Supplementary Information

A metal-free one-pot synthesis of benzo[c]chromen-6-ones from 3, 4- dichlorocoumarin and butadiene by tandem photo-thermal-photo reactions

Yan Zhang†, Yan Tian‡, Pei Xiang§, Ning Huang‡, Jianyi Wang†, Jian-Hua Xu§, Min Zhang* †

†School of Chemistry and Chemical Engineering, Guangxi University, Nanning, Guangxi 530004, China
‡Guangxi Environmental Monitoring Center, Nanning, Guangxi 530028, China
§School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, China
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1. The synthesis details of starting materials.

a) The syntheses of 3, 4-dichlorocoumarins

\[
\begin{align*}
\text{R} & \text{OH} + \begin{array}{c}
\text{Cl} \text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\xrightarrow{1) \text{AlCl}_3, \text{CS}_2}
\text{Cl} \text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{O} \\
\end{align*}
\]

The syntheses of 3, 4-dichlorocoumarins are carried out as described in lit 1. The reaction started from phenols and hexachloropropene catalyzed by AlCl\(_3\) in CS\(_2\) and the solvent was removed. The residue was put in cold dilute H\(_2\)SO\(_4\) and filtered, oven dried. The crude product was purified by silica gel chromatography. The proton NMR for the dichlorocoumarins are given below:

2a

3, 4-dichlorocoumarin (3, 4-dichloro-2H-chromen-2-one)
White needles, m.p. 106-108 °C (Acetone/PE, 2/1, V/V)
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 8.0\) Hz, 1H), 7.66 (t, \(J = 7.8\) Hz, 1H), 7.45 (t, \(J = 7.7\) Hz, 1H), 7.42 (d, \(J = 7.9\) Hz, 1H).

2b

3, 4-dichloro-6-fluoro-2H-chromen-2-one
White needle crystal m.p. 106-108 °C (Acetone/PE, 2/1, V/V)
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.55 (dd, \(J = 8.4, 2.9\) Hz, 1H), 7.40 – 7.36 (m, 1H), 7.34 (m, 1H).

2c

3, 4, 6-trichloro-2H-chromen-2-one
White needles, m.p. 130-132 °C (Acetone/PE, 2/1, V/V)
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 2.4\) Hz, 1H), 7.60 – 7.55 (m, 1H), 7.34 (d, \(J = 8.8\) Hz, 1H).
2d

6-bromo-3,4-dichloro-2H-chromen-2-one
Yellow needles, m.p. 144-146 °C (Acetone/PE, 2/1, V/V)
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.98 (t, $J = 2.1$ Hz, 1H), 7.70 (ddd, $J = 8.8$, 1.5, 0.6 Hz, 1H), 7.27 (d, $J = 8.8$ Hz, 1H).

2e

3, 4-dichloro-6-methyl-2H-chromen-2-one
White needles, m.p. 160-164 °C (Acetone/PE, 2/1, V/V)
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.65 (s, 1H), 7.42 (d, $J = 8.4$ Hz, 1H), 7.28 (d, $J = 8.4$ Hz, 1H), 2.47 (s, 4H).

2f

3, 4-dichloro-6-phenyl-2H-chromen-2-one
White needles, m.p. 146-148 °C (Acetone/PE, 2/1, V/V)
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 2.1$ Hz, 1H), 7.84 (dd, $J = 5.5$, 3.8 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.52 – 7.48 (m, 2H), 7.47 (dd, $J = 8.3$, 4.0 Hz, 1H), 7.45 – 7.40 (m, 1H).

2g

3, 4-dichloro-8-phenyl-2H-chromen-2-one
White flocculent solid, m.p. 148-150 °C (Acetone/PE, 2/1, V/V)
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.90 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.66 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.56 (dt, $J = 8.1$, 1.7 Hz, 2H), 7.49 (ddd, $J = 7.8$, 6.0, 2.5 Hz, 3H), 7.46 – 7.41 (m, 1H).
2h
3, 4, 6, 8-tetrachloro-2H-chromen-2-one
Yellow block crystals, m.p. 158-160 °C (Acetone/PE, 2/1, V/V)
$^1$H NMR (600 MHz, CDCl$_3$) δ 7.75 (d, J = 2.5 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H).

b) The synthesis of 2, 3-dimethoxy-1, 3-butadiene $^2$ (3b)

![2, 3-dimethoxy-1, 3-butadiene]

The synthesis of 3b is carried out as described in the Supporting Information of lit 2: A mixture of biacetyl (17.20 g, 0.20 mol), absolute methanol (25 ml, 1.25 mol), trimethyl orthoformate (63.60 g, 0.60 mol) and concentrated sulfuric acid (5 drops) was refluxed for 10h. The excess of reagents were distilled off and the remaining liquid was vacuum-distilled. Ammonium dihydrogenphosphate (25 mg) and a few crystals of hydroquinone were added and the liquid was heated at 100°C to 110°C. Methanol slowly distilled over, together with some remaining orthoformate. The temperature was raised (160 °C to 170 °C) and the colorless oily liquid collected between 129°C and 132°C (17.30 g or 76% of crude diene). Redistillation gave 2, 3-dimethoxy-1, 3-butadiene (15.50 g, 68%), b. p. 132-132.5 °C.

