Stereocontrol in Palladium-Catalyzed Propargylic Substitutions: Kinetic Resolution to give Enantioenriched 1,5-Enynes and Propargyl Acetates

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Supporting Information

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General Information

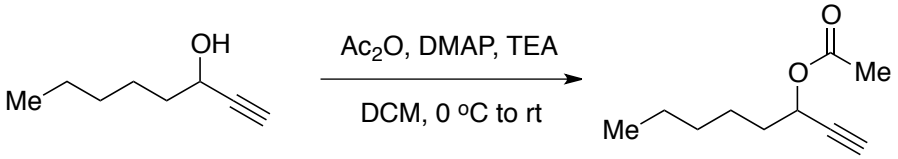
^{1}H NMR spectra were recorded on a Varian Gemini-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, 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 a Varian Gemini-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). ^{31}P NMR spectra were recorded on a Varian Gemini-500 (202 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with phosphoric acid as the external standard (H_3PO_4: 0.0 ppm). Infrared (IR) spectra were recorded on a Bruker alpha spectrophotometer, υ_{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, 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 isopropanol or a 1:1 mixture of isopropanol:hexanes and as the modifier. Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter.

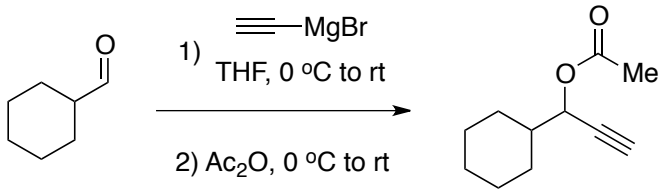
All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), dichloromethane (DCM) and toluene (PhMe) were purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. by passing through two activated alumina columns after being purged with argon. Triethylamine was distilled from calcium hydride. Tris(dibenzylideneacetone) dipalladium(0) [$Pd_2(dba)_3$], bis(benzonitrile)palladium(II) chloride, 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. Allylboronic acid pinacol ester (allyl Bpin) was generously donated by Frontier Scientific. 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 Propargyl Acetates



Representative Procedure A: An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with dichloromethane (20.0 mL), 1-octyn-3-ol (500 mg, 3.96 mmol), and dimethylamino pyridine (catalytic) under nitrogen atmosphere. The solution was cooled to 0 °C and triethylamine (1.2 g, 11.88 mmol) was added, followed by dropwise addition of acetic anhydride ((484.9 mg, 4.7 mmol). The solution was gradually warmed to room temperature and stirred for 2 h. The reaction was concentrated *in vacuo*, and the crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil (599 mg, 90% yield). R_f = 0.60 (10:1 pentane:diethyl ether, stain in PMA). Spectral data is in accordance with the literature.[1]



Representative Procedure B: An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with THF (15 mL) and cyclohexyl carboxaldehyde (336 mg, 3.00 mmol). The solution was cooled to 0 °C and ethynylmagnesium bromide (8.4 mL of a 0.5 M solution in THF, 4.2 mmol) was added dropwise. The solution was stirred for 10 minutes at 0 °C and gradually warmed to room temperature and stirred for 45 minutes. The solution was then cooled to 0 °C and acetic anhydride (432.2 mg, 4.2 mmol) was added dropwise. The solution was allowed to stir for 20 minutes at 0 °C and then gradually warmed to room temperature followed by stirring for one hour. The reaction was recooled to 0 °C and quenched with saturated aqueous ammonium chloride and extracted three times with diethyl ether. The organic layers were combined, dried over sodium sulfate, concentrated *in vacuo* and purified on silica gel (30:1 hexane:ethyl acetate) to afford a clear, colorless oil (392 mg, 73% yield). R_f = 0.64 (5:1 hexane:ethyl acetate, stain in PMA). Spectral data is in accordance with the literature.[2]

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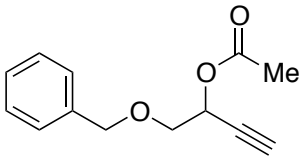
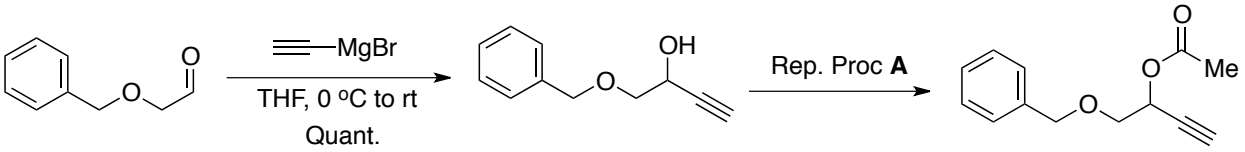
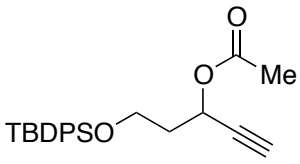
[1]Ghosh, N.; Nayak, S.; Sahoo, A. *J. Org. Chem.* **2011**, *76,* 500.

[2]Detz, R.; Abiri, Z.; Griel, R.; Hiemstra, H.; Maarseveen, J. *Chem. Eur. J.* **2011**, *21*, 5921.

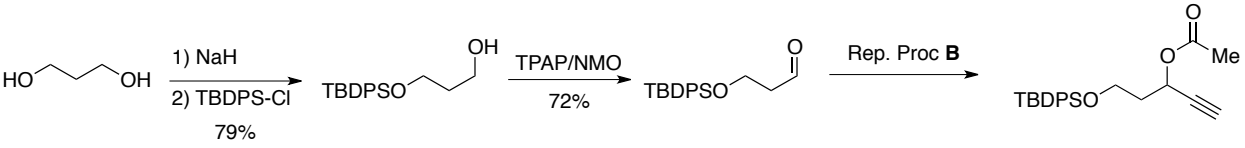


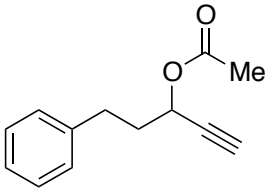
1-(benzyloxy)but-3-yn-2-yl acetate (Compound SI-1). From 1-(benzyloxy)but-3-yn-2-ol, prepared as shown below from commercially available 2-(benzyloxy)acetaldehyde, representative procedure **A** was followed to afford a clear, colorless oil (617 mg, 94% yield). R_f = 0.6 (5:1 pentane:diethyl ether, stain in $KMNO_4$). Spectral data is in accordance with the literature. [3]





5-((tert-butyldiphenylsilyl)oxy)pent-1-yn-3-yl acetate (Compound SI-2). From 3-((*tert*-butyldiphenylsilyl)oxy)propanal, synthesized as shown below utilizing a two-step procedure from commercially available propane-1,3-diol,[4] representative procedure **B** was followed to afford a clear, colorless oil (279 mg, 74% yield). R_f = 0.71 (10:1 pentane:diethyl ether, stain in PMA). Spectral data is in accordance with the literature. [3]





5-phenylpent-1-yn-3-yl acetate (Compound SI-3). From commercially available hydrocinnamaldehyde, representative procedure **B** was followed to afford a clear, colorless oil (763 mg, 88% yield). R_f = 0.80 (5:1 pentane:diethyl ether, stain in PMA). Spectral data is in accordance with the literature. [2]

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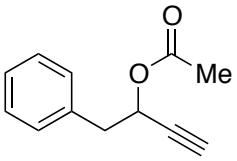
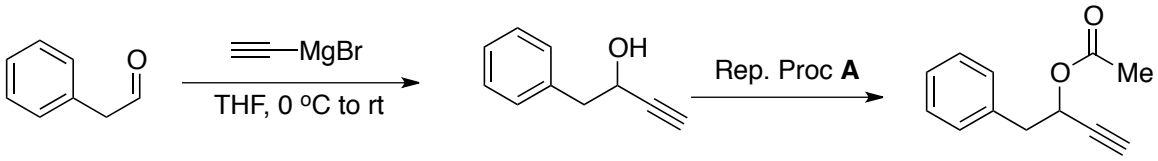
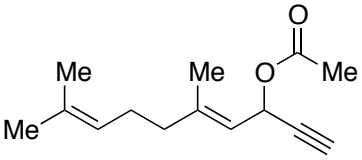
[3]Ardolino, M. J.; Morken, J. P. *J. Am. Chem. Soc.* **2012**, *134*, 8770-8773.

[4] McDougal, P. G.; Rico, J. G.; Oh, Y.-I.; Condon, B. D. *J. Org. Chem.* **1986**, *51*, 3388.

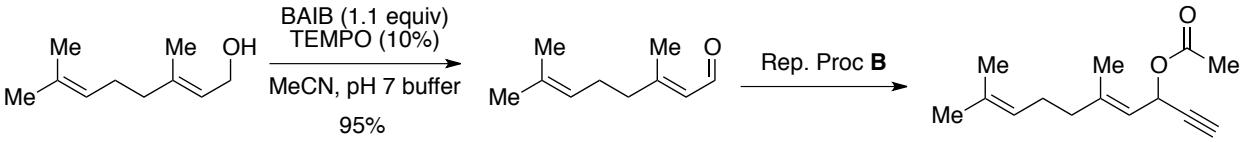


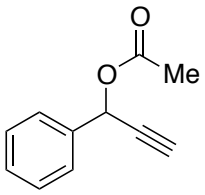
1-phenylbut-3-yn-2-yl acetate (Compound SI-4). From 1-phenylbut-3-yn-2-ol, prepared as shown below from commercially available 2-phenylacetaldehyde, representative procedure **A** was followed to afford a clear, colorless oil (297 mg, 79% yield). R_f = 0.7 (5:1 pentane:diethyl ether, stain in PMA). Spectral data is in accordance with the literature. [1]



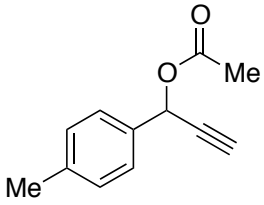


(E)-5,9-dimethyldeca-4,8-dien-1-yn-3-yl acetate (Compound SI-5). From *(E)*-3,7-dimethylocta-2,6-dienal, synthesized as shown below from commercially available geraniol,[5] representative procedure **B** was followed to afford a clear, colorless oil (821 mg, 93% yield). R_f = 0.83 (10:1 pentane:diethyl ether, stain in PMA). Spectral data is in accordance with the literature. [3]





1-phenylprop-2-yn-1-yl acetate (Compound SI-6). From commercially available 1-phenylprop-2-yn-1-ol, representative procedure **A** was followed to afford a clear, colorless oil (938 mg, >96% yield). R_f = 0.39 (10:1 pentane:diethyl ether, stain in PMA). Spectral data is in accordance with the literature. [1]



1-(p-tolyl)prop-2-yn-1-yl acetate (Compound SI-7). From commercially available *p*-tolualdehyde, representative procedure **B** was followed to afford a clear, colorless oil (282 mg, >96% yield). R_f = 0.26 (25:1 hexane:ethyl acetate; stain in PMA). Spectral data is in accordance with literature. [1]

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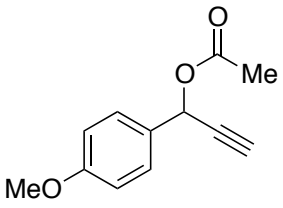
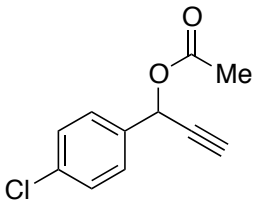
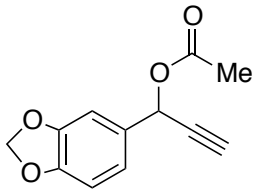
[5]Leonelli, F.; Piancatelli, G. *Org. Syn.* **2009**, *83*, 18.



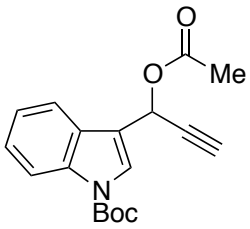
1-(4-methoxyphenyl)prop-2-yn-1-yl acetate (Compound SI-8). From commercially available 4-methoxybenzaldehyde, representative procedure **B** was followed. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, pale yellow oil (741 mg, >96% yield). R_f = 0.4 (10:1 pentane:diethyl ether; stain in CAM). Spectral data is in accordance with the literature. [2]



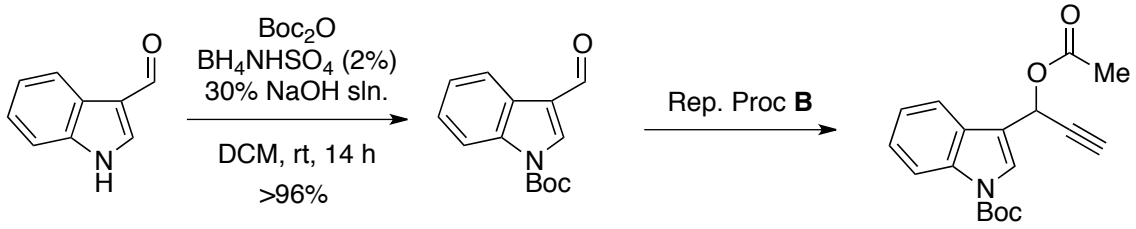
1-(4-chlorophenyl)prop-2-yn-1-yl acetate (Compound SI-9). From commercially available 4-chlorobenzaldehyde, representative procedure **B** was followed to afford a clear, pale yellow oil (574 mg, 92% yield). R_f = 0.32 (10:1 hexane: ethyl acetate, stain in PMA). Spectral data is in accordance with the literature. [1]



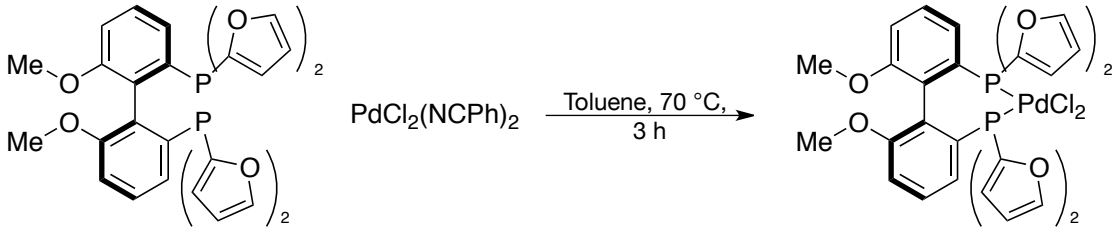
1-(benzo[d][1,3]dioxol-5-yl)prop-2-yn-1-yl acetate (Compound SI-10). From commercially available piperonal, representative procedure **B** was followed to afford a white solid (849 mg, >96% yield). R_f = 0.14 (20:1 hexane: ethyl acetate; stain in PMA). Spectral data is in accordance with the literature.[2]



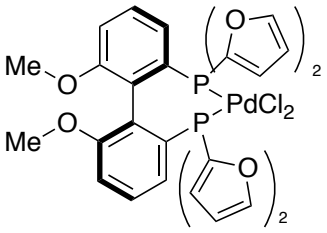
tert-butyl-3-(1-acetoxyprop-2-yn-1-yl)-1H-indole-1-carboxylate (Compound SI-11). From *tert*-butyl 3-formyl-1*H*-indole-1-carboxylate, synthesized as shown below from 1*H*-indole-3-carbaldehyde, representative procedure **B** was followed to afford a pale brown viscous oil (649 mg, 86% yield). R_f = 0.43 (5:1 pentane:diethyl ether, stain in PMA). Spectral data is Spectral data is in accordance with the literature. [3]



Preparation of [*(R)*-(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl]palladium(II) dichloride (3).[6]



An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with bis(benzonitrile)palladium(II) chloride (83.9 mg, .219 mmol) and toluene (12.0 mL) in a dry-box under argon atmosphere to form a rust-brown solution. Also in the dry-box, an oven-dried 2 dram vial equipped with a magnetic stir bar was charged with *(R)*-(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl [*(R)*-Methoxy(furyl)BIPHEP] and toluene (3.0 mL). Both vessels were sealed with septa, removed from the dry box, and heated to 70 °C with stirring under a positive pressure of dry nitrogen. The solution of ligand was added dropwise to the stirring solution of palladium complex over five minutes. The solution was stirred for three hours, over the course of which a bright yellow precipitate formed. The solution was slowly cooled to room temperature, and additional solids were crashed out of solution with the addition of 30 mL pentane. The solids were filtered away from the solution in a Buchner funnel with filter paper and washed with cold diethyl ether to yield a fine, dull yellow powder. This powder was dried for 12 hours under high-vacuum at 60 °C to yield a bright yellow powder (106 mg, 67% yield). The catalyst complex was effective without any further purification. [*(S)*-(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl]palladium(II) dichloride was prepared utilizing the same method with *(S)*-(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl [*(S)*-Methoxy(furyl)BIPHEP].



[*(R)*-(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl]palladium(II) dichloride (3). ^{1}H NMR (500 MHz, CDCl3): δ 7.80 (2H, s), 7.483 (2H, s), 7.22 (2H, dd, J = 3.0 Hz, 3.0 Hz), 7.16 (2H, ddd, J = 8.0 Hz, 8.0 Hz, 3.0 Hz), 6.93 (2H, d, J = 3.0 Hz), 6.85 (2H, dd, J = 12.5 Hz, 8.0 Hz), 6.76 (2H, d, J = 8.0 Hz), 6.45 (2H, ddd, J = 3.0 Hz, 1.5 Hz, 1.5 Hz), 6.24-6.43 (2H, m), 3.60 (6H, s); ^{31}P NMR (202 MHz, CDCl3): δ -11.56; IR (neat): 3109 (m), 3084 (m), 2937 (m), 2835 (w), 2228 (m), 1461 (s), 1267 (s), 1010 (s); A crystal structure of this catalyst complex has also been previously reported.[7]

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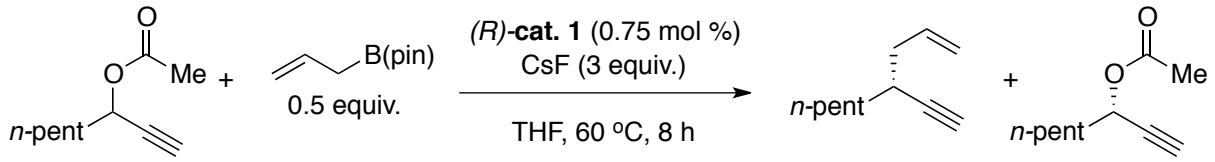
[6] Modified from: Sperrie, M.; Consiglio, G. *J. Am. Chem. Soc.* **1995**, *117*, 12130.

[7] Brozek, L. A.; Ardolino, M. J.; Morken, J. P. *J. Am. Chem. Soc.* **2011**, *133*, 16778.

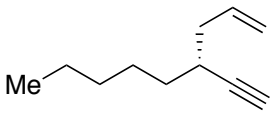
Representative Procedure for Resolution of Propargyl Acetates with Allylboronic acid Pinacol Ester [allyl B(pin)].



An oven-dried scintillation vial equipped with a magnetic stir bar was charged successively with [*(R)*-(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl]palladium(II) dichloride (2.16 mg, 3.0 µmol), THF (0.8 mL), oct-1-yn-3-yl acetate (67.3 mg, 0.40 mmol), allylboronic acid pinacol ester (33.6 mg, 0.20 mmol), and cesium fluoride (182.3 mg, 1.2 mmol) in a dry-box under argon atmosphere. The vial was sealed, removed from the dry-box, and heated to 60 °C while allowing to stir for 8 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*.

Characterization of Products and Analysis of Stereochemistry

Kinetic resolution to give *(R)*-4-ethynylnon-1-ene (Table 2, Entry 1): The representative procedure was followed with oct-1-yn-3-yl acetate.

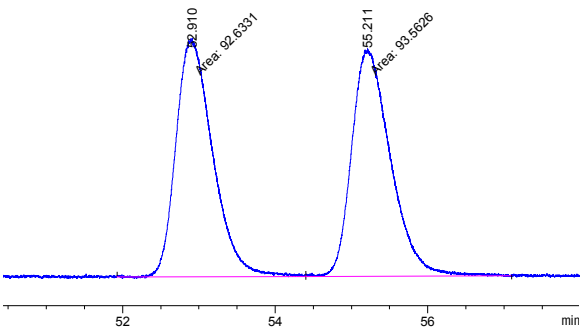


***(R)*-4-ethynylnon-1-ene (Table 2, Entry 1 G)**. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil. R_f = 0.71 (pentane, stain in PMA). $[\alpha]^{22}_D$ = 10.998 (c = 0.20, $CDCl_3$). Spectral data is in accordance with literature. [3]

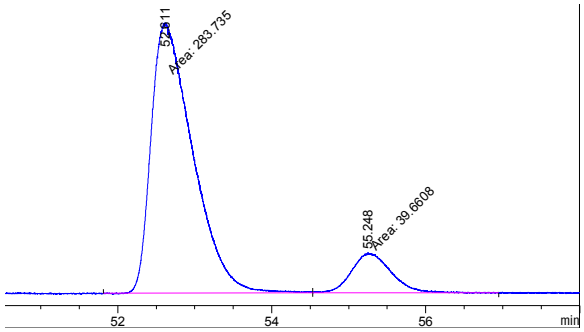
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned as shown below.

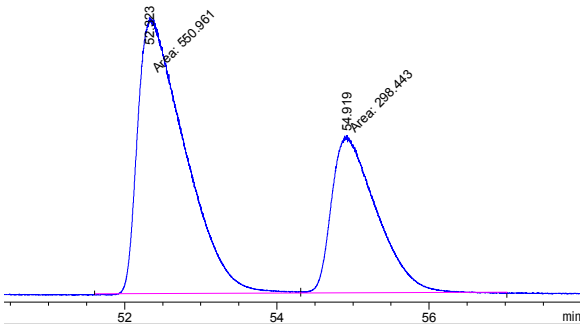
Chiral GLC (CD-BDM, Supelco, 40 °C for 30 min, ramp 0.25 °C/min to 50 °C for 10 min, 20 psi) - analysis of title compound.



Racemic Sample



Enantioenriched Sample

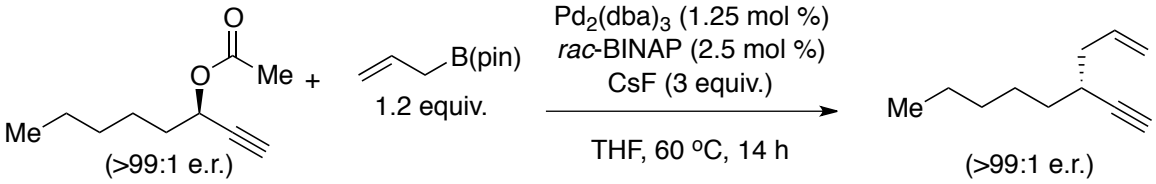


co-injection of racemic and enantioenriched samples

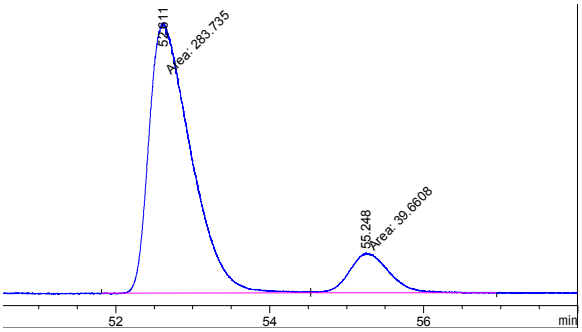
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	52.611	MF	0.6246	283.73468	7.57123	87.73612
2	55.248	FM	0.5893	39.66084	1.12167	12.26388

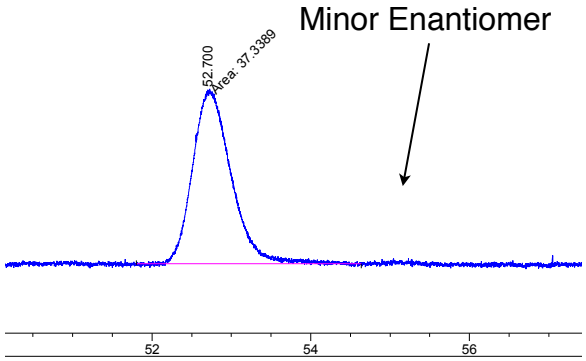
Proof of Absolute Stereochemistry:

In order to determine the absolute stereochemistry, the title compound was compared by GLC analysis to authentic *(R)*-4-ethynylnon-1-ene, prepared by the stereospecific enyne cross coupling as depicted below. [3]



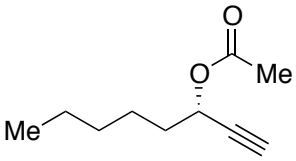
Chiral GLC (CD-BDM, Supelco, 40 °C for 30 min, ramp 0.25 °C/min to 50 °C for 10 min, 20 psi) - analysis of title compound.





Title Compound

authentic (R)-4-ethynylnon-1-ene

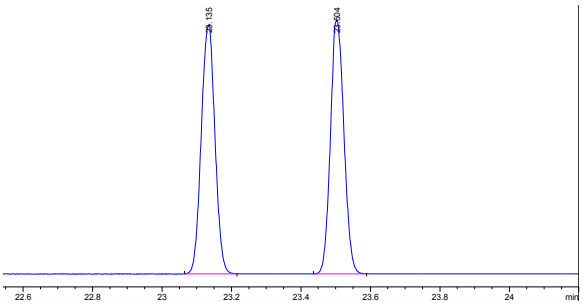


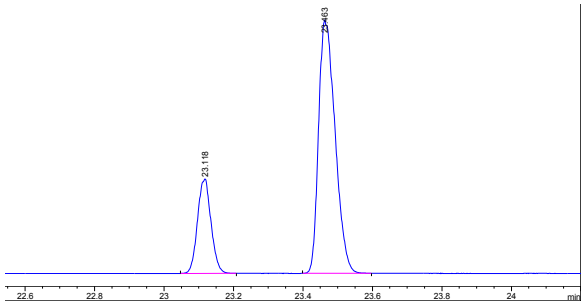
***(S)*-oct-1-yn-3-yl acetate (Table 2, Entry 1 l)**. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil. R_f = 0.60 (10:1 pentane: diethyl ether, stain in PMA). $[\alpha]^{22}_D$ = -19.090 (*c* = 1.06, $CDCl_3$). Spectral data is in accordance with literature. [1]

Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned as shown below.

Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 5 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.

