Lewis Acid-Promoted 3-Aza-Cope Rearrangement of *N*-Alkyl-*N*-allylanilines

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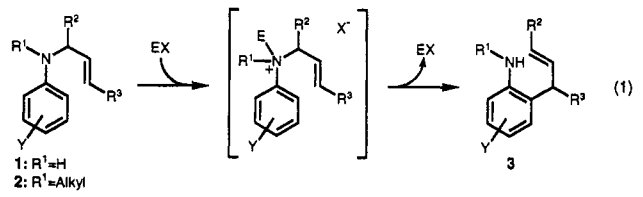
The 3-aza-Cope rearrangement of *N*-alkyl-*N*-allylaniline substrates, which required 250 °C to proceed thermally, was promoted by Lewis acid reagents at 111–140 °C. Systematic studies of this reaction were performed to examine a number of reaction variables such as concentration, the stoichiometry of the Lewis acid with the substrate, the optimum temperature for rearrangement, and the type of Lewis acid reagent. Of the many Lewis acids investigated, $ZnCl_2$ (140 °C) and $Et_2O{\cdot}BF_3$ (111 °C) were the most generally successful reagents for promoting the aromatic 3-aza-Cope rearrangement. With respect to substrate variation, the presence of a methoxy substituent para to the *N*-allyl group slowed the reaction slightly, while a meta substituent accelerated the rate of [3,3] rearrangement and produced moderate site selectivity on the aromatic ring. Lewis acid-promoted rearrangement of an unsymmetrically substituted allyl moiety resulted in [3,3] sigmatropic rearrangement to give the 1-hexen-3-yl substituent on the aromatic ring. Overall, both $ZnCl_2$ and $Et_2O{\cdot}BF_3$ were shown to efficiently accelerate the regiospecific 3-aza-Cope rearrangement of *N*-alkyl-*N*-allylanilines for the purpose of forming a carbon–carbon bond between a secondary alkyl substituent and an aromatic ring.

Introduction

The aromatic 3-aza-Cope rearrangement of *N*-allylaniline substrates **1** and **2** has been of interest for some time as a route to the formation of 2-substituted aniline and indole products, but the utility of this reaction has been greatly limited (eq 1).[1] The severe conditions (200–



(1)

350 °C) required for thermal rearrangement, which produced low yields of 2-allylanilines (**3**) and significant amounts of products resulting from removal of the allyl group, have restricted the utility of this reaction and presented an enormous challenge to synthetic organic chemists.[2] Approaches to overcoming these barriers have focused around one common theme—charge acceleration of the rearrangement process by reaction of *N*-allylaniline substrates with electrophilic reagents through generation of a quaternary intermediate.

The electrophile sources most commonly used for charge acceleration of the aromatic 3-aza-Cope rearrangement have been Brønsted acids, which typically promote rearrangement at temperatures of 140–150 °C. Polyphosphoric acid has been used to promote charge-accelerated 3-aza-Cope rearrangement, but effective use of this reagent was limited to the *N*-crotyl derivatives (R^3 = Me) of **1**[3] and **2**.[4] Two other proton sources, HCl and H_2SO_4, were studied more extensively and have shown greater versatility in promoting this [3,3] sigmatropic rearrangement. The use of HCl to promote the rearrangement of **1** to **3** was achieved by treatment of **1** with either HCl[3b] or $PhNH_2{\cdot}HCl$.[5] Similarly, the treatment of **2** with HCl also gave 2-allylaniline derivatives.[4,6] Rearrangement of both **1** and **2** was promoted effectively with 2 N H_2SO_4.[7] A drawback to the use of strong protic acids has been the tendency of these reagents to produce formation of indole and indoline products from **3**, thus reducing the overall effectiveness of this reaction.[3,4,7c] Generation of the analogous quaternary ammonium salts (E, R^1 = alkyl) produced similar charge acceleration of the aromatic 3-aza-Cope rearrangement at 140 °C; however, significant amounts of substrate deallylation usually occurred.[7d,e,8]

The use of Lewis acids for charge acceleration of the 3-aza-Cope rearrangement appears to be a promising alternative to the use of protic acids. As early as 1957,[2b] $ZnCl_2$ was found to promote the transformation of **1** to **3**, and subsequent examples have produced 37–78% yields of **3**.[5b,d,8a,9] Treatment with $Et_2O{\cdot}BF_3$ was also an effective method of promoting [3,3] rearrangement of **1** at 140

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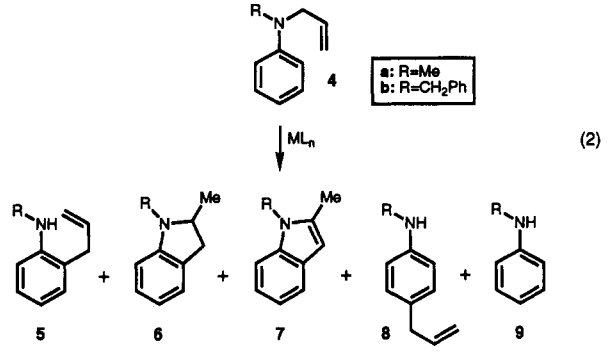
°C,[5d,10] and the use of $Et_2O{\cdot}BF_3$ was the only example of a Lewis acid-promoted 3-aza-Cope rearrangement of **2**.[7d,e] Other catalysts, such as $AlCl_3$, $FeCl_3$, $SnCl_4$, and $TiCl_4$, were less effective at promoting the rearrangement of **1**.[5b,d] A striking feature of studies of the Lewis acid-promoted rearrangement of substrates **2** has been the varying success reported for very similar substrates. Typically, the origin of these differences is a sensitivity of this system to one or many of the reaction conditions.

Our recent investigations in the area of the aliphatic 3-aza-Cope rearrangement have led to the development of proton[11] and Lewis acid[12] charge-accelerated rearrangement of *N*-alkyl-*N*-allylenamines at temperatures ranging from 40 to 110 °C. Organoaluminum complexes were particularly efficient and versatile in promoting the 3-aza-Cope rearrangement, and a recent report of an aromatic Claisen rearrangement accelerated by an organoaluminum reagent provided additional optimism for the ability of organoaluminum complexes to promote the aromatic 3-aza-Cope rearrangement.[13] Herein, we report the systematic investigation of the aromatic 3-aza-Cope rearrangement of *N*-alkyl-*N*-allylanilines promoted by Lewis acids.

