NMR & X-RAY Correlations
WITH AROMATIC DONORS AND THIO(BARBITURIC) ACID ACCEPTORS

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INTRODUCTION

The properties of donor-acceptor dyes with conjugated systems are particularly sensitive to structural modifications. These "tunable" materials have many applications in electronic switching and laser frequency doubling, medicine, and sensors.[1-3] Our research group has synthesized numerous example compounds with (thio)barbituric acid acceptors, and found that the chemistry results in four different products, as confirmed by X-ray analysis. To determine the effects of the location and electronic interaction of groups G on structure and properties of donor-acceptor polyene dyes, we collected experimental data (NMR, IR, UV, fluorescence, and X-ray) for selected members of series 1-4. Here we compare NMR (^{1}H NMR, ^{13}C NMR) for members of series 1-3 taking into account bond lengths and angles from X-ray structures to characterized ground state structures. Since the acceptor and remained constant in all four molecules, the trends were used to compare steric and electronic effects on the 'donor 'on product properties in these series.
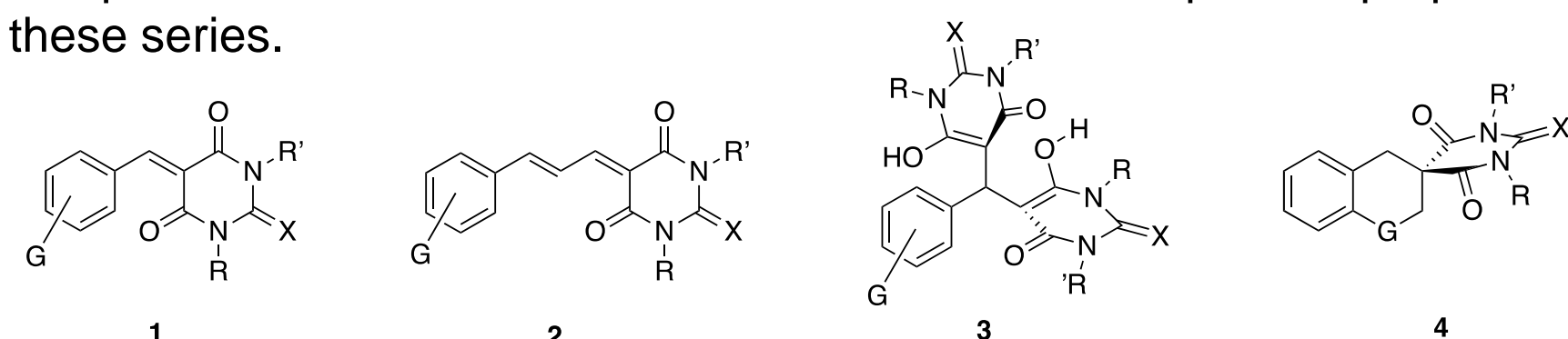

