# Supporting Information

## “Catalyst-Directed Diastereoselectivity in Hydrogenative Couplings of Acetylene to α-Chiral Aldehydes: Formal Synthesis of All Eight L-Hexoses”

Soo Bong Han, Jong Rock Kong and Michael J. Krische*

*University of Texas at Austin*
*Department of Chemistry and Biochemistry*
*Austin, TX 78712*
*USA*

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## I. General.

All reactions were conducted under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred by an oven-dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. BIPHEP, (*R*)-MeO-BIPHEP and (*S*)-MeO-BIPHEP were used as received from Strem Chemicals. Triphenylacetic acid, *m*-nitrobenzoic acid, and pentafluorobenzoic acid were used as received from Aldrich. Acetylene Gas was used as received from PRAXAIR (Atomic Absorption Grade). $[Rh(cod)_2]BARF$[1] was prepared in analogy with the previously reported procedures. 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.[2] 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 + 1) or a suitable fragment ion. 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 (pip) 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.

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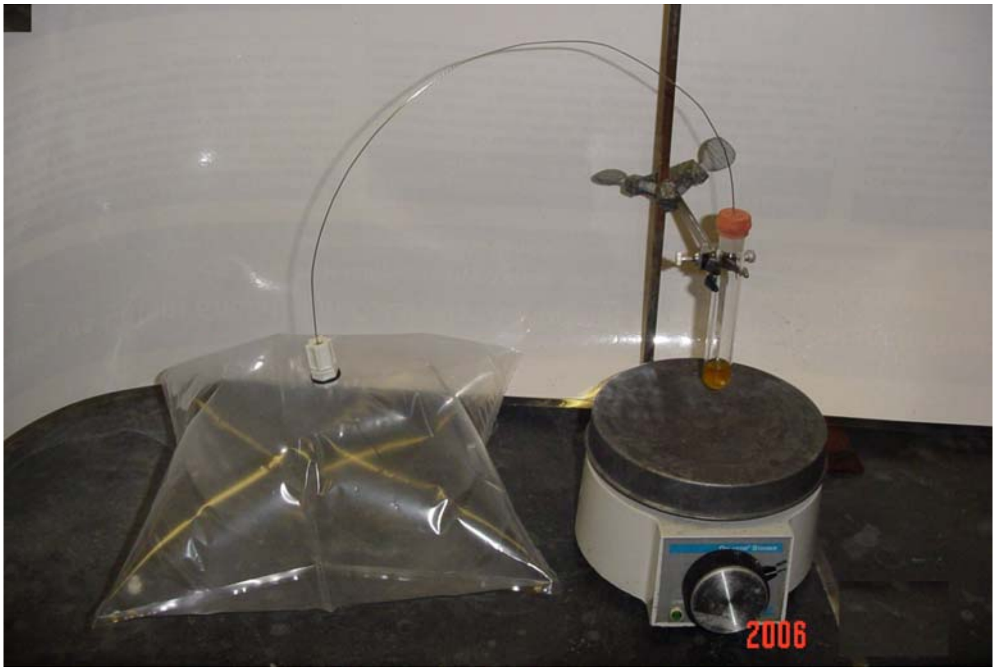
[1] Guzel, B.; Omary, M. A.; Fackler, JP, Jr.; Akgerman, A. *Inorg. Chim. Acta* **2001**, *325*, 45.

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

## II. Experimental Aparatus



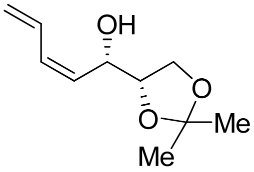
1) Reaction Vessel: 2.0cm (Diameter) * 13.0cm (Length)
2) Gas bag : Tedlar® gas sampling bag (Aldrich)
3) Cannula (Double-tipped needle): 24 in.(Length) – 20 (gauge)

## III. General Procedure for Diastereoselective Reducitve Coupling

To a reaction vessel charged with $[Rh(cod)_2]BARF$ (5 mol%), (*R*)-MeO-BIPHEP or (*S*)-MeO-BIPHEP (5 mol%), petafluoro-benzoic acid (5 mol%), and $Na_2SO_4$ (200 mol%) was added toluene (0.16 M with respect to aldehyde). The reaction mixture was allowed to stir for 15 minutes at 25 $^{o}$C, at which point a 1:1 mixture of hydrogen and acetylene gas was introduced *via* cannula. A solution of aldehyde (100 mol%) in toluene (0.25 M with respect to aldehyde) was added to the reaction vessel. The mixture was allowed to stir at 25 $^{o}$C for 12 hours, at which point the reaction mixture was directly deposited onto a column of silica gel. Flash column chromatography ($SiO_2$) provides the product of aldehyde (*Z*)-butadienylation.

## IV. Detailed Procedure for the Reductive Coupling and Spectral Data

### (*S*,*Z*)-1-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)penta-2,4-dien-1-ol



**1b**

To a reaction vessel charged with [Rh(cod)$_2$]BARF (11.8 mg, 0.01 mmol, 5 mol%), (*S*)-MeO-BIPHEP (5.9 mg, 0.01 mmol, 5 mol%), petafluorobenzoic acid (2.1 mg, 0.01 mmol, 5 mol%), and $Na_2SO_4$ (58 mg, 0.4 mmol, 200 mol%) was added toluene (1.2 mL, 0.16 M). The reaction mixture was allowed to stir for 15 minutes at 25 $^oC$, at which point a 1:1 mixture of hydrogen and acetylene gas was introduced *via* cannula. A toluene solution (0.8 mL, 0.25 M) of L-glyceraldehyde[3] (26 mg, 0.2 mmol, 100 mol%) was added to the reaction mixture *via* syringe. The mixture was allowed to stir at 25 $^oC$ for 12 hours, at which point the reaction mixture was directly deposited onto a column of silica gel. Flash column chromatography ($SiO_2$: $R_f = 0.3$, pentane:ether, 2:1) provides the title compound (28.7 mg, 0.156 mmol) as a colorless oil in 78 % yield (≥ 20:1 dr).

(Spectroscopic data for the major diastereomer)

**$^1$H NMR** (400 MHz, $CDCl_3$): 6.70 – 6.63 (m, 1H), 6.16 (td, *J* = 11.2, 0.8 Hz, 1H), 5.37 – 5.21 (m, 3H), 4.47 (t, *J* = 8.0 Hz, 1H), 4.04 – 4.00 (m, 1H), 3.95 (d, *J* = 6.4 Hz, 1H), 3.93 (d, *J* = 6.4 Hz, 1H), 3.68 (dd, *J* = 8.6, 5.4 Hz, 1H), 2.39 ( br, 1H), 1.45 (s, 3H), 1.35 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): 133.4, 131.5, 128.4, 120.6, 109.9, 79.1, 69.2, 65.7, 26.9, 25.2.

**HRMS** Calcd for $C_{10}H_{17}O_3$ (M+1): 185.1178, Found: 185.1182.

**FTIR** (neat): 3441, 2986, 2887, 1594, 1456, 1371, 1253, 1212, 1154, 1059, 1004, 911, 848, 798, 670 $cm^{-1}$.

**$[\alpha]_D^{25}$**-17$^o$, c = 1.05 in DCM

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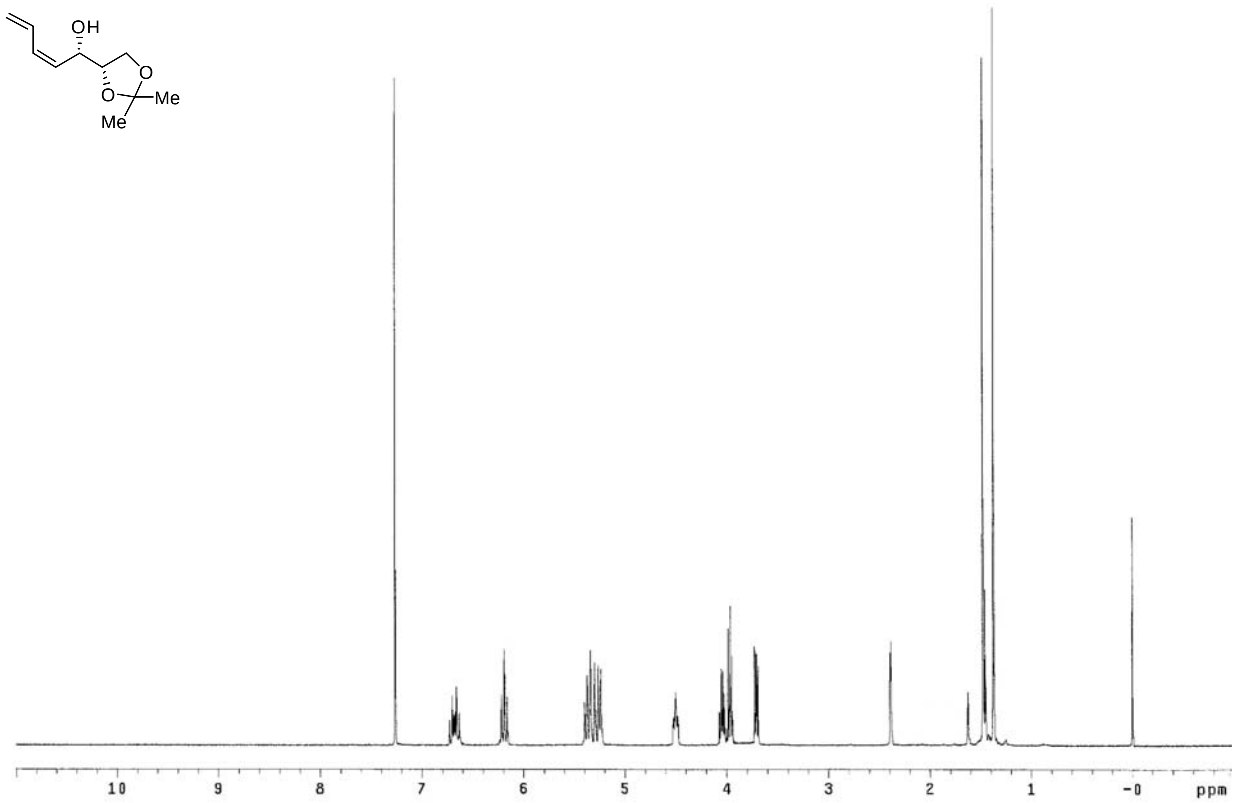
[3] Hubschwerlen, C. *Synthesis* **1986**, 962.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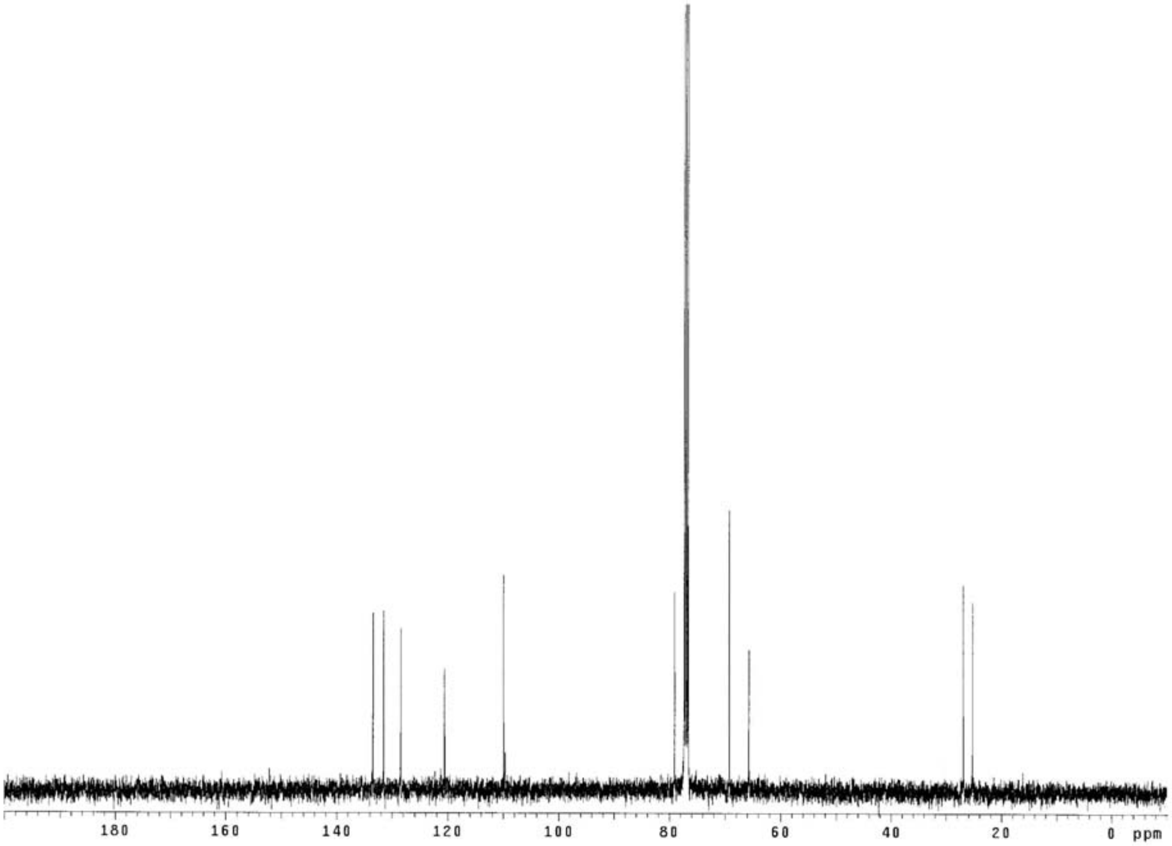
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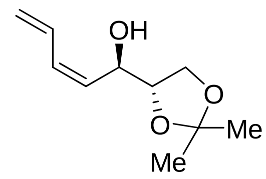
**(*R*,*Z*)-1-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)penta-2,4-dien-1-ol**



**1c**

To a reaction vessel charged with $[Rh(cod)_2]BARF$ (11.8 mg, 0.01 mmol, 5 mol%), (*R*)-MeO-BIPHEP (5.9 mg, 0.01 mmol, 5 mol%), petafluorobenzoic acid (2.1 mg, 0.01 mmol, 5 mol%), and $Na_2SO_4$ (58 mg, 0.4 mmol, 200 mol%) was added toluene (1.2 mL, 0.16 M). The reaction mixture was allowed to stir for 15 minutes at 25 $^{o}$C, at which point a 1:1 mixture of hydrogen and acetylene gas was introduced *via* cannula. A toluene solution (0.8 mL, 0.25 M) of L-glyceraldehyde[3] (26 mg, 0.2 mmol, 100 mol%) was added to the reaction mixture *via* syringe. The mixture was allowed to stir at 4 $^{o}$C for 24 hours, at which point the reaction mixture was directly deposited onto a column of silica gel. Flash column chromatography ($SiO_2$: $R_f$ = 0.3, pentane:ether, 2:1) provides the title compound (30.5 mg, 0.166 mmol) as a colorless oil in 83 % yield (7:1 dr).

(Spectroscopic data for the major diastereomer)

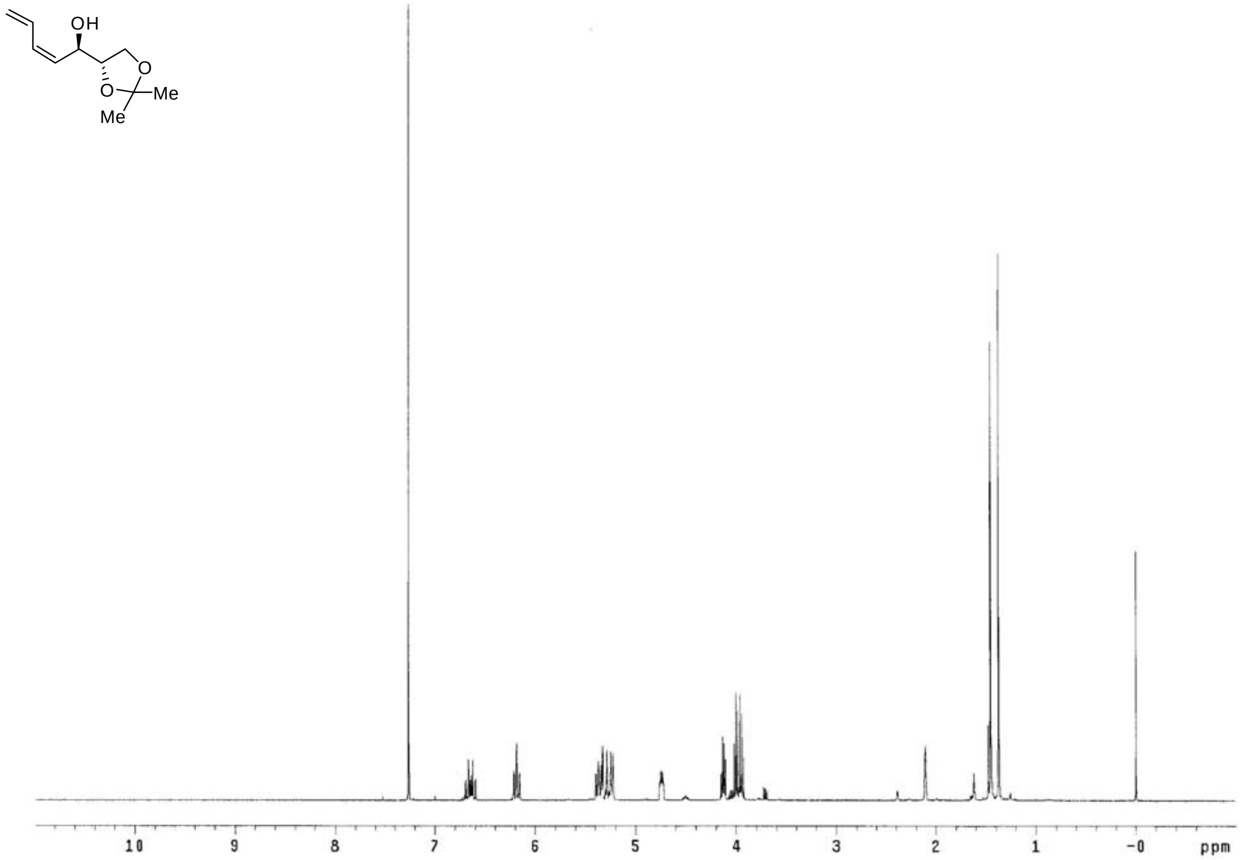
**$^{1}$H NMR** (400 MHz, $CDCl_3$): 6.62 (dtd, *J* = 16.4, 10.6, 1.2 Hz, 1H), 6.16 (td, *J* = 11.2, 0.7 Hz, 1H), 5.34 (t, *J* = 9.8 Hz, 1H), 5.28 (dd, *J* = 16.8, 0.2 Hz, 1H), 5.21 (d, *J* = 10.0 Hz, 1H), 4.73 – 4.71 (m, 1H), 4.10 (td, *J* = 6.6, 4.4 Hz, 2H), 3.98(dd, *J* = 8.2, 6.8 Hz, 1H), 3.92 (dd, *J* = 8.4, 6.8 Hz, 1H), 2.08 (d, *J* = 2.8 Hz, 1H), 1.43 (s, 3H), 1.34 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): 133.0, 131.5, 128.5, 120.3, 109.4, 78.1, 67.5, 64.7, 26.4, 25.1.

