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The Reaction of 2-Chloro-4-nitrophenol and the Isomeric Chloronitrobenzenes With LDA Under Aryne-forming Conditions

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Abstract: The unprecedented base-initiated generation of a nitrobenzyne and subsequent addition of preformed arylacetonitrile anion nucleophiles is reported. In all cases, 2-amino-5-nitro-3-benzo[*b*]furans are obtained as major product with small amounts of 3-arylmethyl-2-cyano-4-nitrophenols. A mechanism involving ring closure of phenoxide and nitrile groups of the initial aryne-nitrile anion adduct is proposed to account for the formation of the benzofurans. The three isomeric chloronitrobenzynes , however, do not give aryne products when treated with LDA, but rather are reduced to the corresponding *bis*-dichloroazoxybenzenes .

Although the role of a wide range of substituents (alkyl, halogeno, alkoxy, CF_3, etc) on the orientation to and reactivity of benzynes toward nucleophilic addition has been extensively studied,[1] little is known concerning the influence of a nitro group on the chemistry of benzynes. The 3- and 4-nitrobenzynes have been postulated to be quite reactive on theoretical grounds,[2] but experimental data have been reported only for 4-nitrobenzyne, and that information is quite limited. In the few reports available, 4-nitrobenzyne was prepared from the decom-position of either 5-nitrobenzenediazonium-2-carboxylate[3,4,5] or 1,2,3-benzothiadiazol-1,1-dioxide.[6] The reactive arynes were trapped with alcohols to give mixtures of *m*- and *p*- substituted nitrophenyl ethers with *m/p* molar ratios varying between 3:1 to 3.8:1, respectively. These product ratios, which are among the highest observed for nucleophilic addition to 4-substituted benzynes, most likely reflect the strong -I effect (electron-withdrawing effect by induction) of the nitro group (Hammett $\sigma_m = 0.71$). [7] Attempts to generate nitrobenzynes by the thermal decomposition of nitrophthalic anhydrides have been unsuccessful.[8] Such decompositions yield benzyne itself with the nitro group being lost during the reaction. The base induced generation of nitrobenzynes from haloarenes, historically one of the most common methods used in aryne chemistry, is conspicuously absent from the chemical literature.

We report here the first example of a base-initiated aryne reaction involving a nitrobenzyne intermediate, specifically 4-nitro-2, 3-dehydrophenoxide. This was accomplished by treating 2-chloro-4-nitrophenol (**1**) with various arylacetonitriles (**3**) in the presence of LDA. The resulting nitrobenzyne (**2**) reacted with α-lithiated arylacetonitriles to give 2-amino-3-aryl-5-nitrobenzo[*b*]furans (**4a-d**) in 21-36% yields and 2-(arylmethyl)-3-

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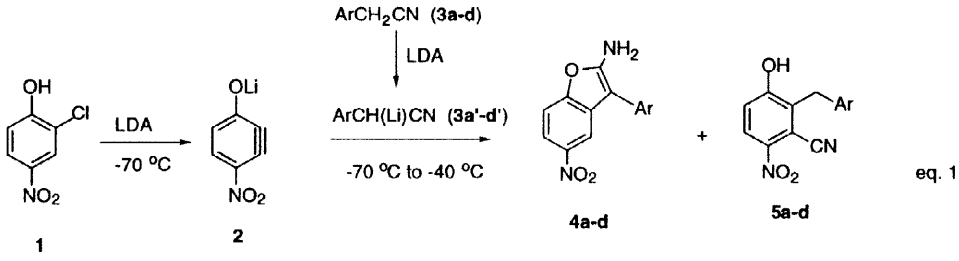
cyano-4-nitrophenols (**5a,c**) in 9-11% yields (eq. 1). In addition, the starting materials (10-15%), p-nitrophenol (10-12%), 2-N,N-diisopropylamino-4-nitrophenol (4-8%) and substantial amounts of intractable



Run 1	a. Ar = C_6H_5	32%	11%
Run 2	b. Ar = 3-MeC_6H_4	36%	trace
Run 3	c. Ar = 4-$MeOC_6H_4$	31%	9%
Run 4	d. Ar = 2-thienyl	21%	trace

tars (~30- 35%) were obtained from all reactions. The ^{1}H NMR spectra and elemental analyses of **4** and **5** are consistent with proposed structures. The NMR spectra of the 2-amino derivatives revealed the absence of tautomeric imino structures. In addition, the amino resonances around δ 4.58 ppm disappeared upon the addition of D_2O. The structure of **4c** was also confirmed by X-ray diffractometry,[9] whose ORTEP drawing is shown in Fig. 1.

