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To cite this article: Mohan R. Shetty , Siddheshwar W. Kshirsagar , Srikanth V. Lanka & Shrinivas D. Samant (2012) Synthesis of *N,N*-diallylanilines by the reaction of anilines and allyl bromide in the presence of Mg–Al hydrotalcites at ambient temperature, Green Chemistry Letters and Reviews, 5:3, 291-301, DOI: [10.1080/17518253.2011.624127](https://doi.org/10.1080/17518253.2011.624127)

To link to this article: <https://doi.org/10.1080/17518253.2011.624127>



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Published online: 05 Dec 2011.



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## RESEARCH LETTER

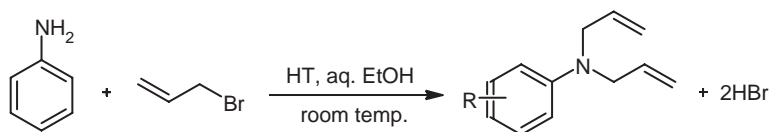
### Synthesis of *N,N*-diallylanilines by the reaction of anilines and allyl bromide in the presence of Mg–Al hydrotalcites at ambient temperature

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(Received 14 April 2011; final version received 9 August 2011)

Anilines react with two equivalents of allyl bromide in aqueous ethanol in the presence of Mg–Al hydrotalcites (Mg/Al = 5, 3, 2) at room temperature to give *N,N*-diallylanilines in good yield. Hydrotalcites (HTs) are mild and efficient catalysts, which can be easily recovered and reused. In this project, efforts are made to check the activity of the calcined and uncalcined HTs. Also, the methodology can be extended for the synthesis of various *N,N*-diallylanilines.



**Keywords:** Mg–Al hydrotalcites; primary amines; diallylation of anilines

#### Introduction

*N,N*-diallylanilines are an important class of compounds which are precursors of nitrogen heterocycles, such as lactams, pyrroles, indoles, and quinolines. These compounds possess a number of biological activities and have been found to show antimalarial, antibacterial, antiasthmatic, antihypertensive, and antiinflammatory activities (1). They are also precursors to many natural products (2). Olefin metathesis has given an impetus to the preparation of the bisallylated compounds as they are useful precursors for the ring closing metathesis to give *N*-aryldihydropyrroles (3).

*N*-allylation of aniline is carried out by the reaction of aniline and allyl bromide in the presence of an acid scavenger, for example  $\text{Na}_2\text{CO}_3$  in ethanol (4), sodium lauryl sulfate,  $\text{NaHCO}_3$  in water (5),  $\text{PhLi}$  in diethyl ether (6),  $\text{N}(\text{Et})_3$  in acetonitrile (7),  $\text{Al}_2\text{O}_3$  zeolite KY in benzene (8), and  $\text{KOH}$  in THF (9). It is also carried out by the reaction of aniline and allyl alcohol using platinum complexes, e.g.  $\text{Pt}(\text{eta}^3\text{-allyl})(\text{xantphos})\text{OTf}$  in DMF (10).  $\text{Pt}(\text{COD})\text{Cl}_2$ , bis[2-(diphenylphosphino)phenyl ether] in dioxane (11) or  $\text{HgO-HBF}_4$  in THF (12). There are few reports on

the *N*-allylation reaction using palladium complex catalyst, for example 1,2-(*p*- $\text{MeOC}_6\text{H}_4$ )<sub>2</sub>cyclobuten[ =  $\text{P}(2,4,6\text{-tri-}t\text{-BuPh})_2$   $\text{PdOTf}$  in toluene (13),  $\text{Mo}_3\text{PdS}_4$  (14),  $\text{Pd}\cdot\text{Et}_3\text{B}$  (15),  $\text{Ti}(\text{O-}i\text{Pr})_4$   $\text{Pd}(\text{OCOCF}_3)_2\text{-dppb}$  in benzene (16), and  $\text{Pd}\{\text{P}(\text{OC}_6\text{H}_5)_3\}_4$  in toluene (17). There is also a recent report on *N*-allylation of amines using silica as a heterogeneous catalyst (18). Though, better results are obtained using homogeneous liquid phase catalysts; these are not environmentally benign. Some of the aforementioned procedures use harsh reaction conditions, use expensive catalysts, and require longer reaction time. Also, catalysts recovery and recyclability is the major issue encountered. Further, the methods are not atom economic. Considering the importance of diallylanilines, a green and efficient method is needed.

Hydrotalcites (HTs) are anionic clays having basic properties. Mg/Al HTs are commonly used as solid base catalysts for a number of organic reactions (19,20). Herein we report a greener method for the preparation of *N,N*-diallylanilines by the reaction of aniline with allyl bromide in the presence of a Mg/Al HTs as solid bases in aqueous ethanol at ambient temperature.