**HRMS** Calcd for $C_{10}H_{17}O_3$ (M+1): ): 185.1178, Found: 185.1176.

**FTIR** (neat): 3439, 2986, 2889, 1594, 1456, 1371, 1252, 1212, 1155, 1057, 1004, 911, 848, 794, 672 cm$^{-1}$.

**$[\alpha]_D^{25}$**-23$^{o}$, c = 0.86 in DCM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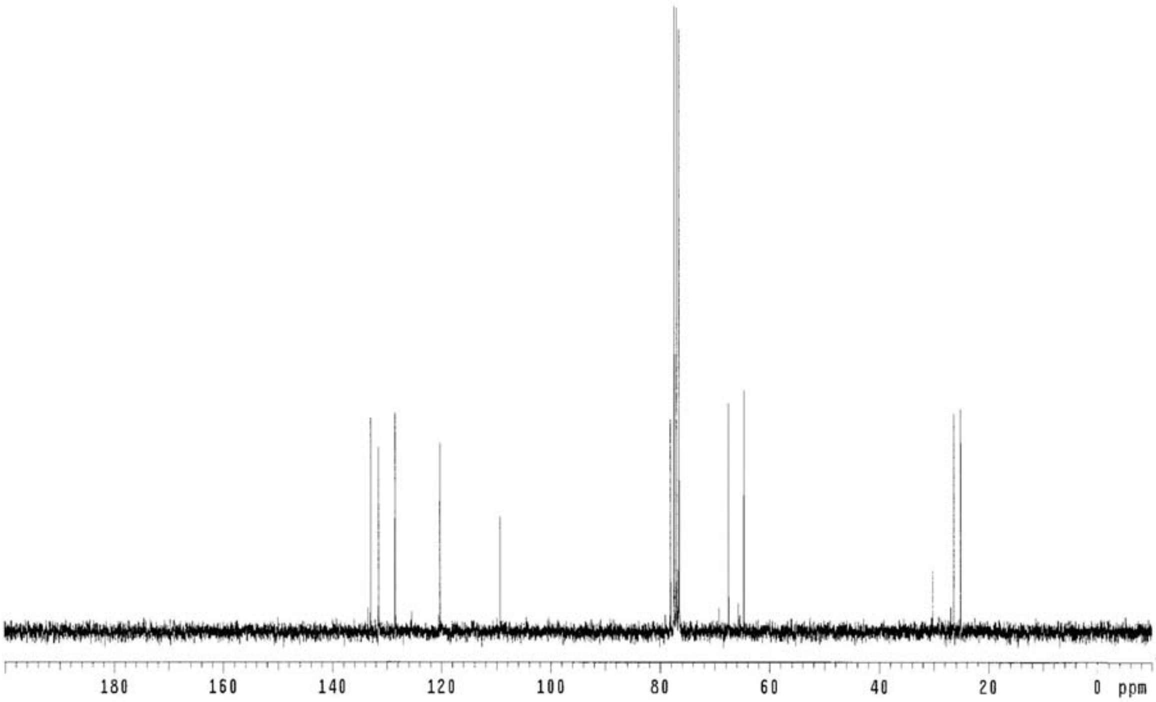
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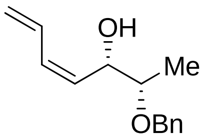
**(2*S*,3*S*,*Z*)-2-(benzyloxy)hepta-4,6-dien-3-ol**



**2b**

To a reaction vessel charged with [Rh(cod)$_2$]BARF (11.8 mg, 0.01 mmol, 5 mol%), (*S*)-MeO-BIPHEP (5.9 mg, 0.01 mmol, 5 mol%), petafluorobenzoic acid (2.1 mg, 0.01 mmol, 5 mol%), and $Na_2SO_4$ (58 mg, 0.4 mmol, 200 mol%) was added toluene (1.2 mL, 0.16 M). The reaction mixture was allowed to stir for 15 minutes at 25 °C, at which point a 1:1 mixture of hydrogen and acetylene gas was introduced *via* cannula. A toluene solution (0.8 mL, 0.25 M) of (*S*)-2-(benzyloxy)propanal[4] (33 mg, 0.2 mmol, 100 mol%) was added to the reaction mixture *via* syringe. The mixture was allowed to stir at 25 °C for 12 hours, at which point the reaction mixture was directly deposited onto a column of silica gel. Flash column chromatography ($SiO_2$: $R_f$ = 0.3, pentane:ether, 2:1) provides the title compound (41.9 mg, 0.19 mmol) as a colorless oil in 95 % yield (11:1 dr).

(Spectroscopic data for the major diastereomer)

**$^1$H NMR** (400 MHz, $CDCl_3$): 7.38 – 7.26 (m, 5H), 6.65 (dtd, *J* = 16.5,10.7, 1.2 Hz, 1H), 6.17 (t, *J* = 11.2 Hz, 1H), 5.38 (t, *J* = 10.0 Hz, 1H), 5.27 (dd, *J* = 16.5, 1.7 Hz, 1H), 5.19 (d, *J* = 11.4 Hz, 1H), 4.46 (d, *J* = 11.4 Hz, 1H), 4.40 (t, *J* = 8.2 Hz, 1H), 3.47 – 3.39 (m, 1H), 2.38 (d, *J* = 2.1 Hz, 1H), 1.14 (d, *J* = 6.3 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): 138.1, 133.2, 132.0, 129.6, 128.54, 127.8, 119.7, 78.6, 71.5, 71.2, 15.4.

**HRMS** Calcd for $C_{14}H_{19}O_2$ (M+1): 219.1385, Found: 219.1383.

**FTIR** (neat): 3434, 3029, 2973, 2871, 1595, 1496, 1454, 1373, 1279, 1228, 1124, 1064, 1027, 909, 848, 795,735, 697 cm$^{-1}$.

**$[\alpha]_D^{25}$** +37°, c = 0.35 in DCM

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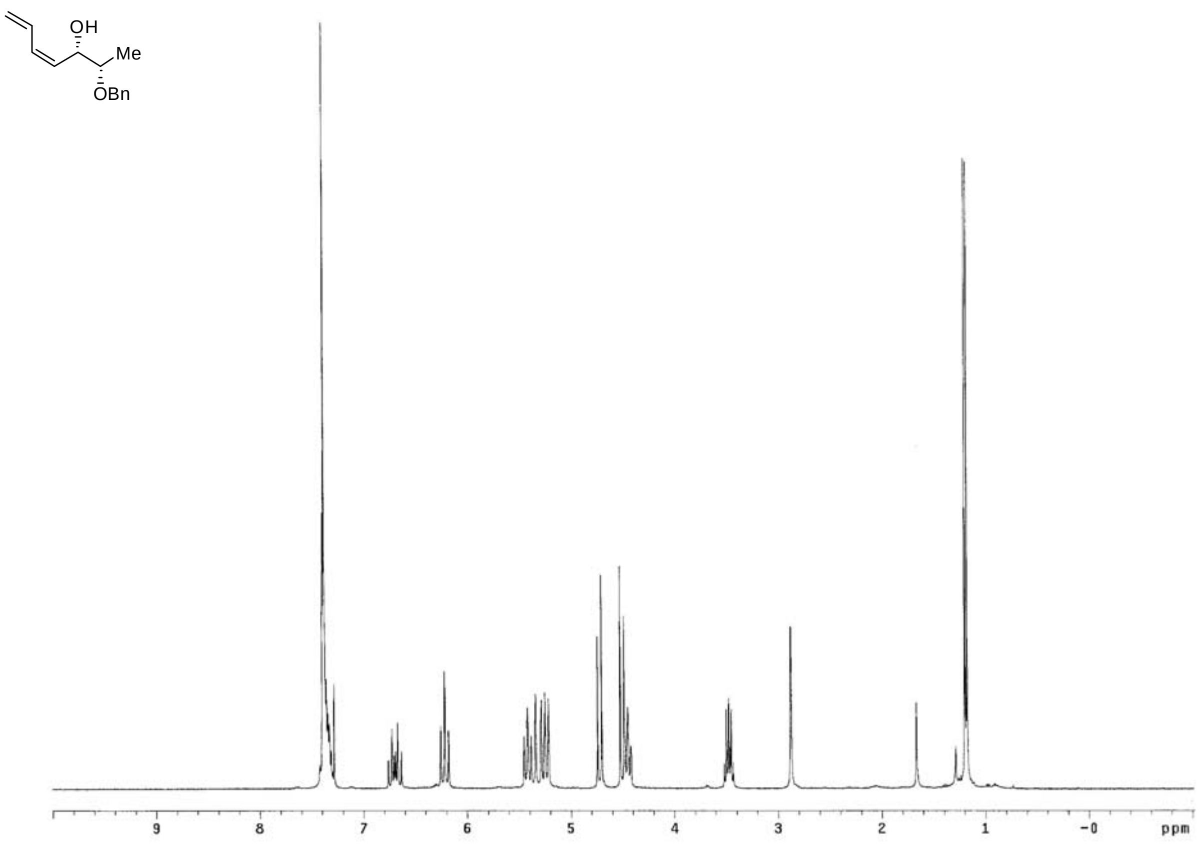
[4] Varelis, P.; Johnson, B. L. *Aust. J. Chem.* **1995**, *48*, 1775.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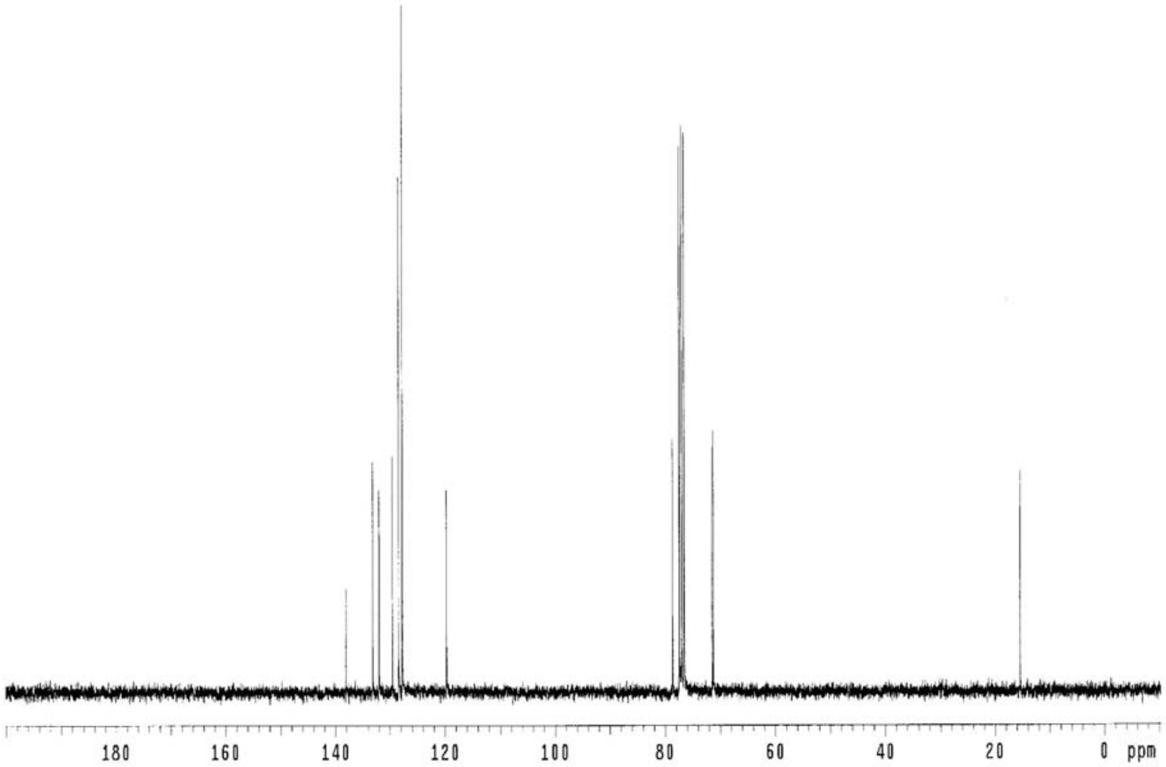
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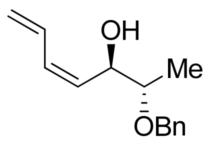
**(2*S*,3*R*,*Z*)-2-(benzyloxy)hepta-4,6-dien-3-ol**



**2c**

To a reaction vessel charged with [Rh(cod)$_2$]BARF (11.8 mg, 0.01 mmol, 5 mol%), (*R*)-MeO-BIPHEP (5.9 mg, 0.01 mmol, 5 mol%), petafluorobenzoic acid (2.1 mg, 0.01 mmol, 5 mol%), and Na$_2$SO$_4$ (58 mg, 0.4 mmol, 200 mol%) was added toluene (1.2 mL, 0.16 M). The reaction mixture was allowed to stir for 15 minutes at 25 $^o$C, at which point a 1:1 mixture of hydrogen and acetylene gas was introduced *via* cannula. A toluene solution (0.8 mL, 0.25 M) of (*S*)-2-(benzyloxy)propanal[4] (33 mg, 0.2 mmol, 100 mol%) was added to the reaction mixture *via* syringe. The mixture was allowed to stir at 25 $^o$C for 12 hours, at which point the reaction mixture was directly deposited onto a column of silica gel. Flash column chromatography (SiO$_2$: R$_f$ = 0.3, pentane:ether, 2:1) provides the title compound (40.5 mg, 0.184 mmol) as a colorless oil in 92 % yield (5:1 dr).

(Spectroscopic data for the major diastereomer)

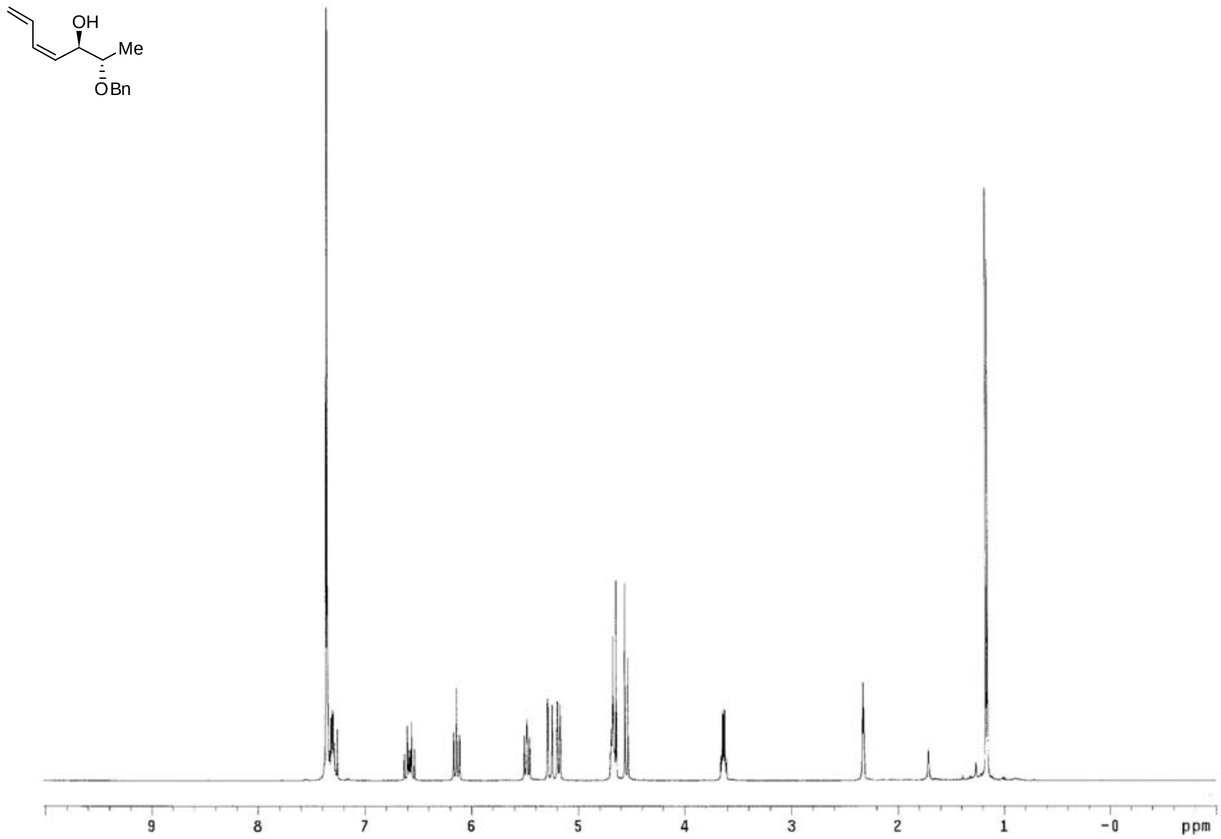
**$^1$H NMR** (400 MHz, CDCl$_3$): 7.36 – 7.24 (m, 5H), 6.61 – 6.51 (m, 1H), 6.12 (t, *J* = 11.0 Hz, 1H), 5.46 (t, *J* = 9.4 Hz, 1H), 5.25 (dt, *J* = 16.8, 0.8 Hz, 1H), 5.16 (d, *J* = 10.4 Hz, 1H), 4.68 – 4.64 (m, 1H), 4.64 (dt, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 3.64 – 3.59 (m, 1H), 2.31 (d, *J* = 4.4 Hz, 1H), 1.14 (d, *J* = 6.4 Hz, 3H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$): 138.4, 131.8, 131.7, 129.8, 128.4, 127.7, 127.6, 119.4, 77.6, 70.9, 69.9, 14.1.

**HRMS** Calcd for $C_{14}H_{19}O_2$ (M+1): 219.1385, Found: 219.1384.

**FTIR** (neat): 3440, 3027, 2971, 2870, 1592, 1490, 1452, 1371, 1284, 1230, 1121, 1060, 1028, 901, 840, 790,733, 698 cm$^{-1}$.

**$[\alpha]_D^{25}$** +31.7$^o$, c = 1.2 in DCM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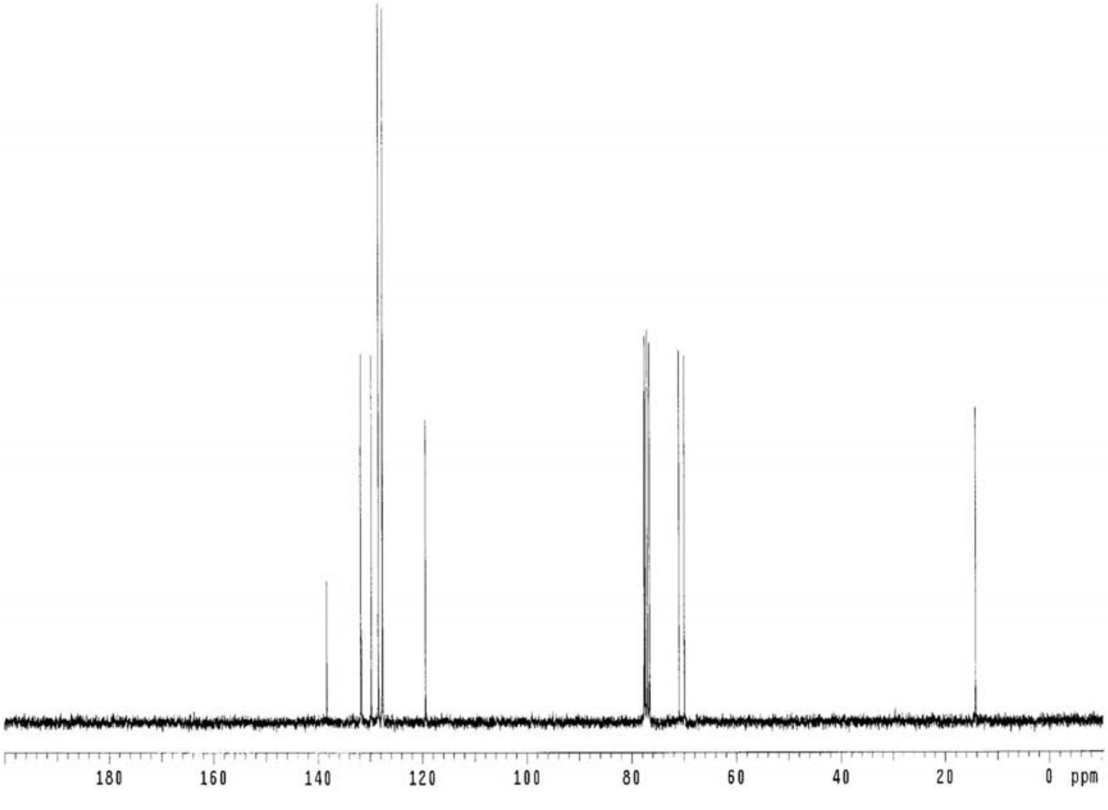
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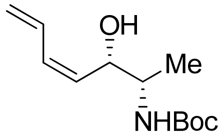
**_tert_-butyl (2_S_,3_S_,_Z_)-3-hydroxyhepta-4,6-dien-2-ylcarbamate**



**3b**

To a reaction vessel charged with [Rh(cod)$_2$]BARF (11.8 mg, 0.01 mmol, 5 mol%), (*S*)-MeO-BIPHEP (5.9 mg, 0.01 mmol, 5 mol%), petafluorobenzoic acid (2.1 mg, 0.01 mmol, 5 mol%), and Na$_2$SO$_4$ (58 mg, 0.4 mmol, 200 mol%) was added toluene (1.2 mL, 0.16 M). The reaction mixture was allowed to stir for 15 minutes at 25 $^{o}$C, at which point a 1:1 mixture of hydrogen and acetylene gas was introduced *via* cannula. A toluene solution (0.8 mL, 0.25 M) of *N*-Boc-L-alaninal[5] (35 mg, 0.2 mmol, 100 mol%) was added to the reaction mixture *via* syringe. The mixture was allowed to stir at 25 $^{o}$C for 12 hours, at which point the reaction mixture was directly deposited onto a column of silica gel. Flash column chromatography (SiO$_2$: R$_f$ = 0.3, pentane:ether, 2:1) provides the title compound (34.1 mg, 0.15 mmol) as a colorless oil in 75 % yield (16:1 dr).

