2-(2-Methoxybenzoyl)-2-*n*-propylpentanenitrile (2m): bp 153-154 °C (2.5 mm); IR ($CHCl_3$) ν 2225 (CN), 1690 cm^{-1} (CO); ^1H NMR δ 0.96 (t, J = 7.3 Hz, 6 H), 1.4-1.7 (m, 4 H), 1.7-1.9 (m, 2 H), 2.0-2.2 (m, 2 H), 3.90 (s, 3 H), 6.9-7.1 (m, 2 H), 7.2-7.3 (m, 1 H), 7.4-7.5 (m, 1 H). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.19; H, 8.15; N, 5.33.

2-(2-Nitrobenzoyl)-2-*n*-propylpentanenitrile (2o): mp 80-81 °C (from cyclohexane); IR ($CHCl_3$) ν 2230 (CN), 1720 cm^{-1} (CO); ^1H NMR δ 1.01 (t, J = 7.3 Hz, 6 H), 1.4-1.7 (m, 4 H), 1.8-2.2 (m, 2 H), 2.0-2.3 (m, 2 H), 7.35 (dd, J = 7.3, 1.5 Hz, 1 H), 7.6-7.9 (m, 2 H), 8.28 (dd?, J = 8.1, 1.5 Hz, 1 H). Anal. Calcd for $C_{15}H_{18}N_2O_3$: C, 65.67; H, 6.61; N, 10.21. Found: C, 65.69; H, 6.61; N, 10.15.

Kinetic Experiments with Hydrazone (1f). The reaction progress in a stream of air or N_2 was examined under conditions indicated in the caption in Figure 1. The reaction was stopped at various times, and the organic layer was passed immediately through a short column of silica gel. The fractions eluted with benzene were analyzed by GLC, and the product yields were determined by the internal standard method using a 1-m FFAP column for **2f** (t_R = 2.3 min; 190 °C, 67 mL/min) and a 2-m FFAP column for 4-heptanone and 2-*n*-propylpentanenitrile (t_R = 1.8 min and 5.1 min; 90 °C, 38 mL/min). Continued elution with benzene-Et_2O (2:1) afforded **3f** as a white solid (R_f = 0.44, benzene-Et_2O (2:1), which was identified by a mixed melting point test with an authentic sample.

Oxidative Conversion of HCN Adduct (3f) into 2f. HCN adduct **3f** (0.65 g, 2.5 mmol) was stirred vigorously in a heterogeneous mixture of aqueous NaCN (0.12 g, 2.5 mmol in 10 mL of H_2O) and the organic solvent in the presence of a quaternary ammonium salt (0.5 mmol) for 3 h in a stream of air. The product yields indicated in Table II and III were determined by the internal standard method as described above.

Decomposition of Diazenes (4, 5). Freshly prepared **4** (0.96 g, 4 mmol) was treated in a mixture of aqueous Na_2CO_3 (0.21 g, 2 mmol in 20 mL H_2O) and cyclohexane (20 mL) at rt. Addition of TOMAC (0.4 g, 1 mmol) brought about vigorous evolution of N_2, and the yellow mixture became colorless. From the organic layer, **2h** was isolated by flash chromatography on silica gel eluting with benzene (0.37 g, 43%), which was identified by spectroscopic comparison with an authentic sample.

Similar treatment of **5** (1.95 g, 10 mmol) gave 0.97 g of cyclohexanecarbonitirle [yield, 87% based on **5**, bp 85-87 °C (23 mm)] and was identified by comparison with an authentic sample prepared previously.[12]

Registry No. **1a**, 3408-16-0; **1b**, 124243-18-1; **1c**, 128721-91-5; **1d**, 124243-16-9; **1e**, 124243-17-0; **1f**, 124243-15-8; **1g**, 24214-78-6; **1h**, 24214-79-7; **1i**, 135664-40-3; **1j**, 135664-41-4; **1k**, 135664-42-5; **1l**, 135664-43-6; **1m**, 135664-44-7; **1n**, 135664-45-8; **1o**, 135664-46-9; **2a**, 7391-73-3; **2b**, 135664-47-0; **2c**, 135664-48-1; **2d**, 135664-49-2; **2e**, 135664-50-5; **2f**, 135664-51-6; **2g**, 135664-52-7; **2h**, 135664-53-8; **2i**, 135664-54-9; **2j**, 135664-55-0; **2k**, 135664-56-1; **2l**, 135664-57-2; **2m**, 135664-58-3; **2n**, 135664-59-4; **2o**, 135664-60-7; **3f**, 128721-94-8; **4**, 27702-92-7; **5**, 33670-04-1; sodium cyanide, 143-33-9; trioctylmethylammonium chloride, 5137-55-3; cyanocyclohexane, 766-05-2; 4-heptanone, 123-19-3; 2-propylpentanenitrile, 13310-75-3; tetrabutylammonium bromide, 1643-19-2; triethylbenzylammonium chloride, 56-37-1; *N*-dodecylpyridinium chloride, 104-74-5; trimethyldodecylammonium chloride, 112-00-5; didodecyldimethylammonium bromide, 3282-73-3.

Supplementary Material Available: ^1H NMR and IR spectral data and elemental analyses for compounds **2b**, **2e**, **2g**, **2l**, and **2n** (1 page). Ordering information is given on any current masthead page.

Catalytic Aminomercuration Reactions of 3-Alken-1-ynes: An Improved Method for the Synthesis of 2-Amino-1,3-butadienes and 1-Aza-1,3-butadienes[1]

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Catalytic aminomercuration of 3-alken-1-ynes leads to 1-aza-1,3-butadienes and 2-amino-1,3-butadienes. Under appropriate reaction conditions it is possible to prepare these compounds via mercuration of 3-alken-1-ynes in the presence of either aromatic or aliphatic primary and secondary amines. Depending on the substituents in the starting 3-alken-1-yne, the mercuration reaction may afford γ-amino enamines instead of 2-amino-1,3-butadienes and 3-imino amines or 4-amino-1-aza-1,3-butadienes instead of 1-aza-1,3-butadienes.

The increasing development of the Diels-Alder reaction in the last 20 years has made 1,3-dienes very important starting materials in organic synthesis through [4 + 2] cycloaddition processes.[2] However, 1-aza-1,3-butadienes[3] and 2-amino-1,3-butadienes[4] have not been studied as extensively as their oxygen analogues.[5] While the preparation of these compounds via condensation reactions between amines and α,β-unsaturated carbonyl compounds is successful in some specific instances,[6] Michael-type addition of the amine often occurs.[6c,7,8]

For many years we have studied the catalytic aminomercuration of terminal C≡C triple bonds leading to en-

