Supplementary Information

"Catalytic C-C Coupling *via* Transfer Hydrogenation: Reverse Prenylation, Crotylation and Allylation from the Alcohol or Aldehyde Oxidation Level"

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Table of Contents

General Experimental Details. All reactions were run under a balloon pressure atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred *via* oven-dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. Dichloroethane, dichloromethane and ethyl acetate were distilled from CaH_2 and sparged with argon immediately prior to use. BIPHEP was used as received from Strem Chemicals. Dimethylallene and methylallene were used as received from Fluka. Isopropanol was used as received from Fisher. Allene gas was used as received from SynQuest. Commercially available aldehydes were purified by distillation or recrystallisation. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F_{254}). Preparative column chromatography employing silica gel was performed according to the method of Still.[1] Solvents for chromatography are listed as volume/volume ratios. Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+H]^+$ or a suitable fragment ion. Melting points were obtained on a Thomas-Hoover Unimelt apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian Gemini (400 MHz or 300MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Gemini 300 (75 MHz) or 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling. Where mixtures of diastereomers have been characterized together, they are referred to as *A* and *B*. *N.B.* Compound numbers used in the experimental section correspond to those employed in the main paper

Procedure for the Preparation of [Ir(cod)BIPHEP]BARF: $\{Ir[Cl(cod)]\}_2$ (100 mg, 0.15 mmol, 100 mol%) and BIPHEP (164 mg, 0.30 mmol, 200 mol%) were dissolved in freshly distilled DCM (1.5 mL, 0.1 M). This solution was added in one portion to a suspension of NaBARF (264 mg, 0.30 mmol, 200 mol%) in freshly distilled DCM (2 mL). The reaction mixture was stirred at room temperature for 45 minutes and then filtered through a pad of $MgSO_4$. *Workup of the reaction mixture did not involve air-free procedures.* Hexane (20 mL) was added causing the precipitation of a brown solid which was isolated by filtration. This material was then was recrystallized from DCM/hexane (1:2) to afford [Ir(cod)BIPHEP]BARF (302 mg, 59% yield) as a burgundy colored powder.

^{1}H NMR (400 MHz, $CDCl_3$): 7.70-7.29 (m, 32H), 7.19-6.94 (m, 8H), 6.34 (d, J = 7.7 Hz, 2H), 4.40 (m, 2H), 4.08 (q, J = 7.4 Hz, 2H), 2.41 (m, 4H), 1.86 (m, 2H), 1.66 (m, 2H).

^{31}P NMR (161 MHz, $CDCl_3$): 14.13

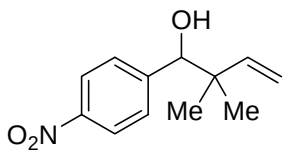
[1] Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Experimental Procedures and Spectroscopic Data for Reverse Prenylated Adducts 1c-6c

General Procedure A for the Coupling of Dimethylallene to Alcohols: To a reaction tube (*ca.* 18 mm × 180 mm including the condenser), fitted with reflux condenser and magnetic stirrer, was added [Ir(cod)BIPHEP]BARF (5 mol%), Cs_2CO_3 (5 mol%) and the corresponding alcohol (0.30 mmol, 100 mol%). DCE-EtOAc (0.30 mL, 1:1 v/v, 1.0 M concentration with respect to the alcohol) and then dimethylallene (1.2 mmol, 400 mol%) were added and the mixture was heated at 75 ^{o}C for the time stated. The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2), under the conditions noted, to afford the corresponding reverse prenylated adduct.

General Procedure B for the Isopropanol Mediated Coupling of Dimethylallene to Carbonyl Compounds: To a reaction tube (*ca.* 18 mm × 180 mm including the condenser), fitted with reflux condenser and magnetic stirrer, was added [Ir(cod)BIPHEP]BARF (5 mol%), Cs_2CO_3 (5 mol%) and the corresponding carbonyl compound (0.30 mmol, 100 mol%). DCE-EtOAc (0.30 mL, 1:1 v/v, 1.0 M concentration with respect to the carbonyl compound), isopropanol (200 mol%) and then dimethylallene (1.2 mmol, 400 mol%) were added and the mixture was heated at 75 ^{o}C for the time stated. The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2), under the conditions noted, to afford the corresponding reverse prenylated adduct.

2,2-Dimethyl-1-(4-nitrophenyl)but-3-en-1-ol (1c)[2]



Procedure A (*via* alcohol 1a): After heating the reaction at 75 °C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (61 mg, 92%) as a colorless, crystalline solid.

Procedure B (*via* carbonyl compound 1b): After heating the reaction at 75 °C for 45 minutes the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (60 mg, 90%) as a colorless, crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.17 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 5.87 (dd, J = 17.4, 10.8 Hz, 1H), 5.19 (dd, J = 10.8, 1.2 Hz, 1H), 5.09 (dd, J = 17.4, 1.2 Hz, 1H), 4.54 (d, J = 2.9 Hz, 1H), 2.21 (d, J = 2.9 Hz, 1H), 1.03 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 148.3, 147.5, 144.3, 128.9, 128.8, 115.2, 79.9, 42.7, 24.4, 21.1.

HRMS (CI) Calcd. for $C_{12}H_{16}NO_3$ $[M+H]^+$: 222.1130, Found: 222.1125.

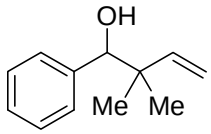
FTIR (neat): 3540, 3082, 2968, 1605, 1518, 1347, 1180, 1055, 1013, 919, 852 cm^{-1}.