References
2. The NMR charts of compounds

1a

$^1$H NMR, 600MHz, CDCl$_3$

$^{13}$C NMR, 151MHz, CDCl$_3$
$^1$H NMR, 600MHz, CDCl$_3$

$^{13}$C NMR, 151MHz, CDCl$_3$
Id
$^{13}\text{C NMR, 151MHz, CDCl}_3$

$^{1}\text{H NMR, 600MHz, CDCl}_3$
$^{13}$C NMR, 151MHz, CDCl$_3$

$^1$H NMR, 600MHz, CDCl$_3$
$^{13}$C NMR, 151MHz, CDCl$_3$

$^1$H NMR, 600MHz, CDCl$_3$
$^1$H NMR, 600 MHz, CDCl$_3$

$^{13}$C NMR, 151 MHz, CDCl$_3$
$^{13}$C NMR, 151 MHz, CDCl$_3$

$^1$H NMR, 600 MHz, CDCl$_3$
$^1$H NMR, 600 MHz, CDCl$_3$

$^{13}$C NMR, 151 MHz, CDCl$_3$
$^{1}H$ NMR, 600 MHz, CDCl$_3$

$^{13}C$ NMR, 151 MHz, CDCl$_3$
$^{19}$F NMR

$^{19}$F NMR, 500MHz, CDCl$_3$

4c

$^1$H NMR, 600MHz, CDCl$_3$
$^{13}$C NMR, 151 MHz, CDCl₃

$^1$H NMR, 600 MHz, CDCl₃
$^1$H NMR, 600MHz, CDCl$_3$

$^1$C NMR, 151MHz, CDCl$_3$
$^{13}$C NMR, 151MHz, CDCl$_3$

$^1$H NMR, 600MHz, CDCl$_3$

S29
4i

$^{13}C$ NMR, 151 MHz, CDCl$_3$

$^1$H NMR, 600 MHz, CDCl$_3$
$^{1}H$ NMR, 600 MHz, CDCl$_3$

$^{13}C$ NMR, 151 MHz, CDCl$_3$
$5c$

\[ \text{\textsuperscript{1}H NMR, 600MHz, CDCl}_3 \]

\[ \text{\textsuperscript{13}C NMR, 151MHz, CDCl}_3 \]
Elemental composition search on mass 295.03

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<th>RDB equiv.</th>
<th>Composition</th>
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D161493 #52  RT: 0.83  AV: 1  NL: 2.16E6
T: FTMS + p ESI Full ms [100.00-1000.00]
3. The crystal data

Crystal data for 1d (Fig. 2): C15H11BrO2, M = 303.15, yellow needle, Bruker CCD diffractometer, Mo-Kα radiation (λ= 0.71073 Å), 0.32 × 0.26 × 0.14mm, T = 293(2) K. Triclinic, space group P-1, a = 7.8650(11) Å, b = 8.6070(11) Å, c = 10.2615(15) Å, α = 92.788(6)º, β = 112.186(6)º, γ = 105.046(4)º, V = 612.75(15) Å³, Z = 2, Dc = 1.643 g cm⁻³, μ = 3.344 mm⁻¹, F(000) = 304. The structure was solved by direct method (SHELXL 97) and refined on F2 by full-matrix least-squares method. A total of 2718 independent reflections [R (int) = 0.0366] were used in the refinement, which converged with R₁ = 0.0564 and wR₂ = 0.1076 (GOF = 1.020).

Fig. 1 ORTEP drawing of 1d, ellipsoids are drawn at 30 % probability level.
Crystal data for 4i (Fig. 1): C15H14Cl2O4, M = 329.16, colorless blocks, Bruker CCD diffractometer, Mo-Kα radiation (λ= 0.71073 Å), 0.32 × 0.28 × 0.26 mm, T = 296(2) K. Monoclinic, space group P21/c, a = 13.0766(3) Å, b = 8.0857(2) Å, c = 14.0760(4) Å, α = 90.00º, β = 90.350(2)º, γ = 90.00º, V = 1488.28(7) Å³, Z = 4, Dc = 1.478 g cm⁻³, μ = 0.448 mm⁻¹, F(000) = 688. The structure was solved by direct method (SHELXL 97) and refined on F2 by full-matrix least-squares method. A total of 3393 independent reflections [R (int) = 0.0389] were used in the refinement, which converged with R1 = 0.0442 and wR2 = 0.1007 (GOF = 1.046).

![ORTEP drawing of 4i](image)

**Fig. 2** ORTEP drawing of 4i, ellipsoids are drawn at 30% probability level.