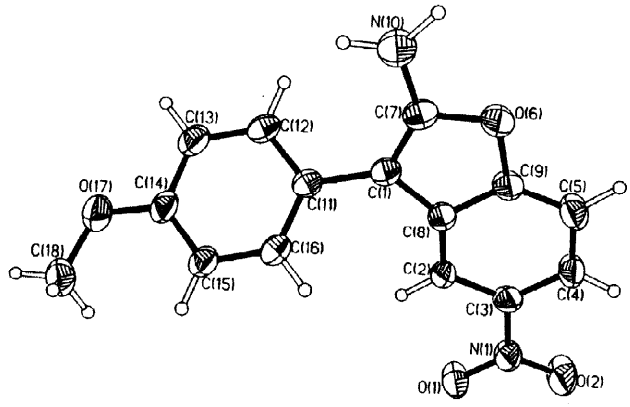
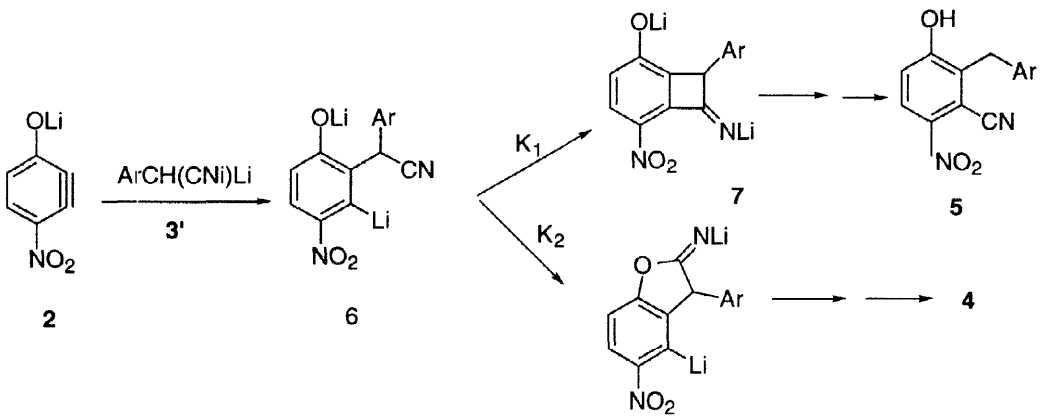


Fig. 1 ORTEP drawing for compound **4c**.

Scheme 1 outlines a possible pathway for the formation of benzofurans **4a-d** and rearranged nitriles **5a-d**. As shown, the arylacetontrile anion (**3'**) adds to the 2-position of 2,3-dehydro-4-nitrophenoxide (**2**) to give adduct **6**, which can be converted to the products (**4** and **5**) in the following ways. First, adduct **6** undergoes cyclization *via* addition of the 3-lithiated phenoxide ring to the α-cyano group (k_1) to give the benzocylo-butenium ring (**7**), the key intermediate in the tandem addition-rearrangement pathway.[10] Intermediate **7** then rearranges to the nitrile product (**5**) by successive ring opening and proton quench. Alternatively, the OLi group attacks the carbon atom of the cyano moiety to give a dilithiated furan intermediate (**8**), which is subsequently converted to the benzofuran (**4**) in a straightforward manner. As shown in Scheme 1, the strong -I effect of the nitro group influences the chemistry of 2,3-dehydrophenoxide in two important ways. First, its -I effect is sufficiently strong to direct nucleophilic addition to the 1-position of **2** (i.e. adjacent to the OLi charged substituent) in spite of the unfavorable electrostatic interactions between the charged substituent and attacking nucleophile present in that addition. The inductive effect of the nitro group