Results and Discussion

An investigation of a number of reaction variables was performed by studying the effect of the relative amount of Lewis acid, concentration of the reaction, reaction time, and the temperature at which rearrangement would occur. The nature of the nitrogen "spectator" substituent on the *N*-allylaniline substrate, as well as substitution on the aromatic ring and the allyl group, were used to probe the features of this reaction.

Studies were initiated by monitoring the rearrangement of **4a** (eq 2) in the presence of varying amounts of $AlCl_3$, a catalyst that was effective for the rearrangement of **1**.



The 3-aza-Cope rearrangement of **4a** gave **5a** in all cases, but the relative amount of $AlCl_3$ was critical to the selectivity of the reaction (Table I). Treatment of **4a** with 1.5 equiv of Lewis acid produced rapid disappearance of starting material, low amounts of **5a**, and further destruction of **5a** over time.[14] With the use of 1.2 equiv, the reaction was slowed to a useful rate, and optimal generation of **5a** was observed. Problems associated with subsequent [3,3] rearrangement to the para position were not encountered. When less than a stoichiometric amount of $AlCl_3$ was used, significant quantities of byproducts, resulting from cyclization of **5a**, were produced during the time necessary to drive the rearrangement to >95% completion. Examination of other Lewis acids showed similar patterns, and in each case, 1.2 equiv of Lewis acid was the optimum amount of reagent.

Table I. Effects of the Amount of $AlCl_3$ on the 3-Aza-Cope Rearrangement of 4a

		yield[b] (%)				
			product formation[c]			
equiv[a]	time (h)	4a	5a	6a	7a	9a
1.5	2	12	38	0	0	0
	4	0	22	0	0	0
	8	0	9	0	0	0
1.2	4	50	49	0	0	0
	8	8	88	0	0	2
	24	6	71	0	0	3
0.75	4	28	68	1	0	0
	8	16	70	6	0	0
	24	11	23	32	5	0
	48	9	4	37	9	1

[a] Rearrangements were run 0.5 M **4a** at reflux in xylenes (140 °C). [b] Values represent GC yields of volatile, nonoligomeric products (ref 14). [c] Formation of no greater than 1% **8a** was observed.

Table II. Effects of Reaction Concentration on the 3-Aza-Cope Rearrangement of 4a Promoted by 1.2 Equiv of $ZnCl_2$

	yield[b] (%)				
		product formation[c]			
condns[a] (M, 4a)	4a	5a	6a	7a	9a
3.0	1	7	19	35	5
2.0	16	37	18	15	7
1.0	19	51	4	6	5
0.75	22	52	4	6	4
0.5	28	53	4	4	3
0.36	69	27	2	0	0

[a] Rearrangements were run at reflux in xylenes (140 °C) for 16 h. In each case, longer reaction times produced lower yields. [b] Values represent % yields as determined by GC analysis (ref 14). [c] Formation of no greater than 1% **8a** was observed.

Another Lewis acid reported to promote the rearrangement of **1**, $ZnCl_2$, showed a greater sensitivity toward reaction conditions and was used to probe the effect of substrate concentration on the product distribution (Table II). Acceleration of the rearrangement with $ZnCl_2$ at concentrations greater than 1.0 M resulted in the generation of substantial quantities of **6a** and **7a**, and reaction concentrations from 0.5 to 1.0 M were found to be optimal. For all subsequent rearrangements described, reactions were performed at 0.5 M of substrate with 1.2 equiv of the corresponding Lewis acid.

Once general reaction conditions were established, a survey of Lewis acids revealed that $AlCl_3$, $ZnCl_2$, and $Et_2O{\cdot}BF_3$ were the most effective reagents for promoting [3,3] rearrangement of **4a** to **5a** (Table III). Treatment of **4a** with $TiCl_4$ or $MgBr_2$ produced consumption of **4a**, but in both cases, **6a** (10–12%) and **7a** (2%) were formed concurrently under these reaction conditions. Alkylaluminum complexes, including the methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) reagent used for the aromatic Claisen rearrangement, produced disappointing results by slow consumption of **4a**, presumably to meth-

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(14) Product distribution and yields for these compounds were determined by capillary gas chromatographic analysis of the quenched reaction mixture (H_2O, NaOH) using internal standards and correcting for detector response.

Table III. Efficiency of Lewis Acids on the 3-Aza-Cope Rearrangement of 4a

reagent[a]	condns temp (°C)	condns time (h)	product formation 5a; yield (%)
$AlCl_3$	140	8	88
$ZnCl_2$	140	16	53
$Et_2O{\cdot}BF_3$	111	44	79
$Et_2O{\cdot}BF_3$	140	24	49
$TiCl_4$	140	16	46
$MgBr_2$	140	40	38
$(ArO)_2AlMe$[c]	140	72	28
$FeCl_3$	140	4	24
Me_2AlCl	140	24	22
$MeAlCl_2$	140	44	16

[a] Rearrangements were run 0.5 M of **4a** with 1.2 equiv of Lewis acid at reflux in toluene (111 °C) or xylenes (140 °C). [b] Values represent GC yields of **5a** (ref 14). [c] ArO = 4-bromo-2,6-di-*tert*-butylphenoxy.

Table IV. Lewis Acid-Promoted 3-Aza-Cope Rearrangement of 4 and 10

substrate	reagent (1.2 equiv)	concns[a] (time(h))	yield (%) isolated[b] (GC)[c]
4a	$AlCl_3$	8	68 (88)
	$ZnCl_2$	16	45 (52)
	$Et_2O{\cdot}BF_3$	48	58 (79)
4b	$AlCl_3$	2	15 (35)
	$ZnCl_2$	24	15 (30)
	$Et_2O{\cdot}BF_3$	24	13 (28)
10a	$ZnCl_2$	16	58 (66)
	$Et_2O{\cdot}BF_3$	72	55 (61)
10b	$ZnCl_2$	24	53 (57)
	$Et_2O{\cdot}BF_3$	48	35 (42)

[a] Rearrangements were run 0.5 M of **4a** with 1.2 equiv of Lewis acid at reflux in toluene (111 °C, $Et_2O{\cdot}BF_3$) or xylenes (140 °C, $AlCl_3$, and $ZnCl_2$). [b] Overall isolated yields of **5** and **11**. [c] Reference 14.

ylated and oligomeric products, without generation of significant amounts of **5a–9a**. In general, these trends were opposite those observed for the aliphatic 3-aza-Cope rearrangement, in which the organoaluminum species were the most efficient reagents, and the metal halides typically used for Freidel–Crafts alkylation produced very poor results.[12] The temperature at which the aromatic 3-aza-Cope rearrangement occurred was also critical to the success of the reaction. The use of decalin (180 °C) resulted in the formation of **6a** and **7a** as the major products in poor yield, and the use of toluene (111 °C) did not provide a high enough temperature at reflux to promote conversion of **4a** to products. Interestingly, the use of $Et_2O{\cdot}BF_3$ was the one exception, and rearrangement in toluene at reflux was more efficient than reaction in xylene.

