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Dimethyl homophthalates to naphthopyrans: the total synthesis of arnottin I and the formal synthesis of (−)-arnottin II†

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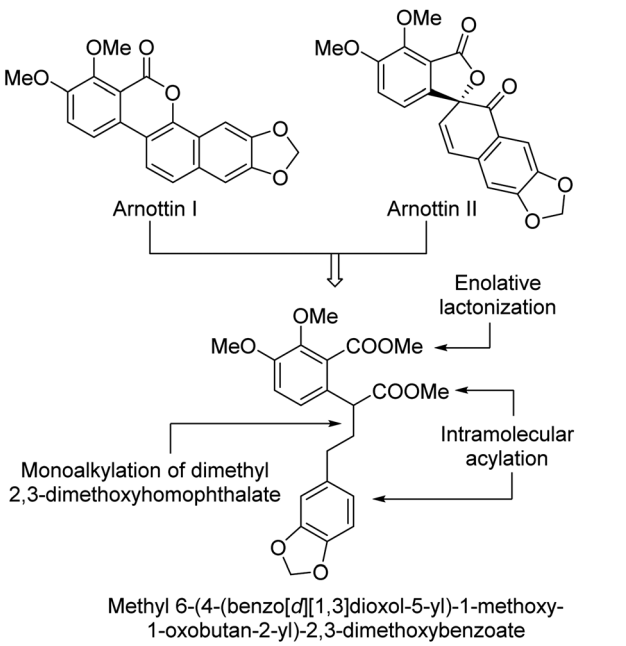
A simple and efficient 3-step synthetic protocol has been reported for dimethyl homophthalates to naphthopyrans. Starting from dimethyl 2,3-dimethoxyhomophthalate, a practical synthesis of arnottin I has been described *via* a base catalyzed mono-alkylation, the selective hydrolysis of an aliphatic ester moiety, two consecutive intramolecular cyclizations and an oxidative aromatization pathway with a very good overall yield. The involved intramolecular acylation followed by an associated enolative lactonization was the decisive step. The synthesis of dihydroarnottin I also completes the formal synthesis of (−)-arnottin II.

The coumarin-based natural products such as gilvocarcins, ravidomycins, chrysomycins and defucogilvocarcins are an important class of antibiotics.[1a–e] Analogous arnottin I and the related (−)-arnottin II were isolated as minor components from the bark of *Xanthoxylum arnottianum Maxim.* (Rutaceae) by Ishikawa and co-workers in 1977.[2] They established their structures in 1993 and 1995 on the basis of spectral data and synthesis.[3a,b] Since then several well-designed synthetic routes involving new carbon–carbon bond forming strategies have been reported for these significant targets.[4a–i] A careful scrutiny of the arnottins I and II structures and their retrosynthetic analysis revealed that the multifunctional methyl 6-(4-(benzo[*d*][1,3]dioxol-5-yl)-1-methoxy-1-oxobutan-2-yl)-2,3-dimethoxybenzoate would be a potential precursor to provide convergent access to both the target compounds (Scheme 1). More specifically, the selective intramolecular acylation of the diester followed by a concomitant enolization–lactonization would be the strategic step in generating rings B and C to obtain the desired advanced common intermediate of arnottins I and II. In continuance of our efforts to synthesize structurally interesting and biologically important natural and unnatural products from cyclic anhydrides and their derivatives as the potential precursors,[5a–e] we herein report a concise and efficient access to naphthopyrans, arnottin I and arnottin II (Scheme 2).

Dimethyl homophthalates **1a,b** on base promoted alkylation with alkyl iodides **2b,c** exclusively furnished the requisite mono-alkylated coupling products **3a–c** in 82–85% yields.[6a,b] The reaction of appropriate precursors **3a,b** with methanesulfonic acid at room temperature directly formed the desired double cyclized products **5a,b** in nearly quantitative yields (98%) *via* the corresponding unisolable tetralone intermediates **4a,b.** As per the planned strategy, an acid-promoted regioselective intramolecular Friedel–Crafts acylation utilizing an aliphatic ester moiety, the instantaneous enolization of the thus formed tetralone intermediates **4a,b** using an acidic α-methine proton and the concurrent δ-lactonization employing a less reactive aromatic ester unit took place in one-pot to deliver the aimed products **5a,b.** Compounds **5a,b** on treatment with SeO_2 in refluxing acetic acid provided the corresponding expected



Scheme 1 The retrosynthetic analysis of arnottins I and II.