(Spectroscopic data for the major diastereomer)

**$^{1}$H NMR** (400 MHz, CDCl$_3$): 6.67 – 6.58 (m, 1H), 6.16 (t, *J* = 11.2 Hz, 1H), 5.45 (t, *J* = 10.0 Hz, 1H), 5.29 (d, *J* = 16.8 Hz, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 4.65 (br, 1H), 4.52 – 4.47 (m, 1H), 3.69 (q, *J* = 6.8 Hz, 1H), 2.57 (br, 1H), 1.45 (s, 9H), 1.15 (d, *J* = 6.8 Hz, 3H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$): 156.3, 132.5, 131.7, 130.4, 120.0, 79.6, 70.8, 51.2, 28.3, 16.9.

**HRMS** Calcd for C$_{10}$H$_{17}$O$_3$ (M+1): 228.1600, Found: 228.1606.

**FTIR** (neat): 3350, 2976, 2931, 1684, 1502, 1453, 1392, 1366, 1247, 1163, 1094, 1041, 1023, 907, 847, 781, 668 cm$^{-1}$.

**$[\alpha]_D^{25}$**-40$^{o}$, c = 0.68 in DCM

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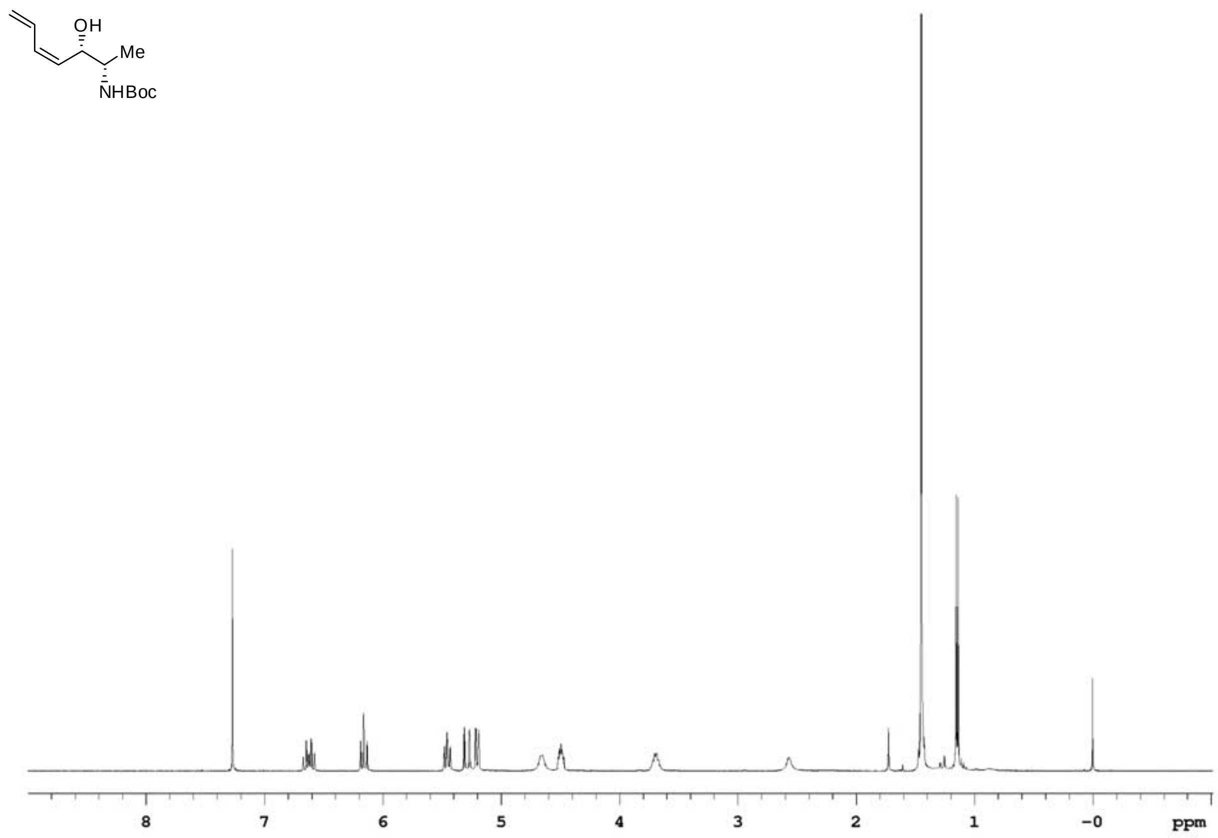
[5] Ocejo, M.; Vicario, J.; Badia, D.; Carrillo, L.; Reyes, E. *Synlett* **2005**, 2110.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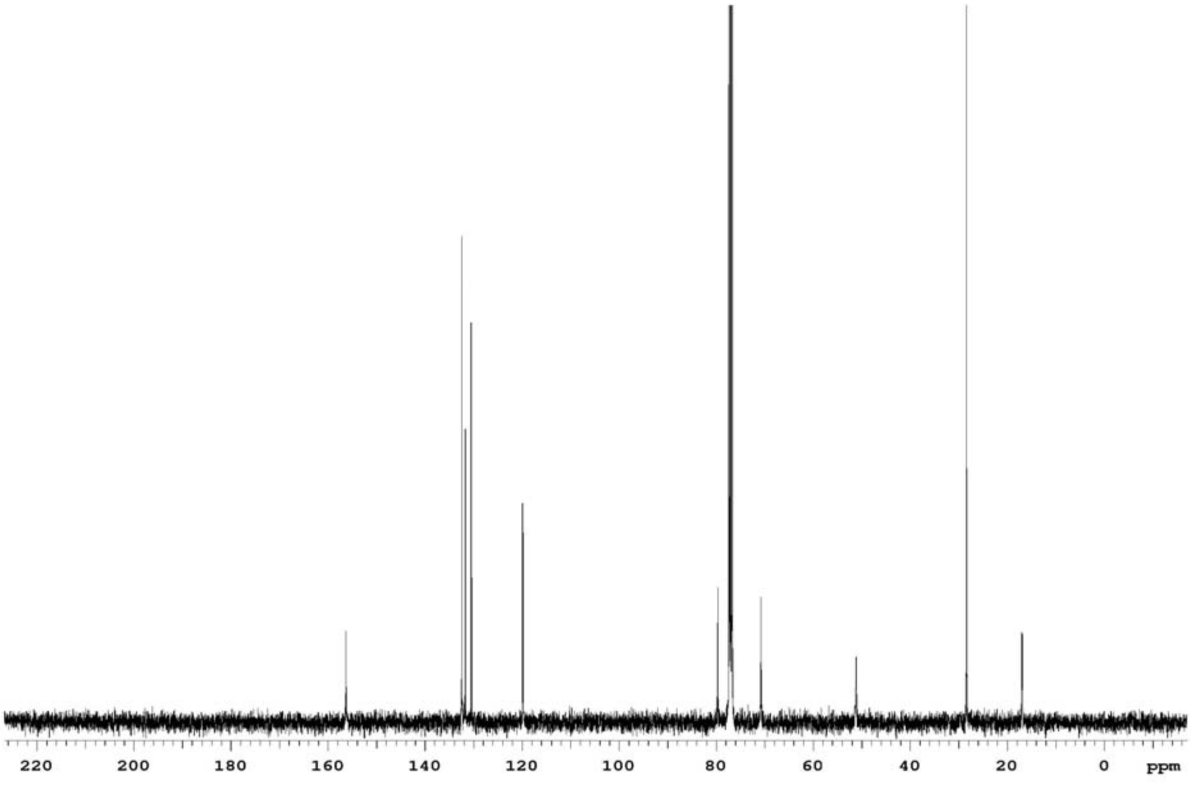
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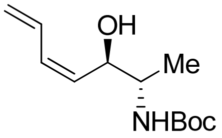
**tert-butyl (2*S*,3*R*,*Z*)-3-hydroxyhepta-4,6-dien-2-ylcarbamate**



**3c**

To a reaction vessel charged with [Rh(cod)$_2$]BARF (11.8 mg, 0.01 mmol, 5 mol%), (*R*)-MeO-BIPHEP (5.9 mg, 0.01 mmol, 5 mol%), petafluorobenzoic acid (2.1 mg, 0.01 mmol, 5 mol%), and $Na_2SO_4$ (58 mg, 0.4 mmol, 200 mol%) was added toluene (1.2 mL, 0.16 M). The reaction mixture was allowed to stir for 15 minutes at 25 $^{o}$C, at which point a 1:1 mixture of hydrogen and acetylene gas was introduced *via* cannula. A toluene solution (0.8 mL, 0.25 M) of *N*-Boc-L-alaninal (35 mg, 0.2 mmol, 100 mol%) was added to the reaction mixture *via* syringe. The mixture was allowed to stir at 25 $^{o}$C for 12 hours, at which point the reaction mixture was directly deposited onto a column of silica gel. Flash column chromatography ($SiO_2$: $R_f$ = 0.3, pentane:ether, 2:1) provides the title compound (30.5 mg, 0.134 mmol) as a colorless oil in 67 % yield (5:1 dr).

(Spectroscopic data for the major diastereomer)

**$^1$H NMR** (400 MHz, $CDCl_3$): 6.71 – 6.60 (m, 1H), 6.14 (t, *J* = 11.2 Hz, 1H), 5.42 (t, *J* = 9.8 Hz, 1H), 5.27 (d, *J* = 16.8 Hz, 1H), 5.21 (d, *J* = 10.0 Hz, 1H), 4.66 – 4.63 (m, 2H), 3.85 – 3.60 (m, 2H), 1.45 (s, 9H), 1.10 (d, *J* = 7.2 Hz, 3H).

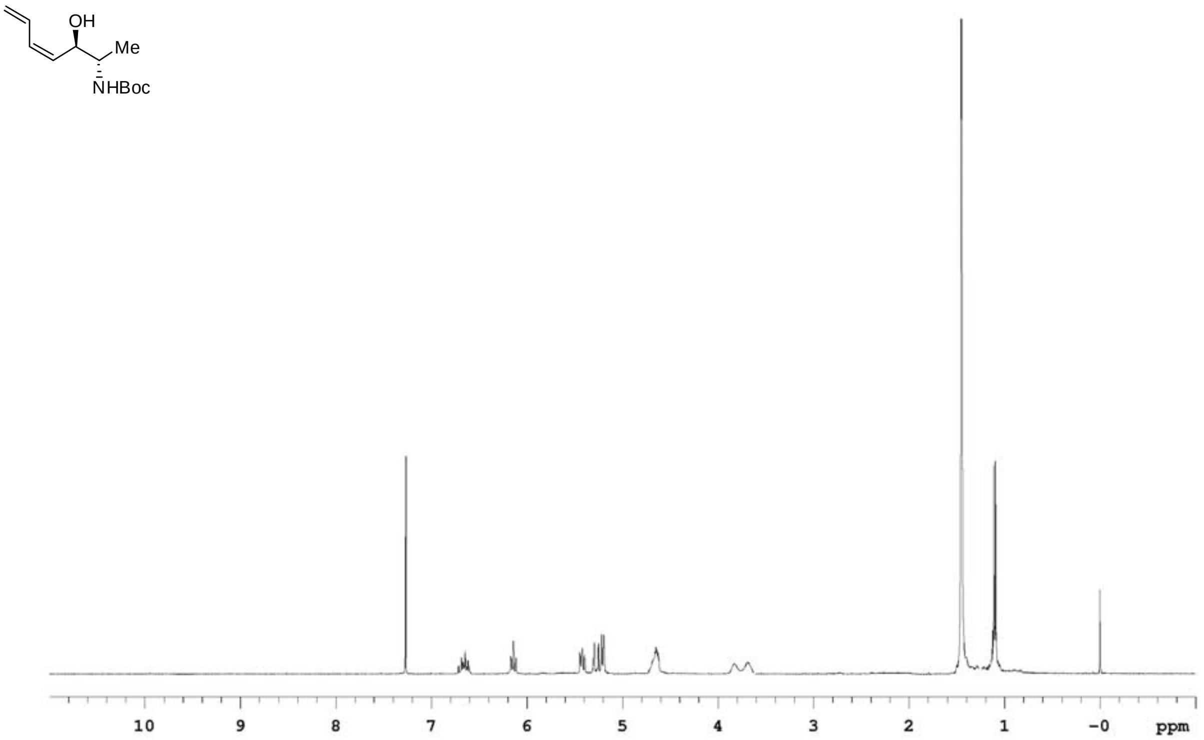
**$^{13}$C NMR** (100 MHz, $CDCl_3$): 156.5, 131.9, 132.1, 130.2, 120.0, 80.0, 71.3, 51.7, 28.6, 15.6.

**HRMS** Calcd for $C_{10}H_{17}O_3$ (M+1): 228.1600, Found: 228.1604.

**FTIR** (neat): 3353, 2970, 2934, 169, 1527, 1448, 1391, 1366, 1326, 1277, 1234, 1163, 1096, 1013, 914, 898, 858, 798, 762 cm$^{-1}$.

**MP**: 106-108 $^{o}$C (dec).

**$[\alpha]_D^{25}$**-9$^{o}$, c = 0.43 in DCM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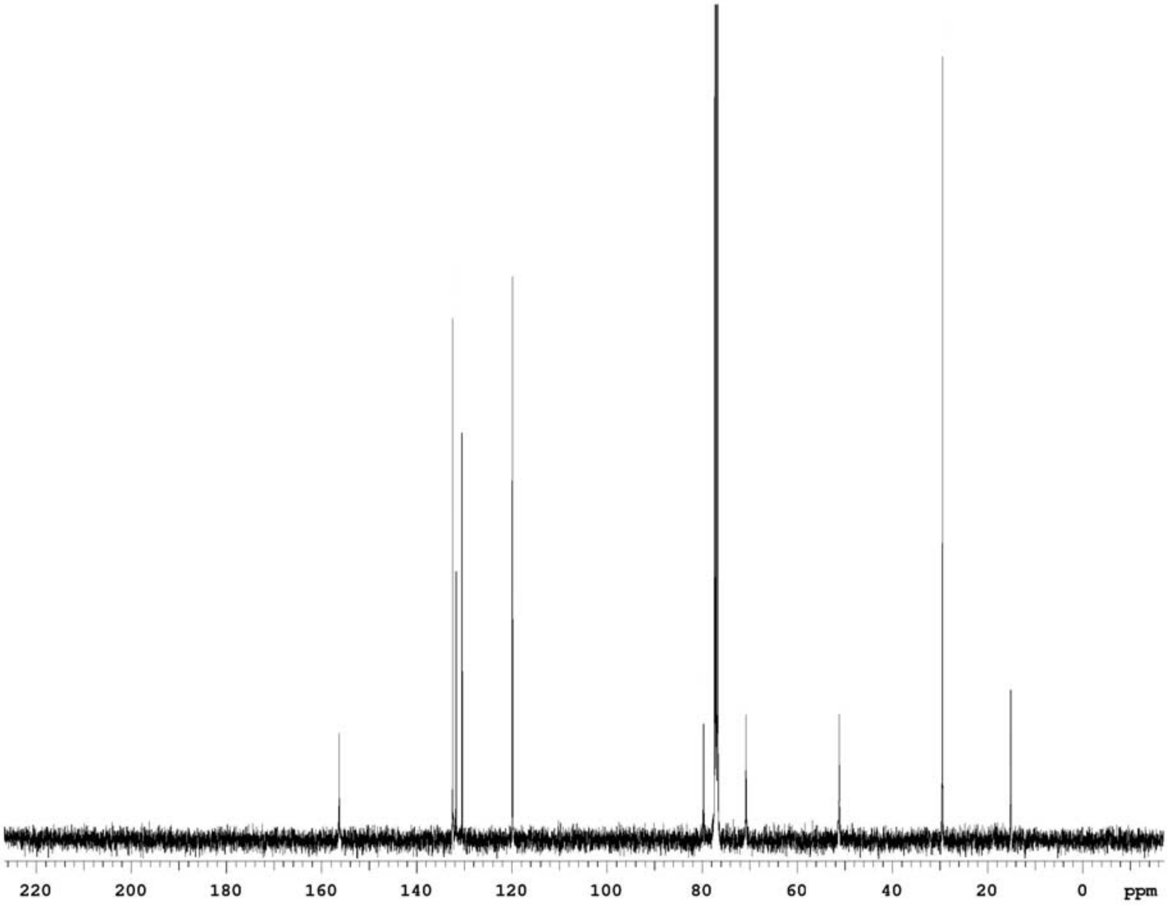
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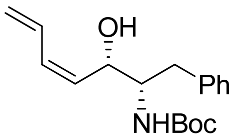
ppm

### ***tert*-butyl (2*S*,3*S*,*Z*)-3-hydroxy-1-phenylhepta-4,6-dien-2-ylcarbamate**



**4b**

To a reaction vessel charged with [Rh(cod)$_2$]BARF (11.8 mg, 0.01 mmol, 5 mol%), (*S*)-MeO-BIPHEP (5.9 mg, 0.01 mmol, 5 mol%), petafluorobenzoic acid (2.1 mg, 0.01 mmol, 5 mol%), and $Na_2SO_4$ (58 mg, 0.4 mmol, 200 mol%) was added toluene (1.2 mL, 0.16 M). The reaction mixture was allowed to stir for 15 minutes at 25 °C, at which point a 1:1 mixture of hydrogen and acetylene gas was introduced *via* cannula. A toluene solution (0.8 mL, 0.25 M) of *N*-Boc-L-phenylalaninal[5] (50 mg, 0.2 mmol, 100 mol%) was added to the reaction mixture *via* syringe. The mixture was allowed to stir at 25 °C for 15 hours, at which point the reaction mixture was directly deposited onto a column of silica gel. Flash column chromatography ($SiO_2$: $R_f = 0.3$, pentane:ether, 2:1) provides the title compound (48.5 mg, 0.16 mmol) as a colorless oil in 80 % yield (12:1 dr).

(Spectroscopic data for the major diastereomer)

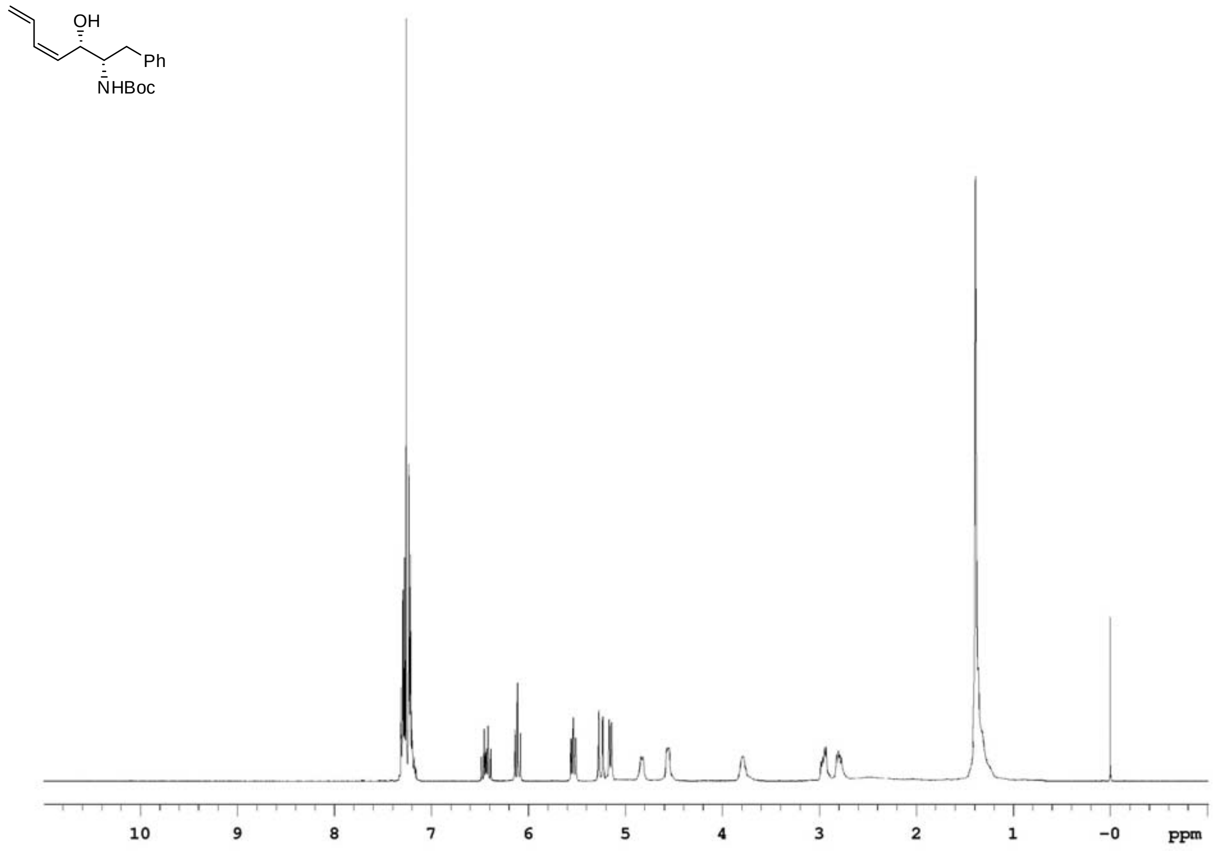
**$^1$H NMR** (400 MHz, $CDCl_3$): 7.31 – 7.21 (m, 5H), 6.48 – 6.39 (m, 1H), 6.11 (t, *J* = 11.2 Hz, 1H), 5.54 (t, *J* = 10.0 Hz, 1H), 5.25 (d, *J* = 16.4 Hz, 1H), 5.15 (d, *J* = 10.0 Hz, 1H), 4.84 – 4.82 (m, 1H), 4.57 – 4.56 (m, 1H), 3.79 (br, 1H), 2.98– 2.77 (m, 2H), 1.39 (s, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): 156.1, 138.1, 132.1, 131.5, 130.7, 129.3, 128.4, 126.4, 120.0, 79.5, 67.9, 56.7, 37.5, 28.3.

