

Cross-Coupling of Aromatic Bromides with Allylic Silanolate Salts

Scott E. Denmark* and Nathan S. Werner

Roger Adams Laboratory, University of Illinois, 600 S. Mathews Avenue, Urbana, Illinois 61801

SUPPORTING INFORMATION

Table of Contents	Page
General Experimental	S1
Response Factors	S4
Literature Preparations	S5
Experimental Procedures	S5
General Cross-Coupling Procedures	S14
Allylation Procedures	S17
Crotylation Procedures	S31
References	S56
¹ H NMR Spectra	S58

General Experimental

All reactions were performed in oven (140 °C) and /or flame dried glassware under an atmosphere of dry argon unless otherwise noted. Reaction solvents tetrahydrofuran (Fisher, HPLC grade), ether (Fisher, BHT stabilized ACS grade) and methylene chloride (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents hexanes (Fisher, OPTIMA grade) and toluene (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Reaction solvents dioxane and benzene were

distilled from sodium, acetonitrile was distilled from CaH_2 , and dimethoxyethane (DME) was distilled from sodium benzophenone ketyl prior to use. Solvents for filtration and chromatography were certified ACS grade. "Brine" refers to a saturated solution of sodium chloride in water. All reaction temperatures correspond to internal temperatures measured with Teflon coated thermocouples.

^1H and ^{13}C NMR spectra were recorded on a Varian Unity-500 MHz (126 MHz, ^{13}C) spectrometer. Spectra are referenced to residual chloroform ($\delta = 7.26$ ppm, ^1H ; 77.0 ppm, ^{13}C) or residual benzene ($\delta = 7.15$ ppm, ^1H ; 128.0 ppm, ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants, J , are reported in Hertz, and integration is provided and assignments are indicated. Mass Spectrometry (MS) was performed by the University of Illinois Mass Spectrometer Center. Electron Impact (EI) spectra were performed at 70 eV using methane as the carrier gas on a Finnegan-MAT C5 spectrometer. Data are reported in the form of m/z (intensity relative to the base peak = 100). Infrared spectra (IR) spectra were recorded on a Perkin-Elmer FT-IR system and peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 0-33% T); m (medium, 34-66% T), w (weak, 67-100% T). Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus in sealed tubes and are corrected. Kugelrohr (bulb-to-bulb) distillations were performed on a Büchi GKR-50 apparatus with boiling points (bp) corresponding to uncorrected air bath temperatures (ABT).

Analytical gas chromatography (GC) was performed using a Hewlett-Packard 5890 Gas Chromatograph fitted with a flame ionization detector. Three GC Methods were used. *GC Method 1* involved injections onto a Hewlett-Packard HP1 (30 m x 0.32 mm) capillary column. Injector temperature was 250 °C and the detector temperature was 300 °C with a H_2 carrier gas

flow of 16 mL/min. The column temperature program was as follows: 175 °C for 5 min, 175 °C to 250 °C at 10 °C/min, then hold for 3 min for a total run time of 13 min. *GC Method 2* involved injections onto a Hewlett-Packard HP1MS (30m x 0.32 mm) capillary column. Injector temperature was 250 °C and the detector temperature was 300 °C with a H₂ carrier gas flow of 16 mL/min. The column temperature program was as follows: 100 °C for 3 min, 100 °C to 260 °C at 40 °C/min, then hold for 7 min for a total run time of 14 min. *GC Method 3* involved injections onto a Hewlett-Packard HP1 (30m x 0.32 mm) capillary column. Injector temperature was 250 °C and the detector temperature was 300 °C with a H₂ carrier gas flow of 16 mL/min. The column temperature program was as follows: 100 °C for 3 min, 100 °C to 260 °C at 40 °C/min, then hold for 7 min for a total run time of 14 min. Retention times (t_R) were obtained using Agilent Chemstation software. Response factors were generated by triplicate runs of three molar ratios of compound and biphenyl dissolved in ethyl acetate.

Commercial reagents were purified by distillation or recrystallization prior to use unless noted. 1-Bromonaphthalene, 4-bromobenzotrifluoride, 4-bromobenzophenone, and 2-bromo-6-methoxynaphthalene were purchased from Alfa Aesar. 4-Bromoanisole, 4-bromo-*N,N*-dimethylaniline, 4-bromobenzoyl chloride, 4-bromochlorobenzene, 4-bromobenzonitrile, 2-bromonaphthalene, 2-bromoanisole, 2-bromo-*N,N*-dimethylaniline, 5-bromo-*m*-xylene, 3-bromobenzyl alcohol, trichlorosilane, crotyl chloride, cyclooctadiene, 1,4-benzoquinone, norbornadiene, maleic anhydride, and tetramethylethylene were purchased from Aldrich. 3,5-bis(Trifluoromethyl)bromobenzene was purchased from Matrix Scientific. Triphenylphosphine, 2-(di-*t*-butylphosphino)biphenyl, triphenylphosphine oxide, (*t*-Bu₃P)₂Pd, 6-bromoindole, 4-bromophenol, triphenylarsine, MeLi (titrated at 1.78 M in ether), diallylcarbonate, (*o*-tol)₃P, 1,3-bis(diphenylphosphino)propane, 1,1'-bis(diphenylphosphino)ferrocene, BINAP, palladium

acetate, palladium bromide and dicyclopentadiene were purchased from Aldrich and used as received. Allyldimethylchlorosilane was purchased from Gelest. *trans, trans*-Dibenzylideneacetone was purchased from Acros and used as received. Tricyclohexylphosphine, Josiphos, and allylchloro[1,3-bis(2,6-di-*i*-propylphenyl)imidazol-2-ylidene]palladium(II) were purchased from Strem and used as received. Palladium chloride was purchased from Pressure Chemical and used as received. Sodium hydride and potassium hydride were purchased from Aldrich as a suspension in mineral oil, washed with hexanes and stored under dry argon.

Response Factors

Response factors for quantitative GC analysis using GC Method 3 were calculated using the following equation and data:

$$\text{Response factor} = (\text{mmol compound} * \text{rel. area biphenyl}) / (\text{mmol biphenyl} * \text{rel. area compound})$$

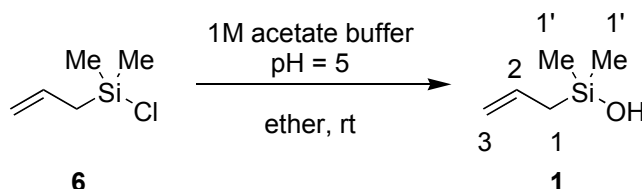
mmol biphenyl	Rel. Area biphenyl	mmol 1-bromonaphthalene	Rel. Area 1-bromonaphthalene	Response Factor
0.113	26.769	0.362	73.231	1.17
0.113	27.007	0.362	72.993	1.19
0.113	27.061	0.362	72.939	1.19
0.119	35.291	0.263	64.709	1.22
0.119	35.279	0.263	64.297	1.22
0.119	35.291	0.263	64.709	1.22
0.191	61.731	0.140	38.269	1.18
0.191	61.828	0.140	38.172	1.19
0.191	61.980	0.140	38.020	1.19
Avg:				1.20

mmol biphenyl	Rel. Area biphenyl	mmol γ - 14h	Rel. Area γ - 14h	Response Factor
0.120	63.900	0.0575	31.136	0.983
0.120	63.684	0.0575	30.975	0.985
0.120	63.626	0.0575	31.084	0.981
0.200	67.830	0.0793	27.760	0.969
0.200	67.871	0.0793	27.739	0.970
0.200	67.920	0.0793	27.689	0.973
0.303	80.549	0.0601	16.483	0.969
0.303	80.648	0.0601	16.448	0.973
0.303	80.515	0.0601	16.501	0.968
Avg:				0.975

Literature Preparations

The following compounds were prepared by literature methods: allylpalladium chloride dimer (APC),¹ Pd(dba)₂,² Pd₂dba₃,² 4-allylbenzophenone,³ 2-butenyltrichlorosilane,⁴ 4,4-dimethylcyclohexa-2,5-diene-1-one,⁵ 2-propenyldimethylchlorosilane,⁶ 2-butenyldimethylchlorosilane,⁷ diallyl ether,⁸ diphenylphosphino-2',6'-dimethoxybiphenyl,⁹ diphenylphosphino-2'4'6'-triisopropylbiphenyl,¹⁰ 6-bromo-*N*-Boc-indole,¹¹ 3-bromotriethylsilylbenzyl ether,¹² *tert*-butyl 4-bromobenzoate,¹³ 4-bromophenyldimethyl(*tert*-butyl)silyl ether,¹⁴ (*E*)-2-butynol,¹⁵ (*E*)-1-chloro-2-butene,¹⁶ (*Z*)-2-butenyltrichlorosilane,⁴ bis(4-methoxybenzylidene)acetone,¹⁷ and bis(4-trifluoromethylbenzylidene)acetone).

Preparation of 1,1-Dimethyl-1-(2-propen-1-yl)silanol (1)



To a single-necked, 1-L, round-bottomed flask equipped with a magnetic stir bar was added 429 mL of 1 M acetate buffer (pH = 5) and ether (43 mL). Allyldimethylchlorosilane (8.75 g, 65.0 mmol) was then dissolved in ether (43 mL) then added by pipette to the vigorously stirring, heterogeneous mixture of acetate buffer and ether. After being stirred for 5 min, the reaction mixture was then poured into a 1-L separatory funnel and diluted with ether (40 mL). The aqueous phase was separated and washed with ether (2 x 30 mL). The three separate organic extracts were then sequentially washed with sat. aq. NaHCO₃ (20 mL) and the pH of the resulting aqueous wash was checked with litmus paper to ensure alkalinity. The organic extracts were then washed with brine, combined, and dried over Na₂SO₄, and then filtered through a pad

of silica gel (5 g) in a glass-fritted funnel (coarse, 5 cm x 7 cm). The filtrate was concentrated (ambient temp., 20 mm Hg) and the residue purified by column chromatography (SiO₂, 30 mm x 20 cm, pentane/Et₂O, 4:1), followed by simple distillation to provide 6.77 g (90%) of **1** as a clear, colorless oil.

Data for (1):

bp: 134 °C (760 mmHg)

¹H NMR: (500 MHz, CDCl₃)

5.82 (ddt, $J = 16.9, 10.1, 8.1$, 1 H, HC(2)), 4.91 (m, 2 H, HC(3)), 1.71 (b, 1 H, HO), 1.63 (d, $J = 8.1$, 2 H, HC(1)), 0.16 (s, 6 H, HC(1')).

¹³C NMR: (126 MHz, CDCl₃)

134.3 C(2), 113.9 C(3), 25.9 C(1), -0.623 C(1').

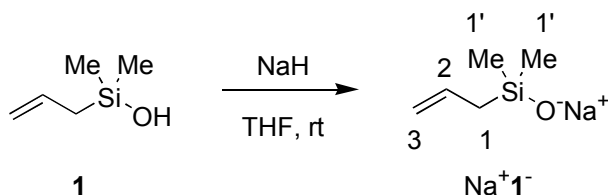
IR: (film)

3294 (s), 3080 (m), 3062 (w), 2998 (w), 2960 (m), 1916 (w), 2886 (w), 1632 (m), 1420 (w), 1393 (w), 1256 (s), 1192 (w), 1160 (m), 1067 (m), 1037 (m), 992 (m), 932 (m), 895 (s), 868 (s), 837 (s), 753 (m), 722 (w), 697 (w), 654 (m), 647 (m).

MS: (EI, 70 eV)

173 (6), 149 (6), 133 (6), 116 (M⁺, 5), 101 (9), 75 (100), 61 (10).

TLC: R_f 0.19 (pentane/Et₂O, 4:1) [silica gel, aqueous KMnO₄]

Preparation of Sodium 1,1-Dimethyl-1-(2-propen-1-yl)silanolate (Na⁺1⁻)

In a dry box, washed NaH (618 mg, 25.8 mmol, 1.1 equiv) and THF (13 mL) were combined in a 50-mL, single-necked, round-bottomed flask containing a magnetic stir bar. In a separate 50-mL, single-necked, round-bottomed flask containing allyldimethylsilanol (2.72 g, 23.4 mmol) was added THF (23 mL), this solution was then mixed and added drop-wise over 10 min to the stirred suspension of NaH. After being stirred for 30 min, the resulting mixture was filtered through a glass-fritted filter (medium, 3.5 cm x 4.5 cm) into a 25-mL Schlenk flask. The filtrate was concentrated (ambient temp., 20 mm Hg) to afford a colorless amorphous solid. Hexane (10 mL) was then added and the resulting solution was concentrated (ambient temp., 0.5 mm Hg) to afford 2.82 g (89%) of Na⁺1⁻ as a white powder.

Data for (Na⁺1⁻):

¹H NMR: (500 MHz, C₆D₆)

6.11 (ddt, *J* = 17.1, 10.0, 8.3, 1 H, HC(2)), 4.93 (m, 2 H, HC(3)), 1.58 (d, *J* = 8.3, 2 H, HC(1)), 0.08 (s, 6 H, HC(1')).

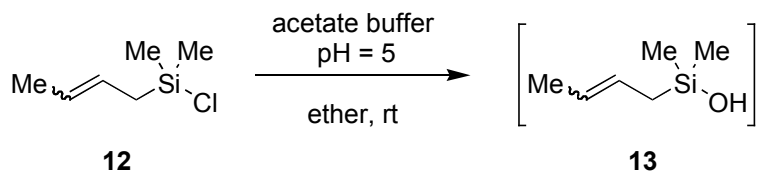
¹³C NMR: (126 MHz, C₆D₆)

141.2 C(2), 110.2 C(3), 30.5 C(1), 3.2 C(1').

Analysis: C₅H₁₁NaOSi (138.22)

Calcd: C, 43.45; H, 8.02

Found: C, 43.06; H, 8.21

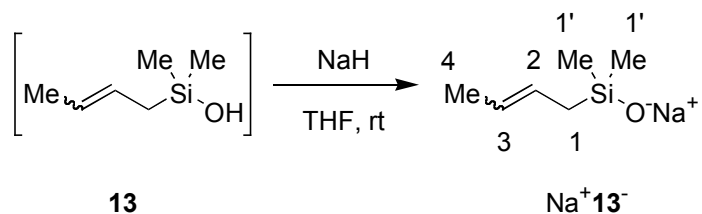
Preparation of 1,1-Dimethyl-1-(2-buten-1-yl)silanol (13)

To a single-necked, 1-L, round-bottom flask equipped with a magnetic stir bar was added 399 mL of 1 M acetate buffer (pH = 5) and ether (40 mL). 2-butenyldimethylchlorosilane (10.0 g, 60.5 mmol) was then dissolved in ether (40 mL) then added by pipette to the vigorously stirring, heterogeneous mixture of acetate buffer and ether. After being stirred for 5 min, the reaction mixture was then poured into a 1-L separatory funnel and diluted with ether (50 mL). The aqueous phase was separated and washed with ether (2 x 50 mL), The three separate organic extracts were then sequentially washed with sat. aq. NaHCO_3 (50 mL) and the pH of the resulting aqueous wash was checked with litmus paper to ensure alkalinity. The organic extracts were then washed with brine (50 mL), combined, dried over Na_2SO_4 , and then filtered through a pad of silica gel (10 g). The filtrate was concentrated (ambient temp., 20 mm Hg) and the residue purified by column chromatography (SiO_2 , 30 mm x 20 cm, pentane/ Et_2O , 4:1). Fractions were combined, concentrated to ~20 mL (ambient temp., 20 mm Hg) and then was transferred to a dry box for conversion to its sodium salt.

Data for (13):

bp: 149 °C (760 mmHg)

TLC: R_f 0.24 (pentane/ Et_2O , 4:1) [silica gel, aqueous KMnO_4]

Preparation of Sodium 1,1-Dimethyl-1-(2-buten-1-yl)silanolate (Na⁺13⁻)

In a dry box, washed NaH (1.84 g, 76.6 mmol, 1.1 equiv) and THF (20 mL) were combined in a 50-mL, single-neck, round-bottomed flask containing a magnetic stir bar. In a separate 50-mL, single-neck, round-bottomed flask containing 2-butenyldimethylsilanol (69.6 mmol) was added THF (10 mL), this solution was then mixed and added drop-wise over 10 min to the stirred suspension of NaH. After being stirred for 30 min, the resulting mixture was filtered through a glass-fritted filter (medium, 3.5 cm x 4.5 cm) into a 100-mL Schlenk flask. The filtrate was concentrated (ambient temp., 20 mm Hg) to afford a colorless amorphous solid. Hexane (10 mL) was then added and the resulting solution was concentrated (ambient temp., 0.5 mm Hg) to afford 8.58 g (81%) of Na⁺13⁻ as a white powder.

Data for (Na⁺13⁻):

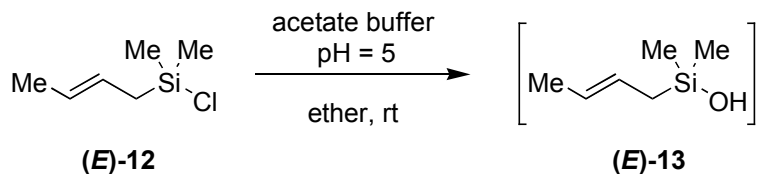
¹H NMR: (500 MHz, C₆D₆)

5.70 (m, 1 H, HC(2)), 5.42 (m, 1 H, HC(3)), 1.72 (dd, *J* = 6.3, 0.9, 3H, HC(4)),

1.52 (d, *J* = 7.9, 2 H, HC(1)), 0.13 (s, 6 H, HC(1')).

