

Supporting Information
Chemo-, Regio-, and Enantioselective Allylations of NH₂OH Under
Iridium Catalysis
Jiteng Chen, Qingchun Liang, Xiaoming Zhao*

School of Chemical Technology and Engineering, Tongji University, 1239 Siping
Road, Shanghai, P. R. China,
200092
E-mail: xmzhao08@mail.tongji.edu.cn

General method: All manipulations were carried out under the argon atmosphere using standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

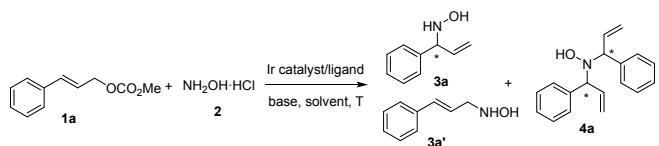
All reagents were obtained from commercial sources and used without further purification. ^1H NMR spectra were obtained at 400 MHz or 600MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent (7.26 ppm for CDCl_3). ^{13}C NMR spectra were obtained at 100 MHz or 151 MHz, and chemical shifts were recorded relative to the solvent resonance (CDCl_3 , 77.0 ppm). ^{19}F NMR spectra were obtained at 377 MHz or 565 MHz. Data for NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration).

The phosphoramidite ligands¹, substituted allylic carbonates², were prepared according to the known procedures. Other chemicals were purchased from commercial suppliers and used without further purification, unless mentioned.

References:

- [1] a) A. Alexakis, S. Rosset, J. Allamand, S. March, F. Guillen, C. Benhaim, *Synlett* **2001**, 9, 1375; b) R. Naasz, L. A. Arnold, A. J. Minnaard, B. L. Feringa, *Angew. Chem. Int. Ed.* **2001**, 40, 927; c) D. Polet, A. Alexakis, *Synthesis* **2004**, 15, 2586.
- [2] P. G. M. Wuts, S. W. Ashford, A. M. Anderson, J. R. Atkins, *Org. Lett.* **2003**, 5, 1483.

Optimization of the reaction conditions for Ir-catalyzed allylation of NH₂OH **2a**.^[a]



entry	solvent	base	T (°C)	3a/3a'	3a (%)	4a	ee (%)
1	DCM	TEA	25	>20/1	15	trace	95
2	DCM	DBU	25	-	-	-	-
3	DCM	DMAP	25	-	-	-	-
4	DCM	TBD	25	-	-	-	-
5	DCM	DIPEA ^[b]	25	>20/1	13	trace	95
6 ^[c]	DMSO	TEA	25	>20/1	70	20	96
7 ^[d]	DMSO	TEA	25	>20/1	55	17	96
8 ^[e]	DMSO	TEA	25	>20/1	47	13	96
9	DMSO	TEA	30	>20/1	72	21	85

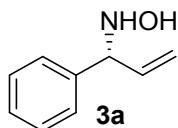
[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), base (0.2 mmol), and solvent (2 mL), 12 h; [b] DIPEA: *N,N*-diisopropylethylamine; [c] 1 mL of DMSO; [d] 1.5 mL of DMSO; [e] 2 mL of DMSO.

General procedure for the synthesis of 3:

[Ir(COD)Cl]₂ (0.004 mmol, 4 mol%), phosphoramidite ligand **L1** (0.008 mmol, 8 mol%) were dissolved in THF (0.5 mL) and *n*-propylamine (0.3 mL) in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a yellow solid. After that, allylic carbonate **1** (0.10 mmol), hydroxylamine hydrochloride **2** (0.40 mmol), triethylamine (TEA, 0.40 mmol), and DMSO (1.0 mL) were added. The reaction was stirring at room temperature for 12 h. Then the reaction mixture was diluted with sat. NH₄Cl solution and extracted with CH₂Cl₂. The combined organic layers were washed with brine and dried with anhydrous Na₂SO₄. And the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give the desired products **3**.

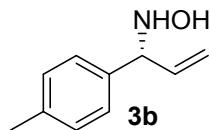
Large-scale synthesis of compound 3o:

[Ir(COD)Cl]₂ (0.16 mmol, 4 mol%), phosphoramidite ligand **L1** (0.32 mmol, 8 mol%) were dissolved in THF (2.0 mL) and *n*-propylamine (1.0 mL) in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a yellow solid. After that, allylic carbonate **1o** (1.08 g, 4.0 mmol), hydroxylamine hydrochloride **2** (0.55 g, 8.0 mmol), triethylamine (0.80 g, 8.0 mmol), and DMSO (10 mL) were added. The reaction was stirring at room temperature for 12 h. Then the reaction mixture was diluted with sat. NH₄Cl solution and extracted with CH₂Cl₂. The combined organic layers were washed with brine and dried with anhydrous Na₂SO₄. And the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give the desired products **3o**.

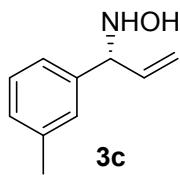


(*R*)-*N*-(1-Phenylallyl)hydroxylamine 3a, white solid; **m.p.** 70-72 °C; 65% yield (9.6 mg); **HPLC ee:** 97% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm];

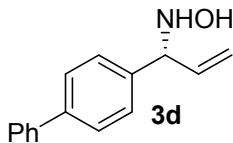
t_R = 17.32 (major), 18.35 (minor) min]. $[\alpha]_D^{20} = +15.8$ (c 1.0, CHCl_3). **1H NMR** (600 MHz, CDCl_3) δ 7.35 (d, J = 4.4 Hz, 4H), 7.32 – 7.27 (m, 1H), 6.01 (ddd, J = 17.5, 10.3, 7.3 Hz, 1H), 5.27 (dd, J = 35.3, 13.8 Hz, 2H), 4.57 (d, J = 7.3 Hz, 1H). **13C NMR** (151 MHz, CDCl_3) δ 139.76 (s), 137.43 (s), 128.68 (s), 127.85 (s), 127.79 (s), 117.75 (s), 69.63 (s). **IR** (KBr): ν_{\max} (cm^{-1}) = 3476, 3414, 3006, 1638, 1618, 1400, 1275, 1260, 750. **HRMS** (ESI $^+$) calcd for $\text{C}_9\text{H}_{11}\text{NNaO}$ [M+Na] $^+$: 172.0736, Found: 172.0733.



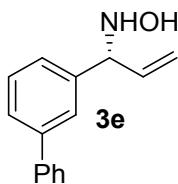
(R)-N-(1-(p-Tolyl)allyl)hydroxylamine 3b, white solid; **m.p.** 110-111 °C; 65% yield (10.6 mg); **HPLC ee:** 95% [Daicel CHIRALCEL IC (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 0.8 mL/min; detection wavelength = 214 nm; t_R = 12.45 (minor), 13.17 (major) min]. $[\alpha]_D^{20} = +209.1$ (c 1.0, CHCl_3). **1H NMR** (600 MHz, CDCl_3) δ 7.20 – 7.12 (m, 2H), 7.08 (d, J = 7.9 Hz, 2H), 5.94 (ddd, J = 17.4, 10.3, 7.3 Hz, 1H), 5.18 (dd, J = 34.4, 13.8 Hz, 2H), 4.45 (d, J = 7.3 Hz, 1H), 2.26 (s, 3H). **13C NMR** (151 MHz, CDCl_3) δ 137.62 (s), 137.59 (s), 136.65 (s), 129.38 (s), 127.72 (s), 117.57 (s), 69.32 (s), 21.15 (s). **IR** (KBr): ν_{\max} (cm^{-1}) = 3414, 3126, 3006, 1637, 1618, 1400, 1275, 1260, 764, 750. **HRMS** (ESI $^+$) calcd for $\text{C}_{10}\text{H}_{13}\text{NNaO}$ [M+Na] $^+$: 186.0922, Found: 186.0889.



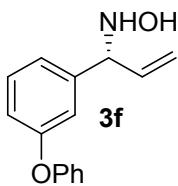
(R)-N-(1-(m-Tolyl)allyl)hydroxylamine 3c, white solid; **m.p.** 128-129 °C; 62% yield (10.1 mg); **HPLC ee:** 96% [Daicel CHIRALCEL IC (0.46 cm × 25 cm); n-hexane/2-propanol = 98/2; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 31.00 (minor), 32.64 (major) min]. $[\alpha]_D^{20} = +46.0$ (c 1.0, CHCl_3). **1H NMR** (600 MHz, CDCl_3) δ 7.17 (dd, J = 13.8, 6.3 Hz, 1H), 7.05 (dd, J = 18.7, 8.2 Hz, 3H), 5.94 (ddd, J = 17.4, 10.3, 7.4 Hz, 1H), 5.19 (dd, J = 36.5, 13.8 Hz, 2H), 4.45 (d, J = 7.3 Hz, 1H), 2.27 (s, 3H). **13C NMR** (151 MHz, CDCl_3) δ 139.59 (s), 138.37 (s), 137.50 (s), 128.65 (s), 128.60 (s), 128.50 (s), 124.81 (s), 117.69 (s), 69.64 (s), 21.45 (s). **IR** (KBr): ν_{\max} (cm^{-1}) = 3475, 3414, 3126, 3006, 1638, 1618, 1276, 750. **HRMS** (ESI $^+$) calcd for $\text{C}_{10}\text{H}_{13}\text{NNaO}$ [M+Na] $^+$: 186.0921, Found: 186.0889.



(R)-N-(1-([1,1'-Biphenyl]-4-yl)allyl)hydroxylamine 3d, white solid; **m.p.** 118–120 °C; 61% yield (13.7 mg); **HPLC ee:** 96% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 27.17 (major), 29.33 (minor) min]. $[\alpha]_D^{20} = +91.95$ (c 1.0, CHCl_3). **¹H NMR** (600 MHz, CDCl_3) δ 7.57 (d, J = 8.1 Hz, 4H), 7.42 (dd, J = 14.8, 7.7 Hz, 4H), 7.34 (t, J = 7.4 Hz, 1H), 6.04 (ddd, J = 17.4, 10.3, 7.3 Hz, 1H), 5.29 (dd, J = 38.9, 13.8 Hz, 2H), 4.61 (d, J = 7.3 Hz, 1H). **¹³C NMR** (151 MHz, CDCl_3) δ 140.81 (d, J = 12.1 Hz), 138.75 (s), 137.29 (s), 128.80 (s), 128.25 (s), 127.41 (d, J = 13.5 Hz), 127.13 (s), 117.95 (s), 69.30 (s). **IR** (KBr): ν_{\max} (cm^{-1}) = 3477, 3415, 3006, 1638, 1618, 1276, 1261, 750. **HRMS** (ESI $^+$) calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}$ [M+Na] $^+$: 248.1048, Found: 248.1046.



(R)-N-(1-([1,1'-Biphenyl]-3-yl)allyl)hydroxylamine 3e, pale yellow wax; 70% yield (15.7 mg); **HPLC ee:** 92% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 23.13 (minor), 26.33 (major) min]. $[\alpha]_D^{20} = +27.38$ (c 1.0, CHCl_3). **¹H NMR** (600 MHz, CDCl_3) δ 7.60 – 7.54 (m, 3H), 7.52 (d, J = 7.7 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.37 – 7.30 (m, 2H), 6.03 (ddd, J = 17.4, 10.3, 7.3 Hz, 1H), 5.28 (dd, J = 41.2, 13.8 Hz, 2H), 4.62 (d, J = 7.3 Hz, 1H). **¹³C NMR** (151 MHz, CDCl_3) δ 141.67 (s), 140.95 (s), 140.29 (s), 137.29 (s), 129.11 (s), 128.79 (s), 127.42 (s), 127.23 (s), 126.83 – 126.60 (m), 117.98 (s), 69.66 (s). **IR** (KBr): ν_{\max} (cm^{-1}) = 3476, 3414, 3006, 2989, 1638, 1618, 1276, 1260, 764, 750. **HRMS** (ESI $^+$) calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}$ [M+Na] $^+$: 248.1047, Found: 248.1046.



(R)-N-(1-(3-Phenoxyphenyl)allyl)hydroxylamine 3f, yellow wax; 72% yield (17.3 mg); **HPLC ee:** 95% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm);

n-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 25.91 (major), 33.33 (minor) min]. $[\alpha]_D^{20} = +17.16$ (c 1.0, CHCl_3). **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.31 (dt, J = 21.7, 7.7 Hz, 3H), 7.12 – 7.06 (m, 2H), 7.02 (dd, J = 18.0, 4.8 Hz, 3H), 6.90 (dd, J = 7.8, 2.0 Hz, 1H), 5.95 (ddd, J = 17.5, 10.3, 7.4 Hz, 1H), 5.25 (dd, J = 29.3, 13.8 Hz, 2H), 4.52 (d, J = 7.4 Hz, 1H). **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ 157.54 (s), 157.01 (s), 141.89 (s), 137.02 (s), 129.87 (d, J = 19.4 Hz), 123.38 (s), 122.53 (s), 118.99 (s), 118.16 (d, J = 10.9 Hz), 117.98 (s), 69.31 (s). **IR** (KBr): ν_{max} (cm^{-1}) = 3475, 3414, 3006, 2990, 1638, 1618, 1400, 1260, 764, 750. **HRMS** (ESI $^+$) calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}_2$ [M+Na] $^+$: 264.1005, Found: 264.0995.

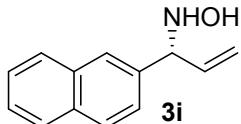


(R)-N-(1-(3-(Allyloxy)phenyl)allyl)hydroxylamine 3g, colorless oil; 70% yield (14.4 mg); **HPLC ee**: 94% [Daicel CHIRALCEL OD-H (0.46 cm \times 25 cm); n-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 13.36 (minor), 21.32 (major) min]. $[\alpha]_D^{20} = +30.76$ (c 1.0, CHCl_3). **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.26 (t, J = 7.9 Hz, 1H), 6.94 (d, J = 7.5 Hz, 2H), 6.84 (dd, J = 7.4, 1.7 Hz, 1H), 6.05 (ddd, J = 22.4, 10.5, 5.3 Hz, 1H), 5.97 (ddd, J = 17.4, 10.3, 7.4 Hz, 1H), 5.42 (dd, J = 17.2, 1.4 Hz, 1H), 5.30 (dd, J = 9.4, 8.3 Hz, 2H), 5.23 (d, J = 10.3 Hz, 1H), 4.53 (d, J = 5.6 Hz, 3H). **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ 158.87 (s), 141.38 (s), 137.25 (s), 133.23 (s), 129.69 (s), 120.22 (s), 117.85 (s), 117.74 (s), 114.13 (s), 113.98 (s), 69.57 (s), 68.78 (s). **IR** (KBr): ν_{max} (cm^{-1}) = 3476, 3413, 3007, 2990, 1638, 1618, 1400, 1276, 1261, 764, 750. **HRMS** (ESI $^+$) calcd for $\text{C}_{12}\text{H}_{15}\text{NNaO}_2$ [M+Na] $^+$: 228.1002, Found: 228.0995.

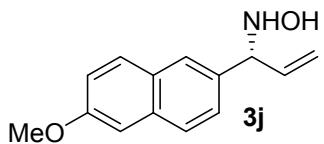


(R)-N-(1-(4-Methoxyphenyl)allyl)hydroxylamine 3h, white solid; **m.p.** 69-70 °C; 66% yield (11.8 mg); **HPLC ee**: 95% [Daicel CHIRALCEL OD-H (0.46 cm \times 25 cm); n-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 9.85 (minor), 11.78 (major) min]. $[\alpha]_D^{20} = +134.95$ (c 1.0, CHCl_3). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.29 – 7.24 (m, 2H), 6.89 (d, J = 8.5 Hz, 2H), 6.00 (ddd, J = 17.4, 10.3, 7.2 Hz, 1H), 5.25 (dd, J = 20.9, 13.8 Hz, 2H), 4.52 (d, J = 7.1 Hz, 1H),

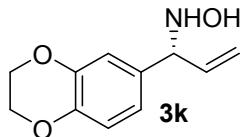
3.80 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 159.27 (s), 137.63 (s), 131.72 (s), 128.96 (s), 117.38 (s), 114.08 (s), 68.92 (s), 55.29 (s). **IR** (KBr): ν_{max} (cm⁻¹) = 3550, 3476, 3415, 3007, 2990, 1638, 1618, 1400, 1276, 1261, 764, 750. **HRMS** (ESI⁺) calcd for C₁₀H₁₃NNaO₂ [M+Na]⁺: 202.0828, Found: 202.0838.



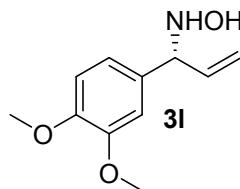
(R)-N-(1-(Naphthalen-2-yl)allyl)hydroxylamine 3i, white solid; **m.p.** 88-89 °C; 72% yield (14.3 mg); **HPLC ee:** 94% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 26.68 (minor), 31.86 (major) min]. [α]_D²⁰ = +139.53 (c 1.0, CHCl₃). **¹H NMR** (600 MHz, CDCl₃) δ 7.84 – 7.74 (m, 4H), 7.46 (dt, *J* = 16.7, 7.4 Hz, 3H), 6.06 (ddd, *J* = 17.4, 10.3, 7.2 Hz, 1H), 5.27 (dd, *J* = 35.3, 13.8 Hz, 2H), 4.70 (d, *J* = 7.2 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 137.13 (d, *J* = 14.7 Hz), 133.40 (s), 133.23 (d, *J* = 50.5 Hz), 134.85 – 128.04 (m), 130.71 (dd, *J* = 761.2, 61.4 Hz), 220.03 – 125.96 (m), 134.85 – 126.92 (m), 134.85 – 126.30 (m), 125.64 (s), 118.07 (s), 69.62 (s). **IR** (KBr): ν_{max} (cm⁻¹) = 3476, 3415, 3006, 2990, 1638, 1618, 1401, 1276, 1261, 764, 750. **HRMS** (ESI⁺) calcd for C₁₃H₁₃NNaO [M+Na]⁺: 222.0870, Found: 222.0889.



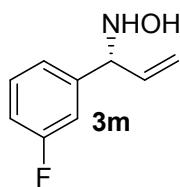
(R)-N-(1-(6-Methoxynaphthalen-2-yl)allyl)hydroxylamine 3j, white solid; **m.p.** 104-106 °C; 76% yield (17.4 mg); **HPLC ee:** 96% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 39.43 (minor), 44.04 (major) min]. [α]_D²⁰ = +209.91 (c 1.0, CHCl₃). **¹H NMR** (600 MHz, CDCl₃) δ 7.70 (dd, *J* = 8.7, 4.5 Hz, 3H), 7.41 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.16 – 7.09 (m, 2H), 6.07 (ddd, *J* = 17.4, 10.3, 7.2 Hz, 1H), 5.28 (dd, *J* = 37.7, 13.8 Hz, 2H), 4.67 (d, *J* = 7.2 Hz, 1H), 3.91 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 157.79 (s), 137.42 (s), 134.75 (s), 134.22 (s), 129.42 (s), 128.86 (s), 127.25 (s), 126.72 (s), 126.19 (s), 119.03 (s), 117.80 (s), 105.62 (s), 69.56 (s), 55.33 (s). **IR** (KBr): ν_{max} (cm⁻¹) = 3475, 3414, 3006, 1637, 1618, 1400, 1275, 1261, 764, 750. **HRMS** (ESI⁺) calcd for C₁₄H₁₅NNaO₂ [M+Na]⁺: 252.1001, Found: 252.0995.



(R)-N-(1-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)allyl)hydroxylamine 3k, white solid; **m.p.** 105–106 °C; 61% yield (12.6 mg); **HPLC ee:** 92% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 55.92 (minor), 64.38 (major) min]. $[\alpha]_D^{20} = +155.96$ (c 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 6.91 – 6.79 (m, 3H), 5.96 (ddd, J = 17.4, 10.3, 7.3 Hz, 1H), 5.25 (dd, J = 25.6, 13.8 Hz, 2H), 4.46 (d, J = 7.2 Hz, 1H), 4.25 (s, 4H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.59 (s), 143.19 (s), 137.49 (s), 133.05 (s), 120.73 (s), 117.41 (s), 116.56 (s), 68.98 (s), 64.36 (s). **IR** (KBr): ν_{\max} (cm⁻¹) = 3476, 3415, 3006, 2990, 1638, 1618, 1401, 1276, 1261, 764, 750. **HRMS** (ESI⁺) calcd for C₁₁H₁₃NNaO₃ [M+Na]⁺: 230.0784, Found: 230.0788.

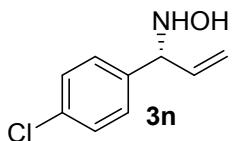


(R)-N-(1-(3,4-Dimethoxyphenyl)allyl)hydroxylamine 3l, pale yellow wax; 65% yield (13.6 mg); **HPLC ee:** 96% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 52.39 (minor), 57.50 (major) min]. $[\alpha]_D^{20} = +60.75$ (c 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 6.95 – 6.80 (m, 4H), 6.00 (ddd, J = 17.4, 10.3, 7.2 Hz, 1H), 5.27 (dd, J = 23.1, 13.8 Hz, 2H), 4.52 (d, J = 7.2 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 149.15 (s), 148.69 (s), 137.55 (s), 132.27 (s), 120.05 (s), 117.48 (s), 111.23 (s), 110.75 (s), 69.28 (s), 55.89 (s). **IR** (KBr): ν_{\max} (cm⁻¹) = 3476, 3415, 3006, 2990, 1638, 1618, 1401, 1276, 1260, 764, 750. **HRMS** (ESI⁺) calcd for C₁₁H₁₅NNaO₃ [M+Na]⁺: 232.0955, Found: 232.0944.

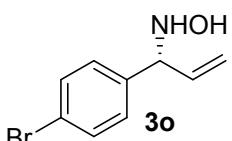


(R)-N-(1-(3-Fluorophenyl)allyl)hydroxylamine 3m, yellow solid; **m.p.** 76–78 °C; 63% yield (10.5 mg); **HPLC ee:** 96% [Daicel CHIRALCEL IC (0.46 cm × 25 cm); n-hexane/2-propanol = 98/2; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 28.98 (major), 32.06 (minor) min]. $[\alpha]_D^{20} = +140.1$ (c 1.0, CHCl₃). **¹H NMR** (600

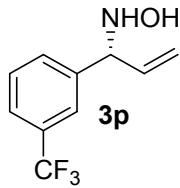
MHz, CDCl₃) δ 7.32 (td, *J* = 7.9, 6.1 Hz, 1H), 7.11 (dd, *J* = 27.4, 8.7 Hz, 2H), 6.98 (td, *J* = 8.3, 2.1 Hz, 1H), 5.95 (ddd, *J* = 17.4, 10.3, 7.4 Hz, 1H), 5.28 (dd, *J* = 27.5, 13.8 Hz, 3H), 4.57 (d, *J* = 7.3 Hz, 1H). **¹⁹F NMR** (565 MHz, CDCl₃) δ -112.78 (s). **¹³C NMR** (151 MHz, CDCl₃) δ 163.83 (s), 162.19 (s), 142.58 (d, *J* = 7.0 Hz), 136.74 (s), 130.13 (d, *J* = 8.2 Hz), 123.40 (d, *J* = 2.8 Hz), 118.31 (s), 114.64 (dd, *J* = 21.5, 12.3 Hz), 69.07 (s). **IR** (KBr): ν_{max} (cm⁻¹) = 3476, 3415, 3006, 2990, 1638, 1618, 1401, 1276, 1261, 764, 750. **HRMS** (ESI⁺) calcd for C₉H₁₁FNO [M+H]⁺: 168.0827, Found: 168.0819.