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## Results and discussion

The reaction of aniline and two equivalents of allyl bromide was carried out without catalyst in aq. ethanol (50% v/v). It was found that the conversion of the aniline was low even after 90 minutes and a mixture of monoallyl and diallyl anilines was formed (Entry 1, Table 1). Mg/Al HTs with different Mg/Al ratios, HT5, HT3, and HT2, were prepared corresponding to Mg/Al = 5, 3, 2 by the reported procedure (21). The HTs were calcined at 550°C to obtain porous metal oxides (HT5C, HT3C, and HT2C). To study the effect of calcined and uncalcined catalyst, the reaction of aniline and two equivalents of allyl bromide was carried in aq. ethanol (50% v/v) (Table 1). All the HTs were found to catalyze the reaction and among them HT5 was found to be the best catalyst which could be reused. There is no much difference in the yield of the product catalyzed by calcined and uncalcined catalyst. The possible reason may be the reaction requires minimum basicity. Also, there is difference in the yields obtained in substrate study (Table 4); the reason here could be the catalysts may be acting as a scavenger of the acid generated in the reaction. In these reactions, diallylanilines were obtained as the sole product; monoallylaniline was found in traces.

The reaction was carried out using different quantities of HT5 (Table 2). The catalyst (20 wt.%) with respect to aniline was found to be optimum, where the aniline conversion was maximum. There was no further increase in the product yield, after increasing the catalyst loading.

Table 1. Reaction of aniline and allyl bromide in the presence of different HTs.

Entry	Catalyst	Conversion of aniline (%)	Yield <sup>a</sup> of (%)	
			Monoallyl aniline	Bisallyl aniline
1	No catalyst	–	17 <sup>b</sup>	48 <sup>b</sup>
2	HT5	90	3	87
3	HT3	85	2	83
4	HT2	85	2	83
5	HT5C	87	3	84
6	HT3C	86	2	83
7	HT2C	84	4	80

Note: Reaction conditions: aniline (10 mmol), allyl bromide (20 mmol), catalyst (20 wt.% of aniline), aq. ethanol (50% v/v, 20 mL), temperature RT (30°C).

<sup>a</sup>The yield reported based on GC.

<sup>b</sup>Isolated yield, time 90 min.

Table 2. Reaction of aniline and allyl bromide in the presence of different quantities of HT5.

Entry	Catalyst quantity (wt.% of aniline)	Conversion of aniline (%)	Yield <sup>a</sup> of (%)	
			Monoallyl aniline	Bisallyl aniline
1	20	90	3	87
2	15	85	4	81
3	10	81	3	79
4	5	78	2	76

Notes: Reaction conditions: aniline (10 mmol), allyl bromide (20 mmol), aq. ethanol (50% v/v, 20 mL), temperature RT (30°C). Time 90 min.

<sup>a</sup>The yield reported based on GC.

To check the reusability, recovered HT5 was reused in the reaction of aniline and allyl bromide (Table 3). After each cycle, the catalyst was filtered, washed with aq. NaHCO<sub>3</sub>, ethyl acetate, and water. After washing, the catalyst was air dried at 60°C and used for the successive cycle. It was found that the catalyst (HT5) could be recycled up to three runs.

Using the optimized quantity of HT5, different anilines were reacted with two equivalent of allyl bromide in ethanol at room temperature to obtain the corresponding *N,N*-diallyl anilines (Table 4). The reaction of *p*-nitroaniline at room temperature was sluggish (Entry 4), so the reaction was carried out at 80°C. In this reaction, the diallyl derivative (44%) was formed, along with the monoallyl derivative. The reaction of ortho-trifluoromethyl aniline with allyl bromide also needed high temperature and was carried out at 80°C. In this reaction, only 10% of the diallyl derivative was formed, while 70% of the monoallyl derivative was formed. The products were isolated by column chromatography and characterized by GC-MS and <sup>1</sup>H NMR.

Table 3. The reaction of aniline and allyl bromide in the presence of HT5.

Entry	Run	Conversion of aniline (%)	Yield of <sup>a</sup> (%)	
			Monoallyl aniline	Bisallyl aniline
1	1	90	3	87
2	2	89	4	84
3	3	87	3	81

Notes: Reaction conditions: aniline (10 mmol), allyl bromide (20 mmol), HT5 (20 wt.% of aniline), aq. ethanol (50% v/v, 20 mL), temperature RT (30°C). Time 90 min.

<sup>a</sup>The yield reported based on GC.

Table 4. Reaction of anilines and allyl bromide in the presence of HT5.