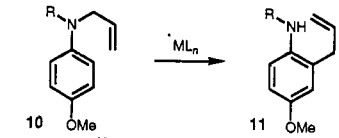
The three optimum catalysts, $AlCl_3$, $ZnCl_2$, and $Et_2O{\cdot}BF_3$, were each used in the studies of substrate variability. Under the optimum conditions for rearrangement, **5a** was isolated from the reaction mixture in 45–68% yield (Table IV). The reaction of Lewis acids with **4b**, having an *N*-benzyl group instead of an *N*-methyl substituent, produced much poorer results. Under similar reaction conditions, a 35% yield was the best that could be obtained from any of the catalysts with **4b**. The disappearance of **4b** without formation of the desired products was suspected to result from reaction of nucleophiles at the benzylic position and concomitant displacement of a quaternary nitrogen during the vigorous reaction conditions. Treatment of the analogous allyl acetamide and sulfonamide substrates with these Lewis acids did not result in [3,3] rearrangement products.

Table V. Lewis Acid-Promoted 3-Aza-Cope Rearrangement of 12

substrate	reagent (1.2 equiv)	condns[a] (time (h))	product formation (%) 13:14[b]	yield[c] (GC)[d]
12a	$ZnCl_2$	8	64:36	70 (77)
	$Et_2O{\cdot}BF_3$	48	66:34	99 (99)
12b	$ZnCl_2$	24	71:29	57 (64)
	$Et_2O{\cdot}BF_3$	48	72:28	38 (47)
12c	$ZnCl_2$	6	73:27	98 (98)
	$Et_2O{\cdot}BF_3$	24	72:28	80 (89)

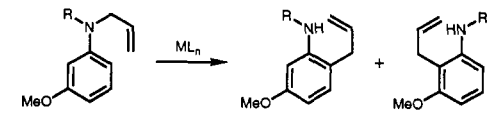
[a] Rearrangements were run 0.5 M of **4a** with 1.2 equiv of Lewis acid at reflux in toluene (111 °C, $Et_2O{\cdot}BF_3$) or xylenes (140 °C, $ZnCl_2$). [b] Ratios of **13**:**14** were determined by GC analysis of the crude reaction mixture. For substrates **b** and **c**, ratios were confirmed by ^1H NMR analysis. [c] Overall isolated yield as the mixture of **13** and **14**. [d] Reference 14.

Rearrangement of substrates containing a methoxy substituent on the aromatic ring provided useful insight into the nature of this Lewis acid-promoted transformation (eqs 3 and 4, Tables IV and V). The most noticeable



(3)

a: R=Me
b: R=CH_2Ph



(4)

a: R=Me
b: R=CH_2Ph
c: R=iBu

difference observed with these substrates was that $AlCl_3$ produced rapid disappearance of **10** and **12**, without the generation of any of the typical [3,3] rearrangement products.[15] Due to the slight deactivation at the position meta to the methoxy substituent, substrate **10** rearranged more slowly than the analogous unsubstituted substrate **4**. However, even though the substituent deactivated the position at which carbon–carbon bond formation occurred, standard conditions for the rearrangement promoted with $ZnCl_2$ and $Et_2O{\cdot}BF_3$ led to comparable or higher isolated yields of **11**.

Rearrangement of substrate **12**, having a methoxy substituent meta to the allylamine substituent, introduced the possibility of regioisomer formation. Depending on the ortho position at which rearrangement took place, two different products resulted, and in each case, reaction occurred at a position activated by the ortho and para directing methoxy substituent (eq 4). Unfortunately, regioselectivity was only moderate, ranging from 64:36 to 73:27 for **13**:**14**, and the product ratio showed little dependence on the Lewis acid used. Formation of the para product analogous to **8a** was not observed. Activation of the aromatic ring by the methoxy substituent had beneficial effects. Not only did rearrangement to products

(15) The treatment of methyl phenyl ethers with $AlCl_3$ and soft nucleophiles has been reported to cleave the methyl ether to produce phenolic products. Node, M.; Nishide, K.; Fuji, K.; Fujita, E. *J. Org. Chem.* **1980**, *45*, 4275. Similar problems have been reported with the use of $Et_2O{\cdot}BF_3$.[7e]

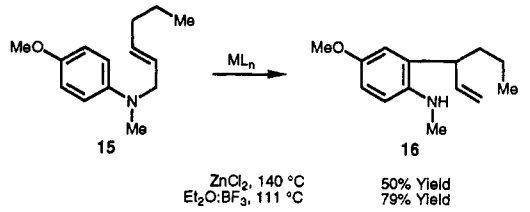
Table VI. Competitive Lewis Acid-Promoted 3-Aza-Cope Rearrangement of 4a and 12a

reagent	condns[a] (time (h))	product formation[b] (%) 13a + 14a	5a	(13a + 14a):5a
$Et_2O{\cdot}BF_3$	2	24	15	62:38
	4	33	22	60:40
	6	49	30	62:38
	8	55	33	63:37
$ZnCl_2$	0.5	17	7	71:29
	1.0	36	10	78:22
	1.5	47	15	76:24
	2.0	55	18	75:25

[a] Rearrangements were run 0.5 M of **4a** with 1.5 equiv of Lewis acid at reflux in toluene (111 °C, $Et_2O{\cdot}BF_3$) or xylenes (140 °C, $ZnCl_2$) with 1.8 equiv of Lewis acid. [b] Ratios were determined by GC analysis of the crude reaction mixture (ref 14).