M.P. 66-68 °C (CH_2Cl_2-hexane)

The spectroscopic properties of this compound were consistent with our previously reported data.[2]

[2] Skucas, E.; Bower, J. F.; Krische, M. J. *J. Am. Chem. Soc.* **2007**, *129*, *in press*.

2,2-Dimethyl-1-phenylbut-3-en-1-ol (2c)[3]



Procedure A (*via* alcohol 2a): After heating the reaction at 75 °C for 16.5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (48 mg, 90%) as a colorless oil.

Procedure B (*via* carbonyl compound 2b): After heating the reaction at 75 °C for 15.5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (43 mg, 81%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.34-7.24 (m, 5H), 5.92 (dd, J = 17.4, 10.8 Hz, 1H), 5.14 (dd, J = 10.8, 1.2 Hz, 1H), 5.08 (dd, J = 17.4, 1.2 Hz, 1H), 4.44 (d, J = 2.9 Hz, 1H), 2.01 (d, J = 2.9 Hz, 1H), 1.02 (s, 3H), 0.96 (s, 3H).

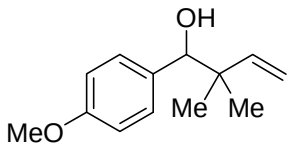
^{13}C NMR (100 MHz, $CDCl_3$): 145.3, 141.0, 128.0, 127.7, 127.6, 114.1, 80.9, 42.5, 24.7, 21.2.

FTIR (neat): 3441, 2964, 1636, 1493, 1452, 1378, 1187, 1050, 1024, 913 cm^{-1}.

The spectroscopic properties of this compound were consistent with the data available in the literature.[3]

[3] Sumida, S.; Ohga, M.; Mitani, J.; Nokami J. *J. Am. Chem. Soc.* **2000**, *122*, 1310.

1-(4-Methoxyphenyl)-2,2-dimethylbut-3-en-1-ol (3c)[4]



Procedure A (*via* alcohol 3a): After heating the reaction at 75 °C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (43 mg, 70%) as a colorless oil.

Procedure B (*via* carbonyl compound 3b): After heating the reaction at 75 °C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (51 mg, 83%) as a colorless oil.

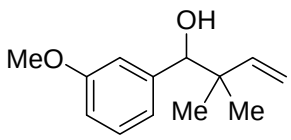
^{1}H NMR (400 MHz, $CDCl_3$): 7.22 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.86 (dd, J = 17.6, 10.8 Hz, 1H), 5.13 (dd, J = 10.8, 1.2 Hz, 1H), 5.07 (dd, J = 17.6, 1.2, 1H), 4.39 (d, J = 2.3, 1H), 3.80 (s, 3H), 1.97 (d, J = 2.3 Hz, 1H), 1.00 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 159.1, 145.4, 133.2, 129.0, 114.0, 113.1, 80.5, 55.5, 42.6, 24.8, 21.2.

The spectroscopic properties of this compound were consistent with the data available in the literature.[4]

[4] Ahn, Y.; Doubleday, W. W.; Cohen, T. *Synth. Commun.* **1995**, *25*, 33.

1-(3-Methoxyphenyl)-2,2-dimethylbut-3-en-1-ol (4c)[5]



Procedure A (*via* alcohol 4a): After heating the reaction at 75 °C for 21 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (47 mg, 76%) as a colorless oil.

Procedure B (*via* carbonyl compound 4b): After heating the reaction at 75 °C for 15.5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (43 mg, 70%) as a colorless oil.

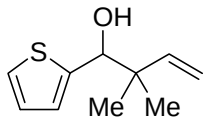
^{1}H NMR (400 MHz, $CDCl_3$): 7.22 (dd, J = 8.0, 7.8 Hz, 1H), 6.89-6.85 (m, 2H), 6.81 (ddd, J = 8.0, 2.7, 1.2 Hz, 1H), 5.86 (dd, J = 17.6, 10.8 Hz, 1H), 5.14 (dd, J = 10.8, 1.2 Hz, 1H), 5.07 (dd, J = 17.6, 1.2 Hz, 1H), 4.40 (d, J = 2.5 Hz, 1H), 3.80 (s, 3H), 2.07 (d, J = 2.5, 1H), 1.02 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 159.2, 145.3, 142.7, 128.6, 120.6, 114.1, 113.8, 112.9, 80.8, 55.4, 42.5, 24.8, 21.4.

The spectroscopic properties of this compound were consistent with the data available in the literature.[5]

[5] Schrekker, H. S.; de Bolster, M. W. G.; Orru, R. V. A.; Wessjohann, L. A. *J. Org. Chem.* **2002**, *67*, 1975.

2,2-Dimethyl-1-thiophen-2-ylbut-3-en-1-ol (5c)[6]



Procedure A (*via* alcohol 5a): After heating the reaction at 75 °C for 15.5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (37 mg, 68%) as a colorless oil.

Procedure B (*via* carbonyl compound 5b): After heating the reaction at 75 °C for 15.5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (44 mg, 81%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.23 (dd, J = 4.7, 1.6 Hz, 1H), 6.98-6.93 (m, 2H), 5.97 (dd, J = 17.6, 10.8 Hz, 1H), 5.17 (dd, J = 10.8, 1.4 Hz, 1H), 5.13 (dd, J = 17.6, 1.4 Hz, 1H), 4.70 (d, J = 3.1 Hz, 1H), 2.16 (d, J = 3.1 Hz, 1H), 1.08 (s, 3H), 1.04 (s, 3H).

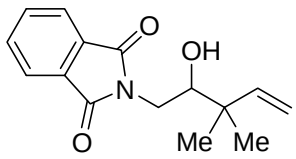
^{13}C NMR (100 MHz, $CDCl_3$): 144.7, 126.3, 125.7, 124.6, 114.6, 77.7, 42.5, 24.5, 21.7 (only 9 signals were observed).