Figure 1. Series of compounds synthesized in this study, some examples exist in the literature.
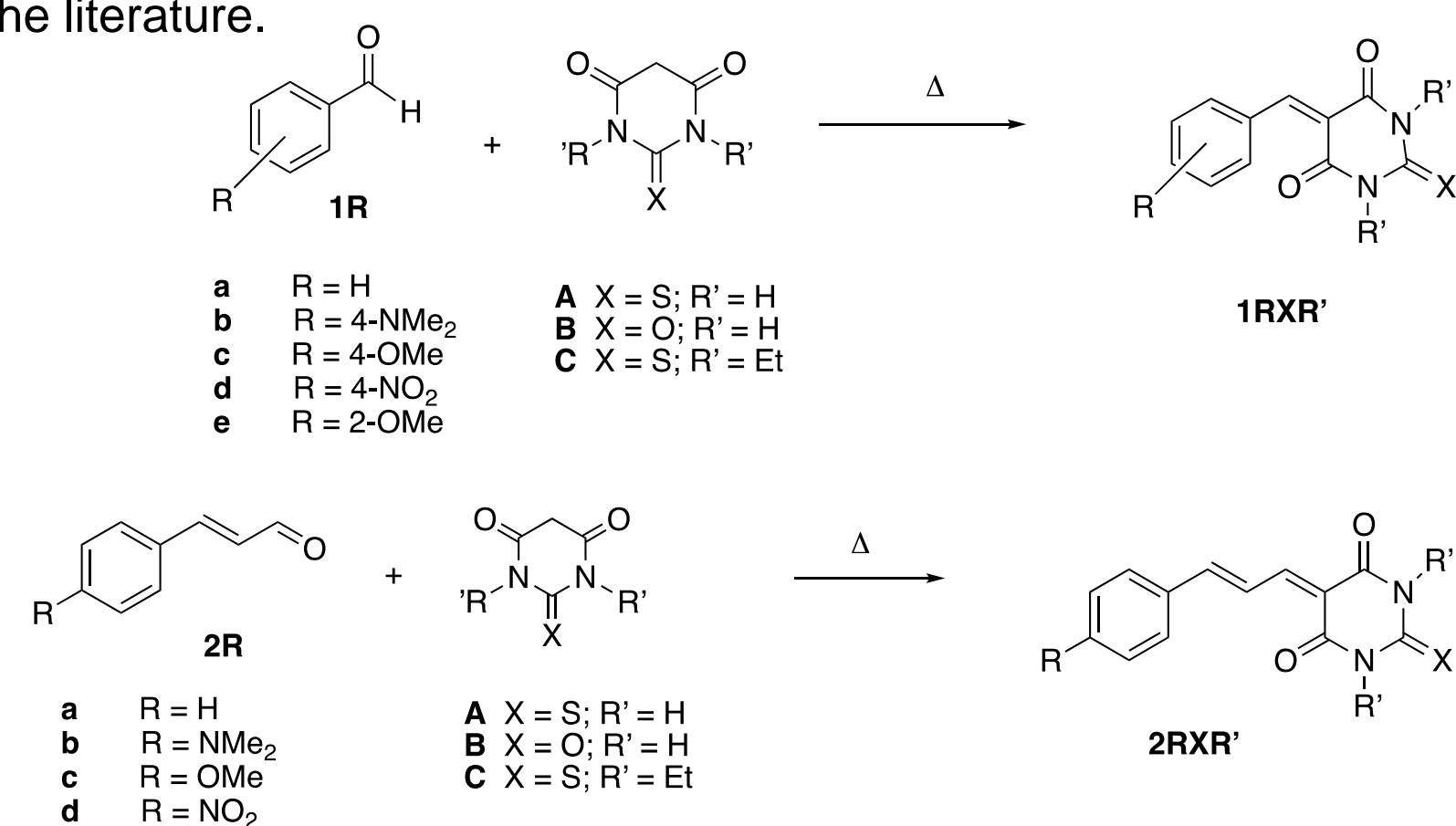

Figure 2. General approach to products **1** and **2** via Knoevenagel reaction.

Series **3** and **4** are side reactions that occur are major product in some examples. For example, **1a** forms **3aA**, **3aB** or **3aC** when heated in ethanol or water with **A**, **B**, or **C**. Similarly, **1j** reacts with **A**, **B**, or **C** to form the **4j** derivative. See X-ray structures below for examples.