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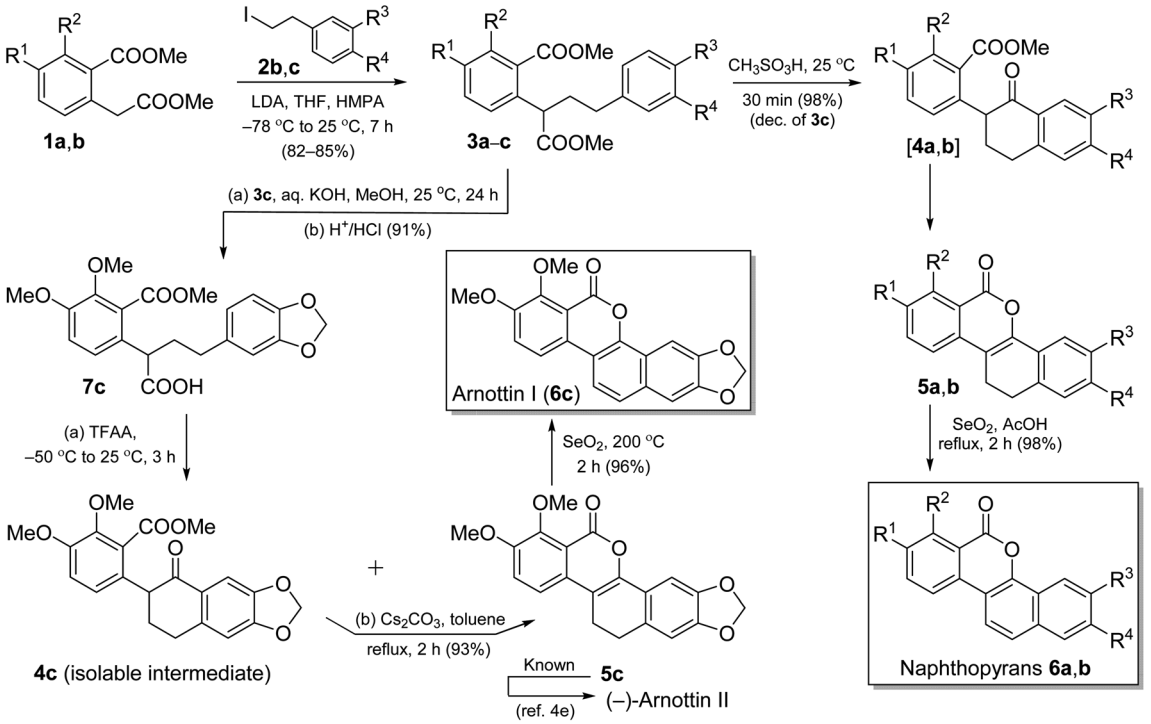

a: $R^1 = R^2 = H$, $R^3 = R^4 = OMe$; **b:** $R^1 = R^2 = R^3 = R^4 = OMe$; **c:** $R^1 = R^2 = OMe$, $R^3 + R^4 = O\text{-}CH_2\text{-}O$

Scheme 2 A general approach to naphthopyrans and the total synthesis of arnottin I.

aromatized products **6a,b** in 2 h with quantitative yield (98%). The aromatization plausibly took place *via* a regioselective introduction of an acetate function at the relatively more reactive allylic site followed by its *in situ* elimination by abstracting the adjacent benzylic proton.[7] Thus starting from dimethyl homophthalates we have developed a new practical approach to the naphthopyran systems and it has advantages in terms of number of steps involved and obtained yields.