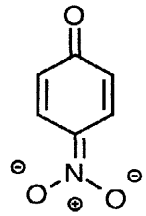
most likely increases the reactivity of the aryne[11] resulting in an early transition state where electrostatic interactions are expected to be less important. Secondly, the nitro group's -I effect apparently decreases the nucleophilicity of the 3-lithiated position in **6** to such an extent that the benzofuran cyclization step (k_2) occurs

Scheme 1



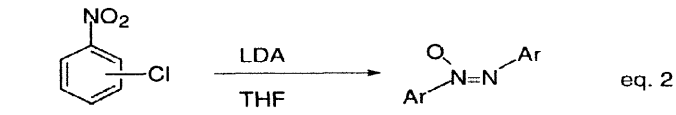
more rapidly than the tandem addition-rearrangement cyclization step (k_1). The unique nucleophilic addition to the 2-position of the 2,3-dehydrophenoxide (**2**) coupled with the decrease in the value of k_1 relative to k_2, which are brought on by the nitro group, result in the formation of the novel benzofuran compounds.

The regioselective addition to the 2-position of aryne **2** may also be due in part to direct resonance interactions between the phenoxide ion and p-nitro group as shown in **9** below. The mutual resonance interactions would enhance addition to the 2-postion by decreasing the negative charge on the phenoxide oxygen while increasing the negative charge on the oxygen atoms of the nitro group.



9

The reaction of LDA with 2-chloro- (**10**), 3-chloro (**11**) and 4-chloronitrobenzene (**12**) with LDA at -70 °C did not give the expected nitrobenzyne products. Instead the corresponding dichloroazoxybenzenes (**13-15**) were produced in modest yields (eq. 2). The structures of **13-15** were deduced from their ^1H



eq. 2

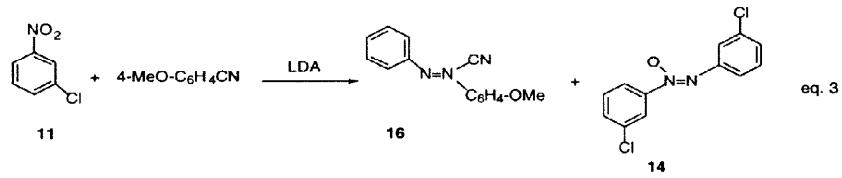
10 = 2-Cl
11 = 3-Cl
12 = 4-Cl

13 Ar = 2-ClC_6H_4 31%
14 Ar = 3-ClC_6H_4 27%
15 Ar = 4-ClC_6H_4 44%

NMR spectroscopy and elemental analysis.

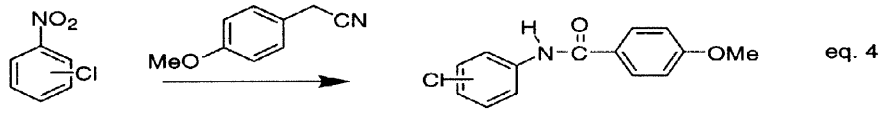
While sodium ethoxide has been shown to reduce nitrobenzene to azoxybenzene,[12] the reduction of the nitro compounds by LDA reported here is unprecedented. Even though LDA is typically viewed as a strong base, it has been shown to function as a single-electron transfer (SET) donor in its reactions with geminal diiodides[9], heterocycles,[10] α-bromo imines,[11] and conjugated acetylenes.[12] It has also found to reduce certain haloarenes, presumably by donating an α-hydrogen to the aryne intermediate.[13]

The sodium ethoxide reduction nitrobenzene is thought to proceed through a one-electron transfer to the nitro groups yielding nitrosobenzene and phenylhydroxylamine, which couple to produce azoxybenene. A similar pathway could take place in eq. 2. This was confirmed by isolating methoxybenzylidene-3-chloroanilines (**16**)[14] and 3,3-dichloroazoxybenzene (**14**) in 15% and 26% yields, respectively from the reaction of 3-chloronitrobenzene (**11**) with LDA in the presence of α-lithiated 4-methoxyphenylacetonitrile as shown in eq. 3.



