Efficient Routes to Acenaphthylene-Fused Polycyclic Arenes/Heteroarenes and Heterocyclic Fluoranthene Analogues

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Dedicated to Prof. Armin de Meijere on the occasion of his 65th birthday

Keywords: Arenes / Annulation / Carbocycles / Heterocycles / Fused-ring systems

The acenaphthenone-derived *α*-oxoketene dithioacetal **2** has been subjected to various [3 + 3] aromatic and heteroaromatic annulation and other heterocyclization reactions previously developed in our laboratory, providing short and efficient routes to a diverse range of known and unknown acenaphtho-annulated linear and angular PAHs, heteroaromatics and five-membered heterocycles in good yields. Thus, benzo- and naphthoannulation of **2** with various allyl and benzyl Grignard reagents afforded substituted fluoranthenes **4a–c** and benzo[*k*]fluoranthene **8**, respectively, in good yields. Similarly, the parent benzo[*j*]fluoranthene **15a** and its substituted derivative **16b** have been synthesized by base-induced conjugate 1,4-addition of arylacetonitriles to **2**, followed by acid-induced cyclization of the conjugate adducts **12a–b** to give **13a–b** and subsequent further transformations. The adducts obtained by 1,4-addition of anions derived from acetophenone and acenaphthenone were subjected to heterocyclization in the presence of ammonium acetate to give 8-arylacenaphtho[1,2-*b*]pyridines **18a–b** and bis(acenaphtho)-annulated pyridine **20**. Heterocyclization of **2** with bifunctional nucleophiles such as 2-picolyllithium and guanidinium nitrate afforded the corresponding acenaphtho[1,2-*b*]quinolizinium salt **23** and acenaphtho[1,2-*d*]pyrimidine **24**, respectively, in high yields. Finally, acenaphtho[1,2-*c*]-fused five-membered heterocycles such as 7-(methylthio)acenaphtho[1,2-*c*]thiophene (**25**), 7-(methylthio)acenaphtho[1,2-*c*]furan (**27**) and 7-(methylthio)acenaphtho[1,2-*c*]pyrrole-2-carboxylic acid (**30**) were obtained in good yields by subjection of **2** to Simmons–Smith reaction conditions or by treatment with dimethylsulfonium methylide or glycinate dianion. Some of these newly synthesized PAHs or fused heterocycles were subjected to Raney Ni desulfurization to furnish sulfur-free compounds.

Introduction

The synthesis of substituted and fused polycyclic aromatic hydrocarbons (PAHs) and the corresponding polycyclic azaarenes is always a fascinating undertaking because representatives of this class of compounds are spread over different fields of organic chemistry from biochemistry (carcinogenic PAHs, DNA intercalators) to materials science and stereochemistry (chiral helicenes).[1] Polycyclic aromatic hydrocarbons and polycyclic azarenes are widespread environmental contaminants that have been extensively studied with regard to their mutagenic and carcinogenic activity.[2] PAHs have also found extensive usage as building blocks for the preparation of materials that can be used as molecular devices such as conductors, ferromagnets, wires,[3] liquid crystalline materials[4] and other electronic and optoelectronic devices.[5] Similarly, the isolation of C_{60} fullerene and higher fullerenes has aroused renewed interest in the chemistry of bowl-shaped PAHs, and many efforts have in recent years been directed towards the synthesis of polynuclear hydrocarbons containing *peri*-fused five- and six-membered ring carbon fragments corresponding to portions of fullerene surfaces (buckybowls).[6] Indeno-annulated polycyclic aromatic hydrocarbons such as fluoranthene, benzo[*j*]fluoranthene and benzo[*k*]fluoranthene have received considerable attention due to their resemblance to partial structures of C_{60} fullerene and its higher homologues, their unusual (photo)physical properties and the carcinogenic activity exhibited by some representative compounds.[2d,7] The heterocyclic analogues of polycyclic aromatic hydrocarbons are also potentially useful organic donors in molecular devices,[8] and heterocyclic compounds with fused aromatic subunits such as porphyrin chromophores may show profound changes in the electronic properties of the porphyrin macrocycles.[9]

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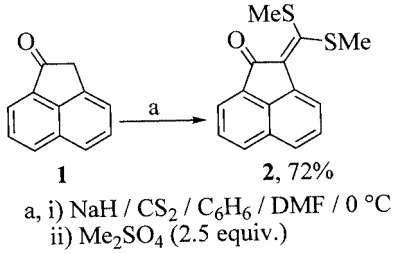
Our own interest in the synthesis of these compounds is based on the application of our aromatic[10] and heteroaromatic annulation[11] methodology involving novel α-oxoketene dithioacetals as three-carbon 1,3-bielectrophilic synthons for the development of efficient synthetic methods for a wide variety of aromatic and heterocyclic compounds of biological and other importance.[10–13a,13b] By making use of these methods, we have previously reported the synthesis of a number of polycyclic aromatic hydrocarbons such as benzo[*a*]anthracene, dibenzo[*a*,*j*]anthracene, dibenzo[*a*,*h*]-anthracene, benzo[*c*]phenanthrene, benzo[*c*]fluorene and their derivatives.[10a,12b] Similarly, the heteroaromatic annulation of α-oxoketene dithioacetals with various heteroallyl anions has provided efficient regiospecific routes to benzoheterocycles such as benzisoxazoles, quinazolines, indazoles, carbazoles, indoles, benzothiophenes and pyrido-[1,2-*a*]benzimidazole derivatives.[11–13a,13b] The presence of two sulfur atoms and other structural features in these α-oxoketene dithioacetals make them attractive substrates for study of their diverse reactivity profile, which has further resulted in the development of new general synthetic routes to a wide variety of substituted and fused five- and six-membered heterocycles.[13c–13e] These reactions, encompassing a wide structural variety both of α-oxoketene dithioacetals, allyl/heteroallyl anions and bifunctional heteronucleophiles, and also of other reactive species to enrich the scope and generality of these methods, have been extensively investigated in our laboratory.[10–13] In continuation of these studies, we now report in this paper the application of aromatic and heteroaromatic annulation and other heterocyclization reactions to 2-[bis(methylthio)methylene]-acenaphthen-2-one (**2**) to provide a diverse array of polycyclic aromatic hydrocarbons, heteroarenes and novel acenaphtho-fused five- and six-membered heterocycles.

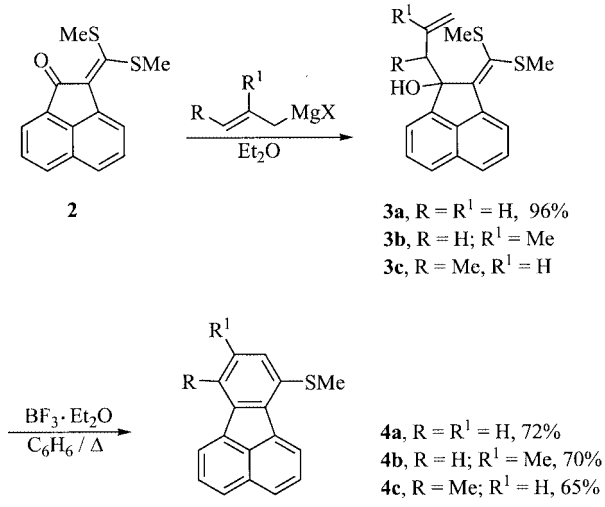
Results and Discussion

The desired α-oxoketene dithioacetal **2** was obtained in 72% yield (Scheme 1) by treatment of acenaphthenone (**1**) with sodium hydride and carbon disulfide in DMF/C_6H_6, followed by alkylation with dimethyl sulfate.[13a]



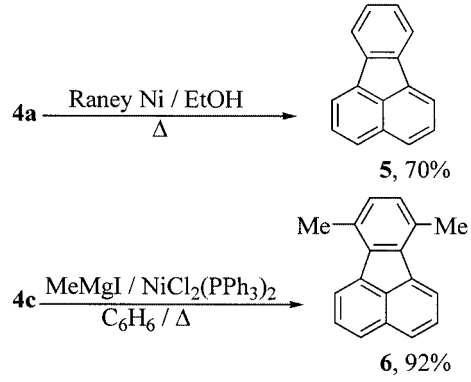
Scheme 1.

