

Iridium Catalyzed Hydro-hydroxyalkylation of Butadiene: Carbonyl Crotylation

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Supporting Information

Table of Contents

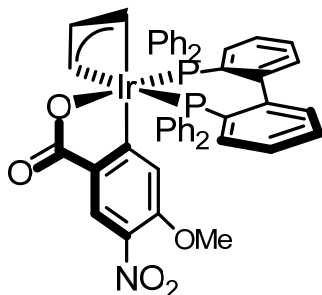
1. General Experimental Details	S2
2. Procedure for the Preparation of Ir-Complex	S3
3. Procedures and Spectroscopic Data for Coupling Products	S4
4. Procedures and Spectroscopic Data for Asymmetric Coupling Products	S22

1. General Methods

Reagents: All reactions were run under an atmosphere of nitrogen. Tetrahydrofuran (THF) and toluene were obtained from Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Anhydrous solvents were transferred by an oven-dried syringe. Sealed tubes (13x100 mm²) were purchased from Fischer Scientific and were dried in an oven overnight and cooled under a stream of nitrogen prior to use. Commercially available alcohols were purified by distillation or recrystallization prior to use. Sodium acetate was purchased from Alfa Aesar and was used directly without further purification. 1,3-Butadiene was purchased from Aldrich and was used directly without further purification. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F254).

Instruments: 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*+1, *M* or *M*-1) or a suitable fragment ion. Nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Varian Gemini (400 MHz) spectrometer in CDCl₃ solution. Chemical shifts are reported as parts per million (ppm) relative to residual CHCl₃ δ_H (7.26 ppm) and CDCl₃ δ_C (77.0 ppm), respectively, as internal standards. Coupling constants are reported in Hertz (Hz).

2. Procedure for the Preparation of Ir-Complex

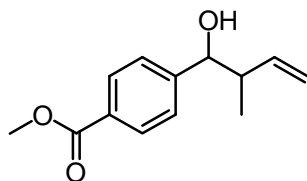


Ir-BIPHEP-1-OMe¹.

To an oven-dried sealed tube under an atmosphere of nitrogen charged with $[\text{Ir}(\text{cod})\text{Cl}]_2$ (100 mg, 0.15 mmol, 100 mol%), BIPHEP (156 mg, 0.3 mmol, 200 mol%), Cs_2CO_3 (195 mg, 0.6 mmol, 400 mol%) and 4-methoxy-3-nitrobenzoic acid (100 mg, 0.6 mmol, 400 mol%) was added THF (3 mL, 0.05 M). The reaction mixture was heated at 80 °C for 30 min and was then allowed to cool to ambient temperature. Allyl acetate (75 mg, 0.75 mmol, 500 mol%) was added and the reaction mixture was allowed to stir for an additional 90 min at 80 °C, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered and washed with THF (15 mL) until all yellow residue was dissolved. The filtrate was concentrated *in vacuo* and hexanes (50 mL) was added. The resulting yellow precipitate was collected by filtration and dried under vacuum (253 mg, 0.266 mmol, 90% yield).

(1) Han, S. B.; Kim, I. S.; Han, H.; Krische, M. J.; *J. Am. Chem. Soc.* **2009**, *131*, 6916–6917.

3. Procedure for the Crotylation



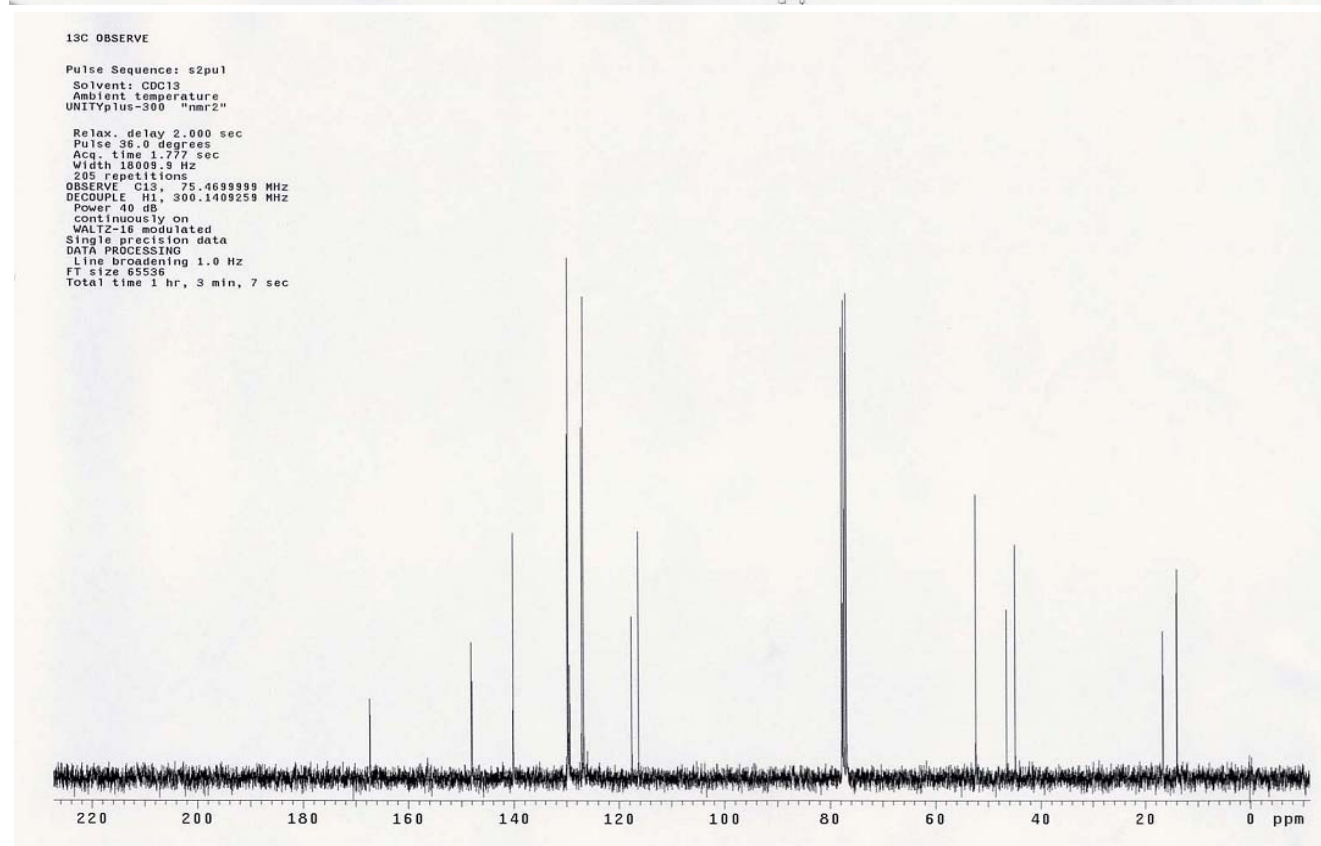
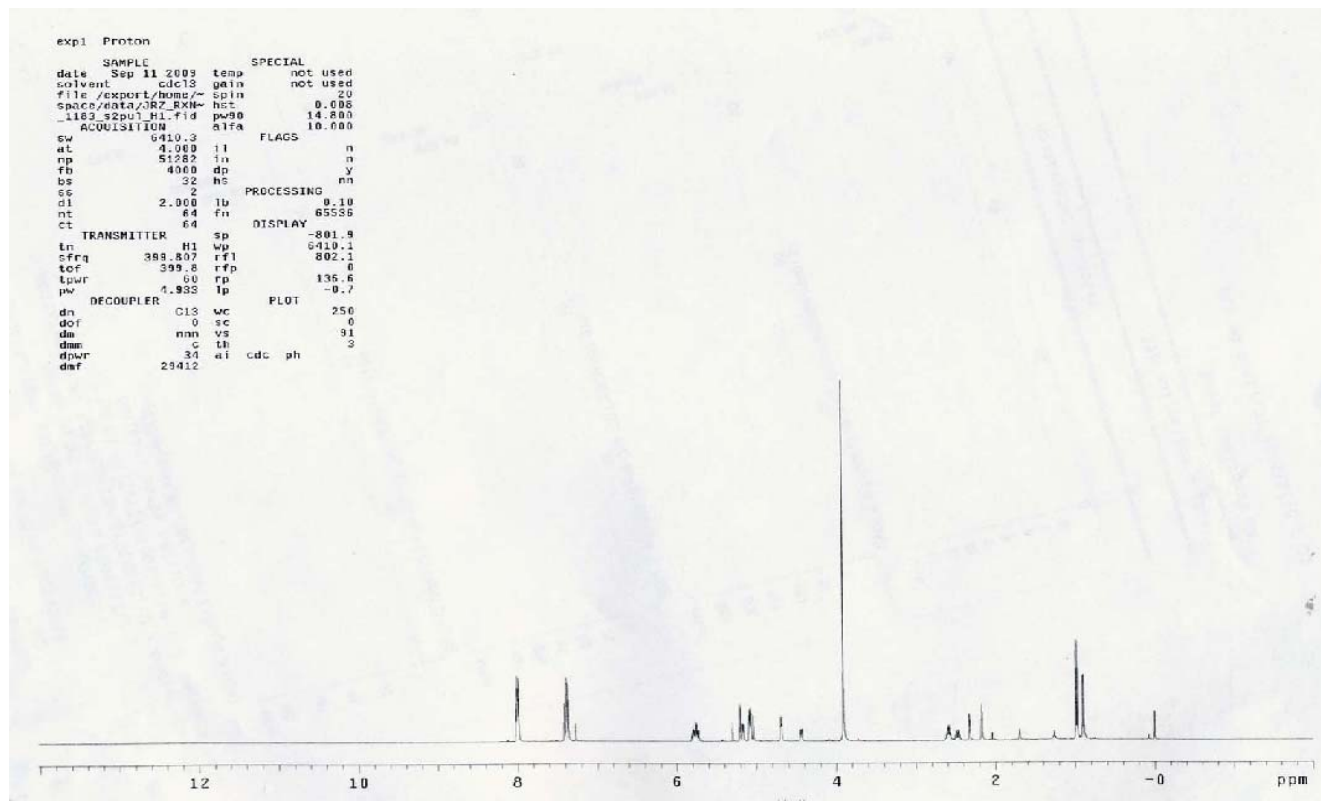
Methyl 4-(1-hydroxy-2-methylbut-3-enyl)benzoate (3a). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **1a** (50 mg, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 °C. The reaction mixture was allowed to stir at 70 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO₂; ethyl acetate:hexanes, 1:10) provides the title compound (53 mg) as a colorless oil in 80% yield (*syn/anti*, 1.4/1.0 dr).

