

## Supporting Information

# Suzuki–Miyaura Cross–Coupling Reactions of Potassium Vinyltrifluoroborate with Aryl- and Heteroaryl Electrophiles

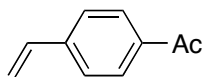
Gary A. Molander\* and Adam R. Brown

*Roy and Diana Vagelos Laboratories, Department of Chemistry, University of  
Pennsylvania, Philadelphia, PA 19104-6323, USA*

[gmolandr@sas.upenn.edu](mailto:gmolandr@sas.upenn.edu)

General Experimental Section.....	S2
Compound Characterization.....	S2
Spectra.....	S15

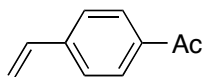
**General.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded at 500MHz,  $^1\text{H}$ ; 125MHz,  $^{13}\text{C}$ , respectively or 360MHz,  $^1\text{H}$ ; 100MHz,  $^{13}\text{C}$ , respectively. Spectra were referenced to internal TMS (0.00 ppm,  $^1\text{H}$ ) and residual chloroform (77.0 ppm,  $^{13}\text{C}$ ). All electrophiles were commercial samples, with the exception of **10i** and **10j**, and were used without further purification.



### General Procedure for Suzuki–Miyaura Cross–Coupling

#### Reactions. Preparation of 1-(4-Vinyl-phenyl)-ethanone (**3a**).<sup>1</sup> A

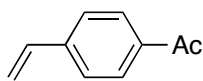
solution of potassium vinyltrifluoroborate (134 mg, 1.00 mmol), PdCl<sub>2</sub> (3.5 mg, 0.02 mmol), PPh<sub>3</sub> (16 mg, 0.06 mmol), Cs<sub>2</sub>CO<sub>3</sub> (978 mg, 3.00 mmol), and 4-bromoacetophenone (199 mg, 1.00 mmol) in THF/H<sub>2</sub>O (9:1) (2 mL) was heated at 85 °C under a N<sub>2</sub> atmosphere in a sealed tube. The reaction mixture was stirred at 85 °C for 22 h, then cooled to rt and diluted with H<sub>2</sub>O (3 mL) followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> (10 mL X 3). The solvent was removed *in vacuo*, and the crude product was purified by silica gel chromatography (eluting with 20:1 *n*-pentane:ether) to yield 1-(4-vinyl-phenyl)-ethanone as a pale yellow solid (123 mg, 0.848 mmol, 85%) mp 33-34 °C. The spectral data obtained were in accordance with those described in the literature.



#### 1-(4-Vinyl-phenyl)-ethanone (**3a**).<sup>1</sup> (From 4-iodoacetophenone).

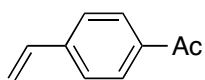
Following the general procedure, potassium trifluoroborate (134 mg, 1.00 mmol) was reacted with 4-iodoacetophenone (246 mg, 1.00 mmol) to yield 1-(4-vinyl-phenyl)-ethanone as a pale yellow solid (130 mg, 0.890 mmol, 89%) mp 33-34 °C. The spectral data obtained were in accordance with those described in the literature.

<sup>1</sup> Denmark, S. E.; Butler, C. R. *Org. Lett.* **2006**, *8*, 63–66.



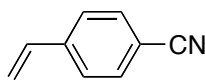
**1-(4-Vinyl-phenyl)-ethanone (3a).**<sup>1</sup> (From 4-acetylphenyl trifluoromethanesulfonate). Following the general procedure,

potassium trifluoroborate (134 mg, 1.00 mmol) was reacted with 4-acetylphenyl trifluoromethanesulfonate (268 mg, 1.00 mmol) to yield 1-(4-vinyl-phenyl)-ethanone as a pale yellow solid (119 mg, 0.815 mmol, 82%) mp 33-34 °C. The spectral data obtained were in accordance with those described in the literature.



**1-(4-Vinyl-phenyl)-ethanone (3a).**<sup>1</sup> (From 4-chloroacetophenone). A solution of potassium vinyltrifluoroborate (134 mg, 1.00 mmol), PdCl<sub>2</sub>

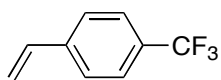
(3.5 mg, 0.02 mmol), RuPhos (28 mg, 0.06 mmol), Cs<sub>2</sub>CO<sub>3</sub> (978 mg, 3.00 mmol), and 4-chloroacetophenone (154 mg, 1.00 mmol) in THF/H<sub>2</sub>O (9:1) (2 mL) was heated at 85 °C under a N<sub>2</sub> atmosphere in a sealed tube. The reaction mixture was stirred at 85 °C for 22 h, then cooled to rt and diluted with H<sub>2</sub>O (3 mL) followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> (10 mL X 3). The solvent was removed *in vacuo*, and the crude product was purified by silica gel chromatography (eluting with 20:1 *n*-pentane:ether) to yield 1-(4-vinyl-phenyl)-ethanone as a pale yellow solid (123 mg, 0.848 mmol, 85%) mp 33-34 °C. The spectral data obtained were in accordance with those described in the literature.



**4-Vinyl-benzonitrile (5a).**<sup>2</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with

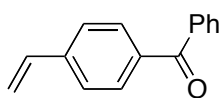
<sup>2</sup> Shirakawa, E.; Yamasaki, K.; Tamerjiro, H. *Synthesis* **1998**, 1544-1549.

4-bromobenzonitrile (182 mg, 1.00 mmol) to yield 4-vinyl-benzonitrile as a clear liquid (107 mg, 0.829 mmol, 83%). The spectral data obtained were in accordance with those described in the literature.



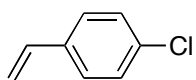
**1-Trifluoromethyl-4-vinylbenzene (5b).**<sup>2</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was

reacted with 1-bromo-4-(trifluoromethyl)benzene (225 mg, 1.00 mmol) to yield 1-trifluoromethyl-4-vinylbenzene as a clear liquid (110 mg, 0.640 mmol, 64%). The spectral data obtained were in accordance with those described in the literature.



**Phenyl-(4-vinyl-phenyl)-methanone (5c).**<sup>2</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was

reacted with (4-bromophenyl)(phenyl)methanone (261 mg, 1.00 mmol) to yield phenyl-(4-vinyl-phenyl)-methanone as a white solid (177 mg, 0.851 mmol, 85%) mp 51-52 °C. The spectral data obtained were in accordance with those described in the literature.

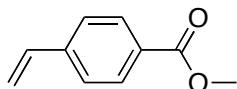


**4-Chloro-4-vinylbenzene (5d).**<sup>3</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 1-

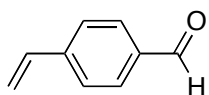
bromo-4-chlorobenzene (191 mg, 1.00 mmol) to yield 4-chloro-4-vinylbenzene as a clear liquid (106 mg, 0.768 mmol, 77%). The spectral data obtained were in accordance with those described in the literature.

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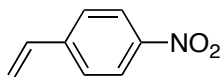
<sup>3</sup> Peyroux, E.; Berthiol, F.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2004**, 1075–1082.



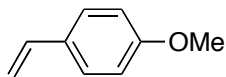
**4-Vinyl-benzoic acid, methyl ester (5e).**<sup>4</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with methyl 4-bromobenzoate (215 mg, 1.00 mmol) to yield 4-vinyl-benzoic acid, methyl ester as a white solid (141 mg, 0.870 mmol, 87%) mp 33-34.5 °C. The spectral data obtained were in accordance with those described in the literature.



**4-Vinyl-benzaldehyde (5f).**<sup>2</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 4-bromobenzaldehyde (185 mg, 1.00 mmol) to yield 4-vinyl-benzaldehyde as a clear liquid (110 mg, 0.833 mmol, 83%). The spectral data obtained were in accordance with those described in the literature.



**1-Nitro-4-vinylbenzene (5g).**<sup>5</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 1-bromo-4-nitrobenzene (202 mg, 1.00 mmol) to yield 1-nitro-4-vinylbenzene as a yellow liquid (125 mg, 0.839 mmol, 84%). The spectral data obtained were in accordance with those described in the literature.

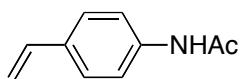


**1-Methoxy-4-vinylbenzene (7a).**<sup>1</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 4-bromoanisole (187 mg, 1.00 mmol) to yield 1-methoxy-4-vinylbenzene as a clear

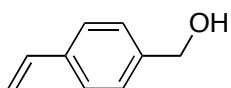
<sup>4</sup> Battace, A.; Zair, T.; Doucet, H.; Santelli, M. *J. Organomet. Chem.* **2005**, *690*, 3790-3801.

<sup>5</sup> Li, J. -H.; Liang, Y.; Wang, D. -P.; Liu, W. -J.; Xie, Y. -X.; Yin, D. -L. *J. Org. Chem.* **2005**, *70*, 2832-2834.

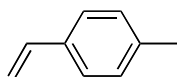
liquid (96 mg, 0.72 mmol, 72%). The spectral data obtained were in accordance with those described in the literature.



***N*-(4-Vinylphenyl)acetamide (7b).**<sup>1</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with *N*-(4-bromophenyl)acetamide (214 mg, 1.00 mmol) to yield *N*-(4-vinylphenyl)acetamide as a white solid (126 mg, 0.783 mmol, 78%) mp 132.5-134 °C. The spectral data obtained were in accordance with those described in the literature.



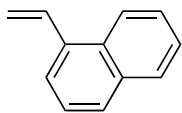
**(4-Vinylphenyl)methanol (7c).**<sup>1</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with (4-bromophenyl)methanol (187 mg, 1.00 mmol) to yield (4-vinylphenyl)methanol as a clear liquid (110 mg, 0.821 mmol, 82%). The spectral data obtained were in accordance with those described in the literature.



**1-Methyl-4-vinylbenzene (7d).**<sup>6</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 1-bromo-4-methylbenzene (171 mg, 1.00 mmol) to yield 1-methyl-4-vinylbenzene as a clear liquid (90 mg, 0.763 mmol, 76%). The spectral data obtained were in accordance with those described in the literature.

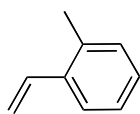
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<sup>6</sup> Mowery, M. E.; Deshong, P. *J. Org. Chem.* **1999**, *64*, 1684-1688.



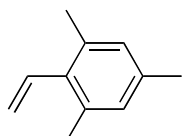
**1-Vinylnaphthalene (7e).**<sup>1</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 1-

bromonaphthalene (207 mg, 1.00 mmol) to yield 1-vinylnaphthalene as a clear liquid (126 mg, 0.818 mmol, 82%). The spectral data obtained were in accordance with those described in the literature.



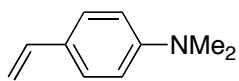
**1-Methyl-2-vinylbenzene (7f).** Following the general procedure,

potassium vinyltrifluoroborate (141 mg, 1.05 mmol) was reacted with 1-bromo-2-methylbenzene (171 mg, 1.00 mmol) to yield 1-methyl-2-vinylbenzene as a clear liquid (97 mg, 0.82 mmol, 82%), containing 7% of 1-bromo-2-methylbenzene by <sup>1</sup>H-NMR analysis. The spectral data obtained were in accordance with those of a commercially available sample.

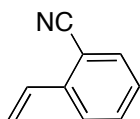


**1, 3, 5-Trimethyl-2-vinylbenzene (7g).**<sup>1</sup> A solution of potassium

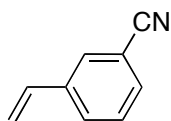
vinyltrifluoroborate (141 mg, 1.05 mmol), PdCl<sub>2</sub> (3.5 mg, 0.02 mmol), RuPhos (27.9 mg, 0.06 mmol), Cs<sub>2</sub>CO<sub>3</sub> (978 mg, 3.00 mmol), and 2-bromo-1,3,5-trimethylbenzene (199 mg, 1.00 mmol) in THF/H<sub>2</sub>O (9:1) (2 mL) was heated at 85 °C under a N<sub>2</sub> atmosphere in a sealed tube. The reaction mixture was stirred at 85 °C for 22 h, then cooled to rt and diluted with H<sub>2</sub>O (3 mL) followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> (10 mL X 3). The solvent was removed *in vacuo*, and the crude product was purified by silica gel chromatography to yield 1,3,5-trimethyl-2-vinylbenzene as a clear liquid (118 mg, 0.808 mmol, 81%). The spectral data obtained were in accordance with those described in the literature.



**Dimethyl-(4-vinyl-phenyl)-amine (7h).**<sup>7</sup> A solution of potassium vinyltrifluoroborate (141 mg, 1.05 mmol), PdCl<sub>2</sub> (3.5 mg, 0.02 mmol), RuPhos (27.9 mg, 0.06 mmol), Cs<sub>2</sub>CO<sub>3</sub> (978 mg, 3.00 mmol), and 4-bromo-*N,N*-dimethylbenzenamine (200 mg, 1.00 mmol) in THF/H<sub>2</sub>O (9:1) (2 mL) was heated at 85 °C under a N<sub>2</sub> atmosphere in a sealed tube. The reaction mixture was stirred at 85 °C for 22 h, then cooled to rt and diluted with H<sub>2</sub>O (3 mL) followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> (10 mL X 3). The solvent was removed *in vacuo*, and the crude product was purified by silica gel chromatography to yield dimethyl-(4-vinyl-phenyl)-amine as a clear liquid (136 mg, 0.925 mmol, 93%). The spectral data obtained were in accordance with those described in the literature.



**2-Vinyl-benzonitrile (9a).**<sup>2</sup> Following the general procedure, potassium vinyltrifluoroborate (141 mg, 1.05 mmol) was reacted with 2-bromobenzonitrile (182 mg, 1.00 mmol) to yield 2-vinyl-benzonitrile as a clear liquid (106 mg, 0.822 mmol, 82%). The spectral data obtained were in accordance with those described in the literature.



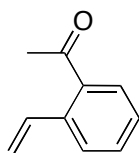
**3-Vinyl-benzonitrile (9b).**<sup>8</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 3-bromobenzonitrile (182 mg, 1.00 mmol) to yield 3-vinyl-benzonitrile as a clear liquid (100 mg, 0.775 mmol, 78%): <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 5.38 (d, 1H, *J*=10.8 Hz),

<sup>7</sup> Su, W.; Urgaonker, S.; McLaughlin, P. A.; Verkade, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 16433-16439.

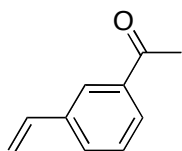
<sup>8</sup> Reynolds, W. F.; Gomes, A.; Maron, A.; MacIntyre, D. W.; Maunder, R. G.; et al. *Can. J. Chem.* **1983**, *61*, 2367-2375.



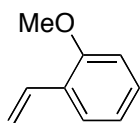
5.81 (d, 1H,  $J=17.6$  Hz), 6.68 (dd, 1H,  $J=17.6$  and 11.2 Hz), 7.42 (t, 1H,  $J=7.5$  Hz), 7.52 (dt, 1H,  $J=7.5$  and 1.8 Hz), 7.59-7.61 (m, 2H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  112.6, 116.5, 118.6, 129.2, 129.6, 130.2, 130.9, 134.7, 138.6. IR (neat): 3092, 2231, 1840, 1632, 1599, 1576, 1478, 1397, 1310, 1280, 1156, 1089, 990, 920, 710, 664. HRMS ( $m/z$ ): calcd. for  $\text{C}_9\text{H}_7\text{N}$ , 129.0578 [ $\text{M}^+$ ]; found, 129.0582.



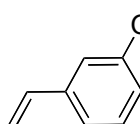
**1-(2-Vinylphenyl)ethanone (9c).**<sup>2</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 2'-bromoacetophenone (199 mg, 1.00 mmol) to yield 1-(2-vinylphenyl)ethanone as a clear liquid (134 mg, 0.918 mmol, 92%), containing 8% of 2'-bromoacetophenone by  $^1\text{H}$ -NMR analysis. The spectral data obtained were in accordance with those described in the literature.



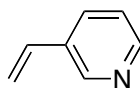
**1-(3-Vinylphenyl)ethanone (9d).**<sup>8</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 3'-bromoacetophenone (199 mg, 1.00 mmol) to yield 1-(3-vinylphenyl)ethanone as a clear liquid (116 mg, 0.794 mmol, 79%):  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  2.59 (s, 3H), 5.32 (d, 1H,  $J=10.8$  Hz), 5.82 (d, 1H,  $J=17.6$  Hz), 6.74 (dd, 1H,  $J=17.6$  and 11.2 Hz), 7.40 (t, 1H,  $J=7.6$  Hz), 7.59 (dt, 1H,  $J=7.9$  and 1.8 Hz), 7.82, (dt, 1H,  $J=7.6$  and 1.8 Hz), 7.96 (t, 1H,  $J=1.8$  Hz);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  26.5, 115.1, 125.9, 127.5, 128.6, 130.4, 135.8, 137.3, 137.9, 197.9. IR (neat): 3352, 3089, 3060, 3007, 1828, 1682, 1632, 1598, 1578, 1480, 1438, 1401, 1357, 1263, 1189, 1082, 1020, 991, 956, 913, 802, 710, 674, 589. HRMS ( $m/z$ ): calcd. for  $\text{C}_{10}\text{H}_{10}\text{O}$ , 146.0732 [ $\text{M}^+$ ]; found 146.0709.



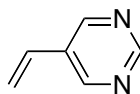
**1-Methoxy-2-vinylbenzene (9e).**<sup>2</sup> Following the general procedure, potassium vinyltrifluoroborate (141 mg, 1.05 mmol) was reacted with 1-bromo-2-methoxybenzene (187 mg, 1.00 mmol) to yield 1-methoxy-2-vinylbenzene as a clear liquid (95 mg, 0.71 mmol, 71%). The spectral data obtained were in accordance with those described in the literature.



**1-Methoxy-3-vinylbenzene (9f).**<sup>2</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 1-bromo-3-methoxybenzene (187 mg, 1.00 mmol) to yield 1-methoxy-3-vinylbenzene as a clear liquid (99 mg, 0.74 mmol, 74%). The spectral data obtained were in accordance with those described in the literature.



**3-Vinylpyridine (11a).**<sup>9</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 3-bromopyridine (158 mg, 1.00 mmol) to yield 3-vinylpyridine as a clear liquid (76 mg, 0.72 mmol, 72%). The spectral data obtained were in accordance with those described in the literature.

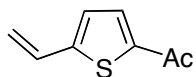


**5-Vinylpyrimidine (11b).**<sup>10</sup> Following the general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 5-bromopyrimidine (159 mg, 1.00 mmol) to yield 5-vinylpyrimidine as a clear liquid (84 mg, 0.792 mmol, 79%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 5.52 (d, 1H, *J*=11.5 Hz), 5.94 (d,

<sup>9</sup> Alunni, S.; Laureti, V.; Ottavi, L.; Ruzziconi, R. *J. Org. Chem.* **2003**, *68*, 718-725.

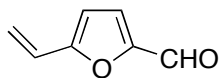
<sup>10</sup> Detert, H.; Sadovski, O.; Sugiono, E. *J. Phys. Org. Chem.* **2004**, *11*, 1046 - 1050.

1H,  $J=17.6$  Hz), 6.67 (dd, 1H,  $J=18$  and 10.8 Hz), 8.77 (s, 2H), 9.10 (s, 1H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  118.4, 130.0, 130.7, 154.0, 157.4. IR (neat): 3028, 1634, 1576, 1553, 1404, 1236, 1189, 1108, 1025, 990, 926, 813, 729, 671, 634. HRMS ( $m/z$ ): calcd. for  $\text{C}_6\text{H}_6\text{N}_2$ , 106.0530 [ $\text{M}^+$ ]; found 106.0526.



**1-(5-Vinylthiophen-2-yl)ethanone (11c).**<sup>11</sup> Following the general

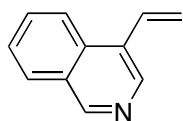
procedure, potassium vinyltrifluoroborate (141 mg, 1.05 mmol) was reacted with 1-(5-bromothiophen-2-yl)ethanone (205 mg, 1.00 mmol) to yield 1-(5-vinylthiophen-2-yl)ethanone as a clear liquid (102 mg, 0.658 mmol, 66%). The spectral data obtained were in accordance with those described in the literature.



**5-Vinylfuran-2-carbaldehyde (11d).** Following the general

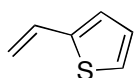
procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 5-bromofuran-2-carbaldehyde (175 mg, 1.00 mmol) to yield 5-vinylfuran-2-carbaldehyde as a yellow liquid (86 mg, 0.70 mmol, 70%):  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  5.48 (d, 1H,  $J=11.5$  Hz), 6.02 (d, 1H,  $J=17.6$  Hz), 6.48 (d, 1H,  $J=3.6$  Hz), 6.58 (dd, 1H,  $J=17.3$  and 11.2 Hz), 7.23 (d, 1H,  $J=3.6$  Hz), 9.60 (s, 1H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  110.1, 118.6, 123.0, 124.1, 151.6, 158.0, 177.2. IR (neat): 3118, 2930, 2831, 1678, 1578, 1518, 1450, 1398, 1371, 1325, 1278, 1187, 1024, 961, 805, 769, 734, 702. HRMS ( $m/z$ ): calcd. for  $\text{C}_7\text{H}_6\text{O}_2$ , 122.0368 [ $\text{M}^+$ ]; found 122.0365.

<sup>11</sup> Molander, G. A., Rivero, M. R. *Org. Lett.* **2002**, *4*, 107–109.



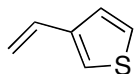
**4-Vinyl-isoquinoline (11e).**<sup>4</sup> Following the general procedure,

potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 4-bromoisoquinoline (208 mg, 1.00 mmol) to yield 4-vinyl-isoquinoline as a clear liquid (136 mg, 0.877 mmol, 88%). The spectral data obtained were in accordance with those described in the literature.



**2-Vinylthiophene (11f).**<sup>12</sup> Following the general procedure, potassium

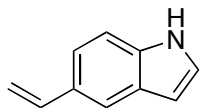
vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 2-bromothiophene (163 mg, 1.00 mmol) to yield 2-vinylthiophene as a clear liquid (70 mg, 0.64 mmol, 64%). The spectral data obtained were in accordance with those described in the literature.



**3-Vinylthiophene (11g).**<sup>4</sup> A solution of potassium vinyltrifluoroborate (134 mg, 1.00 mmol), PdCl<sub>2</sub> (3.5 mg, 0.02 mmol), PPh<sub>3</sub> (16 mg, 0.06 mmol),

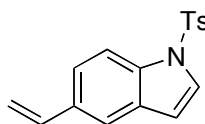
Cs<sub>2</sub>CO<sub>3</sub> (978 mg, 3.00 mmol), and 3-bromothiophene (163 mg, 1.00 mmol) in THF/H<sub>2</sub>O (9:1) (2 mL) was heated at 85 °C under N<sub>2</sub> atmosphere in a sealed tube. The reaction mixture was stirred at 85 °C for 22 h, then cooled to rt and diluted with H<sub>2</sub>O (3 mL) followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> (10 mL X 3). The solvent was removed by distillation, and the crude product was purified by bulb-to-bulb distillation to yield 3-vinylthiophene as a clear liquid (77 mg, 0.70 mmol, 70%), containing 8% 3-bromothiophene and 2% THF by <sup>1</sup>H analysis. The spectral data obtained were in accordance with those described in the literature.

<sup>12</sup> Fauvel, A.; Deleuze, H.; Landais, Y. *Eur. J. Org. Chem.* **2005**, 3900-3910.



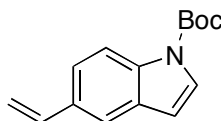
**5-Vinyl-1H-indole (11h).**<sup>13</sup> Following the general procedure,

potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with 5-bromo-1H-indole (196 mg, 1.00 mmol) to yield 5-vinyl-1H-indole as a clear liquid (55 mg, 0.38 mmol, 38%). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 5.16 (d, 1H, *J*=10.8 Hz), 5.72 (d, 1H, *J*=18 Hz), 6.50 (m, 1H), 6.83 (dd, 1H, *J*=18 and 11 Hz), 7.07 (t, 1H, *J*=3.2 Hz), 7.31 (d, 1H, *J*=1.8 Hz), 7.34 (d, 1H, *J*=1.8 Hz), 7.63 (d, 1H, *J*=0.4 Hz), 7.93 (br, 1H); <sup>13</sup>C {<sup>1</sup>H} NMR (90 MHz, CDCl<sub>3</sub>) δ 102.8, 111.0, 111.1, 119.1, 120.2, 124.7, 128.0, 129.8, 135.6, 137.8. IR (neat): 3414, 3084, 1627, 1473, 1450, 1417, 1344, 1325, 1288, 1090, 1066, 991, 893, 810, 766, 731, 612, 559, 490. HRMS (*m/z*): calcd. for C<sub>10</sub>H<sub>9</sub>N. 143.0735 [M<sup>+</sup>]; found 143.0718.



**1-Tosyl-5-vinyl-1H-indole (11i).**<sup>14</sup> Following the general procedure,

potassium vinyltrifluoroborate (67 mg, 0.50 mmol) was reacted with 5-bromo-1-tosyl-1H-indole (175 mg, 0.500 mmol) to yield 1-tosyl-5-vinyl-1H-indole as a viscous oil (131 mg, 0.441 mmol, 88%). The spectral data obtained were in accordance with those described in the literature.



**tert-Butyl 5-vinyl-1H-indole-1-carboxylate (11j).** Following the

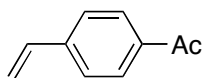
general procedure, potassium vinyltrifluoroborate (134 mg, 1.00 mmol) was reacted with *tert*-butyl 5-bromo-1H-indole-1-carboxylate (294 mg, 1.00 mmol) to yield *tert*-butyl 5-vinyl-1H-indole-1-carboxylate as a white solid (187 mg,

<sup>13</sup> Suvorov, N. N.; Starostenko, N. E.; Zeiberlikh, F. N. *J.Org.Chem.USSR (Engl.Transl.)* **1980**, *16*, 2236-2241.

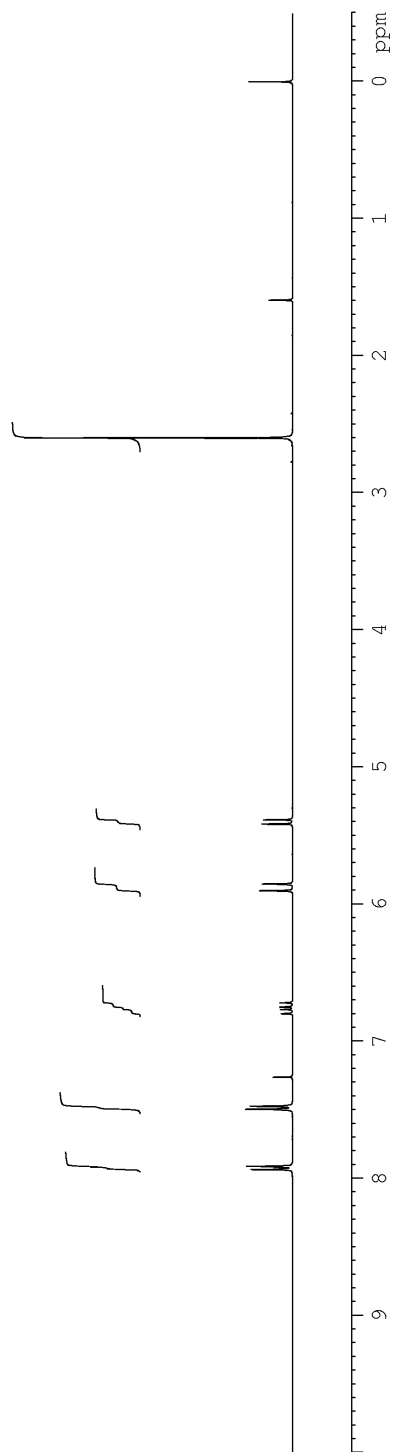
<sup>14</sup> Krolski, M. E.; Renaldo, A. F.; Rudisill, D. E.; Stille, J. K. *J. Org. Chem.* **1988**, *53*, 1170-1176.

0.769 mmol, 77%) mp >240 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.65 (s, 9H), 5.20 (d, 1H, *J*=12 Hz), 5.73 (d, 1H, *J*=17.5 Hz), 6.52 (d, 1H, *J*=4 Hz), 6.79 (dd, 1H, *J*=17.5 and 10 Hz), 7.40 (dd, 1H, *J*=9 and 2 Hz), 7.54 (d, 1H, *J*=1.5 Hz), 7.56 (d, 1H, *J*=3.5 Hz), 8.08 (d, 1H, *J*=8 Hz); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 28.1, 83.7, 107.4, 112.4, 115.1, 118.8, 122.4, 126.3, 130.8, 132.4, 134.9, 137.1, 149.6. IR (neat): 3117, 2979, 2931, 1731, 1537, 1470, 1369, 1255, 1162, 1131, 1083, 1024, 886, 855, 821, 793, 766, 730. HRMS (*m/z*): calcd. for C<sub>15</sub>H<sub>17</sub>NO<sub>2</sub>, 243.1259 [M<sup>+</sup>]; found 243.1254.

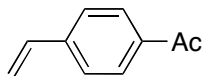
**1-Benzyl-5-vinyl-1*H*-indole (11k).** Following the general procedure, potassium vinyltrifluoroborate (141 mg, 1.05 mmol) was reacted with 1-benzyl-5-bromo-1*H*-indole (286 mg, 1.00 mmol) to yield 1-benzyl-5-vinyl-1*H*-indole as a white solid (166 mg, 0.712 mmol, 71%) mp 40-41 °C. <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 5.12 (dd, 1H, *J*=11 and 1 Hz), 5.28 (s, 2H), 5.67 (dd, 1H, *J*=17.6 and 1 Hz), 6.52 (d, 1H, *J*=3.2 Hz), 6.82 (dd, 1H, *J*=11 and 6.5 Hz), 7.07-7.10 (m, 3H), 7.19-7.31 (m, 5H), 7.64 (d, 1H, *J*=1.4); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 50.1, 102.0, 109.7, 110.9, 119.4, 119.9, 126.7, 127.6, 128.7, 128.8, 128.9, 129.6, 136.2, 137.4, 137.8. IR (neat): 3029, 2916, 1626, 1509, 1483, 1453, 1337, 1311, 1182, 990, 886, 805, 727, 702, 420. HRMS (*m/z*): calcd. for C<sub>17</sub>H<sub>16</sub>N, 234.1282 [MH<sup>+</sup>]; found 234.1281.



