Chemo- and Regioselective Reductive Transposition of Allylic Alcohol Derivatives via Iridium or Rhodium Catalysis

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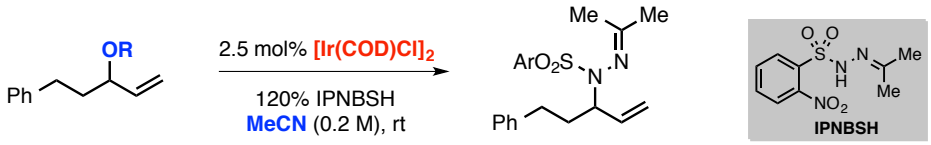
I. General Considerations

Unless noted, all reactions were conducted under inert atmosphere employing standard schlenk technique or by the use of an N_2-filled glovebox. Flash chromatography was performed as described by Still and co-workers[1] (SiliaFlash P60, 40-63μm, 60A silica gel, Silicycle) or by automated flash chromatography (Isolera, HP-SIL or KP-SIL SNAP silica cartridges, Biotage). Analytical thin-layer chromatography was performed using glass plates pre-coated with silica (SiliaPlate G TLC - Glass-Backed, 250μm, Silicycle). TLC plates were visualized by UV light and/or staining with aqueous basic potassium permanganate.

IPNBSH could be used as supplied (Aldrich) and was also prepared on >15 gram scale according to the procedures outlined by Myers[2] and Movassighi.[3] $[Ir(COD)Cl]_2$ and $[Rh(COD)Cl]_2$ could be used as supplied (Strem) and were also prepared according to literature procedures.[4] Anhydrous acetonitrile was used as provided from Sigma-Aldrich. All other reagents were used as received from commercial vendors.

All optimization scale experiments (0.050-0.100 mmol scale) were setup inside an inert atmosphere glovebox. Upon completion of the experiments, the reactions were diluted with EtOAc or Et_2O, passed over a short celite plug, concentrated, and analyzed by ^{1}H NMR spectroscopy using dibenzyl ether as an internal standard.

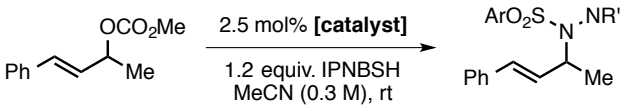
II. Additional Optimization Data



Leaving Group	(conv)	yield (b/l)
OCO_2Me	**(94)**	**91 (>20:1)**
OCO_2Et	(87)	70 (>20:1)
OCO_2tBu	(29)	22 (>20:1)
$OP(O)(OEt)_2$	(>98)	80 (70:10)

Solvent	(conv)	yield (b/l)
MeCN	**(94)**	**91 (>20:1)**
THF	(>98)	25 (>10:1)
CH_2Cl_2	(>98)	40 (>10:1)
EtOH	(>98)	<5

Other Catalysts	(conv)	yield (b/l)
$[Rh(COD)Cl]_2$	(<2)	<2
$[Rh(CO)_2Cl]_2$	(10)	<2
$RhCl(PPh_3)$	(<2)	<2
$RuCp^*(MeCN)_3PF_6$	(>98)	94 (14:80)



entry	[catalyst]	conv. (%)	yield (%)	(regio)
1	**$[Ir(COD)Cl]_2$**	**18**	**17**	**(>95:5)**
2	$[Ir(COD)Cl]_2$ 10% $P(OPh)_3$	16	11	(>95:5)
3	$[Rh(COD)Cl]_2$	<2	<2	nd
4	$[Rh(CO)_2Cl]_2$	<2	<2	nd
5	$Rh(COD)_2]BF_4$	<2	<2	nd
6	**$[Rh(COD)Cl]_2$ 10% $P(OPh)_3$**	**75**	**68**	**(>95:5)**

III. Synthesis of Substrates

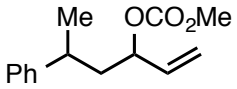
Unless otherwise noted, allylic carbonates were prepared in two steps from the corresponding aldehyde via addition of vinyl magnesium bromide to generate the allylic alcohol followed by treatment with methyl chloroformate and pyridine. Yields were not optimized.

General Procedure for Allylic Alcohol Synthesis To a nitrogen-purged round bottom flask equipped with a rubber septum and stir bar was added vinylmagnesium bromide as a 1.0M solution in THF (1.05 equiv) by syringe. The flask was cooled to 0 °C in an ice water bath. Solid aldehydes were added to a 4 dram vial equipped with a septum and placed under N_2 by evacuating/backfilling three times. The minimum quantity of dry THF required to dissolve the solid was then added by syringe. The aldehyde or aldehyde solution (1.0 equiv) was added dropwise by syringe. The reaction was stirred at 0 °C for 10 minutes, at which time the cooling bath was removed and the reaction was stirred until complete conversion of the aldehyde was observed by TLC. Upon completion, the reaction was quenched by addition of saturated NH_4Cl and the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. If necessary, the product was purified by column chromatography (Hex/EtOAc).

General Procedure for Methyl Carbonate Synthesis To a 4 dram was added allylic alcohol (1.0 equiv) and a stir bar. The vial was purged with N_2 by evacuating/backfilling three times and dry CH_2Cl_2 was added by syringe to make a ~1.0 M solution. Anhydrous pyridine (5.0 equiv) was added by syringe and the reaction was stirred for 10 minutes at room temperature before being cooled to 0 °C in an ice water bath. Methyl chloroformate (2.4

equiv) was slowly added dropwise by syringe and the reaction mixture was stirred at 0 °C for 10 minutes, at which point the cooling bath was removed and the reaction stirred at room temperature until complete conversion of the alcohol was observed by TLC or 5 hours had elapsed. The reaction was quenched by addition of water, diluted with EtOAc and washed with 0.025% aqueous HCl. The organic layer was dried over Na_2SO_4 and if necessary, purified by column chromatography (Hex/EtOAc).

Substrates for Table 2 entry 1,[5] Table 2 entry 3,[6] Table 3 entry 1,[6] Table 3 entry 5,[7] Table 4 entry 1[8] were prepared according to the General Procedure and spectroscopic data agreed with that reported.

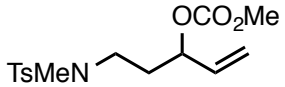


Substrate for Table 2, entry 2 Prepared according to the General Procedure from the corresponding alcohol (934 mg, 6.40 mmol). Isolated in 62% yield (mixture of diastereomers ~1:1) after purification by flash chromatography (Hex/EtOAc gradient) as a colorless oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.14 (m, 3H), 5.77 (m, 1H), 5.28 – 5.13 (m, 2H), 4.96 (m, 0.5H), 4.83 (m, 0.5H), 3.77 (s, 1.5H), 3.74 (s, 1.5H), 2.84 (m, 1H), 2.11 (m, 0.5H), 2.00 (m, 0.5H), 1.83 (m, 1H), 1.29 (d, *J* = 1.47 Hz, 1.5H), 1.27 (d, *J* = 1.47 Hz, 1.5H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.2 (2), 146.3, 146.2, 136.3, 136.0, 128.7 (2), 127.1, 127.0, 126.5, 126.4, 118.2, 117.4, 77.8, 77.6, 54.8, 54.7, 42.9, 42.4, 36.3, 36.1, 22.6 (2);

HRMS (LCMS ESI): calcd for $C_{14}H_{18}NaO_3$ $[M+Na]^+$ 257.1148, found 257.1150.

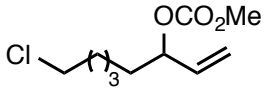


Substrate for Table 2, entry 4 Prepared according to the General Procedure from the corresponding alcohol (360 mg, 1.34 mmol). Isolated in 67% yield after purification by flash chromatography (Hex/EtOAc gradient) as a colorless oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.81 (ddd, *J* = 17.2, 10.5, 6.6 Hz, 1H), 5.35 (m, 1H), 5.26 (m, 1H), 5.15 (m, 1H), 3.78 (s, 3H), 3.16 – 2.98 (m, 2H), 2.72 (s, 3H), 2.43 (s, 3H), 2.01 – 1.82 (m, 2H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.1, 143.5, 135.1, 134.5, 129.8, 127.6, 118.3, 76.3, 54.9, 46.5, 35.3, 32.6, 26.6;

HRMS (LCMS ESI): calcd for $C_{15}H_{21}NNaO_5S$ $[M+Na]^+$ 350.1033, found 350.1032.

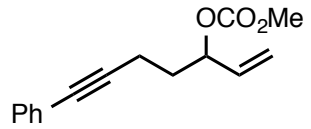


Substrate for Table 2, entry 5 Prepared according to the General Procedure from the corresponding alcohol (1.16 g, 6.00 mmol). Isolated in 87% yield with no purification as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 5.79 (ddd, *J* = 17.2, 10.5, 6.7 Hz, 1H), 5.30 (m, 1H), 5.21 (m, 1H), 5.05 (m, 1H), 3.78 (s, 3H), 3.52 (t, *J* = 6.6 Hz, 2H), 1.82 – 1.68 (m, 3H), 1.63 (m, 1H), 1.52 – 1.32 (m, 4H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.4, 136.0, 117.7, 79.1, 54.8, 45.0, 34.2, 32.6, 26.7, 24.4;

HRMS (LCMS ESI): calcd for $C_{10}H_{21}ClNO_3$ $[M+NH_4]^+$ 238.1204, found 238.1206.

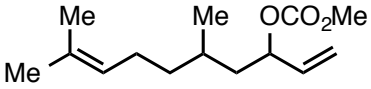


Substrate for Table 2, entry 6 Prepared according to the General Procedure from the corresponding alcohol (145 mg, 0.78 mmol). Isolated in 68% yield after purification by flash chromatography (Hex/EtOAc gradient) as a yellow oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.42 – 7.37 (m, 2H), 7.31 – 7.26 (m, 3H), 5.84 (ddd, *J* = 10.5, 6.8, 3.7 Hz, 1H), 5.38 (m, 1H), 5.30 – 5.23 (m, 2H), 3.78 (s, 3H), 2.58 – 2.44 (m, 2H), 2.03 (m, 1H), 1.93 (m, 1H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.3, 135.4, 131.7, 128.4, 127.9, 123.8, 118.2, 88.5, 81.5, 78.0, 54.9, 33.3, 15.6;

HRMS (LCMS ESI): calcd for $C_{15}H_{16}NaO_3$ $[M+Na]^+$ 267.0992, found 267.0992.

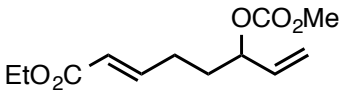


Substrate for Table 2, entry 7 Prepared according to the General Procedure from the corresponding alcohol (4.27 g, 23.5 mmol). Isolated in 64% yield (~1:1 mixture of diastereomers) after purification by flash chromatography (10:1 Hex/EtOAc) as a yellow oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 5.78 (m, 1H), 5.30 (m, 1H), 5.23 – 5.04 (m, 3H), 3.77 (s, 1.5H), 3.77 (s, 1.5H), 2.06 – 1.87 (m, 2H), 1.83 – 1.11 (m, 11H), 0.93 (d, *J* = 2.6 Hz, 1.5H), 0.92 (d, *J* = 2.6 Hz, 1.5H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.5, 155.3, 136.7, 136.3, 131.5 (2), 124.7, 124.6, 117.8, 117.2, 78.1, 77.5, 54.7 (2), 41.7, 41.4, 37.4, 37.0, 28.9, 28.8, 25.8, 25.5, 25.4, 19.8, 19.5, 17.8 (2);

HRMS (LCMS ESI): calcd for $C_{14}H_{24}NaO_3$ $[M+Na]^+$ 263.1618, found 263.1617.

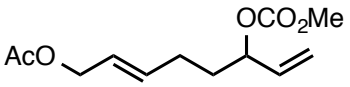


Substrate for Table 2, entry 8 Prepared according to the General Procedure from the corresponding alcohol (240 mg, 1.32 mmol). Isolated in 76% yield after purification by flash chromatography (4:1 Hex/EtOAc) as a colorless oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 6.93 (dt, *J* = 15.7, 6.9 Hz, 1H), 5.86 – 5.74 (m, 2H), 5.32 (m, 1H), 5.25 (m, 1H), 5.07 (m, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.34 – 2.22 (m, 2H), 1.87 (m, 1H), 1.78 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.6, 155.2, 147.5, 135.5, 122.2, 118.2, 78.3, 60.4, 54.9, 32.6, 27.8, 14.4;

HRMS (LCMS ESI): calcd for $C_{12}H_{18}NaO_5$ $[M+Na]^+$ 265.1046, found 265.1051.

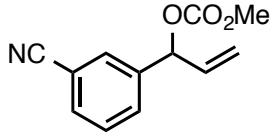


Substrate for Table 2, entry 9 Prepared according to the General Procedure from the corresponding alcohol (500 mg, 2.70 mmol, 85:15 *E*/*Z* mixture). Isolated in 43% yield after purification by flash chromatography (Hex/EtOAc gradient) as a colorless oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 5.82 – 5.72 (m, 2H), 5.59 (m, 1H), 5.30 (m, 1H), 5.22 (m, 1H), 5.06 (m, 1H), 4.50 (d, *J* = 6.4 Hz, 2H), 3.78 (s, 3H), 2.20 – 2.29 (m, 2H), 2.06 (s, 3H), 1.81 (m, 1H), 1.71 (m, 1H);

^{13}C NMR ($CDCl_3$, 176 MHz): δ 170.9, 155.3, 135.8, 134.7, 125.0, 117.9, 78.5, 65.1, 54.8, 33.4, 27.8, 21.1;

HRMS (LCMS ESI): calcd for $C_{12}H_{22}NaO_5$ $[M+Na]^+$ 265.1046 found 265.1041.

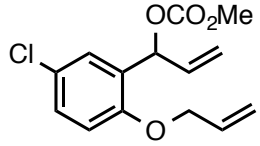


Substrate for Table 3, entry 2 Prepared according to the General Procedure from the corresponding alcohol (1.30 g, 8.10 mmol). Isolated in 52% yield after purification by flash chromatography (4:1 Hex/EtOAc) as colorless oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.67 (m, 1H), 7.63 – 7.59 (m, 2H), 7.48 (m, 1H), 6.08 (d, *J* = 6.2 Hz, 1H), 5.98 (ddd, *J* = 10.3, 6.2, 4.2 Hz, 1H), 5.41 – 5.33 (m, 2H), 3.80 (s, 3H);

^{13}C NMR ($CDCl_3$, 126MHz) δ 154.9, 140.1, 134.8, 132.1, 131.5, 130.7, 129.6, 119.0, 118.5, 113.1, 79.0, 55.2;

HRMS (LCMS ESI): calcd for $C_{12}H_{11}NNaO_3$ $[M+Na]^+$ 240.0631, found 240.0630.

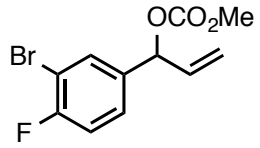


Substrate for Table 3, entry 3 Prepared according to the General Procedure from the corresponding alcohol (687 mg, 3.07 mmol). Isolated in 73% yield after purification by flash chromatography (Hex/EtOAc gradient with 1% NEt_3) as yellow oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.37 (d, *J* = 2.6 Hz, 1H), 7.23 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 1H), 6.51 (m, 1H), 6.09 – 5.98 (m, 2H), 5.47 – 5.23 (m, 4H), 4.61 – 4.56 (m, 2H), 3.82 (s, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.0, 154.0, 134.8, 132.8, 129.2, 129.0, 127.3, 126.2, 117.8, 117.3, 113.5, 74.1, 69.5, 55.0;

HRMS (LCMS ESI): calcd for $C_{14}H_{15}ClNaO_4$ $[M+Na]^+$ 305.0551, found 305.0552.



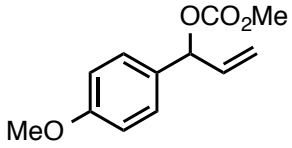
Substrate for Table 3, entry 4 Prepared according to the General Procedure from the corresponding alcohol (2.72 g, 11.8 mmol). Isolated in 69% yield after purification by flash chromatography (Hex/EtOAc gradient) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.58 (dd, *J* = 6.5, 2.3 Hz, 1H), 7.29 (m, 1H), 7.11 (m, 1H), 6.04 – 5.93 (m, 2H), 5.38 – 5.30 (m, 2H), 3.79 (s, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.1 (d, J_{CF} = 248.2 Hz), 155.0, 135.9 (d, J_{CF} = 4.0 Hz), 135.1 (d, J_{CF} = 0.8 Hz), 132.5, 128.0 (d, J_{CF} = 7.5 Hz), 118.4, 116.7 (d, J_{CF} = 21.8 Hz), 109.4 (d, J_{CF} = 21.3 Hz), 78.8, 55.1;

^{19}F NMR ($CDCl_3$, 469 MHz) δ 107.5;

HRMS (LCMS ESI): calcd for $C_{11}H_{10}BrFNaO_3$ $[M+Na]^+$ 310.9690, found 310.9690.

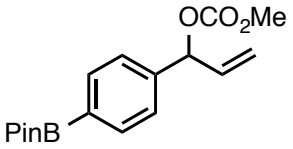


Substrate for Table 3, entry 6 Prepared according to the General Procedure from the corresponding alcohol (1.16 g, 7.04 mmol). Isolated in 77% yield as a pale yellow oil. The product is not stable to silica gel chromatography and will rearrange to the linear methyl carbonate.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.10 – 5.98 (m, 2H), 5.36 – 5.23 (m, 2H), 3.80 (s, 3H), 3.77 (s, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.9, 155.2, 136.0, 130.5, 128.8, 117.2, 114.1, 80.1, 55.4, 54.9;

HRMS (LCMS ESI): calcd for $C_{12}H_{14}NaO_4$ $[M+Na]^+$ 245.0784, found 245.0782.



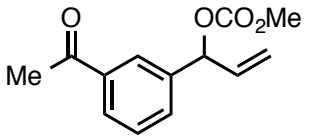
Substrate for Table 3, entry 7 The allylic alcohol was prepared via a modified procedure.

To a round bottom flask was added aldehyde and a stir bar. The flask was then purged with nitrogen by evacuating and backfilling three times and anhydrous THF was added by syringe. The reaction vessel was then cooled to –78 °C in a dry ice/acetone bath, vinylmagnesium bromide was added dropwise while stirring and the reaction was stirred for 1 hour at –78 °C. The reaction was allowed to stir for 30 minutes at room temperature, at which point it was quenched by the addition of saturated NH_4Cl. The resulting mixture was diluted with water (25 mL) and the aqueous layer washed three times with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. The methyl carbonate was prepared according to the General Procedure from the corresponding alcohol (783 mg, 3.00 mmol). Isolated in 83% yield with no purification as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.08 (d, *J* = 6.4 Hz, 1H), 6.01 (ddd, *J* = 16.3, 10.3, 6.1 Hz, 1H), 5.34 (m, 1H), 5.27 (m, 1H), 3.77 (s, 3H), 1.34 (s, 12H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.1, 141.4, 135.8, 135.2, 126.4, 117.9, 84.0, 80.3, 55.0, 25.0 (2);

HRMS (LCMS ESI): calcd for $C_{17}H_{23}BNaO_5$ $[M+Na]^+$ 341.1531, found 341.1534.