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Table I. 2-Amino-1,3-butadienes Prepared

compd	R^1	R^2	R^3	amine	yield,[a] %
2a	CH_3	H	H	morpholine	61
2b	CH_3	CH_2OCH_3	H	morpholine	72
2c	CH_3	$CH_2OSi(CH_3)_3$	H	morpholine	75
2d		$-(CH_2)_4-$	H	morpholine	67
2e[b]	CH_2CH_3	H	CH_3	morpholine	63
2f[b]	CH_3	H	CH_2OCH_3	morpholine	56
2g	CH_3	$CH_2OSi(CH_3)_3$	H	2-(methoxymethyl)pyrrolidine	60
2h	CH_3	CH_2OCH_3	H	2-(methoxymethyl)pyrrolidine	67
3a	CH_3	H	H	*N*-methylaniline	75
3b	CH_3	CH_2OCH_3	H	*N*-methylaniline	69
3c	CH_3	$CH_2OSi(CH_3)_3$	H	*N*-methylaniline	75
3d		$-(CH_2)_4-$	H	*N*-methylaniline	79
3e[b]	CH_3	H	CH_2OCH_3	*N*-methylaniline	62
3f[c]	CH_3	H	CH_2OCH_3	N-allylaniline	55
3g[c]	CH_3	H	CH_2OCH_3	N-(3-butenyl)aniline	49

[a] Isolated yields after high vacuum distillation. [b] Reaction time, 48 h. [c] Yield of the crude reaction product. High vacuum distillation is not necessary.

amines and imines.[9] In previous reports, we have shown that the catalytic aminomercuration of a terminal C≡C triple bond is preferred over the stoichiometric aminomercuration of a double bond.[9b,10,11] We have also reported the synthesis of 2-morpholino-1,3-butadienes and 1-aza-1,3-butadienes by catalytic mercuration of conjugated enynes in the presence of morpholine and primary aromatic amines, respectively.[1]

In previous papers we have demonstrated the use of 2-morpholino-1,3-butadienes as synthetic equivalents for α,β-unsaturated ketones and dienes in [4 + 2] cycloaddition reactions.[12] In most of the cases, 2-morpholino-1,3-butadienes show enamine behavior, in agreement with previous predictions.[13] We became interested in the influence of the amine on the behavior of 2-amino dienes and, in particular, whether the reduced basicity of an aromatic amine may affect the diene or enamine character of these compounds.

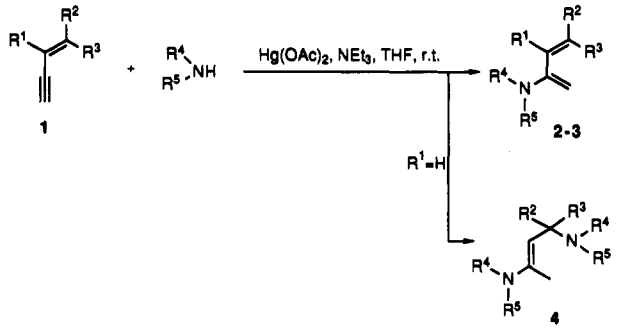
In the present paper, we report a general study of the aminomercuration of conjugated 3-alken-1-ynes with a variety of aliphatic and aromatic primary and secondary amines. We also describe an improved method for the synthesis of 2-amino-1,3-butadienes and 1-aza-1,3-butadienes.

Results and Discussion

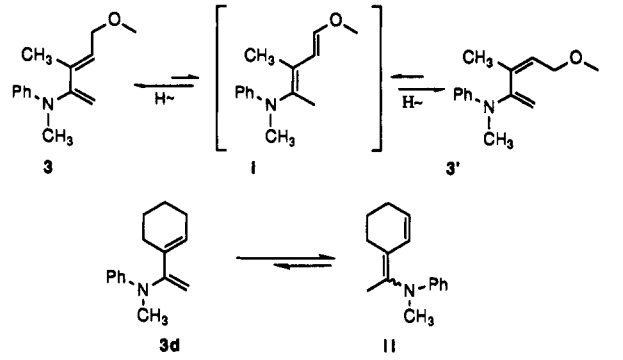
Aminomercuration with Secondary Amines. As we have reported in a previous communication,[1] treatment of 3-alken-1-ynes 1 in dry THF with mercury acetate in the presence of morpholine at room temperature (molar ratio $Hg(OAc)_2$:enyne:amine = 15:20:60) afforded 2-morpholino-1,3-butadienes in yields over 60%. Using the same methodology, we were able to prepare 2-amino-1,3-butadienes with other aliphatic amines, but this procedure failed in the case of aromatic amines.

The need for an excess of amine would be an important drawback in the preparation of chiral 2-aminobutadienes from chiral amines.[14] However, this problem was overcome by using a tertiary amine such as triethylamine as a coreactant. Under these new reaction conditions (molar ratio $Hg(OAc)_2$:enyne:amine:triethylamine = 15:20:20:50), it was possible to employ equimolar quantities of enyne and secondary amine. Some 2-amine-1,3-butadienes 2 prepared by this method are presented in Table I (Scheme I).

Scheme I



Scheme II



The mercury salts in the aminomercuration process can be recovered and reused in another mercuration reaction. Thus, upon completion of the reaction, the volatile components were evaporated and the soluble organic products were extracted with dry hexane. The remaining gummy solid was capable of catalyzing the aminomercuration of fresh reactants. This operation was repeated ten times without apparent loss of activity.

In our first attempts in the mercuration of 3-alken-1-ynes with *N*-methylaniline, we employed the reaction conditions described in a previous paper for the mercuration of terminal acetylenes with secondary aromatic

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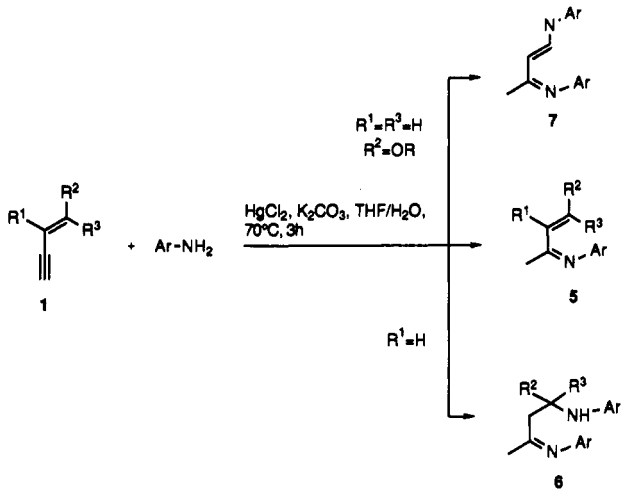
(14) An excess of amine is necessary in order to neutralize the acetic acid liberated in the first step of the catalytic aminomercuration process.

Scheme III



amines[9a] (refluxing THF; molar ratio, $HgCl_2$:3-alken-1-yne:amine = 1:20:100). Under these conditions 2-amino-1,3-butadienes were formed in moderate yields as mixtures of *Z* and *E* isomers (**3**, **3'**). The isomerization reaction between **3** and **3'** may take place via intermediate I.[15] Moreover, when the preparation of diene **3d** was attempted under the same reaction conditions, a mixture of the *cross-conjugated* dienamine **3d** and both isomers of the *extended* dienamine II was obtained. With longer reaction times (6 h) the initially formed *cross-conjugated* dienamine **3d** was converted into the *extended* dienamine II, as a 1:1 mixture of *Z* and *E* isomers (Scheme II).

However, using the method described above for aliphatic amines (molar ratio $Hg(OAc)_2$:enyne:amine:triethylamine = 15:20:20:60), this reaction could be carried out at room temperature to produce 2-(*N*-methylanilino)-1,3-butadienes **3** in good yields (Table I).

