Diastereocontrol in Asymmetric Allyl-Allyl Cross Coupling: Stereocontrolled Reaction of Prochiral Allylboronates with Prochiral Allyl Chlorides

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Supporting Information

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General Information

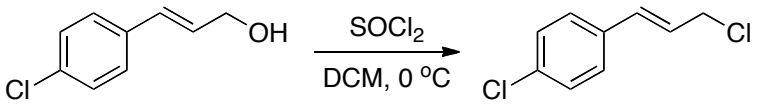
^{1}H NMR spectra were recorded on either a Varian Gemini-500 (500 MHz) or a Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent), and coupling constants (Hz). Coupling constants are reported to the nearest 0.5 Hz. ^{13}C NMR spectra were recorded on either a Varian Gemini-500 (125 MHz) or a Varian Inova-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). Infrared (IR) spectra were recorded on a Bruker alpha spectrophotometer, ν_{max} cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). High resolution mass spectrometry (ESI) was performed at the Mass Spectrometry Facility, Boston College.

Liquid Chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230×450 Mesh) purchased from Silicycle. Thin Layer Chromatography was performed on 25 µm silica gel plates purchased from Silicycle. Visualization was performed using ultraviolet light (254 nm), potassium permanganate ($KMnO_4$) in water, ceric ammonium molybdate (CAM) in water, or phosphomolybdic acid (PMA) in ethanol. Analytical chiral gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 Series chromatograph equipped with a split mode capillary injection system, a flame ionization detector, and a Supelco β-Dex 120 column, a Supelco Chiraldex G-TA, or a Supelco Asta Chiraldex B-DM with helium as the carrier gas. Analytical chiral supercritical fluid chromatography (SFC) was performed on a Thar SFC equipped with a Waters 2998 photodiode array detector and an analytical-2-prep column oven with methanol as the modifier. Analytical high performance liquid chromatography (HPLC) was performed on an Agilent 1120 compact chromatograph equipped with gradient pump and variable wavelength detector. Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), dichloromethane (DCM), and toluene (PhMe) were purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. by passing through two activated alumina columns after being purged with argon. Triethylamine was distilled from calcium hydride. Neutral alumina (Al_2O_3, 32-63 µm) was purchased from Sorbent Technologies. Bis(1,5-cyclooctadiene)nickel(0) [$Ni(cod)_2$], Tris(dibenzylideneacetone) dipalladium(0) [$Pd_2(dba)_3$], tricyclohexylphosphine (PCy_3), 1,2-bis(diphenylphosphino)benzene, (*R*)-(+)-2,2′-bis(di-2-furanylphosphino)-6,6′-dimethoxy-1,1′-biphenyl [(*R*)-MeO(furyl)BIPHEP], (*S*)-(-)-2,2′-bis(di-2-furanylphosphino)-6,6′-dimethoxy-1,1′-biphenyl [(*S*)-MeO(furyl)BIPHEP], and (*R*,*R*)-(-)-2,3-Bis(*t*-butylmethylphosphino)quinoxaline [(*R*,*R*)-QuinoxP*] were purchased from Strem Chemicals, Inc. Pinacolborane (pinBH) was generously donated by BASF. *Trans*-1,3-pentadiene was purchased from ChemSampCo. Bis(pinacolato) diboron [$B_2(pin)_2$] was generously donated by Allychem. All other reagents were purchased from either Fisher or Aldrich and used without further purification.

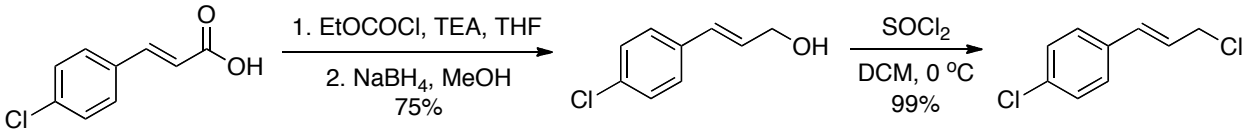
Experimental Procedures

Preparation of Substituted Allylic Chlorides

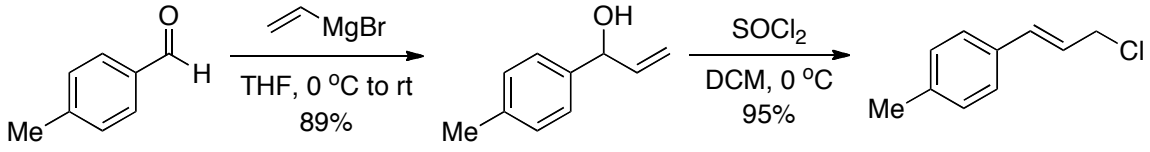


Representative Procedure: An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with dichloromethane (6.0 mL) and 1-(4-chlorophenyl)prop-2-en-1-ol (228 mg, 1.39 mmol) under nitrogen atmosphere. The solution was cooled to 0 °C and thionyl chloride (1.65 g, 13.88 mmol) was added dropwise. The solution was stirred at 0 °C for 2 h, then warmed to rt for 1 h. The reaction was quenched with ice water, extracted into dichloromethane (3 x 20 mL). The combined organics were dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford a clear, colorless oil (155 mg, 99% yield) that was used without further purification.

Preparation of (E)-1-chloro-4-(3-chloroprop-1-en-1-yl)benzene. From (*E*)-3-(4-chlorophenyl)prop-2-en-1-ol, synthesized as shown below,[1] the representative procedure was followed to afford a clear, colorless oil (155 mg, 99% yield). Spectral data is in accordance with the literature.[2]



Preparation of (E)-1-(3-chloroprop-1-en-1-yl)-4-methylbenzene. From 1-(*p*-tolyl)prop-2-en-1-ol, synthesized as shown below, the representative procedure was followed, with the following modification: After reaction work-up, the crude reaction mixture was dissolved in dichloromethane and stirred over activated charcoal, then filtered through celite and concentrated *in vacuo* to afford a clear, colorless oil (428 mg, 95% yield). Spectral data is in accordance with the literature.[2]



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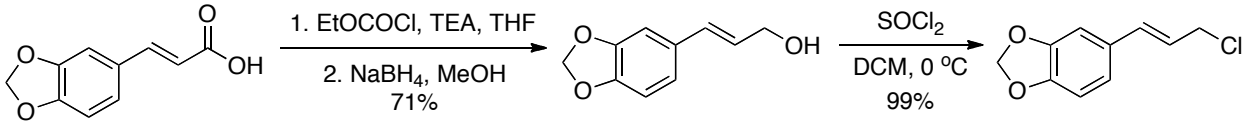
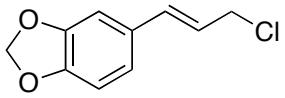
[1] Penjšević, J.; Šukalović, V.; Andrić, D.; Kostić-Rajačić, S.; Šoškić, V.; Roglić, G. *Arch. Pharm. Chem. Life Sci.* **2007**, *340*, 456.

[2] Lölsberg, W.; Ye, S.; Schmalz, H. G. *Adv. Synth. Catal.* **2010**, *352*, 2023.

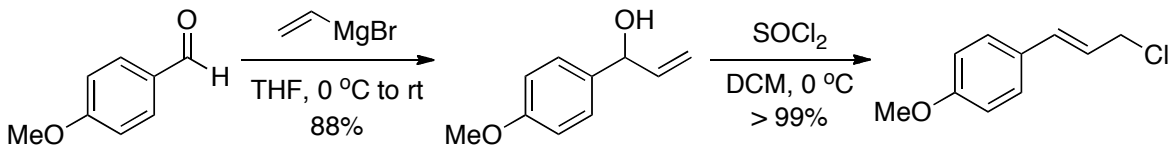
Preparation of (E)-5-(3-chloroprop-1-en-1-yl)benzo[d][1,3]dioxole. From (*E*)-3-(benzo[d][1,2]dioxol-5-yl)prop-2-en-1-ol, synthesized as shown below, the representative procedure was followed.



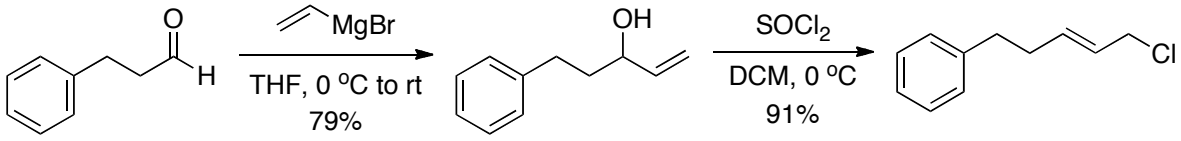


(*E*)-5-(3-chloroprop-1-en-1-yl)benzo[*d*][1,3]dioxole (Compound SI-1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.22 (2H, dd, J = 7.5 Hz, 1.0 Hz), 5.96 (2H, s), 6.15 (1H, dt, J = 15.5 Hz, 7.5 Hz), 6.56 (1H, d, J = 15.5 Hz), 6.76 (1H, d, J = 8.0 Hz), 6.82 (1H, dd, J = 8.5 Hz, 2.0 Hz), 6.93 (1H, d, J = 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 45.6, 101.2, 105.9, 108.3, 121.7, 123.1, 130.3, 133.9, 147.8, 148.1; IR (neat): 1500 (m), 1490 (m), 1447 (m), 1246 (s), 1194 (m), 1100 (m), 1037 (s), 966 (m), 929 (m), 862 (w), 798 (s), 780 (w), 670 (m), 600 (m) cm^{-1}; HRMS-(ESI+) for $C_{10}H_{10}ClO_2$ [M+H]: calculated: 197.0369, found: 197.0374. Upon drying the crude reaction mixture with sodium sulfate, filtration of the solution, and concentration of the mixture *in vacuo*, a viscous yellow oil was obtained (163 mg, 99% yield), and was used in the allyl-allyl coupling reaction without further purification.

Preparation of (E)-1-(3-chloroprop-1-en-1-yl)-4-methoxybenzene. From 1-(4-methoxyphenyl)prop-2-en-1-ol, synthesized as shown below, the representative procedure was followed to afford a clear, colorless oil (265 mg, quantitative yield). Spectral data is in accordance with the literature.[2]

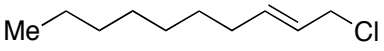


Preparation of (E)-(5-chloropent-1-en-1-yl)benzene. From 5-phenylpent-1-en-3-ol, synthesized as shown below, the representative procedure was followed, with the following modification: The crude reaction mixture was purified on neutral alumina (pentane) to afford a clear, colorless oil (406 mg, 91% yield). Spectral data is in accordance with the literature.[3]



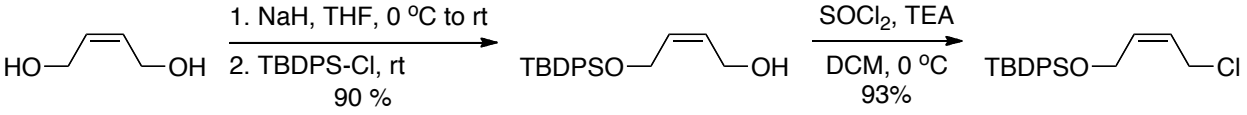
[3] Fuchter, M. J.; Levy, J.-N. *Org. Lett.* **2008**, *10*, 4919.

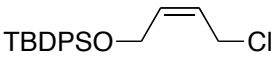
Preparation of (E)-1-chlorodec-2-ene. From commercially available (*E*)-dec-2-en-1-ol, the representative procedure was followed.



(*E*)-1-chlorodec-2-ene (Compound SI-2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, t, *J* = 7.0 Hz), 1.26-1.31 (8H, m), 1.39 (2H, app t, *J* = 7.0 Hz), 2.09-2.13 (2H, m), 4.10 (2H, dd, *J* = 6.5 Hz, 3.0 Hz), 5.63 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 22.6, 27.1, 29.1, 29.2, 29.3, 31.8, 39.6, 125.1, 135.6; IR (neat): 3026 (w), 2957 (m), 2925 (s), 2885 (m), 1652 (w), 1459 (m), 1378 (w), 1250 (m), 757 (s), 724 (m), 676 (w) cm^{-1}. The crude reaction mixture was purified on neutral alumina (pentane) to afford a clear, colorless oil (419 mg, 89% yield). R_f = 0.86 (pentane, stain in $KMnO_4$).

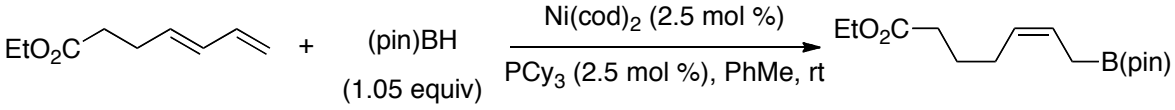
Preparation of (Z)-tert-butyl((4-chlorobut-2-en-1-yl)oxy)diphenylsilane. From (*Z*)-4-((*tert*-butyldiphenylsilyl)oxy)but-2-en-1-ol, synthesized as shown below, the representative procedure was followed, with the following modification: An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with dichloromethane (20.0 mL), distilled triethylamine (0.47 mL, 3.52 mmol), and (*Z*)-4-((*tert*-butyldiphenylsilyl)oxy)but-2-en-1-ol (1.00 g, 3.06 mmol) under nitrogen atmosphere. The solution was cooled to 0 °C and thionyl chloride (0.24 mL, 3.37 mmol) was added dropwise. The solution was warmed to rt and stirred for 1 h. The reaction was quenched with ice water, then extracted into dichloromethane (3 x 20 mL). The mixture was dried over sodium sulfate, filtered, and concentrated *in vacuo*. The crude mixture was purified on a 1" pad of neutral alumina (20:1 pentane:diethyl ether) to afford a clear, colorless oil (978 mg, 93% yield).



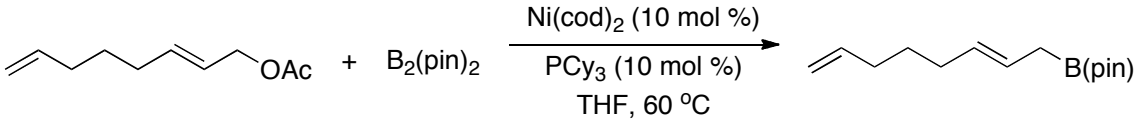


(*Z*)-*tert*-butyl((4-chlorobut-2-en-1-yl)oxy)diphenylsilane (Compound SI-3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.06 (9H, s), 3.96 (2H, dd, *J* = 7.0 Hz, 0.5 Hz), 4.30 (2H, dd, *J* = 6.0 Hz, 1.5 Hz), 5.65 (1H, dtt, *J* = 11.0 Hz, 8.0 Hz, 1.5 Hz), 5.78 (1H, dtt, *J* = 11.0 Hz, 6.0 Hz, 1.0 Hz), 7.39-7.46 (6H, m), 7.69 (4H, dd, *J* = 8.0 Hz, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.1, 26.7, 39.3, 59.9, 126.2, 127.7, 129.7, 133.28, 133.34, 135.5; IR (neat): 3071 (w), 2958 (m), 2931 (m), 2858 (m), 1472 (w), 1428 (m), 1391 (w), 1361 (w), 1256 (w), 1110 (s), 1072 (m), 998 (w), 941 (w), 823 (m), 740 (m), 701 (s), 613 (m), 505 (s), 490 (m) cm^{-1}; HRMS-(ESI+) for $C_{20}H_{26}ClOSi$ [M+H]: calculated: 345.1441, found: 345.1427. The crude reaction mixture was purified on neutral alumina (20:1 pentane:diethyl ether) to afford a clear, colorless oil (978 mg, 93% yield). R_f = 0.73 (5:1 pentane:diethyl ether, stain in $KMnO_4$).

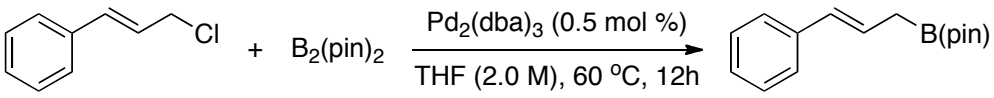
Preparation of Substituted Allyl Boron Reagents



Representative Procedure A:[4] An oven-dried scintillation vial equipped with a magnetic stir bar was charged with bis(1,5-cyclooctadiene)nickel(0) (15 mg, 0.06 mmol), tricyclohexylphosphine (16 mg, 0.055 mmol), and toluene (4.4 mL) in a dry-box under argon atmosphere. The vial was capped and stirred for two minutes, then (*E*)-ethyl hepta-4,6-dienoate (340 mg, 2.205 mmol) was added, followed by pinacolborane (296 mg, 2.32 mmol). The vial was capped with a teflon cone-lined cap, sealed with electrical tape, removed from the dry-box, and allowed to stir at rt for 2 h. The reaction was concentrated *in vacuo*, and the crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, colorless oil (474 mg, 76% yield). R_f = 0.38 (15:1 pentane:diethyl ether, stain in CAM).



Representative Procedure B: An oven-dried scintillation vial equipped with a magnetic stir bar was charged with bis(1,5-cyclooctadiene)nickel(0) (82 mg, 0.30 mmol), tricyclohexylphosphine (83 mg, 0.30 mmol), and tetrahydrofuran (3.0 mL) in a dry box under argon atmosphere. The vial was capped and stirred for two minutes, then (*E*)-octa-2,7-dien-1-yl acetate (500 mg, 2.97 mmol) was added, followed by bis(pinacolato)diboron (754 mg, 2.97 mmol). The vial was capped with a teflon cone-lined cap, sealed with electrical tape, removed from the dry-box, and was heated to 60 °C and allowed to stir for 36 h. At this time, the reaction was concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane, ramped gradually to 20:1 pentane:diethyl ether) to afford a clear, colorless oil (349 mg, 50% yield). R_f = 0.43 (25:1 pentane:diethyl ether, stain in CAM).



Representative Procedure C: An oven-dried scintillation vial equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (18 mg, 0.02 mmol), bis(pinacolato)diboron (1.02 g, 4.02 mmol), and tetrahydrofuran (2.0 mL) in a dry-box under argon atmosphere. The vial was capped and stirred for two minutes, then cinnamyl chloride (610 mg, 4.00 mmol) was added. The vial was capped with a teflon cone-lined cap, sealed with electrical tape, removed from the dry box, and was heated to 60 °C and allowed to stir for 12 h. At this time, the reaction was concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (50:1 pentane:diethyl ether) to afford a clear, colorless oil (627 mg, 65% yield). R_f = 0.44 (50:1 pentane:diethyl ether, stain in $KMnO_4$).

