α-Selective Ni-Catalyzed Hydroalumination of Aryl- and Alkyl-Substituted Terminal Alkynes. Practical Syntheses of Internal Vinyl Aluminums, Halides or Boronates

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SUPPORTING INFORMATION, PART I

General. Infrared (IR) spectra were recorded on a Bruker FT-IR Alpha (ATR mode) spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, bs = broad singlet, bd = broad doublet, bt = broad triplet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). High-resolution mass spectrometry was performed on a JEOL AccuTOF DART (positive mode) at the Mass Spectrometry Facility, Boston College. Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques. Tetrahydrofuran (thf) was purified by distillation from sodium benzophenone ketyl immediately prior to use (the use of unpurified solvent could cause erosion of selectivity by up to 5%, especially for alkyl-substituted alkynes). Except where noted, all work-up and purification procedures were carried out in air. All solvents were purchased from Fisher. Reagent grade (97%) di-*iso*-butylaluminum hydride (dibal–H) was purchased from Aldrich and used as received. Alkynes were purchased from Aldrich and distilled prior to use (or could be used as received without any purification, in some cases with minor erosion of selectivity (<5%)). Deuterium oxide (D incorporation >99.96% with sure seal cap) was purchased from Cambridge Isotope Laboratories, Inc. and used as received. *N*-Bromosuccinimide was purchased from Aldrich and recrystallized from hot water before use. *N*-Iodosuccinimide was purchased from Aldrich and used as received. 2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (MeO–Bpin) was purchased from Aldrich and used as received. Bromine (Br_2) was purchased from Aldrich and treated with basic alumina for 2 hours and filtered through a plug of basic alumina prior to use. Nickel(II) acetylacetonate ($Ni(acac)_2$) and

tetrakis(triphenylphosphine)nickel(0) ($Ni(PPh_3)_4$) were purchased from Aldrich and used as received. Nickel(II) chloride hexahydrate ($NiCl_2•6H_2O$), bis(triphenylphosphine)nickel(II) chloride ($Ni(PPh_3)_2Cl_2$), 1,2-bis(diphenylphosphino)ethane nickel(II) chloride ($Ni(dppe)Cl_2$), and 1,3-bis(diphenylphosphino)propane nickel(II) chloride ($Ni(dppp)Cl_2$) were purchased from Strem and used as received. Bis(1,5-cyclooctadiene)nickel(0) ($Ni(cod)_2$) was purchased from Strem and purified in a N_2 dry box (commercial solid $Ni(cod)_2$ was washed with anhydrous diethyl ether and recrystallized from dry toluene at –50 °C). 1,4-Bis(diphenylphosphino)butane nickel(II) chloride ($Ni(dppb)Cl_2$) was prepared according to a known procedure.[1] Dichloro[1,1'-bis(diphenylphosphino)ferrocene]nickel(II) ($Ni(dppf)Cl_2$) was prepared based on a reported procedure.[2]

■ **Representative Procedure for Catalytic Hydroalumination of Terminal Alkynes with $Ni(dppp)Cl_2$:** Commercial grade 1,3-bis(diphenylphosphino)propane nickel(II) chloride ($Ni(dppp)Cl_2$, 16.3 mg, 0.0300 mmol) is placed in an oven-dried 13x100 test tube equipped with a stir bar. The test tube is sealed with a septum and purged with N_2 for approximately ten minutes. Tetrahydrofuran (thf, 1.0 mL) is added through a syringe, followed by dropwise addition of commercial grade di-*iso*-butylaluminum hydride (dibal–H, 232 μL, 1.30 mmol) at 22 °C (gas evolution occurs as dibal–H was added). The resulting black solution is allowed to cool to 0 °C (ice bath) before phenylacetylene (110 μL, 1.00 mmol) is added slowly over five minutes (please note that reaction is exothermic). The resulting black solution is allowed to warm to 22 °C and stir for an additional two hours. An aliquot of reaction mixture is removed by a syringe and quenched by adding this into a solution of saturated aqueous Rochelle's salt (sodium potassium tartrate; 1.0 mL) at 0 °C (ice bath) and allowed to stir at 0 °C for 30 minutes. The aqueous layer is washed with Et_2O (1.0 mL x 3) and the combined organic layers are passed through a plug of anhydrous $MgSO_4$ and concentrated *in vacuo* to afford the *protonated* product as yellow oil. The remaining reaction mixture is subjected to dropwise addition of D_2O at 0 °C (ice bath) and the resulting mixture is allowed to stir at 0 °C for additional 30 minutes. The aqueous layer is washed with Et_2O (1.0 mL x 3) and the combined organic layers are passed through a plug of anhydrous $MgSO_4$ and concentrated *in vacuo* to afford the crude *deuterated* product as yellow oil. The crude products are subjected to ^1H NMR analysis.

α-Deuteriostyrene (2, Table 1): ^1H NMR (400 MHz, $CDCl_3$): δ 7.43-7.40 (2H, m), 7.34-7.30 (2H, m), 7.27-7.23 (1H, m), 5.74 (1H, dt, J = 2.8, 1.2 Hz), 5.23 (1H, dt, J = 1.6, 1.2 Hz). The spectroscopic data match those reported previously.[3]

Site selectivity (>98:<2 α:β) was determined by analysis of 400 MHz ^1H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with

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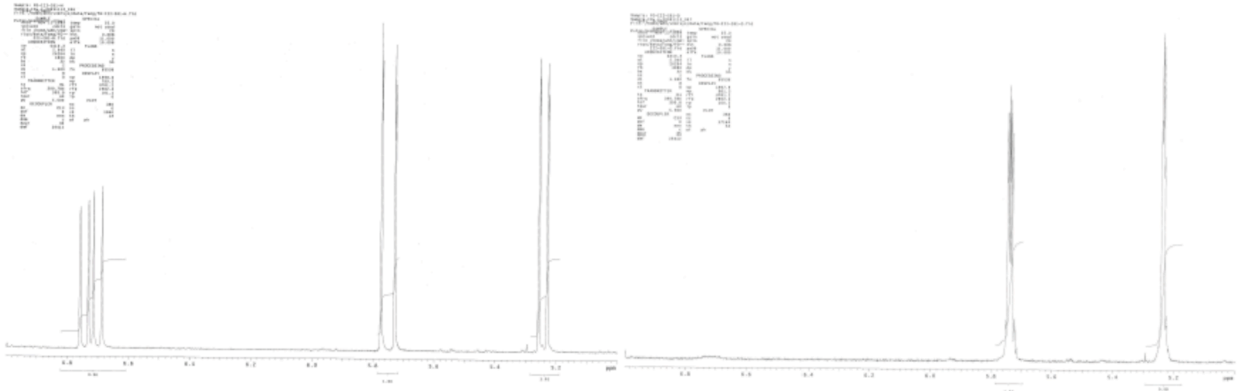
(1) Wille, A.; Tomm, S.; Frauenrath, H. *Synthesis* **1998**, 305–308.

(2) Grant, G. J.; Carter, S. M.; Russell, A. L.; Poullaos, I. M.; VanDerveer D. G. *J. Organomet. Chem.* **2001**, *637-639*, 683–690.

(3) Liard, A.; Marek, I. *J. Org. Chem.* **2000**, *65*, 7218–7220.

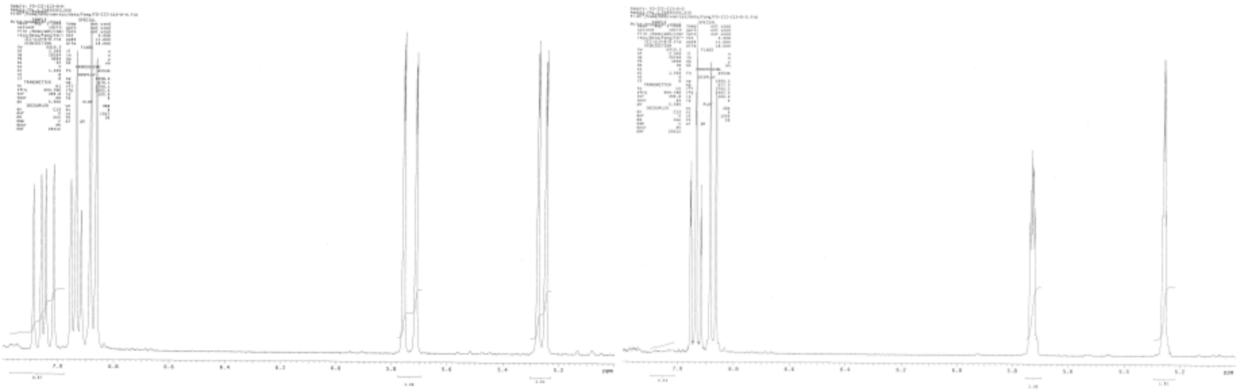
deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.72	0.93	48.2	1	6.70	<0.02	<2.0
3	5.24	1.00	51.8	3	5.23	0.98	>98.0

α-Deuterio-1-methoxy-2-vinylbenzene (Table 2, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (1H, dd, *J* = 7.6, 1.6 Hz), 7.24 (1H, ddd, *J* = 8.0, 8.0, 1.6 Hz), 6.94 (1H, dd, *J* = 7.6, 7.6 Hz), 6.87 (1H, d, *J* = 8.4 Hz), 5.73 (1H, dt, *J* = 1.6, 1.2 Hz), 5.26 (1H, dt, *J* = 1.6, 1.6 Hz), 3.85 (3H, s). The spectroscopic data match those reported previously.[4]

Site selectivity (98:2 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



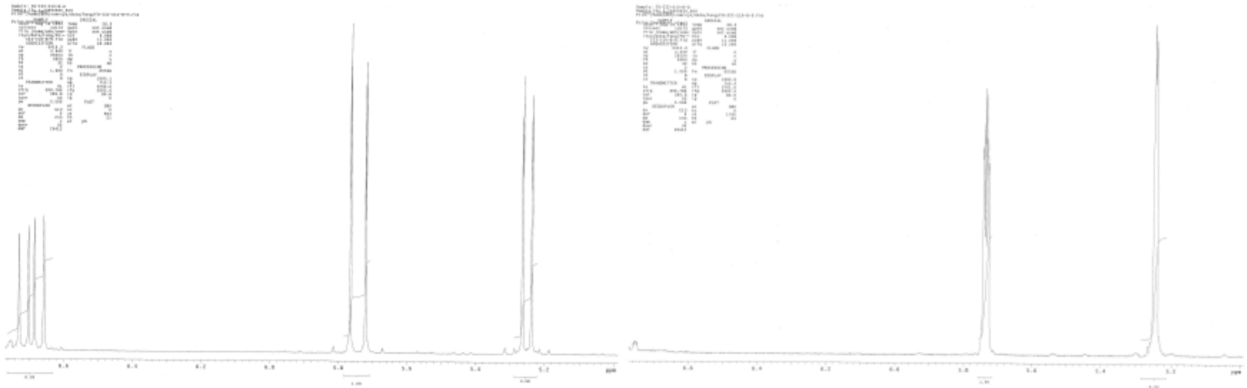
Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	7.05	0.97	49.0	1	7.05	0.02	1.9
4	5.26	1.01	51.0	4	5.26	1.02	98.1

α-Deuterio-1-methoxy-3-vinylbenzene (Table 2, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (1H, dd, *J* = 7.6, 7.6 Hz), 7.02-7.00 (1H, m), 6.95 (1H, dd, *J* = 2.0, 2.0 Hz), 6.82 (1H, ddd, *J* =

(4) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.47 (1H, dd, *J* = 7.6, 1.6 Hz), 7.24 (1H, ddd, *J* = 8.0, 8.0, 1.6 Hz), 7.05 (1H, dd, *J* = 17.6, 11.2 Hz), 6.94 (1H, dd, *J* = 7.6, 7.6 Hz), 6.87 (1H, d, *J* = 8.4 Hz), 5.74 (1H, dd, *J* = 18.0, 1.6 Hz), 5.26 (1H, dd, *J* = 11.2, 1.6 Hz), 3.85 (3H, s); these data match the ^{1}H NMR spectra of the commercially available material.

