Synthesis of 2-Alkynyl-, 4-Alkynyl-, and 2,7-Dialkynyl-1,8-bis(dimethylamino)naphthalenes and the Unexpected Influence of *ortho*-Alkynyl Groups on Their Basicity

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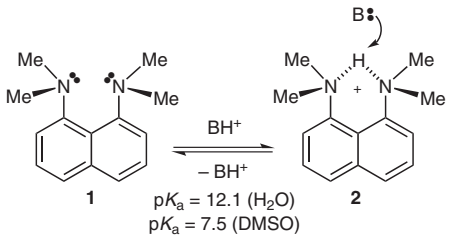
Abstract: Novel 2-alkynyl-, 4-alkynyl-, and 2,7-dialkynyl derivatives of 1,8-bis(dimethylamino)naphthalene ('proton sponge') have been synthesized and their basicity values have been measured by competitive NMR studies in DMSO. These indicate that, while the *para*-alkynyl groups decrease the basicity of the parent proton sponge approximately by one order of magnitude in accordance with their electron-accepting nature, the influence of *ortho*-alkynyl functionalities is unexpectedly base-enhancing. The latter phenomenon has been ascribed to the appearance of a buttressing effect, but some other factors can be also at work.

Key words: amines, proton sponge, cross-coupling, alkynes, buttressing effect, basicity

It is commonly accepted[1] that the exceedingly high basicity (pK_a = 12.1 in water[2] and 7.5 in DMSO[3]) of 1,8-bis(dimethylamino)naphthalene (**1**, 'proton sponge') is mainly caused by two factors: destabilization of free base **1** by steric and electrostatic repulsion of the *peri*-NMe_2 groups and strong intramolecular hydrogen bonding in the protonated form **2** (Scheme 1).



Scheme 1 Protonation–deprotonation of proton sponge **1**

Alder's discovery[4] of proton sponges spurred interest in the area of neutral organic superbases, in particular, promoting a quest to create compounds with the highest basicity.[5] One of the early approaches to this goal consisted in placing the bulky substituents into positions *ortho* to the NMe_2 groups.[6] It was argued that such substituents would bring the *peri*-nitrogen atoms into closer proximity ('buttressing effect') making the resulting base even more destabilized and therefore stronger. Indeed, in several cases this approach turned out to be fruitful. For example, 2,7-dimethoxy derivative **3** (Figure 1) is four orders of magnitude more basic than the parent sponge **1**, and naphthalene-2,7-diolate **4** so strongly holds a proton chelated between the nitrogen atoms that it cannot be removed even by metal hydrides in DMSO.[7] The basicity of **4** has been estimated to be in excess of 25 pK_a units and, currently, it seems to be the most basic arylamine system.

However, several years ago we demonstrated that the high basicity of **3**, **4**, and related compounds resulted not so much from the 'buttressing effect' as from the electron-donor nature of the methoxy and phenolate functionalities.[7,8] The most conclusive evidence in favor of this view is the relatively low basicity of 2,7-bis(trimethylsilyl) derivative **5**, which tallies with the weak electron-acceptor property of the TMS group but not with its steric bulk.[8,9]

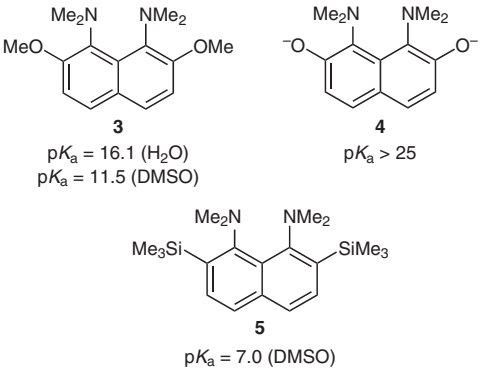


Figure 1 Substituted proton sponges **3**–**5** showing variations in basicity

Starting from this precedent, the main goal of the work reported herein was the preparation of novel 2-alkynyl (**6**), 2,7-dialkynyl (**7**), and 4-alkynyl (**8**) derivatives of 1,8-bis(dimethylamino)naphthalene and a comparative study of their basicity (Figure 2).

We considered that the influence on basicity of *ortho*-alkynyl groups, with the cylindrical symmetry of their triple bonds, weak electron-accepting strength (σ_p = 0.23 and 0.16 for C≡CH and C≡CPh, respectively)[10] and diminished steric bulk could be intriguing, if difficult to predict.

