JOC The Journal of Organic Chemistry

ARTICLE

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Indium-Catalyzed Construction of Polycyclic Aromatic Hydrocarbon Skeletons via Dehydration

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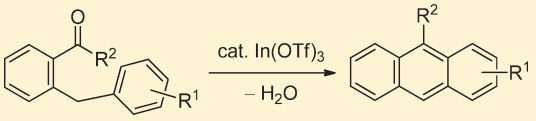
Supporting Information

ABSTRACT: Polycyclic aromatic compounds can be synthesized from 2-benzylic- or 2-allylbenzaldehydes using a catalytic amount of In(III) or Re(I) complexes. By using this method, polycyclic aza-aromatic compounds can also be prepared efficiently. In these reactions, only water is formed as a side product.



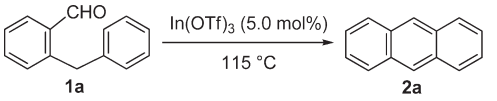
INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are abundant in petroleum and are also basic skeletons in organic molecules. Recently, functional materials based on organic compounds containing PAH skeletons have received much attention,[1] and therefore, many reports have been made on the construction of polycyclic aromatic hydrocarbons.[2] In this paper, we report the synthesis of PAHs and polycyclic aza-aromatic compounds by dehydrative cycloaromatization using a Lewis acid catalyst.

RESULTS AND DISCUSSION

Treatment of 2-benzylbenzaldehyde (**1a**) with a catalytic amount of indium salt $In(OTf)_3$ in toluene at 115 °C for 24 h resulted in cycloaromatization to produce anthracene (**2a**) in 94% yield (eq 1).[3] Scandium triflate, $Sc(OTf)_3$, and a rhenium complex, $[ReBr(CO)_3(thf)]_2$, also showed high catalytic activity in toluene; however, a higher reaction temperature was necessary to complete the reaction (150 °C, 24 h: $Sc(OTf)_3$, 93%; $[ReBr(CO)_3(thf)]_2$, 97%).[4−8] Several other Lewis acids also showed catalytic activity under varying conditions. Conditions A (toluene, 150 °C, 24 h): $Sc(OTf)_3$, 93%; $[ReBr(CO)_3(thf)]_2$, 97%; $ReBr(CO)_5$, 82%; $Re_2(CO)_{10}$, 0%; $MnBr(CO)_5$, 0%; $Mn_2(CO)_{10}$, 0%; $FeCl_3$, 8%; $[IrCl(cod)]_2$, 2%; $Cu(OTf)_2$, 74%; AgOTf, 63%; $InCl_3$, 97%; $In(OTf)_3$, 97%; $Bi(OTf)_3$, 71%. Conditions B (toluene, 115 °C, 24 h): $Sc(OTf)_3$, 73%; $[ReBr(CO)_3(thf)]_2$, 64%; $InCl_3$, 12%. In the case of using $FeCl_3$ as a catalyst, **2a** was formed in only 8%. By adding molecular sieves (100 wt % of $FeCl_3$, a drying agent), $FeCl_3$ worked better and **2a** was obtained in 47% yield. We have carried out the control experiment using triflic acid under the same reaction conditions. As a result, **2a** was provided in 88% and 37% yields, respectively, when 1.0 mol % or 5.0 mol % of triflic acid was used as a catalyst. These results indicate that triflic acid may be generated from $In(OTf)_3$ and water.

Importantly, diphenylmethane was not formed by decarbonylation. It is also noteworthy that $In(OTf)_3$, $Sc(OTf)_3$ and $[ReBr(CO)_3(thf)]_2$ work as Lewis acids even in the presence of water, thus allowing the reaction to proceed well in spite of the formation of water as a side product. Changing the solvent to 1,2-dichloroethane did increase the efficiency, with the reaction proceeding in just 6 h (eq 1). When 1,2-dichloroethane, which was not dried and degassed, was employed as a solvent, anthracene (**2a**) was produced in 96% yield. Therefore, it is not necessary to use dry degassed solvent. When methanol was used as a solvent, anthracene (**2a**) was obtained in 7% yield. In contrast, the cycloaromatization did not proceed in a solvent of THF or DMF.