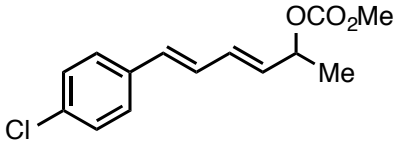


Substrate for Table 3, entry 8 The allylic alcohol was prepared via a modified procedure. To a round bottom flask was added aldehyde and a stir bar. The flask was then purged with nitrogen by evacuating and backfilling three times and anhydrous THF was added by syringe. The reaction vessel was then cooled to –78 °C in a dry ice/acetone bath, vinylmagnesium bromide was added dropwise while stirring and the reaction was stirred for 2 hours at –78 °C. After 2 hours the cooling bath was removed and saturated NH_4Cl was added directly to the cold mixture. The resulting white precipitate was filtered away, washed with Et_2O and the aqueous layer washed three times with Et_2O. The methyl carbonate was prepared according to the general procedure from the alcohol (348 mg, 1.98 mmol). Isolated in 87% yield with no further purification as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.95 (m, 1H), 7.91 (m, 1H), 7.58 (m, 1H), 7.47 (app. t, *J* = 7.7 Hz, 1H), 6.13 (d, *J* = 6.2 Hz, 1H), 6.03 (ddd, *J* = 16.9, 10.6, 6.1 Hz, 1H), 5.37 (m, 1H), 5.32 (m, 1H), 3.79 (s, 3H), 2.61 (s, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.8, 155.1, 139.2, 137.7, 135.4, 131.8, 129.1, 128.5, 127.0, 118.3, 79.8, 55.1, 26.8;

HRMS (LCMS ESI): calcd for $C_{13}H_{14}NaO_4$ $[M+Na]^+$ 257.0784, found 257.0785.

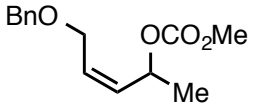


Substrate for Table 4, entry 2 Prepared according to the General Procedure from the corresponding benzyl alcohol (625 mg, 3.00 mmol), which undergoes quantitative isomerization upon methyl carbonate formation/silica gel chromatography. Isolated in 88% yield after purification by flash chromatography (Hex/EtOAc gradient) as a white solid.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.34 – 7.24 (m, 4H), 6.70 (dd, *J* = 15.6, 10.6 Hz, 1H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.43 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.81 (dd, *J* = 15.4, 7.0 Hz, 1H), 5.29 (m, 1H), 3.78 (s, 3H), 1.42 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.3, 135.6, 133.5, 132.7, 132.6, 132.4, 129.0, 128.5, 127.7, 75.0, 54.8, 20.5;

HRMS (LCMS ESI): calcd for $C_{14}H_{15}ClO_3$ [M+Na] 289.0602, found 289.0603.

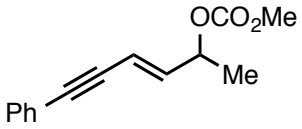


Substrate for Table 4, entry 3 Prepared according to the General Procedure from the corresponding alcohol (950 mg, 3.8 mmol). Isolated in 70% yield after purification by flash chromatography (Hex/EtOAc gradient) as a colorless oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.37 – 7.32 (m, 4H), 7.29 (m, 1H), 5.74 (m, 1H), 5.57 (m, 1H), 5.46 (m, 1H), 4.53 (m, 2H), 4.23 – 4.15 (m, 2H), 3.76 (s, 3H), 1.34 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.2, 138.3, 131.7, 129.7, 128.5, 127.9, 127.8, 72.6, 71.2, 66.1, 54.7, 20.8;

HRMS (LCMS ESI): calcd for $C_{14}H_{18}NaO_4$ [M+Na] 273.1097, found 273.1098.



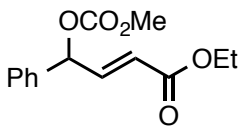
Substrate for Table 4, entry 4 Prepared according to the General Procedure from the corresponding alcohol (1.00 g, 5.81 mmol). Isolated a 5:1 mixture of product and propargylic methyl carbonate in 75% yield after purification by flash chromatography (Hex/EtOAc gradient) as a colorless oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.45 – 7.39 (m, 2H), 7.35 – 7.29 (m, 3H), 6.18 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.98 (dd, 15.8, 1.1 Hz, 1H), 5.28 (m, 1H), 3.79 (m, 3H), 1.42 (d, 6.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 155.0, 140.9, 131.6, 131.5, 128.4, 128.3, 112.2, 91.1, 86.7, 74.7, 54.7, 20.0;

HRMS (LCMS ESI): calcd for $C_{14}H_{14}NaO_3$ [M+Na] 253.0835, found 253.0835.

The synthesis of γ-hydroxy-α,β-unsaturated esters and ketones for Table 3, entries 5 – 8 were achieved via cross-metathesis of ethyl acrylate or vinyl methyl ketone and the corresponding allylic alcohol in a procedure adapted from the literature.[9] To a nitrogen-purged round bottom flask equipped with a rubber septum and stir bar was added CH_2Cl_2, ethyl acrylate (or methyl vinyl ketone, 5 – 10 equiv.) and allylic alcohol (1.0 equiv.) by syringe. The catalyst (Grubbs–Hoveyda 2nd generation, 0.005 – 0.010 equiv.) was dissolved in dry CH_2Cl_2 under N_2 in a separate septum-capped vial and transferred to the reaction vessel via syringe (concentration 0.25 – 0.50 M). The reaction was stirred at 40 °C until the alcohol was fully consumed by TLC. The solvent was removed and the resulting crude mixture purified by flash chromatography (Hex/EtOAc).

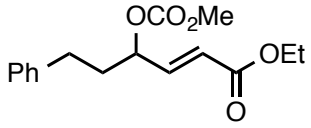


Substrate for Table 4, entry 5 Prepared according to the General Procedure from the corresponding alcohol (850 mg, 4.14 mmol). Isolated in 79% yield after purification by flash chromatography (Hex/EtOAc gradient) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.41 – 7.32 (m, 5H), 7.01 (dd, *J* = 15.7, 5.1 Hz, 1H), 6.22 (dd, *J* = 5.1, 1.7 Hz, 1H), 6.09 (dd, *J* = 15.7, 1.7 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 165.9, 154.9, 143.9, 136.8, 129.2, 129.0, 127.5, 122.2, 78.2, 60.9, 55.2, 14.3;

HRMS (LCMS ESI): calcd for $C_{14}H_{16}NaO_5$ $[M+Na]^+$ 287.0890, found 287.0891.

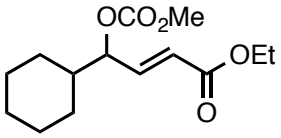


Substrate for Table 4, entry 6 Prepared according to the General Procedure from the corresponding alcohol (3.565 g, 16.3 mmol). Isolated in 63% yield after purification by flash chromatography (Hex/EtOAc gradient) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.31 – 7.27 (m, 2H), 7.20 (m, 1H), 7.18 – 7.15 (m, 2H), 6.87 (dd, *J* = 15.7, 5.5 Hz, 1H), 6.02 (dd, *J* = 15.7, 1.5 Hz, 1H), 5.25 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.77 – 2.65 (m, 2H), 2.07 (m, 1H), 2.01 (m, 1H), 1.29 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 165.9, 155.2, 144.4, 140.7, 128.7, 128.5, 126.4, 122.5, 76.1, 60.8, 55.1, 35.6, 31.2, 14.3;

HRMS (LCMS ESI): calcd for $C_{16}H_{20}NaO_5$ $[M+Na]^+$ 315.1203, found 315.1204.

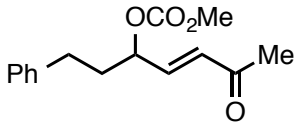


Substrate for Table 4, entry 7 Prepared according to the General Procedure from the corresponding alcohol (610 mg, 2.87 mmol). Isolated in 68% yield after purification by flash chromatography (Hex/EtOAc gradient) as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 6.84 (dd, *J* = 15.7, 5.9 Hz, 1H), 5.98 (dd, *J* = 15.7, 1.5 Hz, 1H), 5.05 (td, *J* = 6.0, 1.4 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3 H), 1.81 – 1.63 (m, 6H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.27 – 1.01 (m, 5H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 166.0, 155.4, 143.8, 122.9, 80.8, 60.7, 55.0, 41.8, 28.6, 28.2, 26.2, 26.0, 26.0, 14.4;

HRMS (LCMS ESI): calcd for $C_{14}H_{22}NaO_5$ $[M+Na]^+$ 293.1359, found 293.1364.

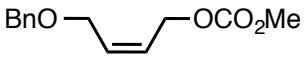


Substrate for Table 4, entry 8 Prepared according to the General Procedure from the corresponding alcohol (908 mg, 4.45 mmol). Isolated in 56% yield after purification by flash chromatography (Hex/EtOAc gradient) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.29 (m, 2H), 7.20 (m, 1H), 7.17 (m, 2H), 6.66 (dd, *J* = 16.1, 5.5 Hz, 1H), 6.24 (dd, *J* = 16.0, 1.4 Hz, 1H), 5.26 (m, 1H), 3.81 (s, 3H), 2.78 – 2.66 (m, 2H), 2.25 (s, 3H), 2.09 (m, 1H), 2.02 (m, 1H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.8, 155.1, 143.0, 140.6, 130.7, 128.7, 128.5, 126.4, 76.2, 55.2, 35.6, 31.3, 27.7;

HRMS (LCMS ESI): calcd for $C_{15}H_{18}NaO_4$ $[M+Na]^+$ 285.1097, found 285.1098.

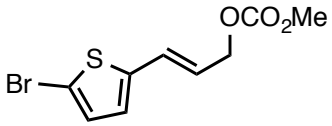


Substrate for Table 4, entry 9 Prepared according to the General Procedure from the corresponding alcohol (890 mg, 5.00 mmol). Isolated in 97% yield after purification by flash chromatography (Hex/EtOAc gradient) as a colorless oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.34 – 7.31 (m, 4H), 7.27 (m, 1H), 5.85 (m, 1H), 5.72 (m, 1H), 4.68 (d, *J* = 6.9 Hz, 2H), 4.50 (s, 2H), 4.12 (d, *J* = 6.2 Hz, 2H), 3.76 (s, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 155.6, 137.9, 131.4, 128.4, 127.8, 127.7, 126.0, 72.4, 65.6, 63.6, 54.8;

HRMS (LCMS ESI): calcd for $C_{13}H_{16}NaO_4$ $[M+Na]^+$ 259.0941, found 259.0942.

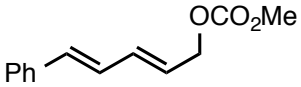


Substrate for Table 4, entry 10 Prepared according to the General Procedure from the corresponding branched allylic alcohol which undergoes isomerization upon methyl carbonate synthesis/silica gel column chromatography (1.19 g, 5.44 mmol). Isolated in 51% yield after purification by flash chromatography (Hex/EtOAc gradient) as a light brown solid.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 6.90 (d, *J* = 3.8 Hz, 1H), 6.71 (d, *J* = 3.8 Hz, 1H), 6.66 (m, 1H), 5.99 (dt, *J* = 15.6, 6.4 Hz, 1H), 4.70 (dd, *J* = 6.4, 1.3 Hz, 2H), 3.78 (s, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 155.5, 142.6, 130.3, 127.2, 127.0, 122.3, 112.1, 67.7, 54.9;

HRMS (LCMS ESI): calcd for $C_9H_9NaO_3S$ $[M+Na]^+$ 298.9348, found 298.9354.



Substrate for Table 4, entry 11 Prepared according to the General Procedure from the corresponding branched allylic alcohol, which undergoes isomerization upon methyl carbonate synthesis/silica gel column chromatography (1.21 g, 7.60 mmol). Isolated in 55% yield after purification by flash chromatography (10:1 Hex/EtOAc) as a white solid.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 5.6 Hz, 2H), 7.25 (m, 1H), 6.77 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.49 (m, 1H), 5.89 (dt, *J* = 15.2, 6.5 Hz, 1H), 4.72 (d, *J* = 6.6, 1.1 Hz, 2H), 3.80 (s, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.8, 137.0, 135.3, 134.4, 128.8, 128.1, 127.7, 126.7, 126.2, 68.3, 55.0;

HRMS (LCMS ESI): calcd for $C_{13}H_{14}NaO_3$ $[M+Na]^+$ 241.0835, found 241.0836.

IV. Ir–Catalyzed Reductive Transposition of Allylic Carbonates

General Procedure (Glovebox) To a 4 dram vial containing a stirbar was added IPNBSH (230 mg, 0.90 mmol, 1.2 equiv.), the allylic carbonate (0.75 mmol, 1.0 equiv.) in MeCN (2 mL), $[Ir(COD)Cl]_2$ (13.0 mg, 0.019 mmol, 0.050 equiv. Ir) in MeCN (2 mL), and dibenzyl ether (14.5 μL 0.075 mmol, 0.10 equiv.). The reaction was stirred for 18 hours, over which time the solution turned from orange to purple to black. After 18 hours the solvent was removed by rotovap and ^{1}H NMR was used to judge the conversion of the allylic carbonate to the allylic sulfonyl hydrazone. The crude reaction mixture was then dissolved in THF (2 mL), and then water (1 mL), TFE (1 mL), and AcOH (110 μL, 2.5 equiv.) were added. The reaction was stirred for 2 hours, after which hexane (50 mL) and saturated sodium bicarbonate (50 mL) was added (EtOAc was used for polar products). The organic layer was washed with brine, dried with Na_2SO_4, concentrated, and purified by column chromatography (generally hexane/EtOAc, or pentane for volatile products). Conducting the reduction step without the removal of MeCN led to a slight reduction (10–15%) in product yield. Unless specifically noted, the *E*/*Z* and regioisomer ratios of the isolated products were ≥95:5.

General Procedure (No Glovebox) To separate 4 dram vials was added IPNBSH (230 mg, 0.90 mmol, 1.2 equiv.), allylic carbonate (0.75 mmol, 1.0 equiv.) and $[Ir(COD)Cl]_2$ (13.0 mg, 0.019 mmol, 0.050 equiv. Ir). Each vial was capped with a PTFE-lined septa cap and evacuated and backfilled with N_2 three times. Anhydrous MeCN (1.5 mL) was added to the vials containing the allylic carbonate and $[Ir(COD)Cl]_2$ via syringe. The MeCN solutions were then transferred to the vial containing IPNBSH via syringe. The remainder of the procedure is identical to that described above.

Gram Scale Reaction (No Glovebox), equation 2. All glassware was rigorously dried under vacuum using a heat gun. To a 4 dram vial was added $[Ir(COD)Cl]_2$ (62 mg, 0.092 mmol, 0.025 equiv. Ir), the vial was capped and placed under N_2 and MeCN was added (10 mL). To a 100 mL round bottom flask under N_2 was added allylic carbonate (2.15 g, 7.4 mmol), followed by the $[Ir(COD)Cl]_2$ solution and an additional 25 mL of MeCN. The solution was stirred for 5 minutes before IPNBSH (2.18 g, 8.53 mmol) was added. The round bottom flask was placed under a positive pressure of N_2 via a balloon and the reaction was stirred for 18 hours. The solvent was then removed and the crude reaction mixture was dissolved in THF (10 mL), TFE (5 mL) and water (5 mL) before adding AcOH (1 mL). The reaction was stirred for 2 hours after which it was diluted with CH_2Cl_2 (100 mL), transferred to a separatory funnel, washed with saturated bicarbonate solution and water. The aqueous extracts where washed with EtOAc, the organic extracts were combined, dried with Na_2SO_4, and concentrated. The product was isolated in 73% yield (1.16 g, 5.4 mmol) after purification by column chromatography (40:1 Hex/EtOAc) as pale yellow oil.

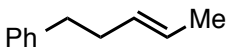


Table 2, entry 1[10] Prepared according to the General Procedure from the corresponding methyl carbonate (165 mg, 0.75 mmol). Isolated in 84% yield after purification by column chromatography (pentane), *E*/*Z* = 93:7, colorless oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.30 – 7.26 (m, 3H), 7.20 – 7.18 (m, 2H), 5.49 – 5.47 (m, 2H), 2.67 (m, 2H), 2.32 – 2.30 (m, 2H), 1.67 – 1.65 (m, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 142.4, 130.8, 128.6, 128.4, 125.9, 125.6, 36.3, 34.4, 18.1;

HRMS (LCMS EI): calcd for $C_{11}H_{14}$ $[M]^+$ 146.1096, found 146.1098.

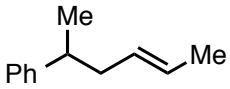


Table 2, entry 2 Prepared according to the General Procedure from the corresponding methyl carbonate (175 mg, 0.75 mmol). Isolated in 68% yield after purification by column chromatography (40:1 Hex/EtOAc), *E*/*Z* = 92:8, 91:9 regioisomer ratio, colorless oil. The yield for a reaction set up without a glovebox was 62%.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 – 7.28 (m, 2H), 7.22 – 7.17 (m, 3H), 5.44 – 5.34 (m, 2H), 2.74 (m, 1H), 2.32 (m, 1H), 2.21 (m, 1H), 1.62 (dd, *J* = 6.2, 1.2 Hz, 3H), 1.24 (d, *J* = 7.0 Hz, 3H);

^{13}C NMR ($CDCl_3$, 124 MHz) δ 147.6, 129.8, 128.4, 127.2, 126.5, 126.0, 41.6, 40.3, 21.6, 18.1;

HRMS (LCMS EI): calcd for $C_{12}H_{16}$ $[M]^+$ 160.1252, found 160.1250.

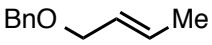


Table 2, entry 3[11] Prepared according to the General Procedure from the corresponding methyl carbonate (177 mg, 0.75 mmol). Isolated in 71% yield after purification by column chromatography (20:1 Hex/EtOAc), colorless oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.36 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 5.74 (m, 1H), 5.64 (m, 1H), 4.50 (s, 2H), 3.97 (d, *J* = 6.3 Hz, 2H), 1.73 (d, *J* = 6.4 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 138.7, 129.8, 128.5, 127.9, 127.7 (2), 78.1, 71.1, 17.9;

HRMS (LCMS EI): calcd for $C_{11}H_{14}O$ $[M]^+$ 162.1045, found 162.1043.

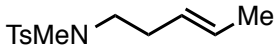


Table 2, entry 4 Prepared according to the General Procedure from the corresponding methyl carbonate (98 mg, 0.30 mmol). Isolated in 88% yield after purification by column chromatography (4:1 Hex/EtOAc) as a thick colorless oil, *E*/*Z* = 94:6.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.48 (m, 1H), 5.34 (m, 1H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.72 (s, 3H), 2.42 (s, 3H), 2.21 (app. q, *J* = 7.8 Hz, 2H), 1.64 (d, *J* = 6.5 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz): δ 143.3, 135.0, 129.8, 127.9, 127.5, 127.1, 50.3, 34.9, 31.3, 21.7, 18.1;

HRMS (LCMS ESI): calcd for $C_{13}H_{19}NNaO_2S$ $[M+Na]^+$ 276.1029, found 276.1030.