8.4, 2.4, 0.8 Hz), 5.74 (1H, dt, *J* = 2.4, 0.8 Hz), 5.25 (1H, d, *J* = 1.2 Hz), 3.82 (3H, s). The spectroscopic data match those reported previously.[5]

Site selectivity (>98:<2 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.69	0.99	50.3	1	6.69	<0.02	<0.02
3	5.25	0.98	49.7	3	5.25	0.99	>98.0

α-Deuterio-1-methoxy-4-vinylbenzene (Table 2, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (2H, ddd, *J* = 8.8, 2.0, 2.0 Hz), 6.86 (2H, ddd, *J* = 8.8, 2.0, 2.0 Hz), 5.60 (1H, dt, *J* = 2.4, 0.8 Hz), 5.12 (1H, dt, *J* = 1.6, 1.2 Hz), 3.81 (3H, s). The spectroscopic data match those reported previously.[6]

Site selectivity (>98:<2 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).

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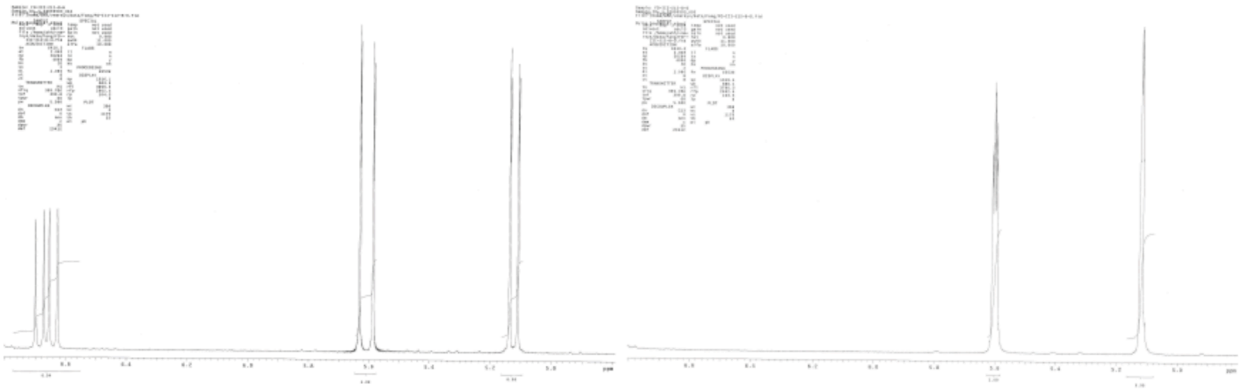
(5) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.24 (1H, dd, *J* = 7.6, 7.6 Hz), 7.02-7.00 (1H, m), 6.95 (1H, dd, *J* = 2.0, 2.0 Hz), 6.82 (1H, ddd, *J* = 8.4, 2.4, 0.8 Hz), 6.69 (1H, dd, *J* = 17.6, 11.2 Hz), 5.74 (1H, dd, *J* = 17.6, 1.2 Hz), 5.25 (1H, dd, *J* = 11.2, 0.8 Hz), 3.82 (3H, s); these data match the ^{1}H NMR spectra of the commercially available material.

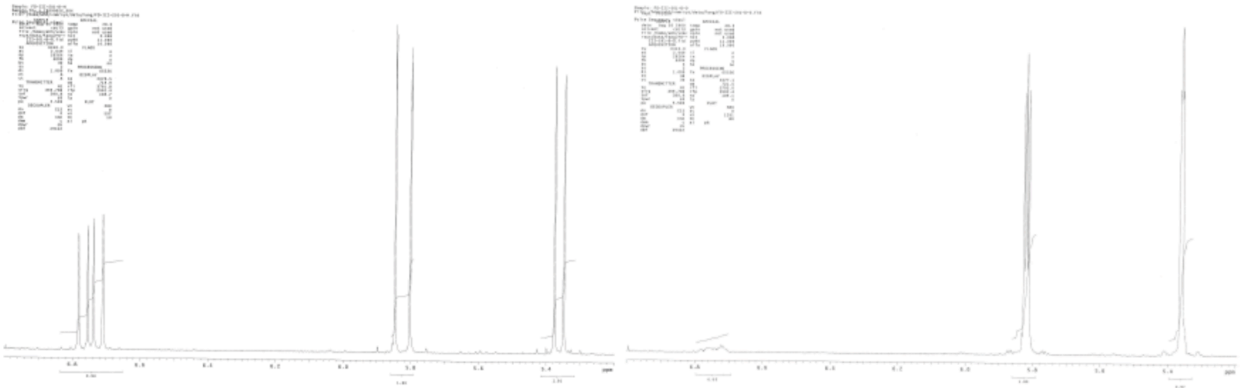
(6) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.35 (2H, ddd, *J* = 8.8, 2.0, 2.0 Hz), 6.86 (2H, ddd, *J* = 8.8, 2.0, 2.0 Hz), 6.66 (1H, dd, *J* = 17.6, 10.8 Hz), 5.61 (1H, dd, *J* = 17.6, 0.8 Hz), 5.12 (1H, dd, *J* = 10.8, 0.8 Hz), 3.81 (3H, s); these data match the ^{1}H NMR spectra of the commercially available material.



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.66	0.94	48.7	1	6.66	<0.02	<2.0
3	5.12	0.99	51.3	3	5.12	0.98	>98.0

α-Deuterio-1-(trifluoromethyl)-3-vinylbenzene (Table 2, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (1H, s), 7.59-7.56 (1H, m), 7.51 (1H, d, *J* = 8.0 Hz), 7.44 (1H, dd, *J* = 7.6, 7.6 Hz), 5.82 (1H, bt, *J* = 2.4 Hz), 5.36 (1H, bt, *J* = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 135.4 (t, *J* = 24.6 Hz), 131.1 (q, *J* = 32.0 Hz), 129.5, 129.1, 124.5 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 270.9 Hz), 123.1 (q, *J* = 3.8 Hz), 115.8; HRMS (ESI$^+$): Calcd for $C_9H_7D_1F_3$ $[M+H]^+$: 174.0641; Found: 174.0641.

Site selectivity (95:5 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.74	0.94	48.2	1	6.74	0.05	4.9
3	5.36	1.01	51.8	3	5.36	0.97	95.1

α-Deuterio-1-(trifluoromethyl)-4-vinylbenzene (Table 2, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (2H, d, *J* = 8.4 Hz), 7.50 (2H, d, *J* = 8.4 Hz), 5.84 (1H, bt, *J* = 2.8 Hz), 5.38 (1H, bt, *J* = 1.2 Hz). The spectroscopic data match those reported previously.[7]

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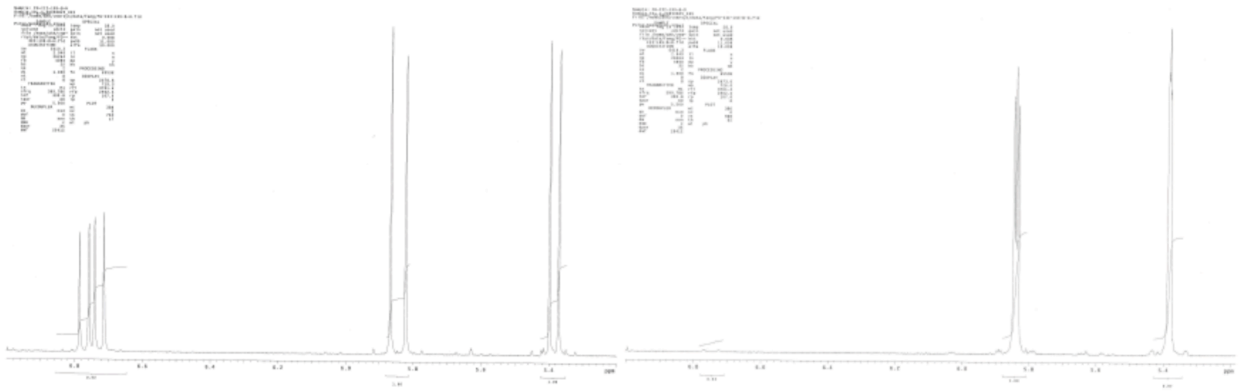
(7) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.58 (2H, d, *J* = 8.4 Hz), 7.50 (2H, d, *J* = 8.4 Hz), 6.75 (1H, dd, *J* = 17.6, 11.2 Hz), 5.85 (1H, d, *J* = 17.6 Hz), 5.39 (1H, d, *J* = 11.2 Hz); these data match the ^{1}H NMR spectra of the commercially available material.

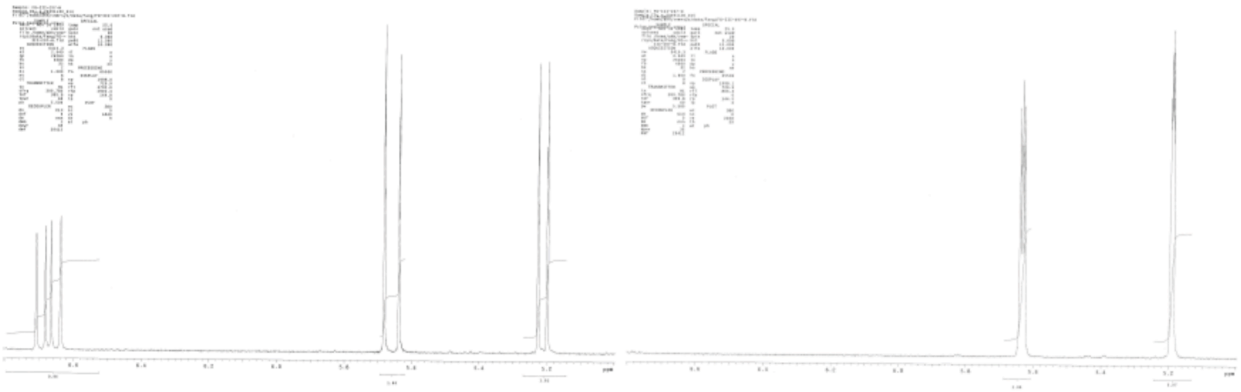
Site selectivity (97:3 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.75	0.92	47.9	1	6.75	0.03	3.0
3	5.39	1.00	52.1	3	5.38	0.97	97.0

α-Deuterio-1-fluoro-4-vinylbenzene (Table 2, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (2H, m), 7.03-6.98 (2H, m), 5.63 (1H, ddt, *J* = 2.8, 0.8, 0.8 Hz), 5.19 (1H, ddt, *J* = 0.8, 0.8, 0.8 Hz). The spectroscopic data match those reported previously.[8]

Site selectivity (>98:<2 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).

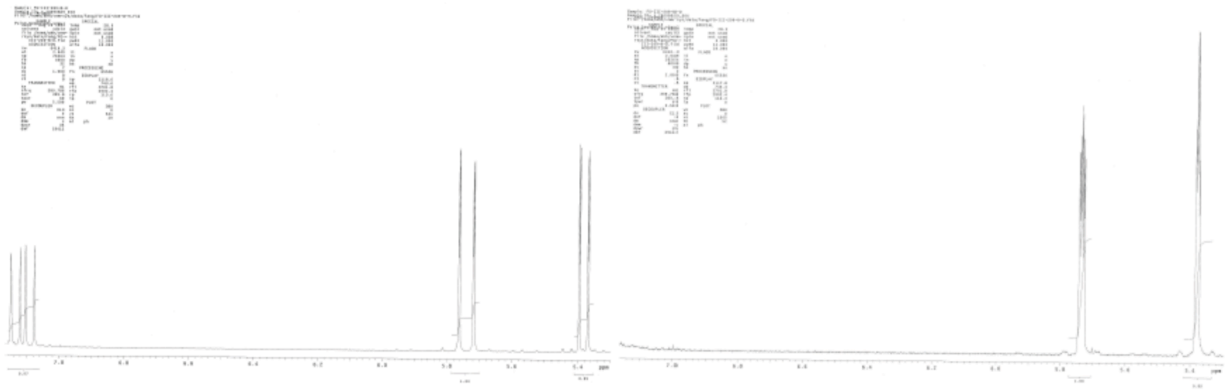


Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.67	0.96	47.9	1	6.66	<0.02	<2.0
3	5.21	1.01	52.1	3	5.19	0.97	>98.0

α-Deuterio-1-chloro-2-vinylbenzene (Table 2, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (1H, dd, *J* = 7.6, 2.0 Hz), 7.35 (1H, dd, *J* = 7.6, 2.0 Hz), 7.26-7.17 (2H, m), 5.74 (1H, dt, *J* = 2.8,

(8) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.39-7.35 (2H, m), 7.03-6.98 (2H, m), 6.67 (1H, dd, *J* = 17.6, 10.8 Hz), 5.66 (1H, ddd, *J* = 17.6, 0.8, 0.8 Hz), 5.21 (1H, ddd, *J* = 11.2, 0.8, 0.8 Hz); these data match the ^{1}H NMR spectra of the commercially available material.