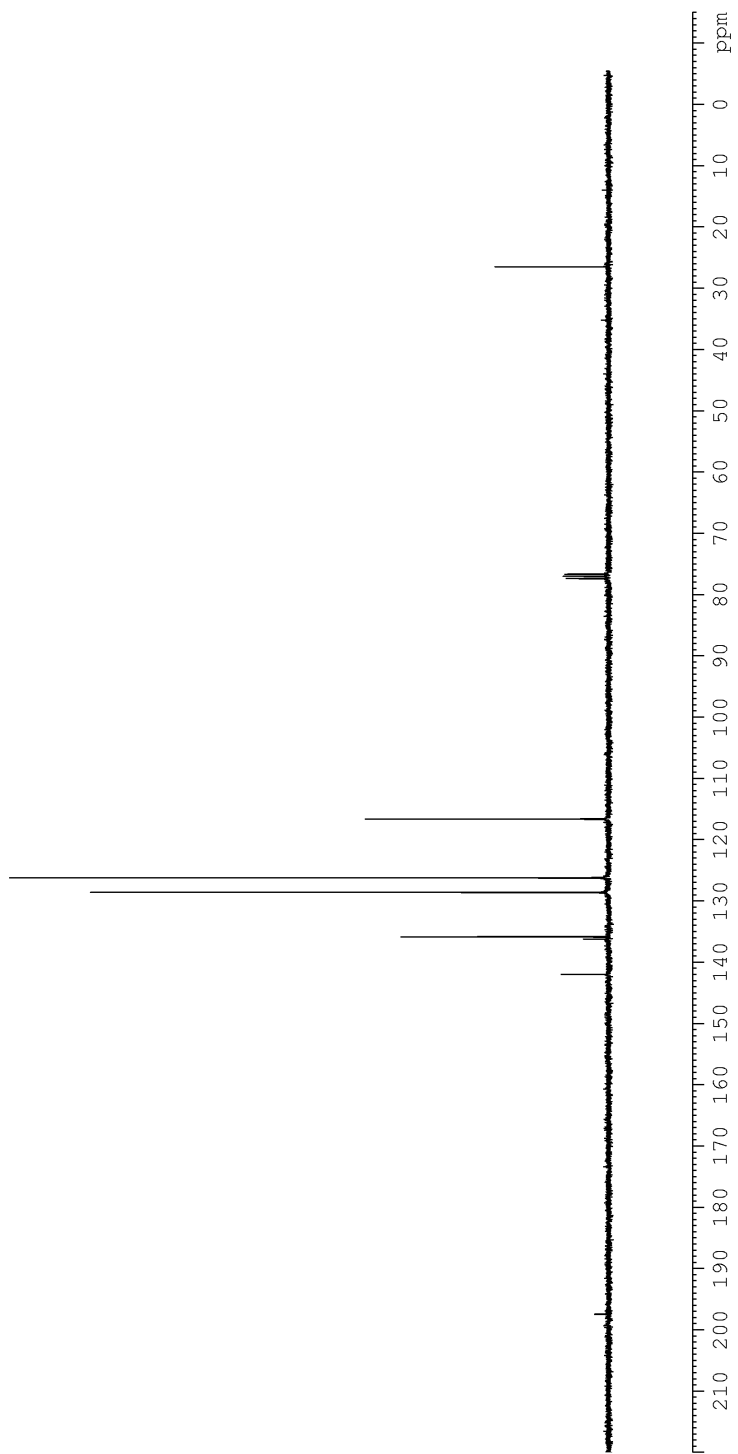
**3a**



<sup>1</sup>H NMR Spectrum of 1-(4-vinyl-phenyl)-ethanone **3a**

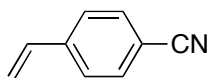


**3a**

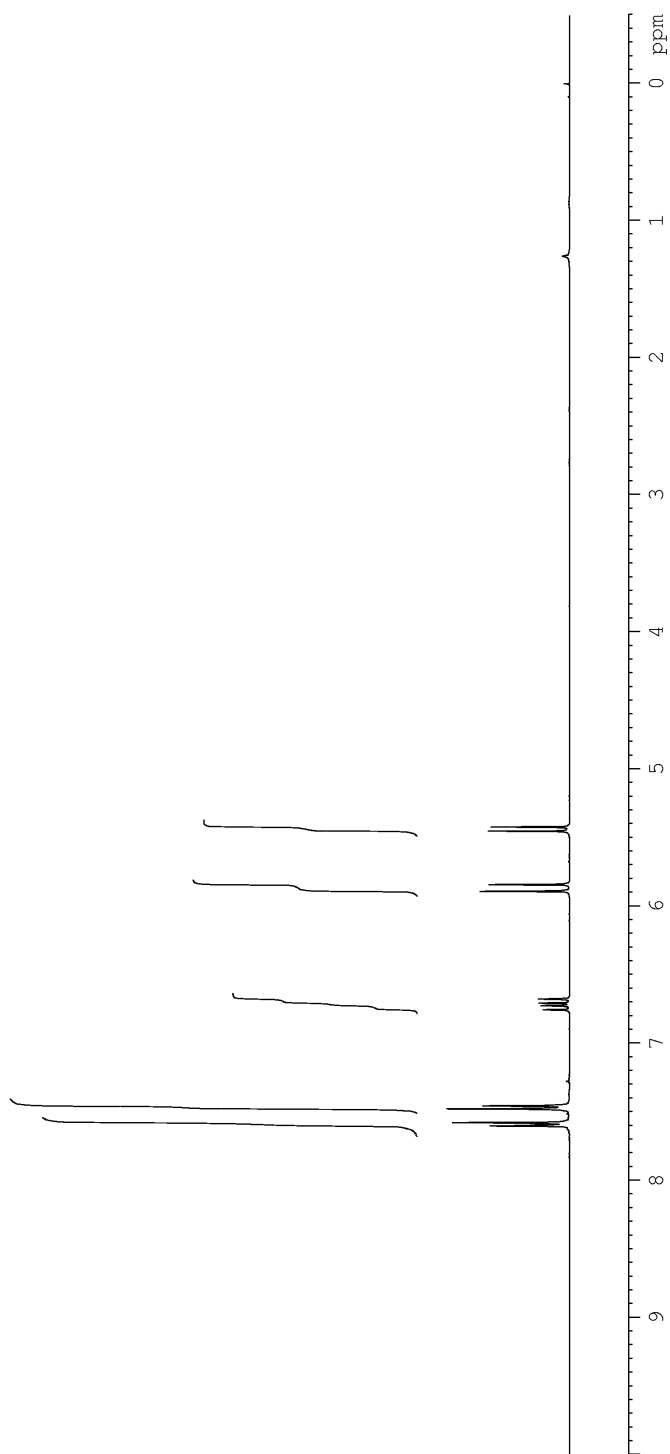


<sup>13</sup>C NMR Spectrum of 1-(4-vinyl-phenyl)-ethanone **3a**

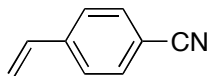




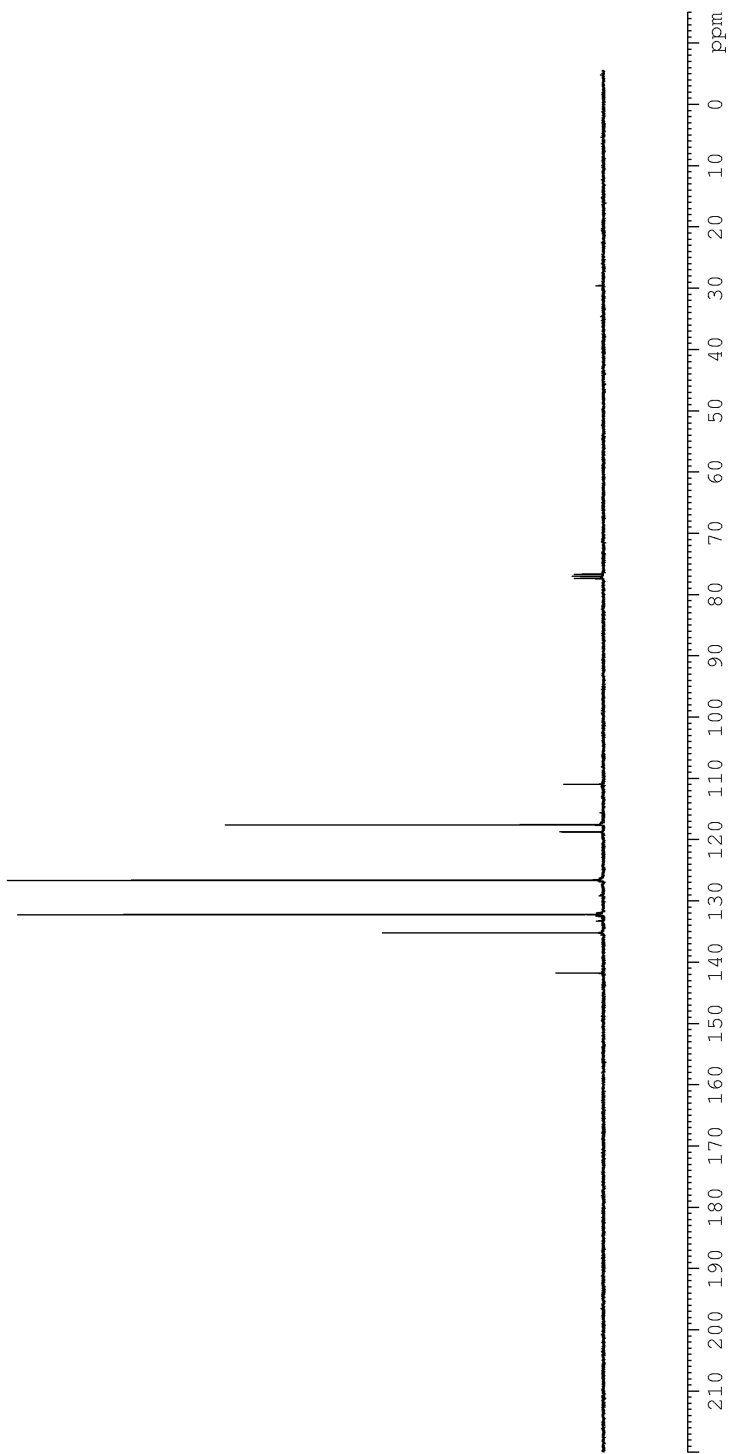
**5a**

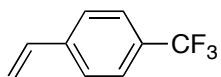


<sup>1</sup>H NMR Spectrum of 4-vinyl-benzonitrile **5a**

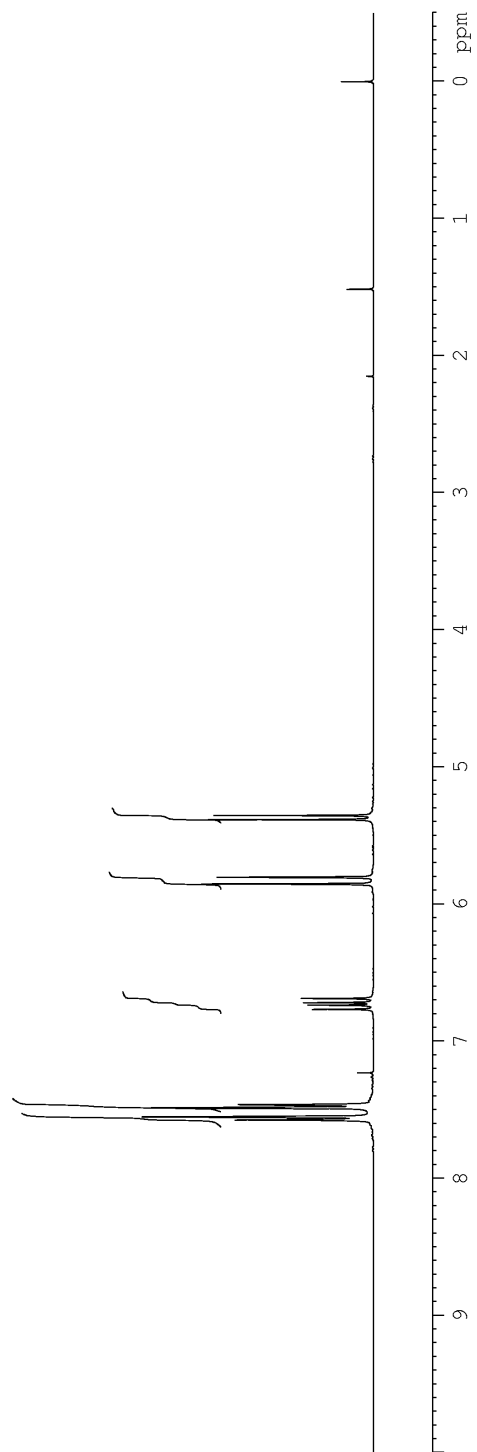


**5a**

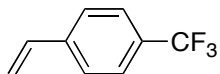




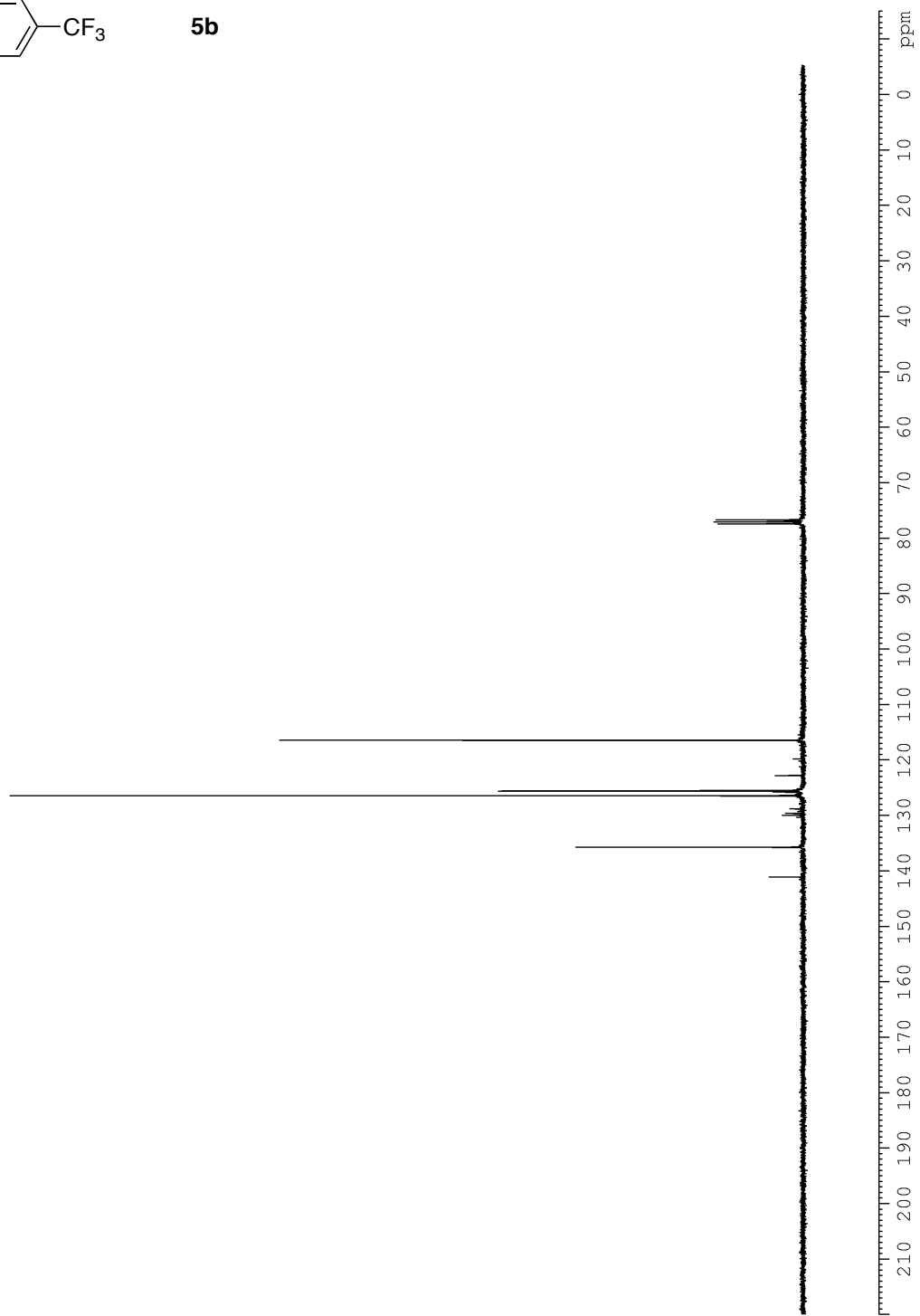
**5b**



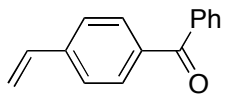
<sup>1</sup>H NMR Spectra of 1-trifluoromethyl-4-vinylbenzene **5b**



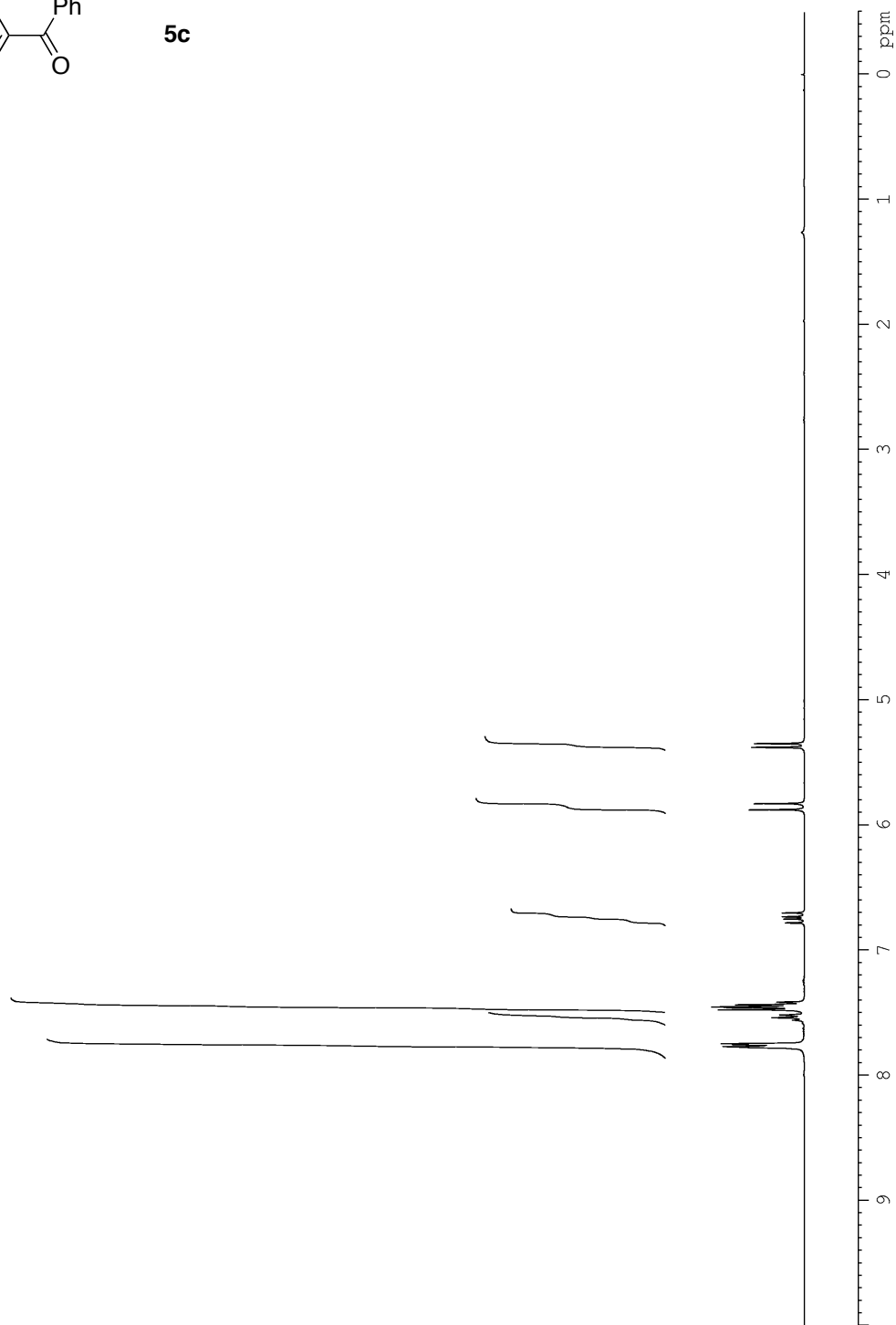
**5b**



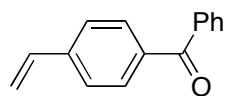
$^{13}\text{C}$  NMR Spectra of 1-trifluoromethyl-4-vinyl-benzene **5b**



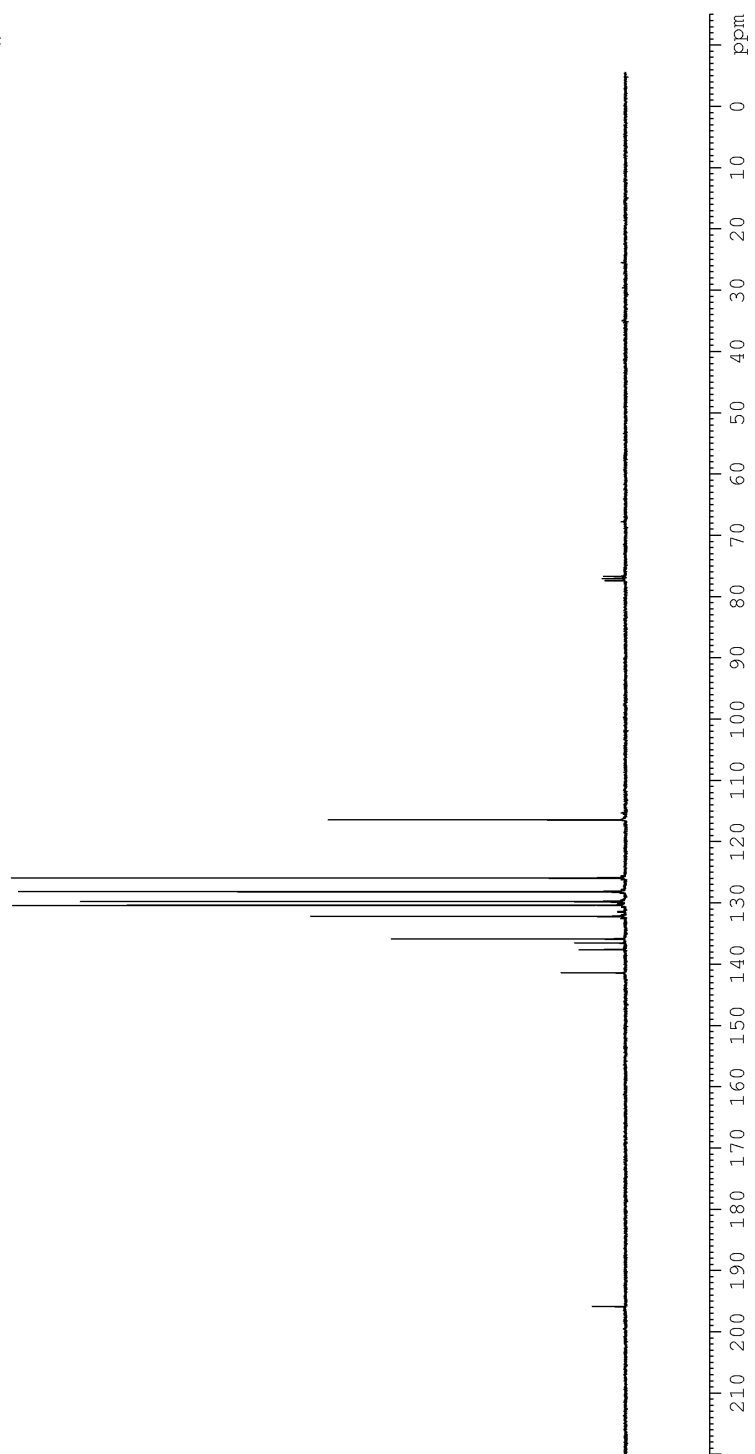
**5c**



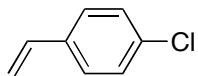
<sup>1</sup>H NMR Spectrum of phenyl-(4-vinyl-phenyl)-methanone **5c**



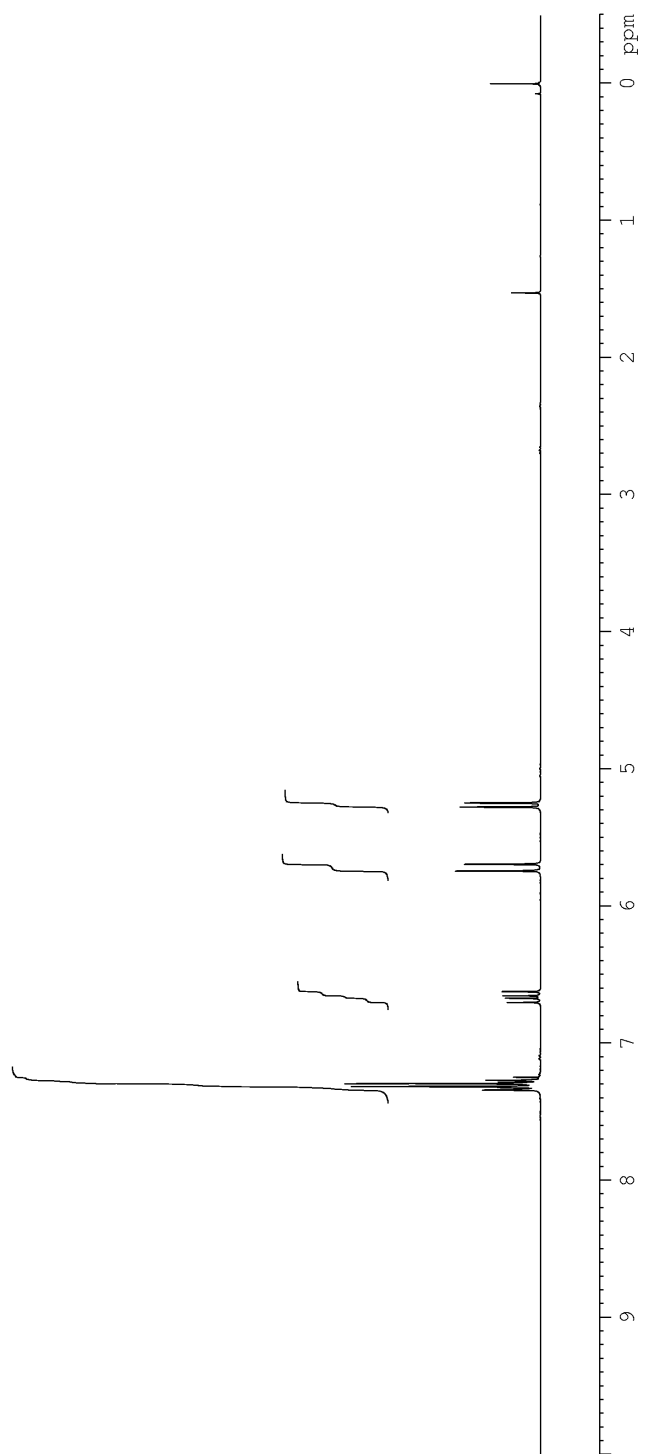
**5c**



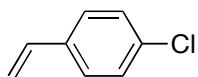
$^{13}\text{C}$  NMR Spectrum of phenyl-(4-vinyl-phenyl)-methanone **5c**



