

## Supporting Information for

### Synthesis of medium sized aryl-fused nitrogen heterocycles *via* sequential aryne aza-Claisen rearrangement/Ring-Closing Metathesis

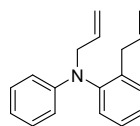
N. S. V. M. Rao Mangina,<sup>†,‡</sup> Ravinder Guduru<sup>†,‡</sup> and Galla V. Karunakar<sup>\*,†,‡</sup>

<sup>†</sup>Crop Protection Chemicals Division, <sup>‡</sup>Academy of Scientific and Innovative Research, and CSIR-Indian Institute of Chemical Technology, Hyderabad, 500007, India.

#### Contents:

|                                                                                                          |    |
|----------------------------------------------------------------------------------------------------------|----|
| 1. Copies of <sup>1</sup> H and <sup>13</sup> C NMR spectra <b>3a-3l</b> , <b>5a-5g</b> and <b>6a-6g</b> | S2 |
| Electronic Supplementary Material (ESI) for Chemical Communications                                      |    |

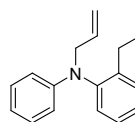
*N*,2-Diallyl-*N*-phenylaniline: **3a**



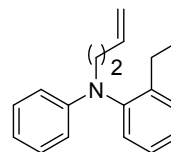
|         |         |
|---------|---------|
| 148,502 | 139,041 |
| 145,340 | 136,870 |
|         | 134,422 |
|         | 130,571 |
|         | 129,674 |
|         | 128,867 |
|         | 127,857 |
|         | 126,781 |
|         | 116,922 |
|         | 116,748 |
|         | 116,086 |
|         | 113,340 |

54.905

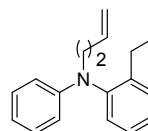
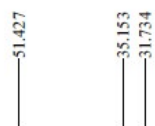
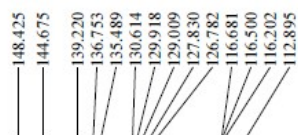
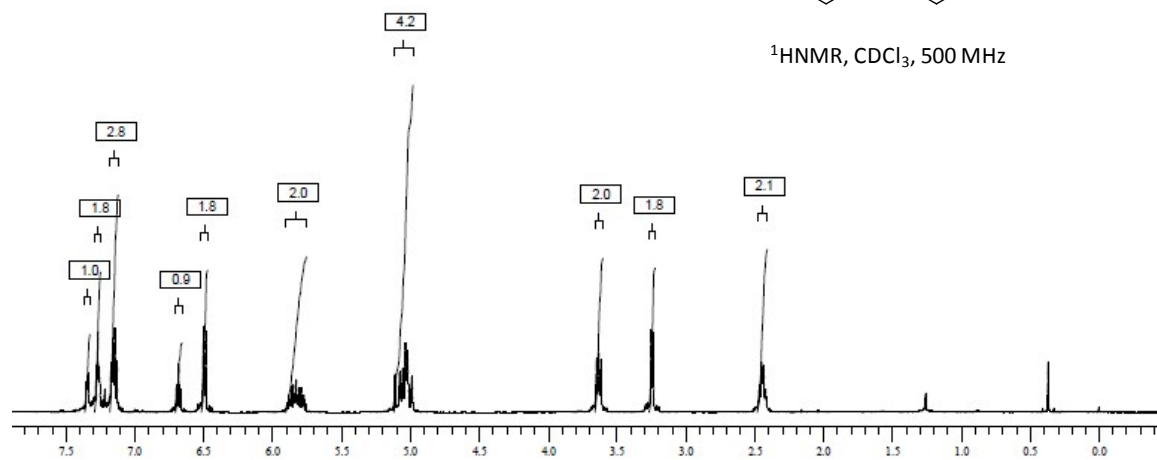
35.353



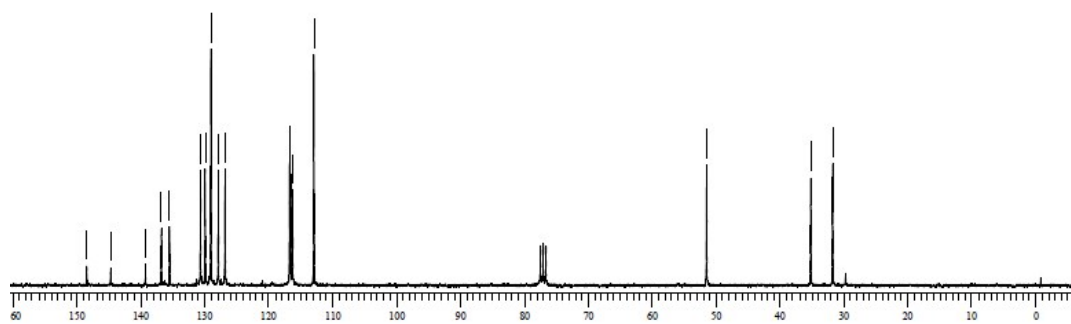
2-Allyl-*N*-(but-3-enyl)-*N*-phenylaniline: **3b**



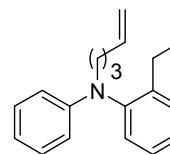
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



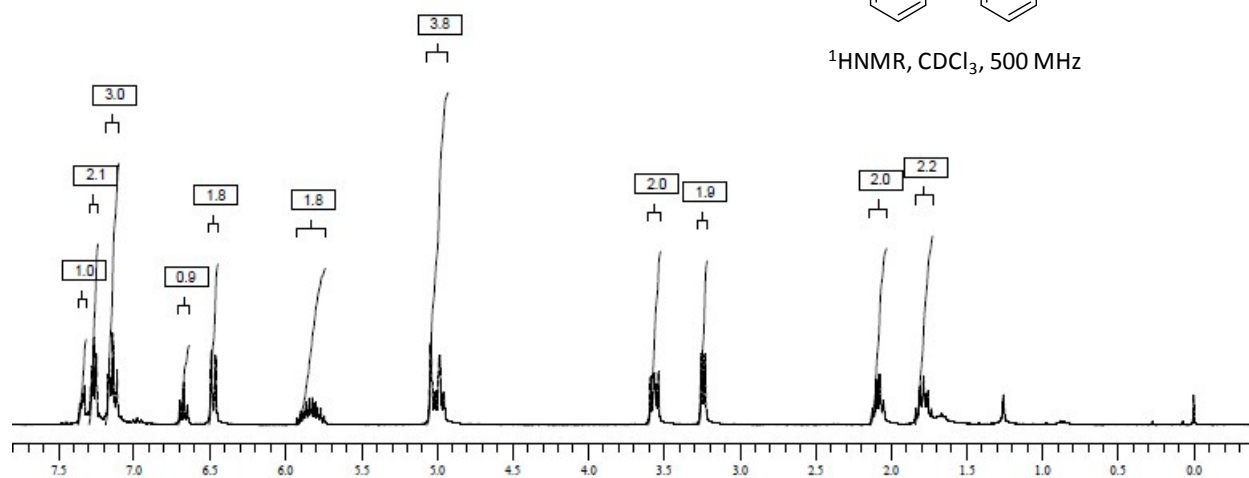
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 75 MHz



2-Allyl-*N*-(pent-4-enyl)-*N*-phenylaniline: **3c**



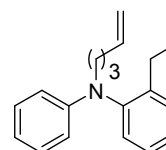
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



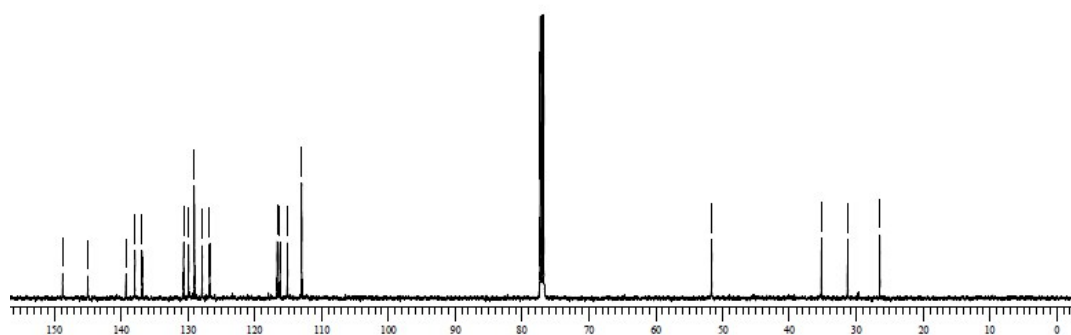
148.671  
144.909  
139.216  
137.881  
136.798  
130.601  
129.851  
128.980  
127.809  
126.688  
116.588  
116.173  
115.048  
112.926

