Expedient Access to Branched Allylic Silanes by Copper-Catalysed Allylic Substitution of Linear Allylic Halides

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Electronic Supplementary Information

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1 General Information

All reactions were performed in flame-dried glassware using Schlenk technique under a static pressure of argon. Liquids and solutions were transferred with syringes. Solvents were purified and dried following standard procedures: diethylether (Et_2O) and dichloromethane (CH_2Cl_2) were distilled from calcium hydride and tetrahydrofuran (THF) was distilled from potassium prior to use. Technical grade solvents for extraction and chromatography (cyclohexane, *n*-pentane and *tert*-butyl methyl ether) were distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on silica gel SIL G-25 glass plates from *Macherey-Nagel*. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Merck* using the indicated solvents. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded in $CDCl_3$ on *Bruker* AV 300 and *Bruker* AV 400 instruments. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 and $CDCl_3$: 77.1 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Infrared (IR) spectra were recorded on a *Varian* 3100 FT-IR spectrophotometer equipped with an ATR unit and are reported (vw = very weak, w = weak, m = medium, s = strong) in wavenumbers (cm^{-1}). Gas liquid chromatography (GLC) was performed on a *Shimadzu* GC-17A gas chromatograph equipped with a SE-54 capillary column (30 m × 0.32 mm, 0.25 µm film thickness) by *CS-Chromatographie Service* using the following program: N_2 carrier gas, injection temperature 250 °C, detector temperature 300 °C; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 5 min. Mass spectral data as well as elemental analysis were obtained from the Analytical Facility at the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster.

2 Experimental Details and General Procedures

2.1 Copper(I)-Catalysed Allylic Silylation of Allylic Bromides and Allylic Chlorides (General Procedures)

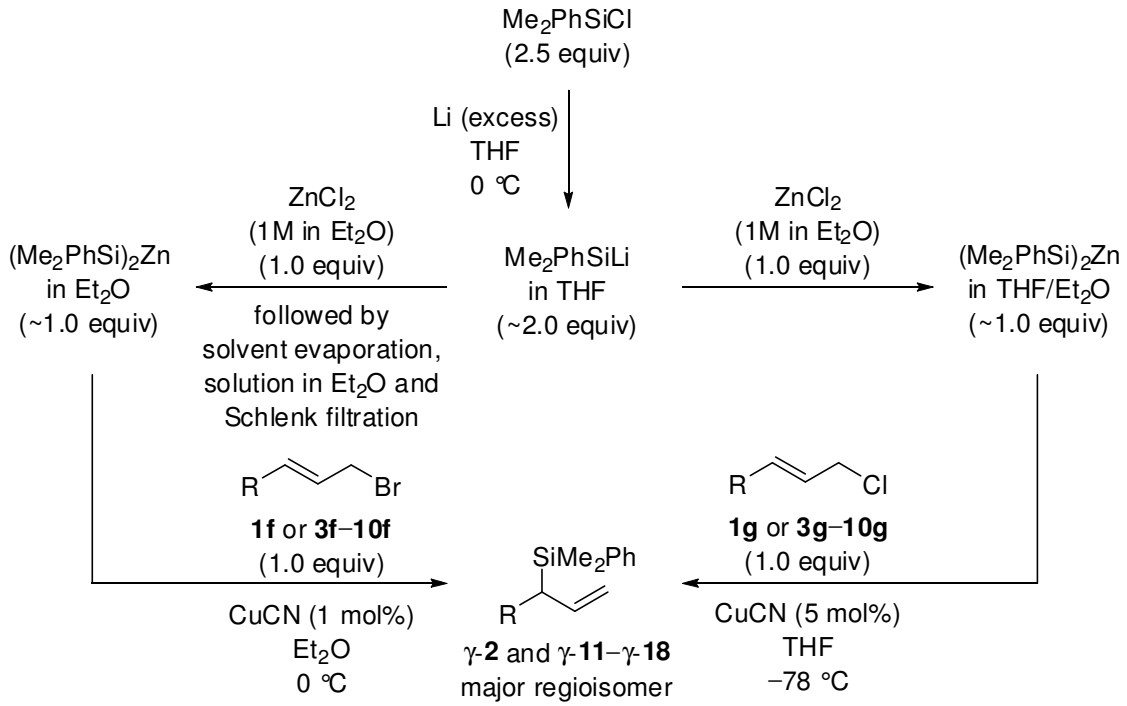


Fig. 1: Generation of the silicon reagent and subsequent copper(I)-catalysed allylic silylation.

General Procedure for Allylic Bromides (**GP1**)

Under argon atmosphere, $Me_2PhSiCl$ (2.5 equiv) is added to a reaction vessel charged with an excess of activated (sodium-rich, 1%) lithium chunks and THF (0.30M based on $Me_2PhSiCl$). The reaction mixture is maintained at 0 °C for 1 h under ultrasonication; the resulting wine-red solution is then maintained for at least 4 h at 0 °C under argon, producing $Me_2PhSiLi$ (~2.0 equiv) at approximately 80% conversion. The reaction mixture is separated from unreacted lithium metal by transfer with a double-ended cannula into a separate flask. Subsequent addition of an etheral solution of $ZnCl_2$ (1.0M in Et_2O, 1.0 equiv) at 0 °C yields the dull yellow solution of $(Me_2PhSi)_2Zn$ (~1.0 equiv), which is maintained at 0 °C for further 0.5 h. The solvents are removed in vacuum, yielding a dark brown residue. Et_2O is then added to this residue, and the suspension is immediately filtered under argon to remove undissolved LiCl. The resultant faint yellow coloured transparent solution in Et_2O (contaminated with THF) is slowly transferred into a pre-cooled reaction vessel (0 °C) charged with a suspension of CuCN (1.0 mol%) and a small volume of Et_2O, forming a dark brown to black coloured solution, which is then allowed to stir for another 0.5 h. The allylic bromide (**1f** or **3f**–**10f**, 1.0 equiv) is added via syringe either neat or as a solution in dry Et_2O. The reaction mixture is maintained at 0 °C and monitored by GLC and TLC analysis, and the reaction is terminated after full conversion by addition of 2M HCl. The aqueous phase is extracted with *tert*-butyl methyl ether (3 × 5 mL). The combined organic layers are back-extracted with $NaHCO_3$ (1 × 10 mL) and H_2O (3 × 10 mL) to remove

lithium and zinc chloride and cyanide salts, washed with brine and dried over Na_2SO_4. Evaporation of the solvents under reduced pressure affords the crude branched allylic silane γ-**2** or γ-**11**–γ-**18** as the major regioisomer.

General Procedure for Allylic Chlorides (**GP2**)

$(Me_2PhSi)_2Zn$ (~1.0 equiv) in THF (contaminated with Et_2O from etheral $ZnCl_2$ solution) is slowly transferred into a pre-cooled vessel (–78 °C) charged with a suspension of CuCN (5.0 mol%) and a small volume of THF, forming a dark brown to black coloured solution which is then allowed to stir for another 0.5 h. The allylic chloride (**1g** or **3g**–**10g**, 1.0 equiv) is added via syringe either neat or as a solution in dry THF. The reaction mixture is maintained at –78 °C and monitored by GLC and TLC analysis. Reaction is terminated after full conversion by addition of 2M HCl, and the aqueous phase is extracted with *tert*-butyl methyl ether (3 × 5 mL). The combined organic layers are back-extracted with $NaHCO_3$ (1 × 10 mL) and H_2O (3 × 10 mL) to remove lithium and zinc chloride and cyanide salts, washed with brine and dried over Na_2SO_4. Evaporation of the solvents under reduced pressure affords the crude branched allylic silane γ-**2** or γ-**11**–γ-**18** as the major regioisomer.

2.2 Preparation of Allylic Bromides, Allylic Chlorides and Requisite Allylic Alcohols (General Procedures)*

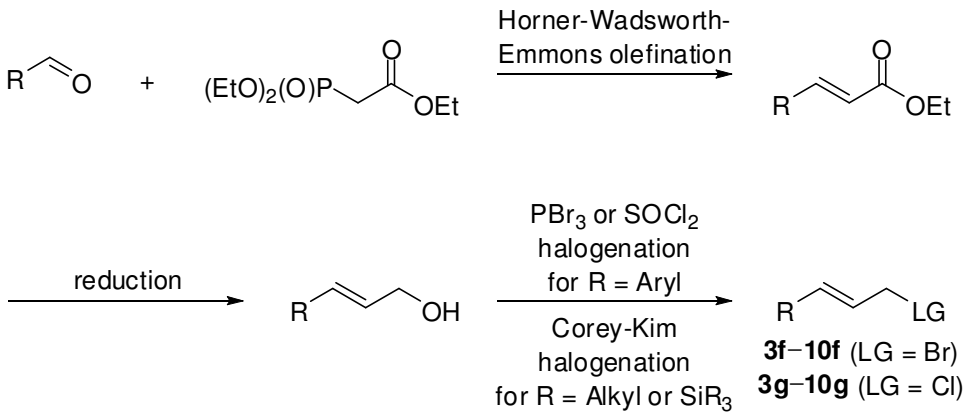


Fig. 2: Preparation of allylic bromides, allylic chlorides and requisite allylic alcohols.

General Procedure for Horner-Wadsworth-Emmons Reaction (**GP3**)

At room temperature, a flame-dried Schlenk flask is charged with LiCl (1.2 equiv) and dry THF under inert atmosphere, followed by addition of neat triethylphosphonoacetate (1.2 equiv). Prior to the addition of DBU (1.1 equiv), the reaction mixture is maintained for 15 min at this temperature. The neat aldehyde (1.0 equiv) is then added to the white suspension, which is allowed to stir for another 2 h at room temperature. After completion of reaction (TLC monitoring), the reaction mixture is quenched by pouring over ice. Standard work-up affords the crude α,β-unsaturated esters (*E*:*Z* > 95:5 as determined by ^1H NMR analysis) in good yields, which are used without further purification.

* Cinnamic bromide (**1f**, *E*:*Z* > 99:1) and cinnamic chloride (**1g**, *E*:*Z* > 99:1) are commercially available.

General Procedure for DIBAL–H Reduction (**GP4**)

In a flame-dried Schlenk flask pre-cooled to –78 °C containing solution of DIBAL–H (1M in cyclohexane, 2.1 equiv) in CH_2Cl_2 is slowly added a solution of the crude α,β-unsaturated ester (1.0 equiv) in dry CH_2Cl_2. After completion (TLC monitoring), the reaction mixture is carefully quenched with 2M HCl solution, and standard work-up furnishes the allylic alcohols in almost quantitative yields after purification by either flash column chromatography on silica gel or crystallisation.

General Procedure for Bromination (with PBr_3) or Chlorination (with $SOCl_2$) (**GP5**)

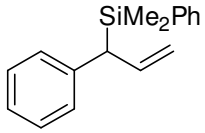
A flame-dried Schlenk flask is charged with the aryl-substituted allylic alcohol (1.0 equiv, neat or as a solution in a minimum quantity of Et_2O = 1.0 mL/1.0 mmol). At 0 °C, neat PBr_3 or $SOCl_2$ (1.1 equiv) is added dropwise, and the reaction mixture is stirred for 0.5 h. After completion of the reaction (TLC monitoring), the reaction mixture is carefully poured over ice, and the aqueous phase is extracted with *tert*-butyl methyl ether. The combined organic layers are washed with $NaHCO_3$ and water, followed by brine. Drying over Na_2SO_4 and evaporation of the solvents under reduced pressure affords the crude aryl-substituted allylic bromides **3f**–**7f** or chlorides **3g**–**7g**. Except for **4g**, **6g** and **7g** (purification by flash chromatography), chemically unstable allylic systems are immediately subjected to the copper(I)-catalysed allylic silylation.

General Procedure for Corey-Kim Bromination (with NBS) or Chlorination (with NCS) (**GP6**)

A flame-dried Schlenk flask is charged with *N*-bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) (1.5 equiv) and CH_2Cl_2. At 0 °C, Me_2S (1.85 equiv) is slowly added to form a yellow suspension. Cooling to –20 °C is then followed by addition of a solution of the alkyl- or silyl-substituted allylic alcohol (1.0 equiv) in CH_2Cl_2. The resultant yellow reaction mixture is allowed to warm to 0 °C and is maintained at this temperature for 2 h. After an additional 1 h at room temperature and completion of reaction (TLC monitoring), the reaction mixture is poured over ice, and the aqueous phase is extracted with *tert*-butyl methyl ether. The combined organic layers are washed with water and brine, followed by drying over Na_2SO_4. Evaporation of the solvents under reduced pressure affords the crude alkyl- or silyl-substituted allylic bromides **8f**–**10f** and chlorides **8g**–**10g**, which are purified by flash column chromatography on silica gel with *n*-pentane. Analytically pure **8f**–**10f** and **8g**–**10g** are obtained in good yields.

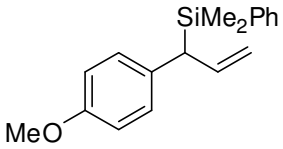
3 Characterisation Data

3.1 Characterisation Data of Branched Allylic Silanes



γ-**2**
$C_{17}H_{20}Si$
M = 252.43 g/mol

Dimethylphenyl(1-phenylallyl)silane (γ-**2**): Table 3, entry 1, left columns (for allylic bromides): Prepared according to **GP1** from cinnamic bromide (**1f**, *E*:*Z* > 99:1, 114 mg, 0.578 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (117 mg, 80%, γ:α = 90:10) as a pale yellow oil. Table 3, entry 1, right columns (for allylic chlorides): Prepared according to **GP2** from cinnamic chloride (**1g**, *E*:*Z* > 99:1, 89 mg, 0.58 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (125 mg, 85%, γ:α = 96:4) as a pale yellow oil. R_f = 0.52 (cyclohexane). IR (ATR): $\tilde{\nu}$ = 3069 (vw), 3025 (vw), 2958 (w), 2362 (vw), 2339 (vw), 1626 (w), 1598 (w), 1491 (w), 1427 (m), 1248 (m), 1189 (w), 1113 (m), 994 (w), 900 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.28 (s, 3H), 0.31 (s, 3H), 3.18 (d, *J* = 9.7 Hz, 1H), 4.90–5.30 (m, 2H), 6.14 (ddd, *J* = 16.9, 9.7, 9.7 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 2H), 7.08–7.15 (m, 1H), 7.18–7.25 (m, 2H), 7.30–7.43 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.7, –4.1, 44.4, 113.2, 124.9, 127.6, 127.6, 128.3, 129.3, 134.5, 136.9, 137.9, 141.8 ppm. HRMS (EI) calcd for $C_{17}H_{20}Si$ ($[M]^+$): 252.1334; Found: 252.1348. GLC (SE-54): t_R = 18.1 min (branched, γ-**2**), t_R = 19.9 min (linear, α-**2**). The γ:α ratio was determined by ^1H NMR analysis of the crude sample.

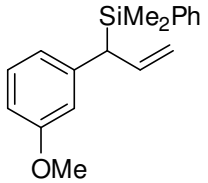


γ-**11**
$C_{18}H_{22}OSi$
M = 282.45 g/mol

[1-(4-Methoxyphenyl)allyl]dimethylphenylsilane (γ-**11**): Table 3, entry 2, left columns (for allylic bromides): Prepared according to **GP1** from crude† *p*-methoxy cinnamic bromide (**3f**, *E*:*Z* > 99:1, 104 mg, 0.633 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (107 mg, 60% over two steps, γ:α = 81:19) as a colourless oil. Table 3, entry 2, right columns (for allylic

† Allylic bromide is chemically unstable and was therefore used without further purification after preparation by bromination of the corresponding allylic alcohol with PBr_3.

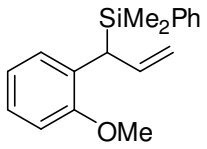
chlorides): Prepared according to **GP2** from crude[‡] *p*-methoxy cinnamic chloride (**3g**, *E*:*Z* > 99:1, 98 mg, 0.60 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (115 mg, 69% over two steps, γ:α = 94:6) as a colourless oil. R_f = 0.60 (cyclohexane:*tert*-butyl methyl ether = 95:5). IR (ATR): $\tilde{\nu}$ = 3070 (vw), 2956 (w), 2834 (vw), 2361 (w), 2340 (w), 1625 (w), 1609 (w), 1508 (s), 1427 (m), 1246 (s), 1179 (m), 1113 (m), 1037 (m), 899 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 3H), 0.27 (s, 3H), 3.09 (d, *J* = 9.5 Hz, 1H), 3.77 (s, 3H), 4.84–4.97 (m, 2H), 6.06 (ddd, *J* = 16.8, 9.7, 9.7 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 7.28–7.41 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –4.7, –4.1, 43.2, 55.4, 112.9, 113.8, 127.6, 128.5, 129.2, 133.8, 134.5, 137.1, 138.3, 157.1 ppm. HRMS (ESI) calcd for $C_{18}H_{22}OSiNa$ ($[M+Na]^+$): 305.1332; Found: 305.1336. Anal. Calcd for $C_{18}H_{22}OSi$: C 76.54; H 7.85; Found: C 76.34; H 7.73. GLC (SE-54): t_R = 20.7 min (branched, γ-**11**), t_R = 22.6 min (linear, α-**11**). The γ:α ratio was determined by GLC analysis.



γ-**12**
$C_{18}H_{22}OSi$
M = 282.45 g/mol

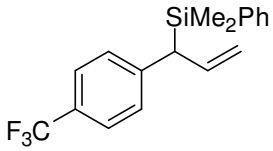
[1-(3-Methoxyphenyl)allyl]dimethylphenylsilane (γ-**12**): Table 3, entry 3, left columns (for allylic bromides): Prepared according to **GP1** from crude[†] *m*-methoxy cinnamic bromide (**4f**, *E*:*Z* > 99:1, 97 mg, 0.59 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (77 mg, 46% over two steps, γ:α = 89:11) as a colourless oil. Table 3, entry 3, right columns (for allylic chlorides): Prepared according to **GP2** from *m*-methoxy cinnamic chloride (**4g**, *E*:*Z* > 99:1, 60 mg, 0.33 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (76 mg, 82%, γ:α = 95:5) as a colourless oil. R_f = 0.58 (cyclohexane:*tert*-butyl methyl ether = 95:5). IR (ATR): $\tilde{\nu}$ = 3069 (w), 2956 (w), 2360 (m), 2338 (w), 1598 (m), 1490 (m), 1247 (s), 1190 (w), 1113 (m), 1048 (w), 900 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 3H), 0.28 (s, 3H), 3.13 (d, *J* = 9.7 Hz, 1H), 3.66 (s, 3H), 4.87–5.02 (m, 2H), 6.09 (ddd, *J* = 16.8, 10.0, 10.0 Hz, 1H), 6.40–6.44 (m, 1H), 6.55 (br d, *J* = 7.6 Hz, 1H), 6.64 (ddd, *J* = 8.2, 2.5, 0.7 Hz, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 7.28–7.42 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –4.7, –4.2, 44.6, 55.1, 110.6, 113.1, 113.2, 120.1, 127.6, 129.2, 129.3, 134.5, 136.9, 137.8, 143.4, 159.5 ppm. HRMS (ESI) calcd for $C_{18}H_{22}OSiNa$ ($[M+Na]^+$): 305.1332; Found: 305.1329. GLC (SE-54): t_R = 20.4 min (branched, γ-**12**), t_R = 22.4 min (linear, α-**12**). The γ:α ratio was determined by GLC analysis.

[‡] Allylic chloride is chemically unstable and was therefore used without further purification after preparation by chlorination of the corresponding allylic alcohol with $SOCl_2$.



γ-**13**
$C_{18}H_{22}OSi$
M = 282.45 g/mol

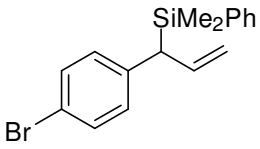
[1-(2-Methoxyphenyl)allyl]dimethylphenylsilane (γ-**13**): Table 3, entry 4, left columns (for allylic bromides): Prepared according to **GP1** from crude[†] *o*-methoxy cinnamic bromide (**5f**, *E*:*Z* > 99:1, 104 mg, 0.633 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (90 mg, 49% over two steps, γ:α = 87:13) as a colourless oil. Table 3, entry 4, right columns (for allylic chlorides): Prepared according to **GP2** from crude[‡] *o*-methoxy cinnamic chloride (**5g**, *E*:*Z* > 99:1, 98 mg, 0.60 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (74 mg, 44% over two steps, γ:α = 94:6) as a colourless oil. R_f = 0.62 (cyclohexane:*tert*-butyl methyl ether = 95:5). IR (ATR): $\tilde{\nu}$ = 3070 (vw), 2957 (w), 1624 (w), 1490 (m), 1240 (s), 1113 (m), 899 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.21 (s, 3H), 0.26 (s, 3H), 3.61 (s, 3H), 3.71 (d, *J* = 9.7 Hz, 1H), 4.86–4.97 (m, 2H), 6.04–6.22 (m, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.84 (ddd, *J* = 7.4, 1.0, 1.0 Hz, 1H), 6.96 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.06 (ddd, *J* = 7.4, 1.7, 1.7 Hz, 1H), 7.27–7.39 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –4.8, –4.2, 35.7, 55.0, 110.3, 113.1, 120.4, 125.5, 127.4, 127.7, 129.0, 130.5, 134.4, 137.8, 137.9, 155.9 ppm. HRMS (ESI) calcd for $C_{18}H_{22}OSiNa$ ($[M+Na]^+$): 305.1332; found: 305.1333. Anal. Calcd for $C_{18}H_{22}OSi$: C 76.54; H 7.85; Found: C 76.79; H 8.06. GLC (SE-54): t_R = 19.8 min (branched, γ-**13**), t_R = 22.0 min (linear, α-**13**). The γ:α ratio was determined by GLC analysis.



γ-**14**
$C_{18}H_{19}F_3Si$
M = 320.42 g/mol

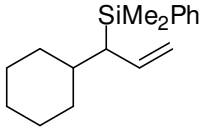
[1-(4-Trifluoromethylphenyl)allyl]dimethylphenylsilane (γ-**14**): Table 3, entry 5, left columns (for allylic bromides): Prepared according to **GP1** from crude[†] *p*-trifluoromethyl cinnamic bromide (**6f**, *E*:*Z* > 99:1, 137 mg, 0.677 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (138 mg, 64% over two steps, γ:α = 79:21) as a colourless oil. Table 3, entry 5, right columns (for allylic chlorides): Prepared according to **GP2** from *p*-trifluoro cinnamic chloride (**6g**, *E*:*Z* > 95:5, 103 mg, 0.466 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane

as eluent afforded the analytically pure product as a mixture of regioisomers (136 mg, 91%, γ:α = 93:7) as a light yellow oil. R_f = 0.46 (cyclohexane). IR (ATR): $\tilde{\nu}$ = 3073 (vw), 2961 (vw), 1615 (m), 1425 (w), 1325 (s), 1251 (m), 1163 (m), 1118 (s), 1069 (s), 1017 (w), 905 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 3H), 0.27 (s, 3H), 3.22 (d, *J* = 9.7 Hz, 1H), 4.89–5.04 (m, 2H), 6.08 (ddd, *J* = 16.8, 10.0, 10.0 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 2H), 7.29–7.40 (m, 5H), 7.42 (d, *J* = 5.5 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –4.7, –4.4, 44.9, 114.0, 124.6 (q, $J_{C,F}$ = 272 Hz), 125.2 (q, $J_{C,F}$ = 3.8 Hz), 127.1 (q, $J_{C,F}$ = 32.5 Hz), 127.6, 127.8, 129.6, 134.4, 136.0, 136.8, 146.3 (m) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.1 ppm. HRMS (EI) calcd for $C_{17}H_{16}F_3Si$ ($[M–CH_3]^+$): 305.0974; Found: 305.1003. Anal. Calcd for $C_{18}H_{19}F_3Si$: C 67.47; H 5.98; Found: C 67.34; H 5.93. GLC (SE-54): t_R = 17.8 min (branched, γ-**14**), t_R = 19.7 min (linear, α-**14**). The γ:α ratio was determined by GLC analysis.



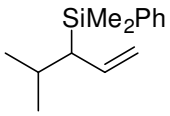
γ-**15**
$C_{17}H_{19}BrSi$
M = 331.32 g/mol

[1-(4-Bromophenyl)allyl]dimethylphenylsilane (γ-**15**): Table 3, entry 6, left columns (for allylic bromides): Prepared according to **GP1** from crude† *p*-bromo cinnamic bromide (**7f**, *E*:*Z* > 99:1, 139 mg, 0.652 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (poor chemical yield, γ:α = 81:19) as a colourless oil. Table 3, entry 6, right columns (for allylic chlorides): Prepared according to **GP2** from *p*-bromo cinnamic chloride (**7g**, *E*:*Z* > 95:5, 25 mg, 0.11 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (30 mg, 84%, γ:α = 96:4) as a colourless oil. R_f = 0.48 (cyclohexane). IR (ATR): $\tilde{\nu}$ = 3070 (w), 2958 (w), 1626 (w), 1486 (s), 1427 (m), 1249 (s), 1186 (m), 1113 (s), 1075 (m), 1008 (s), 950 (vw), 901 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.26 (s, 3H), 0.26 (s, 3H), 3.09 (d, *J* = 9.6 Hz, 1H), 4.87–5.01 (m, 2H), 6.04 (ddd, *J* = 16.8, 10.0, 10.0 Hz, 1H), 6.72–6.81 (m, 2H), 7.27–7.34 (m, 7H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –4.7, –4.4, 44.0, 113.6, 118.4, 127.7, 129.3, 129.5, 131.3, 134.5, 136.3, 137.2, 140.9 ppm. HRMS (EI) calcd for $C_{17}H_{19}BrSi$ ($[M]^+$): 330.0439; Found: 330.0444. GLC (SE-54): t_R = 21.3 min (branched, γ-**15**), t_R = 23.1 min (linear, α-**15**). The γ:α ratio was determined by GLC analysis.



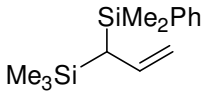
γ-**16**
$C_{17}H_{26}Si$
M = 258.47 g/mol

(1-Cyclohexylallyl)dimethylphenylsilane (γ-**16**): Table 3, entry 7, left columns (for allylic bromides): Prepared according to **GP1** from 3-bromo-1-cyclohexylprop-1-ene (**8f**, *E*:*Z* = 93:7, 136 mg, 0.669 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (152 mg, 88%, γ:α = 88:12) as a colourless oil. Table 3, entry 7, right columns (for allylic chlorides): Prepared according to **GP2** from 3-chloro-1-cyclohexylprop-1-ene (**8g**, *E*:*Z* = 93:7, 92 mg, 0.52 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (126 mg, 84%, γ:α > 99:1) as a colourless oil. R_f = 0.60 (cyclohexane). IR (ATR): $\tilde{\nu}$ = 3071 (w), 2923 (s), 2851 (m), 1623 (w), 1426 (m), 1248 (m), 1113 (s), 896 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.28 (s, 3H), 0.30 (s, 3H), 0.91–1.22 (m, 5H), 1.40–1.52 (m, 2H), 1.56–1.75 (m, 5H), 4.78 (dd, *J* = 16.9, 2.3 Hz, 1H), 4.90 (dd, *J* = 10.0, 2.3 Hz, 1H), 5.71 (ddd, *J* = 16.9, 10.3, 10.3 Hz, 1H), 7.32–7.37 (m, 3H), 7.48–7.53 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –3.3, –2.7, 26.4, 31.5, 34.3, 38.6, 42.4, 113.8, 127.7, 128.8, 134.1, 137.9, 139.1 ppm. HRMS (ESI) calcd for $C_{17}H_{26}SiNa$ ($[M+Na]^+$): 281.1696; Found: 281.1697. Anal. Calcd for $C_{17}H_{26}Si$: C 79.00; H 10.14; Found: C 78.64; H 10.00. GLC (SE-54): t_R = 18.1 min (branched, γ-**16**), t_R = 18.9 min (linear, α-**16**). The γ:α ratio was determined by GLC analysis.



γ-**17**
$C_{14}H_{22}Si$
M = 218.41 g/mol

Dimethyl(4-methylpent-1-ene-3-yl)phenylsilane (γ-**17**): Table 3, entry 8, left columns (for allylic bromides): Prepared according to **GP1** from 1-bromo-4-methylpent-2-ene (**9f**, *E*:*Z* = 95:5, 109 mg, 0.668 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (122 mg, 83%, γ:α = 91:9) as a colourless oil. Table 3, entry 8, right columns (for allylic chlorides): Prepared according to **GP2** from 1-chloro-4-methylpent-2-ene (**9g**, *E*:*Z* = 95:5, 83 mg, 0.70 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (131 mg, 86%, γ:α = 98:2) as a colourless oil. R_f = 0.61 (cyclohexane). IR (ATR): $\tilde{\nu}$ = 3071 (w), 2956 (m), 2361 (vw), 1624 (m), 1428 (m), 1248 (s), 1112 (s), 999 (m), 897 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.30 (s, 3H), 0.32 (s, 3H), 0.86 (d, *J* = 6.8 Hz, 6H), 1.70 (dd, *J* = 10.8, 4.9 Hz, 1H), 1.80–1.93 (m, 1H), 4.84 (dd, *J* = 16.9, 2.3 Hz, 1H), 4.95 (dd, *J* = 10.1, 2.3 Hz, 1H), 5.73 (ddd, *J* = 16.9, 10.6, 10.3 Hz, 1H), 7.33–7.38 (m, 3H), 7.49–7.55 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –3.5, –2.8, 20.8, 24.0, 28.3, 42.9, 114.3, 127.7, 128.9, 134.1, 137.1, 139.0 ppm. HRMS (EI) calcd for $C_{14}H_{22}Si$ ($[M]^+$): 218.1491; Found: 218.1479. Anal. Calcd for $C_{14}H_{22}Si$: C 76.99; H 10.15; Found: C 76.59; H 10.36. GLC (SE-54): t_R = 13.8 min (branched, γ-**17**), t_R = 13.9 min (linear, α-**17**). The γ:α ratio was determined by GLC analysis.



