

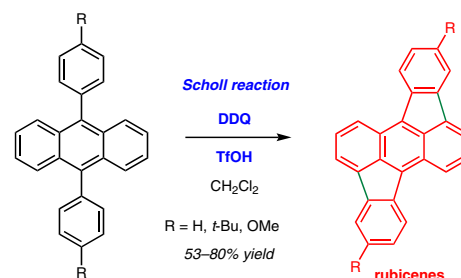
Facile Synthesis of Rubicenes by Scholl Reaction

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Abstract The treatment of 9,10-diphenylanthracenes with DDQ in the presence of TfOH readily gave the corresponding rubicene derivatives in good yields. The effects of oxidant, acid, substituent, and other conditions are discussed. This protocol involving the Scholl reaction is convenient for the preparation of some rubicene derivatives from conventional starting materials.

Key words rubicene, Scholl reaction, DDQ, oxidation, arenes

Rubicene (**1a**, C₂₆H₁₄), a parent aromatic system consisting of five benzene rings and two five-membered rings, has been known for more than a century, and its name originated from its characteristic ruby color (Figure 1).¹ This aromatic compound, which is a substructure of C₇₀,² has recently drawn the attention of chemists engaged in the molecular design of novel aromatic compounds, such as organic electroluminescence and light-emitting diode devices.³ Rubicene was originally synthesized by the reductive dimerization of 9-fluorenone with Mg,⁴ and subsequent synthetic methods include the cyclization of halogenated 9,10-diphenylanthracenes under strongly basic conditions,⁵ the Heck reaction,⁶ and the Friedel–Crafts type reaction (Scheme 1).^{7,8} Although these reactions gave rubicene, harsh conditions were required and the yields were not always high. In order to develop an efficient synthesis of rubicene and its derivatives, we adopted the Scholl reaction⁹ using the readily available starting material, 9,10-diphenylanthracene,¹⁰ a fluorescence standard. The Scholl reaction involves the dehydrogenative coupling between arene compounds and oxidants or Lewis acids, and is widely utilized for the construction of highly fused polyaromatic hydrocarbons (PAHs).¹¹ Recently, Murata's group applied this reaction to the cyclization of 5,11-diphenyltetracene derivatives

to form tetrabenzopyracenes.^{12,13} To the best of our knowledge, there are no reports of a similar approach to rubicene from 9,10-diphenylanthracene. We herein report an efficient synthesis of rubicene and its derivatives by utilizing the Scholl reaction.

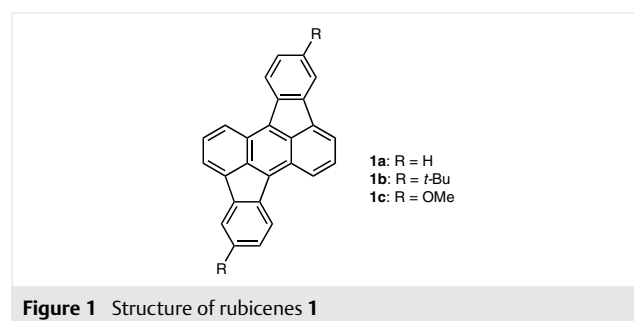
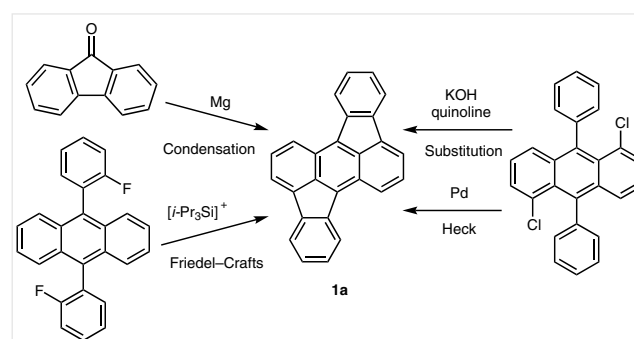


