

Chemoselective vinylation of aminophenols with acetylene catalyzed by sodium aminophenolates in aqueous DMSO

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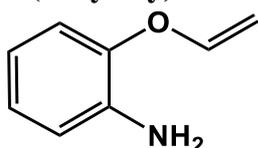
General. The ¹H (400.13 MHz) and ¹³C (100.62 MHz) NMR spectra were recorded with a Bruker DPX-400 and Bruker AV-400 spectrometers in CDCl₃ at ambient temperature. Chemical shifts (δ) are quoted in ppm, to the nearest 0.01 ppm (for ¹H) and 0.1 ppm (for ¹³C), and are referenced to CDCl₃ (7.26 ppm for ¹H) and (77.00 ppm for ¹³C) as an internal standards. Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.1 Hz. The IR spectra were recorded on a Bruker Vertex-70 as thin films. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer. The high-pressure experiments were carried out in a stainless steel, high-pressure batch reactor (Parr 4572, Parr Instrument Co.) equipped with an electrical heating jacket, a gas inlet, a mechanical stirrer and 4848A temperature controller.

Commercially available starting materials were used without further purification.

General Procedure for the Synthesis of Vinyloxyanilines **2.**

A 300 ml pressure reactor equipped with a magnetic stirrer (250 rpm) was charged with sodium phenolate solution in aq. DMSO prepared by stirring a mixture of aminophenol **1** (50 mmol) and NaOH (1.00 g, 25 mmol) in DMSO (40 ml) and H₂O (10 ml) at r.t. for 0.5 h. The reactor was fed with acetylene and then decompressed to atmospheric pressure to remove air. The reactor was fed with acetylene again (initial pressure 14-16 atm) and heated under 90 °C for 3 h. After cooling to r.t. the reaction mixture was poured into ice water (100 ml) and extracted with diethyl ether (5×50 mL). The organic layers were combined, washed with H₂O (3×50 ml) and dried over MgSO₄. After evaporating the diethyl ether, the residue was distilled in vacuum to give vinyl ether **2**.

2-(Vinyloxy)aniline (2a).



Colorless liquid, bp 78 °C/3 Torr, n_D^{20} 1.5692 [Lit.^{S1} bp 66-68 °C/1-2 Torr, n_D^{20} 1.5715]. Yield: 5.24 g, 77%.

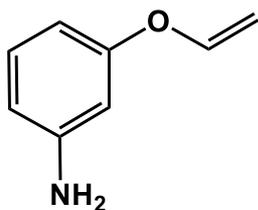
¹H NMR (CDCl₃): δ = 6.96-6.90 and 6.78-6.71 (m, 4 H, H-3,4,5,6, Ar), 6.62 (dd, J = 13.8, 6.1 Hz, 1 H, =CHO), 4.70 (d, J = 13.8 Hz, 1 H, =CH_{trans}), 4.40 (d, J = 6.1 Hz, 1 H, =CH_{cis}), 3.73 (br s, 2 H, NH₂).

¹³C NMR (CDCl₃): δ = 148.8 (=CHO), 143.5 (C-1, Ar), 137.3 (C-2, Ar), 124.2 (C-5, Ar), 118.4 (C-4, Ar), 117.4 (C-3, Ar), 115.9 (C-6, Ar), 93.7 (=CH₂).

IR (film, ν/cm^{-1}): 3466, 3377, 3205, 3115, 3064, 3037, 2959, 2931, 2870, 1638, 1620, 1592, 1503, 1460, 1386, 1304, 1272, 1213, 1152, 1060, 1033, 958, 921, 847, 745, 699, 605, 494, 454.

Calculated for C₈H₉NO (136.163): C, 71.09; H, 6.71; N, 10.36. Found: C, 70.99; H, 6.82; N, 10.45.

3-(Vinyloxy)aniline (2b).



Colorless liquid, bp 101-103 °C /3 Torr, n_D^{20} 1.5773 [Lit.^{S1} bp 92-93 °C/2 Torr, n_D^{20} 1.5820]. Yield: 4.70 g, 69%.