**HRMS** Calcd for $C_{18}H_{26}NO_3$ (M+1): 304.1913, Found: 304.1916.

**FTIR** (neat): 3419, 2977, 2929, 1687, 1497, 1455, 1392, 1366, 1250, 1168, 1044, 1023, 911, 849, 747, 701, 668 cm$^{-1}$.

**$[\alpha]_D^{25}$**-2 °, c = 1.41 in DCM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NHBoc
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9
8
7
6
5
4
3
2
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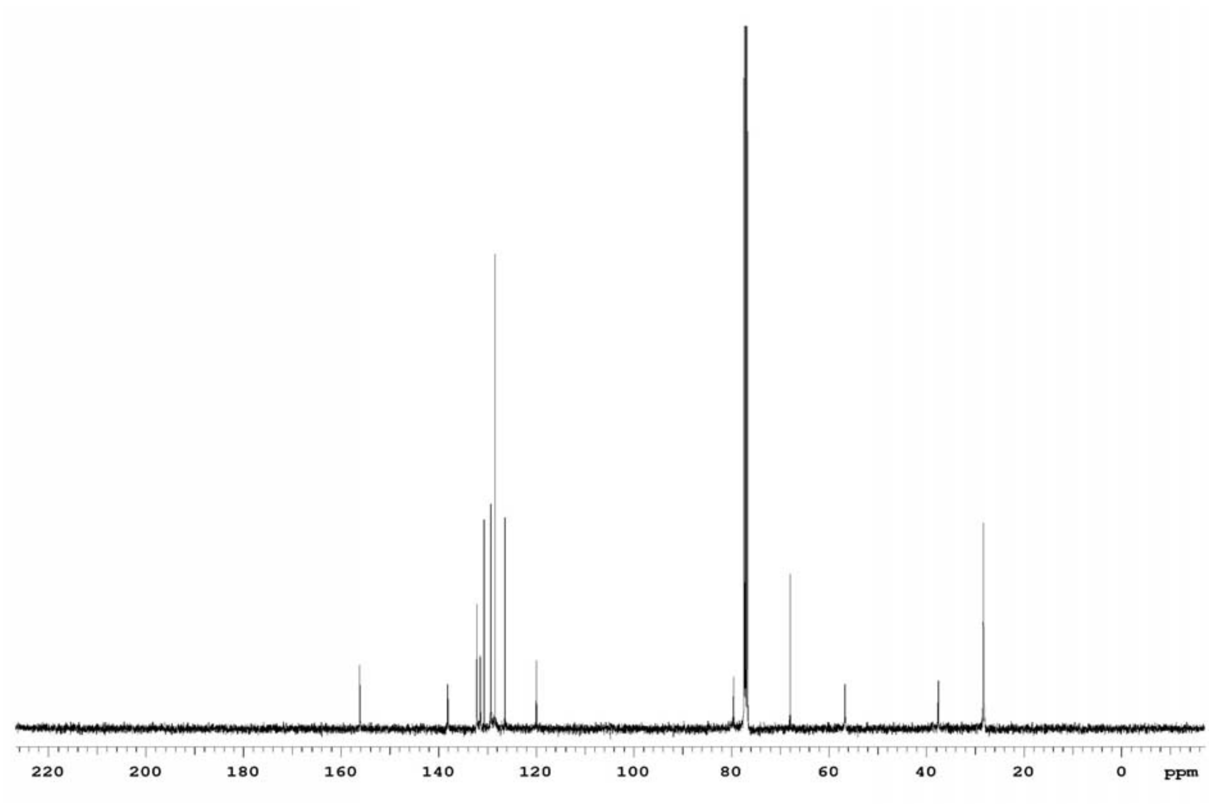
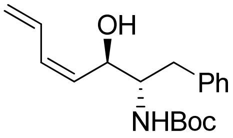
-0
ppm


220
200
180
160
140
120
100
80
60
40
20
0
ppm

**_tert_-butyl (2_S_,3_R_,_Z_)-3-hydroxy-1-phenylhepta-4,6-dien-2-ylcarbamate**



**4c**

To a reaction vessel charged with [Rh(cod)$_2$]BARF (11.8 mg, 0.01 mmol, 5 mol%), (_R_)-MeO-BIPHEP (5.9 mg, 0.01 mmol, 5 mol%), petafluorobenzoic acid (2.1 mg, 0.01 mmol, 5 mol%), and Na$_2$SO$_4$ (58 mg, 0.4 mmol, 200 mol%) was added toluene (1.2 mL, 0.16 M). The reaction mixture was allowed to stir for 15 minutes at 25 $^o$C, at which point a 1:1 mixture of hydrogen and acetylene gas was introduced _via_ cannula. A toluene solution (0.8 mL, 0.25 M) of _N_-Boc-L-phenylalaninal[5] (50 mg, 0.2 mmol, 100 mol%) was added to the reaction mixture _via_ syringe. The mixture was allowed to stir at 25 $^o$C for 15 hours, at which point the reaction mixture was directly deposited onto a column of silica gel. Flash column chromatography (SiO$_2$: R$_f$ = 0.3, pentane:ether, 2:1) provides the title compound (44.3 mg, 0.16 mmol) as a colorless oil in 73 % yield (12:1 dr).

(Spectroscopic data for the major diastereomer)

**$^1$H NMR** (400 MHz, CDCl$_3$): 7.30 – 7.18 (m, 5H), 6.66 – 6.57 (m, 1H), 6.17 (t, _J_ = 11.2 Hz, 1H), 5.51 (t, _J_ = 10.0 Hz, 1H), 5.29 (d, _J_ = 16.4 Hz, 1H), 5.21 (d, _J_ = 10.0 Hz, 1H), 4.68 – 4.56 (m, 2H), 3.97 (br, 1H), 3.17 (br, 1H), 2.90– 2.72 (m, 2H), 1.36 (s, 9H).

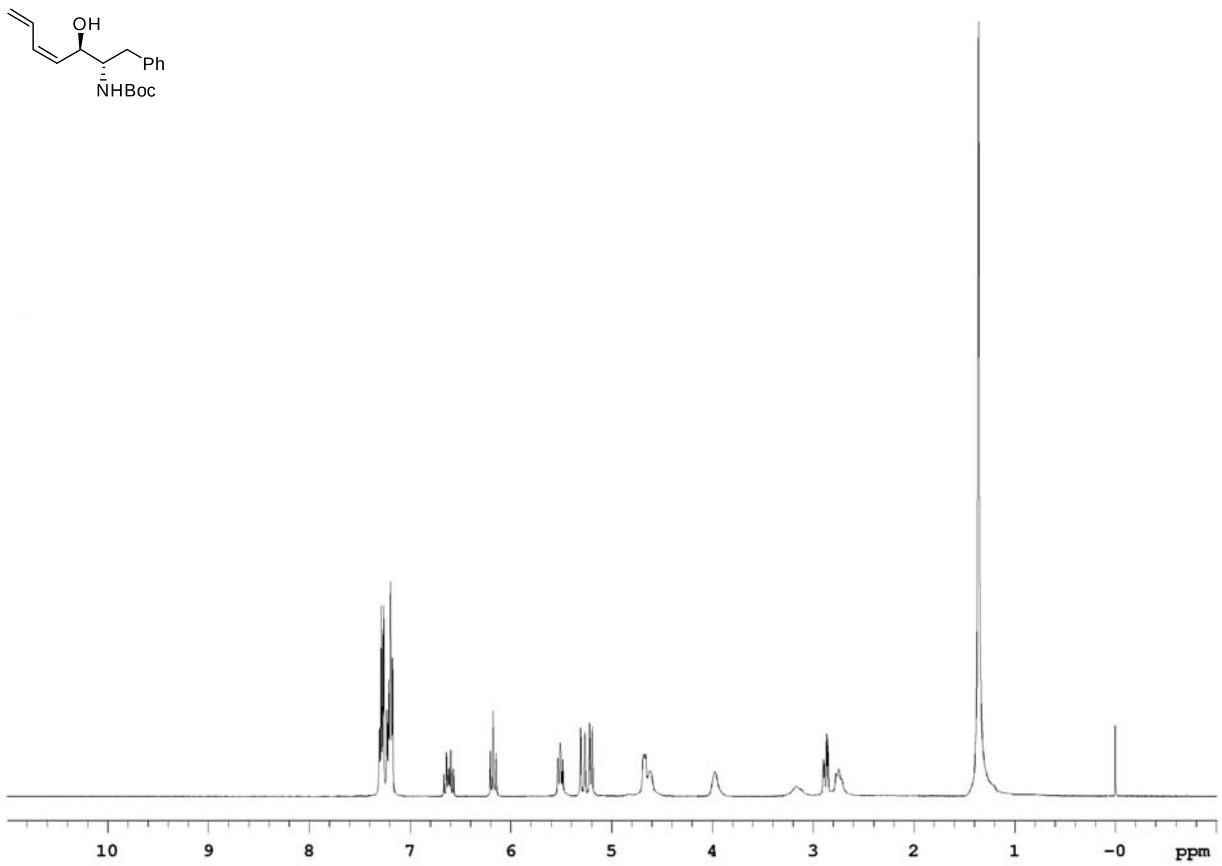
**$^{13}$C NMR** (100 MHz, CDCl$_3$): 156.4, 137.7, 132.3, 131.9, 129.9, 129.2, 128.4, 126.4, 119.9, 79.8, 70.1, 57.0, 35.9, 28.2.

**HRMS** Calcd for C$_{18}$H$_{26}$NO$_3$ (M+1): 304.1913, Found: 304.1919.

**FTIR** (neat): 3358, 2186, 2162, 2036, 1979, 1682, 1533, 1367, 1319, 1172, 1003,754, 700, 669 cm$^{-1}$.

**MP**: 122-125 $^o$C (dec).

**[α]$_D$$^{25}$**-31 $^o$, c = 1.34 in DCM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6
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4
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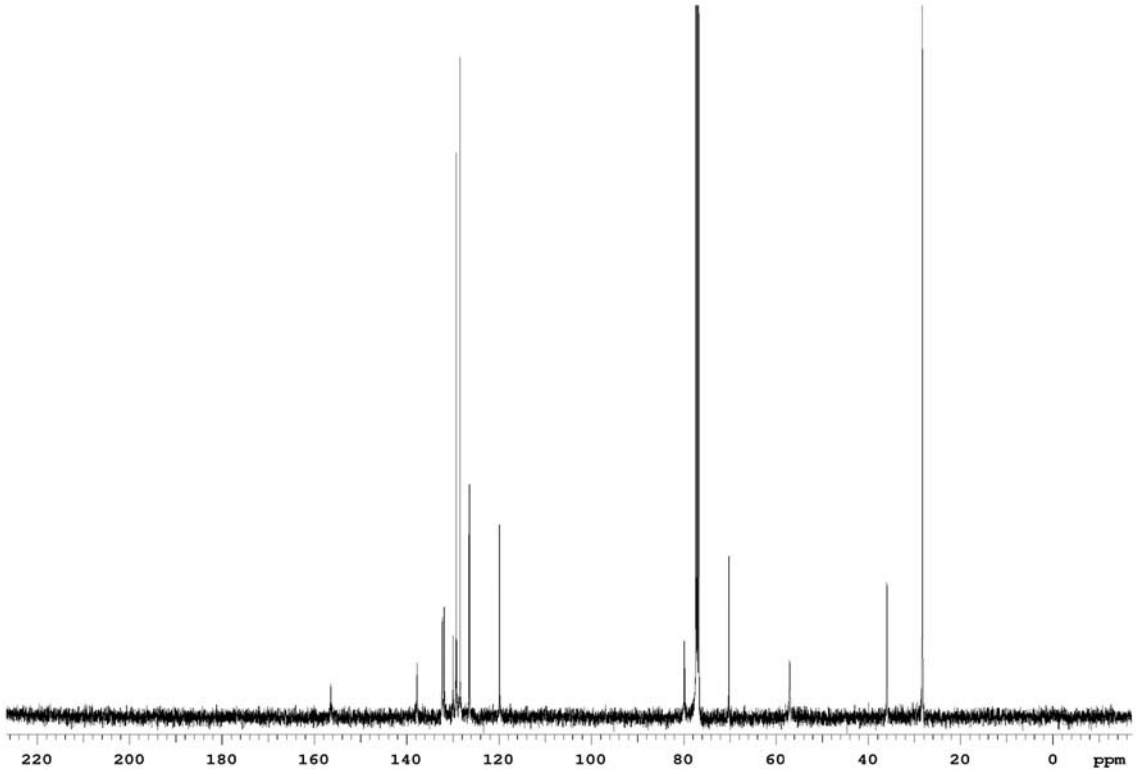
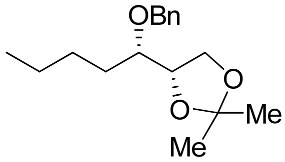
2
1
-0
ppm


220
200
180
160
140
120
100
80
60
40
20
0
ppm

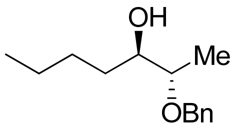
## V. Diene Hydrogenation and Assignment of Relative Stereochemistry

(*S*)-4-((*S*)-1-(benzyloxy)pentyl)-2,2-dimethyl-1,3-dioxolane



To the solution of **5b** (27.1 mg, 0.099 mmol, 100 mol%) in DCM (1.0 ml, 0.1M) at 25 °C was added Crabtree's catalyst (4 mg, 0.005 mmol, 5 mol%). The reaction was purged with argon follow by hydrogen. The reaction was allowed to stir at 25 °C under 1 atm of hydergen for 12 hours. The volatiles were removed under reduced pressure. Flash column chromatography ($SiO_2$: $R_f = 0.3$, pentane:ether, 2:1) provides the title compound (22.6 mg, 0.08 mmol) as a colorless oil in 82 % yield. This compound was identical in all respects to previously prepared material, thus corroborating the assignment of relative stereochemistry.[6]

(2*S*,3*R*)-2-(benzyloxy)heptan-3-ol



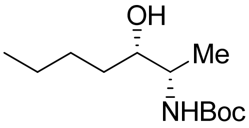
To the solution of **2c** (52.0 mg, 0.238 mmol, 100 mol%) in DCM (2.4 ml, 0.1 M) at at 25 °C was added Crabtree's catalyst (9.6 mg, 0.012 mmol, 5 mol%). The reaction was purged with argon follow by hydrogen. The reaction was allowed to stir at at 25 °C under 1 atm of hydergen for 12 hours. The volatiles were removed under reduced pressure. Flash column chromatography ($SiO_2$: $R_f = 0.3$, pentane:ether, 2:1) provides the title compound (48.2 mg, 0.22 mmol) as a colorless oil in 91 % yield. This compound was identical in all respects to previously prepared material, thus corroborating the assignment of relative stereochemistry.[7]

---

[6] Ito, M.; Kibayashi, C. *Tetrahedron* **1991**, *45*, 9329.

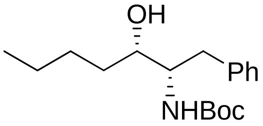
[7] Fujita, M.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 5415.

*tert*-butyl (2*S*,3*S*)-3-hydroxyheptan-2-ylcarbamate



To the solution of **3b** (28.0 mg, 0.123 mmol, 100 mol%) in DCM (1.2 ml, 0.1 M) at 25 °C was added Crabtree's catalyst (4.8 mg, 0.006 mmol, 5 mol%). The reaction was purged with argon follow by hydrogen. The reaction was allowed to stir at 25 °C under 1 atm of hydergen for 48 hours. The volatiles were removed under reduced pressure. Flash column chromatography ($SiO_2$: $R_f = 0.3$, pentane:ether, 2:1) provides the title compound (20.2 mg, 0.087 mmol) as a colorless oil in 71 % yield. This compound was identical in all respects to previously prepared material, thus corroborating the assignment of relative stereochemistry.[8]

*tert*-butyl (2*S*,3*S*)-3-hydroxy-1-phenylheptan-2-ylcarbamate



To the solution of **4b** (30.0 mg, 0.099 mmol, 100 mol%) in DCM (1.0 ml, 0.1M) at 25 °C was added Crabtree's catalyst (4.0 mg, 0.005 mmol, 5 mol%). The reaction was purged with argon follow by hydrogen. The reaction was allowed to stir at 25 °C under 1 atm of hydergen for 48 hours. The volatiles were removed under reduced pressure. Flash column chromatography ($SiO_2$: $R_f = 0.3$, pentane:ether, 2:1) provides the title compound (21.3 mg, 0.07 mmol) as a white solid in 70 % yield. This compound was identical in all respects to previously prepared material, thus corroborating the assignment of relative stereochemistry.[9]

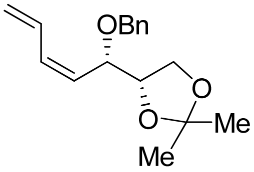
---

[8] Reetz, M. T.; Rolfing, K.; Greibenow, N. *Tetrahedron Lett.* **1994**, 35, 1969.

[9] Barrow, J. C.; Coburn, C. A.; Nantermet, P. G.; Selnick, H. G.; Stachel, S. J.; Stanton, M. G.; Stauffer, S. R.; Zhuang, L.; Davis, J. R. *PCT Int. Appl.* **2005**, 121.

## VI. Formal Synthesis of All Eight L-Hexoses

### (*S*)-4-((*S*,*Z*)-1-(benzyloxy)penta-2,4-dienyl)-2,2-dimethyl-1,3-dioxolane



NaH (17.2 mg, 0.43 mmol, 130 mol%) was added to a solution of **1b** (61 mg, 0.33 mmol, 100 mol%) in anhydrous DMF (2.0 mL, 0.12 M) at 0 °C under argon atmosphere. After 10 min benzyl bromide (78.9 mg, 0.46 mmol, 137 mol% in DMF (0.75 mL) was added in one portion. The reaction mixture was stirred for 2 h, then carefully quenched with saturated $NH_4Cl$ aqueous solution. The mixture was extracted with ether. The combined organic phase was washed with water and brine, dried ($MgSO_4$), filtered and evaporated under reduced pressure. Flash column chromatography ($SiO_2$: $R_f$ = 0.3, hexane:ethyl acetate, 10:1) provides the title compound (80.7 mg, 0.29 mmol) as a colorless oil in 89 % yield.

