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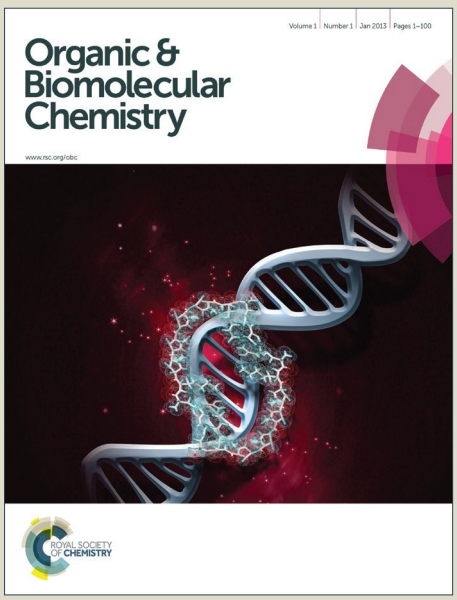

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ARTICLE

Synthesis of Cyclopenta-fused Polycyclic Aromatic Hydrocarbons Utilizing Aryl-substituted Anilines

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Yeojin Choi,[a] Tanmay Chatterjee,[a] Jun Kim,[a] Jun Soo Kim,[b] and Eun Jin Cho*,[a]

Cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs), potentially electronically and biologically highly active materials, were synthesized from readily available 2-aryl-substituted anilines. Reactions occur under extremely mild, room temperature conditions using ^{t}BuONO as the sole reagent. The use of nitrite source generates a reactive diazonium intermediate in situ that then reacts with a tethered polycyclic aromatic moiety by intramolecular aromatic substitution. This protocal could be presented as one of the simplest methods to access CP-PAHs.

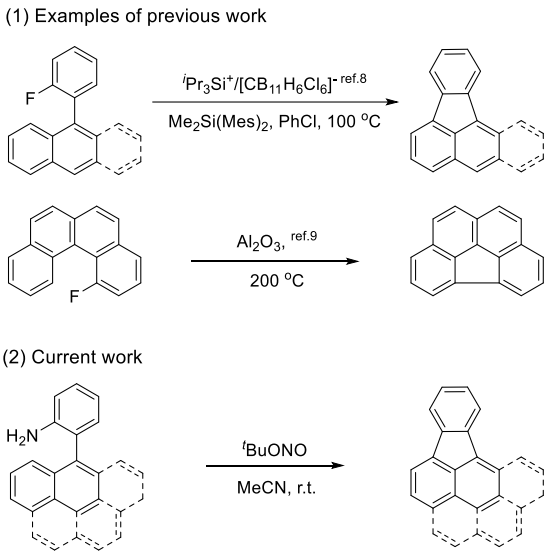
Introduction

Polycyclic aromatic hydrocarbons have received considerable attention as a class of useful materials.[1] Notably, cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) have been of great interest due to their high chemical, physical, and biological activities. These systems show high electron affinities, resulting in their use in many applications including various electronic devices such as organic photovoltaic devices (OPVs) and organic field-effect transistors (OFETs).[1a,1c,1e] In addition, CP-PAHs are important as biologically relevant species.[2] They can be used as DNA intercalators in chemotherapy to inhibit DNA replication in rapidly growing cancer cells.[2b,2c] Furthermore, they have been widely used in the study of biological effects because of their strong mutagenic and carcinogenic activities.[2a,2d]

This extensive use in a wide array of applications has necessitated the development of efficient and practical methods that allow easier access to these compounds. Various CP-PAHs have been synthesized mainly by Pd-catalyzed Heck-type processes,[3] Friedel-crafts reactions,[4] pentannulations,[5] transannular cyclization,[6] or Fe-mediated Scholl[7] reactions. Moreover, several methods were recently developed using silylium-[8] or Al_2O_3[9]-mediated aryl couplings of fluoroarenes [Scheme 1. (1)]. Despite these great advances, many of these methods are still restricted by limited substrate scope and harsh reaction conditions including high temperatures or long reaction times. Herein, we report a metal-free mild protocol for the synthesis of various CP-PAHs using easily accessible 2-aryl-substituted anilines [Scheme 1. (2)]. In this process, the use of a nitrite source generates a reactive diazonium intermediate in situ,[10] that then reacts with a tethered polycyclic aromatic moiety by intramolecular aromatic substitution at room temperature.[11] *Tert*-butyl nitrite (^{t}BuONO) was used as the sole reagent, and the reactivity was controlled by its stoichiometry and substrate concentration.

Results and discussion

We commenced the investigation by using 2-(phenanthren-9-yl)aniline (**1a**) as the model substrate (Table 1). The use of 1.5 equiv. of ^{t}BuONO to diazotize the amine in DMSO (0.25 M) at room temperature produced the desired cyclized compound, benzo[*e*]acephenanthrylene (**2a**), in 54% yield along with deaminated product **3a** (20%) as a side product (Table 1, entry 1). The selection of a suitable solvent was critical to the



Scheme 1 Synthesis of CP-PAHs.