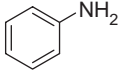
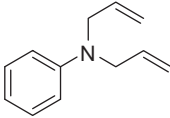
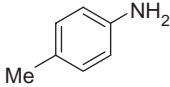
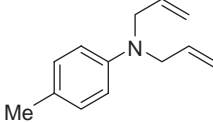
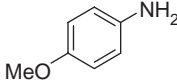
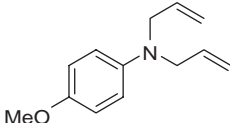
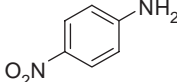
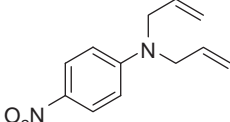
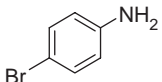
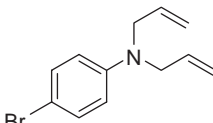
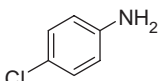
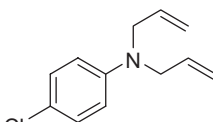
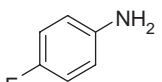
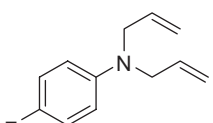
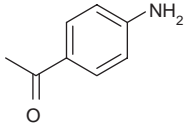
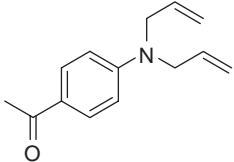
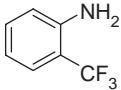
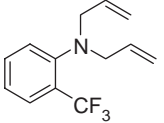
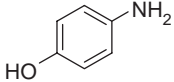
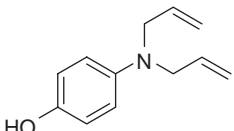
Entry	Amine	Product	Time (min)	Yield <sup>c</sup> (%)
1 <sup>b</sup>			90	80
2			45	71
3 <sup>b</sup>			45	76
4 <sup>a</sup>			120	44
5 <sup>b</sup>			90	70
6			100	69
7			110	63

Table 4 (Continued)

Entry	Amine	Product	Time (min)	Yield <sup>c</sup> (%)
8 <sup>b</sup>			120	62
9 <sup>a</sup>			180	10
10			120	78

Note: Reaction conditions: aniline (10 mmol), allyl bromide (22 mmol), HT5 (20 wt.% of aniline), aq. EtOH (50% v/v, 20 mL), temperature RT (30°C).

<sup>a</sup>Reaction temperature 80°C.

<sup>b</sup>Characterized using <sup>1</sup>H NMR.

<sup>c</sup>Isolated yield.

## Experimental

$^1\text{H}$  NMR spectra of the compounds were recorded on Bruker 400 MHz. GC–MS analysis on Shimadzu-QP 2010 GC–MS having Rt<sub>x</sub> wax capillary column, 30-m length, 0.32-mm diameter, and 0.24-mm inner diameter.

### Catalyst preparation

#### Mg–Al HT-2

An aqueous solution (100 mL) containing  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (25.64 g, 100 mmol) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (18.76 g, 50 mmol) was added drop wise using dropping funnel to a vigorously stirred solution aqueous solution (100 mL) containing NaOH (12 g, 300 mmol) and  $\text{Na}_2\text{CO}_3$  (10.06 g, 100 mmol) taken in a two-necked round bottom flask. After complete addition, the solution was heated at 80°C for 18 h. The solution was allowed to cool to room temperature and filtered. The residue was washed with distilled water several times till the filtrate was neutral (pH paper). The solid was dried in an oven at 60°C in air (electric oven).

Calcination of the dried catalyst at 550°C gave porous metal oxides (HT5C).

Catalysts Mg–Al HT-3 and Mg–Al HT-5 were prepared using above procedure (21).

### General procedure for diallylation of anilines

Aniline (10 mmol), allyl bromide (20 mmol), and HT5 (20 wt.% of aniline) in aqueous ethanol (50% v/v, 20 mL) were stirred in a 25 mL round bottom flask at room temperature. After completion of the reaction, ethanol was evaporated. Ethyl acetate (5 mL) was added to the reaction mass and catalyst was filtered through G4 sintered glass funnel. The solid catalyst was washed with ethyl acetate (2 mL). The filtrate obtained was treated with aq.  $\text{NaHCO}_3$  (5 mL, 20%).

Part A (Tables 1–3): The extract was dried over  $\text{Na}_2\text{SO}_4$  and was collected in a 10 mL-standard volumetric flask. On final dilution, the sample was taken for the GC analysis. The conversion of the reactant and the yield were calculated based on the authentic compounds. GC Analysis was done on Chemito Gas Chromatogram.

Model: GC1000; Column specification: BP10 capillary column, 30-m length, 0.32-mm diameter, and 0.24- $\mu\text{m}$  inner diameter. Detector temperature: 250°C, oven temperature 240°C, Programme: 80°C-0 min-5°C/min-240°C, Flame type: FID.

Part B (Table 4): The extract was evaporated after drying over  $\text{Na}_2\text{SO}_4$ . The product was purified by

column chromatography on silica gel and pet ether as an eluent. The products 1(22), 2(22), 3(18), 4(18), 5(18), 6(2), 7(8) and 10(23) are reported. The products 8 and 9 are new and are characterized by  $^1\text{H}$  NMR and GC–MS, respectively.

### Spectral data

#### 1a: *N,N*-diallylaniline

**Mass spectrum:** ( $\text{C}_{12}\text{H}_{15}\text{N}$ ) 173 ( $\text{M}^+$ ) (base), 158, 146, 130, 117, 104, 91, 51, 41.

