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A Fully Palladium-Mediated Construction of Phenanthrenes and Naphthoxindoles

Luma Nassar-Hardy,[a] Christophe Deraedt,[a] Eric Fouquet,[a] and François-Xavier Felpin*[a]

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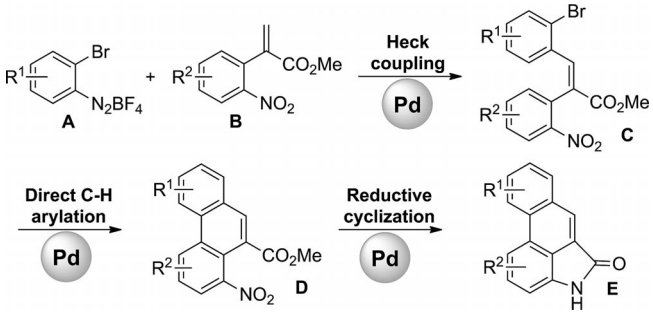
A fully palladium-catalyzed synthesis of unusual naphthoxindole alkaloids through a key intramolecular direct C–H arylation step leading to the formation of the phenanthrene core is described. The three-step process involves a highly efficient Heck coupling of aryl diazonium salts with phenylacrylates, giving the corresponding *cis*-stilbenes. Cyclization of stilbenes into phenanthrenes through a direct intramolecular C–H arylation, followed by a palladium-mediated cyclization of an amino ester, led to the formation of novel naphthoxindoles.

Introduction

The phenanthrene nucleus constitutes an important class of polycyclic aromatic hydrocarbons that is extensively found in natural products and biologically active compounds.[1] It has also been widely used in material science with photophysical applications.[2] As a consequence, there are a variety of available methods for the preparation of phenanthrene-based compounds.[3] Among these strategies, the cyclization of stilbene derivatives into the corresponding phenanthrenes is currently the preferred approach. For instance, oxidative cyclizations have been widely described, but most require electron-rich substrates.[4] Photocyclizations in the presence of an oxidant such as iodine have also been reported; however, this approach suffers from modest group compatibility, although an improved protocol has recently been published that overcomes this lack of generality.[5] Wang and co-workers also recently reported an elegant total synthesis of papilistatin that involved the radical cyclization of a bromostilbene intermediate with a modest yield (30%).[6] In contrast, until now, cyclization of stilbenes by direct C–H arylation has mostly been overlooked.[7] In the context of a medicinal chemistry project, we wish to report our latest investigations, which ultimately led to the preparation of naphthoxindoles **E** through a fully palladium-catalyzed, three-step process, as illustrated in Scheme 1. Naphthoxindoles are unusual tetracyclic constructions that are structurally related to various biologically active natural products (Figure 1).



Scheme 1. General strategy for the preparation of naphthoxindoles.

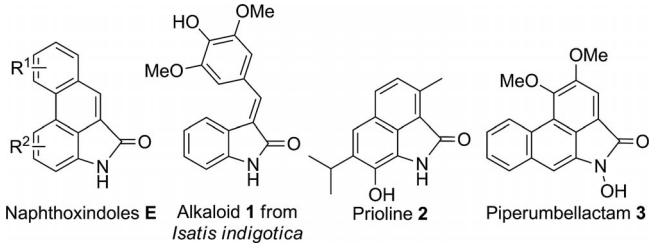


Figure 1. Natural products related to the target naphthoxindoles.

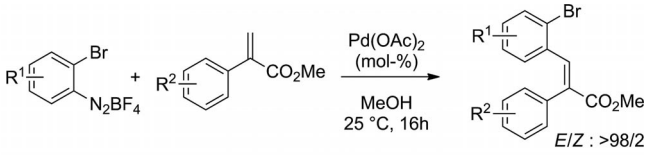
Results and Discussion

Our studies started with the preparation of a variety of bromo-stilbenes **4**–**12** by the coupling of aryl diazonium salts with (2-nitrophenyl)acrylates (Table 1),[8] according to our recently published procedure.[9] The reaction, which was carried out in MeOH at room temperature, proceeds with good to excellent yields under ligand-free and base-free conditions. The simplicity and the robustness of the catalytic system makes this protocol highly reproducible, even for non-specialized chemists. We also prepared stilb-

[a] Université de Bordeaux, CNRS-UMR 5255, Institut des Sciences Moléculaires (ISM),
351, Cours de la Libération, 33405 Talence, France
Fax: +33-5-40006286
E-mail: fx.felpin@ism.u-bordeaux1.fr

enes **10**–**12**, which do not bear a nitro group, to evaluate the scope of the direct C–H arylation, although these compounds could not be further transformed into the target naphthoxindoles. It was observed that the preparation of cyano-stilbene **10** required higher palladium loading. We assumed that strong complexation of cationic palladium intermediates with the cyano group could explain this lower activity. As expected, complete control of the olefin geometry in favor of the *cis*-stilbenes was consistently obtained, and the *trans*-stilbenes were never observed by ^{1}H NMR analysis of the crude reaction mixture. The *E* geometry of *cis*-stilbenes prepared in this study was assigned by analyzing the ^{1}H NMR shift of the olefinic proton (ca. 8 ppm vs. ca. 7 ppm for the *Z* isomer) and by analogy with structurally related stilbenes previously prepared in our laboratory. This behavior was rationalized by DFT calculations[9] that showed that a lower activation barrier is predicted for structures having the two phenyl groups in a *cis* relation in the transition state, which leads to the corresponding *cis*-stilbene.

Table 1. Preparation of stilbenes by Heck coupling.



