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Synthesis of musafluorone: a naphthoxanthenone isolated from *Musa acuminata*

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ABSTRACT

5-Methoxy-3*H*-naphtho[2,1,8-*mna*]xanthen-3-one (musafluorone, **1**), the only naphthoxanthenone reported so far from Musaceae, was synthesized starting from 2-naphthol in nine steps and resulted in an overall yield of 3%. Grignard addition of phenylmagnesium bromide to 4-methoxyperinaphthenone afforded the corresponding 4-methoxy-9-phenylphenalenone which, after epoxidation and methyl transposition, was subjected to a photochemical cyclization procedure to furnish **1**.

Naphthoxanthenones constitute a rare group of natural pigments characterized by the formation of intensely fluorescent solutions in polar solvents.[1] Of the five members reported as natural products,[1] four were isolated from Haemodoraceae plants with a common 1*H*-naphtho[2,1,8-*mna*]xanthen-1-one skeleton.[1] Musafluorone (5-methoxy-3*H*-naphtho[2,1,8-*mna*]xanthen-3-one, **1**) is the only naphthoxanthenone isolated from *Musa acuminata* with an isomeric 3*H*-naphtho[2,1,8-*mna*]xanthen-3-one core nucleus.[1d] There are no reports concerning the biological activity of naphthoxanthenones; however, evidence exist that the extracts of *Lachnanthes tinctoria* containing among their major constituents 2,5-dihydroxy-1*H*-naphtho[2,1,8-*mna*]xanthen-1-one (lachnanthofluorone) exhibit photodynamic activity against *Staphylococcus epidermidis*.[2] The phototoxic potential of naphthoxanthenones can be further suspected by their relationship with perinaphthenone, which due to its nearly 100% yield of $^1O_2$ production[2] possesses a high photosensitizing capacity.[2] The phototoxic effects of various perinaphthenones against *Mycosphaerella fijiensis* recently have been demonstrated.[2]

Because of their minute occurrence in only a few phenylphenalenone-producing plants, naphthoxanthenones are almost inaccessible from natural sources. At the extreme is musafluorone (**1**), of which 0.5 mg was isolated from 80 kg of fresh rhizomes of *M. acuminata* after laborious purification procedures.[1d] Therefore, it is important to develop synthetic routes for these kinds of compounds in order to guarantee their accessibility for biological assays.

In the previous work, we stated that 4-methoxy-1*H*-phenalen-1-one (4-methoxyperinaphthenone, **6**) could be used as a starting material for the synthesis of oxabenzochrysenones (naphthoxanthenones).[3] Here, we report the use of **6** in the preparation of **1**, employing a Grignard addition as a C–C bond-forming reaction and a photochemical cyclization as the key steps in the generation of the naphthoxanthenone nucleus.

Biosynthetically, it is presumed that musafluorone (**1**) and related naphthoxanthenones are derived from 9-phenylphenalenones by oxidative phenol coupling.[1d] Interestingly, typical EI-MS spectra of 9-phenylphenalenones present an $[M-1]^+$ ion as the base peak.

This $[M-1]^+$ ion is supposed to be of naphthoxanthenium structure.[1a] Therefore, combining both biomimetic and retro mass spectrometric strategies provides an interesting approach to the naphthoxanthenone nucleus.[4] This approach has been applied successfully in the case of lachnanthofluorone and structural analogs.[1a,c]

The general features of the musafluorone synthesis are outlined retrosynthetically in Scheme 1.