Benzo- and naphthoannulation of **2** with allyl and benzyl anions was first investigated with a view to synthesize indeno-annulated polycyclic aromatic hydrocarbons (indeno-PAHs) such as fluoranthene, benzo[*j*]fluoranthene and benzo[*k*]fluoranthene (see Schemes 2–5). Thus, treatment of **2** with allylmagnesium chloride[14a] resulted in the formation of the corresponding carbinol acetal **3a** in nearly quantitative yield. Cycloaromatization of the carbinol **3a** in the presence of $BF_3{\cdot}Et_2O$ at reflux in benzene proceeded smoothly to afford 7-(methylthio)fluoranthene (**4a**) in 72% yield. Similarly, the corresponding 8-methyl-10-(methylthio)- and 7-methyl-10-(methylthio)fluoranthenes **4b** and **4c** were formed readily in high yields under the same conditions from the corresponding carbinols **3b**–**c**, obtained by 1,2-addition of methacryl and crotoylmagnesium chlorides, respectively, to **2** (Scheme 2). It is pertinent to note that the addition of **2** with crotylmagnesium chloride is highly regioselective, exclusively yielding the carbinol **3c** in quantitative yield.[15]



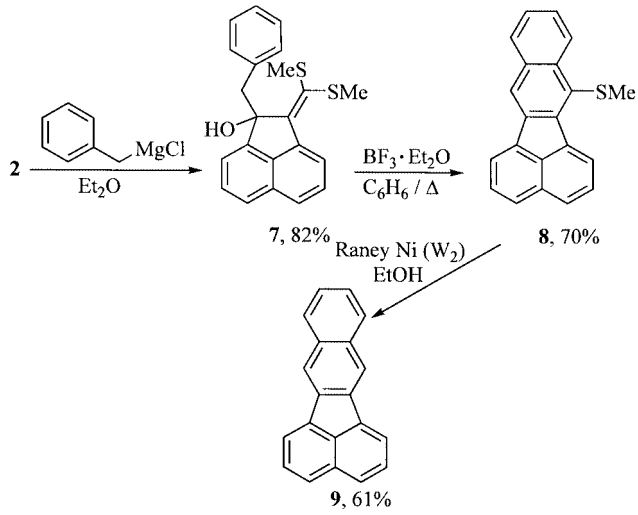
Scheme 2.

The 7-(methylthio)fluoranthene (**4a**) was converted into the parent fluoranthene **5** in 70% yield by reductive dethiomethylation with Raney Ni (Scheme 3). Moreover, the 7-methylthio group in one of the fluoranthenes, **4c**, could be replaced by a methyl group by treatment with methylmagnesium iodide in the presence of bis(triphenylphosphanyl)-nickel dichloride to give 7,10-bis(methyl)fluoranthene (**6**) in 92% yield. This compound is a potential precursor for corannulene synthesis[16] (Scheme 3).



Scheme 3.

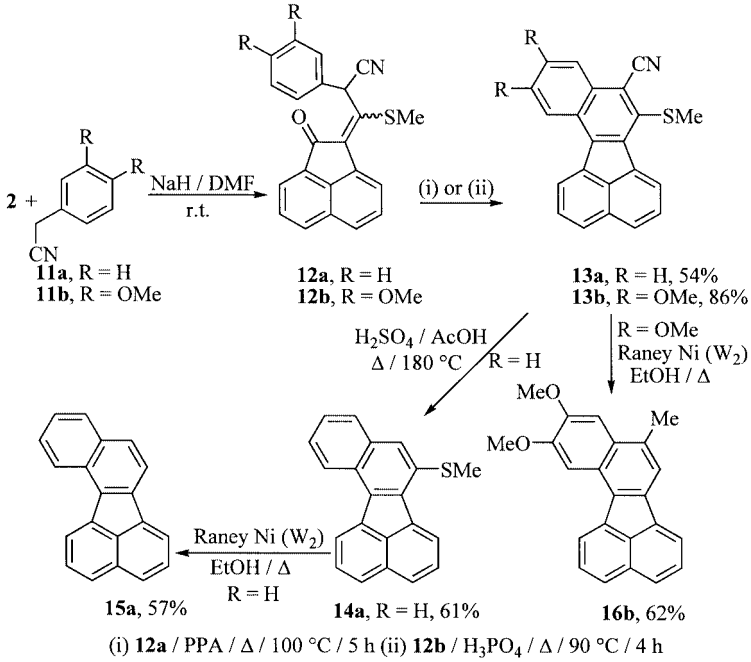
Naphthoannulation of **2** with benzylmagnesium chloride was next investigated (Scheme 4).[10a,14b,14c] It is pertinent to note that benzylmagnesium chloride had previously been shown to undergo sequential 1,4- and 1,2-addition with various oxoketene dithioacetals to give carbinol adducts, which on subsequent $BF_3{\cdot}Et_2O$-induced cycloaromatization yield naphthoannulated products with an undesired benzylic substituent.[14b] Interestingly, treatment of **2** with benzylmagnesium chloride under the previously reported conditions furnished only the carbinol **7**, the product of exclusive 1,2-addition. The carbinol **7** was efficiently transformed into 7-(methylthio)benzo[*k*]fluoranthene (**8**, 70%) through $BF_3{\cdot}Et_2O$-promoted cycloaromatization under the standard reaction conditions. Subsequent Raney Ni dethiomethylation of **8** gave the parent benzo[*k*]fluoranthene (**9**) in 61% yield (Scheme 4).[17]



Scheme 4.

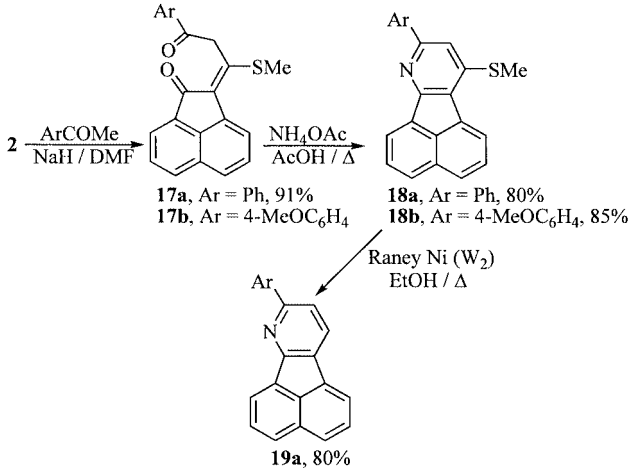
We further elaborated our naphthoannulation studies for the synthesis of angularly fused benzo[*j*]fluoranthene (**15a**) through our conjugate 1,4-addition/cyclization methodology with the corresponding stabilized benzyl anions derived from phenylacetonitrile, as depicted in Scheme 5. Base-induced conjugate addition of phenylacetonitrile (**11a**) to ketene dithioacetal **2** gave the conjugate adduct **12a**, which was subsequently converted into the corresponding 7-(methylthio)-8-cyanobenzo[*j*]fluoranthene (**13a**) in 54% yield through intramolecular cyclocondensation in the presence of PPA (Scheme 5). Subsequent acid-assisted hydrolytic decarboxylation of **13a** provided the nitrile-free 7-(methylthio)benzo[*j*]fluoranthene (**14a**) in good yield. Raney nickel dethiomethylation of **14a** afforded the parent benzo[*j*]fluoranthene (**15a**) in 57% yield (Scheme 5). Similarly, the corresponding adduct **12b**, obtained by conjugate addition of 3,4-dimethoxyphenylacetonitrile to **2** in the presence of NaH, underwent facile intramolecular cyclization in the presence of hot H_3PO_4 to provide the corresponding bis(methoxy)benzo[*j*]fluoranthene derivative **13b** in 86% yield (Scheme 5). Reductive dethiomethylation of dimethoxy derivative **13b** yielded the corresponding 8-methyl-10,11-bis(methoxy)benzo[*j*]fluoranthene (**16b**) formed by concomitant reduction of the nitrile group to a methyl group (Scheme 5).

The α-oxoketene dithioacetal **2** was subjected to various heteroaromatic annulation and heterocyclization reactions with a view to synthesize a variety of acenaphthylene-fused five- and six-membered heterocycles as shown in Schemes 6–10. Pyridine annulation was achieved through our previously reported method[18] involving base-induced conjugate addition of acetophenones to afford the adducts



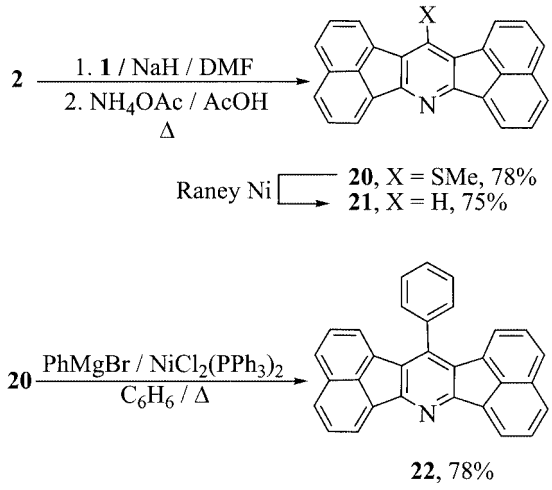
Scheme 5.

17a–**b** in high yields (Scheme 6). The adducts **17a**–**b** were transformed into the corresponding 10-(methylthio)-8-arylacenaphtho[1,2-*b*]pyridines **18a** and **18b** on heating with ammonium acetate/acetic acid, in 80% and 85% yields, respectively. One of the products (**18a**) was converted into the sulfur-free acenaphthopyridine **19a**[19] on treatment with Raney Ni under standard reaction conditions (Scheme 6).



Scheme 6.