1.2 Hz), 5.38 (1H, dt, *J* = 1.6, 0.8 Hz). The spectroscopic data match those reported previously.[9]
Site selectivity (>98:<2 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).

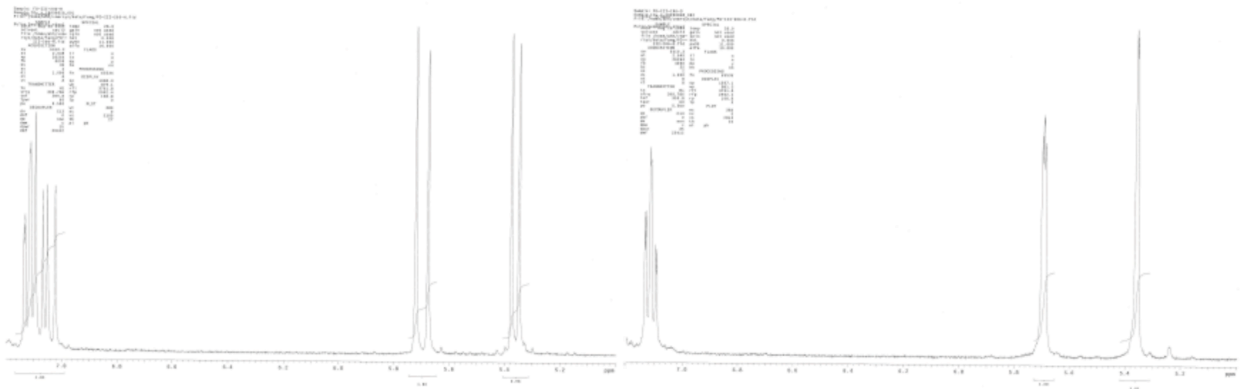


Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	7.11	0.97	49.5	1	7.11	<0.02	<2.0
3	5.38	0.99	50.5	3	5.38	0.99	>98.0

α-Deuterio-1-bromo-2-vinylbenzene (Table 2, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (2H, d, *J* = 8.0 Hz), 7.28 (1H, dd, *J* = 8.0, 8.0 Hz), 7.11 (1H, ddd, *J* = 7.6, 7.6, 1.6 Hz), 5.69 (1H, bt, *J* = 2.4 Hz), 5.36 (1H, bd, *J* = 1.6 Hz). The spectroscopic data match those reported previously.[10]
Site selectivity (>98:<2 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).

(9) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.57 (1H, dd, *J* = 7.6, 2.0 Hz), 7.35 (1H, dd, *J* = 7.6, 2.0 Hz), 7.26-7.17 (2H, m), 7.11 (1H, dd, *J* = 17.6, 10.8 Hz), 5.74 (1H, dd, *J* = 17.6, 1.2 Hz), 5.38 (1H, dd, *J* = 11.2, 1.2 Hz); these data match the ^{1}H NMR spectra of the commercially available material.

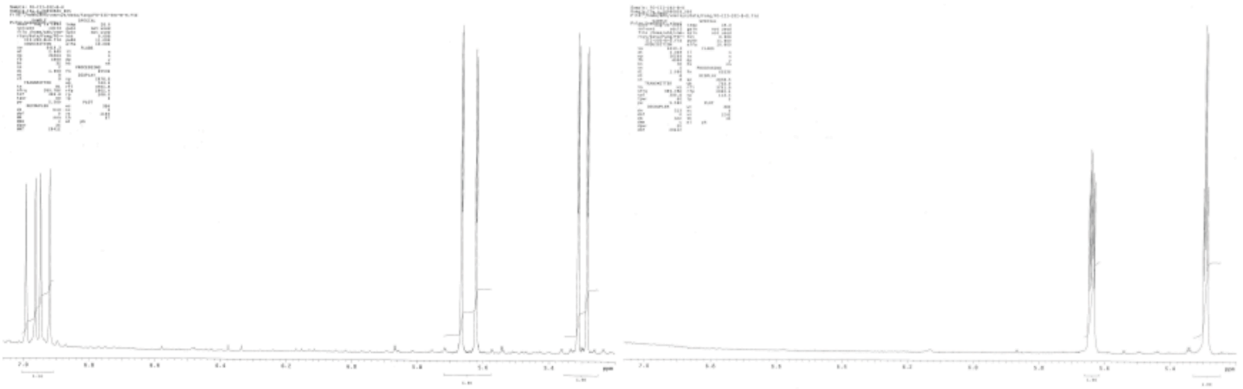
(10) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.55 (2H, d, *J* = 8.0 Hz), 7.28 (1H, dd, *J* = 8.0, 8.0 Hz), 7.14-7.02 (2H, m), 5.70 (1H, d, *J* = 17.2 Hz), 5.36 (1H, d, *J* = 11.2 Hz); these data match the ^{1}H NMR spectra of the commercially available material.



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
2	7.05	0.93	48.7	2	7.05	<0.02	<2.0
4	5.36	0.98	51.3	4	5.36	1.01	>98.0

α-Deuterio-1-methyl-2-vinylbenzene (Table 2, entry 9): ^{1}H NMR (400 MHz, $CDCl_3$): 7.49-7.47 (1H, m), 7.19-7.15 (3H, m), 5.64 (1H, dt, *J* = 2.8, 1.6 Hz), 5.29 (1H, dt, *J* = 1.6, 1.6 Hz), 2.36 (3H, s). The spectroscopic data match those reported previously.[11]

Site selectivity (>98:<2 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.96	1.14	53.3	1	6.95	<0.02	<2.0
3	5.30	1.00	46.7	3	5.29	1.00	>98.0

α-Deuterio-3-vinylpyridine (Table 2, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (1H, s), 8.48 (1H, d, *J* = 3.2 Hz), 7.72 (1H, d, *J* = 7.6 Hz), 7.24 (1H, dd, *J* = 7.6, 2.0 Hz), 5.82 (1H, bt, *J* = 2.4 Hz), 5.38 (1H, bs). The spectroscopic data match those reported previously.[12]

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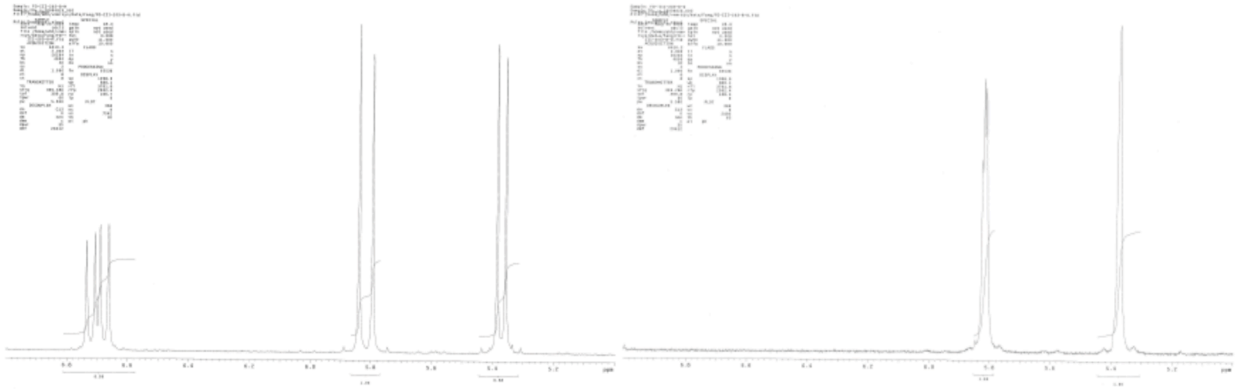
(11) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.49-7.47 (1H, m), 7.19-7.15 (3H, m), 6.96 (1H, dd, *J* = 17.6, 11.2 Hz), 5.64 (1H, ddd, *J* = 17.6, 0.8, 0.8 Hz), 5.30 (1H, ddd, *J* = 10.8, 0.8, 0.8 Hz), 2.36 (3H, s); these data match the ^{1}H NMR spectra of the commercially available material.

(12) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.61 (1H, s), 8.48 (1H, d, *J* = 3.2 Hz), 7.72 (1H, d, *J* = 7.6 Hz), 7.24 (1H, dd, *J* = 7.6, 2.0 Hz), 6.70 (1H, dd, *J* = 17.6, 10.8 Hz),

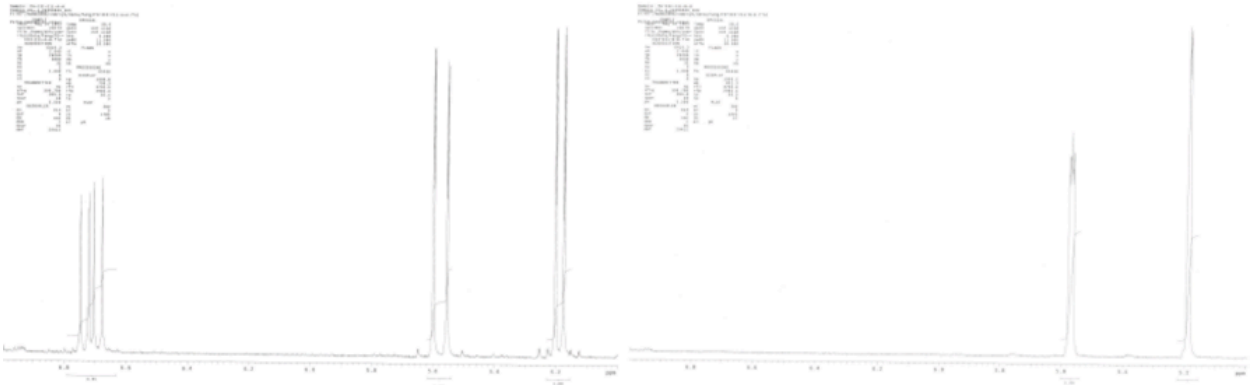
Site selectivity (>98:<2 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.70	0.99	50.3	1	6.70	<0.02	<2.0
3	5.37	0.98	49.7	3	5.38	1.00	>98.0

α-Deuterio-3-vinylthiophene (Table 2, entry 11): ^{1}H NMR (400 MHz, $CDCl_3$): 7.28-7.23 (2H, m), 7.18-7.17 (1H, m), 5.57 (1H, bt, J = 2.8 Hz), 5.19 (1H, bd, J = 1.6 Hz). The spectroscopic data match those reported previously.[13]

Site selectivity (>98:<2 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



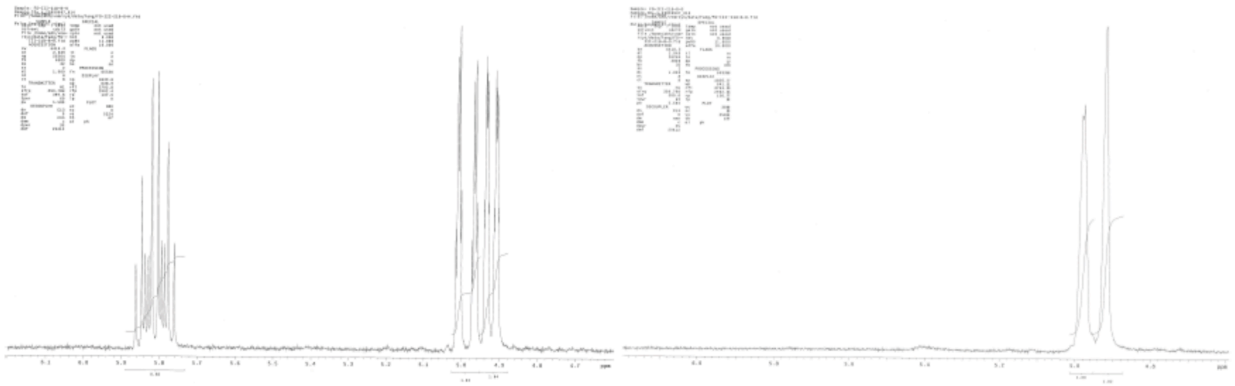
Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.71	0.95	48.7	1	6.71	<0.02	<2.0
3	5.19	1.00	51.3	3	5.19	0.98	>98.0

5.82 (1H, d, J = 17.6 Hz), 5.37 (1H, d, J = 10.8 Hz); these data match the ^{1}H NMR spectra of the commercially available material.

(13) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.23 (2H, m), 7.18-7.17 (1H, m), 6.71 (1H, dd, J = 17.6, 10.8 Hz), 5.58 (1H, dd, J = 17.6, 1.2 Hz), 5.19 (1H, dd, J = 10.8, 1.2 Hz); this matches the data reported previously. See: Tominaga, Y.; Lee, M. L.; Castle, R. N. *J. Heterocyclic Chem.* **1981**, *18*, 967–972.