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $d_{\text{H}}$ : 3.89–4.00 (m, 4H, 2 $\text{CH}_2$ ), 5.17–5.23(m, 4H, 2 $\text{CH}_2$ =), 5.84–5.94 (m, 2H, 2 $\text{CH}$ =), 6.69–6.74 (m, 2H, 3ArH), 7.21–7.2 (m, 2H, 2ArH) ppm.

#### 2a: *N,N*-diallyl-4-methylaniline

**Mass spectrum:** ( $\text{C}_{13}\text{H}_{17}\text{N}$ ). 187 ( $\text{M}^+$ ) (base), 172, 160, 144, 130, 118, 105, 91, 77, 65.

#### 3a: *N,N*-diallyl-4-methoxyaniline

**Mass spectrum:** ( $\text{C}_{13}\text{H}_{17}\text{NO}$ ). 203 ( $\text{M}^+$ ) (base), 188, 176, 162, 146, 135, 120, 107, 92, 77, 65.

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $d_{\text{H}}$ : 3.75 (s, 3H,  $\text{CH}_3$ ), 3.81–3.92 (m, 4H, 2 $\text{CH}_2$ ), 5.14–5.21(m, 4H, 2 $\text{CH}_2$ =), 5.82–5.90 (m, 2H, 2 $\text{CH}$ =), 6.68–7.26 (m, 4H, 4ArH) ppm.

#### 4a: *N,N*-diallyl-4-nitroaniline

**Mass spectrum:** ( $\text{C}_{12}\text{H}_{14}\text{NO}$ ) 218 ( $\text{M}^+$ ) (base), 203, 191, 171, 157, 145, 130, 117, 103, 91, 77.

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $d_{\text{H}}$ : 3.97–4.07 (m, 4H, 2 $\text{CH}_2$ ), 5.15–5.30 (m, 4H, 2 $\text{CH}_2$ ), 5.80–5.89 (m, 2H, 2 $\text{CH}$ =), 6.57–6.69 (m, 2H, 2ArH), and 8.09–8.16 (m, 2H, 2ArH) ppm.

#### 5a: *N,N*-diallyl-4-bromoaniline

**Mass spectrum:** ( $\text{C}_{12}\text{H}_{10}\text{BrN}$ ) 251 (1:1,  $\text{M}^+$ ) (base), 226, 224, 210, 186, 182, 157, 145, 130, 117, 103, 90, 76, 63, 50.

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $d_{\text{H}}$ : 3.85–3.96 (m, 4H, 2 $\text{CH}_2$ ), 5.14–5.24 (m, 4H, 2 $\text{CH}_2$ =), 5.79–5.88 (m, 2H, 2 $\text{CH}$ =), 6.53–6.63 (m, 2H, 2ArH), and 7.27–7.32 (m, 2H, 2ArH) ppm.

#### 6a: *N,N*-diallyl-4-chloroaniline

**Mass spectrum:** ( $\text{C}_{12}\text{H}_{14}\text{ClN}$ ). 207 ( $\text{M}^+$ ) (base), 182, 180, 164, 140, 130, 113, 111, 89, 75, 63, 51.

#### 7a: *N,N*-diallyl-4-fluoroaniline

**Mass spectrum:** ( $\text{C}_{12}\text{H}_{14}\text{FN}$ ). 191 ( $\text{M}^+$ ) (base), 176, 164, 148, 135, 122, 109, 95, 75, 68.

#### 8a: 1-(4-(diallylamino)phenyl)ethanone

**Mass spectrum:** ( $\text{C}_{14}\text{H}_{17}\text{NO}$ ) 215 ( $\text{M}^+$ ) (base), 200, 188, 172, 158, 146, 130, 118, 103, 91, 77, 65.

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $d_{\text{H}}$ : 2.5 (s, 3H, 1 $\text{CH}_3$ ), 3.94–4.05 (m, 4H, 2 $\text{CH}_2$ ), 5.14–5.26 (m, 4H, 2 $\text{CH}_2$ =), 5.81–5.90 (m, 2H, 2 $\text{CH}$ =), 6.60–6.72 (m, 2H, 2ArH), and 7.80–7.99 (m, 2H, 2ArH) ppm.

#### 9a: *N,N*-diallyl-2-(trifluoromethyl)aniline

**Mass spectrum:** ( $\text{C}_{13}\text{H}_{14}\text{F}_3\text{N}$ ). 201 ( $\text{M}^+$ ) (base), 180, 154, 145, 127, 114, 95, 77, 65.

**10a: 4-(diallylamino)phenol**

**Mass spectrum:** (C<sub>12</sub>H<sub>15</sub>NO). 189 (M<sup>+</sup>) (base), 174, 162, 146, 133, 120, 1075, 93, 77, 65.