51.599

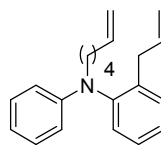
35.159  
31.237  
26.445



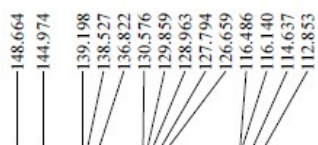
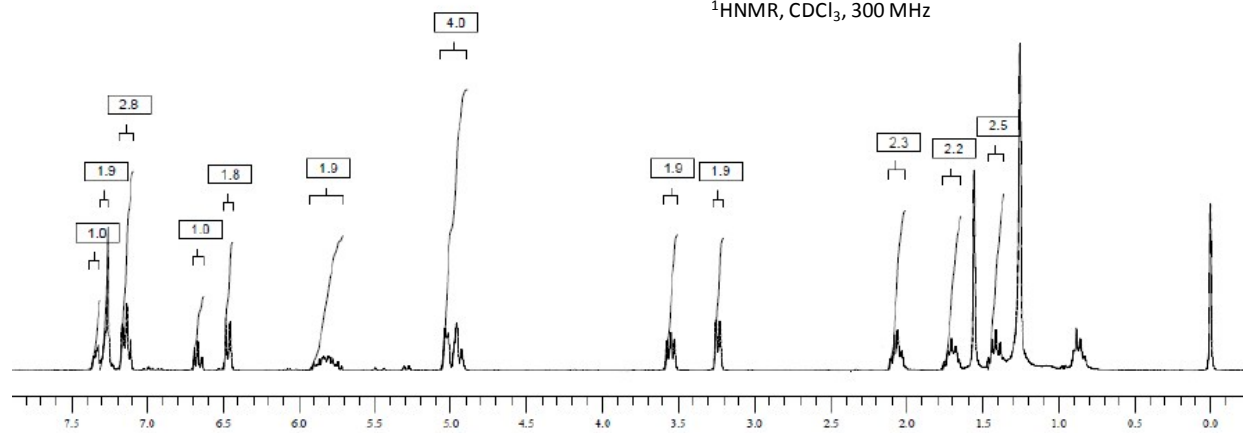
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 75 MHz



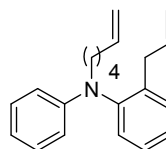
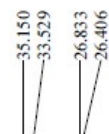
2-Allyl-*N*-(hex-5-enyl)-*N*-phenylbenzenamine: **3d**



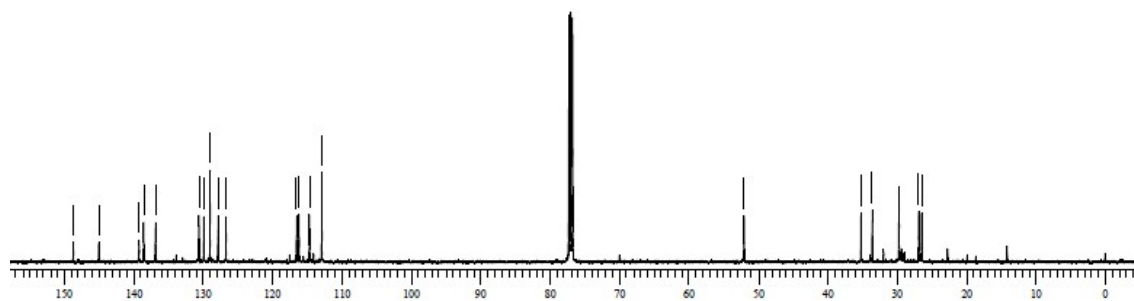
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 300 MHz

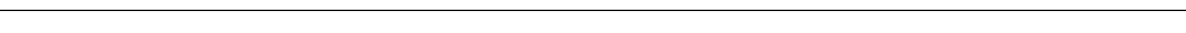


52.014

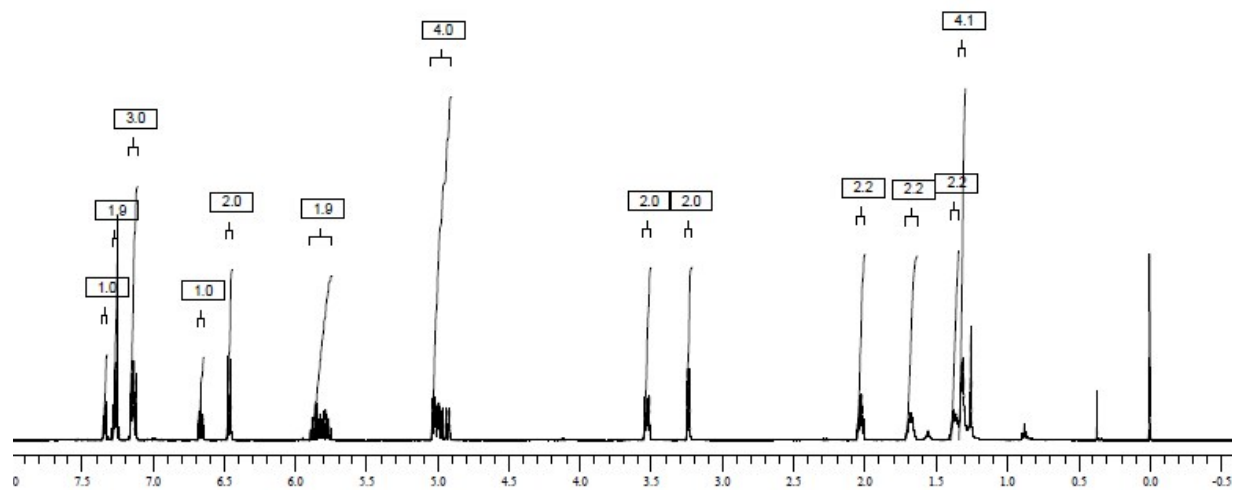
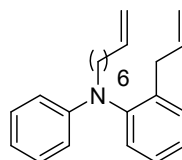


$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125 MHz



2-Allyl-*N*-(hept-6-enyl)-*N*-phenylbenzenamine: **3e**

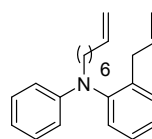
2-Allyl-*N*-(oct-7-enyl)-*N*-phenylbenzenamine: **3f**



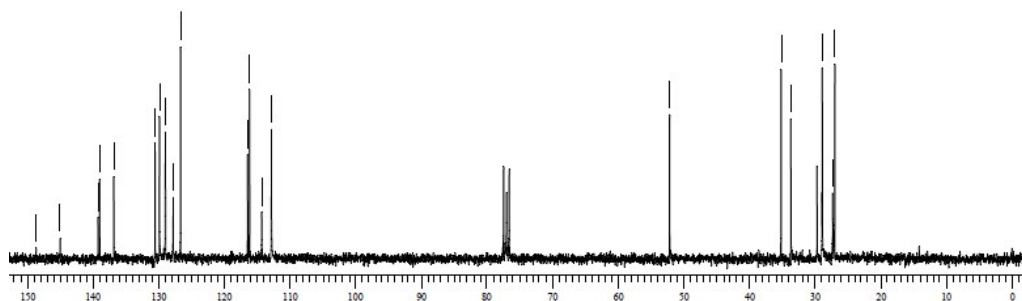
148.659  
144.994  
139.205  
138.972  
136.819  
130.535  
129.865  
128.963  
127.768  
126.637  
116.424  
116.135  
114.272  
112.785

52.132

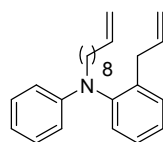
35.142  
33.658  
28.859  
27.284  
26.967



