

Amination of Allylic *Alcohols* in Water at Room Temperature

Takashi Nishikata and Bruce H. Lipshutz*
Department of Chemistry & Biochemistry
University of California
Santa Barbara, CA 93106

Supporting Information

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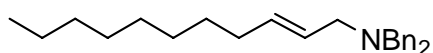
General Information

PTS (Polyoxyethanyl- α -tocopheryl sebacate) was obtained from Zymes, LLC (PTS is also obtained from Sigma-Aldrich, catalog #698717), [Pd(allyl)Cl]₂, Biphep (2,2'-bis(diphenylphosphino)-1,1'-biphenyl) and Dppf (1,1'-bis(diphenylphosphino)ferrocene) from STREM. These and all commercially available chemicals were used as supplied. For TLC analyses precoated Kieselgel 60 F₂₅₄ plates (Merck, 0.25 mm thick) were used; for column chromatography Silica *Flash*® P60 (SiliCycle, 40-63 μ m) was used. Reactions were monitored using a Hewlett-Packard HP6890 gas chromatograph. ¹H and ¹³C NMR spectra were obtained using a Varian UNITY INOVA 400 MHz NMR spectrometer. High resolution mass analyses were obtained using a VG70 double-focusing magnetic sector instrument (VG Analytical) for EI and a PE Sciex QStar Pulsar quadrupole/TOF instrument (API) for ESI.

General procedure

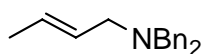
Allylic alcohol **1** (0.75 mmol), amine **2** (0.5 mmol), dppf (0.025 mmol), base (1.5 mmol) and [Pd(allyl)Cl]₂ (0.0125 mmol) were sequentially added under argon to a reaction tube equipped with a stir bar and a septum. PTS solution (1.0 mL, 2 wt %), and HCO₂Me (2.0 mmol) were added by syringe and vigorously stirred for 20 h. After the reaction, the contents of the flask were diluted with brine and extracted with EtOAc. The solution obtained was dried over anhydrous MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography eluting with hexane/EtOAc to afford the product.

Compounds **3a**,^[1] **3b**,^[2] **3c**,^[3] **3d**,^[4] and **3g**,^[5] are known.



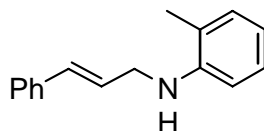
(*E*)-*N,N*-Dibenzyl-2-undecenylamine (**3e**).

Following the general procedure, using **1d** (256 mg, 1.5 mmol), **2a** (99 mg, 0.5 mmol), [Pd(allyl)Cl]₂ (4.5 mg, 0.0125 mmol), Biphep (13 mg, 0.025 mmol), K₂CO₃ (207 mg, 1.5 mmol), 2 wt % PTS solution (1.0 mL) and HCO₂Me (0.12 mL, 2 mmol), yielded the allylic amine **3e** (148 mg, 84%), ¹H NMR (CDCl₃) δ : 0.88 (t, 6.9 Hz, 3H), 0.12-0.13 (m, 12H), 2.03 (dd, J = 6.5 and 13.5 Hz, 2H), 3.01 (d, J = 6.2 Hz, 2H), 3.57 (s, 4H), 5.52 (dt, J = 6.2 and 15.3 Hz, 1H), 5.59 (dt, J = 6.5 and 15.3 Hz, 1H), 7.23 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.4 Hz, 4H), 7.37 (d, J = 7.2 Hz, 4H). ¹³C NMR (CDCl₃) δ : 14.34, 22.89, 29.39, 29.51, 29.59, 29.67, 32.09, 32.67, 55.72, 57.79, 126.8, 127.2, 128.3, 128.9, 134.4, 140.0; HREIMS calcd for C₂₅H₃₅N(M⁺): 349.2769; found 349.2761.



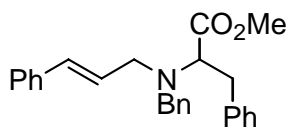
(*E*)-*N,N*-Dibenzyl-2-butenylamine (**3f**).

Following the general procedure, using **1e** (108 mg, 1.5 mmol), **2a** (99 mg, 0.5 mmol), [Pd(allyl)Cl]₂ (4.5 mg, 0.0125 mmol), Biphep (13 mg, 0.025 mmol), K₂CO₃ (207 mg, 1.5 mmol), 2 wt % PTS solution (1.0 mL) and HCO₂Me (0.12 mL, 2 mmol), yielded the allylic amine **3f** (101 mg, 81%), ¹H NMR (CDCl₃) δ: 1.70 (dd, *J* = 1.0 and 6.1 Hz, 3H), 3.00 (d, *J* = 5.9 Hz, 2H), 3.57 (s, 4H), 5.56 (dtq, *J* = 1.3, 6.1 and 18.3 Hz, 1H), 5.61 (qt, *J* = 6.0 and 18.3 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 4H), 7.37 (d, *J* = 7.4 Hz, 4H). ¹³C NMR (CDCl₃) δ: 18.08, 55.63, 57.7, 126.8, 128.2, 128.5, 128.9, 140.0; HREIMS calcd for C₁₈H₂₁N(M⁺): 251.1674; found 251.1602.



(*E*)-*N*-(3-phenyl-2-propenyl)-2-methylaniline (**3h**).

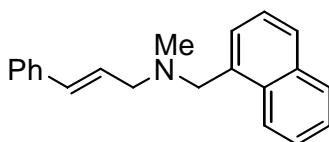
Following the general procedure, using **1a** (100 mg, 0.75 mmol), **2c** (53 mg, 0.5 mmol), [Pd(allyl)Cl]₂ (4.5 mg, 0.0125 mmol), Dppf (14 mg, 0.025 mmol), K₂CO₃ (207 mg, 1.5 mmol), 2 wt % PTS solution (1.0 mL) and HCO₂Me (0.12 mL, 2 mmol), yielded the allylic amine **3h** (89 mg, 80%), ¹H NMR (CDCl₃) δ: 2.22 (s, 3H), 3.73 (brs, 1H), 4.02 (dd, *J* = 1.5 and 6.3 Hz, 2H), 6.42 (dt, *J* = 5.8 and 15.9 Hz, 1H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.73 (t, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.3 Hz, 2H). ¹³C NMR (CDCl₃) δ: 17.51, 46.14, 109.9, 117.1, 122.0, 126.2, 127.0, 127.1, 127.5, 128.5, 130.0, 131.5, 136.7, 145.8; HREIMS calcd for C₁₆H₁₇N(M⁺): 223.1361; found 223.1359.



