Facile one-pot synthesis of 10-aryl derivatives of 9-aminoanthracenes and 9,10-dihydroanthracen-9-imines

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Abstract

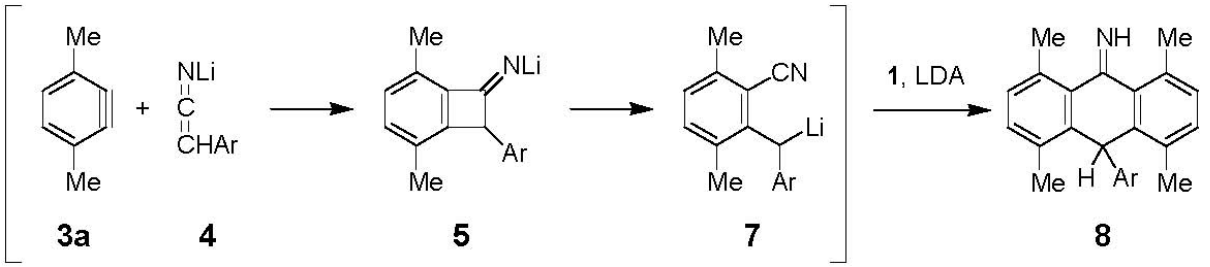
A series of 9-amino-10-arylanthracenes was easily prepared from bromobenzene and arylacetonitriles *via* benzyne and α-lithiated 2-arylmethylbenzonitrile intermediates. In addition, several mono-, di-, tri-, and tetra-*peri*-substituted derivatives of 10-aryl-9-aminoanthracenes and 9,10-dihydroanthracen-9-imines were obtained from the reaction of the respective bromoarenes as precursors of *in situ* generated benzyne, 3-methoxy-, 6-methoxy-3-methyl-, and 3-,6-dimethoxybenzyne with preformed α-lithiated 2-arylmethyl-benzonitriles.

Keywords: Benzyne, nucleophilic addition, amine-imine tautomerism, *peri*-substituted anthracene derivatives

Introduction

Substituted benzynes (generated *in situ* by the reaction of a bromoarene with LDA) generally react with α-lithiated arylacetonitriles yielding the rearrangement products 2-benzylbenzonitriles by a tandem addition-rearrangement pathway[1,2] or α-arylated arylacetonitriles by the usual aryne mechanism.[3] However, 3,6-dimethylbenzyne **3a** reacts with lithiated arylacetonitriles **4** to give 1,4,5,8-tetramethyl-9,10-dihydroanthracen-9-imines **8** (Scheme 1).[4] Presumably, the imines **8** are formed by an initial non-concerted [2+2]

cycloaddition of **3a** and **4** to give the benzocyclobutene intermediate **5** which fragments to the α-lithiated 2-benzyl-3,6-dimethylbenzonitrile **7**. Usually, α-lithiated 2-benzonitriles simply await protonation to give 2-arylbenzonitriles. However, **7** undergoes [4+2] cycloaddition with another molecule of **3a** to give the observed product **8**. We have extended this reaction to include the preparation of 10-aryl derivatives of 9-amino-anthracenes and 9,10-dihydroanthracen-9-imines, and report the results herein.



Scheme 1

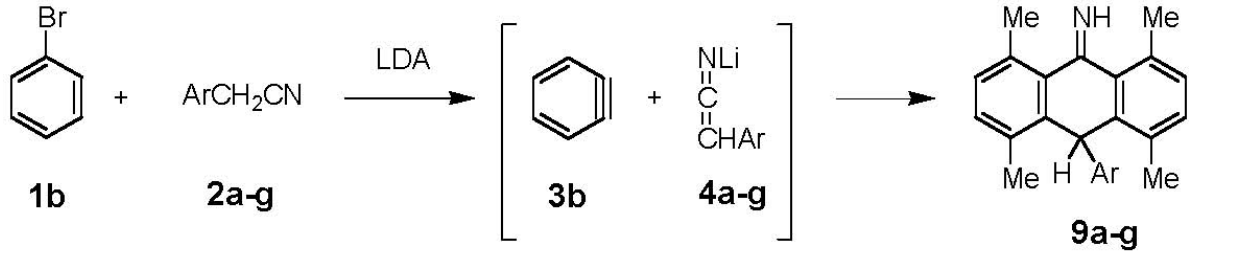
Prior to this study the only reported synthesis of 9-amino-10-phenylanthracene **9a** involved the successive nitration and reduction of 9-phenylanthracene which is commercially available though quite expensive.[5] Furthermore, the synthesis of 9-phenylanthracene involves a multi-step synthesis:[6] (a) Friedel-Crafts alkylation of 10-bromo-9-anthrone with benzene to give 10-phenyl-9-anthrone; (b) reduction of phenylanthrone to 9-phenylanthracene by distillation from zinc (c) nitration of phenylanthracene to 9-nitro-10-phenylanthracene; (d) reduction of the nitro group by stannous chloride. Furthermore, the method is not general because the initial Friedel-Craft reaction is limited to benzene; using other arenes like toluene, xylenes results only in formation of resinous products.

Results and Discussion

9-Amino-10-arylanthracenes

The reaction of bromobenzene **1b** with arylacetonitriles **2a-g** in the presence of LDA afforded 9-amino-10-arylanthracenes **9a**-g (52-79% yields) *via* benzyne **3b** and lithiated arylacetonitriles **4a-g** (Scheme 2). In addition, treatment of **1b** with 3-thienylacetonitrile **2h**

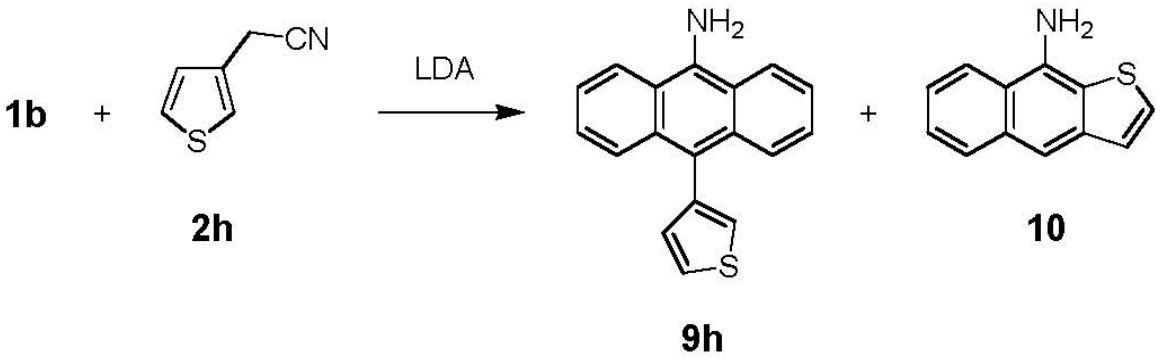
gave the corresponding 9-amino-10-(3-thienyl)anthracene **9h** and naphtho[2,3-*b*]thiophen-9-amine **10** (Scheme 3). Elemental analyses, melting points (sealed, evacuated tube) and yields of compounds **9** and **10** are given in Table 1. These compounds are air and light sensitive and should be stored in evacuated amber containers in order to prevent decomposition.



