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m-CPBA/TFA: an efficient nonmetallic reagent for oxidative coupling of 1,2-diarylethylenes

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ABSTRACT

A mild synthesis of a series of phenanthrenes with different substituents on the phenanthrene ring is described. The method involves intramolecular oxidative coupling of a variety of 1,2-diarylethylene derivatives in the presence of *m*-chloroperoxybenzoic acid (*m*-CPBA) in trifluoroacetic acid (TFA) to yield phenanthrenes in high yields. The present approach solves a key step for the synthesis of polycyclic structures related to an alkaloid tylophorine.

1. Introduction

The phenanthroindolizidine and phenanthroquinolizidine alkaloids are structurally related groups of pentacyclic natural products.[1] Since the first isolation of (−)-tylophorine in 1935,[2] more than 60 alkaloids and their seco analogues have been reported.[3] These alkaloids exhibit interesting pharmacological properties.[1,3,4] Among these interesting biological activities, antitumor activity is most notable,[3,4g,5] and thus, it is responsible for synthetic attention.[3,6] The synthesis of polymethoxy-substituted phenanthrene unit is the key step in the preparation of these alkaloids.[3,6] Therefore, development of an effective protocol to access polymethoxy-substituted phenanthrenes is noteworthy. Pschorr proposed the first synthesis of phenanthrene core in 1896,[7] the first step of this reaction was a Perkin condensation between the sodium salt of phenylacetic acid and *o*-nitrobenzaldehyde; *o*-nitro-α-phenylcinnamic acid was formed. The nitro group was then reduced using an ammoniacal solution of ferrous sulfate, and the amino acid produced was diazotized. On shaking the diazonium salt with dilute sulfuric acid and copper powder, nitrogen was eliminated and ring closure led to the formation of 9-phenanthrenecarboxylic acid. When heated, this acid lost carbon dioxide and formed phenanthrene. And the Pschorr reaction has been widely used and become a classical method to synthesize phenanthrene ring system.[8] But the long linear sequence and low overall yields restrict the practical application of this method. The main limitations to the Pschorr synthesis are difficulties in obtaining starting materials and in decarboxylating the phenanthrene derivative. Problems connected with the preparation of *o*-nitrobenzaldehydes are sometimes the determining factors in the usefulness of the Pschorr synthesis. Metal-based intramolecular oxidative coupling to yield the phenanthrene ring by using vanadium oxytrifluoride (VOF_3),[6d,9] thallium(III) triflouroacetate (TTFA),[10] lead(IV) tetraacetate ($Pb(OAc)_4$)[11] has been developed. However, these coupling reactions require large excess amount of metal salts, extensive application of these organic metallic reagents has been limited by high toxicity, severe conditions, and low yields. Moreover, these heavy metals can contaminate the final products. We have recently reported the use of large excess iron(III) chloride ($FeCl_3$) and catalytic amount of $FeCl_3$ for the synthesis of polymethoxy-substituted phenanthrene derivatives by oxidative coupling of substituted methyl (*E*)-α-phenyl cinnamates.[12] These two methods also suffer from difficulty in separation of organic and inorganic products relatively due to introducing metallic reagent. Therefore, the development of more efficient organic nonmetallic coupling reagents for the construction of phenanthrene derivatives is highly desirable.

m-Chloroperoxybenzoic acid (*m*-CPBA) is the one of choice for laboratory-scale experiments because it is very efficient and it can be easily and safely handled in very clean reactions. *m*-CPBA has been extensively investigated as an oxidizing agent for oxidation of unsaturated compounds, organic sulfur compounds, organic nitrogen compounds, aldehydes, ketones, quinones, organic iodine compounds, and so on. *m*-CPBA has also been used for the

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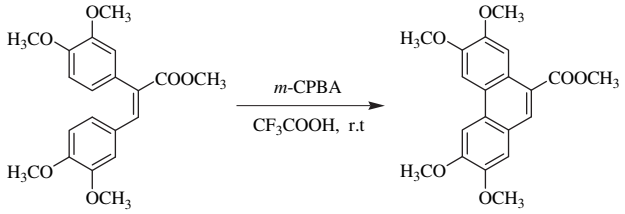
determination of structure and analysis of organic compounds.[13] However, the use of nonmetallic *m*-CPBA as sole oxidative coupling reagent for the direct construction of phenanthrenes rather than epoxy compounds and its scope and limitations remain unknown. In this paper, we report the efficiency of the system *m*-CPBA/TFA for oxidative coupling of 1,2-diarylethylenes to phenanthrenes under very mild conditions.

