Construction of 1,5-Enynes by Stereospecific Pd-Catalyzed Allyl-Propargyl Cross-Couplings

Michael J. Ardolino, and James P. Morken*

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467

Supporting Information

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General Information

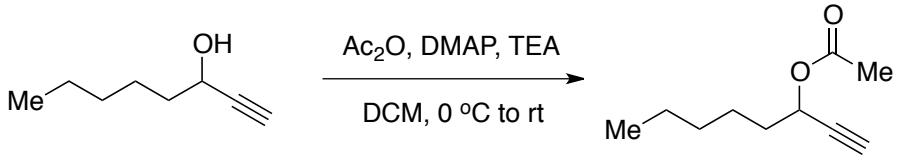
^{1}H NMR spectra were recorded on a Varian Gemini-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, 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). 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. Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter.

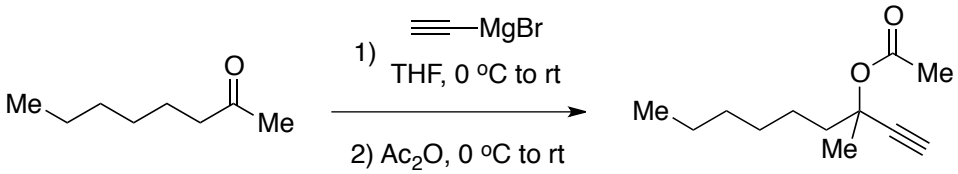
All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), Toluene (PhMe), and dichloromethane (DCM) were purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. by passing through two activated alumina columns after being purged with argon. Triethylamine (TEA) and Ethyl Acetate (EtOAc) were distilled from calcium hydride. Tris(dibenzylideneacetone) dipalladium(0) [$Pd_2(dba)_3$], Bis(1,5-cyclooctadiene)nickel(0) [$Ni(cod)_2$], Tris(dibenzylideneacetone) dipalladium(0) [$Pd_2(dba)_3$], tricyclohexylphosphine (PCy_3), 1,2-bis(diphenylphosphino)benzene (dpp-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], (*S*,*S*)-(-)-2,3-Bis(*t*-butylmethylphosphino)quinoxaline [(*S*,*S*)-QuinoxP*], and (*R*,*R*)-(-)-2,3-Bis(*t*-butylmethylphosphino)quinoxaline [(*R*,*R*)-QuinoxP*] were purchased from Strem Chemicals, Inc. Pinacolborane (pinBH) was generously donated by BASF. 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

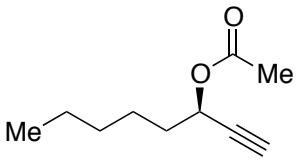
Preparation of Substituted Propargyl Acetates



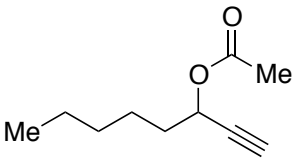
Representative Procedure A: An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with dichloromethane (20.0 mL), 1-octyn-3-ol (500 mg, 3.96 mmol), and dimethylamino pyridine (catalytic) under nitrogen atmosphere. The solution was cooled to 0 °C and triethylamine (1.2 g, 11.88 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).



Representative Procedure B: An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with THF (18 mL) and 1-octanone (388 mg, 3.00 mmol). The solution was cooled to 0 °C and ethynylmagnesium bromide (9.0 mL of a 0.5 M solution in THF, 4.50 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 (612.5 mg, 6.0 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 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 (10:1 pentane:diethyl ether) to afford a clear, colorless oil (481 mg, 82% yield). R_f = 0.75 (10:1 pentane:diethyl ether, stain in CAM).



(R)-oct-1-yn-3-yl acetate. From commercially available *(R)*-oct-1-yn-3-ol, representative procedure **A** was followed to afford a clear, colorless oil (232 mg, 90% yield). R_f = 0.60 (10:1 pentane:diethyl ether, stain in PMA). $[\alpha]^{22}_D$ = 77.787 (*c* = 0.635, $CHCl_3$). Spectral data is in accordance with the literature.[1]

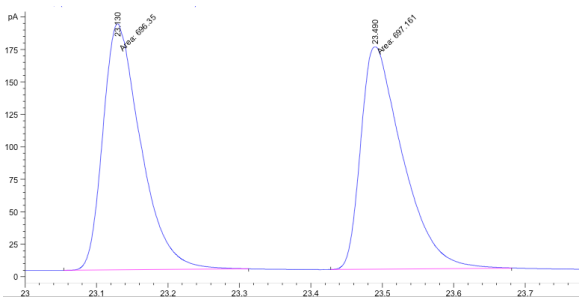


oct-1-yn-3-yl acetate. From commercially available oct-1-yn-3-ol, representative procedure **A** was followed to afford a clear, colorless oil (599 mg, 90% yield).

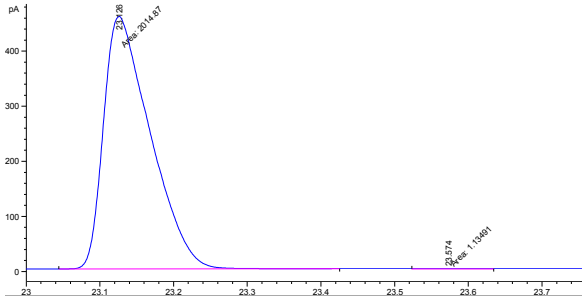
Analysis of Stereochemistry:

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

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



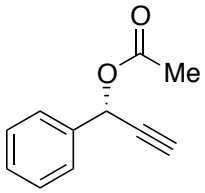
Racemic Sample



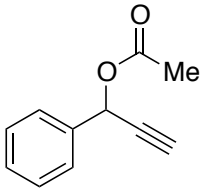
Enantioenriched Sample

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	23.126	MM	0.0733	2014.87195	458.27991	99.94371
2	23.574	MM	0.0561	1.13491	3.37070e-1	0.05629

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



(R)-1-phenylprop-2-yn-1-yl acetate. From commercially available *(R)*-1-phenylprop-2-yn-1-ol, representative procedure **A** was followed to afford a clear, colorless oil (740 mg, 96% yield). R_f = 0.39 (10:1 pentane:diethyl ether, stain in PMA). $[\alpha]^{22}_D$ = 4.852 (*c* = 0.915, $CHCl_3$). Spectral data is in accordance with the literature. [1]

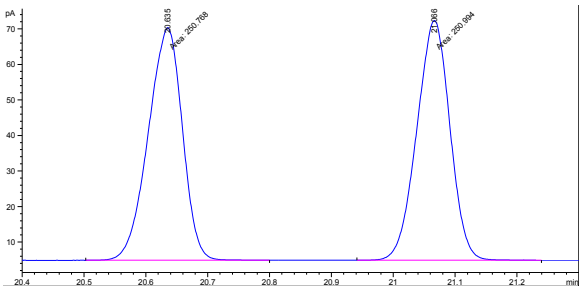


1-phenylprop-2-yn-1-yl acetate. From commercially available 1-phenylprop-2-yn-1-ol, representative procedure **A** was followed to afford a clear, colorless oil (938 mg, >96% yield).

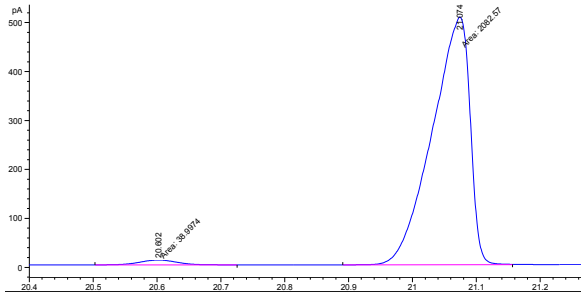
Analysis of Stereochemistry:

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

Chiral GLC (β-dex, Supelco, 100 °C for 10 min, ramp 3 °C/min to 150 °C for 10 min, 20 psi)-analysis of title compound.



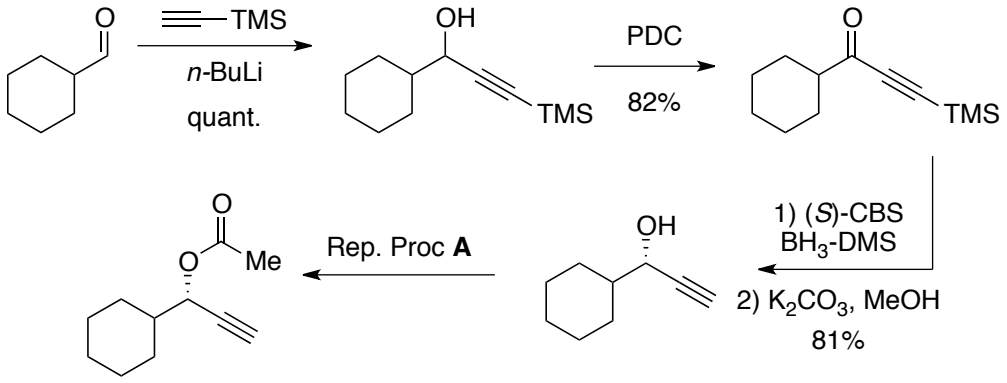
Racemic Sample



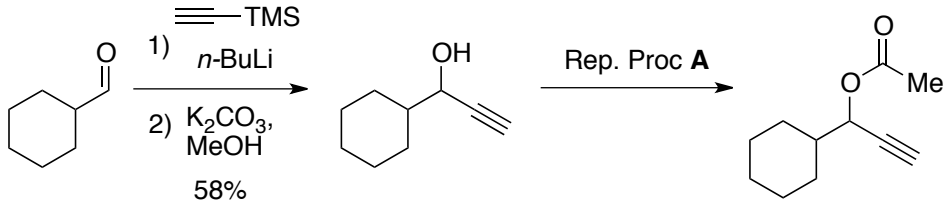
Enantioenriched Sample

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	20.602	MM	0.0659	38.99739	9.86351	1.83814
2	21.074	MF	0.0685	2082.57373	506.66437	98.16186

(S)-1-cyclohexylprop-2-yn-1-yl acetate. From *(S)*-1-cyclohexylprop-2-yn-1-ol, prepared *via* the three step sequence shown below, representative procedure **A** was followed to afford a clear, colorless oil (57 mg, 74% yield). R_f = 0.78 (10:1 pentane:diethyl ether, stain in PMA). $[\alpha]^{22}_D$ = –47.280 (*c* = 0.67, $CHCl_3$). Spectral data is in accordance with the literature.[2]



1-cyclohexylprop-2-yn-1-yl acetate. From 1-cyclohexylprop-2-yn-1-ol, prepared as shown below, representative procedure **A** was followed to afford a clear, colorless oil (171 mg, 87% yield).

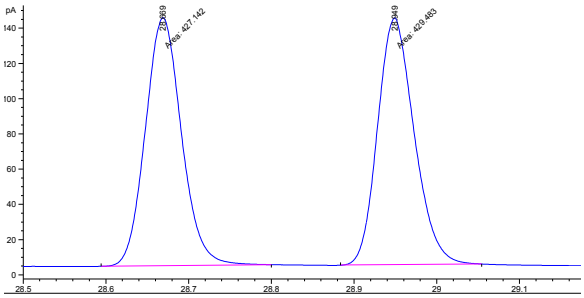


[2]Detz, R.; Abiri, Z.; Griel, R.; Hiemstra, H.; Maarseveen, J. *Chem. Eur. J.* **2011**, *21*, 5921.

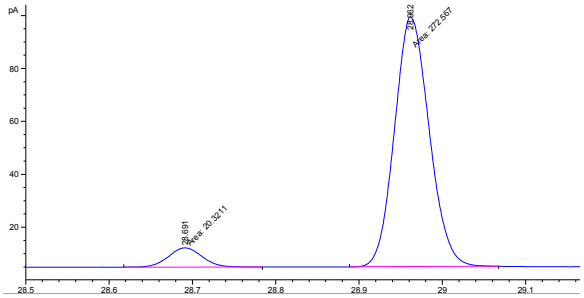
Analysis of Stereochemistry:

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

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



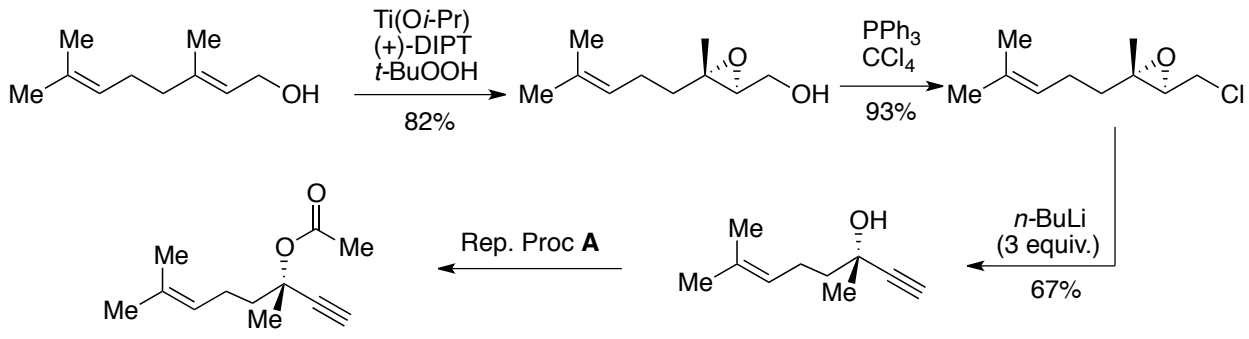
Racemic Sample



Enantioenriched Sample

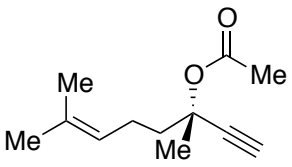
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.691	MM	0.0466	20.32110	7.26293	6.93818
2	28.962	MM	0.0482	272.56686	94.27633	93.06182

(S)-3,7-dimethyloct-6-en-1-yn-3-yl acetate. From *(S)*-3,7-dimethyloct-6-en-1-yn-3-ol, synthesized from commercially available geraniol *via* the previously reported three step procedure shown below,[3] representative procedure **A** was followed.



[3]Mohapatra, D.; Pramanik, C.; Chorghade, M.; Gurjar, M. *Eur. J. Org. Chem.* **2007**, *30*, 5059.

3,7-dimethyloct-6-en-1-yn-3-yl acetate. From commercially available 6-methylhept-5-en-2-one, representative procedure **B** was followed to afford a clear, colorless oil (265 mg, 50% yield). R_f = 0.56 (10:1 pentane:diethyl ether, stain in PMA).

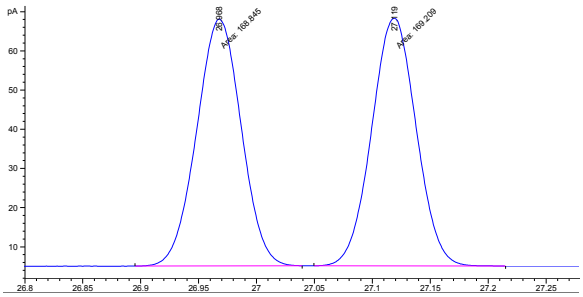


***(S)-3,7-dimethyloct-6-en-1-yn-3-yl acetate* (Table 2, Compound 7).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.11 (1H, ddqq (app tp), *J* = 7.5 Hz, 7.5 Hz, 1.0 Hz, 1.0 Hz), 2.56 (1H, s), 2.23-2.11 (2H, m), 2.03 (3H, s), 1.95 (1H, ddd, J = 13.5 Hz, 11.0 Hz, 6.0 Hz), 1.81 (1H, ddd, *J* = 13.5 Hz, 11.5 Hz, 6.0 Hz), 1.68 (6H, s), 1.62 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 132.3, 123.2, 83.8, 74.7, 73.2, 41.3, 26.4, 25.6, 22.9, 21.9, 17.6; IR (neat): 3288 (w), 2967 (w), 2927 (m), 2861 (w), 1745 (s), 1445 (m), 1368 (m), 1232 (s), 1168 (m), 1111 (m), 1081 (m), 1015 (m), 832 (w), 662 (m) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{19}O_2$ [M+H]: calculated: 195.1385, found: 195.1393. $[\alpha]^{22}_D$ = –21.3926 (*c* = 1.72, $CHCl_3$). The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil (176 mg, 87% yield). R_f = 0.56 (10:1 pentane:diethyl ether, stain in PMA).

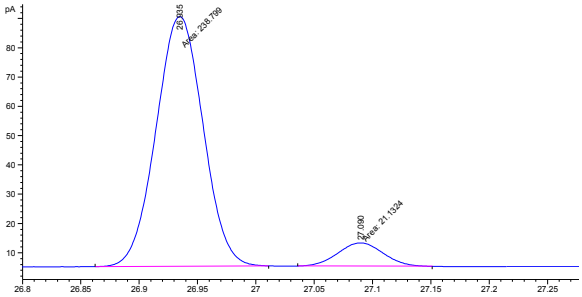
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound prepared from the enantioenriched alcohol as compared to the racemic acetate.

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



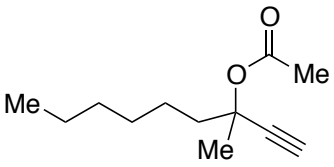
Racemic Sample



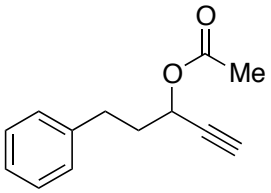
Enantioenriched Sample

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.935	MM	0.0466	238.79890	85.41997	91.87002
2	27.090	MM	0.0445	21.13236	7.90767	8.12998

3-methylnon-1-yn-3-yl acetate. From commercially available 2-octanone representative procedure **B** was followed.

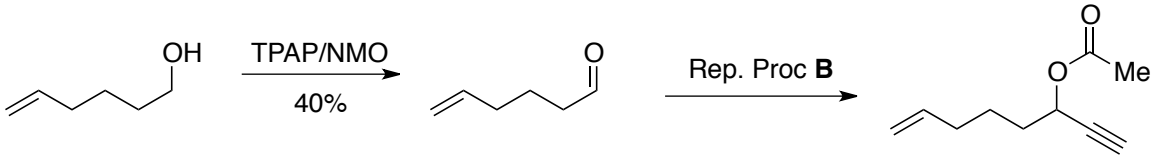


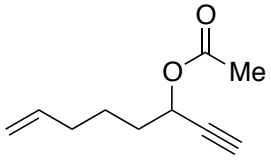
***3-methylnon-1-yn-3-yl acetate* (Compound SI-1).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.53 (1H, s), 2.02 (3H, s), 1.93 (1H, ddd, J = 13.5 Hz, 11.5 Hz, 5.0 Hz), 1.79 (1H, ddd, J = 13.5 Hz, 12.0 Hz, 5.5 Hz), 1.66 (3H, s), 1.53-1.39 (4H, m), 1.33-1.28 (4H, m), 0.89 (3H, dd (app t), J = 7.0 Hz, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 84.0, 74.9, 73.0, 41.3, 31.7, 29.2, 26.4, 24.0, 22.6, 21.9, 14.0; IR (neat): 3310 (w), 2930 (m), 2858 (m), 1744 (s), 1462 (m), 1367 (m), 1238 (s), 1178 (m), 1152 (m), 1059 (m), 660 (m), 611 (m), 537 (w) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{21}O_2$ [M+H]: calculated: 197.1542, found: 197.1537. The crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear colorless oil (481 mg, 82% yield). R_f = 0.75 (10:1 pentane:diethyl ether, stain in CAM).



5-phenylpent-1-yn-3-yl acetate. 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]

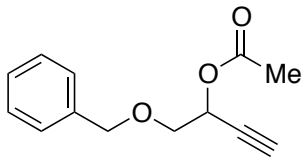
oct-7-en-1-yn-3-yl acetate. From hex-5-enal, synthesized as shown below from commercially available hex-5-en-1-ol, representative procedure **B** was followed.





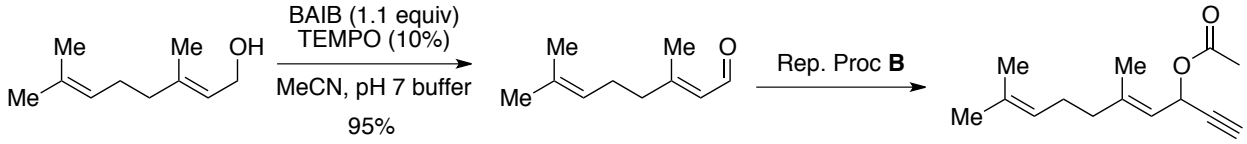
***oct-7-en-1-yn-3-yl acetate* (Compound SI-2).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79 (1H, dddd (app ddt), J = 17.0 Hz, 10.0 Hz, 6.5 Hz, 6.5 Hz), 5.35 (1H, ddd (app dt), J = 6.5 Hz, 6.5 Hz, 2.5 Hz), 5.02 (1H, ddd, J = 17.0 Hz, 3.5 Hz, 2.0 Hz), 4.96 (1H, dddd (app ddt), J = 10.0 Hz, 2.0 Hz, 1.0 Hz, 1.0 Hz), 2.45 (1H, d, J = 2.5 Hz), 2.12-2.07 (2H, m), 2.08 (3H, s), 1.81-1.76 (2H, m), 1.56 (2H, dddd (app tt), J = 7.5 Hz, 7.5 Hz, 7.5 Hz, 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 138.0, 115.1, 81.2, 73.5, 63.6, 33.9, 33.1, 24.1, 21.0; IR (neat): 3289 (w), 2928 (w), 2858 (w), 1738 (s), 1454 (m), 1370 (s), 1227 (s), 1157 (m), 1128 (m), 1089 (m), 1019 (m), 937 (w), 910 (w), 748 (m) cm^{-1}; HRMS-(ESI+) for $C_{10}H_{15}O_2$ [M+H]: calculated: 167.1072, found: 167.1081. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil (115 mg, 46% yield). R_f = 0.75 (10:1 pentane:diethyl ether, stain in PMA).

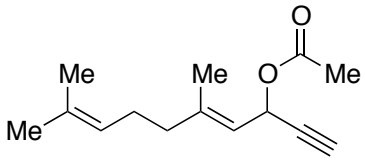
1-(benzyloxy)but-3-yn-2-yl acetate. From commercially available 2-(benzyloxy)acetaldehyde, representative procedure **B** was followed.



***1-(benzyloxy)but-3-yn-2-yl acetate* (Compound SI-3).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.28 (5H, m), 5.58 (1H, ddd, J = 7.0 Hz, 4.5 Hz, 2.5 Hz), 4.63 (1H, d, J = 12.0 Hz), 4.59 (1H, d, J = 12.0 Hz), 3.72 (1H, dd, J = 11.0 Hz, 7.0 Hz), 3.69 (1H, dd, J = 11.0 Hz, 4.5 Hz), 2.48 (1H, d, J = 2.5 Hz), 2.12 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 137.5, 128.4, 127.8, 127.7, 78.6, 74.5, 73.3, 70.9, 62.6, 20.9; IR (neat): 3283 (w), 2866 (w), 1741 (s), 1496 (w), 1370 (m), 1223 (s), 1123 (m), 1094 (m), 1043 (m), 1025 (m), 738 (m), 697 (s) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{15}O_3$ [M+H]: calculated: 219.1021, found: 219.1029. The crude reaction mixture was purified on silica gel (5:1 pentane:diethyl ether) to afford a clear, colorless oil (341 mg, 78% yield). R_f = 0.34 (5:1 pentane:diethyl ether, stain in PMA).

