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Supporting Information

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Primary *tert*- and *sec*-Allylamines via Palladium-Catalyzed Hydroamination and Allylic Substitution with Hydrazine and Hydroxylamine Derivatives **

Adam M. Johns, Zhijian Liu, and John F. Hartwig*

Department of Chemistry, University of Illinois Urbana-Champaign, 600 South Mathews Ave, Urbana, IL 61801 and Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107

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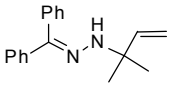
General Experimental Procedure and Reagent Availability.

All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. Tetrahydrofuran and diethyl ether were obtained as HPLC grade without inhibitors; dichloromethane was obtained as ACS reagent grade. All solvents were degassed by purging with nitrogen for 45 min and dried with a solvent purification system containing a 1 m column of activated alumina. Tetrahydrofuran-d_8 and CD_2Cl_2 were dried over appropriate drying agents and vacuum transferred prior to use. Geraniol ethyl carbonate[1] and ethyl 3-methylbut-2-enyl carbonate[2] were prepared following published procedures. All other reagents and solvents were obtained from commercial sources and used without further purification. ^{1}H NMR spectra were obtained at 400 or 500 MHz and recorded relative to residual protio-solvent. ^{13}C NMR spectra were obtained at 101 or 126 MHz, and chemical shifts were recorded relative to the solvent resonance. ^{31}P NMR spectra were obtained at 162 or 202 MHz and chemical shifts are reported relative to 85% H_3PO_4.

General Procedure for the Hydroamination of Isoprene with Benzophenone Hydrazone (Table 1). In a drybox allylpalladiumchloride dimer (1.9 mg, 0.0052 mmol), bisphosphine (0.010 mmol), isoprene (50 μL, 0.50 mmol), and benzophenone hydrazone (98 mg, 0.50 mmol) were placed into a small vial, dissolved in 0.50 mL dichloromethane, and sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 23 ºC for 24 h, and yields were determined by gas chromatography.

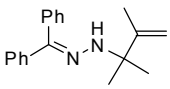
General Procedure for the Hydroamination of 1,3-Dienes with H_2N-X Nucleophiles (Table 2). In a drybox allylpalladiumchloride dimer (3.7 mg, 0.010 mmol), Xantphos (11.6 mg, 0.020 mmol), 1,3-diene (1.0 mmol), the H_2N-X nucleophile (1.00 mmol) and dodecane (10 uL, 0.044 mmol) as an internal standard were placed into a small vial, dissolved in 1.00 mL dichloromethane, and sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 23 ºC for 24 h. Upon completion, as determined by gas chromatography, the reaction mixture was purified by flash chromatography using a solvent gradient ranging from 3:97 v/v ethyl acetate/hexanes to 20:80 v/v ethyl acetate/hexanes.

1-(diphenylmethylene)-2-(2-methylbut-3-en-2-yl)hydrazine (Table 2, Entry 1).



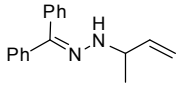
The general procedure was followed with isoprene (68.1 mg, 1.00 mmol) and benzophenone hydrazone (196 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 251 mg (95%) of the hydroamination product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 6H), 4.99 (dd, J = 10.8, 1.0 Hz, 1H), 5.06 (dd, J = 17.5, 1.0 Hz, 1H), 5.26 (s,1H), 6.00 (dd, J = 17.5, 10.8 Hz, 1H), 7.19-7.28 (m, 5H), 7.42 (m, 1H), 7.48-7.52 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 26.5, 57.6, 111.7, 126.2, 127.4, 127.9, 128.6, 129.0, 129.3, 133.7, 139.1, 144.7, 145.7.

1-(2,3-dimethylbut-3-en-2-yl)-2-(diphenylmethylene)hydrazine (Table 2, Entry 2).



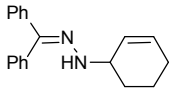
The general procedure was followed with 2,3-dimethyl-1,3-butadiene (82.1 mg, 1.00 mmol) and benzophenone hydrazone (196 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 251 mg (90%) of the hydroamination product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (s, 6H), 1.74 (s, 3H), 4.81 (m, 1H), 4.86 (dd, J = 1.4, 0.7 Hz, 1H), 5.34 (s, 1H), 7.20-7.31 (m, 5H), 7.45 (m, 1H), 7.47-7.55 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 19.4, 26.4, 59.7, 110.0, 126.1, 127.2, 127.9, 128.6, 129.1, 129.3, 133.7, 139.2, 143.7, 151.1; Anal. Calcd for $C_{19}H_{22}N_2$: C, 81.97; H, 7.97; N, 10.06 Found: C, 82.14; H, 7.98; N, 9.85.

1-(but-3-en-2-yl)-2-(diphenylmethylene)hydrazine (Table 2, Entry 3).