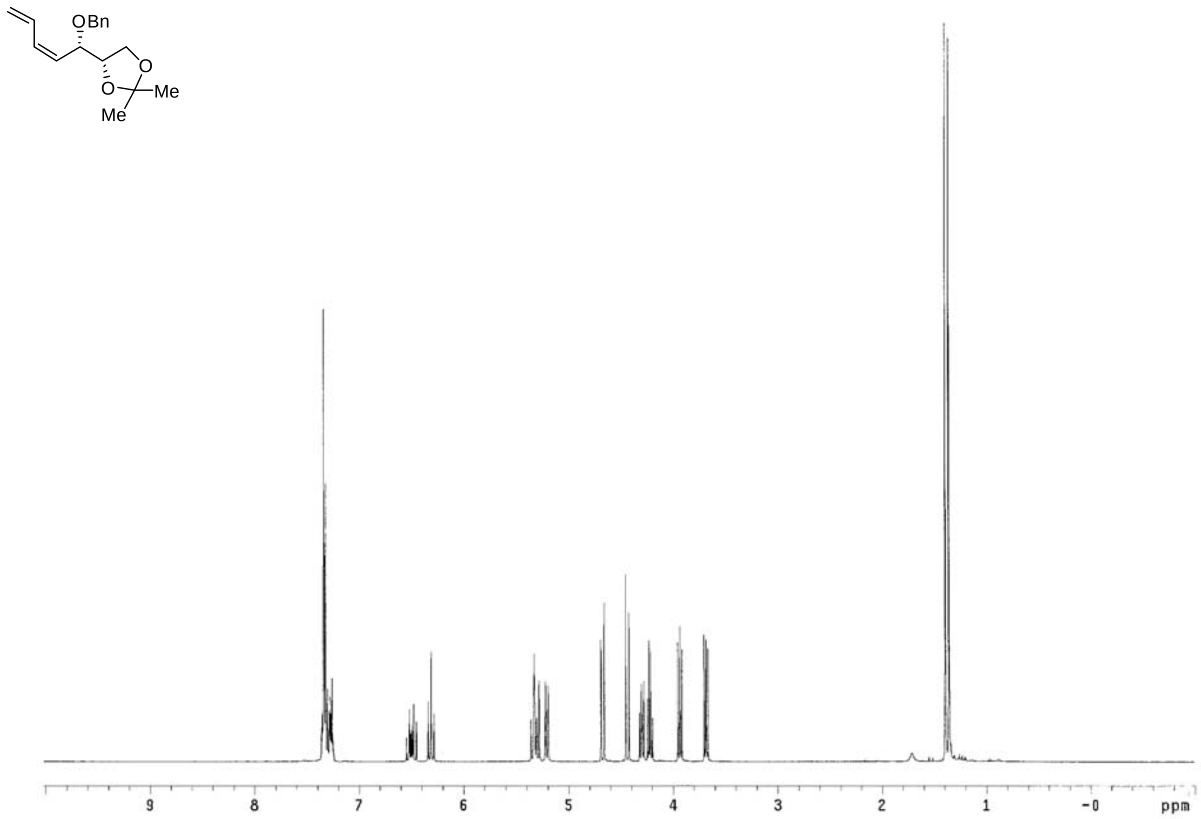
**$^1$H NMR** (400 MHz, $CDCl_3$): 7.36 – 7.24 (m, 5H), 6.50 (dtd, *J* = 16.8, 10.0, 0.8 Hz, 1H), 6.31 (td, *J* = 11.2, 0.4 Hz, 1H), 5.36 – 5.28 (m, 2H), 5.21 (d, *J* = 10.4 Hz, 1H), 4.67 (d, *J* = 12.4, 1H), 4.44 (d, *J* = 12.4 Hz, 1H), 4.32 (ddd, *J* = 9.6, 6.8, 0.8 Hz, 1H), 4.22 (q, *J* = 6.4 Hz, 1H), 3.94 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.69 (dd, *J* = 10.0, 6.0 Hz, 1H), 1.39 (s, 3H), 1.36 (s, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): 138.1, 135.0, 131.7, 128.2, 127.9, 127.5, 127.2, 120.4, 109.8, 77.9, 74.9, 70.0, 65.7, 26.5, 25.3.

**HRMS** Calcd for $C_{17}H_{23}O_3$ (M+1): 275.1647, Found: 275.1646.

**FTIR** (neat): 2985, 2883, 1592, 1496, 1454, 1380, 1369, 1256, 1211, 1155, 1067, 1028, 999, 911, 849, 801, 735, 697 cm$^{-1}$.

**$[\alpha]_D^{25}$**-17°, c = 1.10 in DCM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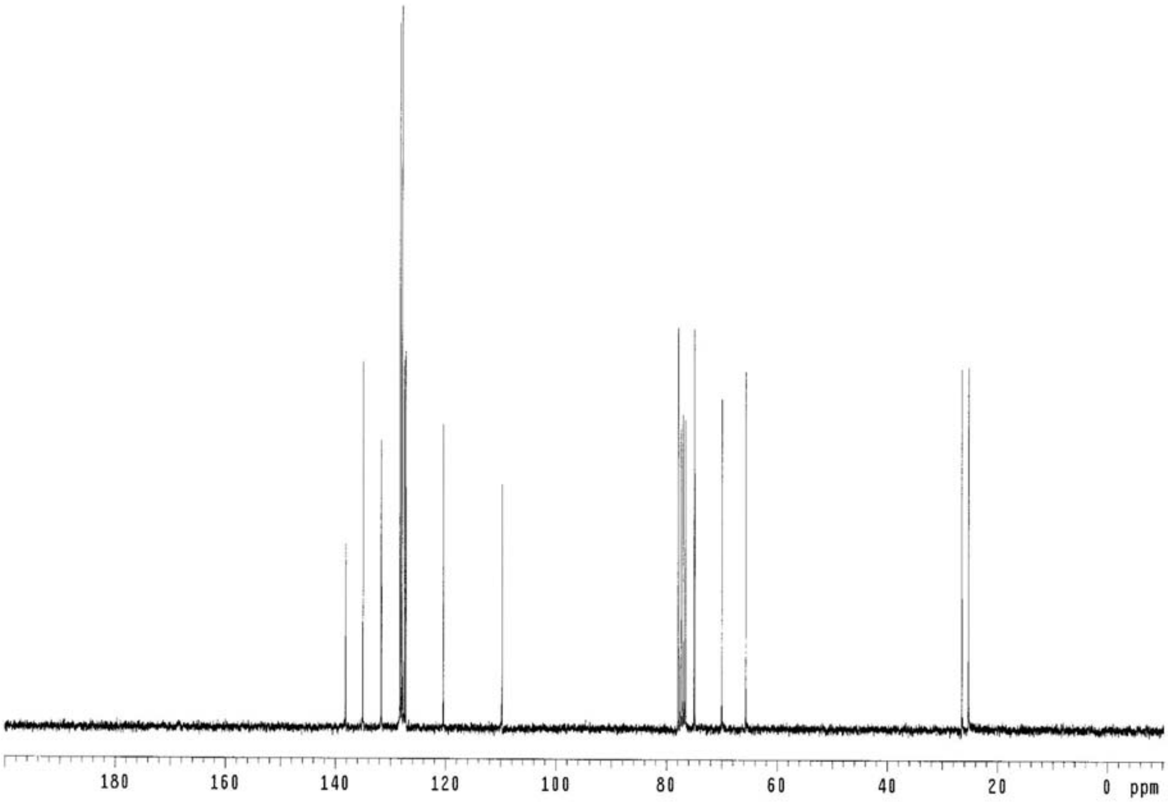
180
160
140
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100
80
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20
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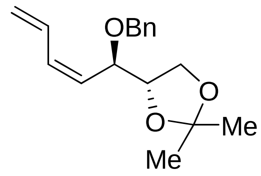
ppm

**(*S*)-4-((*R*,*Z*)-1-(benzyloxy)penta-2,4-dienyl)-2,2-dimethyl-1,3-dioxolane**



NaH (17.2 mg, 0.43 mmol, 130 mol%) was added to a solution of **1c** (61 mg, 0.33 mmol, 100 mol%) in anhydrous DMF (2.0 mL, 0.12 M) at 0 °C under argon atmosphere. After 10 min benzyl bromide (78.9 mg, 0.46 mmol, 137 mol% in DMF (0.75mL)) was added in one portion. The reaction mixture was stirred for 2h, then carefully quenched with saturated $NH_4Cl$ aqueous sloution. The mixture was extracted with ether, the combined organic phase washed with water and brine, dried ($MgSO_4$), filtered and evaporated under reduced pressure. Flash column chromatography ($SiO_2$: $R_f$ = 0.3, hexane:ethyl acetate, 10:1) provides the title compound (83.6 mg, 0.30 mmol) as a colorless oil in 92 % yield.

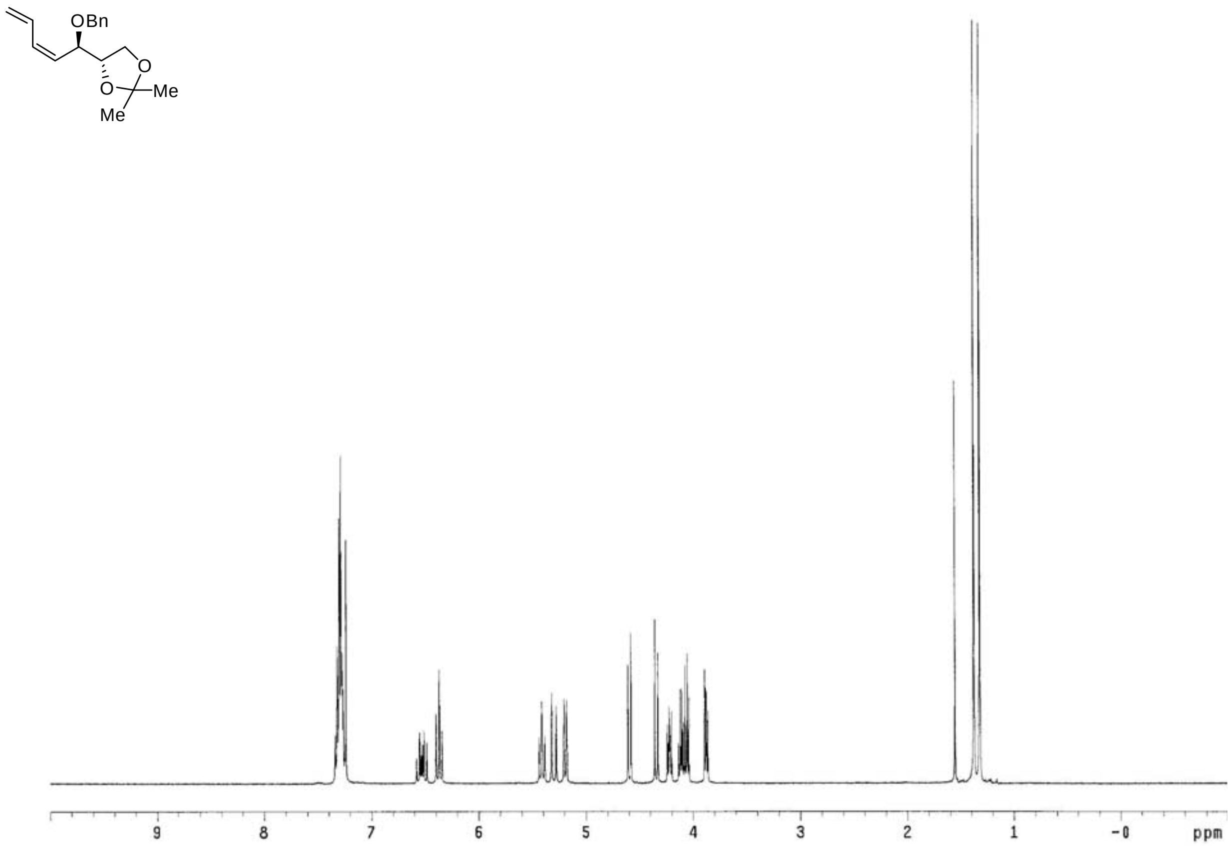
**$^1$H NMR** (400 MHz, $CDCl_3$): 7.35 – 7.24 (m, 5H), 6.54 (dt, *J* = 16.8, 11.0 Hz, 1H), 6.38 (t, *J* = 11.0 Hz, 1H), 5.43 (t, *J* = 10.2, 1H), 5.31 (d, *J* = 16.4 Hz, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 4.61 (d, *J* = 12.0, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.23 (dd, *J* = 9.2, 6.4 Hz, 1H), 4.12 (dd, *J* = 11.6, 6.4 Hz, 1H), 4.06 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.89 (dd, *J* = 8.4, 5.6 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): 138.0, 134.8, 131.5, 128.4, 128.3, 127.9, 127.6, 120.1, 109.4, 77.5, 74.7, 70.1, 66.7, 26.4, 25.1.

**HRMS** Calcd for $C_{17}H_{23}O_3$ (M+1): 275.1647, Found: 275.1646.

**FTIR** (neat): 2986, 2879, 1593, 1497, 1454, 1380, 1370, 1254, 1209, 1156, 1068, 1028, 998, 911, 847, 796, 736, 698 $cm^{-1}$.

**$[\alpha]_D^{25}$**-22°, c = 0.86 in DCM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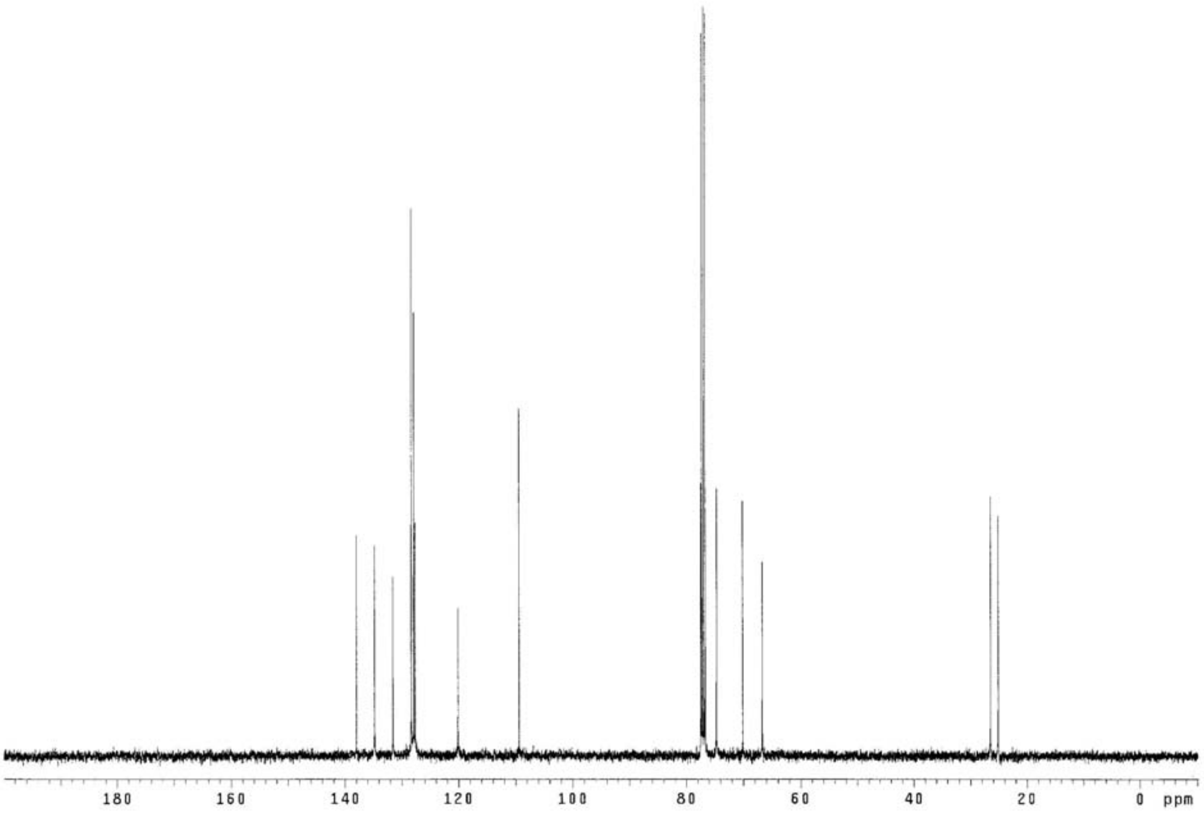
180
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100
80
60
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20
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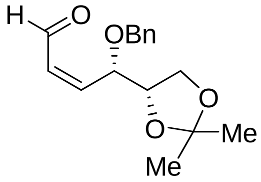
ppm

**(*S*,*Z*)-4-(benzyloxy)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)but-2-enal**



**5b**

To a mixture of THF and water (11.7 mL, 0.05 M, THF:water = 2.5:1), $OsO_4$ (3.0 mg, 0.01 mmol, 5 mol%) and the benzyl protected diene (64.0 mg, 0.23 mmol, 100 mol%) was added and then stirred for 5 minutes. While the temperature of the stirred mixture was maintained at 24 – 26 °C, $NaIO_4$ (110.0 mg, 0.51 mmol, 220 mol%) was added in portions over a period of 40 minutes. The solution was stirred for an additional 2 hours. The mixture was extracted thoroughly with ether and the combined organic layers were dried ($Na_2SO_4$), filtered and evaporated. Flash column chromatography ($SiO_2$: $R_f$ = 0.3, hexane:ethyl acetate, 2:1) provides the title compound (50.4 mg, 0.20 mmol) as a colorless oil in 85 % yield.

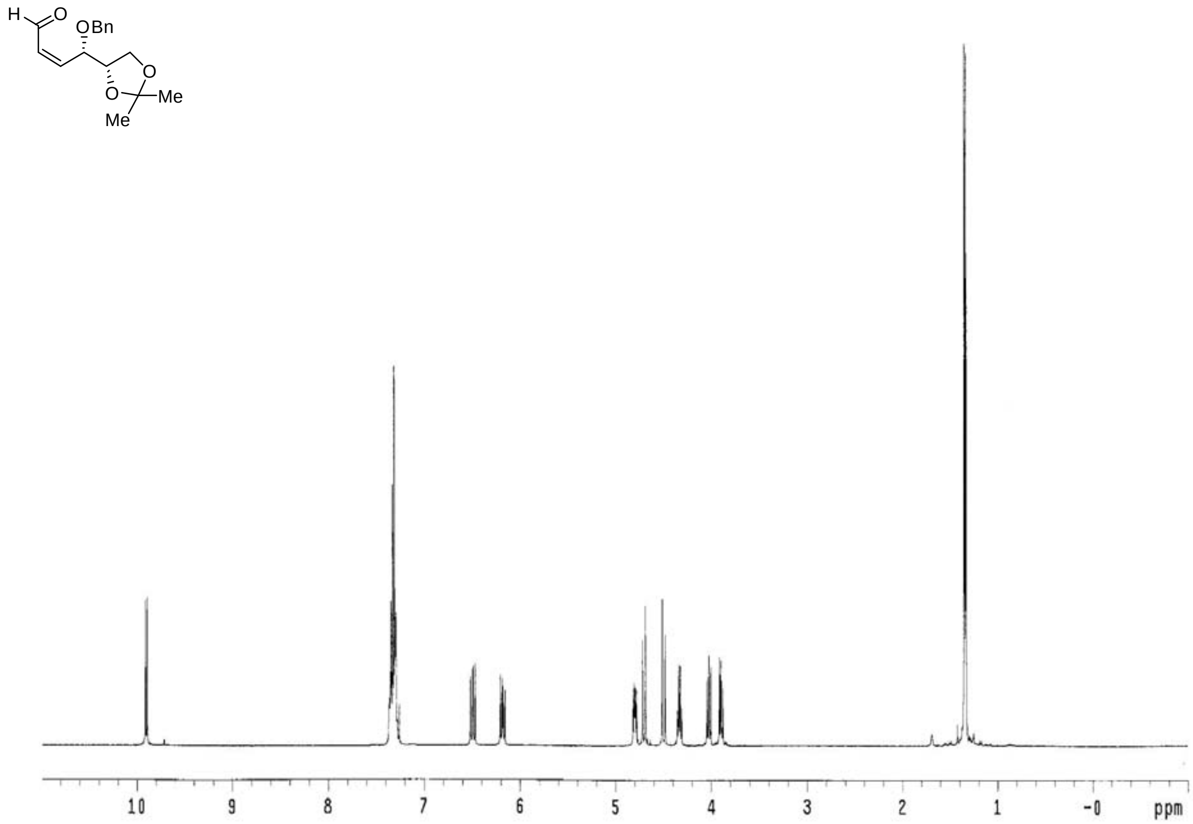
**$^1$H NMR** (400 MHz, $CDCl_3$): 9.89 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.24 (m, 5H), 6.47 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.17 (dd, *J* = 11.6, 7.6 Hz, 1H), 4.78 (dd, *J* = 9.2, 5.2 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.31 (q, *J* = 6.0 Hz, 1H), 3.99 (dd, *J* = 8.6, 7.0 Hz, 1H), 3.87 (dd, *J* = 9.0, 5.8 Hz, 1H), 1.33 (s, 3H), 1.31 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): 191.0, 146.6, 137.1, 133.6, 128.5, 128.1, 127.8, 110.0, 73.9, 71.5, 65.0, 26.1, 25.0.