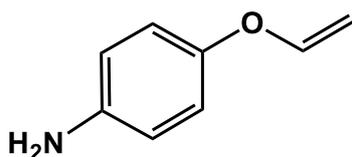
¹H NMR (CDCl₃): δ = 7.09 (t, J = 8.0 Hz, 1 H, H-5, Ar), 6.63 (dd, ³ J = 13.7, 6.1 Hz, 1 H, =CHO), 6.42-6.40 and 6.34-6.33 (m, 3 H, H-2,4,6 Ar), 4.77 (d, J = 13.7 Hz, 1 H, =CH_{trans}), 4.41 (d, J = 6.1 Hz, 1 H, =CH_{cis}), 3.68 (br s, 2 H, NH₂).

¹³C NMR (CDCl₃): δ = 157.9 (C-1, Ar), 148.0 (=CHO), 147.8 (C-3, Ar), 130.2 (C-5, Ar), 110.9 (C-6, Ar), 106.8 (C-4, Ar), 103.8 (C-2, Ar), 94.8 (=CH₂).

IR (film, ν/cm^{-1}): 3458, 3376, 3220, 3056, 3034, 2981, 1604, 1492, 1467, 1388, 1320, 1288, 1189, 1160, 1070, 993, 952, 917, 846, 772, 687, 615, 584, 524, 455.

Calculated for C₈H₉NO (136.163): C, 71.09; H, 6.71; N, 10.36. Found: C, 71.21; H, 6.92; N, 10.51.

4-(Vinylloxy)aniline (2c).



Colorless liquid, bp = 95 °C/3 Torr, n_D^{20} 1.5748 [Lit.^{S1} bp 118 °C/10 Torr, n_D^{20} 1.5765]. Yield: 5.78 g, 85%.

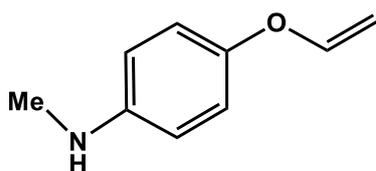
¹H NMR (CDCl₃): δ = 6.84 (d, J = 8.7 Hz, 2 H, H-3,5, Ar), 6.64 (d, J = 8.6 Hz, 2 H, H-2,6, Ar), 6.58 (dd, J = 13.8, 6.2 Hz, 1 H, =CHO), 4.61 (dd, J = 13.8, 1.3 Hz, 1 H, CH=), 4.30 (dd, J = 6.2, 1.3 Hz, 1 H, CH=), 3.55 (br s, 2 H, NH₂).

¹³C NMR (CDCl₃): δ = 149.7 (CHO), 149.0 (C-1, Ar), 142.3 (C-4, Ar), 118.6 (C-2,6, Ar), 115.9 (C-3,5, Ar), 92.7 (CH₂).

IR (film, ν/cm^{-1}): 3436, 3362, 3220, 3116, 3042, 3015, 1639, 1507, 1437, 1387, 1308, 1279, 1228, 1168, 1149, 1081, 1011, 959, 832, 728, 692, 564, 511, 434.

Calculated for C₈H₉NO (136.163): C, 71.09; H, 6.71; N, 10.36. Found: C, 71.01; H, 6.79; N, 10.29.

N-Methyl-4-(vinylloxy)aniline (2d).



Colorless liquid, bp = 93 °C/3 Torr, n_D^{20} 1.5673 [Lit.^{S2} bp 104-105 °C/4 Torr, n_D^{20} 1.5685]. Yield: 5.37 g, 72%.

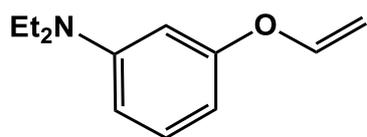
¹H NMR (CDCl₃): δ = 6.90 (d, J = 8.7 Hz, 2 H, H-3,5, Ar), 6.66-6.57 (m, 3 H, H-2,6 Ar, =CHO), 4.61 (dd, J = 13.8, 1.3 Hz, 1 H, =CH_{trans}), 4.30 (dd, J = 6.1, 1.3 Hz, 1 H, =CH_{cis}), 3.51 (br s, 1 H, NH), 2.82 (s, 3 H, Me).

¹³C NMR (CDCl₃): δ = 150.0 (=CHO), 148.2 (C-1, Ar), 145.6 (C-4, Ar), 118.8 (C-2,6, Ar), 113.0 (C-3,5, Ar), 92.4 (=CH₂), 31.0 (Me).

IR (film, ν/cm^{-1}): 3417, 3114, 3055, 3028, 2981, 2930, 2885, 2812, 1639, 1513, 1449, 1389, 1312, 1228, 1173, 1151, 1102, 1060, 1006, 959, 826, 748, 693, 622, 518, 462.