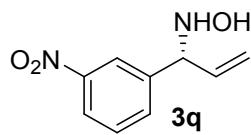
(R)-N-(1-(4-Chlorophenyl)allyl)hydroxylamine 3n, yellow solid; **m.p.** 113-114 °C; 67% yield (12.2 mg); **HPLC ee:** 97% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 0.8 mL/min; detection wavelength = 214 nm; t_R = 23.69 (minor), 27.57 (major) min]. $[\alpha]_D^{20} = +92.7$ (c 1.0, CHCl₃). **¹H NMR** (600 MHz, CDCl₃) δ 7.25 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.88 (ddd, *J* = 17.4, 10.2, 7.3 Hz, 1H), 5.19 (t, *J* = 14.2 Hz, 2H), 4.46 (d, *J* = 7.2 Hz, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 138.23 (s), 136.74 (s), 133.62 (s), 129.22 (s), 128.82 (s), 118.27 (s), 68.79 (s). **IR** (KBr): ν_{max} (cm⁻¹) = 3475, 3414, 3006, 2989, 1638, 1618, 1400, 1276, 1261, 764, 750. **HRMS** (ESI⁺) calcd for C₉H₁₁ClNO [M+H]⁺: 184.0530, Found: 184.0524.



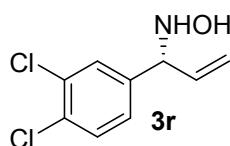
(R)-N-(1-(4-Bromophenyl)allyl)hydroxylamine 3o, yellow solid; **m.p.** 102-104 °C; 65% yield (14.8 mg); **HPLC ee:** 95% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 0.8 mL/min; detection wavelength = 214 nm; t_R = 25.70 (minor), 32.20 (major) min]. $[\alpha]_D^{20} = +37.9$ (c 1.0, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 5.87 (ddd, *J* = 17.4, 10.3, 7.2 Hz, 1H), 5.19 (dd, *J* = 13.7, 10.0 Hz, 2H), 4.44 (d, *J* = 7.2 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 138.87 (s), 136.73 (s), 131.76 (s), 129.55 (s), 121.72 (s), 118.23 (s), 68.86 (s). **IR** (KBr): ν_{max} (cm⁻¹) = 3475, 3413, 3006, 2989, 1637, 1618, 1401, 1276, 1260, 764, 750. **HRMS** (ESI⁺) calcd for C₉H₁₀BrKNO [M+K]⁺: 265.9560, Found: 265.9577.



(R)-N-(1-(3-(Trifluoromethyl)phenyl)allyl)hydroxylamine 3p, yellow wax; 60% yield (13.0 mg); **HPLC ee:** 94% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 12.31 (minor), 13.85 (major) min]. $[\alpha]_D^{20} = +114.3$ (c 1.0, CHCl_3). **¹H NMR** (600 MHz, CDCl_3) δ 7.57 (s, 1H), 7.48 (d, J = 7.7 Hz, 2H), 7.44 – 7.36 (m, 1H), 5.88 (ddd, J = 13.5, 10.3, 7.3 Hz, 1H), 5.23 (dd, J = 23.5, 13.8 Hz, 2H), 4.57 (d, J = 7.3 Hz, 1H). **¹⁹F NMR** (565 MHz, CDCl_3) δ -62.53 (s). **¹³C NMR** (151 MHz, CDCl_3) δ 141.15 (s), 136.49 (s), 131.23 (s), 131.08 (s), 130.87 (s), 129.07 (s), 125.00 (s), 124.58 (dq, J = 7.8, 3.8 Hz), 123.19 (s), 118.61 (s), 69.10 (s). **IR** (KBr): ν_{max} (cm^{-1}) = 3475, 3414, 3007, 2990, 1637, 1618, 1401, 1275, 1261, 764, 750. **HRMS** (ESI⁺) calcd for $\text{C}_{10}\text{H}_{11}\text{F}_3\text{NO}$ [$\text{M}+\text{H}]^+$: 218.0796, Found: 218.0787.

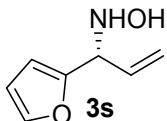


(R)-N-(1-(3-Nitrophenyl)allyl)hydroxylamine 3q, pale yellow wax; 65% yield (12.6 mg); **HPLC ee:** 94% [Daicel CHIRALCEL OD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 9.40 (minor), 10.56 (major) min]. $[\alpha]_D^{20} = +47.41$ (c 1.0, CHCl_3). **¹H NMR** (400 MHz, CDCl_3) δ 8.27 (s, 1H), 8.15 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.53 (t, J = 7.9 Hz, 1H), 5.94 (ddd, J = 17.4, 10.2, 7.4 Hz, 1H), 5.32 (t, J = 13.0 Hz, 2H), 4.70 (d, J = 7.3 Hz, 1H). **¹³C NMR** (101 MHz, CDCl_3) δ 148.56 (s), 142.60 (s), 135.95 (s), 134.00 (s), 129.48 (s), 122.74 (s), 119.08 (s), 68.69 (s). **IR** (KBr): ν_{max} (cm^{-1}) = 3475, 3414, 3006, 2989, 1638, 1618, 1400, 1276, 764, 750. **HRMS** (ESI⁺) calcd for $\text{C}_9\text{H}_{10}\text{N}_2\text{NaO}_3$ [$\text{M}+\text{Na}]^+$: 217.0594, Found: 217.0584.

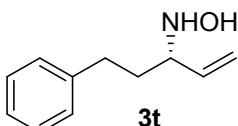


(R)-N-(1-(3,4-Dichlorophenyl)allyl)hydroxylamine 3r, yellow wax; 60% yield (13.1 mg); **HPLC ee:** 92% [Daicel CHIRALCEL OD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 7.67 (minor), 8.30 (major) min]. $[\alpha]_D^{20} = +43.34$ (c 1.0, CHCl_3). **¹H NMR**

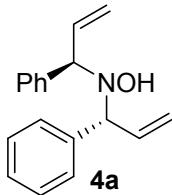
(600 MHz, CDCl₃) δ 7.47 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.19 (dd, *J* = 8.2, 1.8 Hz, 1H), 5.90 (ddd, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.28 (t, *J* = 13.9 Hz, 2H), 4.53 (d, *J* = 7.3 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 140.37 (s), 136.16 (s), 132.70 (s), 131.71 (s), 130.58 (s), 129.76 (s), 127.19 (s), 118.74 (s), 68.43 (s). IR (KBr): ν_{max} (cm⁻¹) = 3476, 3415, 3006, 2990, 1638, 1618, 1401, 1276, 1260, 764, 750. HRMS (ESI⁺) calcd for C₉H₁₀Cl₂NO [M+H]⁺: 218.0138, Found: 218.0134.



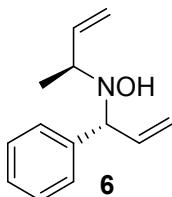
(R)-N-(1-(Furan-2-yl)allyl)hydroxylamine 3s, brown wax; 69% yield (9.5 mg); HPLC *ee*: 97% [Daicel CHIRALCEL AD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 16.00 (major), 18.02 (minor) min]. $[\alpha]_D^{20}$ = +85.40 (c 1.0, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 7.34 (dd, *J* = 9.1, 8.5 Hz, 1H), 7.19 (s, 1H), 6.32 – 6.25 (m, 1H), 6.20 (t, *J* = 8.3 Hz, 1H), 5.97 (ddd, *J* = 17.5, 10.3, 7.4 Hz, 1H), 5.36 – 5.21 (m, 2H), 4.57 (dd, *J* = 28.2, 7.7 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 152.45 (s), 142.38 (s), 134.12 (s), 119.32 (s), 110.34 (s), 107.88 (s), 63.12 (s). IR (KBr): ν_{max} (cm⁻¹) = 3475, 3414, 3006, 2989, 1638, 1618, 1400, 1276, 1260, 764, 750. HRMS (ESI⁺) calcd for C₇H₁₀NO₂ [M+H]⁺: 140.0706, Found: 140.0706.



(S)-N-(5-Phenylpent-1-en-3-yl)hydroxylamine 3t, colorless oil; 87% yield (14.5 mg); HPLC *ee*: 92% [Daicel CHIRALCEL OD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 8.93 (minor), 10.95 (major) min]. $[\alpha]_D^{20}$ = +82.61 (c 1.0, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 7.20 (dd, *J* = 13.3, 5.8 Hz, 2H), 7.12 (t, *J* = 7.0 Hz, 3H), 5.73 – 5.64 (m, 1H), 5.23 – 5.15 (m, 2H), 3.35 (dd, *J* = 13.4, 8.0 Hz, 1H), 2.65 – 2.50 (m, 2H), 1.91 – 1.59 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 141.79 (s), 138.03 (s), 128.42 (s), 128.39 (s), 125.92 (s), 118.49 (s), 65.03 (s), 33.30 (s), 32.01 (s). IR (KBr): ν_{max} (cm⁻¹) = 3476, 3415, 3006, 2990, 1638, 1618, 1401, 1276, 1261, 764, 750. HRMS (ESI⁺) calcd for C₁₁H₁₆NO [M+H]⁺: 178.1226, Found: 178.1226.



N,N-Bis((R)-1-phenylallyl)hydroxylamine 4a, white solid; **m.p.** 121-123 °C; 80% yield (21.2 mg); **HPLC ee:** 80% [Daicel CHIRALCEL OD-H (0.46 cm × 25 cm); n-hexane/2-propanol = 98/2; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 6.53 (major), 7.45 (minor) min]. $[\alpha]_D^{20} = +131.24$ (c 1.0, CHCl_3). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.37 (d, J = 7.4 Hz, 4H), 7.28 (t, J = 7.5 Hz, 4H), 7.22 – 7.17 (m, 2H), 6.18 – 6.01 (m, 2H), 5.20 (t, J = 14.8 Hz, 4H), 4.48 (d, J = 8.7 Hz, 2H), 1.50 (s, 4H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 141.44 (s), 136.42 (s), 128.43 (s), 128.06 (s), 127.18 (s), 118.32 (s), 70.94 (s). **IR (KBr):** ν_{max} (cm^{-1}) = 3476, 3414, 3006, 2990, 1638, 1618, 1401, 1276, 1261, 764, 750. **HRMS (ESI⁺)** calcd for $\text{C}_{18}\text{H}_{19}\text{NNaO}$ [M+Na^+]: 288.1364, Found: 288.1379.

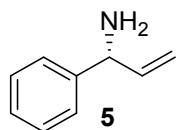


N-((S)-But-3-en-2-yl)-N-((R)-1-phenylallyl)hydroxylamine 6, colorless oil; 90% yield (18.0 mg); $[\alpha]_D^{20} = +98.47$ (c 1.0, CHCl_3). **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.32 (d, J = 7.4 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.18 (d, J = 7.3 Hz, 1H), 6.02 – 5.92 (m, 1H), 5.92 – 5.84 (m, 1H), 5.18 – 4.99 (m, 4H), 4.36 (d, J = 8.8 Hz, 1H), 4.13 (s, 1H), 3.54 – 3.42 (m, 1H), 1.20 (d, J = 6.6 Hz, 3H). **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ 142.05 (s), 138.00 (s), 137.28 (s), 128.58 (s), 127.79 (s), 127.18 (s), 117.55 (s), 116.77 (s), 72.34 (s), 60.98 (s), 18.09 (s). **IR (KBr):** ν_{max} (cm^{-1}) = 3476, 3414, 3007, 2990, 1638, 1618, 1401, 1275, 1261, 764, 750. **HRMS (ESI⁺)** calcd for $\text{C}_{13}\text{H}_{17}\text{NNaO}$ [M+Na^+]: 226.1206, Found: 226.1202.

Procedure for the synthesis of 5:[1-2]

3a (44.7 mg, 0.3 mmol) was dissolved in a mixture of H_2O and AcOH (1 mL:1 mL), then Zn powder (384 mg, 6 mmol) was added and the solution was stirred for 12h at 25 °C. After quenched with aq. sat. NaHCO_3 , the mixture was extracted with CH_2Cl_2 and the combined organic layers were washed with brine and dried with anhydrous Na_2SO_4 . The solvent was distilled under reduced pressure and the

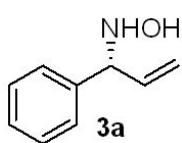
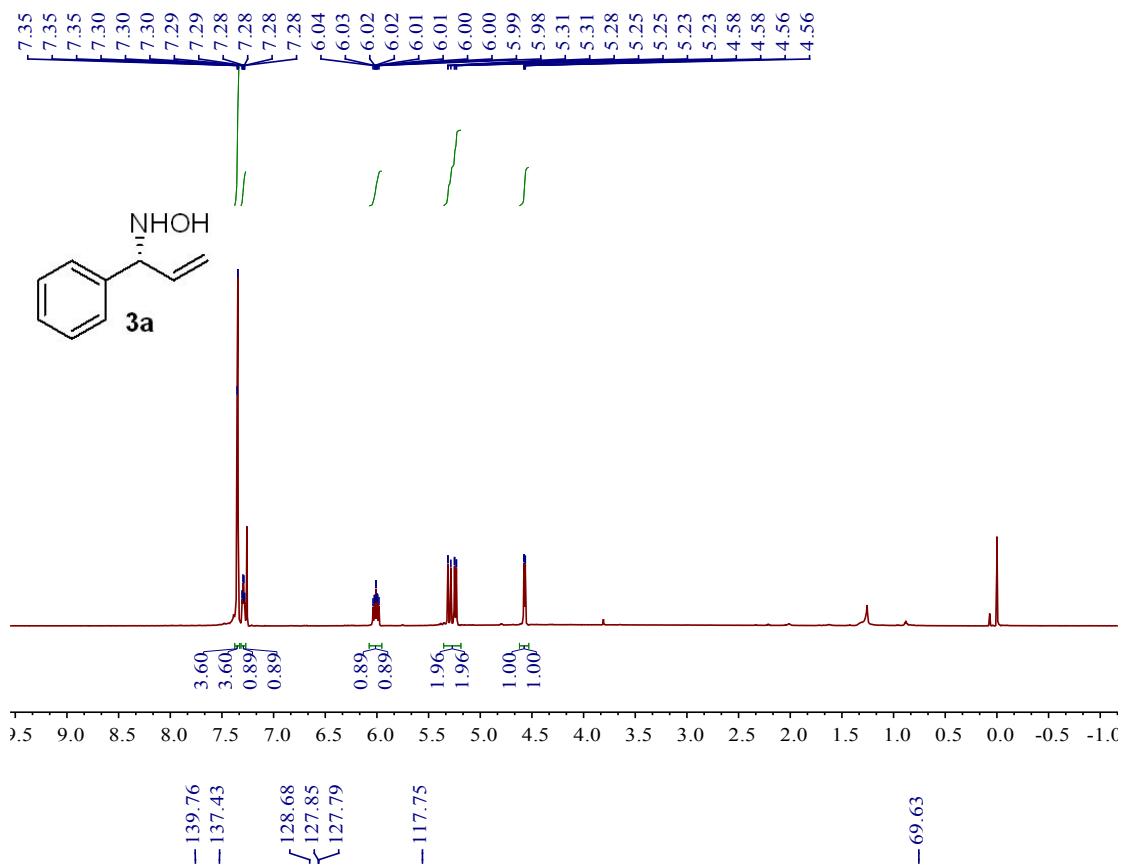
resulting yellow oil was obtained without further purification.

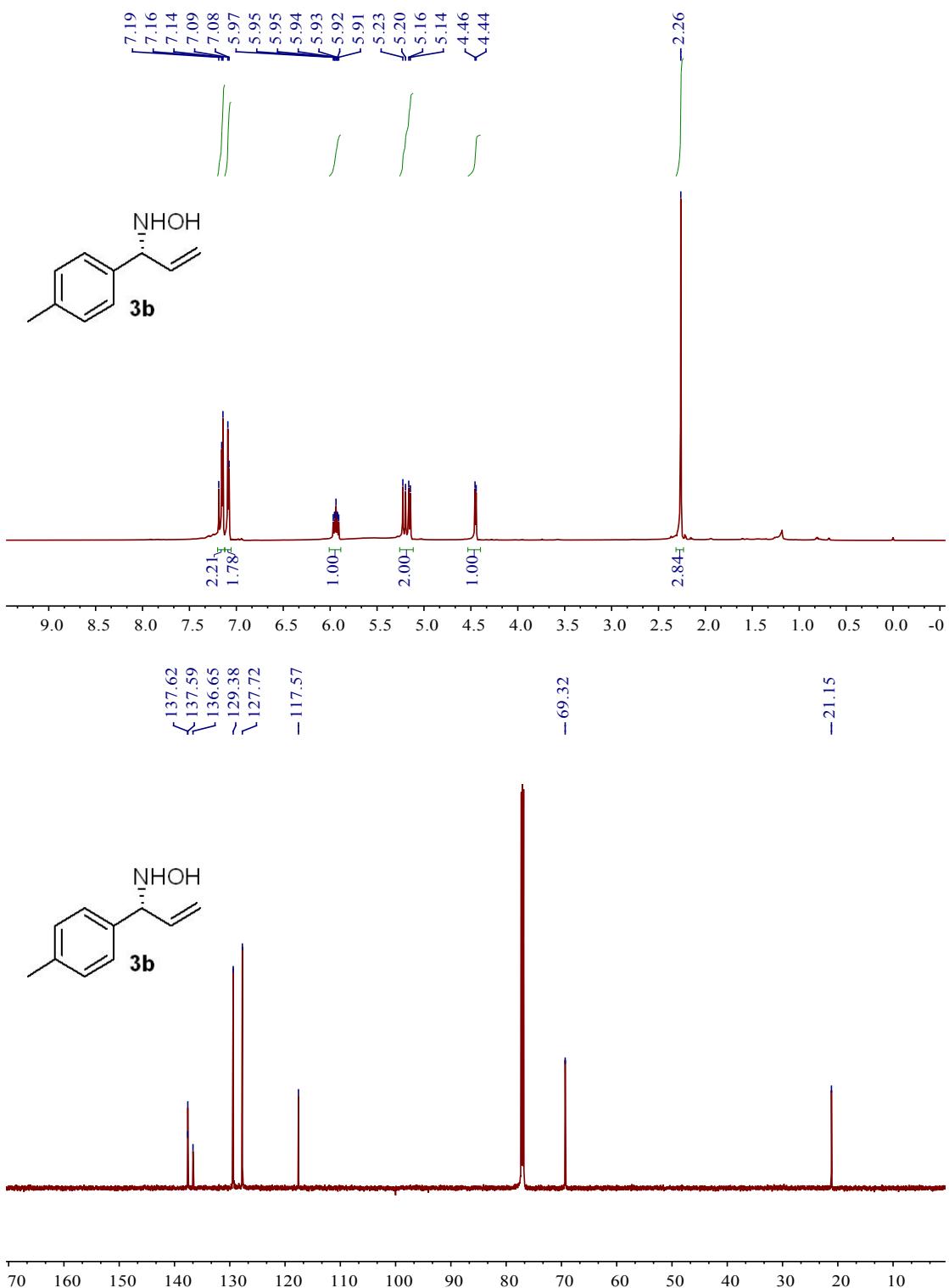


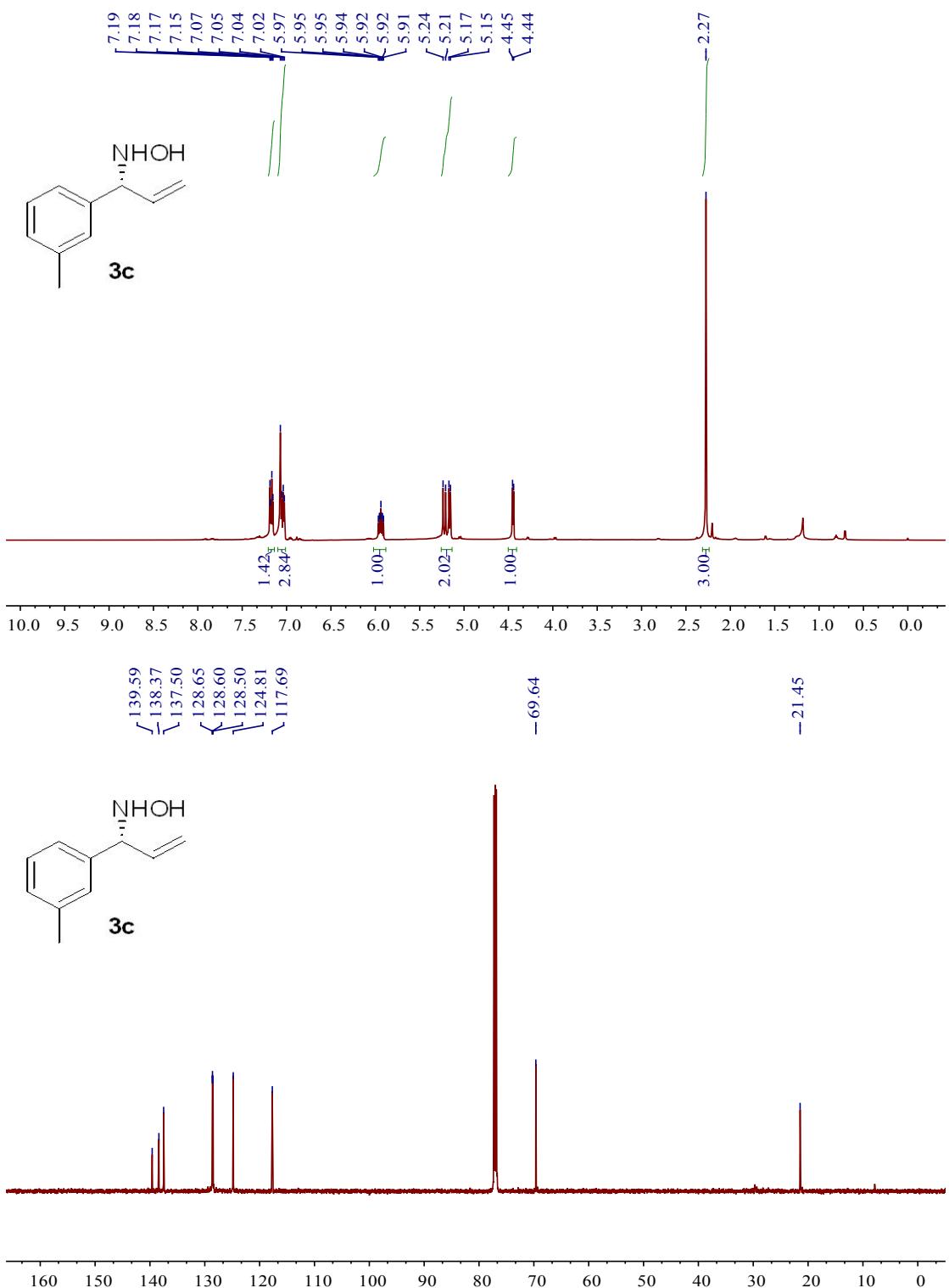
(R)-1-Phenylprop-2-en-1-amine 5, yellow oil; 95% yield (39.8 mg); $[\alpha]_D^{20} = +10.70$ (c 1.0, CHCl₃). **¹H NMR** (600 MHz, CDCl₃) δ 7.34 (d, *J* = 4.4 Hz, 4H), 7.26 (d, *J* = 2.9 Hz, 1H), 6.03 (ddd, *J* = 16.6, 10.2, 6.1 Hz, 1H), 5.24 (d, *J* = 17.1 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 4.53 (d, *J* = 6.1 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 144.37 (s), 142.19 (s), 128.58 (s), 127.15 (s), 126.65 (s), 113.77 (s), 58.39 (s). **HRMS** (ESI⁺) calcd for C₉H₁₂N [M+H]⁺: 134.0975, Found: 134.0964.