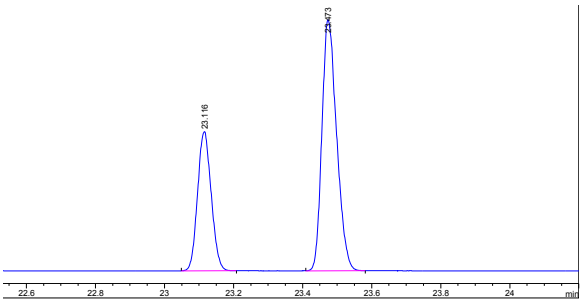




Racemic Sample

Enantioenriched Sample

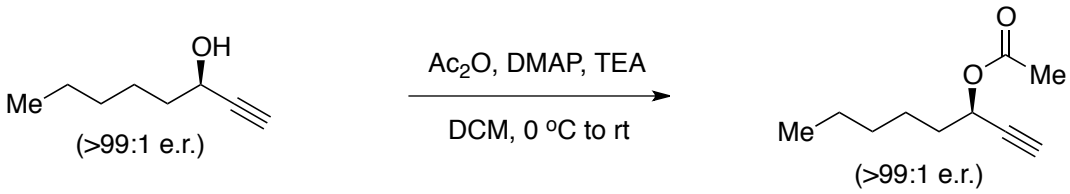
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	23.118	BB	0.0346	168.23032	62.15095	23.41013
2	23.463	BB	0.0412	550.39166	166.93874	76.58987



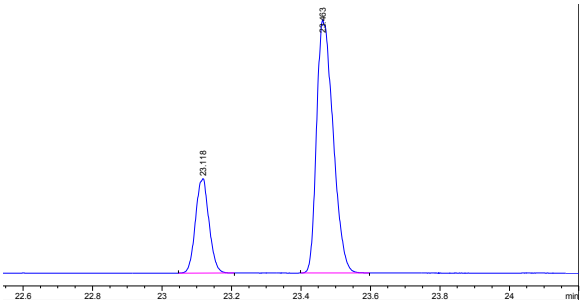
co-injection of racemic and enantioenriched samples

Proof of Absolute Stereochemistry:

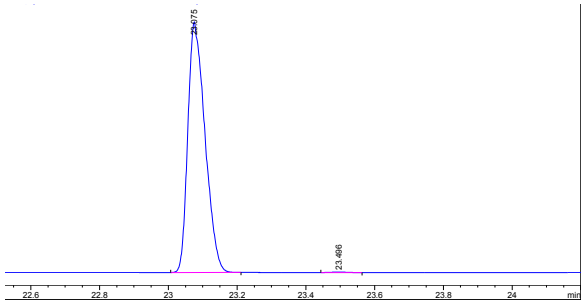
In order to determine the absolute stereochemistry, the title compound was compared by GLC analysis to authentic *(R)*-oct-1-yn-3-yl acetate prepared from commercially available *(R)*-oct-1-yn-3-ol as shown below.



Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 5 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.

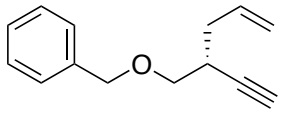


Title Compound



(R)-oct-1-yn-3-yl acetate

Kinetic resolution to give *(R)*-(((2-ethynylpent-4-en-1-yl)oxy)methyl)benzene (Table 2, Entry 2): The representative procedure was followed with 1-(benzyloxy)but-3-yn-2-yl acetate on a 0.2 mmol scale.

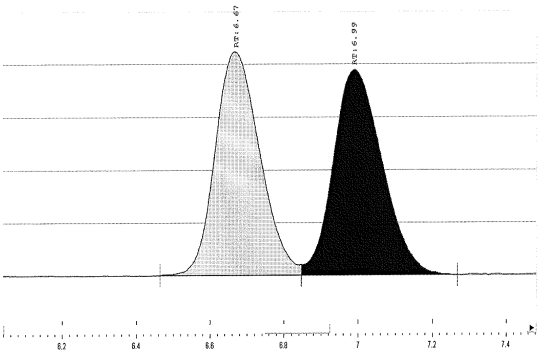


***(R)*-(((2-ethynylpent-4-en-1-yl)oxy)methyl)benzene (Table 2, Entry 2 G)**. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil. R_f = 0.86 (10:1 pentane:diethyl ether, stain in $KMNO_4$). $[\alpha]^{22}_D$ = -8.461 (c = 0.73, $CHCl_3$). Spectral data is in accordance with the literature. [3]

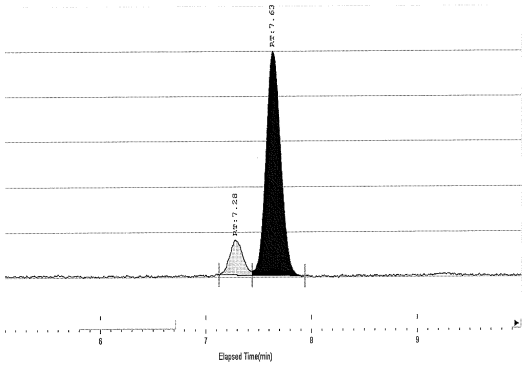
Analysis of Stereochemistry:

Optical purity was determined by SFC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-4-ethynylnon-1-ene (Table 2, Entry 1 G).

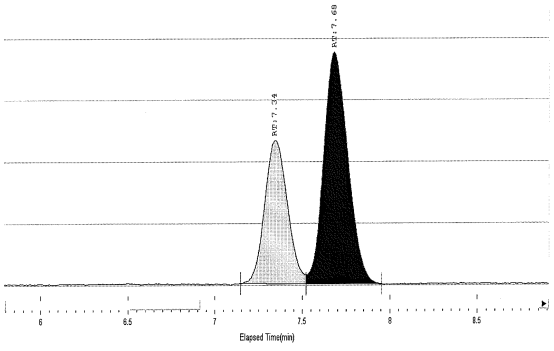
Chiral SFC (OJ-H, Chiralpak, 215 nm, 1.0 mL/min, 1.0% 1:1 i-PrOH:Hexanes, 100 bar, 35 °C) - analysis of title compound.



Racemic Sample

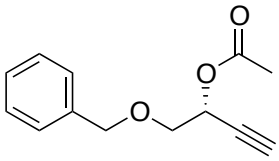


Enantioenriched Sample



co-injection of racemic and enantioenriched samples

Peak No	% Area	Area	RT (min)
1	12.1609	133.3423	7.28
2	87.8391	963.1384	7.63
Total:	100	1096.4807	

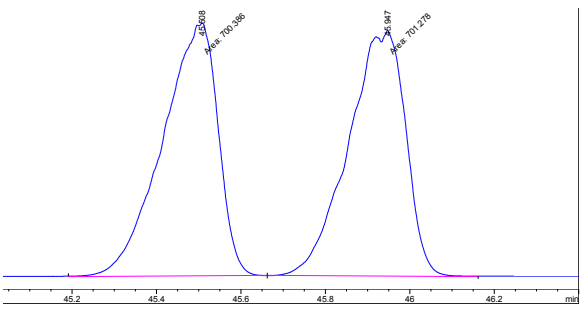


***(R)*-1-(benzyloxy)but-3-yn-2-yl acetate (Table 2, Entry 2 l)**. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil. R_f = 0.24 (10:1 pentane:diethyl ether, stain in $KMNO_4$). $[\alpha]^{22}_D$ = -28.339 (*c* = 10.76, $KMNO_4$). Spectral data is in accordance with the literature. [3]

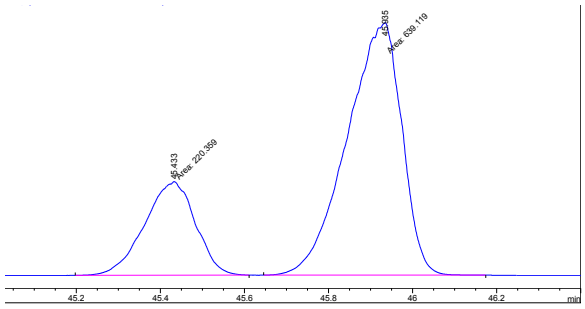
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(S)*-oct-1-yn-3-yl acetate (Table 2, Entry 1 l).

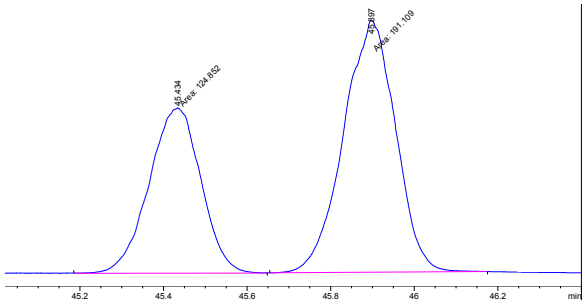
Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 5 °C/min to 160 °C for 20 min, 20 psi) - analysis of title compound.



Racemic Sample



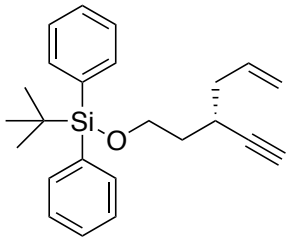
Enantioenriched Sample



co-injection of racemic and enantioenriched samples

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	45.433	MM	0.1399	220.35901	26.25463	25.63870
2	45.935	MM	0.1506	639.11896	70.73759	74.36130

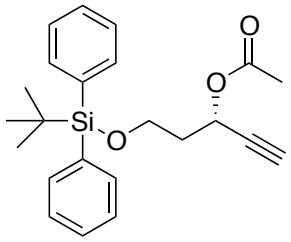
Kinetic resolution to give *(S)*-tert-butyl((3-ethynylhex-5-en-1-yl)oxy)diphenylsilane (Table 2, Entry 3): The representative procedure was followed with 5-((tert-butyldiphenylsilyl)oxy)pent-1-yn-3-yl acetate with the following modification: the reaction was run for 12 hours on a 0.2 mmol scale.



***(S)*-tert-butyl((3-ethynylhex-5-en-1-yl)oxy)diphenylsilane (Table 2, Entry 3 G)**. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil. R_f = 0.95 (10:1 pentane:diethyl ether, stain in $KMNO_4$). $[\alpha]^{22}_D$ = 13.981 (c = 1.52, $CHCl_3$). Spectral data is in accordance with the literature. [3]

Analysis of Stereochemistry:

The absolute stereochemistry was assigned by analogy to *(R)*-4-ethynylnon-1-ene (Table 2, Entry 1 G).

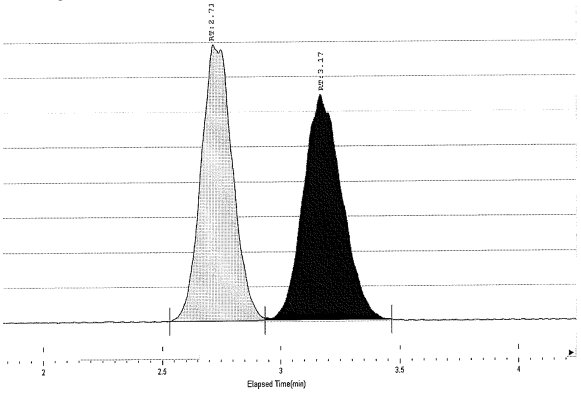


***(S)*-5-((tert-butyldiphenylsilyl)oxy)pent-1-yn-3-yl acetate (Table 2, Entry 3 I)**. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil. R_f = 0.35 (10:1 pentane:diethyl ether, stain in $KMNO_4$). $[\alpha]^{22}_D$ = -18.147 (c = 1.52, $CHCl_3$). Spectral data is in accordance with the literature. [3]

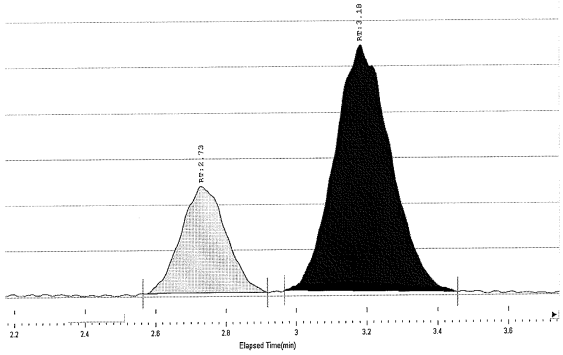
Analysis of Stereochemistry:

Optical purity was determined by SFC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(S)*-oct-1-yn-3-yl acetate (Table 2, Entry 1 I).

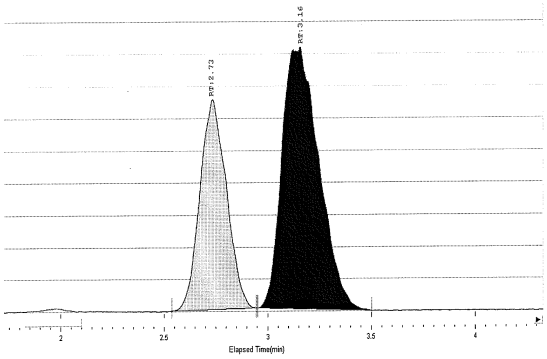
Chiral SFC (OJ-H, Chiralpak, 215 nm, 5.0 mL/min, 1.0% 1:1 i-PrOH:Hexanes, 100 bar, 35 °C) - analysis of title compound.



Racemic Sample



Enantioenriched Sample

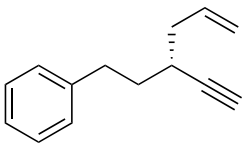


co-injection of racemic and enantioenriched samples

Peak Info					
Peak Name	Number	Concentration	Area %	Area	Area Sum
Peak1	1	0	25.8179	1036.9514	
Peak2	2	0	74.1821	2979.4555	4016.407

RT (min)	St. (min)	End (min)	Height
2.73	2.5644	2.9162	116.5486
3.18	2.9661	3.4545	268.681

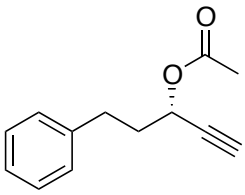
Kinetic resolution to give *(R)*-(3-ethynylhex-5-en-1-yl)benzene (Table 2, Entry 4): The representative procedure was followed with 5-phenylpent-1-yn-3-yl acetate on a 0.2 mmol scale.



***(R)*-(3-ethynylhex-5-en-1-yl)benzene (Table 2, Entry 4 G)**. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil. R_f = 0.37 (pentane, stain in PMA). $[\alpha]^{22}_D$ = 34.614 (*c* = 0.58, $CHCl_3$). Spectral data is in accordance with the literature. [3]

Analysis of Stereochemistry:

The absolute stereochemistry was assigned by analogy to *(R)*-4-ethynylnon-1-ene (Table 2, Entry 1 G).

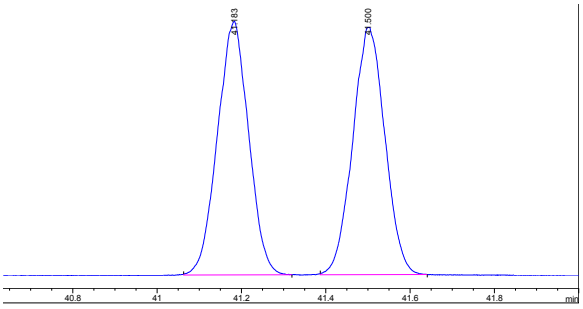


***(S)*-5-phenylpent-1-yn-3-yl acetate (Table 2, Entry 4 l)**. The crude reaction mixture was purified on silica gel (10:1 pentane: diethyl ether) to afford a clear, colorless oil. R_f = 0.21 (15:1 hexane: ethyl acetate, stain in PMA). $[\alpha]^{22}_D$ = -9.086 (*c* = 0.63, $CHCl_3$). Spectral data is in accordance with the literature. [2]

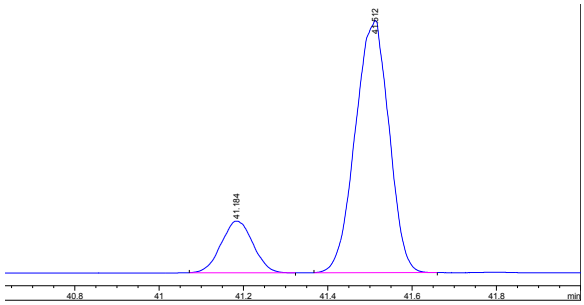
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(S)*-oct-1-yn-3-yl acetate (Table 2, Entry 1 l).

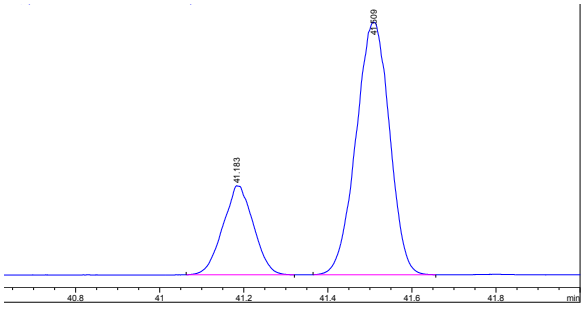
Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 4 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.



Racemic Sample



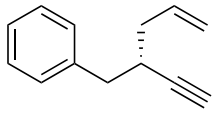
Enantioenriched Sample



co-injection of racemic and enantioenriched samples

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	41.184	BB	0.0661	60.81909	11.52059	16.33605
2	41.512	BB	0.0657	311.48068	56.19104	83.66395

Kinetic resolution to give *(S)*-(2-ethynylpent-4-en-1-yl)benzene (Table 2, Entry 5): The representative procedure was followed with 1-phenylbut-3-yn-2-yl acetate on a 0.2 mmol scale.

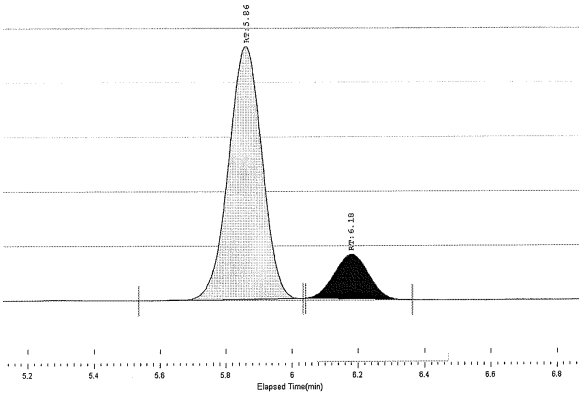


***(S)*-(2-ethynylpent-4-en-1-yl)benzene (Table 2, Entry 5 G)**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.32 (2H, m), 7.21-7.25 (3H, m), 5.92 (1H, ddddd (app dtt), *J* = 17.0 Hz, 8.5 Hz, 7.0 Hz, 7.0 Hz, 1.0 Hz), 5.12-5.13 (1H, m), 5.10 (1H, m), 2.79-2.80 (2H, m), 2.70 (1H, ddddd (app ddtd), *J* = 8.5 Hz, 8.5 Hz, 6.5 Hz, 6.5 Hz, 2.5 Hz), 2.25 (2H, m), 2.10 (1H, d, *J* = 2.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.2, 135.5, 129.2, 129.2, 128.2, 128.2, 126.4, 117.0, 86.6, 70.4, 40.5, 38.4, 33.3; IR (neat): 3300 (w), 3064 (m), 3028 (m), 2979 (m), 2924 (m), 2858 (w), 1641 (m), 1604 (m), 1495 (m), 1441 (m), 915 (s), 698 (s), 632 (s) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{15}$ [M+H]: calculated: 171.1174, found: 171.1176. $[\alpha]^{22}_D$ = 3.214 (*c* = 0.53, $CDCl_3$). The crude reaction was purified on silica gel (pentane) to afford colorless oil. R_f = 0.21 (pentane; stain in PMA).

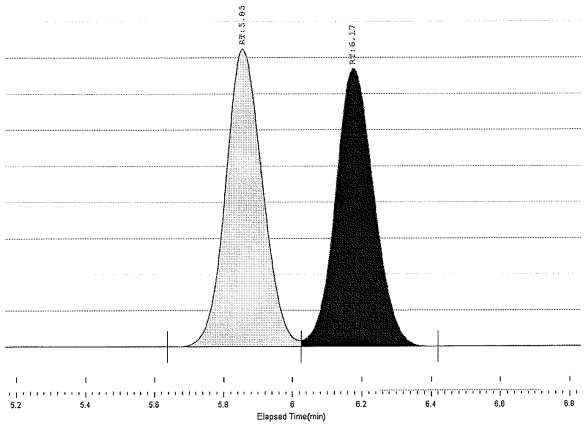
Analysis of Stereochemistry:

Optical purity was determined by SFC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-4-ethynylnon-1-ene (Table 2, Entry 1 G).

Chiral SFC (OJ-H, Chiralpak, 215 nm, 3.0 mL/min, 1.5% i-PrOH, 100 bar, 35 °C) - analysis of title compound.

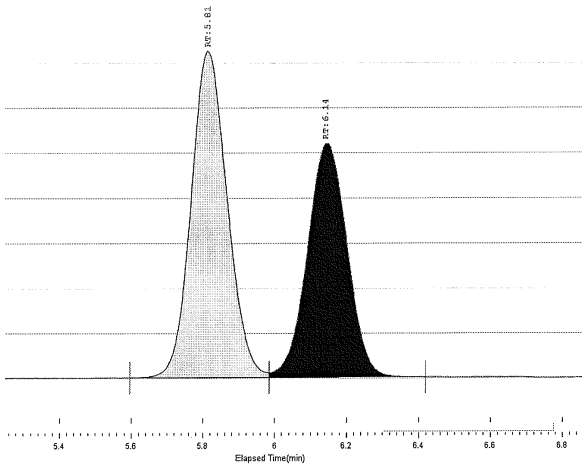


Racemic Sample

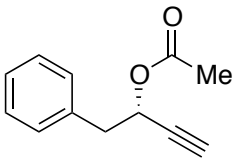


Enantioenriched Sample

Peak No	% Area	Area	RT (min)
1	84.6896	3257.8362	5.86
2	15.3104	588.9614	6.18
Total:	100	3846.7976	



co-injection of racemic and enantioenriched samples

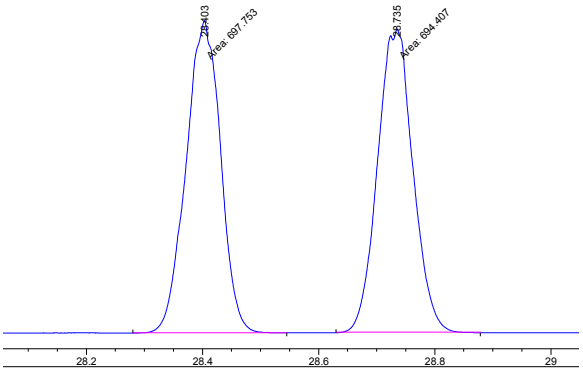


***(S)*-1-phenylbut-3-yn-2-yl acetate (Table 2, Entry 5 l)**. The crude reaction mixture was purified on silica gel (10:1 pentane: diethyl ether) to afford a clear, colorless oil. R_f = 0.7 (5:1 pentane: diethyl ether; stain in PMA). $[\alpha]^{22}_D$ = -7.968 (*c* = 1.33, $CDCl_3$). Spectral data is in accordance with the literature. [1]

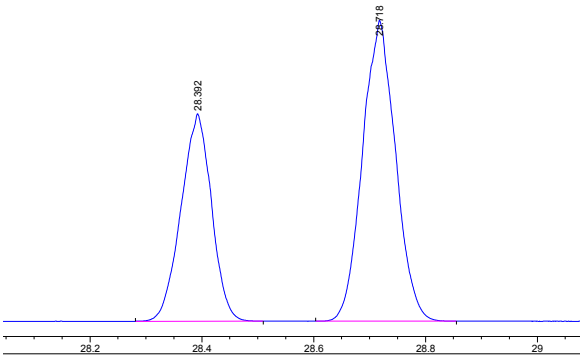
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(S)*-oct-1-yn-3-yl acetate (Table 2, Entry 1 l).

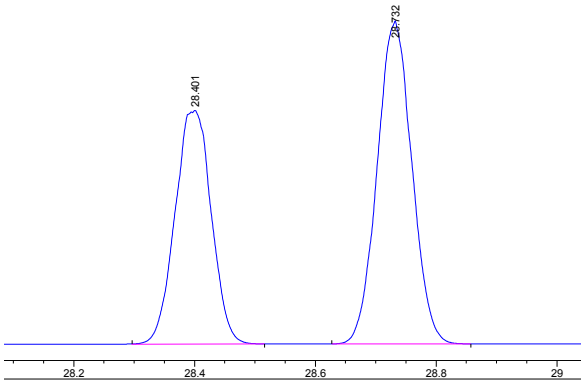
Chiral GLC (β-dex, Supelco, 100 °C for 10 min, ramp 3 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.



Racemic Sample



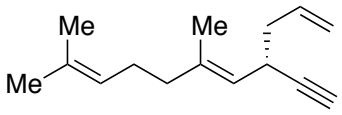
Enantioenriched Sample



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.392	BB	0.0471	436.78180	114.99051	38.95276
2	28.718	BB	0.0499	684.52972	166.75691	61.04724

co-injection of racemic and enantioenriched samples

Kinetic resolution to give *(S,E)*-4-ethynyl-6,10-dimethylundeca-1,5,9-triene (Table 2, Entry 6): The representative procedure was followed with *(E)*-5,9-dimethyldeca-4,8-dien-1-yn-3-yl acetate with the following modification: the reaction was run for 1.5 hours at 0.5% catalyst loading on a 0.2 mmol scale.



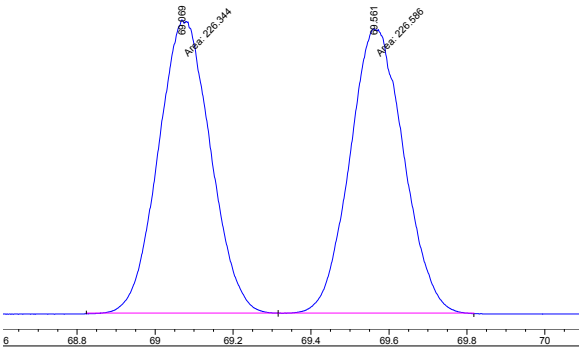
3

***(S,E)*-4-ethynyl-6,10-dimethylundeca-1,5,9-triene (Table 2, Entry 6 G)**. The crude reaction mixture was purified on silica gel (20:1 pentane: diethyl ether) to afford a clear, pale yellow oil. R_f = 0.97 (20:1 pentane: diethyl ether, stain in $KMNO_4$). $[\alpha]^{22}_D$ = 32.525 (c = 0.79, $CHCl_3$). Spectral data is in accordance with the literature.