2. Results and discussion

As a starting point, we chose (*E*)-methyl-2,3-bis(3,4-dimethoxyphenyl)acrylate (**1a**) as standard substrate to investigate suitable reaction conditions for the desired intramolecular oxidative coupling reaction. The results are summarized in Table 1.

Table 1
Effect of amount of *m*-CPBA on coupling of **1a**[a]



1a **1b**

Entry	*m*-CPBA (equiv)	*t* (h)	LC conv.[b] (%)	LC yield[b] (%)
1	1.1	6	73	57
2	1.2	6	80	70
3	1.3	6	91	84
4	1.4	1.2	98	90
5	1.5	1.2	100	94

[a] Conditions: **1a** (358 mg, 1.0 mmol), CF_3COOH (10 mL) acts as solvent.
[b] Conversion and yield were determined by HPLC.

The desired coupling product **1b** was not obtained with *m*-CPBA as sole oxidant when dichloromethane acts as solvent. When organic acid trifluoroacetic acid (CF_3COOH) acts as solvent, the coupling reaction proceeded successfully at room temperature (Table 1), showing that acidic environment is an indispensable condition for intramolecular coupling of **1a**. Increasing the amount of *m*-CPBA had great influence on the conversions and yields (Table 1, entries 1–5). Quantitative conversion and almost quantitative yield were obtained by using 1.5 equiv of *m*-CPBA as oxidant (Table 1, entry 5).

Concentration effect on coupling reaction of **1a** is shown in Table 2, which shows that the reaction can be performed in a wide range of concentration with excellent yields at room temperature. The yields of **1b** also increased gradually when the concentration decreased.

Table 2
Effect of concentration on coupling of **1a**[a]

Entry	Concn (mol/L)	*t* (h)	LC conv. (%)	LC yield (%)
1	0.1	1.0	98	93
2	0.05	1.0	100	92
3	0.025	0.7	100	95
4	0.01	0.5	100	99

[a] Conditions: **1a** (358 mg, 1.0 mmol), 1.5 equiv of *m*-CPBA, CF_3COOH act as solvent, room temperature.

In order to further optimize the reaction conditions, the reaction was studied with different temperatures as shown in Table 3. Reaction times were shorter when the temperature became higher. Almost quantitative yield was obtained at room temperature (Table 3, entry 3), which evidences the efficiency of the *m*-CPBA/TFA system to get the intramolecular oxidative coupling.

Considering operational simplicity and large-scale synthesis, the optimized reaction conditions were summarized as follows: 1.5 equiv of *m*-CPBA, TFA as solvent, the concentration of the substrate was 0.05 mol/L, at room temperature.

Table 3
Effect of temperature on coupling of **1a**[a]

Entry	Temp (°C)	*t* (h)	LC conv. (%)	LC yield (%)
1	−15	18	67	66
2	0	6	91	89
3	25	2	100	98
4	40	0.25	100	94
5	70	0.25	100	95

[a] Conditions: **1a** (358 mg, 1.0 mmol), 1.5 equiv of *m*-CPBA, CF_3COOH act as solvent, 0.01 mol/L.

Subsequently, various simple structure 1,2-diarylethylenes were tested as substrates for the intramolecular oxidative coupling to form phenanthrene rings under the above optimized conditions (Table 4). To avoid side-reactions such as epoxidation of the ethylene

Table 4
Substrate scope of intramolecular oxidative coupling using *m*-CPBA[a]

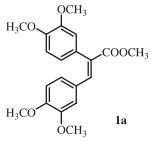
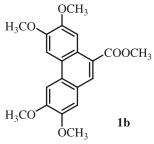
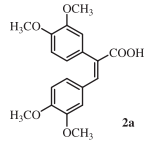
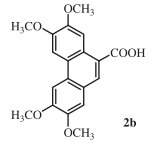
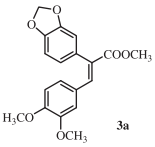
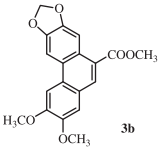
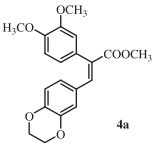
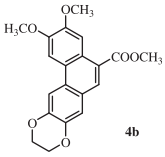
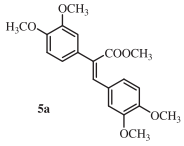
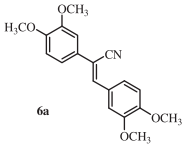
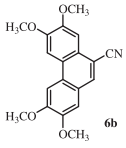
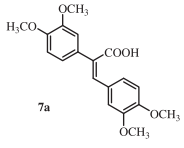
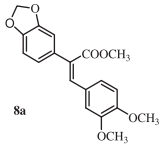
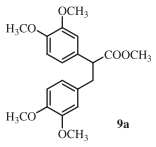
Entry	Substrate	Product	*t* (h)	Yield[b] (%)
1			0.5	96
2			0.7	92
3			1.3	96
4			0.5	86
5		**1b**	0.7	96
6			0.75	95
7		**2b**	0.85	93
8		**3b**	2.5	82