FTIR (neat): 3443, 3081, 2964, 2869, 1638, 1466, 1382, 1021, 914, 853, 829 cm^{-1}.

The spectroscopic properties of this compound were consistent with the data available in the literature.[6]

[6] Sinha, P.; Roy, S. *Chem. Commun.* **2001**, 1798.

2-(2-Hydroxy-3,3-dimethylpent-4-enyl)-isoindole-1,3-dione (6c)[2]



Procedure A (*via* alcohol 6a): In a modification to Procedure A, increased loadings of [Ir(cod)BIPHEP]BARF (10 mol%) and Cs_2CO_3 (10 mol%) were employed. After heating the reaction at 75 ^oC for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, hexanes/EtOAc 4/1) to afford the title compound (65 mg, 84%) as a colorless oil.

Procedure B (*via* carbonyl compound 6b): In a modification to Procedure B, increased loadings of [Ir(cod)BIPHEP]BARF (10 mol%), Cs_2CO_3 (10 mol%), isopropanol (400 mol%) and dimethylallene (800 mol%) were employed. After heating the reaction at 75 ^oC for 15.5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, hexanes/EtOAc 4/1) to afford the title compound (44 mg, 57%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.85 (dd, J = 5.5, 3.1 Hz, 2H), 7.72 (dd, J = 5.5, 3.1 Hz, 2H), 5.94 (dd, J = 17.6, 11.0 Hz, 1H), 5.17-5.10 (m, 2H), 3.89 (d, J = 11.7, 1H), 3.69-3.62 (m, 2H), 2.23 (d, J = 5.9, 1H), 1.14 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 169.2, 143.9, 134.3, 132.2, 123.6, 114.2, 77.0, 41.2 (2 signals), 23.5, 22.7.

HRMS (CI) Calcd. for $C_{15}H_{18}NO_3$ $[M+H]^+$: 260.1287, Found: 260.1288.

FTIR (neat): 3512, 2965, 1771, 1711, 1397, 1189, 1078, 1024, 913, 717 cm^{-1}.

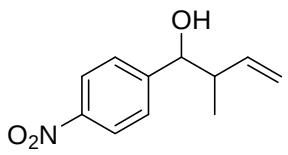
The spectroscopic properties of this compound were consistent with our previously reported data.[2]

Experimental Procedures and Spectroscopic Data for Crotylated Adducts 1d-3d

General Procedure C for the Coupling of Methylallene to Alcohol Compounds: To a reaction tube (*ca.* 18 mm × 180 mm including the condenser), fitted with reflux condenser and magnetic stirrer, was added [Ir(cod)BIPHEP]BARF (7.5 mol%), Cs_2CO_3 (7.5 mol%), the corresponding alcohol (0.30 mmol, 100 mol%), and a mixture of DCE-EtOAc (0.50 mL, 1:1 v/v, 0.6 M concentration with respect to the alcohol). Methylallene (*ca.* 1.2 mmol, *ca.* 100 μL, 400 mol %) was condensed into a 1 dram vial at -78 ^{o}C and dissolved in DCE-EtOAc (0.50 mL, 1:1 v/v). This solution was then immediately transferred to the reaction tube and the resulting mixture was heated at 75 ^{o}C for the time stated. The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2), under the conditions noted, to afford the corresponding crotylated adduct.

General Procedure D for the Isopropanol Mediated Coupling of Methylallene to Carbonyl Compounds: To a reaction tube (*ca.* 18 mm × 180 mm including the condenser), fitted with reflux condenser and magnetic stirrer, was added [Ir(cod)BIPHEP]BARF (7.5 mol%), Cs_2CO_3 (7.5 mol%), the corresponding carbonyl compound (0.30 mmol, 100 mol%), isopropanol (400 mol%) and a mixture of DCE-EtOAc (0.50 mL, 1:1 v/v, 0.6 M concentration with respect to the carbonyl compound). Methylallene (*ca.* 1.2 mmol, *ca.* 100 μL, 400 mol %) was condensed into a 1 dram vial at -78 ^{o}C and dissolved in DCE-EtOAc (0.50 mL, 1:1 v/v). This solution was then immediately transferred to the reaction tube and the resulting mixture was heated at 75 ^{o}C for the time stated. The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2), under the conditions noted, to afford the corresponding crotylated adduct.

2-Methyl-1-(4-nitrophenyl)but-3-en-1-ol (1d)[7]



Procedure C (*via* alcohol 1a): After heating the reaction at 75 °C for 14 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 9/1) to afford the title compound (51 mg, 82%, 1.5:1 d.r. *A:B*) as a yellow oil.

Procedure D (*via* carbonyl compound 1b): After heating the reaction at 75 °C for 14 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 9/1) to afford the title compound (52 mg, 83%, 1.3:1 d.r. *A:B*) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.19-8.16 (m, 4H), 7.49-7.45 (m, 4H), 5.80-5.67 (m, 2H), 5.21-5.04 (m, 4H), 4.76-4.74 (m, 1H *of B*), 4.49 (dd, *J* = 7.2, 2.2 Hz, 1H *of A*), 2.60-2.56 (m, 1H *of B*), 2.47-2.41 (m, 1H *of A*), 2.30 (d, *J* = 2.2 Hz, 1H *of A*), 2.11 (d, *J* = 3.4 Hz, 1H *of B*), 0.94 (d, *J* = 6.8 Hz, 3H *of B*), 0.91 (d, *J* = 6.8 Hz, 3H *of A*)

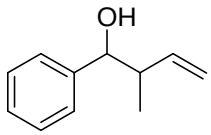
^{13}C NMR (100 MHz, $CDCl_3$): 149.8, 149.7, 146.3, 146.2, 139.3, 139.2, 127.6, 127.2, 123.4, 123.3, 118.0, 116.7, 76.8, 76.0, 46.6, 44.6, 16.3, 13.2.