(E)-5,9-dimethyldeca-4,8-dien-1-yn-3-yl acetate. From *(E)*-3,7-dimethylocta-2,6-dienal, synthesized as shown below from commercially available geraniol,[4] representative procedure **B** was followed.

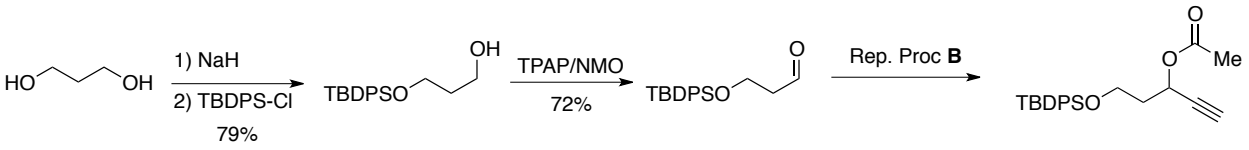


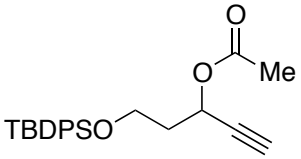


***(E)-5,9-dimethyldeca-4,8-dien-1-yn-3-yl acetate.* (Compound SI-4).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.98 (1H, dd, J = 9.0 Hz, 2.5 Hz), 5.25 (1H, ddd, J = 9.0 Hz, 7.0 Hz, 1.0 Hz), 5.02-4.98 (1H, m), 2.42 (1H, d, J = 2.0 Hz), 2.01 (3H, s), 2.07-1.96 (4H, m), 1.69 (3H, d, J = 1.5 Hz), 1.61 (3H, d, J = 1.0 Hz), 1.53 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7, 142.7, 132.0, 123.5, 120.1, 81.1, 73.1, 60.8, 39.3, 26.1, 25.6, 21.0, 17.7, 16.8; IR (neat): 3291 (w), 2967 (w), 2919 (w), 2857 (w), 1738 (s), 1667 (w), 1442 (w), 1370 (m), 1225 (s), 1009 (m), 931 (m), 907 (m), 814 (w) cm^{-1}; HRMS-(ESI+) for $C_{14}H_{21}O_2$ [M+H]: calculated: 221.1542, found: 221.1547. The crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, colorless oil (821 mg, 93% yield). R_f = 0.83 (10:1 pentane:diethyl ether, stain in PMA).

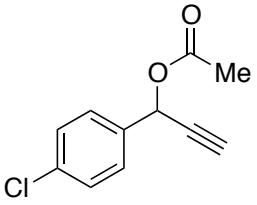
[4] Leonelli, F.; Piancatelli, G. *Org. Syn.* **2009**, *83*, 18.

5-((tert-butyldiphenylsilyl)oxy)pent-1-yn-3-yl acetate. From 3-((*tert*-butyldiphenylsilyl)oxy)propanal, synthesized as shown below utilizing a two-step procedure from commercially available propane-1,3-diol,[5] representative procedure **B** was followed.

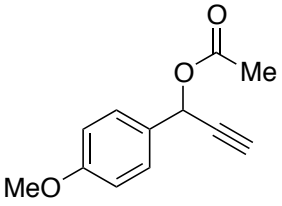




5-((tert-butyldiphenylsilyl)oxy)pent-1-yn-3-yl acetate **(Compound SI-5).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (4H, dddd (app tt), J = 8.0 Hz, 8.0 Hz, 1.5 Hz, 1.5 Hz), 7.45-7.36 (6H, m), 5.61 (1H, ddd (app dt), J = 7.0 Hz, 7.0 Hz, 2.0 Hz), 3.81 (1H, ddd, J = 11.0 Hz, 5.5 Hz, 5.5 Hz), 3.75 (1H, dddd, J = 11.0 Hz, 6.5 Hz, 6.5 Hz, 1.5 Hz), 2.43 (1H, d, J = 2.0 Hz), 2.04 (3H, s), 2.11-1.98 (2H, m), 1.05 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7, 135.6, 135.6 (2C), 133.5, 129.7, 129.7, 127.7 (2 C), 81.2, 73.6, 61.0, 59.4, 37.5, 26.8 (3 C), 20.9, 19.2; IR (neat): 3288 (w), 3071 (w), 2958 (w), 2931 (w), 2883 (w), 2858 (w), 1742 (s), 1472 (w), 1427 (m), 1371 (m), 1227 (s), 1105 (s), 981 (m), 955 (m), 888 (m), 822 (m), 737 (m), 701 (s), 688 (s), 613 (s), 503 (s) cm^{-1}; HRMS-(ESI+) for $C_{23}H_{29}O_3Si$ [M+H]: calculated: 381.1886, found: 381.1888. The crude reaction mixture was purified on silica gel (10:1 pentane:diethyl ether) to afford a clear, colorless oil (279 mg, 74% yield). R_f = 0.71 (10:1 pentane:diethyl ether, stain in PMA).



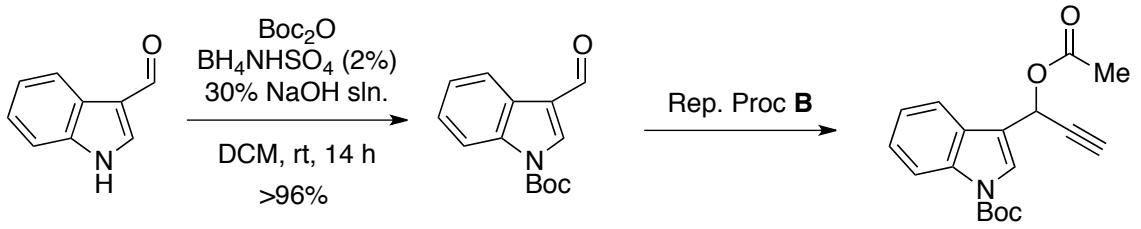
1-(4-chlorophenyl)prop-2-yn-1-yl acetate. From commercially available 4-chlorobenzaldehyde, representative procedure **B** was followed to afford a clear, pale yellow oil (574 mg, 92% yield). Spectral data is in accordance with the literature. [1]

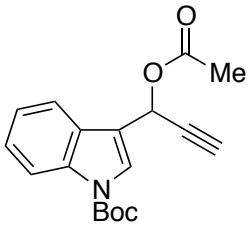


1-(4-methoxyphenyl)prop-2-yn-1-yl acetate. From commercially available 4-methoxybenzaldehyde, representative procedure **B** was followed to afford a clear, pale yellow oil (741 mg, quant.). Spectral data is in accordance with the literature. [2]

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

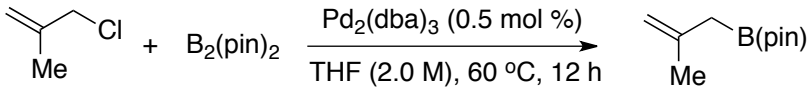
tert-butyl-3-(1-acetoxyprop-2-yn-1-yl)-1H-indole-1-carboxylate. From *tert*-butyl 3-formyl-1*H*-indole-1-carboxylate, synthesized as shown below from 1*H*-indole-3-carbaldehyde, representative procedure **B** was followed.





tert-butyl 3-(1-acetoxyprop-2-yn-1-yl)-1H-indole-1-carboxylate. **(Compound SI-6).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (1H, d J = 8.0 Hz), 7.80 (1H, s), 7.72 (1H, ddd (app dt), J = 8.0 Hz, 1.5 Hz, 1.5 Hz), 7.36 (1H, ddd, J = 8.0 Hz, 7.0 Hz, 1.0 Hz), 7.27 (1H, ddd, J = 7.5 Hz, 7.0 Hz, 1.0 Hz), 6.72 (1H, d, J = 2.5 Hz), 2.65 (1H, d, J = 2.5 Hz), 2.12 (3H, s), 1.67 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 149.4, 135.8, 127.7, 125.7, 124.9, 123.0, 119.6, 116.4, 115.5, 84.2, 79.5, 74.5, 58.5, 28.1, 20.9; IR (neat): 3291 (w), 2979 (w), 1737 (s), 1477 (m), 1453 (w), 1370 (s), 1309 (w), 1219 (s), 1156 (s), 1089 (m), 1017 (m), 937 (w), 909 (w), 677 (m) cm^{-1}; HRMS-(ESI+) for $C_{18}H_{19}N_1O_4$ [M]: calculated: 313.1314, found: 313.1308; The crude reaction mixture was purified on silica gel (2:1 pentane:diethyl ether) to afford a pale brown viscous oil (649 mg, 86% yield). R_f = 0.43 (5:1 pentane:diethyl ether, stain in PMA).

Preparation of 2-Methallylboronic acid Pinacol Ester[6]



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.[7]

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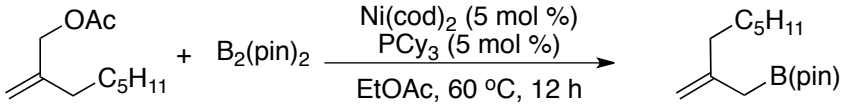
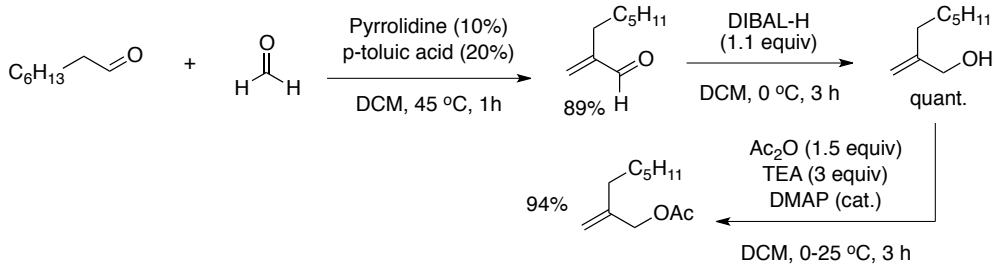
[6] Zhang, P.; Roundtree, I. A.; Morken, J. P. *Org. Lett.* **2012**, *14*, 1416.

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

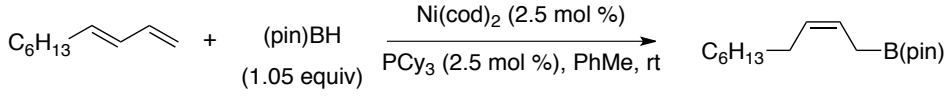
Preparation of 4,4,5,5-tetramethyl-2-(2-methyleneoctyl)-1,3,2-dioxaborolane



An oven-dried scintillation vial equipped with a magnetic stir bar was charged with bis(1,5-cyclooctadiene)nickel(0) (34.4 mg, 0.125 mmol), tricyclohexylphosphine (35.1 mg, 0.125 mmol), and ethyl acetate (2.5 mL) in a dry box under argon atmosphere. The vial was capped and stirred for two minutes, then 2-methyleneoctyl acetate (synthesized from octyl aldehyde as shown below),[8] (460 mg, 2.5 mmol) was added, followed by bis(pinacolato)diboron (635 mg, 2.5 mmol). The vial was capped with a teflon cone-lined cap, sealed with electrical tape, removed from the dry-box, and was heated to 60 °C and allowed to stir for 14 h. At this time, the reaction was concentrated *in vacuo*. The crude reaction mixture was purified on oven-dried silica gel (pentane, ramped quickly to 20:1 pentane:diethyl ether) to afford a clear, colorless oil (473 mg mg, 76% yield). R_f = 0.82 (20:1 pentane:diethyl ether, stain in $KMnO_4$). Spectral data is in accordance with the literature.[7]



Preparation of (Z)-2-(dec-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[9]



An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with bis(1,5-cyclooctadiene)nickel(0) (17.1 mg, 0.0625 mmol), tricyclohexylphosphine (17.5 mg, 0.0625 mmol), and toluene (10 mL) in a dry-box under argon atmosphere. The flask was sealed with a septum and stirred for two minutes, then (E)-deca-1,3-diene (synthesized from nonenal as shown below), (346 mg, 2.25 mmol) was added, followed by pinacolborane (336 mg, 2.625 mmol). The flask was sealed with a rubber septa, removed from the dry-box, and allowed to stir at 25 °C for 3 hours under nitrogen. The reaction was concentrated *in vacuo*, and the crude

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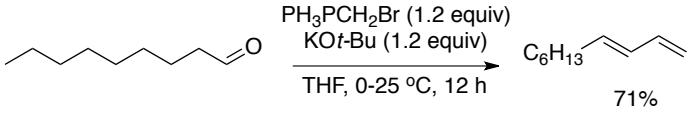
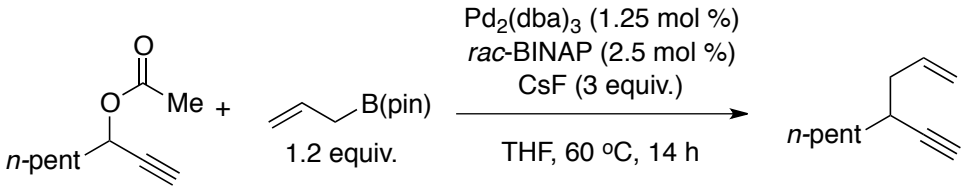
[8]Erkkilä, A.; Pihko, P. M. *Eur. J. Org. Chem.* **2007**, 4205-4216.

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

reaction mixture was purified on oven-dried silica gel (20:1 pentane:diethyl ether) to afford a clear, colorless oil (604 mg, 91% yield). R_f = 0.68 (20:1 pentane:diethyl ether, stain in $KMnO_4$). Spectral data is in accordance with the literature.[10]

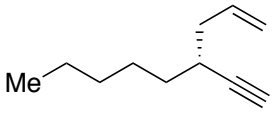


Experimental Procedure for Allyl-Propargyl Coupling



An oven-dried scintillation vial equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (5.7 mg, 6.25 µmol), *racemic*-BINAP (7.8 mg, 12.50 µmol), and THF (1.0 mL) in a dry-box under argon atmosphere. The vial was capped and allowed to stir for five minutes, then oct-1-yn-3-yl acetate (84.1 mg, 0.50 mmol) was added, followed by cesium fluoride (227.4 mg, 1.5 mmol), and allylboronic acid pinacol ester (101.0 mg, 0.60 mmol). The vial was sealed, removed from the dry-box, and heated to 60 °C while allowing to stir for 14 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (70.3 mg, 96% yield).

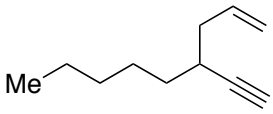
Characterization of Products and Analysis of Stereochemistry



(R)-4-ethynylnon-1-ene **(Table 2, Product 2).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.2 mmol scale with *(R)*-oct-1-yn-3-yl acetate. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.88 (1H, dddd (app ddt), *J* = 17.0 Hz, 10.0 Hz, 7.0 Hz, 7.0 Hz), 5.09 (1H, ddd (app ddt), *J* = 17.0 Hz, 2.0 Hz, 1.0 Hz, 1.0 Hz), 5.06 (1H, dddd (app ddt), *J* = 10.0 Hz, 2.0 Hz, 1.5 Hz, 1.5 Hz), 2.40 (1H, ddddd (app dtt), *J* = 7.0 Hz, 7.0 Hz, 7.0 Hz, 7.0 Hz, 2.5 Hz), 2.45-2.21 (2H, m), 2.07 (1H, d, *J* = 2.5 Hz), 1.56-1.23 (8H, m), 0.89 (3H, dd (app t), *J* = 7.5 Hz, 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.9, 116.5, 87.5, 69.3, 39.2, 34.3, 31.6, 31.4, 26.8, 22.6, 14.0; IR (neat): 2956 (s), 2930 (s), 2857 (m), 1969 (w), 1458 (m), 1378 (w), 997 (w), 914 (m), 644 (w), 631 (m), 613 (w) cm^{-1}; HRMS-(ESI+) for $C_{19}H_{11}$ [M+H]: calculated: 151.1487, found: 151.1489. $[\alpha]^{22}_D$ = 14.140 (*c* = 1.26, $CHCl_3$). The crude

[10] Brozek, L. A.; Ardolino, M. J.; Morken, J. P. *J. Am. Chem. Soc.* **2011**, *133*, 16778-16781.

reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (28.0 mg, 93% yield). R_f = 0.71 (pentane, stain in PMA).

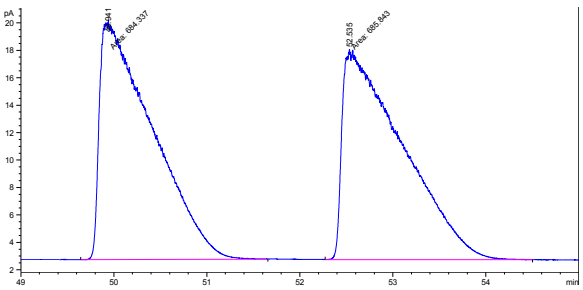


4-ethynylnon-1-ene. The title compound was prepared *via* the representative procedue for allyl-propargyl coupling with oct-1-yn-3-yl acetate. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (72.0 mg, 96% yield). R_f = 0.71 (pentane, stain in PMA).

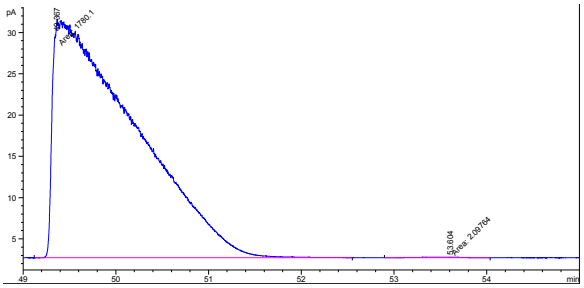
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound prepared from enantioenriched acetate as compared to product prepared with racemic material. The absolute stereochemistry was assigned by analogy to products **2** (*(S)*-hex-5-en-1-yn-3-ylbenzene) and **3** (*(R)*-hex-5-en-1-yn-3-ylcyclohexane), Table 2.

Chiral GLC (CD-BDM, Supelco, 40 °C for 30 min, ramp 0.25 °C/min to 100 °C for 10 min, 20 psi) - analysis of title compound.

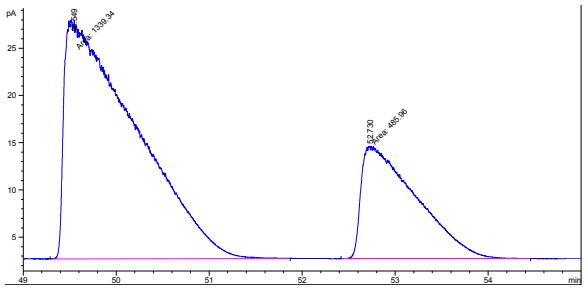


Racemic Sample

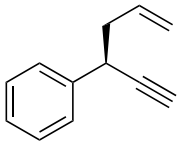


Enantioenriched Sample

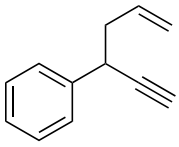
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	49.367	MM	1.0262	1780.09680	28.91143	99.88230
2	53.604	MM	0.4383	2.09764	7.97637e-2	0.11770



co-injection of racemic and enantioenriched samples



***(S)-hex-5-en-1-yn-3-ylbenzene* (Table 2, Product 4).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale with *(R)*-1-phenylprop-2-yn-1-yl acetate utilizing (2.5 mol %) [*(R)*-MeO(furyl)BIPHEP] as the ligand. Spectral data is in accordance with the literature.[11] $[\alpha]^{22}_{D}$ = 29.05 (*c* = 1.05, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (28.1 mg, 90% yield). R_f = 0.43 (pentane, stain in PMA).



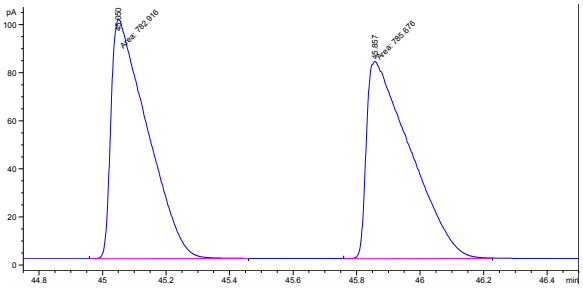
***hex-5-en-1-yn-3-ylbenzene*.** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling with 1-phenylprop-2-yn-1-yl acetate. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (71.0 mg, 91% yield). R_f = 0.43 (pentane, stain in PMA).

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

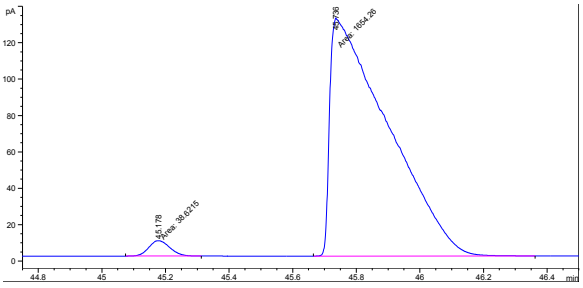
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound prepared from enantioenriched acetate as compared to product prepared with racemic material. The absolute stereochemistry was assigned as shown below.

Chiral GLC (CD-BDM, Supelco, 40 °C for 20 min, ramp 2.5 °C/min to 100 °C for 10 min, 20 psi) - analysis of title compound.

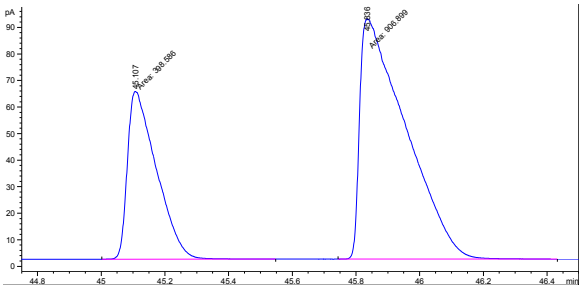


Racemic Sample



Enantioenriched Sample

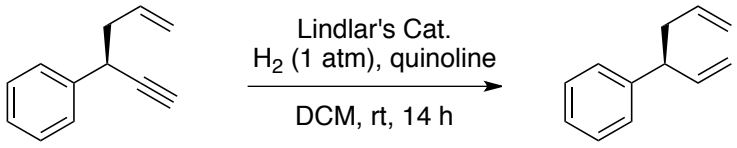
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	45.178	MM	0.0764	38.62150	8.42845	2.28141
2	45.736	MM	0.2105	1654.25708	131.00157	97.71859

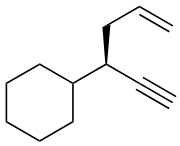


co-injection of racemic and enantioenriched samples

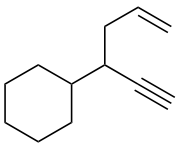
Proof of Structure and Stereochemistry:

The title compound was subjected to selective hydrogenation of the alkyne utilizing Lindlar's catalyst to afford the previously reported 1,5-diene as depicted below. Spectral data is in accordance with the literature.[7] In order to determine the absolute stereochemistry, the optical rotation of the 1,5-diene derived from the propargyl-allyl coupling product ($[\alpha]^{22}_D$ = 21.558 (*c* = 1.295, $CHCl_3$) was compared to the rotation of authentic (*S*)-hexa-1,5-dien-3-ylbenzene ($[\alpha]^{20}_D$ = 12.237 (*c* = 0.44, $CHCl_3$)) as previously reported in the literature.[7]





(*R)-hex-5-en-1-yn-3-ylcyclohexane* (Table 2, Product 6). The title compound was prepared *via* the representative procedure for allyl-propargyl coupling with *(S)*-1-cyclohexylprop-2-yn-1-yl acetate on a 0.10 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.89 (1H, dddd (app ddt), *J* = 17.0 Hz, 10.0 Hz, 7.0 Hz, 7.0 Hz), 5.09 (1H, dddd (app ddt), *J* = 17.0 Hz, 2.0 Hz, 1.5 Hz, 1.5 Hz), 5.05 (dddd (app dt), *J* = 10.0 Hz, 2.0 Hz, 1.0 Hz, 1.0 Hz), 2.31-2.23 (3H, m), 2.07 (1H, d, *J* = 2.5 Hz), 1.85-1.82 (1H, m), 1.78-1.64 (4H, m), 1.40-1.35 (1h, m), 1.28-1.10 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.4, 116.2, 86.2, 70.3, 40.4, 37.8, 36.5, 31.3, 28.9, 26.4, 26.4, 26.2; IR (neat): 3310 (w), 2925 (s), 2853 (m), 1449 (m), 996 (m), 912 (m), 631 (m) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{19}$ [M+H]: calculated: 163.1487, found: 163.1491. $[\alpha]^{22}_D$ = 2.548 (*c* = 0.65, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (14.1 mg, 87% yield). R_f = 0.80 (pentane, stain in PMA).

