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Direct One-Pot Synthesis of Phenanthrenes via Suzuki−Miyaura Coupling/Aldol Condensation Cascade Reaction

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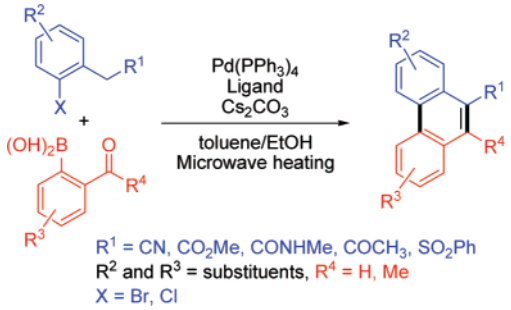

We have developed an efficient cascade reaction, a Suzuki−Miyaura coupling followed by an aldol condensation, for the construction of phenanthrene derivatives using microwave irradiation. For example, the reaction of methyl 2-bromophenylacetamide with 2-formylphenylboronic acid in the presence of a palladium catalyst and a base provided a biaryl intermediate, which underwent in situ cyclization to afford the corresponding phenanthrene in high yield.

Introduction

Phenanthrenes belong to an important skeleton of organic compounds due to their core structure in natural products[1] and interesting biological activities such as antimalarial,[2] anticancer,[3] and emetic activity.[4] They also serve as a common structural motif in materials science based on their photoconducting, photochemical, and electroluminescent properties.[5] For the last several decades, much attention has focused on the development of synthetic methods for the construction of phenanthrene derivatives. These strategies can be divided into three classes that depend upon the order in which the central ring is connected as shown in Figure 1. First, most classical approaches to phenanthrenes require the preparation of a stilbene followed by an intramolecular cyclization via aryl−aryl bond formation such as photocyclization,[6] the Pschorr reaction,[7] and oxidative[8] and radical[9] reactions (connection B and then A). Second, the reverse approaches have also been studied considerably (connection A

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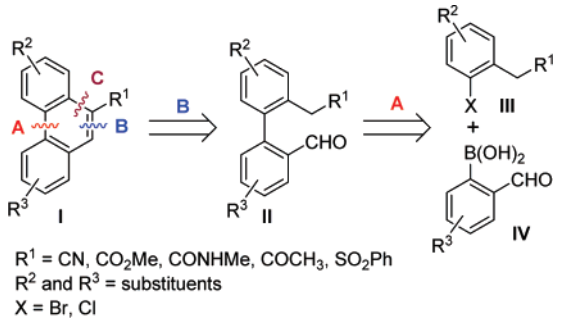
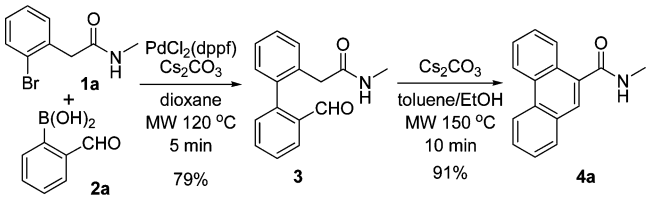


FIGURE 1. Strategy for the construction of phenanthrenes.

then B). Among them, the Suzuki−Miyaura reaction[10] is most frequently utilized in combination with various intramolecular cyclization methods including directed ortho and remote metalation,[11] ring-closing metathesis,[12] and DDQ oxidation.[13] Other examples include Ullman coupling/McMurry cyclization,[14] a Fridel−Crafts-type reaction with quinone/base-mediated condensation,[15] and siloxane coupling/Friedel−Crafts coupling.[16] Third, there are more direct approaches to phenanthrenes based on the metal-induced carbocyclization of alkynylated biaryl derivatives[17] and metal-catalyzed cyclotrimerization of arynes[18] (connection A to C). Despite these advances, there is still demand for methods with improved yields and greater diversity of substituents for the synthesis of highly functionalized phenanthrene derivatives. Thus, we have designed a two-step sequence, Suzuki−Miyaura coupling of **III** with **IV** followed by intramolecular aldol-type condenstion of **II**, for the rapid access of phenanthrenes **I** under microwave irradiation (Figure 1).[19] For feasible aldol condensation and aromatization of **II**, we thought that nitrile, ketone, ester, amide, and sulfone groups would be useful as activating partners.

SCHEME 1. Two-Step Approach to Phenanthrene



Results and Discussion

Two-Step Sequence for the Synthesis of Phenanthrene. To verify our synthetic strategy, we carried out the Suzuki−Miyaura coupling reaction using methods previously developed in our laboratory.[20] Coupling of 2-bromophenylacetamide **1a**[21] with 2-formylphenylboronic acid (**2a**) in the presence of a Pd catalyst provided biaryl **3** in 79% yield (Scheme 1).[22] In this reaction, we observed little or no phenanthrene **4a** based on GC/MS analysis. Then, we attempted the intramolecular aldol-type cyclization under mild basic conditions (Cs_2CO_3) at a higher temperature (150 °C) using microwave heating. This operation successfully afforded the desired phenanthrene **4a** in excellent yield.

Direct One-Pot Synthesis of Phenanthrenes. Having demonstrated the synthesis of phenanthrene **4a**, we envisioned that a cascade reaction of Suzuki−Miyaura coupling/aldol-type condensation in one pot might be possible through a suitable catalyst and base system. The results are illustrated in Table 1. We initially ran the reaction at higher temperature (150 °C) for an extended time period (10 min). In this case, we were able to obtain phenanthrene **4a**, although the reaction yield was very low (entry 1 in Table 1). With the use of $Pd(PPh_3)_4$ as a palladium source, the reaction proceeded in improved 13% yield (entry 2 in Table 1).

