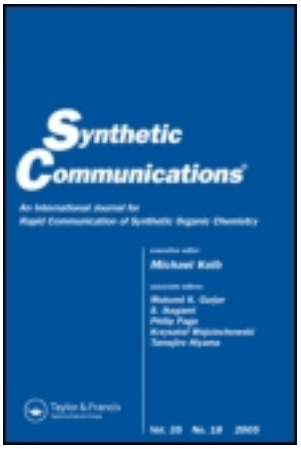

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Simple and Convenient Approach for Synthesis of Tetrahydroquinoline Derivatives and Studies on Aza-Cope Rearrangement

V. S. Prasada Rao Lingam [a b], Abraham Thomas [a], Khagga Mukkanti [b] & Balasubramanian Gopalan [a]

[a] Medicinal Chemistry Division, Glenmark Research Centre, MIDC, Mahape, Mumbai, India

[b] Institute of Science and Technology, Jawaharlal Nehru Technological University, Hyderabad, India

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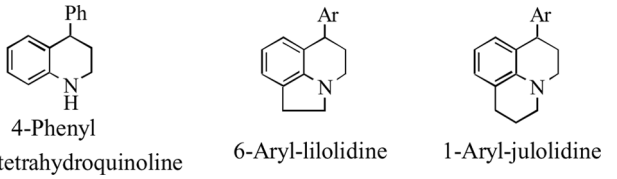
SIMPLE AND CONVENIENT APPROACH FOR SYNTHESIS OF TETRAHYDROQUINOLINE DERIVATIVES AND STUDIES ON AZA-COPE REARRANGEMENT

V. S. Prasada Rao Lingam,[1,2] Abraham Thomas,[1] Khagga Mukkanti,[2] and Balasubramanian Gopalan[1]

[1]*Medicinal Chemistry Division, Glenmark Research Centre, MIDC, Mahape, Mumbai, India*

[2]*Institute of Science and Technology, Jawaharlal Nehru Technological University, Hyderabad, India*

GRAPHICAL ABSTRACT



4-Phenyl 1,2,3,4-tetrahydroquinoline | 6-Aryl-lilolidine | 1-Aryl-julolidine

Abstract *A simple and novel synthesis of 1,2,3,4-tetrahydroquinoline derivatives by polyphosphoric acid–assisted reaction of* N*-aryl allyl anilines prepared from anilines has been reported. The generality and scope of the approach has been demonstrated by extending it to the synthesis of 1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (lilolidine) and 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (julolidine). Further, Lewis acid–mediated aza-Cope rearrangement of various* N*-aryl allyl anilines has been demonstrated.*

Keywords Aza-Cope rearrangement; julolidine; lilolidine; polyphosphoric acid; 1,2,3,4-tetrahydroquinolines

INTRODUCTION

1,2,3,4-Tetrahydroquinoline (THQ) derivatives continue to attract interest because of their importance as key structural elements in several natural products[1] and their uses as farnesyltransferase[2] inhibitors for antimalarial treatment, cardiovascular agents,[3] antihypertesive agents,[4] thrombin inhibitors[5] for anticoagulants, multidrug-resistant (MDR)[6] agents, and antagonists of transient receptor potential vanilloid receptor-1 (TRPV1).[7] The THQ moiety is also a core structure in various fused tricyclic compounds, such as 1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline

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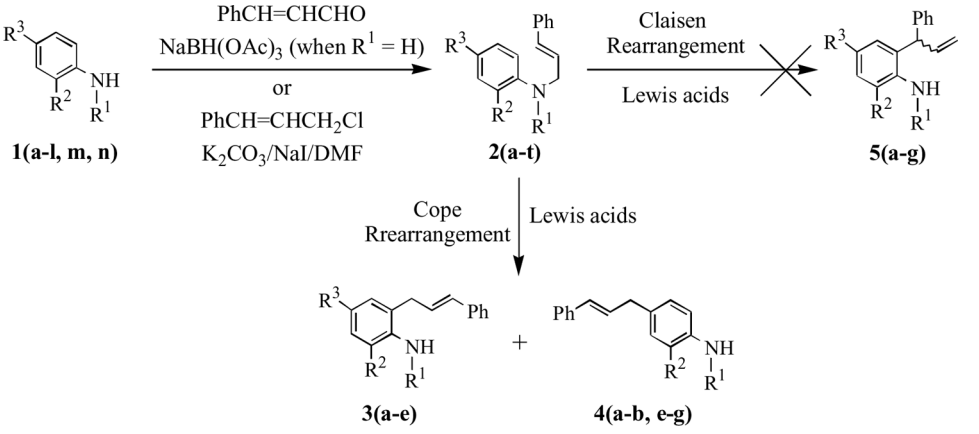
Address correspondence to Khagga Mukkanti, Institute of Science and Technology, Jawaharlal Nehru Technological University, Hyderabad 500 072, India. E-mail: kmukkanti@gmail.com

(lilolidine)[8] and 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (julolidine).[9] Julolidine has been used as an intermediate to synthesize various labeling reagents for carboxylic acids,[10] amines,[11] and laser dyes.[12] Therefore, the preparation of these nitrogen-containing heterocyclic compounds has gained considerable attention in recent years.

The traditional, simple, and very popular synthetic methods for THQs involve the reduction of quinolines,[13] 1,2-dihydroquinolines,[14] or 3,4-dihydroquinolin-2(1H)-one[15] over various transition metals and transition-metal complexes. Other less popular synthetic approaches are intramolecular Friedel–Crafts reaction[16] of 4-anilino-2-butanols, Michael–aldol addition[17] of *o*-carbonylanilines with α,β-unsaturated carbonyl compounds, oxidation of *N*-methylanilines,[18] reaction of α-aminoalkylbenzotriazole[19] with alkenes, and reaction of Schiff base.[20] All of these methods have some good advantages but also have several drawbacks, such as long reaction times, tedious workup procedures, occurrence of several side reaction products, and use of expensive transition metals. Therefore, the search continues for a better and convenient method for the synthesis of THQs in terms of operational simplicity, economic viability, and greater selectivity.

RESULTS AND DISCUSSION

In this article, we report our results on the synthesis of substituted Cope rearranged anilines, THQs, lilolidine, and julolidine from substituted *N*-allylanilines. As outlined in Scheme 1, the required starting materials **2a–i** for this study were synthesized by reductive amination of *trans*-cinnamaldehyde with anilines **1a–i** using sodium triacetoxyborohydride in a mixture of acetic acid and 1,2-dichloroethane. The allyl anilines **2j–t** bearing additional substitutions on the nitrogen were prepared by alkylation of *N*-substituted anilines **1j–l**, indoline (**1m**), and THQ (**1n**) with various substituted allyl chlorides[21] using anhydrous potassium carbonate in the presence of catalytic amounts of sodium iodide in *N,N*-dimethylformamide.



Scheme 1. Studies on aza-Cope rearrangement.

Attempted amino-Claisen rearrangement of **2a** by pyrolysis[22] at 250–270 °C for 2 h under solvent-free conditions resulted in a tarry material, which on chromatographic purification yielded the starting aniline (**1a**) in 40% isolated yield, probably formed via cleavage of C-N bond at high temperature. Refluxing a solution of **2a** in diphenyl ether (~250 °C) resulted in an unidentifiable more polar product along with the unreacted allyl aniline **2a**. Attempted rearrangement of **2a** using 2*N* sulfuric acid[22] at 120 °C for 12 h resulted in the formation of sulfate salt quantitatively. Compound **2a** on refluxing in tetrahydrofuran (Table 1, entry 1) for 36 h in the presence of borontrifluoride etherate[23] (2 equivalents) resulted in a mixture of aza-Cope rearranged anilines **3a** and **4a** in 8% and 15% yields respectively but no Claisen rearranged product **5a**, as shown in Scheme 1. Increasing the reaction temperature by using 1,4-dioxane resulted in reduction of reaction time to 8 h with significantly improved yields of up to 28% of **3a** and 41% of **4a** (Table 1, entry 2). To investigate the scope of this rearrangement, different Lewis acids such as $AlCl_3$, $ZnCl_2$, $FeCl_3$, and $AgBF_4$ were tried, but Claisen rearranged products **5a–g** were not obtained with any of the Lewis acids and resulted in poor yields of **3a** and **4a** (Table 1, entries 3–7). From Table 1, it is evident that boron trifluoride is the best catalyst in terms of product yields. To further explore the scope of aza-Cope rearrangement, a variety of fluoro and *N*-alkyl substituted allyl anilines were subjected to this reaction, although the Claisen rearranged products **5a**–**g** were not observed in all the cases studied. The details of these reaction conditions and the product distributions are summarized in Table 1.