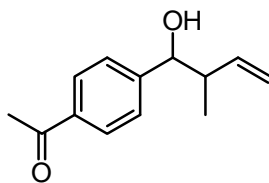
¹H NMR (400 MHz, CDCl₃): δ 8.02–7.98 (m, 4H), 7.44–7.36 (m, 4H), 5.82–5.70 (m, 2H), 5.24–5.04 (m, 4H), 4.70 (d, $J = 4.8$ Hz, 1H of *syn*), 4.40 (d, $J = 7.2$ Hz, 1H of *anti*), 3.92 (s, 6H), 2.64–2.58 (m, 1 H of *syn*), 2.56–2.44 (m, 1H of *anti*), 2.24 (br, 1H of *anti*), 2.04 (br, 1H of *syn*), 0.97 (d, $J = 6.8$ Hz, 3H of *syn*), 0.90 (d, $J = 6.8$ Hz, 3H of *anti*) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 167.3, 148.1, 147.9, 140.2, 140.1, 129.8, 129.6, 129.3, 127.0, 126.7, 117.5, 116.3, 77.6, 76.9, 52.3, 46.5, 44.9, 16.6, 13.9 ppm.

The spectroscopic properties of this compound were consistent with the data available in the literature.²

(2) Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2005**, *7*, 3577–3579.





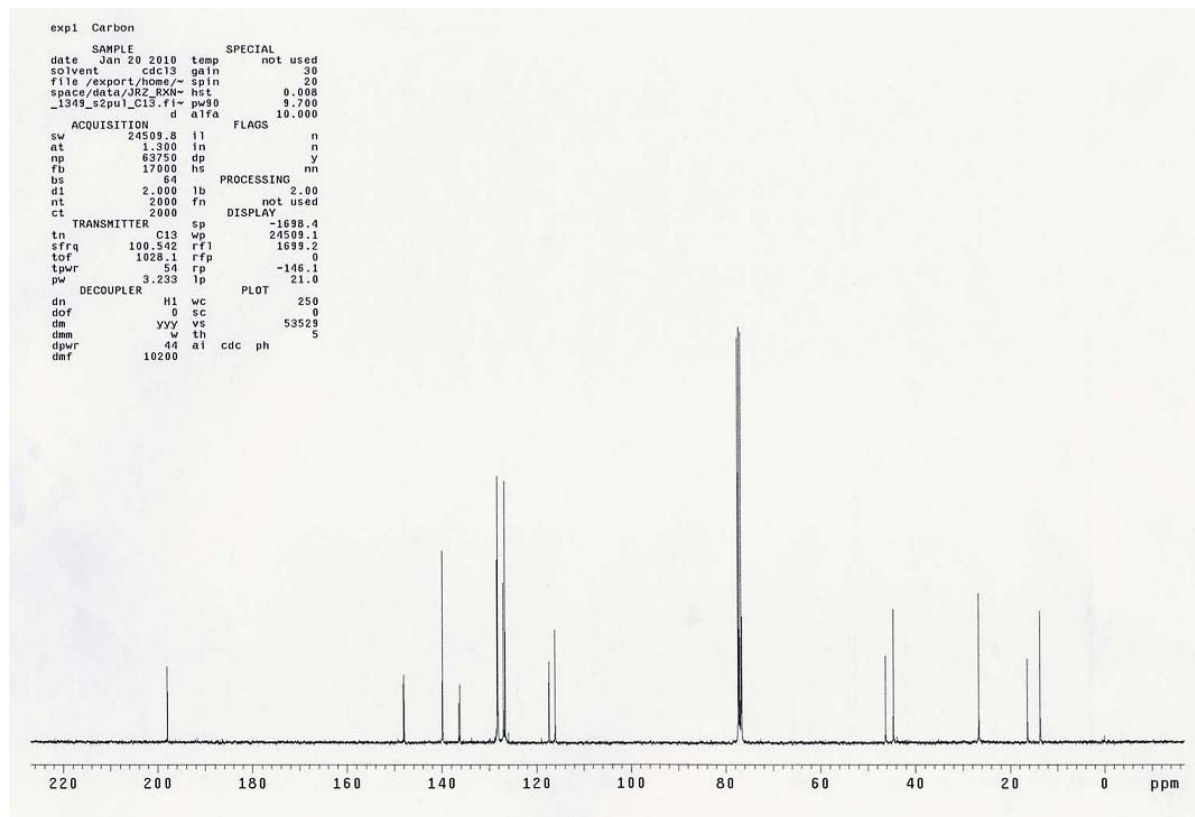
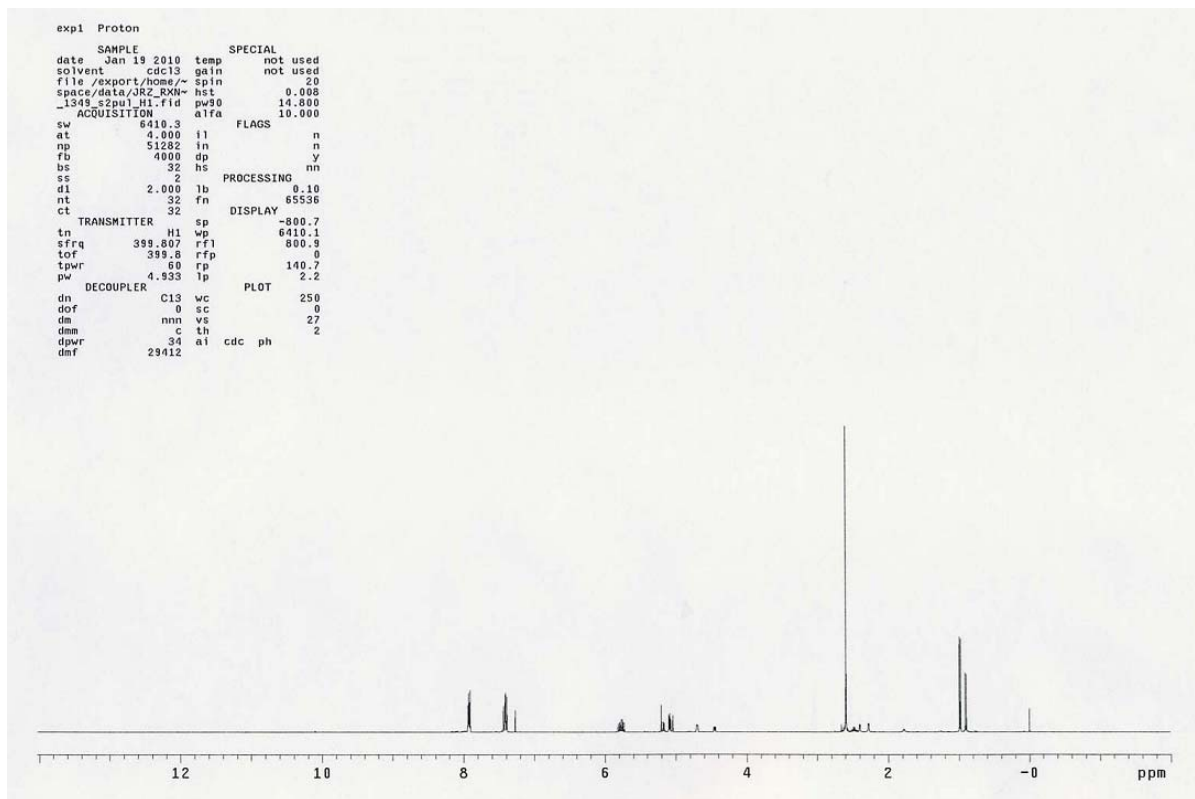
1-(4-Acetylphenyl)-2-methyl-but-3-en-1-ol (3b). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **1b** (45 mg, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 °C. The reaction mixture was allowed to stir at 70 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ethyl acetate:hexanes, 1:10) provides the title compound (50 mg) as a colorless oil in 82% yield (*syn/anti*, 1.4/1.0 dr).

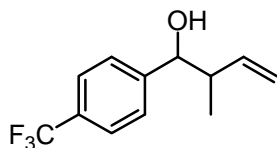
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.94–7.90 (m, 4H), 7.44–7.38 (m, 4H), 5.82–5.72 (m, 2H), 5.22–5.04 (m, 4H), 4.70 (dd, $J = 4.8, 2.4$ Hz, 1H of *syn*), 4.45 (dd, $J = 7.2, 2.0$ Hz, 1H of *anti*), 2.59 (s, 6H), 2.64–2.54 (m, 1H of *syn*), 2.51–2.42 (m, 1H of *anti*), 2.40 (d, $J = 2.4$ Hz, 1H of *anti*, OH), 2.28 (d, $J = 3.6$ Hz, 1H of *syn*, OH), 0.98 (d, $J = 6.8$ Hz, 3H of *syn*), 0.90 (d, $J = 6.8$ Hz, 3H of *anti*) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 198.0, 148.0, 147.9, 139.8, 136.4, 136.2, 128.3, 128.2, 127.0, 126.6, 117.3, 116.0, 77.3, 76.6, 46.2, 44.6, 26.6, 16.3, 13.6 ppm.

IR (thin film): $\nu = 3442, 2971, 2872, 1673, 1606, 1572, 1455, 1412, 1358, 1304, 1267, 1198, 1179, 1100, 1013, 958, 914, 856, 826, 721, 675$ cm^{-1} .

HRMS (ESI): m/z : calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2$: 205.1229; found: 205.1228 [$M+H$] $^+$.