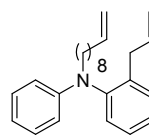
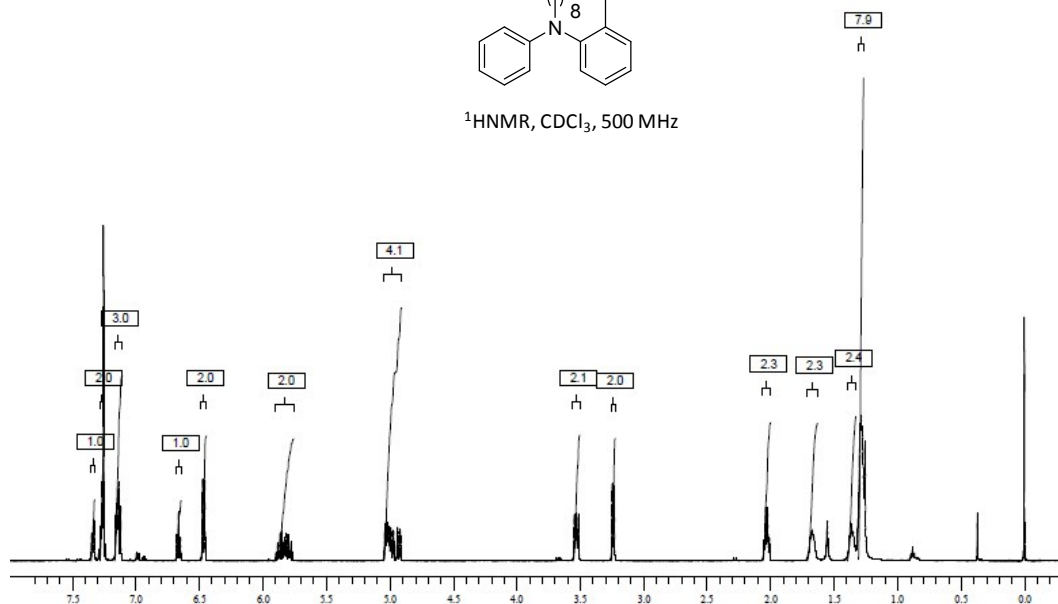
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 75 MHz



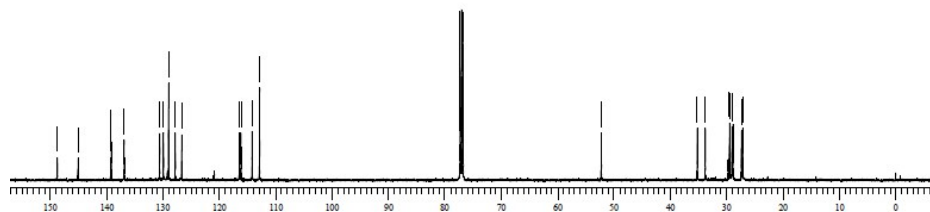
2-Allyl-*N*-(dec-9-enyl)-*N*-phenylbenzenamine: **3g**



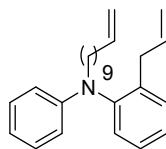
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



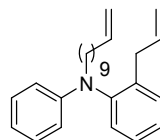
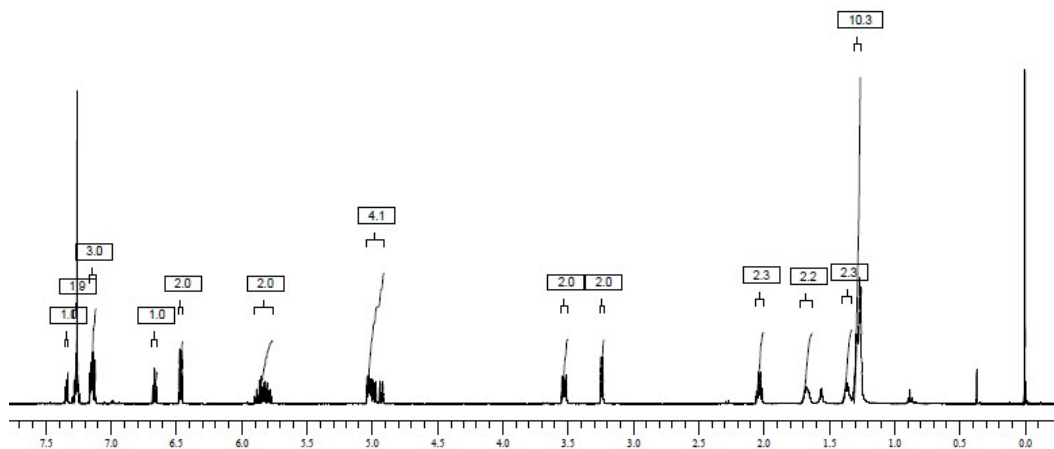
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125 MHz



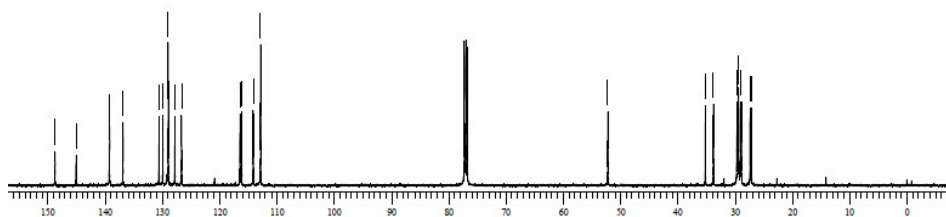
2-Allyl-*N*-phenyl-*N*-(undec-10-enyl)benzenamine: **3h**



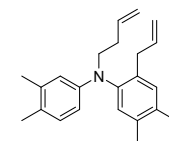
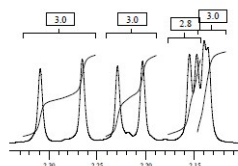
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



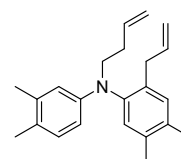
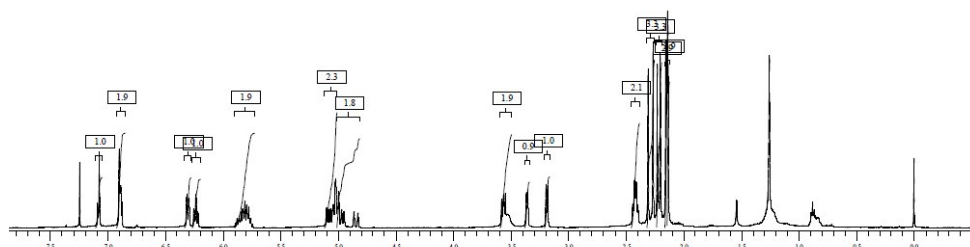
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125 MHz



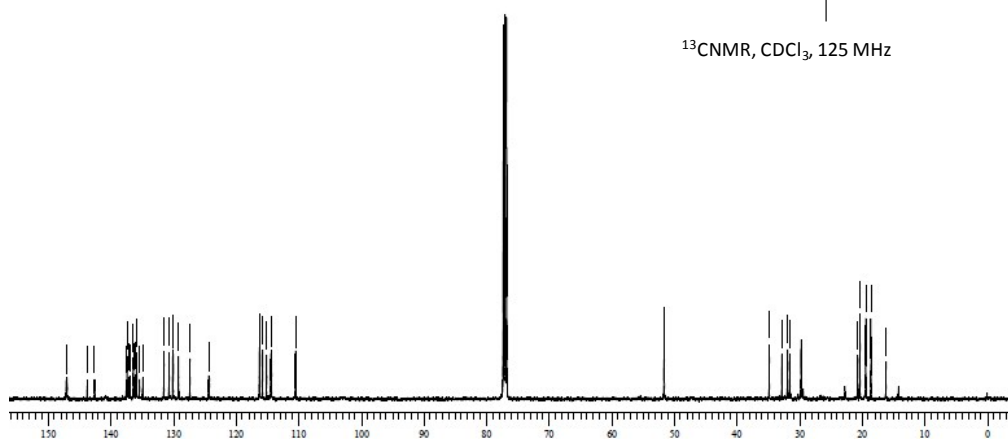
2-Allyl-*N*-(but-3-enyl)-*N*-(3,4-dimethylphenyl)-4,5-dimethylbenzenamine: **3i**