The desired acetylenes **6**–**8** were obtained from the corresponding iodides **9**–**11**[8,11] and 1-alkynes by Sonogashira coupling[12] using $Pd_2(dba)_3$, CuI, Ph_3P, K_2CO_3, and DMF or $Pd_2(dba)_3$, CuI, Ph_3P, and Et_3N catalytic systems (Scheme 2).[13] Unfortunately, proton sponge bromides,

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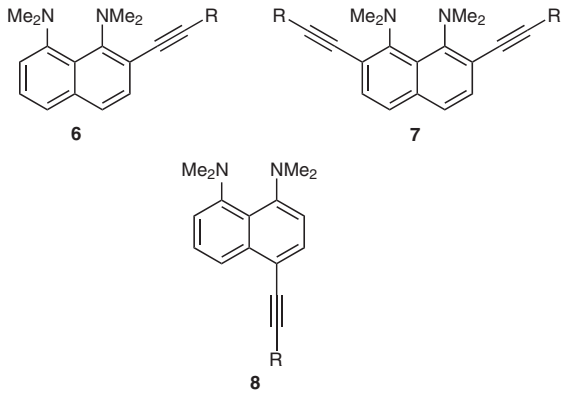
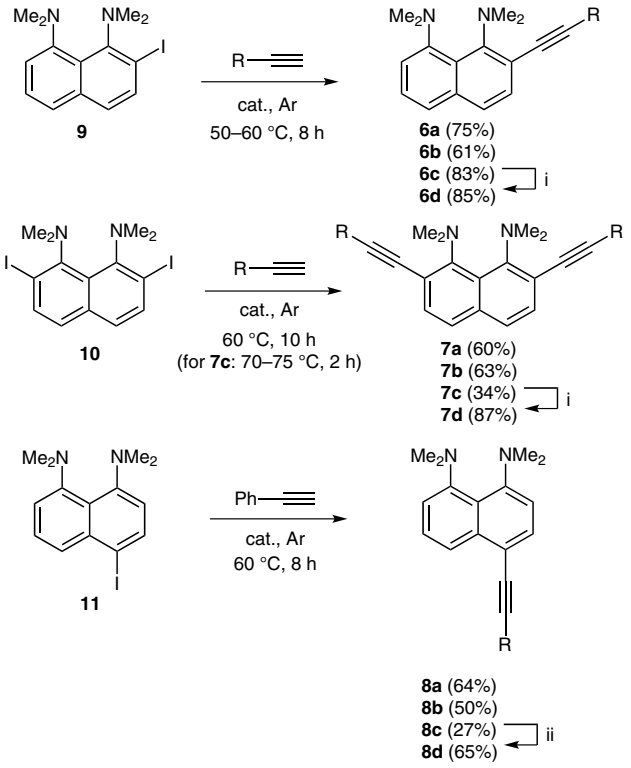


Figure 2 Structural motifs of new acetylenic compounds **6**–**8**

which are generally more accessible,[11,14] were non-reactive. Even using iodides **9**–**11** as starting materials, the reactions required warming to 50–60 °C and reaction times of 8–10 hours in order to furnish alkynes **6**–**8** in moderate to good yields. Trimethylsilylacetylenes **6c** and **7c** were then desilylated with KF in aqueous methanol producing ethynyl derivatives **6d** and **7d**, respectively. Interestingly, coupling 2-iodo-1,8-bis(dimethylamino)naphthalene (**9**) with phenylacetylene took place without need for added K_2CO_3 giving phenylethynyl derivative **6a** in 30% yield. Probably, compound **9** serves as the base. This shows that the high basicity of proton sponges can, in principle, be used for self-catalysis in cross-coupling reactions.

The pK_a values of acetylenes **6**–**8** were determined in DMSO-d_6 with the help of ^{1}H NMR analysis by the competitive transprotonation between a base and a cation of two compounds comparable in their pK_a values (usually an equimolar mixture of **1** and the perchlorate of the corresponding monoprotonated acetylene).[8,15] The data obtained are presented in Table 1. As expected, 4-ethynyl derivatives **8a**,**b**,**d** are 1–1.5 pK_a units less basic than **1**. In contrast, 2-ethynyl-, and especially 2,7-diethynyl derivatives, are notably more basic than the parent proton sponge. With a high degree of probability, this can be attributed to the 'buttressing effect' caused by the *ortho*-alkynyl groups. As we have previously reported on the basis of X-ray single-crystal measurements performed for compound **7b** and its perchlorate, the N···N distance in the former (2.76 Å) is somewhat shorter than that in **1** (2.80 Å).[16] This should lead to the extra destabilization of molecules **7** thus increasing their basicity in spite of the electron-accepting character of the ethynyl groups.