Calculated for C₉H₁₁NO (149.193): C, 72.46; H, 7.43; N, 9.39. Found: C, 72.61; H, 7.32; N, 9.39.

***N,N*-Diethyl-3-(vinylloxy)aniline (2e).**



Colorless liquid, bp = 120 °C/6 Torr, n_D^{20} 1.5478 [Lit.^{S3} bp 100 °C/3 Torr, n_D^{20} 1.5480]. Yield: 5.92 g, 62%.

¹H NMR (CDCl₃): δ = 7.15 (t, J = 8.1 Hz, 1 H, H-5, Ar), 6.68 (dd, J = 13.7, 6.1 Hz, 1 H, =CHO), 6.42 (d, J = 7.2 Hz, 1 H, H-6, Ar), 6.32-6.30 (m, 2 H, H-2,4, Ar), 4.76 (dd, J = 13.7, 1.3 Hz, 1 H, =CH_{trans}), 4.39 (dd, J = 6.1, 1.2 Hz, 1 H, =CH_{cis}), 3.35 (q, J = 7.0 Hz, 4 H, NCH₂), 1.18 (t, J = 7.1 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃): δ = 158.2 (C-1, Ar), 149.1 (C-, Ar), 148.4 (=CHO), 129.9 (C-5, Ar), 106.8 (C-6, Ar), 103.3 (C-4, Ar), 100.7 (C-2, Ar), 94.1 (=CH₂). 44.3 (CH₂), 12.4 (CH₃).

IR (film, ν/cm^{-1}): 3072, 3033, 2971, 2930, 2890, 1635, 1606, 1573, 1500, 1462, 1381, 1355, 1310, 1276, 1209, 1158, 1079, 1026, 993, 951, 853, 787, 756, 869, 449.

Calculated for C₁₂H₁₇NO (191.270): C, 75.35; H, 8.96; N, 7.32. Found: C, 75.41; H, 9.02; N, 7.45.

References

- [S1] M. F. Shostakovskii, G. G. Skvortsova, M. Ya. Samoiloa and Yu. M. Fayershteyn, *Zh. Obshch. Khim.*, 1961, **31**, 3226 (in Russian).
- [S2] G. G. Skvortsova, M. Ya. Samoiloa, Z. M. Kolbina and Z. V. Stepanova, *Zh. Org. Khim.*, 1965, **1**, 111 (in Russian).
- [S3] P. I. Grebneva, G. G. Skvortsova, G. V. Rassolova and D. E. Stepanov, *Izv. SO Akad. Nauk SSSR, Ser. Khim. Nauk*, 1980, **5** (12), 122 (in Russian).