Since aldol condensation with inorganic bases requires polar reaction media,[23] we decided to use a protic solvent environment. Reaction in dioxane/H_2O, however, provided no desired product as well as a lower coupling yield (entry 3 in Table 1). We were pleased to find that the reaction in toluene/EtOH (2:1 v/v) provided the phenanthrene **4a** in excellent yield with complete consumption of biphenyl intermediate **3** (entry 4 in Table 1).[24] We next examined temperature and base effects, but the reaction yields were inferior to those of the previous reaction (entries 5−8 in Table 1). Additionally, we observed

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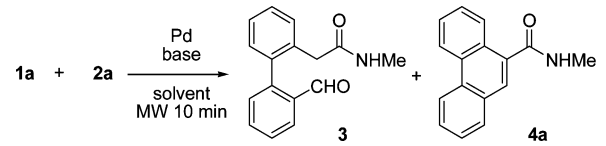
TABLE 1. Synthesis of Phenanthrene via Suzuki−Miyaura Coupling/Aldol Condensation Cascade Reaction[a]



entry	Pd	base	solvents	temp (°C)	yield (%)[b] 3	4a
1	$Pd(PPh_3)_2Cl_2$	Cs_2CO_3	dioxane	150	63	3
2	$Pd(PPh_3)_4$	Cs_2CO_3	dioxane	150	53	13
3	$Pd(PPh_3)_4$	Cs_2CO_3	dioxane/H_2O[c]	150	27	0
4	**$Pd(PPh_3)_4$**	**Cs_2CO_3**	**toluene/EtOH[d]**	**150**	**0**	**87**
5	$Pd(PPh_3)_4$	Cs_2CO_3	toluene/EtOH[d]	130	0	83
6	$Pd(PPh_3)_2Cl_2$	Cs_2CO_3	toluene/EtOH[d]	150	0	75
7	$Pd(PPh_3)_4$	Na_2CO_3	toluene/EtOH[d]	150	30	0
8	$Pd(PPh_3)_4$	K_3PO_4	toluene/EtOH[d]	150	17	27
9	$Pd(PPh_3)_4$	Cs_2CO_3	toluene/EtOH[d]	150[e]	0	81

[a] Reaction conditions: aryl bromide **1a** (0.5 mmol), boronic acid **2a** (0.6 mmol, 1.2 equiv), Pd (4 mol %), base (1.5 mmol), solvents (3 mL), MW, 10 min. [b] Isolated yield. [c] Dioxane/H_2O = 9:1. [d] Toluene/EtOH = 2:1. [e] Oil bath heating, 2 h.

TABLE 2. Solvent Effects: Reaction of 1a with 2a[a]

entry	ratio (toluene/EtOH)	GC yields (%) 3	4a
1	9:1	69	16
2	4:1	0	84 (71)[b]
3	2:1	0	87[b]
4	1:1	0	73

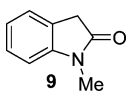
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (4 mol %), Cs_2CO_3 (1.5 mmol), solvents (3 mL), MW 150 °C, 10 min. [b] Isolated yields.

that the thermal reaction in an oil bath for 2 h smoothly proceeded to furnish the phenanthrene **4a** in 81% yield (entry 9 in Table 1).

The ratio of toluene/EtOH is crucial for achieving high yields of the phenanthrene. As illustrated in Table 2, we examined various ratios of toluene and ethanol (9:1, 4:1, 2:1, and 1:1). When a larger proportion of toluene was used, the reaction was less effective for the aldol condensation (entry 1 in Table 2). On the contrary, increasing amounts of ethanol equal to toluene (1:1) resulted in loss of reaction yield (entry 4 in Table 2). We found that the optimum ratio was 2:1 (entry 3 in Table 2).

To study the scope and limitations of the cascade reaction, we examined a variety of aryl halides with substituted 2-formylphenylboronic acids (Table 3).[25] Reactions of an aryl bromide possessing an amide or ester moiety with boronic acids provided the corresponding phenanthrenes in good yields. In the case of methyl ester **1e**, however, transesterification with ethanol occurred significantly. Decreasing the reaction temperature to 130 °C reduced transesterification (entry 6 in Table 3).

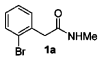
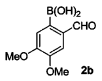
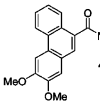
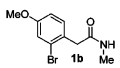
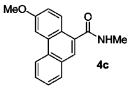
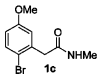
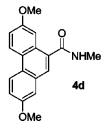
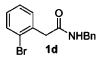
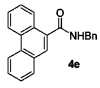
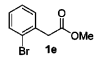
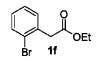
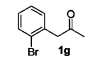
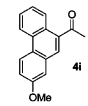
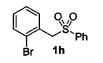
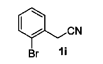
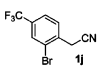
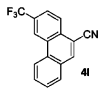
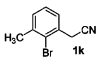
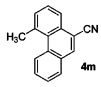
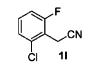
(24) On the basis of GC/MS analysis, we observed that dehalogenated product was obtained as a major side product (~5%) and that intramolecular cyclization product **9** was not detected under these conditions, see: Yang, B. H.; Buchwald, S. L. *Org. Lett.* **1999**, *1*, 35−38.



9

(25) In cases of aryl bromides such as 2-bromobenzyl methyl ether and *N*-(2-bromobenzyl)acetamide, we failed to obtain the corresponding phenanthrenes.

