

# The Synthesis of Homoallylic Amines via the Palladium-catalyzed Decarboxylative Coupling of Amino Acid Derivatives.

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## Experimental

**Materials.** Toluene and THF were dried over activated alumina. 1,4-Dioxane was dried over 4 Å molecular sieves and then vacuum distilled. All other materials were used as received. Imines **1a-1o** were synthesized from the appropriate Boc protected amino acid by an EDCI/ DMAP catalyzed coupling with the appropriate allylic alcohol<sup>1</sup>, followed by

<sup>1</sup> Neises, B., Steglich, W. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 522.

TFA deprotection and condensation of the HCl salt with benzophenone imine<sup>2</sup>. <sup>1</sup>H NMR spectra were referenced to residual protio solvent signals. Structural assignments are based on <sup>1</sup>H, <sup>13</sup>C, DEPT-135, COSY, and HMQC spectroscopies.

**Procedure for the synthesis of protected homoallylic amines and N-allyl aziridines:**

A 0.1 M solution of allylic ester was prepared in a flame-dried Schlenk tube under argon. 5 mol % Pd<sub>2</sub>(dba)<sub>3</sub> and 10 mol % ligand were added and the reaction was stirred under argon for the indicated reaction time at the appropriate temperature. The solvent was then removed under reduced pressure and the crude material was purified by flash chromatography (0.5 to 1% ethyl acetate in hexane on SiO<sub>2</sub>).

**Impact of electron withdrawing groups: 4,4'-Dichlorobenzophenone Derivative**

Alternatively, 4,4'-dichlorobenzophenone was added to a solution of phenylglycine allyl ester (10 equivalents) and TiCl<sub>4</sub> in benzene under Argon.<sup>3</sup> Stirring for 4 days at room temperature led to formation of the ketimine of the amino acid allyl ester formation. Following chromatography on neutral alumina, the imino ester was subjected to the catalytic system of 5% Pd<sub>2</sub>(dba)<sub>3</sub> and 10% dppf in THF-d<sup>6</sup> at room temperature. After 15 minutes <sup>1</sup>H NMR indicated complete consumption of starting ester and a 2:1 ratio of α:γ allylation products.

**Attempted decarboxylation of the ketimine carboxylates derived from 5-H.**

Independent treatment of the diphenylketimine of phenylalanine (**5-H**) with either Cs<sub>2</sub>CO<sub>3</sub> or NaH in toluene led to formation of the carboxylate salt, which precipitated out of solution and was shown not to decarboxylate after refluxing for 2 hours.

**Stoichiometric [Pd(allyl)(dppf)]BF<sub>4</sub> decarboxylations:**

Imino acid **5-H** was prepared by addition of 1 equivalent of benzophenone imine to a 0.1M solution of phenylalanine HCl in methylene chloride with molecular sieves. After the reaction was stirred for 24 hours, filtration of the resulting yellow suspension of NH<sub>4</sub>Cl and evaporation of solvent yield the desired product. The imino acid was then dissolved in toluene (dried over sodium) under Argon and 1.5 equivalents of NaH (60% in mineral oil) were added. Following deprotonation, 1 equivalent of [Pd(allyl)(dppf)]BF<sub>4</sub> was added<sup>4</sup> and the reactions were refluxed for 2 hours. The crude reaction mixture was analyzed by <sup>1</sup>H NMR. The dppb complex was synthesized in a similar manner<sup>5</sup> and gave identical results.

Alternatively, after refluxing for 2 hours imino ester **2k** was added to the reaction mixture and heating continued. After an additional hour at reflux <sup>1</sup>H NMR indicated formation of **4k**, confirming the existence of a catalytically active system derived from [Pd(allyl)(dppf)]BF<sub>4</sub>.

<sup>2</sup> Tullis, J. et.al. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 1975.

<sup>3</sup> Moretti, Il; Torre, G. *Synthesis*, **1970**, 141.

<sup>4</sup> Amatore, C.; Jutand, A.; Meyer, G.; Mottier, L. *Chem. Eur. J.* **1999**, *5*, 466. Amatore, C.; Gamez, S.; Jutand, A. *Chem. Eur. J.* **2001**, *7*, 1273.

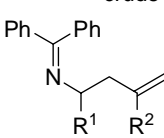
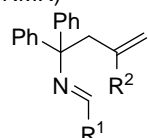
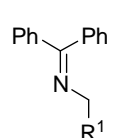
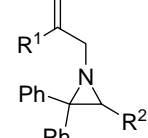
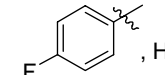
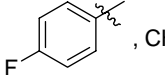
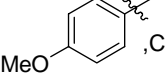
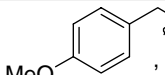
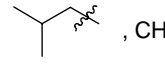
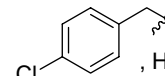
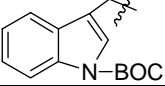
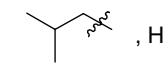
<sup>5</sup> Shigeru, M.; Hidenori, K.; Susumu, A. European Patent # 0112727, **1984**.

**Results of preliminary screening of chiral ligands.****Table 1: Enantioselectivity in the conversion of **1g** to **2g****

Ligand	Conditions	% ee	Ligand	Conditions	% ee
(R,R) MeDuPhos	A	NR	(S,S)-DIOP	A	5%
(R,S)-JosiPhos	A	NR	(S,S)-ChiraPhos	A	7%
(R)-BINAP	A	22%	(S)-tBuPHOx	A	NR
(R)-BINAP	B	30%	(R)-Tol-BINAP	A	20%
(R)-Xylyl-BINAP	A	0%	(R)-SynPhos	A	24%
(R)-Cl-MeO-BIPHEP	A	18%	(R)-SynPhos	C	35%

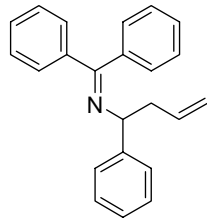
Reactions run with 5 mol% Pd<sub>2</sub>dba<sub>3</sub> and 10 mol% chiral ligand. Conditions: A = 0.1M **1g** in toluene at 110 °C; B = 0.1M **1g** in dioxane at 100 °C; C = 0.1M **1g** in dioxane at 90 °C.

**Table 2: Product distributions for Pd-catalyzed decarboxylation reactions**

Substrate	R <sup>1</sup> , R <sup>2</sup>	Yields (estimated from crude <sup>1</sup> H NMR)			
					
<b>1a</b>	Ph, H	67%	(17%)	---	---
<b>1b</b>	Ph, CH <sub>3</sub>	81%	(10%)	---	---
<b>1c</b>	Ph, Ph	75%	(10%)	---	---
<b>1d</b>	 , H	66%	(17%)	---	---
<b>1e</b>	 , CH <sub>3</sub>	93%	(7%)	---	---
<b>1f</b>	 , CH <sub>3</sub>	85%	(15%)	---	---
<b>1g</b>	Bn, CH <sub>3</sub>	63%	(17%)	(12%)	---
<b>1h*</b>	Bn, Ph	43%	---	(14%)	---
<b>1i</b>	 , H	67%	---	(16%)	(5%)
<b>1j*</b>	 , CH <sub>3</sub>	26%	---	---	(25%)
<b>1k</b>	Bn, H	(13%)	---	(8%)	68%
<b>1l</b>	 , H	(31%)	---	---	59%
<b>1m*</b>	 , H	---	---	---	87%
<b>1n</b>	 , H	---	---	---	>95%

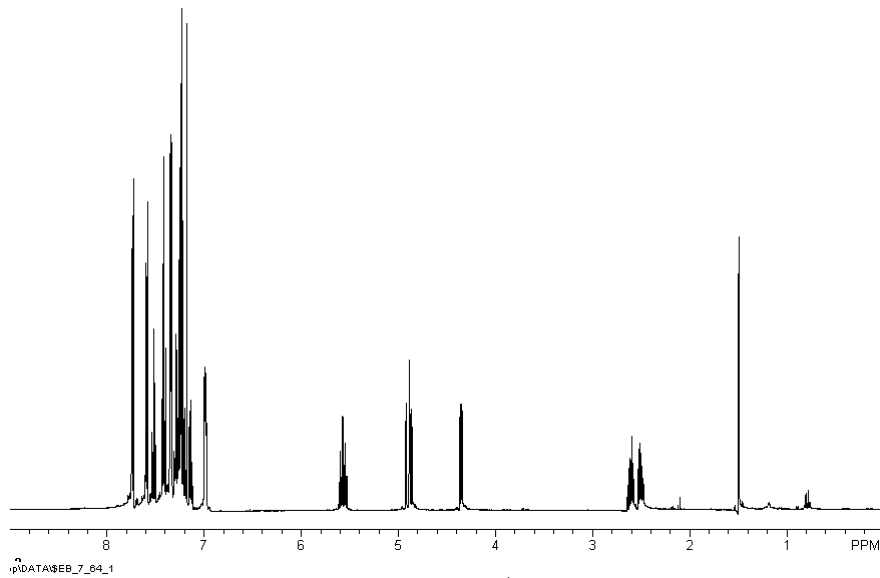
\* crude <sup>1</sup>H NMR also indicated a significant amount of unidentifiable side products

## Spectral Characterization

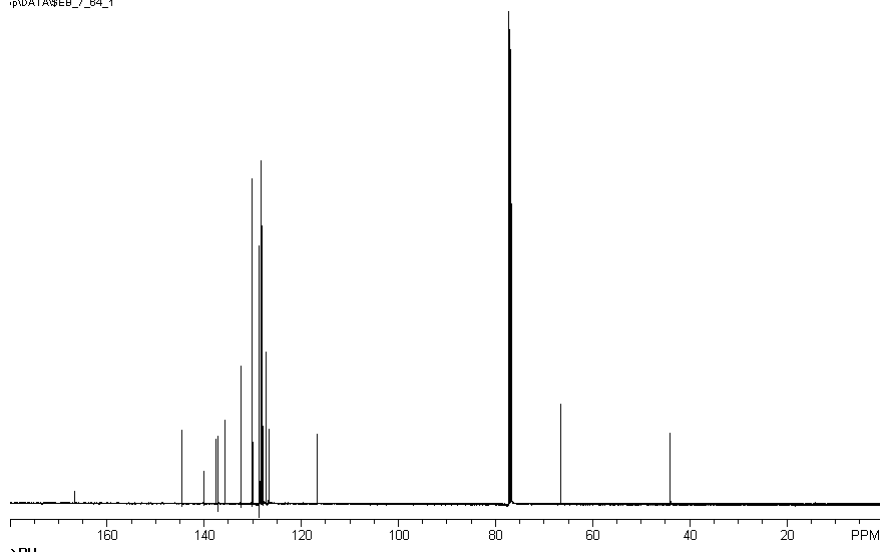


**2a**

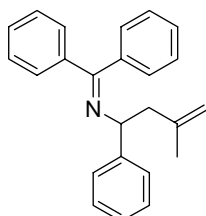
*N*-(diphenylmethylene)-1-phenylbut-3-en-1-amine



