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Three components synthesis of homoallylic amines catalyzed by bismuth(III) nitrate pentahydrate

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ABSTRACT

Bismuth (III) nitrate pentahydrate catalyzes efficiently the three-component condensation of aldehydes, amines, and allyltributylstannane at rt to afford the corresponding homoallylic amines in excellent yield.

1. Introduction

Homoallylic amines are important fundamental building blocks for the synthesis of many nitrogen containing natural products[1] and biologically or synthetically active compounds.[2] Moreover, *N*-aryl homoallylic amines show potent antifungal activity[3] and hence the syntheses of these compounds are highly useful. Nucleophilic addition of allylic organometallic (Si, Sn, Ge) reagents[4] to imines in the presence of catalyst is straightforward method for the synthesis of homoallylic amines. In recent years the Lewis acids such as $TiCl_4$,[5a] $BF_3{\cdot}OEt_2$,[5a] $PdCl_2(Ph_3P)_2/PtCl_2(Ph_3P)_2$,[5b] bis-π-allyl palladium complex,[5c] $Yb(OTf)_3$,[5d] $Sc(OTf)_3$,[5e] $LiClO_4$,[5f] $TaCl_5$,[5g] $ZrOCl_2{\cdot}8H_2O$,[5h] and CuI[5i] have been employed for this purpose.[5] The solid catalysts such as sulfamic acid and $PMA{\cdot}SiO_2$ were also used.[6]

Some of the reactions were carried out in one-pot operation with poor yields because water formed during the imine formation can decompose or deactivate the Lewis acid.[5a,b] Other methods have involved the use of strong acidic condition[5a,d,e] and extended reaction time.[5b,e,f,h,i] Several lanthanide triflates were used as catalysts that is however strongly acidic and highly expensive.[5d,e] Therefore, the development of less expensive and high yielding catalytic method is desired. Recently, $Bi(NO_3)_3{\cdot}5H_2O$ has emerged as a very effective catalyst for various organic transformations[7] because of inexpensive and oxygen/moisture tolerant nature. In continuation of work on the development of useful synthetic methodologies,[8] we report herein a three-component synthesis of homoallylic amines using $Bi(NO_3)_3{\cdot}5H_2O$ as the catalyst (Eq. 1).

2. Results and discussions

Several parameters including catalyst and its amount, allylating source, solvent, and temperature were optimized, which are summarized in Table 1. Several Lewis acids (bismuth, rhodium, ruthenium, and thallium salts) were screened and bismuth nitrate pentahydrate [$Bi(NO_3)_3{\cdot}5H_2O$] and thallium nitrate trihydrate [$Tl(NO_3)_3{\cdot}3H_2O$] were proved suitable catalysts (Table 1). $Bi(NO_3)_3{\cdot}5H_2O$ is the better catalyst because of non-toxicity. To a mixture of benzaldehyde (1 mmol), *p*-anisidine (1 mmol), and $Bi(NO_3)_3{\cdot}5H_2O$ (10 mol % based on the amount of benzaldehyde) in CH_2Cl_2 at rt the allyltributylstannane (1 mmol) was added. The reaction was monitored by TLC. After 2 h of reaction time, the yield of the homoallylic amine has been found to give 73% yield. The remarkable improvement of the reaction yield (92%) was observed by changing the ratio reactants, benzaldehyde (1 mmol), *p*-anisidine (1.5 mmol), and allyltributylstannane (1.2 mmol).[9a] Allyltrimethylsilane and allyltributylstannane were also examined for the allylation reaction as allylating source. The allyltributylstannane is more effective allyl source compared to allyltrimethylsilane in terms of reaction time and yield. Furthermore

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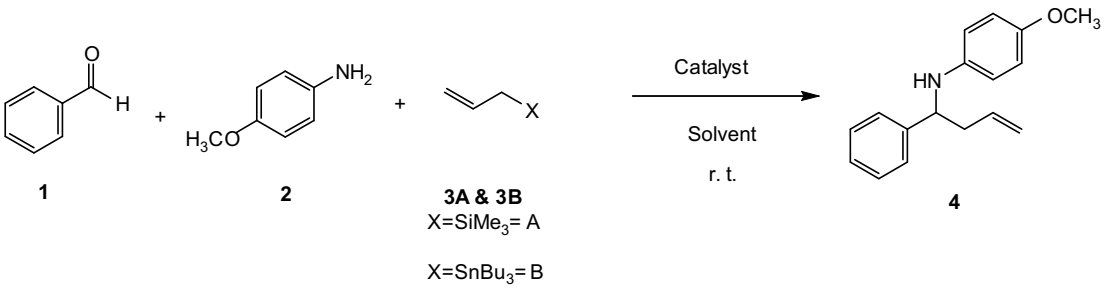


(1)

Table 1
Synthesis of homoallylic amines from benzaldehyde and *p*-ansidine under various reaction conditions[a]