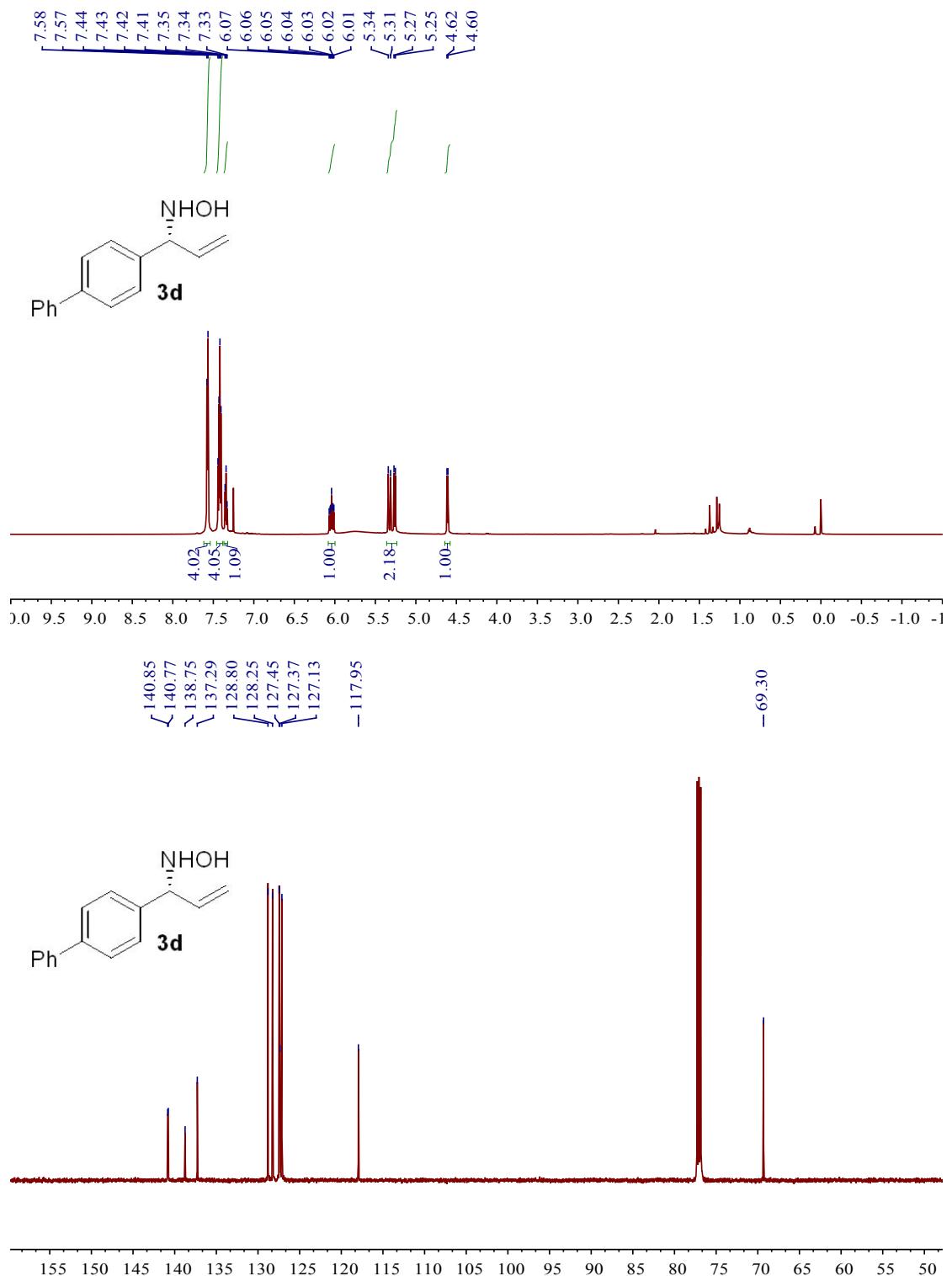
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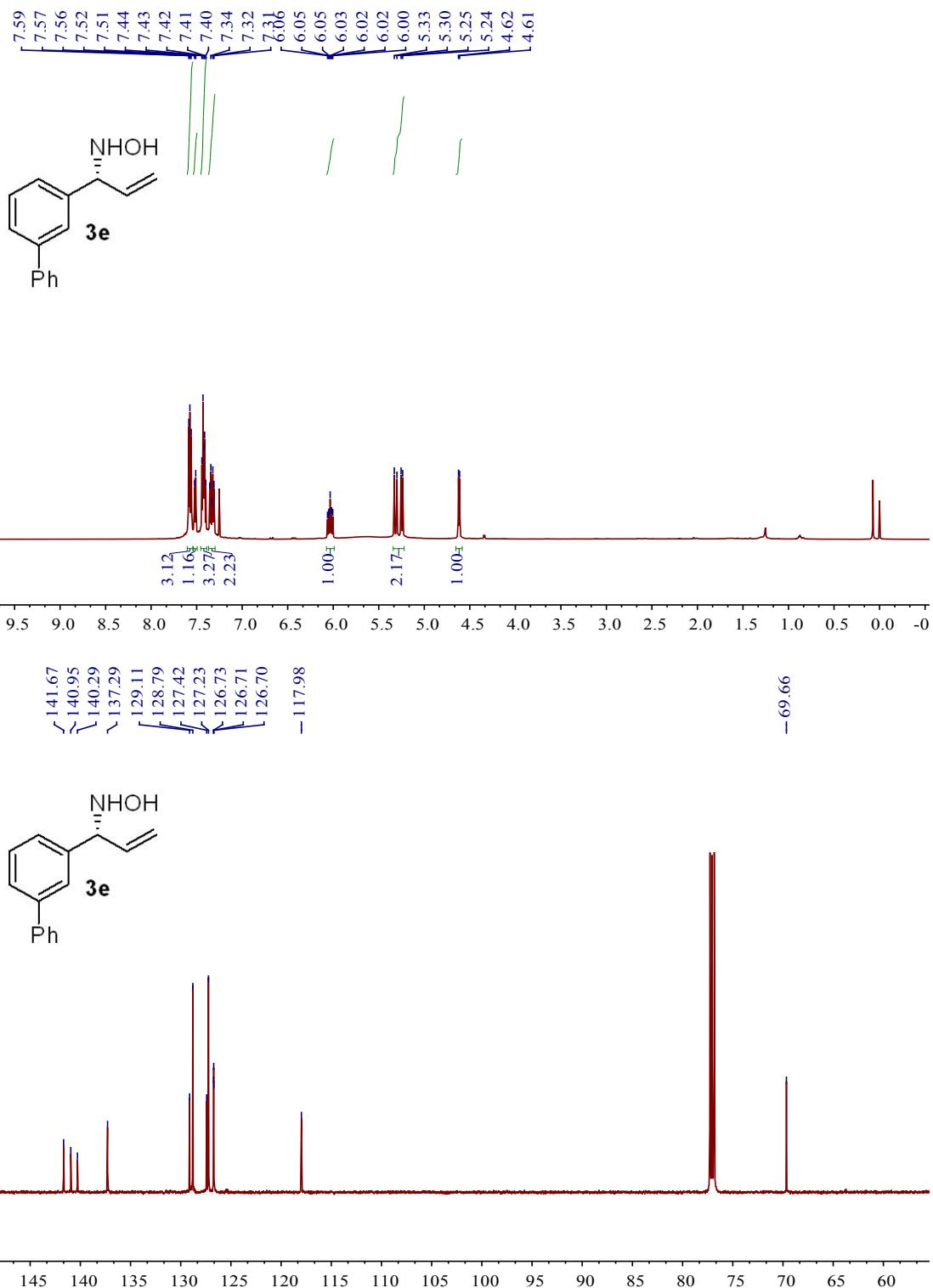
- [1] C. J. Moody, P. T. Gallagher, A. P. Lightfoot, A. M. Z. Slawin, *J. Org. Chem.*, **1999**, 64, 4419;
- [2] H. Miyabe, A. Masumura, K. Moriyama, Y. Takemoto, *Org. Lett.*, **2004**, 6, 463

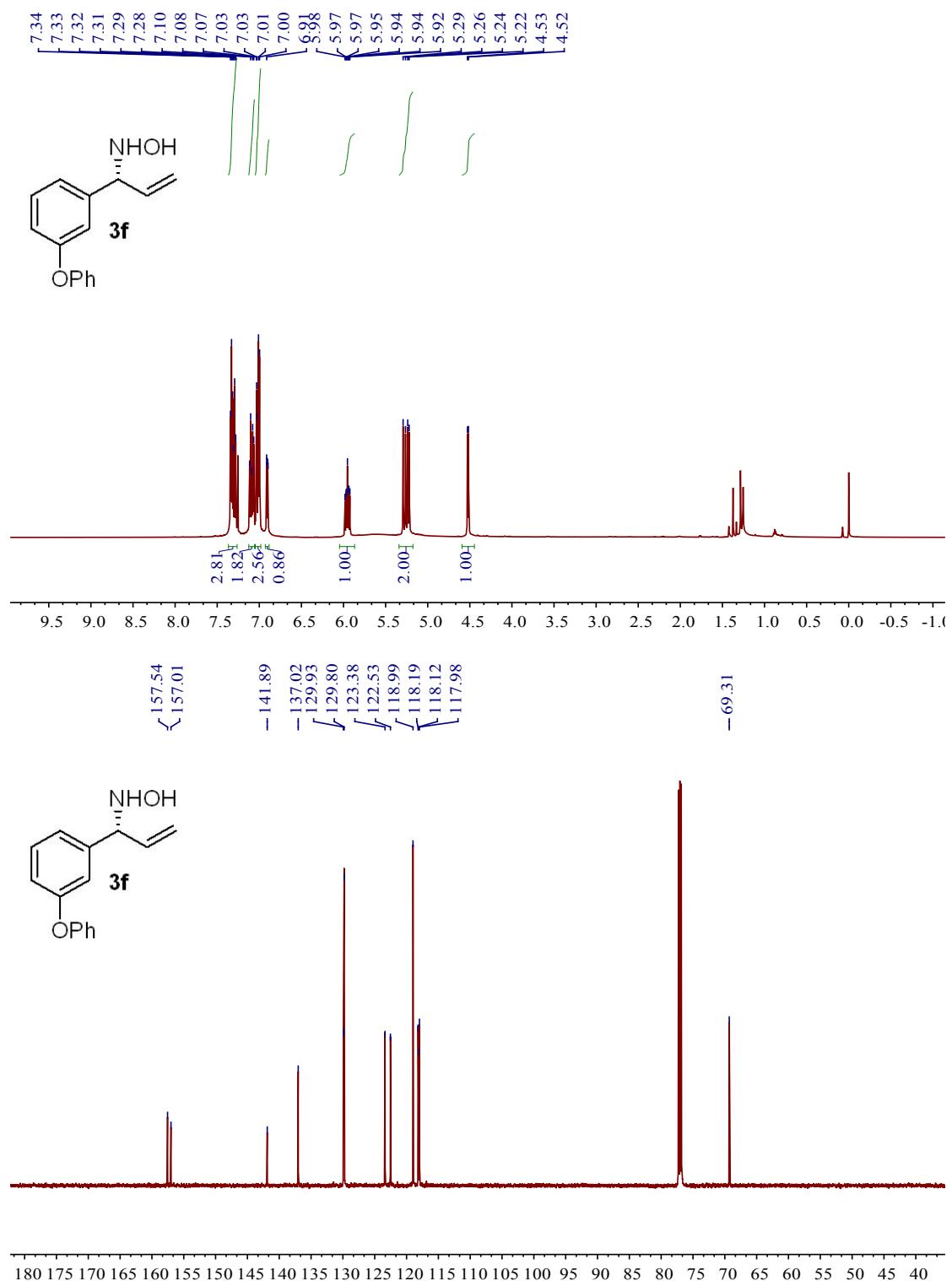


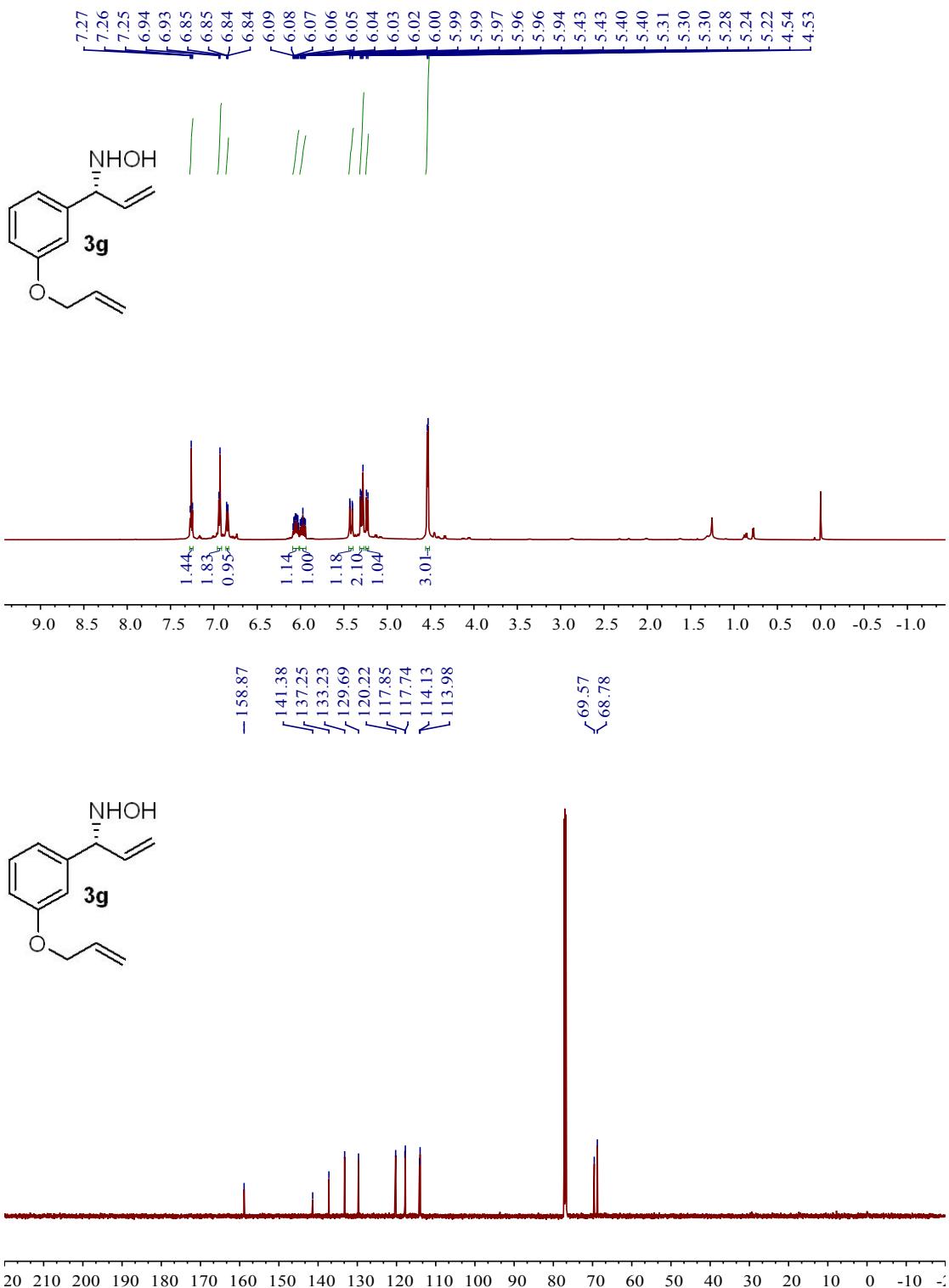


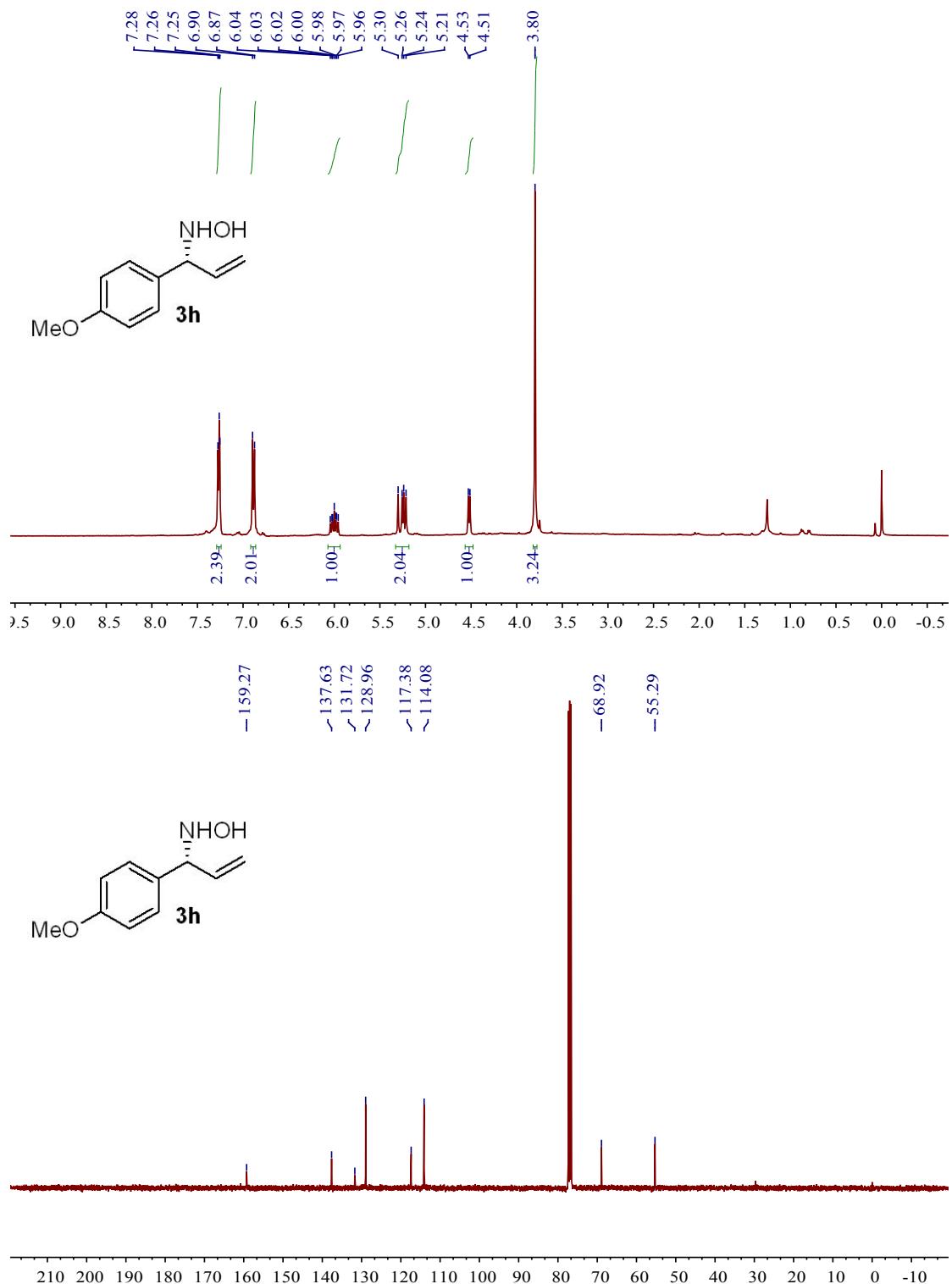


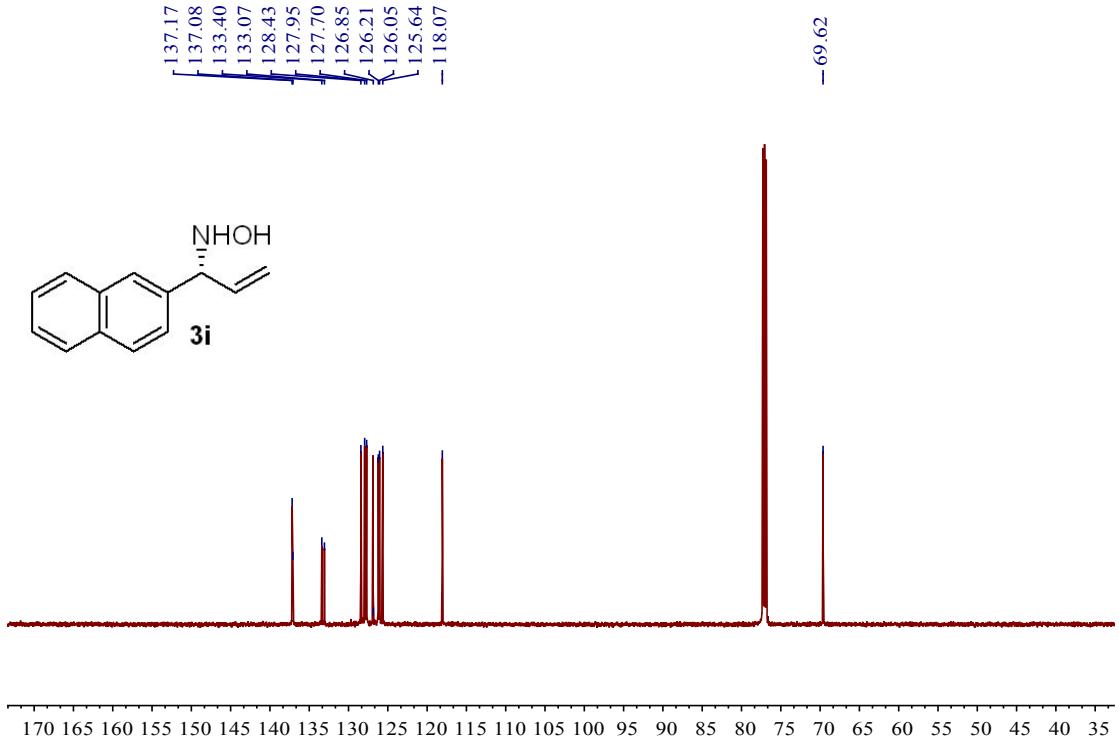
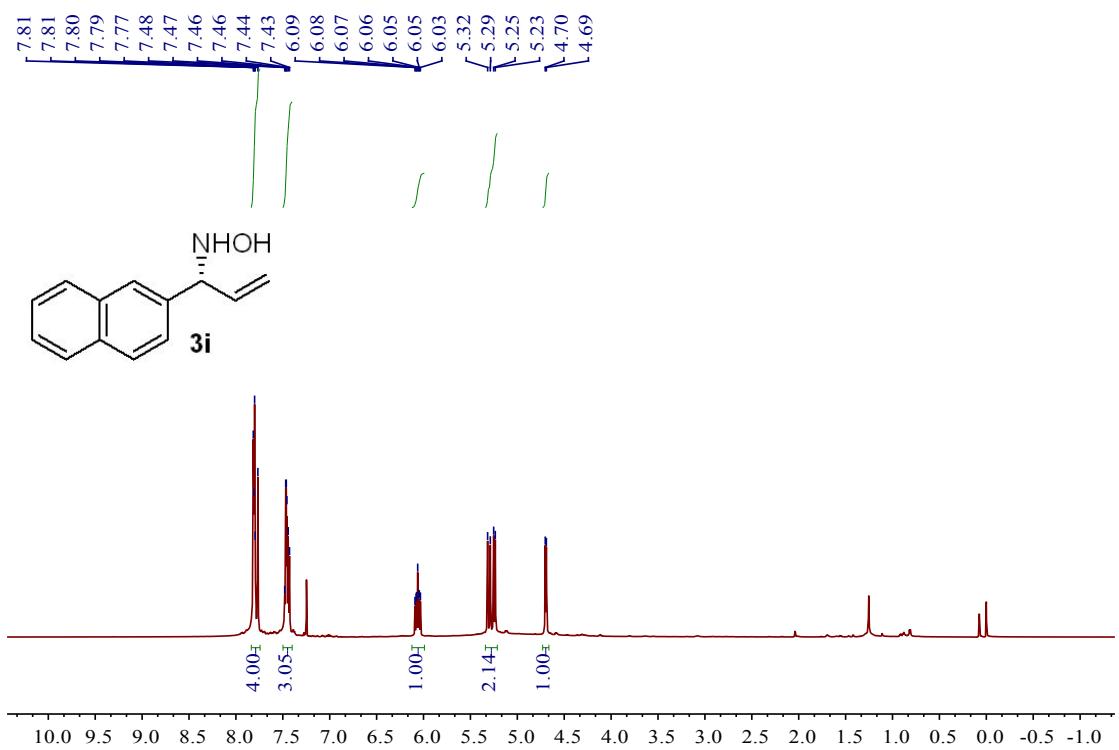