HRMS (CI) Calcd. for $C_{11}H_{14}NO_3$ $[M+H]^+$: 208.0978, Found: 208.0974.

The spectroscopic properties of this compound were consistent with the data available in the literature.[7]

2-Methyl-1-phenylbut-3-en-1-ol (2d)[7]

[7] Jiang, S.; Agoston, E. G.; Chen, T.; Cabal, M.-P.; Turos. E. *Organometallics* **1995**, *14*, 4697.



Procedure C (*via* alcohol 2a): After heating the reaction at 75 ^{o}C for 14 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, pentane/Et_2O 9/1) to afford the title compound (34 mg, 69%, 1:1 d.r.) as a yellow oil.

Procedure D (*via* carbonyl compound 2b): After heating the reaction at 75 ^{o}C for 14 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, pentane/Et_2O 9/1) to afford the title compound (38 mg, 77%, 1:1 d.r.) as a yellow oil.

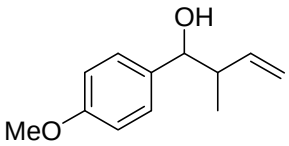
^{1}H NMR (400 MHz, $CDCl_3$): 7.28-7.17 (m, 10H), 5.78-5.64 (m, 2H), 5.16-5.93 (m, 2H), 5.01-4.95 (m, 2H), 4.54 (dd, J = 5.3, 3.5 Hz, 1H), 4.28 (dd, J = 8.0, 2.5 Hz, 1H), 2.55-2.47 (m, 1H), 2.45-2.36 (m, 1H), 2.10 (d, J = 2.5 Hz, 1H), 1.91 (d, J = 3.5 Hz, 1H), 0.93 (d, J = 6.8 Hz, 3H), 0.79 (d, J = 6.8 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 142.5, 142.3, 140.6, 140.2, 128.2, 128.0, 127.6, 127.3, 126.8, 126.4, 116.8, 115.5, 77.8, 77.2, 46.3, 44.6, 16.5, 13.9.

HRMS (CI) Calcd. for $C_{11}H_{15}O$ $[M+H]^+$: 163.1124, Found: 163.1123.

The spectroscopic properties of this compound were consistent with the data available in the literature.[7]

1-(4-Methoxyphenyl)-2-methylbut-3-en-1-ol (3d)[7]



Procedure C (*via* alcohol 3a): After heating the reaction at 75 ^{o}C for 14 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 9/1) to afford the title compound (42 mg, 72%, 1.3:1 d.r. *A:B*) as a yellow oil.

Procedure D (*via* carbonyl compound 3b): After heating the reaction at 75 ^{o}C for 14 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 9/1) to afford the title compound (46 mg, 79%, 1.3:1 d.r. *A:B*) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.25-7.18 (m, 4H), 6.87-6.84 (m, 4H), 5.84-5.66 (m, 2H), 5.21-5.14 (m, 2H), 5.04-4.99 (m, 2H), 4.51 (dd, *J* = 5.7, 1.6 Hz, 1H *of B*), 4.27 (d, *J* = 8.0 Hz, 1H *of A*), 3.78 (s, 6H), 2.57-2.49 (m, 1H *of B*), 2.48-2.38 (m, 1H *of A*), 2.14 (d, *J* = 2.0 Hz, 1H *of A*), 1.94 (d, *J* = 2.6 Hz, 1H *of B*), 1.00 (d, *J* = 6.7 Hz, 3H *of B*), 0.82 (d, *J* = 6.8 Hz, 3H *of A*).

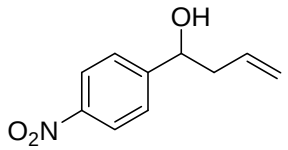
^{13}C NMR (100 MHz, $CDCl_3$): 159.0, 158.8, 140.9, 140.3, 134.7, 134.5, 127.9, 127.6, 116.7, 115.4, 113.6, 113.4, 77.4, 77.1, 55.2 (2 signals), 46.4, 44.6, 16.5, 14.3

HRMS (CI) Calcd. for $C_{12}H_{17}O_2$ $[M+H]^+$: 193.1232, Found: 193.1229.

The spectroscopic properties of this compound were consistent with the data available in the literature.[7]

Experimental Procedures and Spectroscopic Data for Allylated Adduct 1e

1-(4-Nitrophenyl)-but-3-en-1-ol (1e)[8]



***Via* alcohol 1a:** To a reaction tube (*ca.* 18 mm × 180 mm including the condenser), fitted with reflux condenser and magnetic stirrer, was added [Ir(cod)BIPHEP]BARF (5 mol%), Cs_2CO_3 (5 mol%), the corresponding alcohol (0.30 mmol, 100 mol%) and a mixture of DCE-EtOAc (0.30 mL, 1:1 v/v, 1.0 M concentration with respect to the alcohol). A 1.6 L gas sampling bag (Aldrich) was charged with allene gas and this was bubbled directly, *via* cannula (20 gauge), into the reaction mixture which was held at 75 ^oC for 14 hours. During this time a slight positive pressure was applied to the allene gas bag by means of a small weight (*ca.* 85 g) and pressure relief from the reaction vessel was provided by an additional, empty gas bag. This ensured a continual flow of allene through the mixture for the entire reaction period (no recharging of the gas bag was necessary). The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (14 mg, 23%) as a yellow oil.