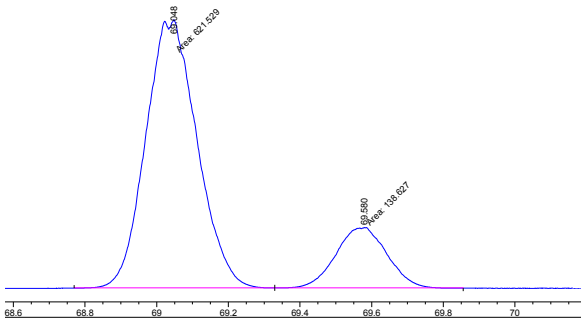
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-4-ethynylnon-1-ene (Table 2, Entry 1 G).

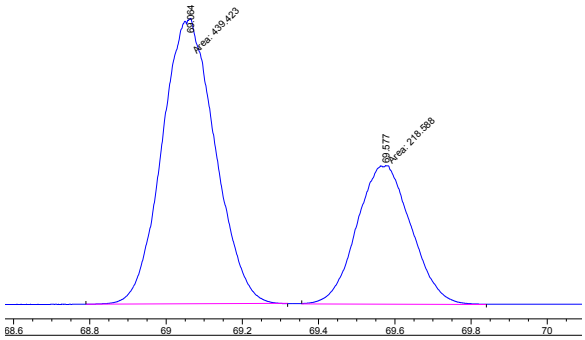
Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 1 °C/min to 140 °C for 40 min, 20 psi) - analysis of title compound.



Racemic Sample

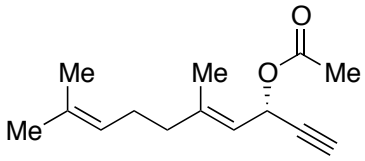


Enantioenriched Sample



co-injection of racemic and enantioenriched samples

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	69.048	MM	0.1661	621.52887	62.35764	81.76338
2	69.580	MM	0.1646	138.62669	14.03614	18.23662

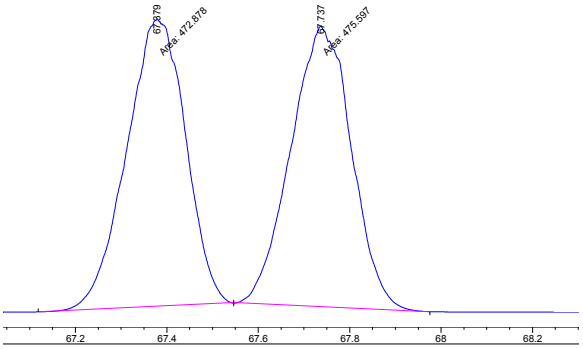


***(S,E)*-5,9-dimethyldeca-4,8-dien-1-yn-3-yl acetate (Table 2, Entry 6 l)**. The crude reaction mixture was purified on silica gel (20:1 pentane: diethyl ether) to afford a clear, pale yellow oil. R_f = 0.49 (20:1 pentane: diethyl ether, stain in $KMNO_4$). $[\alpha]^{22}_D$ = 15.497 (c = 1.12, $CHCl_3$). Spectral data is in accordance with the literature. [3]

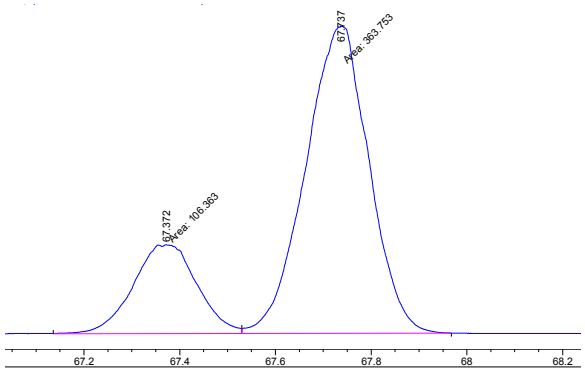
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(S)*-oct-1-yn-3-yl acetate (Table 2, Entry 1 l).

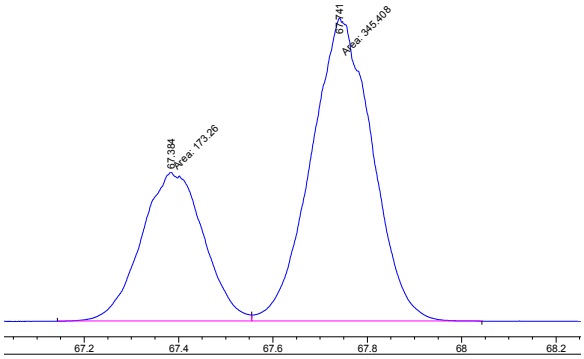
Chiral GLC (β-dex, Supelco, 80 °C for 10 min, ramp 1 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.



Racemic Sample



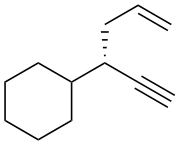
Enantioenriched Sample



co-injection of racemic and enantioenriched samples

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	67.372	MF	0.1552	106.36320	11.42260	22.62488
2	67.737	FM	0.1532	363.75287	39.56961	77.37512

Kinetic resolution to give *(S)*-hex-5-en-1-yn-3-ylcyclohexane (Table 2, Entry 7): The representative procedure was followed with 1-cyclohexylprop-2-yn-1-yl acetate on a 0.2 mmol scale.

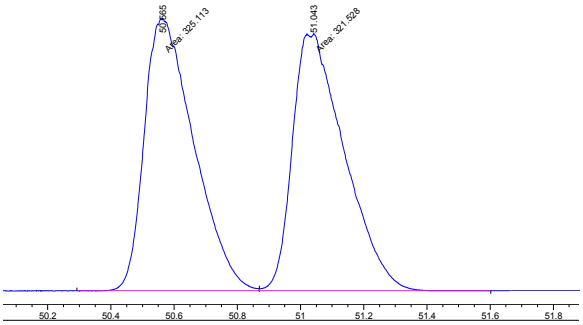


***(S)*-hex-5-en-1-yn-3-ylcyclohexane (Table 2, Entry 7 G)**. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil. R_f = 0.64 (5:1 hexane: ethyl acetate, stain in PMA). $[\alpha]^{22}_D$ = 6.163 (*c* = 0.31, $CHCl_3$). Spectral data is in accordance with the literature. [3]

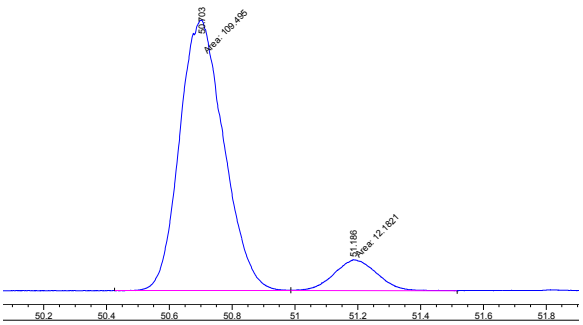
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-4-ethynylnon-1-ene (Table 2, Entry 1 G).

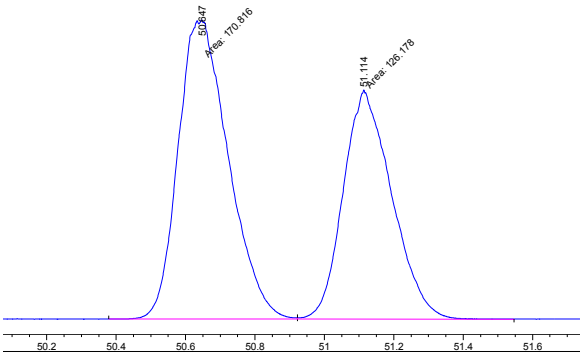
Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 1 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.



Racemic Sample

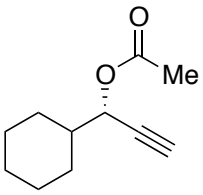


Enantioenriched Sample



co-injection of racemic and enantioenriched samples

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	50.703	MF	0.1627	109.49494	11.21545	89.98819
2	51.186	FM	0.1586	12.18208	1.28046	10.01181

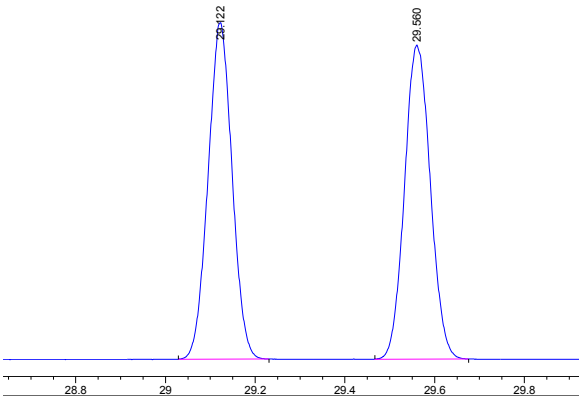


***(S)*-1-cyclohexylprop-2-yn-1-yl acetate (Table 2, Entry 7 I)**. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil. R_f = 0.51 (pentane, stain in PMA). $[\alpha]^{22}_D$ = -5.022 (*c* = 1.76, $CHCl_3$). Spectral data is in accordance with the literature. [2]

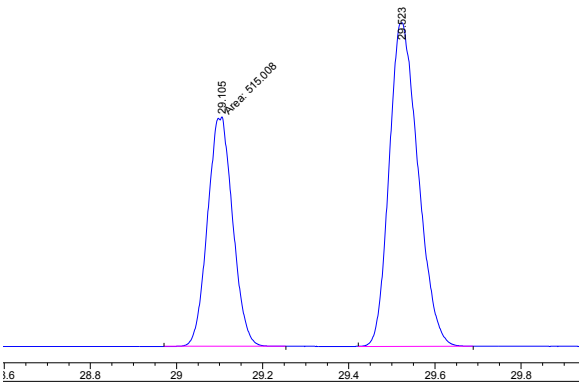
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(S)*-oct-1-yn-3-yl acetate (Table 2, Entry 1 I).

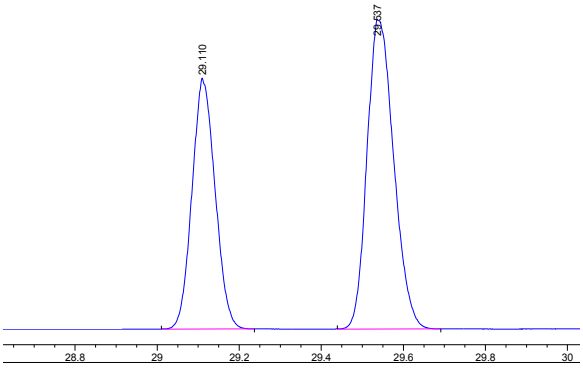
Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 5 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.



Racemic Sample



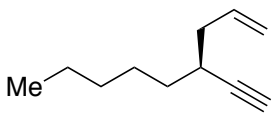
Enantioenriched Sample



co-injection of racemic and enantioenriched samples

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.105	MM	0.0675	515.00781	127.15060	38.15054
2	29.523	BB	0.0573	834.92798	179.27284	61.84946

Kinetic resolution to give *(S)*-4-ethynylnon-1-ene (Table 2, Entry 8): The representative procedure was followed with oct-1-yn-3-yl acetate with the following modification: *(S)*-**cat 1** (0.75 mol %) was used on a 0.2 mmol scale.

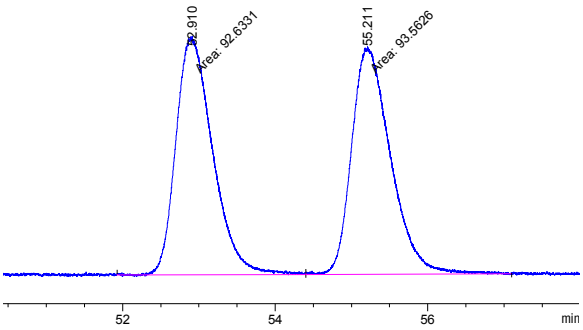


***(S)*-4-ethynylnon-1-ene (Table 2, Entry 8 G)**. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil. R_f = 0.71 (pentane, stain in PMA). Spectral data is in accordance with literature.[3]

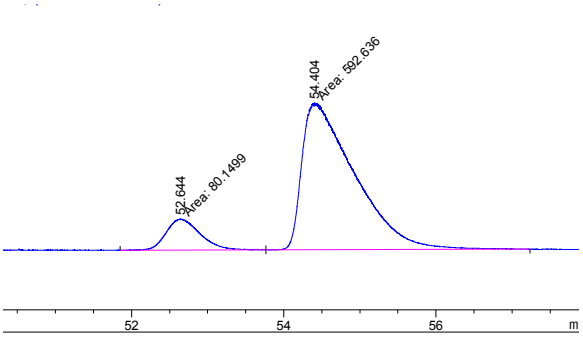
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by comparison to to *(R)*-4-ethynylnon-1-ene (Table 2, Entry 1 G).

Chiral GLC (CD-BDM, Supelco, 40 °C for 30 min, ramp 0.25 °C/min to 50 °C for 10 min, 20 psi) - analysis of title compound.

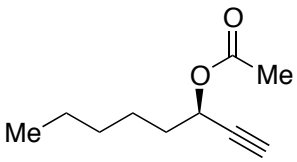


Racemic Sample



Enantioenriched Sample

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	52.644	MF	0.5080	80.14990	2.62966	11.91313
2	54.404	FM	0.7952	592.63623	12.42084	88.08687

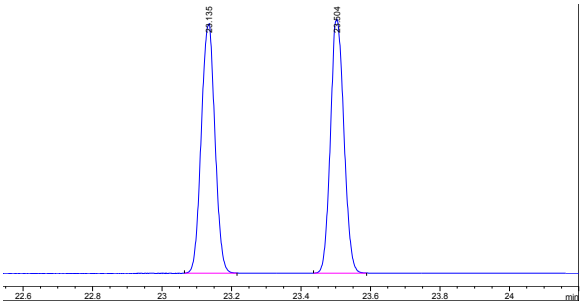


***(R)*-oct-1-yn-3-yl acetate (Table 2, Entry 8 l)**. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil. R_f = 0.60 (10:1 pentane: diethyl ether, stain in PMA). Spectral data is in accordance with literature. [11]

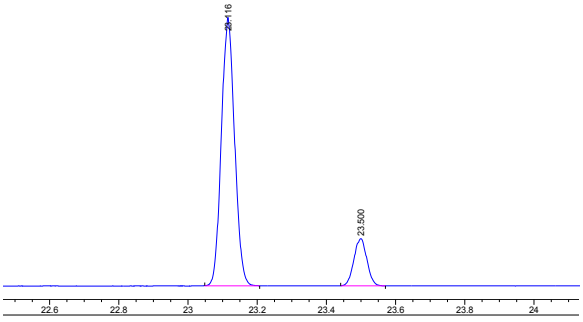
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by comparison to *(S)*-oct-1-yn-3-yl acetate (Table 2, Entry 1 l).

Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 5 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.



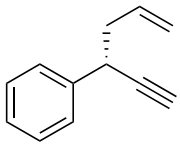
Racemic Sample



Enantioenriched Sample

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	23.116	BB	0.0358	157.85902	59.36190	85.29798
2	23.500	BB	0.0345	27.20868	10.41043	14.70202

Kinetic resolution to give *(R)*-hex-5-en-1-yn-3-ylbenzene (Table 2, Entry 9): The representative procedure was followed with 1-phenylprop-2-yn-1-yl acetate with the following modification: the reaction was run for 2 hours at 0.5% catalyst loading on a 0.2 mmol scale.



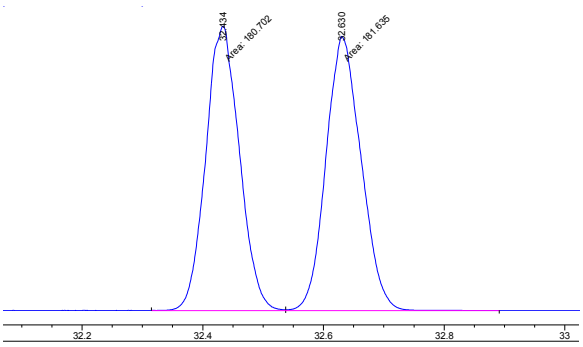
***(R)*-hex-5-en-1-yn-3-ylbenzene (Table 2, Entry 9 G)**. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil. R_f = 0.43 (pentane, stain in PMA). $[\alpha]^{22}_D$ = -15.235 (*c* = 0.31, $CHCl_3$). Spectral data is in accordance with the literature.[8]

Analysis of Stereochemistry:

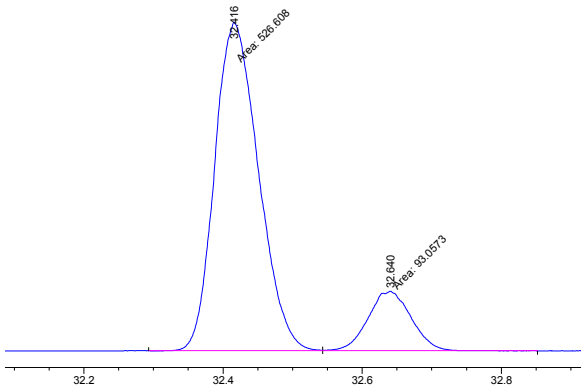
Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned as shown below.

[8] Zhan, Z.; Yo, J.; Liu, H.; Cui, Y.; Yang, R.; Yang, W.; Li, Y. *J. Org. Chem.* **2006**, *71*, 8298.

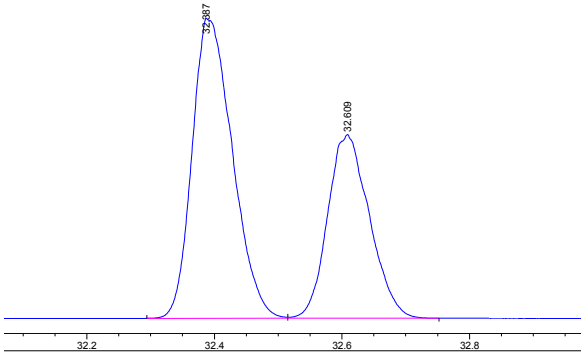
Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 3 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.



Racemic Sample



Enantioenriched Sample

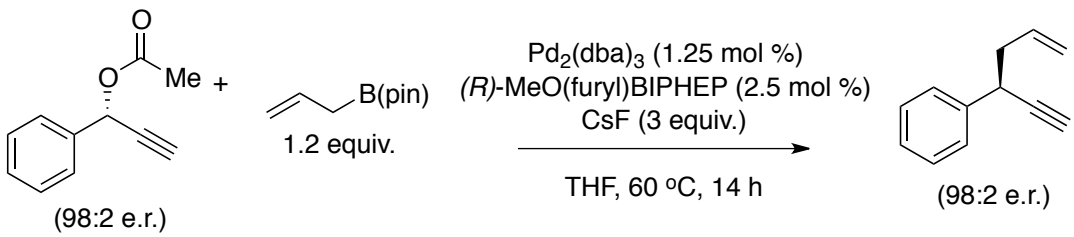


co-injection of racemic and enantioenriched samples

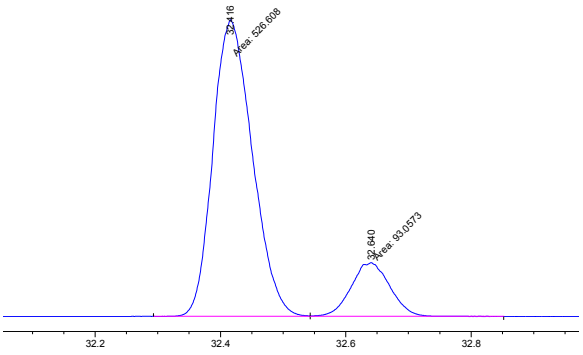
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	32.416	MF	0.0727	526.60809	120.75000	84.98265
2	32.640	FM	0.0711	93.05730	21.80412	15.01735

Proof of Absolute Stereochemistry:

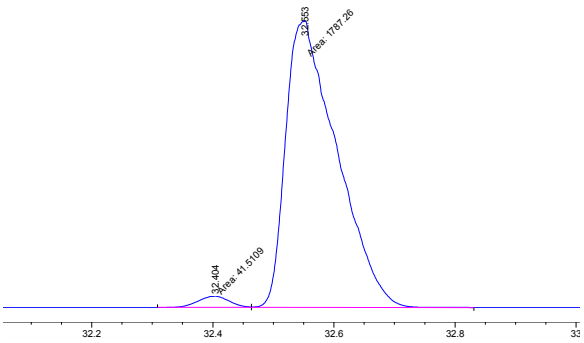
In order to determine the absolute stereochemistry, the title compound was compared by GLC analysis to authentic *(S)*-hex-5-en-1-yn-3-ylbenzene, prepared by the stereospecific enyne cross coupling as depicted below. [3]



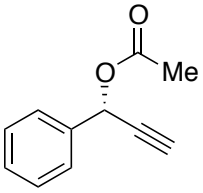
Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 3 °C/min to 140 °C for 10 min, 20 psi)-analysis of title compound.



Title Compound



authentic *(S)*-hex-5-en-1-yn-3-ylbenzene

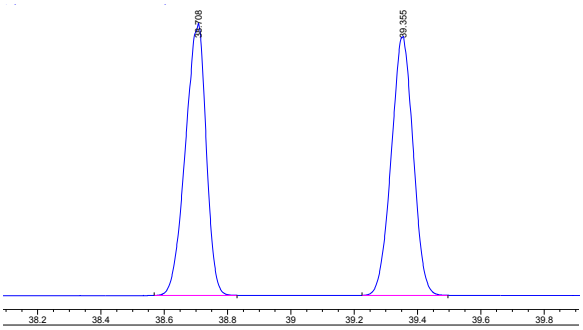


***(R)*-1-phenylprop-2-yn-1-yl acetate (Table 2, Entry 9 l)**. The crude raction mixture was purified on silica gel (pentane) to afford a clear, colorless oil. R_f = 0.27 (25:1 hexane: ethyl acetate, stain in PMA). $[\alpha]^{22}_D$ = 2.176 (*c* = 0.45, $CHCl_3$). Spectral data is in accordance with the literature.[2]

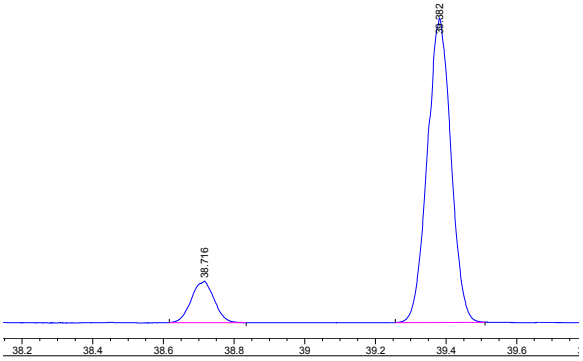
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned as shown below.

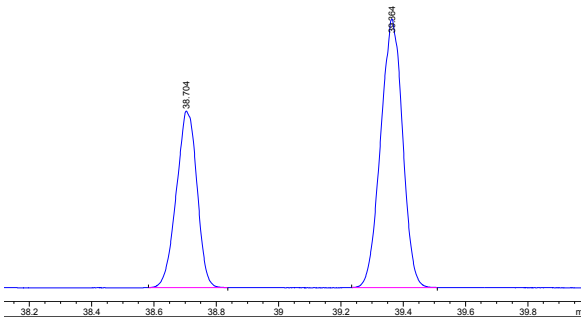
Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 3 °C/min to 140 °C for 20 min, 20 psi) - analysis of title compound.



Racemic Sample



Enantioenriched Sample

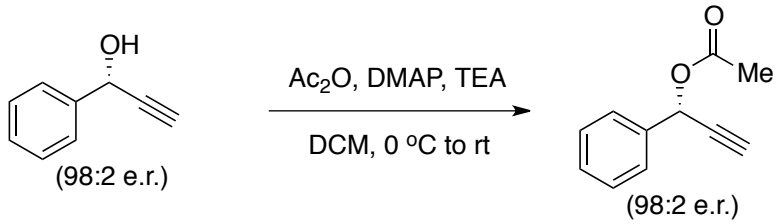


co-injection of racemic and enantioenriched samples

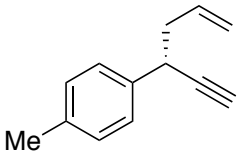
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	38.716	BB	0.0548	19.52114	4.33718	11.65692
2	39.382	BB	0.0573	147.94279	31.80352	88.34308

Proof of Absolute Stereochemistry:

In order to determine the absolute stereochemistry, the optical rotation of the title compound [$[\alpha]^{22}_D$ = 2.176 (*c* = 0.45, $CHCl_3$), 88:11 e.r.] was compared to authentic *(R)*-1-phenylprop-2-yn-1-yl acetate prepared from commercially available *(R)*-1-phenylprop-2-yn-1-ol as shown below [$[\alpha]^{22}_D$ = 4.852 (*c* = 0.915, $CHCl_3$), 98:2 e.r.]



Kinetic resolution to give *(R)*-1-(hex-5-en-1-yn-3-yl)-4-methylbenzene (Table 2, Entry 10): The representative procedure was followed with 1-(p-tolyl)prop-2-yn-1-yl acetate with the following modification: the reaction was run for 2 hours at 0.5% catalyst loading on a 0.2 mmol scale.