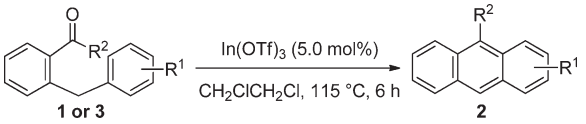
(1)

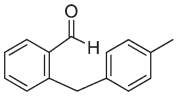
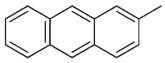
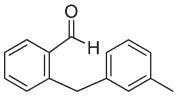
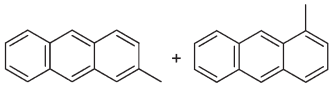
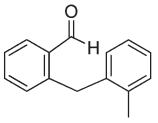
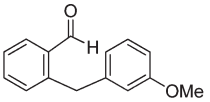
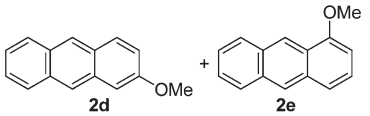
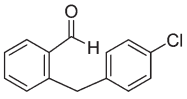
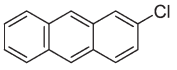
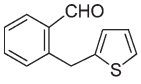
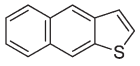
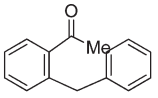
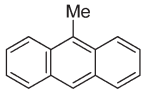
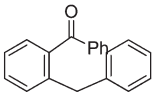
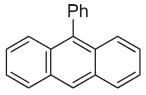
conditions	yield / %
toluene, 24 h	94
CH_2ClCH_2Cl, 6 h	96

To clarify the scope and limitations of the reaction in terms of substrates, we investigated several 2-benzylic aromatic aldehydes (Table 1). Substrates with a methyl group at the *para* or *ortho* position, **1b** and **1d**, produced anthracene derivatives **2b** and **2c** in 94% and 96% yields, respectively (entries 1 and 3). When a 2-benzylic aromatic aldehyde with a methyl group at the *meta* position (**1c**) was used, however, a mixture of anthracene derivatives **2b** and **2c** was obtained in 97% yield (entry 2). The reaction occurred regioselectively at the position with less steric hindrance and was also influenced by an electronic effect. The corresponding anthracene derivative **2d** (and **2e** as a minor product) was obtained in 93% yield at 25 °C for 1 h using 2-benzylic benzaldehyde **1e** bearing an electron-donating group (entry 4), while reaction of a 2-benzylic benzaldehyde having an electron-withdrawing substituent such as a trifluoromethyl group at the *meta* position did not proceed. Chlorine substituents, on the other hand,

Received: April 28, 2011
Published: July 18, 2011

Table 1. Investigation of Several 2-Benzylic Aromatic Aldehydes 1 and 2-Benzylic Aromatic Ketones 3



entry	1 or 3	temp / °C	time / h	yield / %[a]
1	 **1b**	115	6	 **2b** 94 (>99)
2	 **1c**	80	24	 **2b** + **2c** 97 (>99) [93 : 7][b]
3	 **1d**	115	6	**2c** 96 (>99)
4	 **1e**	25	1	 **2d** + **2e** 93 (>99) [95:5][c]
5	 **1f**	115	12	 **2f** 96 (>99)
6	 **1g**	25	12	 **2g** 95 (95)
7[d]		25	9	95 (95)
8	 **3a**	115	24	 **2h** 97 (>99)
9	 **3b**	135	6	 **2i** 96 (97)

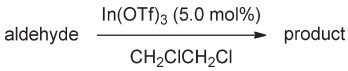
[a] Isolated yield. Yield determined by ^{1}H NMR is reported in parentheses. [b] The ratio of **2b** and **2c** is given in square brackets. [c] The ratio of **2d** and **2e** is given in square brackets. [d] $[ReBr(CO)_3(thf)]_2$ (2.5 mol %).