[a]*Department of Chemistry, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu, Seoul 06974, Republic of Korea. E-mail: ejcho@cau.ac.kr, http://ejcho.cau.ac.kr*
[b] *Department of Chemistry & Nanoscience, Ewha Womans University, Seoul 03760, Republic of Korea.*

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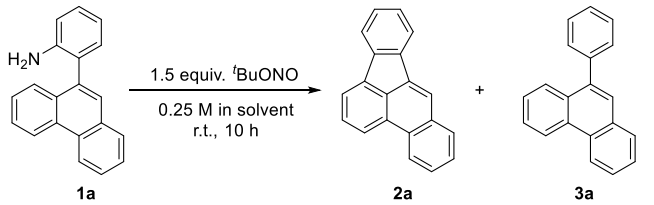
reactivity of the process. Among the various solvents tested (including DMSO, DMF, DCM, dimethyl carbonate, THF, MeOH, and MeCN), MeCN afforded the best results (**2a** in 80% yield; Table 1, entries 1-7). The use of isopentyl nitrite as the diazotization reagent also produced the desired product **2a**, but the process required longer reaction times (Table 1, entries 8 and 9). The rate of diazonium salt generation might be slower with isopentyl nitrite than with ^{t}BuONO. We further conducted optimization studies including the stoichiometry of ^{t}BuONO, substrate concentration, and addition of additives. While the amount of ^{t}BuONO did not significantly affect the efficiency in terms of yield (Table 1, entries 7 and 10-12), the concentration was found to be critical in the reaction; the yield decreased greatly at higher concentrations (Table 1, entries 7 and 13-16). The additional use of an inorganic base (K_3PO_4) and higher temperature (80 °C) prevented the desired transformation, resulting only in the formation of deaminated product **3a** (Table 1, entries 17 and 18). The reaction was also attempted with a triscyclometalated Ir(III) complex, *fac*-Ir(ppy)$_3$ which is known to be activated by visible light and leads to a variety of radical-mediated photoredox catalysis (Table 1, entry 19).[12,13] However, the use of a photocatalyst did not affect the reactivity and **2a** was afforded in similar yield. Interestingly, the reactivity decreased under oxygen atmosphere with slower conversion (Table 1, entry 20).[14] A variety of 2-aryl-substituted aniline derivatives were investigated under these optimized conditions. First, 2-(phenanthren-9-yl)aniline derivatives were tested in 0.5 mmol scale (Scheme 2). While **1a** and **1b** smoothly underwent cyclization to afford **2a** and **2b**, respectively, the substrates containing electron-withdrawing substituents on the aniline ring (**1c** and **1d**) exhibited less reactivity toward the transformation. The corresponding 6-substituted benzo[*e*]acephenanthrylenes **2c** and **2d** were generated in low yield. It is likely that the electron withdrawing substituent affected reactivity in the diazotization step. Interestingly, a regioisomer **2ci** (10%) was also detected in the reaction of **1c**, indicating that radical species might be involved in the transformation by a minor radical pathway despite very low yield of **1c'**.[15]

The compound 2-(anthracen-9-yl)aniline (**4**) also reacted to afford benzo[*a*]aceanthrylene (**5**), but the product showed partial decomposition during the purification process (Scheme 3).[8]

The electron density of the polycyclic aromatic part might also affect the reactivity. Pyrenyl-substituted substrates (**6a** and **6b**) showed slightly higher reactivity than phenanthrenyl-substituted substrates to afford the corresponding indeno[1,2,3-*cd*]pyrene derivatives, **7a** and **7b** (Scheme 4). In the case of **6c** containing Cl substituent, the reaction showed low conversion, providing 18% yield of cyclized product **7c** along with 50% of deaminated product and 24% of recovered starting substrate **6c**.

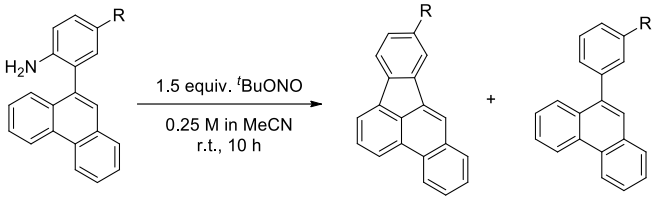
Table 1 Optimization of the reaction conditions[a]



1a 2a 3a

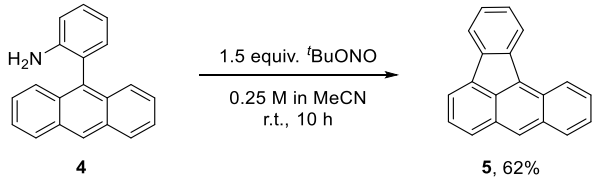
Entry	Solvent	Variations	Yield(%)[b]	
			2a	3a
1	DMSO		54	20
2	DMF		12	61
3	DCM		29	46
4	dimethyl carbonate		trace	72
5	THF		trace	91
6	MeOH		-	-
7	MeCN		80	6
8	MeCN	1.5 equiv. isopentyl nitrite	40	3
9	MeCN	1.5 equiv. isopentyl nitrite, 24 h	65	7
10	MeCN	1.2 equiv. ^{t}BuONO	65	25
11	MeCN	2 equiv. ^{t}BuONO	75	5
12	MeCN	3 equiv. ^{t}BuONO	73	12
13	MeCN	1.0 M	49	6
14	MeCN	0.5 M	65	6
15	MeCN	0.2 M	79	4
16	MeCN	0.1 M	77	4
17	MeCN	2 equiv. K_3PO_4	-	45
18	MeCN	80 °C	-	88
19	MeCN	1 mol% *fac*-Ir(ppy)$_3$, visible light	78	10
20	MeCN	O_2 bubbling	36	4

[a]Reaction scale: **1a** (0.1 mmol); [b]the yield was determined by gas chromatography.



