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Synthesis of 10-Arylanthracenes from 2-Fluorobenzophenones and Arylacetonitriles *via* a One-Pot S_NAr and Anionic Cyclization Cascade†

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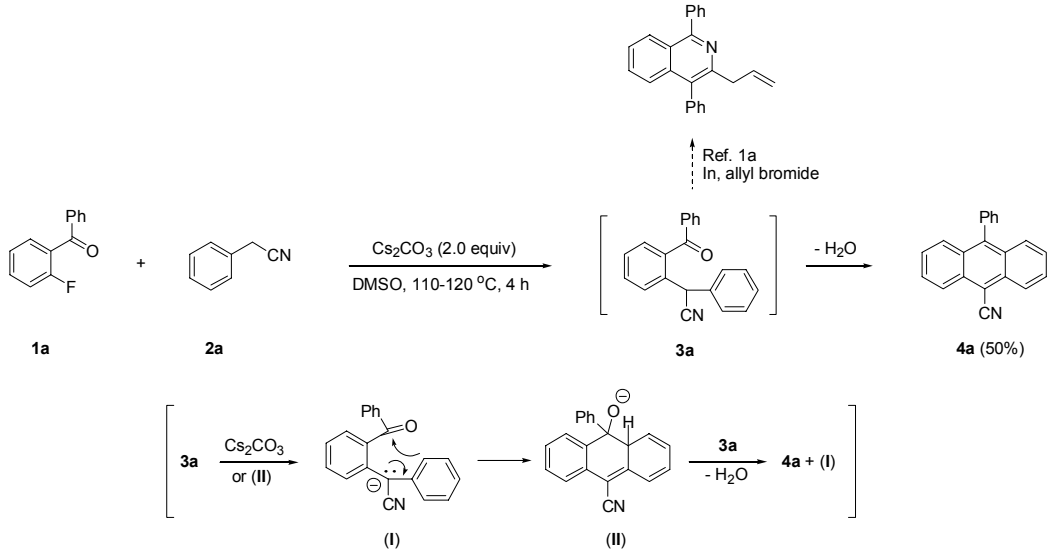
During our recent studies on the indium-mediated Barbier reaction for the synthesis of isoquinoline derivatives,[1a] we tried the synthesis of **3a** *via* an S_NAr reaction from 2-fluorobenzophenone (**1a**) and phenylacetonitrile (**2a**) in order to make 3-allyl-1,4-phenylisoquinoline (see Scheme 1). However, we did not observe the formation of our desired compound **3a** under the conditions of Cs_2CO_3 in DMSO. Instead, 9-cyano-10-phenylanthracene (**4a**)[2] was isolated as the major product (*vide infra*, entry 2 in Table 1, 110 ~ 120 °C, 4 h, 50%). The plausible reaction mechanism for the formation of **4a** is depicted in Scheme 1. The reaction of **1a** and **2a** must produce carbanion (**I**) which is stabilized by the α-cyano group (*vide infra*).[3] The attack of *ortho*-carbon of arene moiety onto the benzoyl group resulted in effective bond-formation to form (**II**) and eventually **4a** after dehydration.

Anthracenes has been incorporated into a variety of applications for sensing metal ions, simple inorganic anions, and small organic molecules, as well as for cell-surface labeling and medical diagnosis.[2,4,5] Especially, 9-cyano-10-arylanthracenes and related compounds have been synthesized and studied extensively due to their π-conjugated donor-acceptor properties.[2] In these respects, various synthetic procedures of anthracene scaffold have been developed including the use of Diels-Alder reaction,[4f] Bergman cycloaromatization,[4e] and AuCl-catalyzed [4+2] benzannulation.[4c,d] We thought that our serendipitous finding could provide an easy and efficient protocol for the synthesis of various 10-arylanthracenes in a one-pot reaction.