**HRMS** Calcd for $C_{16}H_{20}O_4$ (M): 276.1365, Found: 276.1362.

**FTIR** (neat): 2986, 2924, 1682, 1497, 1455, 1381, 1371, 1259, 1213, 1156, 1068, 1028, 945, 847, 738, 698 cm$^{-1}$.

**$[\alpha]_D^{25}$** +25°, c = 0.36 in DCM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Me
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7
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5
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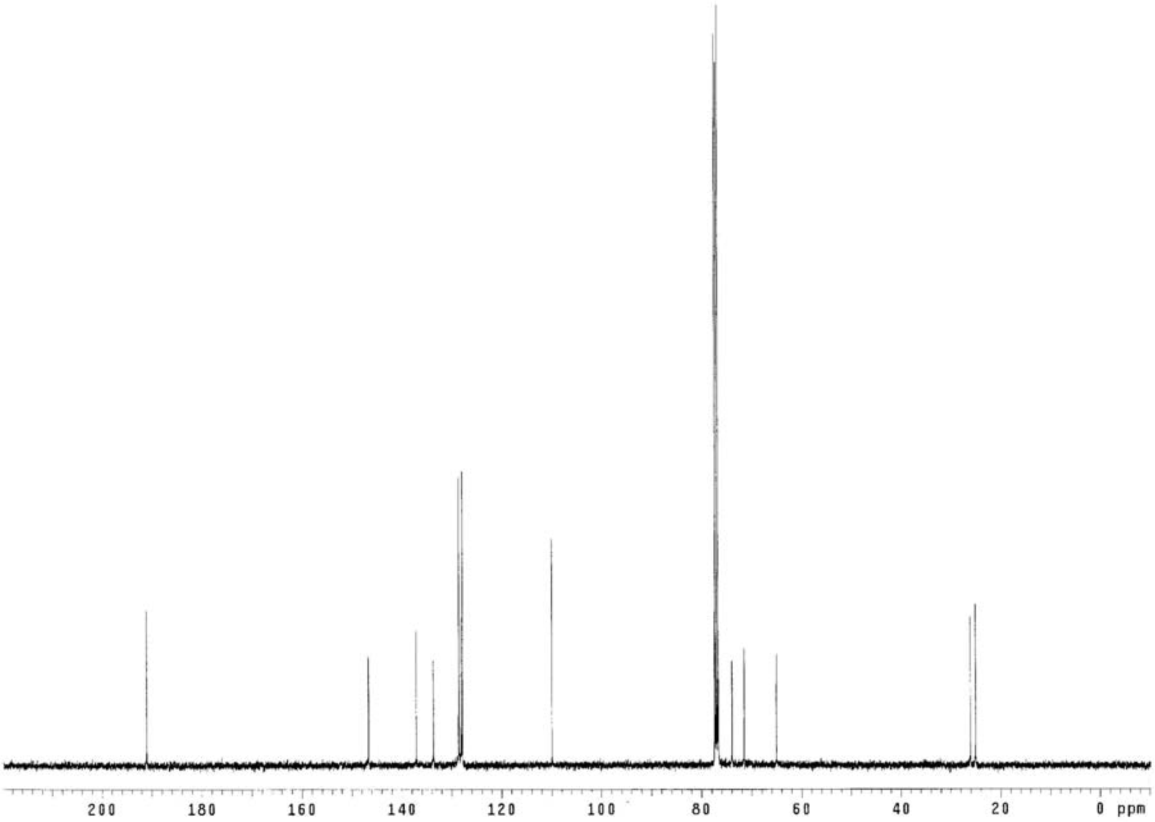
-0
ppm


200
180
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80
60
40
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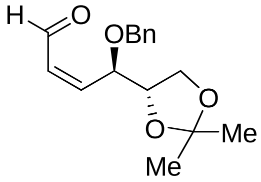
0 ppm

### (*R*,*Z*)-4-(benzyloxy)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)but-2-enal



**5c**

To a mixture of THF and water (11.7 mL, 0.05 M, THF:water = 2.5:1), $OsO_4$ (3.0 mg, 0.01 mmol, 5 mol%) and the benzyl protected diene (64.0 mg, 0.23 mmol, 100 mol%) was added and then stirred for 5 minutes. While the temperature of the stirred mixture was maintained at 24 – 26 °C, $NaIO_4$ (110.0 mg, 0.51 mmol, 220 mol%) was added in portions over a period of 40 minutes. The solution was stirred for an additional 2 hours. The mixture was extracted thoroughly with ether and the combined organic layers were dried ($Na_2SO_4$), filtered and evaporated. Flash column chromatography ($SiO_2$: $R_f = 0.3$, hexane:ethyl acetate, 4:1) provides the title compound (48.9 mg, 0.17 mmol) as a colorless oil in 77 % yield.

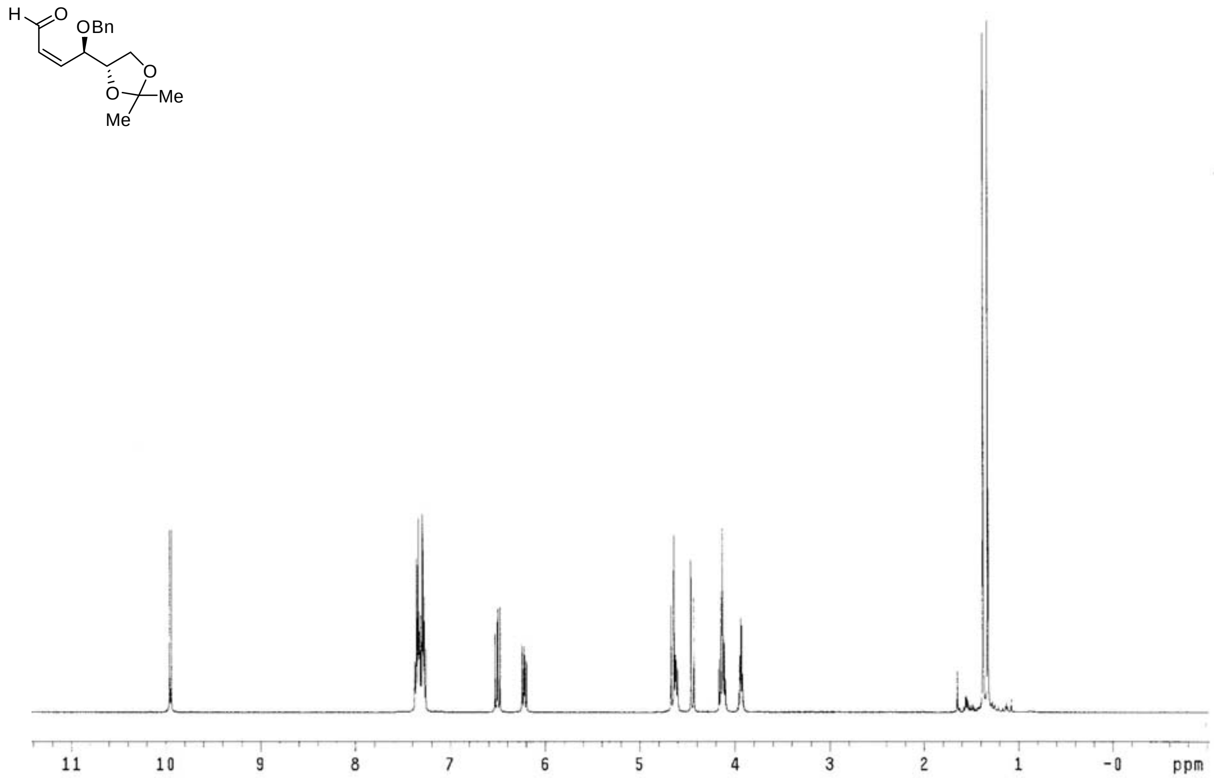
**$^1$H NMR** (400 MHz, $CDCl_3$): 9.93 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.26 (m, 5H), 6.48 (dd, *J* = 11.6, 8.8 Hz, 1H), 6.19 (ddd, *J* = 11.5, 7.5, 0.9 Hz, 1H), 4.64 (d, *J* = 11.6, 1H), 4.61 (d, *J* = 8.8 Hz, 1H), 4.61 (q, *J* = 8.8, 1H), 4.43 (d, *J* = 11.6, 7.0 Hz, 1H), 4.15 – 4.07 (m, 1H), 3.94 – 3.89 (m, 1H), 1.36 (s, 3H), 1.31 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): 190.7, 148.0, 136.9, 133.6, 128.6, 128.2, 128.0, 109.9, 76.5, 75.0, 71.4, 67.1, 26.4, 24.9.

**HRMS** Calcd for $C_{16}H_{20}O_4$ (M+1): 277.1440, Found: 277.1437.

**FTIR** (neat): 2986, 2928, 1683, 1497, 1455, 1371, 1258, 1211, 1154, 1070, 1028, 966,845, 738, 699 cm$^{-1}$.

**$[\alpha]_D^{25}$** -43°, c = 0.28 in DCM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7
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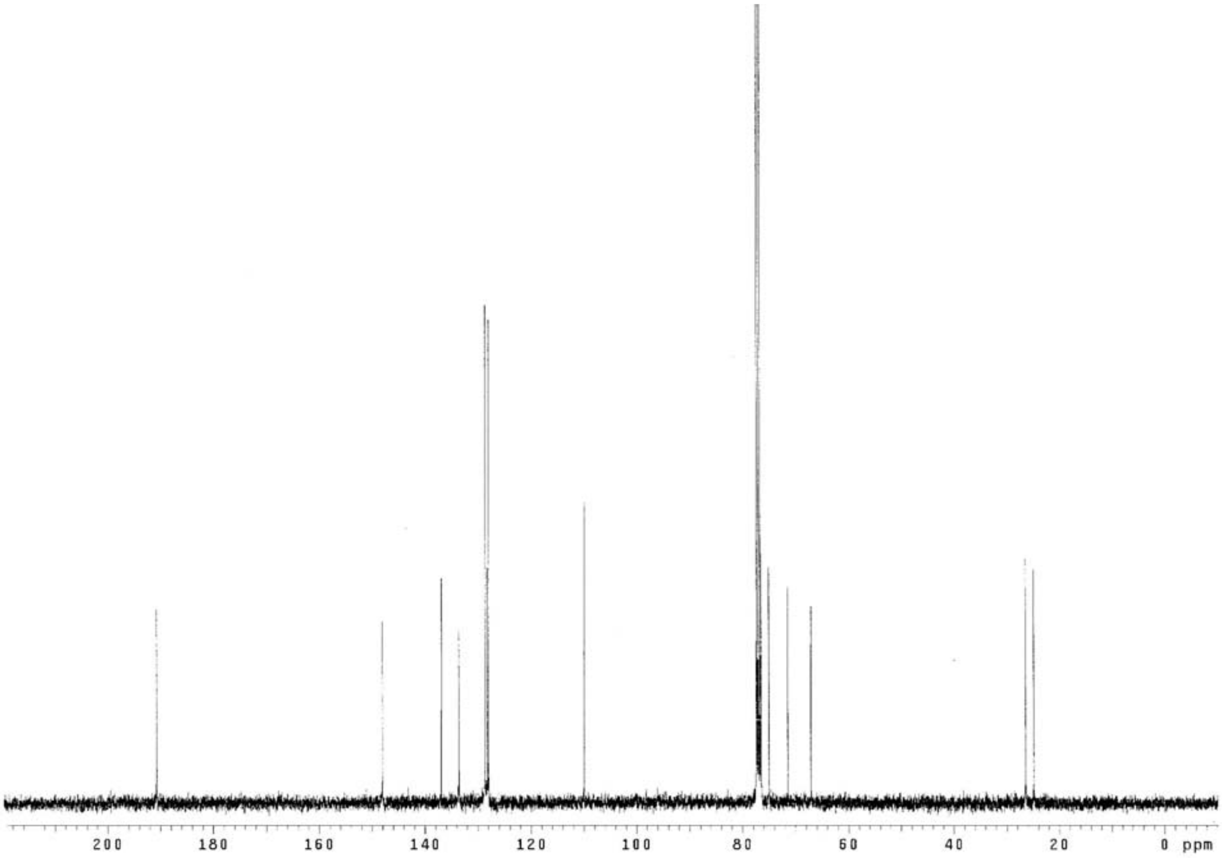
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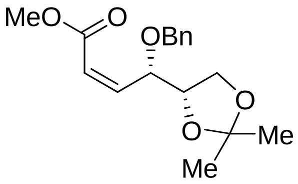
**(*S*,*Z*)-methyl 4-(benzyloxy)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)but-2-enoate**



**6b**

To a solution of **5b** (37.9 mg, 0.137 mmol, 100 mol%) in MeOH (2.74 mL, 0.05 M) were added manganese dioxide (280 mg, 2.74 mmol, 2000 mol%), sodium cyanide (28.3 mg, 0.55 mmol, 400 mol%) and acetic acid (2.5 mg, 0.007 mmol, 5 mol%). The resulting suspension was stirred at 25 $^{o}$C for 3 hours, filtered (Celite) and the filtrate was evaporated under reduced pressure. The residue was redissolved in water and extracted with ether. The combined organic extracts were dried ($Na_2SO_4$), filtered and evaporated. Flash column chromatography ($SiO_2$: $R_f$ = 0.3, hexane:ethyl acetate, 6:1) provides the title compound (39.0 mg, 0.13 mmol) as a colorless oil in 93 % yield.

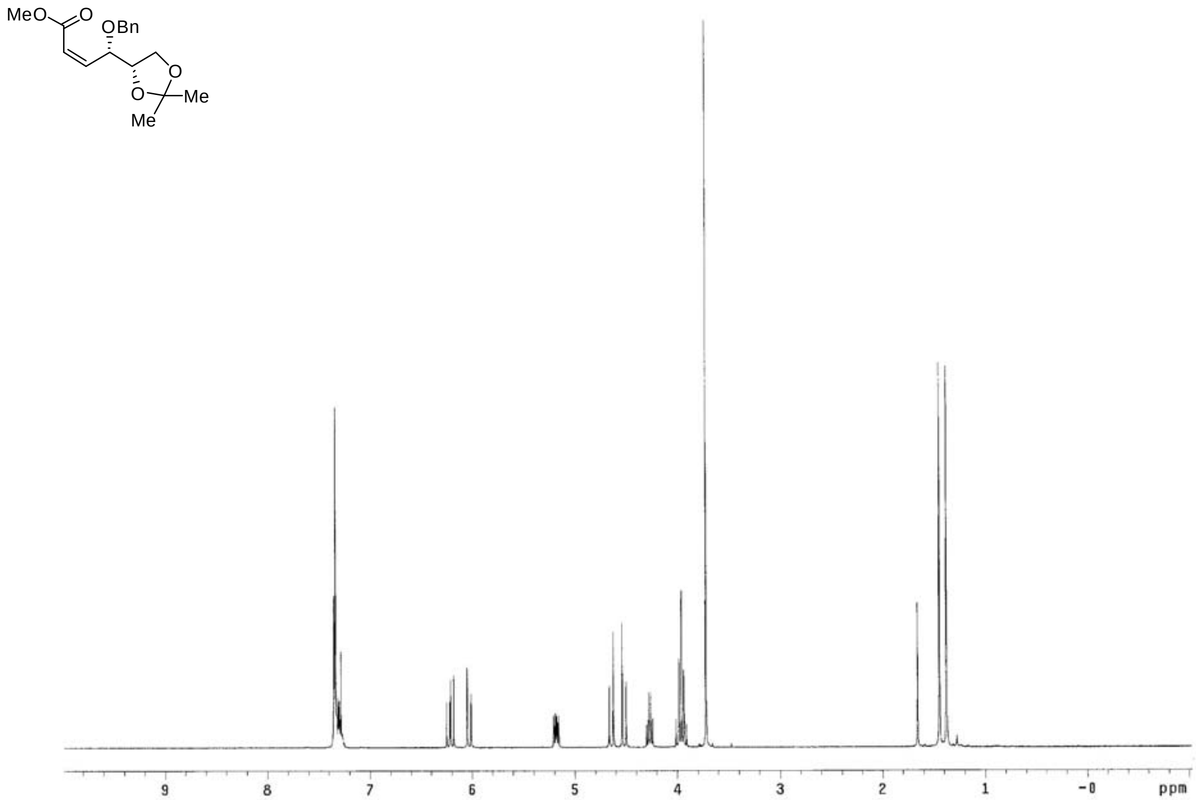
**$^{1}$H NMR** (300 MHz, $CDCl_3$): 7.31 – 7.23 (m, 5H), 6.17 (dd, *J* = 12.0, 9.0 Hz, 1H), 5.99 (dd, *J* = 11.7, 0.9 Hz, 1H), 5.14 (ddd, *J* = 9.2, 5.2, 1.1, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.26 – 4.20 (m, 1H), 3.97 – 3.87 (m, 2H), 3.68 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): 166.1, 146.2, 138.1, 128.2, 127.8, 127.6, 123.1, 109.8, 77.6, 74.4, 71.5, 65.3, 51.5, 26.2, 25.5.

**HRMS** Calcd for $C_{17}H_{23}O_5$ (M+1): 307.1545, Found: 307.1543.

**FTIR** (neat): 3030, 3013, 2990, 2955, 2892, 1730, 1654, 1499, 1454, 1437, 1400, 1229, 1203, 1180, 1154, 1125, 1070, 1209, 994, 909, 845,826 cm$^{-1}$.

**$[\alpha]_D^{25}$** +1.2$^{o}$, c = 1.2 in DCM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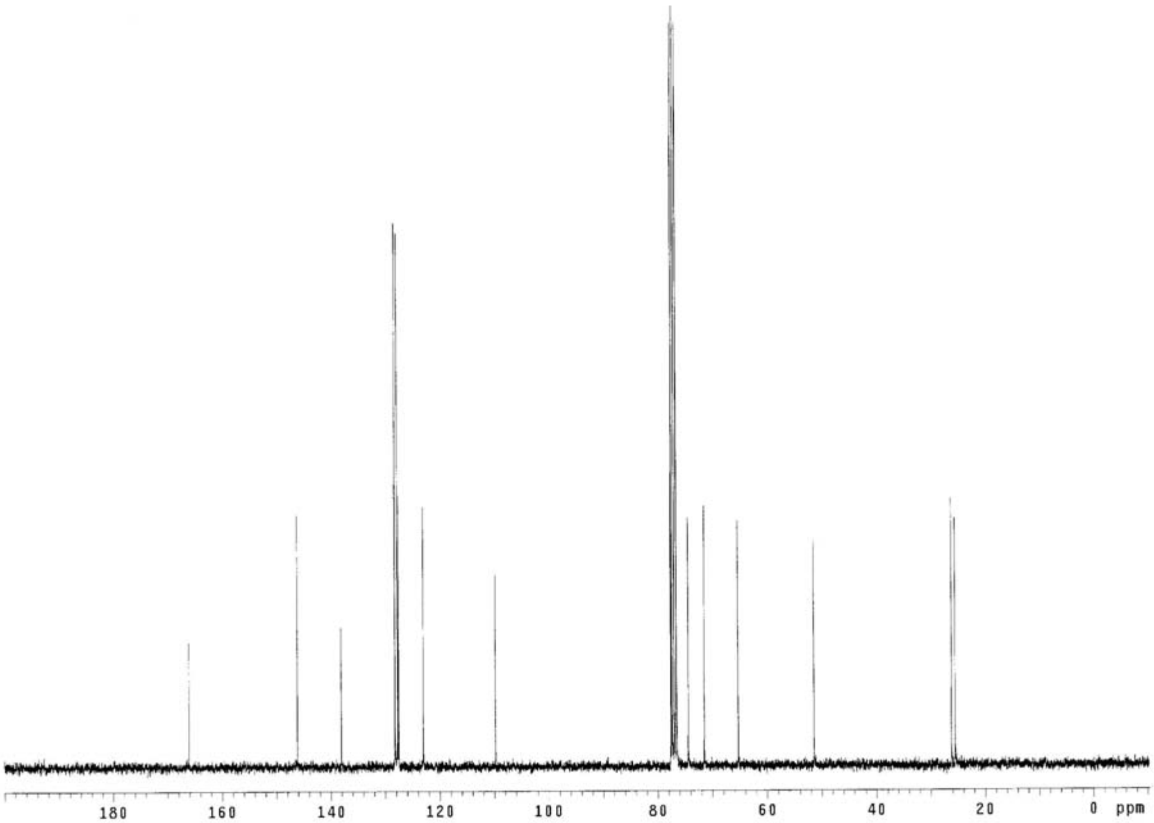
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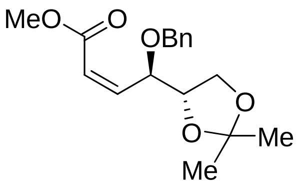
**(*R*,*Z*)-methyl 4-(benzyloxy)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)but-2-enoate**



**6c**

To a solution of **5c** (42.4 mg, 0.15 mmol, 100 mol%) in MeOH (3.0 mL, 0.05M) were added manganese dioxide (313.9 mg, 3.07 mmol, 2000 mol%) and sodium cyanide (31.6 mg, 0.61 mmol, 400 mol%) and acetic acid (2.8 mg, 0.008 mmol, 5 mol%). The resulting suspension was stirred at 25 °C for 3 hours, filtered (Celite) and the filtrate was evaporated. The residue was redissolved in water and extracted with ether. The combined organic extracts were dried ($Na_2SO_4$), filtered and evaporated. Flash column chromatography ($SiO_2$: $R_f$ = 0.3, hexane:ethyl acetate, 6:1) provides the title compound (40.0 mg, 0.13 mmol) as a colorless oil in 82 % yield.