In the second part of our studies, we planned the synthesis of arnottin I and (−)-arnottin II by using the below defined synthetic protocol. The pivotal arnottin antecedent compound **3c** on similar treatment with methanesulfonic acid underwent an unfortunate instantaneous decomposition under the several sets of reaction conditions. We also tried various conditions to effect the transformation of **3c** to **5c** utilizing reagents such as acetic acid, trifluoroacetic acid and *p*-TSA, but this always resulted in the isolation of the starting material and/or decomposition. The cause for the decomposition of compound **3c** under acidic conditions was the presence of a labile dioxymethylene bridge attached to ring D. To circumvent the above specified difficulty, we initially performed a base catalyzed regioselective mono-hydrolysis of an aliphatic ester moiety in compound **3c** and obtained the product **7c** in a 91% yield, as the synthesis of the corresponding dicarboxylic acid followed by treatment with dehydrating agents would form the cyclic anhydride and demand sequential synthetic steps to transform compound **3c** into the essential product **5c**. The acid-ester **7c** on treatment with trifluoroacetic anhydride at −50 °C to 25 °C formed a reactive mixed anhydride intermediate and delivered a mixture of the corresponding simple acylation product; the known tetralone intermediate **4c** and the desired double cyclized advanced intermediate **5c** in quantitative yield[4e] (~7 : 3 ratio, by ^{1}H NMR). Herein the second cyclization step was relatively slow due to the mesomeric deactivation of an aromatic ester function by the corresponding *ortho*-methoxy group. An increase in the reaction temperature and/or extending the reaction time again resulted in some decomposition. The above specified mixture of the tetralone intermediate **4c** and compound **5c** was silica gel column chromatographically inseparable. Thus to ensure the complete transformation into the essential compound **5c**, the above mixture of products was further treated with Cs_2CO_3 in refluxing toluene (93% yield). Starting from the advanced common intermediate **5c**, the synthesis of arnottin I by employing DDQ-oxidation in benzene and the synthesis of (−)-arnottin II *via* the Sharpless asymmetric dihydroxylative spiro-lactonization route have been known in the literature.[4e] Similarly, we repeated the DDQ-oxidation of **5c** in refluxing toluene and obtained the natural product arnottin I (**6c**) in a quantitative yield (98%). However, analogous to the **5a,b** to **6a,b** transformation, the SeO_2 oxidation of compound **5c** in refluxing acetic acid resulted in the decomposition of the reaction mixture. Alternatively, the performed SeO_2 oxidation of compound **5c** in refluxing benzene, toluene and freshly distilled acetic anhydride was very slow and provided the silica gel column chromatographically inseparable mixture of the starting material **5c** and arnottin I (**6c**) in 48 h.

The ^{1}H NMR spectra of above specified mixtures indicated only 10 to 20% conversions into the desired product **6c**. As anticipated, the neat SeO_2 (10.00 equiv.) induced oxidative aromatization of dihydronaphthopyran **5c** at 200 °C took place in 2 h without any decomposition and provided the desired natural naphthopyran **6c** in a 96% yield. The analytical and spectral data obtained for arnottin I was in complete agreement with the reported data.[3a,4e] Arnottin I was obtained in four steps by using two different oxidizing agents at the ultimate step with 71% and 69% overall yields, respectively.

In summary, we have demonstrated a bio-inspired protection-free concise and efficient total synthesis of arnottin I and the formal synthesis of (−)-arnottin II. The present transition metal free diversity oriented robust 3-step new approach to the imperative naphthopyran architectures is general in nature and will be useful to design several focused mini-libraries of their natural and unnatural analogues and congeners for SAR studies. Our present approach also provides an efficient access to several corresponding isoquinoline alkaloids.[6b,8]

Experimental section

The melting points are uncorrected. The mass spectra were taken on an MS-TOF mass spectrometer. HRMS (ESI) were taken on an Orbitrap (quadrupole plus ion trap) and TOF mass analyzer. The IR spectra were recorded on an FT-IR spectrometer. The starting materials **1a,b** and **2b,c** were prepared by using known literature procedures.[4h,9] Commercially available chemicals and reagents were used.