***Via* carbonyl compound 1b:** To a reaction tube (*ca.* 13 mm × 180 mm including the condenser), fitted with reflux condenser and magnetic stirrer, was added [Ir(cod)BIPHEP]BARF (5 mol%), Cs_2CO_3 (5 mol%), the corresponding carbonyl compound (0.30 mmol, 100 mol%), isopropanol (400 mol%) and a mixture of DCE-EtOAc (0.30 mL, 1:1 v/v, 1.0 M concentration with respect to the carbonyl compound). A 1.6 L gas sampling bag (Aldrich) was charged with allene gas and this was bubbled directly, *via* cannula (20 gauge), into the reaction mixture which was held at 75 ^oC for 14 hours. During this time a slight positive pressure was applied to the allene gas bag by means of a small weight (*ca.* 85 g) and pressure relief from the reaction vessel was provided by an additional, empty gas bag. This ensured a continual flow of allene through the mixture for the entire reaction period (no recharging of the gas bag was necessary). The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (29 mg, 50%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.21 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 5.79 (m, 1H), 5.22-5.17 (m, 2H), 4.87 (m, 1H), 2.58 (m, 1H), 2.46 (m, 1H), 2.25 (m, 1H).

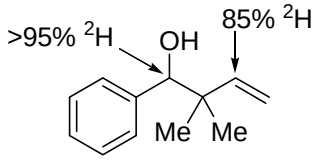
^{13}C NMR (100 MHz, $CDCl_3$): 151.1, 147.2, 133.2, 126.5, 123.6, 119.7, 72.1, 43.9.

The spectroscopic properties of this compound were consistent with the data available in the literature.[8]

[8] Yao, Q.; Sheets, M. *J. Org. Chem.* **2006**, *71*, 5384.

Experimental Details for Mechanistic Studies

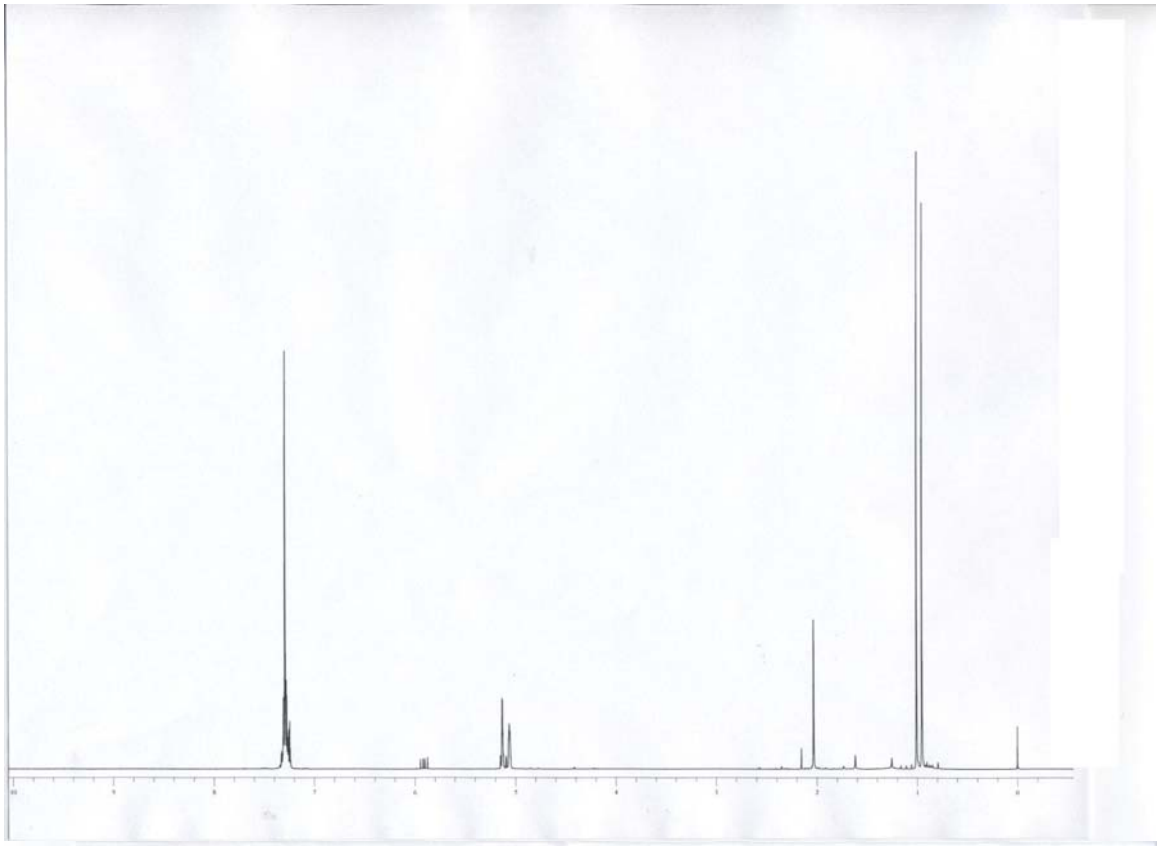
1,3-*Deuterio*-2,2-dimethyl-1-phenylbut-3-en-1-ol (*deuterio*-2c)