Entry	Catalyst	Allyl source[b]	Catalyst amount[c]	Solvent	Reaction time (h)	Isolated yield[d] (%)
1	—	A	—	CH_2Cl_2	—	NR
2	$Bi(OTf)_3$	A	10.0	CH_2Cl_2	6.0	<25
		B	10.0	CH_2Cl_2	5.0	42
3	Bi_2O_3	B	10.0	CH_2Cl_2	7.0	NR
4	$BiBr_3$	A	10.0	CH_2Cl_2	3.0	75
		B	10.0		3.0	81
5	$BiCl_3$	B	10.0	CH_2Cl_2	3.5	80
		A	10.0		5.0	68
6	$Bi(NO_3)_3{\cdot}5H_2O$	B	10.0	CH_2Cl_2	2.0	73[e]
		B	10.0		1.5	90
		B	5.0		1.5	87
7	$RhI_3{\cdot}H_2O$	B	10.0	CH_2Cl_2	6.0	NR[f]
8	$Ru(acac)_3$	B	10.0	CH_2Cl_2	7.0	NR
9	$TlCl_3{\cdot}3H_2O$	B	10.0	CH_2Cl_2	2.5	80
10	$Tl(NO_3)_3{\cdot}3H_2O$	A	10.0	CH_2Cl_2	1.5	76
		B	10.0	CH_2Cl_2	1.5	90
		B	5.0	CH_2Cl_2	1.5	84
12	*$Bi(NO_3)_3{\cdot}5H_2O$*	*B*	*5.0*	*CH_3CN*	*1.5*	*92*
			2.0		3.5	68
13	$Bi(NO_3)_3{\cdot}5H_2O$	B	3.0	CH_3CN	3.0	82
			4.0		1.5	90
				$CHCl_3$	5.0	57
				MeOH	5.0	NR[f]
14	$Bi(NO_3)_3{\cdot}5H_2O$	B	5.0	EtOH	6.0	Trace
				H_2O	6.0	NR[f]
				Neat	3.0	24

[a] Benzaldehyde (1 mmol), 1.5 mmol of *p*-anisidine, and 1.2 mmol of allyltributylstannane were used.
[b] The allyl source, A is allyltrimethylsilane and B is allyltributylstannane.
[c] The amount of catalyst was used with respect to aldehyde.
[d] Isolated yields after chromatography purification.
[e] Benzaldehyde (1 mmol), 1.0 mmol of *p*-anisidine, and 1.0 mmol of allyltributylstannane were used.
[f] Only formation of imines was observed.

the synthesis of homoallylic amines has also been reported with allyltributylstannane.[5,6] The effect of various solvents such as CH_2Cl_2, $CHCl_3$, MeOH, EtOH, H_2O, CH_3CN, and solvent-free condition has been studied. CH_3CN is found to be the solvent of choice in terms of yield and reaction time (Table 1).

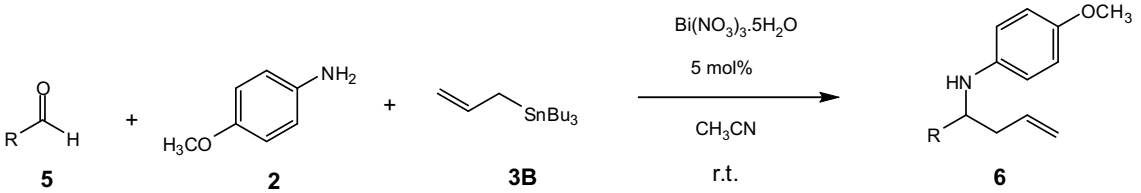
A variety of aldehydes and *p*-ansidine were coupled with allyltributylstannane in CH_3CN at rt so as to give the desired products in excellent yield (Eq. 2 and Table 2). The aldehydes containing electron-donating substituents in the aromatic ring afford the reaction products in excellent yield (entries 2–4). The reactions of *o*, *m*, and *p*-chlorobenzaldehydes with *p*-ansidine give corresponding homoallylic amines in 83, 91, and 87% yield, respectively (entries 6–8). *o*-Chloro isomer indicates slight steric effect that is responsible for the less yield. The reaction of aldehydes containing electron-withdrawing group such as NO_2, CN at *m* or *p*-position in aromatic ring with *p*-ansidine gave no reaction products at all. This indicates that strongly electron-withdrawing group hardly induces the reaction at all (entries 10–12). The acid sensitive heteroaromatic aldehydes such as 2-furaladehyde, 2-thiophenaldehyde, 2-pyridinecarboxaldehyde, and cinnamaldehyde react with *p*-ansidine to offer the corresponding homoallylic amines in considerably good yield (entries 14–16). The reaction of cyclohexane carboxaldehyde and butaraldehyde gives the corresponding products in 80 and 60%, respectively (entries 18 and 19).