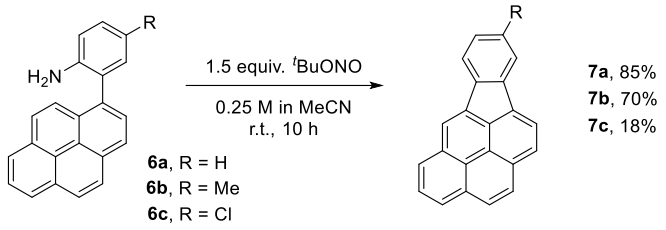
1a, R = H — **2a**, 75% — **3a**, 5%
1b, R = Me — **2b**, 55% — **3b**, 23%
1c, R = Cl — **2c**, 20% — **3c**, 55%
1d, R = CO_2Me — **2d**, 39% — **3d**, 41%

Scheme 2 Synthesis of benzo[*e*]acephenanthrylene derivatives (**2a**-**2d**); **1** (0.5 mmol scale), isolated yield.

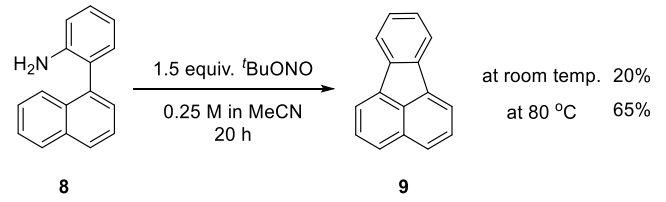


4 **5**, 62%

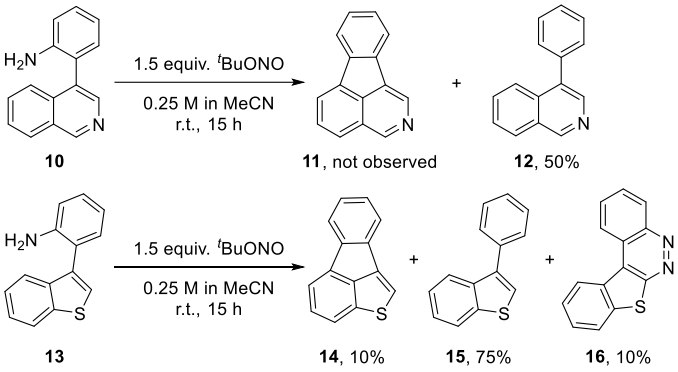
Scheme 3 Synthesis of benzo[*a*]aceanthrylene (**5**); **4** (0.5 mmol scale).



Scheme 4 Synthesis of indeno[1,2,3-*cd*]pyrene derivatives (**7a**-**7c**); **6** (0.5 mmol scale), isolated yield.



Scheme 5 Synthesis of fluoranthene (**9**); **8** (0.5 mmol scale), isolated yield.



Scheme 6 Reactions of benzofused-heterocycle-substituted anilines.

On the other hand, 2-(naphthalen-1-yl)aniline (**8**) exhibited less reactivity so that its reaction did not proceed well at room temperature. Thus, it afforded fluoranthene (**9**) in only 20% yield. When the temperature was increased to 80 °C, **9** was obtained in 65% yield after 20 h (Scheme 5).

Benzo-fused heterocycle-substituted anilines were also tested as possible substrates for this transformation (Scheme 6). However, these reactions did not display good reactivity toward the intramolecular substitution reaction. The compound 2-(isoquinolin-4-yl)aniline (**10**) did not undergo cyclization, but afforded the deaminated product (**12**). The reaction of 2-(benzo[*b*]thiophen-3-yl)aniline (**13**) provided the desired product (**14**) only in 10% yield. The deaminated product (**15**, 75% yield) and benzo[4,5]thieno[2,3-*c*]cinnoline[16] (**16**, 10% yield) were also formed.

To understand the difference in reactivity dependent on the tethered polycyclic aromatic ring, the density functional theory (DFT, B3LYP/6-31G(d)) calculations were conducted. The orbital coefficients of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of diazonium intermediates, generated from **8**, **1a**, **6a**, and **13**,