2-Amino-1,3-butadienes are colorless liquids that can be distilled under high vacuum. These compounds must be handled and stored under an inert atmosphere with exclusion of air and moisture. Otherwise hydrolysis will occur to afford α,β-unsaturated ketones.

It is noteworthy that when the aminomercuration reaction was carried out with 3-alken-1-ynes lacking a substituent at C-3 (R^1 = H), the corresponding 2-amino-1,3-butadienes were not obtained. The absence of a bulky substituent apparently favors the planarity of the conjugated system, allowing Michael addition of a second molecule of amine to take place. In this way, γ-amino enamines **4** are formed as we have previously reported.[11]

Aminomercuration with Primary Amines. In a previous paper, we reported the synthesis of 1-aza-1,3-butadienes[1] **5** from 3-alken-1-ynes and primary aromatic amines (Scheme III). Since these compounds are stable in aqueous media, the reaction can be carried out in aqueous K_2CO_3. The reactions are best performed in 4:1 THF:H_2O % vol with a molar ratio of $HgCl_2$:3-alken-1-yne:amine:K_2CO_3 = 5:10:40:10. The usual workup of the reaction mixture involves reduction of the mercuric species with $NaBH_4$ in alkaline solution, which facilitates product isolation and improves the yields (Table II).

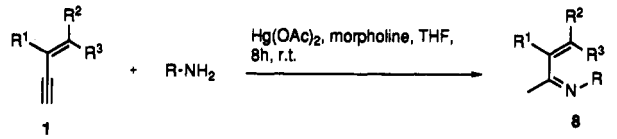
As with secondary amines, it was not possible to prepare 1-aza dienes **5** when R^1 = H, since the Michael-type addition of a second molecule of amine occurs and β-amino imines **6** were obtained. Moreover, 3-alken-1-ynes **1** with R^1 = H and R^2 = OR did not afford 4-alkoxy-1-aza-1,3-butadienes; instead, 4-amino-1-aza-1,3-butadienes **7** were isolated after the usual workup. The formation of the latter compounds can be understood through the Michael-type addition of a second molecule of amine to the alkoxy aza diene followed by elimination of a molecule of alcohol (Scheme III, Table II).

Table II. 1-Aza-1,3-butadienes, 4-Amino-1-aza-1,3-butadienes, and 3-Imino Amines Prepared

compd	R^1	R^2	R^3	Ar/R	yield,[a] %
5a	CH_3	H	H	Ph	79
5b	CH_3	CH_2OCH_3	H	Ph	72
5c	CH_3	H	H	2-$CH_3C_6H_4$	61
5d	—$(CH_2)_4$—		H	Ph	78
5e	—$(CH_2)_4$—		H	2-$CH_3C_6H_4$	45
5f	—$(CH_2)_3$—		H	Ph	47
5g	CH_3	H	H	3-$CH_3C_6H_4$	66
6a	H	CH_3	H	Ph	57
6b	H	CH_2CH_3	H	Ph	75
7a				Ph	55
7b				2-$CH_3C_6H_4$	58
7c				4-$CH_3C_6H_4$	59
7d[c]				4-ClC_6H_4	61
8a	CH_3	CH_2OCH_3	H	$Ph(CH_3)CH$	69
8b	CH_3	CH_2OCH_3	H	$PhCH_2$	73
8c	CH_3	$CH_2OSi(CH_3)_3$	H	$PhCH_2$	75
8d	—$(CH_2)_4$—		H	^nBu	62

[a] Isolated yields after high vacuum distillation. [b] Recrystallized from ethanol. [c] Recrystallized from hexane.

Scheme IV



The aminomercuration reaction of 3-alken-1-ynes **1** with primary aliphatic amines under the reaction conditions used for primary aromatic amines leads to the formation of dialkenynyl mercurials,[16] which do not progress toward 1-aza-1,3-butadienes. On the other hand, the instability of these compounds in aqueous media makes the aforementioned procedure, which is effective for aromatic amines, completely useless for aliphatic amines. It has not been possible thus far to prepare 1-azabutadienes by direct aminomercuration of enynes by using primary aliphatic amines. However, it is possible to prepare these compounds in the presence of a catalytic amount of a secondary aliphatic amine; thus, treatment of 3-alken-1-yne **1** with $Hg(OAc)_2$ and a mixture of morpholine and a primary aliphatic amine (molar ratio $Hg(OAc)_2$:enyne:primary amine:morpholine = 15:20:45:10) in dry THF for 8 h afforded 1-aza-1,3-butadienes **8** as yellow, moisture-sensitive oils, which can be distilled under high vacuum (Scheme IV, Table II).

In this reaction, addition of a molecule of morpholine to the monoalkenynylmercurial[9b] presumably gives rise to the corresponding 2-amino-1,3-butadiene. Subsequent exchange of amine in the preformed enamine would account for the formation of 1-aza-1,3-butadiene.[17]

Conclusion

We have studied the catalytic mercuration reaction of 1,3-enynes in the presence of primary and secondary ali-

(15) The acidic medium resulting from liberation of hydrochloric acid in the course of the mercuration induces the transposition of H for Hg. This same effect was also observed when **3e** was heated at reflux in THF over 3 h in the absence of acidic medium.

(16) Formation of dialkenynyl mercurials ($R^2R^3CH{=}CHR^1C{\equiv}C)_2Hg$ are favored under basic conditions. For further information, see ref 9b.

(17) In face, **8b** was obtained through an amine interchange process when **2b** was treated with benzylamine in the presence of *p*-toluenesulfonic acid.

phatic and aromatic amines as a general route to 2-amino-1,3-butadienes and 1-aza-1,3-butadienes. The availability of the starting enynes[18] and the good yields attainable make this aminomercuration reaction a very useful procedure for the preparation of these dienes on a multigram scale. The major limitation of this procedure is associated with the inability to prepare 2-amino-1,3-butadienes of 1-aza-1,3-butadienes having R^1 = H because the Michael-type addition takes place rapidly to form a 2:1 (amine:enyne) adduct.

Experimental Section

General Methods. NMR spectra were recorded on a Varian FT-80 or a Brücker AC-300 spectrometer.

Materials. All reactions were run under an Ar or N_2 atmosphere. All amines were refluxed over NaOH, distilled, and stored under N_2. THF was distilled from sodium benzophenone prior to use and hexane was distilled over P_2O_5 prior to use. Mercury salts were dried under high vacuum and kept under Ar. All other reagents were of the best commercial grade available and used without further purification. All 3-alken-1-ynes were prepared as described,[18] except the previously unknown 3-methyl-5-[(trimethylsilyl)oxy]-3-penten-1-yne ($R^1 = CH_3$, $R^2 = CH_2OSi(CH_3)_3$, R^3 = H), which was prepared as follows.