We extend our studies of synthesis of other homoallylic amines by allylation of benzaldimines (benzaldehyde and various amines) with allyltributylstannane (Eq. 3 and Table 3). The results are summarized in Table 3, which show that aromatic amines containing electron-donating substituents afford the corresponding homoallylic amines in good yields (entries 2–4). The reactions of 4-chloro- and 4-fluoroaniline with benzaldehyde afford the corresponding homoallylic amines in 85 and 87%, respectively (entries 5 and 6). Under similar reaction condition the reaction of sterically hindered 2,6-diisopropyl aniline, 2-aminopyridine, cyclohexylamine, benzylamine or benzyl carbamate rarely produce desired products at all.

The generality and the excellence of $Bi(NO_3)_3{\cdot}5H_2O$ in terms of the catalyst loading, allylating source, reaction time, and yield can be easily clarified from the comparison of the data with the literature results as is shown in Table 4.

3. Summary

A convenient method for the synthesis of homoallylic amines through three-component coupling reaction has been described. The major advantages of the method are that operational simplicity and low catalyst loading at rt.



(2)

Table 2
Bismuth(III) nitrate pentahydrate catalyzed synthesis of homoallylic amines with different aldehydes[a,b]

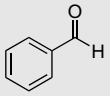
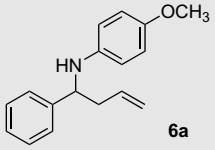
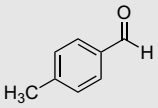
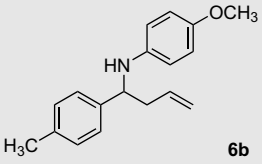
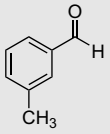
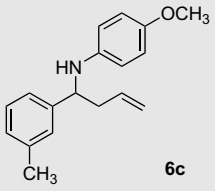
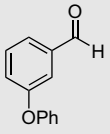
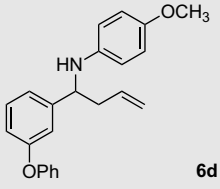
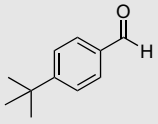
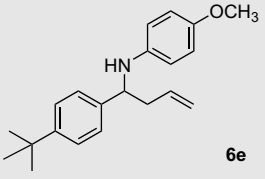
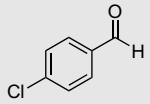
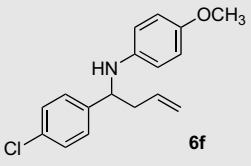
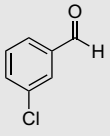
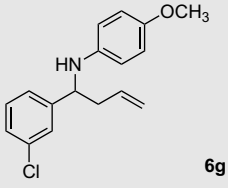
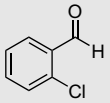
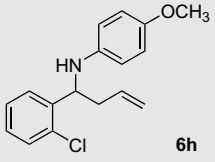
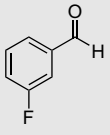
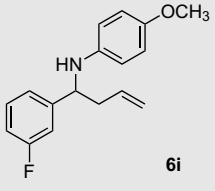
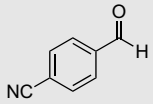
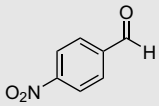
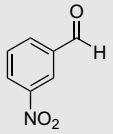
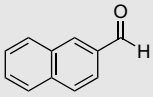
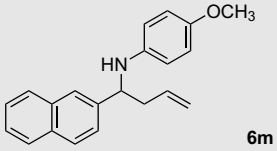
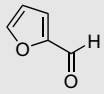
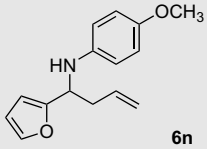
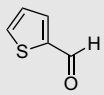
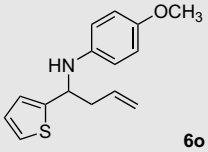
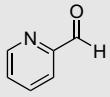
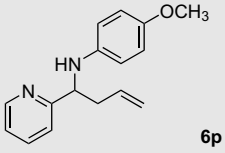
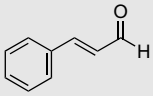
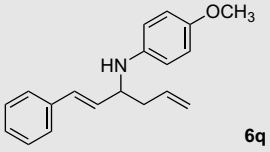
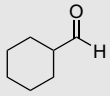
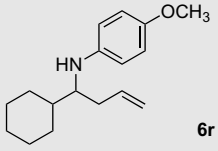
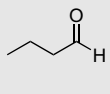
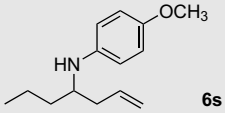
Entry	RCHO	Product	Reaction time (h)	Isolated yields[c] (%)
1		 **6a**	1.5	92
2		 **6b**	1.5	90
3		 **6c**	1.5	90
4		 **6d**	1.5	83
5		 **6e**	1.5	87
6		 **6f**	1.5	87
7		 **6g**	2.0	91
8		 **6h**	2.0	83
9		 **6i**	1.5	88

Table 2 (*continued*)