Methyl 2-(4-(3,4-dimethoxyphenyl)-1-methoxy-1-oxobutan-2-yl)-benzoate (3a)

A fresh solution of LDA was prepared from diisopropylamine (0.87 mL, 6.24 mmol) and *n*-BuLi (1.60 M in hexane, 4.20 mL, 6.72 mmol) in THF (5 mL) under an argon atmosphere at 0 °C. This was added to a solution of compound **1a** (1.00 g, 4.80 mmol) in THF (10 mL) and HMPA (10 mL) mixture at −78 °C under an argon atmosphere and the reaction mixture was further stirred at the same temperature for 30 min. To the above reaction mixture a solution of compound **2b** (1.54 g, 5.28 mmol) in THF (5 mL) was added in a dropwise fashion. The reaction mixture was allowed to gradually attain room temperature in 7 h. The reaction was quenched with a saturated NH_4Cl solution and the solvent was removed *in vacuo*. The obtained residue was dissolved in ethyl acetate and the organic layer was washed with water, brine and dried over Na_2SO_4. The concentration of the organic layer *in vacuo* followed by silica gel (60–120 mesh) column chromatographic purification of the resulting residue using ethyl acetate–petroleum ether (1 : 3) as an eluent gave the pure product **3a** as a thick oil (1.46 g, 82%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.95–2.25 (m, 1H), 2.35–2.70 (m, 3H), 3.68 (s, 3H), 3.87 (s, 6H), 3.88 (s, 3H), 4.64 (t, J = 8 Hz, 1H), 6.69 (s, 1H), 6.72 (t, J = 8 Hz, 1H), 6.78 (t, J = 8 Hz, 1H), 7.27–7.42 (m, 1H), 7.42–7.60 (m, 2H), 7.92 (dd, J = 8, 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 33.4, 35.2, 46.5, 52.0, 52.1, 55.7, 55.9, 111.1, 111.7, 120.2, 126.9, 128.7, 129.8, 130.7, 132.2, 134.0, 140.2, 147.2, 148.7, 167.8, 174.3; ESIMS (m/z) 395 [M + Na]$^+$; HRMS (ESI) calcd for $C_{21}H_{25}O_6$ 373.1646, found 373.1639; IR ($CHCl_3$) ν_{max} 1732, 1721, 1602 cm^{-1}.

The products **3b** and **3c** were similarly obtained by using the above specified procedure.

Methyl 6-(4-(3,4-dimethoxyphenyl)-1-methoxy-1-oxobutan-2-yl)-2,3-dimethoxybenzoate (3b)

Thick oil (1.33 g, 83%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.90–2.15 (m, 1H), 2.25–2.68 (m, 3H), 3.55 (t, J = 8 Hz, 1H), 3.67 (s, 3H), 3.82 (s, 3H), 3.85 (s, 6H), 3.86 (s, 3H), 3.88 (s, 3H), 6.62–6.74 (m, 2H), 6.79 (d, J = 8 Hz, 1H), 6.94 (d, J = 8 Hz, 1H), 7.15 (d, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 33.2, 35.3, 46.5, 52.0, 52.1, 55.7, 55.8 (2C), 61.4, 111.1, 111.6, 113.7, 120.2, 123.1, 128.3, 129.4, 133.7, 145.8, 147.1, 148.7, 151.5, 167.5, 173.9; ESIMS (m/z) 455 [M + Na]$^+$; HRMS (ESI) calcd for $C_{23}H_{29}O_8$ 433.1857, found 433.1851; IR ($CHCl_3$) ν_{max} 1735, 1610 cm^{-1}.