3-Methyl-5-[(trimethylsilyl)oxy]-3-penten-1-yne. To a solution of commercial 3-methyl-2-penten-4-yn-1-ol (100 mmol, 10 mL) in dry Et_2O (100 mL) was added a mixture of $ClSiMe_3$ (100 mmol, 12.7 mL) and 1,1,1,3,3,3-hexamethyldisilazane (100 mmol, 23 mL). After 1 h, the hydrochloride salts were separated by filtration and Et_2O was removed by distillation. The resultant liquid was distilled under reduced pressure: bp 95–100 °C (50 Torr); yield 16.8 g (95%); ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 1.84 (s, 3 H), 2.82 (s, 1 H), 4.22 (d, J = 6.3 Hz, 2 H), 6.01 (t, J = 6.3 Hz, 1 H); ^{13}C NMR (neat) δ 04 (q), 16.6 (q), 58.9 (t), 75.3 (d), 86.1 (s), 118.3 (s), 137.9 (d). Anal. Calcd for $C_9H_{16}OSi$: C, 64.22; H, 9.58. Found: C, 64.37; H, 9.43.

General Preparative Procedure for 2-Amino-1,3-butadienes 2 and 3. To a mixture of 3-alken-1-yne (20 mmol), Et_3N (50 mmol, 7 mL), and $Hg(OAc)_2$ (15 mmol, 4.78 g) in 40 mL of THF at room temperature was added dropwise a solution of secondary amine (20 mmol) in 10 mL of THF. The reaction mixture was vigorously stirred for 8 h and filtered under Ar, and the filtrate was concentrated under reduced pressure (0.05 Torr). The resulting liquid was treated with dry n-hexane (3 × 30 mL) filtered under Ar, and the filtrate was concentrated in vacuo (0.05 Torr). The crude reaction product was an essentially pure pale yellow or brown liquid, which was trap-to-trap condensed in high vacuum (10^{-3} Torr).

***N*-(2-Methyl-1-methylene-2-propenyl)morpholine (2a)**: 3-methyl-3-buten-1-yne (2 mL), morpholine (1.75 mL); yield 1.96 g (61%); bp 55–60 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 1.80 (s, 3 H), 2.55–2.80 (m, 4 H), 3.40–3.70 (m, 4 H), 3.85 (s, 1 H), 4.05 (s, 1 H), 4.85 (s, 1 H), 5.05 (s, 1 H); ^{13}C NMR (neat) δ 21.9 (q), 50.6 (t), 67.2 (t), 90.2 (t), 115.1 (t), 143.4 (s), 159.0 (s); MS m/z = 153 (M^+). Anal. Calcd for $C_9H_{15}NO$: C, 70.56; H, 9.88; N, 9.13. Found: C, 70.55; H, 9.97; N, 9.01.

***(E)*-*N*-(4-Methoxy-2-methyl-1-methylene-2-butenyl)morpholine (2b)**: (*E*)-5-methoxy-3-methyl-3-penten-1-yne (2.4 mL), morpholine (1.75 mL); yield 2.83 g (72%); bp 65–70 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 1.75 (s, 3 H), 2.70 (m, 4 H), 3.45 (s, 3 H), 3.6–3.8 (m, 4 H), 3.95 (d, J = 6.4 Hz, 2 H), 4.0 (s, 1 H), 4.25 (s, 1 H), 5.80 (t, J = 6.4 Hz, 1H); ^{13}C NMR (neat) δ 16.3 (q), 50.5 (t), 58.1 (q), 67.3 (t), 69.5 (t), 89.5 (t), 127.4 (d), 137.4 (s), 168.4 (s). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.98; H, 9.71; N, 7.11. Found: C, 66.70; H, 9.87; N, 7.05.

***(E)*-*N*-[2-Methyl-1-methylene-4-[(trimethylsilyl)oxy]-2-butenyl]morpholine (2c)**: 3-methyl-5-[(trimethylsilyl)oxy]-3-penten-1-yne (3.36 g), morpholine (1.75 mL); yield 3.80 g (75%); bp 80–88 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 0.5 (s, 9 H), 1.75 (s, 3 H), 2.6–2.8 (m, 4 H), 3.6–3.8 (m, 4 H), 3.85 (s, 1 H), 4.1 (d, J = 6.3 Hz, 2 H), 4.15 (s, 1 H), 5.80 (t, J = 6.3 Hz, 1H); ^{13}C NMR (neat) δ 2.2 (q), 17.9 (q), 52.2 (t), 61.8 (t), 69.0 (t), 91.3 (t), 132.1 (d), 132.9 (s), 162.1 (s). Anal. Calcd for $C_{13}H_{25}NO_2Si$: C, 61.12; H, 9.86; N, 5.48. Found: C, 61.38; H 9.73; N, 5.41.

***N*-(1-Cyclohex-1-enylethenyl)morpholine (2d)**: 1-ethynylcyclohexene (2.4 mL), morpholine (1.75 mL); reaction time 48 h; yield 2.57 g (67%); bp 65–70 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 1.5–1.75 (m, 4 H), 1.85–2.25 (m, 4 H), 2.55–2.8 (m, 4 H), 3.45–3.7 (m, 4 H), 3.75 (s, 1 H), 3.95 (s, 1 H), 5.85 (s br, 1 H); ^{13}C NMR (neat) δ 13.2 (t), 13.7 (t), 16.1 (t), 18.5 (t), 40.7 (t), 57.4 (t), 78.4 (t), 116.9 (d), 127.2 (s), 150.1 (s). Anal. Calcd for $C_{12}H_{19}NO$: C, 74.51; H, 9.87; N, 7.20. Found: C, 74.72; H, 9.91; N, 7.43.

***(Z)*-*N*-(2-Ethyl-1-methylene-2-butenyl)morpholine (2e)**: (*Z*)-3-ethyl-3-penten-1-yne (2.4 mL), morpholine (1.75 mL); reaction time 48 h; yield 2.72 g (75%); bp 60–65 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 1.4 (t, J = 8.1 Hz, 3 H), 2.05 (d, J = 6.6 Hz, 3 H), 2.5 (q, J = 8.5 Hz, 2 H), 3.2 (t, J = 5.8 Hz, 4 H), 4.05 (t, J = 5.8 Hz, 4 H), 4.15 (s, 1 H), 4.40 (s, 1 H), 5.85 (q, J = 6.6 Hz, 1 H); ^{13}C NMR (neat) δ 13.6 (q), 15.3 (q), 30.9 (t), 49.0 (t), 67.3 (t), 88.6 (t), 120.3 (d), 123.6 (s), 142.0 (s). Anal. Calcd for $C_{11}H_{19}NO$: C, 72.89; H, 10.54; N, 7.73. Found: C, 72.72; H, 10.32; N, 7.61.

***(Z)*-*N*-(4-Methoxy-2-methyl-1-methylene-2-butenyl)morpholine (2f)**: (*Z*)-5-methoxy-3-methyl-3-penten-1-yne (2.4 mL), morpholine (1.75 mL); reaction time 48 h; yield 2.20 g (56%); bp 65–70 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 1.78 (s, 3 H), 2.6–2.8 (m, 4 H), 3.3 (s, 3 H), 3.4–3.6 (m, 4 H), 3.7 (s, 1 H), 3.9 (s, 1 H), 4.05 (d, J = 6.3 Hz, 2 H), 5.5 (t, J = 6.3 Hz, 1 H); ^{13}C NMR (neat) δ 24.2 (q), 47.5 (t), 56.4 (q), 65.9 (t), 69.0 (t), 87.4 (t), 127.5 (d), 137.2 (s), 154.3 (s). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.98 H, 9.71; N, 7.11. Found: C, 66.70; H, 9.87; N, 7.05.