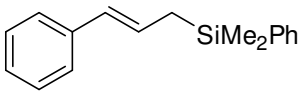
γ-**18**

$C_{14}H_{24}Si_2$

M = 248.51 g/mol

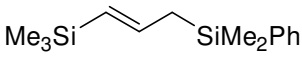
Dimethyl[1-(trimethylsilyl)allyl]phenylsilane (γ-**18**): Table 3, entry 9, left columns (for allylic bromides): Prepared according to **GP1** from 3-bromo-1-trimethylsilylprop-1-ene (**10f**, *E*:*Z* > 99:1, 126 mg, 0.652 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (137 mg, 85%, γ:α = 58:42) as a colourless oil. Table 3, entry 9, right columns (for allylic chlorides): Prepared according to **GP2** from 3-chloro-1-trimethylsilylprop-1-ene (**10g**, *E*:*Z* > 99:1, 86 mg, 0.58 mmol, 1.0 equiv); purification by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product as a mixture of regioisomers (129 mg, 89%, γ:α = 76:24) as a colourless oil. R_f = 0.63 (cyclohexane). IR (ATR): $\tilde{\nu}$ = 3071 (w), 2955 (m), 1605 (w), 1428 (w), 1248 (s), 1113 (m), 933 (w) cm^{-1}. ^1H NMR and ^{13}C NMR resonance signals for both regioisomers were assigned with the aid of 2D NMR spectroscopy. ^1H NMR (400 MHz, $CDCl_3$): δ = –0.11 (s, 9H), 0.30 (s, 3H), 0.33 (s, 3H), 1.34 (d, *J* = 11.7 Hz, 1H), 4.73 (dd, *J* = 16.7, 2.1 Hz, 1H), 4.83 (dd, *J* = 10.0, 2.1 Hz, 1H), 5.69 (ddd, *J* = 16.7, 11.7, 10.0 Hz, 1H), 7.30–7.39 (m, 3H), 7.46–7.55 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –2.0, –1.9, –0.5, 26.9, 112.9, 127.7, 129.1, 134.0, 136.6, 139.5 ppm. HRMS (EI) calcd for $C_{14}H_{24}Si_2$ ($[M]^+$): 248.1417; Found: 248.1428. GLC (SE-54): t_R = 13.9 min (linear, α-**18**), t_R = 14.7 min (branched, γ-**18**). The γ:α ratio was determined by GLC analysis.

3.2 Characterisation Data of Linear Allylic Silanes



α-**2**
$C_{17}H_{20}Si$
M = 252.43 g/mol

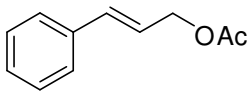
(*E*)-Dimethylphenyl(3-phenylallyl)silane (α-**2**, Table 1): Colourless oil. IR (ATR): $\tilde{\nu}$ = 3023 (w), 2955 (w), 2362 (w), 2339 (vw), 1641 (m), 1600 (vw), 1496 (w), 1427 (w), 1248 (m), 1147 (w), 1113 (m), 1072 (w), 1020 (w), 961 (m), 908 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.37 (s, 6H), 1.95 (d, *J* = 6.5 Hz, 2H), 6.19–6.34 (m, 2H), 7.15–7.25 (m, 1H), 7.29–7.33 (m, 4H), 7.38–7.45 (m, 3H), 7.54–7.61 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.2, 23.2, 125.7, 126.4, 127.3, 127.9, 128.6, 129.1, 129.2, 133.8, 138.5, 138.7 ppm. HRMS (EI) calcd for $C_{17}H_{20}Si$ ($[M]^+$): 252.1334; Found: 252.1314. Anal. Calcd for $C_{17}H_{20}Si$: C 80.89; H 7.99; Found: C 80.55; H 7.90. GLC (SE-54): t_R = 19.9 min.



α-**18**
$C_{14}H_{24}Si_2$
M = 248.51 g/mol

(*E*)-Dimethyl[3-(trimethylsilyl)allyl]phenylsilane (α-**18**, Table 3, entry 9): ^1H NMR (400 MHz, $CDCl_3$): δ = 0.01 (s, 9H), 0.27 (s, 6H), 1.85 (dd, *J* = 7.8, 1.2 Hz, 2H), 5.44 (dt, *J* = 18.4, 1.2 Hz, 1H), 5.99 (dt, *J* = 18.4, 7.8 Hz, 1H), 7.30–7.39 (m, 3H), 7.46–7.55 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –3.4, –0.9, 27.6, 127.8, 129.0, 129.1, 133.8, 138.8, 143.1 ppm.

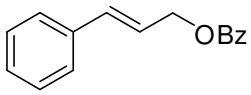
3.3 Characterisation Data of Allylic Substrates with an Oxygenated Leaving Group



1a

$C_{11}H_{12}O_2$
M = 176.21 g/mol

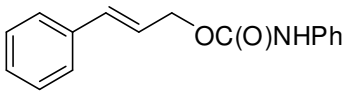
(*E*)-Cinnamic acetate (**1a**, Table 1, entry 1): Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.03 (s, 3H), 4.66 (dd, *J* = 6.4, 1.3 Hz, 2H), 6.22 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 7.15–7.37 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 65.0, 123.1, 126.6, 128.0, 128.6, 134.1, 136.2, 170.7 ppm. GLC (SE-54): t_R = 14.3 min. *E*:*Z* > 99:1 determined by GLC analysis.



1b

$C_{16}H_{14}O_2$
M = 238.28 g/mol

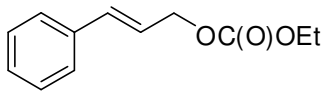
(*E*)-Cinnamic benzoate (**1b**, Table 1, entry 2): Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.9 (d, *J* = 6.4 Hz, 2H), 6.34 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 7.14–7.31 (m, 3H), 7.31–7.42 (m, 4H), 7.44–7.52 (m, 1H), 8.00–8.08 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 65.5, 123.3, 126.7, 128.1, 128.4, 128.7, 129.7, 130.3, 133.0, 134.3, 136.3, 166.4 ppm. GLC (SE-54): t_R = 21.6 min. *E*:*Z* > 99:1 determined by GLC analysis.



1c

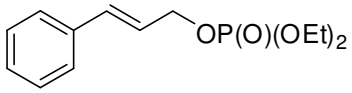
$C_{16}H_{15}NO_2$
M = 253.3 g/mol

(*E*)-Cinnamic *N*-phenyl carbamate (**1c**, Table 1, entry 3): White crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.84 (dd, *J* = 6.4, 1.2 Hz, 2H), 6.34 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.65–6.76 (m, 2H), 7.03–7.12 (m, 1H), 7.22–7.46 (m, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 65.9, 118.9, 123.5, 123.7, 126.8, 128.2, 128.8, 129.2, 134.4, 136.3, 137.9, 153.4 ppm. *E*:*Z* > 95:5 determined by ^{1}H NMR analysis.



1d
$C_{12}H_{14}O_3$
M = 206.24 g/mol

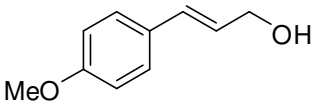
(*E*)-Cinnamic ethyl carbonate (**1d**, Table 1, entry 4): Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.1 Hz, 3H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.69–4.78 (m, 2H), 6.17–6.31 (m, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 7.16–7.38 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3, 64.1, 68.2, 122.6, 126.7, 128.2, 128.7, 134.7, 136.1, 155.1 ppm. GLC (SE-54): t_R = 16.6 min. *E*:*Z* > 99:1 determined by GLC analysis.



1e
$C_{13}H_{19}O_4P$
M = 270.26 g/mol

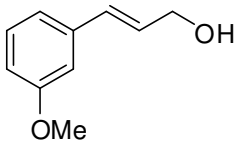
(*E*)-Cinnamic diethyl phosphate (**1e**, Table 1, entry 5): Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.1 Hz, 6H), 4.06–4.19 (m, 4H), 4.65–4.75 (m, 2H), 6.30 (dt, *J* = 15.8, 6.2, Hz, 1H), 6.68 (d, *J* = 15.8 Hz, 1H), 7.22–7.43 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.3 (d, $J_{C,P}$ = 6.8 Hz), 64.0 (d, $J_{C,P}$ = 5.8 Hz), 68.1 (d, $J_{C,P}$ = 5.5 Hz), 123.7 (d, $J_{C,P}$ = 6.7 Hz), 126.8, 128.3, 128.8, 134.0, 136.2 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = –0.77 ppm. HRMS (ESI) calcd for $C_{13}H_{19}O_4PNa$ ($[M+Na]^+$): 293.0913; Found: 293.0909. GLC (SE-54): t_R = 20.0 min. *E*:*Z* > 99:1 determined by GLC analysis.

3.4 Characterisation Data of Aryl-Substituted Allylic Alcohols (Precursors for Chemically Unstable, Aryl-Substituted Allylic Bromides and Chlorides)



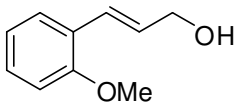
$C_{10}H_{12}O_2$
M = 164.20 g/mol

(*E*)-*p*-Methoxy cinnamic alcohol (for **3f** and **3g**): Crystalline white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.82 (br s, 1H), 3.80 (s, 3H), 4.28 (d, *J* = 5.8 Hz, 2H), 6.22 (dt, *J* = 15.8, 5.9 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.81–6.90 (m, 2H), 7.27–7.36 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.5, 64.0, 114.1, 126.5, 127.9, 129.6, 131.1, 159.5 ppm. GLC (SE-54): t_R = 16.0 min. *E*:*Z* > 99:1 determined by GLC analysis.



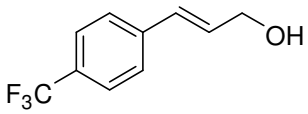
$C_{10}H_{12}O_2$
M = 164.20 g/mol

(*E*)-*m*-Methoxy cinnamic alcohol (for **4f**): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.41 (br s, 1H), 3.81 (s, 3H), 4.32 (d, *J* = 5.5 Hz, 2H), 6.37 (dt, *J* = 15.9, 5.5 Hz, 1H), 6.60 (d, *J* = 15.9, 1H), 6.84 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.96 (s, 1H), 7.01(d, *J* = 7.7 Hz, 1H), 7.22–7.32 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.0, 63.1, 111.8, 113.1, 119.0, 129.0, 129.5, 130.4, 138.2, 159.6 ppm. GLC (SE-54): t_R = 16.0 min. *E*:*Z* > 99:1 determined by GLC analysis.



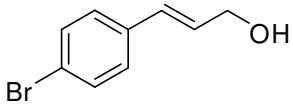
$C_{10}H_{12}O_2$
M = 164.20 g/mol

(*E*)-*o*-Methoxy cinnamic alcohol (for **5f** and **5g**): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47 (br s, 1H), 3.85 (s, 3H), 4.33 (dd, *J* = 5.9, 1.4 Hz, 2H), 6.39 (dt, *J* = 16.0, 5.9 Hz, 1H), 6.83–6.99 (m, 3H), 7.19–7.29 (m, 1H), 7.44 (dd, *J* = 7.6, 1.6 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3, 63.8, 110.8, 120.6, 125.0, 125.8, 126.9, 128.6, 129.4, 156.6 ppm. GLC (SE-54): t_R = 15.5 min. *E*:*Z* > 99:1 determined by GLC analysis.



$C_{10}H_9F_3O$
M = 202.17 g/mol

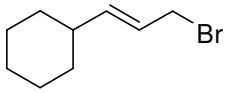
(*E*)-*p*-Trifluoromethyl cinnamic alcohol (for **6f** and **6g**): White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 1H), 4.35 (dd, *J* = 5.3, 1.4 Hz, 2H), 6.43 (dt, *J* = 16.0, 5.3 Hz, 1H), 6.58–6.71 (d, *J* = 16.0 Hz, 1H), 7.40–7.48 (d, *J* = 8.2 Hz, 2H), 7.50–7.58 (d, *J* = 8.2 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.3, 124.3 (q, $J_{C,F}$ = 272 Hz), 125.7 (q, $J_{C,F}$ = 3.8 Hz), 126.7, 129.3, 129.7, 129.5 (q, $J_{C,F}$ = 32.5 Hz), 140.3 (m) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.5 ppm. GLC (SE-54): t_R = 12.8 min. *E*:*Z* > 99:1 determined by GLC analysis.



C_9H_9BrO
M = 213.07 g/mol

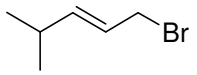
(*E*)-*p*-Bromo cinnamic alcohol (for **7f** and **7g**): White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (s, 1H), 4.31 (d, *J* = 4.6 Hz, 2H), 6.34 (dt, *J* = 15.9, 5.5 Hz, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 7.19–7.28 (m, 2H), 7.40–7.46 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.6, 121.6, 128.1, 129.4, 129.9, 131.8, 135.7 ppm. GLC (SE-54): t_R = 16.5 min. *E*:*Z* > 99:1 determined by GLC analysis.

3.5 Characterisation Data of Alkyl-Substituted Allylic Bromides



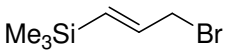
8f
$C_9H_{15}Br$
M = 203.12 g/mol

(*E*)-3-Bromo-1-cyclohexylprop-1-ene (**8f**, Table 3, entry 7): Prepared from 3-cyclohexylprop-2-en-1-ol (*E*:*Z* = 95:5, 1.20 g, 8.56 mmol, 1.0 equiv) according to **GP6**. Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the analytically pure product (1.23 g, 70%, *E*:*Z* = 93:7) as a light yellow oil. R_f = 0.71 (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96–1.36 (m, 5H), 1.59–1.80 (m, 5H), 1.91–2.07 (m, 1H), 3.95 (d, *J* = 7.0 Hz, 2H), 5.57–5.77 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.0, 26.2, 32.6, 34.2, 40.3, 124.1, 142.3 ppm. GLC (SE-54): t_R = 12.4 min. The *E*:*Z* ratio was determined by GLC analysis.



9f
$C_6H_{11}Br$
M = 163.06 g/mol

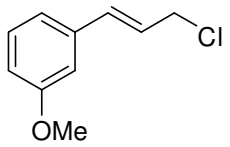
(*E*)-1-Bromo-4-methylpent-2-ene (**9f**, Table 3, entry 8): Prepared from 4-methylpent-2-en-1-ol (*E*:*Z* = 95:5, 0.935 g, 9.33 mmol, 1.0 equiv) according to **GP6**. Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the analytically pure product (1.01 g, 68%, *E*:*Z* = 95:5) as a colorless oil. R_f = 0.80 (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.0 (d, *J* = 6.7 Hz, 6H), 2.23–2.41 (m, 1H), 3.95 (d, *J* = 7.2 Hz, 2H), 5.57–5.80 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1, 30.8, 33.9, 123.9, 143.4 ppm. GLC (SE-54): t_R = 6.2 min. The *E*:*Z* ratio was determined by GLC analysis.



10f
$C_6H_{13}BrSi$
M = 193.16 g/mol

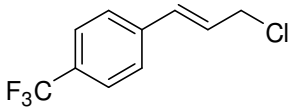
(*E*)-3-Bromo-1-trimethylsilylprop-1-ene (**10f**, Table 3, entry 9): Prepared from 3-trimethylsilylprop-2-en-1-ol (*E*:*Z* > 99:1, 500 mg, 3.84 mmol, 1.0 equiv) according to **GP6**. Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the analytically pure product (539 mg, 73%, *E*:*Z* > 99:1) as a colourless oil. R_f = 0.82 (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08 (s, 9H), 3.94 (dd, *J* = 6.7, 1.0 Hz, 2H), 5.94 (dt, *J* = 18.2, 1.0 Hz, 1H), 6.08–6.20 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.4, 35.3, 135.8, 140.8 ppm. GLC analysis: t_R = 7.3 min. The *E*:*Z* ratio was determined by GLC analysis.

3.6 Characterisation Data of Aryl-Substituted Allylic Chlorides



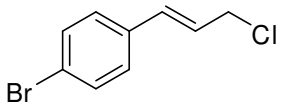
4g
$C_{10}H_{11}ClO$
M = 182.65 g/mol

(*E*)-*m*-Methoxy cinnamic chloride (**4g**, Table 3, entry 3): Prepared from *m*-methoxy cinnamic alcohol (*E*:*Z* > 99:1, 98 mg, 0.66 mmol, 1.0 equiv) according to **GP5**. Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the analytically pure product (60 mg, 55%, *E*:*Z* > 99:1) as a colourless oil. R_f = 0.62 (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3H), 4.22 (dd, *J* = 7.1, 1.0 Hz, 2H), 6.30 (dt, *J* = 15.6, 7.1 Hz, 1H), 6.62 (d, *J* = 15.6, 1H), 6.82 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.90–6.93 (m, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 7.19–7.27 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.5, 55.4, 112.2, 114.1, 119.5, 125.4, 129.8, 134.2, 137.5, 160.0 ppm. GLC analysis: t_R = 15.7 min. The *E*:*Z* ratio was determined by GLC analysis.



6g
$C_{10}H_8ClF_3$
M =220.62 g/mol

(*E*)-*p*-Trifluoromethyl cinnamic chloride (**6g**, Table 3, entry 5): Prepared from *p*-trifluoromethyl cinnamic alcohol (*E*:*Z* = 95:5, 121 mg, 0.600 mmol, 1.0 equiv) according to **GP5**. Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the analytically pure product (103 mg, 78%, *E*:*Z* > 95:5) as a colourless oil. R_f = 0.80 (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.25 (dd, *J* = 7.0, 1.0 Hz, 2H), 6.41 (dt, *J* = 15.7, 7.0 Hz, 1H), 6.69 (d, *J* = 15.7 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.9, 124.2 (q, $J_{C,F}$ = 272 Hz), 125.8 (q, $J_{C,F}$ = 3.8), 127.0, 127.7, 130.2 (q, $J_{C,F}$ = 32.5 Hz), 132.7, 139.6 (m) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.6 ppm. The *E*:*Z* ratio was determined by ^{1}H NMR analysis.

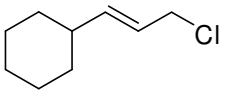


7g
C_9H_8BrCl
M = 231.52 g/mol

(*E*)-*p*-Bromo cinnamic chloride (**7g**, Table 3, entry 6): Prepared from *p*-bromo cinnamic alcohol (*E*:*Z* > 99:1, 128 mg, 0.600 mmol, 1.0 equiv) according to **GP5**. Purification by flash column

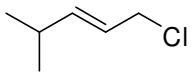
chromatography on silica gel using *n*-pentane as eluent afforded the analytically pure product (100 mg, 51%, *E*:*Z* > 95:5) as a colourless oil. R_f = 0.82 (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.22 (dd, *J* = 7.1, 1.1 Hz, 2H), 6.30 (dt, *J* = 15.6, 7.1 Hz, 1H), 6.58 (d, *J* = 15.7 Hz, 1H), 7.21–7.27 (m, 2H), 7.41–7.48 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.3, 122.3, 125.8, 128.3, 131.9, 133.0, 134.9 ppm. The *E*:*Z* ratio was determined by ^{1}H NMR analysis.

3.7 Characterisation Data of Alkyl-Substituted Allylic Chlorides



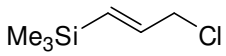
8g
$C_9H_{15}Cl$
M = 158.67 g/mol

(*E*)-3-Chloro-1-cyclohexylprop-1-ene (**8g**, Table 3, entry 7): Prepared from 3-cyclohexylprop-2-en-1-ol (*E*:*Z* = 95:5, 650 mg, 4.63 mmol, 1.0 equiv) according to **GP6**. Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the analytically pure product (608 mg, 83%, *E*:*Z* = 93:7) as a light yellow oil. R_f = 0.68 (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98–1.35 (m, 5H), 1.59–1.79 (m, 5H), 1.90–2.06 (m, 1H), 4.30 (d, *J* = 7.0 Hz, 2H), 5.49–5.61 (m, 1H), 5.66–5.76 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.0, 26.2, 32.6, 40.3, 46.0, 123.6, 141.9 ppm. GLC (SE-54): t_R = 11.1 min. The *E*:*Z* ratio was determined by GLC analysis.



9g
$C_6H_{11}Cl$
M = 118.6 g/mol

(*E*)-1-Chloro-4-methylpent-2-ene (**9g**, Table 3, entry 8): Prepared from 4-methylpent-2-en-1-ol (*E*:*Z* = 95:5, 1.08 g, 10.8 mmol, 1.0 equiv) according to **GP6**. Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the analytically pure product (0.637 g, 50%, *E*:*Z* = 95:5) as a colorless oil. R_f = 0.82 (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.0 (d, *J* = 6.8 Hz, 6H), 2.23–2.40 (m, 1H), 4.03 (dd, *J* = 7.0, 0.8 Hz, 2H), 5.49–5.63 (m, 1H), 5.69–5.79 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1, 30.8, 45.8, 123.2, 143.0 ppm. GLC (SE-54): t_R = 5.1 min. The *E*:*Z* ratio was determined by GLC analysis.



10g

$C_6H_{13}ClSi$

M = 148.71 g/mol

(*E*)-3-Chloro-1-trimethylsilylprop-1-ene (**10g**, Table 3, entry 9): Prepared from 3-trimethylsilylprop-2-en-1-ol (*E*:*Z* > 99:1, 1.0 g, 7.7 mmol, 1.0 equiv) according to **GP6**. Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the analytically pure product (819 mg, 72%, *E*:*Z* > 99:1) as a colourless oil. R_f = 0.82 (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09 (s, 9H), 4.07 (dd, *J* = 5.5, 1.0 Hz, 2H), 5.94–6.02 (m, 1H), 6.09 (dt, *J* = 18.4, 5.6 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.4, 47.5, 134.9, 140.6 ppm. GLC analysis: t_R = 6.1 min. The *E*:*Z* ratio was determined by GLC analysis.

4 Preparation and Characterisation of (*Z*)-Configured Cinnamic Bromide (1f)

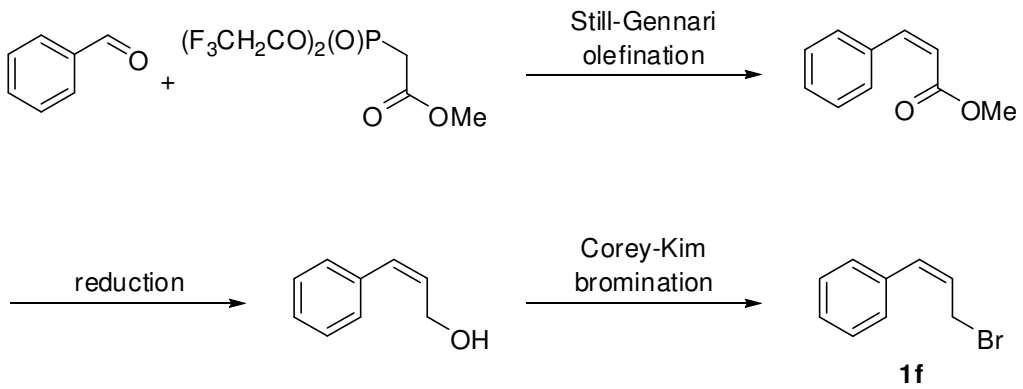
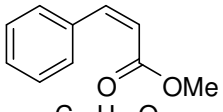


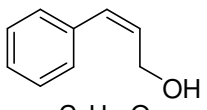
Fig. 3: Three-step preparation of (*Z*)-cinnamic bromide (**1f**).



$C_{10}H_{10}O_2$
M = 162.19 g/mol

According to the Still-Gennari protocol, a flame-dried Schlenk flask was charged with Still-Gennari reagent (1.37 g, 4.33 mmol, 1.40 equiv) and 18-crown-6 (2.04 g, 7.72 mmol, 2.50 equiv) in THF. At –78 °C, KHMDS (16% w/w solution in toluene, 0.857 g, 4.33 mmol, 1.40 equiv) was slowly added, and the reaction mixture was stirred for 0.5 h. To this suspension, a solution of benzaldehyde (0.328 g, 3.09 mmol, 1.0 equiv) in THF was added, and the reaction mixture was maintained at –78 °C. After completion of reaction (TLC monitoring), the reaction mixture was quenched with saturated NH_4Cl. Standard work-up and flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether (95:5) as eluent gave the analytically pure α,β-unsaturated ester (0.424 g, 2.60 mmol, 84%, *Z*:*E* > 99:1). The *Z*:*E* ratio was determined by GLC analysis.

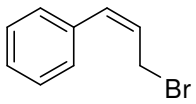
(*Z*)-Cinnamic methyl carboxylate: Colourless oil. R_f = 0.55 (cyclohexane:*tert*-butyl methyl ether = 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.72 (s, 3H), 5.96 (d, *J* = 12.6 Hz, 1H), 6.97 (d, *J* = 12.6 Hz, 1H), 7.32–7.41 (m, 3H), 7.56–7.63 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.5, 119.4, 128.2, 129.2, 129.8, 134.9, 143.6, 166.7 ppm. HRMS (EI) calcd for $C_{10}H_{10}O_2$ ($[M]^+$): 162.0681; Found 162.0667. GLC (SE-54): t_R = 12.3 min.



$C_9H_{10}O$
M = 134.18 g/ mol

(*Z*)-Cinnamic alcohol: Prepared from the above α,β-unsaturated ester (*Z*:*E* > 99:1, 424 mg, 2.60 mmol, 1.0 equiv) according to **GP4**. Purification by flash column chromatography on silica gel using

cyclohexane:*tert*-butyl methyl ether (95:5) as eluent afforded the analytically pure allylic alcohol (300 mg, 86%, *Z*:*E* > 99:1) as a colorless oil. R_f = 0.21 (cyclohexane:*tert*-butyl methyl ether = 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63 (t, *J* = 4.9 Hz, 1H), 4.40–4.48 (m, 2H), 5.88 (dt, *J* = 11.8, 6.4 Hz, 1H), 6.58 (d, *J* = 11.7 Hz, 1H), 7.18–7.40 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 59.8, 127.4, 128.4, 128.9, 131.2, 131.3, 136.6 ppm. HRMS (EI) calcd for $C_9H_{10}O$ ($[M]^+$): 134.0732: Found 134.0735. GLC (SE-54): t_R = 11.7 min. The *Z*:*E* ratio was determined by GLC analysis.



1f

C_9H_9Br

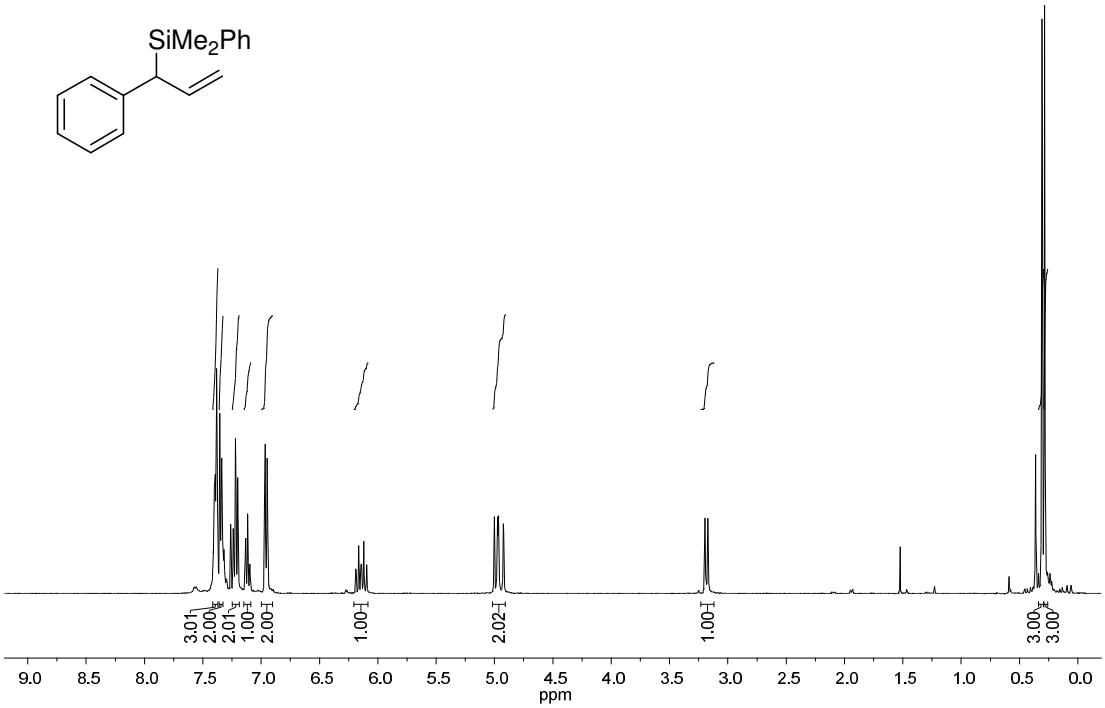
M = 197.07 g/mol

(*Z*)-Cinnamic bromide (**1f**, Scheme 1): Prepared from the above allylic alcohol (*Z*:*E* > 99:1, 205 mg, 1.52 mmol, 1.0 equiv) according to **GP6** (double bond isomerisation is seen with **GP5**). Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the analytically pure product (195 mg, 65%, *Z*:*E* > 95:5) as a colorless oil. R_f = 0.60 (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.18 (dd, *J* = 8.7, 0.8 Hz, 2H), 6.00 (dt, *J* = 11.3, 8.6 Hz, 1H), 6.61 (d, *J* = 11.2 Hz, 1H), 7.27–7.45 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.0, 127.1, 127.8, 128.7, 128.8, 133.6, 135.7 ppm. GLC (SE-54): t_R = 12.6 min. The *Z*:*E* ratio was determined by ^{1}H NMR and ^{13}C NMR analysis.