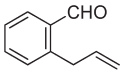
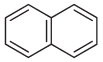
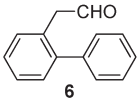
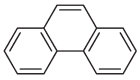
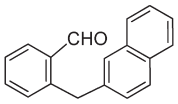
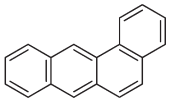
are tolerated in the reaction (entry 5). Naphtho[2,3-*b*]thiophene (**2g**) was obtained in 95% yield from 2-(thiophene-2-ylmethyl)-benzaldehyde (**1g**) as is a heteroaromatic substrate (entry 6).[9] In this reaction, the catalytic activity of rhenium complex $[ReBr(CO)_3(thf)]_2$ is higher than that of $In(OTf)_3$ (entry 7). For substrates bearing a substituent at the R^2 position (2-benzylic aromatic ketones **3a** and **3b**), the cycloaromatization reaction also proceeds, providing the corresponding anthracene derivatives **2h** and **2i** in 97% and 96% yields, respectively (entries 8 and 9).

In the above reactions, anthracenes were synthesized by activating an *aromatic* C−H bond. We postulated that a similar transformation using *olefinic* C−H bonds would provide access to other types of polycyclic aromatic hydrocarbons. Gratifyingly, this assumption was proved correct. By heating 2-allylbenzaldehyde (**4**) in the presence of a catalytic amount of $In(OTf)_3$, naphthalene (**5**) was obtained in 70% yield (Table 2, entry 1).[10] The reaction proceeded in good yield even though the substrate lacks a C2 alkyl or aryl group that would stabilize the cationic intermediate. Using this method, bent polycyclic aromatic compounds can also be synthesized. After treatment of 2-biphenylacetaldehyde (**6**) with a catalytic amount of $[ReBr(CO)_3(thf)]_2$, phenanthrene (**7**) was afforded in 95% yield even at 25 °C (Table 2, entry 2). In Table 2, entry 2, the cyclization also proceeded using $In(OTf)_3$ as a catalyst; however, the yield of phenanthrene (**7**) was 48%. When 2-(2-naphthylmethyl)benzaldehyde (**8**) was employed as the substrate, tetraphene (**9**) was produced in 90% yield (Table 2, entry 3). While the reaction can potentially proceed at either the 1- or 3-positions of the 2-naphthyl moiety, it occurs regioselectively at the 1-position.

At present we do not have enough experimental evidence to support a definitive reaction mechanism. However, because the

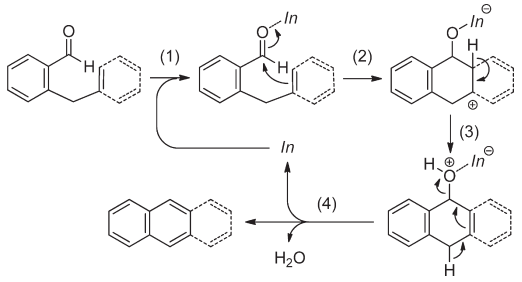
Table 2. Synthesis of Several Aromatic Compounds from the Corresponding Aldehydes



entry	aldehyde	temp / °C	time / h	yield / %[a]
1	 **4**	80	24	 **5** 70 (75)
2[b]	 **6**	25	24	 **7** 95 (97)
3	 **8**	80	6	 **9** 90 (>99)

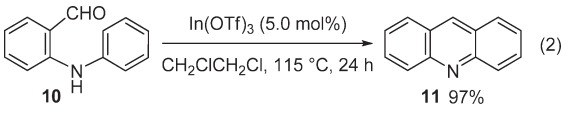
[a] Isolated yield. Yield determined by ^{1}H NMR is reported in parentheses. [b] $[ReBr(CO)_3(thf)]_2$ (2.5 mol %).

Scheme 1. Proposed Mechanism for the Formation of Oligoarenes

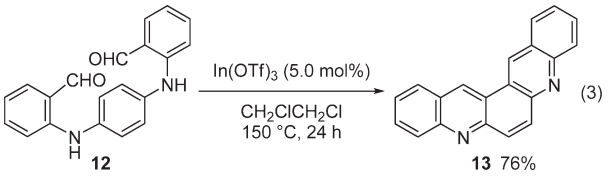


reactivity of the 2-benzylic aromatic aldehyde with an electron-withdrawing group is much less than that of the substrate bearing an electron-donating group and similar reactions are mediated by several different Lewis acids, we are tempted to assume that the transformation proceeds via an electrophilic substitution reaction (in the case of 2-benzylic aromatic aldehydes and ketones, a Friedel–Crafts-type reaction).[11] The possible mechanism is shown in Scheme 1: (1) activation of the carbonyl group of 2-benzylic or 2-allylic aromatic aldehydes or ketones by an indium catalyst; (2) intramolecular nucleophilic attack to generate a cyclic zwitterionic intermediate; (3) deprotonation and protonation to form an alcoholic intermediate; and (4) dehydration catalyzed by the indium complex to give the polycyclic aromatic hydrocarbon. In this reaction, water is formed as a side product. Therefore, it is important to use Lewis acids that are stable and show high reactivity even in the presence of water.