X-ray Structures for Examples of 3 and 4

Series **3** was reported previously when a large excess of thiobarbituric acid used with electron deficient benzaldehydes (G = CN, NO₂, H).[9] The intramolecular rearrangement of dialkylaminobenzenes to form spirolinkages to active methylene acceptors is well known[10] and our X-rays structure of **4jA** demonstrates a new example occurs as the only product of **1j** and **A**.
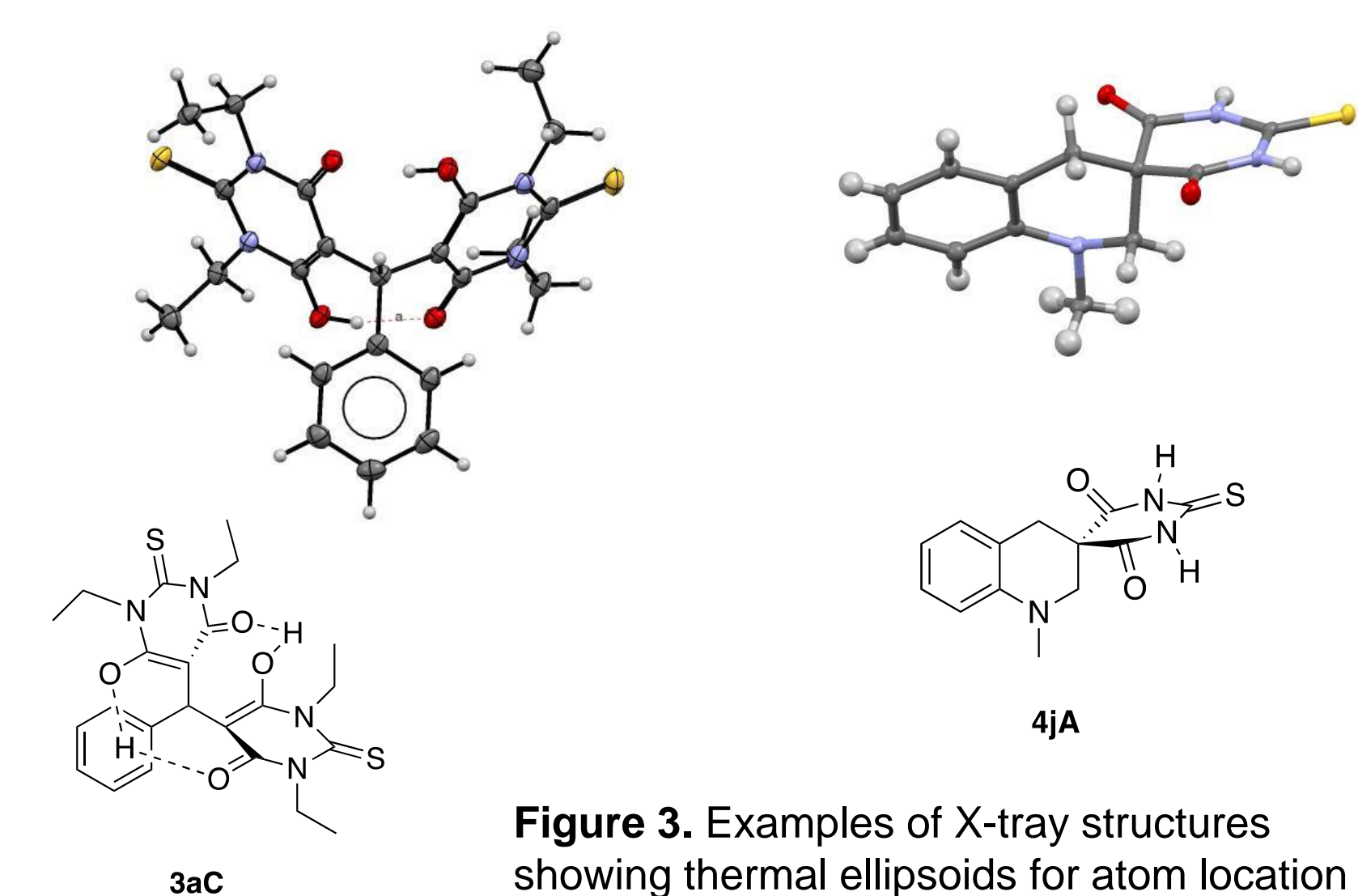

Figure 3. Examples of X-tray structures showing thermal ellipsoids for atom location in unexpected products **3aC** and **4jA**.

EXPERIMENTAL METHODS

Materials. Compounds were synthesized according to a three step method[2] described for julolidine in the companion poster.

Nuclear Magnetic Resonance Spectroscopy. ^{1}H NMR analysis was run on a JEOL ECM 500 NMR using DMSO-d₆, \and referenced to the residual protons. ^{13}C NMR analysis was run on a JEOL ECM 500 NMR (10,000 scans). 2-D methods literature and MestreNova were used to determine [1]H -^{13}C chemical shifts and coupling constants.

Calculations. NMR spectra were qualitatively modeled with ChemDraw Professional 16.0 (an empirical program that sums contributions to fragments). They were also modeled with using Gaussian 09 (B3LYP) using DMSO solvent.