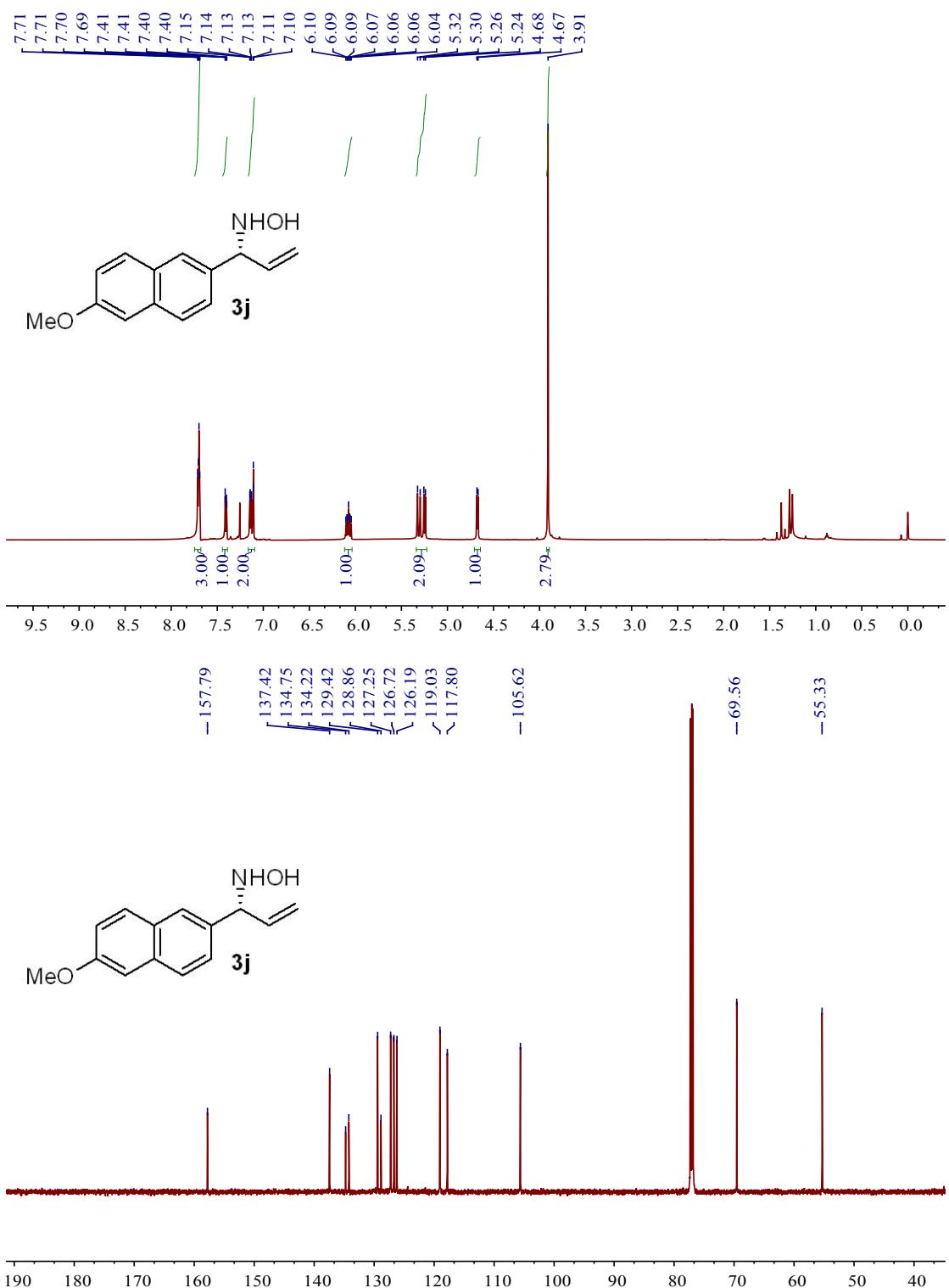


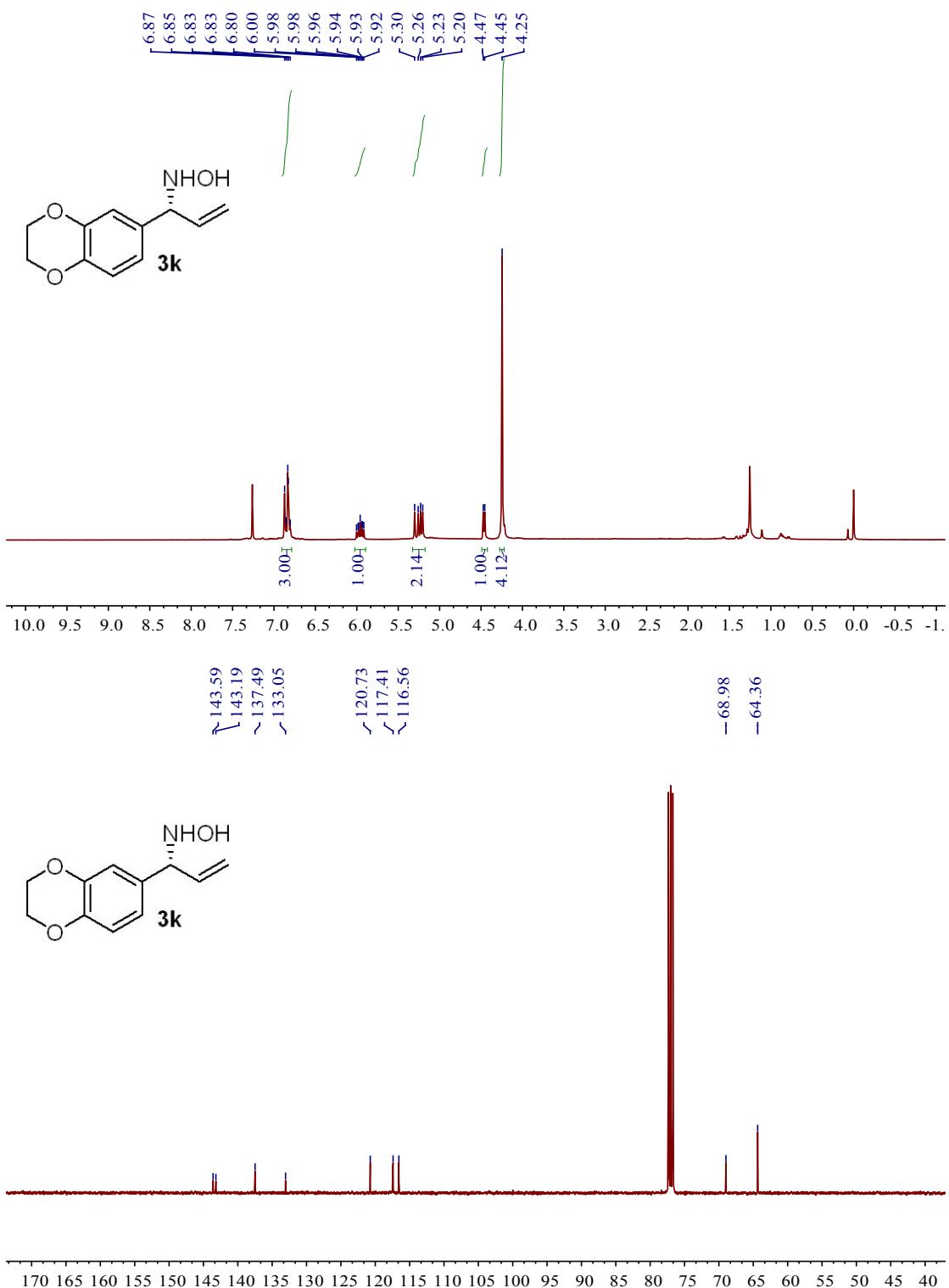


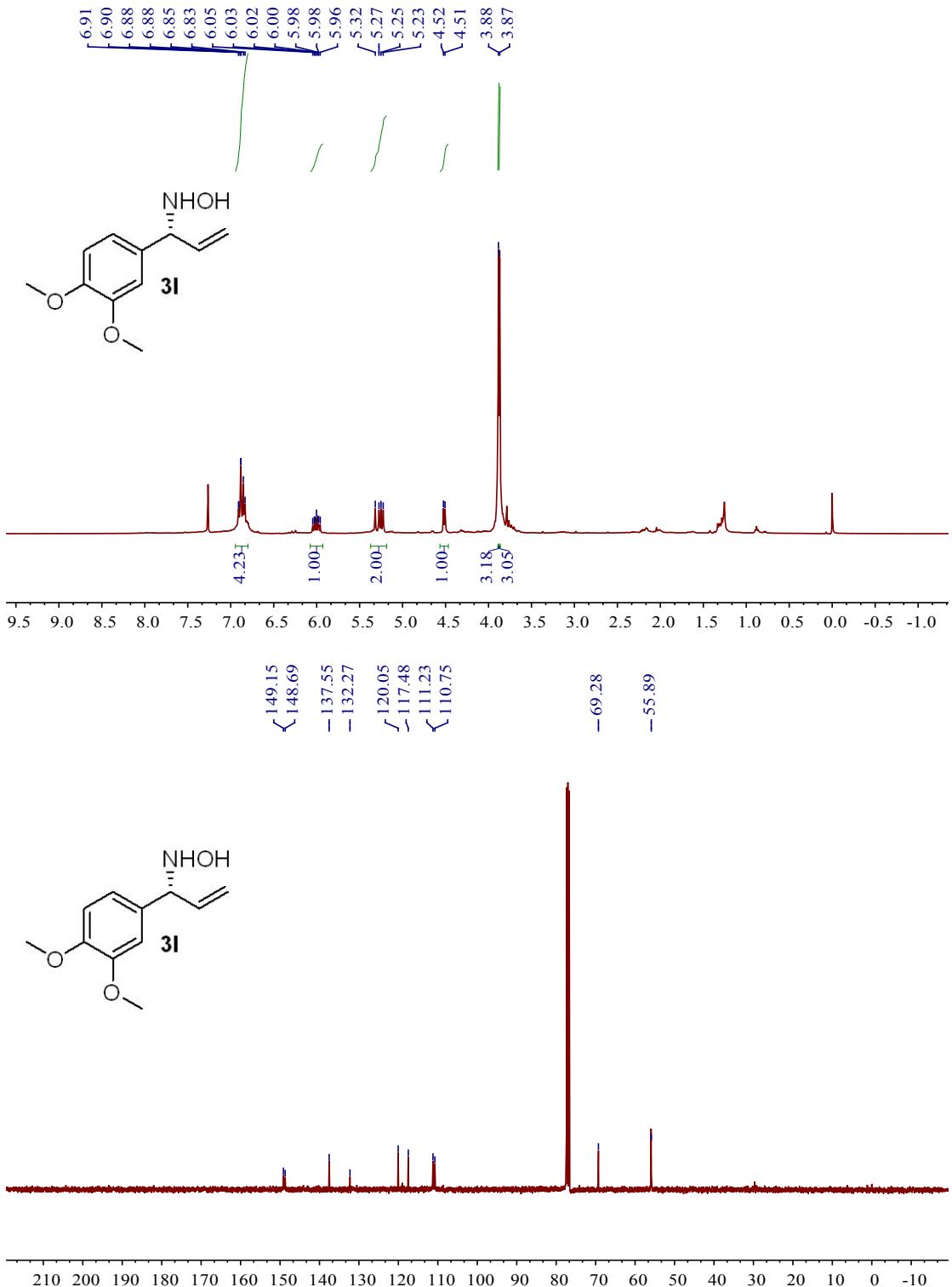


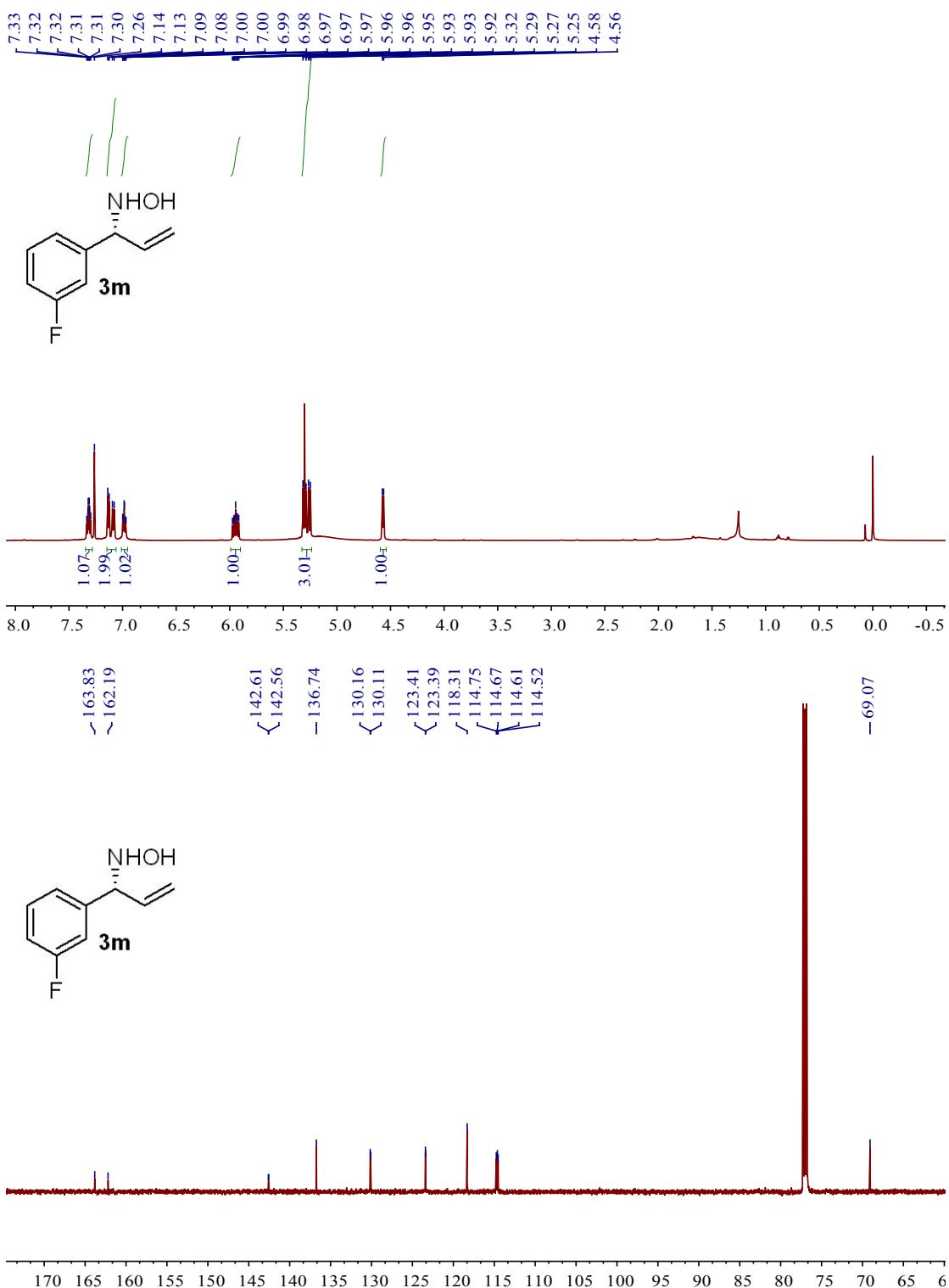


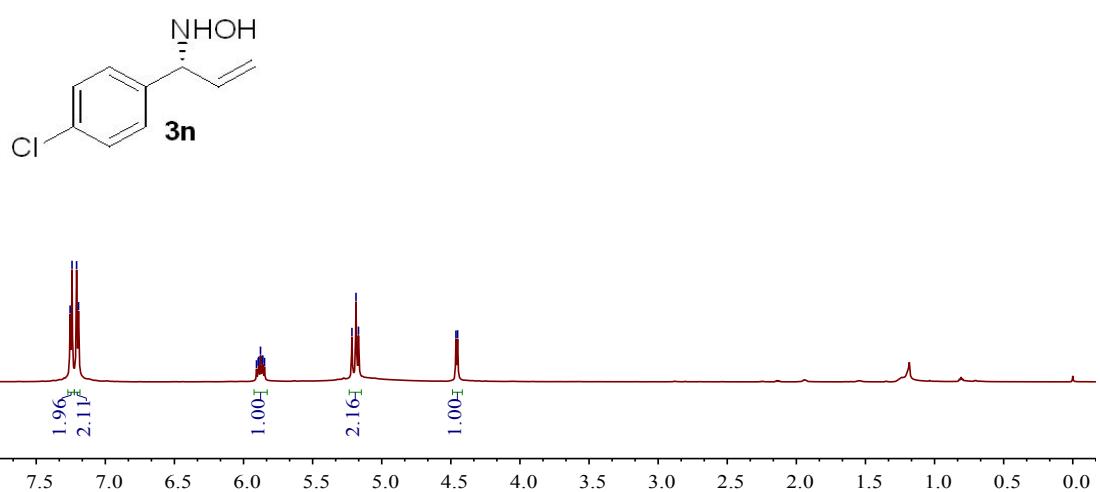
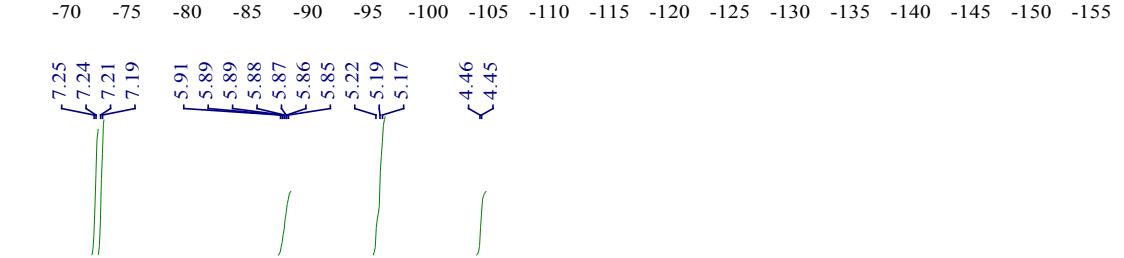
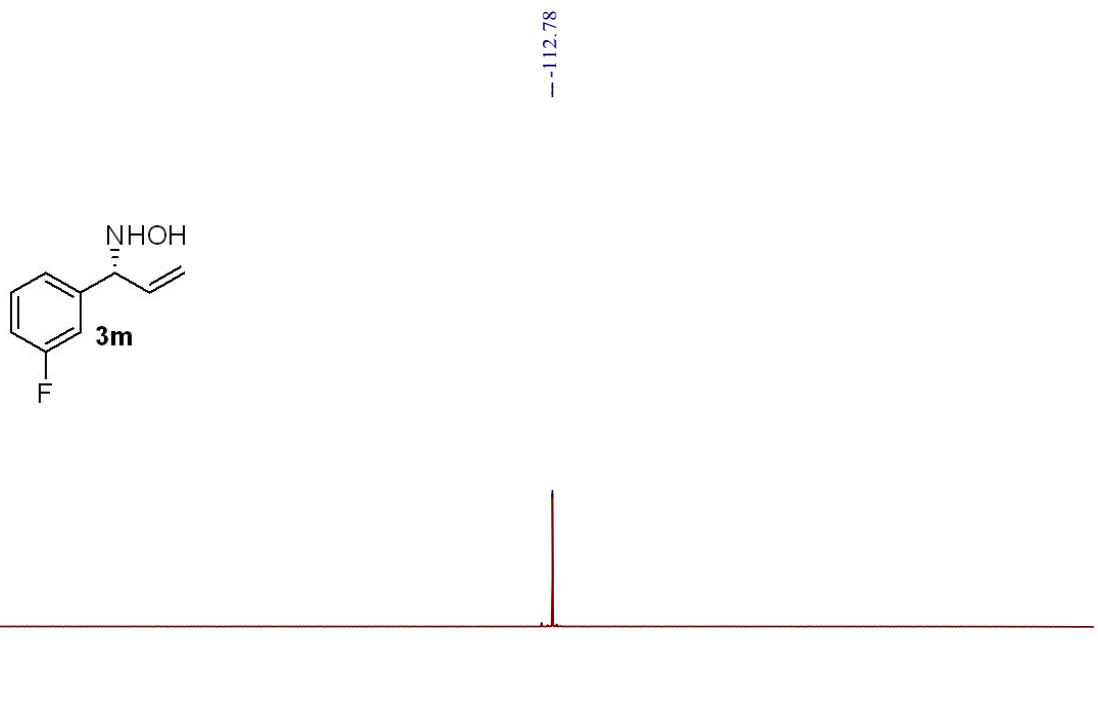