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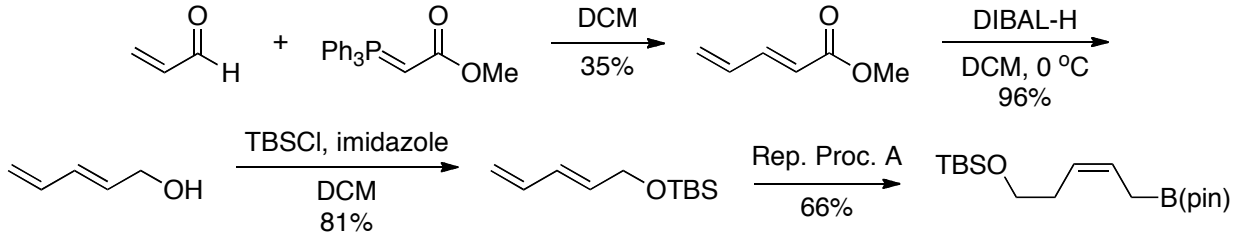
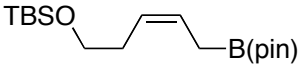
[4] Ely, R. J.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 2534.

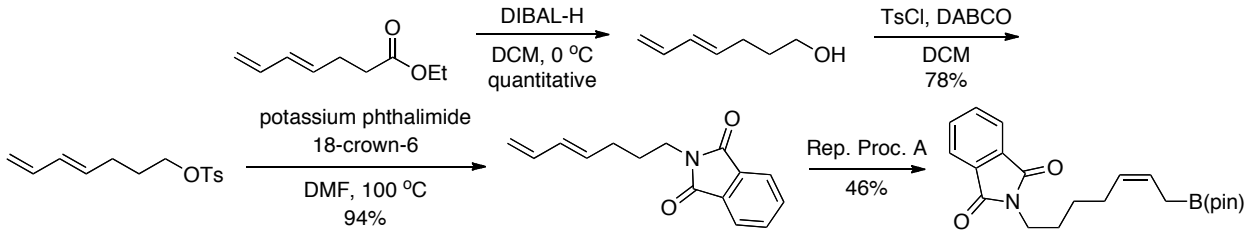
Preparation of (Z)-tert-butyldimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaboronlan-2-yl)pent-3-en-1-yl)oxy)silane. From (*E*)-*tert*-butyldimethyl(penta-2,4-dien-1-yloxy)silane, synthesized as shown below, representative procedure A was followed.

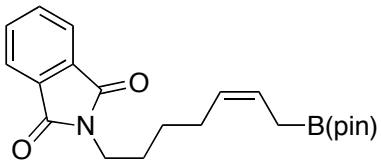




(*Z*)-*tert*-butyldimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-1-yl)oxy)silane (Compound SI-4). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.05 (6H, s), 0.89 (9H, s), 1.24 (12H, s), 1.69 (2H, d, J = 8.0 Hz), 2.27 (2H, app qd, J = 7.0 Hz, 1.5 Hz), 3.60 (2H, t, J = 7.0 Hz), 5.39 (1H, dtt, J = 10.5 Hz, 7.0 Hz, 1.5 Hz), 5.57 (1H, dtt, J = 10.5 Hz, 8.0 Hz, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ -5.24, 18.4, 24.8, 26.0, 31.0, 62.9, 83.2, 125.5, 126.1; IR (neat): 2978 (w), 2955 (w), 2929 (m), 2857 (m), 1718 (w), 1471 (w), 1379 (m), 1371 (m), 1326 (s), 1254 (m), 1215 (w), 1144 (s), 1097 (s), 1006 (w), 968 (w), 936 (w), 884 (w), 835 (s), 775 (s), 743 (w), 664 (w) cm^{-1}; HRMS-(ESI+) for $C_{17}H_{36}BO_3Si$ [M+H]: calculated: 327.2527, found: 327.2527. The crude reaction mixture was purified on silica gel (25:1 hexanes:ethyl acetate) to afford a clear, colorless oil (326 mg, 66% yield). R_f = 0.24 (20:1 pentane:diethyl ether, stain in CAM).

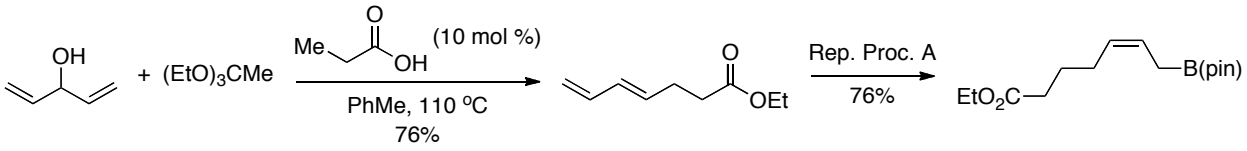
Preparation of (Z)-2-(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-5-en-1-yl)isoindoline-1,3-dione. From (*E*)-2-(hepta-4,6-dien-1-yl)isoindoline-1,3-dione,[4] synthesized as shown below, representative procedure A was followed.

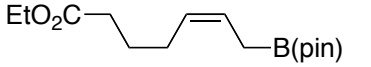




(*Z*)-2-(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-5-en-1-yl)isoindoline-1,3-dione (Compound SI-5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (12H, s), 1.37-1.43 (2H, m), 1.65 (2H, d, *J* = 7.0 Hz), 1.65-1.71 (2H, m), 2.06 (2H, app q, *J* = 7.5 Hz), 3.67 (2H, t, *J* = 7.5 Hz), 5.34 (1H, dtt, *J* = 10.5 Hz, 7.0 Hz, 1.5 Hz), 5.47 (1H, dtt, *J* = 10.5 Hz, 8.0 Hz, 1.5 Hz), 7.69 (2H, dd, *J* = 5.0 Hz, 3.0 Hz), 7.83 (2H, dd, *J* = 5.5 Hz, 3.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.7, 26.5, 26.8, 28.2, 38.0, 83.2, 123.1, 124.7, 129.1, 132.2, 133.8, 168.4; IR (neat): 2977 (w), 2934 (w), 2862 (w), 1772 (w), 1712 (s), 1467 (w), 1437 (w), 1395 (m), 1370 (m), 1326 (m), 1144 (m), 1109 (w), 1040 (w), 847 (w), 720 (m), 530 (w) cm^{-1}; HRMS-(ESI+) for $C_{21}H_{29}BNO_4$ [M+H]: calculated: 370.2190, found: 370.2182. The crude reaction mixture was purified on silica gel (4:1 pentane:diethyl ether) to afford a clear, light yellow oil (71 mg, 46% yield). R_f = 0.34 (3:1 pentane:diethyl ether, stain in CAM).

Preparation of (Z)-ethyl 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-5-enoate. From (*E*)-ethyl hepta-4,5-dienoate, synthesized as shown below,[5] representative procedure A was followed.





(*Z*)-ethyl 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-5-enoate (Compound SI-6). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23 (12H, s), 1.24 (3H, t, *J* = 7.0 Hz), 1.65 (2H, d, *J* = 8.0 Hz), 1.68 (2H, app p, *J* = 7.5 Hz), 2.06 (2H, app q, *J* = 7.0 Hz), 2.29 (2H, t, *J* = 7.5 Hz), 4.11 (2H, q, *J* = 7.0 Hz), 5.35 (1H, dtt, *J* = 10.5 Hz, 7.0 Hz, 1.5 Hz), 5.53 (1H, dtt, *J* = 10.5 Hz, 8.0 Hz, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 24.7, 24.8, 26.4, 33.8, 60.1, 83.2, 125.3, 128.5, 173.7; IR (neat): 2979 (m), 2934 (w), 1735 (s), 1448 (w), 1371 (m), 1326 (s), 1273 (w), 1241 (w), 1215 (w), 1165 (m), 1144 (s), 1110 (w), 1033 (w), 968 (w), 881 (w), 847 (m), 737 (w) cm^{-1}; HRMS-(ESI+) for $C_{15}H_{28}BO_4$ [M+H]: calculated: 283.2081, found: 283.2091. The crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, colorless oil (474 mg, 76% yield). R_f = 0.38 (15:1 pentane:diethyl ether, stain in CAM).

Preparation of (Z)-2-(dec-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. This compound was prepared following literature procedure, and spectral data is in accordance with reported values.[6]

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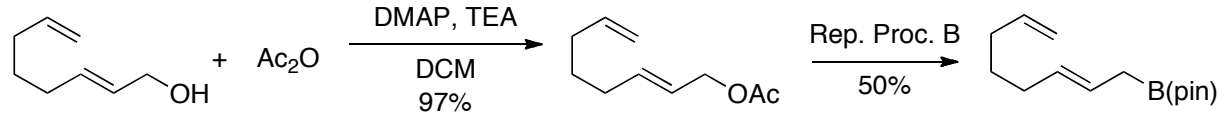
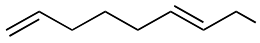
[5] Spino, C.; Crawford, J.; Bishop, J. *J. Org. Chem.* **1995**, *60*, 844.

[6] Ely, R. J.; Morken, J. P. *Org. Synth.* **2011**, *88*, 342.

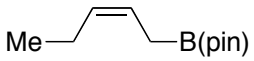
Preparation of (E)-4,4,5,5-tetramethyl-2-(octa-2,7-dien-1-yl)-1,3,2-dioxaborolane. From (*E*)-octa-2,7,-dien-1-yl acetate, synthesized as shown below, representative procedure B was followed.





(*E*)-4,4,5,5-tetramethyl-2-(octa-2,7-dien-1-yl)-1,3,2-dioxaborolane (Compound SI-7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (12H, s), 1.43 (2H, app p, J = 7.5 Hz), 1.64 (2H, d, J = 7.0 Hz), 1.97-2.06 (4H, m), 4.91-4.95 (1H, m), 4.99 (1H, app dq, J = 17.0 Hz, 2.0 Hz), 5.34-5.48 (2H, m), 5.80 (1H, app ddt, J = 17.0 Hz, 10.5 Hz, 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.7, 28.8, 32.1, 33.2, 83.1, 114.3, 125.2, 130.5, 139.0; IR (neat): 2978 (m), 2927 (w), 2857 (w), 1640 (w), 1369 (m), 1323 (s), 1272 (w), 1214 (w), 1144 (s), 967 (m), 909 (w), 883 (w), 847 (w), 673 (w) cm^{-1}; HRMS-(ESI+) for $C_{14}H_{26}BO_2$ [M+H]: calculated: 237.2026, found: 237.2036. The crude reaction mixture was purified on silica gel (pentane, ramped gradually to 20:1 pentane:diethyl ether) to afford a clear, colorless oil (349 mg, 50% yield). R_f = 0.43 (25:1 pentane:diethyl ether, stain in CAM).

Preparation of (Z)-4,4,5,5-tetramethyl-2-(pent-2-en-1-yl)-1,3,2-dioxaborolane. From commercially available *trans*-1,3-pentadiene, representative procedure A was followed.



(*Z*)-4,4,5,5-tetramethyl-2-(pent-2-en-1-yl)-1,3,2-dioxaborolane (Compound SI-8). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96 (3H, t, J = 7.5 Hz), 1.25 (12H, s), 1.67 (2H, d, J = 8.0 Hz), 2.03 (2H, app pd, J = 7.5 Hz, 1.0 Hz), 5.36-5.41 (1H, m), 5.43-5.49 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 20.3, 24.7, 83.2, 123.4, 131.6; IR (neat): 2977 (m), 2934 (w), 2875 (w), 1463 (w), 1371 (w), 1322 (s), 1273 (w), 1214 (w), 1165 (w), 1144 (s), 1112 (w), 966 (m), 887 (w), 848 (m), 738 (w), 672 (w) cm^{-1}; HRMS-(ESI+) for $C_{11}H_{22}BO_2$ [M+H]: calculated: 197.1713, found: 197.1718. The crude reaction mixture was purified on silica gel (1:1 pentane:dichloromethane) to afford a clear, colorless oil (711 mg, 83% yield). R_f = 0.58 (1:1 pentane:dichloromethane, stain in CAM).

Preparation of 2-cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. From commercially available cinnamyl chloride, procedure C was followed. Spectral data is in accordance with reported values.[7]

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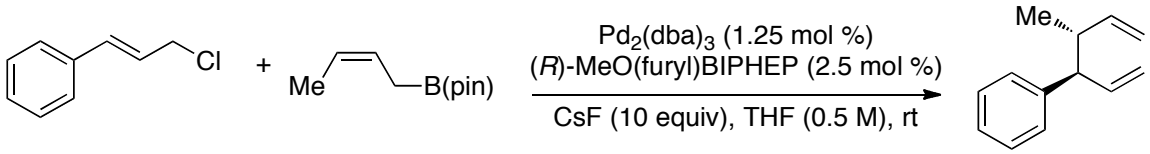
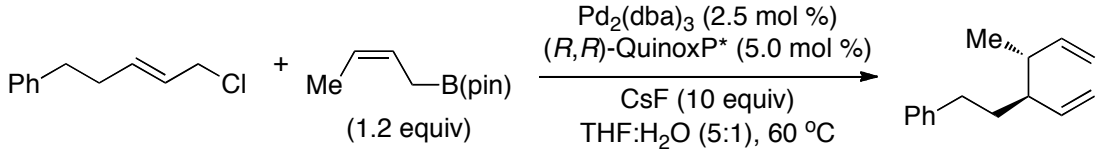
[7] Selander, N.; Paasch, J. R.; Szabó, K. J. *J. Am. Chem. Soc.* **2011**, *133*, 409.

Experimental Procedures for Diastereoselective Allyl-Allyl Coupling

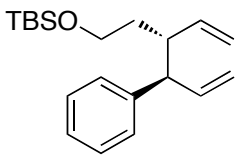


Representative Procedure A: An oven-dried two-dram vial equipped with magnetic stir bar was charged with $Pd_2(dba)_3$ (1.1 mg, 1.25 µmol), (*R*)-MeO(furyl)BIPHEP (1.4 mg, 2.50 µmol), and THF (0.2 mL) in a dry-box under argon atmosphere. The vial was capped and stirred for five minutes, then cinnamyl chloride (15.3 mg, 0.10 mmol) was added, followed by cesium fluoride (152.0 mg, 1.0 mmol), and *cis*-crotylboronic acid pinacol ester (21.8 mg, 0.12 mmol). The vial was sealed, removed from the dry-box, and allowed to stir at ambient temperature for 14 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (15.6 mg, 90% yield). R_f = 0.56 (pentane, stain in PMA).



Representative Procedure B: An oven-dried two-dram vial equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (2.3 mg, 2.5 µmol), (*R*,*R*)-QuinoxP* (1.7 mg, 5.0 µmol), and THF (0.2 mL) in a dry-box under an argon atmosphere. The vial was capped and stirred for five minutes, then (*E*)-(5-chloropent-3-en-1-yl)benzene (18.0 mg, 0.1 mmol) was added, followed by cesium fluoride (152.0 mg, 1.0 mmol), and *cis*-crotylboronic acid pinacol ester (21.8 mg, 0.12 mmol). The vial was sealed with a rubber septum, removed from the dry box, and put under nitrogen atmosphere. Then 40 µL of deoxygenated water was added, the septum was replaced with a screw cap, and the reaction was heated to 60 °C and allowed to stir for 14 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (12.9 mg, 64% yield). R_f = 0.63 (pentane, stain in PMA).

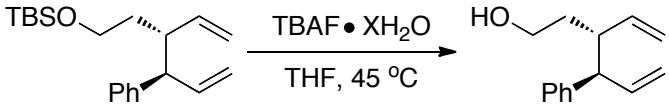
Characterization of Products and Analysis of Stereochemistry



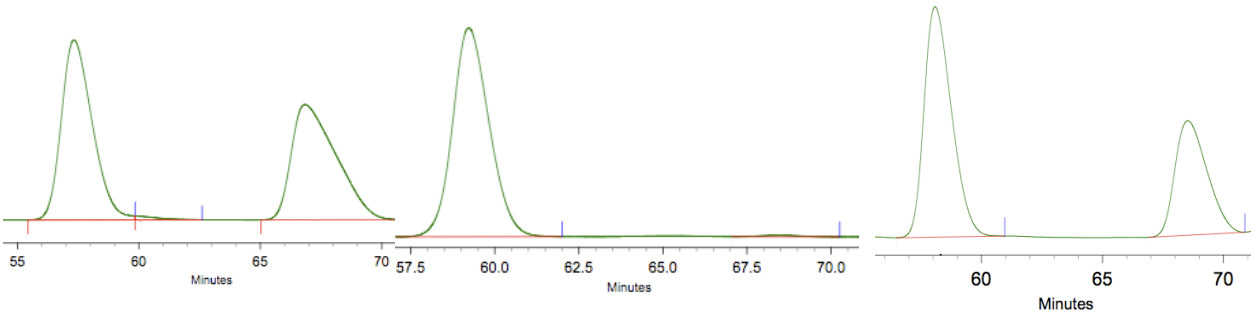
***tert*-butyldimethyl(((3*R*,4*R*)-4-phenyl-3-vinylhex-5-en-1-yl)oxy)silane (Table 2, compound 1).** The title compound was prepared *via* representative procedure A for allyl-allyl coupling, with the following modification: 2.5 mol % $Pd_2(dba)_3$ and 5.0 mol % (*R*)-MeO(furyl)BIPHEP were used. ^{1}H NMR (500 MHz, $CDCl_3$): δ -0.04 (3H, s), -0.02 (3H, s), 0.86 (9H, s), 1.25-1.32 (1H, m), 1.53-1.60 (1H, m), 2.55 (1H, app dq, *J* = 10.0 Hz, 3.5 Hz), 3.19 (1H, app t, *J* = 8.5 Hz), 3.46-3.50 (1H, m), 3.57 (1H, ddd, *J* = 10.0 Hz, 7.5 Hz, 4.5 Hz), 4.94-4.95 (1H, m), 4.97-4.98 (1H, m), 5.02 (1H, app dq, *J* = 10.0 Hz, 1.0 Hz), 5.07 (1H, dd, *J* = 10.5 Hz, 2.0 Hz), 5.55 (1H, ddd, *J* = 17.5 Hz, 10.5 Hz, 9.5 Hz), 5.98 (1H, ddd, *J* = 17.5 Hz, 10.5 Hz, 9.0 Hz), 7.16-7.20 (3H, m), 7.29 (2H, app t, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ -5.4, -5.3, 18.2, 25.9, 35.2, 45.3, 54.8, 60.8, 115.3, 116.2, 126.2, 128.2, 128.3, 140.4, 140.6, 143.1; IR (neat): 2954 (m), 2928 (m), 2894 (w), 2857 (m), 1472 (m), 1418 (w), 1388 (w), 1361 (w), 1255 (s), 1099 (s), 994 (w), 938 (w), 913 (m), 835 (s), 775 (s), 758 (w), 725 (w), 699 (m) cm^{-1}; HRMS-(ESI+) for $C_{20}H_{33}OSi$ [M+H]: calculated: 317.2301, found: 317.2296. $[\alpha]^{22}_D$ = -40.369 (*c* = 1.87, $CHCl_3$, from (*S*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (100:1 pentane:diethyl ether) to afford a clear, colorless oil (41.3 mg, 87% yield). R_f = 0.48 (50:1 pentane:diethyl ether, stain in PMA).