Methyl 6-(4-(benzo[*d*][1,3]dioxol-5-yl)-1-methoxy-1-oxobutan-2-yl)-2,3-dimethoxybenzoate (3c)

Thick oil (1.32 g, 85%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.65–2.10 (m, 1H), 2.20–2.65 (m, 3H), 3.54 (t, J = 8 Hz, 1H), 3.65 (s, 3H), 3.85 (s, 9H), 5.89 (s, 2H), 6.58 (dd, J = 8, 2 Hz, 1H), 6.64 (d, J = 2 Hz, 1H), 6.71 (d, J = 8 Hz, 1H), 6.94 (d, J = 10 Hz, 1H), 7.13 (d, J = 10 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 33.3, 35.3, 46.5, 51.9, 52.1, 55.8, 61.4, 100.6, 108.0, 108.8, 113.8, 121.1, 123.1, 128.2, 129.4, 135.0, 145.6, 145.8, 147.4, 151.5, 167.5, 173.8; ESIMS (m/z) 439 [M + Na]$^+$; HRMS (ESI) calcd for $C_{22}H_{25}O_8$ 417.1544, found 417.1537; IR ($CHCl_3$) ν_{max} 1733, 1604 cm^{-1}.

2,3-Dimethoxy-11,12-dihydro-6*H*-dibenzo[*c*,*h*]chromen-6-one (5a)

To compound **3a** (372 mg, 1.00 mmol) CH_3SO_3H (4 mL) was added at room temperature under an argon atmosphere and the reaction mixture was stirred for 30 min. The reaction mixture was poured on crushed ice and the obtained precipitate was filtered, washed with water and 10% aqueous $NaHCO_3$ and dried using a vacuum pump. The silica gel (60–120 mesh) column chromatographic purification of the resulting compound using ethyl acetate–petroleum ether (3 : 7) as an eluent gave the pure product **5a** as a yellow solid (302 mg, 98%). Mp 167–169 °C (ref. 10, 105 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.85–3.00 (m, 4H), 3.92 (s, 3H), 3.96 (s, 3H), 6.75 (s, 1H), 7.38 (s, 1H), 7.45 (t, J = 8 Hz, 1H), 7.57 (d, J = 8 Hz, 1H), 7.75 (t, J = 8 Hz, 1H), 8.33 (d, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 26.9, 56.0, 56.3, 106.1, 107.6, 110.9, 120.4, 121.3, 121.8, 127.1, 129.7, 130.2, 134.7, 137.6, 148.0, 148.3, 149.8, 162.3; ESIMS (m/z) 331 [M + Na]$^+$; IR ($CHCl_3$) ν_{max} 1733, 1722, 1631, 1603 cm^{-1}.

The product **5b** was similarly obtained by using the above specified procedure.

2,3,7,8-Tetramethoxy-11,12-dihydro-6*H*-dibenzo[*c*,*h*]chromen-6-one (5b)

Yellow solid (360 mg, 98%); mp 172–174 °C (ref. 11, 171–172 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.80–3.02 (m, 4H), 3.93 (s, 3H), 3.96

(s, 3H), 3.98 (s, 3H), 4.00 (s, 3H), 6.75 (s, 1H), 7.30 (d, $J = 10$ Hz, 1H), 7.38 (s, 1H), 7.39 (d, $J = 10$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.6, 27.0, 56.0, 56.3, 56.6, 61.5, 105.8, 106.9, 110.9, 115.0, 117.7, 119.9, 121.3, 129.1, 132.2, 146.6, 147.9, 149.3, 151.5, 152.1, 158.7; ESIMS (*m*/*z*) 391 $[M + Na]^+$; IR ($CHCl_3$) ν_{max} 1730 cm^{-1}.

2,3-Dimethoxy-6*H*-dibenzo[*c*,*h*]chromen-6-one (6a)