^1H and ^{13}C spectra of the synthesized products

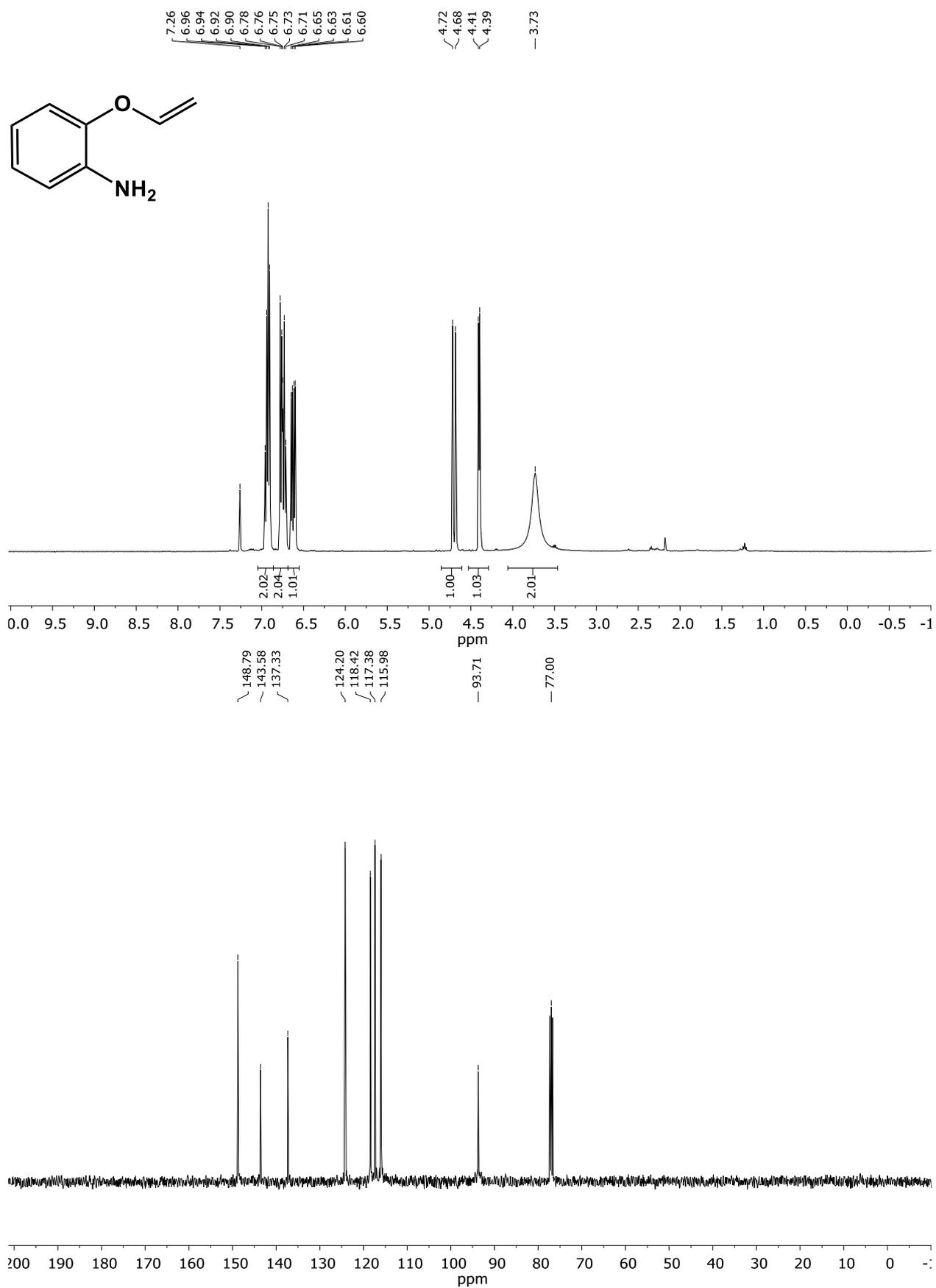


Figure S1. ^1H and ^{13}C NMR spectra for 2-(vinylloxy)aniline (**2a**).