¹H NMR

^{1}H NMR chemical shifts of protons A-G assigned using ^{1}H NMR spectra, literature,[5] and ChemDraw (Chem Office).
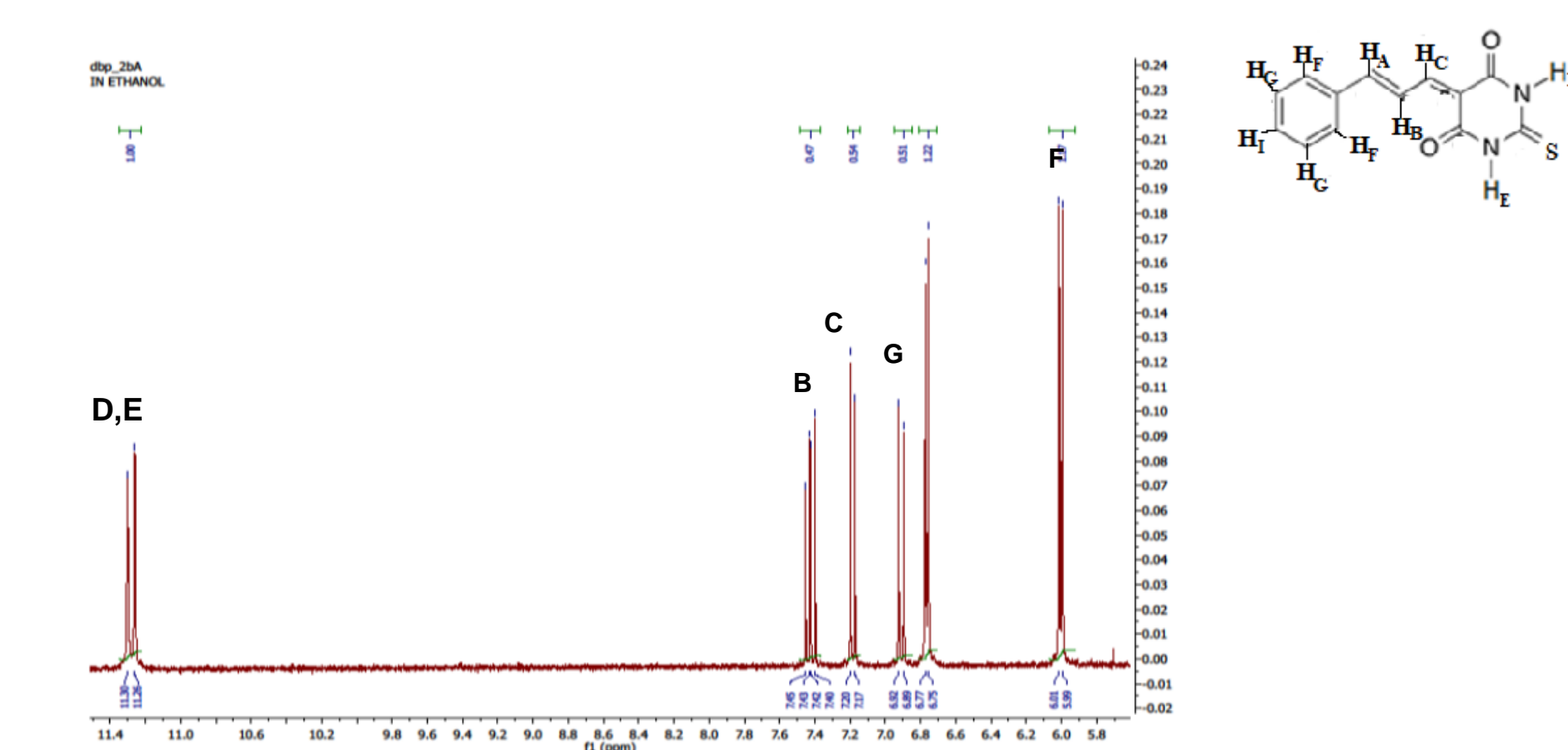