	Ar
a	C_6H_5
b	4-$MeOC_6H_4$
c	2-$MeOC_6H_4$
d	3-MeC_6H_4
e	1-naphthyl
f	3,4-$(MeO)_2C_6H_3$
g	2-pyridyl

Scheme 2

The structures of **9a-h** and **10** were established by IR, ^{1}H NMR, ^{13}C NMR, and UV spectra. For example, the IR spectra of **9a-h** exhibit two NH stretching absorption bands at about 3490 and 3410 cm^{-1}; the ^{1}HNMR spectra reveal signals at δ ~ 6.6 (NH) and a doublet at δ 8.3. The latter signal is attributed to deshielding of the peri-protons (*i.e.* 1,8-protons) by the lone pair electrons of the 9-amino group.



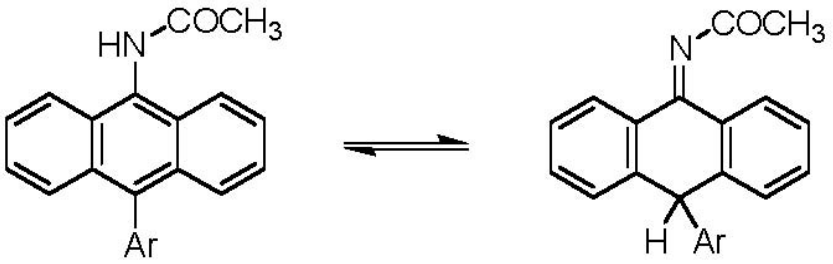
Scheme 3

Table 1. Yields, mp, and elemental analyses of compounds **9-11**

Compound (formula)	Yield %	mp °C	C, % Found (Calcd)	H, % Found (Calcd)	N, % Found (Calcd)
9a	74	165-166[a]			
9b ($C_{21}H_{17}NO$)	63	175-177	84.21 (84.25)	5.80 (5.72)	4.7 4(4.68)
9c ($C_{21}H_{17}NO$)	59	213-215	84.29 (84.25)	5.68 (5.72)	4.62 (4.68)
9d ($C_{21}H_{17}N$)	64	203-205	88.79 (89.01)	6.22 (6.05)	4.98 (4.94)
9e ($C_{24}H_{17}N$)	64	167-168.5	90.41 (90.25)	5.33 (5.46)	4.44 (4.39)
9f ($C_{22}H_{19}NO_2$)	79	240-242	80.04 (80.22)	6.03 (5.81)	4.32 (4.25)
9g ($C_{19}H_{14}N_2$)	75	177.5-179	84.6 (84.42)	5.13 (5.22)	10.28 (10.36)
9h ($C_{18}H_{13}NS$)	52	177-179	78.80 (78.51)	4.84 (4.76)	5.04 (5.09)[c]
10 ($C_{12}H_9NS$)	31	122-124	72.40 (72.33)	4.59 (4.55)	7.09 (7.03)[d]
11a	90	262-263[b]			
11b ($C_{23}H_{19}NO_2$)	83	274-276	80.93 (80.92)	5.69 (5.61)	4.18(4.10)
11c ($C_{23}H_{19}NO_2$)	85	229-231	80.99 (80.92)	5.60 (5.61)	4.13(4.10)
11d $C_{23}H_{19}NO$)	62	233-235	84.77 (84.89)	5.97 (5.89)	4.37 (4.30)
11e ($C_{26}H_{19}$)NO	86	327-329	86.44 (86.40)	5.43 (5.30)	3.95 (3.88)
11f ($C_{24}H_{21}NO_3$)	64	310-312	77.65 (77.61)	5.78 (5.70)	3.87 (3.77)
11g ($C_{20}H_{15}NOS$)	74	287-289	75.75 (75.68)	4.50 (4.76)	4.43 (4.41)

[a] lit[4] mp 162-163 ºC. [b] lit.[4] mp 261 ºC. [c] %S: 11.70 (11.61). [d] %S = 16.21 (16.09).

Subsequently, we found that compounds **9a-f,h** can be easily converted into air-stable *N*-acyl derivatives **11a-f,h** (62-90% yields) by treatment with acetic anhydride at 0 ºC (Table 1). Although these amides **11a-f,h** are stable in dimethylsulfoxide solution, they undergo partial tautomerization to the corresponding 9,10-dihydroanthracen-9-imine **12a-f,h** in deuterochloroform (eq. 1).