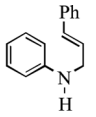
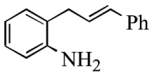
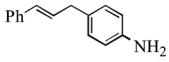
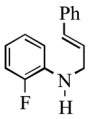
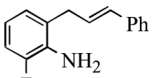
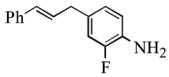
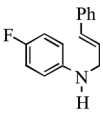
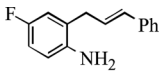
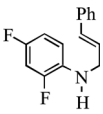
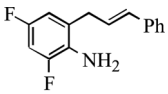
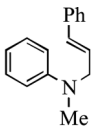
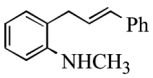
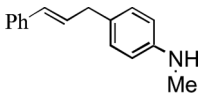
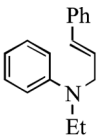
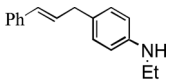
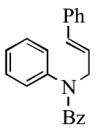
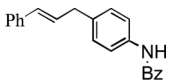
After several experiments, in contrast to other Lewis acids, the compound **2a**, on treatment with excess polyphosphoric acid at 100 °C under a nitrogen atmosphere for 10 min, formed 4-phenyl-1,2,3,4-tetrahydroquinoline (**6a**) in 71% isolated yield as shown in Scheme 2 (physical and spectral characteristics are comparable with the literature data[15]). No trace of Claisen rearranged product (**5a**) was detected in any of these examples.

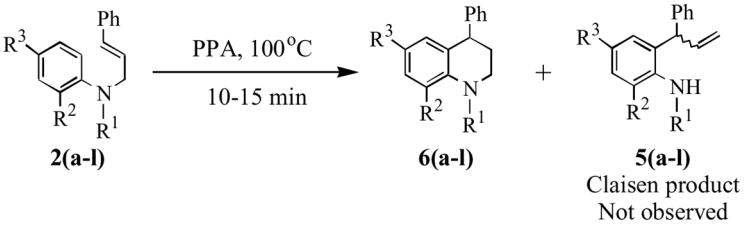
With the viable strategy in place for the synthesis of THQ derivatives, we subjected various *N*-allyl anilines to the described reaction conditions, and the results are given in Table 2. The reaction was found to be very good with *N*-alkyl-*N*-allylaniline (Table 2, entries 10–12), and electron-donating group substitutions on aniline (Table 2, entries 3–5) showed good yields. Anilines with electron–withdrawing group, for example, nitro (Table 2, entries 8 and 9), resulted in deallylation only, with no THQ formation. Both *ortho* and *para* fluorosubstituted aniline (Table 2, entries 2 and 6) provided moderate yields, but difluoroaniline derivative (Table 2, entry 7) was found to give lower yields as a result of cleavage of quaternary ammonium salts to corresponding aniline and allyl cation before its cyclization.

The same conditions were applied to easily synthesized *N*-allylaniline bearing a substitution on nitrogen, which also underwent a facile cyclization; with a view to synthesize polynuclear nitrogen-containing heterocycles. The *N*-allylindolines (**2m** and **2n**) cleanly afforded the corresponding 6-aryl-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolines (6-aryl-lilolidine, **6m** and **6n**) in good yields as shown in Scheme 3.

Similarly, *N*-allyl-1,2,3,4-tetrahydroquinilines **2o**–**t**, when subjected to cyclization in the presence of polyphosphoric acid (PPA) at 100–110 °C for 10–15 min, afforded the desired 1-aryl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline

Table 1. Lewis acid–mediated aza-Cope rearrangement of allyl anilines (**2**) to **3** and **4**

Entry	Substrate	Catalysts	Solvent	Time (h)	Product	
					3	**4**
1	 **2a** (95%)	$BF_3 \cdot Et_2O$	THF	36	 **3a** (8%)	 **4a** (15%)
2	**2a**	$BF_3 \cdot Et_2O$	1,4-Dioxane	8	**3a** (28%)	**4a** (41%)
3	**2a**	$AlCl_3$	Neat	0.5	complex mixture	
4	**2a**	$AlCl_3$	Dichloroethane	6	**3a** (19%)	**4a** (31%)
5	**2a**	$ZnCl_2$	Xylene	18	—	**4a** (10%)
6	**2a**	$FeCl_3$	Dichloroethane	24	—	—
7	**2a**	$AgBF_4$	Dichloroethane	10	—	**4a** (5%)
8	 **2b** (91%)	$BF_3 \cdot Et_2O$	1,4-Dioxane	10	 **3b** (30%)	 **4b** (23%)
9	 **2f** (89%)	$BF_3 \cdot Et_2O$	1,4-Dioxane	8	 **3c** (62%)	—
10	 **2g** (91%)	$BF_3 \cdot Et_2O$	1,4-Dioxane	8	 **3d** (51%)	—
11	 **2h** (79%)	$BF_3 \cdot Et_2O$	1,4-Dioxane	8	 **3e** (5%)	 **4e** (53%)
12	 **2i** (84%)	$BF_3 \cdot Et_2O$	1,4-Dioxane	10	—	 **4f** (62%)
13	 **2j** (87%)	$BF_3 \cdot Et_2O$	1,4-Dioxane	14	—	 **4g** (69%)



Scheme 2. Synthesis of 1,2,3,4-tetrahydroquinolines.

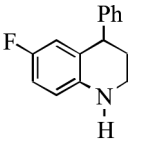
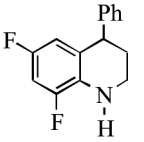
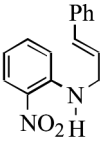
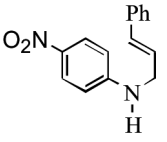
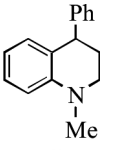
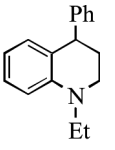
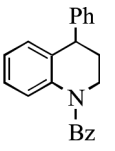
(1-aryl-julolidines[24]) **6o–t** (Scheme 4) in fairly good yields, demonstrating the scope of the approach, and the results obtained in all these reactions are summarized in Table 3.

Table 2. Synthesis of 4-phenyl-1,2,3,4-tetrahydroquinoline

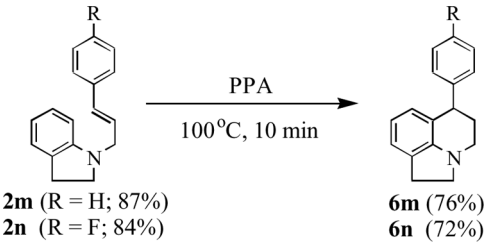
Entry	Allylaniline	Products	Yield (%)[a]
1	**2a**	**6a**	71
2	**2b**	**6b**	52
3	**2c** (87%)	**6c**	68
4	**2d** (90%)	**6d**	66
5	**2e** (96%)	**6e**	85

(*Continued*)

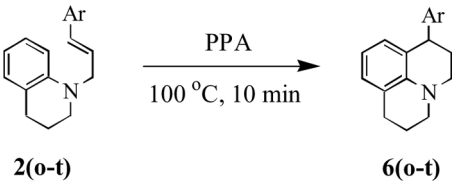
Table 2. Continued

Entry	Allylaniline	Products	Yield (%)[a]
6	**2f**	 **6f**	58
7	**2g**	 **6g**	30
8	 **2h** (85%)	Loss of allyl	0
9	 **2i** (91%)	Loss of allyl	0
10	**2j**	 **6j**	88
11	**2k**	 **6k**	84
12	**2l**	 **6l**	85

[a]All reactions completed within 10–15 min under a nitrogen atmosphere.



Scheme 3. Synthesis of 6-aryl-lilolidines.



Scheme 4. Synthesis of 1-aryl-julolidines.