(*E*)-*N*-Benzyl-*N*-(3-phenyl-2-propenyl)phenylalanine methyl ester (**3i**).

Following the general procedure, using **1h** (67 mg, 0.5 mmol), **2d** (160 mg, 0.6 mmol), [Pd(allyl)Cl]₂ (4.5 mg, 0.0125 mmol), Biphep (13 mg, 0.025 mmol), K₂CO₃ (207 mg, 1.5 mmol), 2 wt % PTS solution (1.0 mL) and HCO₂Me (0.12 mL, 2 mmol), yielded the allylic amine **3i** (154 mg, 80%), ¹H NMR (CDCl₃) δ: 2.97 (dd, *J* = 8.3 and 13.8 Hz, 1H), 3.11 (dd, *J* = 7.0, and 13.8 Hz, 1H), 3.25 (dd, *J* = 7.8, and 10.6 Hz, 1H), 3.50 (dd, *J* = 5.0, and 14.6 Hz,

1H), 3.60 (d, $J = 14.3$ Hz, 1H), 3.70 (s, 3H), 3.76 (t, $J = 8.2$ Hz, 1H), 4.02 (d, $J = 14.3$ Hz, 1H), 6.02 (ddd, $J = 5.0, 7.7$ and 15.9 Hz, 1H), 6.46 (d, $J = 15.9$ Hz, 1H), 7.11-7.29 (m, 15H). ^{13}C NMR (CDCl_3) δ : 35.8, 51.1, 52.7, 54.3, 63.2, 126.1, 126.7, 127.2, 127.7, 128.08, 128.09, 128.3, 128.4, 129.3, 132.1, 136.9, 138.3, 139.3, 172.9 ; HRESIMS calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_2(\text{MH}^+)$: 386.2120; found 386.2106.



Naftifine (**3j**).

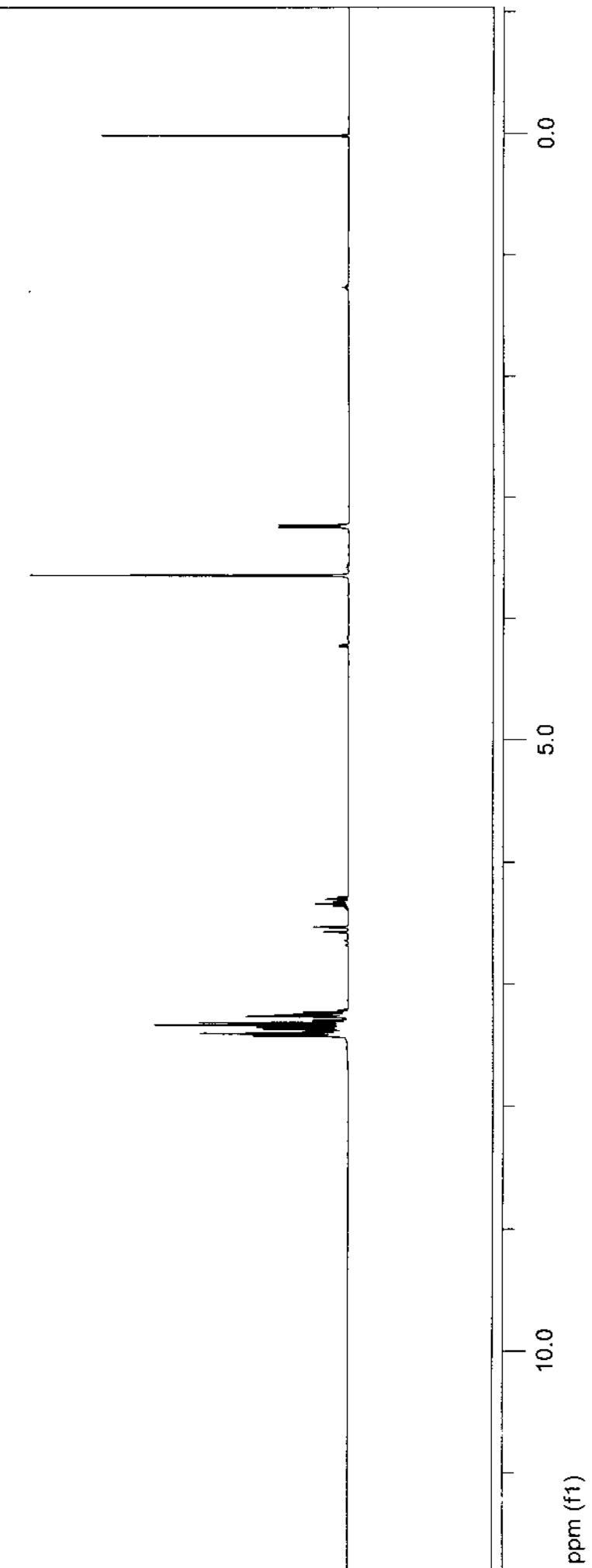
Following the general procedure, using **1h** (67 mg, 0.5 mmol), **2e** (128 mg, 0.75 mmol), $[\text{Pd}(\text{allyl})\text{Cl}]_2$ (4.5 mg, 0.0125 mmol), Biphep (13 mg, 0.025 mmol), K_2CO_3 (207 mg, 1.5 mmol), 2 wt % PTS solution (1.0 mL) and HCO_2Me (0.12 mL, 2 mmol), yielded the allylic amine **3j** (118 mg, 83%), ^1H NMR (CDCl_3) δ : 2.29 (s, 3H), 3.29 (d, $J = 6.4$ Hz, 2H), 3.96 (s, 2H), 6.38 (dt, $J = 6.4, 16.0$ Hz, 1H), 6.60 (d, $J = 16.0$ Hz, 1H), 7.23-7.57 (m, 9H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 8.31 (d, $J = 7.2$ Hz, 1H). ^{13}C NMR (CDCl_3) δ : 42.4, 60.0, 60.32, 124.5, 125.0, 125.5, 125.8, 126.2, 127.30, 127.37, 127.5, 127.8, 128.3, 128.4, 132.4, 132.5, 133.8, 134.8, 137.0; HREIMS calcd for $\text{C}_{21}\text{H}_{21}\text{N}(\text{M}^+)$: 287.1670; found 287.1684.