¹³C NMR: (126 MHz, C₆D₆)

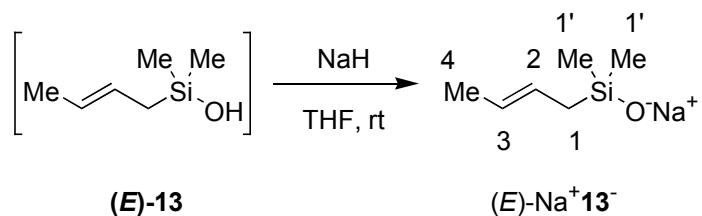
131.3 C(2), 121.6 C(3), 28.3 C(1), 18.2 C(4), 3.1 (C(1')).

Preparation of (*E*)-1,1-Dimethyl-1-(2-buten-1-yl)silanol ((*E*)-13)

To a single-necked, 1-L, round-bottom flask equipped with a magnetic stir bar was added 250 mL of 1 M acetate buffer (pH = 5) and ether (20 mL). (*E*)-2-butenyldimethylchlorosilane (5.84 g, 39.3 mmol) was then dissolved in ether (33 mL) then added by pipette to the vigorously stirring, heterogeneous mixture of acetate buffer and ether. After being stirred for 5 min, the reaction mixture was then poured into a 1-L separatory funnel and diluted with ether (50 mL). The aqueous phase was separated and washed with ether (2 x 50 mL). The three separate organic extracts were then sequentially washed with sat. aq. NaHCO₃ (50 mL) and the pH of the resulting aqueous wash was checked with litmus paper to ensure alkalinity. The organic extracts were then washed with brine (50 mL), combined, dried over Na₂SO₄, and then filtered through a pad of silica gel (10 g). The filtrate was concentrated (ambient temp., 20 mm Hg) and the residue purified by column chromatography (SiO₂, 30 mm x 20 cm, pentane/Et₂O, 4:1). Fractions were combined, concentrated to ~20 mL (ambient temp., 20 mm Hg) and then was transferred to a dry box for conversion to its sodium salt.

Data for ((*E*)-13):

TLC: R_f 0.24 (pentane/Et₂O, 4:1) [silica gel, aqueous KMnO₄]

Preparation of Sodium (*E*)-1,1-Dimethyl-1-(2-buten-1-yl)silanolate (Na⁺(*E*)-13**⁻)**

In a dry box, washed NaH (1.04 g, 43.2 mmol, 1.1 equiv) and THF (10 mL) were combined in a 50-mL, single-neck, round-bottomed flask containing a magnetic stir bar. In a separate 50-mL, single-neck, round-bottomed flask containing (*E*)-2-butenyldimethylsilanol (39.3 mmol) was added THF (10 mL), this solution was then mixed and added drop-wise over 10 min to the stirred suspension of NaH. After being stirred for 30 min, the resulting mixture was filtered through a glass-fritted filter (M, 3.5 cm x 4.5 cm) into a 100-mL Schlenk flask. The filtrate was concentrated (ambient temp., 20 mm Hg) to afford a colorless amorphous solid. Hexane (10 mL) was then added and the resulting solution was concentrated (ambient temp., 0.5 mm Hg) to afford 5.00 g (84%) of Na⁺(*E*)-**13**⁻ as a white powder.

Data for (Na⁺(*E*)-**13**⁻):

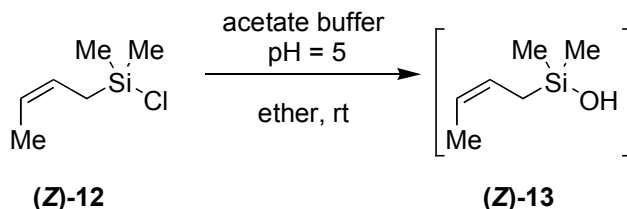
¹H NMR: (500 MHz, C₆D₆)

5.70 (m, 1 H, HC(2)), 5.42 (m, 1 H, HC(3)), 1.72 (dd, *J* = 6.3, 1.2, 3H, HC(4)),

1.52 (d, *J* = 7.9, 2 H, HC(1)), 0.13 (s, 6 H, HC(1')).

¹³C NMR: (126 MHz, C₆D₆)

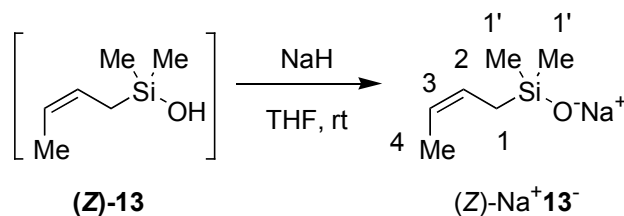
131.6 C(2), 121.7 C(3), 28.5 C(1), 18.4 C(4), 3.2 (C(1')).

Preparation of (Z)-1,1-Dimethyl-1-(2-buten-1-yl)silanol ((Z)-13)

To a single-necked, 1-L, round-bottom flask equipped with a magnetic stir bar was added 198 mL of 1 M acetate buffer (pH = 5) and ether (15 mL). (Z)-2-Butenyldimethylchlorosilane (4.46 g, 30.0 mmol) was then dissolved in ether (25 mL) then added by pipette to the vigorously stirring, heterogeneous mixture of acetate buffer and ether. After being stirred for 5 min, the reaction mixture was then poured into a 1-L separatory funnel and diluted with ether (50 mL). The aqueous phase was separated and washed with ether (2 x 50 mL), The three separate organic extracts were then sequentially washed with sat. aq. NaHCO₃ (50 mL) and the pH of the resulting aqueous wash was checked with litmus paper to ensure alkalinity. The organic extracts were then washed with brine (50 mL), combined, dried over Na₂SO₄, and then filtered through a pad of silica gel (10 g). The filtrate was concentrated (ambient temp., 20 mm Hg) and the residue purified by column chromatography (SiO₂, 30 mm x 20 cm, pentane/Et₂O, 4:1). Fractions were combined, concentrated to ~20 mL (ambient temp., 20 mm Hg) and then was transferred to a dry box for conversion to its sodium salt.

Data for ((Z)-13):

TLC: R_f 0.24 (pentane/Et₂O, 4:1) [silica gel, aqueous KMnO₄]

Preparation of Sodium (Z)-1,1-Dimethyl-1-(2-buten-1-yl)silanolate (Na⁺(Z)-13**⁻)**

In a dry box, washed NaH (800 mg, 33.0 mmol, 1.1 equiv) and THF (10 mL) were combined in a 50-mL, single-neck, round-bottomed flask containing a magnetic stir bar. In a separate 50-mL, single-neck, round-bottomed flask containing (Z)-2-butenyldimethylsilanol (30.0 mmol) was added THF (10 mL), this solution was then mixed and added drop-wise over 10 min to the stirred suspension of NaH. After being stirred for 30 min, the resulting mixture was filtered through a glass-fritted filter (M, 3.5 cm x 4.5 cm) into a 100-mL Schlenk flask. The filtrate was concentrated (ambient temp., 20 mm Hg) to afford a colorless amorphous solid. Hexane (10 mL) was then added and the resulting solution was concentrated (ambient temp., 0.5 mm Hg) to afford 3.88 g (85%) of Na⁺(Z)-**13**⁻ as a colorless solid.

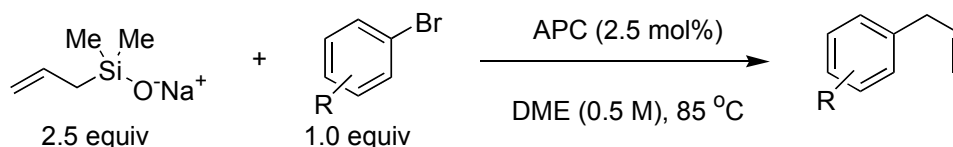
Data for (Na⁺(Z)-**13**⁻):

¹H NMR: (500 MHz, C₆D₆)

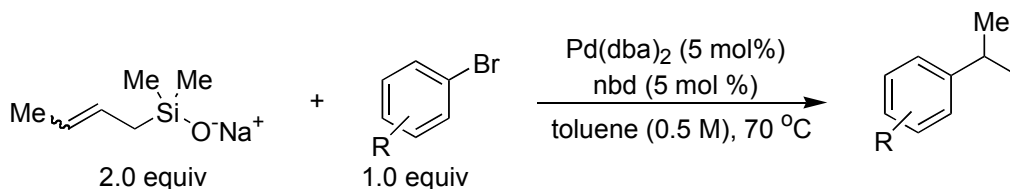
5.74 (m, 1 H, HC(2)), 5.49 (m, 1 H, HC(3)), 1.66 (d, *J* = 6.6, 3H, HC(4)), 1.55 (d, *J* = 8.6, 2 H, HC(1)), 0.12 (s, 6 H, HC(1')).

¹³C NMR: (126 MHz, C₆D₆)

130.1 C(2), 120.6 C(3), 23.3 C(1), 12.9 C(4), 3.6 (C(1')).

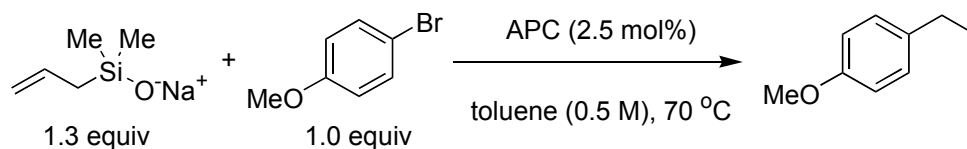
General Procedure I. Preparative Cross-coupling of Sodium 2-Propenyldimethylsilanolate with Aryl Bromides

To a 5-mL, single-necked, round-bottomed flask containing a magnetic stir bar, equipped with a reflux condenser and an argon inlet capped with a septum was added allylpalladium chloride dimer (APC, 9.2 mg, 0.025 mmol, 0.025 equiv). The flask was then sequentially evacuated and filled with argon three times. The aryl bromide (1.0 mmol) was then added by syringe. Sodium 2-propenyldimethylsilanolate (346 mg, 2.5 mmol, 2.5 equiv), pre-weighed into a 10-mL, two-necked, round-bottomed flask in a dry-box, was then dissolved in DME (2.0 mL) then added to the aryl bromide by syringe. The reaction mixture was heated in a preheated oil bath to 85 °C under argon. After complete consumption of the aryl bromide was observed by GC analysis, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) in a glass-fritted filter (coarse, 2 cm x 5 cm) and the filter cake washed with ether (3 x 10 mL). The filtrate was concentrated (ambient temp., 20 mm Hg) and the residue was purified by column chromatography (silica gel or C-18 reverse phase) followed by Kugelrohr distillation or recrystallization to afford the product.

General Procedure II. Preparative Cross-Coupling of Sodium 2-Butenyldimethylsilanolate with Aryl Bromides

To an oven dried, 5-mL, single-neck, round-bottomed flask, containing a magnetic stir bar, equipped with a reflux condenser and an argon inlet capped with a septum was added $\text{Pd}(\text{dba})_2$ (28.8 mg, 0.05 mmol, 0.05 equiv). The flask was then sequentially evacuated and filled with argon three times. The aryl bromide (1.0 mmol) was then added by syringe. Sodium 2-butenyldimethylsilanolate (308 mg, 2.0 mmol, 2.0 equiv), pre-weighed into a 10-mL, two-necked, round-bottomed flask in a dry-box, was then dissolved in toluene (2.0 mL) and then norbornadiene (nbd, 5.2 μL , 0.05 mmol, 0.050 equiv) was added by syringe. The solution of $\text{Na}^+\mathbf{13}^-$ and nbd in toluene was then added to the aryl bromide by syringe. The reaction mixture was heated under argon to 70 °C in a preheated oil bath. After complete consumption of the aryl bromide was observed by GC analysis, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) in a glass-fritted filter (C, 2 cm x 5 cm) and the filter cake washed with ether (3 x 10 mL). The filtrate was concentrated (ambient temp., 20 mm Hg) and the residue was purified by column chromatography (silica gel or C-18 reverse phase) followed by Kugelrohr distillation or recrystallization to afford the product.

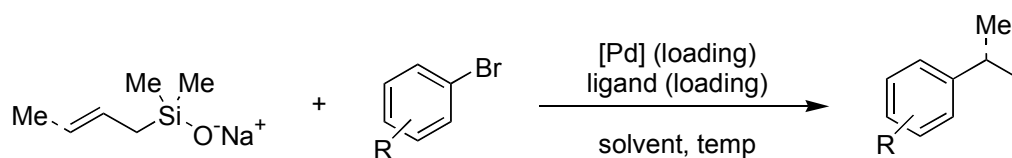
General Procedure III. Small-scale Cross-coupling of Sodium 2-Propenyldimethylsilanolate with 4-Bromoanisole (Dry-Box Set-Up)



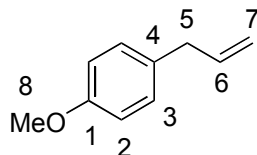
In a 5-mL, single-necked, round-bottomed flask containing a magnetic stir bar, equipped with a reflux condenser was combined APC (4.0 mg, 0.010 mmol, 0.025 equiv), biphenyl (40 mg, 0.26 mmol), 4-bromoanisole (75.0 mg, 0.40 mmol), toluene (0.80 mL) and Sodium 2-propenyldimethylsilanolate (72 mg, 0.52 mmol, 1.3 equiv). The flask was then sealed with a

septum, removed from the dry-box, and heated in a preheated oil bath to 70 °C under argon using a stainless steel 16 gauge needle. Aliquots (50 μ L) were removed from the reaction mixture by syringe, then were quenched with 10% 2-(dimethylamino)ethanethiol hydrochloride solution (0.25 mL), and were extracted with EtOAc (1 mL). The organic extract was then filtered through a small plug of silica gel in a pipette (0.5 cm x 1.0 cm) and the filter cake washed with EtOAc (0.5 mL). The sample was then analyzed by GC or GC/MS using Methods 1, 2, or 3.

General Procedure IV. Small-scale Cross-coupling of Sodium 2-Propenyldimethylsilanolate or Sodium 2-Butenyldimethylsilanolate with Aryl Bromides (Bench-Top Set-Up)



In a 5-mL, single-necked, round-bottomed flask containing a magnetic stir bar, equipped with a reflux condenser was combined palladium catalyst, ligand, and biphenyl (internal standard). The flask was then sequentially evacuated and filled with argon three times. The aryl bromide (1.0 equiv) was then added by syringe. The silanolate pre-weighed into a 10-mL, two-necked, round-bottomed flask in a dry-box, was then dissolved in solvent, and added to the aryl bromide by syringe. The reaction mixture was heated under argon in a preheated oil bath. Aliquots (50 μ L) were removed from the reaction mixture by syringe, quenched with 10% 2-(dimethylamino)ethanethiol hydrochloride solution (0.25 mL), and were extracted with EtOAc (1 mL). The organic extract was then filtered through a small plug of silica gel (0.5 cm x 1.0 cm) and the filter cake washed with EtOAc (0.5 mL). The sample was then analyzed by GC or GC/MS using Methods 1, 2, or 3.

1-Methoxy-4-(2-propen-1-yl)benzene (8a)

Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), 4-bromoanisole (187 mg, 1.0 mmol), Na^+I^- (346 mg, 2.5 mmol, 2.5 equiv), and DME (2.0 mL) were combined and heated to 85 °C. After 3 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (20 cm X 20 mm, hexane/EtOAc, gradient 100:0 to 20:1) followed by Kugelrohr distillation afforded 119 mg (80%) of **8a** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.¹⁸

Data for (8a):

bp: 90 °C (10 mmHg, ABT)

¹H NMR: (500 MHz, CDCl_3)

7.14 (d, $J = 8.5$, 2 H, HC(3)), 6.87 (d, $J = 8.5$, 2 H, HC(2)), 5.99 (ddt, $J = 16.8$, 10.3, 6.6, 1 H, HC(6)), 5.09 (m, 2 H, HC(7)), 3.81 (s, 3 H, HC(8)), 3.36 (d, $J = 6.6$, 2 H, HC(5)).

¹³C NMR: (126 MHz, CDCl_3)

158.2 C(1), 138.2 C(6), 132.4 C(4), 129.8 C(3), 115.7 C(7), 114.1 C(2), 55.5 C(8), 39.6 C(5).

IR: (film)

3077 (m), 3032 (m), 3003 (m), 2978 (m), 2954 (m), 2934 (m), 2906 (m), 2835 (m), 1639 (m), 1611 (s), 1584 (m), 1511 (s), 1464 (s), 1441 (m), 1321 (w), 1301 (s), 1247 (s), 1177 (s), 1111 (m), 1038 (s), 1012 (w), 995 (m), 914 (s), 842 (m),

830 (m), 815 (m), 761 (m), 708 (w), 639 (m), 624 (m).

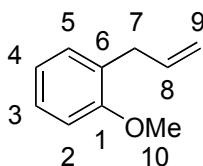
MS: (EI, 70eV)

148 (M^+ , 100), 133 (19), 121 (30), 105 (17), 91 (15), 77 (16).