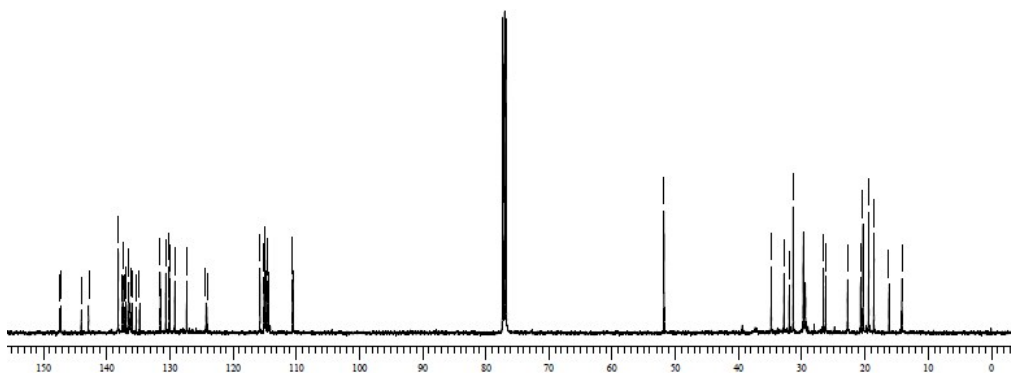


$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz

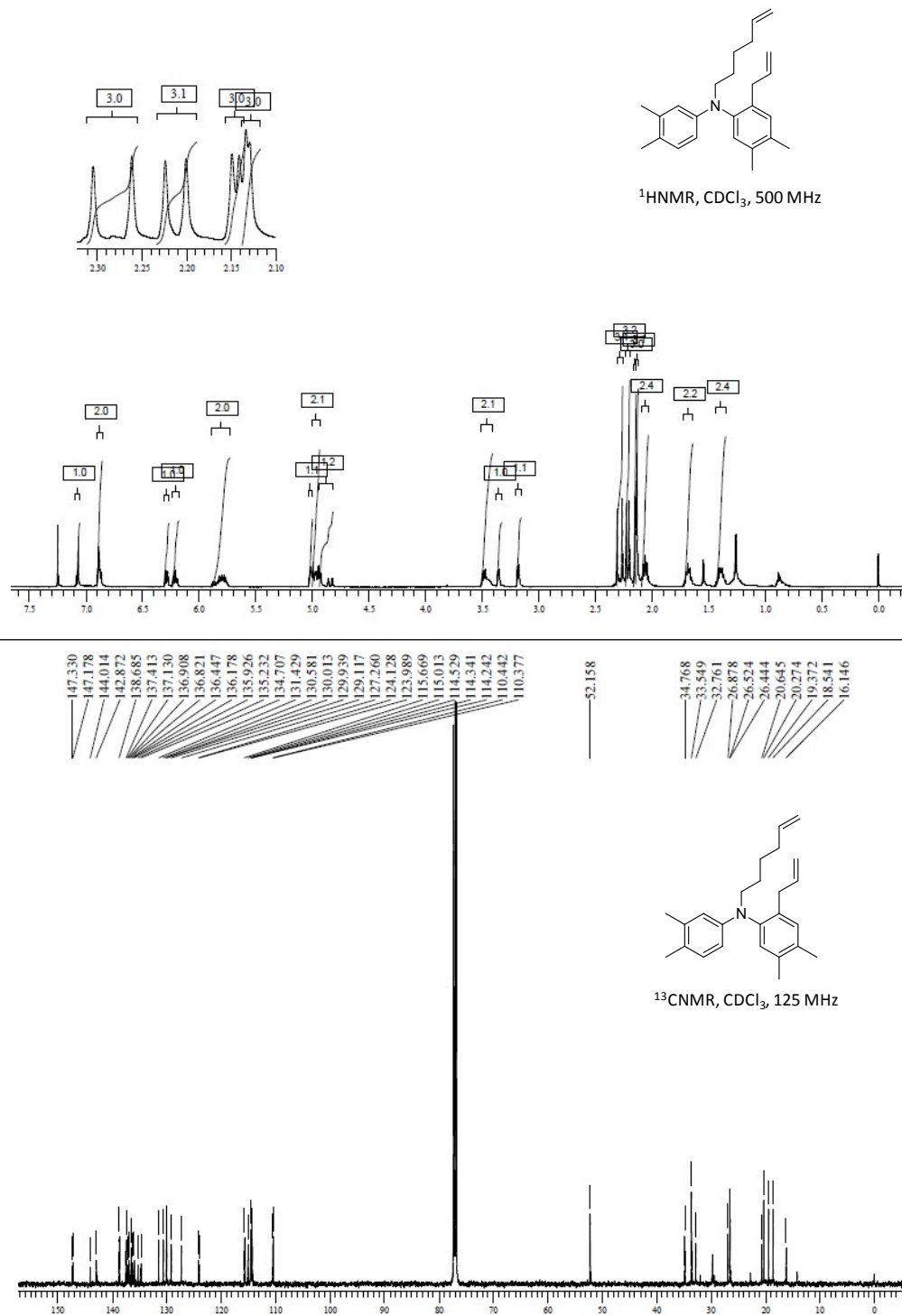


$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125 MHz

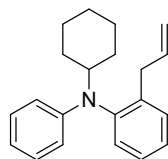




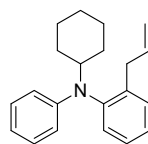
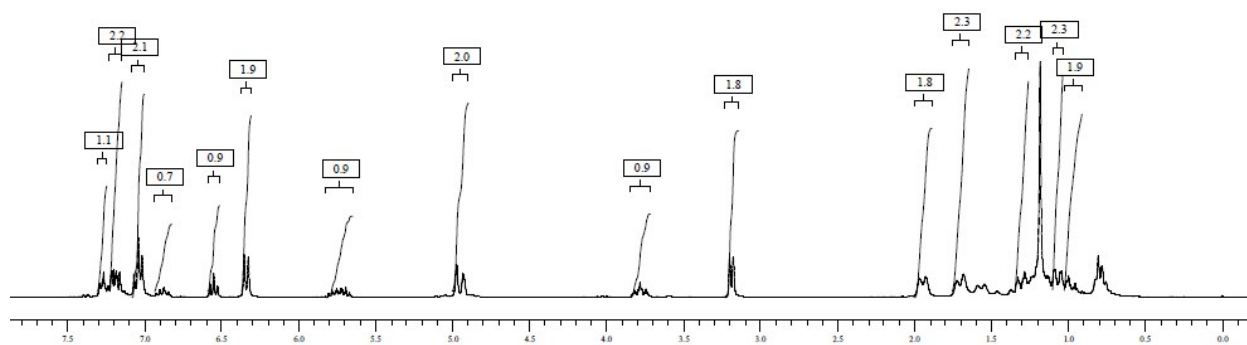
2-Allyl-*N*-(3,4-dimethylphenyl)-*N*-(hex-5-enyl)-4,5-dimethylbenzenamine: **3k**



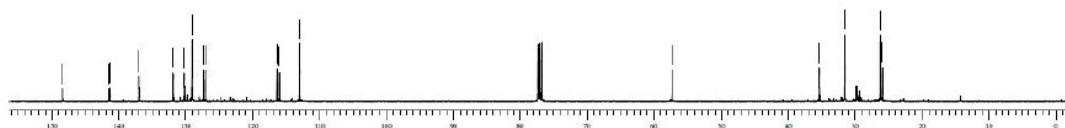
2-Allyl-*N*-cyclohexyl-*N*-phenylaniline: **31**



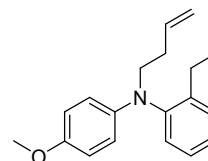
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 300 MHz



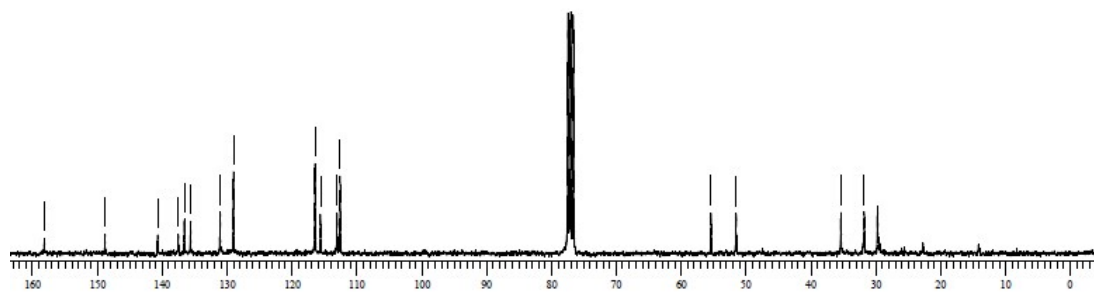
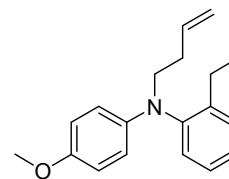
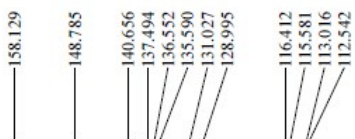
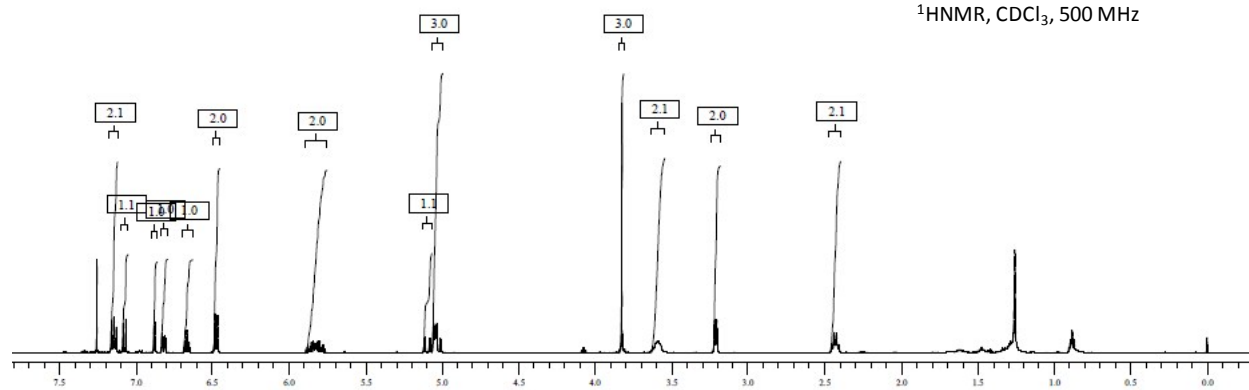
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 75 MHz



