

Synthesis of a Coumarin Compound from Phenanthrene by TiO₂-Photocatalyzed Reaction

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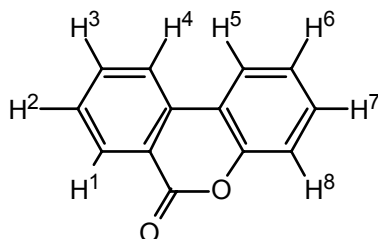
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Electronic Supplementary Material

Methods: The authentic sample of **2** was purchased from Wako Pure Chemical and that of **4** was synthesized from phenanthrene via ozonolysis, and **3** was isolated from the reaction products. Their ¹H and ¹³C NMR spectra were measured on a JEOL JNM-AL400 NMR spectrometer. HH-COSY and CH-COSY spectra of **3** were measured on a Varian-Unity INOVA 500 NMR spectrometer.



3 ¹H NMR (400MHz, CDCl₃) δ 8.42(1H, d.d, *J* = 8.0 Hz, 1.2 Hz, H¹), 8.14(1H, d, *J* = 8.0 Hz, H⁴), 8.08(1H, d, *J* = 8.0 Hz, H⁵), 7.84(1H, t.d, *J* = 8.0 Hz, 1.2 Hz, H³), 7.59(1H, t.d, *J* = 8.0 Hz, 1.2 Hz, H²), 7.49(1H, t.d, *J* = 8.0 Hz, 1.2 Hz, H⁷), 7.38(1H, d.d *J* = 8.0 Hz, 1.2 Hz, H⁸), 7.35(1H, t.d, *J* = 8.0 Hz, 1.2 Hz, H⁶). ¹³C NMR (100MHz, CDCl₃) δ 161.06, 151.21, 134.75, 134.71, 130.52, 130.37, 128.81, 124.48, 122.69, 121.61, 121.23, 118.00, 117.74.

4 ¹H NMR (400MHz, CDCl₃) δ 9.83(2H, s, CHO), 8.06(2H, d, *J* = 7.4 Hz, 5-ArH), 7.67(2H, t, *J* = 7.4 Hz, 4-ArH), 7.60(2H, t, *J* = 7.4 Hz, 3-ArH), 7.36(2H, d, *J* = 7.4 Hz, 2-ArH). ¹³C NMR (100MHz, CDCl₃) δ 190.75(CHO), 141.04(1-Ar), 134.39(6-Ar), 133.28(2-Ar), 131.56(5-Ar), 128.39(3-Ar), 128.40(4-Ar).

HH-COSY and CH-COSY(Varian-Unity INOVA 500) of **3** are shown below.