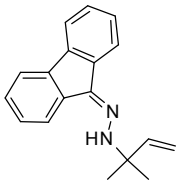
The general procedure was followed with 1,3-butadiene (54.1 mg, 1.00 mmol) and benzophenone hydrazone (196 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 223 mg (89%) of the hydroamination product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (d, *J* = 6.7 Hz, 3H), 4.11 (dd, *J* = 10.2, 6.0 Hz, 1H), 5.14 (td, *J* = 10.4, 1.1 Hz, 1H), 5.21 (td, *J* = 17.3, 1.2 Hz, 1H), 5.31 (d, *J* = 2.4 Hz, 1H), 5.98 (m, 1 H), 7.28-7.39 (m, 5H), 7.48-7.62 (m, 5H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 19.7, 57.4, 114.3, 126.2, 127.5, 127.9, 128.6, 128.9, 129.3, 133.7, 138.8, 141.2, 145.2.

1-(cyclohex-2-enyl)-2-(diphenylmethylene)hydrazine (Table 2, entry 4).



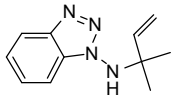
The general procedure was followed with 1,3-cyclohexadiene (80.1 mg, 1.00 mmol) and benzophenone hydrazone (196 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 271 mg (98%) of the hydroamination product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30-1.39 (m, 3H), 1.63-1.74 (m, 3H), 3.83 (br s, 1H), 4.98 (d, J = 7.6 Hz, 1H), 5.46-5.57 (m, 2H), 6.94-7.05 (m, 5H), 7.16 (t, J = 7.5 Hz, 1H), 7.21-7.29 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 19.3, 24.9, 29.2, 54.8, 126.0, 127.3, 127.8, 128.0, 128.5, 128.8, 129.3, 130.2, 133.7, 138.7, 145.1; Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14 Found: C, 82.23; H, 7.48; N, 9.89.

1-(9*H*-fluoren-9-ylidene)-2-(2-methylbut-3-en-2-yl)hydrazine (Table 2, entry 5).



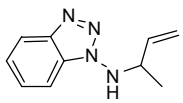
The general procedure was followed with isoprene (68.1 mg, 1.00 mmol) and fluorenone hydrazone (194 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 252 mg (96%) of the hydroamination product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.53 (s, 6H), 5.14 (dd, *J* = 10.7, 0.7 Hz, 1H), 5.26 (dd, *J* = 17.5, 0.8 Hz, 1H), 6.18 (dd, *J* = 17.5, 10.7 Hz, 1H), 6.63 (s, 1H), 7.33 (m, 2H), 7.36 (m, 1H), 7.43 (dt, *J* = 7.5, 0.8 Hz, 1H), 7.68 (m, 1H), 7.81 (t, *J* = 8.4 Hz, 2H), 7.84 (dd, *J* = 4.6, 1.7 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 26.5, 58.7, 112.5, 119.3, 120.4, 120.5, 124.4, 127.3, 127.4, 127.5, 128.8, 130.4, 137.6, 138.3, 140.2, 140.9, 145.2; Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68 Found: C, 82.47; H, 7.02; N, 10.43.

N-(2-methylbut-3-en-2-yl)-1*H*-benzo[*d*][1,2,3]triazol-1-amine (Table 2, entry 6).



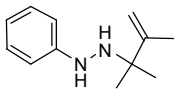
The general procedure was followed with isoprene (68.1 mg, 1.00 mmol) and *N*-aminobenzotriazole (134 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 196 mg (97%) of the hydroamination product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 6H), 5.05 (d, *J* = 10.8 Hz, 1H), 5.09 (d, *J* = 17.5 Hz, 1H), 5.57 (s, 1H), 6.11 (dd, *J* = 17.5, 10.8 Hz, 1H), 7.32 (dd, *J* = 7.9, 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.59 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.98 (dd, *J* = 8.4, 0.4 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 25.8, 60.5, 110.5, 114.3, 119.7, 123.8, 127.5, 133.4, 143.0, 144.0; Anal. Calcd for $C_{11}H_{14}N_4$: C, 65.32; H, 6.98; N, 27.70 Found: C, 65.08; H, 7.11; N, 27.80.

N-(but-3-en-2-yl)-1*H*-benzo[*d*][1,2,3]triazol-1-amine (Table 2, entry 7).



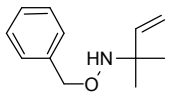
The general procedure was followed with 1,3-butadiene (54.1 mg, 1.00 mmol) and *N*-aminobenzotriazole (134 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 166 mg (88%) of the hydroamination product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (d, *J* = 6.4 Hz, 3H), 4.21 (m, 1H), 4.91 (ddd, *J* = 10.2, 1.2, 0.6 Hz, 1H), 5.00 (dt, *J* = 17.2, 1.0 Hz, 1H), 5.76 (ddd, *J* = 17.2, 10.2, 7.9 Hz, 1H), 5.89 (d, *J* = 2.8 Hz, 1H), 7.26 (ddd, *J* = 7.8, 7.8, 1.0 Hz, 1H), 7.40 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.54 (td, *J* = 8.3, 0.9 Hz, 1H), 7.92 (td, *J* = 8.4, 0.8 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 18.8, 60.5, 109.9, 117.7, 119.5, 123.8, 127.4, 132.7, 138.0, 143.9; Anal. Calcd for $C_{10}H_{12}N_4$: C, 63.81; H, 6.43; N, 29.77 Found: C, 63.84; H, 6.33; N, 29.81.