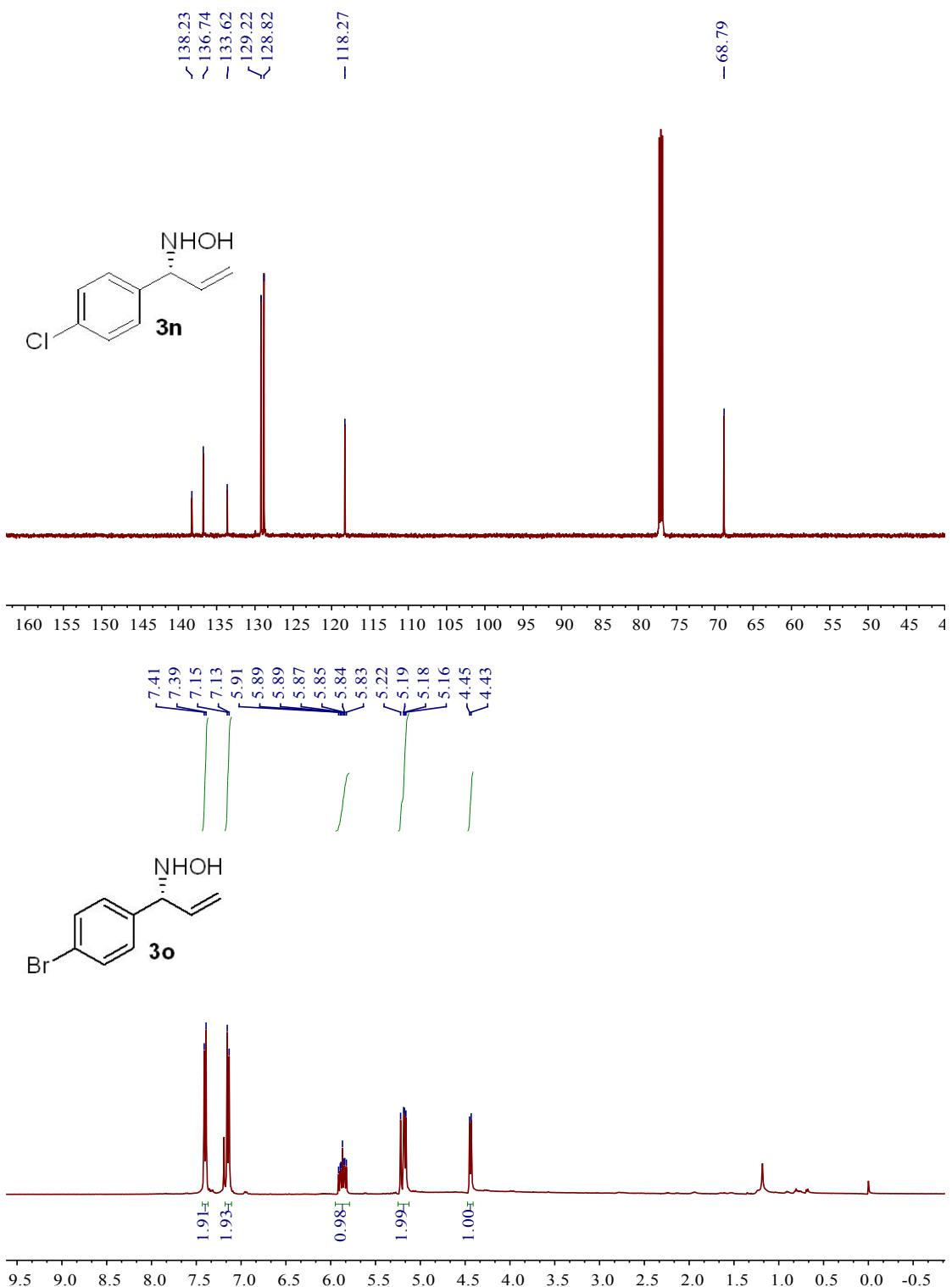


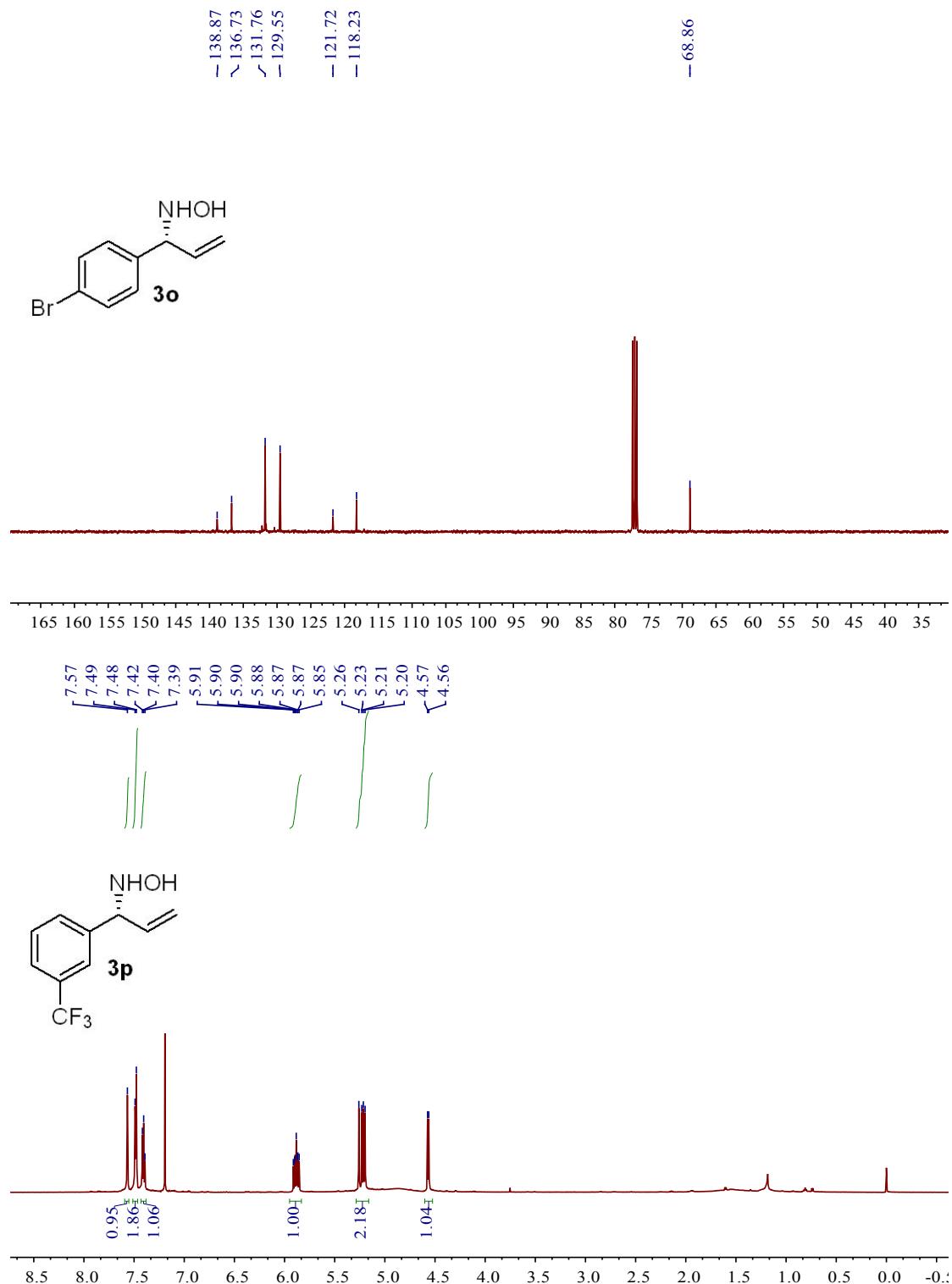


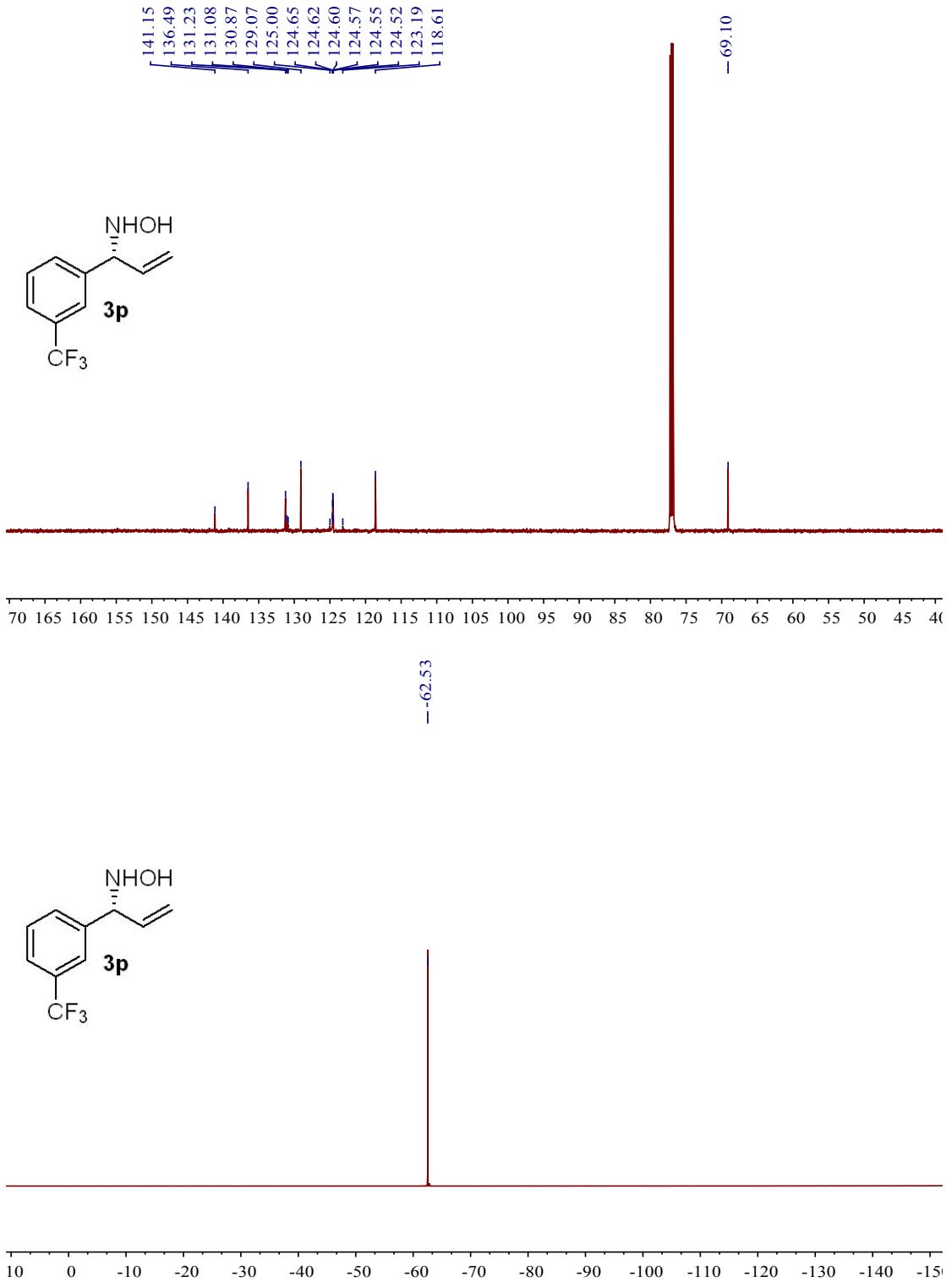


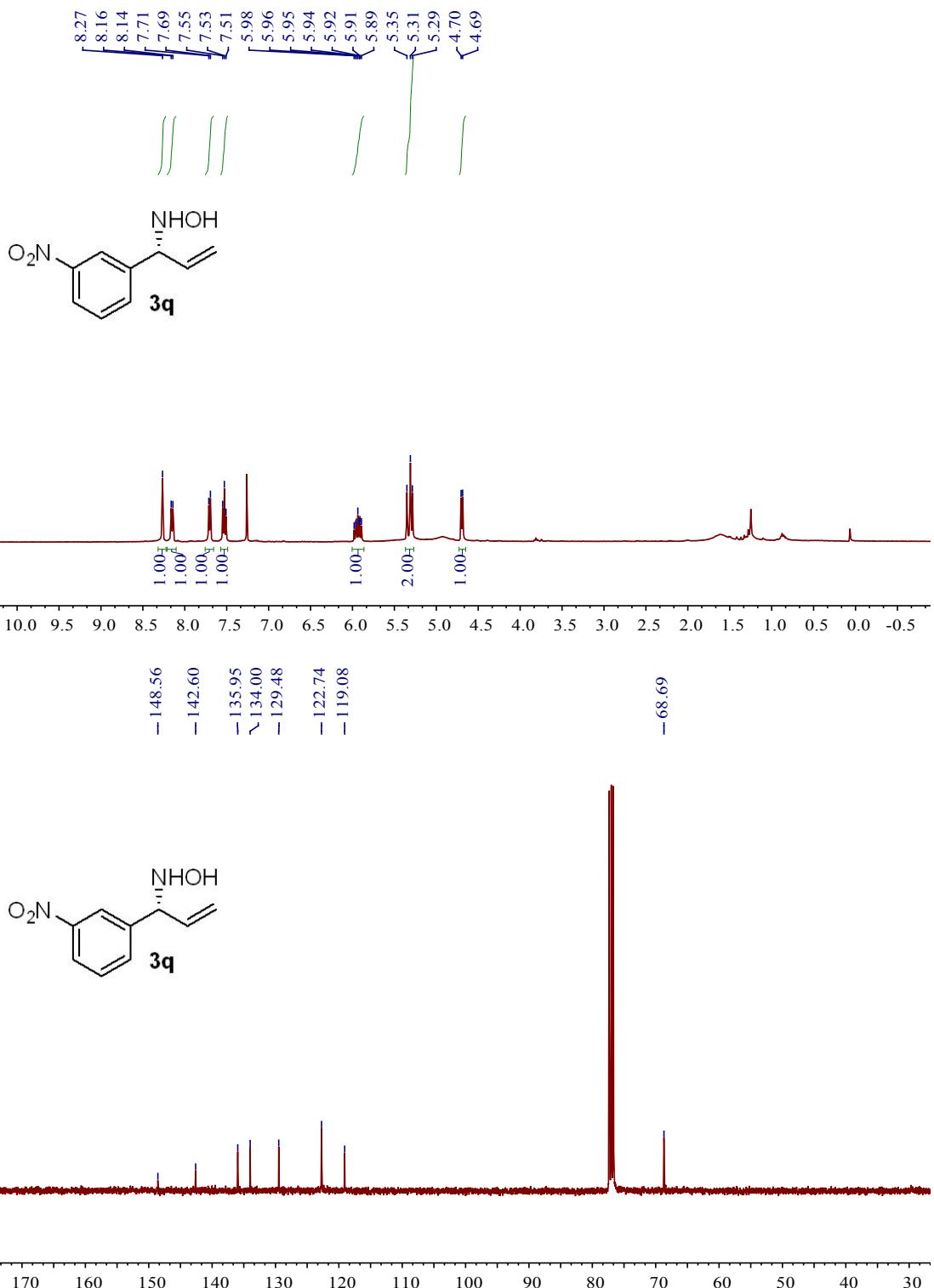


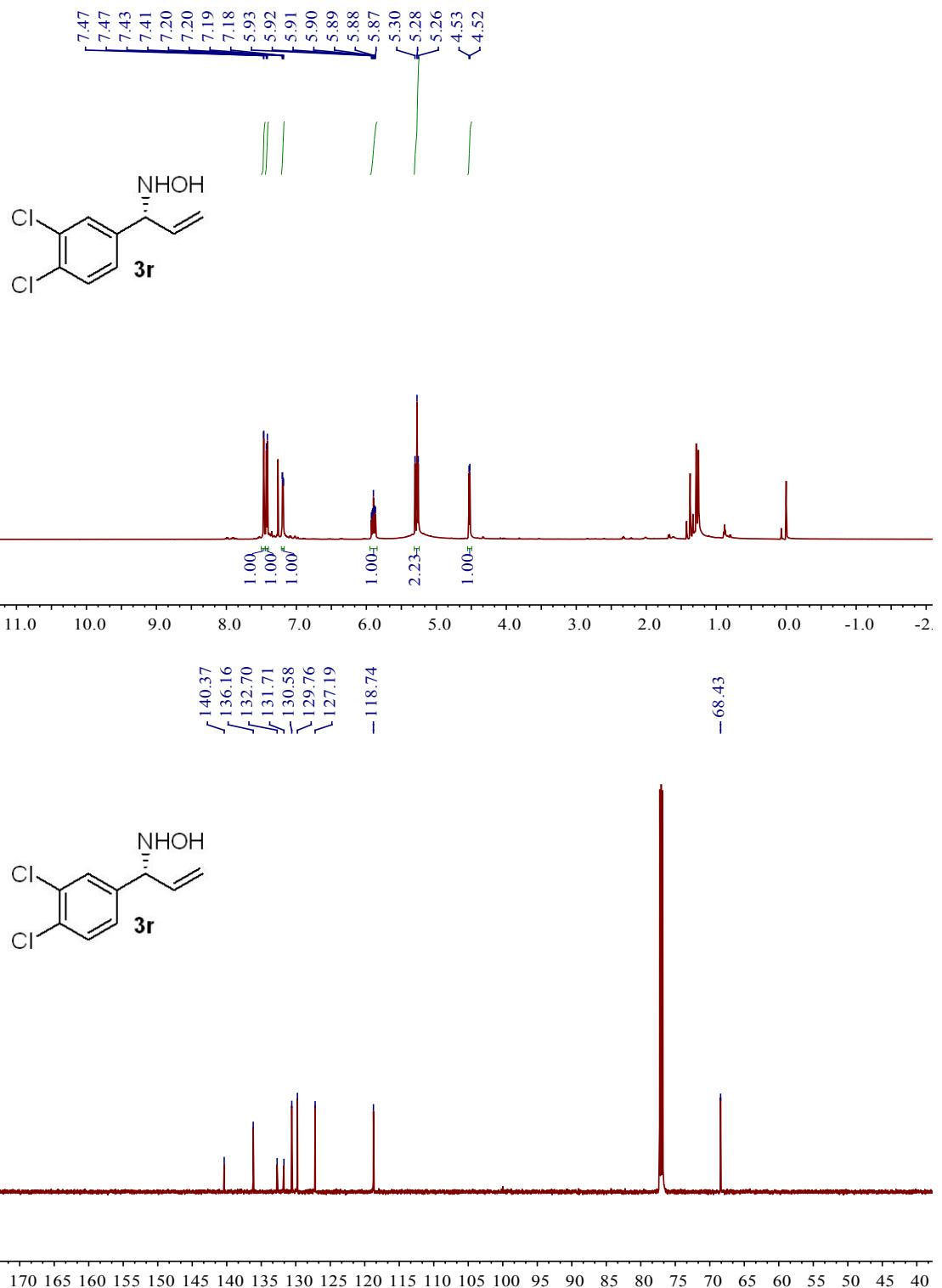


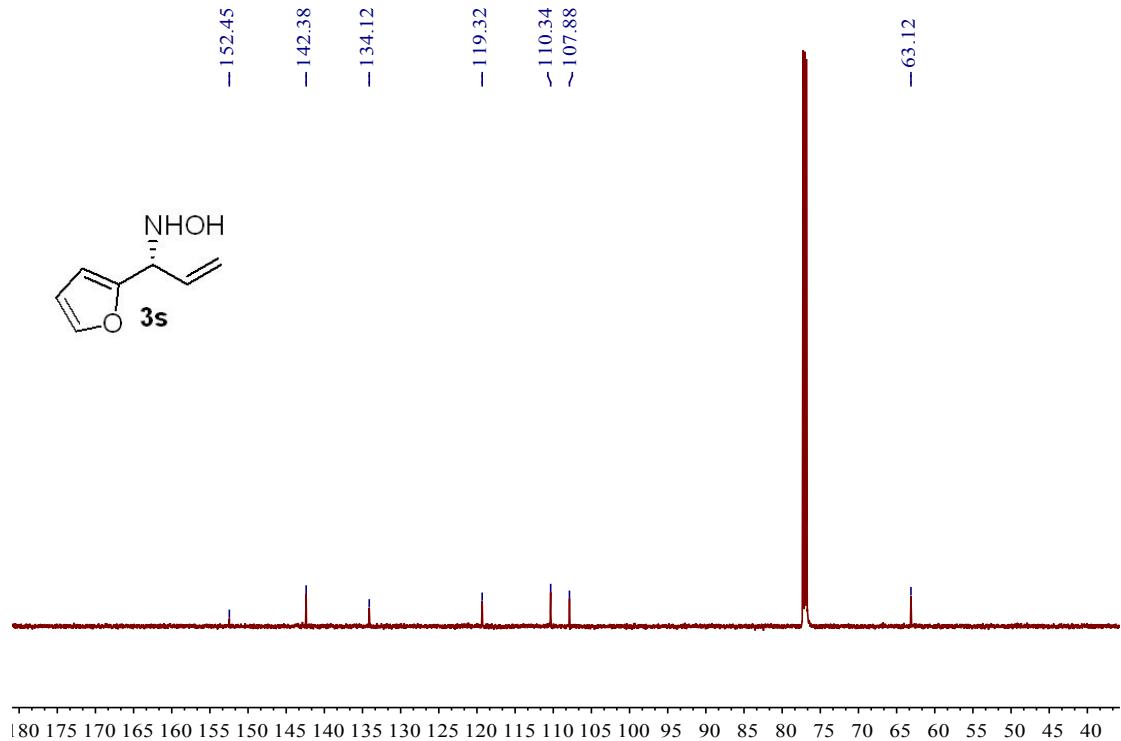
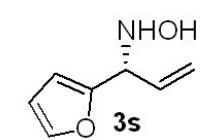
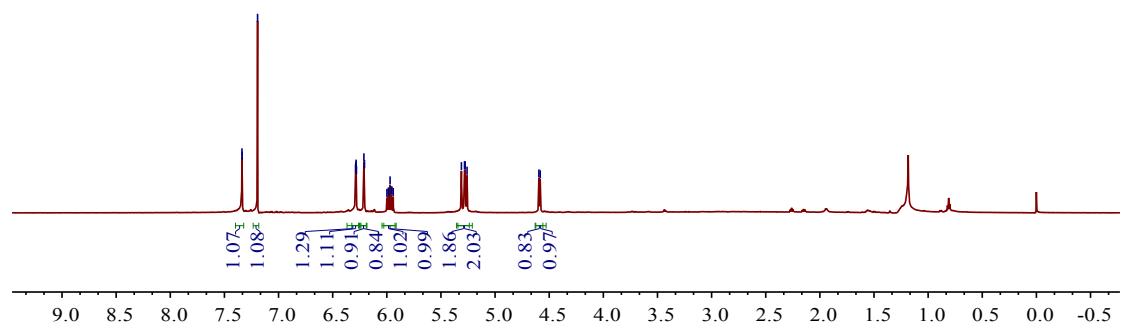
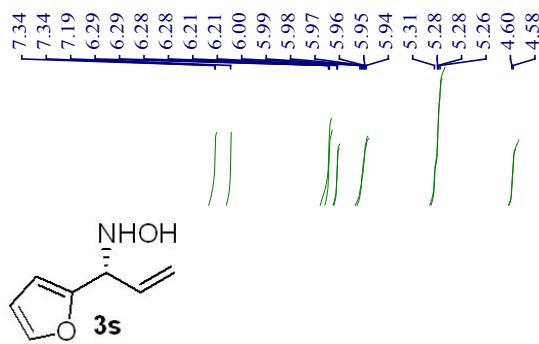