Analysis of Stereochemistry:

The title compound was subjected to TBAF-mediated deprotection of the silyl ether to afford the primary alcohol for HPLC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.



Chiral HPLC (OJ-H, Chiralcel, 0.5 mL/min, 1.5% isopropanol, 220 nm) - analysis of primary alcohol.

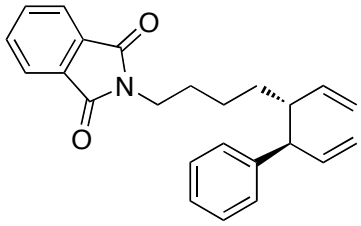


racemic

alcohol from (*S*)-MeO(furyl)BIPHEP

alcohol from allyl-allyl coupling product + racemic co-injection

Retention Time	Area	Area %	Height	Height %
59.223	90773475	99.31	1198525	99.34
68.457	627879	0.69	8012	0.66

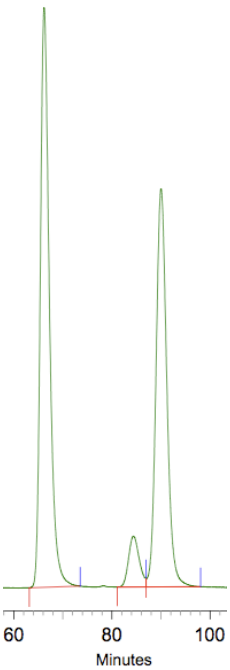


2-((5*R*,6*R*)-6-phenyl-5-vinyloct-7-en-1-yl)isoindoline-1,3-dione (Table 2, compound 2). The title compound was prepared *via* representative procedure A for allyl-allyl coupling, with the following modification: 2.5 mol % $Pd_2(dba)_3$ and 5.0 mol % (*R*)-MeO(furyl)BIPHEP were used. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.10-1.24 (2H, m), 1.26-1.40 (2H, m), 1.45-1.53 (1H, m), 1.56-1.64 (1H, m), 2.33 (1H, app qd, *J* = 9.0 Hz, 3.5 Hz), 3.14 (1H, app t, *J* = 8.5 Hz), 3.58 (2H, t, *J* = 7.5 Hz), 4.90-4.92 (1H, m), 4.93-4.95 (1H, m), 5.00 (1H, app dq, *J* = 10.5 Hz, 1.0 Hz), 5.04 (1H, dd, *J* = 10.5 Hz, 1.5 Hz), 5.51 (1H, ddd, *J* = 17.0 Hz, 10.5 Hz, 9.5 Hz), 5.97 (1H, ddd, *J* = 17.0 Hz, 10.5 Hz, 8.5 Hz), 7.14-7.19 (3H, m), 7.25-7.29 (2H, m), 7.69 (2H, dd, *J* = 5.5 Hz, 3.0 Hz), 7.82 (2H, dd, *J* = 5.5 Hz, 3.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.3, 28.3, 31.8, 37.9, 49.0, 55.0, 115.2, 116.2, 123.1, 126.2, 128.1, 128.4, 132.2, 133.8, 140.6, 143.3, 168.4; IR (neat): 2930 (m), 2860 (w), 1772 (m), 1712 (s), 1639 (w), 1467 (w), 1453 (w), 1437 (w), 1396 (s), 1369 (m), 1168 (w), 1048 (w), 995 (w), 914 (m), 761 (w), 720 (s), 702 (m), 530 (w) cm^{-1}; HRMS-(ESI+) for $C_{24}H_{26}NO_2$ [M+H]: calculated: 360.1964, found: 360.1960. $[\alpha]^{22}_D$ = +34.804 (*c* = 0.57, $CHCl_3$, from (*R*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (20:1 to 15:1 pentane:diethyl ether) to afford a clear, colorless oil (32.5 mg, 76% yield). R_f = 0.15 (16:1 pentane:diethyl ether, stain in PMA).

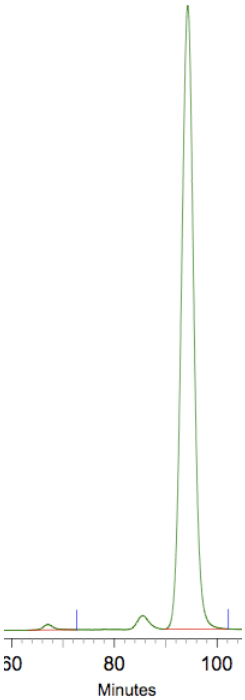
Analysis of Stereochemistry:

Enantioselectivity was determined by HPLC analysis of the title compound as compared to racemic material, prepared by mixing a 1:1 ratio of allyl-allyl coupling products derived from the (*R*) and (*S*) enantiomers of MeO(furyl)BIPHEP. Absolute stereochemistry was assigned by analogy to compounds **7** and **8**.

Chiral HPLC (OJ-H, Chiralcel, 0.5 mL/ min, 1.0% isopropanol, 220 nm) - analysis of title compound.

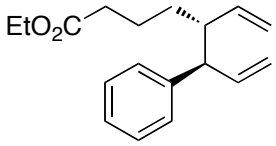


PDT from (S) ligand mixed with PDT from (R)



from (*S*)-MeO(furyl)BIPHEP

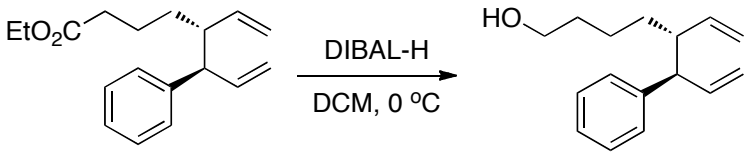
Retention Time	Area	Area %
67.033	6857466	0.75
94.290	908677585	99.25



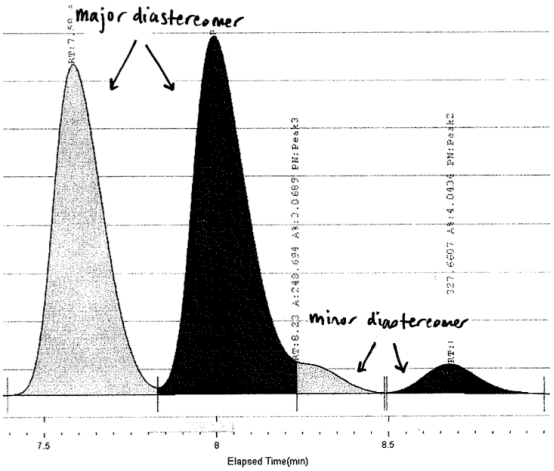
(5*R*,6*R*)-ethyl 6-phenyl-5-vinyloct-7-enoate (Table 2, compound 3). The title compound was prepared *via* representative procedure A for allyl-allyl coupling, with the following modification: 2.5 mol % $Pd_2(dba)_3$ and 5.0 mol % (*R*)-MeO(furyl)BIPHEP were used. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.10-1.17 (1H, m), 1.20 (3H, app t, *J* = 7.0 Hz), 1.22-1.33 (1H, m), 1.42-1.48 (1H, m), 1.62-1.70 (1H, m), 2.11-2.23 (2H, m), 2.34 (1H, app qd, *J* = 9.0 Hz, 3.0 Hz), 3.16 (1H, app t, *J* = 8.5 Hz), 4.06 (2H, q, *J* = 7.5 Hz), 4.91-4.92 (1H, m), 4.95-4.96 (1H, m), 4.99-5.03 (1H, m), 5.09 (1H, dd, *J* = 10.0 Hz, 1.5 Hz), 5.54 (1H, ddd, *J* = 17.5 Hz, 10.5 Hz, 9.5 Hz), 5.97 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 8.5 Hz), 7.15-7.21 (3H, m), 7.29 (2H, app t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 22.6, 31.8, 34.2, 49.1, 54.9, 60.1, 115.3, 116.4, 126.2, 128.1, 128.4, 140.4, 140.5, 143.2, 173.6; IR (neat): 3077 (w), 2978 (w), 2928 (w), 1733 (s), 1638 (w), 1373 (w), 1246 (w), 1164 (m), 1076 (w), 994 (w), 913 (m), 759 (w), 701 (s) cm^{-1}; HRMS-(ESI+) for $C_{18}H_{25}O_2$ [M+H]: calculated: 273.1854, found: 273.1844. $[\alpha]^{22}_D$ = -51.664 (*c* = 0.60, $CHCl_3$, from (*S*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (40:1 pentane:diethyl ether) to afford a clear, colorless oil (31.5 mg, 77% yield). R_f = 0.31 (40:1 pentane:diethyl ether, stain in PMA).

Analysis of Stereochemistry:

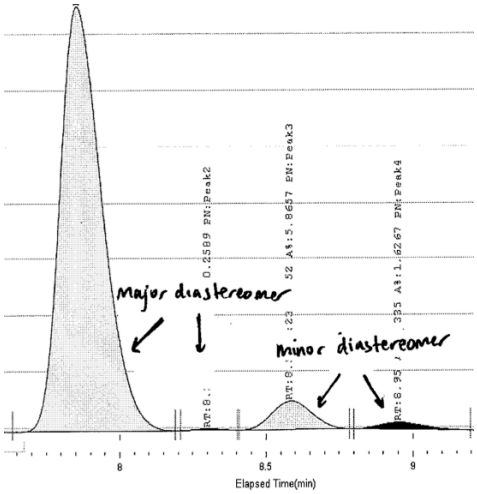
The title compound was subjected to DIBAL-H reduction to afford the primary alcohol for SFC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.



Chiral SFC (AD-H, Chiralpak, 215 nm, 2.0 mL/min, 3.0% MeOH, 100 bar, 35 °C) - analysis of primary alcohol.

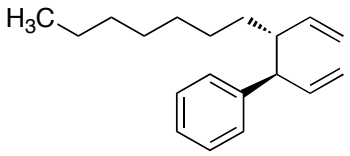


racemic



from (*S*)-MeO(furyl)BIPHEP

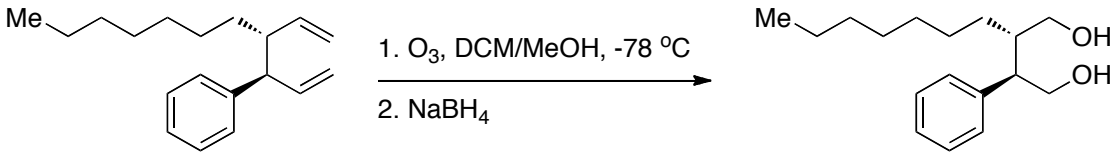
Peak No	% Area	Area	RT (min)
1	92.2487	3761.7756	7.85
2	0.2589	10.5558	8.3
3	5.8657	239.1952	8.58
4	1.6267	66.335	8.95



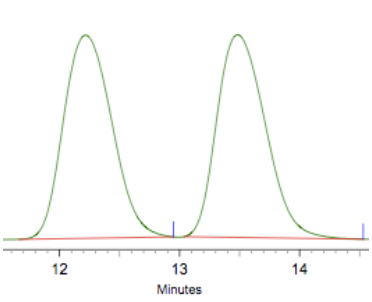
((3*R*,4*R*)-4-vinylundec-1-en-3-yl)benzene (Table 2, compound 4). The title compound was prepared *via* representative procedure A for allyl-allyl coupling, with the following modification: 2.5 mol % $Pd_2(dba)_3$ and 5.0 mol % (*R*)-MeO(furyl)BIPHEP were used. ^1H NMR (500 MHz, $CDCl_3$): δ 0.86 (3H, t, *J* = 6.5 Hz), 1.07-1.28 (12H, m), 2.33 (1H, app dq, *J* = 9.0 Hz, 3.0 Hz), 3.17 (1H, app t, *J* = 8.5 Hz), 4.92-4.97 (2H, m), 5.01 (1H, ddd, *J* = 10.5 Hz, 2.0 Hz, 1.0 Hz), 5.06 (1H, dd, *J* = 10.5 Hz, 2.0 Hz), 5.55 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 9.0 Hz), 5.99 (1H, ddd, *J* = 17.0 Hz, 10.5 Hz, 8.5 Hz), 7.16-7.28 (3H, m), 7.30 (2H, app t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 22.6, 27.0, 29.2, 29.4, 31.8, 32.3, 49.2, 55.0, 115.1, 115.8, 126.1, 128.1, 128.3, 140.7, 141.0, 143.5; IR (neat): 3077 (w), 2977 (m), 2928 (m), 1733 (s), 1638 (w), 1452 (w), 1419 (w), 1372 (w), 1246 (w), 1164 (m), 1115 (w), 1031 (w), 994 (w), 913 (m), 759 (w), 729 (w), 701 (s) cm^{-1}; HRMS-(ESI+) for $C_{19}H_{29}$ [M+H]: calculated: 257.2269, found: 257.2276. $[\alpha]^{22}_D$ = -52.976 (*c* = 0.87, $CHCl_3$, from (*S*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (27.3 mg, 71% yield). R_f = 0.43 (pentane, stain in PMA).

Analysis of Stereochemistry:

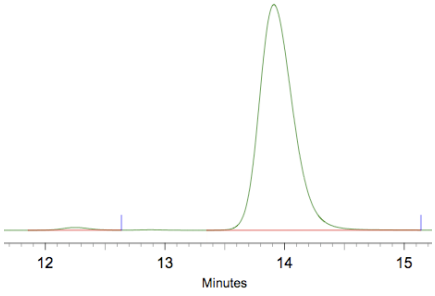
The title compound was subjected to ozonolysis and reduction to afford the 1,4-diol for HPLC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.



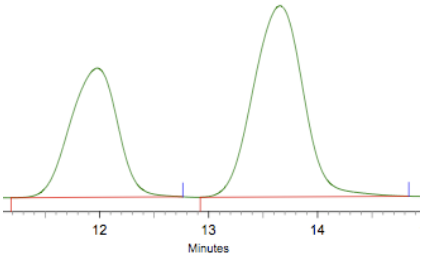
Chiral HPLC (OJ-H, Chiralcel, 0.5 mL/min, 5.0% isopropanol, 217 nm) - analysis of 1,4-diol.



racemic

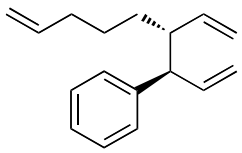


diol from (*S*)-MeO(furyl)BIPHEP



diol from allyl-allyl coupling product + racemic co-injection

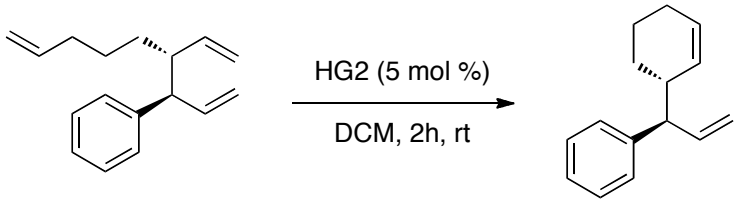
Retention Time	Area	Area %	Height	Height %
12.250	2095438	0.98	130102	1.20
13.910	211932281	99.02	10754123	98.80



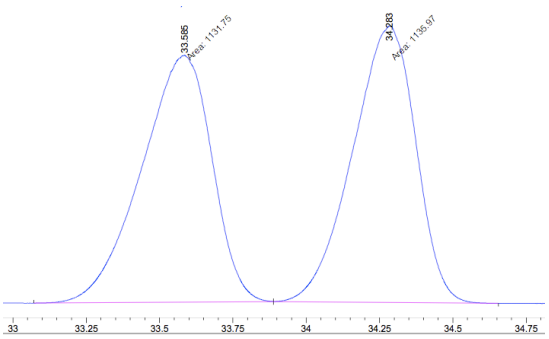
((3*R*,4*R*)-4-vinylnona-1,8-dien-3-yl)benzene (Table 2, compound 5). The title compound was prepared *via* representative procedure A for allyl-allyl coupling, with the following modification: 2.5 mol % $Pd_2(dba)_3$ and 5.0 mol % (*R*)-MeO(furyl)BIPHEP were used. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.10-1.17 (1H, m), 1.19-1.33 (2H, m), 1.36-1.44 (1H, m), 1.86-1.92 (1H, m), 1.94-2.01 (1H, m), 2.34 (1H, app qd, *J* = 9.5 Hz, 3.5 Hz), 3.17 (1H, app t, *J* = 8.5 Hz), 4.88 (1H, app dp, *J* = 10.5 Hz, 1.0 Hz), 4.90-4.94 (3H, m), 5.02 (1H, dd, *J* = 10.0 Hz, 1.5 Hz), 5.07 (1H, dd, *J* = 10.0 Hz, 2.0 Hz), 5.55 (1H, ddd, *J* = 17.5 Hz, 10.5 Hz, 9.5 Hz), 5.72 (1H, app ddt, *J* = 17.0 Hz, 10.0 Hz, 6.5 Hz), 5.99 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 8.5 Hz), 7.16-7.21 (3H, m), 7.30 (2H, app t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.4, 31.9, 33.6, 49.1, 55.0, 114.2, 115.2, 116.0, 126.1, 128.1, 128.3, 138.9, 140.6, 140.8, 143.4; IR (neat): 3076 (w), 2976 (w), 2927 (m), 2856 (w), 1639 (m), 1494 (w), 1452 (w), 1417 (w), 993 (m), 966 (w), 911 (s), 759 (m), 700 (s) cm^{-1}; HRMS-(ESI+) for $C_{17}H_{23}$ [M+H]: calculated: 227.1800, found: 227.1809. $[\alpha]^{22}_D$ = -59.585 (*c* = 0.39, $CHCl_3$, from (*S*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (18.3 mg, 54% yield). R_f = 0.39 (pentane, stain in PMA).