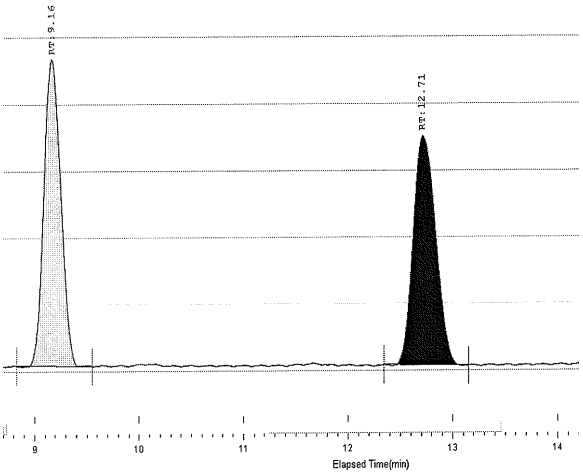


***(R)*-1-(hex-5-en-1-yn-3-yl)-4-methylbenzene (Table 2, Entry 10 G)**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (2H, ddd, J = 8.0 Hz, 2.0 Hz, 2.0 Hz), 7.14 (2H, d, J = 8.0 Hz), 5.85 (1H, dddd (app ddt), J = 17.0 Hz, 10.0 Hz, 6.5 Hz, 6.5 Hz), 5.09 (1H, ddd, J = 1.5 Hz, 1.5 Hz, 1.5 Hz), 5.04 - 5.07 (1H, m), 3.69 (1H, ddd (app dt), J = 7.0 Hz, 7.0 Hz, 2.5 Hz), 2.50 (2H, dddd (app ddt), J = 6.5 Hz, 6.5 Hz, 2.5 Hz, 1.5 Hz), 2.33 (3H, s), 2.28 (1H, d, J = 2.5); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.8, 136.5, 135.3, 129.2, 129.2, 127.3, 127.3, 117.1, 85.6, 71.2, 42.4, 37.3, 21.1; IR (neat): 3299 (w), 3051(m), 3007 (m), 2923 (w), 2857 (m), 1513 (m), 1022 (m), 915 (m), 813 (m), 634 (s) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{15}$ [M+H]: calculated: 171.1174, found: 171.1179. $[\alpha]^{22}_{D}$ = -59.989 (c = 0.05, $CHCl_3$). The crude reaction was purified on silica gel (pentane) to afford a clear, colorless oil. R_f = 0.23 (pentane; stain in PMA).

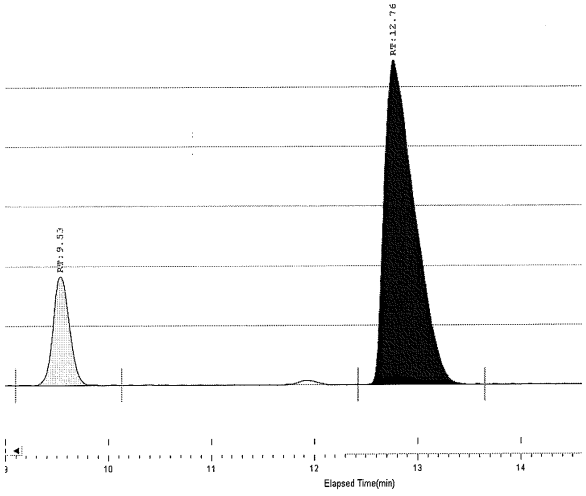
Analysis of Stereochemistry:

Optical purity was determined by SFC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-hex-5-en-1-yn-3-ylbenzene (Table 2, Entry 9 G).

Chiral SFC (OJ-H, Chiralpak, 215 nm, 3.0 mL/min, 1% 1:1 i-PrOH:Hexanes, 100 bar, 35 °C) - analysis of title compound.

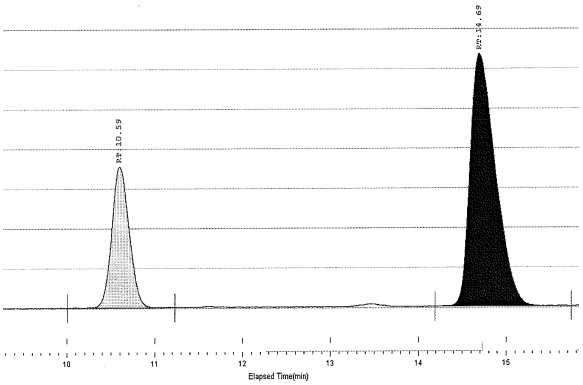


Racemic Sample

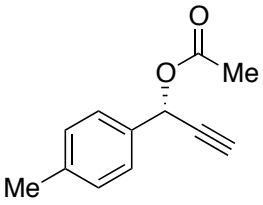


Enantioenriched Sample

Peak No	% Area	Area	RT (min)
1	15.3555	4031.9559	9.53
2	84.6445	22225.3857	12.76
Total:	100	26257.3416	



co-injection of racemic and enantioenriched samples

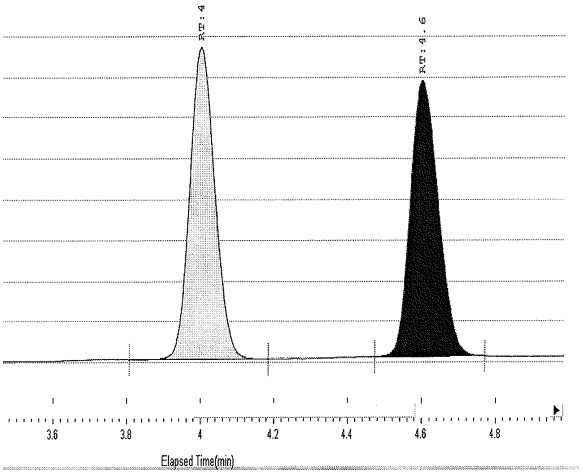


***(R)*-1-(p-tolyl)prop-2-yn-1-yl acetate (Table 2, Entry 10 l)**. The crude reaction mixture was purified on silica gel (10:1 pentane: diethyl ether) to afford a clear, colorless oil. R_f = 0.26 (25:1 hexane: ethyl acetate; stain in PMA). $[\alpha]^{22}_D$ = 26.177 (*c* = 0.11, $CHCl_3$). Spectral data is in accordance with the literature. [1]

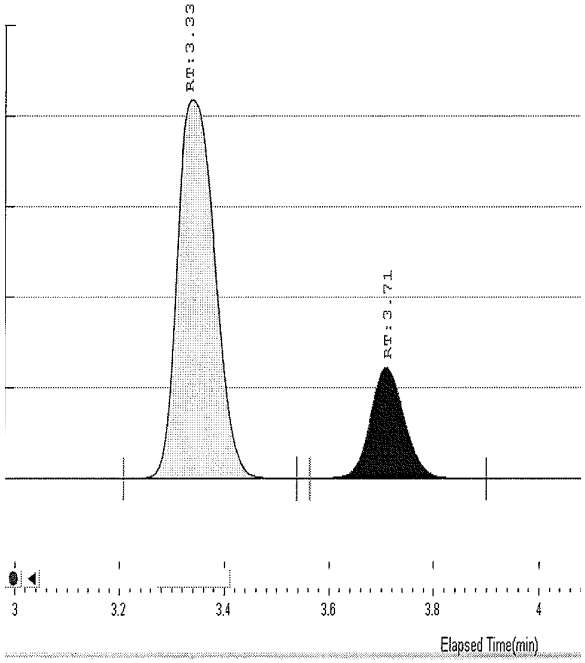
Analysis of Stereochemistry:

Optical purity was determined by SFC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-1-phenylprop-2-yn-1-yl acetate (Table 2, Entry 9 l).

Chiral SFC (OJ-H, Chiralpak, 215 nm, 3.0 mL/min, 3% i-PrOH, 100 bar, 35 °C) - analysis of title compound.

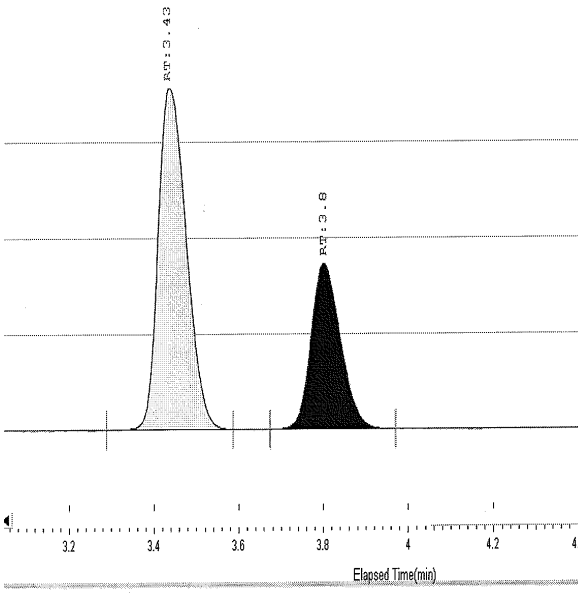


Racemic Sample



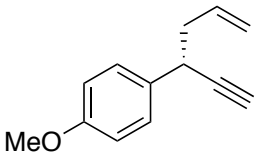
Enantioenriched Sample

Peak No	% Area	Area	RT (min)
1	78.8757	10298.8407	3.33
2	21.1243	2758.2045	3.71
Total:	100	13057.0452	



co-injection of racemic and enantioenriched samples

Kinetic resolution to give *(R)*-1-(hex-5-en-1-yn-3-yl)-4-methoxybenzene (Table 2, Entry 11): The representative procedure was followed with 1-(4-methoxyphenyl)prop-2-yn-1-yl acetate with the following modification: the reaction was run for 1 hour at 0.5% catalyst loading on a 0.2 mmol scale.

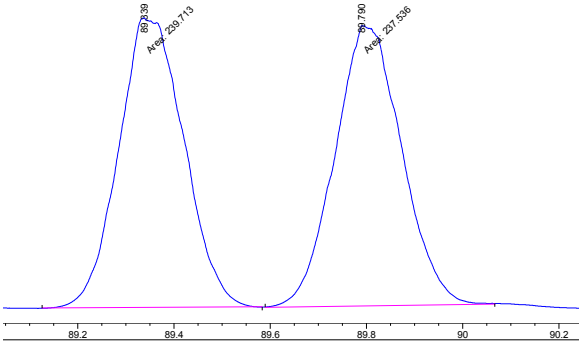


***(R)*-1-(hex-5-en-1-yn-3-yl)-4-methoxybenzene (Table 2, Entry 11 G)**. The crude reaction mixture was purified on silica gel (10:1 pentane: diethyl ether) to afford a clear, colorless oil. R_f = 0.86 (10:1 pentane: diethyl ether, stain in $KMNO_4$). $[\alpha]^{22}_D$ = 13.916 (c = 0.73, $CHCl_3$). Spectral data is in accordance with the literature. [3]

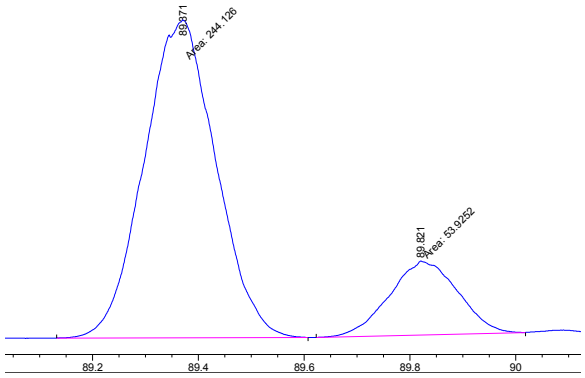
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-hex-5-en-1-yn-3-ylbenzene (Table 2, Entry 9 G).

Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 1 °C/min to 160 °C for 20 min, 20 psi) - analysis of title compound.

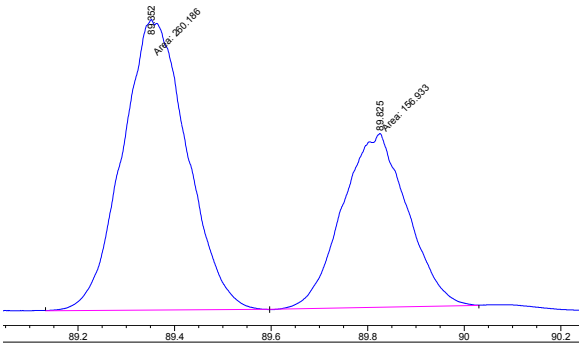


Racemic Sample

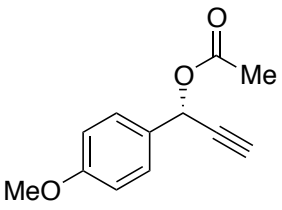


Enantioenriched Sample

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	89.371	MM	0.1571	244.12610	25.89414	81.90742
2	89.821	MM	0.1491	53.92517	6.02781	18.09258



co-injection of racemic and enantioenriched samples

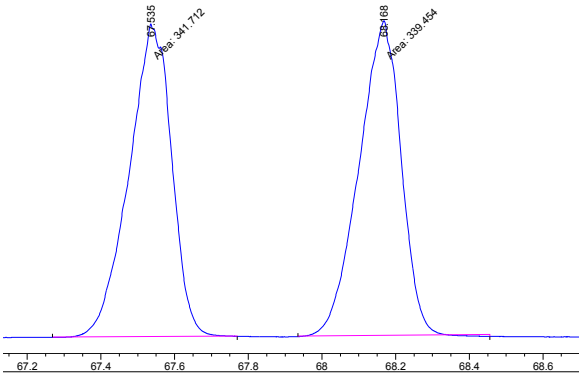


***(R)*-1-(4-methoxyphenyl)prop-2-yn-1-yl acetate (Table 2, Entry 11 l)**. The crude reaction mixture was purified on silica gel (10:1 pentane: diethyl ether) to afford a clear, colorless oil. R_f = 0.39 (10:1 pentane: diethyl ether, stain in $KMNO_4$). $[\alpha]^{22}_D$ = 20.301 (c = 0.92, $CHCl_3$). Spectral data is in accordance with the literature. [3]

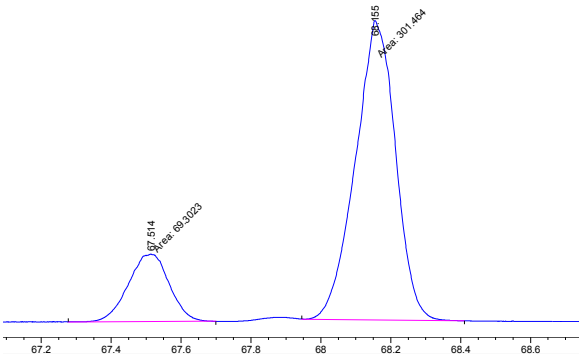
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-1-phenylprop-2-yn-1-yl acetate (Table 2, Entry 9 l).

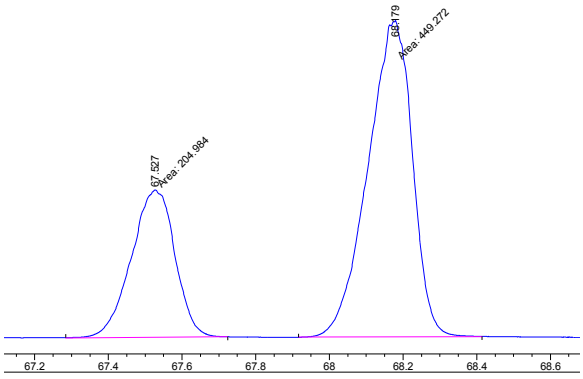
Chiral GLC (β-dex, Supelco, 40 °C for 10 min, ramp 2.5 °C/min to 160 °C for 20 min, 20 psi) - analysis of title compound.



Racemic Sample



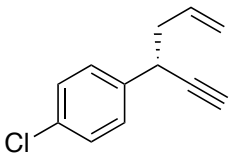
Enantioenriched Sample



co-injection of racemic and enantioenriched samples

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	67.514	MM	0.1357	69.30232	8.51125	18.69166
2	68.155	MM	0.1332	301.46375	37.73237	81.30834

Kinetic resolution to give *(R)*-1-chloro-4-(hex-5-en-1-yn-3-yl)benzene (Table 2, Entry 12): The representative procedure was followed with 1-(4-chlorophenyl)prop-2-yn-1-yl acetate with the following modification: the reaction was run for 2 hours at 0.5% catalyst loading on a 0.2 mmol scale.

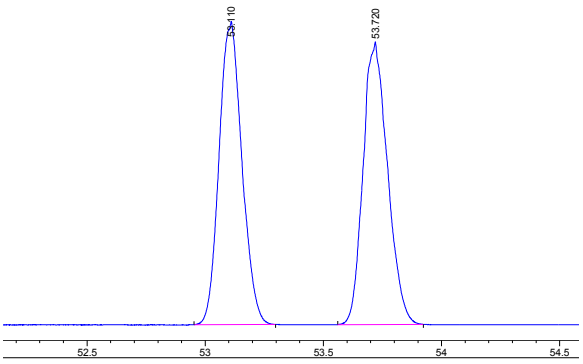


***(R)*-1-chloro-4-(hex-5-en-1-yn-3-yl)benzene (Table 2, Entry 12 G)**. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil. R_f = 0.37 (pentane, stain in PMA). $[\alpha]^{22}_D$ = -5.646 (*c* = 0.60, $CHCl_3$). Spectral data is in accordance with the literature. [3]

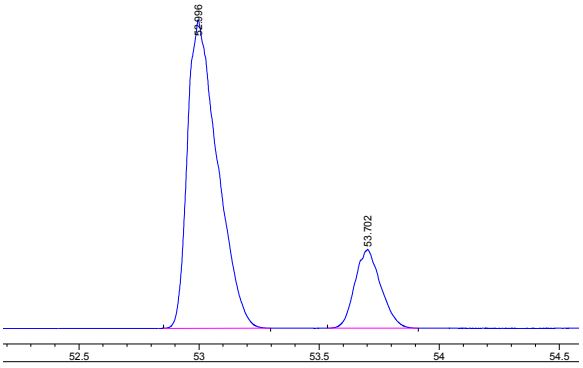
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-hex-5-en-1-yn-3-ylbenzene (Table 2, Entry 9 G).

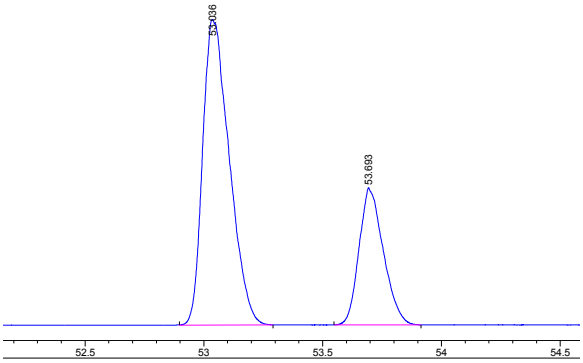
Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 2 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.



Racemic Sample

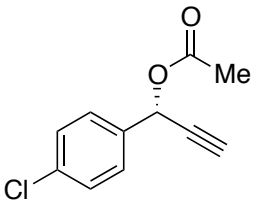


Enantioenriched Sample



co-injection of racemic and enantioenriched samples

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	52.996	BB	0.1041	1385.26355	159.45381	81.93271
2	53.702	BB	0.0887	305.46964	40.77204	18.06729

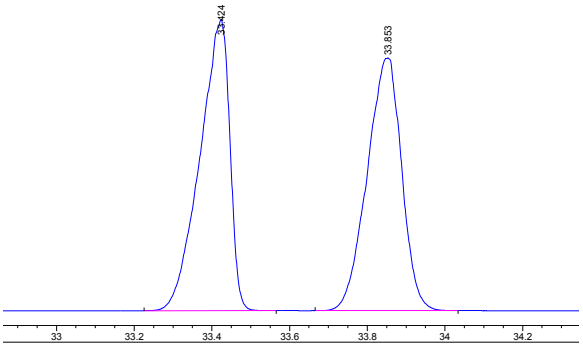


***(R)*-1-(4-chlorophenyl)prop-2-yn-1-yl acetate (Table 2, Entry 12 l)**. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl either) to afford a clear, colorless oil. R_f = 0.32 (10:1 hexane: ethyl acetate, stain in PMA). $[\alpha]^{22}_D$ = 9.834 (*c* = 1.22, $CHCl_3$). Spectral data is in accordance with the literature. [1]

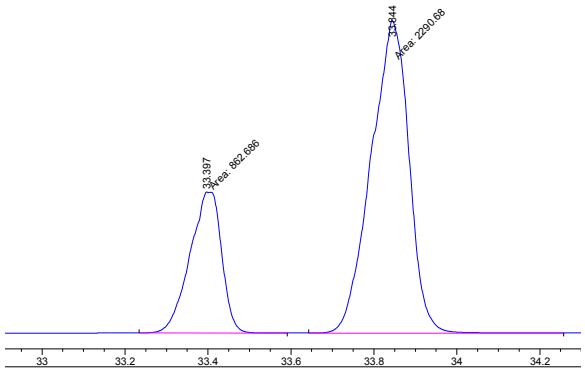
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-1-phenylprop-2-yn-1-yl acetate (Table 2, Entry 9 l).

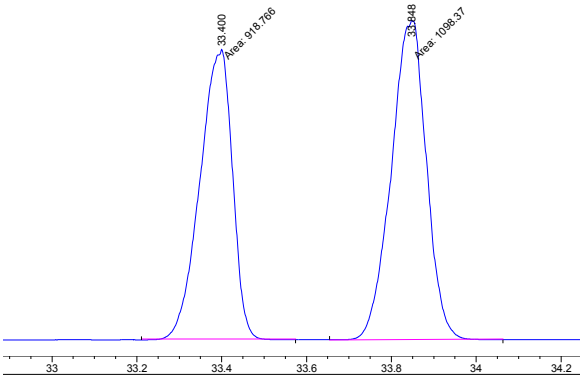
Chiral GLC (β-dex, Supelco, 100 °C for 10 min, ramp 3 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.



Racemic Sample



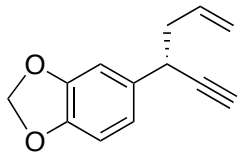
Enantioenriched Sample



co-injection of racemic and enantioenriched samples

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	33.397	MM	0.0885	862.68561	162.41209	27.35757
2	33.844	MM	0.1061	2290.68481	359.74545	72.64243

Kinetic resolution to give *(R)*-5-(hex-5-en-1-yn-3-yl)benzo[d][1,3]dioxole (Table 2, Entry 13): The representative procedure was followed with 1-(benzo[d][1,3]dioxol-5-yl)prop-2-yn-1-yl acetate with the following modification: the reaction was run for 2 hours at 0.5% catalyst loading on a 0.2 mmol scale.

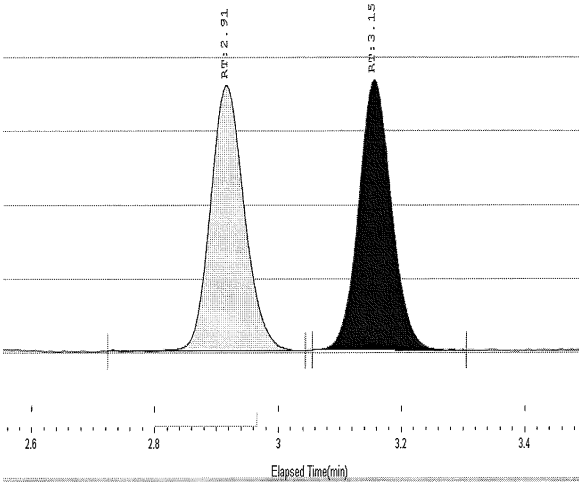


***(R)*-5-(hex-5-en-1-yn-3-yl)benzo[d][1,3]dioxole (Table 2, Entry 13 G)**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 (1H, d, *J* = 2.0 Hz), 6.80 (1H, dd, *J* = 8.0 Hz, 2.0 Hz), 6.75 (1H, d, *J* = 8.0 Hz), 5.94 (2H, dd, *J* = 2.0 Hz, 2.0 Hz), 5.83 (1H, dddd (app ddt), *J* = 17.0 Hz, 10.5 Hz, 7.0 Hz, 7.0 Hz), 5.07-5.09 (1H, m), 5.04-5.06 (1H, m), 3.32 (1H, ddd (app dt), *J* =7.0 Hz, 7.0 Hz, 2.5 Hz), 2.46-4.50 (2H, m), 2.94 (1H, d, *J* = 2.5 Hz) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.7, 146.4, 135.0, 134.6, 120.5, 117.2, 108.1, 107.9, 101.0, 85.4, 71.3, 42.5, 37.4; IR (neat): 3293 (m), 3077 (w), 2979 (w), 2895 (m), 1485 (m), 2439 (s), 1245 (s), 918 (m), 634 (s) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{13}O_2$ [M+H]: calculated: 200.0837, found: 200.0837. $[\alpha]^{22}_D$ = 28.318 (*c* = 0.37, $CHCl_3$). The crude reaction was purified on silica gel (60:1 pentane:diethyl ether) to afford a clear, colorless oil. R_f = 0.10 (pentane; stain in PMA).

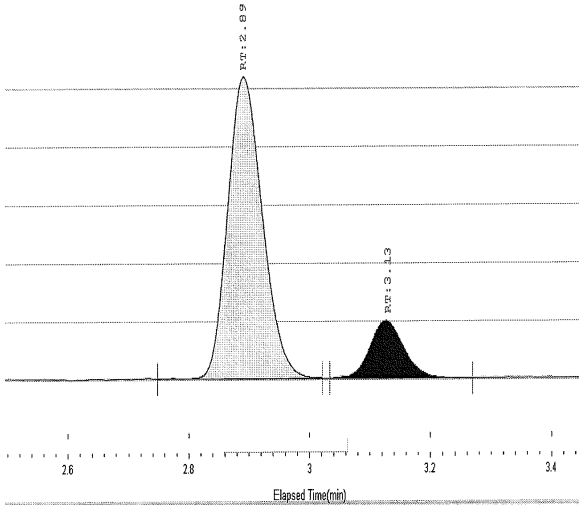
Analysis of Stereochemistry:

Optical purity was determined by SFC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-hex-5-en-1-yn-3-ylbenzene (Table 2, Entry 9 G).

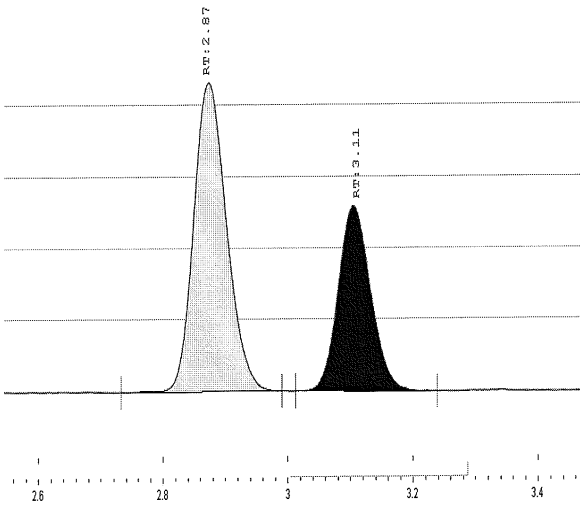
Chiral SFC (AD-H, Chiralpak, 215 nm, 3.0 mL/min, 3% i-PrOH, 100 bar, 35 °C) - analysis of title compound.