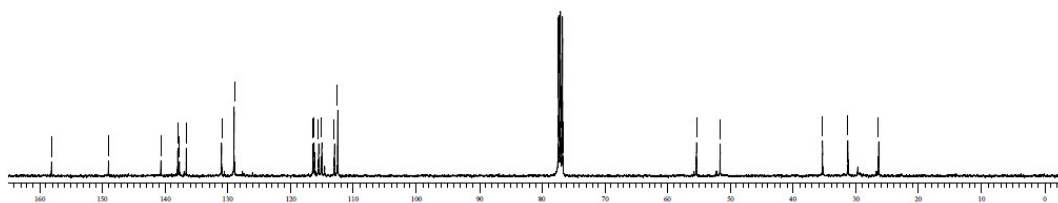
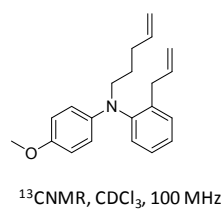
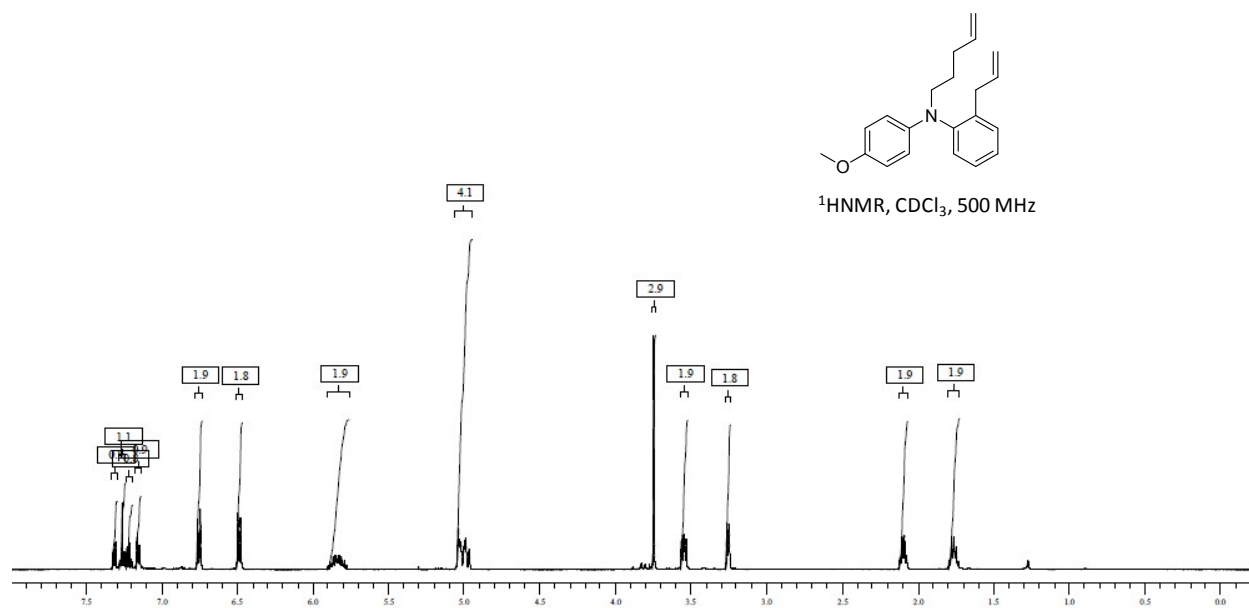
2-Allyl-*N*-(but-3-enyl)-*N*-(4-methoxyphenyl)aniline: **5a**



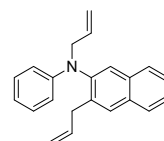
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



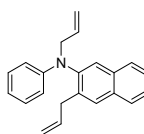
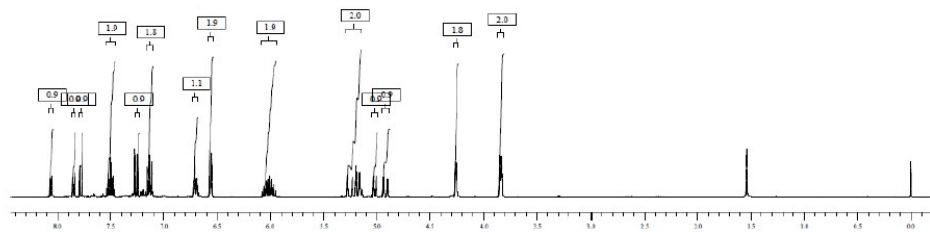
2-Allyl-*N*-(4-methoxyphenyl)-*N*-(pent-4-en-1-yl)aniline: **5b**



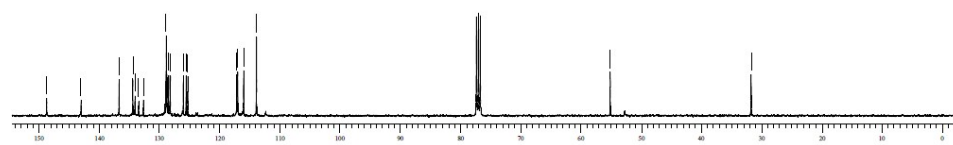
*N*,3-Diallyl-*N*-phenylnaphthalen-2-amine: **5c**



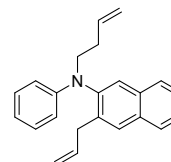
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 400 MHz



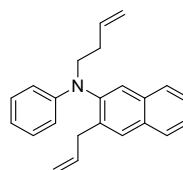
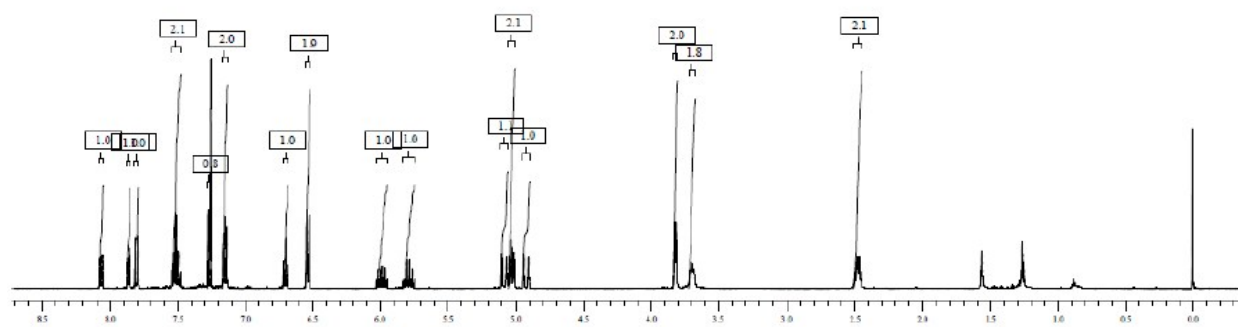
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 100 MHz



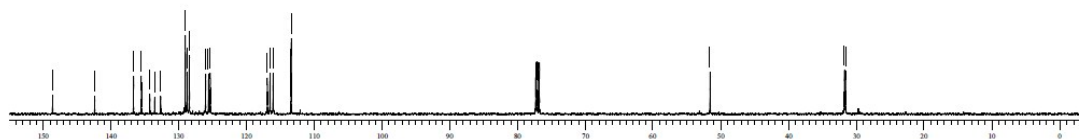
3-Allyl-*N*-(but-3-enyl)-*N*-phenylnaphthalen-2-amine: **5d**



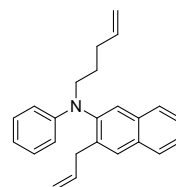
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