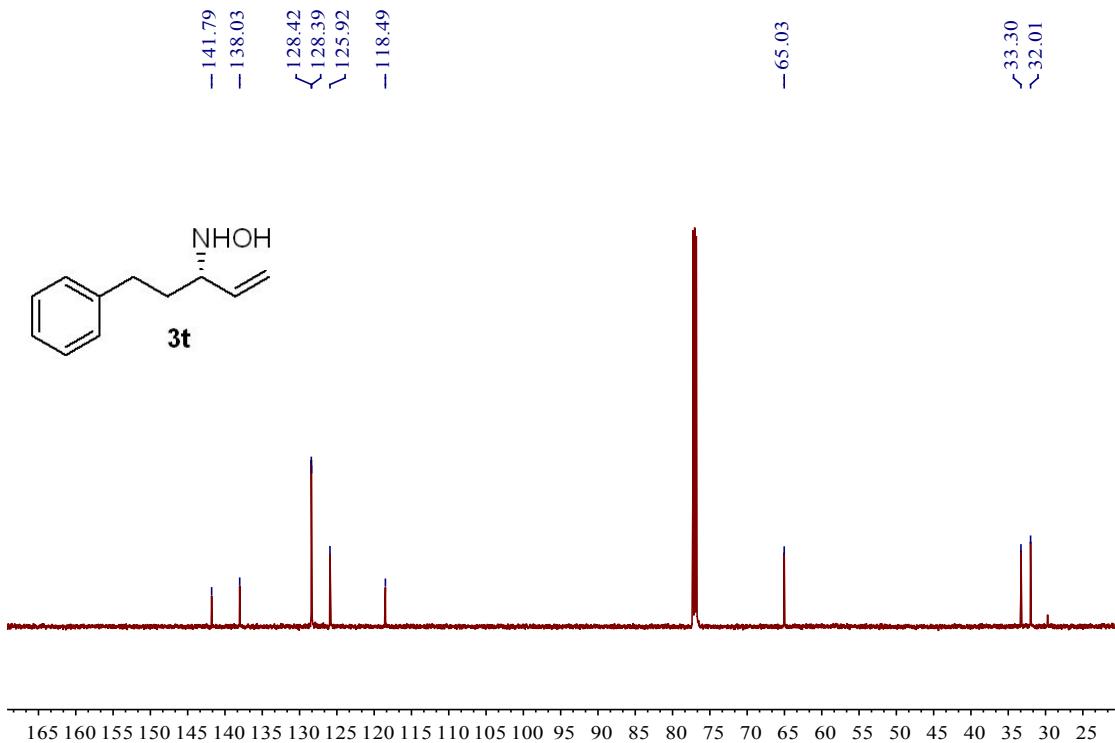
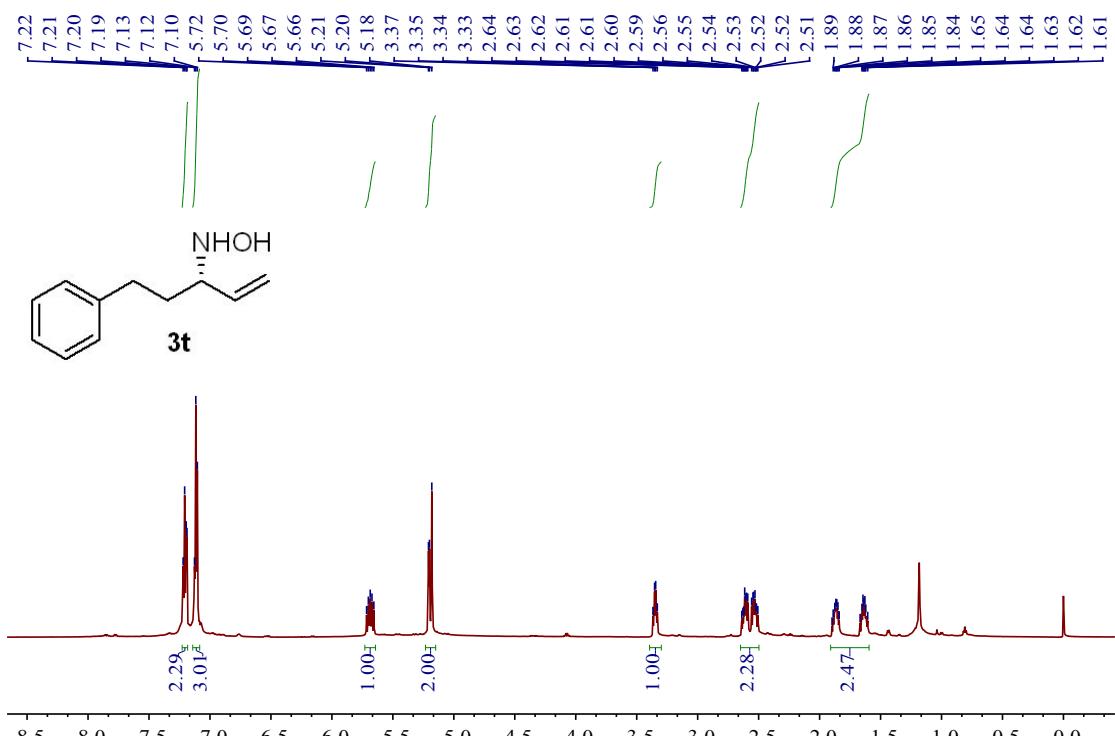


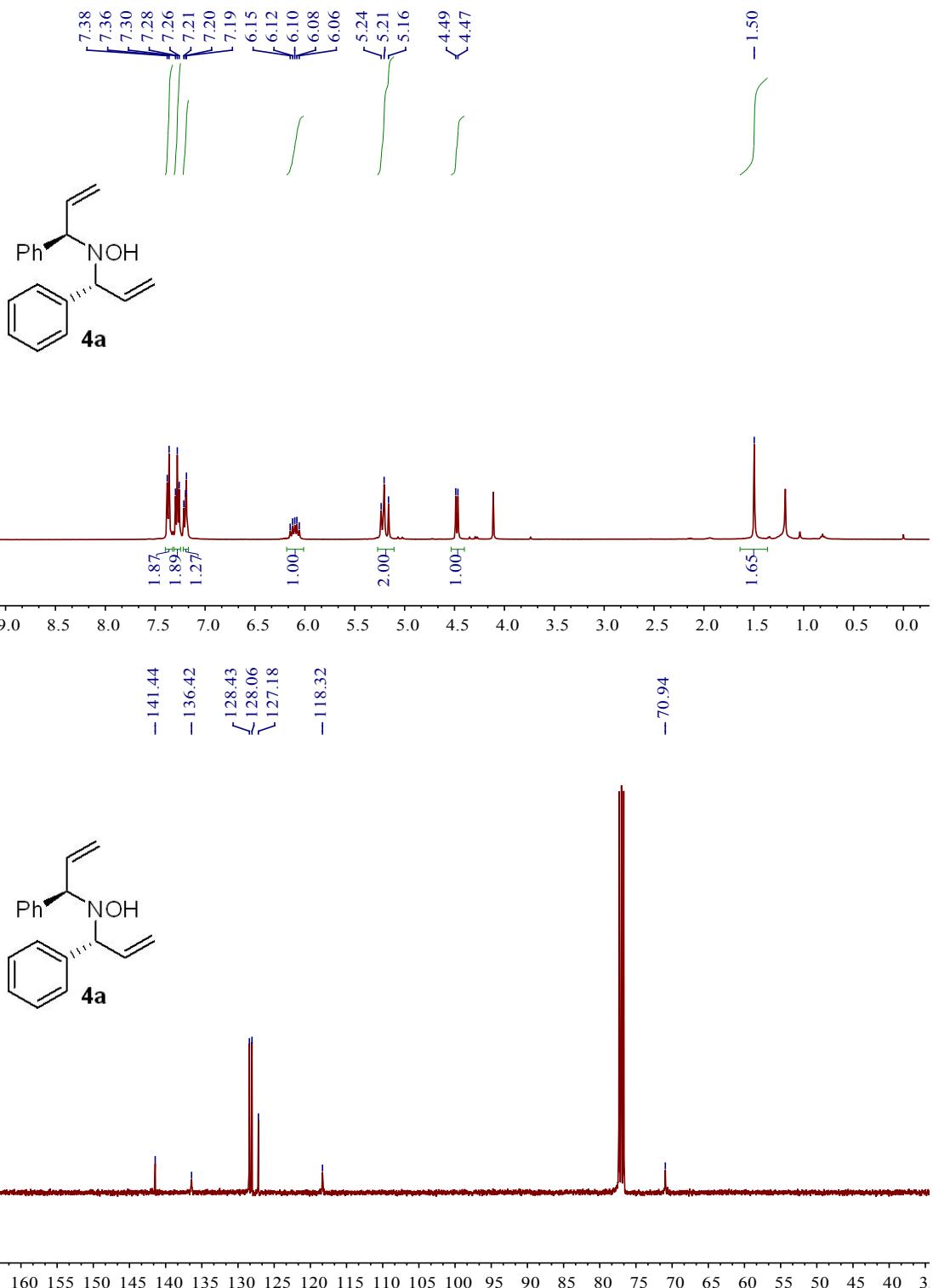


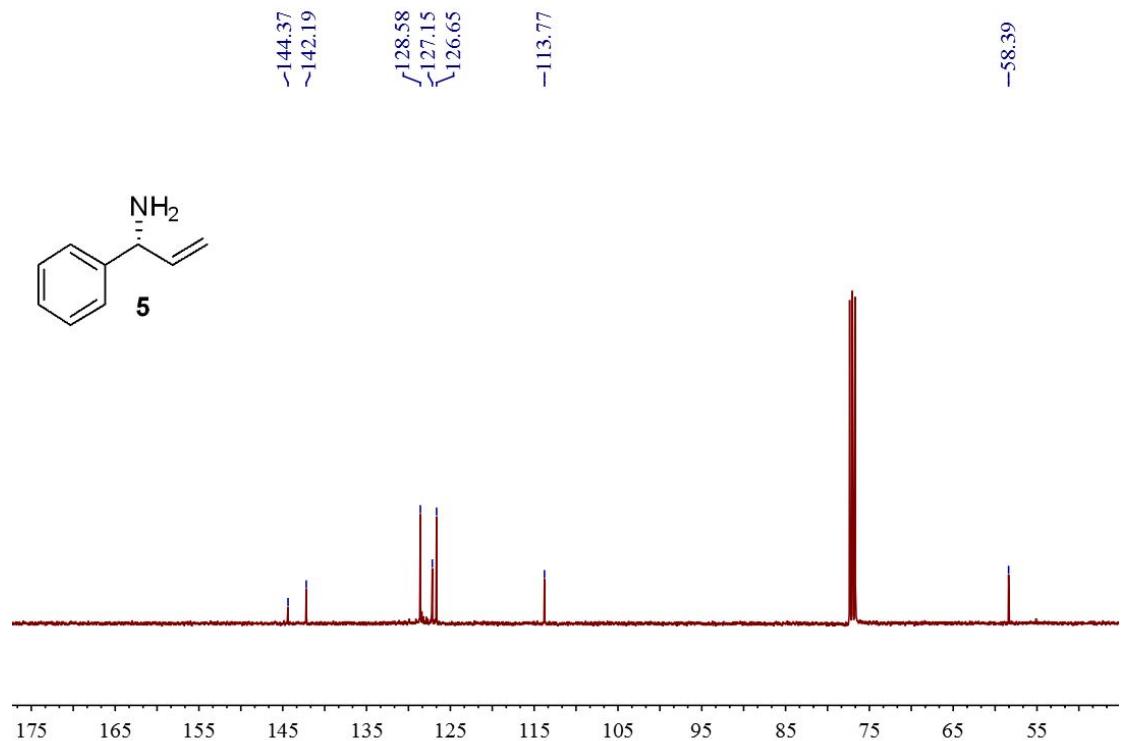
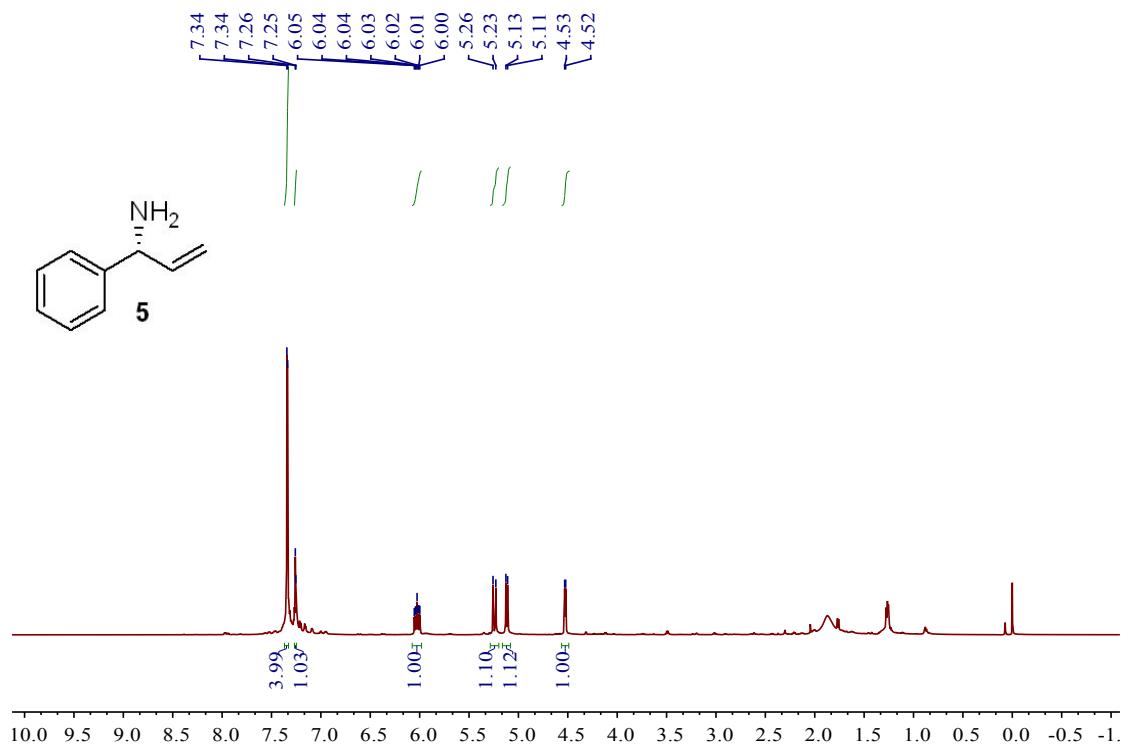


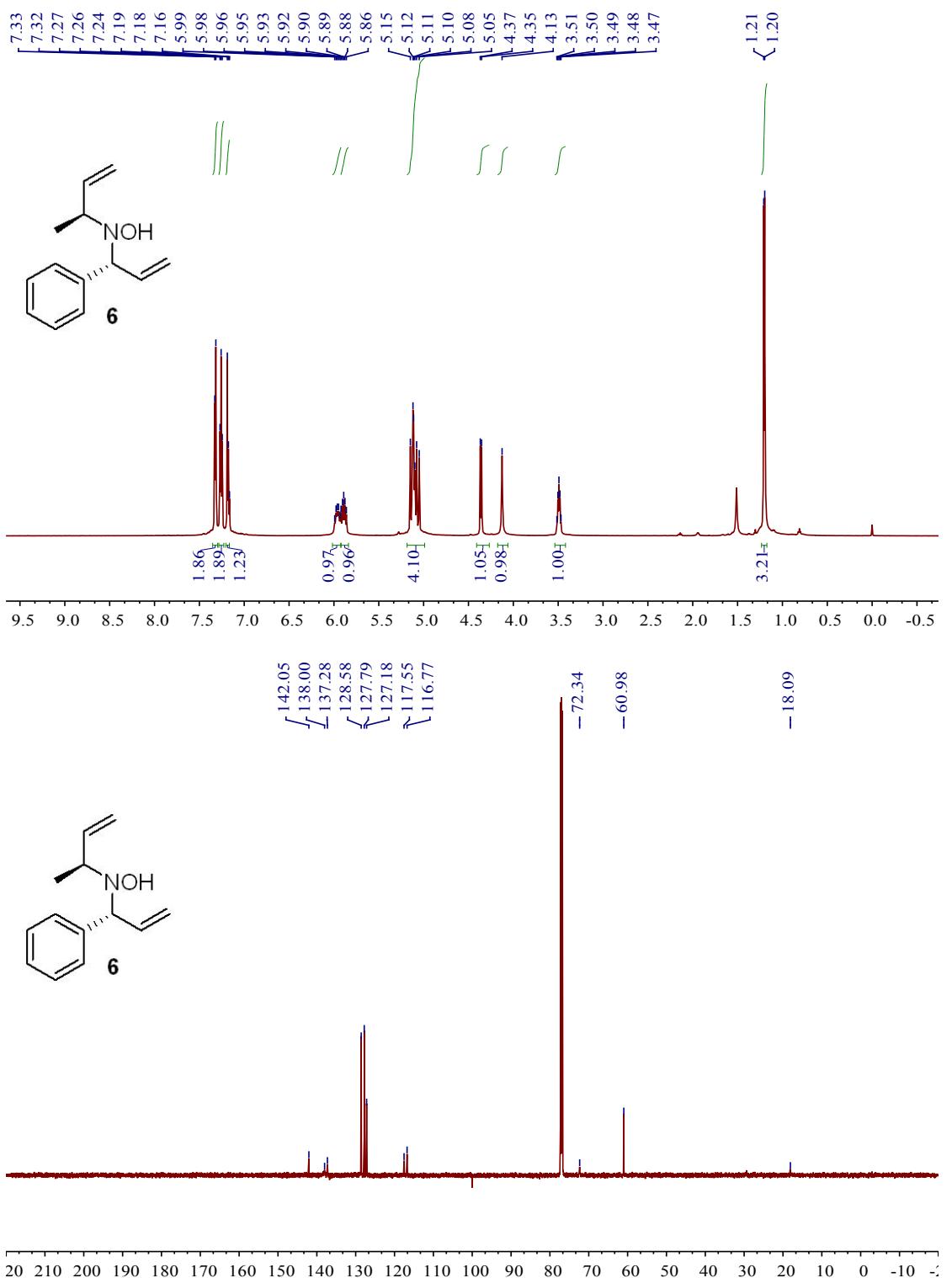


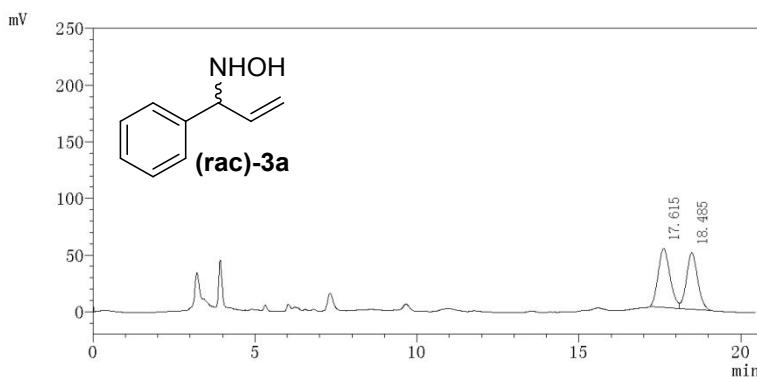




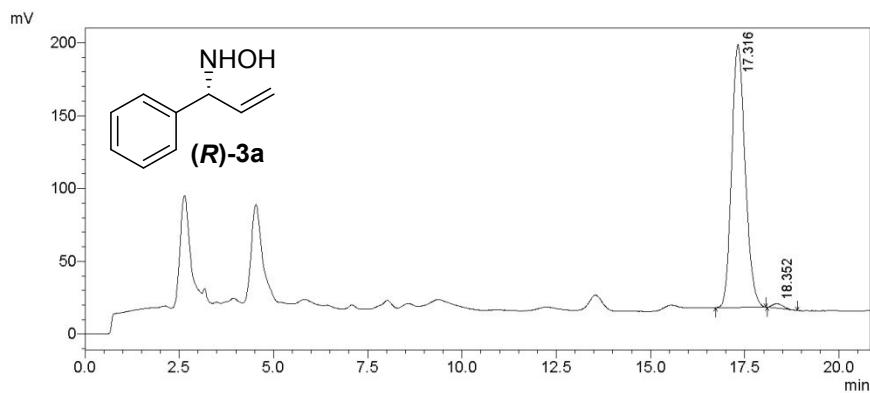




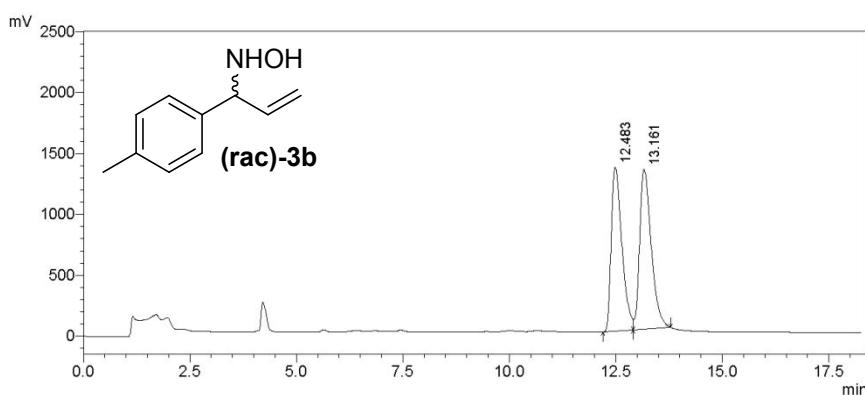




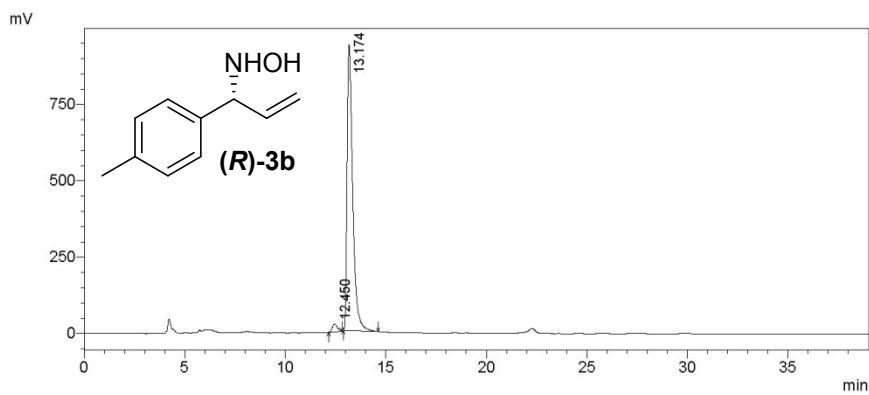
Peak No.	R. Time	Peak Area	Percent
1	17.615	1314490	52.241
2	18.485	1201699	47.759
Total		2516190	100.000