4-Methoxyperinaphthenone (**6**) can be conveniently prepared by a one-pot cyclization procedure of 3-(2-methoxy-1-naphthyl)propanoic acid.[3] This precursor can be obtained in good yield through the use of a Heck–Fujiwara coupling between 1-bromo-2-methoxynaphthalene and ethyl acrylate.[3] However, hydrolysis of 3-(2-methoxynaphthalen-1-yl)propanenitrile (**8**) can provide the same precursor,[6] with the advantage that **8** can be obtained from

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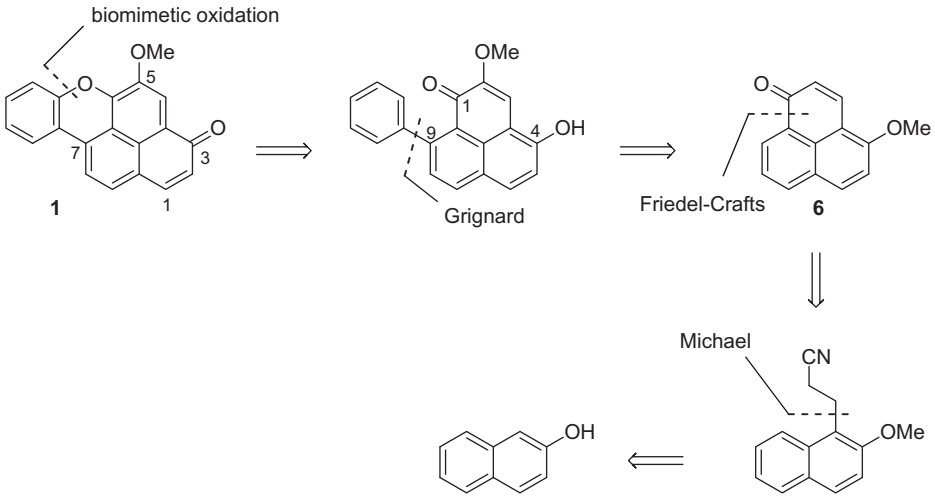


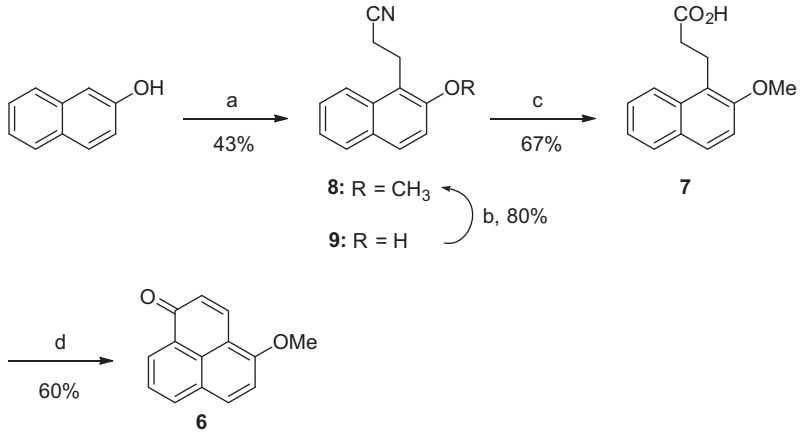
Scheme 1. Retrosynthetic analysis of musafluorone (**1**).[5]

2-naphthol in two steps without the use of palladium and on a multigram scale.[6] Thus, refluxing acrylonitrile with a basic solution of 2-naphthol in benzene according to the method reported by Hardman[6a] (Scheme 2) afforded 3-(2-hydroxynaphthalen-1-yl)propanenitrile (**9**) in 43% yield (84% based on recovered 2-naphthol) after flash column chromatography.[7] Treatment of **9** with iodomethane produced the methyl ether **8** (80%)[8] which, after basic hydrolysis, afforded the corresponding 3-(2-methoxynaphthalen-1-yl)propanoic acid (**7**) in 67% yield after acidic workup and in suitable purity for the next step.[9] Friedel–Crafts cyclization of **7** using our previously reported method[3] completed the synthesis of 4-methoxyperinaphthenone (**6**, 60%) on the gram scale.

