extracted with ethyl acetate (100 mL), and the organic layer was washed with water (100 mL), saturated sodium bicarbonate solution (100 mL), water (100 mL), brine (100 mL), and dried over anhydrous MgSO₄. After filtration and concentration, the residue was purified by column chromatography (20:80 EtOAc:hex) to give **23** as white solid (0.9 g, 78%). Mp 150-152°C. ¹H-NMR (400 MHz, CDCl₃): δ 10.95 (s, 1H, NH), 9.06 (s, 1H, NH), 8.05 -8.03 (d, 1H, *J* = 7.9 Hz), 7.91-7.89 (d, 1H, *J* = 7.8 Hz), 7.56 (s, 1H), 7.54 (s, 1H), 7.52-7.50 (t, 1H, *J* = 6.6 Hz), 7.45-7.35 (m, 10H), 5.36 (s, 2H), 5.24 (s, 2H), 3.94 (s, 3H). ¹³C-NMR (100.6 MHz, CDCl₃): δ 167.2, 160.8, 160.3, 143.3, 142.6, 136.3, 135.9, 131.6, 131.3, 130.8, 129.0, 128.7, 128.6, 128.5, 128.4, 128.1, 125.8, 122.7, 78.3, 77.8, 52.5. IR (KBr): 3448, 3246, 1697, 1681, 1534, 1000, 754 cm⁻¹. Elemental Analysis: Calcd for C₂₆H₂₄N₄O₆: C, 63.93; H, 4.95; N, 11.48. Found: C, 63.94; H, 4.80; N, 11.37.

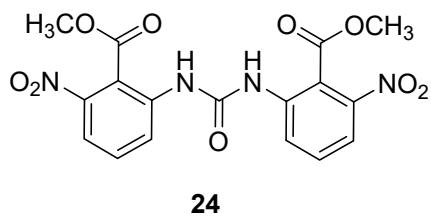
2-(2-Benzyloxyimino-acetylamino)-6-[[1,3]dithiolane-2-carbonyl]-amino]-benzoic acid methyl ester (23)



methyl ester (23): In the manner described above, the compound **20** (0.25 g, 0.76 mmol) was treated with 1,3-dithiolane-2-carbonyl chloride¹⁶ (141 mg, 0.84 mmol) in presence of 0.212 mL (154 mg, 1.5 mmol) of triethylamine at 0°C in 20 mL of dichloromethane. Column chromatography (30:70 EtOAc:hex) to give **21** as pale

yellow solid (225 mg, 64%). Mp 170-172°C. ¹H-NMR (400 MHz, CDCl₃): δ 10.91 (s, 1H, NH), 10.69 (s, 1H, NH), 8.27-8.25 (d, 1H, *J* = 7.9 Hz), 8.20-8.18 d, 1H, *J* = 7.6 Hz), 7.59 (s, 1H), 7.52-7.50 (t, 1H, *J* = 7.7 Hz), 7.42 (m, 5H), 5.31 (s, 2H), 5.03 (s, 1H), 3.93 (s, 3H), 3.43-3.40 (m, 4H). ¹³C-NMR (100.6 MHz, CDCl₃): δ 169.1, 167.5, 144.6, 139.7, 138.9, 136.6, 134.2, 129.0, 128.9, 128.6, 118.1, 118.1, 109.1, 78.1, 55.1, 53.2, 39.6. IR (KBr): 3448, 3290, 2948, 1695, 1684, 1659, 1534, 1500, 1467, 1287, 806 cm⁻¹. Elemental Analysis: Calcd for C₂₁H₂₁N₃O₅S₂: C, 54.89; H, 4.61; N, 9.14. Found: C, 54.13; H, 4.45; N, 8.88.

Dimethyl 6,6'-(carbonylbis(azanediy))-bis(2-nitrobenzoate) (24)



g, 10.0 mmol) in aqueous glacial acetic acid (10 mL/5 mL) and heated at 110°C until no more nitrogen gas evolved (2 h). Poured the reaction mixture into crushed ice (100 g) and stirred for 30 minutes to precipitate the product. Filtered and

washed well with water (250 mL). After dry obtained 1.9 g of essentially pure product in 91% yield. ¹H-NMR (DMSO-d₆, 400): δ 9.10 (s, 1H, NH urea), 8.12-8.10 (d, 1H, *J* = 7.6 Hz, CH alpha to Nitro), 7.87-7.85 (d, 1H, *J* = 7.6 Hz, CH alpha to urea), 7.73-7.71 (1H, *J* = 7.4 Hz, CH meta), 3.83 (s, 3H, COOCH₃). ¹H-NMR (CDCl₃, 400 MHz): δ 9.02 (s, 1H, NH urea), 8.51-8.49 (d, 1H, *J* = 7.6 Hz, CH alpha to Nitro), 7.63-7.54 (m, 2H, alpha to urea, CH meta), 3.93 (s, 3H,

COOCH₃). ¹³C-NMR (DMSO-d₆, 400 MHz): δ 165.4 (CO, ester), 153.3 (CO, Urea), 148.3 (C-Nitro), 138.0 (C-NH-Urea), 132.2 (CH, alpha to Nitro), 130.4 (CH alpha to urea), 120.6 (C-COOMe), 120.2 (CH meta), 54.3 (CH₃, COOCH₃).

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