Supporting Information

A Cascade Process for the Synthesis of ortho-Formyl Allyl Aryl Ethers and 2H-Chromen-2-ol Derivatives from Arynes via Trapping of o-Quinone Methide with Activated Alkene

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Copies of \textsuperscript{1}H, \textsuperscript{13}C NMR and HRMS spectra
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)

S2
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
$^{1}$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)

3ad
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
$^1$H-NMR (500 MHz, CDCl$_3$)

$^1$C-NMR (126 MHz, CDCl$_3$)
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
\[ \text{\(^1H-NMR (500 MHz, CDCl\textsubscript{3})} \]

\[ \text{\(^{13}C-NMR (126 MHz, CDCl\textsubscript{3})} \]
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)

S12
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)

S13
\[ ^1H-NMR \ (500 \text{ MHz, CDCl}_3) \]

\[ ^{13}C-NMR \ (126 \text{ MHz, CDCl}_3) \]
**1H-NMR (500 MHz, CDCl₃)**

![1H-NMR spectrum]

**13C-NMR (126 MHz, CDCl₃)**

![13C-NMR spectrum]
**1H-NMR (500 MHz, CDCl₃)**

**13C-NMR (126 MHz, CDCl₃)**
$^{1}H$-NMR (500 MHz, CDCl$_3$)

$^{13}C$-NMR (126 MHz, CDCl$_3$)
**1^H-NMR (500 MHz, CDCl₃)**

**13^C-NMR (126 MHz, CDCl₃)**

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S21
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
**1H-NMR (500 MHz, CDCl₃)**

![1H-NMR Spectrum](image)

**13C-NMR (126 MHz, CDCl₃)**

![13C-NMR Spectrum](image)
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)

CHO

3fb
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
$^{1}H$-NMR (500 MHz, CDCl$_3$)

$^{13}C$-NMR (126 MHz, CDCl$_3$)
$^{1}$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
$^{1}$H-NMR (500 MHz, CDCl$_3$)

$^{13}\text{C-NMR (126 MHz, CDCl}_3\text{)}$
$^{13}$C-NMR (126 MHz, CDCl$_3$)

S33
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
\textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3})

\textsuperscript{13}C-NMR (126 MHz, CDCl\textsubscript{3})
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
$^1$H-NMR (500 MHz, CDCl$_3$)

$^1$C-NMR (126 MHz, CDCl$_3$)
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)

S44
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (126 MHz, CDCl$_3$)
**HRMS of 3ba**

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<tr>
<td>271.0820</td>
<td>224.0179</td>
<td>269.0229</td>
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<td>2.19 ε 958</td>
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**HRMS of 3bb**

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<td>295.0761</td>
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![Image of 3ba](image1.png)

![Image of 3bb](image2.png)
HRMS of 3bc

![HRMS of 3bc]

HRMS of 3bd

![HRMS of 3bd]
HRMS of 3ca

\[
\text{CHO} \quad \text{OMe} \quad \text{CH}_2
\]

HRMS of 3cb

\[
\text{CHO} \quad \text{OEt}
\]
HRMS of 3ja

HRMS of 3da & 3d’a
<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Structure</th>
<th>Formula</th>
<th>Mass (m/z)</th>
<th>Charge State</th>
</tr>
</thead>
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<td>3db</td>
<td><img src="image" alt="3db Structure" /></td>
<td>Me-CHO-OEt</td>
<td>347.0798</td>
<td>4+</td>
</tr>
<tr>
<td>3d'b</td>
<td><img src="image" alt="3d'b Structure" /></td>
<td>Me-CHO-OEt</td>
<td>347.0798</td>
<td>4+</td>
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<tr>
<td>3dc</td>
<td><img src="image" alt="3dc Structure" /></td>
<td>Me-CHO</td>
<td>343.0674</td>
<td>4+</td>
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<td>3d'c</td>
<td><img src="image" alt="3d'c Structure" /></td>
<td>Me-CHO</td>
<td>343.0674</td>
<td>4+</td>
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</table>