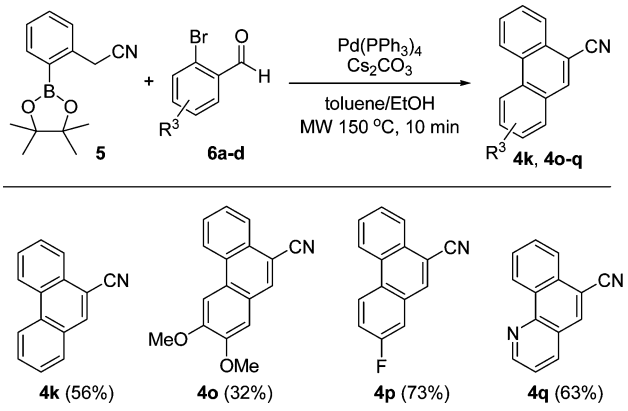
TABLE 3. Synthesis of Phenanthrene Derivatives[a]

entry	aryl halide	boronic acid	product	yield[b] (%)
1				87
2	**1a**			80
3		**2a**		86
4				58
5		**2a**		73
6		**2a**		57[c]
7		**2a**		87[d]
8		**2a**		72
9	**1g**	**2c**		66
10		**2a**		85
11		**2a**		83
12		**2a**		90
13		**2a**		56[e]
14		**2a**		80[e]

[a] Reaction conditions: aryl halide (0.5 mmol), boronic acid (0.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (4 mol %), Cs_2CO_3 (1.5 mmol), toluene/EtOH (2 mL/1 mL), MW 150 °C, 10 min. [b] Isolated yield. [c] MW 130 °C, 10 min, **4g** was isolated (18%). [d] DavePhos (6 mol %) was added, MW 120 °C, 5 min → MW 150 °C, 10 min. [e] SPhos (6 mol %) was added.

When ethyl ester **1f** was used, the phenanthrene ethyl ester **4g** was obtained in excellent yield (entry 7 in Table 3). The coupling of 2-bromoacetophenone (**1g**) with boronic acids

SCHEME 2. Synthesis of Phenanthrene Using Arylboronate

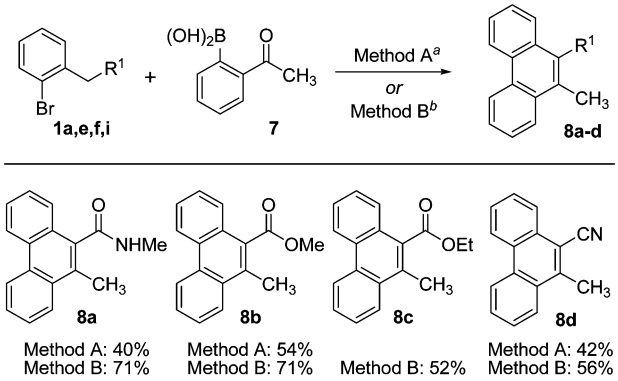


provided phenanthrenes in good yields (entries 8−9 in Table 3). Phenyl sulfone **1h** also proved to be an excellent coupling partner in this type of cascade reaction, with 85% yield (entry 10 in Table 3). Additionally, efficient cascade reactions of phenylacetonitriles **1i**−**l** with 2-formylphenylboronic acid were achieved (entries 11−14 in Table 3). In the case of aryl bromide **1k**,[26] having the hindered *o*-methyl group, we were able to obtain 5-methylphenanthrene **4m** in moderate yield (entry 13 in Table 3). Importantly, **1l** having the chloride moiety also served as a good Suzuki−Miyaura coupling partner, in the presence of additional SPhos ligand,[27] to provide phenanthrene **4n** in 80% yield (entry 14).

Reverse Approach Using Boronate Ester. Despite the successful utilization of the cascade reaction, limitations still exist. For example, *o*-formylphenylboronic acids **2** are difficult to synthesize.[28] We recognized that this drawback could be overcome by the use of boronate ester **5**[29] and 2-haloaryl carboxaldehyde counterparts **6**, which are commercially available (Scheme 2). The cascade reaction of pinacol boronate ester **5** with 2-bromobenzaldehyde (**6a**) under the same conditions afforded the phenanthrene **4k** in slightly lower yield than that of aryl bromide **1i** with boronic acid **2a**. Additionally, with the use of 2-bromo-4,5-dimethoxybenzaldehyde (**6b**) possessing electron-donating groups, the cascade reaction of **5** proceeded sluggishly. On the other hand, 2-bromo-5-fluorobenzaldehyde (**6c**), which contains an electron-withdrawing group, afforded the phenanthrene **4p** in 73% yield. Furthermore, this strategy employing a boronate ester allowed the use of heteroaryl carboxaldehydes such as 2-bromonicotinaldehyde (**6d**) for the synthesis of benzoquinoline **4q** in good yield.

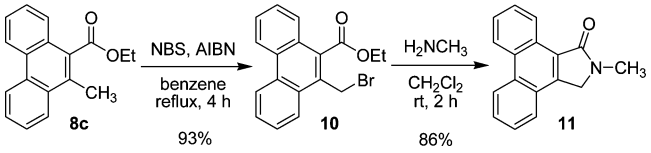
Synthesis of 10-Methylphenanthrenes. To further challenge the scope of the cascade reaction, we employed 2-acetylphenylboronic acid **7**, which contains a ketone as an aldol acceptor (Scheme 3). Using the previously optimized conditions (method A), we obtained the desired product **8a** only in 40% yield. In this result, we believe that the primary factor affecting the reaction yield of phenanthrene is the efficiency of the Suzuki−Miyaura coupling. After screening a number of reaction

SCHEME 3. Synthesis of Phenanthrene Using 2-Acetylphenylboronic Acid



[a] Method A: aryl halide (0.5 mmol), **7** (0.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (4 mol %), Cs_2CO_3 (1.5 mmol), toluene/EtOH (2 mL/1 mL), MW 150 °C, 10 min. [b] Method B: Method A + DavePhos (6 mol %), MW 120 °C, 5 min → MW 150 °C, 10 min.