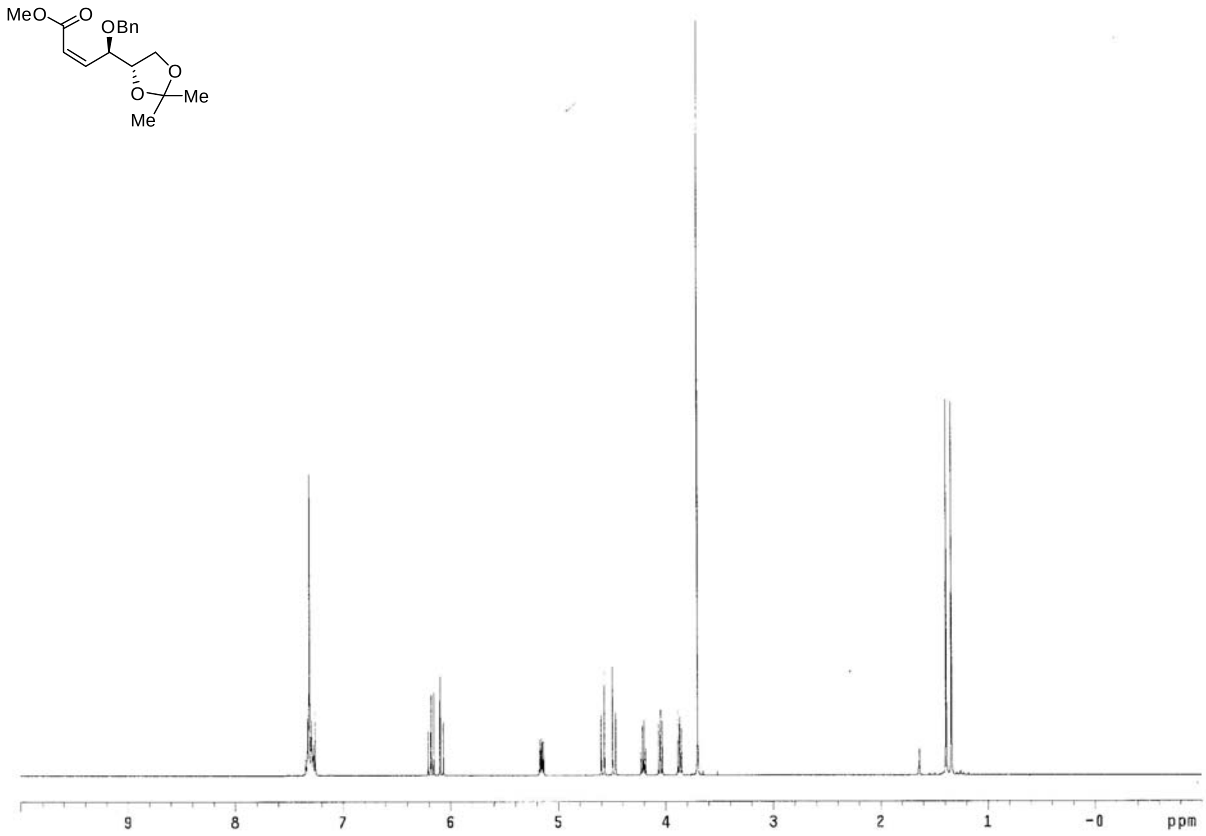
**$^1$H NMR** (400 MHz, $CDCl_3$): 7.33 – 7.25 (m, 5H), 6.16 (dd, *J* = 12.2, 9.0 Hz, 1H), 6.06 (dd, *J* = 11.6, 0.8 Hz, 1H), 5.14 (ddd, *J* = 9.2, 5.6, 0.8, 1H), 4.57 (d, *J* = 12.4 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.19 (q, *J* = 6.0 Hz, 1H), 4.03 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.84 (dd, *J* = 8.6, 6.2 Hz, 1H), 3.68 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): 166.1, 145.5, 137.9, 128.3, 128.0, 127.7, 123.8, 109.6, 77.0, 74.4, 71.5, 66.3, 51.4, 26.2, 25.2.

**HRMS** Calcd for $C_{17}H_{23}O_5$ (M+1): 307.1545, Found: 307.1545.

**FTIR** (neat): 3032, 3014, 2990, 2951, 2890, 1725, 1654, 1454, 1439, 1389, 1375, 1212, 1185, 1154, 1071, 995, 909, 845,826 $cm^{-1}$.

**$[\alpha]_D^{25}$**-8.3°, c = 1.2 in DCM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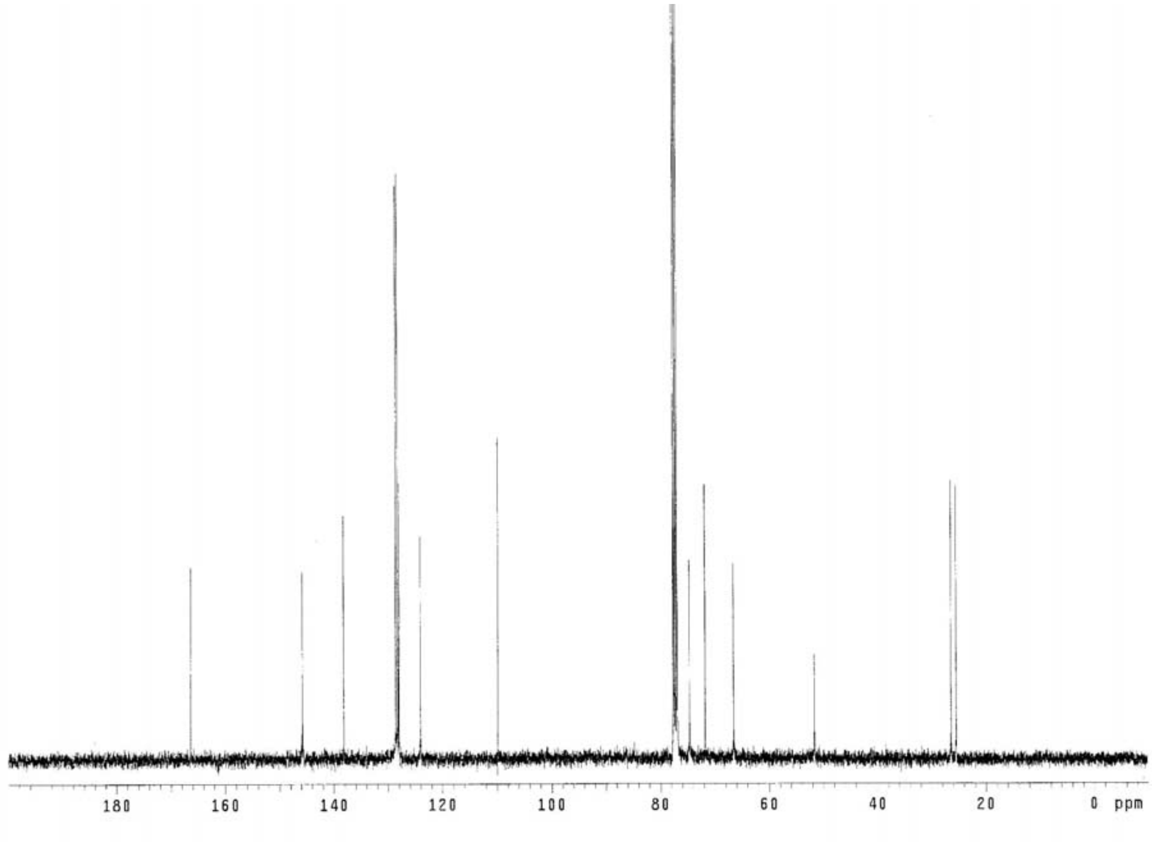
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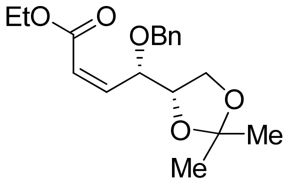
ppm

**(*S*,*Z*)-ethyl 4-(benzyloxy)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)but-2-enoate**



**7b**

To a solution of **5b** (49.2 mg, 0.178 mmol, 100 mol%) in EtOH (9.0 mL, 0.05 M) were added manganese dioxide (364.2 mg, 3.56 mmol, 2000 mol%) and sodium cyanide (36.7 mg, 0.712 mmol, 400 mol%) and acetic acid (3.3 mg, 0.009 mmol, 5 mol%). The resulting suspension was stirred at 25 °C for 3 hours, filtered (Celite) and the filtrate was evaporated. The residue was redissolved in water and extracted with ether. The combined organic extracts were dried ($Na_2SO_4$), filtered and evaporated. Flash column chromatography ($SiO_2$: $R_f$ = 0.3, hexane:ethyl acetate, 6:1) provides the title compound (49.0 mg, 0.15 mmol) as a colorless oil in 86 % yield.

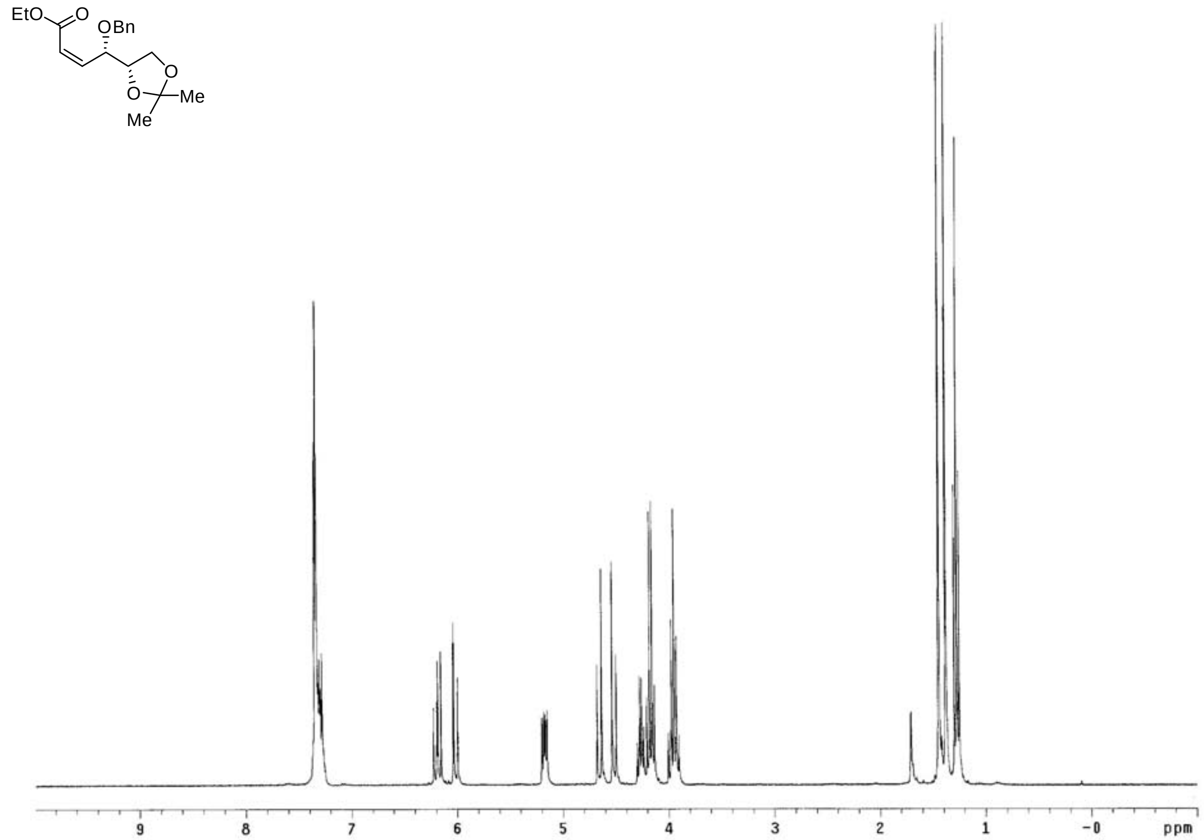
**$^1$H NMR** (300 MHz, $CDCl_3$): 7.32 – 7.22 (m, 5H), 6.15 (dd, *J* = 11.6, 9.2 Hz, 1H), 5.97 (d, *J* = 12.2 Hz, 1H), 5.13 (dd, *J* = 9.0, 2.4 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.25 – 4.19 (m, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.96 – 3.86 (m, 2H), 1.40 (s, 3H), 1.34 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): 165.7, 145.7, 138.1, 128.2, 127.8, 127.6, 123.6, 109.8, 77.6, 74.4, 71.4, 65.3, 60.4, 26.2, 25.5, 14.1.

**HRMS** Calcd for $C_{18}H_{25}O_5$ (M+1): 321.1702, Found: 321.1706.

**FTIR** (neat): 2927, 2856, 1983, 1722, 1605, 1457, 1419, 1371, 1255, 1189, 1073, 1027, 849, 823, 737, 693 cm$^{-1}$.

**$[\alpha]_D^{25}$** +0.9°, c = 1.1 in DCM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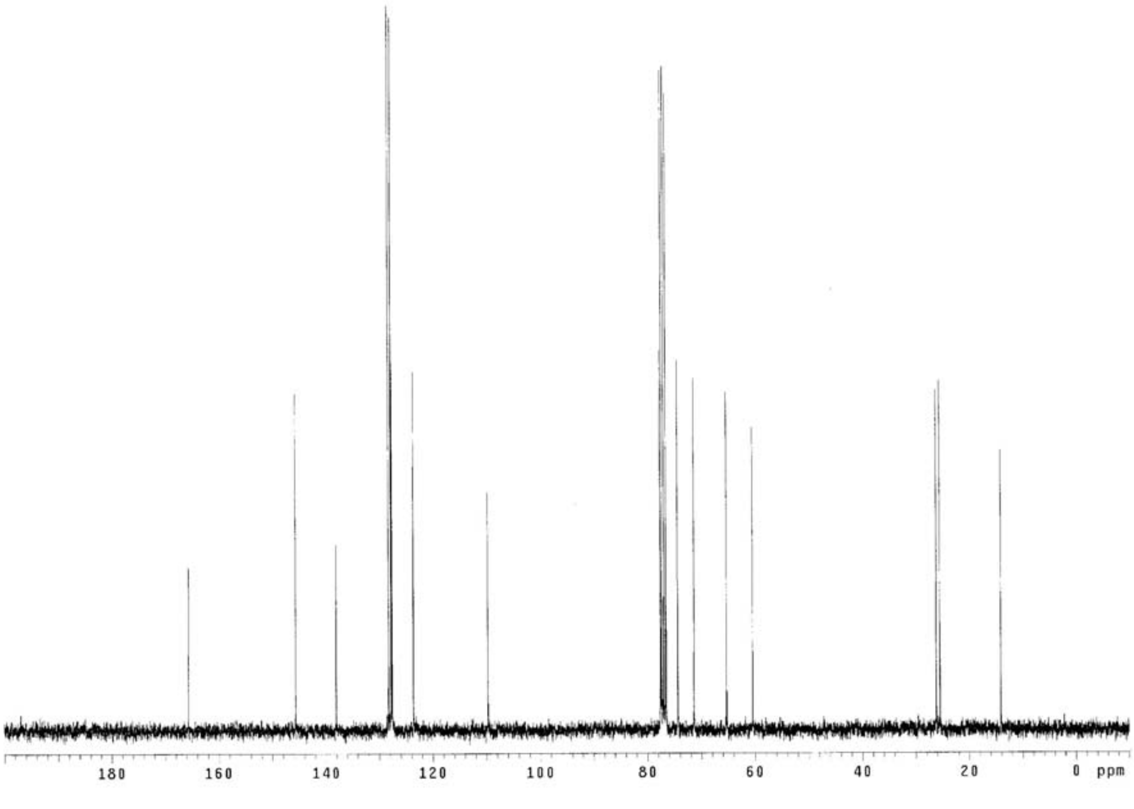
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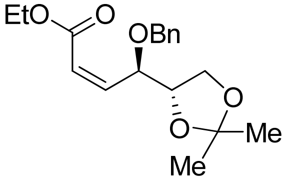
**(*R*,*Z*)-ethyl 4-(benzyloxy)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)but-2-enoate**



**7c**

To a solution of **5c** (73.2 mg, 0.26 mmol, 100 mol%) in EtOH (3.3 mL, 0.05 M) were added manganese dioxide (541.9 mg, 5.30 mmol, 2000 mol%) and sodium cyanide (54.7 mg, 1.10 mmol, 400 mol%) and acetic acid (4.8 mg, 0.013 mmol, 5 mol%).The resulting suspension was stirred at 25 °C for 3 hours,filtered (Celite) and the filtrate was evaporated. The residue was redissolved in water and extracted with ether. The combined organic extracts were dried ($Na_2SO_4$), filtered and evaporated. Flash column chromatography ($SiO_2$: $R_f$ = 0.3, hexane:ethyl acetate, 6:1) provides the title compound (65.8 mg, 0.21 mmol) as a colorless oil in 79 % yield.

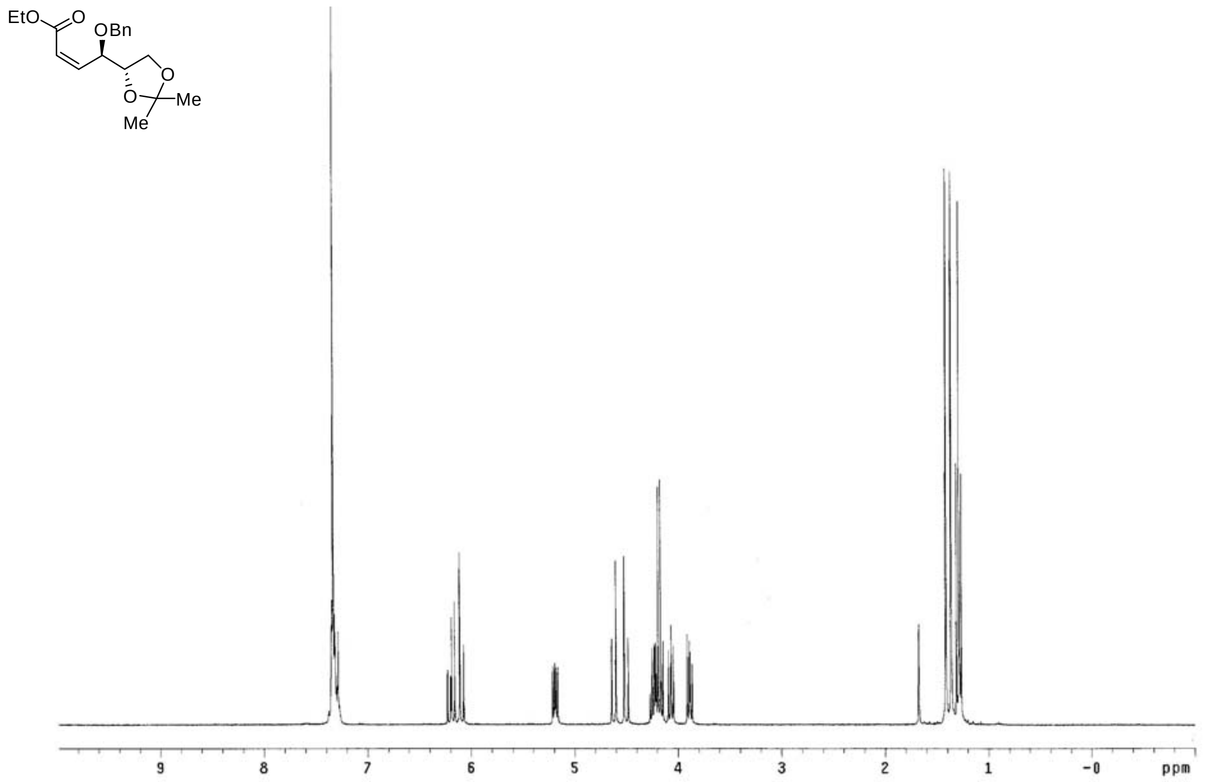
**$^1$H NMR** (300 MHz, $CDCl_3$): 7.31 – 7.25 (m, 5H), 6.15 (dd, *J* = 11.7, 8.7 Hz, 1H), 6.05 (d, *J* = 11.7 Hz, 1H), 5.15 (dd, *J* = 9.0, 5.4 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.22 – 4.10 (m, 2H), 4.02 (dd, *J* = 8.4, 6.6 Hz, 1H), 3.85 (dd, *J* = 11.6, 5.9 Hz, 1H), 1.37 (s, 3H), 1.32 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): 165.7, 145.2, 138.0, 128.3, 127.9, 127.7, 124.3, 109.5, 77.4, 74.3, 71.5, 66.3, 60.4, 26.2, 25.2, 14.1.