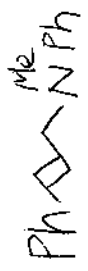
References

- (1) Miyabe, H.; Matsumura, A.; Moriyama, K.; Takemoto, Y. *Org. Lett.* **2004**, *6*, 4631.
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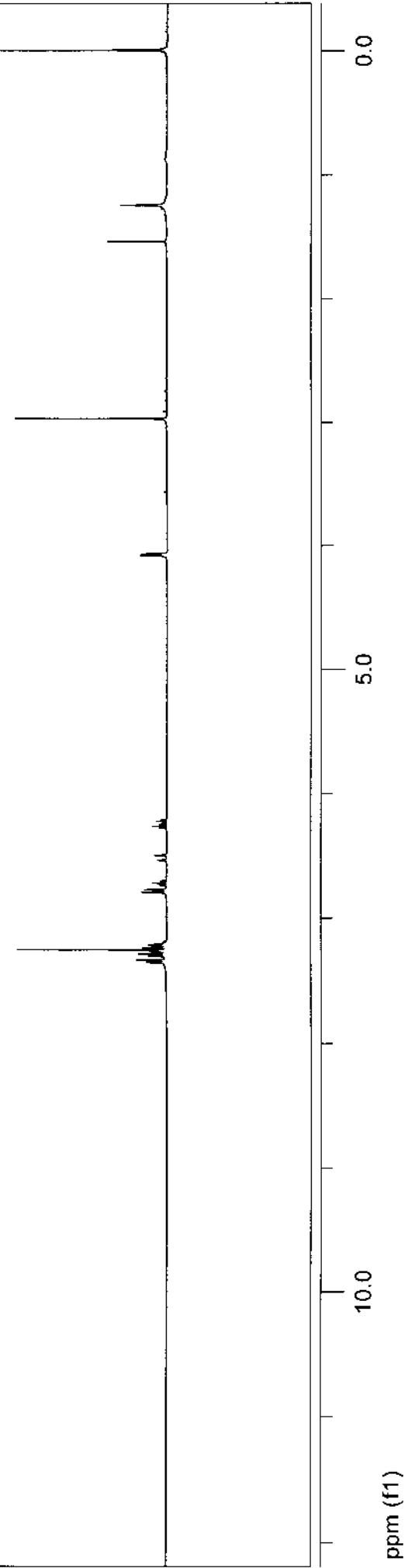