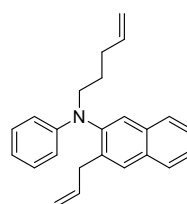
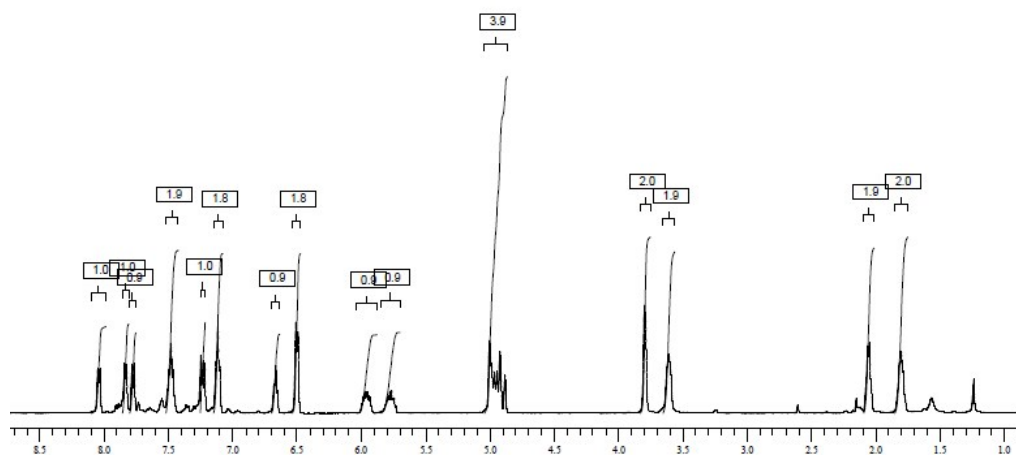
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125 MHz



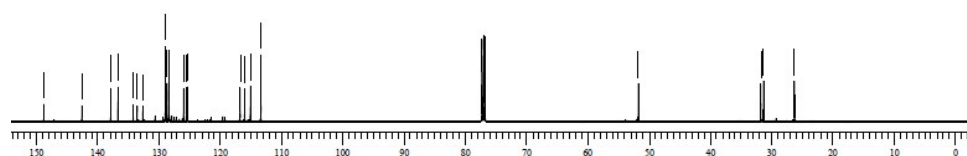
3-Allyl-*N*-(pent-4-enyl)-*N*-phenylnaphthalen-2-amine: **5e**



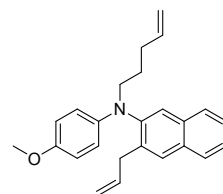
$^1\text{H NMR}$ ,  $\text{CDCl}_3$ , 500 MHz



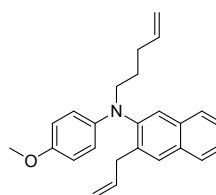
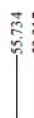
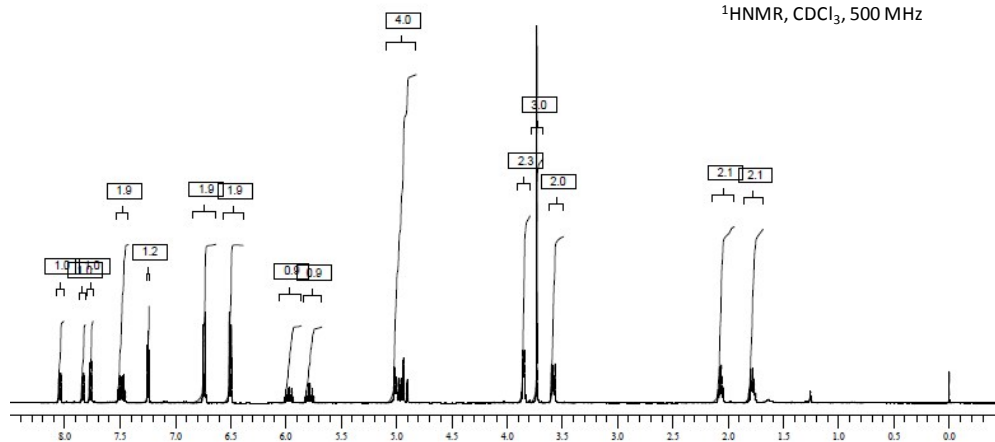
$^{13}\text{C NMR}$ ,  $\text{CDCl}_3$ , 125 MHz



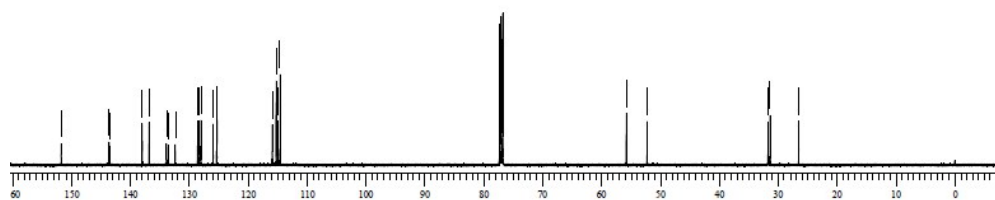
3-Allyl-*N*-(4-methoxyphenyl)-*N*-(pent-4-enyl)naphthalen-2-amine: **5f**



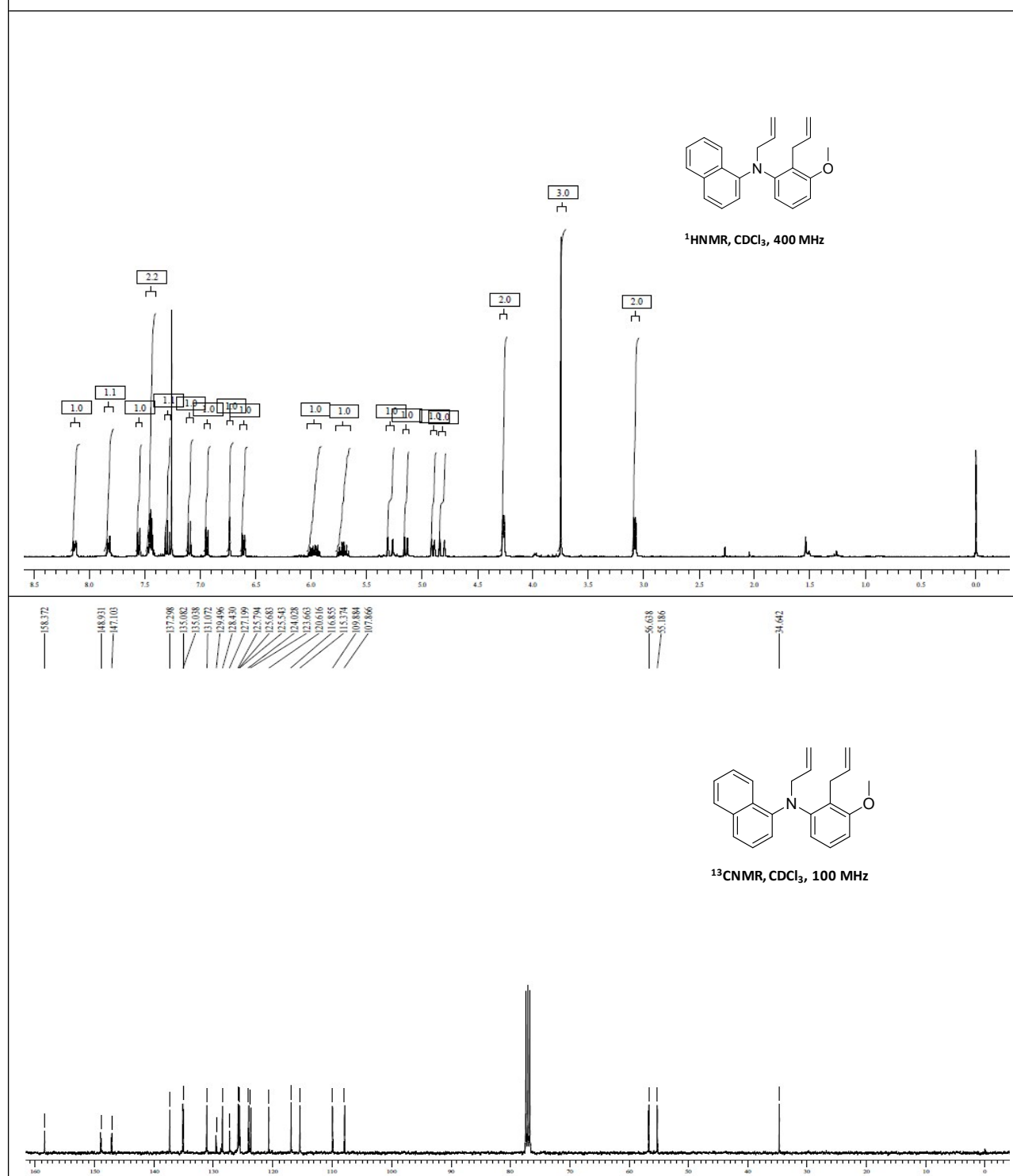
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



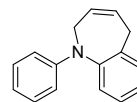
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125 MHz