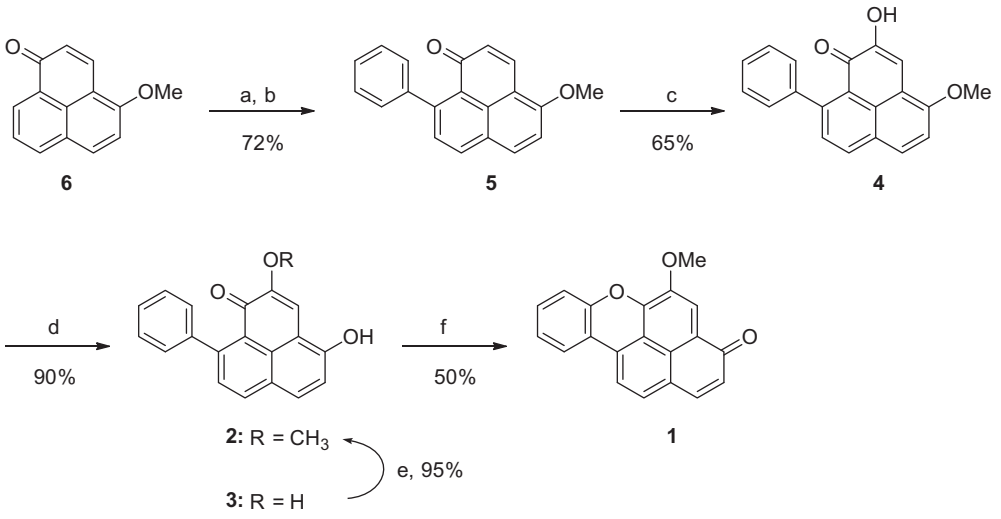
Adding a phenylmagnesium bromide solution to 4-methoxyperinaphthenone (**6**) resulted in 4-methoxy-9-phenyl-1*H*-phenalen-1-one (**5**) after dehydrogenation of the crude product by the action of DDQ (72%, Scheme 3).[10] The double bond in **5** displayed a marked resilience to the epoxidation by the action of alkaline H_2O_2,[11a] *t*-BuOOH/Triton B®,[11b] oxone®,[11c] and Na_2O_2.[11d] This phenomenon was previously observed for a closely related compound (6-methoxy-9-phenylphenalen-1-one) for which the Jacobsen–Katsuki epoxidation proved to be a convenient solution.[12] In the present case, the epoxidation of **5** using $Ca(OCl)_2$ as an oxidizing agent and (salen)Mn as a catalyst furnished 2-hydroxy-4-methoxy-9-phenyl-1*H*-phenalen-1-one (**4**) in 50% yield after preparative TLC.[13] The immediate color change from pale yellow to red that occurred during the application of the crude dichloromethane extract to TLC plates was indicative of the lability of the epoxide to acid treatment and therefore no attempt was made to isolate it.

Demethylation of **4** with HBr produced the desired 2,4-dihydroxy-9-phenyl-1*H*-phenalen-1-one (4-hydroxyanigorufone, **3**, 84%), which is identical to the compound isolated from *Anigozanthos flavidus* and *Monochoria elata*.[14] Treatment of **3** with an ethereal solution of diazomethane afforded 4-hydroxy-2-methoxy-9-phenyl-1*H*-phenalen-1-one (**2**) in 95% and set the stage for the photochemical key step.[15] Transformation of **2** into musafluorone (**1**) was achieved in a yield of 56% upon irradiation of a methanolic solution in an open air atmosphere with an overhead projector lamp.[16]

In summary, we have developed a nine-step synthesis of 5-methoxy-3*H*-naphtho[2,1,8-*mna*]xanthen-3-one (musafluorone, **1**) starting from 2-hydroxynaphthalene in a 3% global yield using photochemical cyclization as a key step. The use of 4-hydroxy-2-methoxy-9-phenyl-1*H*-phenalen-1-one (**2**) in the photochemical cyclization process supports the hypothesis that **2** is the natural precursor of **1** in *Musa*.