11 16 14

In addition, 2-chloro (**10**) and 4-chloronitrobenzene (**12**) were found to react with 4-methoxy-phenylacetonitrile to give N-(2-chlorophenyl)-4-methoxybenzamide (**17**) and N-(4-chlorophenyl)-4-methoxybenzamide (**18**) in 15% and 18% yields, respectively (see eq. 4). The co-products in these reactions were the corresponding azoxy compounds **13** (24%) and **15** (37%). The amides were most likely the result of hydrolysis during aqueous work up of the initially formed α-cyanobenzylanilines.



10, 12

17, 2-chloro
18, 4-chloro

That LDA behaves as a base rather than a reducing agent towards 2-chloro-4-nitrophenol most likely is due to direct resonance interactions shown in **9**. This contributing structure, which resembles a nitrate ion, would be expected to decrease the reduction potential of the nitro group.

In conclusion, the reaction of the 2,3-dehydro-4-nitrophenoxide intermediate in the presence of lithiated arylacetonitriles results in the facile introduction of the 2-amino and 3-aryl (or hetaryl) groups with the concommitant construction of a benzo[*b*] ring onto a furan ring. The facile one-step synthesis may prove valuable in studying the chemistry of furans, which recently has been a lively area of research.[13] Scott[14] has reported the synthesis of arylfurans by the addition of 2-lithiofuran to arynes. However, that base-induced reaction can not be easily extended to the synthesis of aminobenzofurans, since lithiation of the aminofuran would preferentially occur on nitrogen. Additionally, LDA has been shown to reduce chloronitrobenzenes to azoxybenzenes at low temperatures. This azoxybenzene synthesis should complement the currently used room temperature nitroarene reduction methodologies (e.g.$NaBH_4$ catalytic reduction[15] and $BiCl_3$-Zn promoted reduction).[16]

Experimental Section

General Data: Melting points were taken on a Mel-Temp capillary apparatus and are uncorrected with respect to stem correction. IR spectra were recorded on a Nicolet Magna-IR™ 550 FTIR spectrometer and the ^1H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker AVANCE DRX-400 Multi-nuclear NMR spectrometer; chemical shifts were referenced to TMS as internal standard. Elemental analyses were obtained from E + R Microanalytical Laboratories, Inc., Corona, NY. 2-Chloro-4-nitrophenol (**1**), arylacetonitriles (**2**) n-BuLi and lithium diisopropylamine were purchased from Aldrich Chemical Company. The latter was dried and distilled from Na/benzophenone immediately prior to use. The glassware used in the aryne reactions were dried overnight in an oven at 150 °C. All reactions were done under an atmosphere of dry O_2-free N_2 *via* balloon.

X-ray Single Crystal Analysis of 4c. All data were collected on a Nicolet R3m/V diffractometer using the q-2q scan technique, Mo-Ka radiation (l = 0.71073Å), scan speed 3.0-15 deg min^{-1}, scan range 3.5-50.0^0 and a graphite monochromator. Data were corrected for Lorentz, absorption, and polarization effects. The structures were solved by direct methods using SHELXS-86,[15] and the model was refined by using full-matrix least-squares techniques. Pertinent data are given in the Table 2.