SCHEME 4. Synthesis of Phenanthrene Lactam



conditions,[30] we found that additional DavePhos ligand (6 mol %) and lower reaction temperature (120 °C) for the Suzuki−Miyaura coupling step resulted in an improved 71% yield (method B). In addition, the cascade reactions of **1e**, **1f**, and **1i** also afforded the corresponding phenanthrenes **8b**, **8c**, and **8d** in 71, 52, and 56% yields, respectively.

Synthesis of Phenanthrene Excimer. Finally, we utilized our approach for the synthesis of a fluorescent excimer **11**, which was previously reported by the Lewis group.[5a] Retrosynthetically, we have envisioned the synthesis starting from 10-methylphenanthrene ethyl ester **8c**. As shown in Scheme 4, phenanthrene **8c** was treated with NBS/AIBN to afford methyl bromide **10** in 93% yield. Subsequent lactamization of **10** using methyl amine furnished phenanthrene lactam **11** in excellent yield. This protocol can be applied to the synthesis of novel fluorescent phenanthrene excimers.

Conclusion

In summary, we have demonstrated that a one-pot cascade reaction of Suzuki−Miyaura coupling/aldol condensation can be a mild, simple, and efficient method for the synthesis of highly functionalized phenanthrenes. This one-pot method has also proved to be a robust and rapid route to construct a central ring of phenanthrenes from readily available ortho substituted aryl bromides and *o*-formyl- or *o*-acetyl-arylboronic acids. Furthermore, applications of this protocol toward the total synthesis of natural products and polycyclic aromatic compounds will be reported in due course.

Experimental Section

2-(2′-Formylbiphenyl-2-yl)-*N*-methylacetamide (3). To a solution of aryl bromide **1a** (114 mg, 0.5 mmol) in 3 mL of dioxane was added boronic acid **2a** (90 mg, 0.6 mmol), $Pd(PPh_3)_2Cl_2$ (14

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(27) (a) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685−4696. (b) Billingsley, K. Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358−3366.

(28) (a) Geen, G. R.; Mann, I. S.; Mullane, M. V.; McKillop, A. *Tetrahedron* **1998**, *54*, 9875−9894. (b) Hall, D. G. *Boronic Acids*; Wiley-VCH: Weinheim, Germany, 2005.

(29) Baudoin, O.; Guénard, D.; Guéritte, F. *J. Org. Chem.* **2000**, *65*, 9268−9271.

(30) We have evaluated reaction conditions using a variety of palladium sources ($Pd(PPh_3)_4$, $Pd(OAc)_2$, and $PdCl_2$) and ligands (DavePhos, XPhos, and SPhos).

mg, 4 mol %), and Cs_2CO_3 (489 mg, 1.5 mmol). The mixture was irradiated at 120 °C for 5 min using a microwave reactor and cooled to room temperature. The mixture was diluted with EtOAc and filtered through a short Celite pad. The solution was concentrated in vacuo and purified by flash column chromatography (10% → 50% EtOAc/hexanes) to provide biphenyl **3** (101 mg, 79%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.00 (dd, 1H, J = 7.6, 1.2 Hz), 7.63 (td, 1H, J = 7.4, 1.5 Hz), 7.54 (td, 1H, J = 7.6, 0.6 Hz), 7.46−7.20 (m, 5H), 5.29 (bs, 1H), 3.43 (d, A of ABq, 2H, J = 15.9 Hz), 3.34 (d, B of ABq, 2H, J = 15.9 Hz), 2.63 (d, 3H, J = 4.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2, 171.0, 143.9, 138.6, 134.2, 133.9, 133.6, 131.2, 131.0, 130.9, 129.1, 129.0, 128.6, 127.4, 41.5, 26.6; IR (neat) 3305, 1691, 1644, 1254 cm^{-1}; MS (EI) *m*/*z* 253 (M^+, 2), 235 (22), 195 (33), 181 (16), 178 (34), 165 (100), 152 (42), 139 (16), 115 (13); HRMS (EI) calcd for $C_{16}H_{15}NO_2$ [M^+] 253.1103, found 253.1128.

***N*-Methylphenanthrene-9-carboxamide (4a).** To a solution of biphenyl **3** (100 mg, 0.4 mmol) in toluene/EtOH (2 mL/1 mL) was added Cs_2CO_3 (390 mg, 1.2 mmol). The suspension was irradiated at 150 °C for 10 min using a microwave reactor and cooled to room temperature. The mixture was diluted with EtOAc and filtered through a short Celite pad. The solution was concentrated in vacuo, and the residue was purified by silica gel flash column chromatography (10% → 50% EtOAc/hexanes) to afford phenanthrene **4a** (86 mg, 91%) as a white solid: mp 160 °C (lit.[5b] 191−192 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73−8.67 (m, 2H), 8.35−8.31 (m, 1H), 7.89 (dd, 2H, J = 3.8, 1.4 Hz), 7.86−7.59 (m, 4H), 6.09 (bs, 1H), 3.13 (d, 1H, J = 4.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 133.8, 131.2, 130.8, 130.6, 129.3, 128.8, 128.1, 127.4, 127.3, 127.2, 126.5, 126.4, 123.1, 122.9, 27.7; IR (neat) 3272, 1631, 1548, 1320 cm^{-1}; MS (EI) *m*/*z* 235 (M^+, 100), 234 (11), 206 (11), 205 (79), 178 (13), 177 (79), 176 (51), 151 (22), 150 (20); HRMS (EI) calcd for $C_{16}H_{13}NO$ [M^+] 235.0997, found 235.0993.

