A Simple and Efficient Oxidative Coupling of Aromatic Nuclei Mediated by Manganese Dioxide

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Abstract: Oxidative intramolecular coupling of the aryl rings of various stilbenes for direct construction of the phenanthrene ring system is promoted efficiently by manganese dioxide–trifluoroacetic acid at room temperature in excellent yields. This approach is also applied to the intermolecular biaryl coupling of 2-naphthols, 2-naphthalenethiol, 2-naphthylamine, a phenol ether and a phenol under very mild conditions. An electron-transfer mechanism is proposed in which manganese dioxide acts as a two-electron oxidant.

Key words: oxidative coupling, aromatic nuclei, manganese dioxide, phenanthrenes, intermolecular biaryl coupling

The construction of biaryl bonds has been studied in detail, and various methods have been developed to synthesize natural products and important chiral auxiliaries for asymmetric synthesis via biaryl bond formation.[1,2] Examples include phenanthroindo(quino)lizidine alkaloids and 1,1′-binaphthalene derivatives. The synthesis of the phenanthrene ring system is a key step in the preparation of such alkaloids.[3] Some of the reported methods require substrates bearing suitable functionalization.[4] Metal-based intramolecular oxidative couplings to yield phenanthrene rings, without prior functionalization, using thallium(III) trifluoroacetate (TTFA),[1a,5] iron(III) chloride, iron(III) perchlorate,[6] lead(IV) tetraacetate [$Pb(OAc)_4$],[7] vanadium oxytrifluoride (VOF_3) and vanadium oxytrichloride ($VOCl_3$)[8] have also been developed. 1,1′-Binaphthols (BINOL) have gained considerable attention in asymmetric synthesis.[2] They are typically prepared using iron(III) or copper(II) transition metal complexes, although the use of titanium(IV), vanadium(V) and ruthenium(III) has also been reported.[9] Extensive application of these coupling reagents is often limited by their high toxicity, the need for harsh reaction conditions, problems with catalyst–product separation, and low yields.

The most common method for biaryl carbon–carbon bond construction is via cross-coupling between two suitably functionalized starting materials.[10,11] However, taking into consideration operational simplicity, the availability of starting materials, and environmental factors, a more attractive approach to phenanthrenes and biaryls would involve direct oxidative coupling of two unfunctionalized arenes.[1a,5–9,12] In such a transformation, both starting materials could be used directly without prior functionalization, and the sole by-product would be two equivalents of hydrogen cations (H^+). As such, the development of highly regioselective methods for the construction of carbon–carbon bonds starting from arenes remains an ongoing synthetic challenge.

Manganese(IV) dioxides have been extensively investigated as oxidants, ion exchangers, and as soft magnetic and electrode materials in lithium–manganese dioxide batteries.[13] They have been used for a wide range of industrial applications such as ozone decomposition, photocatalytic oxidation of organic pollutants, nitric oxide reduction, selective oxidation of carbon monoxide, decomposition of hydrogen peroxide, and so on.[14] However, to the best of our knowledge, relatively little is known about manganese(IV) dioxide mediated intramolecular and intermolecular biaryl coupling reactions.[15] Herein, we report a manganese(IV) dioxide mediated oxidative coupling of aromatic nuclei to form a new carbon–carbon bond from unfunctionalized arenes under very mild conditions.

In order to establish mild reaction conditions for the oxidative coupling, we examined the intramolecular coupling of methyl (2*E*)-2,3-bis(3,4-dimethoxyphenyl)acrylate (**1a**) as a model compound (Table 1).

The desired coupling product **1b** was not obtained using two equivalents of manganese dioxide as the oxidant (Table 1, entry 1). When organic acids such as trifluoroacetic acid, trichloroacetic acid and tribromoacetic acid were added, the coupling reaction proceeded successfully and gave phenanthrene **1b** in 99%, 99% and 86% yields, respectively (Table 1, entries 2–4), showing that an acidic environment was essential. The reaction time was significantly longer when trichloroacetic acid and tribromoacetic acid were used. *p*-Toluenesulfonic acid and methanesulfonic acid were efficient acids giving **1b** in 89% and 73% yields, respectively (Table 1, entries 5 and 8). Acetic acid and cyanoacetic acid did not promote any coupling – probably due to their weak acidity which was insufficient to activate the manganese dioxide (Table 1, entries 6 and 7). Decreasing the amount of manganese dioxide greatly influenced the conversions and yields; a quantitative yield of **1b** was obtained using one equivalent (Table 1, entry 9), while the use of 0.8 and 0.5 equivalents gave **1b** in 76% and 62% yields, respectively (Table 1, entries 10 and 11). The coupling also proceeded in quantitative

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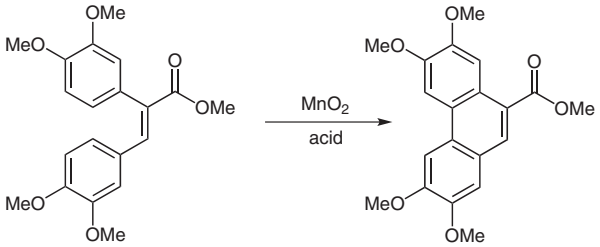
yield under an inert atmosphere (Table 1, entry 12). The use of the mineral acids, concentrated hydrochloric acid and dilute sulfuric acid (25%) gave **1b** in 69% and 77% yields, respectively, which indicated that this reaction was not sensitive to water (Table 1, entries 13 and 14).