In summary, 2-alkynyl-, 4-alkynyl-, and 2,7-dialkynyl derivatives of the proton sponge have been synthesized for the first time. It has been shown that 4-alkynyl groups exhibit their usual inherent electron-withdrawing effect, lowering the proton sponge basicity on one pK_a unit and more. At the same time, the *ortho*-alkynyl substituents, contrary to their electronic nature, enhance the basicity by 0.1–0.8 pK_a units. This can be attributed to the electrostatic repulsion of the free nitrogen electron pairs and the π-electrons of the triple bonds ('buttressing effect').



Scheme 2 Synthesis of compounds **6**–**8**. *Reagents and conditions*: i) KF, H_2O, MeOH, r.t., 12 h; (ii) KOH, H_2O, MeOH, r.t., 1 h. Catalyst for R = Ph, 4-Tol: $Pd_2(dba)_3$, CuI, Ph_3P, K_2CO_3, DMF; catalyst for R = TMS: $Pd(dba)_3$, CuI, Ph_3P, Et_3N.

Table 1 Basicity Constants (pK_a) of Alkynyl Derivatives of 1,8-Bis(dimethylamino)naphthalene[a]

Compd	R	pK_a
1	–	7.5
6a	Ph	7.6
6b	4-Tol	7.6
6d	H	7.5
7a	Ph	7.9
7b	4-Tol	8.3
7d	H	7.8
8a	Ph	6.5
8b	4-Tol	6.6
8d	H	5.9