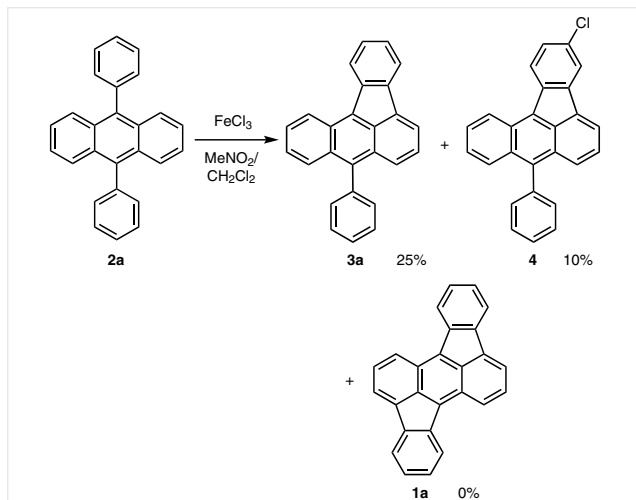
Figure 1 Structure of rubicenes **1**



Scheme 1 Previous synthetic methods of rubicene (**1a**)

We first reacted 9,10-diphenylanthracene (**2a**) with FeCl₃, utilizing the reaction conditions for 5,11-diphenyltetracene (Scheme 2).^{12a} The reaction with 8.0 equivalents of FeCl₃ at room temperature for 24 hours gave only a trace amount of rubicene (**1a**) and 8-phenylbenzo[*a*]fluoranthene (**3a**), a

monocyclization product, in 25% yield. Another product was also obtained in 10% yield, and its structure was determined by single crystal X-ray analysis to be 3-chloro-8-phenylbenzo[*a*]fluoranthene (**4**), as shown in Figure 2. The formation of this product means that the chlorination by FeCl_3 competes with the second cyclization.¹⁴



Scheme 2 Scholl reaction of **2a** with FeCl_3

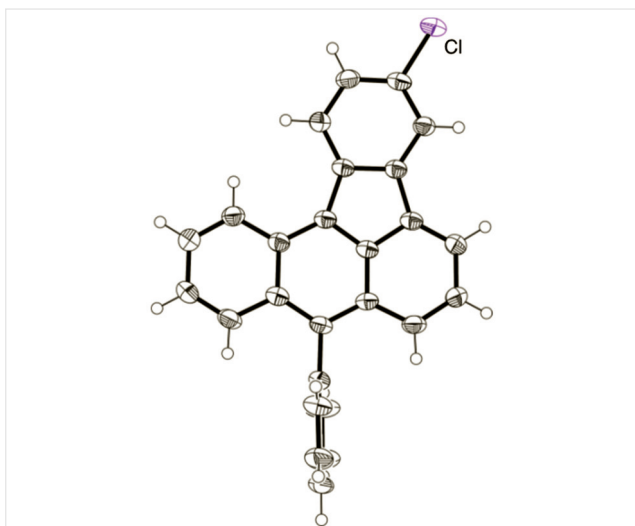
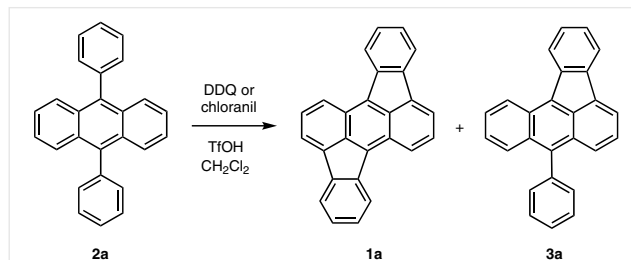


Figure 2 An ORTEP drawing of the X-ray crystal structure of **4**; thermal ellipsoids are set at 50% probability

Then, 2,3-dichloro-4,5-dicyano-1,4-benzoquinone (DDQ) was used as the oxidant in trifluoromethanesulfonic acid (TfOH) according to the literature method.¹⁵ When **2a** was treated with 3.0 equivalents of DDQ in the presence of TfOH in CH_2Cl_2 , the reaction proceeded smoothly at 0 °C and was completed within 10 minutes (Scheme 3). Quenching followed by column chromatography on silica gel afforded pure **1a** in 80% isolated yield as a deep red solid and no iso-

rubicene was found in the reaction products. This simple protocol readily gave rubicene in high yield from the conventional starting material.