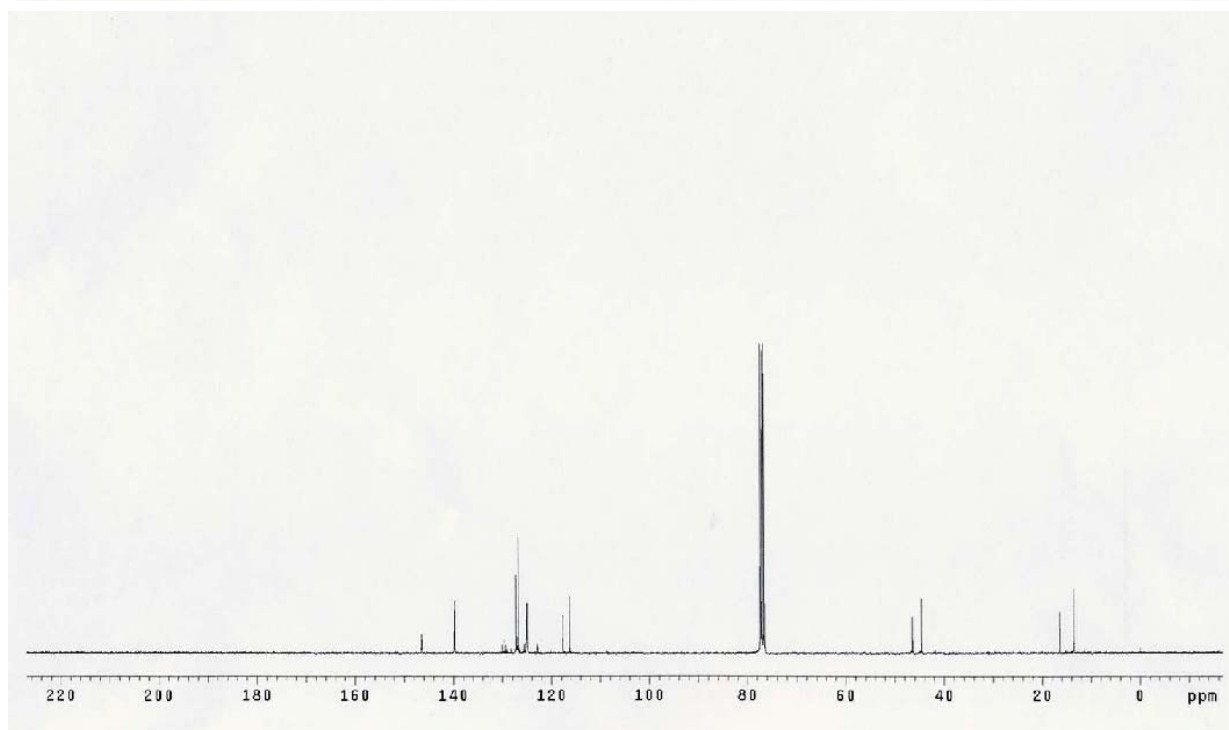
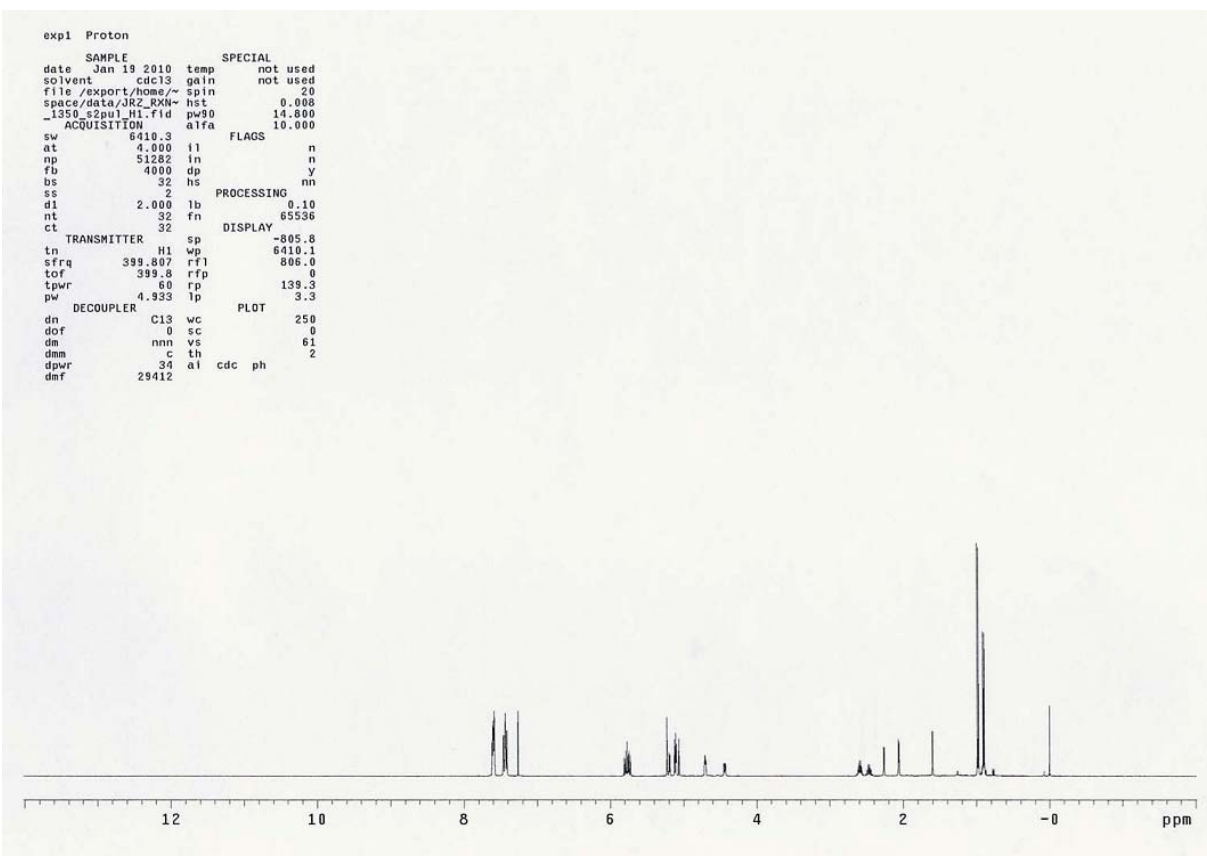
1-(4-Trifluoromethylphenyl)-2-methyl-but-3-en-1-ol (3c). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **1c** (53 mg, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 °C. The reaction mixture was allowed to stir at 70 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO₂; ethyl acetate:hexanes, 1:10) provides the title compound (59 mg) as a colorless oil in 86% yield (*syn/anti* 1.4/1.0 dr).

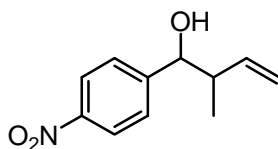
¹H NMR (400 MHz, CDCl₃): δ 7.61–7.58 (m, 4H), 7.46–7.41 (m, 4H), 5.82–5.72 (m, 2H), 5.24–5.05 (m, 4H), 4.70 (t, $J = 4.0$ Hz, 1H of *syn*), 4.43 (dd, $J = 7.2, 2.4$ Hz, 1H of *anti*), 2.63–2.55 (m, 1H of *syn*), 2.51–2.42 (m, 1H of *anti*), 2.26 (d, $J = 2.8$ Hz, 1H of *anti*, OH), 2.06 (d, $J = 2.8$ Hz, 1H of *syn*, OH), 0.98 (d, $J = 6.8$ Hz, 3H of *syn*), 0.90 (d, $J = 6.8$ Hz, 3H of *anti*) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 146.5, 146.3, 139.8, 139.7, 129.7 (q, $J = 32$ Hz), 127.2, 126.8, 124.0 (q, $J = 271$ Hz), 125.2 (q, $J = 3.7$ Hz), 125.0 (q, $J = 3.7$ Hz), 117.6, 116.3, 77.2, 76.4, 46.4, 44.6, 16.4, 13.5 ppm.

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

(3) For *syn* isomer, Denmark, S. E.; Fu, J.; Lawler, M. J.; *J. Org. Chem.* **2006**, *71*, 1523–1536. For *anti* isomer, Takada, Y.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K.; *Org. Lett.* **2006**, *8*, 2515–2517.





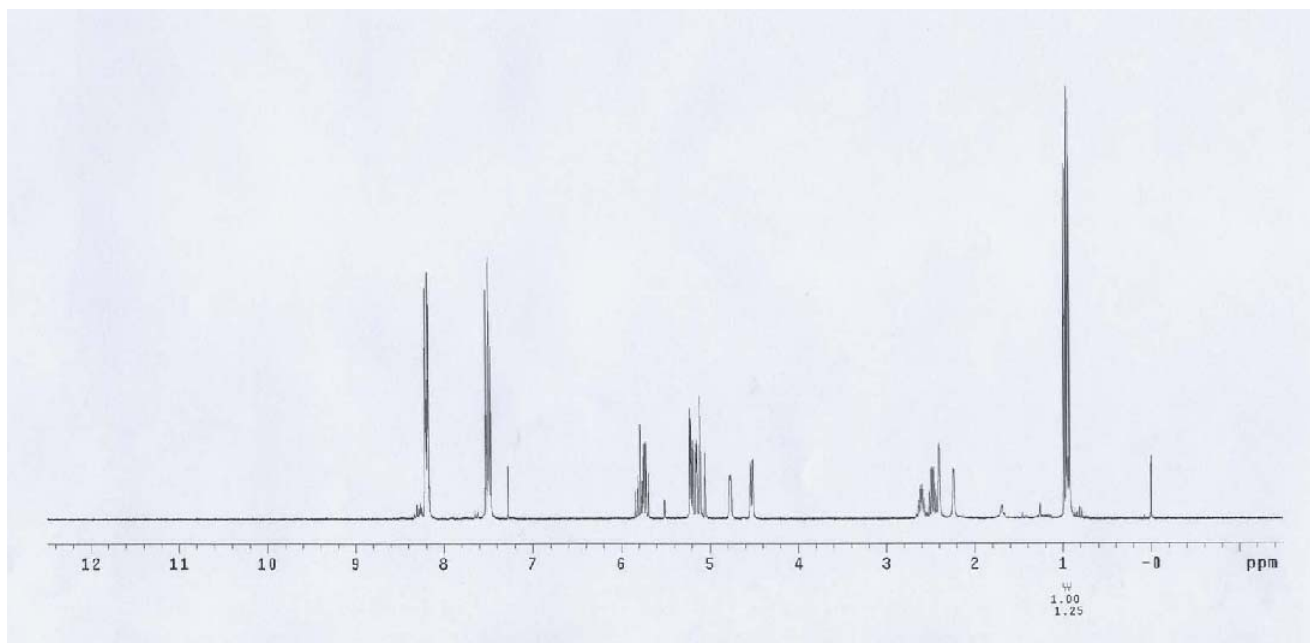
2-Methyl-1-(4-nitrophenyl)but-3-en-1-ol (3d). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **1d** (46 mg, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 °C. The reaction mixture was allowed to stir at 70 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO₂; ethyl acetate:hexanes, 1:9) provides the title compound (44 mg, 0.21 mmol) as a colorless oil in 70% yield (*syn/anti*, 1.0/1.3 dr).