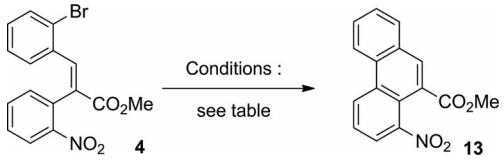
4 - 0.25 mol-%, 83% **5** - 0.5 mol-%, 99% **6** - 0.5 mol-%, 78%

7 - 1 mol-%, 97% **8** - 1 mol-%, 90% **9** - 1 mol-%, 88%

10 - 3.5 mol-%, 98% **11** - 1 mol-%, 96% **12** - 0.5 mol-%, 99%

With a set of bromo-stilbenes **4**–**12** in hand, the direct C–H arylation step was then studied. The optimization trials were conducted with stilbene **4** as the model substrate (Table 2). Because direct C–H arylation of non-heterocyclic substrates frequently require high palladium loading (typically more than 5 mol-%),[10] we initially screened heterogeneous palladium sources so that the palladium metal could be recovered after completion (Table 2). Unfortunately, all the charcoal-supported palladium catalysts tested were ineffective for the desired transformation (Table 2, Entries 1–5).[11] Even the use of Pearlman's catalyst [$Pd(OH)_2$/C], which has previously been successfully used for the C–H arylation of heterocycles,[12] was inactive with this substrate. In contrast, the use of $Pd(OAc)_2$ (10 mol-%) furnished phenanthrene **13** with good yield in dimethylacetamide (DMAc) with K_2CO_3 as base at 130 °C (Table 2, Entry 6). Decreasing the palladium loading to 2 mol-% slightly improved the yield, but a lower loading (1 mol-%) was detrimental for the conversion (Table 2, Entry 9). A large impact of the base on the reaction outcome was observed; K_2CO_3 was by far superior to AcOK, Na_2CO_3, and *t*BuOK (Table 2, Entries 8 vs. 10–12). The choice of solvent was also found to be critical; DMAc proved to be more effective than both *N*-methyl-2-pyrrolidinone (NMP) and *N*,*N*-dimethylformamide (DMF), whereas no conversion was observed with either xylene or dioxane (Table 2, Entries 13–16). The temperature also considerably impacted the reaction outcome and the reagent stability; at 150 °C, extensive decomposition products were observed (Table 2, Entry 17), whereas at 90 °C the conversion was rather low (Table 2, Entry 19). After careful optimization, we found that, for this substrate, the reaction was best performed at 110 °C (Table 2, Entry 17). Because we were still interested in performing this transformation with a heterogeneous catalyst,

Table 2. Optimization studies of the intramolecular direct C–H arylation.



4 **13**

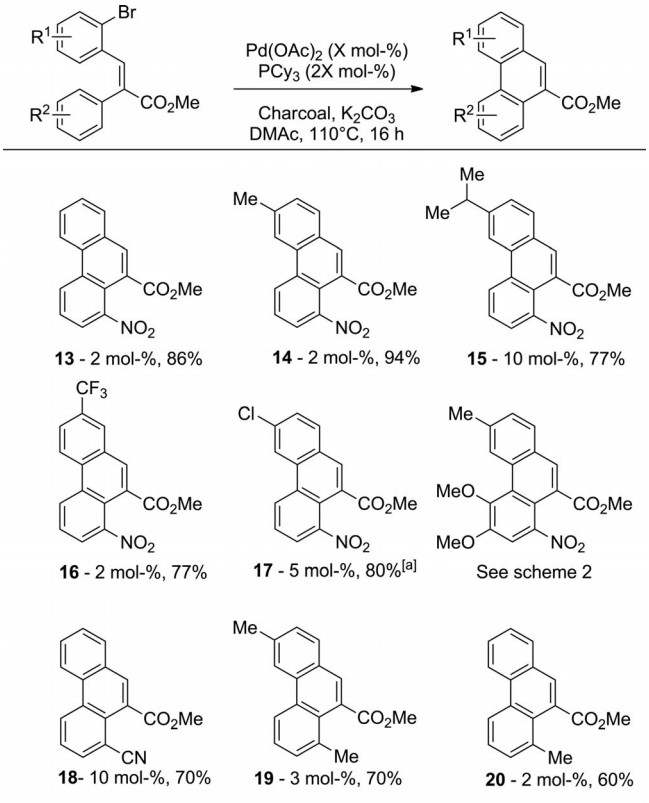
Entry	Palladium	Loading [mol-%]	Solvent	Base (3 equiv.)	*T* [°C]	Yield [%][a]
1	$P^{II}/C_{eggshell}$	10	DMAc	K_2CO_3	130	(<5)
2	$P^{II}/C_{uniform}$	10	DMAc	K_2CO_3	130	0
3	$P^{0}/C_{eggshell}$	10	DMAc	K_2CO_3	130	0
4	$P^{0}/C_{uniform}$	10	DMAc	K_2CO_3	130	0
5	$Pd(OH)_2$	10	DMAc	K_2CO_3	130	(<5)
6	$Pd(OAc)_2$	10	DMAc	K_2CO_3	130	70
7	$Pd(OAc)_2$	5	DMAc	K_2CO_3	130	72
8	$Pd(OAc)_2$	2	DMAc	K_2CO_3	130	74
9	$Pd(OAc)_2$	1	DMAc	K_2CO_3	130	(50)
10	$Pd(OAc)_2$	2	DMAc	AcOK	130	63
11	$Pd(OAc)_2$	2	DMAc	Na_2CO_3	130	(32)
12	$Pd(OAc)_2$	2	DMAc	*t*BuOK	130	(98)[b]
13	$Pd(OAc)_2$	2	DMF	K_2CO_3	130	(72)
14	$Pd(OAc)_2$	2	Xylene	K_2CO_3	130	66
15	$Pd(OAc)_2$	2	Dioxane	K_2CO_3	130	0
16	$Pd(OAc)_2$	2	DMAc	K_2CO_3	130	0
17	$Pd(OAc)_2$	2	DMAc	K_2CO_3	150	31
18	$Pd(OAc)_2$	2	DMAc	K_2CO_3	110	75
19	$Pd(OAc)_2$	2	DMAc	K_2CO_3	90	(38)
20[c]	$Pd(OAc)_2$	2	DMAc	K_2CO_3	110	78
21[d]	$Pd(OAc)_2$	2	DMAc	K_2CO_3	110	86

[a] Yield of isolated product. Conversion in parentheses, estimated by ^{1}H NMR spectroscopic analysis. [b] The starting material was completely degraded. [c] Charcoal was added. [d] Charcoal and PCy_3 were added.