1-(2,3-dimethylbut-3-en-2-yl)-2-phenylhydrazine (Table 2, entry 8).



The general procedure was followed with 2,3-dimethyl-1,3-butadiene (94.2 mg, 1.00 mmol) and phenylhydrazine (108 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 148 mg (78%) of the hydroamination product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 6H), 1.83 (s, 3H), 3.53 (br s, 1H), 4.94 (br s, 1H), 4.96 (dd, *J* = 1.3, 0.7 Hz, 1H), 5.07 (m, 1H), 6.76 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.96 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.21 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 18.9, 24.9, 60.2, 112.3, 112.6, 118.2, 128.8, 147.9, 150.7.

O-benzyl-*N*-(2-methylbut-3-en-2-yl)hydroxylamine (Table 2, Entry 9).

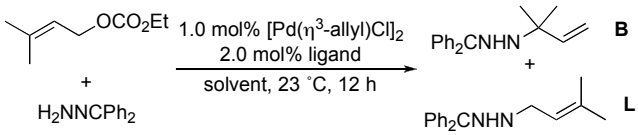


In a drybox, allylpalladiumchloride dimer (3.7 mg, 0.010 mmol), ^{t}BuXantphos (13.8 mg, 0.020 mmol), isoprene (68.1 mg, 1.0 mmol), and *O*-benzylhydroxylamine (123 mg, 1.00 mmol) were placed into a small vial, dissolved in 1.00 mL tetrahydrofuran, and the vial was sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 23 ºC for 24 h. Upon completion, the reaction mixture was purified by flash chromatography to give 135 mg (76%) of the hydroamination product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (s, 6H), 4.76 (s, 2H), 5.11 (d, *J* = 10.8 Hz, 1H), 5.18 (d, *J* = 17.6 Hz, 1H), 5.28 (br s, 1H), 6.00 (dd, *J* = 17.6, 10.8 Hz, 1H), 7.30-7.41 (m, 5H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 24.3, 58.8, 77.2, 112.8, 127.6, 128.1, 128.2, 138.0, 144.1; Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32 Found: C, 75.62; H, 8.85; N, 7.52.

Effect of ligands on the Allylic Amination of Prenyl Ethyl Carbonate with Benzophenone Hydrazone (Table S1).

In a drybox, allylpalladiumchloride dimer (3.7 mg, 0.010 mmol), bisphosphine (0.020 mmol), prenyl ethyl carbonate (158 mg, 1.00 mmol), benzophenone hydrazone (196 mg, 1.00 mmol) and dodecane (20 uL, 0.088 mmol) as an internal standard were placed into a small vial, dissolved in 1.00 mL of the appropriate solvent, and sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 23 ºC for 12 h and yields and product ratios were determined by gas chromatography.

Table S1. The Effect of Bisphosphine Identity and Solvent on the Yield and Regioselectivity of the Palladium Catalyzed Addition of Benzophenone Hydrazone to Prenyl Ethyl Carbonate.[a]

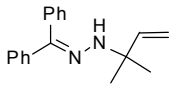


entry	ligand	solvent	yield[b]	B:L
1	Xantphos	CH_2Cl_2	100	98:2
2	DPEphos	CH_2Cl_2	87	97:3
3	Binap	CH_2Cl_2	14	98:2
4	DPPF	CH_2Cl_2	75	96:4
5	DPPpent	CH_2Cl_2	44	96:4
6	Xantphos	THF	98	93:7
7	Xantphos	Toluene	89	95:5
8	Xantphos	Dioxane	85	92:8
9	Xantphos	CH_3CN	84	95:5

[a] Reaction conditions: 1.0 mmol of benzophenone hydrazone, 1.0 mmol of prenyl ethyl carbonate, 1.0 mL of the appropriate solvent, 12 h at 23 ºC. [b] GC yields, in percent.

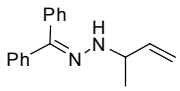
General Procedure for the Addition of H_2N-X Nucleophiles to Allylic Carbonates (Table 3). In a drybox, allylpalladiumchloride dimer (3.7 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), allylic carbonate (1.0 mmol), and the H_2N-X nucleophile (1.00 mmol or 1.30 mmol) were placed into a small vial, dissolved in 1.00 mL dichloromethane, and the vial was sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 23 ºC for 12 h. Upon completion, as determined by gas chromatography, crude product mixtures were assayed by GC/MS and ^{1}H NMR spectroscopy to determine the ratio of isomers. The major isomer was purified by flash chromatography using 3:97 v/v ethyl acetate/hexanes.