The effect of temperature and concentration on the intramolecular coupling reaction of biaryl **1a** is shown in Table 2. The results illustrate that the coupling could be performed over wide temperature (0–72 °C) and concentration (0.01–0.5 mol/L) ranges to afford excellent yields of phenanthrene **1b**.

Consequently, the optimized reaction conditions for the oxidative coupling were as follows: one equivalent of manganese dioxide, a substrate concentration of 0.1 mol/L, room temperature, and trifluoroacetic acid as the promoter and solvent.

Table 1 Effect of Acids on the Intramolecular Manganese Dioxide Mediated Coupling of **1a**[a]



1a **1b**

Entry	MnO_2 (equiv)	Acid (equiv)	Time (h)	Conversion (%)[b]	Yield (%)[b]
1	2	none	6	0	0
2	2	TFA[c]	1	100	99
3	2	Cl_3CCOOH (10)	24	100	99
4	2	Br_3CCOOH (10)	36	93	86
5	2	PTSA (10)	23	97	89
6	2	MeCOOH[c]	15	0	0
7	2	$NCCH_2COOH$ (10)	15	0	0
8	2	MsOH[c]	6	100	73
9	1	TFA[c]	2	100	100
10	0.8	TFA[c]	10	77	76
11	0.5	TFA[c]	6	63	62
12[d]	1	TFA[c]	2	100	100
13[e]	1	concd HCl (1 mL)	24	94	69
14[e]	1	25% H_2SO_4 (2 mL)	15	78	77

[a] Reaction conditions: MnO_2, acid, **1a** (0.5 mmol, 0.1 mol/L), CH_2Cl_2 (5.0 mL) (unless otherwise noted), r.t.
[b] Conversion and yield were determined by HPLC.
[c] The acid also acts as the solvent.
[d] Reaction under an N_2 atmosphere.
[e] MeCN was used as the solvent.

Table 2 Effect of Temperature and Concentration on the Intramolecular Coupling of **1a**[a]

Entry	Concn (mol/L)	Temp (°C)	Time (h)	Conversion (%)[b]	Yield (%)[b]
1	0.1	0	6	100	100
2	0.1	25	2	100	99
3	0.1	72	0.5	100	93
4	0.01	25	2.7	89	89
5	0.02	25	2	100	100
6	0.05	25	2.6	99	99
7	0.2	25	2	99	99
8	0.5	25	2.3	100	100

[a] Reaction conditions: **1a** (0.5 mmol), MnO_2 (0.5 mmol), TFA as solvent.
[b] Conversion and yield were determined by HPLC.

Various stilbenes were tested as substrates in intramolecular oxidative couplings using the optimized conditions to give the corresponding phenanthrenes (Table 3). Both *E*- and *Z*-stilbenes possessing an electron-withdrawing group at the double bond were found to react smoothly to give the corresponding coupled products in excellent yields (Table 3, entries 1–6). In addition, a large-scale reaction (50-fold scale) gave an identical result to that obtained from the small-scale procedure. Interestingly, oxidative coupling and dehydrogenation of **7a** was successfully achieved in one pot using two equivalents of manganese dioxide to give phenanthrene **1b** in 93% yield (Table 3, entry 7). By contrast, stilbene **8a** with no substituent on the aryl groups, and stilbene **9a** possessing an electron-withdrawing group on one of the aromatic rings did not give the corresponding coupled products (Table 3, entries 8 and 9).

We have also applied this approach to intermolecular biaryl coupling reactions (Table 4). Various 2-naphthols **10a–12a** reacted to give the corresponding 1,1′-binaphthols **10b–12b**, respectively (Table 4, entries 1–5). The use of methanesulfonic acid instead of trifluoroacetic acid resulted in increased yields of the coupled products (Table 4, entries 1–4). Simultaneous carbon–carbon and sulfur–sulfur bond formation in naphthalene-2-thiol (**13a**) was accomplished readily to give 3,4-dithia-dibenzo[*c*,*g*]phenanthrene (**13b**) in 76% yield (Table 4, entry 6). Naphthalen-2-amine (**14a**) was coupled using manganese dioxide to give 1,1′-binaphthyl-2,2′-diamine (**14b**) in 55% yield (Table 4, entry 7). A similar reaction of 3,4-dimethoxytoluene (**15a**) gave the coupled biphenyl **15b** in 56% yield (Table 4, entry 8). As a preliminary attempt to further the application of manganese dioxide, the coupling reaction of 2,6-di-*tert*-butylphenol (**16a**) was carried out to yield diphenoquinone **16b** in 88% yield (Table 4, entry 9), however, none of the expected biphenol was detected. This reaction would appear to be similar to the enzymatic reaction of laccase.[16]