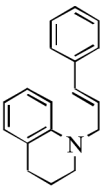
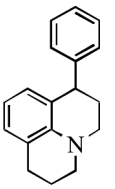
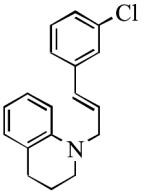
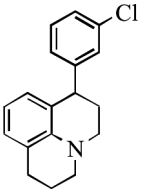
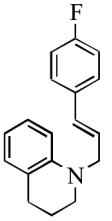
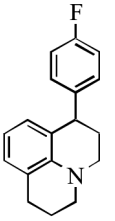
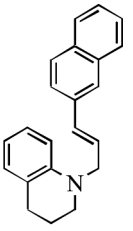
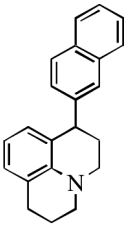
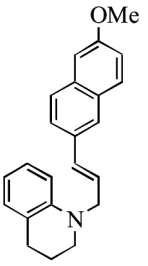
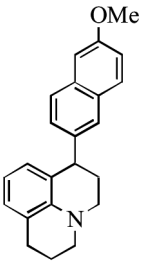
Mechanism of Aza-Cope Rearrangements

The possible reaction pathways for these rearrangements based on these results and literature reports[25] are discussed herein. To the best of our knowledge, the proposed [3,3] rearrangement mechanism is essentially a charge-accelerated reaction, as given in Scheme 5. Thus, an initial aniline-BF_3 complex (**A**) can either cleave to aniline with loss of allyl cation and intermolecular allyl transfer, or undergo [3,3] rearrangement through a charge-delocalized transition state (**B**) to the *ortho* imine intermediate (**C**). The enolization of **C** and deprotonation of boron complex to Claisen product (**5a**) usually occurs rapidly with respect to other potential rearrangements in this species, but if the [3,3] migration terminus does not bear a hydrogen, the *ortho* imine (**C**) once again either undergoes [3,3] rearrangement leading to formation of *para* imine (**D**), which on enolization gives thermodynamically more stable Cope rearranged aniline (**4a**), or undergoes [1,2] migration to form meta *imine* (**E**). The unstable intermediate (**E**) rearranges to more stable *ortho* imine (**D**) or *para* imine (**F**) via [3,3]-sigmatropic rearrangement followed by deprotonation of the boron complex to give Cope anilines **4a** and **3a**, respectively. The formation of Claisen rearranged product (**6a**) or 1,2,3,4-tetrahydroquinolines (**5a**) was not observed in any of the Lewis acid cases studied.

CONCLUSION

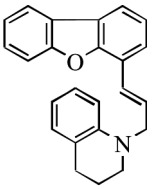
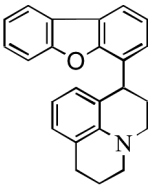
This paper highlights the utility of polyphosphoric acid in cyclization of *N*-aryl allyl anilines. By employing this approach, 4-phenyl-1,2,3,4-tetrahydroquinolines, 6-aryl-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolines, and 4-aryl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolines were prepared from easily accessible

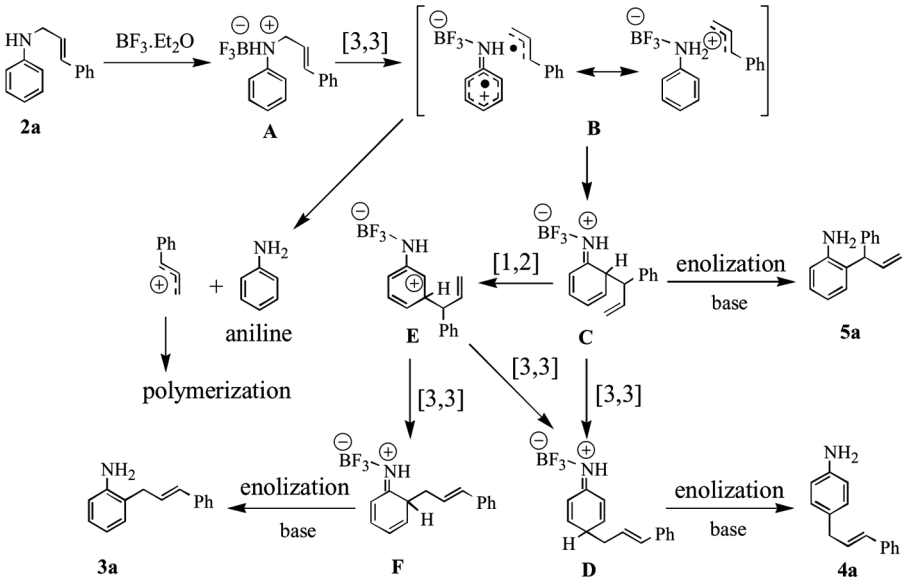
Table 3. Synthesis of 1-aryl-julolidines

Entry	Allylaniline	Products	Yield (%)[a]
1	 **2o** (91%)	 **6o**	69
2	 **2p** (90%)	 **6p**	70
3	 **2q** (88%)	 **6q**	74
4	 **2r** (91%)	 **6r**	65
5	 **2s** (89%)	 **6s**	63

(*Continued*)

Table 3. Continued

Entry	Allylaniline	Products	Yield (%)[a]
6	 **2t** (90%)	 **6t**	71



Scheme 5. Mechanism of Cope rearrangements.

3-arylprop-2-en-1-yl amine derivatives. We believe that this methodology would be a valuable addition to the existing methods for the synthesis of polynuclear nitrogen-containing heterocycles. $BF_3 \cdot Et_2O$-mediated Cope rearrangement of *N*-aryl allyl anilines also has been established with moderate yields.

EXPERIMENTAL

General Procedure for Preparation of *N*-Allylanilines (Reductive Amination)

Sodium triacetoxyborohydride (2 equivalent) was added to a stirred solution of anilines (1 equivalent), *trans*-cinnamaldehyde (1 equivalent), and acetic acid

(1 equivalent) in 1,2-dichloroethane (30 mL/g), and the mixture was stirred at room temperature until both the starting materials were completely consumed (5–10 h) as determined by thin-layer chromatography (TLC; 20% EtOAc in n-hexane). The reaction mixture was slowly quenched with aqueous sodium bicarbonate solution and diluted with chloroform (50 mL). The layers were separated, and the aqueous layer was extracted with chloroform (25 mL). The combined organic layers were washed with water (3 × 100 mL) followed by brine (50 mL) and dried over anhydrous sodium sulfate. The residue obtained after evaporation of the solvent was purified by silica-gel column chromatography using a mixture of 15–30% of EtOAc in petroleum ether as eluent to afford the title compounds.

Selected Data for 2a–2i

***N*-[(2*E*)-3-Phenylprop-2-en-1-yl]aniline (2a).** Oil; IR (neat) 3413, 3059, 2924, 1601, 1493, 1452, 1324, 1180, 1069, 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.82 (br s, 1H, exchangeable with D_2O), 3.93 (d, $J = 5.7$ Hz, 2H), 6.33 (dt, $J = 4.5$, 5.7 Hz, 1H), 6.58–6.73 (m, 4H), 7.14–7.21 (m, 3H), 7.26–7.36 (m, 4H); MS m/z (+ cAPCI): 209.56 $(M)^+$ (209.29 calcd. for $C_{15}H_{15}N$).

2-Fluoro-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2b). Off-white solid; mp 56–58 °C; IR (KBr) 3430, 3057, 2847, 1620, 1513, 1446, 1334, 1248, 1187, 1113, 966 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.70 (br s, 1H, exchangeable with D_2O), 3.96 (d, $J = 5.4$ Hz, 2H), 6.30 (dt, $J = 4.5$, 5.4 Hz, 1H), 6.58–6.50 (m, 2H), 6.73 (t, $J = 7.8$ Hz, 1H), 6.92–6.99 (m, 2H), 7.18–7.36 (m, 5H); MS m/z (+c APCI): 228.26 $(M + H)^+$ (227.28 calcd. for $C_{15}H_{14}FN$).

2-Methyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2c). Off-white solid; mp 40–42 °C; IR (neat) 3435, 3054, 2915, 1605, 1512, 1447, 1317, 1255, 1129, 1052 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.16 (s, 3H), 3.65 (br s, 1H, exchangeable with D_2O), 3.97 (d, $J = 6.0$ Hz, 2H), 6.35 (dt, $J = 4.2$, 5.4 Hz, 1H), 6.58–6.68 (m, 3H), 7.09–7.13 (m, 2H), 7.18–7.37 (m, 5H); MS m/z (+ cAPCI): 224.14 $(M + H)^+$ (223.31 calcd. for $C_{16}H_{17}N$).