2-Deuterio-oct-1-ene (Table 3, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.98 (1H, bs), 4.92 (1H, bs), 2.03 (2H, bt, J = 7.2 Hz), 1.39-1.24 (8H, m), 0.88 (3H, t, J = 6.4 Hz). The spectroscopic data match those reported previously.[14]

Site selectivity (>98:<2 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.81	0.98	48.5	1	5.81	<0.02	<2.0
3	4.92	1.04	51.5	3	4.92	1.02	>98.0

4-Deuterio-pent-4-en-1-ol **(Table 3, entry 2):** ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.05-5.03 (1H, m), 4.99-4.97 (1H, m), 3.67 (2H, t, J = 6.4 Hz), 2.15 (2H, t, J = 7.6 Hz), 1.68 (2H, tt, J = 7.6, 6.8 Hz), 1.29 (1H, br). The spectroscopic data match those reported previously.[15]

Site selectivity (97:3 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).

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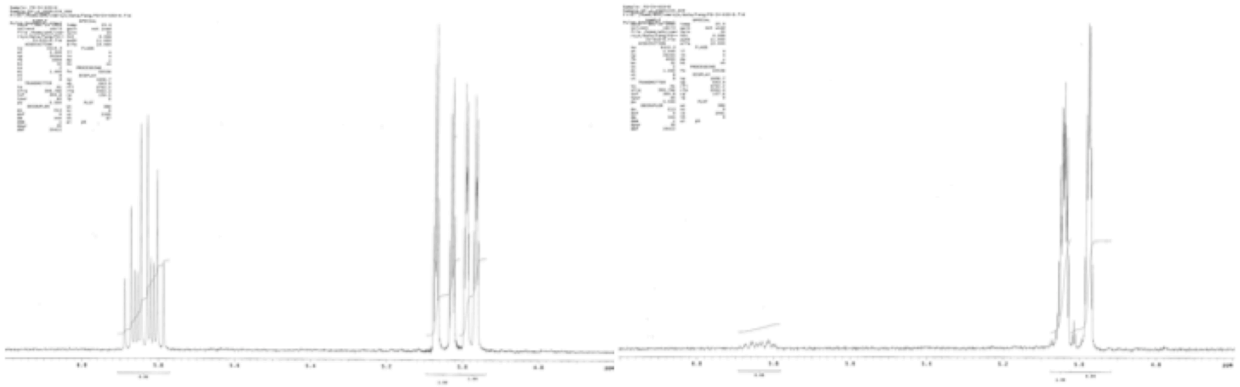
(14) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (1H, ddt, J = 16.8, 10.0, 6.4 Hz), 4.99 (1H, ddt, J = 16.8, 2.0, 1.6 Hz), 4.92 (1H, ddt, J = 10.0, 1.2, 1.2 Hz), 2.04 (2H, dtt, J = 7.6, 7.6, 1.2 Hz), 1.39-1.24 (8H, m), 0.88 (3H, t, J = 6.4 Hz); these data match the ^{1}H NMR spectra of the commercially available material.

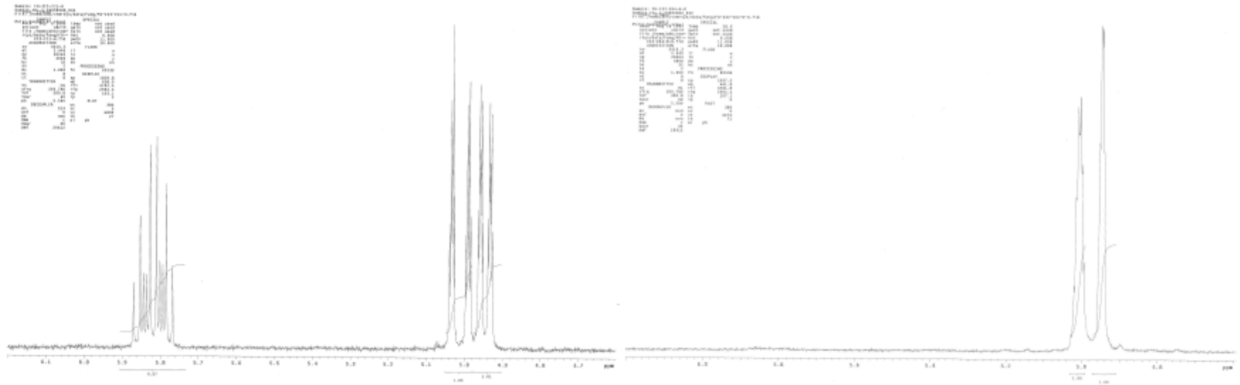
(15) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.84 (1H, ddt, J = 16.8, 10.0, 6.8 Hz), 5.08-5.02 (1H, m), 5.00-4.96 (1H, m), 3.67 (2H, t, J = 6.4 Hz), 2.15 (2H, t, J = 7.6 Hz), 1.68 (2H, tt, J = 7.6, 6.8 Hz), 1.29 (1H, br); these data match the ^{1}H NMR spectra of the commercially available material.



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.84	0.96	49.0	1	5.84	0.03	2.9
3	4.98	1.00	51.0	3	4.98	0.99	97.1

***tert*-Butyldimethyl(4-deuterio-pent-4-en-1-yloxy)silane (Table 3, entry 3):** ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.01-5.00 (1H, m), 4.95-4.94 (1H, m), 3.60 (2H, t, J = 6.8 Hz), 2.08 (2H, bt, J = 7.2 Hz), 1.63-1.56 (2H, m), 0.88 (9H, s), 0.04 (6H, s). The spectroscopic data match those reported previously.[16]

Site selectivity (>98:<2 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



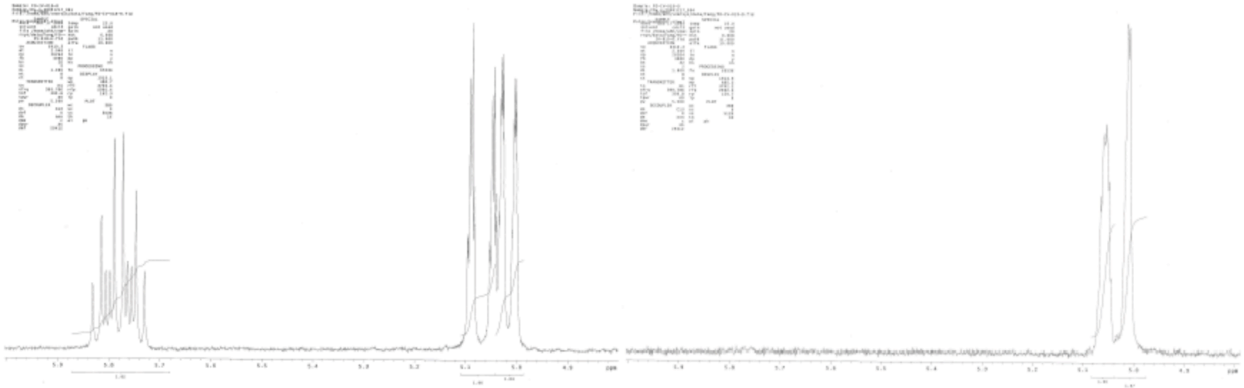
Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.82	0.97	48.5	1	5.82	<0.02	<2.0
3	4.95	1.01	51.5	3	4.95	1.00	>98.0

2-Deuterio-5-chloropent-1-ene (Table 3, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.07-5.05 (1H, m), 5.01 (1H, bd, J = 1.2 Hz), 3.55 (2H, t, J = 6.4 Hz), 2.14 (2H, bt, J = 7.2 Hz), 1.89-1.84

(16) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (1H, ddt, J = 16.8, 10.4, 6.8 Hz), 5.04-4.98 (1H, m), 4.97-4.93 (1H, m), 3.61 (2H, t, J = 6.4 Hz), 2.10 (2H, dtt, J = 7.2, 7.2, 1.2 Hz), 1.64-1.57 (2H, m), 0.89 (9H, s), 0.04 (6H, s); this matches the data reported previously. See: Grotjahn, D. B.; Larsen, C. R.; Gustafson, J. L.; Nair, R.; Sharma, A. *J. Am. Chem. Soc.* **2007**, *129*, 9592–9593.

(2H, m). The spectroscopic data match those reported previously.[17]

Site selectivity (>98:<2 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.78	1.02	49.5	1	5.78	<0.02	<2.0
3	5.01	1.04	50.5	3	5.01	1.07	>98.0

(1-Deuteriovinyl)cyclohexane (Table 3, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.93 (1H, bs), 4.87 (1H, bs), 1.97-1.89 (1H, m), 1.73-1.58 (4H, m), 1.31-1.02 (6H, m). The spectroscopic data match those reported previously.[18]

Site selectivity (>98:<2 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).

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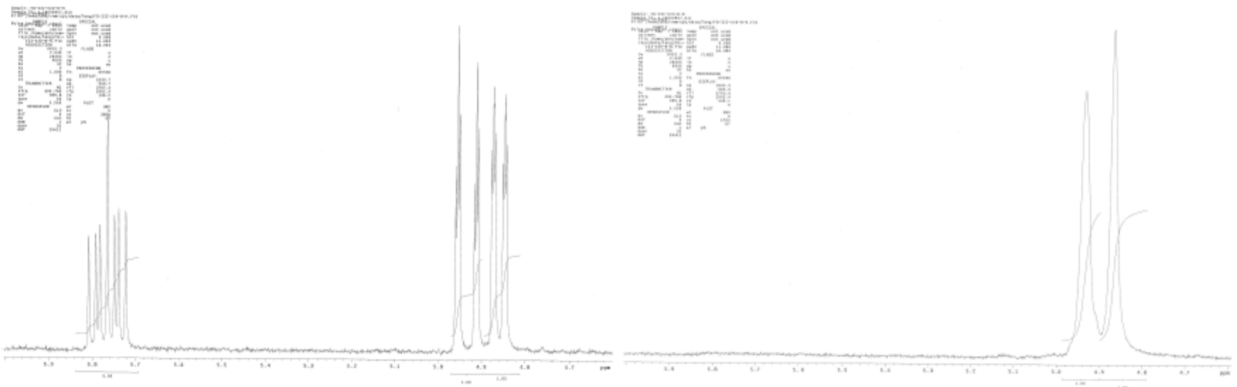
(17) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (1H, ddt, J = 17.2, 10.4, 6.8 Hz), 5.10-5.04 (1H, m), 5.04-5.00 (1H, m), 3.55 (2H, t, J = 6.4 Hz), 2.21 (2H, dt, J = 6.8, 6.8 Hz), 1.89-1.84 (2H, m); this matches the data reported previously. See: Kabalka, G. W.; Gooch, E. E. *J. Org. Chem.* **1980**, *45*, 3578–3580.

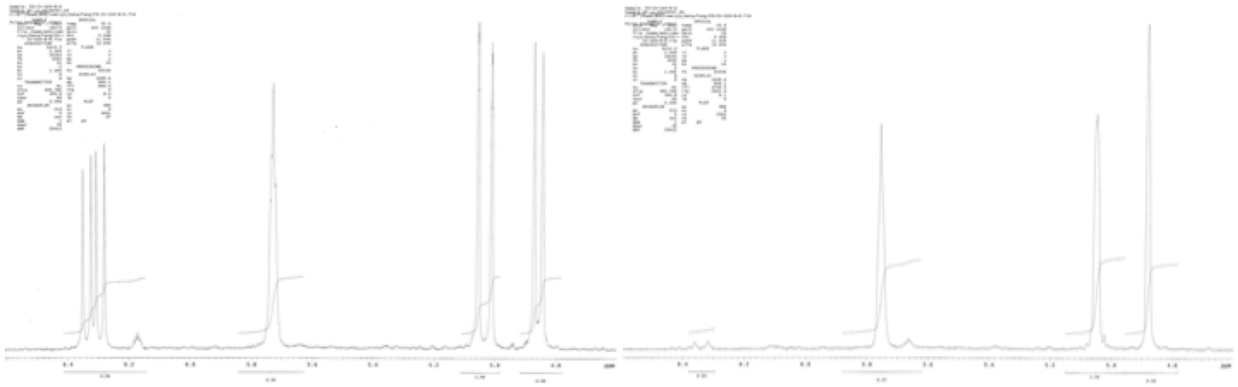
(18) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (1H, ddd, J = 17.2, 10.4, 6.8 Hz), 4.93 (1H, ddd, J = 17.2, 2.0, 2.0 Hz), 4.86 (1H, ddd, J = 10.8, 2.0, 2.0 Hz), 1.97-1.89 (1H, m), 1.73-1.58 (4H, m), 1.31-1.02 (6H, m); these data match the ^{1}H NMR spectra of the commercially available material.