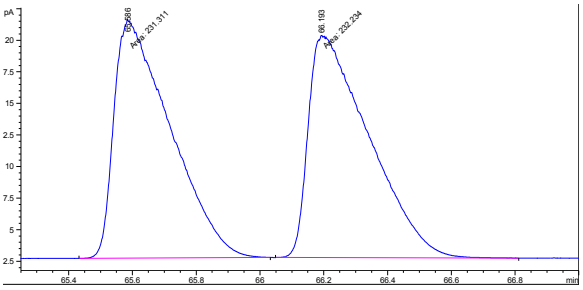


***hex-5-en-1-yn-3-ylcyclohexane*.** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling with 1-cyclohexylprop-2-yn-1-yl acetate on a 0.2 mmol scale. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (33.1 mg, 99% yield). R_f = 0.80 (pentane, stain in PMA).

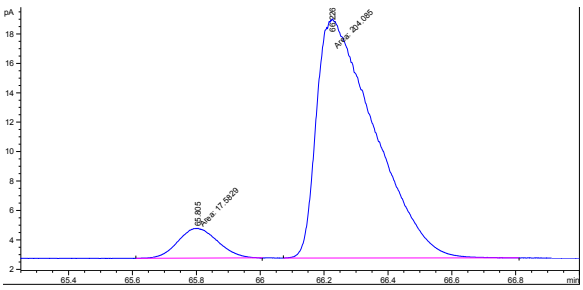
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound prepared from enantioenriched acetate as compared to product prepared with racemic material. The absolute stereochemistry was assigned as shown below.

Chiral GLC (CD-BDM, Supelco, 40 °C for 20 min, ramp 1.0 °C/min to 100 °C for 10 min, 20 psi) - analysis of title compound.

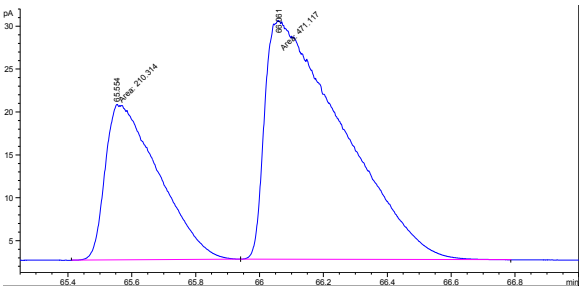


Racemic Sample



Enantioenriched Sample

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	65.805	MM	0.1444	17.58285	2.02874	7.93207
2	66.226	MM	0.2095	204.08516	16.23424	92.06793

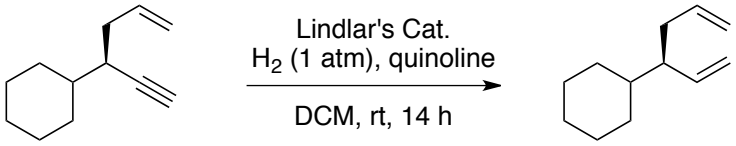


co-injection of racemic and enantioenriched samples

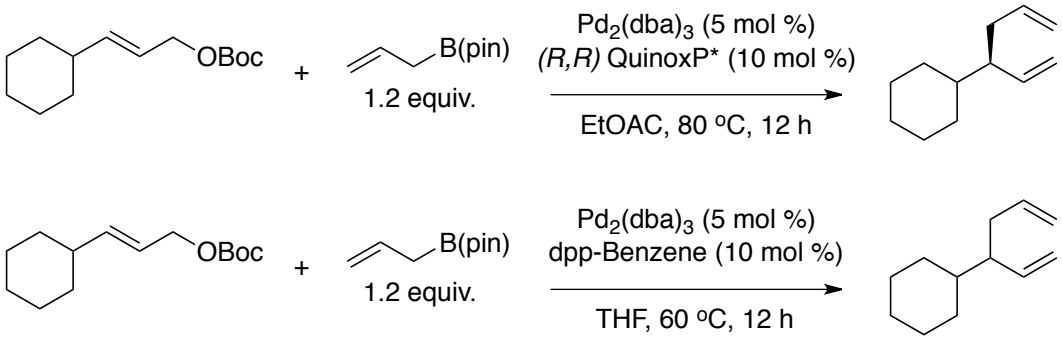
Proof of Structure and Stereochemistry:

The title compound was subjected to selective hydrogenation of the alkyne utilizing Lindlar's catalyst to afford the previously reported 1,5-diene as depicted below. Spectral data is in accordance with the literature.[7] In order to determine the absolute stereochemistry, the resulting diene was compared by GLC analysis to authentic *(S)*-hexa-1,5-dien-3-ylcyclohexane, prepared by allyl-allyl cross coupling as depicted below.

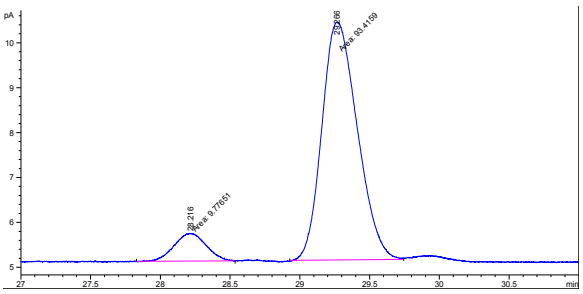
Hydrogenation of Title Compound



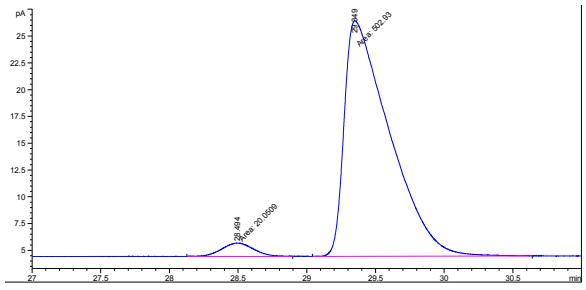
Enantioselective Allyl-Allyl Cross-Coupling[7]



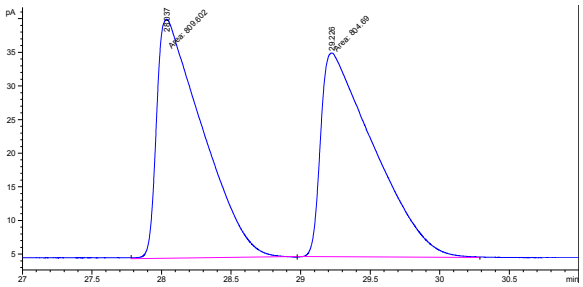
Chiral GLC (β-dex, Supelco, 60 °C for 10 min, ramp 5 °C/min to 160 °C for 10 min, 20 psi)-



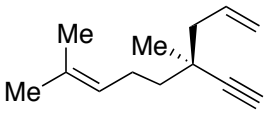
Diene from Lindlar reduction



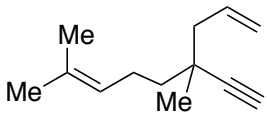
Enantioenriched (S)-hexa-1,5-dien-3-ylcyclohexane from allyl-allyl coupling



Racemic hexa-1,5-dien-3-ylcyclohexane from allyl-allyl coupling



***(S)-4-ethynyl-4,8-dimethylnona-1,7-diene* (Table 2, Product 8).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling with *(S)*-3,7-dimethyloct-6-en-1-yn-3-yl acetate on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.92 (1H, dddd (app ddt), J = 17.5 Hz, 10.0 Hz, 7.0 Hz, 7.0 Hz), 5.14-5.06 (3H, m), 2.28 (1H, ddd (app dt), J = 7.0 Hz, 1.0 Hz, 1.0 Hz), 2.25 (1H, ddd (app dt), J = 7.0 Hz, 1.0 Hz, 1.0 Hz), 2.14 (1H, s), 2.17-2.11 (2H, m), 1.69 (3H, d, J = 1.5 Hz), 1.62 (3H, d, J = 1.0 Hz), 1.47 (1H, ddd, J = 13.5 Hz, 11.0 Hz, 6.0 Hz), 1.35 (1H, ddd, J = 13.5 Hz, 11.5 Hz, 6.0 Hz), 1.17 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.6, 131.6, 124.2, 117.6, 90.3, 69.2, 45.8, 41.1, 34.6, 26.1, 25.7, 23.6, 17.6; IR (neat): 3309 (m), 3077 (w), 2968 (s), 2925 (s), 2856 (m), 1640 (w), 1451 (m), 1376 (m), 1234 (m), 1149 (w), 996 (m), 915 (s), 832 (w), 629 (s) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{21}$ [M+H]: calculated: 177.1643, found: 177.1651. $[\alpha]^{22}_{D}$ = 1.333 (c = 1.65, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (33.8 mg, 96% yield). R_f = 0.67 (pentane, stain in PMA).

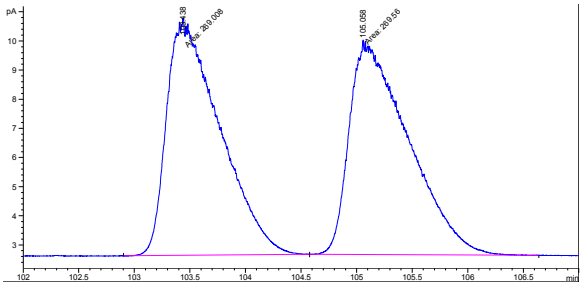


***4-ethynyl-4,8-dimethylnona-1,7-diene*.** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling with 3,7-dimethyloct-6-en-1-yn-3-yl acetate. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (82.8 mg, 94% yield). R_f = 0.67 (pentane, stain in PMA).

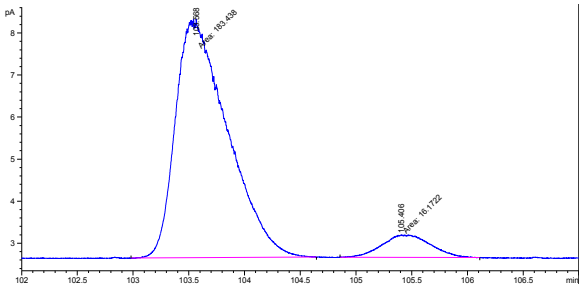
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound prepared from enantioenriched acetate as compared to product prepared with racemic material. The absolute stereochemistry was assigned by analogy to products **2** (*(S)*-hex-5-en-1-yn-3-ylbenzene) and **3** (*(R)*-hex-5-en-1-yn-3-ylcyclohexane), Table 2.

Chiral GLC (CD-BDM, Supelco, 40 °C for 30 min, ramp 0.25 °C/min to 100 °C for 10 min, 20 psi) - analysis of title compound.

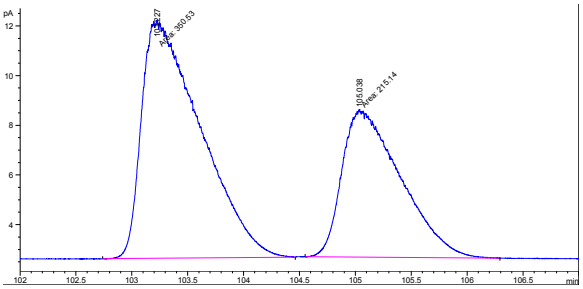


Racemic Sample

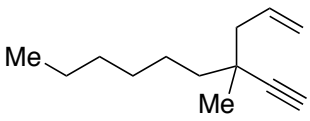


Enantioenriched Sample

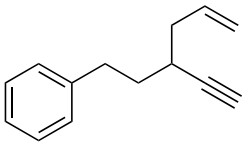
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	103.568	MM	0.5388	183.43817	5.67467	91.89812
2	105.406	MM	0.5029	16.17219	5.35936e-1	8.10188



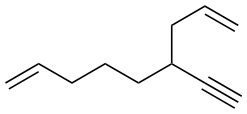
co-injection of racemic and enantioenriched samples



4-ethynyl-4-methyldec-1-ene **(Table 3, Product 9).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.92 (1H, dddd (app ddt), J = 17.0 Hz, 10.0 Hz, 7.0 Hz, 7.0 Hz), 5.09 (1H, dddd (app ddt), J = 10.0 Hz, 2.0 Hz, 1.0 Hz, 1.0 Hz), 5.07 (1H, dddd (app ddt), J = 17.0 Hz, 2.0 Hz, 1.5 Hz, 1.5 Hz), 2.24 (1H, dddd (app ddt), J = 13.0 Hz, 7.0 Hz, 1.0 Hz, 1.0 Hz), 2.13 (1H, dddd (app ddt), J = 13.0 Hz, 8.0 Hz, 1.5 Hz, 1.5 Hz), 2.11 (1H, s), 1.40-1.47 (4H, m), 1.35-1.29 (6H, m), 1.15 (3H, s), 0.89 (3H, dd (app t), J = 7.0 Hz, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.8, 117.5, 90.7, 68.9, 45.8, 41.1, 34.6, 31.8, 29.7, 26.6, 24.7, 22.7, 14.1; IR (neat): 3312 (w), 2956 (m), 2928 (s), 2856 (s), 1462 (w), 1375 (m), 1233 (w), 1110 (m), 996 (m), 914 (m), 793 (w), 701 (w), 633 (m), 506 (w) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{23}$ [M+H]: calculated: 179.1780, found: 179.1807. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (33.1 mg, 93% yield). R_f = 0.88 (pentane, stain in PMA).

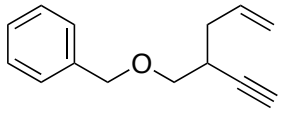


(3-ethynylhex-5-en-1-yl)benzene **(Table 3, Product 10).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (2H, dddd (app tt), J = 8.0 Hz, 8.0 Hz, 2.0 Hz, 2.0 Hz), 7.20 (3H, dddd (app ddt), J = 10.0 Hz, 6.5 Hz, 1.5 Hz, 1.5 Hz), 5.87 (1H, dddd (app ddt), J = 17.0 Hz, 10.0 Hz, 7.0 Hz, 7.0 Hz), 5.11 (1H, dddd (app ddt), J = 17.0 Hz, 2.0 Hz, 1.5 Hz, 1.5 Hz), 5.07 (1H, dddd (app ddt), J = 10.0 Hz, 2.0 Hz, 1.0 Hz, 1.0 Hz), 2.87 (1H, ddd, J = 14.0 Hz, 8.5 Hz, 6.0 Hz), 2.71 (1H, ddd, J = 14.0 Hz, 9.0 Hz, 7.5 Hz), 2.43 (1H, ddddd (app dtt), J = 7.0 Hz, 7.0 Hz, 7.0 Hz, 7.0 Hz, 2.5 Hz), 2.28-2.25 (2H, m), 2.16 (1H, d, J = 2.5 Hz), 1.80-1.74 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.8, 135.6, 128.5, 128.4, 125.9, 116.8, 86.9, 70.1, 39.1, 36.1, 33.4, 30.8; IR (neat): 3302 (m), 3078 (m), 3063 (w), 2925 (m), 2860 (w), 1642 (w), 1603 (w), 1496 (m), 1454 (m), 1030 (w), 944 (m), 745 (m), 699 (s), 634 (s) cm^{-1}; HRMS-(ESI+) for $C_{14}H_{17}$ [M+H]: calculated: 185.1330, found: 185.1331. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (35.3 mg, 96% yield). R_f = 0.44 (pentane, stain in PMA).

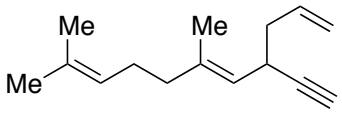


4-ethynylnona-1,8-diene **(Table 3, Product 11).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.88 (1H, dddd (app ddt), J = 17.0 Hz, 10.0 Hz, 7.0 Hz, 7.0 Hz), 5.81 (1H, dddd (app ddt), J = 17.0 Hz, 10.5 Hz, 6.5 Hz, 6.0 Hz), 5.09 (1H, ddd, J = 17.0 Hz, 3.5 Hz, 1.5 Hz), 5.06 (1H, dddd (app ddt), J = 10.0 Hz, 2.0 Hz, 1.0 Hz, 1.0 Hz), 5.02 (1H, ddd, J = 17.0 Hz, 3.5 Hz, 1.5 Hz), 4.96 (1H, dddd (app ddt), J = 10.5 Hz, 2.0 Hz, 1.0 Hz, 1.0 Hz), 2.44-2.38 (1H, m), 2.23 (2H, dddd (app tt), J = 6.5 Hz, 6.5 Hz, 1.5 Hz, 1.5 Hz), 2.07 (1H, d, J = =2.5 Hz), 2.10-2.04 (2H, m), 1.67-1.58 (1H, m), 1.54-1.41 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6, 135.8, 116.6, 114.6, 87.2, 69.5, 39.1, 33.7, 33.5, 31.3, 26.4; IR (neat): 3307 (m), 3078 (w), 2979 (w), 2934 (m), 2860 (w), 1642 (m), 1459 (w), 1441 (m), 1416 (w), 1278 (w), 993 (m), 912 (s), 631 (s) cm^{-1}; HRMS-(ESI+) for $C_{11}H_{17}$ [M+H]: calculated: 149.1330, found: 149.1335. The crude

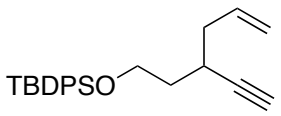
reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (26.3 mg, 89% yield). R_f = 0.69 (pentane, stain in PMA).



***(((2-ethynylpent-4-en-1-yl)oxy)methyl)benzene* (Table 3, Product 12).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (4H, d, *J* = 4.5 Hz), 7.32-7.27 (1H, m), 5.80 (1H, dddd (app ddt), *J* = 17.5 Hz, 10.5 Hz, 7.5 Hz, 7.5 Hz), 5.12 (1H, dddd, *J* = 17.0 Hz, 3.5 Hz, 1.5 Hz, 1.5 Hz), 5.09 (1H, dddd (app ddt), *J* = 10.0 Hz, 3.5 Hz, 1.5 Hz, 1.5 Hz), 4.56 (2H, d, *J* = 1.5 Hz), 3.56 (1H, dd, *J* = 9.0 Hz, 6.0 Hz), 3.47 (1H, dd, *J* = 9.0 Hz, 7.5 Hz), 2.75 (1H, ddddd (app ddq), *J* = 8.0 Hz, 7.5 Hz, 7.0 Hz, 6.0 Hz, 2.5 Hz), 2.41 (1H, ddddd, app pt, *J* = 12.5 Hz, 7.0 Hz, 5.5 Hz, 1.5 Hz, 1.5 Hz), 2.26 (1H, ddddd (app pt), *J* = 12.5 Hz, 8.0 Hz, 7.0 Hz, 1.5 Hz, 1.5 Hz), 2.11 (1H, d, *J* = 2.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 135.1, 128.4 (2 C), 127.6 (3 C), 127.6, 73.1, 71.8, 70.3, 35.6, 32.1; IR (neat): 3300 (m), 3066 (w), 3031 (w), 2909 (m), 2860 (m), 1642 (w), 1496 (m), 1442 (m), 1205 (w), 1102 (s), 1028 (w), 996 (m), 916 (s), 736 (s), 697 (s), 639 (s) cm^{-1}; HRMS-(ESI+) for $C_{14}H_{17}O$ [M+H]: calculated: 201.1279, found: 201.1284. The crude reaction mixture was purified on silica gel (50:1 pentane:diethyl ether) to afford a clear, colorless oil (36.4 mg, 91% yield). R_f = 0.45 (50:1 pentane:diethyl ether, stain in PMA).

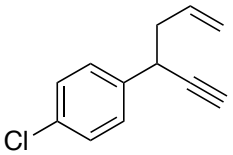


***(E)-4-ethynyl-6,10-dimethylundeca-1,5,9-triene* (Table 3, Product 13).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.85 (1H, dddd (app ddt), *J* = 17.0 Hz, 10.0 Hz, 7.0 Hz, 7.0 Hz), 5.12-5.06 (3H, m), 5.06 (1H, dddd (app ddt), *J* = 10.0 Hz, 2.0 Hz, 1.0 Hz, 1.0 Hz), 3.26 (1H, dddd (app dtd), *J* = 9.5 Hz, 7.0 Hz, 7.0 Hz, 2.5 Hz), 2.31 (1H, ddddd (app tdt), *J* = 14.0 Hz, 7.5 Hz, 7.5 Hz, 1.5 Hz, 1.5 Hz), 2.24 (1H, ddddd (app tdt), *J* = 14.0 Hz, 7.0 Hz, 7.0 Hz, 1.5 Hz, 1.5 Hz), 2.10 (1H, d, *J* = 2.5 Hz), 2.08 (2H, dd (app t), *J* = 7.0 Hz, 7.0 Hz), 2.01 (2H, dd (app t), *J* = 7.5 Hz, 7.5 Hz), 1.68 (3H, d, *J* = 1.0 Hz), 1.65 (3H, d, *J* = 1.5 Hz), 1.60 (3H, d, *J* = 1.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.9, 135.5, 131.6, 124.0, 124.0, 116.7, 86.5, 68.6, 40.0, 39.5, 30.1, 26.4, 25.6, 17.7, 16.4; IR (neat): 3309 (m), 2968 (s), 2916 (s), 2856 (s), 1642 (w), 1440 (m), 1378 (m), 1107 (w), 995 (m), 915 (m), 838 (w), 631 (s) cm^{-1}; HRMS-(ESI+) for $C_{15}H_{23}$ [M+H]: calculated: 203.1780, found: 203.1800. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, pale yellow oil (37.6 mg, 93% yield). R_f = 0.48 (pentane, stain in PMA).