11a-f, h **12a-f, h**

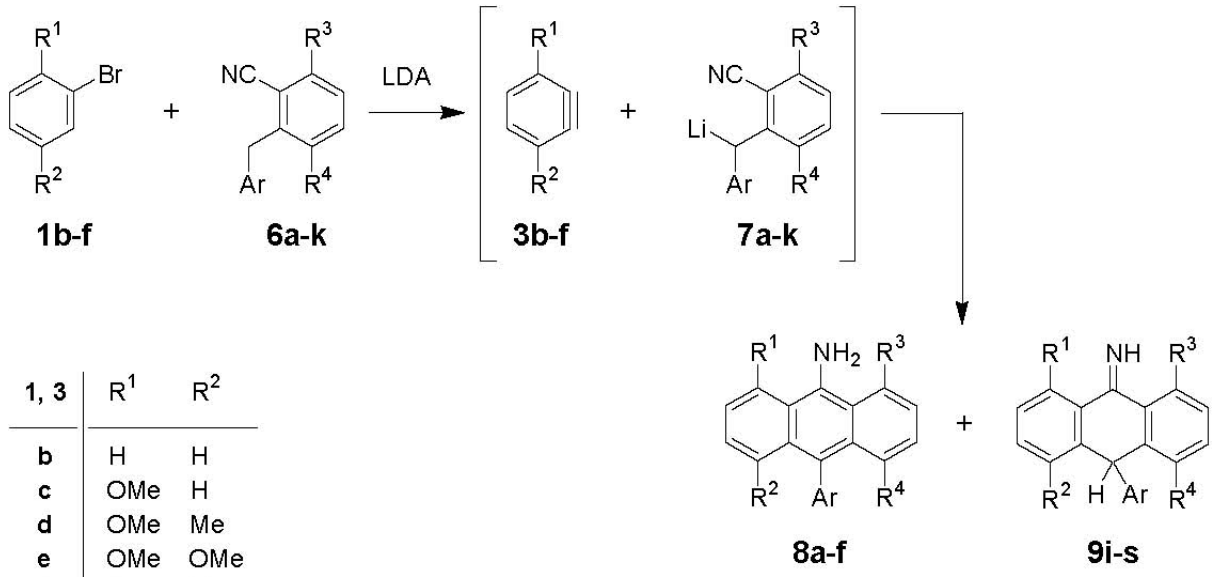
eq. 1

The ^{1}H NMR and ^{13}C NMR spectra of **11a-f,h** in DMSO-d_6 reveal characteristic signals in the range of δ 10.2 – 10.3 (NH), δ ~ 8.13 (1,8-H), and δ ~ 170 (C=O), respectively. However, the ^{1}H NMR and ^{13} C NMR spectra of $CDCl_3$ solutions of **11a-f,h** reveal the additional presence of **12a-f,h**. The ^{1}H NMR spectra of $CDCl_3$ solutions show two signals for the methyl protons of the acetyl group at δ 2.5 and δ ~1.7, two sets of doublets for the *peri* protons at δ ~ 7.9 and δ ~ 9.1, and a considerably broadened amide proton signal as well as a broadened signal in the range of δ 5.5 – 6.0 due to 5-H of the imino tautomers. The ^{13}C NMR spectra in $CDCl_3$ exhibit two methyl signals at δ 20.6 and 23.5 and two carbonyl signals at δ 170.2 and 174.6. The strong preference for the amide tautomers in dimethylsulfoxide solutions probably reflects the hydrogen bonding interactions between the solvent and the 9-amide hydrogen atom. Such interactions, of course, are absent in the imine tautomers.

peri-Substituted 9-amino-10-arylanthracenes

Furthermore, we prepared 1-methoxy- **9i-l** and 1-methoxy-4-methyl-substituted derivatives **9o-s** of 9-amino-10-arylanthracenes by generating benzyne **3b** from **1b** in the presence of α-lithiated 6-methoxy- **7a-d** and 6-methoxy-3-methyl-substituted 2-arylmethylbenzonitriles **7e-i** (Scheme 3 and Table 2). The intermediates **7a-h** were prepared from the corresponding benzonitriles **6a- h** which, in turn, were available from other studies.[7-9] In addition, 3-methoxybenzyne **3c** reacted with **7a** and **7d** to give the respective 10-phenyl- **9m** and 10-(naphth-1-yl)-substituted **9n** derivatives of 9-amino-1,8-dimethoxyanthracene. The reaction of 3,4,5-trimethoxybenzonitrile **6i** with **1d** gave a mixture of the 9-amino derivative **9s** and 9-imino derivative **8a.** These tautomers were readily separated by column chromatography on silica gel using hexane/ethyl acetate (4:1) as eluent. 1,4,5,8-Tetra-substituted 9,10-dihydroanthracen-9-imines **8b-d** were obtained from the reaction of the appropriate

benzonitriles **6i,e**,**f** with **1d** or **1e**, respectively.



1, 3	R^1	R^2
b	H	H
c	OMe	H
d	OMe	Me
e	OMe	OMe
f	Me	H

6, 7	R^3	R^4	Ar
a	OMe	H	Ph
b	OMe	H	4-$MeOC_6H_4$
c	OMe	H	3-MeC_6H_4
d	OMe	H	1-naphthyl
e	OMe	Me	Ph
f	OMe	Me	4-$MeOC_6H_4$
g	OMe	Me	3-MeC_6H_4
h	OMe	Me	1-naphthyl
i	OMe	Me	3,4,5-$(MeO)_3C_6H_2$
j	Me	H	2-$MeOC_6H_4$
k	H	Me	2-$MeOC_6H_4$

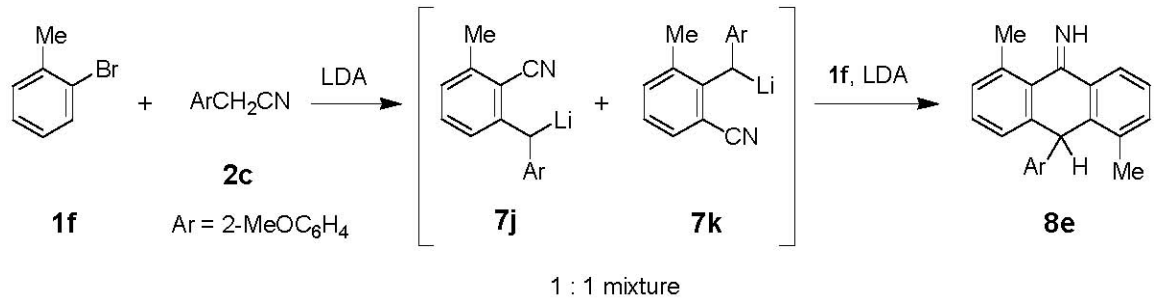
8	R^1	R^2	R^3	R^4	Ar
a	H	H	OMe	Me	3,4,5-$(MeO)_3C_6H_2$
b	OMe	Me	OMe	Me	4-$MeOC_6H_4$
c	OMe	OMe	OMe	Me	Ph
d	OMe	H	OMe	Me	4-$MeOC_6H_4$
e	H	Me	Me	H	2-$MeOC_6H_4$
f	Me	H	OMe	Me	4-$MeOC_6H_4$

9	R^1	R^2	R^3	R^4	Ar
i	H	H	OMe	H	Ph
j	H	H	OMe	H	4-$MeOC_6H_4$
k	H	H	OMe	H	3-MeC_6H_4
l	H	H	OMe	H	1-naphthyl
m	OMe	H	OMe	H	Ph
n	OMe	H	OMe	H	1-naphthyl
o	H	H	OMe	Me	Ph
p	H	H	OMe	Me	4-$MeOC_6H_4$
q	H	H	OMe	Me	3-MeC_6H_4
r	H	H	OMe	Me	1-naphthyl
s	H	H	OMe	Me	3,4,5-$(MeO)_3C_6H_2$

Scheme 4

The products were identified on the basis of IR, ^{1}H NMR, ^{13}C NMR and UV spectra. The UV spectra of the bright yellow 9-aminoanthracene derivatives exhibit characteristic absoprtion bands at λ_{max} 420, 380, 340 nm. The ^{1}H NMR spectra of **9i-9s** display characteristic downfield shifts (δ ~ 8.1) and coupling patterns (doublet of doublet) characteristic of *peri* protons (resulting from ^{3}J and ^{4}J). These coupling patterns are absent in the ^{1}H NMR spectra of 1,8-dimethoxy-substituted 9-aminoanthracenes **9m** and **9n**. Interestingly, ^{1}H NMR spectra of these two aminoanthracenes **9m** and **9n** are particularly revealing: the signals of the 9-amino protons occur at δ 8.10 and 8.26, respectively. These signals are considerably shifted downfield (approximately 1.5-1.75 ppm) as compared to those of the other 9-aminoanthracenes reported in this study. This shift probably reflects extended intramolecular H-bonding between the two amino hydrogen atoms and the adjacent 1,8-dimethoxy substituents. On the other hand, the ^{1}H NMR spectra of the imines **8a-d** exhibit a characteristic NH signal at δ ~ 11.0, and a 10-H singlet at δ 5.5, whereas the ^{13}C NMR spectra show characteristic C=N signals at δ ~ 186.