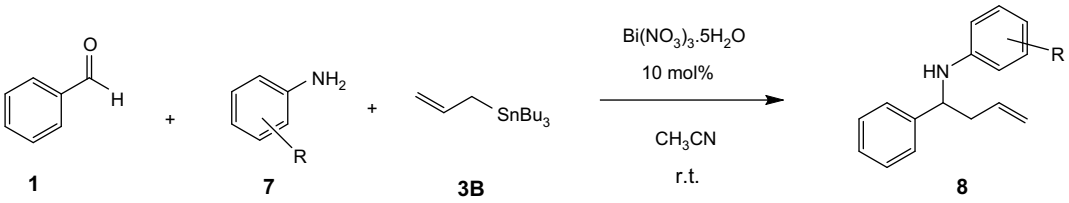
Entry	RCHO	Product	Reaction time (h)	Isolated yields[c] (%)
10		—**6j**	3.0	NR[d]
11		—**6k**	3.0	NR[d]
12		—**6l**	3.0	NR[d]
13		 **6m**	1.5	90
14		 **6n**	2.0	85
15		 **6o**	2.0	88
16		 **6p**	2.0	90
17		 **6q**	2.0	81
18		 **6r**	1.5	80
19		 **6s**	2.0	60

[a] Aldehyde (1 mmol), 1.5 mmol of *p*-anisidine, and 1.2 mmol of allyltributylstannane were used.

[b] The structures of the products were settled from spectral (^{1}H, ^{13}C NMR, MS) data. The spectral data (^{1}H, ^{13}C NMR, and MS) of the compounds are compared with the literature values.

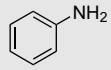
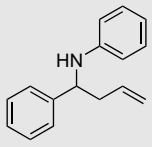
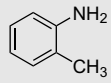
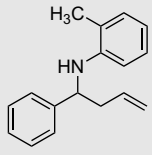
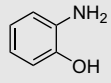
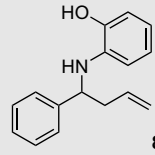
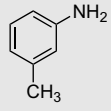
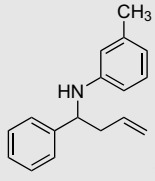
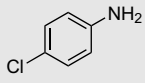
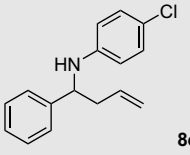
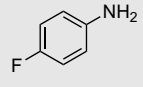
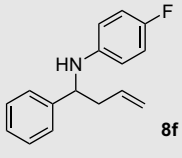
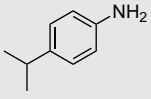
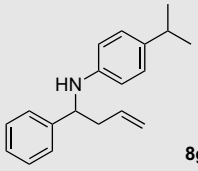
[c] Isolated yields after chromatography purification.

[d] In case of the imine containing electron-withdrawing substituents (*p*-NO_2, *m*-NO_2, and *p*-CN), allyltributylstannane reacts with aldehyde to give homoallylic alcohol instead of forming the homoallylic amines between the reaction of the imine and the allyltributylstannane.



(3)

Table 3
Bismuth(III) nitrate pentahydrate catalyzed synthesis of homoallylic amines with different amines[a,b]

Entry	Amine	Product	Reaction time (h)	Isolated yields[c] (%)
1		 **8a**	2.0	91
2		 **8b**	3.0	87
3		 **8c**	3.0	90
4		 **8d**	3.0	90
5		 **8e**	3.0	85
6		 **8f**	3.0	87
7		 **8g**	3.0	89

[a] Benzaldehyde (1 mmol), 1.5 mmol of amines, and 1.2 mmols of allyltributylstannane were used.
[b] The structures of the products were settled from spectral (^{1}H, ^{13}C NMR, MS) data. The spectral data (^{1}H, ^{13}C NMR, and MS) of the compounds are compared with the literature values.
[c] Isolated yields after chromatography purification.

Table 4
$Bi(NO_3)_3\cdot 5H_2O$ catalyzed synthesis of *N*-(1-phenylbut-3-enyl)aniline (**8a**) in comparison with other literatures

Entry	Catalyst/equiv	Allyltributyl stannane (equiv)	Reaction temperature	Reaction time (h)	Isolated yield[a,b] (%)	Reference
1	$BF_3\cdot OEt_2$/1.0	2.0	−78 °C	2.5	73	5a
2	$TiCl_4$/1.0	2.0	−78 °C	2.5	53	5a
3	$PdCl_2(PPh_3)_2$/0.1	1.0	rt	4 days	64	5b
4	$PtCl_2(PPh_3)_2$/0.1	1.0	rt	4 days	90	5b
5	Bis-allylpalladium complex/0.05	1.2	0	20	70	5c
6	$Yb(OTf)_3$/0.2	1.0	−45 °C	12	81	5d
7	$Sc(OTf)_3$/0.2 and SDS/0.2	1.5	rt	20	83	5e
8	$LiClO_4$/0.2	1.0	rt	3.0	90	5f
9	$TaCl_5$/1.0	2.0	−78 °C	3.0	92	5g
10	$ZrOCl_2\cdot 8H_2O$/0.2	1.2	60 °C	5.0	87	5h
11	Sulfamic acid/0.05	1.2	rt	1.0	90	6a
12	$Bi(NO_3)_3\cdot 5H_2O$/0.1	1.2	rt	2.0	91	Present method

[a] Isolated yields after chromatography purification.
[b] Other substrates have also shown similar trend of the yield.