Scheme 2. Reagents and conditions: (a) acrylonitrile, NaOH, benzene, 3 h reflux then HCl 10% until pH ~2; (b) CH_3I, K_2CO_3, acetone, 4 h reflux; (c) NaOH 20%, 8 h reflux then HCl 10% until pH ~1; (d) $SOCl_2$, 30 °C until dryness then CH_2Cl_2, $AlCl_3$ (3 equiv) 10 min, DDQ (1.3 equiv) 15 min.



Scheme 3. Reagents and conditions: (a) PhMgBr (1 M in THF), −70 °C to 25 °C in 30 min, then $NH_4Cl_{(aq)}$; (b) DDQ, CH_2Cl_2, reflux 10 min; (c) (salen)Mn, CH_2Cl_2, 4-phenylpyridine-*N*-oxide, 30% $Ca(OCl)_2$, 0 °C, 4 h, then silica gel; (d) 45% HBr, AcOH, reflux 6 h; (e) 1 equiv CH_2N_2; (f) MeOH, irradiation (ENX lamp, 82 V, 360 W, 2500 lumens), 8 h.

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4. (a) Kametani, T.; Fukumoto, K. *Acc. Chem. Res.* **1976**, *9*, 319–325; For a different synthesis of naphthoxanthenones, see: (b) Cooke, R. G.; Merrett, B. K.; ÓLoughlin, G. J.; Pietersz, G. A. *Aust. J. Chem.* **1980**, *33*, 2317–2324.
5. Numbering of musafluorone (**1**) was taken over from Opitz et al.[1d]
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7. In our case, recrystallization of the crude product **9** from ethanol as reported by Hardman[6a] did not afford satisfactory results. Therefore, flash column chromatography was conducted using CH_2Cl_2 as an eluent. ^{1}H NMR (C_3D_6O, 500.13 MHz) δ 8.80 (s, –OH), 8.03 (d, *J* = 8.5 Hz, H-8′), 7.81 (d, *J* = 8.1 Hz, H-5′), 7.72 (d, *J* = 8.9 Hz, H-4′), 7.50 (ddd, *J* = 8.5, 6.9, 1.2 Hz, H-7′), 7.31 (ddd, *J* = 8.1, 6.9, 1.2 Hz, H-6′), 7.24 (d, *J* = 8.9 Hz, H-3′), 3.45 (t, *J* = 7.7 Hz, H-3), 2.76 (t, *J* = 7.7 Hz, H-2); ^{13}C NMR (C_3D_6O, 125.75 MHz) δ 153.6 (C-2′), 134.1 (C-8a′), 130.0 (C-4a′), 129.6 (C-4′), 129.5 (C-5′), 127.5 (C-7′), 123.6 (C-6′), 123.2 (C-8′), 120.4 (C-1), 118.6 (C-3′), 117.4 (C-1′), 21.9 (C-3), 17.2 (C-2). HREIMS *m/z* 197.084343 (calcd for $C_{13}H_{11}NO$, 197.084064).
8. *Experimental procedure*: Compound **9** (5.0 g, 25 mmol), K_2CO_3 (5.2 g), and CH_3I (2.12 mL, 37.5 mmol) were refluxed in acetone (30 mL) for 4 h. The reaction mixture was filtered, the solvent removed under vacuum, and the crude extract submitted to flash column chromatography using a CH_2Cl_2–*n*-hexane mixture (2:1) as eluent to give 4.2 g (80%) of 3-(2-methoxynaphthalen-1-yl)propanenitrile (**8**) as a yellow oil. ^{1}H NMR, (C_3D_6O, 500.13 MHz) δ 8.06 (d, *J* = 8.6 Hz, H-8′), 7.88 (d, *J* = 9.0 Hz, H-4′), 7.86 (d, *J* = 8.1 Hz, H-5′), 7.52 (ddd, *J* = 8.6, 6.8, 1.3 Hz, H-7′), 7.45 (d, *J* = 9.0 Hz, H-3′), 7.36 (ddd, *J* = 8.1, 6.8, 1.1 Hz, H-6′), 4.01 (s, –OCH_3), 3.45 (t, *J* = 7.7 Hz, H-3), 2.73 (t, *J* = 7.7 Hz, H-2); ^{13}C NMR, (C_3D_6O, 125.75 MHz) δ 155.9 (C-2́), 133.5 (C-8a′), 130.2 (C-4a′), 129.9 (C-4′), 129.5 (C-5′), 127.6 (C-7′), 124.2 (C-6′), 123.4 (C-8′), 120.3 (C-1), 120.2 (C-1′), 114.1 (C-3′), 56.8 (–OCH_3), 21.6 (C-3), 17.4 (C-2). HREIMS *m/z* 211.098701 (calcd for $C_{14}H_{13}NO$, 211.099714).
9. *Experimental procedure*: Compound **8** (5.55 g, 26 mmol) was refluxed with NaOH (20%, 50 mL) for 8 h until evolution of ammonia ceased. The dropwise addition of a 10% HCl solution afforded 3-(2-methoxynaphthalen-1-yl)propanoic acid (**7**, 6.0 g, 67%) as a white solid after filtration. ^{1}H NMR, (C_3D_6O, 500.13 MHz) δ 8.04 (d, *J* = 8.8 Hz, H-8′), 7.84 (d, *J* = 8.1 Hz, H-5′), 7.82 (d, *J* = 8.8 Hz, H-4′), 7.51 (dd, *J* = 8.8, 7.6 Hz, H-7′), 7.42 (d, *J* = 8.8 Hz, H-3′), 7.34 (dd, *J* = 8.1, 7.6 Hz, H-6′), 3.98 (s, –OCH_3), 3.39 (t, *J* = 8.3 Hz, H-3), 2.55 (t, *J* = 8.3 Hz, H-2); ^{13}C NMR (C_3D_6O, 125.75 MHz) δ 174.2 (C-1 155.5 (C-2́), 133.6 (C-8a′), 130.2 (C-4á), 129.4 (C-5′), 129.0 (C-4′), 127.3 (C-7′), 124.0 (C-6′), 123.6 (C-8′), 122.3 (C-1′), 114.2 (C-3′), 56.8 (–OCH_3), 34.4 (C-2), 21.3 (C-3). HREIMS *m/z* 256.094212 (calcd for $C_{14}H_{14}O_3$, 256.094294).