We were also able to introduce methyl group/s into the anthracene ring using 2-bromotoluene **1f** as aryne precursor in two ways. First, **1f** was treated with (2-methoxyphenyl)acetonitrile **2c** and LDA to yield a 1:1 mixture (determined by GC/MS and by integration of the respective aromatic hydrogen signals of each regioisomer) of lithiated 2-(2-methoxyphenylmethyl)-6-methylbenzonitrile **7j** and 2-(2-methoxy-phenylmethyl)-3-methylbenzonitrile **7k** (Scheme 5). This is consistent with the weak inductive effect of the methyl group in 3-methylbenzyne.[10] No attempt was made to separate the mixture, it rather was made to react with 2-bromotoluene **1f** and LDA to give a single product, 10-(2-methoxy-phenyl)-1,5-dimethyl-9,10dihydroanthracen-9-imine **8e** (62% yield); none of the 1,8- or 1,5-dimethyl regioisomers was detected. The structure of **8e** was confirmed by single crystal X-Ray spectrometry, the ORTEP[7] drawing is shown in Figure 1.



Scheme 5

Most likely, the exclusive formation of **8e** involves the regioselective addition of α-lithiated 5-methylbenzonitrile **7j** to the 2-position of the aryne **3f** and the opposite addition of **7k** to the 3-position of **3f** (Scheme 5). The regioselectve formation of **8e** from both isomeric α-lithiated nitrile intermediates **7j** and **7k** is caused by steric effects. Obviously, the carbanion **7j** adds exclusively to the 2-position of 3-methylbenzyne **3f**, whereas the carbanion **7k** adds to the 3-position of **3f**. The opposite regioselective additions by the two isomeric nucleophiles **7j** and can not be explained on the basis of the inductive effect of the methyl (which is weak) but rather on the steric effect of the methyl. Inspection of molecular models reveals that steric interactions between the methyl groups and the 9-imino and 10-aryl group in **8e** are less severe than those in which the two methyl groups flank either the 9-imino or the 10-aryl group. Consequently, the tricyclic ring in **8e** is not strongly puckered, and hence, it is more stabilized by resonance as compared to the situation of the other two possible isomers.

Table 2. Yields, mp, and elemental analyses of compounds **9i-9s** and **8a-f**

Compound (formula)	Yield (%)	mp °C	C, % Found (Calcd)	H, % Found (Calcd)	N, % Found (Calcd)
9i ($C_{21}H_{17}NO$)	57	175-177	84.31 (84.25)	5.77 (5.72)	4.60 (4.68)
9j ($C_{22}H_{19}NO_2$)	52	136-139	80.27 (80.22)	5.88 (5.82)	4.27 (4.25)
9k ($C_{21}H_{17}NO$)	32	157-159	84.40 (84.31)	6.15 (6.11)	4.50 (4.47)

Table 2. Continued

9l ($C_{25}H_{19}NO$)	48	152-155	85.88 (85.92)	5.53 (5.48)	4.05 (4.01)
9m ($C_{22}H_{19}NO_2$)	63	157-159	80.29 (80.22)	5.87 (5.81)	4.22 (4.25)
9n ($C_{26}H_{21}NO_2$)	38	214-216	82.37 (82.30)	5.59 (5.58)	3.72 (3.69)
9o ($C_{22}H_{19}NO$)	35	147-149	84.38 (84.31)	6.15 (6.11)	4.54 (4.47)
9p ($C_{23}H_{21}NO_2$)	68	212-214	84.45 (84.44)	6.11 (6.16)	4.14 (4.08)
9q ($C_{23}H_{21}NO$	64	204-205	84.42 (84.37)	6.49 (6.46)	4.31 (4.28)
9r ($C_{26}H_{21}NO$	51	188-190	86.01 (85.92)	5.88 (5.82)	3.88 (3.85)
9s ($C_{25}H_{25}NO_4$)	43	106-108	74.38 (74.42)	6.28 (6.25)	3.55 (3.47)
8a ($C_{25}H_{25}NO_4$)	21	178-180	74.50 (74.42)	6.32 (6.25)	3.52 (3.47)
8b $C_{25}H_{25}NO_3$)	68	221-223	77.55 (77.49)	6.62 (6.50)	3.66 (3.61)
8c ($C_{24}H_{23}NO_3$)	47	182-183	77.25 (77.19)	6.16 (6.21)	3.77 (3.75)
8d ($C_{23}H_{21}NO_2$)	54	191-193	80.46 (80.44)	6.22 (6.16)	4.11 (4.08)
8e($C_{23}H_{21}NO$)	62	180-182	84.43 (84.37)	6.70 (6.46)	4.32 (4.28)
8f ($C_{24}H_{23}NO_2$)	57	177-179	80.70 (80.64)	6.44 (6.49)	3.99 (3.92)