¹H NMR (400 MHz, CDCl₃): 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 *syn*), 4.49 (dd, $J = 7.2, 2.2$ Hz, 1H of *anti*), 2.60-2.56 (m, 1H of *syn*), 2.47-2.41 (m, 1H of *anti*), 2.30 (d, $J = 2.2$ Hz, 1H of *anti*), 2.11 (d, $J = 3.4$ Hz, 1H of *syn*), 0.94 (d, $J = 6.8$ Hz, 3H of *syn*), 0.91 (d, $J = 6.8$ Hz, 3H of *anti*) ppm.

¹³C NMR (100 MHz, CDCl₃): 149.9, 149.8, 147.3, 147.1, 139.3, 139.1, 127.5, 127.2, 123.7, 123.4, 123.2, 117.9, 116.6, 76.6, 76.0, 46.3, 44.6, 16.2, 13.3 ppm.

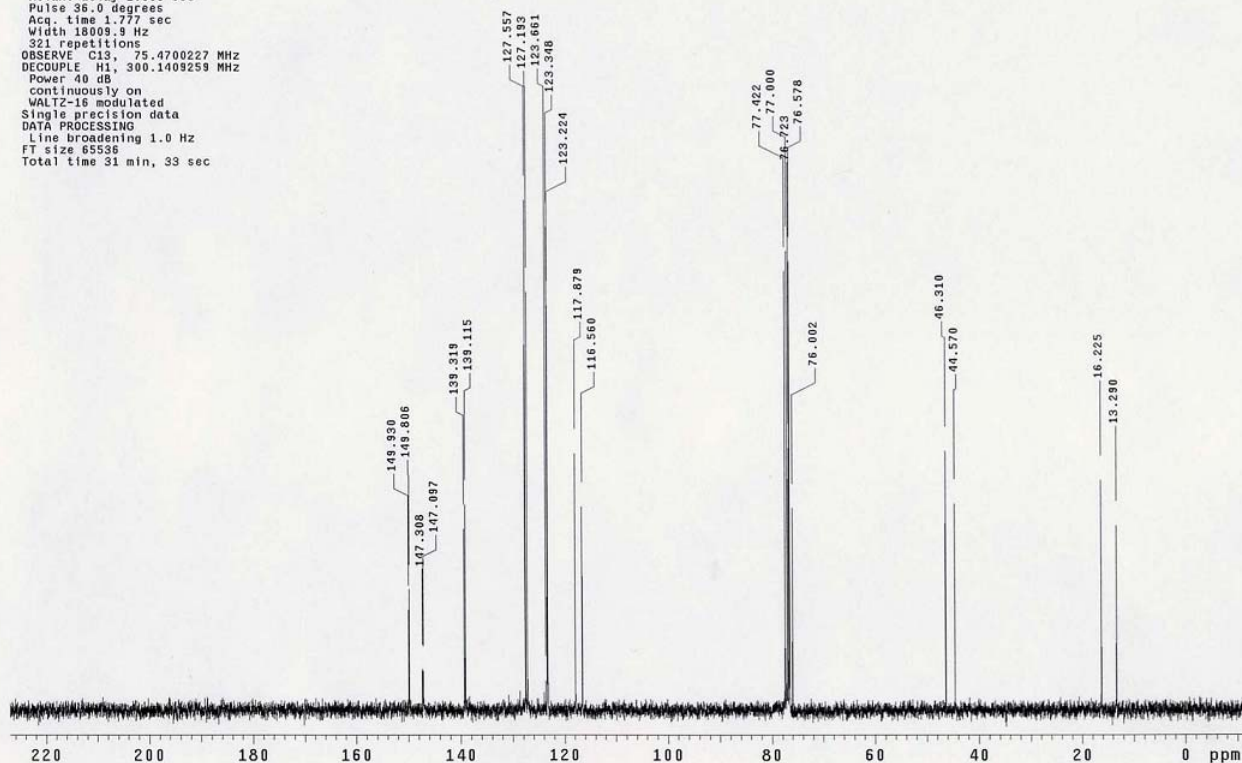
The spectroscopic properties of this compound were consistent with the data available in the literature.⁴

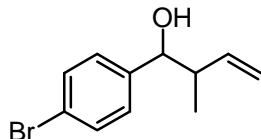
(4) Jiang, S.; Agoston, E. G.; Chen, T.; Cabal, M.-P.; Turos, E. *Organometallics* **1995**, *14*, 4697.



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 Continuously on
 WALTZ-16 modulated
 Single precision data
 DATA PROCESSING
 Line broadening 1.0 Hz
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 Total time 31 min, 33 sec





2-Methyl-1-(4-bromophenyl)but-3-en-1-ol (3e). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **1e** (56 mg, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 °C. The reaction mixture was allowed to stir at 70 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ethyl acetate:hexanes, 1:10) provides the title compound (45 mg) as a colorless oil in 62% yield (*syn/anti*, 1.7/1 dr).

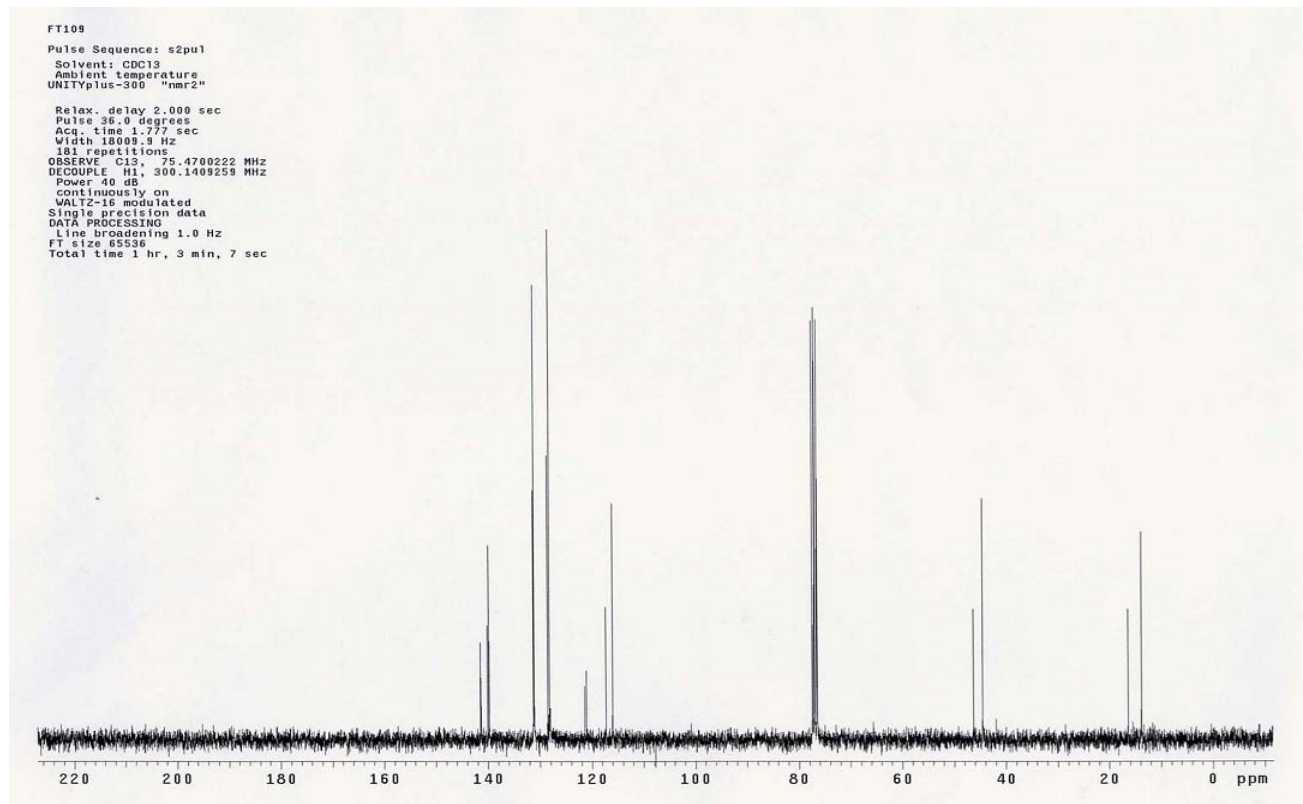
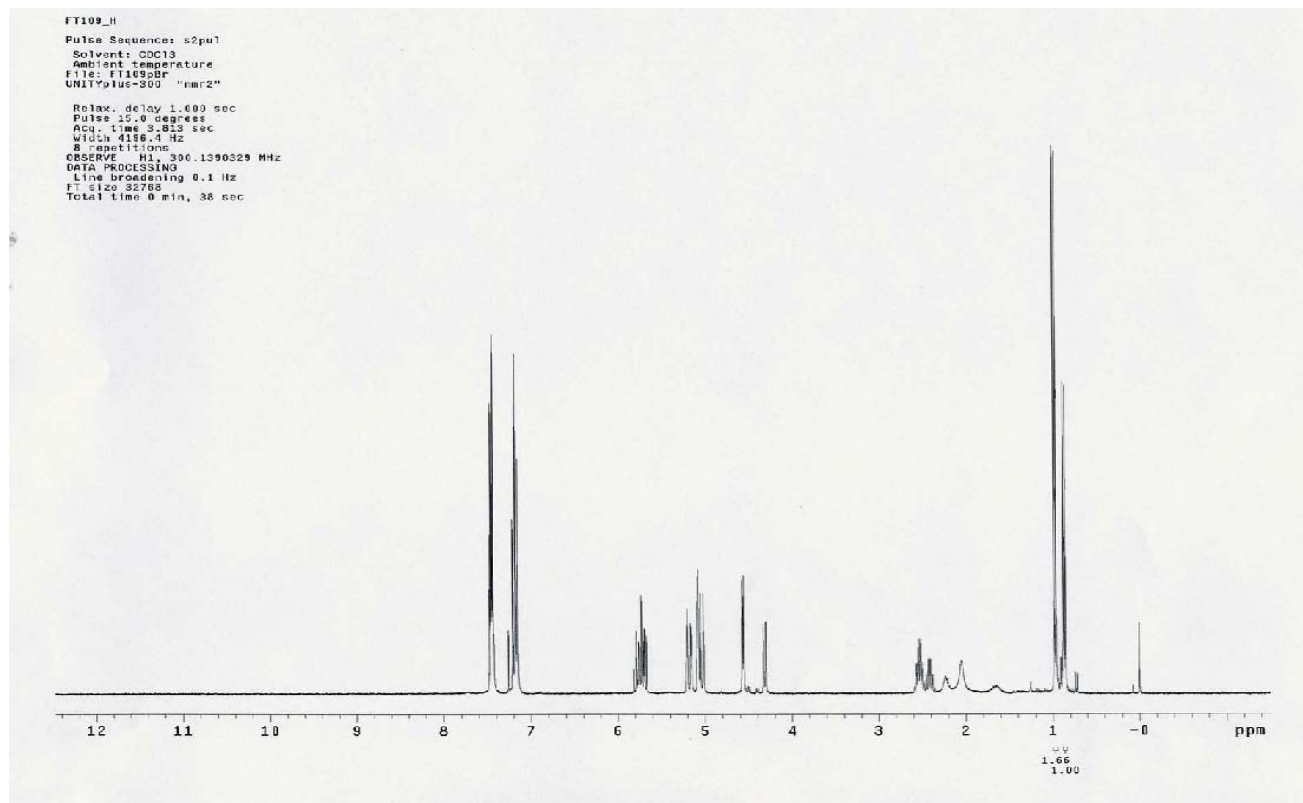
Corresponding Aldehyde Coupling: An oven-dried sealed tube under an atmosphere of nitrogen was charged with aldehyde **2e** (55.0 mg, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14.0 mg, 0.015 mmol, 5 mol%), sodium acetate (25.1 mg, 0.30 mmol, 100 mol%), 1,4-butanediol (27.0 μl , 0.30 mmol, 100 mol%) and toluene (2.0 M, 0.15 mL). 1,3-Butadiene (0.10 ml, 1.2 mmol, 400 mol%) was added at -78 °C. The reaction mixture was allowed to stir at 70 °C for 72 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ethyl acetate:hexanes, 93:7) provides the title compound (56.7 mg) as a colorless oil in 78% yield (*syn/anti*, 1.7/1 dr).