Typical Procedure for Direct One-Pot Synthesis of Phenanthrenes. Method A: to a thick-well borosilicate glass vial (3 mL) was added aryl bromide (0.5 mmol), boronic acid (0.6 mmol), Pd(PPh_3)$_4$ (4 mol %), and Cs_2CO_3 (1.5 mmol) sequentially. The mixture was suspended in toluene/EtOH (2 mL/1 mL). Then, the reaction vial was sealed and placed into a microwave reactor and irradiated at 150 °C for 10 min (Usually, the average microwave power ranged from 60 to 80 W and the internal pressure was 6−8 bar). After being cooled to room temperature, the mixture was diluted with EtOAc and filtered through a short Celite pad. The solution was concentrated in vacuo, and the residue was purified by silica gel flash column chromatography (EtOAc/hexanes) to afford a phenanthrene product.

2,3-Dimethoxy-*N*-methylphenanthrene-9-carboxamide (4b). Yield 80%, white solid, mp 198∼200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, 1H, J = 7.7 Hz), 8.31 (d, 1H, J = 8.1 Hz), 7.92 (d, 1H, J = 2.2 Hz), 7.73 (d, 1H, J = 3.0 Hz), 7.66−7.53 (m, 2H), 7.14 (d, 1H, J = 3.5 Hz), 6.16 (s, 1H), 4.10 (s, 3H), 3.99 (s, 3H), 3.11 (d, 3H, J = 4.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 150.0, 149.3, 131.5, 129.9, 127.9, 126.6, 126.4, 126.1, 125.7, 125.5, 125.3, 122.3, 108.5, 103.0, 56.0, 55.9, 26.9; IR (neat) 3377, 1660, 1504, 1464, 1435, 1249, 1151 cm^{-1}; MS (EI) *m*/*z* 296 (22), 295 (M^+, 100), 265 (74), 207 (11), 165 (11), 151 (14); HRMS (EI) calcd for $C_{18}H_{17}NO_3$ [M^+] 295.1208, found 295.1214.

6-Methoxy-*N*-methylphenanthrene-9-carboxamide (4c). Yield 86%, white solid, mp 166∼168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, 1H, J = 8.1 Hz), 8.27 (d, 1H, J = 9.1 Hz), 8.05 (d, 1H, J = 2.5 Hz), 7.85 (dd, 1H, J = 6.7, 3.7 Hz), 7.71−7.57 (m, 3H), 7.26 (dd, 1H, J = 9.0, 2.5 Hz), 6.16 (bs, 1H), 4.02 (s, 3H), 3.11 (d, 3H, J = 4.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 158.7, 133.4, 132.3, 130.9, 129.2, 128.0, 127.5, 127.4, 127.2, 124.0, 123.3, 122.8, 116.9, 55.6, 26.9; IR (neat) 3281, 2835, 1620, 1530, 1234 cm^{-1}; MS (EI) *m*/*z* 265 (M^+, 100), 235 (78), 207 (58), 163 (61), 125 (11); HRMS (EI) calcd for $C_{17}H_{15}NO_2$ [M^+] 265.1103, found 265.1097.

2,7-Dimethoxy-*N*-methylphenanthrene-9-carboxamide (4d). Yield 58%, white solid, mp 205∼206 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (t, 2H, J = 8.3 Hz), 7.75 (s, 1H), 7.73 (d, 1H, J = 2.6 Hz), 7.31−7.25 (m, 2H), 7.17 (d, 1H, J = 2.6 Hz), 6.16 (bs, 1 H), 3.93 (s, 6H), 3.10 (d, 3H, J = 4.9 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 169.8, 158.2, 157.9, 134.0, 131.3, 129.5, 127.2, 125.4, 125.2, 124.7, 118.9, 117.7, 109.8, 107.7, 55.9, 55.8, 26.8; IR (neat) 3287, 2935, 1618, 1467 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{17}NO_3$ [M^+] 295.1208, found 295.1209.

***N*-Benzylphenanthrene-9-carboxamide (4e).** Yield 73%, white solid, mp 154∼156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (t, 2H, J = 9.5 Hz), 8.35 (dd, 1H, J = 7.8, 1.1 Hz), 7.86−7.83 (m, 2H), 7.72−7.56 (m, 4H), 7.44−7.29 (m, 5H), 6.46 (bs, 1H), 4.74 (d, 2H, J = 5.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 138.4, 133.4, 131.2, 130.8, 130.5, 129.3, 129.1, 128.7, 128.2, 128.1, 127.9, 127.4, 127.3, 127.2, 126.5, 123.1, 122.9, 44.3; IR (neat) 3268, 1631, 1528, 1450, 1261 cm^{-1}; MS (EI) *m*/*z* 312 (14), 311 (M^+, 61), 205 (78), 87 (100), 151 (26), 104 (26), 91 (37); HRMS (EI) calcd for $C_{22}H_{17}NO$ [M^+] 311.1310, found 311.1310.

Methyl Phenanthrene-9-carboxylate (4f). The reaction mixture was irradiated for 10 min at 130 °C. Yield 57%, white solid, mp 76∼80 °C (lit.[5b] 115 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.91 (m, 1H), 8.71 (t, 2H, J = 8.4 Hz), 8.47 (d, 1H, J = 6.3 Hz), 7.97 (d, 1H, J = 7.8 Hz), 7.75−7.46 (m, 4H), 4.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 132.7, 132.4, 130.9, 130.3, 130.2, 129.3, 129.2, 127.7, 127.3, 127.1, 126.8, 126.4, 1231, 122.9, 52.5; IR (neat) 1705, 1444, 1432, 1252 cm^{-1}; MS (EI) *m*/*z* 237 (19), 236 (M^+, 100), 205 (88), 177 (78), 176 (74), 151 (25), 150 (23); HRMS (EI) calcd for $C_{16}H_{12}O_2$ [M^+] 236.0837, found 236.0837.