Table 1. Optimization of reaction conditions for the synthesis of **4a**[a]

entry	base[b]	solvent	temp (°C)	time (h)	**1a** (%)[c]	**4a** (%)[d]
1	Cs_2CO_3	DMSO	70 ~ 80	5	95	0
2	Cs_2CO_3	DMSO	110 ~ 120	4	0	50
3[e]	Cs_2CO_3	DMSO	130 ~ 140	3	0	62
4	Cs_2CO_3	DMF	130 ~ 140	4	0	45
5	Cs_2CO_3	NMP	130 ~ 140	4	0	41
6	K_2CO_3	DMSO	130 ~ 140	5	0	44
7	CsF	DMF	140 ~ 150	5	72	4
8[f]	*t*-BuOK	DMF[g]	100 ~ 110	3	0	66

[a]Compounds **1a** (1.0 equiv) and **2a** (2.0 equiv) were used. [b]Base (2.0 equiv) was used. [c]Recovered **1a** and isolated yield. [d]Isolated yield. [e]Conditions A. [f]Conditions B. [g]Dry DMF was required, otherwise the yield of **4a** was decreased to 45%.

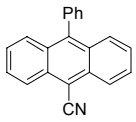
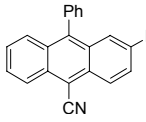
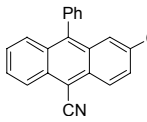
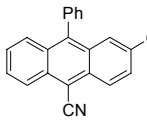
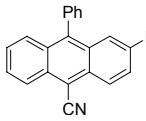
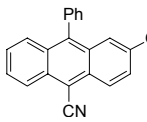
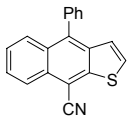
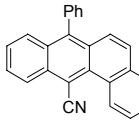
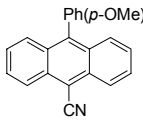
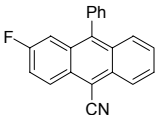


Scheme 1

†This paper is dedicated to Professor Sunggak Kim on the occasion of his honorable retirement.

As described above, the reaction of **1a** and **2a** under the influence of Cs_2CO_3 in DMSO at 110 ~ 120 °C afforded **4a** in 50% yield (entry 2 in Table 1). At lower temperature (70 ~ 80 °C) **4a** was not formed at all (entry 1) while the yield of **4a** was increased to 62% at 130 ~ 140 °C (entry 3). The use of DMF or NMP was less effective (entries 4 and 5). The use of K_2CO_3 and CsF was found to be also less effective (entries 6 and 7). However, compound **4a** was isolated in an increased yield (66%) when we used *t*-BuOK in DMF (entry 8). Thus, we selected two conditions, namely conditions A (entry 3) and conditions B (entry 8), and examined the synthesis of 10-arylanthracenes with various substrates, as shown in Figure 1. The results for the syntheses of 10-arylanthracene derivatives **4a-j** are summarized in Table 2.

Table 2. Synthesis of 10-arylanthracenes

entry	substrate[a]	conditions[b]	product (%)
1	**1a** + **2a**	A, 3 h B, 3 h	 **4a**: A (62) B (66)
2	**1a** + **2b**	A, 3 h	 **4b**: (67)
3	**1a** + **2c**	A, 5 h	 **4c**: (44)
4	**1a** + **2d**	A, 5 h B, 3 h	 **4d**: A (38) B (50)
5	**1a** + **2e**	A, 6 h B, 6 h	 **4e**: A (0) B (0)
6	**1a** + **2f**	A, 8 h B, 5 h	 **4f**: A (19) B (43)
7	**1a** + **2g**	A, 2 h B, 2 h	 **4g**: A (21) B (8)
8	**1a** + **2h**	A, 3 h	 **4h**: (62)
9	**1b** + **2a**	A, 3 h B, 3 h	 **4i**: A (52) B (60)
10	**1c** + **2a**	A, 3 h B, 3 h	 **4j**: A (16) B (38)

[a]Compound **2** was used in 2.0 equiv. [b]Condition A: DMSO, Cs_2CO_3 (2.0 equiv), 130 ~ 140 °C; Condition B: DMF, *t*-BuOK (2.0 equiv), 100 ~ 110 °C.