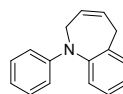
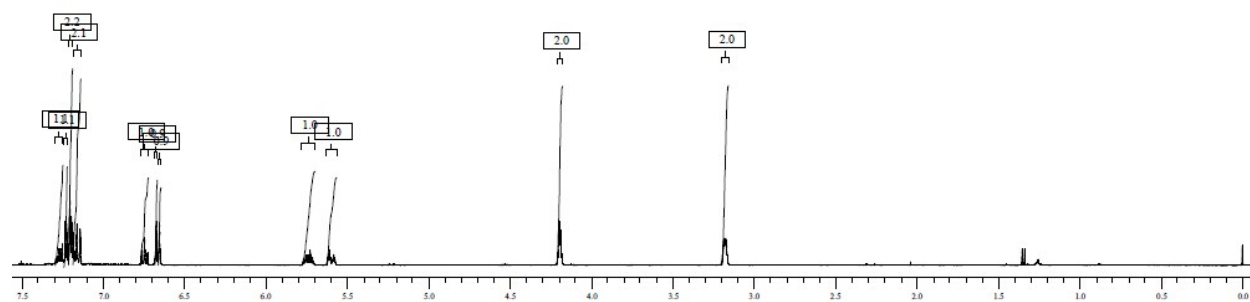
*N*-Allyl-*N*-(2-allyl-3-methoxyphenyl)naphthalen-1-amine: **5g**



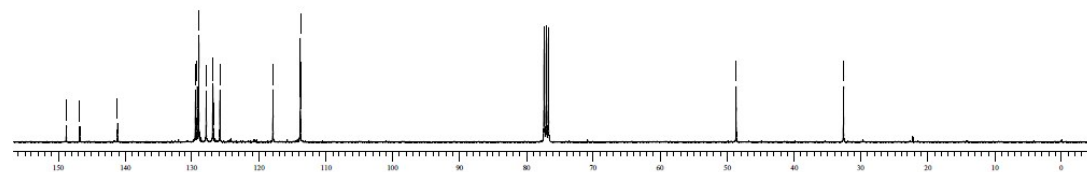
1-Phenyl-2,5-dihydro-1*H*-benzo[*b*]azepine: **6a**



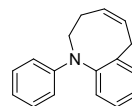
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 400 MHz



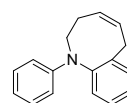
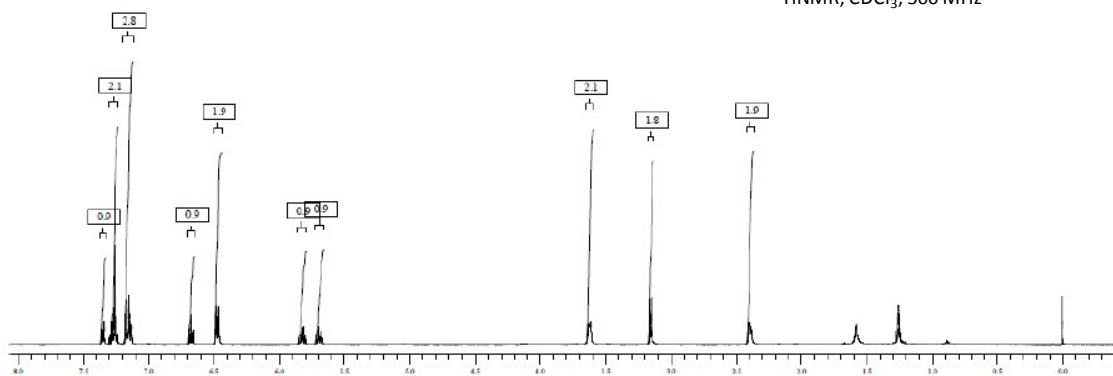
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 100 MHz



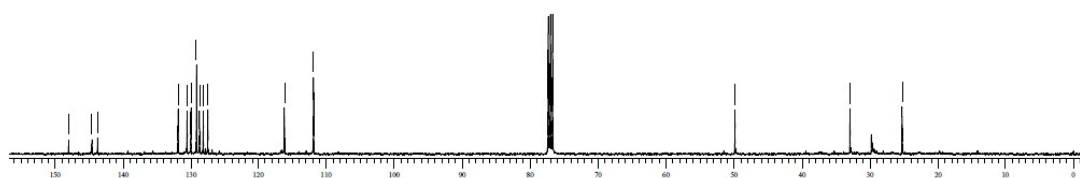
(Z)-1-Phenyl-1,2,3,6-tetrahydrobenzo[*b*]azocine: **6b**



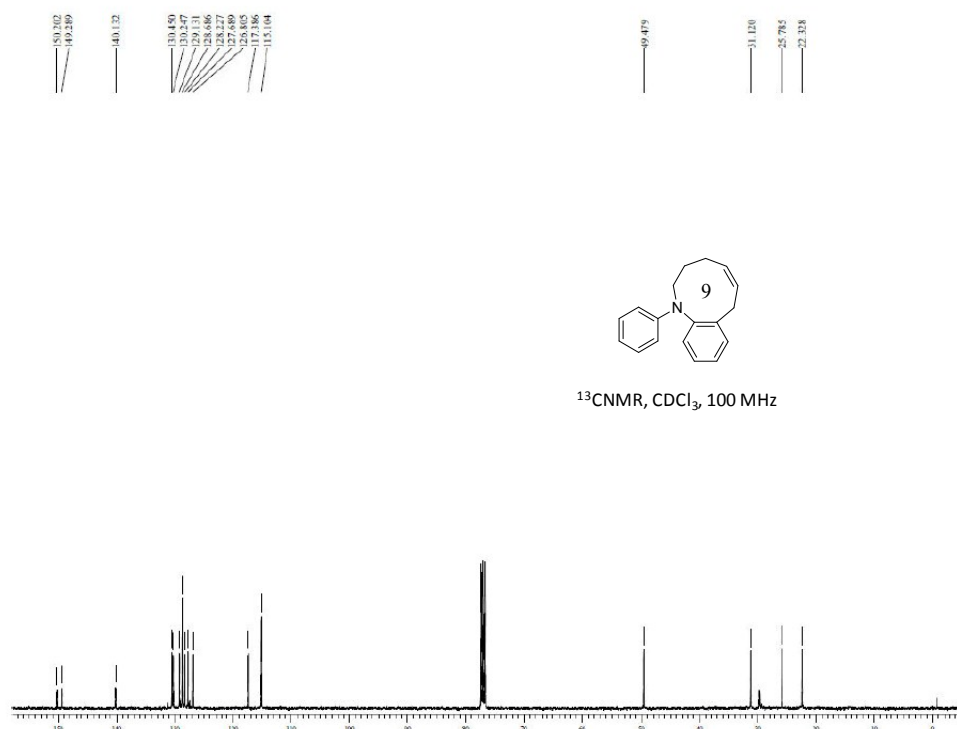
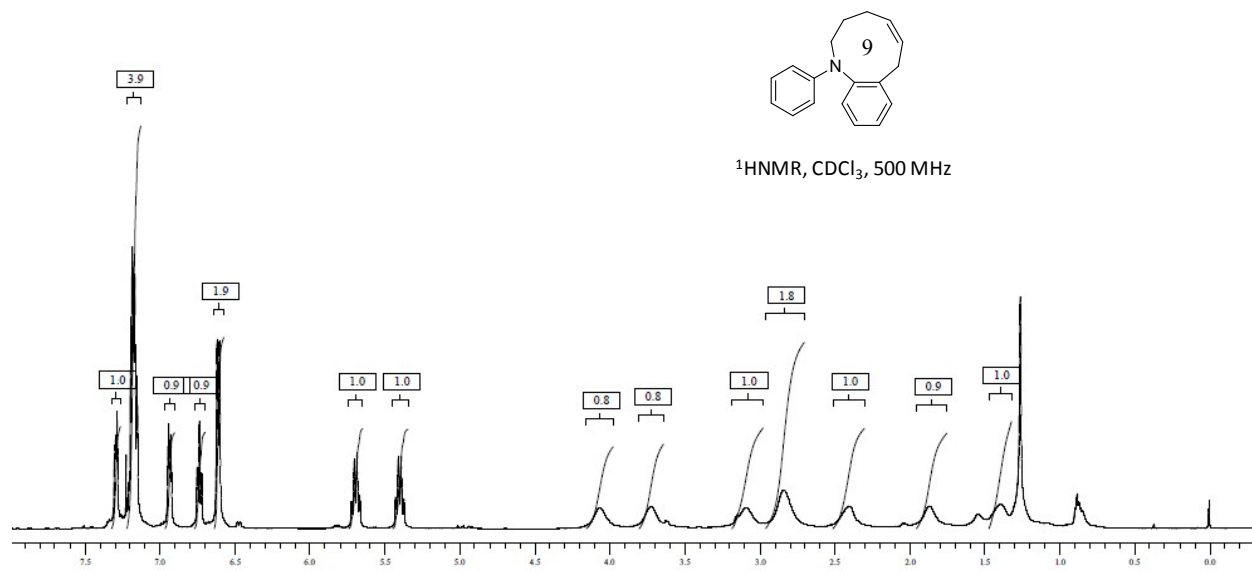
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