***(E)*-*N*-[2-Methyl-1-methylene-4-[(trimethylsilyl)oxy]-2-butenyl]-2-(methoxymethyl)pyrrolidine (2g)**: 3-methyl-5-[(trimethylsilyl)oxy]-3-penten-1-yne (3.36 g), 2-(methoxymethyl)pyrrolidine (2.3 g); yield 3.4 g (60%); bp = 92–96 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 0.5 (s, 9 H), 1.7–2.0 (m, 7 H), 2.9–3.5 (m, 5 H), 3.32 (s, 3 H), 3.60 (s, 1 H), 3.80 (s, 1 H), 4.1 (d, J = 6.5 Hz, 2 H), 5.80 (t, J = 6.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.2 (q), 16.3 (q), 23.24 (t), 28.8 (t), 49.0 (t), 56.86 (d), 58.8 (q), 59.5 (t), 73.3 (t), 83.2 (t), 128.2 (d), 135.9 (s), 155.6 (s). Anal. Calcd for $C_{15}H_{29}NO_2Si$: C, 63.55; H, 10.31; N, 4.94. Found: C, 63.62; H, 10.23; N, 5.01.

***(E)*-*N*-(4-Methoxy-2-methyl-1-methylene-2-butenyl)-2-(methoxymethyl)pyrrolidine (2h)**: (*E*)-5-methoxy-3-methyl-3-penten-1-yne (2.4 mL), 2-(methoxymethyl)pyrrolidine (2.3 g); yield 3.05 g (67%); bp 82–88 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 1.7–2.0 (m, 7 H), 2.8–3.6 (m, 5 H), 3.30 (s, 3 H), 3.41 (s, 3 H), 3.81 (s, 1 H), 3.93 (s, 1 H), 4.10 (d, J = 6.5 Hz, 2 H), 5.80 (t, J = 6.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.8 (q), 25.9 (t), 31.4 (t), 51.6 (t), 58.6 (d), 59.7 (q), 60.9 (q), 71.2 (t), 75.9 (t), 86.5 (t), 128.3 (d), 140.7 (s), 157.7 (s). Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.28; N, 6.21. Found: C, 69.34; H, 10.33; N, 6.04.

***N*-(2-Methyl-1-methylene-2-propenyl)-*N*-methylaniline (3a)**: 2-methyl-1-buten-3-yne (2 mL), *N*-methylaniline (2.15 mL); yield 2.59 g (75%); bp 65–72 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 1.90 (s, 3 H), 3.11 (s, 3 H), 4.80 (s, 1 H), 4.90 (s, 1 H), 5.00 (s, 1 H), 5.15 (s, 1 H) 6.8–6.9 (m, 3 H), 7.2–7.3 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.5 (q), 42.2 (q), 106.49 (t), 117.5 (t), 119.7 (d), 121.5 (d), 130.9 (d), 143.1 (s), 151.3 (s), 156.9 (s). Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.25; H, 8.62; N, 8.12.

***(E)*-*N*-(4-Methoxy-2-methyl-1-methylene-2-butenyl)-*N*-methylaniline (3b)**: (*E*)-5-methoxy-3-methyl-3-penten-1-yne (2.4 mL), *N*-methylaniline (2.15 mL); yield 2.99 g (69%); bp 86–90 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 1.80 (s, 3 H), 3.10 (s, 3 H), 3.20 (s, 3 H), 4.02 (d, J = 6.5 Hz, 2 H), 4.8 (s, 1 H), 5.04 (s, 1 H), 5.97 (t, J = 6.5 Hz, 1 H), 6.85 (m, 3 H), 7.2–7.3 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.5 (q), 40.1 (q), 57.7 (q), 69.0 (t), 103.6 (t), 117.3 (d), 118.9 (d), 128.5 (d), 129.05 (d), 132.5 (s), 148.9 (s), 155.5 (s). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.44. Found: C, 77.49; H, 8.73; N, 6.51.

***(E)*-*N*-[2-Methoxy-1-methylene-4-[(trimethylsilyl)oxy]-2-butenyl]-*N*-methylaniline (3c)**: 3-methyl-5-[(trimethylsilyl)oxy]-3-penten-1-yne (3.36 g), *N*-methylaniline (2.15 mL); yield 4.12 g (75%); bp 95–100 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 2.2 (s, 3 H), 3.00 (s, 3 H), 4.21 (d, J = 6.4 Hz, 2 H), 4.74 (s, 1 H), 4.90 (s, 1 H), 5.77 (t, J = 6.4 Hz, 1 H), 6.8–7.2 (m, 5H);

(18) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1971; pp 124, 136–137.

^{13}C NMR ($CDCl_3$) δ 0.4 (q), 14.3 (q), 39.9 (q), 59.8 (t), 103.5 (t), 117.5 (d), 118.8 (d), 128.5 (d), 129.1 (d), 133.1 (s), 148.9 (s), 155.6 (s). Anal. Calcd for $C_{16}H_{25}NOSi$: C, 69.76; H, 9.15; N, 5.08. Found: C, 69.66; H, 9.17; N, 5.14.

***N*-(1-Cyclohex-1-enylethenyl)-*N*-methylaniline (3d)**: 1-ethynylcyclohexene (2.4 mL), *N*-methylaniline (2.15 mL); reaction time 48 h; yield 3.36 g (79%); bp 80–84 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 1.0–1.2 (m, 4 H), 2.0–2.2 (m, 4 H), 3.05 (s, 3 H), 4.75 (s, 1 H), 4.95 (s, 1 H), 5.90 (s br, 1 H), 6.7–6.9 (m, 3 H), 7.1–7.2 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.9 (t), 23.4 (t), 26.1 (t), 26.7 (t), 40.3 (q), 103.2 (t), 117.0 (d), 119.0 (d), 127.3 (d), 129.0 (d), 134.6 (s), 149.7 (s), 155.8 (s). Anal. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98; N, 6.57. Found: C, 84.64; H, 8.99; N, 6.34.

(*Z*)-*N*-(4-Methoxy-2-methyl-1-methylene-2-butenyl)-*N*-methylaniline (3e): 5-methoxy-3-methyl-3-penten-1-yne (2.4 mL), *N*-methylaniline (2.15 mL); reaction time 48 h: yield 2.68 g (62%); bp 60–70 °C (10^{-3} Torr); ^1H NMR ($CDCl_3$) δ 1.72 (s, 3 H), 3.05 (s, 3 H), 3.3 (s, 3 H), 4.09 (d, J = 6.3 Hz, 2 H), 4.23 (s, 1 H), 4.48 (s, 1 H), 5.46 (t, J = 6.3 Hz, 1 H), 6.89 (m, 3 H), 7.19 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.7 (q), 39.9 (q), 57.8 (q), 70.0 (t), 96.7 (t), 121.2 (d), 121.6 (d), 127.5 (d), 128.5 (d), 137.8 (s), 147.9 (s), 150.9 (s). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.44. Found: C, 77.44; H, 8.91; N, 6.29.