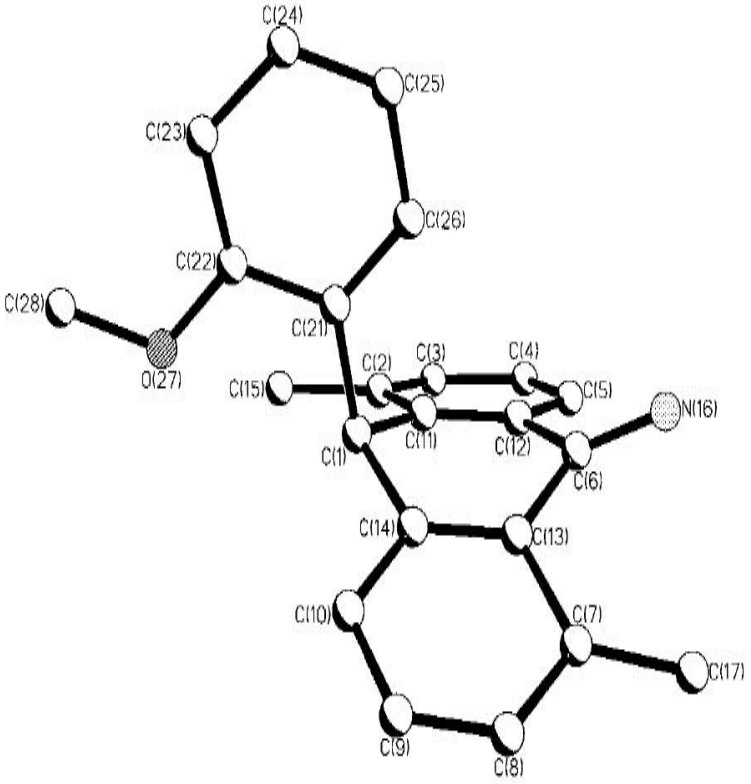
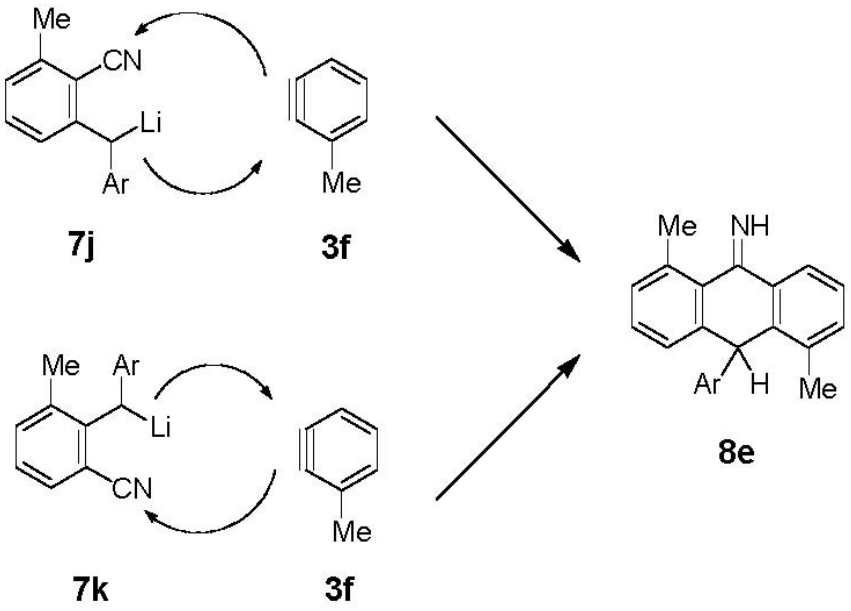
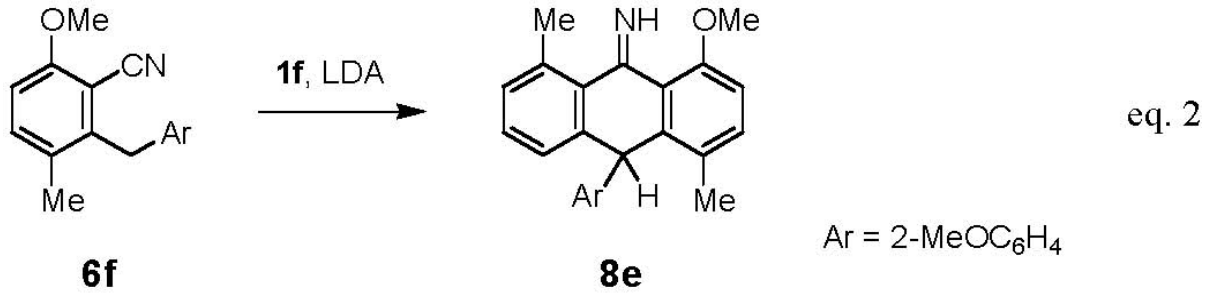


Figure 1. ORTEP drawing of **8e**



Scheme 6

Similarly, the reaction of bromotoluene **1f** with **6f** and LDA gave a single product, 1-methoxy-10-(4-methoxyphenyl)-4,8-dimethyl-9,10-dihydroanthracen-9-imine **8f** (57% yield) (eq 2). Again, nucleophilic addition occurred in such a way to place the two methyl groups on opposite sides of the tricyclic ring.



6f **8e** eq. 2

In conclusion, the otherwise not easily accessible 10-aryl-substituted derivatives of 9-aminoanthacenes **9** and 9,10-dihydroanthracen-9-imines **8** are readily prepared by the one-pot synthesis described herein. Utilizing readily available and inexpensive starting materials provides an efficient access to these products in multi-gram quantities.

Experimental Section

General Procedures. Melting points were taken on a Mel-Temp II capillary apparatus, and are uncorrected with respect to stem correction. IR spectra were recorded on a Nicolet Magna-IR^{TM} 550 FTIR spectrometer and the ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker AVANCE DRX-400 Multi-nuclear NMR spectrometer; chemical shifts were referenced to TMS as internal standard. The UV/VIS spectra were recorded on a Beckman DU 660 Spectrometer. Elemental analyses were obtained from SMU Analytical Services Laboratories.

Bromobenzene, arylacetonitriles, diisopropylamine, 2,2,6,6-tetramethylpiperidine, and *n*-BuLi were purchased from Aldrich Chemical Company. Diisopropylamine and 2,2,6,6-tetramethylpiperidine were refluxed over and distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from Na/benzophenone immediately prior to use. The glassware was

heated at 125 ^{o}C in an oven overnight prior to use. Benzyne reactions were carried out under an atmosphere of dry O_2-free N_2 utilizing a balloon.

General procedure for the preparation of 10-aryl-9-aminoanthracenes 9a-h

The reactions and the work-up were carried out in subdued light. Fresh LDA (40 mmol) was prepared in a flame-dried flask flushed with nitrogen by adding *n*-BuLi (40 mmol, 2.5 M in hexane) to a solution of diisopropylamine (4.0 g, 40 mmol) in THF (50 mL) at –70 ºC. After stirring for 10 min, the appropriate arylacetonitrile **2** (10 mmol) was added, and stirring was contiuned for 20 min to ensure complete anion formation. Bromobenzene **1b** (0.312 g, 20 mmol) was added, the resulting solution was allowed to warm to room temperature and was stirred for 6 h. The reaction was then quenched with saturated NH_4Cl solution (30 mL) and extracted with methylene chloride. The combined extracts were washed with dilute HCl then dried (Na_2SO_4) and concentrated (rotary evaporator) to give a crude material. Chromatography of this material on silica gel (hexane/ethyl acetate, 4:1) gave the pure product **9a-h**. The yields, mp and elemental analyses for **9a-h** are shown in Table 1 and spectral data of **12ag** are given below.