The yields of **4a**, **4b**, **4h**, and **4i** were good to moderate (entries 1, 2, 8, and 9). When we used arylacetonitriles having an electron withdrawing substituent at the *para*-position (entries 3 and 4), the yields of products were low (44 ~ 50%). The reaction of 4-nitrophenylacetonitrile (**2e**) did not produce any trace amounts of **4e** presumably due to low nucleophilicity of the *ortho*-carbon atom of arene moiety by the delocalization of electrons to the nitro group (entry 5). However, the yield of **4f** was also low unfortunately, although the starting material **2f** has an electron-donating −OMe group (entry 6). Actually, in this case severe decomposition of *p*-methoxybenzylcyanide (**2f**) was observed on TLC and this might be the major reason for the low yield of **4f**. The situation was similar for 2-thiopheneacetonitrile (**2g**) as in entry 7. When we used 2-chlorobenzophenone (**1d**) instead of **1a**, the yield of **4a** was decreased to 25%, and the starting material **1d** was recovered in 47%. As a next experiment, we examined the synthesis of bi-anthracene **6** as shown in Scheme 2. The reaction of **1a** and **2i** afforded very low yield of **6** (7 ~ 9%), unfortunately, along with anthracene **5** (10 ~ 14%).

In order to clarify the reaction mechanism, we tried the synthesis of intermediate (**I**) but failed (*vide supra*, Scheme 1) under various conditions. Thus we checked the presence of (**I**) in the reaction mixture, as a next choice. During the column separation process of **4a**, we collected the remaining spots all together, and the mixture was subjected under the same conditions (Cs_2CO_3/DMSO, 130 ~ 140 °C). However, we could not observe the formation of any trace amounts of **4a**. The results stated that intermediate (**I**), once formed, readily converted to **4a** under the reaction conditions.

The anionic cyclization pathway has not been reported much, although the reaction can provide an easy route to many cyclic compounds. Wrobel and co-workers reported an interesting anionic cyclization in their synthesis of acridine and related compounds.[6] The *ortho*-carbon of arene moiety attack the nitroso group in an intramolecular fashion in the intermediate stage, as shown in Scheme 3.[7] Based on the reported papers and our results, the mechanism for the formation of anthracene can be regarded as a one-pot domino process involving the nucleophilic aromatic substitution (S_NAr) and an anionic cyclization.

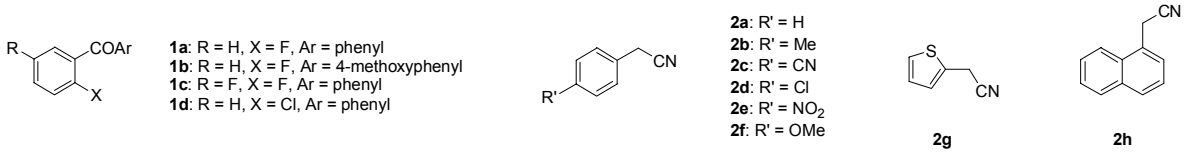
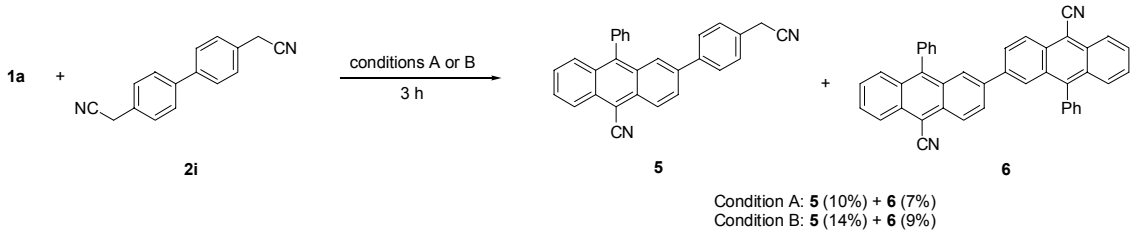
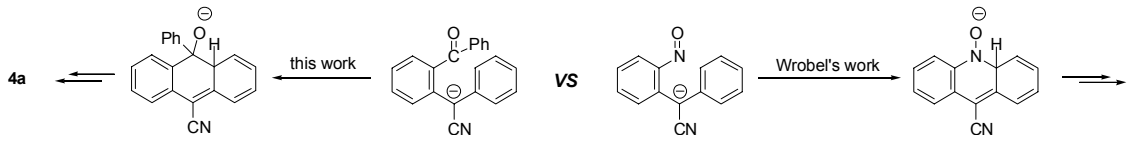