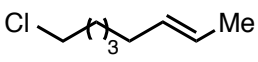


Table 2, entry 5[12] Prepared according to the General Procedure from the corresponding methyl carbonate (499 mg, 2.27 mmol). Isolated in 71% yield after purification by column chromatography (pentane) as a colorless oil, *E*/*Z* = 92:8.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 5.50 – 5.33 (m, 2H), 3.53 (t, *J* = 6.8 Hz, 2H), 2.05 – 2.00 (m, 2H) 1.80 – 1.68 (m, 5H), 1.48 –1.36 (m, 4H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 131.2, 125.2, 45.3, 32.7, 32.5, 29.0, 26.6, 18.1;

HRMS (LCMS ESI): calcd for $C_8H_{15}Cl$ $[M]^+$ 146.0862, found 146.0863.

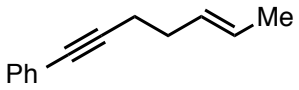


Table 2, entry 6 Prepared according to the General Procedure from the corresponding methyl carbonate (100 mg, 0.40 mmol). Isolated in 74% yield after purification by column chromatography (Hex/EtOAc gradient) as a thick colorless oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.41 – 7.38 (m, 2H), 7.30 – 7.24 (m, 3H), 5.59 – 5.51 (m, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.32 – 2.26 (m, 2H), 1.72 – 1.66 (m, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 131.7, 129.6, 128.3, 127.7, 126.5, 124.2, 90.1, 81.0, 32.1, 20.1, 18.1;

HRMS (LCMS ESI): calcd for $C_{13}H_{14}$ $[M]^+$ 170.1096, found 170.1093.

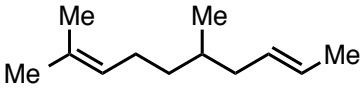


Table 2, entry 7 Prepared according to the General Procedure from the corresponding methyl carbonate (180 mg, 0.75 mmol). Isolated in 57% yield after purification by column chromatography (pentane), colorless oil, *E*/*Z* = 94:6.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 5.41 – 5.39 (m, 2H), 5.10 (m, 1H), 2.01 – 1.94 (m, 3H), 1.85 – 1.78 (m, 1H), 1.67 (s, 3H), 1.66 – 1.65 (m, 3H), 1.59 (s, 3H), 1.44 (m, 1H), 1.33 (m, 1H), 1.12 (m, 1H), 0.85 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 131.2, 130.2, 126.0, 125.1, 40.2, 36.8, 32.9, 25.9, 25.8, 19.6, 18.0, 17.8;

HRMS (LCMS EI): calcd for $C_{12}H_{22}$ $[M]^+$ 166.1722, found 166.1722.

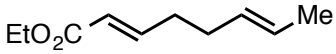


Table 2, entry 8 Prepared according to the General Procedure from the corresponding methyl carbonate (73 mg, 0.30 mmol). Isolated in 75% yield after purification by column chromatography (10:1 Hex/EtOAc) as a thick, colorless oil, E/Z = 94:6.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 6.93 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.80 (d, *J* = 15.7 Hz, 1H), 5.48 – 5.35 (m, 2H), 4.17 (q, *J* = 7.0 Hz, 2H), 2.23 (m, 2H), 2.12 (m, 2H), 1.62 (d, *J* = 6.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 166.7, 148.7, 129.6, 126.0, 121.5, 60.1, 32.2, 31.0, 17.8, 14.2;

HRMS (LCMS ESI): calcd for $C_{10}H_{16}NaO_2$ $[M+Na]^+$ 191.1043, found 191.1042.

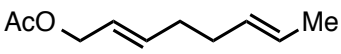


Table 2, entry 9 Prepared according to the General Procedure from the corresponding methyl carbonate (145 mg, 0.60 mmol, 85:15 *E*/*Z* mixture). Isolated in 65% yield (85:15 *E*/*Z* of allylic acetate alkene, >95:5 *E*/*Z* of newly formed alkene) after purification by flash chromatography (20:1 to 10:1 Hex/EtOAc) as a colorless oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 5.77 (m, 1H), 5.57, (m, 1H), 5.47 – 5.37 (m, 2H), 4.50 (d, *J* = 6.5 Hz, 2H), 2.18 – 2.03 (m, 7H), 1.64 (d, *J* = 5.8 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.0, 136.1, 130.5, 125.6, 124.2, 65.4, 32.4, 32.1, 21.2, 18.0;

HRMS (LCMS ESI): calcd for $C_{10}H_{16}NaO_2$ $[M+Na]^+$ 191.1040 found 191.1043.

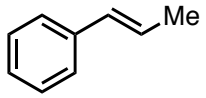


Table 3, entry 1[10] Prepared according to the General Procedure from the corresponding methyl carbonate (192 mg, 1.00 mmol). Isolated in 69% yield after purification by column chromatography (pentane). Spectroscopic data agrees with commercially available material.

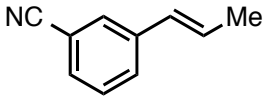


Table 3, entry 2 Prepared according to the General Procedure from the corresponding methyl carbonate (163 mg, 0.75 mmol). Isolated in 63% yield after purification by column chromatography (Hex/EtOAc gradient), regioisomer ratio = 93:7.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.58 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.38 (m, 1H), 6.38 – 6.29 (m, 2H), 1.91 (dd, *J* = 6.4, 1.4 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 139.3, 130.2 (2), 129.9, 129.4, 129.2, 129.0, 119.1, 112.8, 18.7;

HRMS (LCMS EI): calcd for $C_{10}H_9N$ $[M]^+$ 143.0735, found 143.0736.

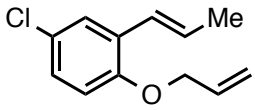


Table 3, entry 3 Prepared according to the General Procedure from the corresponding methyl carbonate (212 mg, 0.75 mmol). Isolated in 71% yield after purification by column chromatography (10:1 Hex/EtOAc), regioisomer ratio = 94:6. The yield for a reaction set up without a glovebox was 64%.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.36 (d, *J* = 2.7 Hz, 1H), 7.09 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 6.68 (d, *J* = 16 Hz, 1H), 6.24 (m, 1H), 6.06 (m, 1H), 5.41 (m, 1H), 5.29 (m, 1H), 4.57 (m, 2H), 1.90 (dd, *J* = 1.7, 6.7 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 153.9, 133.3, 129.2, 128.0, 127.2, 126.3, 126.1, 124.6, 117.7, 113.7, 69.7, 19.1;

HRMS (LCMS EI): calcd for $C_{12}H_{13}OCl$ $[M]^+$ 210.0626, found 210.0634.

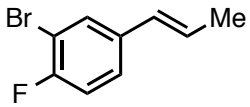


Table 3, entry 4 Prepared according to the General Procedure from the corresponding methyl carbonate (292 mg, 1.01 mmol). Isolated in 94% yield after purification by column chromatography (10:1 Hex/EtOAc), colorless oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.50 (dd, *J* = 6.7, 2.1 Hz, 1H), 7.21 (m, 1H), 7.02 (app. t, *J* = 16.1 Hz, 1H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.16 (dq, *J* = 16.1, 6.5 Hz, 1H), 1.87 (dd, *J* = 6.6, 1.7 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 158.6 (J_{CF} = 246 Hz), 135.8 (J_{CF} = 3.5 Hz), 130.7, 128.8 (J_{CF} = 0.7 Hz), 127.2 (J_{CF} = 2.3 Hz), 126.3 (J_{CF} = 6.9 Hz), 116.5 (J_{CF} = 22.3 Hz), 109.2 (J_{CF} = 21.3 Hz), 18.5;

HRMS (LCMS EI): calcd for C_9H_8FBr $[M]^+$ 215.9773, found 215.9770.

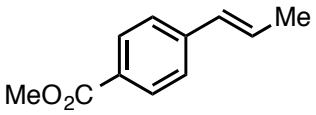


Table 3, entry 5[13] Prepared according to the General Procedure from the corresponding methyl carbonate (176 mg, 0.70 mmol). Isolated in 56% yield after purification by column chromatography (Hex/EtOAc gradient) as a colorless solid, regioisomer ratio = 83:17.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.99 – 7.96 (m, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.45 – 6.35 (m, 2H), 3.93 (s, 3H), 1.93 (dd, *J* = 6.3, 1.0 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.0, 142.5, 130.4, 129.9, 128.8, 128.2, 125.7, 52.0, 18.6;

HRMS (LCMS ESI): calcd for $C_{11}H_{12}NaO_2$ $[M+Na]^+$ 199.0730, found 199.0728.

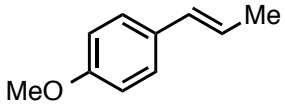


Table 3, entry 6[13] Prepared according to the General Procedure from the corresponding methyl carbonate (167 mg, 0.75 mmol). Isolated in 45% yield after purification by column chromatography (10:1 Hex/EtOAc).

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.27 – 7.25 (m, 2H), 6.85 – 6.83 (m, 2H), 6.34 (d, *J* = 15 Hz, 1H), 6.09 (dq, *J* = 16, 6.6 Hz, 1H), 3.80 (s, 3H), 1.86 (dd, *J* = 6.4, 1.8 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 158.8, 131.0, 130.5, 127.0, 123.7, 114.1, 55.4, 18.6;

HRMS (LCMS EI): calcd for $C_{10}H_{12}O$ $[M]^+$ 148.0888, found 148.0887.

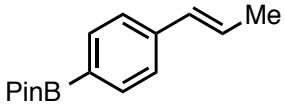


Table 3, entry 7[14] Prepared according to the General Procedure from the corresponding methyl carbonate (200 mg, 0.63 mmol). Isolated in 55% yield after purification by column chromatography (20:1 Pent/Et_2O) as a yellow oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.41 (m, 1H), 6.31 (m, 1H), 1.89 (dd, *J* = 6.4, 1.5 Hz, 3H), 1.34 (s, 12H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.8, 135.2, 131.3, 127.1, 125.3, 83.8, 25.0, 18.7;

HRMS (LCMS EI): calcd for $C_{15}H_{21}BO_2$ $[M]^+$ 244.1635, found 244.1636.

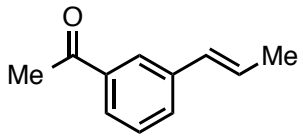


Table 3, entry 8 Prepared according to the General Procedure from the corresponding methyl carbonate (176 mg, 0.75 mmol). Isolated in 77% yield after purification by column chromatography (2:1 Pent/Et_2O) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 498 MHz): δ 7.90 (m, 1H), 7.77 (m, 1H), 7.52 (m, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 6.45 (m, 1H), 6.33 (m, 1H), 2.60 (s, 3H), 1.91 (dd, *J* = 6.5, 1.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 198.4, 138.6, 137.5, 130.4, 130.3, 128.8, 127.4, 126.8, 125.8, 26.8, 18.6;

HRMS (LCMS EI): calcd for $C_{11}H_{12}O$ $[M]^+$ 160.0888, found 160.0890.

V. Rh–Catalyzed Reductive Transposition of Allylic Carbonates

General Procedure (Glovebox) To a 1 dram vial was added $[Rh(COD)Cl]_2$ (0.050 equiv. Rh), triphenylphosphite (0.10 equiv.) and MeCN (200 μL). The solution was stirred for five minutes. To a second 1 dram vial containing the allylic carbonate (1.00 equiv) was added the $Rh/P(OPh)_3$ solution, followed by an MeCN rinsing (100 μL). The solution was stirred for 15 minutes (NOTE: adequate pre-activation time is important). Then, to a 2-dram vial containing IPNBSH (1.2 equiv.) and K_2CO_3 (2.0 equiv.), the allylic carbonate/$Rh/P(OPh)_3$ solution was added, followed by an MeCN rinsing (to make a 0.30 M solution). The vial was capped with a PTFE-lined septum cap, removed from the glovebox and stirred at the indicated temperature. After 18 hours the solvent was removed and the crude reaction mixture was dissolved in THF (2 mL), water (1 mL), TFE (1 mL), and AcOH (220 μL, 5.0 equiv.) were added. The reaction was stirred for 2 hours after which hexane (50 mL) and saturated bicarbonate (50 mL) was added (EtOAc was used for polar products). The organic layer was washed with brine, dried with Na_2SO_4, concentrated, and purified by column chromatography (generally hexane/EtOAc, or pentane for volatile products). Unless specifically noted, the E/Z and regioisomer ratios were ≥95:5.

General Procedure (No Glovebox) All glassware was rigorously dried under vacuum using a heat gun. To a 1 dram vial was added $[Rh(COD)Cl]_2$ (0.050 – 0.075 equiv. Rh; a slight increase in catalyst loading was required for the more slowly reacting substrate in Table 3, entry 1 to ensure >90% conversion and >85% yield of aminated product), the vial was capped with a PTFE lined septa cap and placed under N_2. MeCN (150 μL) and $P(OPh)_3$ (0.10 – 0.15 equiv.) was added via syringe and the solution was stirred for 5 minutes before being transferred to a vial containing allylic carbonate (1.0 equiv.) using MeCN (150μL). To a 1 dram vial was added IPNBSH (1.2 equiv.) and K_2CO_3 (2.0 equiv.). The vial was then placed under N_2. The solution of catalyst and allylic carbonate was transferred to the IPNBSH-containing vial by syringe using 200μL MeCN after stirring for 15 minutes. The reaction was stirred for 24 hours at 40 °C (Table 3, entry 1) or room temperature (Table 3, entry 6). The remainder of the procedure is identical to that described above.

General Procedure Gram Scale Reaction (No Glovebox), equation 3 To a 4 dram vial was added $[Rh(COD)Cl]_2$ (100 mg, 0.20 mmol, 0.05 equiv. Rh), the vial was capped with a PTFE lined septa cap and placed under N_2. MeCN (10 mL) and $P(OPh)_3$ (220 μL, 0.84 mmol) was

added via syringe and the solution was stirred for 5 minutes before the allylic carbonate (2.30 g, 7.88 mmol) was added as a MeCN solution (5 mL). To a round bottom flask was under N_2 was added IPNBSH (2.28 g, 8.80 mmol) and K_2CO_3 (2.25 g, 16.3 mmol). The solution of catalyst and allylic carbonate was added via syringe after stirring for 15 minutes to the round bottom flask along with additional MeCN (20 mL). The reaction was stirred under a positive pressure of N_2 for 24 hours, after which the reaction was diluted with CH_2Cl_2 (100 mL) and passed over a plug of celite and concentrated. The crude reaction mixture was dissolved in THF/TFE/water (2:1:1, 30 mL total) and AcOH was added (1 mL). The reaction was stirred for 2 hours after which CH_2Cl_2 (100 mL) was added along with saturated aqueous $NaHCO_3$. The organic layer was collected and the aqueous layer was washed with additional CH_2Cl_2 (2 x 50 mL). The combined organic fractions were dried with Na_2SO_4, concentrated and the product was isolated by column chromatography (20:1 to 10:1 Hex/EtOAc) in 81% yield (1.40 g) as a pale yellow oil.

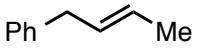


Table 4, entry 1[10] Prepared according to the General Procedure from the corresponding methyl carbonate (165 mg, 0.70 mmol) at 40 °C. Isolated in 62% yield after purification by column chromatography (pentane) as a colorless oil, *E*/*Z* = 94:6.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.31 – 7.28 (m, 2H), 7.21 – 7.18 (m, 3H), 5.63 – 5.57 (m, 1H), 5.55 – 5.51 (m, 1H), 3.33 (d, *J* = 6.8 Hz, 2H), 1.70 (m, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 141.3, 130.2, 128.6, 128.5, 126.5, 126.0, 39.2, 18.0;

HRMS (LCMS EI): calcd for $C_{10}H_{12}$ $[M]^+$ 132.0939, found 139.0940.

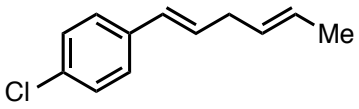


Table 4, entry 2 Prepared according to the General Procedure from the corresponding methyl carbonate (106 mg, 0.40 mmol). Isolated in 57% yield after purification by column chromatography (40:1), *E*/*Z* = 94:6.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.25 – 7.22 (m, 4H), 6.31 (d, *J* = 15.9 Hz, 1H), 6.17 (dt, *J* = 15.8, 6.7 Hz, 1H), 5.50 – 5.47 (m, 2H), 2.87 – 2.85 (m, 2H), 1.68 (d, *J* = 5.1, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 136.4, 132.6, 130.2, 129.2, 128.8 (2), 127.4, 126.7, 36.1, 18.1;

HRMS (LCMS EI): calcd for $C_{12}H_{13}Cl$ $[M]^+$ 192.0706, found 192.0700.

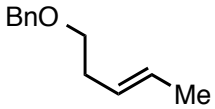


Table 4, entry 3[15] Prepared according to the General Procedure from the corresponding methyl carbonate (100 mg, 0.40 mmol) at 40 °C with 5% $[Rh(COD)Cl]_2$ and 20% $P(OPh)_3$. Isolated in 79% yield after purification by column chromatography (20:1 Hex/EtOAc) as a colorless oil (*E*/*Z* = 94:6).

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.35 – 7.32 (m, 4H), 7.28 (m, 1H), 5.57 – 5.42 (m, 2H), 4.52 (s, 2H), 3.48 (t, *J* = 6.9 Hz, 2H), 2.32 (m, 2H), 1.66 (dd, *J* = 8.1, 1.4 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 138.8, 128.5, 127.8, 127.7 (2), 127.1, 73.1, 70.4, 35.3, 18.2;
HRMS (LCMS EI): calcd for $C_{12}H_{16}O$ $[M]^+$ 176.1201, found 176.1200.

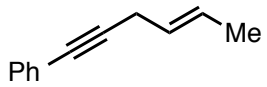


Table 4, entry 4 Prepared according to the General Procedure from the corresponding methyl carbonate (161 mg, 0.70 mmol) at 40 °C with 5% $[Rh(COD)Cl]_2$ and 20% $P(OPh)_3$. Isolated in 64% yield after purification by column chromatography (Hex/EtOAc gradient).

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.43 – 7.41 (m, 2H), 7.29 – 7.26 (m, 3H), 5.77 (m, 1H), 5.51 (m, 1H), 3.13 (m, 2H), 1.72 (m, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 131.7, 128.3, 127.8, 127.1, 125.2, 124.0, 87.8, 82.3, 22.8, 17.8;
HRMS (LCMS EI): calcd for $C_{12}H_{12}$ $[M]^+$ 156.0939, found 156.0942.

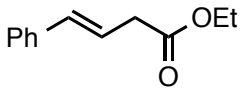


Table 4, entry 5[16] Prepared according to the General Procedure from the corresponding methyl carbonate (106 mg, 0.40 mmol) at room temperature. Isolated in 66% yield after purification by column chromatography (Pent/Et_2O gradient) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.24 (m, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.24 (d, *J* = 7.7 Hz, 2H), 1.29 (q, *J* = 7.0 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 171.8, 137.1, 133.5, 128.7, 127.7, 126.5, 122.1, 61.0, 38.7, 14.4;
HRMS (LCMS ESI): calcd for $C_{12}H_{14}NaO_2$ $[M+Na]^+$ 213.0886, found 213.0887.