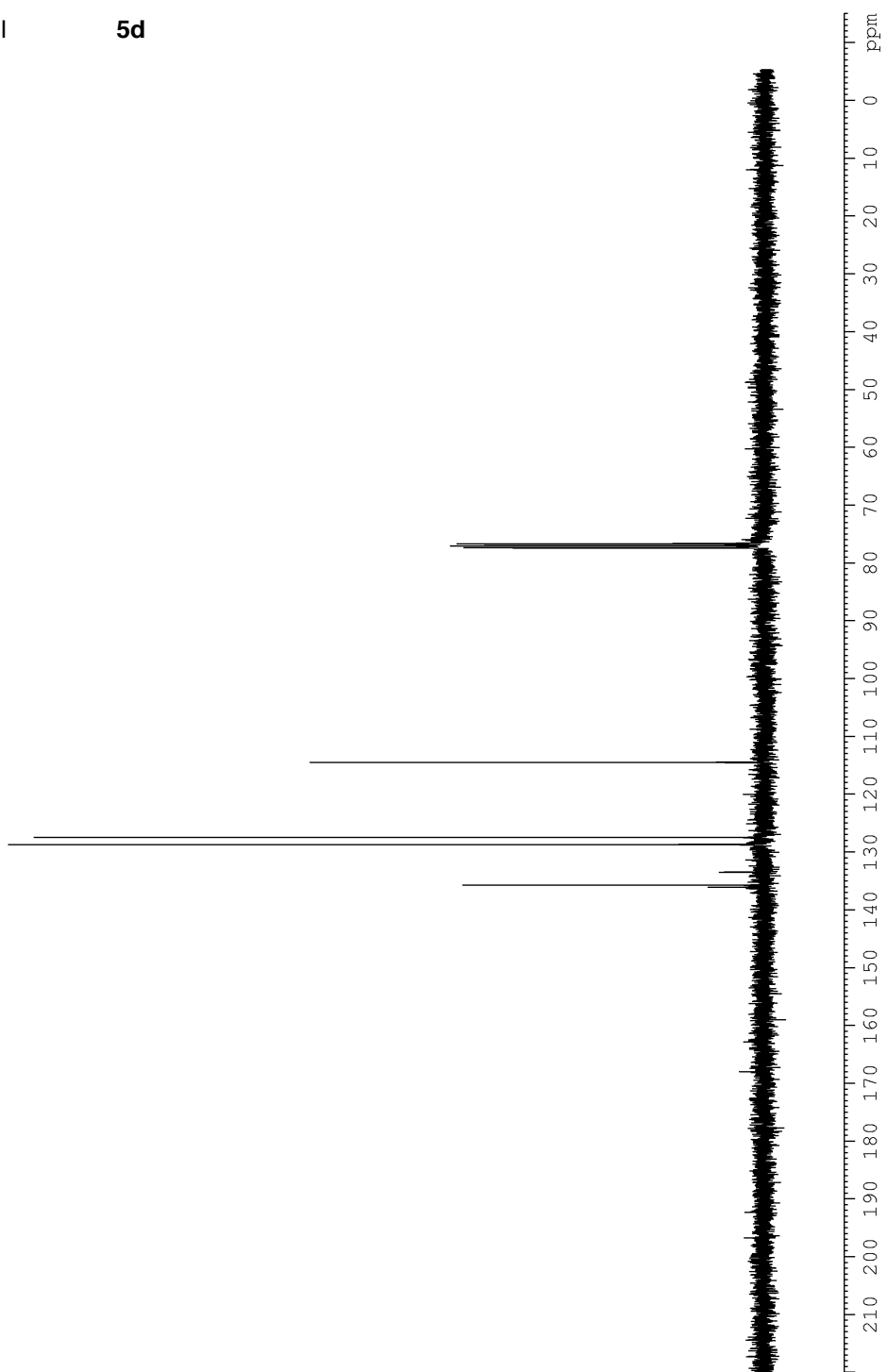
**5d**



<sup>1</sup>H NMR Spectrum of 1-chloro-4-vinyl-benzene **5d**

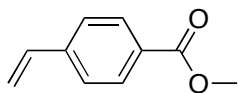


**5d**

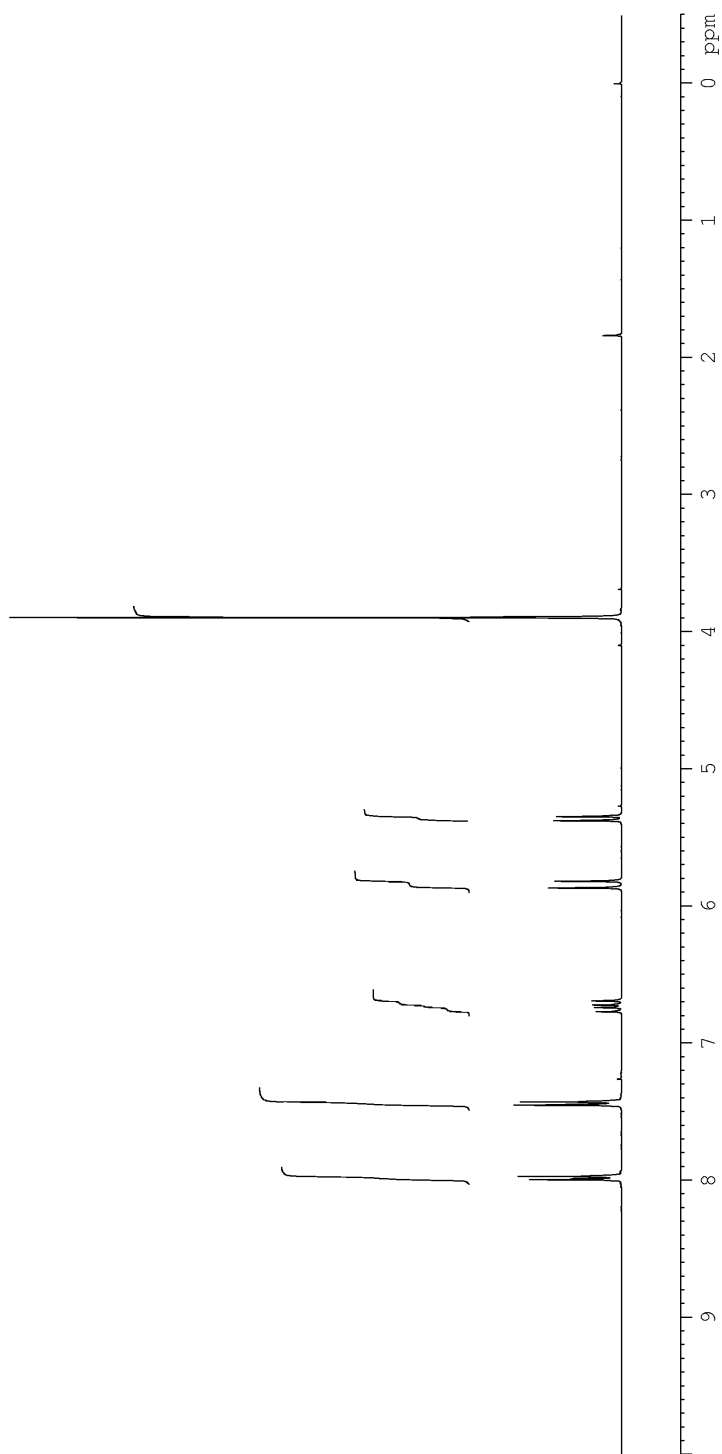


$^{13}\text{C}$  NMR Spectrum of 1-chloro-4-vinylbenzene **5d**

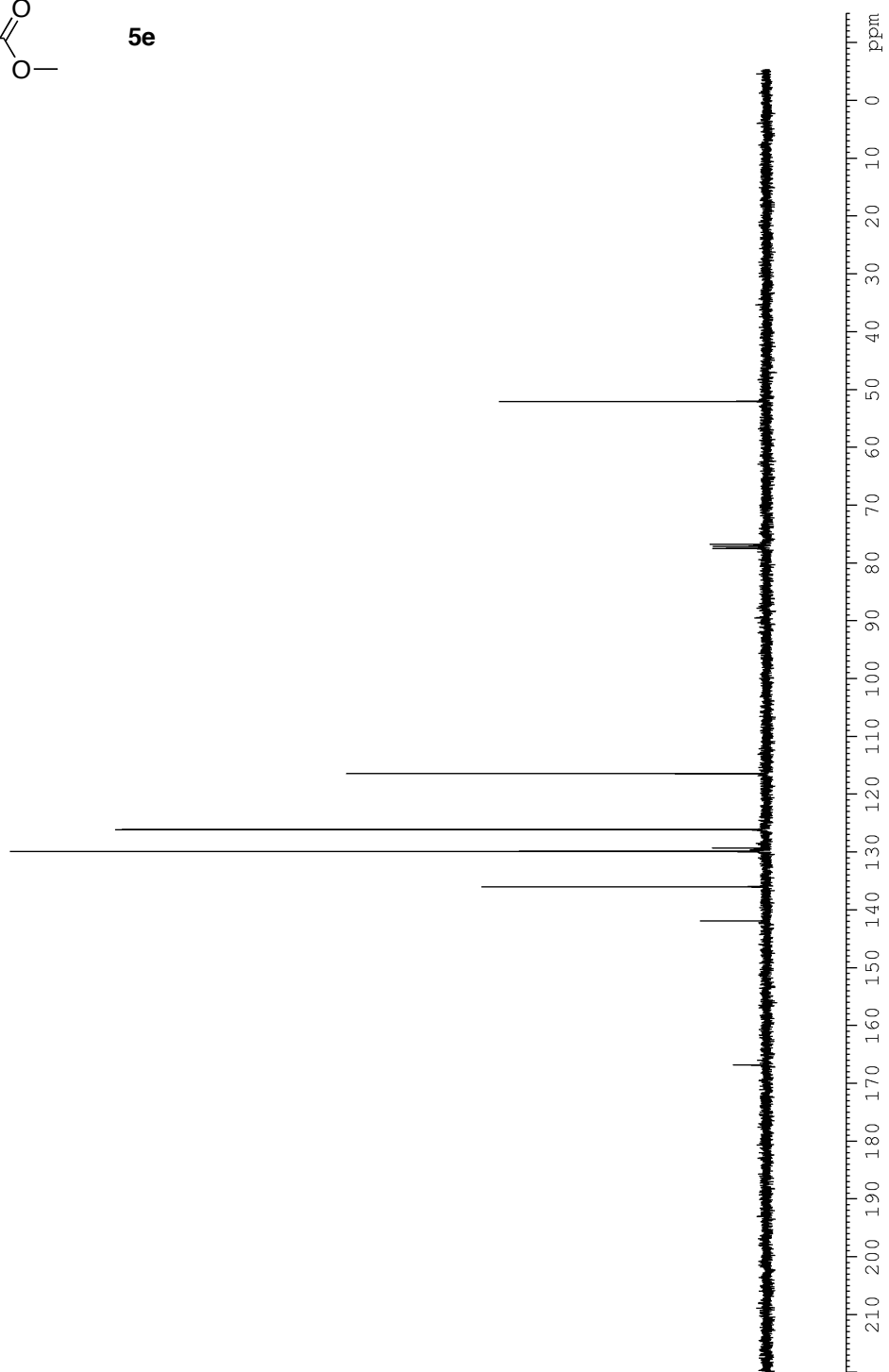
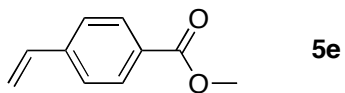




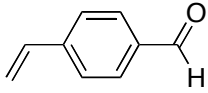
**5e**



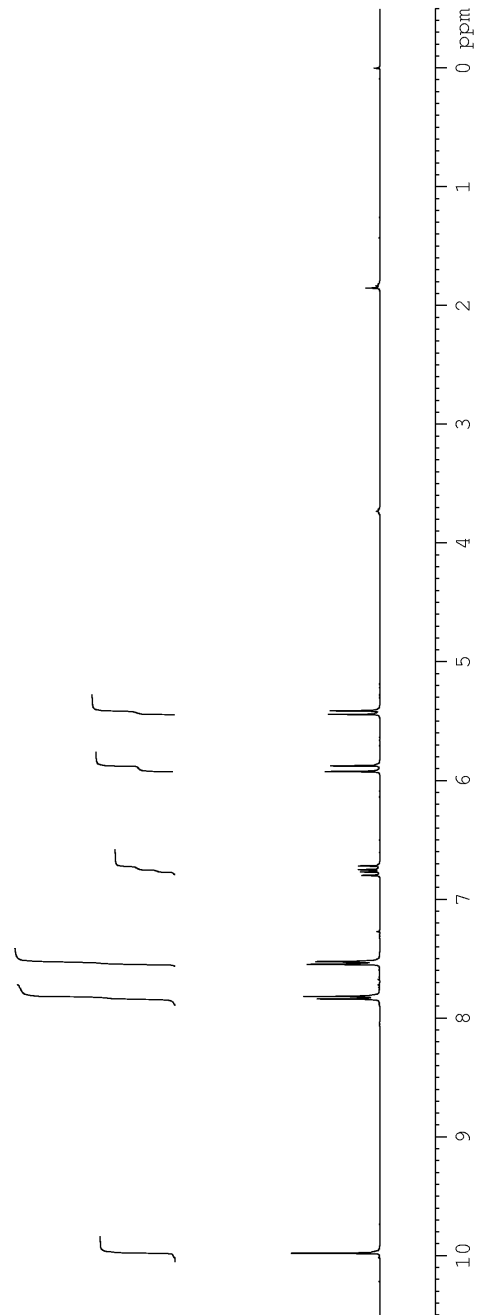
<sup>1</sup>H NMR Spectrum of 4-vinylbenzoic acid methyl ester **5e**



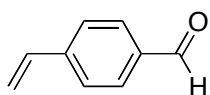
$^{13}\text{C}$  Spectrum of 4-vinyl-benzoic acid methyl ester **5e**



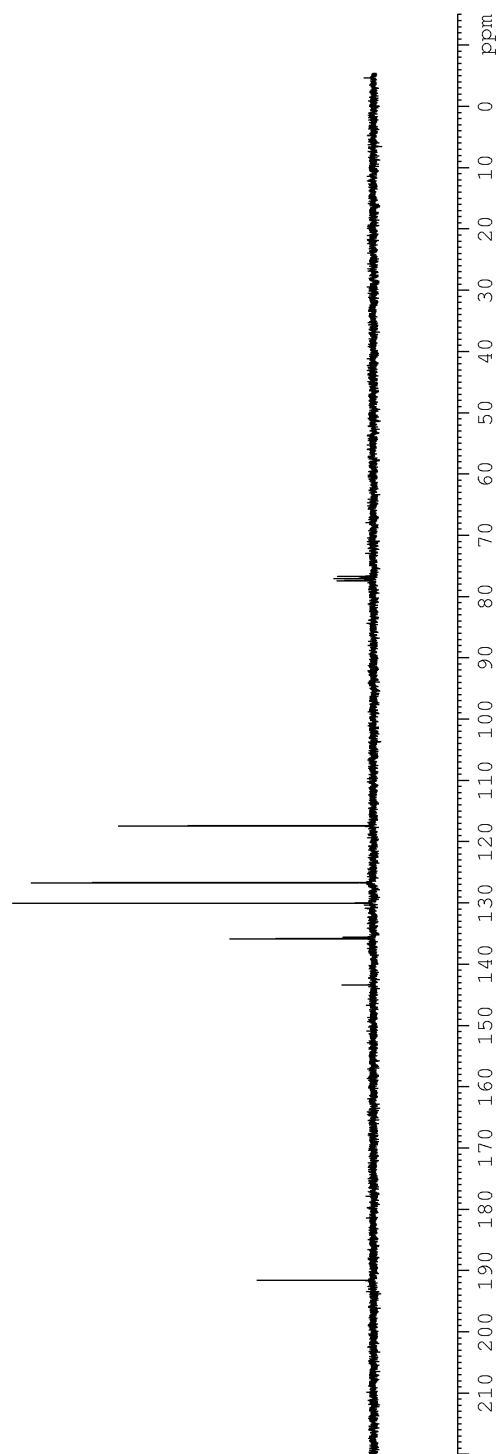
**5f**



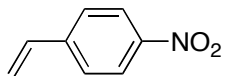
<sup>1</sup>H NMR Spectrum of 4-vinyl-benzaldehyde **5f**



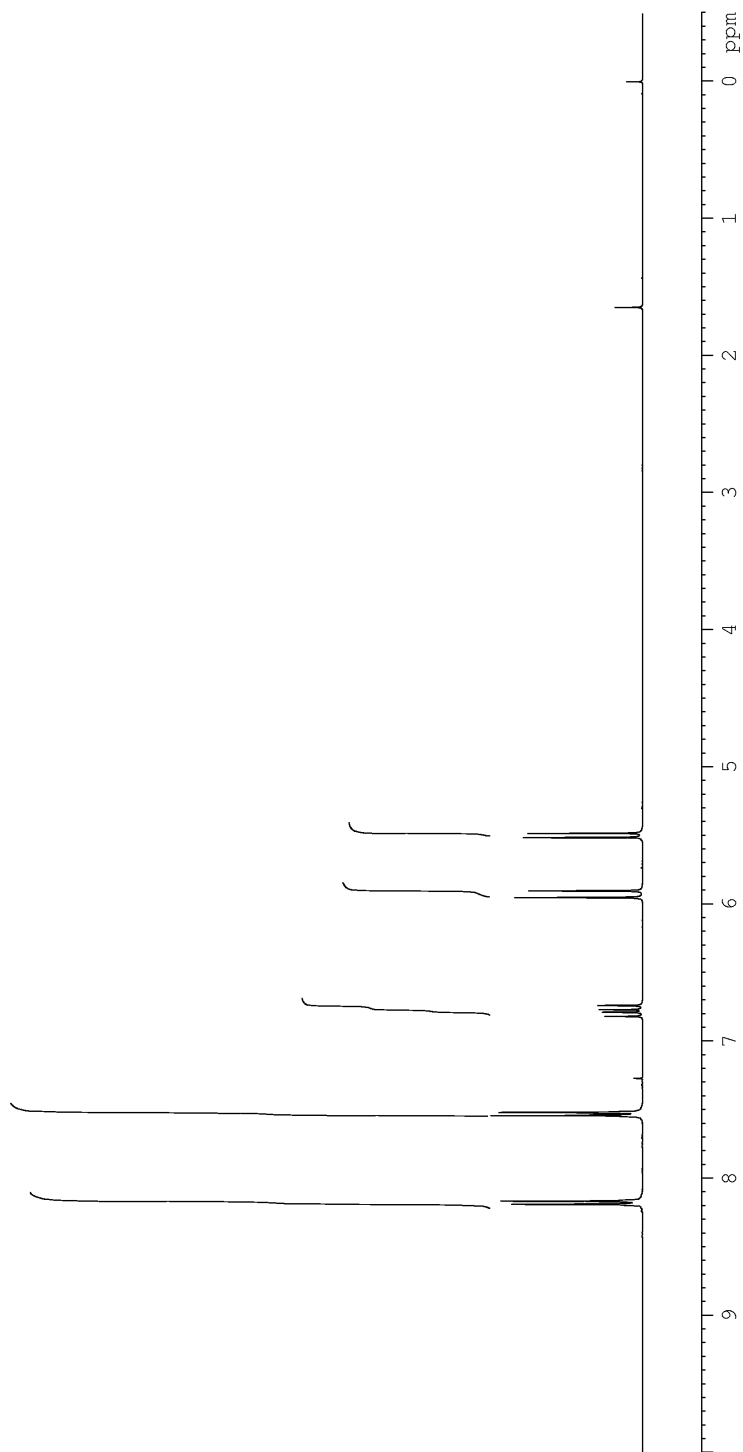
**5f**



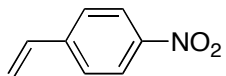
$^{13}\text{C}$  NMR Spectrum of 4-vinyl-benzaldehyde **5f**



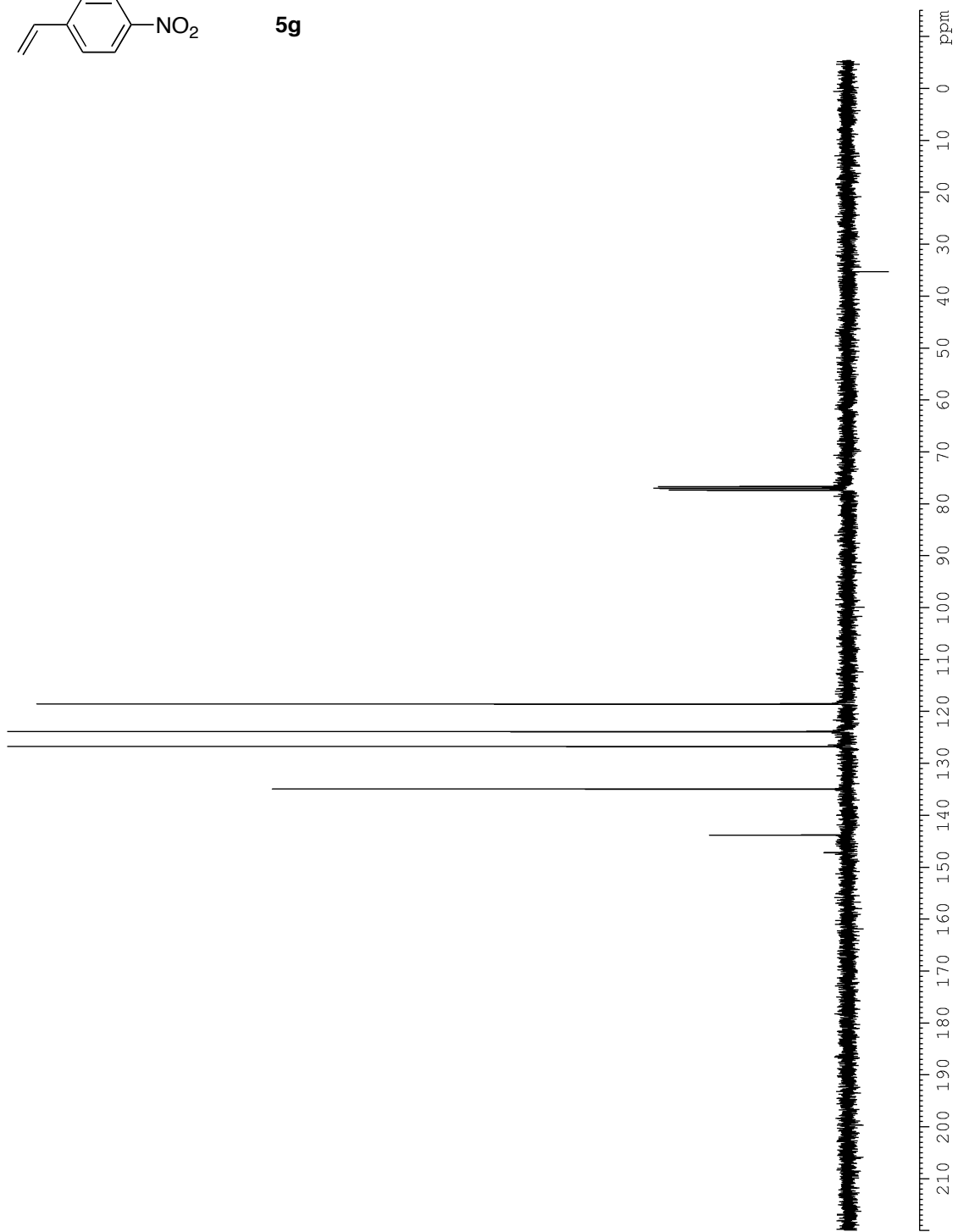
**5g**



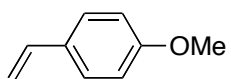
<sup>1</sup>H NMR Spectrum of 1-nitro-4-vinylbenzene **5g**



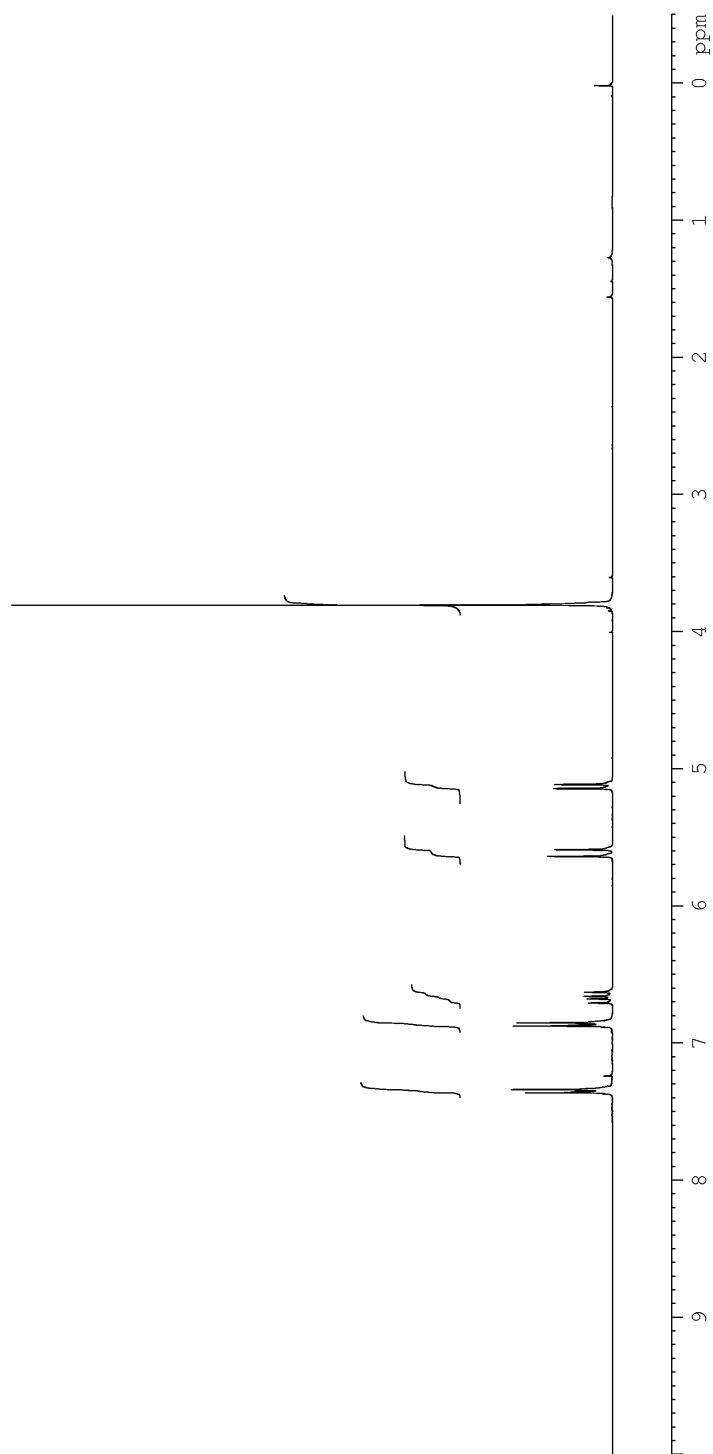
**5g**



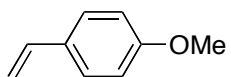
$^{13}\text{C}$  NMR Spectrum of 1-nitro-4-vinylbenzene **5g**



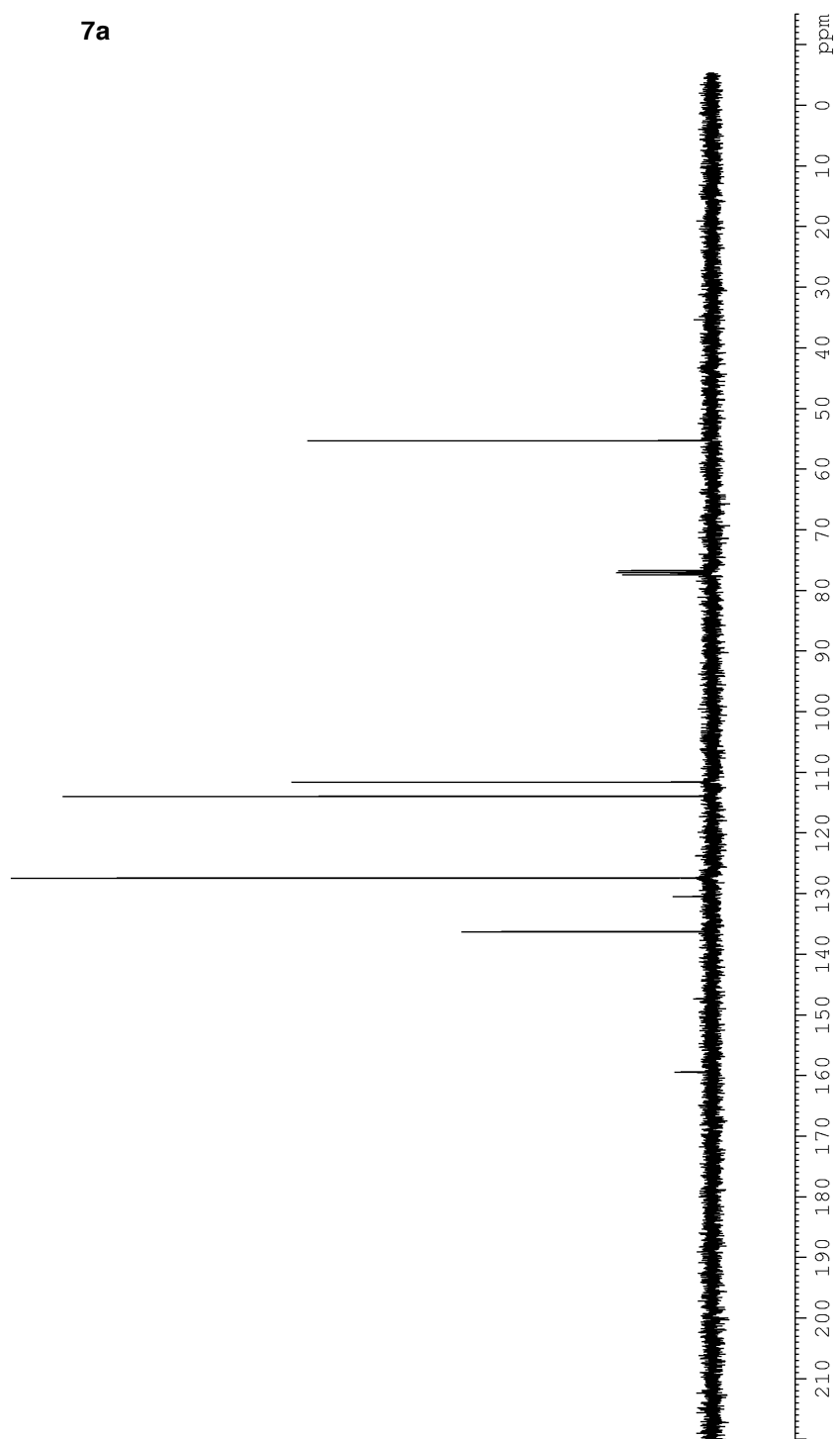
**7a**



<sup>1</sup>H NMR Spectrum of 1-methoxy-4-vinyl-benzene **7a**

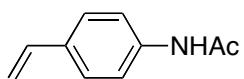


**7a**

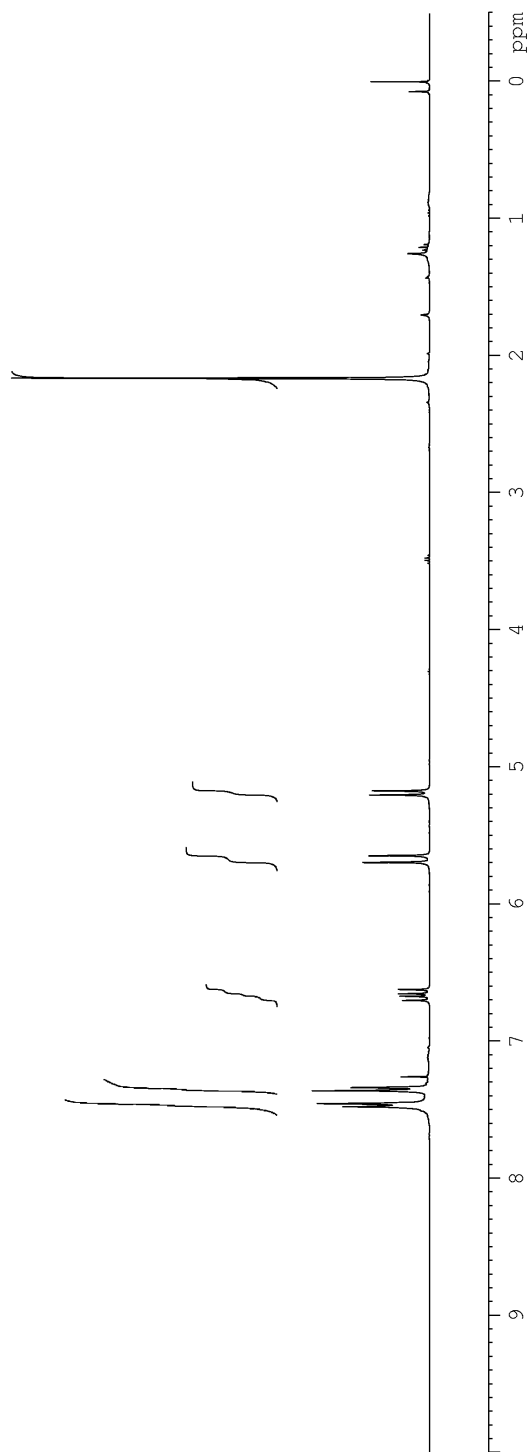


$^{13}\text{C}$  NMR Spectrum of 1-methoxy-4-vinylbenzene **7a**

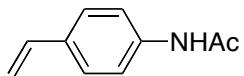




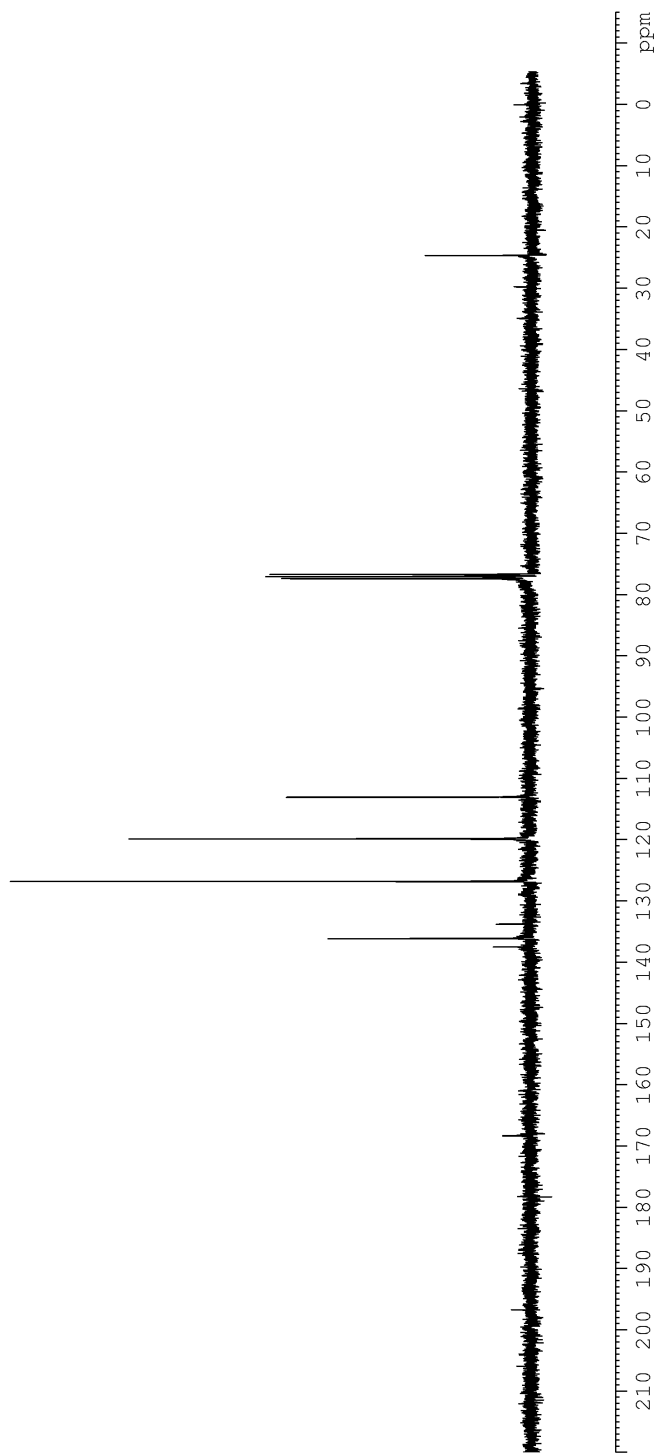
**7b**



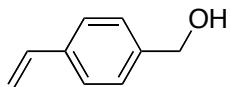
$^1\text{H}$  NMR Spectrum of *N*-(4-vinyl-phenyl)-acetamide **7b**