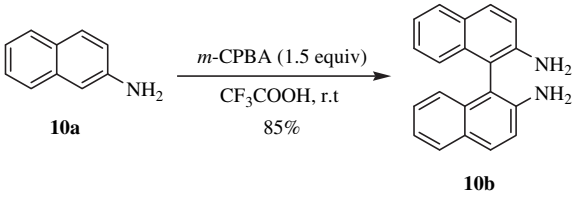
Table 4 (*continued*)

Entry	Substrate	Product	*t* (h)	Yield[b] (%)
9	**2a**/**7a**=1:1	**2b**	1	94
10[c]	 **9a**	**1b**	0.85	93

[a] Substrate: 1.0 mmol.
[b] Yield of the isolated products.
[c] *m*-CPBA (3.0 equiv) was used.

unit, we deactivated the double bond by introduction of a carbonyl or cyano substituent. Both *E*-isomer substrates **1a**–**4a** and *Z*-isomer substrates **5a**–**8a**, which have an electron-withdrawing group on the double bond and electron-donating groups on the phenyls were found to react smoothly and gave the corresponding coupling products rather than epoxy products in excellent yields (82–96%), suggesting that configuration of the double bond has no effect to the intramolecular oxidative coupling. As we all know, Perkin condensation of the appropriate benzeneacetic acid with the corresponding aromatic aldehyde invariably yield a mixture of *E*-isomer as the main product and *Z*-isomer as the minor product,[9a,14] such as **2a** and **7a**. So we selected the mixture of **2a** and **7a** as substrate to test this method and gave the same oxidative coupling product **2b** in the presence of *m*-CPBA at room temperature in 94% yield (Table 4, entry 9). In contrast to the Pschorr synthesis of phenanthrene, the reaction makes full use of the minor (*Z*)-isomer **7a**, which was a byproduct in the Pschorr reaction. In addition, a larger-scale reaction (50-fold scaled up) showed the same result as for the small one. There are also certain very definite limitations to the Pschorr synthesis. Some of the limitations arise as a result of side reaction: reduction and/or hydroxylation may replace coupling, and where the α-phenyl nucleus of the cinnamic acid derivative is unsymmetrically substituted, two isomeric coupling products are possible. Interestingly, oxidative coupling and dehydrogenation of **9a** was successfully achieved in one pot by using 3.0 equiv of *m*-CPBA and gave **1b** in 93% yield (Table 4, entry 10). Thus, this facile and efficient synthesis of phenanthrene derivatives by using *m*-CPBA/TFA system solved the key step for the synthesis of polycyclic structures related to an alkaloid tylophorine.

To our delight, the *m*-CPBA/TFA system has become successful as an effective organic nonmetallic oxidant for intermolecular C–C bond formation, initiating an oxidative aniline coupling reaction between 2-naphthylamine (**10a**) moieties at room temperature and gave binaphthyl amine (**10b**) in 85% isolated yield. The coupling of 2-naphthylamine has been investigated via complex process with low yields[15] and our simple reaction scheme is given below (Scheme 1).



Scheme 1. Synthesis of binaphthyl amine (**10b**).

No mechanism has yet been formulated for the above coupling reactions employing *m*-CPBA/TFA reagent. The nonstereospecificity of our coupling reaction (Table 4, entries 1–8) implied that the reaction proceed via free radical species. To further clarify the mechanism of the present *m*-CPBA-mediated oxidative coupling, the ESR spectrum was then measured for the coupling of **1a**. As shown in Fig. 1, a signal at g=2.006 was observed, which is assignable to a radical species derived from **1a** and it has no hyperfine splitting (Fig. 1a). The signal was not observed after the treatment of **1a** in CH_2Cl_2 (Fig. 1b). Acidic environment is indispensable for protonation of *m*-CPBA and increases its oxidation ability.