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.77	0.98	48.3	1	5.78	<0.02	<2.0
3	4.86	1.05	51.7	3	4.87	1.02	>98.0

(1-Deuteriovinyl)cyclohex-1-ene (Table 3, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (1H, bs), 5.05 (1H, bs), 4.88 (1H, bs), 2.15-2.12 (4H, m), 1.71-1.57 (4H, m). The spectroscopic data match those reported previously.[19]

Site selectivity (98:2 α*:*β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.32	0.96	49.5	1	6.32	0.02	2.1
4	4.86	0.98	50.5	4	4.88	0.92	97.9

(2-Deuterioallyl)cyclopentane (Table 3, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.98 (1H, bt, *J* = 1.2 Hz), 4.93 (1H, bs), 2.03 (2H, bd, *J* = 6.0 Hz), 1.77-1.69 (1H, m), 1.63-1.48 (6H, m), 1.17-1.09 (2H, m). The spectroscopic data match those reported previously.[20]

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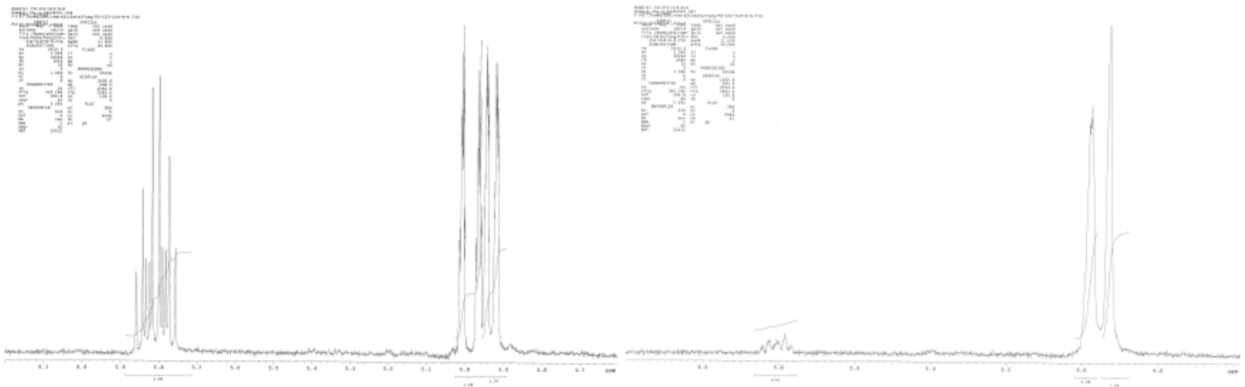
(19) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.32 (1H, dd, *J* = 17.2, 10.8 Hz), 5.74-5.72 (1H, m), 5.03 (1H, ddd, *J* = 16.8, 0.8, 0.4 Hz), 4.86 (1H, d, *J* = 10.4 Hz), 2.15-2.12 (4H, m), 1.71-1.57 (4H, m); these data match the ^{1}H NMR spectra of the commercially available material.

(20) The spectroscopic data for the corresponding protonated alkene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (1H, ddt, *J* = 17.2, 9.6, 7.6 Hz), 5.02-4.96 (1H, m), 4.95-4.91 (1H, m), 2.05 (2H, dd, *J* = 6.8, 6.8 Hz), 1.77-1.69 (1H, m), 1.63-1.48 (6H, m), 1.17-1.09 (2H, m); these data match the ^{1}H NMR spectra of the commercially available material.

Site selectivity (96.5:3.5 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



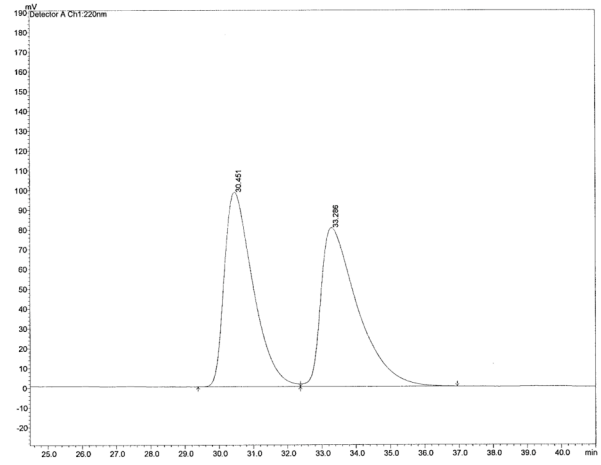
Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.81	1.00	48.3	1	5.81	0.04	3.7
3	4.93	1.07	51.7	3	4.93	1.04	96.3

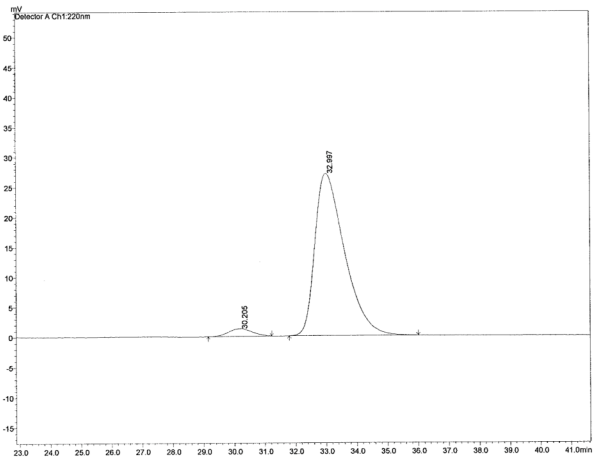
■ **Representative Procedure for Ni-catalyzed Hydroalumination of Terminal Alkynes and Functionalization of the Resulting Vinylaluminum Reagent with NHC-Cu Catalyzed Enantioselective Allylic Alkylation**:

A 13 x 100 mm test tube equipped with a stir bar is charged with NHC•Ag complex (2.8 mg, 0.0020 mmol) in an N_2-filled glovebox. The test tube is sealed with a septum and removed from the glovebox. Tetrahydrofuran (1.0 mL) and a solution of $CuCl_2$•$2H_2O$ (0.02 M in thf, 200 μL, 0.004 mmol) are added to the test tube at 22 °C. The resulting blue solution is allowed to cool to –78 °C (dry ice/acetone), followed by the addition of the vinylaluminum reagent **1** (0.745 M in thf, 200 μL, 0.150 mmol) and a solution of (*E*)-4-(3-((diethoxyphosphoryl)oxy)prop-1-en-1-yl)phenyl 4-methylbenzenesulfonate in thf (44.0 mg, 0.100 mmol in 1.0 mL thf). The mixture is allowed to warm to –15 °C and stir for 3 h, after which time, the reaction is quenched by addition of a saturated aqueous solution of Rochelle's salt (2.0 mL) and allowed to stir for 1 h at 22 °C. Layers are separated, and the aqueous layer is washed with Et_2O (2.0 mL x 3). The combined organic layers are passed through a short plug of $MgSO_4$, and concentrated under reduced pressure. The resulting yellow oil is purified by silica gel chromatography to give the product **4** as colorless oil (36.3 mg, 0.0930 mmol, 93%). **(*S*, *E*)-4-(1-Phenylpenta-1, 4-dien-3-yl)phenyl 4-methylbenzenesulfonate (4, Scheme 1):** IR (neat): 3060 (w), 3027 (w), 1635 (w), 1499 (s), 1373 (s), 1198 (s), 1177 (s), 1153 (s), 1093 (w), 1018 (w), 969 (w), 921 (s), 864 (m), 814 (s), 752 (m), 694 (m), 670 (m), 567 (s), 552 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (2H, ddd, *J* = 8.4, 2.0, 1.6 Hz), 7.37-7.34 (2H, m), 7.32-7.28 (4H, m), 7.24-7.20 (1H, m), 7.19-7.16 (2H, m), 6.93 (2H, ddd, *J* = 8.4, 3.2, 2.0 Hz), 6.40 (1H, d, *J* = 16.0 Hz), 6.32 (1H, dd, *J* = 16.0, 6.4 Hz), 6.04 (1H, ddd, *J* = 17.2, 10.4, 6.8 Hz), 5.19 (1H, ddd, *J* = 10.4, 1.6, 1.2 Hz), 5.10 (1H, ddd, *J* = 17.2, 1.6, 1.2 Hz), 4.19 (1H, dd, *J* = 6.8, 6.8 Hz), 2.45 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ

148.3, 145.4, 141.7, 139.6, 137.2, 132.7, 131.2, 131.2, 129.9, 129.3, 128.7, 128.7, 127.6, 126.4, 122.5, 116.3, 51.8, 21.9; HRMS (ESI$^+$): Calcd for $C_{24}H_{23}S_1O_3$ [M+H]$^+$: 391.1368; Found: 391.1385. Specific rotation: $[\alpha]_D^{20}$ –3.32 (*c* = 1.25, $CHCl_3$) for an enantiomerically enriched sample of 93:7 er.

Enantiomer ratio was determined by HPLC analysis in comparison with authentic racemic material (chiralcel column OD-H, 99% hexanes: 1% *iso*propanol, 1.0 mL/min, 220nm). A sample with 96:4 er is shown below:





PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.451	5733719	98424	49.059	55.086
2	33.286	5953587	80248	50.941	44.914
Total		11687305	178672	100.000	100.000

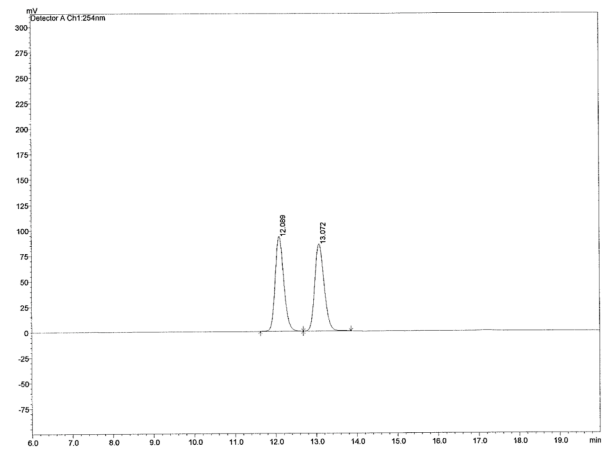
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.205	68152	1263	3.607	4.466
2	32.997	1821225	27024	96.393	95.534
Total		1889376	28287	100.000	100.000

(*S*)-*tert*-Butyldimethyl((7-phenyl-6-vinyloct-7-en-1-yl)oxy)silane (5, Scheme 1): IR (neat): 2929 (m), 2856 (m), 1471 (w), 1254 (m), 1099 (s), 1005 (w), 912 (m), 834 (s), 774 (s), 703 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.35 (2H, m), 7.33-7.29 (2H, m), 7.28-7.24 (1H, m), 5.83 (1H, ddd, *J* = 17.0, 10.0, 8.0 Hz), 5.28 (1H, d, *J* = 1.6 Hz), 5.09-5.03 (3H, m), 3.58 (2H, t, *J* = 6.8 Hz), 3.19 (1H, ddd, *J* = 8.4, 8.4, 8.4 Hz), 1.63-1.57 (1H, m), 1.53-1.46 (3H, m), 1.39-1.27 (4H, m), 0.90 (9H, s), 0.05 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 142.7, 141.7, 128.2, 127.3, 126.8, 114.8, 112.8, 63.4, 48.8, 34.1, 32.9, 27.4, 26.1, 25.9, 18.5, -5.11; HRMS (ESI$^+$): Calcd for $C_{22}H_{37}Si_1O_1$ [M+H]$^+$: 345.2614; Found: 345.2607. Specific rotation: $[\alpha]_D^{20}$ +5.82 (*c* = 0.91, $CHCl_3$) for an enantiomerically enriched sample of 93:7 er.