Figure 1



Scheme 2



Scheme 3

In summary, we found an efficient one-pot approach for the synthesis of 9-cyano-10-arylanthracenes involving a tandem S_NAr and interesting anionic cyclization of arene moiety. Although the yields of anthracenes were low to moderate, synthesis of pentacene derivatives and the study on optimization of yield are currently underway.

Experimental Section

Typical procedure for the synthesis of compounds 4a (method A). To a stirred solution of 2-fluorobenzophenone (**1a**, 200 mg, 1.0 mmol) and benzyl cyanide (**2a**, 234 mg, 2.0 mmol) in DMSO (2 mL) was added Cs_2CO_3 (651 mg, 2.0 mmol) and heated to 130 ~ 140 °C for 3 h. The reaction mixture was poured into dilute aqueous HCl, extracted with EtOAc, dried with $MgSO_4$, and removed the solvent. Column chromatographic purification process (hexanes/diethyl ether/CH_2Cl_2, 84:1:15) afforded compound **4a** (173 mg, 62%) as a yellow solid.

Typical procedure for the synthesis of compounds 4a (method B). To a solution of **1a** (200 mg, 1.0 mmol) and **2a** (234 mg, 2.0 mmol) in dry DMF (2 mL) was added *t*-BuOK (224 mg, 2.0 mmol) and heated to 100 ~ 110 °C for 3 h. The reaction mixture was poured into dilute aqueous HCl, extracted with EtOAc, dried with $MgSO_4$, and removed the solvent. Column chromatographic purification process (hexanes/diethyl ether/CH_2Cl_2, 84:1:15) afforded compound **4a** (184 mg, 66%) as a yellow solid.

Other compounds were prepared similarly by using method A and/or method B (see Table 2). Known compounds **4a**[2a] and **4i**[2a] were identified by their ^{1}H and ^{13}C NMR data. The spectroscopic data of unknown compounds are as follows.

Compound 4b: Yellow solid, mp 176 ~ 177 °C; IR (KBr) 2213, 1632, 1601, 1446 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.41 (s, 3H), 7.31-7.42 (m, 4H), 7.49 (dd, J = 8.7 and 1.8 Hz, 1H), 7.55-7.65 (m, 5H), 8.34 (d, J = 8.7 Hz, 1H), 8.40-8.44 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.98, 105.26, 117.54, 125.18, 125.31, 125.81, 126.01, 127.62, 128.06, 128.09, 128.47, 129.68, 129.74, 130.56, 131.35, 131.69, 132.43, 136.09, 137.38, 142.55; ESIMS *m/z* 294 (M^++1). Anal. Calcd for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.77. Found: C, 90.33; H, 5.21; N, 4.56.