Table 2 X-ray data collection and processing parameters for **4c**

formula	$C_{15}H_{12}N_2O_4$
crystal dmns, cm^{-3}	0.30 X 0.20 X 0.15
Space Group	$P2_1/c$
a (Å)	17,507(1)
b (Å)	10.631(1)
c (Å)	7.212(1)
β (°)	97,103(1)
V (Å^3)	1331,91.9(3)
Z-value	4
D calc (g-cm^3)	1.417
abs coeff, mm^{-1}	0.105
T (K)	228
decay, %	3.94
Data collected	2566
Unique reflections	1203
R_{int}	0.063
Parameters	191
R, R_W	0.063, 0.057
$(\Delta/\sigma)_{max}$	<0,01
$\rho_{max};\rho_{min}$ (eÅ^{-3})	0.28; -.0.25
GOF	1.82

General Procedure for Aryne Reactions. Fresh LDA (15 mmol) in THF (30 mL) was placed in a flame-dried flask, flushed with nitrogen, at -70 °C. After stirring for 10 min, 2-chloro-4-nitrophenol (**1**) (5 mmol) in THF (30 mL) was added dropwise over 5 min, and the stirring was continued for 10 min at -70 °C. The appropriate arylacetonitrile (**3**) was then added over a period of 5 min during which time the solution developed a deep red color. The resulting solution was stirred for an additional 30 min, then was allowed to warm to room temperature. After stirring an additional 2 h, the solution was quenched with sat. aq. NH_4Cl (30 mL), the THF was evaporated under reduced pressure, and the remaining residue extracted with methylene chloride (3 X 20 mL). The combined extracts were washed with dilute HCl (1 X 20 mL), brine (2 X 20 mL), dried (Na_2SO_4), and concentrated (rotary evaporator) to provide a crude solid material. The crude mixture was purified by flash column chromatography (silica gel) using a mixture of hexane/acetone (6:4) as the eluent. The products were recrystallized from EtOAc. The mp, elemental analyses and NMR spectral data of compounds (**4** and **5**) are given below.

2-Amino-3-phenyl-5-nitrobenzo[*b*]furan (4a): colorless solid, mp 173-176 °C, ^{1}H NMR ($CDCl_3$) δ 4.58 (s, 2 H), 7.31 (d, *J* = 4.8 Hz, 2 H), 7.50-7.52 (m, 4 H), 7.98 (d, *J* = 2.0 Hz, 1 H), 8.00 (d, *J* = 2.0 Hz, 1 H), 8.33 (d, *J* = 2.2 Hz, 1 H). The signal at δ 4.58 disappeared upon the addition of D_2O. ^{13}C NMR ($CDCl_3$) δ 94.1, 109.8, 113.0, 117.0, 126.9, 127.4, 129.5, 130.9, 131.7, 144.7, 153.0, 156.0. Anal. Calcd for $C_{14}H_{10}N_2O_3$: C, 66.14; H, 3.96; N, 11.02. Found: C, 66.01; H, 3.95, N, 11.19.

2-Amino-3-(3'-methylphenyl)-5-nitrobenzo[*b*]furan (4b): colorless solid, mp 162-164 °C; ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 3 H), 4.58 (s, 2 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.36-7.44 (m, 4 H), 8.03 (d,d *J* = 8.0 Hz, 2.4 Hz, 1 H), 8.36 (d, *J* = 2.4 Hz, 1 H). The signal at δ 4.58 disappeared upon the addition of D_2O. ^{13}C NMR ($CDCl_3$) δ 21.63, 109.8, 113.1, 116.9, 124.5, 127.7, 128.0, 129.4, 131.3, 132.5, 135.0, 139.3, 145.0, 154.4, 156.0. Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.20; H, 4.42; N, 10.35.

2-Amino-3-(4'-methoxyphenyl)-5-nitrobenzo[*b*]furan (4c): colorless solid, mp 174-175 °C; ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 3 H), 5.07 (s, 2 H), 6.90-6.92 (dd, *J* = 8.8 Hz, 3.4 Hz, 2 H), 7.17-7.20 (dd, *J* = 8.8 Hz, 3.6 Hz, 1 H), 7.31-7.33 (dd, *J* = 8.8 Hz, 3.4 Hz, 2 H), 7.81-7.83 (dd, *J* = 8.8 Hz, 1 H), 8.10-8.11 (m, 1 H). The signal at δ 5.07 disappeared upon the addition of D_2O. ^{13}C NMR ($CDCl_3$) δ 55.5, 93.9, 109.8, 112.9, 115.0, 116.9, 123.7, 128.8, 131.3, 144.7, 153.0, 155.6, 158.7. Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.43; H, 4.25; N, 9.71. Found: C, 63.38; H, 4.22; N, 9.85.