occur in shorter time periods, but higher product yields resulted due to the increased rate of the transformation of **12** to **13** and **14** relative to the competitive formation of byproducts. As was observed in the reaction of **10**, $AlCl_3$ resulted in consumption of **12** without producing **13** or **14**.[15] Comparison of relative reaction rates was observed by the direct competition of 1.0 equiv each of **4a** and **12a** promoted by 1.8 equiv of Lewis acid. Results from this study showed that formation of **13a** and **14a** was approximately 1.5 times faster than that of **5a** when promoted by $Et_2O{\cdot}BF_3$ and roughly 3.0 faster in the presence of $ZnCl_2$ (Table VI).[16]

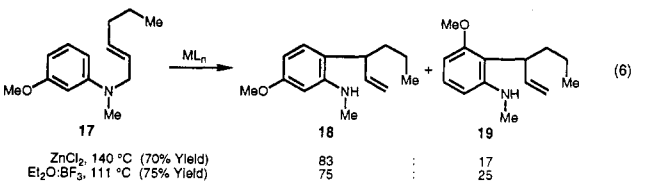
A final set of substrates was examined in order to determine the regioselectivity of the rearrangement with an unsymmetrical allylic substituent, enhance regioselective reaction on the aromatic ring, and establish a potential route to a methoxy-substituted variety of naturally occurring alkaloids. These substrates were prepared with an unsymmetrical *N*-((*E*)-2-hexen-1-yl) substituent on the aniline (eq 5). Rearrangement of **15** with $ZnCl_2$ at



(5)

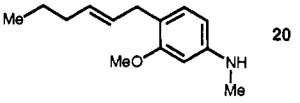
140 °C or $Et_2O{\cdot}BF_3$ at 111 °C produced **16** in 50% and 79% isolated yields, respectively. Compared to the analogous rearrangement of **10a**, the use of $ZnCl_2$ was similar, while the reaction promoted by $Et_2O{\cdot}BF_3$ was far more efficient. In both reactions, only [3,3] rearrangement was evident from analysis of the reaction products; carbon–carbon bond formation resulting from [1,3] rearrangement of the substrate through a nonconcerted pathway was not observed. Most importantly, these reagents efficiently promoted the regiospecific 3-aza-Cope rearrangement of *N*-alkyl-*N*-allylanilines and produced carbon–carbon bond formation between an aromatic ring and a secondary alkyl substituent.

The rearrangement of the corresponding substrate having a methoxy substituent meta to the amine, **17**, produced results similar to those observed for the rearrangement of **12a** and **15a** (eq 6). As was observed for

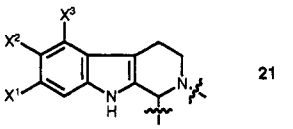


(6)

12a, a mixture of regioisomers was obtained. In the case of **17**, however, slightly increased product selectivities of 75:25 and 83:17 for **18**:**19** were obtained for rearrangement with $Et_2O{\cdot}BF_3$ and $ZnCl_2$, respectively. However, in contrast to previous rearrangement with the *N*-allyl substituents, further [3,3] Cope rearrangement of **18** and/or **19** in the presence of $ZnCl_2$ produced **20**, which could be separated from **18** and **19** in 11% isolated yield. This product appeared to result from two sequential [3,3] rearrangements giving only the (*E*)-2-hexen-1-yl aromatic substituent. Because of the different rates at which **20**



was generated from **18** versus **19**, the regioselectivity ratio based on the direct observation of product distribution might not directly reflect the actual selectivity of the relative reaction rates. The similarities in structure of **16**, **18**, and **19** to the indole alkaloids **21** such as acricine (X^1 = X^3 = H, X^2 = OMe),[17] reserpinine (X^1 = OMe, X^2 = X^3 = H),[17] ochropposinine (X^1 = X^2 = OMe, X^3 = H),[18] and mitragynaline (X^1 = X^2 = H, X^3 = OMe)[19] are striking and provide some intriguing possibilities for future application of this methodology.



Summary

Systematic studies of the aromatic 3-aza-Cope rearrangement have been used to examine a number of reaction variables, and results have shown that reaction conditions having a substrate concentration of 0.5 M and treatment with 1.2 equiv of Lewis acid were optimum for obtaining the desired product. Of the many Lewis acids investigated, $ZnCl_2$ (140 °C) and $Et_2O{\cdot}BF_3$ (111 °C) were the most generally successful reagents for promoting the 3-aza-Cope rearrangement. The presence of a methoxy substituent para to the *N*-allyl group slowed the reaction slightly, while a meta substituent greatly accelerated the rate of rearrangement to the position ortho or para to the methoxy group. In this case, site selectivity on the aromatic ring was moderate. Rearrangement of an unsymmetrically substituted allyl moiety resulted in regioselective [3,3] rearrangement to produce a 1-hexen-3-yl substituent on the aromatic ring. Overall, both $ZnCl_2$ and $Et_2O{\cdot}BF_3$ were demonstrated to efficiently accelerate the regiospecific 3-aza-Cope rearrangement of *N*-alkyl-*N*-allylanilines for

(16) These values illustrate the presence of this general trend, but the accuracy of these values is somewhat limited by the differing efficiencies of these reactions.

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the purpose of forming a carbon–carbon bond between a secondary alkyl substituent and an aromatic ring.

Experimental Section

General Methods. All reactions were carried out performing standard inert atmosphere techniques to exclude moisture and oxygen.[20] Benzene, toluene, tetrahydrofuran (THF), and Et_2O were distilled from sodium/benzophenone immediately prior to use. Xylenes and decalin were heated over calcium hydride for a minimum of 12 h and then distilled prior to use. Petroleum ether (35–60 °C boiling range) was used without further purification. $LiAlH_4$ (1 M in THF) was obtained from Aldrich Chemical Co. 1-Bromo-2-hexene[21] and all secondary alkylanilines were prepared by literature methods.[22] Compound **8a** was prepared through an independent route.[23]

For reactions in which a Dean-Stark trap was used, the trap was filled with 4-Å molecular sieves to a level below that of returning solvent turbulence. The sieves were changed during reactions in which additional reagent was added during the course of the reaction. Molecular sieves were activated by heating in a 150 °C oven for at least 24 h prior to use. Unless specified, concentration of mixtures after workup was performed using a Büchi rotary evaporator.