Racemic Sample

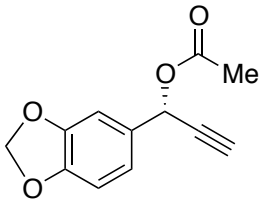


Enantioenriched Sample



Peak Info			
Peak No	% Area	Area	RT (min)
1	84.386	1026.7635	2.89
2	15.614	189.9822	3.13
Total:	100	1216.7457	

co-injection of racemic and enantioenriched samples

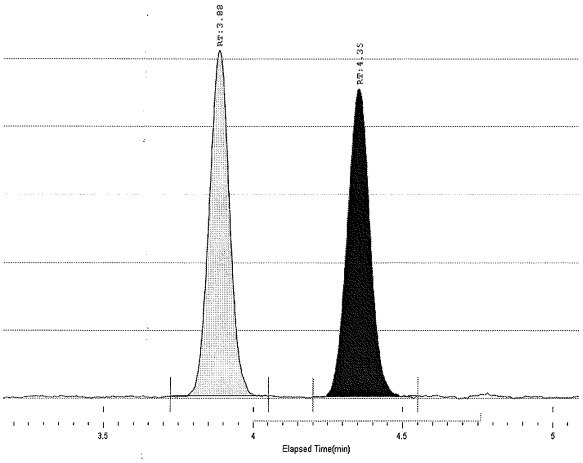


***(R)*-1-(benzo[d][1,3]dioxol-5-yl)prop-2-yn-1-yl acetate (Table 2, Entry 13 l)**. The crude reaction was purified on silica gel (10:1 pentane:diethyl ether) to afford a white solid. R_f = 0.14 (20:1 hexane: ethyl acetate; stain in PMA). $[\alpha]^{22}_D$ = 3.744 (*c* = 0.38, $CHCl_3$). Spectral data is in accordance with the literature.[3]

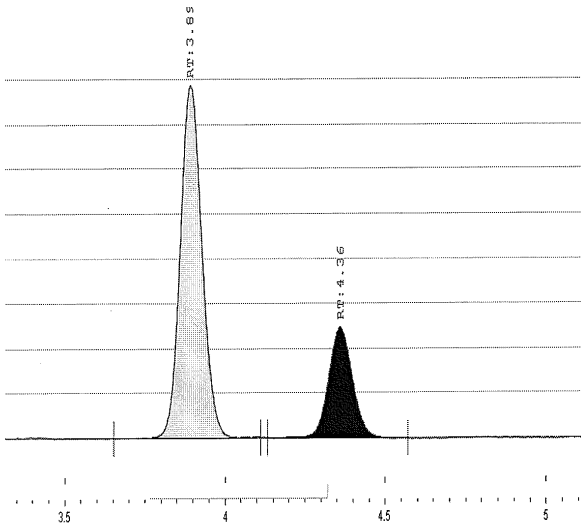
Analysis of Stereochemistry:

Optical purity was determined by SFC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-1-phenylprop-2-yn-1-yl acetate (Table 2, Entry 9 l).

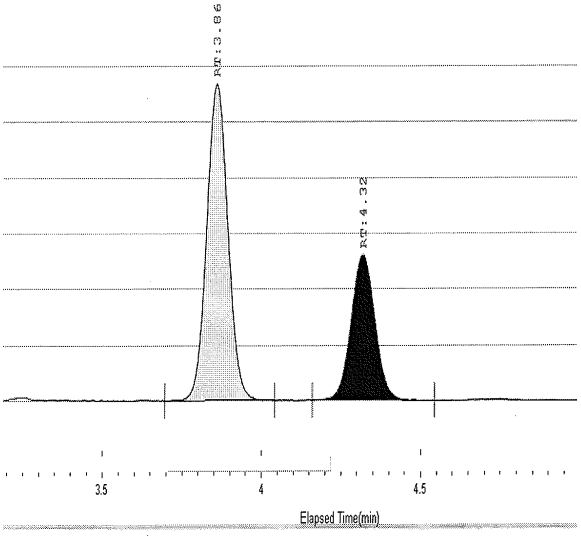
Chiral SFC (OJ-H, Chiralpak, 215 nm, 3.0 mL/min, 3% i-PrOH, 100 bar, 35 °C) - analysis of title compound.



Racemic Sample



Enantioenriched Sample

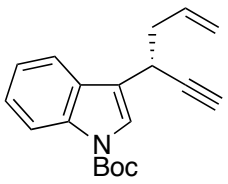


co-injection of racemic and enantioenriched samples

Peak Info

Peak No	% Area	Area	RT (min)
1	74.5721	1853.3292	3.89
2	25.4279	631.9564	4.36
Total:	100	2485.2856	

Kinetic resolution to give *(R)*-tert-butyl 3-(hex-5-en-1-yn-3-yl)-1H-indole-1-carboxylate (Table 2, Entry 14): The representative procedure was followed with tert-butyl 3-(1-acetoxyprop-2-yn-1-yl)-1H-indole-1-carboxylate with the following modification: the reaction was run for 1 hour at 0.5% catalyst loading on a 0.2 mmol scale.

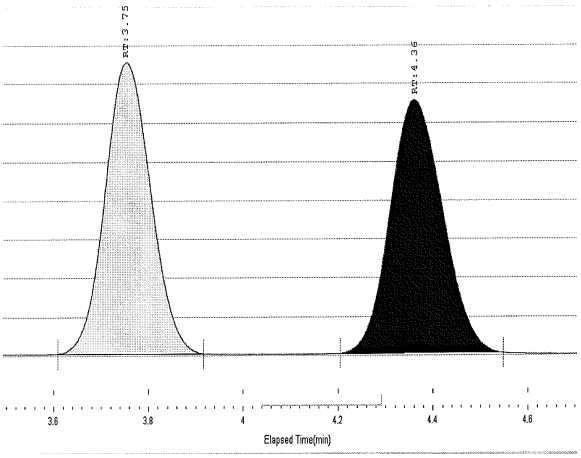


***(R)*-tert-butyl 3-(hex-5-en-1-yn-3-yl)-1H-indole-1-carboxylate (Table 2, Entry 14 G)**. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl either) to afford a clear, colorless oil. R_f = 0.93 (10:1 pentane:diethyl either, stain in $KMNO_4$). $[\alpha]^{22}_D$ = -4.112 (c = 0.73, $CHCl_3$). Spectral data is in accordance with the literature. [3]

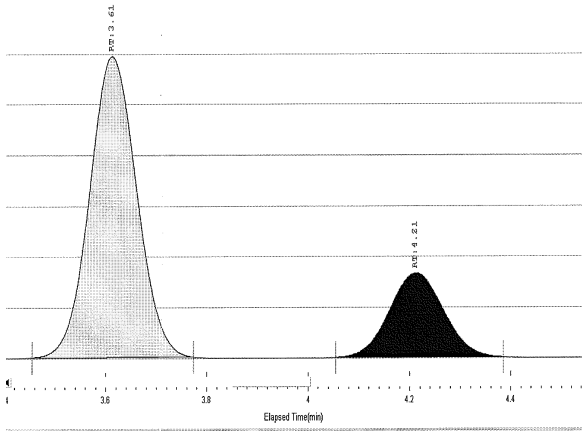
Analysis of Stereochemistry:

Optical purity was determined by SFC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-hex-5-en-1-yn-3-ylbenzene (Table 2, Entry 9 G).

Chiral SFC (OJ-H, Chiralpak, 215 nm, 3.0 mL/min, 1% 1:1 i-PrOH:Hexanes, 100 bar, 35 °C) - analysis of title compound.



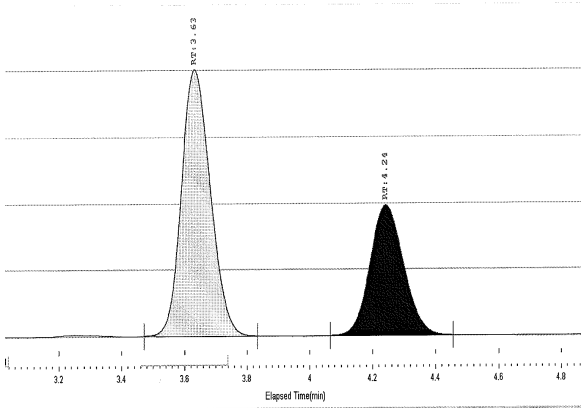
Racemic Sample



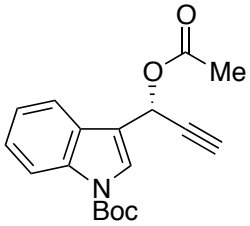
Enantioenriched Sample

Peak Info			
Peak Name	**Number**	**Concentration**	**Area %**
Peak1	1	0	75.6151
Peak2	2	0	24.3849

RT (min)	**St. (min)**	**End (min)**	**Height**
3.61	3.4547	3.7714	1187.8859
4.21	4.0547	4.383	332.7256



co-injection of racemic and enantioenriched samples

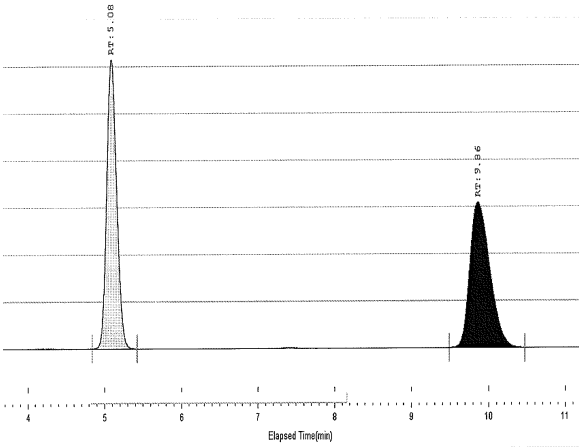


***(R)-tert*-butyl 3-(1-acetoxyprop-2-yn-1-yl)-1H-indole-1-carboxylate (Table 2, Entry 14 l)**. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl either) to afford a clear, colorless oil. R_f = 0.35 (10:1 pentane:diethyl either, stain in $KMNO_4$). $[\alpha]^{22}_D$ = -2.350 (c = 1.15, $CHCl_3$). Spectral data is in accordance with the literature. [3]

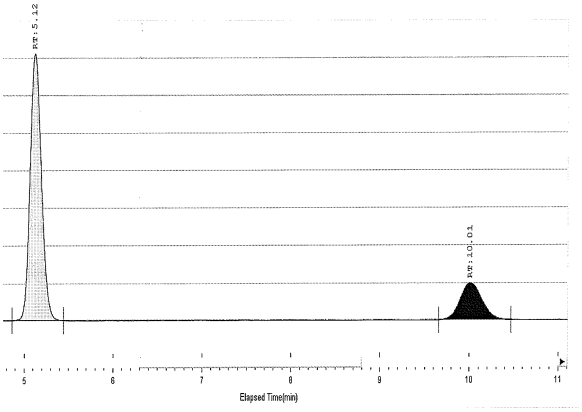
Analysis of Stereochemistry:

Optical purity was determined by SFC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-1-phenylprop-2-yn-1-yl acetate (Table 2, Entry 9 l).

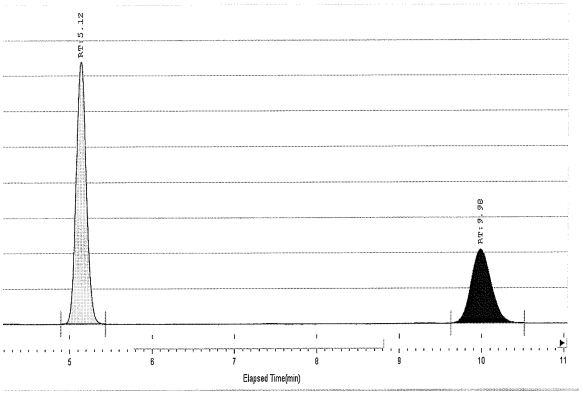
Chiral SFC (OJ-H, Chiralpak, 215 nm, 3.0 mL/min, 1% 1:1 i-PrOH:Hexanes, 100 bar, 35 °C) - analysis of title compound.



Racemic Sample



Enantioenriched Sample

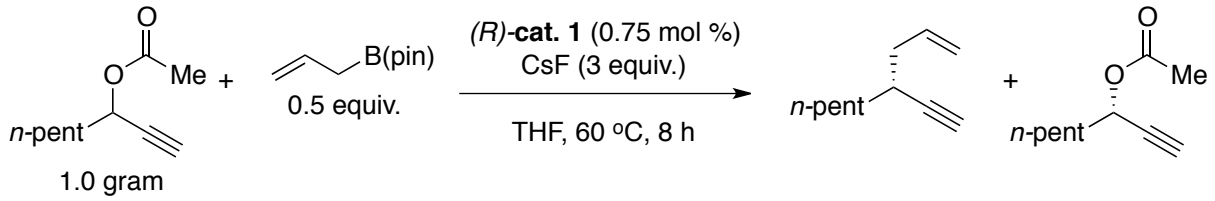


co-injection of racemic and enantioenriched samples

Peak Info

Peak No	% Area	Area	RT (min)
1	79.0279	6306.2126	5.12
2	20.9721	1673.5195	10.01
Total:	100	7979.7321	

Gram-Scale Resolution (Scheme 2, eq 3)



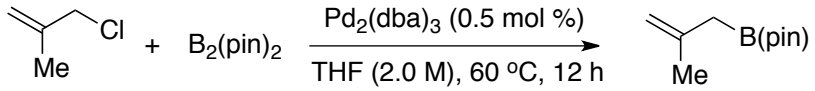
An oven-dried 100-mL airfree pressure vessel equipped with a magnetic stir bar was charged successively with [*(R)*-(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl]palladium(II) dichloride (32.1 mg, 44.6 µmol), THF (11.9 mL), oct-1-yn-3-yl acetate (1.0 g mg, 5.95 mmol), allylboronic acid pinacol ester (500 mg, 2.97 mmol), and cesium fluoride (2.71 g, 17.8 mmol) in a dry-box under argon atmosphere. The vessel was sealed, removed from the dry-box, and heated to 60 °C while allowing to stir for 8 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 a silica gel with a solvent gradient from 20:1 to 10:1 pentane:diethyl ether and the enyne product and recovered propargyl acetate were collected separately:

Enyne Product: clear colorless oil, 373.83 mg (93% yield based on 46% conversion) 89:11 e.r.

Recovered Acetate: Pale yellow oil, 391.26 mg (73% recovery based on 46% conversion) 82:18 e.r.; the *s* value was calculated to be 15.5 at the calculated 46% conversion.

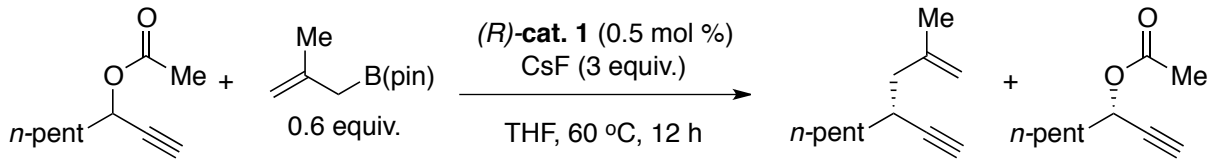
Preparation of 2-Methallylboronic acid Pinacol Ester



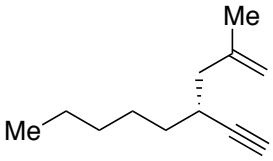
An oven-dried scintillation vial equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (13.7 mg, 0.015 mmol), bis(pinacolato)diboron (762.6 mg, 3.00 mmol), and tetrahydrofuran (1.5 mL) in a dry-box under argon atmosphere. The vial was capped and stirred for two minutes, then 3-chloro-2-methylpropane (271.7 mg, 3.00 mmol) was added. The vial was capped with a teflon cone-lined cap, sealed with electrical tape, removed from the dry-box, and heated to 60 °C and allowed to stir for 12 h. The reaction was then concentrated *in vacuo* and the crude reaction mixture was purified rapidly on oven-dried silica gel (50:1 pentane:diethyl ether) to afford a clear, colorless oil (341 mg, 63% yield). R_f = 0.63 (50:1 pentane:diethyl ether, stain in $KMnO_4$). Spectral data is in accordance with the literature.[9]

[9] Zhang, P.; Brozek, L. A.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 10686.

Kinetic Resolution to Give *(R)*-4-ethynyl-2-methylnon-1-ene (Scheme 2, eq 4):



An oven-dried scintillation vial equipped with a magnetic stir bar was charged successively with [*(R)*-(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl]palladium(II) dichloride (0.72 mg, 1.0 µmol), THF (0.4 mL), oct-1-yn-3-yl acetate (33.6 mg, 0.20 mmol), 2-methallylboronic acid pinacol ester (21.8 mg, 0.12 mmol), and cesium fluoride (91.9 mg, 0.6 mmol) in a dry-box under argon atmosphere. The vial was sealed, removed from the dry-box, and heated to 60 °C while allowing to stir for 12 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*.

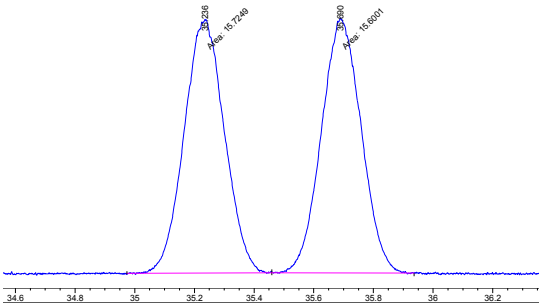


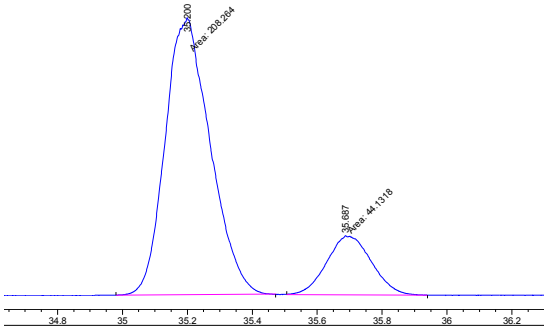
***(R)*-4-ethynyl-2-methylnon-1-ene**: The crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, colorless oil. R_f = 0.95 (20:1 pentane:diethyl ether, stain in $KMNO_4$). Spectral data is in accordance with the literature.[3]

Analysis of Stereochemistry:

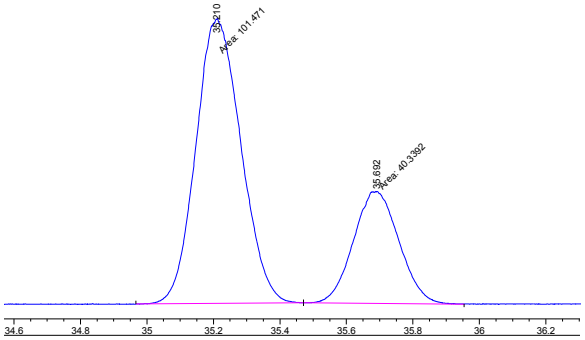
Optical purity was determined by GLC analysis of the title compound as compared to racemic product. The absolute stereochemistry was assigned by analogy to *(R)*-4-ethynylnon-1-ene (Table 2, Entry 1 G). **Note:** The enantiomer ratios values presented in the report are an average of two runs.

Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 1 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.





Racemic Sample *Enantioenriched Sample*

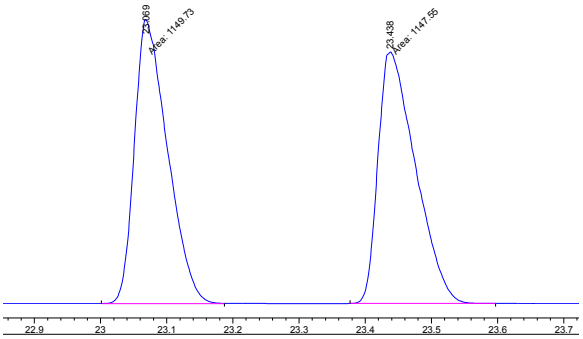


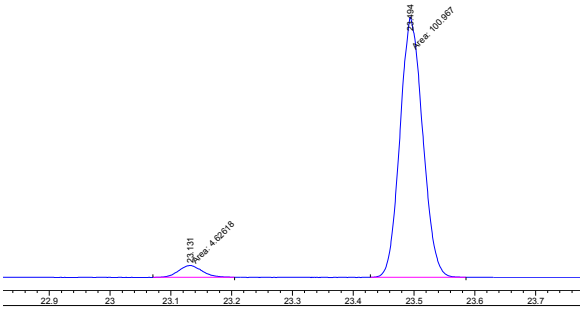
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	35.200	MM	0.1606	208.26378	21.60966	82.51483
2	35.687	MM	0.1594	44.13179	4.61521	17.48517

co-injection of racemic and enantioenriched samples

Recovered *(S)*-oct-1-yn-3-yl acetate:

Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 1 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.



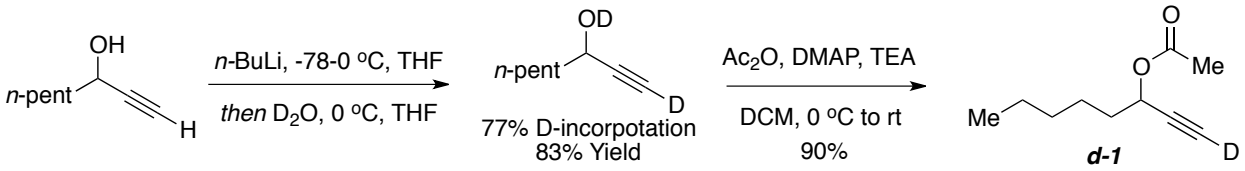


Racemic Sample *Enantioenriched Sample*

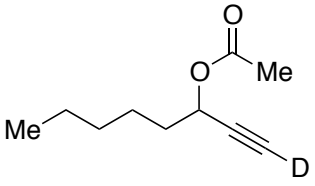
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	23.131	MM	0.0441	4.62618	1.74884	4.38112
2	23.494	MM	0.0435	100.96746	38.71632	95.61888

Kinetic Isotope Labeling Study (Scheme 3)

The kinetic isotope effect was measured experimentally through a competition experiment between authentic oct-1-yn-3-yl acetate and its deuterated analogue, prepared from commercially available oct-1-yn-3-ol via the two step procedure as shown below:



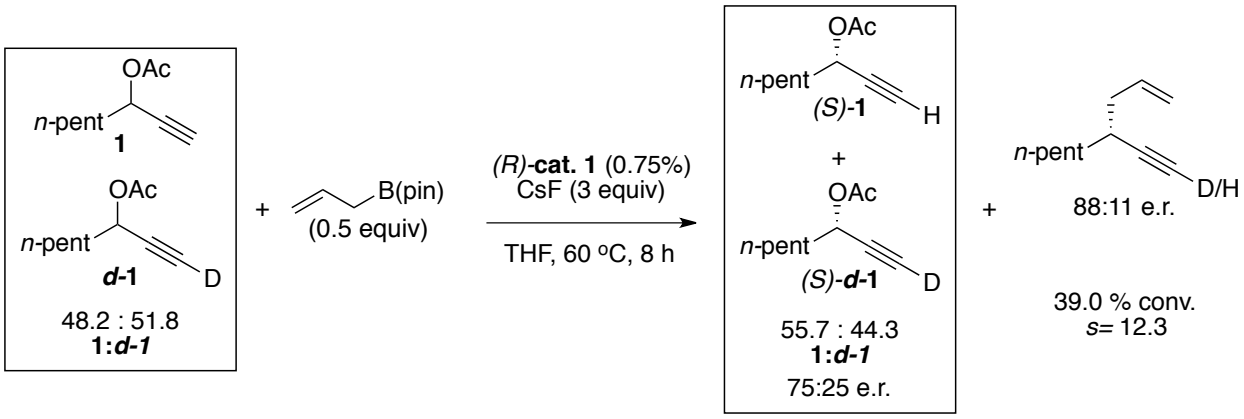
A flame-dried round-bottomed flask with a magnetic stir bar was charged with THF (50 mL) and oct-1-yn-3-ol (631 mg, 5.0 mmol) under nitrogen, and the solution was stirred and cooled to –78° C. *n*-butyllithium (5.0 mL of a 2.5 M solution, 12.5 mmol) was added dropwise and the solution was stirred for 15 min at –78° C and then slowly warmed to 0° C. A separate solution of D_2O (501 mg, 25.0 mmol) and THF (25 mL) was prepared under nitrogen in a separate flame-dried round-bottomed flask under nitrogen and sparged with a steady flow of nitrogen gas for 30 minutes. This solution was then added dropwise to the solution of alcohol and butyl lithium at 0° C under nitrogen, and the solution was stirred and slowly warmed to room temperature for three hours. The solution was recooled to 0° C, quenched with an aqueous saturated ammonium chloride solution, extracted three times with diethyl ether, dried with magnesium sulfate, filtered and concentrated *in vacuo*. The resulting crude mixture was purified on silica gel (2:1 pentane:diethyl ether) to give 531.5 mg of the desired labeled alcohol (83% yield, 77.3% D-incorporation by ^{1}H-NMR). R_f = 0.72 (2:1 pentane:diethyl ether; stain in CAM). Representative procedure A was then followed to afford the desired labeled acetate (457 mg, 90% yield). R_f = 0.34 (20:1 pentane:diethyl ether, stain in $KMNO_4$).



d-oct-1-yn-3-yl acetate. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.34 (1H, dd (app t), *J* = 6.5 Hz, 6.5 Hz), 2,09 (3H, s), 1.74-1.79 (2H, m), 1.42-1.48 (2H, m), 1.29-1.35 (4H, m), 0.89 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 81.4, 73.3, 63.8, 34.5, 31.2, 24.5, 24.5, 21.0, 13.9; IR (neat): 3294 (w), 2956 (w), 2931 (m), 2863 (w), 1740 (s), 1371 (m), 1227 (s), 1020 (s), 962 (w), 892 (w) cm^{-1}; HRMS-(ESI+) for $C_{10}H_{16}D_1O_2$ [M+H]: calculated: 170.12913, found: 170.12897.