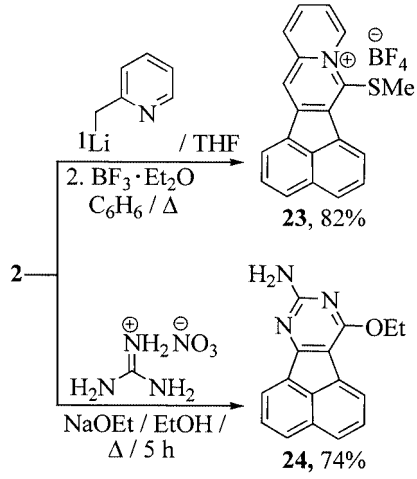
Interestingly, this pyridine annulation strategy could also be elaborated for the synthesis of bis(acenaphtho)-annulated pyridine derivatives **21** and **22**, as shown in Scheme 7. The adduct obtained through base-induced conjugate addition of acenaphthenone **1** to oxoketene dithioacetal **2** underwent facile heterocyclization in the presence of ammonium acetate/acetic acid to afford the symmetrical methylthio-substituted polycyclic heteroarene **20** in high yield (Scheme 7). The methylthio group in the product **20** could be removed reductively (Raney Ni) or replaced by a phenyl group through nickel-catalysed cross-coupling with phenyl



Scheme 7.

Grignard reagent, to furnish either the parent sulfur-free diacenaphtho[1,2-*b*:1′,2′-*e*]pyridine (**21**) or the corresponding 14-phenyl derivative **22**[20] in good yields (Scheme 7). The structures of the products **20**–**22** were unequivocally confirmed with the help of spectral and analytical data.

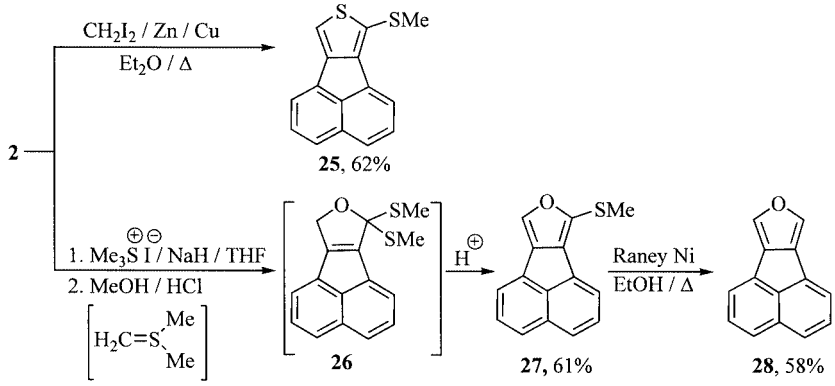
The ketene dithioacetal **2** underwent facile heterocyclization with bifunctional nucleophiles such as 2-picolyllithium[21] and guanidinium nitrate[22] under our previously reported conditions to yield the corresponding acenaphtho[1,2-*b*]quinolizinium salt **23**[23] or the corresponding acenaphtho[1,2-*d*]pyrimidine derivative **24**[24] in good yields, as shown in Scheme 8.



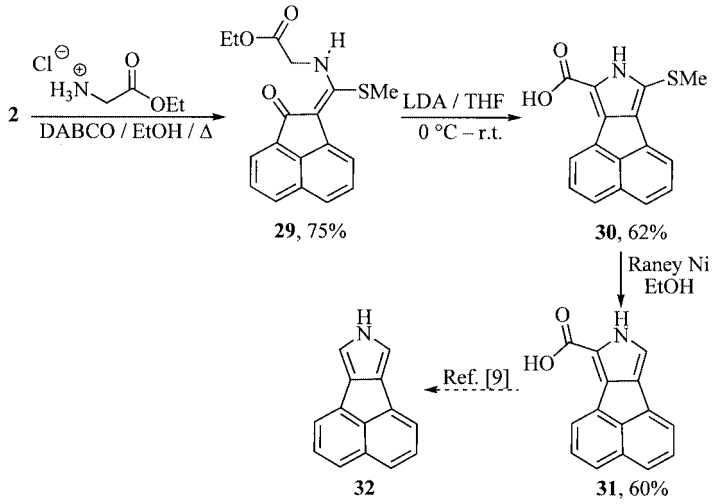
Scheme 8.

The oxoketene dithioacetal **2** was further transformed into the various acenaphtho[1,2-*c*]-fused five-membered heterocycles as shown in Schemes 9 and 10 through a series of standard reactions previously developed in our laboratory. Treatment of **2** with methylene iodide and Zn–Cu couple afforded the corresponding 7-(methythio)acenaptho[1,2-*c*]thiophene (**25**,[25] 62%), in line with our earlier observations on Simmons–Smith reactions of α-oxoketene dithioacetals.[26] Treatment of **2** with dimethylsulfonium methylide followed by acid workup similarly afforded 7-(methythio)acenaphtho[1,2-*c*]furan (**27**) in good yields, as observed previously by Okazaki and co-workers.[27] Subsequent Raney Ni-induced dethiomethylation of **27** yielded the hitherto unknown parent acenaphtho[1,2-*c*]furan (**28**) in 58% yield (Scheme 9).

Finally, the corresponding 9-(methythio)-8*H*-acenaphtho[1,2-*c*]pyrrole-7-carboxylic acid (**30**) was synthesized in 62% yield through a two-step base-catalysed addition/intramolecular aldol condensation of **2** with ethyl glycinate as shown in Scheme 10. Subsequent dethiomethylation of **30** furnished the corresponding acid **31**, which has previously been converted into the parent acenaphtho[1,2-*c*]pyrrole (**32**) by thermal decarboxylation in the presence of copper powder.[9]



Scheme 9.



Scheme 10.

Conclusions

In summary, [3 + 3] aromatic and heteroaromatic annulation and other heterocyclization studies on the acenaphthenone-derived α-oxoketene dithioacetal **2** with various bifunctional nucleophiles have provided short and efficient routes to a diverse range of both known and unknown acenaphtho-annulated linear and angular polycyclic aromatic hydrocarbons, heteroaromatics and five-membered heterocycles with potential biological activity. Some of these compounds may be useful for the preparation of more complex structural motifs, which is under investigation in our laboratory.

Experimental Section

General: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ or [D_6]DMSO, with TMS as an internal reference. Melting points are uncorrected. Chromatographic purification was conducted by column chromatography on 60–120 mesh silica gel obtained from Acme Synthetic Chemicals. DMF was distilled from over CaH_2 and stored over molecular sieves. THF was distilled from over sodium/benzophenone prior to use. Chemically pure diisopropylamine, ethanol, *n*BuLi (15% in hexane), H_2SO_4, AcOH, H_3PO_4 (85%), PPA, DABCO, diethyl ether and ammonium acetate were purchased from standard firms and further dried, whenever needed, by standard procedures. The synthesis of 2-[bis-(methylthio)methylene]acenaphthen-1-one has been reported previously.[12a]

General Procedure for the Cycloaromatization of 2-[Bis(methylthio) methylene]acenaphthen-1-one with Allylic and Benzylic Grignard Reagents. Synthesis of Substituted Fluoranthenes 4a–c and benzo-[*k*]fluoranthene 8: A solution of **2** (1.36 g, 5 mmol) in dry THF (30 mL) was added dropwise to a stirred solution of allyl/methallyl/crotyl/benzylmagnesium chloride [chloride (10 mmol) and magnesium turnings [(0.5 g, 20.8 mmol)] in dry ether (75 mL)], and the reaction mixture was further stirred at room temperature for 5 h. It was then poured into saturated NH_4Cl solution (200 mL) and extracted with $CHCl_3$ (2 × 100 mL), and the combined organic layers were washed with water, dried (Na_2SO_4) and evaporated under reduced pressure to give the crude carbinols as viscous residues. The crude carbinols were dissolved in dry benzene (50 mL), followed by addition of $BF_3{\cdot}Et_2O$ (1.25 mL, 10 mmol). The reaction mixture was then heated at reflux for 5 h (monitored by TLC), cooled, poured into saturated $NaHCO_3$ solution (100 mL), extracted with chloroform (2 × 100 mL), washed with water (2 × 100 mL) and dried (Na_2SO_4), and the solvent was evaporated to give crude products, which were purified by silica gel column chromatography with hexane/ethyl acetate (98:2) as eluent to give fluoranthenes **4a**–**c** and **8**. The carbinols **3a**–**d** decomposed on purification by column chromatography over silica gel, whereas the car-

binol **7** derived from benzylic Grignard reagent could be obtained as an analytically pure sample by column chromatography over silica gel with hexane/EtOAc (10:1) as eluent.