4. Experimental

4.1. General methods

In all the cases the ^{1}H NMR spectra were recorded with Varian Gemini 200 or 400 MHz instrument. Chemical shifts are reported in parts per million in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR data were collected on Varian Gemini 200 or 400 MHz instrument (50 or 100 MHz). Compounds have been also identified by HRMS (EI) with Jeol DMX 303.

4.2. General experimental procedure

To a mixture of aldehyde (1 mmol) and amine (1.5 mmol) in acetonitrile (2 mL) was added bismuth(III) nitrate pentahydrate (5–10 mol %) that was stirred for 5 min at rt. Then allyltributylstannane (1.2 mmol) was added that was stirred at rt. The progress of the reaction mixture was monitored by TLC. After completion of the reaction, the mixture was filtered. The filtrate was concentrated and the viscous mass was subjected to silica gel column chromatography using 0.5% EtOAc in *n*-hexane as eluent.

4.3. The spectral data of the products

*4.3.1. 4-Methoxy-N-(1-phenylbut-3-enyl)aniline (**6a**)*

Yellow viscous mass; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.38–7.16 (5H, m), 6.67 (2H, d, J=8.8 Hz), 6.44 (2H, d, J=8.8 Hz), 5.82–5.71 (1H, m), 5.20–5.10 (2H, m), 4.28 (1H, dd, J=8.0, 4.6 Hz), 3.91 (1H, br s), 3.66 (3H, s), 2.60–2.40 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.9, 143.7, 141.5, 134.7, 128.5, 126.9, 126.3, 118.1, 114.6, 114.5, 57.9, 55.6, 43.3. Analytical data are consistent with reported literature values.[9a]

*4.3.2. 4-Methoxy-N-(1-p-tolylbut-3-enyl)aniline (**6b**)*

Light yellow viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21 (2H, d, J=8.4 Hz), 7.07 (2H, d, J=8.4 Hz), 6.65 (2H, d, J=8.9 Hz), 6.41 (2H, d, J=8.9 Hz), 5.79–5.69 (1H, m), 5.18–5.09 (2H, m), 4.24 (1H, dd, J=8.2, 4.8 Hz), 3.94 (1H, br s), 3.67 (3H, s), 2.59–2.55 (1H, m), 2.53–2.41 (1H, m), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 141.5, 140.7, 136.1, 134.9, 129.2, 126.2, 118.0, 114.7, 114.6, 96.2, 57.7, 43.4, 21.1; HRMS-EI (m/z): $[M]^+$ calcd for $C_{18}H_{21}NO$: 267.1623, found: 267.1624.

*4.3.3. 4-Methoxy-N-(1-m-tolylbut-3-enyl)aniline (**6c**)*

Light yellow viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23–7.16 (3H, m), 7.05 (1H, d, J=8.5 Hz), 6.70 (2H, d, J=8.7 Hz), 6.48 (2H, d, J=8.7 Hz), 5.74–5.72 (1H, m), 5.21–5.13 (2H, m), 4.28 (1H, dd, J=8.0, 4.5 Hz), 3.97 (1H, br s), 3.85 (3H, s), 2.63–2.58 (1H, m), 2.54–2.42 (1H, m), 2.38 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.9, 143.8, 141.7, 138.1, 134.9, 128.4, 127.7, 126.9, 123.4, 118.1, 114.7, 114.6, 57.9, 55.7, 43.4, 21.5; HRMS-EI (m/z): $[M]^+$ calcd for $C_{18}H_{21}NO$: 267.1623, found: 267.1624.

*4.3.4. 4-Methoxy-N-(1-(3-phenoxyphenyl)but-3-enyl)aniline (**6d**)*

Colorless viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33–7.21 (3H, m), 7.12–7.04 (3H, m), 6.95 (2H, d, J=8.4 Hz), 6.85 (1H, dd, J=8.4, 1.5 Hz), 6.67 (2H, d, J=8.7 Hz), 6.43 (2H, d, J=8.7 Hz), 5.81–5.68 (1H, m), 5.20–5.10 (2H, m), 4.27 (1H, dd, J=8.0, 4.0 Hz), 3.68 (3H, s), 2.60–2.52 (1H, m), 2.47–2.42 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.9, 157.2, 152.0, 146.0, 141.2, 134.5, 129.8, 129.6, 123.0, 121.3, 118.5, 118.3, 117.3, 117.0, 114.7, 114.6, 57.7, 55.7, 43.1; HRMS-EI (m/z): $[M]^+$ calcd for $C_{23}H_{23}NO_2$: 345.1728, found: 345.1721.