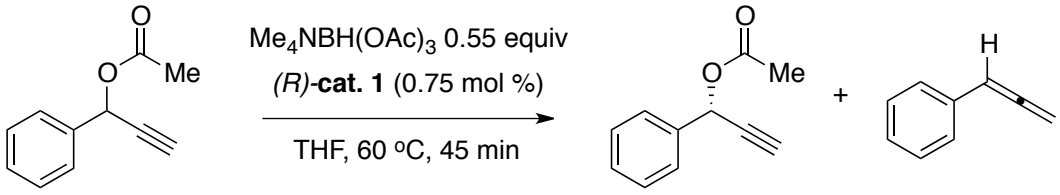
In order to test for the kinetic isotope effect, Representative Procedure **C** was followed on a 0.2 mmol scale with a mixture of labeled and unlabeled oct-1-yn-3-yl acetate as shown below. The change in ratio of labeled and unlabeled acetate in the recovered enriched sample

was compared with the ratio in the starting material, and average rates for each were determined.

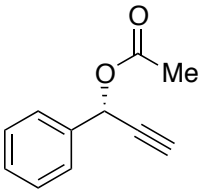


Run	Total Conv. (%)	Conv. 1 (%)	Conv *d-1* (%)	Rate 1 [M]/min	Rate *d*-1 [M]/min	k_H/k_D
1	39.0	16.6	22.4	0.864×10^{-4}	1.168×10^{-4}	0.74
2	50.1	20.6	29.6	1.073×10^{-4}	1.541×10^{-4}	0.70
3	52.9	21.8	32.1	1.135×10^{-4}	1.670×10^{-4}	0.68

Representative Procedure D: Resolution of Propargyl Acetates with Tetramethylammonium Triacetoxyborohydride.



An oven-dried scintillation vial equipped with a magnetic stir bar was charged with [*(R)*-(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl]palladium(II) dichloride (2.16 mg, 3.0 µmol), tetramethylammonium triacetoxyborohydride (57.9 mg, 0.22 mmol), and THF (1.0 mL) in a dry-box under argon atmosphere. The vial was capped and allowed to stir for five minutes, over which time the solution turned a deep red color. 1-phenylprop-2-yn-1-yl acetate (69.6 mg, 0.40 mmol) was added and the vial was sealed, removed from the dry-box, and heated to 60 °C while allowing to stir for 45 minutes. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*.

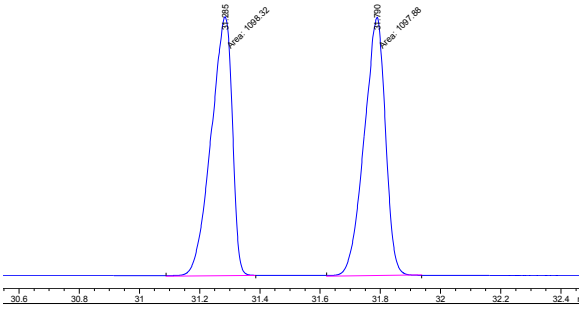


***(R)*-1-phenylprop-2-yn-1-yl acetate (Table 3, Entry 1 I)**. The crude raction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil (28.7 mg, 96% yield). R_f = 0.48 (10:1 pentane:diethyl ether, stain in $KMNO_4$).

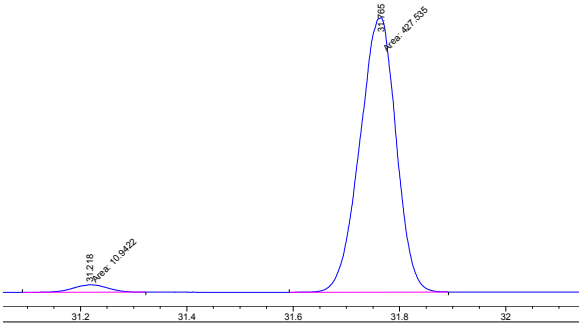
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product.

Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 5 °C/min to 140 °C for 15 min, 20 psi) - analysis of title compound.

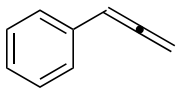


Racemic Sample



Enantioenriched Sample

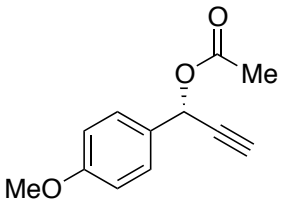
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.218	MM	0.0741	10.94217	2.46253	2.49549
2	31.765	MF	0.0792	427.53540	89.94408	97.50451



propa-1,2-dien-1-ylbenzene (Table 3, Entry 1 L). Clear, pale yellow oil. R_f = 0.88 (10:1 pentane:diethyl ether, stain in $KMNO_4$). Spectral data is in accordance with the literature.[10]

[10] F. Gagosz, B. Bolte, Y. Odabachian, *J. Am. Chem. Soc.* **2010**, *132*, 7294.

***(R)*-1-(4-methoxyphenyl)prop-2-yn-1-yl acetate (Table 3, Entry 2):** The representative procedure was followed with 1-(4-methoxyphenyl)prop-2-yn-1-yl acetate with the following modification: the reaction was run for 1 hour with 0.5 equivalents of tetramethylammonium triacetoxyborohydride.

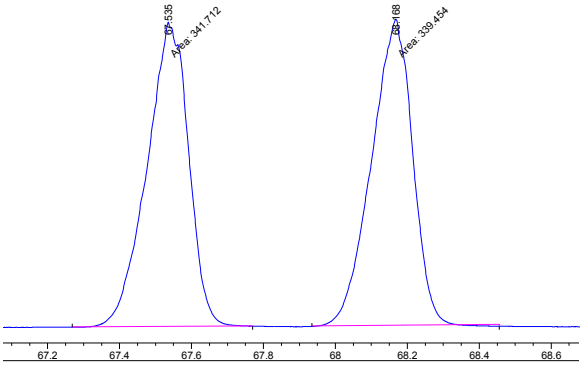


***(R)*-1-(4-methoxyphenyl)prop-2-yn-1-yl acetate (Table 3, Entry 2 I)**. The crude raction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil (40.8 mg, 90% yield). R_f = 0.33 (10:1 pentane:diethyl ether, stain in $KMNO_4$).

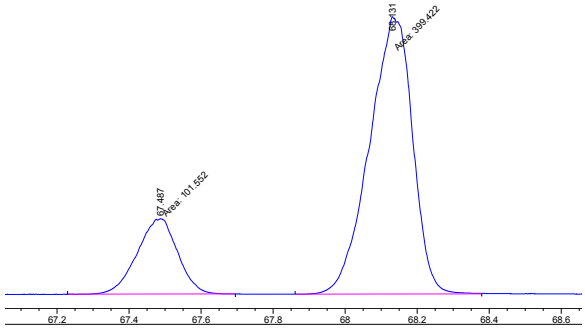
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product.

Chiral GLC (β-dex, Supelco, 40 °C for 10 min, ramp 2.5 °C/min to 140 °C for 20 min, 20 psi) - analysis of title compound.

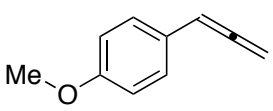


Racemic Sample



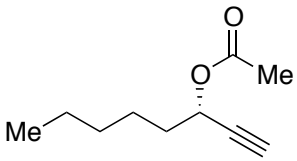
Enantioenriched Sample

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	67.487	MM	0.1302	101.55161	13.00158	20.27083
2	68.131	MF	0.1390	399.42249	47.89069	79.72917



1-methoxy-4-(propa-1,2-dien-1-yl)benzene (Table 3, Entry 2 L). Clear, pale yellow oil. R_f = 0.85 (10:1 pentane:diethyl ether, stain in $KMNO_4$). Spectral data is in accordance with the literature. [10]

Kinetic resolution to give *(S)*-oct-1-yn-3-yl acetate (Table 3, Entry 3): The representative procedure was followed with oct-1-yn-3-yl acetate with the following modification: the reaction was run for 4.5 hours at with 0.6 equivalents of tetramethylammonium triacetoxyborohydride.

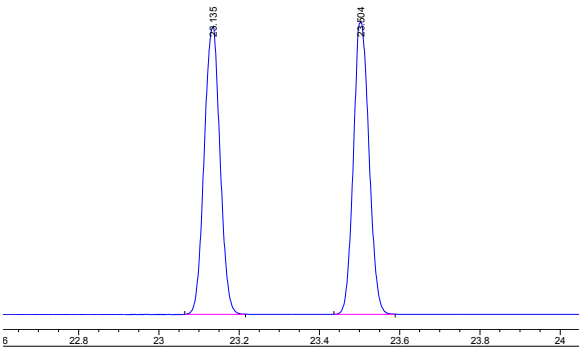


***(S)*-oct-1-yn-3-yl acetate (Table 2, Entry 3 l)**. The crude raction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, colorless oil (19.7 mg, 70% yield). R_f = 0.31 (20:1 pentane:diethyl ether, stain in $KMNO_4$).

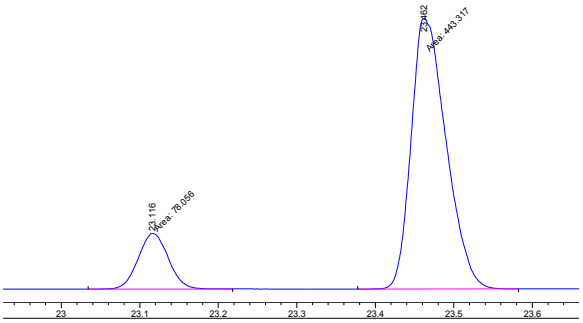
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product.

Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 5 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.

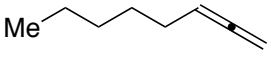


Racemic Sample



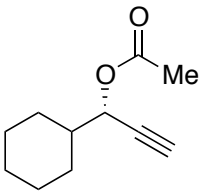
Enantioenriched Sample

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	23.116	MM	0.0442	78.05604	29.44047	14.97124
2	23.462	MF	0.0517	443.31720	143.00038	85.02876



octa-1,2-diene (Table 3, Entry 3 L). Clear, pale yellow oil. R_f = 0.94 (20:1 pentane:diethyl ether, stain in $KMNO_4$). Spectral data is in accordance with the literature. [10]

Kinetic resolution to give *(S)*-1-cyclohexylprop-2-yn-1-yl acetate (Table 3, Entry 4): The representative procedure was followed with 1-cyclohexylprop-2-yn-1-yl acetate with the following modification: the reaction was run for 6.5 hours at 1.0% catalyst loading with 0.75 equivalents of the tetramethylammonium triacetoxyborohydride.

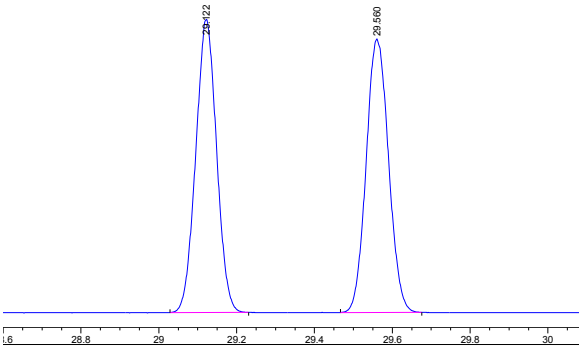


***(S)*-1-cyclohexylprop-2-yn-1-yl acetate (Table 3, Entry 4 l)**. The crude raction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, colorless oil (28.5 mg, 88% yield). R_f = 0.38 (20:1 pentane:diethyl ether, stain in $KMNO_4$).

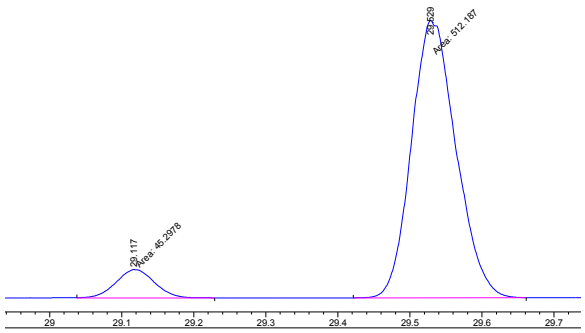
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product.

Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 5 °C/min to 140 °C for 10 min, 20 psi) - analysis of title compound.

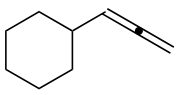


Racemic Sample



Enantioenriched Sample

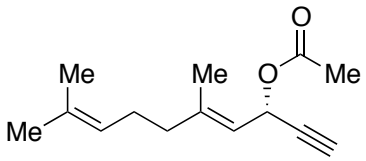
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.117	MM	0.0619	45.29784	12.20295	8.12539
2	29.529	MM	0.0716	512.18719	119.22504	91.87461



propa-1,2-dien-1-ylcyclohexane (Table 3, Entry 4 L). Clear, pale yellow oil. R_f = 0.94 (20:1 pentane:diethyl ether, stain in $KMNO_4$). Spectral data is in accordance with the literature.[11]

[11] N. Nishima, Y. Yamamoto, *Angew. Chem. Int. Ed.* **2006**, *45*, 3314.

Kinetic resolution to give *(S,E)*-5,9-dimethyldeca-4,8-dien-1-yn-3-yl acetate (Table 3, Entry 5): The representative procedure was followed with *(E)*-5,9-dimethyldeca-4,8-dien-1-yn-3-yl acetate with the following modification: the reaction was run with 0.5 equivalents of tetramethylammonium triacetoxyborohydride.

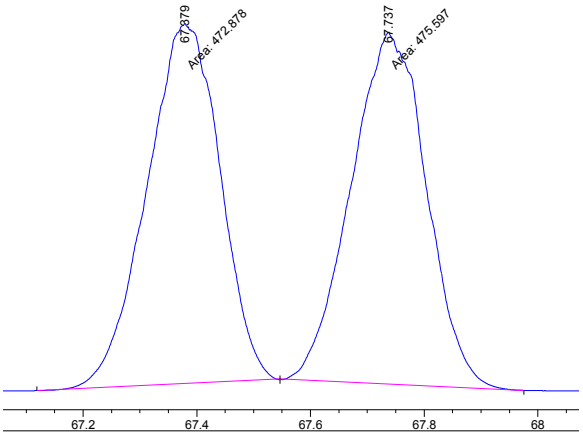


***(S,E)*-5,9-dimethyldeca-4,8-dien-1-yn-3-yl acetate (Table 3, Entry 5 l)**. The crude raction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, yellow oil (44.0 mg, 94% yield). R_f = 0.24 (20:1 pentane:diethyl ether, stain in $KMnO_4$).

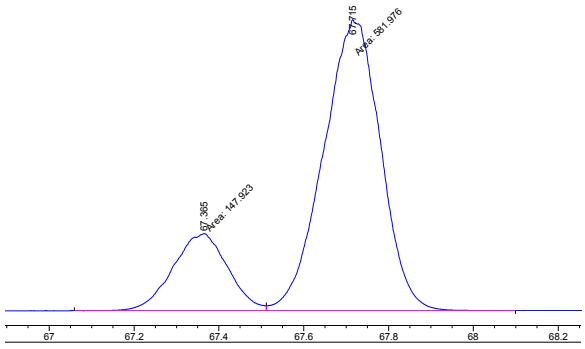
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound as compared to racemic product.

Chiral GLC (β-dex, Supelco, 80 °C for 10 min, ramp 1 °C/min to 160 °C for 10 min, 20 psi) - analysis of title compound.

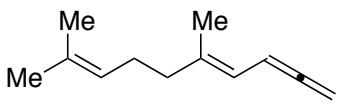


Racemic Sample



Enantioenriched Sample

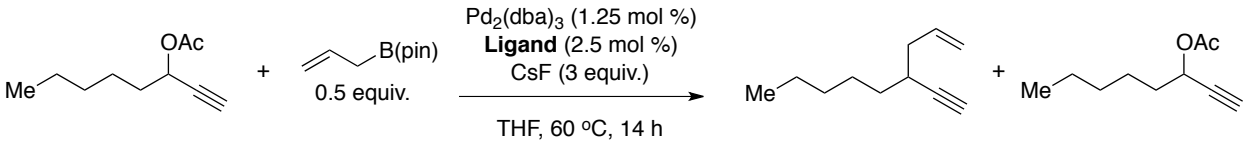
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	67.365	MF	0.1499	147.92336	16.44899	20.26626
2	67.715	FM	0.1561	581.97632	62.11814	79.73374



***(E)-5,9-dimethyldeca-1,2,4,8-tetraene* (Table 3, Entry 5 L).** ^1H NMR (500 MHz, $CDCl_3$): δ 6.01 (1H, ddd (app dt), *J* = 11.0 Hz, 7.0 Hz, 7.0 Hz), 5.63 (1H, *J* = 11.0 Hz, 2.5 Hz, 1.5 Hz), 5.10 (1H, dddd (app tt), *J* = 7.0 Hz, 7.0 Hz, 1.5 Hz, 1.5 Hz), 4.88 (2H, dddd (app

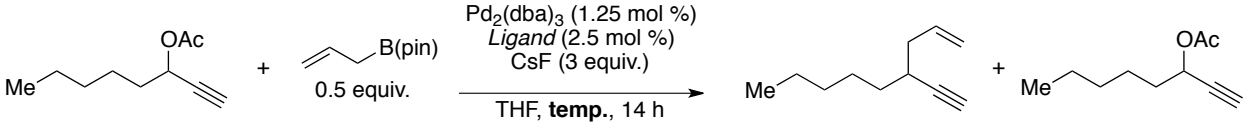
ddt), J = 7.5 Hz, 2.5 Hz, 1.5 Hz, 1.5 Hz), 2.05-2.13 (4H, m), 1.72 (3H, d, J = 1.5 Hz), 1.69 (3H, d, J = 1.0 Hz), 1.61 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ , 211.9, 138.0, 131.7, 123.9, 118.4, 89.8, 75.7, 39.9, 26.6, 25.7, 17.7, 16.5; IR (neat): 2968 (w), 2915 (m), 2855 (w), 1937 (m), 1443 (m), 1377 (m), 876 (m), 845 (s), 818 (w) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{19}$ [M+H]: calculated: 163.14868, found: 163.14926. The crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, pale yellow oil. R_f = 0.84 (20:1 pentane:diethyl ether, stain in $KMNO_4$).

Additional Optimization Tables:
Ligand Screen:



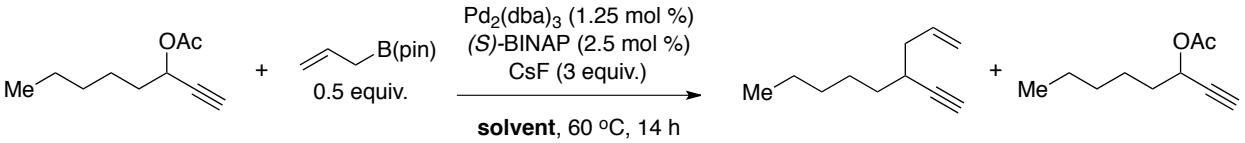
Ligand	e.r. enyne	e.r. recovered acetate	Conversion	*s*
(R)-MFB	89:11	11:89	50%	18.6
(S)-MFB	12:88	90:10	56%	16.9
(R)-SEGPHOS	82:18	23:77	46%	7.7
(R,R)-QuinoxP*	85:15	37:63	27%	7.3
(R)-MeO-BIPHEP	77:23	16:84	56%	6.6
(R)-C_3-Tunephos	76:24	29:71	45%	4.7
(R)-Ph-Garphos	70:30	17:83	63%	4.2
(S)-BINAP	29:71	73:27	52%	3.8
(R)-Cl-MeO-BIPHEP	67:33	25:75	60%	3.1
(R)-xylyl-BINAP	60:20	39:61	52%	1.9
(R,R)-Me-DUPHOS	64:36	48:52	13%	1.8

Temperature Studies:



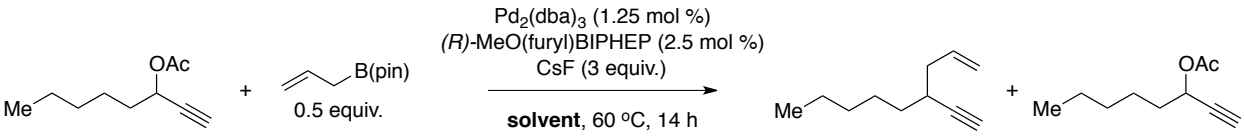
Ligand	Temperature (°C)	e.r. enyne	e.r. recovered acetate	conversion	*s*
(R)-MFB	40	94:6	40:60	18%	17.3
	60	89:11	11:89	50%	18.6
	80	--	not recovered	--	--
(S)-BINAP	RT	21:79	51:49	3%	3.8
	40	25:75	62:38	33%	3.7
	60	29:71	73:27	52%	3.8

Solvent Screen (with *(S)*-BINAP):



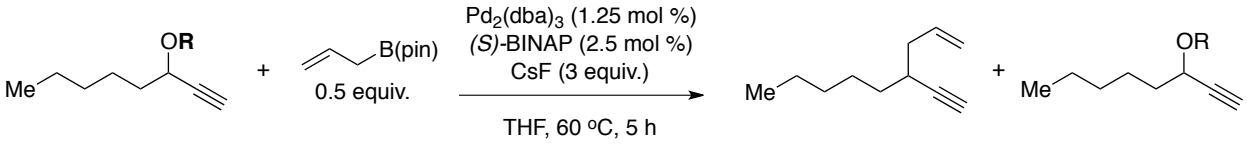
Solvent	e.r. enyne	e.r. recovered acetate	conversion	*s*
1,4-dioxane	27:73	73:27	50%	4.2
THF	29:71	73:27	52%	3.7
ethylacetate	30:70	67:33	46%	3.2
acetonitrile	35:65	70:30	57%	2.7
dichloromethane	40:60	60:40	50%	1.9
toluene	--	--	--	--

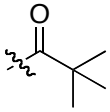
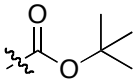
Solvent Screen (with *(R)*-MeO(furyl)BIPHEP):



Solvent	e.r. enyne	e.r. recovered acetate	conversion	*s*
THF	89:11	11:89	50%	18.6
Me-THF	88:12	11:89	51%	17.1
TBME	92:8	39:61	20%	14.0
acetonitrile	90:10	40:60	20%	11.3
dichloromethane	84:16	15:85	51%	10.8
1,4-dioxane	85:15	41:59	19%	6.7
DMF	66:34	20:80	65%	3.4
dibutyl ether	--	--	--	--

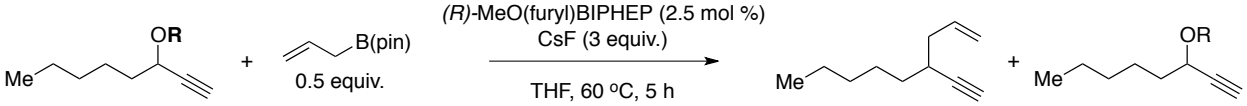
Protecting Group Survey (with *(S)*-BINAP):

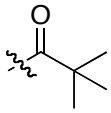
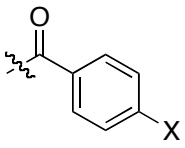
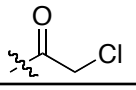
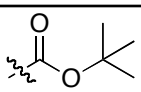


R	e.r. enyne	e.r. starting material	conversion	*s*
	31:69	11:89	67%	4.9
	29:71	70:30	52%	3.6
	46:54	n.d.	52%	1.3
TBS		No reaction		
TBDPS		No reaction		

a) reaction run for 14h b) reaction run with *rac*-BINAP

Protecting Group Survey (with *(R)*-MeO(furyl)BIPHEP):



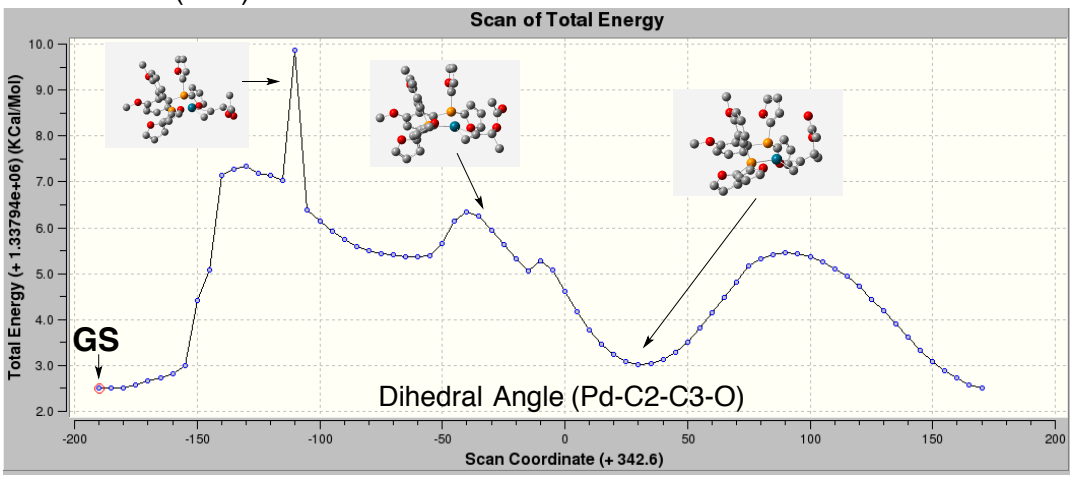
R	X	time (h)	e.r. enyne	e.r. starting material	conv.	*s*
		14	84:16 84:16	98:2 97:3	59% 58%	20.0 17.9
		14	89:11	11:89	50%	18.6
	H	5	92:8	59:41	18%	12.5
	OCH_3	5	81:19	98:2	61%	15.0
	Br	5	92:8	44:56	14%	12.3
		2	74:26	1:99	67%	10.5
		5	89:11	n.d.	19%	2.7

Computational Details

All calculations were performed using Gaussian 09 with all geometry optimizations, energies and frequencies were calculated at the DFT level utilizing the B3LYP hybrid functional.[12, 13] The 6-31G** basis set was used for the elements C, H, P, and O in conjunction with the LANL2DZ relativistic pseudopotential for Pd. The two oxygens and carbonyl carbon of the acetate group were augmented with diffuse functions. All free energies were calculated at 333.15 K. The PCM model was used to estimate the effect of solvation (THF).[14] The frequency calculations for transition states demonstrated one imaginary frequency each, and were found to connected with the correct ground states through IRC calculations. NBO analysis was carried out with Gaussian NBO version 3.1.[15] The three-dimensional structures presented in Figure 1 were visualized utilizing CYLview.[16]

Conformational Analysis about C2-C3 bond:

Begin with dihedral at -172.6, scan 73 steps at +5°/step, optimize maximum 10 cycles/ step at B3LYP-PCM(THF)/LANL2DZ-6-31G**.