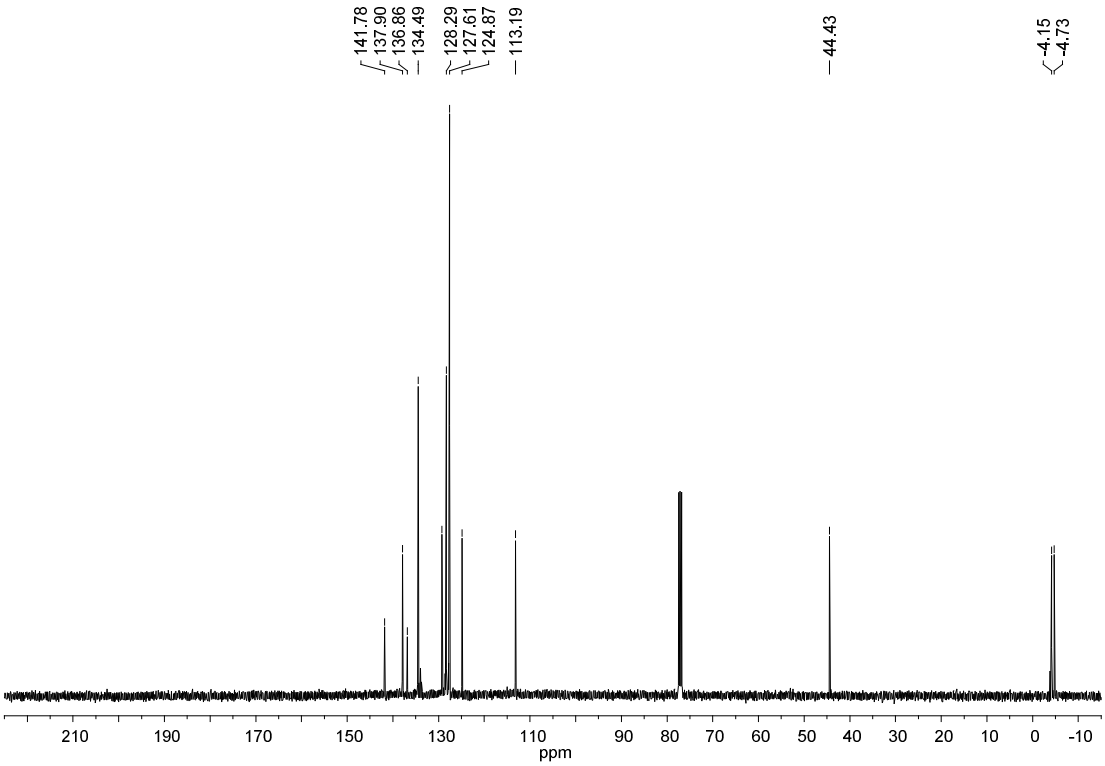
5 NMR Spectra of All Compounds

Dimethylphenyl(1-phenylallyl)silane (γ-**2**)

^{1}H NMR:

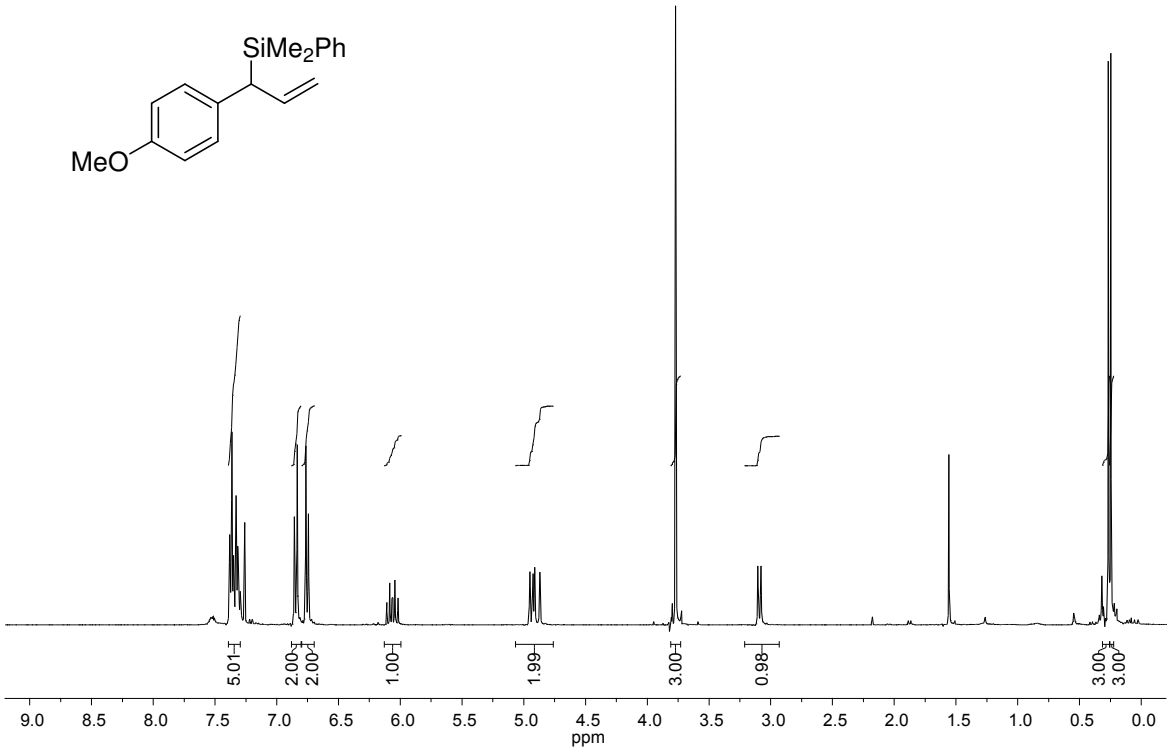


^{13}C NMR:

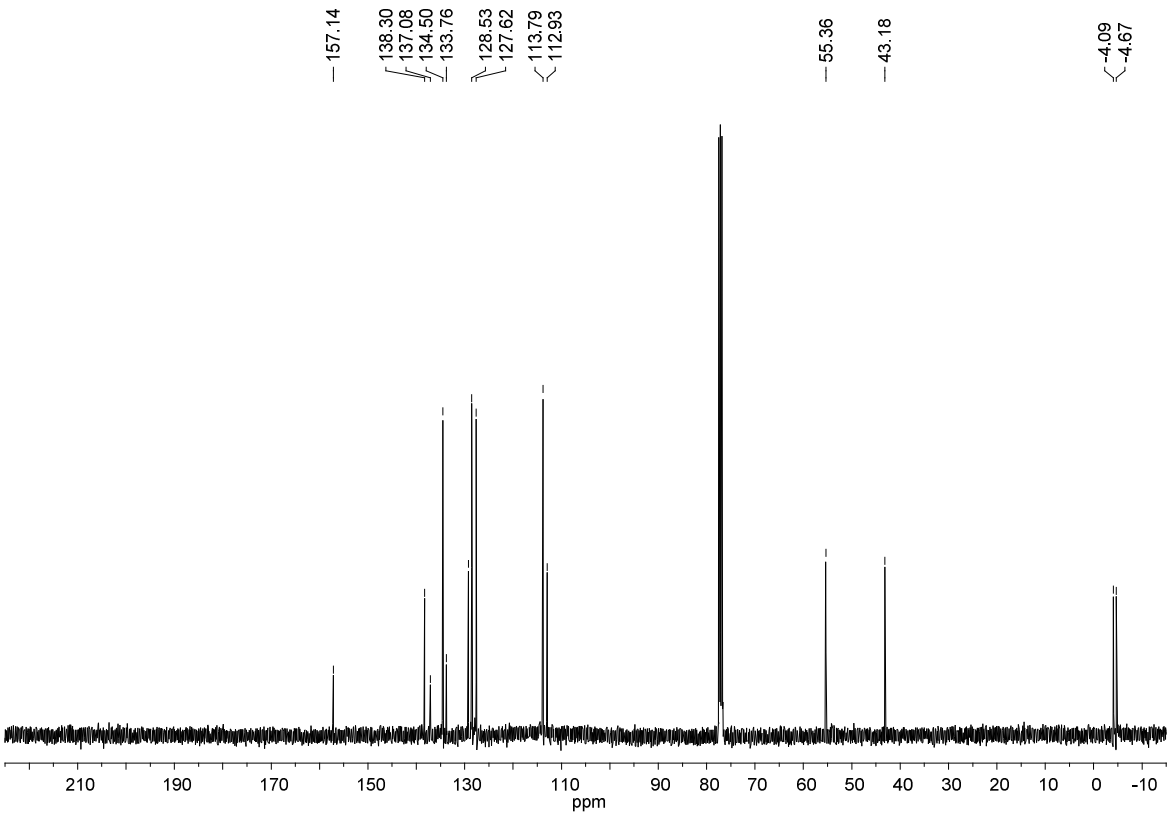


[1-(4-Methoxyphenyl)allyl]dimethylphenylsilane (γ-**11**)

^{1}H NMR:

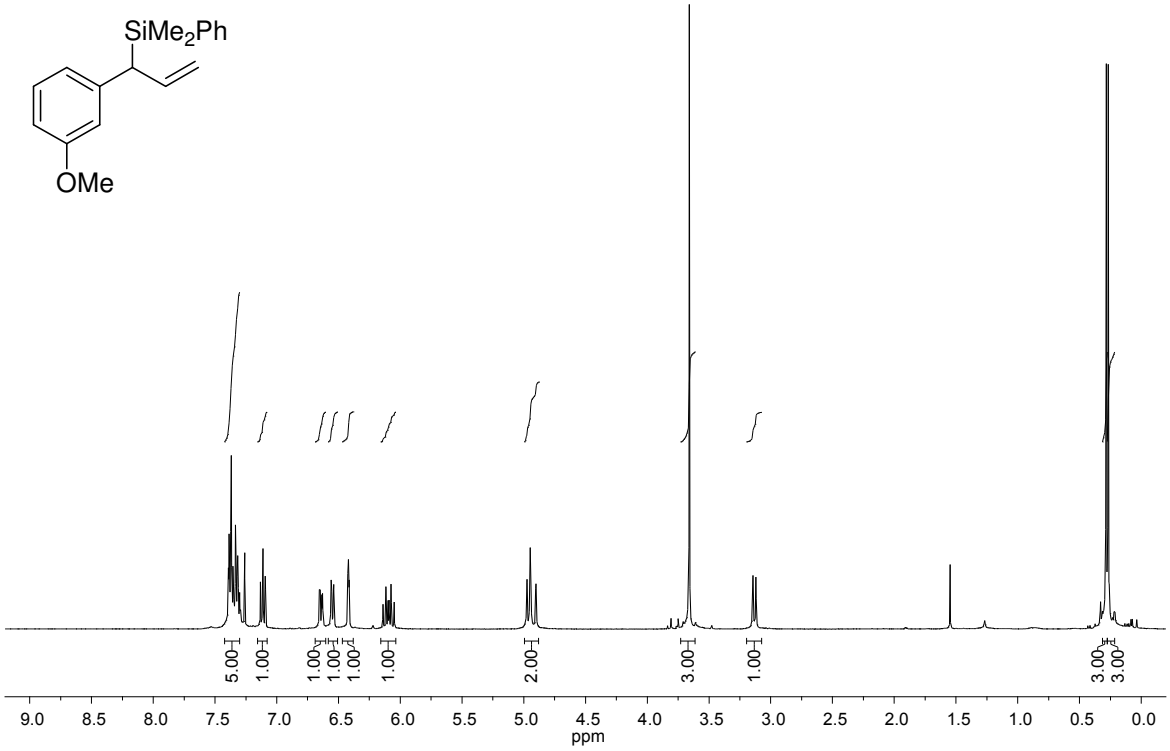


^{13}C NMR:

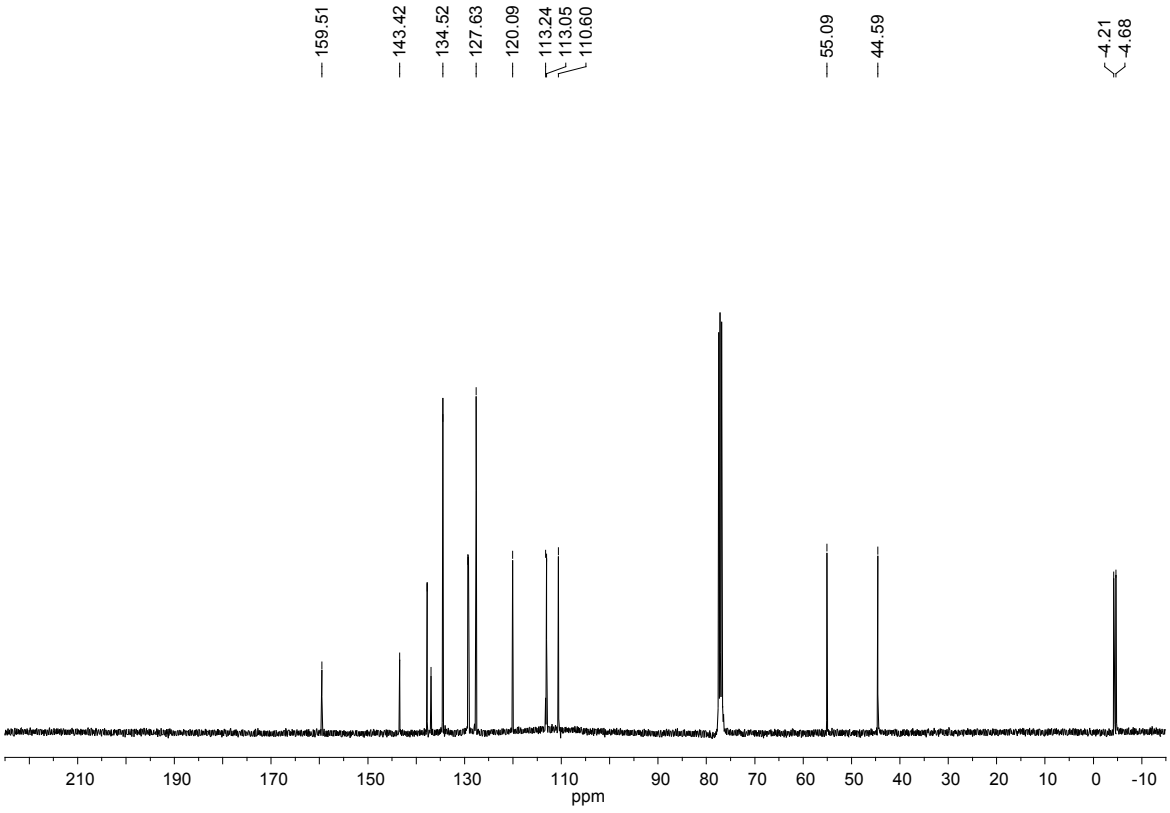


[1-(3-Methoxyphenyl)allyl]dimethylphenylsilane (γ-**12**)

^{1}H NMR:

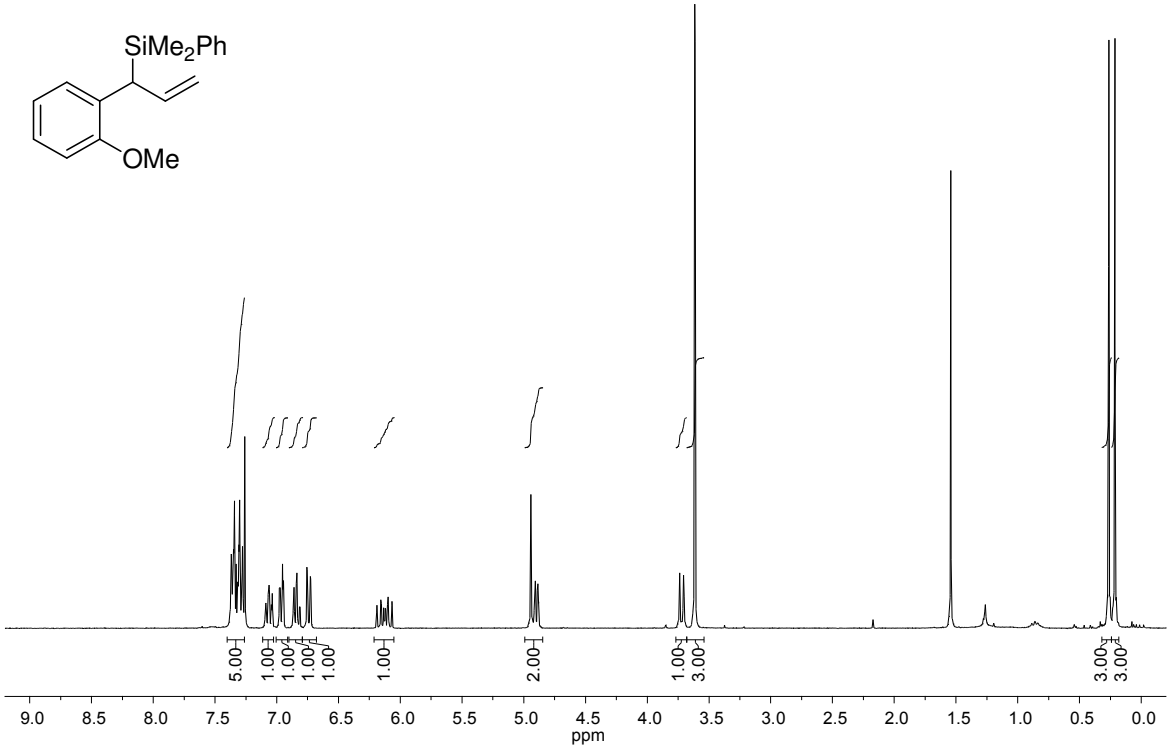


^{13}C NMR:

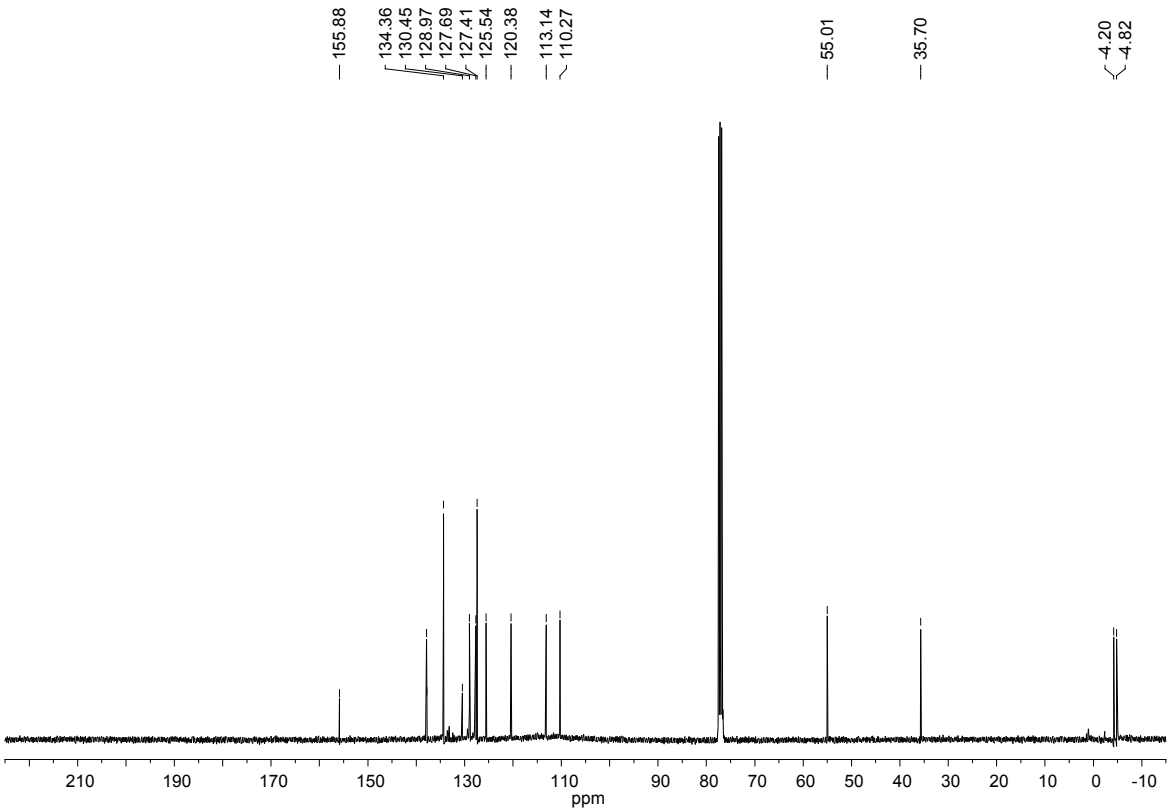


[1-(2-Methoxyphenyl)allyl]dimethylphenylsilane (γ-**13**)

^{1}H NMR:

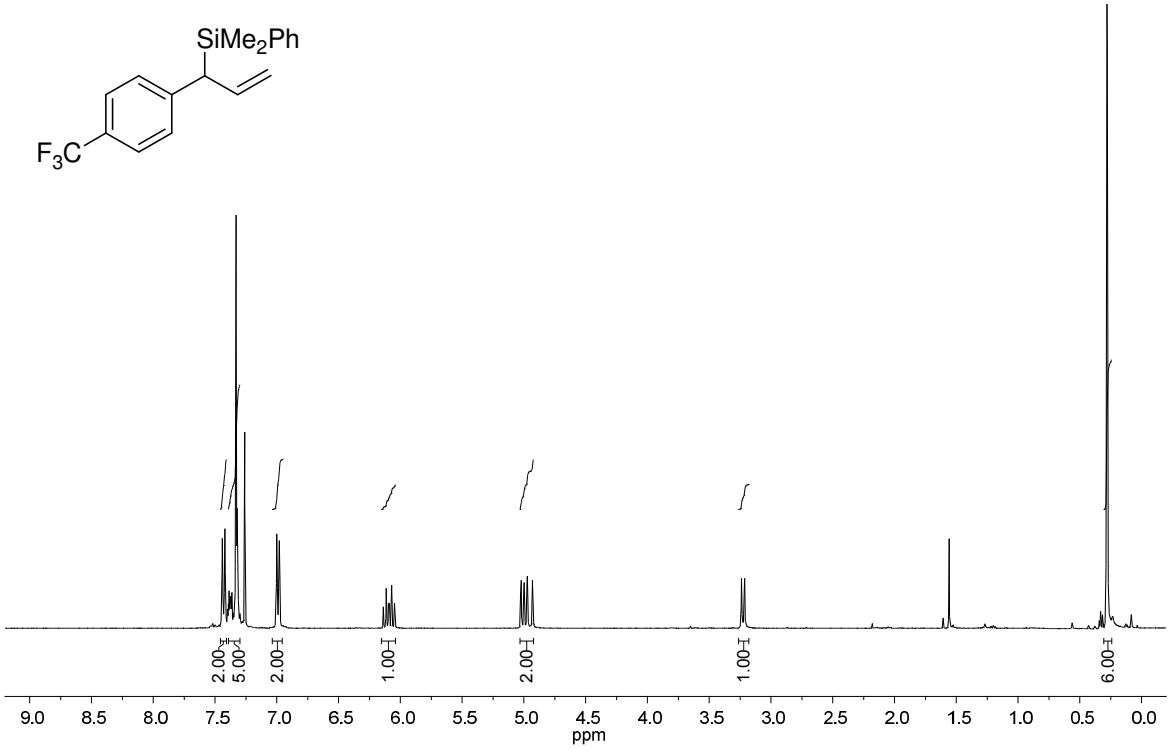


^{13}C NMR:

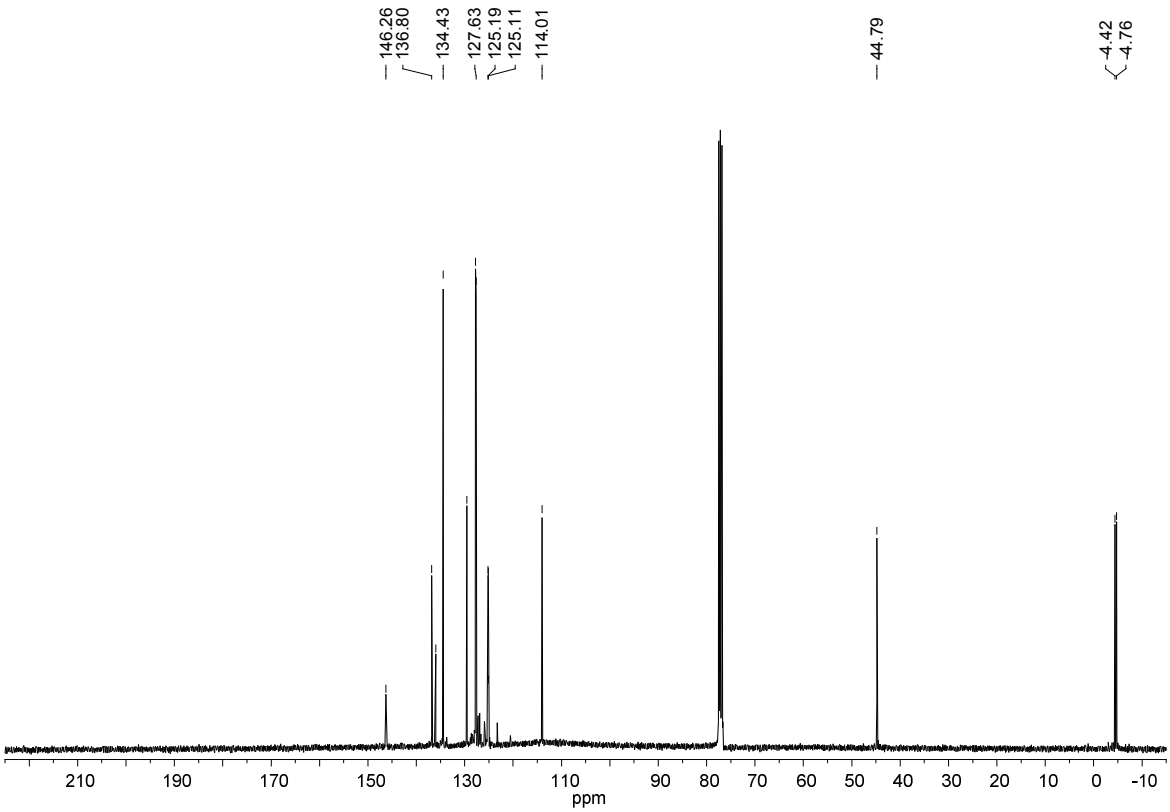


[1-(4-Trifluoromethylphenyl)allyl]dimethylphenysilane (γ-**14**)

^{1}H NMR:

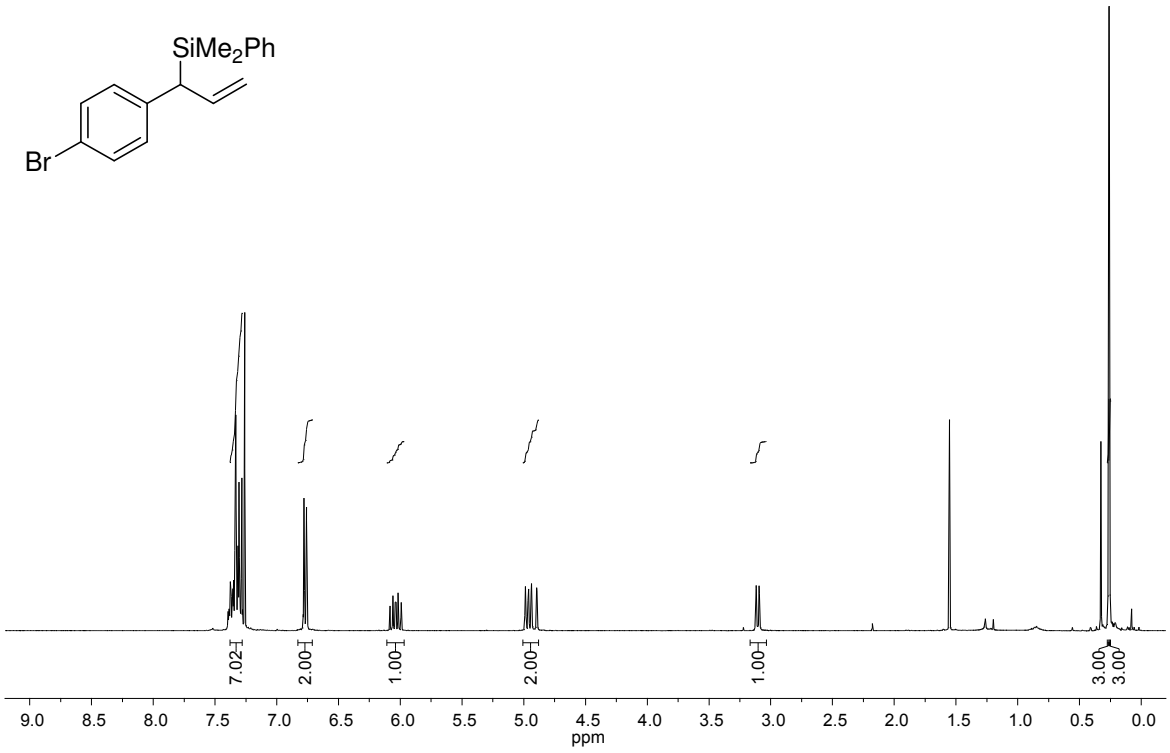


^{13}C NMR:

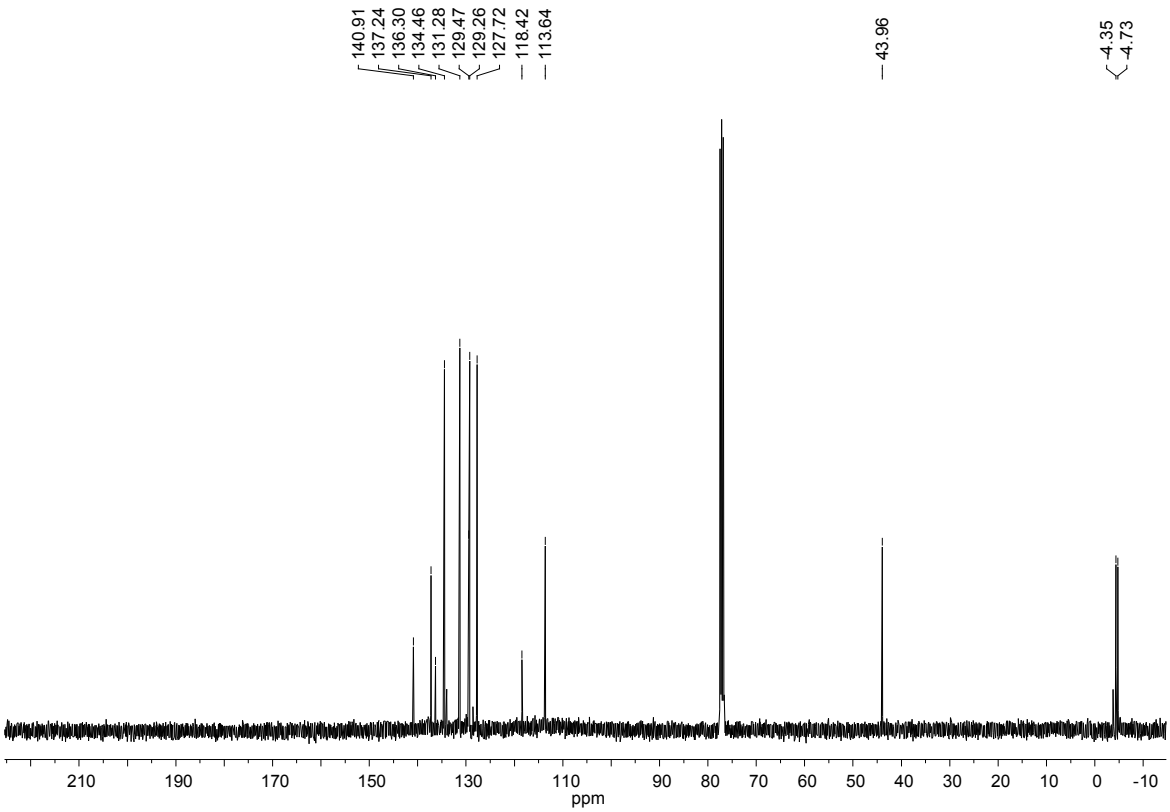


[1-(4-Bromophenyl)allyl]dimethylphenylsilane (γ-**15**)

