Supplementary Material (ESI) for Chemical Science

Supporting Information

Mild and Selective Boronic Acid Catalyzed 1,3-Transposition of Allylic Alcohols and Meyer-Schuster Rearrangement of Propargylic Alcohols

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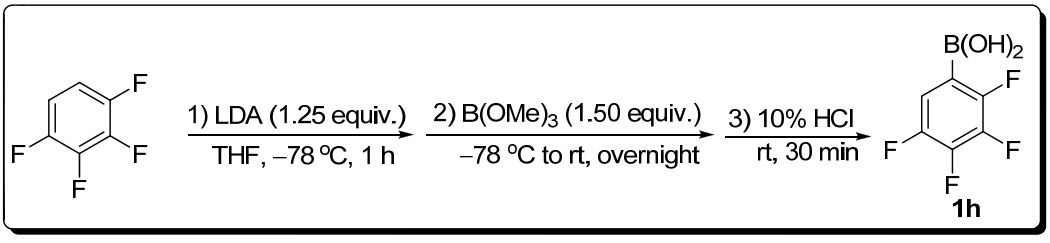
1. Experimental Details and Compound Characterization Data

1.1 General information

Unless otherwise stated, all reactions were performed under a nitrogen atmosphere using flame-dried glassware. Toluene, THF, DMF, MeOH and dichloromethane were treated by Fisher Scientific-MBraun MB SPS* solvent purification system prior to use. All commercially available aldehydes and acrylic acid were purified by Kugelrohr distillation prior to use. Thin layer chromatography (TLC) was performed on Merck Silica Gel 60 F254 plates and was visualized with UV light and $KMnO_4$ stain. NMR spectra were recorded on Varian INOVA-400 or MERCURY-400 MHz instruments. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ^1H NMR data are presented as follows: chemical shift in ppm (δ) downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; qnt, quintet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; qq, quartet of quartets; m, multiplet. High-resolution mass spectra (HRMS) were recorded by the University of Alberta mass spectrometry services laboratory using either electron impact (EI) or electrospray ionization (ESI) techniques. Infrared spectra (IR) were obtained on a Nicolet Magna-IR with frequencies expressed in cm^{-1}. Powdered 4 Å molecular sieves (< 5 micron, Aldrich) were dried overnight in a vacuum oven (250 ^oC) prior to use. 4 Å molecular sieves (1/16 inch pellets) were dried overnight in a vacuum oven (250 ^oC) prior to use. All Grignard reagents were purchased from Sigma-Aldrich.

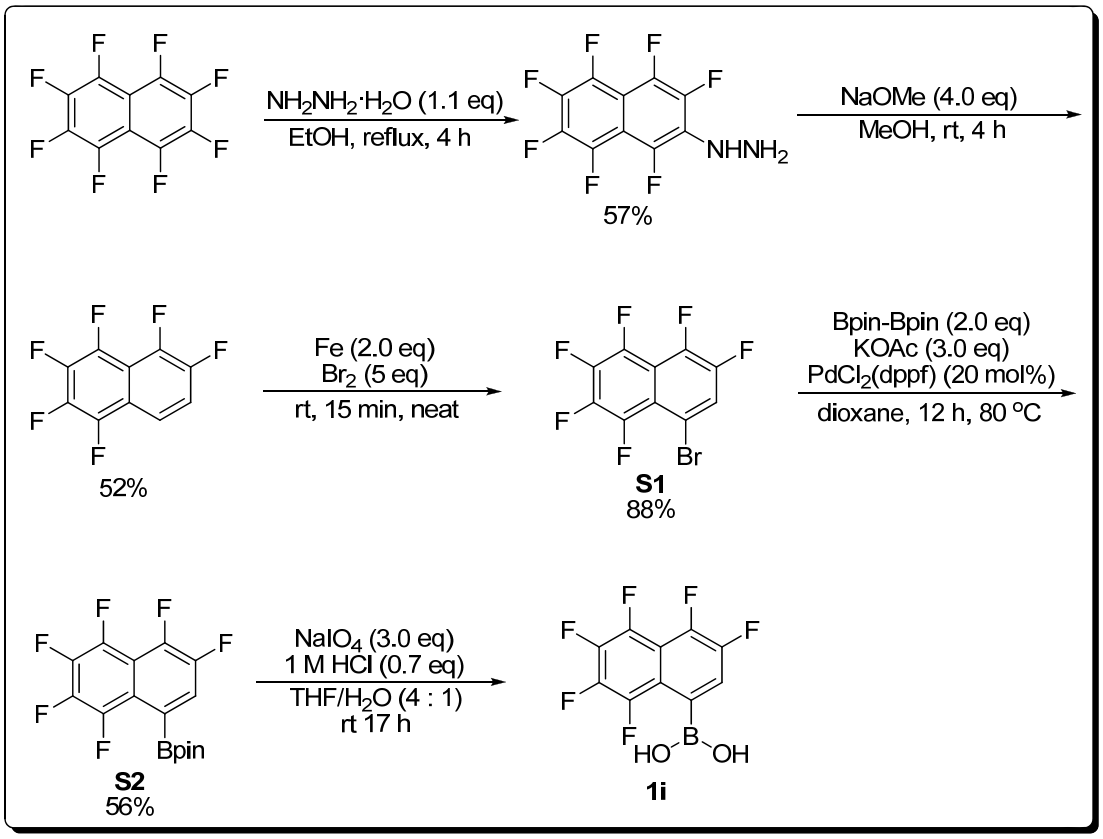
1.2 Preparation of arylboronic acid catalysts

1.2.1 Preparation of 2,3,4,5-Tetrafluorophenyl boronic acid (1h)



2,3,4,5-Tetrafluorophenyl boronic acid **1h** was made following a literature procedure (90% yield).[1]

1.2.2 Preparation of 3,4,5,6,7,8-hexafluoronaphthalen-1-ylboronic acid (1i)



8-Bromo-1,2,3,4,5,6-hexafluoronaphthalene (S1, step 1–3)

8-Bromo-1,2,3,4,5,6-hexafluoronaphthalene **S1** was made following a literature procedure (24% over three steps).[2]

3,4,5,6,7,8-Hexafluoronaphthalen-1-ylboronic acid pinacol ester (S2, step 4)

To a suspension of 8-bromo-1,2,3,4,5,6-hexafluoronaphthalene (**S1**, 933 mg, 3.0 mmol), KOAc (880 mg, 3.0 mmol) and B_2pin_2 (1.52 g, 6.0 mmol) in 1,4-dioxane (20 mL) at room temperature was added $PdCl_2$dppf (490 mg, 0.6 mmol). The reaction mixture was stirred at 80 °C for 12 hours. Then the reaction mixture was filtered through Celite and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:20) to give

[1] Lewis, S. P.; Chai, J.; Collins, S.; Sciarone, T. J. J.; Henderson, L. D.; Fan, C.; Parvez, M.; Piers, W. E. *Organometallics* **2009**, *28*, 249-263.
[2] Morrison, D. J.; Riegel, S. D.; Piers, W. E.; Parvez, M.; McDonald, R. *Chem. Commun.* **2006**, 2875-2877.

the title boronic acid pinacol ester **S2** (565 mg, 52% yield) in pure form.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 9.5, 7.8 Hz, 1H), 1.42 (s, 12 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5, 144.7, 144.6, 143.0, 141.4, 139.2, 138.2, 124.2, 119.6, 112.1, 85.1, 24.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –138.8 (m, 1F), –139.0 (t, *J* = 16.0 Hz, 1F), –142.9 (m, 1F), –146.3 (dddd, *J* = 57.7, 17.5, 15.1, 5.7 Hz, 1F), –155.8 (t, *J* = 18.7 Hz, 1F), –157.5 (tdd, *J* = 19.0, 7.6, 4.2 Hz, 1F); **^{11}B NMR** (128 MHz, $CDCl_3$) 31.1; **IR** (Microscope, cm^{-1}) 2988, 2935, 1667, 1638, 1527, 1500; **HRMS** (EI) for $C_{16}H_{13}{}^{11}BF_6O_2$: calcd. 362.09128; found 362.09160.

3,4,5,6,7,8-Hexafluoronaphthalen-1-ylboronic acid (1i, step 5)

To a solution of boronic acid pinacol ester **S2** (360 mg, 1.0 mmol) in THF/H_2O (10 mL, 4:1) at room temperature was added $NaIO_4$ (642 mg, 3.0 mmol). The resulting mixture was stirred at room temperature for 30 minutes. Then 1 N HCl (0.7 mL) was added and the resulting reaction mixture was stirred at room temperature for 17 hours. The mixture was extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with H_2O (2 × 20 mL), brine (20 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was washed with hexanes to give the title boronic acid **1i** (168 mg, 60% yield) in pure form.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.55 (br s, 2H), 7.77-7.70 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.2, 142.6, 142.3, 140.5, 138.4, 137.1, 130.8, 121.7, 118.6, 111.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –139.2 (m, 1F), –139.8 (m, 1F), –147.8 (m, 2F), –156.6 (t, *J* = 17.2 Hz, 1F), –159.4 (t, *J* = 17.8 Hz, 1F); **^{11}B NMR** (128 MHz, $CDCl_3$) 29.0; **IR** (Microscope, cm^{-1}) 3299, 1667, 1637, 1525; **HRMS** (EI) for $C_{10}H_3{}^{11}BF_6O_2$: calcd. 280.01303; found 280.01308.

1.2.3 Preparation of the other arylboronic acids (Table 1)

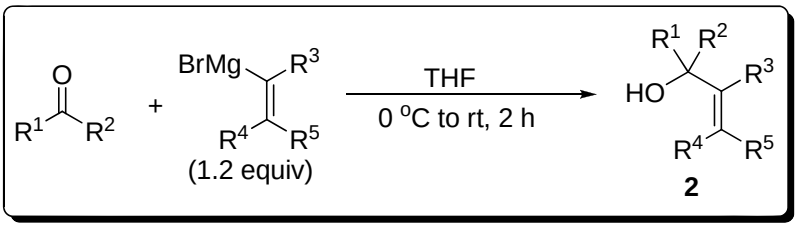
2-Nitrophenylboronic acid was made following a literature procedure. [3] 2-Iodophenylboronic acid was prepared based on a previous literature procedure reported by our group.[4] The other arylboronic acids were obtained from commercial

[3] a) Seaman, W.; Johnson, J. R. *J. Am. Chem. Soc.* **1931**, *53*, 711-723; b) Groziak, M. P.; Canguly, A. D.; Robinsons, P. D. *J. Am. Chem. Soc.* **1994**, *116*, 7597-7605.
[4] Al-Zoubi, R.; Marion, O.; Hall, D. G. *Angew. Chem. Int. Ed.* **2008**, *47*, 2876-2879.

sources (purchased from either Combi-Blocks Inc. or Sigma-Aldrich).

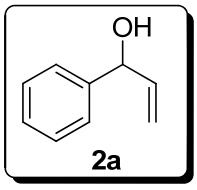
1.3 Preparation of allylic alcohols 2

1.3.1 General procedure for the preparation of allylic alcohols



To a solution of aldehyde or ketone (5.0 mmol) in THF (10 mL) at 0 °C was added Grignard reagent solution (1.0 M in THF, 6.0 mL, 6.0 mmol) dropwise. The reaction mixture was stirred at 0 °C for 30 minutes. Then the reaction mixture was allowed to warm to room temperature and further stirred at room temperature for 2 hours. A saturated aqueous NH_4Cl solution (20 mL) was added to quench the reaction and the reaction mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:15) to give the title allylic alcohols in pure form.

1.3.2 1-Phenylprop-2-en-1-ol (2a)

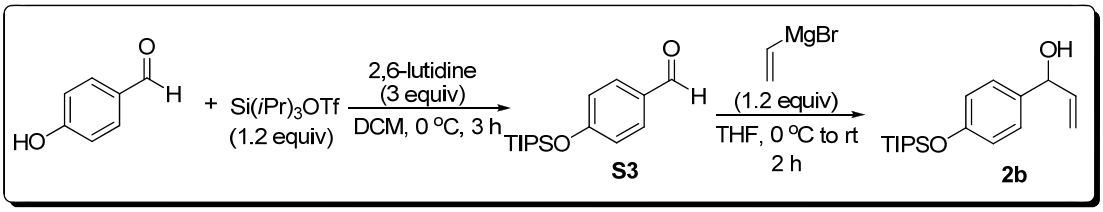


The title compound was prepared using the general procedure for allylic alcohols (81% yield).

The characterization data for this compound matched that of a previous report.[5]

[5] a) Bouziane, A.; Helou, M.; Carboni, B.; Carreaux, F.; Demerseman, B.; Bruneau, C.; Renaud, J. *Chem. Eur. J.* **2008**, *14*, 5630-5637; b) Kim, J. W.; Koike, T.; Kotani, M.; Yamaguchi, K.; Mizuno, N. *Chem. Eur. J.* **2008**, *14*, 4104-4109.

1.3.3 1-(4-(Triisopropylsilyloxy)phenyl)prop-2-en-1-ol (2b)



Step 1: To a solution of *p*-hydroxybenzaldehyde (366 mg, 3.0 mmol) in DCM (12 mL) at 0 °C was slowly added 2,6-lutidine (963 mg, 9.0 mmol). The reaction mixture was stirred at 0 °C for 15 minutes and triisopropylsilyl trifluoromethanesulfonate (1.10 g, 3.6 mmol) was added dropwise. Then the reaction mixture was stirred at 0 °C for 3 hours. Et_2O (100 mL) was added to dilute the reaction mixture. The reaction mixture was washed with saturated aqueous $NaHCO_3$ solution (2 × 50 mL), brine (50 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:50) to give 4-(triisopropylsilyloxy)benzaldehyde **S3** (802 mg, 96% yield) in pure form.

The characterization data for **S3** matched that of a previous report.[6]

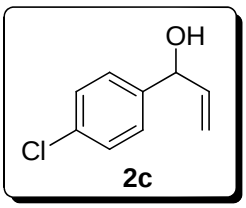
Step 2: To a solution of 4-(triisopropylsilyloxy)benzaldehyde **S3** (557 mg, 2.0 mmol) in THF (5 mL) at 0 °C was added Grignard reagent solution (1.0 M in THF, 2.4 mL, 2.4 mmol) dropwise. The reaction mixture was stirred at 0 °C for 30 minutes. Then the reaction mixture was allowed to warm to room temperature and further stirred at room temperature for 2 hours. NH_4Cl solution (10 mL) was added to quench the reaction and the reaction mixture was extracted with EtOAc (2 × 25 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:15) to give the title allylic alcohols **2b** (564 mg, 92% yield) in pure form.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 6.90-6.86 (m, 2H), 6.07 (ddd, *J* = 17.4, 10.6, 6.1 Hz, 1H), 5.34 (dt, *J* = 17.1, 1.6 Hz, 1H), 5.20 (dd, *J* = 10.3, 1.5 Hz, 1H), 5.16 (dd, *J* = 5.6, 4.4 Hz, 1H), 1.96 (br s, 1H), 1.27 (dq, *J* = 7.3, 1.9 Hz, 3H), 1.12 (d, *J* = 7.3 Hz, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.0, 140.7, 135.3, 127.8,

[6] Ischay, M. A.; Lu, Z.; Yoon, T. P. *J. Am. Chem. Soc.* **2010**, *132*, 8572-8574.

120.1, 114.9, 75.2, 18.2, 12.9; **IR** (Microscope, cm^{-1}) 3330, 3080, 2945, 2893, 2868, 1607, 1582, 1510, 1464, 1416; **HRMS** (EI) for $C_{18}H_{30}O_2Si$: calcd. 306.20151; found 306.20195.

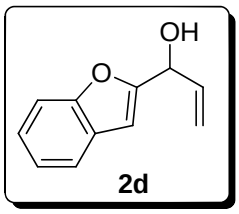
1.3.4 1-(4-Chlorophenyl)prop-2-en-1-ol (2c)



The title compound was prepared using the general procedure for allylic alcohols (84% yield).

The characterization data for this compound matched that of a previous report.[5a]

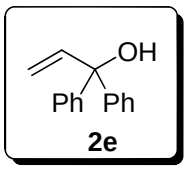
1.3.5 1-(Benzofuran-2-yl)prop-2-en-1-ol (2d)



The title compound was prepared using the general procedure for allylic alcohols (90% yield).

The characterization data for this compound matched that of a previous report.[7]

1.3.6 1,1-Diphenylprop-2-en-1-ol (2e)

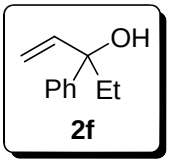


The title compound was prepared using the general procedure for allylic alcohols (95% yield).

The characterization data for this compound matched that of a previous report.[8]

[7] Morrill, C.; Beutner, G. L.; Grubbs, R. H. *J. Org. Chem.* **2006**, *71*, 7813-7825.
[8] Marion, N.; Gealageas, R.; Nolan, S. P. *Org. Lett.* **2007**, *9*, 2653-2656.

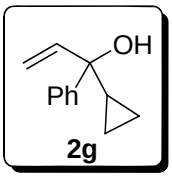
1.3.7 3-Phenylpent-1-en-3-ol (2f)



The title compound was prepared using the general procedure for allylic alcohols (79% yield).

The characterization data for this compound matched that of a previous report.[7]

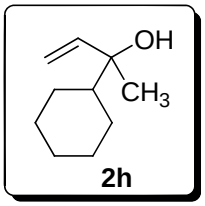
1.3.8 1-Cyclopropyl-1-phenylprop-2-en-1-ol (2g)



The title compound was prepared using the general procedure for allylic alcohols (87% yield).

The characterization data for this compound matched that of a previous report.[9]

1.3.9 2-Cyclohexylbut-3-en-2-ol (2h)

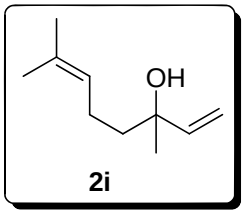


The title compound was prepared using the general procedure for allylic alcohols (64% yield).

The characterization data for this compound matched that of a previous report.[10]

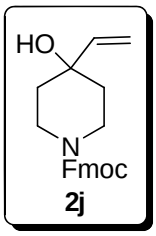
[9] Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1539-1546.
[10] Morrill, C.; Grubbs, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 2842-2843.

1.3.10 Linalool (2i)



Linalool **2i** was purchased from Fluka Analytical (Sigma-Aldrich).

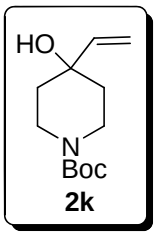
1.3.11 9*H*-Fluoren-9-yl)methyl 4-hydroxy-4-vinylpiperidine-1-carboxylate (2j)



The title compound was prepared using the general procedure for allylic alcohols (57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dt, *J* = 7.6, 0.8 Hz, 2H), 7.61 (ddd, *J* = 7.4, 1.9, 0.9 Hz, 2H), 7.43 (ddt, *J* = 7.5, 1.1, 0.7 Hz, 2H), 7.34 (dt, *J* = 7.4, 1.2 Hz, 2H), 5.95 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.29 (dd, *J* = 17.4, 1.0 Hz, 1H), 5.13 (dd, *J* = 10.8, 1.0 Hz, 1H), 4.48 (d, *J* = 6.9 Hz, 2H), 4.27 (t, *J* = 6.7 Hz, 1H), 4.00-3.78 (m, 2H), 3.36-3.27 (m, 2H), 1.73-1.53 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.4, 145.1, 144.4, 141.6, 127.9, 127.3, 125.2, 120.2, 112.8, 70.2, 67.4, 47.7, 40.2, 36.8; **IR** (Microscope, cm^{-1}) 3436, 3066, 3008, 2949, 1912, 1681, 1580, 1477, 1450; **HRMS** (EI) for $C_{22}H_{23}NO_3$: calcd. 349.16779; found 349.16725.

1.3.12 *tert*-Butyl 4-hydroxy-4-vinylpiperidine-1-carboxylate (2k)

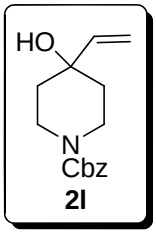


The title compound was prepared using the general procedure for allylic alcohols (22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (dd, *J* = 17.3, 11.3 Hz, 1H), 5.25 (dd, *J* = 17.4,

0.9 Hz, 1H), 5.06 (dd, *J* = 10.7, 0.8 Hz, 1H), 3.88-3.66 (m, 2H), 3.28-3.12 (m, 2H), 2.05 (br s, 1H), 1.70-1.58 (m, 2H), 1.56-1.48 (m, 2H), 1.43 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.4, 144.6, 111.9, 79.0, 69.5, 39.7, 36.2, 28.0; **IR** (Microscope, cm^{-1}) 3434, 3087, 3007, 2977, 2945, 2876, 1695, 1671; **HRMS** (EI) for $C_{12}H_{21}NO_3$: calcd. 227.15215; found 227.15229.

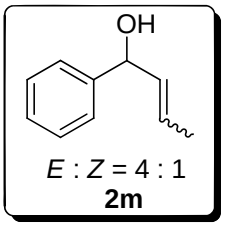
1.3.13 Benzyl 4-hydroxy-4-vinylpiperidine-1-carboxylate (2l)



The title compound was prepared using the general procedure for allylic alcohols (61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 5H), 5.94 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.28 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.14 (s, 2H), 5.11 (dd, *J* = 10.8, 1.0 Hz, 1H), 4.00-3.81 (m, 2H), 3.32 (t, *J* = 12.6 Hz, 2H), 1.91 (s, 1H), 1.75-1.63 (m, 2H), 1.61-1.52 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.5, 145.1, 137.1, 128.8, 128.2, 128.1, 112.7, 70.1, 67.3, 40.2, 36.8; **IR** (Microscope, cm^{-1}) 3438, 3088, 3065, 3033, 3007, 2948, 2876, 1699, 1679, 1587, 1497, 1474, 1435; **HRMS** (EI) for $C_{15}H_{19}NO_3$: calcd. 261.13651; found 261.13649.

1.3.14 1-Phenylbut-2-en-1-ol (2m)

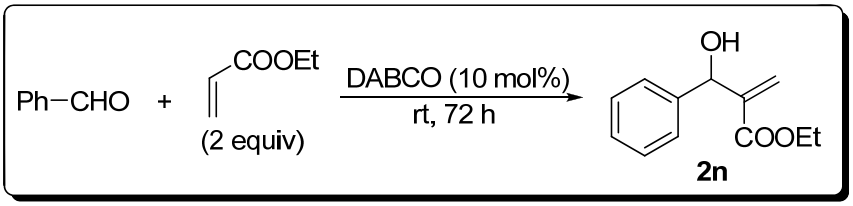


The title compound was prepared using the general procedure for allylic alcohols (86% yield, *E* : *Z* = 4 : 1, determined by ^{1}H NMR).

The characterization data for this compound matched that of a previous report.[11]

[11] Stevens, B. D.; Bungard, C. J.; Nelson, S. G. *J. Org. Chem.* **2006**, *71*, 6397-6402.

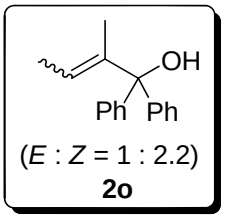
1.3.15 Ethyl 2-(hydroxy(phenyl)methyl)acrylate (2n)



A mixture of ethyl acrylate (2.00 g, 20.0 mmol), benzaldehyde (1.06 g, 10.0 mmol) and DABCO (112 mg, 1.0 mmol) was stirred at room temperature for 72 hours. Then the reaction mixture was directly purified by silica gel column chromatography (EtOAc/Hexanes = 1:5) to give the title allylic alcohol **2n** (1.75 g, 85% yield) in pure form.

The characterization data for **2n** matched that of a previous report.[12]

1.3.16 2-Methyl-1,1-diphenylbut-2-en-1-ol (2o)



The title compound was prepared using the general procedure for allylic alcohols (80% yield, *E* : *Z* = 1 : 2.2, determined by ^{1}H NMR).

Z isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.26 (m, 10H), 5.67 (qq, *J* = 7.3, 1.4 Hz, 1H), 2.53 (br s, 1H), 1.74 (quin, *J* = 1.5 Hz, 3H), 1.24 (dq, *J* = 7.4, 1.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 140.6, 128.3, 127.8, 127.4, 124.8, 82.3, 24.4, 15.7.

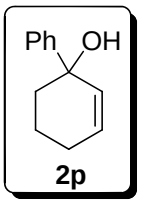
E isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.26 (m, 10H), 5.24 (qq, *J* = 6.6, 1.2 Hz, 1H), 2.50 (br s, 1H), 1.71 (quin, *J* = 1.1 Hz, 3H), 1.24 (dq, *J* = 6.7, 1.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.7, 140.3, 128.1, 128.0, 127.3, 124.5, 84.1, 14.3, 13.9.

IR (Microscope, cm^{-1}) 3476, 3059, 3025, 2969, 2946, 2919, 1599, 1491, 1447; **HRMS** (EI) for $C_{17}H_{18}O$: calcd. 238.13577; found 238.13564.

[12] Ferreira, B. R. V.; Pirovani, R. V.; Souza-Filho, L. G.; Coelho, F. *Tetrahedron* **2009**, *65*, 7712-7717.

1.3.17 1-Phenylcyclohex-2-enol (2p)



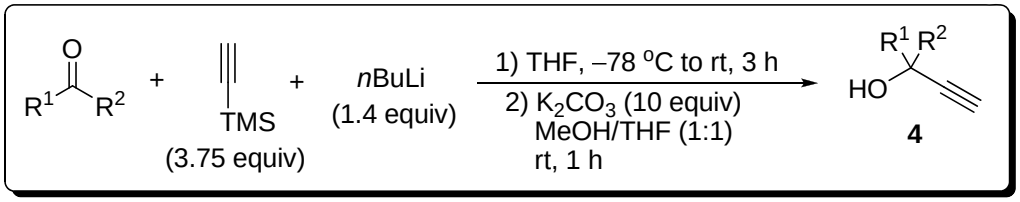
Compound **2p** was made following a literature procedure.[13]

The characterization data for **2p** matched that of a previous report.[13]

1.4 Preparation of propargylic alcohols 4

1.4.1 General procedure for the preparation of propargylic alcohols

Method A:

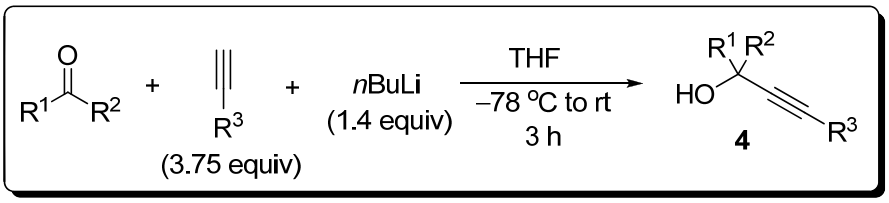


To a solution of alkyne (18.0 mmol) in THF (15 mL) at –78 °C was added *n*BuLi solution (2.5 M in hexanes, 2.8 mL, 6.8 mmol). The solution was allowed to warm to 0 °C over 1 hour and stirred at 0 °C for 30 minutes. Then the solution was cooled to –78 °C and aldehyde or ketone (4.8 mmol) was added. The reaction mixture was allowed to warm to room temperature over 1 hour and stirred at room temperature for 3 hours. NH_4Cl solution (20 mL) was added to quench the reaction and the reaction mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with H_2O (20 mL), saturated $NaHCO_3$ solution (20 mL), brine (20 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure to give the crude product. The crude propargylic alcohol bearing trimethylsilyl substituent was dissolved in MeOH/THF (1:1, 20 mL). Then K_2CO_3 (6.63 g, 48.0 mmol) was added and the resulting mixture was stirred at room temperature for 1 hour. The reaction mixture was filtered and evaporated. The residue was dissolved in EtOAc (30 mL) and washed with saturated NH_4Cl solution (10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The

[13] Shlbuya, M.; Tomlzawa, M.; Iwabuchl, Y. *Org. Lett.* **2008**, *10*, 4715-4718.

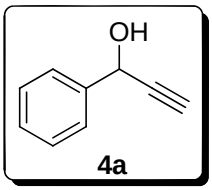
residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:15) to give the title propargylic alcohols **4** in pure form.

Method B:



To a solution of alkyne (18.0 mmol) in THF (15 mL) at –78 °C was added *n*BuLi solution (2.5 M in hexanes, 2.8 mL, 6.8 mmol). The solution was allowed to warm to 0 °C over 1 hour and stirred at 0 °C for 30 minutes. Then the solution was cooled to –78 °C and aldehyde or ketone (4.8 mmol) was added. The reaction mixture was allowed to warm to room temperature over 1 hour and stirred at room temperature for 3 hours. NH_4Cl solution (20 mL) was added to quench the reaction and the reaction mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with H_2O (20 mL), saturated $NaHCO_3$ solution (20 mL), brine (20 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:15) to give the title propargylic alcohols **4** in pure form.

1.4.2 1-Phenylprop-2-yn-1-ol (4a)

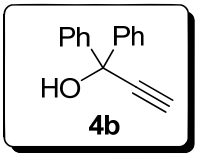


The title compound was prepared using the general procedure (Method A) for propargylic alcohols (92% yield).

The characterization data for this compound matched that of a previous report.[14]

[14] Ye, L.; He, W.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 8550-8551.

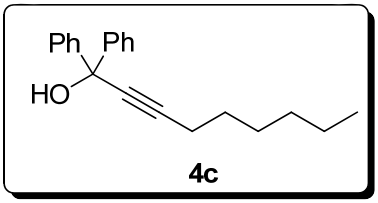
1.4.3 1,1-Diphenylprop-2-yn-1-ol (4b)



The title compound was prepared using the general procedure (Method A) for propargylic alcohols (98% yield).

The characterization data for this compound matched that of a previous report.[15]

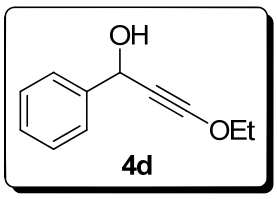
1.4.4 1,1-Diphenylnon-2-yn-1-ol (4c)



The title compound was prepared using the general procedure (Method B) for propargylic alcohols (97% yield).

The characterization data for this compound matched that of a previous report.[16]

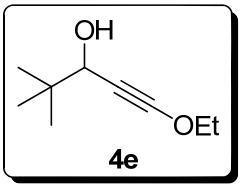
1.4.5 3-Ethoxy-1-phenylprop-2-yn-1-ol (4d)



The title compound was prepared using the general procedure (Method B) for propargylic alcohols (100% yield).

The characterization data for this compound matched that of a previous report.[17]

1.4.6 1-Ethoxy-4,4-dimethylpent-1-yn-3-ol (4e)



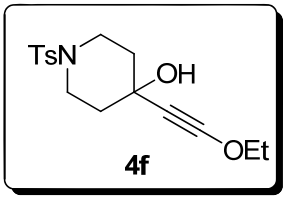
The title compound was prepared using the general procedure (Method B) for

[15] Zhang, X.; Teo, W. T.; Chan, P. W. H. *Org. Lett.* **2009**, *11*, 4990-4993.
[16] Kuwajima, I.; Nakamura, E.; Hashimoto, K. *Tetrahedron* **1983**, *39*, 975-982.
[17] Raucher, S.; Bray, B. L. *J. Org. Chem.* **1987**, *52*, 2332-2333.

propargylic alcohols (97% yield).

The characterization data for this compound matched that of a previous report.[18]

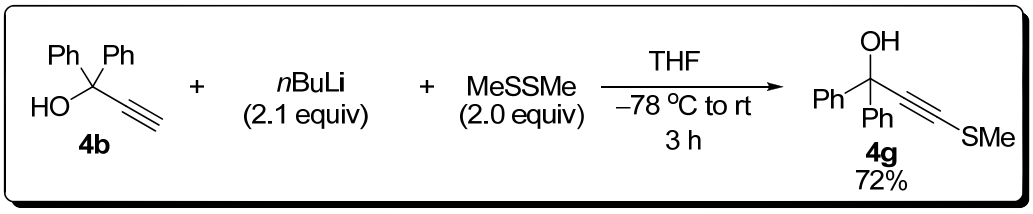
1.4.7 4-(Ethoxyethynyl)-1-tosylpiperidin-4-ol (4f)



The title compound was prepared using the general procedure (Method B) for propargylic alcohols (91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.31 (dd, *J* = 8.5, 0.5 Hz, 2H), 3.96 (q, *J* = 7.4 Hz, 2H), 3.25 (ddd, *J* = 11.0, 6.6, 3.9 Hz, 2H), 2.96 (dt, *J* = 11.2, 3.1 Hz, 2H), 2.41 (s, 3H), 2.25-2.17 (m, 1H), 1.85 (ddd, *J* = 12.9, 6.6, 3.9 Hz, 4H), 1.24 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7, 133.6, 129.9, 127.9, 94.2, 74.9, 65.7, 43.5, 40.7, 39.4, 21.7, 14.4; **IR** (Microscope, cm^{-1}) 3495, 2959, 2931, 2861, 2415, 2260, 1924, 1720, 1597, 1494, 1466; **HRMS** (EI) for $C_{17}H_{21}NO_4S$: calcd. 323.11914; found 323.11974.

1.4.8 3-(Methylthio)-1,1-diphenylprop-2-yn-1-ol (4g)



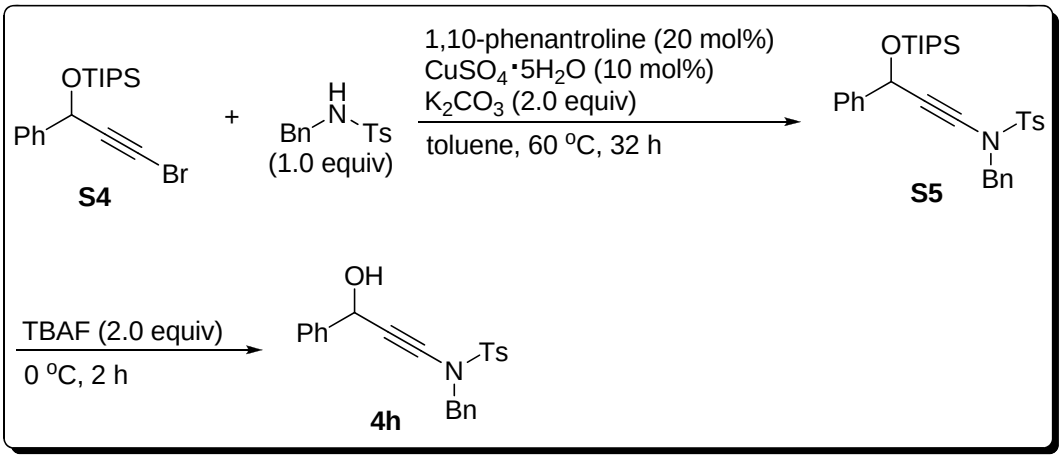
To a solution of 1,1-diphenylprop-2-yn-1-ol **4b** (415 mg, 2.0 mmol) in THF (15 mL) at –78 °C was added *n*BuLi solution (2.5 M in hexanes, 1.68 mL, 4.2 mmol). The solution was stirred at –78 °C for 1 hour. Then MeSSMe (375 mg, 4.0 mmol) was added. The reaction mixture was allowed to warm to room temperature over 1 hour and stirred at room temperature for 3 hours. NH_4Cl solution (20 mL) was added to quench the reaction and the reaction mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with H_2O (20 mL), brine (20 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was

[18] Engel, D. A.; Lopez, S. S.; Dudley, G. B. *Tetrahedron* **2008**, *64*, 6988-6996.

purified by silica gel column chromatography (EtOAc/Hexanes = 1:9) to give the title propargylic alcohol **4g** (356 mg, 72% yield) in pure form.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.60 (m, 4H), 7.38-7.27 (m, 6H), 2.84 (br s, 1H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.1, 128.5, 127.9, 126.3, 95.2, 79.9, 75.4, 19.3; **IR** (Microscope, cm^{-1}) 3542, 3447, 3059, 3085, 3026, 2927, 2168, 1953, 1890, 1813, 1767, 1597, 1490, 1449; **HRMS** (EI) for $C_{16}H_{14}OS$: calcd. 254.07654; found 254.07647.

1.4.9 3-(Methylthio)-1,1-diphenylprop-2-yn-1-ol (4h)



(3-Bromo-1-phenylprop-2-ynyloxy)triisopropylsilane **S4** (85% yield over 3 steps from benzaldehyde) was made following a literature procedure.[19]

***N*-Benzyl-*N*-(3-hydroxy-3-phenylprop-1-ynyl)-4-methylbenzenesulfonamide (S5, step 1)**

To a solution of **S4** (130 mg, 0.5 mmol) in toluene (1 mL) at room temperature was added 1,10-phenantroline (18 mg, 0.1 mmol), $CuSO_4$·$5H_2O$ (12 mg, 0.05 mmol) and *N*-benzyl-4-methylbenzene-sulfonamide (130 mg, 0.5 mmol). The suspension was stirred at 60 °C for 32 hours. The mixture was diluted with DCM (10 mL), filtered through Celite and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:9) to give the title ynamine **S5** (240 mg, 88% yield) in pure form.