To a stirred solution of compound **5a** (154 mg, 0.50 mmol) in AcOH (5 mL) SeO_2 (165 mg, 1.50 mmol) was added and the reaction mixture was refluxed for 2 h under an argon atmosphere. It was allowed to reach room temperature and was concentrated *in vacuo*. The obtained residue was dissolved in ethyl acetate (20 mL) and the organic layer was washed with water, a saturated solution of $NaHCO_3$ and brine and dried over Na_2SO_4. The concentration of the organic layer *in vacuo* followed by the silica gel (60–120 mesh) column chromatographic purification of the resulting residue using ethyl acetate–petroleum ether (3 : 7) as an eluent gave the pure product **6a** as a faint yellow solid (150 mg, 98%). Mp 217–220 °C (ref. 10, 213 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.02 (s, 3H), 4.09 (s, 3H), 7.10 (s, 1H), 7.54 (t, $J = 8$ Hz, 1H), 7.56 (d, $J = 8$ Hz, 1H), 7.74 (s, 1H), 7.82 (dt, $J = 8$, 2 Hz, 2H), 7.87 (d, $J = 10$ Hz, 1H), 8.11 (d, $J = 10$ Hz, 1H), 8.41 (d, $J = 8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 55.8, 56.2, 100.7, 106.1, 111.5, 117.2, 118.6, 120.3, 121.5, 122.6, 127.8, 130.1, 130.2, 134.6, 135.4, 146.0, 149.9, 150.5, 161.2; ESIMS (*m*/*z*) 306 $[M]^+$; IR ($CHCl_3$) ν_{max} 1732, 1629, 1607 cm^{-1}.

The product **6b** was similarly obtained by using the above specified procedure.

2,3,7,8-Tetramethoxy-6*H*-dibenzo[*c*,*h*]chromen-6-one (6b)

Faint yellow solid (179 mg, 98%); mp 230–232 °C (ref. 12, 218–220 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.00 (s, 3H), 4.05 (s, 6H), 4.12 (s, 3H), 7.15 (s, 1H), 7.46 (d, $J = 8$ Hz, 1H), 7.58 (d, $J = 8$ Hz, 1H), 7.80 (s, 1H), 7.86 (d, $J = 8$ Hz, 1H), 7.91 (d, $J = 8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.9, 56.3, 56.4, 61.5, 100.9, 106.3, 111.5, 115.1, 117.4, 117.7, 118.6, 119.5, 122.5, 129.70, 129.74, 145.4, 150.0, 150.4, 151.5, 152.8, 157.9; ESIMS (*m*/*z*) 389 $[M + Na]^+$; IR ($CHCl_3$) ν_{max} 1735, 1633 cm^{-1}.

4-(Benzo[d][1,3]dioxol-5-yl)-2-(3,4-dimethoxy-2-(methoxycarbonyl)phenyl)butanoic acid (7c)

To a stirred solution of compound **3c** (1.25 g, 3.00 mmol) in MeOH (25 mL) 2% aqueous KOH (25 mL) was added at 0 °C. The reaction mixture was allowed to gradually attain room temperature and was further stirred for 24 h. It was acidified with 2 N HCl and the formed product was extracted in ethyl acetate (25 mL × 2). The organic layer was washed with water and brine and dried over Na_2SO_4. The concentration of the organic layer *in vacuo* followed by the silica gel (60–120 mesh) column chromatographic purification of the resulting residue using ethyl acetate–petroleum ether (4 : 6) as an eluent gave the pure product **7c** as a thick oil (1.10 g, 91%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.90–2.15 (m, 1H), 2.20–2.60 (m, 3H), 3.52 (t, $J = 8$ Hz, 1H), 3.86 (s, 9H), 5.89 (s, 2H), 6.57 (dd, $J = 8$, 2 Hz, 1H), 6.62 (d, $J = 2$ Hz, 1H), 6.70 (d, $J = 8$ Hz, 1H), 6.96 (d, $J = 10$ Hz, 1H), 7.14 (d, $J = 8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 33.1, 34.5, 46.4, 52.4, 55.9, 61.4, 100.7, 108.1, 108.9, 114.2, 121.2, 123.2, 127.7, 129.3, 134.8, 145.7, 146.1, 147.5, 151.8, 168.2, 177.9; ESIMS (*m*/*z*) 425 $[M + Na]^+$; HRMS (ESI) calcd for $C_{21}H_{22}O_8Na$ 425.1207, found 425.1204; IR ($CHCl_3$) ν_{max} 2700–2500, 1731, 1709, 1606 cm^{-1}.