1-(diphenylmethylene)-2-(2-methylbut-3-en-2-yl)hydrazine (Table 3, Entry 1).



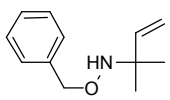
The general procedure was followed with ethyl 3-methylbut-2-enyl carbonate (158 mg, 1.00 mmol) and benzophenone hydrazone (196 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 259 mg (98%) of the allylic substitution product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 6H), 4.99 (dd, J = 10.8, 1.0 Hz, 1H), 5.06 (dd, J = 17.5, 1.0 Hz, 1H), 5.26 (s, 1H), 6.00 (dd, J = 17.5, 10.8 Hz, 1H), 7.19-7.28 (m, 5H), 7.42 (m, 1H), 7.48-7.52 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 26.5, 57.6, 111.7, 126.2, 127.4, 127.9, 128.6, 129.0, 129.3, 133.7, 139.1, 144.7, 145.7.

1-(but-3-en-2-yl)-2-(diphenylmethylene)hydrazine (Table 3, Entry 2).



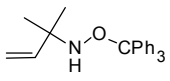
The general procedure was followed with ethyl 3-methylbut-2-enyl carbonate (144 mg, 1.00 mmol) and benzophenone hydrazone (196 mg, 1.00 mmol). The reaction was completed in 2 h. The reaction mixture was purified by flash chromatography to give 193 mg (77%) of the hydroamination product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (d, J = 6.7 Hz, 3H), 4.11 (dd, J = 10.2, 6.0 Hz, 1H), 5.14 (td, J = 10.4, 1.1 Hz, 1H), 5.21 (td, J = 17.3, 1.2 Hz, 1H), 5.31 (d, J = 2.4 Hz, 1H), 5.98 (m, 1 H), 7.28-7.39 (m, 5H), 7.48-7.62 (m, 5H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 19.7, 57.4, 114.3, 126.2, 127.5, 127.9, 128.6, 128.9, 129.3, 133.7, 138.8, 141.2, 145.2.

O-benzyl-*N*-(2-methylbut-3-en-2-yl)hydroxylamine (Table 3, Entry 3).



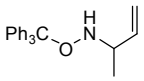
The general procedure was followed with ethyl 3-methylbut-2-enyl carbonate (158 mg, 1.00 mmol) and *O*-benzylhydroxylamine (160 mg, 1.30 mmol). The reaction mixture was purified by flash chromatography to give 172 mg (90%) of the allylic substitution product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (s, 6H), 4.76 (s, 2H), 5.11 (d, J = 10.8 Hz, 1H), 5.18 (d, J = 17.6 Hz, 1H), 5.28 (br s, 1H), 6.00 (dd, J = 17.6, 10.8 Hz, 1H), 7.30-7.41 (m, 5H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 24.3, 58.8, 77.2, 112.8, 127.6, 128.1, 128.2, 138.0, 144.1; Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32 Found: C, 75.62; H, 8.85; N, 7.52.

N-(2-methylbut-3-en-2-yl)-*O*-tritylhydroxylamine (Table 3, Entry 4).



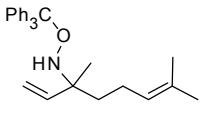
The general procedure was followed with ethyl 3-methylbut-2-enyl carbonate (158 mg, 1.00 mmol) and *O*-tritylhydroxylamine (275 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 258 mg (75%) of the allylic substitution product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (s, 6H), 4.82 (br s, 1H), 4.94 (dd, J = 10.8, 1.3 Hz, 1H), 5.04 (dd, J = 17.6, 1.2 Hz, 1H), 5.74 (dd, J = 17.6, 10.8 Hz, 1H), 7.21-7.32 (m, 9H), 7.37-7.42 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 24.3, 58.4, 88.7, 112.1, 126.9, 127.4, 129.4, 144.1, 144.9; Anal. Calcd for $C_{24}H_{25}NO$: C, 83.93; H, 7.34; N, 4.08 Found: C, 83.68; H, 7.08; N, 3.95.

N-(but-3-en-2-yl)-*O*-tritylhydroxylamine (Table 3, Entry 5).



The general procedure was followed with ethyl 3-methylbut-2-enyl carbonate (144 mg, 1.00 mmol) and *O*-tritylhydroxylamine (275 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 270 mg (82%) of the allylic substitution product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (d, *J* = 6.6 Hz, 3H), 3.14 (p, *J* = 6.5 Hz, 1H), 4.82 (br s, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 5.04 (td, *J* = 17.3, 1.3 Hz, 1H), 5.63 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 7.19-7.30 (m, 9H), 7.37-7.43 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 17.5, 58.4, 89.1, 115.1, 126.8, 127.4, 129.1, 140.2, 144.2; ^{1}H NMR: Fig. **S1**, ^{13}C NMR: Fig. **S2**.