TLC: R_f 0.35 (hexanes/EtOAc, 20:1) [silica gel, UV]

GC: t_R : 6.21 min (GC Method 1).

1-Methoxy-2-(2-propen-1-yl)benzene (**8b**)



Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), 2-bromoanisole (187 mg, 1.0 mmol), Na^+1^- (346 mg, 2.5 mmol, 2.5 equiv), and DME (2.0 mL) were combined and heated to 85 °C. After 12 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (20 cm X 20 mm, hexane/EtOAc, gradient 100:0 to 50:1) followed by Kugelrohr distillation afforded 116 mg (78%) of **8b** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.¹⁹

Data for (**8b**):

bp: 85 °C (11 mmHg, ABT)

1H NMR: (500 MHz, $CDCl_3$)

7.21 (td, $J = 8.2$ and 1.7 , 1 H, HC(3)), 7.15 (dd, $J = 7.4$ and 1.7 , 1 H, HC(5)), 6.92 (td, $J = 7.4$ and 1.0 , 1 H, HC(4)), 6.87 (d, $J = 8.2$, 1 H, HC(2)), 6.01 (ddt, $J = 16.8, 10.3, 6.6$, 1 H, HC(8)), 5.06 (m, 2 H, HC(9)), 3.84 (s, 3 H, HC(10)), 3.40 (d, $J = 6.6$, 2 H, HC(7)).

¹³C NMR: (126 MHz, CDCl₃)

157.5 C(1), 137.3 C(8), 130.0 C(5), 128.8 C(6), 127.6 C(2), 120.7 C(3), 115.6 C(4), 110.6 C(9), 55.6 C(10), 34.5 C(7).

IR: (film)

3077 (m), 3003 (m), 2938 (m), 2836 (m), 1638 (m), 1600 (m), 1493 (s), 1464 (s), 1439 (m), 1290 (m), 1245 (s), 1174 (m), 1126 (m), 1050 (m), 1032 (s), 996 (m), 752 (s).

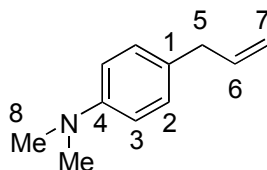
MS: (EI, 70eV)

148 (M⁺, 100), 133 (25), 119 (22), 115 (30), 105 (33), 91 (45), 77 (18), 65 (10), 55 (4).

TLC: *R_f* 0.23 (hexanes/EtOAc, 50:1) [silica gel, UV]

GC: *t_R*: 4.626 min (GC Method 2).

***N,N*-Dimethyl-4-(2-propen-1-yl)benzenamine (**8c**)**



Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), 4-bromo-*N,N*-dimethylaniline (200 mg, 1.0 mmol), Na⁺**1**⁻ (346 mg, 2.5 mmol, 2.5 equiv), and DME (2.0 mL) were combined and heated to 85 °C. After 7 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (20 cm X 20 mm, pentane/ether, gradient 100:0 to 50:1) followed by Kugelrohr distillation afforded 135 mg (84%) of **8c** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.²⁰

Data for (8c):

bp: 105 °C (5 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.08 (d, $J = 8.6$, 2 H, HC(2)), 6.73 (d, $J = 8.6$, 2 H, HC(3)), 5.97 (ddt, $J = 16.8$, 10.0, 6.7 1 H, HC(6)), 5.05 (m, 2 H, HC(7)), 3.32 (d, $J = 6.7$, 2 H, HC(5)), 2.93 (s, 6 H, HC(8)).

¹³C NMR: (126 MHz, CDCl₃)

149.5 C(4), 138.6 C(6), 129.4 C(1), 128.5 C(2), 115.3 C(7), 113.3 C(3), 41.2 C(8), 39.5 C(5).

IR: (film)

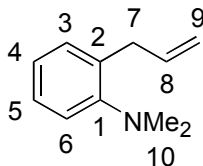
3076 (m), 3003 (m), 2976 (m), 2892 (m), 2845 (m), 2799 (m), 1638 (m), 1615 (s), 1567 (w), 1521 (s), 1479 (m), 1443 (m), 1412 (w), 1346 (s), 1278 (w), 1227 (m), 1190 (w), 1163 (m), 1132 (m), 1060 (w), 994 (m), 948 (m), 911 (m), 825 (m), 802 (s).

MS: (EI, 70eV)

161 (M⁺, 100), 134 (46), 117 (18), 91 (12),

TLC: R_f 0.25 (pentane/ether, 50:1) [silica gel, UV]

GC: t_R : 5.78 min (GC Method 2).

***N,N*-Dimethyl-2-(2-propenyl)benzenamine (8d)**

Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), 2-bromo-*N,N*-dimethylaniline (200 mg, 1.0 mmol), Na⁺1⁻ (346 mg, 2.5 mmol, 2.5 equiv), DME (2.0 mL) were combined and heated to 85 °C. After 12 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (20 cm X 20 mm, hexane/EtOAc, gradient 100:0 to 50:1) followed by Kugelrohr distillation afforded 135 mg (84%) of **8d** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.²¹

Data for (8d):

bp: 85 °C (9 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.20 (d, *J* = 7.4, 1 H, HC(3)), 7.19 (t, *J* = 7.6, 1 H, HC(5)), 7.10 (d, *J* = 7.8, 1 H, HC(4)), 7.02 (t, *J* = 7.3, 1 H, HC(4)), 6.01 (ddt, *J* = 16.8, 10.3, 6.6, 1 H, HC(8)), 5.11 (m, 2 H, HC(9)), 3.50 (d, *J* = 6.6, 2 H, HC(7)), 2.69 (s, 6 H, HC(10)).

¹³C NMR: (126 MHz, CDCl₃)

152.8 C(1), 138.1 C(8), 134.7 C(2), 130.4 C(5), 127.1 C(4), 123.3 C(3), 119.4 C(6), 115.9 C(9), 45.2 C(10), 35.2 C(7).

IR: (film)

3075 (m), 3021 (m), 2978 (m), 2939 (s), 2888 (m), 2860 (m), 2826 (s), 2784 (s), 2610 (w), 2236 (w), 1908 (w), 1826 (w), 1638 (m), 1598 (m), 1493 (s), 1451 (s),

1306 (m), 1188 (m), 1156 (s), 1096 (m), 1049 (m), 995 (m), 950 (s), 912 (s), 766 (s).

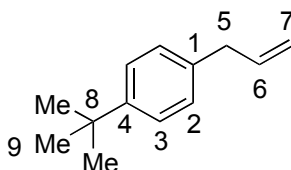
MS: (EI, 70eV)

161 (M^+ , 100), 146 (52), 132 (77), 118 (30), 104 (7), 91 (25), 77 (13), 65 (10).

TLC: R_f 0.12 (hexanes/EtOAc, 50:1) [silica gel, UV]

GC: t_R : 4.971 min (GC Method 2).

1-(1,1-Dimethylethyl)4-(2-propen-1-yl)benzene (8e)



Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), 4-bromo-*tert*-butylbenzene (213 mg, 1.0 mmol), Na^+1^- (346 mg, 2.5 mmol, 2.5 equiv), and DME (2.0 mL) were combined and heated to 85 °C. After 9 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (20 cm X 20 mm, pentane) and C-18 reverse phase chromatography (20 cm x 10 mm, MeCN/H₂O, 9:1) followed by Kugelrohr distillation afforded 128 mg (74%) of **8e** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.²²

Data for (8e):

bp: 85 °C (5 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.34 (d, J = 8.3, 2 H, HC(3)), 7.14 (d, J = 8.3, 2 H, HC(2)), 5.99 (ddt, J = 16.9, 10.0, 6.8 1 H, HC(6)), 5.09 (m, 2 H, HC(7)), 3.38 (d, J = 6.8, 2 H, HC(5)), 1.32 (s, 9 H, HC(9)).

¹³C NMR: (126 MHz, CDCl₃)

149.1 C(4), 137.9 C(6), 137.3 C(1), 128.4 C(3), 125.6 C(2), 115.9 C(7), 40.0 C(5), 34.6 C(8), 31.7 C(9).

IR: (film)

3079 (w), 3057 (w), 3025 (w), 3004 (w), 2964 (m), 2905 (m), 2869 (m), 1638 (w), 1515 (m), 1499 (w), 1475 (w), 1460 (w), 1432 (w), 1414 (w), 1393 (w), 1364 (w), 1269 (w), 1203 (w), 1110 (w), 1020 (w), 993 (w), 913 (w), 848 (w), 833 (w), 806 (w).

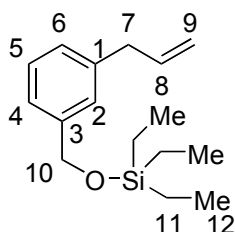
MS: (EI, 70eV)

174 (32), 153 (M⁺, 100), 131 (12), 117 (13), 105 (10), 91 (18), 57 (13).

TLC: *R_f* 0.58 (pentane) [silica gel, UV]

GC: *t_R*: 5.26 min (GC Method 2).

1-[(Triethylsilyl)oxy]methyl-3-(2-propenyl)benzene (8f)



Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), 3-bromotriethylsilylbenzyl ether (301 mg, 1.0 mmol), Na⁺1⁻ (346 mg, 2.5 mmol, 2.5 equiv), and DME (2.0 mL) were combined and heated to 85 °C. After 4 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (20 cm X 20 mm, hexane/EtOAc, gradient 100:0 to 20:1) followed by Kugelrohr distillation afforded 225 mg (86%) of **8f** as a clear, colorless oil.

Data for (8f):

bp: 170 °C (2 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.26 (t, $J = 7.6$, 1 H, HC(5)), 7.18 (d, $J = 7.9$, 2 H, HC(4), HC(6)), 7.08 (d, $J = 7.6$, 1 H, HC(2)), 5.97 (ddt, $J = 16.9, 10.1, 6.7$, 1 H, HC(8)), 5.08 (m, 2 H, HC(9)), 4.72 (s, 2 H, HC(10)), 3.39 (d, $J = 6.7$, 2 H, HC(7)), 0.98 (t, $J = 7.9$, 9 H, HC(12)), 0.65 (q, $J = 7.9$, 6 H, HC(11)).

¹³C NMR: (126 MHz, CDCl₃)

141.7 C(1), 140.2 C(3), 137.7 C(8), 128.5 C(4), 127.5 C(6), 126.7 C(5), 124.3 C(2), 116.0 C(9), 65.0 C(10), 40.5 C(7), 7.0 C(12), 4.7 C(11).

IR: (film)

3059 (m), 3005 (m), 2954 (s), 2911 (s), 2876 (s), 2732 (w), 1639 (m), 1609 (m), 1591 (w), 1488 (m), 1458 (m), 1414 (m), 1372 (m), 1239 (s), 1153 (s), 1105 (s), 1078 (s), 1006 (s), 974 (m), 913 (s), 820 (s), 743 (s), 700 (s), 669 (m).

MS: (EI, 70eV)

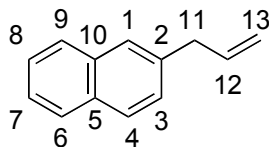
233 ($M^+ - CH_2CH_3$, 100), 203 (13), 175 (16), 131 (44), 115 (11), 91 (17).

HRMS: (CI)

calc for C₁₆H₂₇OSi ($M^+ + H$): 263.1831; found: 263.1830.

TLC: R_f 0.17 (hexanes/EtOAc, 20:1) [silica gel, UV]

GC: t_R : 7.10 min (GC Method 3).

2-(2-Propen-1-yl)naphthalene (8g)

Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), 2-bromonaphthalene (207 mg, 1.0 mmol), Na^+I^- (346 mg, 2.5 mmol, 2.5 equiv), and DME (2.0 mL) were combined and heated to 85 °C. After 9 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (20 cm X 20 mm, pentane) and C-18 reverse phase chromatography (20 cm x 10 mm, MeOH/H₂O, 9:1) followed by Kugelrohr distillation afforded 120 mg (71%) of **8g** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.²³

Data for (8g):

bp: 62 °C (0.1 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.82 (m, 3 H, HC(4), HC(6), HC(9)), 7.65 (bs, 1 H, HC(1)), 7.46 (pd, $J = 6.9, 1.5$ 2 H, HC(3), HC(8)), 7.36 (dd, $J = 8.4, 1.7$ 1 H, HC(7)), 6.08 (ddt, $J = 16.8, 10.1, 6.7$, 1 H, HC(12)), 5.16 (m, 2 H, HC(13)), 3.58 (d, $J = 6.7$, 2 H, HC(11)).

¹³C NMR: (126 MHz, CDCl₃)

137.8 C(2), 137.6 C(12), 133.9 C(10), 132.4 C(5), 128.2 C(4), 127.9 C(9), 127.8 C(6), 127.7 C(1), 126.9 C(8), 126.2 C(7), 125.5 C(3), 116.3 C(13), 40.6 C(11).

IR: (film)

3053 (w), 2977 (w), 2900 (w), 2833 (w), 1919 (w), 1831 (w), 1637 (w), 1600 (w), 1560 (w), 1542 (w), 1508 (w), 1431 (w), 1412 (w), 1364 (w), 1268 (w), 1142 (w), 1124 (w), 1018 (w), 994 (w), 960 (w), 913 (w), 851 (w), 814 (w), 771 (w), 752

(w).

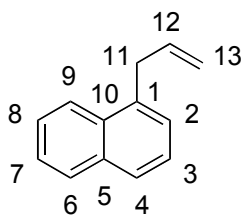
MS: (EI, 70eV)

168 (M^+ , 100), 153 (26), 141 (18), 115 (17).

TLC: R_f 0.25 (pentane) [silica gel, UV]

GC: t_R : 6.31 min (GC Method 2).

1-(2-Propen-1-yl)naphthalene (**8h**)



Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), 1-bromonaphthalene (207 mg, 1.0 mmol), Na^+I^- (346 mg, 2.5 mmol, 2.5 equiv), and DME (2.0 mL) were combined and heated to 85 °C. After 2 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (20 cm x 20 mm, hexane) and C-18 reverse phase chromatography (20 cm x 10 mm, MeOH/H₂O, 9:1) followed by Kugelrohr distillation afforded 143 mg (85%) of **8h** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.²⁴

Data for (**8h**):

bp: 85 °C (1.0 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

8.05 (d, J = 8.1, 1 H, HC(9)), 7.87 (d, J = 7.6, 1 H, HC(6)), 7.76 (d, J = 8.1, 1 H, HC(4)), 7.51 (m, 2 H, HC(8), HC(7)), 7.44 (m, 1 H, HC(3)), 7.36 (d, J = 6.6, 1 H, C(2)), 6.14 (ddt, J = 16.8, 10.5, 6.3, 1 H, HC(12)), 5.12 (m, 2 H, HC(13)), 3.86 (d,

$J = 6.3$, 2 H, HC(11)).

^{13}C NMR: (126 MHz, CDCl_3)

137.2 C(12), 136.4 C(1), 134.1 C(5), 132.2 C(10), 128.9 C(6), 127.2 C(4), 126.5 C(8), 126.1 C(7), 125.9 C(3), 125.8 C(9), 124.3 C(2), 116.4 C(13), 37.5 C(11).

IR: (film)

3046 (m), 3005 (m), 2977 (m), 2912 (m), 2849 (w), 1924 (w), 1831 (w), 1702 (w), 1654 (w), 1638 (m), 1597 (m), 1510 (m), 1430 (w), 1396 (m), 1352 (w), 1296 (w), 1259 (w), 1238 (w), 1218 (w), 1165 (w), 1142 (w), 1076 (w), 1016 (m), 994 (m), 976 (w), 914 (m), 853 (w), 791 (m), 776 (m), 732 (w).

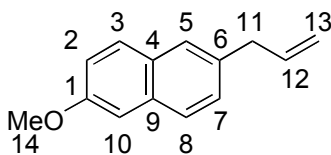
MS: (EI, 70eV)

168 (M^+ 100), 153 (65), 141 (22), 115 (24).

TLC: R_f 0.29 (hexanes) [silica gel, UV]

GC: t_R : 9.496 min (99.7%) (GC Method 1).

2-Methoxy-6-(2-propenyl)naphthalene (**8i**)



Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), 2-bromo-6-methoxynaphthalene (237 mg, 1.0 mmol), $\text{Na}^+\mathbf{1}^-$ (346 mg, 2.5 mmol, 2.5 equiv), and DME (2.0 mL) were combined and heated to 85 °C. After 6 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (20 cm X 20 mm, pentane/ether/ CH_2Cl_2 , gradient 99:0:1 to 97:2:1) followed by recrystallization from pentane afforded 188 mg (95%) of **8i** as white needles. Spectroscopic data

matched those reported in the literature.²⁵

Data for (8i):

mp: 54-55 °C

¹H NMR: (500 MHz, CDCl₃)

7.69 (d, $J = 8.3$, 2 H, HC(3), HC(8)), 7.57 (d, $J = 0.7$, 1 H, HC(5)), 7.31 (dd, $J = 8.3$ and 1.7, 1 H, HC(7)), 6.87 (d, $J = 8.2$, 1 H, HC(2), HC(10)), 6.06 (ddt, $J = 17.1$, 10.2, 6.6, 1 H, HC(12)), 5.13 (m, 2 H, HC(13)), 3.92 (s, 3 H, HC(14)), 3.53 (d, $J = 6.6$, 2 H, HC(11)).