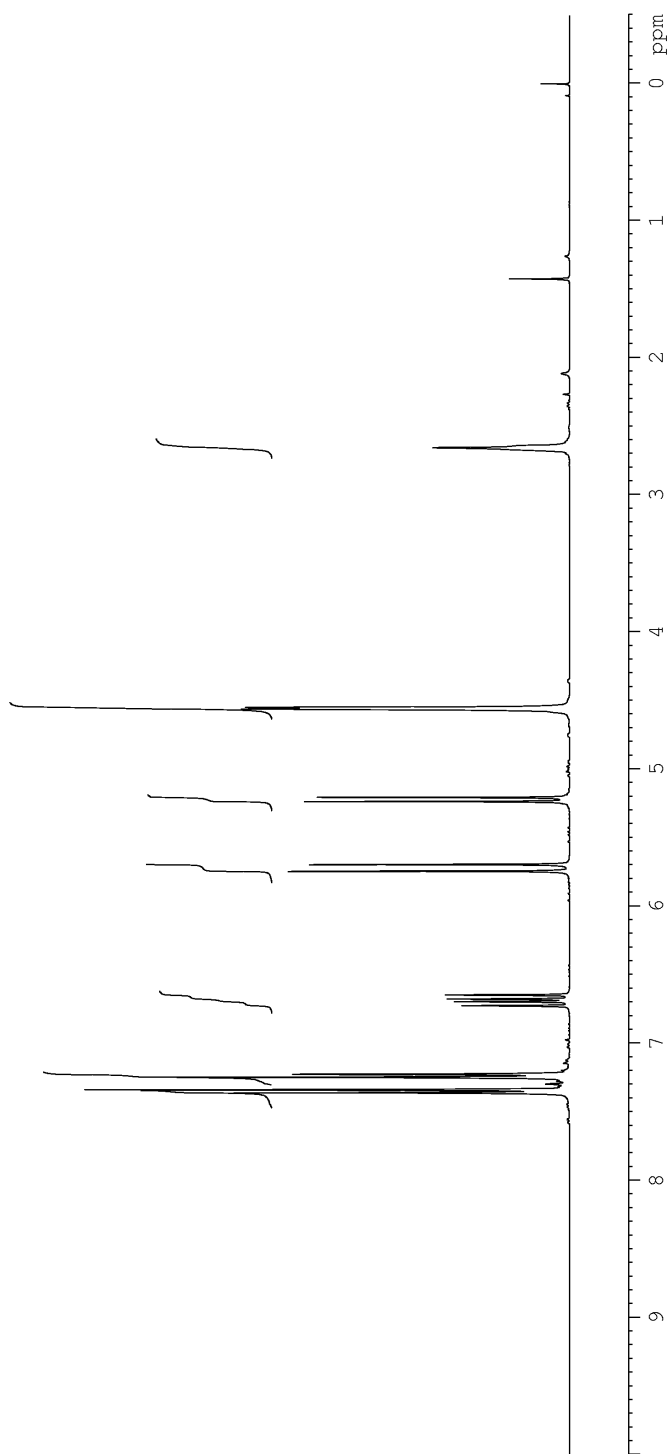
**7b**



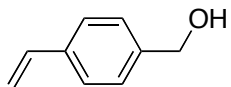
$^{13}\text{C}$  NMR Spectrum of *N*-(4-vinyl-phenyl)-acetamide **7b**



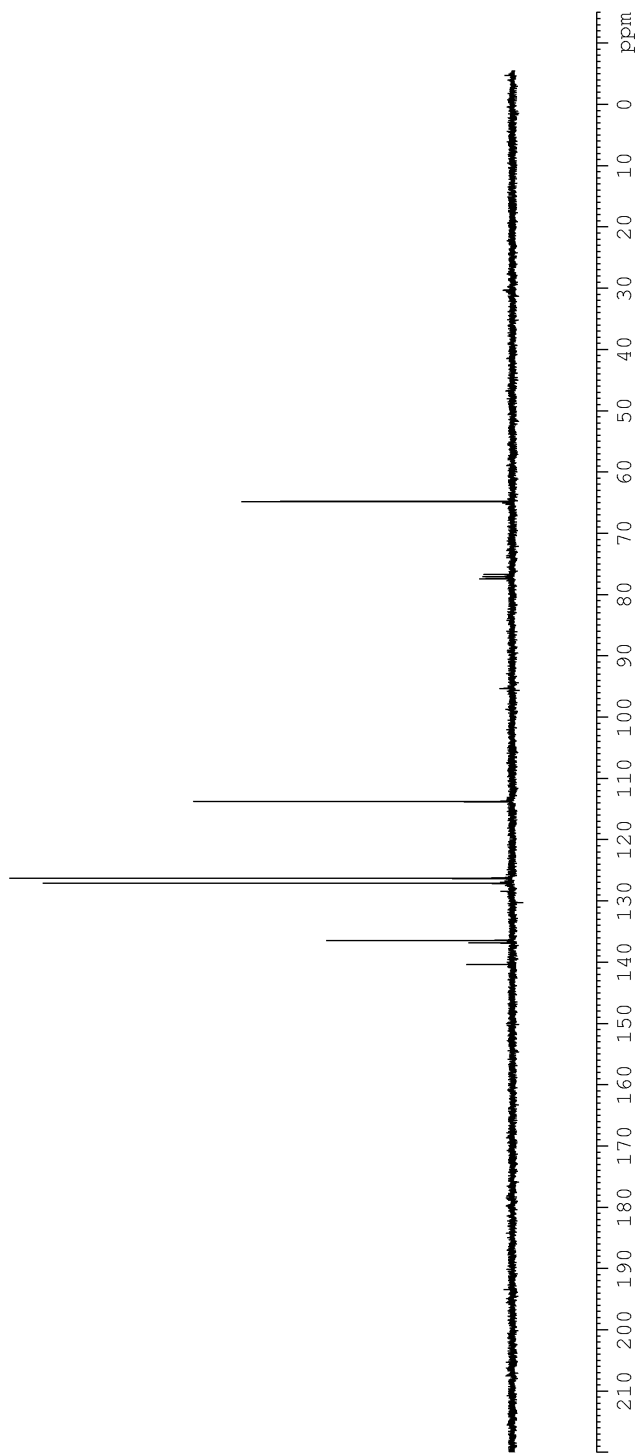
**7c**



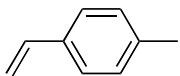
<sup>1</sup>H NMR Spectrum of (4-vinyl-phenyl)-methanol **7c**



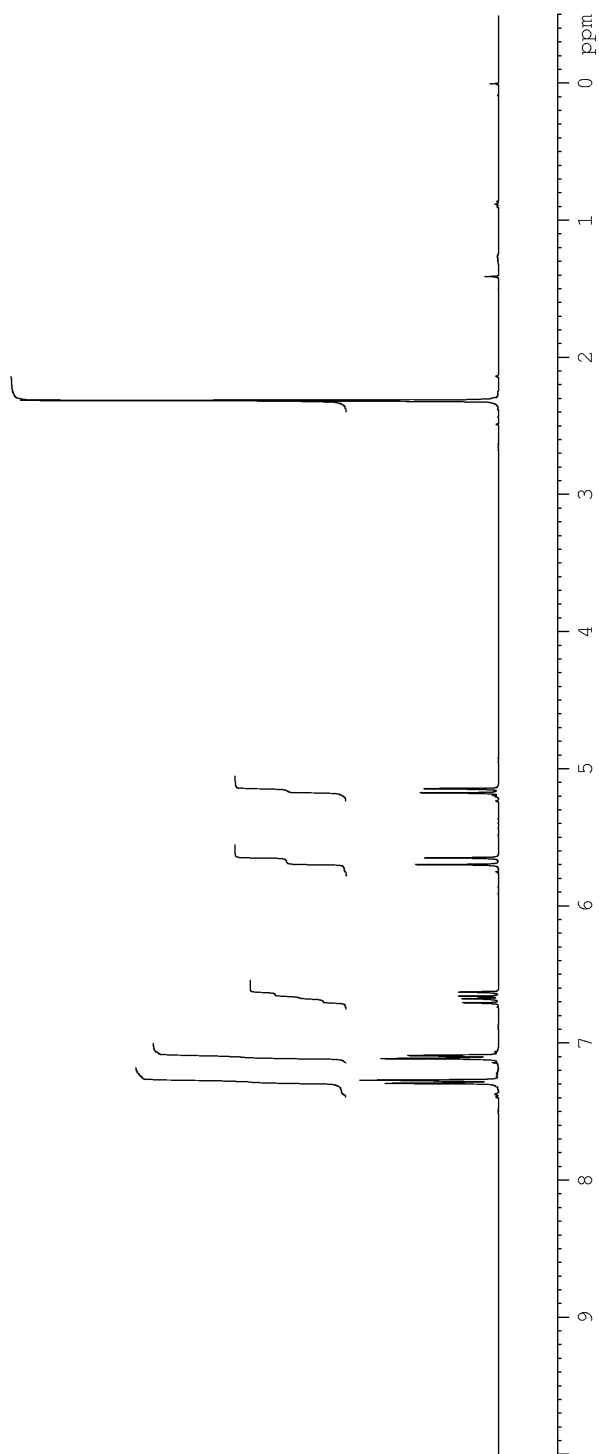
**7c**



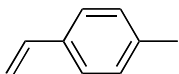
$^{13}\text{C}$  NMR Spectrum of (4-vinyl-phenyl)-methanol **7c**



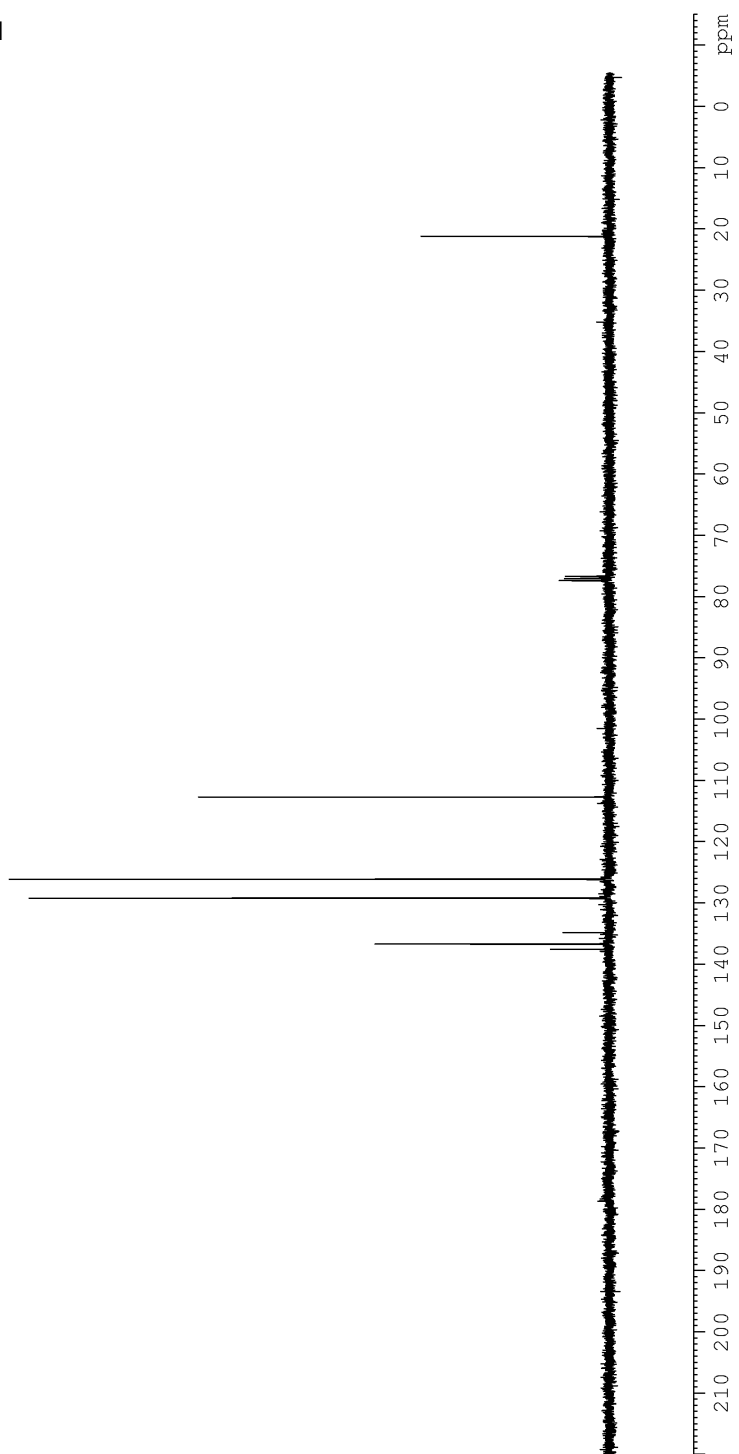
**7d**



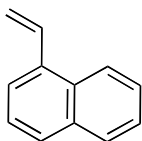
<sup>1</sup>H NMR Spectrum of 1-methyl-4-vinylbenzene **7d**



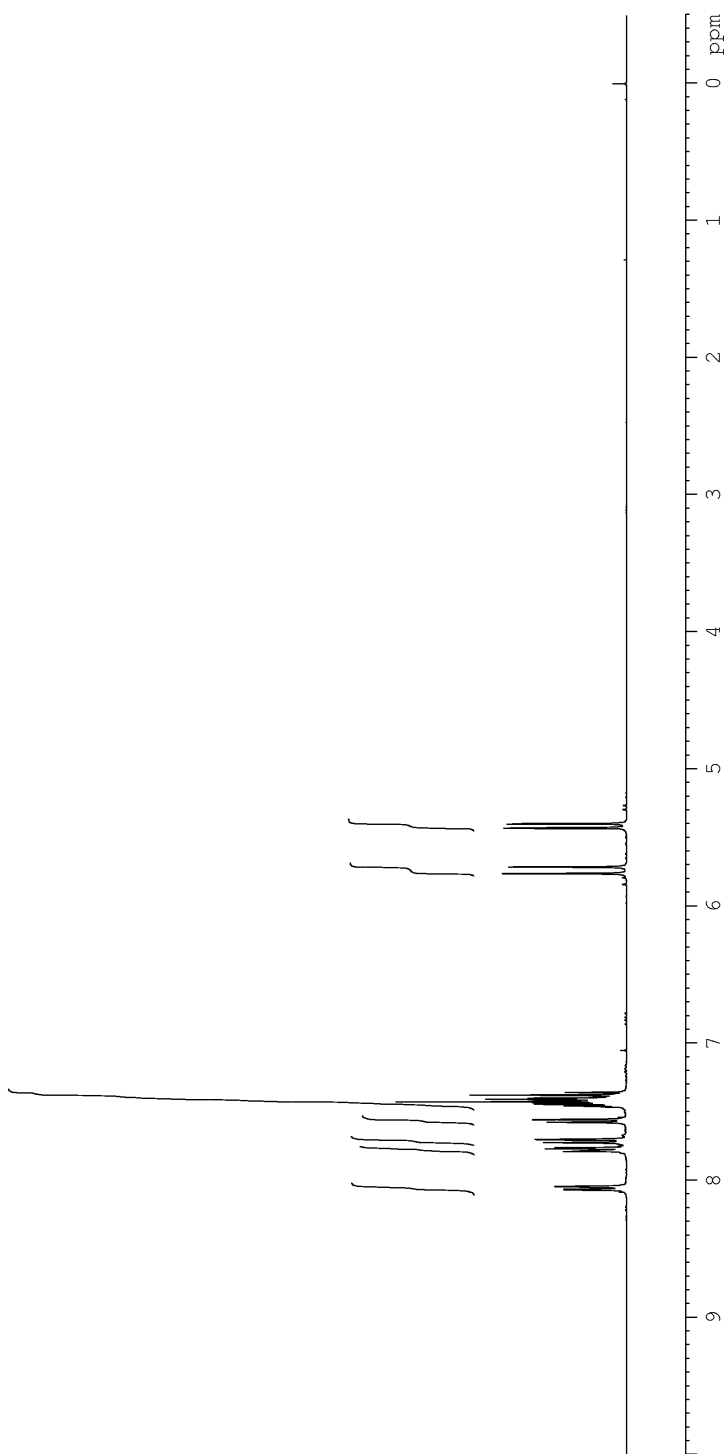
**7d**



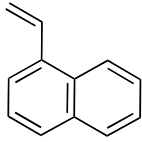
$^{13}\text{C}$  NMR Spectrum of 1-methyl-4-vinylbenzene **7d**



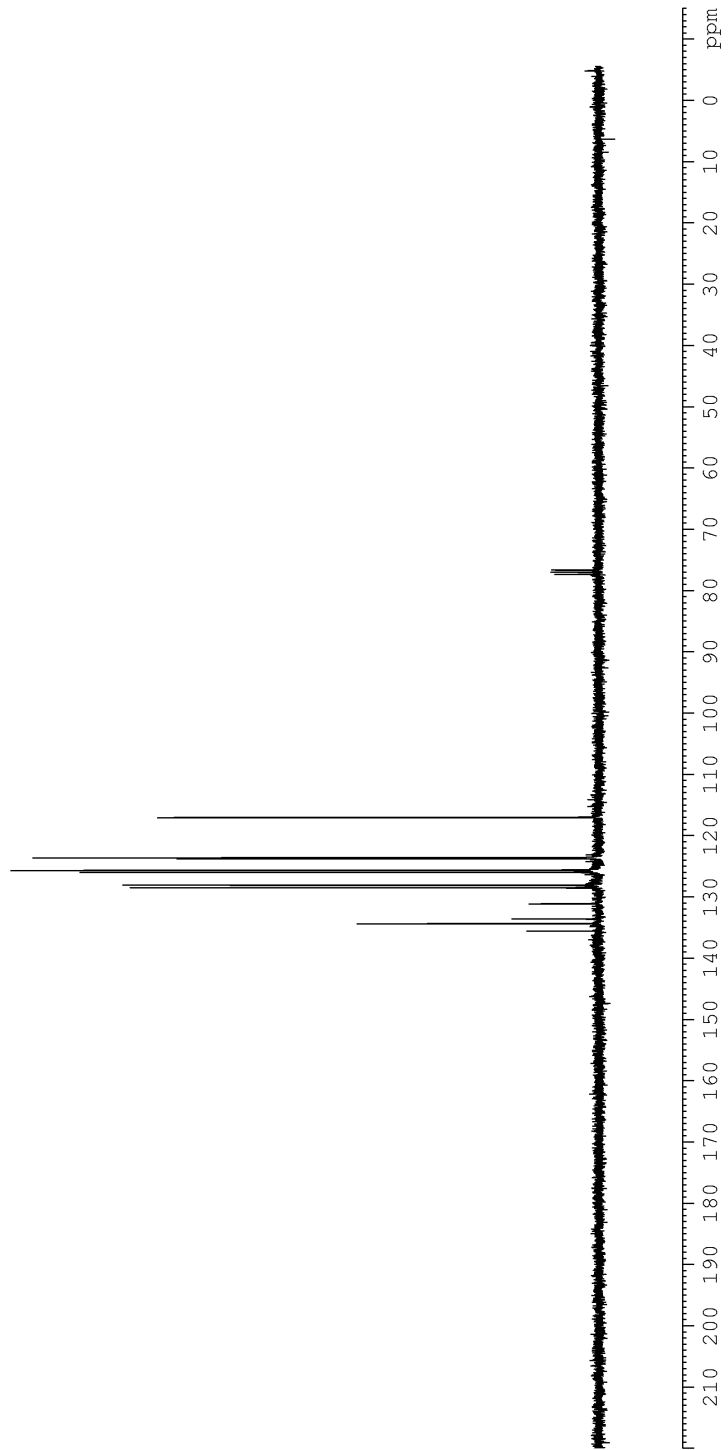
**7e**



<sup>1</sup>H NMR Spectrum of 1-vinyl-naphthalene **7e**

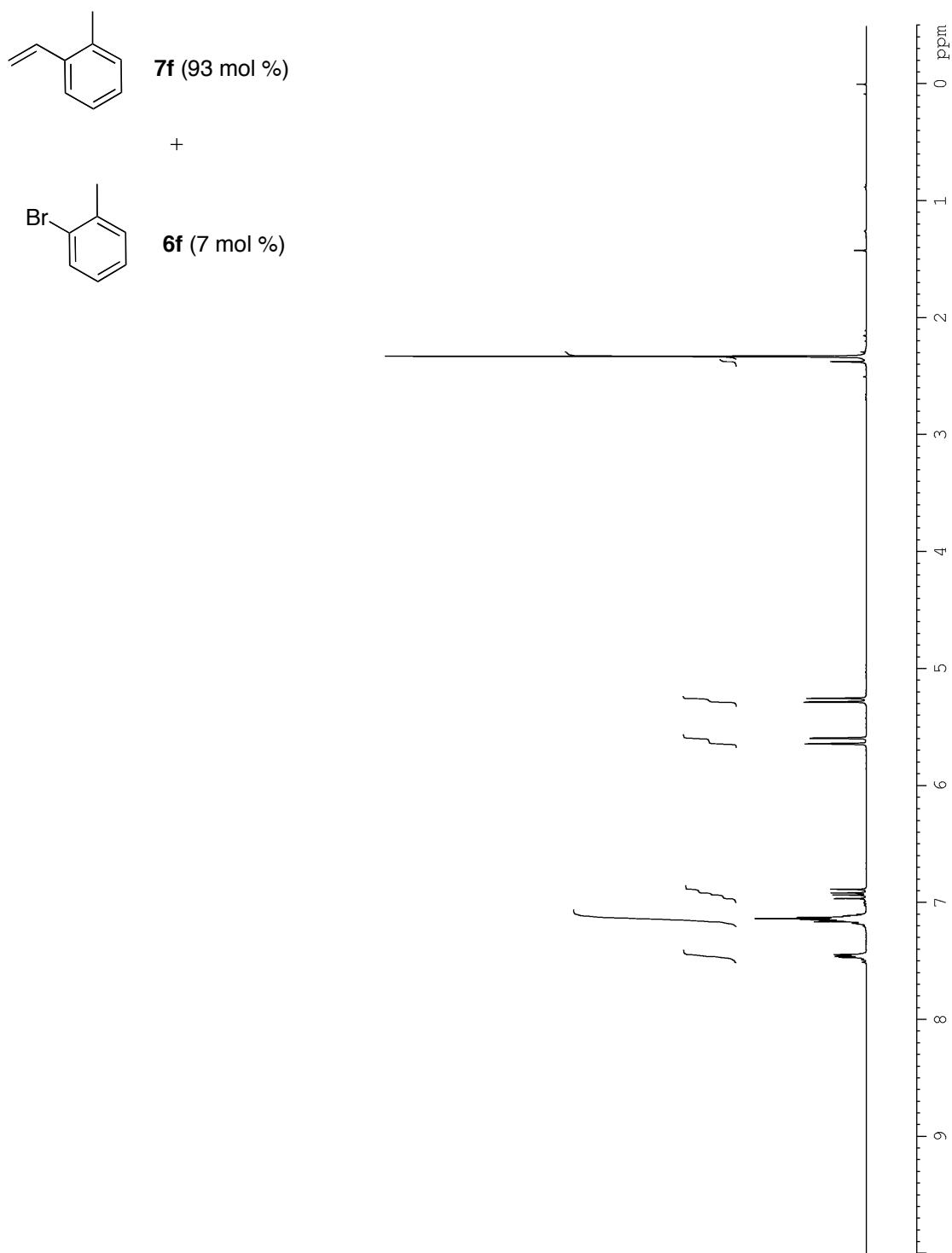


**7e**

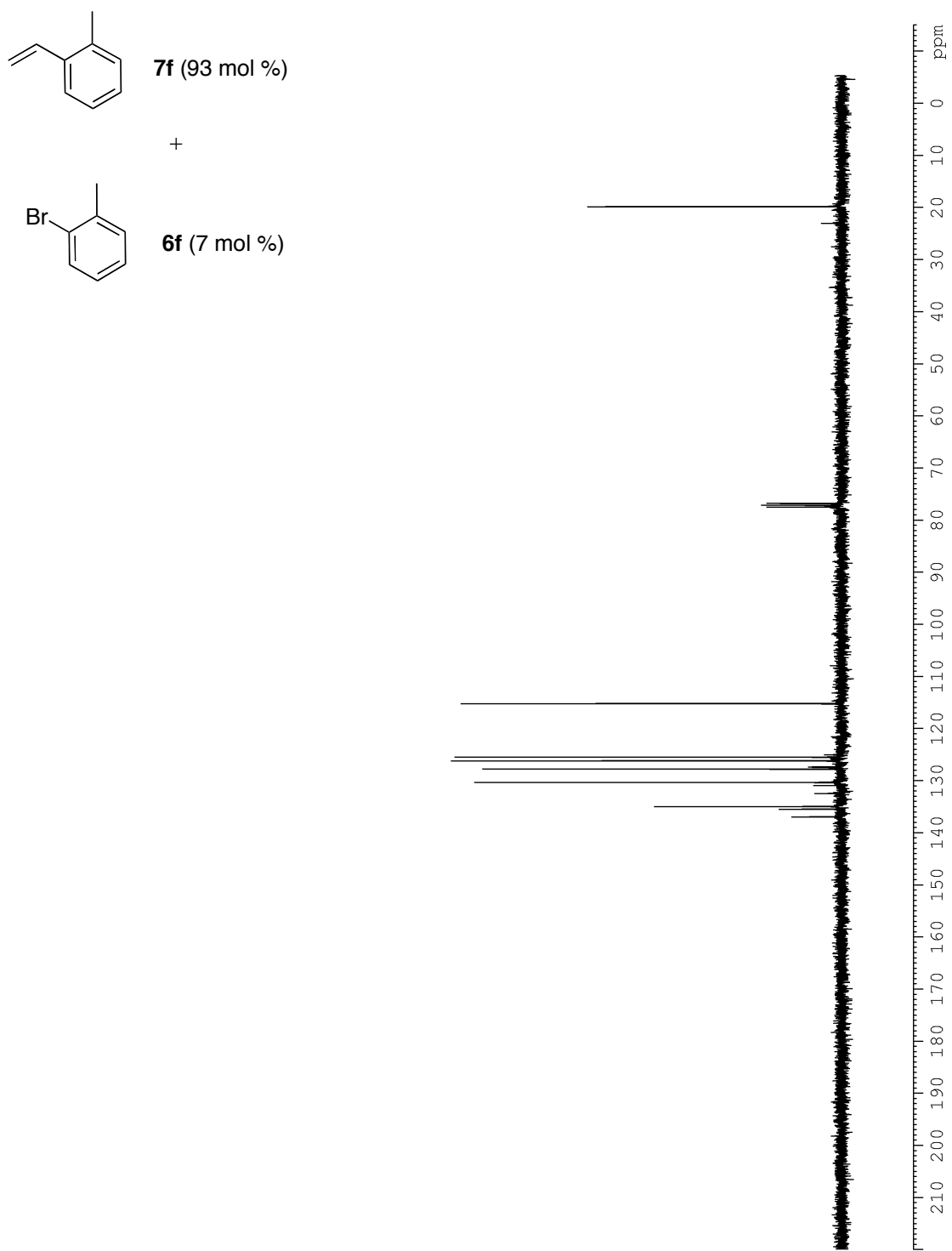


$^{13}\text{C}$  NMR Spectrum of 1-vinyl-naphthalene **7e**

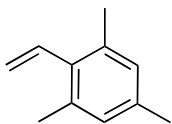




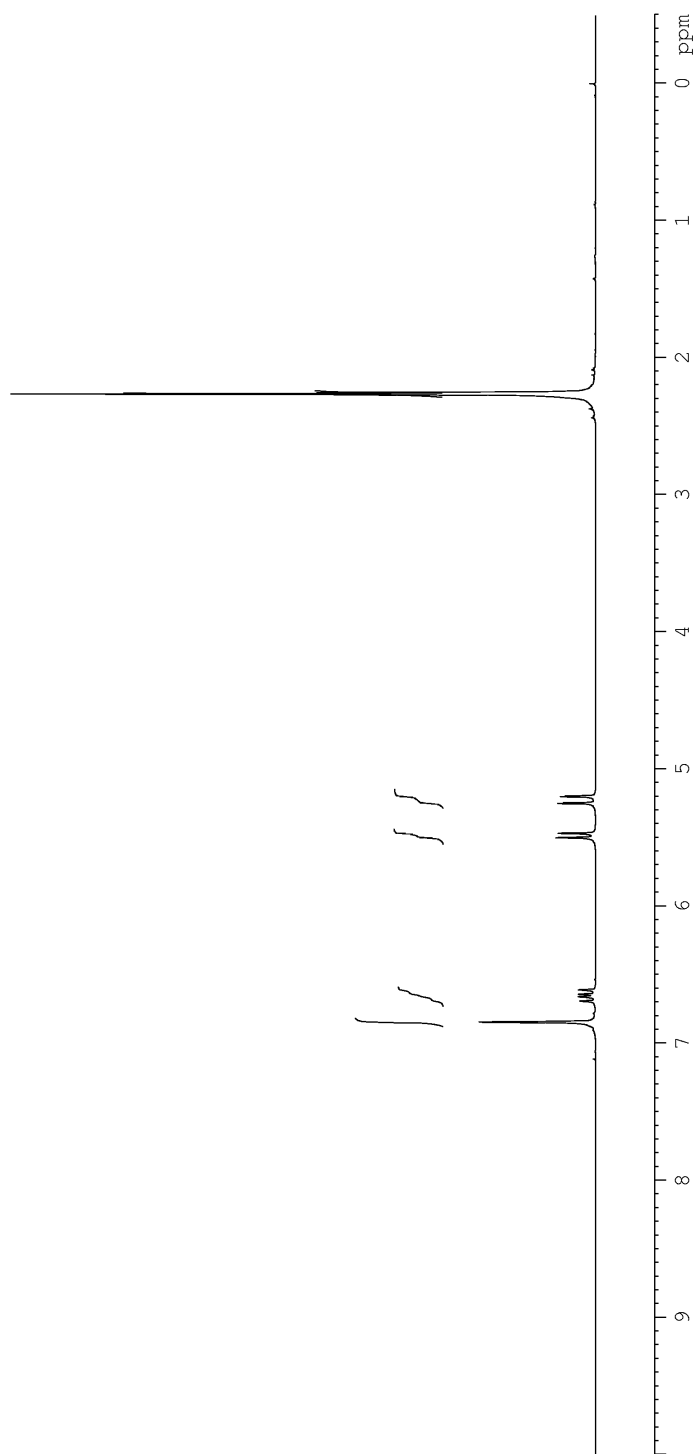
$^1\text{H}$  NMR Spectrum of 1-methyl-2-vinylbenzene **7f** (93%) and 2-bromotoluene **6f** (7%)



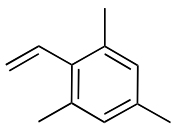
$^{13}\text{C}$  NMR Spectrum of 1-methyl-2-vinylbenzene **7f** (93%) and 2-bromotoluene **6f** (7%)



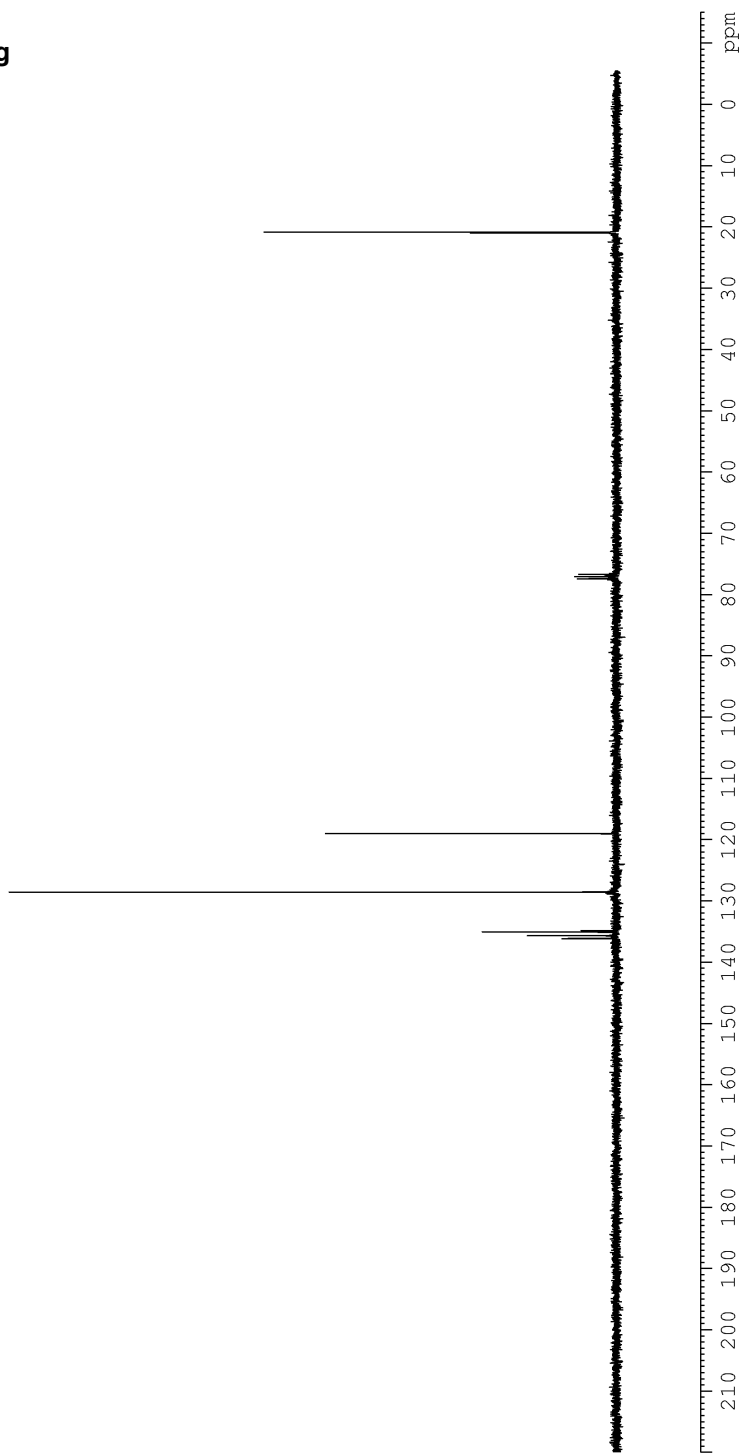
**7g**



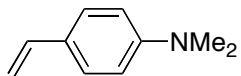
<sup>1</sup>H NMR Spectrum of 1,3,5-trimethyl-2-vinylbenzene **7g**



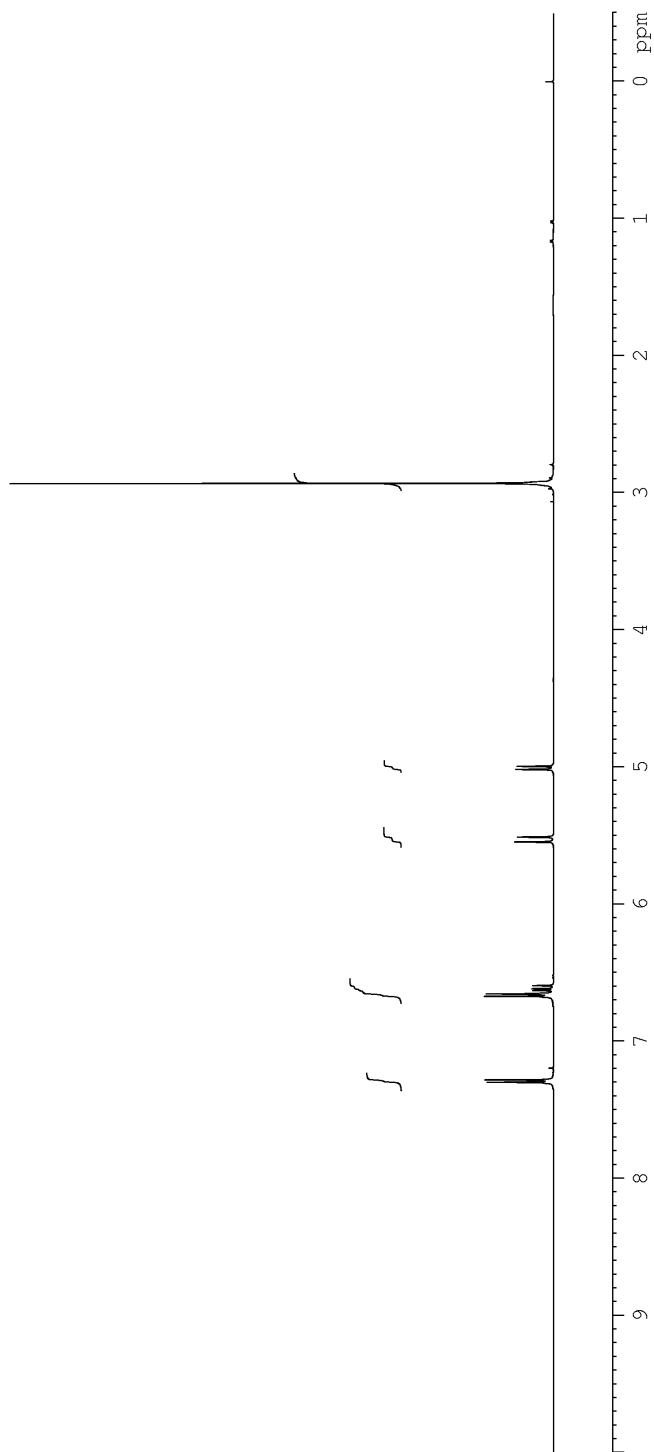
**7g**



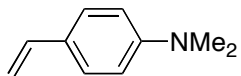
$^{13}\text{C}$  NMR Spectrum of 1,3,5-trimethyl-2-vinylbenzene **7g**



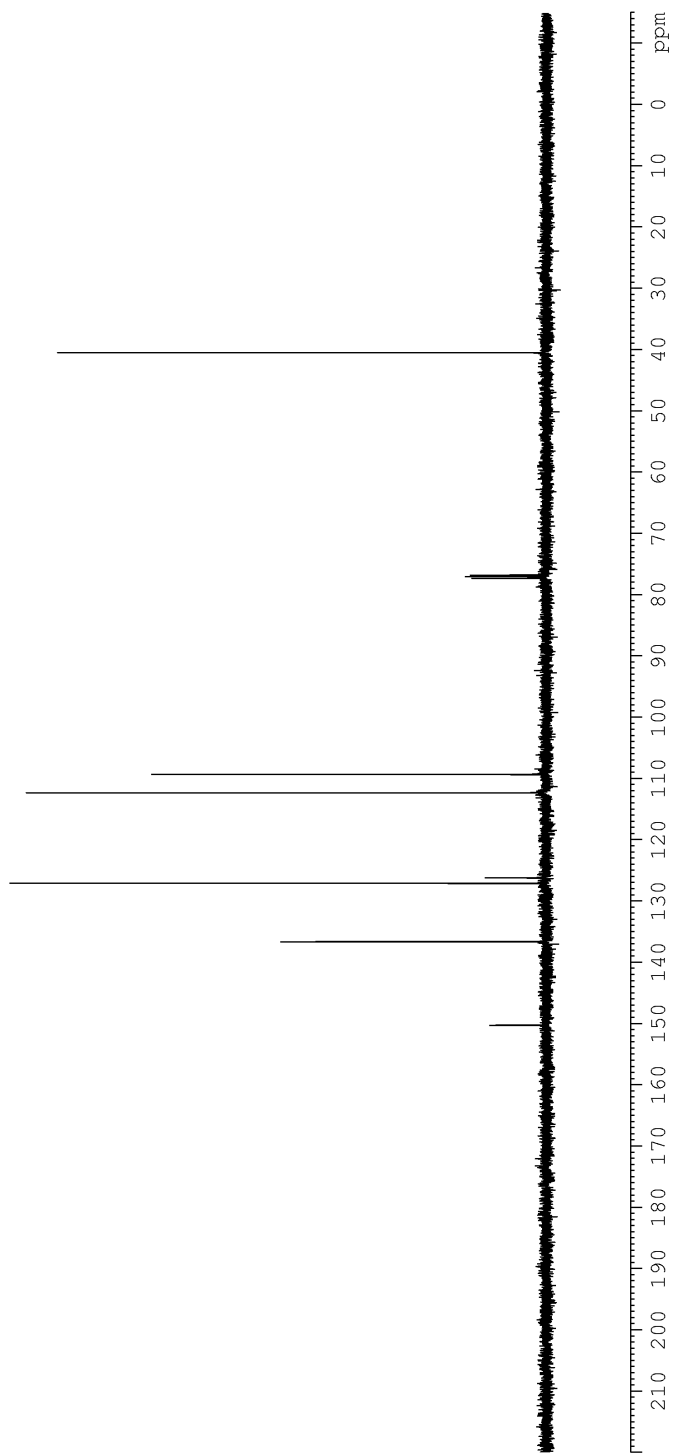
**7h**



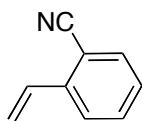
<sup>1</sup>H NMR Spectrum of dimethyl-(4-vinyl-phenyl)-amine **7h**



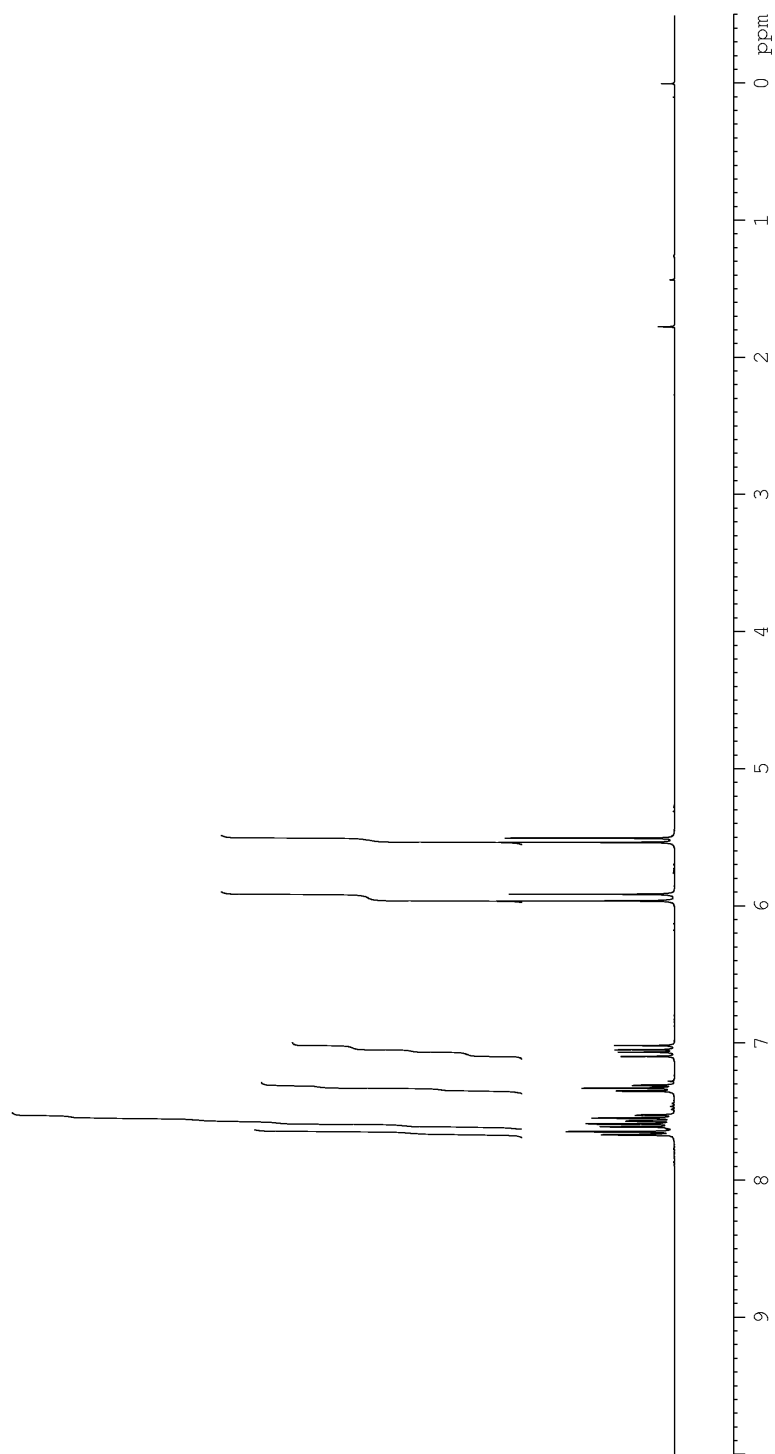
**7h**



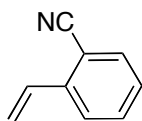
$^{13}\text{C}$  NMR Spectrum of dimethyl-(4-vinyl-phenyl)-amine **7h**



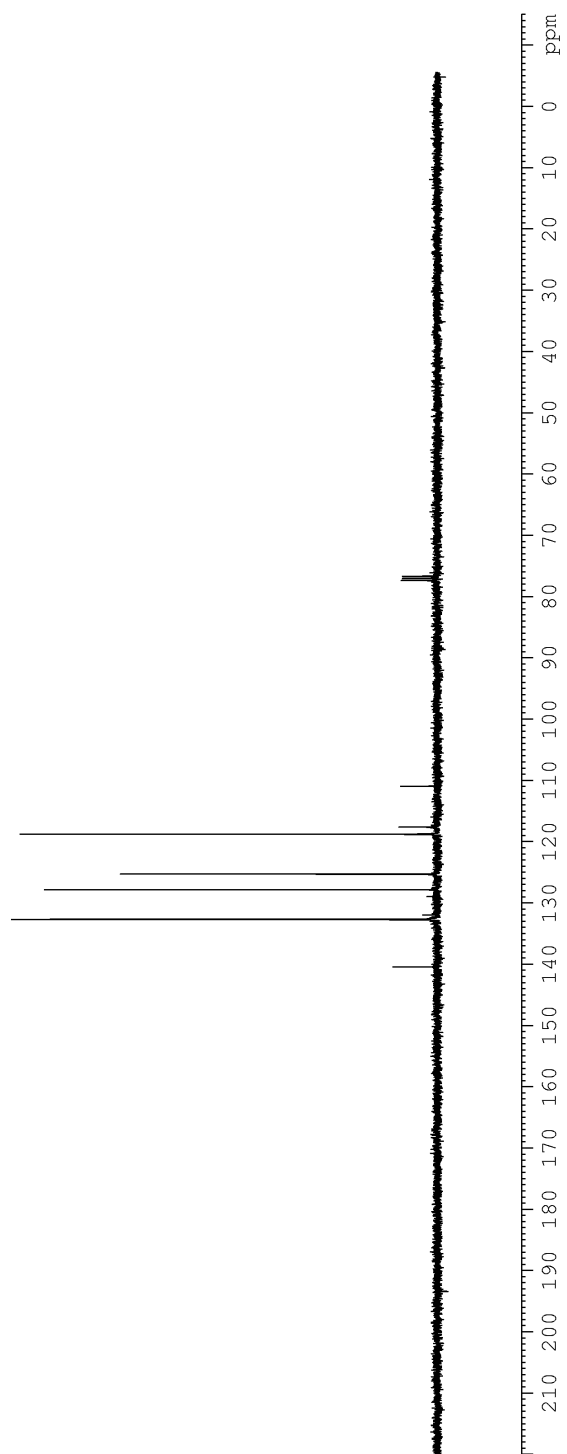
**9a**



$^1\text{H}$  NMR Spectrum of 2-vinyl-benzonitrile **9a**

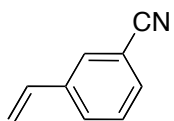


**9a**

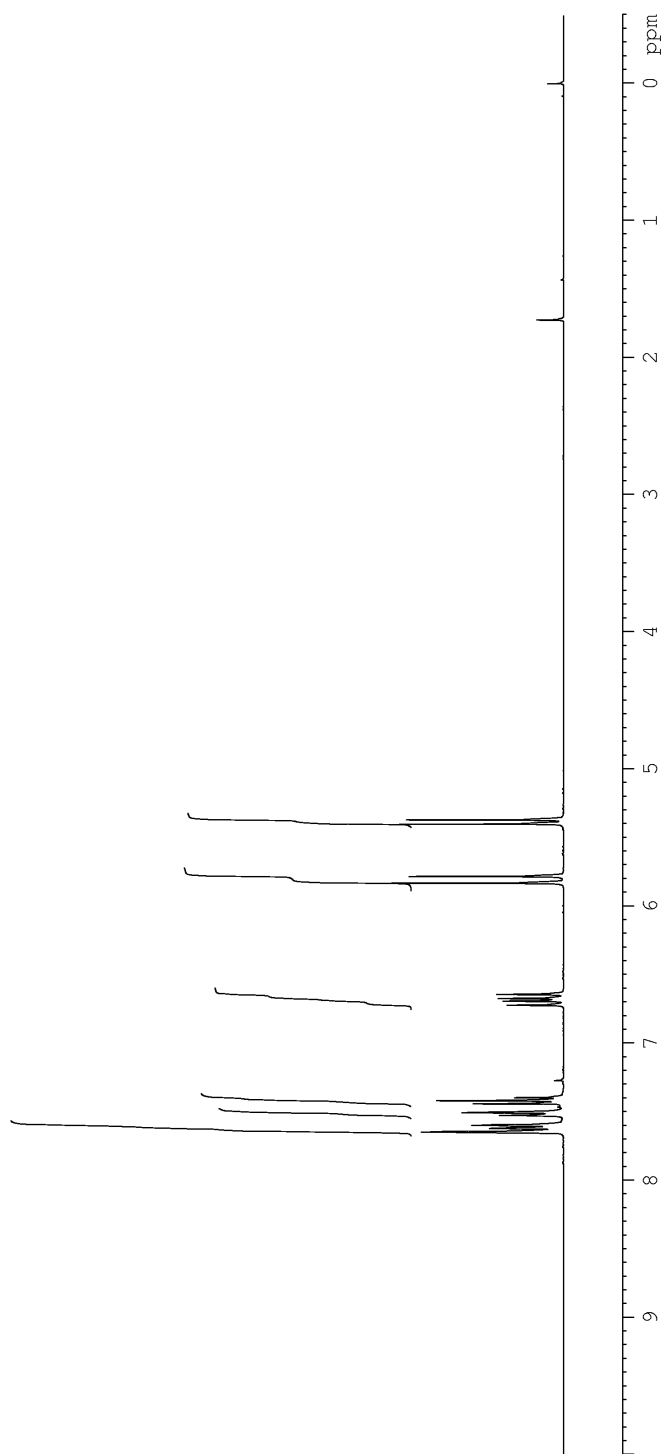


$^{13}\text{C}$  NMR Spectrum of 2-vinyl-benzonitrile **9a**

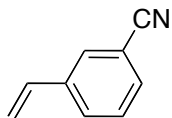




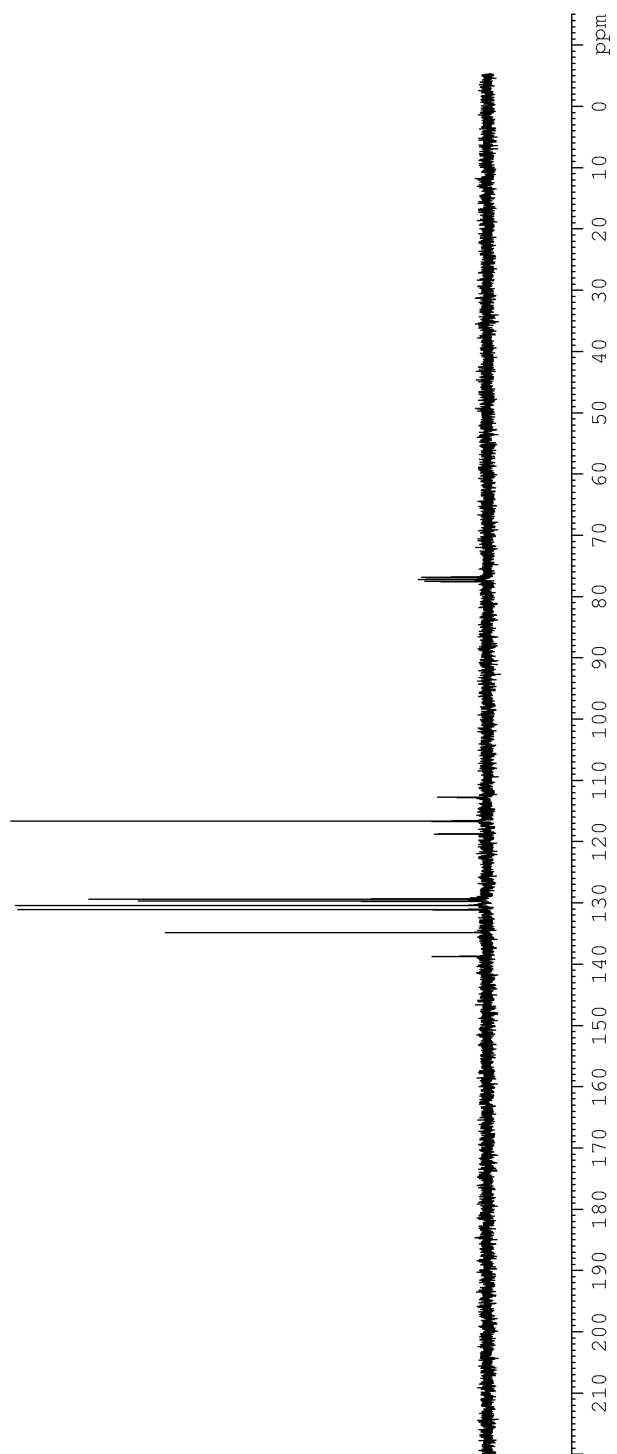
**9b**



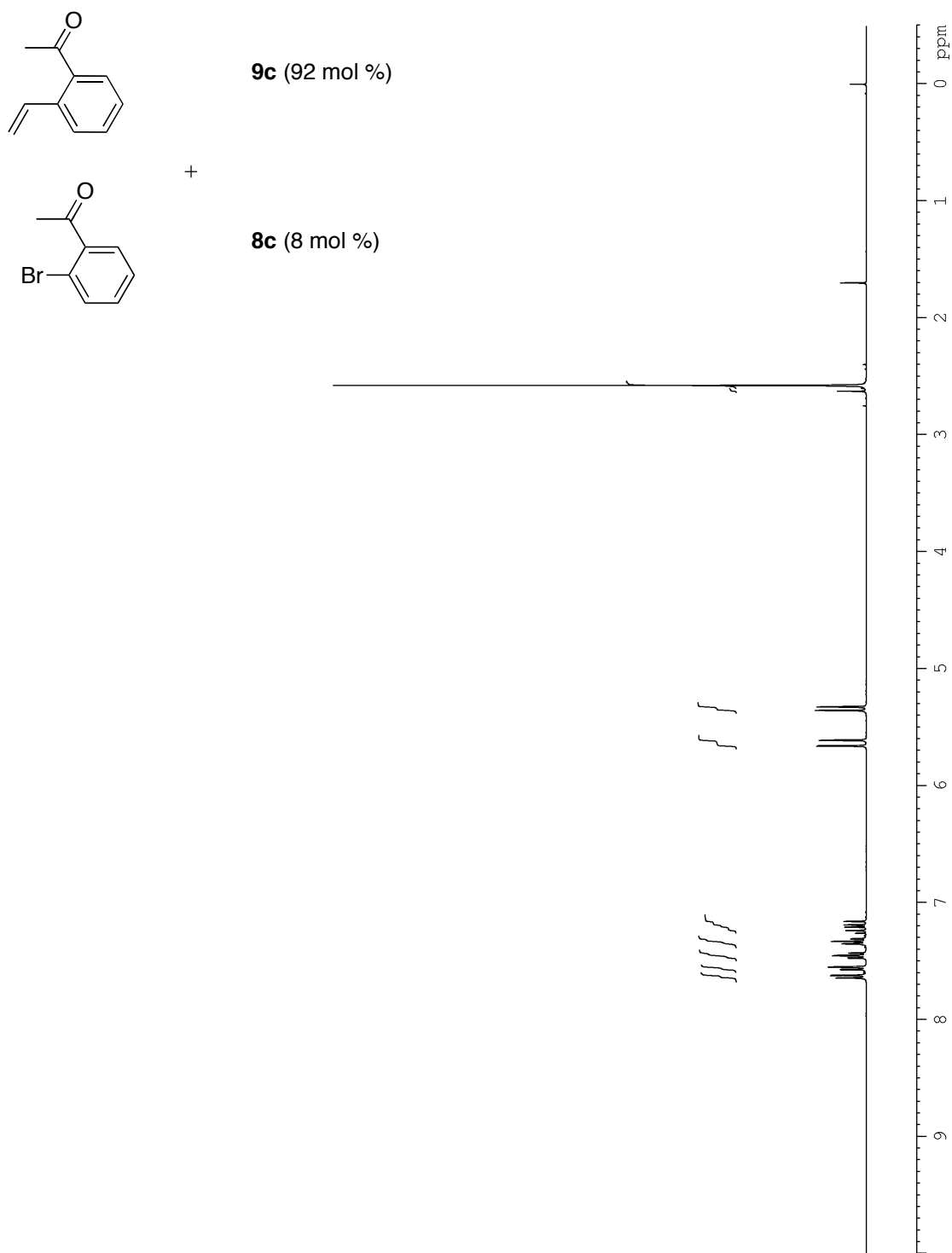
<sup>1</sup>H NMR Spectrum of 3-vinyl-benzonitrile **9b**