1-Benzyl-2-[bis(methylthio)methylene]-1-hydroxyacenaphthene (7): Yield 82% (1.45 g); red, viscous liquid; R_f = 0.35 (hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 3 H, SCH_3), 2.57 (s, 3 H, SCH_3), 3.53 (d, J = 12.9 Hz, 1 H, CH), 3.62 (d, J = 12.9 Hz, 1 H, CH), 4.65 (br. s, 1 H, OH), 6.79 (d, J = 7.3 Hz, 1 H, ArH), 6.96–7.02 (m, 3 H, ArH), 7.23 (d, J = 6.8 Hz, 2 H, ArH), 7.46 (t, J = 7.8 Hz, 1 H, ArH), 7.52 (t, J = 7.8 Hz, 1 H, ArH), 7.60 (d, J = 8.0 Hz, 1 H, ArH) 7.69 (d, J = 8.2 Hz, 1 H, ArH) 8.42 (d, J = 7.3 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8, 17.6, 48.0, 86.1, 118.9, 119.2, 121.7, 122.5, 124.5, 124.9, 126.1, 127.1, 127.3, 127.8, 128.6, 130.1, 131.5, 135.8, 143.3, 151.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3049, 2916, 1678, 1498, 1423 cm^{-1}. MS (*m*/*z*, %): 364 (100) $[M]^+$. $C_{22}H_{20}OS_2$ (364.53): C 72.49, H 5.53%; found C 72.56, H 5.31%.

7-(Methylthio)fluoranthene (4a): Yield 72% (0.89 g); yellow crystals (chloroform/hexane); m.p. 136 °C; R_f = 0.5 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 3 H, SCH_3), 7.23 (d, J = 8.0 Hz, 1 H, ArH), 7.31 (t, J = 7.3 Hz, 1 H, ArH), 7.59 (t, J = 7.3 Hz, 1 H, ArH), 7.65 (t, J = 7.0 Hz, 1 H, ArH), 7.70 (d, J = 7.3 Hz, 1 H, ArH), 7.81 (d, J = 5.4 Hz, 1 H, ArH), 7.83 (d, J = 5.1 Hz, 1 H, ArH), 7.90 (d, J = 6.8 Hz, 1 H, ArH), 8.40 (d, J = 6.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3, 118.1, 120.1, 124.6, 124.8, 126.3, 126.9, 127.5, 127.6, 128.0, 129.6, 132.1, 135.0, 136.0, 136.2, 136.7, 139.9 ppm. IR (KBr): $\tilde{\nu}$ = 3033, 2997, 1876, 1630, 1441 cm^{-1}. MS (*m*/*z*, %): 248 (100) $[M]^+$, 234 (43.9), 233 (33.2), 215 (21.1), 202 (17.9), 201 (14.7), 189 (25.3). $C_{17}H_{12}S$ (248.34): C 82.22, H 4.87%; found C 82.10, H 4.92%.

8-Methyl-10-(methylthio)fluoranthene (4b): Yield 70% (0.91 g); yellow crystals (chloroform/hexane); m.p. 134–135 °C; R_f = 0.4 (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3 H, CH_3), 2.65 (s, 3 H, SCH_3), 7.08 (s, 1 H, ArH), 7.57 (s, 1 H, ArH), 7.59–7.67 (m, 2 H, ArH), 7.80 (d, J = 8.0 Hz, 1 H, ArH), 7.83 (d, J = 8.0 Hz, 1 H, ArH), 7.91 (d, J = 6.8 Hz, 1 H, ArH), 8.35 (d, J = 6.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5, 21.8, 119.4, 119.9, 124.0, 125.7, 125.8, 126.0, 126.9, 127.5, 128.1, 129.7, 132.4, 134.6, 136.4, 136.8, 137,8, 140.3 ppm. IR (KBr): $\tilde{\nu}$ = 1604, 1549, 1434, 766 cm^{-1}. MS (*m*/*z*, %): 262 (100) $[M]^+$, 247 (22.7), 229 (17.9), 215 (13.3), 202 (18.3), 203 (14.0). $C_{18}H_{14}S$ (262.37): C 82.40, H 5.38%; found C 82.23, H 5.49%.

7-Methyl-10-(methylthio)fluoranthene (4c): Yield 65% (0.85 g); yellow crystals (chloroform/hexane); m.p. 97–98 °C; R_f = 0.4 (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3 H, SCH_3), 2.71 (s, 3 H, CH_3), 7.11 (d, J = 8.0 Hz, 1 H, ArH) 7.18 (d, J = 8.0 Hz, 1 H, ArH), 7.61 (t, J = 7.2 Hz, 1 H, ArH), 7.66 (t, J = 7.2 Hz, 1 H, ArH), 7.82 (d, J = 8.0 Hz, 2 H, ArH), 7.96 (d, J = 7.2 Hz, 1 H, ArH), 8.48 (d, J = 7.2 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.9, 20.2, 123.2, 124.7, 125.7, 126.4, 126.5, 127.6, 127.9, 129.5, 130.1, 131.4, 132.1, 132.2, 136.4, 136.6, 137.0, 137.8 ppm. IR (KBr): $\tilde{\nu}$ = 1586, 1428, 1370, 770 cm^{-1}. MS (*m*/*z*, %): 262 (100) $[M]^+$, 247 (43.9), 229 (8.5), 215 (21.1), 203 (17.2), 202 (19.0). $C_{18}H_{14}S$ (262.37): C 82.40, H 5.38%; found C 82.56, H 5.22%.

7-(Methylthio)benzo[*k*]fluoranthene (8): Yield 70% (1.04 g); yellow solid (chloroform/hexanes); m.p. 147–148 °C; R_f = 0.90 (hexanes/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.83 (s, 3 H, SCH_3), 7.52 (dt, J = 7.4, 1.2 Hz, 1 H, ArH), 7.59–7.70 (m, 3 H, ArH), 7.83 (d, J = 8.0 Hz, 1 H, ArH), 7.84 (d, J = 8.3 Hz, 1 H, ArH), 7.95 (s, 1 H, ArH), 7.96 (d, J = 6.8 Hz, 1 H, ArH), 8.10 (d, J = 8.0 Hz, 1 H, ArH), 8.43 (d, J = 7.0 Hz, 1 H, ArH), 8.76 (d, J = 8.2 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 109.4, 113.8, 114.4, 120.6, 120.9, 123.6, 124.8, 125.1, 125.4, 126.4, 126.5, 126.6, 127.2, 127.7, 128.1, 129.5, 132.9, 134.7, 138.0, 160.7 ppm. IR (KBr): $\tilde{\nu}$ = 2937, 2357, 1326, 750 cm^{-1}. MS (*m*/*z*, %): 298 (100) $[M]^+$, 297 (40.1), 283 (91.3), 239 (57.4). $C_{21}H_{14}S$ (298.40): C 84.53, H 4.73%; found C 84.42, H 4.81%.

General Procedure for Base-Induced Conjugate Addition of Arylacetonitriles and Active Methylene Ketones to 2. Preparation of Adducts 12a–b and 17a–b: A solution of the appropriate arylacetonitrile (**11a**–**b**) or ketone (acetophenone/4-methoxyacetophenone/acenaphthenone) (5 mmol) was added dropwise at 0 °C over a period of 15 min. to a stirred suspension of NaH (0.6 g, 60%, 10 mmol) in DMF (10 mL), and the reaction mixture was further stirred at 0 °C for 45 min. A solution of **2** (5 mmol) in DMF (10 mL) was then added dropwise, and the reaction mixture was further stirred at room temperature for 8–10 h. It was then poured into saturated NH_4Cl solution (200 mL) and extracted with $CHCl_3$ (3 × 50 mL). The combined extracts were washed with water (3 × 50 mL), dried (Na_2SO_4) and evaporated to give the 1,4-addition/elimination adducts in nearly quantitative yields. The crude adducts (**12a**–**b**) were found to be unstable towards purification by column chromatography over silica gel.

2-[2-Cyano-1-(methylthio)-2-phenylethylidene]acenaphthen-1-one (12a): Crude adduct; R_f = 0.6 (hexanes/EtOAc, 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, SCH_3), 3.72 (s, 1 H, CH), 7.30–7.39 (m, 3 H, ArH), 7.51 (d, J = 7.6 Hz, 2 H, ArH), 7.67 (t, J = 8.0 Hz, 1 H, ArH), 7.71 (t, J = 7.8 Hz, 1 H, ArH), 7.86 (d, J = 8.3 Hz, 1 H, ArH), 7.98 (d, J = 6.8 Hz, 1 H, ArH), 8.08 (d, J = 8.0 Hz, 1 H, ArH), 8.35 (d, J = 7.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.05, 35.63, 118.14, 122.05, 123.91, 125.81, 126.61, 127.84, 128.07, 128.35, 129.13, 129.23, 130.09, 131.77, 132.52, 132.76, 133.69, 138.45, 147.24, 191.25 ppm. IR (KBr): $\tilde{\nu}$ = 2875, 2241, 1672, 1597, 1425, 767 cm^{-1}.

The adduct **17a** was purified by column chromatography and characterized by its spectral and analytical data. The adduct **17b** from 4-methoxyacetophenone and the adduct from acenaphthenone were used as such for further cyclization.