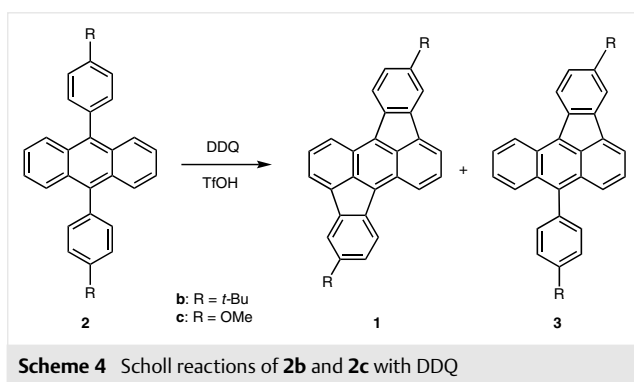
Scheme 3 Scholl reaction of **2a** with DDQ or chloranil

We could control the cyclization step by changing the amount of DDQ (Table 1). The reaction with 1.75 equivalents of DDQ gave **3a** as the major product (64%). The reaction did not work at all when methanesulfonic acid (MsOH) was used as the acid instead of TfOH.^{9c,13a} Therefore, a strong acid is essential for the completion of the cyclization. This result means that protonation in the arenium ion mechanism should play an important role in the overall steps, although the radical cation mechanism cannot be ruled out.^{9c-e} We were able to use chloranil (tetrachloro-1,4-benzoquinone) as the oxidant for the rubicene synthesis as well, although the reaction was slower than that using DDQ under the same conditions. The reaction with 3.0 equivalents of chloranil at 0 °C gave a small amount of **1a** in 10 minutes, but **1a** became the major product in 4 hours. The slow reaction with chloranil is consistent with its oxidizing ability being weaker than that of DDQ.¹⁶

The above method was then applied to the synthesis of some substituted rubicenes from the corresponding diphenylanthracene derivatives (Scheme 4). The reaction of 9,10-bis(4-*tert*-butylphenyl)anthracene (**2b**) with DDQ (3.0 equiv) was slow at 0 °C, and the product ratio of **1b** and **3b** was 72:28 even at 1 hour. Even though the reactions were carried out under various conditions, namely, at room temperature, for a long time, or with an increased amount of DDQ, the product ratios were not improved and the amounts of unidentified byproducts increased. From the reaction mixture under the above conditions (0 °C, 1 h, and 3.0 equiv of DDQ), 5,12-di-*tert*-butylrubicene (**1b**) was obtained in 53% yield as a red solid. The reaction of 9,10-bis(4-methoxyphenyl)anthracene (**2c**) proceeded more slowly than that of **2b**, so the reaction mixture was heated at 60 °C in CHCl_3 . The reaction under the above-mentioned conditions was completed in 2 hours, and 5,12-dimethoxyrubicene (**1c**) was obtained in 76% isolated yield as a purple solid, where most of the loss was attributed to the low solubility during purification.

Table 1 Scholl Reactions of **2a** with DDQ or Chloranil under Various Conditions^a

Entry	Oxidant	Equiv	Acid ^c	Time (Min)	Temp (°C)	Product ratio (%) ^b		
						1a	3a	2a
1	DDQ	3.00	TfOH	10	0	100 (80)	0	0
2	DDQ	2.50	TfOH	10	0	68	32	0
3	DDQ	1.75	TfOH	10	0	19 (14)	74 (64)	7 (5)
4	DDQ	1.00	TfOH	10	0	2	49	49
5	DDQ	3.00	MsOH	2880	r.t.	0	0	100
6	chloranil	3.00	TfOH	10	0	4	42	54
7	chloranil	3.00	TfOH	240	0	84	16	0

^a The reactions were carried out in CH₂Cl₂.^b The ratios of the two products and the starting material were determined by ¹H NMR analysis. Isolated yields in parentheses.^c The solvent/acid ratio was 19:1 (v/v).

In summary, we have found a facile synthetic method for rubicene and its derivatives by using the DDQ/TfOH system under mild conditions. Because some substituted 9,10-diphenylanthracene derivatives can be prepared from anthraquinone or 9,10-dihaloanthracenes, this protocol will be useful for the synthesis of functionalized rubicenes, which would be valuable as core structures of functional materials and the scaffolds for the construction of planar or curved PAH systems.