[19] Lee, T.; Kang, H.-R.; Kim, S.; Kim, S. *Tetrahedron* **2006**, *62*, 4081-4085

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.40-7.20 (m, 12H), 5.60 (s, 1H), 4.55 (d, *J* = 13.9 Hz, 1H), 4.43 (d, *J* = 13.9 Hz, 1H), 2.45 (s, 3H), 1.09 (dq, *J* = 8.4, 6.9 Hz, 3H), 1.02 (dd, *J* = 8.4, 6.9 Hz, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.6, 142.6, 134.9, 134.8, 129.8, 129.0, 128.7, 128.4, 128.3, 128.0, 127.6, 126.2, 79.4, 73.3, 65.2, 55.6, 21.9, 18.3, 12.5; **IR** (Microscope, cm^{-1}) 3089, 3065, 3032, 2943, 2890, 2865, 2725, 2242, 1948, 1884, 1805, 1759, 1598, 1494, 1456; **HRMS** (ESI) for $C_{32}H_{42}NO_3SSi$: calcd. 548.26490; found 548.26510.

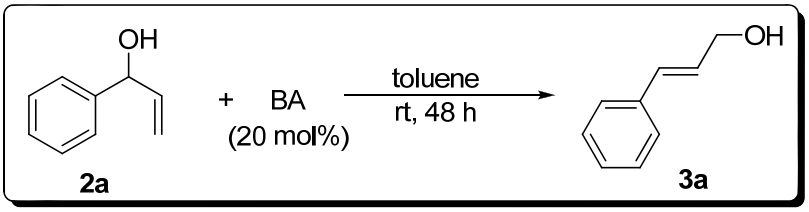
***N*-Benzyl-*N*-(3-hydroxy-3-phenylprop-1-ynyl)-4-methylbenzenesulfonamide (4h, step 2)**

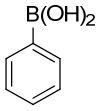
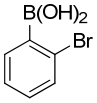
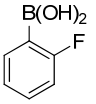
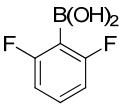
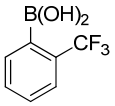
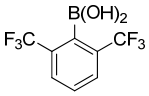
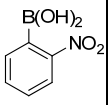
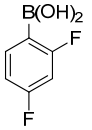
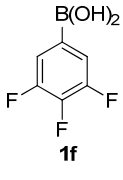
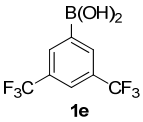
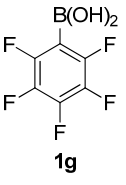
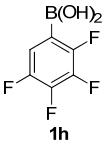
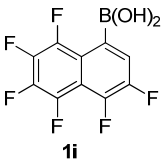
To a solution of **S5** (170 mg, 0.3 mmol) in THF (5 mL) at 0 ^oC was slowly added TBAF (0.6 mL, 1.0 M in THF). The resulting solution was stirred at 0 ^oC for 2 hours. The reaction mixture was diluted with Et_2O (10 mL) and washed with NH_4Cl solution (20 mL), brine (20 mL). The combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:5) to give the title amino alcohol **4h** (117 mg, 97% yield) in pure form.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.34-7.27 (m, 12H), 5.50 (s, 1H), 4.53 (q, *J* = 13.9 Hz, 2H), 2.46 (s, 3H), 2.19 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.0, 140.8, 134.8, 134.5, 130.0, 129.1, 128.8, 128.7, 128.6, 128.4, 127.9, 126.8, 80.6, 71.9, 65.0, 55.6, 21.9; **IR** (Microscope, cm^{-1}) 3497, 3064, 3032, 2928, 2869, 2244, 2191, 2055, 1678, 1635, 1597, 1579, 1494; **HRMS** (ESI) for $C_{23}H_{22}NO_3S$: calcd. 392.13150; found 392.13140.

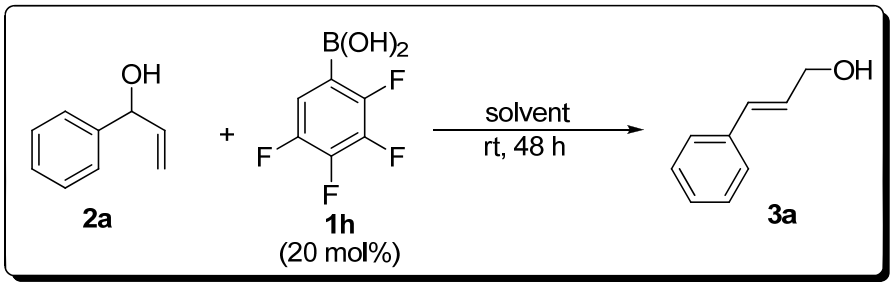
1.5 Full optimization of reaction conditions (Expanded Table 1)

1.5.1 Arylboronic acids screening



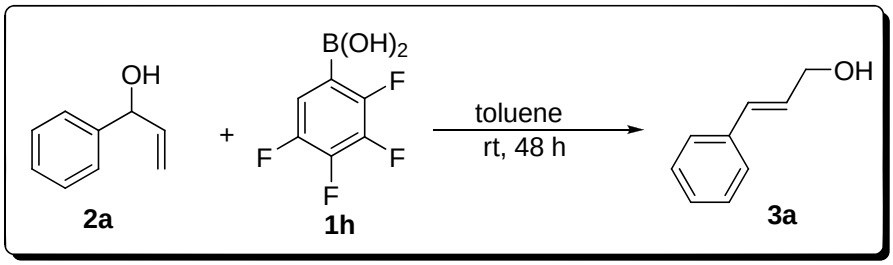
BA	 1a			 1c	 1d	 1b	
Yield	0%	0%	0%	0%	0%	0%	0%
BA			 1f	 1e	 1g	 1h	 1i
Yield	0%	0%	<5%	<5%	10%	36%	**72%**

1.5.2 Solvent screening



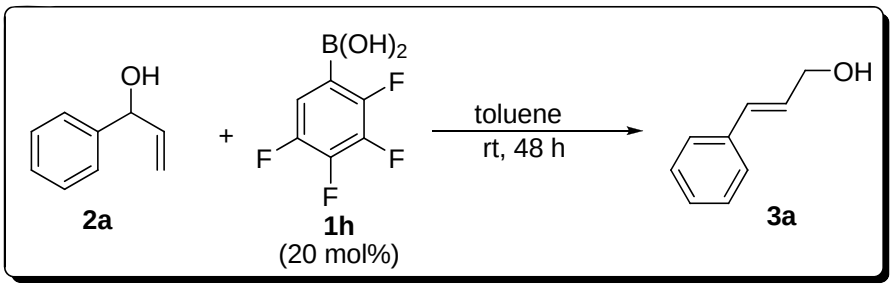
Solvent	MeOH	Acetone	THF	Et_2O	CH_3CN
Yield	0%	13%	7%	5%	trace
Solvent	DMF	EtOAc	DCM	DCE	toluene
Yield	17%	12%	26%	25%	**36%**

1.5.3 Catalyst loading optimization



Catalyst loading	100%	50%	20%	10%	5%
Yield	38%	35%	**36%**	14%	8%

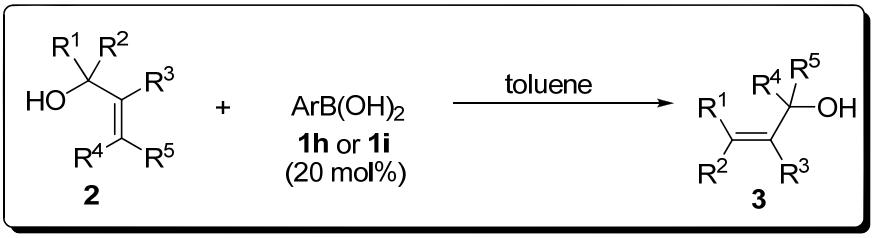
1.5.4 Additive screening



Additive	no additive	with MS	with H_2O (1.0 equiv)	with TsOH (20 mol%)	with $ZrCl_4$ (20 mol%)
Yield	**36%**	18%	5%	25%	complex mixture

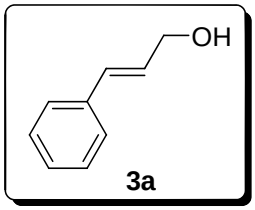
1.6 Boronic acid catalyzed 1,3-transposition of allylic alcohols

1.6.1 General procedure (Table 2)



To a solution of allylic alcohol **2** (0.4 mmol) in toluene (1 mL) at the indicated temperature was added phenyl boronic acid **1h** or **1i** (0.08 mmol). The resulting solution was stirred at the indicated temperature for the indicated period of time. Then the resulting reaction mixture was directly purified by silica gel column chromatography (EtOAc/Hexanes = 1:8) to give the alcohols **3** in pure form.

1.6.2 (*E*)-3-Phenylprop-2-en-1-ol (Table 2, entry 1)



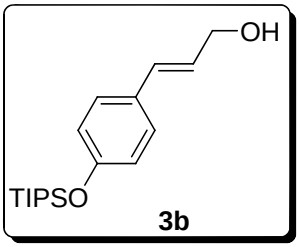
The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols.

The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 48 hours (72% yield, catalyst is **1i**).

The reaction temperature was 50 ^{o}C and the reaction time was 48 hours (93% yield, catalyst is **1i**).

The characterization data for this compound matched that of a previous report.[20]

1.6.3 (*E*)-3-(4-(Triisopropylsilyloxy)phenyl)prop-2-en-1-ol (Table 2, entries 2)



The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols.

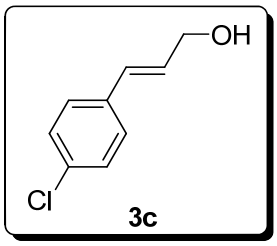
The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 48 hours (68% yield, catalyst is **1h**).

The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 48 hours (75% yield, catalyst is **1i**).

The characterization data for this compound matched that of a previous report.[6]

[20] Mahesh, M.; Murphy, J. A.; Wessel, H. P. *J. Org. Chem.* **2005**, *70*, 4118-4123.

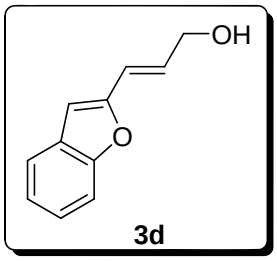
1.6.4 (*E*)-3-(4-Chlorophenyl)prop-2-en-1-ol (Table 2, entry 3)



The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was 50 ^{o}C and the reaction time was 48 hours (67% yield, catalyst is **1i**).

The characterization data for this compound matched that of a previous report.[5a]

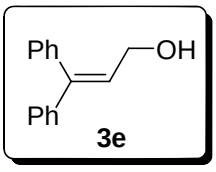
1.6.5 (*E*)-3-(Benzofuran-2-yl)prop-2-en-1-ol (Table 2, entry 4)



The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 48 hours (75% yield, catalyst is **1i**).

The characterization data for this compound matched that of a previous report.[7]

1.6.6 3,3-Diphenylprop-2-en-1-ol (Table 2, entry 5)

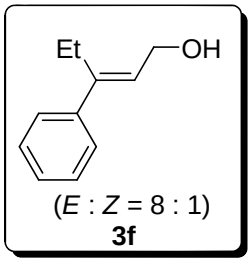


The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 24 hours (80% yield, catalyst is **1h**). Upon completion of the reaction (24 h), adding additional equal amount of starting material also led to 80% yield, which suggested that catalyst **1h** was still active.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.16 (m, 10H), 6.27 (t, *J* = 7.4 Hz, 1H), 4.23 (d, *J*

= 6.8 Hz, 2H), 1.95 (br s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.1, 141.8, 139.1, 129.8, 128.23, 128.20, 128.1, 127.64, 127.60, 127.57, 60.7; **IR** (Microscope, cm^{-1}) 3326, 3080, 3056, 3026, 2926, 2867, 1494, 1444; **HRMS** (EI) for $C_{15}H_{14}O$: calcd. 210.10446; found 210.10441.

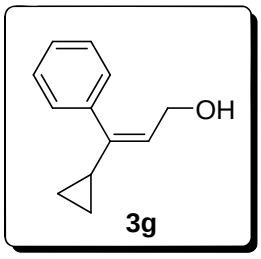
1.6.7 (*E*)-3-Phenylpent-2-en-1-ol (Table 2, entry 6)



The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 24 hours (72% yield, *E* : *Z* = 8 : 1, determined by ^{1}H NMR, catalyst is **1h**).

The characterization data for this compound matched that of a previous report.[7]

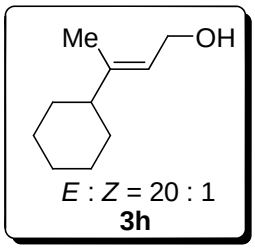
1.6.8 (*Z*)-3-Cyclopropyl-3-phenylprop-2-en-1-ol (Table 2, entry 7)



The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 48 hours (76% yield, catalyst is **1h**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 3H), 7.18-7.12 (m, 2H), 5.65 (t, *J* = 7.0 Hz, 1H), 3.98 (d, *J* = 7.0 Hz, 2H), 1.66-1.57 (m, 1H), 1.28 (br s, 1H), 0.74-0.67 (m, 2H), 0.53-0.46 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.8, 139.1, 128.5, 128.0, 127.1, 123.6, 60.2, 18.2, 5.7; **IR** (Microscope, cm^{-1}) 3323, 3081, 3056, 3011, 2927, 2873, 1648, 1493, 1442; **HRMS** (EI) for $C_{12}H_{14}O$: calcd. 174.10446; found 174.10422.

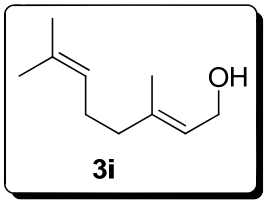
1.6.9 (*E*)-3-Cyclohexylbut-2-en-1-ol (Table 2, entry 8)



The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was 80 ^{o}C and the reaction time was 48 hours (77% yield, *E* : *Z* = 20 : 1, determined by ^{1}H NMR, catalyst is **1i**).

The characterization data for this compound matched that of a previous report.[21]

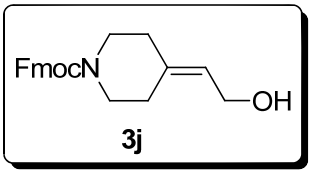
1.6.10 Geraniol (Table 2, entry 9)



The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was 80 ^{o}C and the reaction time was 48 hours (62% yield, *E* : *Z* = 6 : 1, determined by ^{1}H NMR, catalyst is **1i**).

The characterization data for this compound matched that of a previous report.[22]

1.6.11 (9*H*-Fluoren-9-yl)methyl 4-(2-hydroxyethylidene)piperidine-1-carboxylate (Table 2, entry 10)

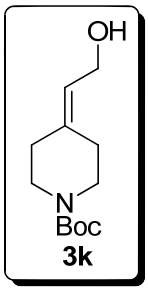


The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was 50 ^{o}C and the reaction time was 12 hours (81% yield, catalyst is **1i**).

[21] Morrill, C.; Grubbs, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 2842-2843.
[22] Grotjahn, D. B.; Larsen, C. R.; Gustafson, J. L.; Nair, R.; Sharma, A. *J. Am. Chem. Soc.* **2007**, *129*, 9592-9593.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.61 (dd, *J* = 7.5, 0.8 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.34 (td, *J* = 7.5, 1.2 Hz, 2H), 5.53 (t, *J* = 7.0 Hz, 1H), 4.48 (d, *J* = 6.8 Hz, 2H), 4.28 (t, *J* = 6.7 Hz, 1H), 4.19 (d, *J* = 6.5 Hz, 2H), 3.58-3.40 (m, 4H), 2.36-2.12 (m, 4H), 1.56 (br s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1, 144.1, 144.0, 141.4, 127.7, 127.1, 125.0, 123.3, 120.0, 67.3, 58.3, 47.4, 45.5, 44.8; **IR** (Microscope, cm^{-1}) 3439, 3066, 2950, 2897, 2871, 1699; **HRMS** (EI) for $C_{22}H_{23}NO_3$: calcd. 349.16779; found 349.16639

1.6.12 *tert*-Butyl 4-(2-hydroxyethylidene)piperidine-1-carboxylate (Table 2, entry 11)

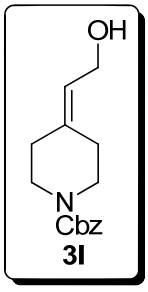


3k

The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was 50 ^oC and the reaction time was 12 hours (72% yield, catalyst is **1i**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (t, *J* = 7.0 Hz, 1H), 4.17 (d, *J* = 6.9 Hz, 2H), 3.46-3.36 (m, 4H), 2.26 (t, *J* = 5.7 Hz, 2H), 2.18 (t, *J* = 5.3 Hz, 2H), 1.65 (br s, 1H), 1.47 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 139.2, 123.0, 79.6, 58.2, 45.1, 35.7, 28.4; **IR** (Microscope, cm^{-1}) 3422, 2974, 2932, 2868, 1696, 1672; **HRMS** (EI) for $C_{12}H_{21}NO_3$: calcd. 227.15215; found 227.15187.

1.6.13 Benzyl 4-(2-hydroxyethylidene)piperidine-1-carboxylate (Table 2, entry 12)

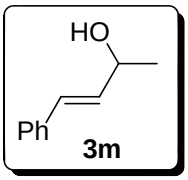


3l

The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was 50 ^{o}C and the reaction time was 12 hours (74% yield, catalyst is **1i**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5H), 5.52 (t, *J* = 6.9 Hz, 1H), 5.16 (s, 2H), 4.18 (d, *J* = 6.7 Hz, 2H), 3.56-3.48 (m, 4H), 2.35-2.18 (m, 4H), 1.57 (br s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 138.7, 136.8, 128.5, 128.0, 127.9, 123.3, 67.2, 58.3, 45.5, 44.8; **IR** (Microscope, cm^{-1}) 3414, 3064, 2942, 2871, 1698; **HRMS** (EI) for $C_{15}H_{19}NO_3$: calcd. 261.13651; found 261.13641.

1.6.14 (*E*)-4-Phenylbut-3-en-2-ol (Table 2, entry 13)

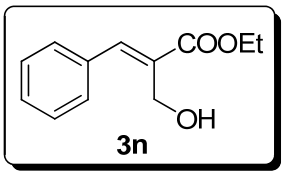


3m

The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 4 hours (73% yield, catalyst is **1h**).

The characterization data for this compound matched that of a previous report.[23]

1.6.15 (*E*)-Ethyl 2-(hydroxymethyl)-3-phenylacrylate (Table 2, entries 14)



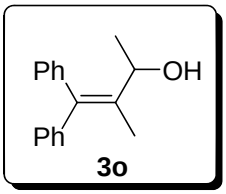
3n

The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was 80 ^{o}C and the reaction time was 48 hours (20% yield, catalyst is **1h**).

The characterization data for this compound matched that of a previous report.[24]

[23] Lu, Z.; Ma, S. *J. Org. Chem.* **2006**, *71*, 2655-2660.
[24] Ramachandran, P. V.; Burghardt, T. E.; Reddy, M. V. R. *Tetrahedron Lett.* **2005**, *46*, 2121-2124.

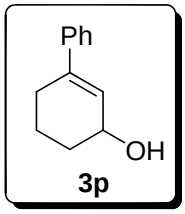
1.6.16 3-Methyl-4,4-diphenylbut-3-en-2-ol (Table 2, entry 15)



3o

The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 48 hours (71% yield, catalyst is **1h**).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.14 (m, 10H), 4.64 (q, *J* = 6.4 Hz, 1H), 1.83 (s, 3H), 1.54 (br s, 1H), 1.34 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.5, 142.1, 139.0, 136.8, 129.4, 129.2, 128.2, 128.0, 126.6, 126.5, 68.1, 21.6, 13.2; **IR** (Microscope, cm^{-1}) 3345, 3078, 3054, 3021, 2976, 2929, 2860, 1598, 1576, 1491, 1442; **HRMS** (EI) for $C_{17}H_{18}O$: calcd. 238.13577; found 238.13604.

1.6.17 3-Phenylcyclohex-2-enol (Table 2, entry 16)

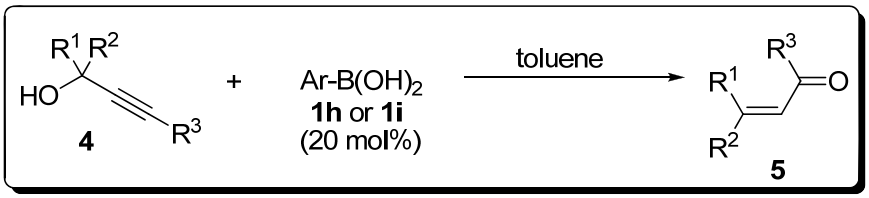


3p

The title compound was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols. The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 14 hours (75% yield, catalyst is **1i**).
The characterization data for this compound matched that of a previous report.[25]

1.7 Boronic acid catalyzed Meyer-Schuster rearrangement

1.7.1 General procedure (Table 3)

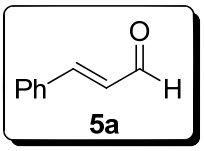


To a solution of propargylic alcohol **4** (0.4 mmol) in toluene (1 mL) at the indicated

[25] Uyanlk, M.; Fukatsu, R.; Ishihara, K. *Org. Lett*. **2009**, *11*, 3470-3473.

temperature was added aryl boronic acid **1h** or **1i** (0.08 mmol). The resulting solution was stirred at the indicated temperature for the indicated period of time. Then the resulting reaction mixture was directly purified by silica gel column chromatography (EtOAc/Hexanes = 1:20) to give the title compounds **5** in pure form.

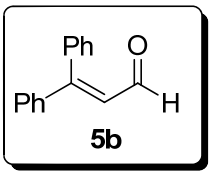
1.7.2 Cinnamaldehyde (Table 3, entry 1)



5a

The title compound was prepared using the general procedure for the boronic acid catalyzed Meyer-Schuster rearrangement of propargylic alcohols. The reaction temperature was 50 ^{o}C and the reaction time was 6 hours (75% yield, catalyst is **1i**).
The characterization data for this compound matched that of a previous report.[26]

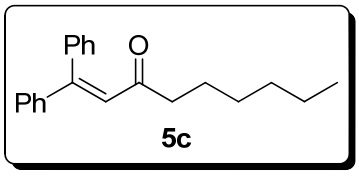
1.7.3 3,3-Diphenylacrylaldehyde (Table 3, entry 2)



5b

The title compound was prepared using the general procedure for the boronic acid catalyzed Meyer-Schuster rearrangement of propargylic alcohols. The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 0.25 hour (87% yield, catalyst is **1h**).
The characterization data for this compound matched that of a previous report.[27]

1.7.4 1,1-Diphenylnon-1-en-3-one (Table 3, entry 3)



5c

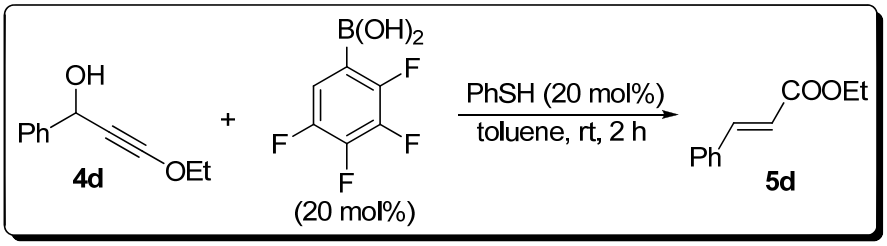
The title compound was prepared using the general procedure for the boronic acid catalyzed Meyer-Schuster rearrangement of propargylic alcohols. The reaction

[26] Liu, J.; Zhu, J.; Jiang, H.; Wang, W.; Li, J. *Chem. Commun.* **2010**, *46*, 415-417.
[27] Yamada, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2005**, *70*, 5471-5474.

temperature was room temperature (25 ^{o}C) and the reaction time was 0.25 hour (90% yield, catalyst is **1h**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.28 (m, 8H), 7.23-7.18 (m, 2H), 6.59 (s, 1H), 2.24 (t, *J* = 7.3 Hz, 2H), 1.54-1.46 (m, 2H), 1.32-1.13 (m, 6H), 0.86 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.6, 153.0, 141.1, 139.1, 129.5, 129.2, 128.5, 128.4 (two carbon signals are overlapping here), 128.2, 126.7, 43.2, 31.5, 28.8, 24.3, 22.4, 14.0; **IR** (Microscope, cm^{-1}) 3080, 3058, 3026, 2955, 2929, 2857, 1691, 1660, 1591, 1575, 1446; **HRMS** (EI) for $C_{21}H_{24}O$: calcd. 292.18271; found 292.18224.

1.7.5 Ethyl cinnamate (Table 3, entry 4)

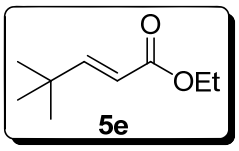


To a solution of propargylic alcohol **4d** (70 mg, 0.4 mmol) and PhSH (9 mg, 0.08 mmol) in toluene (1 mL) at room temperature was added aryl boronic acid **1h** (15 mg, 0.08 mmol). The resulting solution was stirred at room temperature for the 2 hours. Then the resulting reaction mixture was directly purified by silica gel column chromatography (EtOAc/Hexanes = 1:20) to give the title compounds **5d** (59 mg, 84% yield, all *E*) in pure form.

Without PhSH (20 mol%) as additive, the same reaction gave the title product **5d** in 80% yield (*E* : *Z* = 4 : 3, determined by ^{1}H NMR).

The characterization data for this compound matched that of a previous report.[28]

1.7.6 (*E*)-Ethyl 4,4-dimethylpent-2-enoate (Table 3, entry 5)

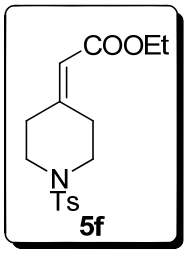


The title compound was prepared using the general procedure for the boronic acid catalyzed Meyer-Schuster rearrangement of propargylic alcohols. The reaction

[28] Cao, P.; Li, C.-Y.; Kang, Y.-B.; Xie, Z.; Sun, X.-L.; Tang, Y. *J. Org. Chem.* **2007**, *72*, 6628-6630.

temperature was 50 °C and the reaction time was 6 hours (78% yield, catalyst is **1i**). The characterization data for this compound matched that of a previous report.[18]

1.7.7 1,1-Diphenylnon-1-en-3-one (Table 3, entry 6)

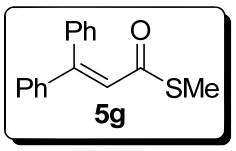


5f

The title compound was prepared using the general procedure for the boronic acid catalyzed Meyer-Schuster rearrangement of propargylic alcohols. The reaction temperature was 50 °C and the reaction time was 1 hour (89% yield, catalyst is **1i**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.60 (m, 2H), 7.34-7.29 (m, 2H), 5.66-5.62 (m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.16-3.02 (m, 6H), 2.42 (s, 3H), 2.41-2.34 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 155.3, 143.7, 133.1, 129.7, 127.6, 116.0, 59.9, 47.3, 46.8, 35.8, 28.6, 21.5, 14.2; **IR** (Microscope, cm^{-1}) 3091, 2978, 2928, 2911, 2848, 1712, 1657, 1598; **HRMS** (ESI) for $C_{16}H_{21}NO_4S$: calcd. 323.11914; found 323.11982.

1.7.8 *S*-Methyl 3,3-diphenylprop-2-enethioate (Table 3, entry 7)



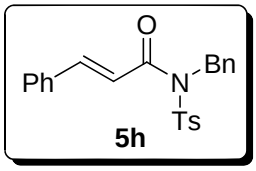
5g

The title compound was prepared using the general procedure for the boronic acid catalyzed Meyer-Schuster rearrangement of propargylic alcohols. The reaction temperature was room temperature (25 °C) and the reaction time was 0.5 hour (88% yield, catalyst is **1i**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.33 (m, 8H), 7.28-7.24 (m, 2H), 6.65 (s, 1H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.4, 153.4, 140.9, 138.9, 129.9, 129.6, 128.8, 128.7, 128.6, 128.2, 123.8, 12.3; **IR** (Microscope, cm^{-1}) 3358, 3079, 3058, 3027, 2925, 2853, 1952, 1886, 1807, 1725, 1677, 1591, 1572, 1490, 1445; **HRMS** (EI)

for $C_{16}H_{14}OS$: calcd. 254.07654; found 254.07634.

1.7.9 *N*-Benzyl-N-tosylcinnamamide (Table 3, entry 8)



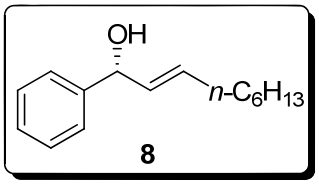
5h

The title compound was prepared using the similar procedure for the boronic acid catalyzed Meyer-Schuster rearrangement of propargylic alcohols **4d** with PhSH (20 mol%) as the additive. The reaction temperature was room temperature (25 ^{o}C) and the reaction time was 24 hours (80%, all *E*, catalyst is **1i**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 15.5 Hz, 1H), 7.35 (m, 12H), 7.29 (d, *J* = 15.5 Hz, 1H), 5.17 (s, 2H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 146.4, 145.1, 137.2, 137.0, 134.7, 130.8, 129.9, 129.2, 128.9, 128.6, 128.3, 128.0, 127.8, 118.4, 49.7, 21.8; **IR** (Microscope, cm^{-1}) 3062, 3030, 2923, 2851, 1678, 1617, 1598, 1577, 1496; **HRMS** (ESI) for $C_{23}H_{21}NO_3SNa$: calcd. 414.11340; found 414.11350.

1.8 Stereochemical study of the 1,3-transposition of allylic alcohols

1.8.1 Preparation of (*R*,*E*)-1-phenylnon-2-en-1-ol (8)



8

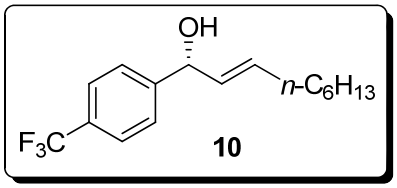
Compound **8** was made following a literature procedure.[21]

The characterization data for compound **8** matched that of a previous report.[21]

$[\alpha]_D^{20}$: –34.4 (c = 1.2, chloroform) for 96.5% ee.

HPLC (Chiralcel OD): 2:98 *i*-PrOH/Hexanes, 1.0 mL/minute, λ = 250 nm, T_{major} = 11.8 min, T_{minor} = 16.9 min, ee = 96.5%.

1.8.2 Preparation of (*R*,*E*)-1-(4-(trifluoromethyl)phenyl)non-2-en-1-ol (10)

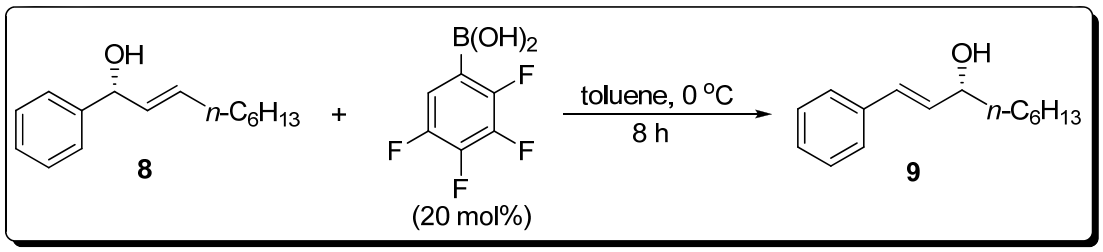


Compound **10** was made following a literature procedure.[7]

The characterization data for compound **10** matched that of a previous report.[7]

$[\alpha]_D^{20}$: –42.5 (c = 1.0, chloroform) for 99% ee.

1.8.3 Boronic acid catalyzed 1,3-transposition of 8 (Scheme 2)



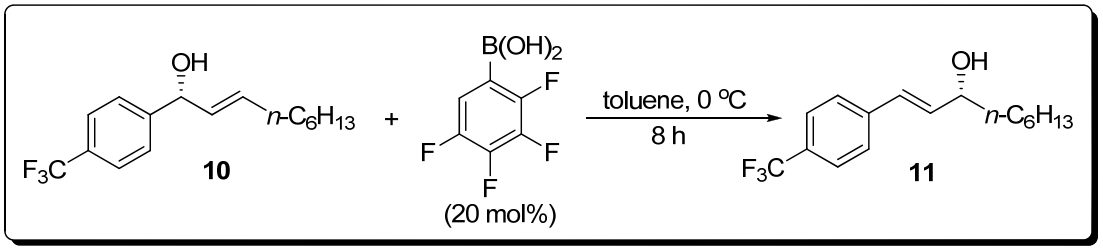
To a solution of allylic alcohol **8** (43 mg, 0.2 mmol) in toluene (1 mL) at 0 °C was added 2,3,4,5-tetrafluorophenyl boronic acid **1h** (8 mg, 0.04 mmol). The resulting solution was stirred at 0 °C for 8 hours. Then the resulting reaction mixture was directly purified by silica gel column chromatography (EtOAc/Hexanes = 1:8) to give (*R*,*E*)-1-phenylnon-1-en-3-ol **9** (33.5 mg, 78% yield) in pure form.

The characterization data for compound **9** matched that of a previous report.[21]

$[\alpha]_D^{20}$: –1.4 (c = 1.2, chloroform) for 23% ee.

HPLC (Chiralcel OD): 3:97 *i*-PrOH/Hexanes, 1.0 mL/minute, λ = 280 nm, T_{major} = 17.1 min, T_{minor} = 33.2 min, ee = 23%.

1.8.4 Boronic acid catalyzed 1,3-transposition of 10 (Scheme 2)



To a solution of allylic alcohol **10** (57 mg, 0.2 mmol) in toluene (1 mL) at 0 °C was

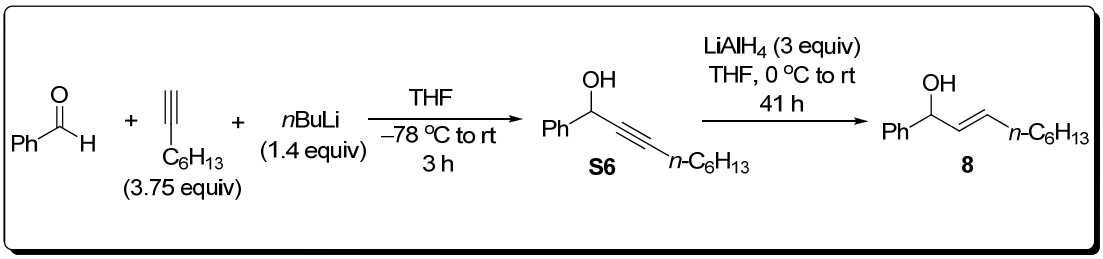
added 2,3,4,5-tetrafluorophenyl boronic acid **1h** (8 mg, 0.04 mmol). The resulting solution was stirred at 0 °C for 8 hours. Then the resulting reaction mixture was directly purified by silica gel column chromatography (EtOAc/Hexanes = 1:8) to give (*R*,*E*)-1-(4-(trifluoromethyl)phenyl)non-1-en-3-ol **11** (42 mg, 74% yield) in pure form. The characterization data for compound **11** matched that of a previous report.[7]

$[\alpha]_D^{20}$: –7.1 (c = 1.7, chloroform) for 87% ee.

HPLC (Chiralcel OD): 1:99 *i*-PrOH/Hexanes, 1.0 mL/minute, λ = 230 nm, T_{major} = 18.8 min, T_{minor} = 28.7 min, ee = 87%.

1.9 Boronic acid catalyzed 1,3-transposition of 8 and 12

1.9.1 Preparation of (*E*)-1-phenylnon-2-en-1-ol (8)



Step 1: To a solution of 1-octyne (1.98 g, 18.0 mmol) in THF (15 mL) at –78 °C was added *n*BuLi solution (2.5 M in hexanes, 2.8 mL, 6.8 mmol). The solution was stirred at –78 °C for 15 minutes and benzaldehyde (509 mg, 4.8 mmol) was added. The reaction mixture was allowed to warm to room temperature over 1 hour and stirred at room temperature for 3 hours. A saturated aqueous NH_4Cl solution (20 mL) was added to quench the reaction and the resulting mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with H_2O (20 mL), saturated $NaHCO_3$ solution (20 mL), brine (20 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:15) to give 1-phenylnon-2-yn-1-ol **S6** (986 mg, 95% yield) in pure form.

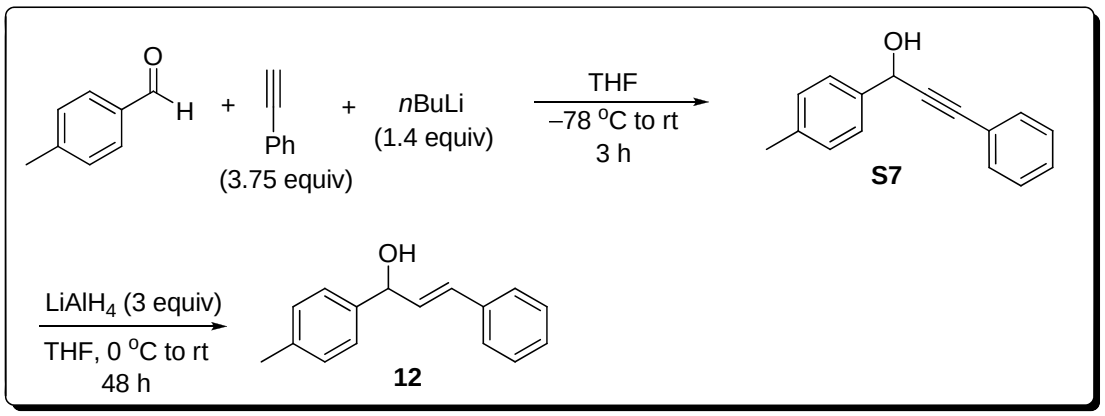
The characterization data for compound **S6** matched that of a previous report.[21]

Step 2: To a solution of 1-phenylnon-2-yn-1-ol **S6** (433 mg, 2.0 mmol) in THF (15

mL) at 0 °C was added $LiAlH_4$ solution (1.0 M in THF, 6.0 mL, 6.0 mmol) dropwise. The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 41 hours. Then the reaction mixture was cooled to 0 °C. EtOAc (20 mL) and $Na_2SO_4 \cdot H_2O$ (1.0 g) were added to the reaction mixture and the reaction mixture was stirred at 0 °C for 20 minutes. The reaction mixture was filtered through Celite and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:15) to give the title allylic alcohols **8** (382 mg, 87% yield) in pure form.

The characterization data for compound **8** matched that of a previous report.[21]

1.9.2 Preparation of (*E*)-3-phenyl-1-*p*-tolylprop-2-en-1-ol (12)



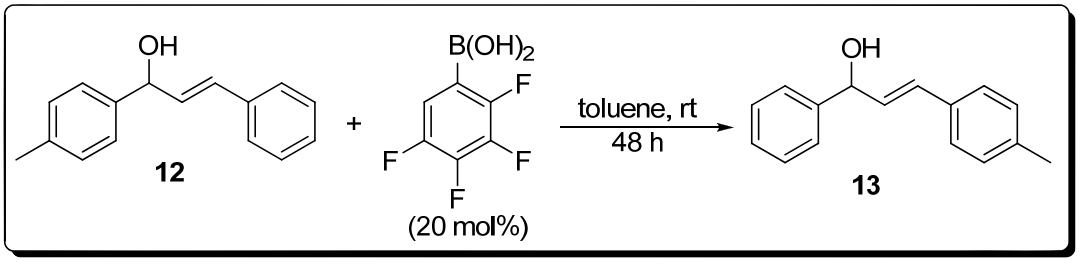
Step 1: To a solution of ethynylbenzene (1.84 g, 18.0 mmol) in THF (15 mL) at –78 °C was added *n*BuLi solution (2.5 M in hexanes, 2.8 mL, 6.8 mmol). The solution was allowed to warm to 0 °C over 1 hour and stirred at 0 °C for 30 minutes. Then the solution was cooled to –78 °C and 4-methylbenzaldehyde (577 mg, 4.8 mmol) was added. The reaction mixture was allowed to warm to room temperature over 1 hour and stirred at room temperature for 3 hours. A saturated aqueous NH_4Cl solution (20 mL) was added to quench the reaction and the reaction mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with H_2O (20 mL), saturated $NaHCO_3$ solution (20 mL), brine (20 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:15) to give 3-phenyl-1-*p*-tolylprop-2-yn-1-ol **S7** (1.05 g, 99% yield) in pure form.

The characterization data for compound **S7** matched that of a previous report.[29]

Step 2: To a solution of 3-phenyl-1-*p*-tolylprop-2-yn-1-ol **S7** (445 mg, 2.0 mmol) in THF (15 mL) at 0 °C was added $LiAlH_4$ solution (1.0 M in THF, 6.0 mL, 6.0 mmol) dropwise. The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 41 hours. Then the reaction mixture was cooled to 0 °C. EtOAc (20 mL) and $Na_2SO_4 \cdot H_2O$ (1.0 g) were added to the reaction mixture and the reaction mixture was stirred at 0 °C for 20 minutes. The reaction mixture was filtered through Celite and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:15) to give the title allylic alcohols **12** (440 mg, 98% yield) in pure form.

The characterization data for compound **12** matched that of a previous report.[30]

1.9.3 Boronic acid catalyzed 1,3-transposition of 12 (Equation 1)

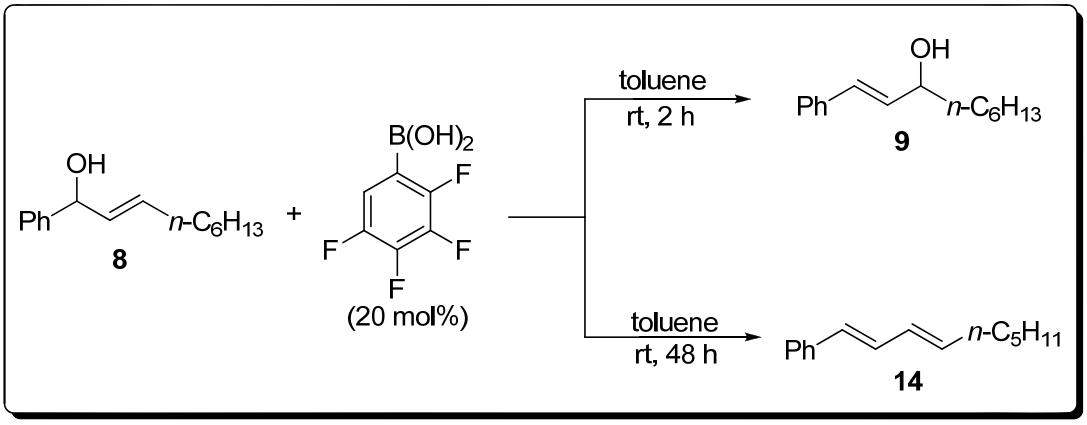


To a solution of allylic alcohol **12** (90 mg, 0.4 mmol) in toluene (1 mL) at room temperature was added 2,3,4,5-tetrafluorophenyl boronic acid **1h** (16 mg, 0.08 mmol). The resulting solution was stirred at room temperature for 48 hours. Then the resulting reaction mixture was directly purified by silica gel column chromatography (EtOAc/Hexanes = 1:20) to give (*E*)-1-phenyl-3-*p*-tolylprop-2-en-1-ol **13** (35 mg, 39% yield) and (*E*)-3-phenyl-1-*p*-tolylprop-2-en-1-ol **12** (46 mg, 51% recovery yield) in pure form.

The characterization data for compound **12** matched that of a previous report.[31]

[29] Downey, C. W.; Mahoney, B. D.; Lipari, V. R. *J. Org. Chem.* **2009**, *74*, 2904-2906.
[30] Von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Ruegger, H.; Pregosin, P. S. *Helv. Chim. Acta*. **1995**, *78*, 265-284.
[31] Schmidt, F.; Rudolph, J.; Bolm, C. *Synthesis* **2006**, *21*, 3625-3630.

1.9.4 Boronic acid catalyzed 1,3-transposition of 8 (Scheme 4)



To a solution of allylic alcohol **8** (87 mg, 0.4 mmol) in toluene (1 mL) at room temperature was added 2,3,4,5-tetrafluorophenyl boronic acid **1h** (16 mg, 0.08 mmol). The resulting solution was stirred at room temperature for 2 hours. Then the resulting reaction mixture was directly purified by silica gel column chromatography (EtOAc/Hexanes = 1:10) to give (*E*)-1-phenylnon-1-en-3-ol **9** (68 mg, 78% yield) in pure form.

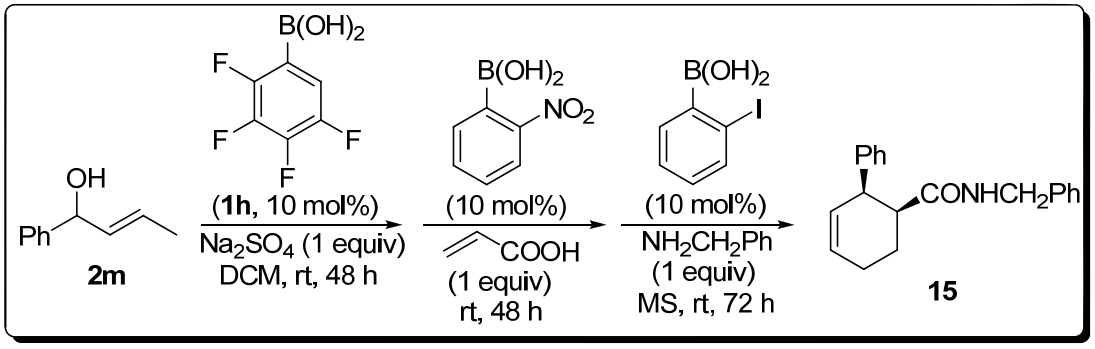
The characterization data for compound **9** matched that of a previous report.[21]

To a solution of allylic alcohol **8** (87 mg, 0.4 mmol) in toluene (1 mL) at room temperature was added 2,3,4,5-tetrafluorophenyl boronic acid **1h** (16 mg, 0.08 mmol). The resulting solution was stirred at room temperature for 48 hours. Then the resulting reaction mixture was directly purified by silica gel column chromatography (100% Hexanes) to give the diene **14** (69 mg, 86% yield) in pure form.

The characterization data for compound **14** matched that of a previous report.[32]

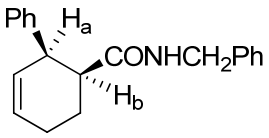
[32] Underiner, T. L.; Goering, H. L. *J. Org. Chem.* **1991**, *56*, 2563-2572.

1.10 Boronic acid catalyzed one-pot multicatalytic reaction (Scheme 5)



To a mixture of the allylic alcohol **2m** (296 mg, 2.0 mmol) and Na_2SO_4 (284 mg, 2.0 mmol) in DCM (5 mL) at room temperature was added 2,3,4,5-tetrafluorophenyl boronic acid (39 mg, 0.2 mmol). The resulting solution was stirred at room temperature for 48 hours. Then acrylic acid (144 mg, 2.0 mmol) and 2-nitrophenylboronic acid (33 mg, 0.2 mmol) were added to the reaction mixture. The reaction mixture was stirred at room temperature for 48 hours. Benzyl amine (214 mg, 2.0 mmol), 4 Å molecular sieves (2.0 g), 2-iodophenylboronic acid (50 mg, 0.2 mmol) and DCM (5 mL) were added to the reaction mixture. The reaction mixture was stirred at room temperature for 72 hours and filtered through Celite. The filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/Hexanes = 1:5) to give *N*-benzyl-2-phenylcyclohex-3-ene-carboxamide **15** (286 mg, 49% yield, *syn*:*anti* = 19:1, determined by 2D NMR) in pure form.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.17 (m, 8H), 6.91-6.84 (m, 2H), 5.90-5.84 (m, 1H), 5.68 (dq, *J* = 10.0, 2.1 Hz, 1H), 5.41 (br s, 1H), 4.36 (dd, *J* = 14.9, 6.4 Hz, 1H), 4.15 (dd, *J* = 14.9, 5.1 Hz, 1H), 3.77-3.70 (m, 1H), 2.29-2.16 (m, 3H), 2.08-1.91 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6, 144.3, 138.1, 130.0, 128.6, 128.4, 128.0, 127.4, 127.2, 127.0, 126.6, 51.3, 45.0, 43.2, 26.2, 24.6; **IR** (Microscope, cm^{-1}) 3294, 3085, 3066, 3029, 2926, 2914, 2883, 2869, 1645, 1558, 1493, 1453; **HRMS** (ESI) for $C_{20}H_{22}NO$: calcd. 292.16961; found 292.16940.

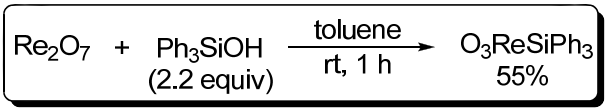


15

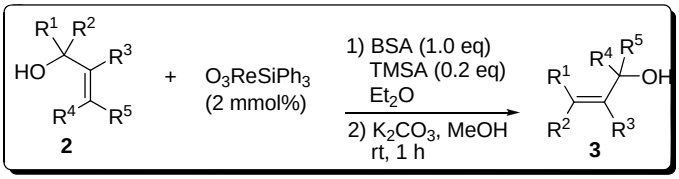
The above stereoisomer was determined by 2D-NMR spectroscopy (see section 3.7). From HSQC and HMBC spectra, H_a and H_b (see the above figure) could be identified as 3.77-3.70 (m, 1H) and 2.29-2.16 (m, 1H) respectively. Then, a strong correlation δ $H_a \leftrightarrow H_b$ on the COSY spectrum showed the desired product was the indicated regioisomer and a strong correlation δ $H_a \leftrightarrow H_b$ on the TROESY spectrum showed that the desired product was *syn*-stereoisomer.

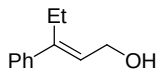
1.11 Transition metal catalyzed variants (Note 19)

1.11.1 Re catalyzed 1,3-transposition of allylic alcohols

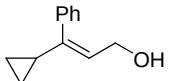


The Re catalyst ($O_3ReSiPh_3$) was prepared following Grubbs' procedure.[7]

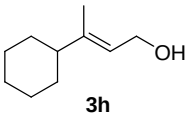




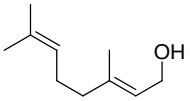
3f
(Table 2, entry 8)
0 °C, 30 min
74% (E/Z = 5:1)



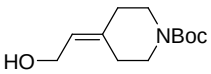
3g
(Table 2, entry 9)
0 °C, 6 h
63% (E/Z = 1:3.5)



3h
(Table 2, entry 10)
0 °C, 30 min
85% (E/Z = 5:1)



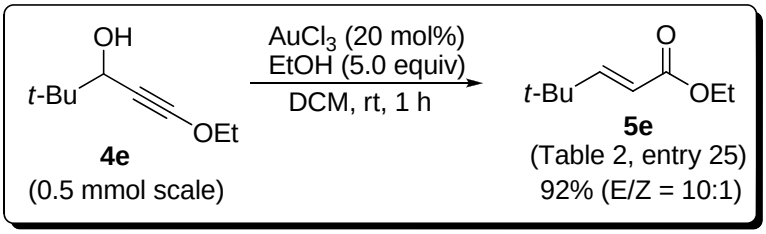
3i
(Table 2, entry 11)
rt, 30 min
81% (E/Z = 3:1)



3k
(Table 2, entry 12)
rt, 12 h
trace

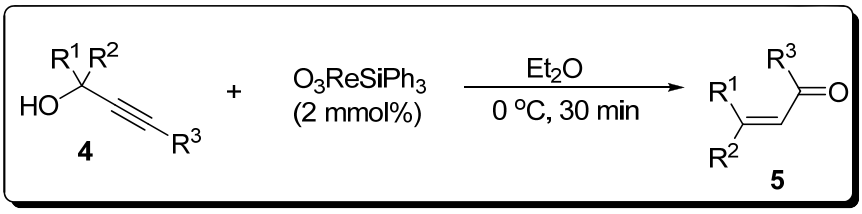
The above Re catalyzed 1,3-transpositions of allylic alcohols (0.4 mmol scale) were performed using Grubbs' protocol.[7]

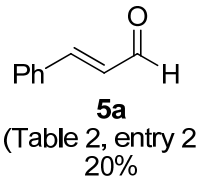
1.11.2 Au catalyzed Meyer-Schuster rearrangement

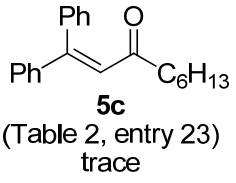


The above Au catalyzed Meyer-Schuster rearrangement (0.5 mmol scale) was performed using Dudley's protocol.[33]

1.11.3 Re catalyzed Meyer-Schuster rearrangements

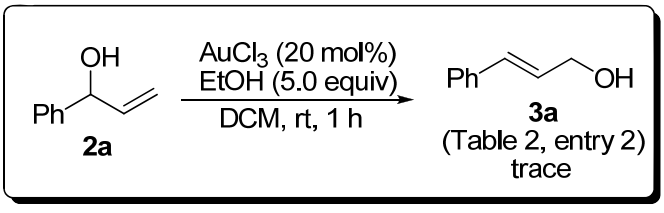






The above Re catalyzed Meyer-Schuster rearrangements (0.4 mmol scale) were performed using Grubbs' protocol which was originally developed for 1,3-transposition of allylic alcohols.[7]

1.11.4 Au catalyzed 1,3-transposition of allylic alcohols

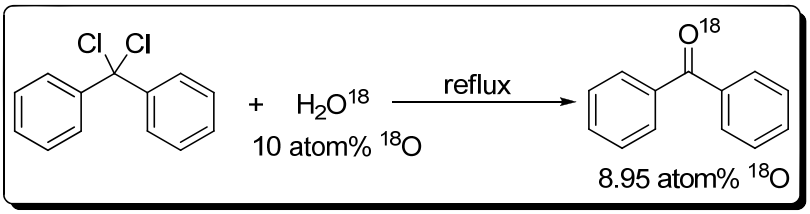


The above Au catalyzed 1,3-transposition of allylic alcohol (0.4 mmol scale) was performed using Dudley's protocol which was originally developed for Meyer-Schuster rearrangement.[33]

[33] Engel, D. A.; Dudley, G. B. *Org. Lett.* **2006**, *8*, 4027-4029

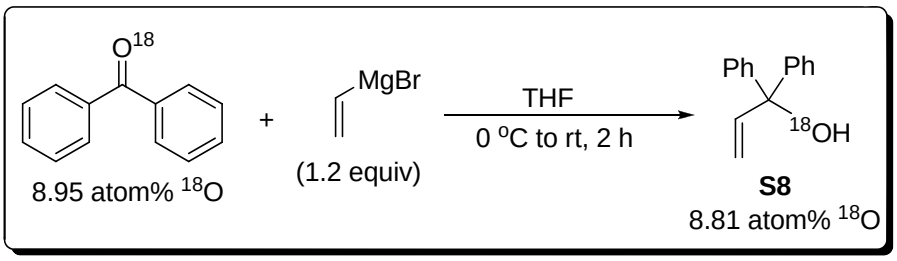
2. ^{18}O Labeling Experiments (Scheme 3)

2.1 Preparation of [^{18}O]benzophenone



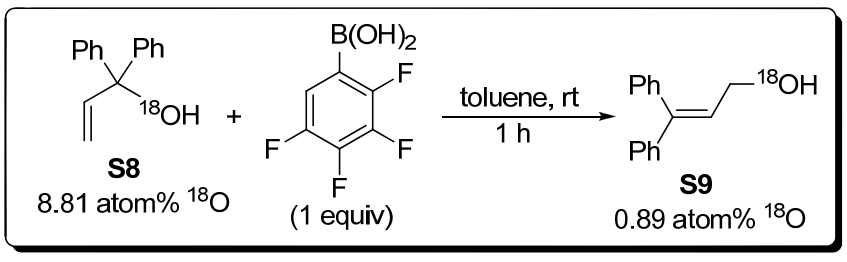
[^{18}O]Benzophenone was made following a literature procedure.[34] Mass spectral analysis indicated 8.95% ^{18}O isotopic incorporation.

2.2 Preparation of [^{18}O]1,1-diphenylprop-2-en-1-ol (S8)



Compound **S8** was prepared using the general procedure for allylic alcohols (83% yield). Mass spectral analysis indicated 8.81% ^{18}O isotopic incorporation.

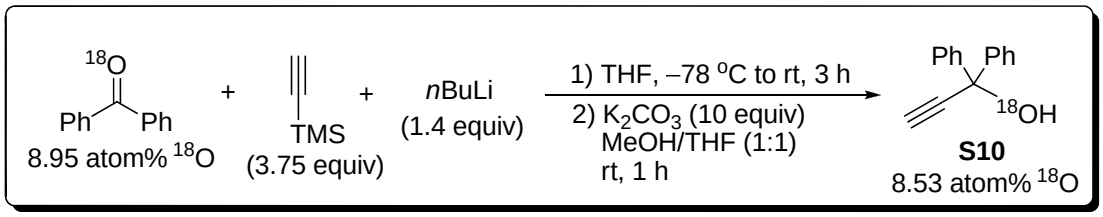
2.3 Boronic acid catalyzed 1,3-transposition of S8



Compound **S9** was prepared using the general procedure for the boronic acid catalyzed 1,3-transposition of allylic alcohols (79% yield). Mass spectral analysis indicated 0.89% ^{18}O isotopic incorporation.

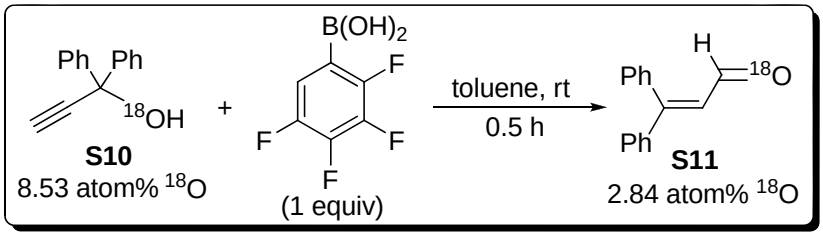
[34] Risley, J. M.; Van Etten, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 4609-4614.

2.4 Preparation of [^{18}O]1,1-diphenylprop-2-yn-1-ol (S10)



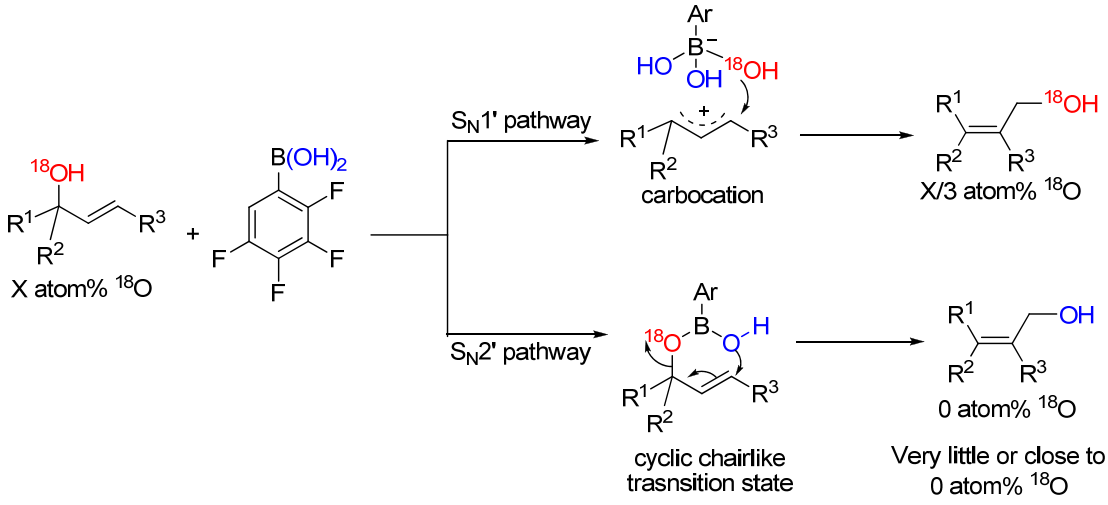
Compound **S10** was prepared using the general procedure (Method A) for propargylic alcohols (82% yield). Mass spectral analysis indicated 8.53% ^{18}O isotopic incorporation.

2.5 Boronic acid catalyzed Meyer-Schuster rearrangement of S10



Compound **S11** was prepared using the general procedure for the boronic acid catalyzed Meyer-Schuster rearrangement of propargylic alcohols (87% yield). Mass spectral analysis indicated 2.84% ^{18}O isotopic incorporation.

2.6 Analysis of ^{18}O labeling experimental data

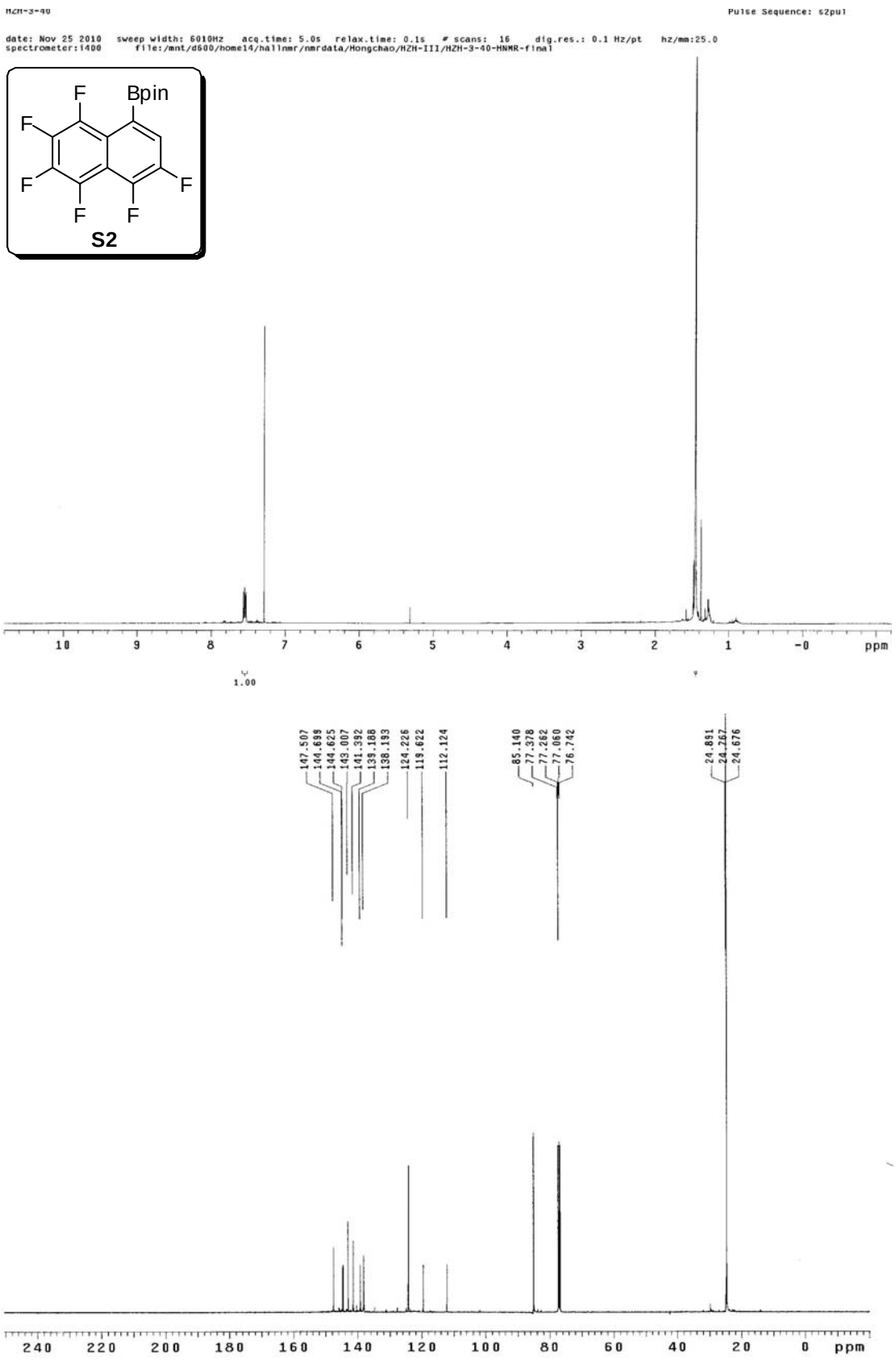


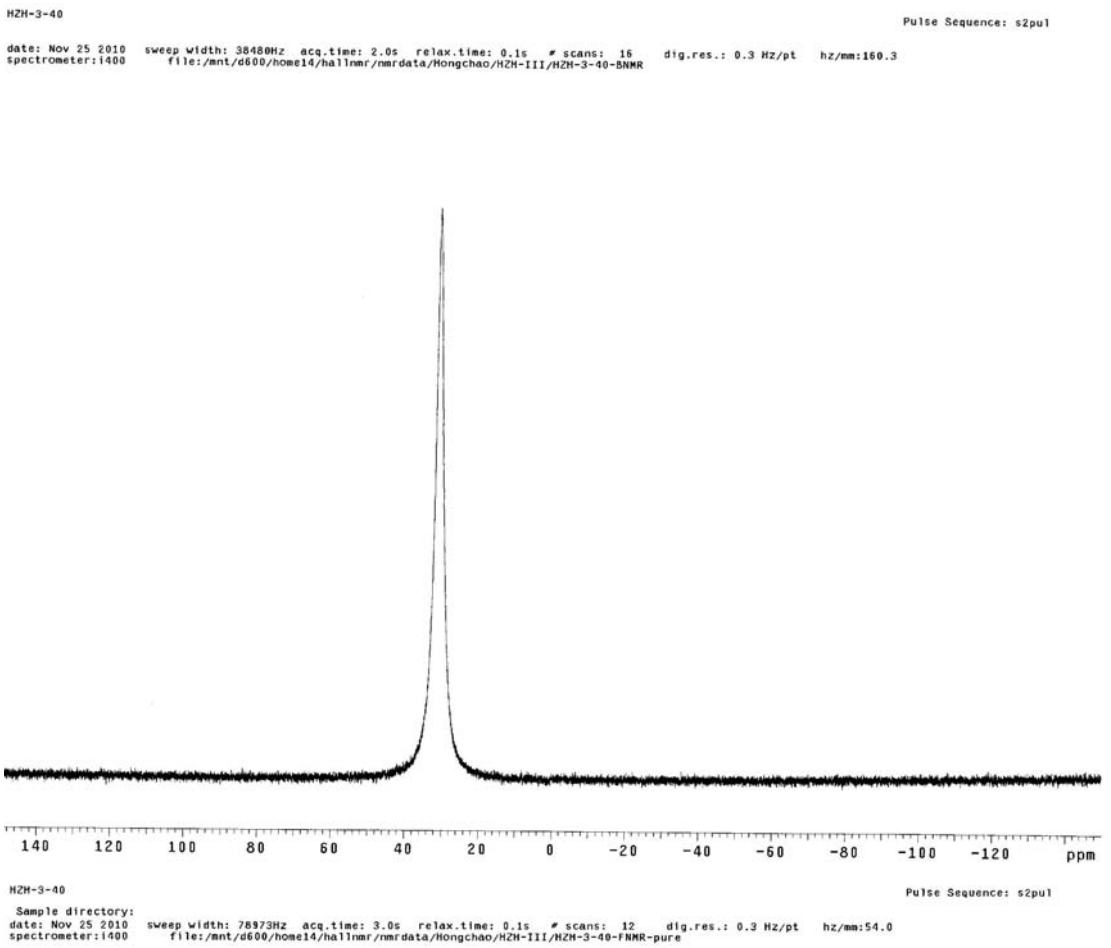
As shown in the above figure, this reaction could proceed through two possible pathways. One is an S_N1' pathway *via* an open transition state and the other is S_N2'

pathway *via* a cyclic chairlike transition state. ^{18}O labeling experiments were used to explore which of these possibilities is the most likely mechanism for the rearrangement. If the reaction proceeds through the S_N1' pathway, the three OH groups in the tetrahedral boronate complex would have an equal chance to attack the intermediate carbocation. Thus, it is statistically expected that **one third** of the labeled oxygen atom would transfer from the starting material to the final product. If the reaction proceeds through a concerted cyclic chairlike transition state, **very little or close to none of** the labeled oxygen atom would be expected to transfer from the starting material to the final product. The experimental data of the boronic acid catalyzed Meyer-Schuster rearrangement shows that 33.2% of the labeled oxygen atom was transferred from **S10** to **S11**, which is consistent with the S_N1' pathway. The experimental data of boronic acid catalyzed 1,3-transposition of allylic alcohols shows that 10.1% of the labeled oxygen atom was transferred from **S8** to **S9**, which suggests that this rearrangement likely proceeds through two parallel (competitive) pathways, an S_N1' pathway and an S_N2' pathway, which is substrate dependent.

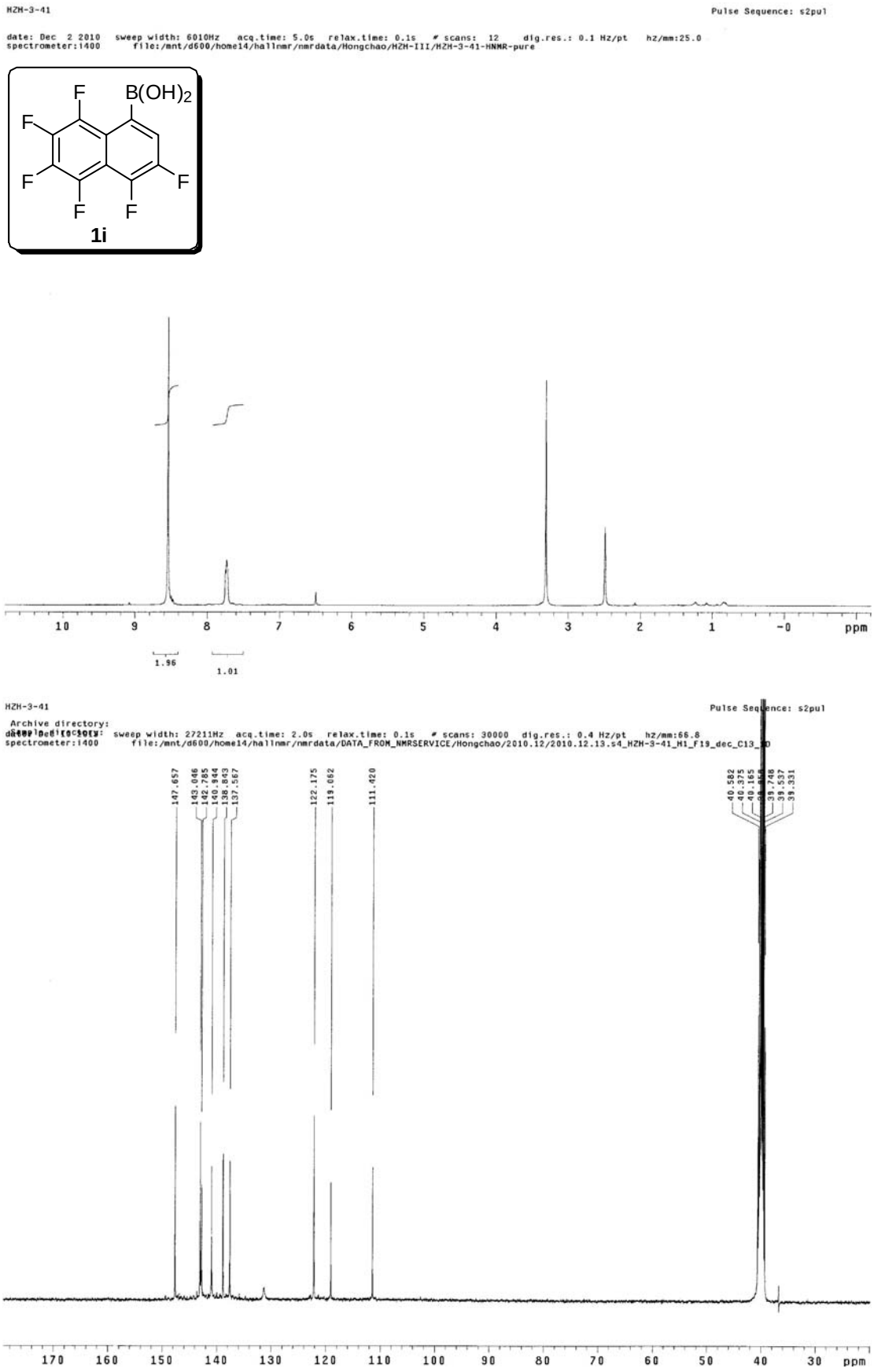
3. NMR Spectra for New Compounds

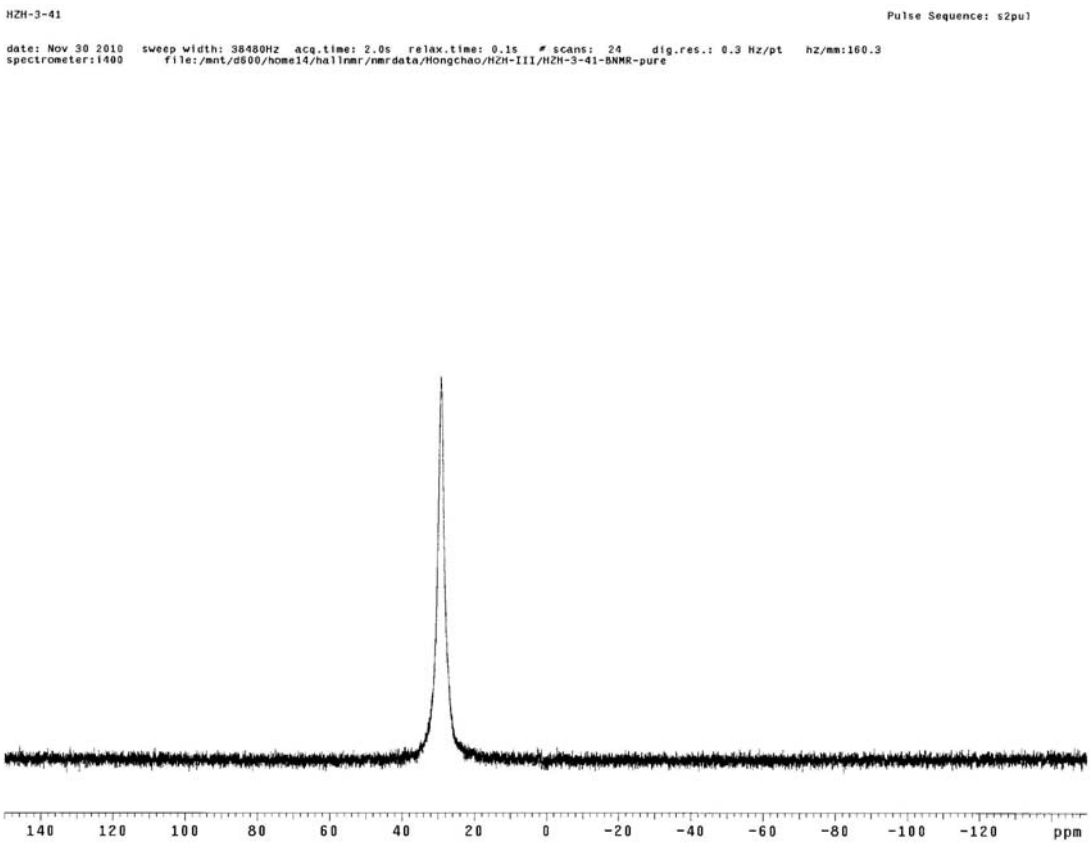
3.1 ^{1}H-, ^{13}C-, ^{11}B- and ^{19}F-NMR of S2 in $CDCl_3$ at 25 ^{o}C



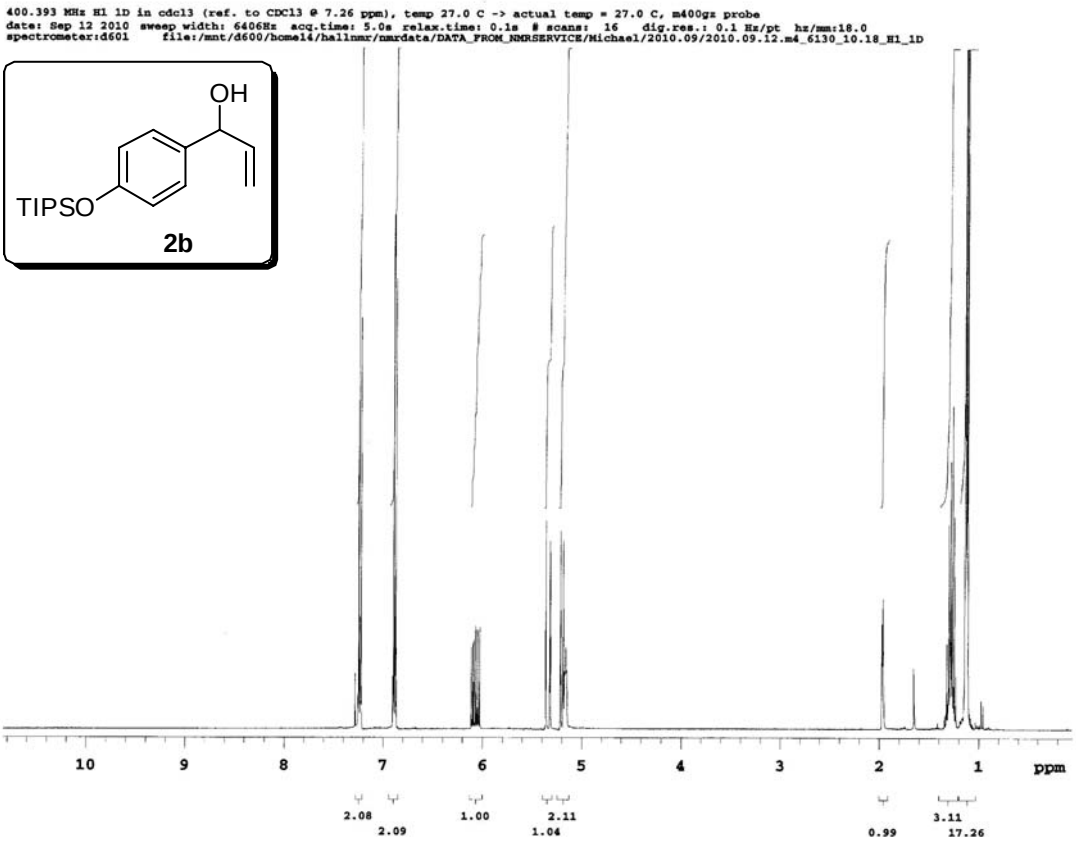

HZH-3-40
Pulse Sequence: s2pul
date: Nov 25 2010 sweep width: 38480Hz acq.time: 2.0s relax.time: 0.1s # scans: 16 dig.res.: 0.3 Hz/pt hz/mm:160.3
spectrometer:i400 file:/mnt/d600/home14/hallnmr/nmrdata/Hongchao/HZH-III/HZH-3-40-BNMR
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 ppm
HZH-3-40
Pulse Sequence: s2pul
Sample directory:
date: Nov 25 2010 sweep width: 76973Hz acq.time: 3.0s relax.time: 0.1s # scans: 12 dig.res.: 0.3 Hz/pt hz/mm:54.0
spectrometer:i400 file:/mnt/d600/home14/hallnmr/nmrdata/Hongchao/HZH-III/HZH-3-40-FNMR-pure
-135 -140 -145 -150 -155 -160 ppm
2.02
1.02
1.00
0.98
1.01

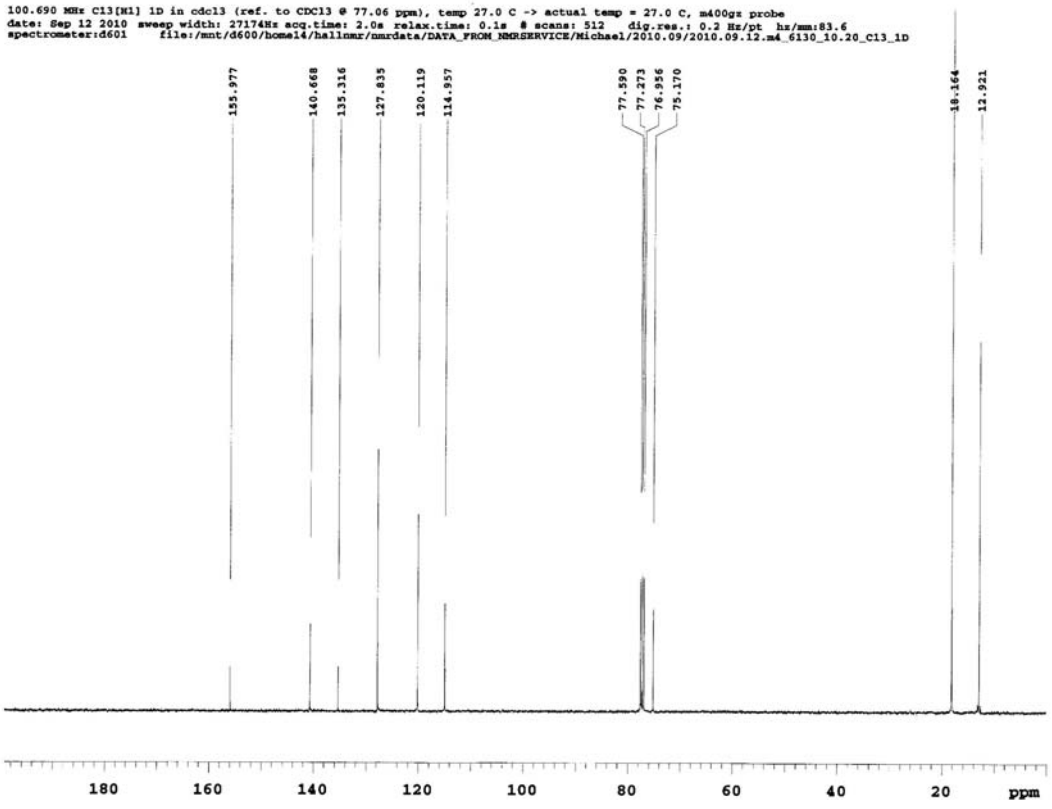
3.2 ^{1}H-, ^{13}C-, ^{11}B- and ^{19}F-NMR of 1i (Table 1) in DMSO-d_6 at 25 ^{o}C



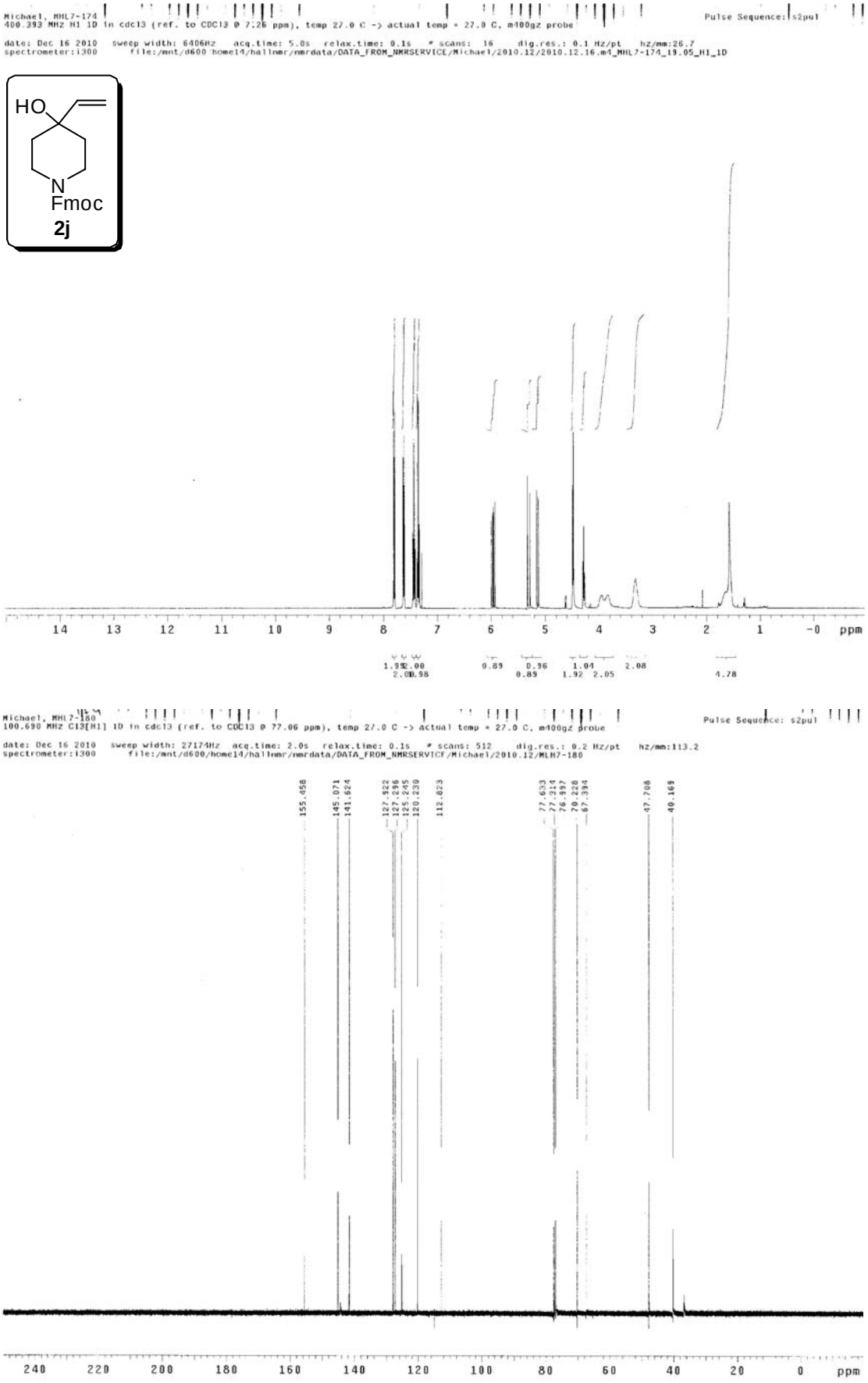

HZH-3-41
Pulse Sequence: s2pul
date: Nov 30 2010 sweep width: 38480Hz acq.time: 2.0s relax.time: 0.1s # scans: 24 dig.res.: 0.3 Hz/pt hz/mm:160.3
spectrometer:i400 file:/mnt/d600/home14/hallnmr/nmrdata/Hongchao/HZH-III/HZH-3-41-BNMR-pure
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 ppm
HZH-3-41
Pulse Sequence: s2pul
Sample directory:
date: Dec 9 2010 sweep width: 79208Hz acq.time: 3.0s relax.time: 0.1s # scans: 32 dig.res.: 0.3 Hz/pt hz/mm:62.8
spectrometer:i400 file:/mnt/d600/home14/hallnmr/nmrdata/DATA_FROM_NMRSERVICE/Hongchao/2010.12/2010.12.09.s4_HZH-3-41_f19_1D
-130 -135 -140 -145 -150 -155 -160 -165 ppm
1.00
1.05
2.01
1.04
1.06

3.3 ^{1}H- and ^{13}C-NMR of 2b in $CDCl_3$ at 25 ^{o}C

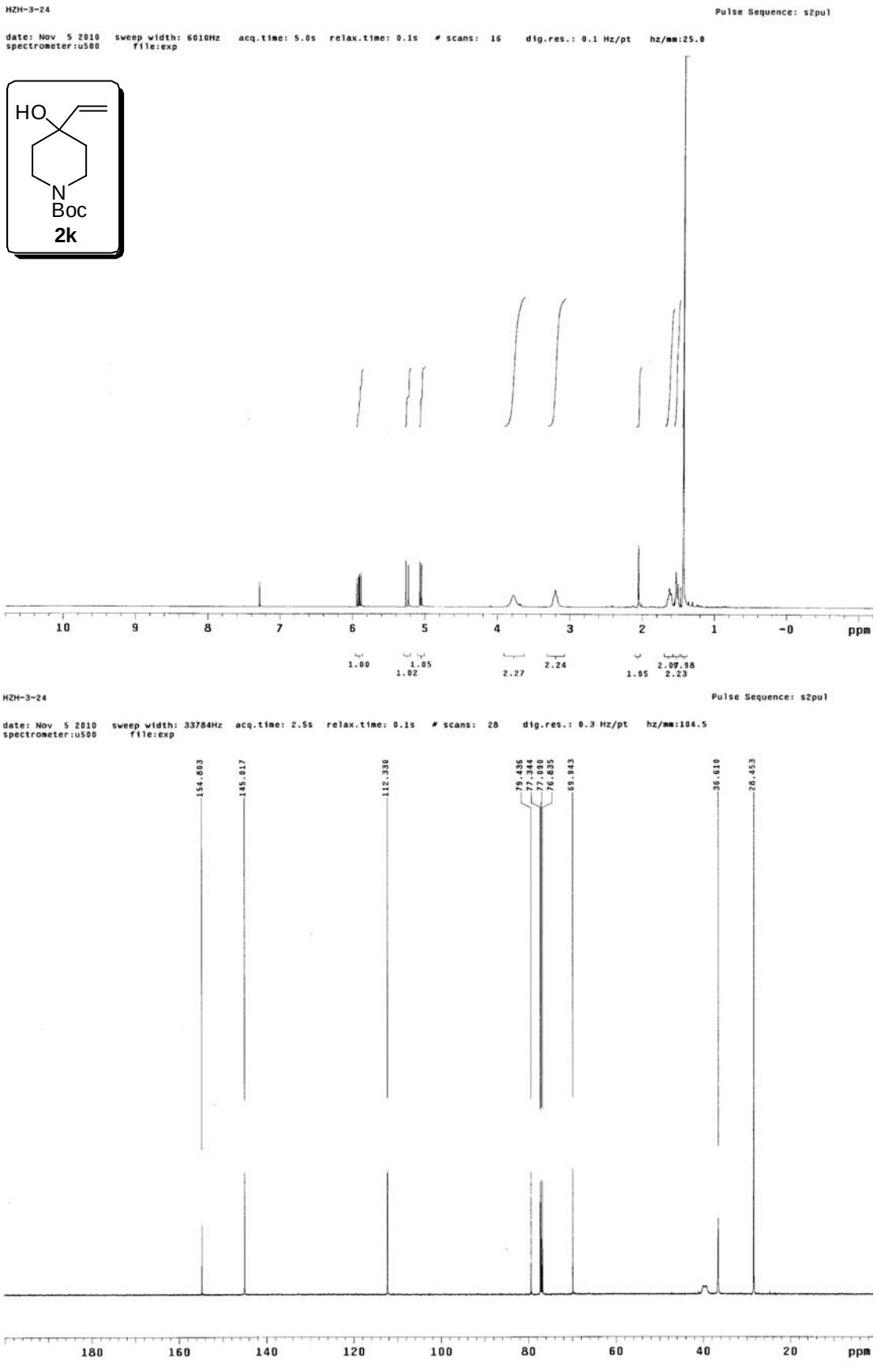




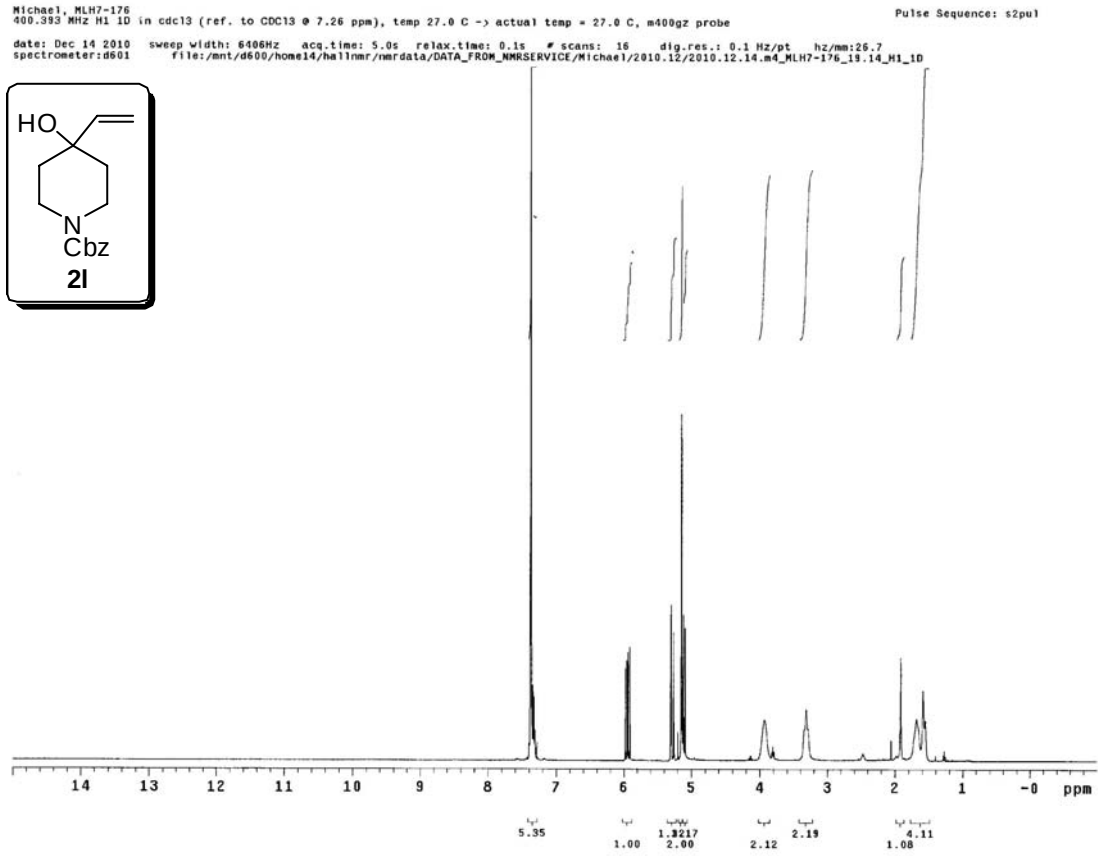
3.4 ^{1}H- and ^{13}C-NMR of 2j in $CDCl_3$ at 25 ^{o}C

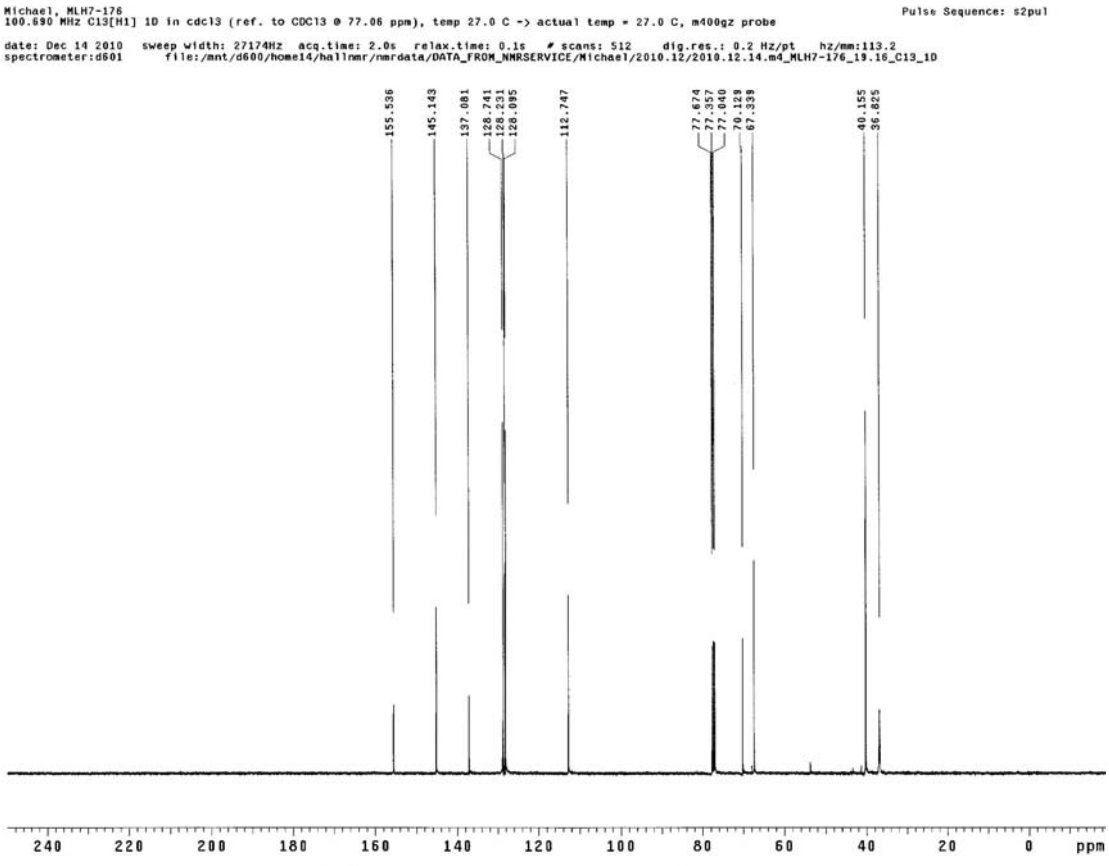


3.5 ^{1}H- and ^{13}C-NMR of 2k in $CDCl_3$ at 25 ^{o}C

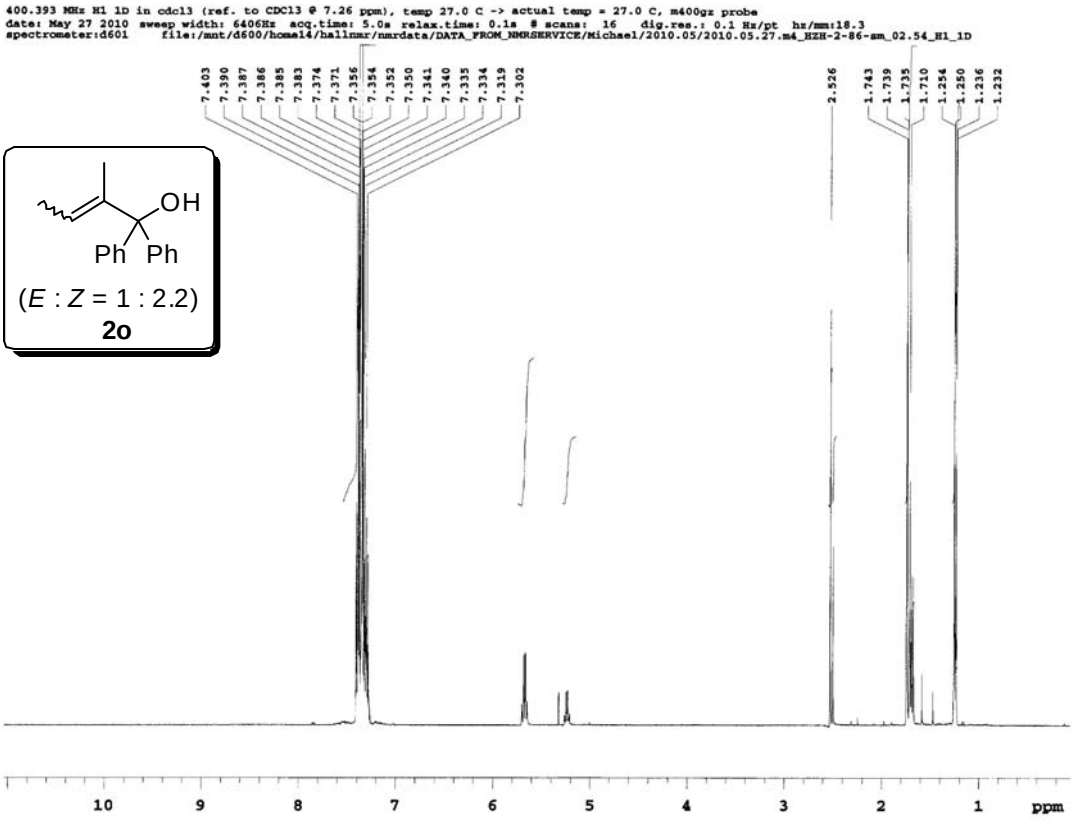


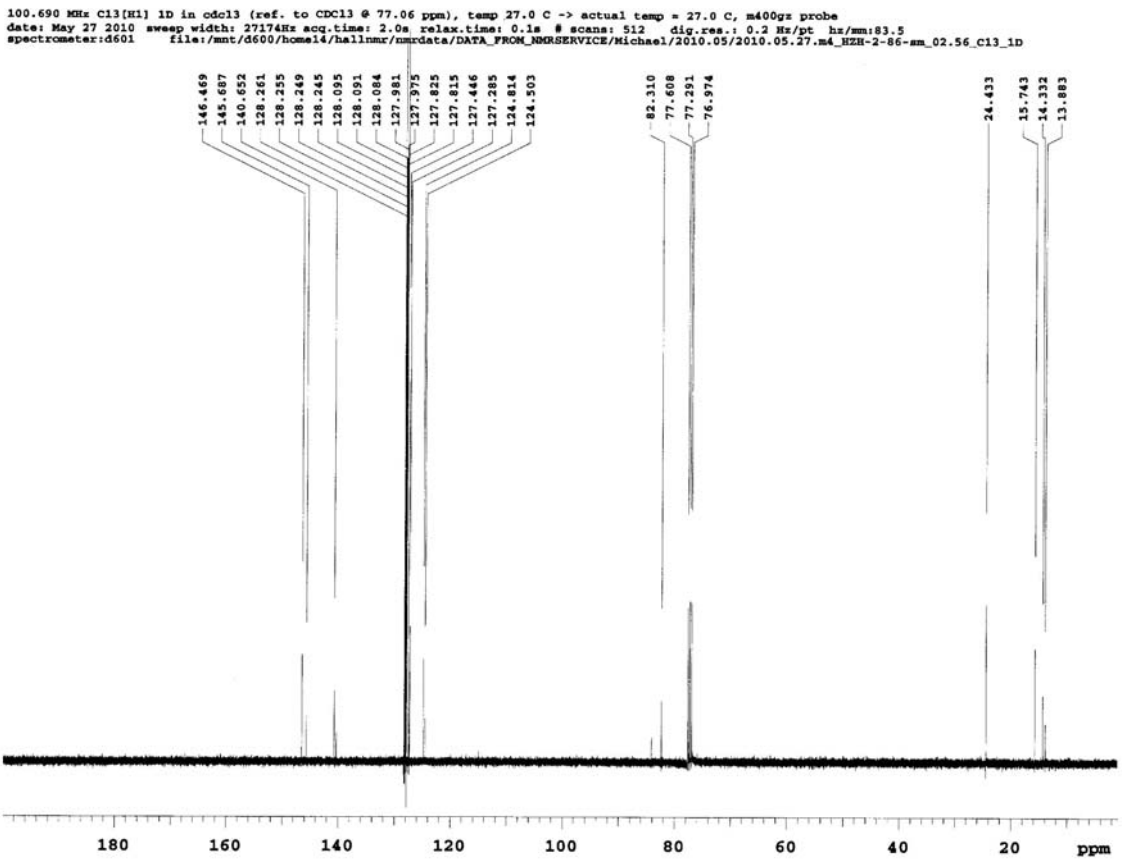
3.6 ^{1}H- and ^{13}C-NMR of 2l in $CDCl_3$ at 25 ^{o}C



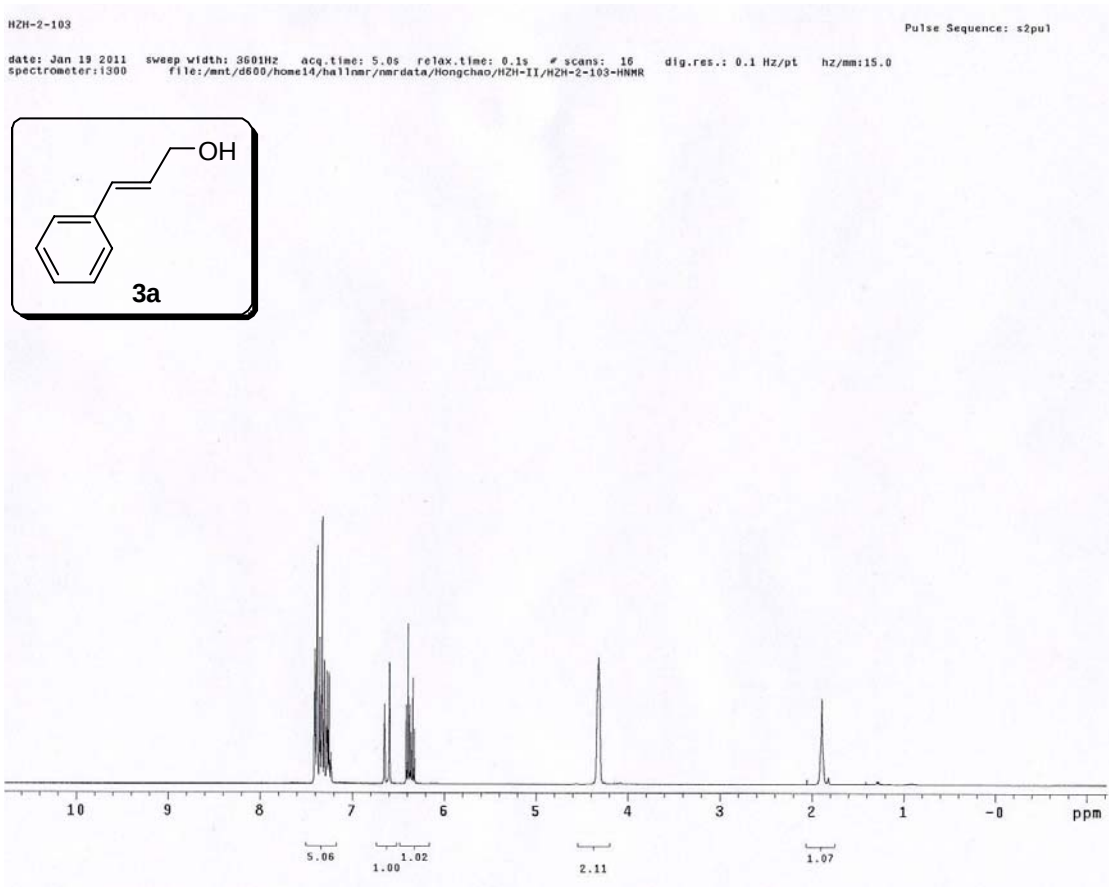


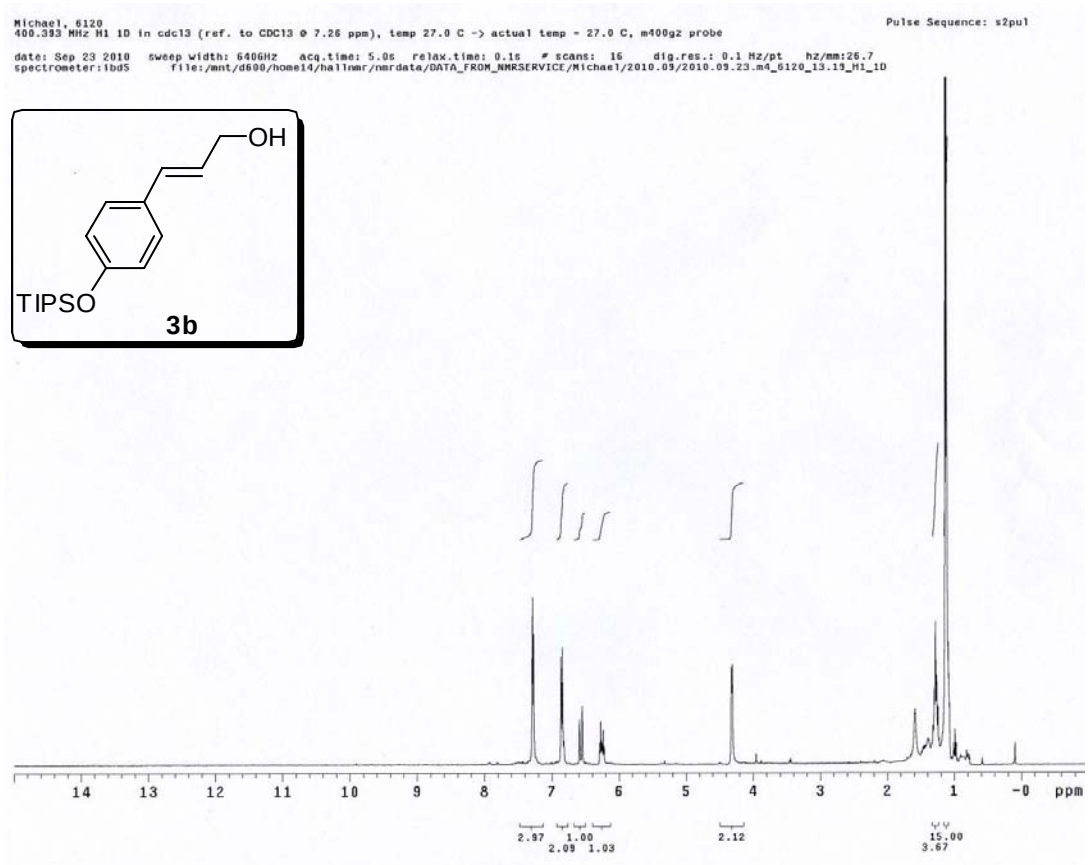
3.7 ^{1}H- and ^{13}C-NMR of 2o in $CDCl_3$ at 25 ^{o}C



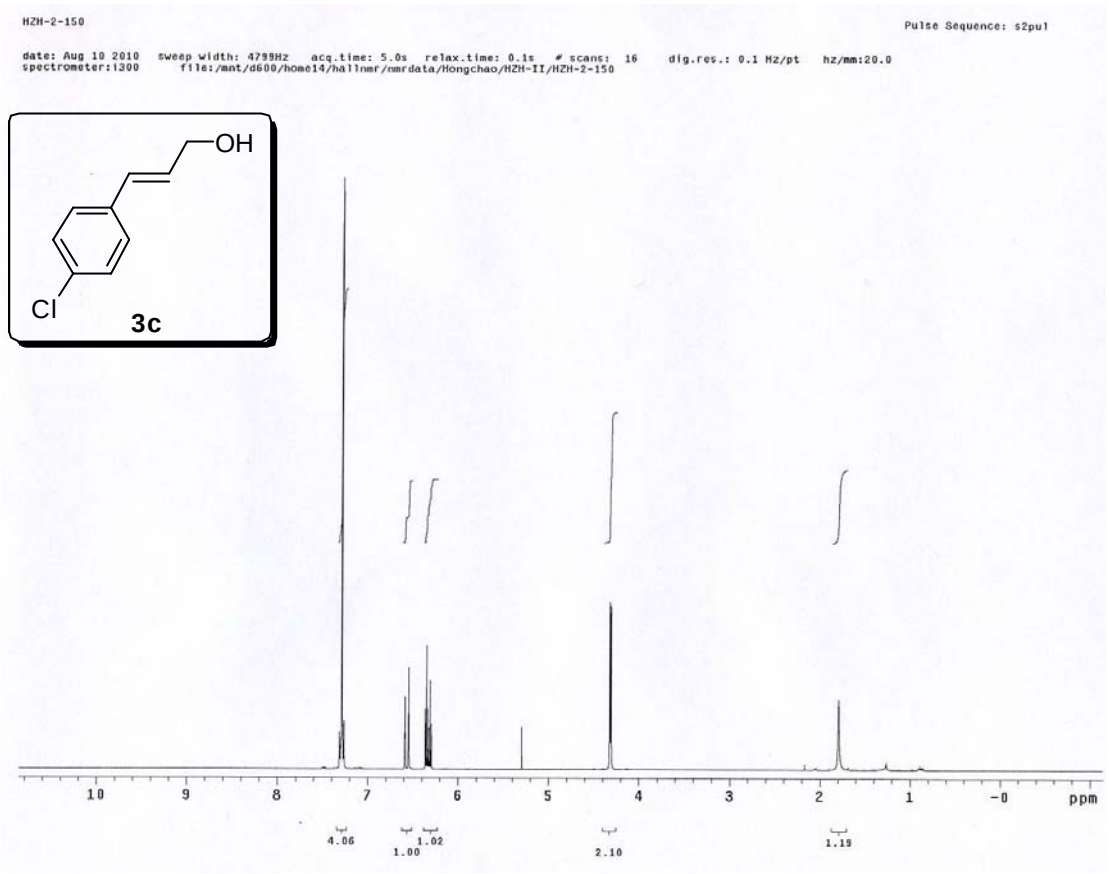


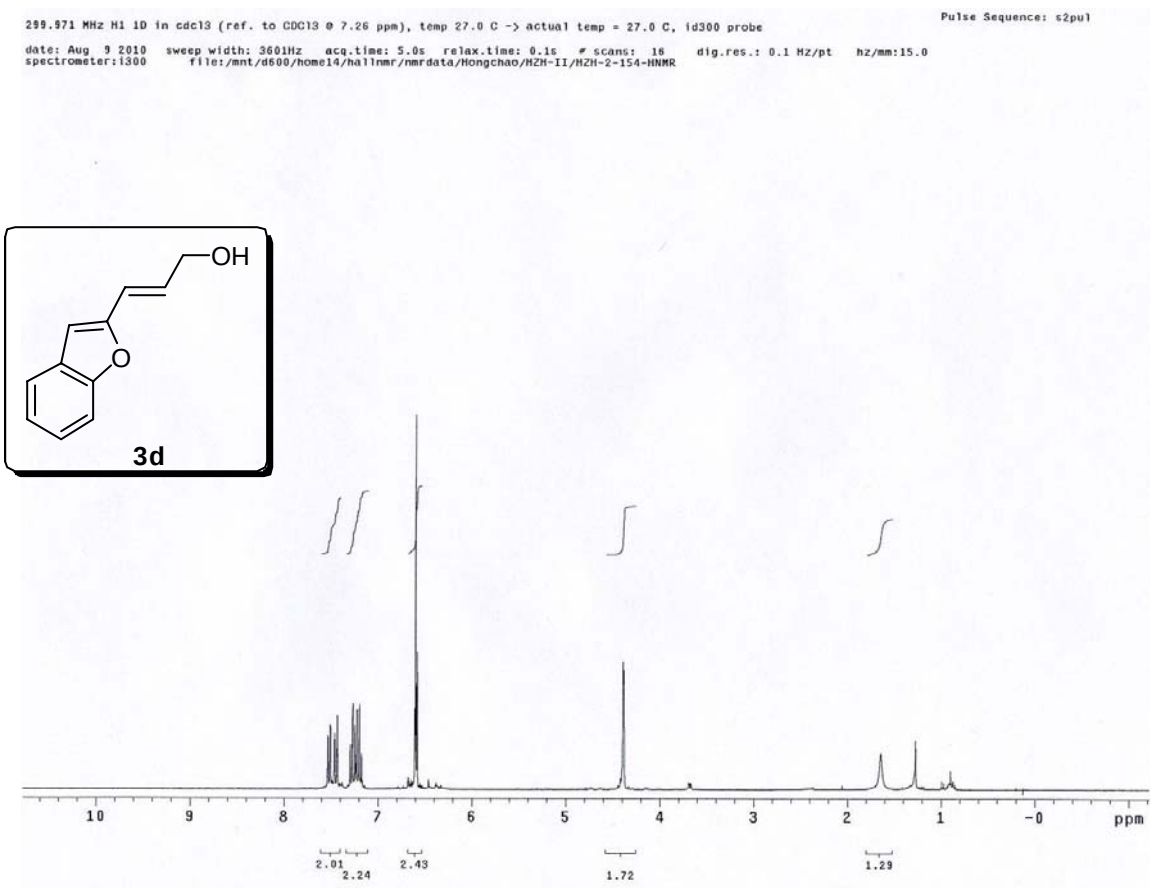
3.8 ^{1}H-NMR of 3a and 3b (Table 2, entries 1–2) in $CDCl_3$ at 25 ^{o}C



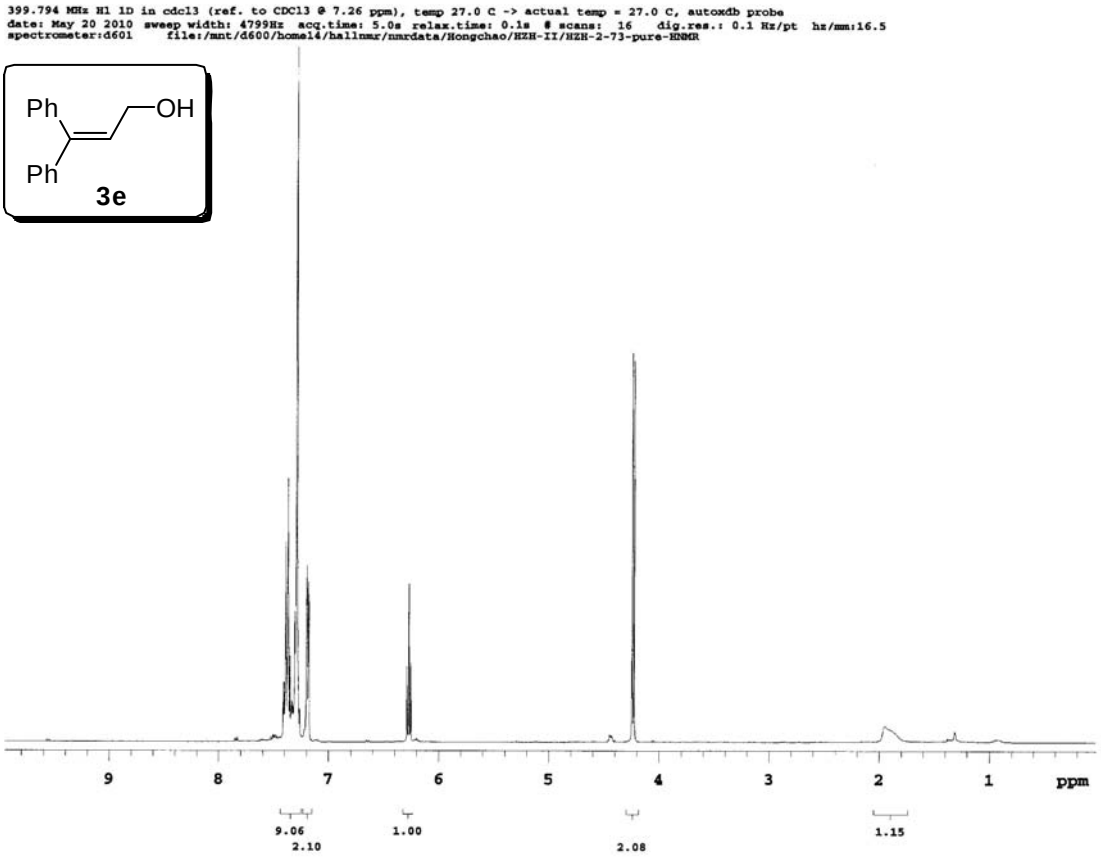


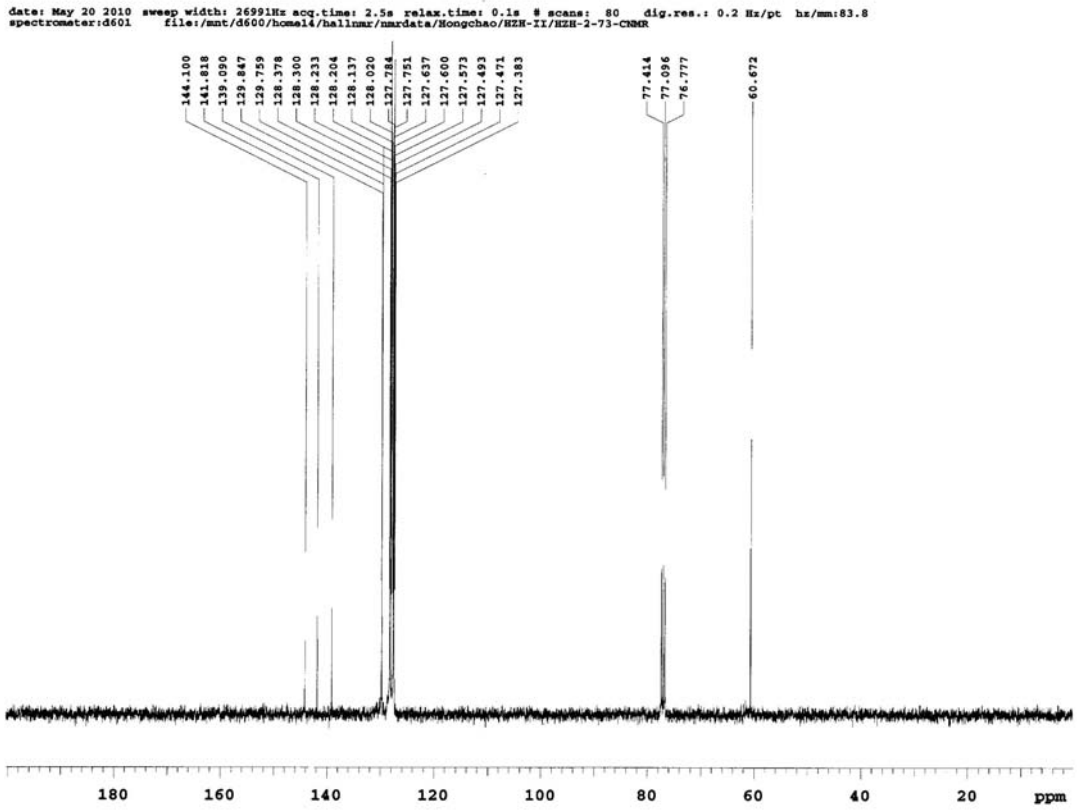
3.9 ^{1}H-NMR of 3c and 3d (Table 2, entries 3–4) in $CDCl_3$ at 25 ^{o}C



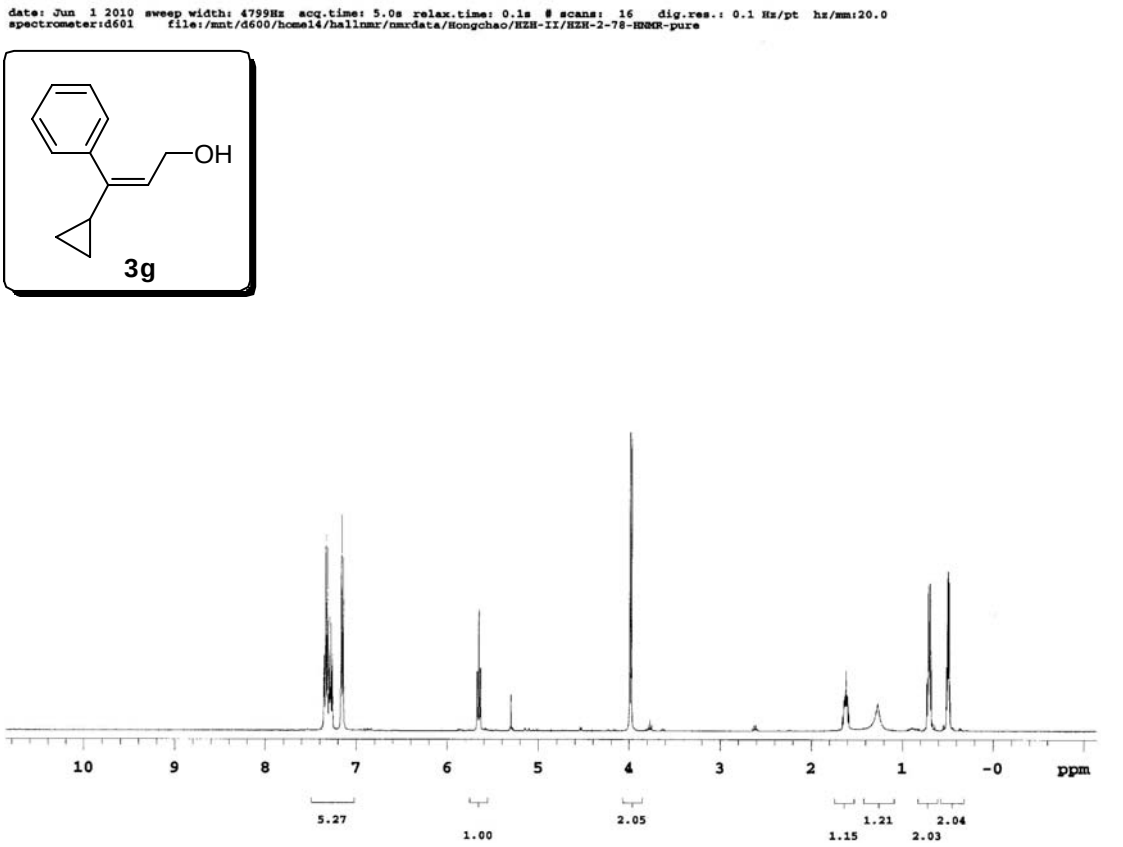


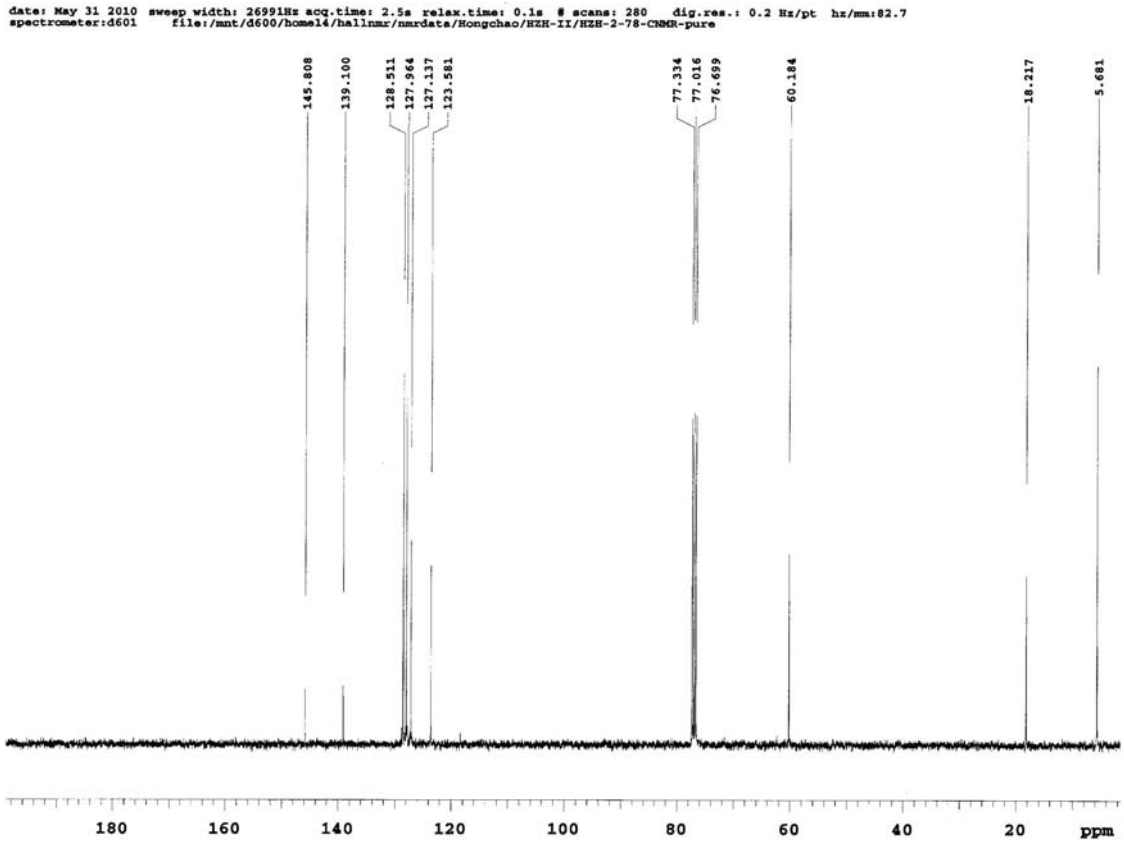
3.10 ^{1}H- and ^{13}C-NMR of 3e (Table 2, entry 5) in $CDCl_3$ at 25 ^{o}C



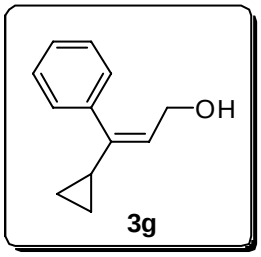


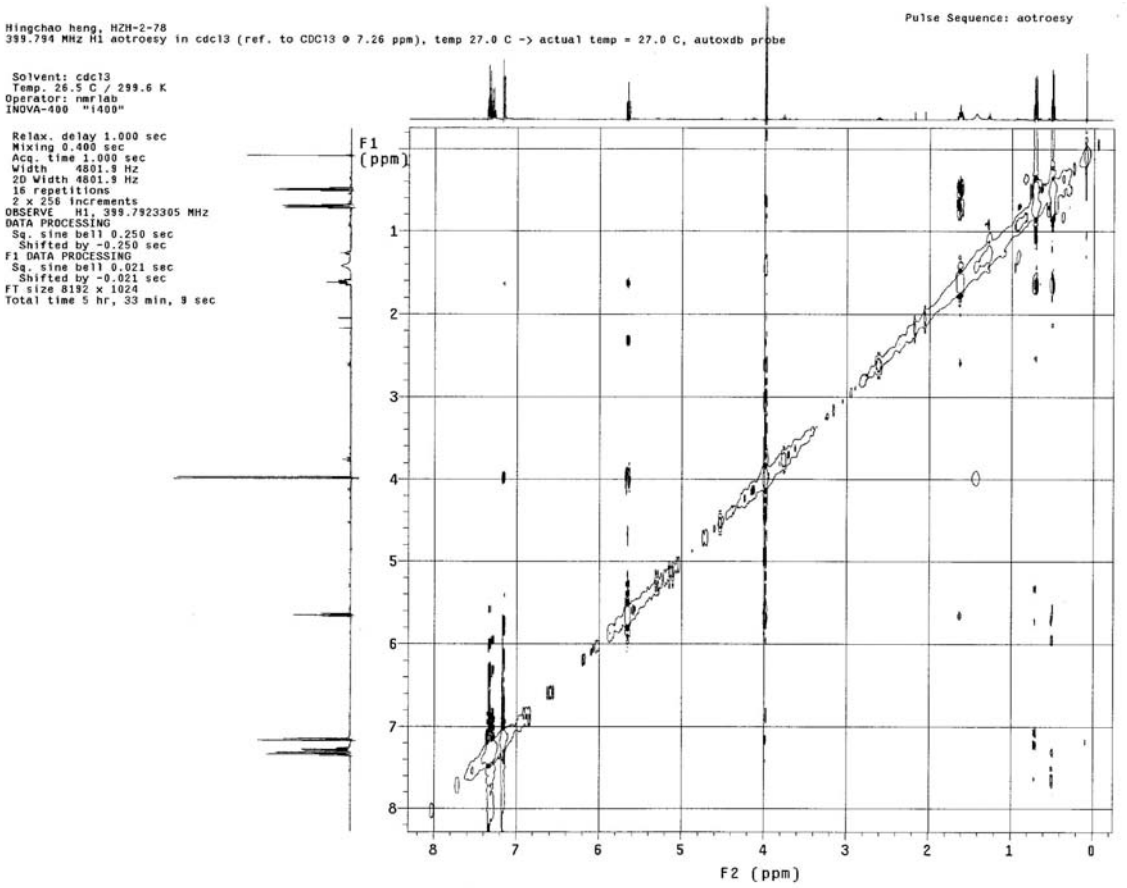
3.11 ^{1}H-, ^{13}C- and TROESY-NMR of 3g (Table 2, entry 7) in $CDCl_3$ at 25 ^{o}C



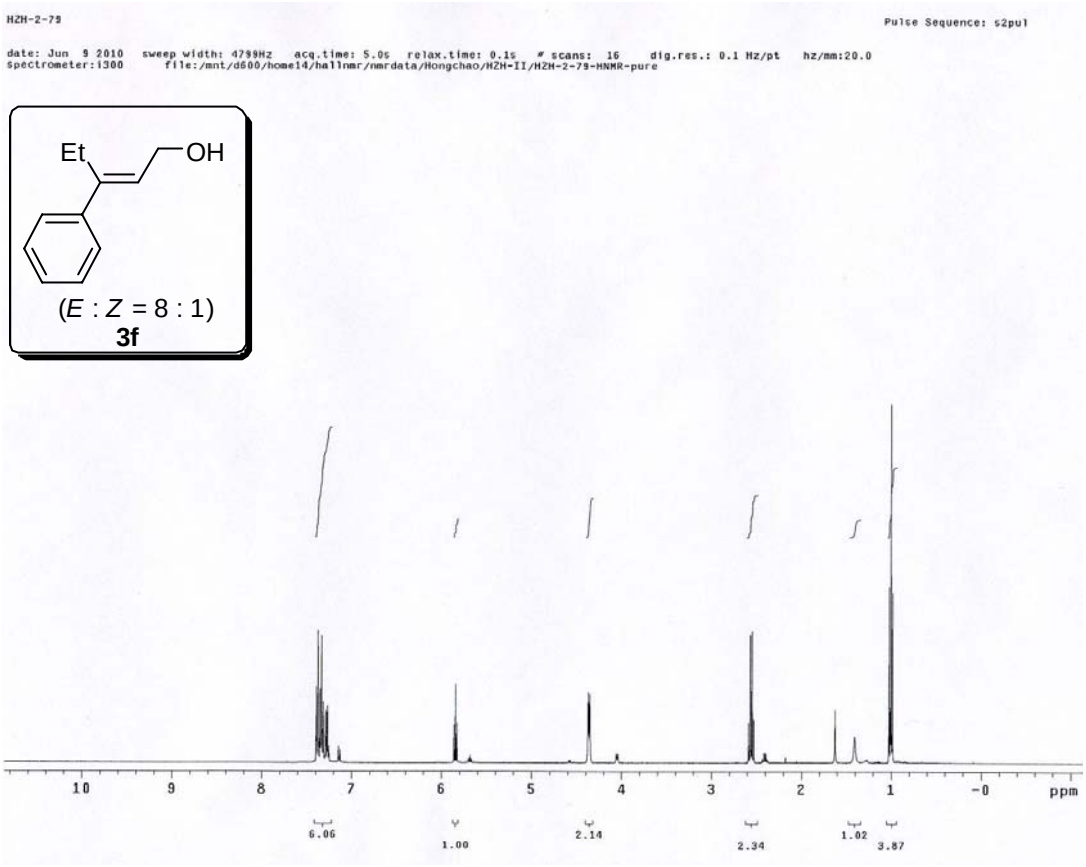


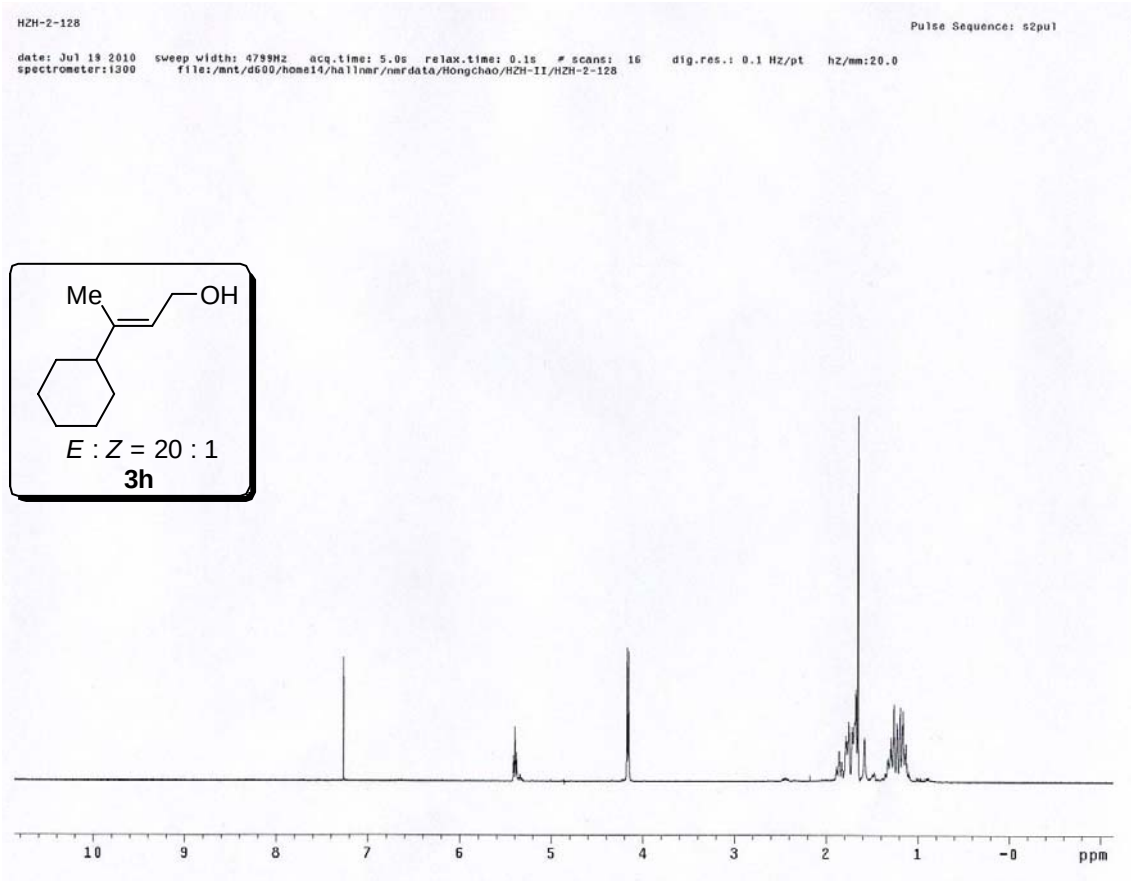
TROESY


OH
3g

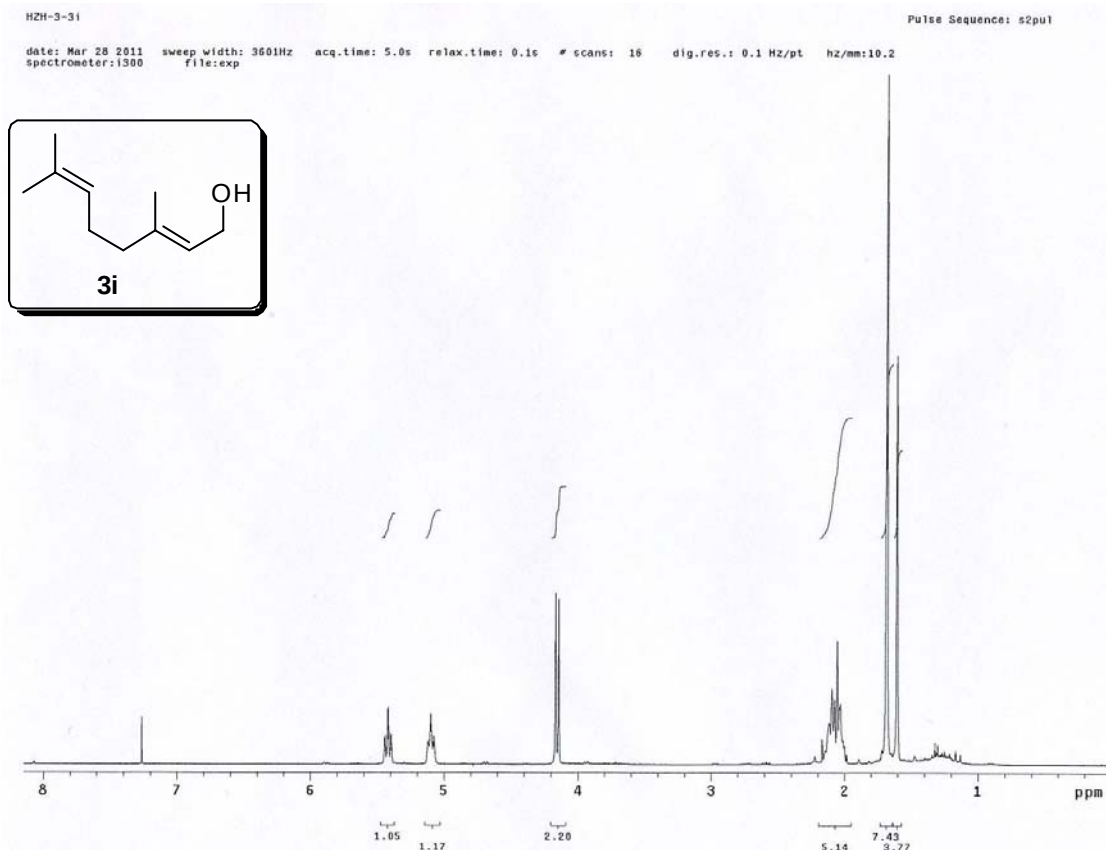

Hingchao heng, HZH-2-78
399.794 MHz H1 aotroesy in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.0 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: aotroesy
Solvent: cdcl3
Temp. 26.5 C / 299.6 K
Operator: nmrlab
INOVA-400 "i400"
Relax. delay 1.000 sec
Mixing 0.400 sec
Acq. time 1.000 sec
Width 4801.9 Hz
2D Width 4801.9 Hz
16 repetitions
2 x 256 increments
OBSERVE H1, 399.7923305 MHz
DATA PROCESSING
Sq. sine bell 0.250 sec
Shifted by -0.250 sec
F1 DATA PROCESSING
Sq. sine bell 0.021 sec
Shifted by -0.021 sec
FT size 8192 x 1024
Total time 5 hr, 33 min, 9 sec
F1 (ppm)
F2 (ppm)

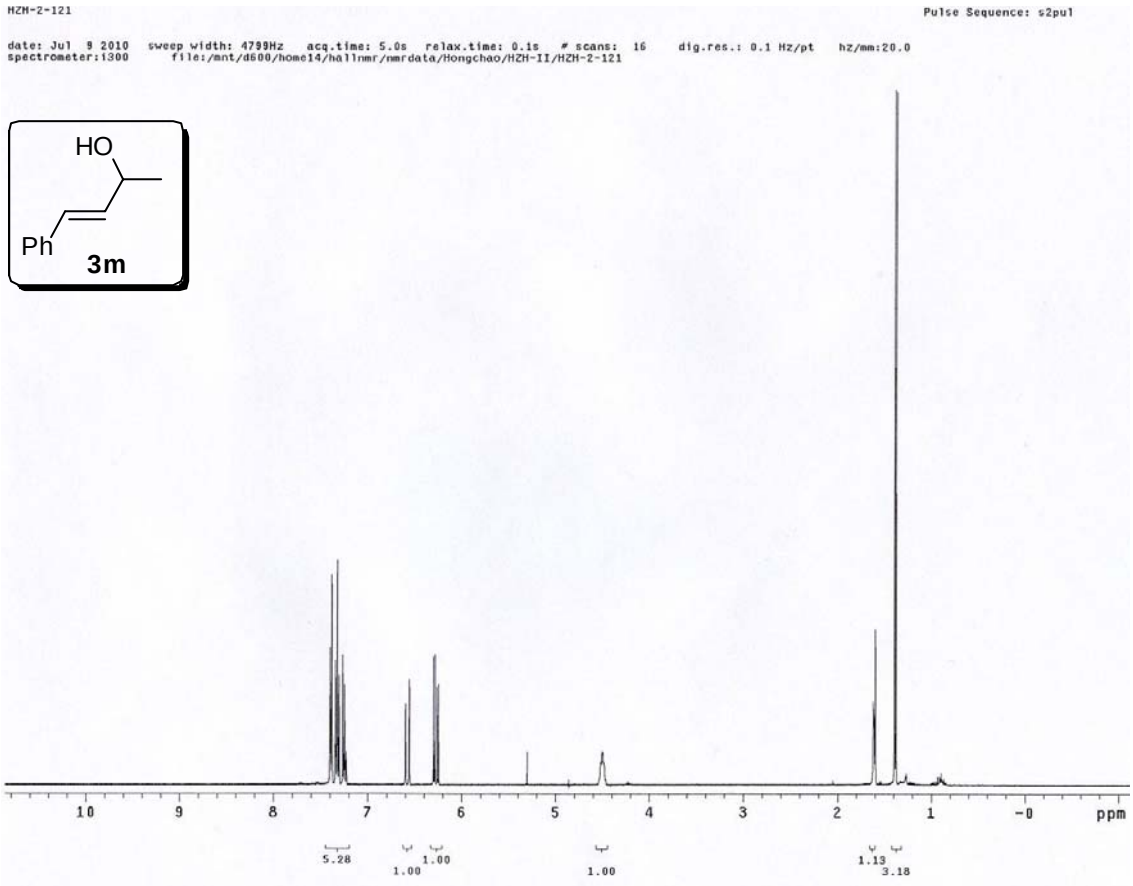
3.12 ^{1}H-NMR of 3f and 3h (Table 2, entries 6 and 8) in $CDCl_3$ at 25 ^{o}C



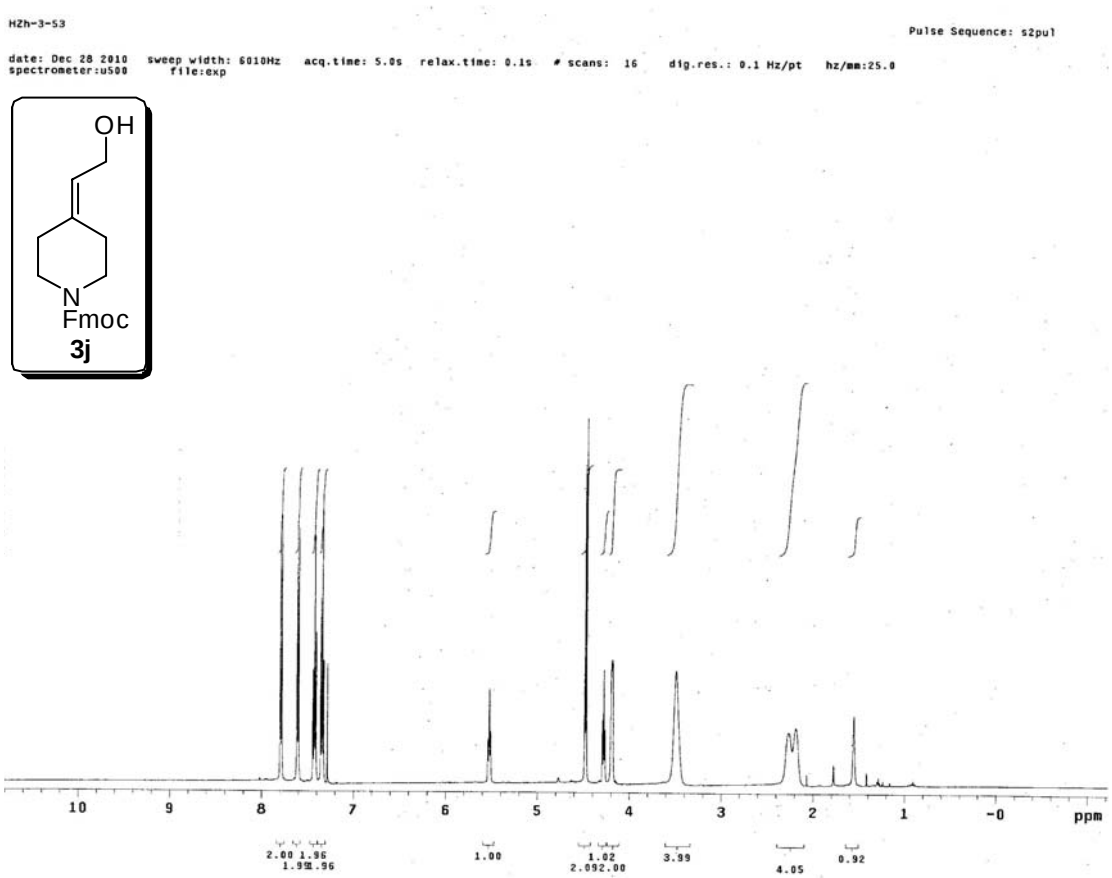


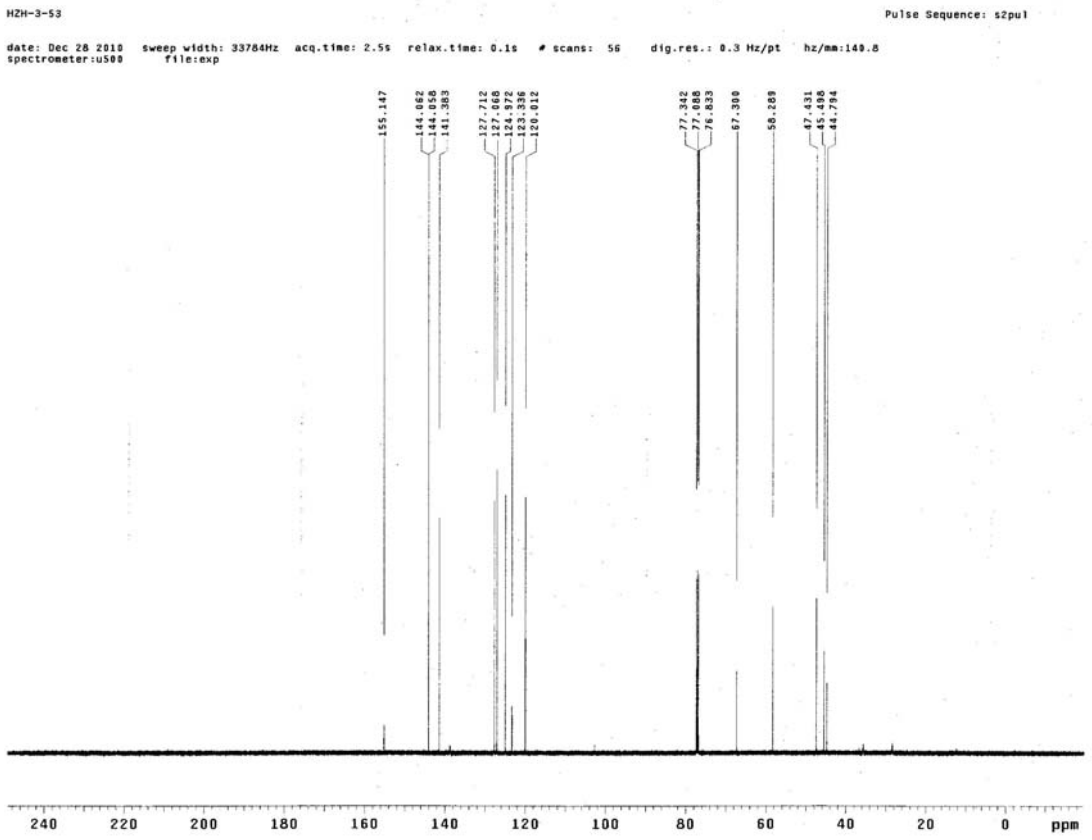
3.13 ^{1}H-NMR of 3i and 3m (Table 2, entries 9 and 13) in $CDCl_3$ at 25 ^{o}C



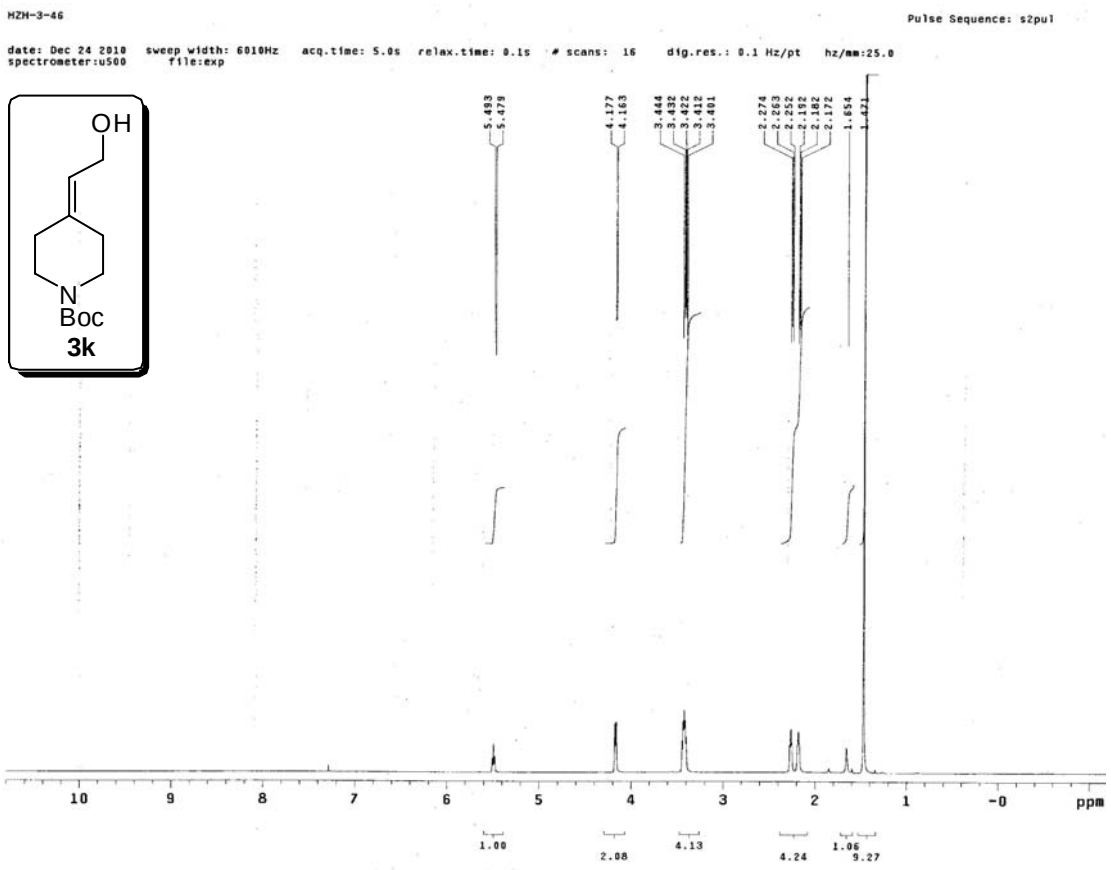


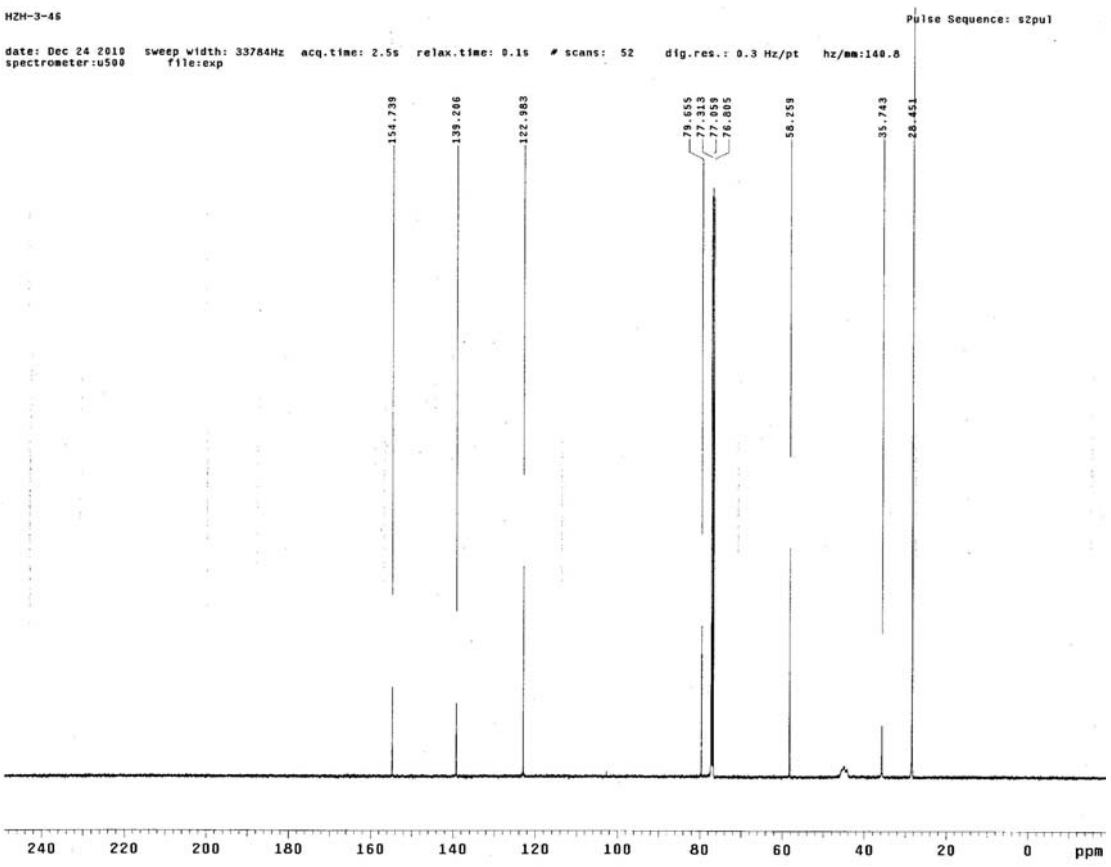
3.14 ^{1}H- and ^{13}C-NMR of 3j (Table 2, entry 10) in $CDCl_3$ at 25 ^{o}C



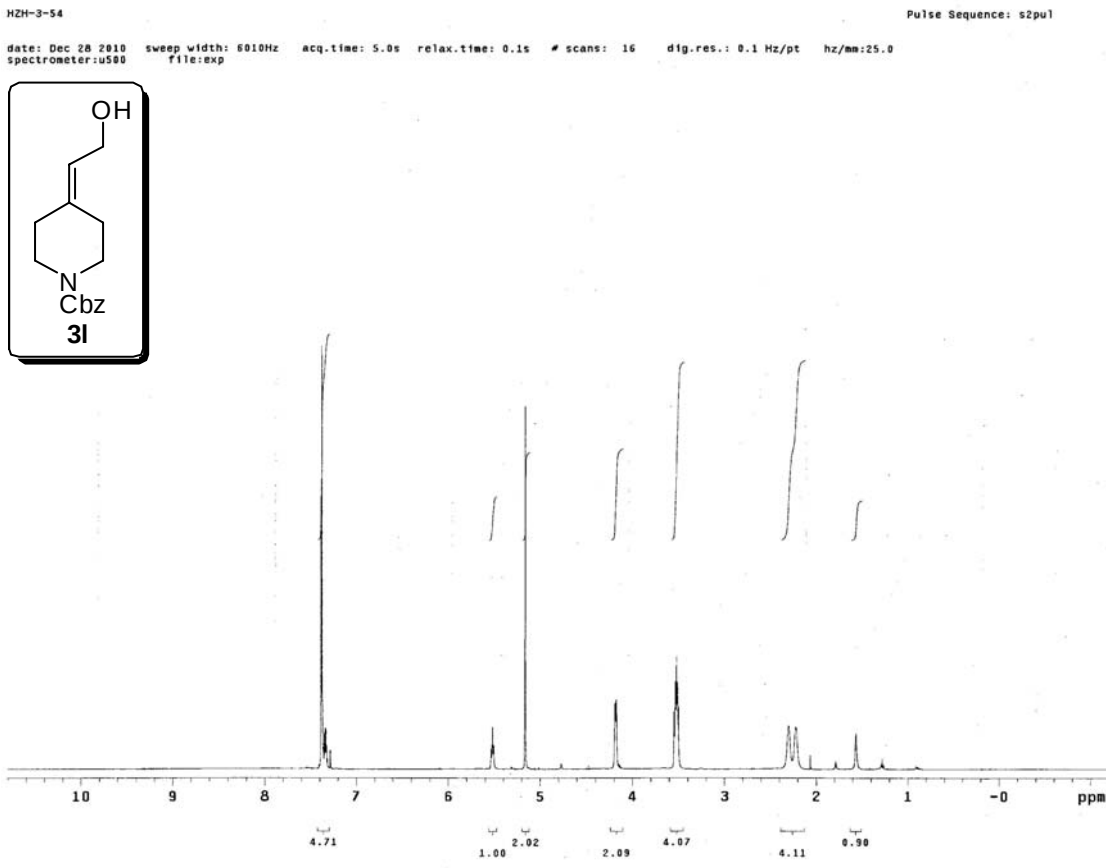


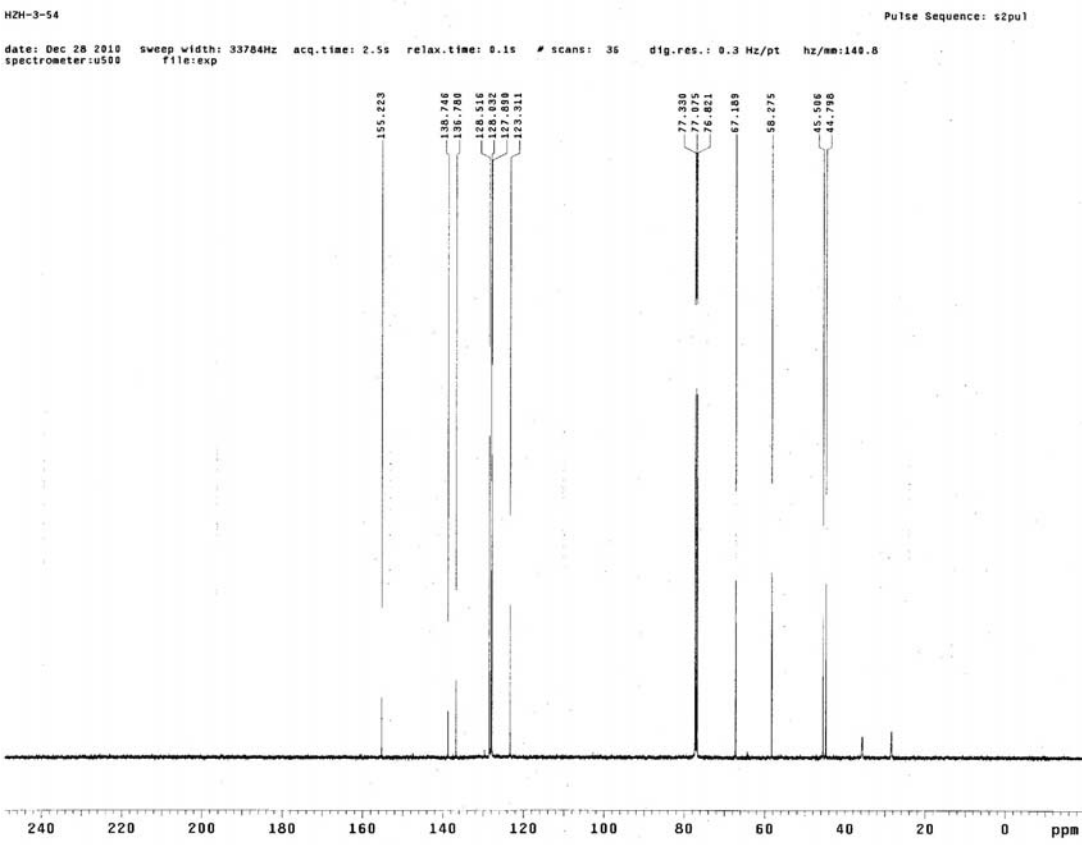
3.15 ^{1}H- and ^{13}C-NMR of 3k (Table 2, entry 11) in $CDCl_3$ at 25 ^{o}C



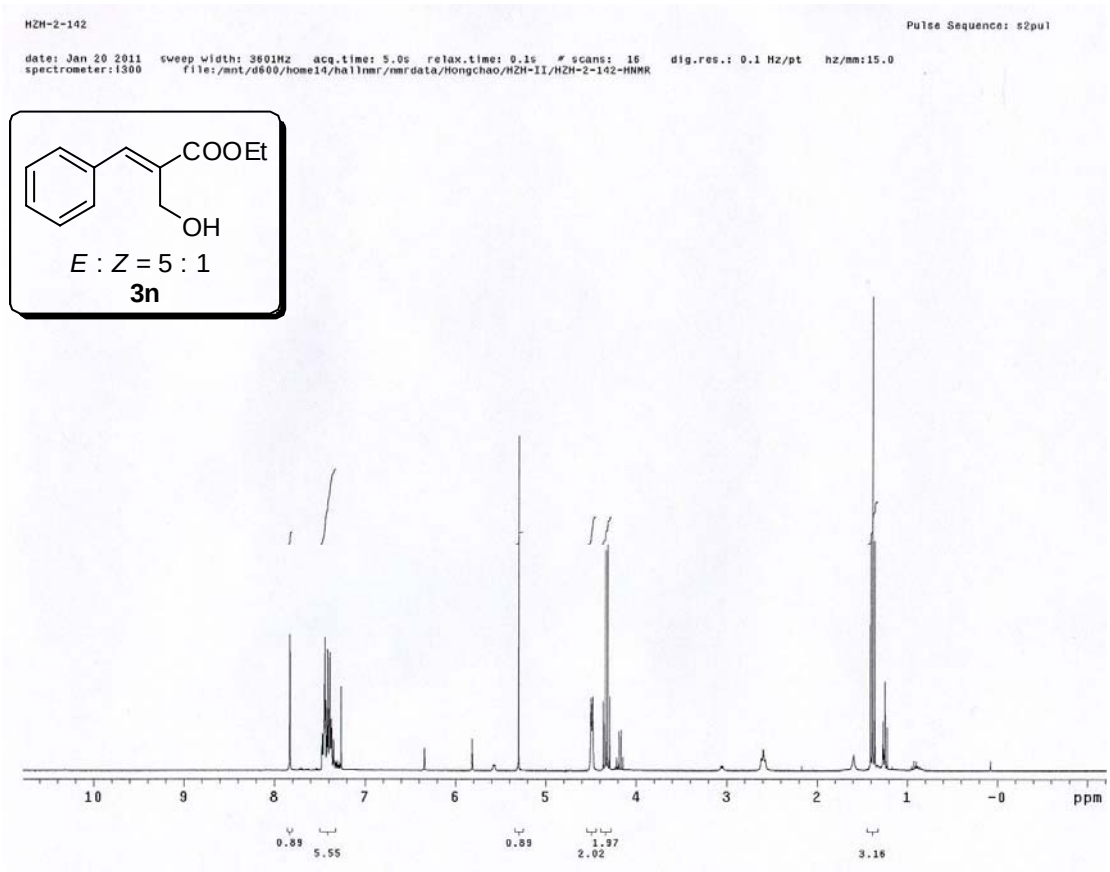


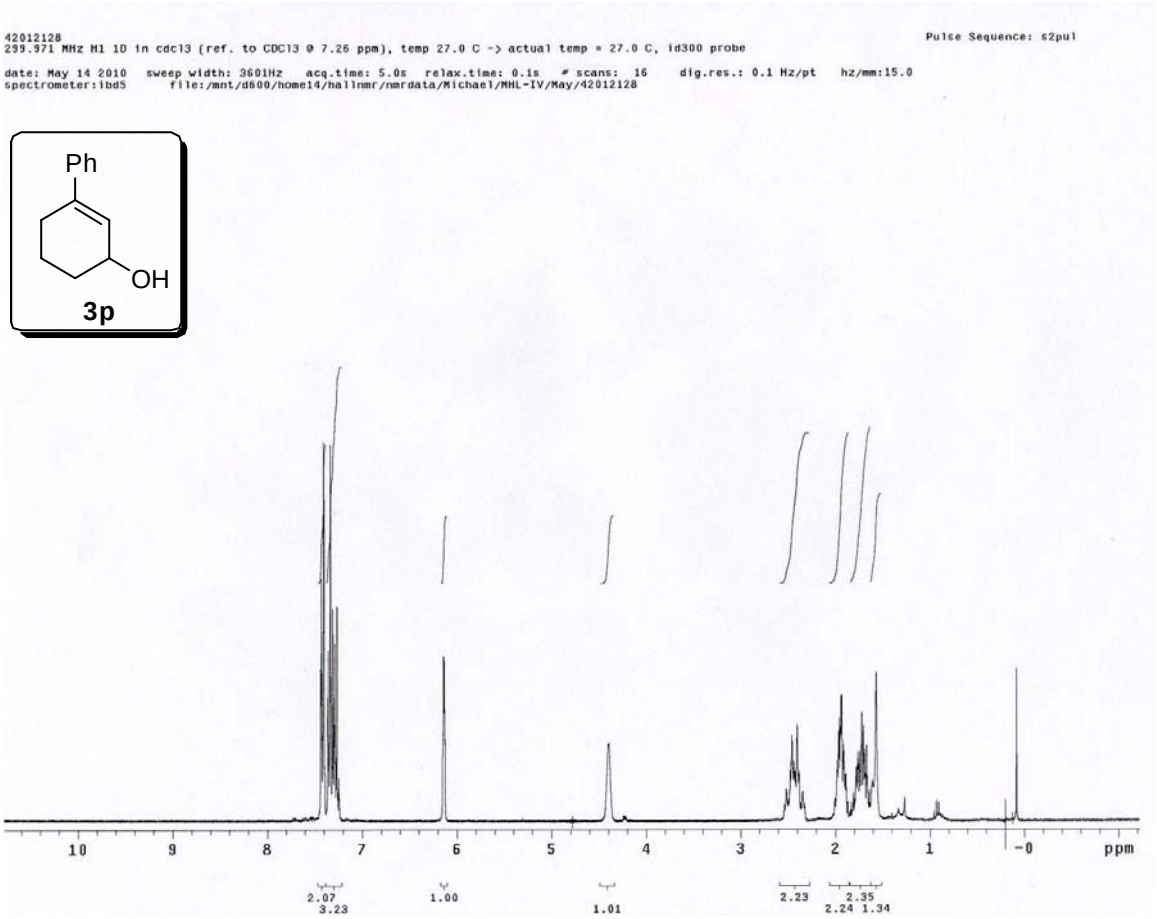
3.16 ^{1}H- and ^{13}C-NMR of 3l (Table 2, entry 12) in $CDCl_3$ at 25 ^{o}C



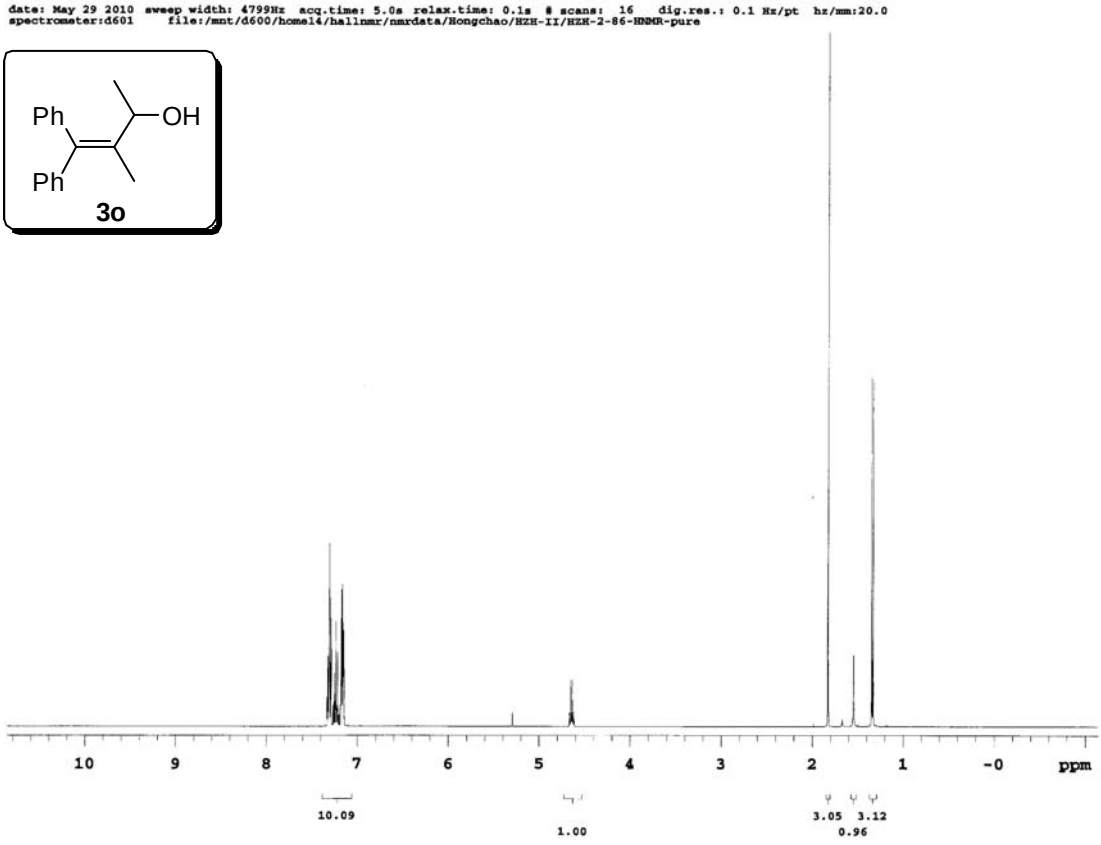


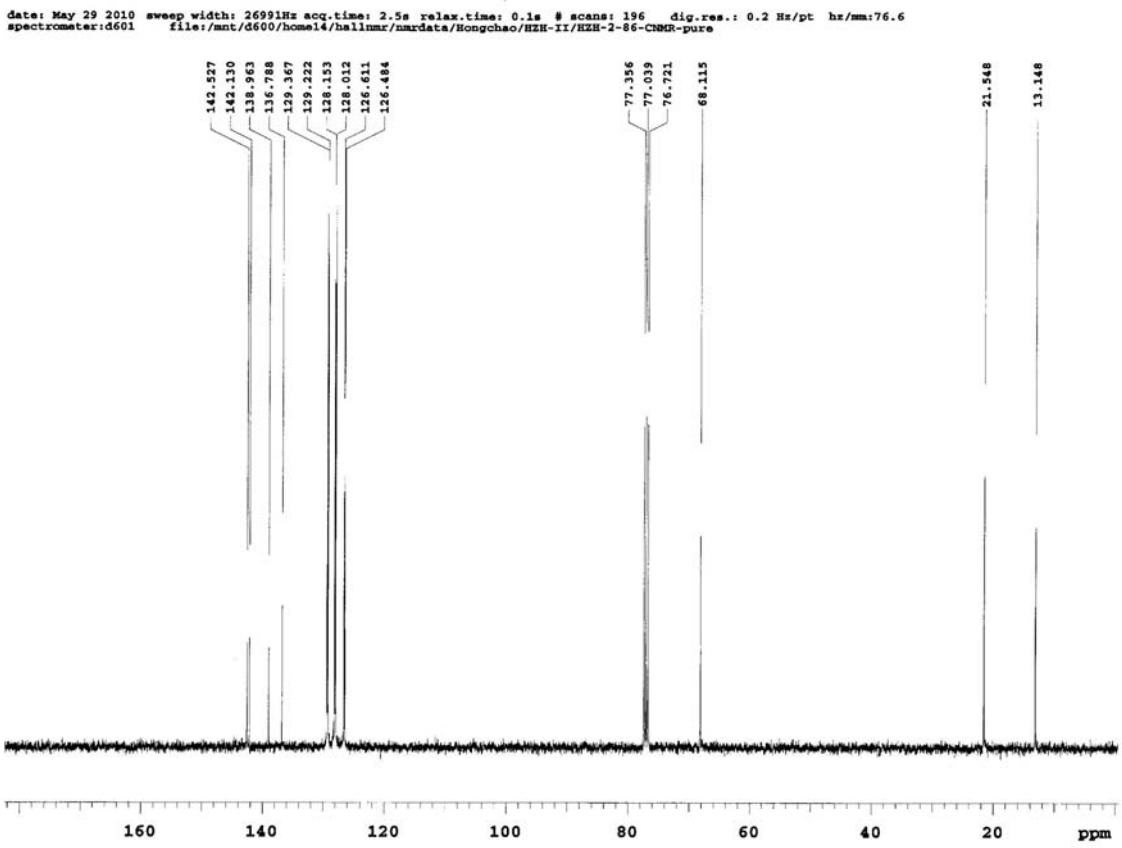
3.17 ^{1}H-NMR of 3n and 3p (Table 2, entries 14 and 16) in $CDCl_3$ at 25 ^{o}C



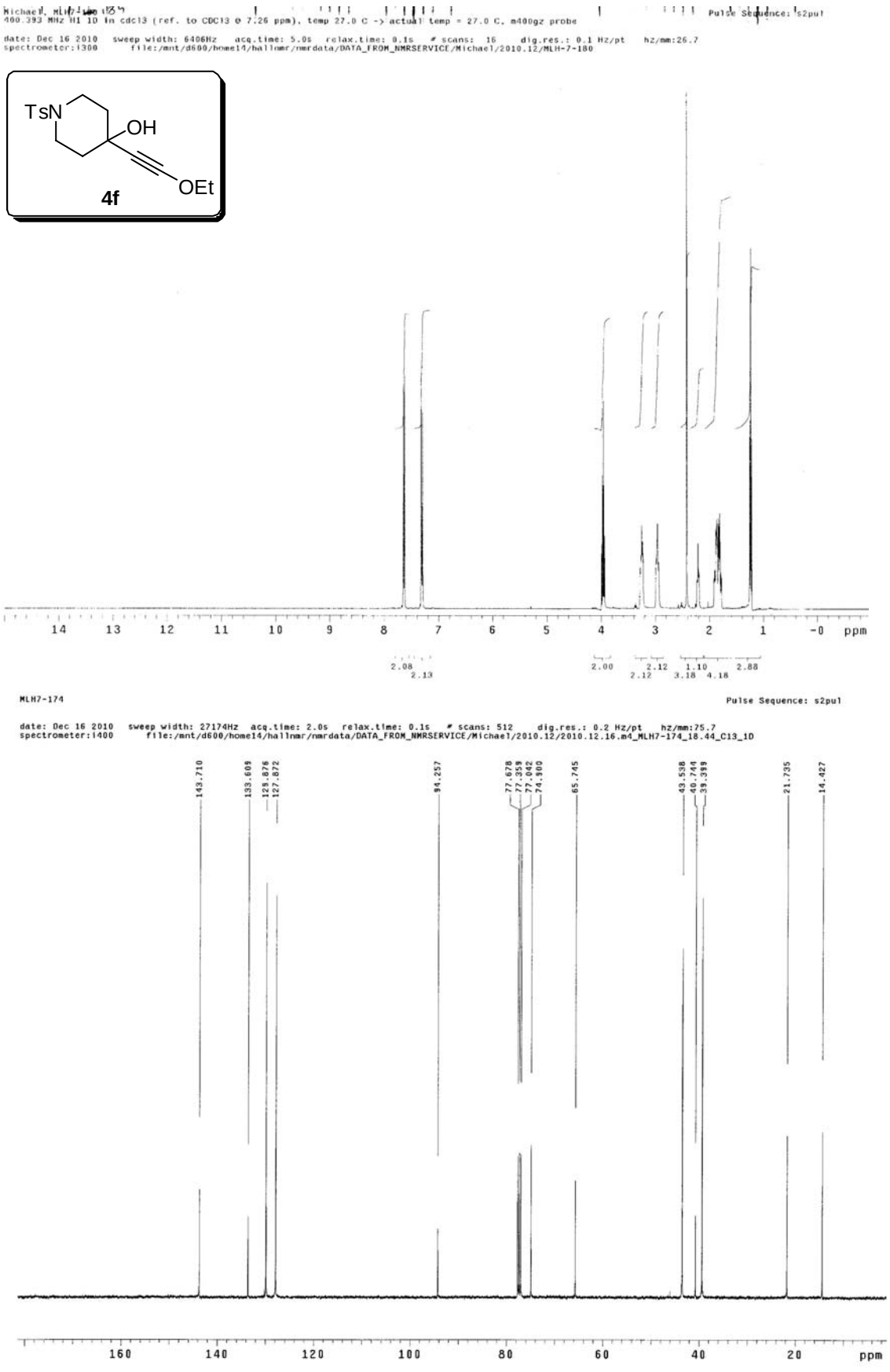


3.18 ^{1}H- and ^{13}C-NMR of 3o (Table 2, entry 15) in $CDCl_3$ at 25 ^{o}C

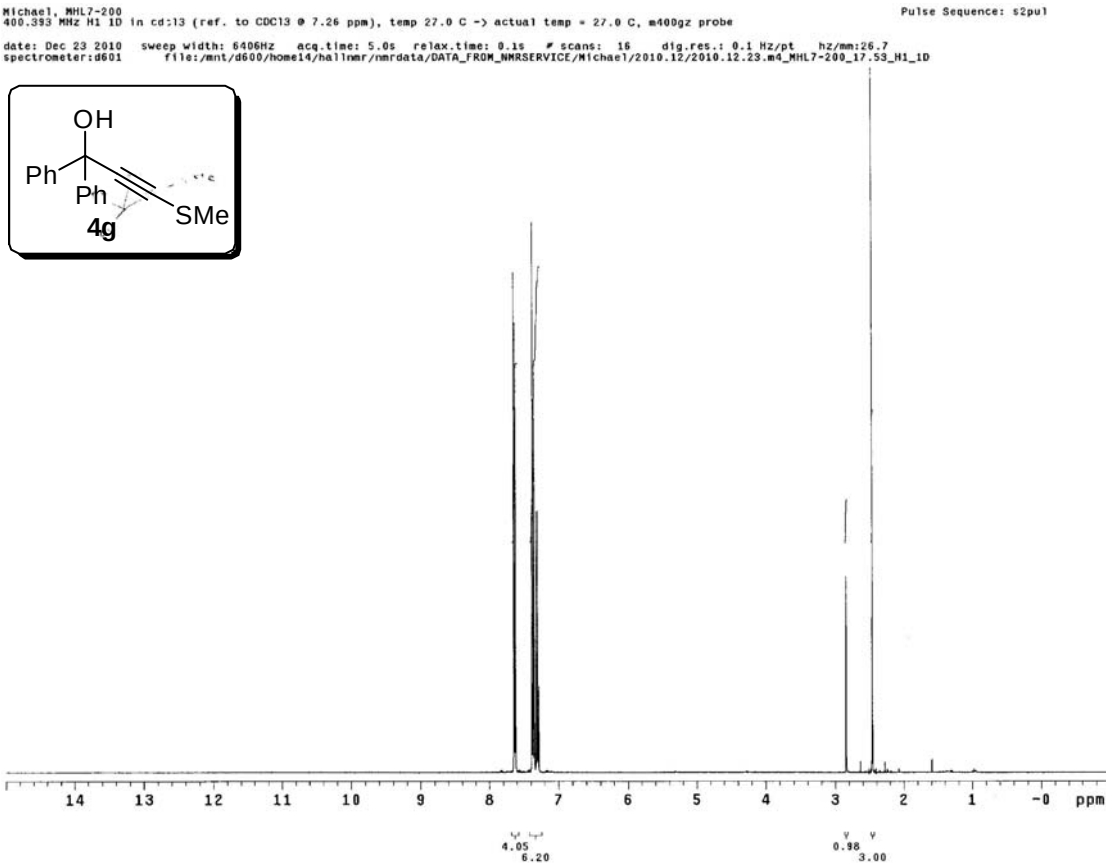


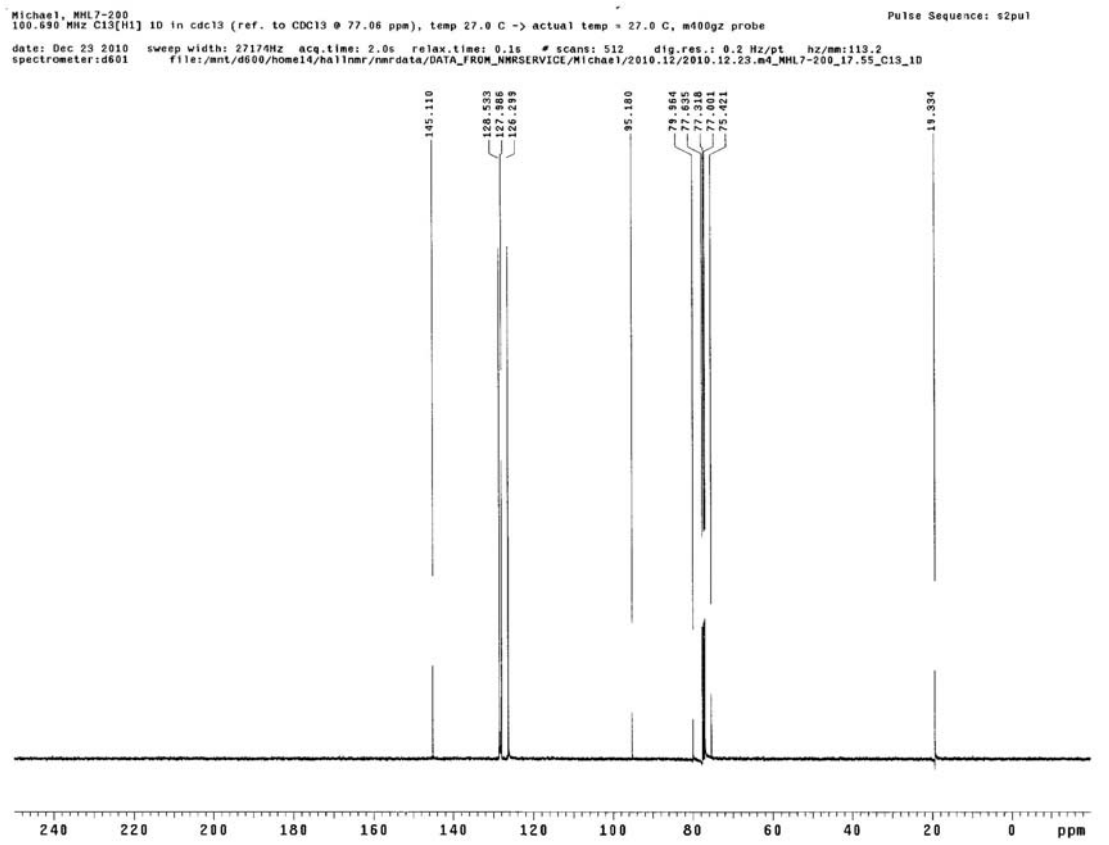


3.19 ^{1}H- and ^{13}C-NMR of 4f in $CDCl_3$ at 25 ^{o}C

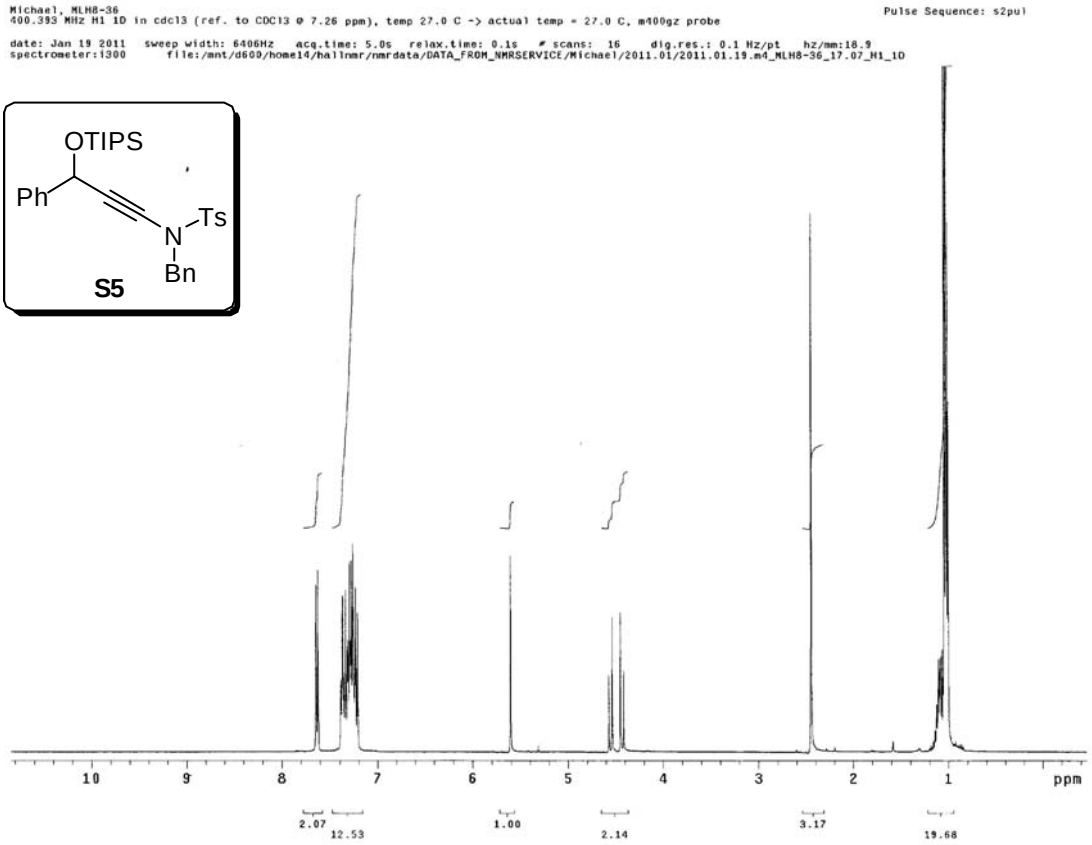


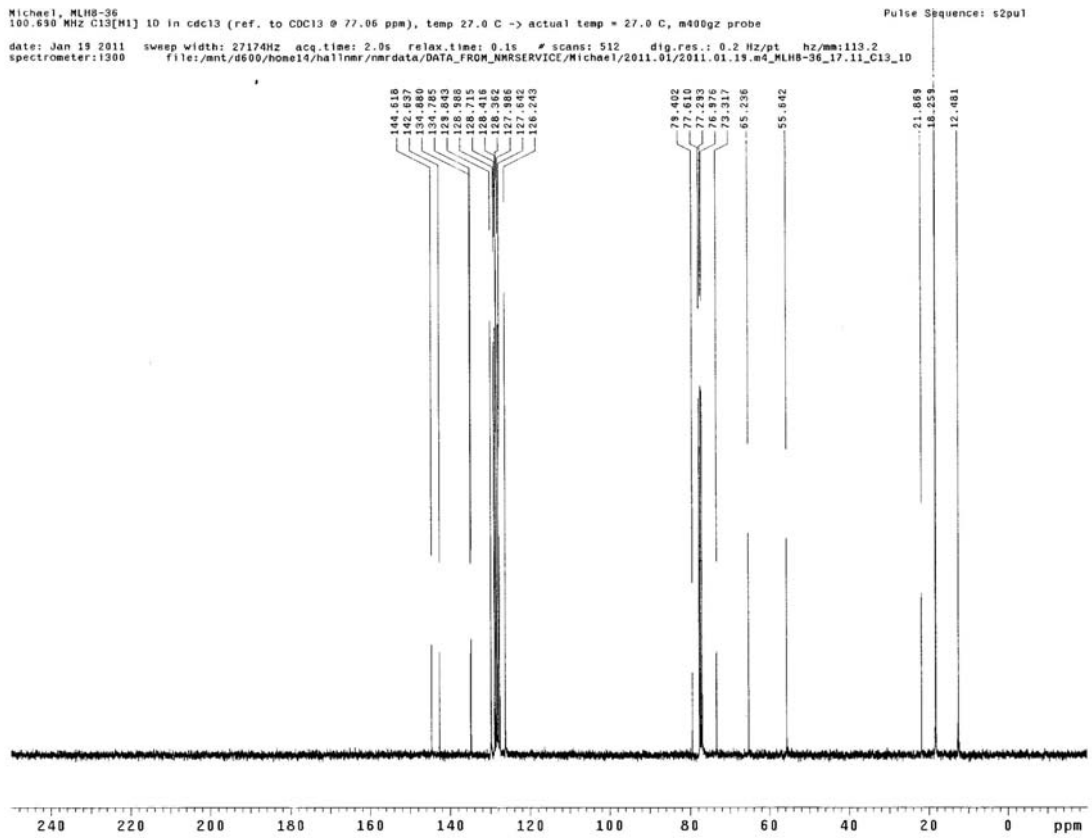
3.20 ^{1}H- and ^{13}C-NMR of 4g in $CDCl_3$ at 25 ^{o}C



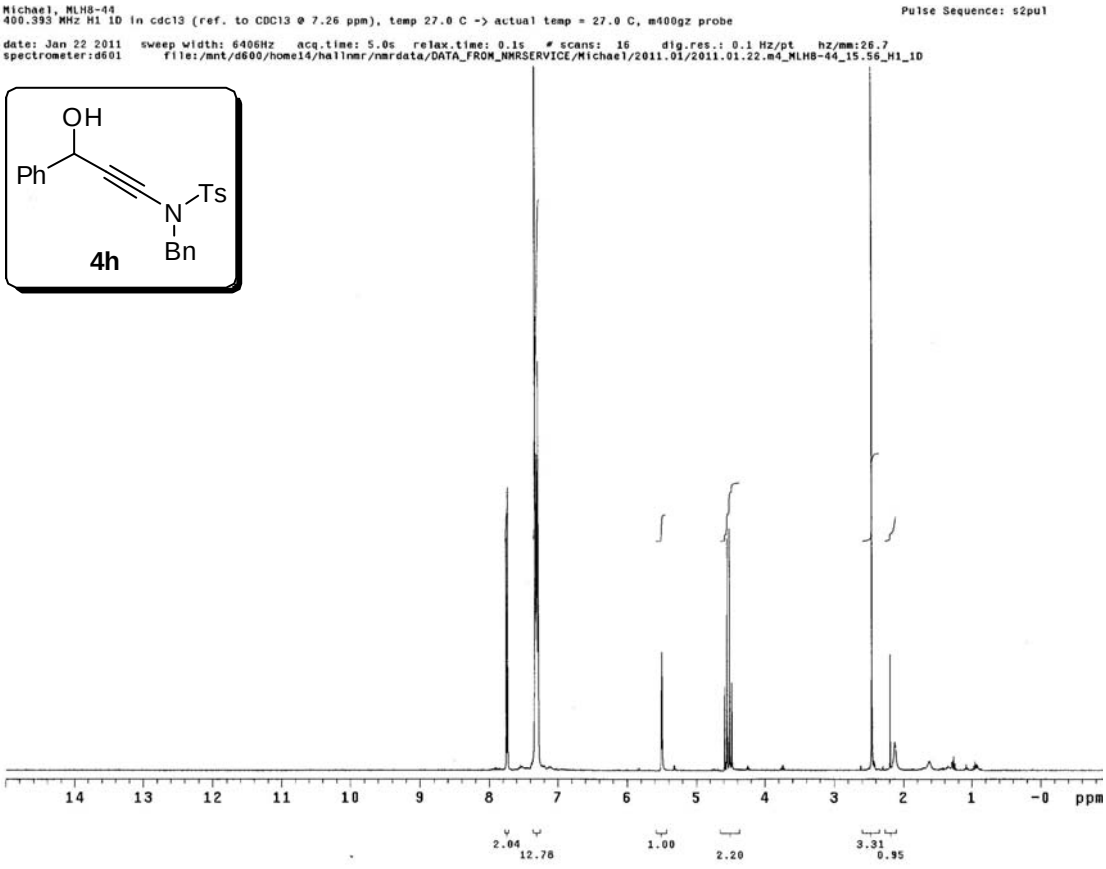


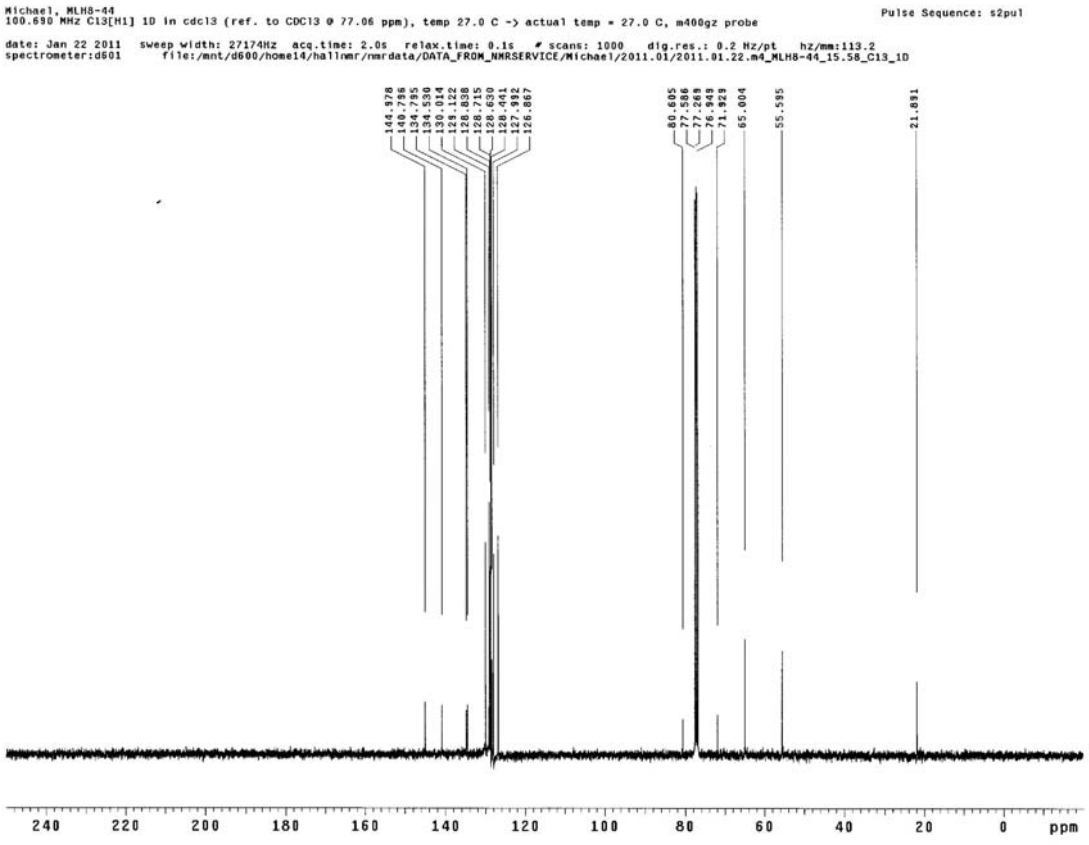
3.21 ^{1}H- and ^{13}C-NMR of S5 in $CDCl_3$ at 25 ^{o}C



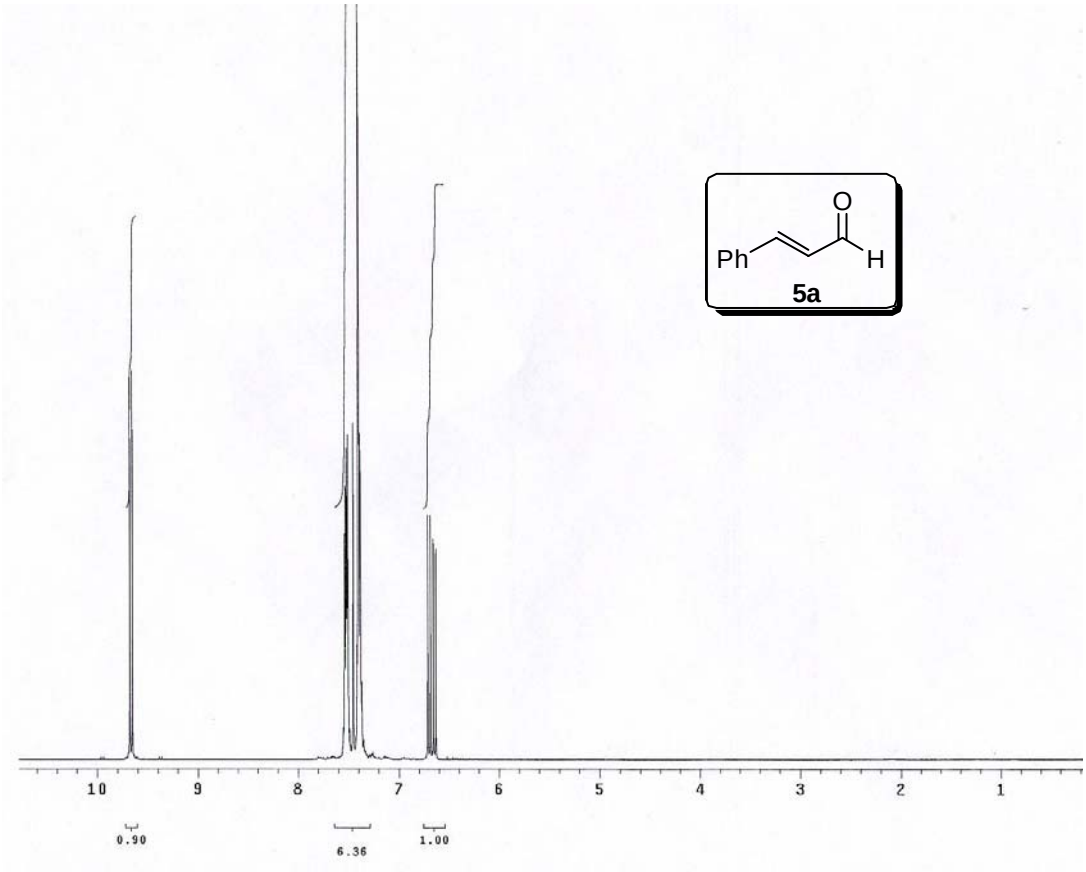


3.22 ^{1}H- and ^{13}C-NMR of 4h in $CDCl_3$ at 25 ^{o}C

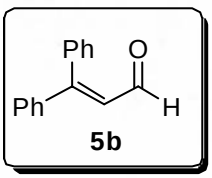


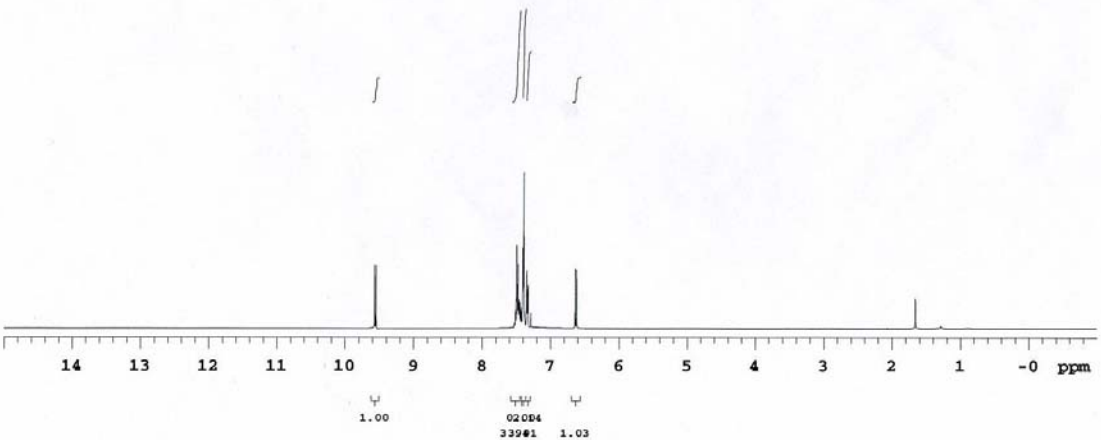


3.23 ^{1}H-NMR of 5a and 5b (Table 3, entries 1 and 2) in $CDCl_3$ at 25 ^{o}C

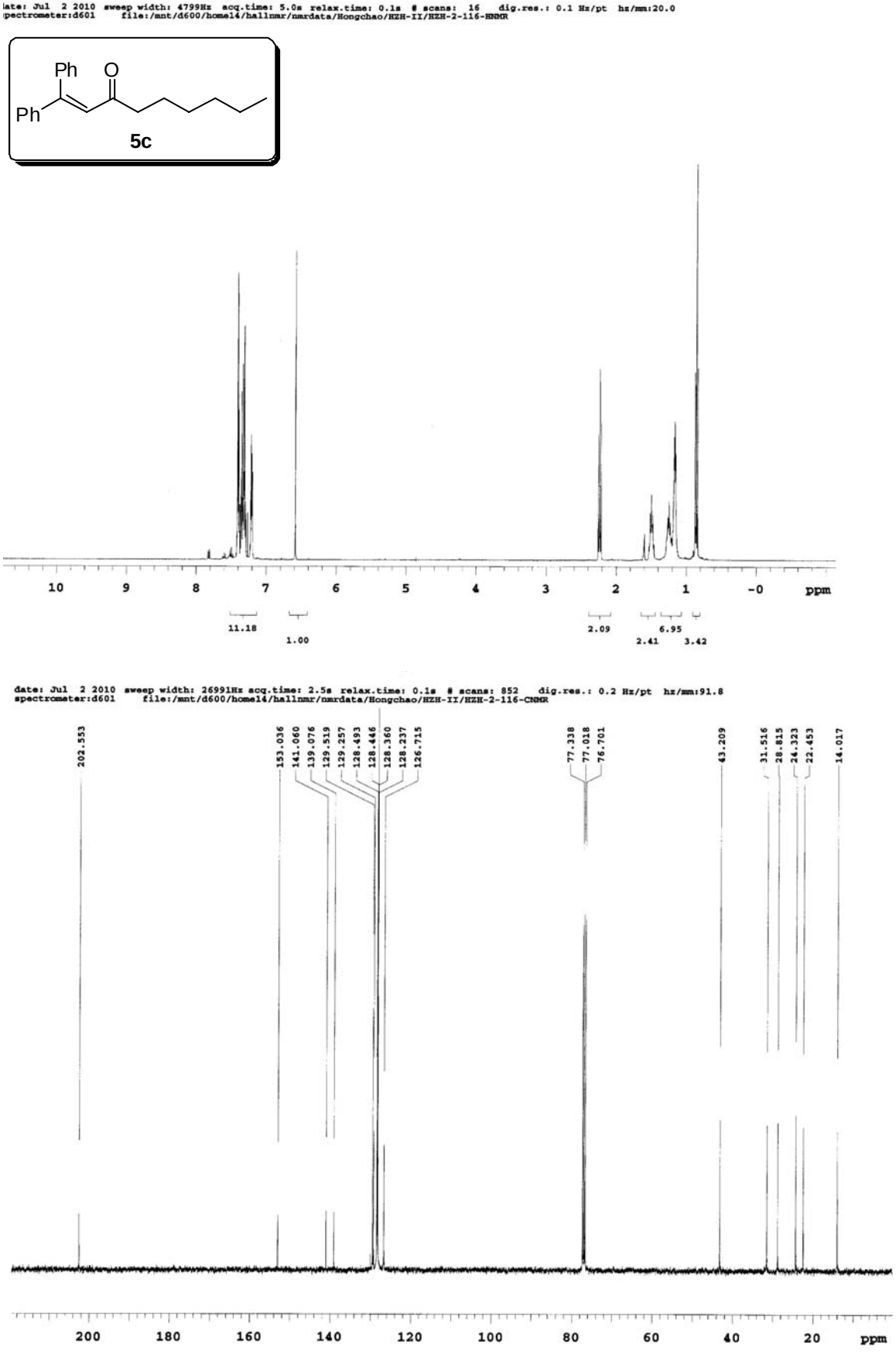


Michael, 5108-1
400.393 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.0 C -> actual temp = 27.0 C, m400gz probe
date: Jun 30 2010 sweep width: 6406Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:26.7
spectrometer:d601 file:/mnt/d600/home14/hallnmr/nmrdata/DATA_FROM_NMRSERVICE/Michael/2010.06/2010.06.30.m4_5108-1_09.17_H1_1D.fid
Pulse Sequence: s2pul

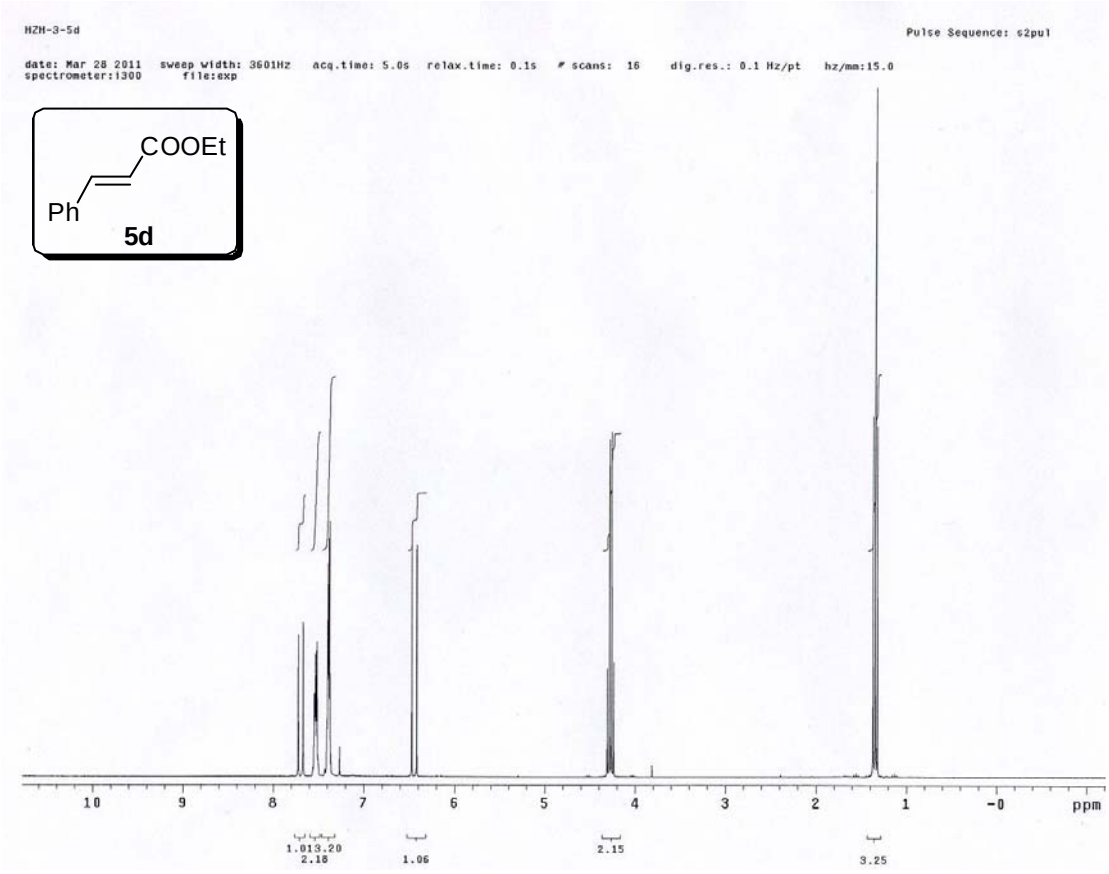


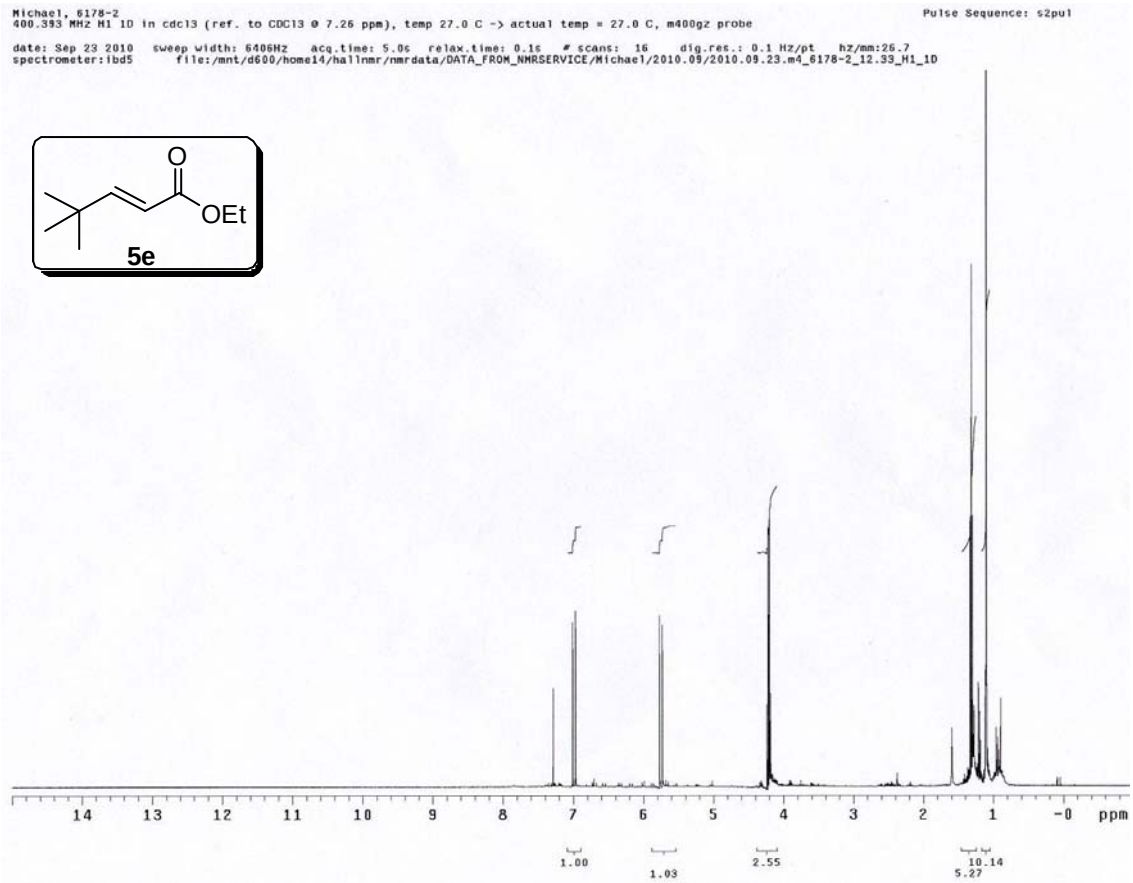


3.24 ^{1}H- and ^{13}C-NMR of 5c (Table 3, entry 3) in $CDCl_3$ at 25 ^{o}C

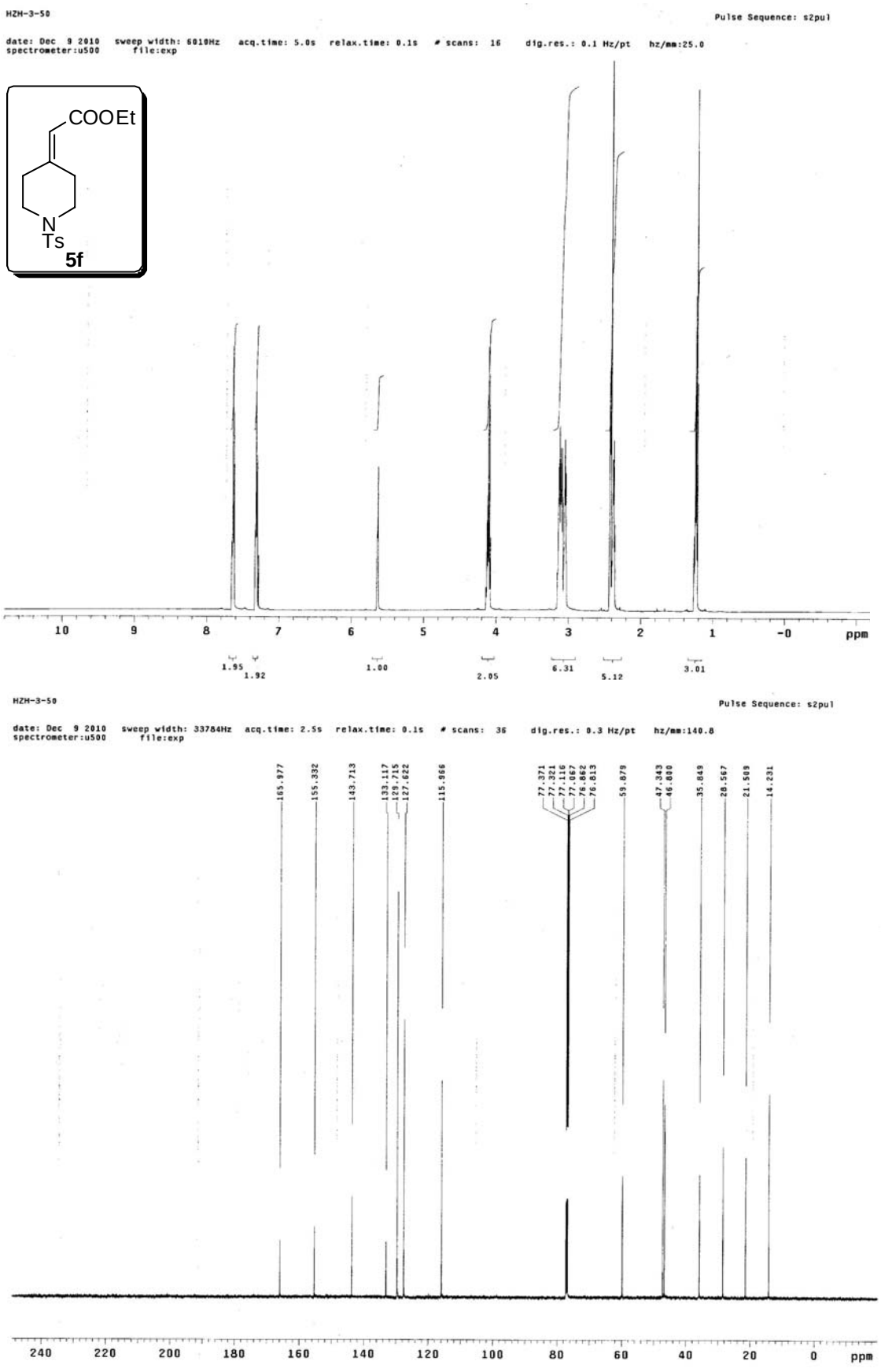


3.25 ^{1}H-NMR of 5d and 5e (Table 3, entries 4 and 5) in $CDCl_3$ at 25 ^{o}C

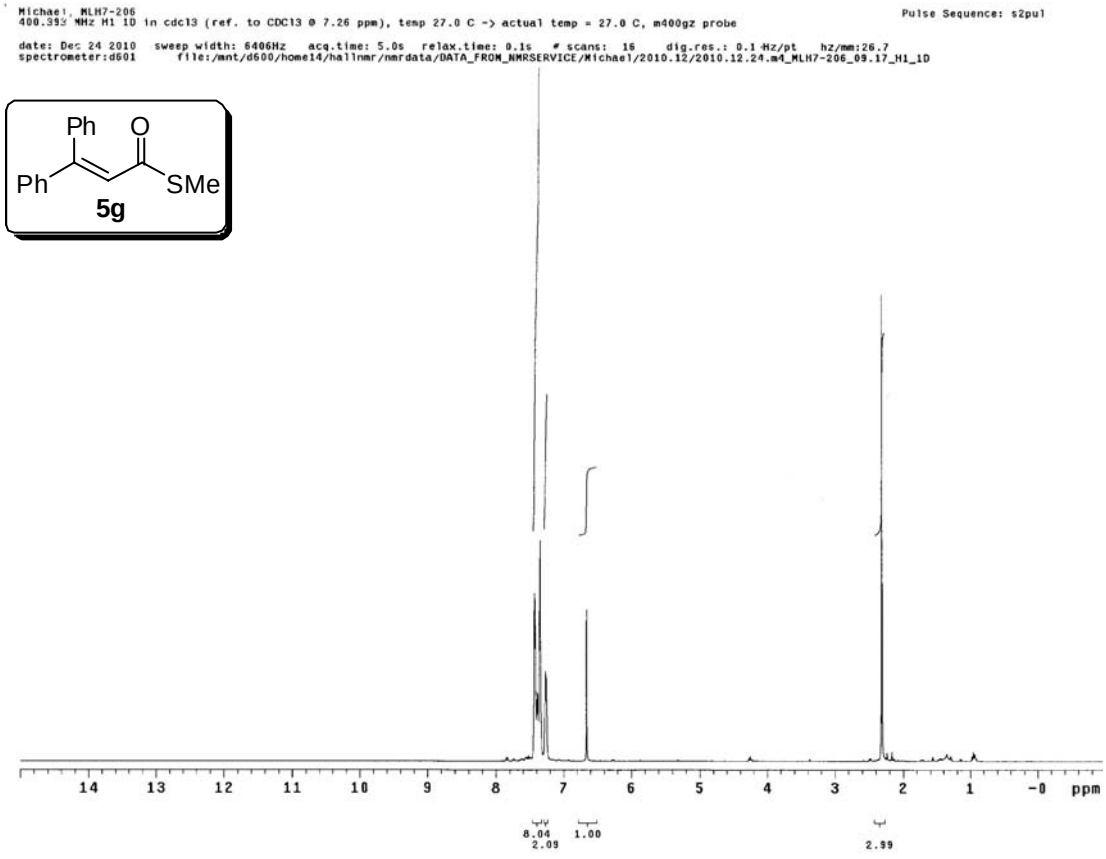


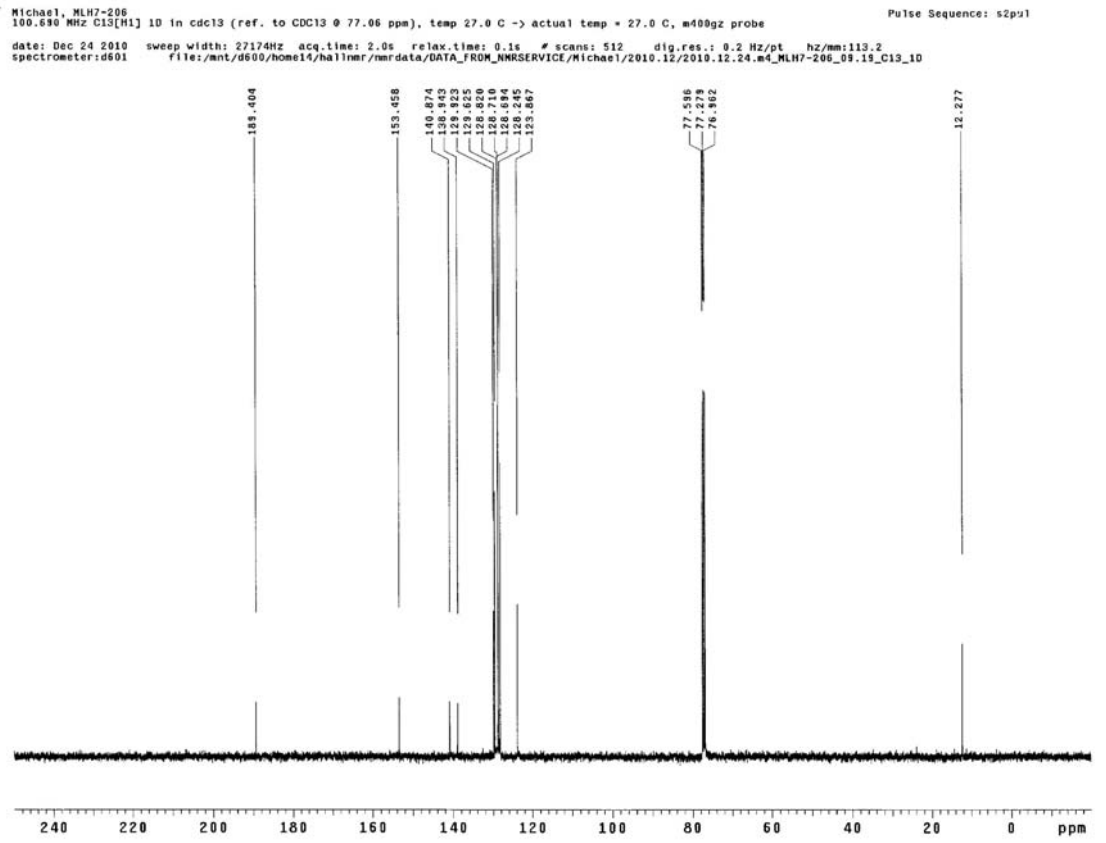


3.26 ^{1}H- and ^{13}C-NMR of 5f (Table 3, entry 6) in $CDCl_3$ at 25 ^{o}C

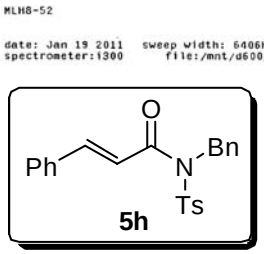


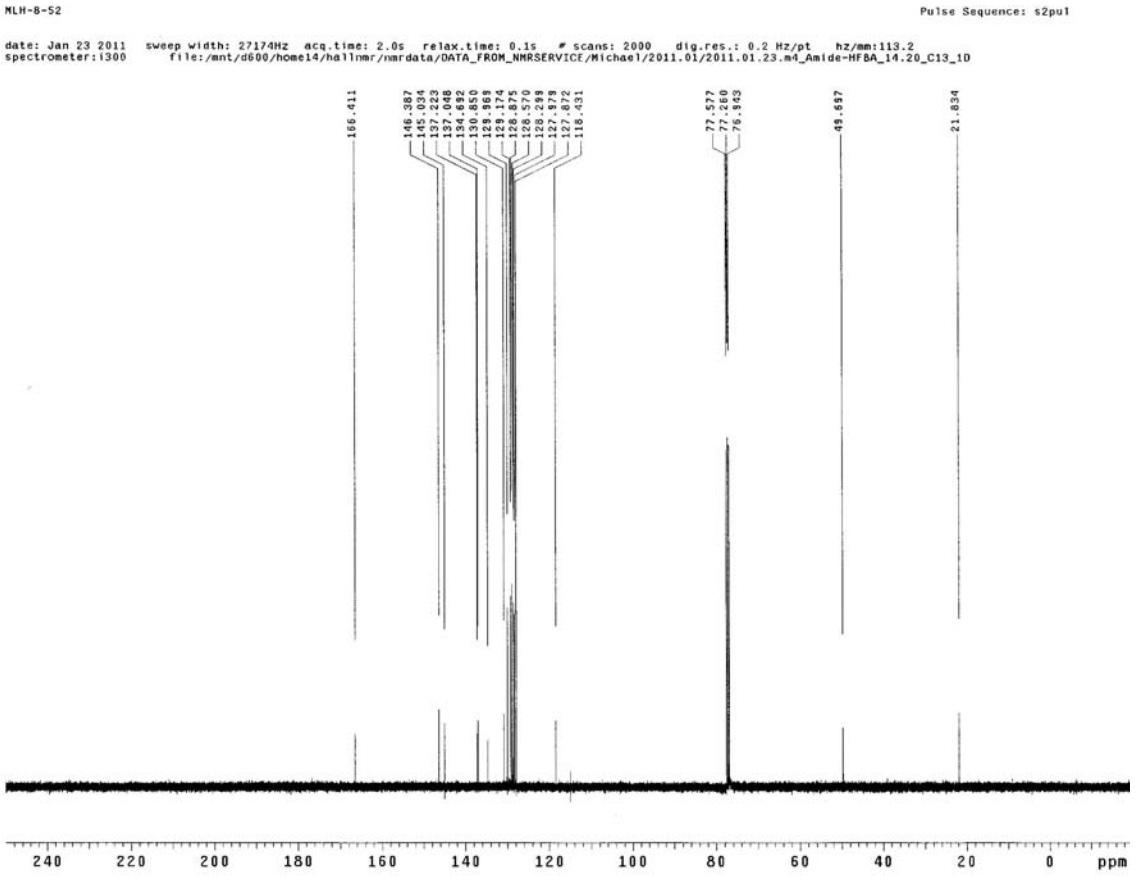
3.27 ^{1}H- and ^{13}C-NMR of 5g (Table 3, entry 7) in $CDCl_3$ at 25 ^{o}C



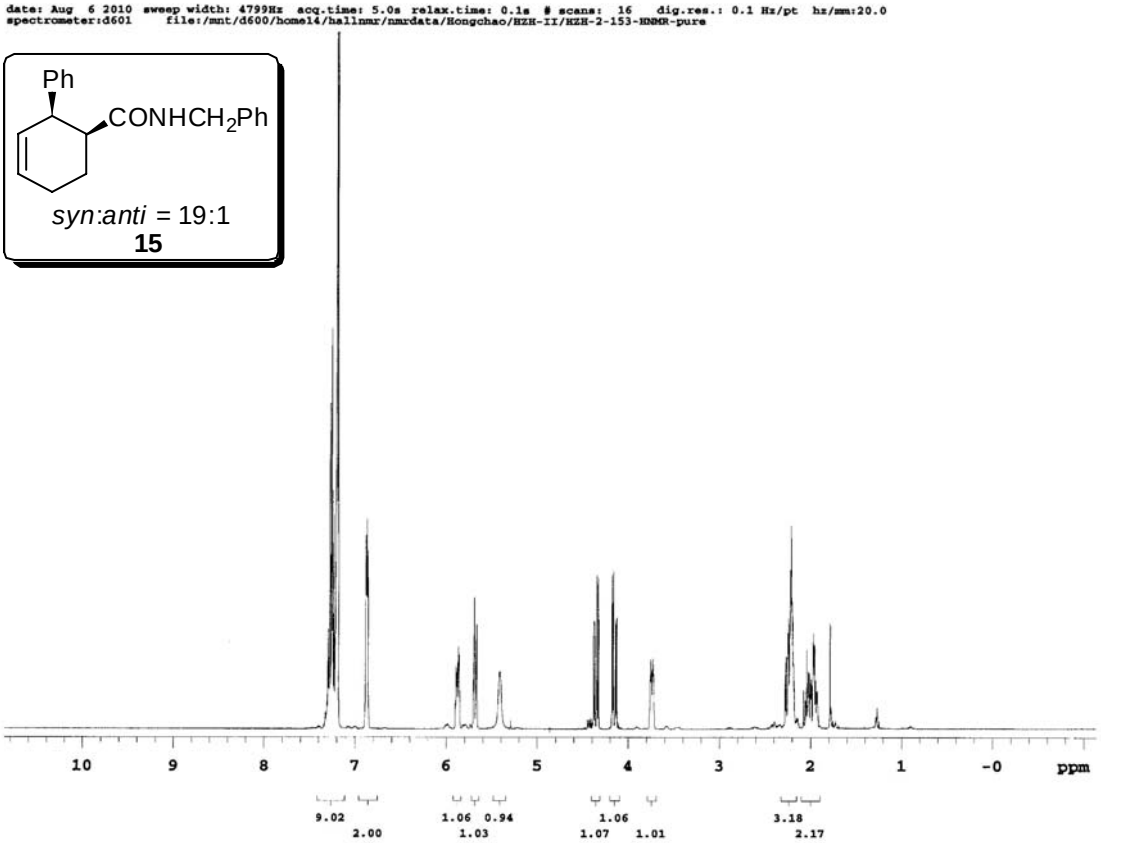


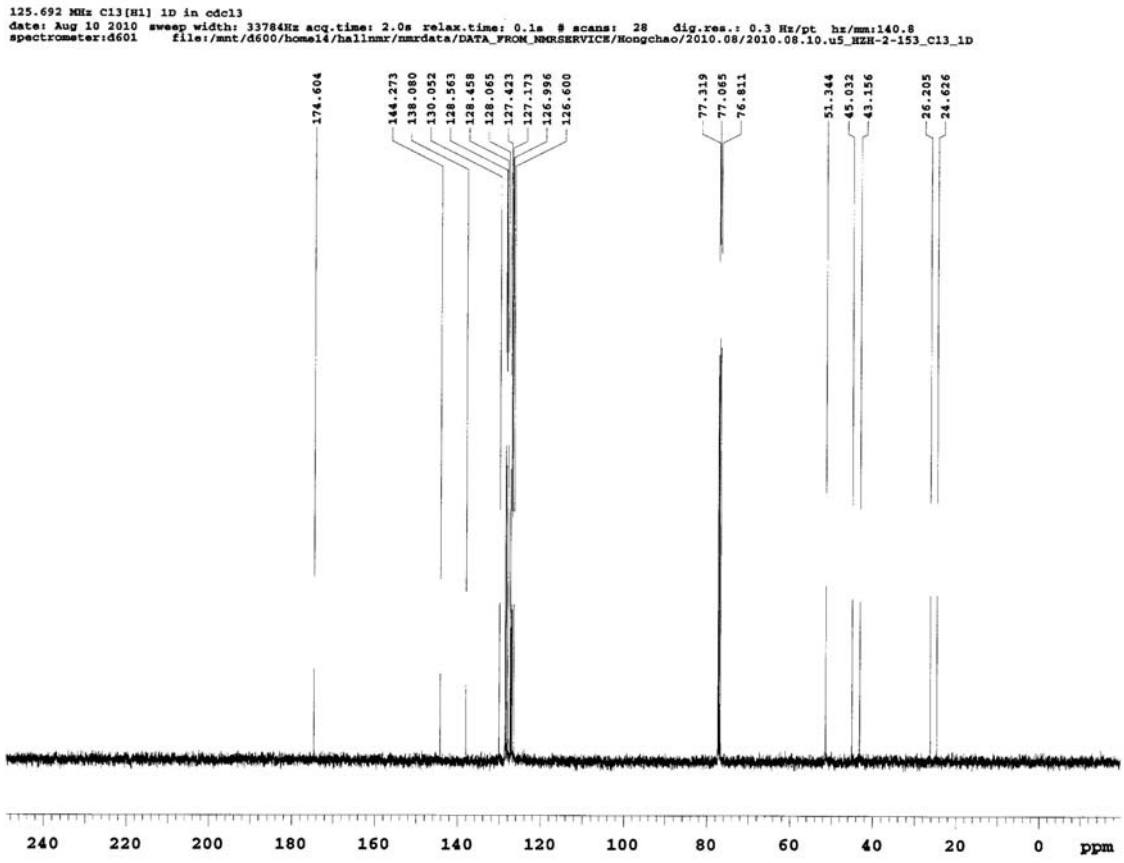
3.28 ^{1}H- and ^{13}C-NMR of 5h (Table 3, entry 8) in $CDCl_3$ at 25 ^{o}C



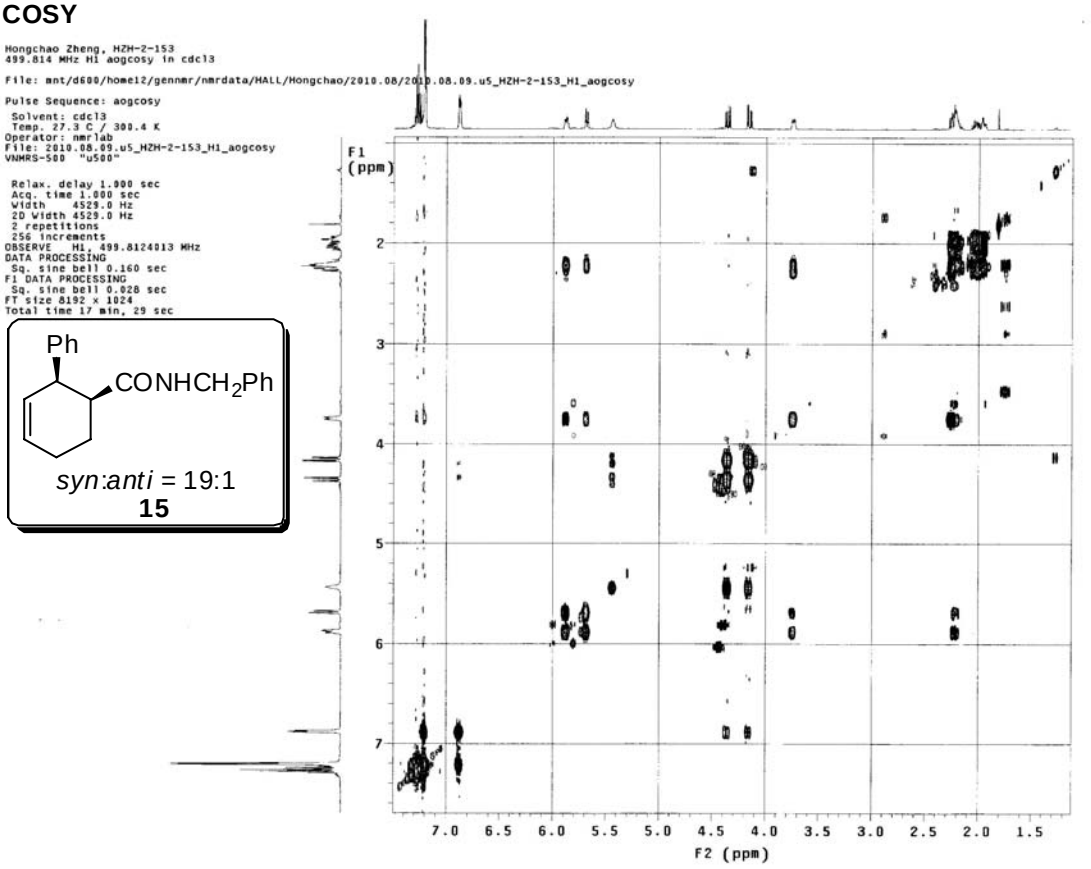


3.29 ^{1}H-, ^{13}C- and 2D-NMR of 15 (Scheme 5) in $CDCl_3$ at 25 ^{o}C

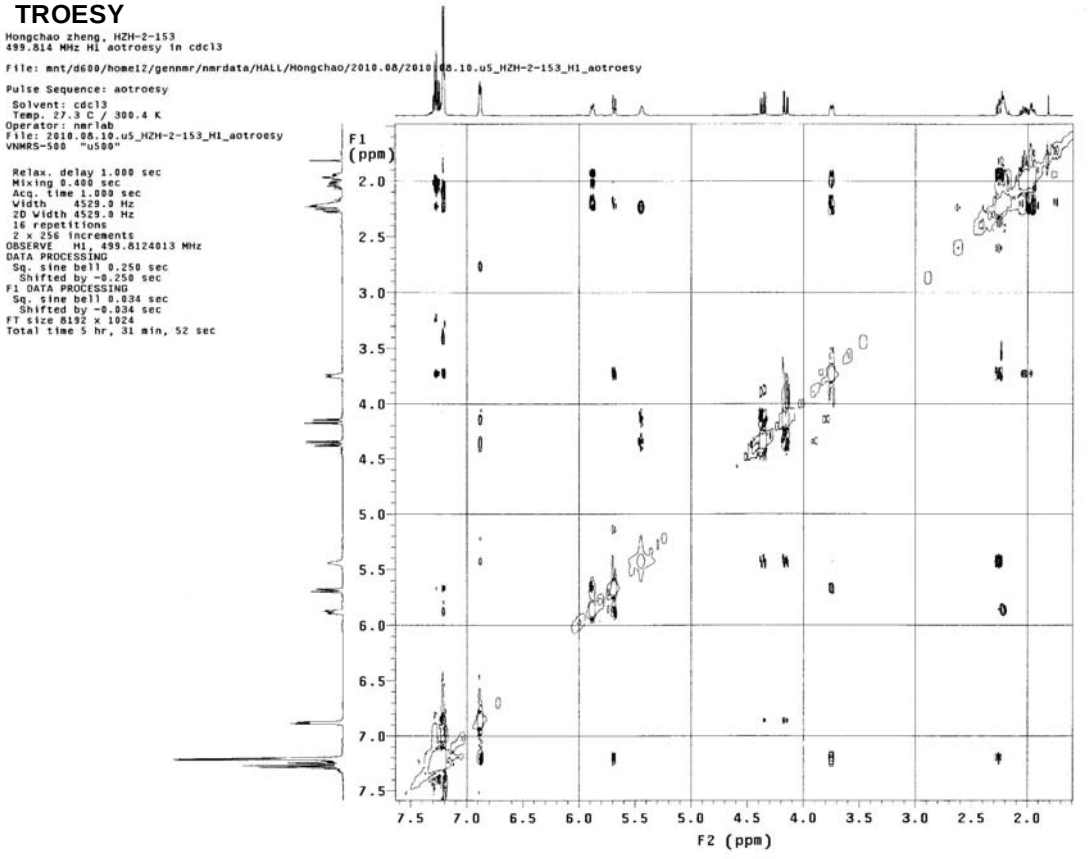




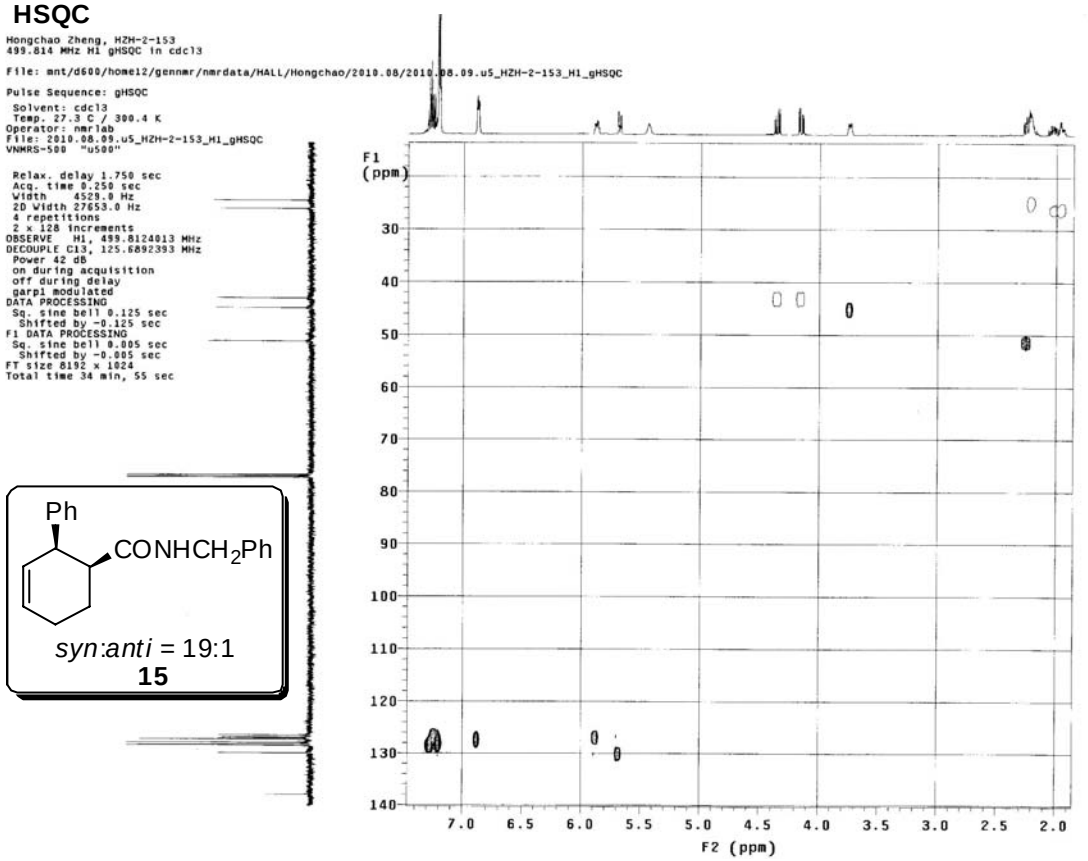
COSY


Hongchao Zheng, HZH-2-153
499.814 MHz H1 aogcosy in cdcl3
File: mnt/d600/home12/gennmr/nmrdata/HALL/Hongchao/2010.08/2010.08.09.u5_HZH-2-153_H1_aogcosy
Pulse Sequence: aogcosy
Solvent: cdcl3
Temp. 27.3 C / 300.4 K
Operator: nmrlab
File: 2010.08.09.u5_HZH-2-153_H1_aogcosy
VNMRS-500 "u500"
Relax. delay 1.000 sec
Acq. time 1.000 sec
Width 4529.0 Hz
2D Width 4529.0 Hz
2 repetitions
256 increments
OBSERVE H1, 499.8124013 MHz
DATA PROCESSING
Sq. sine bell 0.160 sec
F1 DATA PROCESSING
Sq. sine bell 0.028 sec
FT size 8192 x 1024
Total time 17 min, 29 sec
Ph
CONHCH2Ph
syn:anti = 19:1
15
F1 (ppm)
F2 (ppm)

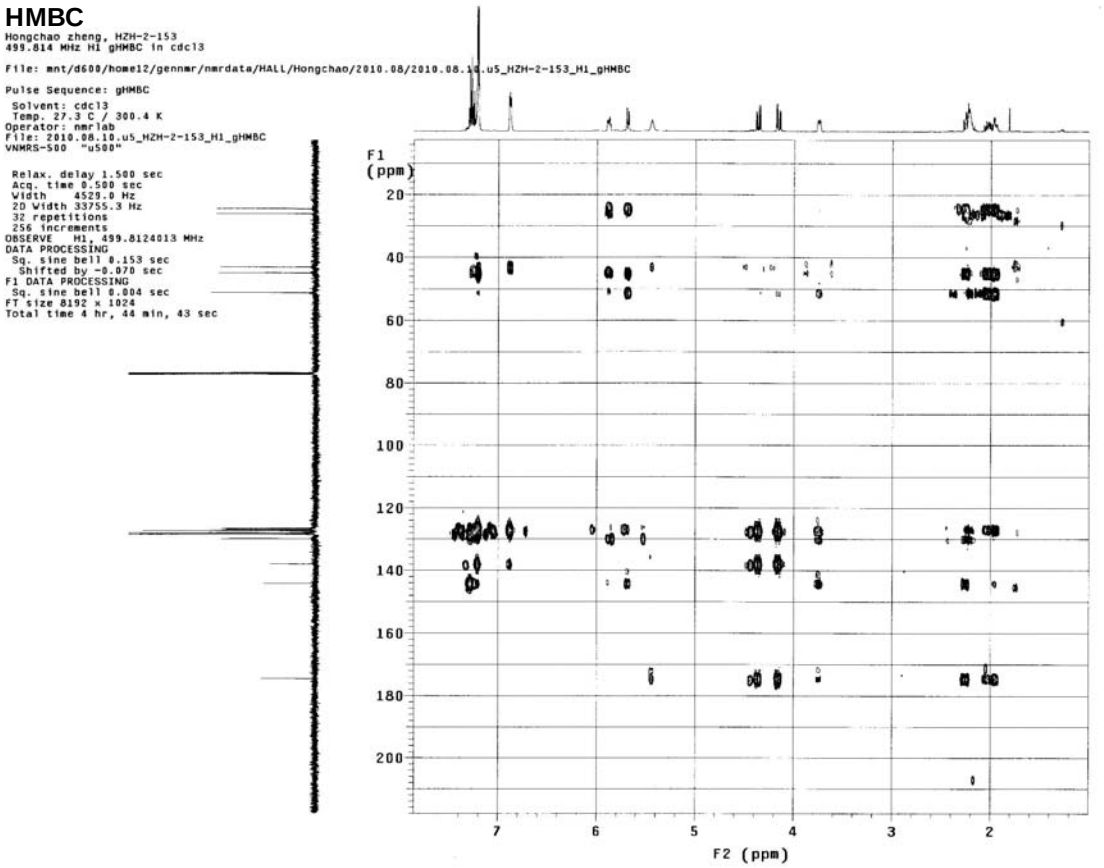
TROESY


Hongchao zheng, HZH-2-153
499.814 MHz H1 aotroesy in cdcl3
File: mnt/d600/home12/gennmr/nmrdata/HALL/Hongchao/2010.08/2010.08.10.u5_HZH-2-153_H1_aotroesy
Pulse Sequence: aotroesy
Solvent: cdcl3
Temp. 27.3 C / 300.4 K
Operator: nmrlab
File: 2010.08.10.u5_HZH-2-153_H1_aotroesy
VNMRS-500 "u500"
Relax. delay 1.000 sec
Mixing 0.400 sec
Acq. time 1.000 sec
Width 4529.0 Hz
2D Width 4529.0 Hz
16 repetitions
2 x 256 increments
OBSERVE H1, 499.8124013 MHz
DATA PROCESSING
Sq. sine bell 0.250 sec
Shifted by -0.250 sec
F1 DATA PROCESSING
Sq. sine bell 0.034 sec
Shifted by -0.034 sec
FT size 8192 x 1024
Total time 5 hr, 31 min, 52 sec
F1 (ppm)
F2 (ppm)

HSQC

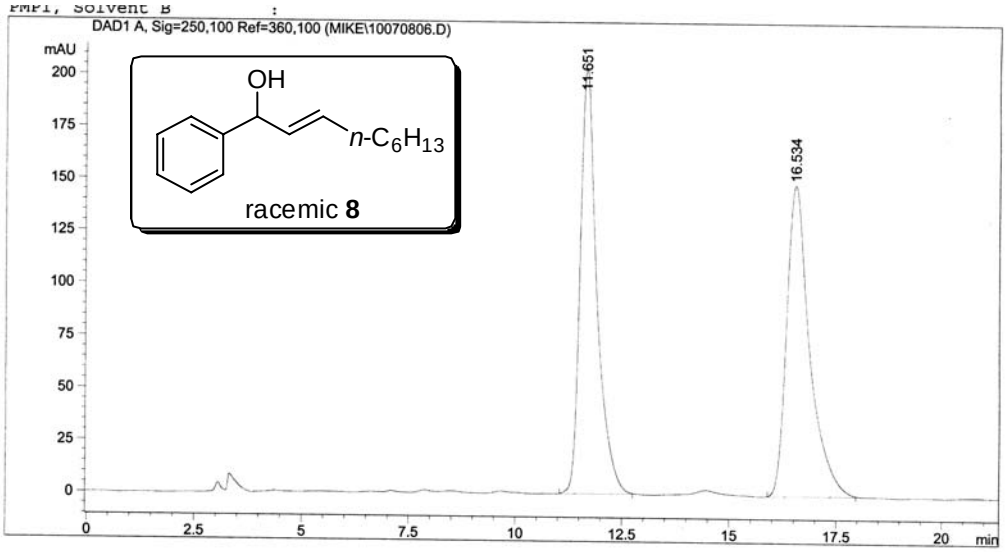

Hongchao Zheng, HZH-2-153
499.814 MHz H1 gHSQC in cdcl3
File: mnt/d600/home12/gennmr/nmrdata/HALL/Hongchao/2010.08/2010.08.09.u5_HZH-2-153_H1_gHSQC
Pulse Sequence: gHSQC
Solvent: cdcl3
Temp. 27.3 C / 300.4 K
Operator: nmrlab
File: 2010.08.09.u5_HZH-2-153_H1_gHSQC
VNMRS-500 "u500"
Relax. delay 1.750 sec
Acq. time 0.250 sec
Width 4529.0 Hz
2D Width 27653.0 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 499.8124013 MHz
DECOUPLE C13, 125.6892393 MHz
Power 42 dB
on during acquisition
off during delay
garp1 modulated
DATA PROCESSING
Sq. sine bell 0.125 sec
Shifted by -0.125 sec
F1 DATA PROCESSING
Sq. sine bell 0.005 sec
Shifted by -0.005 sec
FT size 8192 x 1024
Total time 34 min, 55 sec
Ph
CONHCH2Ph
syn:anti = 19:1
15
F1 (ppm)
F2 (ppm)

HMBC


Hongchao zheng, HZH-2-153
499.814 MHz H1 gHMBC in cdcl3
File: mnt/d600/home12/gennmr/nmrdata/HALL/Hongchao/2010.08/2010.08.10.u5_HZH-2-153_H1_gHMBC
Pulse Sequence: gHMBC
Solvent: cdcl3
Temp. 27.3 C / 300.4 K
Operator: nmrlab
File: 2010.08.10.u5_HZH-2-153_H1_gHMBC
VNMRS-500 "u500"
Relax. delay 1.500 sec
Acq. time 0.500 sec
Width 4529.0 Hz
2D Width 33755.3 Hz
32 repetitions
256 increments
OBSERVE H1, 499.8124013 MHz
DATA PROCESSING
Sq. sine bell 0.153 sec
Shifted by -0.070 sec
F1 DATA PROCESSING
Sq. sine bell 0.004 sec
FT size 8192 x 1024
Total time 4 hr, 44 min, 43 sec
F1 (ppm)
F2 (ppm)

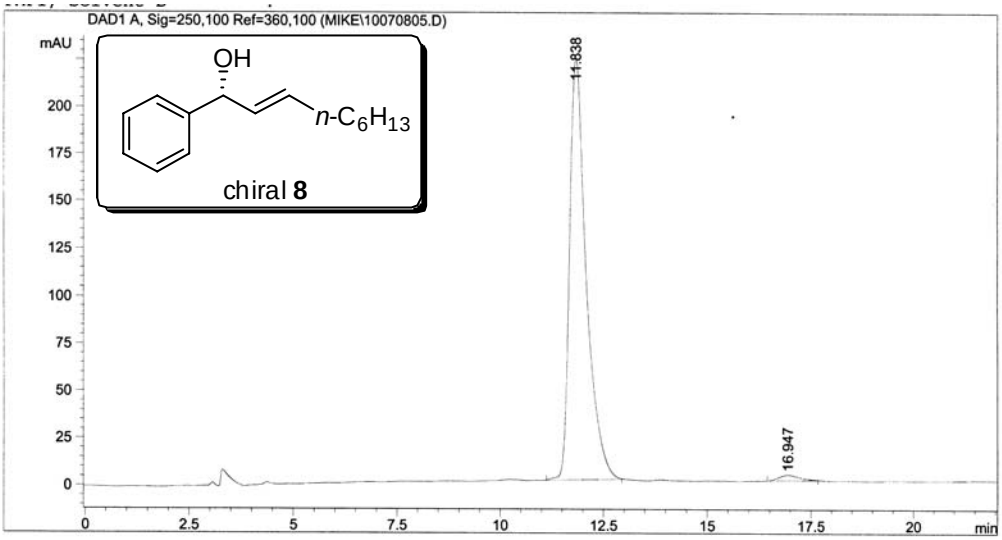
4. Chromatograms for Enantiomeric Excess Measurements

4.1 Racemic (top) and optically enriched (bottom) 8 (Scheme 2)



Signal 1: DAD1 A, Sig=250,100 Ref=360,100

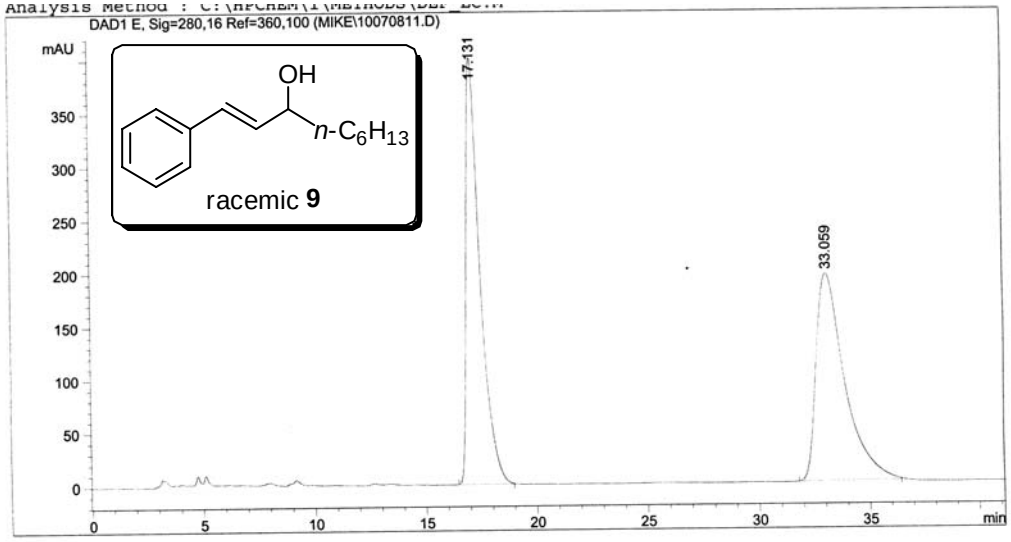
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.651	BB	0.4047	5562.10400	203.63307	49.8425
2	16.534	BB	0.5535	5597.25879	148.56938	50.1575
Totals :				1.11594e4	352.20245	



Signal 1: DAD1 A, Sig=250,100 Ref=360,100

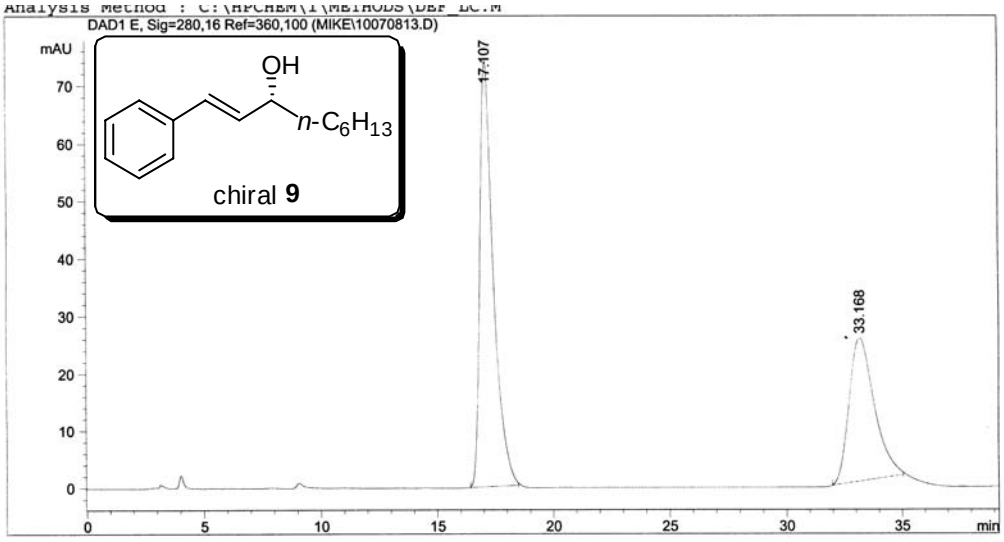
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.838	BB	0.4170	6247.59814	222.88531	98.2907
2	16.947	BB	0.4350	108.64527	3.02533	1.7093
Totals :				6356.24342	225.91065	

4.2 Racemic (top) and optically enriched (bottom) 9 (Scheme 2)



Signal 1: DAD1 E, Sig=280,16 Ref=360,100

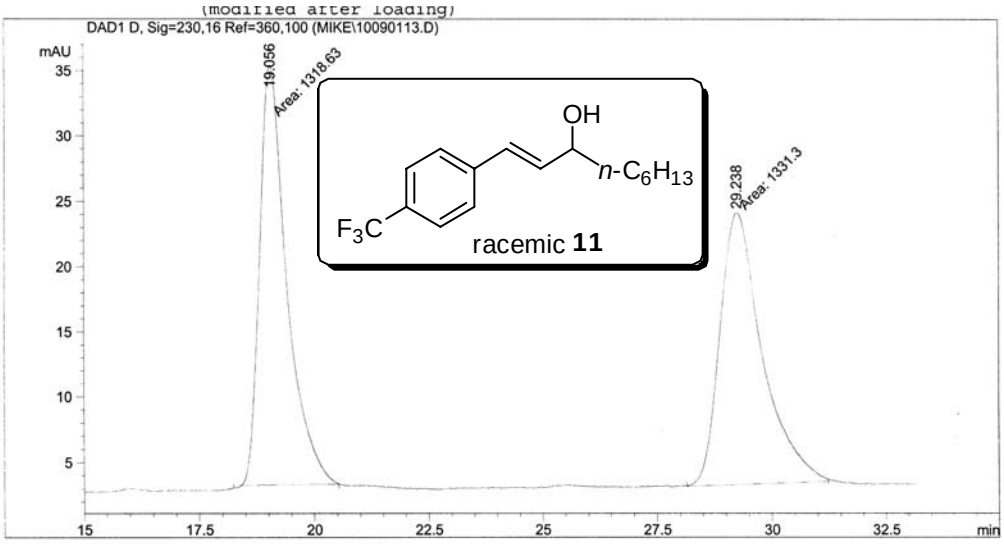
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.131	BB	0.6505	1.74769e4	401.01694	50.1597
2	33.059	BB	1.3229	1.73657e4	195.00877	49.8403
Totals :				3.48426e4	596.02571	



Signal 1: DAD1 E, Sig=280,16 Ref=360,100

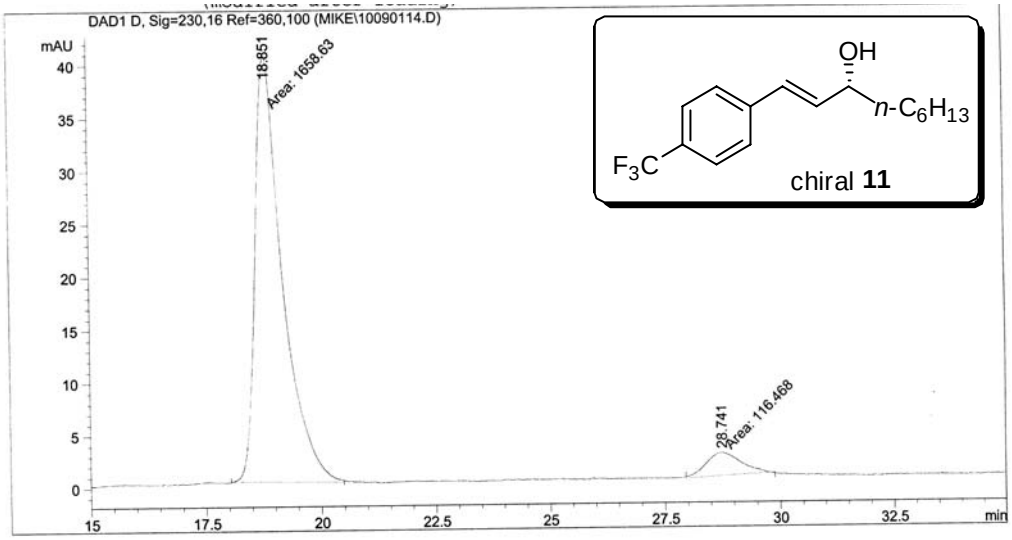
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.107	BB	0.6047	3001.75000	74.08773	61.3093
2	33.168	BB	1.1242	1894.32764	25.05236	38.6907
Totals :				4896.07764	99.14009	

4.3 Racemic (top) and optically enriched (bottom) 11 (Scheme 2)



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.056	MM	0.6834	1318.62646	32.15976	49.7609
2	29.238	MM	1.0646	1331.30017	20.84209	50.2391
Totals :				2649.92664	53.00185	



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.851	MM	0.6866	1658.63354	40.26336	93.4388
2	28.741	MM	0.8739	116.46772	2.22130	6.5612
Totals :				1775.10126	42.48465	