Expanding the regioselective enzymatic repertoire: oxidative mono-cleavage of dialkenes catalyzed by *Trametes hirsuta*

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1. General Information

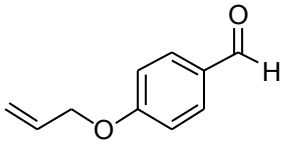
All commercially obtained reagents were used as received unless otherwise noted. 1,4-Dioxane, 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) were dried over sodium with benzophenone. Thin-layer chromatography (TLC) was conducted with Merck Silica Gel 60 F_{254} precoated plates and visualized with UV and potassium permanganate stain. Column chromatography was performed using Merck Silica Gel 60 (230-400 mesh). NMR spectra were recorded on a Bruker DPX-300 or Bruker NAV-300 spectrometer at 300 (^{1}H) and 75 (^{13}C) MHz. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (δ 0.00) using deuterated solvent ($CDCl_3$) as an internal standard. Data reported as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, ap = apparent; coupling constant(s) (*J*) in Hz; integration. GC analyses were carried out on a Varian 3900 gas chromatograph equipped with FID and a DB 1701 capillary column (30 m, 0.25 mm, 0.25 μm film, N_2). GC/MS analyses were performed on a Hewlett Packard 6890 equipped with FID and a HP Mass Selective Detector 5973 attached with a HP 5 MS capillary column (30 m, 0.25 mm, 0.25 μm film) and helium was used as carrier gas. IR spectra were recorded as thin films on NaCl plates on a Perkin-Elmer Spectrum 100 FT-IR and are reported in frequency of absorption (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on a Bruker MicroTofQ by positive electrospray ionization (ESI^+) or atmospheric pressure photoionization ($APPI^+$). When HRMS could not be obtained due to fragmentation of the compound, data were obtained by GC/MS. Ultrasonication was performed in a Branson Digital Sonifier model 250.

2. Experimental Procedures

2.1. General procedure for the allylation of hydroxybenzaldehydes[1]

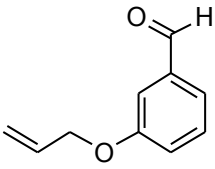
To a solution of 4-, 3- or 2-hydroxybenzaldehyde (16.4 mmol, 1.0 equiv) in acetone (20 mL), K_2CO_3 (6.79 g, 49.1 mmol, 3.0 equiv) and allyl bromide (2.13 mL, 24.6 mmol, 1.5 equiv) were added. The reaction mixture was stirred at room temperature for 2 h and further heated to reflux another 2 h. After cooling to room temperature, the solution was filtered, washed with acetone and concentrated *in vacuo*. Purification by flash chromatography (10% EtOAc / hexanes) afforded the pure products.

4-Allyloxybenzaldehyde (2a)



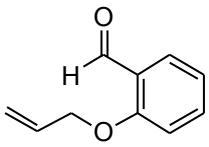
Clear colourless liquid (2.45 g, 95%). R_f (20% EtOAc / hexanes): 0.43; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.05 (ddt, J = 17.2, 10.5, 5.3 Hz, 1H), 5.43 (ap dq, J = 17.3, 1.6 Hz, 1H), 5.32 (ap dq, J = 10.5, 1.4 Hz, 1H), 4.62 (ap dt, J = 5.3, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 163.5, 132.3, 131.8, 129.9, 118.1, 114.9, 68.9; IR (NaCl) ν 3079, 3022, 2987, 2926, 2830, 2739, 1690, 1601, 1576, 1509, 1425, 1313, 1259, 1162, 996, 933, 832 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{10}H_{11}O_2$ $(M+H)^+$: 163.0754, found 163.0751.

3-Allyloxybenzaldehyde (2b)



Clear colourless liquid (2.33 g, 88%). R_f (20% EtOAc / hexanes): 0.45; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.46-7.36 (m, 3H), 7.17 (dt, J = 6.5, 2.7 Hz, 1H), 6.04 (ddt, J = 17.2, 10.5, 5.2 Hz, 1H), 5.42 (ap dq, J = 17.2, 1.5 Hz, 1H), 5.29 (ap dq, J = 10.5, 1.4 Hz, 1H), 4.58 (ap dt, J = 5.2, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 159.2, 137.9, 132.7, 130.1, 123.6, 122.1, 118.1, 113.3, 69.0; IR (NaCl) ν 3083, 3026, 2989, 2921, 2820, 2730, 1699, 1597, 1484, 1450, 1388, 1322, 1263, 1147, 1027, 992, 931, 788 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{10}H_{11}NaO_2$ $(M+Na)^+$: 185.0573, found 185.0590.

2-Allyloxybenzaldehyde (2c)

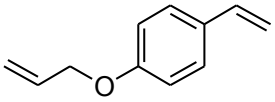


Clear colourless liquid (2.04 g, 77%). R_f (20% EtOAc / hexanes): 0.50; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.76 (dd, J = 7.7, 1.8 Hz, 1H), 7.44 (ddd, J = 8.5, 7.4, 1.8 Hz, 1H), 6.96-6.88 (m, 2H), 6.00 (ddt, J = 17.3, 10.4, 5.1 Hz, 1H), 5.38 (ap dq, J = 17.3, 1.5 Hz, 1H), 5.26 (ap dq, J = 10.5, 1.4 Hz, 1H), 4.57 (ap dt, J = 5.1, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 160.8, 135.7, 132.3, 128.2, 124.9, 120.7, 117.8, 112.8, 69.0; IR (NaCl) ν 3079, 3021, 2986, 2925, 2865, 2763, 1690, 1599, 1483, 1458, 1396, 1286, 1241, 1190, 1163, 1103, 995, 933, 843, 758 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{10}H_{11}NaO_2$ $(M+Na)^+$: 185.0573, found 185.0567.

2.2. General procedure for the Wittig olefination reactions[2]

To a suspension of methyltriphenylphosphonium bromide (4.82 g, 13.5 mmol, 2.25 equiv) or ethyltriphenylphosphonium bromide (5.01 g, 13.5 mmol, 2.25 equiv) in anhydrous THF (54 mL), potassium *tert*-butoxide (1.68 g, 15.0 mmol, 2.5 equiv) was added in three portions under nitrogen atmosphere. The resulting bright yellow or bright orange solution was stirred at room temperature for 3 h. The mixture was subsequently cooled to -78 °C and the corresponding allyloxybenzaldehyde (920 µL, 6.0 mmol, 1.0 equiv) dissolved in anhydrous THF (6 mL) was added dropwise. The resulting solution was allowed to warm to room temperature for 15 h, quenched with saturated aqueous NH_4Cl (20 mL) and extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. Flash chromatography (20% Et_2O / hexanes) afforded the pure products.

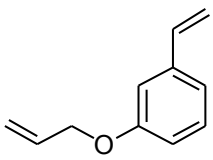
1-Allyloxy-4-vinylbenzene (1a)



Clear colourless liquid (961 mg, 82%). R_f (30% EtOAc / hexanes): 0.73; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.70 (dd, J = 17.6, 10.9 Hz, 1H), 6.08 (ddt, J = 17.2, 10.5, 5.3 Hz, 1H), 5.64 (dd, J = 17.6, 0.9 Hz, 1H), 5.44 (ap dq, J = 17.3, 1.6 Hz, 1H), 5.34 (ap dq, J = 10.5, 1.4 Hz, 1H), 5.18 (dd, J = 10.9, 0.9 Hz, 1H), 4.56 (ap dt, J = 5.3, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 136.3, 133.3, 130.6, 127.5, 117.8, 114.8, 111.7, 68.9; IR (NaCl) ν 3086, 3040, 3007, 2982, 2920, 2862, 1885, 1808, 1628, 1607, 1510, 1429, 1301, 1244, 1176, 1117,

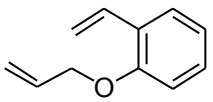
1020, 992, 926, 901, 834 cm^{-1}; GC/MS (EI^+, *m/z*): 160 (M^+, 100), 145 (18), 131 (11), 119 (86), 91 (87).

1-Allyloxy-3-vinylbenzene (1b)



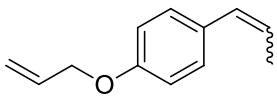
Clear colourless liquid (680 mg, 71%). R_f (20% EtOAc / hexanes): 0.65; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.9 Hz, 1H), 7.06-7.01 (m, 2H), 6.87 (ddd, *J* = 8.1, 2.5, 0.7 Hz, 1H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.11 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.78 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.47 (ap dq, *J* = 17.3, 1.6 Hz, 1H), 5.33 (ap dq, *J* = 10.5, 1.4 Hz, 1H), 5.29 (dd, *J* = 10.9, 0.7 Hz, 1H), 4.59 (ap dt, *J* = 5.3, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 139.2, 136.9, 133.4, 129.6, 119.2, 117.8, 114.3, 114.2, 112.6, 68.9; IR (NaCl) ν 3087, 3009, 2984, 2921, 2863, 1833, 1576, 1488, 1443, 1422, 1286, 1261, 1158, 1025, 991, 913, 876, 783, 715, 668 cm^{-1}; GC/MS (EI^+, *m/z*): 160 (M^+, 100), 145 (39), 131 (20), 117 (51), 91 (61).

1-Allyloxy-2-vinylbenzene (1c)



Clear colourless liquid (714 mg, 74%). R_f (20% EtOAc / hexanes): 0.65; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.28-7.23 (m, 1H), 7.15 (dd, *J* = 17.8, 11.2 Hz, 1H), 6.98 (ap t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.12 (ddt, *J* = 17.2, 10.5, 5.1 Hz, 1H), 5.80 (dd, *J* = 17.8, 1.5 Hz, 1H), 5.49 (ap dq, *J* = 17.3, 1.5 Hz, 1H), 5.34 (ap dq, *J* = 10.6, 1.4 Hz, 1H), 5.31 (dd, *J* = 11.2, 1.5 Hz, 1H), 4.61 (ap dt, *J* = 5.1, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 133.5, 131.8, 128.9, 127.2, 126.6, 121.0, 117.4, 114.5, 112.5, 69.3; IR (NaCl) ν 3085, 3021, 2984, 2919, 2866, 1823, 1626, 1598, 1487, 1451, 1422, 1292, 1241, 1161, 1108, 1018, 997, 912, 750 cm^{-1}; GC/MS (EI^+, *m/z*): 160 (M^+, 25), 145 (33), 131 (28), 119 (50), 91 (100).

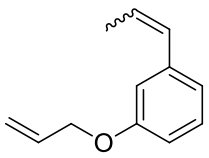
(*Z*)-1-Allyloxy-4-(prop-1-en-1-yl)benzene (1j)



A *Z*/*E* mixture (85:15) was obtained as a clear colourless liquid (770 mg, 74%). R_f (20% EtOAc / hexanes): 0.63; ^1H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ 7.16 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.29 (d, *J* = 11.6 Hz, 1H), 5.99 (ddt, *J* = 17.3, 10.3, 5.6 Hz, 1H), 5.70-5.55 (m, 1H), 5.34 (ap dt, *J* = 17.3, 1.3 Hz, 1H), 5.21 (ap dt, *J* = 10.4, 1.3 Hz, 1H), 4.51-4.41 (m, 2H), 1.82 (ap dt, *J* = 7.3, 1.6 Hz, 3H);

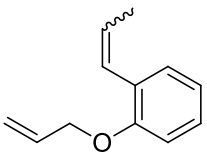
^{13}C NMR (75 MHz, $CDCl_3$, *Z* isomer) δ 157.3, 133.5, 130.6, 130.1, 129.4, 125.3, 117.8, 114.5, 69.0, 14.7; IR (NaCl) ν 3080, 3018, 2914, 2860, 1649, 1606, 1574, 1509, 1456, 1424, 1366, 1302, 1245, 1176, 1117, 1025, 998, 928, 838, 740, 695 cm^{-1}.

(*Z*)-1-Allyloxy-3-(prop-1-en-1-yl)benzene (1k)



A *Z*/*E* mixture (85:15) was obtained as a clear colourless liquid (847 mg, 81%). R_f (20% EtOAc / hexanes): 0.73; ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ 7.25 (ap t, *J* = 7.9 Hz, 1H), 6.92-6.87 (m, 2H), 6.80 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.41 (d, *J* = 11.6 Hz, 1H), 6.08 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.80 (dq, *J* = 11.6, 7.2 Hz, 1H), 5.43 (ap dq, *J* = 17.3, 1.6 Hz, 1H), 5.30 (ap dq, *J* = 10.5, 1.4 Hz, 1H), 4.56 (ap dt, *J* = 5.3, 1.5 Hz, 2H), 1.91 (dd, *J* = 7.2, 1.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, *Z* isomer) δ 158.6, 139.1, 133.6, 129.9, 129.2, 127.2, 121.7, 117.7, 115.4, 113.0, 68.9, 14.8; IR (NaCl) ν 3081, 3018, 2915, 2860, 1649, 1597, 1576, 1489, 1438, 1366, 1234, 1154, 1037, 995, 907, 789, 691 cm^{-1}.

(*Z*)-1-Allyloxy-2-(prop-1-en-1-yl)benzene (1l)



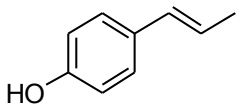
A *Z*/*E* mixture (80:20) was obtained as a clear colourless liquid (774 mg, 74%). R_f (20% EtOAc / hexanes): 0.75; ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer) δ 7.29 (d, *J* = 7.5 Hz, 1H), 7.20 (ap t, *J* = 7.8 Hz, 1H), 6.95 (ap t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.59 (d, *J* = 11.6 Hz, 1H), 6.08 (ddt, *J* = 17.3, 10.4, 5.1 Hz, 1H), 5.85 (dq, *J* = 11.6, 7.1 Hz, 1H), 5.42 (ap dq, *J* = 17.3, 1.7 Hz, 1H), 5.27 (ap dq, *J* = 10.5, 1.5 Hz, 1H), 4.57 (ap dt, *J* = 5.1, 1.6 Hz,, 2H), 1.86 (ap dt, *J* = 7.1, 1.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, *Z* isomer) δ 156.2, 133.6, 130.4, 127.9, 127.8, 126.9, 125.4, 120.3, 117.3, 112.2, 69.2, 14.8; IR (NaCl) ν 3074, 3025, 2914, 2862, 1650, 1598, 1487, 1448, 1288, 1247, 1107, 1022, 998, 928, 751, 700 cm^{-1}.

2.3. General procedure for the Suzuki-Miyaura cross-coupling of bromophenols[3]

A solution of 4- or 3-bromophenol (1.0 equiv) and tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (5% mmol) in anhydrous DME (0.2 M) was stirred at room temperature for 20 min under nitrogen atmosphere. Then, (*E*)-1-propen-1-yl boronic acid (1.2 equiv), distilled water (0.8 M) and Na_2CO_3 (1.0 equiv) were added and the reaction mixture was refluxed for

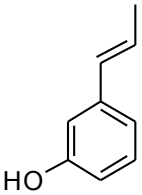
20 h. Afterwards, the reaction mixture was cooled to room temperature, extracted with Et_2O (3 x 10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography (10% Et_2O / hexanes) provided the pure products.

(*E*)-4-(prop-1-en-1-yl)phenol (3)



Clear colourless liquid (145 mg, 63%). R_f (30% Et_2O / hexanes): 0.28; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 6.36 (d, J = 15.8 Hz, 1H), 6.09 (dq, J = 15.7, 6.6 Hz, 1H), 4.67 (s, 1H), 1.86 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 131.2, 130.4, 127.2, 123.7, 115.5, 18.5; IR (NaCl) ν 3344, 3029, 2975, 2932, 2730, 2610, 2492, 1886, 1674, 1611, 1514, 1454, 1377, 1236, 1172, 1107, 966, 838, 788, 733 cm^{-1}; HRMS (APPI$^+$) *m/z* calculated for $C_9H_{10}O$ $(M)^+$: 134.0726, found 134.0709.

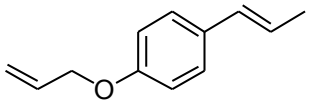
(*E*)-3-(prop-1-en-1-yl)phenol (4)



Clear colourless liquid (215 mg, 70%). R_f (20% Et_2O / hexanes): 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 7.7 Hz, 1H), 6.83-6.79 (m, 1H), 6.68 (ap dd, J = 8.0, 1.7 Hz, 1H), 6.35 (dd, J = 15.8, 1.1 Hz, 1H), 6.22 (dq, J = 15.7, 6.3 Hz, 1H), 4.97 (br s, 1H), 1.88 (dd, J = 6.2, 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 139.8, 130.7, 129.8, 126.4, 118.8, 113.9, 112.6, 18.6; IR (NaCl) ν 3344, 3025, 2964, 2913, 2851, 2731, 2601, 2474, 1926, 1841, 1703, 1656, 1583, 1492, 1446, 1298, 1249, 1157, 963, 770, 687 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_9H_{11}O$ $(M+H)^+$: 135.0804, found 135.0807.

Both compounds **3** and **4** obtained above, as well as the commercially available *ortho*-derivative **5** (obtained from Sigma, mixture of *E* and *Z* configured alkene, 80:20), were subsequently allylated following the same procedure (*vide supra*).

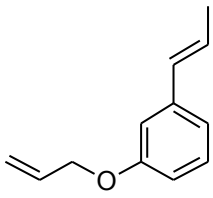
(*E*)-1-Allyloxy-4-(prop-1-en-1-yl)benzene (1g)



Clear colourless liquid (104 mg, 80%). R_f (10% Et_2O / hexanes): 0.65; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.37 (d, J = 15.7 Hz, 1H), 6.16-5.99 (m, 2H), 5.44 (ap dq, J = 17.3, 1.6

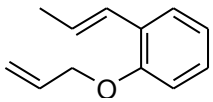
Hz, 1H), 5.30 (ap dq, *J* = 10.5, 1.4 Hz, 1H), 4.54 (ap dt, *J* = 5.3, 1.4 Hz, 2H), 1.87 (dd, *J* = 6.5, 1.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 133.5, 131.1, 130.5, 127.0, 123.7, 117.8, 114.9, 69.0, 18.6; IR (NaCl) ν 3079, 3022, 2964, 2914, 2851, 1651, 1604, 1507, 1453, 1282, 1243, 1178, 1117, 992, 969, 929, 841, 788 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{12}H_{15}O$ $(M+H)^+$: 175.1117, found 175.1112.

(*E*)-1-Allyloxy-3-(prop-1-en-1-yl)benzene (1h)



Clear colourless liquid (456 mg, 84%). R_f (10% Et_2O / hexanes): 0.65; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (ap t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.92-6.90 (m, 1H), 6.78 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.23 (dq, *J* = 15.7, 6.3 Hz, 1H), 6.08 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 5.45 (ap dq, *J* = 17.3, 1.6 Hz, 1H), 5.31 (ap dq, *J* = 10.5, 1.4 Hz, 1H), 4.56 (ap dt, *J* = 5.3, 1.5 Hz, 2H), 1.90 (dd, *J* = 6.4, 1.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 139.6, 133.5, 131.0, 129.5, 126.2, 118.8, 117.7, 113.3, 112.3, 68.9, 18.6; IR (NaCl) ν 3082, 3024, 2914, 2850, 1650, 1598, 1578, 1490, 1440, 1292, 1264, 1159, 1037, 964, 926, 767 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{12}H_{15}O$ $(M+H)^+$: 175.1117, found 175.1128.

(*E*)-1-Allyloxy-2-(prop-1-en-1-yl)benzene (1i)



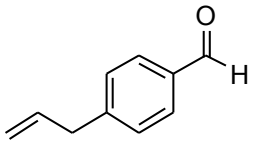
A *Z*/*E* mixture (20:80) was obtained as a clear colourless liquid (927 mg, 89%). Flash chromatography gave two fractions: pure (*E*)-1-(2-allyloxyphenyl)propen-1-yl (460.1 mg, 44%) and a mixture of (*Z*)- and (*E*)-1-(2-allyloxyphenyl)propen-1-yl (36:64, 467.2 mg, 45%).

Characterization of the pure *E* isomer: Clear colourless liquid. R_f (10% Et_2O / hexanes): 0.60; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 1H), 7.16 (ap t, *J* = 7.8 Hz, 1H), 6.92 (ap t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 15.9 Hz, 1H), 6.25 (dq, *J* = 15.8, 6.6 Hz, 1H), 6.10 (ddt, *J* = 17.3, 10.4, 5.1 Hz, 1H), 5.46 (ap dq, *J* = 17.3, 1.5 Hz, 1H), 5.31 (ap dq, *J* = 10.5, 1.5 Hz, 1H), 4.58 (ap dt, *J* = 5.1, 1.6 Hz, 2H), 1.92 (dd, *J* = 6.6, 1.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 133.7, 127.7, 127.5, 126.6, 126.5, 125.8, 121.0, 117.4, 112.4, 69.3, 19.1; IR (NaCl) ν 3073, 3034, 2963, 2913, 2852, 1651, 1597, 1487, 1450, 1239, 1115, 1022, 971, 929, 749 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{12}H_{15}O$ $(M+H)^+$: 175.1117, found 175.1120.

2.4. General procedure for the Suzuki-Miyaura cross-coupling of formylphenylboronic acids[4]

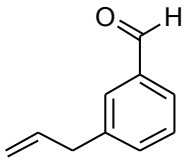
To a solution of 4- or 3-formylphenylboronic acid (450 mg, 3.0 mmol, 1.2 equiv) and $Pd_2(dba)_3$ (11.4 mg, 2.5 x 10^{-2} mmol) in anhydrous 1,4-dioxane (3 mL), triphenylphosphite (6.6 µL, 2.5 x 10^{-2} mmol, 0.01 equiv) and allyl alcohol (170 µL, 2.5 mmol, 1.0 equiv) were added under nitrogen atmosphere. The mixture was refluxed at 100 °C for 3 h, cooled to room temperature, extracted with Et_2O (3 x 10 mL) and washed with brine. The organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography (10% Et_2O / hexanes) afforded the pure products.

4-Allylbenzaldehyde (2d)



Clear colourless liquid (234 mg, 64%). R_f (10% Et_2O / hexanes): 0.60; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.96 (ddt, *J* = 17.1, 10.5, 6.7 Hz 1H), 5.14 (m, 1H), 5.09 (ap dq, *J* = 9.0, 1.6 Hz, 1H), 3.47 (ap d, *J* = 6.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 147.4, 136.1, 130.0, 129.3, 126.3, 116.9, 40.3; IR (NaCl) ν 3081, 2980, 2912, 2828, 2736, 1700, 1606, 1576, 1426, 1389, 1305, 1212, 1168, 995, 919, 827, 785 cm^{-1}.

3-Allylbenzaldehyde (2e)

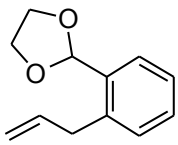


Clear colourless liquid (201 mg, 55%). R_f (20% Et_2O / hexanes): 0.47; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.75-7.69 (m, 2H), 7.48-7.44 (m, 2H), 5.98 (ddt, *J* = 17.1, 10.2, 6.7 Hz 1H), 5.14-5.11 (m, 1H), 5.09 (ap dq, *J* = 8.3, 1.5 Hz, 1H), 3.47 (ap d, *J* = 6.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6, 141.3, 136.8, 136.6, 135.0, 129.8, 129.2, 128.0, 116.9, 39.9; IR (NaCl) ν 3080, 2981, 2916, 2835, 2732, 1699, 1606, 1587, 1441, 1389, 1310, 1238, 1140, 996, 918, 780 cm^{-1}.

2.5. Synthesis of 2-allylbenzaldehyde

2-(2-Allylphenyl)-1,3-dioxolane[5] **(6)**

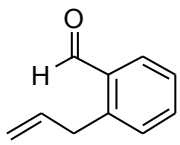
2-(2-Bromophenyl)-1,3-dioxolane (605 µL, 4.0 mmol) and an iodine grain were dissolved in anhydrous THF (2.5 mL, 1.6 M) under nitrogen atmosphere. A small quantity of the solution (ca 500 µL) was added to another flask containing Mg turnings (117 mg, 4.8 mmol) under nitrogen atmosphere and stirred. After the colour of the reaction mixture suddenly faded, the rest of the solution was added dropwise and the mixture was refluxed for 2 h. The reaction mixture was then decanted into a dry flask, cooled in an ice bath and allyl bromide (519 µL, 6.0 mmol) was added. After reaching room temperature, the reaction was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with Et_2O (3 x 30 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Flash chromatography (20% Et_2O / hexanes) afforded the pure product.



Clear colourless liquid (502 mg, 66%). R_f (20% Et_2O / hexanes): 0.45; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.3, 1.6 Hz, 1H), 7.38-7.24 (m, 3H), 6.13-6.00 (m, 2H), 5.15-5.04 (m, 2H), 4.22-4.12 (m, 2H), 4.12-4.01 (m, 2H), 3.61 (d, J = 6.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 137.3, 135.4, 130.0, 129.2, 126.4, 126.2, 115.9, 101.7, 65.3, 36.5; IR (NaCl) ν 3076, 2978, 2887, 2764, 1638, 1606, 1584, 1487, 1454, 1395, 1225, 1070, 969, 945, 759 cm^{-1}; HRMS (ESI$^+$) *m/z* calculated for $C_{12}H_{14}NaO_2$ $(M+Na)^+$: 213.0886, found 213.0895.

2-Allylbenzaldehyde[6] (2f)

To a solution of 2-(2-allylphenyl)-1,3-dioxolane (38 mg, 0.20 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $FeCl_3 \cdot 6H_2O$ (189 mg, 0.71 mmol, 3.5 equiv). The reaction mixture was stirred at room temperature for 15 min, quenched with saturated aqueous $NaHCO_3$ and extracted with Et_2O (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting oil was passed through a short silica gel plug with a minimum amount of Et_2O to remove any remaining iron species. Concentration *in vacuo* afforded the pure product.



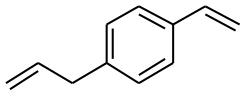
Clear colourless liquid (23 mg, 77%). R_f (20% Et_2O / hexanes): 0.54; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.84 (dd, J = 7.6, 1.5 Hz, 1H), 7.53 (dd, J = 7.5, 1.5 Hz, 1H), 7.39 (ap t, J = 7.5 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 6.03 (ddt, J = 17.1, 10.1, 6.2 Hz, 1H), 5.09 (ap dq, J = 10.2, 1.5 Hz, 1H), 4.99 (ap dq, J = 17.1, 1.7 Hz, 1H), 3.82 (ap dt, J = 6.1, 1.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5,

142.4, 137.1, 134.1, 134.0, 131.7, 131.2, 127.0, 116.5, 36.7; IR (NaCl) ν 3077, 3008, 2979, 2919, 2857, 2738, 1696, 1638, 1599, 1574, 1485, 1453, 1404, 1287, 1209, 996, 917, 755 cm^{-1}; HRMS (ESI^+) *m/z* calculated for $C_{10}H_9O$ $(M-H)^+$: 145.0648, found 145.0652.

2.6. General procedure for Stille coupling[7]

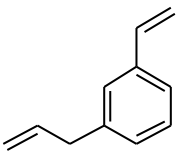
In an oven-dried Schlenk flask $Pd(dba)_2$ (34.5 mg, 0.060 mmol), PCy_3 (33.7 mg, 0.12 mmol), CsF (668 mg, 4.40 mmol) and 4-, 3- or 2-bromostyrene (2.00 mmol) were added under nitrogen atmosphere. Then, allyltributyltin (644 µL, 2.10 mmol) and dioxane (2 mL, 1.0 M) were added. The reaction mixture was stirred and refluxed for 48 h. The solution was then cooled to room temperature and quenched with saturated aqueous NH_4Cl (20 mL), extracted with Et_2O (3 x 30 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by gravimetry chromatography (10% Et_2O / hexanes) afforded the pure products.