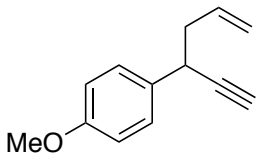


***tert-butyl((3-ethynylhex-5-en-1-yl)oxy)diphenylsilane* (Table 3, Product 14).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (4H, dddd (app ddt), *J* = 8.0 Hz, 6.0 Hz, 1.5 Hz, 1.5 Hz), 7.45-7.37 (6H, m), 5.89 (1H, dddd (app ddt), *J* = 17.0 Hz,

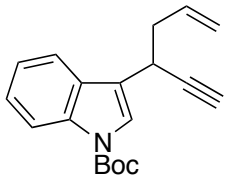
10.0 Hz, 6.5 Hz, 6.5 Hz), 5.10 (1H, ddd, *J* = 17.0 Hz, 3.0 Hz, 1.5 Hz), 5.07-5.09 (1H, m), 3.86 (1H, ddd, *J* = 10.5 Hz, 8.5 Hz, 5.5Hz), 3.79 (1H, ddd, *J* = 11.0 Hz, 6.0 Hz, 5.0 Hz), 2.75 (1H, ddddd, J = 9.5 Hz, 8.0 Hz, 5.5 Hz, 5.0 Hz, 2.5 Hz), 2.31-2.20 (2H, m), 2.04 (1H, d, *J* = 2.5 Hz), 1.78 (1H, dddd, *J* = 13.5 Hz, 8.0 Hz, 6.0 Hz, 5.0 Hz), 1.66 (1H, dddd (app ddt), *J* = 13.5 Hz, 9.5 Hz, 5.0 Hz, 5.0 Hz), 1.06 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.6, 135.6, 135.6, 133.9, 133.8, 129.6, 129.5, 127.6, 127.6, 116.7, 86.8, 69.6, 61.4, 38.9, 37.1, 27.7, 26.9, 19.2; IR (neat): 3306 (w), 3071 (w), 2931 (m), 2858 (m), 1472 (w), 1428 (m), 1361 (w), 1108 (s), 1029 (w), 915 (m), 822 (m), 737 (m), 700 (s), 635 (s), 505 (s) cm^{-1}; HRMS-(ESI+) for $C_{24}H_{31}OSi$ [M +H]: calculated: 363.2144, found: 363.2148. The crude reaction mixture was purified on silica gel (50:1 pentane:diethyl ether) to afford a clear, colorless oil (55.8 mg, 77% yield). R_f = 0.74 (50:1 pentane:diethyl ether, stain in PMA).



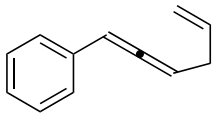
1-chloro-4-(hex-5-en-1-yn-3-yl)benzene **(Table 3, Product 15).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (4H, s), 5.81 (1H, dddd (app ddt), *J* = 16.5 Hz, 11.5 Hz, 7.0 Hz, 7.0 Hz), 5.07-5.08 (1H, m), 5.05 (1H, ddd, *J* = 11.5 Hz, 3.5 Hz, 1.5 Hz), 3.69 (1H, ddd (app dt), *J* = 7.0 Hz, 7.0 Hz, 2.5 Hz), 2.49 (2H, dddd (app ddt), *J* = 7.5 Hz, 7.5 Hz, 2.5 Hz, 1.5 Hz), 2.31 (1H, d, *J* = 2.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.2, 134.6, 132.7, 128.9, 128.6, 117.5, 84.8, 71.7, 42.2, 37.1; IR (neat): 3301 (m), 3079 (w), 2913 (w), 1642 (w), 1491 (s), 1439 (w), 1407 (m), 1274 (w), 1092 (m), 1016 (m), 996 (w), 919 (m), 825 (s), 642 (s), 514 (m), 495 (w) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{12}Cl$ [M+H]: calculated: 191.0628, found: 191.0632. The crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, colorless oil (22.4 mg, 59% yield). R_f = 0.47 (20:1 pentane:diethyl ether, stain in PMA).



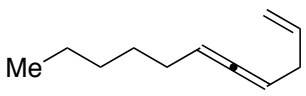
1-(hex-5-en-1-yn-3-yl)-4-methoxybenzene **(Table 3, Product 16).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (2H, ddd (app td), *J* = 8.5 Hz, 2.0 Hz, 2.0 Hz), 6.87 (2H, ddd (app td), *J* = 9.0 Hz, 2.5 Hz, 2.5 Hz), 5.84 (1H, dddd (app ddt), *J* = 17.0 Hz, 10.5 Hz, 7.0 Hz, 7.0 Hz), 5.08 (1H, ddd, *J* = 10.5 Hz, 3.0 Hz, 1.5 Hz), 5.06-5.04 (1H, m), 3.80 (3H, s), 3.66 (1H, ddd (app dt), *J* = 7.0 Hz, 7.0 Hz, 2.5 Hz), 2.51-2.48 (2H, m), 2.29 (1H, d, *J* = 2.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.5, 135.2, 132.9, 128.4, 117.1, 113.9, 85.7, 71.1, 55.3, 42.4, 36.8; IR (neat): 3295 (m), 2935 (w), 2910 (w), 2836 (w), 1641 (w), 1611 (m), 1584 (w), 1510 (s), 1464 (m), 1441 (m), 1302 (w), 1288 (w), 1248 (s), 1177 (m), 1036 (m), 917 (m), 830 (m), 644 (m) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{15}O_1$ [M+H]: calculated: 187.1123, found: 187.1128. The crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, colorless oil (35.3 mg, 95% yield). R_f = 0.61 (20:1 pentane:diethyl ether, stain in PMA).



tert-butyl 3-(hex-5-en-1-yn-3-yl)-1H-indole-1-carboxylate **(Table 3, Product 17).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (1H, d, *J* = 2.0 Hz), 7.64 (1H, ddd (app td), *J* = 7.0 Hz, 1.5 Hz, 1.5 Hz), 7.56 (1H, br s), 7.33 (1H, ddd, *J* = 8.0 Hz, 7.5 Hz, 1.0 Hz), 7.25 (1H, ddd, *J* = 8.5 Hz, 7.5 Hz, 1.0 Hz), 5.94 (1H, dddd (app dt), *J* = 17.0 Hz, 10.0 Hz, 7.0 Hz, 7.0 Hz), 5.14 (1H, ddd, *J* = 17.0 Hz, 3.0 Hz, 1.5 Hz), 5.11 (1H, dddd (app dt), *J* = 10.0 Hz, 3.0 Hz, 1.0 Hz, 1.0 Hz), 3.93 (1H, dddd, *J* = 8.0Hz, 5.5 Hz, 2.5 Hz, 1.0 Hz), 2.70 (1H, ddddd, *J* = 13.5 Hz, 7.0 Hz, 5.5 Hz, 1.5 Hz, 1.5 Hz), 2.64 (1H, ddddd, *J* = 13.5 Hz, 8.0 Hz, 7.0 Hz, 1.5 Hz, 1.5 Hz), 2.28 (1H, d, *J* = 2.5 Hz), 1,68 (1H, d, *J* = 2.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.7, 135.8, 135.1, 128.8, 124.5, 123.2, 122.4, 120.0, 119.3, 117.3, 115.4, 84.5, 83.6, 70.6, 39.6, 28.9, 28.2; IR (neat): 3296 (w), 2979 (w), 2933 (m), 1729 (s), 1641 (w), 1451 (w), 1376 (s), 1308 (m), 1254 (s), 1219 (m), 1153 (s), 1079 (s), 1042 (m), 1018 (m), 994 (m), 916 (m), 765 (s), 839 (m), 641 (s) cm^{-1}; HRMS-(ESI+) for $C_{19}H_{22}N_1O_2$ [M+H]: calculated: 296.1651, found: 296.1665. The crude reaction mixture was purified on silica gel (20:1 pentane:diethyl ether) to afford a clear, colorless oil (33.8 mg, 96% yield). R_f = 0.55 (20:1 pentane:diethyl ether, stain in PMA).



hexa-1,2,5-trien-1-ylbenzene **(Compound Si-6).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale employing triphenylphosphine (2.62 mg, 0.01 mmol, 5 mol %) as the ligand. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.28 (4H, m), 5.91 (1H, dddd (app ddt), *J* = 17.0 Hz, 10.5 Hz, 6.5 Hz, 6.5 Hz), 5.59 (1H, ddd (app dt), *J* = 6.5 Hz, 6.5 Hz, 6.5 Hz), 5.16 (1H, ddd, *J* = 17.0 Hz, 3.0 Hz, 1.5 Hz), 5.06 (1H, ddd, *J* = 10.5 Hz, 3.0 Hz, 1.5 Hz), 2.90 (2H, ddddd (app tp), *J* = 6.5 Hz, 6.5 Hz, 1.5 Hz, 1.5 Hz, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.6, 136.2, 134.8, 128.6, 128.5, 126.8, 126.7 (2 C), 115.6, 95.0, 93.1, 33.1; IR (neat): 3081 (w), 3063 (w), 3031 (m), 3007 (w), 2979 (m), 2906 (w), 1949 (m), 1639 (m), 1598 (w), 1496 (m), 1459 (w), 1431 (w), 1259 (w), 1071 (m), 912 (s), 869 (m), 723 (m), 692 (s), 625 (m), 498 (m) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{13}$ [M+H]: calculated: 157.1017, found: 157.1024. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (7.5 mg, 24% yield). R_f = 0.76 (pentane, stain in PMA).

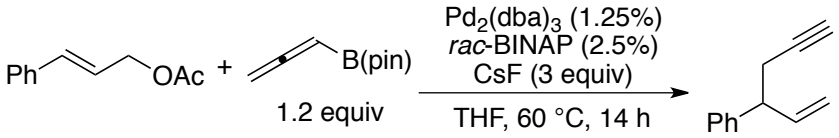


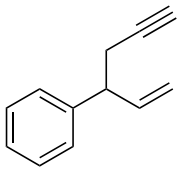
undeca-1,4,5-triene **(Compound Si-7).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling on a 0.20 mmol scale employing triphenylphosphine (2.62 mg, 0.01 mmol, 5 mol%) as the ligand. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.85 (1H, dddd (app ddt), *J* = 16.5 Hz, 10.0 Hz, 6.5 Hz, 6.5 Hz), 5.14-5.06 (3H, m), 5.01 (1H, ddd, *J* = 10.0 Hz, 3.5 Hz, 1.5 Hz), 2.75 (2H, ddddd (app tp), *J* = 6.5 Hz, 6.5 Hz, 1.5 Hz, 1.5 Hz, 1.5 Hz), 1.99 (1H, ddd (app dt), *J* = 7.0 Hz, 7.0 Hz, 3.0 Hz), 1.97 (1H, ddd, *J* = 7.5 Hz, 7.0 Hz, 3.0 Hz), 1.43-1.37 (2H, m), 1.33-1.27 (4H, m), 0.90-0.87 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.3, 136.8, 115.0, 91.5, 88.9, 33.5, 31.3, 28.8, 28.8, 22.5, 14.1; IR (neat): 3079 (w), 2956 (m), 2924 (s), 2856 (m), 1961 (w), 1640 (w), 1459 (m), 1378 (w), 991 (w), 911

(m), 868 (w), 728 (w), 632 (w) cm^{-1}; HRMS-(ESI+) for $C_{11}H_{19}$ [M+H]: calculated: 151.1487, found: 151.1493. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (14.7 mg, 49% yield). R_f = 0.97 (pentane, stain in PMA).

Preparation of *hex-1-en-5-yn-3-ylbenzene*

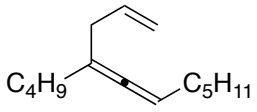
An oven-dried two-dram vial equipped with magnetic stir bar was charged with $Pd_2(dba)_3$ (2.29 mg, 2.50 µmol), *rac*-BINAP (3.11 mg, 5.00 µmol), and THF (0.4 mL) in a dry-box under argon atmosphere. The vial was capped and allowed to stir for five minutes, then cinnamyl acetate (35.2 mg, 0.20 mmol) was added, followed by cesium fluoride (91.4 mg, 0.6 mmol), and allenylboronic acid pinacol ester (39.8 mg, 0.24 mmol). The vial was sealed, removed from the dry-box, and heated to 60 °C and allowed to stir for 14 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (24.0 mg, 77% yield). R_f = 0.28 (pentane, stain in PMA).





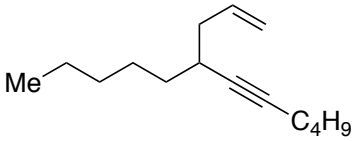
***hex-1-en-5-yn-3-ylbenzene* (Scheme 3, Product 20).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (2H, dddd (app tt), *J* = 7.5 Hz, 7.5 Hz, 1.5 Hz, 1.5 Hz), 7.25-7.22 (3H, m), 6.06 (1H, ddd, *J* = 17.0 Hz, 10.0 Hz, 7.0 Hz), 5.15 (1H, ddd (app td), *J* = 10.0 Hz, 1.5 Hz, 1.5 Hz), 5.12 (1H, ddd, *J* = 17.0 Hz, 1.5 Hz, 1.5 Hz), 3.55 (1H, ddd (app dt), *J* = 7.0 Hz, 7.0 Hz, 7.0 Hz), 2.63 (1H, ddd, *J* = 16.5 Hz, 7.0 Hz, 2.5 Hz), 2.59 (1H, ddd, *J* = 16.5 Hz, 7.0 Hz, 2.5 Hz), 1.97 (1H, dd (app t), *J* = 2.5 Hz, 2.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.5, 140.0, 128.5, 127.6, 126.7, 115.4, 82.5, 69.8, 48.2, 25.1; IR (neat): 3297 (m), 3083 (w), 3063 (w), 3029 (w), 2913 (w), 1638 (w), 1601 (w), 1494 (m), 1453 (w), 1432 (w), 1416 (w), 1029 (w), 918 (m), 755 (m), 699 (s), 639 (s) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{13}$ [M+H]: calculated: 157.1017, found: 157.1018.

***5-allyldodeca-5,6-diene* (Table 1, Entry 9, Product type E).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling with dodec-7-yn-6-yl acetate on a 0.20 mmol scale.



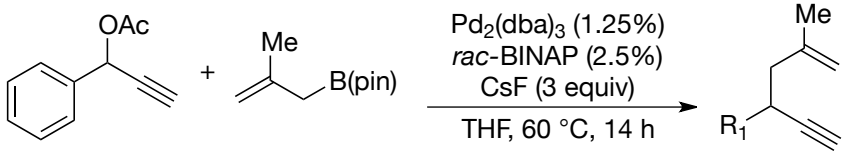
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.82 (1H, dddd (app ddt), *J* = 17.0 Hz, 10.0 Hz, 7.0 Hz, 7.0 Hz), 5.09 (1H, dddd (app tt), *J* = 6.0 Hz, 6.0 Hz, 3.0 Hz, 3.0 Hz), 5.05 (1H, ddd, *J* = 17.0 Hz, 3.5 Hz, 1.5 Hz), 5.00 (1H, dddd (app ddt) *J* = 10.0 Hz, 3.5 Hz, 1.5 Hz, 1.5 Hz), 2.69 (2H, ddd (app dt), *J* = 5.5 Hz, 1.5 Hz, 1.5 Hz), 1.96 (2H, dd, *J* = 8.0 Hz, 6.5 Hz), 1.93 (2H, ddd (app dt), *J* = 7.5 Hz, 3.0 Hz, 3.0 Hz), 1.41-1.29 (10H, m), 0.90 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz), 0.89 (3H, dd (app t), *J* = 7.5 Hz, 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.2, 136.3, 115.3, 102.5, 91.9, 37.8, 32.0, 31.4, 29.8, 29.3, 29.0, 22.5, 22.4, 14.1, 13.9; IR (neat): 2957 (s), 2926 (s), 2872 (s), 2857 (s), 1693 (m), 1465 (m), 1378 (w), 991 (m), 911 (s), 727 (w) cm^{-1}; HRMS-(ESI+) for $C_{15}H_{27}$ [M+H]: calculated: 207.2113, found: 207.2118.

The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (20.5 mg, 50% yield). R_f = 0.93 (pentane, stain in PMA).

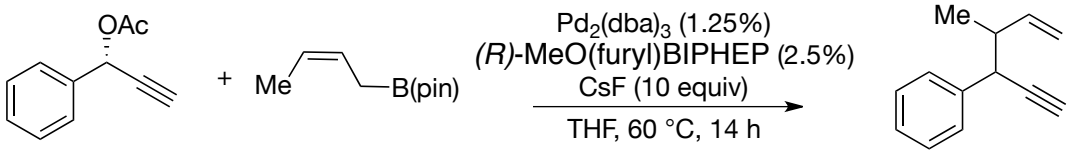


7-allyldodec-5-yne (Table 1, Entry 9, Product type D). The title compound was prepared *via* the representative procedure for allyl-propargyl coupling with dodec-7-yn-6-yl acetate on a 0.20 mmol scale. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.88 (1H, dddd (app ddt), J = 17.5 Hz, 10.5 Hz, 7.5 Hz, 7.5 Hz), 5.06 (1H, dddd (app ddt), J = 17.5 Hz, 2.5 Hz, 1.5 Hz, 1.5 Hz), 5.02 (1H, dddd (app ddt), J = 10.5 Hz, 2.5 Hz, 1.0 Hz, 1.0 Hz), 2.37-2.31 (1H, m), 2.19-2.15 (4H, m), 1.50-1.24 (12H, m), 0.91 (3H, dd (app t), J = 7.5 Hz, 7.5 Hz), 0.89 (3H, dd (app t), J = 7.5 Hz, 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.6, 116.0, 83.1, 81.6, 39.9, 34.8, 31.7, 31.7, 31.3, 26.9, 22.6, 21.9, 18.4, 14.0, 13.6; IR (neat): 2957 (s), 2928 (s), 2858 (s), 1642 (w), 1465 (m), 1378 (w), 1343 (w), 993 (m), 911 (s), 728 (w) cm^{-1}; HRMS-(ESI+) for $C_{25}H_{27}$ [M+H]: calculated: 207.2113, found: 207.2111. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (7.6 mg, 18% yield). R_f = 0.70 (pentane, stain in PMA).

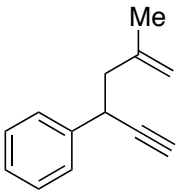
Experimental Procedure for Allyl-Propargyl Coupling with β- and γ-Substituted Allylboron Nucleophiles



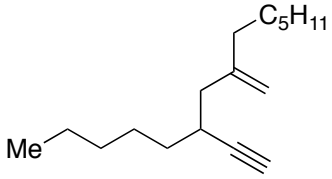
Representative Procedure A: An oven-dried two-dram vial equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (2.28 mg, 2.5 µmol), *racemic*-BINAP (3.11 mg, 5.0 µmol), and THF (0.4 mL) in a dry-box under argon atmosphere. The vial was capped and allowed to stir for five minutes, then 1-phenylprop-2-yn-1-yl acetate (34.8 mg, 0.20 mmol) was added, followed by cesium fluoride (91.4 mg, 0.6 mmol), and methallylboronic acid pinacol ester (43.7 mg, 0.24 mmol). The vial was sealed, removed from the dry-box, and heated to 60 °C while allowing to stir for 14 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (24.6 mg, 83% yield).



Representative Procedure B: An oven-dried two-dram vial equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (2.28 mg, 2.5 µmol), *(R)*-MeO(furyl)BIPHEP (2.71 mg, 5.0 µmol), and THF (0.4 mL) in a dry-box under argon atmosphere. The vial was capped and allowed to stir for five minutes, then (R)-1-phenylprop-2-yn-1-yl acetate (34.8 mg, 0.20 mmol) was added, followed by cesium fluoride (303.8 mg, 2.0 mmol), and *cis*-crotylboronic acid pinacol ester (43.7 mg, 0.24 mmol). The vial was sealed, removed from the dry-box, and heated to 60 °C while allowing to stir for 14 h. After this time, the reaction mixture was diluted with diethyl ether, filtered through a plug of silica gel and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (28.9 mg, 85% yield of a regioisomeric mixture (*vide infra*)).

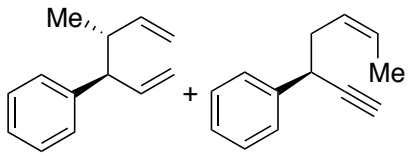


(5-methylhex-5-en-1-yn-3-yl)benzene (Table 4, Product 21). The title compound was prepared *via* representative procedure **A** for allyl-propargyl coupling with β- and γ-substituted allylboron nucleophiles. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.36 (2H, m), 7.35-7.31 (2H, m), 7.25 (1H, tt, *J* = 6.5 Hz, 1.5 Hz), 4.83 (1H, ddd (app dt), *J* = 3.0 Hz, 1.5 Hz, 1.5 Hz), 4.77 (1H, ddd (app dt), *J* = 3.0 Hz, 2.0 Hz, 2.0 Hz), 3.81 (1H, ddd, *J* = 9.0 Hz, 6.0 Hz, 2.5 Hz), 2.51 (1H, ddd, *J* = 13.5 Hz, 9.0 Hz, 1.0 Hz), 2.43 (1H, ddd, *J* = 14.0 Hz, 6.0 Hz, 1.5 Hz), 2.28 (1H, d, *J* = 2.5 Hz), 1.77 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.4, 141.3, 128.5, 128.5, 127.4, 127.4, 126.9, 113.0, 85.7, 71.2, 46.6, 36.4, 22.4; IR (neat): 3298 (m), 3076 (m), 3028 (m), 2969 (m), 2938 (w), 1649 (w), 1493 (m), 1452 (m), 1275 (w), 893 (m), 752 (s), 697 (s), 638 (s), 560 (s) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{15}$ [M+H]: calculated: 171.1174, found: 171.1179. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (24.6 mg, 83% yield). R_f = 0.41 (pentane, stain in PMA).



6-ethynyl-8-methylenetetradecane (Table 4, Product 22). The title compound was prepared *via* representative procedure **A** for allyl-propargyl coupling with β- and γ-substituted allylboron nucleophiles with oct-1-yn-3-yl acetate and 4,4,5,5-tetramethyl-2-(2-methyleneoctyl)-1,3,2-dioxaborolane (60.5 mg, 0.24 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.81 (1H, dd (app t), *J* = 1.0 Hz, 1.0 Hz), 4.80 (1H, dd (app t), *J* = 1.0 Hz, 1.0 Hz), 2.50 (1H, ddddd (app dtt), *J* = 8.0 Hz, 8.0 Hz, 6.5 Hz, 6.5 Hz, 2.5 Hz), 2.22 (1H, ddd, *J* = 14.0 Hz, 8.0 Hz, 1.0 Hz), 2.15 (1H, ddd, *J* = 14.0 Hz, 6.5 Hz, 0.5 Hz), 2.05 (1H, d, *J* = 2.5 Hz), 2.02 (2H, dd (app t), *J* = 7.5 Hz, 7.5 Hz), 1.58-1.36 (16H, m), 0.90 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz), 0.89 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.1, 111.0, 87.9, 69.1, 41.7, 35.8, 34.6, 31.8, 31.7, 29.9, 29.1, 27.7, 26.8, 22.6, 22.6, 14.1, 14.0; IR (neat): 3312 (w), 2956 (m), 2927 (s),

2857 (s), 1645 (w), 1459 (m), 893 (m), 627 (s) cm^{-1}; HRMS-(ESI+) for $C_{17}H_{31}$ [M+H]: calculated: 235.2426, found: 235.2419. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (39.8 mg, 85% yield). R_f = 0.87 (pentane, stain in PMA).