Analysis of Stereochemistry:

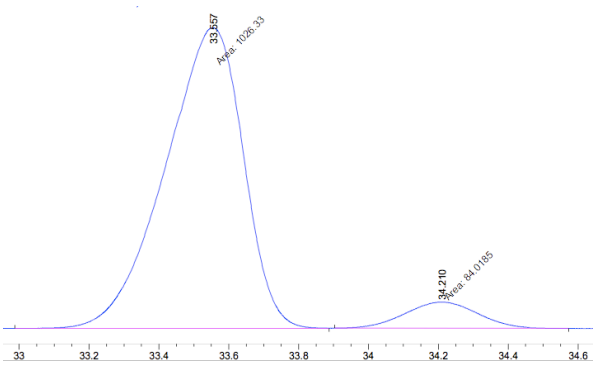
The title compound was treated with Hoveyda-Grubbs second generation catalyst to afford the ring closing metathesis product for GC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.



Chiral GLC (β-dex, Supelco, 135 °C, 20 psi) - analysis of the metathesis product.

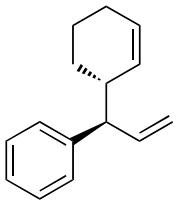


racemic

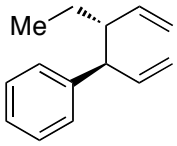


from (*S*)-MeO(furyl)BIPHEP

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	33.557	MM	0.2584	1026.32739	66.20870	92.43313
2	34.210	MM	0.2432	84.01846	5.75815	7.56687



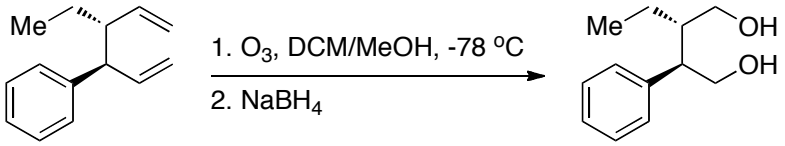
((*R*)-1-((*R*)-cyclohex-2-en-1-yl)allyl)benzene (Compound SI-9). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.09-1.16 (1H, m), 1.41-1.50 (2H, m), 1.66-1.70 (1H, m), 1.95-1.99 (2H, m), 2.42-2.47 (1H, m), 3.04 (1H, app t, *J* = 9.0 Hz), 5.05-5.10 (2H, m), 5.73-5.80 (2H, m), 6.02 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 9.0 Hz), 7.17-7.21 (3H, m), 7.30 (2H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.6, 25.4, 27.7, 39.7, 56.2, 115.6, 126.1, 127.8, 128.1, 128.4, 129.5, 140.6, 143.7; IR (neat): 3025 (w), 2924 (s), 2857 (m), 1713 (w), 1492 (w), 1452 (w), 992 (w), 968 (w), 915 (m), 758 (w), 724 (m), 700 (s) cm^{-1}; HRMS-(ESI+) for $C_{15}H_{19}$ [M+H]: calculated: 199.1487, found: 199.1485. $[\alpha]^{22}_{D}$ = -12.409 (*c* = 0.32, $CHCl_3$, from (*S*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (10.1 mg, 62% yield). R_f = 0.50 (pentane, stain in $KMnO_4$).



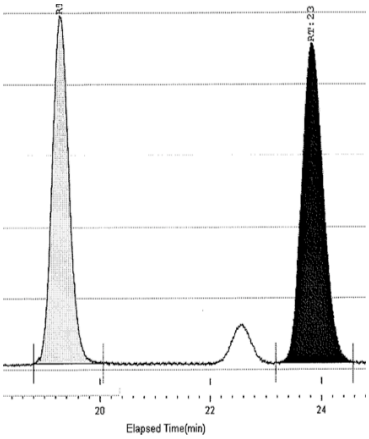
((3*R*,4*R*)-4-ethylhexa-1,5-dien-3-yl)benzene (Table 2, compound 6). The title compound was prepared *via* representative procedure A for allyl-allyl coupling, with the following modification: 2.5 mol % $Pd_2(dba)_3$ and 5.0 mol % (*R*)-MeO(furyl)BIPHEP were used. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.79 (3H, td, *J* = 7.0 Hz, 1.0 Hz), 1.10 (1H, app ddt, *J* = 16.5 Hz, 14.0 Hz, 6.5 Hz), 1.35 (1H, app ddq, *J* = 7.5 Hz, 3.5 Hz, 1.0 Hz), 2.25 (1H, app dq, *J* = 9.0 Hz, 4.0 Hz), 3.19 (1H, app t, *J* = 8.5 Hz), 4.94 (1H, app dt, *J* = 13.0 Hz, 1.0 Hz), 4.97 (1H, app dt, *J* = 13.0 Hz, 1.0 Hz), 5.01 (1H, app dt, *J* = 10.5 Hz, 1.0 Hz), 5.08 (1H, dd, *J* = 10.0 Hz, 1.5 Hz), 5.50 (1H, dtd, *J* = 17.5 Hz, 010.0 Hz, 1.0 Hz), 6.00 (1H, dtd, *J* = 17.5 Hz, 9.5 Hz, 1.0 Hz), 7.17-7.21 (3H, m), 7.30 (2H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.6, 25.2, 51.1, 54.8, 115.1, 116.0, 126.1, 128.1, 128.3, 140.7, 140.8, 143.5; IR (neat): 3078 (m), 3028 (w), 2974 (m), 2927 (w), 2886 (w), 1639 (m), 1601 (w), 1493 (m), 1453 (w), 1416 (w), 1372 (w), 1072 (w), 1030 (m), 992 (w), 911 (s), 758 (m), 722 (w), 670 (s), 527 (w) cm^{-1}; HRMS-(ESI+) for $C_{14}H_{19}$ [M+H]: calculated: 187.1487, found: 187.1487. $[\alpha]^{22}_D$ = +63.112 (*c* = 0.41, $CHCl_3$, from (*R*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (22.6 mg, 81% yield). R_f = 0.49 (pentane, stain in PMA).

Analysis of Stereochemistry:

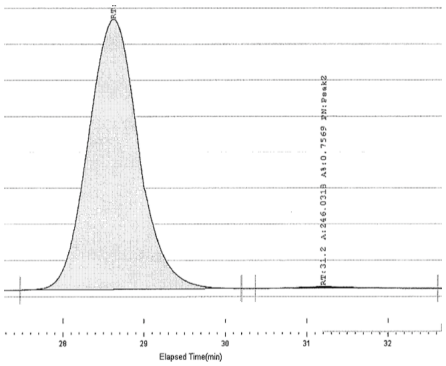
The title compound was subjected to ozonolysis and reduction to afford the 1,4-diol for SFC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.



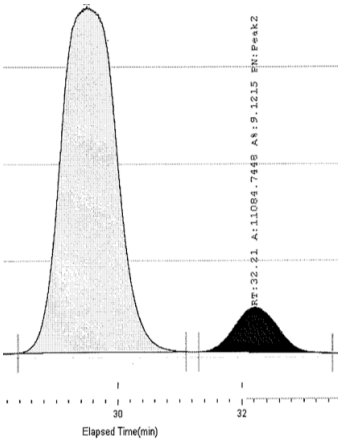
Chiral SFC (AD-H, Chiralpak, total absorbance, 5.0 mL/min, 2.0% MeOH, 100 bar, 35 °C) - analysis of 1,4-diol.



racemic



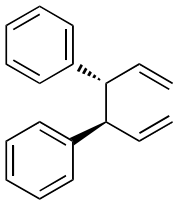
diol from (*R*)-MeO(furyl)BIPHEP



diol from allyl-allyl coupling product + racemic co-injection

Peak Info

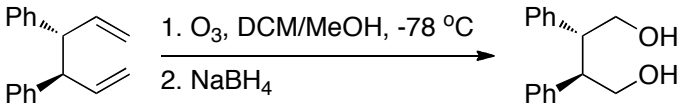
Peak No	% Area	Area	RT (min)
1	99.2431	32259.3864	28.61
2	0.7569	246.0318	31.2
Total:	100	32505.4182	



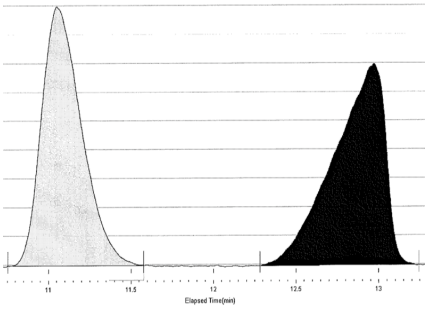
(3*R*,4*R*)-hexa-1,5-diene-3,4-diyldibenzene (Table 2, compound 7). The title compound was prepared *via* representative procedure A for allyl-allyl coupling, with the following modification: the reaction was run at 60 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.64 (2H, dd, *J* = 8.0 Hz, 2.0 Hz), 5.04 (2H, ddd, *J* = 17.0 Hz, 1.5 Hz, 0.5 Hz), 5.11 (2H, ddd, *J* = 10.5 Hz, 1.5 Hz, 0.5 Hz), 6.06-6.17 (2H, m), 7.02-7.37 (10H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.8, 115.8, 126.0, 128.1, 128.2, 140.5, 142.6; IR (neat): 3080 (w), 3062 (w), 3027 (m), 2922 (w), 1637 (w), 1600 (w), 1494 (m), 1452 (m), 1073 (w), 990 (w), 965 (w), 915 (m), 756 (m), 698 (s), 515 (w) cm^{-1}; HRMS-(ESI+) for $C_{18}H_{19}$ [M+H]: calculated: 235.1489, found: 235.1481. $[\alpha]^{22}_D$ = +54.233 (*c* = 0.55, $CHCl_3$, from (*R*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (18.8 mg, 80% yield). R_f = 0.13 (pentane, stain in $KMnO_4$).

Proof of Stereochemistry:

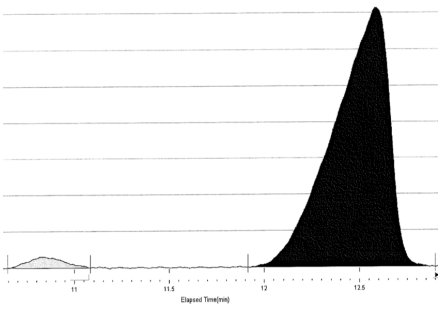
The title compound was subjected to ozonolysis and reduction to afford the 1,4-diol for SFC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. In order to determine the absolute stereochemistry, the optical rotation of the 1,4-diol derived from the allyl-allyl coupling product ($[\alpha]^{20}_D$ = -42.144 (*c* = 0.335, $CHCl_3$, from (*R*)-MeO(furyl)BIPHEP)) was compared to the rotation of authentic (2*R*,3*R*)-2,3-diphenylbutane-1,4-diol ($[\alpha]^{25}_D$ = -48.2 (*c* = 0.249, $CHCl_3$)) as previously reported in the literature.[8]



Chiral SFC (AD-H, Chiralpak, total absorbance, 5.0 mL/min, 5.0% MeOH, 100 bar, 35 °C) - analysis of 1,4-diol.



racemic

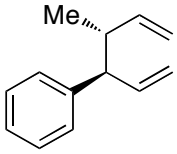


from (*R*)-MeO(furyl)BIPHEP

Peak Name	Number	Concentration	Area %
Peak1	1	0	2.6577
Peak2	2	0	97.3423

RT (min)	St. (min)	End (min)	Height
10.84	10.6452	11.0803	6.0307
12.59	11.9138	12.8974	143.0457

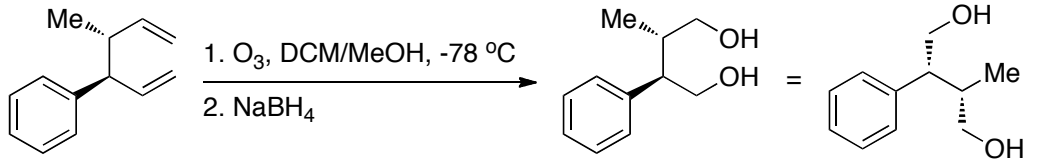
[8] Periasamy, M.; Ramani, G.; Muthukumaragopal, G. P. *Synthesis* **2009**, *10*, 1739.

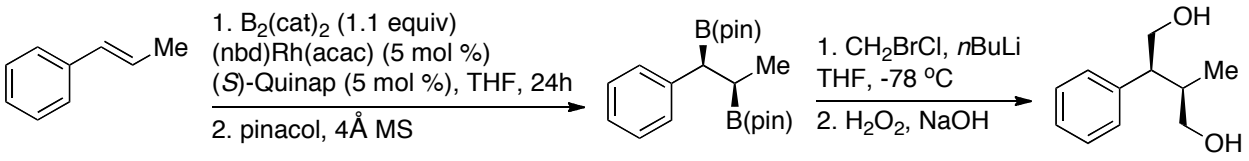


((3*R*,4*R*)-4-methylhexa-1,5-dien-3-yl)benzene (Table 2, compound 8). The title compound was prepared *via* representative procedure A for allyl-allyl coupling. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, d, *J* = 6.5 Hz), 2.53 (1H, br app hextet, *J* = 8.0 Hz), 3.08 (1H, app t, *J* = 8.0 Hz), 4.97 (1H, ddd, *J* = 14.5 Hz, 2.0 Hz, 1.0 Hz), 4.99 (1H, ddd, *J* = 4.5 Hz, 1.5 Hz, 0.5 Hz), 5.02-5.04 (2H, m) 5.77 (1H, ddd, *J* = 16.5 Hz, 11.0 Hz, 8.0 Hz), 6.01 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 8.5 Hz), 7.16-7.22 (3H, m), 7.30 (2H, app tt, *J* = 7.0 Hz, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.6, 42.8, 56.3, 114.0, 115.3, 126.2, 128.1, 128.3, 140.6, 142.5, 143.4; IR (neat): 3077 (w), 3028 (w), 2963 (m), 2931 (w), 2874 (w), 1639 (w), 1601 (w), 1494 (m), 1453 (w), 1418 (w), 1379 (w), 1073 (w), 1030 (w), 993 (m), 911 (s), 757 (w), 727 (m), 699 (s), 525 (w) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{17}$ [M+H]: calculated: 173.1330, found: 173.1337. $[\alpha]^{22}_D$ = +35.997 (*c* = 0.36, $CHCl_3$, from (*R*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (15.6 mg, 90% yield). R_f = 0.56 (pentane, stain in PMA).

Proof of Stereochemistry:

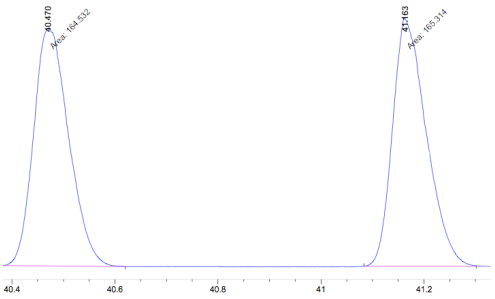
Enantioselectivity was determined by GLC analysis of the title compound as compared to racemic material prepared by using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. Absolute stereochemistry was determined by subjecting the allyl-allyl coupling product to a ozonolysis and reduction to afford a 1,4-diol for HPLC analysis, as shown below. The resulting diol was compared to authentic (2*R*,3*S*)-2-methyl-3-phenylbutane-1,4-diol, prepared by diboration, homologation, and oxidation of β-methylstyrene, as shown below, using chiral HPLC analysis, t.[9]



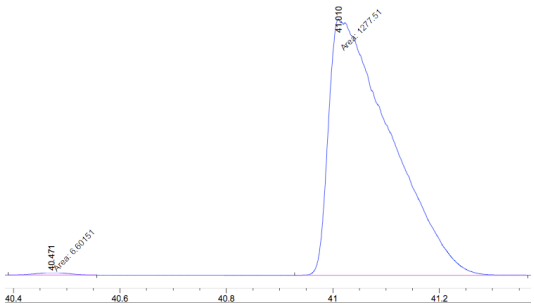


[9] Morgan, J. B.; Miller, S. P.; Morken, J. P. *J. Am. Chem. Soc.* **2003**, *125*, 8702.

Chiral GLC (CD-BDM, Supelco, 50 °C for 20 min, ramp 2.5 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.



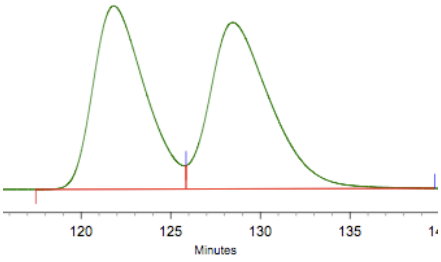
racemic



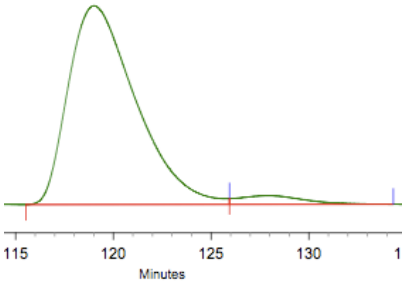
from (*R*)-MeO(furyl)BIPHEP

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	40.471	MM	0.0707	6.60151	1.55683	0.51409
2	41.010	MM	0.1345	1277.50818	158.34184	99.48591

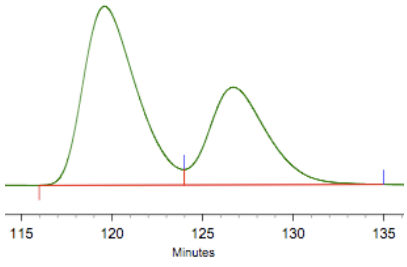
Chiral HPLC (OD-R, Chiralcel, 0.25 mL/min, 3.0% isopropanol, 217 nm) - analysis of 1,4-diol.