General Method for the *N*-Allylation of Secondary Anilines.[22] The aniline (2.0–50.0 mmol, 1.0 equiv) and the alkyl bromide or alkyl chloride (1.2–4.0 equiv) were taken up in a 4:1 $EtOH/H_2O$ mixture (0.5 M relative to the aniline) along with Na_2CO_3 (0.6 equiv). After stirring at room temperature for 14 h, the EtOH was removed under reduced pressure and the crude oil purified by flash column chromatography (silica, 230–400 mesh; eluent 5:95 Et_2O/petroleum ether). The solvents were evaporated and the dialkylated anilines distilled under vacuum.

***N*-Allyl-*N*-methylaniline (4a)**: 91% yield; bp 107–110 °C, <1.5 mmHg; ^1H (300 MHz, $CDCl_3$) δ 2.78 (s, 3H), 3.76 (dt, J = 5.0, 1.7 Hz, 2H), 5.05 (dq, J = 17.0, 1.7 Hz, 1H), 5.07 (dq, J = 10.4, 1.7 Hz, 1H), 5.73 (ddt, J = 17.0, 10.4, 5.0 Hz, 1H), 6.60–6.68 (m, 3H), 7.11–7.19 (m, 2H); ^{13}C (75.5 MHz, $CDCl_3$) δ 37.57, 54.86, 112.16, 115.70, 116.17, 128.82, 133.60, 149.81; IR (oil/NaCl) 3063, 3027, 2980, 2897, 2815, 1644, 1599, 1449 cm^{-1}; HRMS calcd for $C_{10}H_{13}N$ m/z 147.1049, found m/z 147.1010.

***N*-Allyl-*N*-benzylaniline (4b)**: 85% yield; ^1H NMR (300 MHz, $CDCl_3$) δ 3.85–3.91 (m, 2H), 4.43 (s, 2H), 5.10 (dq, J = 10.5, 1.8 Hz, 1H), 5.12 (dq, J = 17.4, 1.8 Hz, 1H), 5.78 (ddt, J = 17.4, 10.5, 4.8 Hz, 1H), 6.59–6.68 (m, 3H), 7.06–7.24 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.81, 53.76, 112.24, 116.06, 116.43, 126.41, 126.63, 128.40, 128.99, 133.52, 138.76, 148.73; IR (KBr) 3062, 3028, 2862, 1599, 1509 cm^{-1}; HRMS calcd for $C_{16}H_{17}N$ m/z 223.1362, found m/z 223.1382.

***N*-Allyl-*N*-methyl-4-methoxyaniline (10a)**: 66% yield; bp 80–86 °C, <4 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 2.83 (s, 3H), 3.72 (s, 3H), 3.80 (dt, J = 5.3, 1.7 Hz, 2H), 5.14 (dq, J = 10.5, 1.7 Hz, 1H), 5.16 (dq, J = 17.4, 1.7 Hz, 1H), 5.82 (ddt, J = 17.4, 10.5, 5.3 Hz, 1H), 6.67–6.73 (m, 2H), 6.77–6.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.54, 55.55, 56.44, 114.54, 114.59, 116.26, 134.20, 144.38, 151.64; IR (oil/NaCl) 3077, 2936, 2832, 2809, 1642, 1516 cm^{-1}; HRMS calcd for $C_{11}H_{15}NO$ m/z 177.1154, found m/z 177.1148.

***N*-Allyl-*N*-benzyl-4-methoxyaniline (10b)**: 75% yield; bp 128–139 °C, <4 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.92 (dt, J = 5.1, 1.8 Hz, 2H), 4.46 (s, 2H), 5.16 (dq, J = 10.2, 1.8 Hz, 1H), 5.17 (dq, J = 17.2, 1.8 Hz, 1H), 5.87 (ddt, J = 17.2, 10.2, 5.1 Hz, 1H), 6.64–6.71 (m, 2H), 6.74–6.80 (m, 2H), 7.18–7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.78, 54.82, 55.66, 114.35, 114.63, 116.33, 126.71, 126.80, 128.46, 134.17, 139.25, 143.61, 151.53; IR (oil/NaCl) 3085, 2934, 2832, 1512 cm^{-1}; HRMS calcd for $C_{17}H_{19}NO$ m/z 253.1468, found 253.1453.

***N*-Allyl-*N*-methyl-3-methoxyaniline (12a)**: 68% yield; bp 83–87 °C, <4 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 2.91 (s, 3H), 3.76 (s, 3H), 3.88 (dt, J = 5.1, 1.8 Hz, 2H), 5.13 (dq, J = 10.8, 1.8 Hz, 1H), 5.14 (dq, J = 17.1, 1.8 Hz, 1H), 5.82 (ddt, J = 17.1, 10.8, 5.1 Hz, 1H), 6.22–6.29 (m, 2H), 6.30–6.36 (m, 1H), 7.07–7.15 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.96, 54.95, 55.16, 98.90, 101.09, 105.50, 116.01, 129.66, 133.66, 150.79, 160.65; IR (oil/NaCl) 3085, 2998, 2938, 2836, 1609, 1503 cm^{-1}; HRMS calcd for $C_{11}H_{15}NO$ m/z 177.1154, found m/z 177.1156.

***N*-Allyl-*N*-benzyl-3-methoxyaniline (12b)**: 83% yield; bp 130–137 °C, <4 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.96 (dt, J = 4.8, 1.8 Hz, 2H), 4.50 (s, 2H), 5.16 (dq, J = 10.5, 1.8 Hz, 1H), 5.17 (dq, J = 17.1, 1.8 Hz, 1H), 5.85 (ddt, J = 17.1, 10.5, 4.8 Hz, 1H), 6.22–6.35 (m, 3H), 6.32 (ddd, J = 8.4, 2.1, 0.8 Hz, 1H), 7.06 (t, J = 8.4 Hz, 1H), 7.17–7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.03, 53.89, 54.88, 98.91, 101.19, 105.46, 116.21, 126.46, 126.71, 128.48, 129.71, 133.50, 138.77, 150.26, 160.63; IR (oil/NaCl) 3085, 3936, 2836, 1612, 1501, 1453 cm^{-1}; HRMS calcd for $C_{17}H_{21}NO$ m/z 253.1468, found m/z 253.1465.