¹³C NMR: (126 MHz, CDCl₃)

157.5 C(1), 137.8 C(12), 135.4 C(6), 133.4 C(9), 129.4 C(4), 129.2 C(3), 128.1 C(5), 127.1 C(8), 126.8 C(7), 119.0 C(2), 116.1 C(13), 105.9 C(10), 55.5 C(14), 40.4 C(11).

IR: (film)

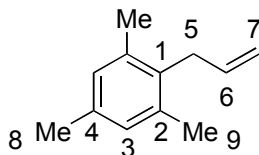
3051 (w), 3013 (w), 2962 (w), 2934 (w), 2904 (w), 2836 (w), 2345 (w), 1636 (w), 1629 (w), 1604 (m), 1505 (w), 1483 (m), 1461 (w), 1432 (w), 1388 (w), 1264 (m), 1236 (m), 1203 (m), 1160 (m), 1120 (w), 1030 (m), 1000 (w), 919 (m), 857 (m), 825 (m).

MS: (EI, 70eV)

198 (M⁺, 100), 183 (17), 167 (18), 155 (21), 139 (6), 128 (17), 115 (7), 99 (4), 87 (2), 76 (4), 63 (5).

TLC: R_f 0.39 (pentane/Et₂O/CH₂Cl₂, 97/2:1) [silica gel, UV]

GC: t_R : 7.196 min (GC Method 2).

1,3,5-Trimethyl-2-(2-propenyl)benzene (8j)

Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), Ph_3PO (14 mg, 0.05 mmol, 0.050 equiv), 2-bromomesitylene (199 mg, 1.0 mmol), Na^+I^- (691 mg, 5.0 mmol, 5.0 equiv), and dioxane (2.0 mL) were combined and heated to 100 °C. After 7 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (20 cm X 20 mm, hexane) and C-18 reverse phase chromatography (20 cm x 10 mm, MeCN/ H_2O , 9:1) followed by Kugelrohr distillation afforded 128 mg (80%) of **8j** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.²⁶

Data for (8j):

bp: 100 °C (10 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

6.86 (s, 2 H, HC(3)), 5.89 (ddt, $J = 17.1, 10.1, 5.7$ 1 H, HC(6)), 4.99 (dq, $J = 10.1, 1.8$, 1 H, $\text{H}_{\text{cis}}\text{C}(7)$), 4.87 (dq, $J = 17.1, 1.8$, 1 H, $\text{H}_{\text{trans}}\text{C}(7)$), 3.37 (dt, $J = 5.7, 1.8$, 2 H, HC(5)), 2.27 (s, 9 H, HC(8), HC(9)).

^{13}C NMR: (126 MHz, CDCl_3)

136.8 C(6), 135.8 C(1), 135.6 C(4), 133.3 C(2), 129.0 C(3), 114.9 C(7), 33.6 C(5), 21.1 C(8), 20.0 C(9).

IR: (film)

3078 (w), 3002 (m), 2973 (m), 2946 (m), 2919 (m), 2861 (m), 2731 (w), 1637 (m), 1613 (w), 1577 (w), 1559 (w), 1484 (m), 1444 (m), 1375 (w), 1257 (w),

1200 (w), 1031 (w), 991 (w), 910 (m), 850 (m), 796 (w), 717 (w).

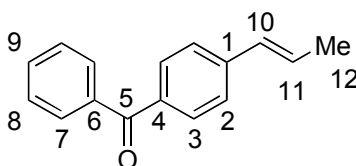
MS: (EI, 70eV)

160 (M^+ , 83), 145 (100), 133 (16), 115 (12), 105 (11), 91 (10).

TLC: R_f 0.58 (pentane) [silica gel, UV]

GC: t_R : 5.14 min (99.7%) (GC Method 3).

Phenyl[4-(1*E*)1-propen-1-ylphenyl]methanone, (9)



Following General Procedure I, APC (9.2 mg, 0.025 mmol, 0.025 equiv), 4-bromobenzophenone (301 mg, 1.0 mmol), Na^+I^- (346 mg, 2.5 mmol, 2.5 equiv), and DME (2.0 mL) were combined and heated to 85 °C. After 1 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether. Purification by silica gel chromatography (30 cm X 30 mm, hexane/EtOAc, gradient 100:0 to 20:1) afforded 169 mg (76%) of **9** as a pale-yellow solid. Spectroscopic data matched those reported in the literature.²⁷

Data for (9):

mp: 62-63 °C

1H NMR: (400 MHz, $CDCl_3$)

7.78 (m, 4 H, HC(7), HC(8)), 7.58 (m, 1 H, HC(9)), 7.48 (m, 2 H, HC(3)), 7.42 (m, 2 H, HC(2)), 6.42 (m, 2 H, HC(10), HC(11)), 1.93 (d, $J = 5.1$, 3 H, HC(12)).

¹³C NMR: (126 MHz, CDCl₃)

196.2 C(5), 142.1 C(1), 137.9 C(6), 135.6 C(4), 132.2 C(9), 130.6 C(3), 130.3 C(11), 129.9 C(7), 129.0 C(10), 128.2 C(8), 125.6 C(2), 18.7 C(12).

IR: (film)

3041 (m), 1651 (s), 1602 (s), 1579 (w), 1447 (m), 1411 (m), 1317 (m), 1283 (s), 1222 (m), 1208 (w), 1177 (m), 1150 (w), 968 (m), 957 (w), 939 (m), 924 (m), 861 (w).

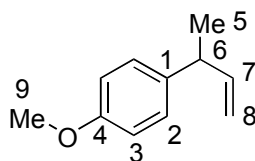
MS: (EI, 70eV)

222 (M⁺, 73), 145 (100), 115 (23), 105 (20), 77 (19).

TLC: *R_f* 0.33 (hexanes/EtOAc, 20:1) [silica gel, UV]

GC: *t_R*: 7.99 min (GC Method 2).

1-Methoxy-4-(1-methyl-2-propen-1-yl)benzene (**14a**)



Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 4-bromoanisole (187 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μL, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 85 °C. After 6 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, hexane/EtOAc, gradient 100:0 to 20:1) followed by Kugelrohr distillation afforded 58 mg (36%) of **14a** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.²⁸

Data for (14a):bp: 120 °C (10 mmHg, ABT)¹H NMR: (500 MHz, CDCl₃)

7.14 (m, 2 H, HC(3)), 5.99 (m, 2 H, HC(2)), 5.99 (ddd, $J = 16.9, 10.3, 6.4$, 1 H, HC(7)), 5.03 (m, 2 H, HC(8)), 3.80 (s, 3 H, HC(9)), 3.43 (ap, $J = 7.0$, 1 H, HC(6)), 1.35 (d, $J = 7.0$, 3 H, HC(5)).

¹³C NMR: (126 MHz, CDCl₃)

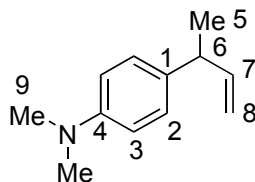
158.2 C(4), 143.9 C(7), 137.9 C(1), 128.4 C(2), 114.0 C(8), 113.0 C(3), 55.5 C(9), 42.6 C(6), 21.1 C(5).

IR: (film)

2962 (m), 2834 (m), 1653 (w), 1636 (m), 1610 (m), 1583 (m), 1512 (m), 1458 (m), 1420 (w), 1369 (w), 1245 (m), 1178 (m), 1109 (w), 1038 (m), 912 (m), 830 (m), 739 (w).

MS: (EI, 70eV)

162 (M^+ , 62), 147 (100), 131 (12), 115 (11), 91 (27).

TLC: R_f 0.43 (hexane/EtOAc, 20:1) [silica gel, UV]GC: γ - t_R : 5.15 min, α - t_R : 5.45 and 5.53 min (29:1 [2.7:1], γ : α [E or Z]) (GC Method 3).***N,N*-Dimethyl-4-(1-Methyl-2-propen-1-yl)benzenamine (14c)**

Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 4-bromo-*N,N*-dimethylaniline (200 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μ L,

0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 85 °C. After 20 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, pentane/ether, gradient 100:0 to 20:1) followed by Kugelrohr distillation afforded 58 mg (33%) of **14c** as a clear, colorless oil.

Data for (14c):

bp: 110 °C (10 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.11 (m, 2 H, HC(3)), 6.74 (m, 2 H, HC(2)), 6.00 (ddd, $J = 17.0, 10.3, 6.5$, 1 H, HC(7)), 5.02 (m, 2 H, HC(8)), 3.40 (ap, $J = 7.0$, 1 H, HC(6)), 2.93 (s, 6 H, HC(9)), 1.35 (d, $J = 7.0$, 3 H, HC(5)).

¹³C NMR: (126 MHz, CDCl₃)

144.2 C(7), 128.0 C(1), 126.9 C(2), 113.3 C(8), 112.6 C(3), 42.4 C(9), 41.2 C(6), 21.0 C(5).

IR: (film)

2963 (m), 2874 (w), 2798 (w), 1614 (m), 1521 (s), 1477 (w), 1444 (w), 1347 (m), 1224 (w), 1165 (w), 1060 (w), 948 (w), 910 (w), 817 (m).

MS: (EI, 70eV)

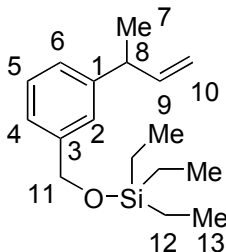
175 (M⁺, 100), 160 (98), 144 (20), 115 (12).

HRMS: (EI, 70eV)

calc for C₁₂H₁₇N (M⁺): 175.1361; found: 175.1363

TLC: R_f 0.30 (pentane/ether, 20:1) [silica gel, UV]

GC: γ - t_R : 6.00 min, α - t_R : 6.30, 6.52 min (8.5:1 [1.4:1], γ : α [*E* or *Z*]) (GC Method 3).

1-[[Triethylsilyl]oxy]methyl]-3-(1-methyl-2-propen-1-yl)benzene (14f**)**

Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), triethylsilyl 3-bromobenzyl ether (301 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μ L, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 4 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, hexane/EtOAc, gradient 100:0 to 20:1) followed by Kugelrohr distillation afforded 218 mg (79%) of **14f** as a clear, colorless oil.

Data for (**14f**):

bp: 145 °C (1.0 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.27 (t, *J* = 7.6, 1 H, HC(5)), 7.18 (m, 2 H, HC(4) and HC(6)), 7.10 (d, *J* = 7.6, 1 H, HC(2)), 6.00 (ddd, *J* = 17.1, 10.3, 6.8, 1 H, HC(9)), 5.04 (m, 2 H, HC(10)), 4.72 (s, 2 H, HC(11)), 3.47 (ap, *J* = 6.8, 1 H, HC(8)), 1.36 (d, *J* = 6.8, 3 H, HC(7)), 0.98 (t, *J* = 7.9, 9 H, HC(13)), 0.65 (q, *J* = 7.9, 6 H, HC(12)).

¹³C NMR: (126 MHz, CDCl₃)

145.5 C(1), 143.2 C(9), 141.4 C(3), 128.3 C(4), 125.9 C(6), 124.1 C(5), 123.3 C(2), 113.0 C(10), 64.8 C(11), 43.2 C(8), 20.7 C(7), 6.8 C(13), 4.5 C(12).

IR: (film)

2956 (m), 2875 (m), 1636 (w), 1607 (w), 1487 (w), 1457 (w), 1457 (w), 1413 (m), 1372 (w), 1239 (w), 1160 (w), 1082 (m), 1016 (m), 911 (w), 819 (w), 741 (m), 704 (w).

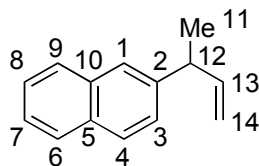
MS: (EI, 70eV)

275 (M-1, 8), 261 (36), 247 (79), 217 (11), 205 (22), 191 (12), 165 (14), 145 (36), 131 (42), 117 (33), 103 (100), 91 (22), 75 (72).

TLC: R_f 0.41 (hexane/EtOAc, 20:1) [silica gel, UV]

GC: γ - t_R : 7.25 min, α - t_R : 7.43 and 7.52 min (15:1 [2.4:1], γ : α [*E* or *Z*]) (GC Method 3).

2-(1-Methyl-2-propen-1-yl)naphthalene (**14g**)



Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 2-bromonaphthalene (207 mg, 1.0 mmol), Na⁺**13**⁺ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μ L, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 6 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, pentane) and C-18 reverse phase chromatography (20 cm x 10 mm, MeOH/H₂O, 9:1) followed by Kugelrohr distillation afforded 145 mg (80%) of **14g** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.²⁹

Data for (**14g**):

bp: 160 °C (5 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.80 (m, 3 H, HC(4), HC(6), HC(9)), 7.66 (s, 1 H, HC(1)), 7.45 (m, 2 H, HC(3), HC(8)), 7.38 (m, 1 H, HC(7)), 6.10 (ddd, $J = 16.9, 10.3, 6.9$, 1 H, HC(13)), 5.11 (m, 2 H, HC(14)), 3.65 (ap, $J = 6.9$, 1 H, HC(12)), 1.47 (d, $J = 6.9$, 3 H, HC(11)).

¹³C NMR: (126 MHz, CDCl₃)

143.4 C(13), 143.2 C(2), 133.9 C(10), 132.4 C(5), 128.2 C(4), 127.9 C(9), 127.8 C(6), 126.5 C(1), 126.1 C(8), 125.5 C(7), 125.4 C(3), 113.7 C(14), 43.5 C(12), 20.9 C(11).

IR: (film)

3055 (m), 3013 (w), 2965 (m), 2930 (w), 2874 (w), 1632 (w), 1600 (w), 1507 (w), 1452 (w), 1412 (w), 1374 (w), 1257 (m), 1126 (w), 1032 (m), 997 (w), 963 (w), 949 (w), 912 (m), 893 (w), 855 (m), 817 (s), 748 (s).

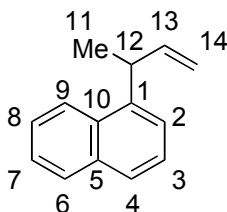
MS: (EI, 70eV)

182 (M⁺, 69), 167 (100), 152 (22), 128 (11).

TLC: R_f 0.39 (pentane) [silica gel, UV]

GC: γ - t_R : 6.50 min, α - t_R : 6.71 and 6.79 min (25:1 [1.9:1], γ : α [E or Z]) (GC Method 3).

1-(1-Methyl-2-propen-1-yl)naphthalene (14h)



Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 1-bromonaphthalene (207 mg, 1.0 mmol), Na⁺**13**⁻ (386 mg, 2.5 mmol, 2.5 equiv), nbd (5.2 μ L, 0.05

mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 6 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, pentane) followed by Kugelrohr distillation afforded 116 mg (63%) of **14h** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.³⁰

Data for (14h):

bp: 120 °C (1 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

8.15 (d, *J* = 8.4, 1 H, HC(9)), 7.88 (d, *J* = 7.9, 1 H, HC(6)), 7.74 (d, *J* = 8.1, 1 H, HC(4)), 7.49 (m, 4 H, HC(2), HC(3), HC(7), HC(8)), 6.18 (ddd, *J* = 17.7, 10.0, 5.8 1 H, HC(13)), 5.15 (m, 2 H, HC(14)), 4.32 (ap, *J* = 7.0, 1 H, HC(12)), 1.53 (d, *J* = 7.0, 3 H, HC(11)).

¹³C NMR: (126 MHz, CDCl₃)

143.1 C(13), 141.7 C(1), 134.2 C(5), 131.7 C(10), 129.1 C(6), 127.0 C(4), 126.0 C(3), 125.8 C(9), 125.6 C(7), 123.9 C(8), 123.7 C(2), 113.9 C(14), 38.1 C(12), 20.5 C(11).

IR: (film)

3048 (m), 2967 (m), 2931 (m), 2874 (m), 1923 (w), 1830 (w), 1700 (w), 1684 (w), 1653 (w), 1636 (m), 1596 (m), 1509 (m), 1452 (m), 1410 (m), 1395 (m), 1369 (m), 1250 (m), 1235 (w), 1167 (w), 1016 (m), 997 (m), 912 (m), 859 (w), 797 (m), 777 (m).

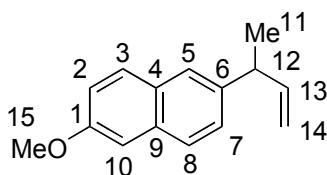
MS: (EI, 70eV)

182 (M⁺, 63), 167 (100), 152 (24), 128 (13).

TLC: R_f 0.42 (pentane) [silica gel, UV]

GC: γ - t_R : 6.50 min, α - t_R : 6.67 and 6.78 min (13:1 [1.5:1], γ : α [*E* or *Z*]) (GC Method 3).

2-Methoxy-6-(1-methyl-2-propen-1-yl)naphthalene (**14i**)



Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 2-bromo-6-methoxynaphthalene (237 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μ L, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 3 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, pentane/ether/CH₂Cl₂, gradient 99:0:1 to 97:2:1) followed by Kugelrohr distillation afforded 146 mg (69%) of **14i** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.³¹

Data for (**14i**):

bp: 170 °C (5 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.70 (dd, J = 8.5, 2.4, 2 H, HC(3), HC(8)), 7.58 (s, 1 H, HC(5)), 7.34 (dd, J = 8.5, 1.8, 1 H, HC(7)), 7.13 (m, 2 H, HC(2), HC(10)), 6.09 (ddd, J = 16.8, 10.3, 6.4, 1 H, HC(13)), 5.09 (m, 2 H, HC(14)), 3.92 (s, 3 H, HC(15)), 3.61 (ap, J = 7.0, 1 H, HC(12)), 1.45 (d, J = 7.0, 3 H, HC(11)).