**HRMS of 3db & 3d'b**

**HRMS of 3dc & 3d'c**
HRMS of 3dd & 3d'd

3dd

3d'd

HRMS of 3ea & 3e'a

3ea

3e'a
### HRMS of 3eb & 3e'b

![HRMS of 3eb & 3e'b](image)

### HRMS of 3ec & 3e'c

![HRMS of 3ec & 3e'c](image)
HRMS of 3fa

CHO \rightarrow CH_{2}O

3fa

HRMS of 3fb

CHO \rightarrow CH_{2}OEt

3fb
HRMS of 3ga

![HRMS of 3ga image]

HRMS of 3g’a

![HRMS of 3g’a image]
HRMS of 3gb

HRMS of 3g'b
HRMS of 3gc

![Compound 3gc](image)

HRMS of 3g’c

![Compound 3g’c](image)
HRMS of 3ha

![Graph of 3ha](image)

HRMS of 3aa(D)

![Graph of 3aa(D)](image)
HRMS of 4af

HRMS of 4bf
### HRMS of 4if

**Molecular Formula:** C₂₀H₁₇NO₄SMe

**Exact Mass:** 339.0480

**Elemental Composition:**
- C: 54.93%
- H: 4.12%
- N: 3.58%
- O: 21.76%
- S: 10.42%

**Isotopic Abundance:**
- [C₂₀H₁₇NO₄SMe]⁺ 100%
- [C₂₀H₁₆NO₄SMe]⁺ 31.4%
- [C₁₉H₁₆NO₄SMe]⁺ 9.3%
- [C₁₉H₁₅NO₄SMe]⁺ 0.3%

### HRMS of 4ag

**Molecular Formula:** C₂₁H₂₀NO₄SMe

**Exact Mass:** 334.0972

**Elemental Composition:**
- C: 56.96%
- H: 4.80%
- N: 3.07%
- O: 24.34%
- S: 10.21%

**Isotopic Abundance:**
- [C₂₁H₂₀NO₄SMe]⁺ 100%
- [C₂₁H₁₹NO₄SMe]⁺ 21.4%
- [C₂₀H₂₀NO₄SMe]⁺ 6.7%
- [C₂₀H₁₉NO₄SMe]⁺ 0.3%

HRMS of 4ah

HRMS of 4ch
HRMS of 3ai

![HRMS Graph]

**3ai**

![Chemical Structure of 3ai]
Assignment of product obtained from unsymmetrical arynes.

The products 3da/3d'a - 3ec/3e'c obtained from unsymmetrical arynes 1d and 1e are isolated as inseparable mixtures of two regioisomers. The regioisomers are not separated into individual isomers and their ratio was determined by $^1$H NMR data.

In order to confirm the product 3fa obtained from unsymmetrical arynes 1f, we have carried out an independent experiment to synthesize the same compound 3fa alternatively using 2-hydroxy-1-napthaldehyde and activated alkene methyl-2-(bromomethyl)acrylate. The product obtained from this independent experiment was characterized by $^1$H and $^{13}$C NMR data. This spectroscopic data resemble with our synthesized compound 3fa, which confirmed our proposed structure. This suggests that the product obtained from 1f results in single regioisomer 3fa which is attributed to preferential attack of carbonyl oxygen atom of DMF at the less sterically hindered carbon atom of naphthalyne.

The assignment of products 3ga and 3g'a obtained from unsymmetrical aryne precursor 1g when treated with methyl-2-(bromomethyl)acrylate could be explained from $^1$H NMR data. In case of compound 3ga, the proton (3) resonates at 7.33 ppm whereas in case of compound 3g'a, the proton (6) resonates at 6.47 ppm which appears to be more upfield due to the presence of ether groups on the adjacent position of the proton. This information from $^1$H NMR data helps us to confirm our proposed structure.

The structure of the compound 3ha was characterized by using 1D ($^1$H and $^{13}$C) and 2D ($^1$H-$^1$H NOESY experiment) NMR analysis.

The NOESY correlation between H-4/OMe-3 (Aromatic-ortho) protons and H-6/H-3' protons suggests that they are in spatial proximity which confirmed our proposed structure.
NOESY of 3ha