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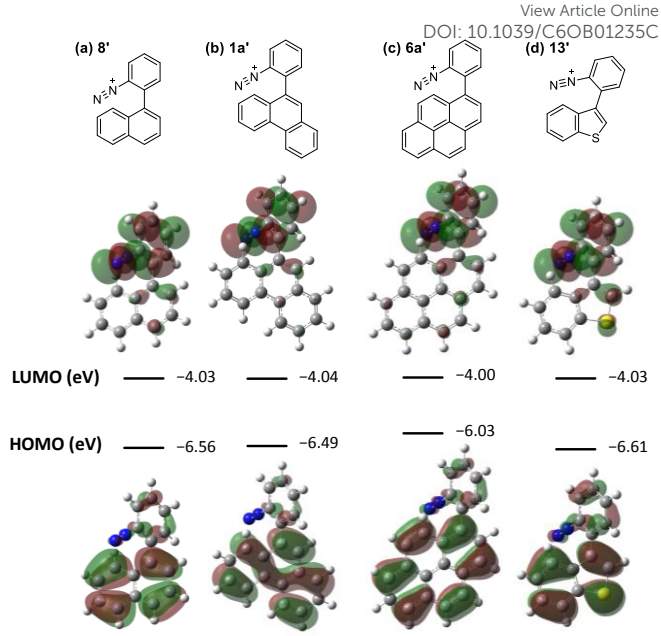
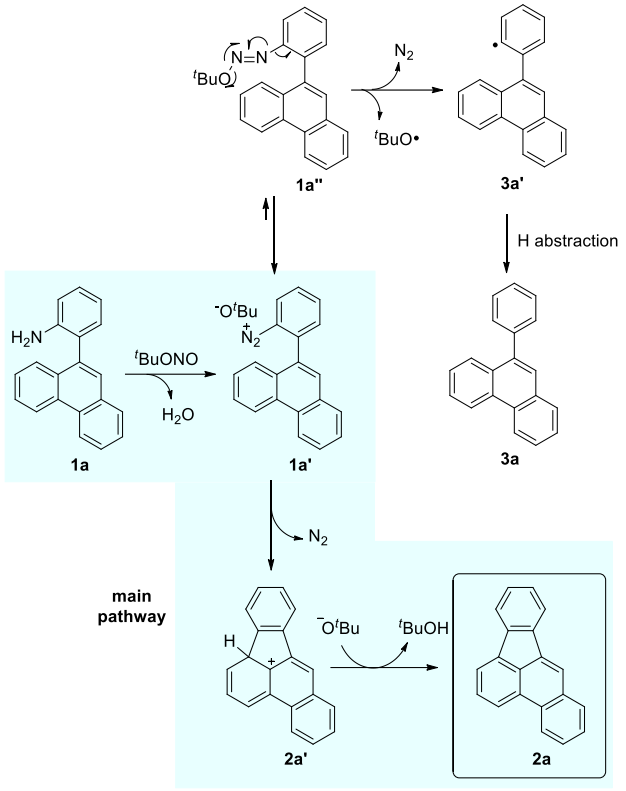


Figure 1 Calculated frontier molecular orbital profiles and energy levels for diazonium intermediates, **8'**, **1a'**, **6a'**, and **13'**, obtained by the DFT calculations with B3LYP functional and 6-31G(d) basis set.

are presented in Figure 1, as well as the HOMO-LUMO energy separation. In the figure, it is shown that the electron density in HOMO are localized mostly in the polycyclic aromatic ring whereas that in LUMO is in the diazotized aryl ring, implying the possibility of the charge transfer from the polycyclic aromatic ring to the diazotized aryl ring via the HOMO-LUMO interaction. When the HOMO-LUMO energy separation is reduced, the reactivity of CP-PAH synthesis becomes enhanced due to the higher efficiency of the charge transfer. In Figure 1, the HOMO-LUMO energy separation decreases in order of the intermediates **13'**> **8'**> **1a'**> **6a'**, consistent with our experimental findings that the reactivity is the greatest for **6a'** (containing pyrene moiety) followed by **1a'** (containing phenanthrene moiety), **8'** (containing naphthalene moiety) and **13'** (containing benzothiophene moiety). It is noted that the agreement is only qualitative. The difference in the HOMO-LUMO energy separation is not very significant between **8'** and **1a'** and there must be some other factors that additionally affect the reactivity. However, the HOMO-LUMO energy separation provides the qualitative explanation on the dependence of the reactivity on the polycyclic aromatic ring.

A proposed mechanism for this reaction, using **1a**, is outlined in Scheme 7. This process is initiated by the ^{t}BuONO-mediated diazotization of **1a** to form the corresponding diazonium compound (**1a'**) in situ. Its subsequent intramolecular aromatic substitution with the tethered phenanthrene moiety generates the corresponding benzo[*e*]acephenanthrylene, **2a**. However, considering the formation of deaminated side product (**3a**), we cannot exclude the radical pathway where the aryl radical (**3a'**) could be generated by a homolytic cleavage from compound (**1a''**) that is in equilibrium with **1a'**. The formation of **3a** is



Scheme 7 Proposed mechanism.

likely a result of hydrogen atom abstraction of aryl radical **3a'**. In addition, **3a'** could also undergo intramolecular cyclization by radical aromatic substitution to provide the desired product **2a** as a minor pathway (See *Scheme S1* in the SI).

Conclusions

We developed a simple method for the preparation of CP-PAHs. The process, based on in situ generation of diazonium salts, transforms readily available 2-aryl-substituted anilines into the target products by an intramolecular aromatic substitution. Notably, the reactions occur under extremely mild, room temperature conditions using ^{t}BuONO as the sole reagent. We present our protocol as one of the simplest methods to access potentially electronically and biologically highly valuable molecules, CP-PAHs.

Experimental

General reagent information

Anhydrous DCM and MeCN were purchased from Sigma-Aldrich chemical company in Sure-Seal bottles and degassed by repeated sonication under light vacuum and replenishing the atmosphere with argon. ^{t}BuONO was purchased from Acros Organics. All other reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI companies or Combi-Blocks. Gravity column chromatography was performed using Merck silica gel 60 (70-230 mesh).