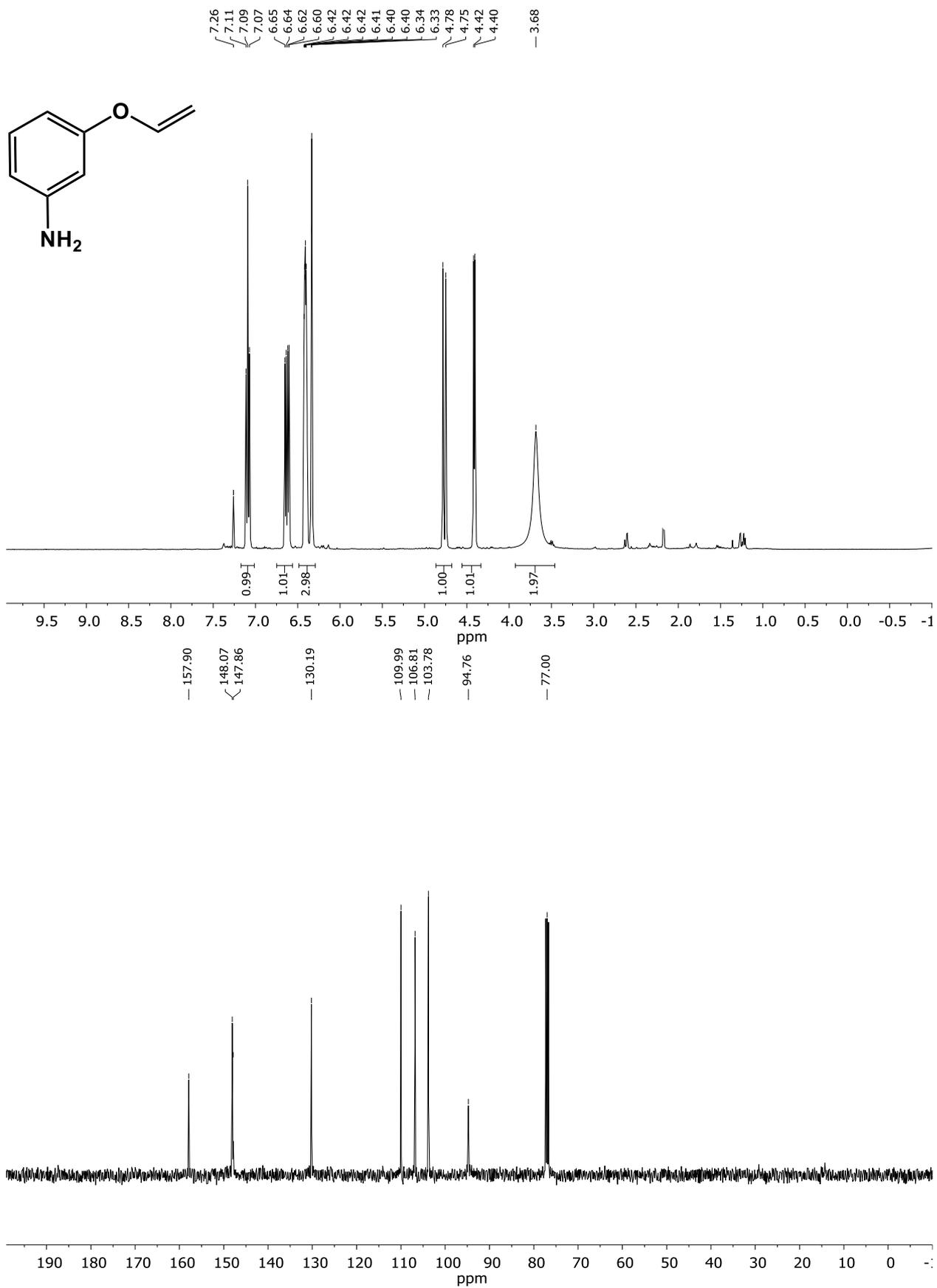


Figure S2. ¹H and ¹³C NMR spectra for 3-(vinylloxy)aniline (**2b**).

