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A one-pot tandem chemoselective allylation/cross-coupling via temperature control of a multi-nucleophile/electrophile system

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Contents

1. General

All reagents and solvents were obtained from commercial suppliers and were used without further purification unless otherwise stated. Purification was carried out according to standard laboratory methods.

1.1 Purification of Solvents

Dry solvents for reactions were either obtained from a PureSolv SPS-400-5 solvent purification system (PhMe, THF, CH_2Cl_2). Et_2O, EtOAc, and petroleum ether 40-60 °C for purification purposes were used as obtained from suppliers without further purification.

1.2 Experimental Details

Reactions were carried out using conventional glassware (preparation of intermediates) or in capped 5 mL microwave vials. The glassware was oven-dried (150 °C) and purged with N_2 before use. Purging refers to a vacuum/nitrogen-refilling procedure. Room temperature was generally *ca.* 18 °C. Reactions were carried out at elevated temperatures using a temperature-regulated hotplate/stirrer.

1.3 Purification of Products

Thin layer chromatography was carried out using Merck silica plates coated with fluorescent indicator UV254. These were analyzed under 254 nm UV light or developed using potassium permanganate solution. Normal phase flash chromatography was carried out using ZEOprep 60 HYD 40-63 μm silica gel.

1.4 Analysis of Products

Fourier Transformed Infra-Red (FTIR) spectra were obtained on a Shimadzu IRAffinity-1 machine. ^{19}F NMR spectra were obtained on a Bruker AV 400 spectrometer at 376 MHz. ^{1}H and ^{13}C NMR spectra were obtained on either a Bruker AV 400 at 400 MHz and 101 MHz, respectively, or Bruker DRX 500 at 500 MHz and 126 MHz, respectively. Chemical shifts are reported in ppm and coupling constants are reported in Hz with $CDCl_3$ referenced at 7.26 (^{1}H) and 77.16 ppm (^{13}C) and DMSO-d_6 referenced at 2.50 (^{1}H) and 39.5 (^{13}C). High-resolution mass spectra were obtained through analysis at the EPSRC UK National Mass Spectrometry Facility at Swansea University.

2. General Experimental Procedures

General Procedure A: For example, for the preparation of compound 5a

An oven dried 5 mL microwave vial was charged with 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (66 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), and K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.). The microwave vial was capped and purged with N_2 before adding PhMe (1 mL, 0.25 M), H_2O (225 μL, 50.0 equiv.) and allylBPin (60 μL, 0.31 mmol, 1.25 equiv.). The reaction mixture was stirred at 0 °C for 7 h before allowed to warm up to room temperature and stirred for another 2 h. The reaction mixture was then heated to 90 °C for 16 h. The crude mixture was filtered through a short pad of Celite, the filter cake was rinsed with EtOAc (10 mL x 2) and the resulting filtration was washed with sat. ammonium chloride solution (20 mL). The aqueous phase was extracted with EtOAc (10 mL x 2) and the combined organic phase was passed through a hydrophobic frit and concentrated under reduced pressure before being purified by flash chromatography (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless solid (49 mg, 87%).

General Procedure B: For example, for the preparation of compound 5c

An oven dried 5 mL microwave vial was charged with 3-bromo-5-(trifluoromethyl) benzaldehyde (63 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (102 mg, 0.50 mmol, 2.0 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), and K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.). The microwave vial was capped and purged with N_2 before adding PhMe (1 mL, 0.25 M), H_2O (225 μL, 50.0 equiv.) and allylBPin (60 μL, 0.31 mmol, 1.25 equiv.). The reaction mixture was stirred at 0 °C for 7 h before allowed to warm up to room temperature and stirred for another 2 h. The reaction mixture was then heated to 90 °C for 16 h. The crude mixture was filtered through a short pad of Celite, the filter cake was rinsed with EtOAc (10 mL x 2) and the resulting filtration was washed with sat. ammonium chloride solution (20 mL). The aqueous phase was extracted with EtOAc (10 mL x 2) and the combined organic phase was passed through a hydrophobic frit and concentrated under reduced pressure before being purified by flash chromatography (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow solid (68 mg, 92%).

General Procedure C: For example, for the preparation of compound 5r

An oven dried 5 mL microwave vial was charged with 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (153 mg, 0.75 mmol, 3.0 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), and K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.). The microwave vial was capped and purged with N_2 before adding PhMe (1 mL, 0.25 M), H_2O (225 μL, 50.0 equiv.) and 2-(2-chloroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (101 mg, 0.50 mmol, 2.0 equiv.). The reaction mixture was stirred at 0 °C for 7 h before allowed to warm up to room temperature and stirred for another 2 h. The reaction mixture was then heated to 90 °C for 16 h. The crude mixture was filtered through a short pad of Celite, the filter cake was rinsed with EtOAc (10 mL x 2) and the resulting filtration was washed with sat. ammonium chloride solution (20 mL). The aqueous phase was extracted with EtOAc (10 mL x 2) and the combined organic phase was passed through a hydrophobic frit and concentrated under reduced pressure before being purified by flash chromatography (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (59.5 mg, 95%).

3. Temperature study

Reactions carried out using 4-bromobenaldehyde (1 equiv.), allyl BPin (1 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (4 mol%), K_3PO_4 (3 equiv.), H_2O (5 equiv.) and THF (0.25 M). Reactions were stirred at **x** K for 3 h then quenched with sat. NH_4Cl solution. Extraction of the organic phase with ethyl acetate and concentration gave the crude mixture. The conversion was determined by using 1,4-dinitrobenzene as internal standard.

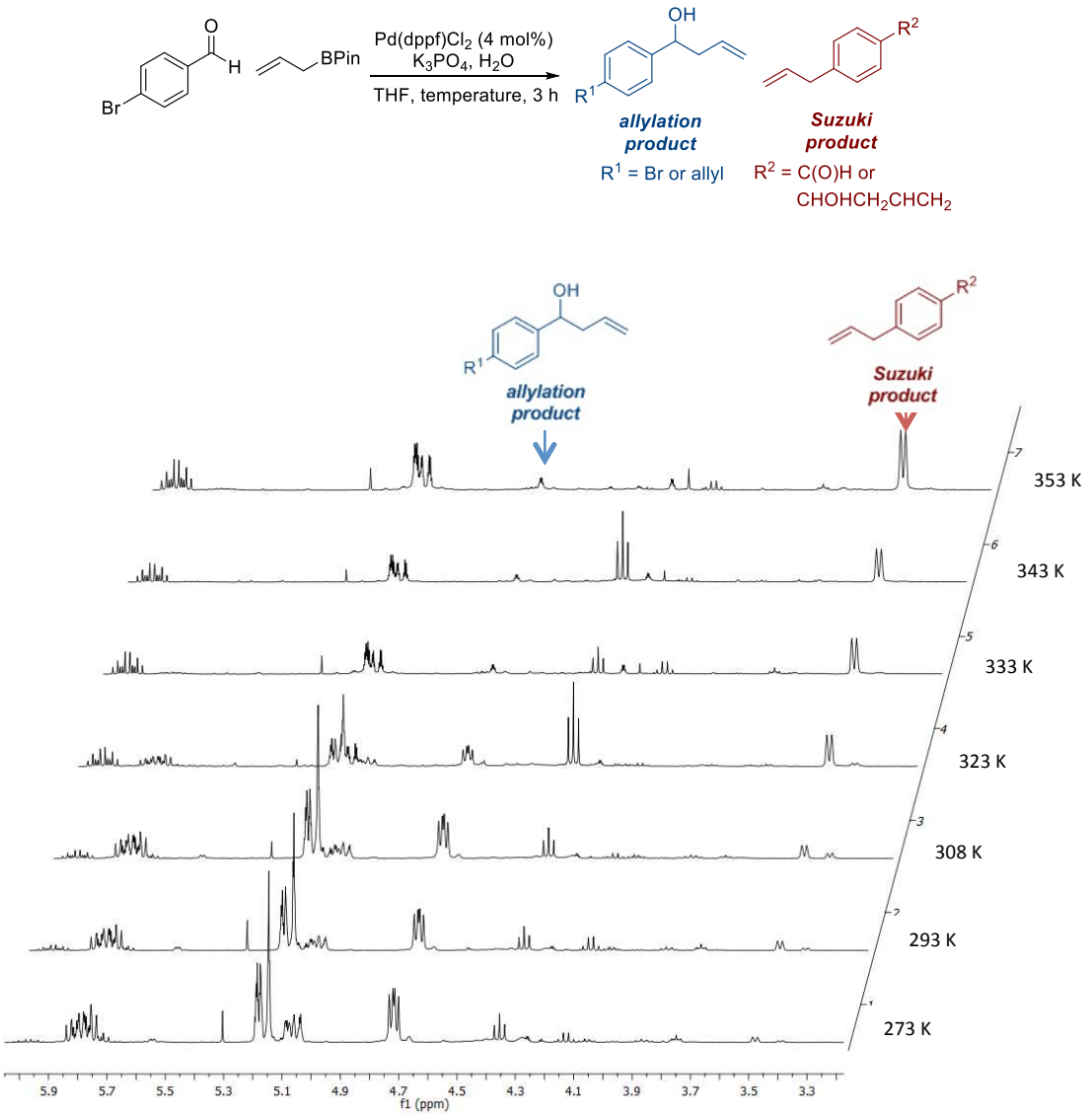


Fig. 1 Staged ^1H NMR spectra of temperatures study

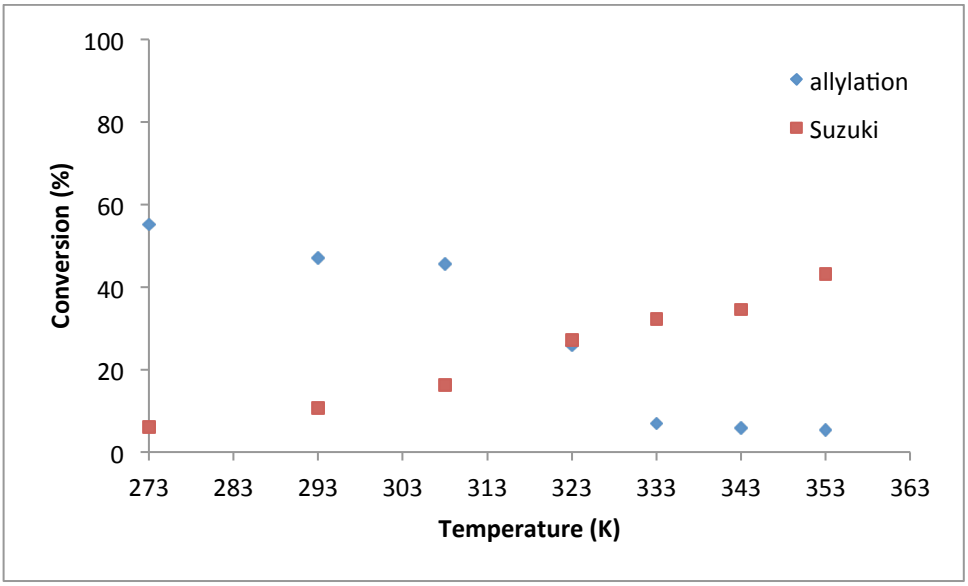


Chart 1 Conversion vs. temperature

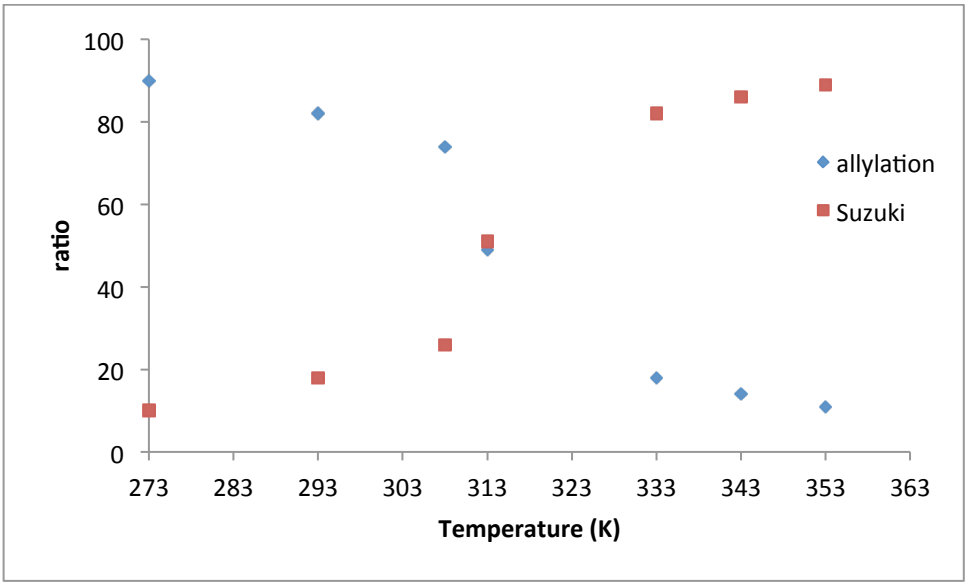
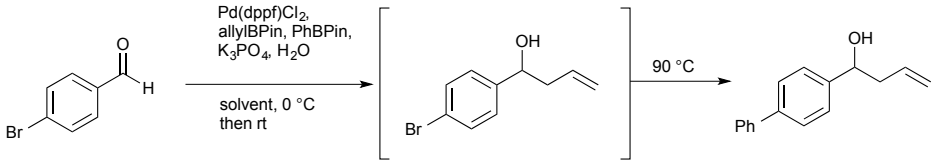


Chart 2 Product ratio vs. temperature

4. Reaction Optimization Data (Table 1)

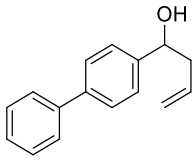
Reactions carried out according to General Procedure using 4-bromobenaldehyde (46 mg, 0.25 mmol, 1 equiv.), phenylboronic acid pinacol ester (**x** equiv.), allyl boronic acid pinacol ester (**x** equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (**x** mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), H_2O (**x** equiv.) and solvent (0.25 M). Reactions were stirred at 0 °C for **a** h then rt for **b** h followed by heating at 90 °C for 16 h.



Entry	Solvent	H_2O	$Pd(dppf)Cl_2$	allylBPin	PhBPin	Time (a+b)	Yield
1	THF	50 equiv.	4 mol%	1.1	0.9	0 + 5	48%
2	THF	50 equiv.	4 mol%	1.1	0.9	3 + 2	35%
3	THF	50 equiv.	4 mol%	1.4	0.9	3 + 2	67%
4	THF	50 equiv.	4 mol%	2.2	1.1	3 + 2	49%
5	THF	50 equiv.	4 mol%	1.6	1.1	3 + 2	71%
6	CH_2Cl_2	50 equiv.	2 mol%	1.1	1.3	3 + 2	70%
7	PhMe	50 equiv.	2 mol%	1.1	1.3	3 + 2	72%
8	PhMe	50 equiv.	4 mol%	1.2	1.3	3 + 2	58%
9	PhMe	50 equiv.	3 mol%	1.2	1.3	3 + 2	67%
10	PhMe	50 equiv.	2 mol%	1.2	1.3	3 + 2	70%
11	PhMe	50 equiv.	1 mol%	1.2	1.3	3 + 2	76%
12	THF	50 equiv.	1 mol%	1.2	1.3	3 + 2	68%
13	PhMe	5 equiv.	1 mol%	1.2	1.3	3 + 2	56%
14	PhMe	50 equiv.	0.5 mol%	1.2	1.3	3 + 2	77%
15	PhMe	50 equiv.	0.5 mol%	1.2	1.3	7 + 2	79%
16	**PhMe**	**50 equiv.**	**0.5 mol%**	**1.25**	**1.3**	**7 + 2**	**87%**
17	**PhMe**	**50 equiv.**	**0.5 mol%**	**1.25**	**1.4**	**7 + 2**	**89%**
18	PhMe	50 equiv.	0.5 mol%	1.25	1.3	0 + 9	69%
19	PhMe	50 equiv.	0.5 mol%	1.3	1.4	7 + 2	76%
20	PhMe	50 equiv.	0.5 mol%	1.2	1.3	7 + 0	74%
21	PhMe	50 equiv.	0.5 mol%	1.25	1.3	7 + 0	79%

5. Characterization Data for compounds

1-([1,1'-biphenyl]-4-yl)but-3-en-1-ol, **5a**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (66 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 µmol, 0.5 mol%), allylBPin (60 µL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 µL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless solid (49 mg, 87%).

υ_{max} (solid): 3373 (br), 3071, 2972, 2930, 2859, 1430, 1049, 700 cm^{-1}.

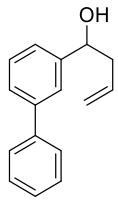
^1H NMR (500 MHz, $CDCl_3$): δ 7.64–7.58 (m, 4H), 7.49–7.41 (m, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 5.92 – 5.81 (m, 1H), 5.24 – 5.15 (m, 2H), 4.78 (t, *J* = 6.8 Hz, 1H), 2.62–2.51 (m, 2H), 2.42 (brs, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.0, 140.9, 140.5, 134.5, 128.8, 127.3, 127.2, 127.1, 126.4, 118.4, 73.2, 43.8.

HRMS(NSI): exact mass calculated for $[M+Na]^+$ ($C_{15}H_{16}ONa$) requires *m/z* 247.1093, found *m/z* 247.1093.

The spectral data were consistent with those previously reported in the literature.[1]

1-([1,1'-biphenyl]-3-yl)but-3-en-1-ol, **5b**



Prepared according to General Procedure A using 3-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (66 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 µmol, 0.5 mol%), allylBPin (60 µL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 µL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless solid (50 mg, 89%).

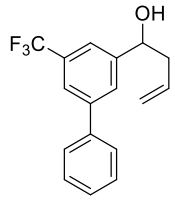
υ_{max} (solid): 3368 (br), 3072, 2977, 2929, 2858, 1572, 1430, 1049, 999, 787, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.59 (m, 3H), 7.54 – 7.50 (m, 1H), 7.48 – 7.41 (m, 3H), 7.40 – 7.32 (m, 2H), 5.93 – 5.78 (m, 1H), 5.24 – 5.13 (m, 2H), 4.82 (dd, *J* = 7.8, 5.1 Hz, 1H), 2.64 – 2.50 (m, 2H), 2.05 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.6, 141.6, 141.3, 134.6, 129.0, 128.9, 127.5, 127.3, 126.5, 124.9, 124.8, 118.7, 73.5, 44.1.

HRMS (NSI): exact mass calculated for $[M+NH_4]^+$ ($C_{15}H_{20}ON$) requires *m/z* 242.1539, found *m/z* 242.1541.

1-(5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)but-3-en-1-ol, **5c**



Prepared according to General Procedure B using 3-bromo-5-(trifluoromethyl)benzaldehyde (63 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (102 mg, 0.50 mmol, 2.0 equiv.), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), allylBPin (60 μL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure B (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow solid (68 mg, 92%).

υ_{max} (solid): 3373 (br), 3080, 2977, 2925, 1352, 1265, 1166, 1126, 767 cm^{-1}.

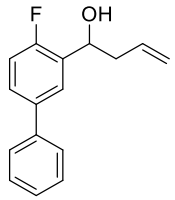
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.76 (s, 1H), 7.64 – 7.59 (m, 3H), 7.48 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 5.90 – 5.79 (m, 1H), 5.26 – 5.18 (m, 2H), 4.87 (dd, *J* = 7.6, 4.8 Hz, 1H), 2.65 – 2.48 (m, 2H), 2.27 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 145.6, 142.4, 139.9, 133.8, 131.5 (q, J^2 = 32.1 Hz), 129.1, 128.2, 128.0, 127.4, 123.2 (q, J^3 = 3.7 Hz), 121.6 (q, J^3 = 3.6 Hz), 119.4, 72.8, 44.2. (CF_3 signal was not observed)

^{19}F NMR (471 MHz, $CDCl_3$): δ -62.5.

HRMS (NSI): exact mass calculated for $[M-H]^-$ ($C_{17}H_{14}OF_3$) requires *m/z* 291.0997, found *m/z* 291.0991.

1-(4-fluoro-[1,1'-biphenyl]-3-yl)but-3-en-1-ol, **5d**



Prepared according to General Procedure A using 5-bromo-2-fluorobenzaldehyde (50.5 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (66 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 µmol, 0.5 mol%), allylBPin (60 µL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 µL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow solid (42 mg, 70%).

υ_{max} (film): 3388 (br), 3068, 3031, 2931, 1484, 765 cm^{-1}.

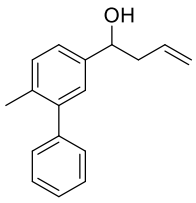
^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 7.0, 2.4 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.49 – 7.41 (m, 3H), 7.38 – 7.32 (m, 1H), 7.09 (dd, *J* = 10.1, 8.5 Hz, 1H), 5.94 – 5.79 (m, 1H), 5.23 – 5.16 (m, 2H), 5.12 (dd, *J* = 7.8, 4.6 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.59 – 2.49 (m, 1H), 2.19 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5 (d, J^1 = 246.2 Hz), 140.4, 137.7 (d, J^4 = 2.8 Hz), 134.2, 131.2 (d, J^2 = 13.8 Hz), 128.9, 127.6 (d, J^3 = 8.4 Hz), 127.4, 127.2, 126.2 (d, J^3 = 4.4 Hz), 119.0, 115.7 (d, J^2 = 22.2 Hz), 67.5, 42.8.

^{19}F NMR (471 MHz, $CDCl_3$): δ -122.2.

HRMS (NSI): exact mass calculated for $[M-H]^-$ ($C_{15}H_{14}OF$) requires *m/z* 241.1034, found *m/z* 241.1033.

1-(6-methyl-[1,1'-biphenyl]-3-yl)but-3-en-1-ol, **5e**



Prepared according to General Procedure A using 3-bromo-4-methylbenzaldehyde (49.5 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (66 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 µmol, 0.5 mol%), allylBPin (60 µL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 µL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow solid (26 mg, 44%).

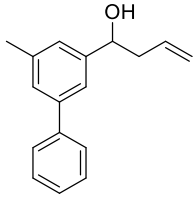
υ_{max} (solid): 3358 (br), 3055, 2975, 2923, 1488, 705 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.20 – 7.14 (m, 3H), 5.82 – 5.71 (m, 1H), 5.14 – 5.05 (m, 2H), 4.67 (dd, *J* = 7.8, 5.1 Hz, 1H), 2.53 – 2.40 (m, 2H), 2.19 (s, 3H), 1.92 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.1, 142.0, 141.5, 134.8, 134.7, 130.6, 129.3, 128.2, 127.5, 127.0, 124.8, 118.6, 73.2, 43.9, 20.3.

HRMS (NSI): exact mass calculated for $[M-H]^-$ ($C_{17}H_{17}O$) requires *m/z* 237.1290, found *m/z* 237.1285.

1-(5-methyl-[1,1'-biphenyl]-3-yl)but-3-en-1-ol, **5f**



Prepared according to General Procedure A using 3-bromo-5-methylbenzaldehyde (49.5 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (66 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), allylBPin (60 μL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow solid (39 mg, 65%).

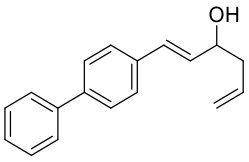
υ_{max} (solid): 3531, 3381(br), 3029, 2974, 2918, 2855, 1051, 765 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (m, 2H), 7.46 – 7.41 (m, 2H), 7.39 (s, 1H), 7.36 – 7.31 (m, 2H), 7.18 (s, 1H), 5.90 – 5.80 (m, 1H), 5.23 – 5.15 (m, 2H), 4.78 (dd, *J* = 7.9, 5.0 Hz, 1H), 2.62 – 2.50 (m, 2H), 2.43 (s, 3H), 2.05 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 144.6, 141.6, 141.4, 138.7, 134.7, 128.9, 127.4, 127.4, 127.4, 125.6, 122.1, 118.6, 73.5, 44.1, 21.7.

HRMS (NSI): exact mass calculated for $[M+NH_4]^+$ ($C_{17}H_{22}ON$) requires *m/z* 256.1696, found *m/z* 256.1698.

(*E*)-1-([1,1'-biphenyl]-4-yl)hexa-1,5-dien-3-ol, **5g**



Prepared according to General Procedure A using (*E*)-3-(4-bromophenyl)acrylaldehyde (52 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (66 mg, 0.33 mmol, 1.3 equiv.),

Pd(dppf)Cl_2·CH_2Cl_2 (1.0 mg, 1.2 μmol, 0.5 mol%), allylBPin (60 μL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow solid (44 mg, 71%).

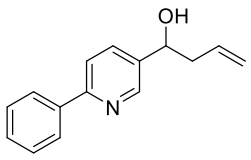
υ_{max} (film): 3344 (br), 3063, 3029, 2979, 2929, 2855, 973, 765 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (dt, *J* = 8.2, 1.6 Hz, 2H), 7.58 – 7.55 (m, 2H), 7.48 – 7.42 (m, 4H), 7.37 – 7.33 (m, 1H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.30 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.94 – 5.83 (m, 1H), 5.20 (ddt, *J* = 6.3, 1.8, 1.2 Hz, 2H), 4.39 (td, *J* = 6.7, 1.0 Hz, 1H), 2.51 – 2.37 (m, 2H), 1.84 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 140.8, 140.6, 135.9, 134.2, 131.8, 130.1, 128.9, 127.5, 127.4, 127.1, 127.1, 118.7, 71.9, 42.2.

HRMS (NSI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{18}ONa$) requires *m/z* 273.1250, found *m/z* 273.1252.

1-(6-phenylpyridin-3-yl)but-3-en-1-ol, **5h**



Prepared according to General Procedure B using 6-bromonicotinaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid pinacol ester (102 mg, 0.5 mmol, 2.0 equiv.), Pd(dppf)Cl_2·CH_2Cl_2 (1.0 mg, 1.2 μmol, 0.5 mol%), allylBPin (60 μL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure B (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow solid (15 mg, 27%).

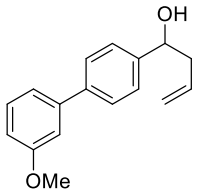
υ_{max} (solid): 3347 (br), 3072, 2923, 2853, 1477, 746 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65 (d, *J* = 2.0 Hz, 1H), 8.01 – 7.96 (m, 2H), 7.78 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 5.89 – 5.76 (m, 1H), 5.21 (dd, *J* = 11.0, 6.3 Hz, 2H), 4.84 (dd, *J* = 7.8, 5.1 Hz, 1H), 2.57 (m, 2H), 2.22 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 157.0, 147.9, 139.3, 137.5, 134.5, 133.8, 129.1, 128.9, 127.0, 120.4, 119.5, 71.1, 43.9.

HRMS (NSI): exact mass calculated for $[M+H]^+$ ($C_{15}H_{16}ON$) requires *m/z* 226.1226, found *m/z* 226.1227.

1-(3'-methoxy-[1,1'-biphenyl]-4-yl)but-3-en-1-ol, **5i**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 2-(3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (76 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 µmol, 0.5 mol%), allylBPin (60 µL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 µL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (56.4 mg, 89%).

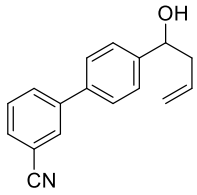
υ_{max} (film): 3420 (br), 3072, 2974, 2935, 2834, 1601, 1482, 1215, 1055, 837 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.36 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.15 – 7.13 (m, 1H), 6.91 (dd, *J* = 7.9, 2.2 Hz, 1H), 5.85 (ddt, *J* = 17.1, 10.2, 7.1 Hz, 1H), 5.24 – 5.14 (m, 2H), 4.84 – 4.75 (m, 1H), 3.87 (s, 3H), 2.63 – 2.49 (m, 2H), 2.21 (brs, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.1, 143.2, 142.5, 140.4, 134.5, 129.9, 127.3, 126.4, 119.7, 118.6, 113.0, 112.8, 73.2, 55.4, 43.9.

HRMS (NSI): exact mass calculated for $[M+Na]^+$ ($C_{17}H_{18}O_2Na$) requires *m/z* 277.1199, found *m/z* 277.1200.

4'-(1-hydroxybut-3-en-1-yl)-[1,1'-biphenyl]-3-carbonitrile, **5j**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (74.5 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 µmol, 0.5 mol%), allylBPin (60 µL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 µL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (59.5 mg, 95%).

υ_{max} (film): 3433 (br), 3072, 2977, 2925, 2230, 1481, 1055, 800 cm^{-1}.

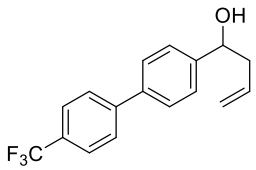
^1H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 1.5, 1.5 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.63 – 7.59 (m, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.51 (m, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 5.89 – 5.76

(m, 1H), 5.22 – 5.11 (m, 2H), 4.80 (dd, *J* = 7.8, 5.0 Hz, 1H), 2.61 – 2.47 (m, 2H), 2.27 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 144.3, 142.2, 138.1, 134.3, 131.5, 130.8, 130.7, 129.7, 127.2, 127.2, 127.1, 126.7, 118.9, 118.9, 113.0, 72.9, 44.0.

HRMS (NSI): exact mass calculated for $[M+Na]^+$ ($C_{17}H_{15}ONNa$) requires *m/z* 272.1046, found *m/z* 272.1047.

1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)but-3-en-1-ol, **5k**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (88 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 µmol, 0.5 mol%), allylBPin (60 µL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 µL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow solid (56 mg, 77%).

υ_{max} (solid): 3407 (br), 3077, 2979, 2931, 1328, 1125, 825 cm^{-1}.

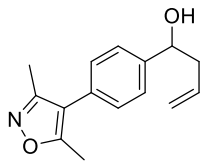
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (aps, 4H), 7.62 – 7.57 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 5.92 – 5.78 (m, 1H), 5.26 – 5.16 (m, 2H), 4.81 (dd, *J* = 7.8, 5.1 Hz, 1H), 2.64 – 2.49 (m, 2H), 2.19 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.5, 144.1, 139.1, 134.4, 130.0, 129.5 (q, J^2 = 32.3 Hz), 127.4, 127.4, 126.6, 125.9 (q, J^3 = 3.55 Hz), 118.9, 73.0, 44.0. (CF_3 signal was not observed).

^{19}F NMR (471 MHz, $CDCl_3$): δ -62.4.

HRMS (NSI): exact mass calculated for $[M-H]^-$ ($C_{17}H_{14}OF_3$) requires *m/z* 291.0997, found *m/z* 291.0993.

1-(4-(3,5-dimethylisoxazol-4-yl)phenyl)but-3-en-1-ol, **5l**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 3,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isoxazole (75.8 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), allylBPin (60 μL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow oil (50.8 mg, 84%).

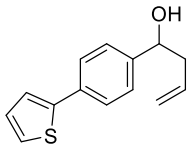
υ_{max} (film): 3384 (br), 3072, 2975, 2927, 2853, 1639, 1427, 1241, 1003, 843 cm^{-1}.

^1H NMR (500 MHz, CD_2Cl_2): δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.91 – 5.81 (m, 1H), 5.21 – 5.12 (m, 2H), 4.77 (dd, *J* = 8.0, 4.9 Hz, 1H), 2.59 – 2.46 (m, 2H), 2.39 (s, 3H), 2.28 (s, 1H), 2.24 (s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 165.2, 158.6, 143.5, 134.6, 129.6, 129.0, 126.2, 118.1, 116.3, 72.9, 43.9, 11.3, 10.6.

HRMS (NSI): exact mass calculated for $[M+H]^+$ ($C_{15}H_{18}O_2N$) requires *m/z* 244.1332, found *m/z* 244.1333.

1-(4-(thiophen-2-yl)phenyl)but-3-en-1-ol, **5m**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (66 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), allylBPin (60 μL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow oil (50.6 mg, 88%).

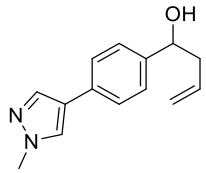
υ_{max} (film): 3373 (br), 3072, 3029, 2975, 2927, 2853, 822, 700.

^1H NMR (500 MHz, CD_2Cl_2): δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 3.7 Hz, 1H), 7.30 (d, *J* = 5.0 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.84 (ddt, *J* = 17.1, 10.2, 7.1 Hz, 1H), 5.19 – 5.11 (m, 2H), 4.74 (dd, *J* = 7.6, 5.3 Hz, 1H), 2.58 – 2.45 (m, 2H), 2.19 (brs, 1H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 144.5, 144.0, 135.0, 133.9, 128.5, 126.9, 126.8, 126.8, 126.2, 126.1, 125.2, 123.5, 118.5, 118.4, 118.4, 73.3, 44.2.

HRMS (NSI): exact mass calculated for $[M+H]^+$ ($C_{14}H_{15}OS$) requires *m/z* 231.0838, found *m/z* 231.0840.

1-(4-(1-methyl-1*H*-pyrazol-4-yl)phenyl)but-3-en-1-ol, **5n**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (67.6 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 µmol, 0.5 mol%), allylBPin (60 µL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 µL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless solid (48.4 mg, 85%).

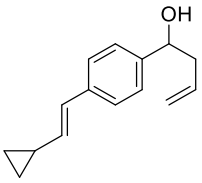
υ_{max} (solid): 3388 (br), 2925, 2856, 1198, 1059, 843, 811 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.57 (s, 1H), 7.45 – 7.39 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.81 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.18 – 5.10 (m, 2H), 4.72 (t, *J* = 6.5 Hz, 1H), 3.90 (s, 3H), 2.57 (s, 1H), 2.54 – 2.45 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.3, 136.8, 134.6, 131.9, 127.0, 126.5, 125.6, 123.0, 118.3, 73.2, 43.8, 39.1.

HRMS (NSI): exact mass calculated for $[M+H]^+$ ($C_{14}H_{17}ON_2$) requires *m/z* 229.1335, found *m/z* 229.1336.

(*E*)-1-(4-(2-cyclopropylvinyl)phenyl)but-3-en-1-ol, **5o**



Prepared according to General Procedure B using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), (*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (97 mg, 0.50 mmol, 2.0 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 µmol, 0.5 mol%), allylBPin (60 µL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 µL, 12.5 mmol, 50.0 equiv). The reaction mixture was subjected to the purification outlined in the General Procedure B (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (53.4 mg, 97%).

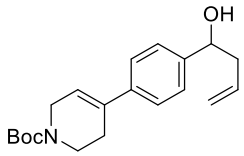
υ_{max} (film): 3373 (br), 3078, 3005, 2977, 2927, 1049, 954 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 5.79 – 5.59 (m, 2H), 5.12 – 4.99 (m, 2H), 4.65 – 4.55 (m, 1H), 2.46 – 2.34 (m, 2H), 2.02 (s, 1H), 1.54 – 1.43 (m, 1H), 0.77 – 0.70 (m, 2H), 0.46 – 0.38 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 142.2, 137.3, 135.0, 134.6, 127.1, 126.1, 125.7, 118.4, 73.3, 43.8, 14.6, 7.4, 7.4.

HRMS (NSI): exact mass calculated for $[M+Na]^+$ ($C_{15}H_{18}ONa$) requires *m/z* 237.1250, found *m/z* 237.1250.

tert-butyl 4-(4-(1-hydroxybut-3-en-1-yl)phenyl)-3,6-dihydropyridine-1-carboxylate, **5p**



Prepared according to General Procedure B using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), *tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dihydro pyridine-1(2*H*)-carboxylate (155 mg, 0.50 mmol, 2.0 equiv.), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), allylBPin (60 μL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure B (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow oil (77.8 mg, 91%).

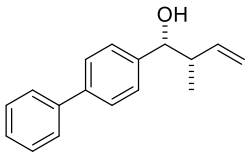
υ_{max} (film): 3438 (br), 3074, 2975, 2929, 1694, 1678, 1423, 1168 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.34 (m, 2H), 7.34 – 7.30 (m, 2H), 6.03 (app s, 1H), 5.87 – 5.74 (m, 1H), 5.20 – 5.11 (m, 2H), 4.74 (m, 1H), 4.07 (d, *J* = 2.9 Hz, 2H), 3.63 (t, *J* = 5.7 Hz, 2H), 2.56 – 2.48 (m, 4H), 2.08 (d, *J* = 2.0 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.0, 143.0, 140.1, 135.2, 134.5, 126.1, 125.1, 120.9, 118.6, 79.8, 73.1, 43.9, 43.9, 40.0, 28.6, 27.5

HRMS (NSI): exact mass calculated for $[M-H]^-$ ($C_{20}H_{26}O_3N$) requires *m/z* 328.1907, found *m/z* 328.1908.

(1*R**,2*S**)-1-([1,1'-biphenyl]-4-yl)-2-methylbut-3-en-1-ol, **5s**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (66 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), (*Z*)-2-(but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (64 μL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica

gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (45 mg, 75%).

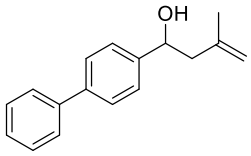
υ_{max} (film): 3565, 3399 (br), 3074, 3026, 2964, 2923, 2869, 1486, 767 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.56 (m, 4H), 7.49 – 7.42 (m, 2H), 7.41 – 7.32 (m, 3H), 5.91 – 5.75 (m, 1H), 5.12 (ddd, *J* = 5.3, 2.7, 1.6 Hz, 1H), 5.10 – 5.05 (m, 1H), 4.68 (d, *J* = 5.4 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.05 (s, 1H), 1.07 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.7, 141.0, 140.4, 140.3, 128.9, 127.4, 127.2, 127.1, 126.9, 115.8, 77.2, 44.7, 14.2.

HRMS (NSI): exact mass calculated for $[M+Na]^+$ ($C_{17}H_{18}ONa$) requires *m/z* 261.1250, found *m/z* 261.1252.

1-([1,1'-biphenyl]-4-yl)-3-methylbut-3-en-1-ol, **5q**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (66 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), 4,4,5,5-tetramethyl-2-(2-methylallyl)-1,3,2-dioxaborolane (57 mg, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (44 mg, 70%).

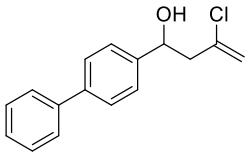
υ_{max} (film): 3544, 3394 (br), 3074, 3026, 2966, 2930, 1488, 767 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (m, 4H), 7.48 – 7.41 (m, 4H), 7.37 – 7.32 (m, 1H), 4.98 – 4.94 (m, 1H), 4.90 (d, *J* = 0.9 Hz, 1H), 4.87 (t, *J* = 6.5 Hz, 1H), 2.48 (d, *J* = 6.5 Hz, 2H), 1.83 (s, 3H). (OH not observed).

^{13}C NMR (126 MHz, $CDCl_3$): δ 142.9, 142.2, 140.7, 140.3, 128.6, 127.1, 127.0, 126.9, 126.1, 114.0, 71.0, 48.2, 22.2.

HRMS (NSI): exact mass calculated for $[M-H]^-$ ($C_{17}H_{17}O$) requires *m/z* 237.1285, found *m/z* 237.1285.

1-([1,1'-biphenyl]-4-yl)-3-chlorobut-3-en-1-ol, **5r**



Prepared according to General Procedure C using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (153 mg, 0.75 mmol, 3.0 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), 2-(2-chloroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (101 mg, 0.50 mmol, 2.0 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure C (silica gel, EtOAc:petroleum ether, 1:20) to afford the desired product as a colourless oil (43.7 mg, 68%).

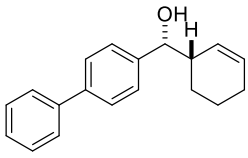
υ_{max} (film): 3567, 3399 (br), 3057, 3027, 2949, 2922, 2855, 1639, 1488, 769, 700 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.61 – 7.58 (m, 4H), 7.48 – 7.43 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 5.32 (s, 1H), 5.27 (s, 1H), 5.12 – 5.07 (m, 1H), 2.82 (dd, *J* = 14.4, 8.9 Hz, 1H), 2.72 (dd, *J* = 14.4, 4.2 Hz, 1H), 2.12 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 142.1, 141.0, 140.9, 139.0, 128.9, 127.5, 127.5, 127.2, 126.4, 115.7, 71.1, 49.4.

HRMS (NSI): exact mass calculated for $[M+Cl]^-$ ($C_{15}H_{15}OCl_2$) requires *m/z* 293.0505, found *m/z* 293.0506.

(*R**)-[1,1'-biphenyl]-4-yl((*S**)-cyclohex-2-en-1-yl)methanol, **5t**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (66 mg, 0.33 mmol, 1.3 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), 2-(cyclohex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (65 mg, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (56 mg, 85%).

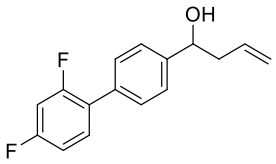
υ_{max} (film): 3550, 3388 (br), 3054, 3024, 2922, 2855, 1488, 1010, 769, 700 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 7.63 – 7.58 (m, 4H), 7.47 – 7.41 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 5.91 – 5.81 (m, 1H), 5.45 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.64 (d, *J* = 6.6 Hz, 1H), 2.56 (dd, *J* = 5.5, 2.8 Hz, 1H), 2.02 (s, 3H), 1.79 (qd, *J* = 10.7, 5.0 Hz, 2H), 1.66 – 1.47 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 142.1, 141.0, 140.4, 130.6, 128.9, 128.1, 127.4, 127.2, 127.1, 127.1, 77.3, 43.1, 25.4, 24.0, 21.3.

The spectral data were consistent with those previously reported in the literature.[2]

1-(2',4'-difluoro-[1,1'-biphenyl]-4-yl)but-3-en-1-ol, **5u**



Prepared according to General Procedure A using 4-bromobenzaldehyde (46 mg, 0.25 mmol, 1.0 equiv.), 2-(2,4-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (78 mg, 0.33 mmol, 1.3 equiv.), Pd(dppf)Cl_2·CH_2Cl_2 (1.0 mg, 1.2 μmol, 0.5 mol%), allylBPin (60 μL, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50.0 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure A (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (59.5 mg, 92%).

υ_{max} (film): 3394 (br), 3076, 2931, 1618, 1496, 1144, 967 cm^{-1}.

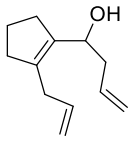
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.00 – 6.86 (m, 2H), 5.91 – 5.78 (m, 1H), 5.22 – 5.16 (m, 2H), 4.79 (dd, *J* = 7.8, 5.0 Hz, 1H), 2.63 – 2.48 (m, 2H), 2.19 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.4 (dd, J^1 = 248.9 Hz, J^3 = 11.9 Hz), 159.9 (dd, J^1 = 250.4 Hz, J^3 = 11.8 Hz), 143.6, 134.5, 131.5 (dd, J^3 = 9.4 Hz, J^3 = 5.0 Hz), 129.1, 129.0, 126.2, 125.2 (dd, J^2 = 13.7 Hz, J^4 = 3.7 Hz), 118.7, 111.7 (dd, J^2 = 21.1 Hz, J^4 = 3.6 Hz), 104.5 (dd, J^2 = 26.0 Hz, J^2 = 26.0 Hz), 73.1, 43.9.

^{19}F NMR (471 MHz, $CDCl_3$): δ -111.5 (d, *J* = 7.6 Hz), -113.5 (d, *J* = 7.6 Hz).

The spectral data were consistent with those previously reported in the literature.[3]

1-(2-allylcyclopent-1-en-1-yl)but-3-en-1-ol, **10**



An oven dried 5 mL microwave vial was charged with 2-bromocyclopent-1-ene-1-carbaldehyde (44 mg, 0.25 mmol, 1.0 equiv.), Pd(dppf)Cl_2·CH_2Cl_2 (1.0 mg, 1.2 μmol, 0.5 mol%), and K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.). The microwave vial was capped and purged with N_2 before adding PhMe (1 mL, 0.25 M), H_2O (22.5 μL, 5.0 equiv.) and allylBPin (144 μL, 0.75 mmol, 3.0 equiv.). The reaction mixture was stirred at 0 °C for 7 h before allowed to warm up to room temperature and stirred for another 2 h. The reaction mixture

was then heated to 90 °C for 16 h. The crude mixture was filtered through a short pad of Celite, the filter cake was rinsed with EtOAc (10 mL x 2) and the resulting filtration was washed with sat. ammonium chloride solution (20 mL). The aqueous phase was extracted with EtOAc (10 mL x 2) and the combined organic phase was passed through a hydrophobic frit and concentrated under reduced pressure before being purified by flash chromatography (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (38 mg, 86%).

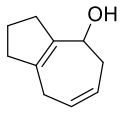
υ_{max} (film): 3394 (br), 3076, 2927, 2853, 1641, 1443, 1048, 995, 915 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 5.90 – 5.54 (m, 2H), 5.19 – 4.91 (m, 4H), 4.52 (dd, *J* = 7.5, 6.3 Hz, 1H), 2.86 (d, *J* = 1.4 Hz, 2H), 2.49 (dt, *J* = 6.2, 5.0 Hz, 1H), 2.43 – 2.21 (m, 5H), 1.85 – 1.73 (m, 2H), 1.69 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.6, 137.2, 136.2, 134.9, 117.7, 115.4, 67.8, 40.5, 36.5, 33.1, 31.1, 21.8.

HRMS (NSI): exact mass calculated for $[M+H]^+$ ($C_{12}H_{19}O$) requires *m/z* 179.1430, found *m/z* 179.1432.

1,2,3,4,5,8-hexahydroazulen-4-ol, **11**



An oven dried 50 mL round bottom flask was charged with 1-(2-allylcyclopent-1-en-1-yl)but-3-en-1-ol (**11**) (35 mg, 0.20 mmol, 1.0 equiv.), GII catalyst (6.7 mg, 7.9 μmol, 4 mol%), and CH_2Cl_2 (20 mL, 0.01 M). The reaction mixture was stirred at 40 °C for 6 h before allowed to cool down to room temperature. The reaction mixture was then concentrated under reduced pressure and purified by flash chromatography (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (27 mg, 90%).

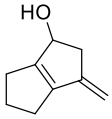
υ_{max} (film): 3381 (br), 3026, 2951, 2925, 2851, 1720, 1648, 1445, 1046 cm^{-1}.

^1H NMR (400 MHz, CD_2Cl_2): δ 5.91 (dt, *J* = 10.5, 5.3 Hz, 1H), 5.75 (dtt, *J* = 10.5, 6.6, 1.3 Hz, 1H), 4.16 (ap.s, 1H), 2.85 – 2.75 (m, 2H), 2.70 – 2.59 (m, 1H), 2.51 – 2.44 (m, 2H), 2.40 – 2.27 (m, 3H), 1.80 – 1.69 (m, 2H). (OH signal not observed).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 138.2, 136.3, 132.3, 126.5, 67.9, 40.2, 36.7, 34.9, 29.6, 21.4.

HRMS (NSI): exact mass calculated for $[M+H-H_2O]^+$ ($C_{10}H_{13}$) requires *m/z* 133.1012, found *m/z* 133.1011.

3-methylene-1,2,3,4,5,6-hexahydropentalen-1-ol, **12**



An oven dried 5 mL microwave vial was charged with 2-bromocyclopent-1-ene-1-carbaldehyde (44 mg, 0.25 mmol, 1.0 equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), and K_3PO_4 (159 mg, 0.75 mmol, 3.0 equiv.). The microwave vial was capped and purged with N_2 before adding PhMe (1 mL, 0.25 M), H_2O (225 μL, 50.0 equiv.) and allylBPin (60 μL, 0.31 mmol, 1.25 equiv.). The reaction mixture was stirred at 0 °C for 7 h before allowed to warm up to room temperature and stirred for another 2 h. The reaction mixture was then heated to 90 °C for 16 h. The crude mixture was filtered through a short pad of Celite, the filter cake was rinsed with EtOAc (10 mL x 2) and the resulting filtration was washed with sat. ammonium chloride solution (20 mL). The aqueous phase was extracted with EtOAc (10 mL x 2) and the combined organic phase was passed through a hydrophobic frit and concentrated under reduced pressure before being purified by flash chromatography (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a colourless oil (17.7 mg, 52%).

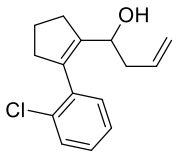
υ_{max} (film): 3371 (br), 2925, 2851, 1310, 1254, 1157, 1038 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 4.76 (d, *J* = 5.1 Hz, 2H), 4.71 (m, 1H), 4.68 (m, 1H), 3.28 (ddd, *J* = 16.8, 5.1, 1.6 Hz, 1H), 2.69 (dd, *J* = 16.8, 1.9 Hz, 1H), 2.57 – 2.43 (m, 1H), 2.42 – 2.22 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 157.5, 151.8, 145.8, 101.7, 71.7, 46.3, 28.0, 27.9, 26.0.

HRMS (NSI): exact mass calculated for $[M+H]^+$ ($C_9H_{13}O$) requires *m/z* 137.0959, found *m/z* 137.0961.

1-(2-(2-chlorophenyl)cyclopent-1-en-1-yl)but-3-en-1-ol, **14**



Prepared according to General Procedure B using 2-bromocyclopent-1-ene-1-carbaldehyde (87 mg, 0.50 mmol, 1.0 equiv), 2-(2-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (297 mg, 1.25 mmol, 2.5 equiv), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (2.0 mg, 2.5 μmol, 0.5 mol%), allylBPin (202 mg, 1.00 mmol, 2.0 equiv), K_3PO_4 (318 mg, 1.50 mmol, 3 equiv), PhMe (2 mL, 0.25 M), and H_2O (450 μL, 25.00 mmol, 50 equiv). The reaction mixture was subjected to the purification outlined in the General Procedure B (silica gel, EtOAc:petroleum ether, 1:20) to afford the desired product as a colourless oil (80.4 mg, 65%).

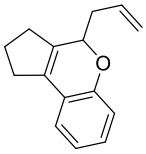
υ_{max} (film): 3366 (br), 3070, 2925, 2843, 1471, 1429, 1040, 756 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.35 (m, 1H), 7.25 – 7.18 (m, 2H), 7.12 (d, *J* = 6.6 Hz, 1H), 5.69 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.16 – 4.95 (m, 2H), 4.21 – 4.09 (m, 1H), 2.76 – 2.59 (m, 3H), 2.56 – 2.47 (m, 1H), 2.39 – 2.24 (m, 2H), 2.06 – 1.95 (m, 2H), 1.61 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 141.9, 138.0, 137.5, 134.8, 134.8, 130.5, 129.7, 128.5, 126.8, 117.7, 68.2, 40.0, 38.2, 31.0, 22.7.

HRMS (NSI): exact mass calculated for $[M+O_2-H]^-$ ($C_{15}H_{16}O_3Cl$) requires *m/z* 279.0793, found *m/z* 279.0795.

4-allyl-1,2,3,4-tetrahydrocyclopenta[c]chromene, **15**



An oven dried 5 mL microwave vial was charged with 1-(2-(2-chlorophenyl)cyclopent-1-en-1-yl)but-3-en-1-ol (**15**) (62 mg, 0.25 mmol, 1.0 equiv.), $Pd(OAc)_2$ (2.2 mg, 10 µmol, 4 mol%), and K_3PO_4 (106 mg, 0.50 mmol, 2.0 equiv.). The microwave vial was capped and purged with N_2 before adding 1,4-dioxane (1 mL, 0.25 M). The reaction mixture was heated to 120 °C for 24 h. The crude mixture was filtered through a short pad of Celite, the filter cake was rinsed with EtOAc (10 mL x 2) and the resulting filtration was washed with sat. ammonium chloride solution (20 mL). The aqueous phase was extracted with EtOAc (10 mL x 2) and the combined organic phase was passed through a hydrophobic frit and concentrated under reduced pressure before being purified by flash chromatography (silica gel, EtOAc:petroleum ether, 1:15 to 1:10) to afford the desired product as a pale yellow oil (15 mg, 28%).

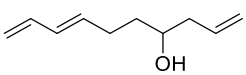
υ_{max} (film): 2951, 2907, 2845, 1492, 1200, 1036, 751 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 – 7.03 (m, 1H), 6.96 – 6.91 (m, 1H), 6.84 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.94 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.16 – 5.04 (m, 3H), 2.72 – 2.57 (m, 2H), 2.55 – 2.38 (m, 4H), 2.09 – 2.01 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.6, 135.4, 134.0, 131.8, 128.3, 123.2, 121.8, 120.8, 117.7, 115.5, 77.3, 39.0, 33.5, 30.7, 22.6.

HRMS (NSI): exact mass calculated for $[M+H]^+$ ($C_{15}H_{17}O$) requires *m/z* 213.1279, found *m/z* 213.1276.

(*E*)-deca-1,7,9-trien-4-ol, **18**



Prepared according to General Procedure B using (*E*)-5-iodopent-4-enal (**17**)[4] (52 mg, 0.25 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (77 mg, 0.50 mmol, 2.0

equiv.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 0.5 mol%), allylBPin (53 mg, 0.31 mmol, 1.25 equiv.), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), PhMe (1 mL, 0.25 M), and H_2O (225 μL, 12.5 mmol, 50 equiv.). The reaction mixture was subjected to the purification outlined in the General Procedure B (silica gel, EtOAc:petroleum ether, 1:20) to afford the desired product as a colourless oil (28.5 mg, 75%).

υ_{max} (film): 3377(br), 3078, 2974, 2925, 2851, 1005, 915 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 6.31 (dt, *J* = 17.0, 10.3 Hz, 1H), 6.14 – 6.04 (m, 1H), 5.88 – 5.77 (m, 1H), 5.77 – 5.67 (m, 1H), 5.17 – 5.07 (m, 3H), 5.01 – 4.93 (m, 1H), 3.71 – 3.60 (m, 1H), 2.35 – 2.10 (m, 5H), 1.61 – 1.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.3, 134.8, 134.7, 131.6, 118.4, 115.3, 70.2, 42.1, 36.3, 28.9.

HRMS (NSI): exact mass calculated for $[M+NH_4]^+$ ($C_{10}H_{20}NO$) requires *m/z* 170.1539, found *m/z* 170.1542.

6. References

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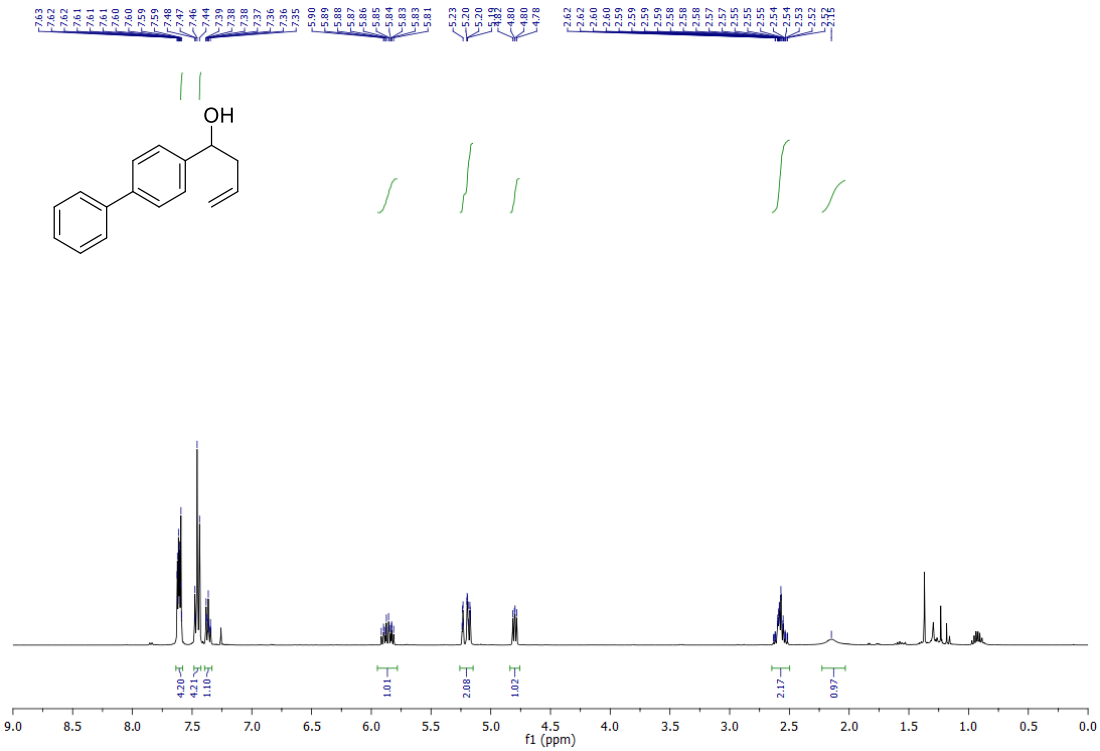
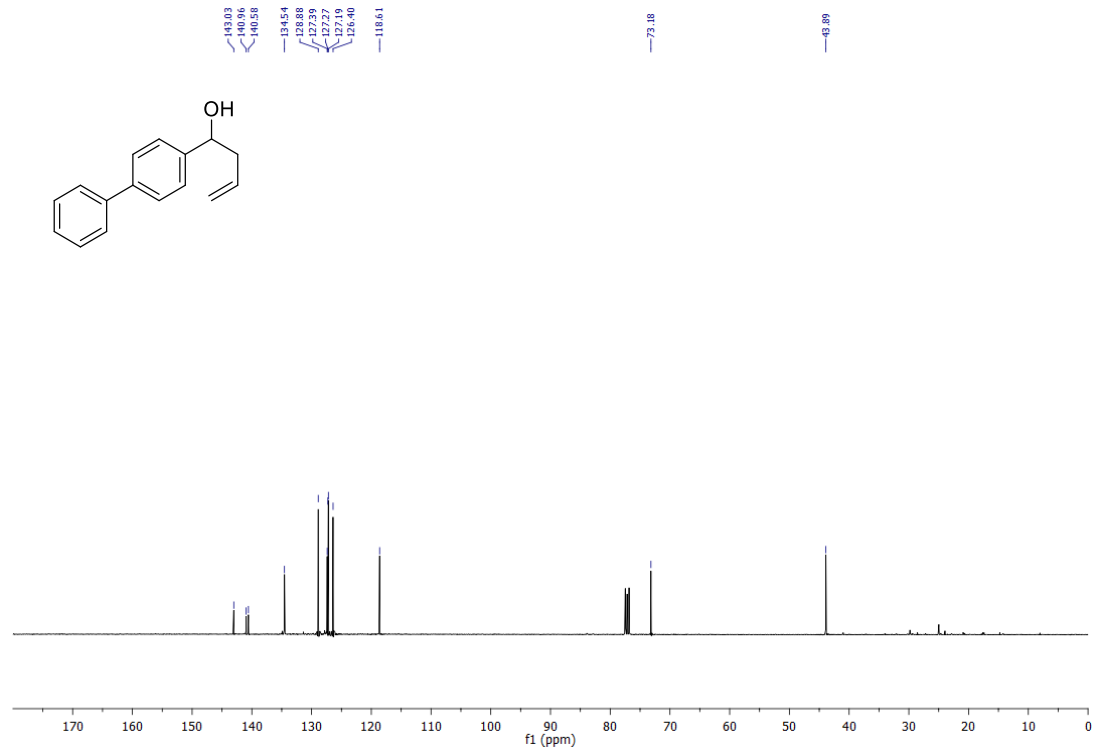
7. NMR spectra

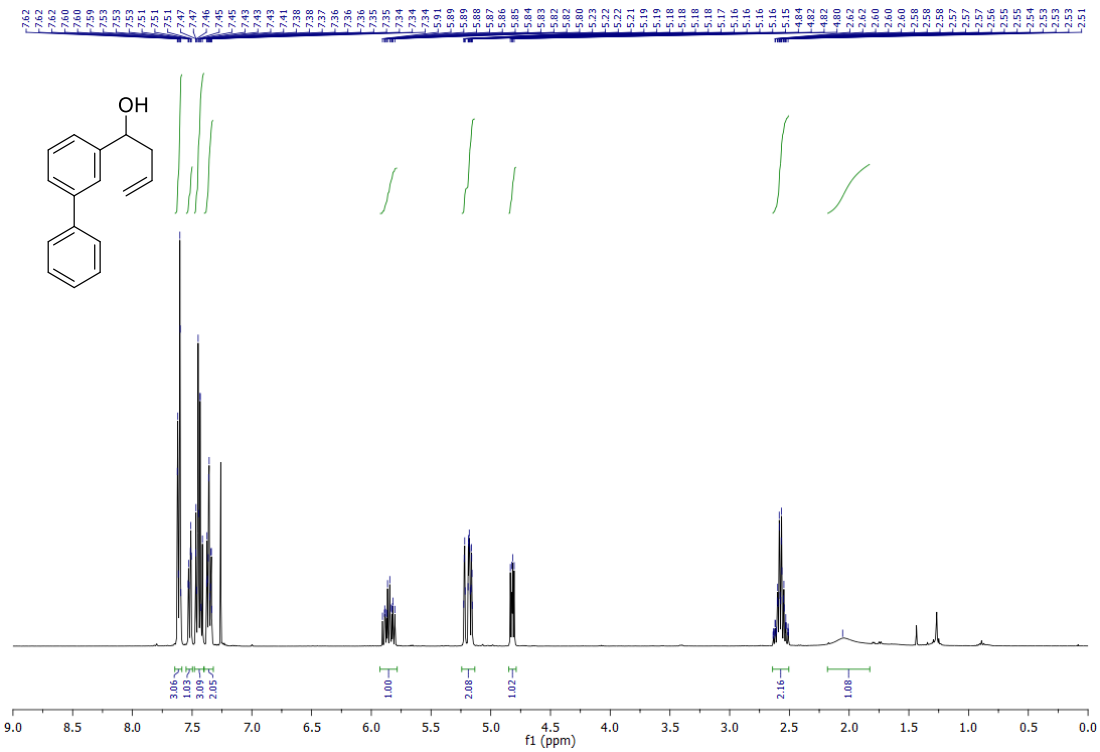
^{1}H NMR of 5a



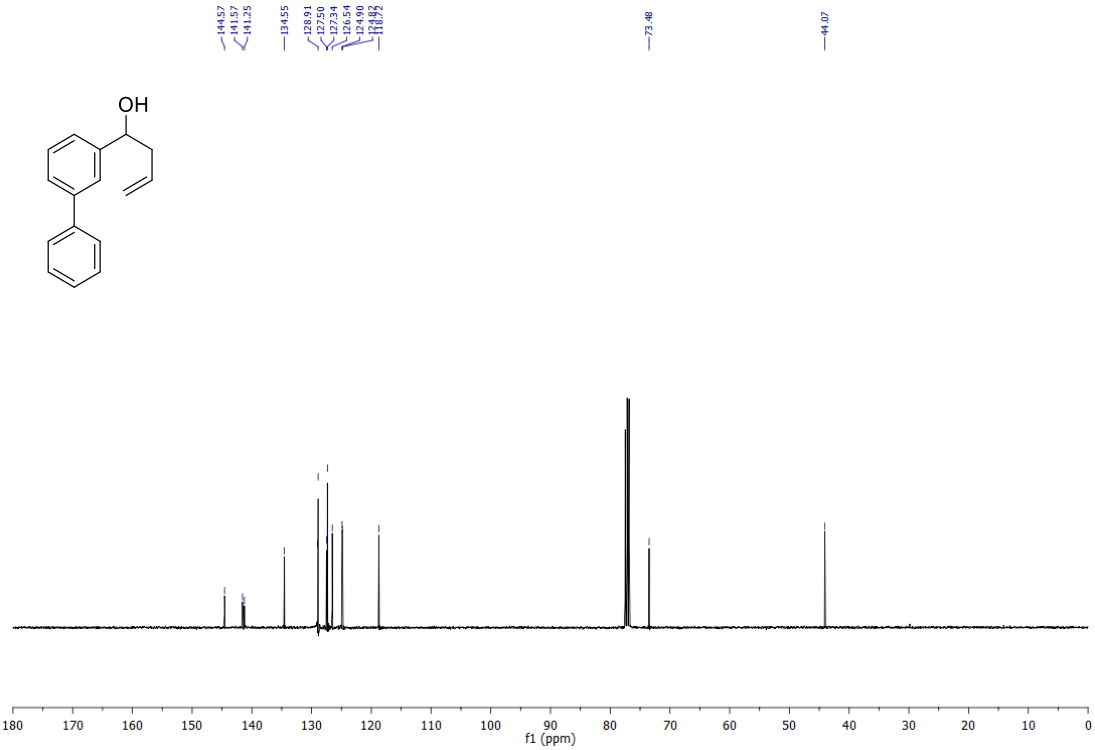
^{13}C NMR of 5a



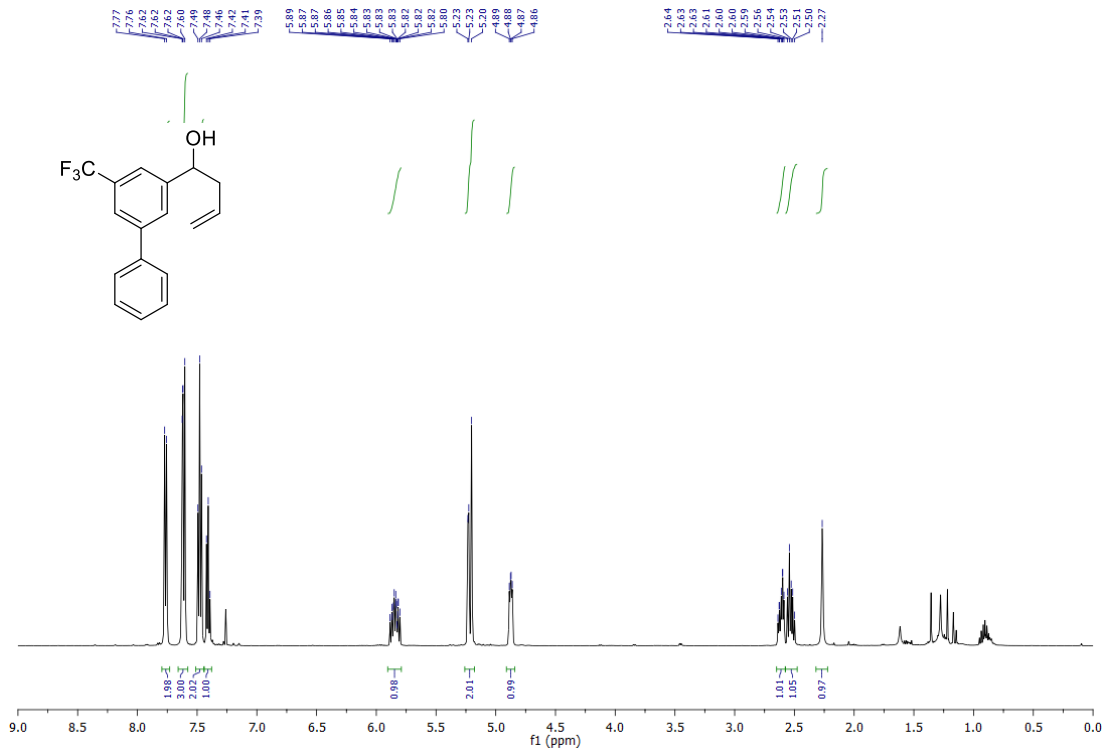
^{1}H NMR of 5b



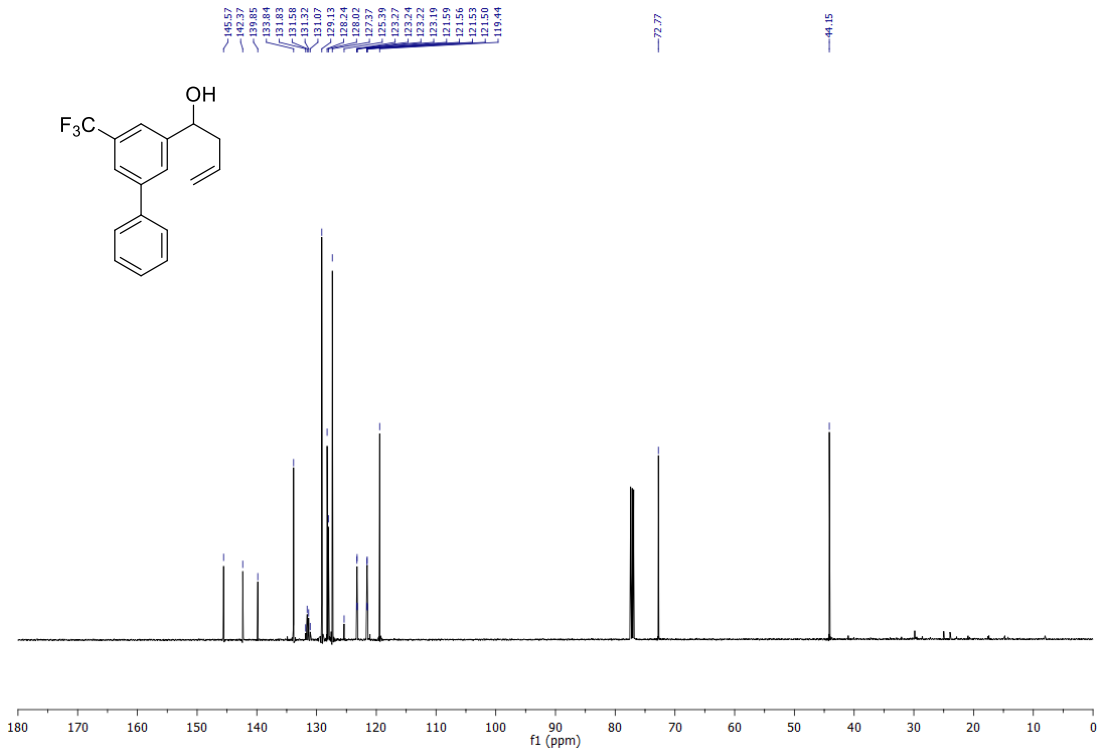
^{13}C NMR of 5b



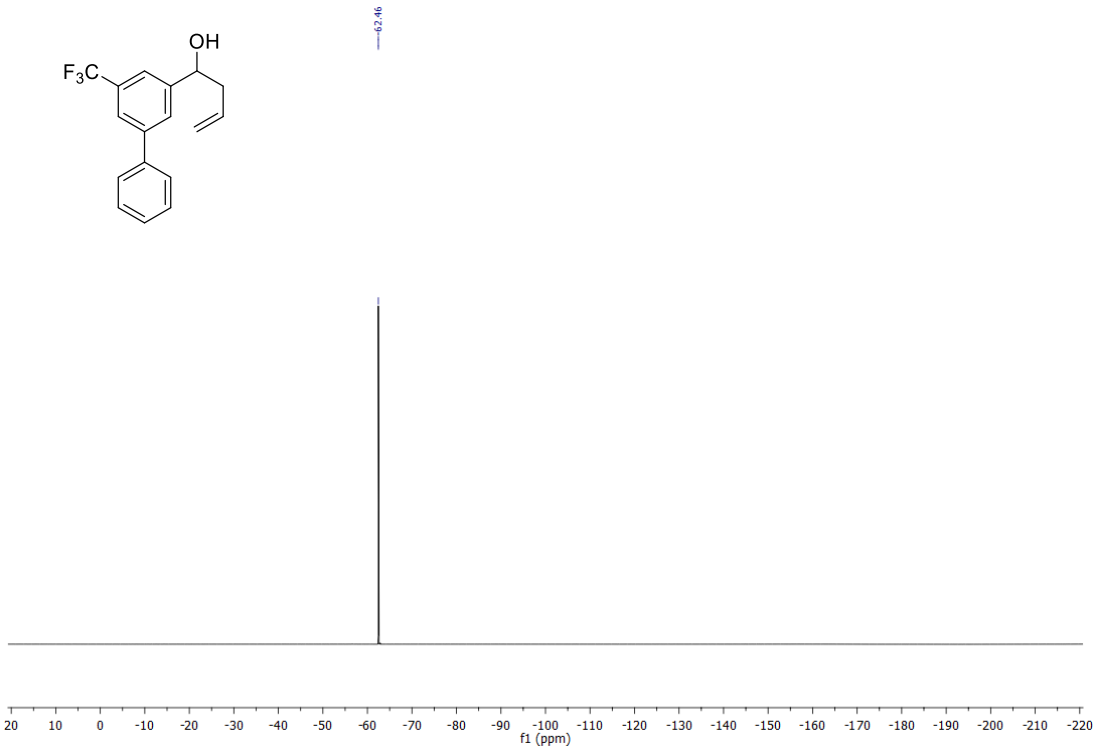
^{1}H NMR of 5c



^{13}C NMR of 5c



^{19}F NMR of 5c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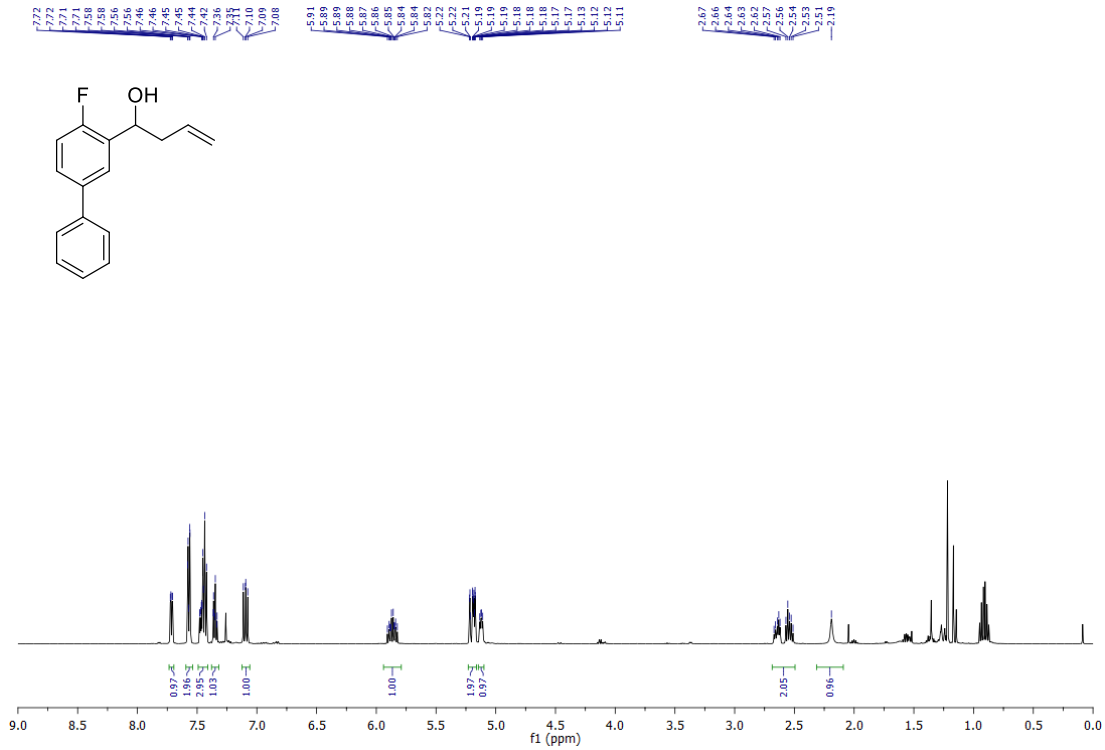
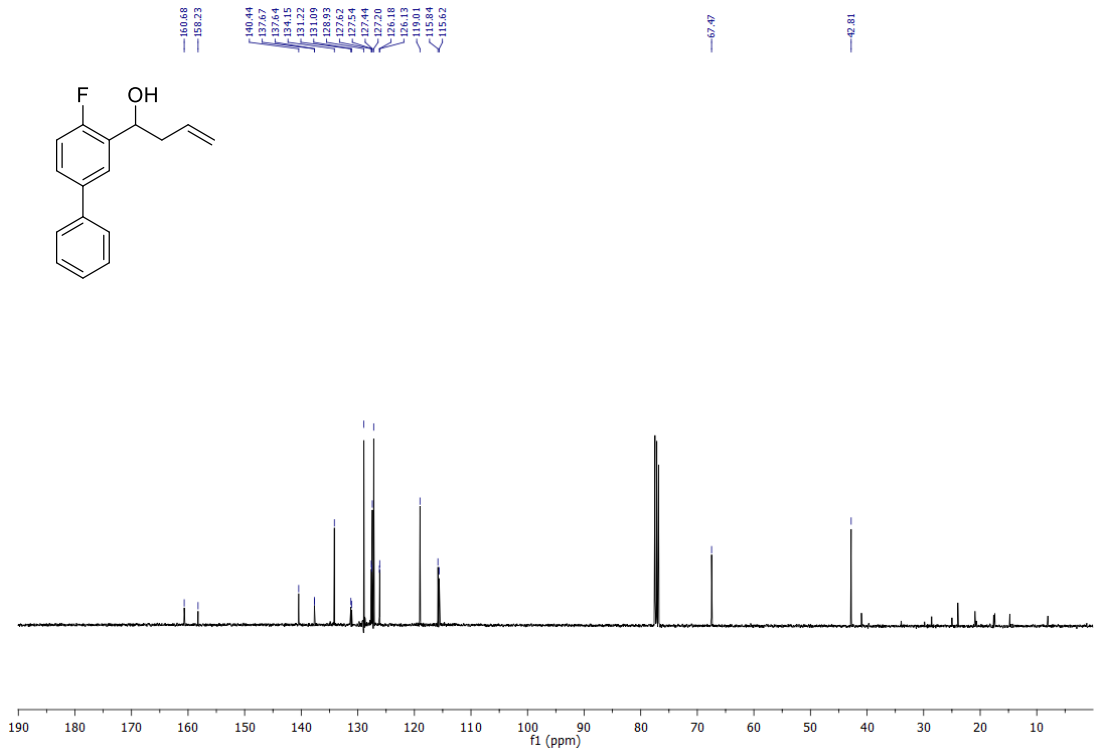
F3C
-62.46
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

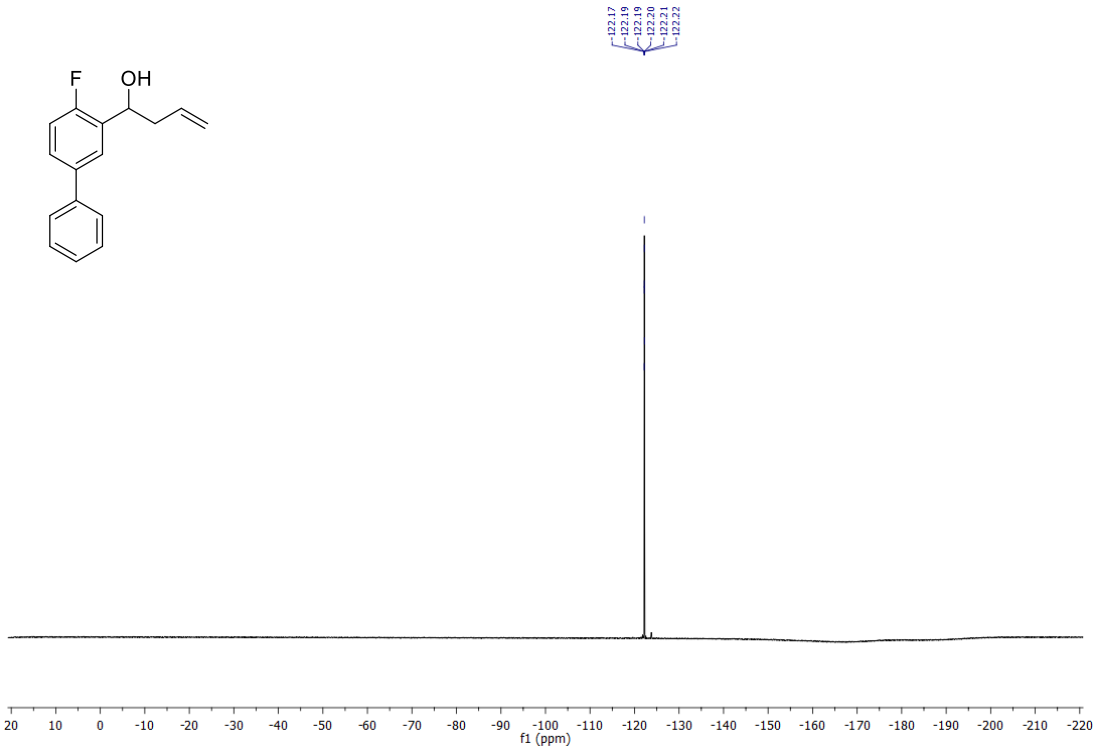
^{1}H NMR of 5d



^{13}C NMR of 5d



^{19}F NMR of 5d


F
OH
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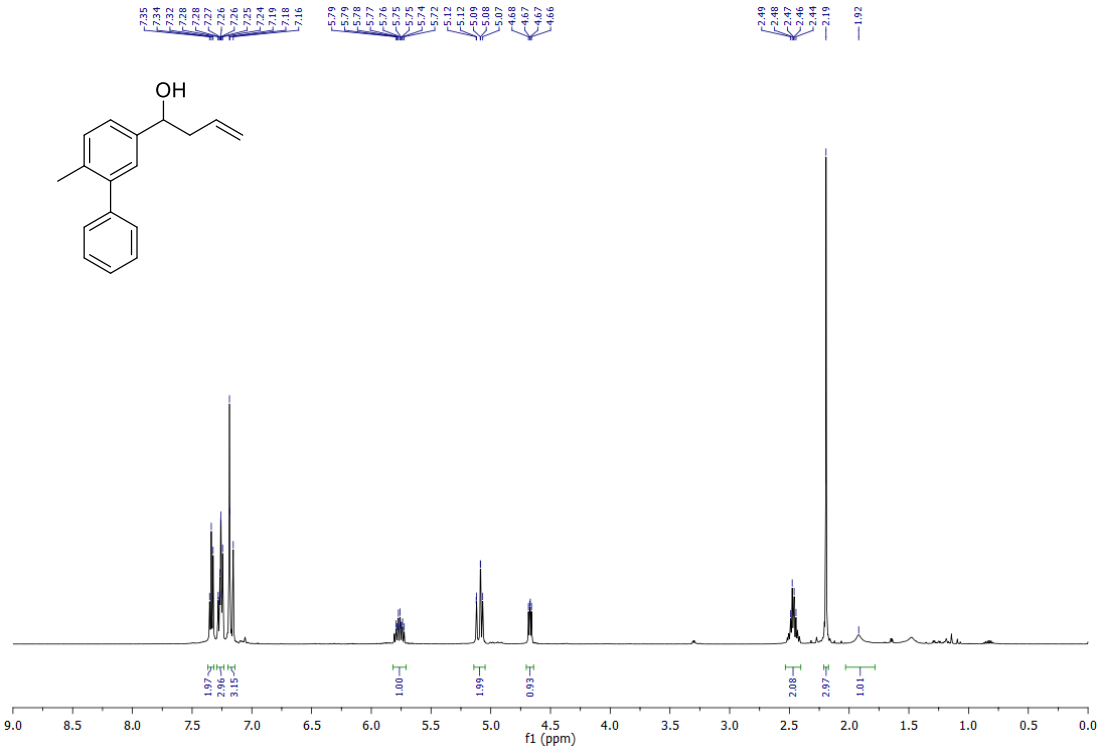
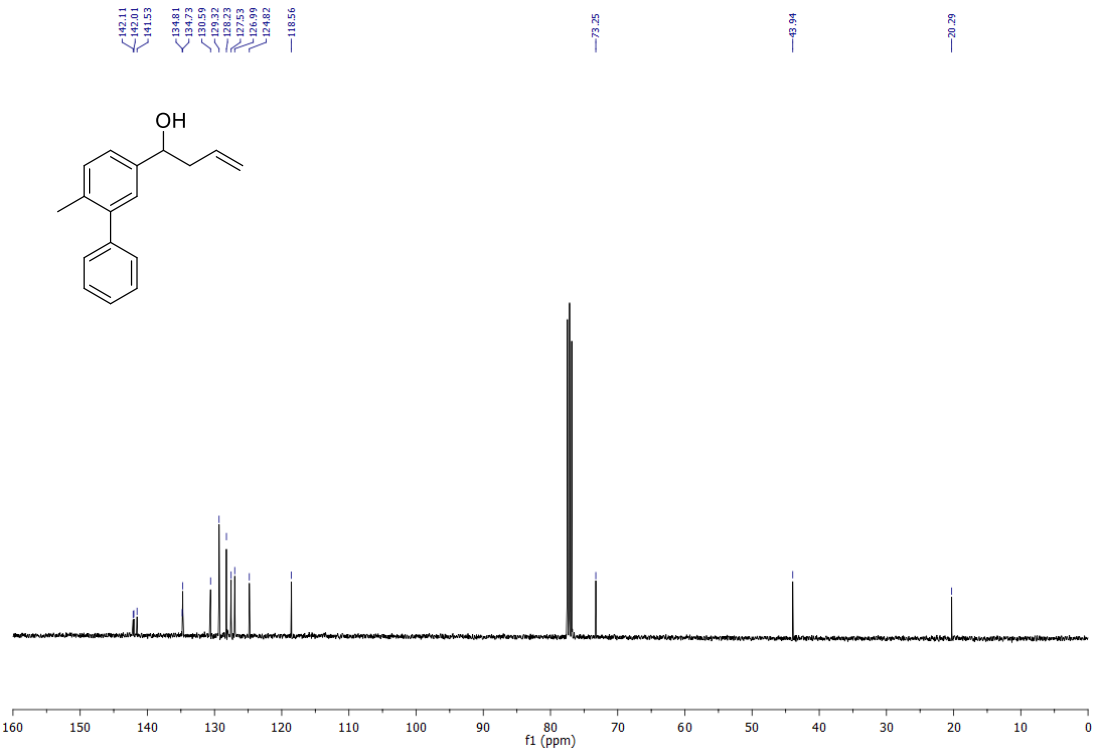
-122.19
-122.19
-122.20
-122.21
-122.22
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

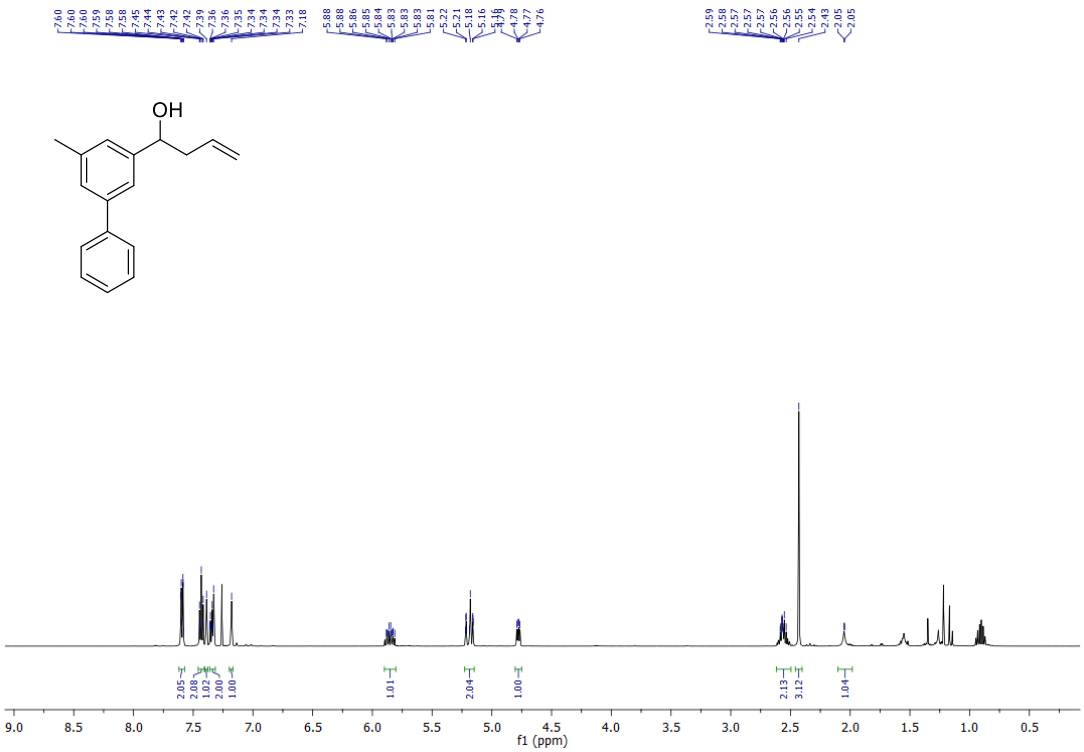
^{1}H NMR of 5e



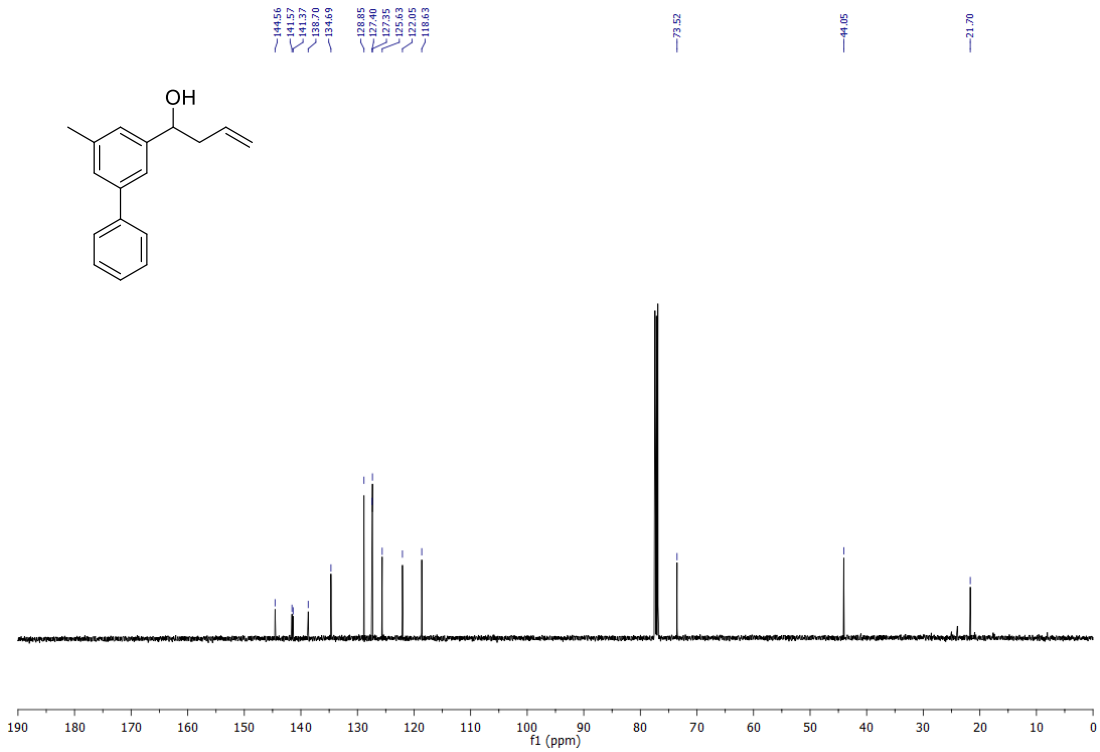
^{13}C NMR of 5e



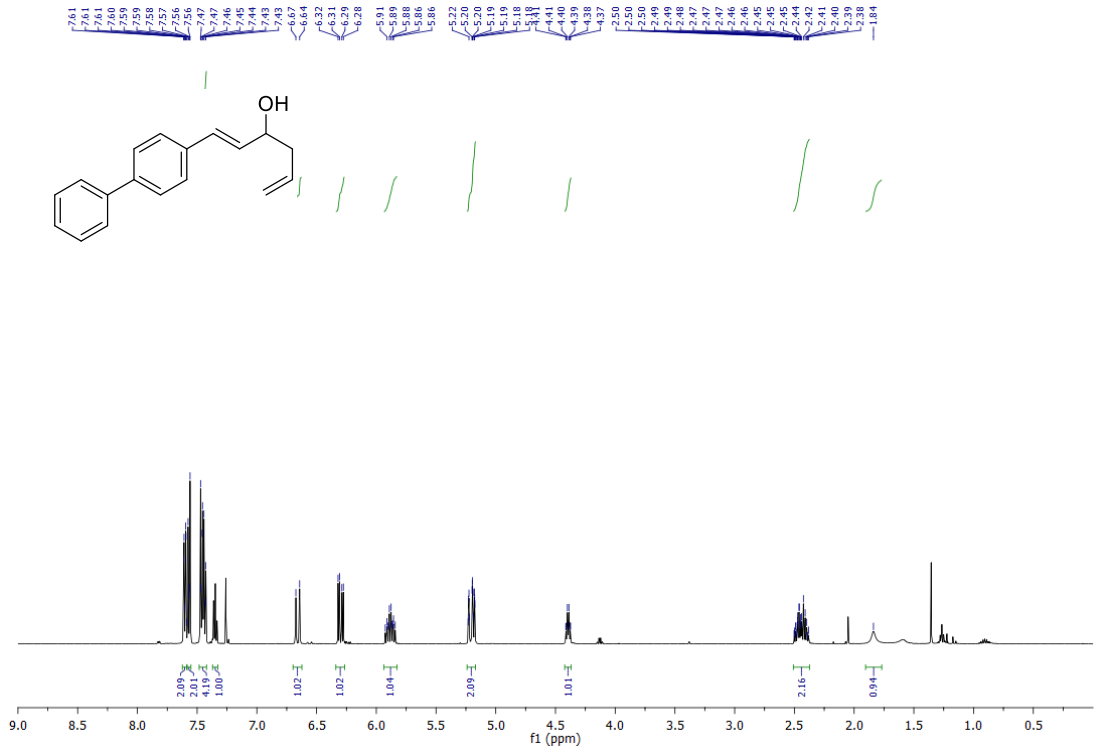
^{1}H NMR of 5f



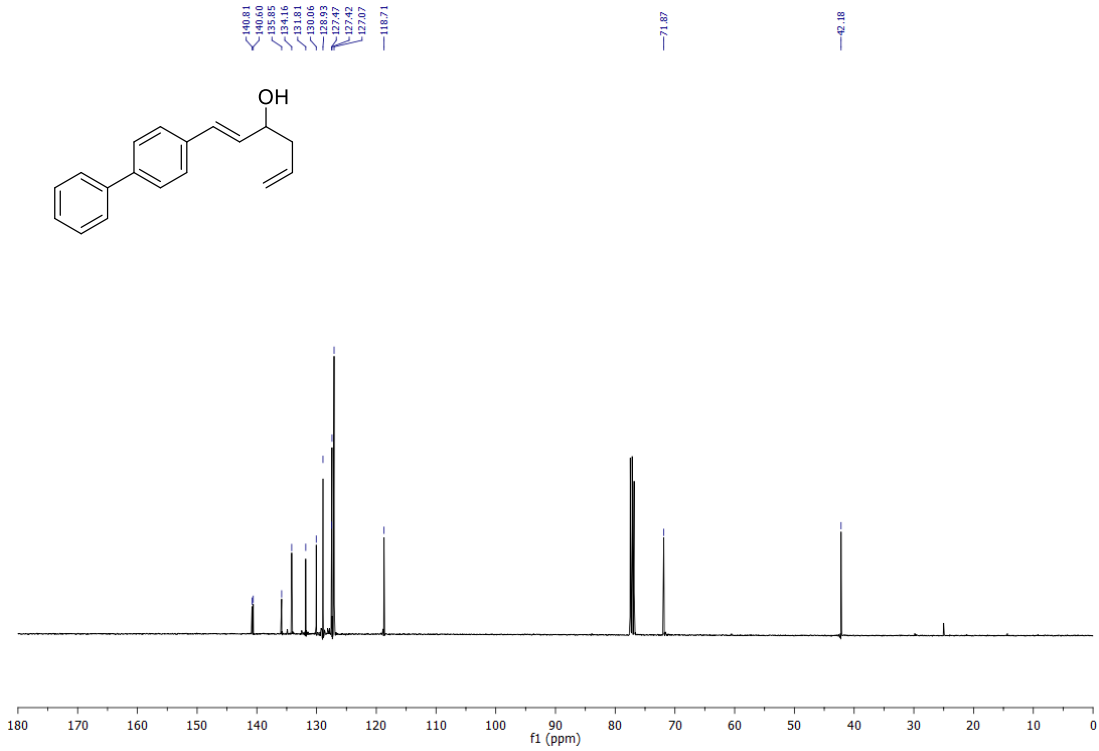
^{13}C NMR of 5f



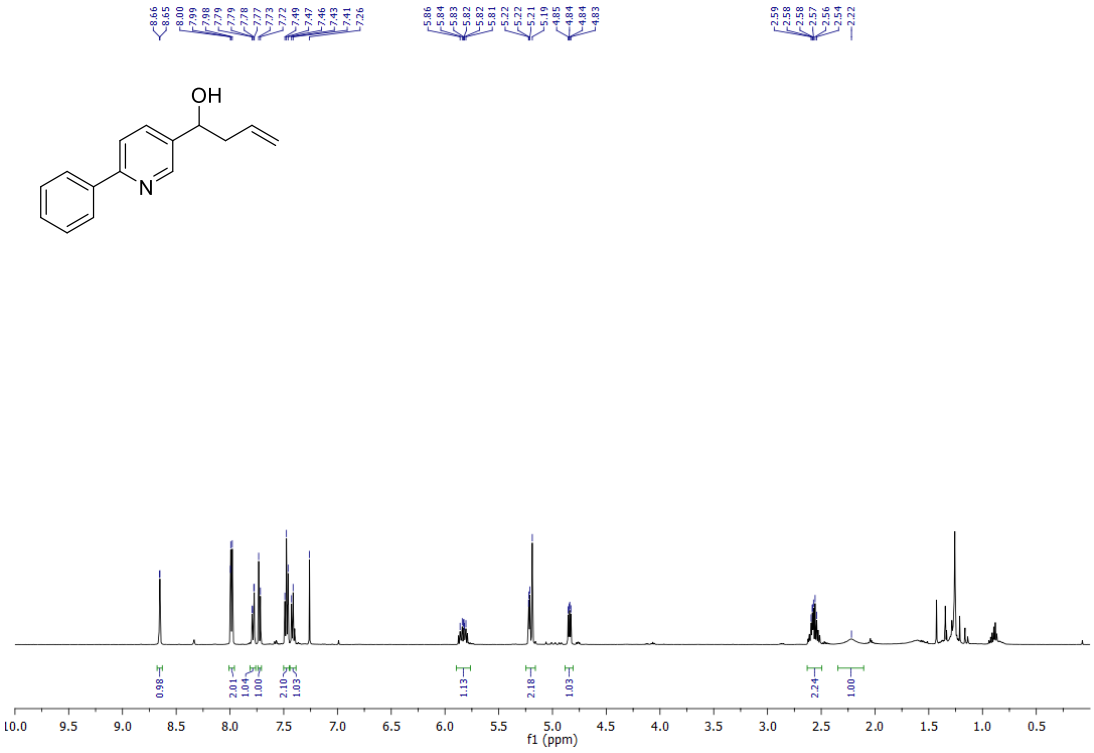
^{1}H NMR of 5g



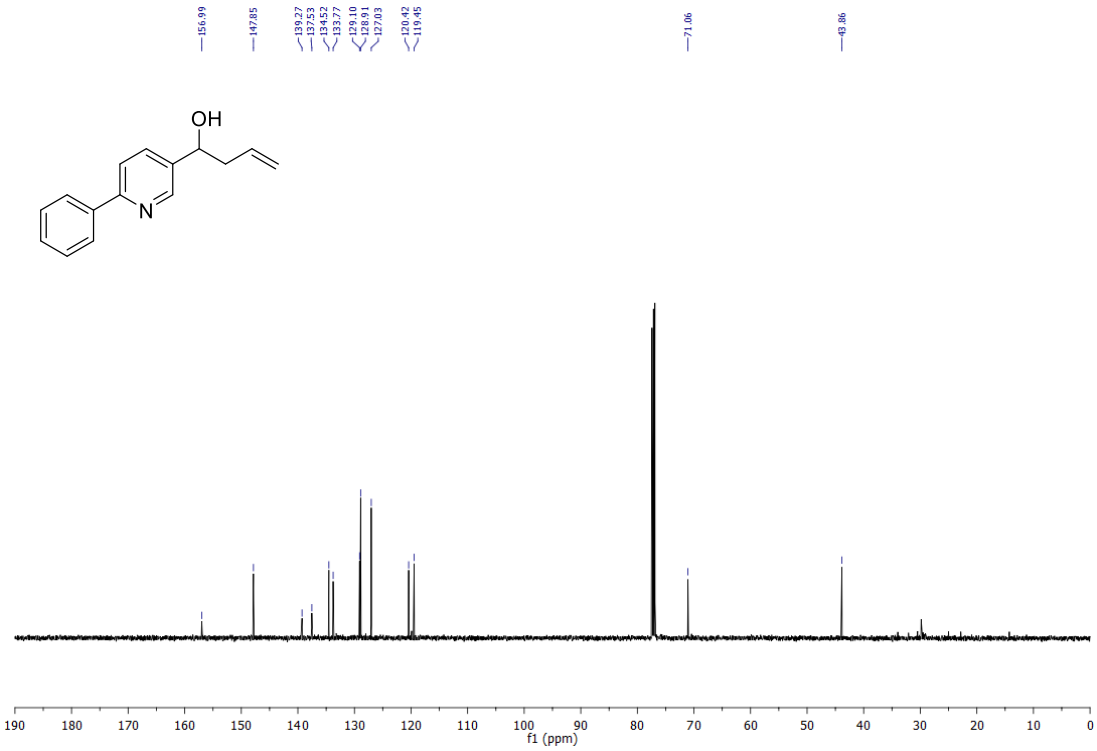
^{13}C NMR of 5g



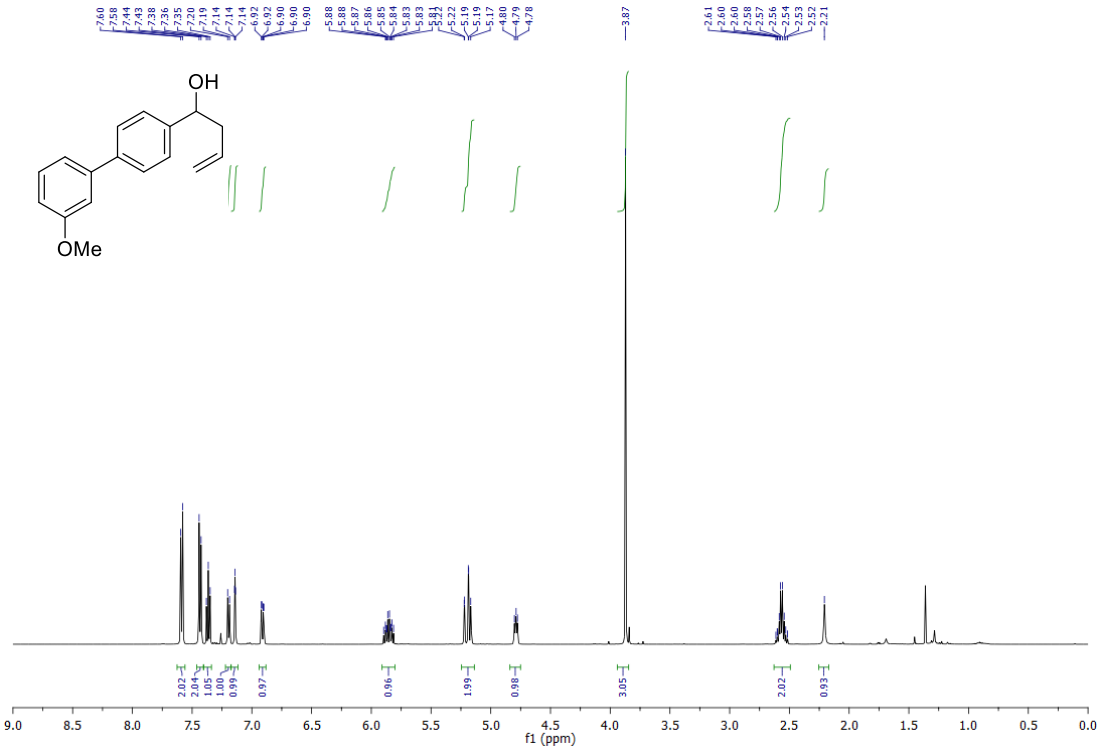
^{1}H NMR of 5h



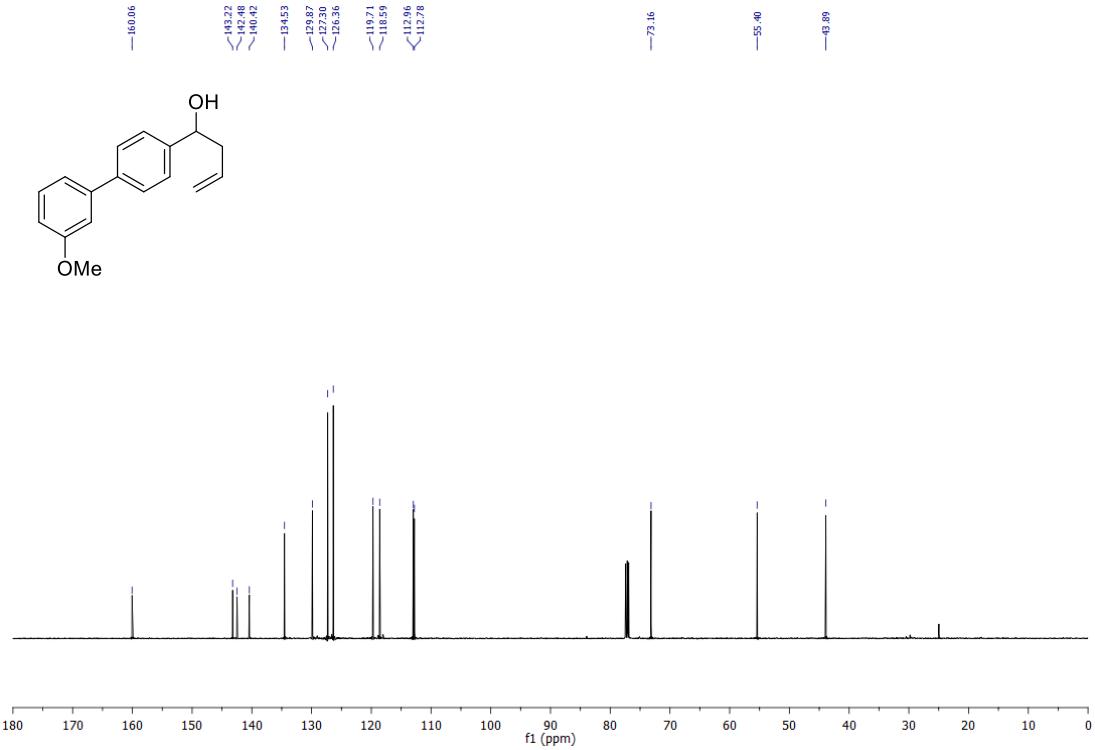
^{13}C NMR of 5h



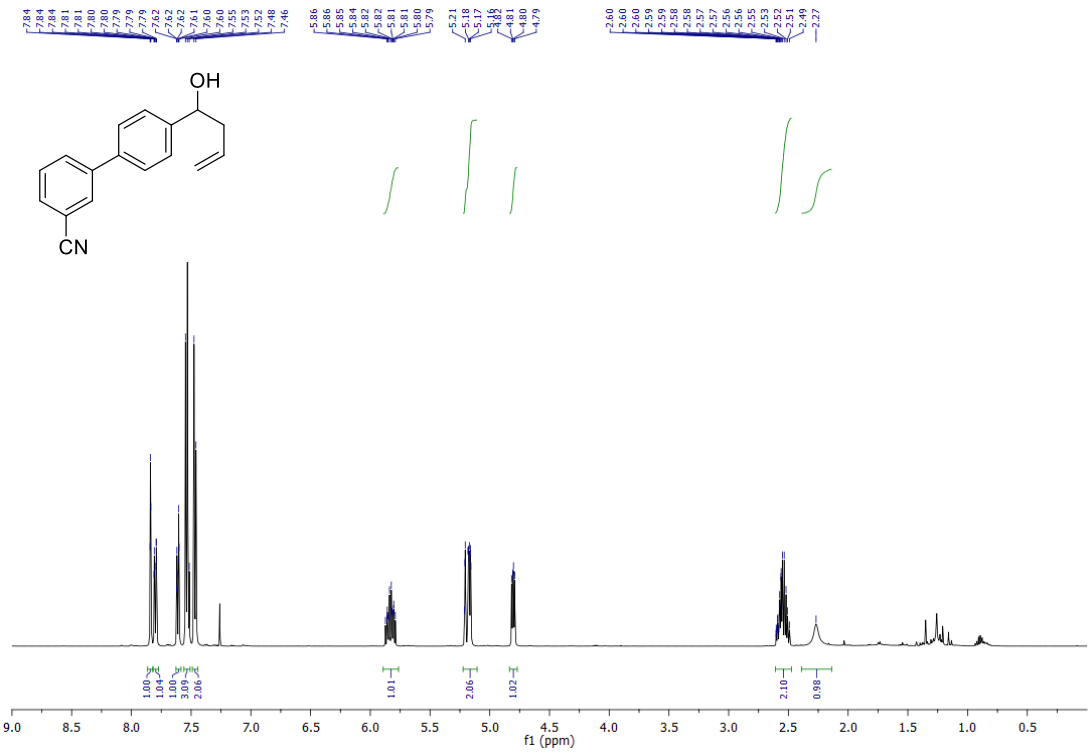
^{1}H NMR of 5i



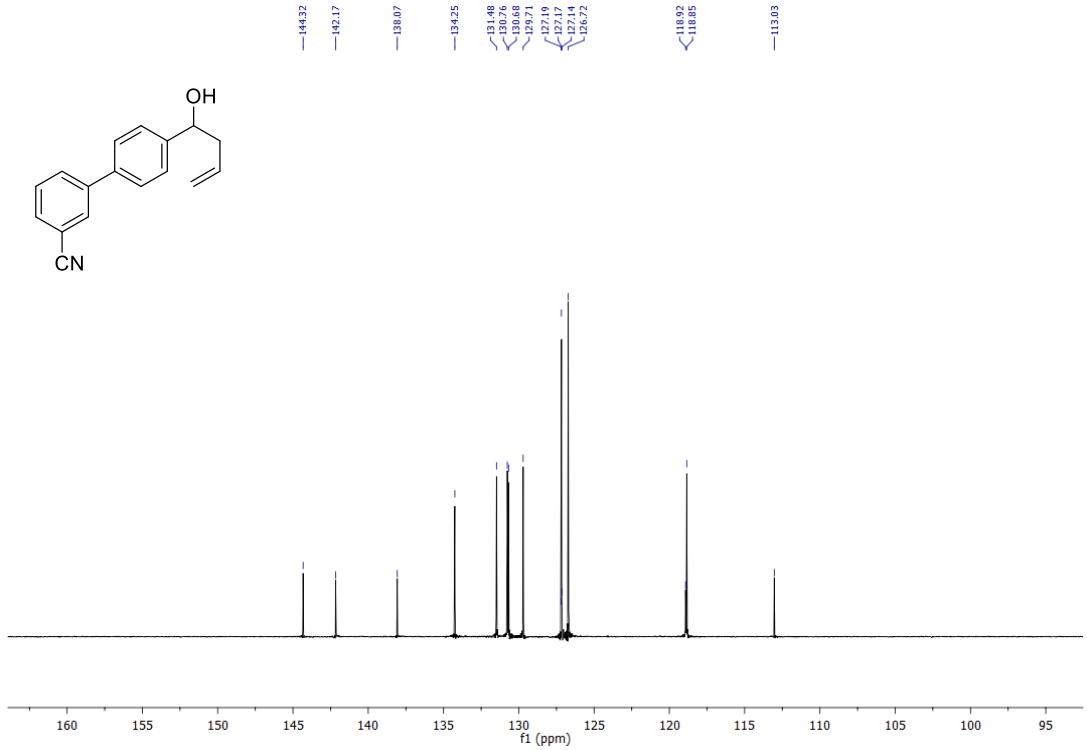
^{13}C NMR of 5i



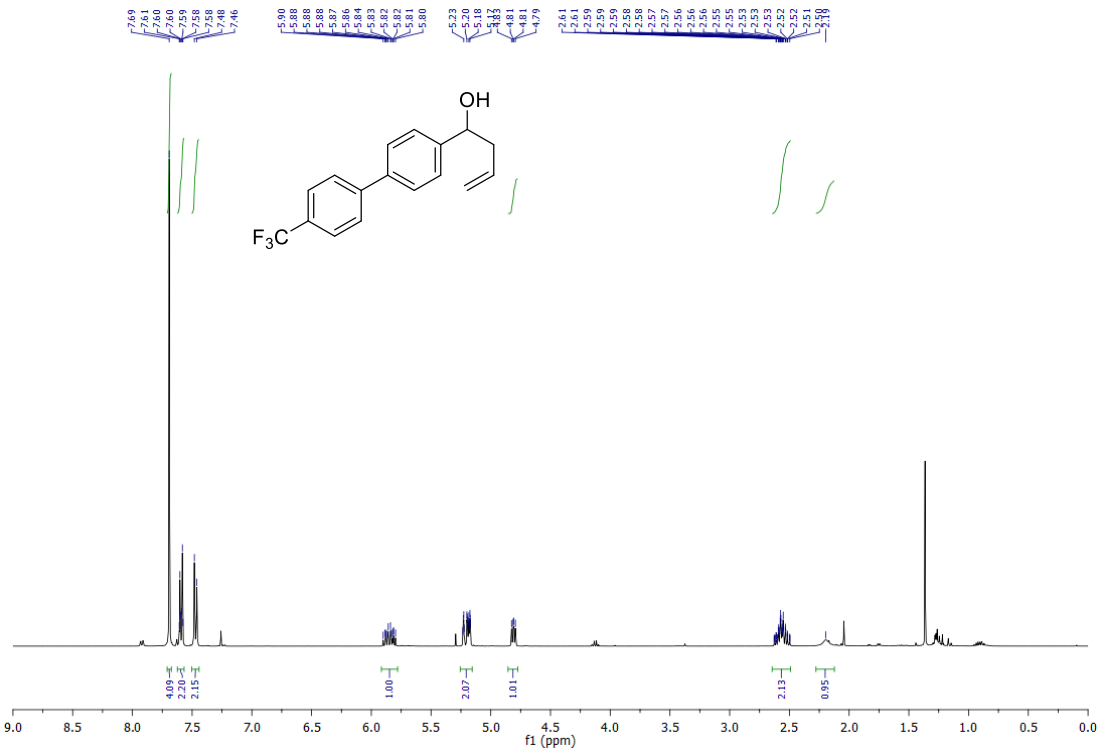
^{1}H NMR of 5j



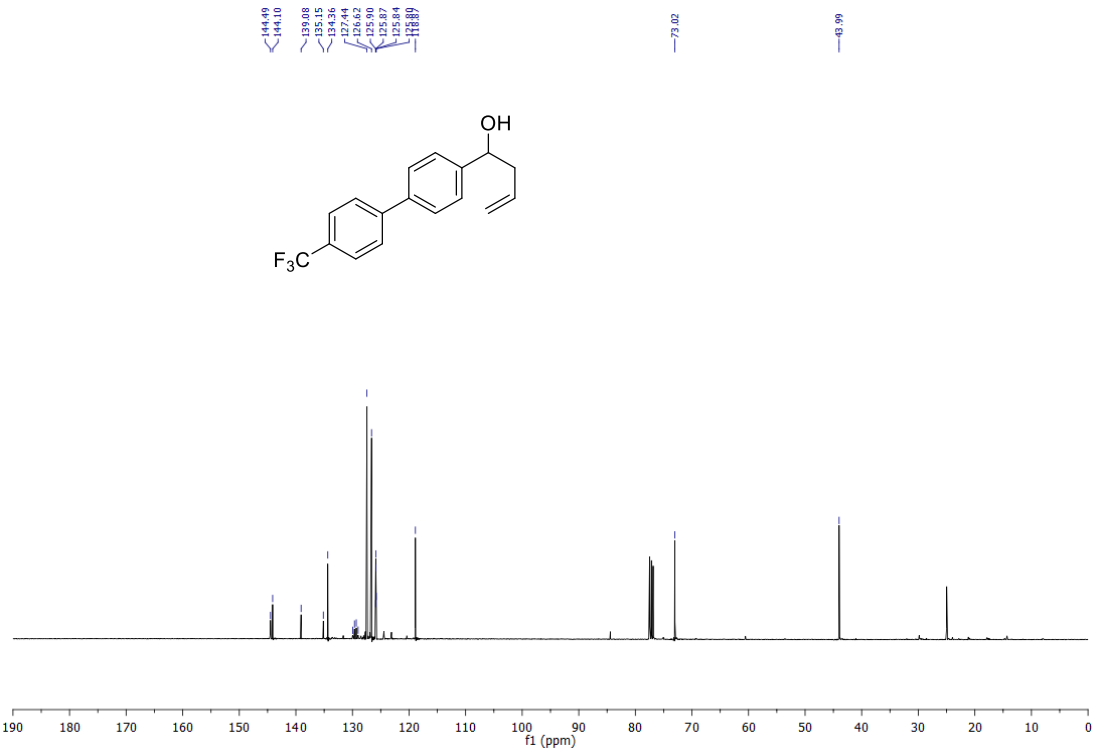
^{13}C NMR of 5j



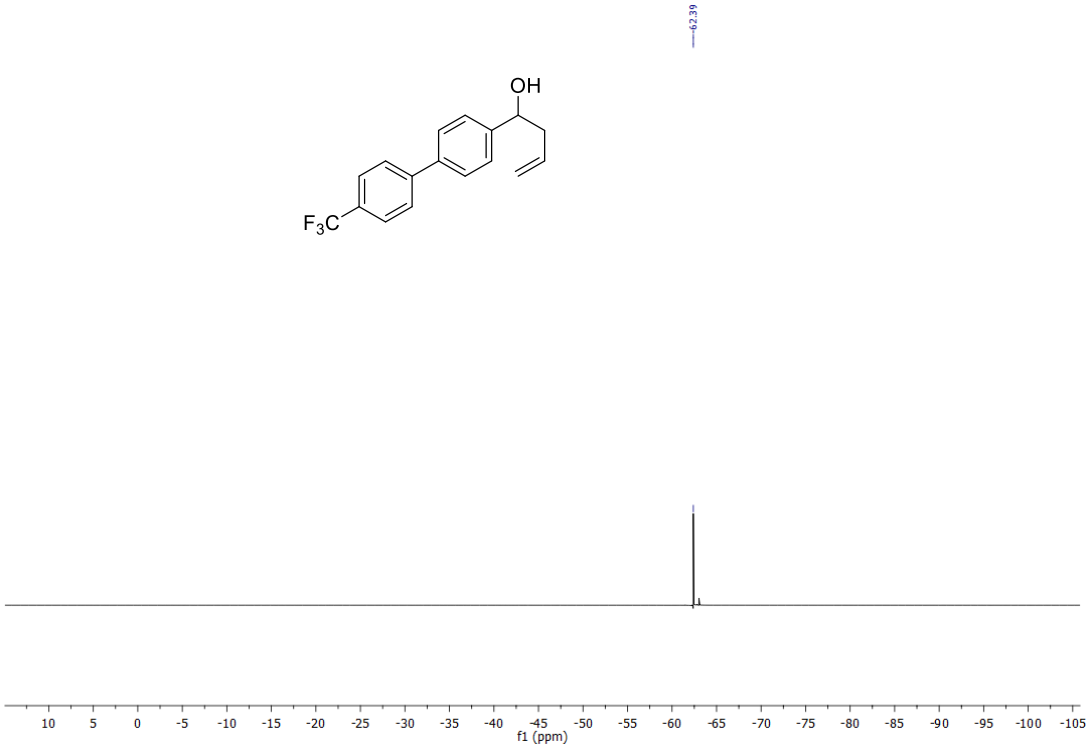
^{1}H NMR of 5k



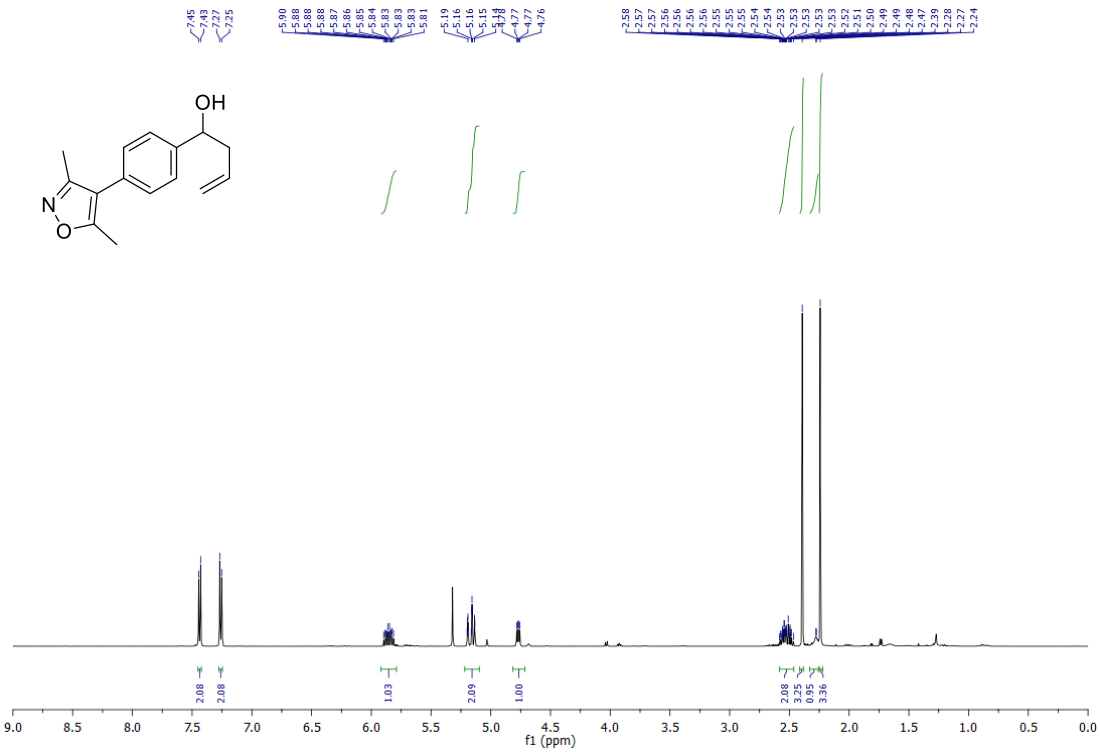
^{13}C NMR of 5k



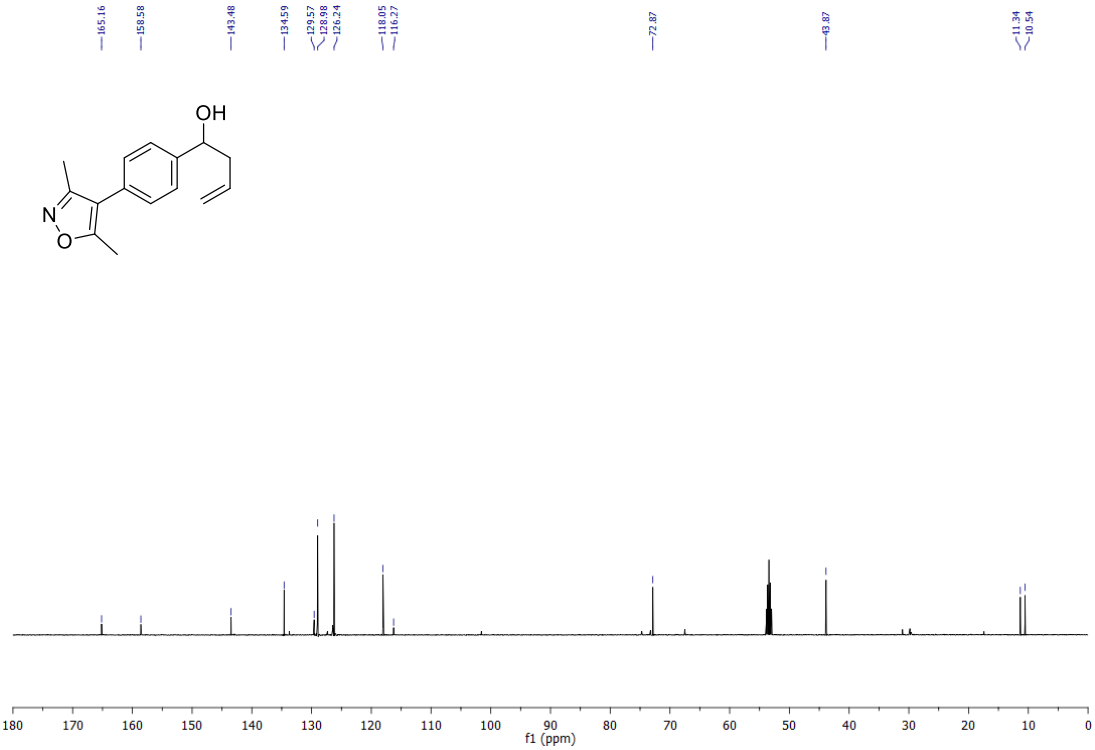
^{19}F NMR of 5k


-62.39
OH
F3C
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105
f1 (ppm)

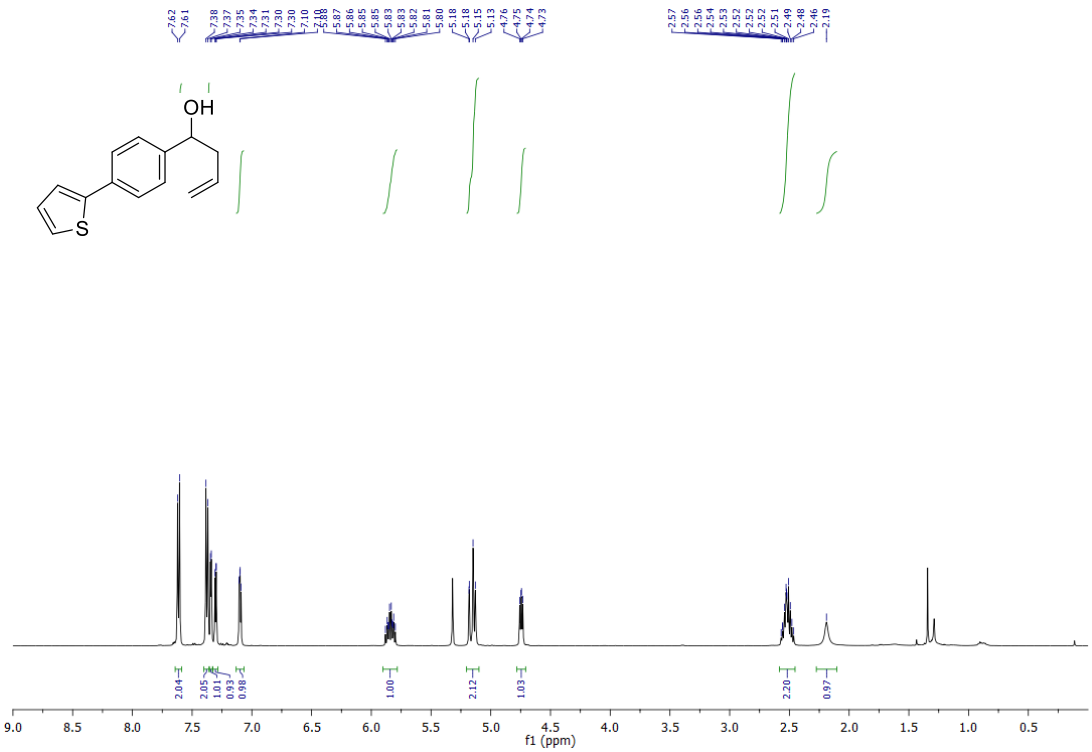
^{1}H NMR of 5l



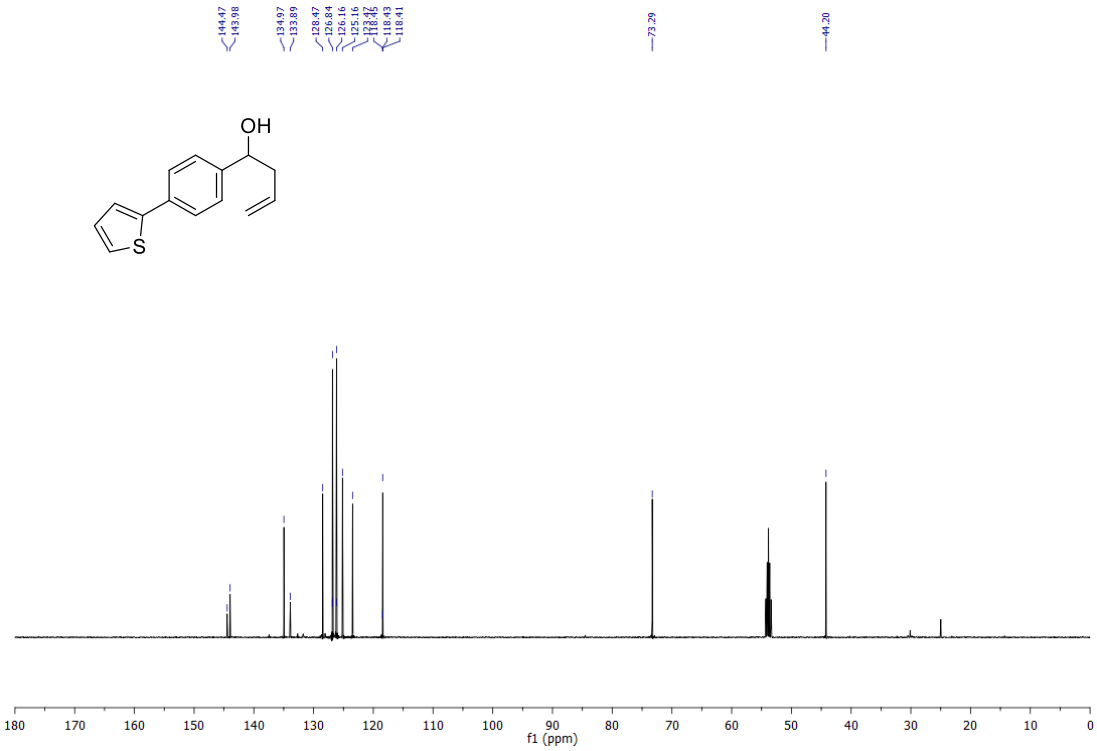
^{13}C NMR of 5l



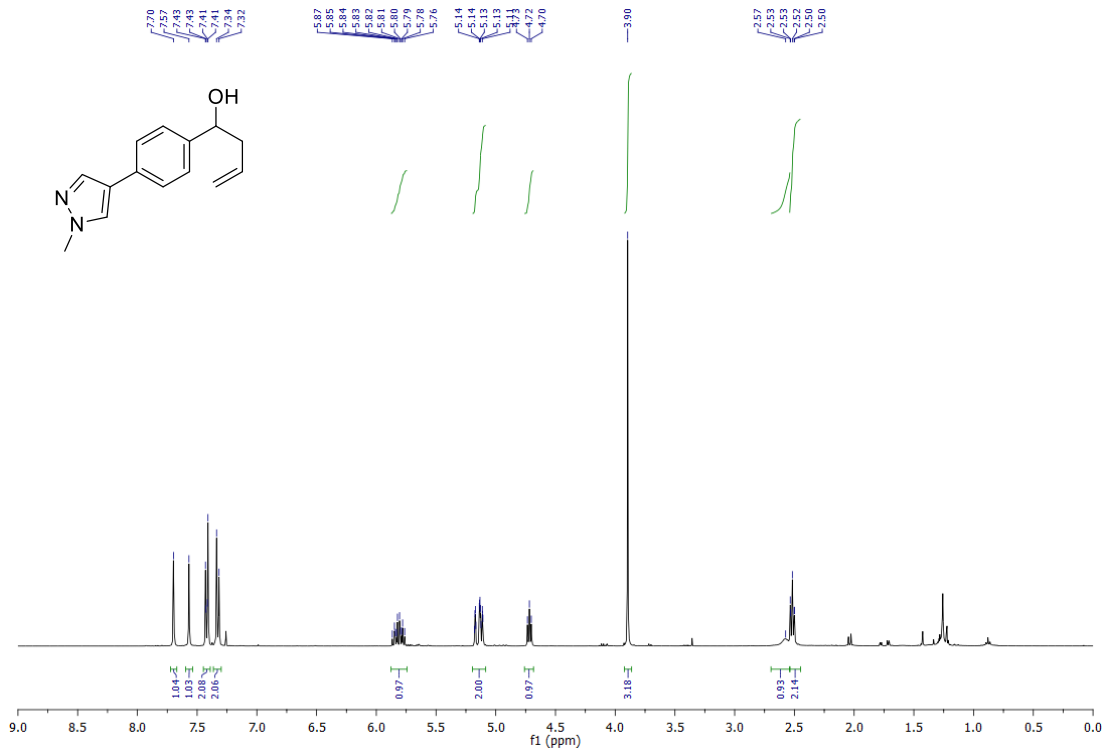
^{1}H NMR of 5m



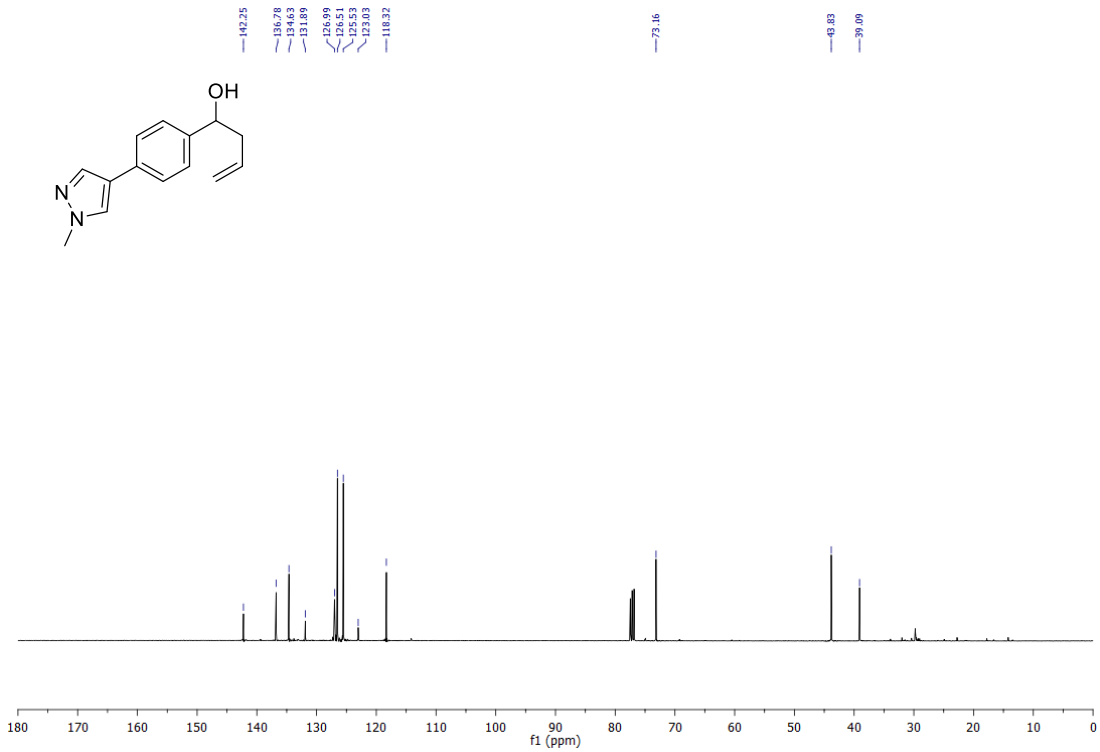
^{13}C NMR of 5m



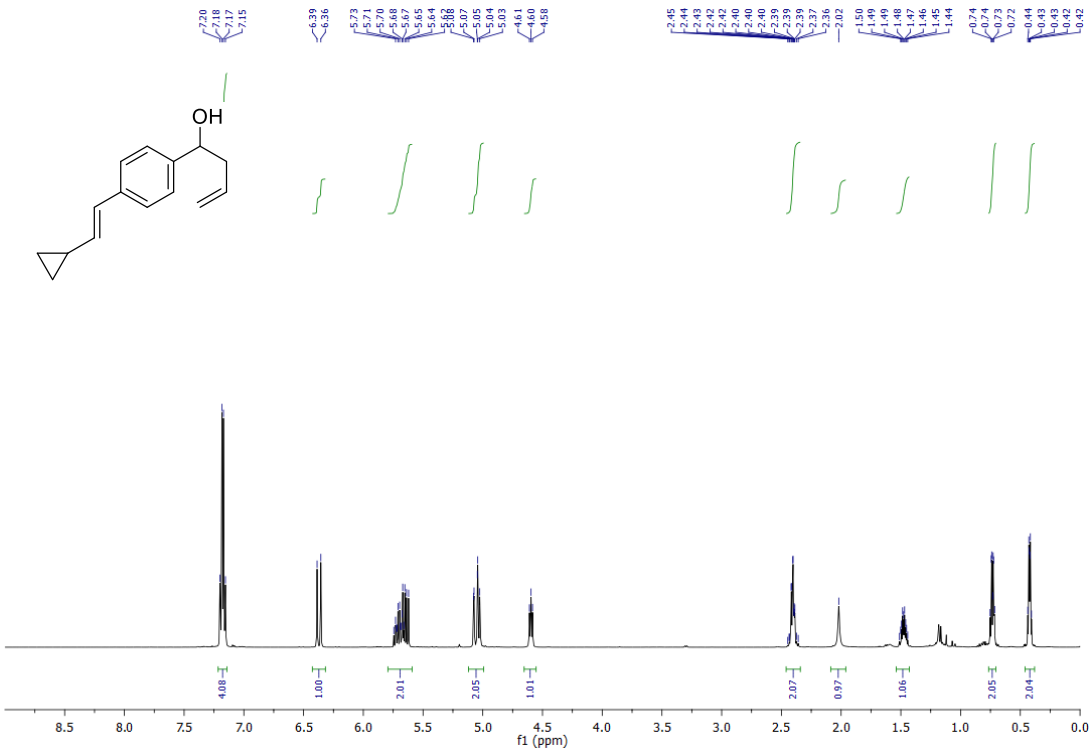
^{1}H NMR of 5n



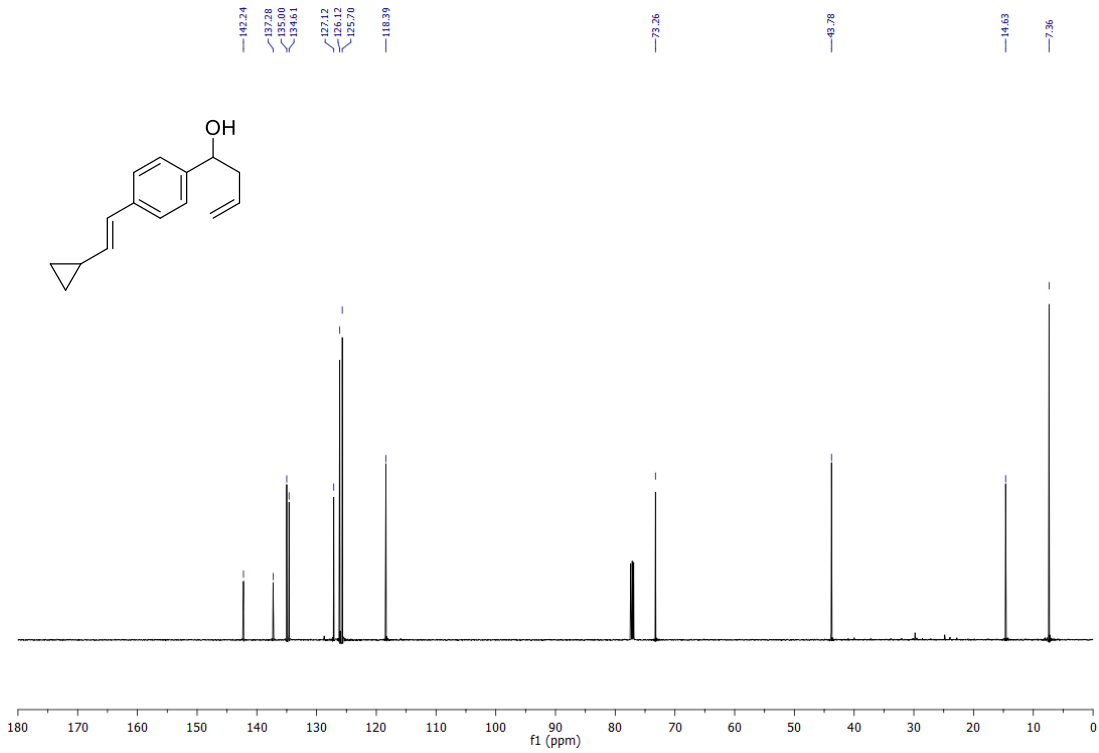
^{13}C NMR of 5n



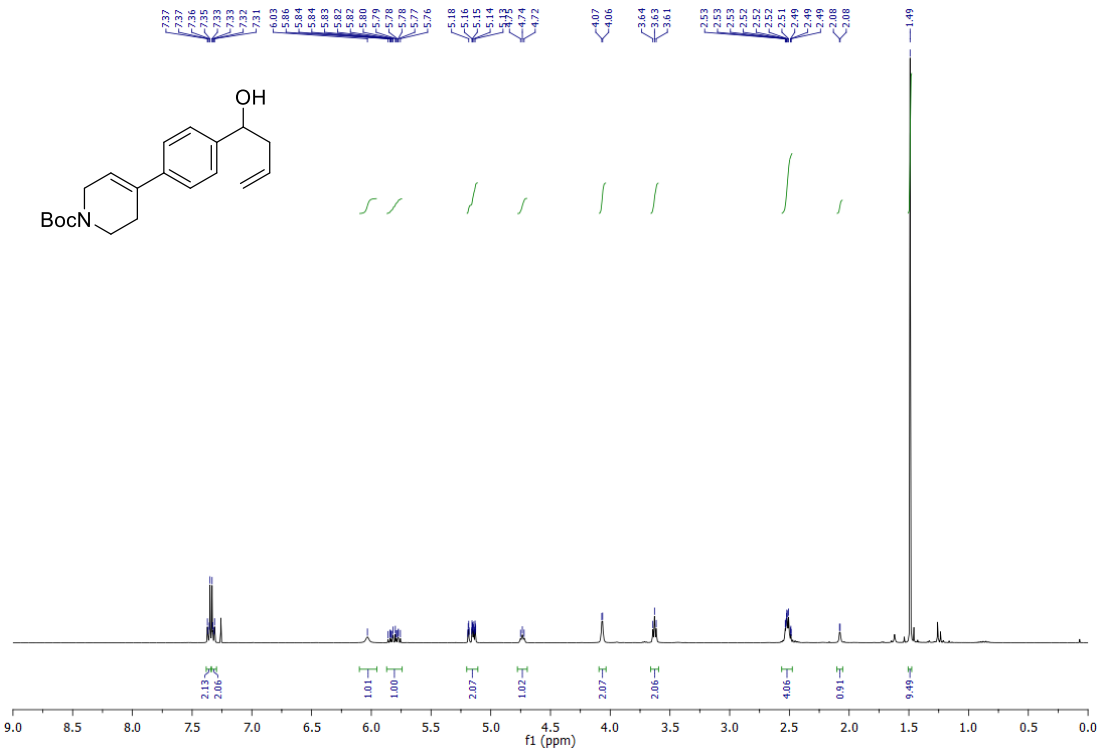
^{1}H NMR of 5o



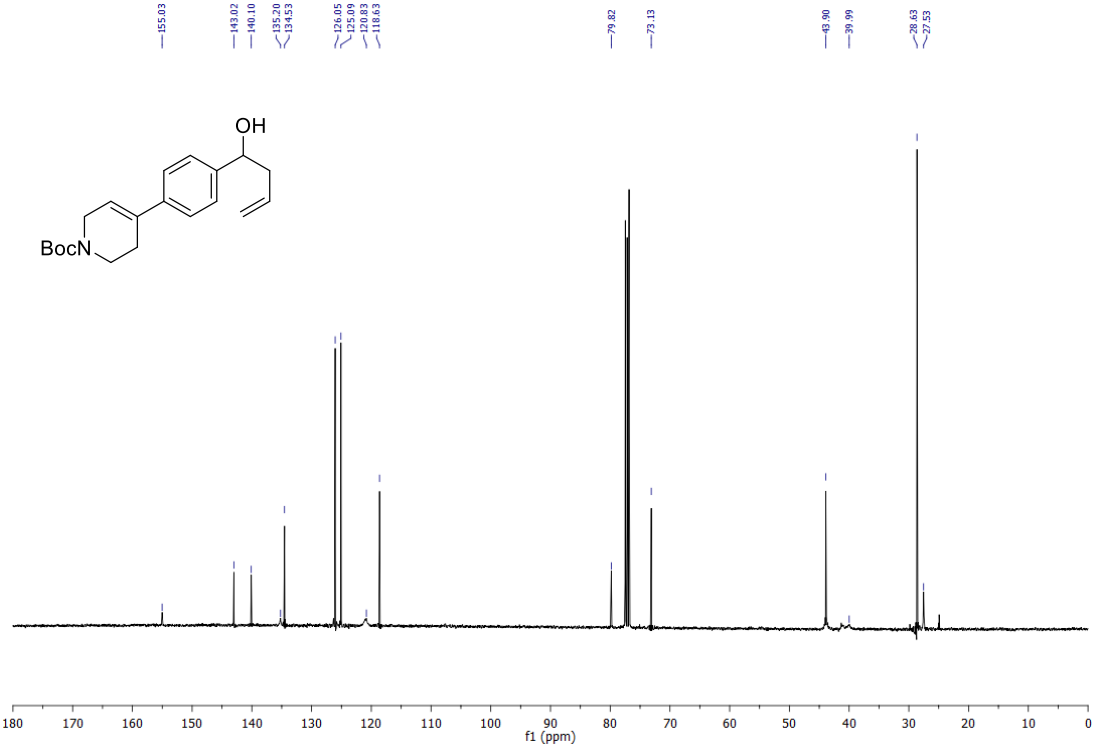
^{13}C NMR of 5o



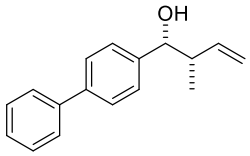
^{1}H NMR of 5p

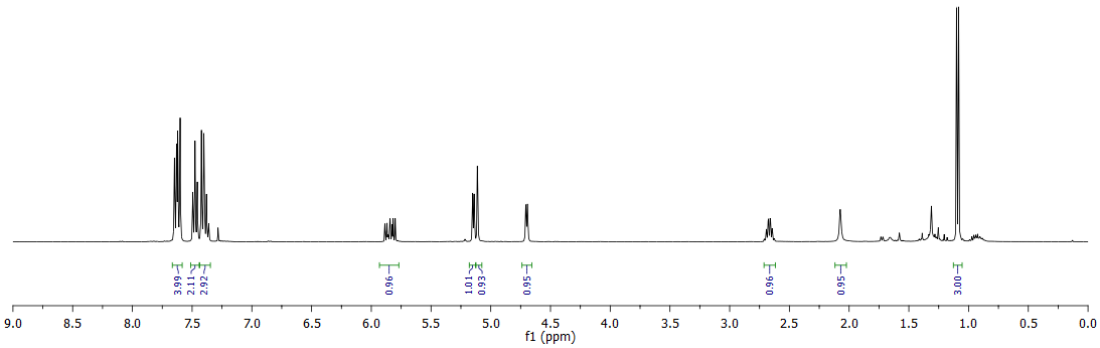


^{13}C NMR of 5p

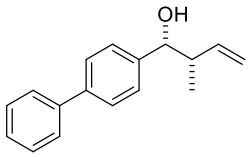


^{1}H NMR of 5s

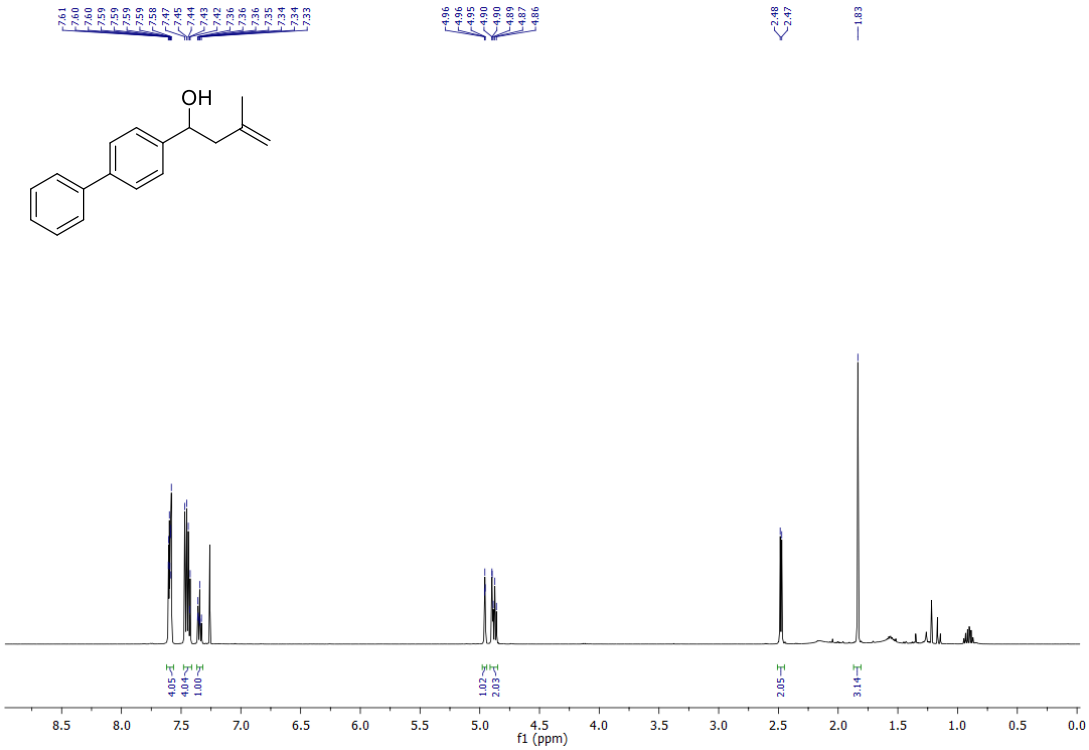




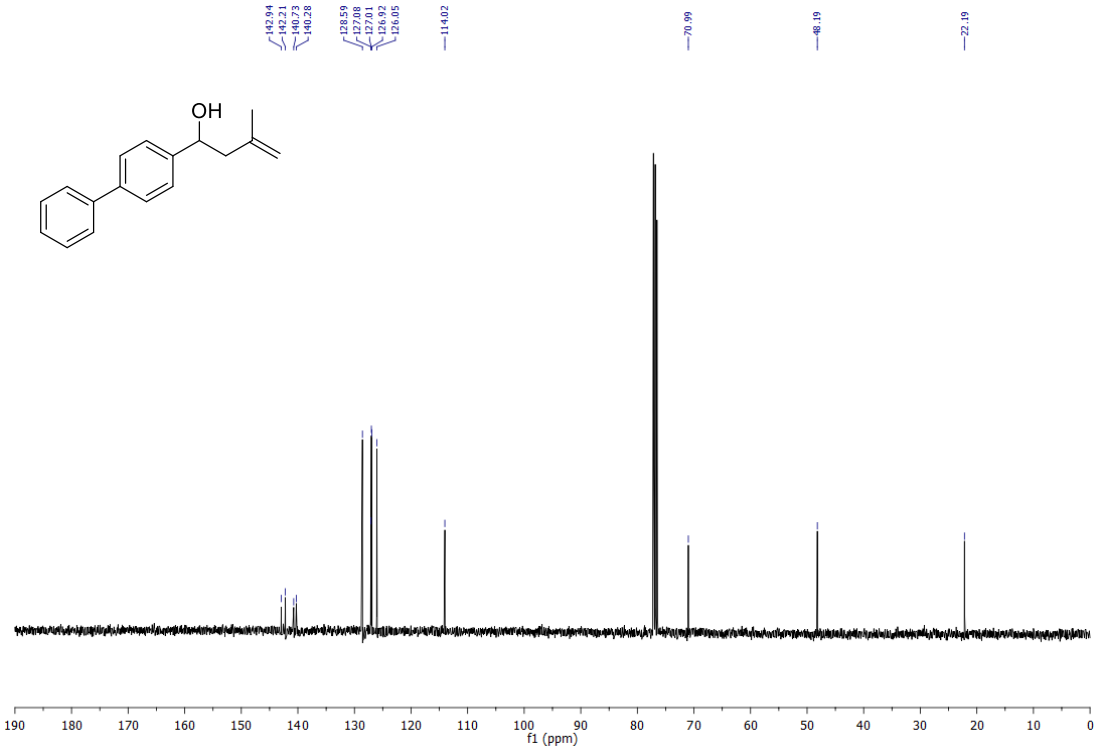
^{13}C NMR of 5s



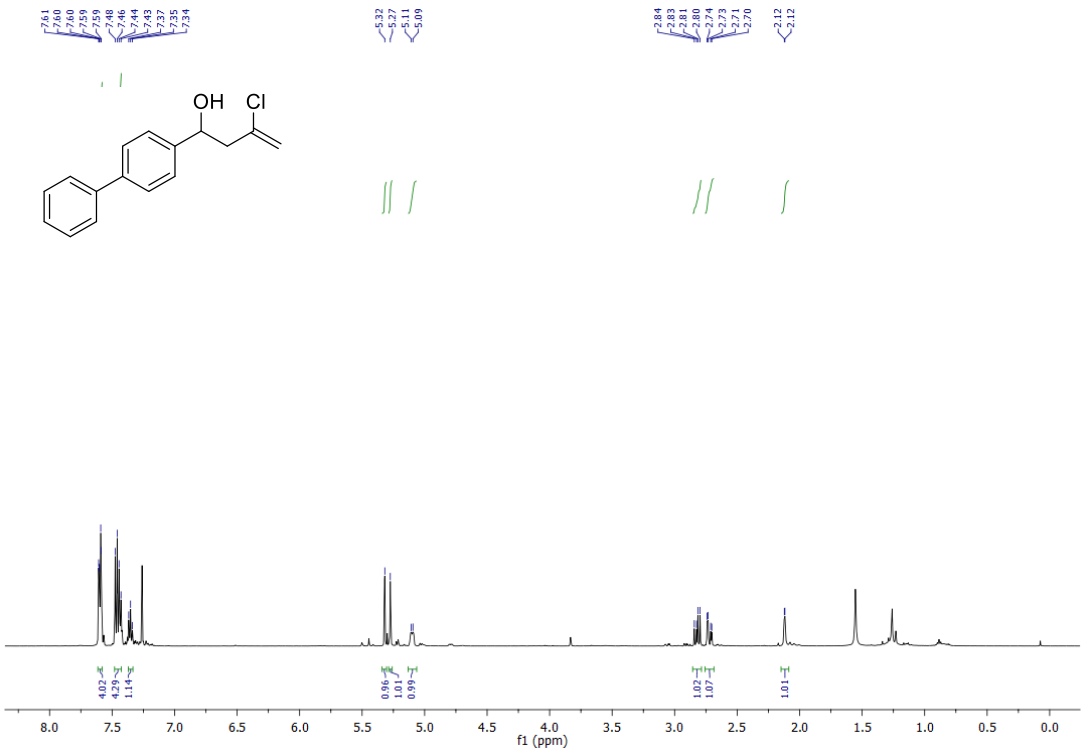
^{1}H NMR of 5q



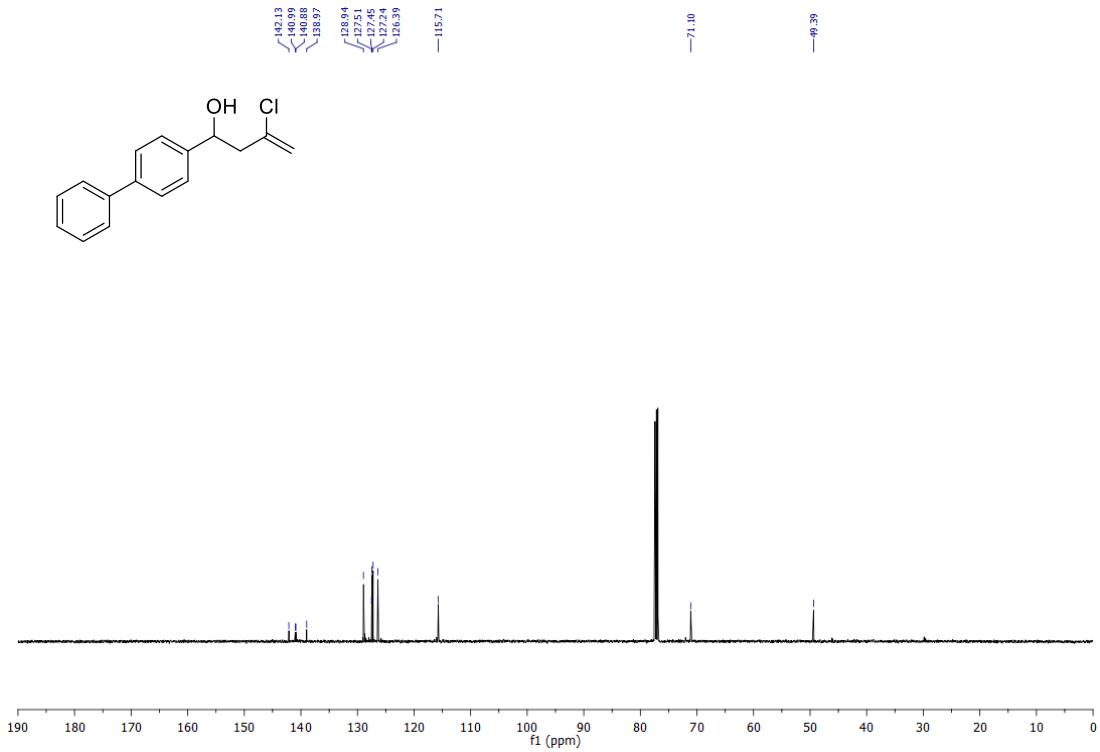
^{13}C NMR of 5q



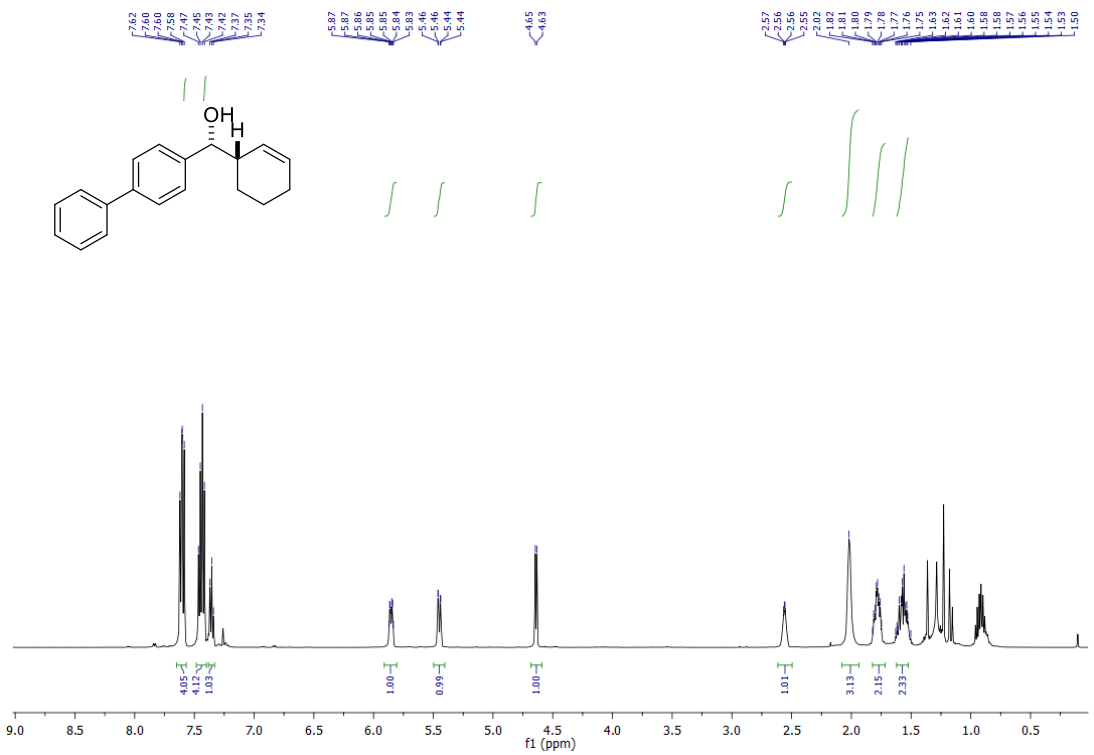
^{1}H NMR of 5r



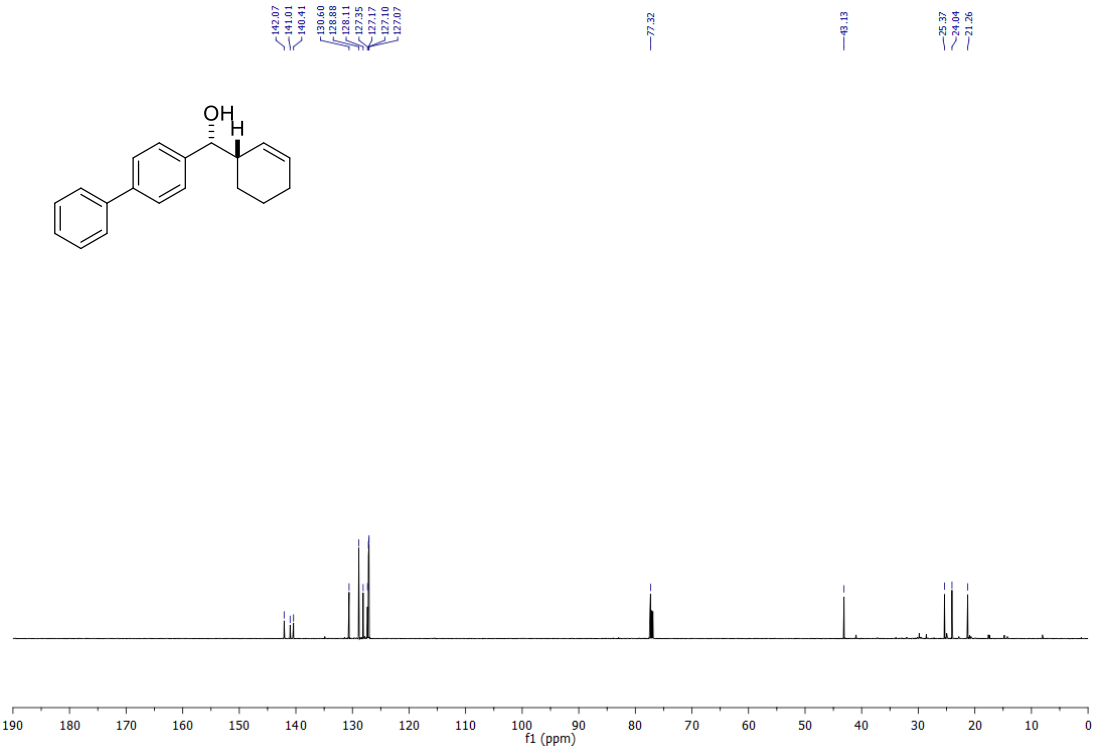
^{13}C NMR of 5r



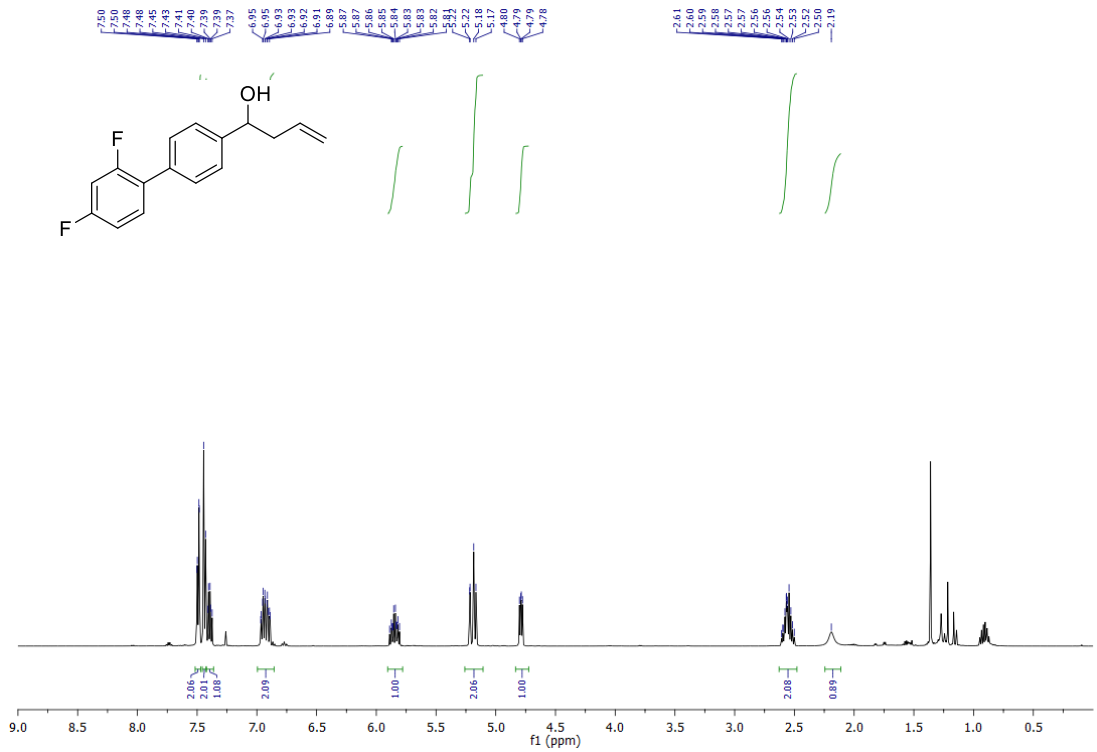
^{1}H NMR of 5t



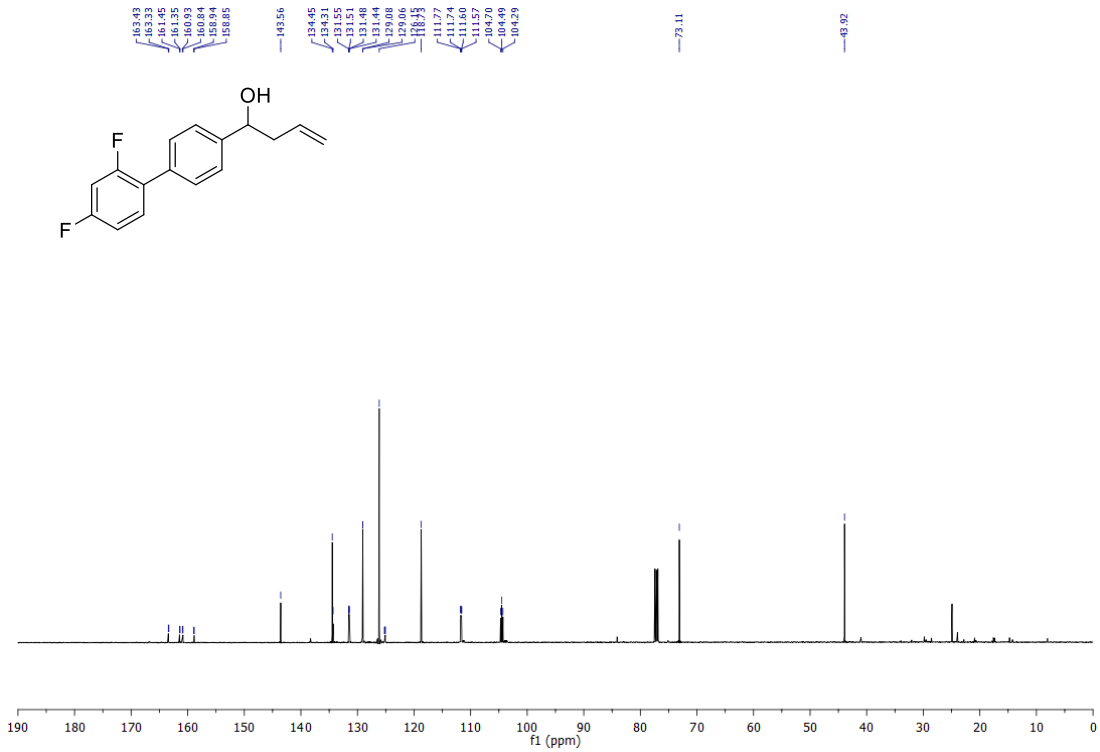
^{13}C NMR of 5t



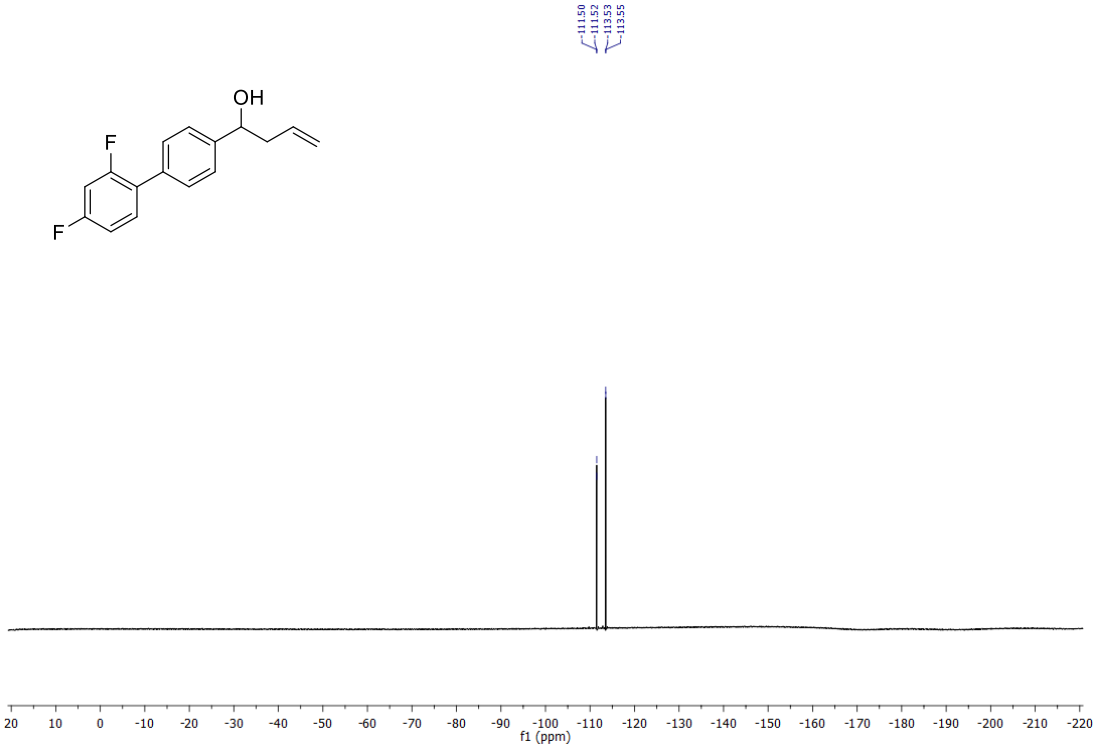
^{1}H NMR of 5u



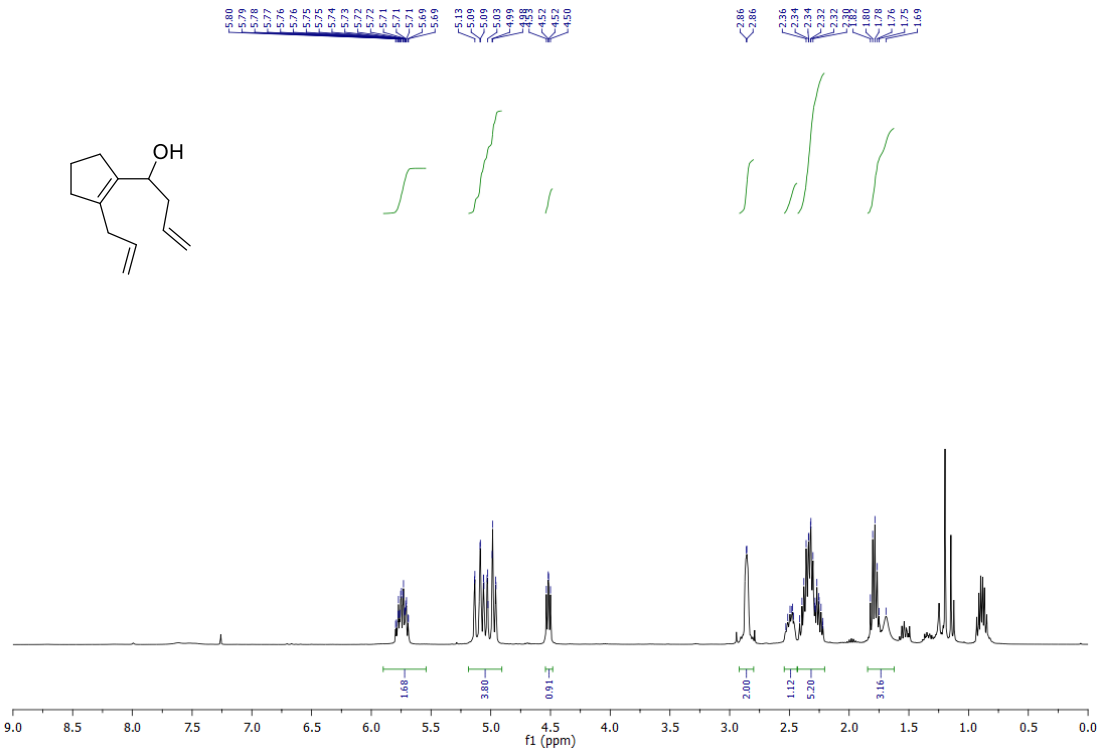
^{13}C NMR of 5u



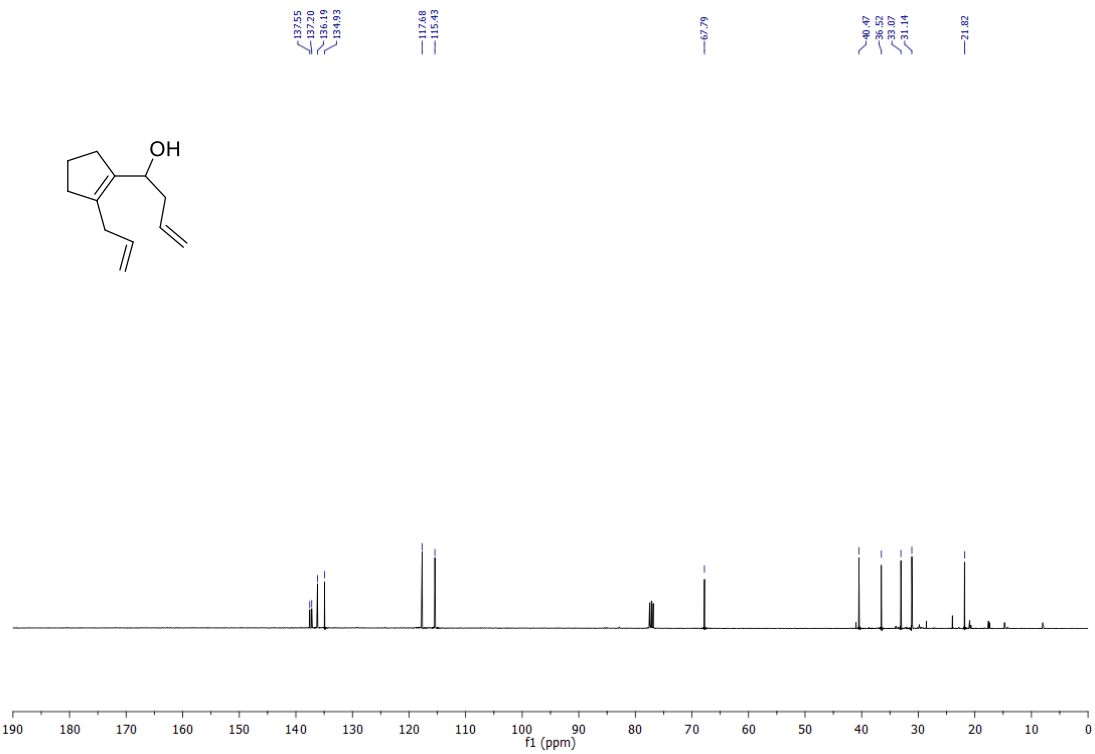
^{19}F NMR of 5u


-111.50
-111.52
-113.53
-113.55
OH
F
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

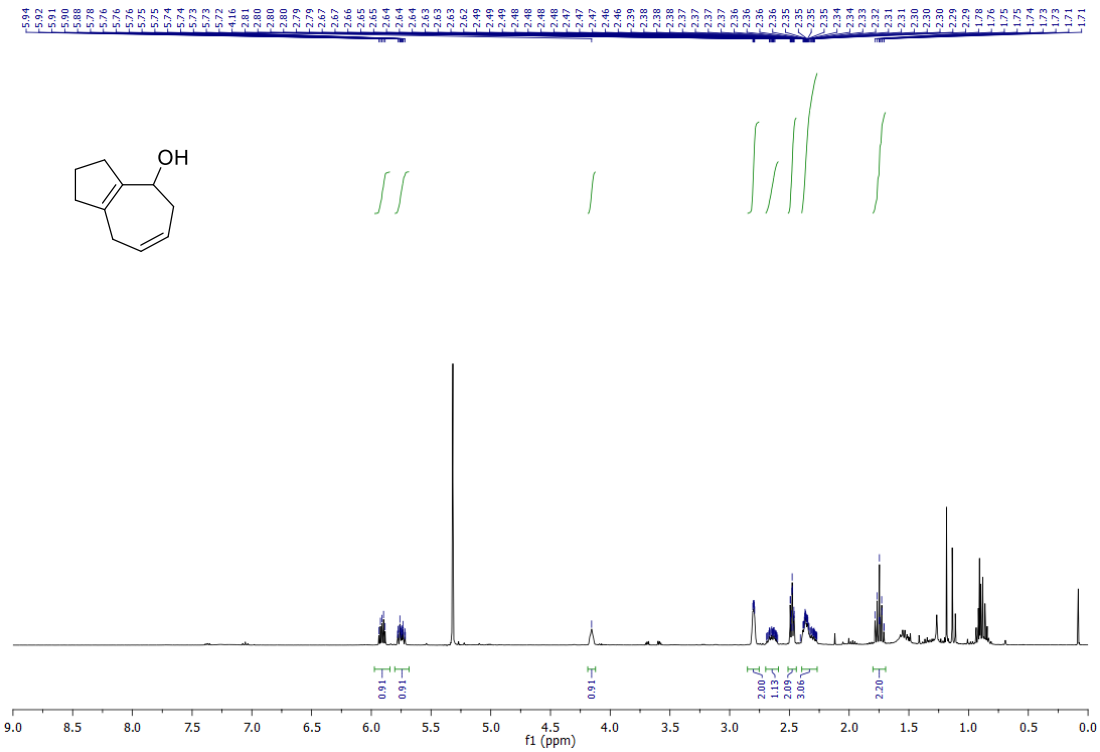
^{1}H NMR of 10



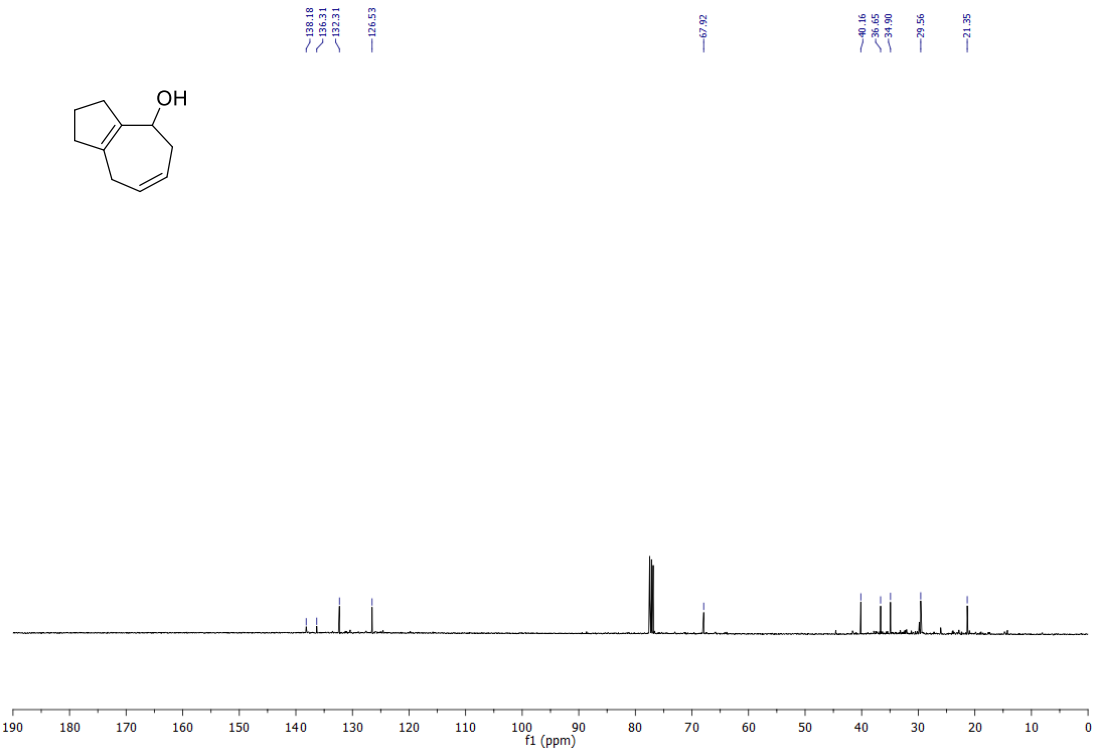
^{13}C NMR of 10



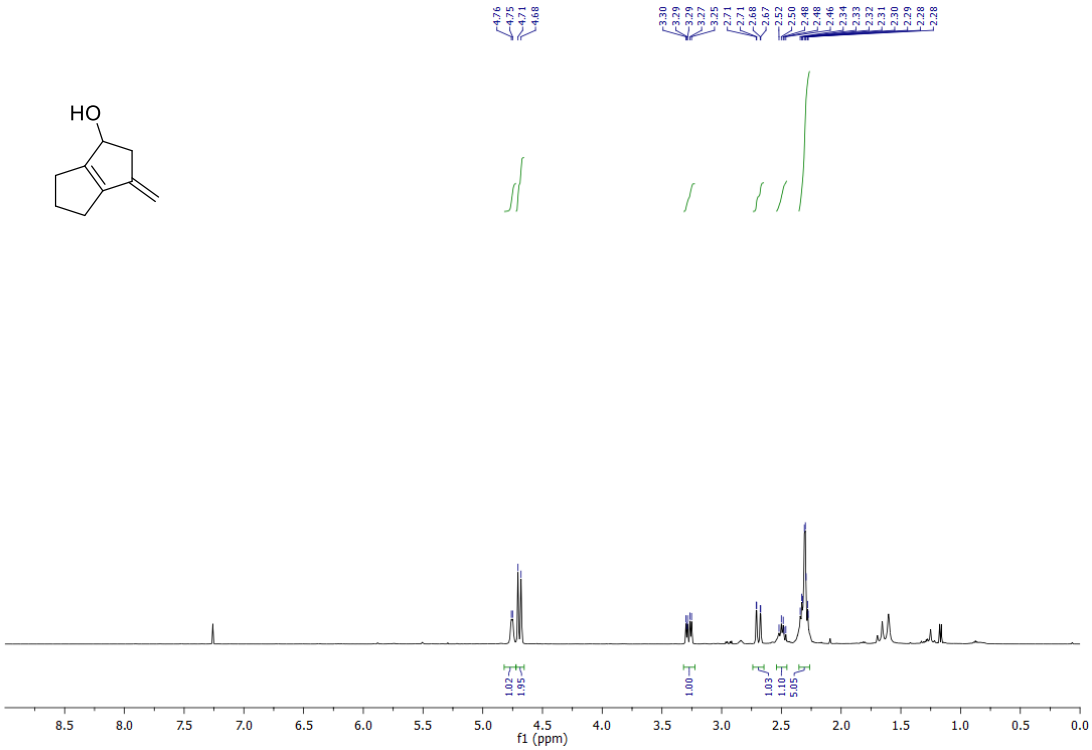
^{1}H NMR of 11



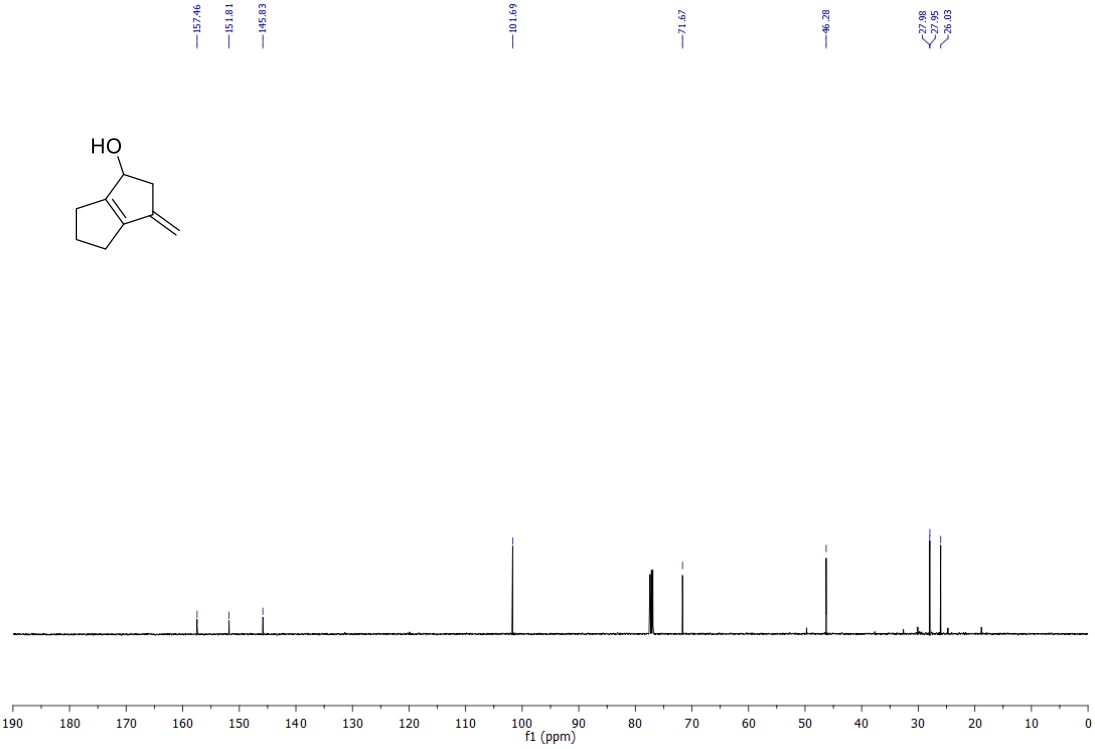
^{13}C NMR of 11



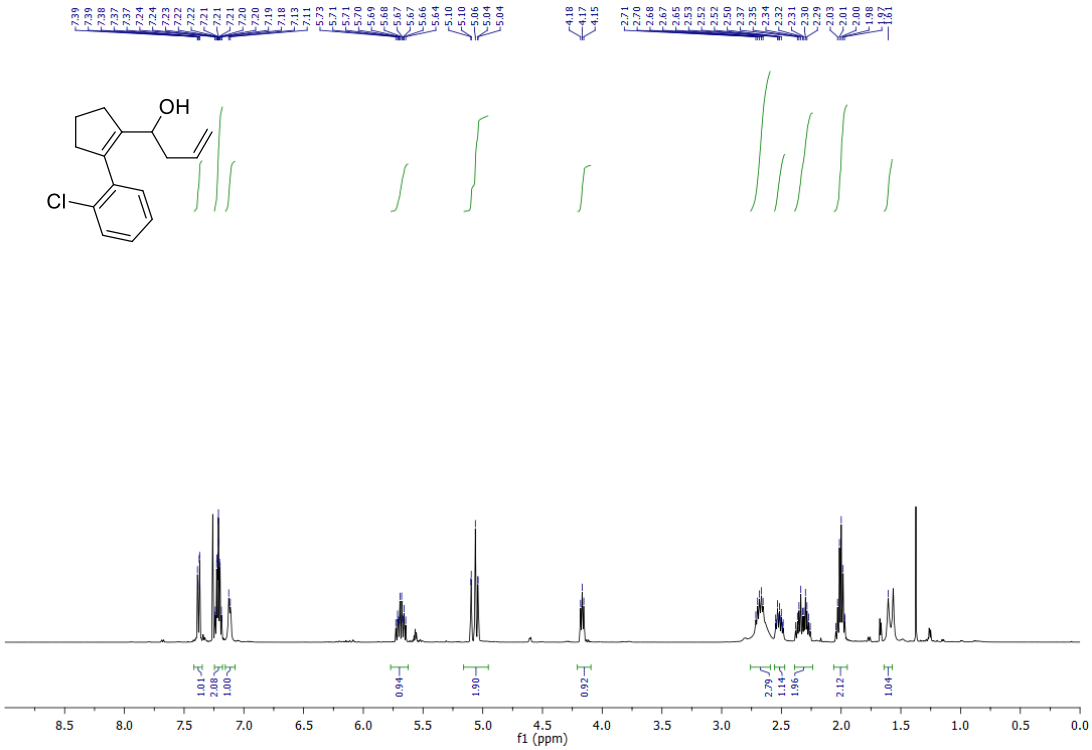
^{1}H NMR of 12



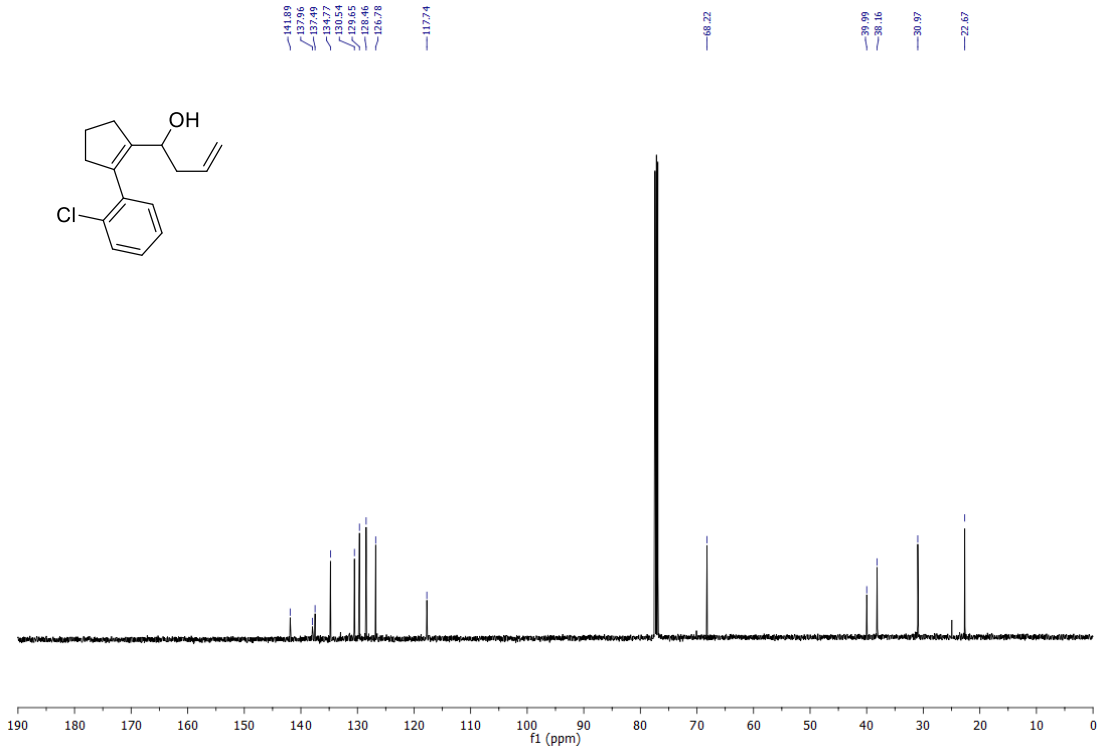
^{13}C NMR of 12



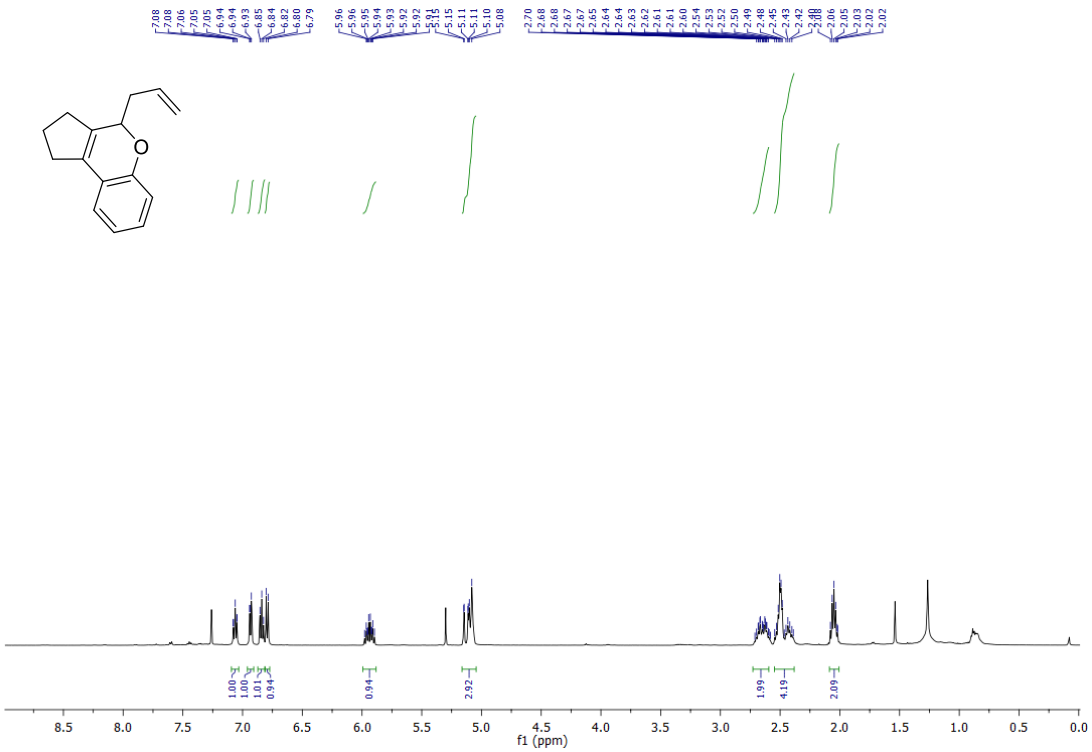
^{1}H NMR of 14



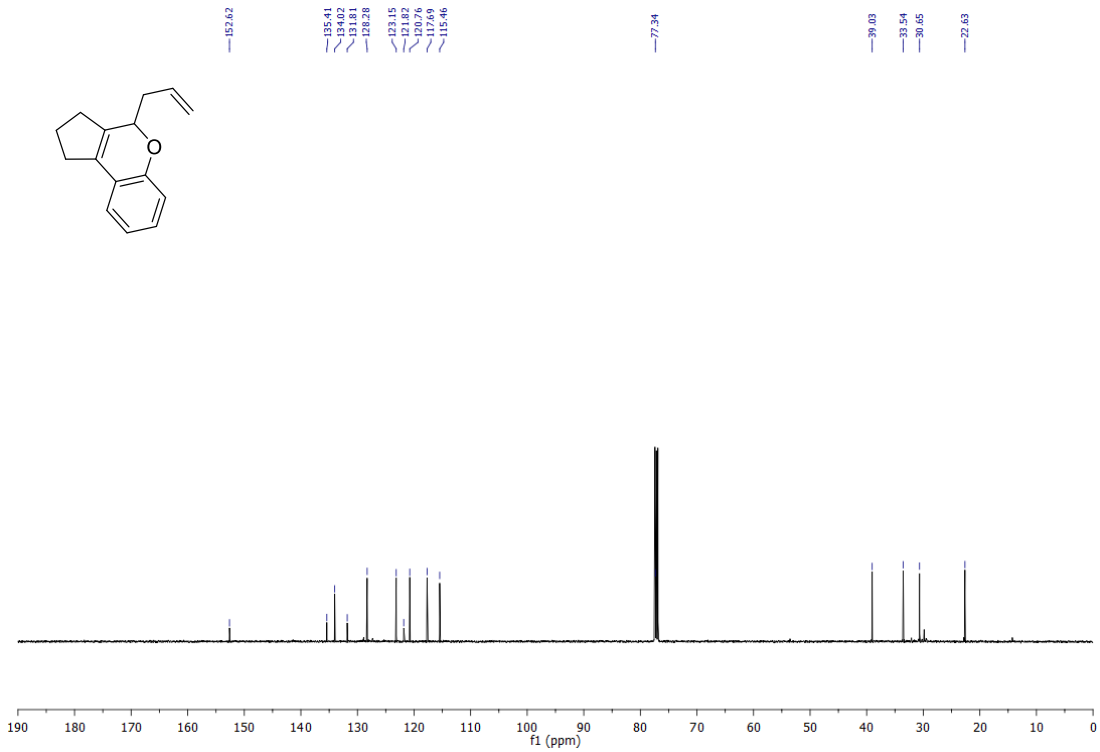
^{13}C NMR of 14



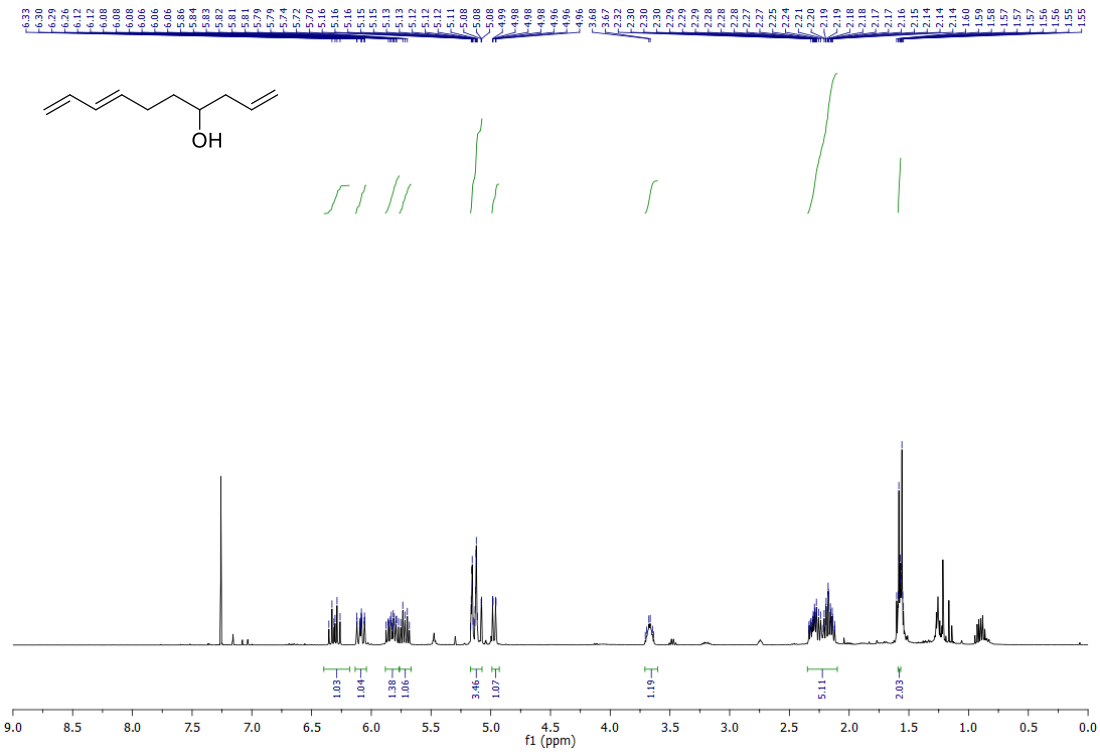
^{1}H NMR of 15



^{13}C NMR of 15



^{1}H NMR of 18



^{13}C NMR of 18