Synthesis M. Kawamura et al. Paper

# Facile Synthesis of Rubicenes by Scholl Reaction

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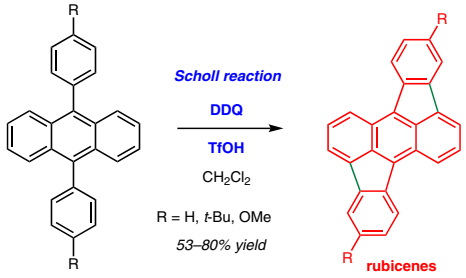


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**Abstract** The treatment of 9,10-diphenylanthracenes with DDQ in the presence of TfOH readily gave the corresponding rubicene derivatives in good yields. The effects of oxidant, acid, substituent, and other conditions are discussed. This protocol 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**, $C_{26}H_{14}$), 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 $C_{70}$,[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 reaction[9] 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 tetrabenzopyracylenes.[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.

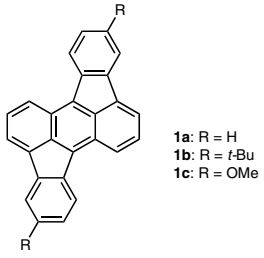
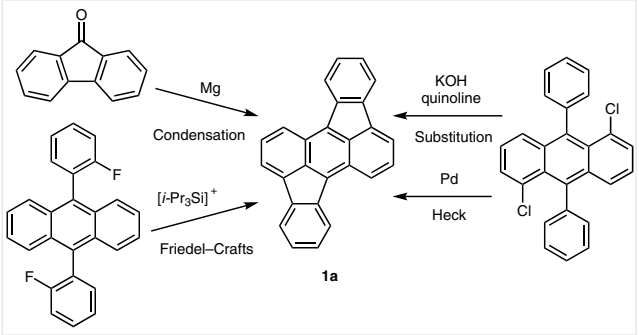


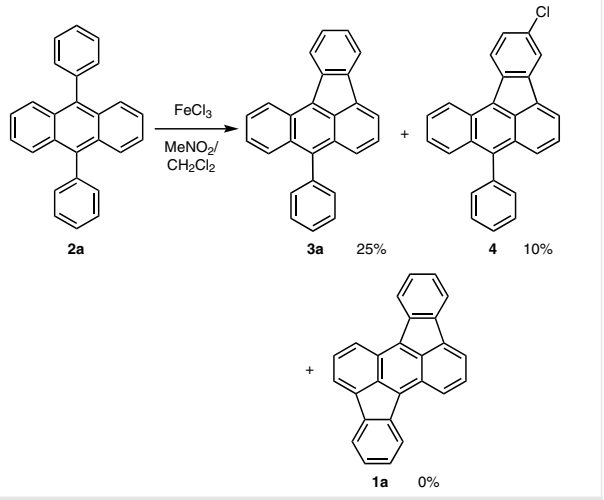

**Figure 1** Structure of rubicenes **1**




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

We first reacted 9,10-diphenylanthracene (**2a**) with $FeCl_3$, utilizing the reaction conditions for 5,11-diphenyltetracene (Scheme 2).[12a] The reaction with 8.0 equivalents of $FeCl_3$ 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 $FeCl_3$

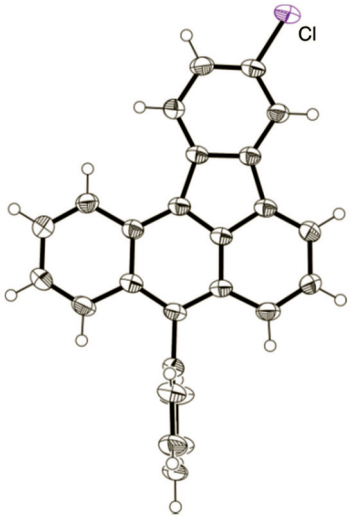
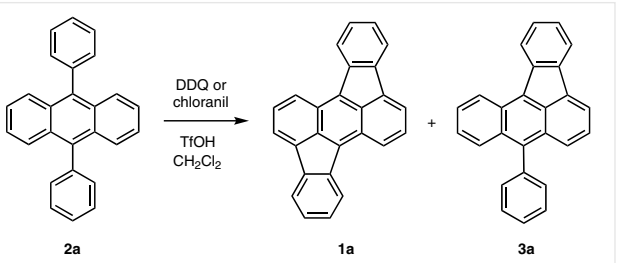



**Figure 2** An ORTEP drawing of the X-ray crystal structure of **4**; thermal ellipsoids are set at 50% probability

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 isorubicene 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

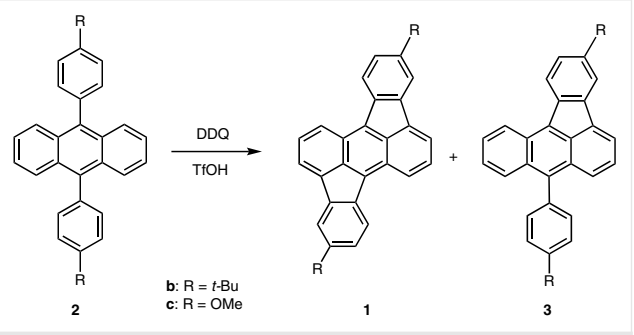
We could control the cyclization step by changing the amount of DDQ (Table 1). The reaction with 1.75 equivalents of DDQ gave **3a** as the major product (64%). The reaction did not work at all when methanesulfonic acid (MsOH) was used as the acid instead of TfOH.[9c,13a] Therefore, a strong acid is 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 $CH_2Cl_2$.
[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).




**Scheme 4** Scholl reactions of **2b** and **2c** with DDQ

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, $^{13}C$: 100 MHz) or JNM-ECZ500R spectrometer ($^1H$: 500 MHz, $^{13}C$: 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 $FeCl_3$

In a 10 mL flask, $FeCl_3$ (78.5 mg, 484 µmol) and $MeNO_2$ (1 mL) were added to a solution of 9,10-diphenylanthracene (**2a**; 20.0 mg, 60.5 µmol) in $CH_2Cl_2$ (2 mL). The deep blue solution was stirred for 24 h at r.t. The reaction was quenched with $H_2O$ (5 mL), and the whole was added to $H_2O$ (50 mL). The organic materials were extracted with $CH_2Cl_2$ (3 × 40 mL). The combined organic layers were dried ($Na_2SO_4$) 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/$CH_2Cl_2$ 3:2).

$^1H$ NMR (400 MHz, $CDCl_3$): 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).

$^{13}C$ NMR (125 MHz, $CDCl_3$): 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 $C_{26}H_{16}$ $[M]^+$: 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/$CH_2Cl_2$ 3:2).

$^1H$ NMR (400 MHz, $CDCl_3$): 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).

$^{13}C$ NMR (100 MHz, $CDCl_3$): 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 $C_{26}H_{15}{}^{35}Cl$ $[M]^+$: 362.0862; found: 362.0819.

### X-ray Crystal Structure Analysis of 4[18]

A single crystal of **4** was prepared by recrystallization from $CHCl_3$/MeOH. Diffraction data were collected on a Rigaku Varimax with Saturn system equipped with a Rigaku GNNP low-temperature device using Mo*K*α 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 program[19] 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)°, $V$ = 1739.3(2) Å$^3$, $Z$ = 4, $d$ = 1.3856 g cm$^{-3}$, $\mu$(Mo$K\alpha$) = 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, w$R_2$ = 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 $CH_2Cl_2$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 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.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 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).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 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).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 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 $C_{34}H_{32}$ [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).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 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).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 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).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 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 $C_{28}H_{20}O_2$ [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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