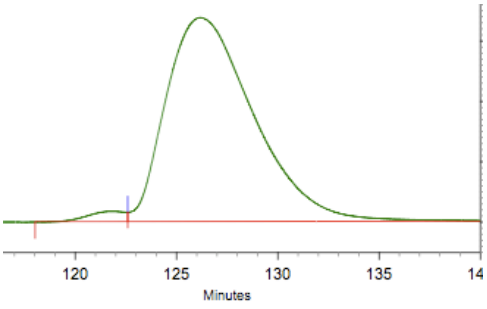
racemic



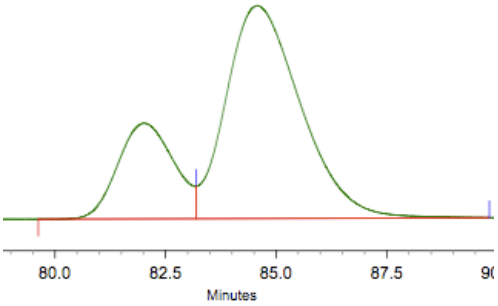
diol from allyl-allyl coupling product; with (*R*)-MeO(furyl)BIPHEP



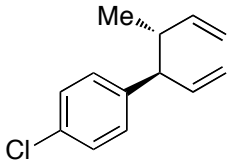
diol from allyl-allyl coupling product + racemic co-injection



diol from alkene diboration; with (*S*)-Quinap



diol from alkene diboration + racemic co-injection

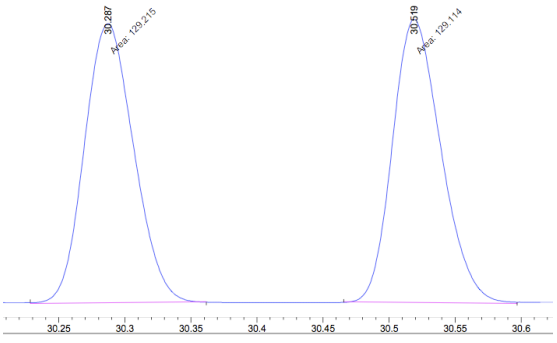


1-chloro-4-((3*R*,4*R*)-4-methylhexa-1,5-dien-3-yl)benzene (Table 2, compound 9). The title compound was prepared *via* representative procedure A for allyl-allyl coupling. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, d, *J* = 7.0 Hz), 2.49 (1H, br app hextet, *J* = 7.5 Hz), 3.07 (1H, app t, *J* = 8.0 Hz), 4.94-5.08 (4H, m), 5.74 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 7.5 Hz), 5.97 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 8.5 Hz), 7.09-7.12 (2H, m), 7.26-7.28 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.5, 42.8, 55.5, 114.4, 115.8, 128.5, 129.5, 131.8, 140.0, 141.8, 142.0; IR (neat): 3079 (w), 2975 (w), 2926 (w), 1639 (m), 1491 (s), 1455 (w), 1406 (w), 1373 (s), 1299 (w), 1092 (s), 1015 (m), 992 (m), 913 (s), 817 (m), 726 (w), 680 (w), 625 (w), 562 (w), 524 (w) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{16}Cl$ [M+H]: calculated: 207.0941, found: 207.0948. $[\alpha]^{22}_D$ = +97.733 (*c* = 0.67, $CHCl_3$, from (*R*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (19.9 mg, 96% yield). R_f = 0.76 (pentane, stain in PMA).

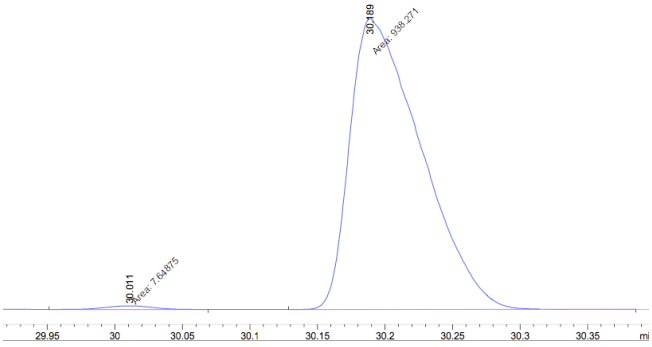
Analysis of Stereochemistry:

Enantioselectivity was determined by GLC analysis of the title compound as compared to racemic material, prepared by using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.

Chiral GLC (CD-BDM, Supelco, 50 °C for 10 min, ramp 5 °C/min to 160 °C for 60 min, 20 psi) - analysis of title compound.

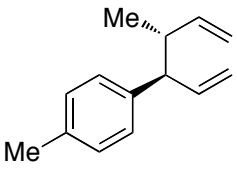


racemic



from (*R*)-MeO(furyl)BIPHEP

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	30.011	MM	0.0402	7.64875	3.17182	0.80860
2	30.189	MM	0.0611	938.27069	255.81476	99.19140

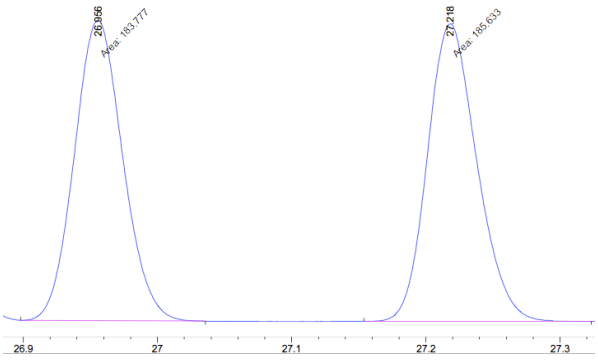


1-methyl-4-((3*R*,4*R*)-4-methylhexa-1,5-dien-3-yl)benzene (Table 2, compound 10). The title compound was prepared *via* representative procedure A for allyl-allyl coupling. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, dd, *J* = 7.0 Hz, 1.0 Hz), 2.32 (3H, s), 2.51 (1H, br app hextet, *J* = 7.5 Hz), 3.07 (1H, app t, *J* = 8.0 Hz), 4.84-5.05 (4H, m), 5.77 (1H, dddd, *J* = 17.5 Hz, 10.5 Hz, 9.0 Hz, 1.0 Hz), 5.99 (1H, dddd, *J* = 17.0 Hz, 10.0 Hz, 9.0 Hz, 1.0 Hz), 7.04-7.12 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.6, 21.0, 42.7, 55.9, 113.9, 115.1, 127.9, 129.0, 135.6, 140.3, 140.8, 142.7; IR (neat): 3077 (w), 2974 (m), 2961 (m), 2924 (w), 2868 (w), 1638 (m), 1513 (m), 1455 (w), 1416 (w), 1372 (w), 1110 (w), 992 (m), 911 (s), 810 (m), 722 (w), 528 (w) cm^{-1}; HRMS-(ESI+) for $C_{14}H_{19}$ [M+H]: calculated: 187.1487, found: 187.1479. $[\alpha]^{22}_{D}$ = +114.360 (*c* = 0.57, $CHCl_3$, from (*R*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (17.4 mg, 93% yield). R_f = 0.60 (pentane, stain in PMA).

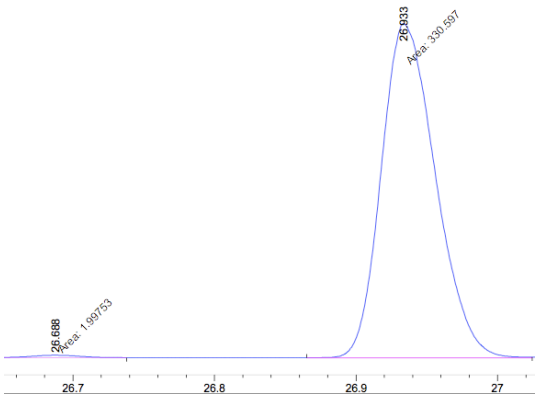
Analysis of Stereochemistry:

Enantioselectivity was determined by GLC analysis of the title compound as compared to racemic material, prepared by using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.

Chiral GLC (CD-BDM, Supelco, 50 °C for 10 min, ramp 5 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.

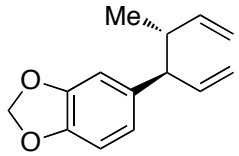


racemic



from (*R*)-MeO(furyl)BIPHEP

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.688	MM	0.0379	1.99753	8.78039e-1	0.60059
2	26.933	MF	0.0442	330.59680	124.62852	99.39941

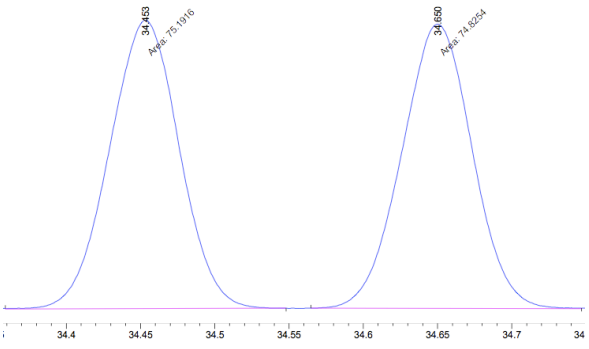


5-((3*R*,4*R*)-4-methylhexa-1,5-dien-3-yl)benzo[*d*][1,3]dioxole (Table 2, compound 11). The title compound was prepared *via* representative procedure A for allyl-allyl coupling, with the following modification: the reaction was run at 60 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, d, *J* = 6.5 Hz), 2.45 (1H, br app hextet, *J* = 7.5 Hz), 3.00 (1H, app t, *J* = 8.5 Hz), 4.94-5.05 (4H, m), 5.71-5.79 (1H, m), 5.91-5.98 (1H, m), 5.93 (2H, s), 6.62 (1H, ddd, *J* = 7.5 Hz, 1.5 Hz, 0.5 Hz), 6.68 (1H, d, *J* = 2.0 Hz), 6.74 (1H, d, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.5, 42.9, 55.9, 100.8, 108.0, 108.1, 108.3, 114.0, 115.2, 121.1, 131.3, 140.6, 142.5, 147.6; IR (neat): 3076 (w), 2974 (w), 2924 (w), 2891 (m), 1638 (w), 1504 (m), 1487 (s), 1441 (m), 1041 (s), 994 (w), 934 (m), 914 (m), 816 (w), 808 (m), 686 (w) cm^{-1}; HRMS-(ESI+) for $C_{14}H_{17}O_2$ [M +H]: calculated: 217.1229, found: 217.1239. $[\alpha]^{22}_D$ = +75.827 (*c* = 0.49, $CHCl_3$, from (*R*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (50:1 pentane:diethyl ether) to afford a clear, colorless oil (18.2 mg, 84% yield). R_f = 0.67 (50:1 pentane:diethyl ether, stain in PMA).

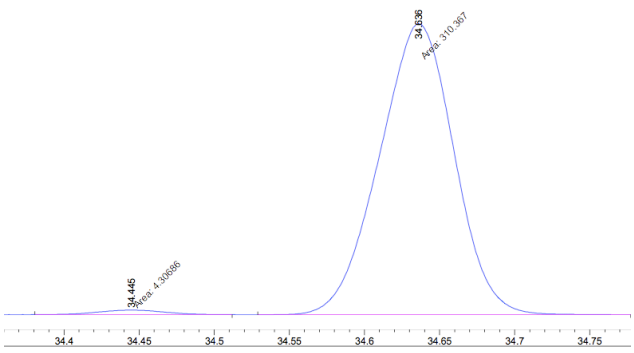
Analysis of Stereochemistry:

Enantioselectivity was determined by GLC analysis of the title compound as compared to racemic material, prepared by using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.

Chiral GLC (CD-BDM, Supelco, 50 °C for 10 min, ramp 5 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.

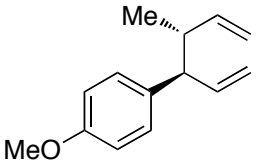


racemic



from (*R*)-MeO(furyl)BIPHEP

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	34.445	MM	0.0513	4.30686	1.40058	1.36867
2	34.636	MM	0.0575	310.36737	89.95261	98.63133

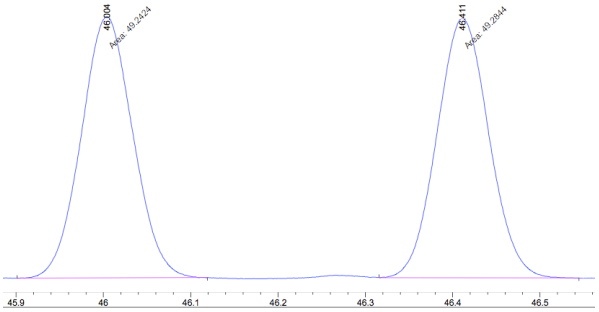


1-methoxy-4-((3*R*,4*R*)-4-methylhexa-1,5-dien-3-yl)benzene (Table 2, compound 12). The title compound was prepared *via* representative procedure A for allyl-allyl coupling, with the following modification: the reaction was run at 60 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (3H, d, *J* = 6.5 Hz), 2.49 (1H, br app hextet, *J* = 7.0 Hz), 3.04 (1H, app t, *J* = 8.0 Hz), 3.79 (3H, s), 4.93-5.05 (4H, m), 5.31-5.78 (1H, m), 5.99 (1H, ddd, *J* = 10.5 Hz, 8.5 Hz, 2.0 Hz), 6.82-6.86 (2H, m), 7.06-7.13 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.5, 42.9, 55.2, 55.3, 113.8, 113.9, 115.0, 115.1, 129.0, 135.4, 140.7, 140.9; IR (neat): 3076 (w), 2959 (w), 2932 (m), 2835 (w), 1638 (w), 1610 (m), 1583 (w), 1510 (s), 1464 (w), 1302 (w), 1245 (s), 1178 (m), 1107 (w), 1037 (m), 993 (m), 910 (s), 824 (m), 778 (w), 678 (w), 648 (w), 540 (w) cm^{-1}; HRMS-(ESI+) for $C_{14}H_{19}O$ [M+H]: calculated: 203.1436, found: 203.1441. $[\alpha]^{22}_{D}$ = +96.204 (*c* = 1.84, $CHCl_3$, from (*R*)-MeO(furyl)BIPHEP). The crude reaction mixture was purified on silica gel (50:1 pentane:diethyl ether) to afford a clear, colorless oil (17.1 mg, 84% yield). R_f = 0.84 (50:1 pentane:diethyl ether, stain in PMA).

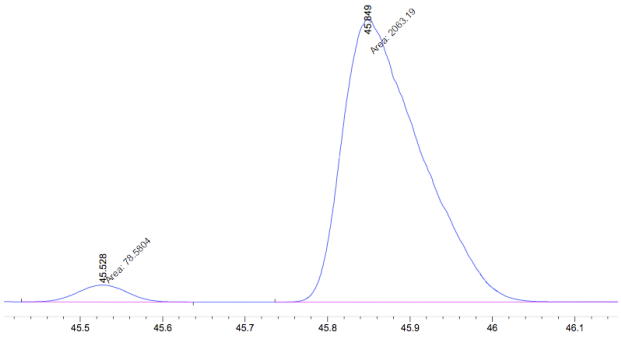
Analysis of Stereochemistry:

Enantioselectivity was determined by GLC analysis of the title compound as compared to racemic material, prepared by using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.

Chiral GLC (CD-BDM, Supelco, 50 °C for 10 min, ramp 2.5 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.

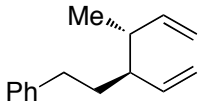


racemic



from (*R*)-MeO(furyl)BIPHEP

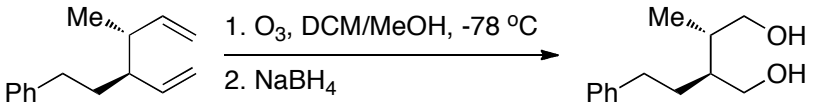
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	45.528	MM	0.0695	78.58038	18.84259	3.66894
2	45.849	MM	0.1095	2063.19287	313.92480	96.33106



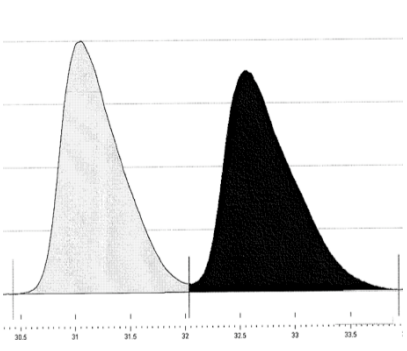
((3*R*,4*R*)-4-methyl-3-vinylhex-5-en-1-yl)benzene (Table 2, compound 13). The title compound was prepared *via* representative procedure B for allyl-allyl coupling. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.98 (3H, d, *J* = 7.0 Hz), 1.54-1.62 (1H, m), 1.72 (1H, app dtd, *J* = 17.5 Hz, 6.5 Hz, 4.0 Hz), 1.99 (1H, app heptet, *J* = 5.0 Hz), 2.21-2.27 (1H, m), 2.49 (1H, ddd, *J* = 13.5 Hz, 10.5 Hz, 6.5 Hz), 2.65 (1H, ddd, *J* = 14.0 Hz, 10.5 Hz, 5.0 Hz), 4.94-5.03 (3H, m), 5.11 (1H, dd, *J* = 10.0 Hz, 2.0 Hz), 5.61 (1H, app dt, *J* = 17.5 Hz, 10.0 Hz), 5.72 (1H, ddd, *J* = 16.5 Hz, 11.0 Hz, 8.0 Hz), 7.15-7.18 (2H, m), 7.25-7.29 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.7, 33.8, 34.0, 41.7, 49.0, 114.0, 116.2, 125.6, 128.2, 128.2, 128.4, 139.9, 141.6; IR (neat): 3075 (w), 3027 (w), 3000 (w), 2962 (m), 2925 (m), 2865 (m), 1639 (w), 1604 (w), 1496 (m), 1454 (m), 1422 (w), 1373 (w), 1030 (w), 996 (m), 912 (s), 748 (m), 698 (s) cm^{-1}; HRMS-(ESI+) for $C_{15}H_{21}$ [M+H]: calculated: 201.1643, found: 201.1645. $[\alpha]^{22}_D$ = +9.586 (*c* = 0.63, $CHCl_3$, from (*R*,*R*)-QuinoxP*). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (12.9 mg, 64% yield). R_f = 0.63 (pentane, stain in PMA).

Analysis of Stereochemistry:

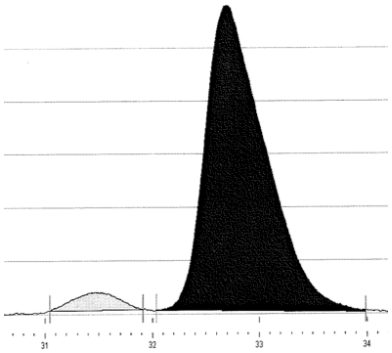
The title compound was subjected to ozonolysis and reduction to afford the 1,4-diol for SFC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.