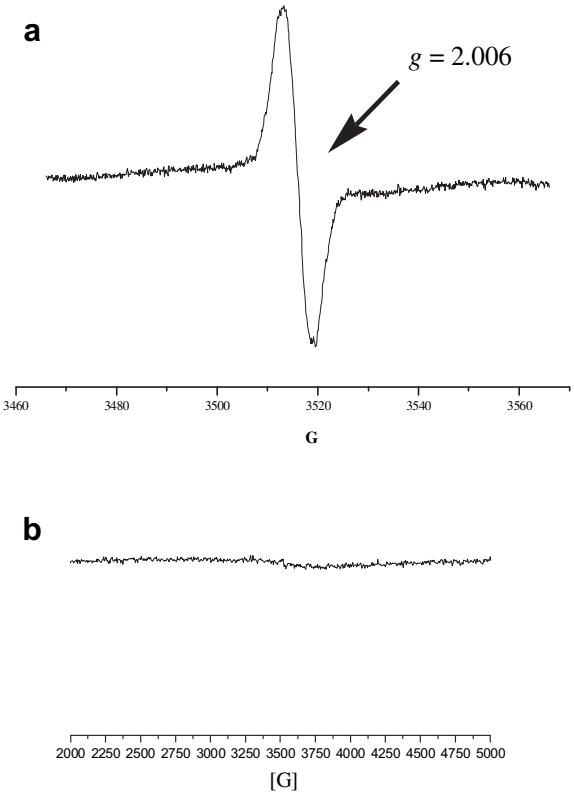
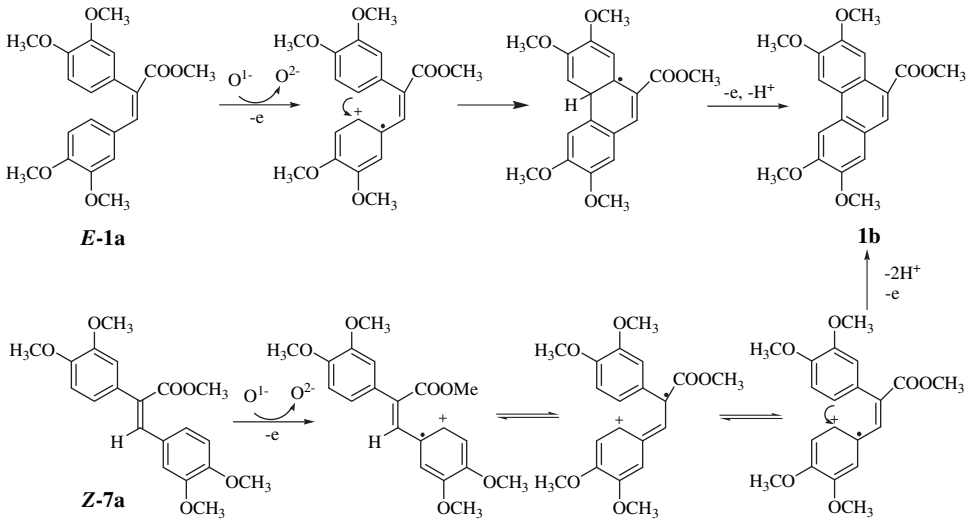


Fig. 1. ESR spectra of *m*-CPBA-mediated oxidative coupling. (a) *m*-CPBA/TFA was treated with **1a**, after 6 min, the spectrum was measured. (b) Compound **1a** was dissolved in CH_2Cl_2 and the spectrum was measured.

Based on the above experimental results, we propose the reaction mechanism for the present oxidative coupling (Scheme 2). This reaction can be divided into three steps. The first step proceeds via a one-electron transfer from substrate *E*-**1a** or *Z*-**7a** to *m*-CPBA to give the reduced form *m*-chlorobenzoic acid and radical cationic species, which was attacked by another rich-electronic phenyl ring to form new C–C bond. At last, one electron is lost and dehydroaromatization to give the corresponding biaryl coupling product **1b**. Compound *Z*-**7a** also proceeds via C–C bond rotation.