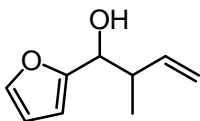
$^1\text{H NMR}$ (400 MHz, CDCl_3): 7.47–7.42 (m, 4H), 7.20–7.13 (m, 4H), 5.80–5.67 (m, 2H), 5.20–5.02 (m, 4H), 4.54 (dd, $J = 5.0, 4.0$ Hz, 1H of *syn*), 4.30 (dd, $J = 8.0, 2.5$ Hz, 1H of *anti*), 2.60–2.50 (m, 1H of *syn*), 2.50–2.40 (m, 1H of *anti*), 2.25 (br, 1H of *anti*, OH), 2.12 (br, 1H of *syn*, OH), 0.97 (d, $J = 7.0$ Hz, 3H of *syn*), 0.86 (d, $J = 7.0$ Hz, 3H of *anti*) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): 141.5, 141.3, 140.1, 139.8, 131.3, 131.1, 128.5, 128.2, 121.4, 121.1, 117.3, 116.0, 77.1, 76.5, 46.3, 44.5, 16.4, 13.8 ppm.

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

(5) Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. *Tetrahedron* **2001**, *57*, 835.





Methyl 4-(1-hydroxy-2-methylbut-3-enyl)benzoate (3f). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **2f** (26 μ l, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 °C. The reaction mixture was allowed to stir at 95 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ether:pentanes, 1:10) provides the title compound (33mg) as a colorless oil in 80% yield (*syn/anti*, 1.1/1.0 dr).

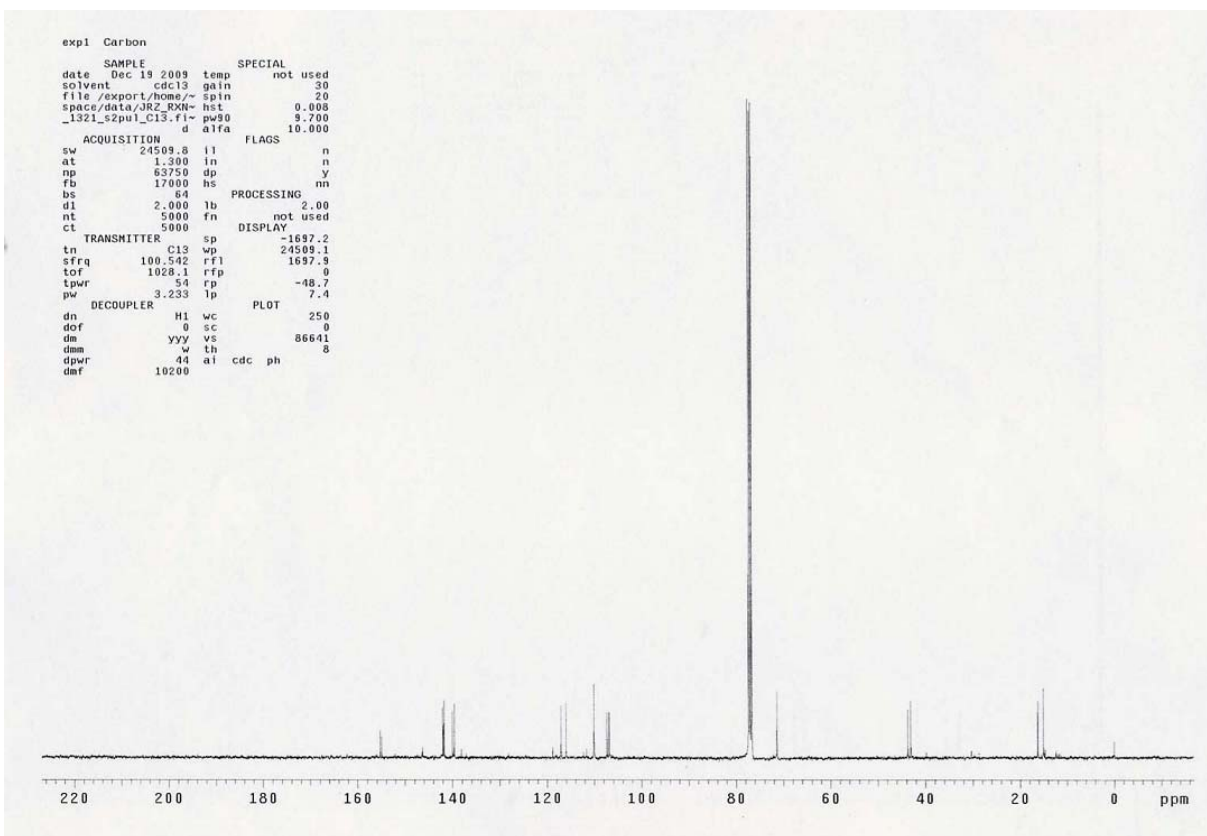
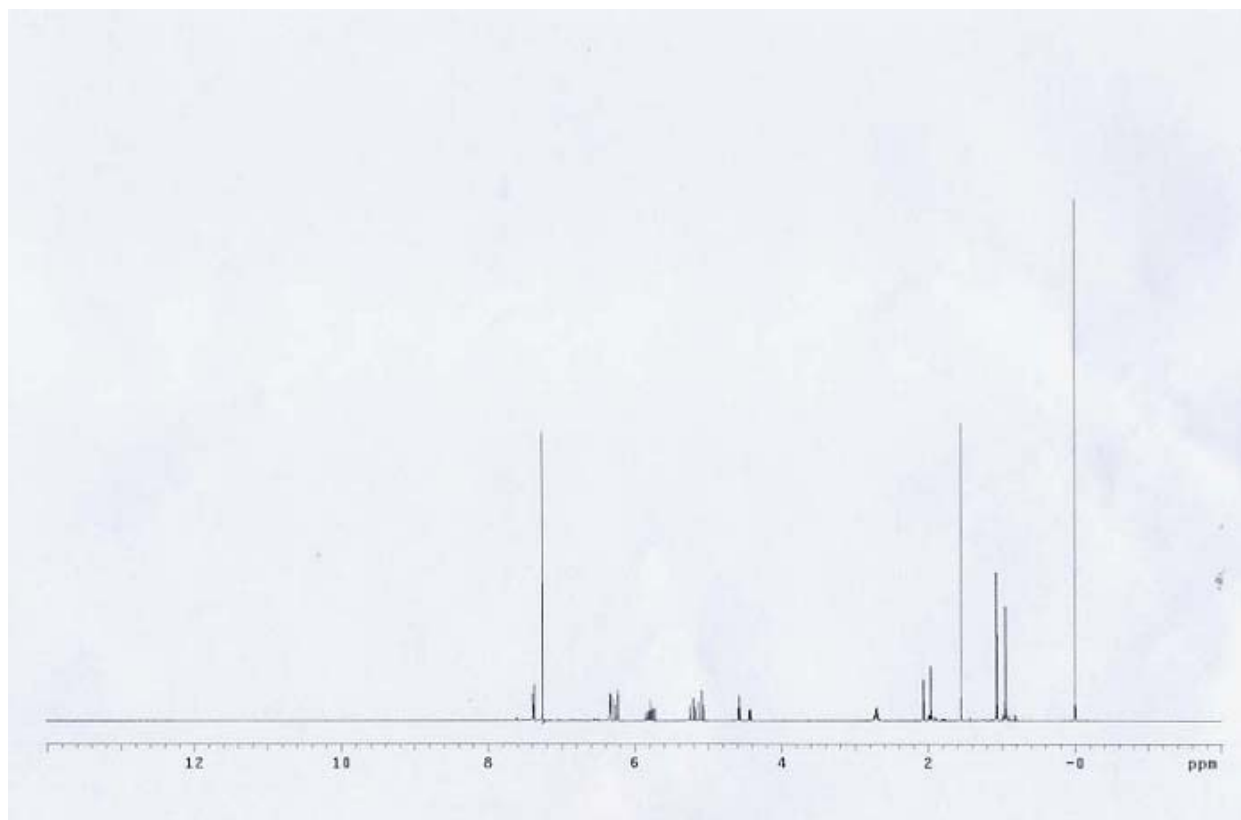
Corresponding Aldehyde Coupling: An oven-dried sealed tube under an atmosphere of nitrogen was charged with aldehyde **2f** (25 μ l, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%), 1,4-butanediol (27 μ l, 0.30 mmol, 100 mol%) and toluene (2.0 M, 0.15 mL). 1,3-butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 °C. The reaction mixture was allowed to stir at 70 °C for 72 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ethyl acetate:hexanes, 5:95) provides the title compound (35mg) as a colorless oil in 76% yield (*syn/anti*, 1.7/1.0 dr).