Table 3 An Investigation of the Substrate Scope of the Intramolecular Oxidative Coupling Using MnO_2[a]

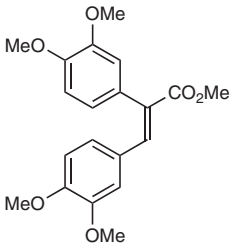
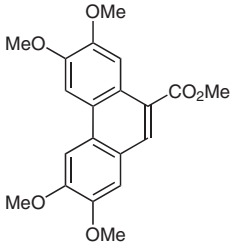
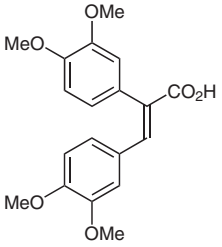
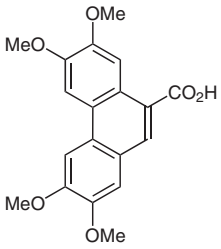
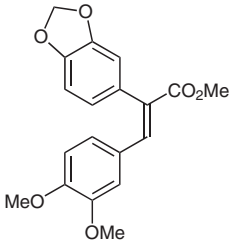
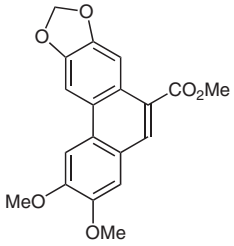
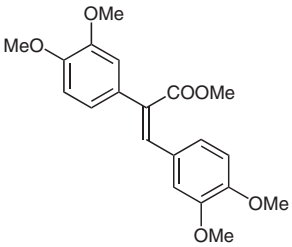
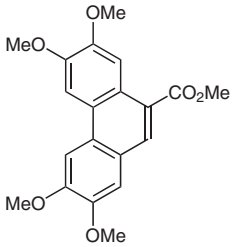
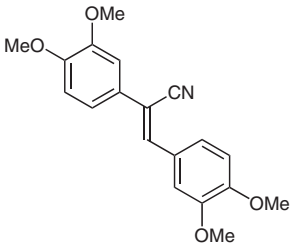
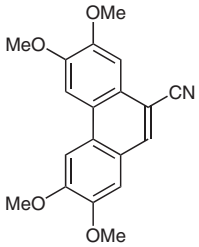
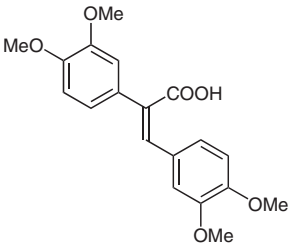
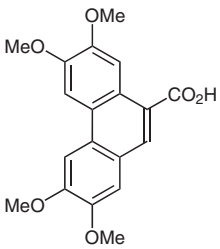
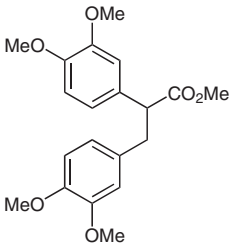
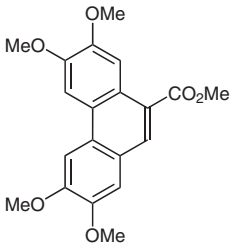
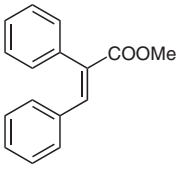
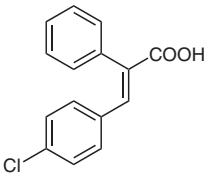
Entry	Substrate	Product	Time (h)	Conversion (%)[b]	Yield (%)[c]
1	**1a** 	**1b** 	2	100	98
2	**2a** 	**2b** 	8	100	94
3	**3a** 	**3b** 	2	97	95
4	**4a** 	**1b** 	2	99	98
5	**5a** 	**5b** 	12	99	91
6	**6a** 	**2b** 	6	100	95

Table 3 An Investigation of the Substrate Scope of the Intramolecular Oxidative Coupling Using MnO_2[a] (continued)

Entry	Substrate	Product	Time (h)	Conversion (%)[b]	Yield (%)[c]
7[d]	**7a** 	**1b** 	4.5	98	93
8	**8a** 	no product	6	0	0
9	**9a** 	no product	6	0	0

[a] MnO_2 (0.5 mmol).
[b] Conversion was determined by HPLC.
[c] Yield of isolated product.
[d] MnO_2 (1.0 mmol).