10. *Experimental procedure*: To a −70 °C THF solution of **6** (1.41 g, 6.7 mmol in 10 mL) was slowly added (5 min) 1.3 equiv of phenylmagnesium bromide (9 mL, 1.0 M in THF) under nitrogen. The reaction mixture was stirred for 10 min at −70 °C before being warmed up to 25 °C (total stirring time 30 min). The reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2 (20 mL). The organic phase was dried (Na_2SO_4), filtered, mixed with 1.5 g of DDQ (6.5 mmol), and boiled for 15 min. The product was purified by flash column chromatography using CH_2Cl_2 as an eluent to afford 4-methoxy-9-phenyl-1*H*-phenalen-1-one (**5**, 1.38 g, 72%) as a yellow solid. ^{1}H NMR, (C_3D_6O, 500.13 MHz) δ 8.27 (d, *J* = 8.2 Hz, H-7), 8.26 (d, *J* = 9.1 Hz, H-6), 8.21 (d, *J* = 10.0 Hz, H-3), 7.62 (d, *J* = 9.1 Hz, H-5), 7.43 (d, *J* = 8.2 Hz, H-8), 7.38 (m, H-2′/6′), 7.33 (m, H-4′), 7.32 (m, H-3′/5′), 6.45 (d, *J* = 10.0 Hz, H-2), 4.18 (s, –OCH_3); ^{13}C NMR, (C_3D_6O, 125.75 MHz) δ 185.0 (C-1), 160.0 (C-4), 149.0 (C-9), 144.6 (C-1′), 135.5 (C-6), 134.6 (C-7), 134.0 (C-3), 130.5 (C-9b), 130.3 (C-8), 129.2 (C-2), 129.0 (C-3′/5′), 128.7 (C-2′/6′), 128.3 (C-6a), 127.5 (C-4′), 126.5 (C-9a), 114.7 (C-3a), 114.5 (C-5), 57.1 (–OCH_3). HREIMS *m/z* 286.099380 (calcd for $C_{20}H_{14}O_2$, 286.100510).
11. Experimental procedures were performed as described in the following papers. No attempts were made for optimization: (a) Forte, G. J.; Zito, J. A.; Edwards, J. M. *Lloydia* **1976**, *39*, 192–196; (b) Yang, N. C.; Finnegan, R. A. *J. Am. Chem. Soc.* **1958**, *80*, 5845–5848; (c) Rani, S.; Vankar, Y. D. *Tetrahedron Lett.* **2003**, *44*, 907–909; (d) Reddy, V. K.; Haritha, B.; Yamashita, M. *Lett. Org. Chem.* **2005**, *2*, 128–131.
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13. *Experimental procedure*: Compound **5** (325 mg, 1.1 mmol), (*S*,*S*)-(+)-*N*,*N*′-bis-(3,5-di-*tert*-butylsalicylidene)-1,2-diamino-cyclohexane manganese-(III)-chloride ((salen)Mn, 30 mg, 0.05 mmol), and 4-phenylpyridine-*N*-oxide (47 mg, 0.3 mmol) were dissolved in CH_2Cl_2 (10 mL) and the resulting solution was cooled in an ice-water bath. A 30% slurry of $Ca(OCl)_2$ in water (10 mL) buffered with 5 mL of a sodium phosphate solution (0.05 M) was added in one portion under vigorous stirring and the reaction was maintained at 0 °C for 2 h. The mixture was separated and the organic layer dried and applied directly to a preparative TLC plate. Separation using CH_2Cl_2 as an eluent resulted in a red zone (R_f = 0.74), which gave 165 mg (50%) of 2-hydroxy-4-methoxy-9-phenyl-1*H*-phenalen-1-one (**4**). ^{1}H NMR (C_3D_6O, 500.13 MHz) δ 8.33 (d, *J* = 8.2 Hz, H-7), 8.15 (d, *J* = 9.0 Hz, H-6), 7.61 (d, *J* = 9.0 Hz, H-5), 7.51 (s, H-3), 7.46 (d, *J* = 8.2 Hz, H-8), 7.34–7.45 (br m, H-2′–H-6′), 4.17 (s, –OCH_3); ^{13}C NMR (C_3D_6O, 125.75 MHz) δ 179.7 (C-1), 159.1 (C-4), 150.7 (C-2), 150.2 (C-9), 144.1 (C-1′), 136.1 (C-7), 133.1 (C-6), 129.9 (C-8), 129.0 (C-3′/5′), 128.7 (C-2′/6′), 128.2 (C-6a), 127.7 (C-4′), 126.8 (C-9b), 124.2 (C-9a), 115.2 (C-3a), 114.7 (C-5), 106.9 (C-3), 57.1 (–OCH_3). HREIMS *m/z* 302.093636 (calcd for $C_{20}H_{14}O_3$, 302.094294).
14. (a) Hölscher, D.; Schneider, B. *Phytochemistry* **1999**, *50*, 155–161; (b) Hölscher, D.; Reichert, M.; Görls, H.; Ohlenschläger, O.; Bringmann, G.; Schneider, B. *J. Nat. Prod.* **2006**, *69*, 1614–1617. *Experimental procedure*: To a refluxing solution of compound **4** (180 mg, 0.6 mmol) in AcOH (18 mL) was added 300 μL of aqueous HBr (48%). This addition was repeated over intervals of 15 min until a