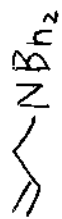
3a



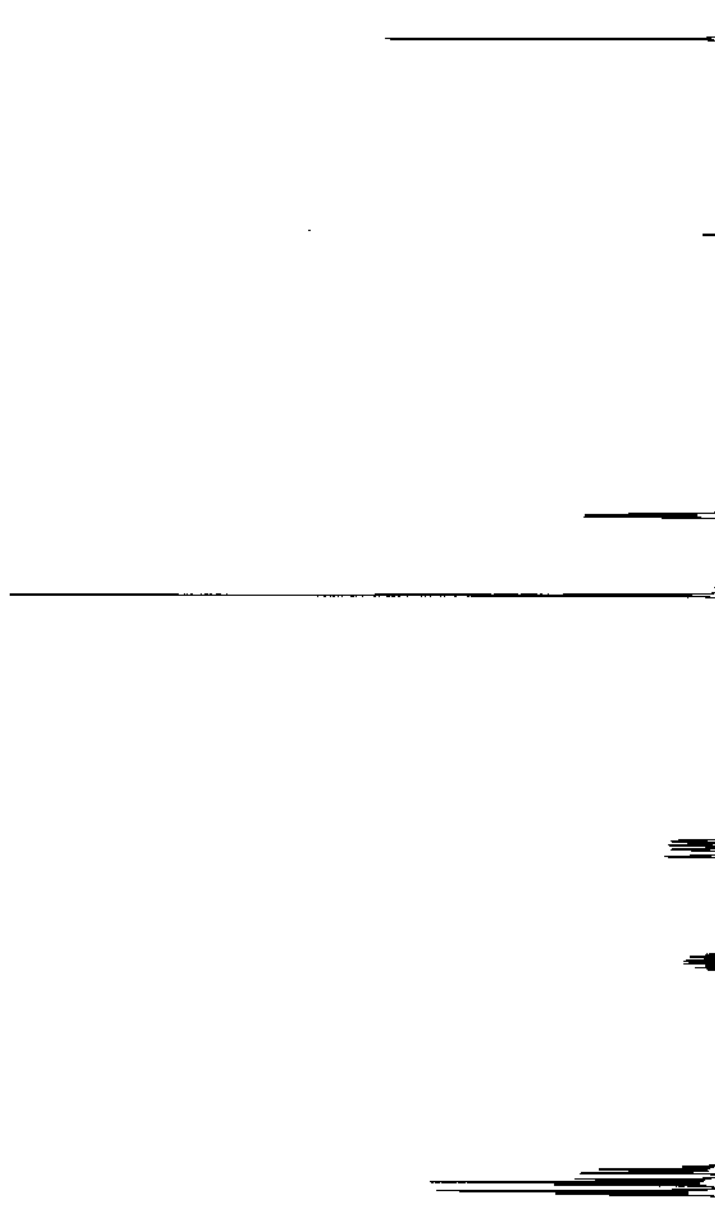


3b





3c

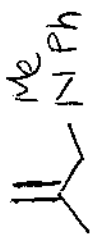


0.0

5.0

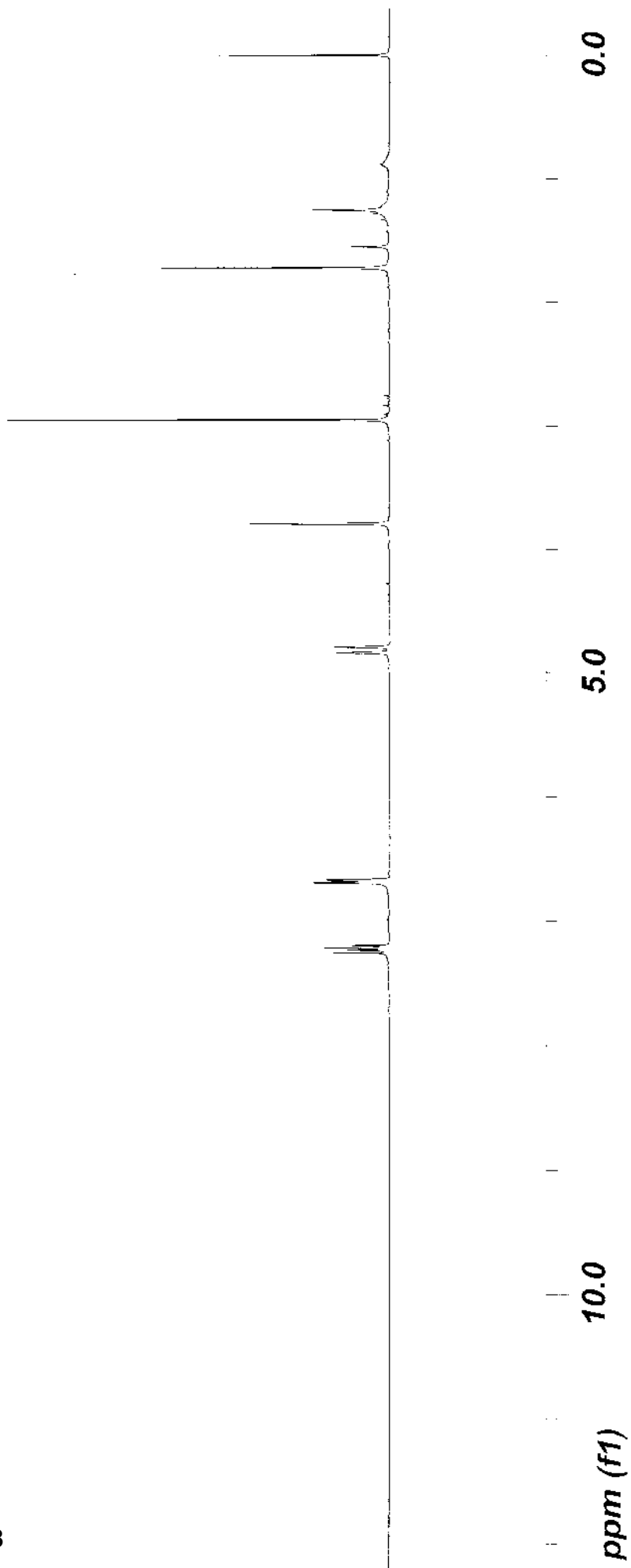
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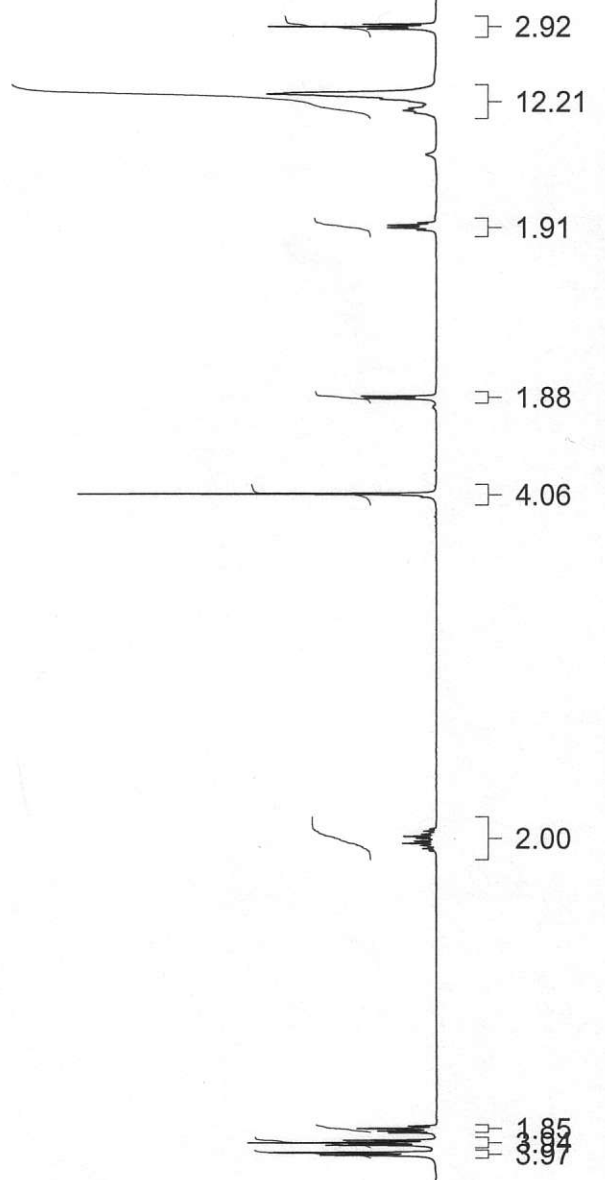
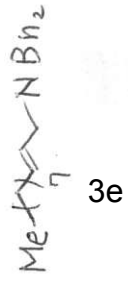
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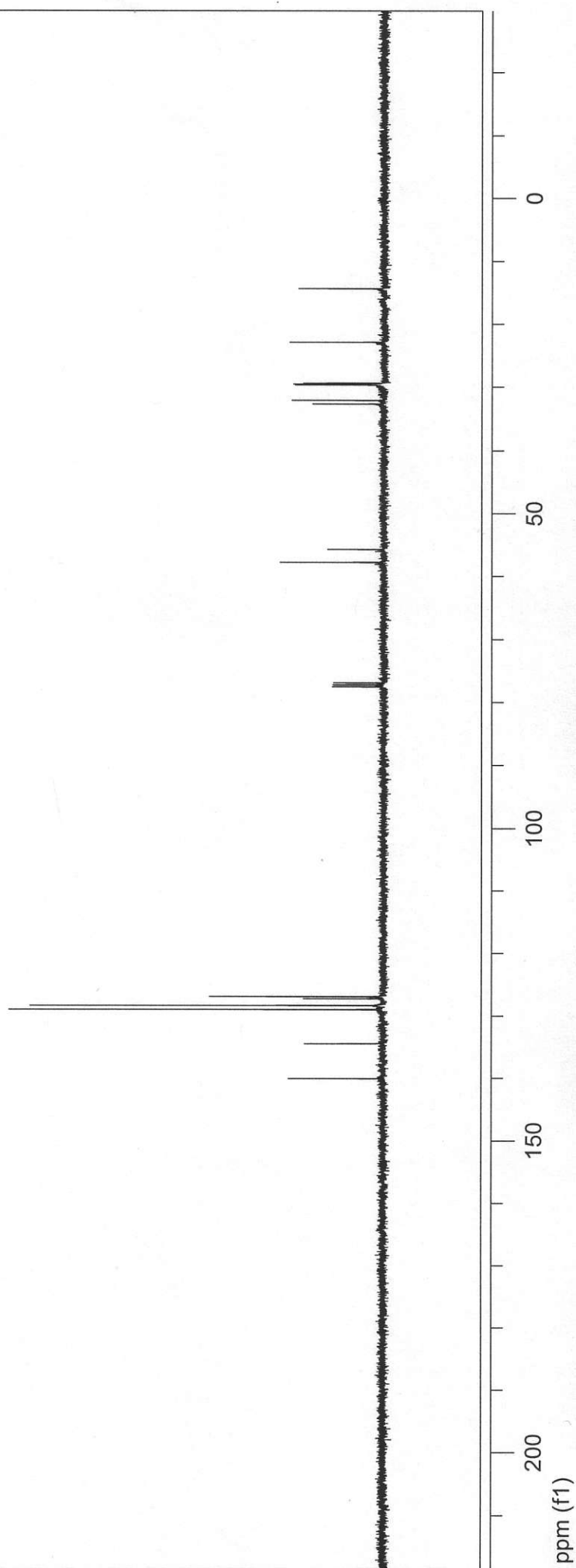
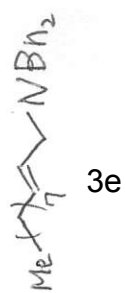