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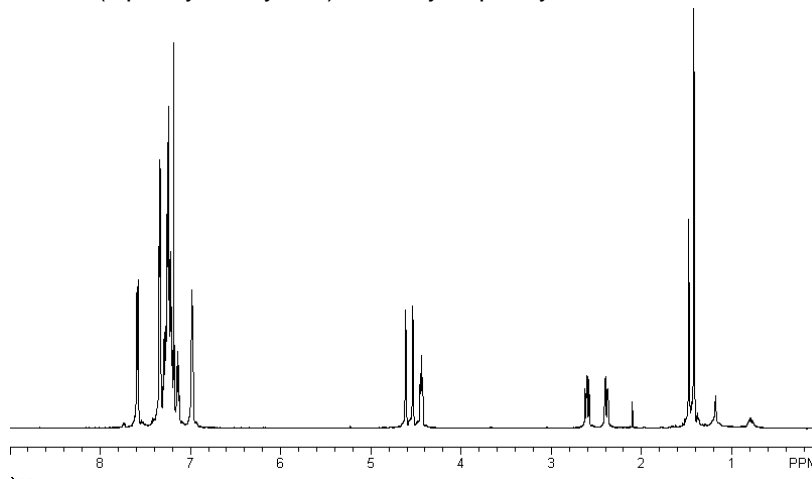


**2a**<sup>6</sup>: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8 Hz, 1H: arom. CH), 7.59 (m, 2H: arom. CH), 7.52 (t, *J* = 7 Hz, 1H: arom. CH), 7.41 (t, *J* = 8 Hz, 2H: arom. CH), 7.35 (overlapping m, 3H: arom. CH), 7.21 (overlapping m, 3H: arom. CH), 6.99 (m, 2H: arom. CH), 5.57 (ddt, *J* = 7 Hz, 10 Hz, 17 Hz, 1H: CH=CH<sub>2</sub>), 4.90 (d, *J* = 17 Hz, 1H: CH=CH(*H*)<sub>trans</sub>), 4.88 (d, *J* = 10 Hz, 1H: CH=CH(*H*)<sub>cis</sub>), 4.36 (dd, *J* = 5 Hz, 8 Hz, 1H: CH), 2.61 (ddd, *J* = 7 Hz, 8 Hz, 14 Hz, 1H: diastereotopic allylic CH<sub>2</sub>), 2.50 (ddd, *J* = 5 Hz, 7 Hz, 14 Hz, 1H: diastereotopic allylic CH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.69 (C=N), 145.50 (arom. C), 140.06 (arom. C), 137.61 (arom. C), 135.78 (=CH), 132.45 (arom. CH), 130.10 (arom. CH), 129.87 (arom. CH), 128.60 (arom. CH), 128.30 (arom. CH), 127.99 (arom. CH), 127.92 (arom. CH), 127.16 (arom. CH), 126.72 (arom. CH), 116.70 (=CH<sub>2</sub>), 66.49 (CH), 43.96 (CH<sub>2</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub>): ν<sub>max</sub> 1658, 1622, 1446, 999, 920. HRMS calcd for C<sub>23</sub>H<sub>22</sub>N [M+H] = 312.1752, found 312.1721. Reaction time = 3 hours.

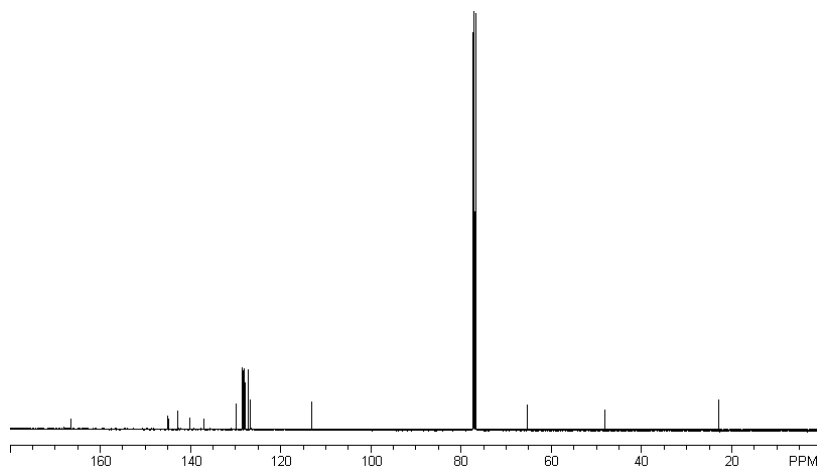


**2b**

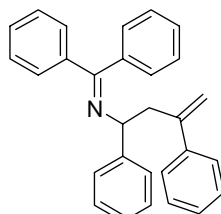
*N*-(diphenylmethylene)-3-methyl-1-phenylbut-3-en-1-amine



<sup>6</sup> Cainelli, G.; Giacomini, D.; Trere, A.; Boyd, P. *J. Org. Chem.* **1996**, *61*, 5134.

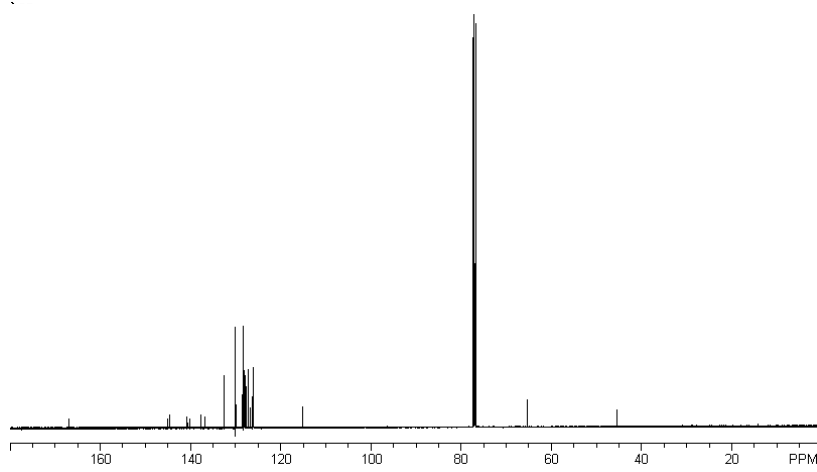
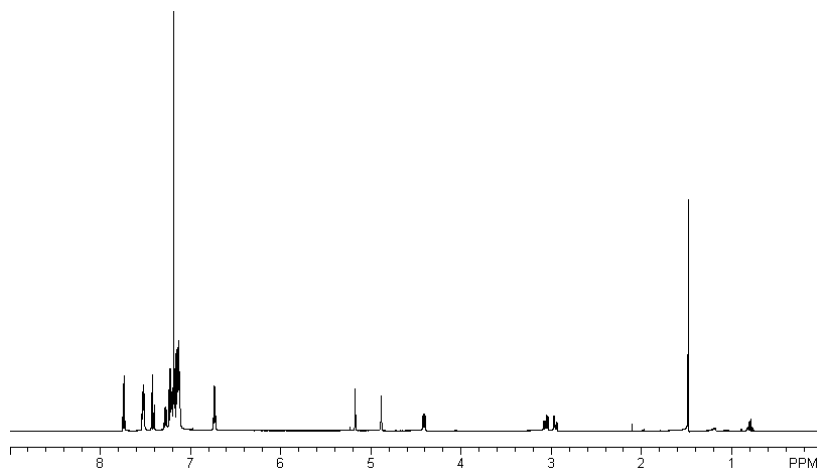


**2b:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 7$  Hz, 2H: arom. CH), 7.34 (overlapping m, 4H: arom. CH), 7.26 (overlapping m, 7H: arom. CH), 7.19 (d,  $J = 3$  Hz, 2H: arom. CH), 4.61 (s, 1H: diastereotopic  $=\text{CH}_2$ ), 4.54 (s, 1H: diastereotopic  $=\text{CH}_2$ ), 4.44 (m, 1H: CH), 2.60 (dd,  $J = 8$  Hz, 13 Hz, 1H: diastereotopic allylic  $\text{CH}_2$ ), 2.39 (dd,  $J = 5$  Hz, 13 Hz, 1H: diastereotopic allylic  $\text{CH}_2$ ), 1.42 (s, 3H:  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.48 (C=N), 144.92 (arom. C), 142.72 (arom. C), 140.13 (arom. C), 136.96 (=C), 130.09 (arom. CH), 129.79 (arom. CH), 128.60 (arom. CH), 128.27 (arom. CH), 128.20 (arom. CH), 128.08 (arom. CH), 127.95 (arom. CH), 127.12 (arom. CH), 126.65 (arom. CH), 113.14 ( $=\text{CH}_2$ ), 65.21 (CH), 48.13 ( $\text{CH}_2$ ), 22.86 ( $\text{CH}_3$ ). IR ( $\text{CD}_2\text{Cl}_2$ ):  $\nu_{\text{max}}$  1647, 895, 696. HRMS calcd for  $\text{C}_{24}\text{H}_{23}\text{N}$  [ $\text{M}+\text{H}$ ] = 326.1909, found 326.1883. Separated enantiomers on Diacel Chiralpak OD-H HPLC column (99.5% Hexane/IPA, 1.0 mL/min) -  $t_r$  = 3.8, 4.4 min. Reaction time = 3 hours.

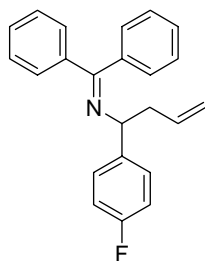


**2c**

*N*-(diphenylmethylene)-1,3-diphenylbut-3-en-1-amine

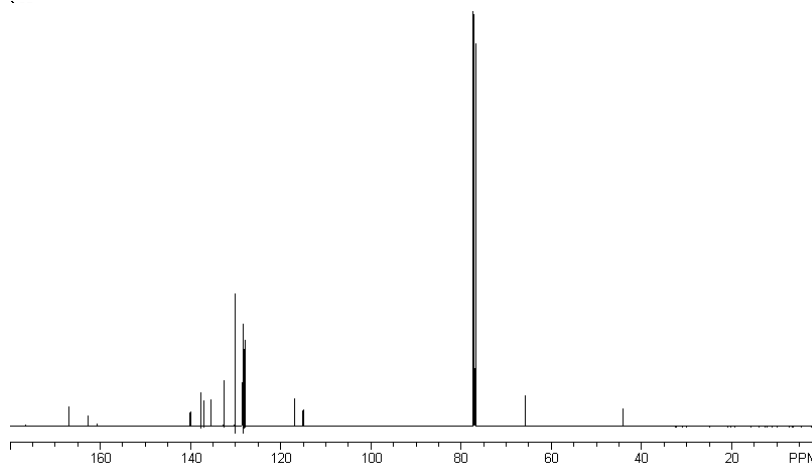
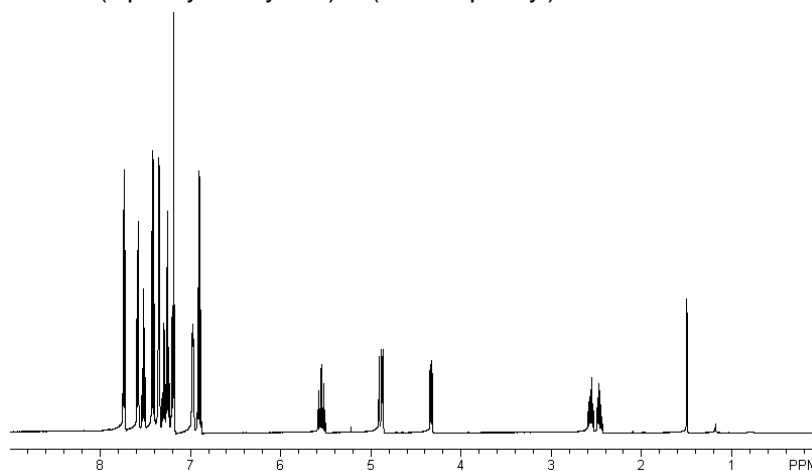


**2c:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8$  Hz, 2H: arom. CH), 7.52 (overlapping m, 3H: arom. CH), 7.42 (t,  $J = 8$  Hz, 2H: arom. CH), 7.20 (overlapping m, 11H: arom. CH), 6.73 (d,  $J = 7$  Hz, 2H: arom. CH) 5.12 (s, 1H: diastereotopic  $=\text{CH}_2$ ), 4.89 (s, 1H: diastereotopic  $=\text{CH}_2$ ), 4.41 (dd,  $J = 6$  Hz, 8 Hz, 1H: CH), 3.06 (dd,  $J = 8$  Hz, 14 Hz, 1H: diastereotopic allylic  $\text{CH}_2$ ), 2.95 (dd,  $J = 6$  Hz, 14 Hz, 1H: diastereotopic allylic  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.95 (C=N), 145.12 (arom. C), 144.66 (arom. C), 140.68 (arom. C), 140.05 (arom. C), 136.70 ( $=\text{C}$ ), 132.45 (arom. CH), 130.09 (arom. CH), 129.79 (arom. CH), 128.57 (arom. CH), 128.30 (arom. CH), 128.22 (arom. CH), 128.13 (arom. CH), 128.00 (arom. CH), 127.90 (arom. CH), 127.73 (arom. CH), 127.19 (arom. CH), 126.17 (arom. CH), 115.14 ( $=\text{CH}_2$ ), 65.21 (CH), 45.49 ( $\text{CH}_2$ ). IR ( $\text{CD}_2\text{Cl}_2$ ):  $\nu_{\text{max}}$  1658, 1622, 1446, 894. HRMS calcd for  $\text{C}_{29}\text{H}_{26}\text{N}$  [ $\text{M}+\text{H}$ ] = 388.2065, found 388.2051. Reaction time = 2 hours.



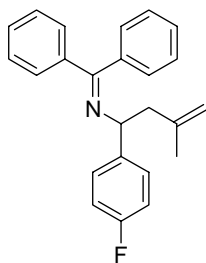
**2d**

*N*-(diphenylmethylene)-1-(4-fluorophenyl)but-3-en-1-amine



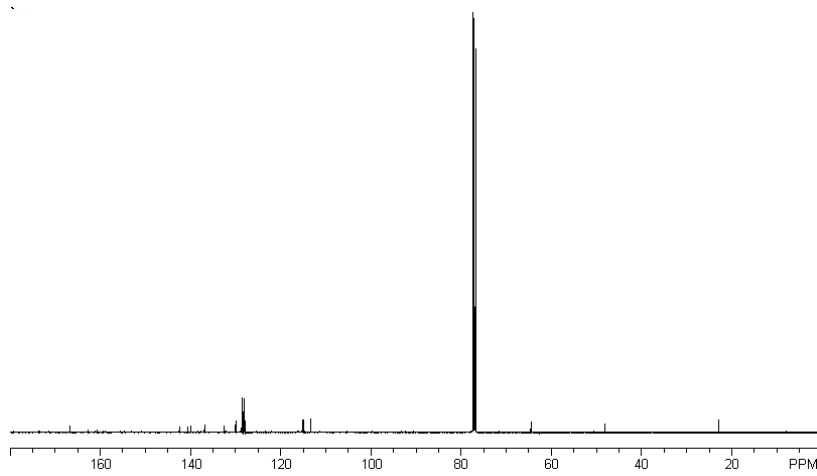
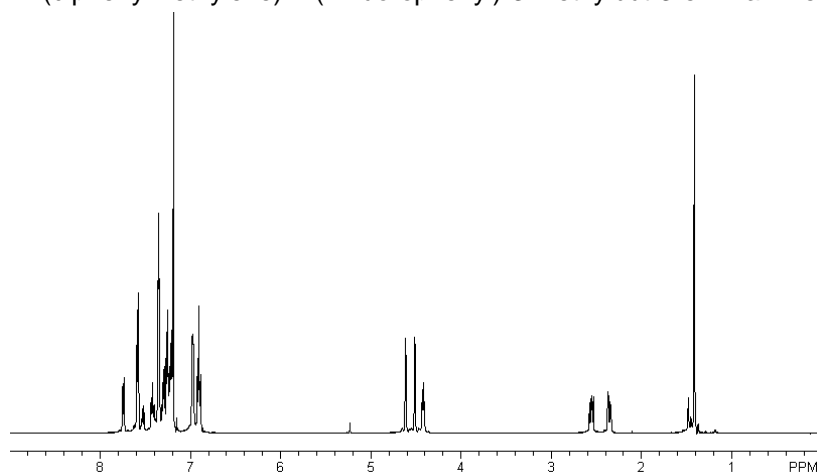
**2d:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (m, 2H: arom. CH), 7.59 (m, 2H: arom. CH), 7.52 (t,  $J = 7$  Hz, 1H: arom. CH), 7.30 (overlapping m, 5H: arom. CH) 6.97 (m, 2H: arom. CH), 6.90 (t,  $J = 7$  Hz 2H: arom. CH), 5.55 (ddt,  $J = 7$  Hz, 10 Hz, 17 Hz, 1H:  $\text{CH}=\text{CH}_2$ ), 4.89 (d,  $J = 17$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{trans}}$ ), 4.88 (d,  $J = 10$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{cis}}$ ), 4.33 (dd,  $J = 6$  Hz, 8 Hz, 1H: CH), 2.57 (ddd,  $J = 7$  Hz, 7 Hz, 14 Hz, 1H: diastereotopic allylic  $\text{CH}_2$ ), 2.46 (ddd,  $J = 6$  Hz, 7 Hz, 14 Hz, 1H: diastereotopic allylic  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.84 (C=N), 161.67 (d,  $J = 244$  Hz, C-F), 140.18 (arom. C), 137.61 (arom. C), 137.00 (arom C), 135.46 (=CH), 132.45 (arom. CH), 130.10 (arom. CH), 128.58 (arom. CH), 128.37 (arom. CH), 128.31 (arom. CH), 128.03 (arom. CH), 127.80 (arom. CH), 116.92 (=CH<sub>2</sub>), 115.04 (d,  $J = 21$  Hz, arom CH), 65.74

(CH), 44.02 (CH<sub>2</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\max}$  1639, 1600, 995. HRMS calcd for C<sub>23</sub>H<sub>21</sub>FN [M+H] = 330.1658, found 330.1641. Reaction time = 2 hours.