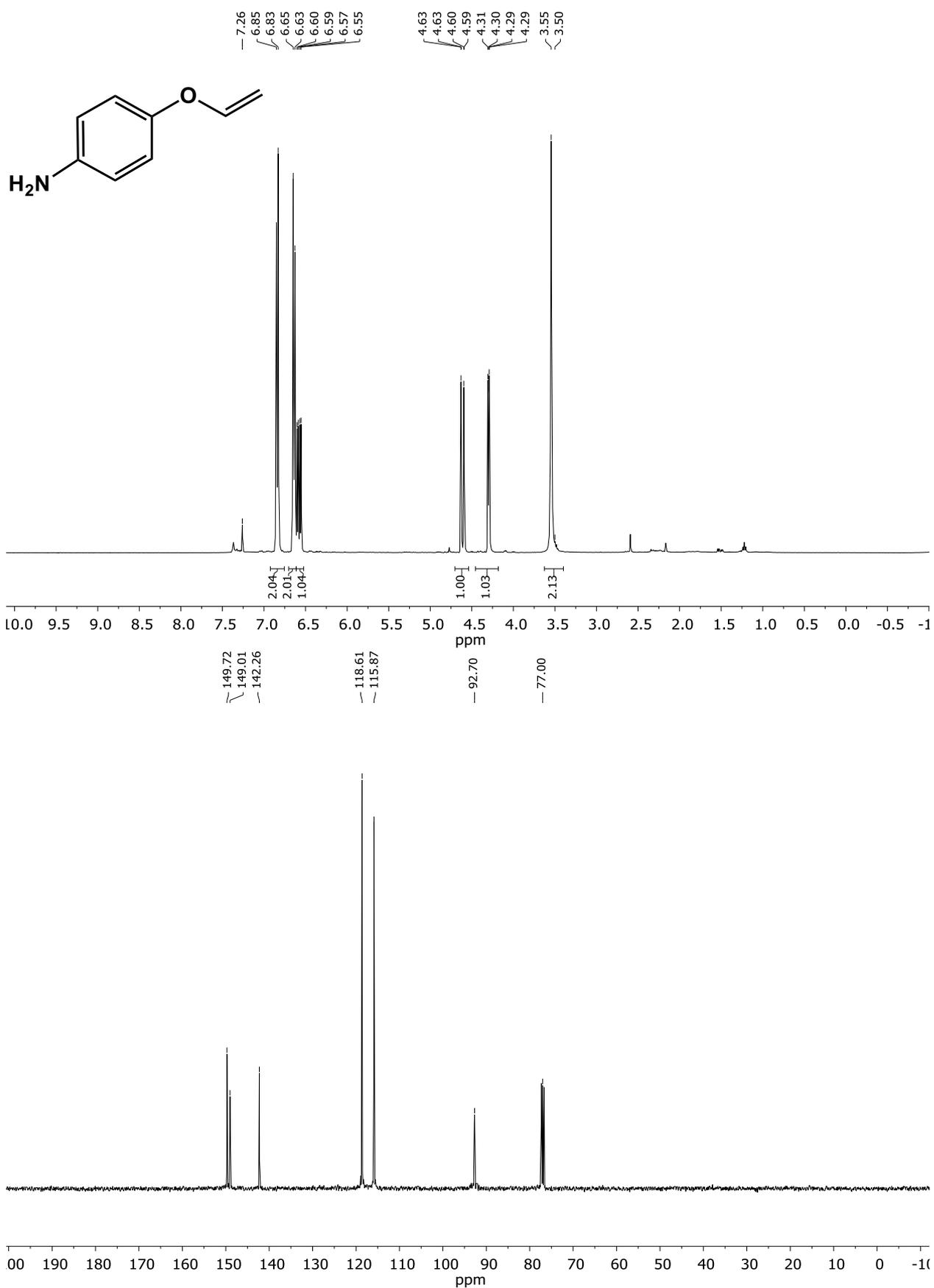


Figure S3. ¹H and ¹³C NMR spectra for 4-(vinylloxy)aniline (**2c**).