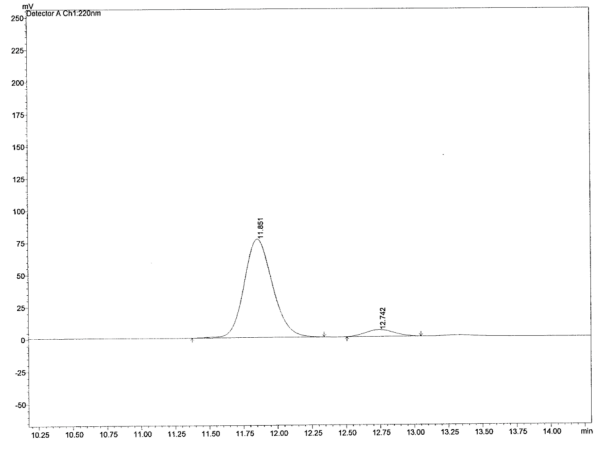
Enantiomer ratio was determined by HPLC analysis in comparison with authentic racemic material (chiralcel column OD-H, 100% hexanes, 0.5 mL/min, 220nm). A sample with 93:7 er is shown below:



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.089	1363072	92781	50.067	52.114
2	13.072	1359406	85253	49.933	47.886
Total		2722478	178035	100.000	100.000



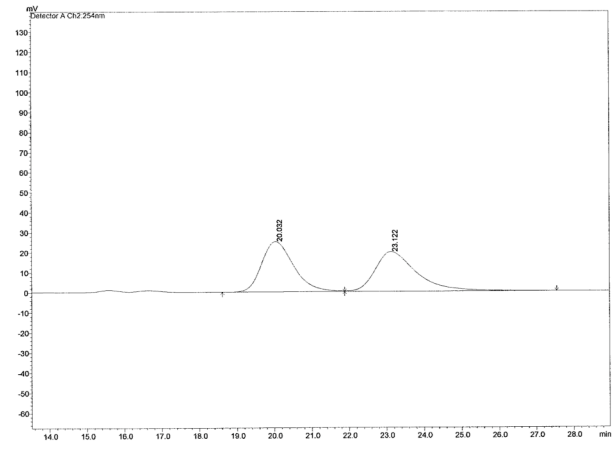
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.851	1104189	76379	93.581	93.568
2	12.742	75738	5251	6.419	6.432
Total		1179927	81629	100.000	100.000

(*R*)-4-(2-(Cyclohex-1-en-1-yl)penta-1, 4-dien-3-yl)phenyl 4-methylbenzenesulfonate (6, Scheme 1): IR (neat): 2928 (m), 2858 (w), 1599 (w), 1499 (s), 1375 (s), 1198 (s), 1177 (s), 1153 (s), 1094 (m), 1019 (w), 919 (w), 866 (s), 814 (m), 747 (m), 666 (m), 578 (m), 552 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (2H, dd, *J* = 8.4, 2.0 Hz), 7.29-7.26 (2H, m), 7.09 (2H, dd, *J* = 8.8, 2.0 Hz), 6.90-6.87 (2H, m), 6.04 (1H, ddd, *J* = 16.8, 10.0, 6.4 Hz), 5.74 (1H, t, *J* = 4.0 Hz), 5.26 (1H, s), 5.10 (1H, ddd, *J* = 10.0, 1.6, 1.2 Hz), 4.84 (1H, s), 4.75 (1H, ddd, *J* = 16.8, 1.6, 1.2 Hz), 4.42 (1H, d, *J* = 6.8 Hz), 2.44 (3H, s), 2.16-1.97 (4H, m), 1.64-1.47 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 148.1, 145.3, 141.6, 140.8, 135.7, 132.6, 129.8, 129.7, 128.7, 125.8, 122.1, 116.0, 112.1, 51.2, 26.7, 25.9, 23.0, 22.2, 21.8; HRMS (ESI^+): Calcd for $C_{24}H_{27}S_1O_3$ $[M+H]^+$: 395.1681; Found: 395.1677. Specific rotation: $[\alpha]_D^{20}$ –37.44 (*c* = 1.95, $CHCl_3$) for an enantiomerically enriched sample of 91.5:8.5 er.

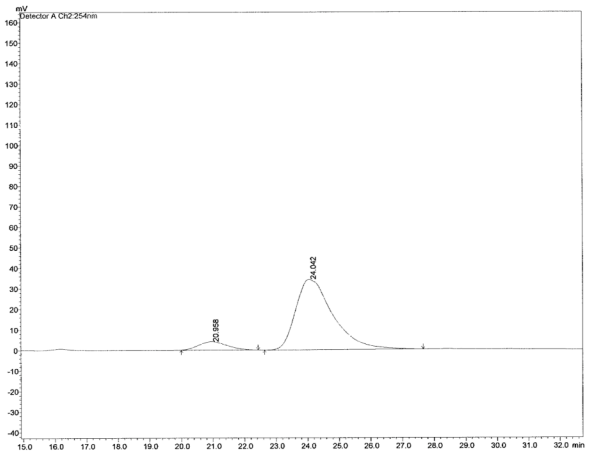
Enantiomer ratio was determined by HPLC analysis in comparison with authentic racemic material (chiralcel column OJ-H, 98.5% hexanes: 1.5% *iso*propanol, 1.0 mL/min, 254nm). A sample with 91.5:8.5 er is shown below:



PeakTable

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.032	1494292	25057	49.590	55.805
2	23.122	1519026	19844	50.410	44.195
Total		3013318	44901	100.000	100.000



PeakTable

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.958	253618	4071	8.316	10.661
2	24.042	2796223	34120	91.684	89.339
Total		3049841	38191	100.000	100.000

■ Representative Procedure for Ni(dppp)Cl_2 Catalyzed Hydroalumination of Terminal Alkynes and Functionalization of the Resulting Vinylaluminum Reagent with *N*-bromosuccinamide or *N*-iodosuccinamide

Commercial grade 1,3-bis(diphenylphosphino)propane nickel(II) chloride (Ni(dppp)Cl_2, 16.3 mg, 0.0300 mmol) is placed in an oven-dried 13x100 test tube equipped with a stir bar. The test tube is sealed with a septum and purged with N_2 for approximately ten minutes. Tetrahydrofuran (thf, 1.0 mL) is added through a syringe, followed by dropwise addition of dibal–H (232 μL, 1.30 mmol) at 22 °C (gas evolution occurs as dibal–H is added). The resulting black solution is allowed to cool to 0 °C (ice bath) before 1-ethynyl-3-methoxybenzene (127 μL, 1.00 mmol) is added slowly over five minutes (reaction is exothermic). The resulting black solution is allowed to warm to 22 °C and stir for an additional two hours. In a separate 10 mL pear shape flask, a solution (orange color) of *N*-bromosuccinamide (356.0 mg, 2.0 mmol) in thf (3.0 mL) is prepared and transferred with a syringe into hydroalumination reaction mixture at 0 ºC (ice bath). The resulting dark brown solution is allowed to warm up to 22 ºC and stir for one hour. At this point, the reaction is quenched by adding the mixture into a separatory funnel, which contains a saturated solution of Rochelle's salt (sodium potassium tartrate; 5.0 mL) and Et_2O (5.0 mL). The organic layer is separated and the aqueous layer is washed with Et_2O (5.0 mL x 2). The combined organic layers are dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford yellow oil, which is purified by basified (with triethylamine) silica gel chromatography or basic alumina (100% hexanes) to furnish the desired product **7** as light yellow oil (185.4 mg, 0.87 mmol, 87% yield). **1-(1-Bromovinyl)-3-methoxybenzene (7, Scheme 2):** The compound is sensitive to acidic condition (It will decompose in regular chloroform; therefore, chloroform basified with K_2CO_3 is needed to acquire the NMR spectra). IR (neat): 2924 (s), 2853 (m), 1577 (m), 1485 (m), 1463 (m), 1428 (m), 1288 (m), 1259 (s), 1164 (w), 1045 (m), 883 (m), 780 (w), 707 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (1H, dd, J = 8.0, 8.0 Hz), 7.18 (1H, ddd, J =

7.6, 1.6, 0.8 Hz), 7.13 (1H, dd, *J* = 2.4, 2.4 Hz), 6.88 (1H, ddd, *J* = 8.4, 2.4, 1.2 Hz), 6.12 (1H, d, *J* = 2.0 Hz), 5.78 (1H, d, *J* = 2.4 Hz), 3.84 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 140.1, 130.8, 129.4, 119.9, 118.1, 114.8, 113.3, 55.5; HRMS (ESI$^+$): Calcd for $C_9H_{10}Br_1O_2$ [M+OH]$^+$: 228.9864; Found: 228.9874.

(1-Iodovinyl)benzene (8, Scheme 2): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.49 (2H, m), 7.34-7.28 (3H, m), 6.47 (1H, d, *J* = 1.6 Hz), 6.09 (1H, d, *J* = 2.0 Hz); HRMS (ESI$^+$): Calcd for $C_8H_8I_1$ [M+H]$^+$: 230.9671; Found: 230.9671. The spectroscopic data match those reported previously.[21]

2-Bromooct-1-ene (9, Scheme 2): IR (neat): 2956 (m), 2928 (s), 2858 (m), 1713 (w), 1629 (m), 1459 (w), 1188 (w), 882 (s), 726 (w), 640 (w), 568 (w), 531 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.55 (1H, d, *J* = 1.6 Hz), 5.38 (1H, d, *J* = 1.2 Hz), 2.41 (2H, dt, *J* = 7.2, 0.8 Hz), 1.57-1.51 (2H, m), 1.34-1.24 (6H, m), 0.91-0.86 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.1, 116.3, 41.6, 31.7, 28.2, 28.0, 22.7, 14.2; HRMS (ESI$^+$): Calcd for $C_8H_{16}Br_1$ [M+H]$^+$: 191.0435; Found: 191.0435.

4-Iodopent-4-en-1-ol (10, Scheme 2): The compound is prepared through the use of the general halogenation procedure except that 2.3 equiv of dibal–H and 3.0 equiv of *N*-iodosuccinamide are used (iodination occurs at 0 °C for one hour). IR (neat): 3316 (b), 2941 (m), 2874 (w), 1617 (m), 1429 (w), 1184 (w), 1112 (w), 1057 (s), 1037 (s), 894 (s), 494 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07 (1H, q, *J* = 1.2 Hz), 5.72 (1H, s), 3.67 (2H, t, *J* = 6.4 Hz), 2.50 (2H, dt, *J* = 7.2, 0.8 Hz), 1.78 (2H, tt, *J* = 7.6, 6.4 Hz), 1.47 (1H, bs); ^{13}C NMR (100 MHz, $CDCl_3$): δ 126.0, 111.6, 61.3, 41.8, 32.1; HRMS (ESI$^+$): Calcd for $C_5H_{10}I_1O_1$ [M+H]$^+$: 212.9776; Found: 212.9773.

***tert*-Butyl((4-iodopent-4-en-1-yl)oxy)dimethylsilane (11, Scheme 2):** IR (neat): 2952 (w), 2928 (w), 2856 (w), 1617 (w), 1471 (w), 1253 (m), 1098 (s), 969 (w), 891 (w), 832 (s), 773 (s), 661 (w), 494 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03 (1H, q, *J* = 1.6 Hz), 5.70 (1H, s), 3.62 (2H, t, *J* = 6.4 Hz), 2.47 (2H, dt, *J* = 7.2, 1.2 Hz), 1.72 (2H, tt, *J* = 7.6, 6.4 Hz), 0.90 (9H, s), 0.05 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.7, 112.1, 63.1, 41.9, 32.2, 26.1, 18.4, -5.2; HRMS (ESI$^+$): Calcd for $C_{11}H_{24}I_1O_1Si_1$ [M+H]$^+$: 327.0641; Found: 327.0633.