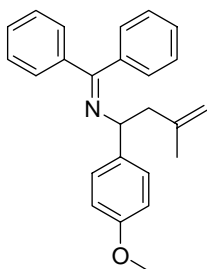
**2e**

*N*-(diphenylmethylene)-1-(4-fluorophenyl)-3-methylbut-3-en-1-amine



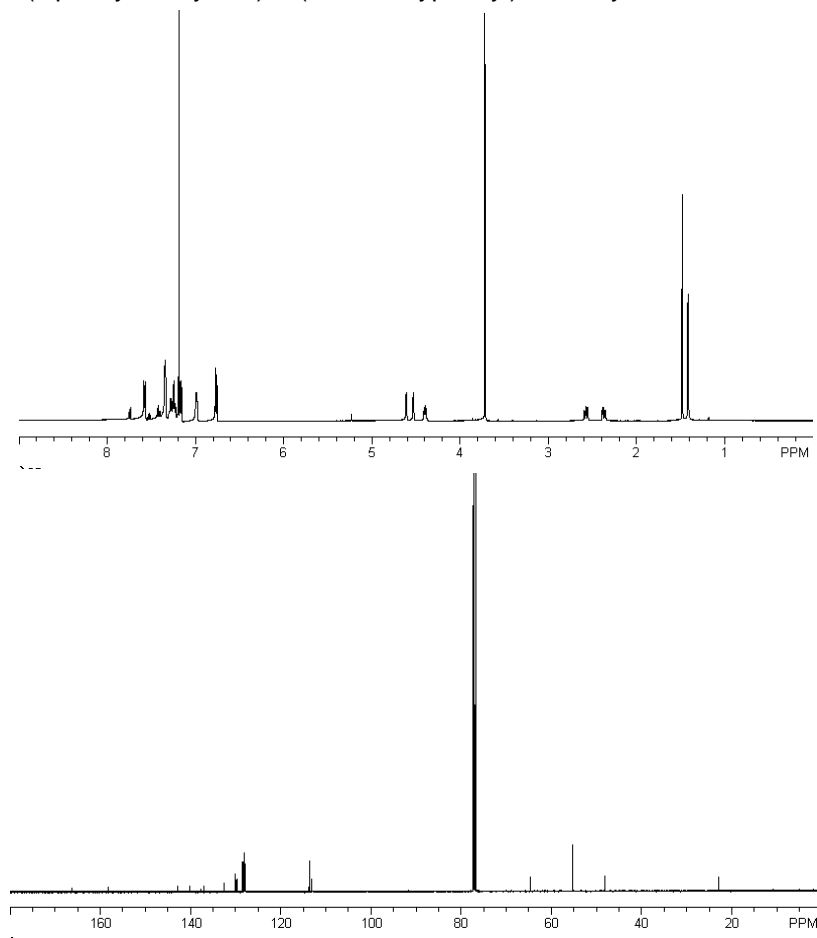
**2e:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d,  $J$  = 8 Hz, 1H: arom. CH), 7.54 (d,  $J$  = 8 Hz, 2H: arom. CH), 7.31 (overlapping m, 7H: arom. CH), 6.98 (m, 2H: arom. CH), 6.90 (t,  $J$  = 8 Hz, 2H: arom. CH), 4.61 (s, 1H: diastereotopic =CH<sub>2</sub>), 4.51 (s, 1H: diastereotopic =CH<sub>2</sub>), 4.24 (dd,  $J$  = 5 Hz, 8 Hz, 1H: CH), 2.55 (dd,  $J$  = 8 Hz, 13 Hz, 1H: diastereotopic allylic CH<sub>2</sub>), 2.36 (dd,  $J$  = 5 Hz, 13 Hz, 1H: diastereotopic allylic CH<sub>2</sub>), 1.42 (s, 3H: CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  166.62 (C=N), 161.64 (d,  $J$  = 244 Hz, C-F), 142.44 (arom. C), 140.57 (arom. C), 139.97 (C), 136.87 (=C), 132.45 (arom. CH), 130.10

(arom. CH), 129.92 (arom. CH), 128.59 (arom. CH), 128.28 (arom. CH), 128.00 (arom. CH), 127.96 (arom. CH), 115.02 (d,  $J = 21$  Hz, arom. CH), 113.32 (=CH<sub>2</sub>), 64.51 (CH), 48.19 (CH<sub>2</sub>), 22.85 (CH<sub>3</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\max}$  1620, 894, 761, 696. HRMS calcd for C<sub>24</sub>H<sub>23</sub>FN [M+H] = 344.1815, found 344.1800. Reaction time = 3 hours.



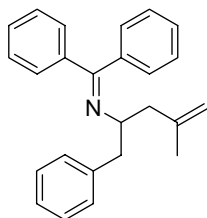
**2f**

*N*-(diphenylmethylene)-1-(4-methoxyphenyl)-3-methylbut-3-en-1-amine



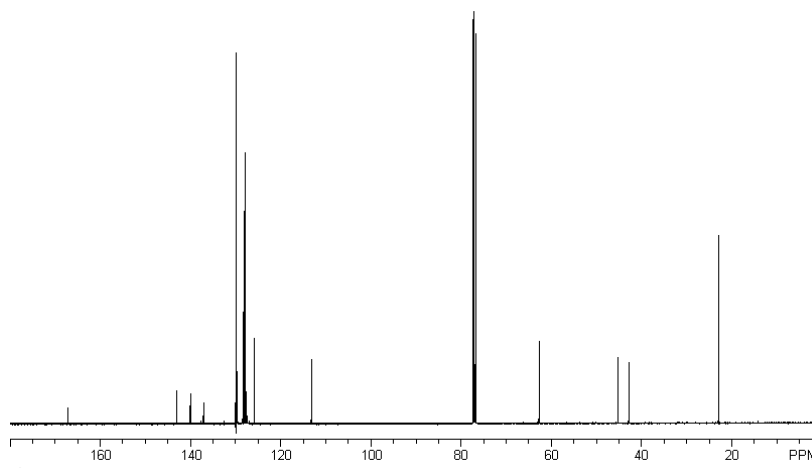
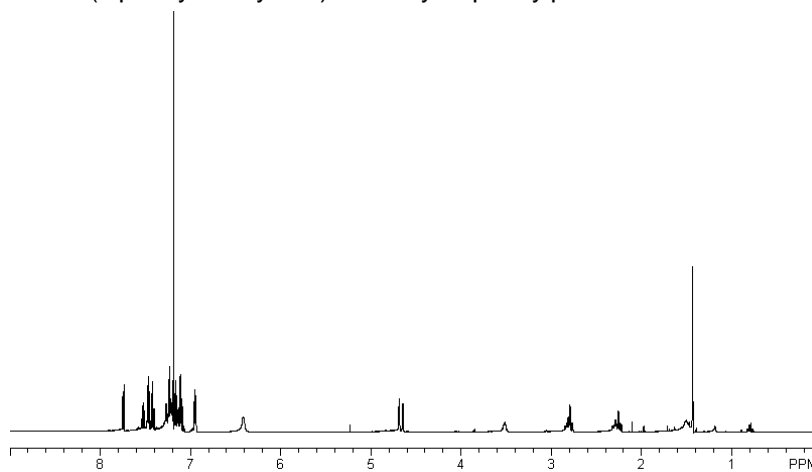
**2f:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (d,  $J = 7$  Hz, 2H: arom. CH), 7.34 (overlapping m, 3H: arom. CH), 7.26 (overlapping m, 3H: arom. CH), 7.17 (d,  $J = 8$  Hz, 2H: arom. CH), 6.98 (m, 2H: arom. CH), 6.77 (d,  $J = 8$  Hz, 2H: arom. CH), 4.61 (s, 1H: diastereotopic =CH<sub>2</sub>), 4.53 (s, 1H: diastereotopic =CH<sub>2</sub>), 4.40 (dd,  $J = 5$  Hz, 8 Hz, 1H:

CH), 3.72 (s, 3H: O-CH<sub>3</sub>), 2.57 (dd,  $J = 8$  Hz, 13 Hz, 1H: diastereotopic allylic CH<sub>2</sub>), 2.37 (dd,  $J = 5$  Hz, 13 Hz, 1H: diastereotopic allylic CH<sub>2</sub>), 1.42 (s, 3H: CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  166.16 (C=N), 158.28 (arom. C), 142.82 (arom. C), 140.17 (arom. C), 137.09 (C), 137.02 (C), 132.45 (arom. CH), 130.09 (arom. CH), 129.74 (arom. CH), 128.58 (arom. CH), 128.20 (arom. CH), 128.07 (arom. CH), 127.94 (arom. CH), 113.64 (arom. CH), 113.05 (=CH<sub>2</sub>), 64.58 (CH), 55.24 (O-CH<sub>3</sub>), 48.09 (CH<sub>2</sub>), 22.89 (CH<sub>3</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\max}$  1647, 1443, 897, 762. HRMS calcd for C<sub>25</sub>H<sub>26</sub>NO [M+H] = 356.2014, found 356.2000. Reaction time = 12 hours.



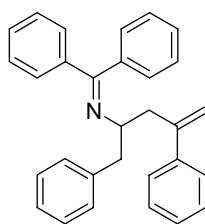
**2g**

*N*-(diphenylmethylene)-4-methyl-1-phenylpent-4-en-2-amine



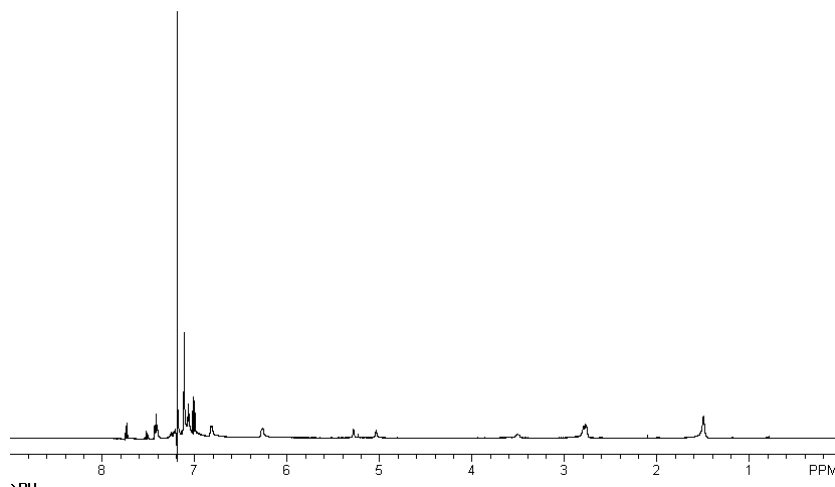
**2g:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d,  $J = 8$  Hz, 1H: arom. CH), 7.47 (m, 3H: arom. CH), 7.18 (overlapping m, 7H: arom. CH), 6.95 (d,  $J = 8$  Hz, 1H: arom. CH) 6.41 (m,