total of 2.4 mL had been added and the reaction was refluxed for a further 20 min. Extraction with CH_2Cl_2 and purification by preparative TLC (CH_2Cl_2–AcOEt 4:1, R_f = 0.83) afforded 146 mg (84%) of 2,4-dihydroxy-9-phenyl-1*H*-phenalen-1-one (**3**), which rapidly decomposes in the presence of light and oxygen. ^{1}H NMR (C_3D_6O, 500.13 MHz) δ 8.26 (d, J = 8.2 Hz, H-7), 7.99 (d, J = 8.7 Hz, H-6), 7.59 (s, H-3), 7.42 (d, J = 8.2 Hz, H-8), 7.34–7.44 (br m, H-2′–H-6′), 7.40 (d, J = 8.7 Hz, H-5); ^{13}C NMR (C_3D_6O, 125.75 MHz) δ 179.4 (C-1), 158.4 (C-4), 150.2 (C-2), 149.6 (C-9), 144.3 (C-1′), 135.7 (C-7), 133.0 (C-6), 129.3 (C-8), 129.0 (C-3′/5′), 128.7 (C-2′/6′), 128.1 (C-6a), 127.6 (C-4′), 127.5 (C-9b), 124.2 (C-9a), 119.8 (C-5), 113.1 (C-3a), 107.2 (C-3). HREIMS m/z 288.078911 (calcd for $C_{19}H_{12}O_3$, 288.078644)..