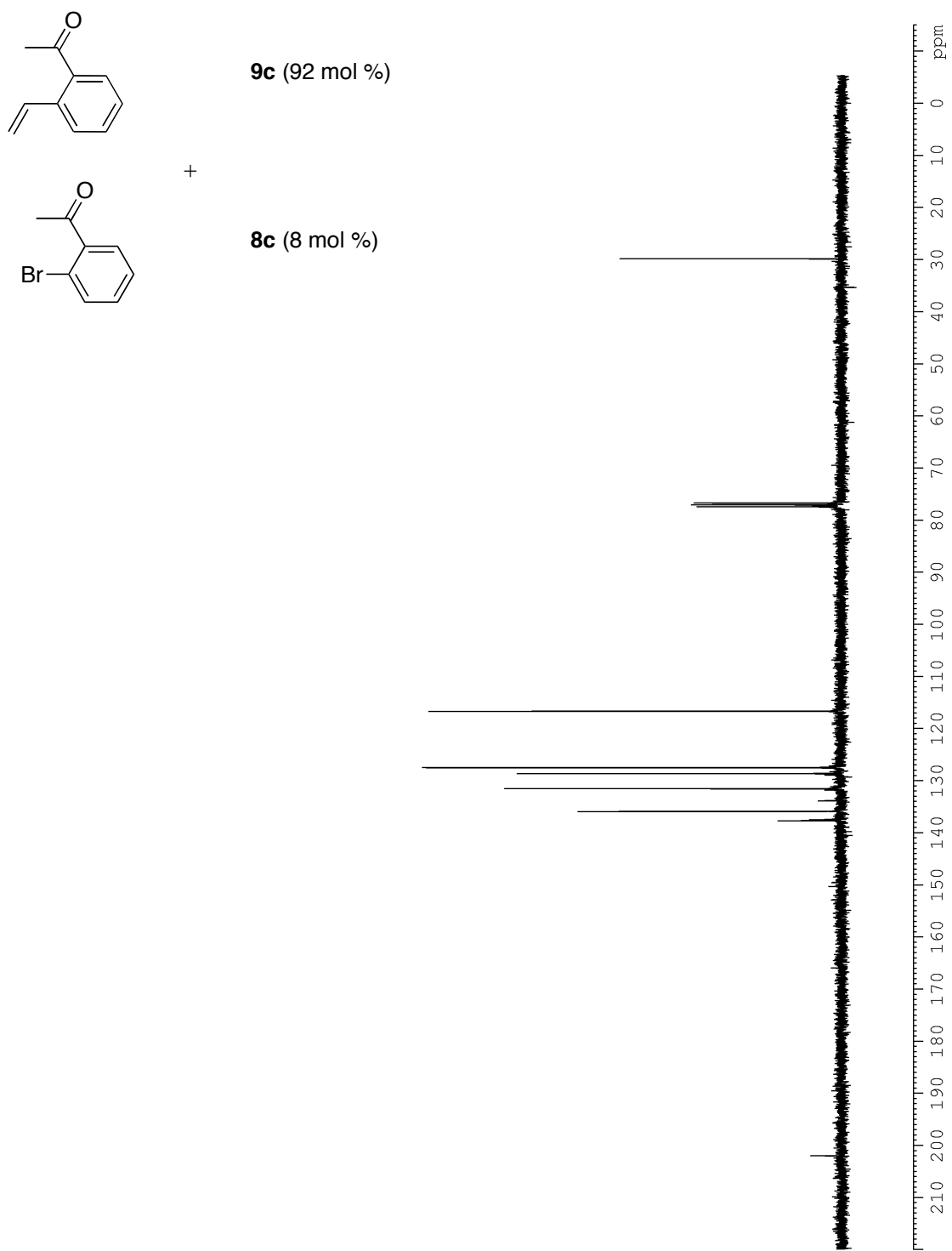
**9b**



$^{13}\text{C}$  NMR Spectrum of 3-vinyl-benzonitrile **9b**

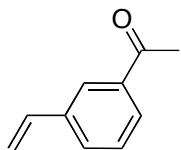


<sup>1</sup>H NMR Spectrum of 1-(2-vinyl-phenyl)-ethanone **9c** (92%) and 2-bromoacetophenone **8c** (8%)

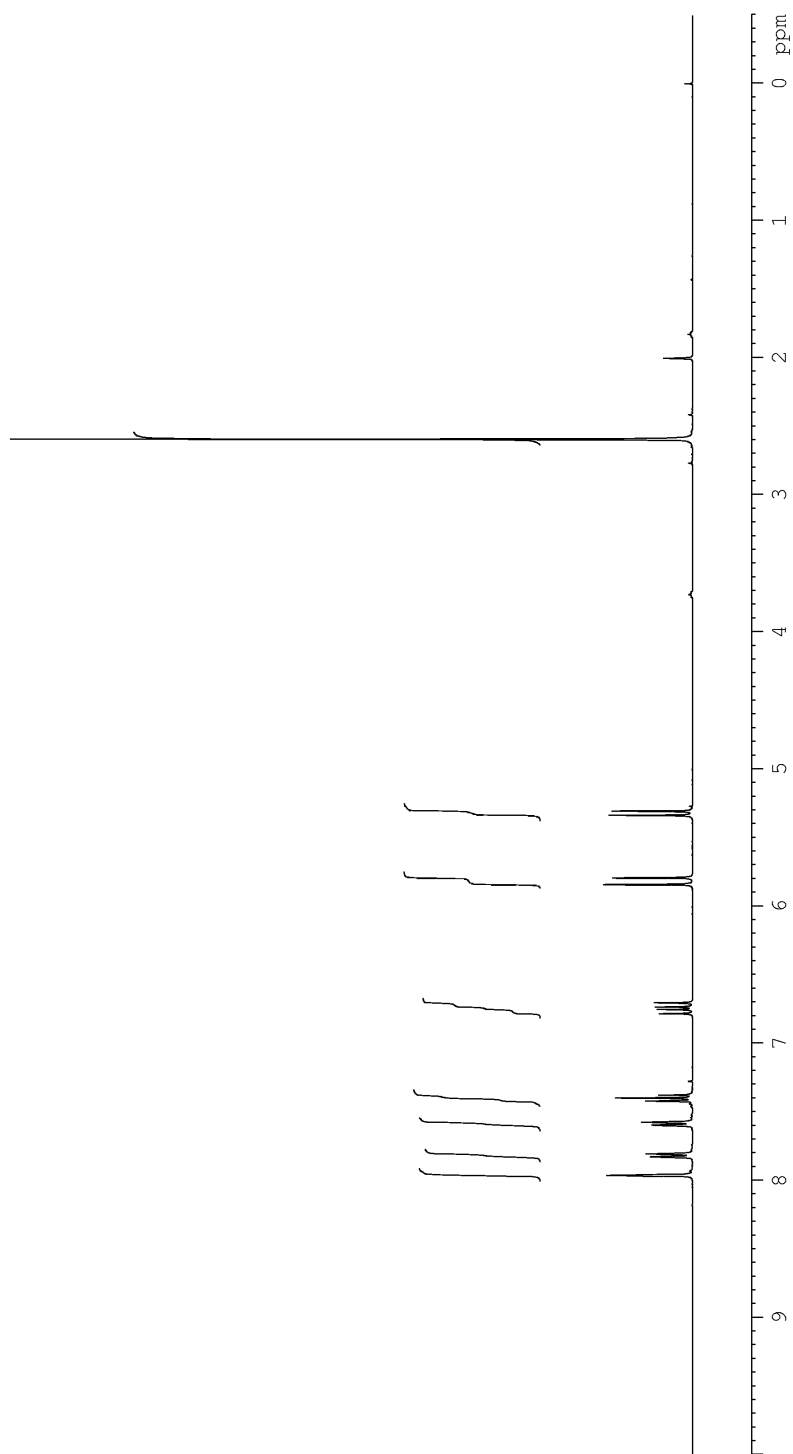


$^{13}\text{C}$  NMR Spectrum of 1-(2-vinyl-phenyl)-ethanone **9c** (92%) and 2-bromoacetophenone

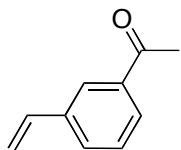
**8c** (8%)



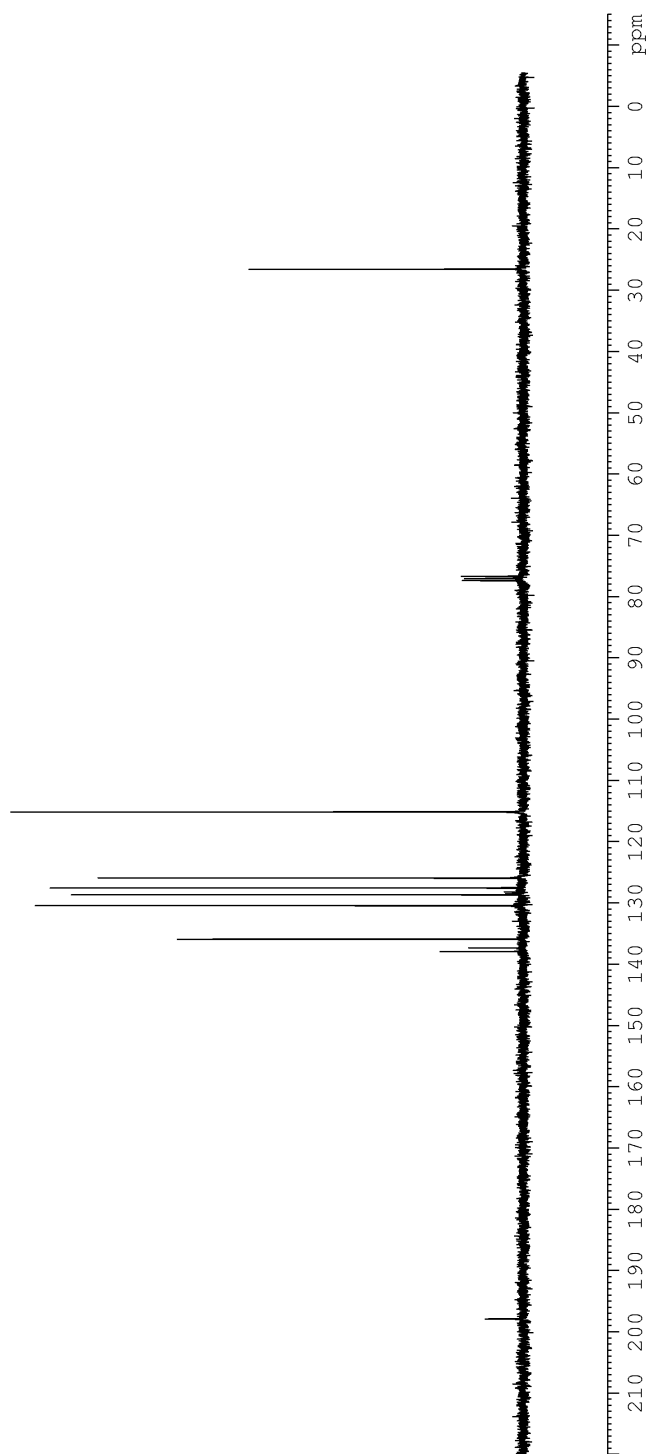
**9d**



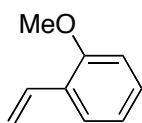
<sup>1</sup>H NMR Spectrum of 1-(3-vinyl-phenyl)-ethanone **9d**



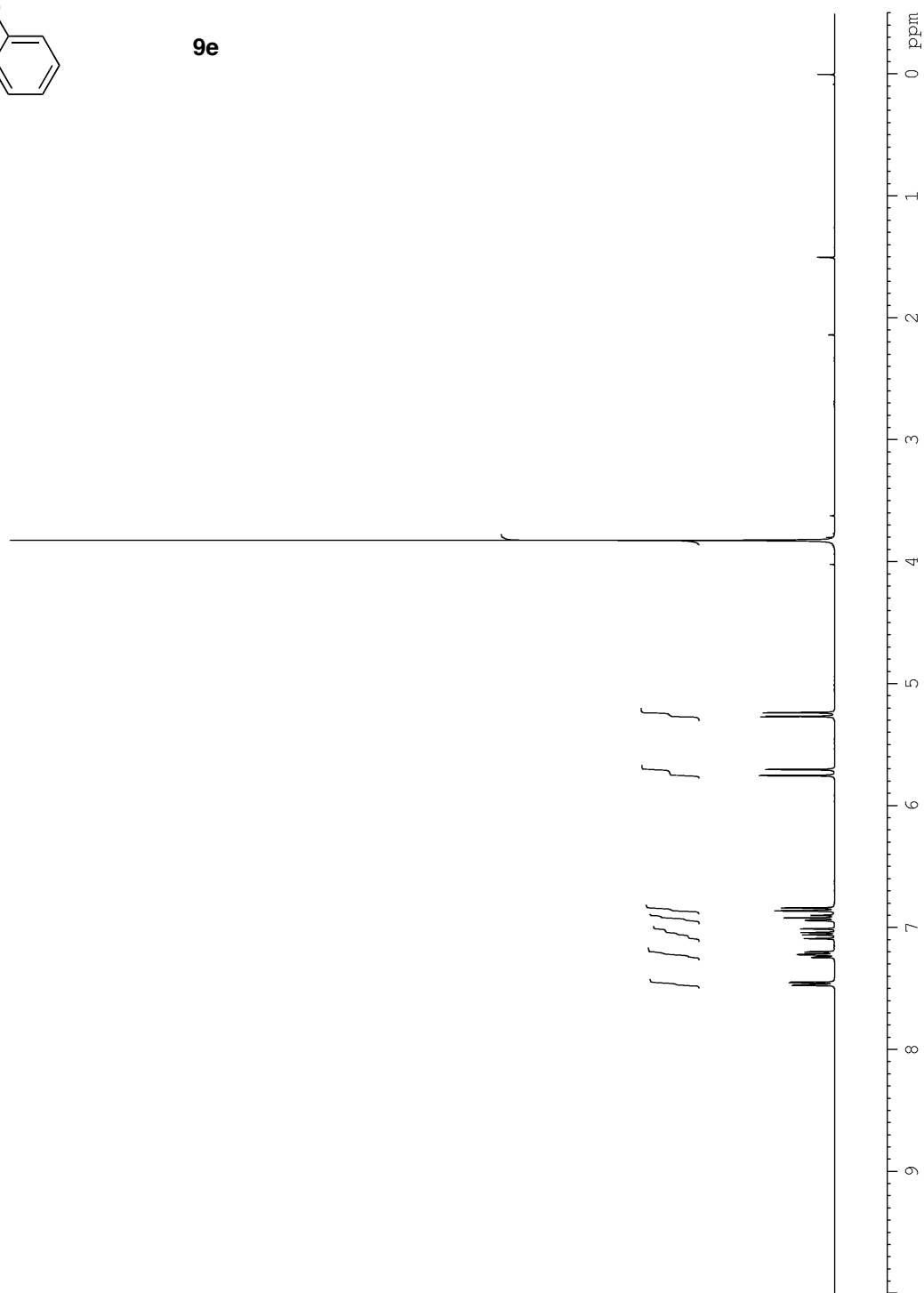
**9d**



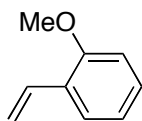
$^{13}\text{C}$  NMR Spectrum of 1-(3-vinyl-phenyl)-ethanone **9d**



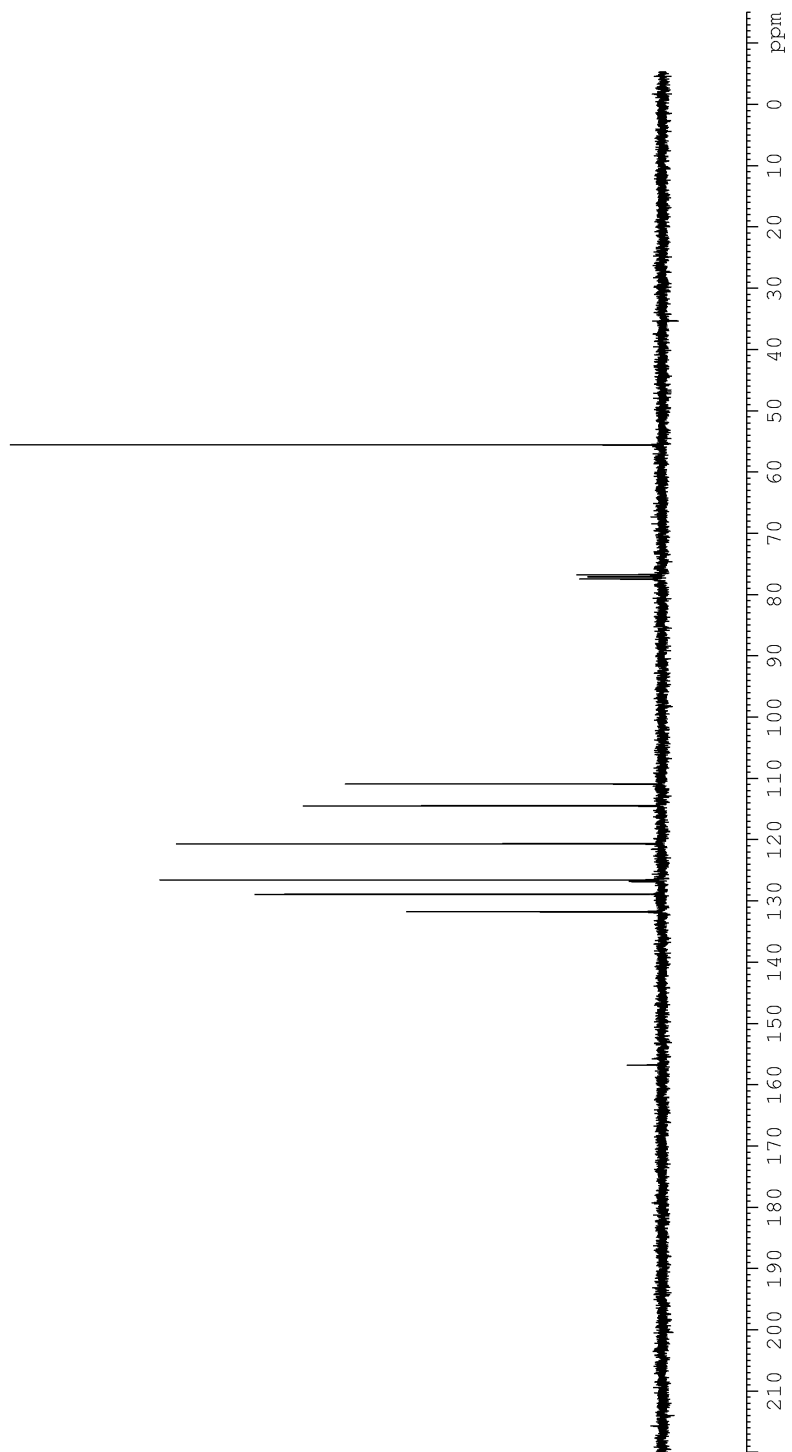
**9e**



<sup>1</sup>H NMR Spectrum of 1-methoxy-2-vinyl-benzene **9e**

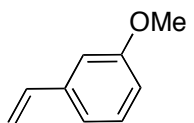


**9e**

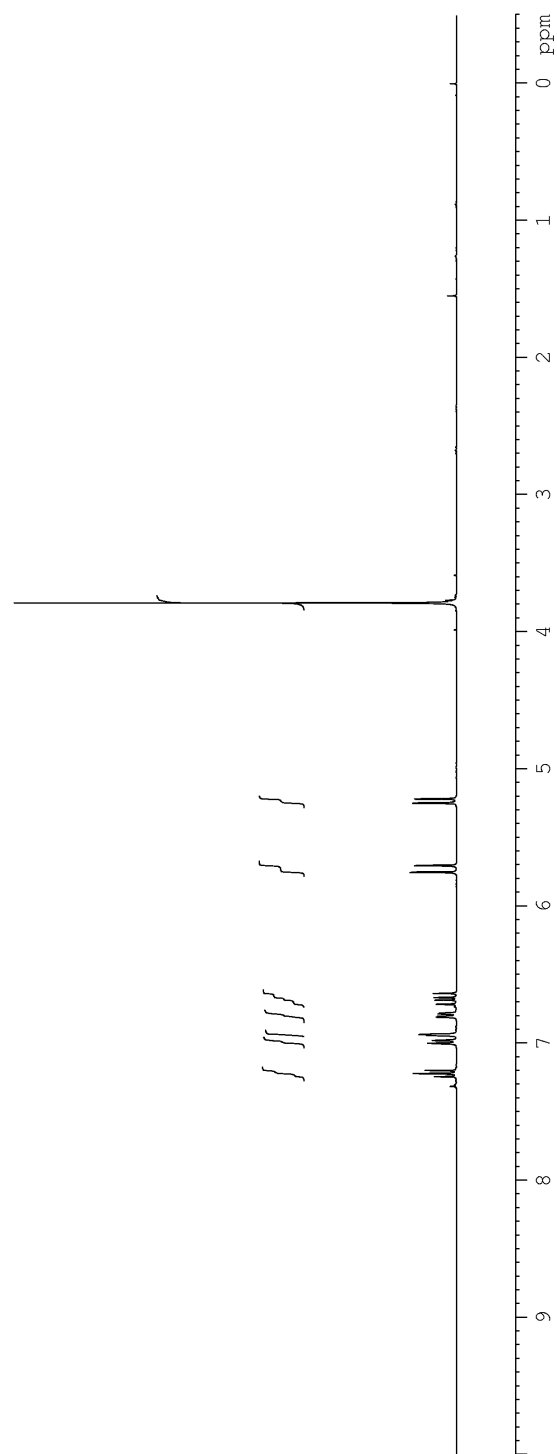


$^{13}\text{C}$  NMR Spectrum of 1-methoxy-2-vinylbenzene **9e**

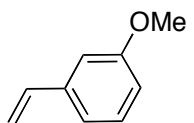




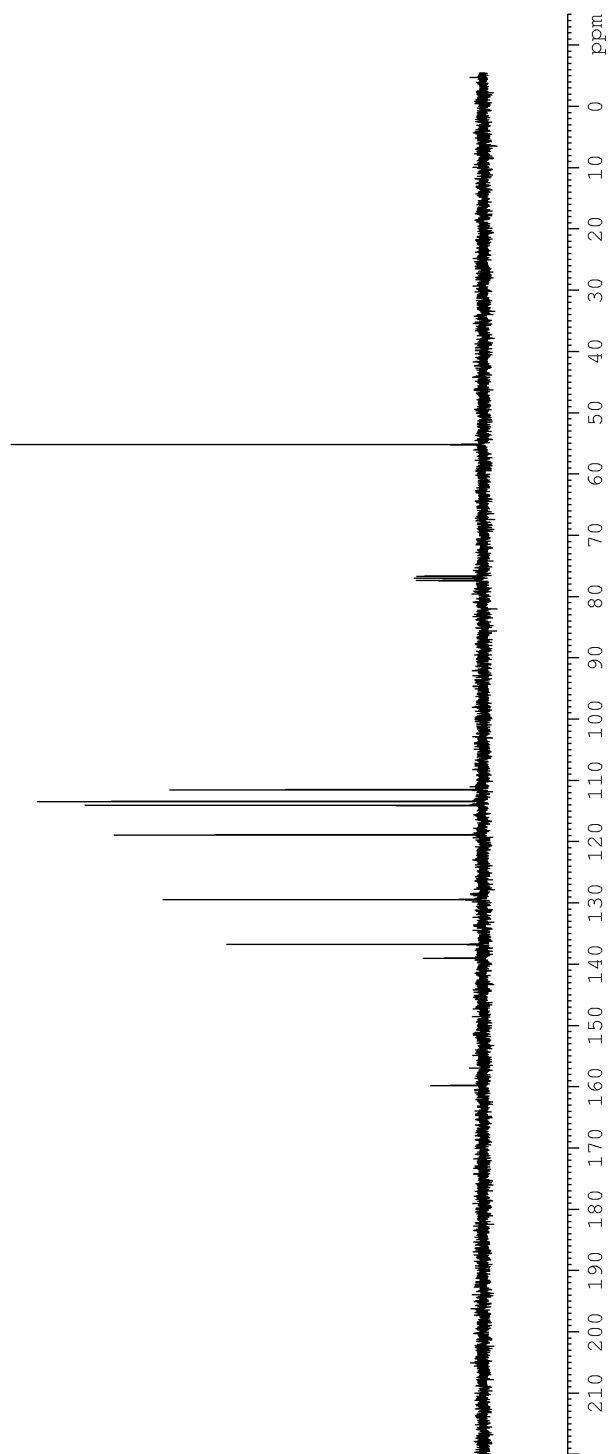
**9f**



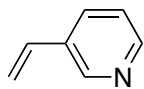
<sup>1</sup>H NMR Spectrum of 1-methoxy-3-vinyl-benzene **9f**



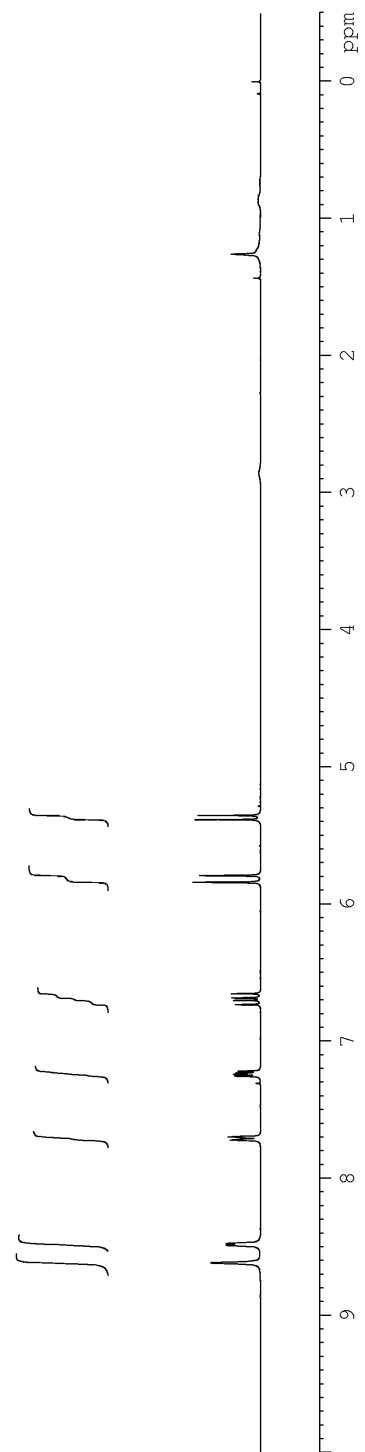
**9f**



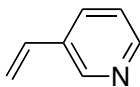
$^{13}\text{C}$  NMR Spectrum of 1-methoxy-3-vinylbenzene **9f**



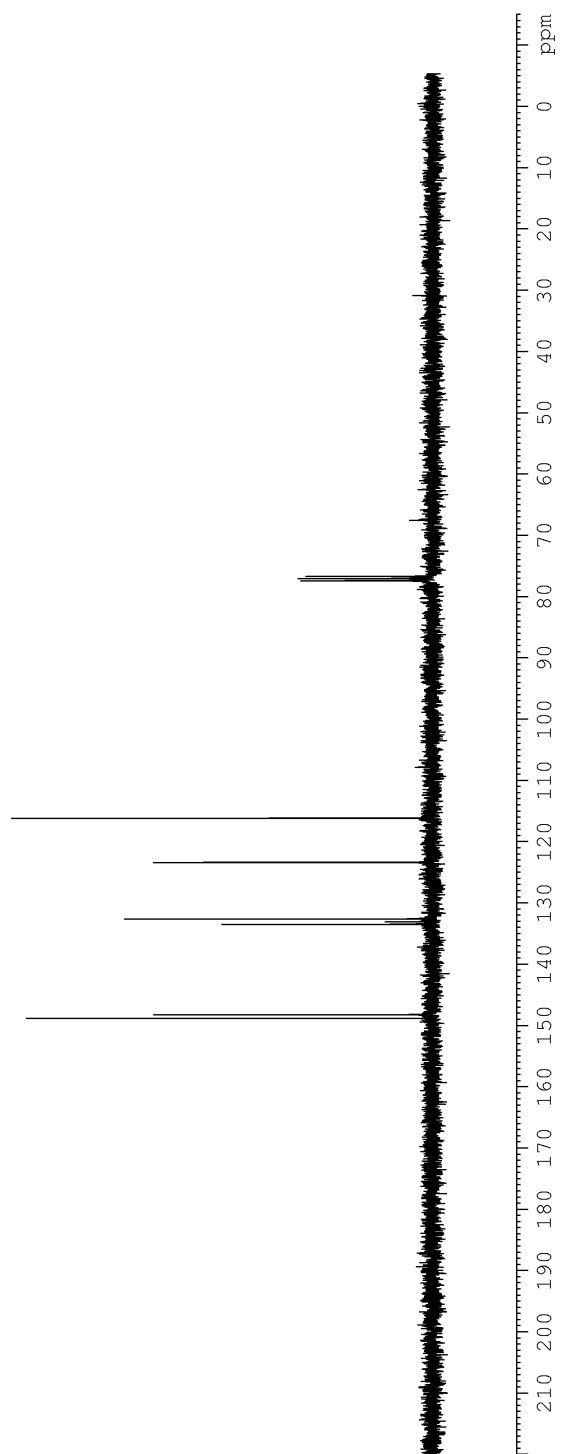
**11a**



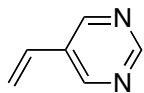
<sup>1</sup>H NMR Spectrum of 3-vinyl-pyridine **11a**