¹³C NMR: (126 MHz, CDCl₃)

157.5 C(1), 143.6 C(13), 140.9 C(6), 133.4 C(9), 129.4 C(4), 129.3 C(3), 127.1 C(5), 127.0 C(8), 125.3 C(7), 118.9 C(2), 113.5 C(14), 105.9 C(10), 55.5 C(15), 43.3 C(12), 20.9 C(11).

IR: (film)

3057 (w), 3000 (w), 2963 (m), 2838 (w), 1636 (m), 1606 (s), 1506 (m), 1483 (m), 1464 (w), 1437 (w), 1415 (w), 1391 (m), 1369 (w), 1266 (m), 1231 (m), 1214 (m), 1195 (w), 1177 (w), 1162 (m), 1034 (m), 927 (w), 912 (w), 889 (w), 851 (m), 810 (m).

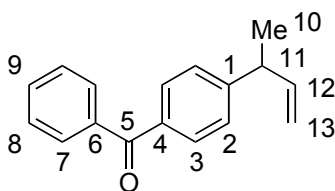
MS: (EI, 70eV)

236 (M⁺, 98), 197 (100), 165 (49), 153 (28), 141 (13), 113 (33), 84 (22).

TLC: *R_f* 0.29 (pentane/ether/CH₂Cl₂, 97/2:1) [silica gel, UV]

GC: γ -*t_R*: 7.44 min, α -*t_R*: 7.64 and 7.74 min (24:1 [1.5:1], γ : α [*E* or *Z*]) (GC Method 3).

[4-(1-Methyl-2-propen-1-yl)phenyl]phenylmethanone (14k)



Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 4-bromobenzophenone (261 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μ L, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 20 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm,

hexane/EtOAc, gradient 100:0 to 20:1) followed by Kugelrohr distillation afforded 187 mg (81%) of **14k** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.³²

Data for (14k):

bp: 170 °C (5 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.79 (m, 4 H, HC(7), HC(8)), 7.58 (m, 1 H, HC(9)), 7.48 (m, 2 H, HC(3)), 7.33 (m, 2 H, HC(2)), 6.02 (m, 1 H, HC(12)), 5.10 (m, 2 H, HC(13)), 3.56 (ap, $J = 7.0$, 1 H, HC(11)), 1.41 (d, $J = 7.0$, 3 H, HC(10)).

¹³C NMR: (126 MHz, CDCl₃)

196.7 C(5), 150.8 C(1), 142.5 C(12), 138.1 C(4), 135.8 C(6), 132.5 C(9), 130.7 C(7), 130.2 C(3), 128.5 C(8), 127.5 C(2), 114.2 C(13), 43.5 C(11), 20.8 C(10).

IR: (film)

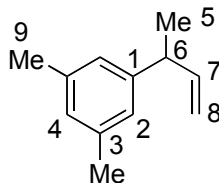
3059 (m), 2967 (m), 2930 (m), 2875 (m), 1653 (s), 1604 (s), 1577 (m), 1447 (m), 1412 (m), 1370 (w), 1316 (s), 1278 (s), 1177 (m), 1149 (m), 1111 (w), 1070 (m), 1017 (m), 1000 (m), 938 (m), 923 (m), 850 (m), 795 (m), 738 (m), 700 (m).

MS: (EI, 70eV)

236 (M⁺, 96), 159 (66), 131 (27), 105 (100), 77 (45).

TLC: R_f 0.24 (hexane/EtOAc, 20:1) [silica gel, UV]

GC: γ - t_R : 8.24 min, α - t_R : 8.48 and 8.61 min (14:1 [3.4:1], γ : α [*E* or *Z*]) (GC Method 3).

1,3-Dimethyl-5-(1-methyl-2-propenyl)benzene (14l)

Following General Procedure II, Pd(dba)₂ (57.6 mg, 0.10 mmol, 0.050 equiv), 5-bromo-*o*-xylene (370 mg, 2.0 mmol), Na⁺**13**⁻ (617 mg, 4.0 mmol, 2.0 equiv), nbd (10.4 μL, 0.10 mmol, 0.050 equiv), and toluene (4.0 mL) were combined and heated to 70 °C. After 3 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 30 mm, pentane) followed by Kugelrohr distillation afforded 215 mg (69%) of **14l** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.³³

Data for (14l):

bp: 140 °C (10 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

6.88 (m, 3 H, HC(2), HC(4)), 6.04 (ddd, *J* = 17.1, 10.3, 6.5, 1 H, HC(7)), 5.08 (m, 2 H, HC(8)), 3.43 (ap, *J* = 7.0, 1 H, HC(6)), 2.34 (s, 6 H, HC(9)), 1.38 (d, *J* = 7.0, 3 H, HC(5)).

¹³C NMR: (126 MHz, CDCl₃)

145.8 C(1), 143.7 C(7), 138.1 C(3), 128.0 C(4), 125.3 C(2), 113.1 C(8), 43.4 C(6), 21.6 C(9), 21.0 C(5).

IR: (film)

3081 (w), 3013 (m), 2965 (s), 2918 (m), 2870 (m), 2730 (w), 1636 (w), 1602 (m), 1454 (m), 1410 (m), 1370 (w), 1305 (w), 1257 (m), 1164 (w), 1036 (m), 997 (m),

964 (w), 911 (m), 848 (s), 819 (m), 799 (m), 719 (m), 702 (m).

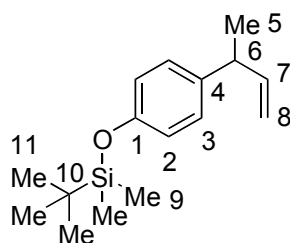
MS: (EI, 70eV)

160 (M^+ , 52), 145 (100), 130 (19), 115 (10).

TLC: R_f 0.54 (pentane) [silica gel, UV]

GC: γ - t_R : 4.80 min, α - t_R : 5.13 and 5.23 min (21:1 [1.6:1], γ : α [*E* or *Z*]) (GC Method 3).

1-[(1,1-Dimethylethyl)dimethylsilyl]oxy]-4-(1-methyl-2-propen-1-yl)benzene (14m**)**



Following General Procedure II, $\text{Pd}(\text{dba})_2$ (28.8 mg, 0.05 mmol, 0.050 equiv), 4-bromophenol *tert*-butyldimethylsilyl ether (287 mg, 1.0 mmol), $\text{Na}^+\mathbf{13}^-$ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μL , 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 8 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, hexane/DCM, 4:1) followed by Kugelrohr distillation afforded 199 mg (76%) of **14m** as a clear, colorless oil.

Data for (**14m**):

bp: 145 °C (5 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

7.06 (m, 2 H, HC(3)), 6.77 (m, 2 H, HC(3)), 5.98 (ddd, $J = 17.0, 10.3, 6.4$, 1 H, HC(7)), 5.01 (m, 2 H, HC(8)), 3.41 (ap, $J = 7.0$, 1 H, HC(6)), 1.33 (d, $J = 7.0$, 3 H, HC(5)), 0.98 (s, 9 H, HC(11)), 0.19 (s, 6 H, HC(9)).

¹³C NMR: (126 MHz, CDCl₃)

153.8 C(4), 143.7 C(7), 138.1 C(1), 128.1 C(3), 119.8 C(2), 112.7 C(8), 42.4 C(6), 25.7 C(11), 20.8 C(5), 18.2 C(10), -4.4 C(9).

IR: (film)

2959 (m), 2930 (m), 2885 (w), 2859 (m), 1636 (w), 1607 (w), 1509 (s), 1472 (m), 1463 (w), 1390 (w), 1362 (w), 1257 (s), 1171 (w), 917 (s), 839 (s), 808 (m).

MS: (EI, 70eV)

262 (M⁺, 46), 205 (100), 163 (27), 151 (26), 73 (18), 55 (28).

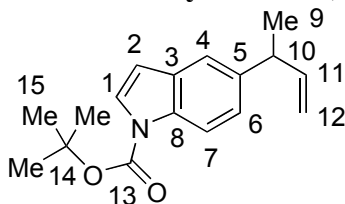
HRMS: (EI, 70eV)

calc for C₁₆H₂₆OSi (M⁺): 262.1753; found: 262.1752

TLC: *R_f* 0.40 (hexane/DCM, 4:1) [silica gel, UV]

GC: γ -*t_R*: 6.73 min, α -*t_R*: 6.92 and 7.00 min (13:1 [2.6:1], γ : α [*E* or *Z*]) (GC Method 3).

5-(1-Methyl-2-propen-1-yl)1H-indole-1-carboxylic Acid 1,1-Dimethylethyl Ester (14n)



Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 6-bromo-*N*-boc-indole (296 mg, 1.0 mmol), Na⁺**13**⁺ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μ L, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. The reaction was monitored by TLC. After 3.5 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, hexane/EtOAc, gradient 100:0 to 20:1) afforded 225 mg (83%) of **14n** as a clear, colorless oil.

Data for (14n):

¹H NMR: (500 MHz, CDCl₃)

8.07 (d, $J = 7.7$, 1 H, HC(7)), 7.59 (d, $J = 3.3$, 1 H, HC(4)), 7.41 (d, $J = 1.7$, 1 H, HC(1)), 7.20 (m, 1 H, HC(6)), 6.54 (d, $J = 3.7$, 1 H, HC(2)), 6.08 (m, 1 H, HC(11)), 5.07 (m, 2 H, HC(12)), 3.58 (ap, $J = 7.0$, 1 H, HC(10)), 1.68 (s, 9 H, HC(15)), 1.43 (d, $J = 7.0$, 3 H, HC(9)); (19:1 [1.9:1], γ : α [E or Z]).

¹³C NMR: (126 MHz, CDCl₃)

149.8 C(13), 143.7 C(11), 140.0 C(3), 133.7 C(5), 130.8 C(8), 126.0 C(1), 123.9 C(4), 119.1 C(6), 115.0 C(12), 112.8 C(7), 107.2 C(2), 83.5 C(14), 43.0 C(10), 28.2 C(15), 21.1 C(9).

IR: (film)

3151 (w), 3081 (w), 2976 (m), 2932 (w), 2872 (w), 1732 (s), 1636 (w), 1580 (w), 1538 (w), 1471 (s), 1373 (s), 1349 (s), 1253 (s), 1193 (m), 1163 (s), 1136 (s), 1084 (m), 1041 (m), 1023 (m), 998 (w), 911 (m), 885 (w), 838 (w), 820 (w), 767 (w).

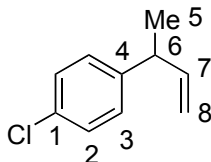
MS: (EI, 70eV)

271 (M^+ , 49), 215 (99.7), 200 (59), 171 (49), 156 (100), 129 (13), 117 (11), 84 (16).

HRMS: (EI, 70eV)

calc for C₁₇H₂₁NO₂ (M^+): 271.1572; found: 271.1572

TLC: R_f 0.32 (hexane/EtOAc, 20:1) [silica gel, UV]

1-Chloro-4-(1-methyl-2-propenyl)benzene (14o)

Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 4-bromochlorobenzene (191 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μL, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 5 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, hexane) followed by Kugelrohr distillation afforded 111 mg (67%) of **13o** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.³⁴

Data for (14o):

bp: 105 °C (10 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.29 (m, 2 H, H(C(2))), 5.16 (m, 2 H, HC(3)), 5.98 (m, 1 H, HC(7)), 5.06 (m, 2 H, HC(8)), 3.47 (ap, *J* = 7.0, 1 H, HC(6)), 1.36 (d, *J* = 7.0, 3 H, HC(5)).

¹³C NMR: (126 MHz, CDCl₃)

144.0 C(4), 142.7 C(7), 131.7 C(1), 128.6 C(2), 128.5 C(3), 113.5 C(8), 42.5 C(6), 20.6 C(5).

IR: (film)

3076 (w), 2969 (m), 2924 (w), 2872 (w), 1684 (w), 1636 (w), 1592 (w), 1491 (s), 1454 (w), 1406 (m), 1370 (w), 1258 (m), 1093 (s), 1014 (s), 916 (m), 828 (s).

MS: (EI, 70eV)

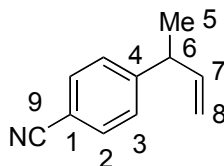
166 (M⁺, 49), 151 (71), 139 (41), 131 (100), 115 (57), 103 (18), 91 (15), 75 (17),

63 (10).

TLC: R_f 0.53 (hexane) [silica gel, KMnO_4]

GC: γ - t_R : 4.80 min, α - t_R : 5.14 and 5.24 min (12:1 [3.4:1], γ : α [*E* or *Z*]) (GC Method 3).

4-(1-Methyl-2-propenyl)benzonitrile (**14p**)



Following General Procedure II, $\text{Pd}(\text{dba})_2$ (28.8 mg, 0.05 mmol, 0.050 equiv), 4-bromobenzonitrile (182 mg, 1.0 mmol), $\text{Na}^+\mathbf{13}^-$ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μL , 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 $^\circ\text{C}$. After 8 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, hexane/EtOAc, gradient 100:0 to 20:1) followed by Kugelrohr distillation afforded 102 mg (65%) of **14p** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.³⁵

Data for (**14p**):

bp: 105 $^\circ\text{C}$ (10 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

7.59 (m, 2 H, H(C(2))), 7.32 (m, 2 H, HC(3)), 5.95 (ddd, $J = 16.9, 10.3, 6.4$, 1 H, HC(7)), 5.08 (m, 2 H, HC(8)), 3.52 (ap, $J = 7.0$, 1 H, HC(6)), 1.37 (d, $J = 7.0$, 3 H, HC(5)).

^{13}C NMR: (126 MHz, CDCl_3)

151.0 C(4), 141.6 C(7), 132.3 C(2), 128.1 C(3), 119.0 C(9), 114.5 C(8), 110.0

C(1), 43.2 C(6), 20.4 C(5).

IR: (film)

3070 (w), 2970 (m), 2932 (w), 2873 (w), 2228 (s), 1675 (w), 1607 (m), 1503 (m),
1454 (w), 1413 (w), 1372 (w), 1261 (w), 1178 (w), 1069 (w), 1017 (m), 997 (w),
969 (w), 920 (m), 839 (m).

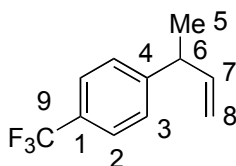
MS: (EI, 70eV)

157 (M^+ , 91), 142 (100), 130 (29), 115 (69), 103 (17), 89 (18), 77 (17), 63 (13).

TLC: R_f 0.39 (hexane/EtOAc, 20:1) [silica gel, UV]

GC: γ - t_R : 5.54 min, α - t_R : 5.80 and 5.88 min (3.5:1 [6.7:1], γ : α [*E* or *Z*]) (GC Method 3).

1-(1-Methyl-2-propen-1-yl)4-(trifluoromethyl)benzene (**14q**)



Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 4-bromobenzotrifluoride (225 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μ L, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 4 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, hexane/ether, gradient 100:0 to 10:3) followed by Kugelrohr distillation afforded 130 mg (65%) of **14q** as a clear, colorless oil.

Data for (**14q**):

bp: 95 °C (10 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.56 (m, 2 H, H(C(3))), 7.33 (m, 2 H, HC(2)), 5.98 (m, 1 H, HC(7)), 5.07 (m, 2 H, HC(8)), 3.53 (s, 3 H, HC(9)), 3.43 (ap, $J = 7.0$, 1 H, HC(6)), 1.38 (d, $J = 7.0$, 3 H, HC(5)).

¹³C NMR: (126 MHz, CDCl₃)

151.1 C(4), 141.5 C(7), 132.3 C(2), 128.2 q, $J = 274$, C(9), 128.1 C(3), 114.48 C(1), 114.47 C(8), 43.2 C(6), 20.4 C(5)

IR: (film)

3080 (w), 2973 (w), 2924 (w), 2877 (w), 1693 (w), 1636 (w), 1607 (m), 1503 (w), 1454 (w), 1412 (w), 1261 (w), 1178 (w), 1070 (w), 1018 (w), 914 (m), 839 (m).

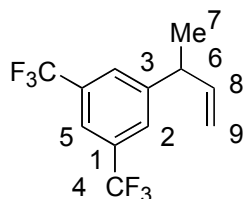
MS: (EI, 70eV)

200 (M⁺, 48), 185 (64), 165 (48), 149 (16), 131 (100), 115 (26), 55 (28).

TLC: R_f 0.69 (hexane/ether, 10/3) [silica gel, UV]

GC: γ - t_R : 3.39 min, α - t_R : 3.96 and 4.09 min (12:1 [2.2:1], γ : α [E or Z]) (GC Method 3).

1,3-Bis(trifluoromethyl)5-(1-methyl-2-propen-1-yl)benzene (14r)



Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 3,5-bis(trifluoromethyl)bromobenzene (293 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μ L, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 3 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm,

hexane) followed by Kugelrohr distillation afforded 168 mg (62%) of **14r** as a clear, colorless oil.