2-(1-Methylthio-3-oxo-3-phenylpropylidene)acenaphthen-1-one (17a): Yield 91% (1.56 g); yellow solid (chloroform/hexane); m.p. 166–167 °C; R_f = 0.4 (8:2 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, SCH_3), 5.26 (s, 2 H, CH_2), 7.51 (t, J = 8.0 Hz, 2 H, ArH), 7.58–7.64 (m, 3 H, ArH), 7.77 (d, J = 7.4 Hz, 1 H, ArH), 7.85 (d, J = 7.0 Hz, 1 H, ArH), 8.00 (d, J = 8.0 Hz, 1 H, ArH), 8.11 (d, J = 8.0 Hz, 2 H, ArH), 8.24 (d, J = 7.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 40.3, 121.3, 122.4, 122.8, 124.4, 127.5, 128.2, 128.7, 129.1, 130.0, 131.0, 133.4, 133.7, 135.1, 136.5, 137.7, 151.3, 191.0, 195.3 ppm. IR (KBr): $\tilde{\nu}$ = 3052, 2921, 1677, 1550, 769 cm^{-1}. MS (*m*/*z*, %): 344 (100) $[M]^+$. $C_{22}H_{16}O_2S$ (344.43): C 76.72, H 4.68; N; found C 76. 64, H 4.76.

Procedure for Cycloaromatization of the Adducts 12a–b to 13a–b. Synthesis of Benzo[*j*]fluoranthenes 13a–b: The crude adduct **12a** (ca. 5 mmol) was mixed with PPA (25 mL), whereas the adduct **12b** was dissolved in H_3PO_4 (25 mL). Both reaction mixtures were heated at 90–100 °C for 5–6 h (monitored by TLC). Each was then cooled, poured into ice-cold water (150 mL) and extracted with $CHCl_3$ (3 × 50 mL). The combined organic layers were washed with water (3 × 50 mL) and dried over Na_2SO_4. The solvent was distilled off to give crude products (**13a** or **13b**), which were purified by column chromatography with hexane/ethyl acetate (97:3) as eluent.

8-Cyano-7-(methylthio)benzo[*j*]fluoranthene (13a): Yield 54% (0.87 g); orange solid (chloroform/hexanes); m.p. 223–224 °C; R_f =

0.55 (hexanes/EtOAc, 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 3 H, SCH_3), 7.40 (t, J = 7.5 Hz, 1 H, ArH), 7.47 (t, J = 7.3 Hz, 2 H, ArH), 7.53–7.60 (m, 2 H, ArH), 7.63 (d, J = 7.3 Hz, 1 H, ArH), 7.79 (d, J = 8.3 Hz, 1 H, ArH), 7.95 (d, J = 7.5 Hz, 2 H, ArH), 8.25 (d, J = 6.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.5, 117.2, 121.7, 123.4, 126.0, 126.4, 127.4, 127.7, 128.1, 128.2, 128.3, 128.40, 128.43, 128.5, 130.7, 130.73, 130.8, 131.9, 134.8, 152.5, 157.7, 161.0 ppm. IR (KBr): $\tilde{\nu}$ = 2215, 1693, 1496, 1422 cm^{-1}. MS (*m*/*z*, %): 324 (100) $[M + 1]^+$. $C_{22}H_{13}NS$ (323.41): C 81.70, H 4.05, N 4.33%; found C 81.62, H 4.12, N 4.19%.

8-Cyano-10,11-dimethoxy-7-(methylthio)benzo[*j*]fluoranthene (13b): Yield 86% (1.64 g); yellow crystals (chloroform/hexanes); m.p. 283–284 °C; R_f = = 0.1 (hexanes/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.62 (s, 3 H, SCH_3), 4.09 (s, 3 H, OCH_3), 4.16 (s, 3 H, OCH_3), 7.45 (s, 1 H, ArH), 7.69 (t, J = 7.8 Hz, 1 H, ArH), 7.72 (t, J = 7.8 Hz, 1 H, ArH), 7.86 (s, 1 H, ArH), 7.90 (d, J = 8.0 Hz, 1 H, ArH), 7.96 (d, J = 8.0 Hz, 1 H, ArH), 8.30 (d, J = 7.3 Hz, 1 H, ArH), 8.85 (d, J = 7.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 56.1, 56.2, 103.0, 104.9, 117.2, 124.7, 126.0, 126.1, 127.5, 127.6, 127.8, 127.9, 128.5, 128.6, 128.7, 128.8, 134.2, 134.3, 135.1, 135.5, 137.3, 151.3 157.3 ppm. IR (KBr): $\tilde{\nu}$ = 2916, 2217, 1620, 1508, 1491 cm^{-1}. MS (*m*/*z*, %): 383 (100) $[M]^+$, 368 (20.2). $C_{24}H_{17}NO_2S$ (383.46): C 75.17, H 4.47, N 3.65%; found C 75.29, H 4.51, N 3.42%.

Procedure for Acid-Induced Hydrolysis/Decarboxylation of 13a. Synthesis of 7-(Methylthio)benzo[*j*]fluoranthene (14a): A suspension of **13a** (1.6 g, 5 mmol) in water (5 mL), AcOH (5 mL) and concentrated H_2SO_4 (5 mL) was heated at reflux with stirring at 180 °C for 6 h (monitored by TLC). It was then cooled, poured into ice-cold water (25 mL), neutralized with saturated $NaHCO_3$ solution and extracted with $CHCl_3$ (3 × 50 mL). The combined organic layer was dried (Na_2SO_4) and evaporated to give a crude viscous residue, which was purified by column chromatography over silica gel with hexane/EtOAc (98:2) as eluent.

Yield 61% (0.91 g); yellow solid (chloroform/hexanes); m.p. 114–115 °C; R_f = 0.5 (hexanes/EtOAc, 8:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.83 (s, 3 H, SCH_3), 7.52 (t, J = 8.0 Hz, 1 H, ArH), 7.63 (t, J = 8.0 Hz, 2 H, ArH), 7.68 (t, J = 8.0 Hz, 1 H, ArH), 7.83 (d, J = 8.1 Hz, 1 H, ArH), 7.85 (d, J = 8.0 Hz, 1 H, ArH), 7.92 (s, 1 H, ArH), 7.98 (d, J = 6.8 Hz, 1 H, ArH), 8.08 (d, J = 8.0 Hz, 1 H, ArH), 8.41 (d, J = 7.0 Hz, 1 H, ArH), 8.74 (d, J = 8.2 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 120.6, 120.9, 123.6, 124.8, 125.1, 125.4, 126.5, 126.6, 127.2, 127.7, 128.1, 129.5, 130.7, 131.9, 132.7, 132.9, 134.7, 137.3, 137.4, 138.0 ppm. IR (KBr): $\tilde{\nu}$ = 3053, 2923, 2358, 1646, 1556, 1424 cm^{-1}. MS (*m*/*z*, %): 298 $[M]^+$ (58), 283 (10), 252 (20). $C_{21}H_{14}S$ (298.40): C 84.53, H 4.73%; found C 84.69, H 4.52%.

General Procedure for the Heterocyclization of the Adducts 17a–b with Ammonium Acetate. Synthesis of Acenaphtho[1,2-*b*]pyridines 18a–b and 14-(Methylthio)diacenaphtho[1,2-*b*:1′,2′-*e*]pyridine (20): NH_4OAc (1.2 g, 15 mmol) was added to a solution of adducts **17a** or **17b** (5.0 mmol) or the adduct (5.0 mmol) from acenaphthenone and **2** in glacial acetic acid (50 mL), and the reaction mixture was heated at reflux with stirring for 12–15 h (monitored by TLC). It was then cooled, poured into ice-cold water (200 mL), extracted with $CHCl_3$ (3 × 50 mL) and dried (Na_2SO_4), and the solvent was evaporated under reduced pressure to give the crude products (**18a–b**, **20**), which were purified by column chromatography with hexane/ethyl acetate (94:6) as eluent.

10-Methylthio-8-phenylacenaphtho[1,2-*b*]pyridine (18a): Yield 80% (1.30 g); brown solid (chloroform/hexanes); m.p. 118–119 °C; R_f = 0.6 (hexanes/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.72 (s, 3 H, SCH_3), 7.42–7.54 (m, 4 H, ArH), 7.64–7.74 (m, 2 H, ArH), 7.88 (d, J = 8.3 Hz, 1 H, ArH), 7.96 (d, J = 8.1 Hz, 1 H, ArH), 8.14 (d, J = 7.3 Hz, 2 H, ArH), 8.21 (d, J = 6.6 Hz, 1 H, ArH), 8.36 (d, J = 6.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 113.3, 122.2, 124.6, 127.0, 127.2, 127.3, 128.0, 128.3, 128.7, 128.8, 128.9, 129.3, 132.0, 133.7, 135.4, 139.8, 145.3, 155.78, 158.6 ppm. IR (KBr): $\tilde{\nu}$ = 1550, 1420, 1330, 790 cm^{-1}. MS (*m*/*z*, %): 326 $[M + 1]^+$ (100), 311 (10), 279 (10). $C_{22}H_{15}NS$ (325.43): C 81.20, H 4.65, N 4.30%; found C 81.48, H 4.51, N 4.19%.