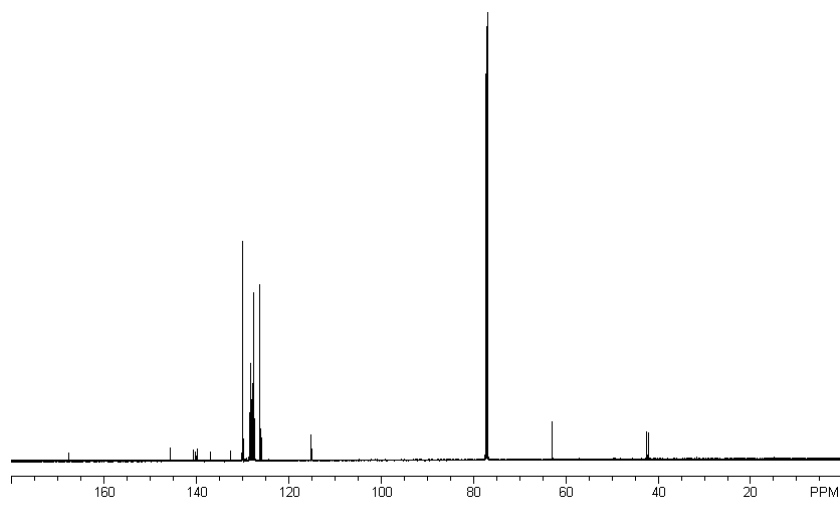
2H: arom. CH), 4.69 (s, 1H: diastereotopic =CH<sub>2</sub>), 4.65 (s, 1H: diastereotopic =CH<sub>2</sub>), 3.52 (m, 1H: CH), 2.83 (dd, *J* = 8 Hz, 13 Hz, 1H: diastereotopic benzylic CH<sub>2</sub>), 2.78 (dd, *J* = 4 Hz, 13 Hz, 1H: diastereotopic benzylic CH<sub>2</sub>), 2.30 (dd, *J* = 7 Hz, 13 Hz, 1H: diastereotopic allylic CH<sub>2</sub>), 2.24 (dd, *J* = 6 Hz, 13 Hz, 1H: diastereotopic allylic CH<sub>2</sub>), 1.43 (s, 3H: CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.08 (C=N), 142.98 (arom. C), 140.11 (arom. C), 139.88 (arom. C), 137.09 (=C), 129.88 (arom. CH), 129.59 (arom. CH), 128.35 (arom. CH), 128.08 (arom. CH), 127.97 (arom. CH), 127.85 (arom. CH), 127.76 (arom. CH), 127.74 (arom. CH), 125.86 (arom. CH), 113.18 (=CH<sub>2</sub>), 62.71 (CH), 45.17 (allylic CH<sub>2</sub>), 42.83 (benzylic CH<sub>2</sub>), 22.97 (CH<sub>3</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub>): ν<sub>max</sub> 1624, 895, 696. HRMS calcd for C<sub>25</sub>H<sub>26</sub>N [M+H] = 340.2065, found 340.2047. Reaction time = 6 hours.



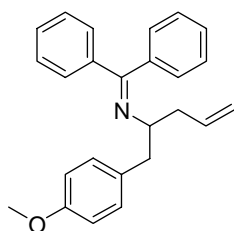
**2h**

*N*-(diphenylmethylene)-1,4-diphenylpent-4-en-2-amine



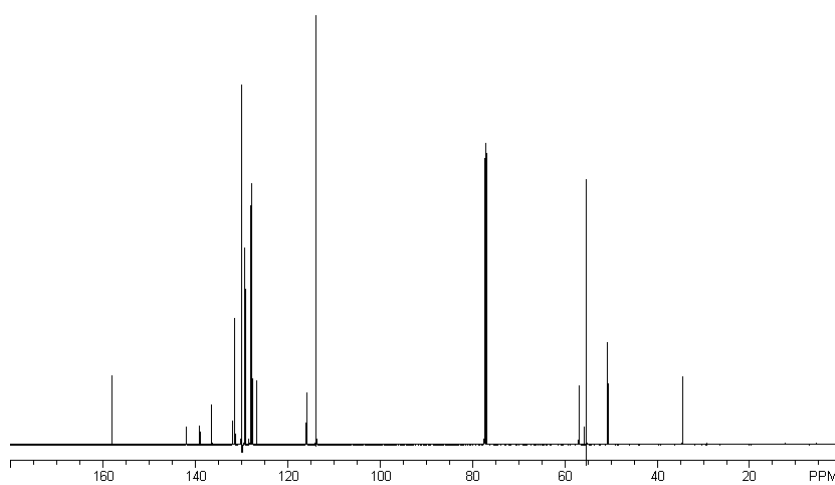
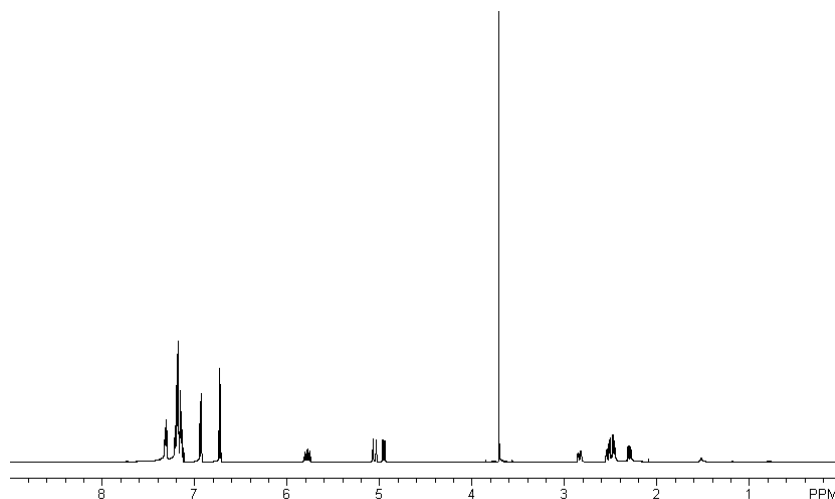


**2h:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (m, 2H: arom. CH), 7.23 (overlapping m, 6H: arom. CH), 7.09 (overlapping m, 6H: arom. CH), 7.01 (t,  $J = 8$  Hz, 1H: arom. CH) 6.82 (d,  $J = 6$  Hz, 2H: arom. CH), 6.28 (d,  $J = 7$  Hz, 2H: arom. CH), 5.28 (s, 1H: diastereotopic  $=\text{CH}_2$ ), 5.04 (s, 1H: diastereotopic  $=\text{CH}_2$ ), 3.50 (p,  $J = 7$  Hz, 1H: CH), 2.79 (overlapping m, 2H: benzylic  $\text{CH}_2$ ), 2.79 (overlapping m, 2H: allylic  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.45 (C=N), 145.46 (arom. C), 140.58 (arom. C), 139.99 (arom. C), 139.66 (arom. C), 136.82 ( $=\text{C}$ ), 132.45 (arom. CH), 129.79 (arom. CH), 128.33 (arom. CH), 128.13 (arom. CH), 128.06 (arom. CH), 127.93 (arom. CH), 127.76 (arom. CH), 127.59 (arom. CH), 127.43 (arom. CH), 127.20 (arom. CH), 126.10 (arom. CH), 125.86 (arom. CH), 114.99 ( $=\text{CH}_2$ ), 49.53 (CH), 42.46 ( $\text{CH}_2$ ), 42.10 ( $\text{CH}_2$ ). IR ( $\text{CD}_2\text{Cl}_2$ ):  $\nu_{\text{max}}$  1600, 895, 760, 696. HRMS calcd for  $\text{C}_{30}\text{H}_{28}\text{N}$  [ $\text{M}+\text{H}$ ] = 402.2222, found 402.2210. Reaction time = 3 hours.

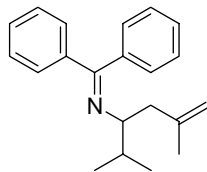


**2i**

*N*-(diphenylmethylene)-1-(4-methoxyphenyl)pent-4-en-2-amine

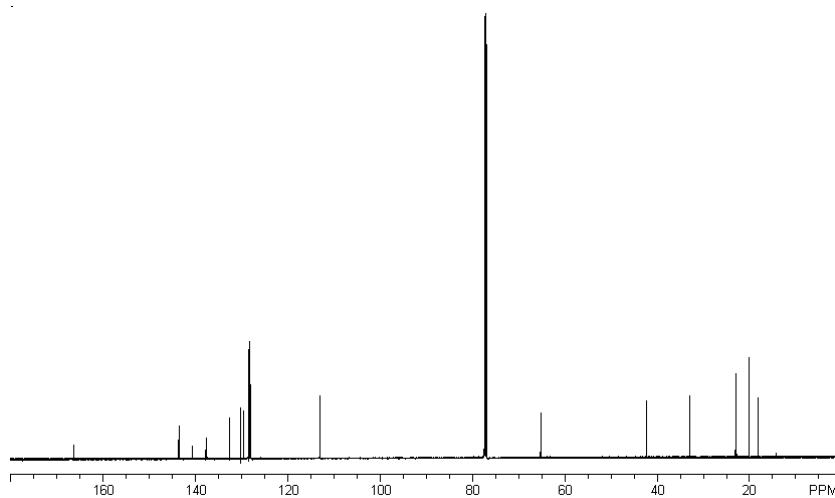
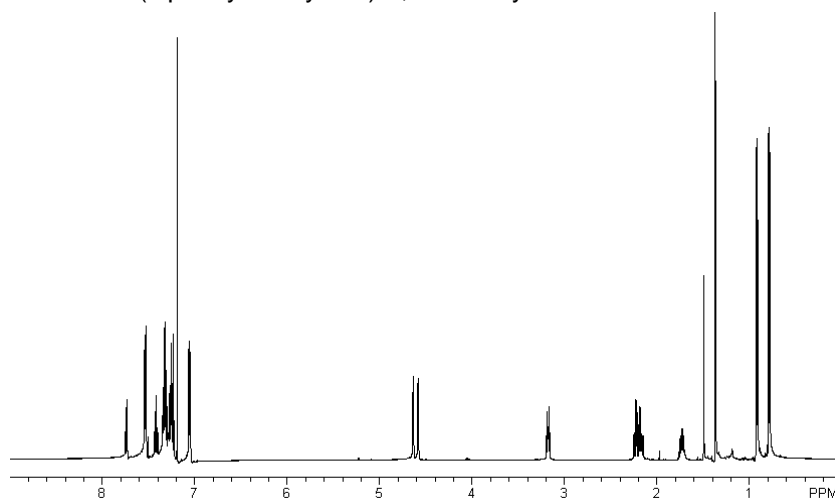