2-Methoxy-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2d). Off-white solid; mp 60–62 °C; IR (KBr) 3418, 3062, 1601, 1512, 1452, 1245, 1222, 1123, 1026 871 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.94 (dd, $J = 0.9$, 4.5 Hz, 2H), 4.45 (br s, 1H, exchangeable with D_2O), 6.33 (dt, $J = 3.0$, 4.5 Hz, 1H), 6.61 (d, $J = 17.7$ Hz, 1H), 6.66–6.69 (m, 2H), 6.67 (d, $J = 7.8$ Hz, 1H), 6.85 (td, $J = 0.9$, 6.3 Hz,1H), 7.17–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.85, 55.30, 109.22, 110.03, 116.50, 121.11, 12613 (2C), 127.03, 127.23, 128.34 (2C), 131.09, 136.73, 137.75, 146.63; MS m/z (+c APCI): 240.09 $(M + H)^+$ (239.31 calcd. for $C_{16}H_{17}NO$).

4-Ethyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2e). Oil; IR (KBr) 3412, 5057, 2961, 1617, 1519, 1449, 1316, 1258, 1183, 1127, 966 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, $J = 7.5$ Hz, 3H), 2.54 (q, $J = 7.2$ Hz, 2H), 3.70 (br s, 1H, exchangeable with D_2O), 3.90 (d, $J = 5.7$ Hz, 2H), 6.32 (dt, $J = 3.3$, 4.5 Hz, 1H), 6.55–6.61 (m, 3H), 7.01 (d, $J = 8.7$ Hz, 2H), 7.17–7.35 (m, 5H). MS m/z (-cAPCI): 236.51 $(M - H)^-$ (237.34 calcd. for $C_{17}H_{19}N$).

4-Fluoro-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2f). Off-white solid; mp 74–76 °C; IR (KBr) 3305, 2915, 1508, 1311, 1221, 1116 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.73 (br s, 1H, exchangeable with D_2O), 3.88 (d, $J = 5.4$ Hz, 2H), 6.29 (dt, $J = 4.2$, 6.0 Hz, 1H), 6.55–6.62 (m, 3H), 6.87 (t, $J = 8.7$ Hz, 2H), 7.18–7.35 (m, 5H); MS m/z (-c APCI): 226.36 $(M - H)^-$ (227.28 calcd. for $C_{15}H_{14}FN$).

2,4-Difluoro-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2g). Off-white solid; mp 68–70 °C; IR (KBr) 3419, 3062, 2824, 1600, 1519, 1427, 1221, 1200, 1142, 1065, 960 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.15 (br s, 1H, exchangeable with D_2O), 3.92 (d, $J = 6.0$ Hz, 2H), 6.28 (dt, $J = 4.5$, 5.7 Hz, 1H), 6.60 (d, $J = 16.8$ Hz, 1H), 6.47–6.80 (m, 3H), 7.18 (m, 5H); MS m/z (-c APCI): 244.51 $(M - H)^-$ (245.27 calcd. for $C_{15}H_{13}F_2N$).

2-Nitro-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2h). Yellow solid; mp 68–70 °C; IR (KBr) 3394, 2850, 1620, 1567, 1513, 1359, 1258, 1153 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 4.21 (t, $J = 5.1$ Hz, 2H), 6.39 (dt, $J = 5.1$, 5.7 Hz, 1H), 6.58–6.72 (m, 2H), 7.05 (d, $J = 8.4$ Hz, 1H), 7.21 (d, $J = 6.9$ Hz, 1H), 7.25–7.41 (m, 4H), 7.49 (t, $J = 7.8$ Hz, 1H), 8.08 (d, $J = 8.4$ Hz, 1H), 8.41 (br s, 1H, exchangeable with D_2O); MS m/z (+c APCI): 255.23 $(M + H)^+$ (254.28 calcd. for $C_{15}H_{14}N_2O_2$).

4-Nitro-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2i). Yellow solid; mp 142–144 °C; IR (KBr) 3357, 1602, 1537, 1471, 1325, 1295, 1108 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 4.06 (t, $J = 5.1$ Hz, 2H), 6.35 (dt, $J = 5.2$, 5.7 Hz, 1H), 6.59 (d, $J = 15.9$ Hz, 1H), 6.70 (d, $J = 9.3$ Hz, 2H), 7.23–7.43 (m, 5H), 7.60 (br s, 1H, exchangeable with D_2O), 8.00 (d, $J = 9.3$ Hz, 2H); MS m/z (+c APCI): 255.20 $(M + H)^+$ (254.28 calcd. for $C_{15}H_{14}N_2O_2$).

General Procedure for Preparation of *N*-Alkyl-*N*-allylanilines

Anhydrous potassium carbonate (1.5 equivalent) was added to a well-stirred solution of *N*-alkyl-anilines, lindoline, or 1,2,3,4-tetrahydroquinilines (1 equivalent) in dry dimethylformamide (DMF; 10 mL/g), followed by a catalytic amount of sodium iodide (0.01 equivalents), under an atmosphere of nitrogen. Allyl chloride (1–1.2 equivalent) was added, and the reaction mixture was stirred until the completion of starting materials (18–24 h) as judged by TLC (10% EtOAc in *n*-hexanes). The reaction mixture was partitioned between EtOAc and water, and the layers were separated. The aqueous layer was extracted with EtOAc, and the combined organic extracts were washed with water and brine and dried over anhydrous sodium sulfate. The organic layer was concentrated under reduced pressure to afford crude products. The crude was purified on silica-gel column chromatography using a mixture of 5–15% of EtOAc in petroleum ether as eluent to afford the title compounds.

Selected Data for 2j–2t

***N*-Methyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2j).** Sticky solid; IR (neat) 3025, 2926, 1598, 1505, 1447, 1353, 1200, 1117, 1034, 963 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.96 (s, 3H), 4.06 (d, $J = 4.8$ Hz, 2H), 6.24 (dt, $J = 5.1$,

5.4 Hz, 1H), 6.49 (d, $J = 15.0$ Hz, 1H), 6.69 (t, $J = 6.9$ Hz, 1H), 6.76 (d, $J = 7.8$ Hz, 2H), 7.19–7.33 (m, 7H); MS m/z (+ cAPCI): 224.12 $(M + H)^+$ (223.31 calcd. for $C_{16}H_{17}N$).

***N*-Ethyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2k).** White solid; mp 48–50 °C; IR (KBr) 3050, 2967, 1594, 1503, 1444, 1349, 1270, 1178, 966 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, $J = 7.5$ Hz, 3H), 3.42 (q, $J = 7.2$ Hz, 2H), 4.04 (d, $J = 4.8$ Hz, 2H), 6.24 (dt, $J = 4.5$, 4.8 Hz, 1H), 6.49 (d, $J = 15.6$ Hz, 1H), 6.65 (t, $J = 6.9$ Hz, 1H), 6.72 (d, $J = 7.8$ Hz, 2H), 7.16–7.33 (m, 5H); MS m/z (+ cAPCI): 238.09 $(M + H)^+$ (237.34 calcd. for $C_{17}H_{19}N$).

***N*-Benzyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (2l).** White solid; mp 110–112 °C; IR (KBr) 3029, 2907, 1598, 1505, 1367, 1357, 1232, 1175, 970 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.16 (d, $J = 4.5$ Hz, 2H), 4.59 (s, 2H), 6.26 (dt, $J = 3.0$, 4.5 Hz, 1H), 6.49 (d, $J = 15.6$ Hz, 1H), 6.68 (t, $J = 7.5$ Hz, 1H), 6.76 (d, $J = 8.4$ Hz, 2H), 7.15–7.33 (m, 12H); MS m/z (+c APCI): 300.14 $(M + H)^+$ (299.41 calcd. for $C_{22}H_{21}N$).

1-[(2*E*)-3-Phenylprop-2-en-1-yl]indoline (2m). Viscous oil; IR (neat) 3024, 2844, 1606, 1487, 1459, 1356, 1266, 1223, 1155, 1022, 966 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.96 (t, $J = 8.1$ Hz, 2H), 3.70 (t, $J = 8.1$ Hz, 2H), 3.85 (d, $J = 6.0$ Hz, 2H), 6.28 (dt, $J = 5.7$, 6.0 Hz, 1H), 6.53–6.67 (m, 3H), 7.01–7.04 (m, 1H), 7.22–7.36 (m, 6H); MS m/z (+c APCI): 236.07 $(M + H)^+$ (235.32 calcd. for $C_{17}H_{17}N$).