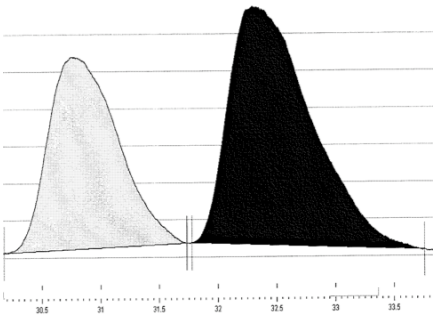
Chiral SFC (OJ-H, Chiralpak, total absorbance, 3.0 mL/min, 2.0% MeOH, 100 bar, 35 °C) - analysis of 1,4-diol.



racemic

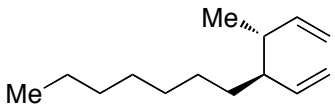


diol derived from allyl-allyl coupling product; from (*R*,*R*)-QuinoxP*



diol from allyl-allyl coupling product + racemic co-injection

Peak Name	Area %	Area	RT (min)
Peak1	4.2855	201.1763	31.46
Peak2	95.7145	4493.226	32.7

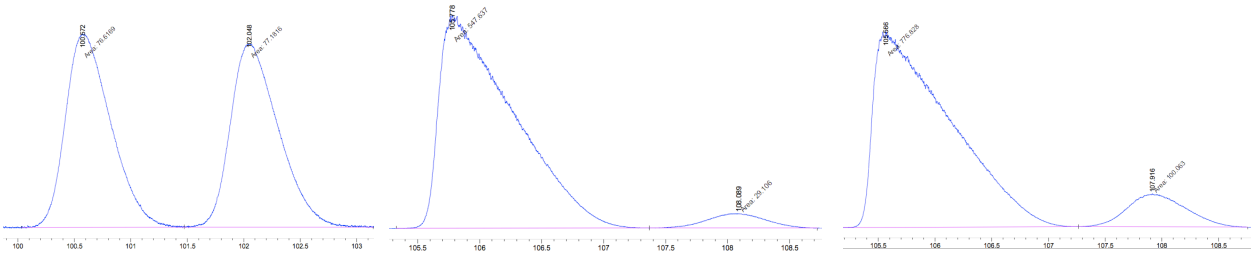


(3*R*,4*R*)-3-methyl-4-vinylundec-1-ene (Table 2, compound 14). The title compound was prepared *via* representative procedure B for allyl-allyl coupling. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, t, *J* = 6.5 Hz), 0.97 (3H, dd, *J* = 6.5 Hz, 0.5 Hz), 1.19-1.39 (12H, m), 1.90 (1H, app heptet, *J* = 4.5 Hz), 2.20 (1H, app hextet, *J* = 7.0 Hz), 4.92-4.94 (1H, m), 4.95-4.97 (2H, m), 5.01 (1H, dd, *J* = 10.5 Hz, 2.0 Hz), 5.45 (1H, app dt, *J* = 17.0 Hz, 10.0 Hz), 5.73 (1H, dddd, *J* = 17.0 Hz, 10.5 Hz, 8.0 Hz, 0.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 17.7, 22.7, 27.5, 29.3, 29.7, 31.9, 32.0, 41.6, 49.5, 113.7, 115.4, 140.6, 141.9; IR (neat): 2958 (m), 2924 (s), 2854 (m), 1462 (w), 911 (w), 455 (w) cm^{-1}; HRMS-(ESI+) for $C_{14}H_{27}$ [M+H]: calculated: 195.2112, found: 195.2114. $[\alpha]^{22}_{D}$ = -3.140 (*c* = 0.45, $CHCl_3$, from (*R*,*R*)-QuinoxP*). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (13.1 mg, 67% yield). R_f = 0.95 (pentane, stain in PMA).

Analysis of Stereochemistry:

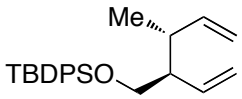
Enantioselectivity was determined by GLC analysis of the title compound as compared to racemic material, prepared by using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.

Chiral GLC (CD-BDM, Supelco, 50 °C for 10 min, ramp 0.25 °C/min to 80 °C for 80 min, 20 psi) - analysis of title compound.



racemic | from (*R*,*R*)-QuinoxP* | allyl-allyl coupling product + racemic spike

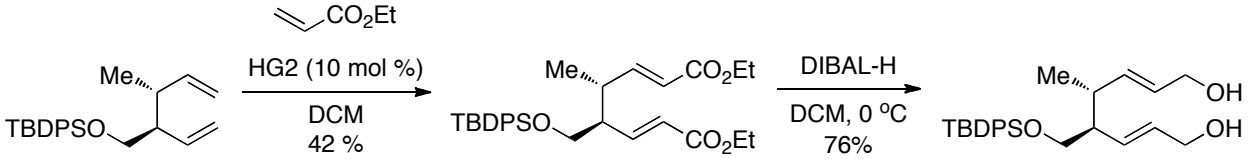
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	105.778	MM	0.6886	547.63739	13.25515	94.95339
2	108.089	MM	0.5416	29.10597	8.95651e-1	5.04661



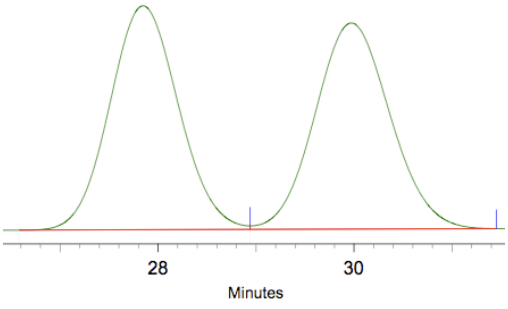
***tert*-butyl(((2*R*,3*R*)-3-methyl-2-vinylpent-4-en-1-yl)oxy)diphenylsilane (Table 2, compound 15).** The title compound was prepared *via* representative procedure A for allyl-allyl coupling, with the following modification: 2.5 mol % $Pd_2(dba)_3$ and 5.0 mol % (*R,R*)-QuinoxP* were used, and the reaction was run at 60°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.99 (3H, d, *J* = 7.0 Hz), 1.06 (9H, s), 2.18-2.21 (1H, m), 2.58 (1H, app hextet, *J* = 5.0 Hz), 3.61 (1H, dd, *J* = 10.0 Hz, 6.0 Hz), 3.65 (1H, dd, *J* = 10.0 Hz, 7.0 Hz), 4.95-5.03 (3H, m), 5.06 (1H, dd, *J* = 10.5 Hz, 2.0 Hz), 5.61 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 9.0 Hz), 5.70 (1H, ddd, *J* = 17.0 Hz, 10.5 Hz, 8.0 Hz), 7.33-7.45 (6H, m), 7.66-7.68 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.0, 19.3, 26.0, 26.9, 27.3, 37.4, 51.8, 65.2, 114.3, 116.9, 127.2, 127.6, 127.9, 129.3, 129.5, 130.2, 134.4, 135.6, 137.2, 141.2; IR (neat): 3072 (w), 3050 (w), 2960 (m), 2931 (m), 2892 (w), 2858 (m), 1472 (w), 1428 (m), 1390 (w), 1361 (w), 1111 (s), 1027 (w), 998 (m), 915 (m), 822 (m), 739 (m), 701 (s), 613 (m), 505 (s), 487 (m) cm^{-1}; HRMS-(ESI+) for $C_{24}H_{33}OSi$ [M+H]: calculated: 365.2301, found: 365.2291. $[\alpha]^{22}_D$ = +9.905 (*c* = 1.07, $CHCl_3$, from (*R,R*)-QuinoxP*). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (27.9 mg, 51% yield). R_f = 0.64 (45:1 pentane:diethyl ether, stain in $KMnO_4$).

Analysis of Stereochemistry:

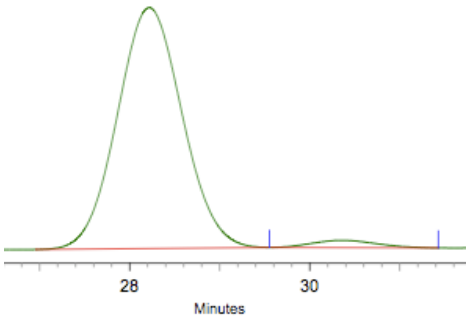
The title compound was subjected to cross metathesis and reduction to afford the diol for HPLC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using 1,2-bis(diphenylphosphino)benzene as the achiral ligand in the allyl-allyl coupling reaction. The absolute stereochemistry was assigned by analogy to compounds **7** and **8**.



Chiral HPLC (OD-H, Chiralcel, 2.5 mL/min, 0.5% isopropanol, 220 nm) - analysis of diol.

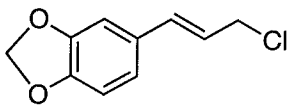


racemic

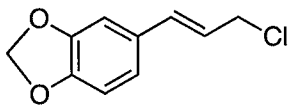


diol derived from allyl-allyl coupling product; from (*R,R*)-QuinoxP*

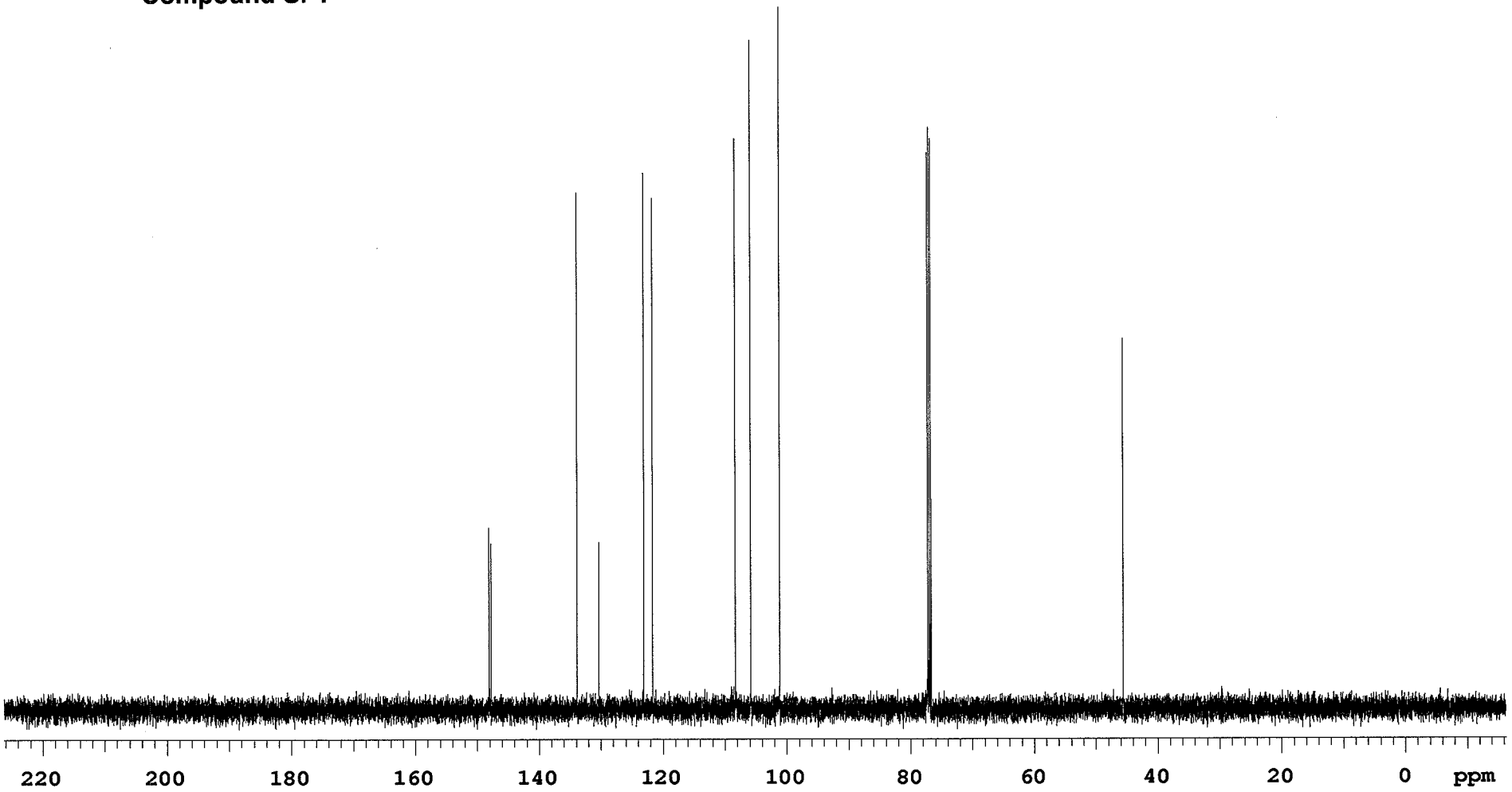
Retention Time	Area	Area %	Height	Height %
28.217	47538691	97.09	946461	97.05
30.357	1422558	2.91	28731	2.95