Data for (14r):

bp: 110 °C (10 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.67 (bm, 3 H, HC(2)), HC(5)), 5.97 (ddd, $J = 17.0, 10.3, 6.4$, 1 H, HC(8)), 5.13 (m, 2 H, HC(9)), 3.61 (ap, $J = 7.0$, 1 H, HC(6)), 1.42 (d, $J = 7.0$, 3 H, HC(7)).

¹³C NMR: (126 MHz, CDCl₃)

148.0 C(3), 141.1 C(8), 131.6 (q, $J = 33$, C(1)), 127.5 (q, $J = 2.8$, C(2)), 123.4 (q, $J = 27.3$, C(4)), 120.3 (m, C(5)), 115.1 C(9), 42.8 C(6), 20.4 C(7).

IR: (film)

3085 (w), 2976 (w), 2873 (w), 1623 (w), 1465 (w), 1378 (s), 1279 (s), 1174 (s), 1134 (s), 990 (w), 968 (w), 923 (m), 896 (m), 847 (m), 708 (m), 695 (w), 683 (m).

MS: (EI, 70eV)

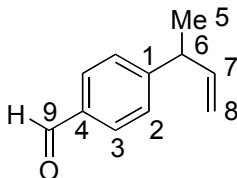
268 (M⁺, 100), 253 (88), 240 (23), 227 (59), 213 (35), 184 (23), 164 (26), 151 (13), 115 (13).

HRMS: (EI, 70eV)

calc for C₁₂H₁₀F₆ (M⁺): 268.0686; found: 268.0687

TLC: R_f 0.45 (hexane) [silica gel, KMnO₄]

GC: γ - t_R : 4.23 min, α - t_R : 4.69 and 4.80 min (3.4:1 [5.2:1], γ : α [*E* or *Z*]) (GC Method 3).

4-(1-Methyl-2-propen-1-yl)benzaldehyde (14s)

Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 4-bromobenzaldehyde (185 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μL, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 1.5 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, hexane/EtOAc, gradient 100:0 to 20:1) followed by Kugelrohr distillation afforded 64 mg (40%) of **14s** as a clear, colorless oil.

Data for (14s):

bp: 115 °C (10 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

9.98 (s, 1 H, HC(9)), 7.82 (m, 2 H, HC(3)), 7.38 (m, 2 H, HC(2)), 5.99 (m, 1 H, HC(7)), 5.08 (m, 2 H, HC(8)), 3.55 (ap, *J* = 7.0, 1 H, HC(6)), 1.39 (d, *J* = 7.0, 3 H, HC(5)).

¹³C NMR: (126 MHz, CDCl₃)

192.0 C(9), 152.8 C(1), 141.9 C(7), 134.7 C(4), 130.0 C(3), 128.0 C(2), 114.2 C(8), 43.4 C(6), 20.5 C(5).

IR: (film)

3075 (w), 3049 (w), 2968 (w), 2929 (w), 2873 (w), 2825 (w), 2732 (w), 1699 (s), 1637 (w), 1606 (s), 1575 (w), 1456 (w), 1423 (w), 1390 (w), 1305 (w), 1212 (m),

1169 (m), 1068 (w), 1016 (w), 917 (w), 828 (m), 761 (w).

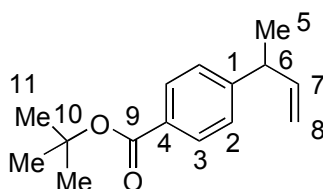
MS: (EI, 70eV)

160 (M^+ , 100), 131 (99), 117 (99), 103 (15), 91 (72), 84 (62), 77 (29), 63 (13).

TLC: R_f 0.23 (hexane/EtOAc, 20:1) [silica gel, UV]

GC: γ - t_R : 5.47 min, α - t_R : 5.74 and 5.82 min (14:1 [2.1:1], γ : α [E or Z]) (GC Method 3).

4-(1-Methyl-2-propen-1-yl)benzoic Acid, 1,1-Dimethylethyl Ester (**14t**)



Following General Procedure II, $\text{Pd}(\text{dba})_2$ (28.8 mg, 0.05 mmol, 0.050 equiv), 4-bromo-*tert*-butylbenzoate (257 mg, 1.0 mmol), $\text{Na}^+ \mathbf{13}^-$ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μL , 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 $^\circ\text{C}$. After 6 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, hexane/EtOAc, gradient 100:0 to 20:1) followed by Kugelrohr distillation afforded 155 mg (67%) of **14t** as a clear, colorless oil.

Data for (**14t**):

bp: 155 $^\circ\text{C}$ (5 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

7.93 (m, 2 H, HC(3)), 7.26 (m, 2 H, HC(2)), 5.98 (ddd, $J = 17.7, 9.8, 6.4$, 1 H, HC(7)), 5.05 (m, 2 H, HC(8)), 3.51 (ap, $J = 7.0$, 1 H, HC(6)), 1.59 (s, 1 H, HC(11)), 1.37 (d, $J = 7.0$, 3 H, HC(5)).

¹³C NMR: (126 MHz, CDCl₃)

166.0 C(9), 150.6 C(1), 142.7 C(7), 130.2 C(4), 129.9 C(3), 127.4 C(2), 114.0 C(8), 81.0 C(10), 43.3 C(6), 28.5 C(11), 20.8 C(5).

IR: (film)

2975 (m), 2931 (m), 1718 (s), 1700 (m), 1636 (w), 1610 (m), 1578 (w), 1507 (w), 1477 (m), 1457 (m), 1413 (m), 1392 (m), 1368 (m), 1291 (s), 1256 (m), 1167 (m), 1117 (m), 1017 (m), 915 (m), 849 (m), 771 (m), 708 (m).

MS: (EI, 70eV

232 (M⁺, 12), 176 (48), 159 (53), 131 (100), 117 (37), 84 (18).

TLC: *R_f* 0.33 (hexane/EtOAc, 20:1) [silica gel, UV]

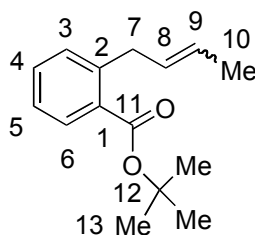
GC: γ -*t_R*: 6.70 min, α -*t_R*: 6.88 and 6.95 min (25:1 [3.2:1], γ : α [*E* or *Z*]) (GC Method 3).

Analysis: C₁₅H₂₀O₂ (232.32)

Calcd: C, 77.55; H, 8.68

Found: C, 77.28; H, 8.72

2-(1-Methyl-2-propen-1-yl)benzoic Acid 1,1-Dimethylethyl Ester (14u)



Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 2-bromo-*tert*-butylbenzoate (257 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), nbd (5.2 μ L, 0.05 mmol, 0.050 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 20 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) and the filter cake washed with ether (3 x 10 mL). Purification by silica gel chromatography (20 cm x 20 mm, hexane/EtOAc,

gradient 100:0 to 20:1) followed by Kugelrohr distillation afforded 191 mg (82%) of **14u** as a clear, colorless oil.

Data for (14u):

bp: 150 °C (1.0 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.75 (m, 1 H, HC(6)), 7.38 (m, 1 H, HC(4)), 7.24 (m, 2 H, HC(3) and HC(5)),
5.62 (m, 1 H, HC(8)), 5.46 (m, 1 H, HC(9)), 3.64 (d, $J = 6.5$, 2 H, HC(7)), 1.60 (d,
 $J = 2.2$, 3 H, HC(10)), 1.59 (s, 9 H, HC(13)).

¹³C NMR: (126 MHz, CDCl₃)

167.4 C(11), 141.5 C(2), 132.0 C(1), 131.7 C(4), 130.6 C(5), 130.09 C(6), 130.05
C(8), 126.1 C(9), 125.8 C(3), 81.2 C(12), 37.1 C(7), 28.2 C(13), 17.9 C(10).

IR: (film)

3064 (w), 2977 (s), 2932 (m), 1716 (s), 1636 (w), 1600 (m), 1575 (m), 1478 (m),
1447 (m), 1393 (m), 1368 (s), 1298 (s), 1254 (s), 1173 (m), 1132 (m), 1076 (s),
968 (m), 914 (w), 849 (m), 800 (w), 750 (s), 712 (m).

MS: (EI, 70eV)

176 (100), 158 (63), 147 (68), 134 (32), 131 (46), 115 (28), 91 (20), 77 (10), 56
(54).

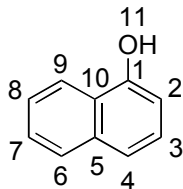
TLC: R_f 0.34 (hexane/EtOAc, 20:1) [silica gel, UV]

GC: γ - t_R : 6.25 min, α - t_R : 6.51 and 6.59 min (1:2.5 [8.3:1], γ : α [E/Z]) (GC Method 3).

Analysis: C₁₅H₂₀O₂ (232.32)

Calcd: C, 77.55; H, 8.68

Found: C, 77.23; H, 8.75

1-Naphthalenol (17)

Following General Procedure II, Pd(dba)₂ (28.8 mg, 0.05 mmol, 0.050 equiv), 1-bromonaphthalene (207 mg, 1.0 mmol), Na⁺**13**⁻ (308 mg, 2.0 mmol, 2.0 equiv), t-Bu₂(2-biphenyl)P (29.8 mg, 0.10 mmol, 0.010 equiv), and toluene (2.0 mL) were combined and heated to 70 °C. After 6 h, the mixture was cooled to rt, diluted with 15 mL EtOAc, and transferred to a 60 mL separatory funnel and 30 mL sat. aq. NH₄Cl was added. The aqueous phase was separated and washed with EtOAc (2 x 15 mL). The three separate organic extracts were then sequentially washed with H₂O (30 mL) then brine (30 mL). The combined organic extracts were dried over Na₂SO₄, and then filtered. Purification by silica gel chromatography (20 cm x 20 mm, hexane/EtOAc, gradient 100:0 to 4:1) followed by sublimation (80 °C, 1.0 mmHg) and recrystallization (hexane) afforded 81 mg (56%) of **17** as colorless, needle crystals.

Data for (17):

mp: 91-92 °C (hexane)

¹H NMR: (500 MHz, CDCl₃)

8.18 (m, 1 H, HC(9)), 7.82 (m, 1 H, HC(6)), 7.50 (m, 2 H, HC(8)), 7.45 (d, *J* = 8.3, 1 H, HC(7)), 7.31 (m, 1 H, HC(3)), 6.82 (dd, *J* = 7.4, 0.7 1 H, HC(2)), 5.18 (s, 1 H, HO(11)).

¹³C NMR: (126 MHz, CDCl₃)

151.3 C(1), 134.7 C(5), 127.7 C(6), 126.4 C(7), 125.8 C(3), 125.3 C(8), 124.3 C(10), 121.5 C(9), 120.7 C(4), 108.6 C(2).

IR: (film)

3304 (b), 1685 (w), 1654 (w), 1598 (w), 1517 (w), 1387 (m), 1270 (w), 1083 (w),
1044 (w), 1015 (w), 877 (w).

MS: (EI, 70eV)

144 (M^+ , 100), 115 (71).

TLC: R_f 0.29 (hexane/EtOAc, 4:1) [silica gel, UV]

GC: t_R : 6.26 min (GC Method 3).

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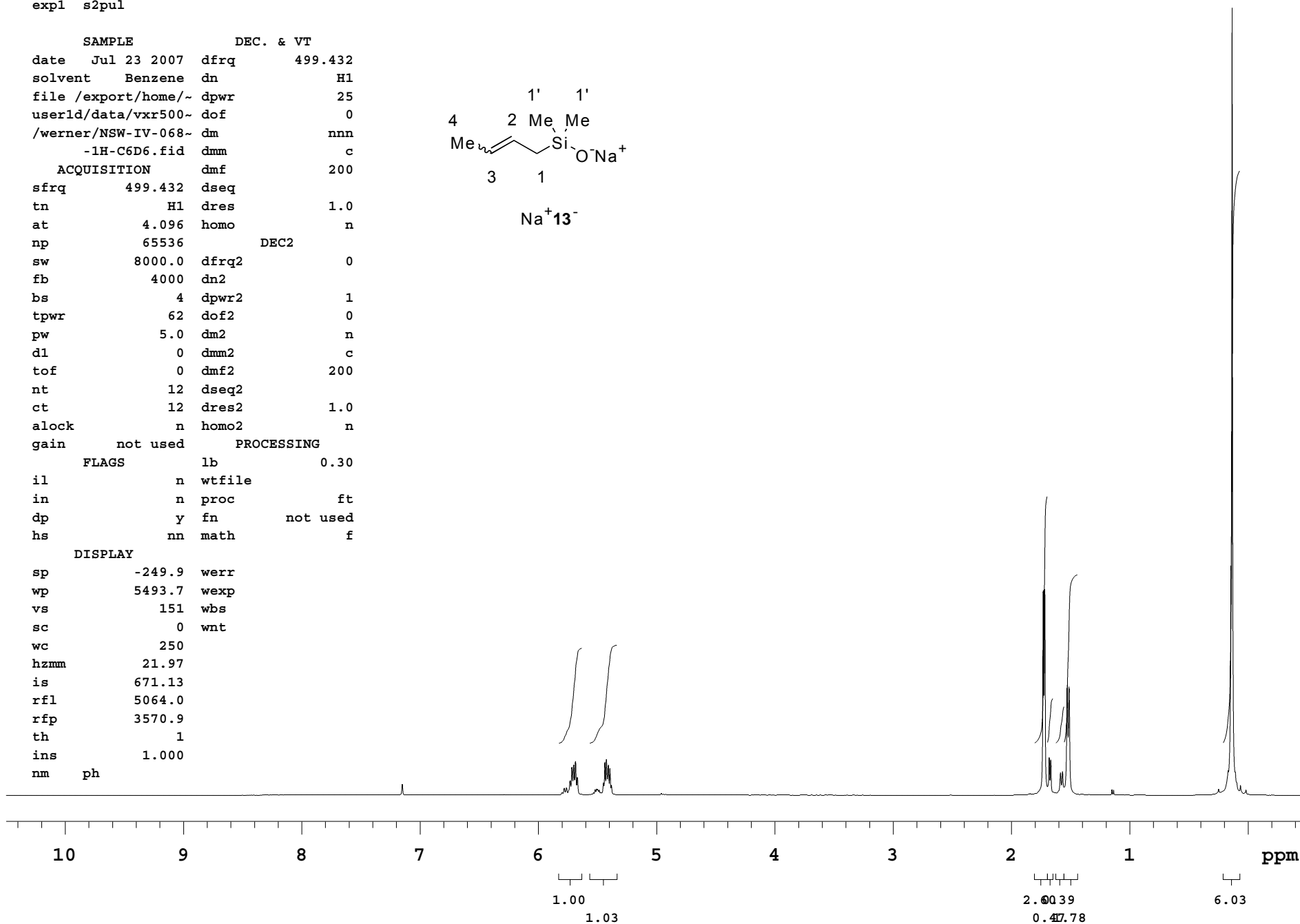
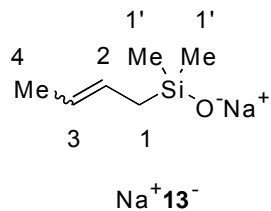
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NSW-IV-068-1H-C6D6

exp1 s2pul

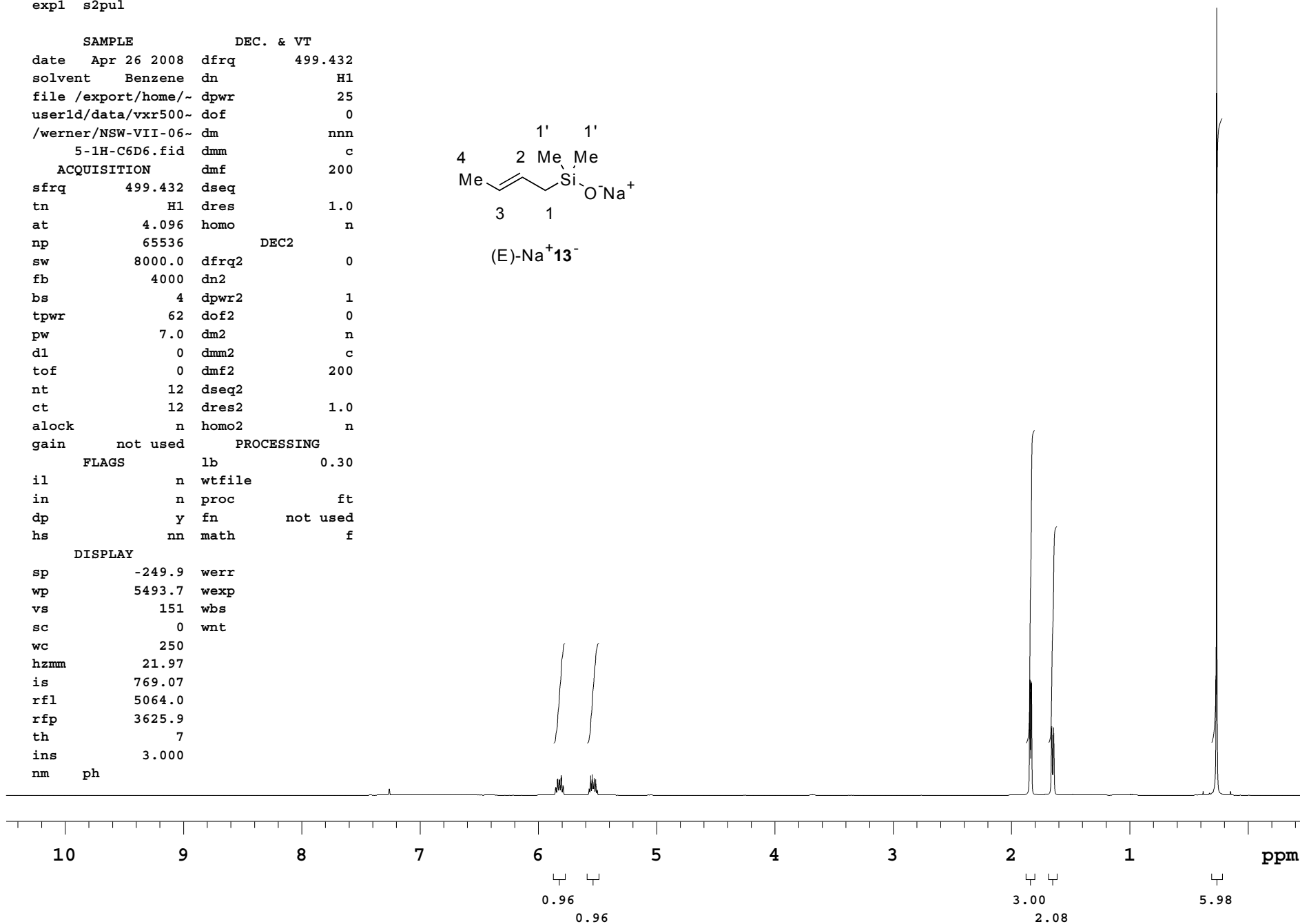
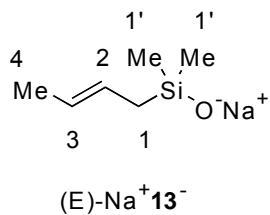
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tn	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	62	dof2	0
pw	5.0	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	12	dseq2	
ct	12	dres2	1.0
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dp	y	fn	not used
hs	nn	math	f
DISPLAY			
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wp	5493.7	wexp	
vs	151	wbs	
sc	0	wnt	
wc	250		
hzmm	21.97		
is	671.13		
rfl	5064.0		
rfp	3570.9		
th	1		
ins	1.000		
nm	ph		