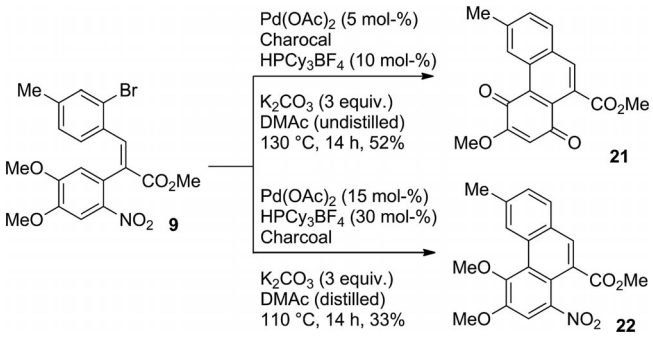
we added charcoal to the reaction mixture and found that the yield was slightly improved (Table 2, Entry 20). Interestingly, the use of PCy_3 as ligand, in the presence of charcoal, led to a much cleaner crude reaction mixture and to the isolation of **13** in 86% yield (Table 2, Entry 21). We believe that charcoal acts as a stabilizer for active palladium species and as a sponge for inactive species that would otherwise form palladium black. ICP-MS analysis of the crude mixture after simple filtration showed that at least 80% of the palladium initially introduced was adsorbed on the charcoal, allowing its recovery for further reprocessing.

We then applied the optimized conditions to the set of bromo-stilbenes **4**–**12** (Table 3). A higher palladium loading was required for the intramolecular C–H arylation of stilbene **6** leading to phenanthrene **15** due to the competitive palladium-mediated debromination reaction that was observed at a lower loading. In the absence of phosphane, the protocol was found to be selective for reaction at the bromine atom; no reaction occurred at the chlorine atom on substrate **8**. However, it should be noted that the use of PCy_3 with stilbene **8** led to a much lower yield of **17** (56 vs. 80%) due to side-reactions at the chlorine atom. As already noted for the Heck reaction, the cyano-substituted stilbene **10** was much less reactive and required a higher palladium loading for optimal conversion and good yield of **18**. The case of the methoxylated stilbene **9** was quite interesting, because the major reaction product was highly dependent on the quality of the DMAc used (Scheme 2). When undistilled DMAc was used, only the unexpected and highly unstable quinone **21** was observed (52% yield) along with degradation products. On the other hand, with twice-distilled DMAc we were able to isolate the target phenanthrene **22** with modest yield (33%) along with a trace of quinone **21**. The mode of formation of quinone **21** is still unclear at this time; however, in the absence of palladium we did not observe its formation. We assume that a push–pull effect would give a highly hydrolyzable intermediate **23**, which would ultimately furnish quinone **21** in the presence of water (Scheme 3).

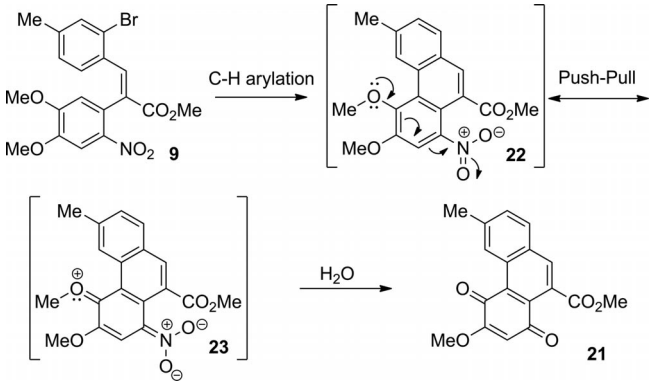
Table 3. Scope of the intramolecular direct C–H arylation.



[a] PCy_3 was omitted.



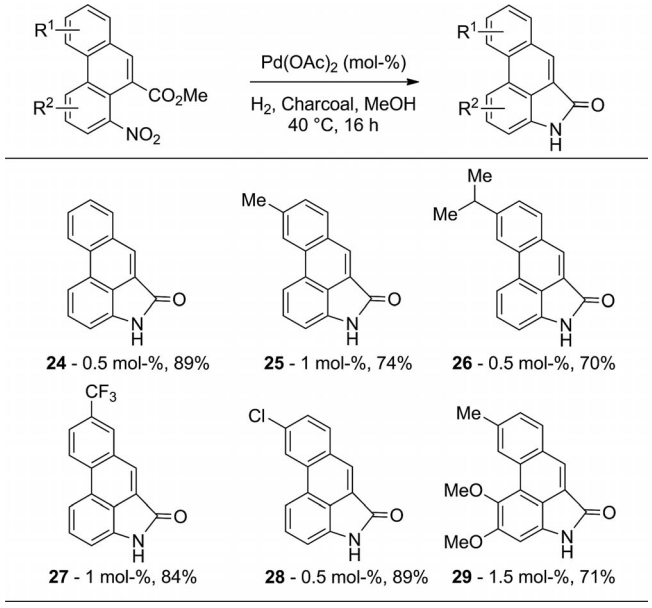
Scheme 2. Unexpected formation of quinone **21** in undistilled DMAc.



Scheme 3. Mechanistic rationale for the formation of quinone **21**.

Lastly, phenanthrenes **13**–**17** and **22** were converted with good yields into the target naphthoxindoles **24**–**29** through a palladium-mediated reductive cyclization (Table 4). This step was conducted according to an extension of our recently published procedure for the hydrogenation of olefins and the hydrogenolysis of benzyl ethers.[13] The catalytic system proceeds through the formation of a highly active Pd^0/C catalyst that was prepared in situ from $Pd(OAc)_2$ and charcoal. This strategy allows the use of low palladium loadings and avoids the need to handle pyrophoric Pd/C catalysts. ICP-MS analyses of the crude mixtures after a single filtration showed only trace amounts (2–3 ppb) of residual palladium species in the supernatant, which means that more than 99.9% of the palladium initially introduced was adsorbed on the charcoal.