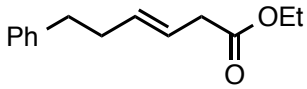


Table 4, entry 6[17] Prepared according to the General Procedure from the corresponding methyl carbonate (117 mg, 0.40 mmol) at room temperature. Isolated in 71% yield after purification by column chromatography (10:1 Hex/EtOAc) as a light yellow oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.30 – 7.26 (m, 2H), 7.20 – 7.17 (m, 3H), 5.59 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.02 (q, *J* = 6.1 Hz, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.37 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 172.3, 142.0, 133.9, 128.6, 128.5, 126.0, 122.5, 60.7, 38.3, 35.8, 34.4, 14.4;

HRMS (LCMS ESI): calcd for $C_{14}H_{18}NaO_2$ $[M+Na]^+$ 241.1199, found 241.1199.

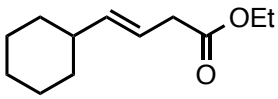


Table 4, entry 7[18] Prepared according to the General Procedure from the corresponding methyl carbonate (190 mg, 0.68 mmol) at room temperature with 5% $[Rh(COD)Cl]_2$ and 20%

$P(OPh)_3$. Isolated in 69% yield after purification by column chromatography (Hex/EtOAc gradient) as a colorless oil.

^{1}H NMR ($CDCl_3$, 700 MHz) δ 5.52 – 5.46 (m, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.00 (d, *J* = 5.6 Hz, 2H), 1.95 (m, 1H), 1.74 – 1.56 (m, 6H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.19 – 1.02 (m, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 172.4, 140.6, 119.3, 60.5, 40.7, 38.3, 32.9, 26.2, 26.1, 14.3;

HRMS (LCMS ESI): calcd for $C_{12}H_{20}NaO_2$ $[M+Na]^+$ 219.1356, found 219.1357.

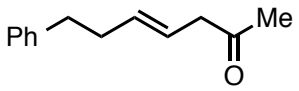


Table 4, entry 8 Prepared according to the General Procedure from the corresponding methyl carbonate (176 mg, 0.60 mmol) at room temperature. Isolated in 56% yield after purification by column chromatography (10:1 Hex/EtOAc).

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.30 – 7.26 (m, 2H), 7.20 – 7.16 (m, 3H), 5.62– 5.52 (m, 2H), 3.10 (d, *J* = 6.1 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.38 (m, 2H), 2.10 (s, 3H);

^{13}C NMR ($CDCl_3$, 176 MHz) δ 207.6, 141.8, 134.6, 128.6, 128.5, 126.0, 122.7, 47.8, 25.8, 34.4, 29.5;

HRMS (LCMS EI): calcd for $C_{13}H_{16}O$ $[M]^+$ 188.1201, found 188.1203.

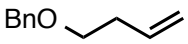


Table 4, entry 9 Prepared according to the General Procedure from the corresponding methyl carbonate (142 mg, 0.60 mmol) at 40 °C with 5% $[Rh(COD)Cl]_2$ and 20% $P(OPh)_3$. Isolated in 78% yield after purification by column chromatography (Hex/EtOAc 40:1) as a colorless oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.38 – 7.33 (m, 4H), 7.30 (m, 1H), 5.85 (m, 1H), 5.14 – 5.05 (m, 2H), 4.54 (s, 2H), 3.54 (t, *J* = 5.2 Hz, 2H), 2.41 – 2.38 (m, 2H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.6, 135.4, 128.5, 127.8, 127.7, 116.5, 73.0, 69.7, 34.4;

HRMS (LCMS EI): calcd for $C_{11}H_{14}O$ $[M]^+$ 162.1045, found 162.1042.

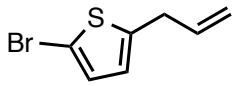


Table 4, entry 10 Prepared according to the General Procedure from the corresponding methyl carbonate (83 mg, 0.30 mmol) at 40 °C with 5% $[Rh(COD)Cl]_2$ and 20% $P(OPh)_3$. Isolated in 52% yield after purification by column chromatography (Hex/EtOAc gradient) as a colorless oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 6.87 (d, *J* = 3.7 Hz, 1H), 6.57 (dt, *J* = 3.7, 1.1 Hz, 1H), 5.93 (m, 1H), 5.19 – 5.10 (m, 2H), 3.50 (m, 2H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.6, 135.6, 129.6, 125.0, 116.8, 109.6, 34.5;

HRMS (LCMS EI): calcd for C_7H_7SBr $[M]^+$ 203.9431, found 203.9431.

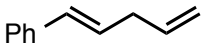


Table 4, entry 11 Prepared according to the General Procedure from the corresponding methyl carbonate (131 mg, 0.60 mmol) at 40 °C with 5% $[Rh(COD)Cl]_2$ and 20% $P(OPh)_3$. Isolated in 65% yield after purification by column chromatography (Hex/EtOAc 40:1) as a colorless oil.

^{1}H NMR ($CDCl_3$, 498 MHz) δ 7.38 – 7.18 (m, 5H), 6.43 (d, *J* = 12.8 Hz, 1H), 6.24 (dt, *J* = 12.8, 5.2 Hz, 1H), 5.92 (m, 1H), 5.15 – 5.07 (m, 2H), 2.99 – 2.96 (m, 2H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.8, 136.6, 131.0, 128.6, 128.3, 127.1, 126.2, 115.8, 37.1;

HRMS (LCMS EI): calcd for $C_{11}H_{12}$ $[M]^+$ 144.0939, found 144.0941.

VI. References

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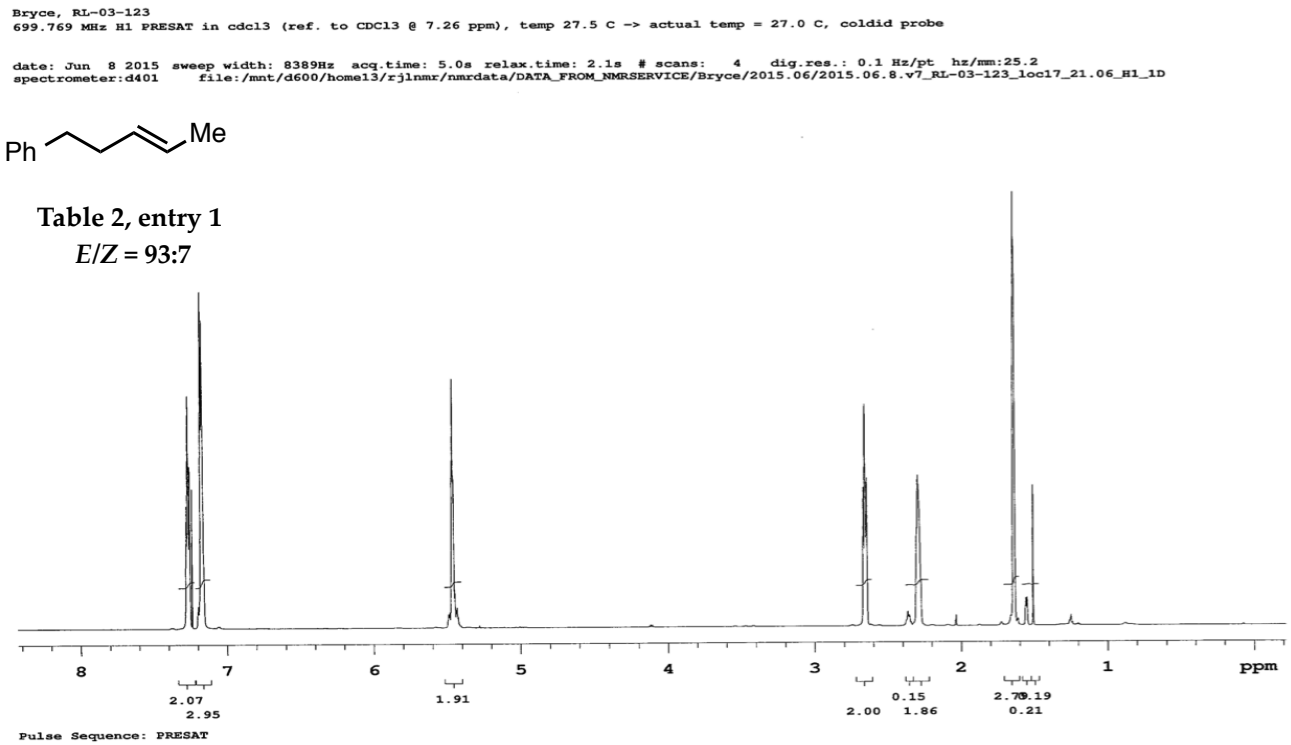
VII. ^{1}H NMR Spectra



Bryce, RL-04-035-A
699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid probe

date: Jun 8 2015 sweep width: 8389Hz acq.time: 5.0s relax.time: 2.1s # scans: 4 dig.res.: 0.1 Hz/pt hz/mm:26.9
spectrometer:d401 file:/mnt/d600/home13/rjlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bryce/2015.06/2015.06.8.v7_RL-04-035-A_loc22_22.17_H1_1D

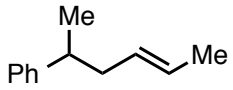
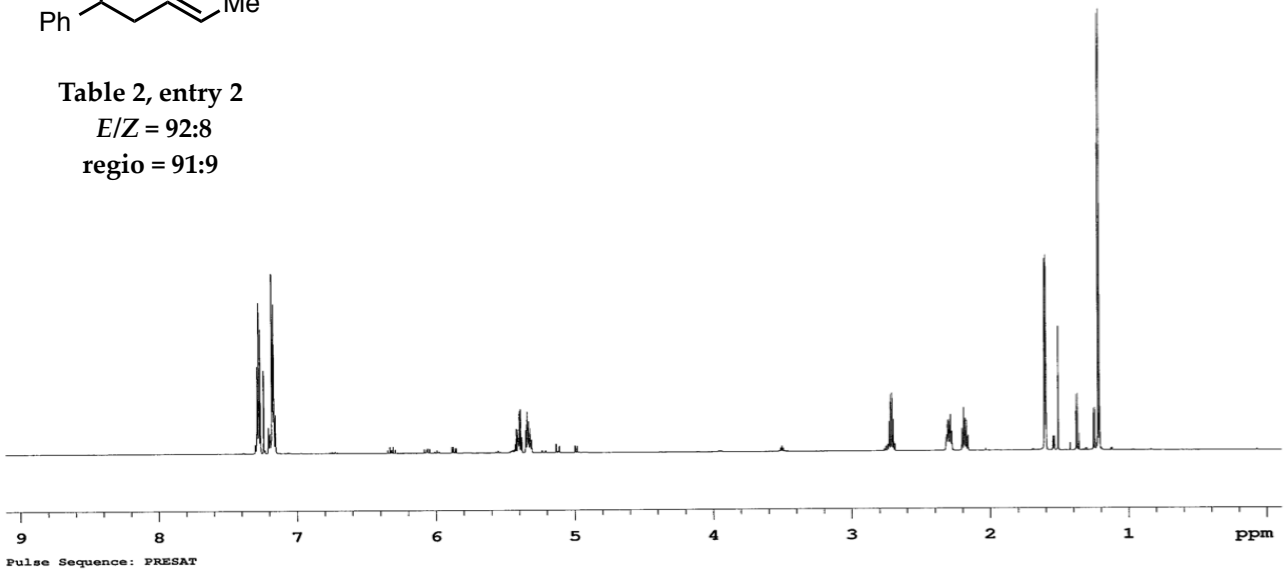


Table 2, entry 2
***E*/*Z* = 92:8**
regio = 91:9



Pulse Sequence: PRESAT

Bryce, RL-03-177-A
699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid probe

date: Jun 8 2015 sweep width: 8389Hz acq.time: 5.0s relax.time: 2.1s # scans: 4 dig.res.: 0.1 Hz/pt hz/mm:27.3
spectrometer:d401 file:/mnt/d600/home13/rjlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bryce/2015.06/2015.06.8.v7_RL-03-177-A_loc15_20.34_H1_1D

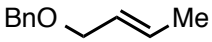
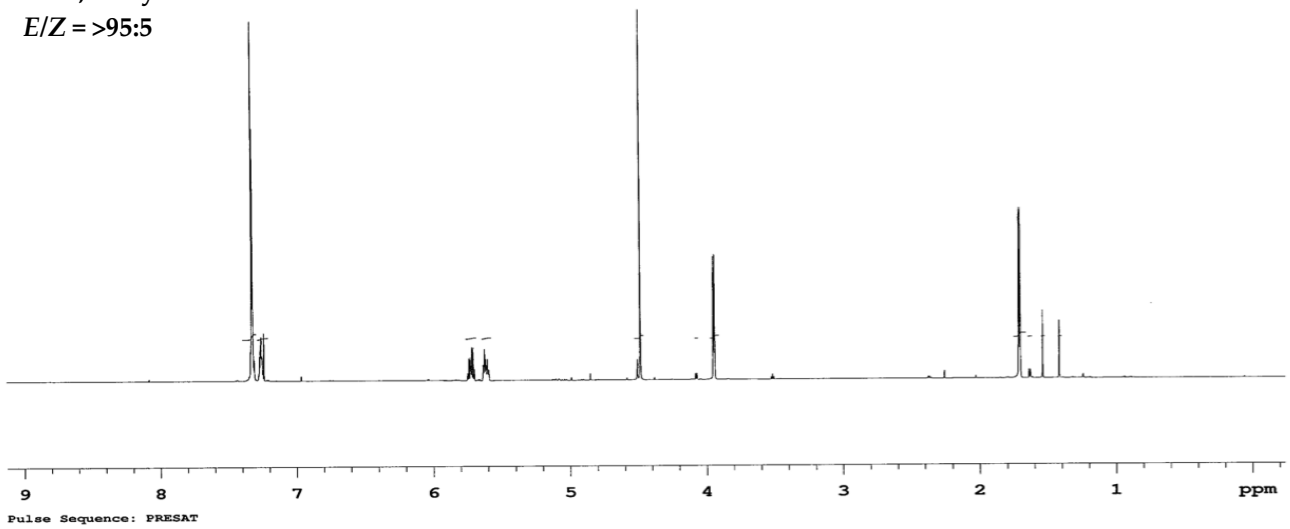


Table 3, entry 3

***E*/*Z* = >95:5**



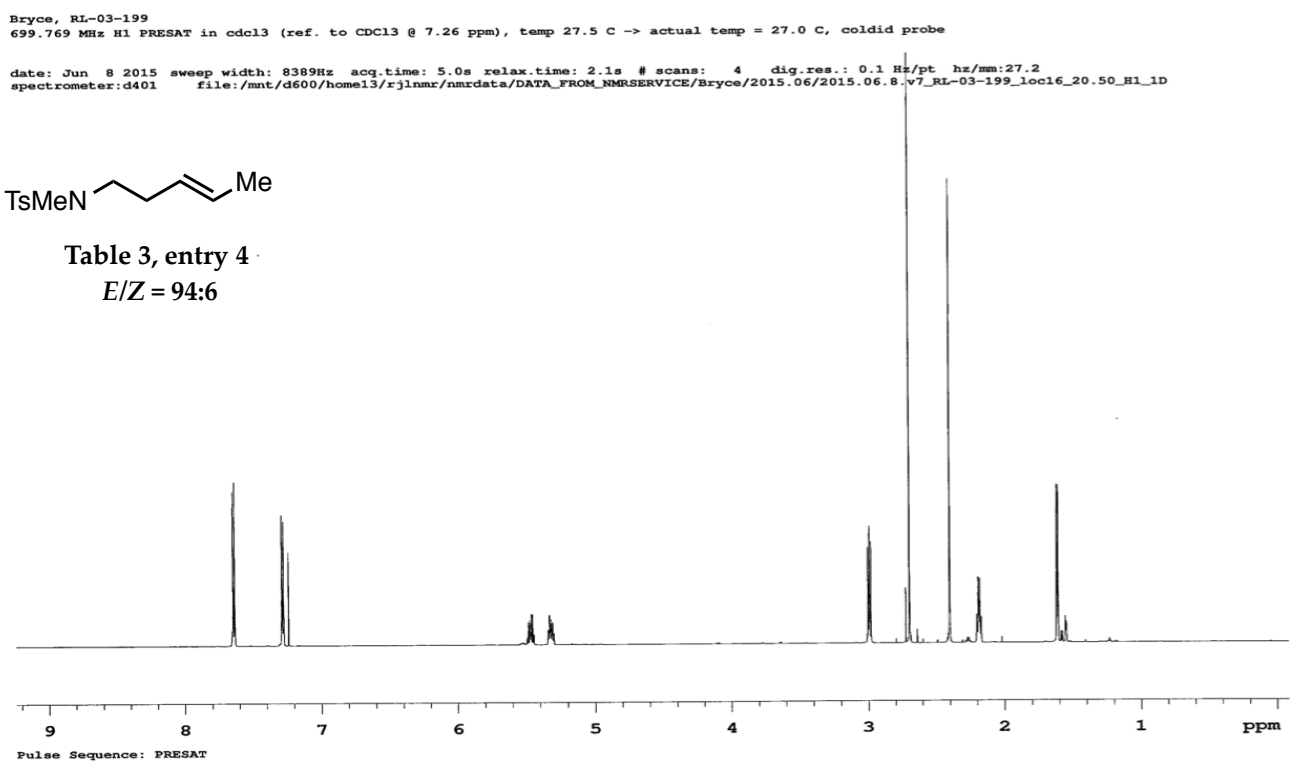


Table 3, entry 4

***E*/*Z* = 94:6**

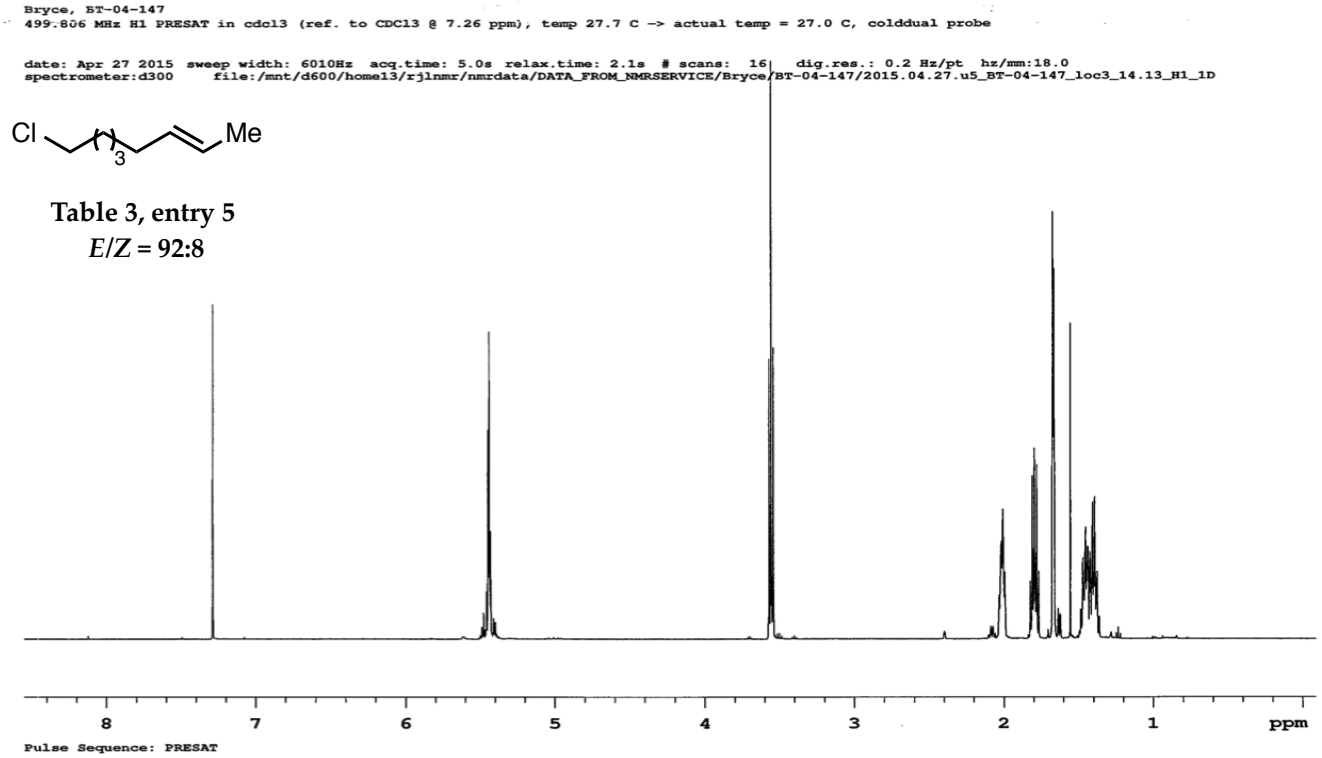


Table 3, entry 5

***E*/*Z* = 92:8**

Bryce, RL-03-187
699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid probe

date: Jun 9 2015 sweep width: 8389Hz acq.time: 5.0s relax.time: 2.1s # scans: 4 dig.res.: 0.1 Hz/pt hz/mm:25.5
spectrometer:d401 file:/mnt/d600/home13/rjlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bryce/2015.06/2015.06.9.v7_RL-03-187_loc7_21.39_H1_1D