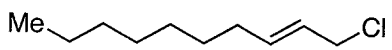


Compound Si-1

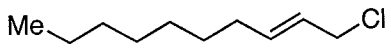


Compound Si-1

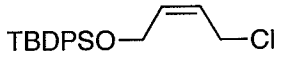




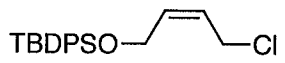
Compound Si-2



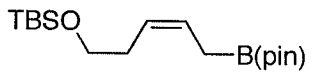
Compound Si-2



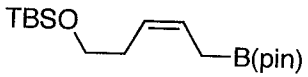
Compound Si-3



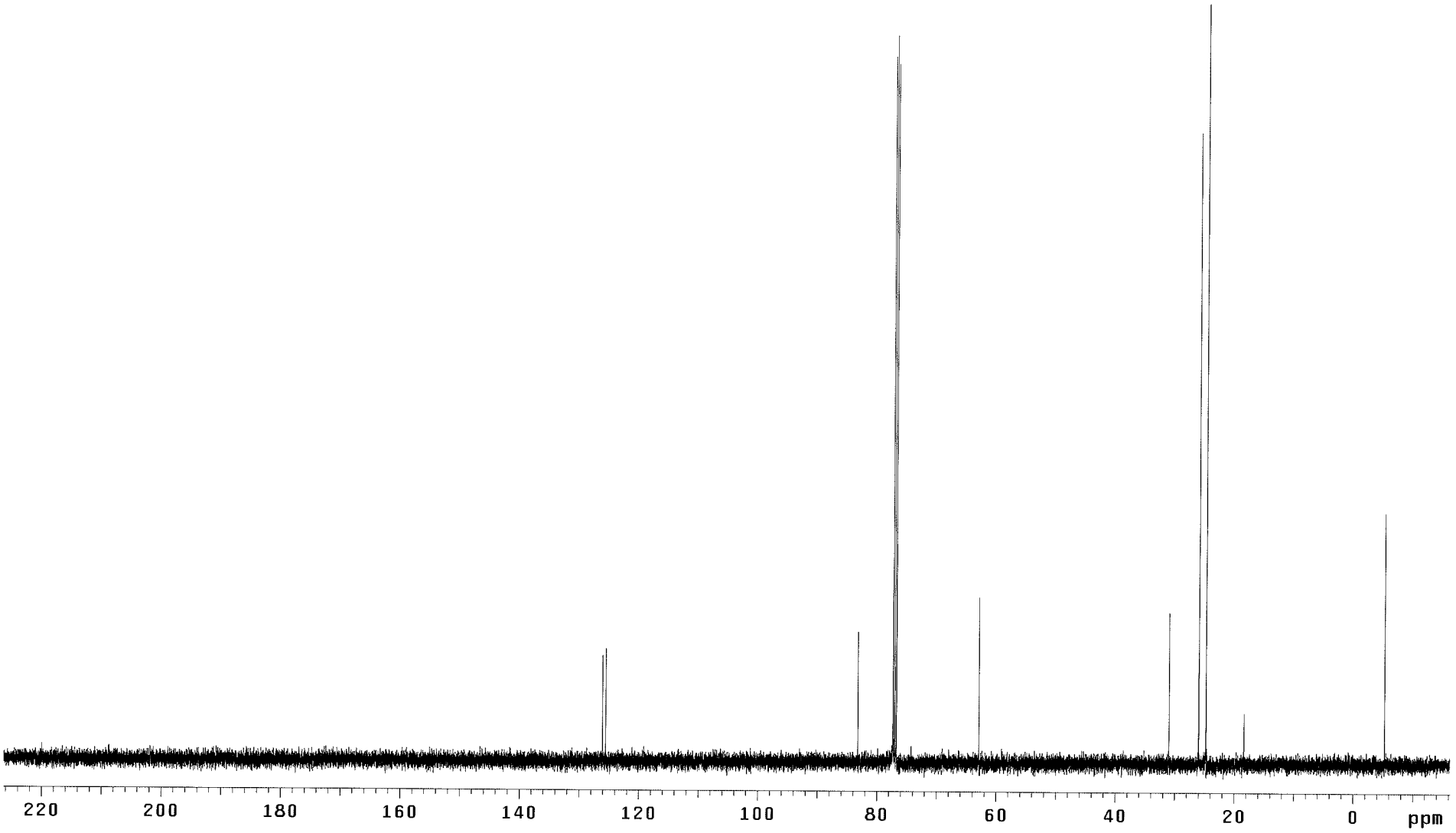
Compound Si-3

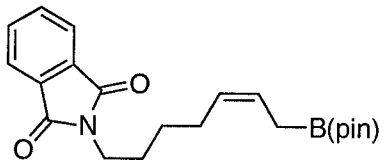


Compound Si-4

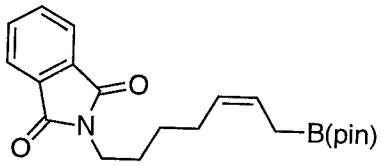


Compound Si-4

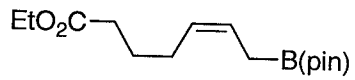




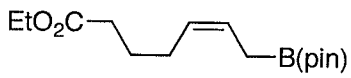
Compound Si-5



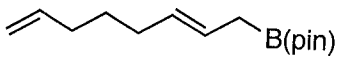
Compound Si-5



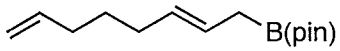
Compound Si-6



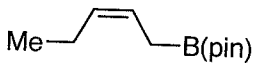
Compound Si-6



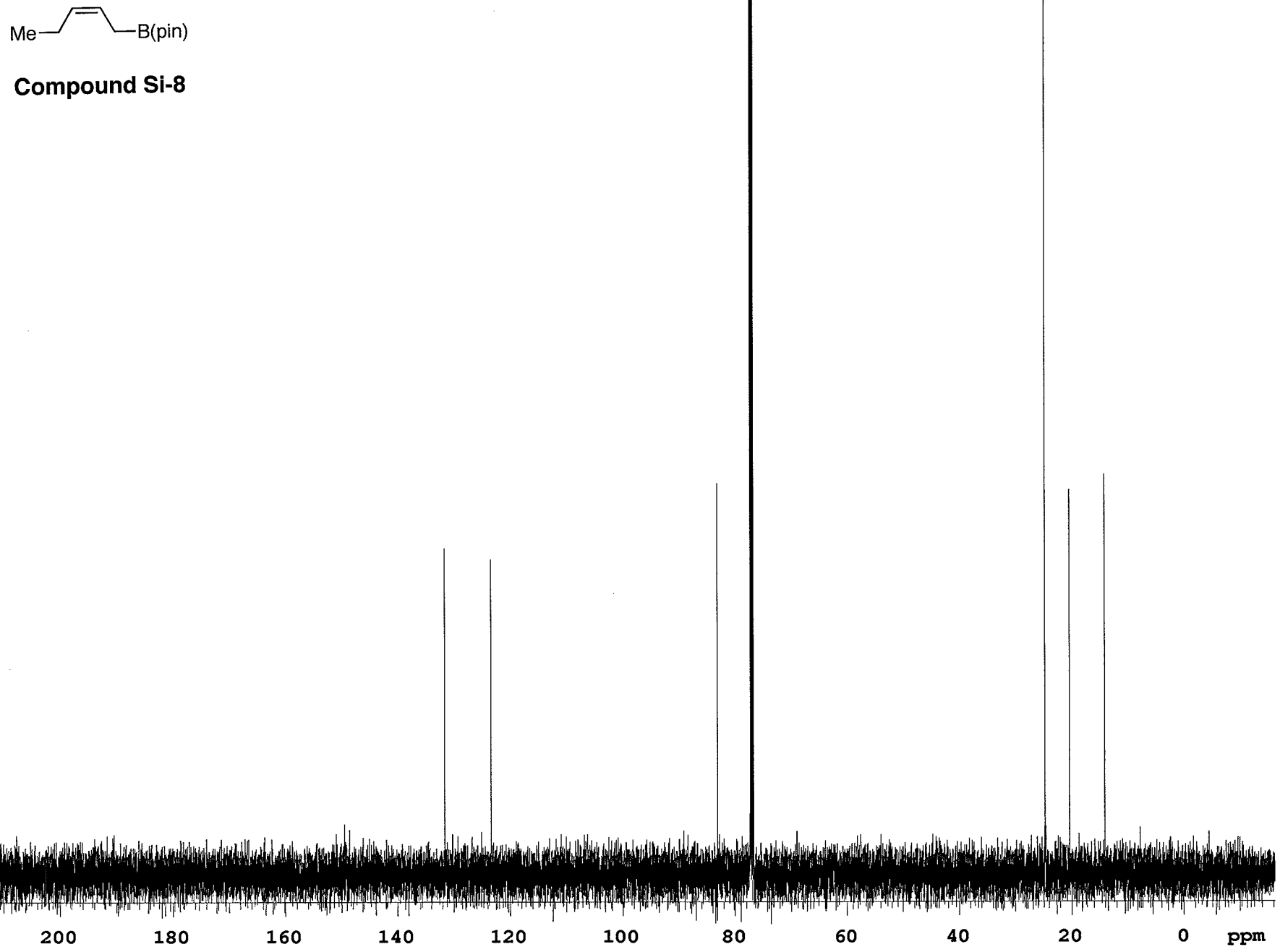
Compound Si-7



Compound Si-7



Compound Si-8


Me
B(pin)
Compound Si-8
220
200
180
160
140
120
100
80
60
40
20
0
ppm

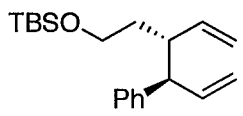


Table 2
Compound 1

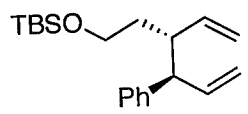


Table 2
Compound 1

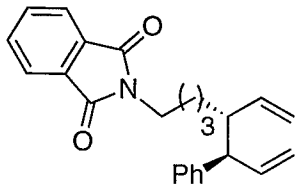


Table 2
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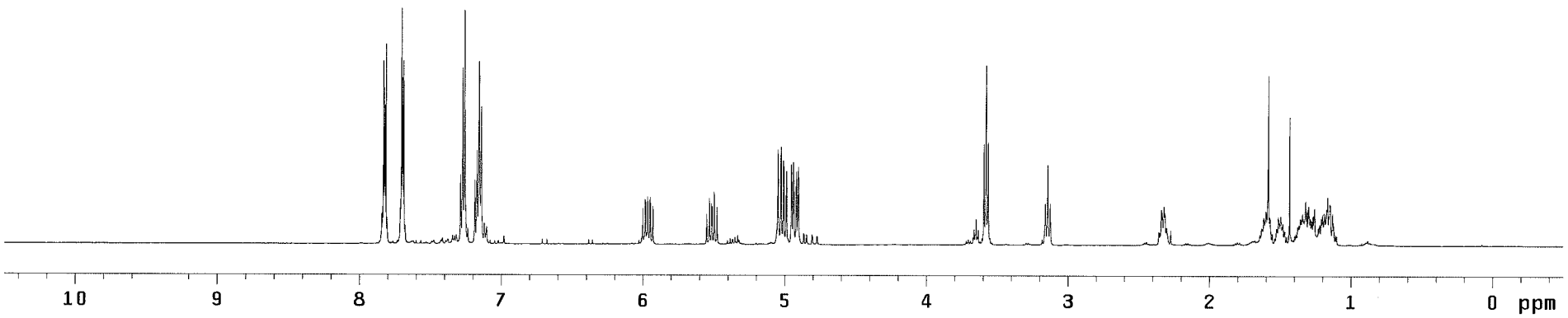


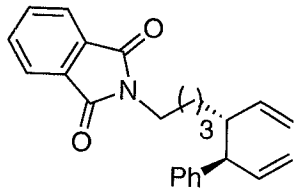
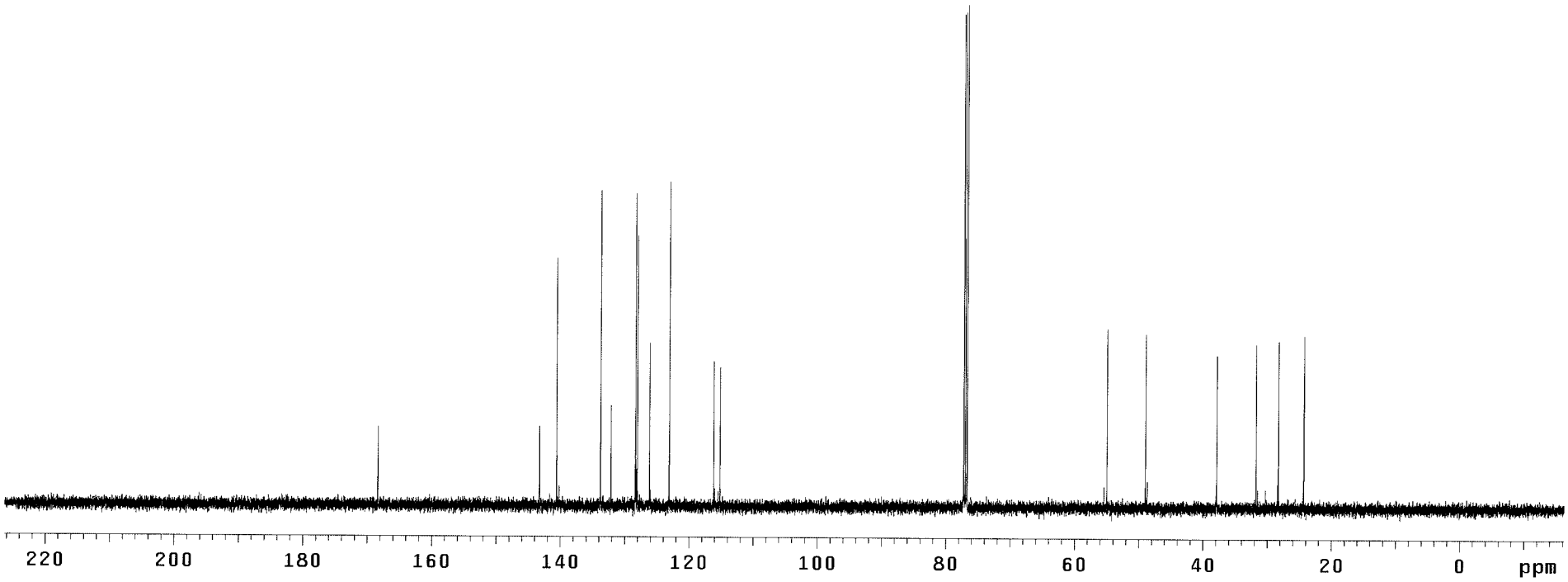


Table 2
Compound 2



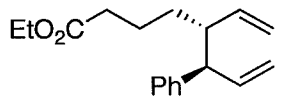
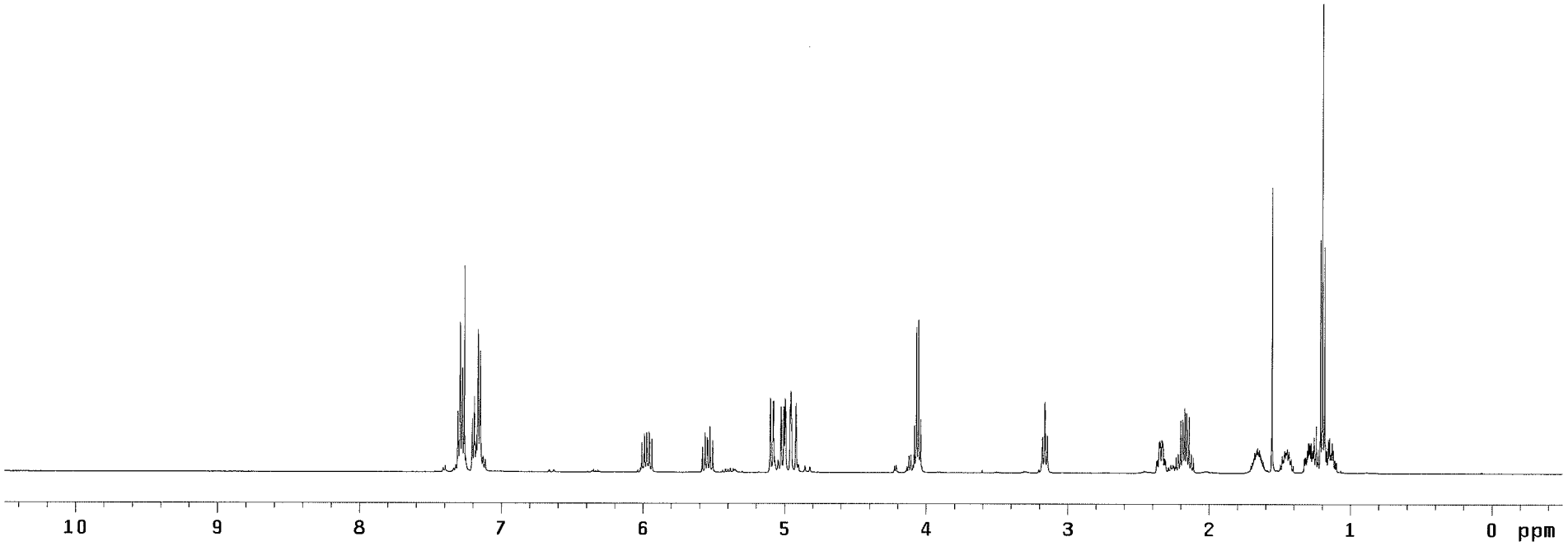


Table 2
Compound 3



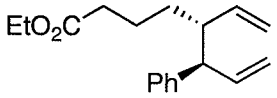


Table 2
Compound 3

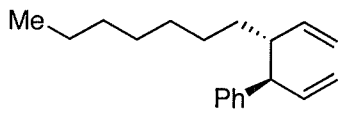


Table 2
Compound 4

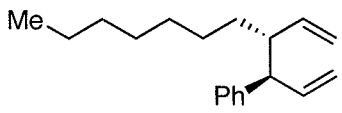
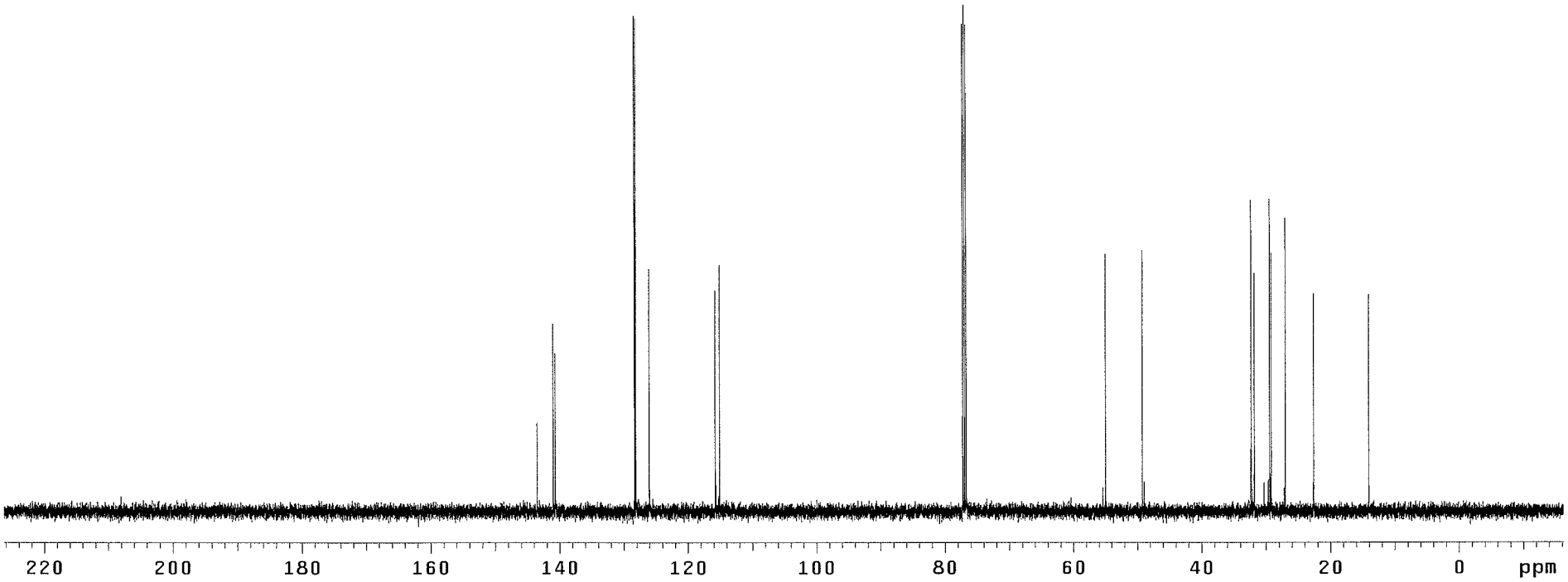


Table 2
Compound 4



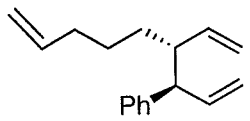
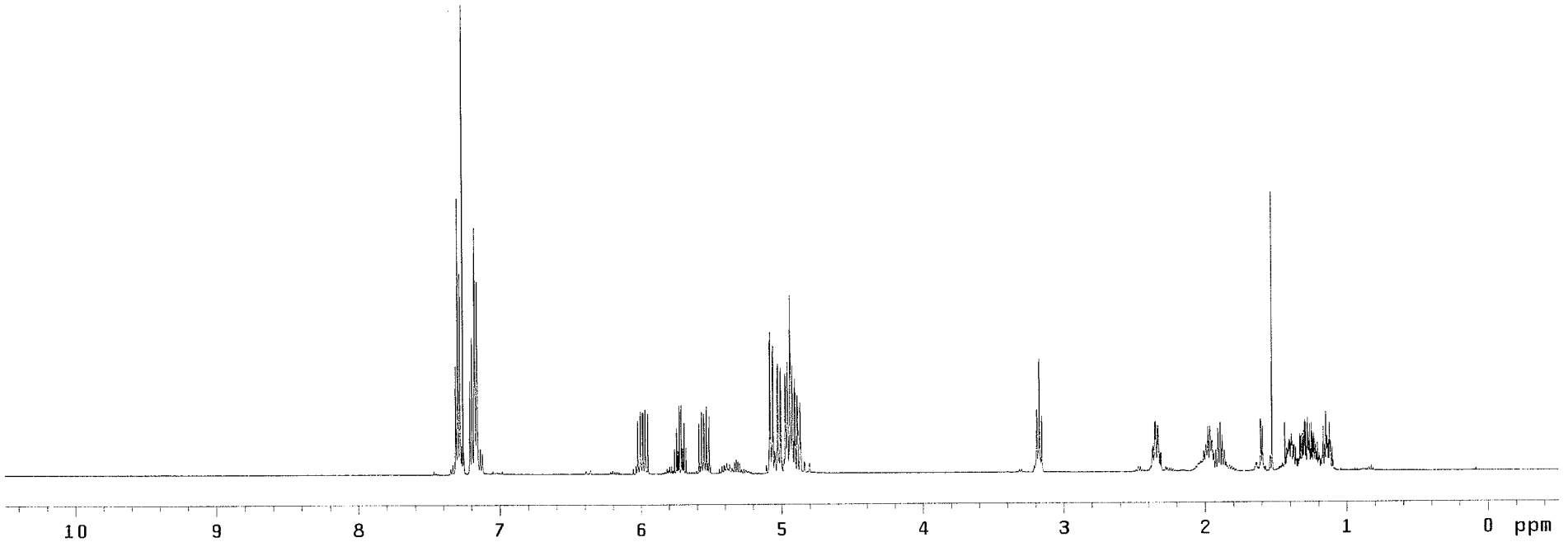