**HRMS** Calcd for $C_{16}H_{20}O_4$ (M): 321.1702, Found: 321.1698.

**FTIR** (neat): 2924, 2855, 1980, 1721, 1605, 1455, 1414, 1370, 1252, 1188, 1071, 1028, 848, 827, 735, 698 $cm^{-1}$.

**$[\alpha]_D^{25}$** +4°, c = 0.60 in DCM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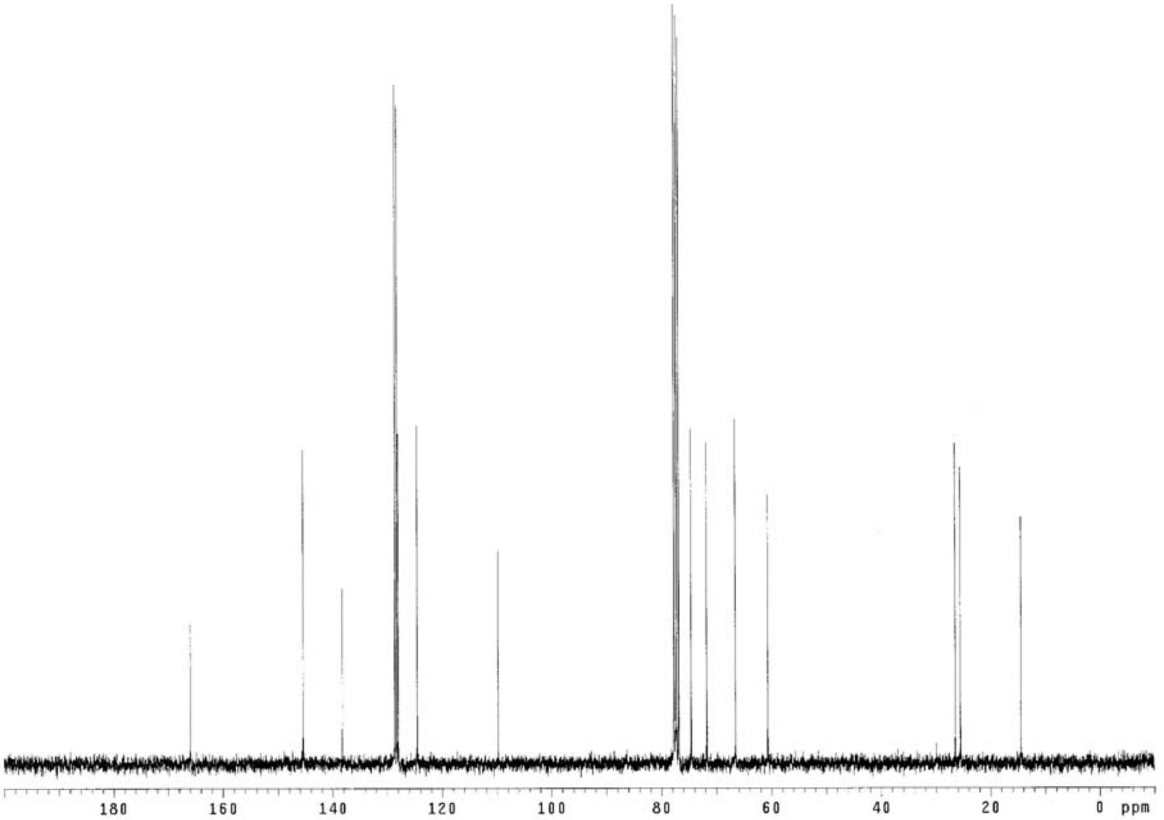
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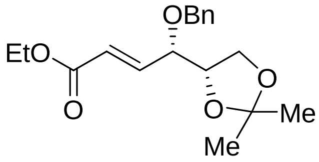
### (*S*,*E*)-ethyl 4-(benzyloxy)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)but-2-enoate



**8b**

To a solution of **7b** (31.5 mg, 0.098 mmol, 100 mol%) in *t*-BuOH (4.9 mL, 0.05M) was added trimethylphosphine in toluene (39.2μL, 0.039 mmol, 40 mol%). The resulting solution was stirred at 35 °C for 12 hours, at which point the volatiles were evaporated. Flash column chromatography ($SiO_2$: $R_f = 0.3$, hexane:ethyl acetate, 6:1) provides the title compound (28.9 mg, 0.09 mmol) as a colorless oil in 92 % yield.

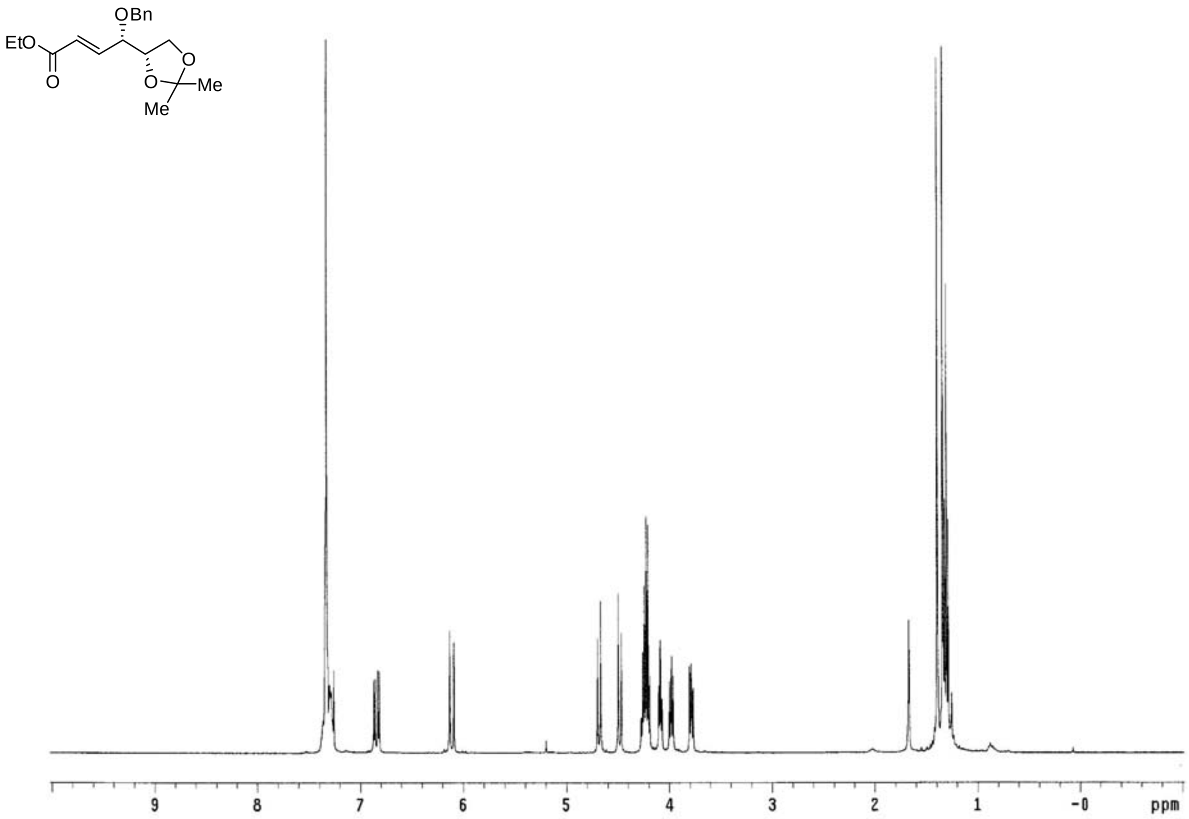
**$^1$H NMR** (400 MHz, $CDCl_3$): 7.35 – 7.25 (m, 5H), 6.82 (dd, *J* = 15.8, 6.2 Hz, 1H), 6.09 (d, *J* = 15.6 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.25 – 4.17 (m, 3H), 4.07 (t, *J* = 6.4 Hz, 1H), 3.96 (dd, *J* = 8.6, 6.6 Hz, 1H), 3.77 (dd, *J* = 8.6, 6.2 Hz, 1H), 1.37 (s, 3H), 1.32 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): 165.8, 143.4, 137.6, 128.4, 127.8, 127.7, 124.4, 109.8, 78.2, 71.5, 65.3, 60.6, 26.2, 25.1, 14.2.

**HRMS** Calcd for $C_{18}H_{25}O_5$ (M+1): 321.1702, Found: 321.1701.

**FTIR** (neat): 3030, 3013, 2987, 2936, 2891, 2876, 1721, 1660, 1499, 1452, 1381, 1370, 1302, 1276, 1180, 1155, 1072, 1042, 981, 913, 848 $cm^{-1}$.

**$[\alpha]_D^{25}$** +20.3°, c = 1.3 in DCM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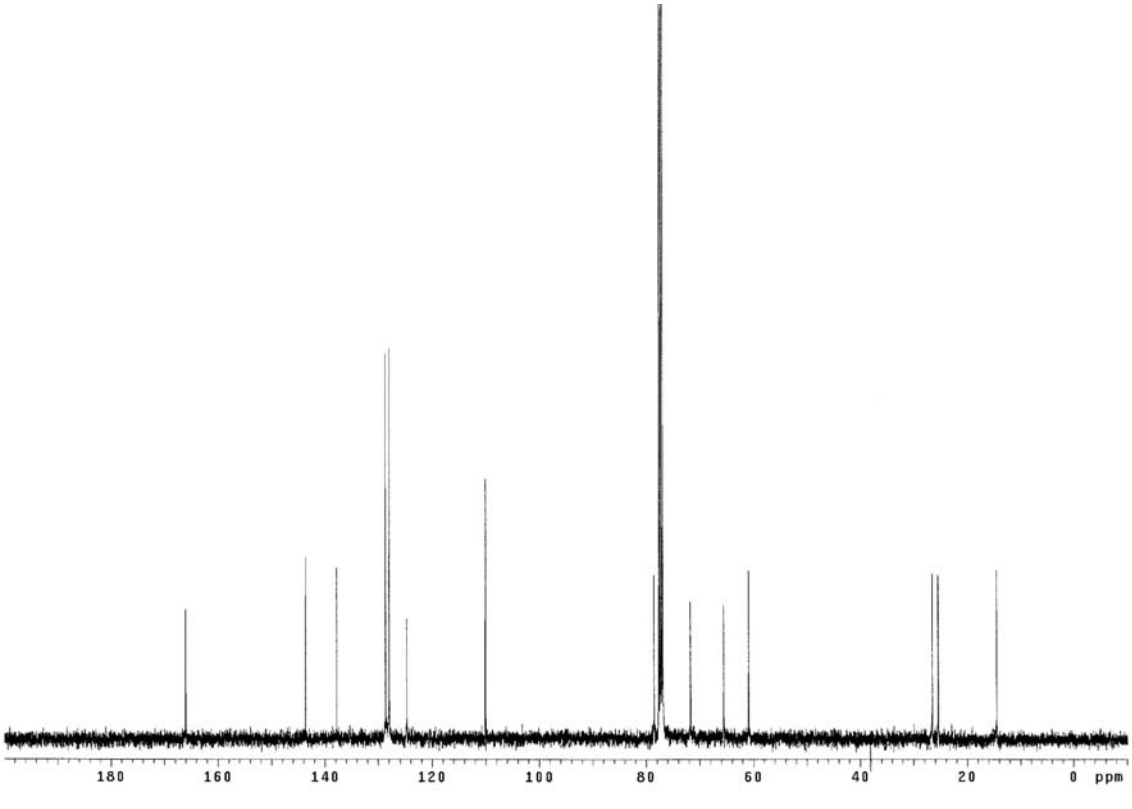
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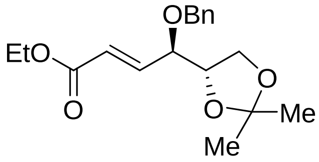
**(*R*,*E*)-ethyl 4-(benzyloxy)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)but-2-enoate**



**8c**

To a solution of **7c** (39.4 mg, 0.12 mmol, 100 mol%) in *t*-BuOH (6.5 mL, 0.05M) was added trimethylphosphine in toluene (40μL, 0.50 mmol, 40 mol%). The resulting solution was stirred at 35 °C for 12 hours, at which point the volatiles were evaporated. Flash column chromatography ($SiO_2$: $R_f = 0.3$, hexane:ethyl acetate, 10:1) provides the title compound (31.1mg, 0.10 mmol) as a colorless oil in 81 % yield.

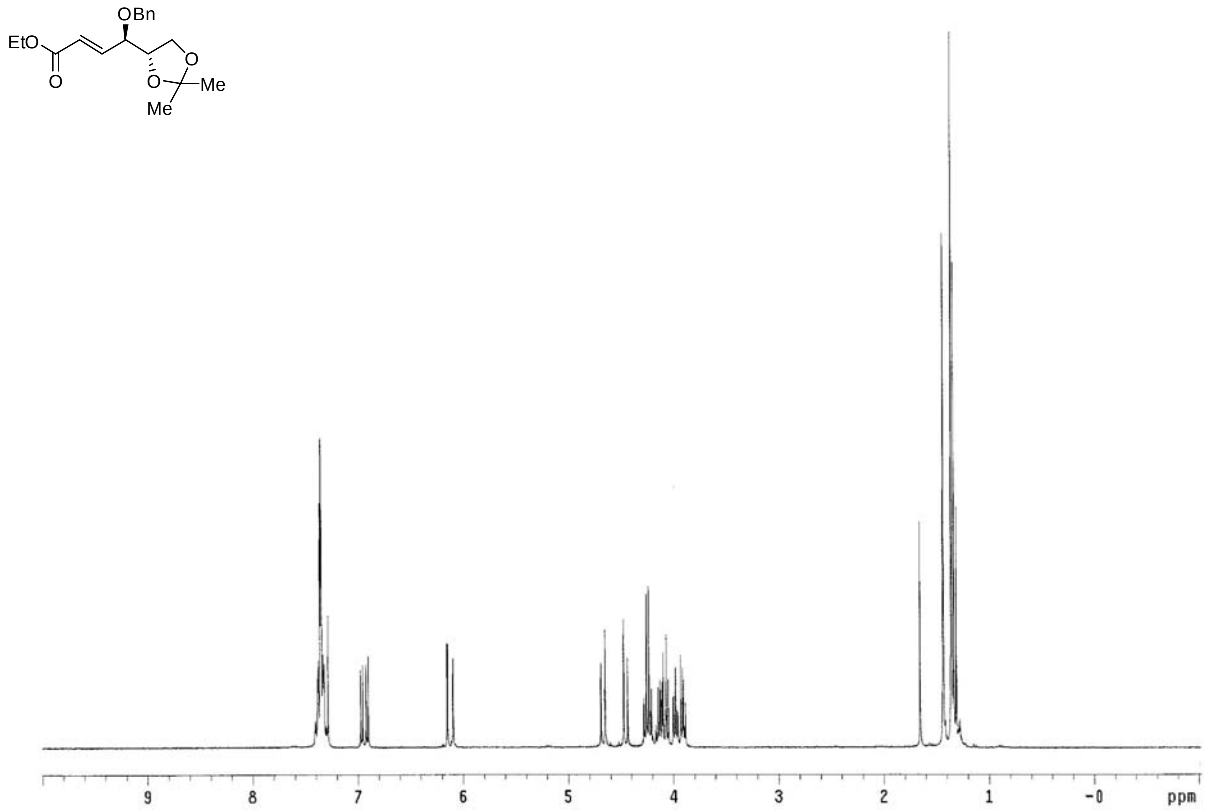
**$^1$H NMR** (300 MHz, $CDCl_3$): 7.36 – 7.25 (m, 5H), 6.89 (dd, *J* = 15.9, 6.0 Hz, 1H), 6.08 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.12 – 4.00 (m, 2H), 3.94 (td, *J* = 6.3, 1.1 Hz, 1H), 3.87 (dd, *J* = 8.1, 5.1 Hz, 1H), 1.39 (s, 3H), 1.32 (s, 3H), 1.29 (t, *J* = 6.9 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): 165.9, 144.6, 137.4, 128.5, 127.9, 124.1, 109.8, 78.8, 77.2, 71.7, 66.6, 60.6, 26.2, 25.2, 14.2.

**HRMS** Calcd for $C_{18}H_{25}O_5$ (M+1): 321.1702, Found: 321.1703.

**FTIR** (neat): 3027, 2985, 2937, 2891, 2875, 1721, 1659, 1454, 1370, 1302, 1299, 1270, 1213, 1178, 1073, 984, 848 $cm^{-1}$.

**$[\alpha]_D^{25}$** -19.2°, c = 0.87 in DCM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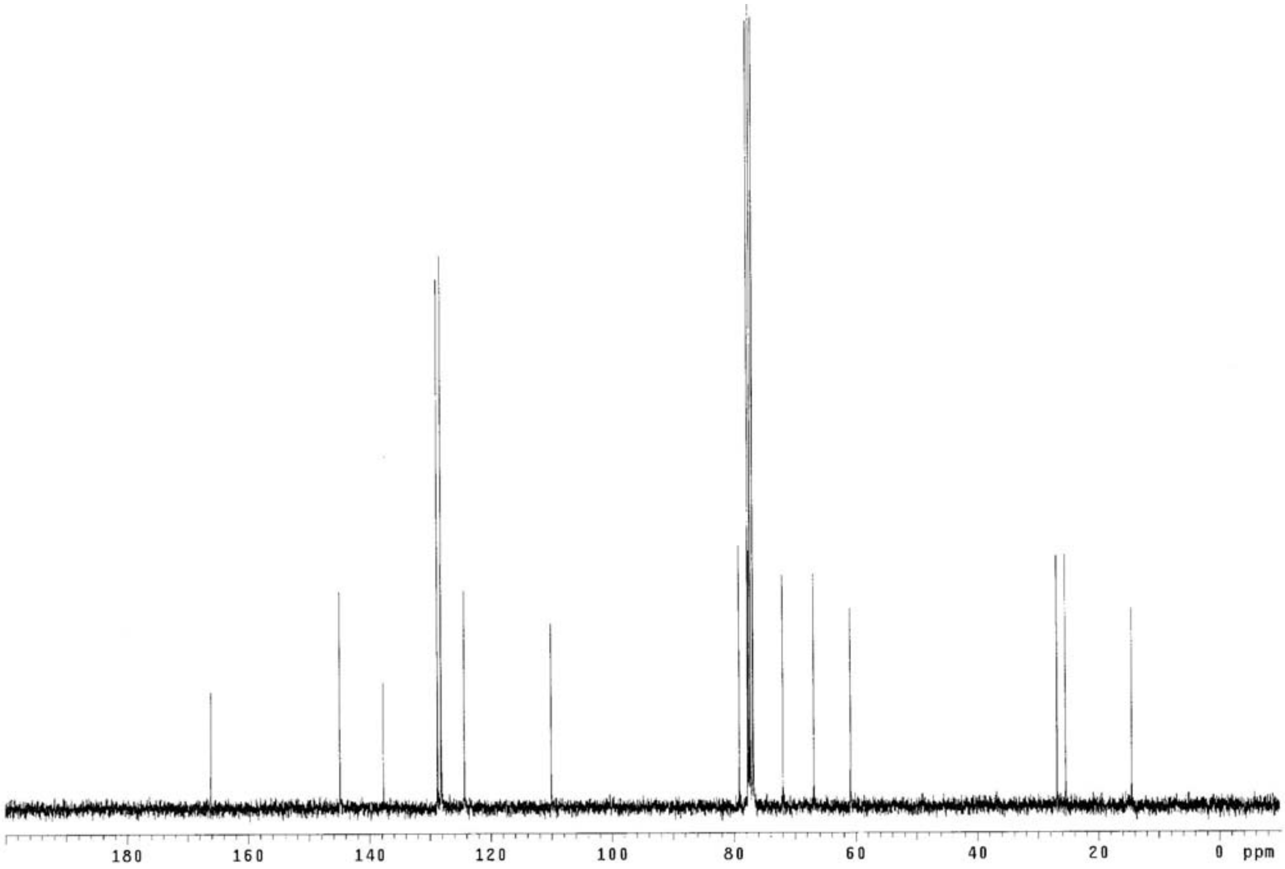
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