**Conclusion**

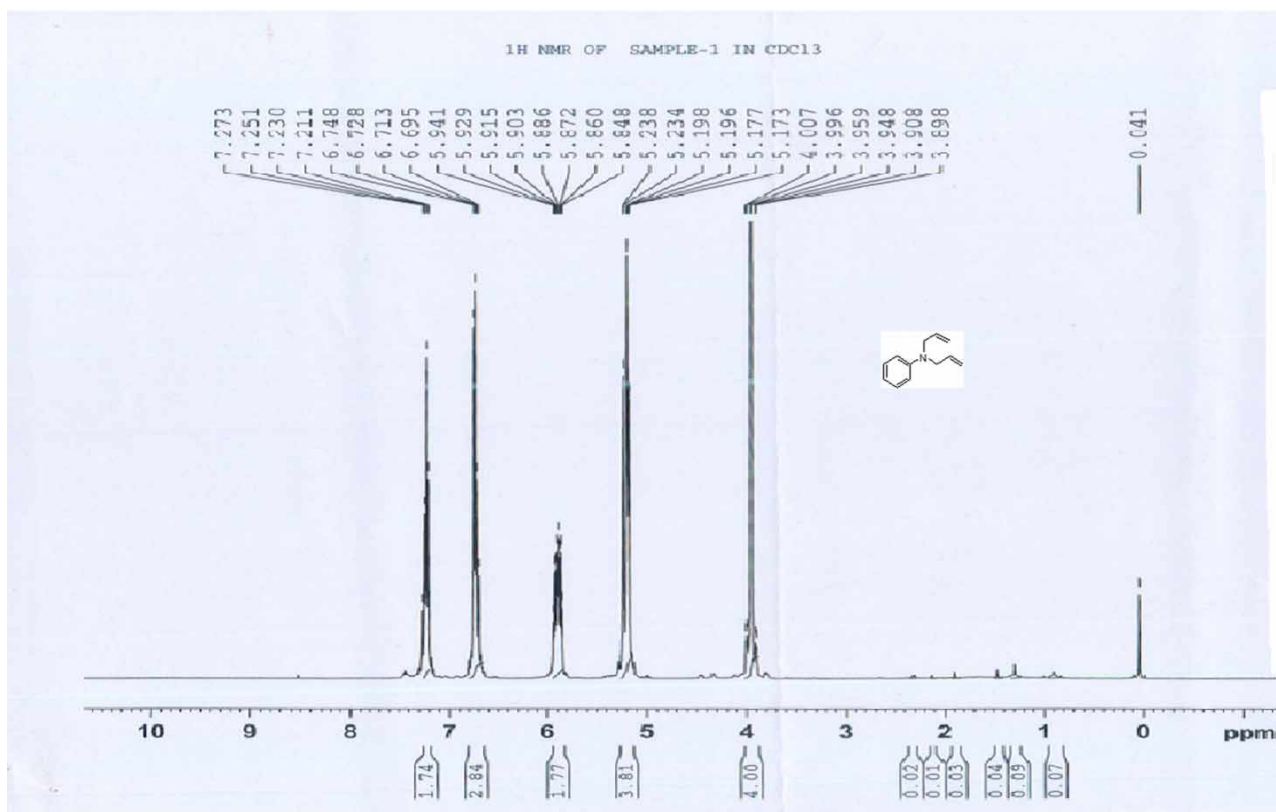
Aromatic primary amines can be effectively diallylated by reacting them with two equivalents of allyl bromide in the presence of Mg/Al HTs (Mg/Al = 5) at room temperature in aqueous ethanol. This method is environmentally benign, convenient to carry out, and the catalyst is recyclable up to three cycles.

**Acknowledgements**

MRS is thankful to the UGC, New Delhi, for a fellowship under UGC-SAP programme.