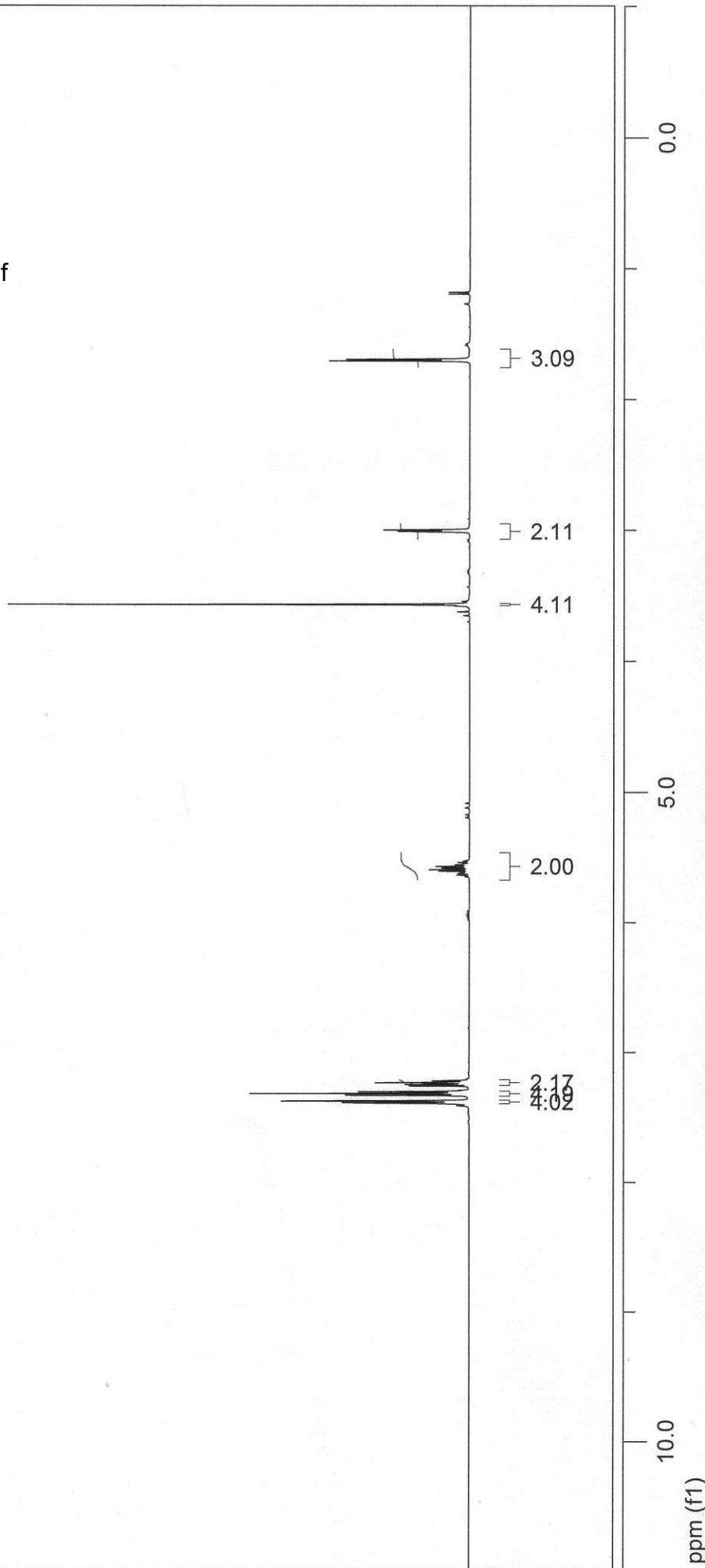
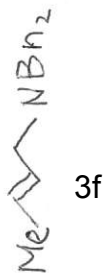
3d