9-Amino-10-phenylanthracene (9a). IR (KBr): ν_{max} 3487, 3407 cm^{-1} (NH_2); UV ($CHCl_3$): λ_{max} [nm] (log ε): 272 (5.07) [lit.[5] 2.72 {5.07}], 360 (3.79), [lit. [5] 381 {3.74}] 420 (4.00) [lit.[5] 420 {4.00}]; ^{1}H NMR (DMSO-d_6): δ 6.60 (s, 2H), 7.32-7.34 (m, 2H), 7.40-7.42 (m, 5H), 7.51-7.57 (m, 4H), 8.33 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ117.9, 121.1, 123.7, 125.3, 125.9, 127.1, 127.4, 128.4, 130.6, 132.1, 137.9, 139.6

9-Amino-10-(4-methoxyphenyl)anthracene (9b). IR (KBr): ν_{max} 3474, 3388 cm^{-1} (NH_2); UV ($CHCl_3$): λ_{max} [nm] (log ε): 270 (4.59), 360 (3.55), 380 (3.73), 420 (3.78); NMR (DMSO-d_6): δ 3.95 (s, 3H), 6.64 (s, 2H), 7.09, 7.11 (AA' of 4-MeOC_6H_4), 7.27, 7.29 (BB'), 7,.31-7.35 (m, 2H), 7.42 (m, 2 H), 7.44 (d, *J* -= 8.8 Hz, 2H), 8.38 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.4, 113.9, 117.9, 121.1, 123.7, 125.2, 126.9, 127.2, 127.7, 130.9, 131.6, 133.1, 137.8, 158.8.

9-Amino-10-(2-methoxyphenyl)anthracene (9c). IR (KBr): ν_{max} 3490, 3403, 1665 cm^{-1} (NH_2); UV: ($CHCl_3$) λ_{max} [nm] (log ε): 269 (4.91), 360 (3.55), 3.80 (3.87), 420 (3.91); ^{1}H NMR (DMSO-d_6): δ 3.57 (s, 3H), 6.60 (s, 2 H), 7.12-7.13 (m, 2 H), 7.19-7.22 (m, 2 H), 7.24-7.30 (m, 6 H), 7.48-7.49 (m, 1 H), 8.32 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$): δ 55.8,

111.4, 118.1, 120.8, 121.2, 123.6, 125.2, 125.9, 127.5, 128.1, 129.0, 130.6, 133.8, 138.0, 158.6.

9-Amino-10-(3-methylphenyl)anthracene (9d). IR (KBr): ν_{max} 3476, 3386 cm^{-1} (NH_2); UV ($CHCl_3$): λ_{max} nm (log ε) 270 (4.79), 380 (3.49), 420 (3.85); ^{1}H NMR (DMSO-d_6): δ 2.44 (s, 3H), 6.65 (s, 2H), 7.10-7.11(m, 2H), 7.29-7.32 (m, 5H), 7.40- 7.44 (m, 3H), 8.40 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 21.6, 117.9, 121.1, 123.7, 125.2, 127.5, 127.8, 127.9, 128.3, 129.2, 130.5, 137.8, 138.0, 139.5.

9-Amino-10-(naphth-1-yl)anthracene (9e). IR (KBr): ν_{max} 3494, 3404 cm^{-1} (NH_2): UV ($CHCl_3$): λ_{max} [nm] (log ε) 270 (4.87), 360, (3.59), 380 (3.85), 420 (3.890; ^{1}H NMR (DMSO-d_6): δ 6.60 (s, 1H), 6.96-6.99 (m, 2H), 7.18-7.24 (m, 5H), 7.45-7.49 (m, 4H), 8.40 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ 118.0, 121.2, 123.8, 124.6, 125.5, 125.8, 126.0, 126.2, 126.9, 127.7, 127.9, 128.3, 130.0, 131.3, 133.9, 134.2, 127.3, 138.3.

9-Amino-10-(3,4-dimethoxyphenyl)anthracene (9f). IR (KBr): ν_{max} 3494, 3401 cm^{-1} (NH_2); UV ($CHCl_3$): λ_{max} [nm] (log ε) 272 (4.93), 360 (3.52) 380 (3.84), 420 (3.87); ^{1}H NMR (DMSO-d_6): δ 3.69 (s, 3H), 3.85 (s, 3H), 6.63 (s, 2H), 6.81 (dd, *J* = 8.0 Hz,1H), 6.84(s, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.26-7.29 (m, 4H), 7.45-7.48 (m, 2H), 7.47, 8.37 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ 56.0, 56.1, 111.2, 115.2, 117.9, 121.1, 123.7, 124.3, 125.3, 126.9, 127.7, 130.8, 132.9, 137.9, 148.2, 148.9.

9-Amino-10-(pyrid-2-yl)anthracene (9g). IR (KBr) ν_{max} 3493, 3401 cm^{-1} (NH_2); UV ($CHCl_3$): λ_{max} [nm] (log ε) 270 (4.91), 360 (3.51), 279 (3.88), 420 (3.91); ^{1}H NMR (DMSO-d_6): δ 6.60 (s, 2H), 7.30-7.35 (m, 4H), 7.45-7.46 (m, 4H), 7.90-7.91 (m, 1H), 8.35 (d, *J*= 8.8 Hz, 2H), 8.80 (br s, 1H); ^{13}C NMR ($CDCl_3$:) δ 117.7, 121.3, 122.0, 123.5, 125.1, 125.7, 125.9, 126.6, 127.7, 130.5, 136.3, 139.1, 150.1, 159.2. Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; 5.22; N, 10.36. Found: C, 84.49; H, 5.25; N, 10.42.

9-Amino-10-(thien-3-yl)anthracene (9h). IR (KBr): ν_{max} 3495, 3407 cm^{-1} (NH_2); UV ($CHCl_3$): λ_{max} [nm] (log ε) 270 (4.89), 361 (3.52), 379 (3.85), 420 (3.96): ^{1}H NMR (DMSO-d_6): δ 6.69 (s, 2H), 7.11 (m, 1H), 7.27-7.32 (m, 4H), 7.49-7.52 (m, 2H), 7.56-7.78 (m, 1H), 8.38 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 117.9, 121.1, 121.6, 123.8, 125.1, 125.2, 125.4, 127.5, 131.2, 131.6, 138.1, 139.26.

General procedure for the preparation of *N*-acetyl derivatives 11a-f,h

A 100 mg sample of the appropriate 9-aminoanthracene **9** was added to 5 mL of acetic

anhydride which was previously cooled to 0 ºC. Within 10 min, crystals of the amide precipitated. The crystals were collected by vacuum filtration, washed first with water then cold acetone, and dried. The amides were sufficiently pure for analysis. The spectral data for **11a-f,h** are given below.