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[12] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

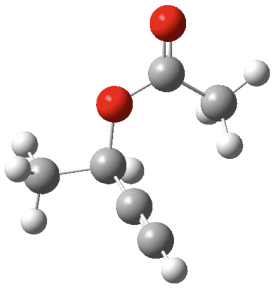
[13] (a) A. D. Becke, *Phys. Rev. A* 1988, *38*, 3098; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, *37*, 785.

[14] (a) S. Miertus, E. Scrocco, J. Tomassi, *Chem. Phys.* **1981**, *55*, 117. (b) V. Barone, M. Cossi, J. Tomassi, *Chem. Phys.* **1997**, *107*, 3210.

[15] NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.

[16] CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org).

Substrate_1



Cartesian coordinates (Angstroms):

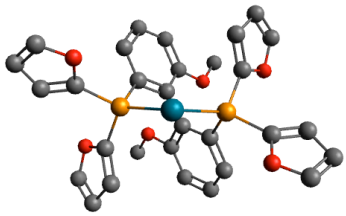
C -1.495 0.802 -0.127
C -2.014 1.812 -0.541
C -0.872 -0.424 0.381
O 0.347 -0.718 -0.368
C 1.517 -0.069 -0.135
C 1.587 0.938 0.988
O 2.465 -0.354 -0.842
H 0.825 1.714 0.875
H 2.577 1.393 0.979
H 1.430 0.449 1.955
C -1.769 -1.650 0.228
H -0.615 -0.295 1.437
H -2.474 2.702 -0.910
H -2.002 -1.823 -0.826
H -2.701 -1.497 0.776
H -1.260 -2.529 0.632

	1	2	3
	A	A	A
Frequencies --	68.3435	82.6680	163.7823
Red. masses --	3.4125	6.4939	1.4562

ZERO-POINT CORRECTION= 0.126910 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.137866
Thermal correction to Enthalpy= 0.138921
Thermal correction to Gibbs Free Energy= 0.087702
Sum of electronic and zero-point Energies= -383.735811
Sum of electronic and thermal Energies= -383.724854
Sum of electronic and thermal Enthalpies= -383.723799
Sum of electronic and thermal Free Energies= -383.775018

ITEM	VALUE	THRESHOLD	CONVERGED?
MAXIMUM FORCE	0.000041	0.000450	YES
RMS FORCE	0.000008	0.000300	YES

Catalyst_a



Cartesian coordinates (Angstroms):

Pd 0.000 -2.186 -0.000
P 1.930 -0.943 -0.041
O 3.377 0.782 1.596
O -1.118 3.159 -1.141
O 3.482 -2.436 -1.696
C 2.487 -0.269 1.549
C 2.195 -0.668 2.826
H 1.518 -1.467 3.094
C 2.939 0.177 3.708
H 2.952 0.150 4.788
C 3.635 1.034 2.909
H 4.325 1.840 3.107
C 1.401 0.527 -1.063
C 0.330 1.363 -0.677
C -0.106 2.360 -1.585
C 0.481 2.503 -2.847
H 0.135 3.261 -3.538
C 1.528 1.658 -3.210
H 1.990 1.767 -4.187
C 1.987 0.684 -2.331
H 2.804 0.040 -2.634
C -1.608 4.182 -2.000
H -0.825 4.906 -2.254
H -2.397 4.687 -1.442
H -2.028 3.764 -2.923
C 3.538 -1.412 -0.771
C 4.758 -2.698 -2.091
H 4.872 -3.482 -2.825
C 5.636 -1.882 -1.444
H 6.711 -1.874 -1.558
C 4.848 -1.047 -0.591
H 5.199 -0.271 0.072
P -1.930 -0.943 0.041
O -3.377 0.782 -1.596
O 1.118 3.159 1.141
O -3.482 -2.436 1.696
C -2.487 -0.269 -1.549
C -2.195 -0.668 -2.826
H -1.518 -1.467 -3.094
C -2.939 0.177 -3.708
H -2.952 0.150 -4.788
C -3.635 1.034 -2.909
H -4.325 1.840 -3.107
C -1.401 0.527 1.063
C -0.330 1.363 0.677

C 0.106 2.360 1.585
C -0.481 2.503 2.847
H -0.135 3.261 3.538
C -1.528 1.658 3.210
H -1.990 1.767 4.187
C -1.987 0.684 2.331
H -2.804 0.040 2.634
C 1.608 4.182 2.000
H 0.825 4.906 2.254
H 2.397 4.687 1.442
H 2.028 3.764 2.923
C -3.538 -1.412 0.771
C -4.758 -2.698 2.091
H -4.872 -3.482 2.825
C -5.636 -1.882 1.444
H -6.711 -1.874 1.558
C -4.848 -1.047 0.591
H -5.199 -0.271 -0.072

	1	2	3
	A	A	A
Frequencies --	-5.3361	22.6076	34.1663
Red. masses --	6.9580	6.1620	4.9712

Zero-Point Correction= 0.472240 (Hartree/Particle)
Thermal correction to Energy= 0.515390
Thermal correction to Enthalpy= 0.516445
Thermal correction to Gibbs Free Energy= 0.389564
Sum of electronic and zero-point Energies= -2417.878386
Sum of electronic and thermal Energies= -2417.835236
Sum of electronic and thermal Enthalpies= -2417.834180
Sum of electronic and thermal Free Energies= -2417.961062

Item	Value	Threshold	Converged?
Maximum Force	0.000000	0.000002	YES
RMS Force	0.000000	0.000001	YES

NOTE: We were unable to optimize the geometry to remove the small negative frequency listed (-5.3361) despite use of Ultrafine integration and Verytight convergence criteria. Its effect on the free energy of the complex should be negligible however the total energy of the unbound catalyst and substrate could be slightly lower than the 4.9 kcal/mol listed in the report.

GS_fast

Cartesian coordinates (Angstroms):

Pd 1.384 0.700 -0.275
P 0.466 -1.492 -0.017
O -0.840 -3.480 -1.448
O -4.314 -0.147 1.529
O 2.555 -2.368 1.507
C -0.133 -2.299 -1.523
C 0.035 -1.953 -2.837
H 0.545 -1.070 -3.195
C -0.600 -2.970 -3.618
H -0.668 -3.024 -4.695
C -1.112 -3.864 -2.726
H -1.669 -4.783 -2.832
C -0.955 -1.506 1.176
C -2.172 -0.864 0.872
C -3.157 -0.769 1.887
C -2.929 -1.290 3.165
H -3.684 -1.214 3.938
C -1.715 -1.915 3.443
H -1.537 -2.323 4.434
C -0.734 -2.024 2.463
H 0.204 -2.511 2.702
C -5.336 0.011 2.507
H -5.701 -0.957 2.870
H -6.149 0.536 2.005
H -4.988 0.609 3.357
C 1.577 -2.786 0.630
C 3.289 -3.464 1.849
H 4.096 -3.291 2.545
C 2.818 -4.572 1.212
H 3.210 -5.576 1.291
C 1.706 -4.135 0.425
H 1.075 -4.741 -0.208
P -0.713 1.845 -0.175
O -2.597 2.760 1.646
O -3.862 -2.264 -0.694
O 0.003 3.657 -2.081
C -1.329 2.249 1.479
C -0.707 2.172 2.697
H 0.293 1.801 2.870
C -1.637 2.658 3.669
H -1.489 2.740 4.736
C -2.762 2.997 2.977
H -3.718 3.405 3.267

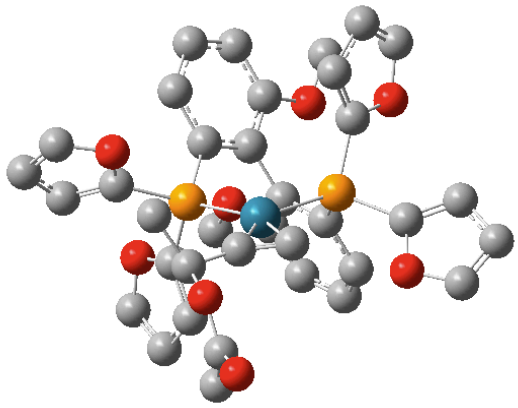
C -2.071 0.891 -1.007
C -2.532 -0.335 -0.487
C -3.449 -1.094 -1.256
C -3.884 -0.648 -2.508
H -4.582 -1.232 -3.094
C -3.411 0.566 -3.003
H -3.751 0.917 -3.974
C -2.514 1.331 -2.266
H -2.158 2.270 -2.672
C -4.787 -3.075 -1.410
H -5.730 -2.546 -1.593
H -4.977 -3.941 -0.775
H -4.369 -3.413 -2.366
C -0.791 3.484 -0.968
C -0.161 4.941 -2.502
H 0.403 5.225 -3.377
C -1.032 5.602 -1.688
H -1.342 6.633 -1.780
C -1.443 4.658 -0.695
H -2.137 4.822 0.115
C 3.484 0.784 -0.473
C 3.041 1.976 -0.480
C 4.599 -0.187 -0.524
O 5.900 0.500 -0.502
C 6.438 0.990 0.635
C 5.739 0.734 1.951
O 7.489 1.604 0.550
H 4.692 1.044 1.913
H 6.261 1.286 2.732
H 5.766 -0.334 2.193
H 3.218 3.036 -0.539
C 4.608 -1.026 -1.800
H 4.548 -0.853 0.342
H 5.447 -1.727 -1.781
H 4.700 -0.382 -2.678
H 3.675 -1.589 -1.875

	1	2	3
	A	A	A
Frequencies --	11.2295	17.6838	22.5356
Red. masses --	6.7711	7.2334	6.6926

ZERO-POINT CORRECTION= 0.601030 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.657588
Thermal correction to Enthalpy= 0.658643
Thermal correction to Gibbs Free Energy= 0.499264
Sum of electronic and zero-point Energies= -2801.644974
Sum of electronic and thermal Energies= -2801.588416
Sum of electronic and thermal Enthalpies= -2801.587361
Sum of electronic and thermal Free Energies= -2801.746740

ITEM	VALUE	THRESHOLD	CONVERGED?
MAXIMUM FORCE	0.000034	0.000450	YES
RMS FORCE	0.000003	0.000300	YES

GS_slow



Cartesian coordinates (Angstroms):

Pd -1.433 0.524 -0.377
P -0.320 -1.589 -0.172
O 0.673 -3.262 1.806
O 4.606 0.066 -0.517
O -1.766 -2.875 -2.098
C -0.106 -2.160 1.533
C -0.649 -1.688 2.699
H -1.292 -0.825 2.787
C -0.182 -2.540 3.748
H -0.405 -2.466 4.803
C 0.613 -3.472 3.150
H 1.180 -4.312 3.521
C 1.381 -1.575 -0.922
C 2.419 -0.789 -0.382
C 3.643 -0.704 -1.094
C 3.820 -1.374 -2.308
H 4.755 -1.304 -2.850
C 2.777 -2.141 -2.825
H 2.913 -2.664 -3.767
C 1.568 -2.242 -2.144
H 0.770 -2.840 -2.568
C 5.859 0.201 -1.178
H 6.361 -0.767 -1.292
H 6.464 0.847 -0.540
H 5.745 0.669 -2.163
C -1.084 -3.070 -0.916
C -2.277 -4.081 -2.476
H -2.839 -4.085 -3.398
C -1.952 -5.042 -1.568
H -2.228 -6.086 -1.609
C -1.176 -4.390 -0.558
H -0.732 -4.840 0.317
P 0.543 1.842 -0.152
O 2.793 2.677 -1.546
O 3.688 -1.825 1.765
O -0.786 3.817 1.184

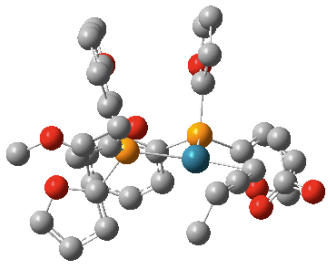
C 1.550 2.089 -1.635
C 1.266 1.826 -2.949
H 0.362 1.361 -3.316
C 2.389 2.272 -3.713
H 2.516 2.221 -4.785
C 3.281 2.776 -2.813
H 4.260 3.222 -2.907
C 1.678 1.145 1.138
C 2.345 -0.080 0.939
C 3.058 -0.646 2.024
C 3.095 -0.013 3.271
H 3.639 -0.451 4.099
C 2.424 1.196 3.446
H 2.455 1.690 4.412
C 1.719 1.773 2.395
H 1.200 2.711 2.552
C 4.412 -2.458 2.815
H 5.232 -1.826 3.177
H 4.823 -3.371 2.384
H 3.755 -2.717 3.654
C 0.301 3.570 0.375
C -0.814 5.156 1.430
H -1.619 5.502 2.059
C 0.220 5.779 0.797
H 0.439 6.837 0.811
C 0.946 4.752 0.115
H 1.835 4.867 -0.486
C -3.554 0.586 -0.544
C -3.095 1.772 -0.537
C -4.719 -0.326 -0.608
O -5.979 0.414 -0.421
C -6.409 0.812 0.795
C -5.634 0.392 2.023
O -7.429 1.479 0.849
H -3.251 2.837 -0.553
H -4.578 0.659 1.936
H -5.698 -0.693 2.161
H -6.069 0.885 2.892
C -4.859 -1.016 -1.963
H -4.653 -1.084 0.177
H -5.724 -1.686 -1.955
H -3.958 -1.593 -2.172
H -4.992 -0.271 -2.753

	1	2	3
	A	A	A
Frequencies --	11.0995	17.5785	24.2125
Red. masses --	6.9213	5.1950	6.5240

ZERO-POINT CORRECTION= 0.601564 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.657801
Thermal correction to Enthalpy= 0.658856
Thermal correction to Gibbs Free Energy 0.501656
Sum of electronic and zero-point Energies= -2801.643521
Sum of electronic and thermal Energies= -2801.587284
Sum of electronic and thermal Enthalpies= -2801.586229
Sum of electronic and thermal Free Energies= -2801.743429

ITEM	VALUE	THRESHOLD	CONVERGED?
MAXIMUM FORCE	0.000011	0.000450	YES
RMS FORCE	0.000002	0.000300	YES

TS_fast



Cartesian coordinates (Angstroms):

Pd 1.361 0.501 -0.269
P 0.242 -1.604 0.020
O -1.177 -3.509 -1.394
O -4.363 0.290 1.479
O 2.270 -2.523 1.585
C -0.386 -2.386 -1.482
C -0.176 -2.077 -2.800
H 0.402 -1.242 -3.169
C -0.874 -3.060 -3.569
H -0.933 -3.130 -4.645
C -1.461 -3.897 -2.667
H -2.081 -4.776 -2.764
C -1.184 -1.456 1.191
C -2.313 -0.680 0.861
C -3.296 -0.464 1.859
C -3.151 -1.004 3.141
H -3.903 -0.835 3.901
C -2.024 -1.767 3.441
H -1.913 -2.189 4.436
C -1.044 -1.992 2.480
H -0.173 -2.585 2.734
C -5.392 0.546 2.429
H -5.860 -0.382 2.776
H -6.135 1.151 1.907
H -5.011 1.106 3.291
C 1.276 -2.925 0.719
C 2.952 -3.640 1.962
H 3.767 -3.482 2.652
C 2.430 -4.745 1.359
H 2.777 -5.762 1.471
C 1.342 -4.284 0.555
H 0.686 -4.879 -0.063
P -0.556 1.842 -0.188
O -2.317 2.892 1.656
O -4.116 -1.901 -0.725
O 0.424 3.566 -2.057
C -1.101 2.272 1.477
C -0.476 2.130 2.687
H 0.488 1.670 2.849
C -1.351 2.691 3.669

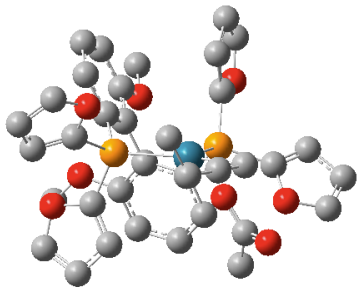
H -1.187 2.751 4.735
C -2.447 3.134 2.989
H -3.360 3.623 3.291
C -1.980 1.025 -1.037
C -2.585 -0.132 -0.509
C -3.565 -0.795 -1.291
C -3.918 -0.319 -2.558
H -4.665 -0.830 -3.152
C -3.301 0.826 -3.059
H -3.578 1.197 -4.041
C -2.338 1.496 -2.312
H -1.867 2.382 -2.720
C -5.093 -2.632 -1.460
H -5.975 -2.019 -1.680
H -5.384 -3.466 -0.820
H -4.679 -3.022 -2.397
C -0.417 3.473 -0.970
C 0.405 4.862 -2.470
H 1.023 5.092 -3.325
C -0.418 5.606 -1.678
H -0.618 6.663 -1.771
C -0.954 4.705 -0.705
H -1.651 4.935 0.087
C 3.576 0.816 -0.501
C 2.893 1.886 -0.452
C 4.208 -0.398 -0.542
O 6.355 0.039 -0.489
C 6.959 0.616 0.490
C 6.172 0.816 1.791
O 8.149 1.001 0.438
H 2.964 2.960 -0.475
H 5.917 -0.158 2.225
H 5.233 1.345 1.599
H 6.763 1.378 2.516
C 4.338 -1.207 -1.802
H 4.346 -0.921 0.398
H 4.253 -0.578 -2.690
H 3.550 -1.968 -1.832
H 5.303 -1.716 -1.808

	1	2	3
	A	A	A
Frequencies --	-196.5413	11.2047	17.9448
Red. masses --	6.7132	6.6021	7.8575

ZERO-POINT CORRECTION= 0.597855 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.655029
Thermal correction to Enthalpy= 0.656084
Thermal correction to Gibbs Free Energy= 0.494517
Sum of electronic and zero-point Energies= -2801.618847
Sum of electronic and thermal Energies= -2801.561673
Sum of electronic and thermal Enthalpies= -2801.560618
Sum of electronic and thermal Free Energies= -2801.722185

ITEM	VALUE	THRESHOLD	CONVERGED?
MAXIMUM FORCE	0.000006	0.000450	YES
RMS FORCE	0.000001	0.000300	YES

TS_Slow



Cartesian coordinates (Angstroms):

Pd -1.404 0.318 -0.319
P -0.067 -1.688 -0.120
O 1.110 -3.201 1.875
O 4.607 0.532 -0.597
O -1.435 -3.097 -2.015
C 0.215 -2.195 1.589
C -0.371 -1.761 2.749
H -1.106 -0.973 2.827
C 0.191 -2.538 3.809
H -0.034 -2.469 4.864
C 1.080 -3.390 3.223
H 1.736 -4.157 3.605
C 1.598 -1.489 -0.910
C 2.543 -0.576 -0.403
C 3.733 -0.357 -1.141
C 3.964 -1.025 -2.348
H 4.874 -0.856 -2.910
C 3.012 -1.920 -2.830
H 3.192 -2.442 -3.765
C 1.836 -2.153 -2.124
H 1.107 -2.850 -2.519
C 5.829 0.796 -1.279
H 6.437 -0.110 -1.380
H 6.362 1.522 -0.663
H 5.649 1.226 -2.271
C -0.715 -3.225 -0.846
C -1.836 -4.349 -2.379
H -2.415 -4.410 -3.288
C -1.402 -5.271 -1.476
H -1.578 -6.336 -1.509
C -0.672 -4.544 -0.483
H -0.171 -4.946 0.385
P 0.374 1.828 -0.134
O 2.434 2.852 -1.655
O 3.969 -1.433 1.718
O -1.106 3.660 1.250
C 1.265 2.124 -1.673
C 0.953 1.791 -2.965
H 0.094 1.216 -3.278
C 1.983 2.339 -3.790
H 2.067 2.271 -4.865

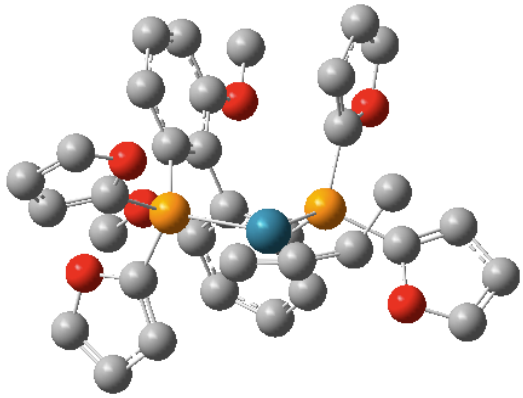
C 2.850 2.968 -2.946
H 3.765 3.519 -3.097
C 1.594 1.258 1.131
C 2.409 0.129 0.914
C 3.204 -0.342 1.989
C 3.181 0.293 3.235
H 3.790 -0.070 4.053
C 2.363 1.406 3.423
H 2.346 1.900 4.390
C 1.571 1.887 2.387
H 0.936 2.748 2.557
C 4.789 -1.970 2.752
H 5.530 -1.240 3.098
H 5.303 -2.823 2.310
H 4.187 -2.309 3.603
C -0.057 3.519 0.369
C -1.270 4.994 1.471
H -2.065 5.262 2.150
C -0.362 5.712 0.753
H -0.266 6.788 0.731
C 0.428 4.758 0.040
H 1.253 4.959 -0.626
C -3.669 0.559 -0.503
C -2.987 1.630 -0.458
C -4.347 -0.627 -0.542
O -6.510 -0.123 -0.419
C -7.079 0.452 0.580
C -6.245 0.648 1.852
O -8.271 0.836 0.574
H -3.075 2.703 -0.432
H -5.298 1.144 1.624
H -6.007 -0.328 2.292
H -6.796 1.238 2.587
C -4.562 -1.397 -1.812
H -4.485 -1.156 0.394
H -5.480 -1.982 -1.736
H -3.722 -2.080 -1.967
H -4.629 -0.727 -2.672

	1	2	3
	A	A	A
Frequencies --	-165.6350	11.7929	19.9046
Red. masses --	7.3473	6.8965	6.0386

ZERO-POINT CORRECTION= 0.598051 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.655139
Thermal correction to Enthalpy= 0.656194
Thermal correction to Gibbs Free Energy= 0.495641
Sum of electronic and zero-point Energies= -2801.617730
Sum of electronic and thermal Energies= -2801.560641
Sum of electronic and thermal Enthalpies= -2801.559586
Sum of electronic and thermal Free Energies= -2801.720140

ITEM	VALUE	THRESHOLD	CONVERGED?
MAXIMUM FORCE	0.000002	0.000450	YES
RMS FORCE	0.000000	0.000300	YES

Int_a_fast



Cartesian coordinates (Angstroms):

Pd 0.694 -1.939 -0.144
P 1.742 0.176 -0.145
O 2.554 2.112 1.628
O -2.436 3.150 -0.902
O 3.556 -0.637 -2.012
C 2.080 0.828 1.499
C 1.986 0.245 2.735
H 1.638 -0.758 2.939
C 2.424 1.222 3.681
H 2.483 1.114 4.754
C 2.754 2.329 2.956
H 3.131 3.305 3.221
C 0.762 1.431 -1.076
C -0.479 1.890 -0.594
C -1.250 2.743 -1.422
C -0.789 3.120 -2.688
H -1.379 3.773 -3.319
C 0.442 2.651 -3.141
H 0.800 2.948 -4.122
C 1.217 1.809 -2.349
H 2.168 1.452 -2.723
C -3.256 4.029 -1.668
H -2.740 4.972 -1.884
H -4.132 4.230 -1.051
H -3.573 3.563 -2.608
C 3.381 0.184 -0.920
C 4.846 -0.483 -2.425
H 5.135 -1.067 -3.285
C 5.501 0.404 -1.626
H 6.533 0.712 -1.717
C 4.552 0.840 -0.649
H 4.712 1.554 0.145
P -1.499 -1.109 0.022
O -3.435 -0.016 -1.585
O -0.412 3.787 1.326
O -2.232 -3.171 1.649
C -2.222 -0.663 -1.563

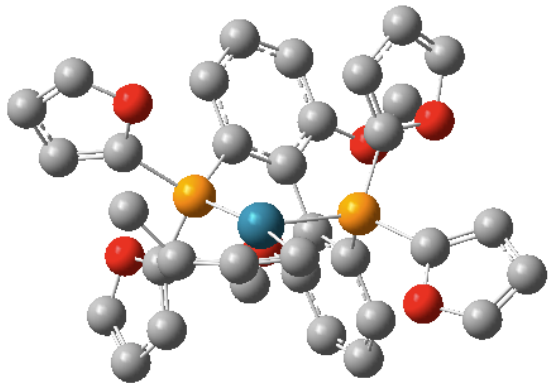
C -1.799 -0.897 -2.845
H -0.878 -1.383 -3.129
C -2.804 -0.363 -3.708
H -2.807 -0.363 -4.789
C -3.766 0.157 -2.894
H -4.705 0.658 -3.078
C -1.586 0.354 1.139
C -1.009 1.585 0.775
C -0.981 2.626 1.736
C -1.513 2.433 3.017
H -1.491 3.230 3.749
C -2.076 1.203 3.351
H -2.491 1.057 4.344
C -2.114 0.164 2.426
H -2.552 -0.785 2.708
C -0.349 4.881 2.238
H -1.350 5.204 2.547
H 0.140 5.691 1.696
H 0.243 4.628 3.125
C -2.692 -2.296 0.691
C -3.280 -3.970 1.996
H -3.072 -4.716 2.748
C -4.393 -3.634 1.286
H -5.364 -4.103 1.353
C -4.015 -2.546 0.440
H -4.640 -2.012 -0.260
C 1.471 -3.998 -0.305
C 0.212 -4.067 -0.335
C 2.644 -3.279 -0.196
H -0.684 -4.652 -0.408
C 3.480 -3.268 1.061
H 3.158 -3.032 -1.123
H 4.018 -2.320 1.150
H 4.233 -4.066 1.012
H 2.872 -3.423 1.954

	1	2	3
	A	A	A
Frequencies --	17.8034	32.8908	37.5770
Red. masses --	6.3208	4.7296	4.8137

ZERO-POINT CORRECTION= 0.548680 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.599446
Thermal correction to Enthalpy= 0.600501
Thermal correction to Gibbs Free Energy= 0.456784
Sum of electronic and zero-point Energies= -2573.045691
Sum of electronic and thermal Energies= -2572.994926
Sum of electronic and thermal Enthalpies= -2572.993871
Sum of electronic and thermal Free Energies= -2573.137588

ITEM	VALUE	THRESHOLD	CONVERGED?
MAXIMUM FORCE	0.000006	0.000450	YES
RMS FORCE	0.000001	0.000300	YES

Int_a_slow



Cartesian coordinates (Angstroms):