[a] Conditions: DMSO-d_6, 25 °C.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(13) **1,8-Bis(dimethylamino)-2-(phenylethynyl)naphthalene (6a)**
Yellow solid; mp 98–100 °C (from EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.78 (6 H, s, NMe_2), 3.16 (6 H, s, NMe_2), 6.95 (1 H, dd, *J* = 6.0, 2.8 Hz, H_{arom}), 7.28–7.40 (7 H, m, H_{arom}), 7.54 (2 H, dd, *J* = 7.7, 1.8 Hz, H_{arom}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 45.0, 45.2, 91.5, 94.5, 114.2, 114.7, 122.0, 123.0, 124.8, 126.8, 128.0, 128.8, 131.0, 131.3, 138.2, 152.0, 152.5. MS: *m/z* (%) = 314 (90) $[M]^+$, 299 (24), 282 (72), 268 (77), 254 (29), 226 (35), 207 (37), 196 (27), 167 (26), 157 (25), 149 (29), 141 (29), 133 (25), 127 (53), 113 (38), 103 (26), 91 (70), 77 (68), 58 (72), 51 (35). 44 (100). Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.87; H, 7.23; N, 9.03.
1,8-Bis(dimethylamino)-2-(*p*-tolylethynyl)naphthalene (6b)
Yellow solid; mp 89–92 °C (from EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.37 (3 H, s, CMe), 2.79 (6 H, s, NMe_2), 3.18 (6 H, s, NMe_2), 6.95 (1 H, dd, *J* = 6.3, 2.4 Hz, H_{arom}), 7.16 (2 H, d, *J* = 8.1 Hz, *p*-Tol), 7.24–7.40 (4 H, m, H_{arom}), 7.43 (2 H, d, *J* = 8.1 Hz, 4-Tol). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.0, 45.0, 45.2, 91.0, 94.8, 114.0, 115.0, 119.2, 121.8, 122.1, 123.0, 126.8, 129.8, 131.0, 131.2, 138.2, 138.3, 152.0, 152.1. MS: *m/z* (%) = 328 (100) $[M]^+$, 313 (25), 296 (74), 282 (66), 268 (17), 206 (18), 196 (20), 164 (21), 149 (22), 141 (17), 134 (18), 127 (20). Anal. Calcd for $C_{23}H_{24}N_2$: C, 84.11; H, 7.37; N, 8.53. Found: C, 84.24; H, 7.26; N, 8.37.
1,8-Bis(dimethylamino)-2-(trimethylsilylethynyl)-naphthalene (6c)
Dark yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.25 (9 H, s, $SiMe_3$), 2.78 (6 H, s, NMe_2), 3.09 (6 H, s, NMe_2), 6.91 (1 H, m, H_{arom}), 7.24–7.35 (4 H, m, H_{arom}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.5, 45.0, 45.1, 82.4, 99.1, 107.3, 114.0, 122.0, 122.7, 126.8, 131.3, 138.4, 138.5, 152.1, 153.1. IR: 2140 (C≡C), 1553 (ring) cm^{-1}. MS: *m/z* (%) = 310 (51) $[M]^+$, 295 (29), 279 (24), 264 (22), 238 (30), 221 (17), 206 (51), 192 (30), 73 (100). Anal. Calcd for $C_{19}H_{26}N_2Si$: C, 73.49; H, 8.44; N, 9.02. Found: C, 73.58; H, 8.29; N, 9.23.
2-Ethynyl-1,8-bis(dimethylamino)naphthalene (6d)
Dark yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.86 (6 H, s, NMe_2), 3.20 (6 H, s, NMe_2), 3.45 (1 H, s, ≡CH), 7.04 (1 H, m, H_{arom}), 7.31–7.45 (4 H, m, H_{arom}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 45.0, 45.2, 82.4, 85.6, 113.6, 114.2, 122.1, 122.9, 123.0, 126.9, 131.4, 138.5, 152.1, 153.3. IR: 3303 (≡CH), 2093 (C≡C), 1600, 1553 (ring) cm^{-1}. MS: *m/z* (%) = 238 (95) $[M]^+$, 223 (18), 206 (70), 192 (83), 178 (21), 165 (18), 152 (31), 139 (15), 111 (21), 103 (23), 89 (25), 76 (33), 63 (34), 58 (69), 32 (100). Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.50; H, 7.79; N, 11.81.
1,8-Bis(dimethylamino)-2,7-bis(phenylethynyl)-naphthalene (7a)
Yellow solid, mp 156–157 °C (from EtOH or *n*-octane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.20 (12 H, s, 2 NMe_2), 7.33–7.47 (10 H, m, H_{arom}), 7.55–7.62 (4 H, m, H_{arom}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 45.0, 91.0, 94.5, 117.0, 123.5, 124.4, 126.3, 128.0, 128.5, 131.0, 131.5, 138.0, 153.0. IR: 2211 (C≡C) cm^{-1}. MS: *m/z* (%) = 414 (94) $[M]^+$, 399 (39), 382 (100), 368 (31), 307 (25), 91 (29), 58 (23). Anal. Calcd for $C_{30}H_{26}N_2$: C, 86.92; H, 6.32; N, 6.76. Found: C, 87.09; H, 6.17; N, 6.84.
1,8-Bis(dimethylamino)-2,7-bis(*p*-tolylethynyl)-naphthalene (7b)
Yellow-orange solid, mp 155–156 °C (from *i*-PrOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.36 (6 H, s, 2 CMe), 3.15 (12 H, s, 2 NMe_2), 7.17 (4 H, d, *J* = 7.9 Hz, 4-Tol), 7.32 (2 H, d, *J* = 8.5 Hz, H_{arom}), 7.40 (2 H, d, *J* = 8.5 Hz, H_{arom}), 7.43 (4 H, d, *J* = 7.9 Hz, 4-Tol). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.0, 45.0, 90.5, 95.0, 117.5, 121.5, 124.0, 126.8, 129.5, 131.5, 131.8, 138.0, 138.5, 153.0. IR: 2210 (C≡C) cm^{-1}. MS: *m/z* (%) = 442 (100) $[M]^+$, 427 (40), 410 (89), 396 (33), 320 (22), 221 (20), 205 (21), 191 (17), 175 (26). Anal. Calcd for $C_{32}H_{30}N_2$: C, 86.84; H, 6.83; N, 6.33. Found: C, 87.00; H, 6.95; N, 6.23.
1,8-Bis(dimethylamino)-2,7-bis(trimethylsilylethynyl)-naphthalene (7c)
Dark yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.24 (18 H, s, 2 $SiMe_3$), 3.06 (12 H, s, 2 NMe_2), 7.20 (2 H, d, *J* = 8.5 Hz, H_{arom}), 7.27 (2 H, d, *J* = 8.5 Hz, H_{arom}). IR: 2133 (C≡C), 1525 (ring) cm^{-1}. Anal. Calcd for $C_{24}H_{34}N_2Si_2$: C, 70.88; H, 8.43; N, 6.89. Found: C, 71.04; H, 8.54; N, 6.71.
2,7-Diethynyl-1,8-bis(dimethylamino)naphthalene (7d)
Yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.09 (12 H, s, 2 NMe_2), 3.37 (1 H, s, ≡CH), 7.27 (2 H, d, *J* = 8.9 Hz, H_{arom}), 7.33 (2 H, d, *J* = 8.95 Hz, H_{arom}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 45.2, 83.0, 85.0, 115.8, 123.6, 126.1, 132.5, 138.4, 154.0. IR: 3300 (≡CH), 2090 (C≡C), 1540 (ring) cm^{-1}. MS: *m/z* (%) = 262 (100) $[M]^+$, 230 (59), 216 (41). Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.62; H, 6.71; N, 10.78.
1,8-Bis(dimethylamino)-4-(phenylethynyl)naphthalene (8a)
Yellow solid; mp 147–149 °C (from EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.80 (6 H, s, NMe_2), 2.85 (6 H, s, NMe_2), 6.87 (1 H, d, *J* = 8.0 Hz, H_{arom}), 6.97 (1 H, d, *J* = 7.7 Hz,