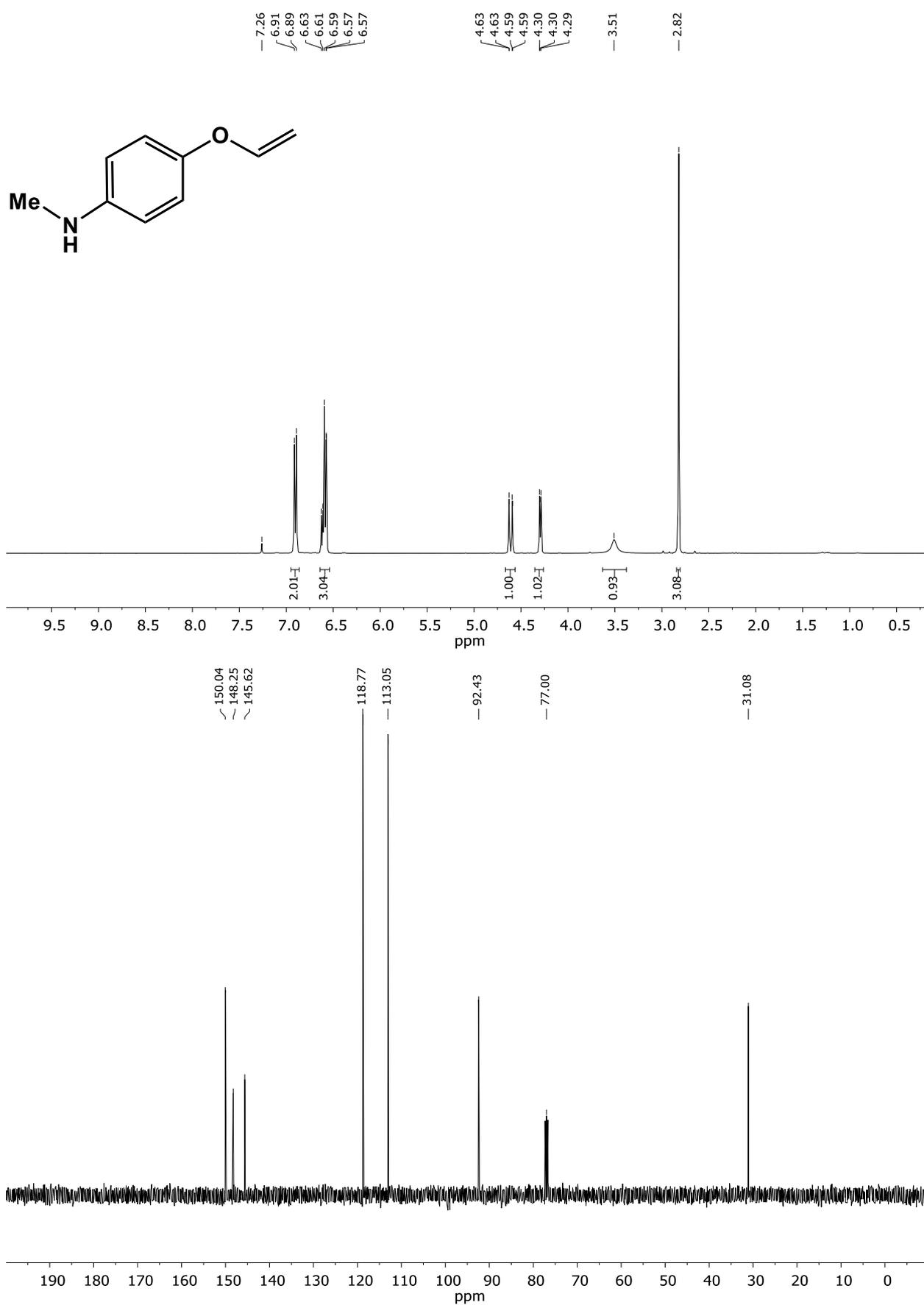


Figure S4. ¹H and ¹³C NMR spectra for *N*-methyl-4-(vinyl-oxy)aniline (**2d**).