■ Representative Procedure for Ni(dppp)Cl_2 Catalyzed Hydroalumination of Terminal Alkynes and Functionalization of the Resulting *Internal* Vinylaluminum Reagent with Bromine:

Commercial grade 1,3-bis(diphenylphosphino)propane nickel dichloride (Ni(dppp)Cl_2, 5.4 mg, 0.0100 mmol) is placed in a flame-dried 50 mL round bottom flask. The vessel is sealed with a septum and purged with N_2 for approximately ten minutes. Tetrahydrofuran (thf, 10.0 mL) is added through a syringe followed by dropwise addition of dibal–H (1.96 mL, 11.0 mmol) at 22 °C (gas evolution occurs as dibal–H is introduced). The resulting light brown solution is allowed to cool to 0 °C (ice bath) before phenylacetylene (1.10 mL, 10.0 mmol) is added slowly over approximately five minutes (reaction is exothermic). The resulting light brown solution is

(21) Cheung, L. L. W.; Yudin, A. K. *Org. Lett.* **2009**, *11*, 1281–1284.

allowed to warm to 22 °C and stir for two hours. The mixture is allowed to cool to –78 °C (dry ice-acetone bath), and bromine (Br_2; 0.771 mL, 15.0 mmol) is added through a syringe slowly in a dropwise manner (reaction is vigorous) over approximately ten minutes. Tetrahydrofuran (thf, 5.0 mL) is used to wash off the residue on the sidewall of the flask. The resulting yellow solution is allowed to warm to 22 °C and kept at this temperature for one additional hour before the reactions is quenched at 0 °C through dropwise addition of a saturated solution of Rochelle's salt (sodium potassium tartrate; 10.0 mL) over a period of ten minutes. The mixture is allowed to stir at 22 °C for 30 minutes and layers are separated. The aqueous layer is washed with Et_2O (20.0 mL x 3) and the combined organic layers are dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum to give light yellow oil. Purification with basified (with triethylamine) silica gel chromatography (100% hexanes) affords **12** as light yellow oil (1.26 g, 6.60 mmol, 69% yield). **(1-Bromovinyl)benzene (12, Equation 2):** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.58 (2H, m), 7.37-7.32 (3H, m), 6.12 (1H, d, J = 2.0 Hz), 5.78 (1H, d, J = 2.0 Hz). The spectroscopic data match those reported previously.[22]

■ **Representative Procedure for Ni(dppp)Cl_2 catalyzed Hydroalumination of Terminal Alkynes and Functionalization of the Resulting Vinylaluminum Reagent with MeO-Bpin**:

Commercial grade 1,3-bis(diphenylphosphino)propane nickel(II) chloride (Ni(dppp)Cl_2, 16.3 mg, 0.0300 mmol) is placed in an flame-dried 10 mL round bottom flask equipped with a stir bar and a refluxing condenser. The apparatus is sealed with a septum and purged with N_2 for approximately ten minutes. Tetrahydrofuran (thf, 3.0 mL) is added through a syringe, followed by dropwise addition of dibal–H (232 μL, 1.30 mmol) at 22 °C (gas evolution occurs as dibal–H is added). The resulting black solution is allowed to cool to 0 °C (ice bath) before phenylacetylene (110 μL, 1.00 mmol) is added slowly over five minutes (reaction is exothermic). The resulting black solution is allowed to warm to 22 °C and stir for an additional two hours. After two hours, 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (MeO-Bpin; 492 μL, 3.00 mmol) is added dropwise through a syringe into the reaction solution at 0 °C (ice bath). The resulting solution is allowed to be heated to 80 °C and stir for 24 hours before the reaction is quenched by dropwise addition of water (3.0 mL) at 0 °C (ice bath). The mixture is allowed to warm to 22 °C and stir for one additional hour before it is washed with Et_2O (5.0 mL x 3). The combined organic layers are passed through a plug of anhydrous $MgSO_4$ and concentrated under vacuum to afford yellow oil, which is purified by silica gel chromatography (40/1 hexanes/ethyl acetate) to afford the desired product **13** as colorless oil (173.0 mg, 0.752 mmol, 75% yield). **4,4,5,5-Tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (13, Scheme 3):** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.46 (2H, m), 7.34-7.29 (2H, m), 7.27-7.22 (1H, m), 6.08-6.05 (2H, m), 1.33 (12H, s); HRMS (ESI$^+$): Calcd for $C_{14}H_{20}B_1O_2$ $[M+H]^+$: 231.1556; Found: 231.1568. The spectroscopic data match those reported previously.[23]

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(22) Spaggiari, A.; Vaccari, D.; Davoli, P.; Torre, G.; Prati, F. *J. Org. Chem.* **2007**, *72*, 2216–2219.

(23) Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, *124*, 8001–8006.

2-(1-(3-Fluorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14, Scheme 3): Purification of this compound from a byproduct *iso*butyl-Bpin could be tedious. IR (neat): 2979 (w), 1578 (w), 1372 (m), 1316 (m), 1238 (m), 1142 (s), 933 (w), 868 (m), 844 (w), 788 (w), 743 (w), 673 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (2H, m), 7.24-7.21 (1H, m), 6.96-6.91 (1H, m), 6.11 (2H, bs), 1.33 (12H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, J = 243.3 Hz), 143.7 (d, J = 8.2 Hz), 132.0, 129.6 (d, J = 8.9 Hz), 122.9 (d, J = 2.3 Hz), 114.2 (d, J = 21.6 Hz), 113.8 (d, J = 21.6 Hz), 84.1, 24.9; HRMS (ESI^+): Calcd for $C_{14}H_{19}B_1O_2F_1$ $[M+H]^+$: 249.1462; Found: 249.1472.

2-(1-(2-Chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15, Scheme 3): The compound is prepared as described in the general procedure, except that the reaction is carried out with 5 equivalent of MeOBpin and heated for 48 hours (all characterizations are carried out in the presence of 4% corresponding β isomer). IR (neat): 2979 (m), 2932 (w), 1471 (m), 1371 (s), 1319 (s), 1262 (m), 1210 (m), 1145 (s), 1101 (m), 1046 (m), 966 (m), 849 (m), 745 (m), 698 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (1H, m), 7.25-7.17 (3H, m), 6.12 (1H, bd, J = 3.2 Hz), 5.85 (1H, bd, J = 2.8 Hz), 1.31 (12H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 132.7, 132.7, 129.8, 129.1, 128.4, 127.1, 84.1, 24.9; HRMS (ESI^+): Calcd for $C_{14}H_{19}B_1O_2Cl_1$ $[M+H]^+$: 265.1167; Found: 265.1167.

4,4,5,5-Tetramethyl-2-(oct-1-en-2-yl)-1,3,2-dioxaborolane (16, Scheme 3): The compound is prepared as described in the general procedure, except that the reaction is carried out at 0 °C for 24 h. ^1H NMR (400 MHz, $CDCl_3$): δ 5.75 (1H, d, J = 3.2 Hz), 5.59 (1H, bs), 2.14 (2H, t, J = 7.6 Hz), 1.43-1.36 (2H, m), 1.34-1.22 (6H, m), 1.27 (12H, s), 0.88 (3H, t, J = 6.4 Hz); HRMS (ESI^+): Calcd for $C_{14}H_{28}B_1O_2$ $[M+H]^+$: 239.2182; Found: 239.2188. The spectroscopic data match those reported previously.[24]

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (17, Scheme 3): The compound is prepared as described in the general procedure, except that the reaction is carried out at 22 °C for 24 h. IR (neat): 3422 (br), 2978 (m), 2932 (w), 1617 (w), 1429 (m), 1370 (s), 1309 (s), 1213 (w), 1141 (s), 1048 (m), 948 (w), 863 (m), 672 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.90 (1H, bd, J = 3.6 Hz), 5.71 (1H, bs), 3.68 (2H, t, J = 6.0 Hz), 2.43 (2H, t, J = 6.0 Hz), 2.03 (1H, bs), 1.27 (12H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.5, 83.9, 62.7, 39.5, 24.9; HRMS (ESI^+): Calcd for $C_{10}H_{20}B_1O_3$ $[M+H]^+$: 199.1506; Found: 199.1509.

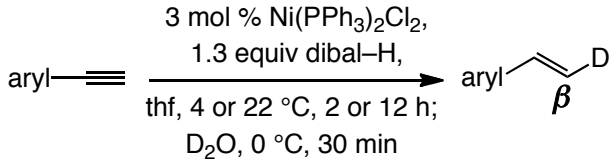
***tert*-Butyldimethyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)oxy)silane (18, Scheme 3):** The compound is prepared as described in the general procedure, except that the reaction is carried out at 22 °C for 24 h. IR (neat): 2954 (w), 2929 (w), 2857 (w), 1369 (m), 1308 (m), 1253 (m), 1142 (s), 1097 (s), 968 (w), 939 (w), 833 (s), 773 (s), 669 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.77 (1H, d, J = 3.6 Hz), 5.61 (1H, bs), 3.60 (2H, t, J = 6.8 Hz), 2.17 (2H, t, J = 8.0 Hz), 1.65 (2H, tt, J = 7.6, 7.6 Hz), 1.26 (12H, s), 0.90 (9H, s), 0.05 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.3, 83.4, 63.1, 32.5, 31.7, 26.1, 24.9, 18.5, -5.1; HRMS (ESI^+): Calcd for

(24) Moran, M. J.; Morken, J. P. *Org. Lett.* **2006**, *8*, 2413–2415.

$C_{17}H_{36}B_1O_3Si_1$ $[M+H]^+$: 327.2527; Found: 327.2540.

■ Tables and Characterizations of the Terminal Vinylaluminums Derived from Hydroalumination of Terminal Alkynes Catalyzed by $Ni(PPh_3)_2Cl_2$:

Table S1. *β*-Selective Ni-Catalyzed Hydroalumination of Arylacetylenes[a]

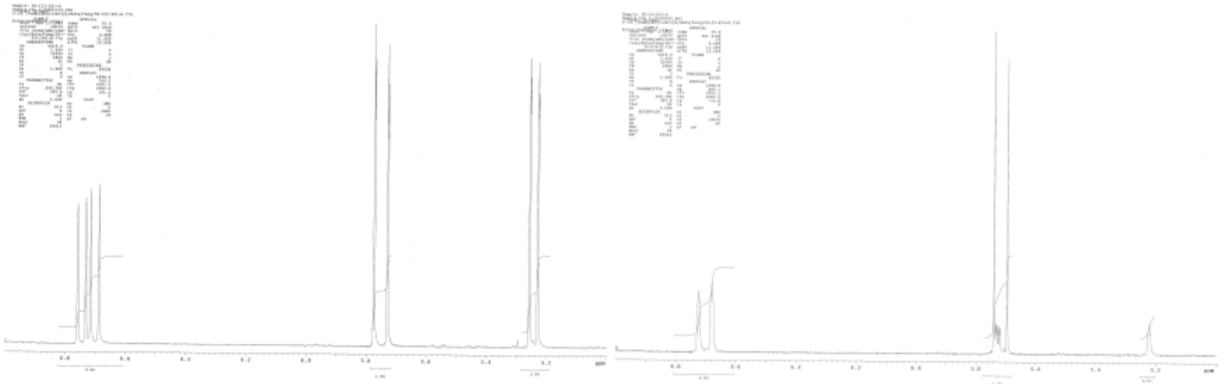


entry	aryl	temp (°C); time (h)[b]	conv (%)[c]	β:α[c]
1	*o*-$OMeC_6H_4$	4; 12	>98	97:3
2	*m*-$OMeC_6H_4$	22; 2	>98	94:6
3	*p*-$OMeC_6H_4$	4; 12	>98	>98:2
4	*m*-$CF_3C_6H_4$	4; 12	>98	98:2
5	*p*-$CF_3C_6H_4$	22; 2	>98	88:12
6	*p*-FC_6H_4	22; 2	>98	92:8
7	*o*-ClC_6H_4	22; 2	>98[d]	95.5:4.5
8	*o*-BrC_6H_4	4; 12	>98[d]	96:4
9	*o*-MeC_6H_4	4; 12	83[d]	>98:2
10	3-pyridyl	22; 2	>98[d]	85.5:14.5
11	3-thienyl	22; 2	>98	96:4

[a] Reactions under N_2 atm. [b] Reaction times correspond to hydroalumination portion of the process (not including D_2O quench). [c] By analysis of 400 MHz ^1H NMR spectra of unpurified mixtures (after D_2O). [d] 5~10% alkynylaluminum oberved.