NSW-VII-065-1H-C6D6

exp1 s2pul

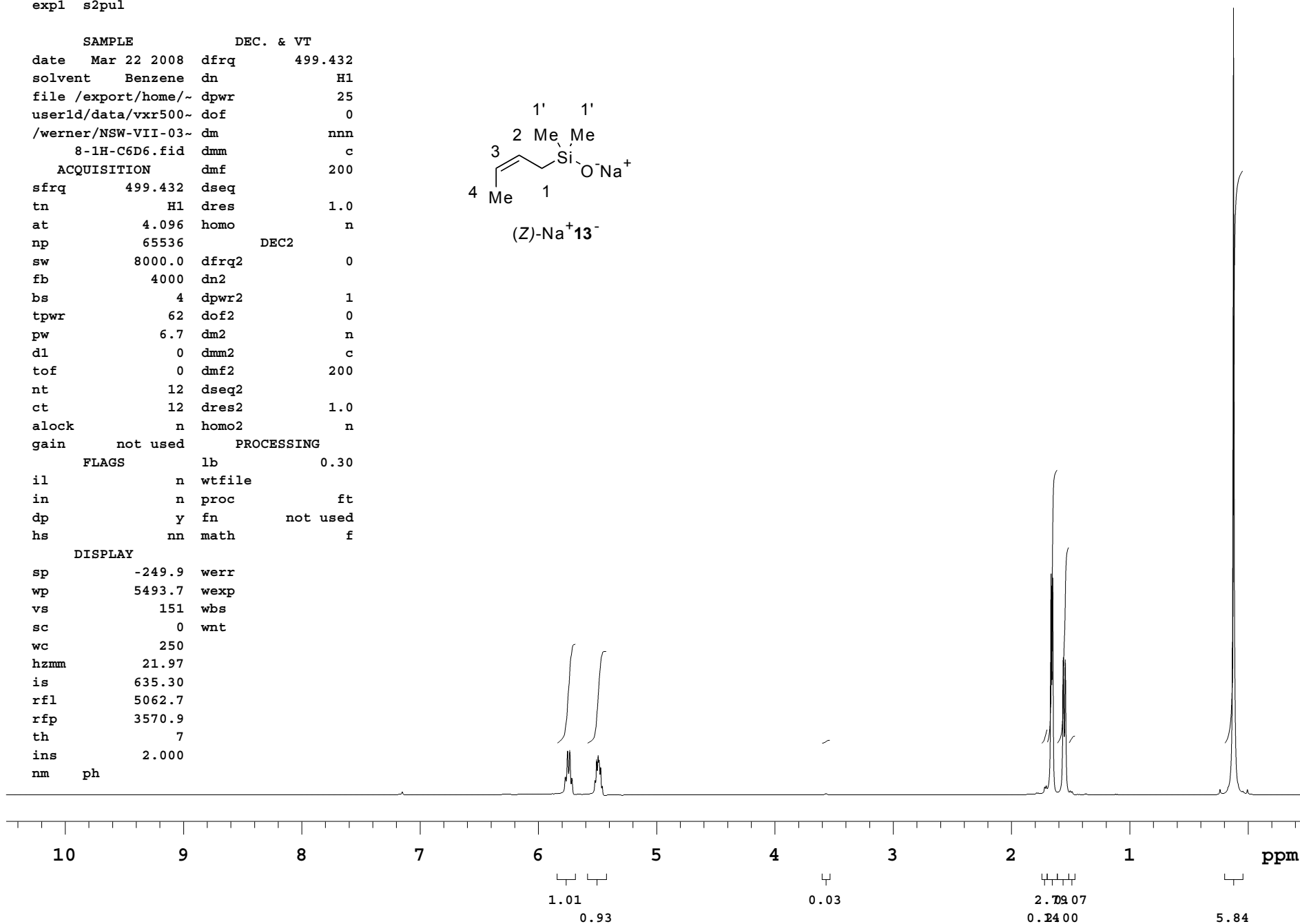
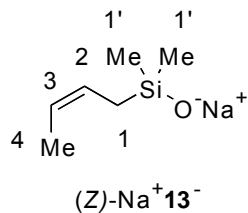
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5-1H-C6D6.fid		dmm	c
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at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	62	dof2	0
pw	7.0	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
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alock	n	homo2	n
gain	not used	PROCESSING	
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DISPLAY			
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wp	5493.7	wexp	
vs	151	wbs	
sc	0	wnt	
wc	250		
hzmm	21.97		
is	769.07		
rfl	5064.0		
rfp	3625.9		
th	7		
ins	3.000		
nm	ph		



NSW-VII-038-1H-C6D6

exp1 s2pul

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tn	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	62	dof2	0
pw	6.7	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	12	dseq2	
ct	12	dres2	1.0
alock	n	homo2	n
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hs	nn	math	f
DISPLAY			
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wp	5493.7	wexp	
vs	151	wbs	
sc	0	wnt	
wc	250		
hzmm	21.97		
is	635.30		
rfl	5062.7		
rfp	3570.9		
th	7		
ins	2.000		
nm	ph		



NSW-II-065-distilled-1H-CDC13

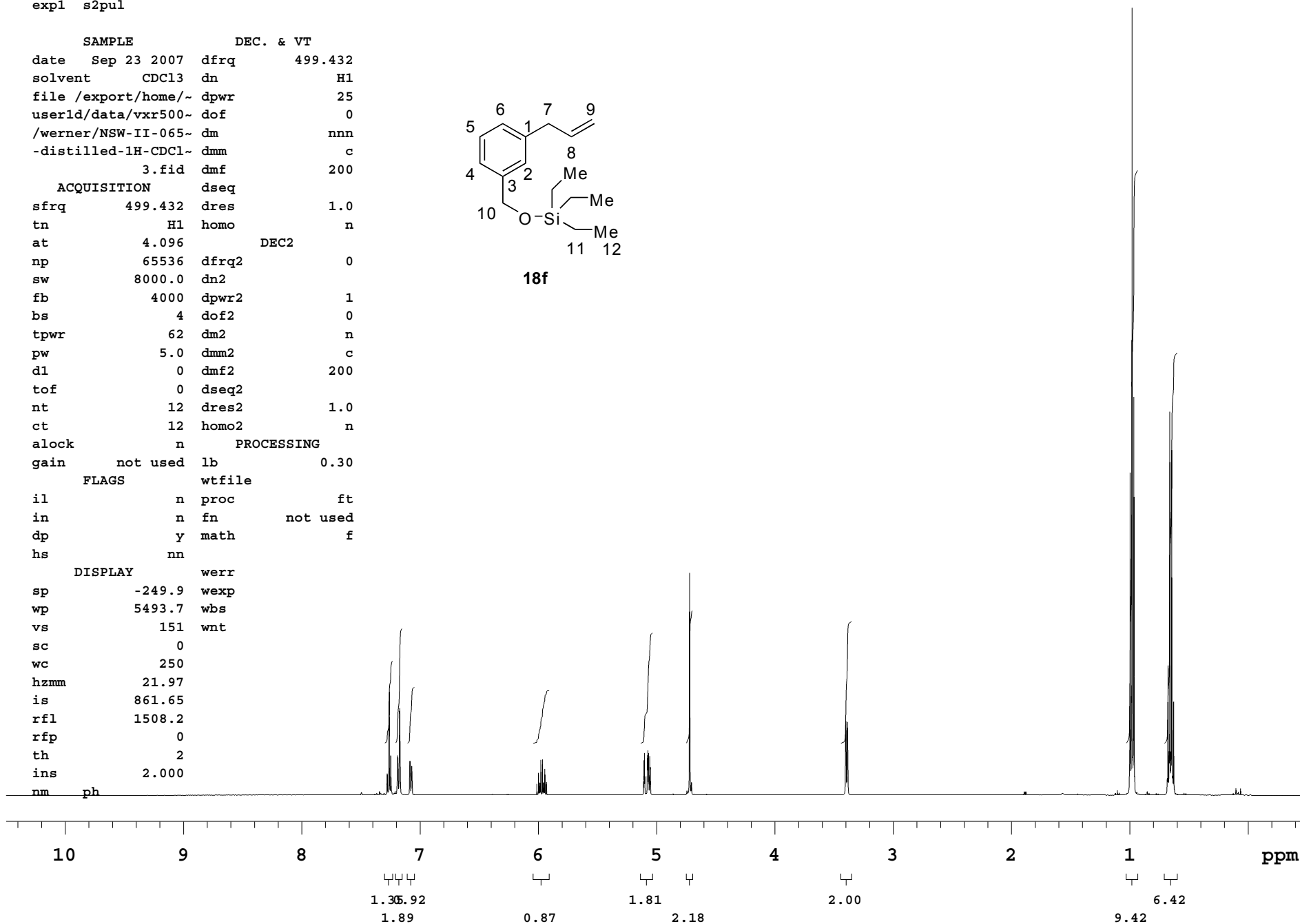
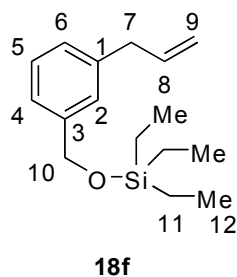
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3.fid dmf 200

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tn H1 homo n
at 4.096 DEC2
np 65536 dfrq2 0
sw 8000.0 dn2
fb 4000 dpwr2 1
bs 4 dof2 0
tpwr 62 dm2 n
pw 5.0 dmm2 c
dl 0 dmf2 200
tof 0 dseq2
nt 12 dres2 1.0
ct 12 homo2 n

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in n fn not used
dp y math f
hs nn

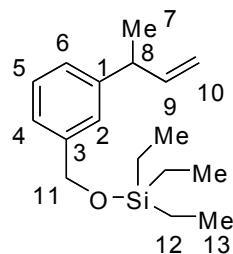
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rfp 0
th 2
ins 2.000
nm ph



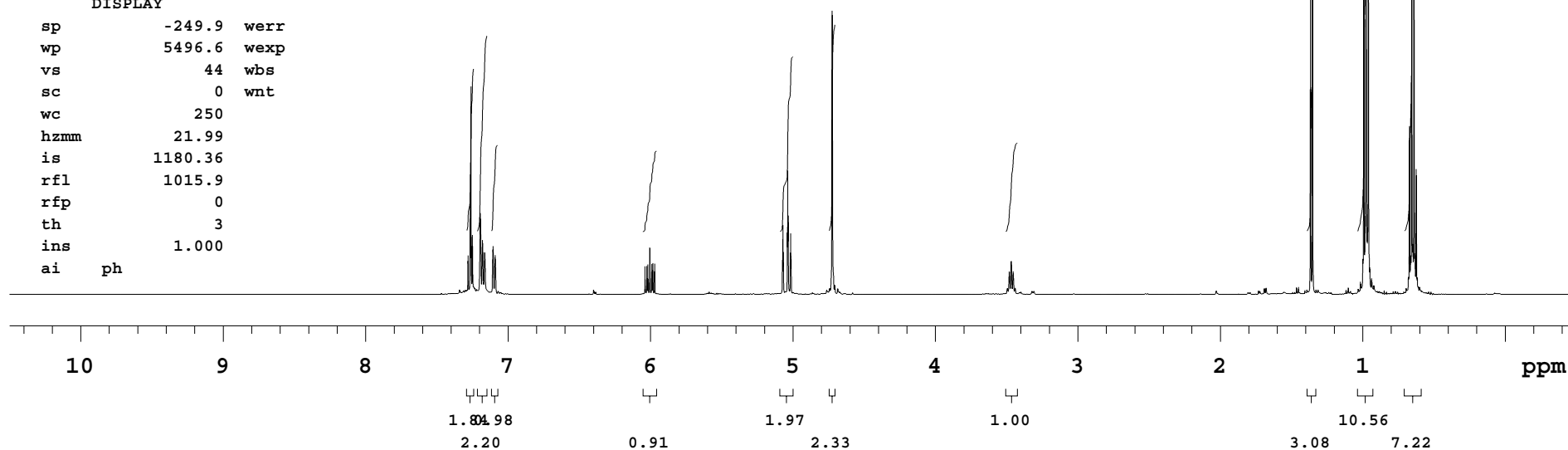
NSW-VII-026-dist-1H-CDC13

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erner/NSW-VII-026~	dm	nnn	
dist-1H-CDC13.fid	dmm	c	
ACQUISITION	dmf	200	
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tn	H1	dres	1.0
at	4.665	homo	n
np	65536	DEC2	
sw	7024.9	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	63	dof2	0
pw	6.5	dm2	n
d1	0	dmm2	c
tof	2.0	dmf2	200
nt	12	dseq2	
ct	12	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb	0.30	
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
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wp	5496.6	wexp	
vs	44	wbs	
sc	0	wnt	
wc	250		
hzmm	21.99		
is	1180.36		
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rfp	0		
th	3		
ins	1.000		
ai	ph		



14d



exp1 s2pul

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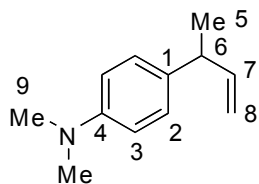
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np	65536	dfrq2	0
sw	8000.0	dn2	
fb	4000	dpwr2	1
bs	4	dof2	0
tpwr	62	dm2	n
pw	5.0	dmm2	c
d1	0	dmf2	200
tof	0	dseq2	
nt	12	dres2	1.0
ct	12	homo2	n

PROCESSING	
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gain	not used
lb	0.30