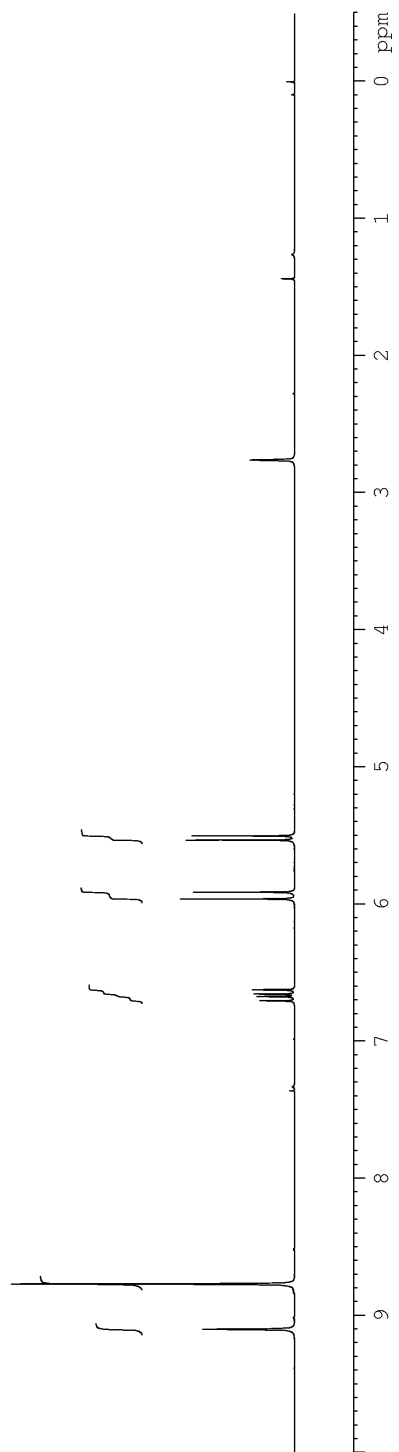
**11a**



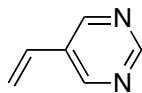
$^{13}\text{C}$  NMR Spectrum of 3-vinyl-pyridine **11a**



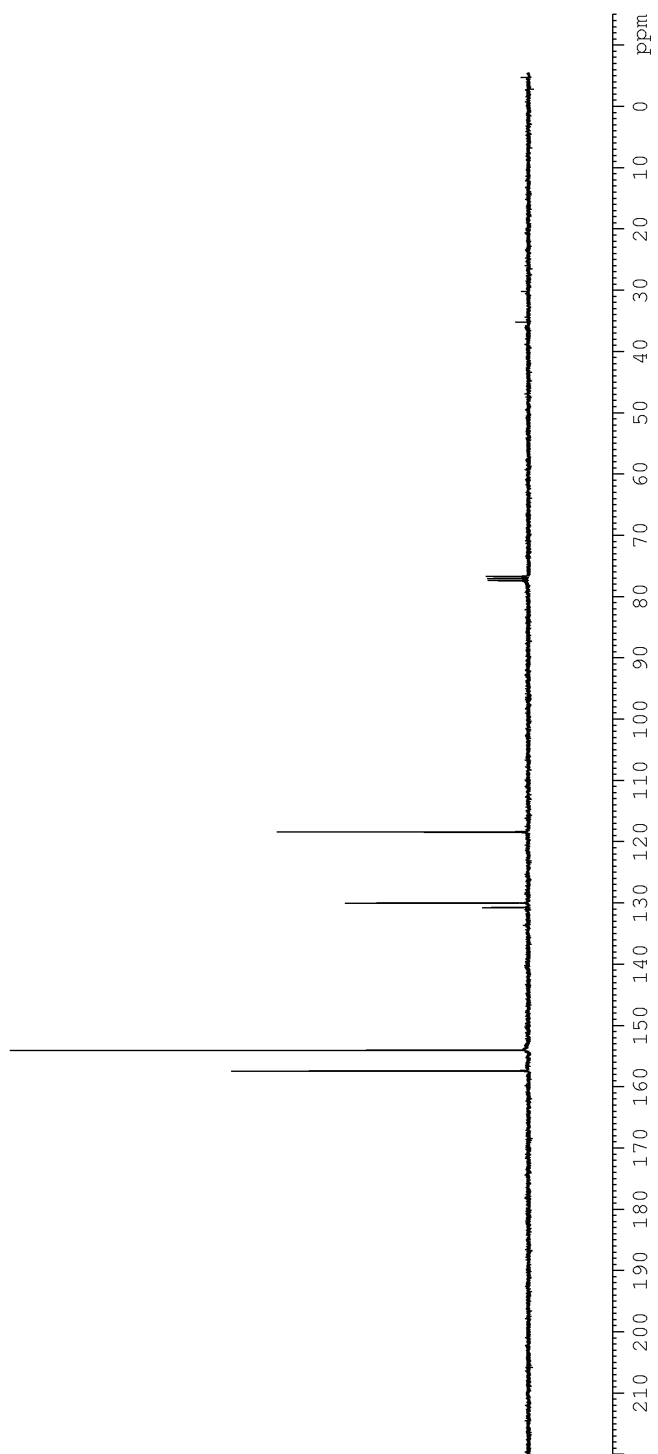
**11b**



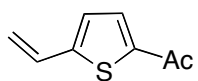
<sup>1</sup>H NMR Spectrum of 5-vinyl-pyrimidine **11b**



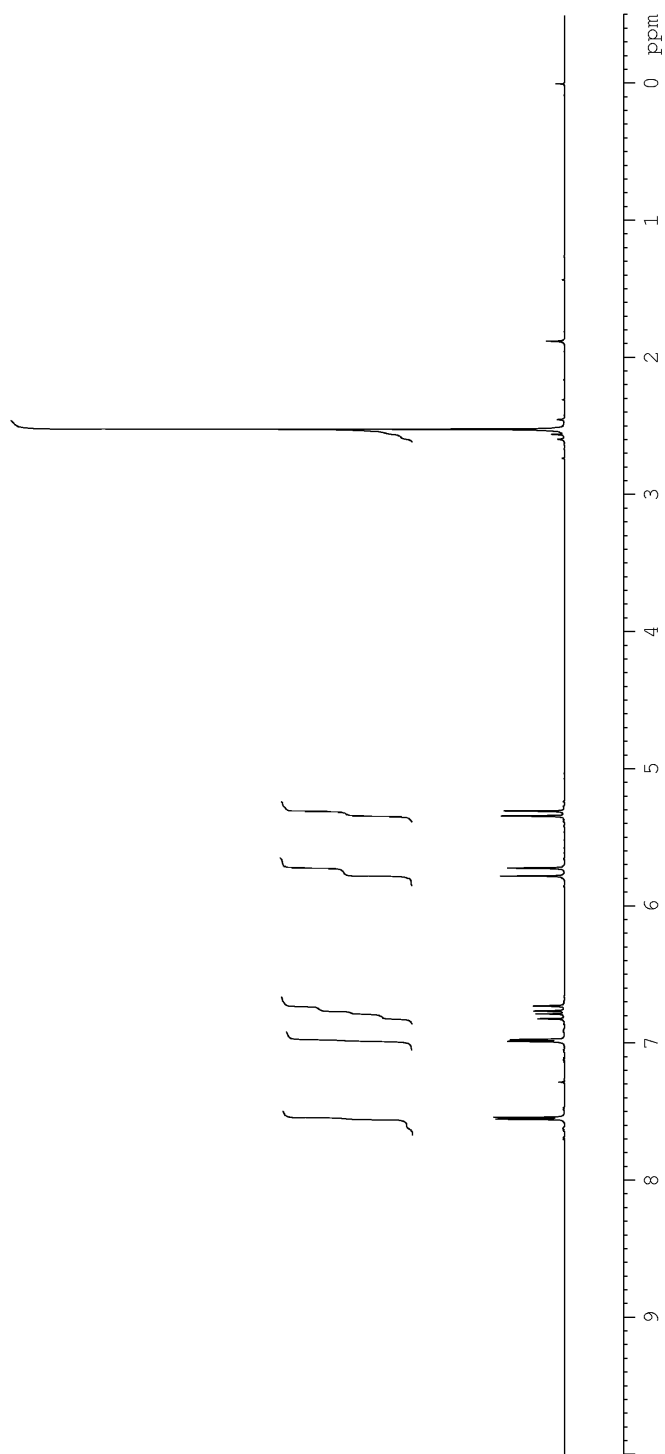
**11b**



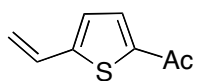
$^{13}\text{C}$  NMR Spectrum of 5-vinyl-pyrimidine **11b**



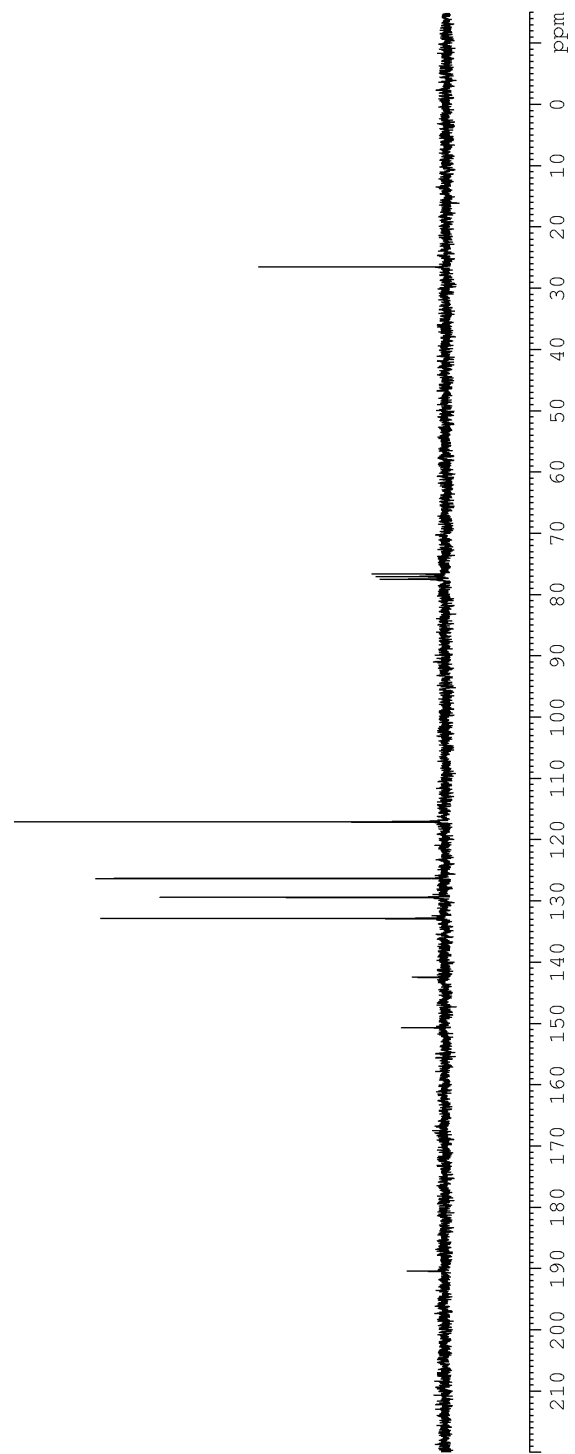
**11c**



<sup>1</sup>H NMR Spectrum of 1-(5-vinyl-thiophen-2-yl)-ethanone **11c**

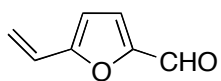


**11c**

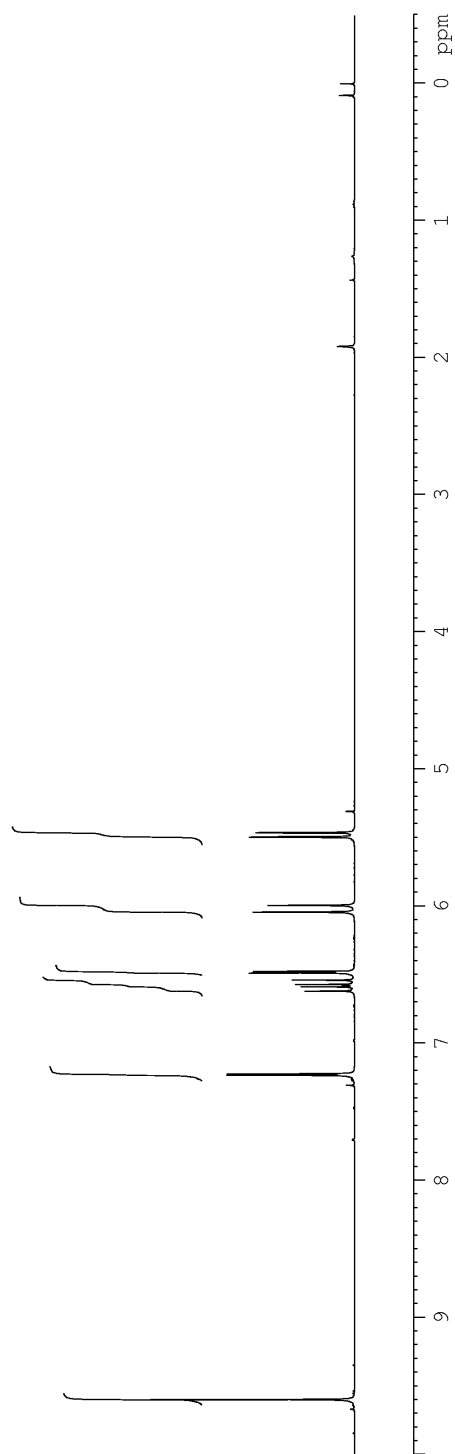


<sup>13</sup>C NMR Spectrum of 1-(5-vinyl-thiophen-2-yl)-ethanone **11c**

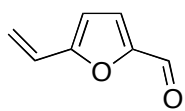




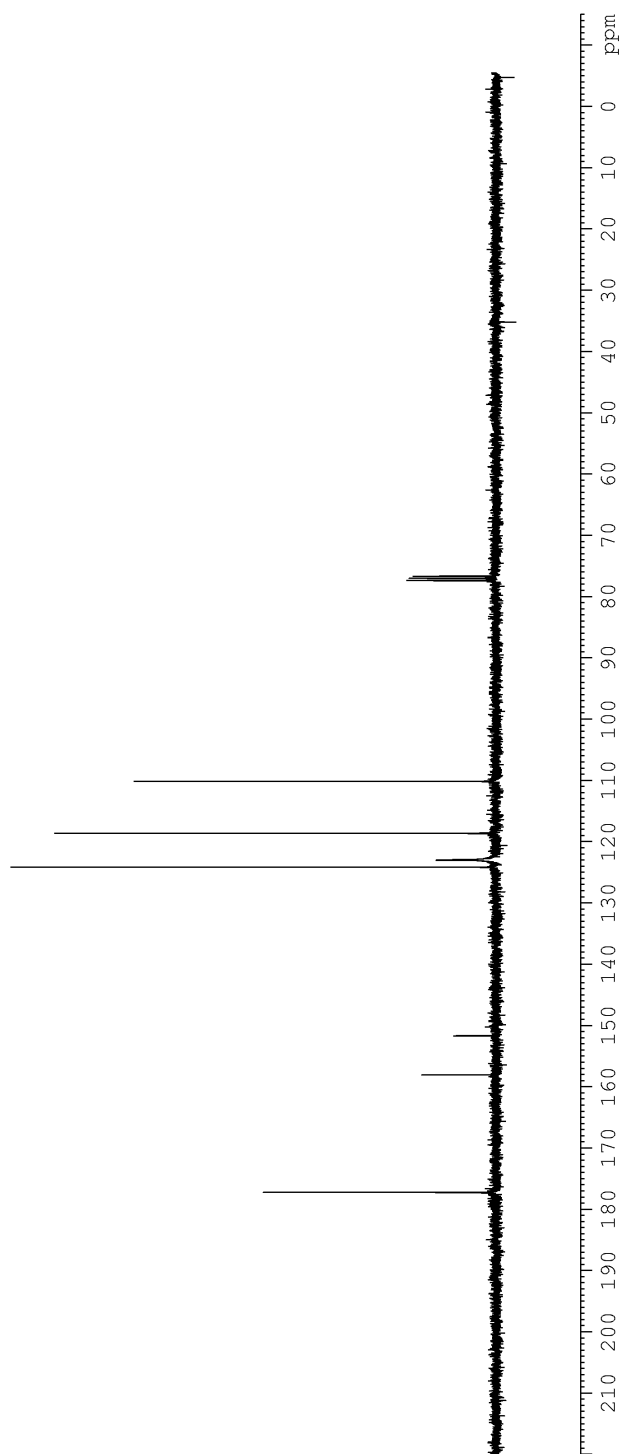
**11d**



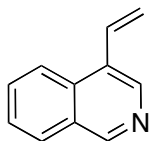
<sup>1</sup>H NMR Spectrum of 5-vinyl-furan-2-carbaldehyde **11d**



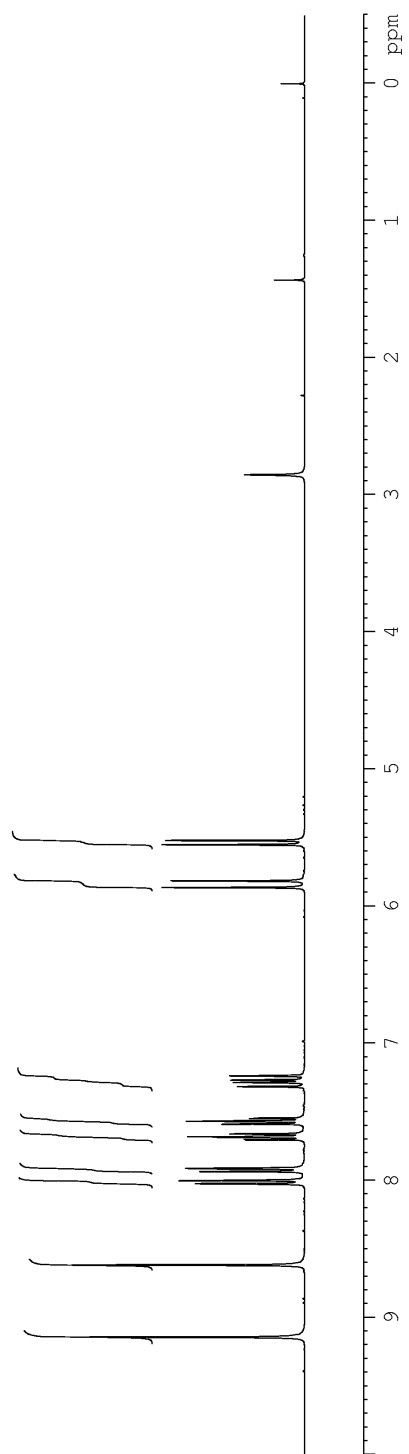
**11d**



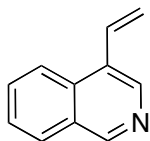
$^{13}\text{C}$  NMR Spectrum of 5-vinyl-furan-2-carbaldehyde **11d**



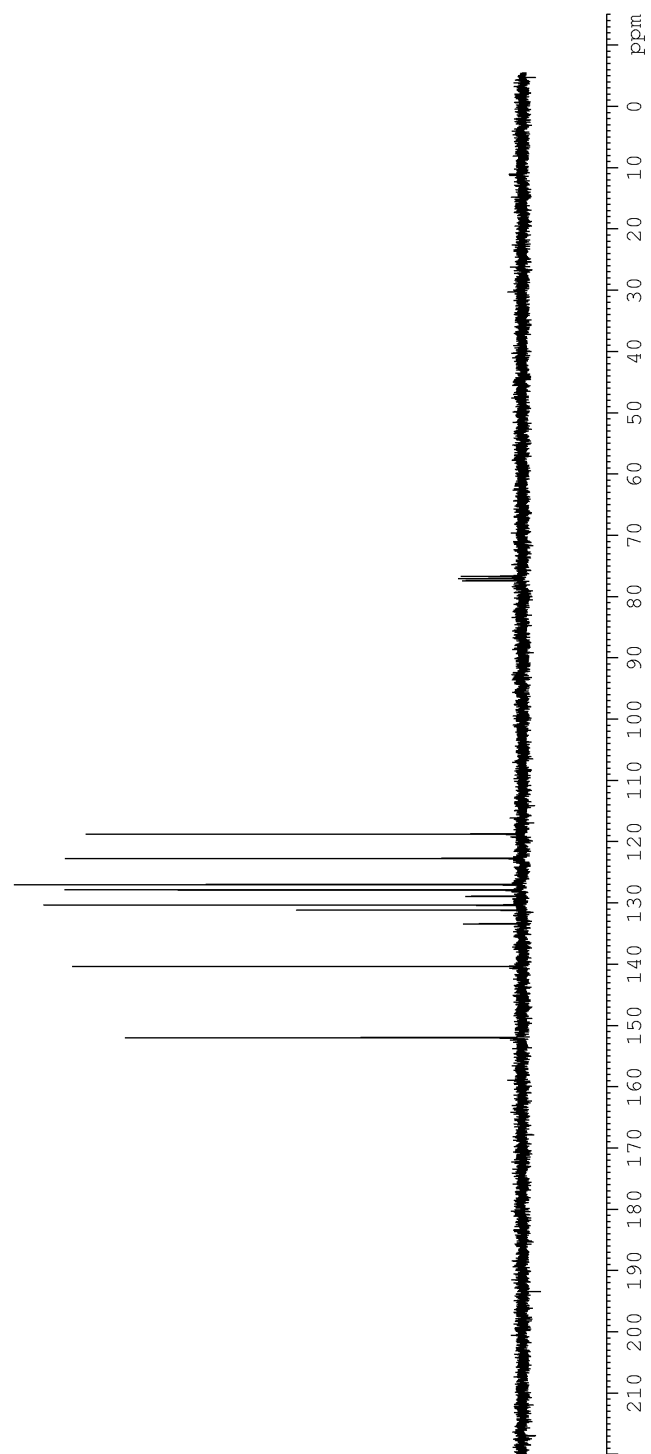
**11e**



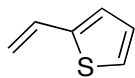
<sup>1</sup>H NMR Spectrum of 4-vinyl-isoquinoline **11e**



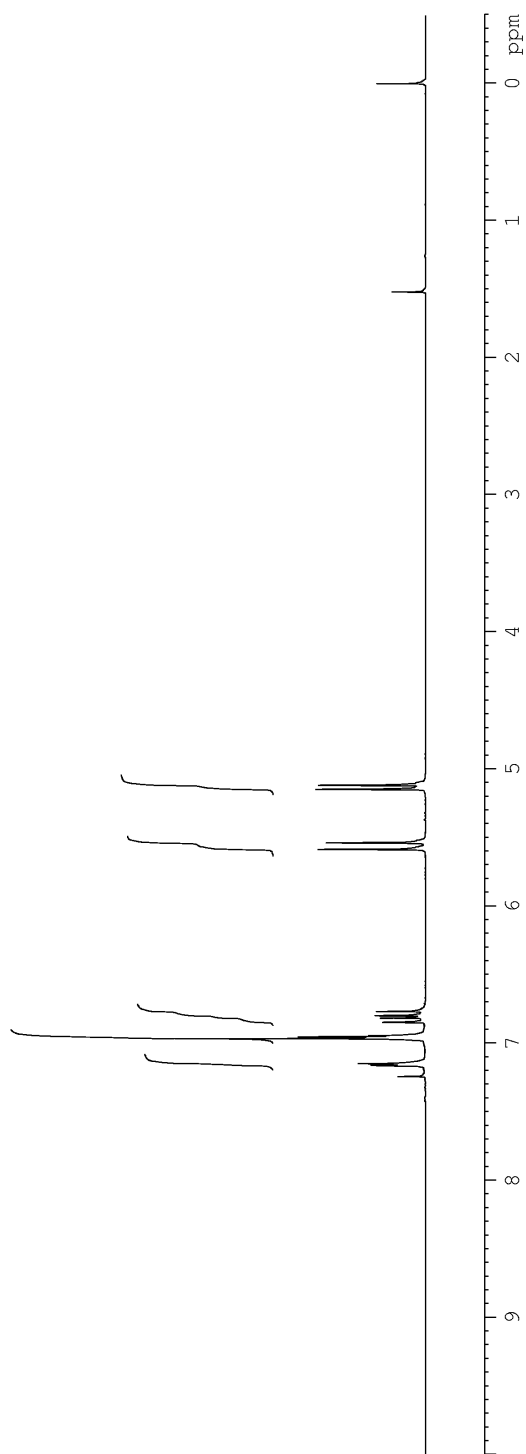
**11e**



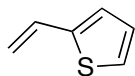
$^{13}\text{C}$  NMR Spectrum of 4-vinyl-isoquinoline **11e**



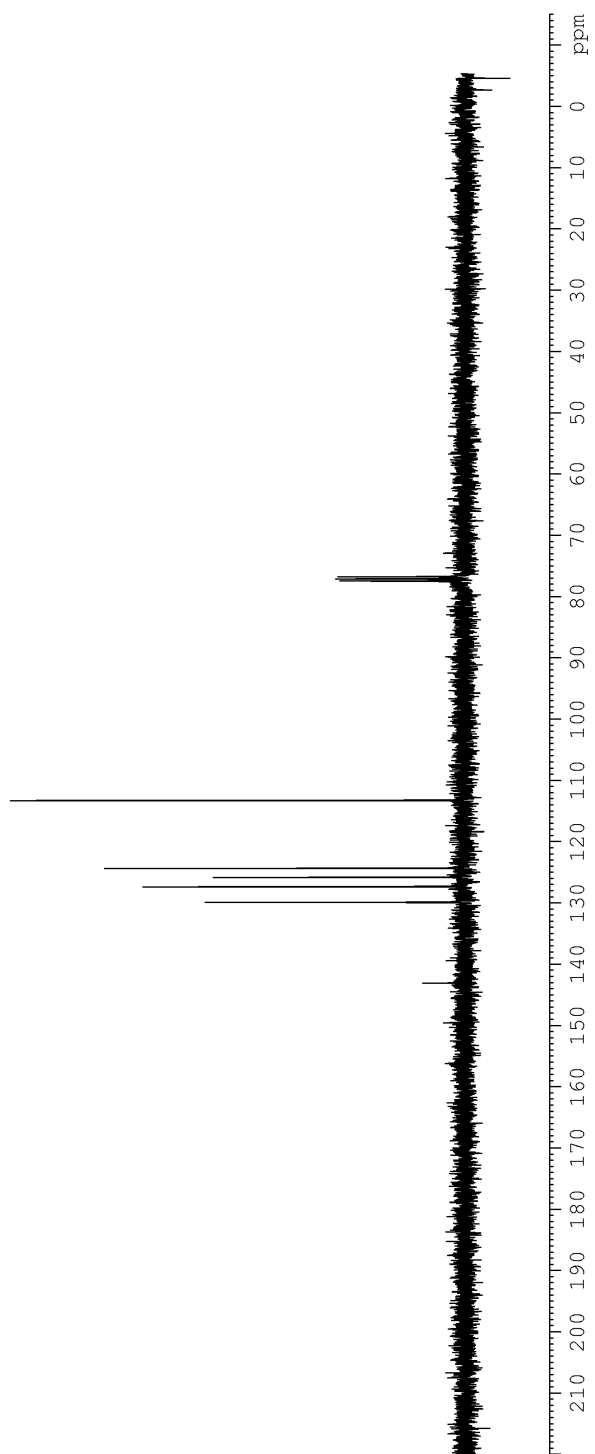
**11f**



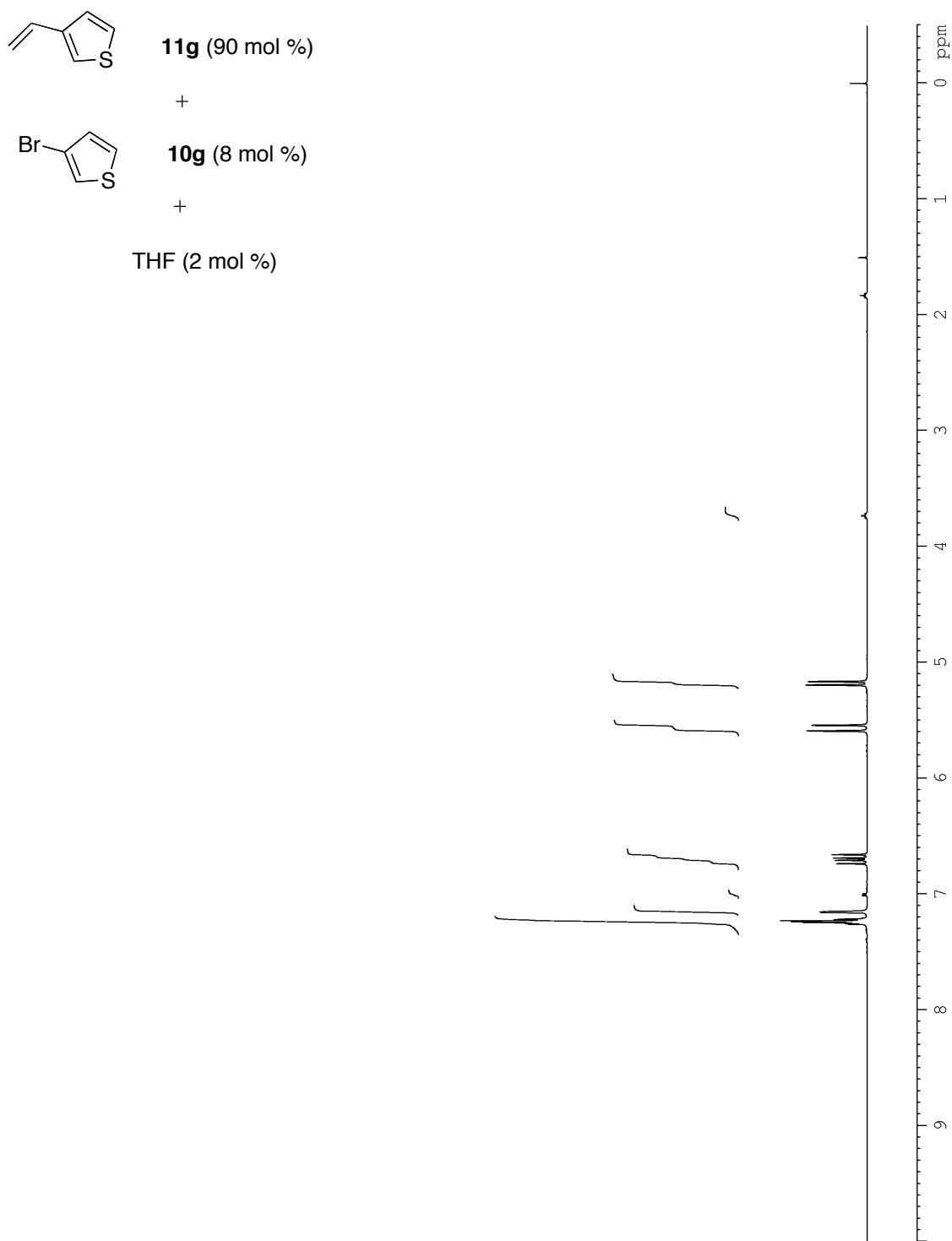
$^1\text{H}$  NMR Spectrum of 2-vinylthiophene **11f**