**2i:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 7$  Hz, 2H: arom. CH), 7.17 (overlapping m, 8H: arom. CH), 6.94 (d,  $J = 8$  Hz, 2H: arom. CH), 6.73 (d,  $J = 8$  Hz, 2H: arom. CH), 5.78 (ddt,  $J = 6$  Hz, 10 Hz, 17 Hz, 1H:  $\text{CH}=\text{CH}_2$ ), 5.07 (d,  $J = 17$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{trans}}$ ), 4.96 (d,  $J = 10$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{cis}}$ ), 3.71 (s, 3H:  $\text{OCH}_3$ ), 2.84 (dd,  $J = 6$  Hz, 15 Hz, 1H: CH), 2.53 (dd,  $J = 6$  Hz, 15 Hz, 1H: diastereotopic allylic  $\text{CH}_2$ ), 2.47 (m, 1H: CH), 2.47 (m, 1H: diastereotopic  $\text{CH}_2$ ), 2.30 (dd,  $J = 6$  Hz, 13 Hz, 1H: diastereotopic benzylic  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.93 (C=N), 141.87 (arom. C), 138.91 (arom. C), 136.33 (=CH), 132.45 (arom. C), 131.82 (arom. C), 131.32 (arom. CH), 129.79 (arom. CH), 129.11 (arom. CH), 127.97 (arom. CH), 127.72 (arom. CH), 127.52 (arom. CH), 126.56 (arom. CH), 115.84 (=CH<sub>2</sub>), 113.70 (arom. CH), 56.88 (benzylic  $\text{CH}_2$ ), 55.25 ( $\text{CH}_3$ ), 50.61 (CH), 34.36 (allylic  $\text{CH}_2$ ). IR ( $\text{CD}_2\text{Cl}_2$ ):  $\nu_{\text{max}}$  1610, 1161, 761. HRMS calcd for  $\text{C}_{25}\text{H}_{25}\text{NO}$  [M+H] = 356.2014, found 356.1980. Reaction time = 2 hours.

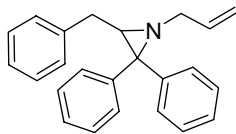


**2j**

*N*-(diphenylmethylene)-2,5-dimethylhex-5-en-3-amine

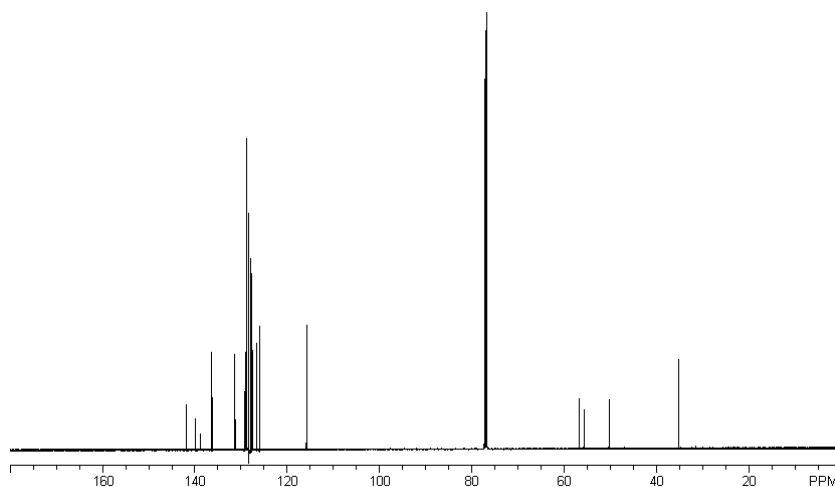
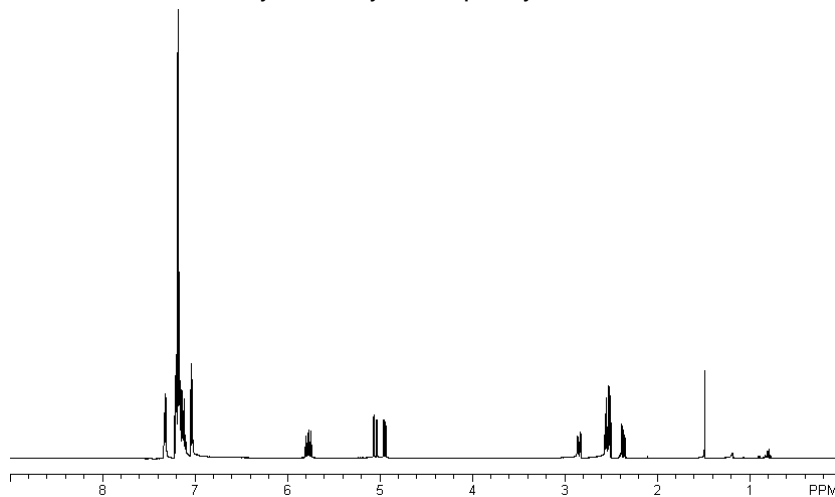


**2j:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 8$  Hz, 2H: arom. CH), 7.29 (overlapping m, 6H: arom. CH), 7.06 (d,  $J = 8$  Hz, 2H: arom. CH), 4.64 (s, 1H: diastereotopic  $=\text{CH}_2$ ), 4.58 (s, 1H: diastereotopic  $=\text{CH}_2$ ), 3.18 (dt,  $J = 5$  Hz, 8 Hz, 1H: N-CH), 2.24 (dd,  $J = 5$  Hz, 13 Hz, 1H: diastereotopic allylic  $\text{CH}_2$ ), 2.17 (dd,  $J = 8$  Hz, 13 Hz, 1H: diastereotopic allylic  $\text{CH}_2$ ), 1.73 (dq,  $J = 5$  Hz, 7 Hz, 1H: *i*-pr CH), 1.37 (s, 3H:  $\text{CH}_3$ ), 0.92 (d,  $J = 7$  Hz, 3H: diastereotopic  $\text{CH}_3$ ), 0.79 (d,  $J = 7$  Hz, 3H: diastereotopic  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.21 (C=N), 143.46 (arom. C), 140.52 (arom. C), 137.39 ( $=\text{C}$ ), 132.45 (arom. CH), 130.09 (arom. CH), 129.49 (arom. CH), 128.42 (arom. CH), 128.03 (arom. CH), 127.95 (arom. CH), 127.95 (arom. CH), 112.97 ( $=\text{CH}_2$ ), 65.16 (N-CH), 42.26 ( $\text{CH}_2$ ), 32.90 (*i*-pr CH), 22.98 ( $\text{CH}_3$ ), 20.03 (0.79)(diastereotopic  $\text{CH}_3$ ), 18.13 (0.92)(diastereotopic  $\text{CH}_3$ ). IR ( $\text{CD}_2\text{Cl}_2$ ):  $\nu_{\text{max}}$  1658, 1444, 1363, 894. HRMS calcd for  $\text{C}_{21}\text{H}_{26}\text{N}$  [M+H] = 292.2065, found 292.2053. Reaction time = 18 hours.



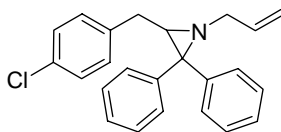
**4k**

1-allyl-3-benzyl-2,2-diphenylaziridine



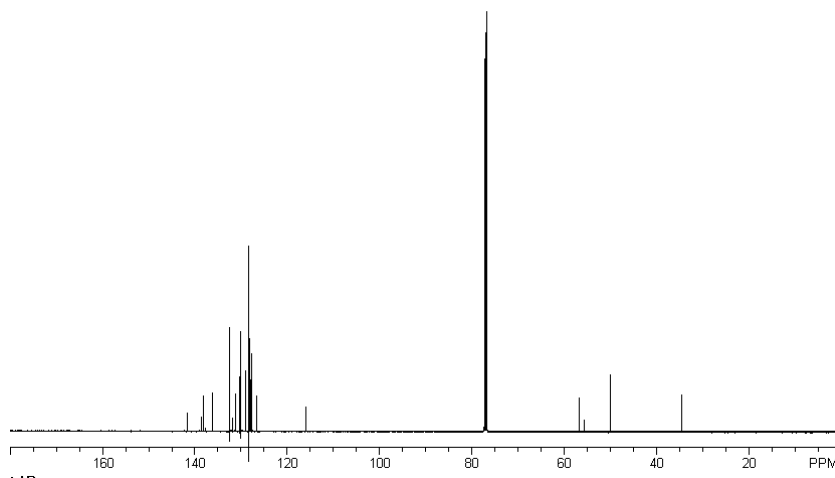
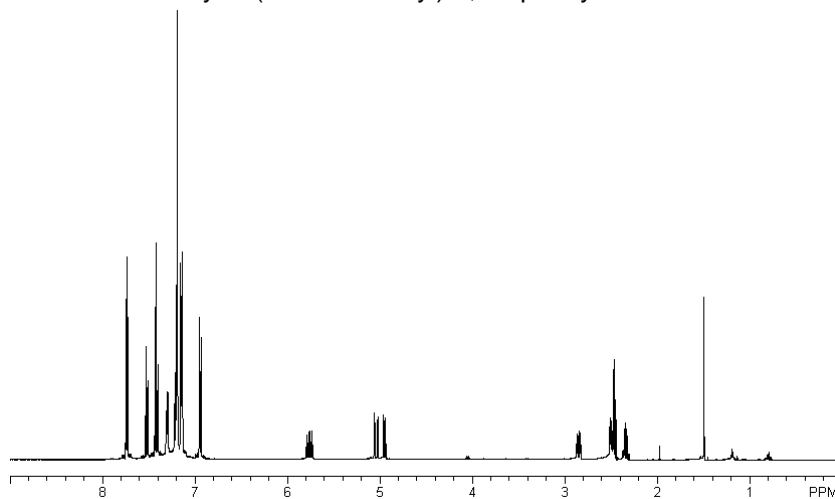
**4k:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 7$  Hz, 2H: arom. CH), 7.17 (overlapping m, 11H: arom. CH), 7.03 (d,  $J = 7$  Hz, 2H: arom. CH), 5.77 (ddt,  $J = 6$  Hz, 10 Hz, 17 Hz, 1H:  $\text{CH}=\text{CH}_2$ ), 5.05 (d,  $J = 17$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{trans}}$ ), 4.95 (d,  $J = 10$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{cis}}$ ), 2.84 (dd,  $J = 6$  Hz, 17 Hz, 1H: diastereotopic allylic  $\text{CH}_2$ ), 2.53 (overlapping m, 1H: diastereotopic allylic  $\text{CH}_2$ ), 2.53 (overlapping m, 1H: CH), 2.53 (overlapping m, 1H: diastereotopic benzylic  $\text{CH}_2$ ), 2.37 (dd,  $J = 6$  Hz, 13 Hz, 1H: diastereotopic benzylic  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.83 (arom. C), 139.79 (arom. C), 138.85 (arom. C), 136.29 ( $=\text{CH}$ ), 131.30 (arom. CH), 129.10 (arom. CH), 128.87 (arom. CH), 128.62 (arom. CH), 127.97 (arom. CH), 127.82 (arom. CH), 127.73 (arom. CH), 126.58 (arom. CH), 126.04 (arom. CH), 115.84 ( $=\text{CH}_2$ ), 56.86 (allylic  $\text{CH}_2$ ),

55.77 (C), 50.35 (CH), 35.31 (benzylic CH<sub>2</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\max}$  1421, 895, 758. HRMS calcd for C<sub>24</sub>H<sub>23</sub>N [M+H] = 326.1909, found 326.1867. Reaction time = 2 hours.