1-[(2*E*)-3-(4-Fluorophenyl)prop-2-en-1-yl]indoline (2n). Off-white solid; mp 59–60 °C; IR (KBr) 3025, 2804, 1599, 1507, 1485, 1371, 1223, 1158, 969 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.96 (t, $J = 7.8$ Hz, 2H), 3.36 (t, $J = 8.4$ Hz, 2H), 3.84 (d, $J = 5.7$ Hz, 2H), 6.19 (dt, $J = 3.3$, 6.6 Hz, 1H), 6.52–6.63 (m, 2H), 6.65 (t, $J = 6.9$ Hz, 1H), 6.94–7.08 (m, 4H), 7.28–7.33 (m, 2H); MS m/z (+ cAPCI): 254.12 $(M + H)^+$ (253.31 calcd. for $C_{17}H_{16}FN$).

1-[(2*E*)-3-Phenylprop-2-en-1-yl]-1,2,3,4-tetrahydroquinoline (2o). Oil; IR (neat) 3060, 2930, 1633, 1574, 1496, 1329, 1277, 1155, 965 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.94–2.02 (m, 2H), 2.77 (t, $J = 6.3$ Hz, 2H), 3.30 (t, $J = 5.7$ Hz, 2H), 4.01 (d, $J = 4.5$ Hz, 2H), 6.23 (dt, $J = 4.8$, 5.4 Hz, 1H), 6.49–6.63 (m, 3H), 6.94 (d, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 7.8$ Hz, 1H), 7.15–7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.37, 28.14, 49.09, 53.36, 110.92, 115.73, 122.33, 125.40, 126.11 (2C), 126.98, 127.14, 128.31 (2C), 128.81, 130.81, 136.73, 145.14; MS m/z (+c APCI): 250.15 $(M + H)^+$ (249.35 calcd. for $C_{18}H_{19}N$).

1-[(2*E*)-3-(3-Chlorophenyl)prop-2-en-1-yl]-1,2,3,4-tetrahydroquinoline (2p). Oil; IR (neat) 2937, 1595, 1492, 1456, 1307, 1216, 1199, 1078 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.97–2.02 (m, 2H), 2.78 (t, $J = 6.3$ Hz, 2H), 3.30 (t, $J = 6.0$ Hz, 2H), 4.01 (d, $J = 3.9$ Hz, 2H), 6.24 (dt, $J = 1.2$, 6.0 Hz, 1H), 6.45 (d, $J = 15.6$ Hz, 1H), 6.57–6.60 (m, 2H), 6.95 (d, $J = 7.5$ Hz, 1H), 7.01 (t, $J = 7.8$ Hz, 1H), 7.17–7.20 (m, 3H), 7.31 (s, 1H). MS m/z (+cAPCI): 284.62 $(M + H)^+$ (283.79 calcd. for $C_{18}H_{18}ClN$).

1-[(2*E*)-3-(4-Fluorophenyl)prop-2-en-1-yl]-1,2,3,4-tetrahydroquinoline (2q). White solid; mp 45–47 °C; IR (KBr) 3064, 2921, 1599, 1507, 1495, 1339, 1226,

1159, 970 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.96–2.00 (m, 2H), 2.77 (t, $J = 6.3$ Hz, 2H), 3.30 (t, $J = 6.0$ Hz, 2H), 4.00 (d, $J = 4.2$ Hz, 2H), 6.13 (dt, $J = 4.8$, 5.7 Hz, 1H), 6.47 (d, $J = 16.2$ Hz, 1H), 6.56–6.16 (m, 2H), 6.92–7.02 (m, 4H), 7.23–7.30 (m, 2H); MS m/z (+c APCI): 268.13 $(M + H)^+$ (267.34 calcd. for $C_{18}H_{18}FN$).

1-[(2*E*)-3-(2-Naphthyl)prop-2-en-1-yl]-1,2,3,4-tetrahydroquinoline (2r). Off-white solid; mp 54–58 °C; IR (neat) 3058, 2923, 1599, 1496, 1330, 1299, 1169, 1153, 971 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.96–2.04 (m, 2H), 2.78 (t, $J = 5.7$ Hz, 2H), 3.33 (t, $J = 5.4$ Hz, 2H), 4.06 (d, $J = 4.8$ Hz, 2H), 6.35 (dt, $J = 5.4$, 5.4 Hz, 1H), 6.54–6.69 (m, 3H), 6.95 (d, $J = 7.5$ Hz, 1H), 7.02 (t, $J = 7.2$ Hz, 1H), 7.35–7.43 (m, 2H), 7.54 (d, $J = 8.1$ Hz, 1H), 7.66 (s, 1H), 7.71–7.75 (m, 3H). MS m/z (+ cAPCI): 300.01 $(M + H)^+$ (299.41 calcd. for $C_{22}H_{21}N$).

1-[(2*E*)-3-(6-Methoxy-2-naphthyl)prop-2-en-1-yl]-1,2,3,4-tetrahydroq-uinoline (2s). White solid; mp 128–130 °C; IR (KBr) 3053, 2933, 1601, 1503, 1482, 1270, 1210, 1166, 1026 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.00 (t, $J = 6.0$ Hz, 2H), 2.78 (t, $J = 6.3$ Hz, 2H), 3.35 (t, $J = 6.0$ Hz, 2H), 3.89 (s, 3H), 4.05 (d, $J = 4.8$ Hz, 2H), 6.29 (dt, $J = 5.1$, 5.4 Hz, 1H), 6.54–6.66 (m, 3H), 6.95 (d, $J = 6.9$ Hz, 1H), 7.01–7.09 (m, 3H), 7.51 (d, $J = 8.7$ Hz, 1H), 7.60–7.65 (m, 3H); MS m/z (+ cAPCI): 330.32 $(M + H)^+$ (329 calcd. for $C_{23}H_{23}NO$).

1-[(2*E*)-3-Dibenzo[*b,d*]furan-4-ylprop-2-en-1-yl]-1,2,3,4-tetrahydroquinoline (2t). White solid; mp 145–148 °C; IR (KBr) 3062, 2928, 1601, 1505, 1450, 1417, 1344, 1186, 1115, 970 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.90–2.06 (m, 2H), 2.80 (t, $J = 6.3$ Hz, 2H), 3.37 (t, $J = 6.0$ Hz, 2H), 4.14 (d, $J = 4.2$ Hz, 2H), 6.57 (t, $J = 7.5$ Hz, 1H), 6.69 (d, $J = 8.4$ Hz, 1H), 6.74–6.91 (m, 2H),6.96 (d, $J = 7.2$ Hz, 1H), 7.03 (t, $J = 7.8$ Hz, 1H), 7.24–7.45 (m, 4H), 7.57 (d, $J = 6.9$ Hz, 1H), 7.77 (d, $J = 7.2$ Hz, 1H), 7.91 (d, $J = 7.5$ Hz, 1H); MS m/z (+ cAPCI): 339.92 $(M)^+$ (339.43 calcd. for $C_{24}H_{21}NO$).

General Procedure for Aza-Cope Rearrangement

A solution of *N*-allylanilines (**2**) (1 equivalent) and boron trifluoride etherate (2 equivalent) in 1,4-dioxane (10 mL) was refluxed under nitrogen atmosphere until the starting material was completely consumed as determined by TLC (20% EtOAc in *n*-hexane mixture). The cold reaction mixture was poured into ice-cold water and basified with 1 N sodium hydroxide solution. The aqueous layer was extracted with EtOAc (2 × 50 mL), and the combined extracts were washed with water (3 × 100 mL) followed by brine (50 mL) and dried over anhydrous sodium sulfate. The crude residue obtained after evaporation of solvent under reduced pressure was chromatographed on silica gel using 15–25% EtOAc and n-hexane mixture to give aza-Cope products.