1-Allyl-4-vinylbenzene (1d)



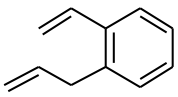
Clear colourless liquid (177.4 mg, 62%). R_f (10% Et_2O / hexanes): 0.75; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.96 (ddt, *J* = 17.2, 10.5, 6.8 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.9 Hz, 1H), 5.12-5.07 (m, 2H), 3.39 (ap d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 137.4, 136.8, 135.7, 128.9, 126.4, 116.0, 113.3, 40.1; IR (NaCl) ν 3081, 3007, 2979, 2908, 2851, 1821, 1639, 1601, 1511, 1407, 990, 908, 823 cm^{-1}; HRMS ($APPI^+$) *m/z* calculated for $C_{11}H_{12}$ $(M)^+$: 144.0934, found 144.0923.

1-Allyl-3-vinylbenzene (1e)

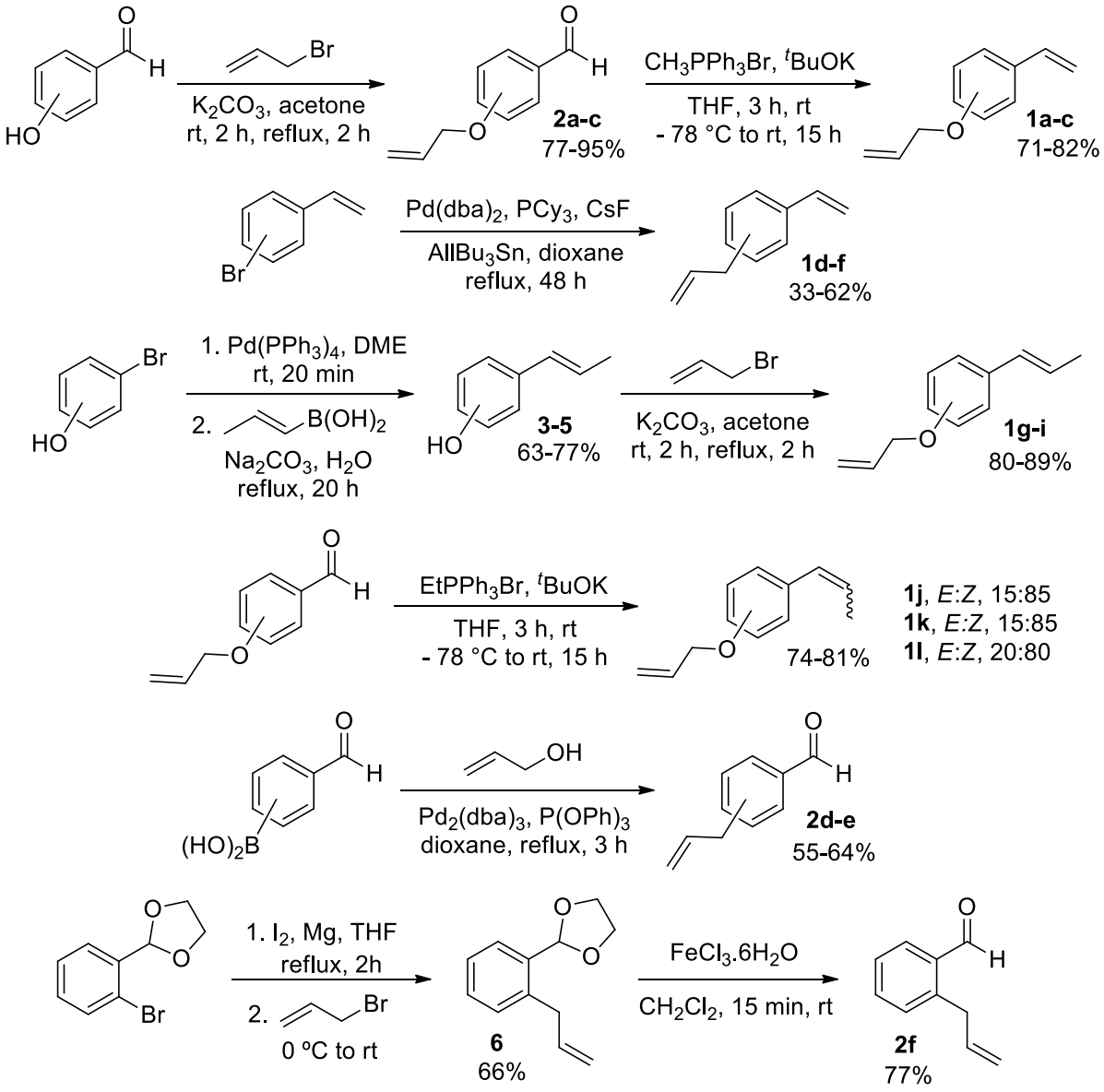


Clear colourless liquid (131.3 mg, 46%). R_f (10% Et_2O / hexanes): 0.73; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27-7.24 (m, 3H), 7.12-7.08 (m, 1H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.98 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.78 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H), 5.13-5.07 (m, 1H), 3.40 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR (75 MHz, CDCl3) δ 140.4, 137.9, 137.5, 137.0, 128.7, 128.3, 126.6, 124.2, 116.0, 113.9, 40.3; IR (NaCl) ν 3081, 3058, 3007, 2979, 2904, 2853, 1822, 1639, 1601, 1581, 1484, 1433, 991, 908, 797, 713 cm^{-1}; HRMS ($APPI^+$) *m/z* calculated for $C_{11}H_{12}$ $(M)^+$: 144.0934, found 144.0925.

1-Allyl-2-vinylbenzene (1f)



Clear colourless liquid (94.8 mg, 33%). R_f (10% Et_2O / hexanes): 0.75; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54-7.48 (m, 1H), 7.24-7.16 (m, 3H), 6.99 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.98 (ddt, *J* = 17.0, 10.5, 6.2 Hz, 1H), 5.66 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.30 (dd, *J* = 11.0, 1.3 Hz, 1H), 5.07 (ap dq, *J* = 10.1, 1.5 Hz, 1H), 4.99 (ap dq, *J* = 17.1, 1.7 Hz, 1H), 3.47 (d, *J* = 6.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 137.0, 136.9, 134.8, 129.8, 128.0, 126.7, 125.9, 116.0, 115.7, 37.6; IR (NaCl) ν 3080, 3060, 3008, 2978, 2906, 1821, 1638, 1509, 1432, 990, 908, 796 cm^{-1}; HRMS ($APPI^+$) *m/z* calculated for $C_{11}H_{13}$ $(M+H)^+$: 145.0994, found 145.1012.



Scheme S1. Summary of the synthetic strategies developed to obtain the dialkene substrates (**1a-l**) and their corresponding mono-aldehyde products (**2a-f**).

3. General procedure for the biocatalytic alkene cleavage

Lyophilized cells of the white-rot fungus *Trametes hirsuta* G FCC 047 were prepared as previously described.[8]

3.1. Microscale

Lyophilized cells from *Trametes hirsuta* G FCC 047 (30 mg) were rehydrated with Bis-Tris buffer (900 µL per sample, 50 mM, pH 6). The cells were disrupted in centrifugal tubes by ultrasonication (amplitude 50%, 1 sec pulse, 4 sec pause, program 1 min 40 sec). The pellet was removed by centrifugation (8000 rpm, 20 min, 4 °C) and the supernatant was transferred into the corresponding reaction well (riplate® sw 10 mL deep-well plate with plastic paraffin film having holes punched through or 4 mL glass vials with septum having a needle punched through). The dialkene substrate (5 µL) and DMSO (10% v v^{-1}) were added in each well and oxygen was flushed through the reaction vessel. The pressure was adjusted to 2 bar. After 24 h at 170 rpm and room temperature, the reaction mixture was extracted with ethyl acetate (2 x 500 µL) and centrifuged after each step (13,000 rpm, 2 min). The combined organic layers were dried with Na_2SO_4 and the resulting crude was analyzed by GC and GC/MS (See Table S1 for retention times). Each reaction was performed in triplicate and with a blank reaction without cells.

3.2. Preparative scale

The lyophilized cells from *Trametes hirsuta* G FCC 047 (600 mg) were rehydrated in Bis-Tris buffer (18 mL, 50 mM, pH 6) on a rotary shaker (25 °C, 150 rpm) for 30 min and transferred to a pressure resistant reaction vessel of a Hydrogen Parr 3910 apparatus. The dialkene substrate (100 µL) mixed with DMSO (2 mL, 10% v v^{-1}) was added and the oxygen pressure was adjusted to 2 bar. After 24 h of lateral agitation at room temperature under constant oxygen pressure, the reaction mixture was extracted with ethyl acetate (3 x 20 mL) and centrifuged after each step (10000 rpm, 15 min, 4 °C). The combined organic layers were dried over Na_2SO_4 and analyzed by GC and GC/MS. Dialkene substrate **1a** was cleaved on a 350 µL scale and the product was isolated by flash column chromatography (20% EtOAc / hexanes) to obtain benzaldehyde **2a** (213 mg, 60%).

4. Analytics

Table S1. Retention times of all substrates and aldehyde products by GC and GC/MS

Compound	GC retention time (min)	GC/MS retention time (min)
1-Allyloxy-4-vinylbenzene **1a**	5.6	7.2
1-Allyloxy-3-vinylbenzene **1b**	5.4	7.0
1-Allyloxy-2-vinylbenzene **1c**	5.2	6.8
1-Allyl-4-vinylbenzene **1d**	3.6	5.6
1-Allyl-3-vinylbenzene **1e**	4.1	6.1
1-Allyl-2-vinylbenzene **1f**	3.6	5.3
(*E*)-1-Allyloxy-4-(prop-1-en-1-yl)benzene **1g**	6.8	8.9
(*E*)-1-Allyloxy-3-(prop-1-en-1-yl)benzene **1h**	6.7	8.7
(*E*)-1-Allyloxy-2-(prop-1-en-1-yl)benzene **1i**	6.2	8.2
(*Z*)-1-Allyloxy-4-(prop-1-en-1-yl)benzene **1j**	6.4	8.4
(*Z*)-1-Allyloxy-3-(prop-1-en-1-yl)benzene **1k**	6.1	8.1
(*Z*)-1-Allyloxy-2-(prop-1-en-1-yl)benzene **1l**	5.7	7.6
4-Allyloxybenzaldehyde **2a**	7.2	8.5
3-Allyloxybenzaldehyde **2b**	6.5	7.8
2-Allyloxybenzaldehyde **2c**	6.9	8.2
4-Allylbenzaldehyde **2d**	4.8	6.6
3-Allylbenzaldehyde **2e**	5.3	7.1
2-Allylbenzaldehyde **2f**	4.8	6.3

GC column: DB-1701 capillary column (50 m, 0.2 mm, 0.33 μm film). GC method: 100/0/15/250/1 [initial temp. (°C)/time (min)/slope (°C/min)/temp. (°C)/time (min)].

GC/MS column: HP 5 MS capillary column (30 m, 0.25 mm, 0.25 μm film). GC/MS method: 1 mL/min, 80/3/30/250/10/30/280, 1 mL/min. [initial temp. (°C)/time (min)/slope (°C/min)/temp. (°C)/time (min)/slope (°C/min)/final temp. (°C)].

5. References

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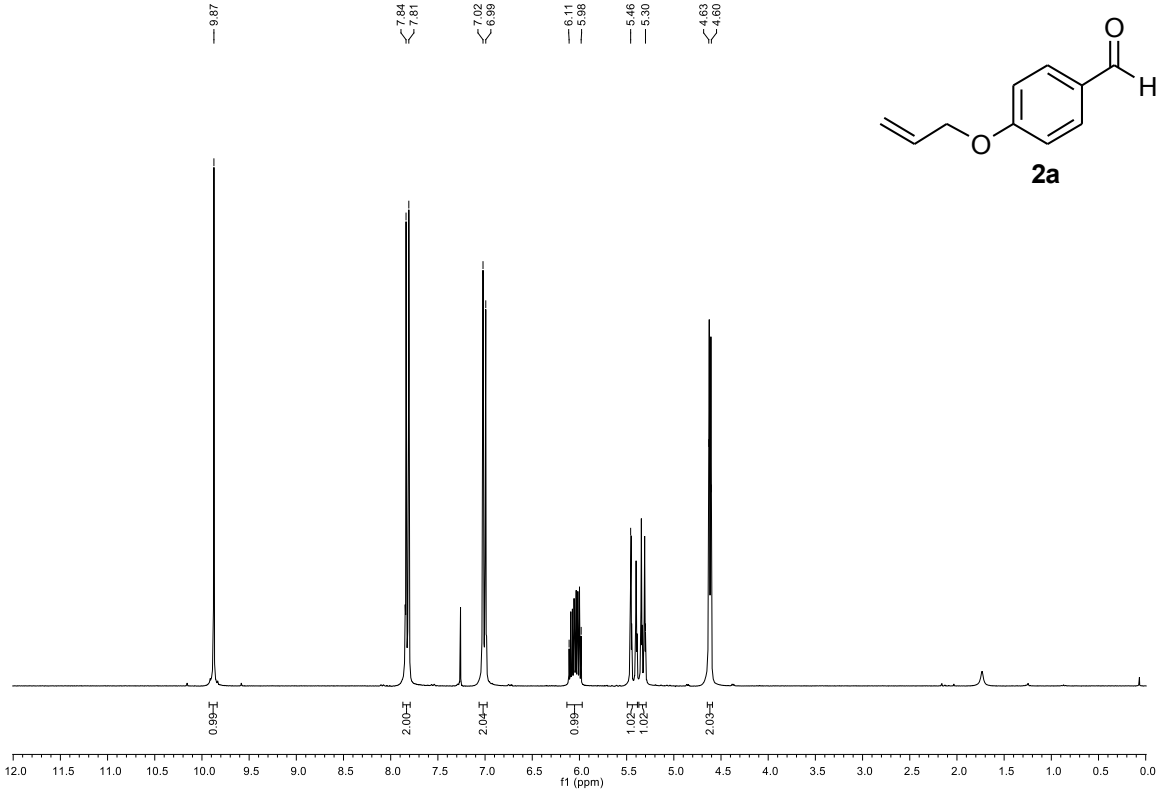
8. (a) H. Mang, J. Gross, M. Lara, C. Goessler, H. E. Schoemaker, G. M. Guebitz and W. Kroutil, *Angew. Chem. Int. Ed.*, 2006, **45**, 5201-5203. (b) H. Mang, J. Gross, M. Lara, C. Goessler, H. E. Schoemaker, G. M. Guebitz and W. Kroutil, *Tetrahedron*, 2007, **63**, 3350-3354.

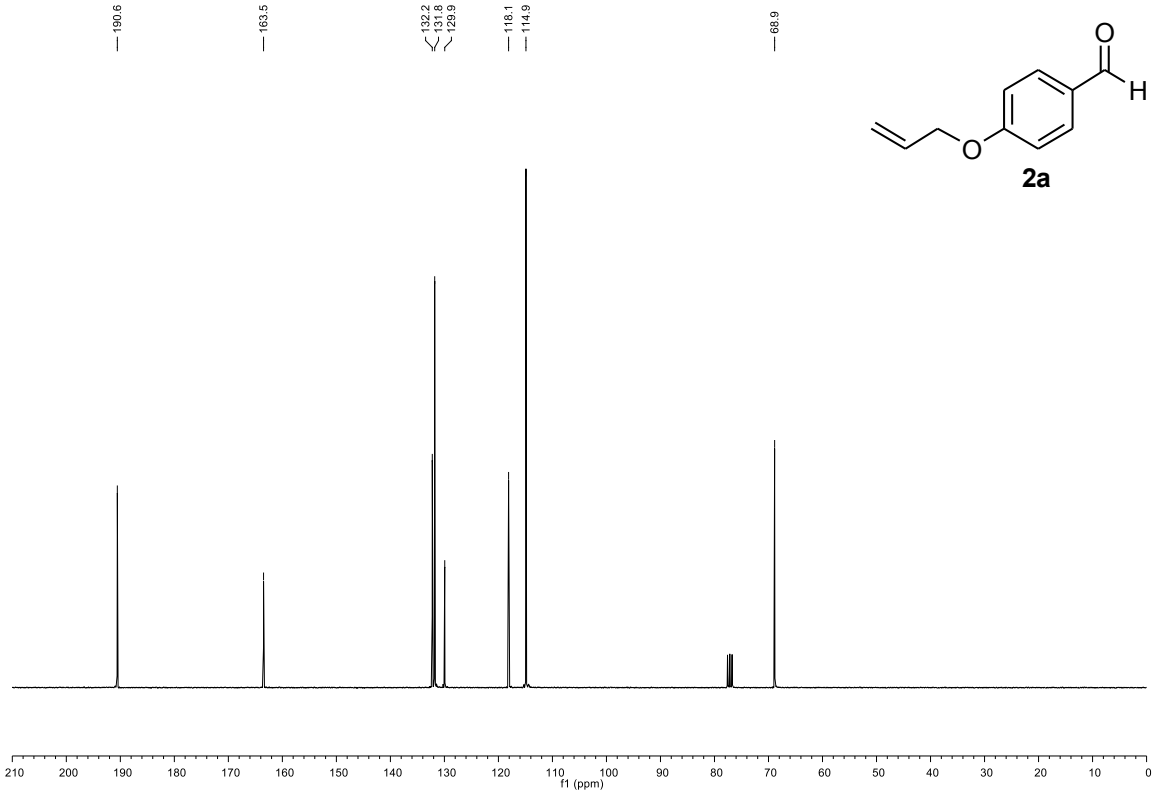
6. NMR spectra

4-Allyloxybenzaldehyde (2a)

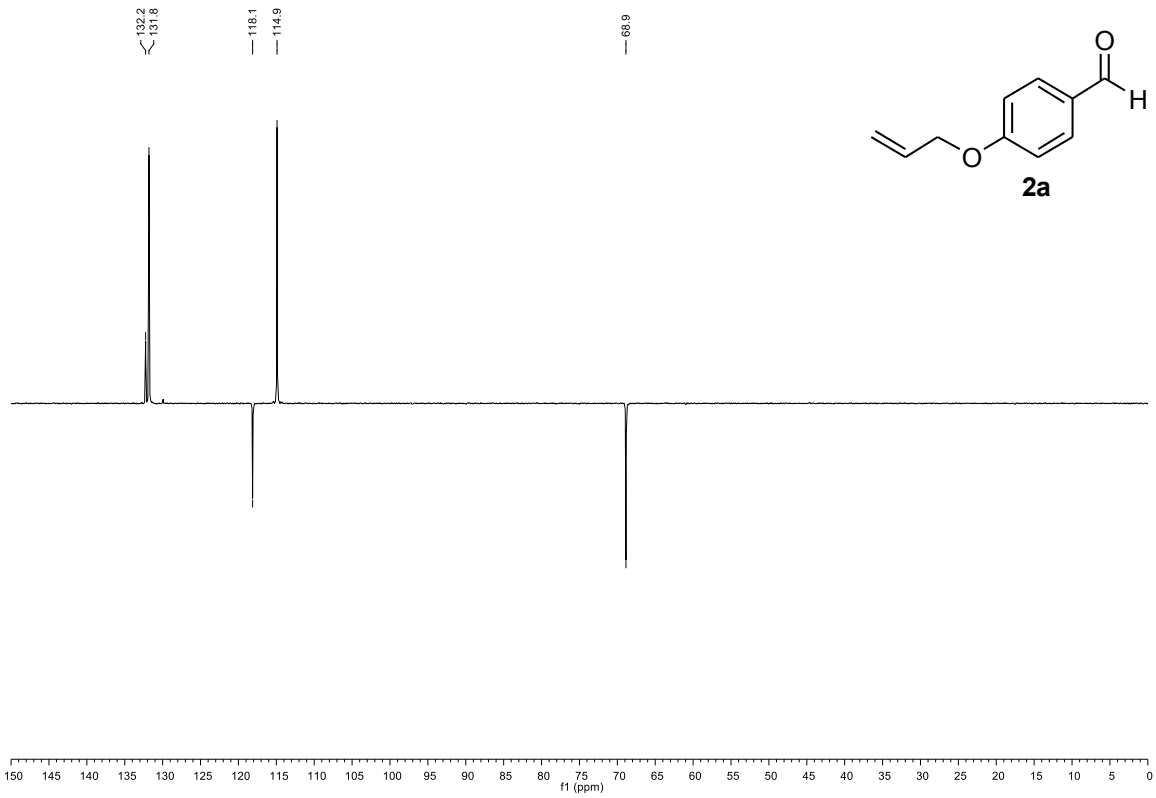
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

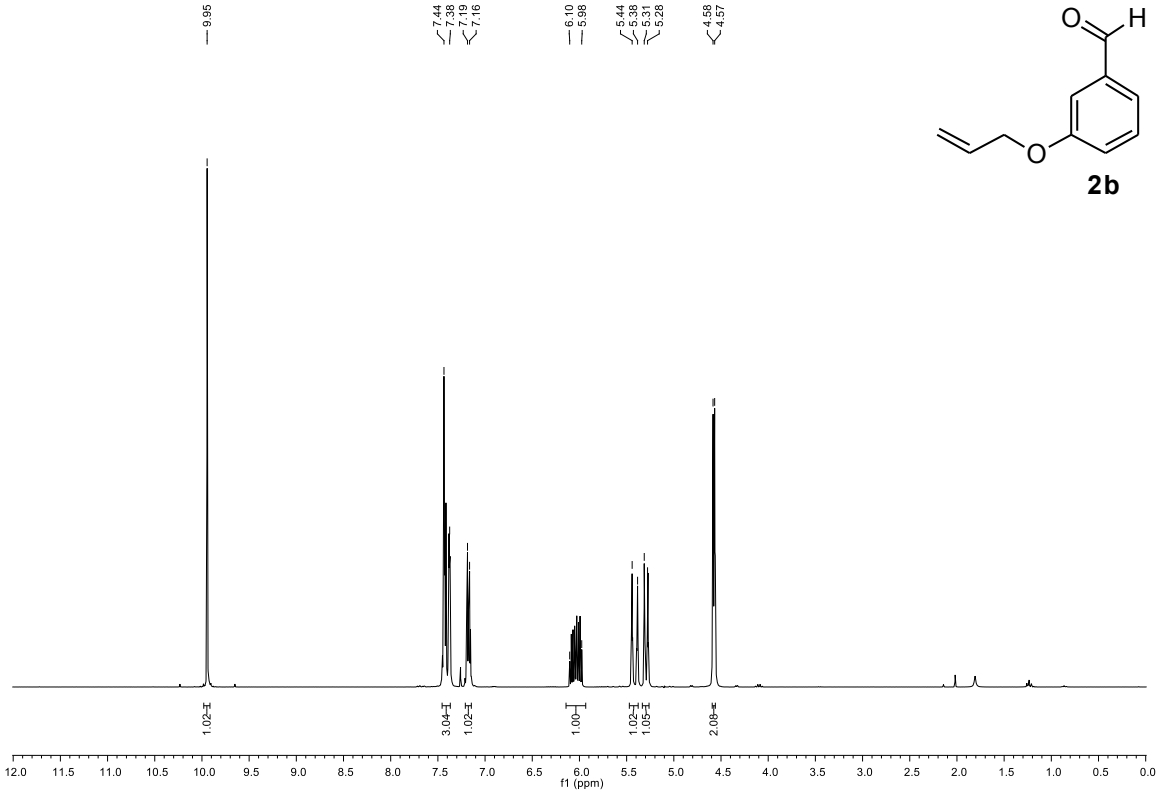


DEPT-135 NMR (75 MHz, $CDCl_3$)



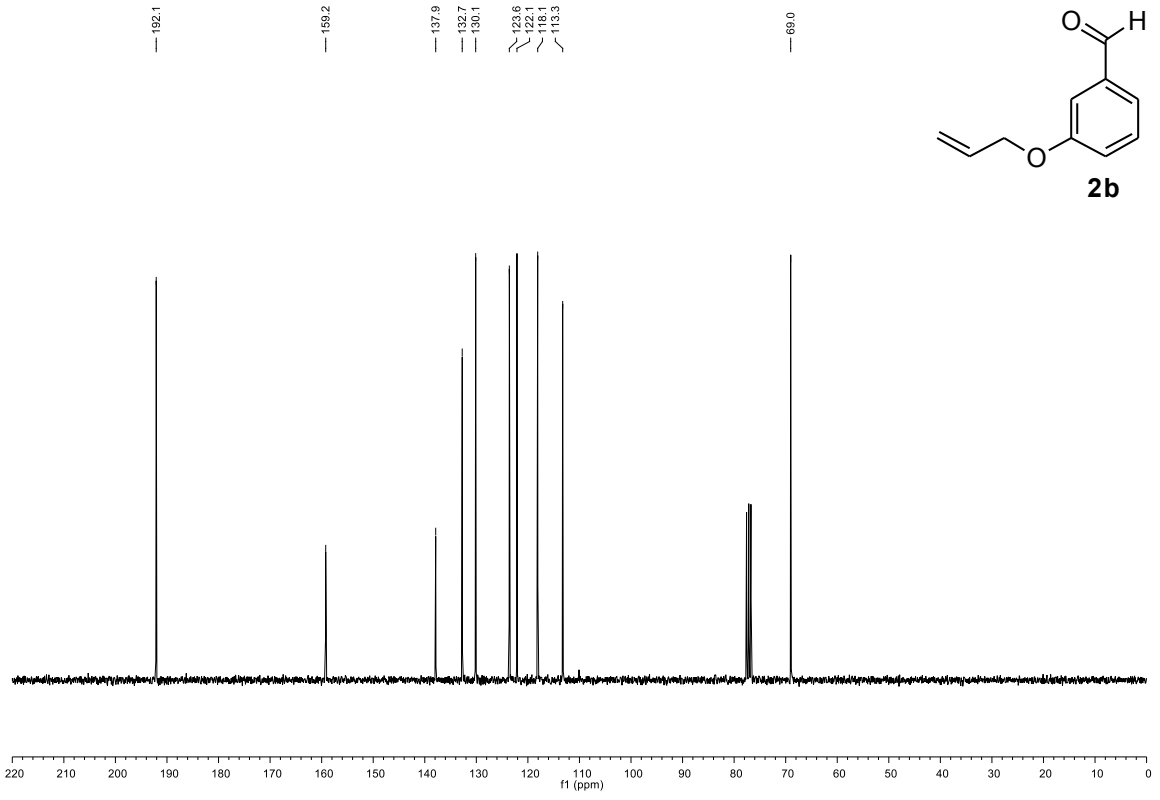
3-Allyloxybenzaldehyde (2b)

^{1}H NMR (300 MHz, $CDCl_3$)



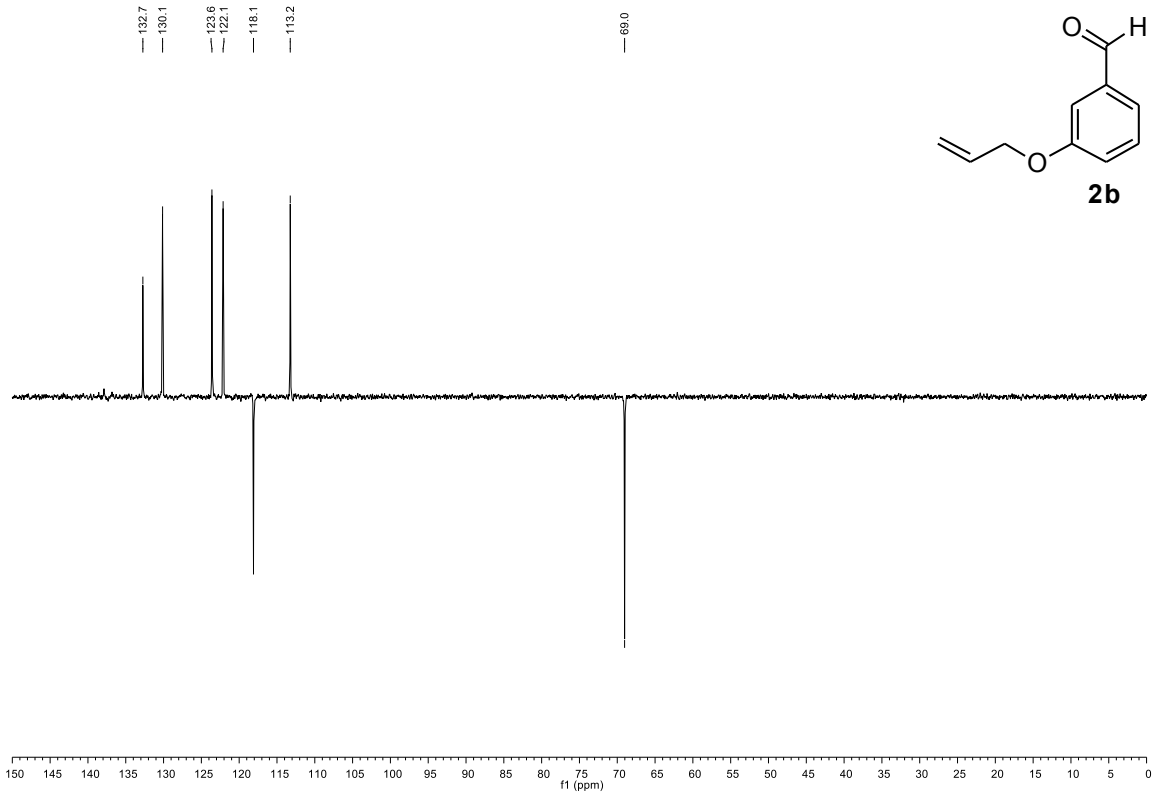
2b

^{13}C NMR (75 MHz, $CDCl_3$)



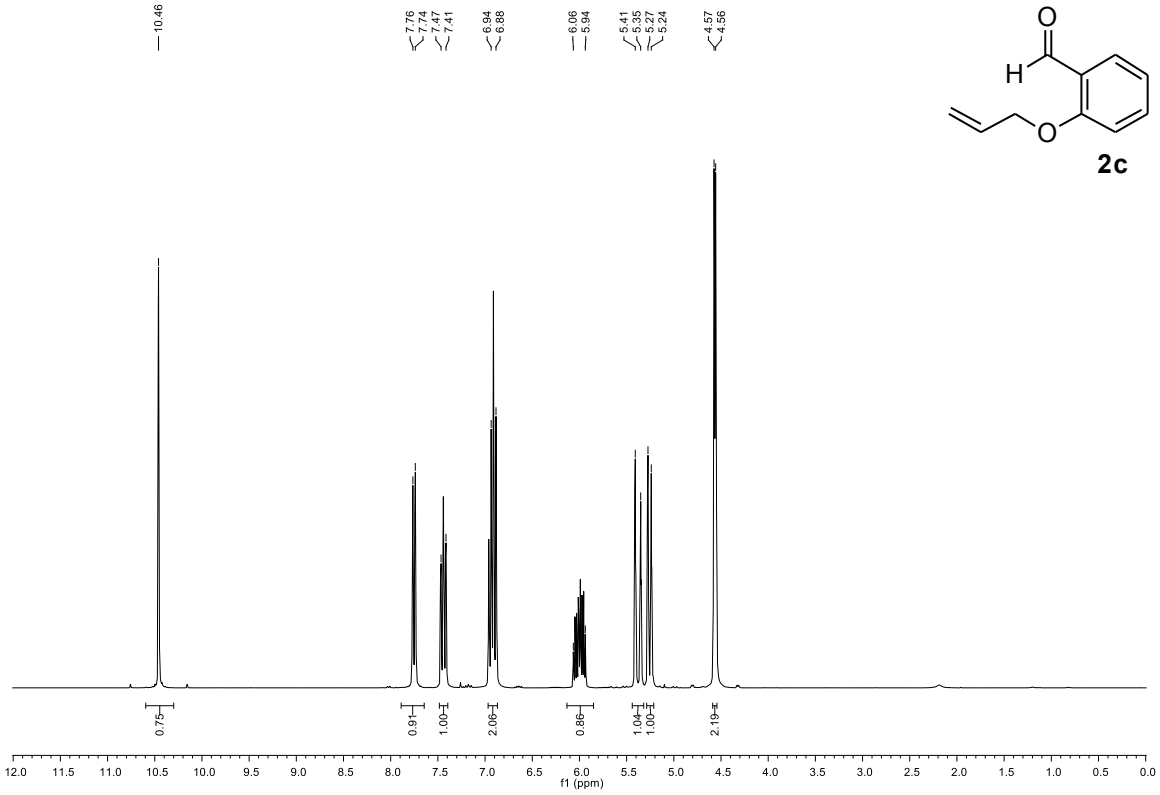
2b

DEPT-135 NMR (75 MHz, $CDCl_3$)



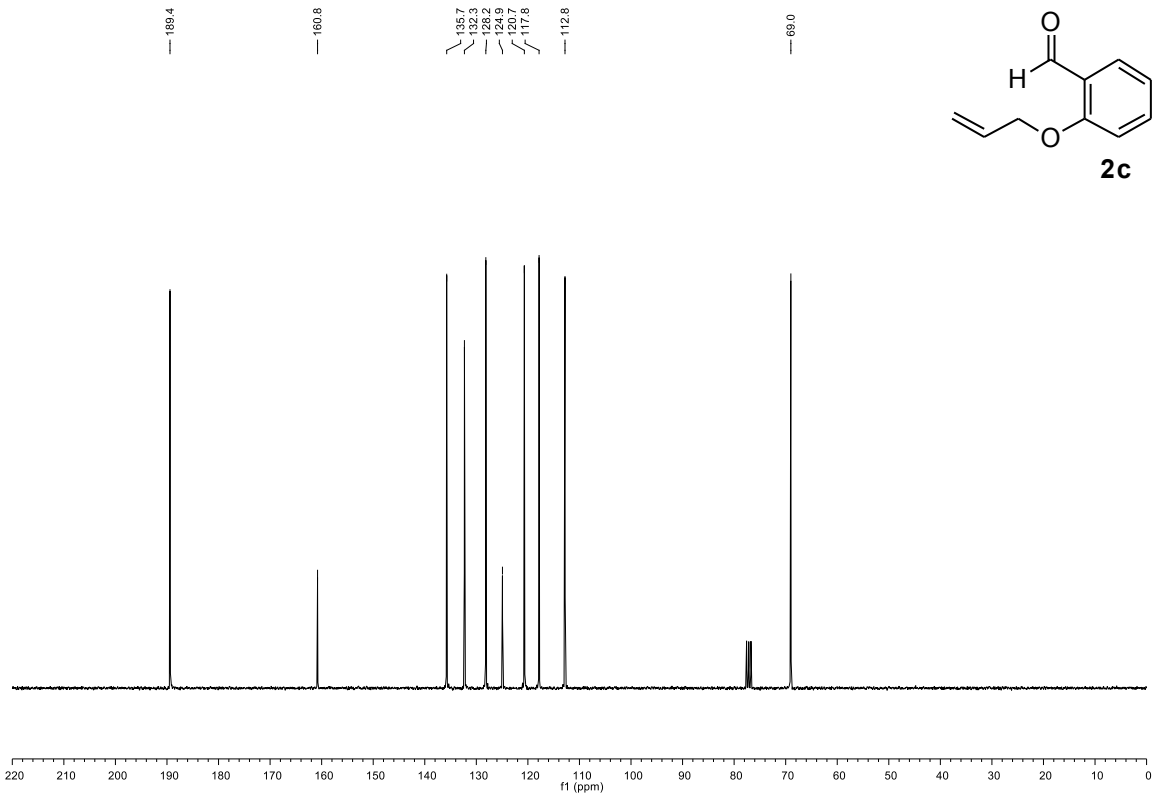
2-Allyloxybenzaldehyde (2c)

^{1}H NMR (300 MHz, $CDCl_3$)



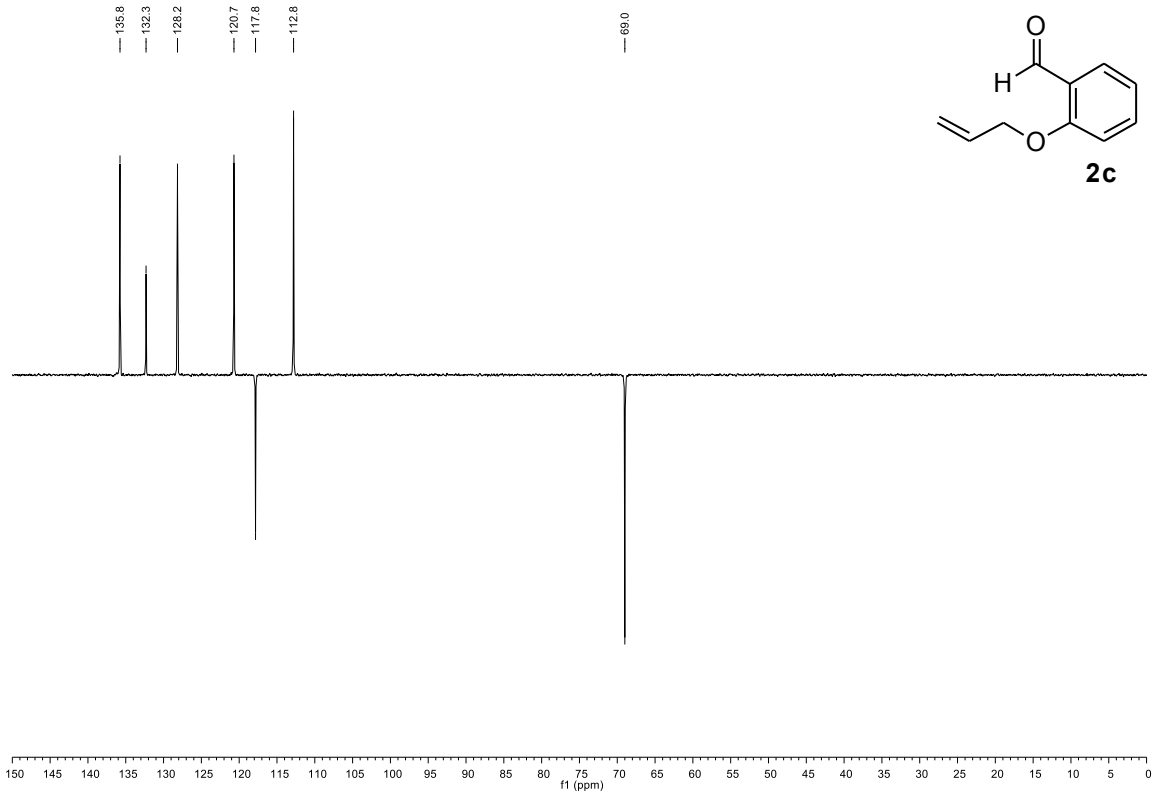
2c

^{13}C NMR (75 MHz, $CDCl_3$)



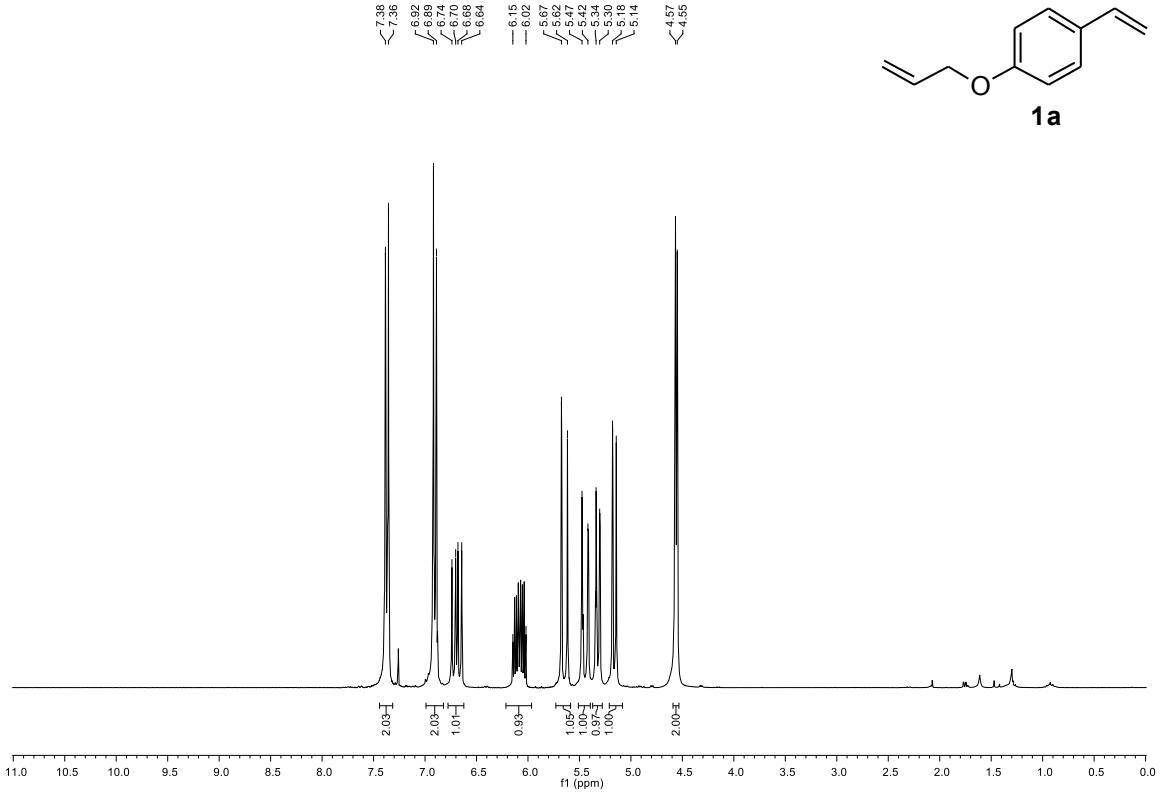
2c

DEPT-135 NMR (75 MHz, $CDCl_3$)



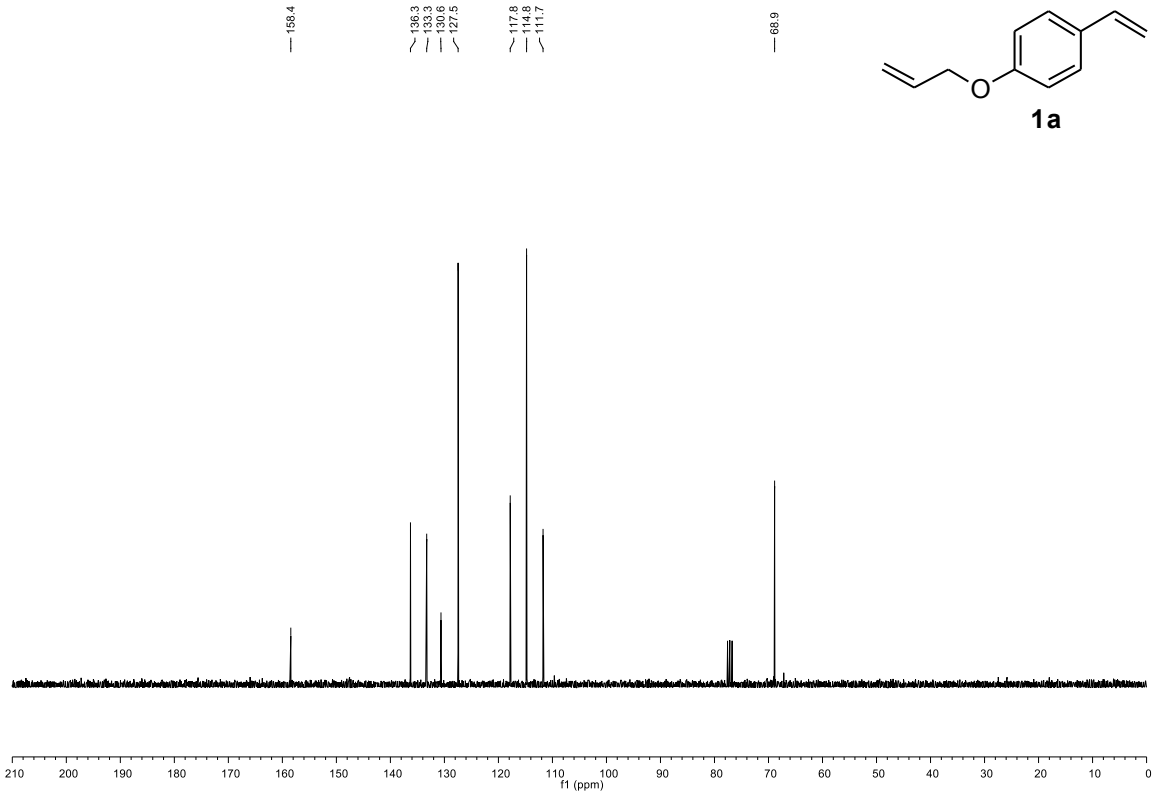
1-Allyloxy-4-vinylbenzene (1a)

^{1}H NMR (300 MHz, $CDCl_3$)



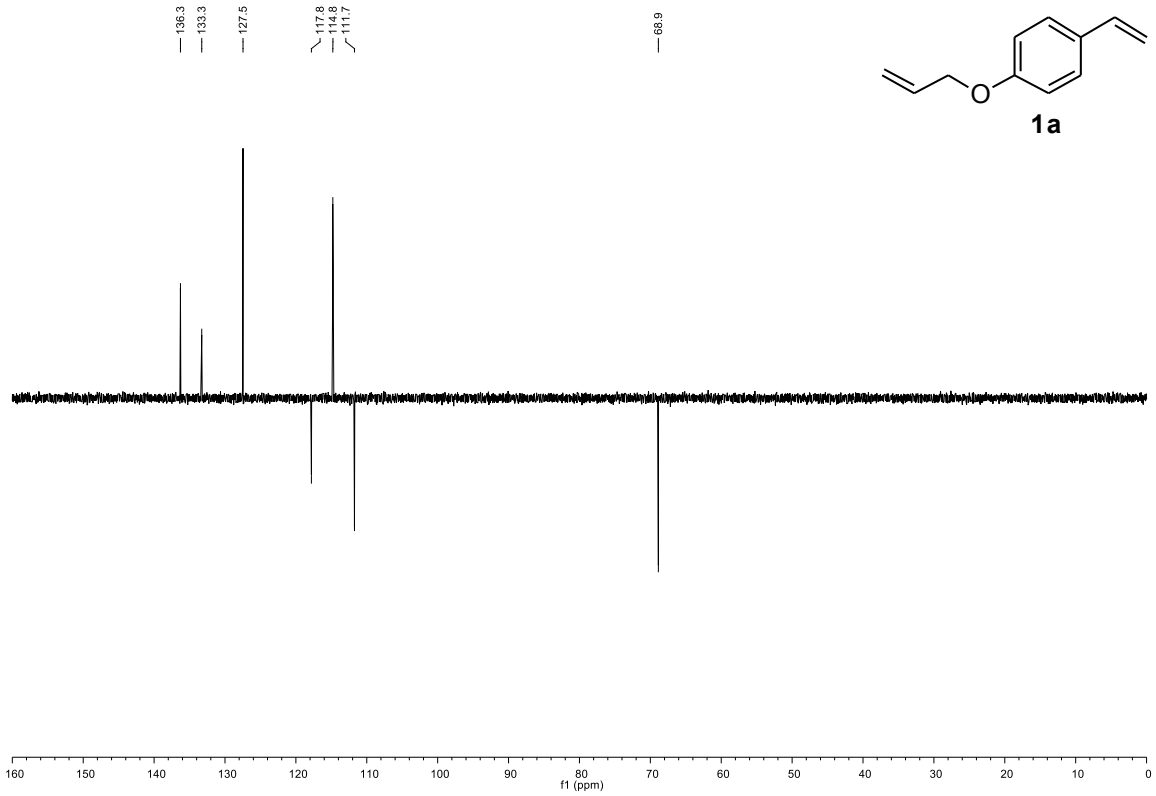
1a

^{13}C NMR (75 MHz, $CDCl_3$)



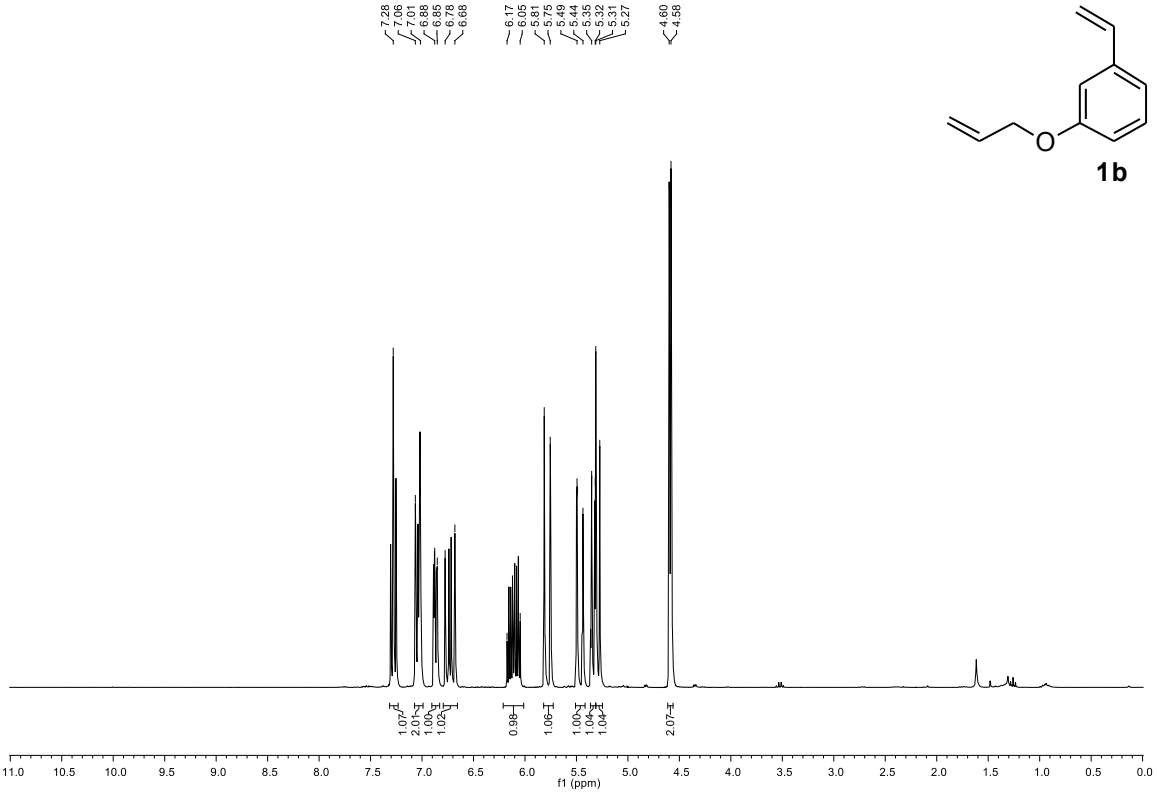
1a

DEPT-135 NMR (75 MHz, $CDCl_3$)



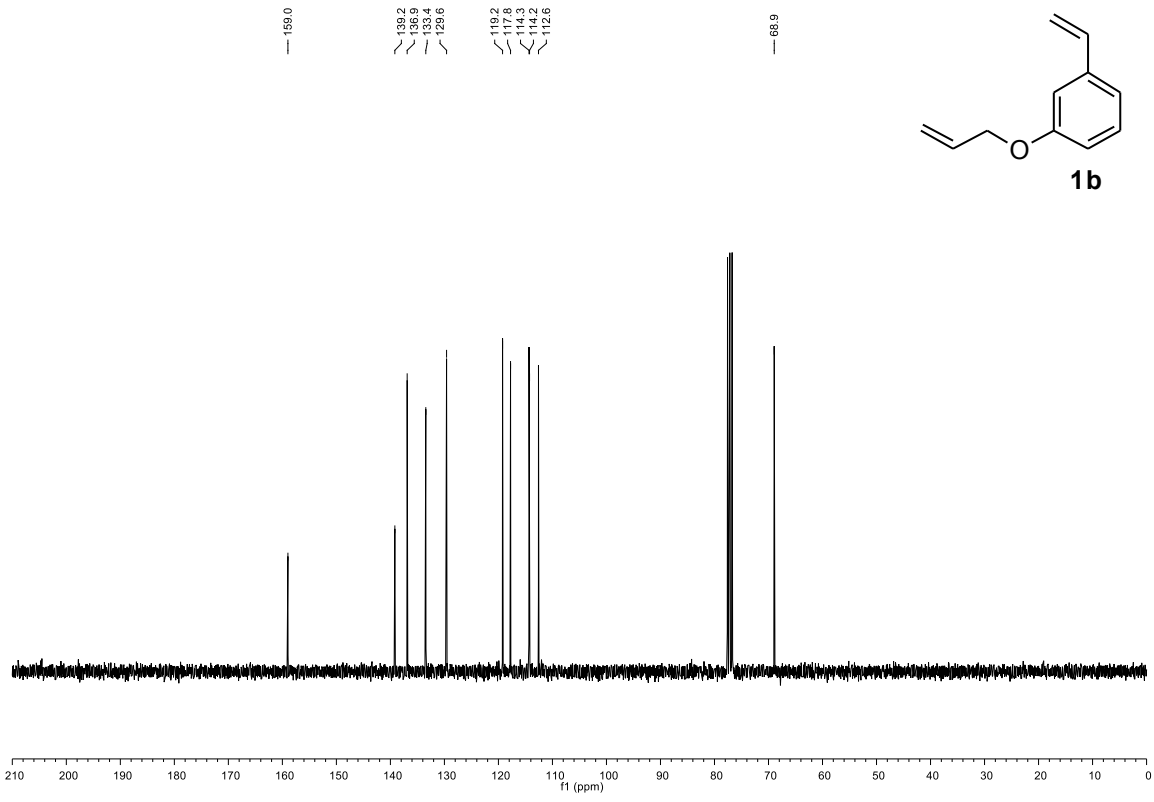
1-Allyloxy-3-vinylbenzene (1b)

^{1}H NMR (300 MHz, $CDCl_3$)



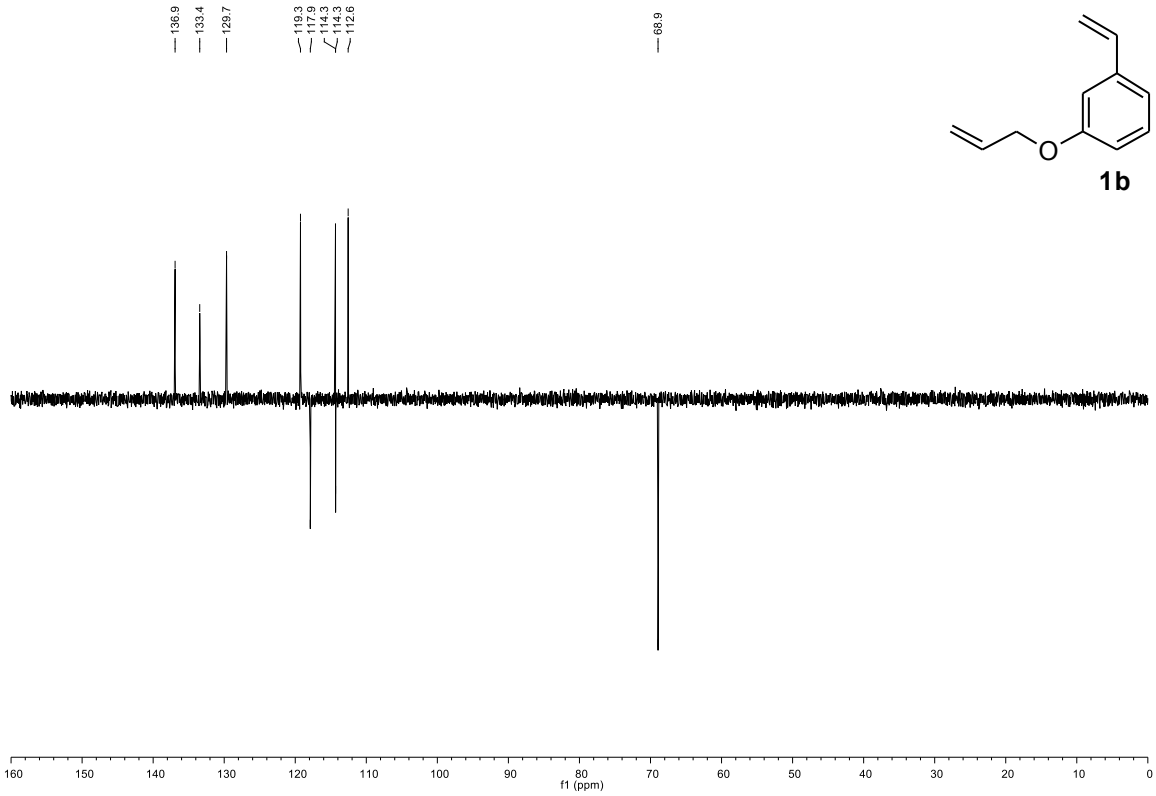
1b

^{13}C NMR (75 MHz, $CDCl_3$)



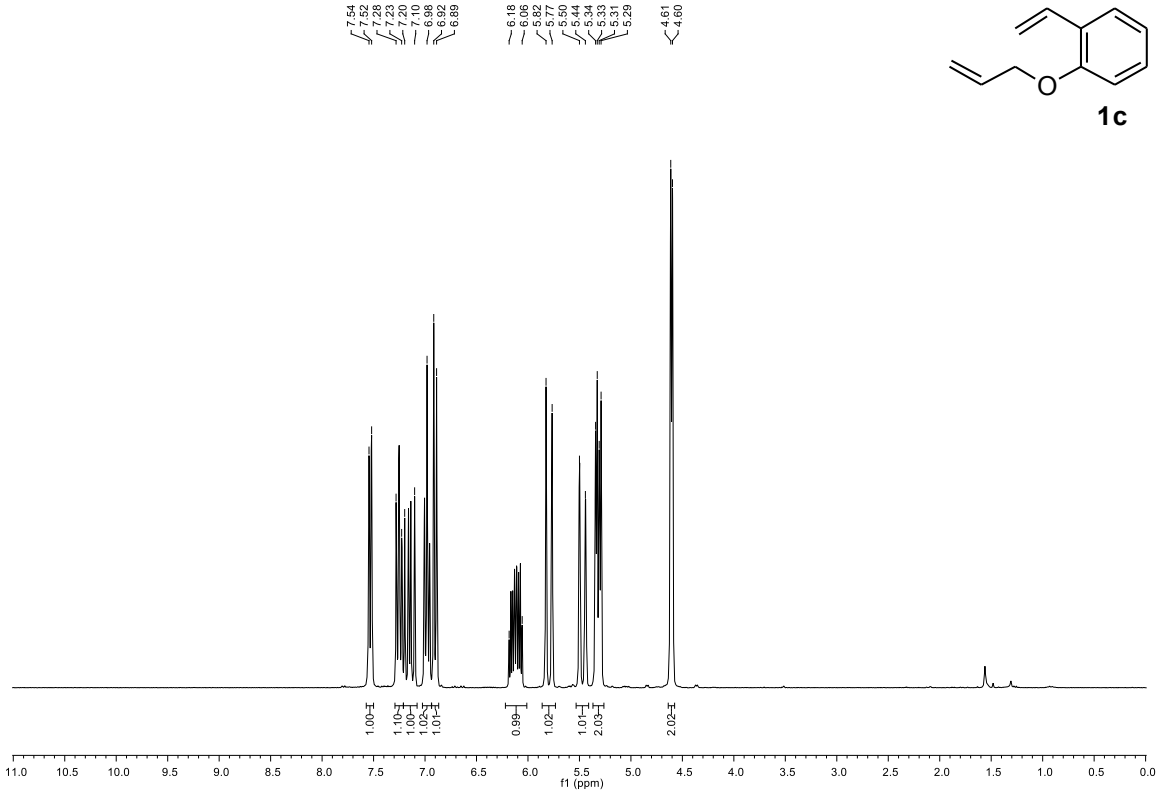
1b

DEPT-135 NMR (75 MHz, $CDCl_3$)



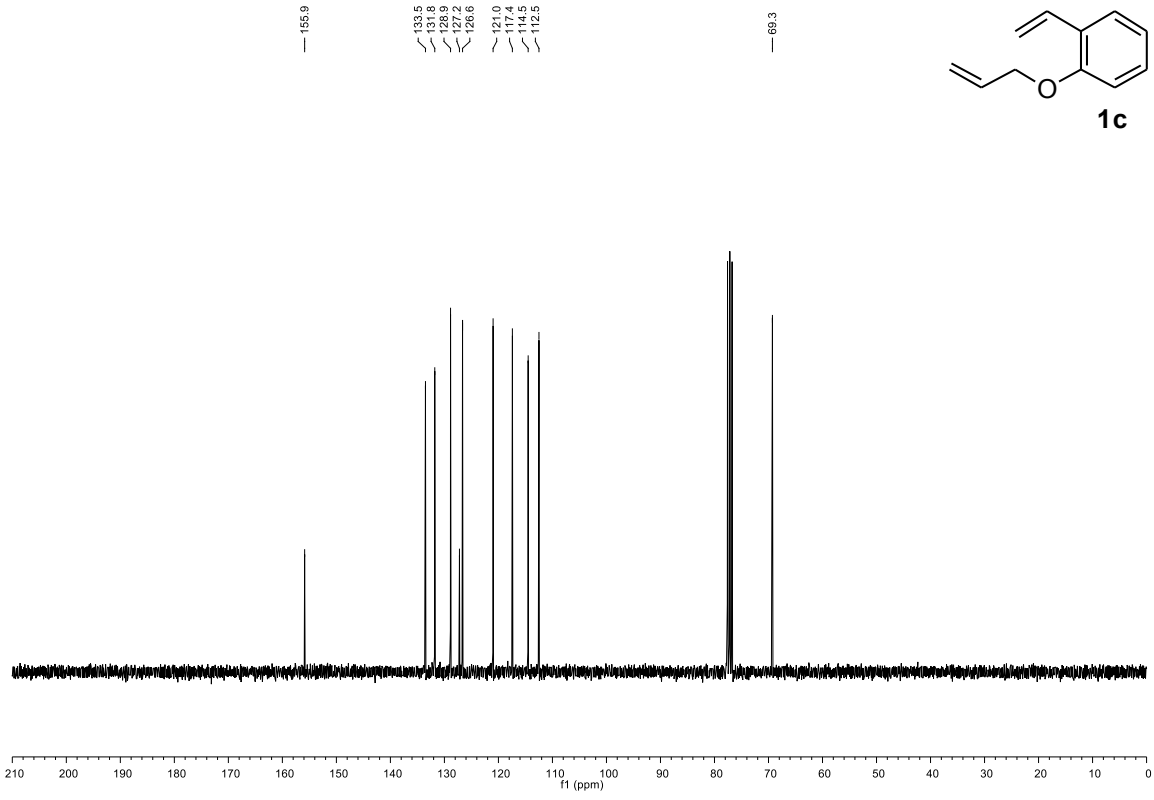
1-Allyloxy-2-vinylbenzene (1c)

^{1}H NMR (300 MHz, $CDCl_3$)



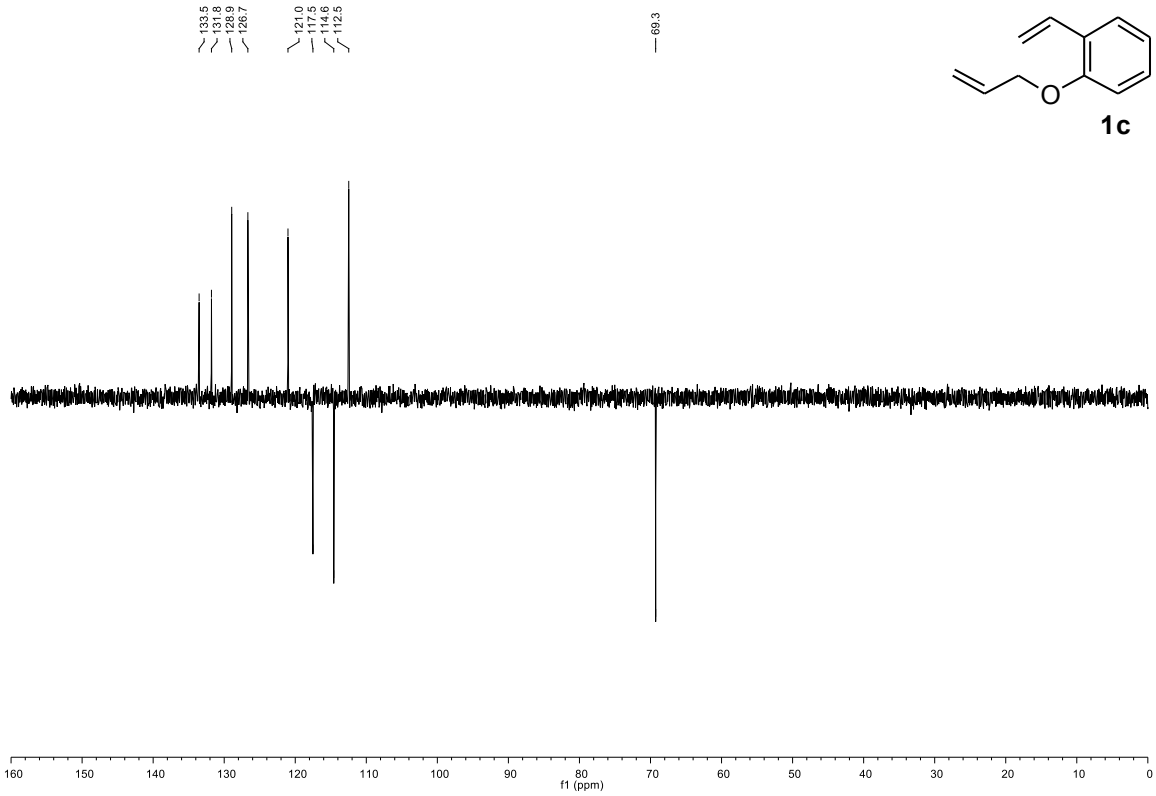
1c

^{13}C NMR (75 MHz, $CDCl_3$)



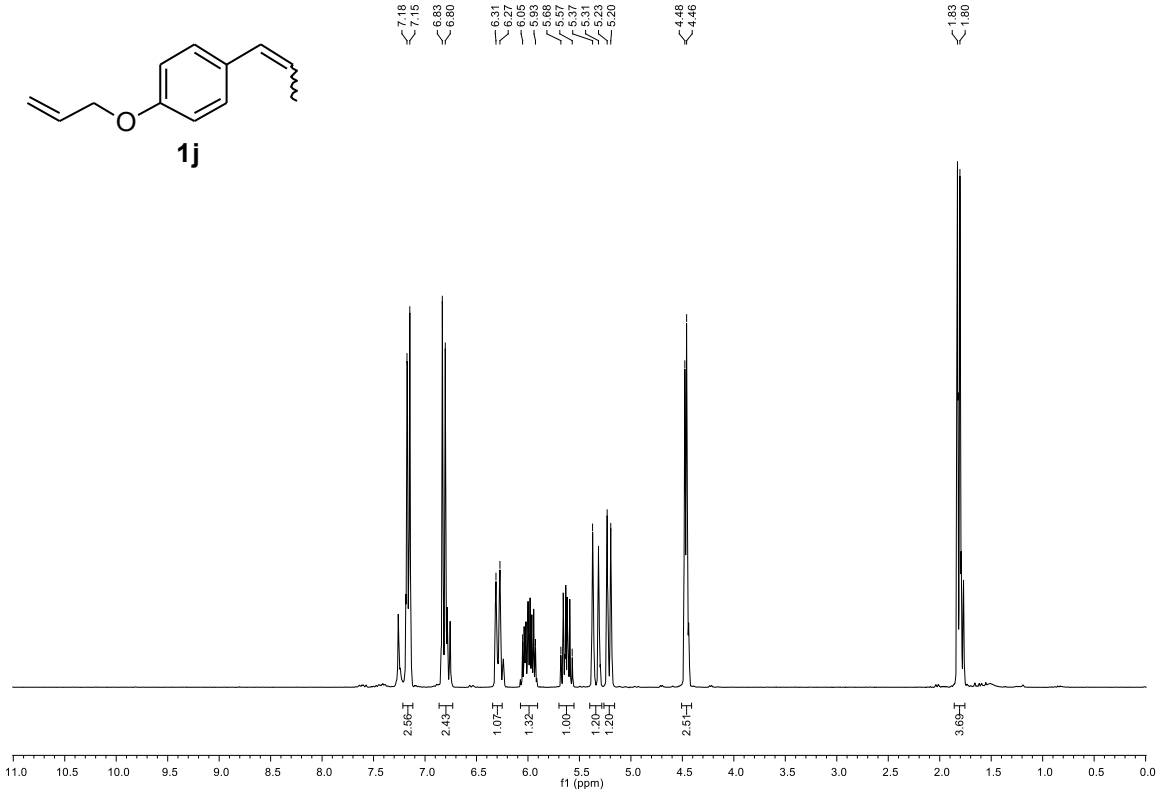
1c

DEPT-135 NMR (75 MHz, $CDCl_3$)



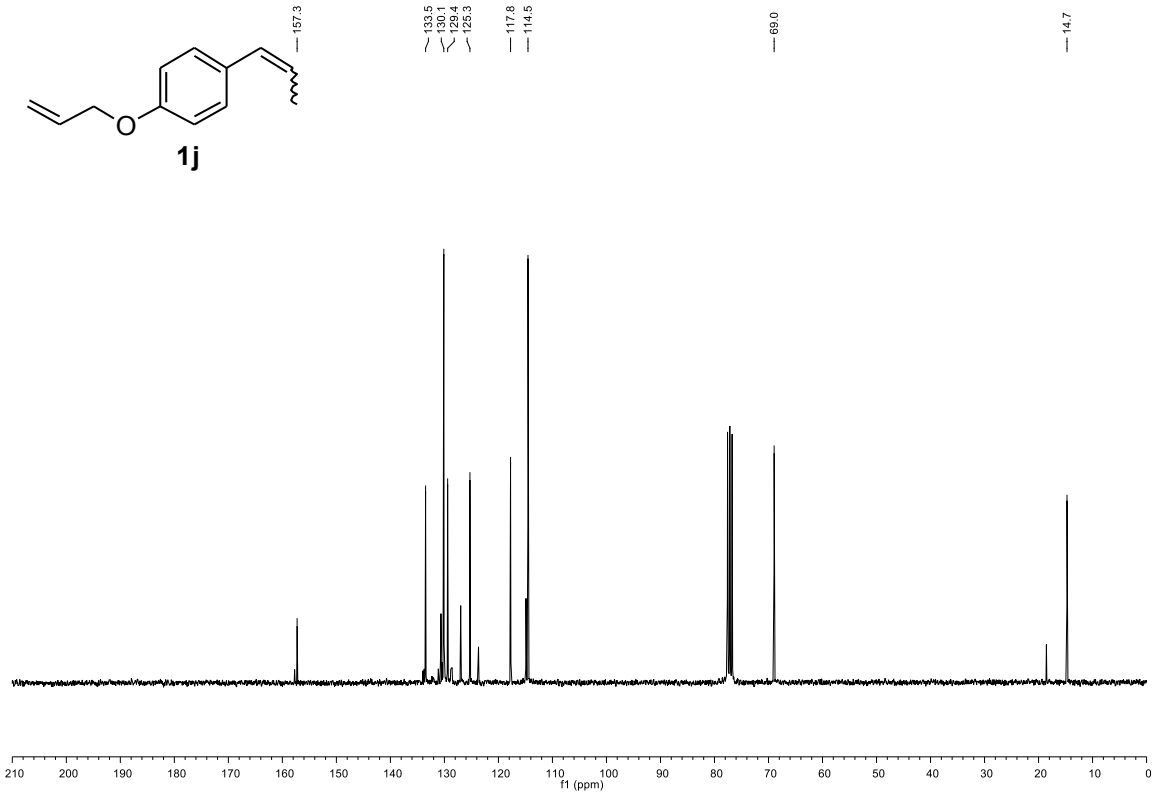
(*Z*)-1-Allyloxy-4-(prop-1-en-1-yl)benzene (1j)

^{1}H NMR (300 MHz, $CDCl_3$)



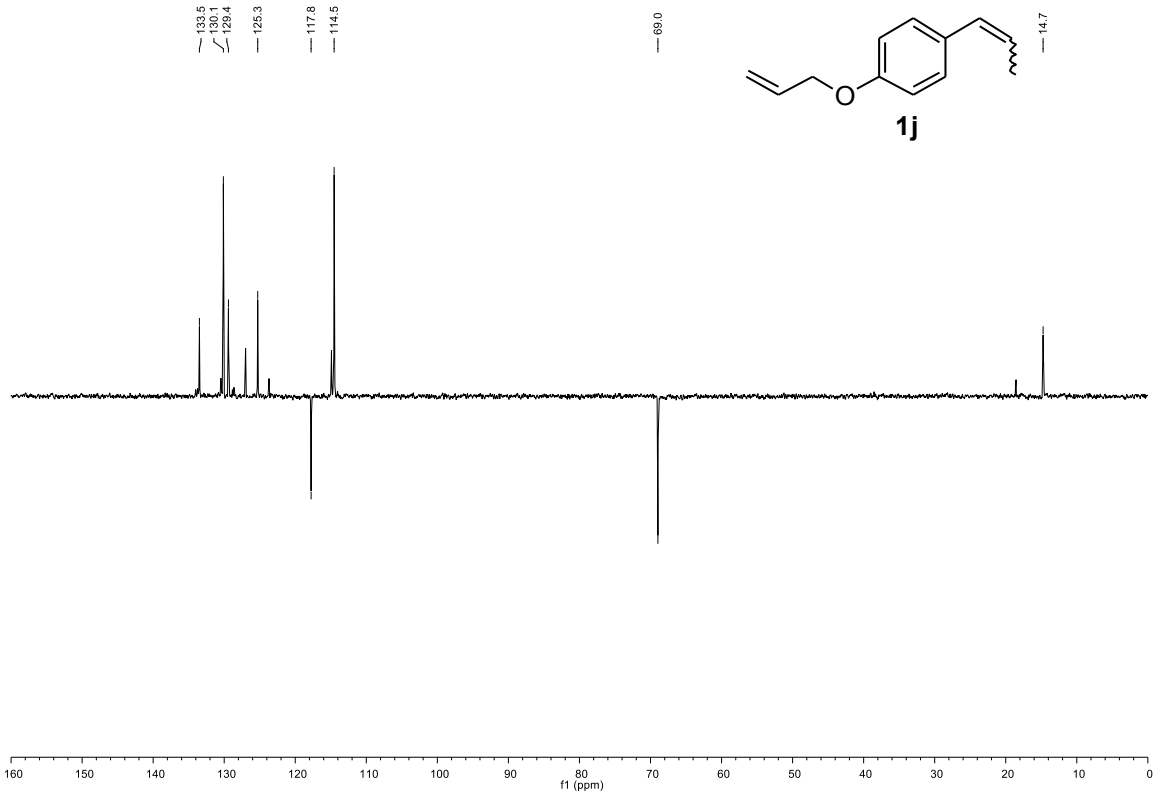
1j

^{13}C NMR (75 MHz, $CDCl_3$)



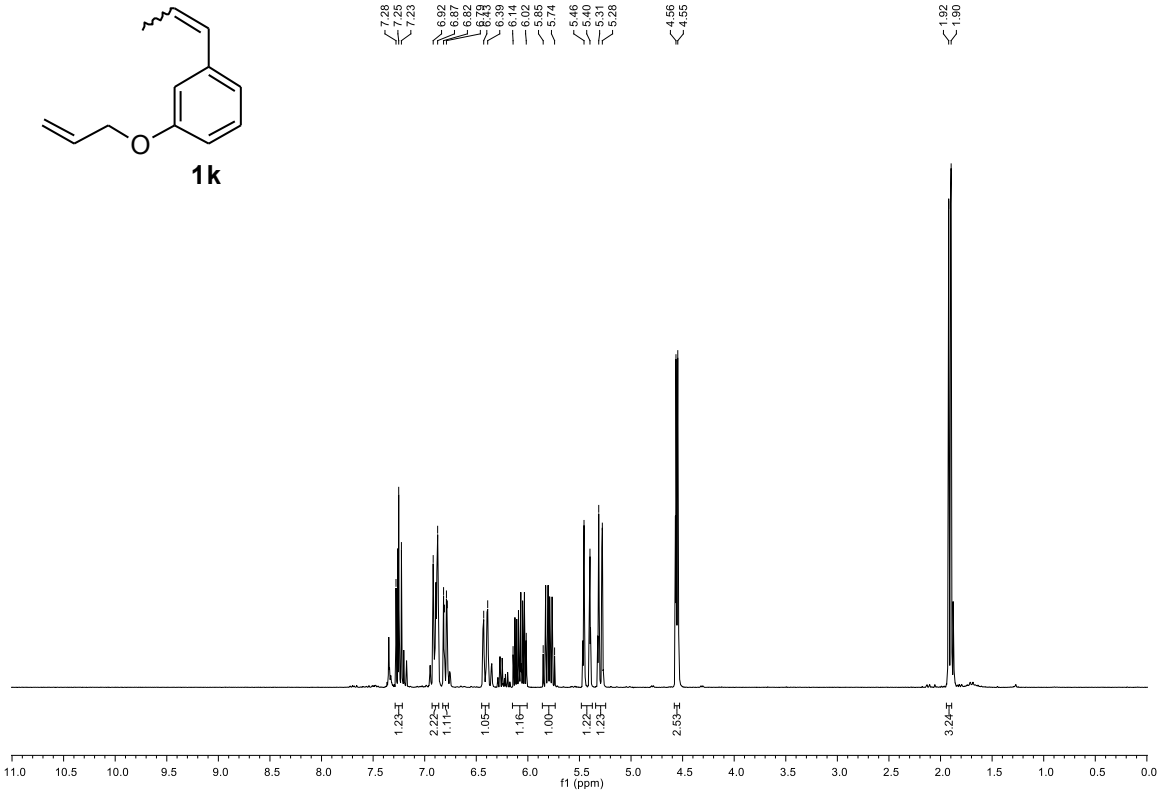
1j

DEPT-135 NMR (75 MHz, $CDCl_3$)



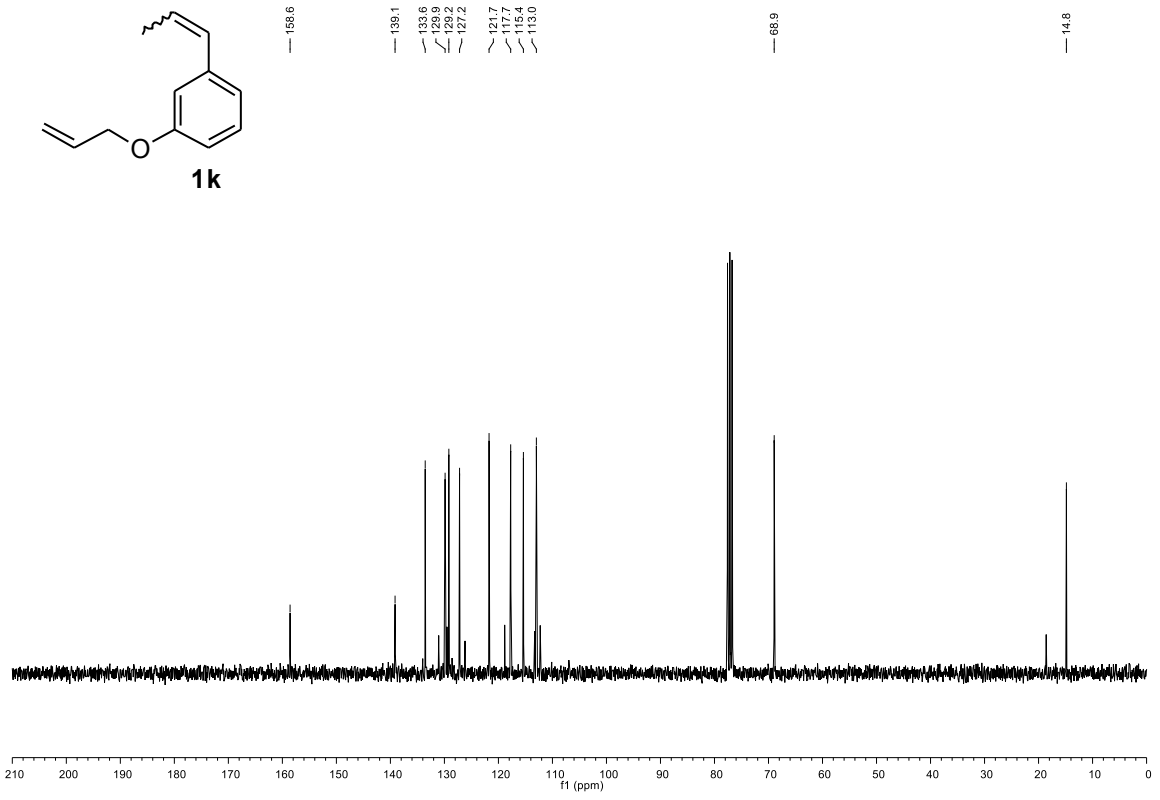
(*Z*)-1-Allyloxy-3-(prop-1-en-1-yl)benzene (1k)

^{1}H NMR (300 MHz, $CDCl_3$)



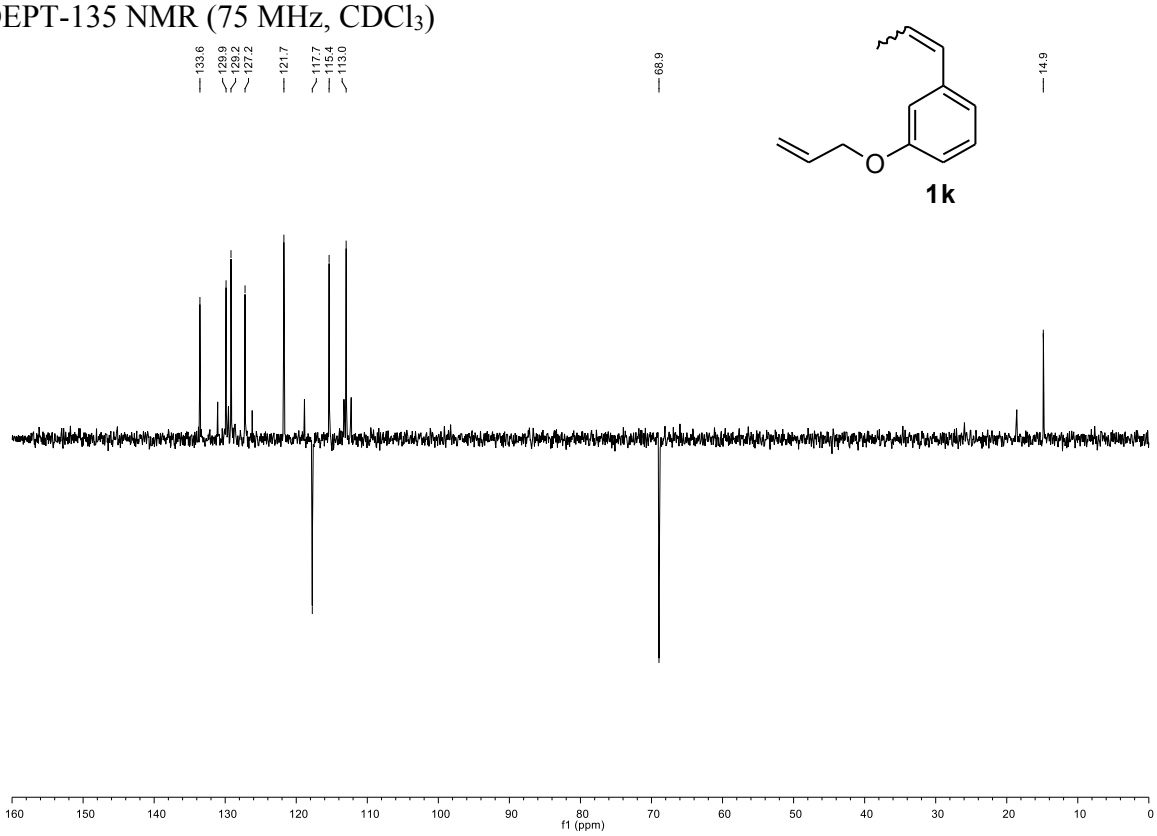
1k

^{13}C NMR (75 MHz, $CDCl_3$)



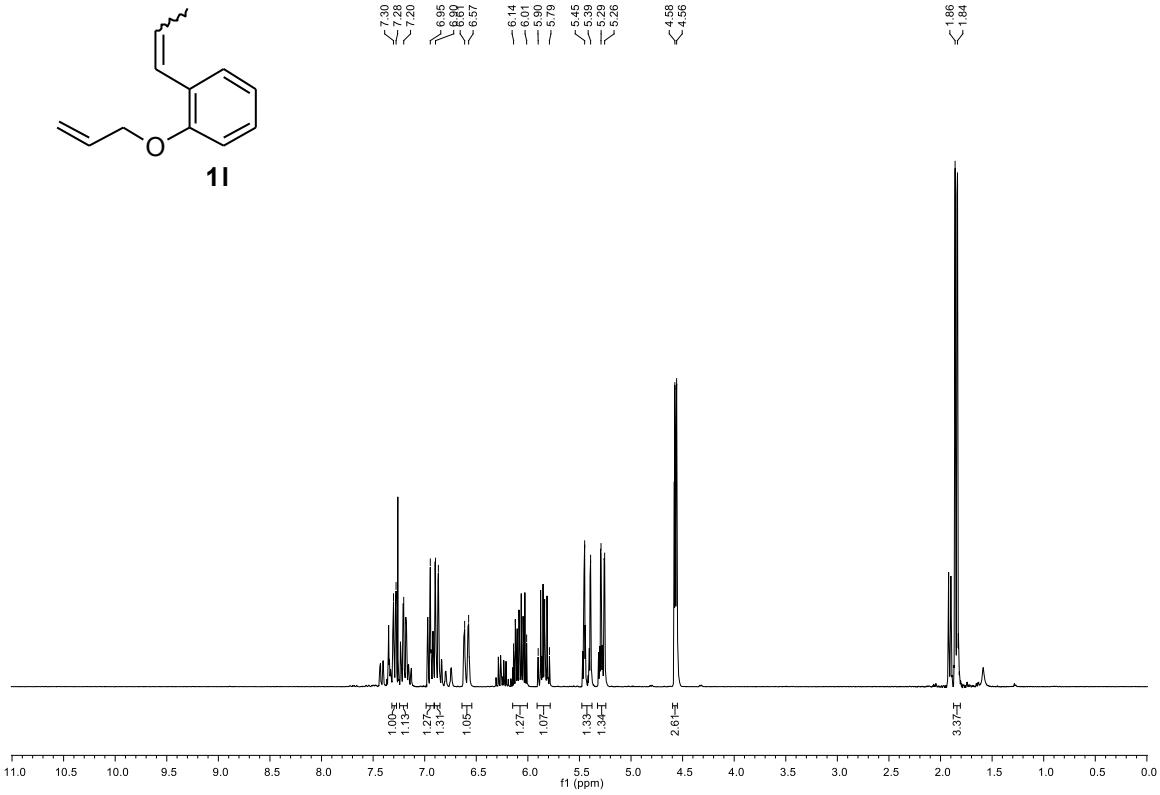
1k

DEPT-135 NMR (75 MHz, $CDCl_3$)



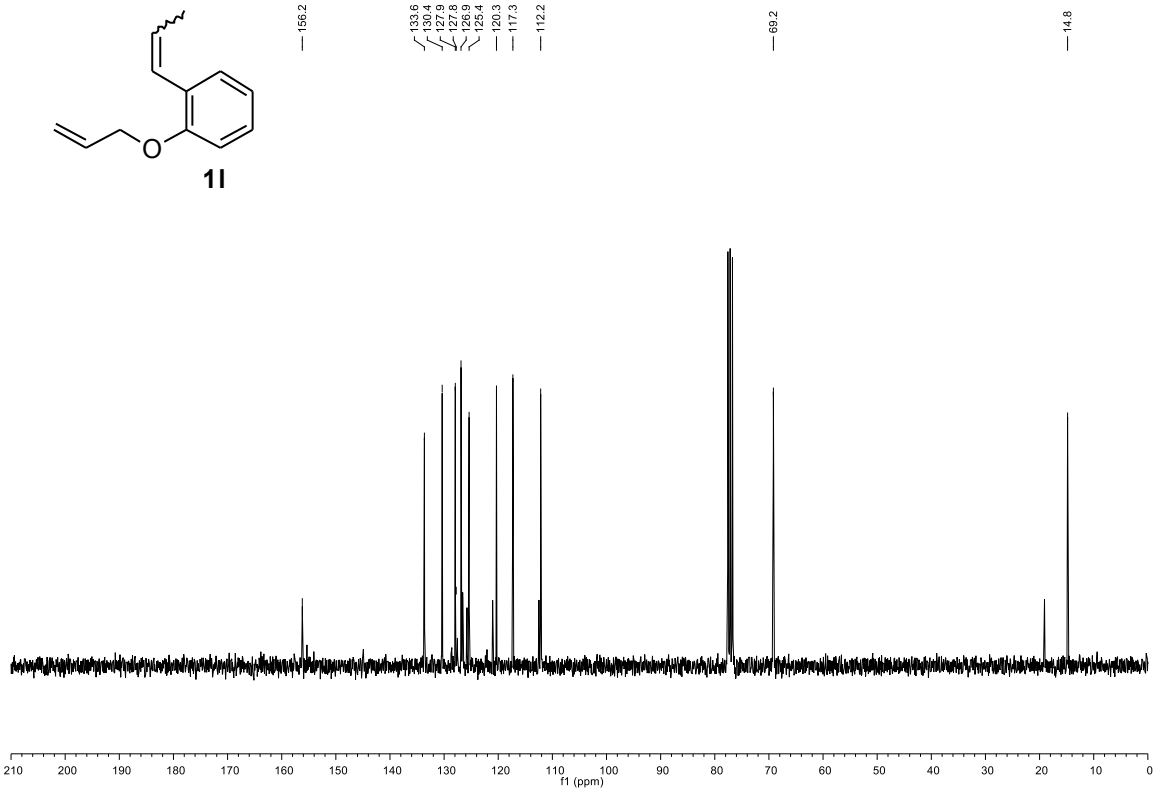
(*Z*)-1-Allyloxy-2-(prop-1-en-1-yl)benzene (1l)

^{1}H NMR (300 MHz, $CDCl_3$)



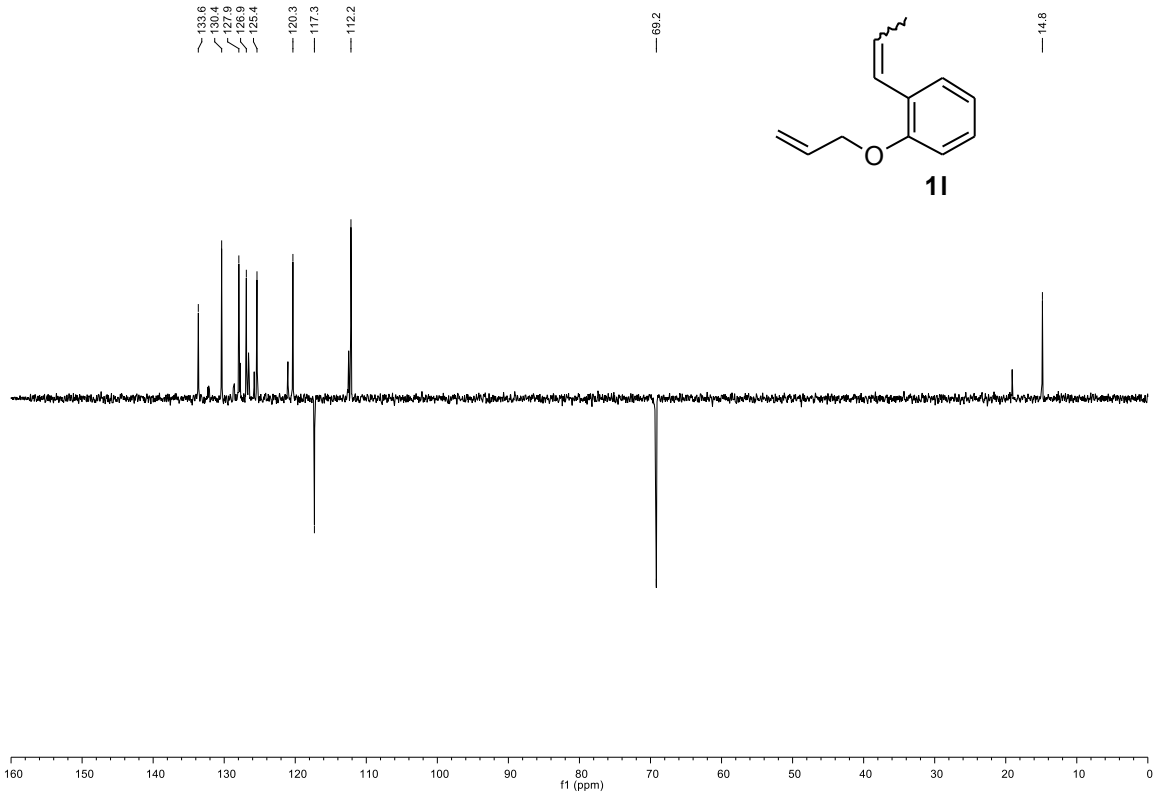
1l

^{13}C NMR (75 MHz, $CDCl_3$)



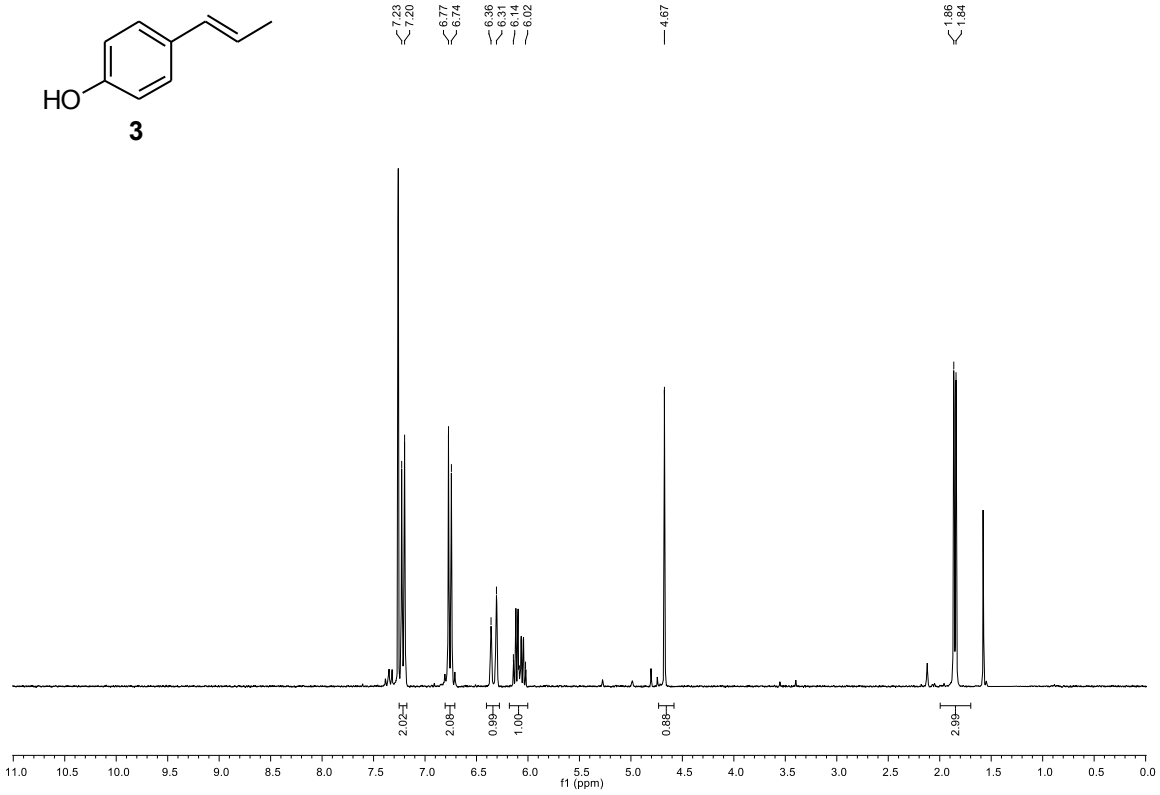
1l

DEPT-135 NMR (75 MHz, $CDCl_3$)

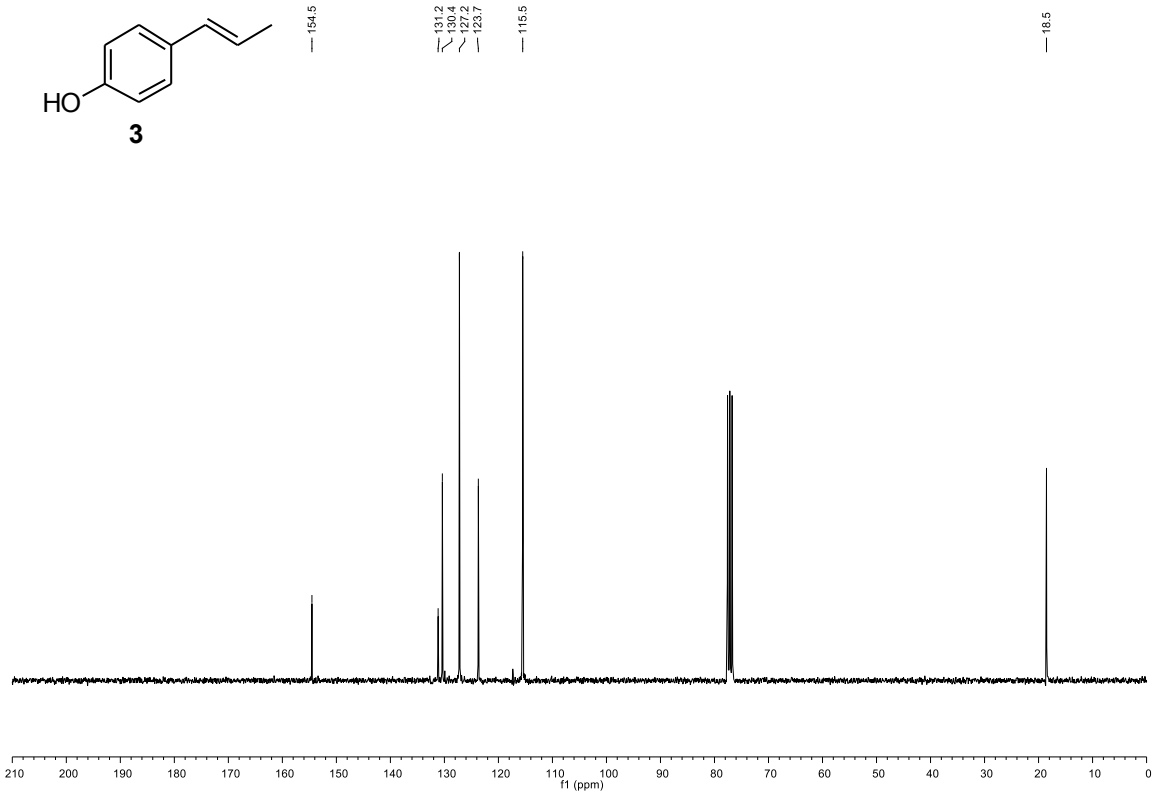


(*E*)-4-(prop-1-en-1-yl)phenol (3)

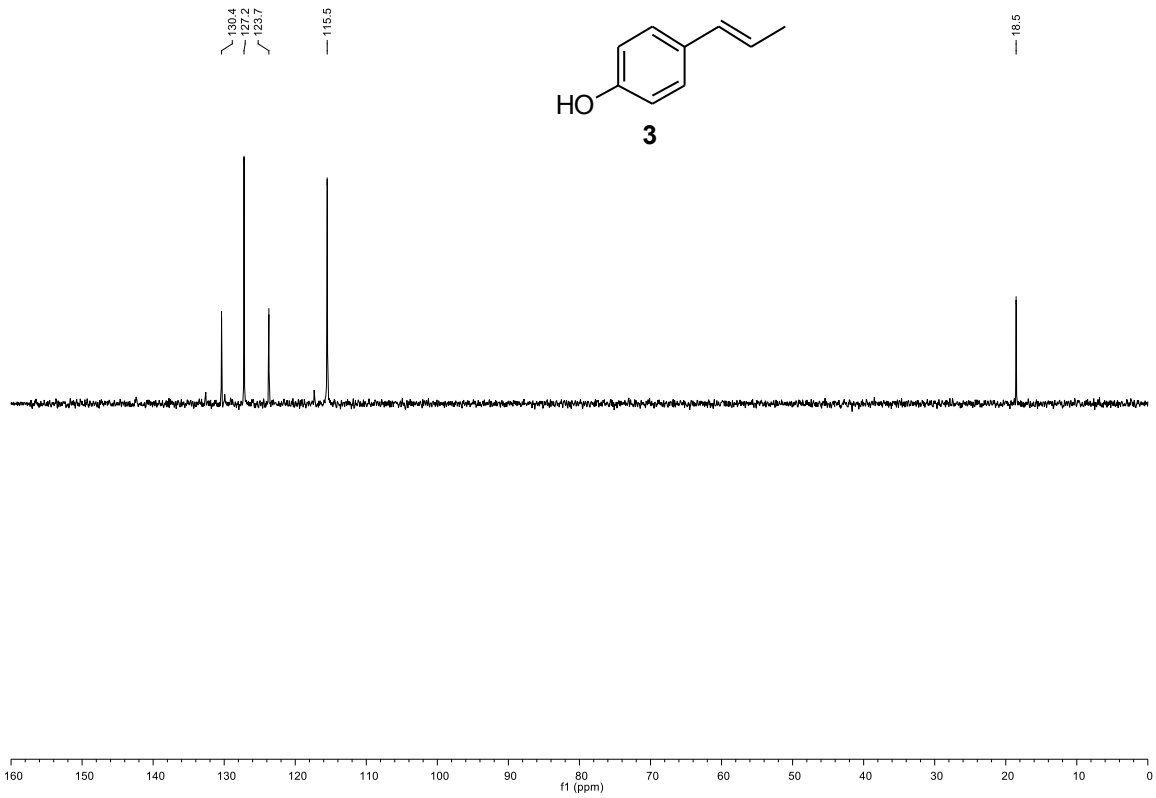
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

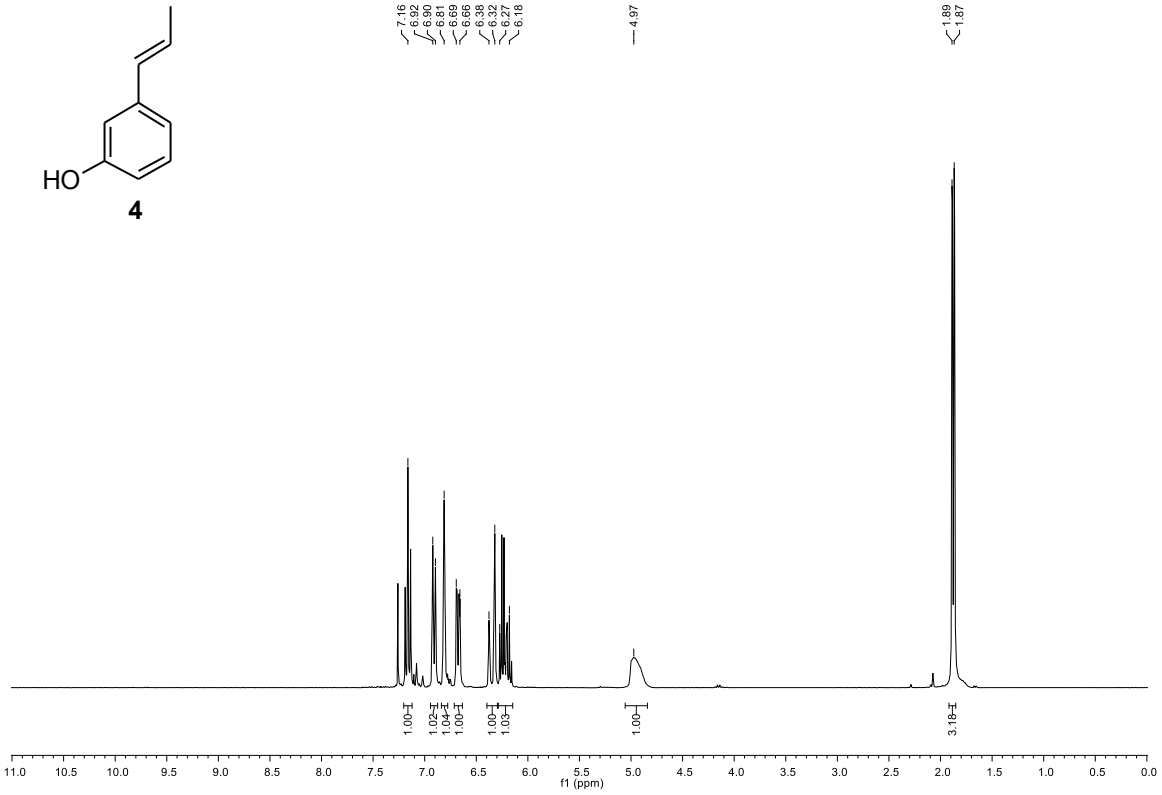


DEPT-135 NMR (75 MHz, $CDCl_3$)

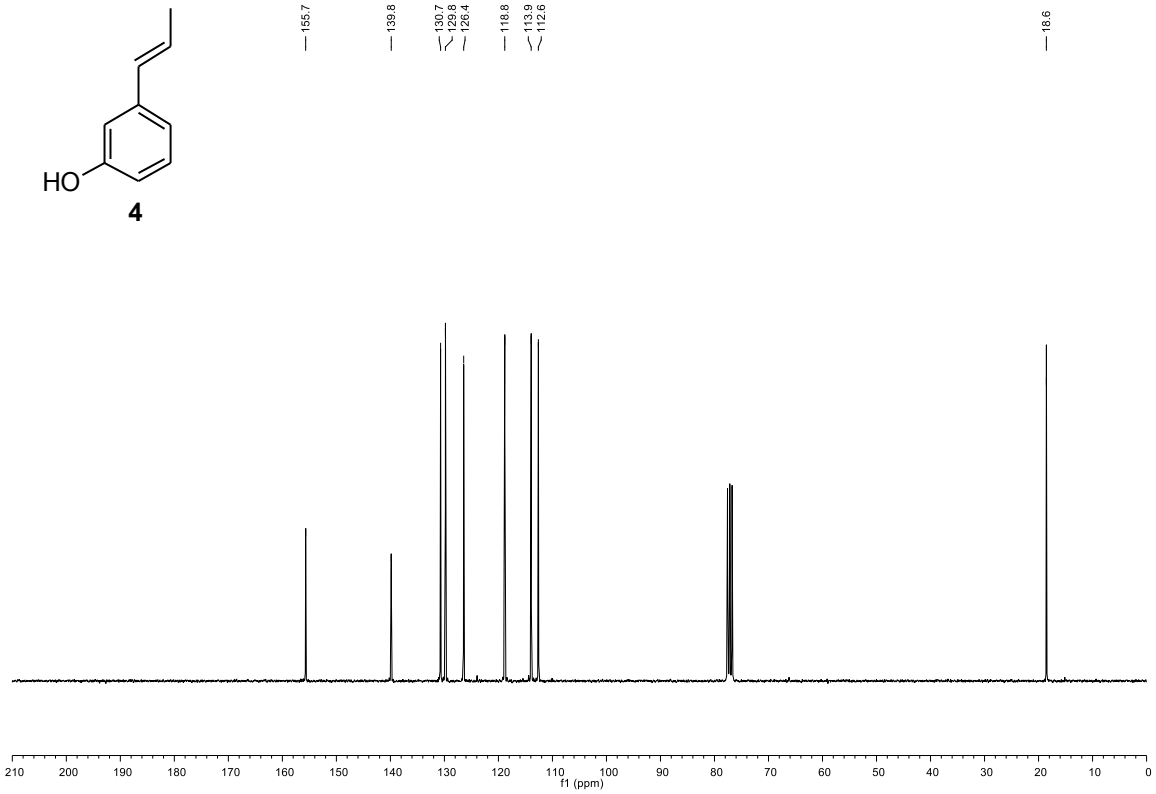


(*E*)-3-(prop-1-en-1-yl)phenol (4)

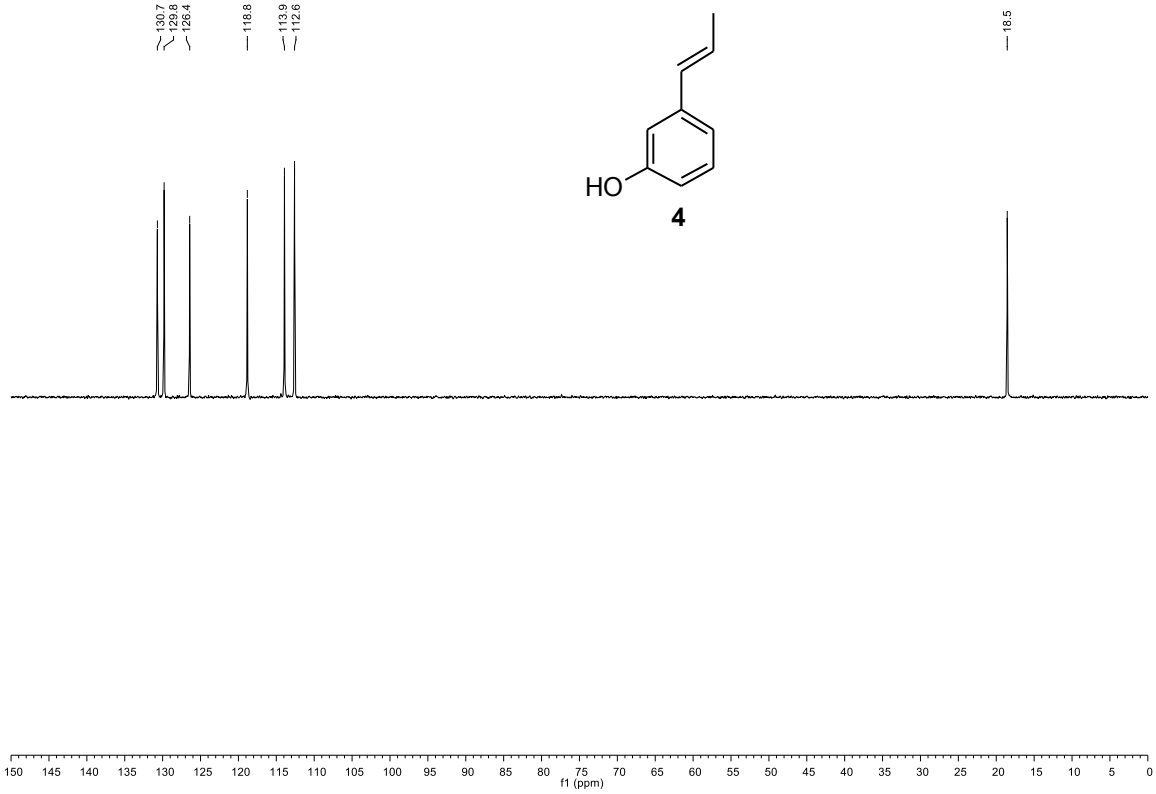
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

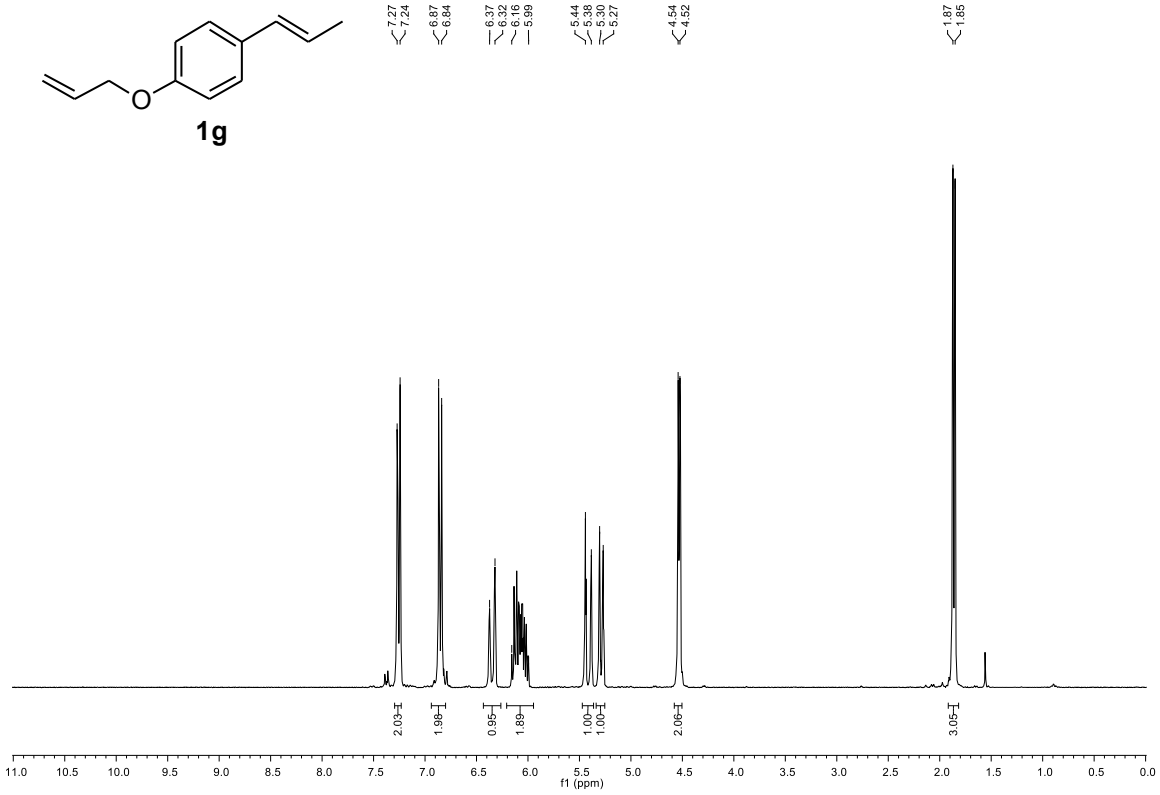


DEPT-135 NMR (75 MHz, $CDCl_3$)

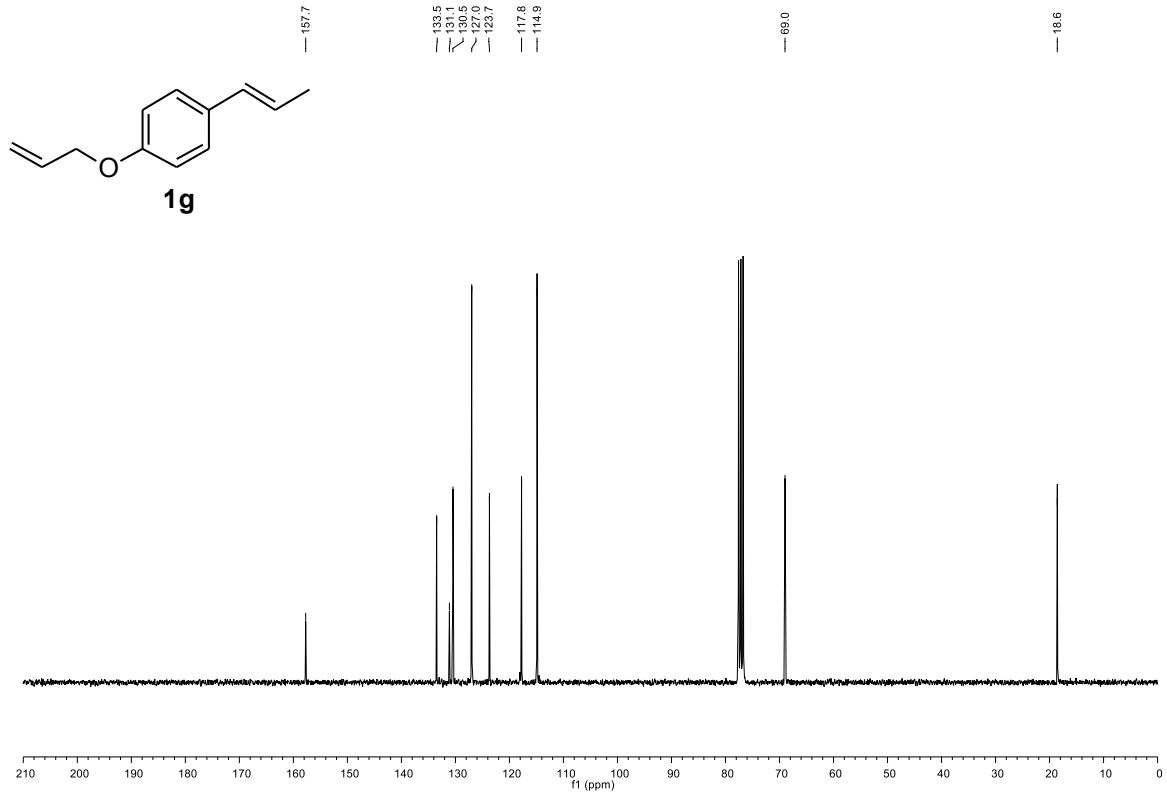


(*E*)-1-Allyloxy-4-(prop-1-en-1-yl)benzene (1g)

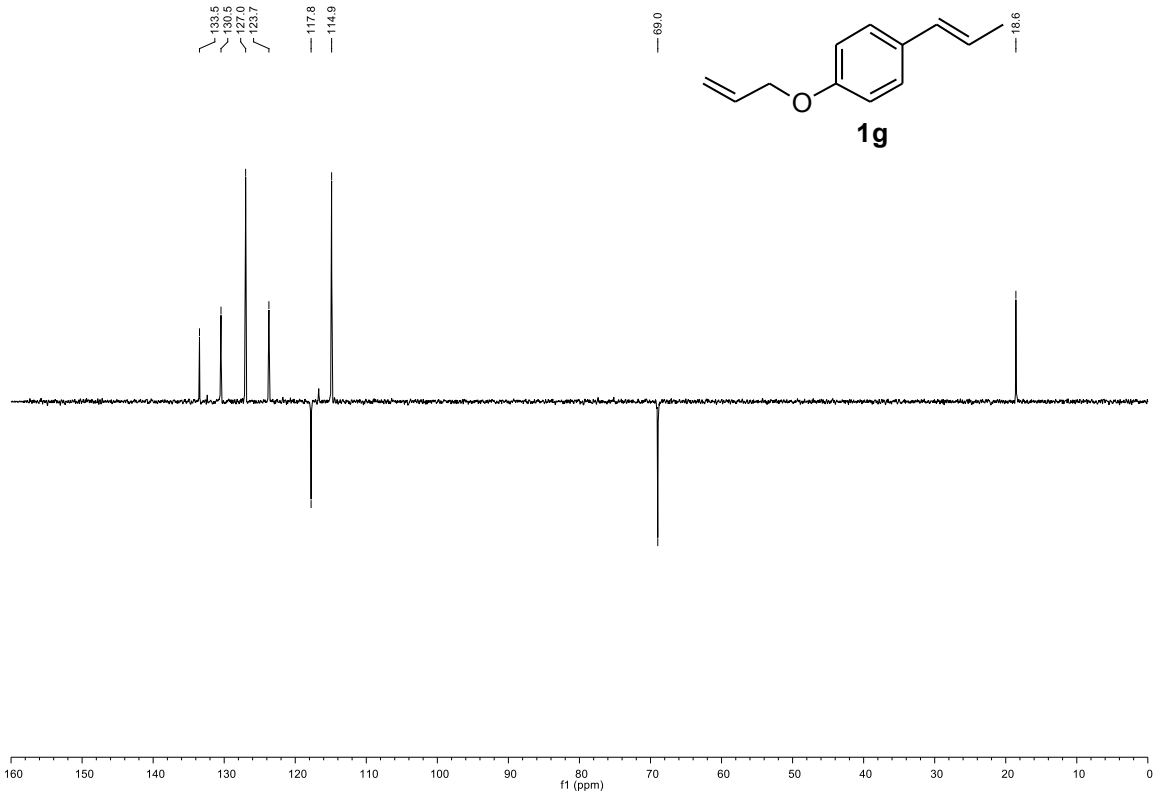
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

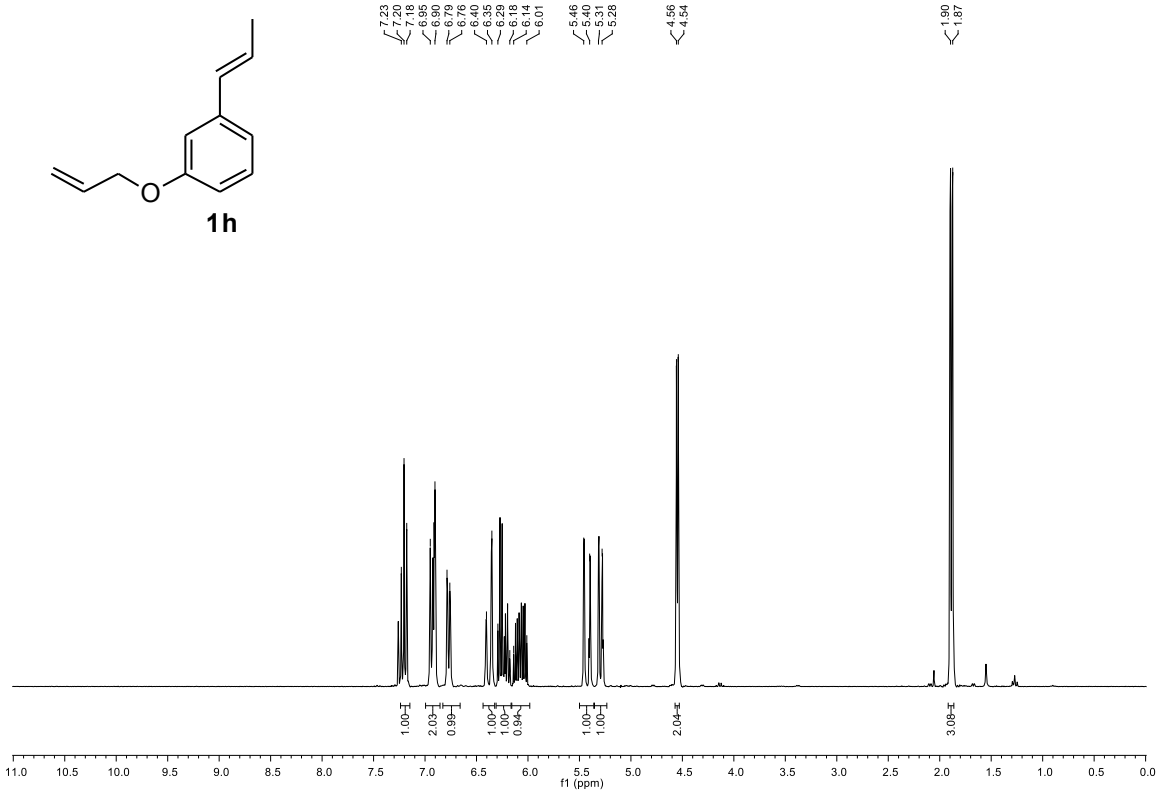


DEPT-135 NMR (75 MHz, $CDCl_3$)



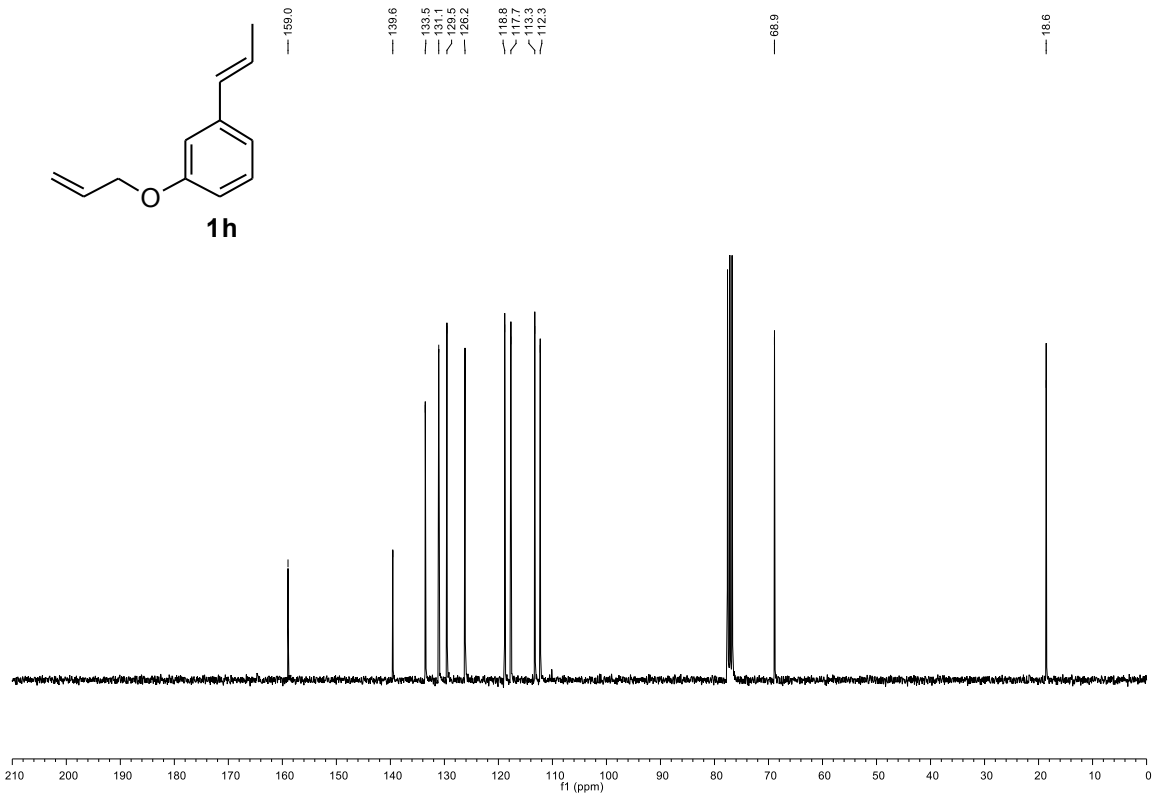
(*E*)-1-Allyloxy-3-(prop-1-en-1-yl)benzene (1h)

^{1}H NMR (300 MHz, $CDCl_3$)



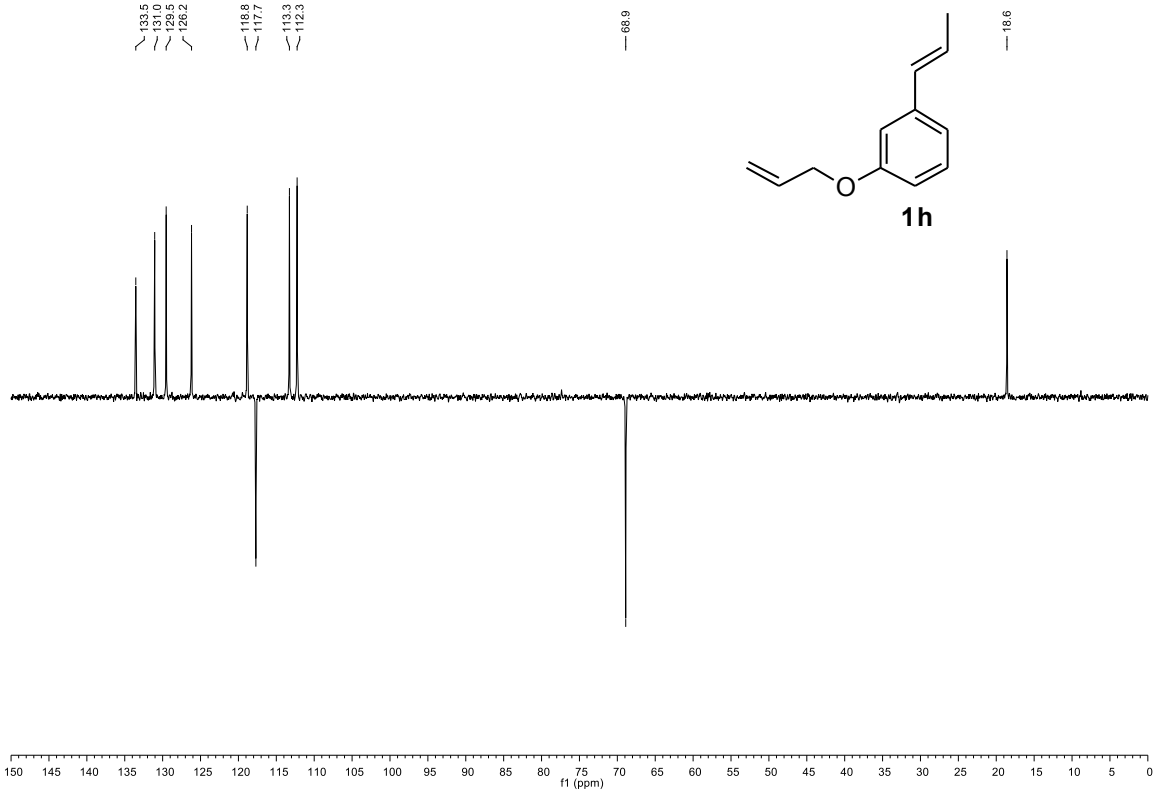
1h

^{13}C NMR (75 MHz, $CDCl_3$)



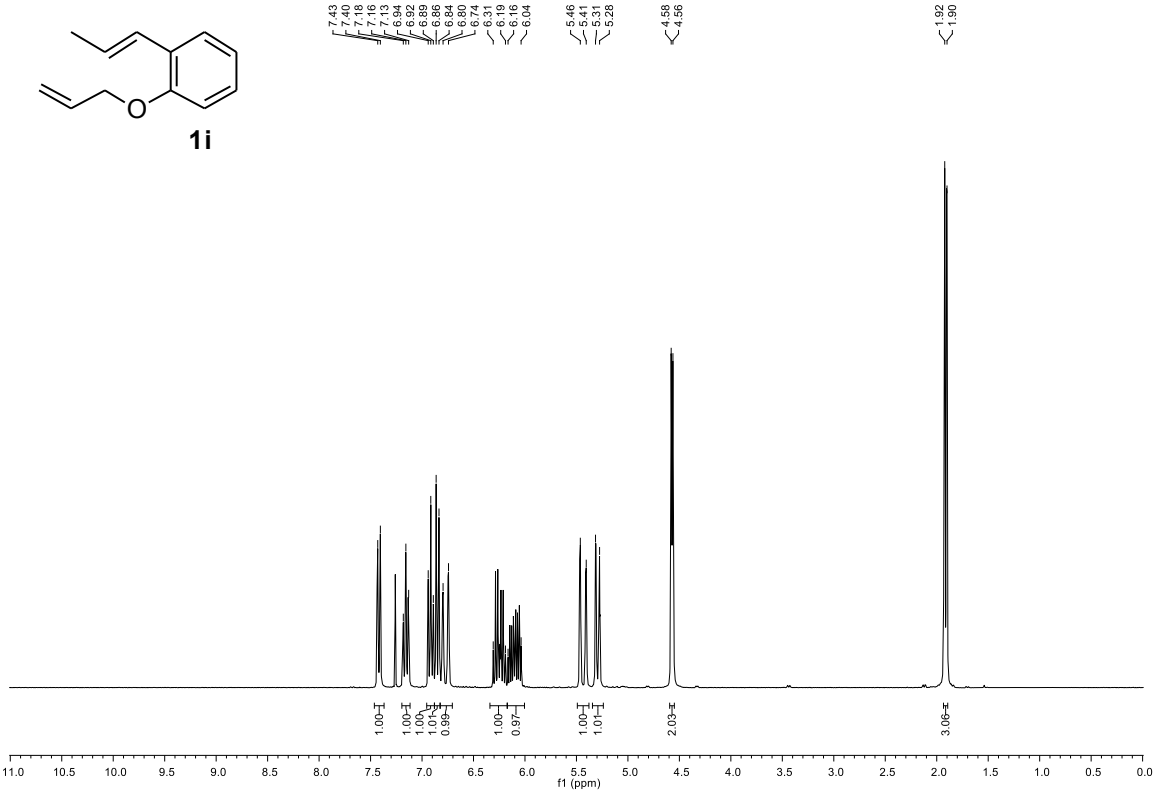
1h

DEPT-135 NMR (75 MHz, $CDCl_3$)



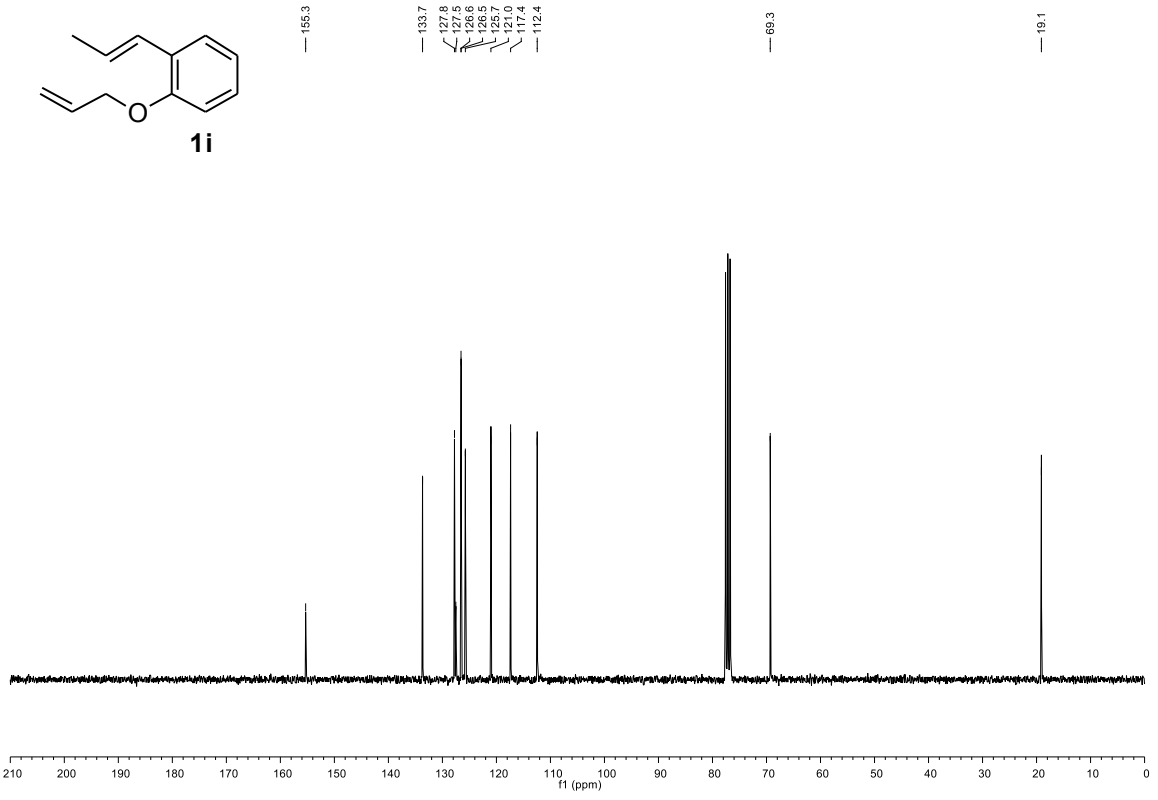
(*E*)-1-Allyloxy-2-(prop-1-en-1-yl)benzene (1i)

^{1}H NMR (300 MHz, $CDCl_3$)



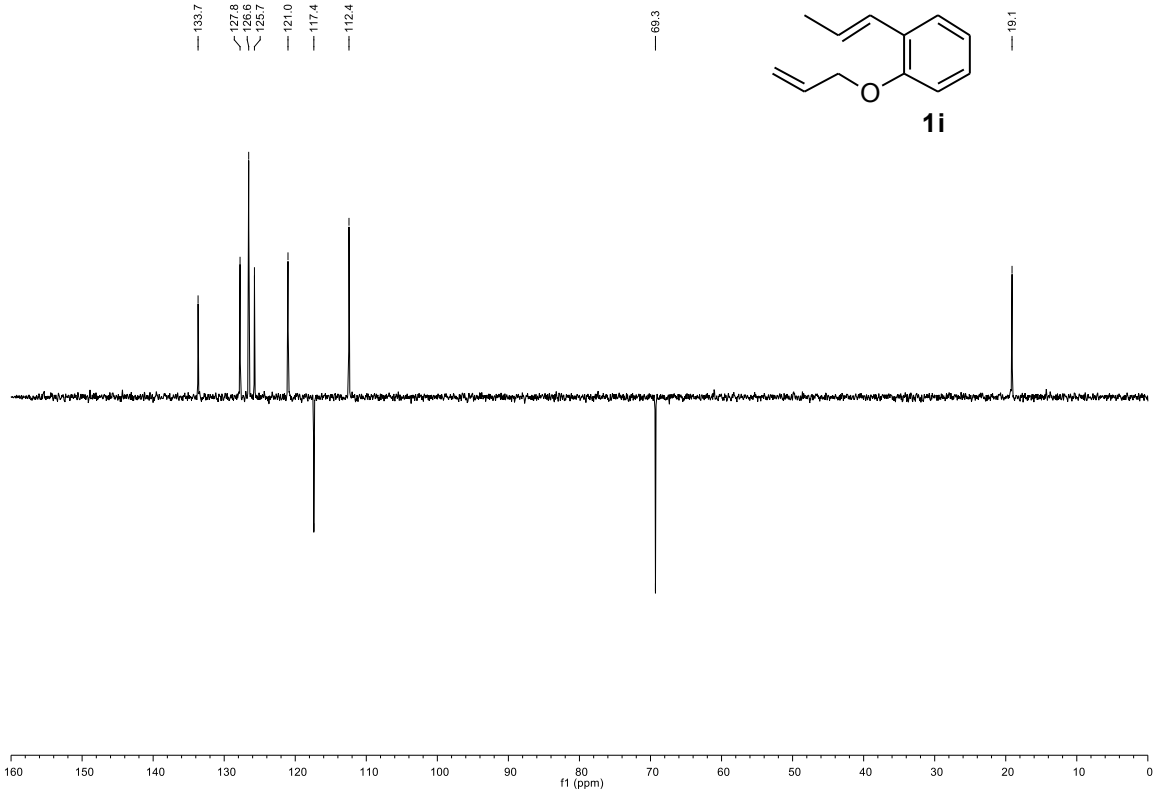
1i

^{13}C NMR (75 MHz, $CDCl_3$)



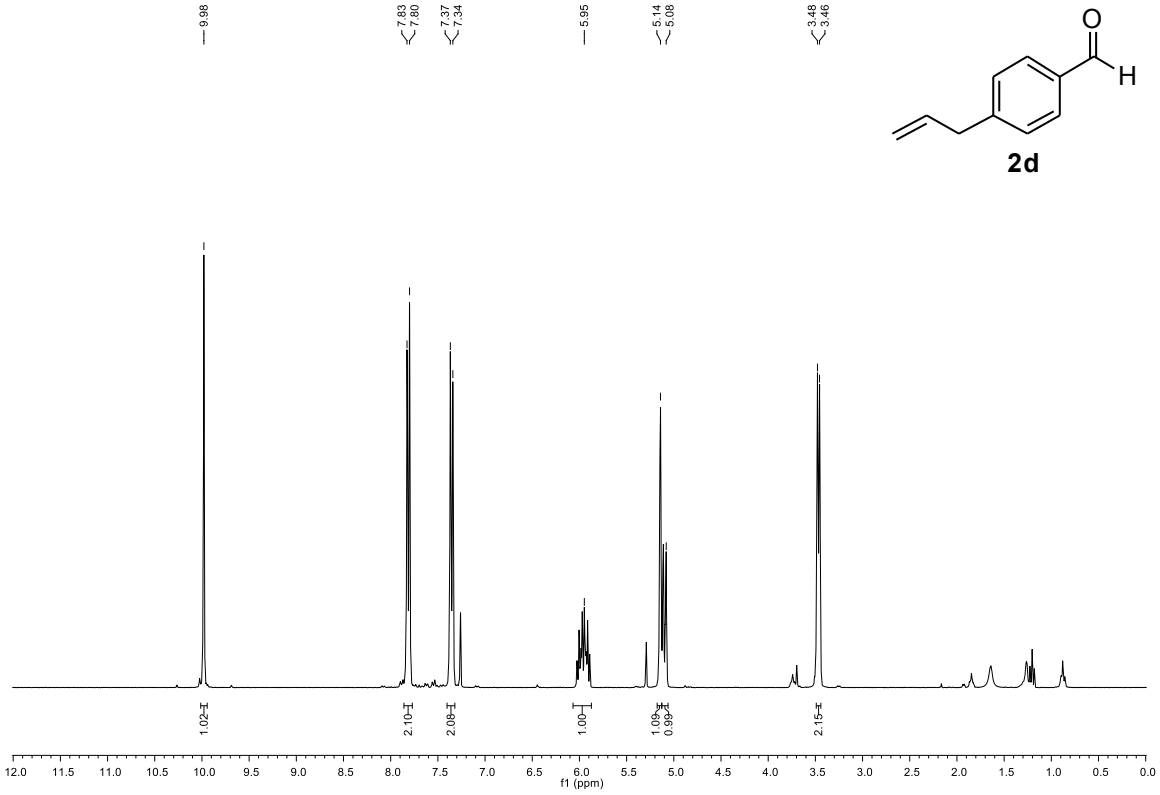
1i

DEPT-135 NMR (75 MHz, $CDCl_3$)

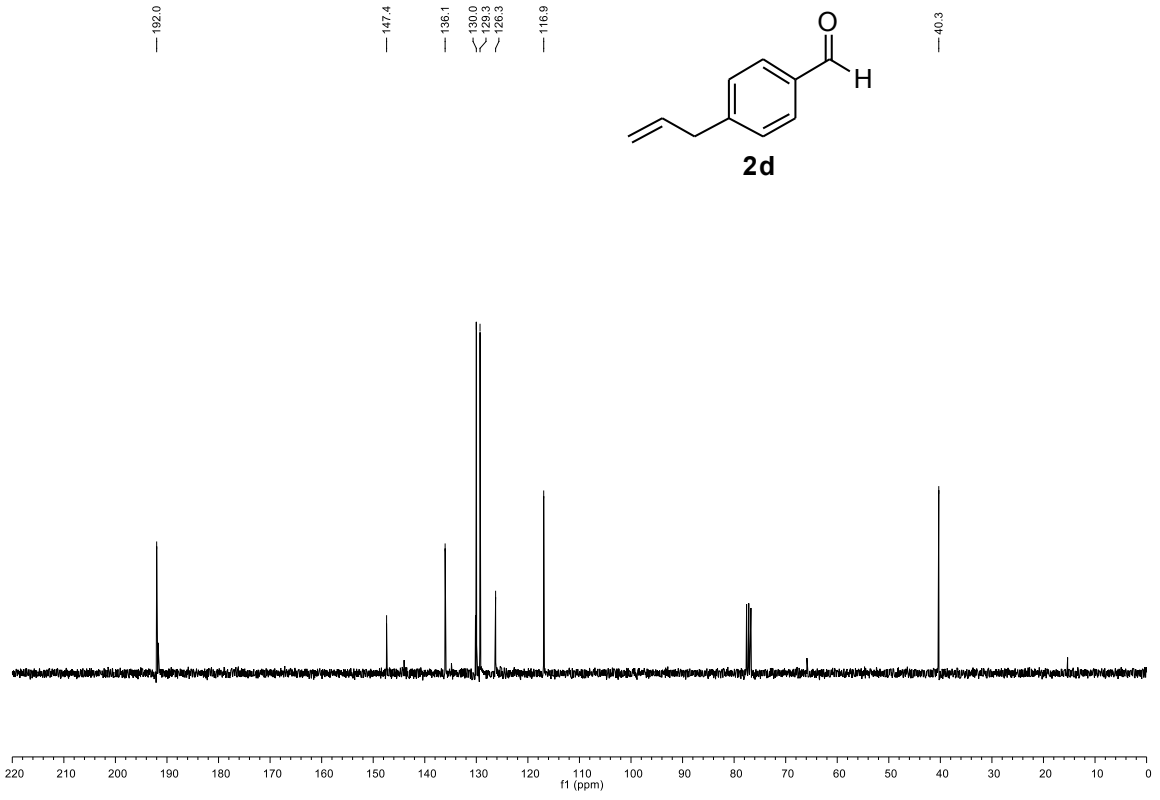


4-Allylbenzaldehyde (2d)

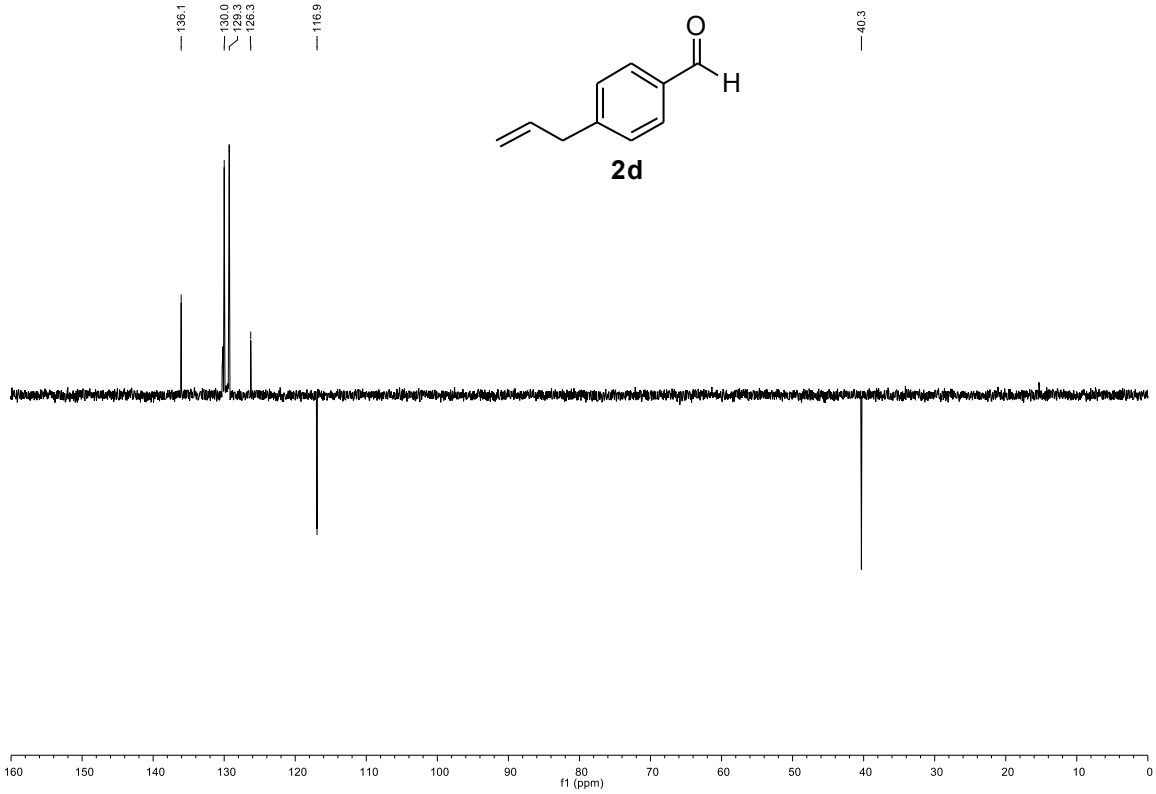
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

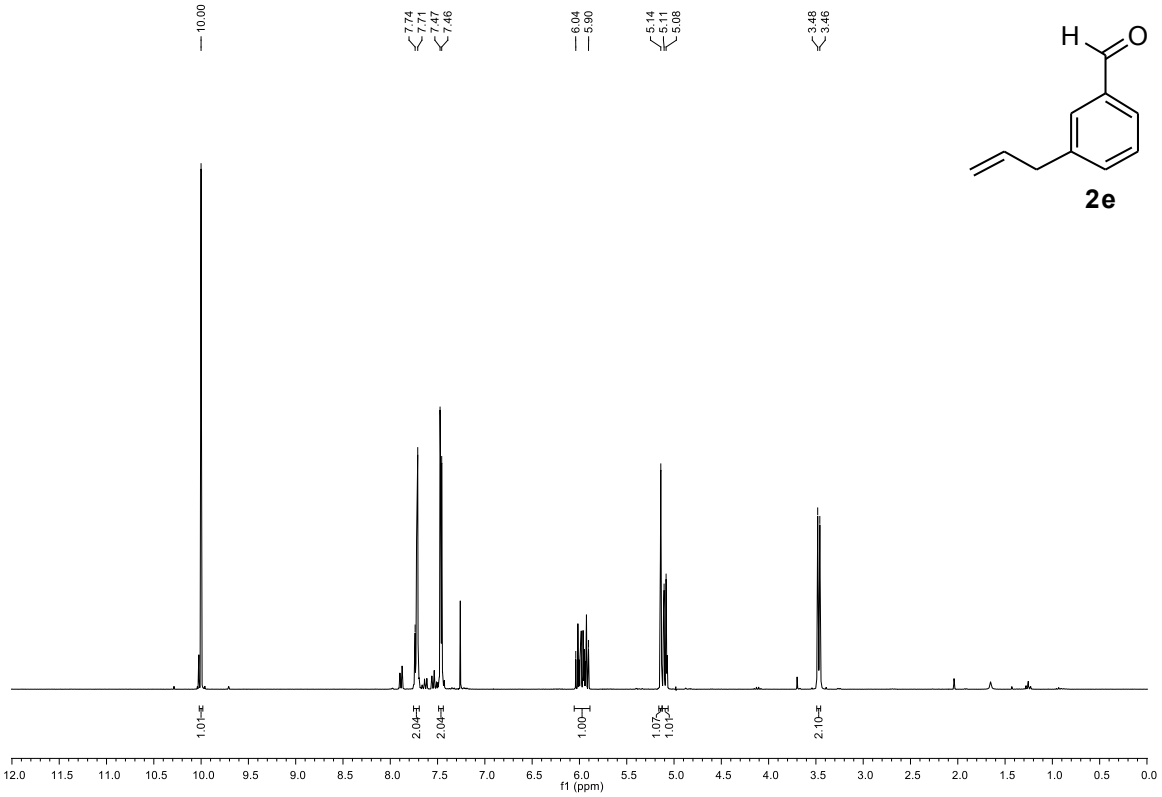


DEPT-135 NMR (75 MHz, $CDCl_3$)

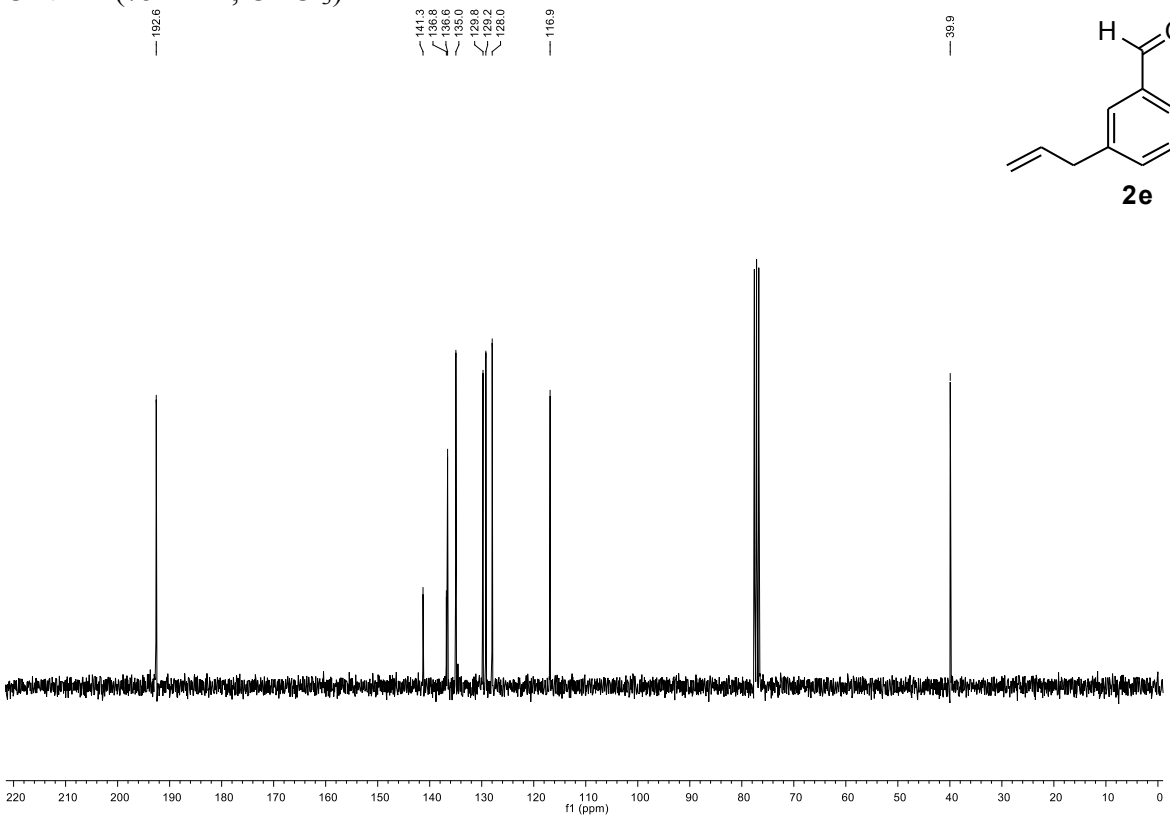


3-Allylbenzaldehyde (2e)

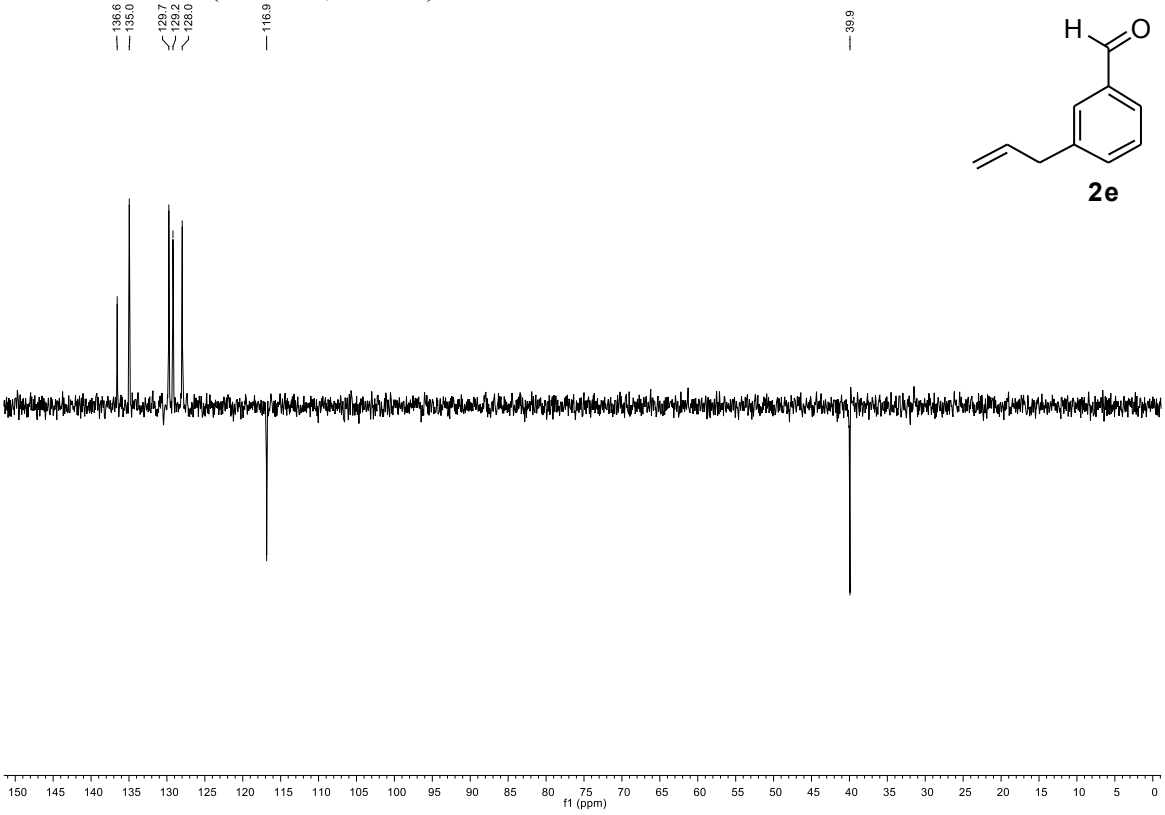
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

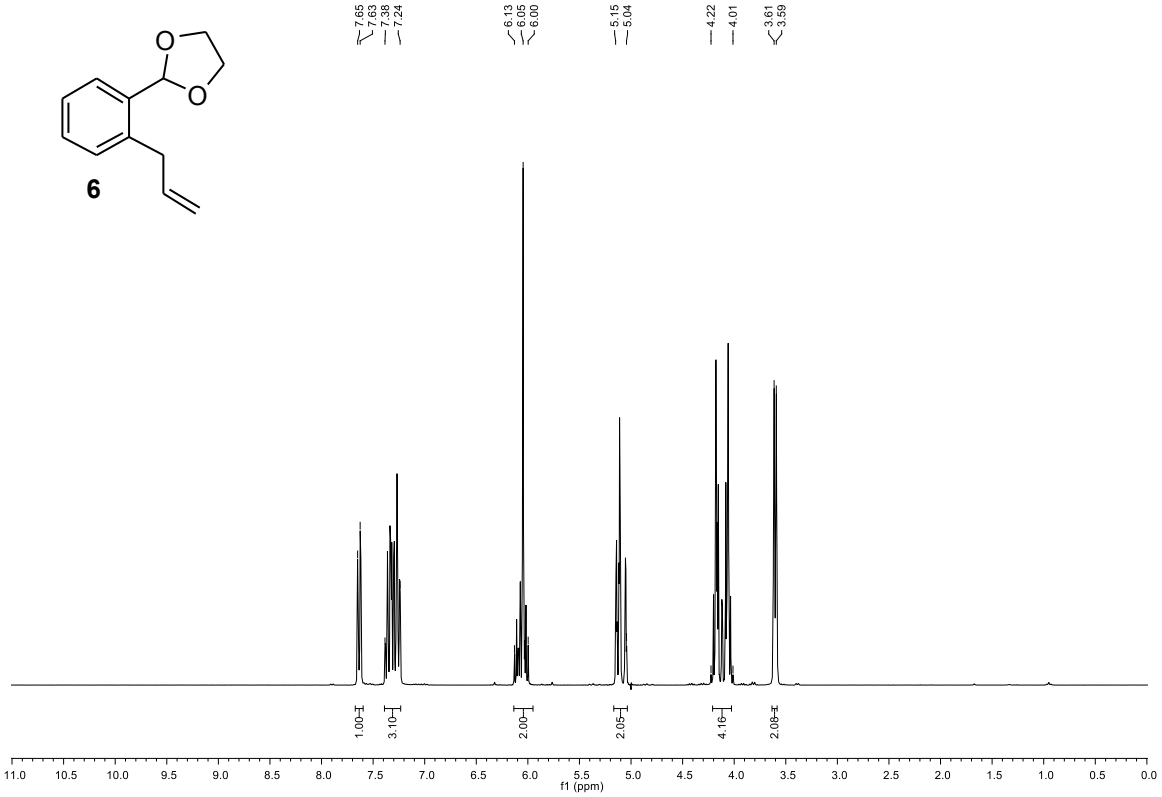


DEPT-135 NMR (75 MHz, $CDCl_3$)

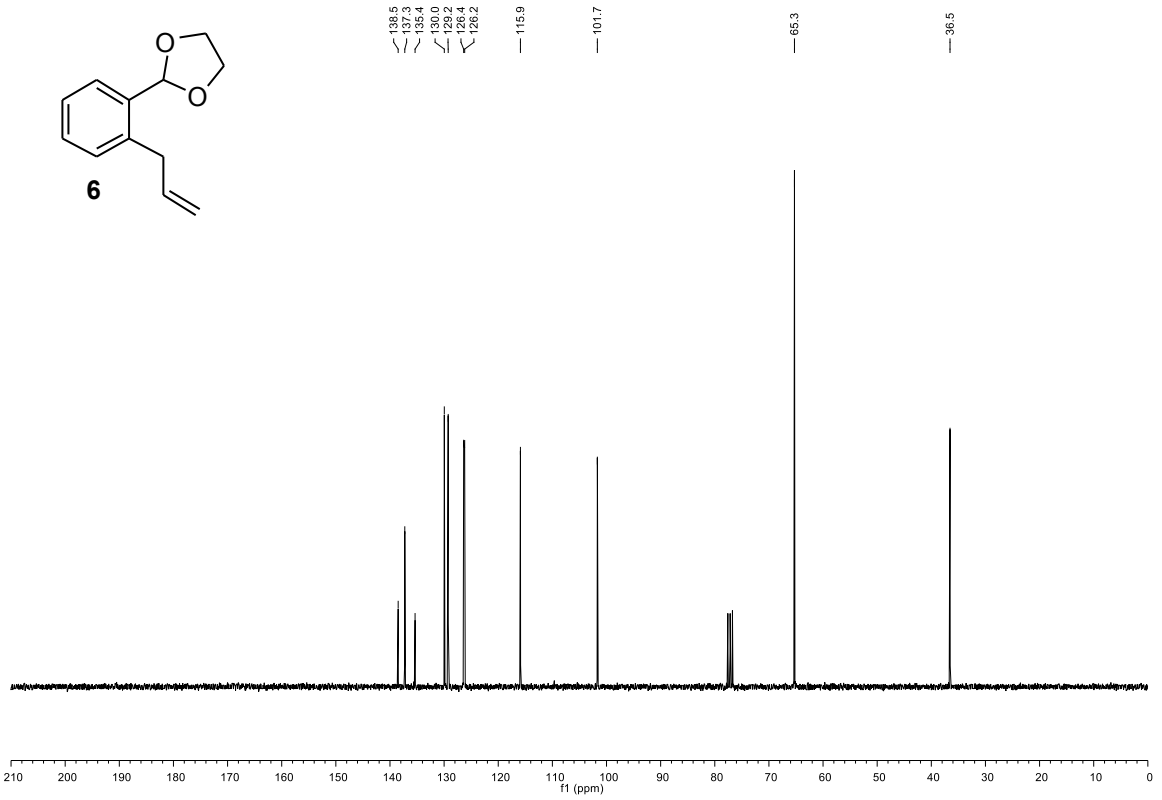


2-(2-Allylphenyl)-1,3-dioxolane (6)

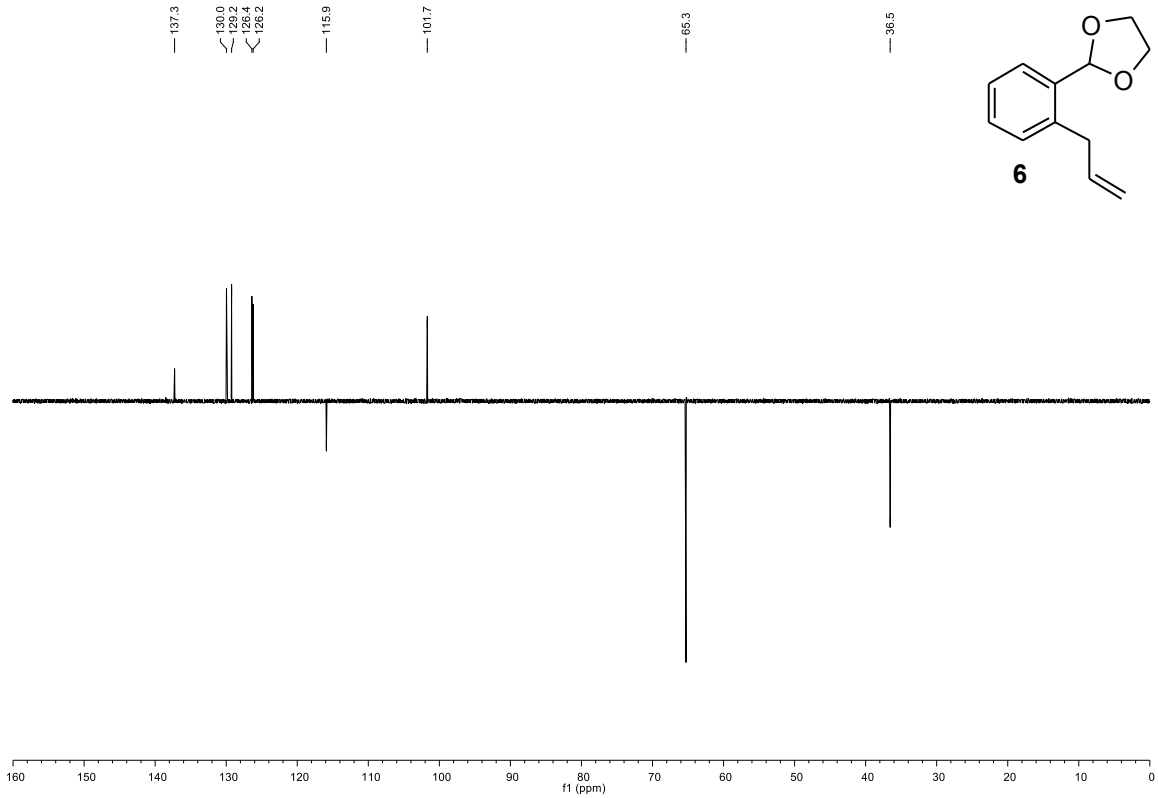
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

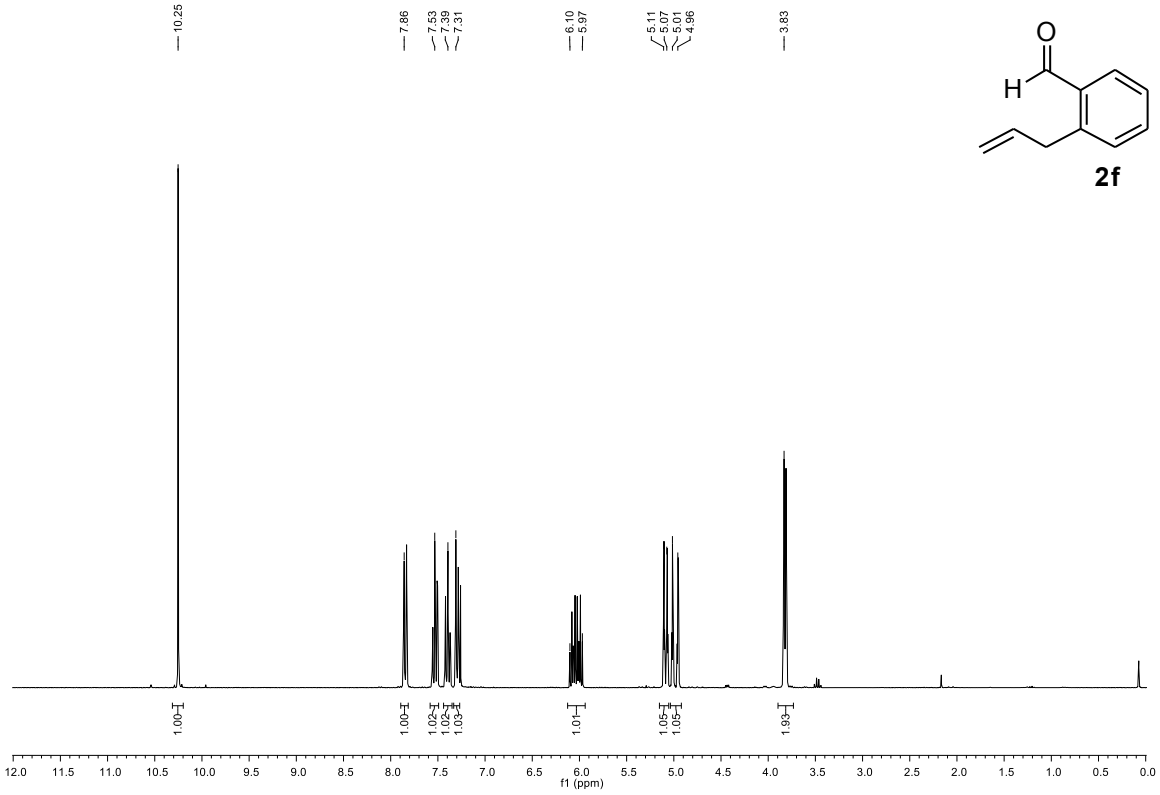


DEPT-135 NMR (75 MHz, $CDCl_3$)



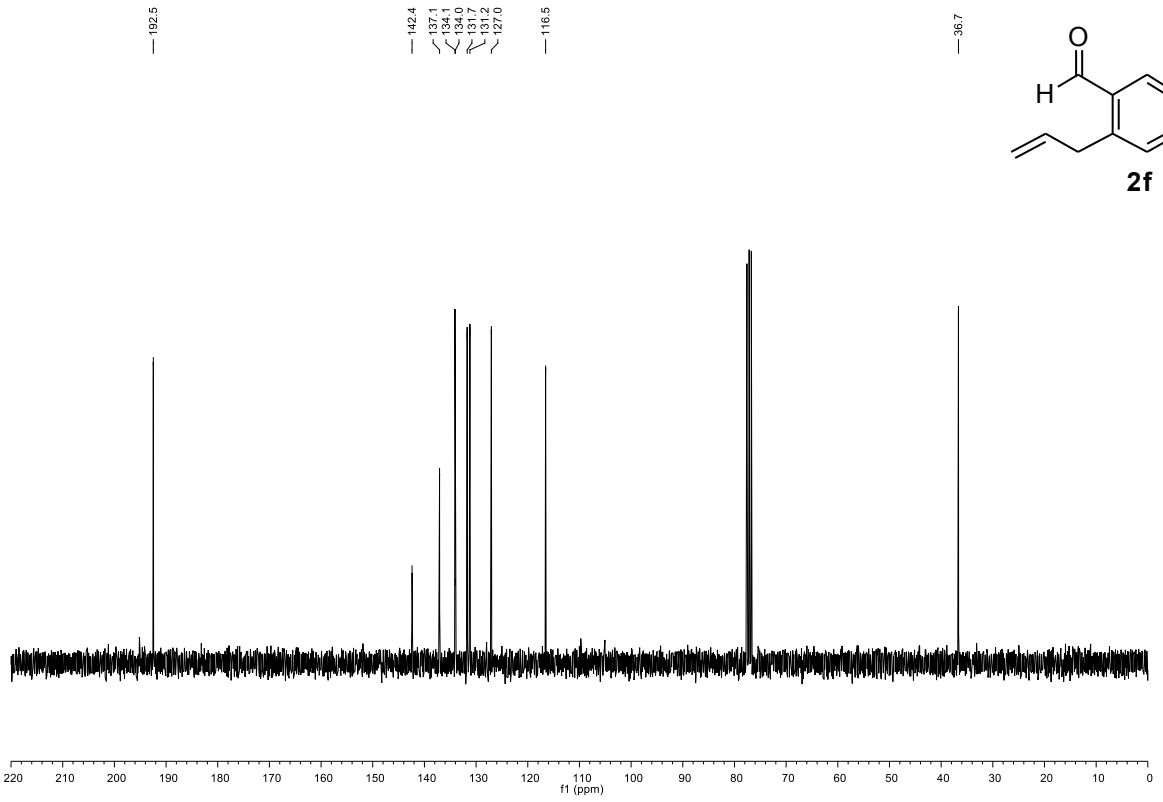
2-Allylbenzaldehyde (2f)

^{1}H NMR (300 MHz, $CDCl_3$)



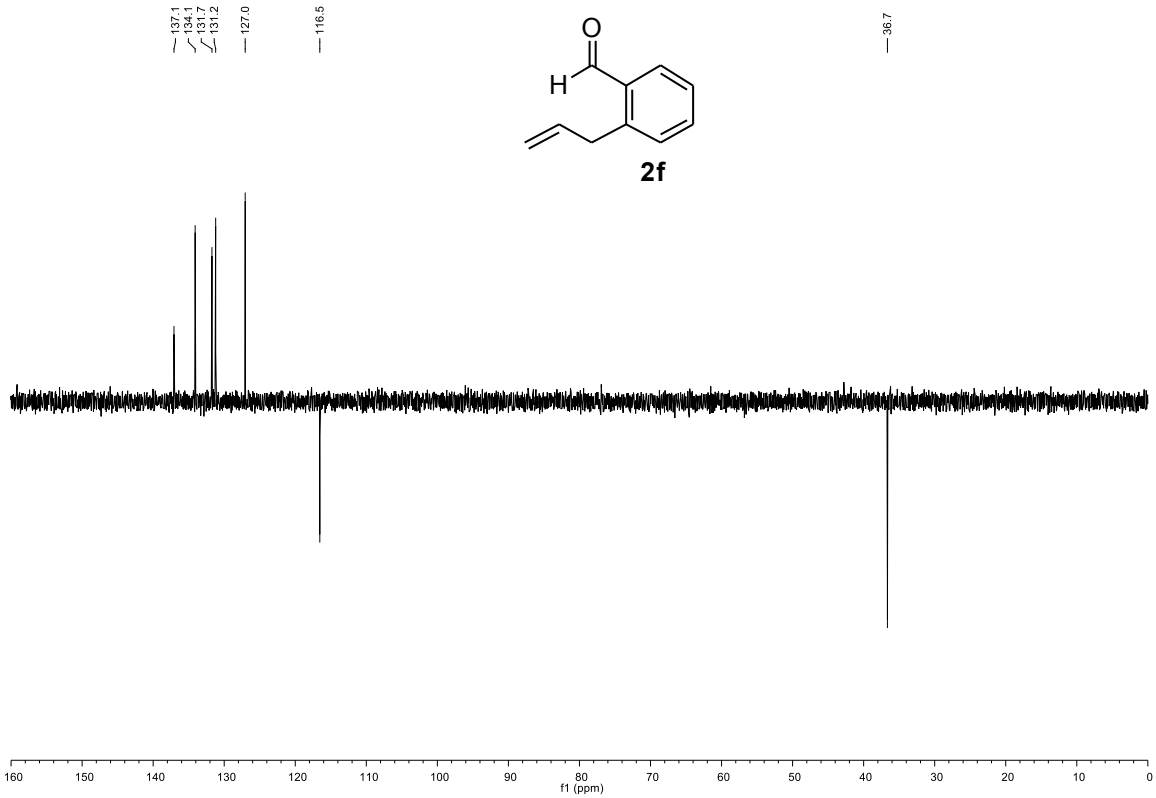
2f

^{13}C NMR (75 MHz, $CDCl_3$)



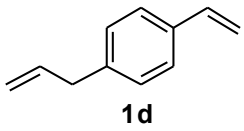
2f

DEPT-135 NMR (75 MHz, $CDCl_3$)



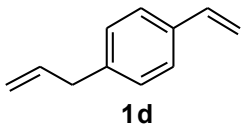
1-Allyl-4-vinylbenzene (1d)

^{1}H NMR (300 MHz, $CDCl_3$)



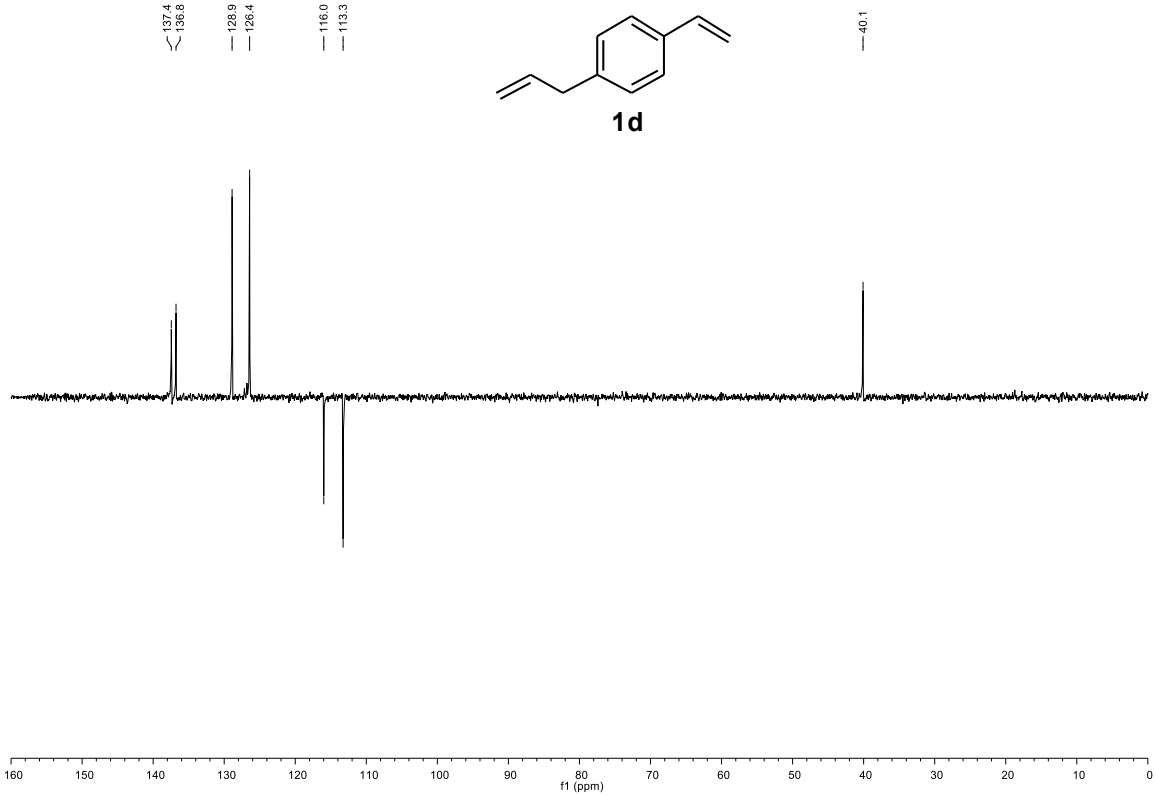
1d

^{13}C NMR (75 MHz, $CDCl_3$)



1d

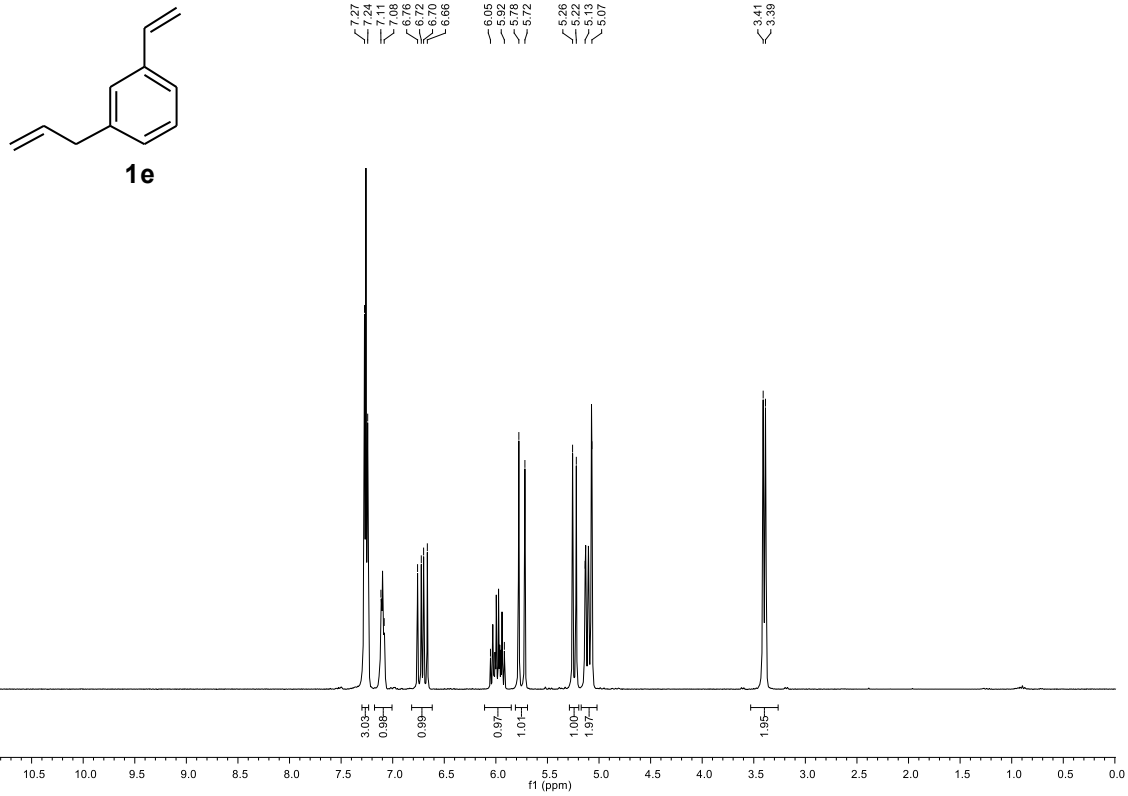
DEPT-135 NMR (75 MHz, $CDCl_3$)



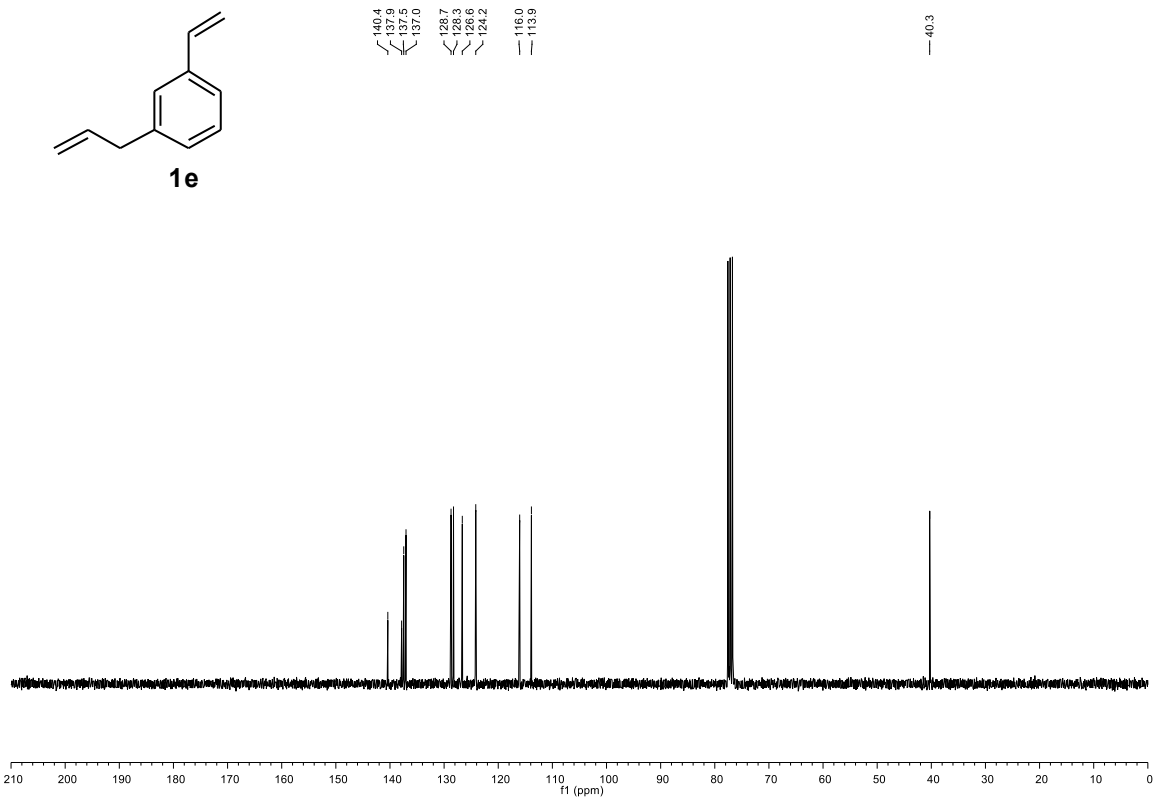
1d

1-Allyl-3-vinylbenzene (1e)

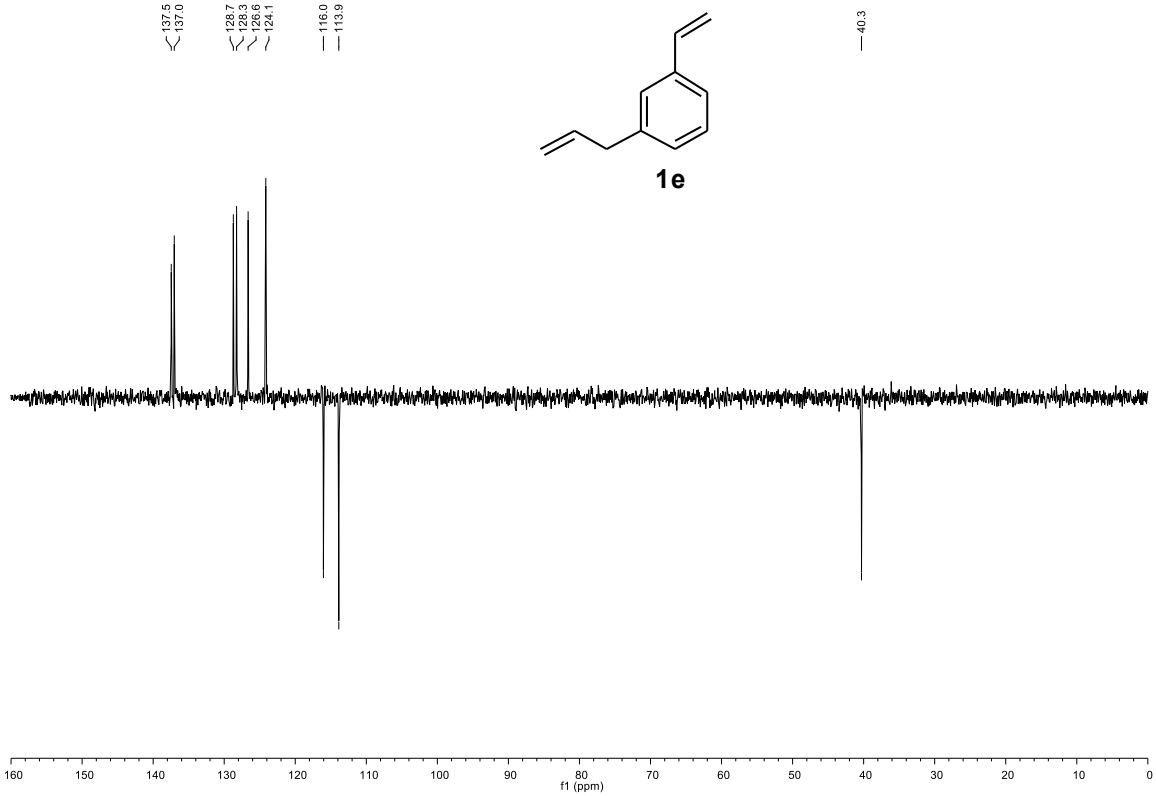
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



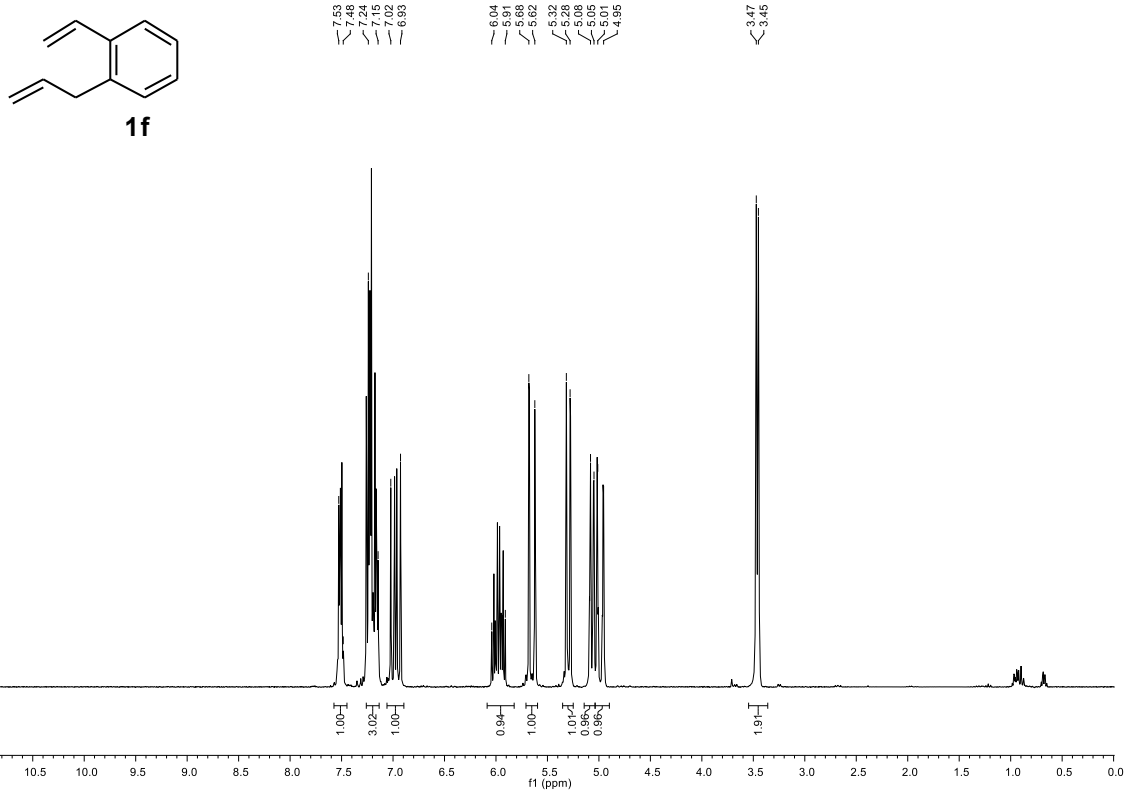
DEPT-135 NMR (75 MHz, $CDCl_3$)



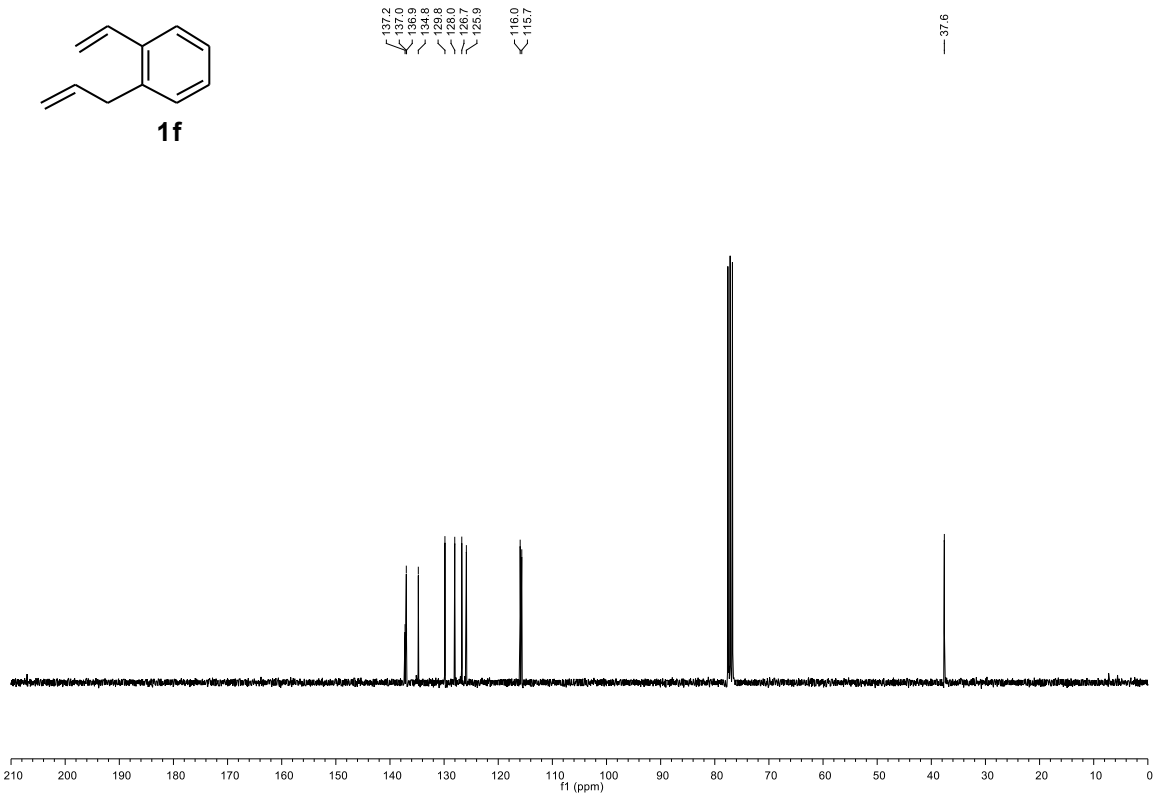
1e

1-Allyl-2-vinylbenzene (1f)

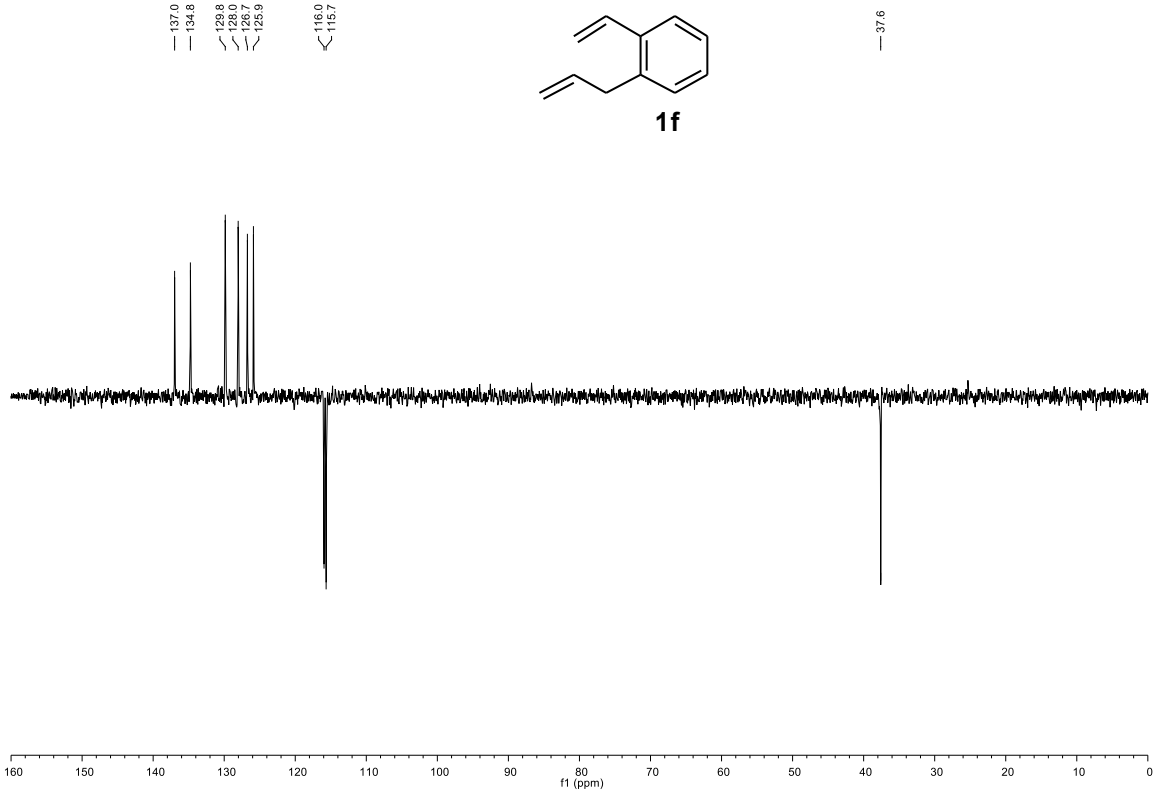
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



DEPT-135 NMR (75 MHz, $CDCl_3$)



1f