(*E*)-*N*-Allyl-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)aniline (3f): (*E*)-5-methoxy-3-methyl-3-penten-1-yne (2.4 mL), *N*-allylaniline (2.67 g); reaction time 12 h; yield 2.67 g (55%); ^1H NMR ($CDCl_3$) δ 1.73 (s, 3 H), 3.22 (s, 3 H), 3.98 (d, J = 6.4 Hz, 2 H), 4.10 (d, J = 5.3 Hz, 2 H), 4.84 (s, 1 H), 5.01 (s, 1 H), 5.15 (m, 2 H), 5.88 (m, 2 H), 6.7–7.3 (m, 5 H_{ar}); ^{13}C NMR ($CDCl_3$) δ 14.5 (q), 54.2 (t), 57.7 (q), 69.0 (t), 105.5 (t), 116.3 (t), 117.0 (d), 118.6 (d), 126.2 (d), 128.5 (d), 134.6 (d), 135.4 (s), 147.8 (s), 153.6 (s). Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.69; N, 5.76. Found: C, 78.81; H, 8.99; N, 5.67.

(*E*)-*N*-(3-Butenyl)-*N*-(4-methoxy-2-methyl-1-methylene-2-butenyl)aniline (3g): (*E*)-5-methoxy-3-methyl-3-penten-1-yne (2.4 mL), *N*-(3-butenyl)aniline (2.90 g); reaction time 12 h; yield 2.52 g (49%); ^1H NMR ($CDCl_3$) δ 1.75 (s, 3 H), 2.30–2.55 (m, 2 H), 3.24 (s, 3 H), 3.30–3.50 (m, 2 H), 4.10 (d, J = 6.4 Hz, 2 H), 4.82 (s, 1 H), 5.05 (m, 2 H), 5.12 (s, 1 H), 5.88 (m, 2 H), 6.7–7.3 (m, 5 H_{ar}); ^{13}C NMR ($CDCl_3$) δ 14.5 (q), 31.6 (t), 51.5 (t), 57.7 (q), 69.0 (t), 105.4 (t), 116.2 (t), 117.0 (d), 118.6 (d), 126.2 (d), 128.6 (d), 135.4 (s), 135.7 (d), 147.8 (s), 153.2 (s). Anal. Calcd for $C_{17}H_{23}NO$: C, 79.33; H, 9.00; N, 5.44. Found: C, 79.49; H, 9.04; N, 5.29.

General Preparative Procedure for 1-Aza 1,3-Dienes 5, 3-Imino Amines 6, and 4-Amino 1-Aza 1,3-Dienes 7. A mixture of K_2CO_3 (10 mmol, 1.40 g), $HgCl_2$ (5 mmol, 1.35 g), 3-alken-1-yne (1) (10 mmol), primary aromatic amine (40 mmol), THF (40 mL), and water (10 mL) was stirred and heated at 70 °C for 3 h. (5e required 6 h.) After cooling, the Hg(II) species were reduced with $NaBH_4$ (5 mmol, 0.19 g) in 2 M aqueous KOH (10 mmol). After 2 h, the metallic mercury was separated and the organic layers were extracted with Et_2O, washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction product was a nearly pure brown oil, which was trap-to-trap condensed (preheated oil bath temperature, 80–130 °C, 0.001 Torr).

***N*-(1,2-Dimethylprop-2-enylidene)aniline (5a)**: 2-methyl-1-buten-3-yne (1 mL), aniline (3.6 mL); yield 1.26 g (79%); ^1H NMR ($CDCl_3$) δ 1.9 (s, 3 H), 2.0 (s, 3 H), 5.5 (s, 1 H), 5.6 (s, 1 H), 6.5–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.8 (q), 19.8 (q), 119.4 (d), 120.2 (t), 123.3 (d), 129.2 (d), 146.2 (s), 152.4 (s), 166.2 (s); MS m/z = 159 M^+. Anal. Calcd for $C_{11}H_{13}N$: C, 82.96; H, 8.25; N, 8.81. Found: C, 82.99; H, 8.10; N, 8.64.

***N*-(1,2-Dimethyl-4-methoxybut-2-enylidene)aniline (5b)**: 5-methoxy-3-methyl-3-penten-1-yne (1.2 mL), aniline (3.6 mL); yield 1.46 g (72%); ^1H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 2.03 (s, 3 H), 3.5 (s, 3 H), 4.25 (d, J = 6.4 Hz, 2 H), 6.36 (t, J = 6.4 Hz, 1 H), 6.6–7.5 (m, 5 H); ^{13}C NMR (neat) δ 13.3 (q), 15.0 (q), 50.3 (q), 70.2 (t), 119.5 (d), 123.1 (d), 129.2 (d), 133.4 (d), 139.0 (s), 152.6 (s), 166.2 (s); MS m/z = 203 M^+. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.80; H, 8.45; N, 6.87. Found: C, 76.56; H, 8.46; N, 6.93.

***N*-(1,2-Dimethylprop-2-enylidene)-*o*-toluidine (5c)**: 2-methyl-1-buten-3-yne (1 mL), *o*-toluidine (4.3 mL); yield 1.05 g (61%); ^1H NMR ($CDCl_3$) δ 1.9 (s, 3 H), 2.05 (s, 3 H), 2.1 (s, 3 H), 5.5 (s, 1 H), 5.6 (s, 1 H) 6.3–6.55 (m, 1 H), 6.7–7.25 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 15.8 (q), 17.9 (q), 19.7 (q), 118.3 (d), 119.6 (t), 123.4 (d), 126.6 (d), 126.8 (s), 130.5 (d), 146.2 (s), 151.0 (s), 165.5 (s); MS m/z = 173 M^+. Anal. Calcd for $C_{12}H_{15}N$: C, 83.18; H, 8.74; N, 8.08. Found: C, 83.03; H, 8.90; N, 8.12.

***N*-(1-Cyclohex-1-enylethylidene)aniline (5d)**: 1-ethynylcyclohexene (1.22 mL), aniline (3.6 mL); yield 1.55 g (78%); ^1H NMR ($CDCl_3$) δ 1.45–1.85 (m, 4 H), 1.9 (s, 3 H), 2.1–2.6 (m, 4 H), 6.3–7.3 (m, 1 H + 5 H_{ar}); ^{13}C NMR ($CDCl_3$) δ 15.8 (q), 22.8 (t), 23.3 (t), 25.3 (t), 26.8 (t), 119.8 (d), 123.0 (d), 129.2 (d), 133.7 (d), 140.2 (s), 153.0 (s), 165.9 (s); MS m/z = 199 M^+. Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.58; N, 7.01. Found: C, 84.25; H, 8.82; N, 7.01.