Table 2
Compound 5



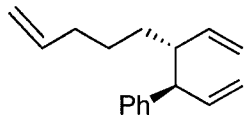
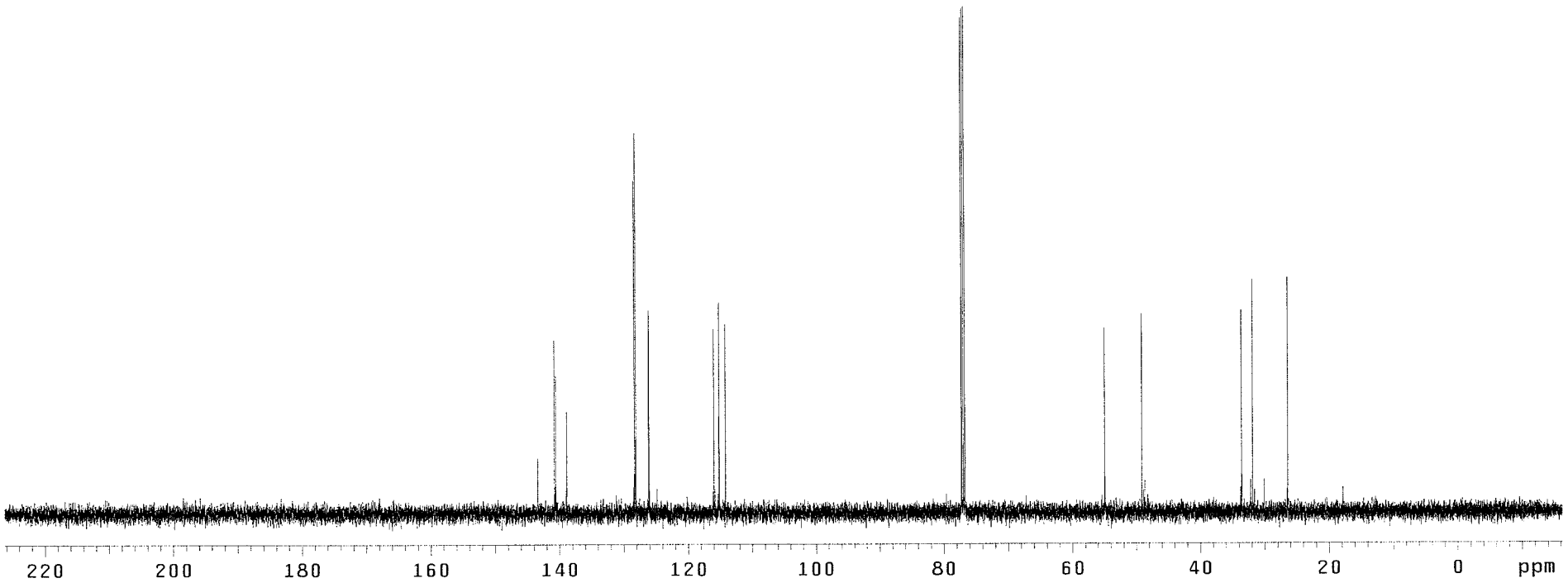
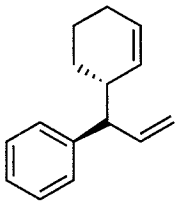
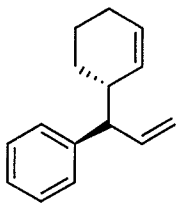


Table 2
Compound 5





Compound Si-9



Compound Si-9

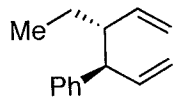
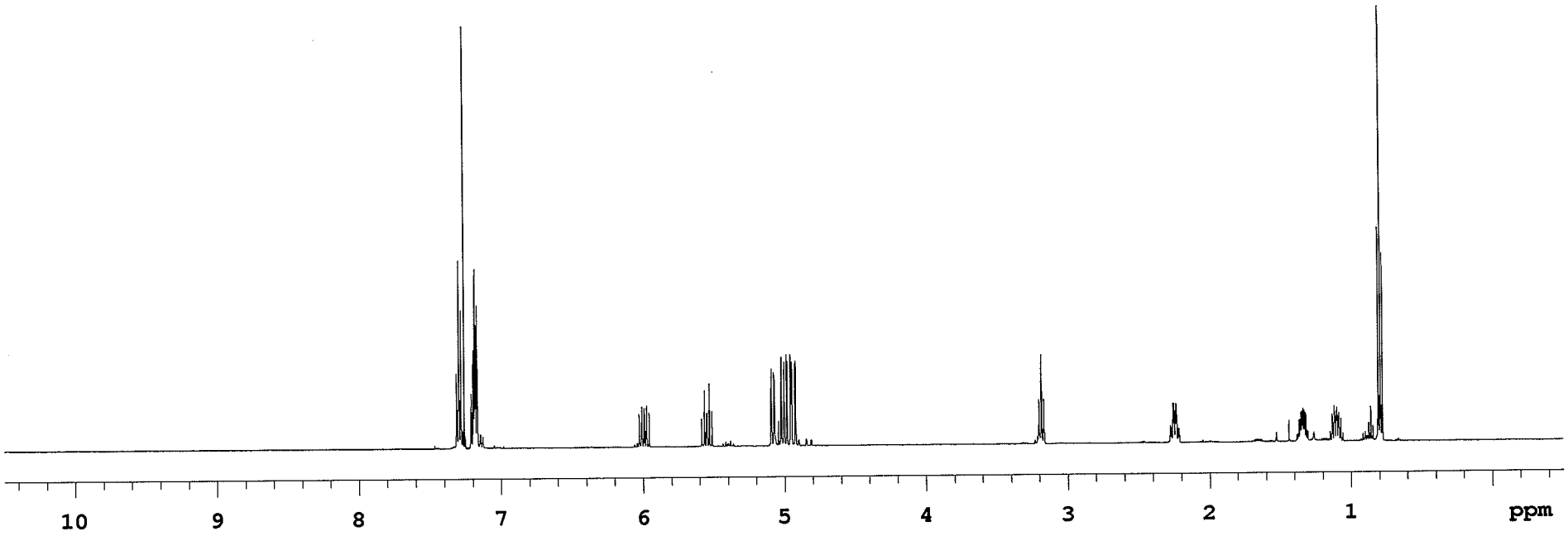


Table 2
Compound 6



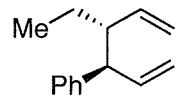


Table 2
Compound 6

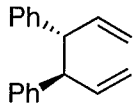
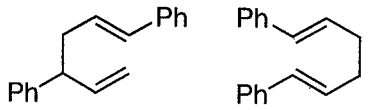
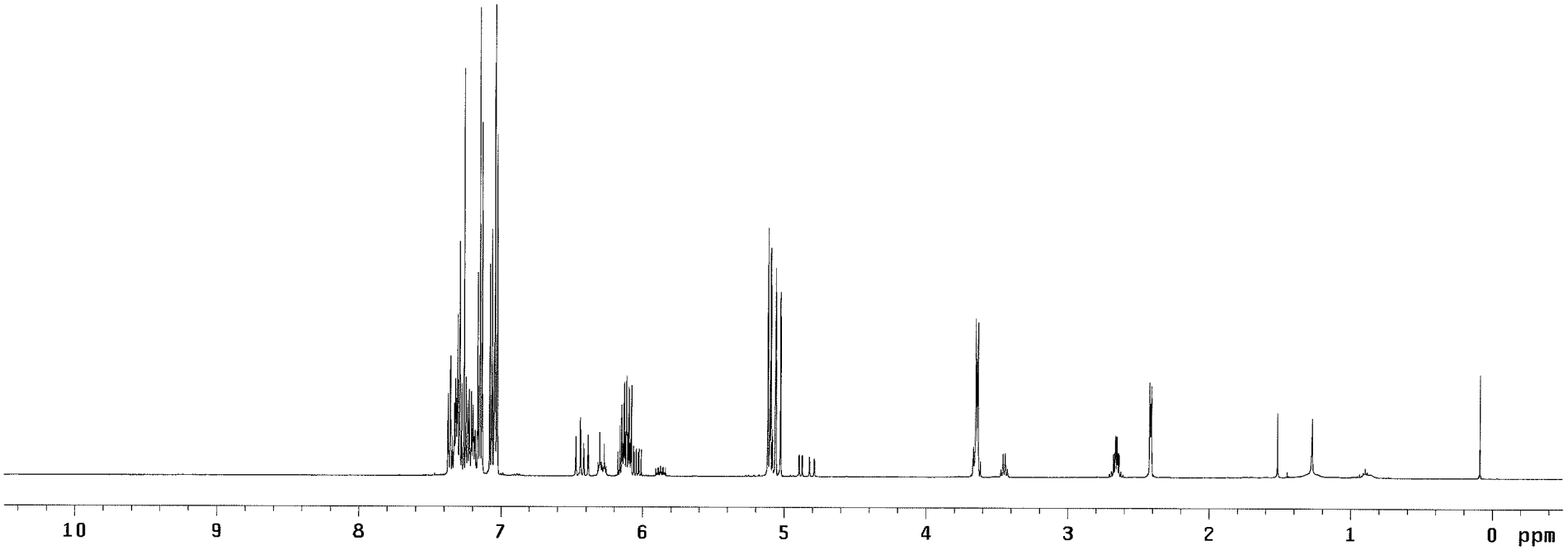


Table 2
Compound 7



Minor Compounds



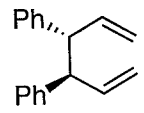


Table 2
Compound 7

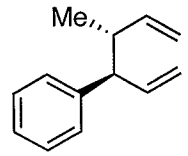


Table 2
Compound 8

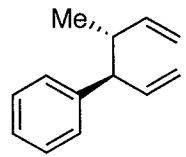


Table 2
Compound 8

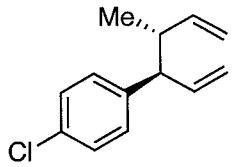


Table 2
Compound 9

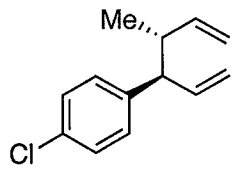
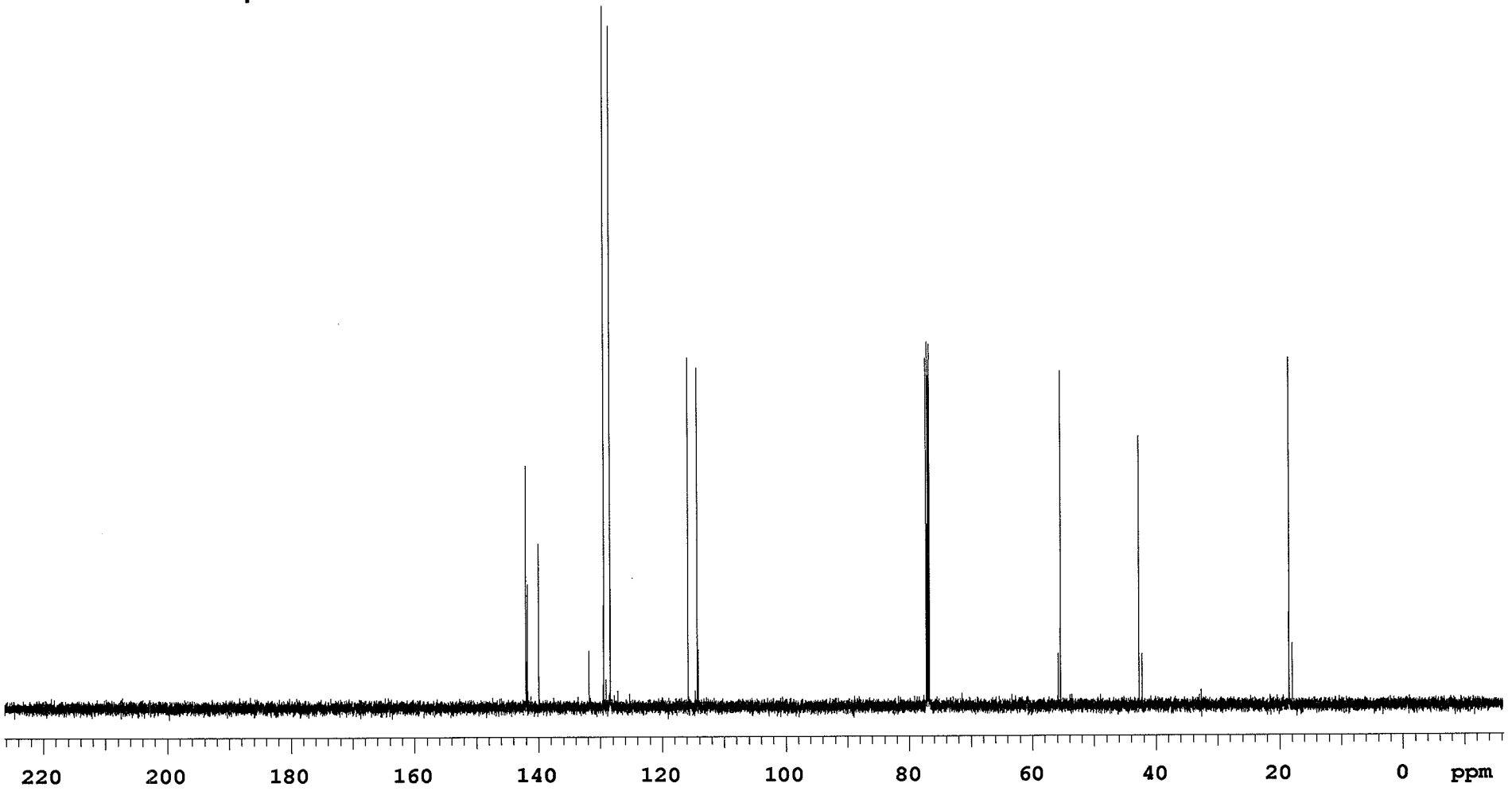


Table 2
Compound 9



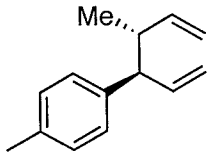
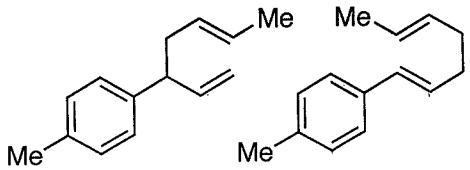


Table 2
Compound 10



Minor Compounds

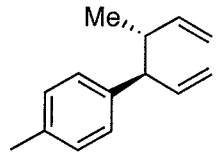


Table 2
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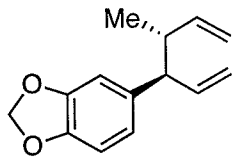
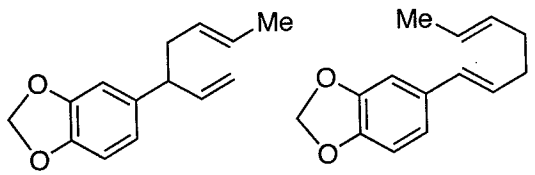
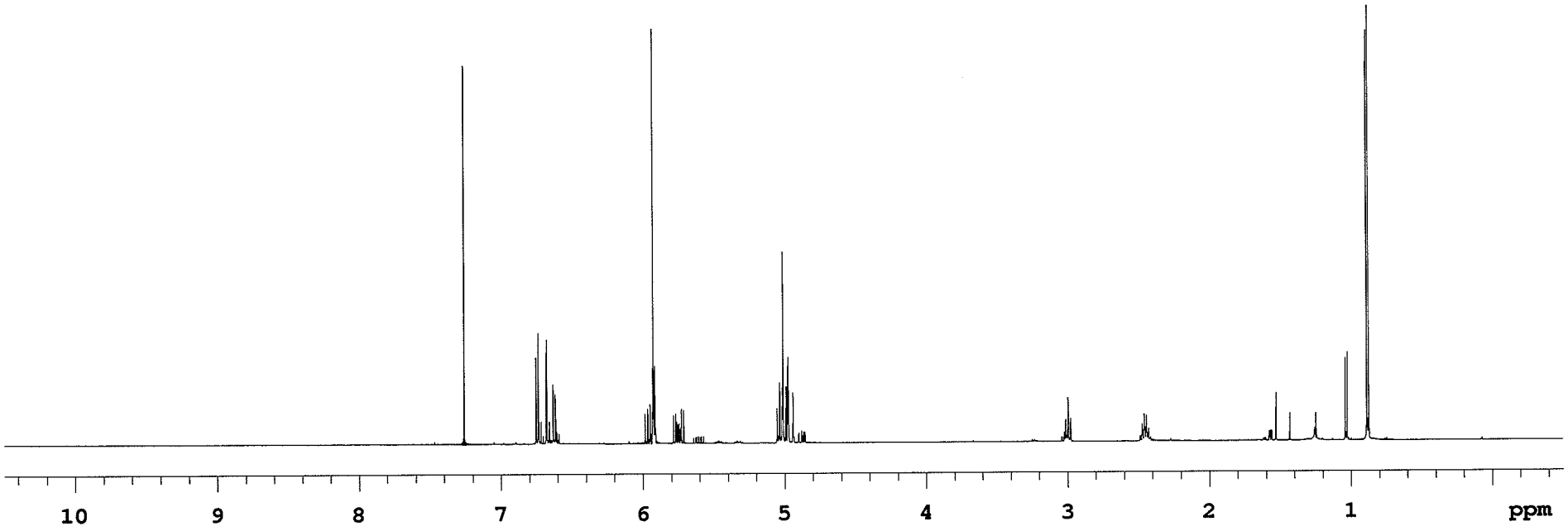
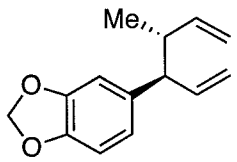


Table 2
Compound 11



Minor Compounds





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Compound 11

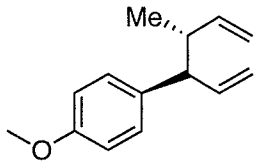
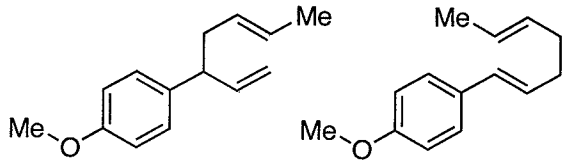


Table 2
Compound 12



Minor Compounds

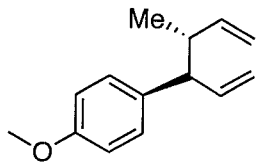


Table 2
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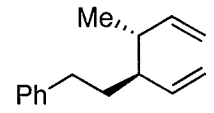
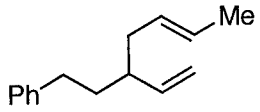
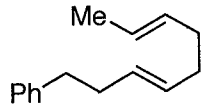


Table 2
Compound 13





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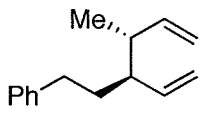


Table 2
Compound 13

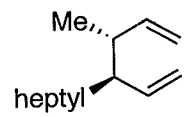
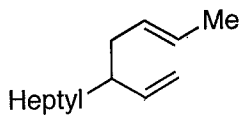
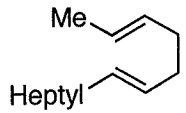
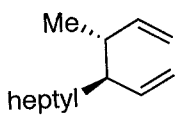


Table 2
Compound 14





Minor Compounds



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Compound 14

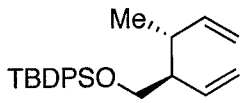

Table 2
Compound 15

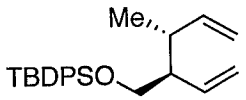

Table 2
Compound 15