General analytical information

The cyclopenta-fused polycyclic aromatic hydrocarbons were characterized by ^{1}H, ^{13}C NMR and FT-IR spectroscopy. NMR spectra were recorded on a Varian 600 MHz instrument (600 MHz for ^{1}H NMR and 151 MHz for ^{13}C NMR) and a Varian 300 MHz instrument (300 MHz for ^{1}H NMR). Copies of ^{1}H and ^{13}C NMR spectra can be found at the end of the Supporting Information. ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ^{1}H decoupling. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Nicolet iS 10 ThermoFisher FT-IR spectrometer. Reactions were monitored by GC-MS using the Agilent GC 7890B/5977A inert MSD with Triple-Axis Detector.

General procedure

Synthesis of substrates (**1a-1d**, **4**, **6a**-**6c**, **8** and **10**)

To 2-iodoaniline (1.10 g, 5 mmol) in toluene–EtOH–H_2O (4:1:1, 40 mL) at room temperature were added K_2CO_3 (1.04 g, 1.50 equiv.), phenanthren-9-ylboronic acid (1.33 g, 1.20 equiv.), and tetrakis(triphenylphosphine)-palladium (289 mg, 5.0 mol%). The reaction mixture was stirred at 100 °C for 4 h. After cooling to room temperature, the phases were separated and the aqueous phase was extracted with EtOAc. The organic layers were combined, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash silicagel-column chromatography, affording the desired product **1a**. Similarly, **1b**, **1c**, **1d**, **4**, **6a**, **6b**, **6c**, **8** and **10** were synthesized, using following substrates. In the case of **1b**, **4**, and **10**, DME–H_2O (1.5:1, 35 mL) was used as the solvent system. And for **13**, $Pd(dba)_2$/XPhos catalytic system was used in *n*-butanol.

For **1b**: 2-bromo-4-methylaniline, phenanthren-9-ylboronic acid
For **1c**: 2-iodo-4-chloroaniline, phenanthren-9-ylboronic acid
For **1d**: 2-methyl-4-amino-3-iodobenzoate, phenanthren-9-ylboronic acid
For **4**: 9-bromoanthracene, 2-aminophenylboronic acid pinacol ester
For **6a**: 2-iodoaniline, pyren-1-ylboronic acid
For **6b**: 2-bromo-4-mehtylaniline, pyren-1-ylboronic acid
For **6c**: 2-iodo-4-chloroaniline, pyren-1-ylboronic acid
For **8**: 2-iodoaniline, naphthalene-1-boronic acid
For **10**: 4-bromoisoquinoline, 2-aminophenylboronic acid pinacol ester
For **13**: 2-boromoaniline, benzo[*b*]thiophen-3-ylboronic acid

Synthesis of CP-PAHs

The oven-dried tube with magnetic bar was charged with the substrate (0.5 mmol) and MeCN (2 mL). After dissolving the substrate (warming with heat gun if there was solubility issue), 1.5 equiv. ^{t}BuONO was added to the tube. The reaction mixture was stirred for 10 h at room temperature (80 °C for **9** and **1c**). The reaction progress was monitored by TLC or gas chromatography. The reaction mixture was concentrated in vacuo and purified by flash silicagel-column chromatography. When required, the product was further purified by recrystallization (using ethanol) or by preparative thin layer chromatography. [For **1d** and **7b**, 0.2 M concentration of MeCN (1.5 mL) and DCM (1 mL) was used due to low solubility of the substrates.]

2-(phenanthren-9-yl)aniline (1a).[17] Light orange solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.84 (d, *J* = 8.0 Hz, 1H), 8.80 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.83 (s, 1H), 7.79–7.71 (m, 2H), 7.70 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.62 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.39 (dd, *J* = 8.0, 7.7 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.02 (dd, *J* = 7.7, 7.4 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 3.54 (s, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.65, 135.73, 131.90, 131.30, 130.87, 130.77, 130.30, 129.02, 128.80, 128.48, 128.46, 126.96, 126.96, 126.90, 126.87, 125.92, 123.06, 122.69, 118.50, 115.44; **IR (neat)**: ν_{max} = 3468, 3376, 2983, 1734, 1237, 1043, 736 cm^{-1}; ***R*$_f$** 0.65 (hex/EtOAc, 4/1).

4-methyl-2-(phenanthren-9-yl)aniline (1b). Light yellow sticky oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.83 (d, *J* = 8.2 Hz, 1H), 8.79 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.81 (s, 1H), 7.76–7.71 (m, 2H), 7.68 (dd, *J* = 8.2, 7.9 Hz, 1H), 7.61 (dd, *J* = 8.2, 8.1 Hz, 1H), 7.19

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(d, *J* = 8.1 Hz, 1H), 7.15 (s, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 3.43 (s, 2H), 2.42 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 142.16, 135.98, 131.96, 131.76, 130.93, 130.78, 130.31, 129.59, 128.80, 128.42, 127.70, 127.05, 126.96, 126.95, 126.85, 126.85, 126.12, 123.07, 122.70, 115.66, 20.65; **IR (neat)**: ν_{max} = 3373, 3015, 1616, 1502, 1285, 904, 722 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{21}H_{17}N$ [M+] 283.1361, found 283.1359; ***R*$_f$** 0.47 (hex/EtOAc, 4/1).