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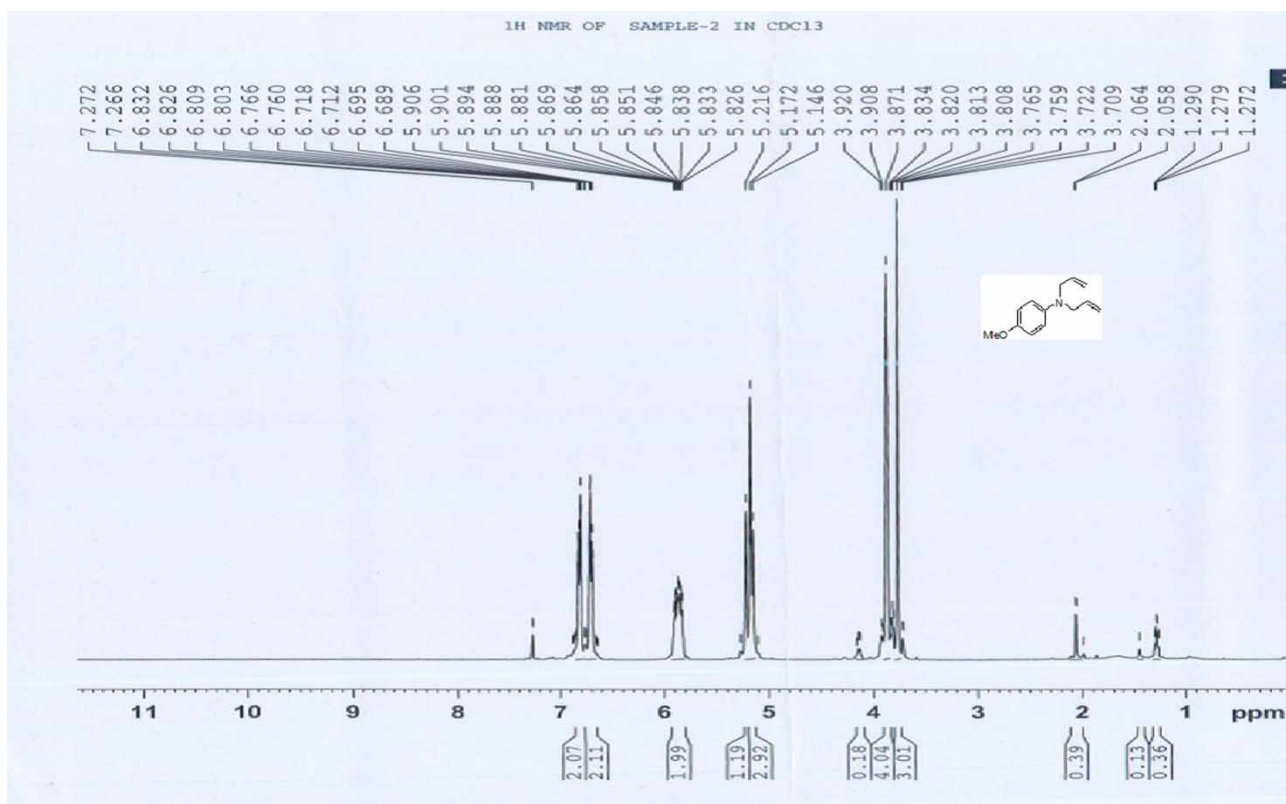
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**1a:**  $^1\text{H}$  NMR of N,N-bisallylaniline

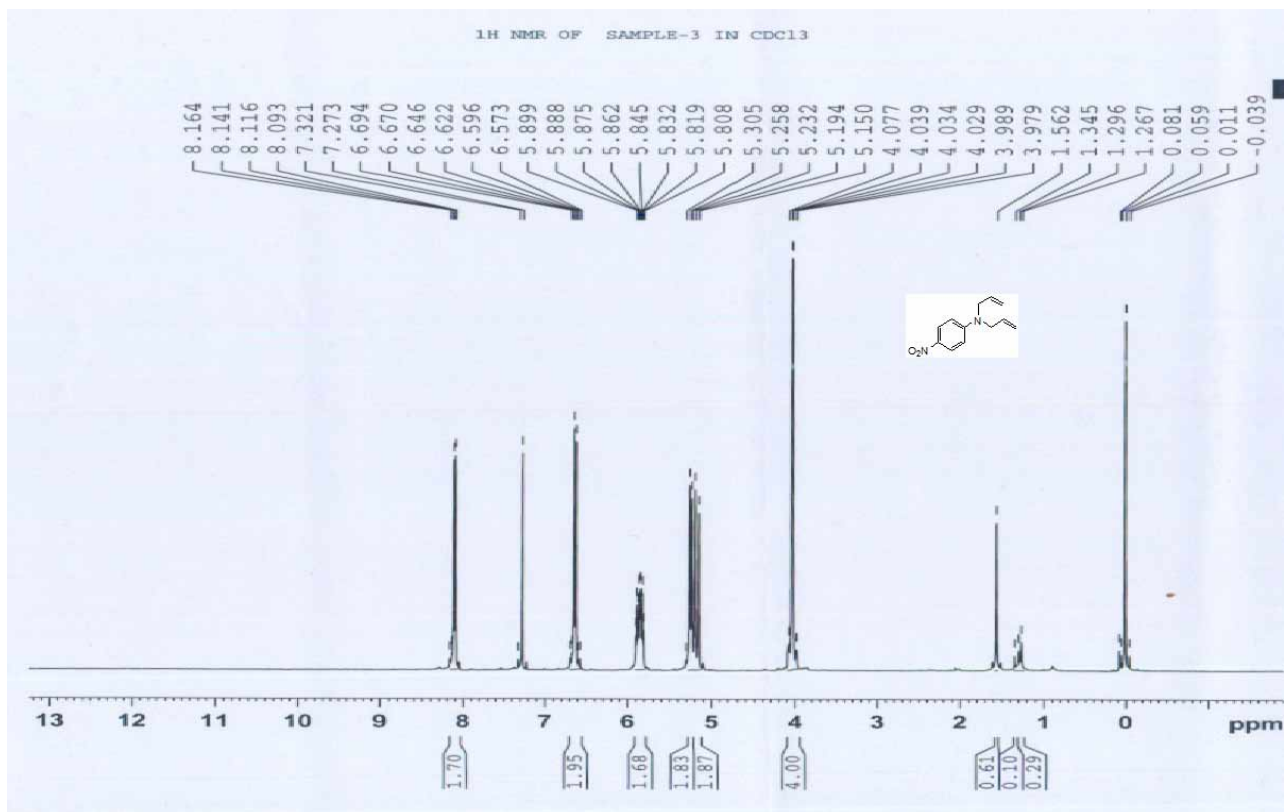
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta\text{H}$ : 3.89–4.00 (m, 4H,  $2\text{CH}_2$ ), 5.17–5.23 (m, 4H,  $2\text{CH}_2 =$ ), 5.84–5.94 (m, 2H,  $2\text{CH} =$ ), 6.69–6.74 (m, 2H,  $3\text{ArH} =$ ), 7.21–7.2 (m, 2H,  $2\text{ArH}$ ) ppm.