Compound 4c: Yellow solid, mp 261 ~ 262 °C; IR (KBr) 2228, 2216, 1637, 1612, 1449 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36-7.41 (m, 2H), 7.55 (ddd, J = 8.4, 6.6, and 1.2 Hz, 1H), 7.64-7.69 (m, 3H), 7.74-7.83 (m, 3H), 8.15 (q, J = 0.9 Hz, 1H), 8.49 (dt, J = 8.4 and 0.9 Hz, 1H), 8.53 (dd, J = 9.0 and 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 106.41, 109.87, 116.42, 118.53, 125.51, 126.96, 127.40, 127.59, 128.09, 128.24, 128.87, 129.04, 130.32, 130.40 (2C), 132.92, 134.32, 135.06, 135.58, 145.38; ESIMS *m/z* 305 (M^++1). Anal. Calcd for $C_{22}H_{12}N_2$: C, 86.82; H, 3.97; N, 9.20. Found: C, 86.97; H, 4.22; N, 9.03.

Compound 4d: Yellow solid, mp 203 ~ 204 °C; IR (KBr) 2216, 1621, 1612, 1442 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31-7.38 (m, 2H), 7.45 (ddd, J = 8.1, 6.9, and 1.2 Hz, 1H), 7.56-7.72 (m, 7H), 8.36-8.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 105.94, 116.96, 125.43, 126.01, 126.80, 127.12, 127.73, 128.53, 128.70, 128.87, 129.68, 129.87, 130.12, 130.47, 131.06, 132.34, 132.89, 136.46, 142.84; ESIMS *m/z* 314 (M^++1). Anal. Calcd for $C_{21}H_{12}ClN$: C, 80.38; H, 3.85; N, 4.46. Found: C, 80.26; H, 3.89; N, 4.35.

Compound 4f: Yellow solid, mp 172 ~ 173 °C; IR (KBr) 2215, 1632, 1615, 1463 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.69 (s, 3H), 6.85 (d, J = 2.4 Hz, 1H), 7.35-7.44 (m, 4H), 7.53-7.65 (m, 5H), 8.37 (dd, J = 9.0 and 0.3 Hz, 1H), 8.41-8.45 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.11, 103.67, 105.56, 117.55, 123.41, 125.44, 126.30, 127.04, 127.25, 127.54, 128.18, 128.69, 129.67, 130.00, 130.45, 130.86, 131.50, 137.62, 141.32, 157.45; ESIMS *m/z* 310 (M^++1). Anal. Calcd for $C_{22}H_{15}NO$: C, 85.41; H, 4.89; N, 4.53. Found: C, 85.69; H, 5.12; N, 4.67.

Compound 4g: Yellow solid, mp 207 ~ 208 °C; IR (KBr) 2217, 1645, 1634, 1487 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.14 (d, J = 5.4 Hz, 1H), 7.42-7.62 (m, 7H), 7.70 (ddd, J = 8.4, 6.9, and 1.2 Hz, 1H), 7.86 (dq, J = 8.7 and 0.6 Hz, 1H), 8.36 (dq, J = 8.4 and 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 101.86, 116.89, 124.12, 124.39, 126.07, 127.44, 128.03, 128.20, 128.42, 128.60, 128.96, 130.18, 131.65, 137.30, 137.73, 139.98, 144.24; ESIMS *m/z* 286 (M^++1). Anal. Calcd for $C_{19}H_{11}NS$: C, 79.97; H, 3.89; N, 4.91. Found: C, 79.66; H, 4.11; N, 4.65.

Compound 4h: Yellow solid, mp 240 ~ 241 °C; IR (KBr) 2207, 1626, 1497, 1409 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32-7.38 (m, 2H), 7.41 (d, J = 9.3 Hz, 1H), 7.47-7.53 (m, 2H), 7.56-7.61

(m, 3H), 7.65-7.83 (m, 5H), 8.69 (dt, J = 8.7 and 0.9 Hz, 1H), 9.96 (dt, J = 8.1 and 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 103.36, 120.37, 125.19, 125.76, 126.47, 126.64, 127.11, 127.58, 127.98, 128.16, 128.57 (2C), 128.63 (2C), 128.93, 128.98, 130.19, 130.60, 131.79, 133.08, 133.51, 137.87, 143.54; ESIMS m/z 330 (M^++1). Anal. Calcd for $C_{25}H_{15}N$: C, 91.16; H, 4.59; N, 4.25. Found: C, 91.04; H, 4.79; N, 4.01.