Pd -0.665 -1.943 -0.177
P -1.719 0.172 0.091
O -2.756 2.170 -1.486
O 2.421 3.183 0.892
O -3.295 -0.734 2.110
C -2.190 0.916 -1.479
C -2.088 0.450 -2.764
H -1.671 -0.501 -3.062
C -2.621 1.469 -3.612
H -2.702 1.450 -4.688
C -3.007 2.483 -2.785
H -3.460 3.448 -2.956
C -0.766 1.439 1.037
C 0.481 1.897 0.573
C 1.225 2.781 1.394
C 0.728 3.194 2.636
H 1.296 3.871 3.261
C -0.512 2.731 3.069
H -0.899 3.056 4.029
C -1.258 1.857 2.284
H -2.216 1.507 2.645
C 3.216 4.088 1.655
H 2.692 5.035 1.826
H 4.110 4.271 1.058
H 3.506 3.651 2.618
C -3.296 0.043 0.974
C -4.563 -0.714 2.609
H -4.722 -1.281 3.513
C -5.375 0.045 1.821
H -6.427 0.234 1.974
C -4.553 0.541 0.759
H -4.851 1.190 -0.051
P 1.523 -1.127 0.027
O 3.195 0.028 1.872
O 0.431 3.741 -1.395
O 2.633 -3.074 -1.545

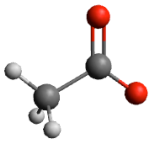
C 2.022 -0.666 1.691
C 1.456 -0.942 2.908
H 0.528 -1.472 3.070
C 2.325 -0.387 3.896
H 2.195 -0.409 4.968
C 3.356 0.188 3.215
H 4.242 0.724 3.520
C 1.651 0.333 -1.092
C 1.049 1.564 -0.773
C 1.033 2.581 -1.760
C 1.608 2.369 -3.018
H 1.596 3.149 -3.769
C 2.202 1.142 -3.306
H 2.652 0.981 -4.281
C 2.224 0.124 -2.358
H 2.680 -0.826 -2.608
C 0.373 4.811 -2.336
H 1.375 5.144 -2.627
H -0.145 5.625 -1.827
H -0.193 4.525 -3.230
C 2.861 -2.241 -0.474
C 3.766 -3.812 -1.726
H 3.740 -4.517 -2.542
C 4.707 -3.478 -0.799
H 5.695 -3.904 -0.703
C 4.123 -2.457 0.014
H 4.580 -1.943 0.846
C -1.434 -3.949 -0.723
C -0.190 -4.028 -0.522
C -2.625 -3.267 -0.789
H 0.703 -4.622 -0.537
H -2.925 -2.905 -1.772
C -3.727 -3.420 0.228
H -4.334 -2.514 0.271
H -3.336 -3.643 1.223
H -4.388 -4.241 -0.077

	1	2	3
	A	A	A
Frequencies --	14.3167	32.5559	36.6284
Red. masses --	6.3825	5.4051	4.0664

ZERO-POINT CORRECTION= 0.548820 (HARTREE/PARTICLE)
Thermal correction to Energy= 0.599547
Thermal correction to Enthalpy= 0.600602
Thermal correction to Gibbs Free Energy= 0.457063
Sum of electronic and zero-point Energies= -2573.043058
Sum of electronic and thermal Energies= -2572.992331
Sum of electronic and thermal Enthalpies= -2572.991276
Sum of electronic and thermal Free Energies= -2573.134815

ITEM	VALUE	THRESHOLD	CONVERGED?
MAXIMUM FORCE	0.000020	0.000450	YES
RMS FORCE	0.000003	0.000300	YES

$^{-}$OAc



Cartesian coordinates (Angstroms):

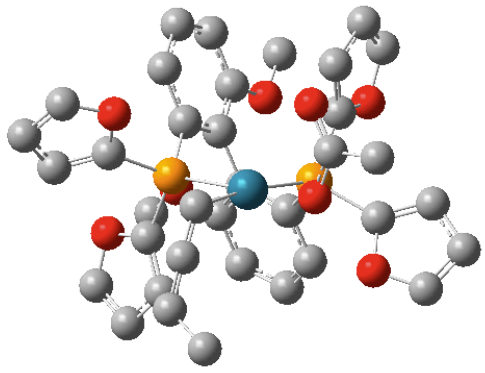
O -0.803 -1.108 0.002
C -0.191 -0.000 -0.008
O -0.721 1.150 0.002
C 1.353 -0.039 -0.003
H 1.741 -1.032 -0.243
H 1.715 0.241 0.994
H 1.757 0.692 -0.710

	1	2	3
	A	A	A
Frequencies --	50.4181	447.5707	611.1940
Red. masses --	1.0873	3.0453	2.7933

Zero-Point Correction= 0.048453 (Hartree/Particle)
Thermal correction to Energy= 0.053585
Thermal correction to Enthalpy= 0.054640
Thermal correction to Gibbs Free Energy= 0.017244
Sum of electronic and zero-point Energies= -228.578257
Sum of electronic and thermal Energies= -228.573125
Sum of electronic and thermal Enthalpies= -228.572070
Sum of electronic and thermal Free Energies= -228.609466

Item	Value	Threshold	Converged?
Maximum Force	0.000001	0.000015	YES
RMS Force	0.000000	0.000010	YES

Int_b_fast



Cartesian coordinates (Angstroms):

Pd 1.730 0.051 -0.244
P 0.103 -1.701 0.324
O -1.713 -3.421 -0.853

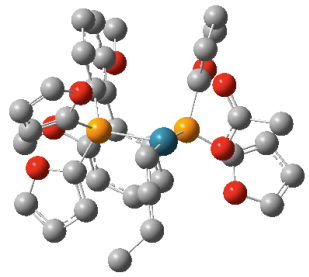
O -4.031 1.296 1.182
O 1.693 -2.684 2.313
C -0.628 -2.598 -1.057
C -0.248 -2.647 -2.373
H 0.594 -2.118 -2.797
C -1.151 -3.548 -3.020
H -1.157 -3.833 -4.062
C -2.013 -3.982 -2.056
H -2.855 -4.658 -2.062
C -1.287 -1.086 1.378
C -2.212 -0.158 0.863
C -3.168 0.407 1.742
C -3.193 0.052 3.095
H -3.924 0.484 3.767
C -2.267 -0.869 3.581
H -2.290 -1.146 4.631
C -1.317 -1.435 2.737
H -0.602 -2.142 3.138
C -5.021 1.901 2.008
H -5.695 1.154 2.441
H -5.589 2.564 1.354
H -4.565 2.490 2.813
C 0.855 -3.044 1.284
C 2.206 -3.833 2.836
H 2.884 -3.709 3.666
C 1.724 -4.918 2.168
H 1.961 -5.954 2.366
C 0.845 -4.408 1.159
H 0.276 -4.978 0.440
P 0.137 1.707 -0.422
O -1.403 3.311 1.203
O -4.199 -1.169 -0.648
O 1.296 2.960 -2.560
C -0.330 2.450 1.151
C 0.257 2.371 2.386
H 1.126 1.778 2.633
C -0.495 3.224 3.250
H -0.323 3.408 4.301
C -1.484 3.764 2.483
H -2.288 4.456 2.686
C -1.393 1.067 -1.243
C -2.291 0.201 -0.590
C -3.365 -0.346 -1.336
C -3.527 -0.042 -2.692
H -4.348 -0.462 -3.259
C -2.620 0.811 -3.317
H -2.744 1.046 -4.370
C -1.559 1.363 -2.607
H -0.862 2.014 -3.118
C -5.301 -1.756 -1.333
H -5.986 -0.993 -1.721
H -5.821 -2.365 -0.593
H -4.966 -2.396 -2.158
C 0.594 3.169 -1.397
C 1.546 4.183 -3.104
H 2.096 4.180 -4.033
C 1.028 5.169 -2.320
H 1.081 6.233 -2.503
C 0.407 4.513 -1.211
H -0.117 4.975 -0.387
C 3.194 1.467 -0.487
C 3.762 2.016 0.541
H 3.497 1.636 -1.518
C 4.317 2.554 1.613
H 3.944 3.517 1.968
C 5.458 1.948 2.394
O 3.299 -1.402 -0.256
C 3.577 -1.918 -1.406
C 4.730 -2.922 -1.403
O 2.988 -1.664 -2.476
H 5.515 -2.570 -2.080
H 4.374 -3.883 -1.786
H 5.150 -3.062 -0.406
H 5.763 0.987 1.971
H 5.175 1.787 3.443
H 6.330 2.614 2.402

	1	2	3
	A	A	A
Frequencies --	11.9377	18.3866	20.7172
Red. masses --	5.5022	4.9158	4.2895

ZERO-POINT CORRECTION= 0.599041
(HARTREE/PARTICLE)
Thermal correction to Energy= 0.656549
Thermal correction to Enthalpy= 0.657604
Thermal correction to Gibbs Free Energy= 0.496349
Sum of electronic and zero-point Energies= -2801.655635
Sum of electronic and thermal Energies= -2801.598127
Sum of electronic and thermal Enthalpies= -2801.597072
Sum of electronic and thermal Free Energies= -2801.758327

ITEM	VALUE	THRESHOLD	CONVERGED?
MAXIMUM FORCE	0.000006	0.000450	YES
RMS FORCE	0.000001	0.000300	YES

Int_b_slow



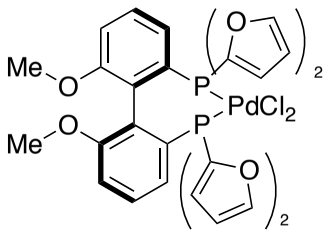
Cartesian coordinates (Angstroms):

Pd -1.730 0.258 -0.223
P 0.171 1.701 0.372
O 2.237 3.103 -0.815
O 3.766 -1.955 1.075
O -1.204 2.904 2.403
C 1.018 2.492 -1.008
C 0.618 2.654 -2.309
H -0.318 2.300 -2.720
C 1.649 3.402 -2.958
H 1.678 3.717 -3.992
C 2.600 3.643 -2.011
H 3.548 4.160 -2.024
C 1.458 0.841 1.382
C 2.207 -0.215 0.828
C 3.072 -0.951 1.674
C 3.179 -0.639 3.034
H 3.841 -1.202 3.680
C 2.429 0.411 3.558
H 2.517 0.657 4.613
C 1.570 1.148 2.747
H 0.990 1.954 3.178
C 4.655 -2.738 1.866
H 5.452 -2.126 2.302
H 5.093 -3.469 1.186
H 4.120 -3.263 2.667
C -0.324 3.132 1.371
C -1.491 4.113 2.962
H -2.171 4.093 3.799
C -0.825 5.109 2.313
H -0.865 6.164 2.541
C -0.065 4.474 1.280
H 0.592 4.948 0.567
P -0.434 -1.638 -0.452
O 0.828 -3.511 1.123
O 4.301 0.513 -0.702
O -1.794 -2.648 -2.601
C -0.074 -2.472 1.103
C -0.607 -2.300 2.353
H -1.341 -1.557 2.629
C 0.001 -3.283 3.194
H -0.175 -3.443 4.248
C 0.858 -3.984 2.399
H 1.528 -4.812 2.576
C 1.168 -1.240 -1.289
C 2.203 -0.545 -0.634
C 3.338 -0.155 -1.390
C 3.428 -0.450 -2.754
H 4.296 -0.151 -3.328
C 2.389 -1.134 -3.380
H 2.458 -1.363 -4.439
C 1.264 -1.527 -2.662
H 0.464 -2.046 -3.173
C 5.462 0.952 -1.402
H 6.020 0.109 -1.824
H 6.080 1.459 -0.662
H 5.203 1.655 -2.202
C -1.141 -2.988 -1.440
C -2.263 -3.803 -3.153
H -2.802 -3.694 -4.081
C -1.933 -4.871 -2.375
H -2.178 -5.906 -2.564
C -1.203 -4.345 -1.262
H -0.772 -4.900 -0.443
C -3.409 -0.889 -0.508
C -4.204 -1.122 0.490
H -3.592 -1.222 -1.526
C -4.995 -1.324 1.529
O -3.015 1.968 -0.162
C -3.216 2.561 -1.290
C -4.164 3.758 -1.232
O -2.701 2.240 -2.380
H -4.968 3.619 -1.962
H -3.617 4.664 -1.517
H -4.594 3.896 -0.239
C -4.943 -2.524 2.444
H -5.764 -0.580 1.748
H -4.788 -2.217 3.486
H -4.135 -3.205 2.163
H -5.887 -3.083 2.418

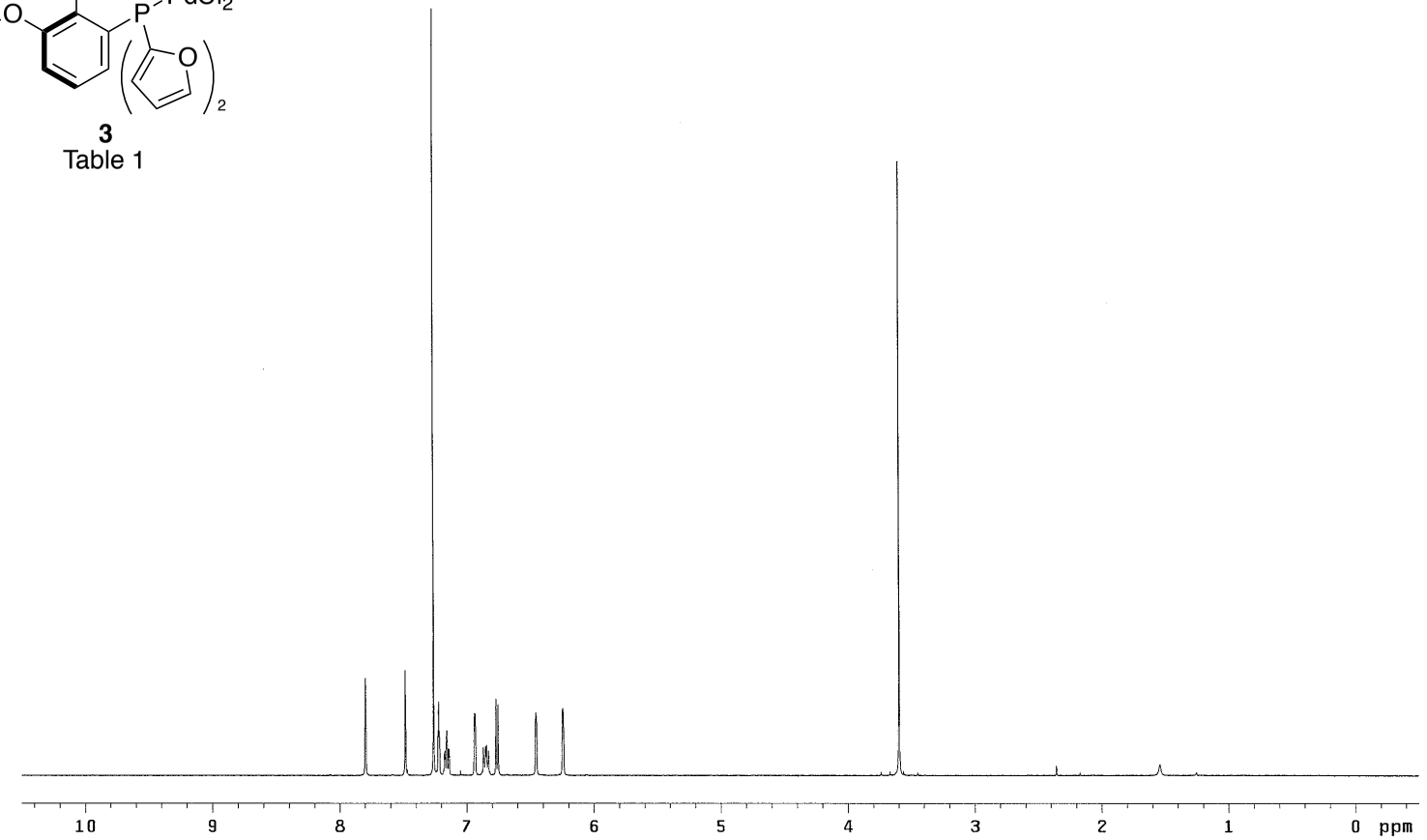
	1	2	3
	A	A	A
Frequencies --	14.0541	18.2832	21.8989
Red. masses --	5.5508	4.0870	5.0110

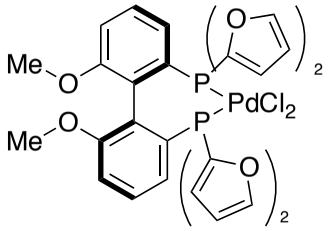
ZERO-POINT CORRECTION= 0.599257
(HARTREE/PARTICLE)
Thermal correction to Energy= 0.656622
Thermal correction to Enthalpy= 0.657677
Thermal correction to Gibbs Free Energy= 0.497330
Sum of electronic and zero-point Energies= -2801.655382
Sum of electronic and thermal Energies= -2801.598016
Sum of electronic and thermal Enthalpies= -2801.596961
Sum of electronic and thermal Free Energies= -2801.757309

ITEM	VALUE	THRESHOLD	CONVERGED?
MAXIMUM FORCE	0.000013	0.000450	YES
RMS FORCE	0.000002	0.000300	YES



3
Table 1




Me
O
Me
O
P
P
PdCl2
O
O
2
2

3
Table 1

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

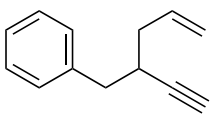


Table 2
Entry 5 G

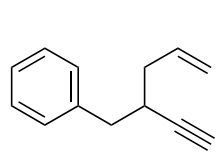
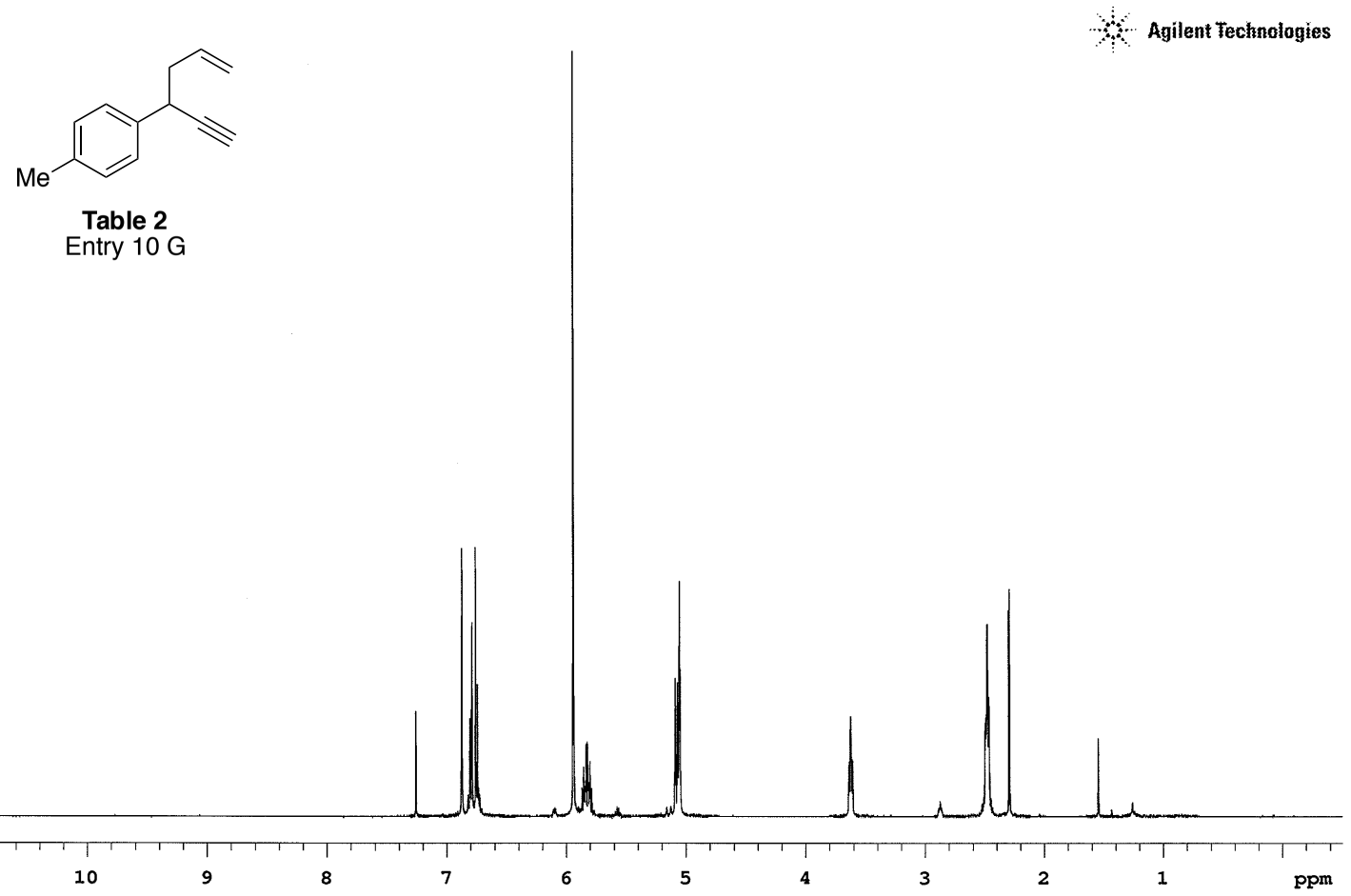


Table 2
Entry 5 G


Me
Table 2
Entry 10 G
Agilent Technologies
10
9
8
7
6
5
4
3
2
1
ppm

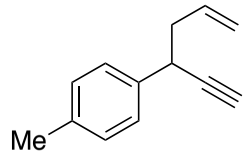


Table 2
Entry 10 G

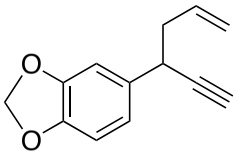


Table 2
Entry 13 G

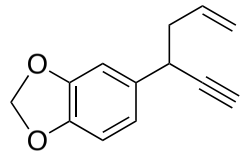
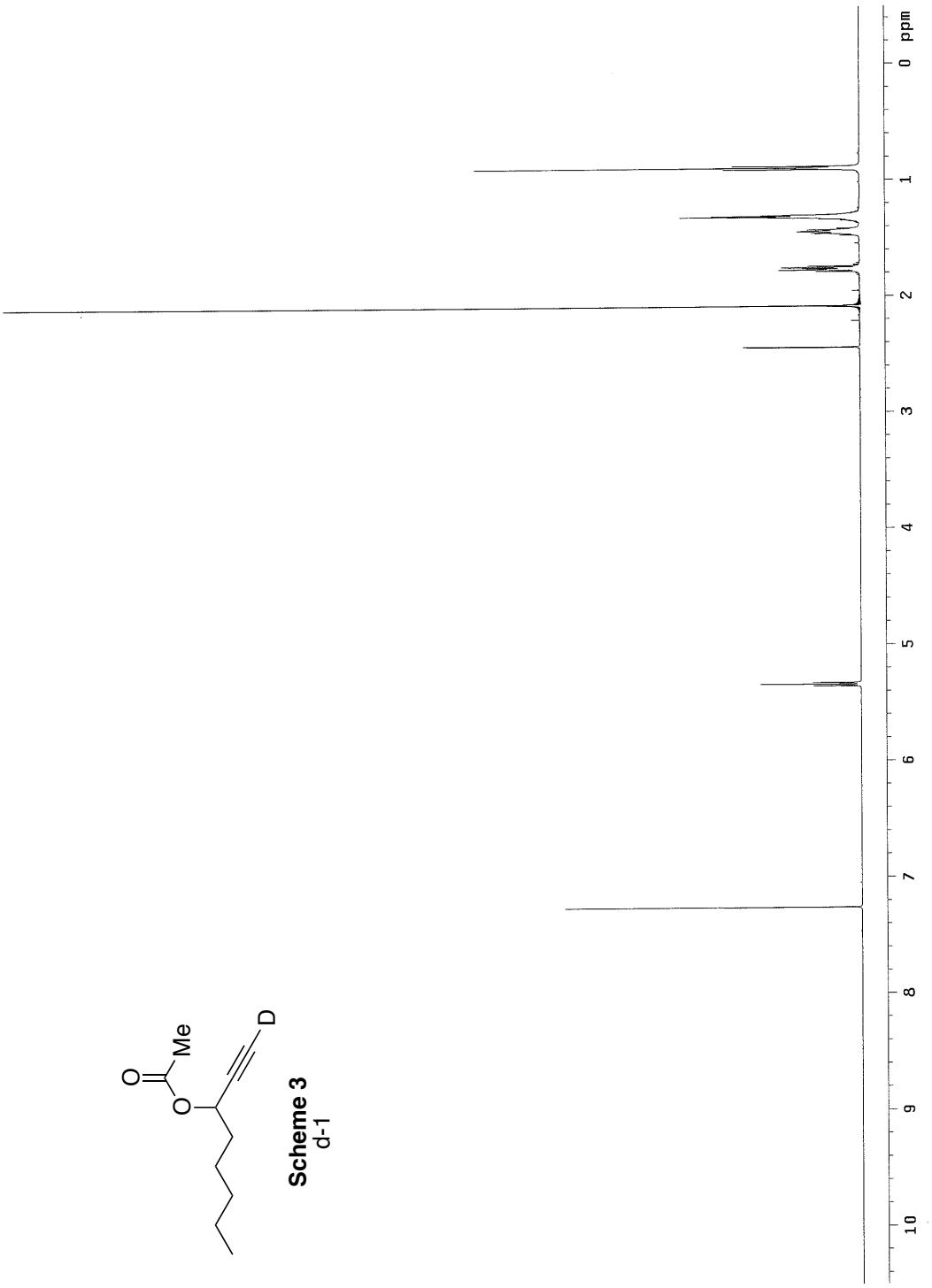
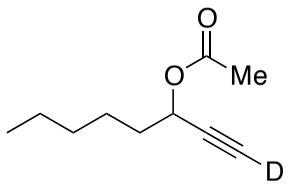


Table 2
Entry 13 G



Scheme 3
d-1



Scheme 3
d-1

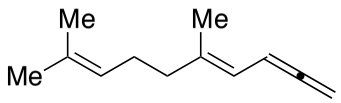


Table 3
Entry 5 L

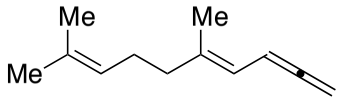


Table 3
Entry 5 L