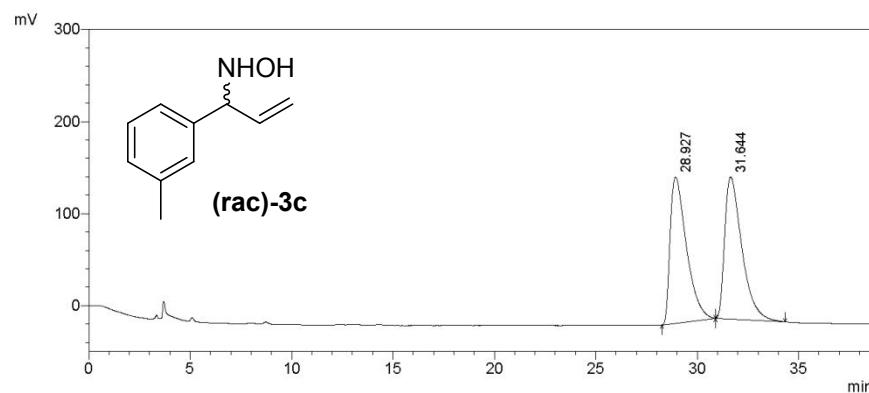
Peak No.	R. Time	Peak Area	Percent
1	17.316	4485002	98.649
2	18.352	61426	1.351
Total		4546428	100.000



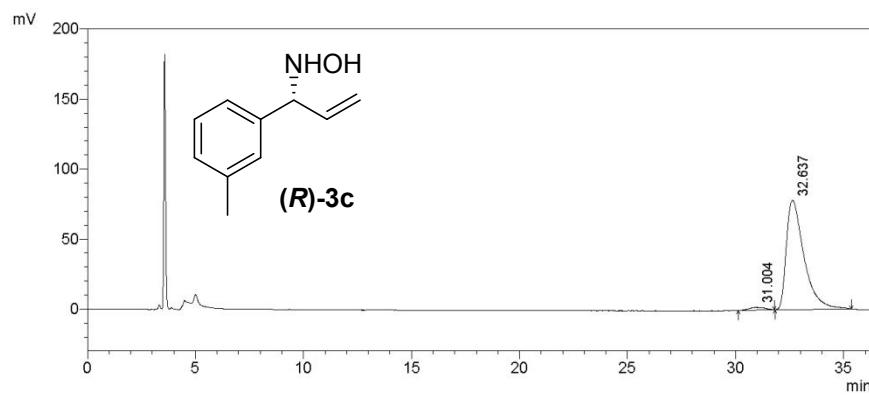
Peak No.	R. Time	Peak Area	Percent
1	12.483	23408745	48.426
2	13.161	24930319	51.574
Total		48339064	100.000



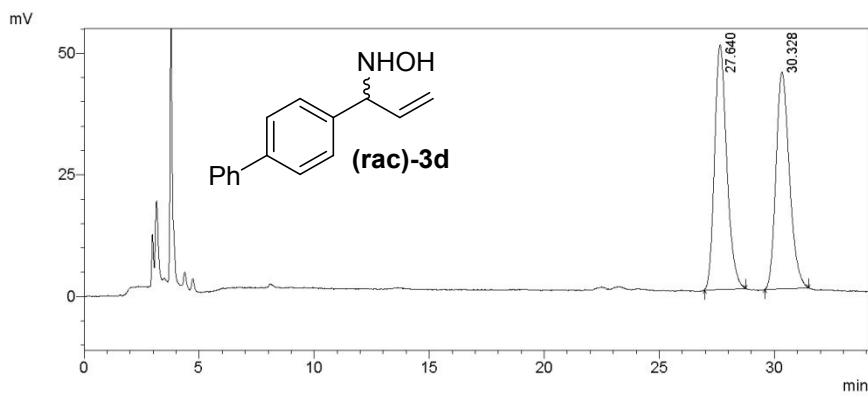
Peak No.	R. Time	Peak Area	Percent
1	12.450	454359	2.422
2	13.174	18305797	97.578
Total		18760156	100.000



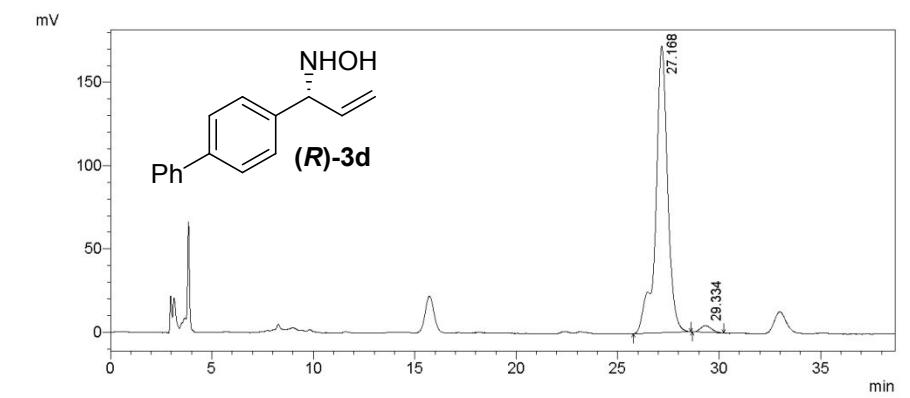
Peak No.	R. Time	Peak Area	Percent
1	28.927	8905269	49.417
2	31.644	9115570	50.583
Total		18020839	100.000



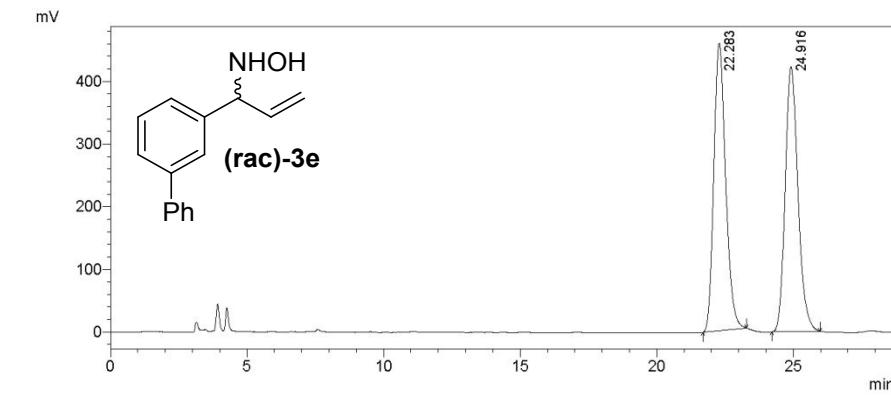
Peak No.	R. Time	Peak Area	Percent
1	31.004	91481	2.028
2	32.637	4418748	97.972
Total		4510229	100.000



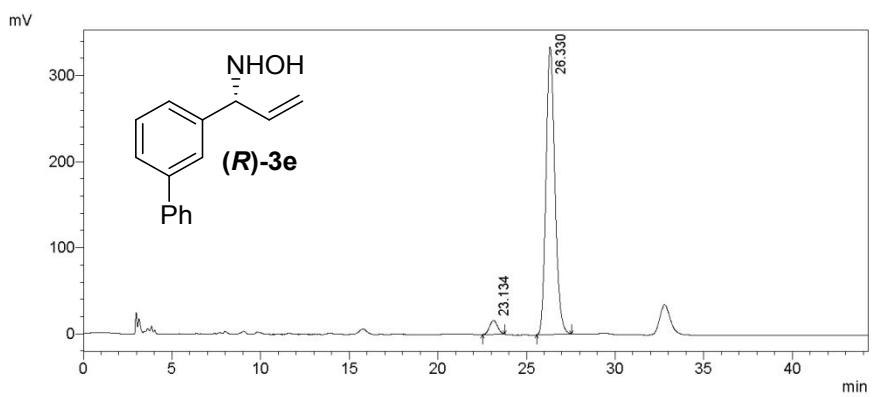
Peak No.	R. Time	Peak Area	Percent
1	27.640	1846653	50.596
2	30.328	1803169	49.404
Total		3649822	100.000



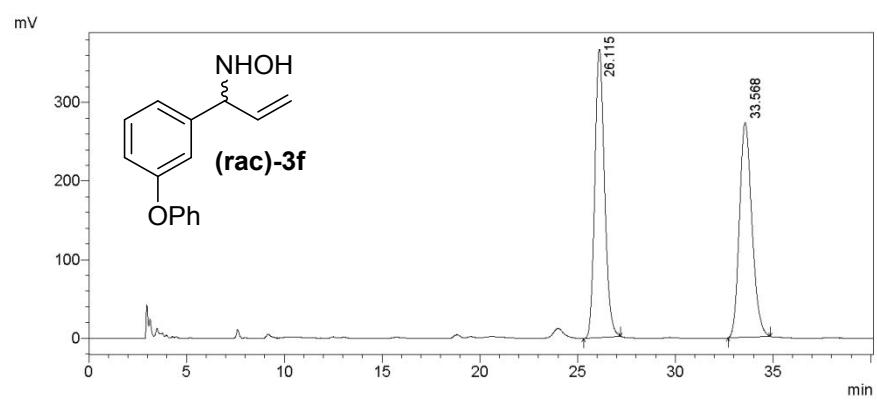
Peak No.	R. Time	Peak Area	Percent
1	27.168	7079386	97.870
2	29.334	154067	2.130
Total		7233453	100.000



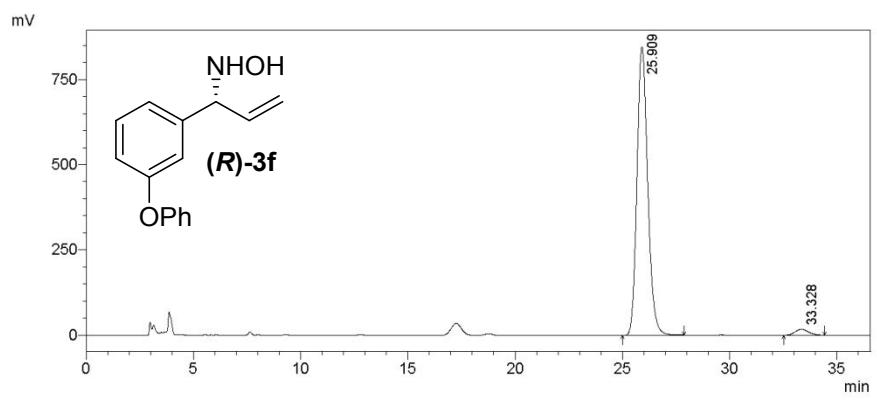
Peak No.	R. Time	Peak Area	Percent
1	22.283	13802903	50.093
2	24.916	13751844	49.900
Total		27554747	100.000



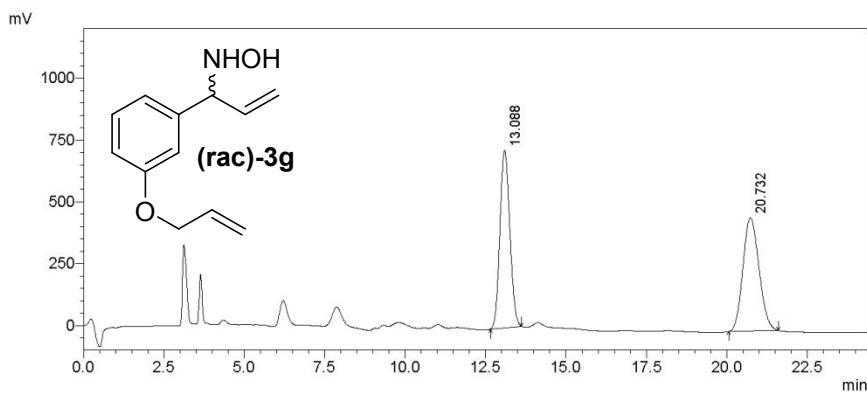
Peak No.	R. Time	Peak Area	Percent
1	23.134	502730	4.133
2	26.330	11662420	95.867
Total		12165150	100.000



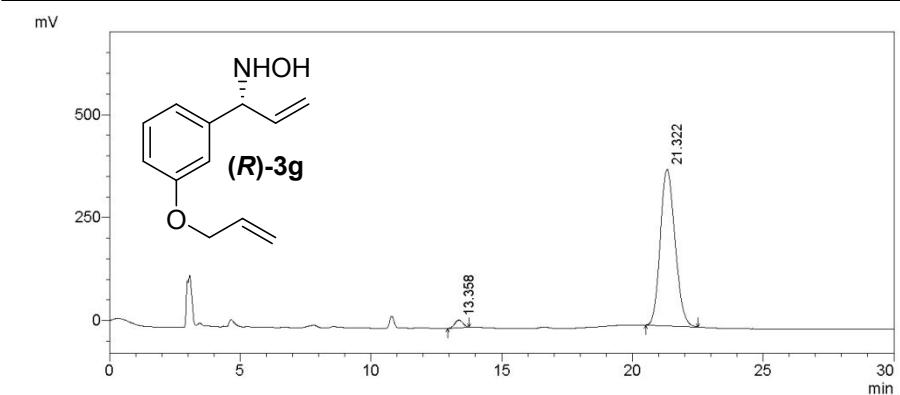
Peak No.	R. Time	Peak Area	Percent
1	26.115	12654543	51.087
2	33.568	12115888	48.913
Total		24770432	100.000



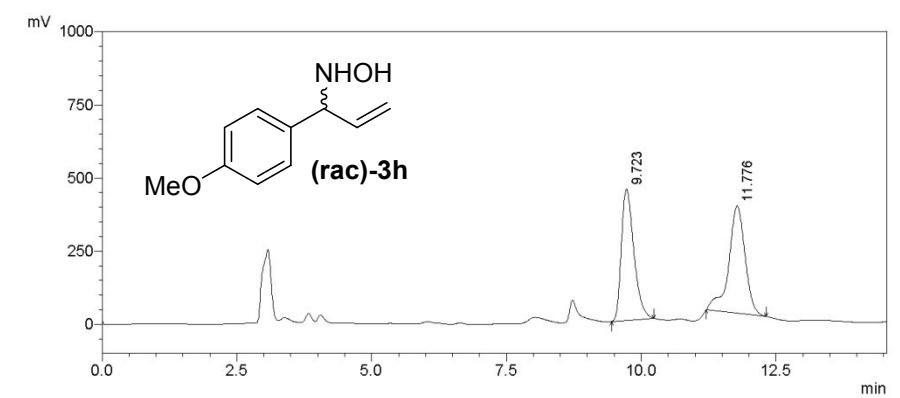
Peak No.	R. Time	Peak Area	Percent
1	25.909	29517583	97.438
2	33.328	776238	2.562
Total		30293821	100.000



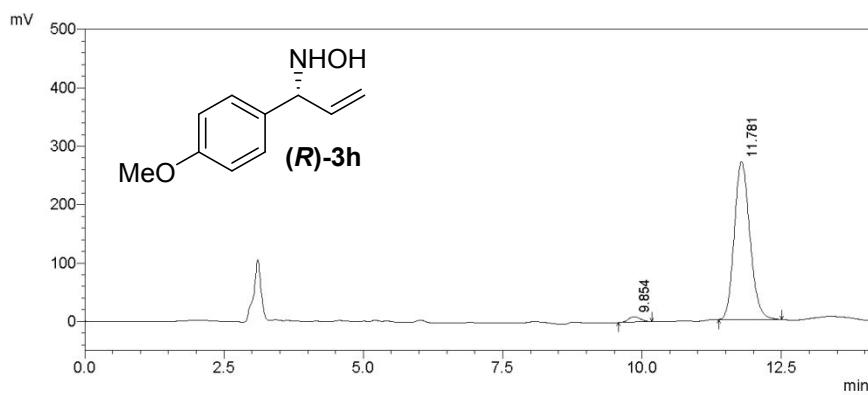
Peak No.	R. Time	Peak Area	Percent
1	13.088	15394948	49.065
2	20.732	1598102	50.935
Total		31376550	100.000



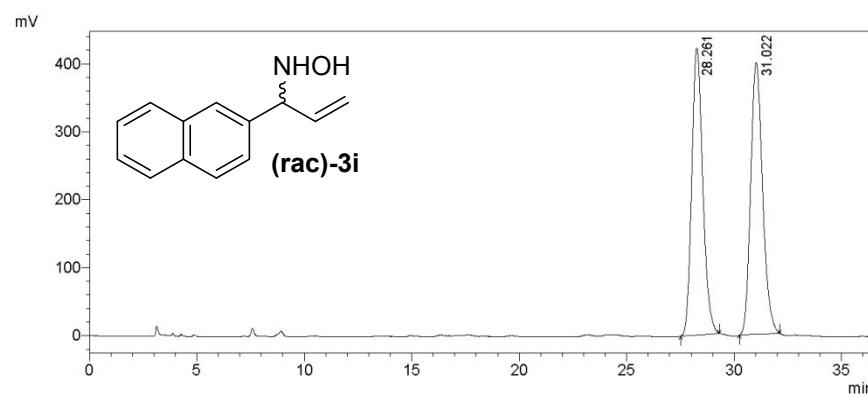
Peak No.	R. Time	Peak Area	Percent
1	13.358	402945	2.634
2	21.322	14892330	97.366
Total		15295275	100.000



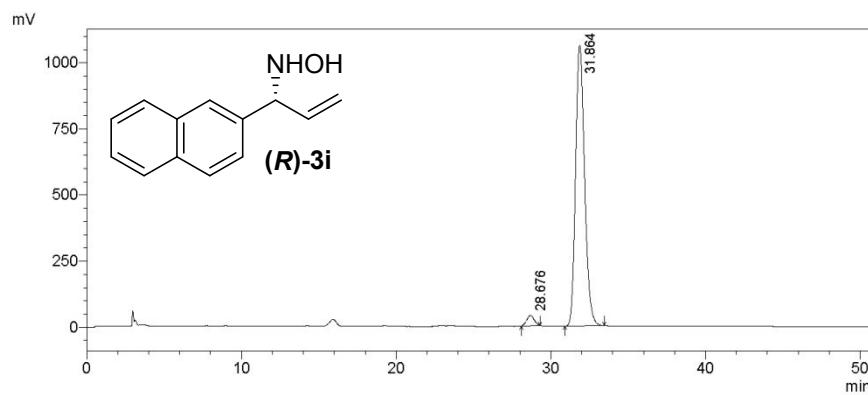
Peak No.	R. Time	Peak Area	Percent
1	9.723	7211936	48.119
2	11.776	7775888	51.881
Total		14987824	100.000



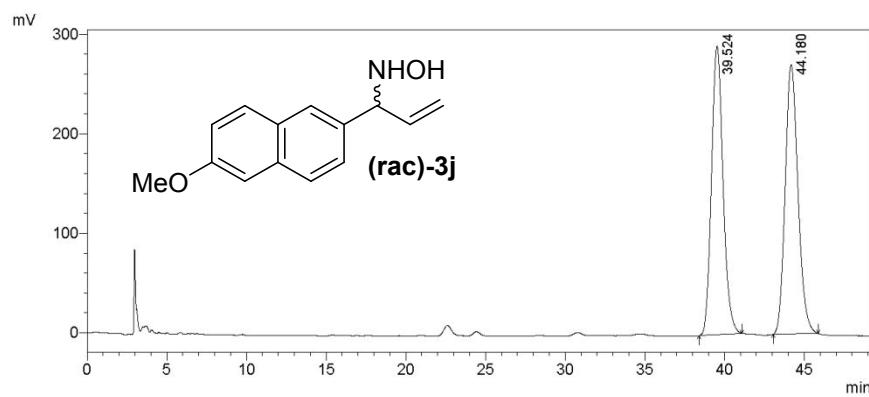
Peak No.	R. Time	Peak Area	Percent
1	9.854	139095	2.582
2	11.781	5247730	97.418
Total		5386825	100.000



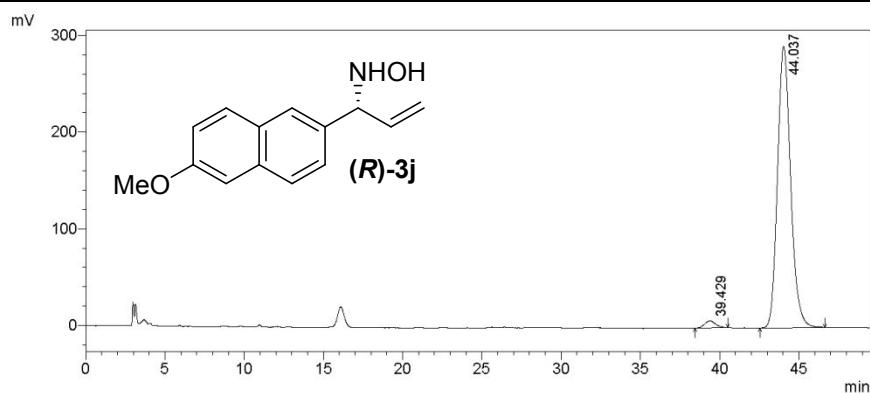
Peak No.	R. Time	Peak Area	Percent
1	28.261	15063577	49.364
2	31.022	15451648	50.636
Total		30515225	100.000



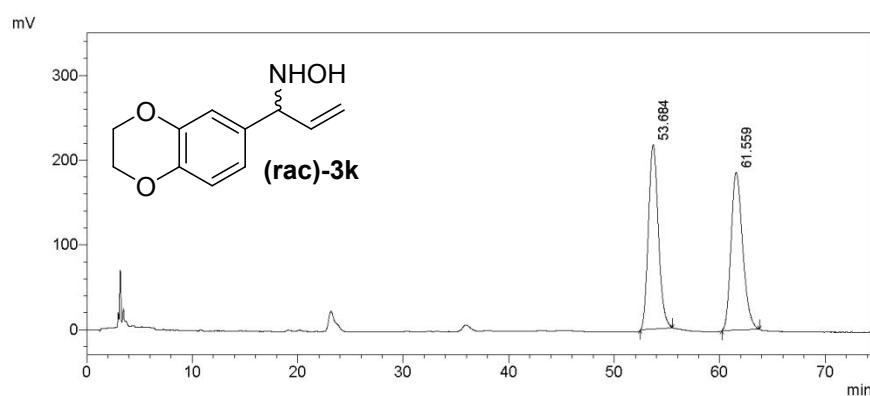
Peak No.	R. Time	Peak Area	Percent
1	28.676	1298973	2.924
2	31.864	43131397	97.076
Total		44430371	100.000



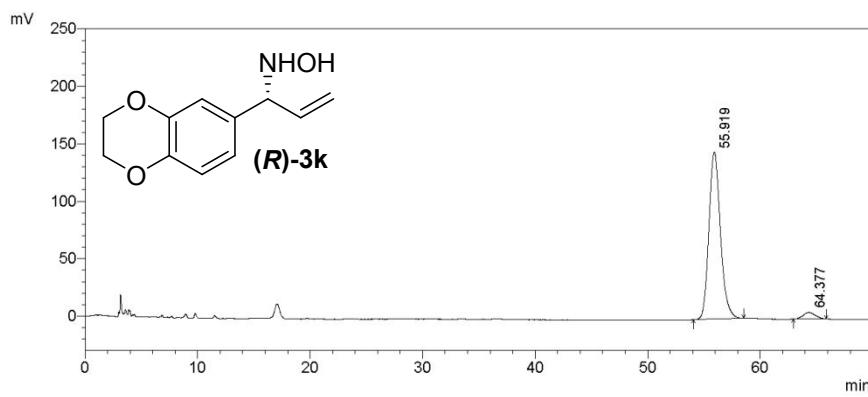
Peak No.	R. Time	Peak Area	Percent
1	39.524	14640064	49.208
2	44.180	15111542	50.792
Total		29751607	100.000