1,2-Dimethoxy-13*H*-[1,3]dioxolo[4′,5′:4,5]benzo[1,2-*h*]benzo[*c*]chromen-13-one (5c)

To compound **7c** (200 mg, 0.49 mmol) TFAA (2 mL) was added at −50 °C and the reaction mixture was stirred under an argon atmosphere at −50 °C to 25 °C for 3 h. The reaction mixture was concentrated *in vacuo* and the obtained residue was dried using a vacuum pump. To the residue toluene (5 mL) and Cs_2CO_3 (326 mg, 1.00 mmol) were added, and the stirred reaction mixture was refluxed for 2 h. It was allowed to reach room temperature and was concentrated *in vacuo*. The obtained residue was dissolved in ethyl acetate (30 mL) and the organic layer was washed with water and brine and dried over Na_2SO_4. The concentration of the organic layer *in vacuo* followed by the silica gel (60–120 mesh) column chromatographic purification of the resulting residue using ethyl acetate–petroleum ether (3 : 7) as an eluent gave the pure product **5c** as a yellow solid (162 mg, 93%). Mp 245–248 °C (ref. 4*e*, 250–251 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.81 (dd, $J = 10$, 2 Hz, 1H), 2.82 (d, $J = 10$ Hz, 1H), 2.91 (d, $J = 10$ Hz, 1H), 2.92 (dd, $J = 10$, 2 Hz, 1H), 3.95 (s, 3H), 3.99 (s, 3H), 5.97 (s, 2H), 6.70 (s, 1H), 7.28 (d, $J = 10$ Hz, 1H), 7.35 (s, 1H), 7.36 (d, $J = 10$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.6, 27.6, 56.6, 61.5, 101.2, 103.5, 107.1, 108.3, 115.2, 117.8, 119.9, 122.7, 130.8, 132.1, 146.6, 146.7, 147.9, 151.6, 152.2, 158.5; ESIMS (*m*/*z*) 375 $[M + Na]^+$; IR ($CHCl_3$) ν_{max} 1734, 1700, 1670 cm^{-1}.

1,2-Dimethoxy-13*H*-[1,3]dioxolo[4′,5′:4,5]benzo[1,2-*h*]benzo[*c*]chromen-13-one (arnottin I, 6c)

A neat mixture of compound **5c** (70 mg, 0.20 mmol) and SeO_2 (220 mg, 2.00 mmol) was heated in the sealed tube at 200 °C for 2 h. It was allowed to reach room temperature and the obtained residue was dissolved in ethyl acetate (20 mL). The organic layer was washed with water, a saturated solution of $NaHCO_3$ and brine and dried over Na_2SO_4. The concentration of the organic layer *in vacuo* provided the pure product **6c** as a yellow solid (67 mg, 96%). The analytically pure sample of **6c** was obtained by recrystallization from chloroform. Mp 296–298 °C (ref. 3*a*, 293–297 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.00 (s, 3H), 4.04 (s, 3H), 6.11 (s, 2H), 7.15 (s, 1H), 7.46 (d, $J = 10$ Hz, 1H), 7.55 (d, $J = 10$ Hz, 1H), 7.86 (d, $J = 10$ Hz, 1H), 7.86 (s, 1H), 7.90 (d, $J = 10$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 56.6, 61.6, 99.1, 101.5, 104.0, 112.1, 115.5, 117.7, 117.8, 119.7, 120.2, 123.2, 129.8, 131.2, 146.1, 148.5, 148.9, 151.7, 153.1, 157.7; ESIMS (*m*/*z*) 373 $[M + Na]^+$; IR ($CHCl_3$) ν_{max} 1734,1651 cm^{-1}.