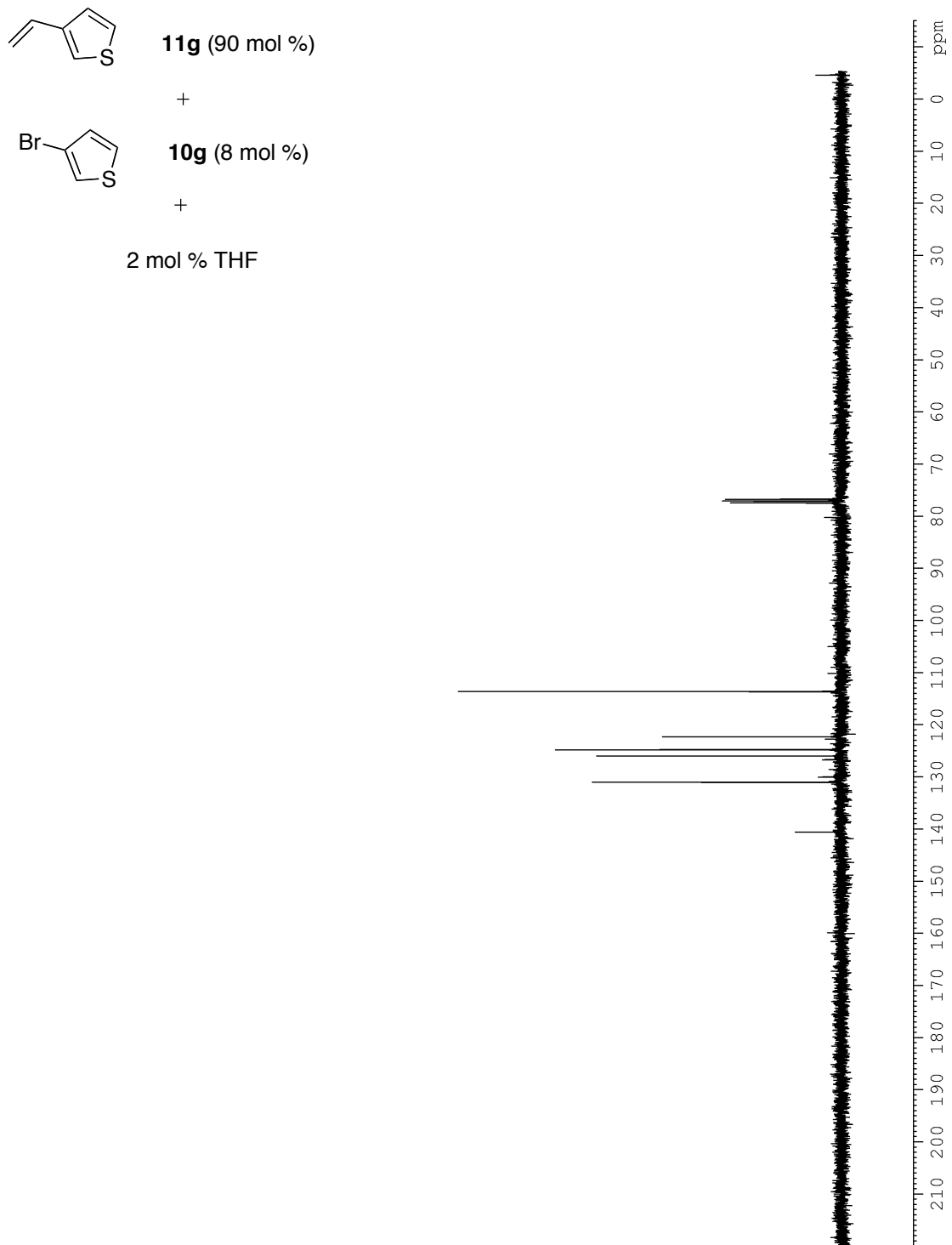
**11f**



$^{13}\text{C}$  NMR Spectrum of 2-vinylthiophene **11f**

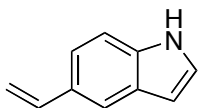


<sup>1</sup>H NMR Spectrum of 3-vinylthiophene **11f** (90%) and 3-bromothiophene **10f** (8%) and THF (2%)

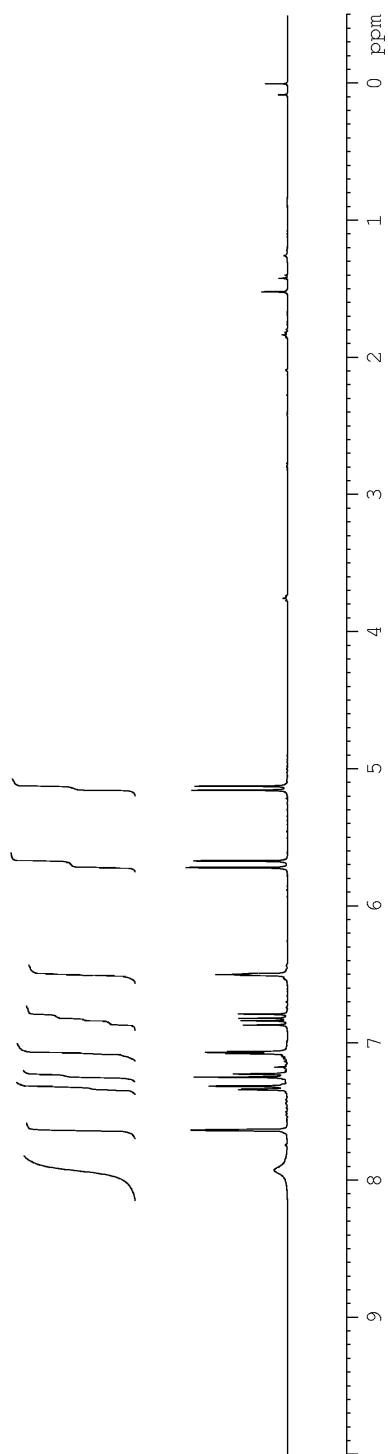


$^{13}\text{C}$  NMR Spectrum of 3-vinylthiophene **11f** (90%) and 3-bromothiophene **10f** (8%) and THF (2%)

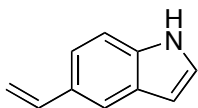




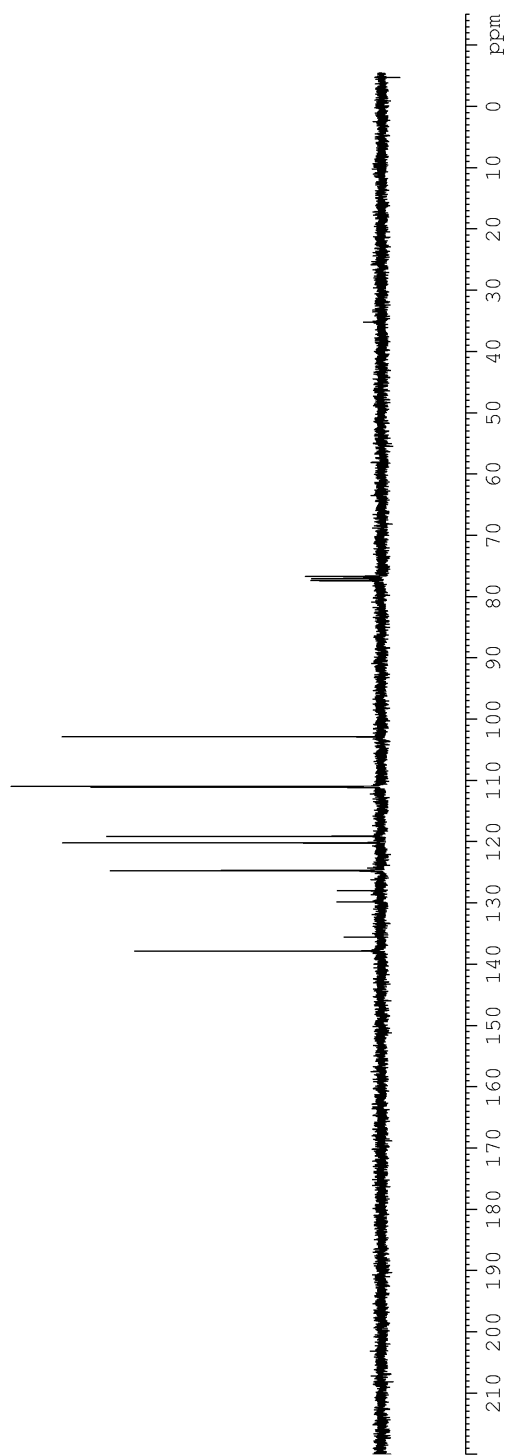
**11h**



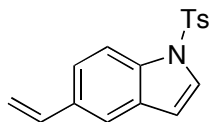
$^1\text{H}$  NMR Spectrum of 5-vinyl-1*H*-indole **11h**



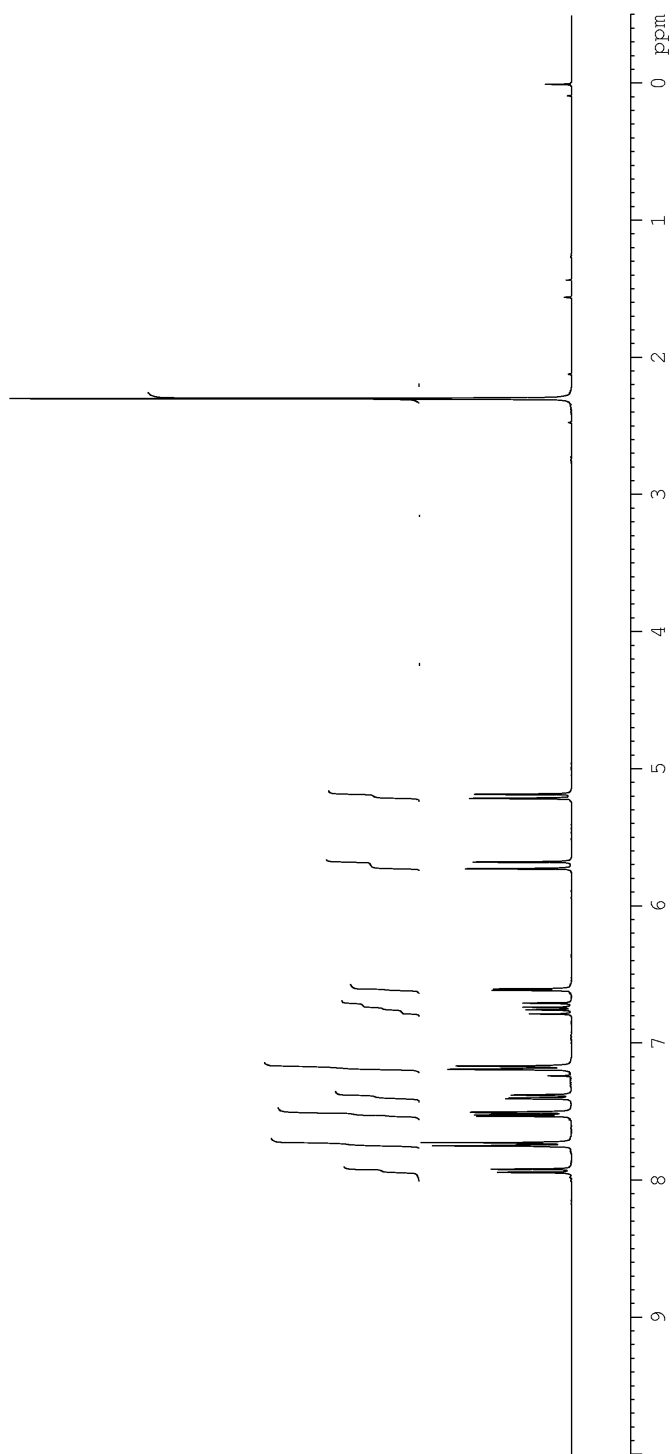
**11h**



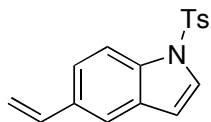
$^{13}\text{C}$  NMR Spectrum of 5-vinyl-1H-indole **11h**



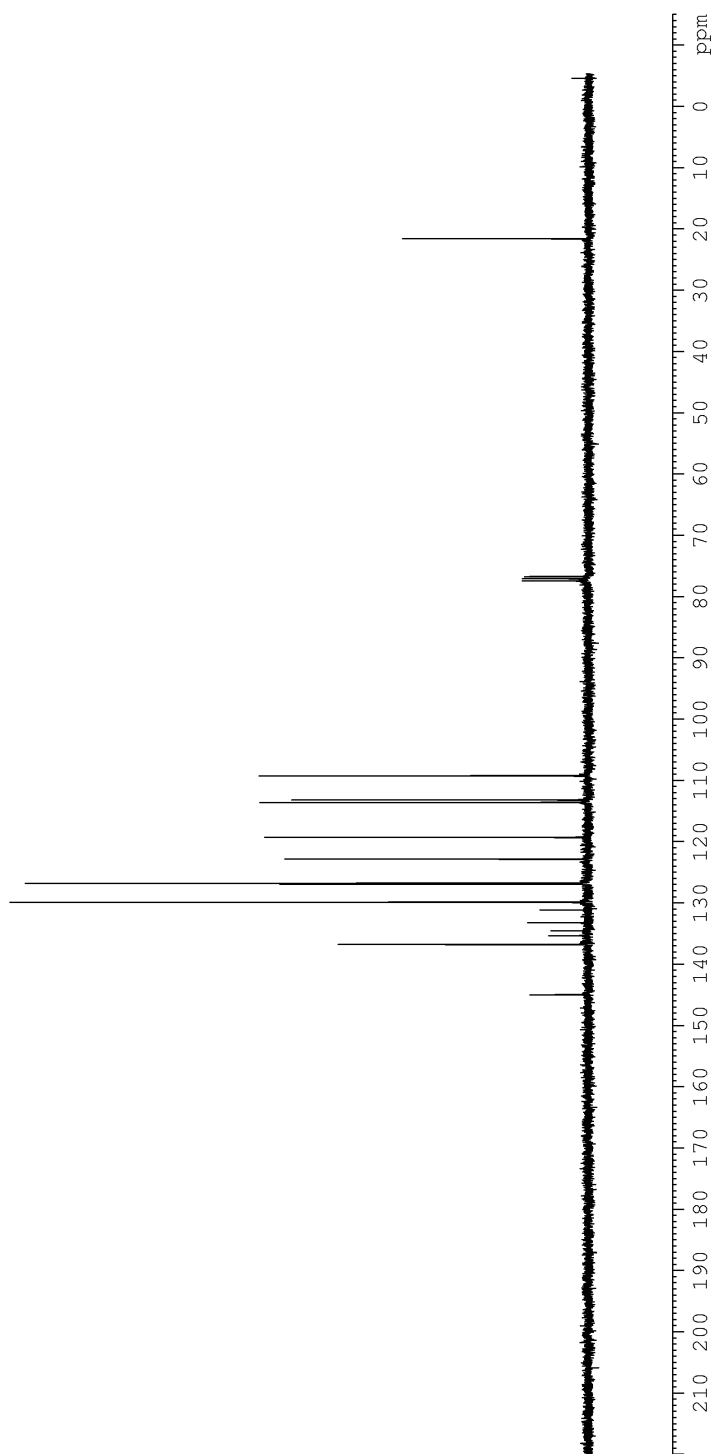
**11i**



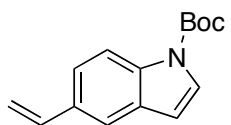
<sup>1</sup>H NMR Spectrum of 1-tosyl-5-vinyl-1*H*-indole **11i**



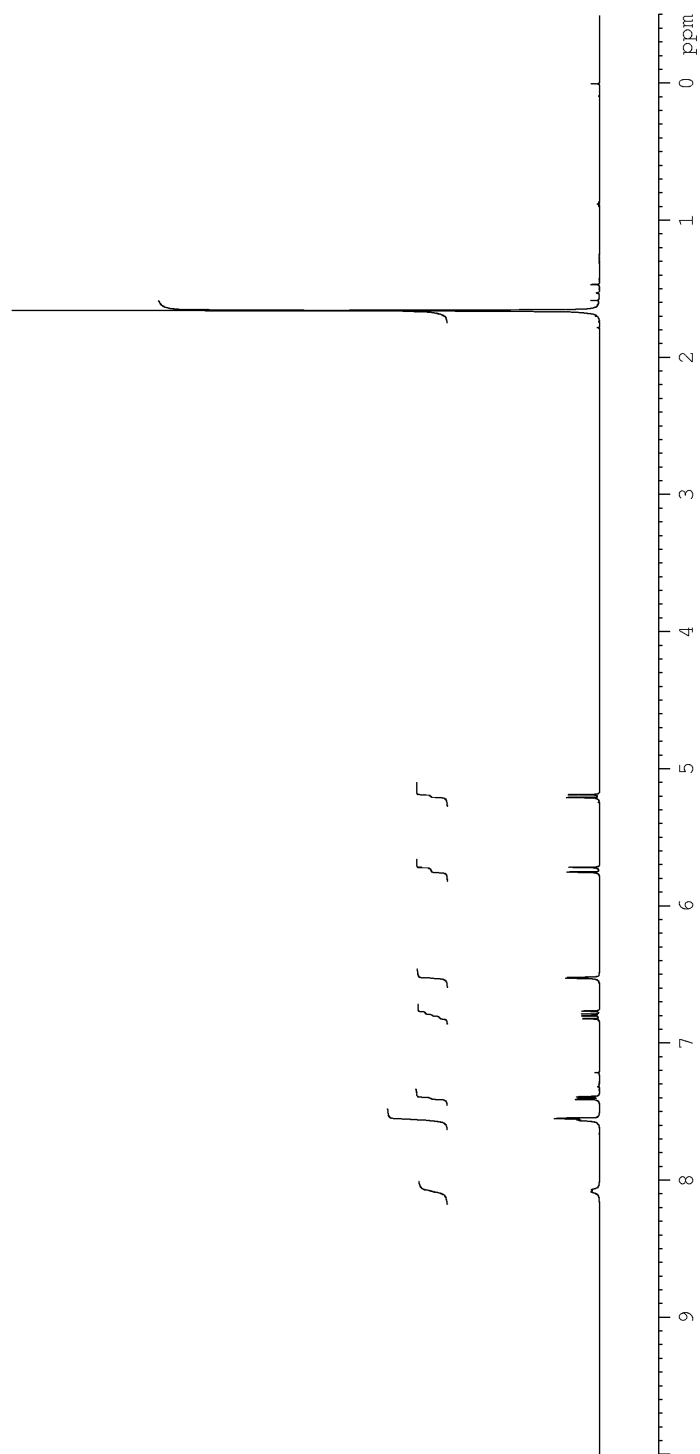
11i



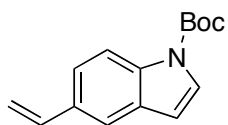
$^{13}\text{C}$  NMR Spectrum of 1-tosyl-5-vinyl-1*H*-indole **11i**



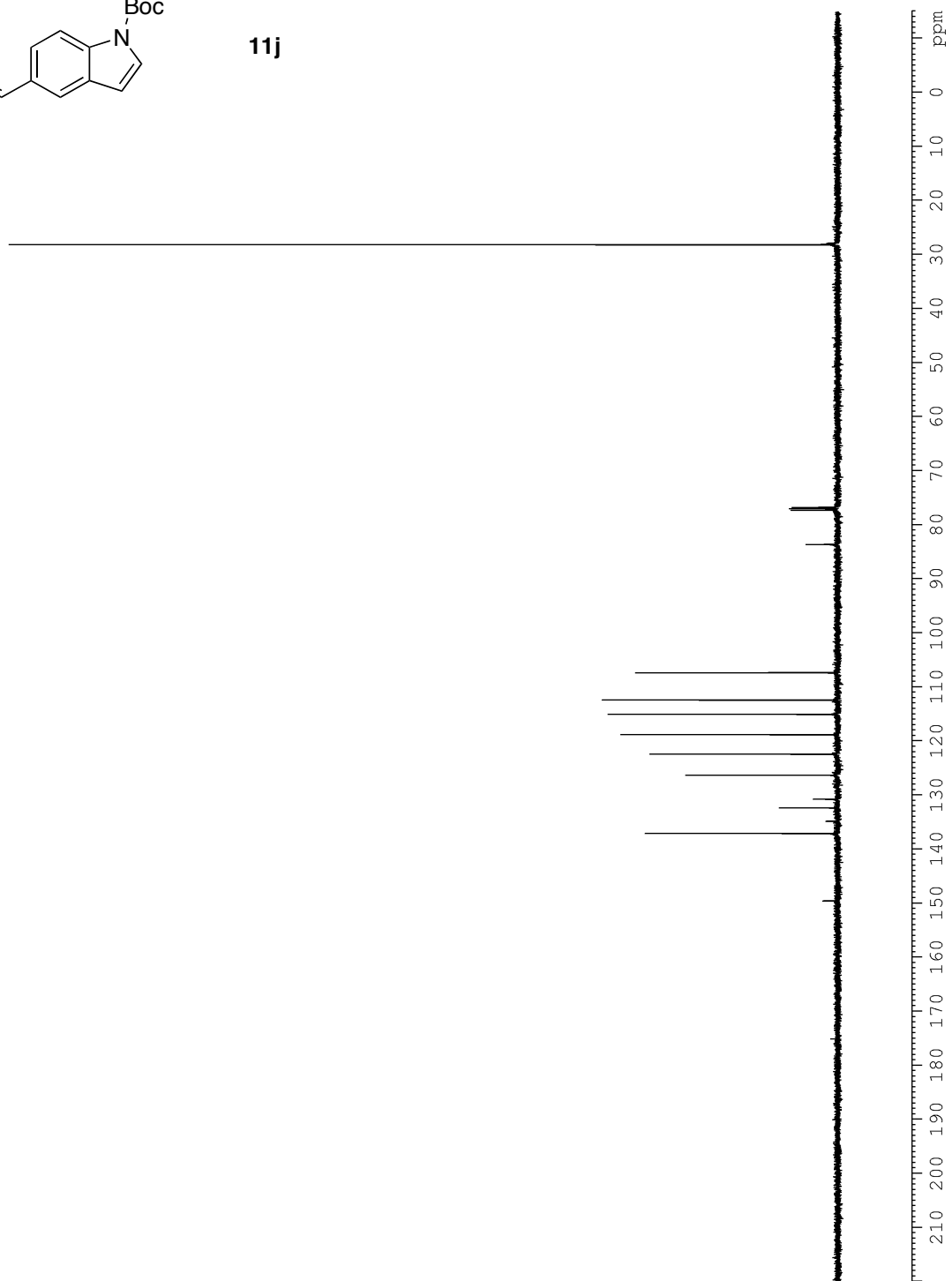
**11j**



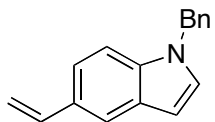
<sup>1</sup>H NMR Spectrum of *tert*-butyl 5-vinyl-1*H*-indole-1-carboxylate **11j**



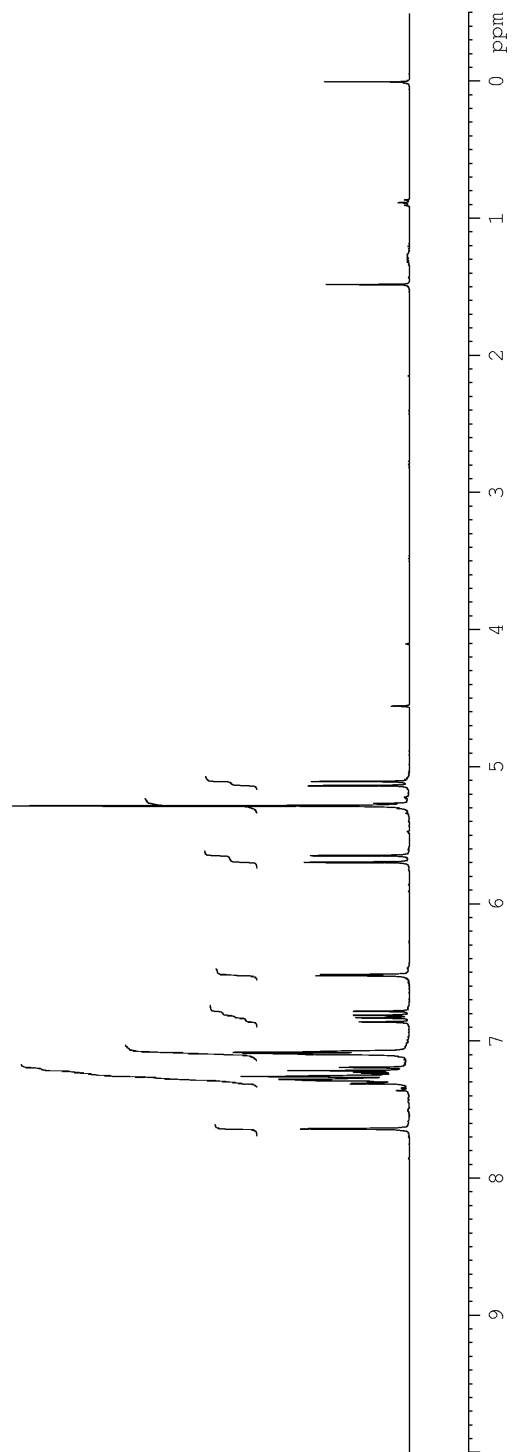
11j



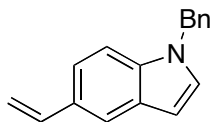
<sup>13</sup>C NMR Spectrum of *tert*-butyl 5-vinyl-1*H*-indole-1-carboxylate **11j**



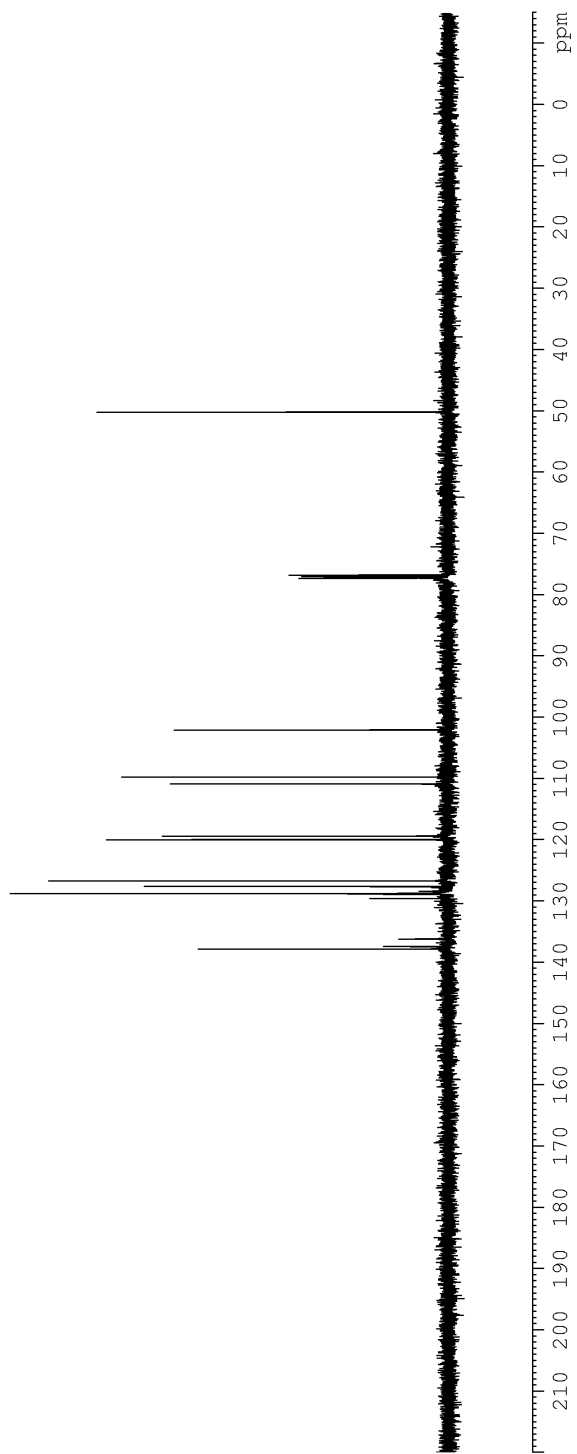
**11k**



<sup>1</sup>H NMR Spectrum of 1-benzyl-5-vinyl-1*H*-indole **11k**



**11k**



<sup>13</sup>C NMR Spectrum of 1-benzyl-5-vinyl-1*H*-indole **11k**