***N*-(1-Cyclohex-1-enylethylidene)-*o*-toluidine (5e)**: 1-ethynylcyclohexene (1.22 mL), *o*-toluidine (4.3 mL); yield 0.96 g (45%); ^1H NMR ($CDCl_3$) δ 1.4–1.75 (m, 4 H), 1.8 (s, 3 H), 2.0 (s, 3 H), 2.05–2.55 (m, 4 H), 6.3–7.25 (m, 1 H + 4 H_{ar}); ^{13}C NMR (neat) δ 16.0 (q), 19.3 (q), 22.8 (t), 23.4 (t), 25.4 (t), 26.8 (t), 119.0 (d), 123.4 (d), 127.7 (s), 130.7 (d), 133.8 (d), 139.9 (d), 145.8 (s), 151.5 (s), 166.1 (s). Anal. Calcd for $C_{15}H_{19}N$: C, 84.47; H, 8.95; N, 6.59. Found: C, 84.35; H, 8.77; N, 6.67.

***N*-(1-Cyclopent-1-enylethylidene)aniline (5f)**: 1-ethynylcyclopentene (0.92 g), aniline (3.6 mL); yield 0.87 g (47%); ^1H NMR ($CDCl_3$) δ 1.4–1.8 (m, 2 H), 1.85 (s, 3 H), 2.3–2.8 (m, 4 H), 6.25 (s br, 1 H), 6.35–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.4 (q), 23.9 (t), 32.8 (t), 34.6 (t), 120.0 (d), 123.5 (d), 129.4 (d), 137.0 (d), 147.8 (s), 152.6 (s), 163.3 (s). Anal. Calcd for $C_{13}H_{15}N$: C, 84.27; H, 8.17; N, 7.56. Found: C, 84.21; H, 8.30; N, 7.71.

***N*-(1,2-Dimethylprop-2-enylidene)-*m*-toluidine (5g)**: 2-methyl-1-buten-3-yne (1 mL), *m*-toluidine (4.3 mL); yield 1.05 g (61%); ^1H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 2.05 (s, 3 H), 2.35 (s, 3 H), 5.5 (s, 1 H), 5.55 (s, 1 H), 6.3– 7.25 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 15.8 (q), 19.7 (q) 21.6 (q), 116.5 (d), 119.8 (t), 120.1 (d), 124.1 (d), 129.0 (d), 138.6 (s), 146.4 (s), 152.5 (s), 165.8 (s). Anal. Calcd for $C_{12}H_{15}N$: C, 83.18 H, 8.74; N, 8.08. Found: C, 83.10; H, 8.85; N, 8.14.

***N*-(3-Anilinio-1-butylidene)aniline (6a)**: 3-penten-1-yne (0.93 mL), aniline (3.6 mL); yield 1.44 g (57%); ^1H NMR ($CDCl_3$) δ 1.20 (d, J = 5.3 Hz, 3 H), 1.70 (s, 3 H), 2.45 (m, 2 H), 3.95 (m, 1 H), 6.45–7.35 (m, 10 H_{ar}); ^{13}C NMR ($CDCl_3$) δ 21.5 (q), 21.7 (q), 40.6 (t), 47.3 (d), 114.2 (d), 117.1 (d), 120.3 (d), 124.0 (d), 129.8 (d), 129.9 (d), 148.4 (s), 150.2 (s), 171.2 (s). Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.90; H, 7.80; N, 11.13.

***N*-(3-Anilinio-1-pentylidene)aniline (6b)**: 3-hexen-1-yne (0.93 mL), aniline (3.6 mL); yield 1.69 g (75%); ^1H NMR ($CDCl_3$) δ 1.0 (t, J = 8.0 Hz, 3 H), 1.75 (s, 3 H), 2.05–2.50 (m, 2 H), 2.60 (d, J = 6.6 Hz, 2 H), 3.65–4.05 (m, 1 H), 6.6–7.7 (m, 10 H_{ar}); ^{13}C NMR ($CDCl_3$) δ 11.1 (q), 20.8 (q), 28.7 (t), 46.6 (t), 53.1 (d), 113.8 (d), 117.6 (d), 120.6 (d), 123.8 (d), 129.6 (d), 130.0 (d), 148.7 (s), 151.9 (s), 171.0 (s). Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.17; H, 8.30; N, 10.50. Found: C, 81.26; H, 8.20; N, 10.36.

***N*,*N*′-(3-Methyl-1-propen-1-yl-3-ylidene)dianiline (7a)**: 1-ethoxy-1-buten-3-yne (0.92 mL), aniline (3.6 mL); yield 1.30 g (55%); mp = 180–181 °C; ^1H NMR (CCl_4) δ 1.9 (s, 3 H), 4.8 (d, J = 8.0 Hz, 1 H), 6.65–7.40 (m, 1 H + 10 H_{ar}); ^{13}C NMR ($CDCl_3$) δ 21.4 (q), 98.6 (d), 116.4 (d), 121.9 (d), 122.5 (d), 123.7 (d), 129.5 (d), 130.0 (d), 139.7 (d), 143.5 (s), 150.4 (s), 166.4 (s). Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.31; H, 6.83; N, 11.84. Found: C, 81.51; H, 6.72 N, 11.83.

***N*,*N*′-(3-Methyl-1-propen-1-yl-3-ylidene)di-*o*-toluidine (7b)**: 1-ethoxy-1-buten-3-yne (0.92 mL), *o*-toluidine (4.3 mL); yield 1.53 g (58%); ^1H NMR ($CDCl_3$) δ 1.8 (s, 3 H), 2.15 (s, 6 H), 5.1 (d, J = 8.2 Hz, 1 H), 6.70–7.50 (m, 1 H + 8 H_{ar}); ^{13}C NMR ($CDCl_3$) δ 18.4 (q), 18.5 (q), 21.4 (q), 78.5 (d), 98.7 (d), 112.9 (d), 121.1 (d), 123.8 (d), 125.6 (d), 127.0 (d), 127.6 (d), 128.6 (d), 130.9 (d), 131.4 (d), 138.5 (d), 141.5 (s), 149.9 (s), 167.1 (s). Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.60; N, 10.61. Found: C, 81.62; H, 7.81; N, 10.53.

***N*,*N*′-(3-Methyl-1-propen-1-yl-3-ylidene)di-*p*-toluidine (7c)**: 1-ethoxy-1-buten-3-yne (0.92 mL), *p*-toluidine (4.5 mL): yield 1.56 g (59%); ^1H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 2.30, (s, 3 H), 2.40 (s, 3 H), 4.95 (d, J = 8.1 Hz, 1 H), 6.65–7.45 (m, 1 H + 8 H_{ar}); ^{13}C NMR ($CDCl_3$) δ 20.9 (q), 21.1 (q), 21.3 (q), 115.7, 116.6, 122.0, 130.1, 130.3, 130.5, 131.7, 132.7, 141.8, 147.2, 165.6 ppm. Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.77; H, 7.60; N, 10.61. Found: C, 81.93; H, 7.60; N, 10.61.

***N,N'*-(3-Methyl-1-propen-1-yl-3-ylidene)di-*p*-chloroaniline (7d)**: 1-methoxy-1-buten-3-ene (0.82 g) or 1-ethoxy-1-buten-3-yne (0.92 mL), *p*-chloroaniline (5.10 g); yield 1.86 g (61%); mp = 93–95 °C, recrystallized from *n*-hexane; ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 5.05 (d, J = 8.5 Hz, 1 H), 6.65–7.50 (m, 1 H + 8 H_{ar}); ^{13}C NMR ($CDCl_3$) δ 21.9 (q), 99.4 (d), 118.0 (d), 123.6 (d), 127.9 (s), 129.4 (s), 129.8 (d), 130.3 (d), 140.2 (d), 142.4 (s), 148.9 (s), 167.3 (s). Anal. Calcd for $C_{16}H_{14}N_2Cl_2$: C, 62.98; H, 4.60; N, 9.20. Found: C, 62.97; H, 4.47; N, 9.36.