3. Conclusion

In summary, as an effort to develop green chemistry in the field of chemical synthesis, we have developed an efficient synthetic approach for the direct construction of polymethoxy-substituted phenanthrene rings using nonmetallic *m*-chloroperoxybenzoic acid (*m*-CPBA) as sole oxidant in trifluoroacetic acid (TFA), which solved the key step in the preparation of polycyclic natural alkaloid tylophorine. This method has also been applied to intermolecular biaryl coupling of 2-naphthylamine in excellent yield. The present system has the following significant advantages: (i) C–C bonds can be formed efficiently starting directly from arenes rather than epoxidation; (ii) simple workup procedures, mild conditions, large-scale preparation, and high yields; (iii) the use of easily available and nontoxic *m*-CPBA as oxidant and TFA can be recycled and reused. Such reactions present the most direct and efficient synthetic methods of C–C bond formation and provide a foundation for the



Scheme 2. Tentative mechanism for *m*-CPBA-mediated intramolecular oxidative coupling.

next generation of chemical syntheses with an eye on green chemistry. Further studies on synthetic applications of *m*-CPBA/TFA system are in progress.

4. Experimental

4.1. General

The melting points were determined on an X-4 binocular microscope melting point apparatus (Beijing Tech Instruments Co., Beijing, China) and uncorrected. ^{1}H NMR spectra were obtained using a Bruker AC-P 300 and a Varian Mercury Plus 400 MHz spectrometers. Chemical shift values (δ) are given in parts per million and are downfield from internal tetramethylsilane. Elemental analysis was performed on an MT-3 elemental analyzer. HRMS was obtained on FT-ICR MS (Ionspec, 7.0 T). HPLC spectra were obtained on a Shimadzu LC-20AT instrument. ESR spectrum was obtained on Bruker EMX-6/1 instrument. All anhydrous solvents were dried and purified by standard techniques just before use. *m*-Chloroperoxybenzoic acid (*m*-CPBA) (a purity of 85%) and trifluoroacetic acid (TFA) were commercially available and used without further purification. Substrate **10a** was commercially available and used without further purification.

4.2. General procedure for the preparation of (*E*)-methyl-2,3-disubstituted phenylacrylate

(*E*)-2,3-Disubstituted phenyl acrylic acids were obtained by condensation of the appropriate aldehyde with the relevant substituted phenyl acetic acid by the method of Halton and co-workers[9a] or by the procedure devised by Baker and co-workers.[14c] Esterification of the above acids with methanol and sulfuric acid in the usual manner afforded the methyl ester, and recrystallization from ethanol afforded the pure product as a white solid.

*4.2.1. Methyl (E)-2,3-bis(3,4-dimethoxyphenyl)acrylate (**1a**).* Yield 92%, mp 127–128 °C (lit.[9a] mp 127–128 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.91 (d, $^3J_{HH}$=8.00 Hz, 1H), 6.81(d, $^4J_{HH}$=2.00 Hz, 1H), 6.80 (d, $^4J_{HH}$=1.60 Hz, 1H), 6.76 (d, $^4J_{HH}$=1.60 Hz, 1H), 6.71 (d, $^3J_{HH}$=8.40 Hz, 1H), 6.51 (d, $^4J_{HH}$=2.00 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.48 (s, 3H).

*4.2.2. (E)-2,3-Bis(3,4-dimethoxyphenyl)acrylic acid (**2a**).* Yield 70%, mp 214–216 °C (lit.[16] mp 216–217 °C); ^{1}H NMR (400 MHz, DMSO) δ 12.50 (br, 1H), 7.68 (s, 1H), 6.54–6.98 (m, 6H), 3.74 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 3.45 (s, 3H).

*4.2.3. Methyl (E)-2-(3,4-methylenedioxyphenyl)-3-(3,4-dimethoxyphenyl)acrylate (**3a**).* Yield 68%, mp 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 6.83–6.87 (m, 2H), 6.72–6.75 (m, 3H), 6.55 (d, $^4J_{HH}$=1.6 Hz, 1H), 5.98 (s, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 55.2, 55.8, 101.1, 108.9, 110.4, 110.5, 112.5, 123.4, 125.4, 127.3, 129.5, 129.9, 140.7, 147.1, 148.0, 148.2, 150.0, 168.5. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{18}O_6Na$ $(M+Na)^+$ 365.0996, found 365.0993.