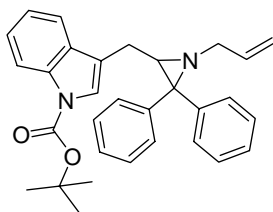
**41**

1-allyl-3-(4-chlorobenzyl)-2,2-diphenylaziridine



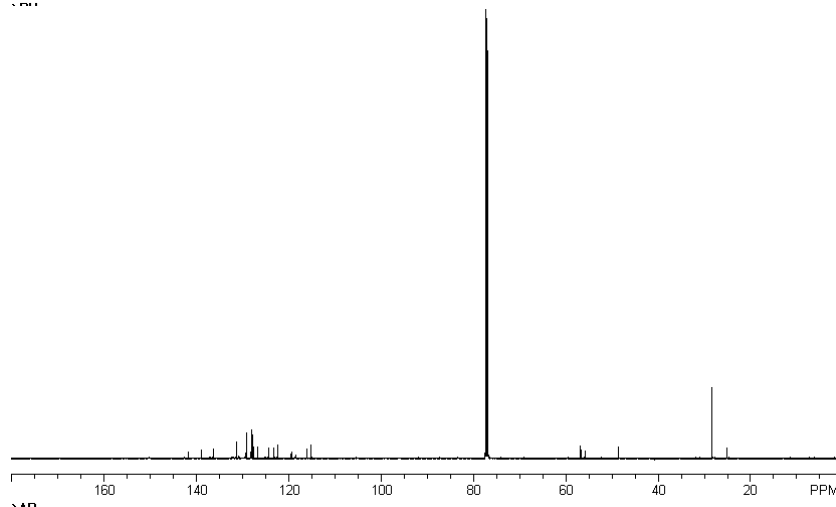
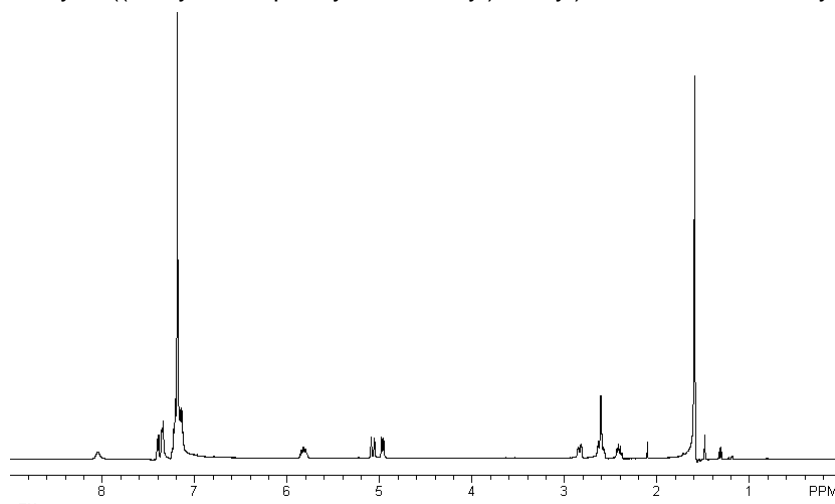
**41:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (m, 2H: arom. CH), 7.48 (t,  $J$  = 8 Hz, 1H: arom. CH), 7.42 (t,  $J$  = 8 Hz, 3H: arom. CH), 7.31 (d,  $J$  = 7 Hz, 2H: arom. CH), 7.21 (m, 3H: arom. CH), 7.14 (m, 2H: arom. CH), 6.95 (d,  $J$  = 8 Hz, 1H: arom. CH), 5.76 (ddt,  $J$  = 6 Hz, 10 Hz, 17 Hz, 1H: CH=CH<sub>2</sub>), 5.04 (d,  $J$  = 17 Hz, 1H: CH=CH(*H*)<sub>trans</sub>), 4.95 (d,  $J$  = 10 Hz, 1H: CH=CH(*H*)<sub>cis</sub>), 2.85 (dd,  $J$  = 6 Hz, 15 Hz, 1H: diastereotopic allylic CH<sub>2</sub>), 2.48 (overlapping m, 1H: diastereotopic allylic CH<sub>2</sub>), 2.48 (overlapping m, 1H: CH), 2.48 (overlapping m, 1H: diastereotopic benzylic CH<sub>2</sub>), 2.34 (dd,  $J$  = 5 Hz, 13 Hz, 1H: diastereotopic benzylic CH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  141.66 (arom. C), 138.65 (arom. C), 138.20 (arom. C), 137.60 (arom. C), 136.18 (=CH), 132.44 (arom. CH),

130.24 (arom. CH), 130.09 (arom. CH), 129.04 (arom. CH), 128.29 (arom. CH), 128.03 (arom. CH), 127.78 (arom. CH), 126.67 (arom. CH), 115.94 (=CH<sub>2</sub>), 56.84 (allylic CH<sub>2</sub>), 55.74 (C), 50.11 (CH), 34.70 (benzylic CH<sub>2</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\max}$  1492, 1446, 895. HRMS calcd for C<sub>24</sub>H<sub>23</sub>ClN [M+H] = 360.1519, found 360.1490. Reaction time = 3 hours.



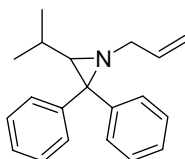
**4m**

*tert*-butyl 3-((1-allyl-3,3-diphenylaziridin-2-yl)methyl)-1*H*-indole-1-carboxylate



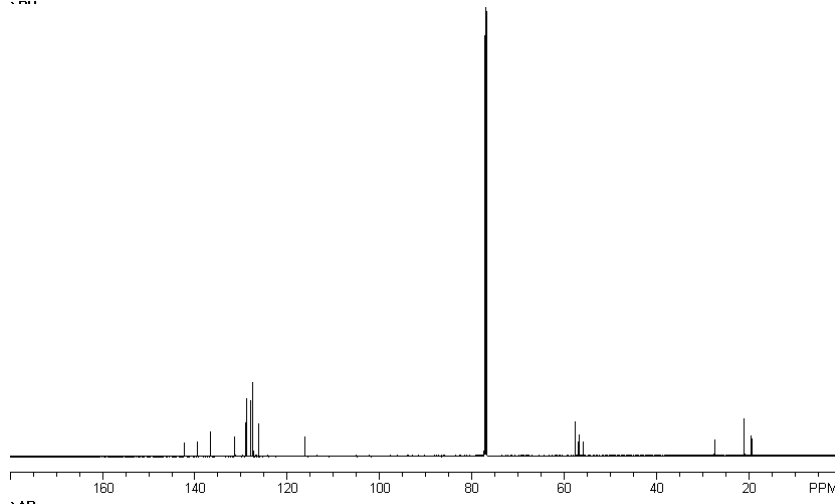
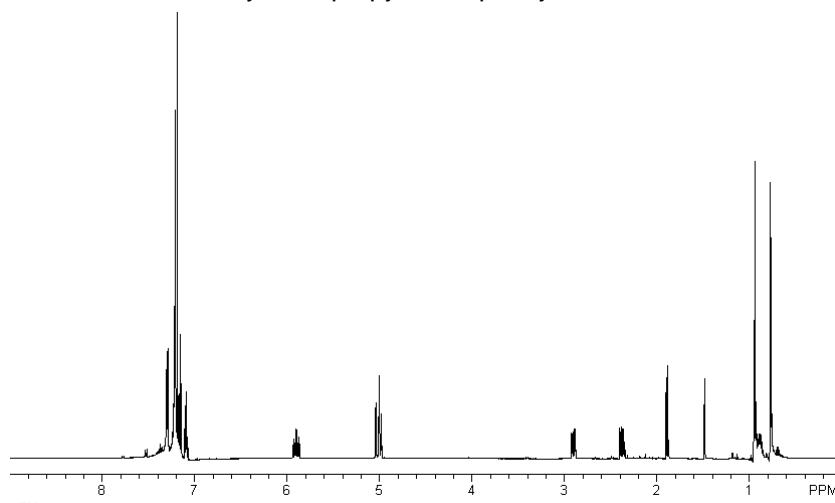
**4m:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (s, 1H: arom. CH), 7.40 (d,  $J = 7$  Hz, 1H: arom. CH), 7.35 (d,  $J = 7$  Hz, 2H: arom. CH), 7.19 (overlapping m, 11H: arom. CH), 5.82 (ddt,  $J = 6$  Hz, 10 Hz, 17 Hz, 1H: CH=CH<sub>2</sub>), 5.07 (d,  $J = 17$  Hz, 1H: CH=CH(*H*)<sub>trans</sub>), 4.97 (d,  $J = 10$  Hz, 1H: CH=CH(*H*)<sub>cis</sub>), 2.84 (dd,  $J = 6$  Hz, 15 Hz, 1H: diastereotopic N-CH<sub>2</sub>),

2.61 (overlapping m, 1H: diastereotopic N-CH<sub>2</sub>), 2.61 (overlapping m, 1H: CH), 2.61 (overlapping m, 1H: diastereotopic CH-CH<sub>2</sub>), 2.41 (dd, *J* = 9 Hz, 18 Hz, 1H: diastereotopic CH-CH<sub>2</sub>), 1.59 (s, 9H: CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.78 (C=O), 141.66 (arom. C), 138.71 (arom. C), 136.25 (=CH), 131.25 (arom. CH), 130.70 (arom. C), 129.09 (arom. CH), 128.01 (arom. CH), 127.79 (arom. CH), 127.58 (arom. CH), 126.64 (arom. CH), 124.28 (arom. CH), 123.04 (arom. CH), 122.33 (arom. CH), 119.32 (arom. CH), 118.44 (arom. C), 115.99 (=CH<sub>2</sub>), 115.10 (arom. CH), 83.28 (O-C), 56.70 (N-CH<sub>2</sub>), 55.76 (C), 48.49 (CH), 28.26 (CH<sub>3</sub>), 25.04 (CH-CH<sub>2</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub>): ν<sub>max</sub> 1713, 1420, 1367, 982. HRMS calcd for C<sub>31</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub> [M+H] = 465.2542, found 465.2518. Reaction time = 12 hours.