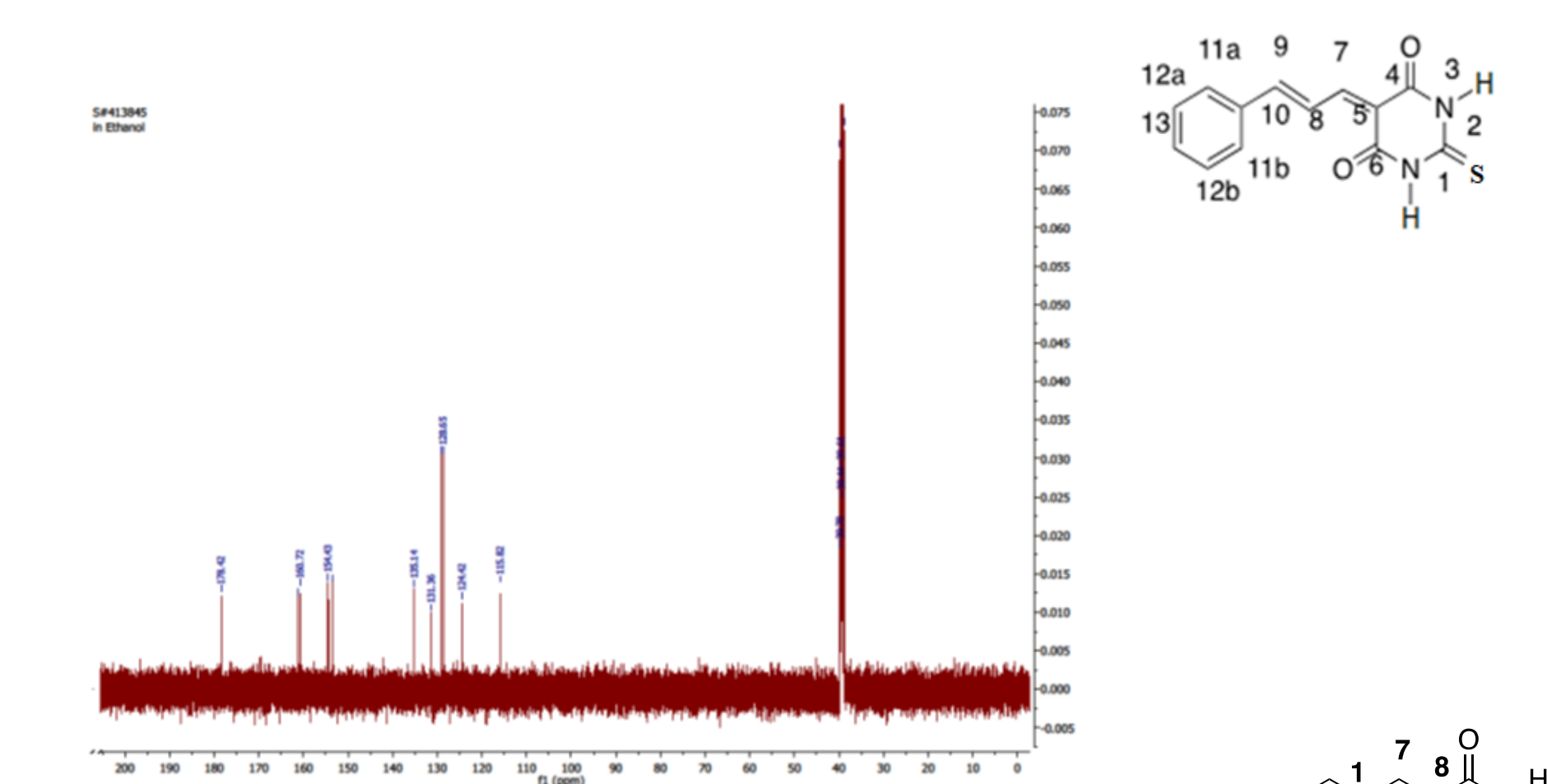**Figure 4.** ^{1}H NMR of **2aA** with vinyl with δ = 6-8 ppm expanded

Figure 5. ([13] C) for **2aA**.

Table 1. Key peaks that indicate **1**, **3** and **4** series.

Compound	C7	C8
1bA	111.4	154.6
3aA	33.5	96.1
4jA	37.8	55.6

¹³C NMR

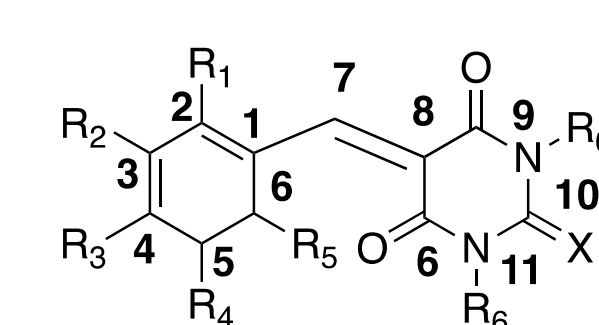[13]C spectra easily distinguish series 1,3, and 4, as illustrated in Table 1.