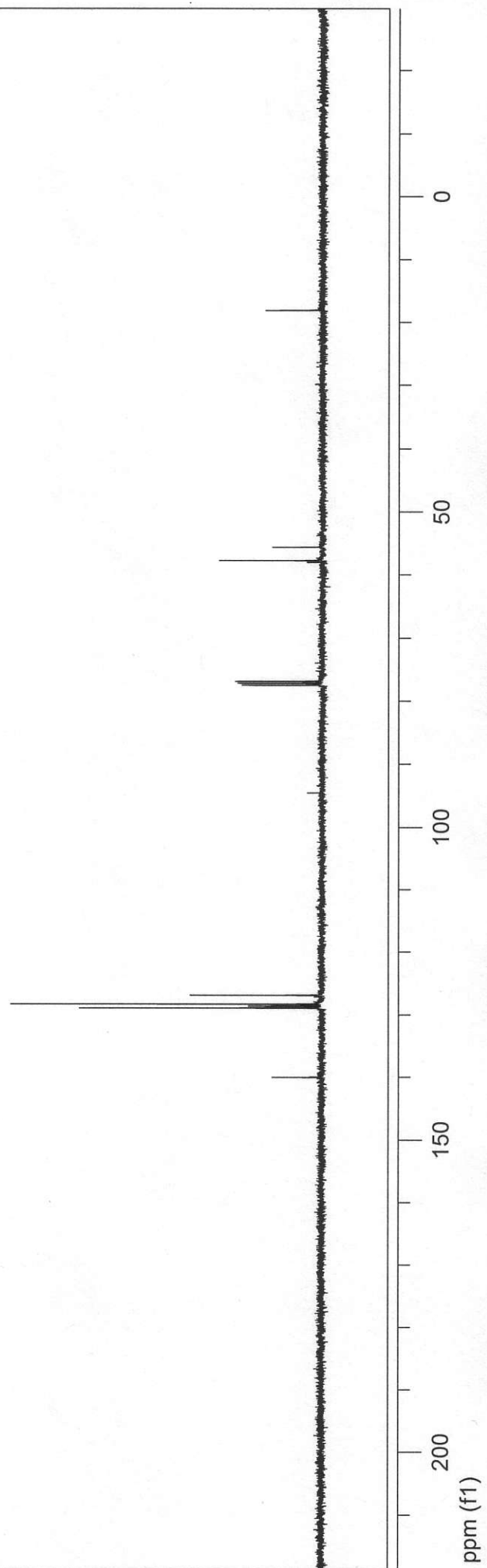
S8







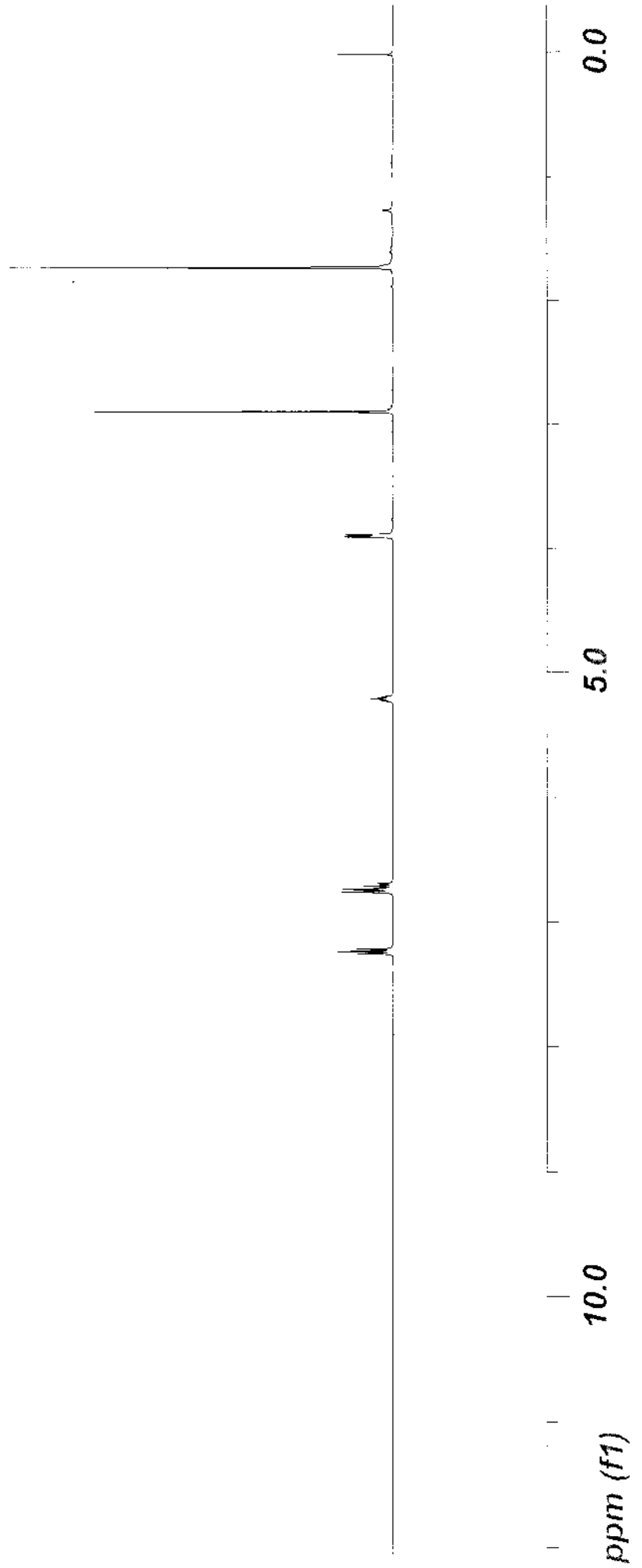






3g

S13





3.24

0.97

2.23

0.97

3.00

2.01

1.02

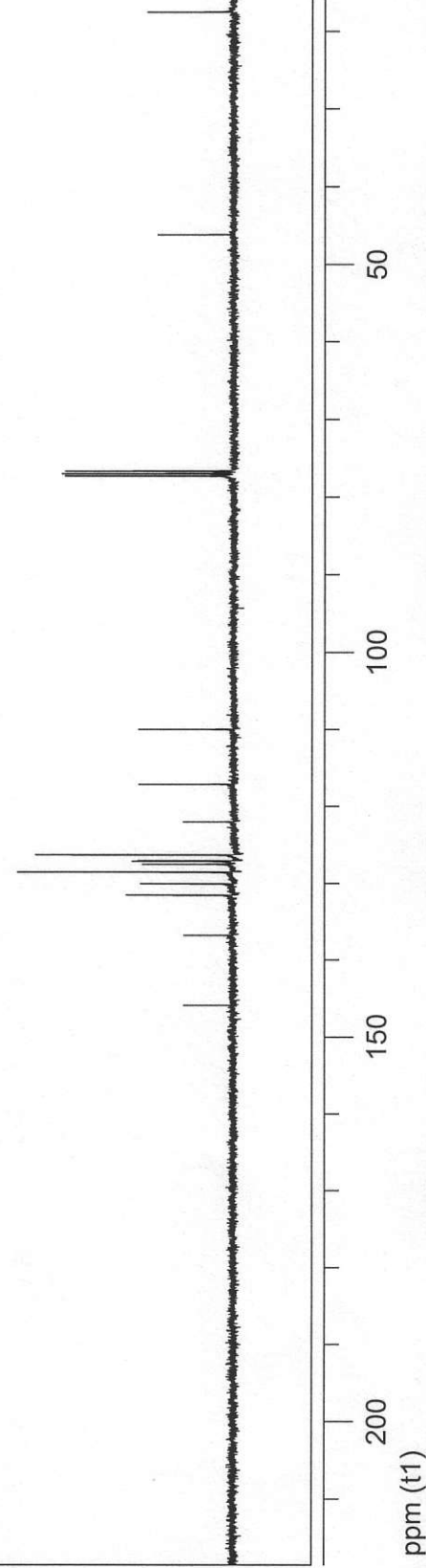
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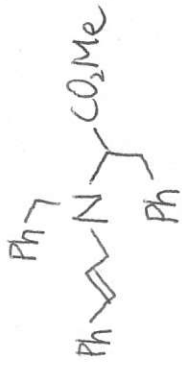