Table 4 An Investigation of the Substrate Scope of the Intermolecular Oxidative Coupling Using MnO_2[a]

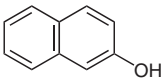
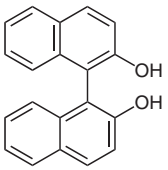
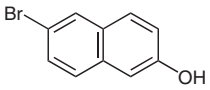
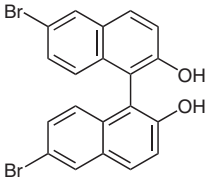
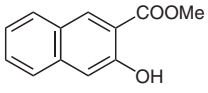
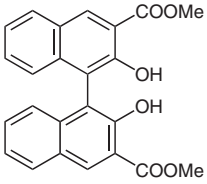
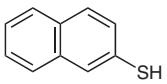
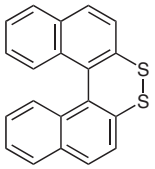
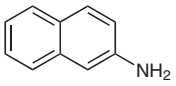
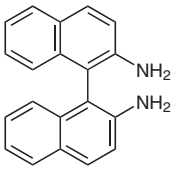
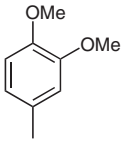
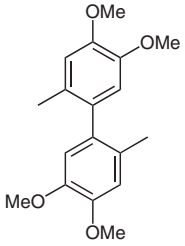
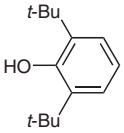
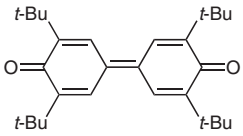
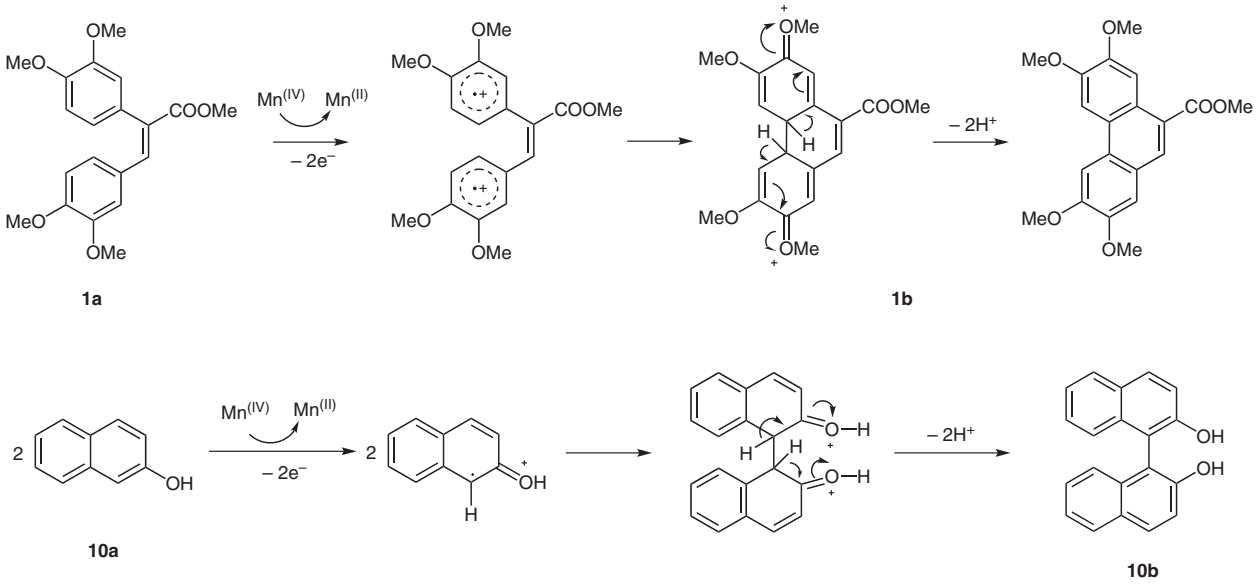
Entry	Substrate	Product	Time (h)	Conversion (%)[b]	Yield (%)[c]
1	**10a** 	**10b** 	5.5	100	56
2[d]			8	100	73
3	**11a** 	**11b** 	17	100	52
4[d]			17	100	64
5	**12a** 	**12b** 	9.5	100	55
6	**13a** 	**13b** 	24	100	76

Table 4 An Investigation of the Substrate Scope of the Intermolecular Oxidative Coupling Using MnO_2[a] (continued)

Entry	Substrate	Product	Time (h)	Conversion (%)[b]	Yield (%)[c]
7	**14a** 	**14b** 	24	100	55
8[e]	**15a** 	**15b** 	1.2	100	56
9[f]	**16a** 	**16b** 	8	100	88

[a] Reaction conditions: substrate (1 mmol), MnO_2 (1 mmol), TFA (10 mmol), CH_2Cl_2 (10 mL), r.t.
[b] Conversion was determined by HPLC.
[c] Yield of isolated product.
[d] MsOH (10 mmol) was used as the acid.
[e] Conversion was determined by GC.
[f] Conversion was determined by ^1H NMR spectroscopy.