Selected Data for 3a–3e and 4a, 4b, 4e–4g

2-[(2*E*)-3-Phenylprop-2-en-1-yl]aniline (3a). Sticky solid; IR (neat) 3445, 3059, 2924, 1601, 1492, 1452, 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.45 (d,

$J = 6.9$ Hz, 2H), 3.68 (br s, 2H, exchangeable with D_2O), 6.30 (dt, $J = 3.9$, 6.0 Hz, 1H), 6.44 (d, $J = 16.2$ Hz, 1H), 6.68 (d, $J = 7.2$ Hz, 1H), 6.75 (t, $J = 7.5$ Hz, 1H), 7.04–7.07 (m, 2H), 7.18–7.33 (m, 5H); MS m/z (+c APCI): 210.25 $(M + H)^+$ (209.29 calcd. for $C_{15}H_{15}N$).

4-[(2*E*)-3-Phenylprop-2-en-1-yl]aniline (4a). Sticky solid; IR (neat) 3365, 3056, 2894, 1621, 1515, 1495, 1277, 1178 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.44 (d, $J = 6.3$ Hz, 2H), 3.57 (br s, 2H, exchangeable with D_2O), 6.23–6.44 (m, 2H), 6.65 (d, $J = 8.4$ Hz, 2H), 7.03 (d, $J = 8.4$ Hz, 2H), 7.12–7.33 (m, 5H); MS m/z (+c APCI): 210.48 $(M + H)^+$ (209.29 calcd. for $C1_5H_{15}N$).

2-Fluoro-6-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (3b). Oil; IR (neat) 3394, 3019, 1629, 1479, 1215, 970 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.45 (br s, 2H, exchangeable with D_2O), 3.49 (d, $J = 6.0$ Hz, 2H), 6.31 (dt, $J = 5.7$ & 9.9 Hz, 1H), 6.45 (d, $J = 16.2$ Hz, 1H), 6.67–6.90 (m, 3H), 7.25–7.33 (m, 5H); MS m/z (+ cAPCI): 228.14 $(M + H)^+$ (227.28 calcd. for $C_{15}H_{14}FN$).

2-Fluoro-4-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (4b). Oil; IR (neat) 3394, 3019, 1636, 1519, 1439, 1215, 966 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.43 (d, $J = 6.3$ Hz, 2H), 3.56 (br s, 2H, exchangeable with D_2O), 6.30 (dt, $J = 6.6$ & 6.9 Hz, 1H), 6.42 (d, $J = 15.6$ Hz, 1H), 6.71–6.89 (m, 3H), 7.18–7.39 (m, 5H); MS m/z (+ cAPCI): 226.26 $(M - H)^-$ (227.28 calcd. for $C_{15}H_{14}FN$).

4-Fluoro-2-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (3c). Sticky solid; IR (neat) 3349, 3058, 2897, 1624, 1597, 1051, 1437, 1235, 1145, 967 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.42 (d, $J = 6.3$ Hz, 2H), 3.55 (br s, 2H, exchangeable with D_2O), 6.29 (dt, $J = 3.3$, 6.3 Hz, 1H), 6.43 (d, $J = 15.6$ Hz, 1H), 6.61 (dd, $J = 3.9$, 4.8 Hz, 1H), 6.74–6.84 (m, 2H), 7.17–7.34 (m, 5H); MS m/z (+ cAPCI): 228.21 $(M + H)^+$ (227.11 calcd. for $C_{15}H_{14}FN$).

2,4-Difluoro-6-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (3d). Oil; IR (neat) 3384, 3020, 1596, 1495, 1215, 1113, 991 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.46 (d, $J = 5.7$ Hz, 2H), 3.58 (br s, 2H, exchangeable with D_2O), 6.29 (dt, $J = 5.7$ & 6.6 Hz, 1H), 6.39 (d, $J = 15.6$ Hz, 1H), 6.67–6.75 (m, 2H), 7.12–7.34 (m, 5H); MS m/z (+ cAPCI): 246.10 $(M + H)^+$ (245.27 calcd. for $C_{15}H_{13}F_2N$).

***N*-Methyl-2-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (3e).** Off-white solid; mp 56–58 °C; IR (KBr) 3418, 3026, 2864, 1602, 1554, 1508, 1461, 1449, 1302, 1258, 978 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.83 (s, 3H), 3.42 (d, $J = 5.4$ Hz, 2H), 3.77 (br s, 1H, exchangeable with D_2O), 6.31 (dt, $J = 5.7$, 6.3 Hz, 1H), 6.42 (d, $J = 15.9$ Hz, 1H), 6.64 (d, $J = 7.8$ Hz, 1H), 6.71 (t, $J = 7.2$ Hz, 1H), 7.08 (d, $J = 6.3$ Hz, 1H), 7.16–7.31 (m, 6H); MS m/z (+ cAPCI): 224.27 $(M + H)^+$ (223.31 calcd. for $C_{16}H_{17}N$).

***N*-Methyl-4-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (4e).** Oil; IR (neat) 3415, 3023, 2891, 1615, 1520, 1495, 1316, 1266, 1181, 1153, 965 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.81 (s, 3H), 3.43 (d, $J = 5.7$ Hz, 2H), 3.61 (br s, 1H, exchangeable with D_2O), 6.33–6.42 (m, 2H), 6.55 (d, $J = 8.1$ Hz, 2H), 7.04 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 6.9$ Hz, 1H), 7.22–7.33 (m, 4H); MS m/z (+ cAPCI): 224.30 $(M + H)^+$ (223.31 calcd. for $C_{16}H_{17}N$).

***N*-Ethyl-4-[(2*E*)-3-phenylprop-2-en-1-yl]aniline (4f).** Sticky solid; IR (neat) 3403, 3024, 2968, 1615, 1519, 1318, 1260, 1147, 965 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.24 (t, $J = 6.9$ Hz, 3H), 3.13 (q, $J = 6.9$ Hz, 2H), 3.42 (d, $J = 6.0$ Hz, 2H), 3.63 (br s, 1H, exchangeable with D_2O), 6.30–6.40 (m, 2H), 6.55 (d, $J = 8.4$ Hz, 2H), 7.03 (d, $J = 8.1$ Hz, 2H), 7.16–7.33 (m, 5H); MS m/z (+ cAPCI): 238.31 $(M + H)^+$ (237.34 calcd. for $C_{17}H_{19}N$).

***N*-Benzyl-4-[(2*e*)-3-phenylprop-2-en-1-yl]aniline (4g).** Oil; IR (neat) 3321, 3029, 2895, 1614, 1519, 1494, 1452, 1322, 1267, 1181, 965 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.42 (d, $J = 6.0$ Hz, 2H), 3.95 (br s, 1H, exchangeable with D_2O), 4.30 (s, 2H), 6.25–6.44 (m, 2H), 6.57 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.1$ Hz, 2H), 7.15–7.35 (m, 10H); MS m/z (+ cAPCI): 300.15 $(M + H)^+$ (299.41 calcd. for $C_{22}H_{21}N$).

General Procedure for Cyclization

A mixture of *N*-allylanilines, *N*-allylindoline, or *N*-allyl-1,2,3,4-tetrahydroquinilines and polyphosphoric acid (6–8 times wt/wt) was heated at 100–110 °C for 10–15 min under an N_2 atmosphere. The reaction mixture was cooled to room temperature, poured into ice-cold water (50 mL), and basified with aqueous ammonia solution. The aqueous layer was extracted with EtOAc (2×25 mL), and the combined organic layer was washed with water (2×20 mL) followed by brine (10 mL) and dried over sodium sulfate. Evaporation of the EtOAc layer under vacuum yielded the crude products. The crude products were purified with silica-gel column chromatography using a solvent mixture of 15–20% EtOAc in n-hexane to obtain pure compounds.

Selected Data for 6a–6g and 6j–6t

4-Phenyl-1,2,3,4-tetrahydroquinoline (6a)[15]. Off-white solid; mp 73–75 °C (literature value 72–74 °C); IR (neat) 3416, 2850, 1601, 1492, 1452, 1313, 1216, 1029 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.99–2.09 (m, 1H), 2.15–2.25 (m, 1H), 3.18–3.32 (m, 2H), 3.92 (br s, 1H, exchangeable with D_2O), 4.13 (t, $J = 5.7$ Hz, 1H), 6.51–6.56 (m, 2H), 6.72 (d, $J = 7.8$ Hz, 1H), 6.98 (t, $J = 7.8$ Hz, 1H), 7.10–7.29 (m, 5H). MS m/z (+c ESI): 210.23 $(M + H)^+$. Anal. calcd. for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.17; H, 7.31; N, 6.61.