*4.2.4. Methyl (E)-2-(3,4-dimethoxyphenyl)-3-(3,4-ethylenedioxyphenyl)acrylate (**4a**).* Yield 62%, mp 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 6.89 (d, $^3J_{HH}$=8.0 Hz, 1H), 6.57–6.79 (m, 5H), 4.16–4.21 (m, 4H), 3.92 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 55.8, 55.9, 64.0, 64.5, 114.4, 112.8, 117.0, 119.6, 122.1, 124.7, 128.2, 128.4, 130.2, 140.0, 143.0, 144.6, 148.6, 149.1, 168.7. Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.31; H, 5.69.

4.3. General procedure for the preparation (*Z*)-2,3-bis(3,4-dimethoxyphenyl)acrylic acid (7a) and (*Z*)-methyl-2,3-bis(3,4-dimethoxyphenyl)acrylate (5a)

In the procedure for the synthesis of (*E*)-2,3-bis(3,4-dimethoxyphenyl)acrylic acid (**2a**), in the last step the aqueous layer was acidified carefully with concentrated hydrochloric acid (pH=5) to afford the main product acid *E*-acrylic acid **2a** as precipitate, which was collected with 70% yield. And then the filtrate was acidified with concentrated hydrochloric acid (pH=3) to afford (*Z*)-2,3-bis(3,4-dimethoxyphenyl)acrylic acid (7**a**) as precipitate with 15% yield. Methylation of **7a** with diazomethane afforded the corresponding methyl ester, and recrystallization from petroleum ether and ethyl acetate afforded the pure **5a** as a white solid with 86% yield.

*4.3.1. (Z)-Methyl-2,3-bis(3,4-dimethoxyphenyl)acrylate (**5a**).* Mp 148–149 °C (lit.[17] mp 148 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99–6.94 (m, 4H), 6.89 (s, 1H), 6.84–6.88 (m, 4H), 3.92 (s, 3H), 3.90 (s, 6H), 3.88 (s, 3H), 3.81 (s, 3H).

*4.3.2. (Z)-2,3-Bis(3,4-dimethoxyphenyl)acrylic acid (**7a**).* Mp 170–171 °C (lit.[17] mp 170–171 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01–7.06

(m, 4H), 6.95 (s, 1H), 6.84–6.90 (m, 2H), 3.92 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H), 3.86 (s, 3H).

*4.3.3. (Z)-2,3-Bis(3,4-dimethoxyphenyl)acrylonitrile (**6a**).* Compound **6a** was prepared according to the known literature in 96% yield,[18] mp 151–152 °C (lit.[18] mp 154–155 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, $^3J_{HH}$=2.01 Hz, 1H), 7.35 (m, 2H), 7.24(dd, $^3J_{HH}$=8.41, $^4J_{HH}$=2.22 Hz, 1H), 7.13 (d, $^3J_{HH}$=2.18 Hz, 1H), 6.93 (dd, $^3J_{HH}$=8.47, 4.54 Hz, 2H), 3.98 (s, 3H), 3.97 (s, 3H), 3.95 (s, 3H), 3.93 (s, 3H).

*4.3.4. Methyl (Z)-2-(3,4-methylenedioxyphenyl)-3-(3,4-dimethoxyphenyl)acrylate (**8a**).* Mp 74–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79–6.94 (m, 7H), 5.98 (s, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 3.80(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.3, 54.7, 54.8, 100.3, 105.5, 107.4, 109.7, 109.9, 119.3, 120.4, 127.4, 128.9, 130.2, 131.7, 146.6, 147.0, 147.7, 148.1, 169.5. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{18}O_6Na$ $(M+Na)^+$ 365.0996, found 365.0993.

*4.3.5. α-(3′,4′-Dimethoxybenzyl)-methyl 3,4-dimethoxyphenylacetate (**9a**).* Compound **9a** was prepared by catalytic hydrogenation of **1a** by 10% Pd/C catalyst and gave a white solid in 96% yield, mp 100–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (m, 3H), 6.71 (d, $^3J_{HH}$=8.1 Hz, 1H), 6.65 (d, $^3J_{HH}$=8.2 Hz, 1H), 6.60 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.80 (s, 3H), 3.75 (dd, $^3J_{HH}$=8.6, 6.9 Hz, 1H), 3.62 (s, 3H), 3.31 (dd, $^2J_{HH}$=13.7 Hz, $^3J_{HH}$=8.6 Hz, 1H), 2.96 (dd, $^2J_{HH}$=13.7 Hz, $^3J_{HH}$=6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.6, 52.0, 53.3, 55.7, 55.8, 55.9, 111.0, 111.1, 111.1, 112.2, 120.3, 120.9, 131.1, 131.6, 147.5, 148.3, 148.6, 149.0, 174.1. HRMS (ESI) *m*/*z* calcd for $C_{20}H_{24}O_6Na$ $(M+Na)^+$ 383.1463, found 383.1468.