***N*-Allyl-*N*-isobutyl-3-methoxyaniline (12c)**: 80% yield; bp 35–36 °C, <4 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (d, J = 6.6 Hz, 6H), 2.06 (sept, J = 6.6 Hz, 1H), 3.06 (d, J = 7.2 Hz, 2H), 3.73 (s, 3H), 3.91 (dt, J = 4.8, 1.8 Hz, 2H), 5.09 (dq, J = 16.8, 1.8 Hz, 1H), 5.10 (dq, J = 11.1, 1.8 Hz, 1H), 5.78 (ddt, J = 16.8, 11.1, 4.8 Hz, 1H), 6.18–6.32 (m, 3H), 7.04–7.11 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.33, 27.30, 53.96, 54.82, 58.93, 98.83, 100.27, 105.39, 115.82, 129.51, 133.82, 149.98, 160.58; IR (oil/NaCl) 2955, 2870, 2836, 1611, 1576, 1499 cm^{-1}; HRMS calcd for $C_{14}H_{21}NO$ m/z 219.1624, found m/z 219.1634.

***N*-((*E*)-2-Hexen-1-yl)-*N*-methyl-4-methoxyaniline (15)**: 73% yield; ^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, J = 7.4 Hz, 3H), 1.36 (sext, J = 7.4 Hz, 2H), 1.98 (q, J = 7.4 Hz, 2H), 2.78 (s, 3H), 3.70 (s, 3H), 3.73 (bd, J = 5.4 Hz, 2H), 5.43 (dtt, J = 15.3, 5.7, 1.1 Hz, 1H), 5.56 (dtt, J = 15.3, 5.7, 1.1 Hz, 1H), 6.67–6.73 (m, 2H), 6.76–6.82 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.46, 22.29, 34.22, 38.21, 55.41, 55.78, 114.41, 114.81, 125.66, 132.91, 144.55, 151.60; IR (oil/NaCl) 2957, 2932, 2872, 2832, 1620, 1562, 1464 cm^{-1}; HRMS calcd for $C_{14}H_{21}NO$ m/z 219.1624, found m/z 219.1618.

***N*-((*E*)-2-Hexen-1-yl)-*N*-methyl-3-methoxyaniline (17)**: 72% yield; ^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, J = 7.4 Hz, 3H), 1.36 (sext, J = 7.4 Hz, 2H), 1.98 (q, J = 7.4 Hz, 2H), 2.85 (s, 3H), 3.74 (s, 3H), 3.81 (dd, J = 5.4, 0.9 Hz, 2H), 5.42 (m, 1H), 5.55 (m, 1H), 6.21–6.28 (m, 2H), 6.31–6.36 (m, 1H), 7.09 (td, J = 8.0, 0.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.48, 22.29, 34.20, 37.57, 54.41, 54.80, 98.91, 100.97, 105.58, 125.18, 129.55, 132.63, 150.88, 160.59; IR (oil/NaCl) 2959, 2872, 2836, 1607, 1503, 1456 cm^{-1}; HRMS calcd for $C_{14}H_{21}NO$ m/z 219.1624, found m/z 219.1639.

General Method for the Lewis Acid-Promoted Rearrangement of *N*-Allyl-*N*-alkylanilines. The aniline (0.5–2.0 mmol, 1.0 equiv) and the catalyst (0.6–2.4 mmol, 1.2 equiv) were added to dry xylenes or toluene (0.5 M relative to the aniline) at −78 °C along with an internal standard of decalin. The reaction was heated to the appropriate temperature and allowed to react as described in the text. The reaction was then quenched at 0 °C by addition of a 15% aqueous NaOH solution, and the organic fractions were combined, separated, dried over $MgSO_4$, and concentrated. The crude products were isolated and purified by flash column chromatography (silica, 230–400 mesh; eluent, 5:95 Et_2O/petroleum ether). Yields for these reactions are provided in the tables.

***N*-Methyl-2-allylaniline (5a)**: ^1H NMR (300 MHz, $CDCl_3$) δ 2.83 (s, 3H), 3.26 (bd, J = 6.1 Hz, 2H), 3.73 (bs, 1H), 5.08 (dq, J = 16.7, 1.8 Hz, 1H), 5.10 (dq, J = 10.4, 1.8 Hz, 1H), 5.93 (ddt, J = 16.7, 10.4, 6.1 Hz, 1H), 6.63 (d, J = 8.2 Hz, 1H), 6.70 (td, J = 7.4, 1.1 Hz, 1H), 7.03 (dd, J = 7.4, 1.1 Hz, 1H), 7.12 (td, J = 7.4, 1.6 Hz, 1H); ^{13}C (75.5 MHz, $CDCl_3$) δ 30.54, 36.21, 109.73, 115.97, 116.93, 123.39, 127.59, 129.47, 135.95, 147.22; IR (oil/

(20) For more detailed General Experimental procedures from these labs, see ref 12.

(21) Prepared from 2-hexen-1-ol by treatment with NBS/PPh_3: (a) Trippett, S. *J. Chem. Soc.* **1962**, 2337. (b) Bose, A. K.; Lai, B. *Tetrahedron Lett.* **1973**, 3937.

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(23) Compound **8a** was prepared from allyl benzene by the following sequence: (a) Br_2, −78 °C (92%);[24] (b) HNO_3, H_2SO_4, 0 °C (72%);[25] (c) NaI, EtOH (69%);[26] (d) H_2O, Fe (95%);[27] (e) MeI, Na_2CO_3 (37%).[22]

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NaCl) 3436 (broad), 3075, 2978, 2894, 2815, 1634, 1605, 1514, 1466 cm^{-1}; HRMS calcd for $C_{10}H_{13}N$ m/z 147.1049, found m/z 147.0994.

***N*-Benzyl-2-allylaniline (5b)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.34 (bd, J = 6.3 Hz, 2H), 4.10 (bs, 1H), 4.34 (s, 2H), 5.07 (dq, J = 16.8, 1.7 Hz, 1H), 5.11 (dq, J = 10.5, 1.7 Hz, 1H), 5.95 (ddt, J = 16.8, 10.5, 6.3 Hz, 1H), 6.62 (d, J = 7.4 Hz, 1H), 6.70 (td, J = 7.4, 0.9 Hz, 1H), 7.06 (dd, J = 7.4, 1.2 Hz, 1H), 7.12 (td, J = 7.4, 1.2 Hz, 1H), 7.22–7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.50, 48.13, 110.69, 116.29, 117.34, 123.49, 127.12, 127.35, 127.68, 128.57, 129.78, 135.93, 139.41, 146.11; IR (oil/NaCl) 3440 (broad), 3031, 2888, 2843, 1633, 1603, 1510 cm^{-1}; HRMS calcd for $C_{16}H_{17}N$ m/z 223.1362, found m/z 223.1373.