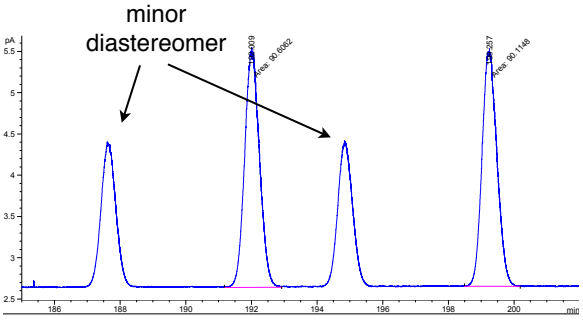
23 H **23 J**

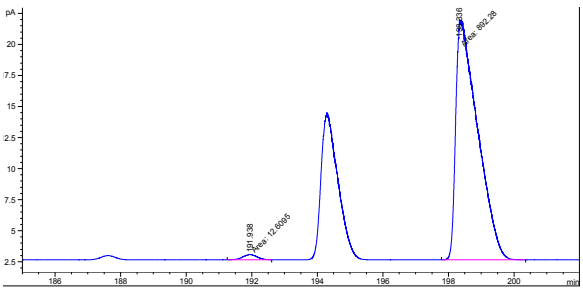
***((3S,4R)*-4-methylhex-5-en-1-yn-3-yl)benzene (Table 4, Product 23 H and J).** The title compound was prepared *via* representative procedure **B** for allyl-propargyl coupling with β- and γ-substituted allylboron nucleophiles. (Characterization for **23 H**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.30 (4H, m), 7.26-7.23 (1H, m), 5.83 (1H, ddd, *J* = 17.5 Hz, 10.0 Hz, 7.5 Hz), 5.00 (1H, dddd (app ddt), *J* = 10.0 Hz, 1.5 Hz, 0.5 Hz, 0.5 Hz), 4.91 (1H, ddd (app dt), *J* = 17.5 Hz, 1.5 Hz, 1.5 Hz), 3.62 (1H, dd, *J* = 6.0 Hz, 2.5 Hz), 2.55 (1H, dqd, *J* = 7.5 Hz, 7.0 Hz, 6.0 Hz), 2.30 (1H, d, *J* = 2.5 Hz), 1.10 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.1, 128.2, 128.2, 128.2, 128.2, 126.8, 126.8, 115.1, 84.2, 72.1, 44.1, 43.9, 18.2; IR (neat): 3302 (m), 3028 (w), 2967 (m), 2928 (m), 2823 (w), 1640 (w), 1493 (m), 1452 (m), 1031 (m), 996 (m), 755 (m), 698 (s), 635 (s) cm^{-1}; HRMS-(ESI+) for $C_{13}H_{15}$ [M +H]: calculated:171.1174, found: 171.1171. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (29.8 mg, 85% yield) as a 3.6:1 mixture of **H:J**. R_f = 0.47 (pentane, stain in PMA).

Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound prepared from enantioenriched acetate and *(R)*-MeO(furyl)BIPHEP as compared to product prepared with racemic acetate and *racemic*-BINAP. The absolute stereochemistry was assigned as shown below.

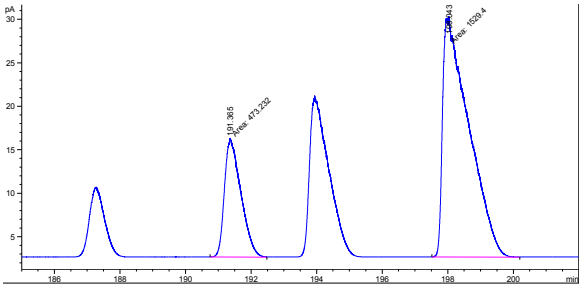
Chiral GLC (β-dex, Supelco, 40 °C for 10 min, ramp 0.25 °C/min to 100 °C for 60 min, 20 psi) - analysis of title compound.





Racemic Sample *Enantioenriched Sample*

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	191.938	MM	0.4955	12.60948	4.24102e-1	1.39348
2	198.336	MM	0.7686	892.28021	19.34984	98.60652
Totals :				904.88969	19.77394	

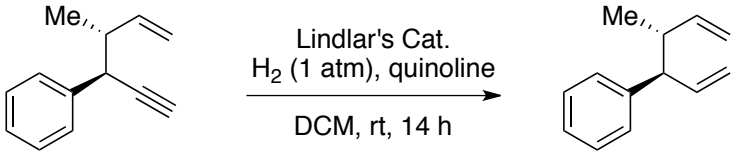


co-injection of racemic and enantioenriched samples

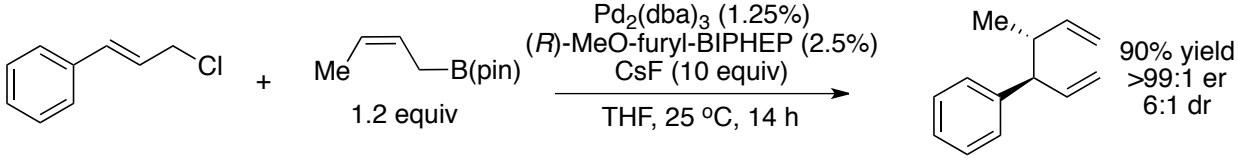
Proof of Structure and Stereochemistry:

The title compound was subjected to selective hydrogenation of the alkyne utilizing Lindlar's catalyst to afford the previously reported 1,5-diene as depicted below. Spectral data is in accordance with the literature.[10] In order to determine the absolute stereochemistry, the resulting diene was compared by GLC analysis to authentic *((3R,4R)*-4-methylhexa-1,5-dien-3-yl)benzene, prepared by asymmetric allyl-allyl cross coupling as depicted below.[10]

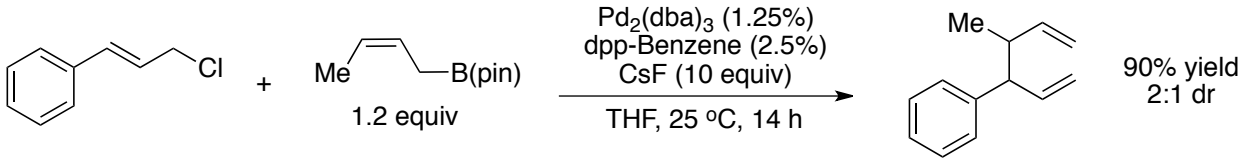
Hydrogenation of Title Compound



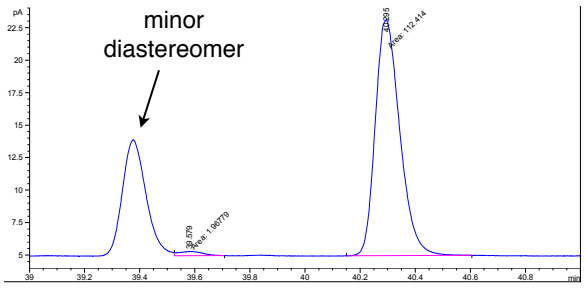
Enantioselective Allyl-Allyl Cross-Coupling



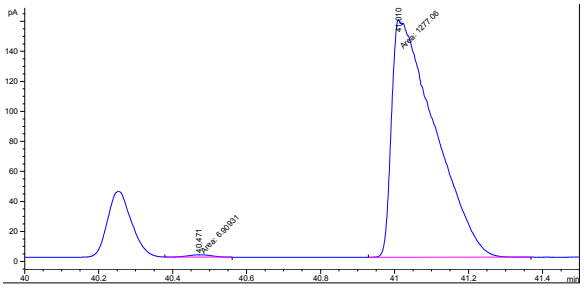
Preparation of Racemic Sample



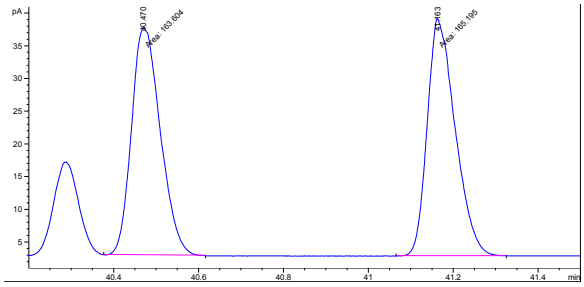
Chiral GLC (CD-BDM, Supelco, 50 °C for 20 min, ramp 2.5 °C/min to 120 °C for 60 min, 25 psi)-



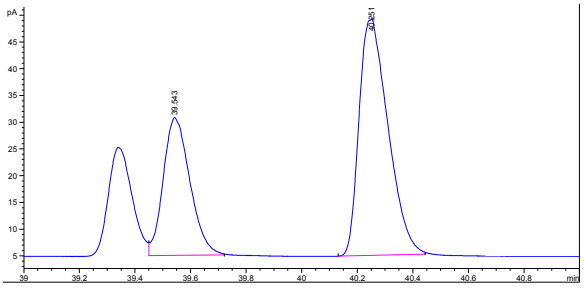
Diene from Lindlar reduction



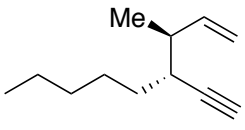
Enantioenriched ((3R,4R)-4-methylhexa-1,5 dien-3-yl)benzene from allyl-allyl coupling



Racemic 4-methylhexa-1,5-dien-3-yl)benzene from allyl-allyl coupling

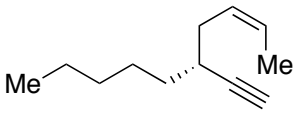


co-injection of racemic and reduced samples

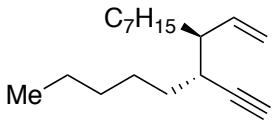


***(3S,4R)*-4-ethynyl-3-methylnon-1-ene (Table 4, Product 24 H).** The title compound was prepared *via* representative procedure **B** for allyl-propargyl coupling with β- and γ-substituted allylboron nucleophiles with *(R)*-oct-1-yn-3-yl acetate utilizing (5 mol%) *(S,S)*-QuinoxP* as the ligand and (2.5mol %) $Pd_2(dba)_3$. ^1H NMR (500 MHz, $CDCl_3$): δ 5.85 (1H, ddd, *J* = 18.5 Hz, 11.5 Hz, 8.0 Hz), 5.04 (1H, d, *J* = 1.0 Hz), 5.01 (1H, ddd, *J* = 6.5 Hz, 1.5 Hz, 1.0 Hz), 2.32 (1H, dddd (app ddt), *J* = 9.0 Hz, 5.0 Hz, 5.0 Hz, 2.5 Hz), 2.29-2.21 (1H, m), 2.06 (1H, d, *J* = 2.5 Hz), 1.23-1.54 (8H, m), 1.12 (3H, d, *J* = 7.0 Hz), 0.89 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.8, 114.7, 86.0, 70.2, 41.2, 37.4, 32.6,

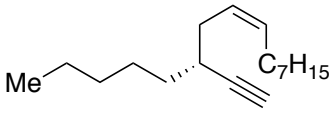
31.6, 27.2, 22.6, 18.5, 14.0; IR (neat): 3311 (w), 2958 (s), 2928 (s), 2859 (s), 1458 (m), 1420 (w), 997 (w), 967 (m), 629 (m) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{21}$ [M+H]: calculated: 165.1643, found: 161.1642. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (13.0 mg, 40% yield). R_f = 0.74 (pentane, stain in PMA). Shown stereochemistry assigned by analogy to Product 23.



***(R,Z)*-5-ethynyldec-2-ene (Table 4, Product 24 J).** The title compound was isolated as a byproduct from allyl-propargyl coupling to generate *(3S,4R)*-4-ethynyl-3-methylnon-1-ene as described above. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.7 (1H, dqdd (app dqt), *J* = 12.5 Hz, 6.5 Hz, 1.5 Hz, 1.5 Hz), 5.49 (1H, dddddd (app dtdt), *J* = 12.5 Hz, 6.5 Hz, 6.5 Hz, 1.5 Hz, 1.5 Hz, 1.5 Hz), 2.40-2.34 (1H, m), 2.24 (2H, dddd (app tt), *J* = 6.5 Hz, 6.5 Hz, 1.5 Hz, 1.5 Hz), 2.05 (1H, d, *J* = 2.5 Hz), 1.63 (3H, dddd (app ddt), *J* = 6.5 Hz, 2.0 Hz, 1.5 Hz, 1.5 Hz), 1.53-1.25 (8H, m), 0.89 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 127.6, 125.7, 87.9, 69.0, 34.3, 32.2, 31.7, 31.7, 26.9, 22.6, 14.0, 13.0; IR (neat): 3311 (m), 2958 (m), 2928 (s), 2859 (s), 1458 (m), 914 (m), 629 (m) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{21}$ [M+H]: calculated: 165.1643, found: 165.1649. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (13.0 mg, 40% yield). R_f = 0.86 (pentane, stain in PMA). Shown stereochemistry assigned by analogy to Product 23.

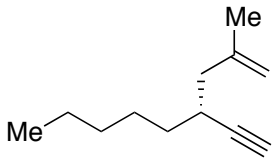


***(6R,7S)*-6-ethynyl-7-vinyltetradecane (Table 4, Product 25 H).** The title compound was prepared *via* representative procedure **B** for allyl-propargyl coupling with β- and γ-substituted allylboron nucleophiles with *(R)*-oct-1-yn-3-yl acetate and *(Z)*-2-(dec-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (63.9 mg, 0.24 mmol) utilizing (5 mol %) *(S,S)*-QuinoxP* as the ligand and (2.5 mol%) $Pd_2(dba)_3$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.73 (1H, ddd, *J* = 17.5 Hz, 10.5 Hz, 9.5 Hz), 5.06 (1H, dd, *J* = 10.5 Hz, 2.0 Hz), 4.99 (1H, ddd, *J* = 17.0 Hz, 2.0 Hz, 1.0 Hz), 2.41-2.36 (1H, m), 2.04 (1H, d, *J* = 2.5 Hz), 2.00 (1H, dddd (app dq), *J* = 7.0 Hz, 7.0 Hz, 7.0 Hz, 4.0 Hz), 1.49-1.45 (4H, m), 1.37-1.24 (16H, m), 0.89 (3H, dd (app t), *J* = 7.0 Hz, 7.0 Hz), 0.88 (3H, dd (app t), *J* = 7.5 Hz, 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.5, 116.0, 85.9, 70.2, 47.4, 35.9, 33.3, 33.3, 31.9, 31.6, 29.6, 29.3, 27.3, 27.2, 22.7, 22.6, 14.1, 14.0; IR (neat): 3312 (m), 3076 (w), 2957 (s), 2925 (s), 2856 (s), 1640 (w), 1466 (m), 1421 (w), 1378 (w), 1240 (w), 998 (m), 913 (s), 628 (s) cm^{-1}; HRMS-(ESI+) for $C_{18}H_{33}$ [M+H]: calculated: 249.2582, found: 249.2578. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (12.3 mg, 25% yield). R_f = 0.93 (pentane, stain in PMA). Shown stereochemistry assigned by analogy to Product 23.

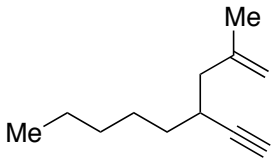


***(R,Z)*-6-ethynylhexadec-8-ene (Table 4, Product 25 J).** The title compound was isolated as a byproduct from allyl-propargyl coupling to generate *(6R,7S)*-6-ethynyl-7-vinyltetradecane as described above. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.51-5.42 (2H, m),

2.41-2.33 (1H, m), 2.23 (2H, dd (app t), J = 6.5 Hz, 6.5 Hz), 2.05 (1H, d, J = 2.5 Hz), 2.05 (2H, ddd (app dt), J = 6.5 Hz, 6.0 Hz, 6.0 Hz), 1.50-1.24 (18H, m), 0.89 (3H, dd (app t), J = 7.0 Hz, 7.0 Hz), 0.88 (3H, dd (app t), J = 7.0 Hz, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.9, 126.5, 69.0, 34.3, 32.5, 31.9, 31.8, 31.7, 31.6, 29.7, 29.3, 29.2, 27.4, 26.9, 22.7, 22.6, 14.1, 14.0; IR (neat): 3312 (m), 2957 (m), 2926 (s), 2856 (m), 1465 (m), 628 (m) cm^{-1}; HRMS-(ESI+) for $C_{18}H_{33}$ [M+H]: calculated: 249.2582, found: 249.2573. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (7.6 mg, 15% yield). R_f = 0.84 (pentane, stain in PMA). Shown stereochemistry assigned by analogy to Product 23.



***(R)-4-ethynyl-2-methylnon-1-ene* (Scheme 5, Product 26).** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling with *(R)*-oct-1-yn-3-yl acetate, utilizing methallylBpin (84.1 mg, 0.60 mmol) as the nucleophile. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.82 (1H, dd, J = 2.0 Hz, 0.5 Hz), 4.70 (1H, dd, J = 2.0 Hz, 1.0 Hz), 2.54-2.48 (1H, m), 2.22 (1H, ddd, J = 14 Hz, 8.5 Hz, 0.5 Hz), 2.16 (1H, ddd, J = 14 Hz, 6.5 Hz, 0.5 Hz), 2.05 (1H, d, J = 2.5 Hz), 1.74 (3H, dd, J = 1.0 Hz, 1.0 Hz), 1.56-1.24 (8H, m), 0.90 (3H, dd (app t), J = 7.0 Hz, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 112.3, 87.8, 69.2, 43.5, 34.5, 31.7, 29.8, 26.8, 22.6, 22.3, 14.0; IR (neat): 3311 (w), 2957 (m), 2930 (s), 2873 (m), 2856 (m), 1455 (m), 1377 (w), 1264 (w), 1068 (w), 891 (m), 722 (m), 699 (m), 631 (m), 531 (w) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{21}$ [M+H]: calculated: 165.1643, found: 165.1648. $[\alpha]^{22}_D$ = 31.376 (c = 1.30, $CHCl_3$). The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (72.4 mg, 85% yield). R_f = 0.61 (pentane, stain in PMA).

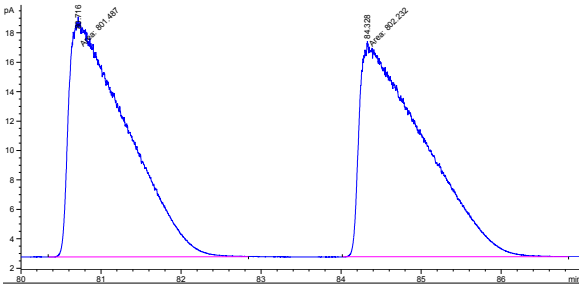


***4-ethynyl-2-methylnon-1-ene*.** The title compound was prepared *via* the representative procedure for allyl-propargyl coupling with oct-1-yn-3-yl acetate on a 0.20 mmol scale. The crude reaction mixture was purified on silica gel (pentane) to afford a clear, colorless oil (29.9 mg, 91% yield). R_f = 0.61 (pentane, stain in PMA).

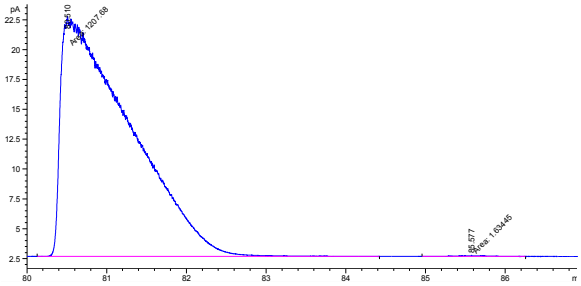
Analysis of Stereochemistry:

Optical purity was determined by GLC analysis of the title compound prepared from enantioenriched acetate as compared to product prepared with racemic material. The absolute stereochemistry was assigned by analogy to products **2** (*(S)*-hex-5-en-1-yn-3-ylbenzene) and **3** (*(R)*-hex-5-en-1-yn-3-ylcyclohexane), Table 2.

Chiral GLC (CD-BDM, Supelco, 40 °C for 30 min, ramp 0.25 °C/min to 100 °C for 10 min, 20 psi) - analysis of title compound.

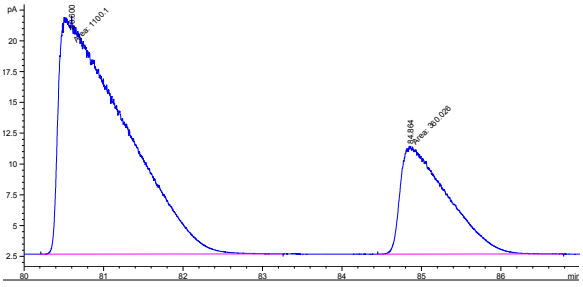


Racemic Sample



Enantioenriched Sample

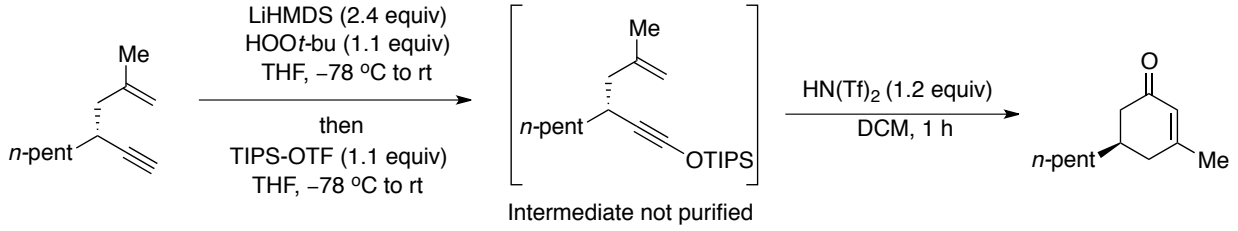
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	80.510	MM	1.0009	1207.67542	20.10914	99.86484
2	85.577	MM	0.2862	1.63445	9.51727e-2	0.13516

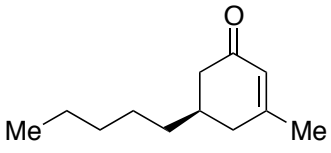


co-injection of racemic and enantioenriched samples

Preparation of *(R)-3-methyl-5-pentylcyclohex-2-enone*

The title compound was prepared *via* the two step literature procedure with slight modification as shown below.[12] The intermediate siloxy alkyne was carried on crude to the second step after workup and was not purified by bulb to bulb distillation as reported in the literature. The crude reaction mixture was purified on silica gel (5:1 pentane:diethyl ether) to afford a clear, colorless oil (41.9 mg, 76% yield). R_f = 0.38 (5:1 pentane:diethyl ether, stain in PMA).





(R)-3-methyl-5-pentylcyclohex-2-enone **(Scheme 4, Product 27).**

Spectral data is in accordance with the literature.[13]

$[\alpha]^{22}_{D}$ = –69.082 *(c* = 1.54, $CHCl_3$).

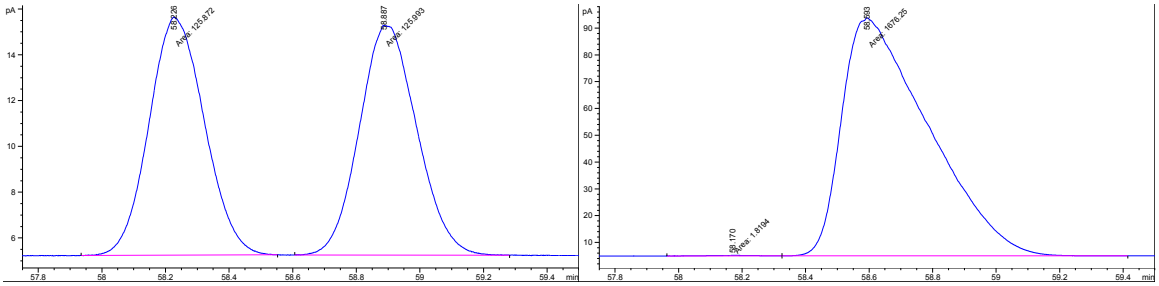
[12] a) Shubinets, V.; Schramm, M.; Kozmin, S. *Org. Syn.* **2010**, *87*, 253. b) Zhang, L.; Kozmin, S. *J. Am. Chem. Soc.* **2004***, 126,* 10204.

[13] Zhou, J.; Wakchaure, V.; Kraft, B., List, B. *Angew. Chem. Int. Ed.* **2008**, *47,* 7656.