***N*-Acetyl-9-amino-10-phenylanthracene (11a).** IR (KBr): ν_{max}**:** 3260, 1658 cm^{-1}; UV ($CHCl_3$): λ_{max} [nm] (log ε): 358 (3.81), 376 (3.93), 396 (3.92) (lit[5] 356 [3.81], 375, [3.93] 397 [3.92]); ^1H NMR ($CHCl_3$): δ 2.37 (s, 3H), 7.40-7.43 (m, 4H), 7.57-7.59 (m, 4H), 7.61-7.65 (m, 3H), 8.16 (d, *J* = 8.8 Hz, 2H), 10.27 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 23.4, 124.7, 126.2, 126.9, 128.4, 128.5, 129.2, 130.2, 130.6, 130.7, 131.4, 136.4, 128.5, 170.4.

***N*-Acetyl-9-amino-10-(4-methoxyphenyl)anthracene (11b).** IR (KBr): ν_{max} 3265, 1658 cm^{-1}; UV ($CHCl_3$): λ_{max} [nm] (log ε) 264 (5.10), 342 (3.61), 360 (3.85), 380 (3.91), 397 (3.93); ^1H NMR (DMSO-d_6): δ 2.36 (s, 3H), 3.88 (s, 3H), 7.18, 7.20 (AA' 4-$MeOC_6H_4$), 7.31 (BB'), 7.41 (t, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 8.5 Hz, 2H), 10.24 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 23.4, 55.7, 114.6, 124.7, 126.1, 126.2, 127.0, 128.4, 130.3, 130.4, 130.5, 133.5, 136.3, 159.3, 170.1.

***N*-Acetyl-9-amino-10-(2-methoxyphenyl)anthracene (11c).** IR (KBr): ν_{max} 3260, 1665 cm^{-1}; UV ($CHCl_3$): λ_{max} [nm] (log ε) 262 (4.98), 340 (3.61), 356 (3.82), 376 (3.97), 397 (3.95); ^1H NMR (DMSO-d_6): δ 2.36 (s, 3H), 3.58 (s, 3H), 7.18-7.20 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 8.4 Hz, 2H), 7.46 (m, 2H 7.51 (t, *J* = 8.4 Hz, 2H), 8.11 (d, *J* = 8.6 Hz, 2H), 10.20 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 23.4, 55.7, 112.1, 121.2, 124.7, 126.0, 126.1, 126.6, 126.7, 126.8, 128.9, 130.4, 132.7, 133.5, 158.0, 170.4.

***N*-Acetyl-9-amino-10-(3-methylphenyl)anthracene (11d).** IR (KBr): ν_{max} 3209, 1655 cm^{-1}; UV ($CHCl_3$): λ_{max} [nm] (log ε) 262 (4.86), 342 (3.54), 358 (3.83), 376 (3.98), 398 (3.94)**;** ^1H NMR (DMSO-d_6): δ 2.35 (s, 3H), 2.47(s, 3H), 7.17-7.20 (m, 2H), 7.39-7.41 (m, 3H), 7.43 (s, 1H), 7.49-7.55 (m, 5H), 8.13 (d, *J* = 8.4 Hz, 2H), 10.24 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 21.6, 23.4, 24.7, 126.1, 126.2, 127.0, 128.3, 128.5, 128.9, 129.0, 130.2, 130.5. 131.9, 136.6, 128.3, 138.5, 170.3.

***N*-Acetyl-9-amino-10-(naphth-1-yl)anthracene (11e).** IR (KBr): ν_{max} 3214, 1650 cm^{-1}; UV ($CHCl_3$): λ_{max} [nm] (log ε): 262 (4.96), 340 (3.56), 357 (3.86), 376 (4.02), 398 (4.01); ^1H NMR (DMSO-d_6): δ 6.82-6.84 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.29-7.33 (m, 3H), 7.48-7.54 (m, 4H, 7.56 (t, *J* = 7.9 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 1H), 8.08-8.20 (m, 4H), 10.30 (s,

1H); ^{13}C NMR (DMSO-d_6): δ 124.8, 126.1, 126.2, 126.4, 126.7, 127.1, 128.4, 128.8, 129.0, 129.5, 130.9, 131.0, 133.3, 133.9, 134.1, 136.0, 170.4.

***N*-Acetyl-9-amino-10-(3,4-dimethoxyphenyl)anthracene (11f).** IR (KBr): ν_{max} 3214 (HN), 1671 cm^{-1} (CO); UV ($CHCl_3$): λ_{max} [nm] (log ε) 262 (4.90), 342 (3.60), 354 (3.86), 376 (4.02), 398 (4.00)**;** ^{1}H NMR (DMSO-d_6): δ 2.34 (s, 3H), 3.71 (s, 3H), 3.86 (s, 3H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.97 (s, 1H), 7.19 ((d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.9 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 10.23 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 23.4, 56.2, 56.3, 112.5, 115.1, 123.6, 124.6, 125.9, 126.1, 127.2, 128.4, 130.3, 130.8, 136.5, 148.9, 149.3, 170.3.

***N*-Acetyl-9-amino-10-(thien-3-yl)anthracene (11h).** IR (KBr): ν_{max} 3261 (HN), 1665 cm^{-1} (CO); UV ($CHCl_3$): λ_{max} [nm] (log ε): 260 (4.98), 342 (3.54), 354 (3.86), 376 (4.01), 398 (3.98); ^{1}H NMR (DMSO-d_6): δ 7.24-7.25 (m, 1H), 7.45 (t, *J* = 7.45 Hz, 2H), 7.54 (t, *J* = 8.4 Hz, 2H), 7.56 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.86-7.88 (m, 1H), 8.14 (d, *J* = 8.8 Hz, 2H), 10.30 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 23.4, 124.7, 126.0, 126.1, 126.3, 126.9, 127.2, 128.4, 130.8, 131.2, 131.6, 138.1, 170.3.

General procedure for the preparation of peri-substituted 10-aryl-9-aminoanthracenes (9i-s) and 10-aryl-9,10-dihydroanthracen-9-imines (8a-f)

The reactions were carried out in similar manner as those described for 9-aminoanthracenes **9a-h** with the exception that the appropriate 2-arylmethylbenzonitrile **6** (10 mmol) and the bromoarene **1** (20 mmol) were added sequentially to a solution containing LDA (50 mmol) in THF (10 mL). The spectral data of the products **9i-s**, **8a-f** are given below.