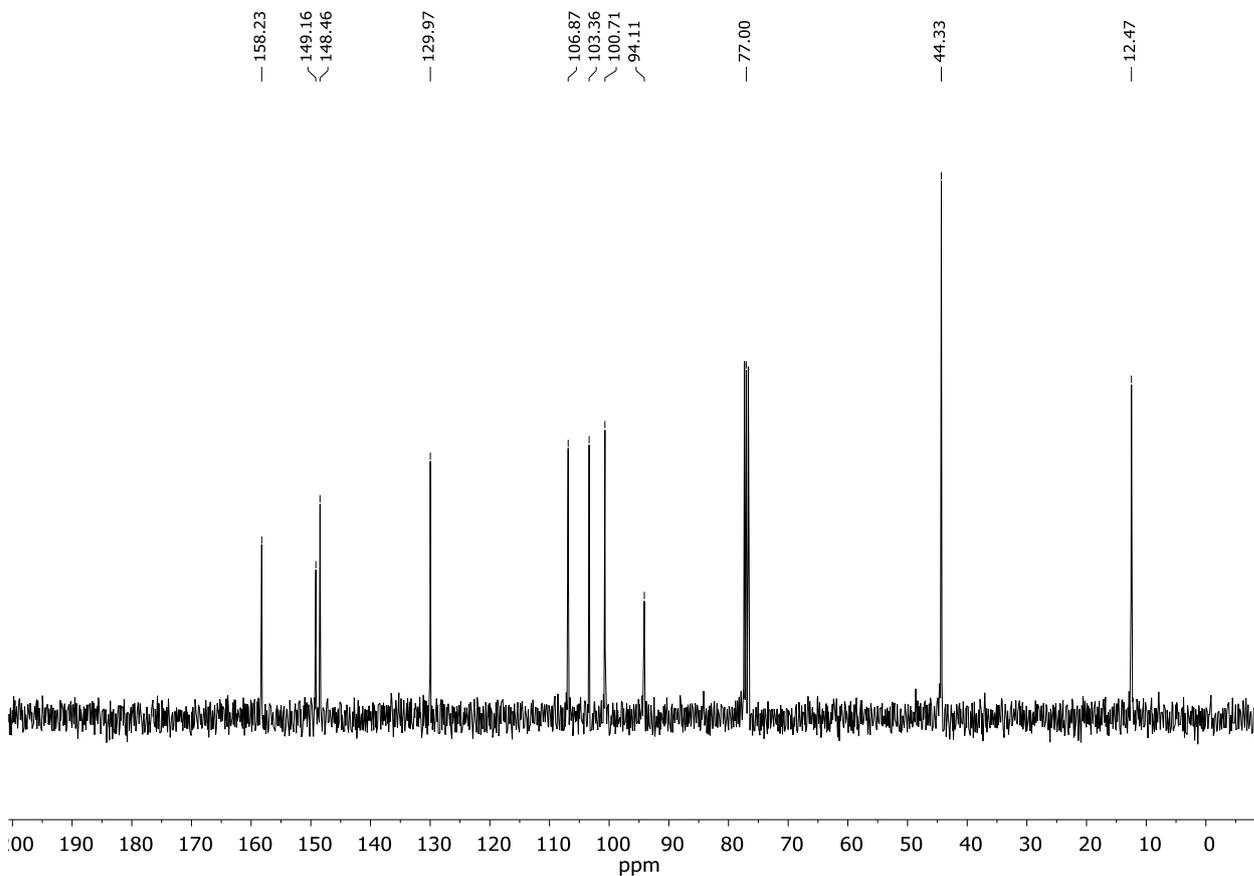
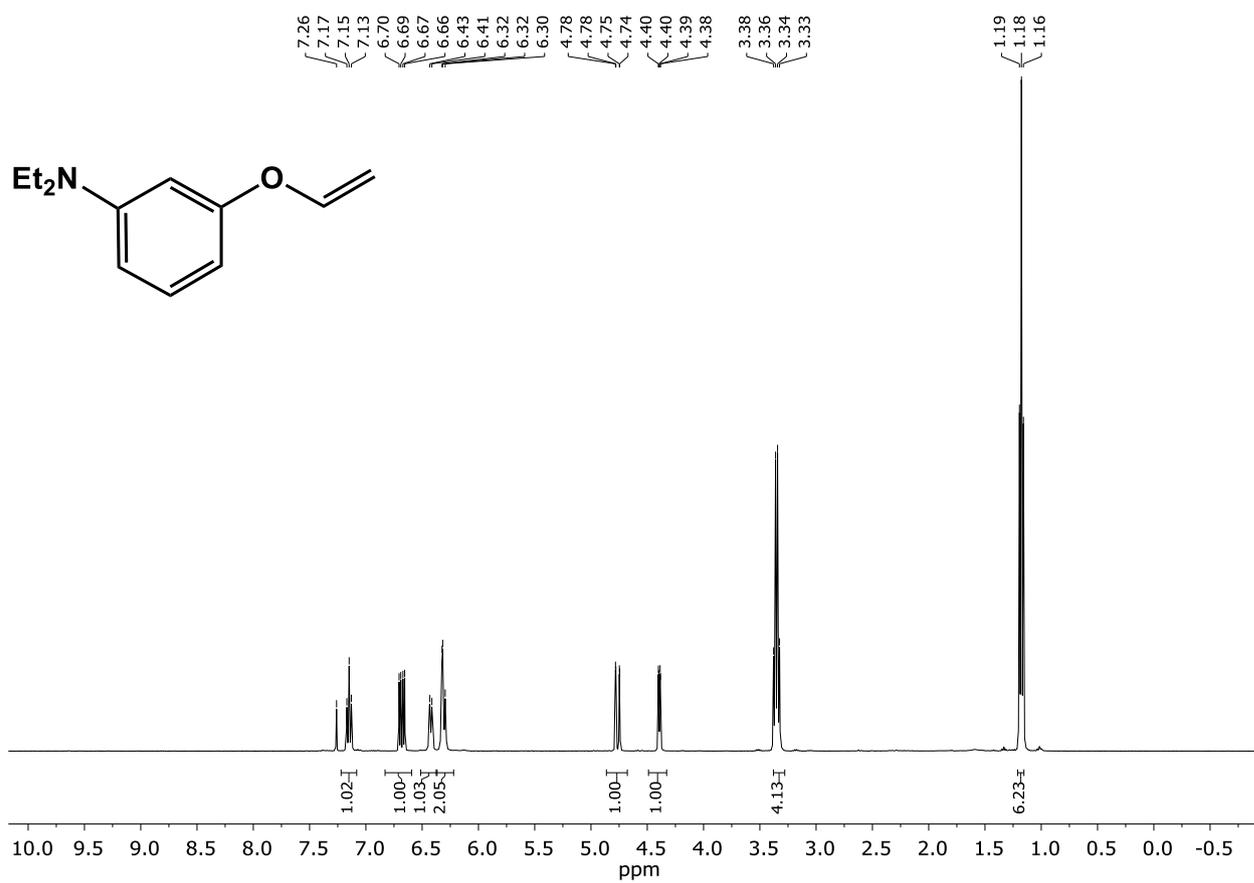


Figure S5. ^1H and ^{13}C NMR spectra for *N,N*-diethyl-3-(vinylloxy)aniline (**2e**).