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5.0

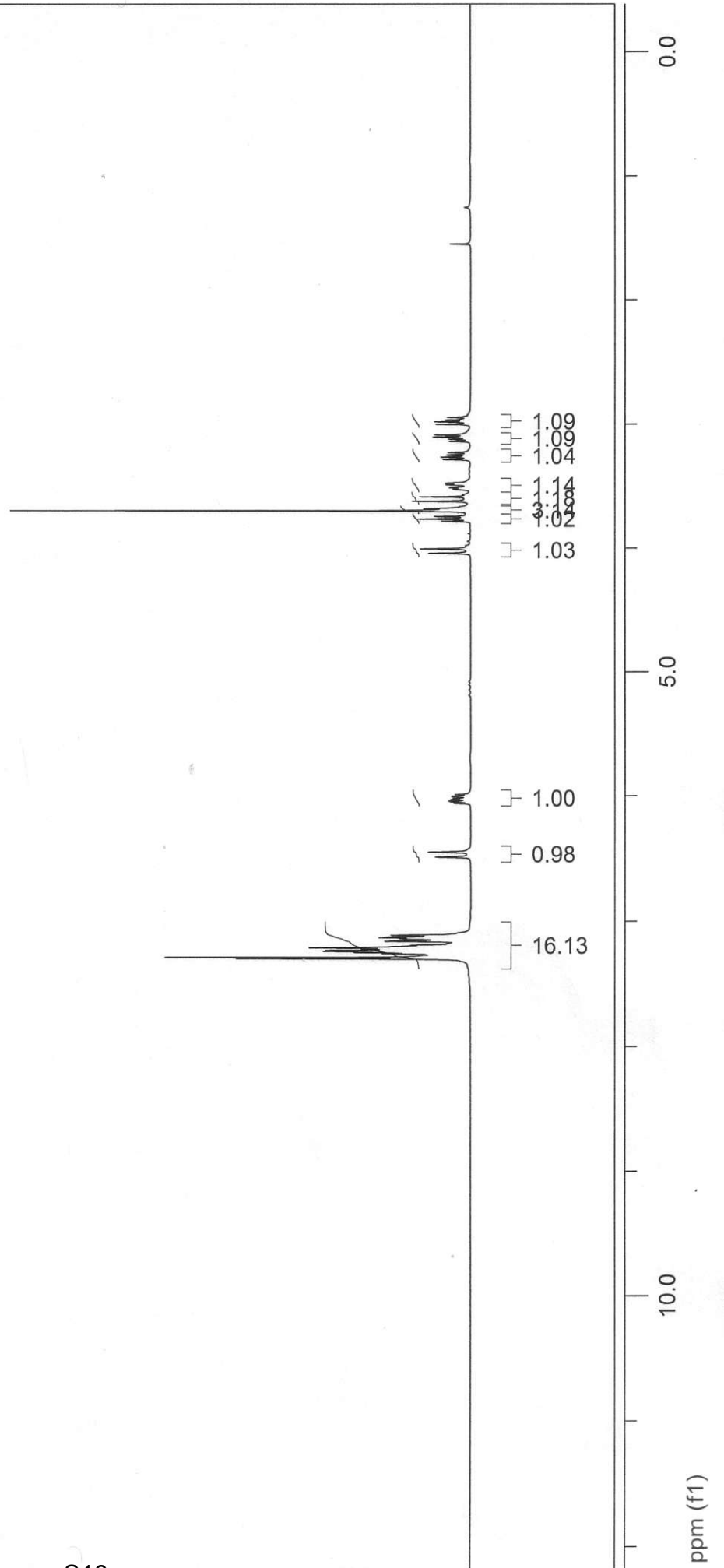
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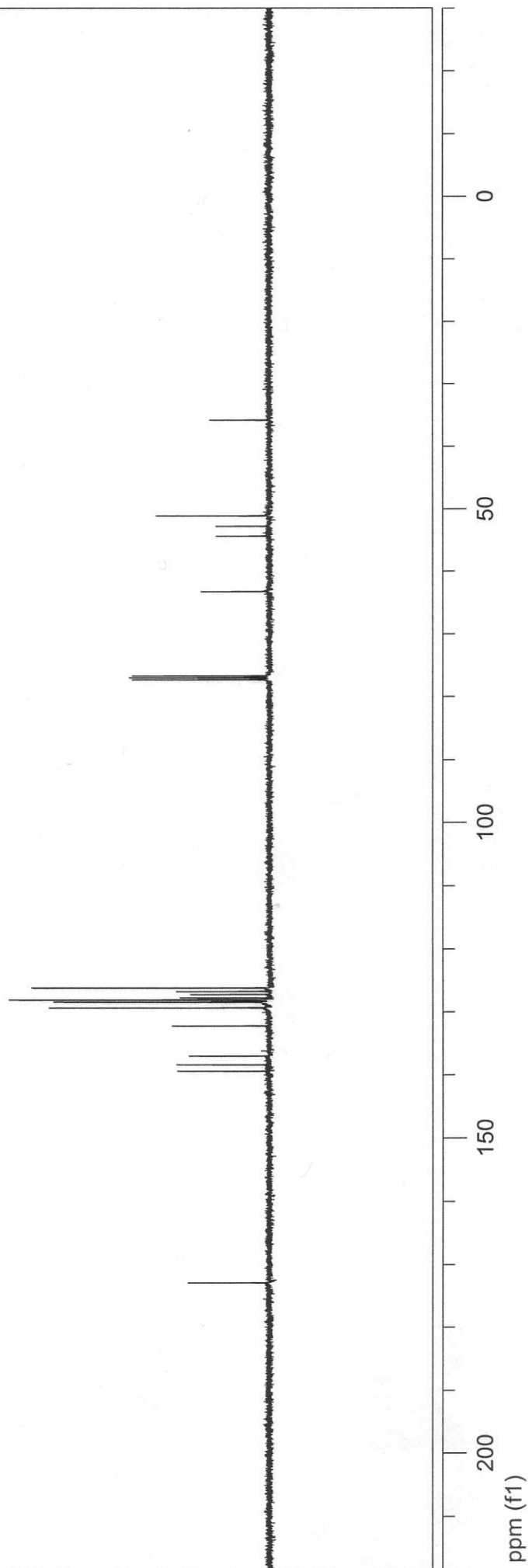
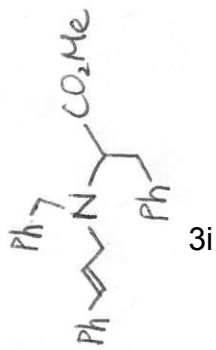
ppm (t1)