No mechanism has yet been postulated for the above coupling reactions employing manganese dioxide, however, similar oxidants such as thallium trifluoroacetate[17] are believed to promote electron transfer and to form radical cations with electron-rich substrates. Taking substrates **1a** and **10a** as examples, the carbon–carbon bond formation could occur via coupling of a pair of radical cations (Scheme 1). Strong evidence for the formation of a bis-radical cation in similar species has been provided by anodic oxidation studies.[18] To further clarify the mechanism of the present manganese dioxide mediated oxidative coupling the electron spin resonance (ESR) spectrum was recorded for the coupling reaction of **1a**. As shown in Figure 1, a sharp signal at $g = 2.005$ was observed, which can be assigned to a bis-radical cation derived from **1a**. Stoichiometrically, one mole of manganese dioxide can



Scheme 1 Proposed mechanisms for the manganese dioxide mediated intra- and intermolecular oxidative coupling reactions

oxidize one mole of stilbene **1a** to give one mole of **1b**, showing that reduction of manganese dioxide is a two-electron transfer process. This was further confirmed by the ESR spectrum shown in Figure 1; the multiple peaks (A = 94 gauss) can be assigned to a manganese center. An acidic environment is required for the protonation of manganese dioxide and to increase its oxidative ability. Based on the above experimental results, we propose the reaction mechanism depicted in Scheme 1 for the present oxidative couplings.

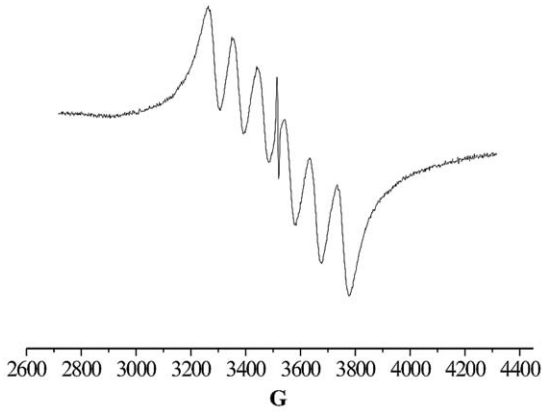


Figure 1 ESR spectrum of the manganese dioxide mediated oxidative coupling. Manganese dioxide (1 equiv) was treated with **1a** (0.5 mmol) in trifluoroacetic acid and the spectrum recorded after 45 minutes

In summary, we have developed manganese dioxide mediated intramolecular and intermolecular oxidative couplings of arenes. The mechanistic investigation suggests that the reaction probably proceeds via homolytic coupling of two radical species with manganese dioxide acting as a two-electron oxidant. The present system has the following advantages: (i) carbon–carbon bonds can be formed from arenes without prior functionalization, (ii) the coupling has been applied to both intramolecular and intermolecular reactions, (iii) the reaction conditions are mild and the work-up procedures are simple with high yields being obtained, (iv) the procedure can be scaled-up, and (v) manganese dioxide is a readily available oxidant. Further studies on the synthetic applications of this carbon–carbon bond forming reaction are in progress.

Melting points were determined on an X-4 binocular microscope melting point apparatus (Beijing Tech Instruments Co., Beijing, China) and are uncorrected. ^{1}H NMR spectra were obtained using Bruker AC-P 300 and Varian Mercury Plus 400 MHz spectrometers. Chemical shifts (δ) are given in ppm and are downfield with respect to the internal standard TMS. ^{13}C NMR spectra were recorded using Bruker AC-P 300 (at 75 MHz) or AV 400 (at 100 MHz) spectrometers with $CDCl_3$ as the solvent. Chemical shifts (δ) are reported in ppm with respect to the solvent peak (77.0 ppm). HRMS spectra were obtained using FT-ICR MS (Ionspec, 7.0T) instrumentation. Elemental analyses were determined on a Yanaco CHN Corder MT-3 elemental analyzer. GC spectra were obtained on an Agilent 6890N instrument. HPLC spectra were recorded using Agilent 1100 and Shimadzu LC-20AT instruments. The ESR spectrum was recorded on a Bruker EMX-6/1 instrument. All solvents were dried and purified by standard techniques prior to use. Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. MnO_2 (99% purity, 2 μm particle size, or powder) is commercially available from J & K Chemical Ltd or Alfa Aesar China (Tianjin Co., Ltd.), respectively, and was used without further purification. Column chromatography was carried out on 400–600 mesh silica gel (Qingdao Haiyang Chemical Co., Ltd., China). Substrates **10a–16a** were purchased from Alfa Aesar China (Tianjin Co., Ltd.). Substrates **1a–9a** were prepared according to the literature[6] and products **1b**, **2b**, **5b**, **10b–12b** and **14b–16b** were identified by comparison of their melting points and ^{1}H NMR spectroscopic data with those reported in the literature (see characterization data for references).