4-chloro-2-(phenanthren-9-yl)aniline (1c). White solid; m. p. 136–138 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.78 (d, *J* = 8.2 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.72 (s, 1H), 7.72–7.66 (m, 3H), 7.64 (dd, *J* = 8.0, 7.9 Hz, 1H), 7.56 (dd, *J* = 8.1, 8.0 Hz, 1H), 7.27–7.21 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 3.52 (s, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 143.46, 134.49, 131.82, 130.94, 130.92, 130.54, 130.47, 128.97, 128.93, 128.73, 127.45, 127.27, 127.21, 127.18, 127.15, 126.74, 123.26, 123.15, 122.81, 116.61; **IR (neat)**: ν_{max} = 3473, 3383, 3061, 1613, 1485, 1282, 904, 725 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_{14}ClN$ [M+] 303.0815, found 303.0812; ***R*$_f$** 0.49 (hex/EtOAc, 4/1).

methyl 4-amino-3-(phenanthren-9-yl)benzoate (1d). White solid; m. p. 215–217 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.79 (d, *J* = 8.3 Hz, 1H), 8.75 (d, *J* = 8.3 Hz, 1H), 7.99 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.75 (s, 1H), 7.73–7.67 (m, 2H), 7.67–7.62 (m, 2H), 7.54 (dd, *J* = 8.0, 7.9 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 2H), 3.86 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 167.42, 149.20, 134.54, 133.43, 131.88, 131.27, 130.95, 130.58, 130.55, 128.95, 127.25, 127.17, 127.13, 126.73, 124.95, 123.26, 122.81, 119.97, 114.41, 51.87 (overlapped peaks present); **IR (neat)**: ν_{max} = 3480, 3362, 1695, 1617, 1289, 1254, 769, 727 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{22}H_{17}NO_2$ [M+] 327.1259, found 327.1259; ***R*$_f$** 0.32 (hex/EtOAc, 4/1).

benzo[*e*]acephenanthrylene (2a).[18] White solid (95 mg, 75%); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.67 (d, *J* = 8.1 Hz, 1H), 8.47 (d, *J* = 8.2 Hz, 1H), 8.23 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 7.4 Hz, 1H), 7.94 (d, *J* = 6.4 Hz, 1H), 7.77 (dd, *J* = 7.6, 8.0 Hz, 1H), 7.70 (dd, *J* = 7.5, 7.6 Hz, 1H), 7.64 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.47–7.38 (m, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 140.92, 138.76, 137.25, 135.33, 134.26, 132.36, 130.96, 130.44, 128.43, 128.33, 127.82, 127.69, 127.26, 127.03, 123.39, 122.15, 121.89, 121.74, 121.61, 119.78; **IR (neat)**: ν_{max} = 2983, 1736, 1235, 1044, 777, 744, 735 cm^{-1}; ***R*$_f$** 0.45 (hex/EtOAc, 20/1).

10-methylbenzo[*e*]acephenanthrylene (2b).[19] Light yellow solid (73 mg, 55%); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.66 (d, *J* = 8.0 Hz, 1H), 8.43 (d, *J* = 8.1 Hz, 1H), 8.19 (s, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 7.0 Hz, 1H), 7.82 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.76–7.73 (m, 1H), 7.68 (dd, *J* = 8.0, 7.9 Hz 1H), 7.63 (dd, *J* = 8.0, 8.1 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 2.52 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.80, 138.16, 137.38, 137.16, 135.22, 134.03, 132.30, 130.74, 130.15, 128.91, 128.18, 127.55, 126.93, 126.71, 123.14, 122.68, 121.23, 121.18, 121.10, 119.12, 21.80; **IR (neat)**: ν_{max} = 2922, 2853, 1734, 1458, 1375, 773, 741 cm^{-1}; ***R*$_f$** 0.47 (hex/EtOAc, 20/1).

10-chlorobenzo[*e*]acephenanthrylene (2c) + 12-chlorobenzo[*e*]acephenanthrylene (2ci). Light yellow solid (28 mg, 20%); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.63 (d, *J* = 8.2 Hz, 1H), 8.61 (d, *J* = 8.1 Hz, 1H), 8.47 (d, *J* = 6.7 Hz, 1H), 8.45 (d, *J* = 7.5 Hz, 1H), 8.40 (d, *J* = 8.1 Hz, 1H), 8.15 (s, 1H), 8.10 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 6.7 Hz, 1H), 7.87 (s, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.77 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.72 (dd, *J* = 7.6, 7.5 Hz, 1H), 7.70 (dd, *J* = 6.8, 6.7 Hz, 1H), 7.69 (dd, *J* = 7.4, 7.3 Hz, 1H), 7.64 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.63 (dd, *J* = 7.0, 6.9 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.31 (dd, *J* = 7.6, 7.5 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 140.79, 140.24, 139.14, 137.44, 136.13, 135.80, 134.14, 134.04, 133.95, 133.84, 133.38, 132.25, 132.01, 131.04, 131.03, 130.57, 130.45, 130.26, 129.30, 128.53, 128.47, 128.28, 128.05, 127.77, 127.60, 127.53, 127.11, 127.05, 123.74, 123.34, 122.45, 122.47, 122.36, 122.30, 122.02, 120.20, 119.82 (overlapped peaks present); **IR (neat)**: ν_{max} = 3071, 2926, 1598, 1446, 903, 733 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_{11}Cl$ [M+] 286.0549, found 286.0550; ***R*$_f$** 0.65 (hex/EtOAc, 10/1).