Melting points are uncorrected. NMR spectra were measured on a JEOL JNM-ECS 400 (¹H: 400 MHz, ¹³C: 100 MHz) or JNM-ECZ500R spectrometer (¹H: 500 MHz, ¹³C: 125 MHz). High-resolution mass spectra were measured with a JEOL JMS-700 MStation mass spectrometer. Column chromatography was carried out with Wako Gel C-300 (45–75 mesh). 9,10-Diphenylanthracene derivatives were prepared from anthraquinone by a Grignard reaction followed by reductive aromatization by the general method.¹⁷

Reaction of 9,10-Diphenylanthracene (**2a**) with FeCl₃

In a 10 mL flask, FeCl₃ (78.5 mg, 484 μmol) and MeNO₂ (1 mL) were added to a solution of 9,10-diphenylanthracene (**2a**; 20.0 mg, 60.5 μmol) in CH₂Cl₂ (2 mL). The deep blue solution was stirred for 24 h at r.t. The reaction was quenched with H₂O (5 mL), and the whole was

added to H₂O (50 mL). The organic materials were extracted with CH₂Cl₂ (3 × 40 mL). The combined organic layers were dried (Na₂SO₄) and evaporated. The crude products were separated by chromatography (silica gel, hexane).

8-Phenylbenzo[a]fluoranthene (**3a**)^{5b}

[CAS Reg. No. 500310-14-5]

Yield: 4.9 mg (25%); yellowish orange solid; mp 185–187 °C (Lit.^{5b} mp 185–186 °C); *R_f* = 0.44 (hexane/CH₂Cl₂ 3:2).

¹H NMR (400 MHz, CDCl₃): δ = 7.42 (t, *J* = 7.6 Hz, 2 H), 7.49–7.62 (m, 7 H), 7.67 (dd, *J* = 4.0, 8.4 Hz, 2 H), 7.94 (d, *J* = 8.8 Hz, 1 H), 8.04 (t, *J* = 7.0 Hz, 2 H), 8.44 (d, *J* = 7.6 Hz, 1 H), 8.85 (d, *J* = 8.4 Hz, 1 H).

¹³C NMR (125 MHz, CDCl₃): δ = 120.1, 121.7, 123.8, 124.3, 124.8, 126.4, 126.7, 127.1, 127.2, 127.6, 127.9, 128.1, 128.9, 129.1, 130.0, 131.0, 131.6, 132.4, 136.8, 137.9, 139.0, 139.1, 140.3.

HRMS (FAB): *m/z* calcd for C₂₆H₁₆ [M]⁺: 328.1252; found: 328.1248.

3-Chloro-8-phenylbenzo[a]fluoranthene (**4**)

Yield: 2.2 mg (10%); yellow solid; mp 193–195 °C; *R_f* = 0.48 (hexane/CH₂Cl₂ 3:2).

¹H NMR (400 MHz, CDCl₃): δ = 7.43 (ddd, *J* = 0.8, 1.6, 6.4 Hz, 1 H), 7.46 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.51 (dd, *J* = 1.2, 7.2 Hz, 1 H), 7.52 (d, *J* = 2.4 Hz, 1 H), 7.54–7.63 (m, 4 H), 7.68 (ddd, *J* = 1.2, 2.0, 6.8 Hz, 1 H), 7.71 (d, *J* = 8.8 Hz, 1 H), 7.94 (d, *J* = 9.2 Hz, 1 H), 7.99 (d, *J* = 2.0 Hz, 1 H), 8.01 (d, *J* = 6.8 Hz, 1 H), 8.32 (d, *J* = 8.0 Hz, 1 H), 8.76 (d, *J* = 8.4 Hz, 1 H).

¹³C NMR (100 MHz, CDCl₃): δ = 120.8, 122.0, 124.1, 124.3, 125.0, 127.0, 127.1, 127.4, 127.4, 127.5, 127.8, 128.1, 129.0, 129.1, 129.9, 130.2, 131.5, 132.2, 132.4, 135.6, 137.7, 138.5, 139.6, 140.5.

HRMS (FAB): *m/z* calcd for C₂₆H₁₅³⁵Cl [M]⁺: 362.0862; found: 362.0819.

X-ray Crystal Structure Analysis of **4**¹⁸

A single crystal of **4** was prepared by recrystallization from CHCl₃/MeOH. Diffraction data were collected on a Rigaku Varimax with Saturn system equipped with a Rigaku GNNP low-temperature device using MoKα radiation (λ = 0.71075 Å) to a maximum 2θ value of 55.0° at 123 K. Equivalent reflections were merged and the images were processed with the Rigaku CrysAlis^{Pro} program. The structure solution was performed using the Yadokari-XG program¹⁹ as a graphical user interface with SHELX-2013 as a set of structure determination pro-

grams. The structure was solved by the direct method (SHELXS) and refined by full-matrix least squares method (SHELXL).²⁰ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in fixed positions. Formula $C_{26}H_{15}Cl$, $M = 362.86$, monoclinic, $P2_1/n$, $a = 14.7056(9)$, $b = 5.4556(4)$, $c = 22.7969(17)$ Å, $\beta = 108.011(7)^\circ$, $V = 1739.3(2)$ Å³, $Z = 4$, $d = 1.3856$ g cm⁻³, $\mu(\text{MoK}\alpha) = 0.227$ mm⁻¹. Number of reflection 3084 (all data), 2227 [$I > 2.0\sigma(I)$], number of reflection used 3084, $R_1 = 0.0543$, $wR_2 = 0.1667$, GOF = 1.105.