N-(3,7-dimethylocta-1,6-dien-3-yl)-*O*-tritylhydroxylamine (Table 3, entry 6).

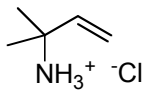


The general procedure was followed with geraniol ethyl carbonate (226 mg, 1.00 mmol) and *O*-tritylhydroxylamine (275 mg, 1.00 mmol). The reaction mixture was purified by flash chromatography to give 313 mg (76%) of the allylic substitution product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (s, 3H), 1.24-1.40 (m, 2H), 1.53 (s, 3H), 1.64 (s, 3H), 1.77 (dd, *J* = 15.8, 7.7 Hz, 2H), 4.92 (br s, 1H), 4.96 (m, 2H), 4.99 (m, 1H), 5.59 (dd, *J* = 17.7, 10.9 Hz, 1H), 7.19-7.29 (m, 9H), 7.37-7.41 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 17.6, 21.6, 22.4, 25.6, 37.7, 60.9, 88.7, 113.0, 124.6, 126.9, 127.4, 129.4, 131.2, 143.7, 144.1; Anal. Calcd for $C_{29}H_{33}NO$: C, 84.63; H, 8.08; N, 3.40 Found: C, 84.43; H, 8.14; N, 3.19.

General Procedure for the Cleavage of RHN-X Bond to Allylic Amine.

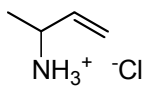
To a suspension of compound **RHN-X** (1.0 mmol) in AcOH-THF-H_2O (3:1:1 v/v/v, 8 mL) was added Zn powder (1.6 g, 24.5 mmol) in several portions at room temperature and stirring was continued for 30 min and then stirring for 4 h at 60 ^{o}C. Upon completion, the reaction mixture was diluted with water. After the reaction mixture was filtered and then extracted with Et_2O. The aqueous layer was neutralized with 6 N NaOH and then extracted with Et_2O. The organic phase was dried over Na_2SO_4 and then HCl (2 N in Et_2O, 0.5 mL) was added and concentrated at reduce pressure affording the pure white salt amine hydrochloride in a good yield.

2-Methyl-3-buten-2-amine hydrochloride.



The general procedure was followed with *O*-benzyl-*N*-(2-methylbut-3-en-2-yl)hydroxylamine (191 mg, 1.00 mmol) and Zn powder (1.6 g, 24.5 mmol). The white solid product was obtained (114.0 mg) in a 93% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55 (s, 6H), 5.26 (d, *J* = 11 Hz, 1H), 5.41 (d, *J* = 18 Hz, 1H), 5.97-6.03 (m, 1H), 8.57 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 26.1, 55.6, 116.3, 139.5.

3-Buten-2-amine hydrochloride.



The general procedure was followed with *N*-(but-3-en-2-yl)-*O*-tritylhydroxylamine (329 mg, 1.00 mmol) and Zn powder (1.6 g, 24.5 mmol). The white solid product was obtained (86.0 mg) in a 79% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (d, *J* = 6.5 Hz, 3H), 3.91 (s, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 5.43 (d, *J* = 17 Hz, 1H), 5.92-5.97 (m, 1H), 8.49 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 19.2, 50.2, 119.5, 134.9.