***N*-Methyl-2-allyl-4-methoxyaniline (11a)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.81 (s, 3H), 3.25 (dt, J = 6.0, 1.7 Hz, 2H), 3.37 (bs, 1H), 3.74 (s, 3H), 5.07 (dq, J = 17.1, 1.7 Hz, 1H), 5.12 (dq, J = 10.2, 1.7 Hz, 1H), 5.93 (ddt, J = 17.1, 10.2, 6.0 Hz, 1H), 6.58 (d, J = 8.7 Hz, 1H), 6.70 (d, J = 3.0 Hz, 1H), 6.76 (dd, J = 8.7, 3.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.37, 36.31, 55.70, 110.96, 112.02, 116.23, 116.50, 125.45, 135.76, 141.65, 151.81; IR (oil/NaCl) 3422 (broad), 2938, 2832, 2808, 1638, 1514, 1464 cm^{-1}; HRMS calcd for $C_{11}H_{15}NO$ m/z 177.1154, found m/z 177.1161.

***N*-Benzyl-2-allyl-4-methoxyaniline (11b)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.29 (dt, J = 6.0, 1.5 Hz, 2H), 3.72 (s, 3H), 3.78 (bs, 1H), 4.28 (s, 2H), 5.06 (dq, J = 17.1, 1.5 Hz, 1H), 5.11 (dq, J = 10.5, 1.5 Hz, 1H), 5.94 (ddt, J = 17.1, 10.5, 6.0 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 6.67 (d, J = 3.0 Hz, 1H), 6.66–6.73 (m, 1H), 7.21–7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.46, 48.89, 55.65, 111.94, 112.02, 116.39, 116.55, 125.50, 127.05, 127.39, 128.51, 135.69, 139.67, 140.34, 151.93; IR (oil/NaCl) 3430 (broad), 3063, 2936, 2832, 1636, 1509, 1466 cm^{-1}; HRMS calcd for $C_{17}H_{19}NO$ m/z 253.1468, found m/z 253.1468.

***N*-Methyl-2-allyl-5-methoxyaniline (13a)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.82 (s, 3H), 3.21 (dt, J = 6.0, 1.8 Hz, 2H), 3.77 (bs, 1H), 3.79 (s, 3H), 5.05 (dq, J = 16.8, 1.8 Hz, 1H), 5.08 (dq, J = 10.8, 1.8 Hz, 1H), 5.91 (ddt, J = 16.8, 10.8, 6.0 Hz, 1H), 6.19–6.27 (m, 2H), 6.93 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.62, 35.69, 55.10, 97.19, 100.74, 115.79, 116.31, 130.17, 136.53, 148.51, 159.83; IR (oil/NaCl) 3438 (broad), 3077, 2938, 2834, 2809, 1617, 1520 cm^{-1}; HRMS calcd for $C_{11}H_{15}NO$ m/z 177.1154, found m/z 177.1145.

***N*-Methyl-2-allyl-3-methoxyaniline (14a)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.84 (s, 3H), 3.38 (dt, J = 6.0, 1.9 Hz, 2H), 3.78 (bs, 1H), 3.80 (s, 3H), 5.02 (dq, J = 17.4, 1.8 Hz, 1H), 5.03 (dq, J = 9.3, 1.8 Hz, 1H), 5.88 (ddt, J = 17.4, 9.3, 6.0 Hz, 1H), 6.35 (d, J = 8.4 Hz, 1H), 6.38 (d, J = 8.4 Hz, 1H), 7.14 (t, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.90, 31.04, 55.78, 100.66, 103.68, 114.76, 125.90, 127.67, 136.05, 148.70, 157.60; IR (oil/NaCl) 3438 (broad), 3077, 2939, 2836, 2815, 1601, 1591, 1478 cm^{-1}; HRMS calcd for $C_{11}H_{15}NO$ m/z 177.1154, found m/z 177.1142.

***N*-Benzyl-2-allyl-5-methoxyaniline (13b)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.25 (dt, J = 6.0, 1.8 Hz, 2H), 3.72 (s, 3H), 4.13 (bs, 1H), 4.31 (s, 2H), 5.05 (dq, J = 17.1, 1.8 Hz, 1H), 5.09 (dq, J = 10.5, 1.8 Hz, 1H), 5.93 (ddt, J = 17.1, 10.5, 6.0 Hz, 1H), 6.19–6.27 (m, 2H), 6.95 (d, J = 8.1 Hz, 1H), 7.20–7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.82, 48.12, 55.04, 97.96, 101.16, 115.95, 116.22, 127.15, 127.38, 128.57, 130.32, 136.41, 139.21, 147.22, 159.68; IR (oil/NaCl) 3438 (broad), 3063, 2834, 1617, 1586, 1520, 1466 cm^{-1}; HRMS calcd for $C_{17}H_{19}NO$ m/z 253.1468, found m/z 253.1492.

***N*-Benzyl-2-allyl-3-methoxyaniline (14b)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.42 (dt, J = 5.4, 1.8 Hz, 2H), 3.79 (s, 3H), 4.16 (bs, 1H), 4.34 (s, 2H), 5.01 (dq, J = 16.8, 1.8 Hz, 1H), 5.02 (dq, J = 11.0, 1.8 Hz, 1H), 5.89 (ddt, J = 16.8, 11.0, 5.4 Hz, 1H), 6.32 (bd, J = 8.4 Hz, 1H), 6.37 (bd, J = 8.4 Hz, 1H), 7.06 (t, J = 8.4 Hz, 1H), 7.21–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.02, 48.35, 55.77, 100.81, 104.50, 114.97, 127.06, 127.30, 127.65, 128.55, 128.62, 135.93, 139.61, 147.43, 157.90; IR (oil/NaCl) 3440 (broad), 2936, 2836, 1634, 1599, 1476 cm^{-1}; HRMS calcd for $C_{17}H_{19}NO$ m/z 253.1468, found m/z 253.1436.