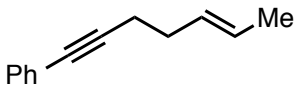
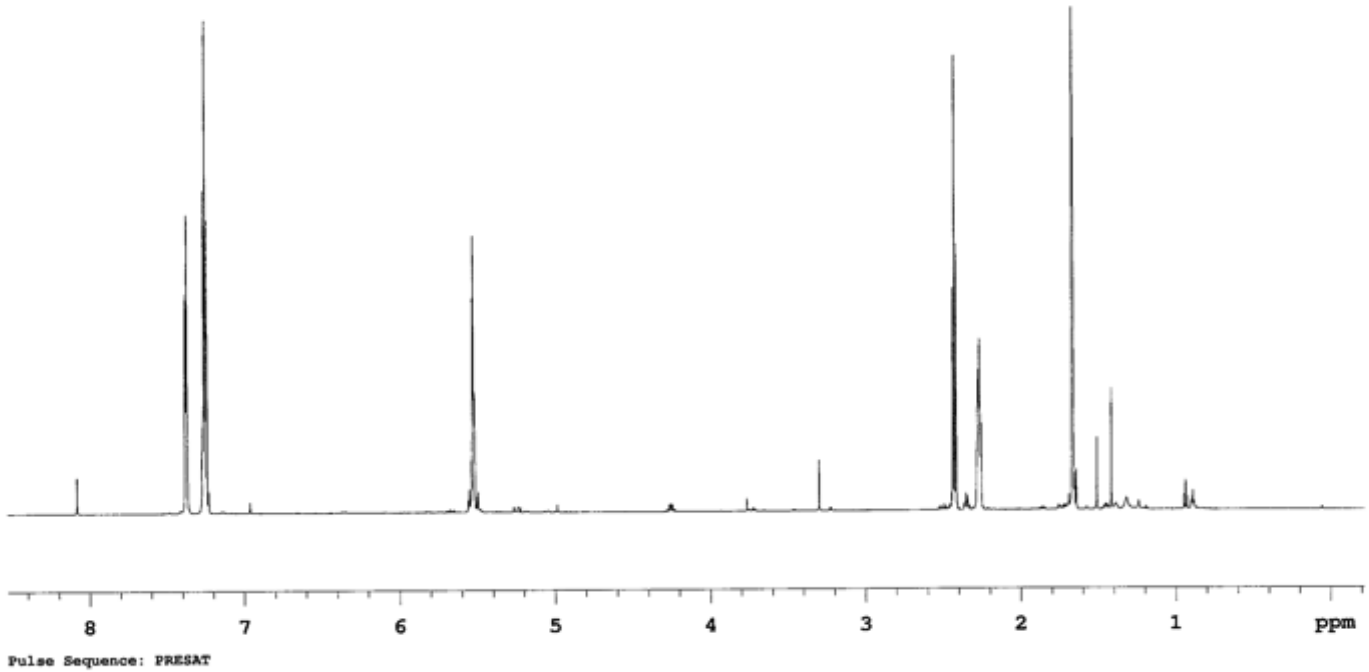


Table 3, entry 6

***E*/*Z* = >95:5**



Pulse Sequence: PRESAT

Bryce, RL-03-143
699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid probe

date: Jun 8 2015 sweep width: 8389Hz acq.time: 5.0s relax.time: 2.1s # scans: 4 dig.res.: 0.1 Hz/pt hz/mm:23.9
spectrometer:d401 file:/mnt/d600/home13/rjlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bryce/2015.06/2015.06.8.v7_RL-03-143_loc13_20.02_H1_1D

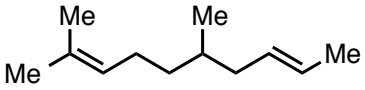
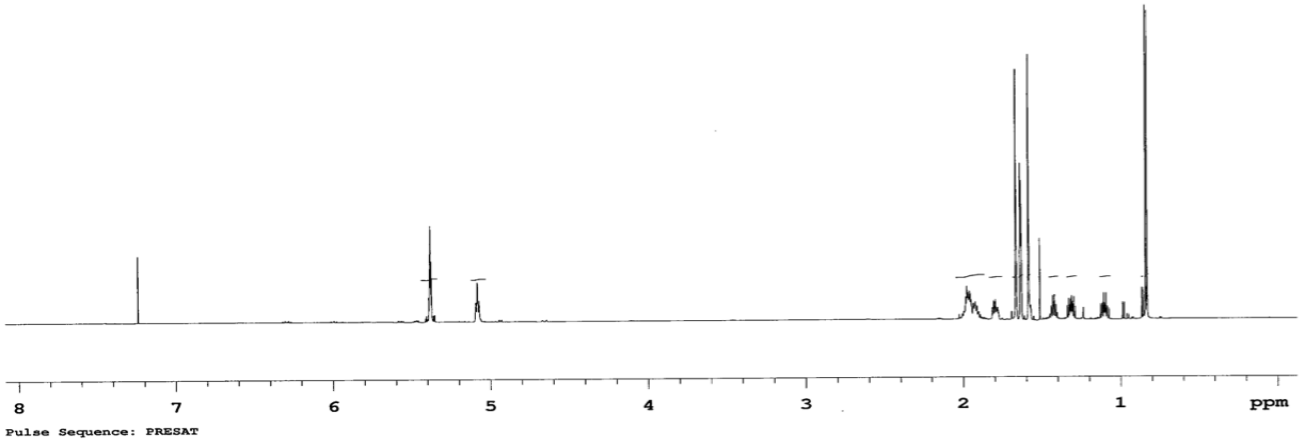


Table 3, entry 7
***E*/*Z* = 94:6**



Pulse Sequence: PRESAT

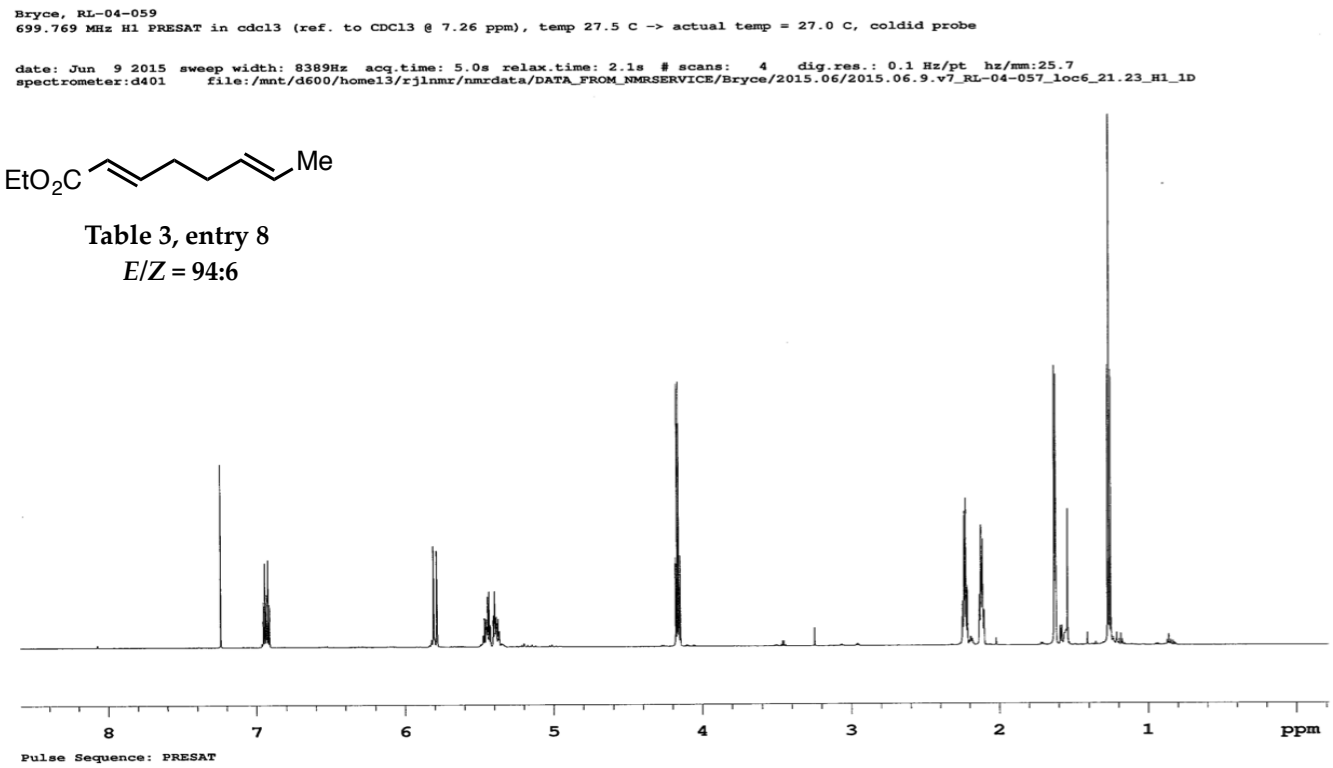


Table 3, entry 8

***E*/*Z* = 94:6**

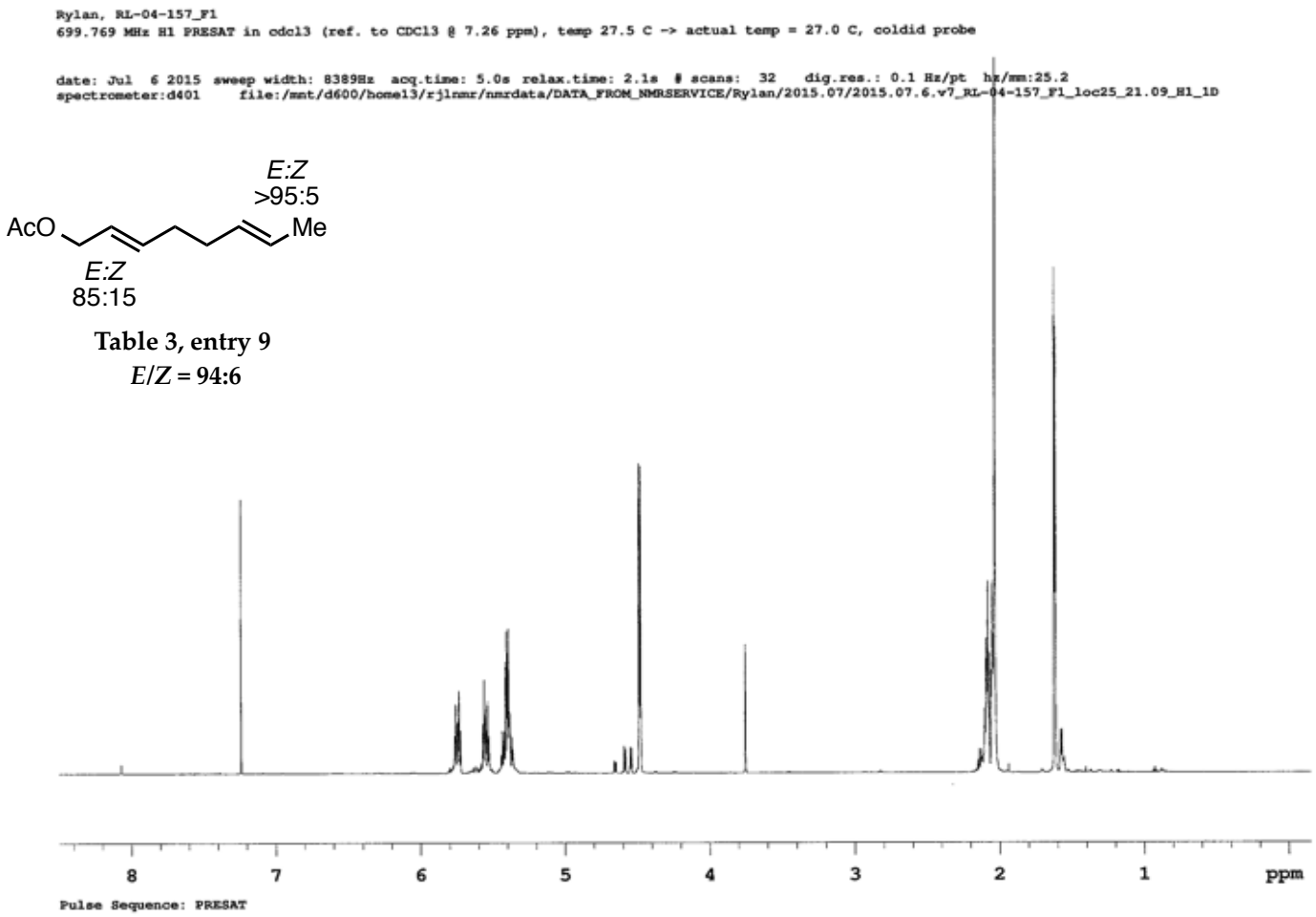


Table 3, entry 9

***E*/*Z* = 94:6**

Bryce, RL-03-171-B
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date: Jun 8 2015 sweep width: 8389Hz acq.time: 5.0s relax.time: 2.1s # scans: 4 dig.res.: 0.1 Hz/pt hz/mm:26.9
spectrometer:d401 file:/mnt/d600/home13/rjlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bryce/2015.06/2015.06.8.v7_RL-03-171-B_loc14_20.18_H1_1D

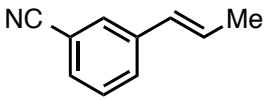
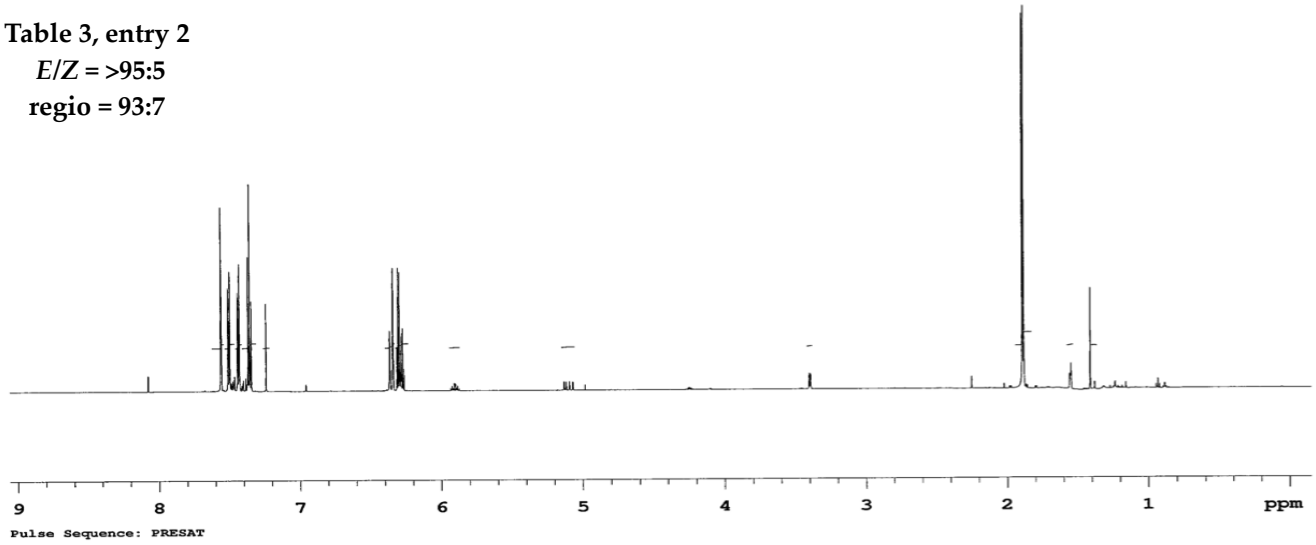


Table 3, entry 2
***E*/*Z* = >95:5**
regio = 93:7



Pulse Sequence: PRESAT

Bryce, RL-04-035-B
699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid probe

date: Jun 8 2015 sweep width: 8389Hz acq.time: 5.0s relax.time: 2.1s # scans: 4 dig.res.: 0.1 Hz/pt hz/mm:27.1
spectrometer:d401 file:/mnt/d600/home13/rjlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bryce/2015.06/2015.06.8.v7_RL-04-035-B_loc21_22.02_H1_1D