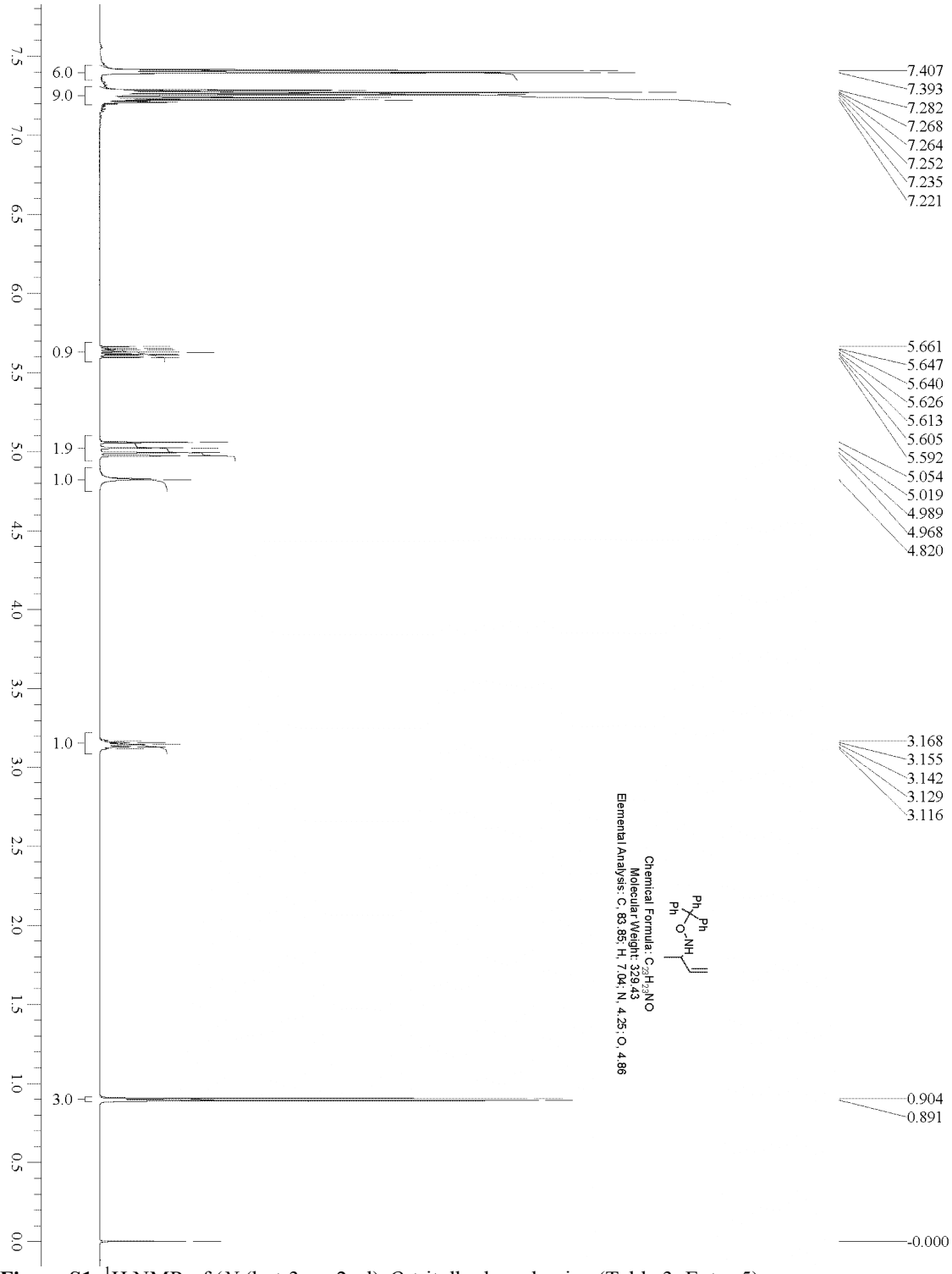


Figure S1. ^{1}H NMR of (*N*-(but-3-en-2-yl)-*O*-tritylhydroxylamine (Table 3, Entry 5).