2-Amino-3-thienyl-5-nitrobenzo[*b*]furan (4d): colorless solid, mp 221-223 °C; ^{1}H NMR ($CDCl_3$) δ 4.43 (s, 2 H), 7.13 (s, 1 H), 7.22 (d, *J* = 8.8 Hz, 1 H), 7.23 (d, *J* =5.6 Hz, 1 H), 7.41 (d, *J* = 5.6 Hz, 1 H), 7.89 (d, *J* = 8.8 Hz, 1 H), 8.20 (s, 1 H). The signal at δ 4.43 disappeared upon the addition of D_2O. Anal. Calcd for $C_{12}H_8N_2O_3S$: C, 55.38; H, 3.10; N, 10.76. Found: C, 55.52; H, 3.24; N, 10.87.

2-Benzyl-3-cyano-4-nitrophenol (5a): viscous oil; ^{1}H NMR ($CDCl_3$) δ 4.40 (s, 2 H), 6.70 (d, *J* = 9.2 Hz, 1 H), 6.92-7.02 (m, 5 H), 7.89 (d, *J* = 9.2 Hz, 1 H). Anal. Calcd for $C_{14}H_{10}N_2O_3$: C, 66.14; H, 3.96;

N, 11.02. Found: C, 66.40; H, 4.04; N, 11.20.

3-Cyano-2-(4'-methoxyphenyl)-4-nitrophenol (5c): yellow solid, mp 232-234 °C, ^{1}H NMR ($CDCl_3$) δ 3.67 (s, 3 H), 4.16 (s, 2 H), 6.71 (d, J = 8.4 Hz, 2 H), 7.09 (d, J = 9.2 Hz, 1 H), 7.24 (J = 8.4 Hz, 2 H), 7.97 (d, J = 9.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 33.4, 55.3, 109.0, 113.9, 114.5, 118.6, 125.7, 129.9, 130.5, 135.7, 140.7, 159.4, 161.6. Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.43; H, 4.25; N, 9.71. Found: C, 63.61; H, 4.33; N, 9.89.

General procedure for the LDA reduction of the isomeric chloronitrobenzenes (10-12). A 12.5 mL portion of a 2.0 M solution of LDA (25 mmol) was added to a flame-dried flask flushed with nitrogen containing 10 ml of THF, and the resulting solution was stirred for 5 min. The appropriate chloronitrobenzene (790 mg, 5 mmol) was then added and the resulting solution was allowed to warm -20 °C where it was quenched with sat. aq. NH_4Cl (30 ml). The resulting crude mixture was dissolved in methylene chloride and dried. The methylene chloride was evaporated (rotary evaporator) and the residue was subjected to flash column chromatography (silica gel, hexane/acetone (6:4) to give the corresponding azoxybenzene (**13-15**). Percentage yields and pertinent physical and spectral data of **13-15** are shown below.

2,2'-Dichloroazoxybenzene (13), 31%, red solid, mp 114-115 °C (lit.,[19] 58-59 °C): IR ν_{max}/(KBr) cm^{-1} 1619 (N=N), 776 and 730 (*o*-substitution), ^{1}H NMR (acetone-d_6) 6.99-7.01 (1 H, m), 7.21-7.22 (1 H, m), 7.44-7.46 (1 H, m), 7.58-7.62 (3 H, m), 8.22 (1 H, d, J= 8.2 Hz). ^{13}C NMR (acetone-d_6) δ 116.3, 118.4, 124.5, 125.9, 126.1, 126.8, 127.6, 128.9, 130.7, 125.6. 136.3, 141.6. Anal. Calcd for $C_{12}H_8N_2OCl_2$: C, 54.0; H, 3.0; 10.5. Found: C, 54.10; H, 3.2; N, 10.53.