Perkin Condensation; Typical Procedure

(3,4-Dimethoxyphenyl)acetic acid (98.0 g, 0.5 mol), 3,4-dimethoxybenzaldehyde (90.0 g, 0.54 mol), Ac_2O (200 mL) and Et_3N (100 mL) were heated at reflux for 20 h with the exclusion of moisture. The soln was allowed to cool to r.t., H_2O (400 mL) was added, and the mixture was stirred for 1 h. The reaction mixture was poured into aq K_2CO_3 soln (350.0 g in 800 mL of H_2O) and heated at reflux until nearly all the gummy material had dissolved. The soln was cooled, extracted with Et_2O (3 × 120 mL), and carefully acidified with concd HCl (pH 4–5) to produce a white precipitate. The solid was collected and recrystallized from MeOH to give acid **2a**.

(2*E*)-2,3-Bis(3,4-dimethoxyphenyl)acrylic Acid (2a)

White solid; yield: 118.7 g (69%); mp 214–216 °C (Lit.[19] mp 216–217 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.50 (br s, 1 H), 7.68 (s, 1 H), 6.98–6.54 (m, 6 H), 3.74 (s, 3 H), 3.69 (s, 3 H), 3.66 (s, 3 H), 3.45 (s, 3 H).

Methyl (2*E*)-2,3-Bis(3,4-dimethoxyphenyl)acrylate (1a)

2,3-Bis(3,4-dimethoxyphenyl)acrylic acid **2a** (3.44 g, 10.0 mmol) was dissolved in a solution of 1.5% concd H_2SO_4 in anhyd MeOH (150 mL), and the resulting solution was heated to reflux for 10 h. After evaporating the solvent under reduced pressure, $CHCl_3$ (100 mL) and H_2O (50 mL) were added to the residual oil. The mixture was washed with 10% $NaHCO_3$ (50 mL), H_2O (40 mL), and brine, and dried over Na_2SO_4. The solvent was evaporated to afford the crude product which was recrystallized from EtOH to give **1a**.

White solid; yield: 3.29 g (92%); mp 127–128 °C (Lit.[8b] mp 127–128 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (s, 1 H), 6.91 (d, $^3J_{HH}$ = 8.0 Hz, 1 H), 6.81 (d, $^4J_{HH}$ = 2.0 Hz, 1 H), 6.80 (d, $^4J_{HH}$ = 1.6 Hz, 1 H), 6.76 (d, $^4J_{HH}$ = 1.6 Hz, 1 H), 6.71 (d, $^3J_{HH}$ = 8.4 Hz, 1 H), 6.51 (d, $^4J_{HH}$ = 2.0 Hz, 1 H), 3.89 (s, 3 H), 3.84 (s, 3 H), 3.81 (s, 3 H), 3.79 (s, 3 H), 3.48 (s, 3 H).

Methyl (2*E*)-2-(1,3-Benzodioxol-5-yl)-3-(3,4-dimethoxyphenyl)acrylate (3a)

White solid; yield: 68%; mp 101–103 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (s, 1 H), 6.87–6.83 (m, 2 H), 6.75–6.72 (m, 3 H), 6.55 (d, $^4J_{HH}$ = 1.6 Hz, 1 H), 5.98 (s, 2 H), 3.86 (s, 3 H), 3.79 (s, 3 H), 3.54 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 150.0, 148.2, 148.0, 147.1, 140.7, 129.9, 129.5, 127.3, 125.4, 123.4, 112.5, 110.5, 110.4, 108.9, 101.1, 55.8, 55.2, 52.4.

HRMS (ESI): *m/z* calcd for $C_{19}H_{18}O_6Na$: 365.0996; found: 365.0993.

Methyl (2*E*)-2,3-Diphenylacrylate (8a)
White solid; yield: 60%; mp 76–77 °C (Lit.[8b] mp 76–77 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1 H), 7.38–7.35 (m, 3 H), 7.23–7.14 (m, 5 H), 7.04–7.02 (m, 2 H), 3.79 (s, 3 H).

(2*E*)-3-(4-Chlorophenyl)-2-phenylacrylic Acid (9a)
White solid; yield: 60%; mp 207–209 °C (Lit.[20] mp 210–211 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.79 (s, 1 H), 7.73 (s, 1 H), 7.38–7.03 (m, 9 H).