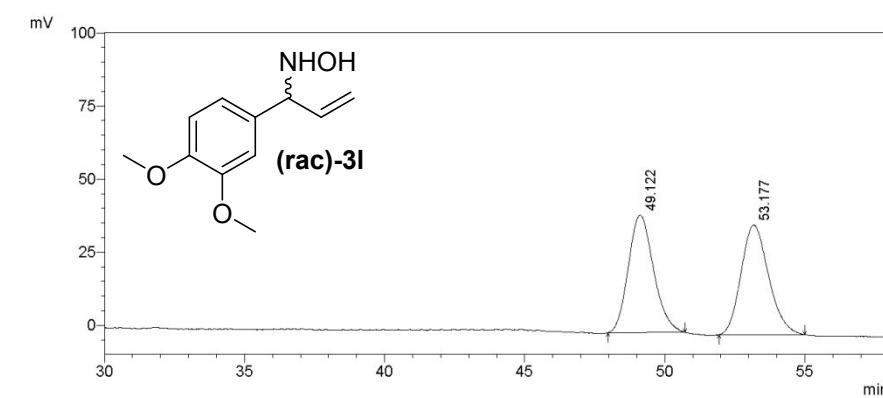
Peak No.	R. Time	Peak Area	Percent
1	39.429	352932	2.064
2	44.037	16742732	97.936
Total		17095664	100.000



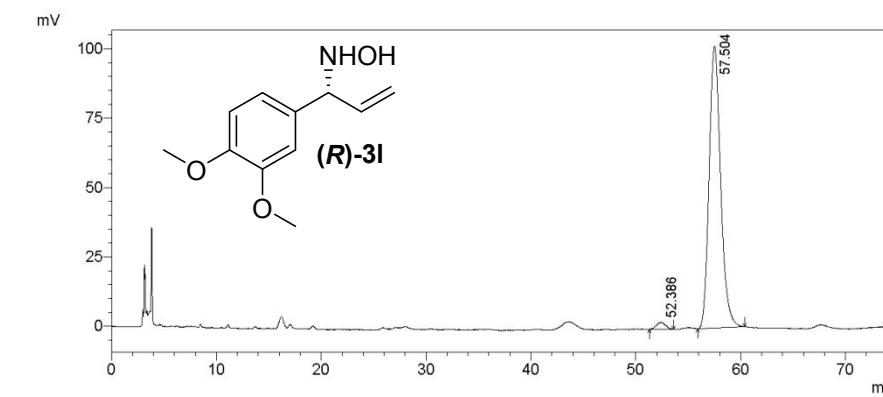
Peak No.	R. Time	Peak Area	Percent
1	53.684	14228798	49.895
2	61.559	14288860	50.105
Total		28517658	100.000



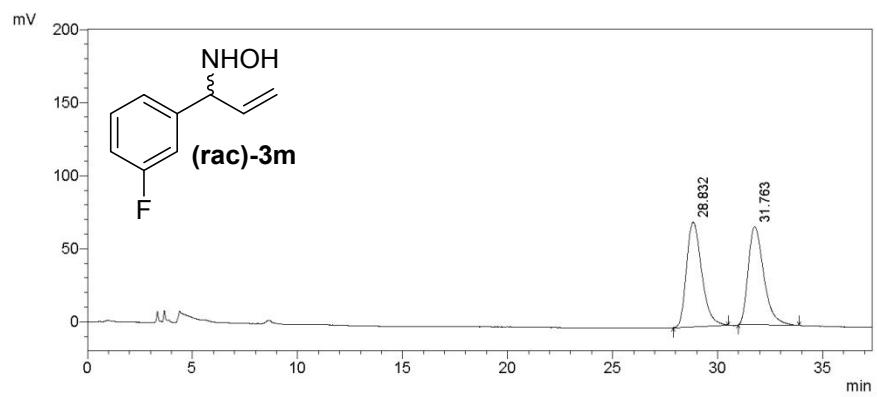
Peak No.	R. Time	Peak Area	Percent
1	55.919	10367450	96.032
2	64.377	428335	3.968
Total		10795785	100.000



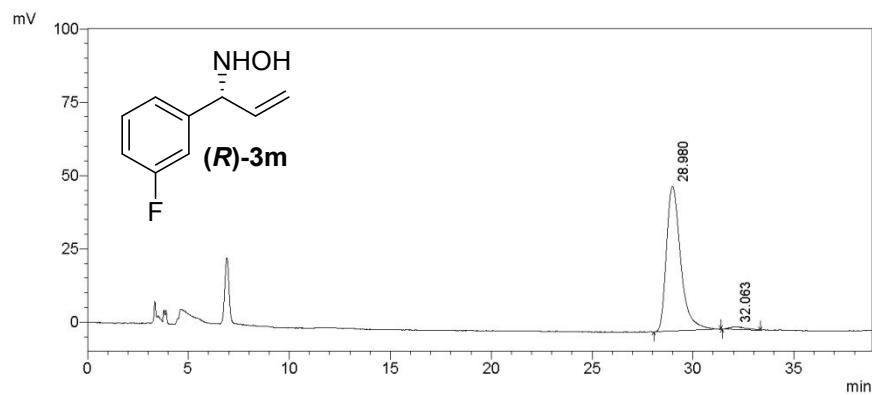
Peak No.	R. Time	Peak Area	Percent
1	49.122	2521378	49.431
2	53.177	2579419	50.569
Total		5100798	100.000



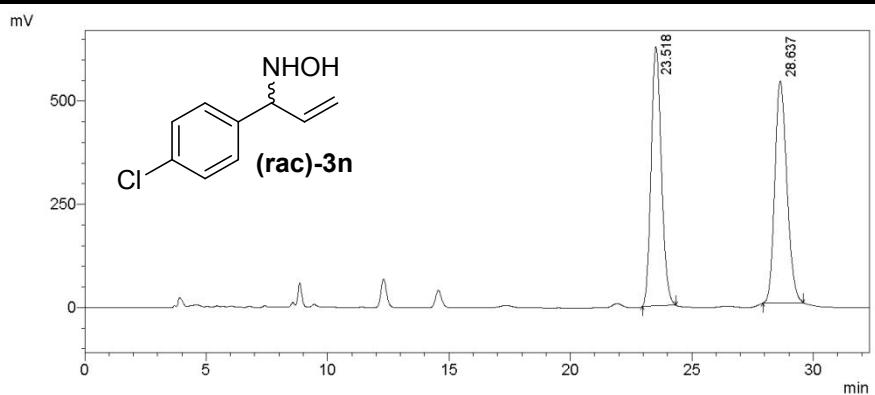
Peak No.	R. Time	Peak Area	Percent
1	52.386	153810	1.942
2	57.504	7764780	98.058
Total		7918590	100.000



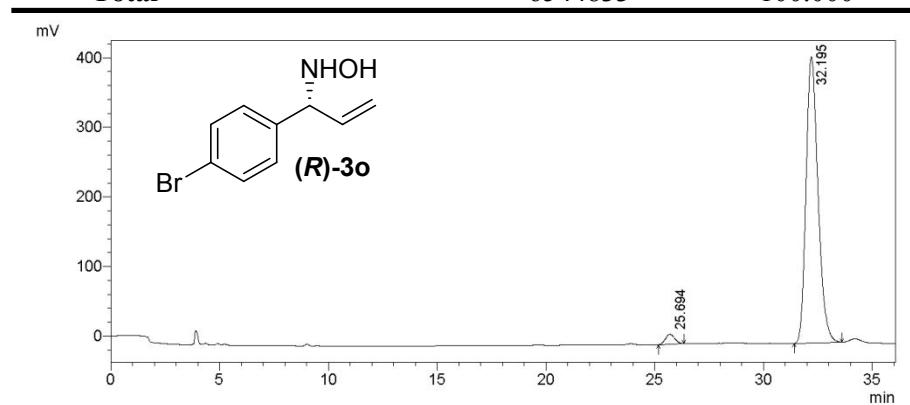
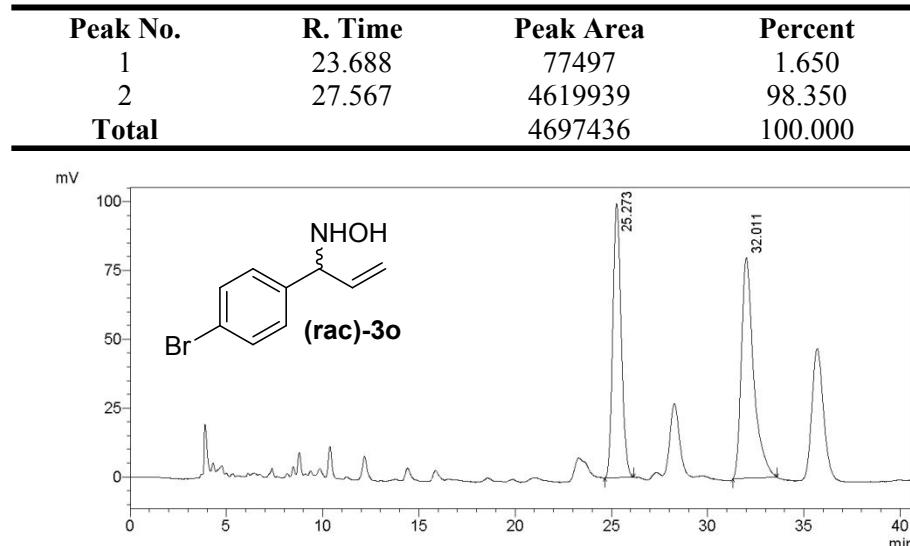
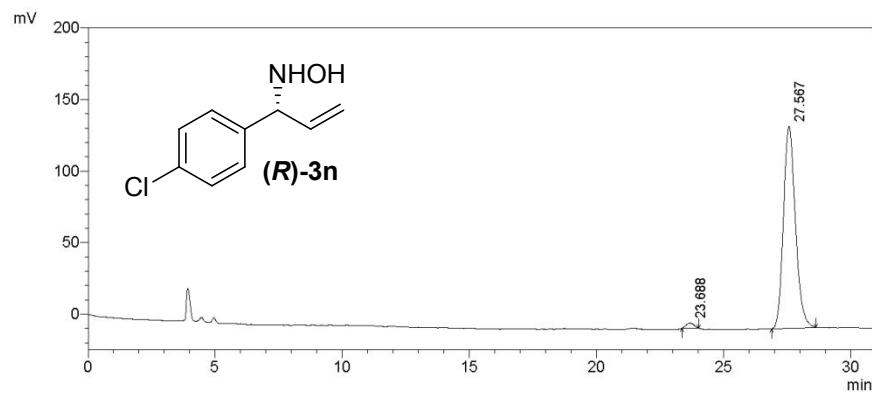
Peak No.	R. Time	Peak Area	Percent
1	28.832	3586299	50.531
2	31.763	3485292	49.286
Total		7071591	100.000

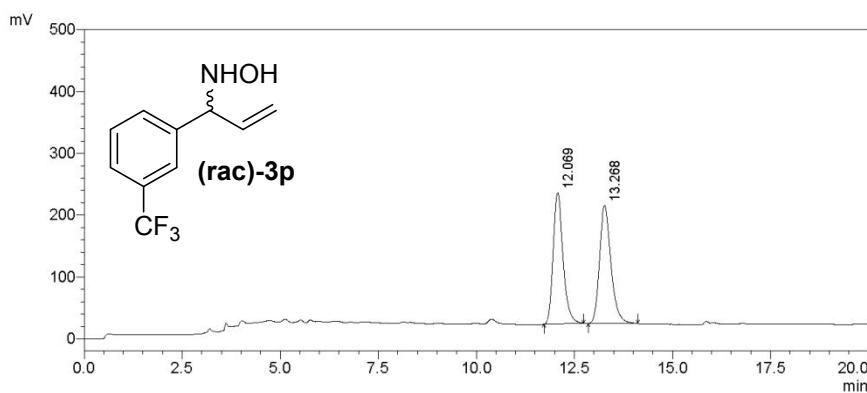


Peak No.	R. Time	Peak Area	Percent
1	28.980	2429487	97.935
2	32.063	51230	2.065
Total		2480717	100.000

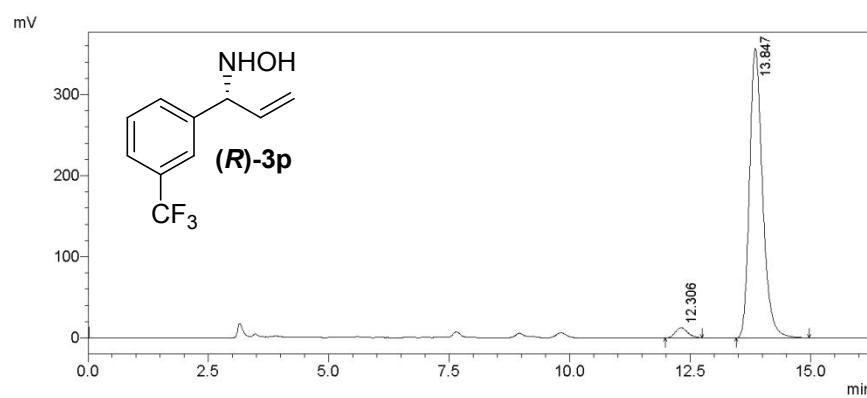


Peak No.	R. Time	Peak Area	Percent
1	23.518	18391901	49.744
2	28.637	18581078	50.256
Total		36972979	100.000

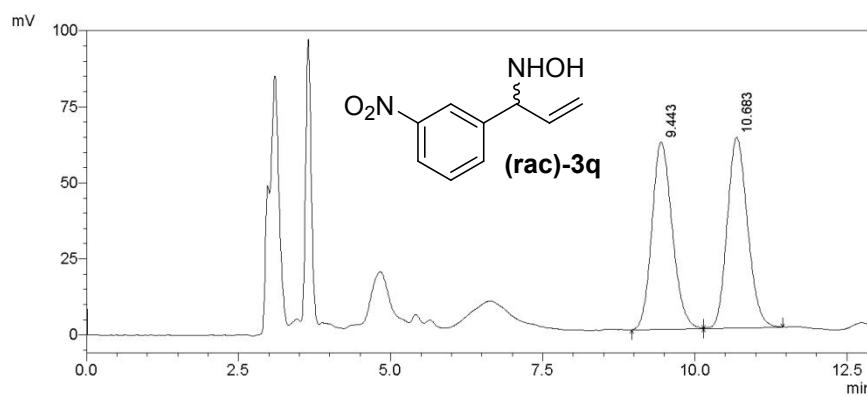




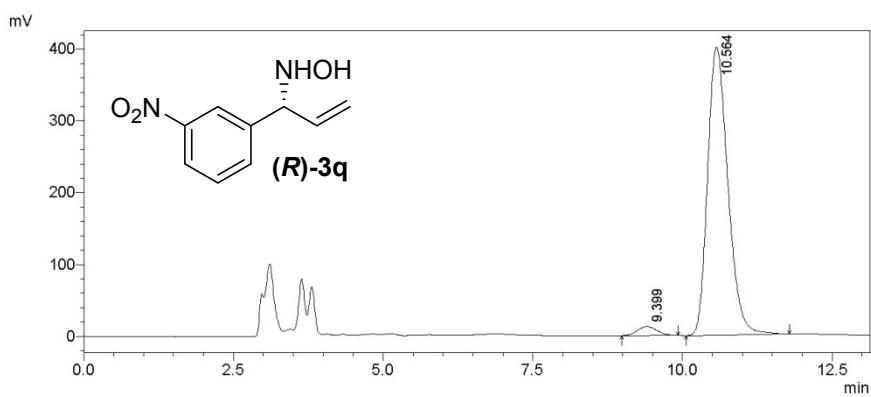
Peak No.	R. Time	Peak Area	Percent
1	12.069	3721328	48.947
2	13.268	3881467	51.053
Total		7602795	100.000



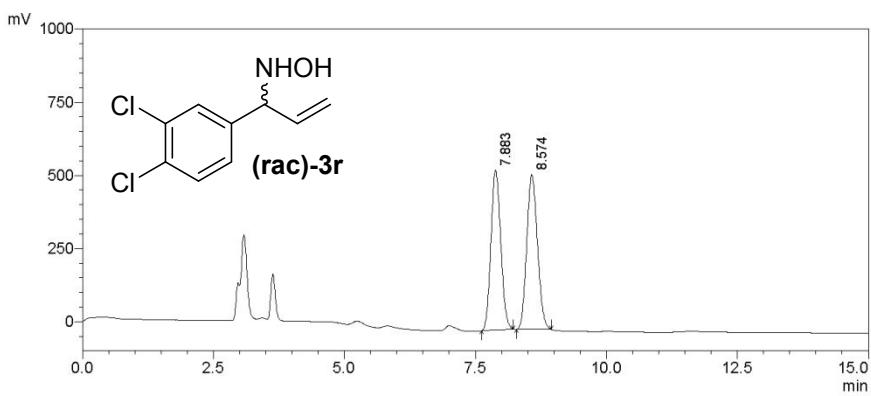
Peak No.	R. Time	Peak Area	Percent
1	12.306	221227	3.194
2	13.847	6704457	96.806
Total		6925685	100.000



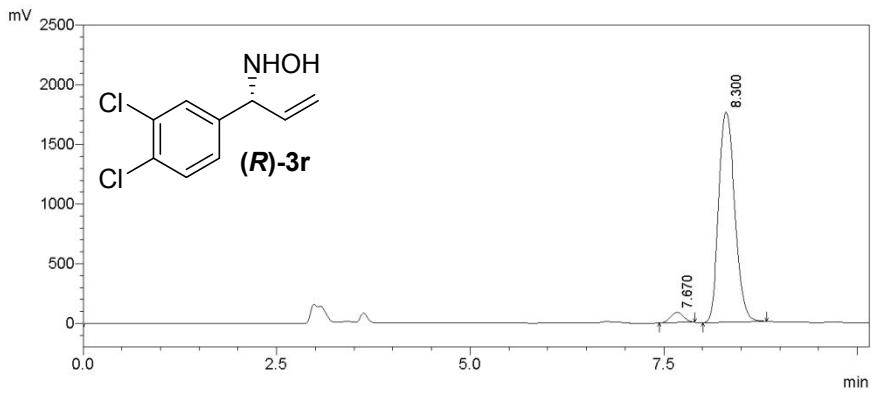
Peak No.	R. Time	Peak Area	Percent
1	9.443	1429830	49.531
2	10.683	1456918	50.469
Total		2886749	100.000



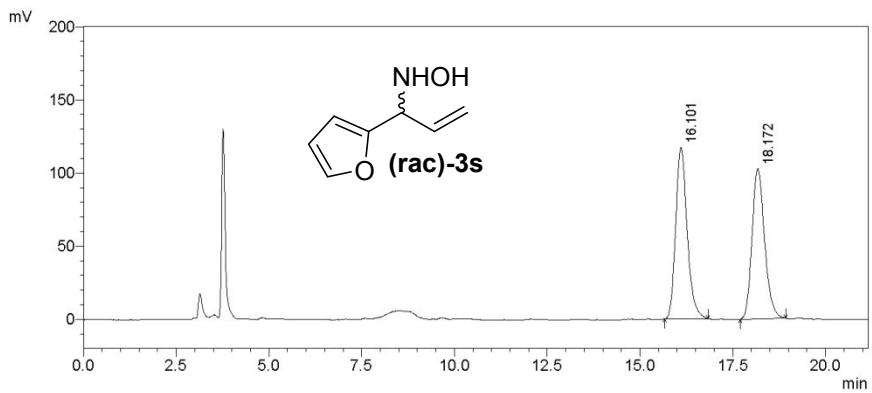
Peak No.	R. Time	Peak Area	Percent
1	9.399	282245	2.897
2	10.564	9461603	97.103
Total		9743849	100.000



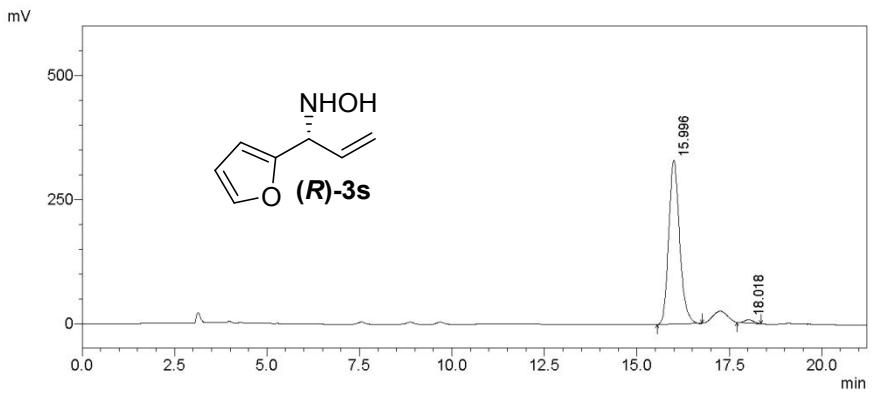
Peak No.	R. Time	Peak Area	Percent
1	7.883	7122849	48.581
2	8.574	7538942	51.419
Total		14661790	100.000



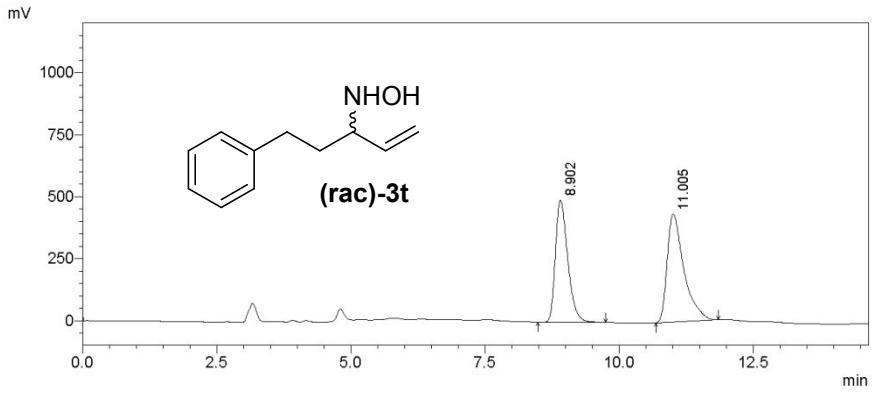
Peak No.	R. Time	Peak Area	Percent
1	7.670	1010436	3.815
2	8.300	25472125	96.185
Total		26482560	100.000



Peak No.	R. Time	Peak Area	Percent
1	16.101	2521633	51.092
2	18.172	2413843	48.709
Total		4935476	100.000



Peak No.	R. Time	Peak Area	Percent
1	15.996	6762853	98.359
2	18.018	112845	1.641
Total		6875697	100.000



Peak No.	R. Time	Peak Area	Percent
1	8.902	7900684	45.456
2	11.005	9480219	54.544
Total		17380903	100.000