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References

1 (*a*) P. R. Nandaluru and G. J. Bodwell, *J. Org. Chem.*, 2012, **77**, 8028; (*b*) I. Hussain, V. T. H. Nguyen, M. A. Yawer, T. T. Dang, C. Fischer, H. Reinke and P. Langer, *J. Org. Chem.*, 2007, **72**, 6255; (*c*) D. K. Rayabarapu, P. Shukla and C.-H. Cheng, *Org. Lett.*, 2003, **5**, 4903; (*d*) D. H. Hua, S. Saha, D. Roche, J. C. Maeng, S. Iguchi and C. Baldwin, *J. Org. Chem.*, 1992, **57**, 399; (*e*) U. Hacksell and G. D. Daves Jr, *Prog. Med. Chem.*, 1985, **22**, 1, and references cited therein 1*a*–*e*.

2 H. Ishii, T. Ishikawa and J. Haginiwa, *Yakugaku Zasshi*, 1977, **97**, 890.

3 (*a*) H. Ishii, T. Ishikawa, M. Murota, Y. Aoki and T. Harayama, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1019; (*b*) T. Ishikawa, M. Murota, T. Watanabe, T. Harayama and H. Ishii, *Tetrahedron Lett.*, 1995, **36**, 4269.

4 (*a*) T. Harayama and H. Yasuda, *Heterocycles*, 1997, **46**, 61; (*b*) T. Ishikawa, K. Hino, T. Yoneda, M. Murota, K. Yamaguchi and T. Watanabe, *J. Org. Chem.*, 1999, **64**, 5691; (*c*) T. Harayama, H. Yasuda, T. Akiyama, Y. Takeuchi and H. Abe, *Chem. Pharm. Bull.*, 2000, **48**, 861; (*d*) S. Madan and C.-H. Cheng, *J. Org. Chem.*, 2006, **71**, 8312; (*e*) F. Konno, T. Ishikawa, M. Kawahata and K. Yamaguchi, *J. Org. Chem.*, 2006, **71**, 9818; (*f*) C. A. James and V. Snieckus, *J. Org. Chem.*, 2009, **74**, 4080; (*g*) C. A. James, A. L. Coelho, M. Gevaert, P. Forgione and V. Snieckus, *J. Org. Chem.*, 2009, **74**, 4094; (*h*) D. Mal, A. K. Jana, P. Mitra and K. Ghosh, *J. Org. Chem.*, 2011, **76**, 3392; (*i*) I. R. Pottie, P. R. Nandaluru, W. L. Benoit, D. O. Miller, L. N. Dawe and G. J. Bodwell, *J. Org. Chem.*, 2011, **76**, 9015.

5 (*a*) P. Mondal and N. P. Argade, *J. Org. Chem.*, 2013, **78**, 6802; (*b*) R. M. Patel and N. P. Argade, *Org. Lett.*, 2013, **15**, 14; (*c*) P. S. Deore and N. P. Argade, *J. Org. Chem.*, 2012, **77**, 739; (*d*) U. A. Kshirsagar, V. G. Puranik and N. P. Argade, *J. Org. Chem.*, 2010, **75**, 2702; (*e*) P. B. Wakchaure, S. Easwar, V. G. Puranik and N. P. Argade, *Tetrahedron*, 2008, **64**, 1786.

6 (*a*) R. Okunaka, T. Honda, M. Kondo, Y. Tamura and Y. Kita, *Chem. Pharm. Bull.*, 1991, **39**, 1298; (*b*) R. Jangir and N. P. Argade, *RSC Adv.*, 2012, **2**, 7087.

7 P. C. Bulman Page and T. J. McCarthy, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 7, p. 83.

8 R. P. Korivi and C.-H. Cheng, *Chem.–Eur. J.*, 2010, **16**, 282.

9 S. Shahane, F. Louafi, J. Moreau, J.-P. Hurvois, J.-L. Renaud, P. V. D. Weghe and T. Roisnel, *Eur. J. Org. Chem.*, 2008, 4622.

10 J. N. Chatterjea, S. C. Bhakta and A. K. Chattopadhyay, *J. Indian Chem. Soc.*, 1974, **LI**, 757.

11 A. S. Bailey and C. R. Worthing, *J. Chem. Soc.*, 1956, 4535.

12 E. Martínez, L. Martínez, M. Treus, J. C. Estévez, R. J. Estévez and L. Castedo, *Tetrahedron*, 2000, **56**, 6023.