(2*Z*)-2,3-Bis(3,4-dimethoxyphenyl)acrylic Acid (6a)
The same procedure as that used for the synthesis of **2a** was followed, except in the last step the aq layer was acidified carefully with concd HCl (pH 5) to afford a precipitate of **2a** as the major product which was obtained in 69% yield after filtration. The filtrate was acidified with concd HCl (pH 3) to afford (*Z*)-2,3-bis(3,4-dimethoxyphenyl)acrylic acid (**6a**) as a precipitate. Recrystallization from a mixture of PE–EtOAc afforded pure **6a**.

White solid; yield: 15%; mp 170–171 °C (Lit.[21] mp 170–171 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06–7.01 (m, 4 H), 6.95 (s, 1 H), 6.90–6.84 (m, 2 H), 3.92 (s, 3 H), 3.91 (s, 3 H), 3.90 (s, 3 H), 3.86 (s, 3 H).

Methyl (2*Z*)-2,3-Bis(3,4-dimethoxyphenyl)acrylate (4a)
To a stirred solution of stilbene **6a** (1.72 g, 5 mmol) in CH_2Cl_2 was added ethereal diazomethane at 0 °C until the substrate **6a** had disappeared, as indicated by TLC; the mixture was stirred at r.t. for an additional 1 h. The solvent was allowed to evaporate and the residue was recrystallized from a mixture of PE–EtOAc to afford methyl ester **4a**.

White solid; yield: 1.54 g (86%); mp 148–149 °C (Lit.[21] mp 148 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.99–6.94 (m, 4 H), 6.89–6.84 (m, 3 H), 3.92 (s, 3 H), 3.90 (s, 6 H), 3.88 (s, 3 H), 3.81 (s, 3 H).

(2*Z*)-2,3-Bis(3,4-dimethoxyphenyl)acrylonitrile (5a)
Compound **5a** was prepared according to a literature procedure.[22]

Yellow solid; yield: 96%; mp 151–152 °C (Lit.[22] mp 154–155 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (s, 1 H), 7.37–7.34 (m, 2 H), 7.24 (d, $^3J_{HH}$ = 8.4 Hz, 1 H), 7.13 (s, 1 H), 6.94–6.90 (m, 2 H), 3.98 (s, 3 H), 3.97 (s, 3 H), 3.95 (s, 3 H), 3.93 (s, 3 H).

Methyl 2,3-Bis(3,4-dimethoxyphenyl)propanoate (7a)
Methyl (2*E*)-2,3-bis(3,4-dimethoxyphenyl)acrylate (**1a**) (358 mg, 1 mmol) was dissolved in EtOH (200 mL) and 10% Pd/C (100 mg) was added. H_2 gas was bubbled through the soln which was stirred for 3 h. The catalyst was removed by filtration and the filtrate was concd in vacuo to afford pure **7a**.

White solid; yield: 96%; mp 100–101 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.83–6.79 (m, 3 H), 6.74 (d, $^3J_{HH}$ = 8.4 Hz, 1 H), 6.65 (d, $^3J_{HH}$ = 8.0 Hz, 1 H), 6.60 (s, 1 H), 3.87 (s, 3 H), 3.86 (s, 3 H), 3.84 (s, 3 H), 3.80 (s, 3 H), 3.74 (t, $^3J_{HH}$ = 7.6 Hz, 1 H), 3.62 (s, 3 H), 3.32 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 8.4 Hz, 1 H), 2.95 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 6.9 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.1, 149.0, 148.6, 148.3, 147.5, 131.6, 131.1, 120.9, 120.3, 112.2, 111.1, 111.1, 111.0, 55.9, 55.8, 55.7, 53.3, 52.0, 39.6.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{24}O_6Na$: 383.1463; found: 383.1468.

Intramolecular Oxidative Coupling; Typical Procedure
To a soln of **1a** (179 mg, 0.5 mmol) in TFA (5.0 mL) was added MnO_2 (44.4 mg, 0.5 mmol) and the reaction mixture was stirred at r.t. for 2 h. The mixture was diluted with CH_2Cl_2 (50 mL) and H_2O (20 mL). The organic phase was washed with H_2O (3 × 20 mL), dried over $MgSO_4$, filtered, and concd in vacuo to yield pure **1b** (as determined by HPLC analysis).

Methyl 2,3,6,7-Tetramethoxyphenanthrene-9-carboxylate (1b)
White solid; yield: 98%; mp 202–203 °C (Lit.[8e] mp 202–204 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 1 H), 8.43 (s, 1 H), 7.81 (s, 1 H), 7.77 (s, 1 H), 7.27 (s, 1 H), 4.14 (s, 3 H), 4.13 (s, 3 H), 4.08 (s, 3 H), 4.04 (s, 3 H), 4.02 (s, 3 H).

2,3,6,7-Tetramethoxyphenanthrene-9-carboxylic Acid (2b)
White solid; yield: 94%; mp 285–287 °C (Lit.[23] mp 280–282 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.87 (br s, 1 H), 8.53 (s, 1 H), 8.40 (s, 1 H), 8.03 (s, 1 H), 7.99 (s, 1 H), 7.55 (s, 1 H), 4.04 (s, 3 H), 4.03 (s, 3 H), 3.89 (s, 3 H), 3.87 (s, 3 H).