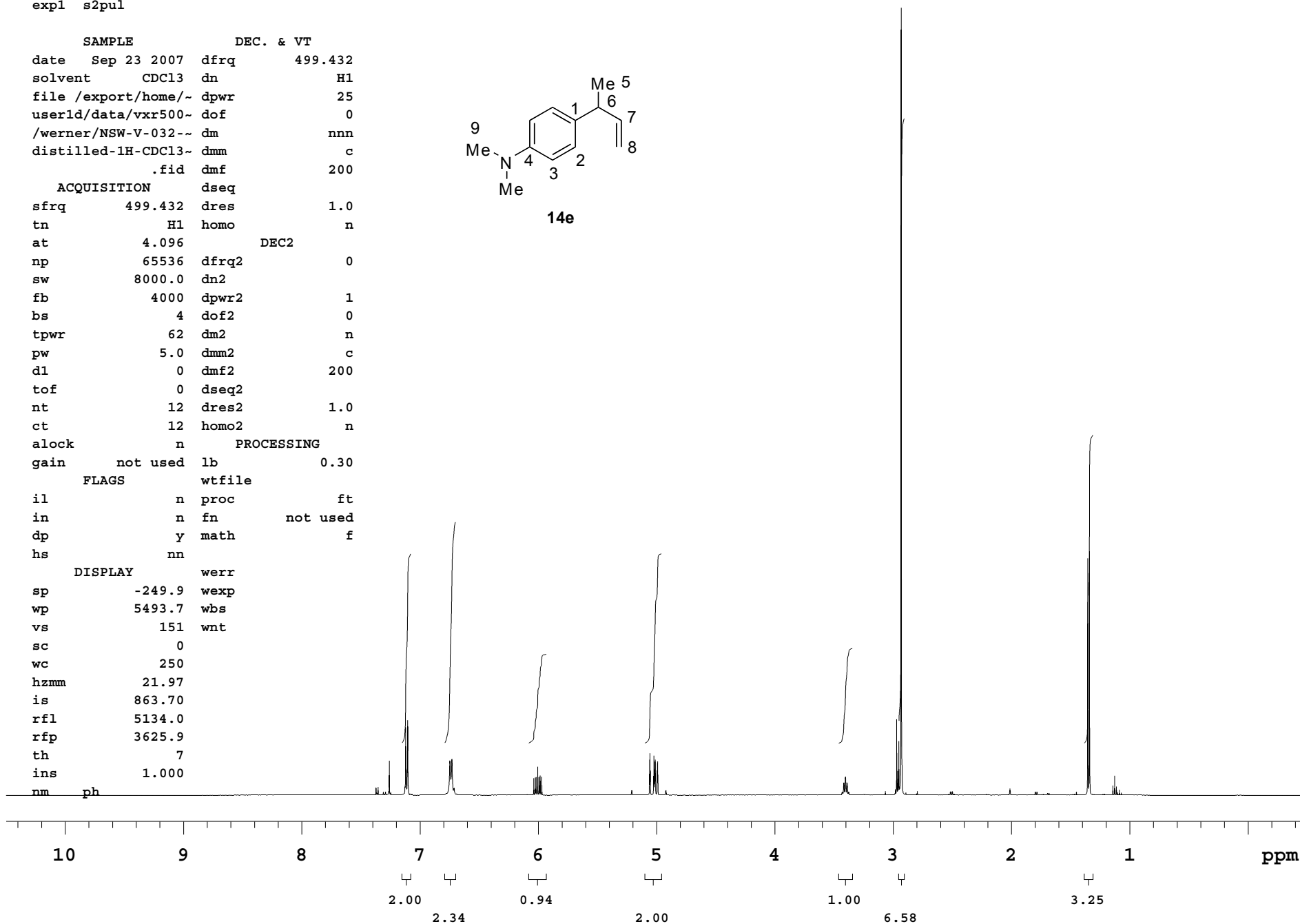
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hs	nn		

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vs	151	wnt	
sc	0		
wc	250		
hzmm	21.97		
is	863.70		
rfl	5134.0		
rfp	3625.9		
th	7		
ins	1.000		

nm ph

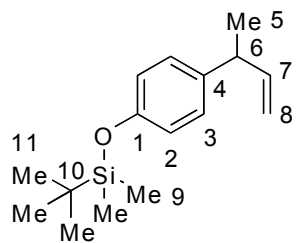


14e

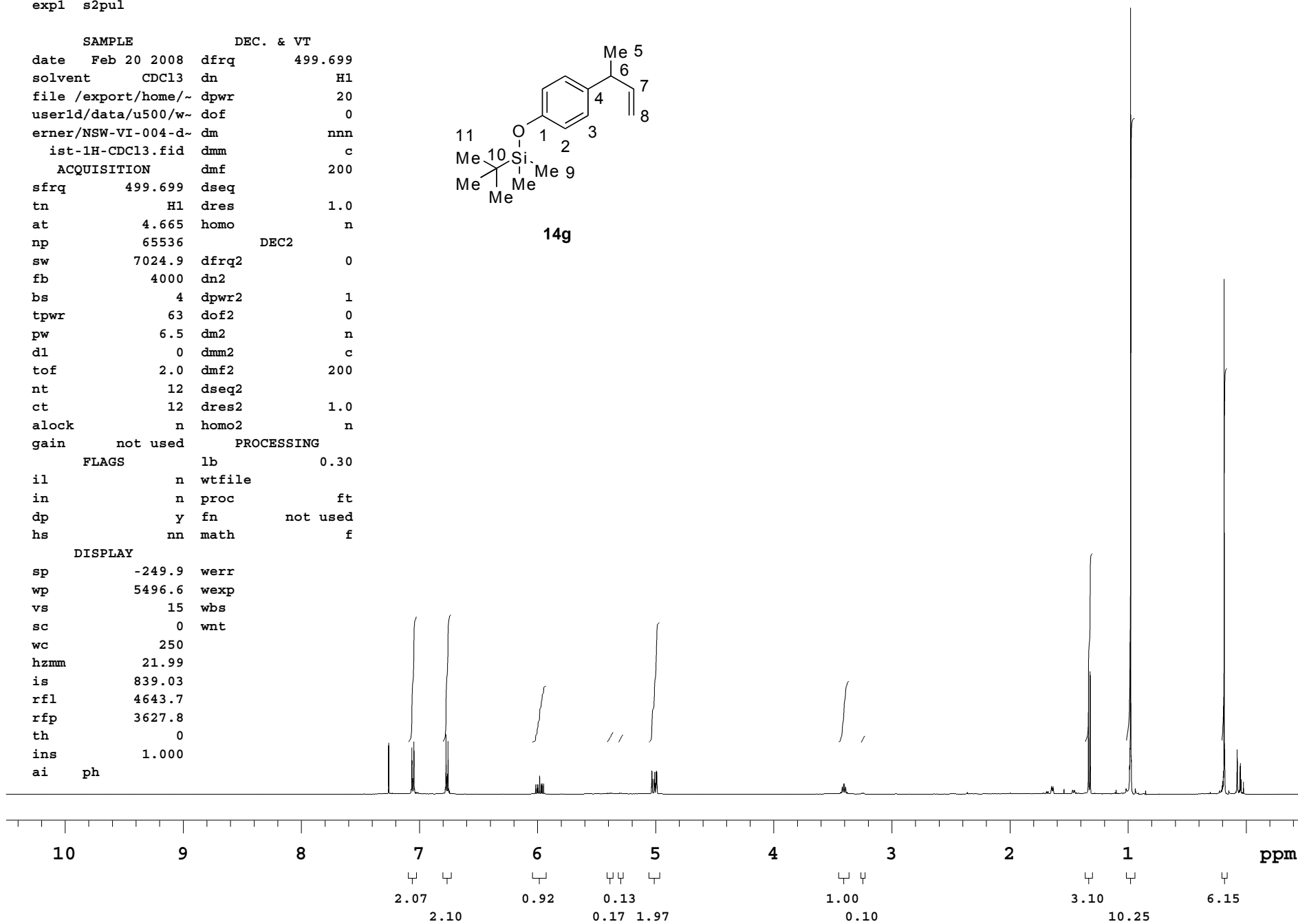


exp1 s2pul

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erner/NSW-VI-004-d-		dm	nnn
ist-1H-CDC13.fid		dmm	c
ACQUISITION		dmf	200
sfrq	499.699	dseq	
tn	H1	dres	1.0
at	4.665	homo	n
np	65536	DEC2	
sw	7024.9	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	63	dof2	0
pw	6.5	dm2	n
dl	0	dmm2	c
tof	2.0	dmf2	200
nt	12	dseq2	
ct	12	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
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in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
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wp	5496.6	wexp	
vs	15	wbs	
sc	0	wnt	
wc	250		
hzmm	21.99		
is	839.03		
rfl	4643.7		
rfp	3627.8		
th	0		
ins	1.000		
ai	ph		

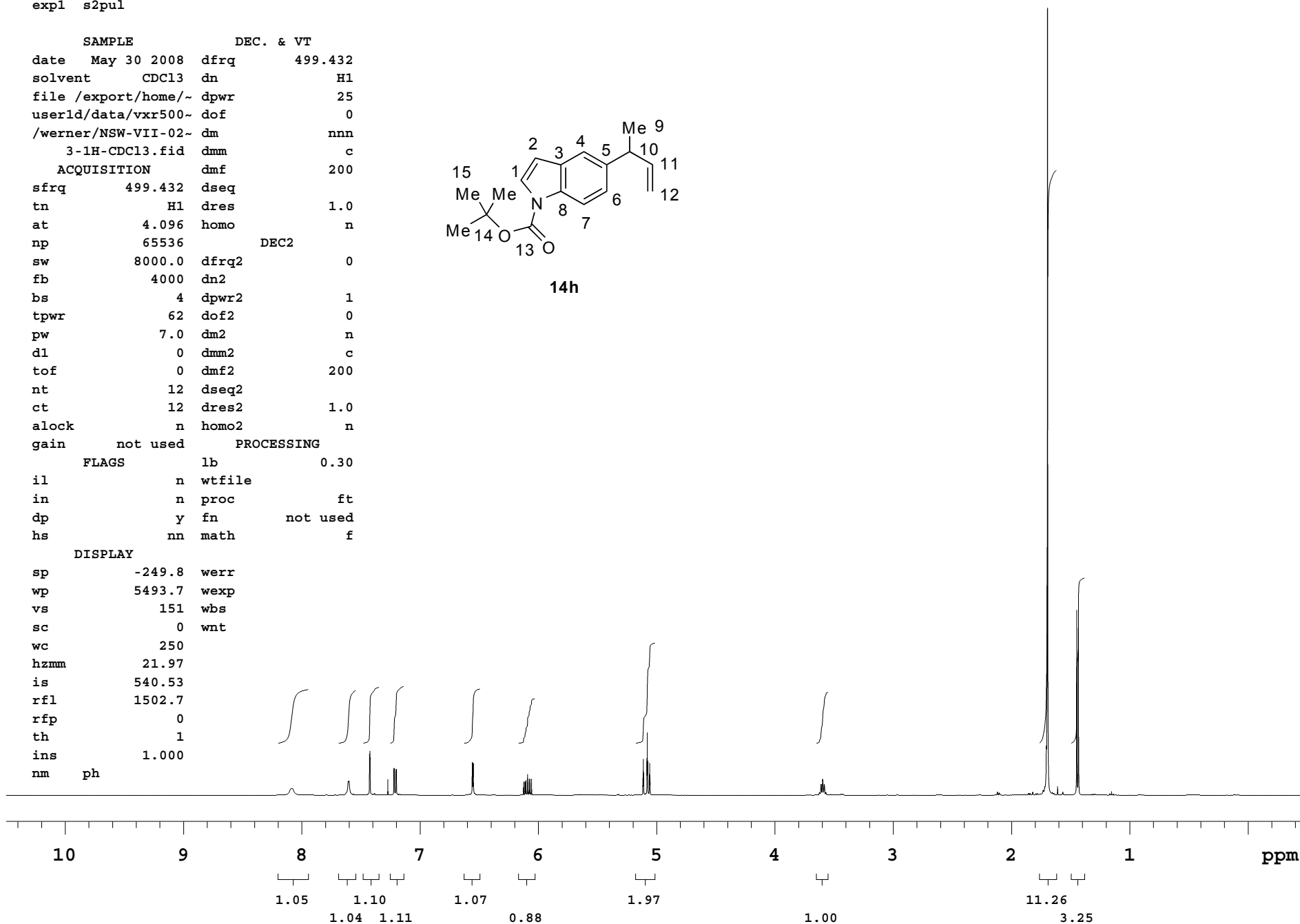
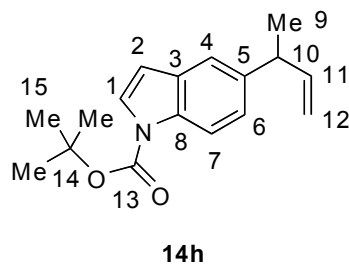


14g



exp1 s2pul

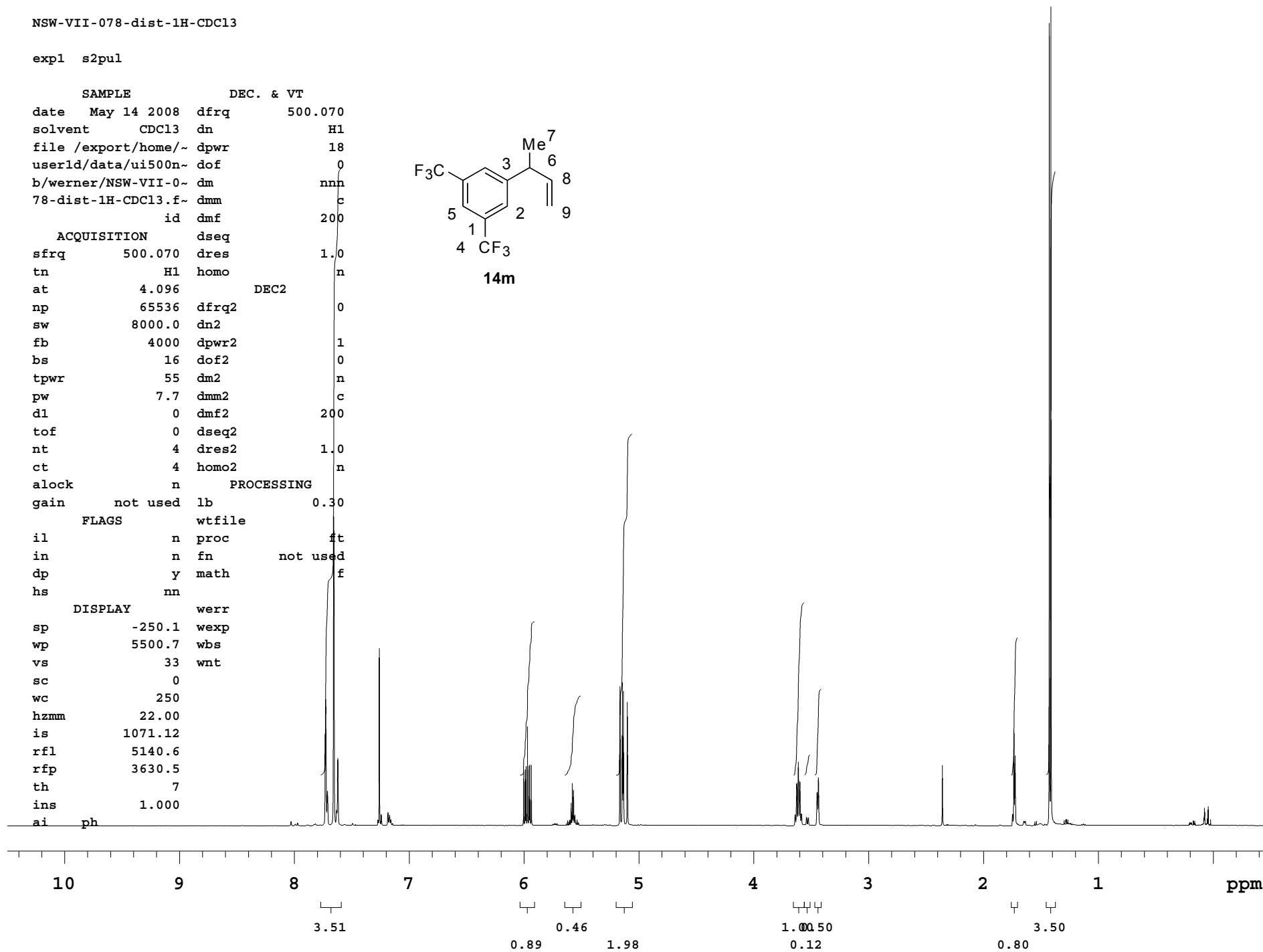
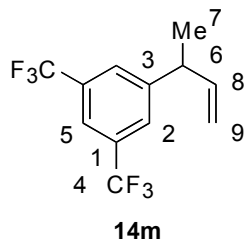
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ACQUISITION		dmf	200
sfrq	499.432	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	62	dof2	0
pw	7.0	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	12	dseq2	
ct	12	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
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in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
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wp	5493.7	wexp	
vs	151	wbs	
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wc	250		
hzmm	21.97		
is	540.53		
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th	1		
ins	1.000		
nm	ph		



NSW-VII-078-dist-1H-CDC13

exp1 s2pul

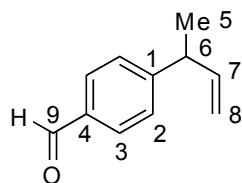
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78-dist-1H-CDC13.f~	dmm		c
	id	dmf	200
ACQUISITION			
sfrq	500.070	dres	1.0
tn	H1	homo	n
at	4.096	DEC2	
np	65536	dfrq2	0
sw	8000.0	dn2	
fb	4000	dpwr2	1
bs	16	dof2	0
tpwr	55	dm2	n
pw	7.7	dmm2	c
d1	0	dmf2	200
tof	0	dseq2	
nt	4	dres2	1.0
ct	4	homo2	n
alock	n	PROCESSING	
gain	not used	lb	0.30
FLAGS			
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in	n	fn	not used
dp	y	math	f
hs	nn		
DISPLAY			
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wp	5500.7	wbs	
vs	33	wnt	
sc	0		
wc	250		
hzmm	22.00		
is	1071.12		
rfl	5140.6		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph		



NSW-VII-027-dist-1H-CDC13

exp1 s2pul

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erner/NSW-VII-027-~	dm	nnn	
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ACQUISITION	dmf	200	
sfrq	499.699	dseq	
tn	H1	dres	1.0
at	4.665	homo	n
np	65536	DEC2	
sw	7024.9	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	63	dof2	0
pw	6.5	dm2	n
d1	0	dmm2	c
tof	2.0	dmf2	200
nt	12	dseq2	
ct	12	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
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il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-249.9	werr	
wp	5496.6	wexp	
vs	37	wbs	
sc	0	wnt	
wc	250		
hzmm	21.99		
is	1378.12		
rfl	4643.7		
rfp	3627.8		
th	3		
ins	1.000		
ai	ph		



140