Ethyl Phenanthrene-9-carboxylate (4g). In addition to the reagents used in method A, DavePhos (6 mol %) was added. The reaction mixture was irradiated for 5 min at 120 °C and then for a further 5 min at 150 °C using a microwave reactor. Yield 87%, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.93−8.89 (m, 1H), 8.75−8.67 (m, 2H), 8.46 (s, 1H), 7.97 (d, 1H, J = 7.8 Hz), 7.78−7.61(m, 4H), 4.52 (q, 2H, J = 7.1 Hz), 1.50 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 132.4, 132.3, 130.9, 130.3, 130.1, 129.3, 129.1, 127.6, 127.2, 127.1, 126.9, 126.8, 123.1, 122.9, 61.5, 14.7; IR (neat) 1713, 1448, 1302, 1252, 1186 cm^{-1}; MS (EI) *m*/*z* 251 (20), 250 (M^+, 100), 222 (21), 205 (89), 177 (89), 151 (28); HRMS (EI) calcd for $C_{17}H_{14}O_2$ [M^+] 250.0994, found 250.1007.

1-(Phenanthren-9-yl)ethanone (4h). Yield 72%, white solid, mp 62 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74−8.67 (m, 3H), 8.21 (s, 1H), 7.96 (d, 1H, J = 7.8 Hz), 7.79−7.63 (m, 4H), 2.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.6, 134.3, 131.8, 130.7, 130.6, 129.7, 129.6, 128.8, 128.2, 127.4, 127.0, 126.9, 126.7, 122.6, 122.5, 30.0; IR (neat) 1670, 1527, 1444, 1352, 1293, 1248, 1212, 1156, 1141 cm^{-1}; MS (EI) *m*/*z* 221 (11), 220 (M^+, 78), 205 (86), 177 (100), 176 (65), 151 (34), 150 (23); HRMS (EI) calcd for $C_{16}H_{12}O$ [M^+] 220.0888, found 220.0729.

1-(2-Methoxyphenanthren-9-yl)ethanone (4i). Yield 66%, white solid, mp 82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67−8.57 (m, 3H), 8.13 (s, 1H), 7.69−7.58 (m, 2H), 7.38 (dd, 1H, J = 9.1, 2.6 Hz), 7.32 (d, 1H, J = 2.6 Hz), 3.99 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.2, 158.8, 135.6, 131.6, 131.2, 130.2, 127.5, 127.4, 127.0, 126.8, 126.6, 124.6, 122.5, 119.8, 109.6, 55.7, 30.3; IR (neat) 2837, 1666, 1572, 1452, 1244 cm^{-1}; MS (EI) *m*/*z* 251 (13), 250 (M^+, 74), 236 (16), 235 (100), 207 (19), 192 (43), 164 (43), 163 (50); HRMS (EI) calcd for $C_{17}H_{14}O$ [M^+] 250.0994, found 250.1009.

9-(Phenylsulfonyl)phenanthrene (4j). Yield 85%, white solid, mp 164∼166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.72−8.61 (m, 3H), 8.11 (dd, 1H, J = 7.8, 1.1 Hz), 8.02−7.99 (m, 2H), 7.85−7.79 (m, 1H), 7.74−7.57 (m, 4H), 7.53−7.44 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 134.4, 133.4, 133.3, 133.0, 131.5, 131.1, 131.0, 130.4, 129.5, 129.4, 127.9, 127.8, 127.6, 126.2, 125.6, 123.6, 123.0; IR (neat) 1444, 1290, 1139, 1086 cm^{-1}; MS

(EI) *m*/*z* 319 (12), 318 (M^+, 43), 253 (47), 176 (60), 165 (100), 151 (24); HRMS (EI) calcd for $C_{20}H_{14}O_2S$ [M^+] 318.0715, found 318.0714.

Phenanthrene-9-carbonitrile (4k). Yield 83%, white solid, mp 100∼106 °C (lit.[31] 105−106 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74−8.69 (m, 2H), 8.33−8.26 (m, 2H), 7.95 (d, 1H, J = 7.8 Hz), 7.84−7.66 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8, 131.9, 130.1, 130.0, 129.9, 129.7, 129.0, 128.4, 128.3, 127.8, 126.2, 1233, 123.0, 118.2, 109.5; IR (neat) 2219, 1527, 1448, 1247 cm^{-1}; MS (EI) *m*/*z* 204 (13), 203 (M^+, 100), 176 (11); HRMS (EI) calcd for $C_{15}H_9N$ [M^+] 203.0735, found 203.0740.

6-(Trifluoromethyl)phenanthrene-9-carbonitrile (4l). Yield 90%, white solid, mp 148∼150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.70 (d, 1H, J = 8.3 Hz), 8.43−8.36 (m, 2H), 8.00−7.86 (m, 3H), 7.77 (t, 1H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 131.5, 130.8, 130.7, 130.4, 130.2, 129.9, 129.8, 128.7, 127.2, 124.3 (J = 271.0 Hz), 124.2 (J = 3.3 Hz), 123.1, 120.8 (J = 2.8 Hz), 117.4, 109.1; IR (neat) 2222, 1320, 1121, 1080, 747 cm^{-1}; MS (EI) *m*/*z* 272 (20), 271 (M^+, 100), 252 (14), 221 (15), 201 (10), 175 (7), 136 (8), 110 (9); HRMS (EI) calcd for $C_{16}H_8F_3N$ [M^+] 271.0609, found 271.0618.