Methyl 2,3-Dimethoxyphenanthro[2,3-*d*][1,3]dioxole-6-oate (3b)
White solid; yield: 95%; mp 209–210 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (s, 1 H), 8.36 (s, 1 H), 7.87 (s, 1 H), 7.72 (s, 1 H), 7.24 (s, 1 H), 6.12 (s, 2 H), 4.12 (s, 3 H), 4.03 (s, 3 H), 4.01 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 151.1, 149.0, 147.8, 147.7, 130.0, 127.3, 126.6, 125.1, 124.5, 123.1, 108.8, 104.4, 102.5, 101.5, 100.1, 56.0, 55.9, 52.1.

Anal. Calcd for $C_{19}H_{16}O_6$: C, 67.05; H, 4.74. Found: C, 66.98; H, 4.60.

2,3,6,7-Tetramethoxyphenanthrene-9-carbonitrile (5b)
Yellow solid; yield: 91%; mp 266–268 °C (Lit.[22] mp 267–269 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.78 (s, 1 H), 7.75 (s, 1 H), 7.57 (s, 1 H), 7.22 (s, 1 H), 4.15 (s, 3 H), 4.14 (s, 3 H), 4.10 (s, 3 H), 4.05 (s, 3 H).

Intermolecular Oxidative Coupling; Typical Procedure
To a soln of **10a** (144 mg, 1.0 mmol) in CH_2Cl_2 (10.0 mL) at r.t. was added MnO_2 (88.9 mg, 1.0 mmol) and TFA (1.14 g, 10.0 mmol). The mixture was stirred at r.t. for 5.5 h and then diluted with CH_2Cl_2 (50 mL) followed by H_2O (20 mL). The organic phase was washed with H_2O (3 × 20 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel (PE–EtOAc, 2:1) to give product **10b**.

1,1′-Binaphthalene-2,2′-diol (10b)
White solid; yield: 56%; mp 216–218 °C (Lit.[24] mp 217–218 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 1 H), 7.95 (s, 1 H), 7.90 (s, 1 H), 7.89 (s, 1 H), 7.40–7.36 (m, 4 H), 7.33–7.29 (m, 2 H), 7.17 (s, 1 H), 7.15 (s, 1 H), 5.06 (s, 2 H).

6,6′-Dibromo-1,1′-binaphthalene-2,2′-diol (11b)
White solid; yield: 52%; mp 200–202 °C (Lit.[25] mp 197–198 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 2 H), 7.90 (s, 1 H), 7.88 (s, 1 H), 7.40–7.36 (m, 4 H), 6.97 (s, 1 H), 6.95 (s, 1 H), 5.04 (s, 2 H).

Dimethyl 2,2′-Dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate (12b)
White solid; yield: 55%; mp 285–287 °C (Lit.[26] mp 280–283 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.73 (s, 2 H), 8.70 (s, 2 H), 7.94–7.91 (m, 2 H), 7.36–7.33 (m, 4 H), 7.18–7.15 (m, 2 H), 4.06 (s, 6 H).

3,4-Dithia-dibenzo[*c*,*g*]phenanthrene (13b)
Light-yellow solid; yield: 76%; mp 180–181 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 1 H), 8.50 (s, 1 H), 7.85 (s, 1 H), 7.83 (s, 1 H), 7.76–7.74 (m, 2 H), 7.67–7.59 (m, 4 H), 7.53–7.50 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.0, 133.3, 133.0, 132.0, 128.4, 127.8, 127.1, 126.5, 126.4, 124.4.

Anal. Calcd for $C_{20}H_{12}S_2$: C, 75.91; H, 3.82. Found: C, 76.11; H, 3.72.

1,1′-Binaphthalene-2,2′-diamine (14b)
Brown solid; yield: 55%; mp 190–192 °C (Lit.[27] mp 189–191 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.78 (m, 4 H), 7.25–7.06 (m, 8 H), 3.88–2.56 (br s, 4 H).

4,4′,5,5′-Tetramethoxy-2,2′-dimethylbiphenyl (15b)
White solid; yield: 56%; mp 121–122 °C (Lit.[28] mp 121–122 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (s, 2 H), 6.65 (s, 2 H), 3.91 (s, 6 H), 3.83 (s, 6 H), 2.02 (s, 6 H).

3,3′,5,5′-Tetra-*tert*-butyl-1,1′-bi(cyclohexa-2,5-dien-1-ylidene)-4,4′-dione (16b)
Red solid; yield: 88%; mp 244–246 °C (Lit.[29] mp 246 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 4 H), 1.37 (s, 36 H).

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