8-Fluoro-4-phenyl-1,2,3,4-tetrahydroquinoline (6b). Oil; IR (neat) 3341, 2925, 1624, 1508, 1499, 1437, 1321, 1222 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.01–2.11 (m, 1H), 2.16–2.26 (m, 1H), 3.10 (br s, 1H, exchangeable with D_2O), 3.12–3.37 (m, 2H), 4.14 (t, $J = 6.3$ Hz, 1H), 6.40–6.47 (m, 1H), 6.52 (d, $J = 7.8$ Hz, 1H), 6.78–6.85 (m, 1H), 7.09 (d, $J = 6.6$ Hz, 2H), 7.16–7.29 (m, 3H). MS m/z (+ cAPCI): 228.12 $(M + H)^+$. Anal. calcd. for $C_{15}H_{14}FN$: C, 79.27; H, 6.21; F, 8.36; N, 6.16. Found: C, 79.12; H, 6.35; N, 6.28.

8-Methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (6c). Off-white solid; mp 56–58 °C; IR (KBr) 3435, 2932, 1599, 1492, 1461, 1359, 1309, 1265, 1061, 1029 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.00–2.09 (m, 1H), 2.13 (s, 3H), 2.15–2.25 (m, 1H), 3.24–3.39 (m, 2H), 3.81 (br s, 1H, exchangeable with D_2O),

4.16 (t, $J = 5.7$ Hz, 1H), 6.48 (t, $J = 6.3$ Hz, 1H), 6.62 (d, $J = 7.8$ Hz, 1H), 6.90 (d, $J = 7.2$ Hz, 1H), 7.10 (d, $J = 6.9$ Hz, 2H), 7.14–7.28 (m, 3H). MS m/z (+ cAPCI): 224.28 $(M + H)^+$. Anal. calcd. for $C_{16}H_{17}N$: C, 80.05; H, 7.67; N, 6.27. Found: C 86.16; H, 7.78; N, 6.21.

8-Methoxy-4-phenyl-1,2,3,4-tetrahydroquinoline (6d). White solid; mp 72–74 °C; IR (KBr) 3425, 2947, 1585, 1508, 1449, 1341, 1250, 1104, 1057, 1013 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.98–2.07 (m, 1H), 2.18–2.26 (m, 1H), 3.22–3.33 (m, 2H), 3.85 (s, 3H), 4.15 (t, $J = 6.0$ Hz, 1H), 4.20 (br s, 1H, exchangeable with D_2O), 6.39 (d, $J = 7.2$ Hz, 1H), 6.50 (t, $J = 7.5$ Hz, 1H), 6.63 (d, $J = 7.8$ Hz, 1H), 7.11 (d, $J = 6.9$ Hz, 2H), 7.17–7.28 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.06, 38.53, 42.53, 55.32, 107.34, 115.42, 122.32, 122.91, 125.84, 128.02 (2C), 128.44 (2C), 134.68, 145.91, 146.56. MS m/z (+ cAPCI): 240.24 $(M + H)^+$. Anal. calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85; O, 6.69. Found: C, 80.18; H, 7.09; N, 5.79.

6-Ethyl-4-phenyl-1,2,3,4-tetrahydroquinoline (6e). Sticky solid; IR (neat) 3401, 2958, 1616, 1508, 1492, 1353, 1312, 1270, 1155, 1029 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.08 (t, $J = 7.2$ Hz, 3H), 1.96–2.06 (m, 1H), 2.16–2.25 (m, 1H), 2.40 (q, $J = 7.8$ Hz, 2H), 3.15–3.29 (m, 2H), 3.87 (br s, 1H, exchangeable with D_2O), 4.12 (t, $J = 5.7$ Hz, 1H), 6.49 (d, $J = 8.4$ Hz, 1H), 6.57 (s, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 7.19–2.29 (m, 5H). MS m/z (+ cAPCI): 238.28 $(M + H)^+$. Anal. calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.21; H, 8.00; N, 5.84.

6-Fluoro-4-phenyl-1,2,3,4-tetrahydroquinoline (6f). Off-white solid; mp 56–58 °C; IR (KBr) 3419, 2918, 1508, 1490, 1315, 1247, 1230, 1140 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.99–2.08 (m, 1H), 2.14–2.24 (m, 1H), 3.18–3.29 (m, 2H), 3.81 (br s, 1H, exchangeable with D_2O), 4.09 (t, $J = 5.7$ Hz, 1H), 6.42–6.48 (m, 2H), 6.70 (dt, $J = 3.0$, 5.7 Hz, 1H), 7.09–7.12 (m, 2H), 7.17–7.30 (m, 3H). MS m/z (+ cAPCI): 228.23 $(M + H)^+$. Anal. calcd. for $C_{15}H_{14}FN$: C, 79.27; H, 6.21; F, 8.36; N, 6.16. Found: C,79.19; H, 6.31; N, 6.03.

6,8-Difluoro-4-phenyl-1,2,3,4-tetrahydroquinoline (6g). Off-white solid; mp 69–72 °C; IR (KBr) 3443, 2963, 1595, 1508, 1423, 1262, 1111, 1080, 958 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.03–2.11 (m, 1H), 2.16 (m, 1H), 3.23–3.18 (m, 2H), 3.31 (br s, 1H, exchangeable with D_2O), 4.09 (t, $J = 6.3$ Hz, 1H), 6.28 (d, $J = 9.3$ Hz, 1H), 6.631 (dt, $J = 2.1$, 8.4 Hz, 1H), 7.09 (d, $J = 6.9$ Hz, 2H), 7.18–7.31 (m, 3H); MS m/z (+ cAPCI): 246.31 $(M + H)^+$. Anal. calcd. for $C_{15}H_{13}F_2N$: C, 73.45; H, 5.34; F, 15.49; N, 5.71. Found: C, 73.38; H, 5.12; N, 5.52.

1-Methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (6j). Oil; IR (neat) 2924, 1602, 1573, 1501, 1458, 1325, 1208, 1027, 1008 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.03–2.11 (m, 1H), 2.24–2.26 (m, 1H), 2.93 (s, 3H), 3.12–3.21 (m, 2H), 4.11 (t, $J = 5.7$ Hz, 1H), 6.53 (t, $J = 6.6$ Hz, 1H), 4.65 (d, $J = 8.4$ Hz, 1H), 6.71 (d, $J = 6.6$ Hz, 1H), 7.07–7.28 (m, 6H). MS m/z (+ cAPCI): 224.29 $(M + H)^+$. Anal. calcd. for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.14; H, 7.59; N, 6.41.

1-Ethyl-4-phenyl-1,2,3,4-tetrahydroquinoline (6k). Sticky solid; IR (neat) 2967, 1601, 1502, 1454, 1343, 1270, 1192, 1076 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, $J = 7.2$ Hz, 3H), 2.04–2.08 (m, 1H), 2.20–2.28 (m, 1H), 3.17 (q, $J = 7.2$ Hz, 2H), 3.30–3.46 (m, 2H), 4.10 (t, $J = 6.0$ Hz, 1H), 6.49 (t, $J = 6.9$ Hz, 1H), 6.66

(d, $J = 8.4$ Hz, 1H), 6.72 (d, $J = 6.9$ Hz, 1H), 7.05–7.07 (m, 3H), 7.16–7.27 (m, 3H). MS m/z (+ cAPCI): 238.27 $(M + H)^+$. Anal. calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.96; H, 8.16; N, 6.01.

1-Benzyl-4-phenyl-1,2,3,4-tetrahydroquinoline (6l). Off-white solid; mp 47–49 °C; IR (neat) 2922, 1601, 1504, 1451, 1337, 1307, 1258, 1169, 1053 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.10–2.22 (m, 1H), 2.28–2.40 (m, 1H), 3.25–3.35 (m, 2H), 4.52 (s, 2H), 6.52 (t, $J = 7.2$ Hz, 1H), 6.58 (d, $J = 8.4$ Hz, 1H), 6.77 (d, $J = 7.2$ Hz, 1H), 6.98 (t, $J = 6.6$ Hz, 1H), 7.11 (d, $J = 6.9$ Hz, 2H), 7.19–7.33 (m, 9H). MS m/z (+ cAPCI): 300.15 $(M + H)^+$. Anal. calcd. for $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68. Found: C, 88.39; H, 7.01; N, 4.75.