5-Methylphenanthrene-9-carbonitrile (4m). In addition to reagents used in method A, SPhos (6 mol %) was added. Yield 56%, white solid, mp 120∼122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (d, 1H, J = 8.6 Hz), 8.27−8.24 (m, 2H), 7.65 (dd, 1H, J = 7.8, 0.9 Hz), 7.78 (dt, 1H, J = 7.6, 1.2 Hz), 7.70−7.63 (m, 3H), 3.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3, 136.2, 133.2, 133.1, 131.2, 130.4, 130.1, 129.9, 129.0, 127.8, 127.5, 127.0, 124.9, 118.6, 110.3, 27.6; IR (neat) 2216, 1450, 1210, 783 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{11}N${M^+] 217.0891, found 217.0896.

8-Fluorophenanthrene-9-carbonitrile (4n). In addition to reagents used in method A, SPhos (6 mol %) was added. Yield 80%, orange solid, mp 142∼144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, 1H, J = 8.4 Hz), 8.48 (d, 1H, J = 8.4 Hz), 8.27 (s, 1H), 7.92 (d, 1H, J = 7.9 Hz), 7.85−7.79 (m, 1H), 7.74−7.65 (m, 2H), 7.39 (ddd, 1H, J = 12.5, 7.9, 0.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6 (J = 252.8 Hz), 138.6, 132,5 (J = 2.6 Hz), 131.0 (J = 2.7 Hz), 130.6, 129.9 (J = 1.0 Hz), 129.7, 128.6 (J = 8.8 Hz), 128.5, 123.4, 119.3 (J = 4.1 Hz), 119.1, 118.6 (J = 11.3 Hz), 113.6 (J = 20.8 Hz), 103.7 (J = 2.4 Hz); IR (neat) 2223, 1241, 1457, 1378 cm^{-1}; MS (EI) *m*/*z* 222 (16), 221 (M^+, 100), 194 (4), 110 (10), 97 (9); HRMS (EI) calcd for $C_{15}H_8FN$ [M^+] 221.0641, found 221.0654.

2,3-Dimethoxyphenanthrene-9-carbonitrile (4o). Yield 32%, white solid, mp 149∼151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (dd, 1H, J = 6.8, 0.5 Hz), 8.26 (dd, 1H, J = 6.2, 1.0 Hz), 8.13 (s, 1H), 7.95 (s, 1H), 7.74−7.65 (m, 2H), 7.23 (s, 1H), 4.14 (s, 3H), 4.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 150.2, 134.4, 129.5, 128.7, 127.8, 127.3, 126.3, 125.2, 122.8, 118.6, 108.8, 107.2, 103.2, 56.3; IR (neat) 2216, 1613, 1506, 1217 cm^{-1}; MS (EI) *m*/*z* 264 (18), 263 (M^+, 100), 220 (18), 202 (160, 190 (20), 177 (51), 150 (20); HRMS (EI) calcd for $C_{17}H_{13}NO_2$ [M^+] 263.0946, found 263.0944.

2-Fluorophenanthrene-9-carbonitrile (4p). Yield 73%, white solid, mp 152∼154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72−8.63 (m, 2H), 8.31 (dd, 1H, J = 3.0 Hz), 8.19 (s, 1H), 7.83−7.73 (m, 2H), 7.60−7.52 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7 (J = 247.9 Hz), 134.6 (J = 3.9 Hz), 131.2 (J = 9.0 Hz), 129.9, 128.8, 128.5 (J = 1.5 Hz), 128.4, 128.2 (J = 0.8 Hz), 126.4, 125.5 (J = 8.7 Hz), 123.1 (J = 0.8 Hz), 119.0 (J = 23.6 Hz), 117.7, 113.7 (J = 20.9 Hz), 111.0; IR (neat) 3073, 2221, 1623, 1530, 1454, 1221 cm^{-1}; MS (EI) *m*/*z* 222 (17), 221 (M^+, 100), 194 (6), 168 (5), 110 (7); HRMS (EI) calcd for $C_{15}H_8FN$ [M^+] 221.0641, found 221.0646.

Benzo[*h*]quinoline-6-carbonitrile (4q). Yield 63%, white solid, mp 150∼152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.36−9.32 (m, 1H), 9.11 (dd, 1H, J = 4.4, 1.7 Hz), 8.31−8.21 (m, 3H), 7.89−7.84 (m, 2H), 7.61 (dd, 1H, J = 8.1, 4.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9, 147.6, 136.8, 134.2, 131.5, 130.7, 129.9, 128.9, 125.6, 125.2, 124.6, 122.9, 117.6, 110.6; IR (neat) 2221, 1591, 1444, 1230 cm^{-1}; MS (EI) *m*/*z* 205 (17), 204 (M^+, 100), 176 (10), 150 (10), 102 (11); HRMS (EI) calcd for $C_{14}H_8N_2$ [M^+] 204.0687, found 204.0704.

Typical Procedure for One-Pot Synthesis of 10-Methylphenanthrenes. Method B: in addition to the reagents used in method A, DavePhos (6 mol %) was added. The reaction mixture was irradiated for 5 min at 120 °C and then for a further 5 min at 150 °C using a microwave reactor.

***N*,10-Dimethylphenanthrene-9-carboxamide (8a).** Yield 71%, white solid, mp 136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71−8.64 (m, 2H), 8.09 (dd, 1H, J = 7.6, 2.0 Hz), 7.83 (dd, 1H, J = 7.7, 1.7 Hz), 7.72−7.55 (m, 4H), 5.96 (bs, 1H), 3.14 (d, 1H, J = 4.8 Hz), 2.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 133.6, 131.3, 130.5, 129.7, 129.3, 128.9, 127.4, 127.3, 127.2, 126.6, 125.8, 125.3, 123.1, 122.9, 26.9, 17.1; IR (neat) 3303, 2924, 1631, 1555, 1276 cm^{-1}; MS (EI) *m*/*z* 249 (M^+, 100), 219 (81), 191 (39), 189 (30), 165 (49); HRMS (EI) calcd for $C_{17}H_{15}NO$ [M^+] 249.1154, found 249.1166.