Table 4. Preparation of naphthoxindoles.



Conclusions

We have reported a novel route to naphthoxindole alkaloids. Our approach entails a fully palladium-catalyzed, three-step sequence composed of a Heck coupling of diazonium salts, direct C–H arylation, and a reductive cyclization. The direct C–H arylation was carried out in the presence of charcoal, which stabilizes active palladium species and adsorbs unstable palladium particles that would otherwise form palladium black. Such a protocol allows the preparation of naphthoxindoles with only parts-per-billion levels of palladium contamination. We believe that this study would be of interest to synthetic chemists involved in palladium catalysis as well as to medicinal chemists concerned by the contamination of biologically active compounds with palladium residues. Moreover, this study provides access to structurally intriguing naphthoxindoles.

Experimental Section

General Remarks: NMR chemical shifts are reported in ppm relative to $CDCl_3$ at δ = 7.26 ppm (^1H) or 77.0 ppm (^{13}C). IR spectra were recorded as neat samples on NaCl plates or with KBr pellets. Yields refer to isolated material determined to be pure by NMR spectroscopy and thin layer chromatography (TLC), unless specified otherwise in the text. Diazonium salts used in this study are all known compounds and were prepared as described in the literature. DARCO G-60 activated charcoal with a 100 mesh particle size, produced from lignin, was used.

General Procedure for the Preparation of Stilbenes 4–12: Acrylate (1 mmol) and $Pd(OAc)_2$ (0.25–3.5 mol-%, see Table 1) were added to a solution of diazonium salt (1.3–1.5 mmol) in MeOH (6 mL) at 25 °C. The resulting mixture was stirred for 18 h and then concentrated under reduced pressure. The crude product was purified by flash chromatography to give the corresponding product.

Methyl (*E*)-3-(2-Bromophenyl)-2-(2-nitrophenyl)acrylate (4): Purification by flash chromatography (15% EtOAc/petroleum ether) gave the desired product **4** as a white solid (300 mg, 83%). M.p. 143 °C. IR (KBr): $\tilde{\nu}$ = 1527, 1709, 2956, 3064 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 3 H), 6.39 (dd, J = 1.1, 7.56 Hz, 1 H), 6.95 (t, J = 7.9 Hz, 1 H), 7.01–7.09 (m, 2 H), 7.38–7.48 (m, 2 H), 7.56 (d, J = 7.9 Hz, 1 H), 8.05 (s, 1 H), 8.16 (dd, J = 2.3, 6.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.5, 124.6, 127.0, 129.1, 130.1, 130.8, 131.2, 132.6, 132.9, 133.6, 135.2, 139.5, 149.0, 165.6 ppm. HRMS (ESI): calcd. for $C_{16}H_{12}NO_4NaBr$ $[M + Na]^+$ 383.9841; found 383.9848.

Methyl (*E*)-3-(2-Bromo-5-methylphenyl)-2-(2-nitrophenyl)acrylate (5): Purification by flash chromatography (20% EtOAc/petroleum ether) gave the desired product **5** as a yellow solid (371 mg, 99%). M.p. 103–104 °C. IR (KBr): $\tilde{\nu}$ = 1526, 1718, 2923, 2952, 3031, 3066 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H), 3.76 (s, 3 H), 6.61 (d, J = 7.9 Hz, 1 H), 6.75 (d, J = 7.9 Hz, 1 H), 7.03–7.06 (m, 1 H), 7.40–7.49 (m, 3 H), 8.04 (s, 1 H), 8.16 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 52.5, 124.7, 124.8, 128.0, 129.2, 130.6, 131.5, 131.9, 132.1, 133.0, 133.2, 133.7, 139.5, 140.9, 149.1, 165.9 ppm. HRMS (ESI): calcd. for $C_{17}H_{14}NO_4NaBr$ $[M + Na]^+$ 397.9998; found 397.9999.

Methyl (*E*)-3-(2-Bromo-4-isopropylphenyl)-2-(2-nitrophenyl)acrylate (6): Purification by flash chromatography (20% EtOAc/petroleum ether) gave the desired product **6** as a yellow solid (315 mg, 78%). M.p. 125 °C. IR (KBr): $\tilde{\nu}$ = 1526, 1717, 2870, 2962, 3030, 3066 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.16 (d, J = 6.9 Hz, 6 H), 2.78 (sept, J = 6.9 Hz, 1 H), 3.76 (s, 3 H), 6.64 (d, J = 8.1 Hz, 1 H), 6.80 (dd, J = 1.7, 8.1 Hz, 1 H), 7.05–7.09 (m, 1 H), 7.40–7.50 (m, 3 H), 8.06 (s, 1 H), 8.13–8.21 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.5, 33.6, 52.5, 124.6, 125.0, 125.4, 129.1, 130.6, 130.7, 131.5, 131.7, 132.2, 132.9, 133.6, 139.4, 149.0, 151.7, 165.8 ppm. HRMS (ESI): calcd. for $C_{19}H_{18}NO_4NaBr$ $[M + Na]^+$ 426.0311; found 426.0317.

Methyl (*E*)-3-[2-Bromo-5-(trifluoromethyl)phenyl]-2-(2-nitrophenyl)-acrylate (7): Purification by flash chromatography (20% EtOAc/petroleum ether) gave the desired product **7** as a yellow solid (417 mg, 97%). M.p. 104–105 °C. IR (KBr): $\tilde{\nu}$ = 1550, 1605, 1723, 2955, 3072 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 6.95 (s, 1 H), 6.99–7.02 (m, 1 H), 7.30 (dd, J = 2.2, 8.4 Hz, 1 H), 7.44–7.49 (m, 2 H), 7.70 (d, J = 8.3 Hz, 1 H), 8.03 (s, 1 H), 8.17 (dd, J = 1.8, 7.4 Hz, 1 H) ppm. HRMS (ESI): calcd. for $C_{17}H_{11}NO_4F_3NaBr$ $[M + Na]^+$ 451.9715; found 451.9713.