3,3'-Dichloroazoxybenzene (14), 27%, light yellow solid, mp 105-106 °C (lit.,[20] 96-97 °C): IR ν_{max}/(KBr) cm^{-1} 1619 (N=N), ^{1}H NMR (acetone-d_6) δ 7.54 (1 H, d, J = 8.0 Hz), 7.60 (1 H, t, J = 8.0 Hz), 7.69 (1 H, t, J = 8.0 Hz), 7.77 (1 H, d, J = 8.0 Hz), 8.07 (1 H, d, J= 8.0 Hz), 8.31 (1 H, s). Anal. Calcd for $C_{12}H_8N_2OCl_2$: C, 54.0; H, 3.0; N, 10.5. Found: C, 54.0; H, 3.1; 10.55.

4,4'-Dichloroazoxybenzene (15), 28%, light yellow solid, mp 158-159 °C (lit.,[21] 158 °C). IR ν_{max}/(KBr) cm^{-1} 1619 (N=N).

General procedure for the LDA reduction of the isomeric chloronitrobenzenes (10-12) in presence of 4-methoxyphenylacetonitrile. LDA was added to a flame-dried flask flushed with nitrogen and containing 30 ml of 2.0 M THF (30 mmol) at -70 °C. The resulting solution was stirred for 5 min after which the appropriate chloronitrobenzene (790 mg, 5 mmol) was added. After stirring an additional 10 min, 4-methoxyphenylacetonitrile (1.1 g, 7.5 mmol) was added to give a light green solution. The appropriate chloronitrobenzene (**1-3**) was then added, and the reaction carried out in similar manner as that described above. Percentage yields and pertinent physical and spectral data of **16-18** follow

α-Cyano-4-methoxybenzylidene-3-chloroaniline (16). 15%, light yellow solid, mp 106-107 °C, ^{1}H NMR (acetone-d_6) δ 3.96 (3 H), 7.18 (1 H, d, J = 8.0 Hz), 7.20 (1 H, d, J = 8.4 Hz), 7.28 (1 H, d J = 8.0 Hz), 7.36 (1 H, d, J= 8.0 Hz), 7.53 (1 H, t, J = 8.0 Hz), 8.11 (2 H, d, J = 8.4 Hz). HRMS: Calcd for $C_{15}H_{11}N_2OCl$: M^+ = 270.0560. Found: 270.0561. Anal. Calcd for $C_{15}H_{11}N_2OCl$: C, 66.55; H, 4.1; N, 10.35 Found: C, 66.7; H, 4.2; 10.35.

N–(2-Chlorophenyl)-4-methoxybenzamide (17). 24%, light yellow solid, mp 145-146 °C: IR ν_{max}/(KBr) cm^{-1} 3278 (NH), 1651 (conj. CONH); ^1H NMR (acetone-d_6) δ 3.90 (3 H, s), 7.1 (2 H, d, *J* = 7.8 Hz), 7.20 (1 H, m), 7.38 (1 H, m), 7.50 (1 H, d, 7.8 Hz), 8.02 (2 H, d, *J* = 7.8 Hz), 8.22 (1 H, t, *J* = 8.0 Hz), 9.51 (1 H, br s) ; HRMS: Calcd for $C_{14}H_{12}NOCl$: M^+ 261.0556. Found: 261.0560.

N–(4-Chlorophenyl)-4-methoxybenzamide (18). 18%, light yellow solid, mp 210-211 °C, IR ν_{max}/(KBr) cm^{-1} 3354 (NH), 1655 (conj CONH). ^1H NMR (acetone-d_6) δ 3.96 (3 H, s), 7.18 (1 H, d, *J* = 8.0 Hz), 7.20 (1 H, d, *J* = 8.4 Hz), 7.20 (2 H, d, *J* = 8.4 Hz), 7.28 (1 H, d, *J* = 8.0 Hz), 7.36 (1 H, d, *J*= 8.0 Hz), 7.53 (1 H, t, *J* = 8.0 Hz), 8.11 (2 H) d, *J* = 8.4 Hz), 9.54 (1 H, br s). HRMS: Calcd for $C_{14}H_{12}NOCl$: M^+ = 261.0556. Found: 261.0561.

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