Rubicene (1a); Typical Procedure

[CAS Reg. No. 197-61-5]

In a two-necked flask (10 mL), a solution of **2a** (100 mg, 303 μmol) and DDQ (210 mg, 909 μmol) in anhyd CH_2Cl_2 (9.5 mL) was stirred for 10 min in an ice bath at 0 °C under N_2 . After the addition of TfOH (0.50 mL, 5.65 mmol), the mixture was stirred for 10 min at 0 °C. The reaction mixture was poured into aq NaHCO_3 (50 mL) and rinsed with H_2O (50 mL). The formed precipitate was collected by filtration, and the solid was washed with H_2O (50 mL), MeOH (50 mL), and hexane (50 mL). The crude product was purified by chromatography (silica gel, hexane/ CH_2Cl_2 1:1); yield: 78.6 mg (80%); red solid; $R_f = 0.37$ (hexane/ CH_2Cl_2 3:2).

The reactions with DDQ or chloranil under various conditions were similarly performed starting from 20.0 mg of **2a**. After the reaction mixture was quenched, the organic material in the reaction mixture was extracted with CH_2Cl_2 .

¹H NMR (400 MHz, CDCl_3): $\delta = 7.40$ (td, $J = 0.8, 7.2$ Hz, 2 H), 7.47 (td, $J = 0.8, 7.2$ Hz, 2 H), 7.79 (dd, $J = 6.6, 8.6$ Hz, 2 H), 7.98 (d, $J = 7.6$ Hz, 2 H), 8.03 (d, $J = 6.4$ Hz, 2 H), 8.33 (d, $J = 7.6$ Hz, 2 H), 8.61 (d, $J = 8.8$ Hz, 2 H).

5,12-Di-tert-butylrubicene (1b)^{5a}

[CAS Reg. No. 219725-19-6]

The reaction was similarly carried out with **2b**²¹ (26.8 mg, 60.5 μmol) and DDQ (41.9 mg, 182 μmol , 3.0 equiv). The reaction mixture was stirred at 0 °C for 1 h. The crude product contained **1b** and **3b** in 72:28 ratio, which was separated by chromatography (silica gel, hexane/ CH_2Cl_2 10:1).

1b

Yield: 14.7 mg (53%); red solid; mp 385–395 °C (dec.) (Lit.^{5a} mp >300 °C); $R_f = 0.57$ (hexane/ CH_2Cl_2 3:2).

When 3.2 equiv of DDQ was used, 16.5 mg (62%) of **1b** was obtained.

¹H NMR (400 MHz, CDCl_3): $\delta = 1.47$ (s, 18 H), 7.50 (dd, $J = 2.0, 7.6$ Hz, 2 H), 7.78 (dd, $J = 6.4, 8.0$ Hz, 2 H), 8.02 (d, $J = 2.0$ Hz, 2 H), 8.04 (d, $J = 6.4$ Hz, 2 H), 8.24 (d, $J = 7.6$ Hz, 2 H), 8.58 (d, $J = 8.0$ Hz, 2 H).

3-tert-Butyl-8-(4-tert-butylphenyl)benzo[a]fluoranthene (3b)

Yield: 4.8 mg (18%), yellow solid; mp 250–252 °C; $R_f = 0.63$ (hexane/ CH_2Cl_2 3:2).

¹H NMR (400 MHz, CDCl_3): $\delta = 1.48$ (s, 9 H), 1.49 (s, 9 H), 7.41 (t, $J = 8.8$ Hz, 1 H), 7.46 (d, $J = 7.6$ Hz, 2 H), 7.52–7.57 (m, 2 H), 7.60 (d, $J = 8.0$ Hz, 2 H), 7.65 (t, $J = 8.8$ Hz, 1 H), 7.71 (d, $J = 8.4$ Hz, 1 H), 7.98 (d, $J = 8.8$ Hz, 1 H), 8.03 (d, $J = 6.4$ Hz, 1 H), 8.07 (s, 1 H), 8.33 (d, $J = 8.0$ Hz, 1 H), 8.81 (d, $J = 9.2$ Hz, 1 H).