8-(4-Methoxyphenyl)-10-(methylthio)acenaphtho[1,2-*b*]pyridine (18b): Yield 85% (1.51 g); yellow crystals (chloroform/hexanes); m.p. 153–154 °C, R_f = 0.4 (hexanes/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.69 (s, 3 H, SCH_3), 3.87 (s, 3 H, OCH_3), 7.03 (d, J = 8.8 Hz, 2 H, ArH), 7.38 (s, 1 H, ArH), 7.64 (t, J = 8.3 Hz, 1 H, ArH), 7.71 (t, J = 8.0 Hz, 1 H, ArH), 7.85 (d, J = 8.2 Hz, 1 H, ArH), 7.93 (d, J = 8.0 Hz, 1 H, ArH), 8.09 (d, J = 8.7 Hz, 2 H, ArH), 8.17 (d, J = 7.0 Hz, 1 H, ArH), 8.33 (d, J = 6.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 55.3, 112.4, 114.1, 122.0, 124.4, 126.8, 127.7, 128.0, 128.1, 128.4, 128.6, 129.3, 131.9, 132.4, 133.9, 135.5, 145.2, 155.4, 158.6, 160.4 ppm. IR (KBr): $\tilde{\nu}$ = 3040, 2961, 1607, 1553 cm^{-1}. MS (*m*/*z*, %): 355 $[M]^+$ (37), 149 (100). $C_{23}H_{17}NOS$ (355.45): C 77.72, H 4.82, N 3.94%; found C 77.91, H 4.63, N 3.72%.

14-(Methylthio)diacenaphtho[1,2-*b*:1′,2′-*e*]pyridine (20): Yield 78% (1.45 g); yellow solid (chloroform/hexane); m.p. 250–251 °C; R_f = 0.2 (hexanes/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.57 (s, 3 H, SCH_3), 7.65 (t, J = 7.3 Hz, 2 H, ArH), 7.72 (t, J = 7.0 Hz, 2 H, ArH), 7.86 (d, J = 8.0 Hz, 2 H, ArH), 7.92 (d, J = 8.0 Hz, 2 H, ArH), 8.69 (d, J = 6.8 Hz, 2 H, ArH), 8.79 (d, J = 6.6 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.6, 119.8, 124.9, 125.5, 126.2, 128.2, 128.3, 128.4, 129.2, 129.7, 132.1, 132.8, 134.8, 159.4 ppm. IR (KBr): $\tilde{\nu}$ = 3050, 2915, 1425, 771 cm^{-1}. MS (*m*/*z*, %): 374 $[M + 1]^+$ (85), 373 (50), 359 (10), 343 (5), 327 (22). $C_{26}H_{15}NS$ (373.47): C 83.62, H 4.05, N 3.75%; found C 83.49, H 4.11, N 3.62%.

General Procedure for Raney Ni Dethiomethylation/Reduction: Raney Ni (W_2) (ca. 3 g) was added to a ethanolic solution (20 mL) of appropriate substrates (**4a, 8, 13b, 14a, 18a, 20, 27** or **30**) (5 mmol), and the suspension was heated at reflux with stirring for 6–7 h (monitored by TLC). It was then filtered through a sintered glass funnel and washed with hot ethanol. The filtrate was concentrated to afford a viscous residue, which was purified by column chromatography over silica gel with hexane/ethyl acetate (99:1) as eluent to give the pure products.

Fluoranthene (5): Yield 70% (0.70 g); white solid (chloroform/hexanes); m.p. 107–108 °C (ref.[28] m.p. 108–109 °C); R_f = 0.8 (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (dd, J = 5.6, 3.1 Hz, 2 H, ArH), 7.62 (t, J = 6.8 Hz, 2 H, ArH), 7.83 (d, J = 8.3 Hz, 2 H, ArH), 7.89–7.95 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.0, 121.5, 126.6, 127.5, 127.9, 129.9, 132.3, 136.9, 139.4 ppm. IR (KBr): $\tilde{\nu}$ = 3039, 2938, 2361, 1435, 774 cm^{-1}. MS (*m*/*z*, %): 202 $[M]^+$ (47). $C_{16}H_{10}$ (202.25): C 95.02, H 4.98%; found C 95.13, H 4.82%.

Benzo[*k*]fluoranthene (9): Yield 61% (0.76 g); light yellow solid (chloroform/hexanes); m.p. 215–216 °C (m.p. 215 °C, ^{1}H, ^{13}C NMR and analytical data as reported in the literature[2d]).

Benzo[*j*]fluoranthene (15a): Yield 57% (0.72 g); light yellow solid (chloroform/hexanes); m.p. 164–165 °C (m.p 165 °C, ^{1}H, ^{13}C NMR and analytical data as reported in the literature[2d]).

10,11-Dimethoxy-8-methylbenzo[*j*]fluoranthene (16b): Yield 62% (1.01 g); yellow crystals (chloroform/hexanes); m.p. 283–284 °C; R_f

= 0.6 (hexanes/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.52 (s, 3 H, CH_3), 4.10 (s, 3 H, OCH_3), 4.18 (s, 3 H, OCH_3), 7.44 (s, 1 H, ArH), 7.74–7.67 (m, 2 H, ArH), 7.83 (s, 1 H, ArH), 7.90 (d, J = 8.0 Hz, 1 H, ArH), 7.92 (s, 1 H, ArH), 7.96 (d, J = 8.0 Hz, 1 H, ArH), 8.30 (d, J = 7.3 Hz, 1 H, ArH), 8.85 (d, J = 7.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.5, 56.2, 56.3, 103.2, 105.1, 124.1, 126.0, 127.6, 127.8, 127.9, 128.1 128.5, 128.6, 128.9, 129.0, 130.1, 134.4, 134.5, 135.3, 135.7, 137.5, 151.3, 157.7 ppm. IR (KBr): $\tilde{\nu}$ = 2918, 1623, 1508, 1494 cm^{-1}. MS (*m*/*z*, %): 326 (100) $[M]^+$, 311 (12), 279 (22). $C_{23}H_{18}O_2$ (326.39): C 84.64, H 5.56%; found C 84.79, H 5.51%.

8-Phenylacenaphtho[1,2-*b*]pyridine (19a): Yield 80% (1.11 g); yellow crystals (chloroform/hexanes); m.p. 134–135 °C; R_f = 0.8 (8:2 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.54 (m, 3 H, ArH), 7.61–7.68 (m, 2 H, ArH), 7.74 (t, J = 7.0 Hz, 1 H, ArH), 7.91 (dd, J = 7.7, 2.6 Hz, 2 H, ArH), 7.95 (d, J = 8.2 Hz, 1 H, ArH), 8.11(d, J = 8.0 Hz, 1 H, ArH), 8.18 (d, J = 8.2 Hz, 2 H, ArH), 8.36 (d, J = 6.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.4, 120.8, 121.8, 126.9, 127.3, 127.9, 128.2, 128.4, 128.6, 128.8, 129.6, 129.7, 131.9, 132.4, 132.5, 135.7, 139.7, 155.9, 159.4 ppm. IR (KBr): $\tilde{\nu}$ = 3044, 1555, 1430, 768 cm^{-1}. MS (*m*/*z*, %): 280 $[M + 1]^+$ (100), 279 (70). $C_{21}H_{13}N$ (279.33): C 90.29, H 4.69, N 5.01%; found C 90.42, H 4.49, N 5.12%.

Diacenaphtho[1,2-*b*:1′,2′-*e*]pyridine (21): Yield 75% (1.22 g); yellow solid (chloroform/hexane); m.p. >300 °C; R_f = 0.1 (8:2 hexanes/EtOAc). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.83 (t, J = 8.0 Hz, 2 H, ArH), 7.86 (t, J = 7.0 Hz, 2 H, ArH), 8.10 (d, J = 8.3 Hz, 2 H, ArH), 8.14 (d, J = 8.2 Hz, 2 H, ArH), 8.30 (d, J = 6.8 Hz, 2 H, ArH), 8.37 (d, J = 7.0 Hz, 2 H, ArH), 9.11 (s, 1 H, ArH) ppm. IR (KBr): $\tilde{\nu}$ = 3047, 1428, 1097, 767 cm^{-1}. MS (*m*/*z*, %): 328 $[M + 1]^+$ (100), 327 (60), 314 (8). $C_{25}H_{13}N$ (327.38): C 91.72, H 4.00, N 4.28%; found C 91.50, H 4.23, N 4.51%.