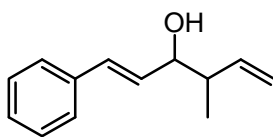
$^1\text{H NMR}$: (400 MHz, CDCl_3) 7.39 (dd, $J = 1.7, 0.7$ Hz, 1H of *anti*), 7.37 (dd, $J = 1.7, 0.7$ Hz, 1H of *syn*), 6.35–6.32 (m, 2H), 6.28 (d, $J = 3.2$ Hz, 1H of *anti*), 6.23 (d, $J = 3.2$ Hz, 1H of *syn*), 5.85–5.71 (m, 2H), 5.25–5.06 (m, 4H), 4.57 (t, $J = 5.6$ Hz, 1H of *syn*), 4.42 (dd, $J = 7.6, 4.0$ Hz, 1H of *anti*), 2.76–2.66 (m, 2H), 2.10 (br, 1H of *anti*, OH), 2.00 (br, 1H of *syn*, OH), 1.07 (d, $J = 6.8$ Hz, 3H of *syn*), 1.07 (d, $J = 6.8$ Hz, 3H of *anti*) ppm.

$^{13}\text{C NMR}$: (100 MHz, CDCl_3) 155.3, 154.9, 142.0, 141.8, 140.0, 139.6, 117.1, 116.0, 110.1, 110.0, 107.3, 106.9, 71.4, 71.3, 43.7, 43.1, 16.3, 15.1 ppm.

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

(6) For *syn* isomer, Denmark, S. E.; Fu, J.; Lawler, M. J.; *J. Org. Chem.* **2006**, *71*, 1523–1536. For *anti* isomer, Fujita, K.; Yorimitsu, H.; Shinokubo, H.; Matsubara, S.; Oshima, K.; *J. Am. Chem. Soc.* **2001**, *123*, 12115–12116.





4-Methyl-1-phenylhexa-(1E,5)-dien-3-ol (3g). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **3g** (39 μ l, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 $^{\circ}$ C. The reaction mixture was allowed to stir at 70 $^{\circ}$ C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ethyl acetate:hexanes, 1:10) provides the title compound (36 mg) as a colorless oil in 64% yield (*syn/anti* 1.5/1 dr).

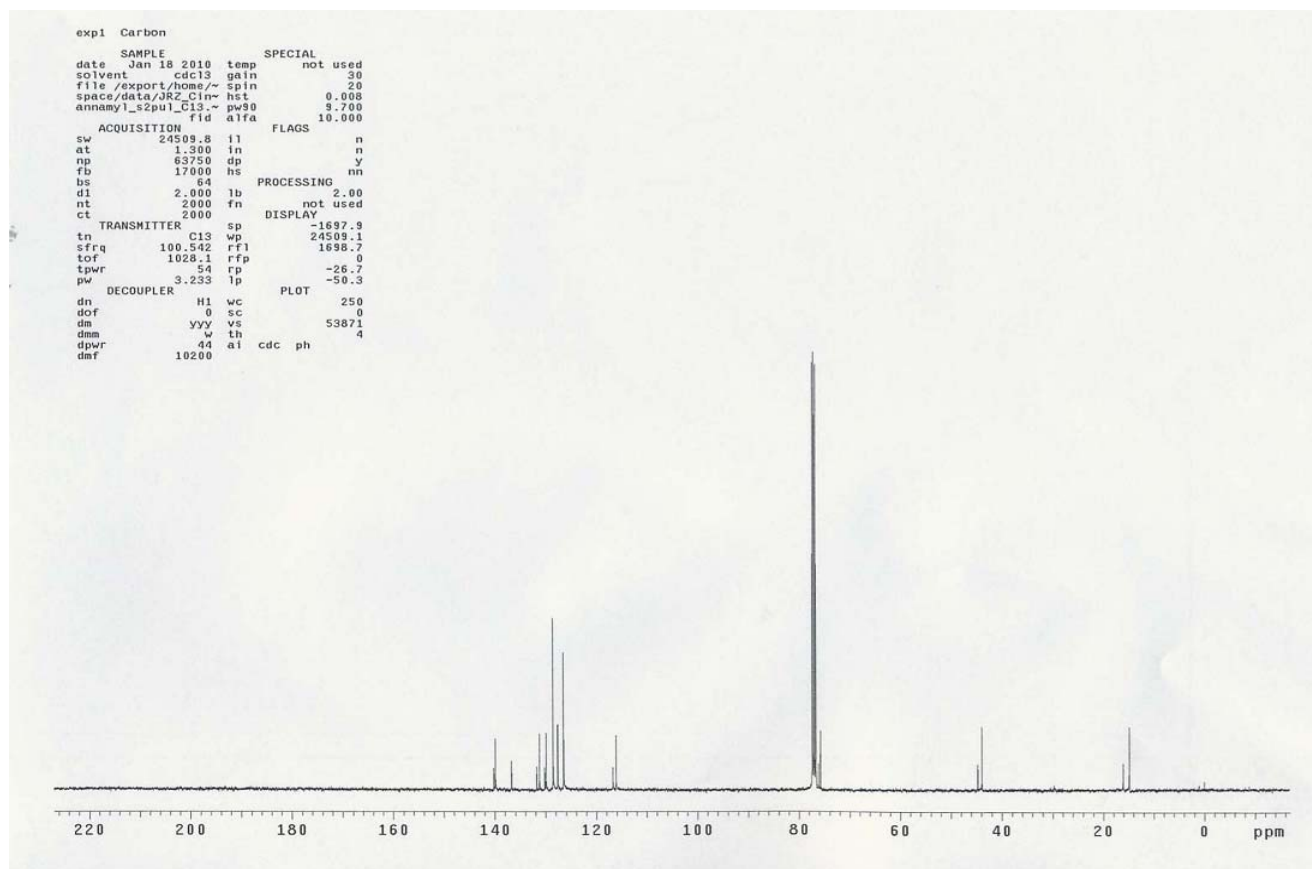
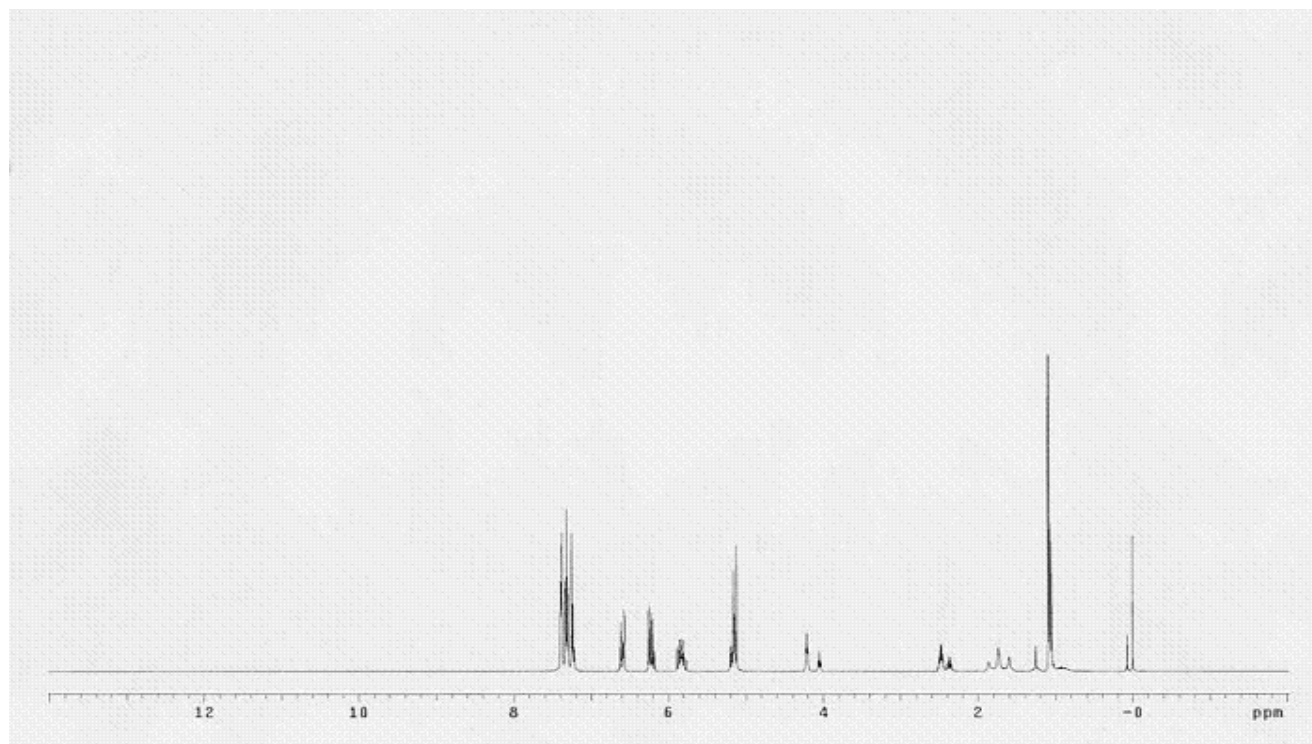
Corresponding Aldehyde Coupling. An oven-dried sealed tube under an atmosphere of nitrogen was charged with aldehyde **2g** (38 μ l, 0.30 mmol, 100 mol%), Ir-complex I (14 mg, 0.015 mmol, 5 mol%), Sodium acetate (25 mg, 0.30 mmol, 100 mol%), 1,4-butanediol (27 μ l, 0.30 mmol, 100 mol%) and Toluene (2.0 M, 0.15 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 $^{\circ}$ C. The reaction mixture was allowed to stir at 70 $^{\circ}$ C for 72 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ether:hexanes, 2:10) provides the title compound (40 mg) as a colorless oil in 72% yield (*syn/anti* 1.8/1 dr).