*4.3.5. N-(1-(4-tert-Butylphenyl)but-3-enyl)-4-methoxyaniline (**6e**)*

Colorless viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (2H, d, J=8.0 Hz), 7. 29 (2H, d, J=8.0 Hz), 6.71 (2H, d, J=8.7 Hz), 6.50 (2H, d, J=8.7 Hz), 5.83–5.76 (1H, m), 5.21–5.14 (2H, m), 4.31 (1H, dd, J=8.4, 4.8 Hz), 3.84 (1H, br s), 3.71 (3H, s), 2.65–2.58 (1H, m), 2.53–2.47 (1H, m), 1.37 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 149.6, 141.8, 140.6, 135.0, 125.9, 125.4, 118.0, 114.7, 114.6, 57.5, 55.7, 43.3, 31.4, 15.3; HRMS-EI (m/z): $[M]^+$ calcd for $C_{21}H_{27}NO$: 309.2092, found: 309.2092.

*4.3.6. N-(1-(4-Chlorophenyl)but-3-enyl)-4-methoxyaniline (**6f**)*

Yellow viscous mass; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.30–7.21 (4H, m), 6.67 (2H, d, J=9.0 Hz), 6.41 (2H, d, J=9.0 Hz), 5.80–5.63 (1H, m), 5.20–5.11 (2H, m), 4.23 (1H, dd, J=8.2, 5.0 Hz), 3.87 (1H, br s), 3.67 (3H, s), 2.60–2.33 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.1, 142.3, 141.2, 134.3, 132.4, 128.7, 127.7, 118.5, 114.7, 114.6, 57.3, 55.6, 43.2. Analytical data are consistent with reported literature values.[9a]

*4.3.7. N-(1-(3-Chlorophenyl)but-3-enyl)-4-methoxyaniline (**6g**)*

Yellow viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (1H, d, J=1.5 Hz), 7.28 (1H, dd, J=8.0, 1.5 Hz), 7.26–7.20 (2H, m), 6.71 (2H, d, J=8.8 Hz), 6.45 (2H, d, J=8.8 Hz), 5.80–5.62 (1H, m), 5.23–5.15 (2H, m), 4.29 (1H, dd, J=8.6, 4.8 Hz), 3.90 (1H, br s), 3.69 (3H, s), 2.62–2.57 (1H, m), 2.55–2.44 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 146.3, 141.2, 134.3, 134.2, 129.8, 127.1, 126.4, 124.5, 118.6, 114.6, 114.5, 57.5, 55.6, 43.2; HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{18}NClO$: 287.1076, found: 287.1080.

*4.3.8. N-(1-(2-Chlorophenyl)but-3-enyl)-4-methoxyaniline (**6h**)*

Yellow viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (1H, d, J=8.0 Hz), 7.39 (1H, d, J=8.0 Hz), 7.21–7.17 (2H, m), 6.70 (2H, d, J=9.0 Hz), 6.41 (2H, d, J=9.0 Hz), 5.86–5.76 (1H, m), 5.26–5.15 (2H, m), 4.81 (1H, dd, J=8.4, 4.5 Hz), 3.99 (1H, br s), 3.67 (3H, s), 2.78–2.69 (1H, m), 2.43–2.38 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.3, 140.4, 139.8, 133.8, 131.9, 129.0, 127.4, 126.9, 126.5, 117.8, 114.0, 113.7, 55.0, 53.4, 40.1; HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{18}NClO$: 287.1076, found: 287.1078.

*4.3.9. N-(1-(3-Fluorophenyl)but-3-enyl)-4-methoxyaniline (**6i**)*

Brown viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.22 (1H, m), 7.12 (1H, d, J=8.0 Hz), 7.06 (1H, dd, J=8.0, 1.2 Hz), 6.89 (1H, td, J=8.5, 4.5 Hz), 6.66 (2H, d, J=8.8 Hz), 6.42 (2H, d, J=8.8 Hz), 5.78–5.68 (1H, m), 5.19–5.10 (2H, m), 4.26 (1H, dd, J=8.4, 4.1 Hz), 3.67 (3H, s), 2.58–2.51 (1H, m), 2.49–2.41 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.6, 152.1, 146.9, 146.8, 141.2, 134.3, 130.1, 129.9, 121.9, 118.6, 114.7, 114.6, 57.5, 55.7, 43.2; HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{18}NFO$: 271.1372, found: 271.1378.

*4.3.10. 4-Methoxy-N-(1-(naphthalene-2-yl)but-3-enyl)aniline (**6m**)*

Brown viscous mass; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.82–7.64 (4H, m), 7.52–7.37 (3H, m), 6.64 (2H, d, J=8.6 Hz), 6.44 (2H, d, J=8.6 Hz), 5.82–5.65 (1H, m), 5.22–5.11 (2H, m), 4.40 (1H, dd, J=8.0, 5.0 Hz), 3.99 (1H, br s), 3.62 (3H, s), 2.72–239 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 141.6, 141.3, 134.7, 133.5, 132.7, 128.3, 127.8, 127.6, 125.9, 125.4, 124.9, 124.7, 118.3, 114.7, 114.6, 58.1, 55.6, 43.3. Analytical data are consistent with reported literature values.[9a]