Using the above method, polycyclic aza-aromatic compounds can also be synthesized (eq 2). Heating a mixture of 2-(phenylamino)-benzaldehyde (**10**) and a catalytic amount of $In(OTf)_3$ afforded acridine (**11**) in 97% yield.[12−14] This reaction was not inhibited by the amino group even though a Lewis acid was used as the catalyst.



Notably, the above reaction can also be applied to the synthesis of dibenzo[*b*,*j*][4,7]phenanthroline (**13**).[15] Double cycloaromatization of dialdehyde **12** proceeded smoothly and provided the desired product **13** in 76% yield (eq 3).



CONCLUSION

We have succeeded in synthesizing polycyclic aromatic hydrocarbons such as naphthalene, anthracene, and naphtho[2,3-*b*]thiophene derivatives via dehydrative intramolecular cycloaromatization. By using 2-biphenylacetaldehyde or 2-(2-naphthylmethyl)benzaldehyde, phenanthrene and tetraphene, bent polycyclic aromatic hydrocarbons, can also be constructed. Furthermore, the method can be used to prepare polycyclic aza-aromatic compounds and can be applied to the synthesis of dibenzo[*b*,*j*][4,7]phenanthroline. In these transformations, generally, $In(OTf)_3$ showed higher catalytic activities compared with other Lewis acid catalysts including $[ReBr(CO)_3(thf)]_2$; however, in some substrates, $[ReBr(CO)_3(thf)]_2$ gave better results. We therefore believe that this transformation will become a useful and powerful method for the synthesis of polycyclic aromatic hydrocarbons and polycyclic aza-aromatic compounds.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under an argon atmosphere. 1,2-Dichloroethane and toluene were purchased and were degassed before use. Indium triflate, $In(OTf)_3$, was purchased and used as received. 2-Benzylic aromatic aldehydes (**1b**–**f** and **8**) were prepared by cross-coupling reactions between *o*-formylbenzyl bromide and aryl boronic acids according to the literature methods.[16] 2-(Thiophene-2-ylmethyl)benzaldehyde (**1g**),[17] 2-benzylacetophenone (**3a**),[18] 2-allylbenzaldehyde (**4**),[19] and 2-(phenylamino)benzaldehyde (**10**)[12] were synthesized according to the literature methods. 2-Benzylbenzaldehyde (**1a**) was prepared by lithiation of 1-benzyl-2-bromobenzene and successive treatment with *N*,*N*-dimethylformamide (DMF). 2-Benzylbenzophenone (**3b**) was synthesized by lithiation of 1-benzyl-2-bromobenzene and treatment of the lithiated intermediate with benzaldehyde followed by oxidation of the formed alcohol. Biphenylacetaldehyde (**6**) was prepared by lithiation of 2-bromobiphenyl and treatment of the lithiated intermediate with ethylene oxide followed by oxidation of the formed alcohol. Dialdehyde (**12**) was prepared by palladium-catalyzed Buchwald–Hartwig amination between 2 equiv of 2-(2-bromophenyl)-1,3-dioxolane and 1,4-phenylenediamine. The structures of these reaction products were determined by comparing the spectrum data of these products with those of **2a**,[20] **2b**,[21] **2c**,[22] **2d**,[23] **2e**,[24] **2f**,[25] **2g**,[26] **2h**,[22] **2i**,[21] **5**,[20] **7**,[20] **9**,[20,27] and **11**.[28]

In ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra, proton chemical shifts are reported relative to Me_4Si ($CDCl_3$) at δ 0.00 ppm or residual solvent peak ($CDCl_3$ at δ 7.26 ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm.