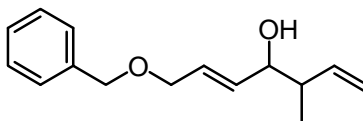
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.41–7.22 (m, 10H), 6.64–6.56 (m, 2H), 6.26–6.18 (m, 2H), 5.89–5.77 (m, 2H), 5.22–5.12 (m, 4H), 4.22 (t, $J = 6.8$ Hz, 1H of *syn*), 4.06 (t, $J = 6.8$ Hz, 1H of *anti*), 2.53–2.44 (m, 1H of *syn*), 2.42–2.32 (m, 1H of *anti*), 1.84 (br, 1H of *syn*, OH), 1.70 (br, 1H of *anti*, OH), 1.09 (d, $J = 6.8$ Hz, 1H of *syn*), 1.06 (d, $J = 6.8$ Hz, 1H of *anti*) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 140.2, 139.9, 136.8, 136.7, 131.8, 131.2, 130.2, 129.9, 128.5, 127.7, 127.6, 126.5, 116.7, 116.1, 76.2, 75.8, 44.7, 43.9, 16.1, 14.8 ppm.

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

(7) Kim, I. S.; Han, S. B.; Krische, M. J.; *J. Am. Chem. Soc.* **2009**, *131*, 2514–2520.





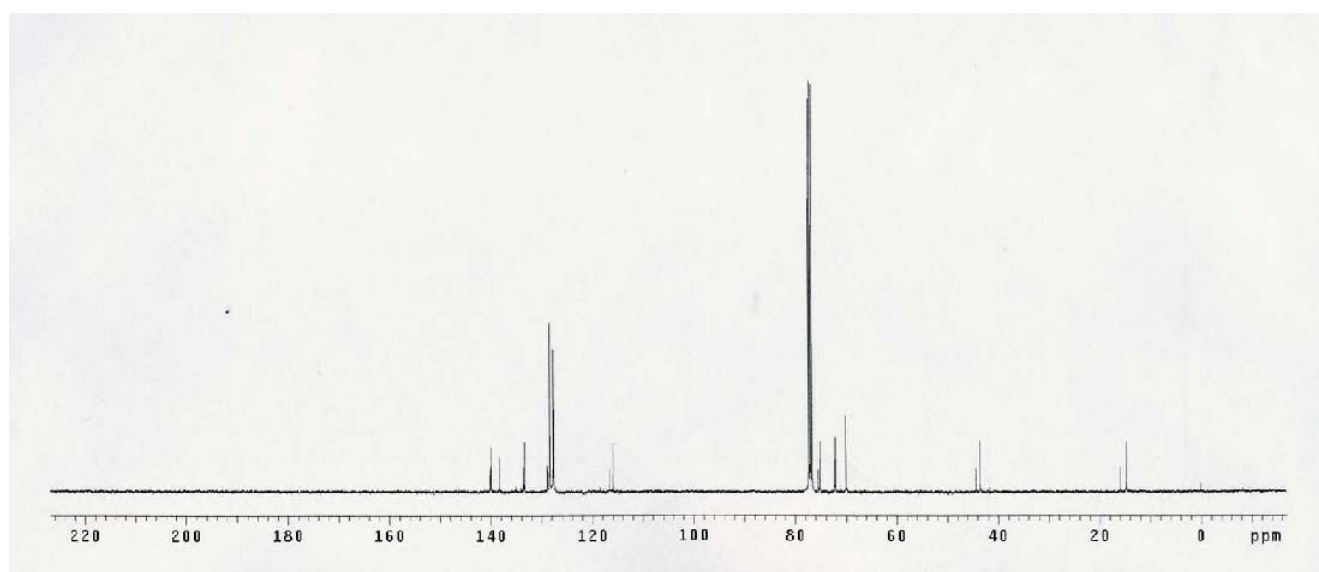
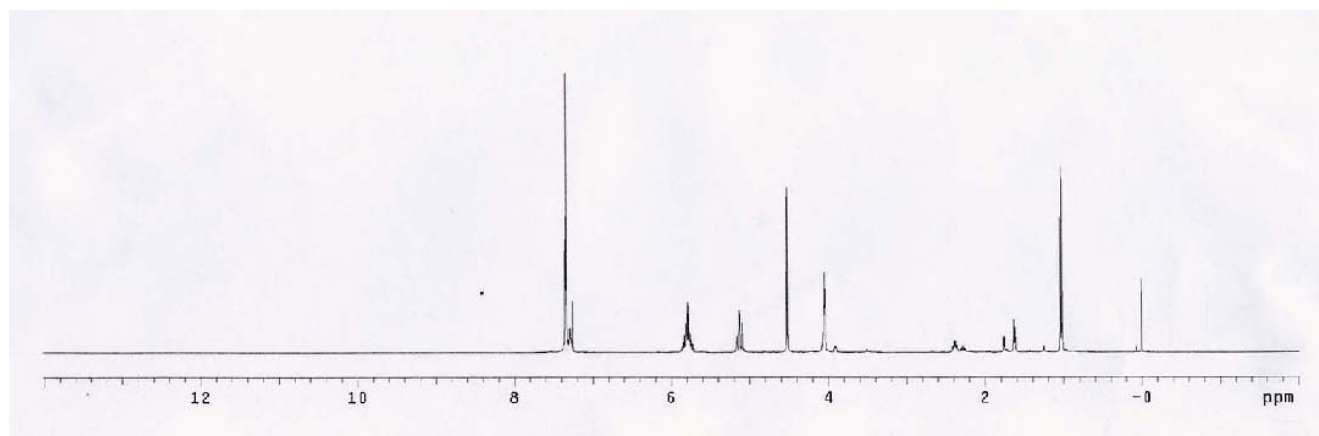
4-Methyl-1-phenylhex-5-en-3-ol (3h). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **1h** (53 mg, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 °C. The reaction mixture was allowed to stir at 70 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ethyl acetate:hexanes, 1:10) provides the title compound (43 mg) as a colorless oil in 62% yield (*syn/anti*, 1.4/1 dr).

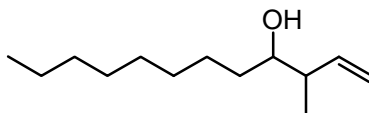
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.26–7.35 (m, 10H), 5.88–5.72 (m, 6H), 5.18–5.06 (m, 4H), 4.52 (s, 4H), 4.08–4.04 (m, 6H), 2.44–2.34 (m, 1H of *syn*), 2.32–2.24 (m, 1H of *anti*), 1.75 (br, 1H of *anti*, OH), 1.63 (br, 1H of *syn*, OH), 1.04 (m, 6H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 140.1, 139.9, 138.2, 133.6, 133.4, 128.9, 128.4, 128.3, 127.7, 127.6, 116.6, 115.9, 75.5, 75.1, 72.2, 72.1, 70.1, 44.3, 43.6, 16.0, 14.7 ppm.

IR (thin film): $\nu = 3410, 3031, 2965, 2857, 2248, 1639, 1454, 1362, 1097, 1068, 971, 908, 731, 697$ cm^{-1} ;

HRMS (ESI): m/z : calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2$: 233.1542; found: 233.1541 [$M+\text{H}$] $^+$.





3-Methyldodec-1-en-4-ol (3i). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **1i** (53 μ l, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 $^{\circ}$ C. The reaction mixture was allowed to stir at 70 $^{\circ}$ C for 72 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ethyl acetate:hexanes, 1:10) provides the title compound (33 mg) as a colorless oil in 52% yield (*syn/anti* 1.5/1 dr).