Analysis of Stereochemistry:

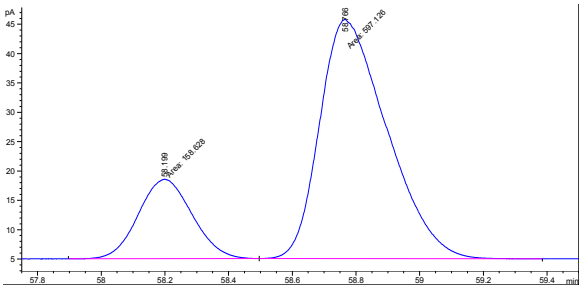
Optical purity was determined by GLC analysis of the title compound prepared from *(R)*-4-ethynyl-2-methylnon-1-ene as compared to product prepared with racemic material. In order to determine the absolute stereochemistry, the optical rotation of the product ($[\alpha]^{20}_D$ = –69.082 (*c* = 1.54, $CHCl_3$) was compared to the rotation of authentic *(R)*-3-methyl-5-pentylcyclohex-2-enone ($[\alpha]^{20}_D$ = –33.59 (*c* = 1.89, $CHCl_3$)) as previously reported in the literature.[14]

Chiral GLC (β-dex, Supelco, 100 °C for 10 min, ramp 1 °C/min to 140 °C for 120 min, 20 psi)--analysis of title compound.



Racemic Sample *Enantioenriched Sample*

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	58.170	MM	0.1532	1.81940	1.97911e-1	0.10842
2	58.593	MM	0.3146	1676.24976	88.79646	99.89158



co-injection of racemic and enantioenriched samples

[14] Buzas, A.; Gagosz, F. *J. Am. Chem. Soc.* **2006**, *128*, 12614.

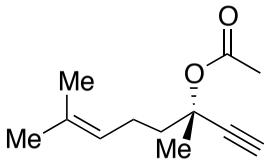


Table 2
Compound 7

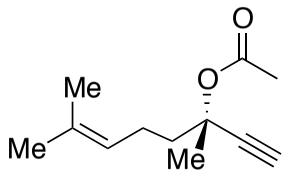
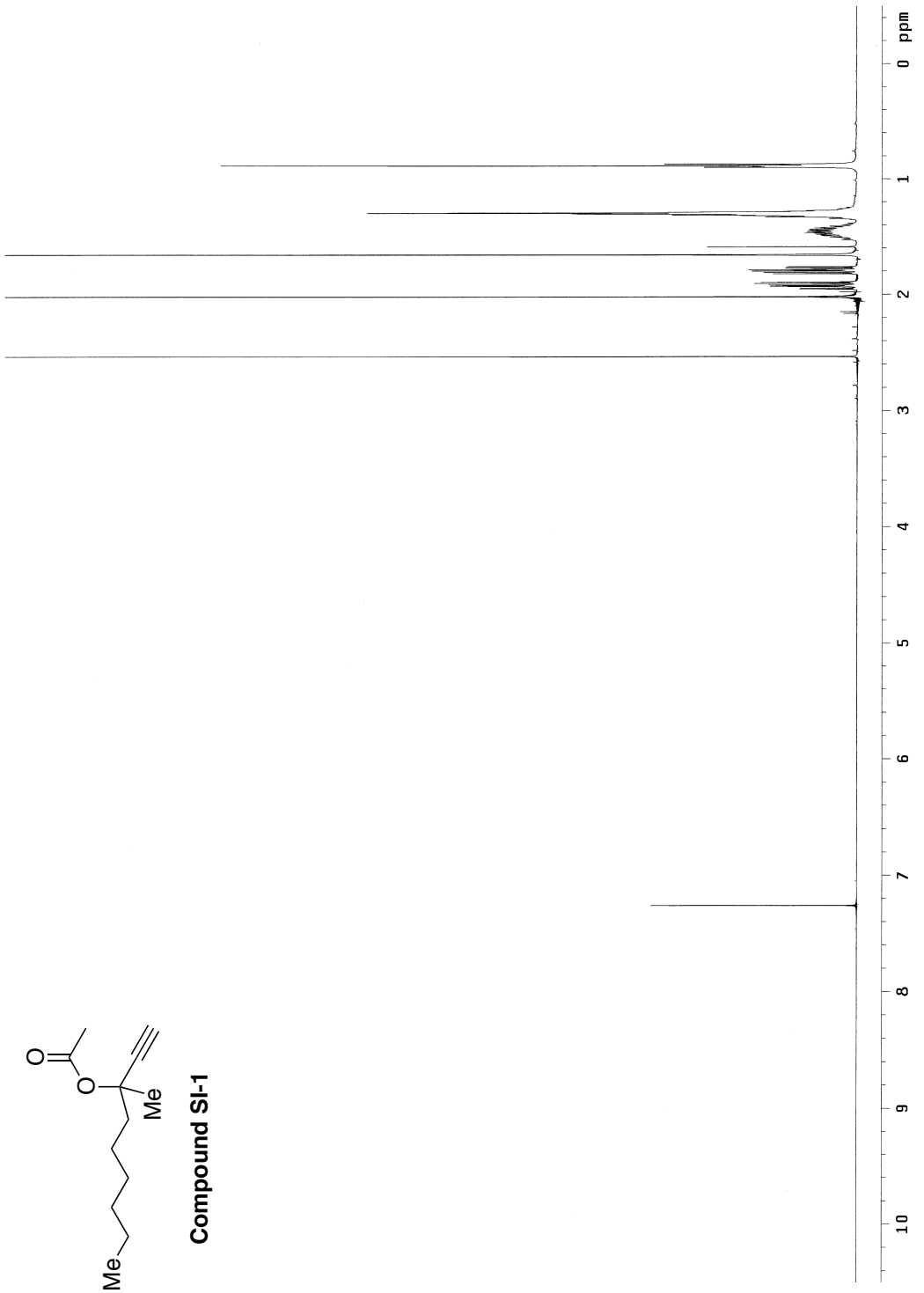
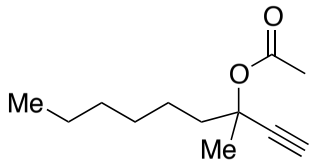


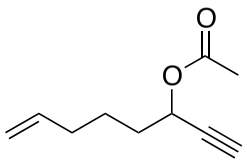
Table 2
Compound 7



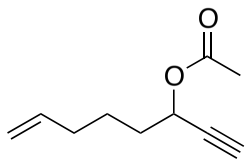
Compound SI-1



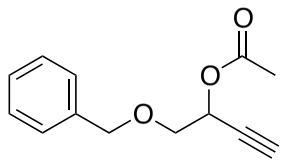
Compound SI-1



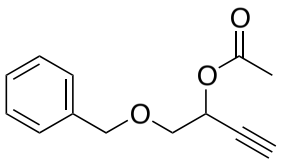
Compound SI-2



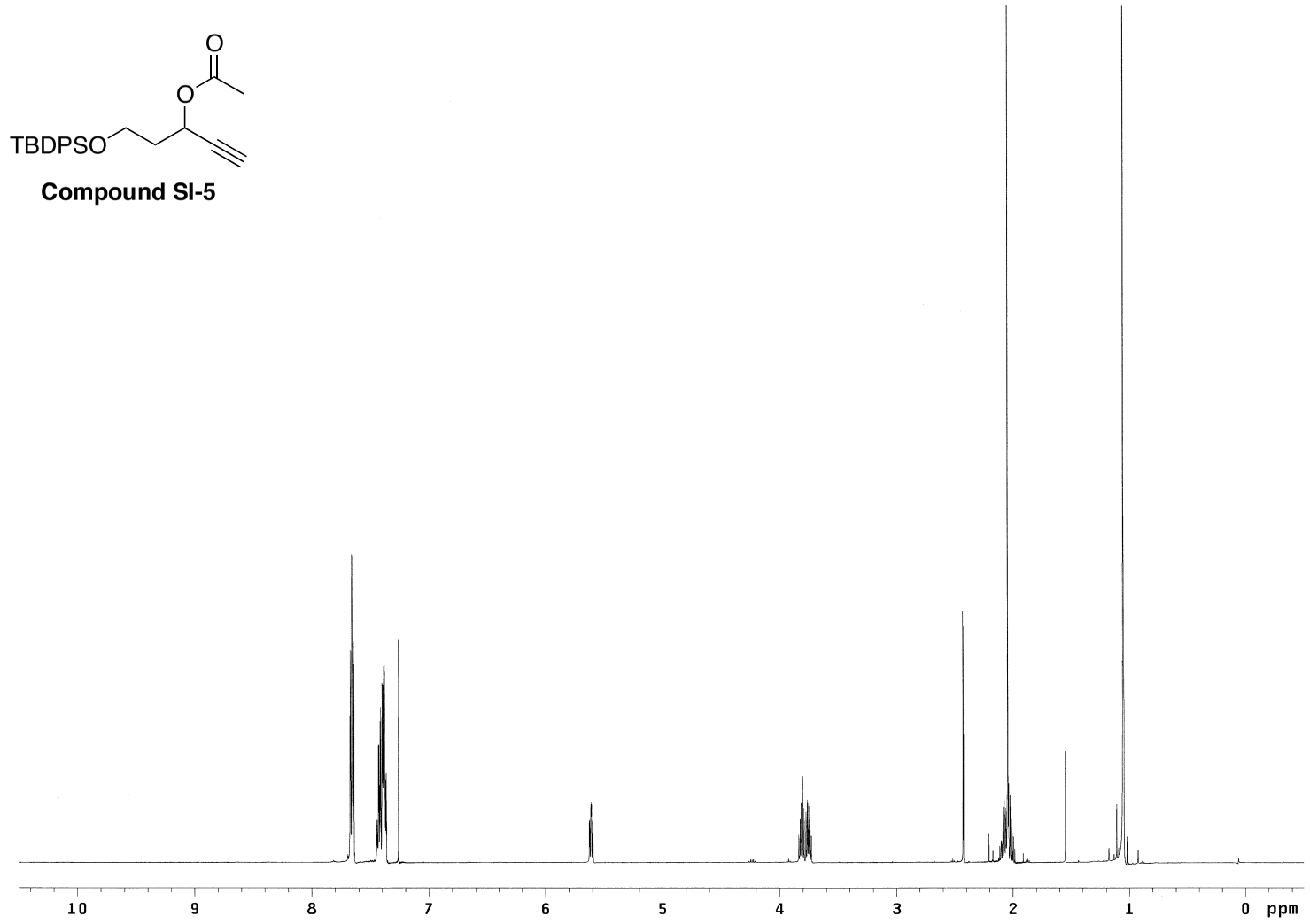
Compound SI-2



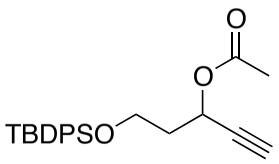
Compound SI-3



Compound SI-3



Compound SI-5



Compound SI-5

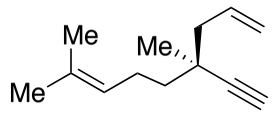


Table 2
Product 8

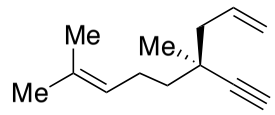
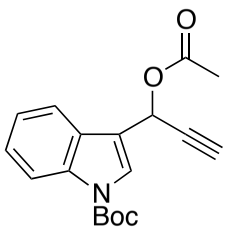


Table 2
Product 8



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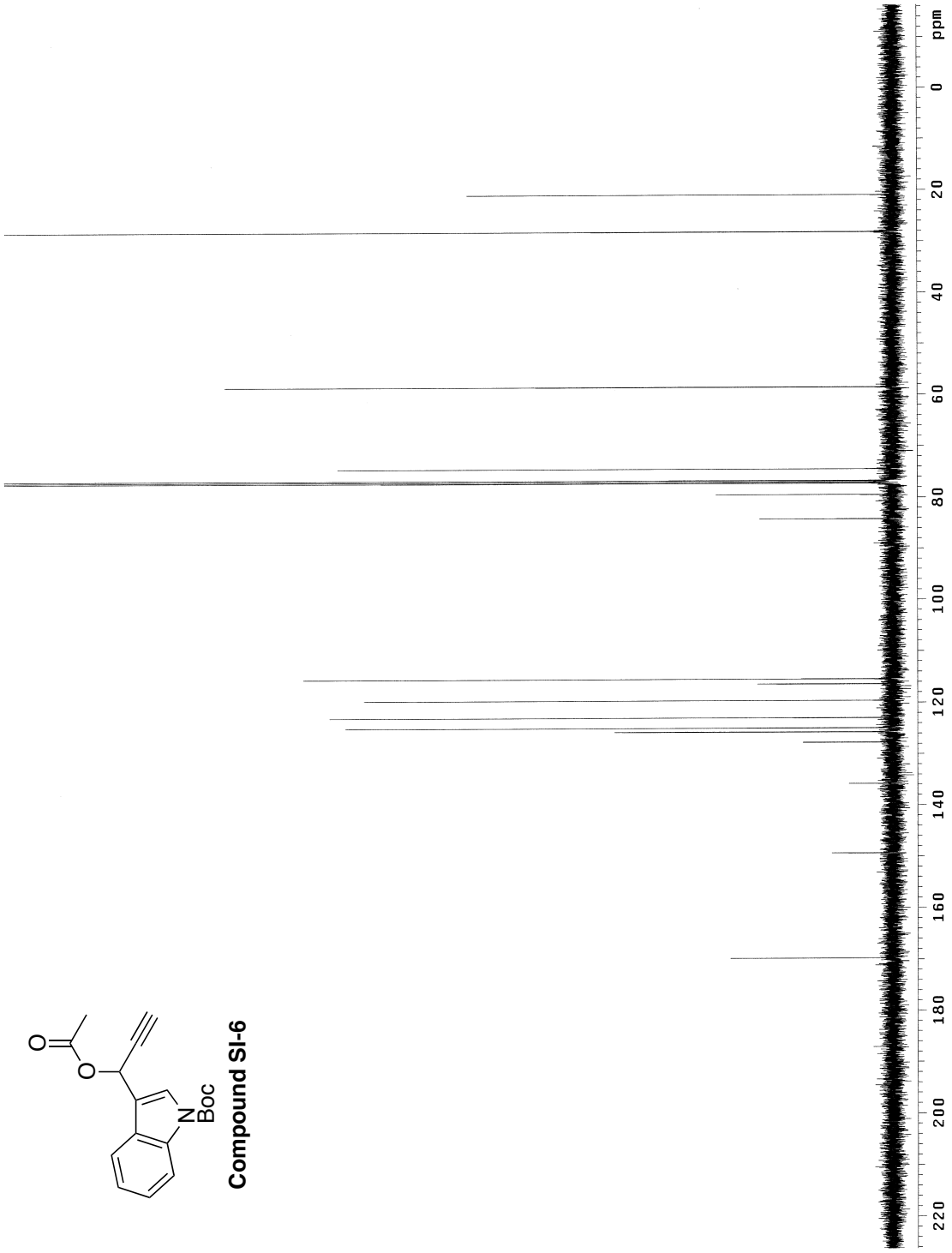
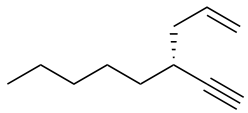


Compound SI-6



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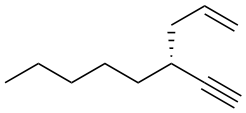

Table 2
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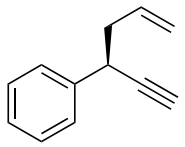
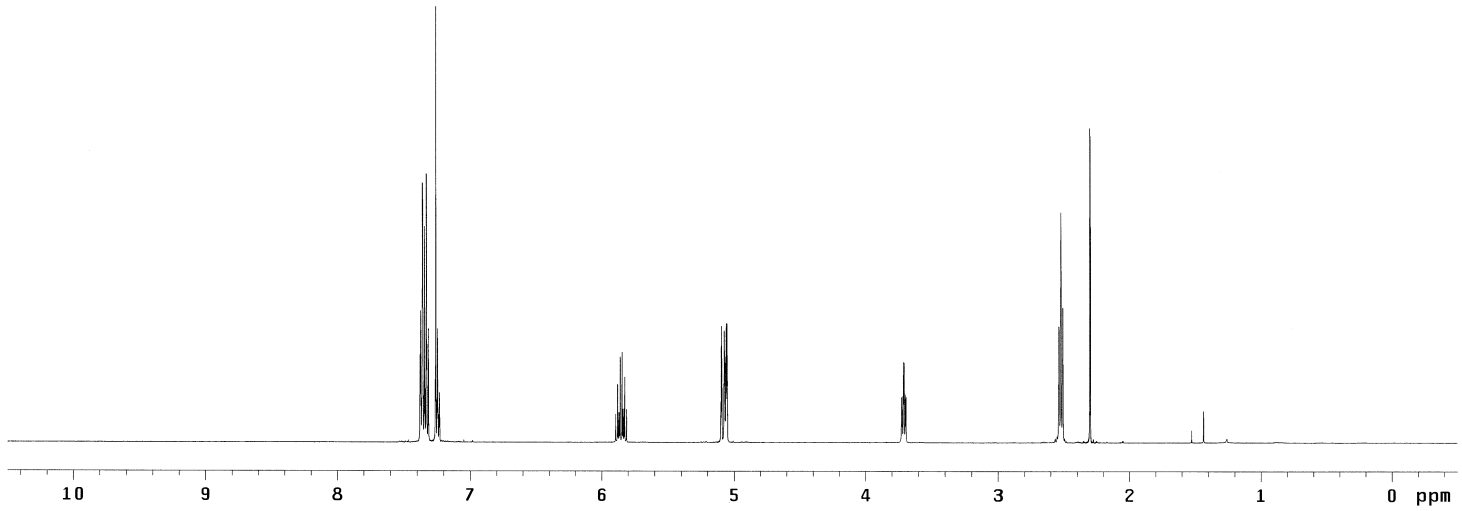


Table 2
Product 4



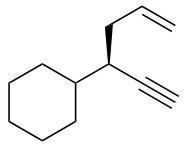


Table 2
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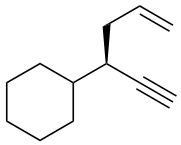
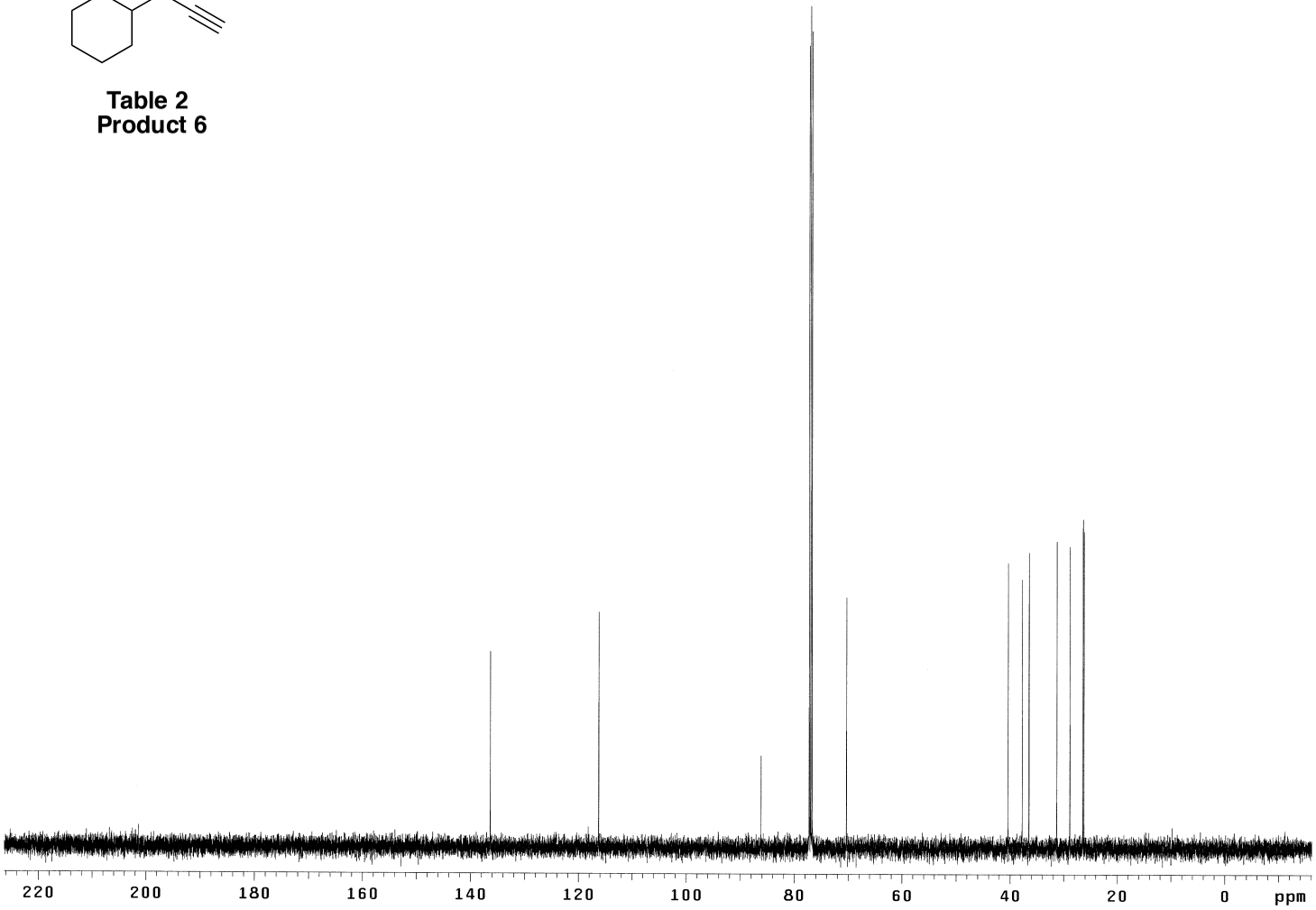