Typical Procedure for the Synthesis of Anthracene (2a). A mixture of *o*-benzylbenzaldehyde (**1a**, 31.0 mg, 0.150 mmol), $In(OTf)_3$ (4.2 mg, 0.0075 mmol), and 1,2-dichloroethane (0.15 mL) was stirred at 115 °C for 6 h in a sealed tube. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel

dx.doi.org/10.1021/jo200861s |*J. Org. Chem.* 2011, 76, 7005–7009

(hexane/AcOEt = 20/1) to give anthracene in 94% yield (**2a**, 25.9 mg, 0.141 mmol).

Anthracene (2a): solid; mp = 210−215 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.47 (m, 4H), 8.00−8.02 (m, 4H), 8.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.3, 126.2, 128.1, 131.6.

2-Methylanthracene (2b). Purification by silica gel column chromatography (hexane/AcOEt = 50/1): TLC (hexane/AcOEt = 50/1) R_f = 0.63; solid; mp = 205−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 3H), 7.27 (d, J = 8.8 Hz, 1H), 7.38−7.43 (m, 2H), 7.70 (s, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.93−7.95 (m, 2H), 8.27 (s, 1H), 8.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 124.9, 125.1, 125.2, 125.9, 126.3, 127.9, 128.0, 128.15, 128.20, 130.3, 131.2, 131.8, 132.0, 134.9.

1-Methylanthracene (2c). Purification by silica gel column chromatography (hexane/AcOEt = 50/1): TLC (hexane/AcOEt = 50/1) R_f = 0.60; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 3H), 7.28 (d, J = 7.2 Hz, 1H), 7.34 (td, J = 8.4 and 2.8 Hz, 1H), 7.45−7.48 (m, 2H), 7.85 (d, J = 7.6 Hz, 1H), 7.97−7.99 (m, 1H), 8.01−8.03 (m, 1H), 8.40 (s, 1H), 8.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 122.7, 125.1, 125.26, 125.31, 125.6, 126.7, 126.8, 127.9, 128.5, 131.3, 131.4, 131.5, 131.8, 134.2.

2-Methoxyanthracene (2d) and 1-Methoxyanthracene (2e). Purification by silica gel column chromatography (hexane/AcOEt = 50/1): TLC (hexane/AcOEt = 50/1) R_f = 0.53; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 3H, **2d**), 4.09 (s, 3H, **2e**), 7.17 (dd, J = 8.8 and 2.4 Hz, 1H, **2d** + **2e**), 7.20 (d, J = 2.4 Hz, 1H, **2d** + **2e**) 7.39−7.48 (m, 2H, **2d** + **2e**), 7.90 (d, J = 8.8 Hz, 1H, **2d** + **2e**), 7.97 (t, J = 8.0 Hz, 2H, **2d** + **2e**), 8.28 (s, 1H, **2d**), 8.35 (s, 1H, **2d**), 8.38 (s, 1H, **2e**), 8.86 (s, 1H, **2e**); ^{13}C NMR (100 MHz, $CDCl_3$, **2d**) δ 55.2, 103.5, 119.3, 120.5, 124.1, 124.4, 124.9, 125.5, 126.2, 127.6, 128.2, 129.8, 130.3, 132.2, 132.7.

2-Chloroanthracene (2f). Purification by silica gel column chromatography (hexane/AcOEt = 50/1): TLC (hexane/AcOEt = 50/1) R_f = 0.63; solid; mp = 221−223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.8 Hz, 1H), 7.47−7.49 (m, 2H), 7.93−7.99 (m, 4H), 8.32 (s, 1H), 8.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.4, 125.7, 126.0, 126.3 (2C), 126.5, 126.6, 128.0, 128.2, 129.9, 131.0, 131.69, 131.73, 132.2.

Naphtho[2,3-*b*]thiophene (2g). Purification by silica gel column chromatography (hexane/AcOEt = 20/1): TLC (hexane/AcOEt = 20/1) R_f = 0.73; solid; mp = 192−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 5.6 Hz, 1H), 7.42−7.48 (m, 3H), 7.88−7.90 (m, 1H), 7.94−7.96 (m, 1H), 8.30 (s, 1H), 8.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.6, 121.8, 123.4, 124.9, 125.2, 127.2, 128.1, 128.2, 130.86, 130.89, 138.2, 138.8.