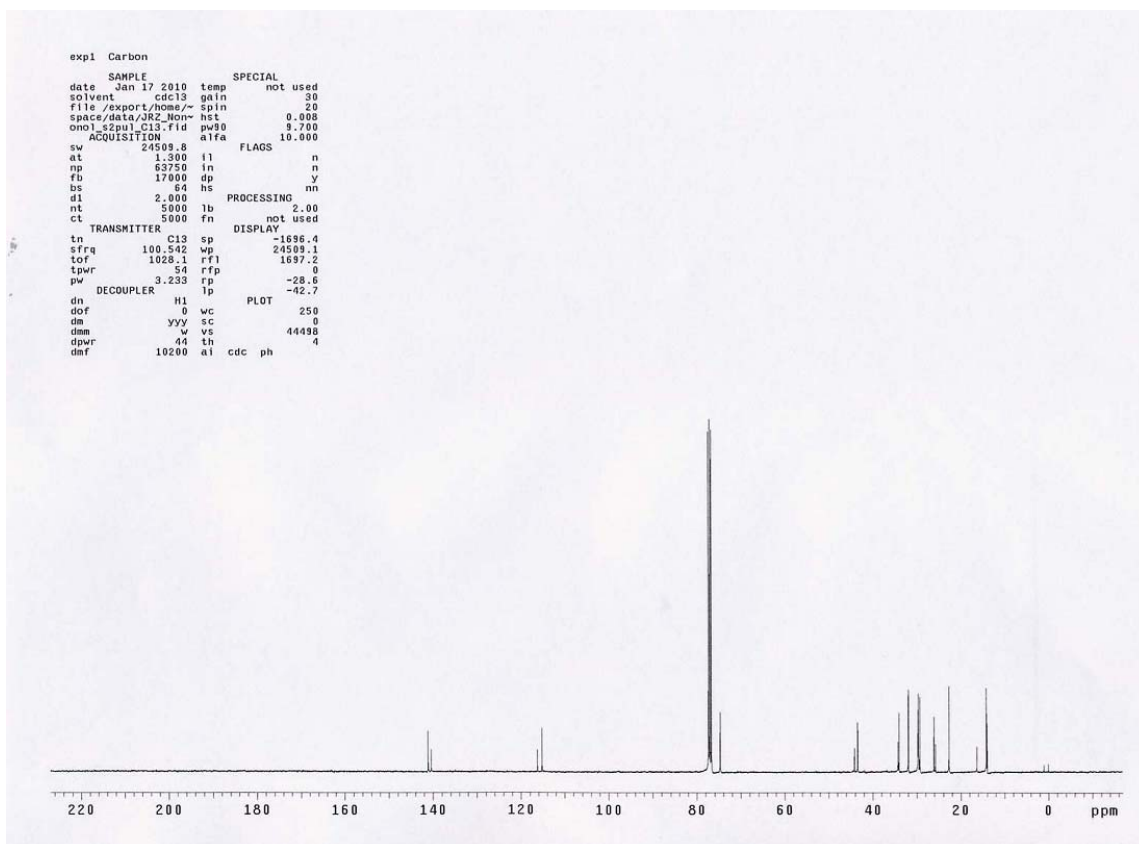
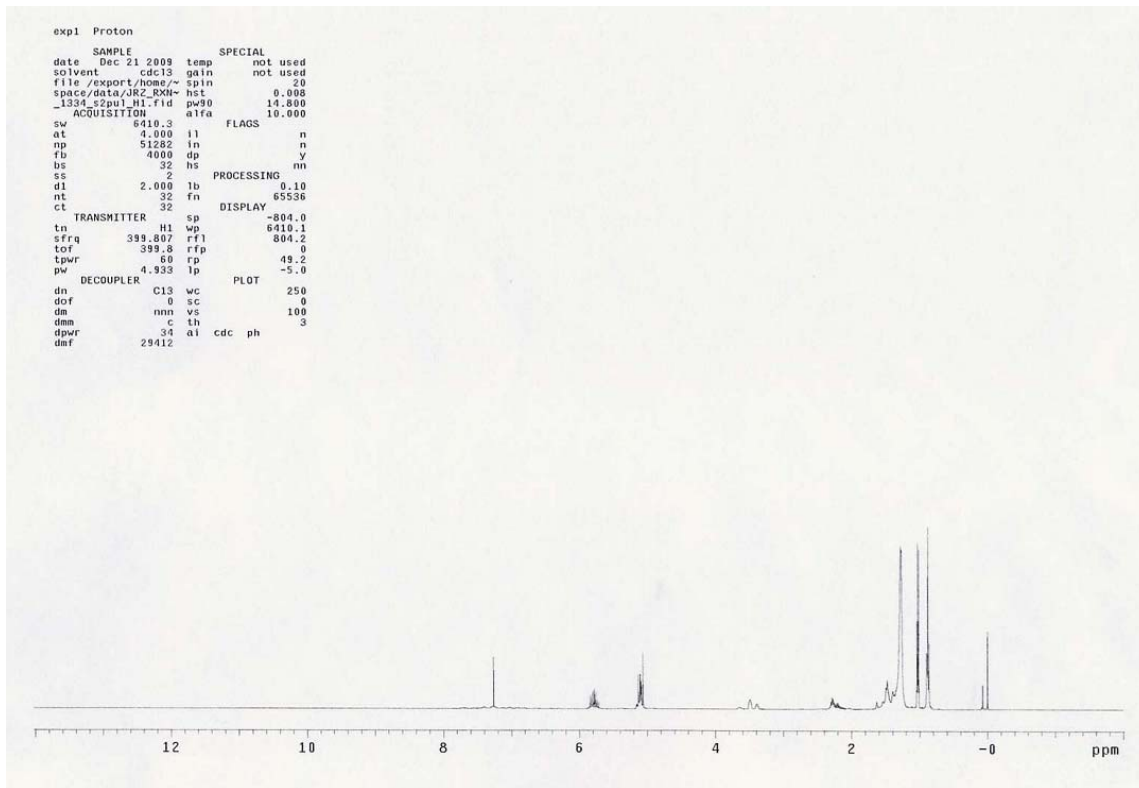
Corresponding Aldehyde Coupling: An oven-dried sealed tube under an atmosphere of nitrogen was charged with aldehyde **2i** (52 μ l, 0.30 mmol, 100 mol%), Ir-BIPHEP-1-OMe (14 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%), 1,4-butanediol (27 μ l, 0.30 mmol, 100 mol%) and toluene (2.0 M, 0.15 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 $^{\circ}$ C. The reaction mixture was allowed to stir at 70 $^{\circ}$ C for 72 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ethyl acetate:hexanes, 3:97) provides the title compound (33 mg) as a colorless oil in 58% yield (*syn/anti* 1.7/1 dr).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 5.85–5.71 (m, 2H), 5.15–5.05 (m, 4H), 3.50–3.35 (m, 2H), 2.34–2.10 (m, 2H), 1.53–1.26 (m, 28H), 1.03 (d, $J = 6.8$ Hz, 3H of *anti*), 1.02 (d, $J = 6.8$ Hz, 3H of *syn*), 0.88 (t, $J = 6.8$ Hz, 6H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 141.1, 140.4, 116.2, 115.2, 74.7, 44.1, 43.4, 34.3, 34.0, 31.9, 29.8, 29.7, 29.6, 29.3, 26.1, 25.7, 26.1, 25.8, 22.7, 16.3, 14.1, 14.0 ppm.

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

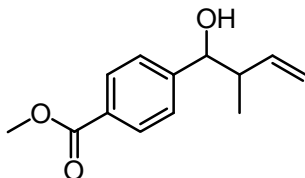
(8) Kim, I. S.; Han, S. B.; Krische, M. J.; *J. Am. Chem. Soc.* **2009**, *131*, 2514–2520.



4. Enantioselective reaction

Ir-Complex with (*S*)–SEGPHOS

Ir complex was prepared according to the General Procedure.



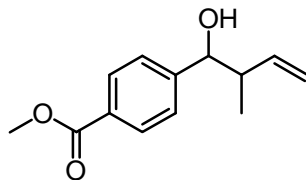
Methyl 4-(1-hydroxy-2-methylbut-3-enyl)benzoate (3a). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **1a** (50 mg, 0.30 mmol, 100 mol%), Ir-(*S*)–SEGPHOS-OMe complex (16 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to stir at $70\text{ }^{\circ}\text{C}$ for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ethyl acetate:hexanes, 1:10) provides the title compound (53 mg) as a colorless oil in 80% yield (*syn/anti*, 1.4/1.0 dr).

HPLC: (Chiralpak AS–H/AD–H column, hexanes:*i*-PrOH = 97:3, 0.5 mL/min, 254 nm),

From Segphos complex catalyst; *syn* ($t_{\text{major}} = 64\text{ min}$, $t_{\text{minor}} = 73\text{ min}$; 87% ee), *anti* ($t_{\text{major}} = 66\text{ min}$, $t_{\text{minor}} = 96\text{ min}$; 62% ee)

Ir-Complex with Walphos (SL–W002–1)

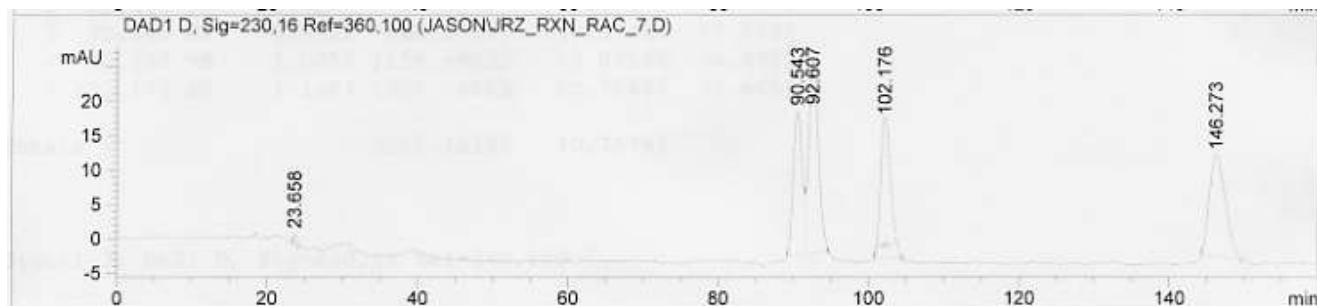
Ir complex was prepared according to the General Procedure.



Methyl 4-(1-hydroxy-2-methylbut-3-enyl)benzoate (3a). An oven-dried sealed tube under an atmosphere of nitrogen was charged with alcohol **1a** (50 mg, 0.30 mmol, 100 mol%), Ir-Walphos-OMe complex (16 mg, 0.015 mmol, 5 mol%), sodium acetate (25 mg, 0.30 mmol, 100 mol%) and toluene (1.0 M, 0.3 mL). 1,3-Butadiene (0.1 ml, 1.2 mmol, 400 mol%) was added at -78 °C. The reaction mixture was allowed to stir at 70 °C for 48 hr, at which point the reaction mixture was concentrated *in vacuo*. Purification of the product by column chromatography (SiO_2 ; ethyl acetate:hexanes, 1:10) provides the title compound (27 mg) as a colorless oil in 40% yield (*syn/anti*, 1.0/2.2 dr).

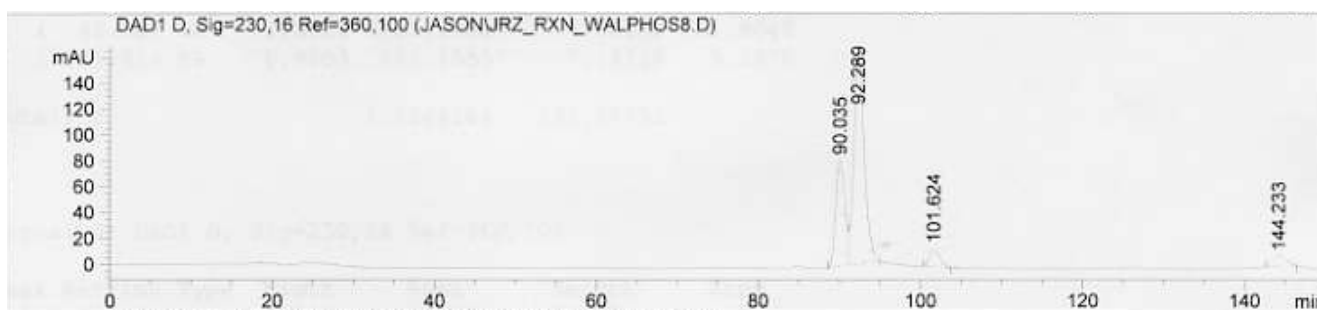
HPLC: (Chiralpak AS–H/AS–H/AD–H column, hexanes:*i*-PrOH = 97:3, 0.5 mL/min, 230 nm), From Walphos complex catalyst; *syn* ($t_{\text{major}} = 90$ min, $t_{\text{minor}} = 102$ min; 68% ee), *anti* ($t_{\text{major}} = 92$ min, $t_{\text{minor}} = 144$ min; 88% ee)

Racemic:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.658	BB	0.3156	31.20956	1.47073	0.3718
2	90.543	BV	1.1517	1743.62085	21.02162	20.7737
3	92.607	VB	1.2643	2521.87207	28.44710	30.0459
4	102.176	BB	1.3150	1937.92969	20.57338	23.0887
5	146.273	BB	1.7307	2158.76782	14.63719	25.7198
Totals :				8393.39999	86.15002	

Chiral:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	90.035	BV	1.2202	6526.96484	81.86084	28.2023
2	92.289	VB	1.3499	1.44421e4	160.18535	62.4029
3	101.624	BB	1.2152	1249.87927	14.22372	5.4006
4	144.233	BB	1.4120	924.41821	7.70343	3.9943
Totals :				2.31434e4	263.97334	