15. *Experimental procedure*: An alcohol-containing ethereal diazomethane solution was prepared using a standard procedure (Aldrich technical bulletin AL-180) and added at a rate of 1 μL/min to 20 mg of compound **3** suspended in ether (500 μL) at room temperature. The addition continued until the disappearance of **3** (as judged by TLC, CH_2Cl_2–AcOEt 4:1, R_f = 0.83). Compound **2** was purified by means of preparative TLC (Et_2O–*n*-hexane 7:1, R_f = 0.35) to give 20 mg (95%) of 4-hydroxy-2-methoxy-9-phenyl-1*H*-phenalen-1-one (**2**) as an orange powder which was used immediately in the next step. Compound **2** is also a natural product isolated from *Musa acuminata* cv. 'Williams'. ^{1}H NMR, (MeOH-d_4, 500.13 MHz) δ 7.96 (s, H-3), 7.93 (d, J = 7.8 Hz, H-7), 7.76 (d, J = 9.3 Hz, H-6), 7.33 (m, H-2′–H-6′), 7.15 (d, J = 7.8 Hz, H-8), 6.97 (d, J = 9.3 Hz, H-5), 3.89 (s, –OCH_3); ^{13}C NMR, (MeOH-d_4, 125.75 MHz) δ 177.0 (C-1), 175.5 (C-4), 151.2 (C-2), 148.0 (C-9), 145.4 (C-1′), 137.3 (C-6), 135.3 (C-7), 130.8 (C-2′/6′), 130.1 (C-4′), 130.0 (C-3′/5′), 128.5 (C-9b), 128.5 (C-8), 128.4 (C-5), 126.2 (C-3a), 126.0 (C-6a), 124.2 (C-9a), 114.5 (C-3), 57.3 (–OCH_3). HREIMS m/z 302.0947 (calcd for $C_{20}H_{14}O_3$, 302.0943).

16. *Experimental procedure*: Compound **2** (10 mg, 0.03 mmol) dissolved in methanol (1 mL) was irradiated for 8 h (quartz cell) on an overhead projector (3M™ 1711 Plus) in an open atmosphere to give 5 mg of musafluorone (**1**) after TLC purification (CH_2Cl_2–AcOEt 5:1, R_f = 0.57). Spectroscopic data were identical with those of the natural compound.[1d]