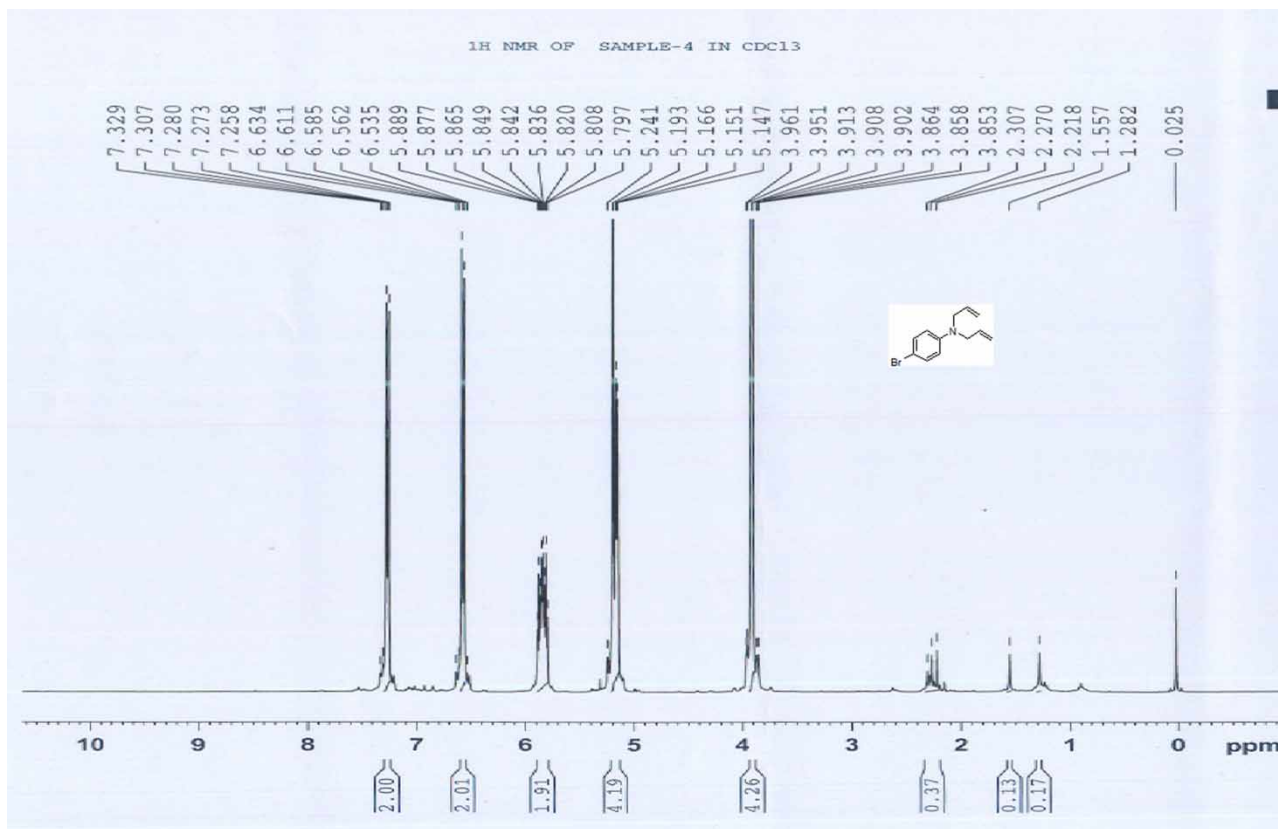
**3a:** <sup>1</sup>H NMR of 4-methoxy N,N-bisallylaniline

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δH: 3.75 (s, 3H, CH<sub>3</sub>), 3.81–3.92 (m, 4H, 2CH<sub>2</sub>), 5.14–5.21 (m, 4H, 2CH<sub>2</sub> =), 5.82–5.90 (m, 2H, 2CH =), 6.68–7.26 (m, 4H, 4ArH) ppm