^{1}H NMR:

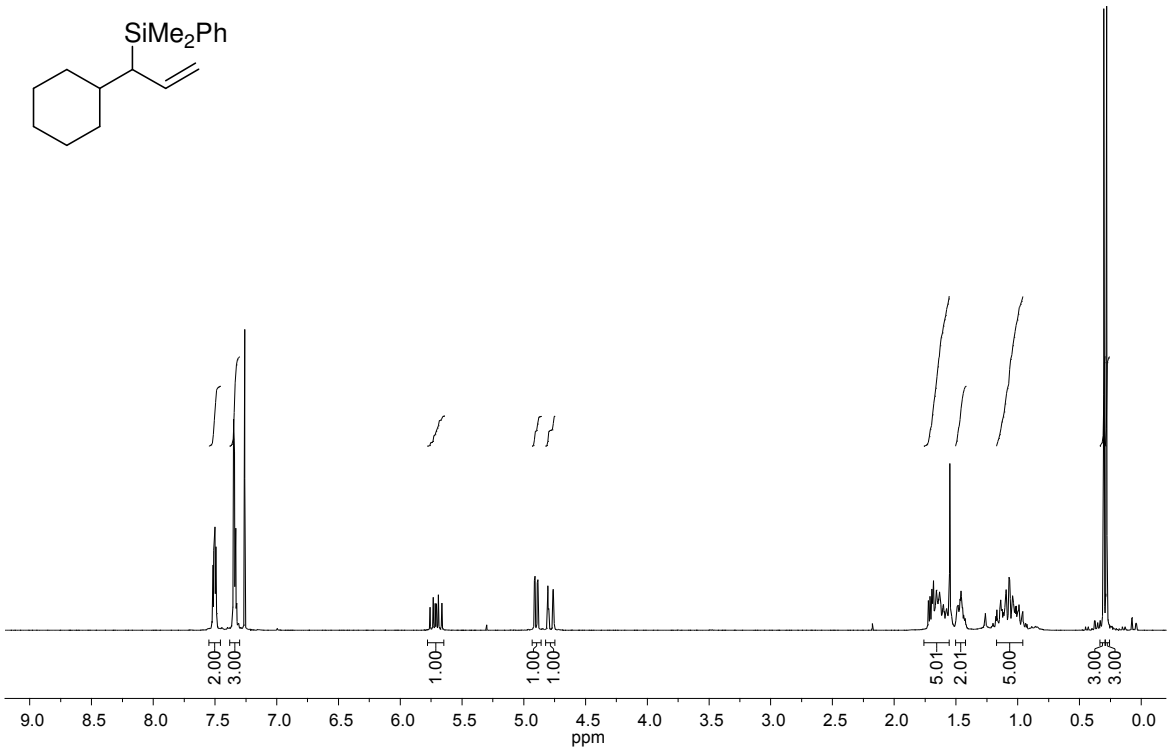


^{13}C NMR:

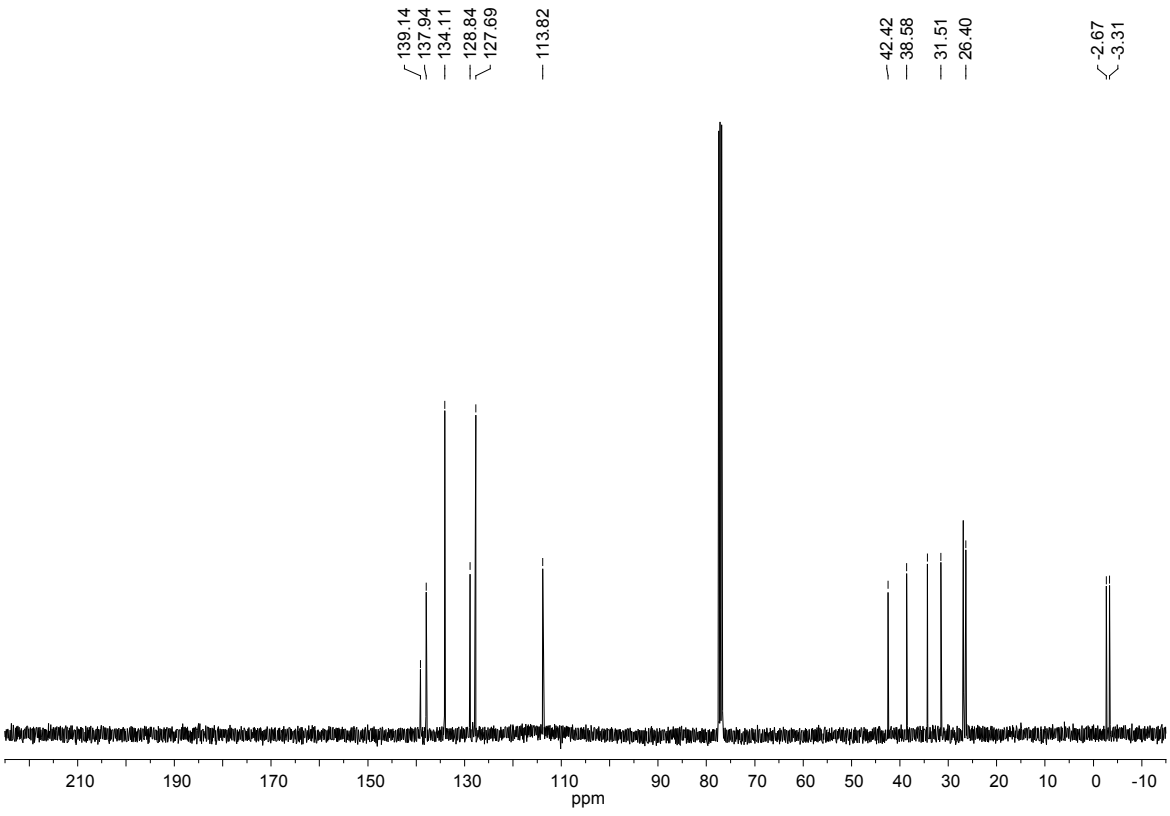


(1-Cyclohexylallyl)dimethylphenylsilane (γ-**16**)

^{1}H NMR:

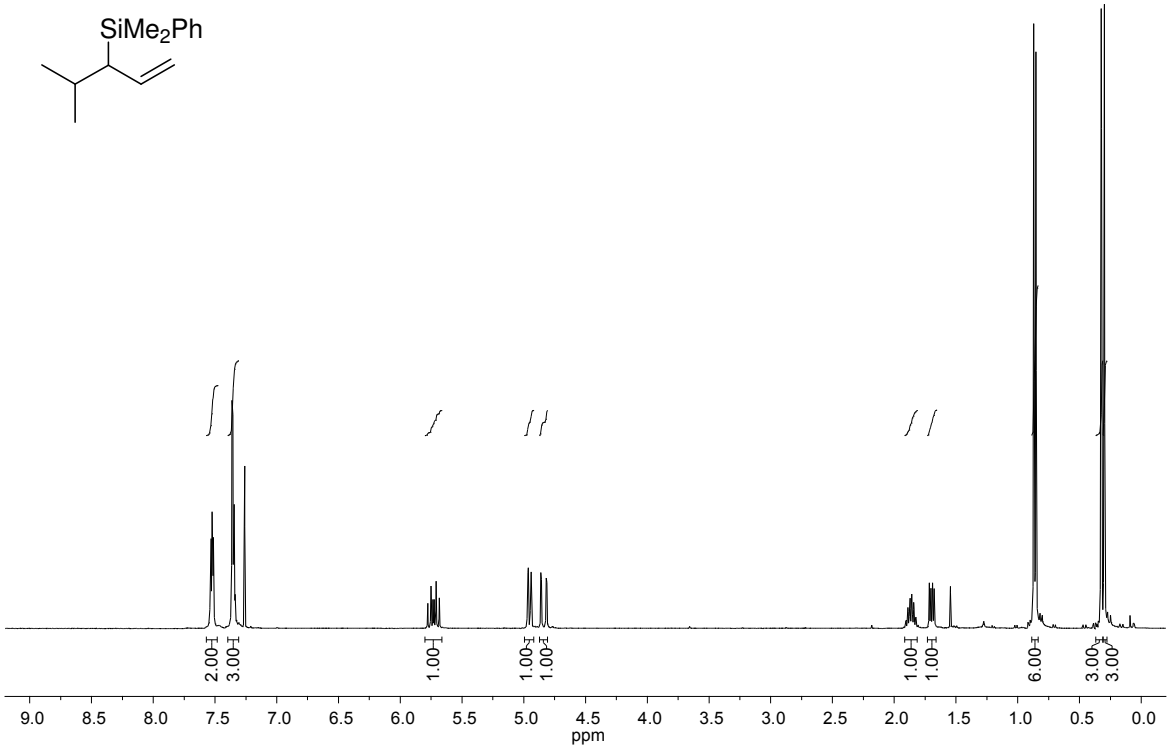


^{13}C NMR:

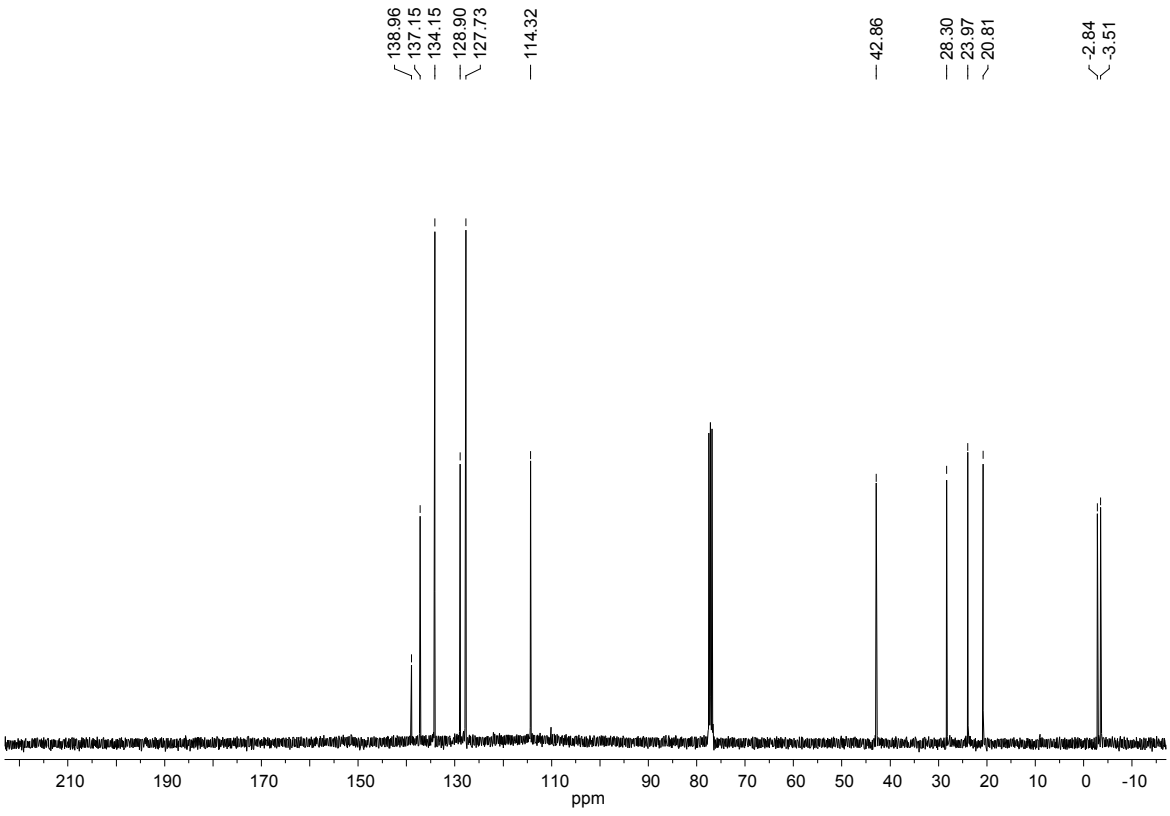


Dimethyl(4-methylpent-1-en-3-yl)phenylsilane (γ-**17**)

^{1}H NMR:

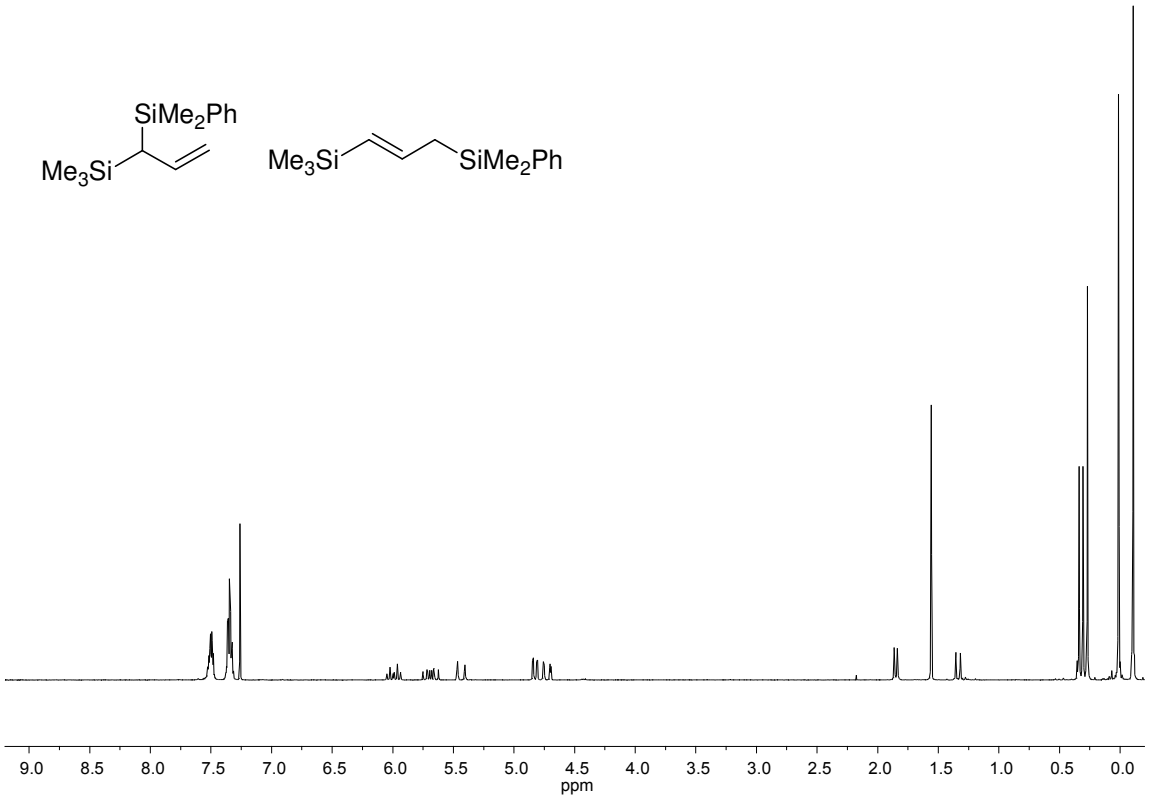


^{13}C NMR:

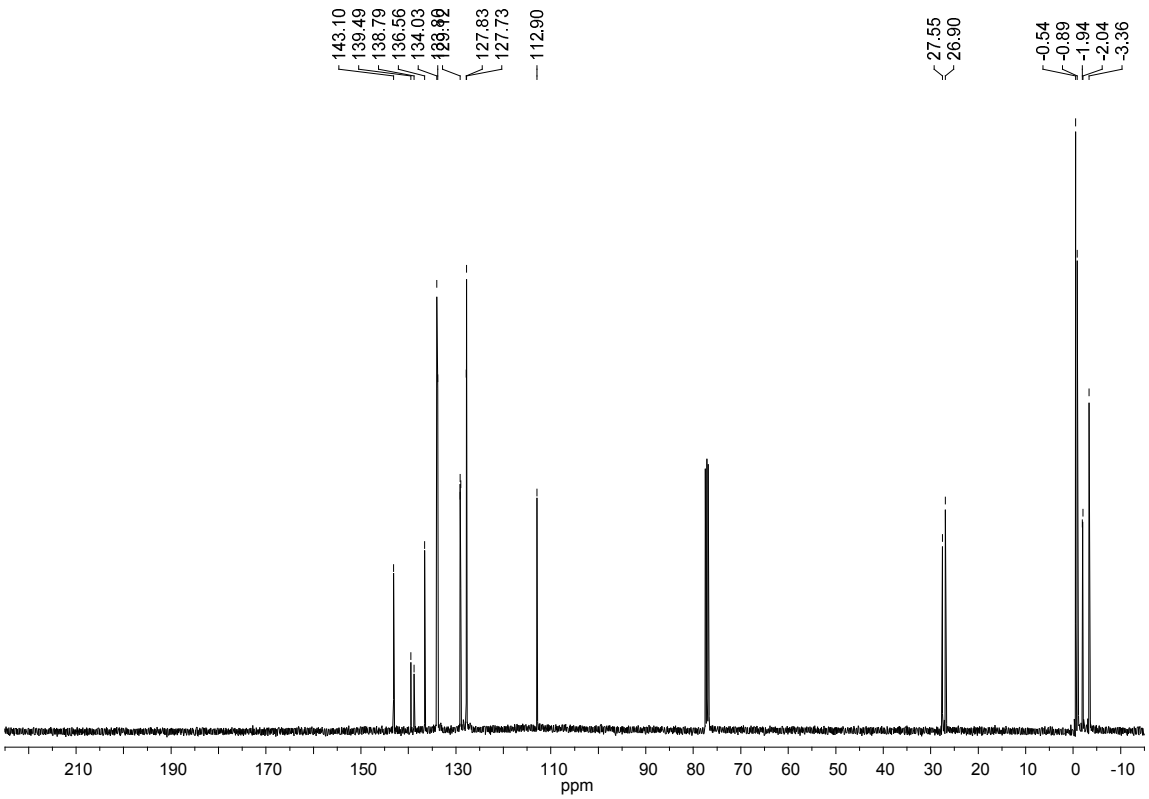


Dimethyl[1-(trimethylsilyl)allyl]phenylsilane (γ-**18**) **and (*E*)-Dimethyl-[3-(trimethylsilyl)allyl]phenylsilane** (α-**18**)

^{1}H NMR:

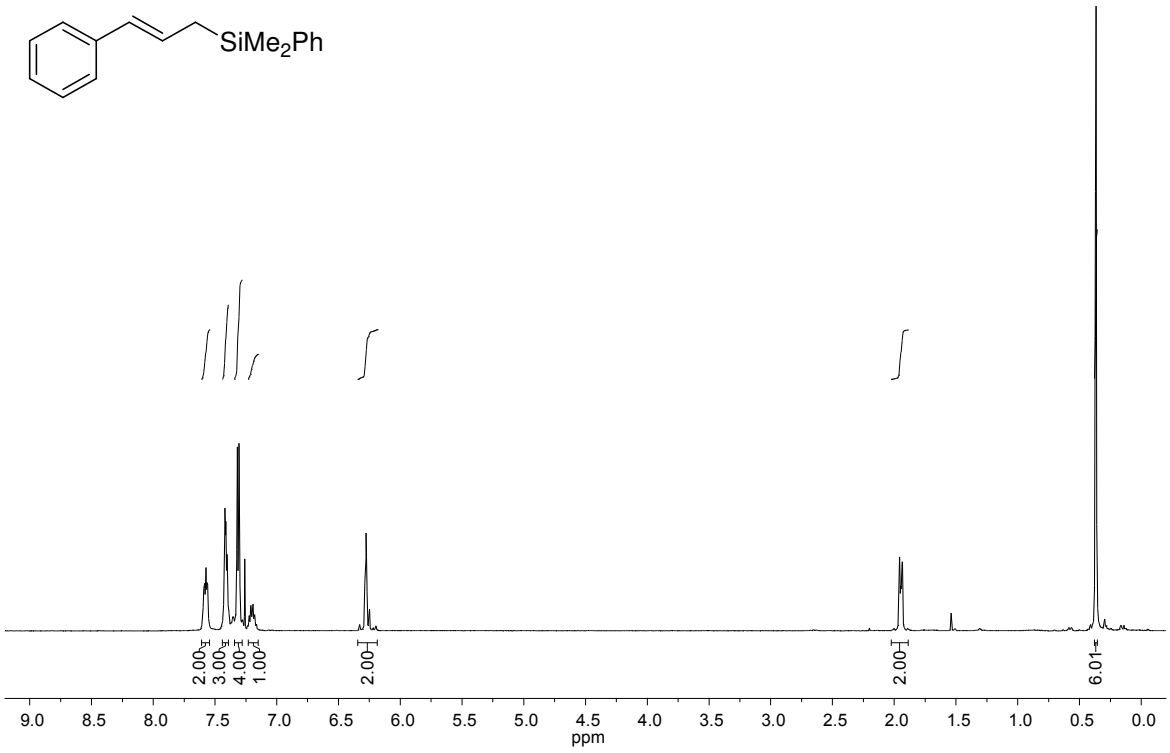


^{13}C NMR:

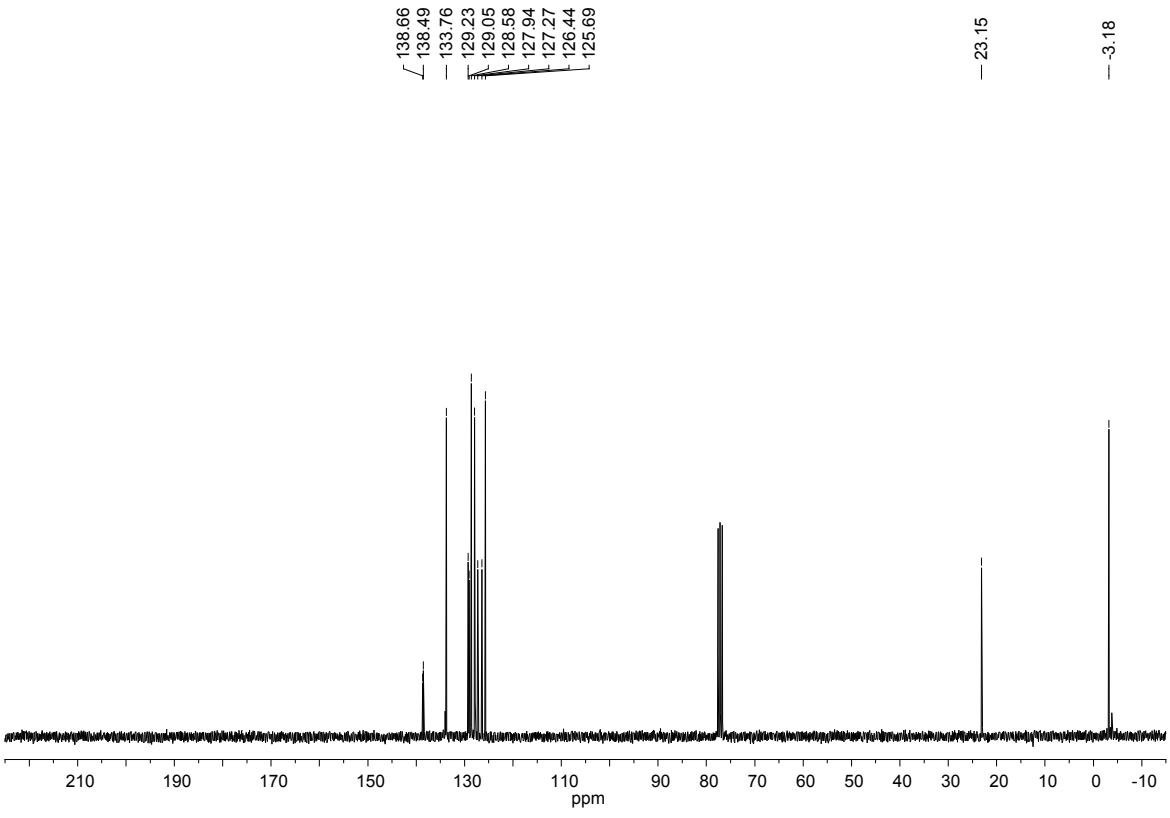


(*E*)-Dimethylphenyl(3-phenylallyl)silane (α-**2**)

^{1}H NMR:

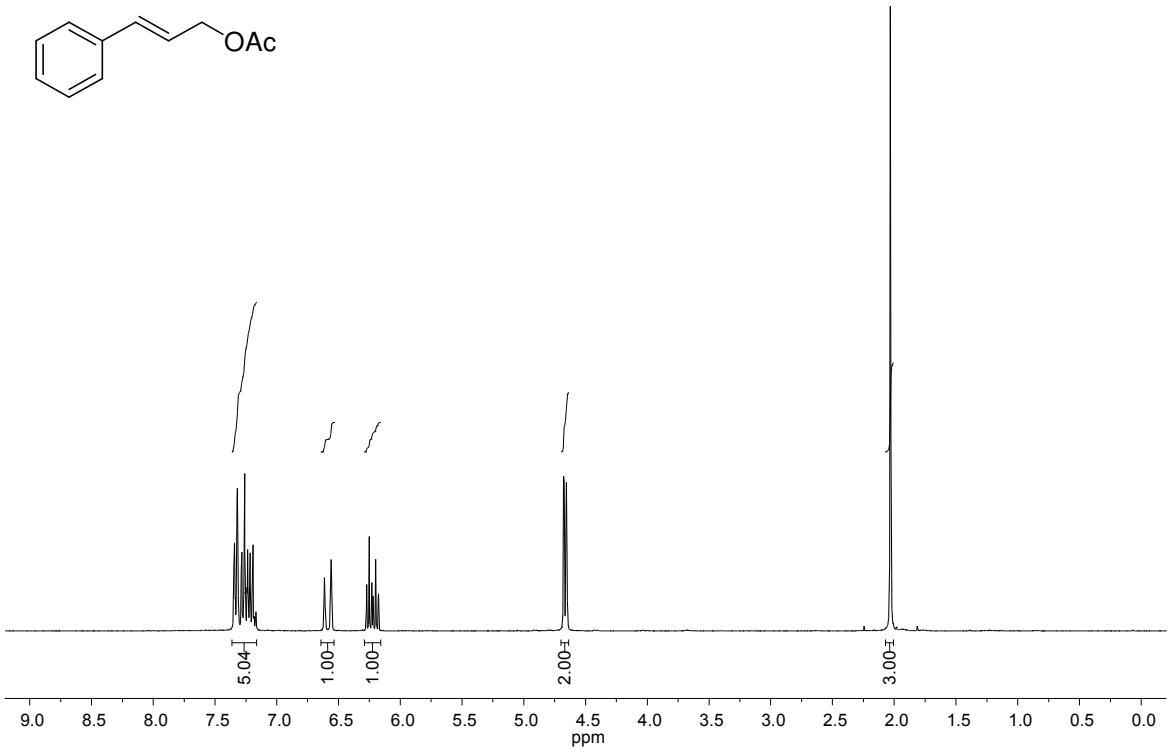


^{13}C NMR:

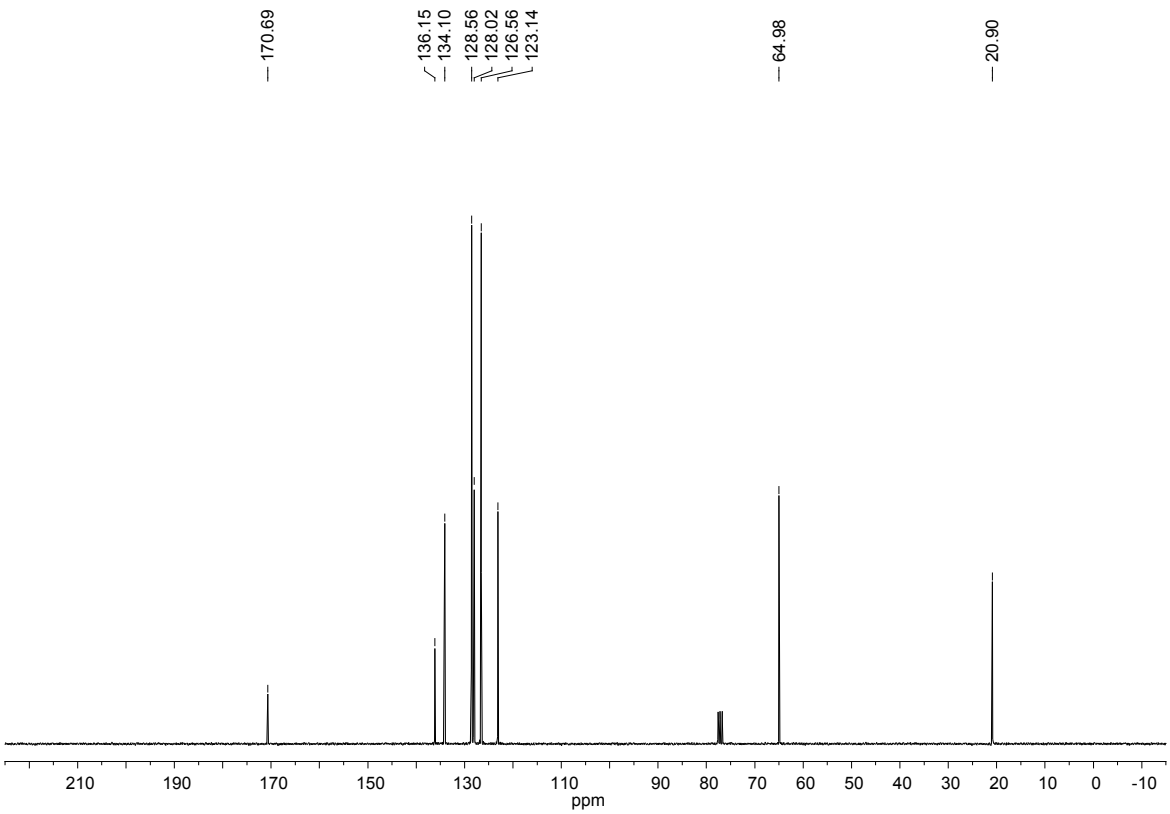


(*E*)-Cinnamic acetate (**1a**)