Compound 4j: Yellow solid, mp 170 ~ 171 °C; IR (KBr) 2217, 1633, 1484, 1453 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30 (ddd, J = 10.8, 2.4, and 0.6 Hz, 1H), 7.35-7.41 (m, 2H), 7.45-7.55 (m, 2H), 7.56-7.66 (m, 3H), 7.68-7.73 (m, 2H), 8.46-8.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 106.07 ($J_{C\text{-}F}$ = 2.0 Hz), 110.10 ($J_{C\text{-}F}$ = 22.6 Hz), 117.18, 120.30 ($J_{C\text{-}F}$ = 27.8 Hz), 125.52, 126.80, 127.48, 128.32 ($J_{C\text{-}F}$ = 8.9 Hz), 128.50, 128.51, 128.53, 128.74, 130.15 ($J_{C\text{-}F}$ = 10.3 Hz), 130.30 ($J_{C\text{-}F}$ = 8.9 Hz), 130.44, 132.51 ($J_{C\text{-}F}$ = 1.7 Hz), 136.83, 142.92 ($J_{C\text{-}F}$ = 7.7 Hz), 160.23 ($J_{C\text{-}F}$ = 248.1 Hz); ESIMS m/z 298 (M^++1). Anal. Calcd for $C_{21}H_{12}FN$: C, 84.83; H, 4.07; N, 4.71. Found: C, 84.65; H, 4.41; N, 4.32.

Compound 5: Yellow solid, mp 190 ~ 191 °C; IR (KBr) 2214, 1637, 1625, 1451 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.79 (s, 2H), 7.38-7.50 (m, 5H), 7.55-7.66 (m, 5H), 7.69-7.74 (m, 2H), 7.88 (dd, J = 1.8 and 0.6 Hz, 1H), 7.95 (dd, J = 9.0 and 1.8 Hz, 1H), 8.48-8.51 (m, 1H), 8.57 (dd, J = 9.0 and 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.33, 105.55, 117.42, 117.60, 125.25, 125.51, 126.31, 126.46, 127.85, 128.04, 128.35, 128.45, 128.57, 128.66, 128.75, 129.51, 129.77, 130.06, 130.61, 132.37, 133.13, 137.05, 137.70, 140.10, 144.06; ESIMS m/z 395 (M^++1). Anal. Calcd for $C_{29}H_{18}N_2$: C, 88.30; H, 4.60; N, 7.10. Found: C, 87.93; H, 4.95; N, 6.86.

Compound 6: Yellow solid, mp 371 ~ 372 °C; IR (KBr) 2215, 1638, 1624, 1444 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36-7.41 (m, 4H), 7.47 (ddd, J = 8.4, 6.9, and 1.2 Hz, 2H), 7.58-7.65 (m, 6H), 7.69-7.74 (m, 4H), 7.89-7.90 (m, 2H), 7.93 (dd, J = 9.0 and 2.1 Hz, 2H), 8.47-8.50 (m, 2H), 8.55 (dd, J = 9.0 and 0.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 105.57, 117.34, 125.54, 125.80, 126.46, 126.52, 127.88, 128.17, 128.41, 128.69, 128.83, 129.75, 130.09, 130.54, 132.39, 133.17, 136.93, 137.58, 144.15; ESIMS m/z 557 (M^++1). Anal. Calcd for $C_{42}H_{24}N_2$: C, 90.62; H, 4.35; N, 5.03. Found: C, 90.31; H, 4.56; N, 4.89.

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