Table 2
Product 6



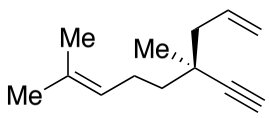


Table 2
Product 8

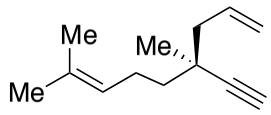
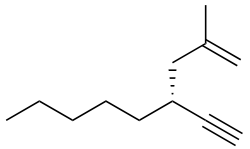
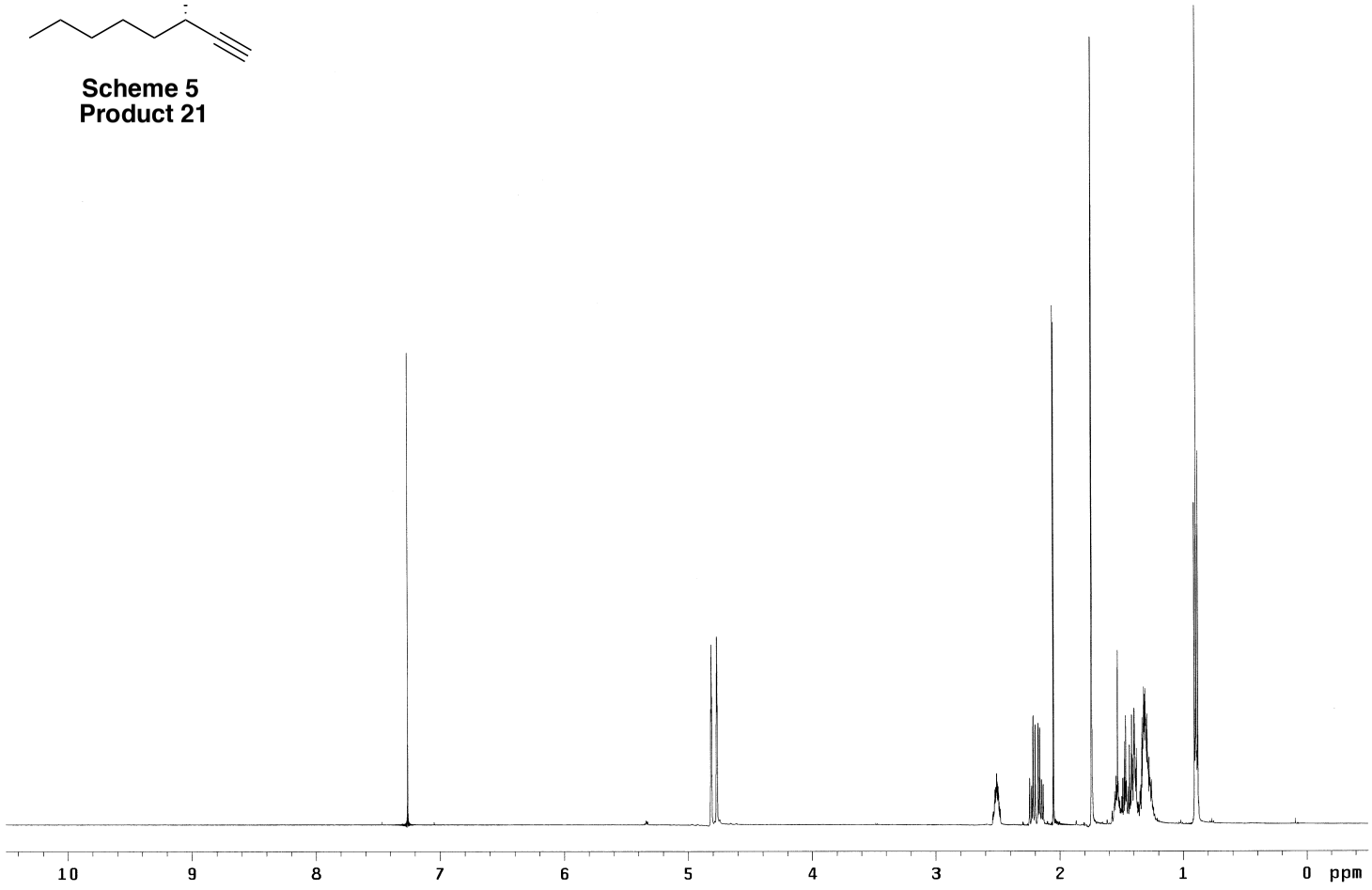
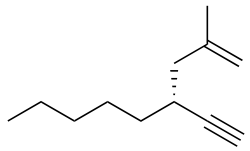


Table 2
Product 8

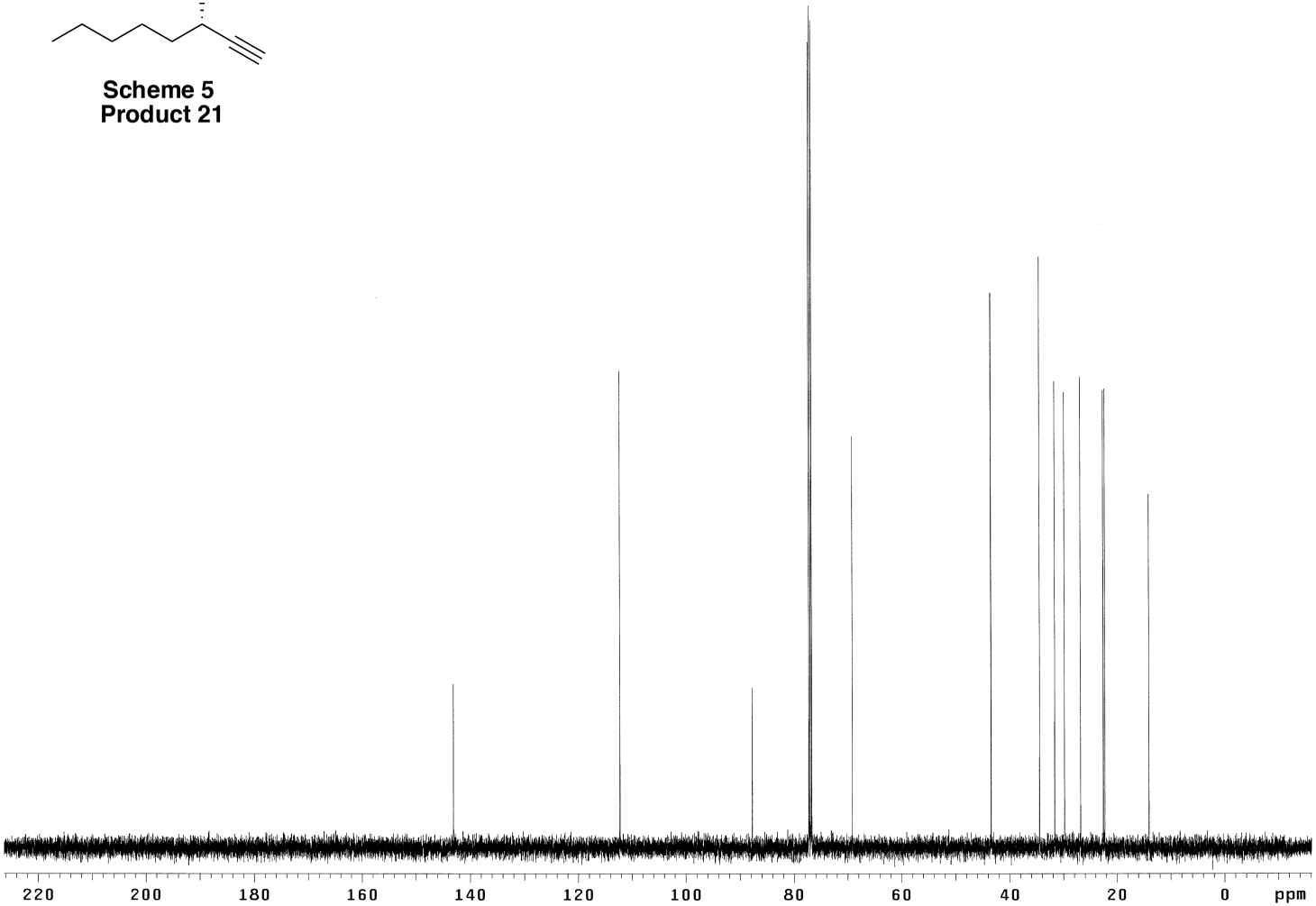


Scheme 5
Product 21





Scheme 5
Product 21



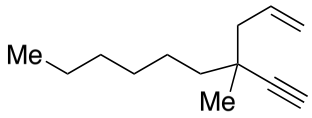


Table 3
Product 9

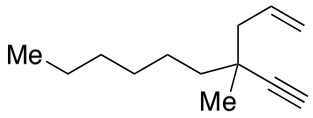


Table 3
Product 9

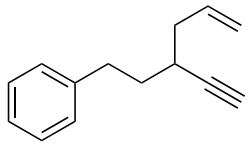
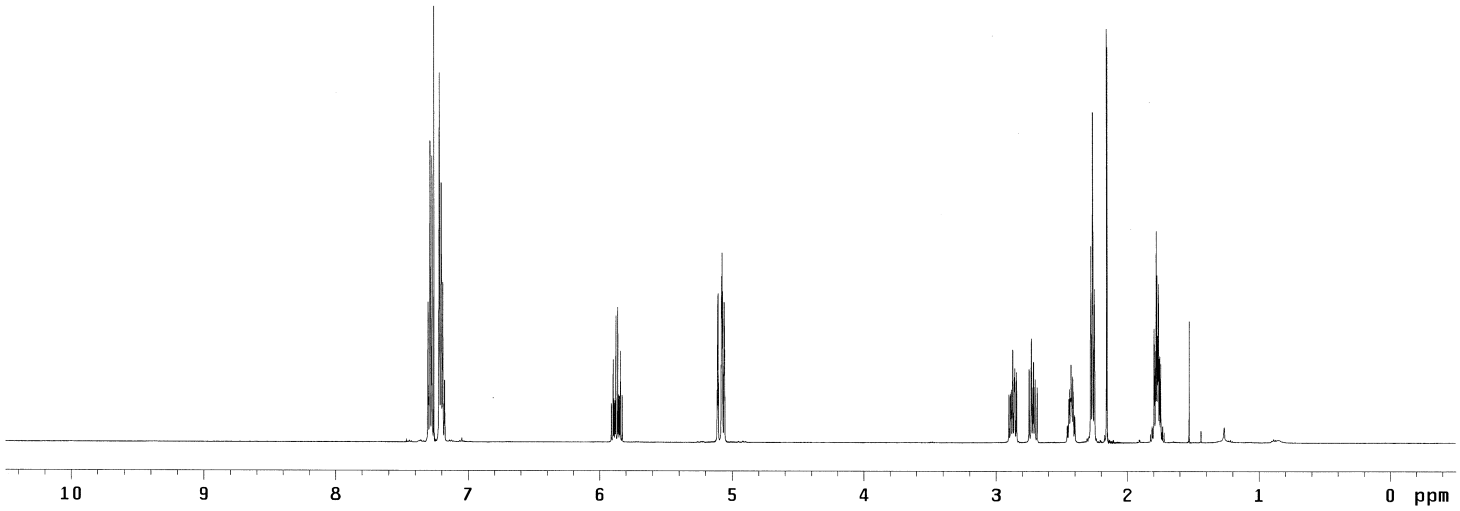


Table 3
Product 10



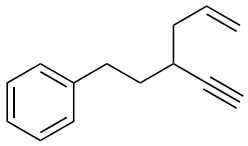


Table 3
Product 10

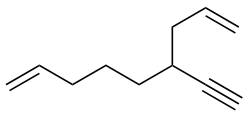
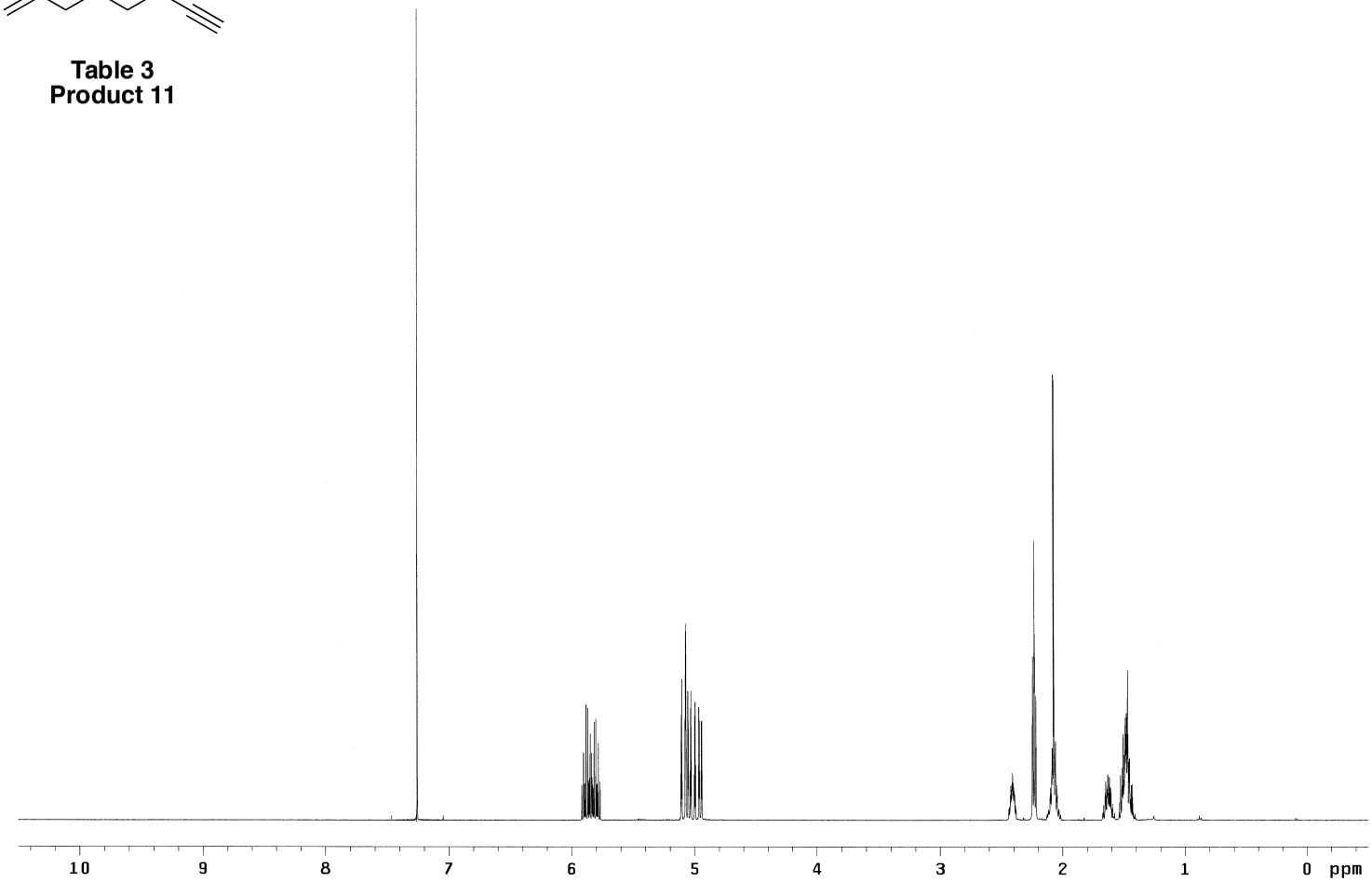


Table 3
Product 11



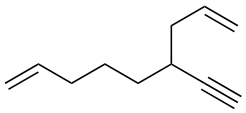
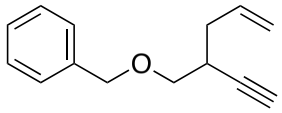


Table 3
Product 11



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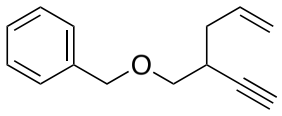
Product 12



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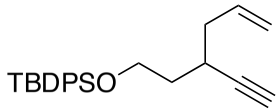
Product 12



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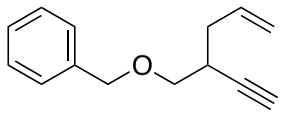

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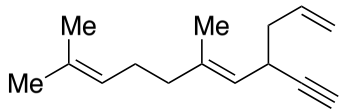
Product 12



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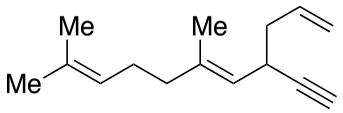

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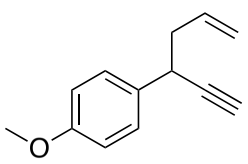

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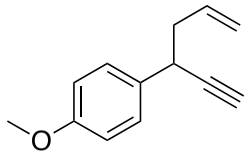

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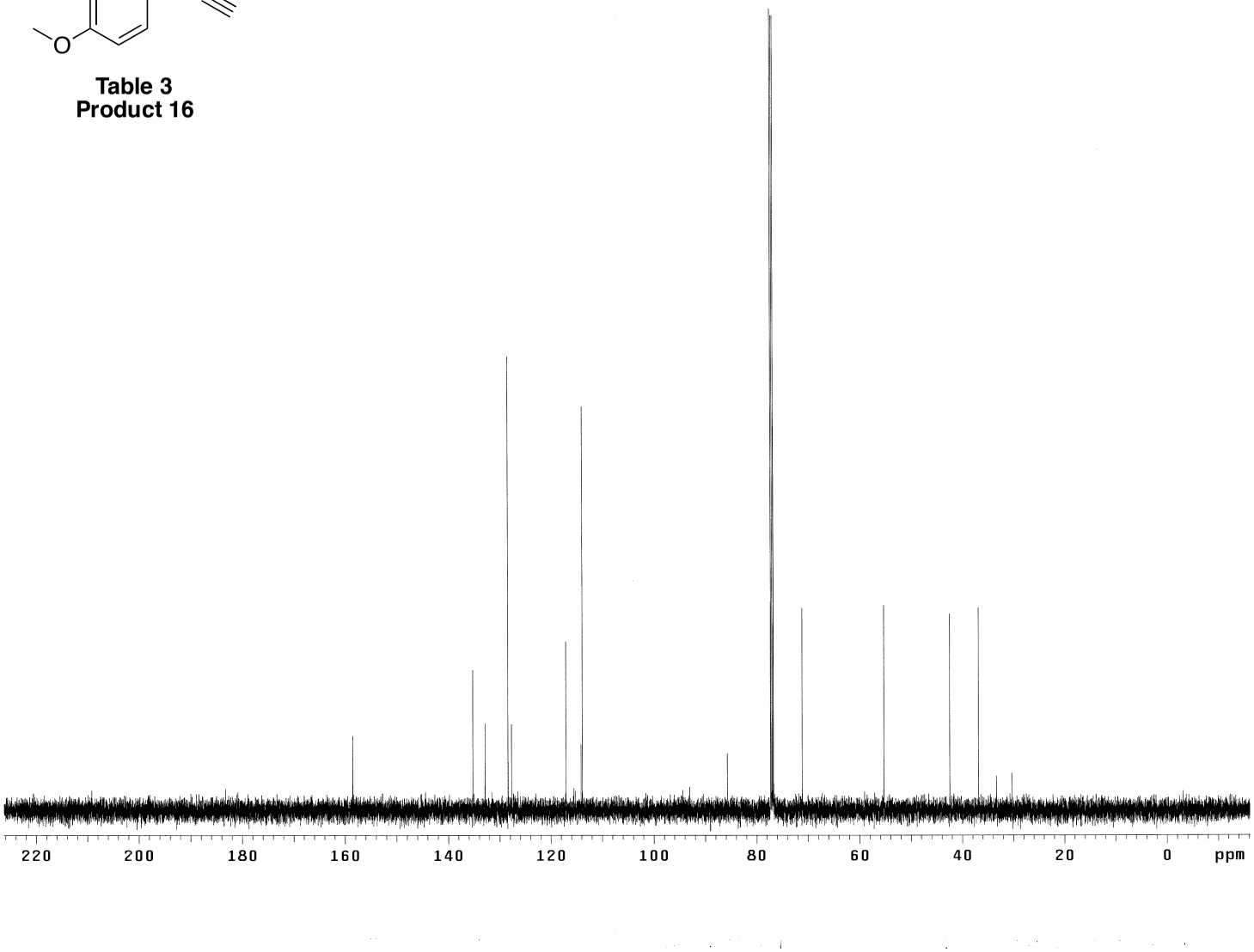

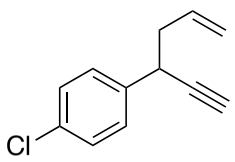

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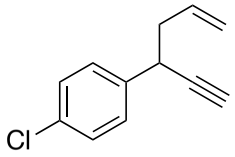

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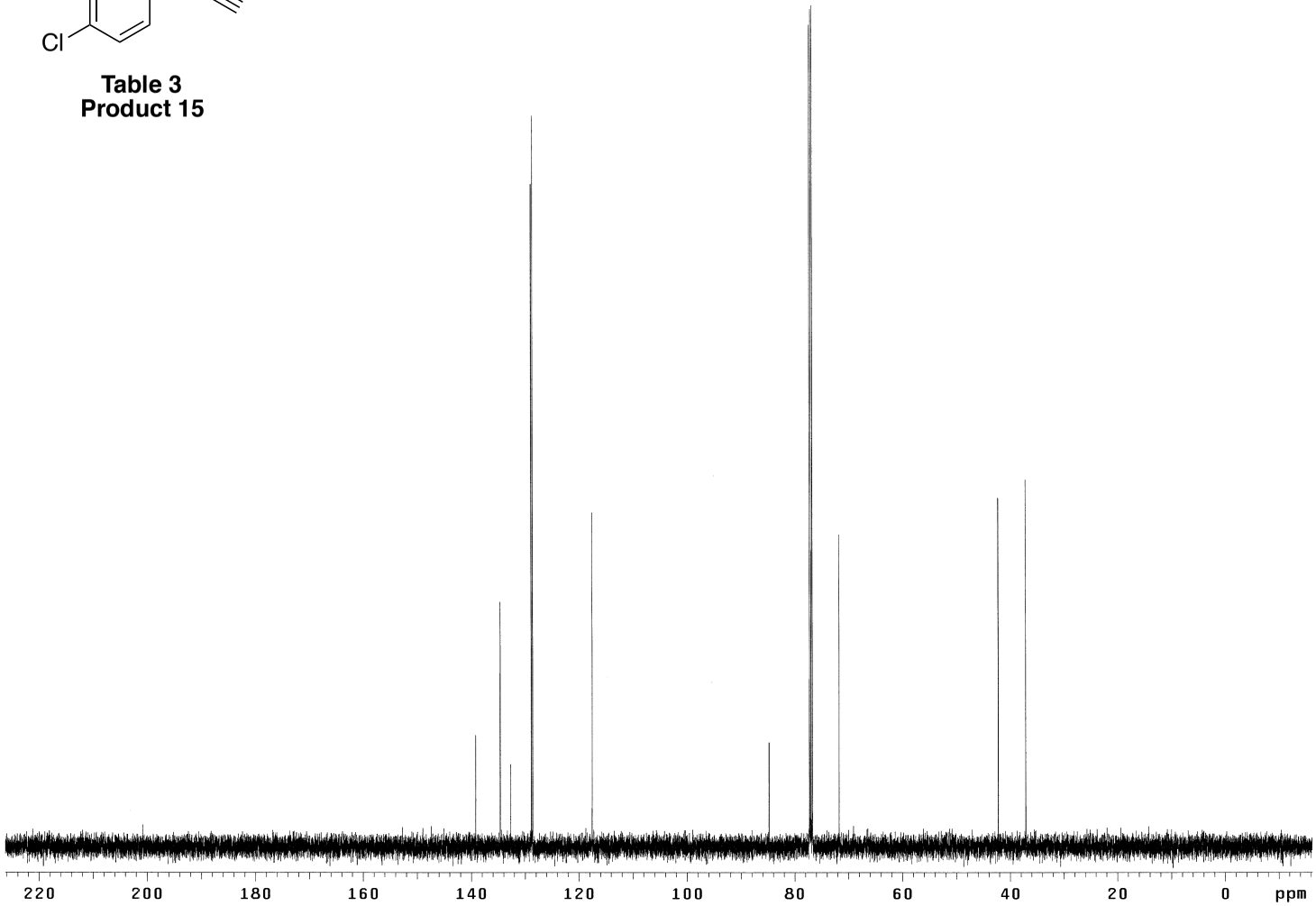
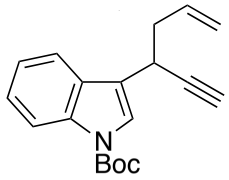
Product 15





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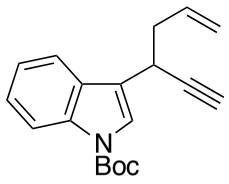