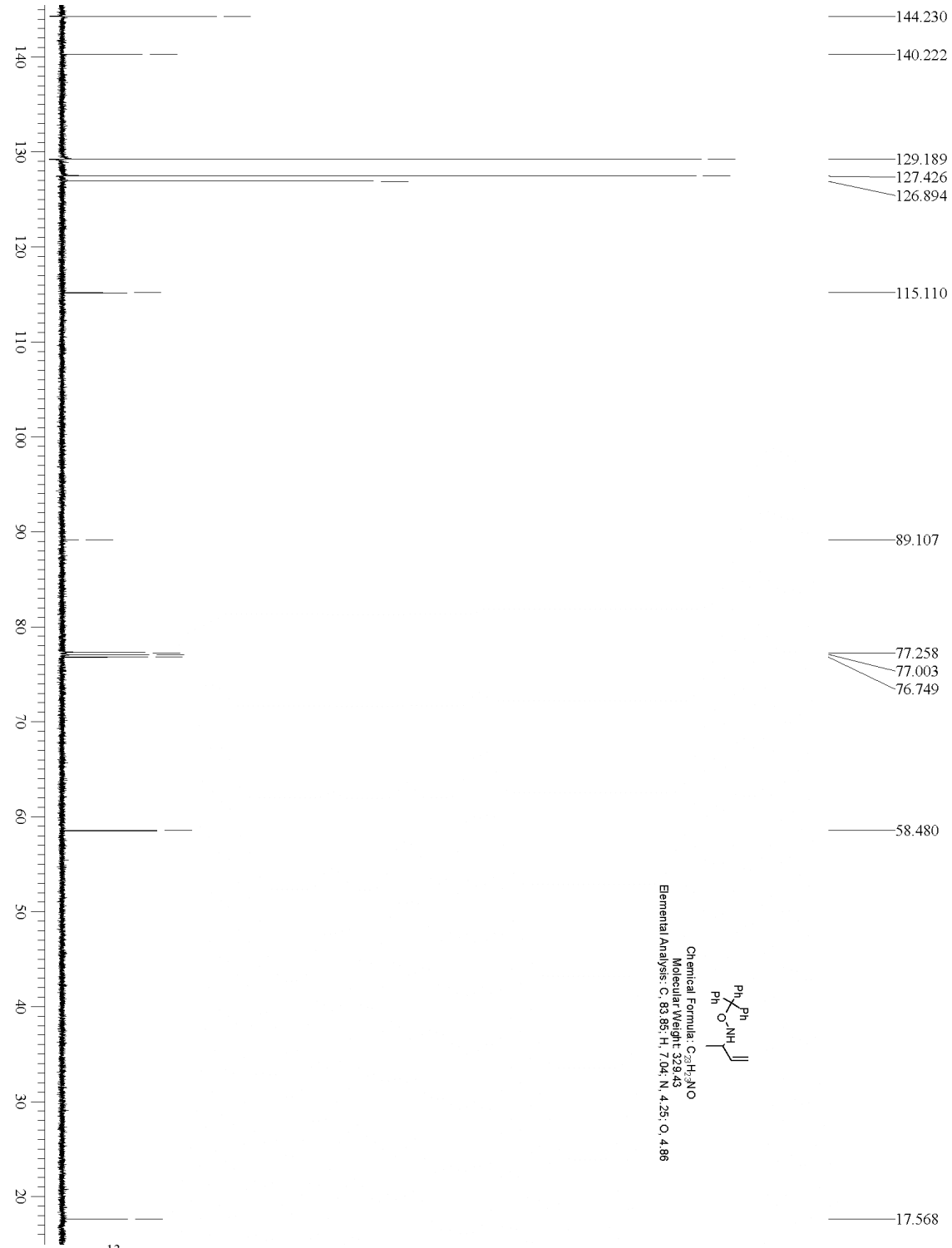


Figure S2. ^{13}C NMR of (*N*-(but-3-en-2-yl)-*O*-tritylhydroxylamine (Table 3, Entry 5).