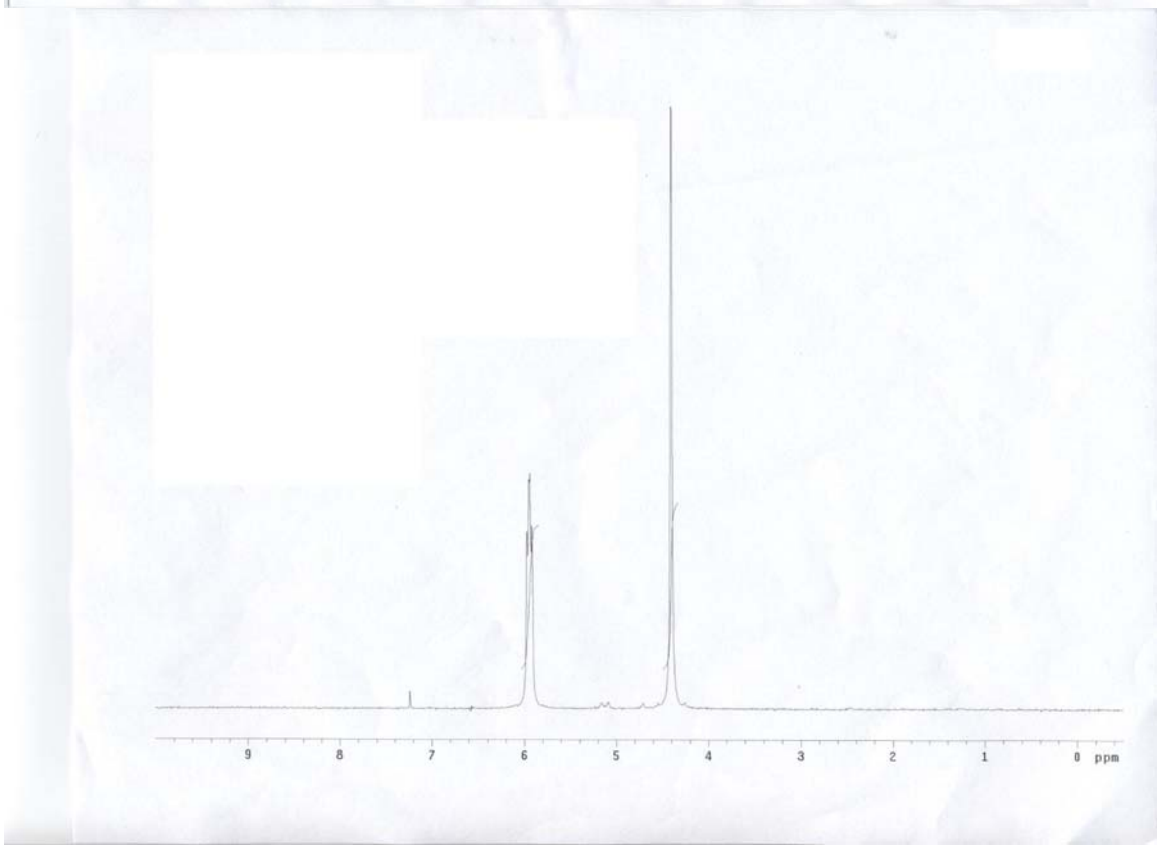


Procedure A (*via* alcohol *deuterio*-2a): d_2-benzyl alcohol (*deuterio*-**2a**, 98% deuterium incorporation) was purchased from Aldrich. After heating the reaction at 75 °C for 16.5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (38 mg, 71%) as a colorless oil.

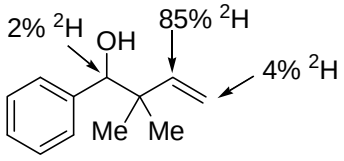
^{1}H NMR (400 MHz, $CDCl_3$): 7.34-7.24 (m, 5H), 5.91 (dd, J = 17.4, 10.8 Hz, 0.15H), 5.13 (m, 1H), 5.07 (m, 1H), 2.04 (d, J = 2.9 Hz, 1H), 1.01 (s, 3H), 0.95 (s, 3H).

^{2}H NMR (77 MHz, $CHCl_3$) 5.94 (m, 0.85^{2}H), 4.41 (s, 1.0^{2}H).




9
8
7
6
5
4
3
2
1
0 ppm

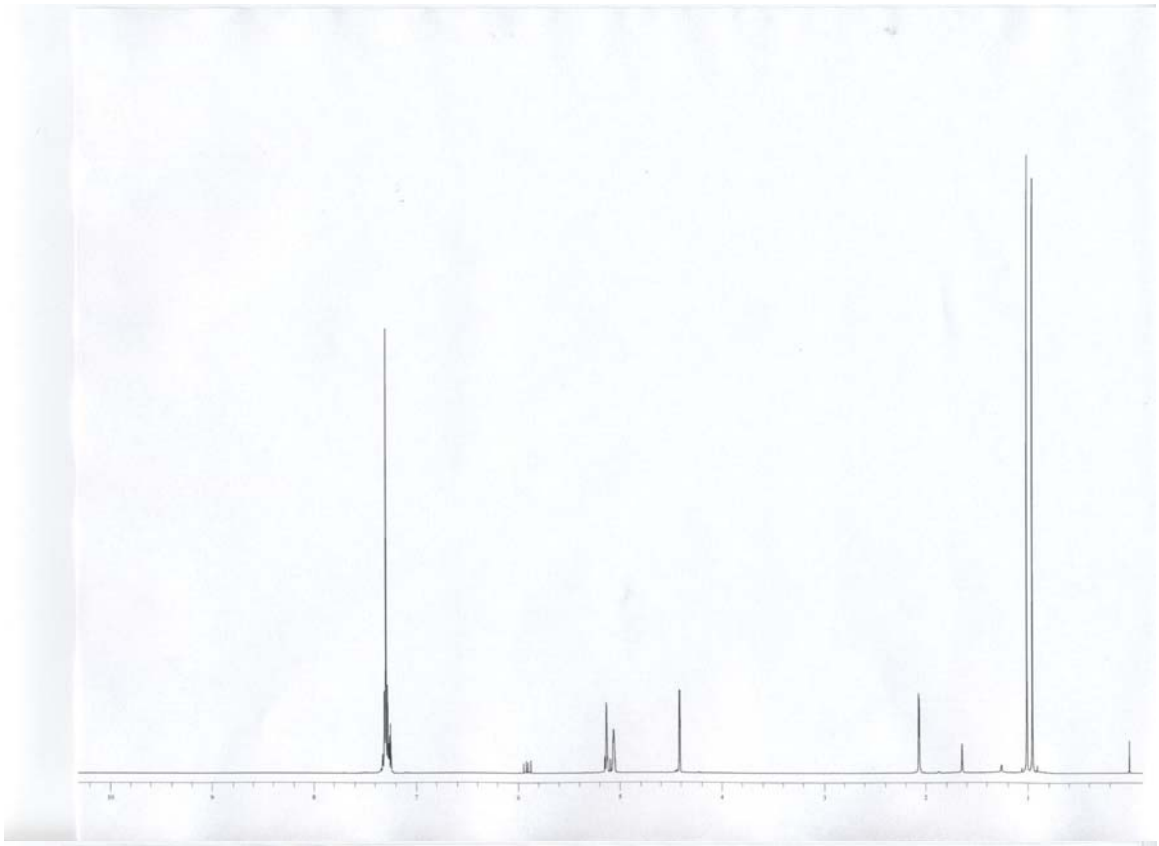
3-*Deuterio*-2,2-dimethyl-1-phenylbut-3-en-1-ol (*deuterio*-2c')