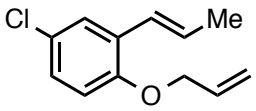
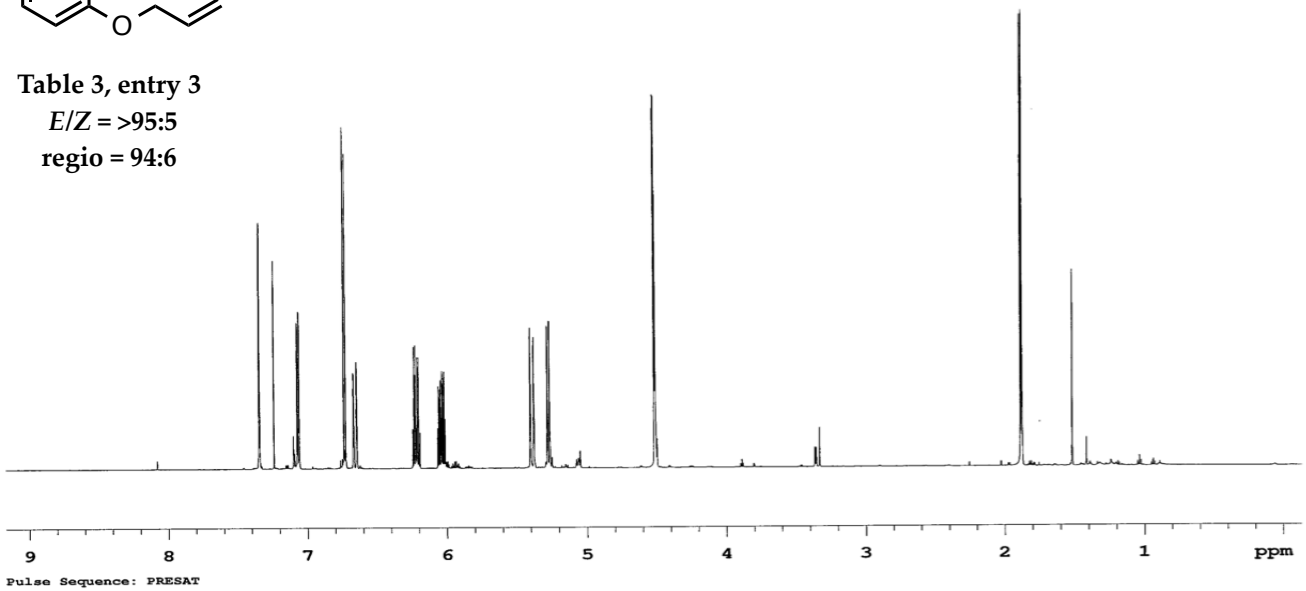


Table 3, entry 3
***E*/*Z* = >95:5**
regio = 94:6



Pulse Sequence: PRESAT

Bryce, RL-04-023
699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid probe

date: Jun 8 2015 sweep width: 8389Hz acq.time: 5.0s relax.time: 2.1s # scans: 4 dig.res.: 0.1 Hz/pt hz/mm:27.2
spectrometer:d401 file:/mnt/d600/home13/rjlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bryce/2015.06/2015.06.8.v7_RL-04-023_loc20_21.45_H1_1D

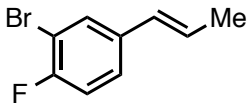
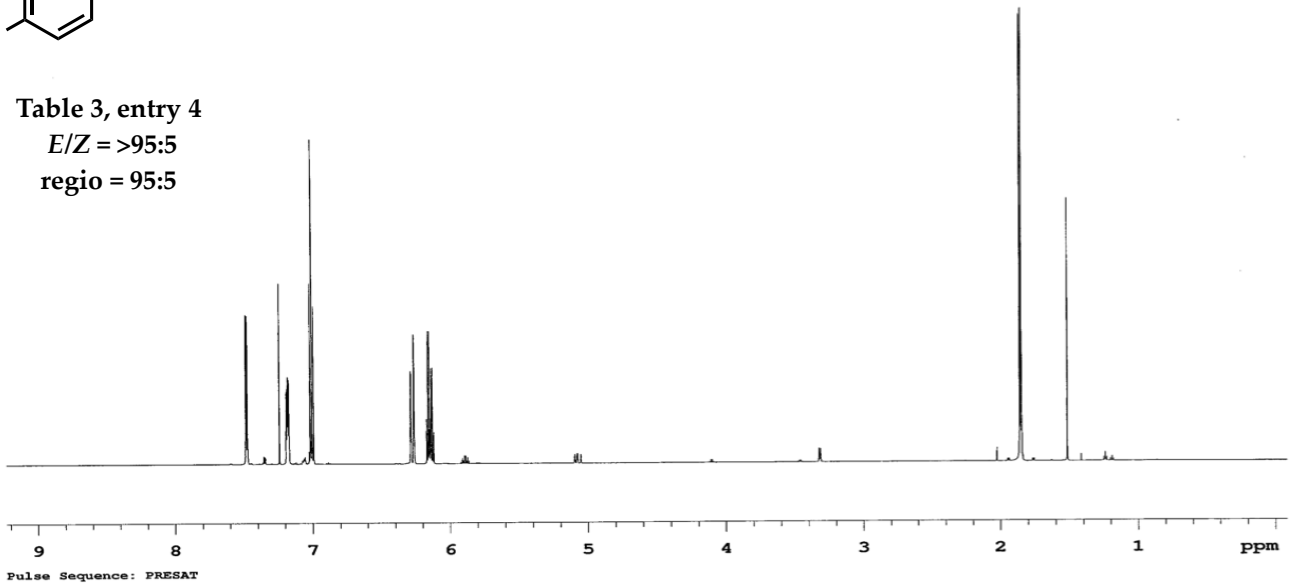