methyl benzo[*e*]acephenanthrylene-10-carboxylate (2d). White solid (61 mg, 39%); m. p. 217–218 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.60 (s, 1H), 8.47 (d, *J* = 8.1 Hz, 1H), 8.23 (s, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.1 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.76 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.70 (dd, *J* = 8.1, 7.4 Hz, 1H), 7.64 (dd, *J* = 7.8, 7.4 Hz, 1H), 4.00 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 167.46, 144.85, 138.64, 136.00, 134.25, 134.09, 132.94, 130.92, 130.62, 129.83, 129.14, 128.48, 127.86, 127.58, 127.20, 123.34, 123.29, 122.93, 122.62, 121.15, 120.78, 52.39; **IR (neat)**: ν_{max} = 2951, 1716, 1433, 1294, 1257, 1232, 1093, 739 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{22}H_{14}O_2$ [M+] 310.0994, found 310.0992; ***R*$_f$** 0.42 (hex/EtOAc, 8/1).

2-(anthracen-9-yl)aniline (4). Orange oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.53 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.51–7.47 (m, 2H), 7.43–7.35 (m, 3H), 7.18 (d, *J* = 7.4 Hz, 1H), 6.99 (dd, *J* = 7.4, 7.3 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 3.32 (s, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 144.97, 133.26, 132.10, 131.68, 130.32, 129.02, 128.53, 127.00, 126.43, 125.82, 125.35, 123.48, 118.49, 115.47; **IR (neat)**: ν_{max} = 3470, 3378, 3049, 1611, 1499, 1452, 1296, 733 cm^{-1}; ***R*$_f$** 0.53 (hex/EtOAc, 4/1).

2-(pyren-1-yl)aniline (6a). Yellowish solid; m. p. 97–99 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.28 (d, *J* = 7.7 Hz, 1H), 8.25 (d, *J* = 6.8 Hz, 1H), 8.21 (d, *J* = 6.8 Hz, 1H), 8.14 (s, 2H), 8.10–7.95 (m, 4H), 7.43–7.31 (m, 2H), 7.08–7.00 (m, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 3.55 (s, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 144.60, 134.44, 131.73, 131.44, 131.15, 130.98, 129.13, 129.01, 128.15, 127.86, 127.64, 127.46, 126.37, 126.19, 125.49, 125.30, 125.23, 125.21, 125.10, 124.92, 118.54, 115.51; **IR (neat)**: ν_{max} = 3468, 3375, 2982, 1734, 1372, 1234, 1043, 848 cm^{-1}; ***R*$_f$** 0.41 (hex/EtOAc, 4/1).

4-methyl-2-(pyren-1-yl)aniline (6b). White solid; m. p. 148–150 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.26 (d, *J* = 7.7 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 1H), 8.12 (s, 2H), 8.06–8.01 (m, 2H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.95 (d, *J* = 9.1 Hz, 1H), 7.15 (d, *J* = 9.1 Hz, 1H), 7.13 (s, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 3.42 (s, 2H), 2.38 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 142.15, 134.74, 132.22, 131.54, 131.25, 131.01, 129.64, 129.18, 128.23, 127.89, 127.84, 127.67, 127.56, 126.64, 126.24, 125.65, 125.34, 125.28, 125.25, 125.15, 125.02, 115.78, 20.74; **IR (neat)**: ν_{max} = 3465, 3374, 3039, 1602, 1498, 1292, 847, 721 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{23}H_{17}N$ [M+] 307.1361, found 307.1363; ***R*$_f$** 0.39 (hex/EtOAc, 4/1).

4-chloro-2-(pyren-1-yl)aniline (6c). Light yellow solid; m. p. 113–114 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.24 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 7.7 Hz, 1H), 8.19 (d, *J* = 7.5 Hz, 1H), 8.13 (d, *J* = 8.9 Hz, 1H), 8.11 (d, *J* = 8.9 Hz, 1H), 8.06–8.02 (m, 2H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 9.1 Hz, 1H), 7.33–7.27 (m, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 3.51 (s, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 143.36, 132.94, 131.46, 131.34, 131.22, 131.13, 129.01, 128.86, 128.24, 127.96, 127.83, 127.46, 126.37, 125.57, 125.46, 125.31, 125.10, 124.88, 123.08, 116.61; **IR (neat)**: ν_{max} = 3343, 3382, 3039, 1611, 1484, 1290, 845, 811, 726 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{22}H_{14}ClN$ [M+] 327.0815, found 327.0816; ***R*$_f$** 0.43 (hex/EtOAc, 4/1).

indeno[1,2,3-*cd*]pyrene (7a).[20] Yellow solid (117 mg, 85%); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.54 (s, 1H), 8.38 (d, *J* = 7.4 Hz, 1H), 8.34 (d, *J* = 7.5 Hz, 1H), 8.25 (d, *J* = 7.7 Hz, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 8.07–8.03 (m, 2H), 8.02 (d, *J* = 6.7 Hz, 1H), 7.48 (dd, *J* = 7.3, 7.4 Hz, 1H), 7.44 (dd, *J* = 7.3, 7.5 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 142.09, 139.23, 135.92, 133.30, 132.25, 130.89, 130.84, 130.66, 128.76, 128.47, 127.38, 127.04, 127.02, 126.88, 126.73, 125.07, 123.44, 122.73, 121.96, 121.76, 121.62, 119.84; **IR (neat)**: ν_{max} = 2984, 1735, 1445, 1372, 1237, 1043, 841, 730 cm^{-1}; ***R*$_f$** 0.42 (hex/EtOAc, 20/1).