General Procedure for Nickel-Catalysed Cross-Coupling Reaction with Methyl/Phenyl Grignard Reagents: A solution of bis(triphenylphosphanyl)nickel dichloride[29] (0.98 g, 15 mol%) in dry benzene (15 mL) was added dropwise under nitrogen to a suspension of methylmagnesium iodide/phenylmagnesium bromide [15 mmol, prepared from 0.36 g (0.015 g atom) of magnesium turnings and 15 mmol of methyl iodide/phenyl bromide] in dry ether (25 mL), and the reaction mixture was stirred at room temperature for 15 min. A solution of **4c** or **20** (5 mmol) in dry benzene (25 mL) was added, and the reaction mixture was heated at reflux for 12 h. It was then cooled, poured into 100 mL of saturated NH_4Cl solution, extracted with diethyl ether (2 × 100 mL), dried (Na_2SO_4) and evaporated to give crude residues of **6** or **22**, which were purified by column chromatography over silica gel with hexane/ethyl acetate (99:1) as eluent.

7,10-Dimethylfluoranthene (6): Yield 92% (1.05 g); white solid (chloroform/hexanes); m.p. 202–203 °C (ref.[28] m.p 202 °C); R_f = 0.6 (hexanes). IR (KBr): $\tilde{\nu}$ = 3039, 1449, 822, 769 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.75 (s, 6 H, 2 × CH_3), 7.10 (s, 2 H, ArH), 7.65 (t, J = 8.2 Hz, 2 H, ArH), 7.84 (d, J = 8.2 Hz, 2 H, ArH), 7.99 (d, J = 7.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 122.8, 126.1, 127.7, 129.6, 129.7, 131.7, 132.3, 137.1, 137.7 ppm. MS (*m*/*z*, %): 230 (100) $[M]^+$, 215 (20). $C_{18}H_{14}$ (230.30): C 93.87, H 6.13%; found C 93.96, H 6.20%.

14-Phenyldiacenaphtho[1,2-*b*:1′,2′-*e*]pyridine (22): Yield 78% (1.57 g); yellow solid (chloroform/hexane); m.p. > 300 °C (ref.[20] m.p. 323–324 °C); R_f = 0.23 (8:2 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (t, J = 7.3 Hz, 1 H, ArH), 7.52 (t, J = 7.5 Hz, 1 H, ArH), 7.75 (dd, J = 7.6, 7.8 Hz, 1 H, ArH), 7.81 (dd, J = 7.0, 7.3 Hz, 1 H, ArH), 7.94 (d, J = 8.0 Hz, 2 H, ArH), 8.05 (d, J = 8.3 Hz, 2 H, ArH), 8.11 (d, J = 8.2 Hz, 2 H, ArH), 8.19 (d, J = 7.0 Hz, 1 H, ArH), 8.23 (t, J = 8.2 Hz, 1 H, ArH), 8.30 (d, J = 6.7 Hz, 1 H, ArH), 8.44 (d, J = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.5, 121.7, 122.1, 126.6, 127.7, 128.6, 128.8, 129.0, 129.4, 130.0, 131.6, 131.7, 132.8, 134.9, 138.8, 154.8, 158.4 ppm. IR (KBr): $\tilde{\nu}$ = 1695, 1497, 1423, 771 cm^{-1}. MS (*m*/*z*, %): 403 (100) $[M]^+$. $C_{31}H_{17}N$ (403.47): C 92.28, H 4.25, N 3.47%; found C 92.36, H 4.41, N 3.20%.

Procedure for the Synthesis of 7-(Methylthio)acenaphtho[1,2-*b*]quinolizinium Tetrafluoroborate (23): *n*BuLi (1.6 M in hexane, 4.5 mL, 7 mmol) was added under nitrogen at –20 °C to a stirred solution of 2-picoline (0.6 mL, 6 mmol) in dry THF (25 mL), and the reaction mixture was stirred at the same temperature for 1 h. A solution of **2** (1.36 g, 5 mmol) in dry THF (25 mL) was then added to the reaction mixture and stirring was continued for another 2.5 h at the same temperature. It was then brought to room temperature and poured into saturated NH_4Cl solution, extracted with chloroform (2 × 100 mL), washed with water (2 × 200 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The residue obtained was dissolved in dry benzene (50 mL), BF_3·Et_2O (2 mL) was added, and the mixture was heated at reflux for 4 h (monitored by TLC). It was then cooled and poured into saturated $NaHCO_3$ solution to give a bright yellow solid, which was filtered and washed with water. The solid was dried and recrystallized from acetic acid to give pure product. Yield 82% (1.58 g); yellow solid (acetic acid); m.p. 285–286 °C; R_f = 0.1 (hexanes/EtOAc, 7:3). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.34 (s, 3 H, SCH_3), 7.83–7.92 (m, 2 H, ArH), 8.16–8.28 (m, 3 H, ArH), 8.44 (d, J = 7.0 Hz, 1 H, ArH), 8.46 (d, J = 8.0 Hz, 1 H, ArH), 8.59 (d, J = 8.2 Hz, 1 H, ArH), 8.84 (d, J = 7.0 Hz, 1 H, ArH), 9.09 (s, 1 H, ArH), 10.11 (d, J = 7.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 16.8, 117.9, 118.8, 124.1, 124.4, 126.9, 128.7, 129.1, 129.2, 129.3, 129.6, 130.0, 130.5, 130.8, 131.2, 134.4, 135.1, 136.9, 138.4, 143.5 ppm. IR (KBr): $\tilde{\nu}$ = 1636, 1563, 1423, 1055 cm^{-1}. MS (*m*/*z*, %): 300 $[M - BF_4]^+$ (100), 285 (12). $C_{20}H_{14}NSBF_4$ (387.20): C 62.04, H 3.64, N 3.62%; found C 62.13, H 3.42, N 3.75%.

Treatment of 2 with Guanidinium Nitrate for the Synthesis of 8-Amino-10-ethoxyacenaphtho[1,2-*b*]pyrimidine (24). Typical Procedure: Guanidinium nitrate (0.61 g, 5 mmol) was added to a solution of sodium ethoxide in ethanol (prepared from 0.4 g of sodium in 60 mL ethanol) and the reaction mixture was stirred for 20 min, followed by addition of a solution of **2** (1.36 g, 5 mmol) in ethanol (30 mL). The reaction mixture was then heated at reflux for 5 h (monitored by TLC), and the solvent was removed under reduced pressure. The residue was treated with water and the solid obtained was filtered, washed with water and dried. The crude compound thus obtained was purified by silica gel column chromatography with hexane/EtOAc (9:1) as eluent. Yield 74% (0.97 g); orange solid; m.p. 200–201 °C; R_f = 0.1 (8:2 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (t, J = 7.0 Hz, 3 H, CH_3), 4.62 (q, J = 7.0 Hz, 2 H, -CH_2), 5.22 (br. s, 2 H, -NH_2), 7.58 (t, J = 7.5 Hz, 1 H, ArH), 7.67 (t, J = 7.4 Hz, 1 H, ArH), 7.75 (d, J = 8.2 Hz, 1 H, ArH), 7.85 (d, J = 6.8 Hz, 1 H,ArH), 7.98 (d, J = 8.0 Hz, 1 H, ArH), 8.17 (d, J = 7.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6, 61.9, 121.5, 122.7, 125.1, 127.6, 128.40, 128.41, 129.4 130.2, 130.8, 132.7, 134.4, 162.8, 165.3, 168.5 ppm. IR (KBr): $\tilde{\nu}$ = 3473, 3290, 3159, 2923, 1627, 1590 cm^{-1}. MS (*m*/*z*, %): 263 $[M]^+$ (20), 262 (100), 247 (42), 234 (51), 217 (34). $C_{16}H_{13}N_3O$ (263.29): C 72.99, H 4.98, N 15.96%; found C 72.91, H 4.80, N 15.71%.

Procedure for Simmons–Smith Reaction with 2. Synthesis of 7-(Methylthio)acenaphtho[1,2-*c*]thiophene (25): A small crystal of I_2

and CH_2I_2 (6.7 g, 25 mmol) were added under nitrogen atmosphere to a well stirred suspension of Zn–Cu couple (4.0 g, 30 mmol) in dry Et_2O (25 mL), and the reaction mixture was heated at reflux for 45 min. A solution of **2** (2.72 g, 10 mmol) in dry THF (15 mL) was added to the reaction mixture, which was further heated at reflux with stirring for 8 h (monitored by TLC). It was then cooled and the solvent was removed under reduced pressure. The residue was diluted with $CHCl_3$ (150 mL) and water (200 mL) and the extract was filtered to remove metal-based residues. The filtrate was extracted with $CHCl_3$ (2 × 25 mL) and the organic extract was washed with saturated NH_4Cl solution (2 × 50 mL), water (2 × 100 mL), dried (Na_2SO_4) and concentrated to give crude **25**, which was purified by column chromatography with hexane as eluent. Yield 62% (1.57 g); red liquid; R_f = 0.85 (hexanes). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 2.54 (s, 3 H, SCH_3), 7.53 (dd, J = 8.2, 7.1 Hz, 1 H, ArH), 7.56 (dd, J = 8.2, 7.0 Hz, 1 H,ArH), 7.61 (d, J = 6.6 Hz, 1 H, ArH), 7.69 (s, 1 H, ArH), 7.71 (d, J = 8.3 Hz, 1 H, ArH), 7.72 (d, J = 8.0 Hz, 1 H, ArH), 7.77 (d, J = 7.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.6, 120.2, 120.3, 125.3, 125.4, 127.7, 127.8, 130.3, 130.5, 131.2, 131.5, 132.8, 135.7, 138.5, 139.2 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3053, 2924, 1642, 1424, 772 cm^{-1}. MS (*m*/*z*, %): 254 (100) $[M]^+$, 239 (25), 223 (5), 208 (27). $C_{15}H_{10}S_2$ (254.37): C 70.83, H 3.96%; found C 70.99, H 3.75%.