Table 3, entry 4
***E*/*Z* = >95:5**
regio = 95:5



Pulse Sequence: PRESAT

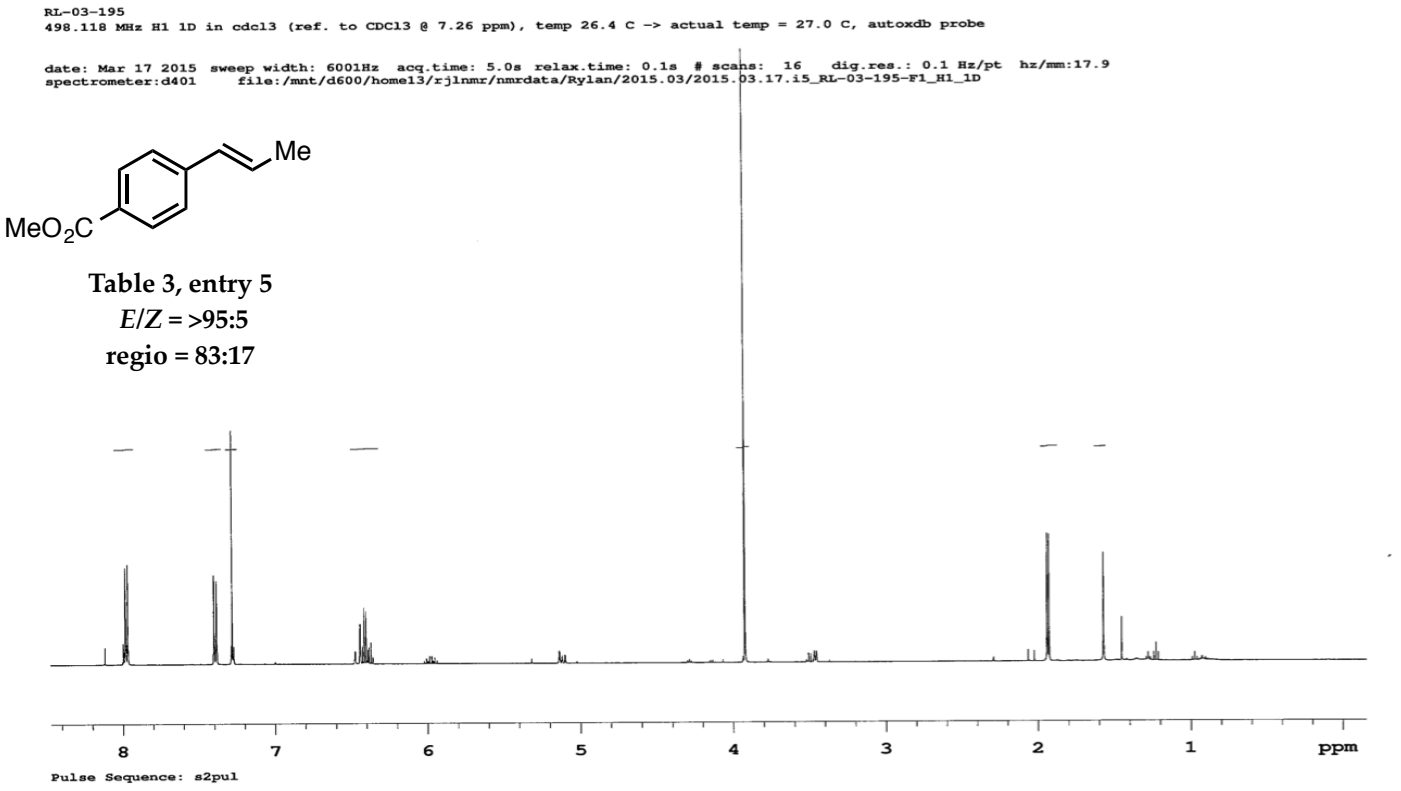


Table 3, entry 5
***E*/*Z* = >95:5**
regio = 83:17

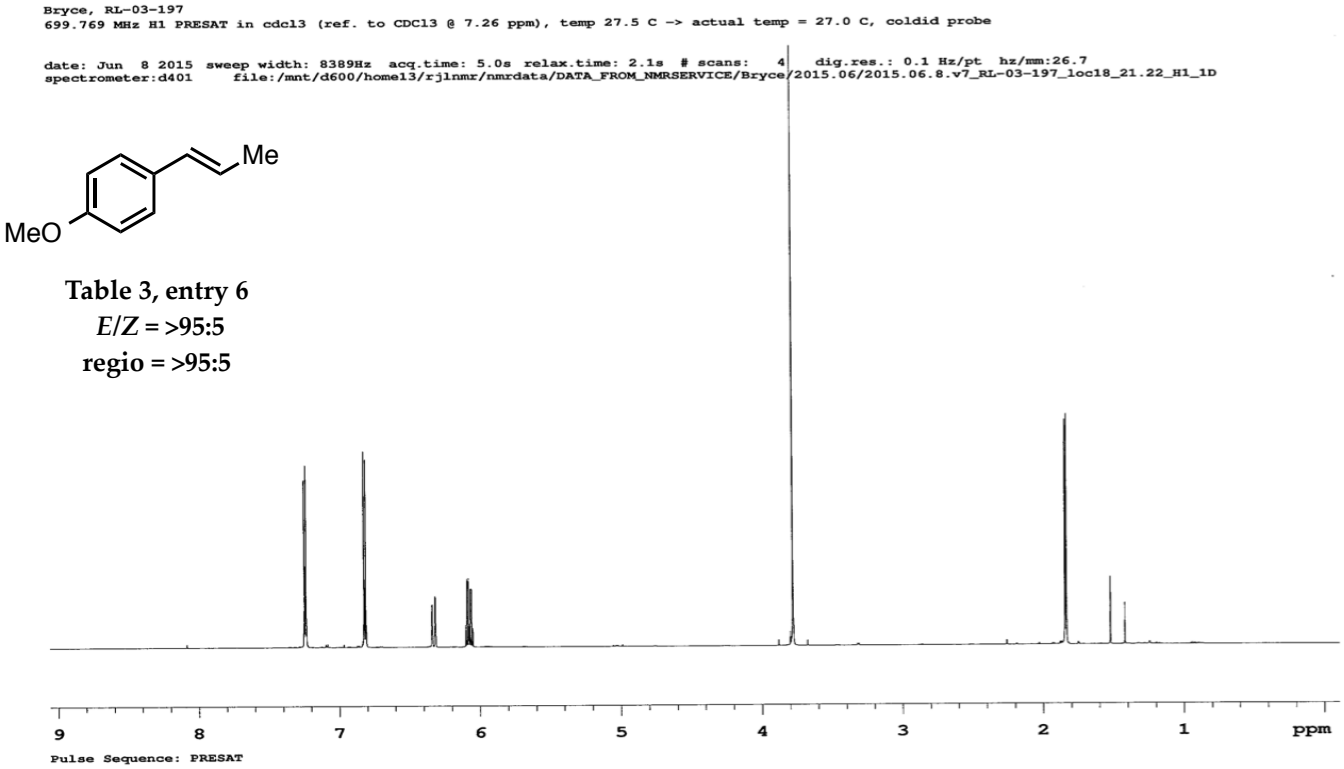


Table 3, entry 6
***E*/*Z* = >95:5**
regio = >95:5

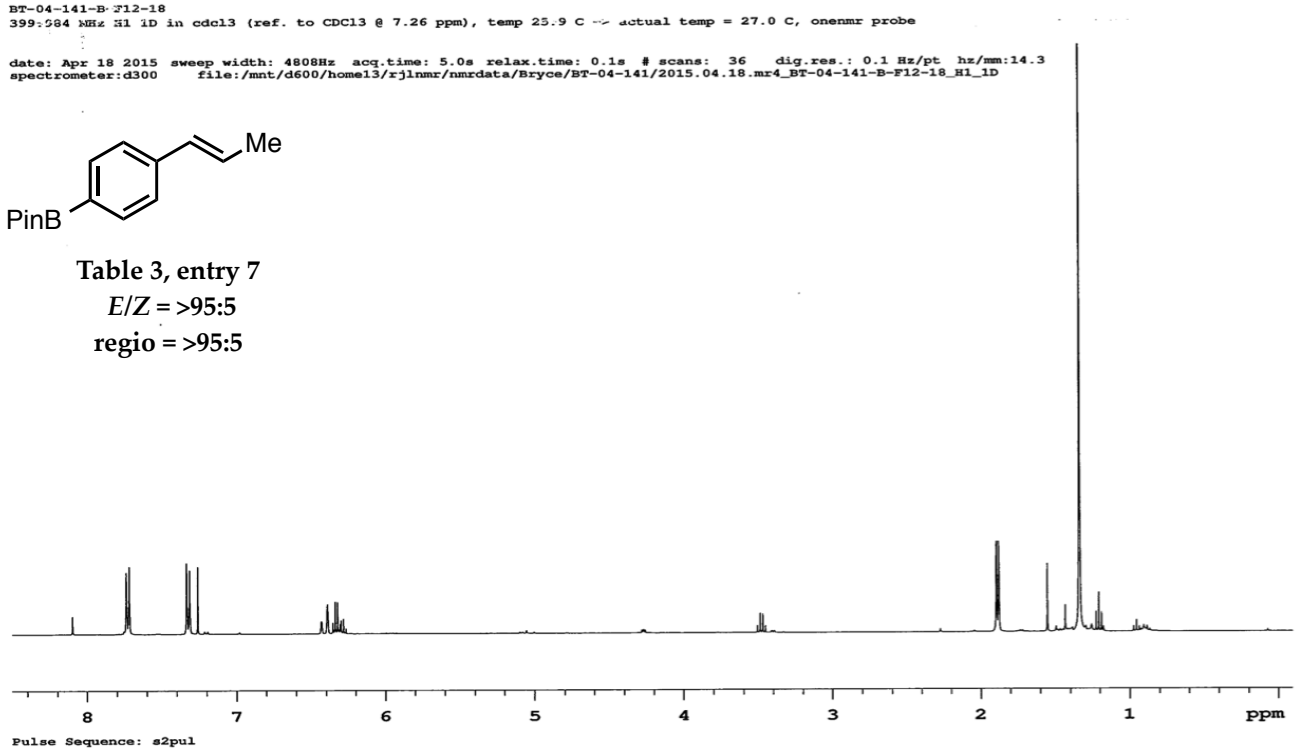


Table 3, entry 7
***E*/*Z* = >95:5**
regio = >95:5

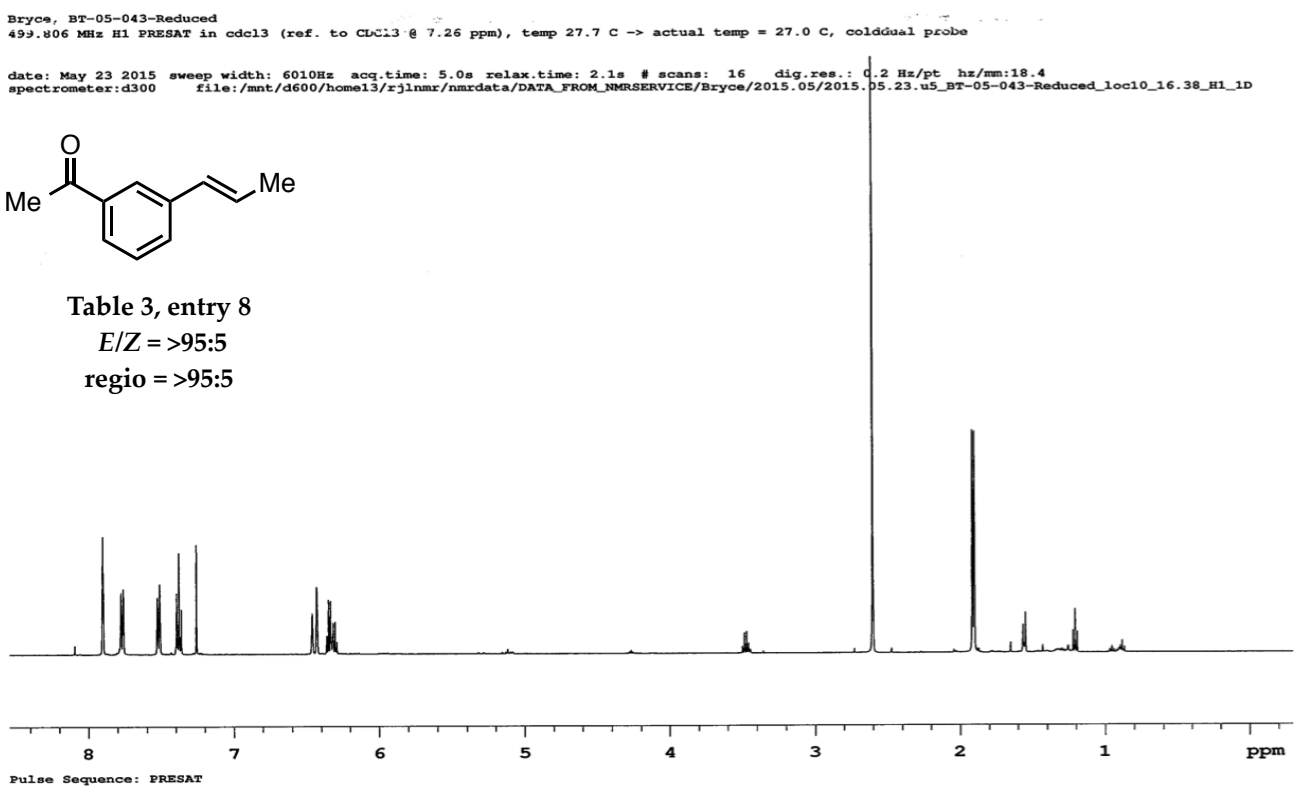


Table 3, entry 8

***E*/*Z* = >95:5**

regio = >95:5

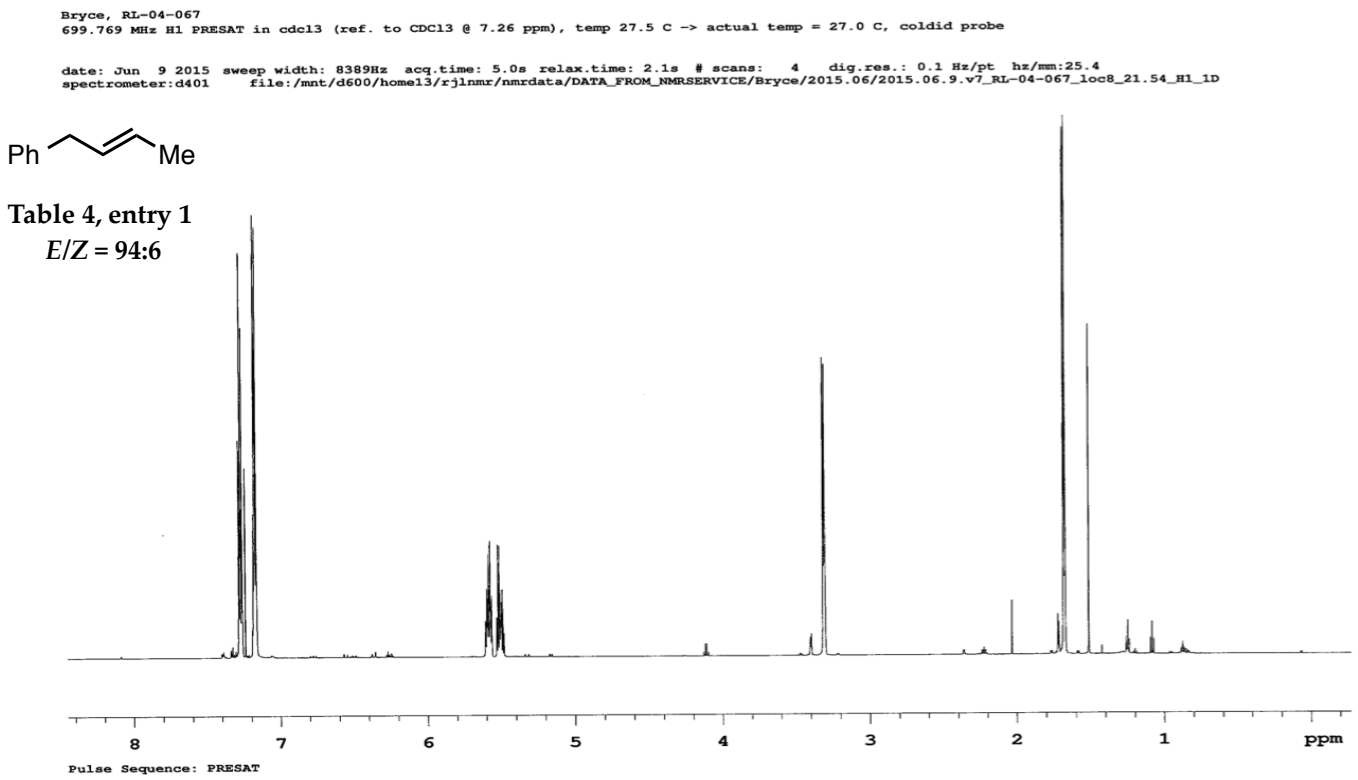
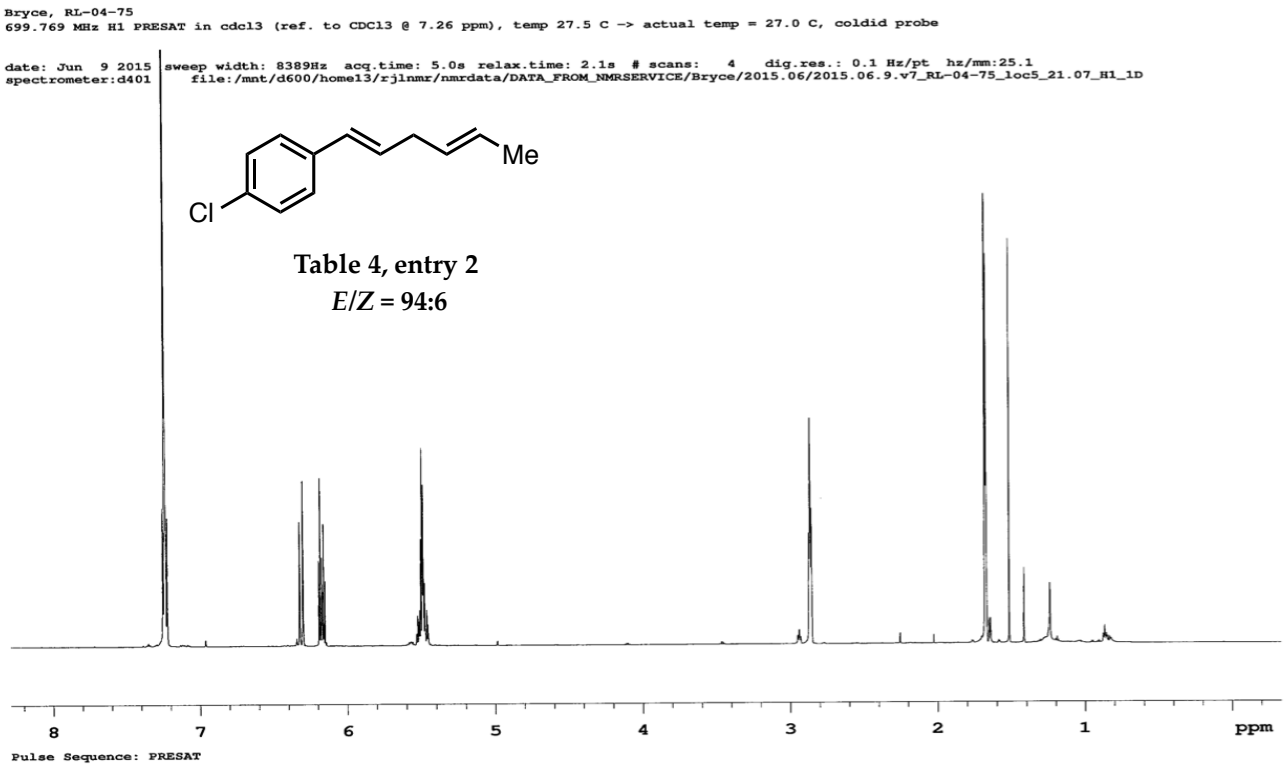


Table 4, entry 1

***E*/*Z* = 94:6**


Bryce, RL-04-75
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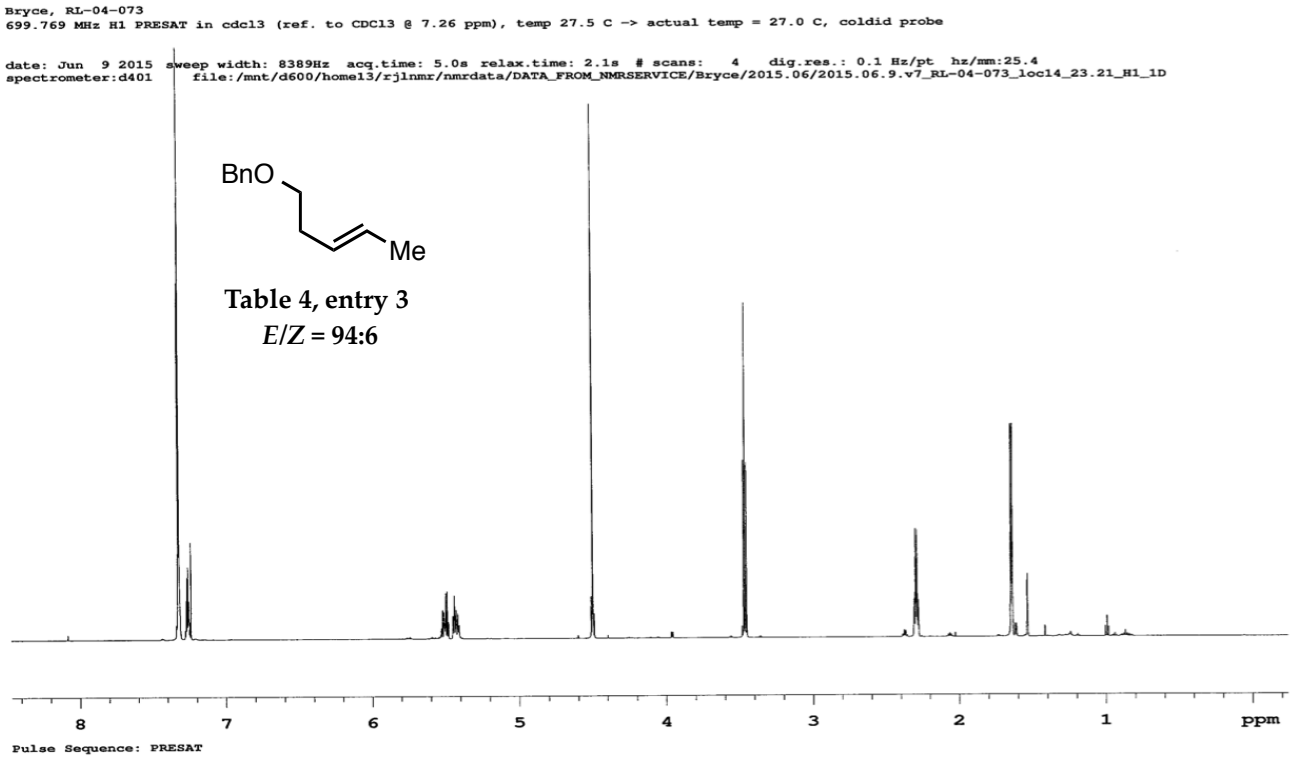
date: Jun 9 2015
spectrometer:d401
sweep width: 8389Hz acq.time: 5.0s relax.time: 2.1s # scans: 4 dig.res.: 0.1 Hz/pt hz/mm:25.1
file:/mnt/d600/home13/rjlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bryce/2015.06/2015.06.9.v7_RL-04-75_loc5_21.07_H1_1D
Cl
Me
Table 4, entry 2
E/Z = 94:6
8
7
6
5
4
3
2
1
ppm
Pulse Sequence: PRESAT


Bryce, RL-04-073
699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid probe
date: Jun 9 2015 sweep width: 8389Hz acq.time: 5.0s relax.time: 2.1s # scans: 4 dig.res.: 0.1 Hz/pt hz/mm:25.4
spectrometer:d401 file:/mnt/d600/home13/rjlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bryce/2015.06/2015.06.9.v7_RL-04-073_loc14_23.21_H1_1D
BnO
Me
Table 4, entry 3
E/Z = 94:6
8
7
6
5
4
3
2
1
ppm
Pulse Sequence: PRESAT

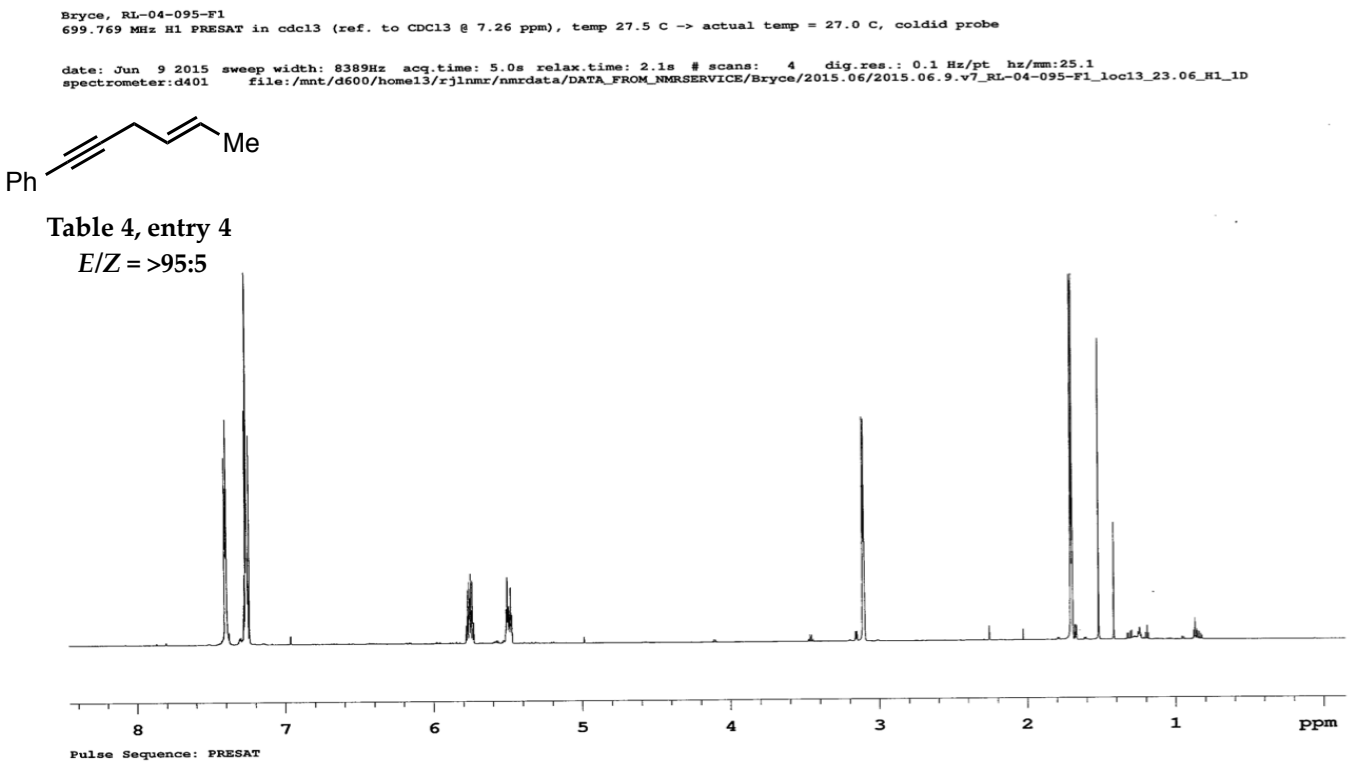


Table 4, entry 4

***E*/*Z* = >95:5**

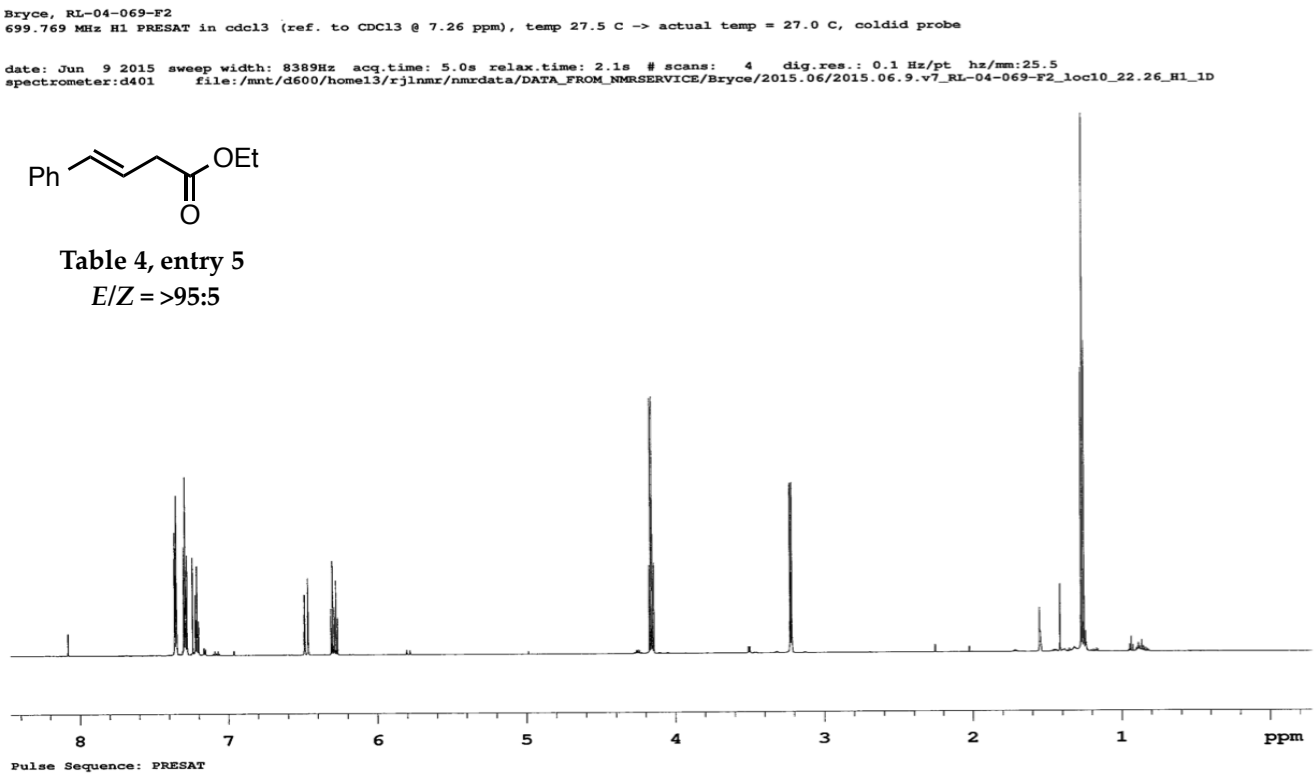


Table 4, entry 5

***E*/*Z* = >95:5**

Bryce, RL-04-079
699.769 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid probe

date: Jun 9 2015 sweep width: 8389Hz acq.time: 5.0s relax.time: 2.1s # scans: 4 dig.res.: 0.1 Hz/pt hz/mm:24.9
spectrometer:d401 file:/mnt/d600/home13/rjlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bryce/2015.06/2015.06.9.v7_RL-04-079_loc12_22.50_H1_1D

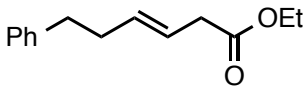
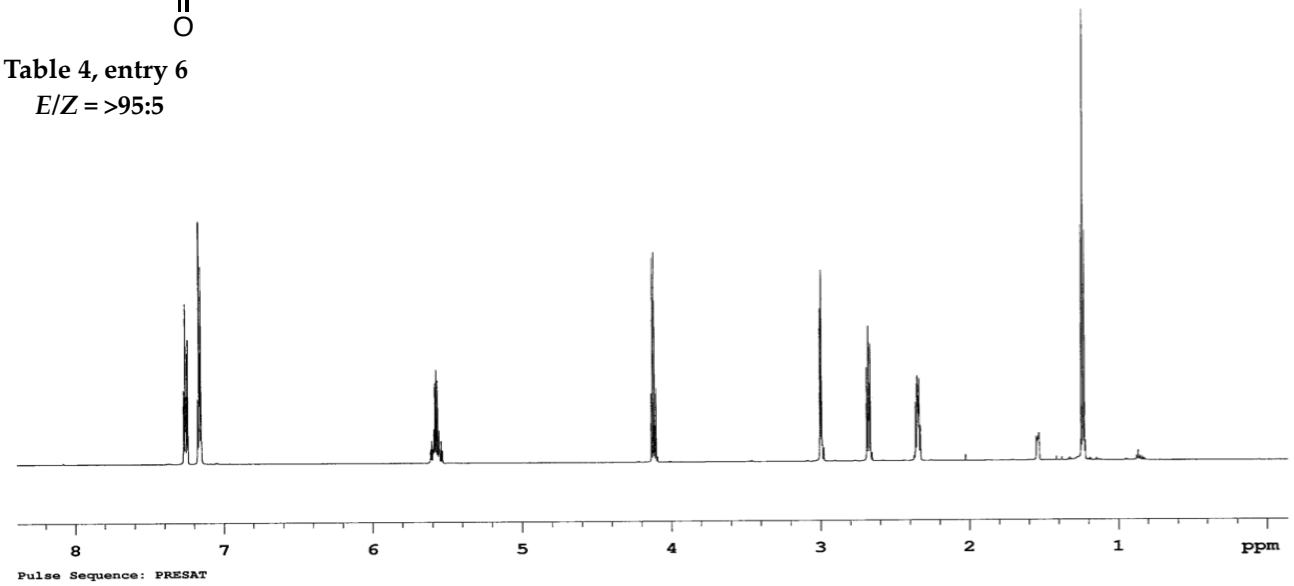