Methyl 10-Methylphenanthrene-9-carboxylate (8b). Yield 71%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74−8.68 (m, 2H), 8.13 (dd, 1H, J = 7.6, 1.2 Hz), 7.74−7.57 (m, 5H), 4.09 (s, 3H), 2.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 131.2, 130.7, 130.4, 130.1, 129.6, 128.4, 127.6, 127.4, 127.3, 126.7, 125.5, 125.4, 123.2, 123.0, 52.7, 17.5; IR (neat) 2949, 1723, 1445, 1205 cm^{-1}; MS (EI) *m*/*z* 251 (20), 250 (M^+, 100), 219 (62), 189 (69), 178 (11), 165 (39), 109 (8); HRMS (EI) calcd for $C_{17}H_{14}O_2$ [M^+] 250.0994, found 250.1004.

Ethyl 10-Methylphenanthrene-9-carboxylate (8c). Yield 52%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72−8.66 (m, 2H), 8.12 (dd, 1H, J = 7.3, 1.9 Hz), 7.76−7.59 (m, 5H), 4.58 (q, 2H, J = 7.1 Hz), 2.70 (s, 3H), 1.48 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 131.2, 130.6, 129.8, 128.4, 127.5, 127.4, 127.3, 126.7, 125.4, 125.3, 123.2, 122.9, 61.7, 17.3, 14.6; IR (neat) 1712, 1446, 1205, 1033 cm^{-1}; MS (EI) *m*/*z* 265 (24), 264 (M^+, 100), 219 (77), 191 (95), 189 (92), 161 (57); HRMS (EI) calcd for $C_{18}H_{16}O_2$ [M^+] 264.1150, found 264.1147.

10-Methylphenanthrene-9-carbonitrile (8d). Yield 56%, white solid, mp 154∼158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69−8.61 (m, 2H), 8.25 (m, 1H), 8.11 (dd, 1H, J = 8.2, 1.3 Hz), 7.81−7.61 (m, 4H), 2.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 131.2, 130.0, 129.2, 129.0, 128.8, 128.0, 127.4, 127.3, 125.8, 125.7, 123.1, 122.7, 117.5, 109.2, 18.9; IR (neat) 2188, 1609, 1434, 1230 cm^{-1}; MS (EI) *m*/*z* 217 (M^+, 100), 216 (27), 189 (27), 110 (13); HRMS (EI) calcd for $C_{16}H_{11}N$ [M^+] 217.0891, found 217.0896.

Ethyl 10-(Bromomethyl)phenanthrene-9-carboxylate (10). To a solution of methylphenanthrene **8c** (100 mg, 0.38 mmol) in 10 mL of benzene was added NBS (81 mg, 0.45 mmol) and AIBN (6 mg, 0.04 mmol). The resulting solution was stirred at reflux temperature for 4 h. After cooling to room temperature, the mixture was filtered while being rinsed with Et_2O. The solution was washed with a 10% aqueous $Na_2S_2O_3$ solution, H_2O, and brine. The organic solution was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (10% EtOAc/hexanes) to give (bromomethyl)phenanthrene **10** (121 mg, 93% yield) as a brown solid. mp 108∼110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69−8.59 (m, 2H), 8.22−8.19 (m, 1H), 7.79 (dd, 1H, J = 7.7, 1.4 Hz), 7.69−7.55 (m, 4H), 4.93 (s, 2H), 4.61 (q, 2H, J = 7.1 Hz), 1.15 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 132.2, 131.3, 130.8, 128.8, 128.7, 128.1, 128.0, 127.9, 127.7, 127.6, 126.4, 125.3, 123.4, 123.1, 62.3, 27.8, 14.6; IR (neat) 1722, 1447, 1247, 1206, 1068 cm^{-1}; MS (EI) *m*/*z* 344 (23), 342 (M^+, 21), 263 (91), 235 (100), 205 (56), 191 (88), 189 (95), 178 (37), 177 (40); HRMS (EI) calcd for $C_{18}H_{15}BrO_2$ [M^+] 342.0255, found 342.0268.

(31) Gore, P. H.; Kamounah, F. S.; Miri, A. Y. *Tetrahedron* **1979**, *35*, 2927−2929.

Phenanthrene-10-aminomethyl-9-carboxamide Lactam (11). To a solution of **10** (100 mg, 0.29 mmol) in 8 mL of CH_2Cl_2 was added methylamine 0.13 mL (1.46 mmol, 40 wt % in water). The solution was stirred at room temperature for 2 h. The mixture was quenched with H_2O (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine solution, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (50% EtOAc/hexanes) to provide phenanthrene lactam **11** (62 mg, 86%) as a white solid. mp 142∼146 °C (lit.[5a] 142−144 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.28 (dd, 2H, J = 7.0, 2.5 Hz), 8.57−8.52 (m, 2H), 7.84 (d, 1H, J = 7.8 Hz), 7.77−7.62 (m, 4H), 4.66 (s, 2H), 3.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 140.8, 131.6, 130.3, 128.3, 127.6, 127.5, 127.1, 127.0, 126.4, 125.3, 124.6, 123.6, 123.5, 122.7, 50.7, 29.5; IR (neat) 1667, 1448, 1392, 1252 cm^{-1}; MS (EI) *m*/*z* 248 (15), 247 (M^+, 87), 218 (100), 189 (17), 176 (24), 108 (14); HRMS (EI) calcd for $C_{17}H_{18}NO$ [M^+] 247.0997, found 247.0996.

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Supporting Information Available: Experimental procedures and spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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