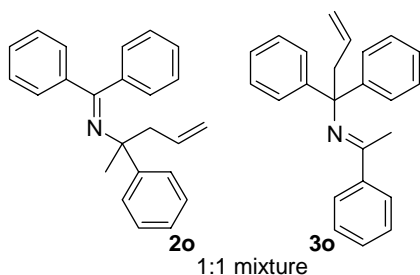


**4n**

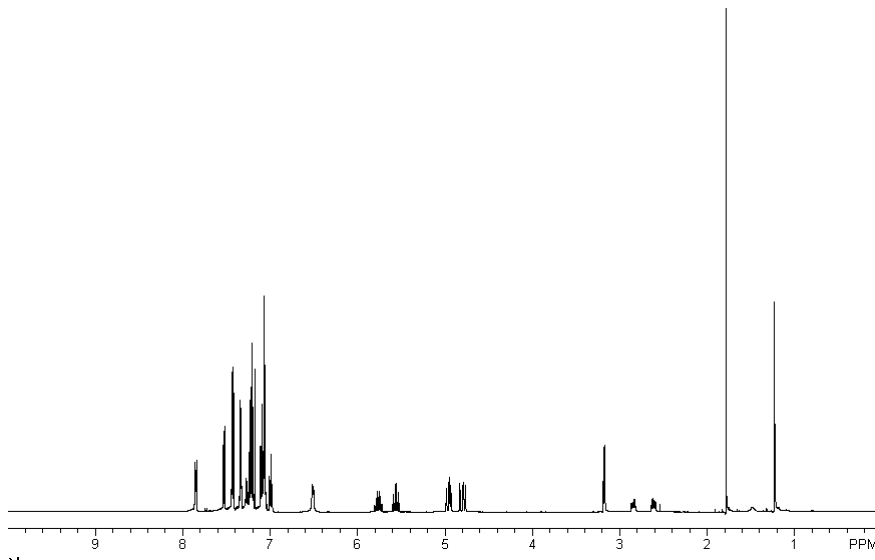
1-allyl-3-isopropyl-2,2-diphenylaziridine

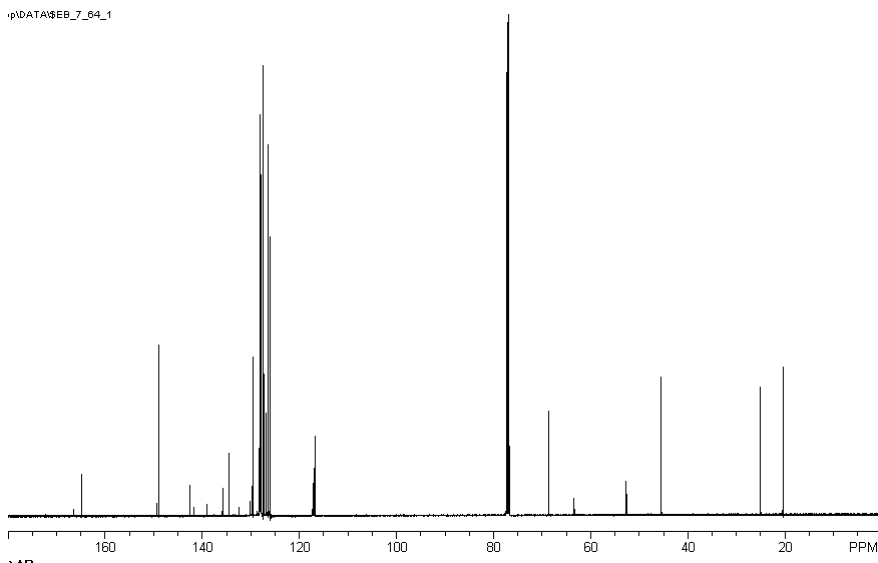


**4n:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J = 7$  Hz, 2H: arom. CH), 7.20 (overlapping m, 5H: arom. CH), 7.16 (t,  $J = 8$  Hz, 2H: arom. CH), 7.09 (t,  $J = 7$  Hz, 1H: arom. CH), 5.90 (ddt,  $J = 6$  Hz, 10 Hz, 17 Hz, 1H:  $\text{CH}=\text{CH}_2$ ), 5.03 (d,  $J = 10$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{cis}}$ ), 5.00 (d,  $J = 17$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{trans}}$ ), 2.90 (dd,  $J = 6$  Hz, 14 Hz, 1H: diastereotopic  $\text{CH}_2$ ), 2.38 (dd,  $J = 6$  Hz, 14 Hz, 1H: diastereotopic  $\text{CH}_2$ ), 1.89 (d,  $J = 9$  Hz, 1H: N-CH), 0.94 (d,  $J = 6$  Hz, 3H: diastereotopic  $\text{CH}_3$ ), 0.89 (m, 1H: *i*pr CH), 0.77 (d,  $J = 6$  Hz, 3H: diastereotopic  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.28 (arom. C), 139.45 (arom. C), 136.65 ( $=\text{CH}$ ), 131.33 (arom. CH), 128.89 (arom. CH), 127.94 (arom. CH), 127.56 (arom. CH), 127.41 (arom. CH), 126.24 (arom. CH), 116.16 ( $=\text{CH}_2$ ), 57.73 ( $\text{CH}_2$ ), 56.91 (N-CH), 55.97 (C), 27.54 (*i*pr CH), 21.05 (diastereotopic  $\text{CH}_3$ ), 19.51 (diastereotopic  $\text{CH}_3$ ). IR ( $\text{CD}_2\text{Cl}_2$ ):  $\nu_{\text{max}}$  1600, 1444, 1363, 997. HRMS calcd for  $\text{C}_{20}\text{H}_{24}\text{N}$  [ $\text{M}+\text{H}$ ] = 278.1909, found 278.1877. Reaction time = 2 hours.



**2o** *N*-(diphenylmethylene)-2-phenylpent-4-en-2-amine  
**3o** 1,1-diphenyl-*N*-(1-phenylethylidene)but-3-en-1-amine





**2o & 3o:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (m, 2H: arom. CH), 7.53 (d,  $J = 7$  Hz, 2H: arom. CH), 7.43 (d,  $J = 8$  Hz, 4H: arom. CH), 7.34 (m, 3H: arom. CH), 7.21 (overlapping m, 7H: arom. CH), 7.09 (overlapping m, 8H: arom. CH), 6.99 (t,  $J = 8$  Hz, 2H: arom. CH), 6.51 (d,  $J = 8$  Hz, 2H: arom. CH), 5.76 (ddt,  $J = 7$  Hz, 10 Hz, 17 Hz, 1H:  $\text{CH}=\text{CH}_2$ ), 5.56 (ddt,  $J = 7$  Hz, 10 Hz, 17 Hz, 1H:  $\text{CH}=\text{CH}_2$ ), 4.97 (d,  $J = 17$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{trans}}$ ), 4.94 (d,  $J = 10$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{cis}}$ ), 4.81 (d,  $J = 17$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{trans}}$ ), 4.78 (d,  $J = 10$  Hz, 1H:  $\text{CH}=\text{CH}(H)_{\text{cis}}$ ), 3.18 (d,  $J = 7$  Hz, 2H:  $\text{CH}_2$  of **3o**), 2.85 (dd,  $J = 7$  Hz, 13 Hz, 1H: diastereotopic  $\text{CH}_2$  of **2o**), 2.61 (dd,  $J = 7$  Hz, 13 Hz, 1H: diastereotopic  $\text{CH}_2$  of **2o**), 1.79 (s, 3H:  $\text{CH}_3$ ), 1.23 (s, 3H:  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.40 (C=N), 164.86 (C=N), 149.28 (arom. C), 148.91 (arom. C), 142.57 (arom. C), 141.71 (arom. C), 139.03 (arom. C), 135.77 (=CH), 134.30 (=CH), 130.11 (arom. CH), 129.69 (arom. CH), 129.51 (arom. CH), 128.24 (arom. CH), 128.15 (arom. CH), 128.08 (arom. CH), 127.92 (arom. CH), 127.79 (arom. CH), 127.48 (arom. CH), 127.29 (arom. CH), 127.24 (arom. CH), 126.86 (arom. CH), 126.36 (arom. CH), 125.98 (arom. CH), 117.21 (=CH<sub>2</sub>), 116.81 (=CH<sub>2</sub>), 68.69 (C), 63.37 (C), 52.63 (CH<sub>2</sub>), 45.41 (CH<sub>2</sub>), 24.97 (CH<sub>3</sub>), 20.37 (CH<sub>3</sub>). IR ( $\text{CD}_2\text{Cl}_2$ ):  $\nu_{\text{max}}$  1637, 1445, 977, 894. HRMS calcd for  $\text{C}_{24}\text{H}_{24}\text{N}$  [M+H] = 326.1909, found 326.1909. Reaction time = 2 hours.