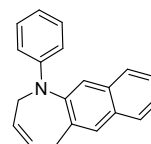
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 100 MHz



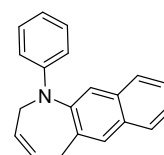
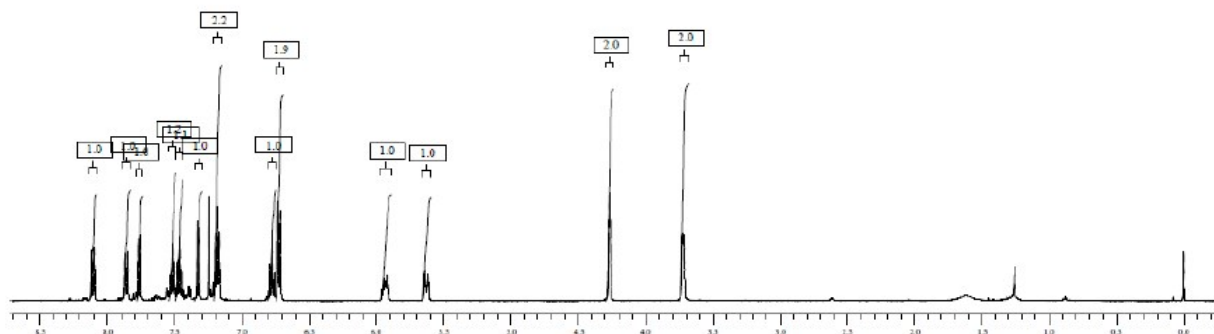
(Z)-1-Phenyl-2,3,4,7-tetrahydro-1H-benzo[b]azonine: **6c**



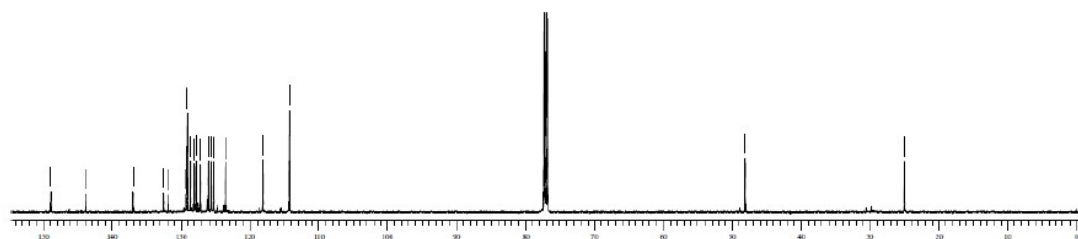
1-Phenyl-2,5-dihydro-1*H*-naphtho[2,3-*b*]azepine: **6d**



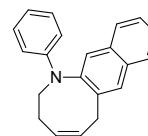
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



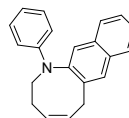
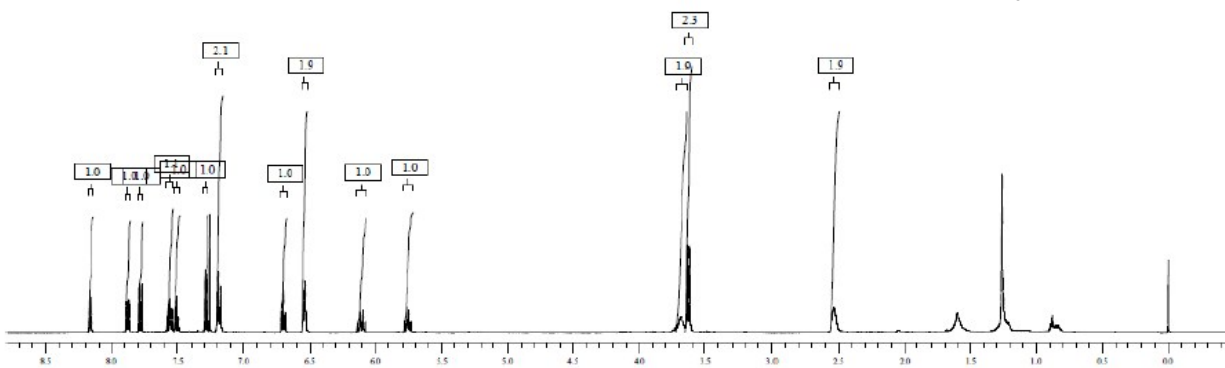
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125 MHz



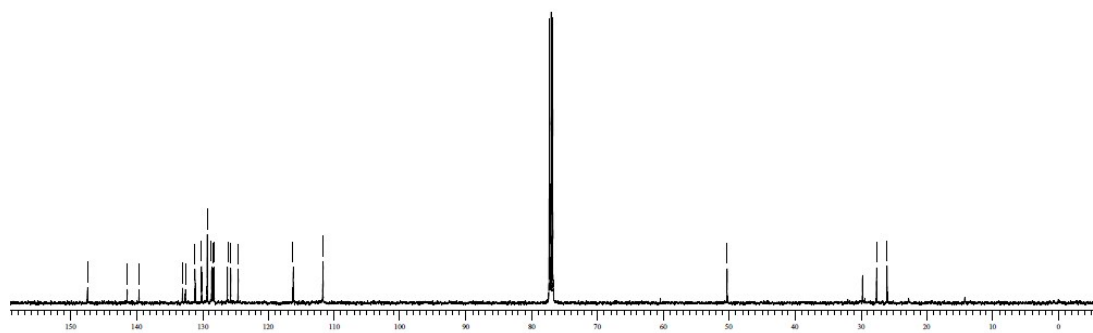
(Z)-1-Phenyl-1,2,3,6-tetrahydronaphtho[2,3-*b*]azocine: **6e**



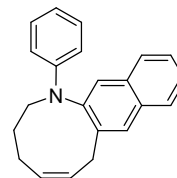
$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



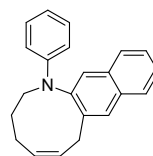
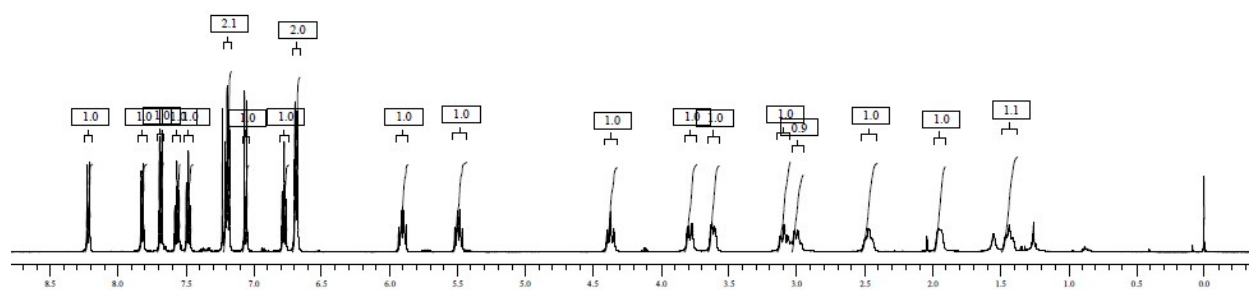
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125 MHz



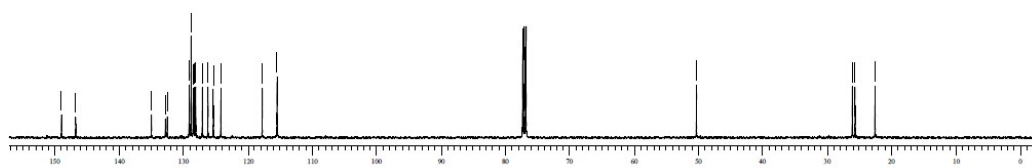
(*Z*)-1-Phenyl-2,3,4,7-tetrahydro-1*H*-naphtho[2,3-*b*]azonine: **6f**



$^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz



$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125 MHz



(Z)-1-(4-Methoxyphenyl)-2,3,4,7-tetrahydro-1H-naphtho[2,3-b]azonine: **6g**