Table 4, entry 6
***E*/*Z* = >95:5**



Pulse Sequence: PRESAT

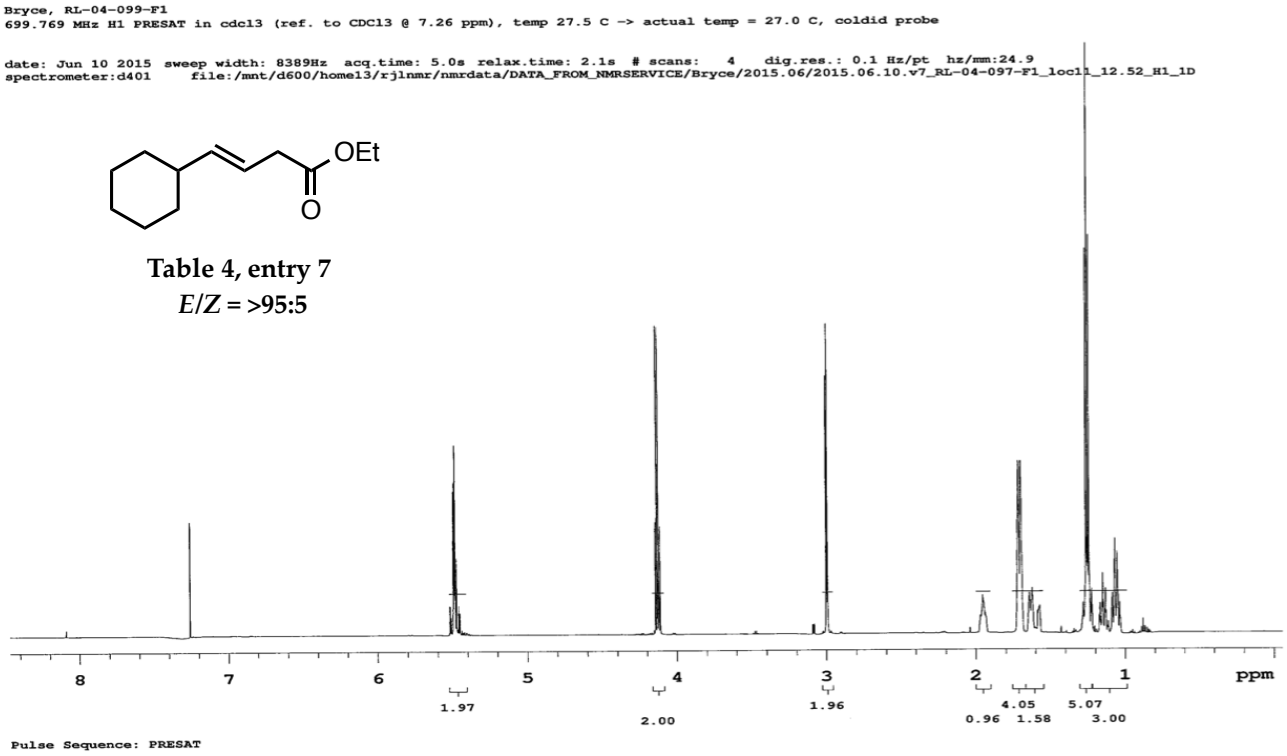


Table 4, entry 7

***E*/*Z* = >95:5**

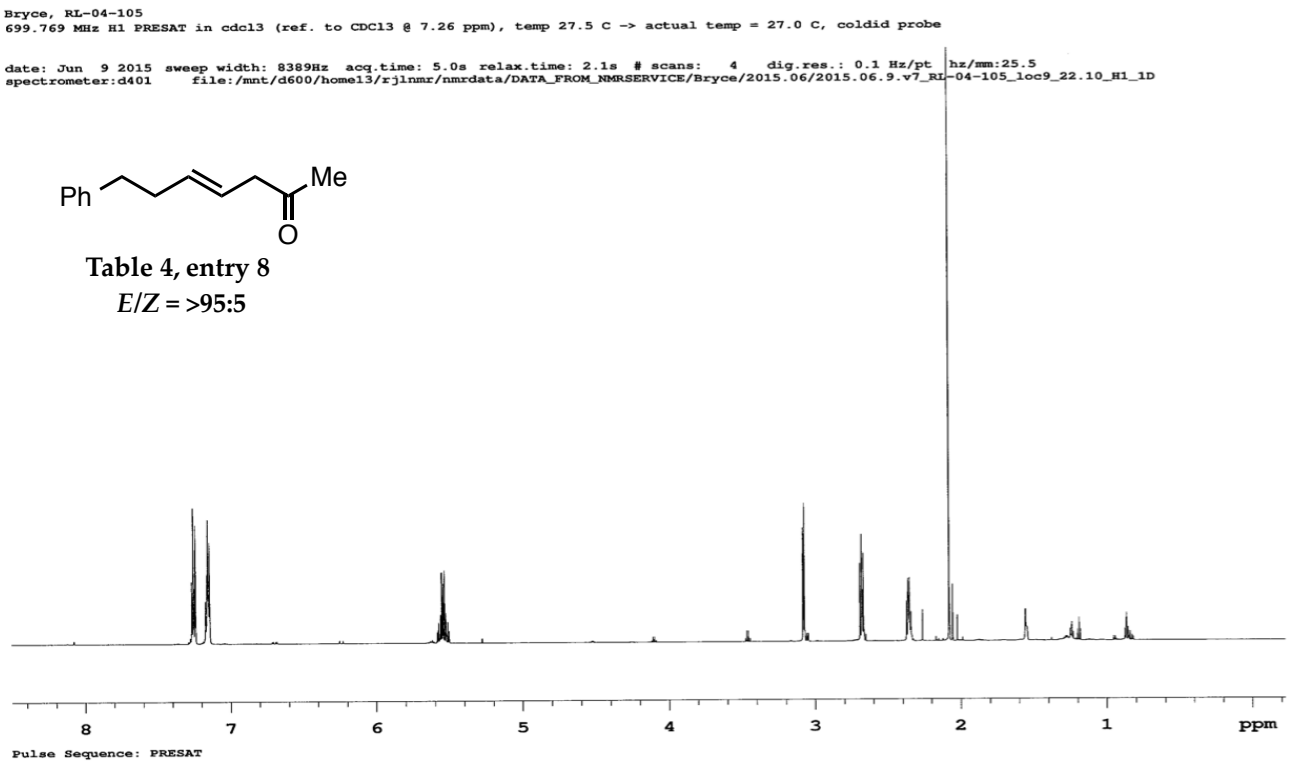
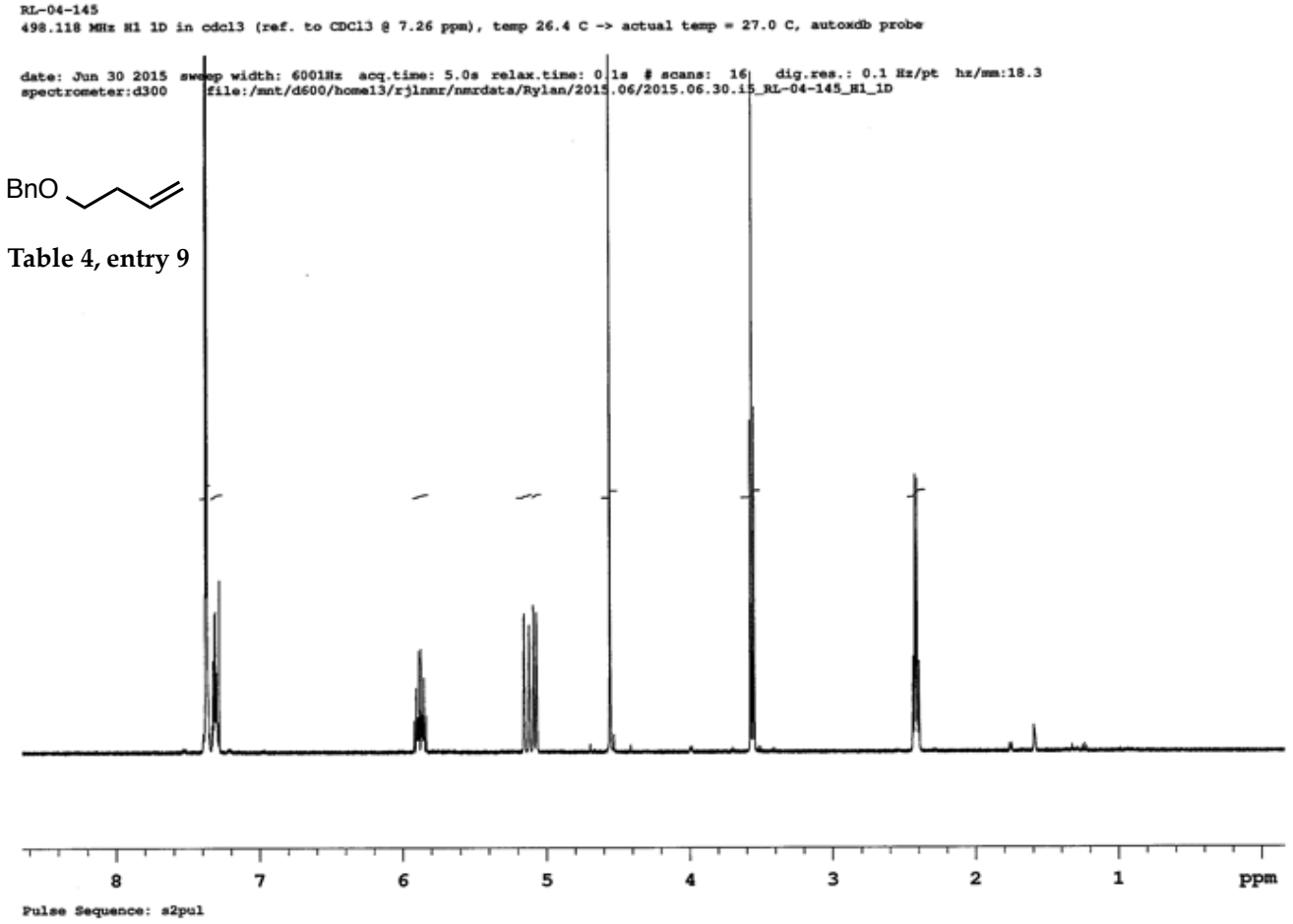


Table 4, entry 8

***E*/*Z* = >95:5**


RL-04-145
498.118 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.4 C -> actual temp = 27.0 C, autoxdb probe
date: Jun 30 2015 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:18.3
spectrometer:d300 file:/mnt/d600/home13/rjlnmr/nmrdata/Rylan/2015.06/2015.06.30.i5_RL-04-145_H1_1D
BnO
Table 4, entry 9
8
7
6
5
4
3
2
1
ppm
Pulse Sequence: s2pul

RL-04-141
399.984 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 25.9 C -> actual temp = 27.0 C, onenmr probe

date: Jun 27 2015 sweep width: 4808Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:14.4
spectrometer:d300 file:/mnt/d600/home13/rjlnmr/nmrdata/Rylan/2015.06/2015.06.27.mr4_RL-04-141_H1_1D

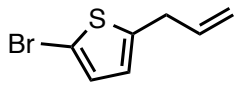
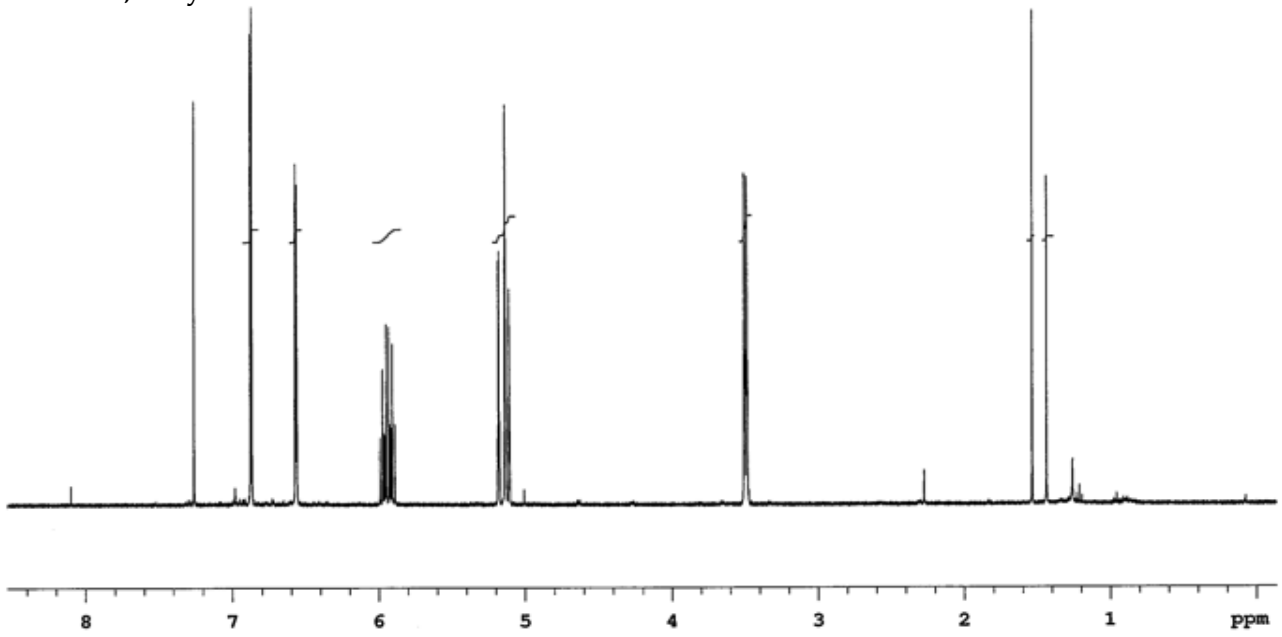
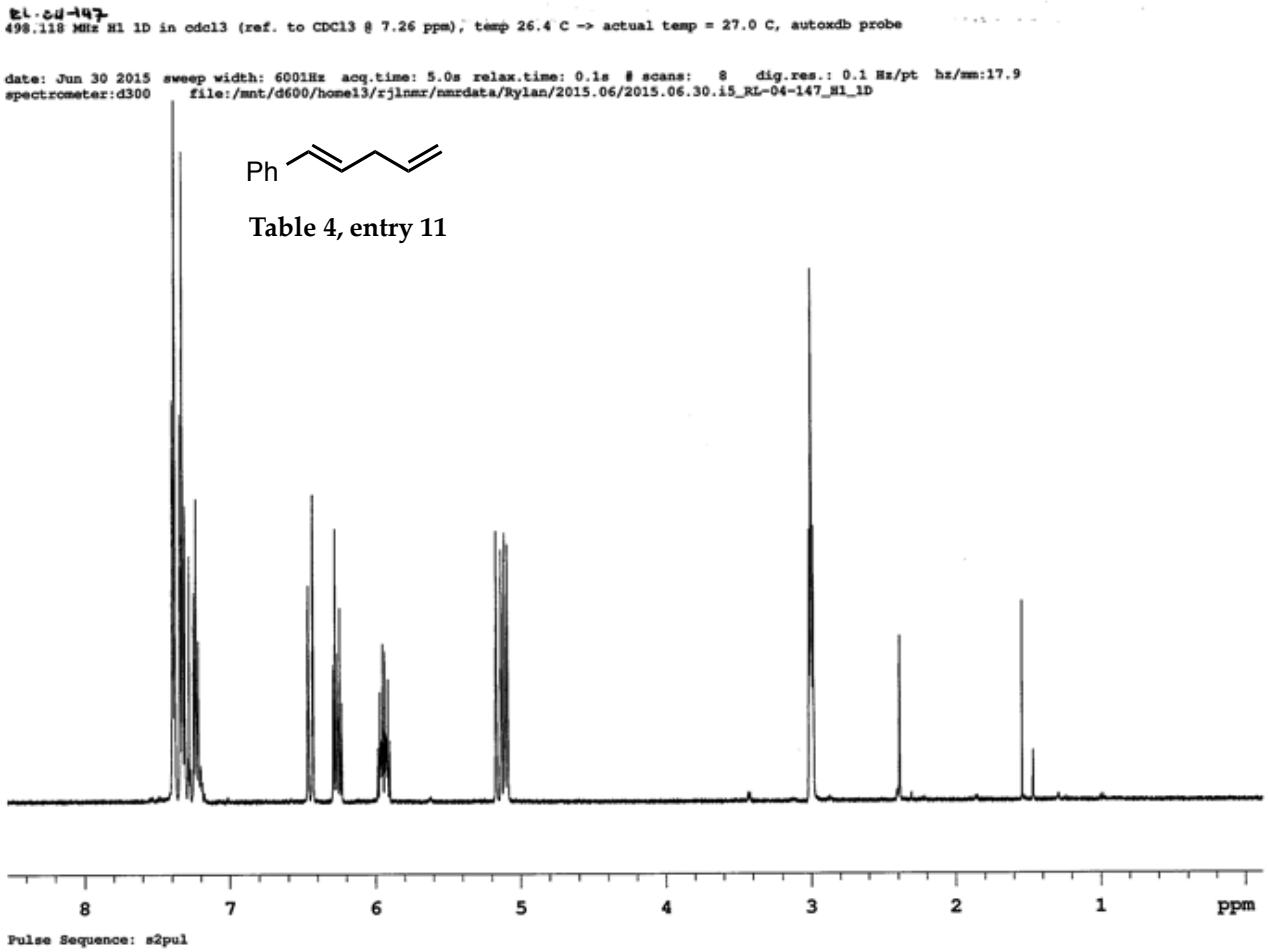


Table 4, entry 10



Pulse Sequence: s2pul


RL-04-147
498.118 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.4 C -> actual temp = 27.0 C, autoxdb probe
date: Jun 30 2015 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 8 dig.res.: 0.1 Hz/pt hz/mm:17.9
spectrometer:d300 file:/mnt/d600/home13/rjlnmr/nmrdata/Rylan/2015.06/2015.06.30.i5_RL-04-147_H1_1D
Ph
Table 4, entry 11
8
7
6
5
4
3
2
1
ppm
Pulse Sequence: s2pul