General Preparative Procedure for 1-Aza 1,3-Dienes 8. A typical procedure for these compounds is an adaptation of that for compounds **2** but using morpholine (20 mmol) instead of triethylamine and the primary amine (40 mmol) instead the secondary amine.

***N*-(4-Methoxy-1,2-dimethylbut-2-enylidene)methylbenzylamine (8a)**: (*E*)-5-methoxy-3-methyl-3-penten-1-yne (2.4 mL), methylbenzylamine (2.40 g); yield 3.18 g (69%); bp = 75–80 °C(10^{-3} Torr); ^{1}H NMR ($CDCl_3$) δ 1.45 (d, J = 5.9 Hz, 3 H), 1.95 (s, 3 H), 2.05 (s, 3 H), 3.41 (s, 3 H), 4.17 (d, J = 6.4 Hz, 2 H), 4.73 (q, J = 5.9 Hz, 1 H), 6.10 (t, J = 6.4 Hz, 1 H), 7.1–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.5 (q), 13.7 (q), 25.9 (q), 58.3 (q), 60.2 (d), 70.6 (t), 126.9 (d), 127.2 (d), 128.8 (d), 130.7 (d), 140.2 (s), 147.3 (s), 163.8 (s). Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.91; H, 9.21; N, 6.00.

***N*-(4-Methoxy-1,2-dimethylbut-2-enylidene)benzylamine (8b)**: (*E*)-5-methoxy-3-methyl-3-penten-1-yne (2.4 mL), benzylamine (2.14 g); yield 3.16 g (73%); bp = 70–76 °C (10^{-3} Torr); ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 2.11 (s, 3 H), 3.36 (s, 3 H), 4.15 (d, J = 6.4 Hz, 2 H), 4.62 (s, 2 H), 6.15 (t, J = 6.4 Hz, 1 H), 7.4–7.1 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.2 (q), 14.00 (q), 55.13 (q), 58.2 (t), 69.8 (t), 126.2 (d), 127.3 (d), 128.1 (d), 129.3 (d), 140.0 (s), 140.6 (s), 166.9 (s). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.44. Found: C, 77.42; H, 8.75; N, 6.29.

***N*-(1,2-Dimethyl-4-[(trimethylsilyl)oxy]but-2-enylidene)benzylamine (8c)**: (*E*)-3-methyl-5-[(trimethylsilyl)oxy]-3-penten-1-yne (3.36 g), benzylamine (2.14 g); yield 4.12 g (75%); bp = 79–85 °C (10^{-3} Torr); ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 1.87 (s, 3 H), 2.12 (s, 3 H), 4.46 (d, J = 6.3 Hz, 2 H), 4.67 (s, 2 H), 6.15 (t, J = 6.3 Hz, 1 H), 7.1–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 0.2 (q), 13.5 (q), 14.0 (q), 55.72 (t), 60.9 (t), 126.7 (d), 128.1 (d), 128.7 (d), 133.6 (d), 138.6 (s), 141.8 (s), 166.2 (s). Anal. Calcd for $C_{16}H_{25}NOSi$: C, 69.76; H, 9.15; N, 5.08. Found: C, 69.66; H, 9.20; N, 5.12.

***N*-(1-Cyclohex-1-enylethylidene)aniline (8d)**: 1-ethynylcyclohexene (1.22 mL), butylamine (1.95 mL); yield 2.24 g (75%); ^{1}H NMR ($CDCl_3$) δ 0.9 (t, J = 5.3 Hz, 3 H), 1.3–1.5 (m, 4 H), 1.6–1.8 (m, 4 H), 1.88 (s, 3 H), 2.2–2.4 (m, 4 H), 3.33 (t, J = 6.6 Hz, 2 H), 6.30 (s br, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.74 (q), 13.58 (q), 20.35 (t), 21.82 (t), 22.30 (t), 24.6 (t), 25.6 (t), 32.8 (t), 51.0 (t), 129.1 (d), 139.8 (s), 165.2 (s). Anal. Calcd for $C_{12}H_{21}N$: C, 80.38; H, 11.81; N, 7.81. Found: C, 80.42; H, 11.90; N, 7.69.

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Registry No. 1 (R_1 = CH_3, R_2 = R_3 = H), 78-80-8; 1 (R_1 = CH_3, R_2 = CH_2OCH_3, R_3 = H), 76681-69-1; 1 (R_1 = CH_3, R_2 = R_2 = $CH_2OSi(CH_3)_3$, R_3 = H), 64700-46-5; 1 (R_1, R_2 = -$(CH_2)_4$-, R_3 = H), 931-49-7; 1 (R_1 = CH_2CH_3, R^2 = H, R_3 = CH_3), 14272-82-3; 1 (R_1 = CH_3, R_2 = H, R_3 = CH_2OCH_3), 86574-08-5; 1 (R_1, R_2 = -$(CH_2)_3$-, R_3 = H), 1610-13-5; 1 (R_1 = R_3 = H, R_2 = CH_3), 2004-69-5; 1 (R_1 = R_3 = H, R_2 = OEt), 18311-19-8; **2a**, 101219-16-3; **2b**, 121405-14-9; **2c**, 124803-50-5; **2d**, 66312-68-3; **2e**, 124803-49-2; **2f**, 129154-86-5; **2g**, 135560-21-3; **2h**, 135523-29-4; **3a**, 135523-30-7; **3b**, 135523-31-8; **3c**, 135523-32-9; **3d**, 135523-33-0; **3e**, 135523-34-1; **3f**, 135523-35-2; **3g**, 135523-36-3; **5a**, 101219-17-4; **5b**, 135523-37-4; **5c**, 101219-18-5; **5d**, 101219-21-0; **5e**, 101219-22-1; **5f**, 101219-20-9; **5g**, 101219-19-6; **6a**, 135523-38-5; **6b**, 135523-39-6; **7a**, 135523-40-9; **7b**, 135523-41-0; **7c**, 135523-42-1; **7d**, 135523-43-2; **8a**, 135523-44-3; **8b**, 135523-45-4; **8c**, 135523-46-5; **8d**, 135523-47-6; $Hg(OAc)_2$, 1600-27-7; $HgCl_2$, 7487-94-7; *p*-$ClC_6H_4NH_2$, 106-47-8; $BuNH_2$, 109-73-9; 3-methyl-2-penten-4-yn-1-ol, 6153-06-6; morpholine, 110-91-8; 2-(methoxymethyl)pyrrolidine, 135523-48-7; *N*-methylaniline, 100-61-8; *N*-allylaniline, 589-09-3; *N*-(3-butenyl)aniline, 29369-71-9; aniline, 62-53-3; *o*-toluidine, 95-53-4; *n*-toluidine, 108-44-1; *p*-toluidine, 106-49-0; 1-phenylethylamine, 98-84-0; benzylamine, 100-46-9.