Table 2. ^{13}C NMR Chemical Shifts of carbons 1-16 assigned using ^{13}C NMR spectra, literature,[4] and ChemDraw (Chem Office).

Carbon	1bA (R3 = NMe2)	1cA (R₃= OMe)	1fA (R₁=R₃ = OMe)	1gA (R₁=R₃ = R₅ = OMe)	1hA (R₁=R₃ = R4 = OMe)
1	120.37	125.22	114.59	106.24	113.01
2	139.6	137.88	160.11	159.05	157.3
3	111.38	114.04	97.59	90.77	96.21
4	156.09	155.90	162.64	160.88	159.3
5	111.38	114.45	106.38	90.77	149.47
6	139.6	137.88	136.01	159.05	113.19
7	109.26	115.55	114.59	117.65	115.92
8	154.67	155.90	159.54	146.78	141.71
9	160.32	163.91	166.76	165.33	160.26
10	177.42	178.21	178.38	178.27	178
11	162.89	164.51	166.76	165.33	162.61

X-Ray Structures

Table 3. Comparison of relevant X-ray bond lengths and angles in **1fA, 1fC, 1gA, 1hA, 1hB,** and **1hC**.
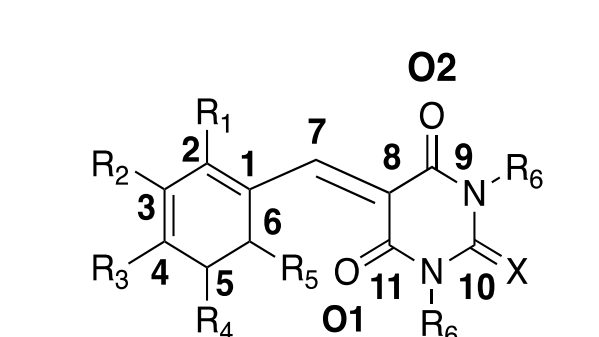
Bond	1fA	1fC	1gA	1hA	1hB	1hC
C1-C2	1.437	1.432	1.420	1.422	1.422	1.431
C2-C3	1.382	1.382	1.384	1.391	1.383	1.394
C3-C4	1.390	1.398	1.399	1.387	1.391	1.388
C4-C5	1.413	1.399	1.391	1.415	1.416	1.421
C5-C6	1.374	1.383	1.390	1.370	1.369	1.374
C6-C1	1.423	1.407	1.418	1.430	1.422	1.416
C1-C7	1.429	1.436	1.435	1.423	1.432	1.426
C7-C8	1.376	1.371	1.360	1.383	1.380	1.386
C8-C9	1.480	1.474	1.473	1.471	1.469	1.470
C8-11	1.449	1.461	1.427	1.468	1.465	1.449
BLA						
Single*	1.427	1.431	1.424	1.424	1.425	1.423
double	1.399	1.371	1.388	1.405	1.400	1.404
D (x10²)	2.8	6.0	3.6	1.9	2.5	1.9
Angles						
Twist	0	28.83	42.91	16.69	4.27	2.96
C1-C7-C8	138.47	135.9	130.54	136.56	137.11	138.48
H-bonding						
2-OMe-H7	2.149	2.249	2.419	2.237	2.215	2.152
O2-H7	2.237	2.278	2.404	2.309	2.262	2.230
O1-C6	2.131	2.224	n/a	2.116	2.030	2.081
N2H-C2	n/a	n/a	2.042	1.998	2.020	n/a
N2H'-C2'	n/a	n/a	1.994	1.989	2.006	n/a
packing	N-Et *trans*					N-Et *cis*

[a] BLA Included bonds between C8 and C9, C11. [b] Planes are defined by C2-C1-C7 and C7-C8-C11

Planar molecules would be expected to be more conjugated, and have less bond length alternation (BLA, difference between single and double bonds). The compounds in Table 1 exhibit twist angles from planarity in the order: **1fA (q= 0°) < 1hC < 1hB < 1hA < 1fE < 1gA**. The twist angle is defined as the angle between planes containing C2-C1-C7 and C11-C8-C7 and corresponds to BLA.