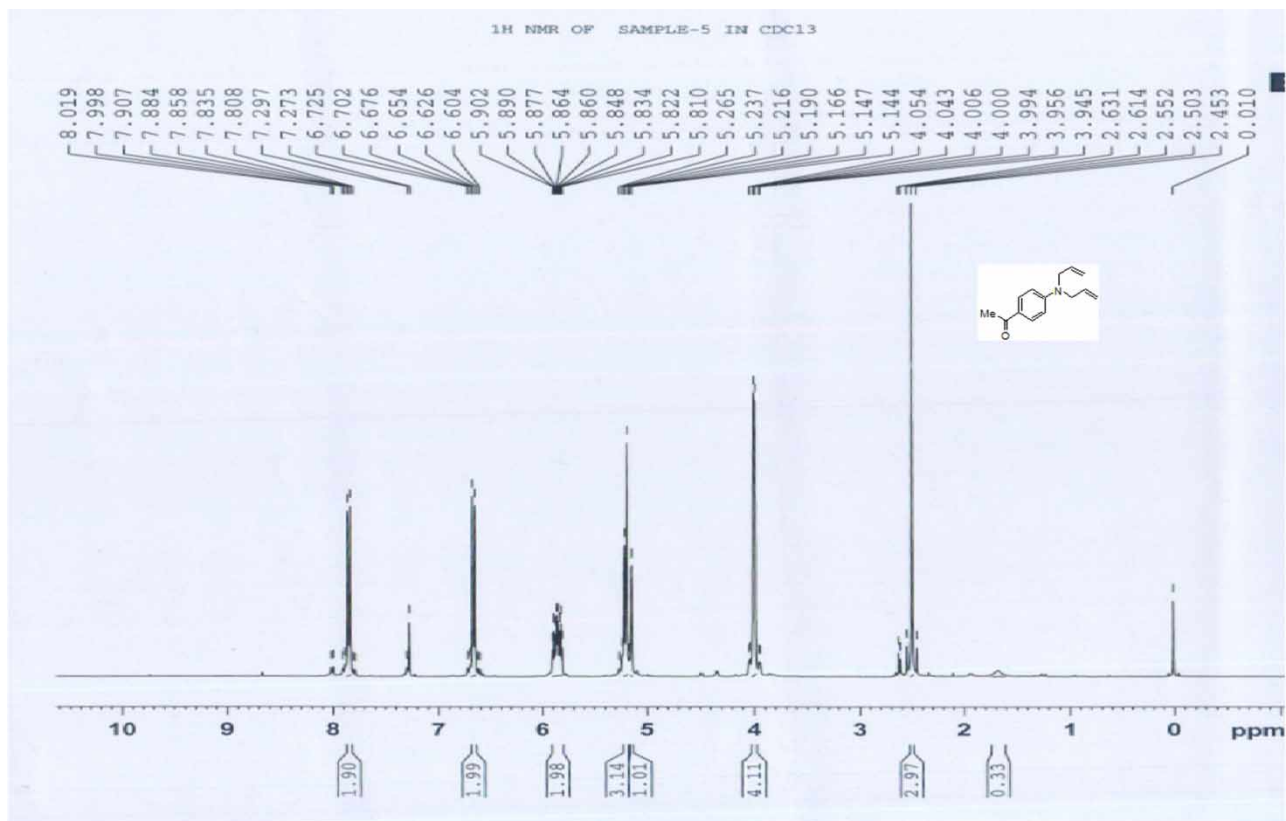
**4a:**  $^1\text{H}$  NMR of 4-nitro N,N-bisallylaniline

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta\text{H}$ : 3.97–4.07 (m, 4H, 2CH<sub>2</sub>), 5.15–5.30 (m, 4H, 2CH<sub>2</sub>), 5.80–5.89 (m, 2H, 2CH = ), 6.57–6.69 (m, 2H, 2ArH), 8.09–8.16 (m, 2H, 2ArH) ppm.



**5a:**  $^1\text{H}$  NMR of 4-bromo N,N-bisallylaniline

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta\text{H}$ : 3.85–3.96 (m, 4H, 2CH<sub>2</sub>), 5.14–5.24 (m, 4H, 2CH<sub>2</sub> =), 5.79–5.88 (m, 2H, 2CH =), 6.53–6.63 (m, 2H, 2ArH), 7.27–7.32 (m, 2H, 2ArH) ppm.



**8a**  $^1\text{H}$  NMR of 1-(4-(diallylamino)phenyl)ethanone

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta\text{H}$ : 2.5 (s, 3H, 1CH<sub>3</sub>), 3.94–4.05 (m, 4H, 2CH<sub>2</sub>), 5.14–5.26 (m, 4H, 2CH<sub>2</sub> =), 5.81–5.90 (m, 2H, 2CH =), 6.60–6.72 (m, 2H, 2ArH), 7.80–7.99 (m, 2H, 2ArH) ppm.