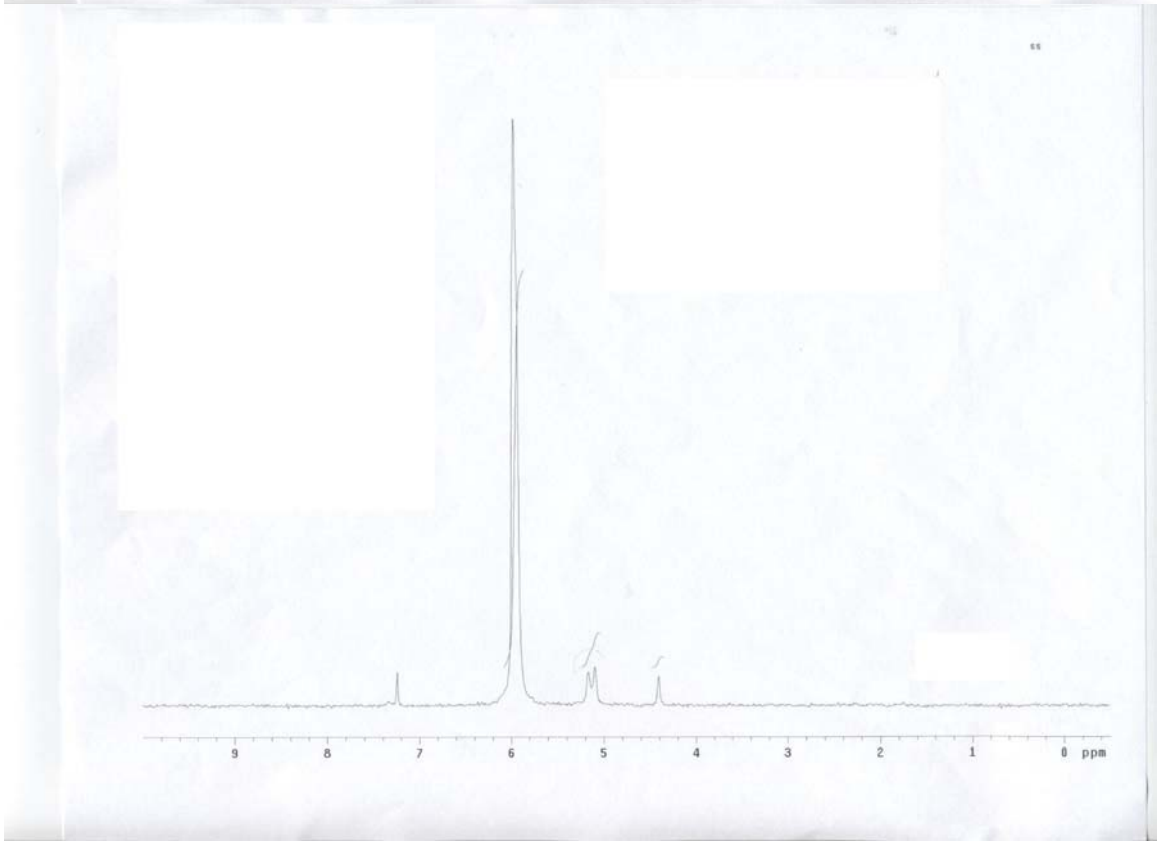


Procedure B (*via* carbonyl compound 2b): In a modification to Procedure B, d_8-isopropanol (instead of isopropanol) was employed as the reductant. After heating the reaction at 75 ^oC for 15.5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc 19/1) to afford the title compound (38 mg, 71%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.34-7.24 (m, 5H), 5.91 (dd, J = 17.4, 10.8 Hz, 0.15H), 5.13 (m, 0.96H), 5.07 (m, 0.96H), 4.41 (d, J = 2.9 Hz, 0.98H), 2.07 (d, J = 2.9 Hz, 1H), 1.01 (s, 3H), 0.95 (s, 3H).