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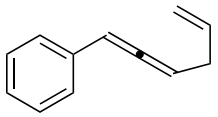
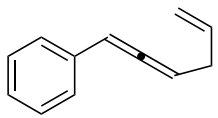
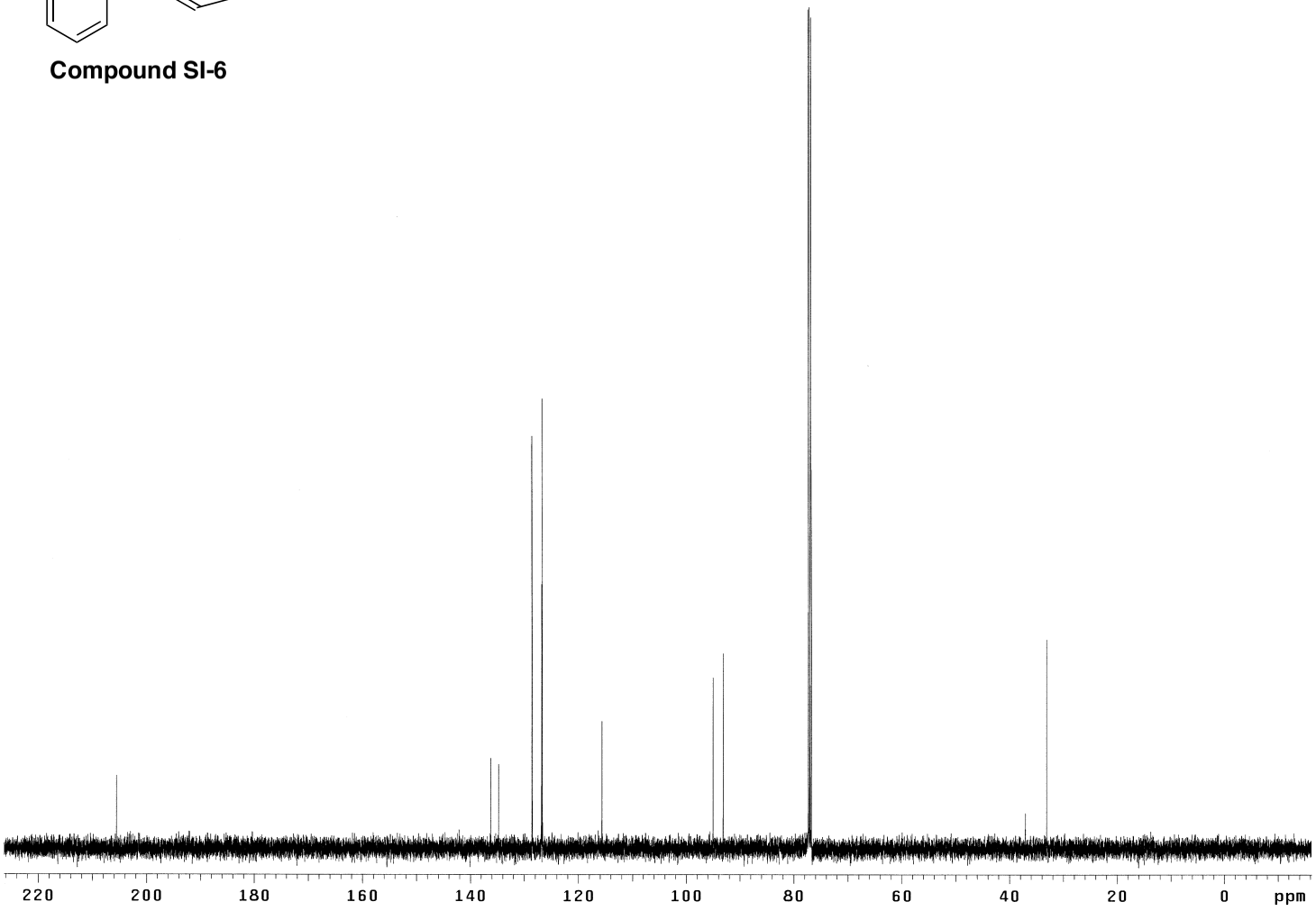
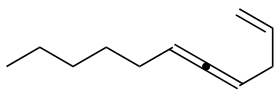


Compound SI-6

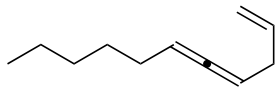


Compound SI-6

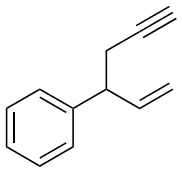




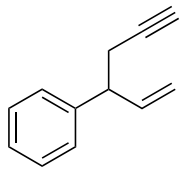
Compound SI-7



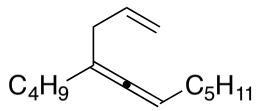
Compound SI-7



Scheme 3
Product 20



Scheme 3
Product 20



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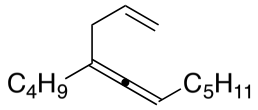
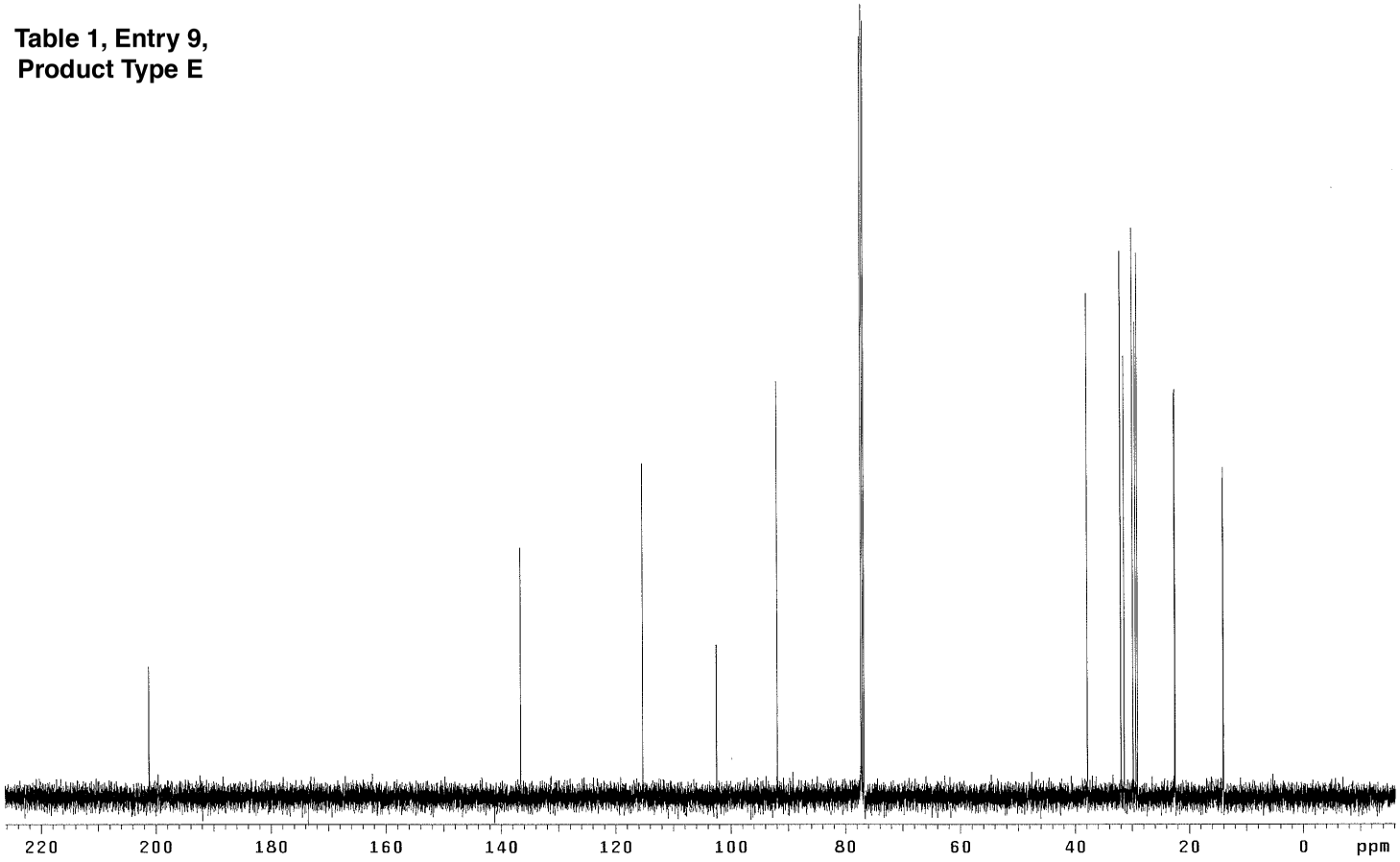
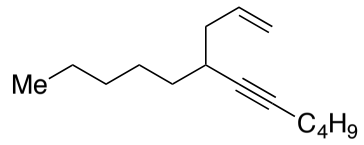


Table 1, Entry 9,
Product Type E





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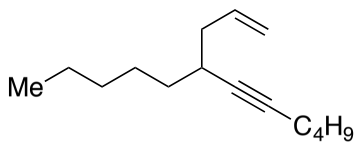


Table 1, Entry 9,
Product Type D

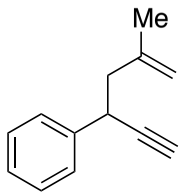
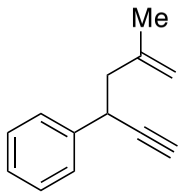


Table 4
Product 21



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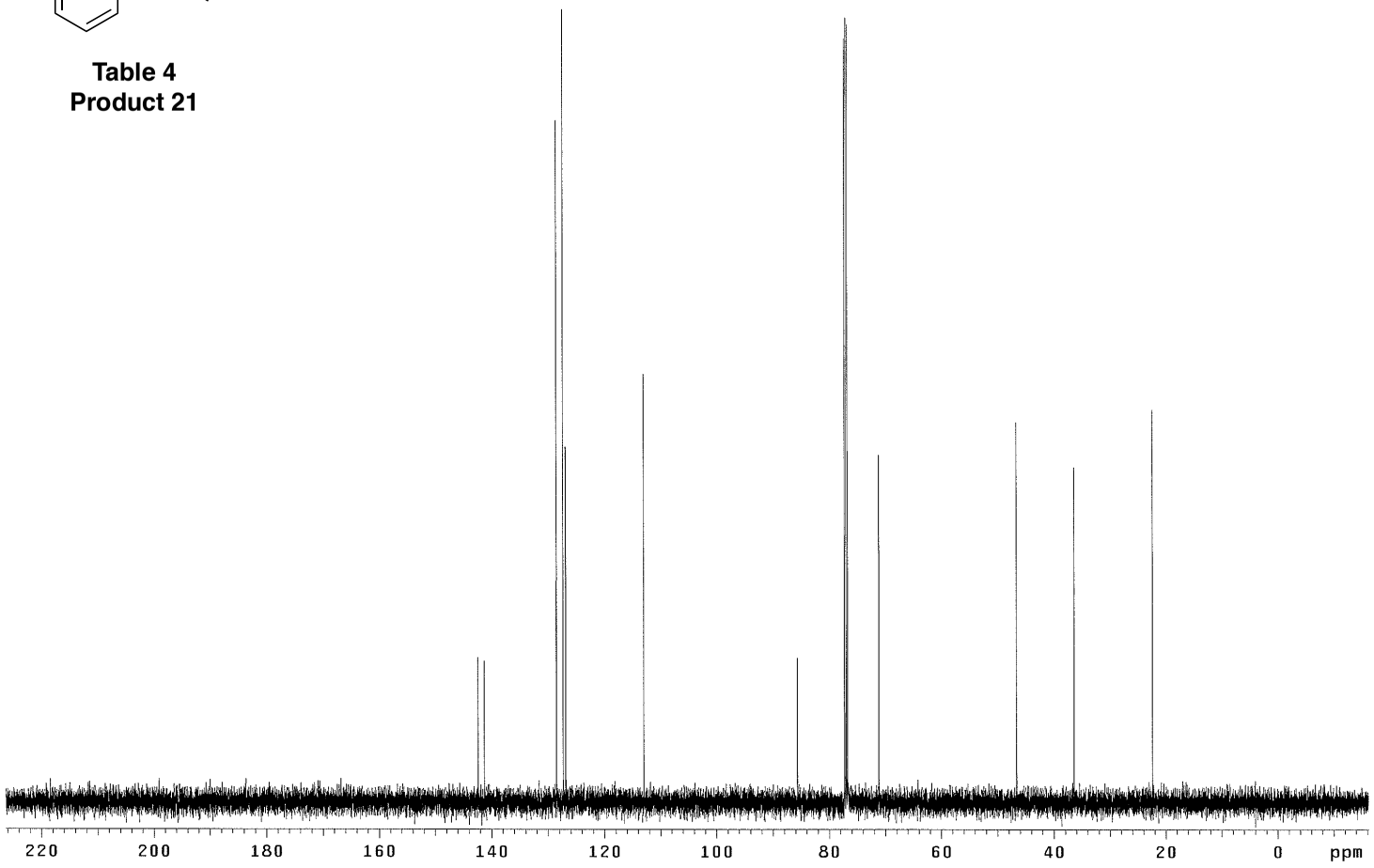

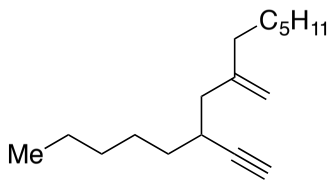

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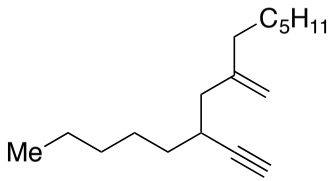

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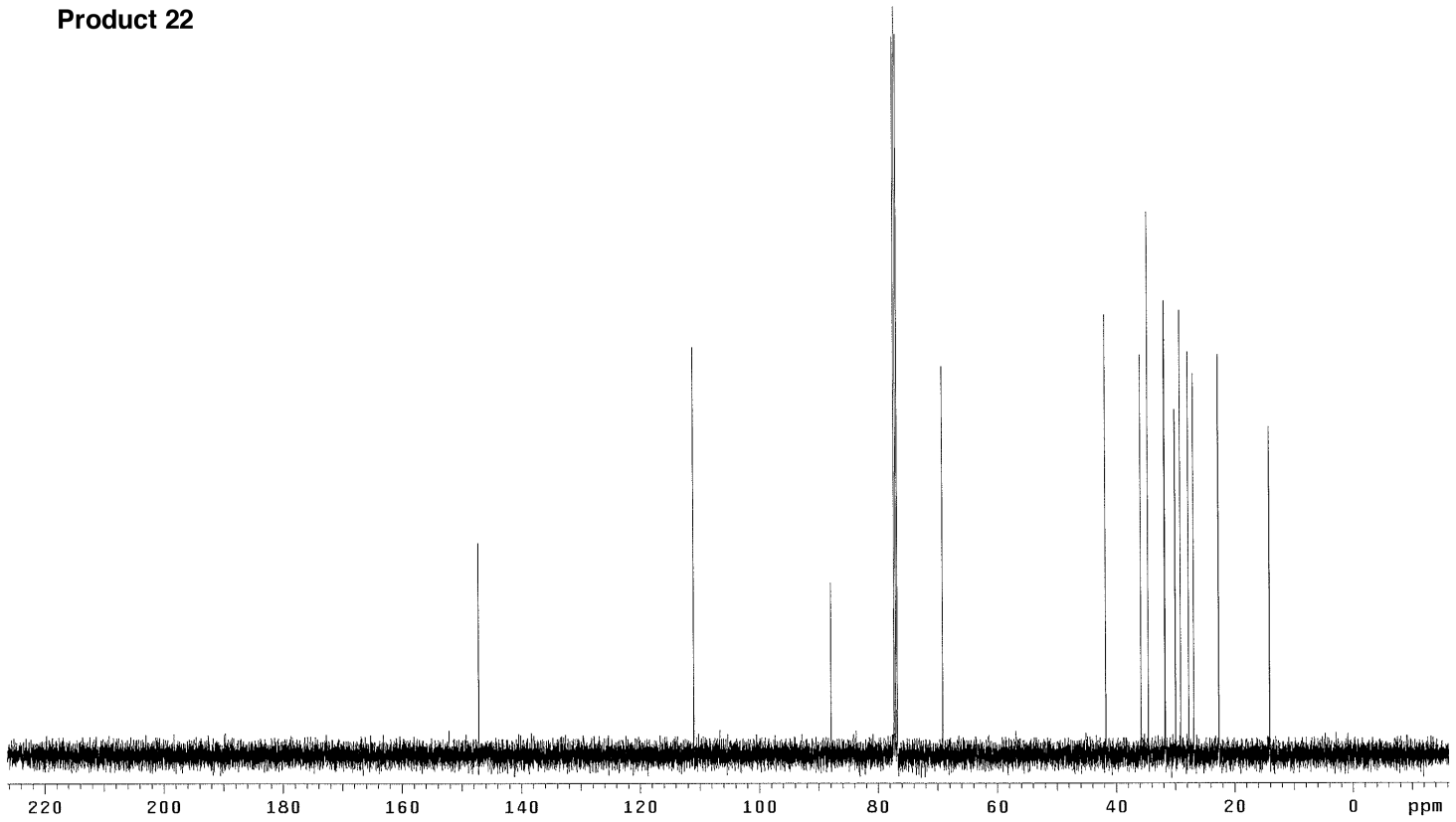
Product 22



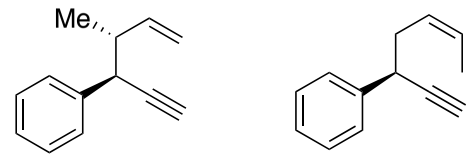


Table 4
Product 23 H

Table 4
Product 23 J

3.6:1 mix
of H:J

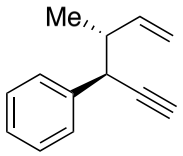


Table 4
Product 23 H

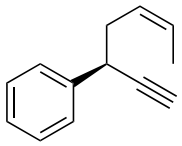
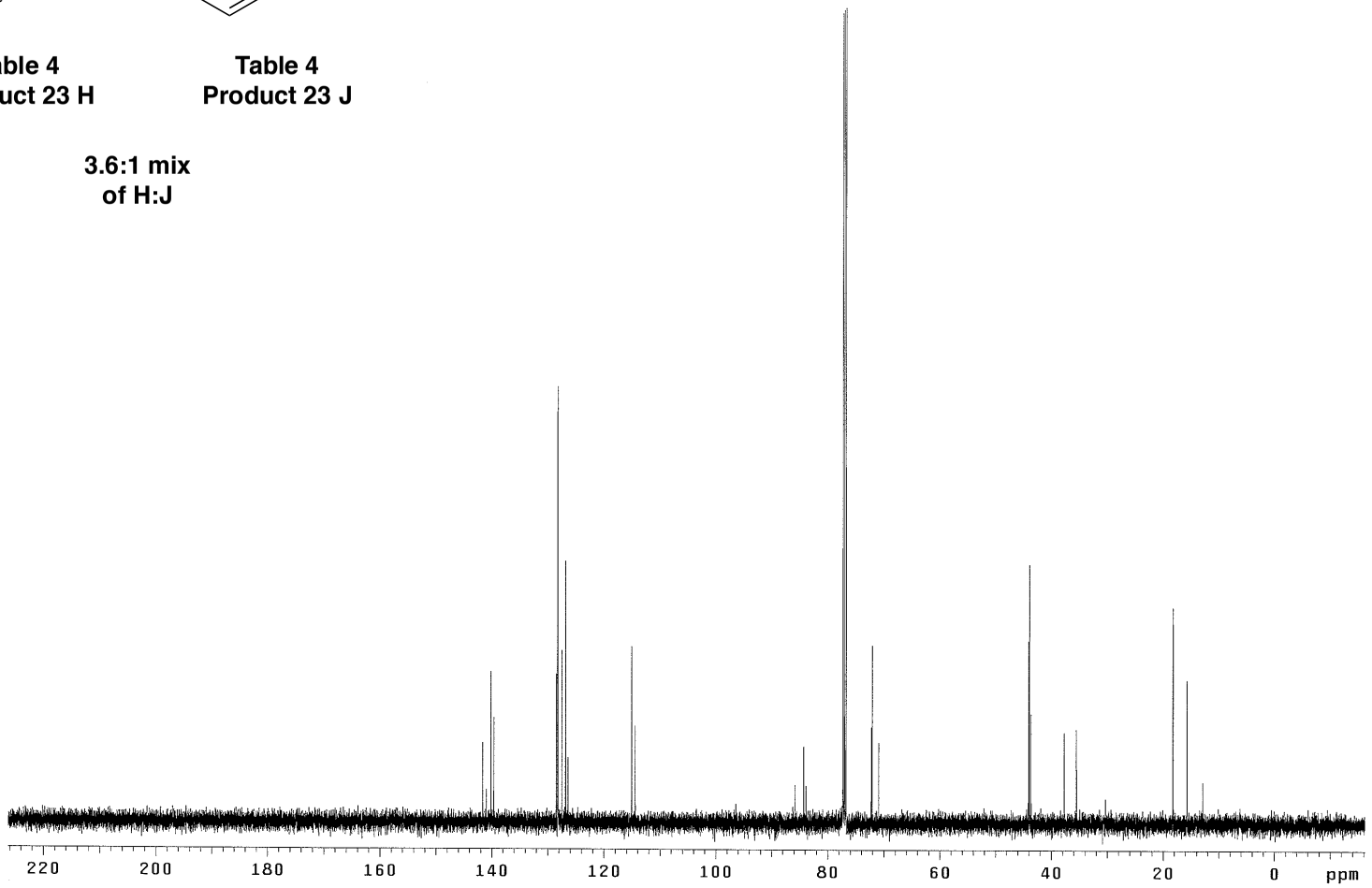
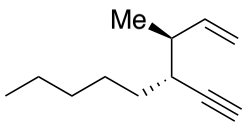


Table 4
Product 23 J

3.6:1 mix
of H:J





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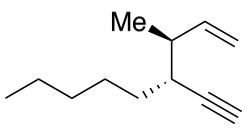
Product 24 H



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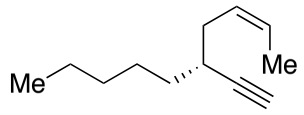
Product 24 H



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Product 24 J

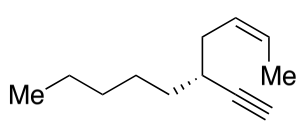


Table 4
Product 24 J

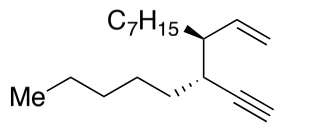
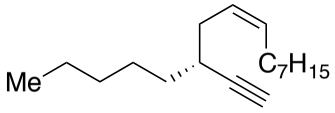
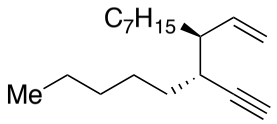


Table 4
Product 25 H



Minor
Compound



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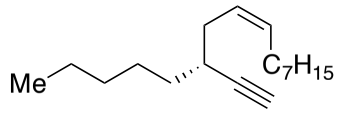
Product 25 H



Minor
Compound

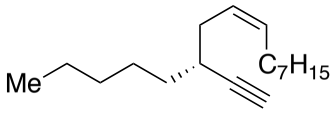
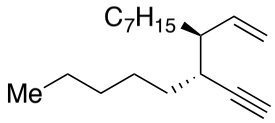


Table 4
Product 25 J



Minor
Compound

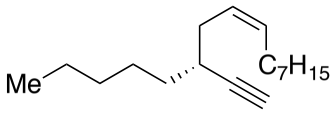
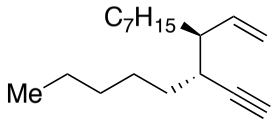
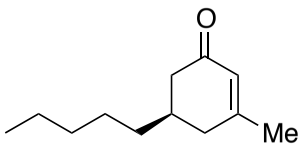


Table 4
Product 25 J



Minor
Compound



Scheme 4
Product 27