9-methylindeno[1,2,3-*cd*]pyrene (7b). Yellow solid (102 mg, 70%); m. p. 154–156 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.50 (s, 1H), 8.38 (d, *J* = 7.5 Hz, 1H), 8.33 (d, *J* = 7.7 Hz, 1H), 8.24 (d, *J* = 7.5 Hz, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 8.03 (dd, *J* = 7.6, 7.5 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.84 (s, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 2.55 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 142.37, 138.56, 136.65, 136.03,

133.41, 132.38, 131.28, 130.81, 130.66, 128.61, 127.82, 127.36, 126.87, 126.81, 126.72, 125.01, 123.34, 122.63, 122.48, 122.01, 120.99, 119.72, 22.18; **IR (neat)**: ν_{max} = 3038, 2919, 1617, 1455, 904, 831, 740 cm^{-1}; R_f 0.40 (hex/EtOAc, 20/1).

9-chloroindeno[1,2,3-*cd*]pyrene (7c). Yellow solid (28 mg, 18%); **IR (neat)**: ν_{max} = 3037, 2926, 1739, 1373, 1230, 1217, 844 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{22}H_{11}Cl$ [M+] 310.0549, found 310.0552; R_f 0.60 (hex/EtOAc, 10/1).

2-(naphthalen-1-yl)aniline (8).[21] White solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.61–7.57 (m, 1H), 7.54 (dd, *J* = 8.3, 8.2 Hz, 1H), 7.49 (d, *J* = 6.9 Hz, 1H), 7.48–7.44 (m, 1H), 7.30 (dd, *J* = 7.7, 7.4 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 6.95–6.90 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.49 (s, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.52, 137.16, 134.01, 131.87, 131.39, 128.95, 128.50, 128.16, 127.77, 126.44, 126.23, 126.20, 126.06, 126.00, 118.49, 115.48; **IR (neat)**: ν_{max} = 3468, 3379, 3056, 1614, 1495, 1297, 779, 751 cm^{-1}; R_f 0.43 (hex/EtOAc, 4/1).

fluoranthene (9).[22] White solid (66 mg, 65%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 7.0 Hz, 2H), 7.94 (dd, *J* = 5.8, 2.8 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.66 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.41 (dd, *J* = 5.8, 2.8 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.65, 137.17, 132.60, 130.20, 128.15, 127.74, 126.84, 121.73, 120.25; **IR (neat)**: ν_{max} = 3051, 1453, 1426, 910, 774, 746, 734 cm^{-1}; R_f 0.36 (hex/EtOAc, 100/1).

2-(isoquinolin-4-yl)aniline (10).[23] Dark brown solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.27 (s, 1H), 8.50 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.69–7.60 (m, 3H), 7.29 (dd, *J* = 7.9, 7.7 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.89 (dd, *J* = 7.5, 7.4 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 3.53 (s, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 152.57, 144.84, 143.84, 134.59, 131.60, 130.85, 130.55, 129.62, 128.62, 128.08, 127.61, 125.30, 122.06, 118.61, 115.66; **IR (neat)**: ν_{max} = 3327, 3201, 3027, 1614, 1489, 1455, 1299, 901, 747 cm^{-1}; R_f 0.30 (hex/EtOAc, 1/1).

2-(benzo[*b*]thiophen-3-yl)aniline (13).[24] Brown sticky oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.47 (s, 1H), 7.45–7.38 (m, 2H), 7.31–7.25 (m, 2H), 6.91 (dd, *J* = 7.5, 7.4 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 3.70 (s, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.82, 140.46, 138.33, 135.05, 131.25, 129.19, 124.82, 124.68, 124.40, 123.55, 122.94, 121.05, 118.39, 115.64; **IR (neat)**: ν_{max} = 3465, 3373, 3057, 1612, 1482, 1449, 1297, 906, 729 cm^{-1}; R_f 0.50 (hex/EtOAc, 4/1).

3-phenylbenzo[*b*]thiophene (15).[25] Yellow oil; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.01–7.85 (m, 2H), 7.65–7.54 (m, 2H), 7.50–7.43 (m, 2H), 7.44–7.31 (m, 4H).

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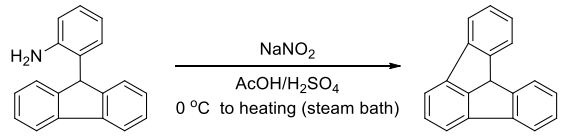

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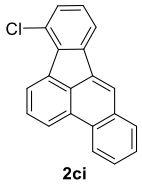

2ci

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