9-Amino-1-methoxy-10-phenylanthracene (9i). IR (KBr): ν_{max} 3488, 3401 cm^{-1} (NH_2); UV ($CHCl_3$); λ_{max} [nm] (log ε): 270 (4.98), 370 (3.86), 388 (4.01), 437 (3.82); ^{1}H NMR (DMSO-d_6): δ 4.00 (s, 3H), 6.63 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 7.07 (t,*J* = 7.6 Hz, 1H), 7.25-7.30, (m,6H), 7.43-7.45 (m, 1H), 7.54 (t, J = 7.0 Hz, 2H), 8.32-8.35 (m, 1H); ^{13}C NMR (DMSO-d_6): δ 56.4, 101.3, 109.1, 117.5, 119.5, 121.9, 122.5, 123.5, 125.7, 126.3, 126.5, 127.4, 129.2, 131.3, 132.3, 133.1, 140.6, 143.6, 158.9.

9-Amino-1-methoxy-10-(4-methoxyphenyl)anthracene (9j). IR (KBr): ν_{max} 3488, 3401 cm^{-1} (NH_2): UV ($CHCl_3$): λ_{max} [nm] (log ε) 270 (4.93), 370 (3.84), 388 (4.02), 437 (3.83); ^{1}H NMR (DMSO-d_6): δ 3.67 (s, 3H), 4.00 (s, 3H), 6.63 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 8.4 Hz,

1H), 7.01, 7.03 (AA' 4-$MeOC_6H_4$), , 7.12, 7.14 (BB'), (d,*J* = 7.6 Hz, 2H), 7.13, (d, J = 7.6 Hz, 1H), 7.40-7.45 (m, 1H), 7.54 (m, 3H), 7.55 (d, *J* = 7.2 Hz, 1H), 8.32 (d, *J* = 7.6 Hz,1H); ^{13}C NMR (DMSO-d_6): δ 55.6, 56.4, 101.3, 109.2, 114.6, 117.6, 119.7, 121.6, 122.5, 123.5, 125.6, 126.4, 131.2, 131.6, 132.5, 133.3, 133.5, 143.4, 158.7, 158.9.

9-Amino-1-methoxy-10-(3-methylphenyl)anthracene (9k). ^{1}H NMR (acetone-d_6): δ 2.16 (s, 3H), 4.00 (s, 3H), 6.92 (t, *J* = 8.8 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 8.8 Hz, 1H), 7.43 (m, 4H), 7.66 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H).

9-Amino-1-methoxy-10-(naphth-1-yl)anthracene (9l). ^{1}H NMR (DMSO-d_6): δ 4.10 (s, 3H), 6.68 (d, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.98 (t, *J* = 8.4 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 3H), 7.20 (m. 3H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.46 (m, 2H), 7.70 (t, *J* = 8.0 Hz, 1H), 8.04 (t, *J* = 8.4 Hz, 2H), 8.33 (d, *J* = 8.0 Hz, 1H).

9-Amino-1,8-dimethoxy-10-phenylanthracene (9m). IR (KBr): ν_{max} : 3489, 3396 cm^{-1} (NH_2); UV ($CHCl_3$): λ_{max} [nm] (log ε) 260 (4.98), 380 (3.86), 399 (4.16), 446 (3.80); ^{1}H NMR (DMSO-d_6): δ 3.98 (s, 6H), 6.62 (d, *J* = 7.2 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.43-7.45 (m, 1 H), 7.51 (t, *J* = 7.2 Hz, 2H), 8.11 (s, 2H); [exchangeable with D_2O). ^{13}C NMR (DMSO-d_6): δ 56.5, 101.5, 109.1, 119.2, 120.3, 126.3, 127.3, 129.3, 132.3, 133.7, 141.4, 146.3, 159.2.

9-Amino-1,8-dimethoxy-10-(napth-1-yl)anthracene (9n). ^{1}H NMR (acetone-d_6): δ 4.06 (s, 6H), 6.59 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.69 (*J* = 7.5 Hz, 1H), 8.04 (t, J^1 = 8.0 Hz, J^2 7.5 Hz, 2 H), 8.26 (s, 2H).

9-Amino-1-methoxy-4-methyl-10-phenylanthracene (9o). UV ($CHCl_3$): λ_{max} [nm] (log ε) 246 (4.93), 273 (6.97), 374 3.62), 392 (3.82), 432 (3.64); ^{1}H NMR (acetone-d_6): δ 1.78 (s, 3H), 4.00 (s, 3H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 7.22-7.25 (m, 1H), 7.28-7.29 (m, 5H), 7.41-7.43 (m, 2H), 8.25 (d, *J* = 8.0 Hz, 1H).

9-Amino-1-methoxy-4-methyl-10-(4-methoxyphenyl)anthracene (9p). UV ($CHCl_3$): λ_{max} [nm] (log ε) 242 (4.40), 270 (4.26), 375 (3.61), 393, (3.90) 440 (3.75); ^{1}H NMR (DMSO-d_6): δ 1.74 (s, 3H), 3.82 (s, 3H), 3.96 (s, 3H), 6.53 (d, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 1H), 6.98, 7.01 (AA' 4-$MeOC_6H_4$), 7.13, 7.15 (BB') 7.25-7.32 (m, 5H), 8.29 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (DMSO-d_6): δ 26.4, 55.6, 56.3, 101.2, 110.1, 113.5, 117.7, 121.9, 122.7, 123.1, 126.3, 126.7, 126.9, 129.4, 132.8, 132.9, 133.8, 135.4, 143.8, 157.7, 158.6.

9-Amino-1-methoxy-4-methyl-10-(3-methylphenyl)anthracene (9q). ^{1}H NMR (DMSO-d_6):

δ 1.75 (s, 3H), 3.60 (s, 3H), 3.96 (s, 3H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.20 (m, 3H), 7.28 (m, 4H), 8.34 (d, *J* = 7.6 Hz, 1H).

9-Amino-1-methoxy-4-methyl-10-(naphth-1-yl)anthracene (9r). ^{1}H NMR (acetone-d_6): δ 1.52 (s, 3H), 4.08 (s, 3H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 7.10 (m. 3H), 7.26 (m, 3H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 8.03 (t, *J* = 8.0 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 1H).

9-Amino-1-methoxy-(3,4,5-trimethoxyphenyl)-4-methylanthracene (9s). UV ($CHCl_3$): λ_{max} [nm] (log ε) 271 (4.55), 373 (3.54), 391 (3.94), 436 (3.76); ^{1}H NMR (DMSO-d_6): δ 1.90 (s, 3H), 3.70 (s, 6H), 3.77 (s, 3H), 4.00 (s, 3H), 6.54 (s, 2H), 6.57 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.29 (m, 5H), 8.29 (d, *J* = 8.8 Hz, 1H).

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