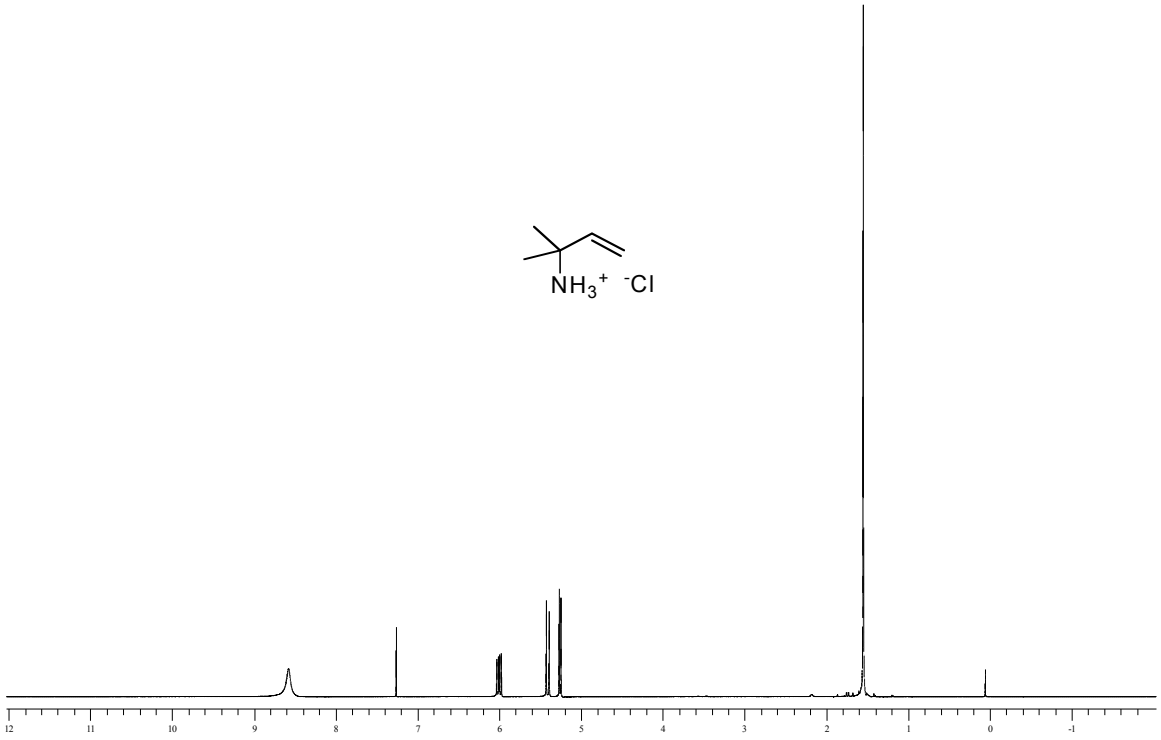


Figure S3. ^{1}H NMR of 2-methyl-3-buten-2-amine hydrochloride

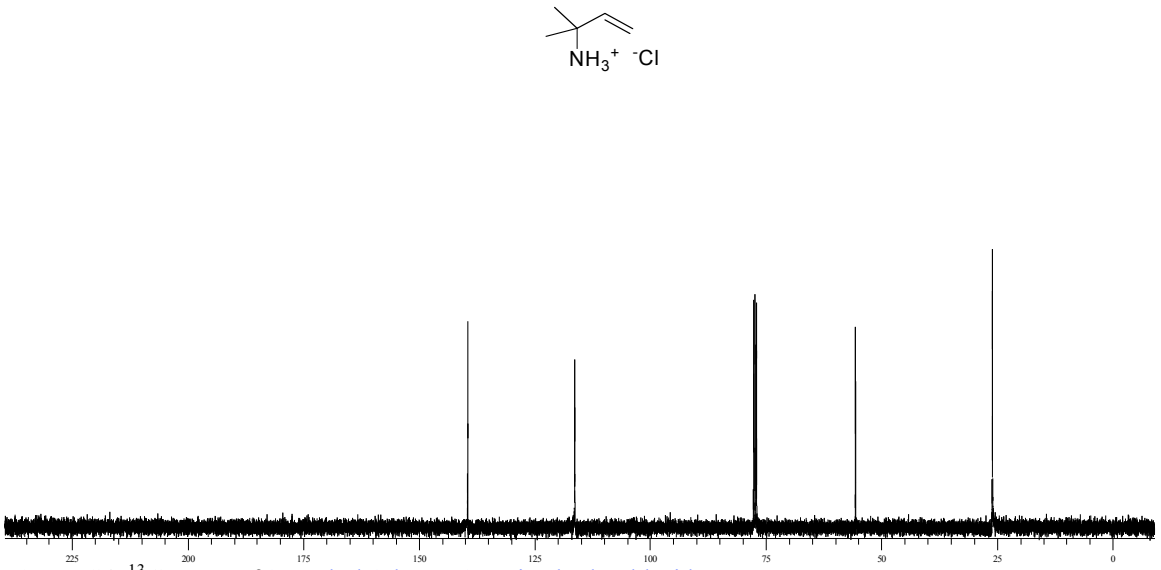
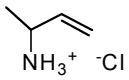


Figure S4. ^{13}C NMR of 2-methyl-3-buten-2-amine hydrochloride



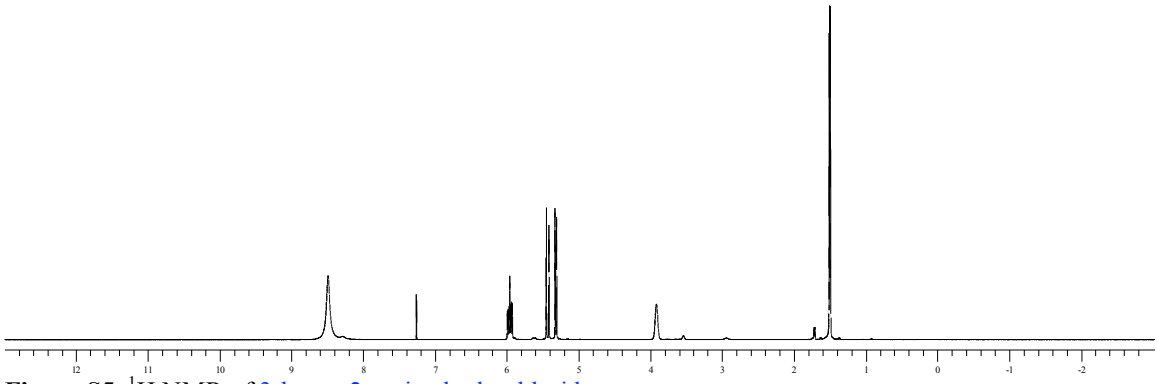
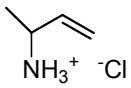


Figure S5. ^{1}H NMR of 3-buten-2-amine hydrochloride



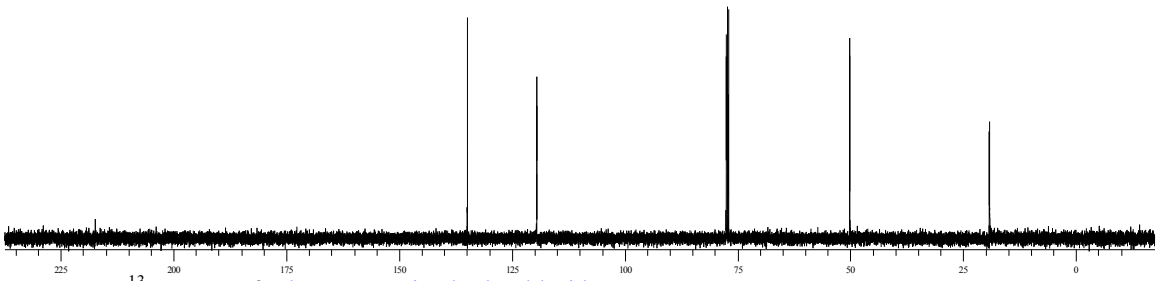


Figure S6. ^{13}C NMR of 3-buten-2-amine hydrochloride

References:

[1] C. Fournier-Ngueface, P. Lhoste, D. Sinou, *Tetrahedron* **1997**, *53*, 4353-4362.
[2] M. Moreno-Mañas, J. Ribas, A. Virgili, *J. Org. Chem.* **1988**, *53*, 5328-5335.