H_{arom}), 7.31–7.41 (4 H, m, H_{arom}), 7.58–7.67 (3 H, m, H_{arom}), 8.04 (1 H, d, J = 8.3 Hz, H_{arom}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.3, 44.5, 89.6, 93.1, 111.9, 112.9, 113.3, 119.9, 120.6, 124.7, 126.8, 128.1, 128.7, 131.1, 131.8, 138.1, 151.5, 151.9. IR: 2201 (C≡C) cm^{-1}. MS: *m/z* (%) = 314 (100) $[M]^+$, 299 (19), 283 (44), 268 (76), 226 (21), 134 (13). Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.92; H, 7.21; N, 9.10.

1,8-Bis(dimethylamino)-4-(*p*-tolylethynyl)naphthalene (8b)

Yellow solid; mp 94–96 °C (from EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.36 (3 H, s, CMe), 2.78 (6 H, s, NMe_2), 2.82 (6 H, s, NMe_2), 6.84 (1 H, d, J = 8.0 Hz, H_{arom}), 6.95 (1 H, dd, J = 7.7, 1.1 Hz, H_{arom}), 7.16 (2 H, d, J = 8.1 Hz, H_{arom}), 7.39 (1 H, dd, J = 7.7, 8.1 Hz, H_{arom}), 7.49 (2 H, dm, J = 8.1 Hz, H_{arom}), 7.57 (1 H, d, J = 8.0 Hz, H_{arom}), 8.00 (1 H, dd, J = 8.1, 1.1 Hz, H_{arom}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.9, 44.4, 44.5, 88.8, 93.2, 112.0, 113.3, 119.8, 119.9, 120.0, 121.6, 126.7, 129.5, 130.9, 131.7, 138.0, 138.1, 151.4, 151.7. IR: 2140 (C≡C) cm^{-1}. MS: *m/z* (%) = 328 (100) $[M]^+$, 313 (19), 297 (44), 284 (38), 268 (14), 239 (18), 149 (21), 140 (30), 134 (14), 127 (13). Anal. Calcd for $C_{23}H_{24}N_2$: C, 84.11; H, 7.37; N, 8.53. Found: C, 84.28; H, 7.15; N, 8.46.

1,8-Bis(dimethylamino)-4-(trimethylsilylethynyl)-naphthalene (8c)

Yellow solid; mp 108–109 °C (from MeOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.27 (9 H, s, $SiMe_3$), 2.74 (6 H, s, NMe_2), 2.79 (6 H, s, NMe_2), 6.77 (1 H, d, J = 8.0 Hz, H_{arom}), 6.91 (1 H, dd, J = 7.6, 1.1 Hz, H_{arom}), 7.36 (1 H, dd, J = 7.6, 8.2 Hz, H_{arom}), 7.51 (1 H, d, J = 8.0 Hz, H_{arom}), 7.88 (1 H, dd, J = 8.2, 1.1 Hz, H_{arom}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.7, 44.3 44.4, 97.5, 105.3, 111.6, 112.7, 113.2, 119.6, 119.8, 126.8, 131.5, 138.2, 151.4, 152.0. IR: 2144 (C≡C) cm^{-1}. Anal. Calcd for $C_{19}H_{26}N_2Si$: C, 73.49; H, 8.44; N, 9.02. Found: C, 73.41; H, 8.27; N, 9.19.

4-Ethynyl-1,8-bis(dimethylamino)naphthalene (8d)

Dark yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.76 (6 H, s, NMe_2), 2.81 (6 H, s, NMe_2), 3.36 (1 H, s, ≡CH), 6.79 (1 H, d, J = 7.9 Hz, H_{arom}), 6.92 (1 H, dm, J = 7.6 Hz, H_{arom}), 7.37 (1 H, dd, J = 7.6, 8.2 Hz, H_{arom}), 7.54 (1 H, d, J = 8.0 Hz, H_{arom}), 7.90 (1 H, dd, J = 8.2, 1.0 Hz, H_{arom}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.3, 44.4, 80.5, 83.8, 105.3, 111.6, 113.3, 119.6, 121.9, 126.9, 131.9, 138.3, 151.5, 152.2. IR: 2085 (C≡C), 3290 (≡CH) cm^{-1}. Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.74; H, 7.47; N, 11.59.

For general procedures and other experimental and analytical details see the Supporting Information.

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