¹³C NMR (125 MHz, CDCl_3): $\delta = 31.5, 31.5, 34.7, 35.0, 118.7, 119.7, 123.2, 124.4, 124.6, 124.9, 124.9, 126.7, 126.8, 127.0, 127.2, 128.9, 129.0, 130.4, 131.0, 131.3, 132.5, 134.8, 137.2, 137.8, 138.8, 139.1, 149.6, 150.4$.

HRMS (FAB): m/z calcd for $\text{C}_{34}\text{H}_{32} [\text{M}]^+$: 440.2504; found: 440.2459.

5,12-Dimethoxyrubicene (1c)^{5a}

[CAS Reg. No. 219725-13-0]

In a Schlenk flask (10 mL), a solution of **2c**²² (47.2 mg, 121 μmol) and DDQ (83.8 mg, 363 μmol , 3.0 equiv) in anhyd CHCl_3 (3.8 mL) was stirred for 10 min at r.t. under N_2 . After the addition of TfOH (0.20 mL, 2.26 mmol), the mixture was stirred for 2 h at 60 °C. The mixture was poured into aq NaHCO_3 (50 mL) and rinsed with H_2O (50 mL). The formed precipitate was collected by filtration, and the solid was washed with H_2O (50 mL), MeOH (50 mL), and hexane (50 mL). The crude product was purified by recrystallization from toluene/MeOH; yield: 35.3 mg (76%); purple solid; mp 358–360 °C (partly sublimed) (Lit.^{5a} mp >300 °C); $R_f = 0.21$ (hexane/ CH_2Cl_2 3:2).

¹H NMR (500 MHz, CDCl_3): $\delta = 3.98$ (s, 6 H), 7.00 (dd, $J = 2.5, 8.5$ Hz, 2 H), 7.54 (d, $J = 2.5$ Hz, 2 H), 7.76 (dd, $J = 2.0, 9.0$ Hz, 2 H), 7.99 (d, $J = 7.0$ Hz, 2 H), 8.21 (d, $J = 8.5$ Hz, 2 H), 8.56 (d, $J = 9.0$ Hz, 2 H).

3-Methoxy-8-(4-methoxyphenyl)benzo[a]fluoranthene (3c)

When the above reaction was performed in CH_2Cl_2 at 40 °C for 14 h, **3c** was formed as the major product. The purification of the crude product by chromatography (silica gel, hexane/ CH_2Cl_2 5:1) gave pure **3c**; yield: 19.5 mg (42%); orange solid; mp 201–205 °C; $R_f = 0.26$ (hexane/ CH_2Cl_2 3:2).

¹H NMR (400 MHz, CDCl_3): $\delta = 3.96$ (s, 3 H), 3.99 (s, 3 H), 7.03 (dd, $J = 2.8, 8.8$ Hz, 1 H), 7.13 (dt, $J = 2.8, 8.8$ Hz, 2 H), 7.40 (ddd, $J = 1.2, 6.8, 9.2$ Hz, 1 H), 7.44 (dt, $J = 2.8, 8.8$ Hz, 2 H), 7.55 (dd, $J = 6.4, 8.8$ Hz, 1 H), 7.60 (d, $J = 2.4$ Hz, 1 H), 7.63 (ddd, $J = 1.2, 6.8, 9.2$ Hz, 1 H), 7.72 (d, $J = 8.4$ Hz, 1 H), 7.96 (d, $J = 8.8$ Hz, 1 H), 7.99 (d, $J = 6.4$ Hz, 1 H), 8.30 (d, $J = 8.8$ Hz, 1 H), 8.75 (d, $J = 8.4$ Hz, 1 H).

¹³C NMR (125 MHz, CDCl_3): $\delta = 55.4, 55.7, 108.0, 112.9, 113.5, 119.9, 124.3, 124.3, 124.7, 126.7, 126.9, 127.0, 127.4, 128.4, 128.8, 130.0, 130.2, 131.0, 132.7, 133.5, 136.7, 137.6, 140.9, 159.0, 159.1$.

HRMS (FAB): m/z calcd for $\text{C}_{28}\text{H}_{20}\text{O}_2 [\text{M}]^+$: 388.1463; found: 388.1431.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0036-1588570>.

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