^{1}H NMR:

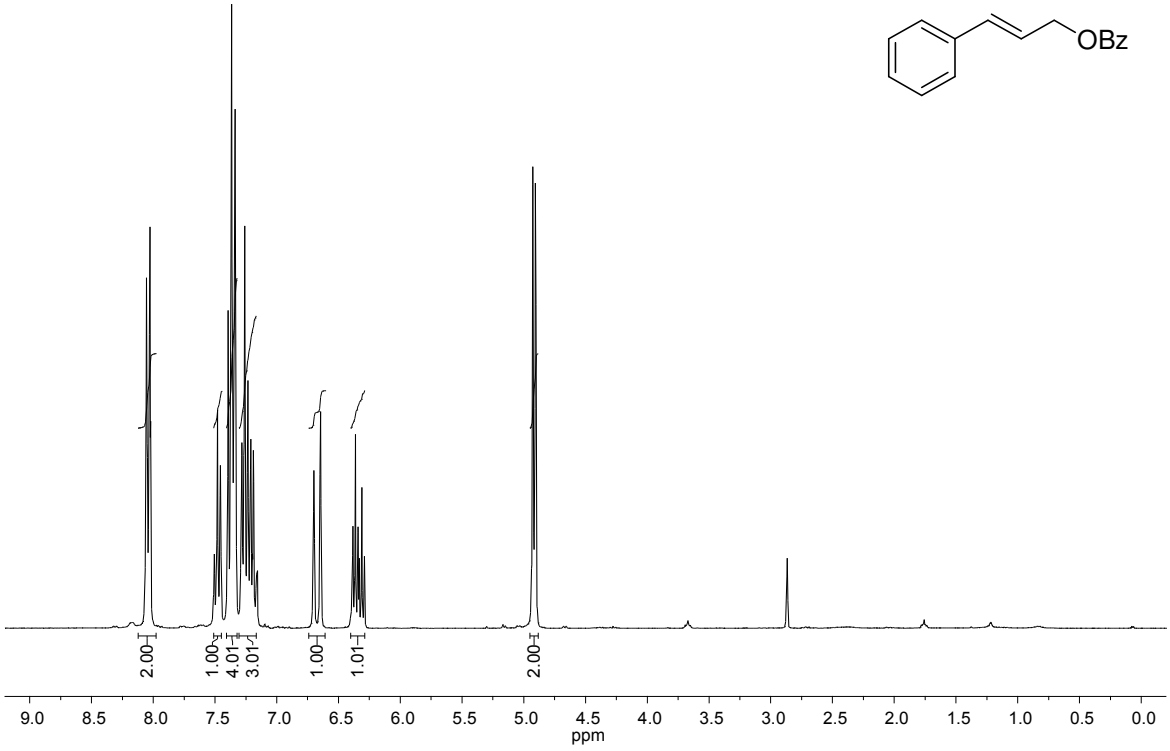


^{13}C NMR:

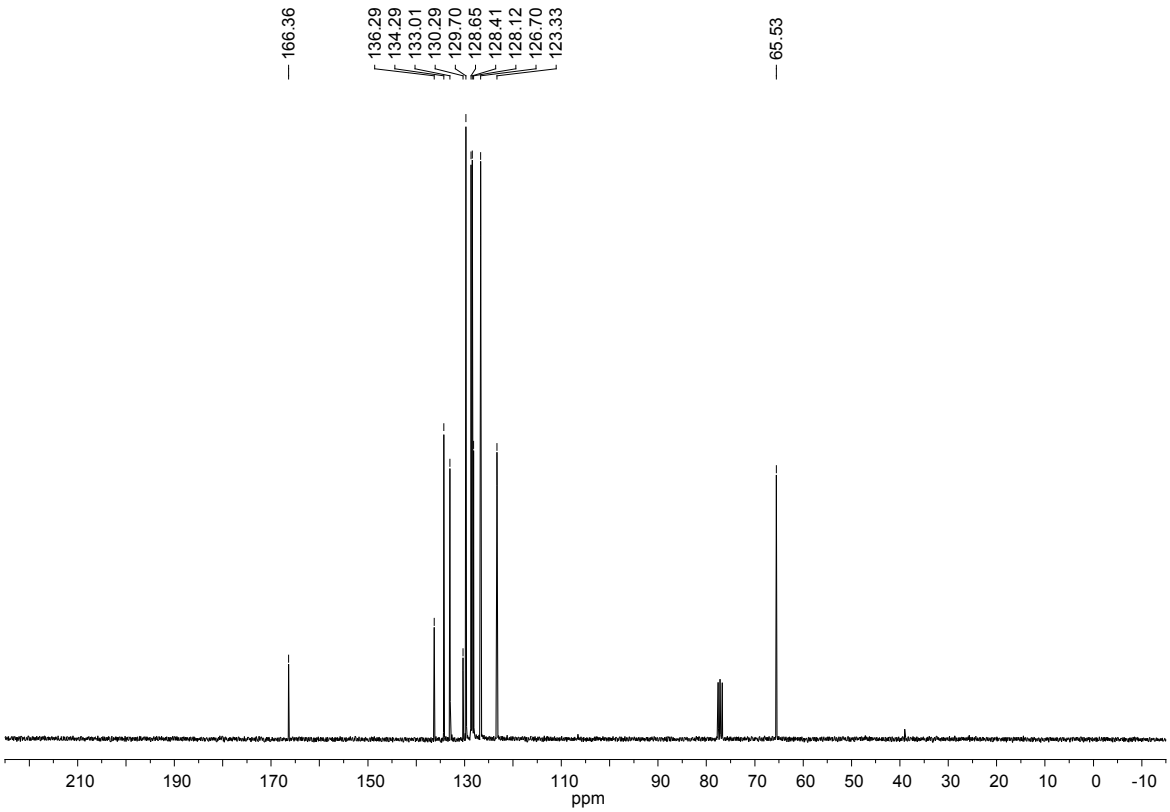


(*E*)-Cinnamic benzoate (**1b**)

^{1}H NMR:

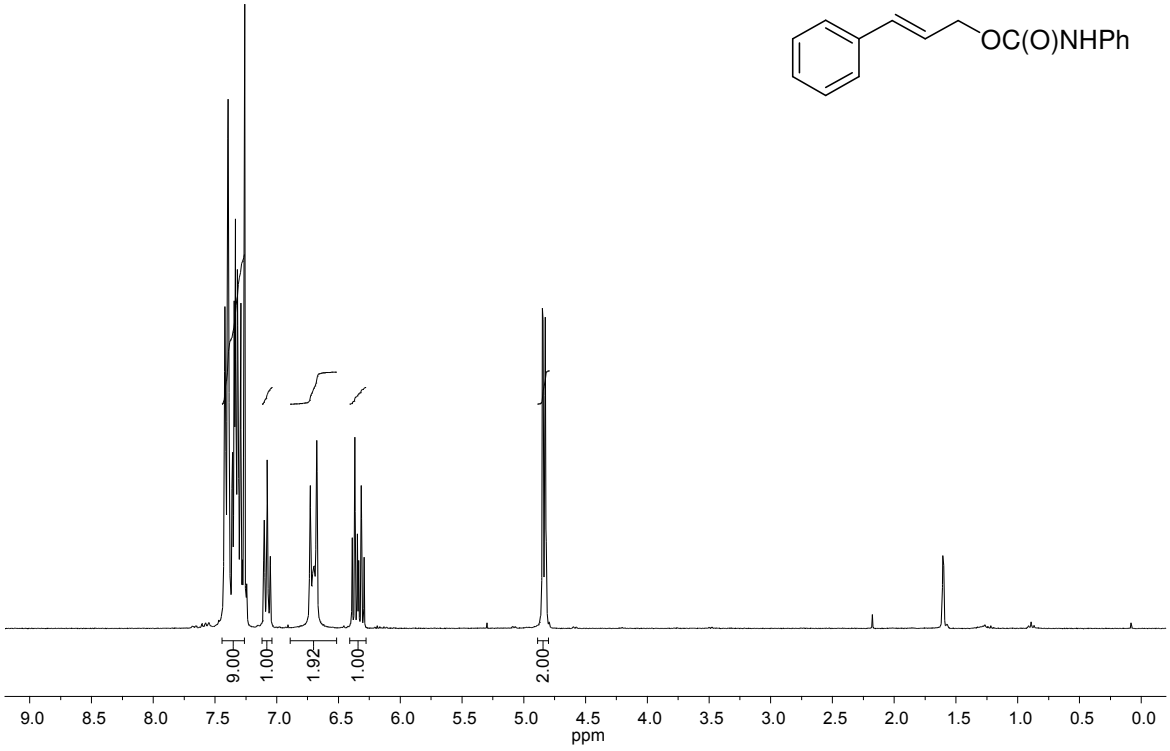


^{13}C NMR:

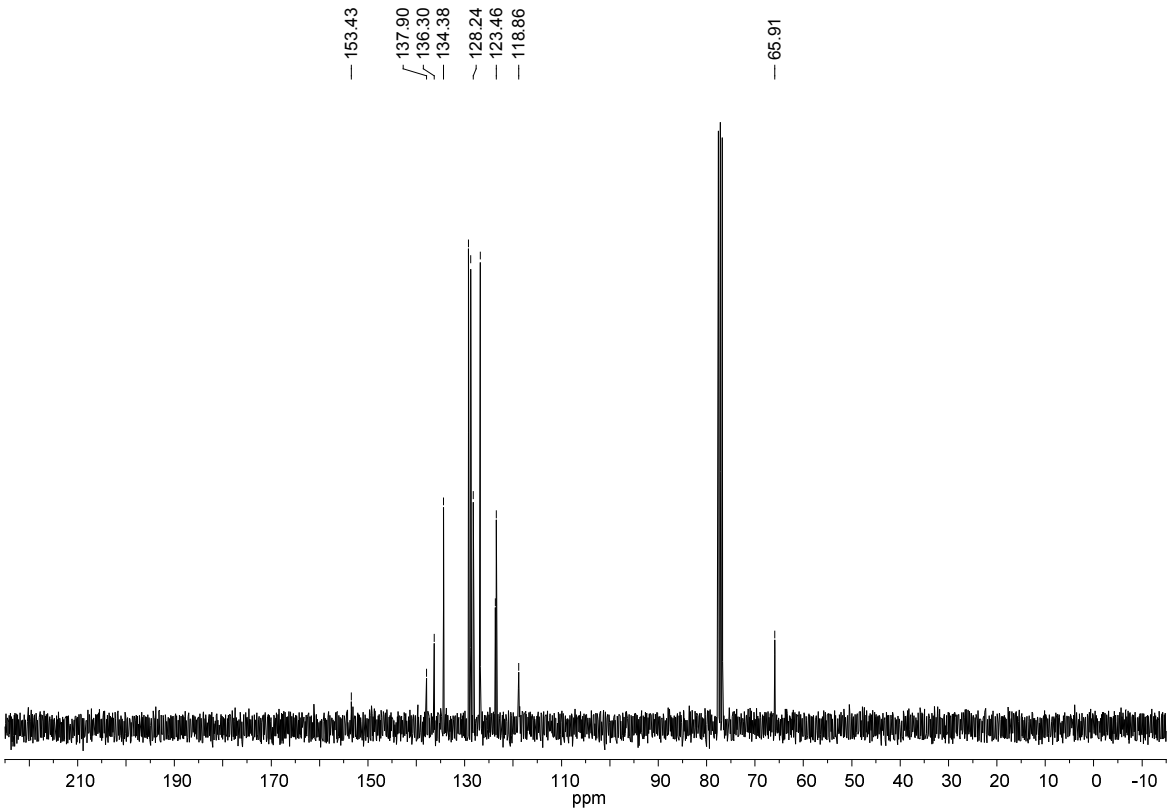


(*E*)-Cinnamic *N*-phenyl carbamate (**1c**)

^{1}H NMR:

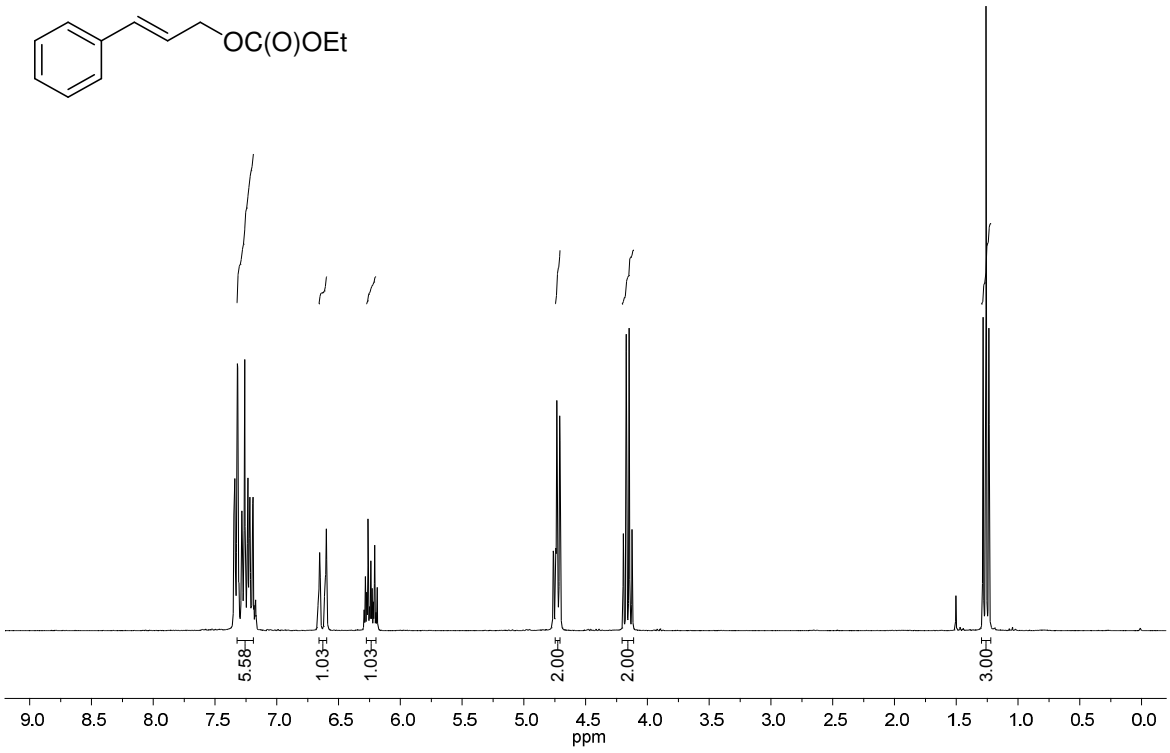


^{13}C NMR:

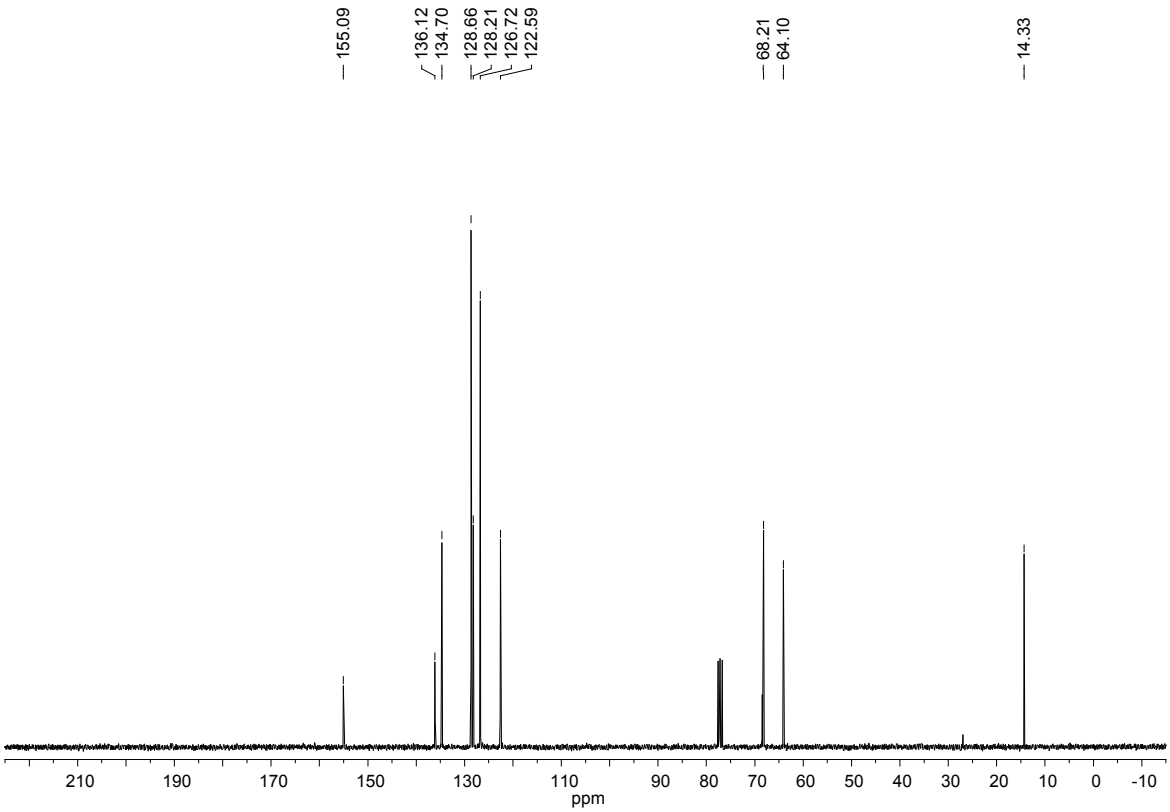


(*E*)-Cinnamic ethyl carbonate (**1d**)

^{1}H NMR:

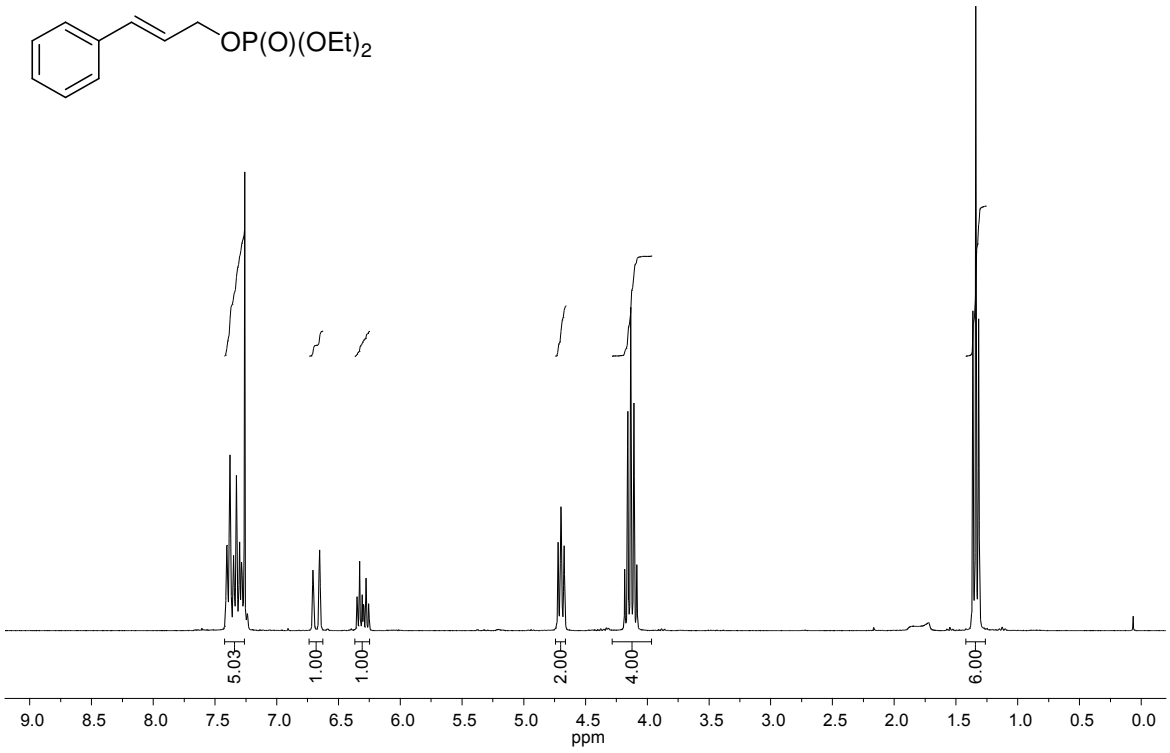


^{13}C NMR:

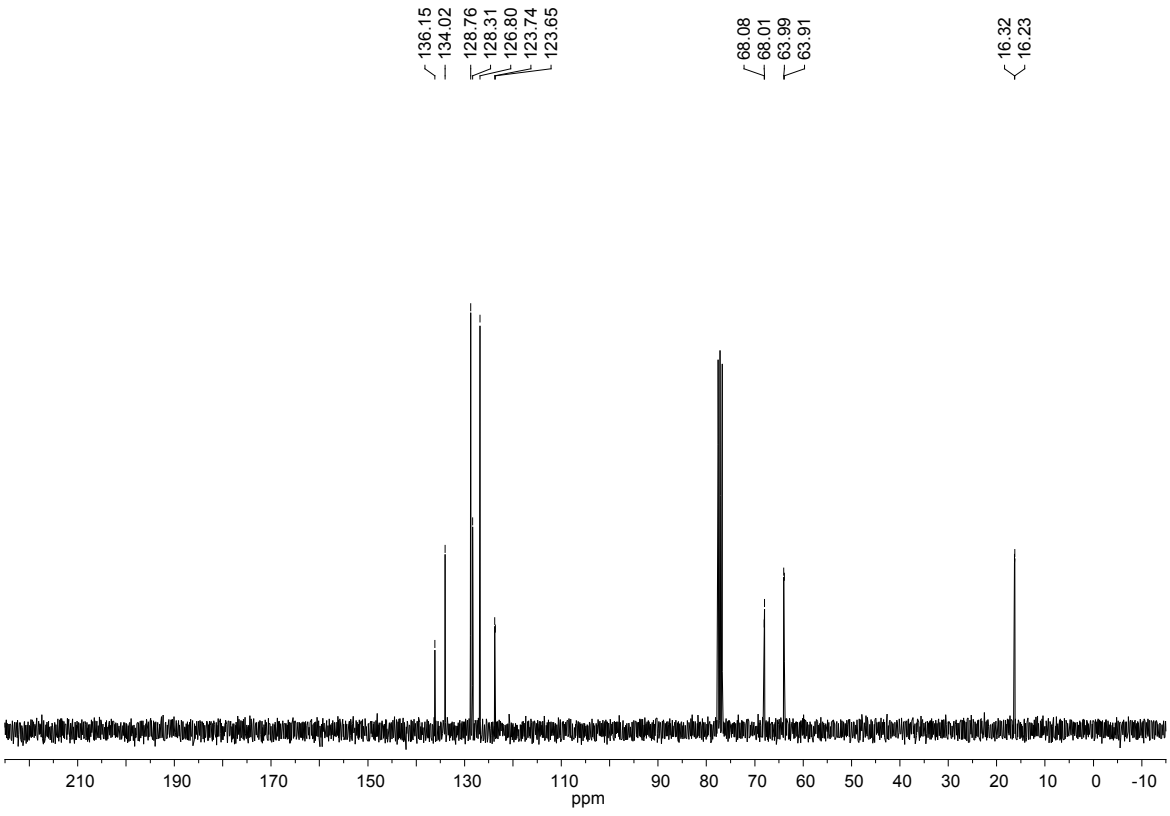


(*E*)-Cinnamic diethyl phosphate (**1e**)

^{1}H NMR:

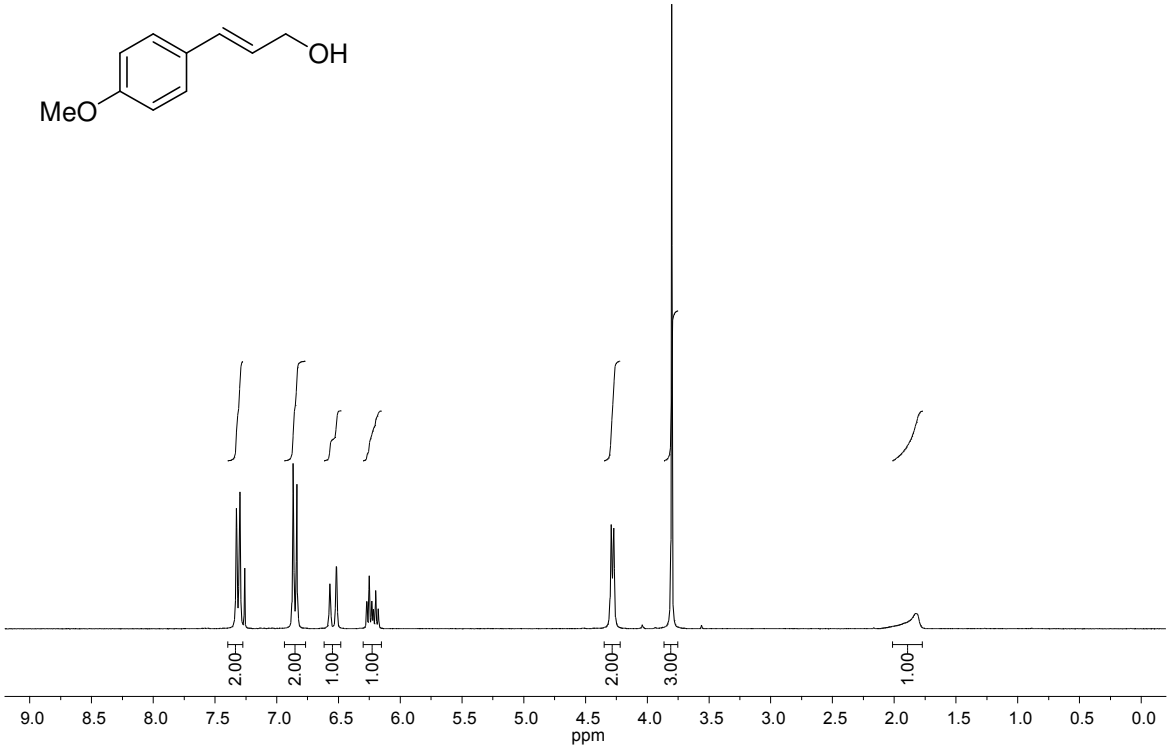


^{13}C NMR:

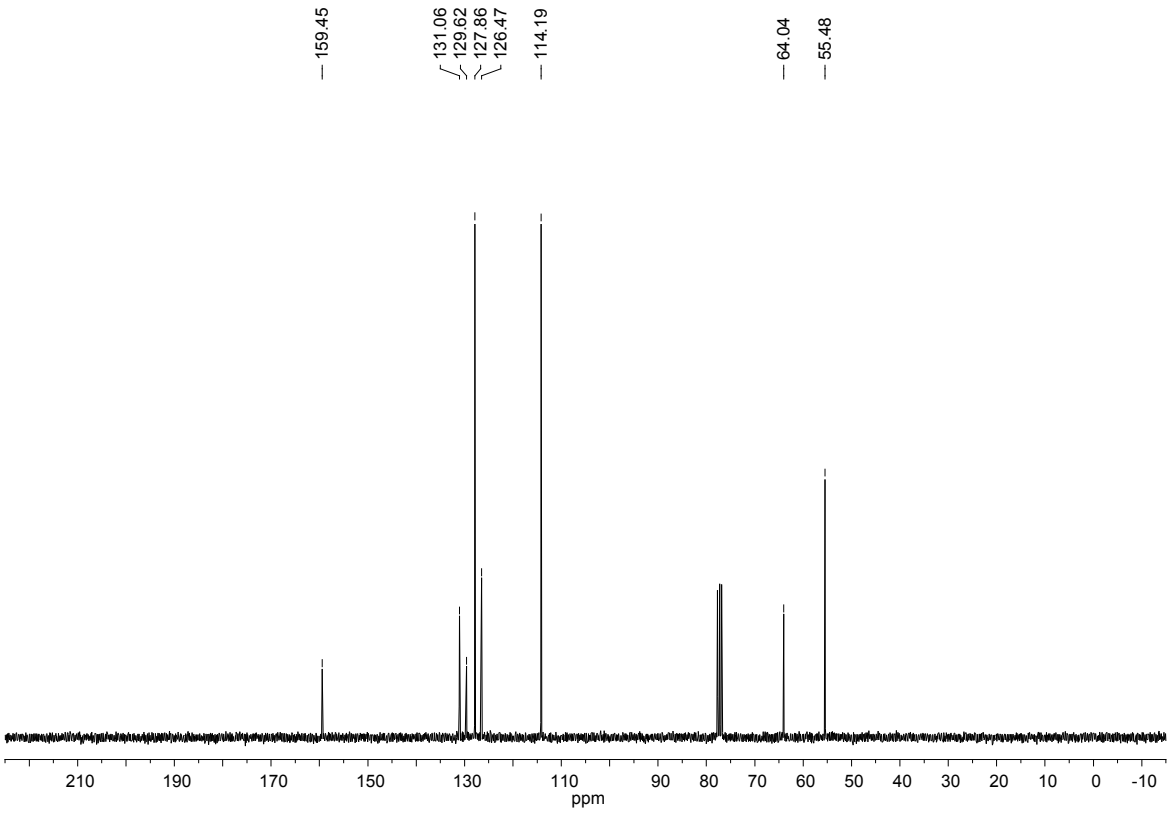


(*E*)-*p*-Methoxy cinnamic alcohol

^{1}H NMR:

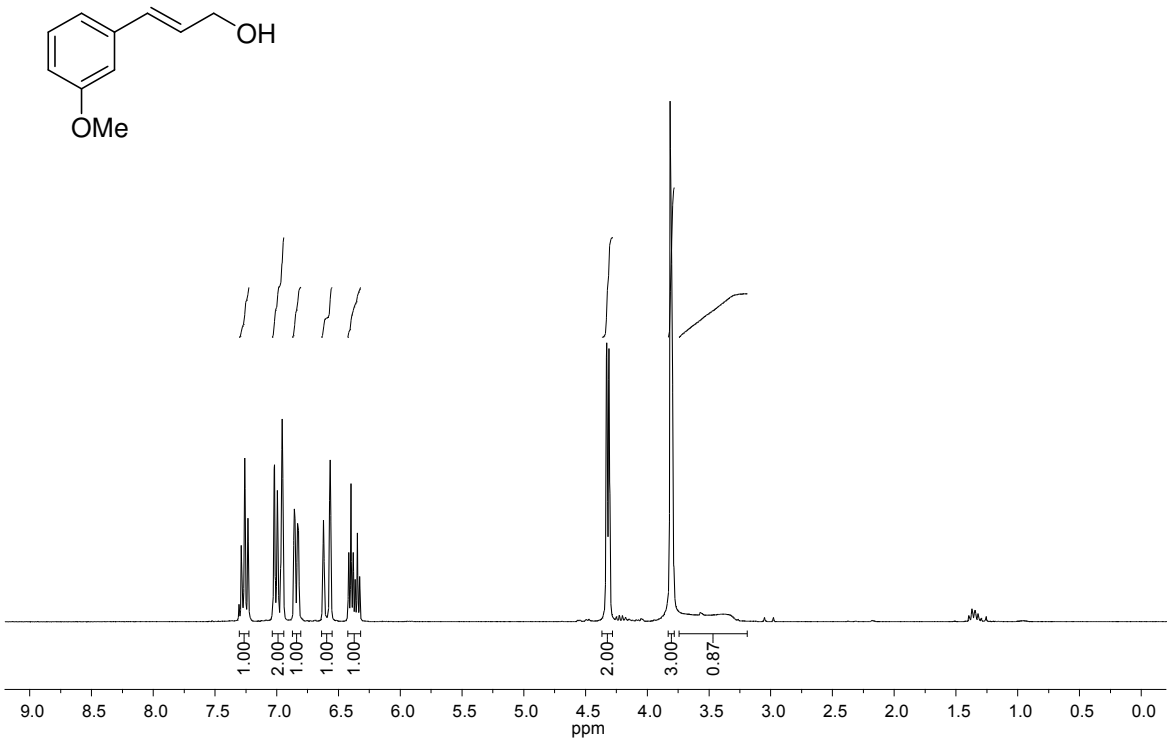


^{13}C NMR:

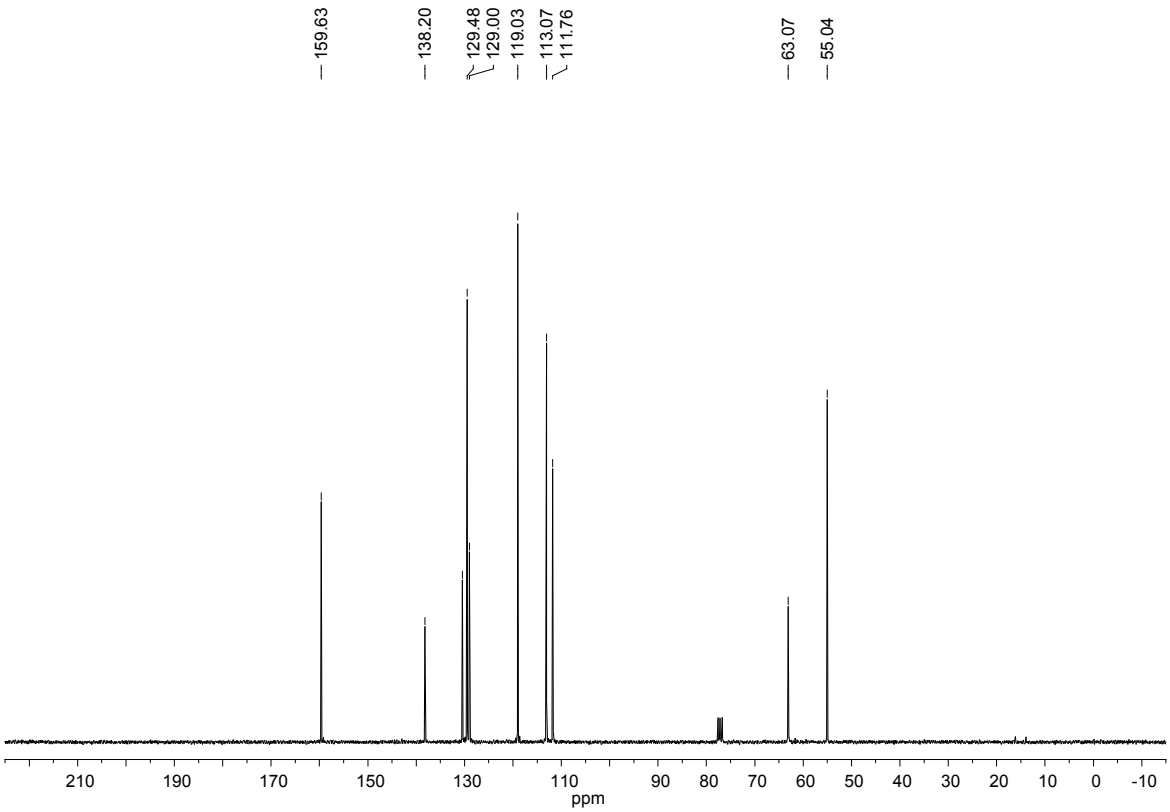


(*E*)-*m*-Methoxy cinnamic alcohol

^{1}H NMR:

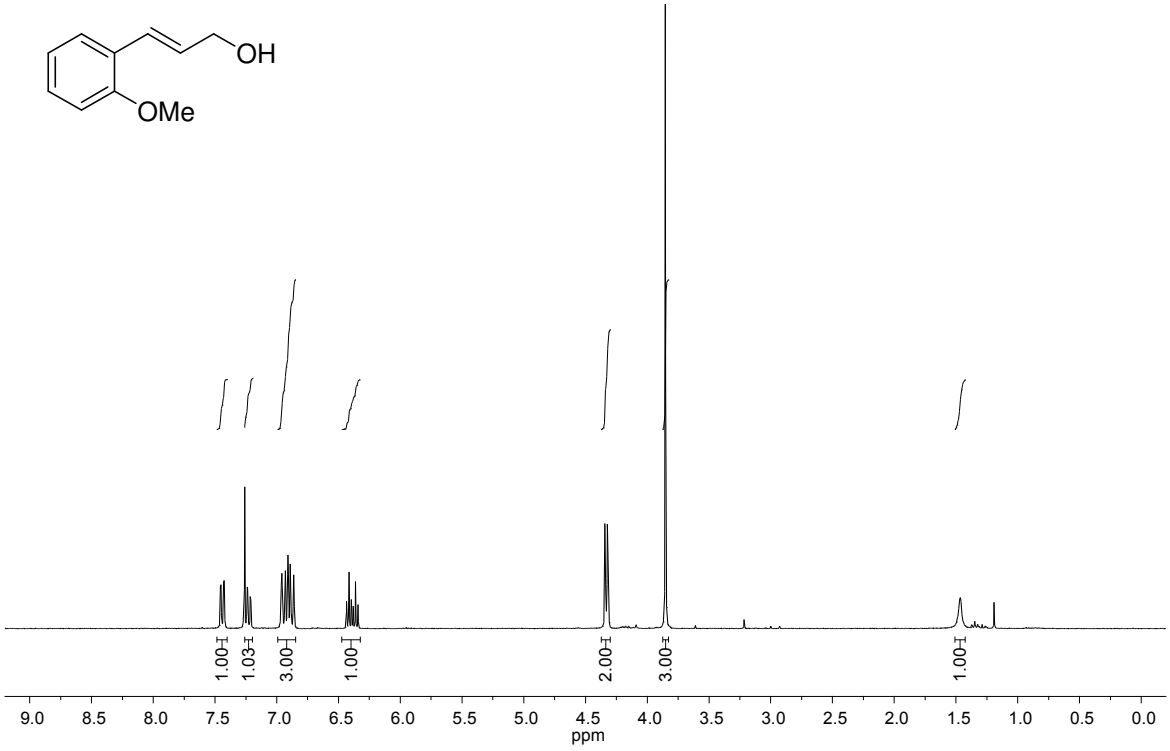


^{13}C NMR:

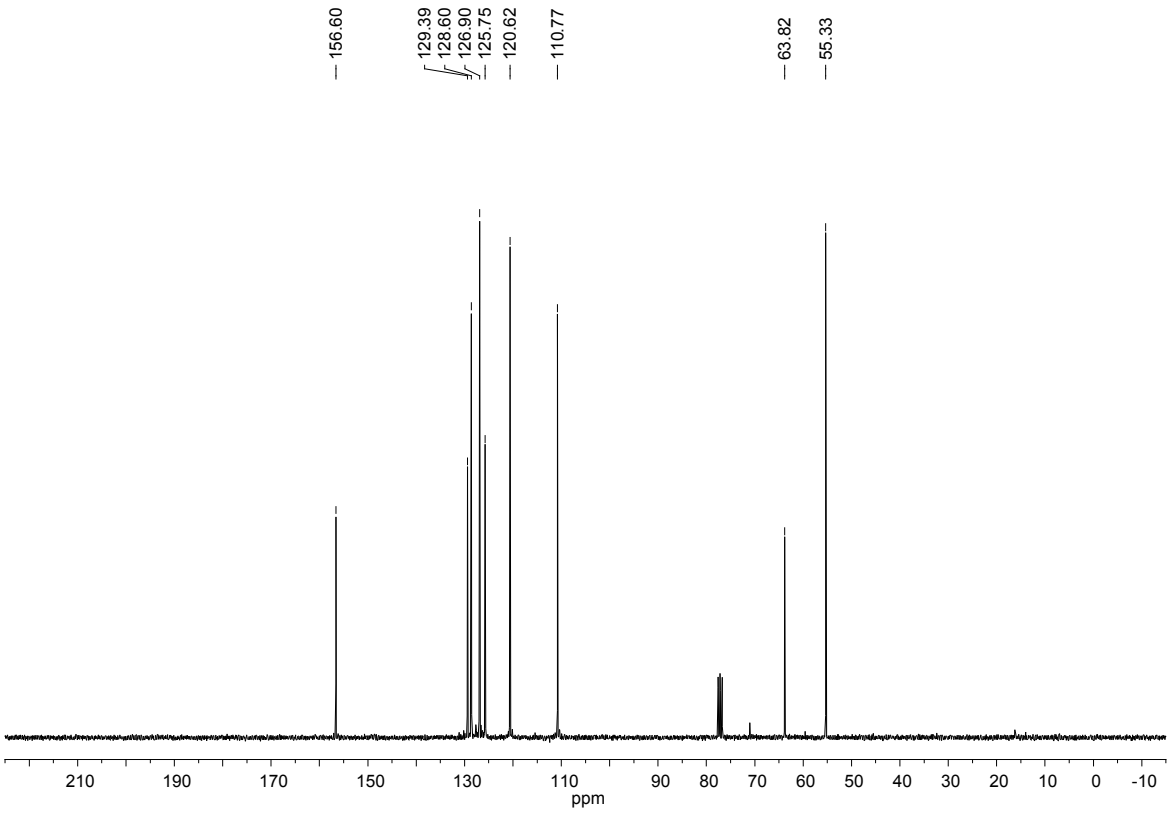


(*E*)-*o*-Methoxy cinnamic alcohol

^{1}H NMR:

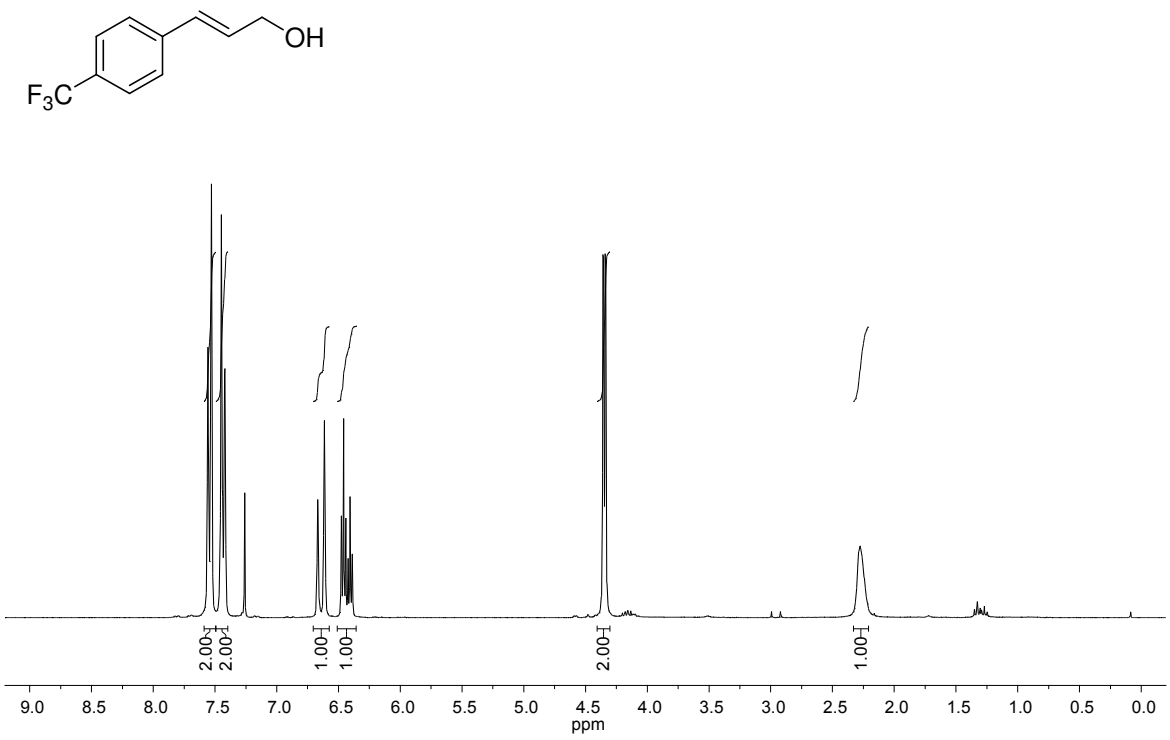


^{13}C NMR:

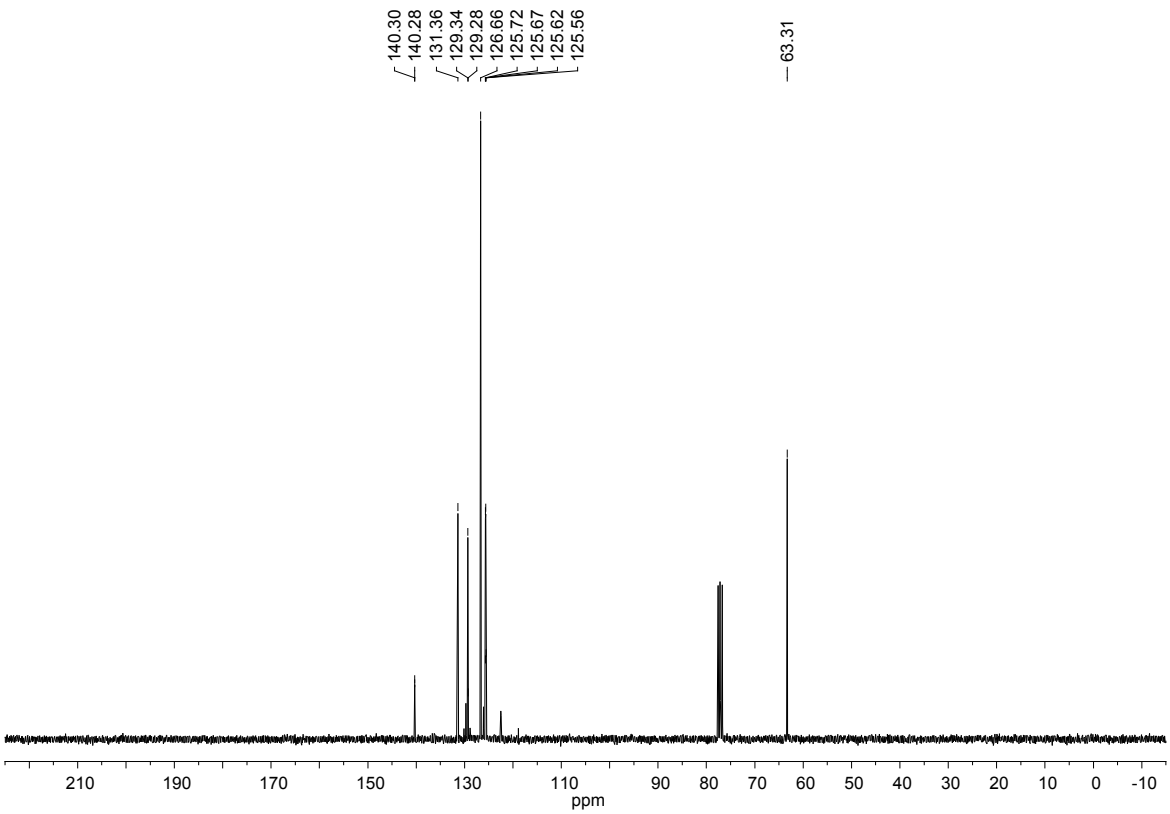


(*E*)-*p*-Trifluoromethyl cinnamic alcohol

^{1}H NMR:

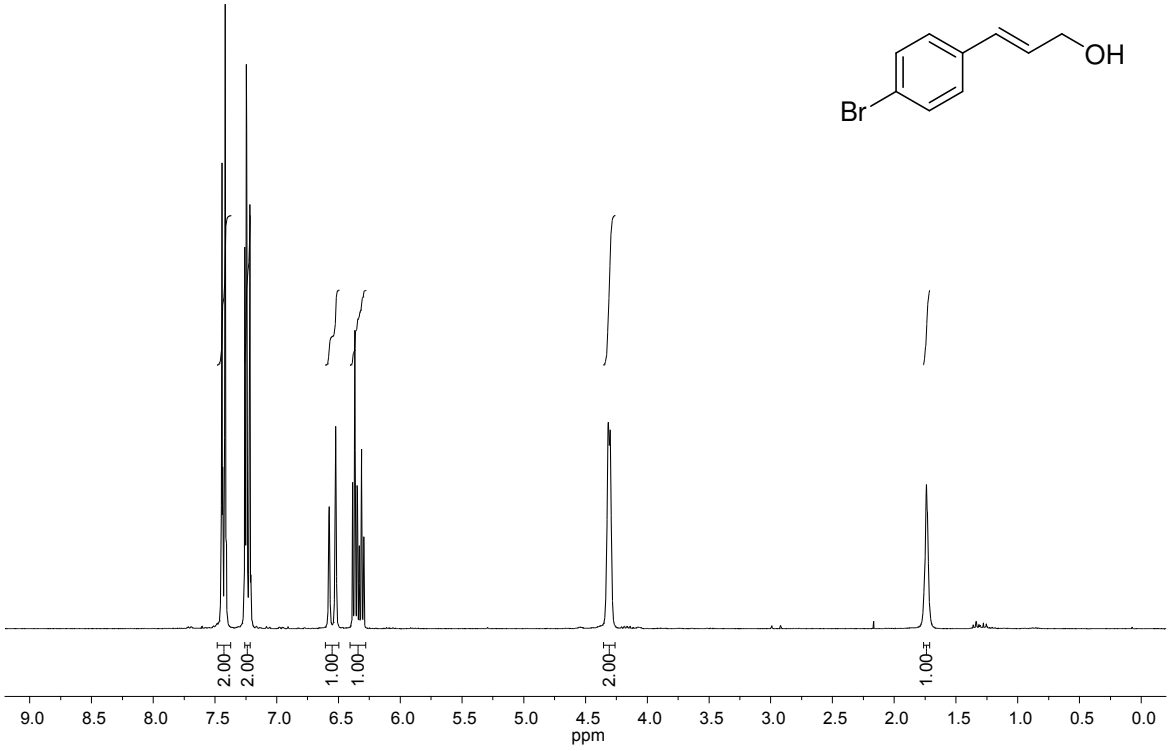


^{13}C NMR:

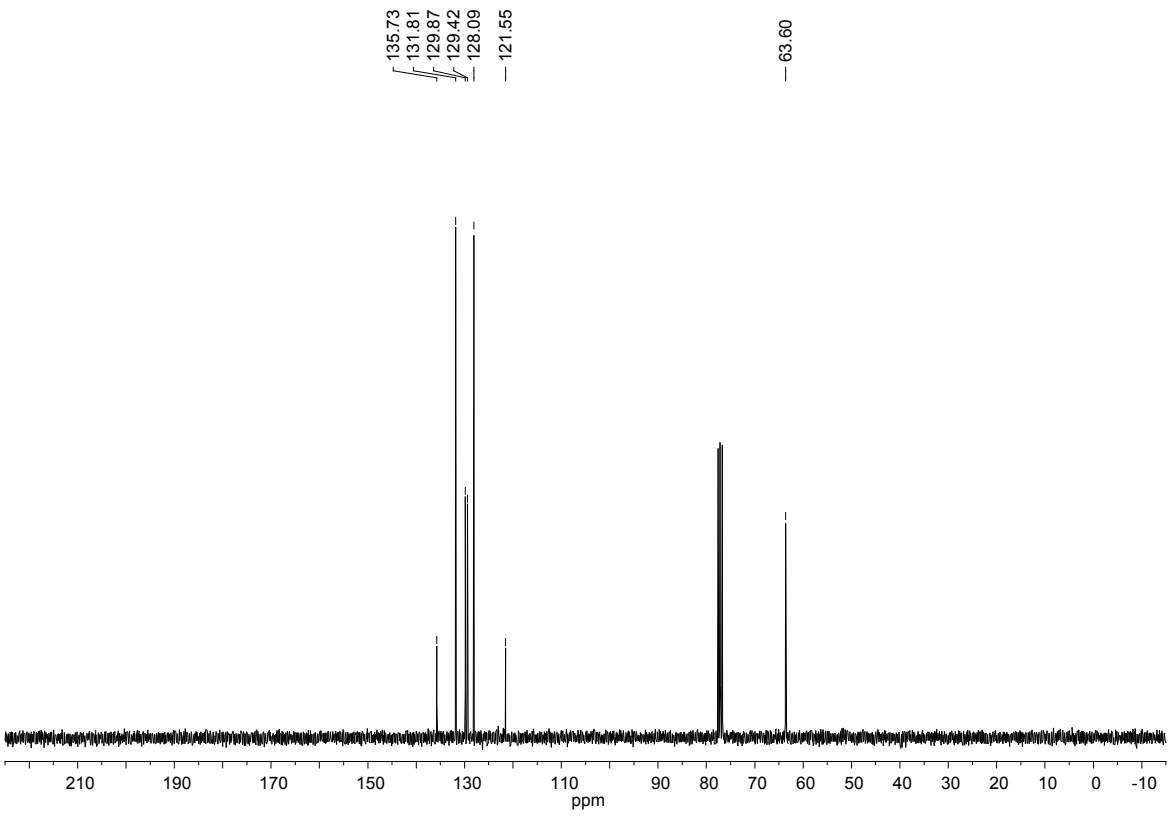


(*E*)-*p*-Bromo cinnamic alcohol

^{1}H NMR:

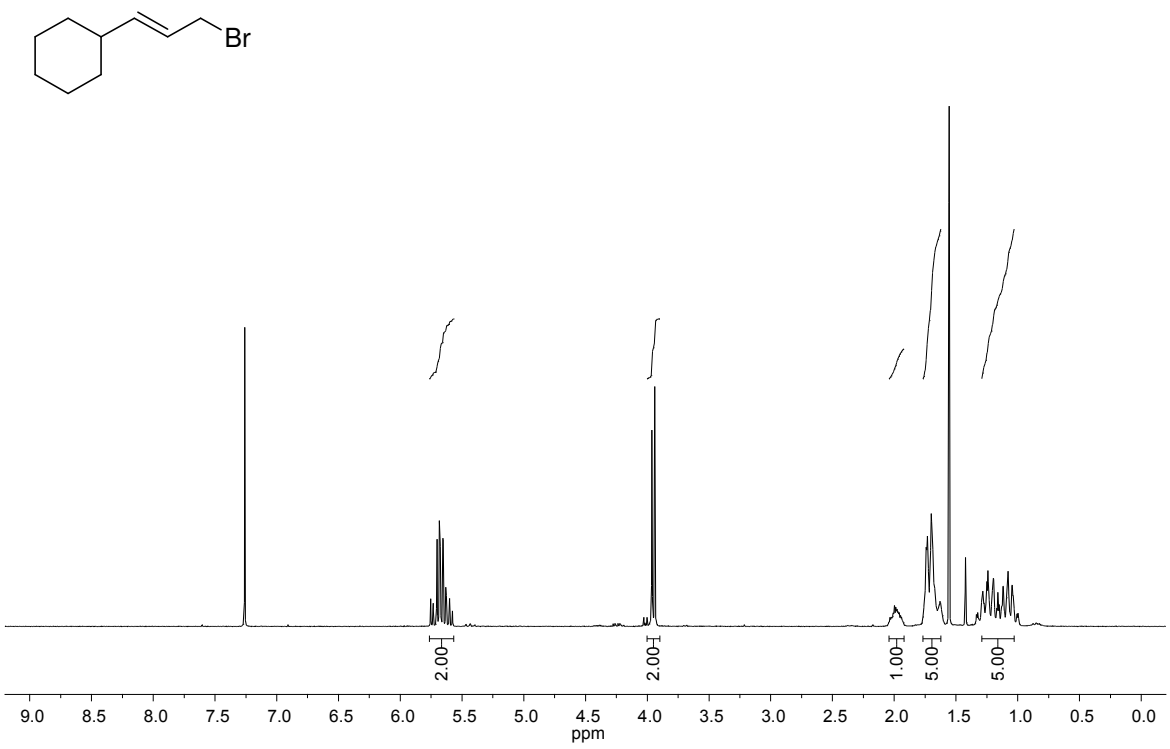


^{13}C NMR:

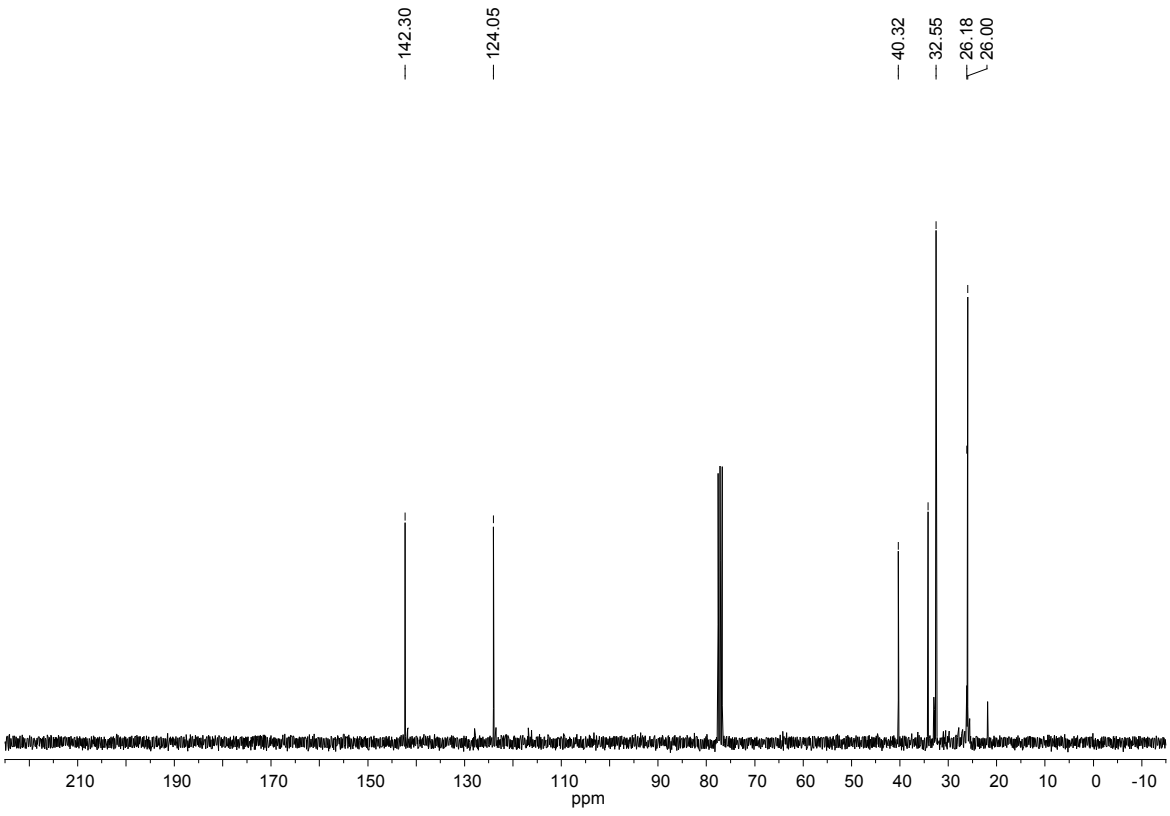


(*E*)-3-Bromo-1-cyclohexylprop-1-ene (**8f**)

^{1}H NMR:

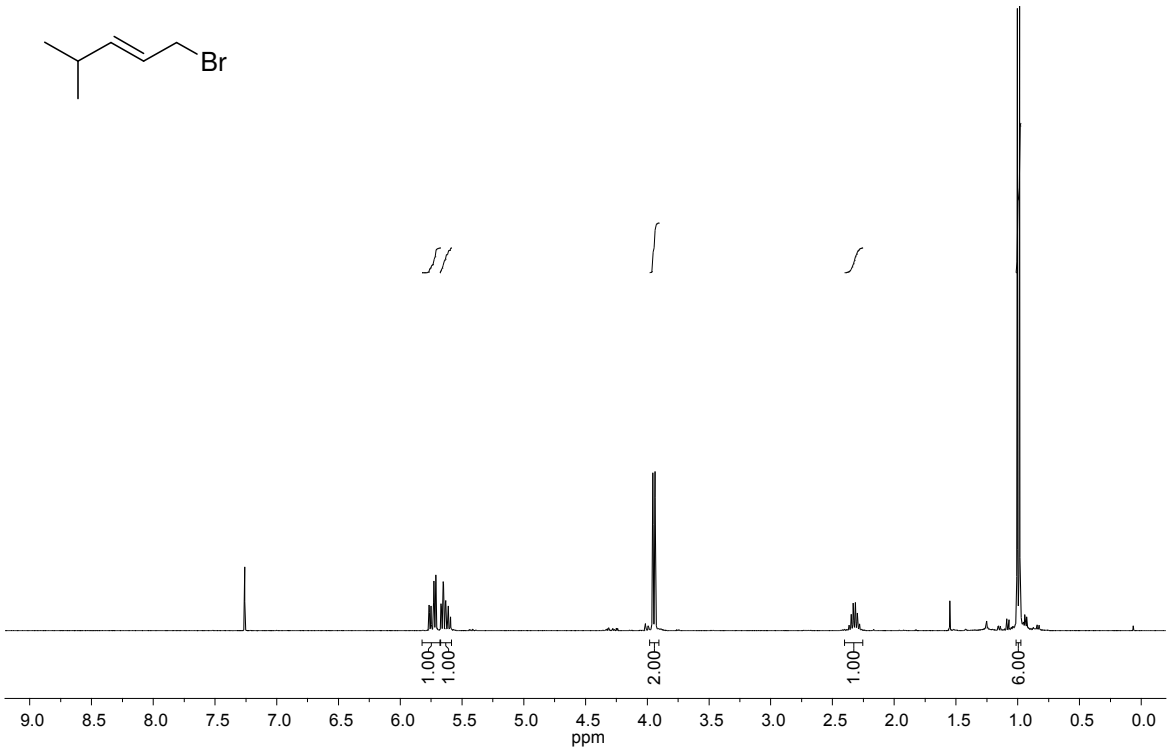


^{13}C NMR:

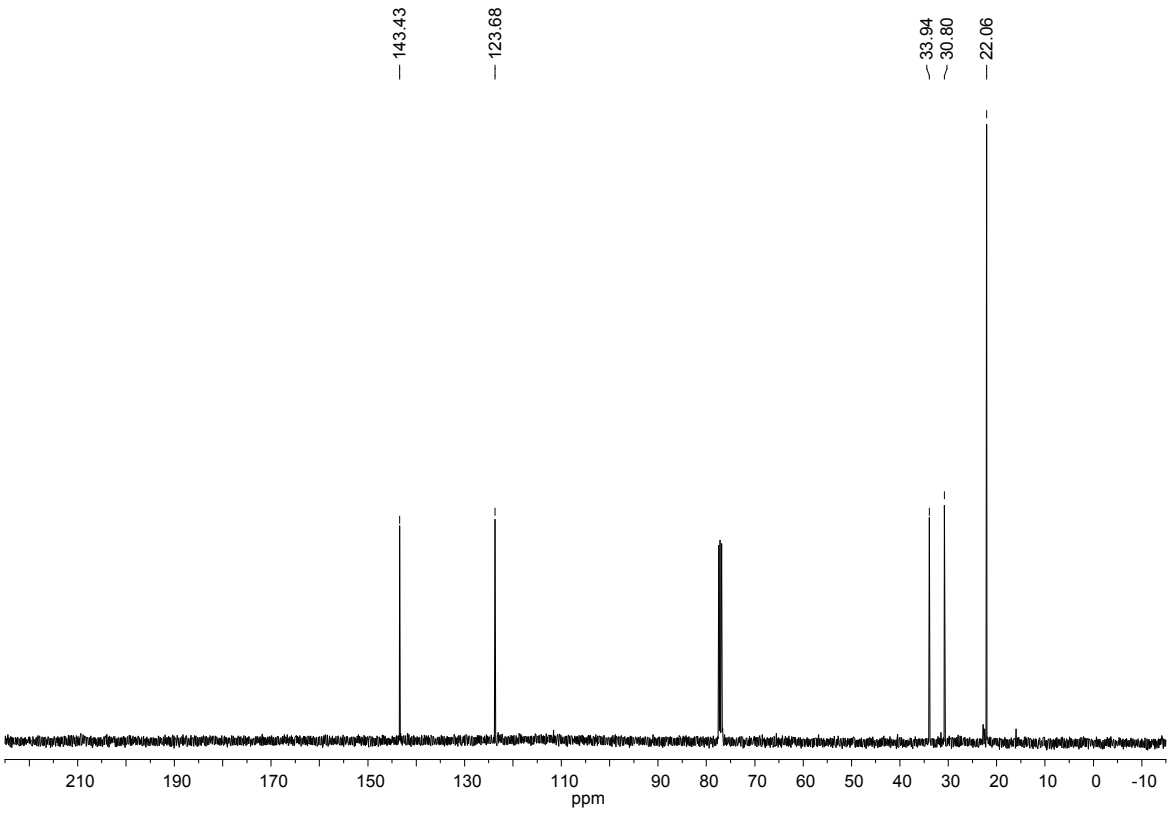


(*E*)-1-Bromo-4-methylpent-2-ene (**9f**)

^{1}H NMR:

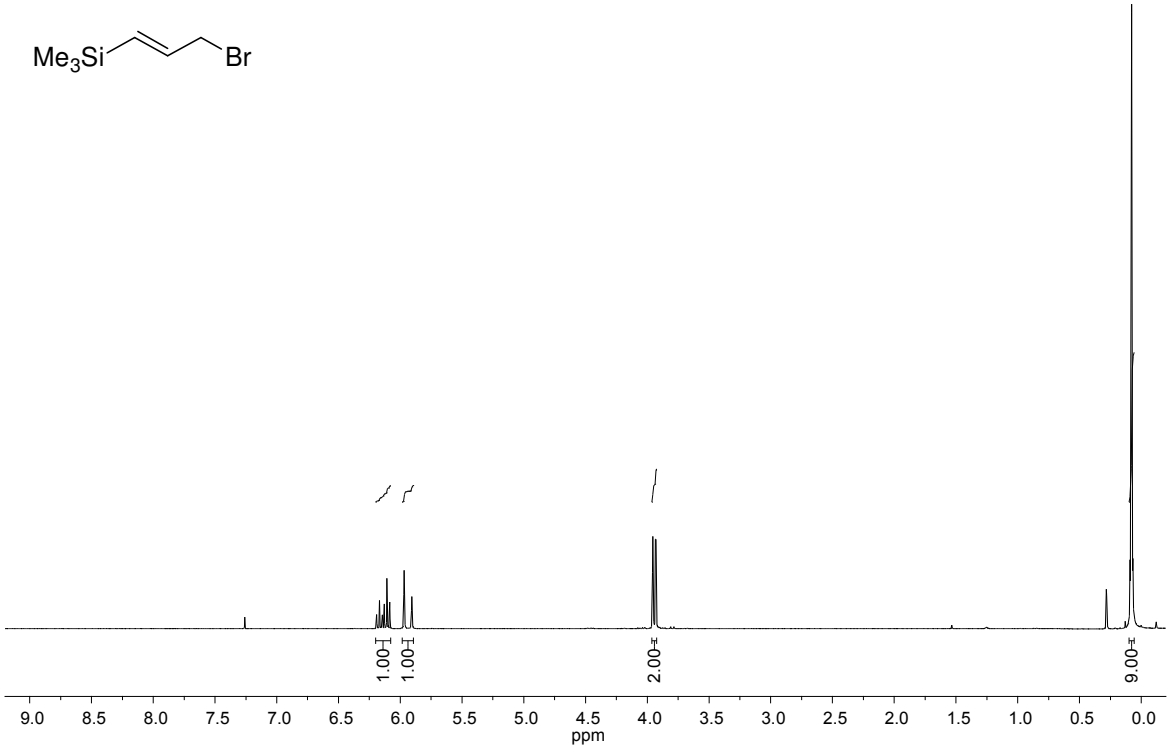


^{13}C NMR:

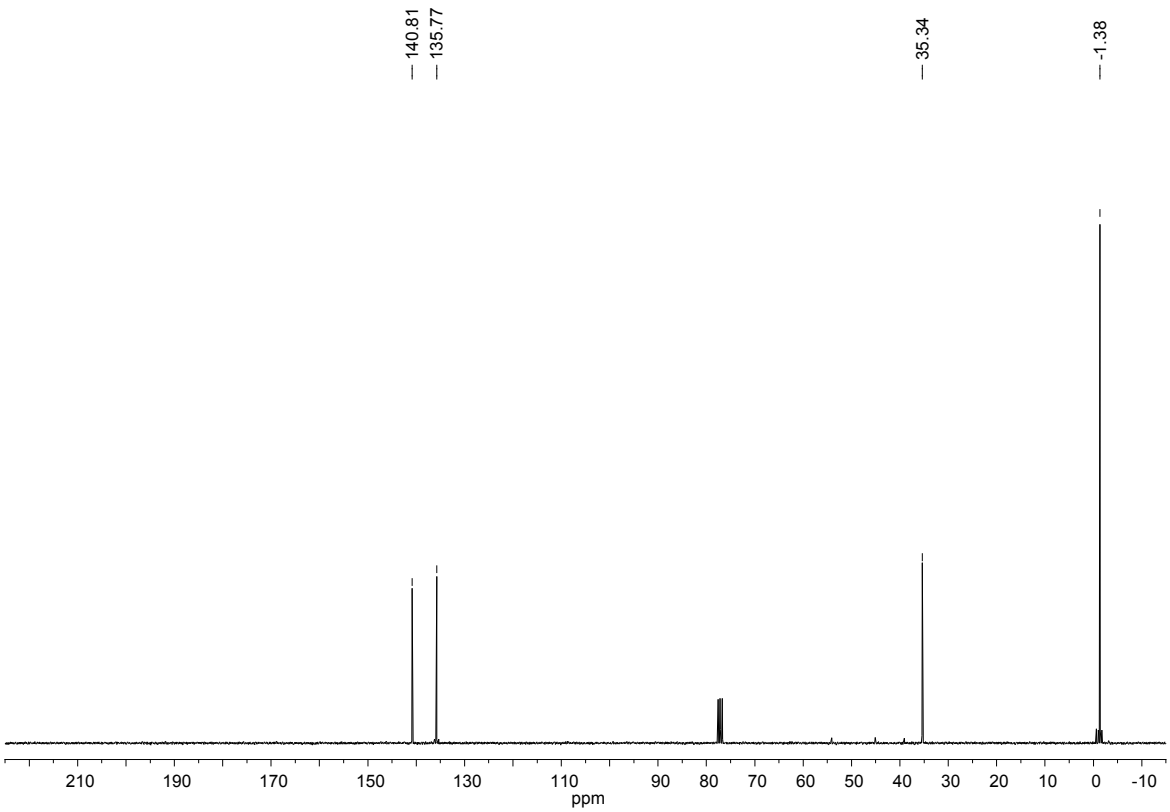


(*E*)-3-Bromo-1-trimethylsilylprop-1-ene (**10f**)

^{1}H NMR:

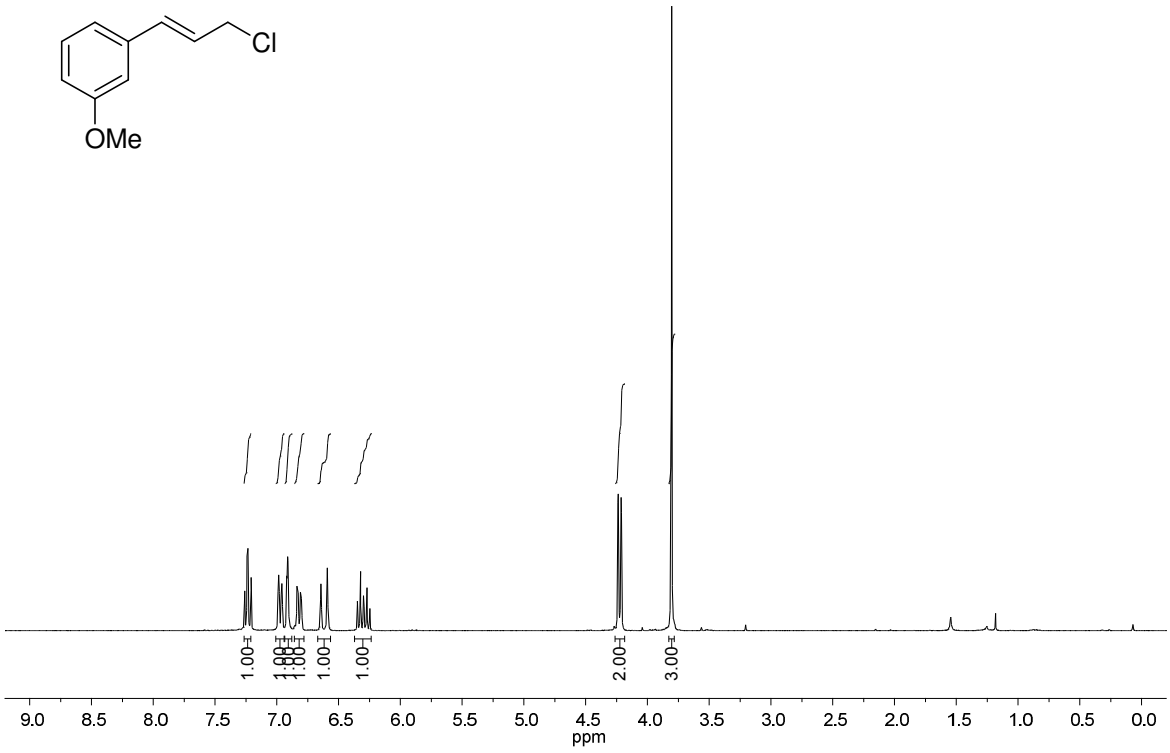


^{13}C NMR:

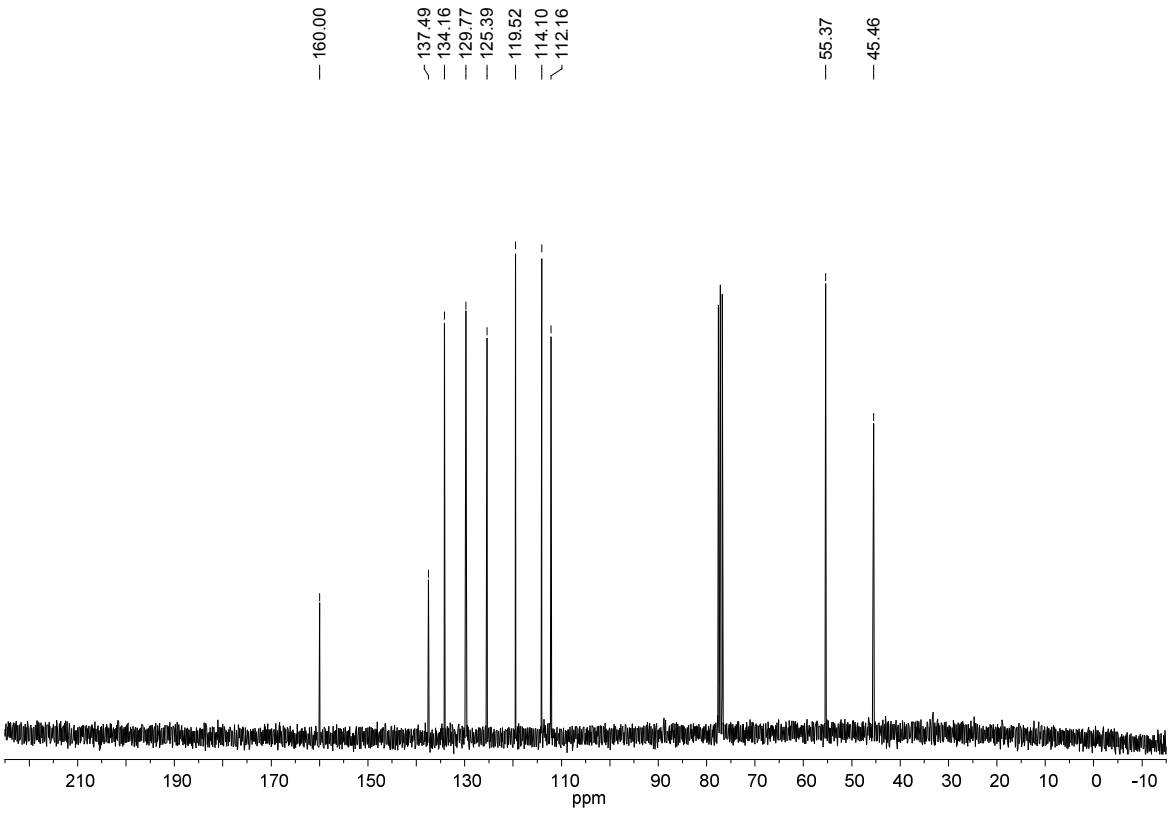


(*E*)-*m*-Methoxy cinnamic chloride (**4g**)

^{1}H NMR:

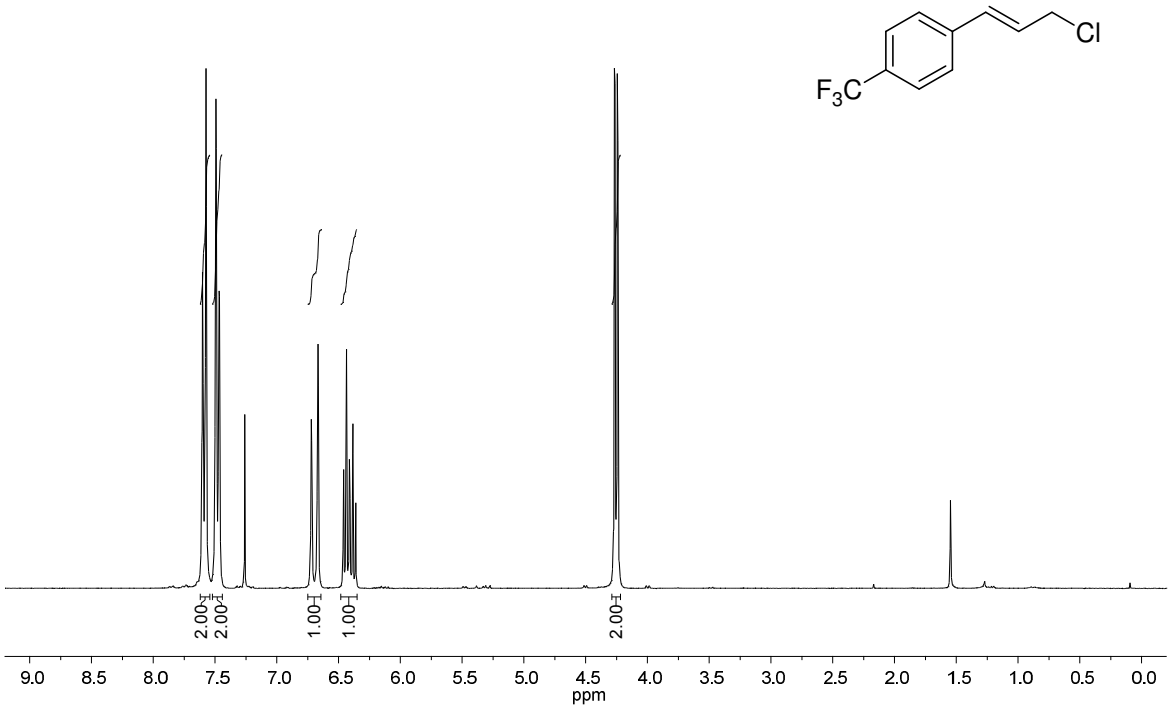


^{13}C NMR:

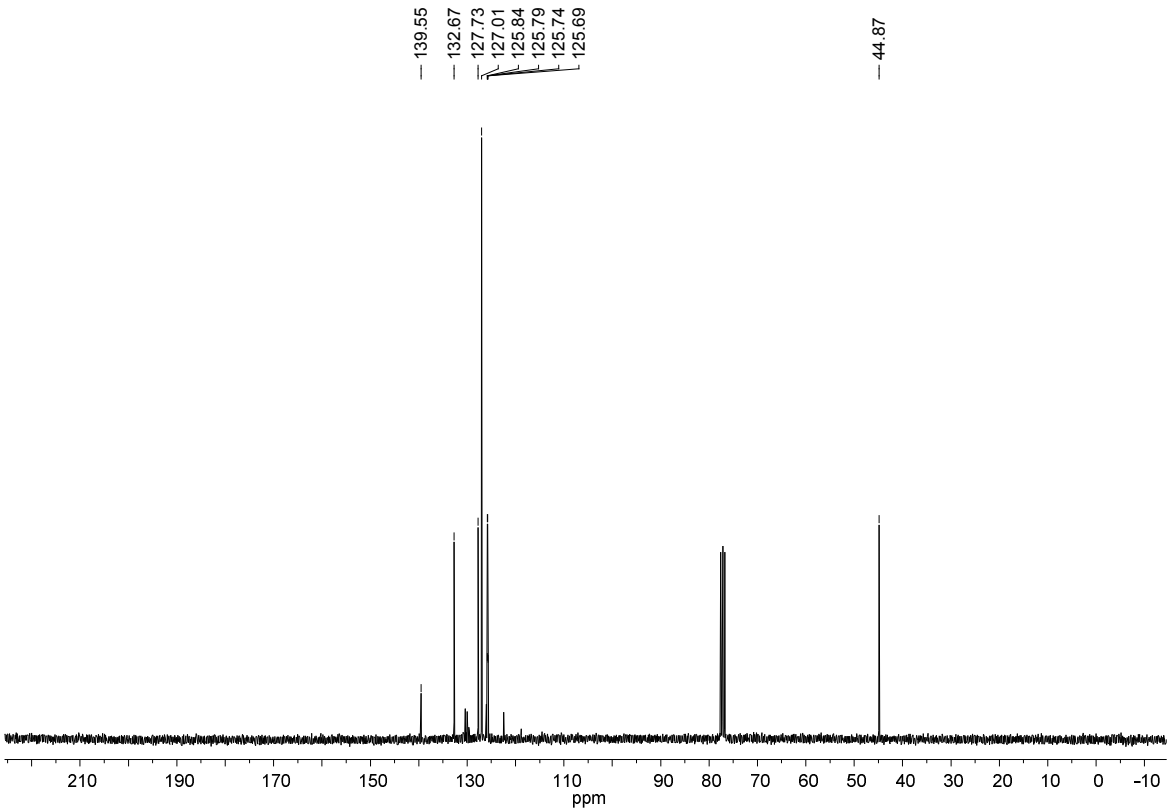


(*E*)-*p*-Trifluoromethyl cinnamic chloride (**6g**)

^{1}H NMR:

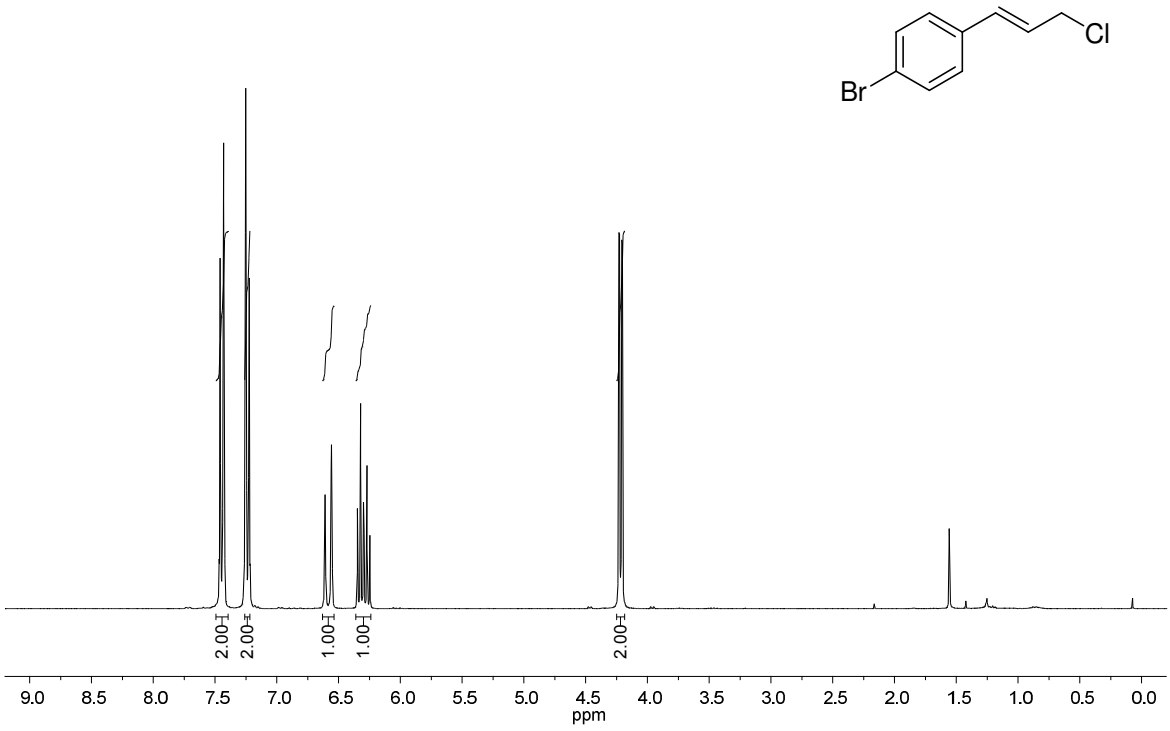


^{13}C NMR:

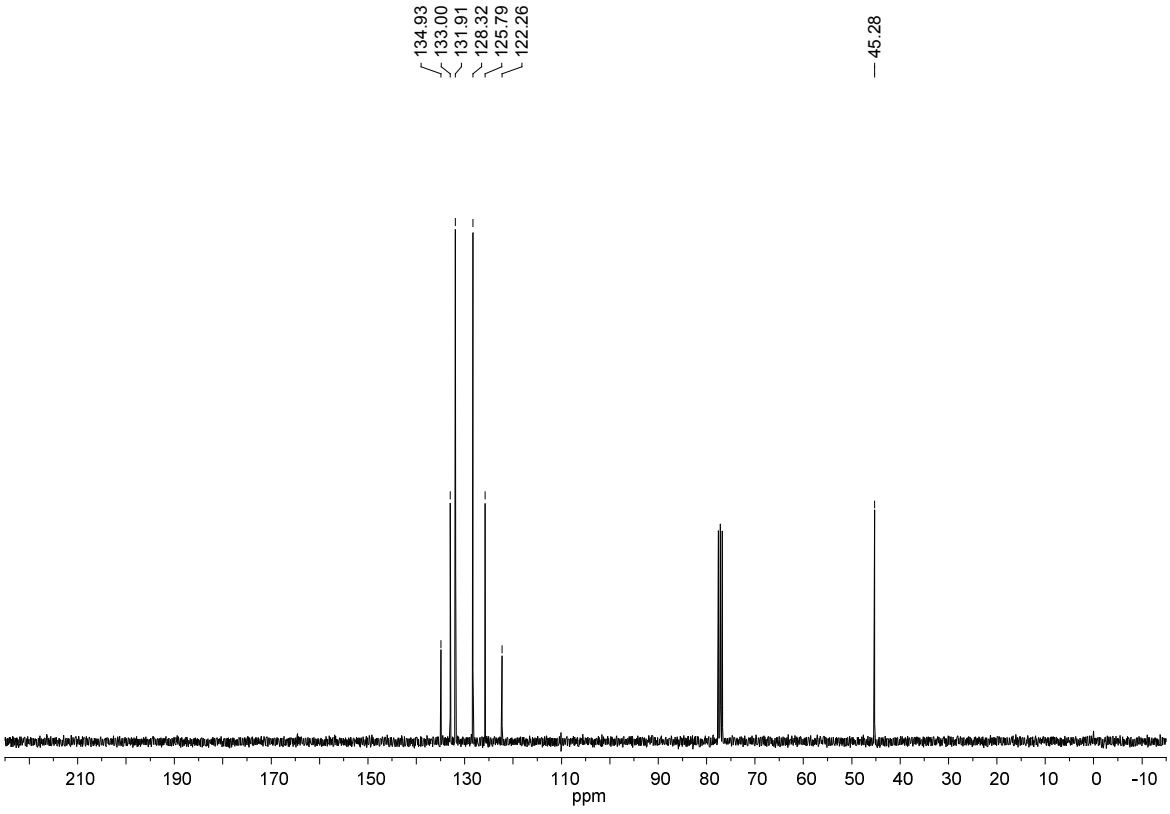


(*E*)-*p*-Bromo cinnamic chloride (**7g**)

^{1}H NMR:

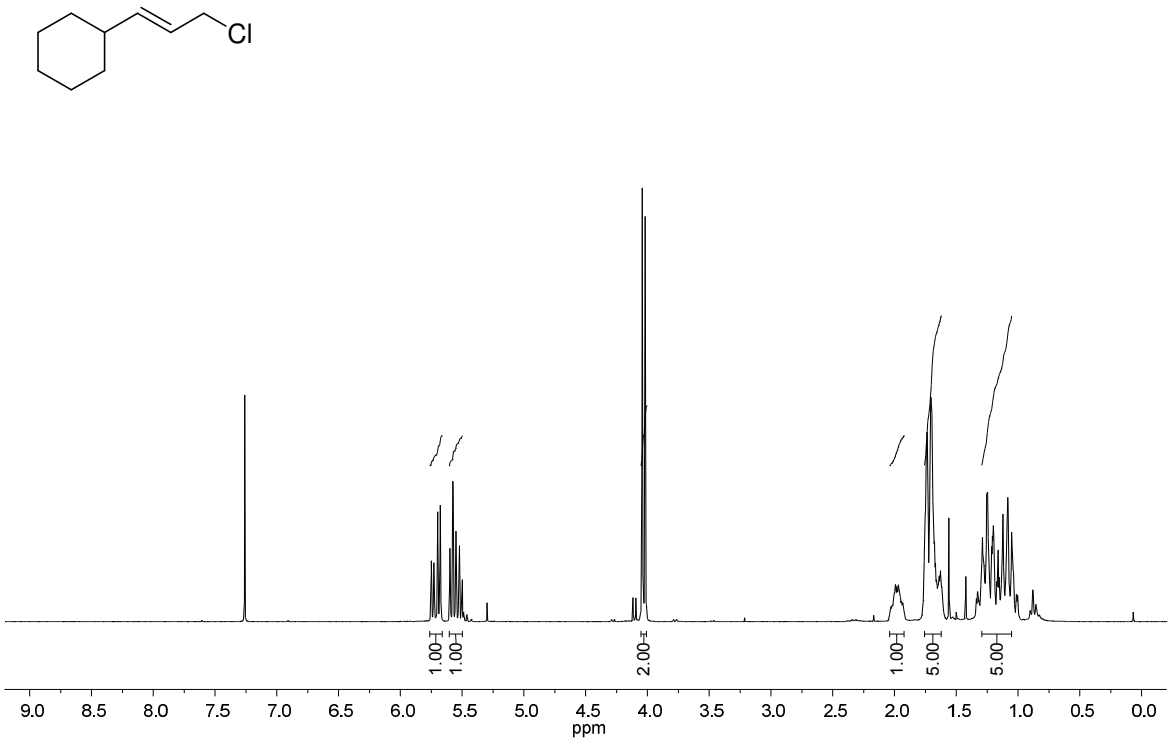


^{13}C NMR:

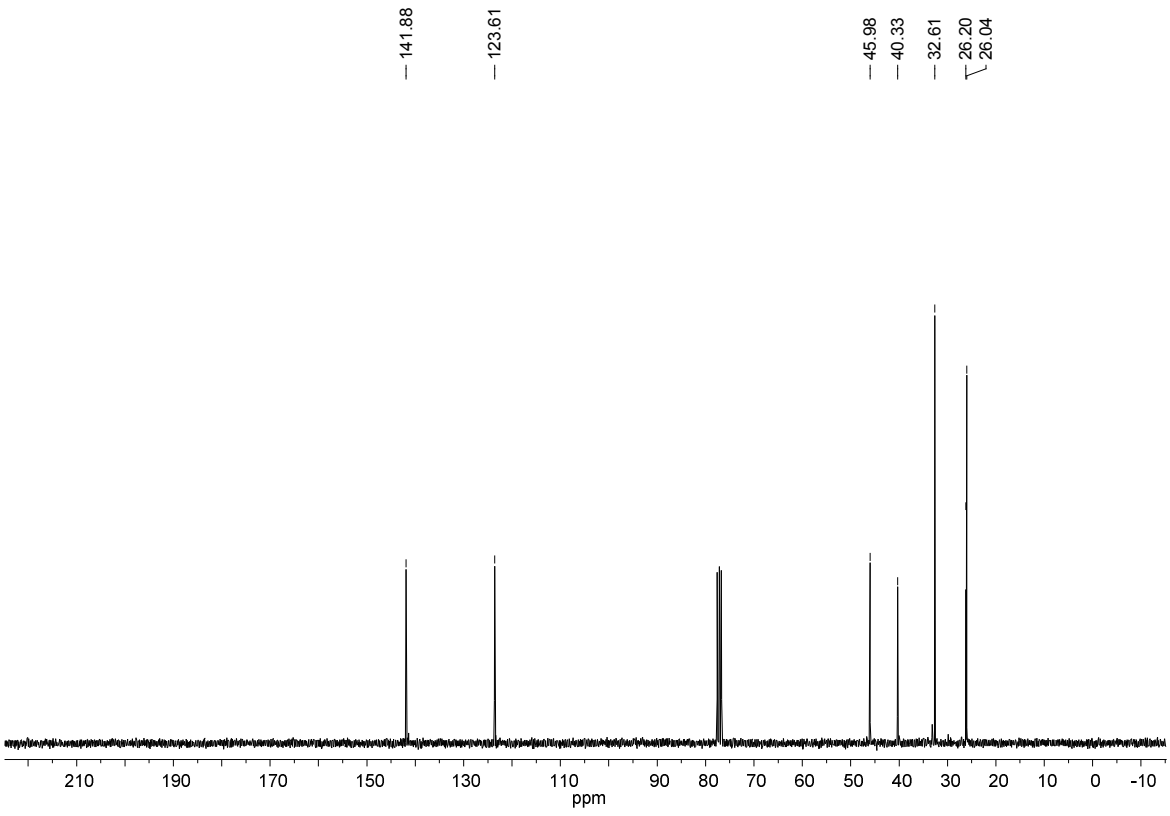


(*E*)-3-Chloro-1-cyclohexylprop-1-ene (**8g**)

^{1}H NMR:

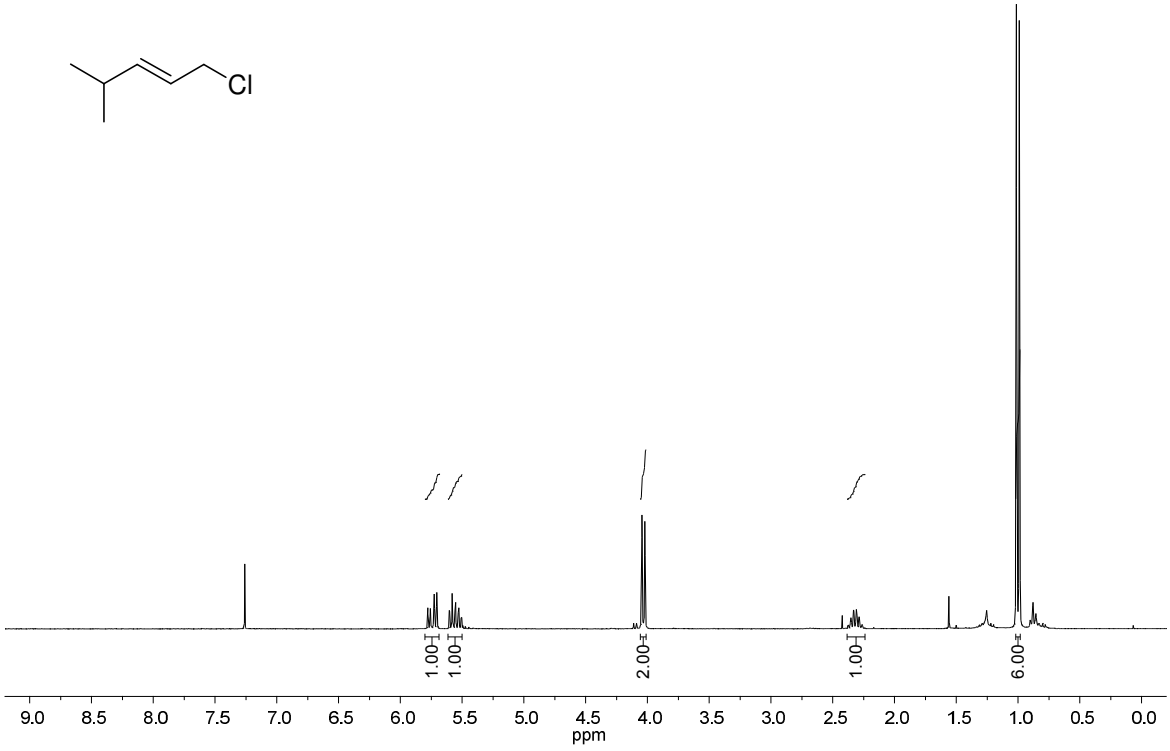


^{13}C NMR:

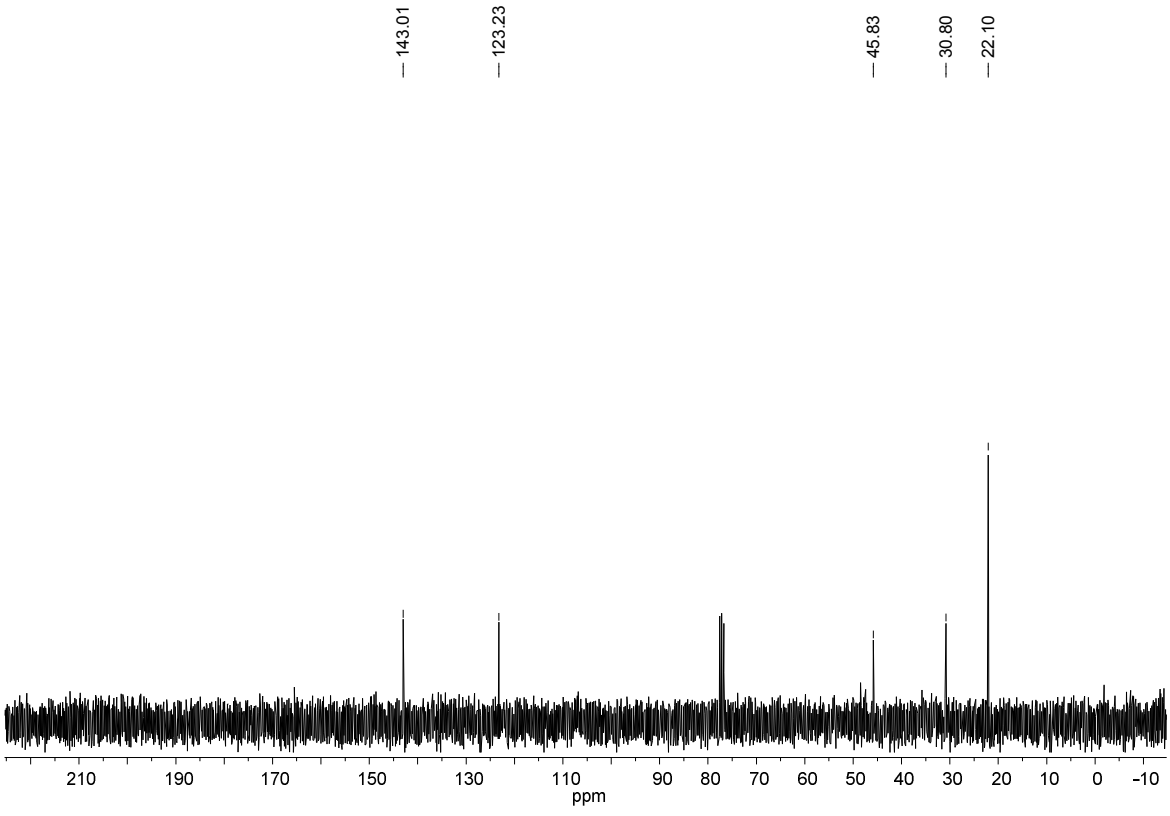


(*E*)-1-Chloro-4-methylpent-2-ene (**9g**)

^{1}H NMR:

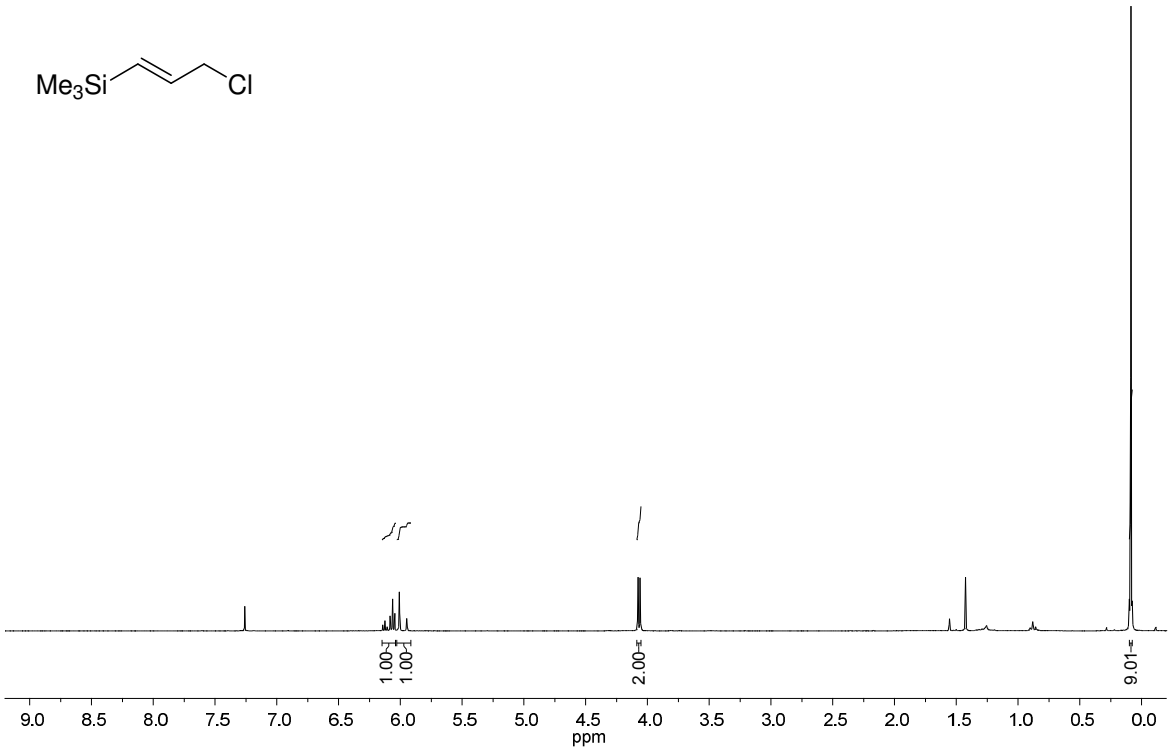


^{13}C NMR:

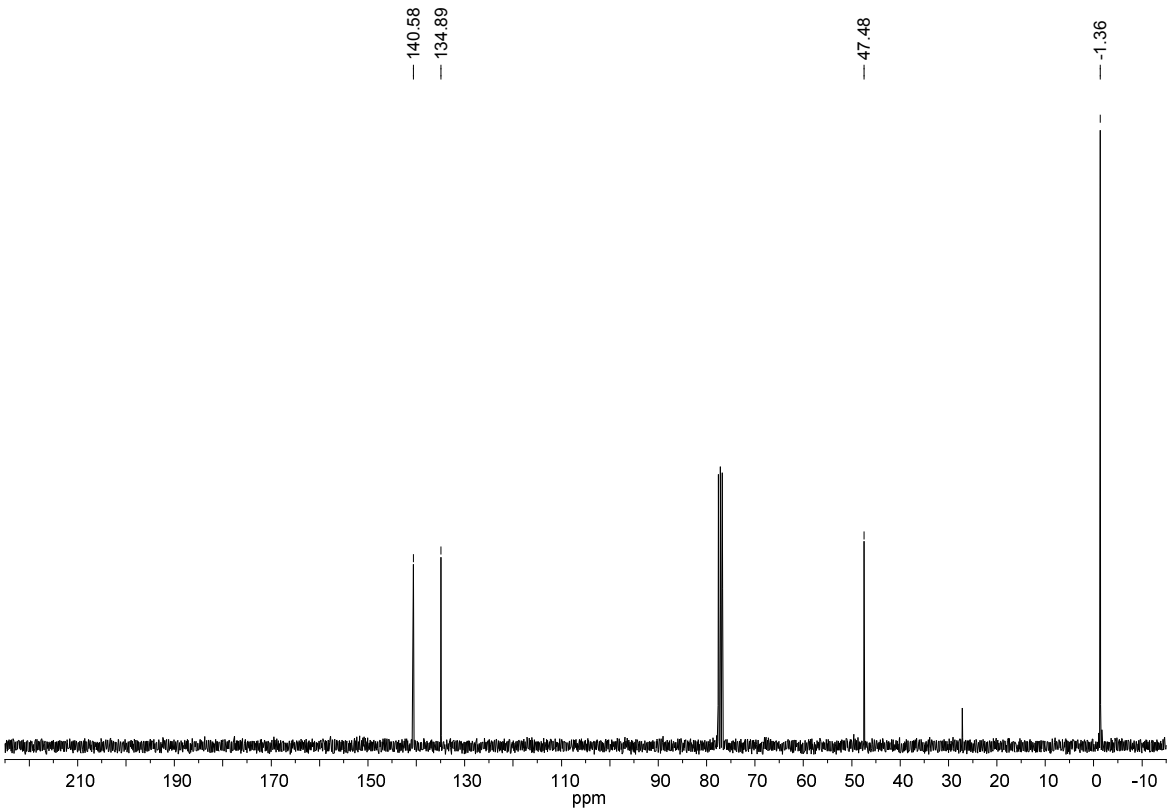


(*E*)-3-Chloro-1-trimethylsilylprop-1-ene (**10g**)

^{1}H NMR:

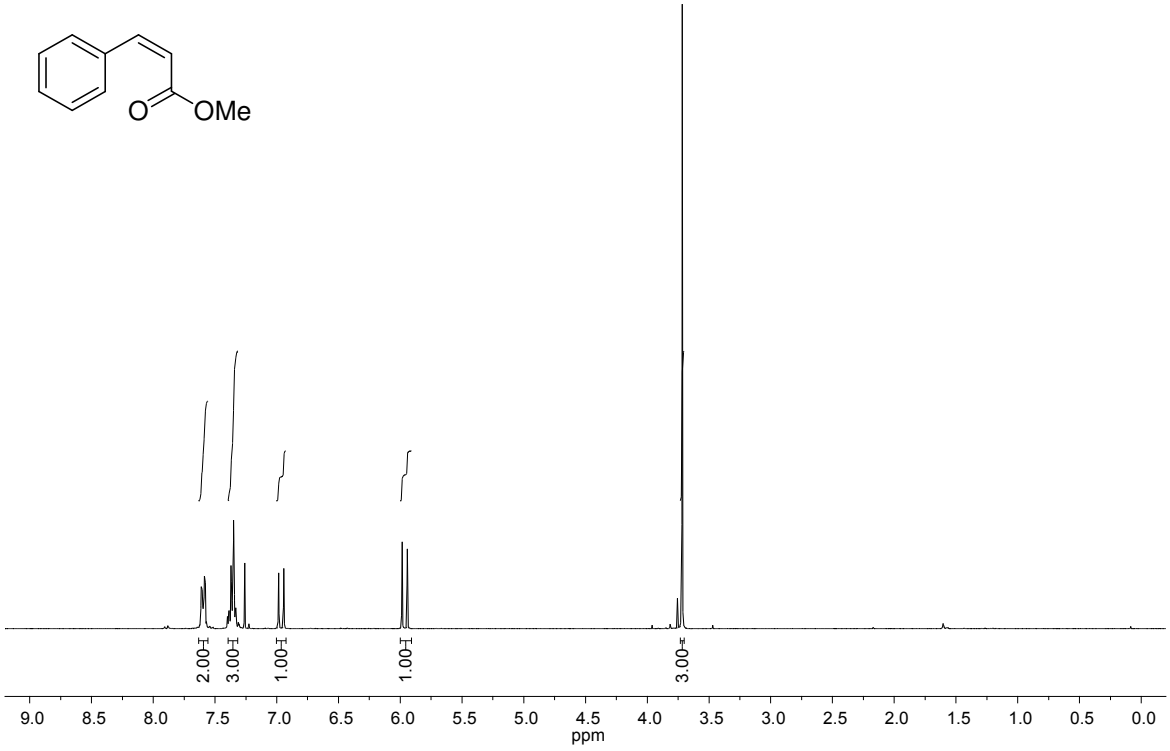


^{13}C NMR:

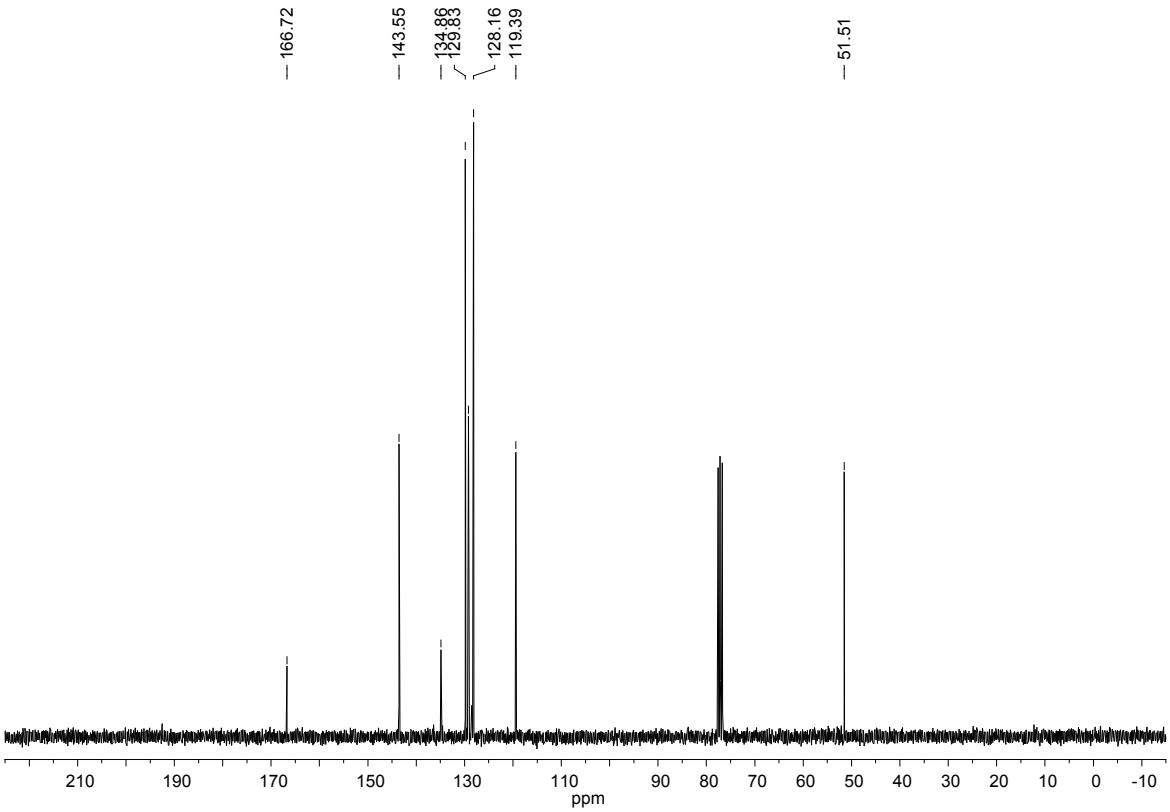


(*Z*)-Cinnamic methyl carboxylate

^{1}H NMR:

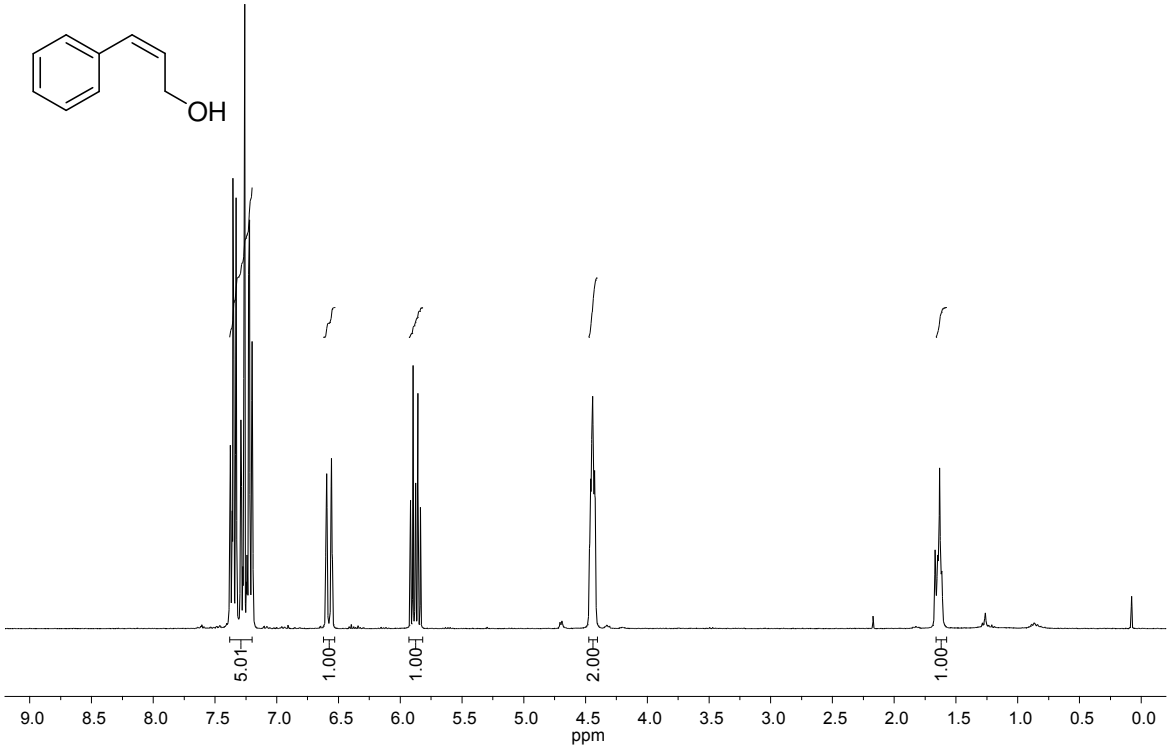


^{13}C NMR:

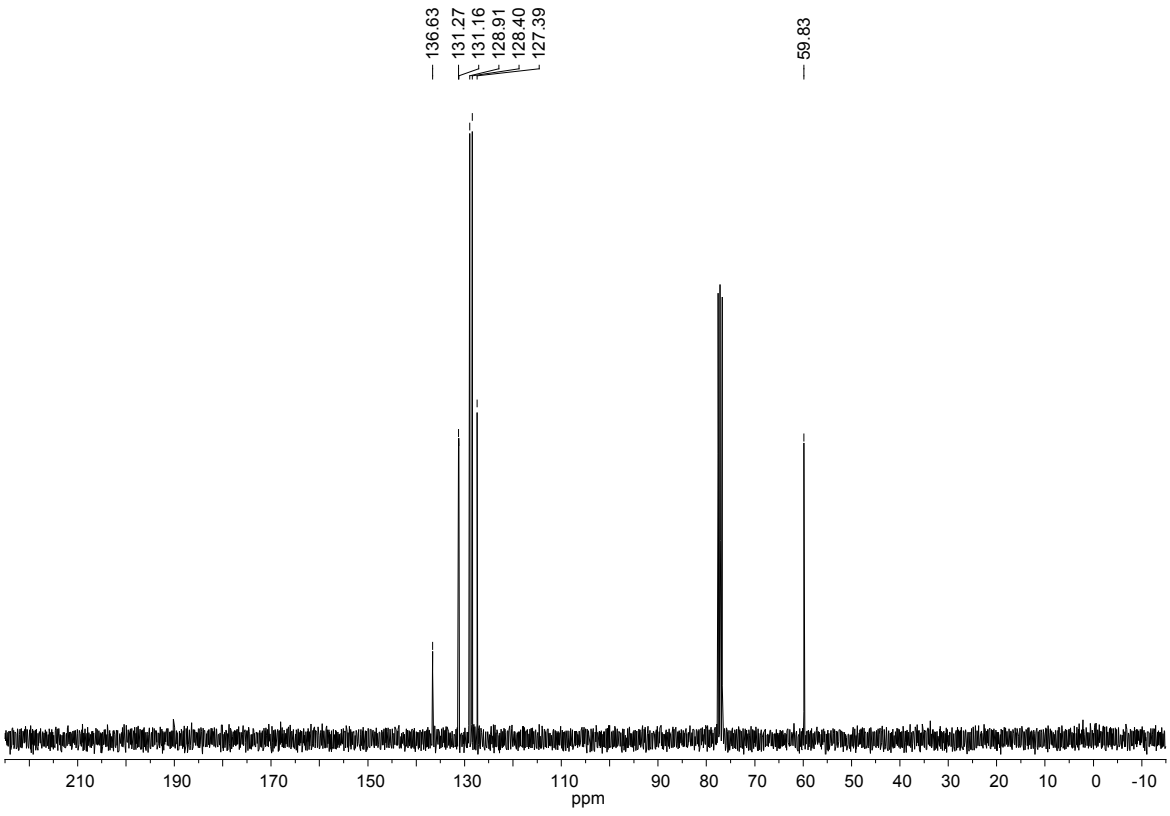


(*Z*)-Cinnamic alcohol

^{1}H NMR:

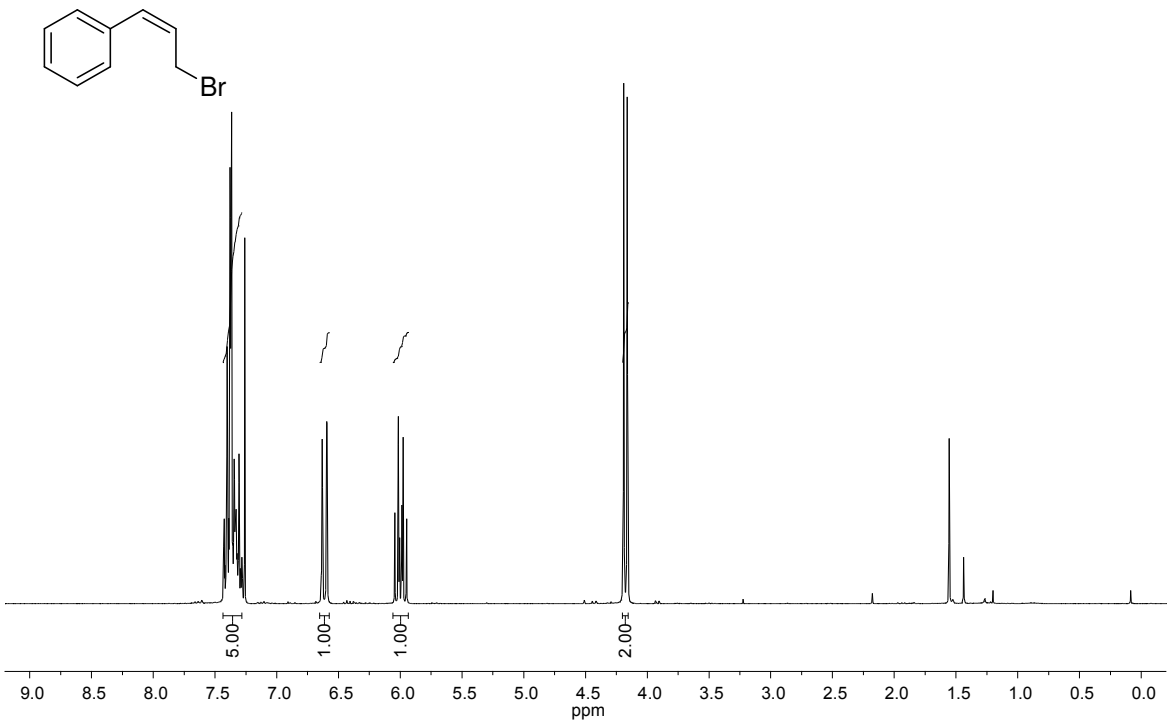


^{13}C NMR:



(*Z*)-Cinnamic bromide (**1f**)

^{1}H NMR:



^{13}C NMR: