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Supporting Information

Enantioselective Barbier-type Allylation of Ketones Using Allyl halide and Indium in Water

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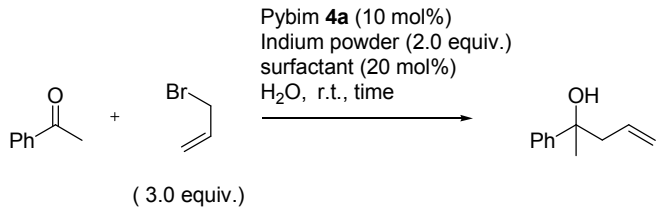
CONTENTS:

Experimental Section

General method: All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or *p*-anisaldehyde in ethanol/heat. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63-210 μm. The ^{1}H NMR (300 MHz), ^{19}F NMR (282 MHz), and ^{13}C NMR (75.5 MHz) spectra for solution in $CDCl_3$ were recorded on Varian Mercury 300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS HPLC analyses were performed on a JASCO LC-2000 plus using 4.6 x 250 mm CHIRALCEL® OD-H, OD-3, and OJ-H column. ESI Mass spectra were recorded on a SHIMADZU LCMS-2020 using positive mode. Optical rotations were measured on a JASCO P-2200. Infrared spectra were recorded on a JASCO FT/IR-4600 spectrometer with ZnSe ATR unit. Bis(imidazoline) catalysts were synthesized by published procedures.[1)]

Optimization of reaction conditions:

Surfactant:

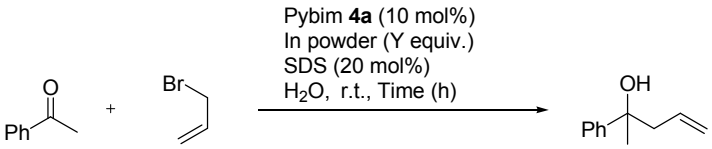


(3.0 equiv.)

Entry	surfactant	Time (h)	Yield (%)	Ee (%)
1	-	36	48	29
2	SDS	2	91	24
3	NH_4Br	30	55	25
4	CTAB[a]	30	99	34
5	18-crown-6	36	67	9
6	SDS / CTAB	36	99	36

a) CTAB : Cetrimonium bromide

Reagent ratio:

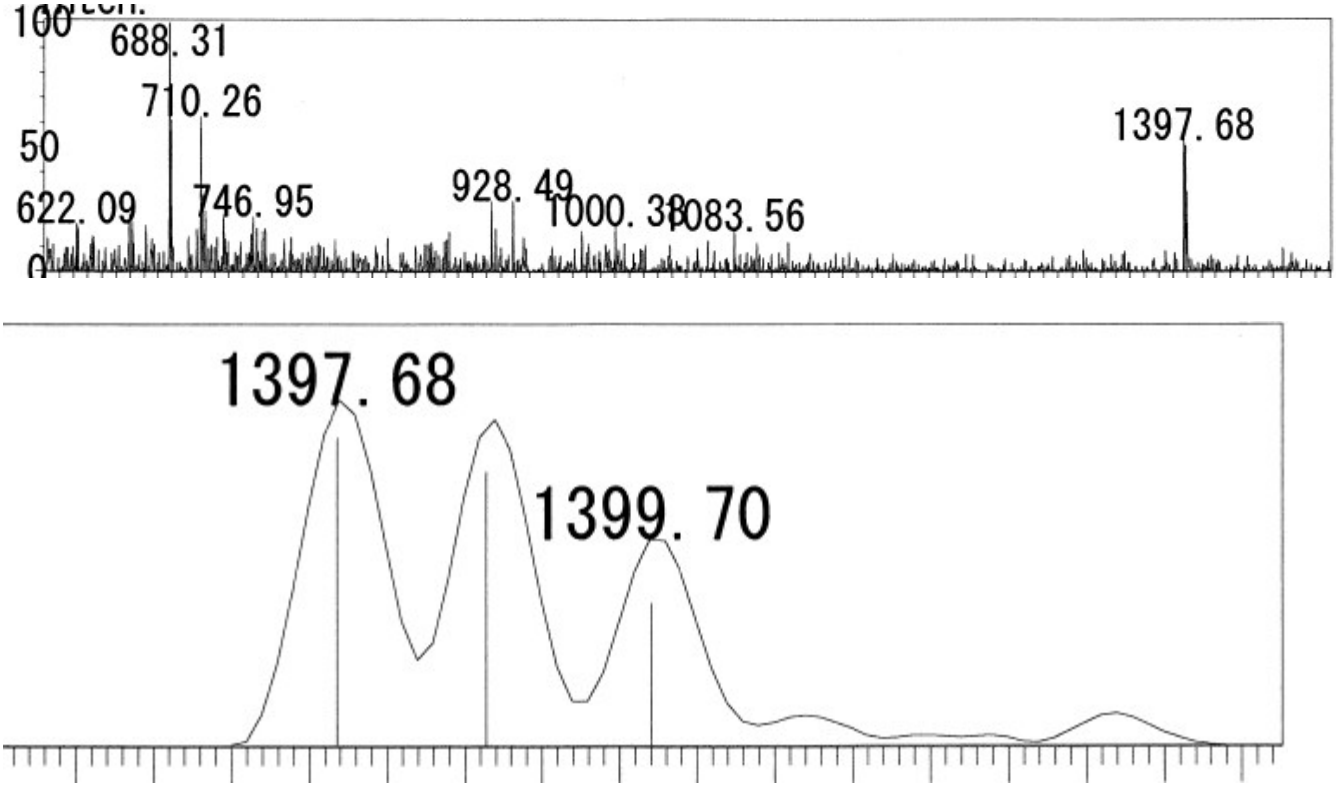


(X equiv.)

Entry	X eq.	Y eq.	Time (h)	Yield (%)	Ee (%)
1	3.0	1.0	36	80	16
2	3.0	2.0	2	91	24
3	3.0	3.0	0.5	99	16
4	3.0	5.0	0.5	90	15
5	2.0	2.0	2	70	17

ESI-Mass spectroscopic analysis:

In order to clarify the assumed reaction mechanism, we also investigated some other spectroscopic analysis. The ESI-Mass spectroscopic analysis of complex **A**; (**2b, 4a**, In, and NaI in a 3:0.1:2:3 ratio in H_2O, cation mode)



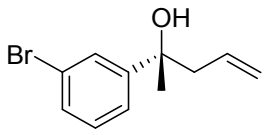
Picture for the reaction mixture:

Start

Finish

Characterization data for products:

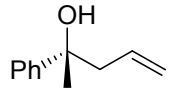
(*R*)-2-(3-Bromophenyl)pent-4-en-2-ol (3a)



3'-Bromoacetophenone (14 μL, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 18 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =1/9) to give **3a** (25.8 mg, 99%, 86% ee) as colorless oil.

$[\alpha]_D^{25}$ +39.1 (*c* 0.35, $CHCl_3$, 86% ee) (lit.[2a] $[\alpha]_D^{25}$ +34.1 (*R*) (*c* 1.03, $CHCl_3$, 89% ee)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 3H, C*H*$_3$), 2.11 (s, 1H, O*H*), 2.44-2.25 (m, 1H, C*H*$_2$), 2.62-2.69 (m, 1H, C*H*$_2$), 5.13-5.17 (m, 2H, C*H*$_2$), 5.56-5.64 (m, 1H, C*H*), 7.18-7.46 (m, 1H, *Ar*), 7.33-7.38 (m, 2H, *Ar*), 7.61 (s, 1H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.9, 48.4, 73.3, 105.0, 120.1, 122.6, 123.5, 128.2, 129.8, 129.8, 133.1, 150.1; HPLC (DAICEL CHIRALCEL OD-H, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 8.1 min (minor), t_R = 9.2 min (major).

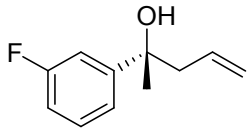
(*R*)-2-Phenylpent-4-en-2-ol (3b)



Acetophenone (12 μL, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 18 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =1/9) to give **3b** (13.7 mg, 86%, 65% ee) as colorless oil.

$[\alpha]_D^{25}$ +26.7 (*c* 0.48, $CHCl_3$, 70% ee) (lit.[2b] $[\alpha]_D^{25}$+37.6 (*R*) (*c* 1.52, $CHCl_3$, 82% ee)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 3H, C*H*$_3$), 2.08 (s, 1H, O*H*), 2.50-2.54 (m, 1H, C*H*$_2$), 2.69-2.73 (m, 1H, C*H*$_2$), 5.11-5.17 (m, 2H, C*H*$_2$), 5.58-5.66 (m, 1H, C*H*), 7.25-7.26 (m, 1H, *Ar*), 7.27-7.35 (m, 2H, *Ar*), 7.37-7.56 (m, 2H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.9, 48.4, 73.6, 119.6, 124.7, 126.6, 128.2, 133.6, 147.6; HPLC (DAICEL CHIRALCEL OJ-H, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 10 min (major), t_R = 12 min (minor).

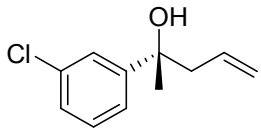
(*R*)-2-(3-Fluorophenyl)pent-4-en-2-ol (3c)



3'-Fluoroacetophenone (12 μL, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 18 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =1/9) to give **3c** (16.0 mg, 89%, 80% ee) as colorless oil.

$[\alpha]_D^{25}$ +40.0 (*c* 0.41, $CHCl_3$, 80% ee) (lit.[2c] $[\alpha]_D^{25}$ −54.9 (*S*) (*c* 1.2, $CHCl_3$, 97% ee)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (s, 3H, C*H*$_3$), 2.14 (s, 1H, O*H*), 2.44-2.52 (m, 1H, C*H*$_2$), 2.63-2.70 (m, 1H, C*H*$_2$), 5.12-5.17 (m, 2H, C*H*$_2$), 5.56-5.61 (m, 1H, C*H*), 6.90-6.95 (m, 1H, *Ar*), 7.17-7.19 (m, 2H, *Ar*), 7.20-7.31 (m, 1H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.9, 48.3, 73.4, 112.0 (d, *J* = 15.0 Hz), 113.3 (d, *J* = 14.1 Hz), 120.3 (d, *J* = 1.7 Hz), 129.6 (d, *J* = 5.6 Hz), 133.2, 150.5 (d, *J* = 4.5 Hz), 161.3, 164.5; HPLC (DAICEL CHIRALCEL OJ-H, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 8.2 min (major), t_R = 8.6 min (minor).

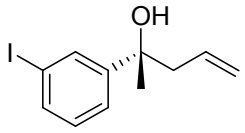
(*R*)-2-(3-Chlorophenyl)pent-4-en-2-ol (3d)



3'-Chloroacetophenone (13 μL, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 48 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =5/95) to give **3d** (13.5 mg, 76%, 76% ee) as colorless oil.

$[\alpha]_D^{25}$ +51.2 (*c* 0.20, $CHCl_3$, 76% ee) (lit.[2b] $[\alpha]_D^{25}$ +41.6 (*R*) (*c* 1.18, $CHCl_3$, 82% ee)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (s, 3H, C*H*$_3$), 2.09 (s, 1H, O*H*), 2.44-2.52 (m, 1H, C*H*$_2$), 2.62-2.69 (m, 1H, C*H*$_2$), 5.13-5.17 (m, 2H, C*H*$_2$), 5.53-5.64 (m, 1H, C*H*), 7.73-7.29 (m, 3H, *Ar*), 7.45 (s, 1H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.9, 48.3, 73.4, 120.0, 123.0, 125.3, 126.8, 129.4, 133.1, 134.2, 149.8; HPLC (DAICEL CHIRALCEL OD-H, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 8.6 min (minor), t_R = 9.3 min (major).

(*R*)-2-(3-Iodophenyl)pent-4-en-2-ol (3e)

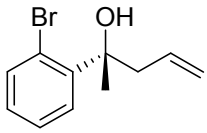


3'-Iodoacetophenone (15 μL, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 18 h, the product was extracted with CH_2Cl_2, and the combined organic layer was

purified through silica gel column chromatography (AcOEt/hexane =5/95) to give **3e** (31.2 mg, 99%, 89% ee) as colorless oil.

$[\alpha]_D^{25}$ +25.6 (*c* 0.41, $CHCl_3$, 89% ee); ^1H NMR (300 MHz, $CDCl_3$) δ 1.51 (s, 3H, C*H*$_3$), 2.13 (s, 1H, O*H*), 2.45-2.50 (m, 1H, C*H*$_2$), 2.61-2.67 (m, 1H, C*H*$_2$), 5.12-5.16 (m, 2H, C*H*$_2$), 5.55-5.64 (m, 1H, C*H*), 7.06 (dd, *J* = 7.5, 7.8 Hz, 2H, *Ar*), 7.37 (d, *J* = 7.5 Hz, 1H, *Ar*), 7.57 (d, *J* = 7.8 Hz, 1H, *Ar*), 7.81 (s, 1H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.9, 48.4, 73.2, 94.6, 120.1, 124.2, 130.0, 133.1, 134.1, 135.7, 150.1; IR (ATR) 3540, 3431, 3073, 3000, 2976, 2929, 1687, 1060, 957, 916, 698 cm^{-1}; MS (ESI) Calcd for $C_{11}H_{13}INaO$ (M+Na) 310.9909; Found 310.9893; HPLC (DAICEL CHIRALPAK IA, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 8.9 min (major), t_R = 9.7 min (minor).

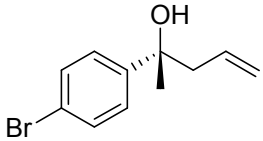
(*R*)-2-(2-Bromophenyl)pent-4-en-2-ol (3f)



2'-Bromoacetophenone (13 μL, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 48 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =5/95) to give **3f** (9.7 mg, 40%, 59% ee) as colorless oil.

$[\alpha]_D^{25}$ +25.0 (*c* 0.21, $CHCl_3$, 59% ee) (lit.[2d] $[\alpha]_D^{25}$ −35.7 (*S*) (*c* 1.34, $CHCl_3$, 97% ee)); ^1H NMR (300 MHz, $CDCl_3$) δ 1.66 (s, 3H, C*H*$_3$), 2.68 (s, 1H, O*H*), 2.68-2.68 (m, 1H, C*H*$_2$), 3.28-3.32 (m, 1H, C*H*$_2$), 5.11-5.48 (m, 2H, C*H*$_2$), 5.51-5.59 (m, 1H, C*H*), 7.09-7.13 (m, 1H, *Ar*), 7.28-7.33 (m, 1H, *Ar*), 7.60 (d, *J* = 9.0 Hz, 1H, *Ar*), 7.71 (d, *J* = 9.6 Hz, 1H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 27.2, 45.9, 74.6, 119.4, 120.0, 127.4, 128.3, 128.6, 133.6, 135.0, 145.0; HPLC (DAICEL CHIRALPAK AD-3, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 8.1 min (major), t_R = 9.6 min (minor).

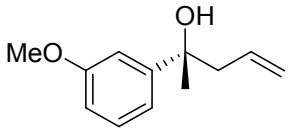
(*R*)-2-(4-Bromophenyl)pent-4-en-2-ol (3g)



4'-Bromoacetophenone (19.9 mg, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 48 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =5/95) to give **3g** (19.1 mg, 78%, 65% ee) as colorless oil.

$[\alpha]_D^{25}$ +14.8 (*c* 0.30, $CHCl_3$, 65% ee) (lit.[2d] $[\alpha]_D^{25}$ −53.6 (*S*) (*c* 1.5, $CHCl_3$, 97% ee)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 3H, C*H*$_3$), 2.06 (s, 1H, O*H*), 2.43-2.51 (m, 1H, C*H*$_2$), 2.61-2.68 (m, 1H, C*H*$_2$), 5.11-5.15 (m, 2H, C*H*$_2$), 5.52-5.63 (m, 1H, C*H*), 7.31 (d, *J* = 8.7 Hz, 2H, *Ar*), 7.45 (d, *J* = 8.7 Hz, 2H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.9, 48.3, 73.4, 120.0, 120.6, 126.7, 131.2, 133.2, 146.7; HPLC (DAICEL CHIRALCEL OJ-H, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 12.0 min (major), t_R = 13.5 min (minor).

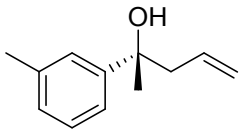
(*R*)-2-(3-Methoxyphenyl)pent-4-en-2-ol (3h)



3'-Methoxyacetophenone (14 μL, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 48 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =5/95) to give **3h** (17.6 mg, 92%, 74% ee) as colorless oil.

$[\alpha]_D^{25}$ +40.1 (*c* 0.41, $CHCl_3$ 74% ee) (lit.[2a] $[\alpha]_D^{25}$ +44.8 (*R*) (*c* 1.02, $CHCl_3$, 93% ee)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (s, 3H, C*H*$_3$), 2.10 (s, 1H, O*H*), 2.45-2.52 (m, 1H, C*H*$_2$), 2.65-2.72 (m, 1H, C*H*$_2$), 5.82 (s, 3H, C*H*$_3$), 5.12-5.17 (m, 2H, C*H*), 5.58-5.64 (m, 1H, C*H*), 6.77-6.99 (m, 1H, *Ar*), 7.01-7.03 (m, 2H, *Ar*), 7.25-7.29 (m, 1H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 28.8, 48.3, 73.6, 111.0, 111.7, 117.2, 119.5, 192.2, 133.6, 149.5, 159.4; HPLC (DAICEL CHIRALCEL OJ-H, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 14.8 min (major), t_R = 17.5 min (minor).

(*R*)-2-(3-Methylphenyl)pent-4-en-2-ol (3i)

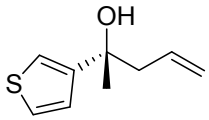


3'-Methylacetophenone (14 μL, 0.10 mmol) and allyl bromide (26 μL, 0.3 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 18 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =5/95) to give **3i** (14.0 mg, 80%, 84% ee), as colorless oil.

$[\alpha]_D^{25}$ +39.6 (*c* 0.19, $CHCl_3$, 84% ee) (lit.[2a] $[\alpha]_D^{25}$ +34.1 (*R*) (*c* 0.86, $CHCl_3$, 51% ee)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 3H, C*H*$_3$), 2.06 (s, 1H, O*H*), 2.46 (s, 3H, C*H*$_3$), 2.48-2.53 (m, 1H, C*H*$_2$), 2.65-2.72 (m, 1H, C*H*$_2$), 5.12-5.17 (m, 2H, C*H*), 5.56-5.69 (m, 1H, C*H*), 7.06 (s, 1H, *Ar*), 7.22-7.27 (m, 3H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6, 28.8, 48.4, 73.6, 119.4, 121.8, 125.5, 127.3, 128.1, 133.8,

137.7, 147.6; HPLC (DAICEL CHIRALCEL OJ-H, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 7.7 min (major), t_R = 8.8 min (minor).

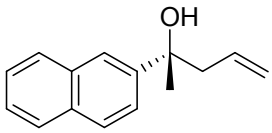
(*R*)-2-(Thiophen-3-yl)pent-4-en-2-ol (3j)



3-Acetylthiophen (12.6 mg, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 24 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =5/95) to give **3j** (15.2 mg, 90%, 55% ee) as colorless oil.

$[\alpha]_D^{25}$ +20.3 (*c* 0.24, $CHCl_3$ 55% ee) (lit.[2d] $[\alpha]_D^{25}$ −49.4 (*S*) (*c* 0.99, $CHCl_3$, 99% ee)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 3H, C*H*$_3$), 2.08 (s, 1H, O*H*), 2.46-2.53 (m, 1H, C*H*$_2$), 2.61-2.68 (m, 1H, C*H*$_2$), 5.12-5.16 (m, 2H, C*H*), 5.63-5.68 (m, 1H, C*H*), 7.07 (s, 1H, *Ar*), 7.16-7.17 (m, 1H, *Ar*), 7.26-7.29 (m, 1H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.5, 48.3, 72.7, 119.4, 119.5, 125.6, 125.9, 133.6; HPLC (DAICEL CHIRALCEL OD-3, hexane:*i*PrOH = 99:1, 0.8 mL/min) t_R = 20.0 min (major), t_R = 21.5 min (minor).

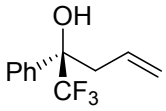
(*R*)-2-(Naphthalen-2-yl)pent-4-en-2-ol (3k)



2-Acetonaphthone (17.0 mg, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 24 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =5/95) to give **3k** (19.9 mg, 94%, 71% ee) as colorless oil.

$[\alpha]_D^{25}$ +47.2 (*c* 0.54, $CHCl_3$, 71% ee) (lit.[2b] $[\alpha]_D^{25}$ −39.8 (*S*) (*c* 0.92, $CHCl_3$, 84% ee)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 3H, C*H*$_3$), 2.20 (s, 1H, O*H*), 2.59-2.62 (m, 1H, C*H*$_2$), 2.80-2.83 (m, 1H, C*H*$_2$), 5.10-5.19 (m, 2H, C*H*), 5.60-5.63 (m, 1H, C*H*), 7.48-7.55 (m, 3H, *Ar*), 7.84-7.92 (m, 4H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 30.0, 48.4, 73.8, 119.6, 121.7, 123.2, 123.5, 125.7, 126.1, 1127.5, 147.9, 128.1, 132.2, 133.2, 133.6, 145.0; HPLC (DAICEL CHIRALCEL OJ-H, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 24.2 min (minor), t_R = 26.8 min (major).

(*R*)-1,1,1-Trifluoro-2-phenylpent-4-en-2-ol (3l)

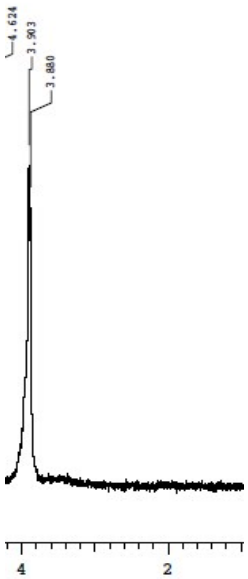


2,2,2-Trifuloroacetophenone (14 μL, 0.10 mmol) and allyl bromide (26 μL, 0.30 mmol) were added to a solution of *t*BuCO-Pybim **4a** (6.9 mg, 0.01 mmol), indium powder (22.8 mg, 0.20 mmol), and sodium iodide (58.4 mg, 0.39 mmol) in pure water (1.0 mL) at 0 °C. After 18 h, the product was extracted with CH_2Cl_2, and the combined organic layer was purified through silica gel column chromatography (AcOEt/hexane =1/9) to give **3l** (16.4 mg, 77%, 86% ee) as colorless oil.

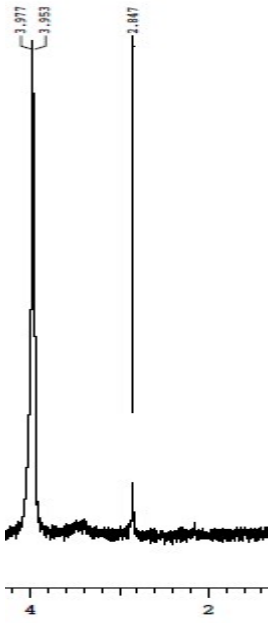
$[\alpha]_D^{25}$ +46.2 (*c* 0,15, Benzene, 86% ee), (lit.[2c] $[\alpha]_D^{25}$ −46.0 (*S*) (*c* 0.34, Benzene, 70% ee)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.61 (s, 1H, O*H*), 2.83-2.88 (m, 1H, CH_2), 2.96-3.02 (m, 1H, CH_2), 5.21-5.28 (m, 2H, C*H*), 5.49-5.60 (m, 1H, C*H*), 7.25-7.41 (m, 3H, *Ar*), 7.56-7.59 (m, 2H, *Ar*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 40.3, 122.1, 123.4, 126.4, 127.2, 128.4, 128.6, 130.4, 163.8; HPLC (DAICEL CHIRALCEL OJ-H, hexane:*i*PrOH = 97:3, 1.0 mL/min) t_R = 15.8 min (major), t_R = 19.9 min (minor).

^{1}H NMR analysis for reaction mixture:

In order to clarify the allylindium intermediate, we investigated NMR analysis. ^{1}H NMR spectrum of the ally bromide in D_2O showed a peak on 3.90 ppm (**spectrum 1**), and the mixture of allyl bromide, indium, NaI and pybim **2a** in D_2O showed new peak on 2.85 ppm (**spectrum 2**).



spectrum 1



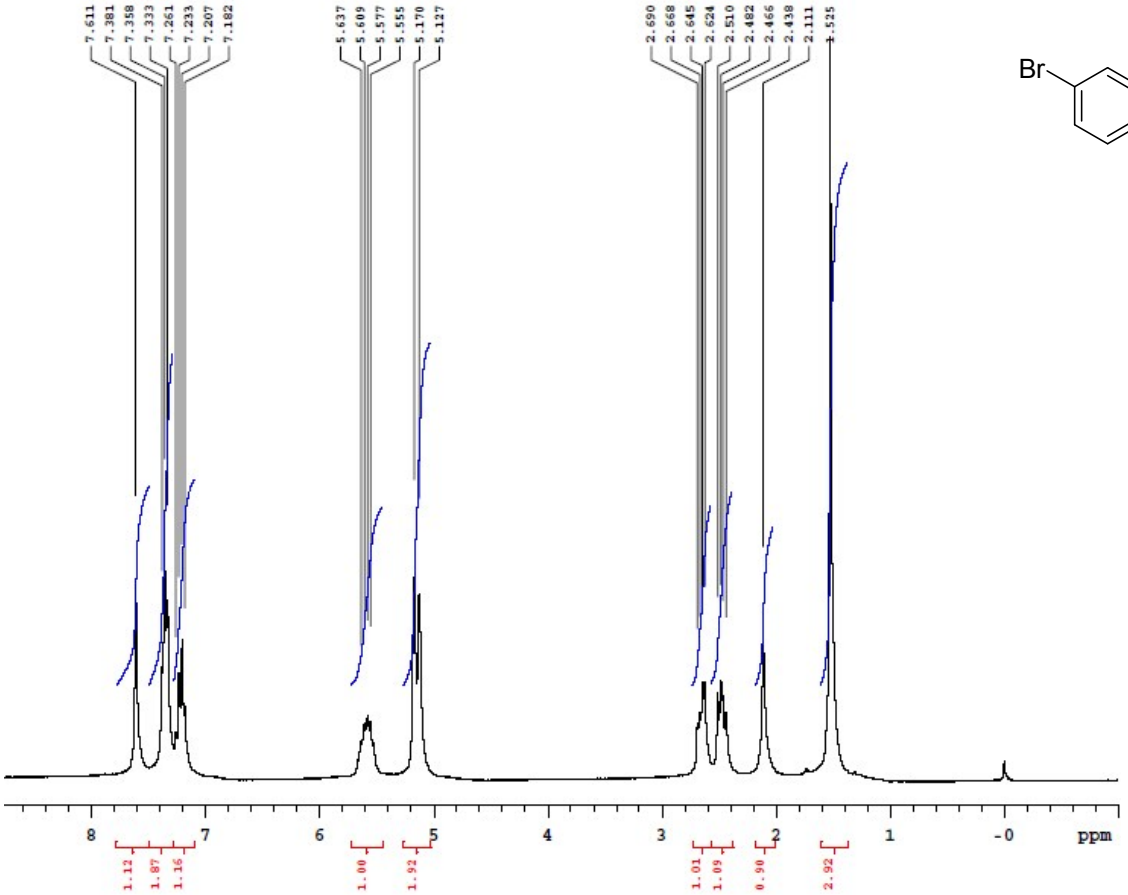
spectrum 2

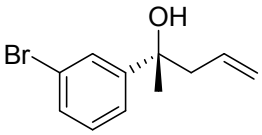
References

1) a) S. Nakamura, M. Ohara, Y. Nakamura, N. Shibata, T. Toru, *Chem. Eur. J.* **2010**, *16*, 2360–2362; b) M. Ohara, Y. Hara, T. Ohnuki, S. Nakamura, *Chem. Eur. J.* **2014**, *20*, 8848–8851.

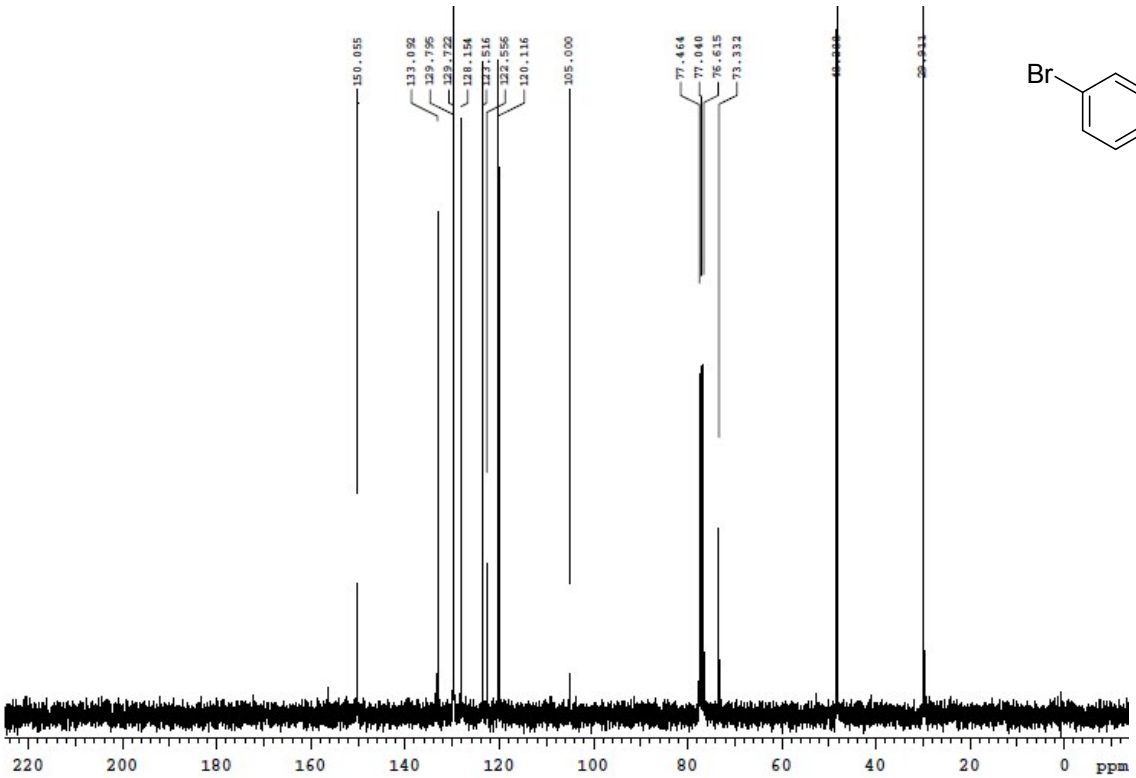
2) a) X.-R. Huang, C. Chen, G.-H. Lee, S.-M. Peng, *Adv. Synth. Catal.* **2009**, *351*, 3089–3095; b) Y.-C. Teo, J.-D. Goh, T.-P. Loh, *Org. Lett.* **2005**, *7,* 2743–2745; c) T.-P. Loh, J.-R. Zhou X.-R. Li, *Tetrahedron Lett.* **1999***, 40*, 9333–9336; d) D. S. Barnett, P. N. Moquist, S. E. Schaus, *Angew. Chem. Int. Ed.* **2009***, 48*, 8679–8682.

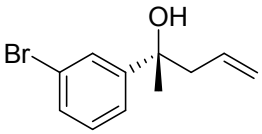
^{1}H and ^{13}C NMR



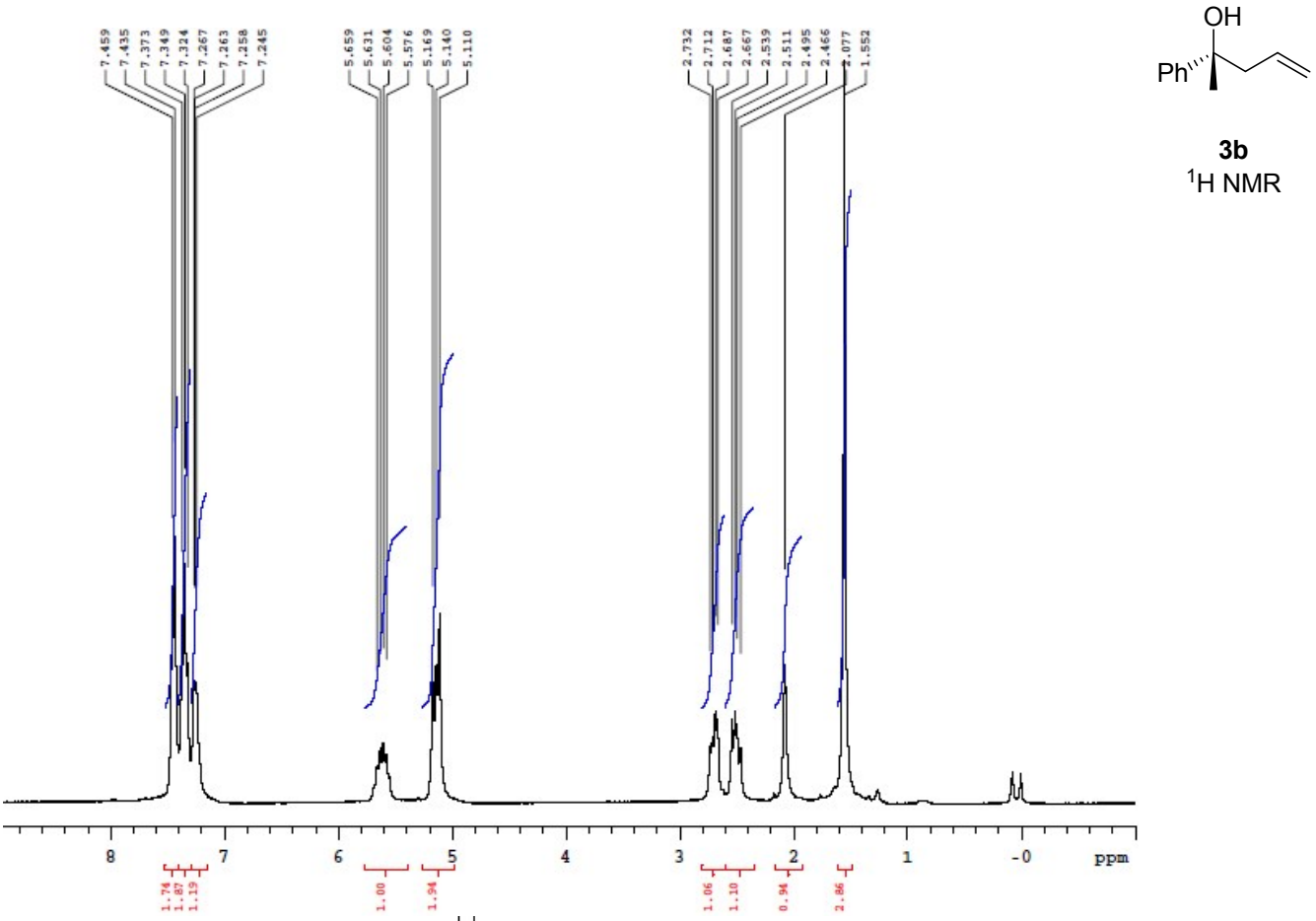


3a
^{1}H NMR

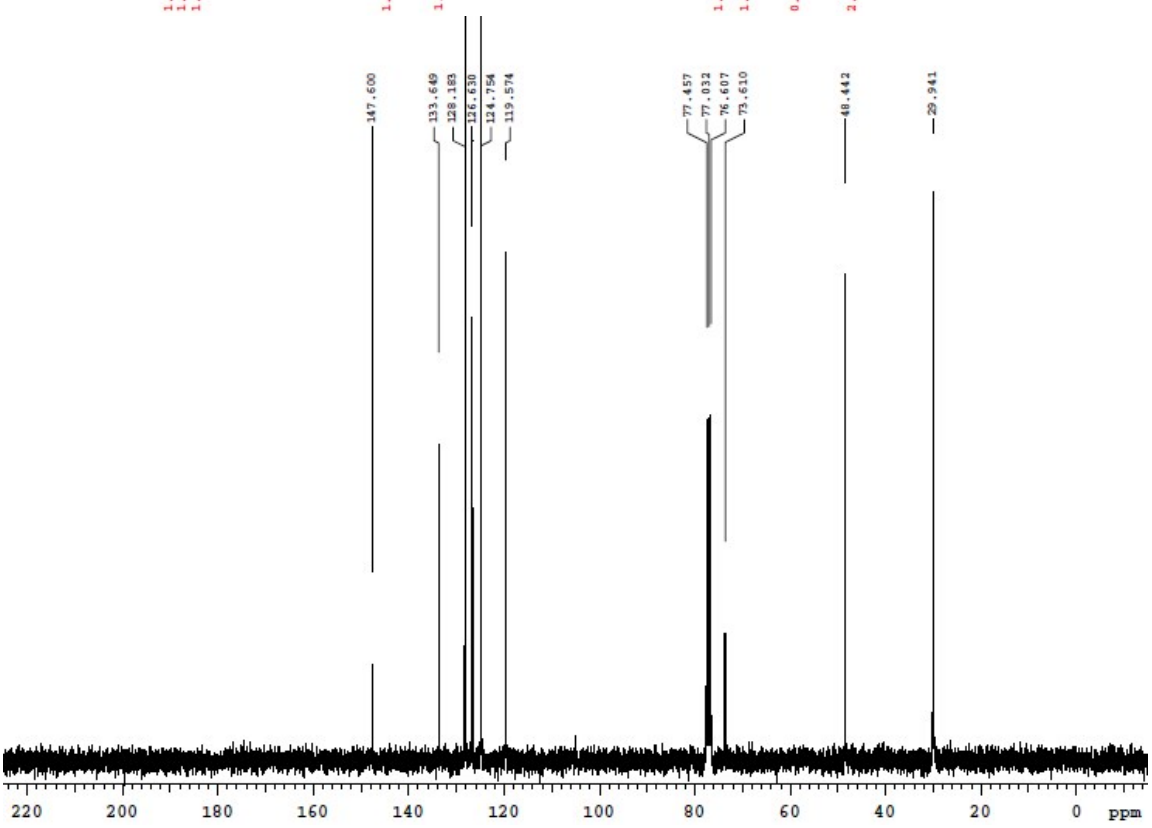


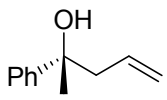


3a
^{13}C NMR



3b
^{1}H NMR





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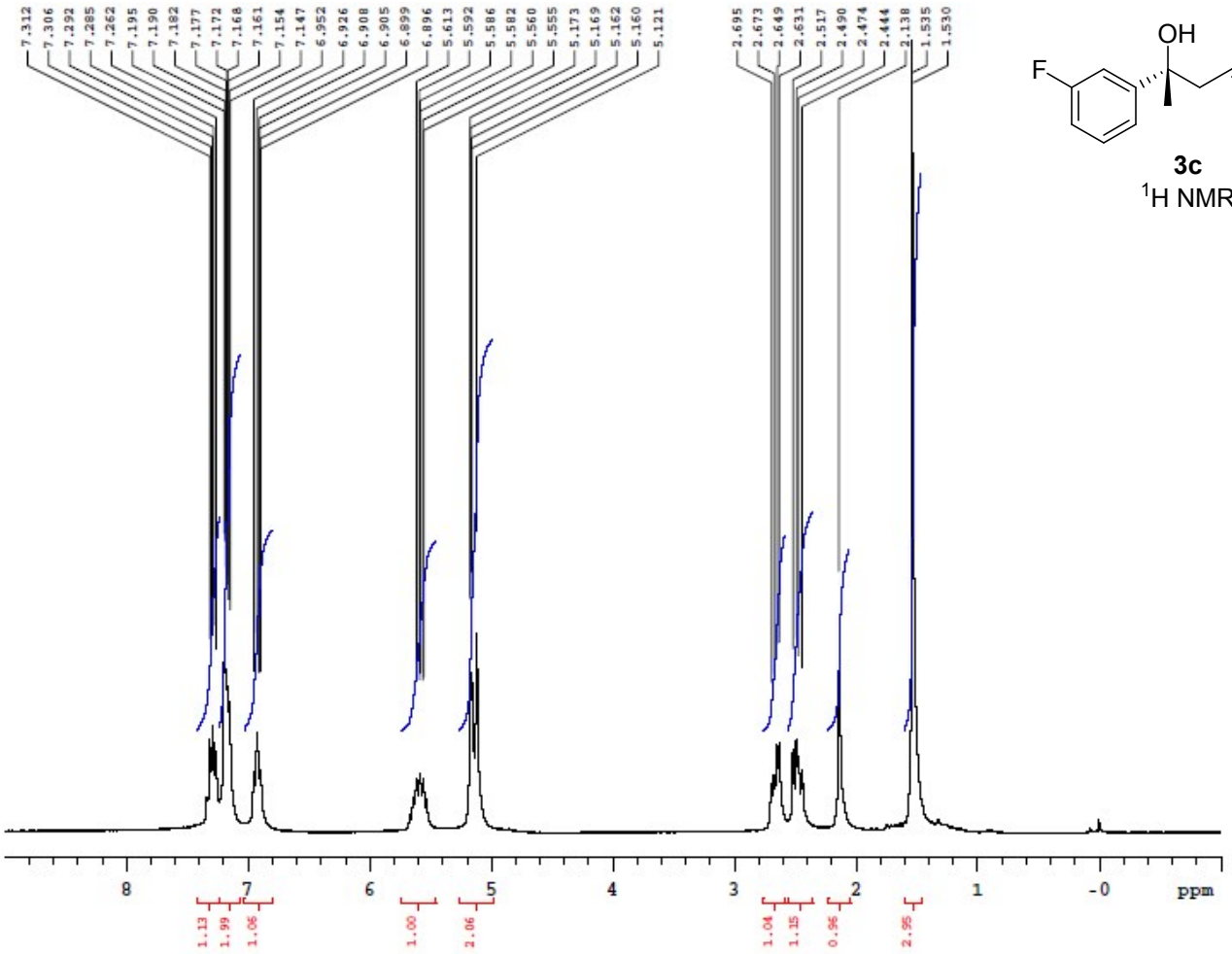
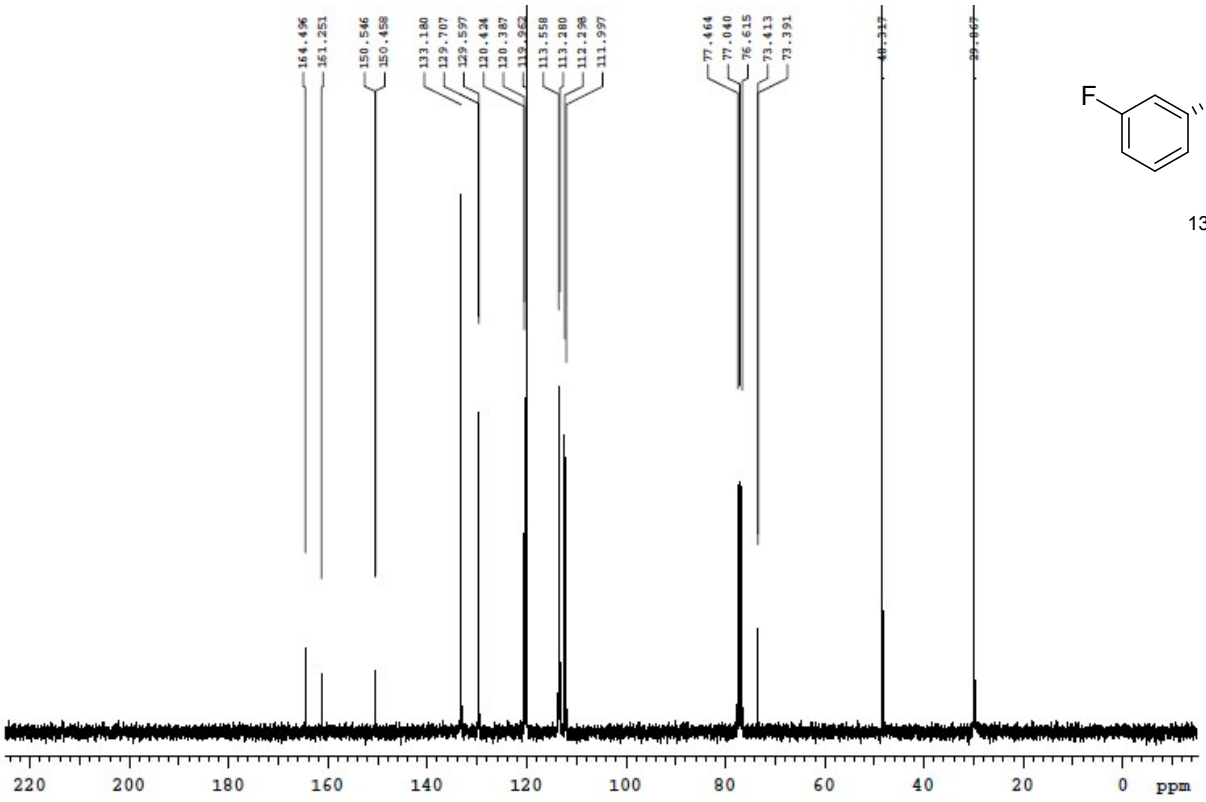
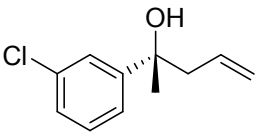
^{13}C NMR



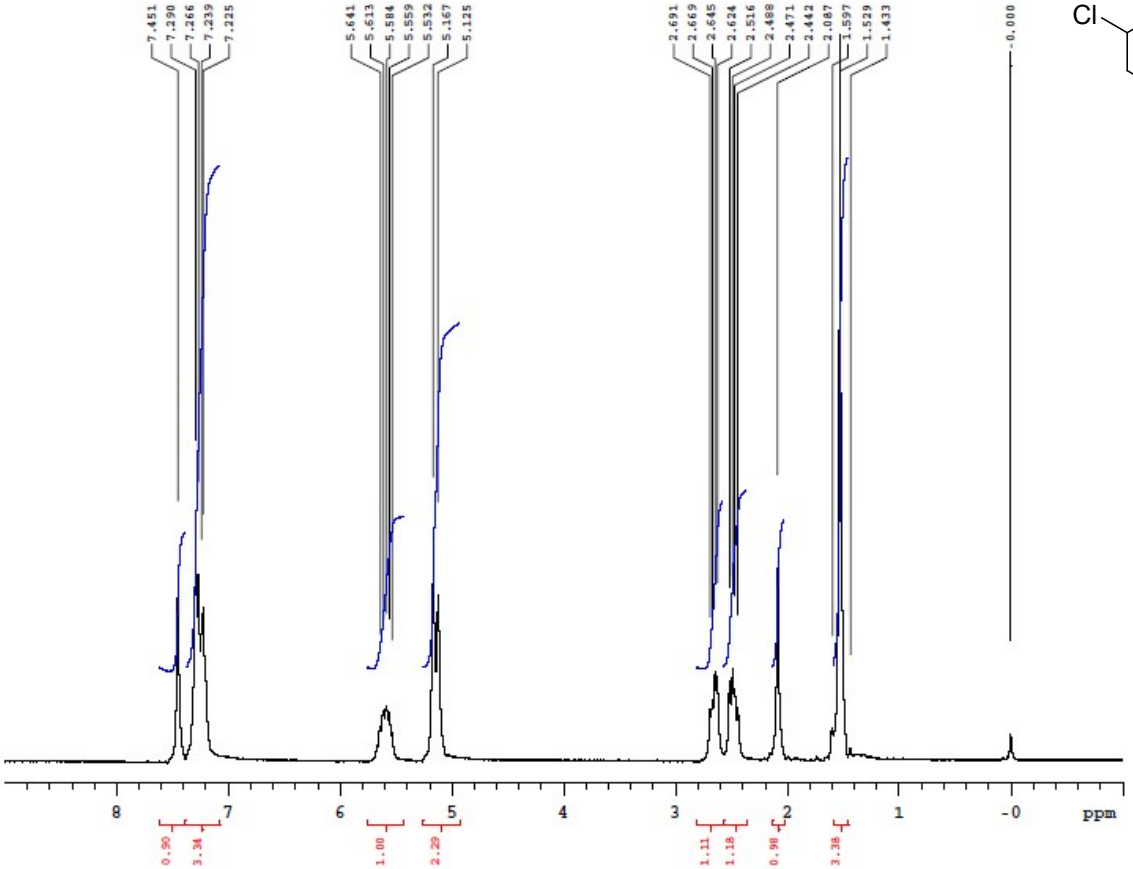
3c
^{1}H NMR

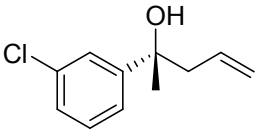


3c
^{13}C NMR



3d
^{1}H NMR





3d
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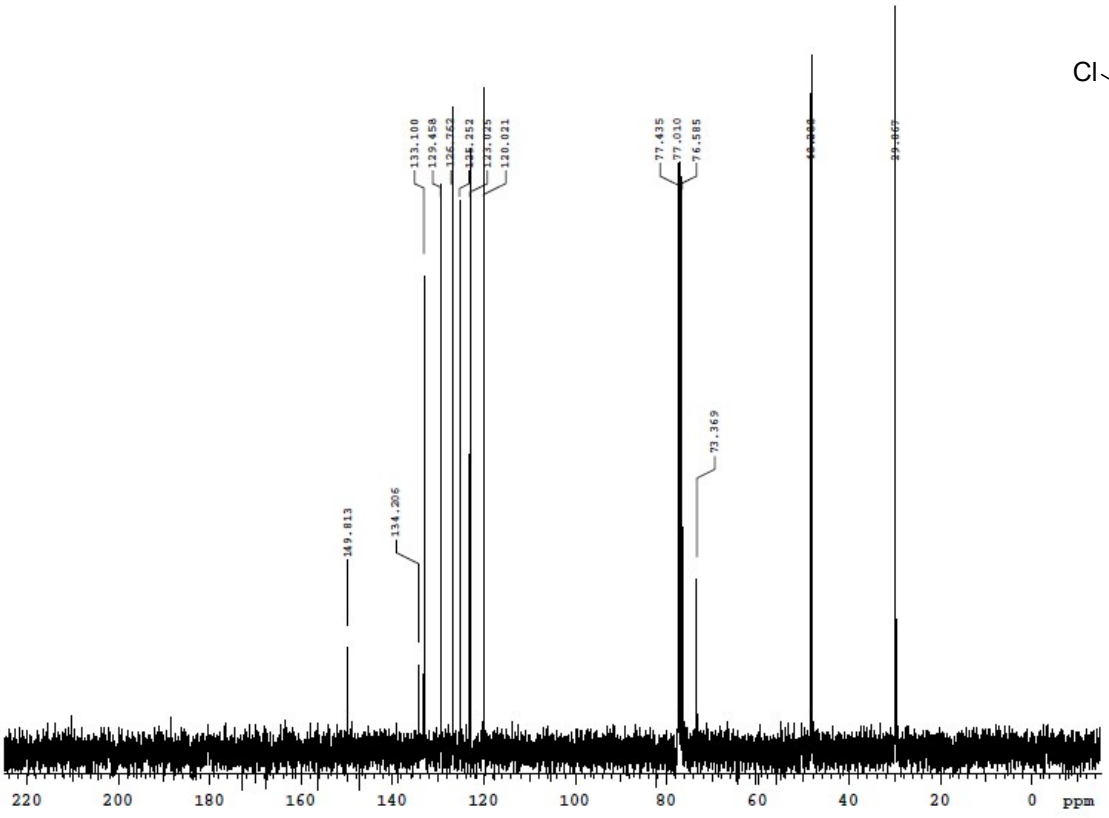
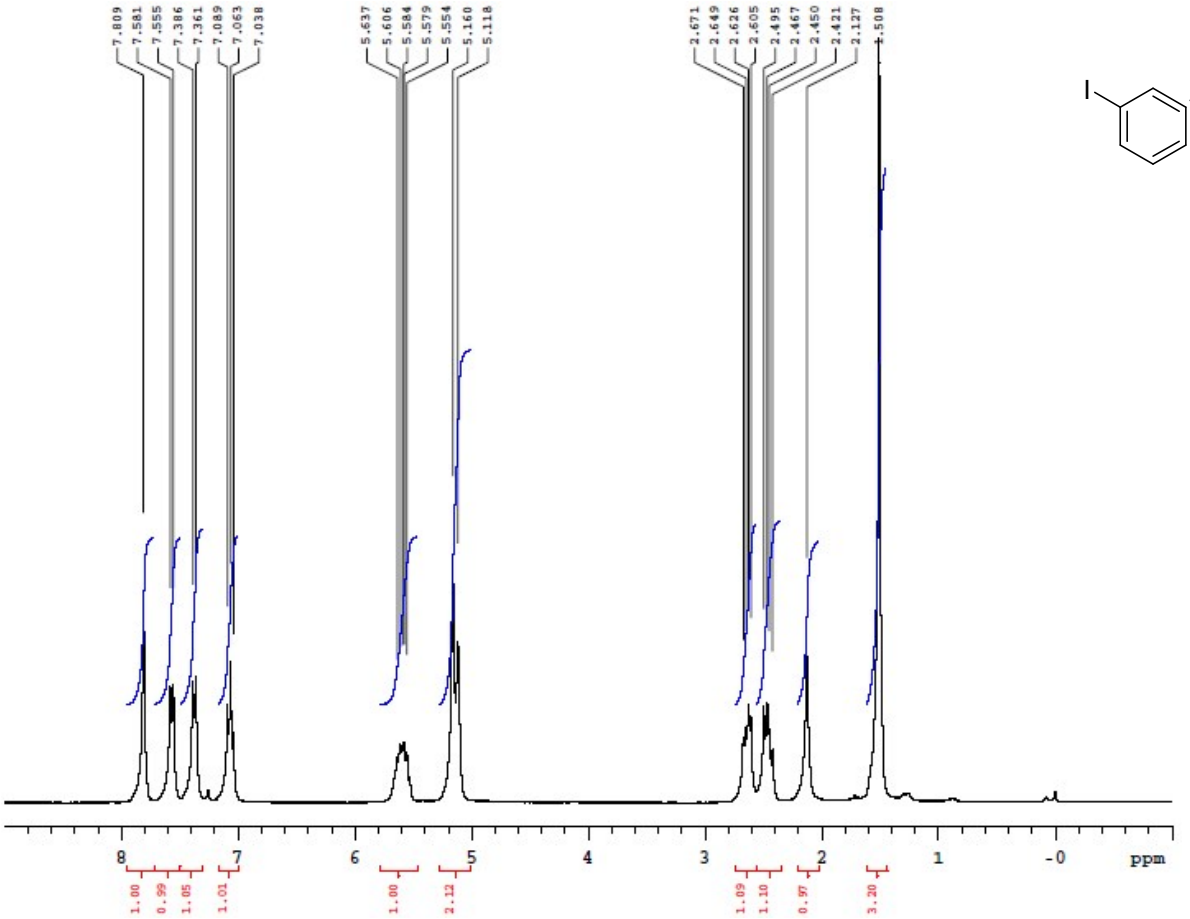
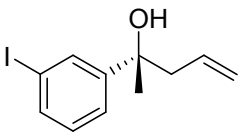
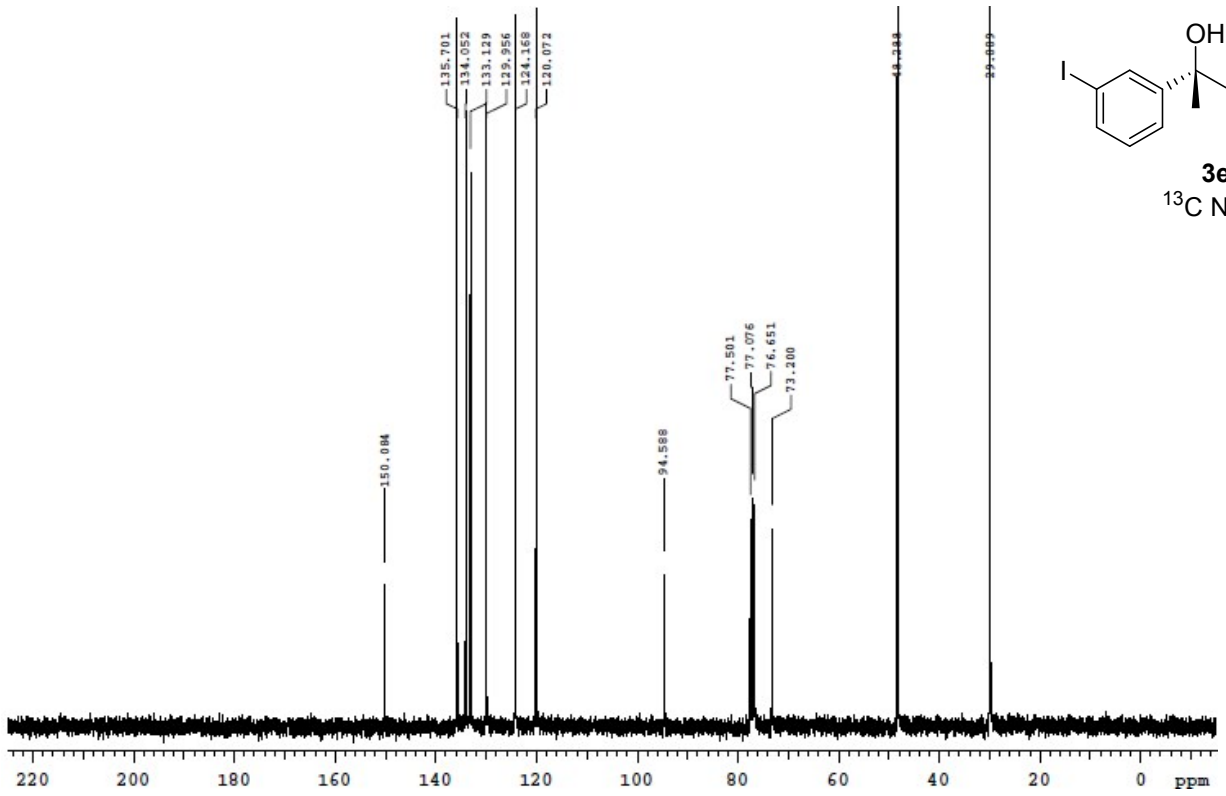


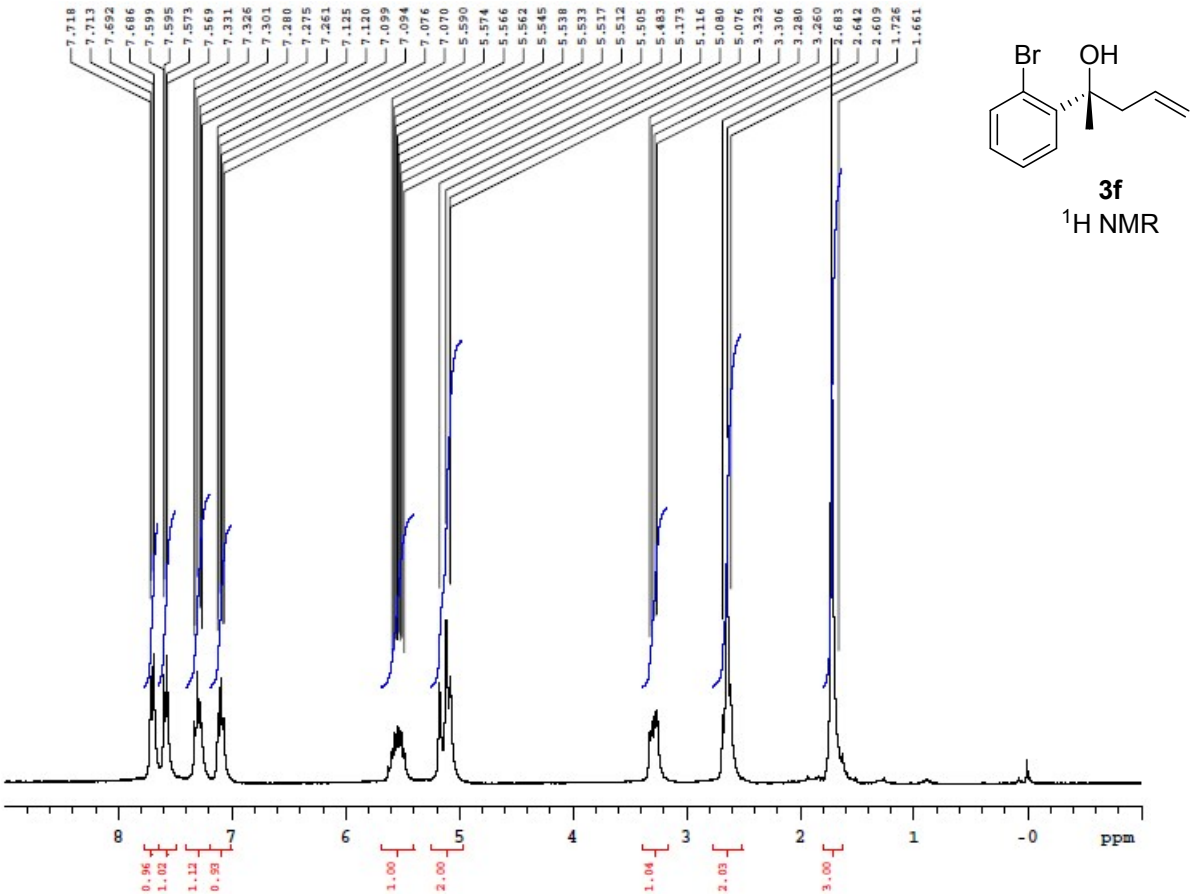




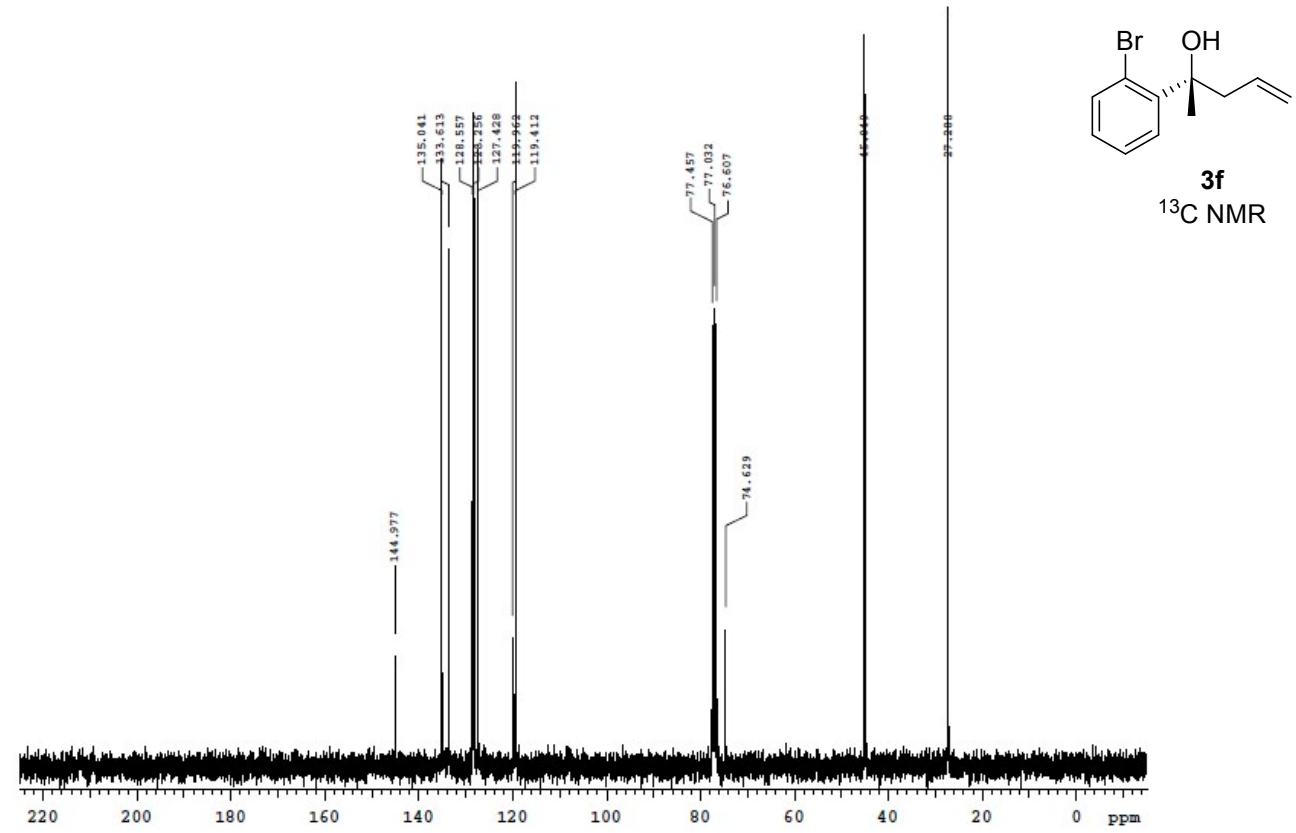
3e
^{1}H NMR



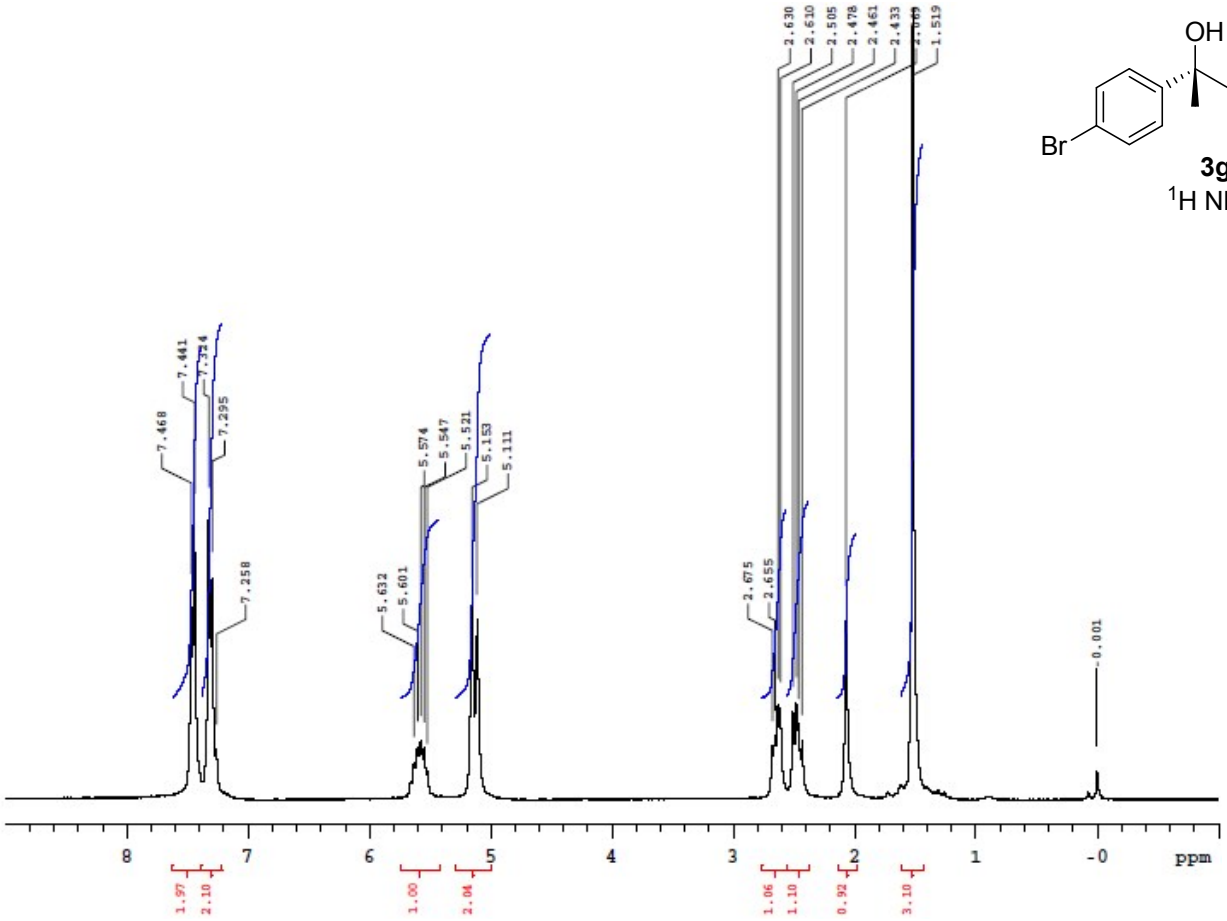
3e
^{13}C NMR

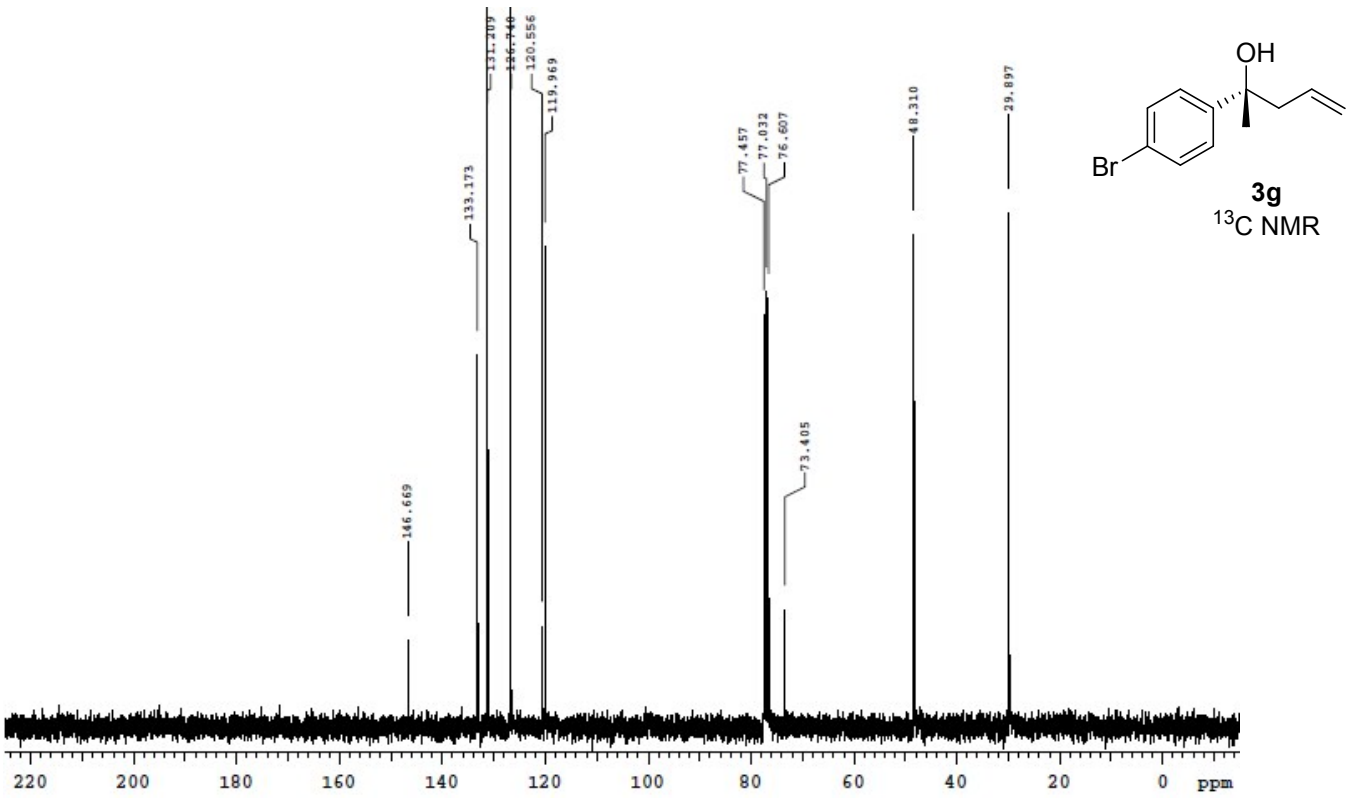


3f
^{1}H NMR



3f
^{13}C NMR


OH
Br
3g
1H NMR
2.630
2.610
2.505
2.478
2.461
2.433
1.519
7.468
7.441
7.324
7.295
7.258
5.632
5.601
5.574
5.547
5.521
5.153
5.111
2.675
2.655
-0.001
8
7
6
5
4
3
2
1
-0
ppm
1.97
2.10
1.00
2.04
1.06
1.10
0.92
3.10


OH
Br
3g
13C NMR
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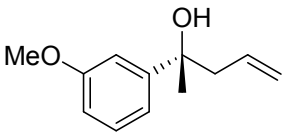
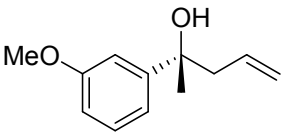
133.173
131.209
126.740
120.556
119.969
77.457
77.032
76.607
73.405
48.310
29.897
220
200
180
160
140
120
100
80
60
40
20
0
ppm



3h
^{1}H NMR



3h
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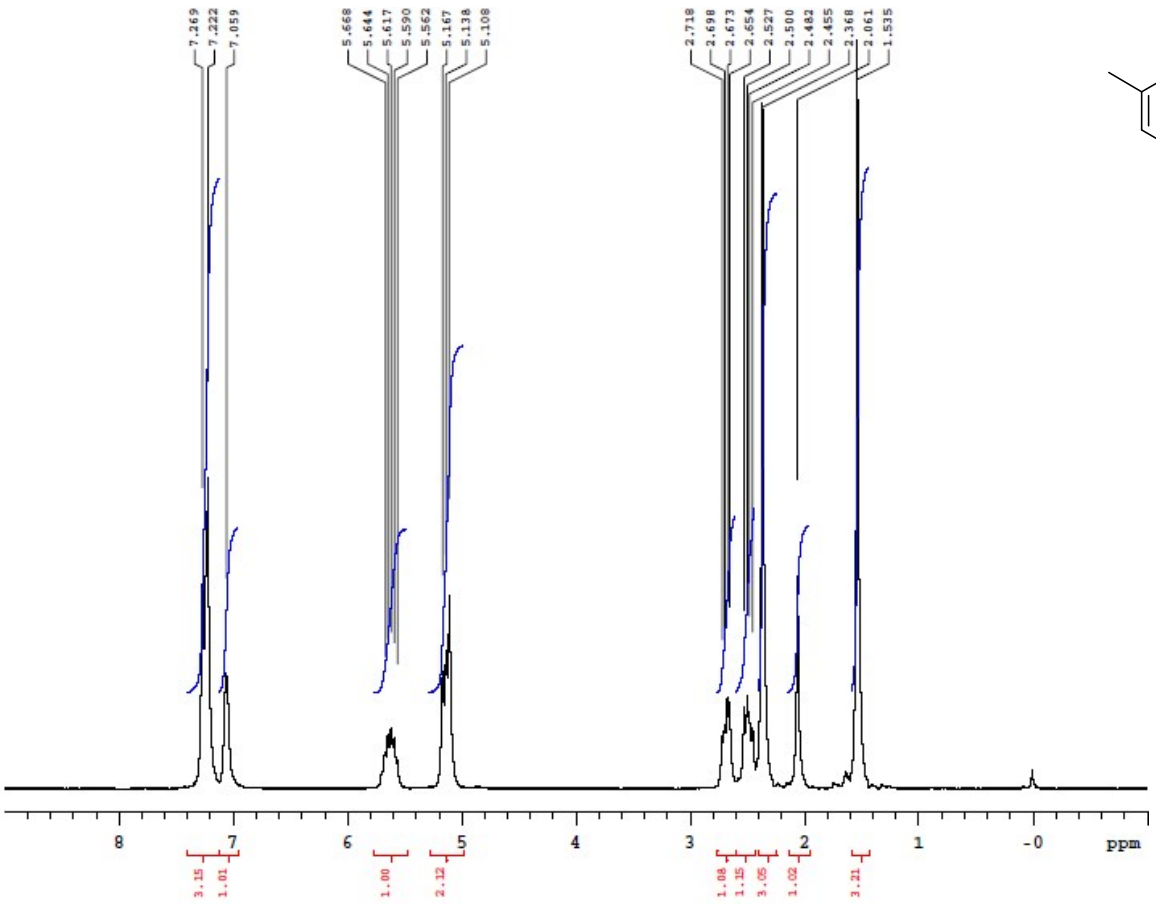
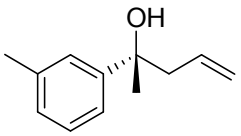
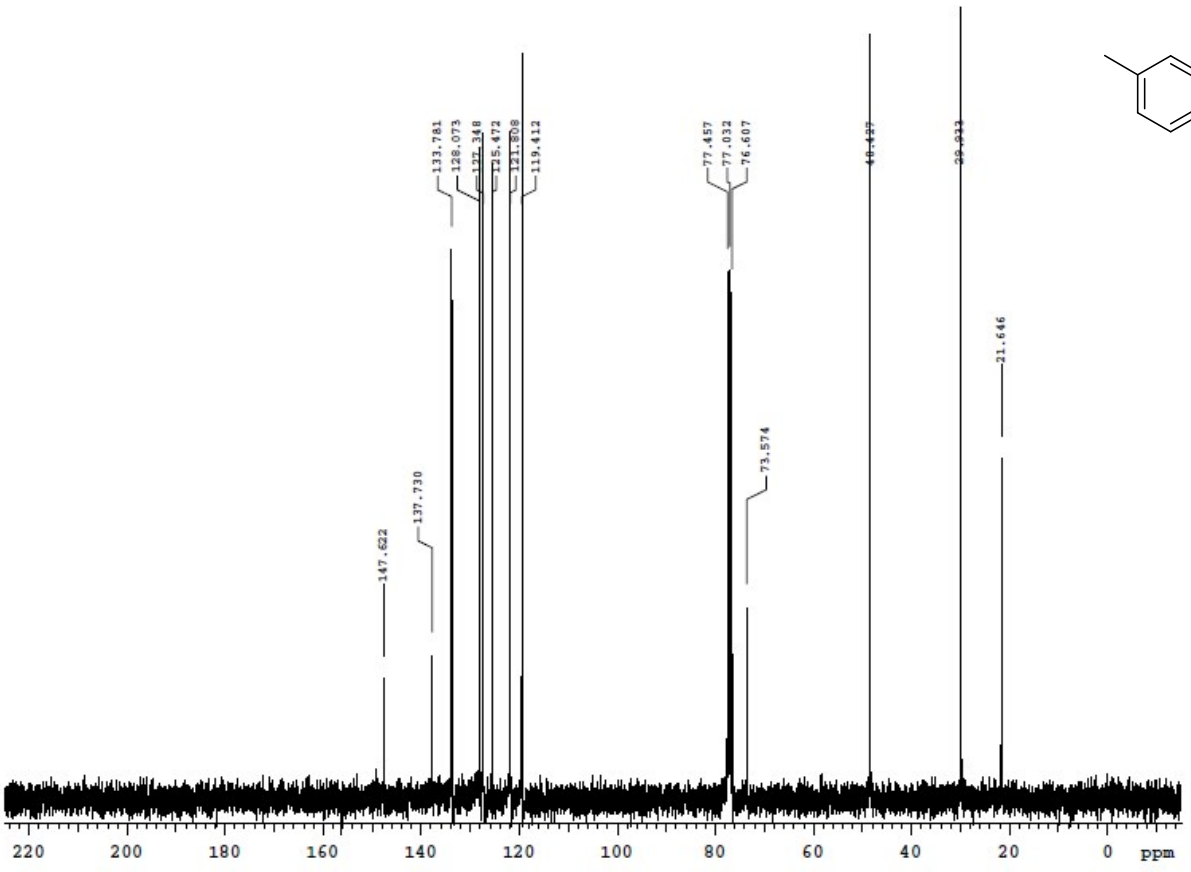
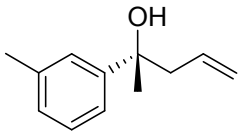


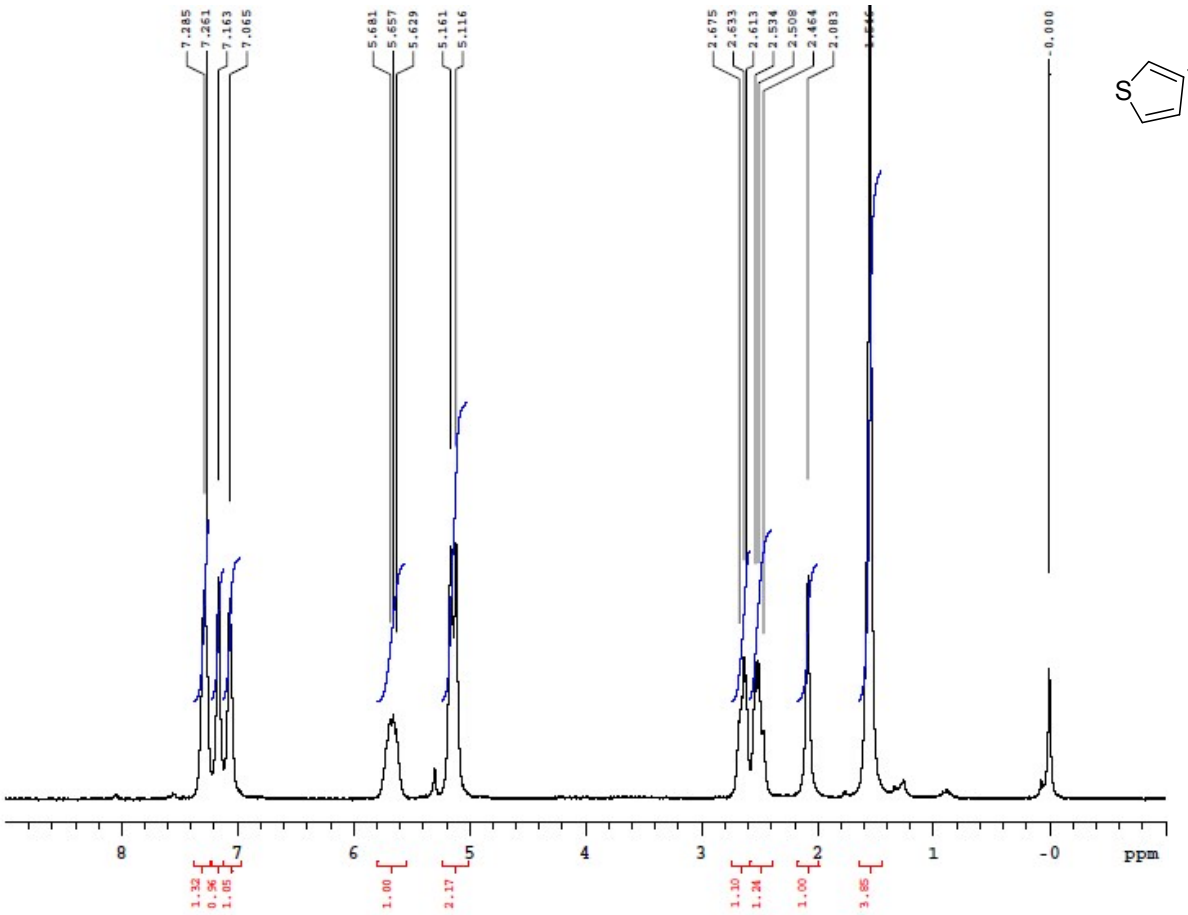


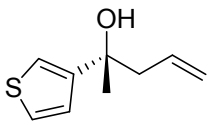
3i
^{1}H NMR





3i
^{13}C NMR





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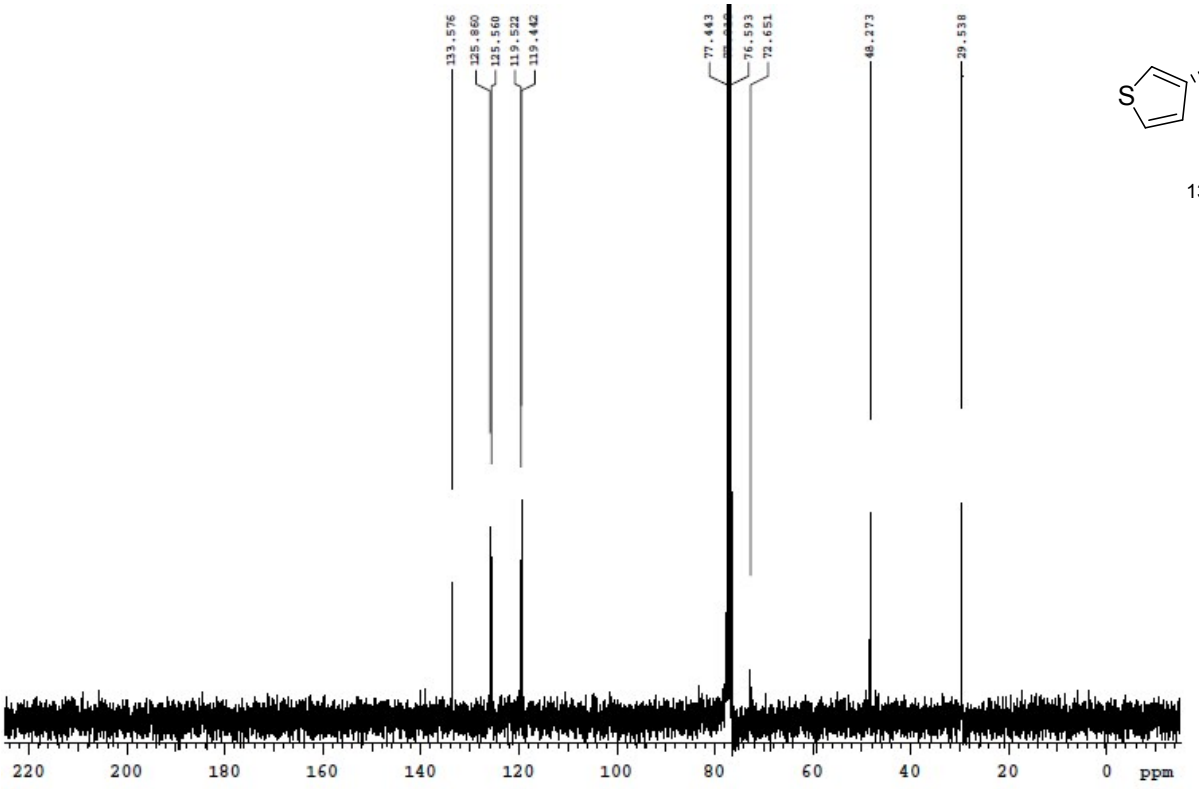

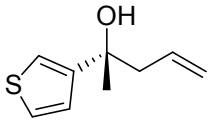

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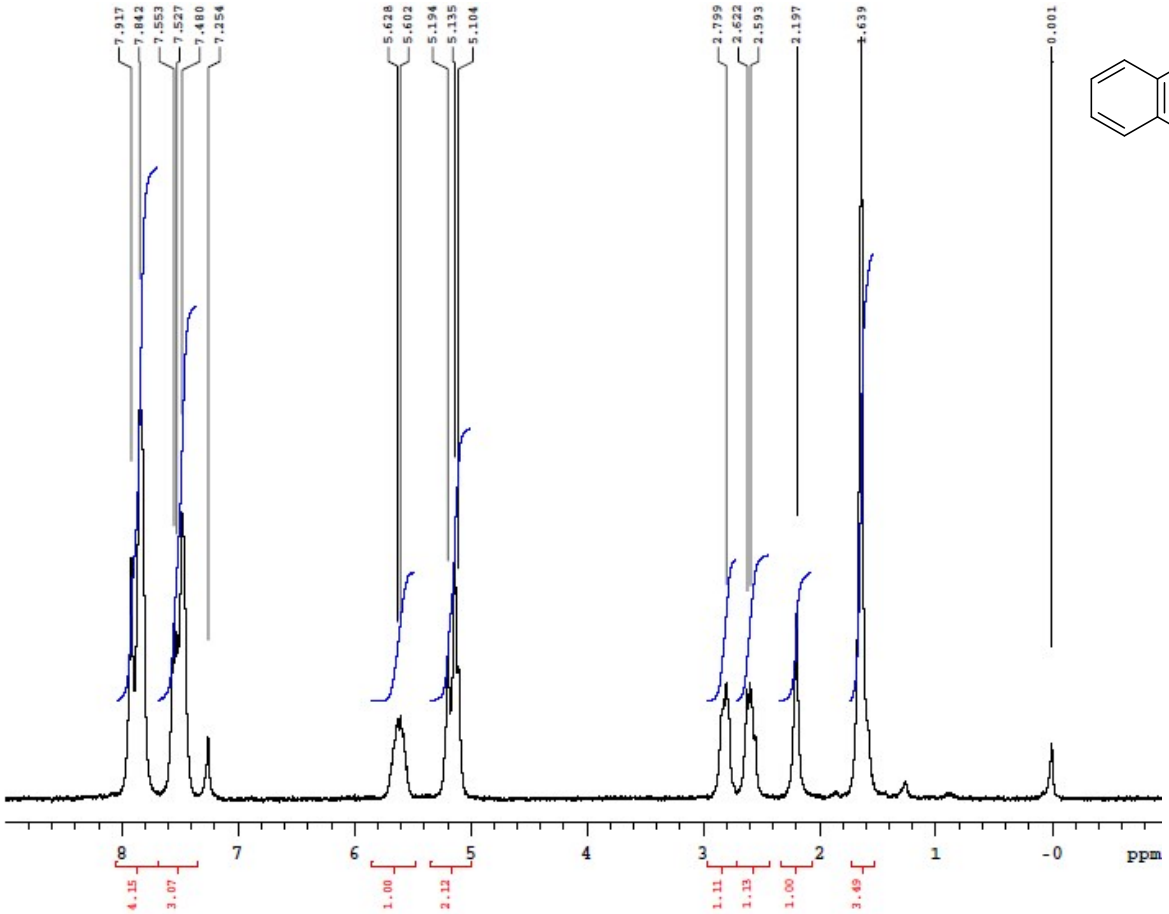
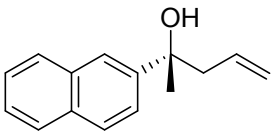
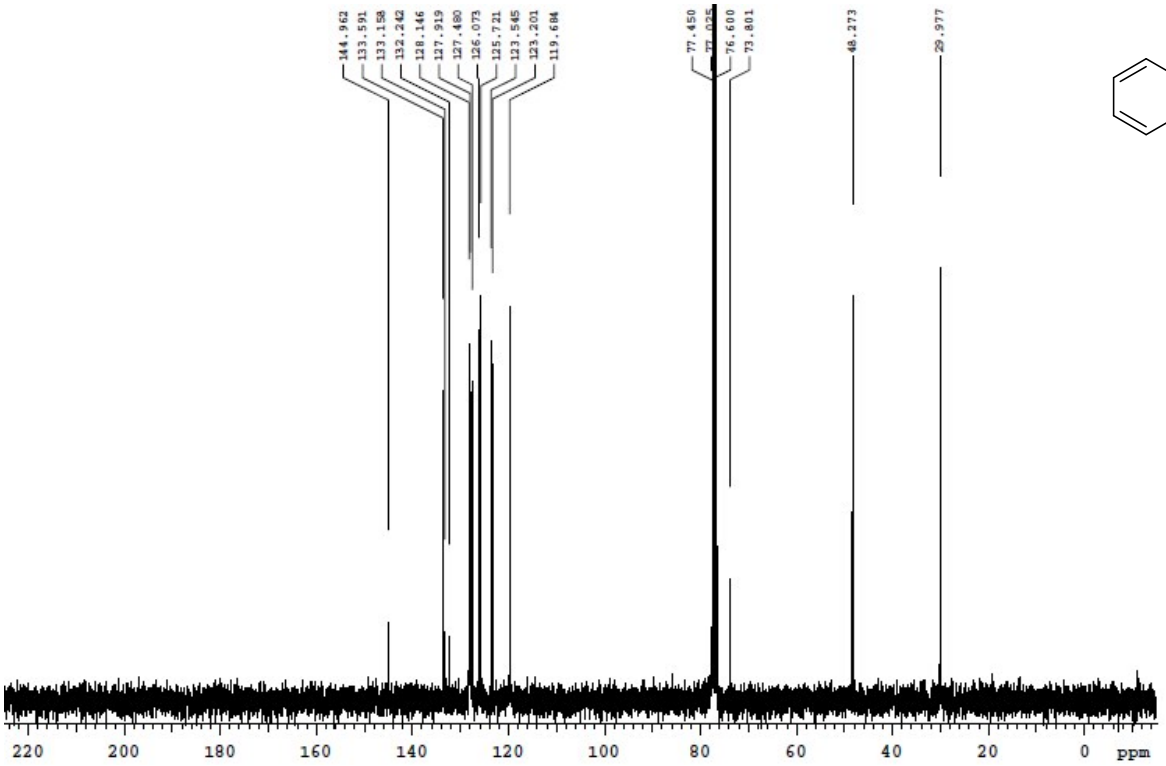
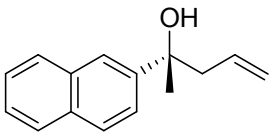




3k
^{1}H NMR





3k
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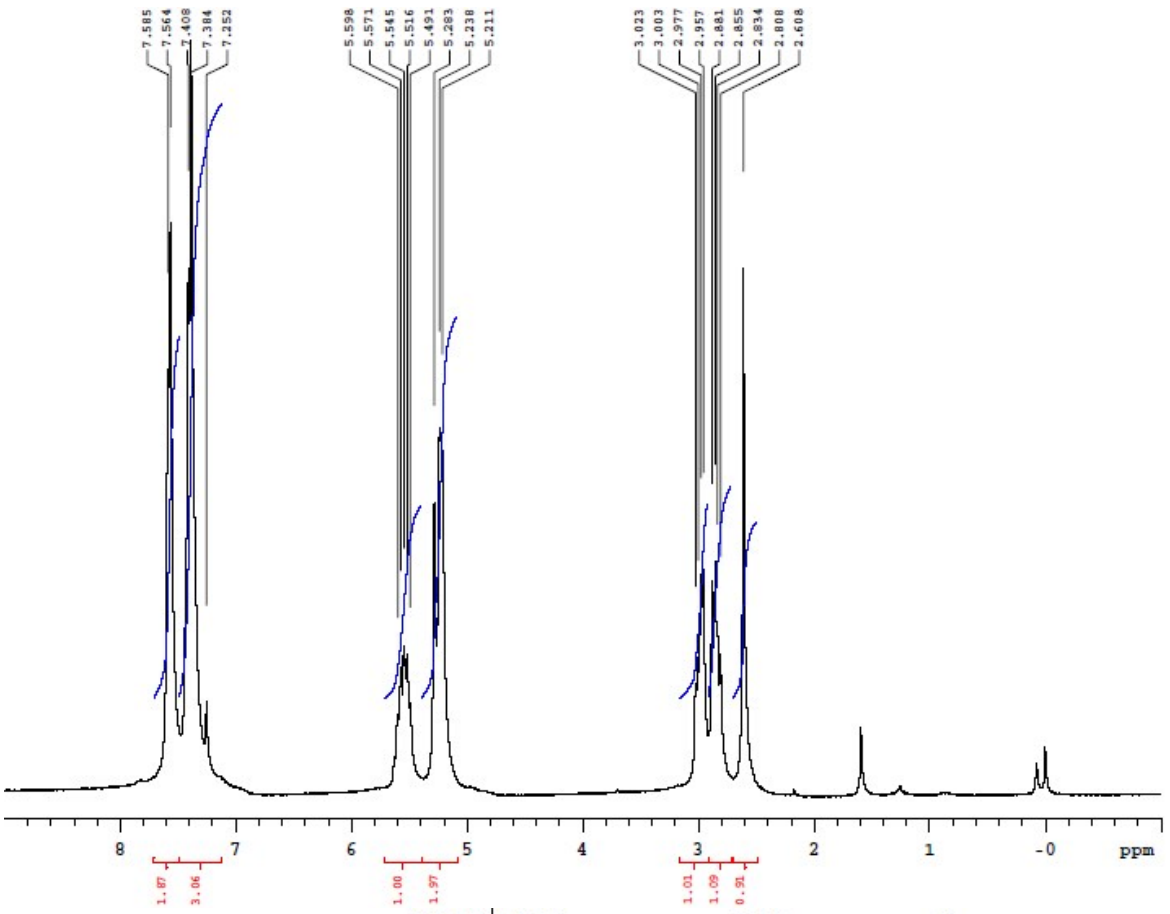
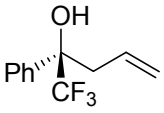
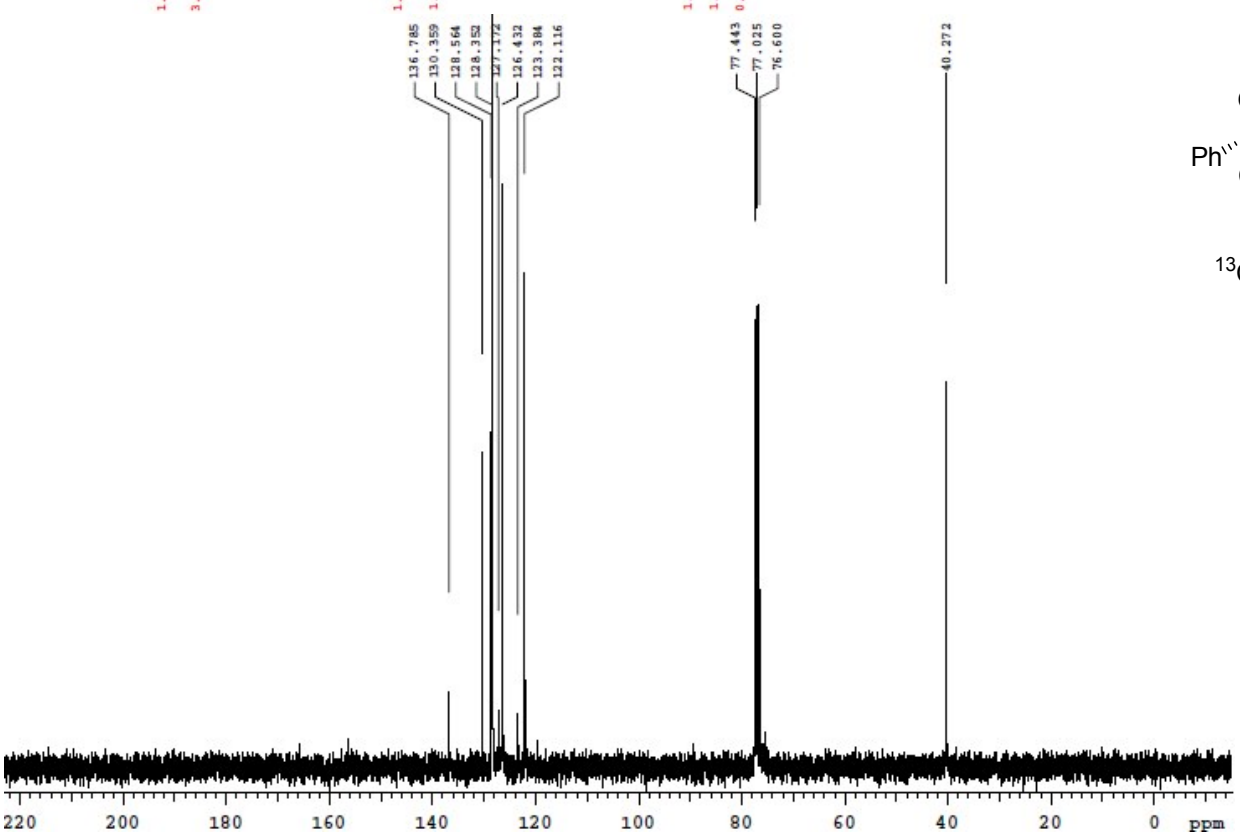
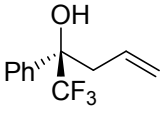




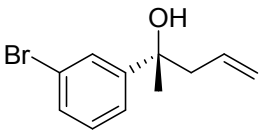
3l
^{1}H NMR



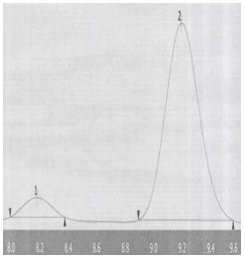


3l
^{13}C NMR

HPLC analysis

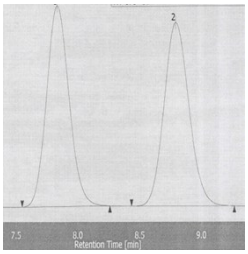


3a-HPLC
DAICEL CHIRALCEL OD-H
hexane:*i*PrOH = 97:3, 1.0 mL/min



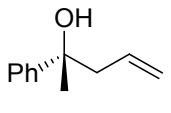
(*R*)-3a

Peak	tR (min)	Area (%)
1	8.2	7.1
2	9.2	92.9

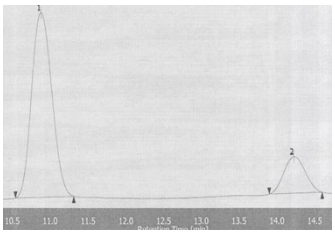


Racemic-3a

Peak	tR (min)	Area (%)
1	7.8	49.9
2	8.8	50.1

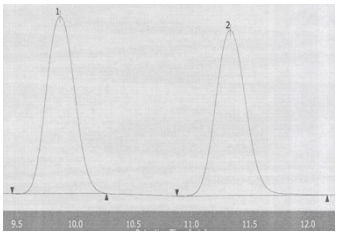


3b-HPLC
DAICEL CHIRALCEL OJ-H
hexane:*i*PrOH = 97:3, 1.0 mL/min



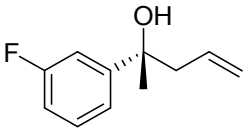
(*R*)-3b

Peak	tR (min)	Area (%)
1	10.9	82.8
2	14.2	17.2

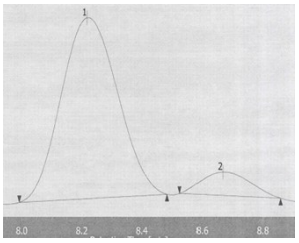


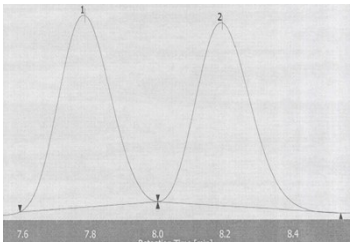
Racemic-3b

Peak	tR (min)	Area (%)
1	9.9	50.1
2	11.3	49.9



3c-HPLC
DAICEL CHIRALCELOJ-H
hexane:*i*PrOH = 97:3, 1.0 mL/min

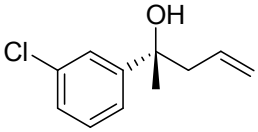




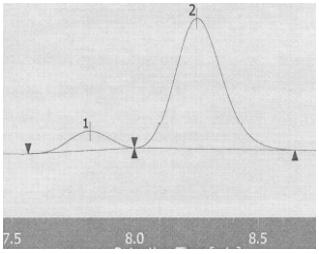
(*R*)-3c **Racemic-3c**

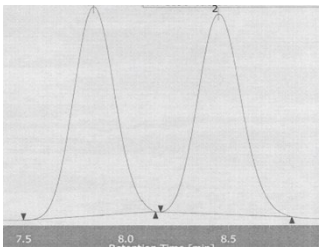
Peak	tR (min)	Area (%)
1	8.2	90.1
2	8.6	9.9

Peak	tR (min)	Area (%)
1	7.8	50.2
2	8.2	49.8



3d-HPLC
DAICEL CHIRALCEL OD-H
hexane:*i*PrOH = 97:3, 1.0 mL/min

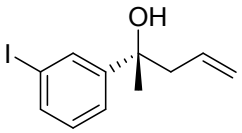




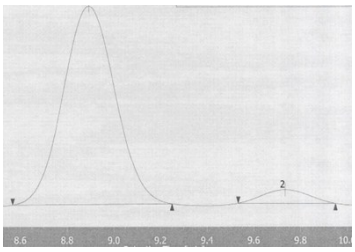
(*R*)-3d **Racemic-3d**

Peak	tR (min)	Area (%)
1	7.8	10.9
2	8.3	89.1

Peak	tR (min)	Area (%)
1	7.8	49.9
2	8.5	50.1

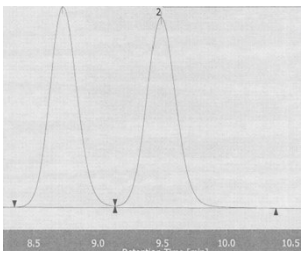


3e-HPLC
DAICEL CHIRALPAK AI
hexane:*i*PrOH = 97:3, 1.0 mL/min



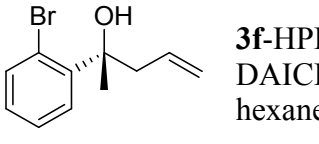
(*R*)-3e

Peak	tR (min)	Area (%)
1	8.9	94.3
2	9.7	5.7

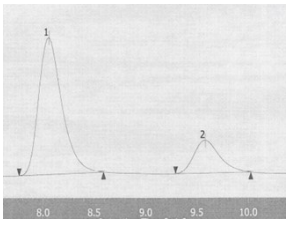


Racemic-3e

Peak	tR (min)	Area (%)
1	8.7	49.9
2	9.5	50.1

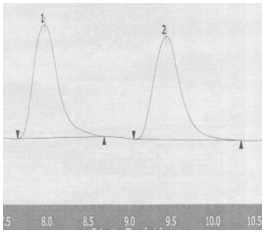


3f-HPLC
DAICEL CHIRALPAK AD-3
hexane:*i*PrOH = 97:3, 1.0 mL/min



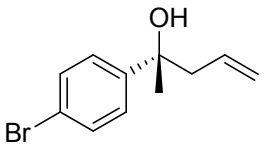
(*R*) 3f

Peak	tR (min)	Area (%)
1	8.1	79.2
2	9.6	20.8

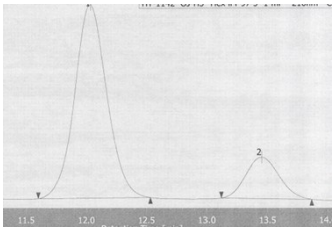


Racemic-3f

Peak	tR (min)	Area (%)
1	8.0	50.1
2	9.4	49.9

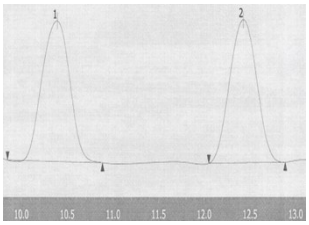


3g-HPLC
DAICEL CHIRALCEL OJ-H
hexane:*i*PrOH = 97:3, 1.0 mL/min



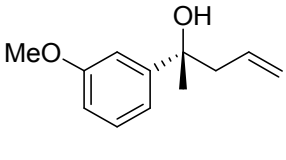
(*R*)-3g

Peak	tR (min)	Area (%)
1	12.0	82.2
2	13.5	17.8

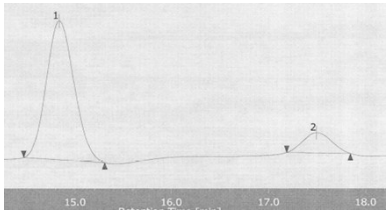


Racemic-3g

Peak	tR (min)	Area (%)
1	10.4	50.1
2	12.4	49.9

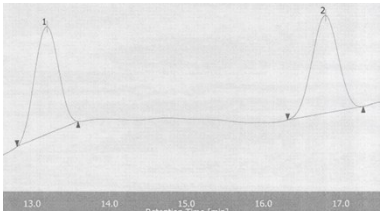


3h-HPLC
DAICEL CHIRALCEL OJ-H
hexane:*i*PrOH = 97:3, 1.0 mL/min



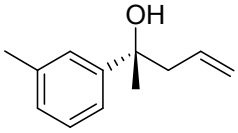
(*R*)-3h

Peak	tR (min)	Area (%)
1	14.8	87.0
2	17.5	13.0

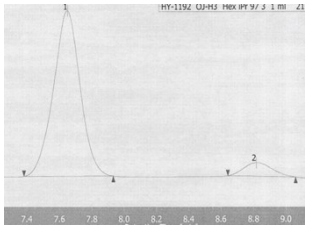


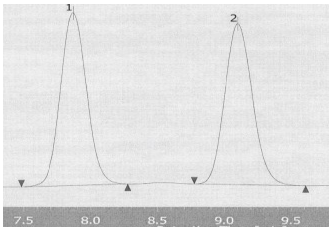
Racemic-3h

Peak	tR (min)	Area (%)
1	13.2	50.1
2	16.8	49.9



3i-HPLC
DAICEL CHIRALCEL OJ-H
hexane:*i*PrOH = 97:3, 1.0 mL/min

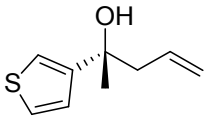




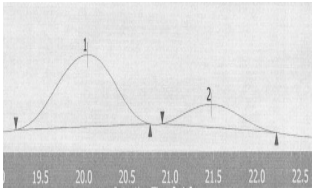
(*R*)-3i **Racemic-3i**

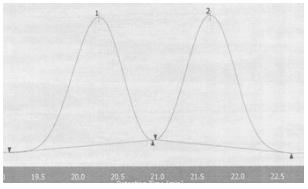
Peak	tR (min)	Area (%)
1	7.7	92.0
2	8.8	8.0

Peak	tR (min)	Area (%)
1	7.9	50.1
2	9.1	49.9



3j-HPLC
DAICEL CHIRALCEL OD-3
hexane:*i*PrOH = 99:1, 0.8 mL/min

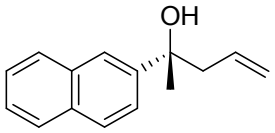




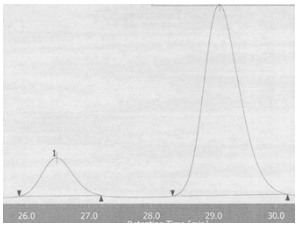
(*R*)-3j **Racemic-3j**

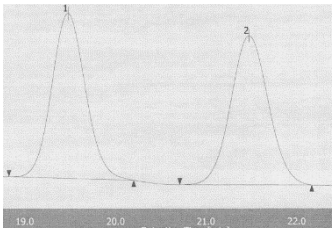
Peak	tR (min)	Area (%)
1	20.0	77.3
2	21.5	22.7

Peak	tR (min)	Area (%)
1	20.3	50.1
2	21.7	49.9



3k-HPLC
DAICEL CHIRALCEL OJ-H
hexane:*i*PrOH = 97:3, 1.0 mL/min



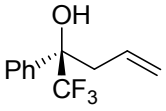


(*R*)-3k

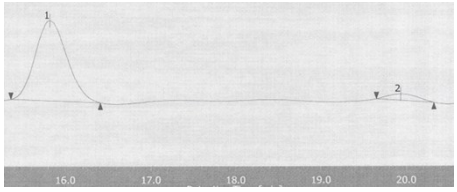
Peak	tR (min)	Area (%)
1	26.5	14.6
2	29.1	85.4

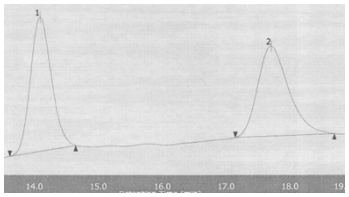
Racemic-3k

Peak	tR (min)	Area (%)
1	19.5	49.8
2	21.5	50.2



3l-HPLC
DAICEL CHIRALCEL OJ-H
hexane:*i*PrOH = 97:3, 1.0 mL/min





(*R*)-3l

Peak	tR (min)	Area (%)
1	15.8	93.2
2	19.9	6.8

Racemic-3l

Peak	tR (min)	Area (%)
1	14.1	50.1
2	17.7	49.9