Methyl (*E*)-3-(2-Bromo-4-chlorophenyl)-2-(2-nitrophenyl)acrylate (8): Purification by flash chromatography (20% EtOAc/petroleum ether) gave the desired product as a yellow solid **8** (356 mg, 90%). M.p. 91–93 °C. IR (KBr): $\tilde{\nu}$ = 1527, 1580, 1719, 2952, 3068 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.75 (s, 3 H), 6.68 (d, J = 8.4 Hz, 1 H), 6.92–7.04 (m, 2 H), 7.41–7.51 (m, 2 H), 7.57 (s, 1 H), 7.97 (s, 1 H), 8.13–8.18 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.6, 124.7, 125.0, 127.4, 129.4, 131.8, 131.4, 132.3, 132.7, 133.1, 133.7, 135.2, 138.1, 149.0, 165.4 ppm. HRMS (ESI): calcd. for $C_{16}H_{11}NO_4NaClBr$ $[M + Na]^+$ 417.9452; found 419.9428.

Methyl (*E*)-3-(2-Bromo-4-methylphenyl)-2-(4,5-dimethoxy-2-nitrophenyl)acrylate (9): Purification by flash chromatography (20% EtOAc/petroleum ether) gave the desired product **9** as a brown solid (384 mg, 88%). M.p. 128–129 °C. IR (KBr): $\tilde{\nu}$ = 1520, 1573, 1604, 1629, 1714, 2837, 2954, 3005, 3065, 3093 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 3.54 (s, 3 H), 3.64 (s, 3 H), 3.83 (s, 3 H), 6.32 (s, 1 H), 6.53 (d, J = 8.1 Hz, 1 H), 6.68 (d, J = 8.5 Hz, 1 H), 7.26 (s, 1 H), 7.65 (s, 1 H), 7.83 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.4, 52.0, 55.9, 107.2, 113.5, 123.8,

125.4, 127.8, 130.0, 132.1, 132.5, 132.6, 138.1, 140.3, 141.0, 148.2, 152.8, 165.5 ppm. HRMS (ESI): calcd. for $C_{19}H_{18}NO_6NaBr$ [M + Na]$^+$ 458.0209; found 458.0217.

Methyl (*E*)-3-(2-Bromophenyl)-2-(2-cyanophenyl)acrylate (10): Purification by flash chromatography (30% EtOAc/petroleum ether) gave the desired product **10** as a yellow solid (335 mg, 98%). M.p. 75–76 °C. IR (KBr): $\tilde{\nu}$ = 1631, 1714, 2225, 2955, 3009, 3065, 3408 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 6.63 (dd, J = 1.7, 7.9 Hz, 1 H), 6.95 (dt, J = 1.1, 7.9 Hz, 1 H), 7.07 (dt, J = 1.9, 7.5 Hz, 1 H), 7.21 (dd, J = 1.1, 7.2 Hz, 1 H), 7.39 (dt, J = 1.5, 7.7 Hz, 1 H), 7.48 (dt, J = 1.5, 7.6 Hz, 1 H), 7.56 (dd, J = 1.1, 7.9 Hz, 1 H), 7.65 (dd, J = 1.1, 7.5 Hz, 1 H), 8.21 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.4, 113.3, 117.1, 124.8, 126.6, 128.2, 130.2, 130.3, 130.9, 131.0, 132.4, 132.6, 132.6, 134.1, 138.7, 142.5, 165.8 ppm. HRMS (ESI): calcd. for $C_{17}H_{12}NO_2NaBr$ [M + Na]$^+$ 363.9943; found 365.9939.

Methyl (*E*)-3-(2-Bromo-4-methylphenyl)-2-*o*-tolylacrylate (8): Purification by flash chromatography (10% EtOAc/petroleum ether) gave the desired product **8** as a pale-yellow oil (331 mg, 96%). IR (NaCl): $\tilde{\nu}$ = 1598, 1622, 1714, 2953, 3021, 3060 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22 (s, 3 H), 2.25 (s, 3 H), 3.83 (s, 3 H), 6.65 (d, J = 8.1 Hz, 1 H), 6.76 (d, J = 8.1 Hz, 1 H), 7.11–7.28 (m, 4 H), 7.44 (s, 1 H), 8.22 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3, 20.5, 52.0, 125.1, 125.7, 127.5, 129.7, 129.9, 131.7, 132.9, 132.9, 134.6, 136.3, 139.2, 140.3, 167.5 ppm. HRMS (ESI): calcd. for $C_{18}H_{17}NO_2NaBr$ [M + Na]$^+$ 367.0304; found 367.0310.

Methyl (*E*)-3-(2-Bromophenyl)-2-*o*-tolylacrylate (9): Purification by flash chromatography (10% EtOAc/petroleum ether) gave the desired product **9** as a pale-yellow oil (328 mg, 99%). IR (NaCl): $\tilde{\nu}$ = 1625, 1716, 2924, 2950, 3020, 3063 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.13 (s, 3 H), 3.82 (s, 3 H), 6.67 (dd, J = 1.6, 7.6 Hz, 1 H), 6.91 (dt, J = 1.3, 7.6 Hz, 1 H), 6.99–7.26 (m, 6 H), 7.56 (dd, J = 1.4, 8.1 Hz, 1 H), 8.10 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.6, 52.5, 125.3, 125.9, 126.7, 128.1, 129.9, 130.0, 130.1, 130.5, 132.7, 133.9, 134.6, 135.0, 136.6, 139.6, 167.8 ppm. HRMS (ESI): calcd. for $C_{17}H_{15}O_2NaBr$ [M + Na]$^+$ 353.0147; found 353.0161.

General Procedure for the Preparation of Phenanthrenes 13–22 from Stilbenes 4–12: Stilbene **1**–**9** (1 mmol), K_2CO_3 (2 mmol), $Pd(OAc)_2$ (2–10 mol-%), charcoal [90 wt.-%/$Pd(OAc)_2$], and $HPCy_3BF_4$ (4–20 mol-%) were mixed in anhydrous DMAc (6 mL). The reaction mixture was stirred at 110 °C in a sealed tube for 15 h and then concentrated under reduced pressure. The crude product was purified by flash chromatography to give the corresponding product.

Methyl 8-Nitrophenanthrene-9-carboxylate (13): Purification by flash chromatography (25% EtOAc/petroleum ether) gave the desired product **13** as a yellow solid (241 mg, 86%). M.p. 140 °C. IR (KBr): $\tilde{\nu}$ = 1523, 1712, 2942, 2993, 3040 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 3 H), 7.63–7.76 (m, 3 H), 7.92 (d, J = 7.9 Hz, 1 H), 8.10 (d, J = 7.7 Hz, 1 H), 8.37 (s, 1 H), 8.54 (d, J = 8.3 Hz, 1 H), 8.83 (d, J = 8.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.0, 120.6, 122.8, 124.0, 125.2, 125.9, 127.7, 128.4, 129.6, 129.8, 130.0, 130.2, 132.4, 134.0, 148.5, 167.5 ppm. HRMS (ESI): calcd. for $C_{16}H_{11}NO_4Na$ [M + Na]$^+$ 304.0580; found 304.0581.

Methyl 3-Methyl-8-nitrophenanthrene-9-carboxylate (14): Purification by flash chromatography (20% EtOAc/petroleum ether, then 30% EtOAc/petroleum ether) gave the desired product **14** as a yellow solid (278 mg, 94%). M.p. 180–181 °C. IR (KBr): $\tilde{\nu}$ = 1512, 1526, 1708, 1733, 2923, 2950 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.61 (s, 3 H), 3.91 (s, 3 H), 7.49 (dd, J = 1.1, 8.1 Hz, 1 H), 7.62 (dd, J = 7.9, 8.3 Hz, 1 H), 7.81 (d, J = 8.1 Hz, 1 H), 8.07 (dd, J = 1.3, 7.7 Hz, 1 H), 8.32 (s, 1 H), 8.33 (s, 1 H), 8.80 (dd, J = 1.0, 8.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.3, 51.9, 120.8, 122.7, 123.9, 124.2, 125.5, 127.6, 128.0, 129.7, 130.1, 130.4, 132.1, 134.0, 140.1, 148.5, 167.7 ppm. HRMS (ESI): calcd. for $C_{17}H_{13}NO_4Na$ [M + Na]$^+$ 318.0736; found 318.0732.

Methyl 3-Isopropyl-8-nitrophenanthrene-9-carboxylate (15): Purification by flash chromatography (20% EtOAc/petroleum ether) gave the desired product **15** as a white solid (249 mg, 77%). M.p. 155 °C. IR (KBr): $\tilde{\nu}$ = 1529, 1718, 2927, 2962, 3055 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (d, J = 7.0 Hz, 6 H), 3.22 (sept, J = 7.0 Hz, 1 H), 3.91 (s, 3 H), 7.63 (dd, J = 1.5, 8.3 Hz, 1 H), 7.74 (dd, J = 7.7, 8.3 Hz, 1 H), 7.94 (d, J = 8.1 Hz, 1 H), 8.15 (dd, J = 1.3, 7.7 Hz, 1 H), 8.42 (s, 1 H), 8.47 (s, 1 H), 8.97 (d, J = 8.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 35.0, 52.0, 120.2, 121.0, 124.0, 124.4, 125.7, 127.7, 128.6, 130.1, 130.6, 132.5, 134.1, 148.7, 150.9, 167.7 ppm. HRMS (ESI): calcd. for $C_{19}H_{17}NO_4Na$ [M + Na]$^+$ 346.1049; found 346.1047.

Methyl 8-Nitro-2-(trifluoromethyl)phenanthrene-9-carboxylate (16): Purification by flash chromatography (10% EtOAc/petroleum ether, then 20% EtOAc/petroleum ether) gave the desired product **16** as a white powder (269 mg, 77%). M.p. 204–205 °C. IR (KBr): $\tilde{\nu}$ = 1523, 1725, 2925, 2957, 3078 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.93 (s, 3 H), 7.85 (dd, J = 7.7, 8.3 Hz, 1 H), 8.02 (dm, J = 8.7 Hz, 1 H), 8.25–8.30 (m, 2 H), 8.49 (s, 1 H), 8.80 (d, J = 8.7 Hz, 1 H), 8.99 (dd, J = 1.1, 8.6 Hz, 1 H) ppm. HRMS (ESI): calcd. for $C_{17}H_{10}NO_4F_3Na$ [M + Na]$^+$ 372.0454; found 372.0453.

Methyl 3-Chloro-8-nitrophenanthrene-9-carboxylate (17): Purification by flash chromatography (20% EtOAc/petroleum ether) gave the desired product **17** as a white solid (252 mg, 80%). M.p. 204–205 °C. IR (KBr): $\tilde{\nu}$ = 1531, 1615, 1709, 1730, 2924, 3098 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 3 H), 7.67 (dd, J = 1.9, 8.5 Hz, 1 H), 7.77 (dd, J = 7.9, 8.3 Hz, 1 H), 7.93 (d, J = 8.5 Hz, 1 H), 8.20 (dd, J = 1.1, 7.7 Hz, 1 H), 8.38 (s, 1 H), 8.59 (t, J = 1.1 Hz, 1 H), 8.83 (dd, J = 1.3, 8.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 52.0, 119.9, 123.4, 125.0, 125.4, 127.2, 128.2, 129.2, 129.5, 131.1, 131.3, 132.0, 133.2, 135.3, 147.7, 166.8 ppm. HRMS (ESI): calcd. for $C_{16}H_{10}NO_4NaCl$ [M + Na]$^+$ 338.0190; found 338.0186.

Methyl 8-Cyanophenanthrene-9-carboxylate (18): Purification by flash chromatography (20% EtOAc/petroleum ether) gave the desired product **18** as a white solid (183 mg, 70%). M.p. 129–130 °C. IR (KBr): $\tilde{\nu}$ = 1726, 2221, 2923, 2953, 3003, 3039 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.1 (s, 3 H), 7.67–7.80 (m, 3 H), 7.93 (d, J = 7.8 Hz, 1 H), 8.02 (d, J = 7.4 Hz, 1 H), 8.15 (s, 1 H), 8.61 (d, J = 8.3 Hz, 1 H), 8.92 (d, J = 8.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.7, 109.8, 118.3, 122.7, 126.4, 127.7, 127.8, 128.2, 128.3, 129.2, 129.6, 130.2, 130.5, 131.3, 132.1, 134.9, 168.9 ppm. HRMS (ESI): calcd. for $C_{17}H_{11}NO_2Na$ [M + Na]$^+$ 284.0681; found 284.0677.

Methyl 3,8-Dimethylphenanthrene-9-carboxylate (19): Purification by flash chromatography (5% EtOAc/petroleum ether) gave the desired product **19** as a white solid (185 mg, 70%). M.p. 116–117 °C. IR (KBr): $\tilde{\nu}$ = 1710, 2948, 2970, 3018, 3058 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.63 (s, 6 H), 4.00 (s, 3 H), 7.42–7.48 (m, 2 H), 7.57 (dd, J = 7.1, 8.1 Hz, 1 H), 7.78 (d, J = 8.1 Hz, 1 H), 7.90 (s, 1 H), 8.46 (s, 1 H), 8.62 (d, J = 8.3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1, 22.3, 52.6, 121.1, 122.7, 126.6, 127.5, 127.6, 128.6, 128.7, 128.8, 129.0, 130.2, 131.1, 131.6, 134.5, 138.1, 171.9 ppm. HRMS (ESI): calcd. for $C_{18}H_{16}O_2Na$ [M + Na]$^+$ 287.1042; found 287.1051.

Methyl 8-Nitrophenanthrene-9-carboxylate (20): Purification by flash chromatography (5% EtOAc/petroleum ether, then 10% EtOAc/petroleum ether) gave the desired product **20** as a white solid (150 mg, 60%). M.p. 70 °C. IR (KBr): $\tilde{\nu}$ = 1712, 2942, 2968, 3058 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.66 (s, 3 H), 4.02 (s, 3 H), 7.48 (dm, J = 6.5 Hz, 1 H), 7.56–7.74 (m, 3 H), 7.89 (dd, J = 1.6, 7.6 Hz, 1 H), 7.94 (s, 1 H), 8.65 (app. t, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.0, 52.6, 121.1, 122.9, 126.8, 127.0, 127.3, 128.1, 128.9, 129.0, 129.6, 129.7, 130.3, 131.4, 131.6, 171.8 ppm. HRMS (ESI): calcd. for $C_{17}H_{14}O_2Na$ [M + Na]$^+$ 273.0886; found 273.0895.

Methyl 6-Methoxy-3-methyl-5,8-dioxo-5,8-dihydrophenanthrene-9-carboxylate (21): Purification by flash chromatography (40% EtOAc/petroleum ether) gave the desired product **21** as a very unstable yellow solid (161 mg, 52%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.60 (s, 3 H), 3.90 (s, 3 H), 4.06 (s, 3 H), 7.48 (d, J = 8.1 Hz, 1 H), 7.81 (d, J = 7.9 Hz, 1 H), 7.87 (s, 1 H), 8.24 (s, 1 H), 9.37 (s, 1 H) ppm. MS (ESI): m/z = 310 [M]$^+$, 296 [M – CH_2]$^+$.

Methyl 5,6-Dimethoxy-3-methyl-8-nitrophenanthrene-9-carboxylate (22): Purification by flash chromatography (20% EtOAc/petroleum ether) gave the desired product **22** as a white solid (117 mg, 33% yield). M.p. 173–175 °C. IR (KBr): $\tilde{\nu}$ = 1514, 1526, 1705, 2955, 3091 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.63 (s, 3 H), 3.89 (s, 3 H), 3.99 (s, 3 H), 4.09 (s, 3 H), 7.53 (d, J = 8.1 Hz, 1 H), 7.84 (d, J = 7.9 Hz, 1 H), 7.94 (s, 1 H), 8.24 (s, 1 H), 9.42 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.7, 52.0, 56.8, 60.3, 110.6, 117.5, 124.1, 126.6, 127.8, 128.9, 129.7, 129.8, 130.0, 133.3, 139.9, 144.1, 150.2, 151.1, 167.7 ppm. HRMS (ESI): calcd. for $C_{19}H_{17}NO_6Na$ [M + Na]$^+$ 378.0948; found 378.0955.

General Procedure for the Preparation of the Naphthoxindoles 21–26: Phenanthrene **10**–**19** (1 mmol), $Pd(OAc)_2$ (0.5–1.5 mol-%), and charcoal [90 wt.-%/$Pd(OAc)_2$] were mixed in MeOH (6 mL). The reaction mixture was stirred at 40 °C under H_2 for 18 h, then concentrated under reduced pressure, and the crude product was purified by flash chromatography to give the corresponding product.

Naphtho[3,2,1-*cd*]indol-5(4*H*)-one (24): Purification by flash chromatography (silica gel; 15% EtOAc/CH_2Cl_2), gave the desired product **24** (195 mg, 89%) as yellow powder. M.p. 230–231 °C. IR (KBr): $\tilde{\nu}$ = 1628, 1707, 2929, 3031, 3069, 3192 cm^{-1}. ^{1}H NMR (300 MHz, DMSO): δ = 7.09 (d, J = 7.1 Hz, 1 H), 7.63 (dd, J = 7.4, 8.3 Hz, 1 H), 7.76 (app. t, J = 8.1 Hz, 1 H), 7.87 (app. t, J = 7.1 Hz, 1 H), 8.25 (d, J = 8.3 Hz, 1 H), 8.34 (d, J = 8.0 Hz, 1 H), 8.52 (s, 1 H), 8.80 (d, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz DMSO): δ = 106.6, 115.5, 122.0, 123.7, 125.4, 126.4, 126.5, 127.2, 129.3, 129.4, 131.4, 131.9, 133.1, 138.4, 168.3 ppm. HRMS (ESI): calcd. for $C_{15}H_9NONa$ [M + Na]$^+$ 242.0576; found 242.0575.

9-Methylnaphtho[3,2,1-*cd*]indol-5(4*H*)-one (25): Purification by flash chromatography (30% EtOAc/petroleum ether) gave the desired product **25** as yellow powder (172 mg, 74%). M.p. 255–256 °C. IR (KBr): $\tilde{\nu}$ = 1606, 1629, 1688, 2921, 3020, 3093, 3184 cm^{-1}. ^{1}H NMR (300 MHz, DMSO): δ = 2.60 (s, 3 H), 7.05 (d, J = 7.1 Hz, 1 H), 7.54–7.62 (m, 2 H), 8.18 (d, J = 8.5 Hz, 2 H), 8.44 (s, 1 H), 8.56 (s, 1 H), 10.82 (s, 1 H) ppm. ^{13}C NMR (75 MHz DMSO): δ = 21.6, 106.5, 115.4, 122.3, 123.2, 124.5, 126.1, 126.3, 128.9, 129.1, 131.0, 131.6, 138.5, 139.4, 168.5 ppm. HRMS (ESI): calcd. for $C_{16}H_{11}NONa$ [M + Na]$^+$ 256.0732; found 256.0738.

9-Isopropylnaphtho[3,2,1-*cd*]indol-5(4*H*)-one (26): Purification by flash chromatography (20% EtOAc/petroleum ether, then 30% EtOAc/petroleum ether) gave the desired product **26** as a yellow solid (183 mg, 70%). M.p. 180–181 °C. IR (KBr): $\tilde{\nu}$ = 1608, 1631, 1707, 2954, 3023, 3071, 3173 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (d, J = 7.0 Hz, 6 H), 3.22 (sept, J = 7.0 Hz, 1 H), 7.11 (d, J = 7.3 Hz, 1 H), 7.56–7.61 (m, 2 H), 8.07 (d, J = 8.5 Hz, 1 H), 8.12 (d, J = 8.3 Hz, 1 H), 8.42 (s, 1 H), 8.45 (s, 1 H), 9.28 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 34.7, 106.9, 115.9, 120.5, 122.9, 124.3, 126.4, 126.9, 127.3, 128.6, 131.7, 131.9, 132.5, 137.5, 150.4, 170.2 ppm. HRMS (ESI): calcd. for $C_{18}H_{15}NONa$ [M + Na]$^+$ 284.1045; found 284.1046.

8-(Trifluoromethyl)naphtho[3,2,1-*cd*]indol-5(4*H*)-one (27): Purification by flash chromatography (5% EtOAc/CH_2Cl_2) gave the desired product **27** as a yellow powder (241 mg, 84%). M.p. 234–235 °C. IR (KBr): $\tilde{\nu}$ = 1624, 1701, 2924, 3025, 3072, 3172 cm^{-1}. ^{1}H NMR (200 MHz, [D_8]THF): δ = 7.07 (d, J = 7.3 Hz, 1 H), 7.63 (app. t, J = 7.3 Hz, 1 H), 8.03 (dd, J = 1.8, 8.5 Hz, 1 H), 8.21 (d, J = 8.4 Hz, 1 H), 8.54 (s, 1 H), 8.63 (s, 1 H), 8.92 (d, J = 8.7 Hz, 1 H), 9.89 (br. s, 1 H) ppm. HRMS (ESI): calcd. for $C_{16}H_8NONaF_3$ [M + Na]$^+$ 288.0630; found 288.0593.

9-Chloronaphtho[3,2,1-*cd*]indol-5(4*H*)-one (28): Purification by flash chromatography (10% EtOAc/CH_2Cl_2), gave the desired product **28** as a yellow powder (225 mg, 89%). M.p. 301 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1603, 1630, 1717, 3093, 3186 cm^{-1}. ^{1}H NMR (200 MHz, DMSO): δ = 7.11 (d, J = 7.2 Hz, 1 H), 7.64 (dd, J = 7.3, 8.4 Hz, 1 H), 7.81 (dd, J = 2.0, 8.5 Hz, 1 H), 8.32 (d, J = 8.4 Hz, 1 H), 8.38 (d, J = 8.7 Hz, 1 H), 8.56 (s, 1 H), 8.91 (d, J = 2.0 Hz, 1 H), 10.9 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz DMSO): δ = 107.3, 115.8, 122.4, 123.3, 125.7, 125.9, 125.9, 127.6, 129.7, 131.7, 132.7, 133.7, 134.4, 138.6, 168.2 ppm. HRMS (ESI): calcd. for $C_{15}H_8NONaCl$ [M + Na]$^+$ 276.0186; found 276.0180.

1,2-Dimethoxy-9-methylnaphtho[3,2,1-*cd*]indol-5(4*H*)-one (29): Purification by flash chromatography (40% EtOAc/petroleum ether, then 10% EtOAc/CH_2Cl_2), gave the desired product **29** as a yellow powder (208 mg, 71%). M.p. 219–221 °C. IR (KBr): $\tilde{\nu}$ = 1635, 1701, 2939, 3061, 3088, 3191 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.67 (s, 3 H), 4.02 (s, 3 H), 4.05 (s, 3 H), 6.94 (s, 1 H), 7.53 (dm, J = 8.1 Hz, 1 H), 8.02 (d, J = 8.3 Hz, 1 H), 8.18 (br. s, 1 H), 8.29 (s, 1 H), 9.20 (s, 1 H) ppm. ^{13}C NMR (75 MHz DMSO): δ = 22.1, 57.0, 59.8, 96.9, 116.4, 120.1, 124.7, 126.6, 128.7, 130.9, 131.7, 131.8, 134.9, 139.1, 140.5, 153.4, 168.8 ppm. HRMS (ESI): calcd. for $C_{18}H_{15}NO_3Na$ [M + Na]$^+$ 316.0944; found 316.0949.

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