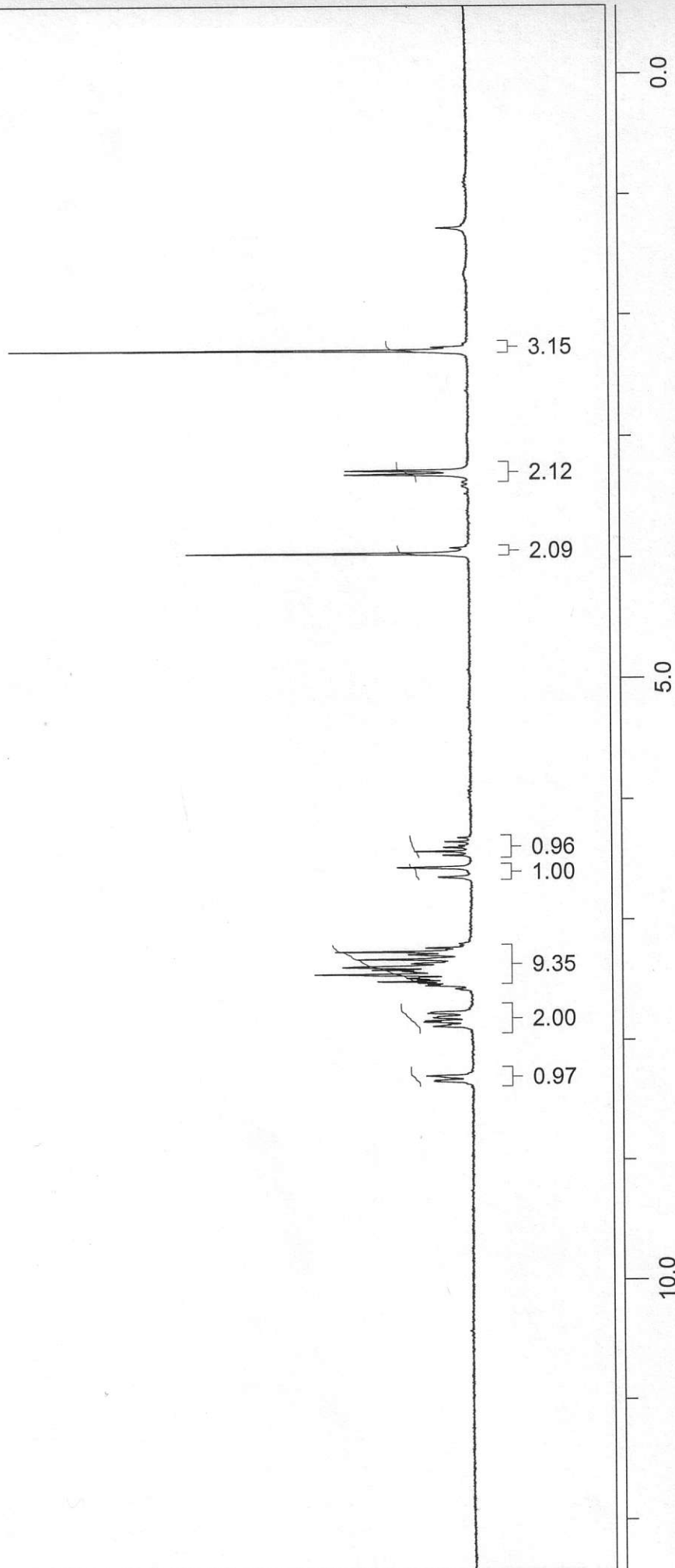
3i







3j





3j