***N*-Isobutyl-2-allyl-5-methoxyaniline (13c)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (d, J = 6.7 Hz, 6H), 1.91 (nonet, J = 6.7 Hz, 1H), 2.91 (d, J = 6.7 Hz, 2H), 3.24 (dt, J = 6.3, 1.8 Hz, 2H), 3.79 (s, 3H), 3.83 (bs, 1H), 5.06–5.16 (m, 2H), 5.93 (ddt, J = 17.7, 9.6, 6.3 Hz, 1H), 6.17–6.24 (m, 2H), 6.94 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.58, 27.84, 36.14, 51.59, 55.12, 97.42, 100.43, 115.88, 116.08, 130.33, 136.82, 147.74, 159.79; IR (oil/NaCl) 3432 (broad), 3079, 2957, 2870, 2834, 1617, 1588, 1520 cm^{-1}; HRMS calcd for $C_{14}H_{21}NO$ m/z 219.1624, found m/z 219.1641.

***N*-Isobutyl-2-allyl-3-methoxyaniline (14c)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (d, J = 6.6 Hz, 6H), 1.89 (nonet, J = 6.6 Hz, 1H), 2.92 (d, J = 6.6 Hz, 2H), 3.39 (dt, J = 5.7, 1.8 Hz, 2H), 3.79 (s, 3H), 3.83 (bs, 1H), 5.03 (dq, J = 10.8, 1.8 Hz, 1H), 5.06 (dq, J = 16.8, 1.8 Hz, 1H), 5.88 (ddt, J = 16.8, 10.8, 5.7 Hz, 1H), 6.31 (d, J = 8.2 Hz, 1H), 6.33 (d, J = 8.2 Hz, 1H), 7.09 (t, J = 8.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.57, 28.00, 28.13, 51.89, 55.76, 100.17, 104.03, 110.84, 114.91, 127.58, 136.30, 147.90, 157.67; IR (oil/NaCl) 3430 (broad), 3076, 2959, 2870, 2836, 1635, 1601, 1476 cm^{-1}; HRMS calcd for $C_{14}H_{21}NO$ m/z 219.1624, found m/z 219.1622.

***N*-Methyl-2-(1-hexen-3-yl)-4-methoxyaniline (16)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3H), 1.22–1.48 (m, 2H), 1.62–1.81 (m, 2H), 2.80 (s, 3H), 3.26 (bq, J = 7.4 Hz, 2H), 3.47 (bs, 1H), 3.75 (s, 3H), 5.02 (dt, J = 17.1, 1.4 Hz, 1H), 5.06 (dt, J = 10.2, 1.4 Hz, 1H), 5.81 (ddd, J = 17.1, 10.2, 7.4 Hz, 1H), 6.57–6.66 (m, 1H), 6.71–6.76 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.03, 20.65, 31.54, 35.52, 43.50, 55.61, 111.10, 111.38, 114.24, 114.49, 129.87, 141.09, 141.35, 152.04; IR (oil/NaCl) 3413 (m-broad), 3077, 2957, 2872, 2832, 2809, 1647, 1510, 1458 cm^{-1}; HRMS calcd for $C_{14}H_{21}NO$ m/z 219.1624, found m/z 219.1487.

***N*-Methyl-2-(1-hexen-3-yl)-5-methoxyaniline (18)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.4, 3H), 1.21–1.48 (m, 2H), 1.62–1.81 (m, 2H), 2.82 (s, 3H), 3.15 (bq, J = 7.4 Hz, 1H), 3.79 (s, 3H), 3.87 (bs, 1H), 5.01 (dt, J = 17.7, 1.4 Hz, 1H), 5.06 (dt, J = 10.5, 1.4 Hz, 1H), 5.81 (ddd, J = 17.7, 10.5, 7.4 Hz, 1H), 6.22 (d, J = 2.4 Hz, 1H), 6.28 (dd, J = 8.4, 2.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.09, 20.75, 30.80, 35.48, 43.19, 55.04, 97.49, 100.92, 114.13, 120.41, 127.59, 141.76, 148.28, 159.31; IR (oil/NaCl) 3438 (broad), 3077, 2959, 2930, 2872, 2836, 2807, 1615, 1586, 1463 cm^{-1}; HRMS calcd for $C_{14}H_{21}NO$ m/z 219.1624, found m/z 219.1650.

***N*-Methyl-2-(1-hexen-3-yl)-3-methoxyaniline (19)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, J = 7.2 Hz, 3H), 1.07–1.37 (m, 2H), 1.70–1.89 (m, 2H), 2.77 (s, 3H), 3.77 (s, 3H), 3.98–4.17 (m, 2H), 5.07 (dt, J = 6.6, 2.4 Hz, 1H), 5.12 (d, J = 2.4 Hz, 1H), 6.11 (m, 1H), 6.30 (bd, J = 8.1 Hz, 2H), 6.37 (bd, J = 8.1 Hz, 1H), 7.10 (t, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.18, 21.11, 31.06, 32.49, 37.58, 55.78, 100.89, 104.45, 113.37, 114.28, 127.58, 141.64, 148.91, 158.10; IR (oil/NaCl) 3426 (broad), 2919, 2848, 1588, 1476 cm^{-1}; HRMS calcd for $C_{14}H_{21}NO$ m/z 219.1624, found m/z 219.1635.

***N*-Methyl-4-((*E*)-2-hexen-1-yl)-3-methoxyaniline (20)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 7.4 Hz, 3H), 1.37 (sext, J = 7.4 Hz, 2H), 1.97 (bq, J = 7.4 Hz, 2H), 2.82 (s, 3H), 3.20 (d, J = 7.4 Hz, 2H), 3.62 (bs, 1H), 3.79 (s, 3H), 5.43 (dtt, J = 15.0, 6.5, 1.4 Hz, 1H), 5.55 (dtt, J = 15.0, 6.5, 1.4 Hz, 1H), 6.13–6.20 (m, 2H), 6.94 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.69, 22.69, 31.03, 32.21, 34.66, 55.25, 96.26, 104.09, 118.56, 129.13, 130.07, 130.70, 149.03, 158.03; IR (oil/NaCl) 3413 (broad), 2957, 2930, 2872, 2836, 1618, 1516, 1464 cm^{-1}.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of all compounds in the Experimental Section (46 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.