6-Phenyl-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (6m). Oil; IR (neat) 2805, 1600, 1489, 1454, 1337, 1281, 1274, 1179, 1063 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.14–2.21 (m, 1H), 2.32–2.38 (m, 1H), 2.93 (m, 3H), 3.06–3.11 (m, 1H), 3.16–3.24 (m, 1H), 3.35–4.40 (m, 1H), 4.08 (t, $J = 6.3$ Hz, 1H), 6.54 (d, $J = 7.2$ Hz, 2H), 6.94 (t, $J = 7.2$ Hz, 1H), 7.13–7.28 (m, 5H). MS m/z (+ cAPCI): 236.21 $(M + H)^+$. Anal. calcd. for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.85; H, 7.08; N, 5.74.

6-(4-Fluorophenyl)-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (6n). White solid; mp 60–61 °C; IR (KBr) 2948, 1598, 1509, 1492, 1338, 1282, 1217, 1159, 1013 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.06–2.18 (m, 1H), 2.28 (m, 1H), 2.88–3.00 (m, 3H), 3.02–3.19 (m, 1H), 3.16–3.24 (m, 1H), 3.35–3.42 (m, 1H), 4.06 (t, $J = 6.9$ Hz, 1H), 6.50–6.54 (m, 2H), 6.92–6.97 (m, 3H), 7.07–7.12 (m, 2H). MS m/z (+ cAPCI): 254.22 $(M + H)^+$. Anal. calcd. for $C_{17}H_{16}FN$: C, 80.60; H, 6.37; F, 7.50; N, 5.53. Found: C, 80.68; H, 6.49; N, 5.47.

1-Phenyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (6o). Sticky solid; IR (neat) 2937, 1597, 1491, 1455, 1309, 1189, 1108 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.98–2.18 (m, 3H), 2.20–2.25 (m, 1H), 2.80 (t, $J = 6.3$ Hz, 2H), 3.08–3.18 (m, 4H), 4.09 (t, $J = 6.0$ Hz, 1H), 6.42 (t, $J = 7.2$ Hz, 1H), 6.53 (d, $J = 7.5$ Hz, 1H), 6.80 (d, $J = 6.9$ Hz, 1H), 7.09–7.26 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.17, 27.86, 30.91, 43.49, 47.36, 50.15, 115.53, 121.36, 123.46, 125.86, 127.24, 127.83, 128.08 (2C), 128.52 (2C), 142.94, 146.77. MS m/z (+ cAPCI): 250.21 $(M + H)^+$. Anal. calcd. for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.63; H, 7.51; N, 5.75.

1-(3-Chlorophenyl)-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (6p). Sticky solid; IR (neat) 2927, 1601, 1505, 1457, 1344, 1193, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.98–2.09 (m, 3H), 2.17–2.24 (m, 1H), 2.78 (t, $J = 6.6$ Hz, 2H), 3.01–3.11 (m, 2H), 3.14–3.17 (m, 2H), 4.07 (t, $J = 6.0$ Hz, 1H), 6.42 (t, $J = 7.5$ Hz, 1H), 6.51 (d, $J = 7.2$ Hz, 1H), 6.80 (d, $J = 7.5$ Hz, 1H), 6.97 (d, $J = 6.9$ Hz, 1H), 7.10–7.22 (m, 3H). MS m/z (+ cAPCI): 284.73 $(M + H)^+$. Anal. calcd. for $C_{18}H_{18}ClN$: C, 76.18; H, 6.39; Cl, 12.49; N, 4.94. Found: C, 76.01; H, 6.46; N, 5.05.

1-(4-Fluorophenyl)-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (6q). Off-white solid; mp 53–55 °C; IR (neat) 2939, 1599, 1506, 1456, 1310, 1220, 1156, 1076, 834 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.96–2.07 (m, 3H), 2.16–2.26 (m, 1H), 2.79 (t, $J = 6.3$ Hz, 2H), 3.00–3.11 (m, 2H), 3.16 (t, $J = 6.0$ Hz, 2H), 4.08

(t, $J = 6.3$ Hz, 1H), 6.42 (t, $J = 7.2$ Hz, 1H), 6.51 (d, $J = 6.6$ Hz, 1H), 6.80 (d, $J = 6.3$ Hz, 1H), 6.94 (t, $J = 8.4$ Hz, 2H), 7.03–7.08 (m, 2H). MS m/z (+ cAPCI): 268.22 $(M + H)^+$. Anal. calcd. for $C_{18}H_{18}FN$: C, 80.87; H, 6.79; F, 7.11; N, 5.24. Found: C, 80.96; H, 6.62; N, 5.31.

1-(2-Naphthyl)-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (6r). White solid; mp 68–71 °C; IR (KBr) 2941, 1597, 1505, 1493, 1455, 1308, 1216 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.99–2.06 (m, 2H), 2.13–2.33 (m, 2H), 2.82 (t, $J = 6.9$ Hz, 2H), 3.06–3.20 (m, 4H), 4.26 (t, $J = 6.6$ Hz, 1H), 6.41 (t, $J = 7.5$ Hz, 1H), 6.54 (d, $J = 7.2$ Hz, 1H), 6.82 (d, $J = 6.9$ Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 1H), 7.37–7.44 (m, 2H), 7.52 (s, 1H), 7.73–7.79 (m, 3H). MS m/z (+ cAPCI): 300.29 $(M + H)^+$. Anal. calcd. for $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68. Found: C, 88.16; H, 7.29; N, 4.56.

1-(6-Methoxy-2-naphthyl)-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]-quinoline (6s). White solid; mp 102–105 °C; IR (KBr) 2929, 1606, 1438, 1330, 1260, 1215, 1104 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.04 (t, $J = 6.0$ Hz, 2H), 2.18–2.30 (m, 2H), 2.82 (t, $J = 6.9$ Hz, 2H), 3.12–3.18 (m, 4H), 3.89 (s, 3H), 4.22 (t, $J = 6.3$ Hz, 1H), 6.41 (t, $J = 7.2$ Hz, 1H), 6.54 (d, $J = 6.3$ Hz, 1H), 6.81 (d, $J = 7.2$ Hz, 1H), 7.08–7.10 (m, 2H), 7.24 (d, $J = 6.9$ Hz, 1H), 7.45 (s, 1H), 7.64 (d, $J = 6.6$ Hz, 2H); ^1H NMR (75 MHz, $CDCl_3$) δ 22.10, 27.77, 30.96, 43.50, 47.65, 50.16, 55.28, 105.55, 115.67, 118.58, 121.53, 123.78, 126.80, 127.10, 127.38, 127.50, 128.13, 128.86, 129.12, 133.12, 142.03, 143.20, 157.25; MS m/z (+ cAPCI): 330.23 $(M + H)^+$. Anal. calcd. for $C_{23}H_{23}NO$: C, 83.85; H, 7.04; N, 4.25; O, 4.86. Found: C, 83.91; H, 7.12; N, 4.17.

Dibenzo[*b,d*]furan-4-yl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (6t). White solid; mp 150–153 °C; IR (KBr) 2936, 1598, 1494, 1451, 1302, 1184, 1108, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.03 (t, $J = 6.0$ Hz, 2H), 2.32–2.38 (m, 2H), 2.79–2.83 (m, 2H), 3.08–3.12 (m, 2H), 3.19 (t, $J = 5.4$ Hz, 2H), 4.82 (t, $J = 6.0$ Hz, 1H), 6.43 (t, $J = 7.5$ Hz, 1H), 6.60 (d, $J = 7.2$ Hz, 1H), 6.83 (d, $J = 6.9$ Hz, 1H), 6.94 (d, $J = 7.2$ Hz, 1H), 7.19 (t, $J = 7.2$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.43 (t, $J = 7.2$ Hz, 1H), 7.56 (d, $J = 7.8$ Hz, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.93 (d, $J = 7.2$ Hz, 1H). MS m/z (+ cAPCI): 340.18 $(M + H)^+$. Anal. calcd. for $C_{24}H_{21}NO$: C, 84.92; H, 6.24; N, 4.13; O, 4.71. Found: C, 84.83; H, 4.13; N, 4.77.

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