9-Methylanthracene (2h). Purification by silica gel column chromatography (hexane/AcOEt = 50/1): TLC (hexane/AcOEt = 50/1) R_f = 0.60; solid; mp = 81−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (s, 3H), 7.50 (d, J = 6.8 Hz, 2H), 7.55 (d, J = 6.4 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 8.32 (d, J = 8.4 Hz, 2H), 8.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 124.6, 124.8 (3C), 125.2, 125.3, 129.0, 130.1, 131.4.

9-Phenylanthracene (2i). Purification by silica gel column chromatography (hexane/AcOEt = 50/1): TLC (hexane/AcOEt = 50/1) R_f = 0.58; solid; mp = 155−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 6.8 Hz, 1H), 7.35 (dd, J = 6.4 and 1.2 Hz, 1H), 7.42−7.46 (m, 4H), 7.51−7.59 (m, 3H), 7.60 (d, J = 8.8 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H), 8.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.1, 125.3, 126.5, 126.8, 127.4, 128.28, 128.34, 130.2, 131.2, 131.3, 137.0, 138.7.

Naphthalene (5). Purification by silica gel column chromatography (hexane/AcOEt = 50/1): TLC (hexane/AcOEt = 50/1) R_f = 0.75; solid; mp = 218−219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.49 (m, 4H), 7.84−7.86 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.8, 127.8, 133.4.

Phenanthrene (7). Purification by silica gel column chromatography (hexane/AcOEt = 50/1): TLC (hexane/AcOEt = 50/1) R_f = 0.63; solid; mp = 224−225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (td, J = 8.0 and 1.6 Hz, 2H), 7.66 (td, J = 8.0 and 1.6 Hz, 2H), 7.74 (s, 2H), 7.89 (dd, J = 8.0 and 1.2 Hz, 2H), 8.69 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.6, 126.5 (3C), 126.9, 128.6, 130.3, 132.0.

Tetraphene (9). Purification by silica gel column chromatography (hexane/AcOEt = 50/1): TLC (hexane/AcOEt = 50/1) R_f = 0.50; solid; mp = 162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.55 (m, 2H), 7.58−7.62 (m, 2H), 7.66 (td, J = 8.0 and 1.2 Hz, 1H), 7.77 (d, J = 9.6 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 8.01−8.04 (m, 1H), 8.09−8.12 (m, 1H), 8.34 (s, 1H), 8.81 (d, J = 8.4 Hz, 1H), 9.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.5, 122.9 (2C), 125.7, 125.8, 126.75, 126.82, 127.0, 127.3, 127.7, 128.4, 128.6 (2C), 128.8, 130.5, 130.6, 131.89, 131.93.

Acridine (11). Purification by silica gel column chromatography (hexane/AcOEt = 20/1): TLC (hexane/AcOEt = 20/1) R_f = 0.30; solid; mp = 111−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, J = 7.2 Hz, 2H), 7.76 (t, J = 6.8 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H), 8.24 (d, J = 8.8 Hz, 2H), 8.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.6, 126.5, 128.1, 129.3, 130.3, 136.0, 148.9.

Dibenzo[*b*,*j*][4,7]phenanthroline (13). Purification by silica gel column chromatography (hexane/AcOEt = 5/1): TLC (hexane/AcOEt = 5/1) R_f = 0.20; solid; mp = 244−245 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, J = 7.2 Hz, 2H), 7.86 (t, J = 8.0 Hz, 2H), 8.12 (d, J = 8.4 Hz, 2H), 8.21 (s, 2H), 8.30 (d, J = 8.4 Hz, 2H), 9.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.4, 126.4, 126.8, 128.0, 129.1, 130.3, 130.4, 134.1, 148.1, 148.7; IR (KBr, ν/cm^{-1}) 3051, 2924, 1341, 1321, 1261, 1190, 1130, 1096, 1013, 957, 905, 860, 835, 804, 783, 746, 741; HRMS (FAB$^+$) calcd for $C_{20}H_{12}N_2$ (M^+) 280.1000, found 280.1009.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra of polycyclic aromatic hydrocarbons **2**, **5**, **7**, and **9** and polycyclic aza-aromatic compounds **11** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan and Okayama University.

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