4.4. General procedure for oxidative coupling

To a solution of **1a**–**8a**, or **10a** (1.0 mmol) in CF_3COOH (20 mL) was added *m*-CPBA (0.3 g, 1.5 mmol, a purity of 85%). The mixture was stirred at room temperature for an appropriate time as shown in Table 4. CF_3COOH was recycled by rotary evaporator. CH_2Cl_2 (100 mL) and water (30 mL) were added and stirred. The organic phase was washed with water (2×20 mL) again, dried over $MgSO_4$, filtered, and concentrated in vacuo and the residue obtained was determined by HPLC analysis and purified by flash chromatography on silica gel to give the desired product.

*4.4.1. Methyl 2,3,6,7-tetramethoxyphenanthrene-9-carboxylate (**1b**).* Yield 96%, mp 202–203 °C (lit.[18] mp 202–204 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.43 (s, 1H), 7.81 (s, 1H), 7.77 (s, 1H), 7.27 (s, 1H), 4.14 (s, 3H), 4.13 (s, 3H), 4.08 (s, 3H), 4.04 (s, 3H), 4.02 (s, 3H).

*4.4.2. 2,3,6,7-Tetramethoxyphenanthrene-9-carboxylic acid (**2b**).* Yield 92%, mp 285–287 °C (lit.[19] mp 280–282 °C); ^{1}H NMR (400 MHz, DMSO) δ 12.87 (br, 1H), 8.53 (s, 1H), 8.40 (s, 1H), 8.03 (s, 1H), 7.99 (s, 1H), 7.55 (s, 1H), 4.04 (s, 3H), 4.03 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H).

*4.4.3. Methyl 2,3-dimethoxy-6,7-methylenedioxyphenanthrene-9-carboxylate (**3b**).* Yield 96%, mp 209–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.36 (s, 1H), 7.87 (s, 1H), 7.72 (s, 1H), 7.24 (s, 1H), 6.12 (s, 2H), 4.12 (s, 3H), 4.03 (s, 3H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.1, 55.9, 56.0, 100.1, 101.5, 102.5, 104.4, 108.8, 123.1, 124.5, 125.1, 126.6, 127.3, 130.0, 147.7, 147.8, 149.0, 151.1, 168.2. Anal. Calcd for $C_{19}H_{16}O_6$: C, 67.05; H, 4.74. Found: C, 66.98; H, 4.60.

*4.4.4. Methyl 2,3-ethylenedioxyphenyl-6,7-dimethoxyphenanthrene-9-carboxylate (**4b**).* Yield 86%, mp 209–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.33 (s, 1H), 7.91 (s, 1H), 7.78 (s, 1H), 7.37 (s, 1H), 4.40 (d, $^4J_{HH}$=1.2 Hz, 4H), 4.09 (s, 3H), 4.06 (s, 3H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.0, 55.8, 64.4, 64.7, 103.0, 106.9, 108.9, 115.6, 122.5, 123.7, 125.0, 127.6, 130.4, 143.4, 145.8, 148.9, 149.2, 168.2. Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.79; H, 5.12. Found: C, 67.90; H, 5.17.

*4.4.5. 2,3,6,7-Tetramethoxyphenanthrene-9-carbonitrile (**6b**).* Yield 95%, mp 266–268 °C (lit.[20] mp 267–269 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.78 (s, 1H), 7.75 (s, 1H), 7.57 (s, 1H), 7.22 (s, 1H), 4.15 (s, 3H), 4.14 (s, 3H), 4.10 (s, 3H), 4.05 (s, 3H).

*4.4.6. 1,1′-Binaphthyl-2,2′-diamine (**10b**).* Yield 85%, mp 190–192 °C (lit.[21] mp 189–191 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.82 (m, 4H), 7.06–7.25 (m, 8H), 2.56–3.88 (br, 4H); HRMS (ESI) *m*/*z* calcd for $C_{20}H_{16}N_2$ $(M+H)^+$ 285.1386, found 285.1390.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.09.101. These data include MOL files and InChIKeys of the most important compounds described in this article.

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