^{2}H NMR (77 MHz, $CHCl_3$): 5.95 (s, 0.85^{2}H), 5.18-5.07 (m, 0.08^{2}H)*, 4.41 (s, 0.02^{2}H).
*(this signal corresponds to 4% total ^{2}H incorporation in the terminal vinylic protons)




9
8
7
6
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2
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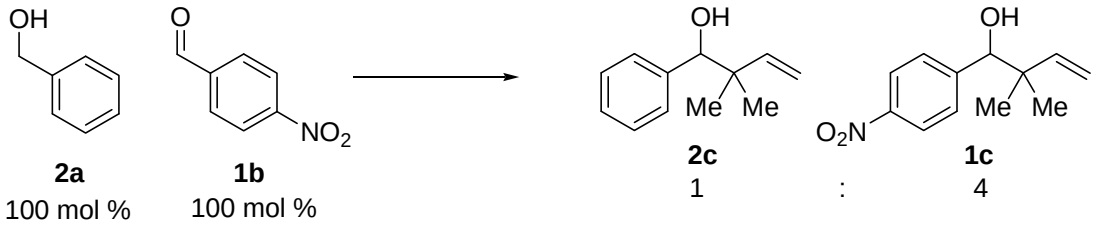
0 ppm



2a 100 mol %

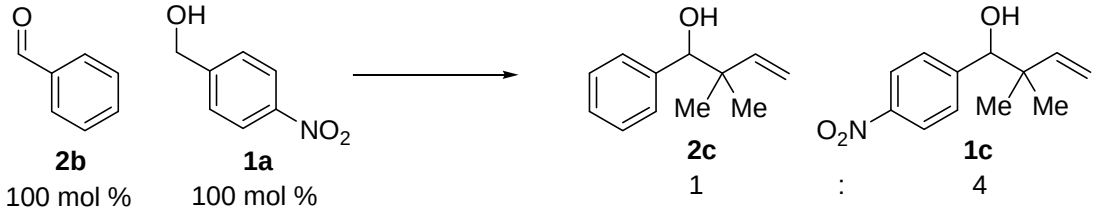
1b 100 mol %

2c : **1c**

1 : 4

ca. 94%
(combined yield based on 100 mol% of alcohol as the limiting reagent)

Competition experiment between aldehyde 1b and alcohol 2a: To a reaction tube (*ca.* 18 mm × 180 mm including the condenser), fitted with reflux condenser and magnetic stirrer, was added [Ir(cod)BIPHEP]BARF (5 mol%), Cs_2CO_3 (5 mol%), alcohol **2a** (0.30 mmol, 100 mol%) and aldehyde **1b** (0.30 mmol, 100 mol%). DCE-EtOAc (1:1, 1.0 M concentration with respect to the alcohol) and then dimethylallene (1.2 mmol, 400 mol%) were added and the mixture was heated at 75 °C for 15 hours. The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc, 19/1) to afford a 4:1 mixture of **1c** and **2c** (62 mg, *ca.* 94%) as a colorless oil. (*N.B.* yield is based upon 100 mol% of alcohol as the limiting reagent and is calculated based upon product stoichiometry).



2b 100 mol %

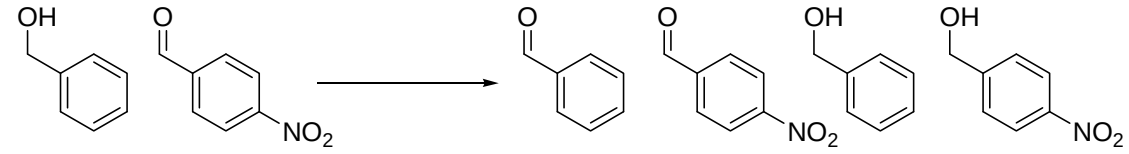
1a 100 mol %

2c : **1c**

1 : 4

ca. 93%
(combined yield based on 100 mol% of alcohol as the limiting reagent)

Competition experiment between aldehyde 2b and alcohol 1a: To a reaction tube (*ca.* 18 mm × 180 mm including the condenser), fitted with reflux condenser and magnetic stirrer, was added [Ir(cod)BIPHEP]BARF (5 mol%), Cs_2CO_3 (5 mol%), alcohol **1a** (0.30 mmol, 100 mol%) and aldehyde **2b** (0.30 mmol, 100 mol%). DCE-EtOAc (1:1, 1.0 M concentration with respect to the alcohol) and then dimethylallene (1.2 mmol, 400 mol%) were added and the mixture was heated at 75 °C for 15 hours. The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe/EtOAc, 19/1) to afford a 4:1 mixture of **1c** and **2c** (61 mg, *ca.* 93%) as a colorless oil. (*N.B.* yield is based upon 100 mol% of alcohol as the limiting reagent and is calculated based upon product stoichiometry).



2a 100 mol % **1b** 100 mol % → **2b** : **1b** : **2a** : **1a** = 4 : 1 : 1 : 4

Equilibration of 2a and 1b: To a reaction tube (*ca.* 18 mm × 180 mm including the condenser), fitted with reflux condenser and magnetic stirrer, was added [Ir(cod)BIPHEP]BARF (5 mol%), Cs_2CO_3 (5 mol%) and alcohol **2a** (0.30 mmol, 100 mol%) and aldehyde **1b** (0.30 mmol, 100 mol%). DCE-EtOAc (1:1, 1.0 M concentration with respect to the alcohol) was added and the mixture was heated at 75 ^{o}C for 15 hours. The mixture was then concentrated *in vacuo* and analyzed directly by ^{1}H NMR to reveal a 4:1:1:4 mixture of **2b**:**1b**:**2a**:**1a**. No significant alcohol or aldehyde derived byproducts were evident.

When the experiment was repeated using alcohol **1a** (100 mol %) and aldehyde **2b** (100 mol %) an identical ratio of products was obtained.

When a mixture of **2b**:**1b**:**2a**:**1a** (4:1:1:4) was subjected to the above reaction conditions in the presence of dimethylallene (400 mol % with respect to **2b** + **1b**) a 4:1 mixture of **1c** and **2c** (84 % yield) was obtained after flash column chromatography.