*4.3.11. N-(1-(Furan-2-yl)but-3-enyl)-4-methoxyaniline (**6n**)*

Yellow viscous mass; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.34–7.32 (1H, m), 6.73 (2H, d, J=9.0 Hz), 6.56 (2H, d, J=9.0 Hz), 6.26 (1H, dd, J=3.5, 2.0 Hz), 6.15 (1H, dd, J=3.5, 2.0 Hz), 5.81–5.68 (1H, m), 5.18–5.07 (2H, m), 4.41 (1H, dd, J=8.0, 4.5 Hz), 3.71 (3H, s), 2.63–2.46 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 152.9, 142.0, 141.7, 134.7, 118.9, 115.7, 115.3, 110.7, 106.7, 56.3, 52.9, 39.9. Analytical data are consistent with reported literature values.[9a]

*4.3.12. 4-Methoxy-N-(1-(thiophen-2-yl)but-3-enyl)aniline (**6o**)*

Brown viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.17 (1H, d, J=5.0 Hz), 6.98–6.93 (2H, m), 6.73 (2H, d, J=8.8 Hz), 6.57 (2H, d, J=8.8 Hz), 5.86–5.78 (1H, m), 5.24–5.16 (2H, m), 4.64 (1H, dd, J=8.0, 4.5 Hz), 3.87 (1H, br s), 3.76 (3H, s), 2.76–2.60 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.4, 149.0, 141.2, 134.1, 126.7, 123.7, 123.3, 118.6, 115.0, 114.6, 55.6, 54.3, 43.2; HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{17}NOS$: 259.1030, found: 259.1027.

*4.3.13. 4-Methoxy-N-(1-(pyridine-2-yl)but-3-enyl)aniline (**6p**)*

Yellow viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (1H, d, J=6.5 Hz), 7.60 (1H, m), 7.35 (1H, d, J=8.0 Hz), 7.12 (1H, m), 6.70 (2H, d, J=8.9 Hz), 6.50 (2H, d, J=8.9 Hz), 5.82–5.69 (1H, m), 5.18–5.09 (2H, m), 4.46 (1H, dd, J=8.2, 4.6 Hz), 4.20 (1H, br s), 3.68 (3H, s), 2.73–2.66 (1H, m), 2.56–2.50 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.7, 152.0, 149.3, 141.3, 136.6, 134.6, 121.9, 120.9, 118.2, 114.7, 114.6, 59.3, 55.6, 41.3; HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{18}N_2O$: 254.1419, found: 254.1401.

*4.3.14. (E)-4-Methoxy-N-(1-phenylhexa-1,5-dien-3yl)aniline (**6q**)*

Light yellow viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.16 (5H, m), 6.75 (1H, d, J=9.0 Hz), 6.65–6.53 (3H, m), 6.18 (1H, dd, J=15.8, 6.0 Hz), 5.91–5.78 (1H, m), 5.22–5.10 (2H, m), 4.26 (1H, dd, J=8.2, 4.6 Hz), 3.72 (3H, s), 2.58–2.51 (1H, m), 2.48–2.41 (1H, m). Analytical data are consistent with reported literature values.[9a]

*4.3.15. N-(1-Cyclohexylbut-3-enyl)-4-methoxyaniline (**6r**)*

Colorless viscous mass; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.75 (2H, d, J=9.0 Hz), 6.53 (2H, d, J=9.0 Hz), 5.86–5.75 (1H, m), 5.10–4.99 (2H, m), 3.80–3.69 (1H, m), 3.74 (3H, s), 3.26 (1H, br s), 3.20 (1H, dd, J=8.0, 4.0 Hz), 2.37–2.10 (2H, m), 1.87–1.60 (5H, m), 1.55–1.43 (1H, m), 1.29–0.97 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.4, 142.6, 135.7, 116.9, 114.8, 114.3, 58.4, 55.7, 41.1, 35.7, 29.3, 29.0, 26.6, 26.4. Analytical data are consistent with reported literature values.[9a]

*4.3.16. N-(1-Hept-1-en-4-yl)-4-methoxyaniline (**6s**)*

Yellow viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.71 (2H, d, J=8.8 Hz), 6.50 (2H, d, J=8.8 Hz), 5.83–5.76 (1H, m), 5.09–4.98 (2H, m), 3.71 (3H, s), 3.22 (1H, br s), 3.14 (1H, J=8.4, 4.0 Hz), 2.30–2.25 (2H, m), 2.18–2.10 (1H, m), 1.86–1.80 (2H, m), 0.87 (3H, t, J=6.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7, 135.8, 117.1, 117.0, 114.9, 114.5, 59.0, 55.8, 35.4, 30.6, 18.6, 15.1; HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{21}NO$: 219.1623, found: 219.1609.