X-Ray Analysis

The most conjugated compounds (BLA = 1.9) are the ones with the strongest donor (**1hA** and **1hC**). 1hB is less conjugated because it has a weaker acceptor. According to this analysis, 1fC would be expected to have a similar BLA to **1fA**. However, in **1fC**, the N-Et groups interrupt packing and force the molecule to twist, decreasing BLA and increasing distances of H-bonding interactions. As expected, **1gA** is the most highly twisted structure due to the 2, 6-dimethoxy substitution pattern that decreases the C1-C7-C8 bond angle and distances between H-bonding interactions.
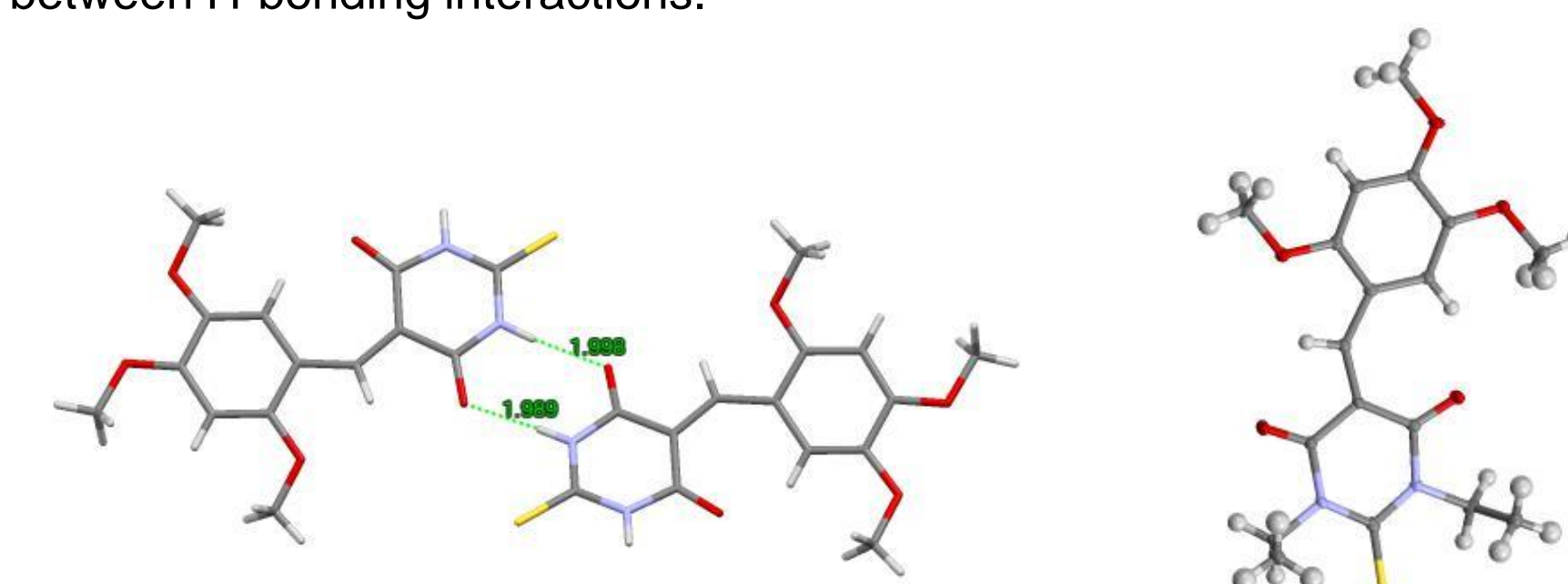

Figure 6. X-ray structures of **1hA** (left) and **1hC**, which have similar electronic structures, but steric differences (see Table 3)

Conclusions

- ^{1}H NMR and ^{13}C NMR, and X-ray analysis were used to characterize soluble and crystalline derivatives **1, 2, 3,** and **4**.
- ^{13}C NMR unambiguously indentifies desired series vs. side product series 3 and 4 by C7 and C8 chemical shifts.
- ^{13}C NMR **C-7** ppm values increase as the number of donating groups increase on aromatic ring.
- The observed molecular torsional angle increases in the series **1fA <1hC < 1hB < 1hA < 1fE < 1gA**, presumably due to a combination of stabilizing packing interactions and degree of conjugation in the molecules.

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