Procedure for the Synthesis of 7-(Methylthio)acenaphtho[1,2-*c*]furan (27): *n*-Butyllithium (1.6 M in hexane, 1.5 mL, 2.4 mmol) was added at –10 °C to a suspension of trimethylsulfonium iodide (0.4 g, 2.4 mmol) in THF (13 mL), and the reaction mixture was stirred for 15 min at this temperature for the generation of dimethylsulfonium methylide. The reaction mixture was then cooled to –78 °C and a solution of **2** (0.54 g, 2.0 mmol) in THF (7 mL) was added over a period of 10 min. The reaction mixture was further stirred at room temperature for 1 h. It was then quenched with a trace of water (0.5 mL) and the solvent was evaporated under reduced pressure below 30 °C. The residue was treated with a saturated solution of NaCl (40 mL) and extracted with diethyl ether, and the organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to give the dihydrofuran derivative **26**. The unstable dihydrofuran derivative **26** was dissolved in methanol (5 mL) and treated with HCl (2 M, 0.2 mL), and the reaction mixture was stirred for 1h. It was then neutralized with saturated Na_2CO_3 solution (5 mL) and extracted with diethyl ether. The combined ethereal solution was washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure to give crude product **27**, which was purified by column chromatography over silica gel with hexane as eluent. Yield 61% (0.29 g); red liquid; R_f = 0.85 (hexane). IR (CH_2Cl_2): $\tilde{\nu}$ = 2923, 2358, 1424, 773 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.52 (s, 3 H, SCH_3), 7.29 (s, 1 H, ArH), 7.45 (t, J = 8.0 Hz, 1 H, ArH), 7.50 (t, J = 8.2 Hz, 1 H, ArH), 7.59 (d, J = 6.8 Hz, 1 H, ArH), 7.65 (d, J = 8.3 Hz, 1 H, ArH), 7.66 (d, J = 8.0 Hz, 1 H, ArH), 7.90 (d, J = 6.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.6, 114.0, 116.9, 119.0, 120.1, 125.5, 125.6, 127.6, 127.9, 131.0, 132.5, 132.6, 139.6, 145.3, 145.3 ppm. MS (*m*/*z*, %): 239 $[M + 1]^+$ (25), 208 (40). $C_{15}H_{10}OS$ (238.31): C 75.60, H 4.23%; found C 75.49, H 4.40%.

Acenaphtho[1,2-*c*]furan (28): This compound was obtained by Raney Ni reduction by the earlier procedure. Yield 58% (0.55 g); low melting solid; R_f = 0.90 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (s, 2 H, ArH), 7.64 (t, J = 7.8 Hz, 2 H, ArH), 7.83 (d, J = 8.3 Hz, 2 H, ArH), 7.99 (d, J = 7.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.4, 128.1, 128.7, 130.1, 138.9, 141.3, 145.1, 155.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3063, 2924, 2858, 1455 cm^{-1}. MS (*m*/*z*, %): 193 $[M + 1]^+$ (75), 192 (40). $C_{14}H_8O$ (192.21): C 87.48, H 4.20%; found C 87.29, H 4.41%.

Preparation of Ethyl 2-[(*E*)-(Methylthio)(1-oxoacenaphthene-2-ylidene)methylamino]acetate (29): DABCO (1.1 g, 10 mmol) was added to an ethanolic solution (50 mL) of **2** (1.1 g, 4 mmol) and glycine ester hydrochloride (1.1 g, 8 mmol), and the reaction mixture was heated at reflux with stirring for 8 h. It was then cooled, concentrated under reduced pressure, poured into ice-cold saturated NH_4Cl solution (200 mL) and extracted with $CHCl_3$ (3 × 50 mL). The combined organic layer was washed with water (2 × 100 mL), dried (Na_2SO_4) and concentrated to give crude **29**, which was purified by column chromatography over silica gel with hexane/ethyl acetate (92:8) as eluent. Yield 75% (0.98 g); yellow solid; m.p. 165–166 °C; R_f = 0.30 (hexanes/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, J = 7.1 Hz, 3 H, CH_3), 2.46 (s, 3 H, SCH_3), 4.24 (q, J = 7.1 Hz, 2 H, CH_2), 4.42 (d, J = 5.8 Hz, 2 H, CH_2) 7.50 (t, J = 8.2 Hz, 1 H, ArH), 7.60 (d, J = 8.5 Hz, 1 H, ArH), 7.61 (t, J = 7.8 Hz, 1 H, ArH), 7.95 (d, J = 7.6 Hz, 2 H, ArH), 8.00 (d, J = 7.0 Hz, 1 H, ArH), 10.76 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 17.9, 46.0, 61.6, 111.1, 118.2, 121.3, 122.3, 127.2, 128.4, 129.8, 130.8, 133.9, 134.1, 135.4, 159.0, 169.6, 192.3 ppm. IR (KBr): $\tilde{\nu}$ = 3453, 3152, 2977, 2931, 1737, 1647, 1192 cm^{-1}. MS (*m*/*z*, %): 327 (100) $[M]^+$. $C_{18}H_{17}NO_3S$ (327.40): C 66.03, H 5.23, N 4.28%; found C 66.12, H 5.10, N 4.44%.

Procedure for Base-Induced Cyclization of *N*,*S*-Acetal 29 to 9-(Methylthio)-8*H*-acenaphtho[1,2-*c*]pyrrole-7-carboxylic Acid (30): A solution of **29** [(1.04 g, 3.2 mmol) in THF (10 mL)] was added at 0 °C to a solution of LDA (8 mmol) [prepared from diisopropylamine (2.5 mL, 8.0 mmol) and *n*BuLi (1.6 M in hexane, 5.1 mL, 8.0 mmol) in 10 mL THF]. The deep red coloured dianion thus formed was further stirred for 1h at 0 °C and then left overnight stirring at room temperature. It was then quenched with ice-cold saturated NH_4Cl solution (50 mL), followed by extraction with $CHCl_3$ (3 × 50 mL). The organic layer was dried (Na_2SO_4) and evaporated to give crude product **30**, which was purified by column chromatography over silica gel with hexane/ethyl acetate (93:7) as eluent. Yield 62% (0.55 g); low melting solid; R_f = 0.30 (9:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.55 (s, 3 H, SCH_3), 7.48 (t, J = 7.7 Hz, 1 H, ArH), 7.57 (d, J = 8.3 Hz, 1 H, ArH), 7.61 (t, J = 7.6 Hz, 1 H, ArH), 7.65 (d, J = 7.1 Hz, 1 H, ArH), 7.94 (d, J = 8.3 Hz, 1 H, ArH), 7.95 (d, J = 6.8 Hz, 1 H, ArH), 9.08 (br. s, 1 H, NH), 10.07 (br. s, 1 H, COOH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.0, 106.0, 117.8, 121.3, 121.7, 127.3, 128.2, 129.6, 129.61, 130.7, 132.9, 134.6, 134.7, 135.9, 160.6, 190.6 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2830, 2557, 1697, 1418, 1286 cm^{-1}. MS (*m*/*z*, %): 281 $[M]^+$ (36). $C_{16}H_{11}NO_2S$ (281.33): C 68.31, H 3.94, N 4.98%; found C 68.50, H 3.71, N 4.83%.

8*H*-Acenaphtho[1,2-*c*]pyrrole-7-carboxylic Acid (31): This compound was obtained by Raney Ni reduction by the earlier procedure. Yield 60% (0.70 g); yellow solid; m.p. 158–159 °C; R_f = 0.10 (8:2 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (d, J = 8.0 Hz, 1 H, ArH), 7.45–7.63 (m, 3 H, ArH), 7.70 (d, J = 8.1 Hz, 1 H, ArH), 7.75 (d, J = 7.5 Hz, 1 H, ArH), 8.12 (d, J = 7.1 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.1, 115.8, 119.6, 123.1, 125.2, 126.5, 127.8, 128.2, 130.6, 130.7, 132.7, 132.9, 133.5, 137.4, 161.3 ppm. IR (KBr): $\tilde{\nu}$ = 3303, 2934, 2379, 1656 cm^{-1}. MS (*m*/*z*, %): 236 $[M + 1]^+$ (100). $C_{15}H_9NO_2$ (235.24): C 76.59, H 3.86, N 5.95%; found C 76. 34, H 3.96, N 5.76%.

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