*4.3.17. N-(1-Phenylbut-3-enyl)aniline (**8a**)*

Light yellow viscous mass; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.30 (5H, m), 7.07 (2H, t, J=8.8 Hz), 6.66 (1H, t, J=7.2 Hz), 6.50 (2H, m), 5.75 (1H, m), 5.15 (2H, m), 4.40 (1H, m), 2.55 (2H, m). Analytical data are consistent with reported literature values.[9b]

*4.3.18. 2-Methyl-N-(1-phenylbut-3-enyl)aniline (**8b**)*

Yellow viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40–7.34 (4H, m), 7.28–7.23 (1H, m), 7.12 (1H, d, J=7.6 Hz), 6.89 (1H, t, J=7.6 Hz), 6.61 (1H, t, J=7.6 Hz), 6.31 (1H, d, J=7.6 Hz), 5.86–5.78 (1H, m), 5.27–5.18 (2H, m), 4.43 (1H, dd, J=8.0, 4.0 Hz), 4.11 (1H, br s), 2.72–2.66 (1H, m), 2.58–2.50 (1H, m), 2.23 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.8, 144.3, 135.6, 130.5, 129.2, 127.5, 126.8, 122.6, 119.0, 117.5, 111.8, 57.5, 44.3, 18.1; HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{19}N$: 237.1517, found: 237.1514.

*4.3.19. 2-(1-Phenylbut-3-enylamino)phenol (**8c**)*

Black viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.21 (6H, m), 6.60 (2H, d, J=9.0 Hz), 6.42–6.37 (1H, m), 5.83–5.78 (1H, m), 5.25–5.16 (2H, m), 4.64 (1H, br s), 4.38 (1H, br s), 2.62–2.53 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 135.9, 134.6, 128.5, 126.9, 126.3, 121.4, 118.2, 117.6, 114.1, 113.6, 57.7, 43.0; HRMS-EI (m/z): $[M]^+$ calcd for $C_{19}H_{23}N$: 239.1310, found: 239.1310.

*4.3.20. 3-Methyl-N-(1-phenylbut-3-enyl)aniline (**8d**)*

Yellow viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.31 (4H, m), 7.29–7.25 (1H, m), 6.98–6.95 (1H, m), 6.48 (1H, d, J=7.8 Hz), 6.39 (1H, s), 6.36 (1H, d, J=7.8 Hz), 5.82–5.74 (1H, m), 5.21–5.17 (2H, m), 4.40 (1H, dd, J=8.0, 4.2 Hz), 4.12 (1H, br s), 2.67–2.59 (1H, m), 2.57–2.48 (1H, m), 2.23 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.0, 144.3, 139.4, 135.3, 129.6, 129.2, 127.5, 126.9, 118.9, 118.8, 114.9, 111.0, 57.7, 43.9, 22.2; HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{19}N$: 237.1517, found: 237.1514.

*4.3.21. 4-Chloro-N-(1-phenylbut-3-enyl)aniline (**8e**)*

Yellow viscous mass; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.38–7.10 (5H, m), 6.97 (2H, d, J=8.5 Hz), 6.35 (2H, d, J=8.5 Hz), 5.82–5.71 (1H, m), 5.25–5.10 (2H, m), 4.32 (1H, dd, J=8.2, 4.6 Hz), 4.08 (1H, br s), 2.69–2.38 (2H, m), 1.87–1.60 (5H, m), 1.55–1.43 (1H, m), 1.29–0.97 (5H, m). Analytical data are consistent with reported literature values.[9c]

*4.3.22. 4-Fluoro-N-(1-phenylbut-3-enyl)aniline (**8f**)*

Brown viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34–7.21 (3H, m), 7.27–7.21 (1H, m), 6.78 (2H, t, J=8.6 Hz), 6.23 (2H, d, J=8.6 Hz), 6.39 (1H, s), 5.78–5.71 (1H, m), 5.20–5.11 (2H, m), 4.29 (1H, dd, J=8.0, 4.2 Hz), 4.14 (1H, br s), 2.64–2.58 (1H, m), 2.51–2.42 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.3, 143.8, 143.7, 134.6, 128.6, 127.1, 126.2, 118.4, 115.7, 115.2, 114.3, 114.1, 57.6, 43.4; HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{16}FN$: 241.1266, found: 241.1265.

*4.3.23. 4-Isopropyl-N-(1-phenylbut-3-enyl)aniline (**8f**)*

Light yellow viscous mass; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44–7.36 (4H, m), 7.31–7.23 (1H, m), 6.99 (2H, d, J=7.8 Hz), 6.50 (2H, d, J=7.8 Hz), 5.86–5.78 (1H, m), 5.22–5.16 (2H, m), 4.38 (1H, dd, J=7.6, 4.0 Hz), 4.11 (1H, br s), 2.81–2.76 (1H, m), 2.66–2.60 (1H, m), 2.51–2.45 (1H, m), 1.20 (6H, d, J=6.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.3, 143.9, 137.7, 134.8, 128.5, 126.9, 126.8, 126.3, 118.2, 113.4, 57.4, 43.4, 33.0, 24.2; HRMS-EI (m/z): $[M]^+$ calcd for $C_{19}H_{23}N$: 265.1830, found: 265.1837.

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