(*E*)-*β*-Deuteriostyrene (1, Table 1): ^1H NMR (400 MHz, $CDCl_3$): δ 7.43-7.40 (2H, m), 7.34-7.30 (2H, m), 7.27-7.23 (1H, m), 6.70 (1H, bd, J = 17.2 Hz), 5.72 (1H, d, J = 17.2 Hz). The spectroscopic data match those reported previously.[3]

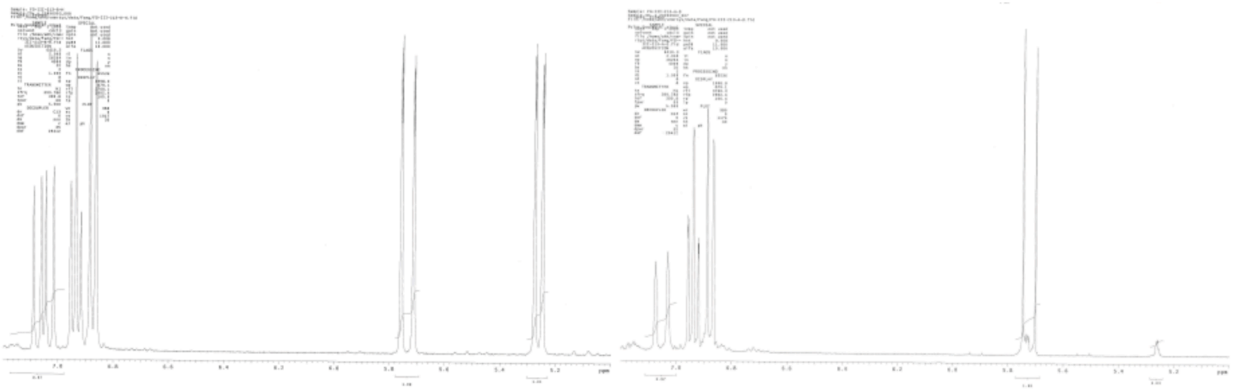
Site selectivity (7:93 α*:β*) was determined by analysis of 400 MHz ^1H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.72	0.93	48.2	1	6.70	0.93	93.0
3	5.24	1.00	51.8	3	5.23	0.07	7.0

(*E*)-*β*-Deuterio-1-methoxy-2-vinylbenzene (Table S1, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (1H, dd, *J* = 7.6, 1.6 Hz), 7.24 (1H, ddd, *J* = 8.0, 8.0, 1.6 Hz), 7.05 (1H, bd, *J* = 17.6 Hz), 6.94 (1H, dd, *J* = 7.6, 7.6 Hz), 6.87 (1H, d, *J* = 8.4 Hz), 5.72 (1H, d, *J* = 18.0 Hz), 3.85 (3H, s). The spectroscopic data match those reported previously.[4]

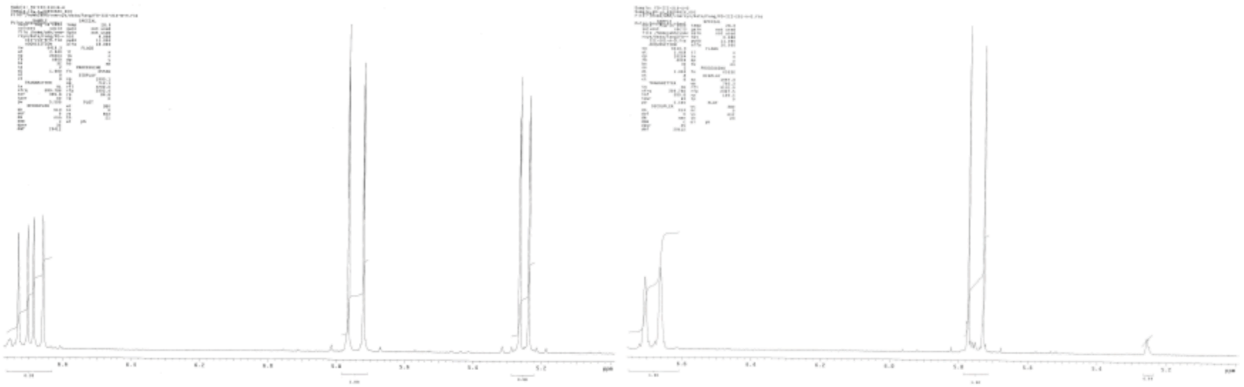
Site selectivity (3:97 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	7.05	0.97	49.0	1	7.05	0.97	97.0
4	5.26	1.01	51.0	4	5.26	0.03	3.0

(*E*)-*β*-Deuterio-1-methoxy-3-vinylbenzene (Table S1, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (1H, dd, *J* = 7.6, 7.6 Hz), 7.02-7.00 (1H, m), 6.95 (1H, dd, *J* = 2.0, 2.0 Hz), 6.82 (1H, ddd, *J* = 8.4, 2.4, 0.8 Hz), 6.69 (1H, bd, *J* = 17.6 Hz), 5.73 (1H, d, *J* = 17.6 Hz), 3.82 (3H, s). The spectroscopic data match those reported previously.[5]

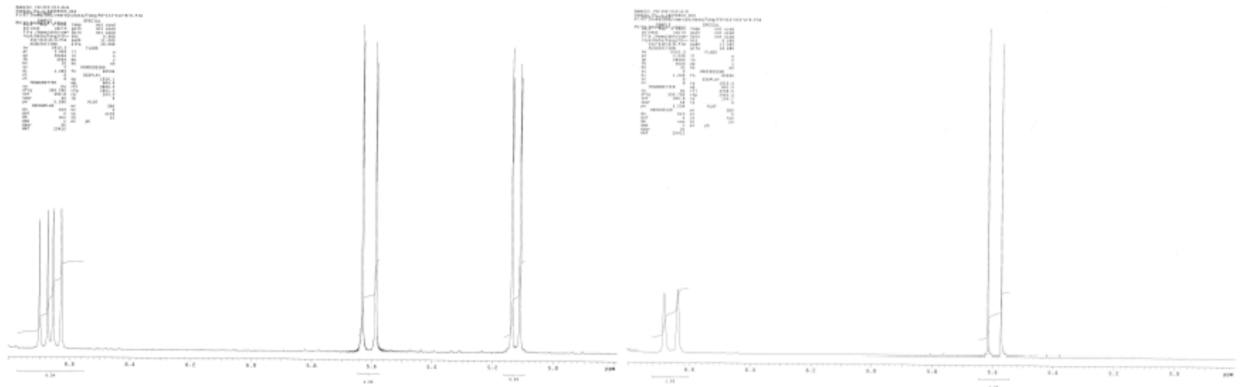
Site selectivity (6:94 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.69	0.99	50.3	1	6.69	1.00	94.3
3	5.25	0.98	49.7	3	5.25	0.06	5.7

(*E*)-*β*-Deuterio-1-methoxy-4-vinylbenzene (Table S1, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (2H, ddd, *J* = 8.8, 2.0, 2.0 Hz), 6.86 (2H, ddd, *J* = 8.8, 2.0, 2.0 Hz), 6.66 (1H, bd, *J* = 17.6 Hz), 5.59 (1H, d, *J* = 17.6 Hz), 3.81 (3H, s). The spectroscopic data match those reported previously.[6]

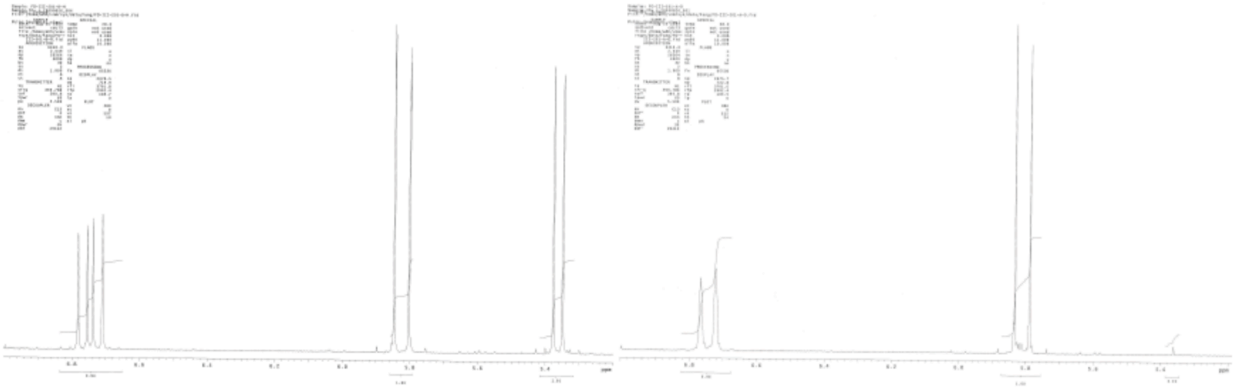
Site selectivity (<2:>98 *α:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.66	0.94	48.7	1	6.66	1.02	>98.0
3	5.12	0.99	51.3	3	5.12	<0.02	<2.0

(*E*)-*β*-Deuterio-1-(trifluoromethyl)-3-vinylbenzene (Table S1, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (1H, s), 7.59-7.56 (1H, m), 7.51 (1H, d, *J* = 8.0 Hz), 7.44 (1H, dd, *J* = 7.6, 7.6 Hz), 6.74 (1H, bd, *J* = 17.6 Hz), 5.81 (1H, d, *J* = 17.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 135.6, 131.1 (q, *J* = 32.0 Hz), 129.5, 129.1, 124.5 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 270.9 Hz), 123.1 (q, *J* = 4.4 Hz), 115.6 (t, *J* = 24.6 Hz); HRMS (ESI^{+}): Calcd for $C_9H_7D_1F_3$ $[M+H]^{+}$: 174.0641; Found: 174.0642.

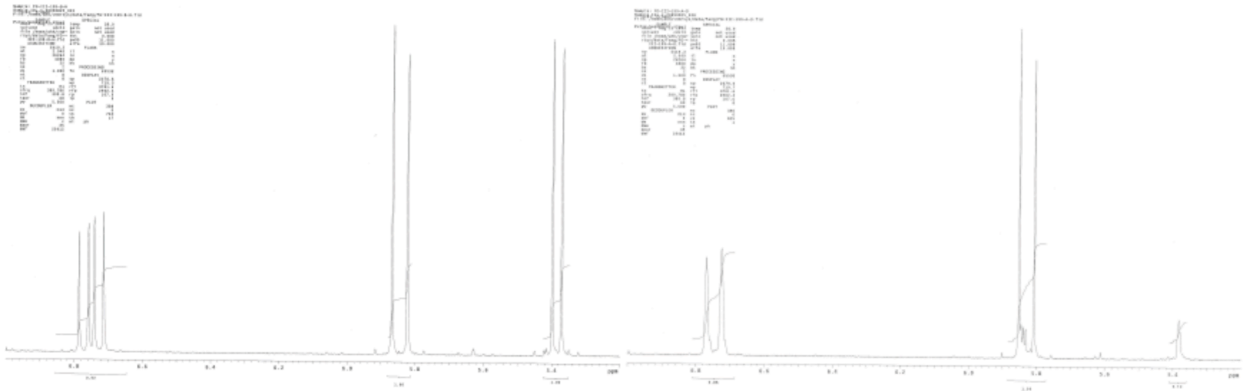
Site selectivity (2:98 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.74	0.94	48.2	1	6.74	0.96	98.0
3	5.36	1.01	51.8	3	5.36	0.02	2.0

(*E*)-*β*-Deuterio-1-(trifluoromethyl)-4-vinylbenzene (Table S1, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (2H, d, *J* = 8.4 Hz), 7.50 (2H, d, *J* = 8.4 Hz), 6.75 (1H, bd, *J* = 17.6 Hz), 5.83 (1H, d, *J* = 17.6 Hz). The spectroscopic data match those reported previously.[7]

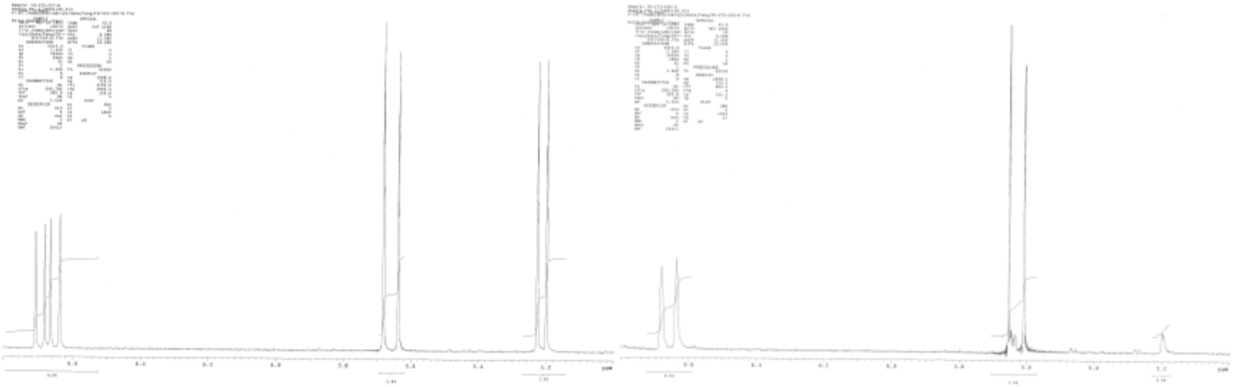
Site selectivity (12:88 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.75	0.92	47.9	1	6.75	0.88	88.0
3	5.39	1.00	52.1	3	5.38	0.12	12.0

(*E*)-*β*-Deuterio-1-fluoro-4-vinylbenzene (Table S1, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (2H, m), 7.03-6.98 (2H, m), 6.66 (1H, bd, *J* = 17.6 Hz), 5.63 (1H, dd, *J* = 17.6, 0.4 Hz). The spectroscopic data match those reported previously.[8]

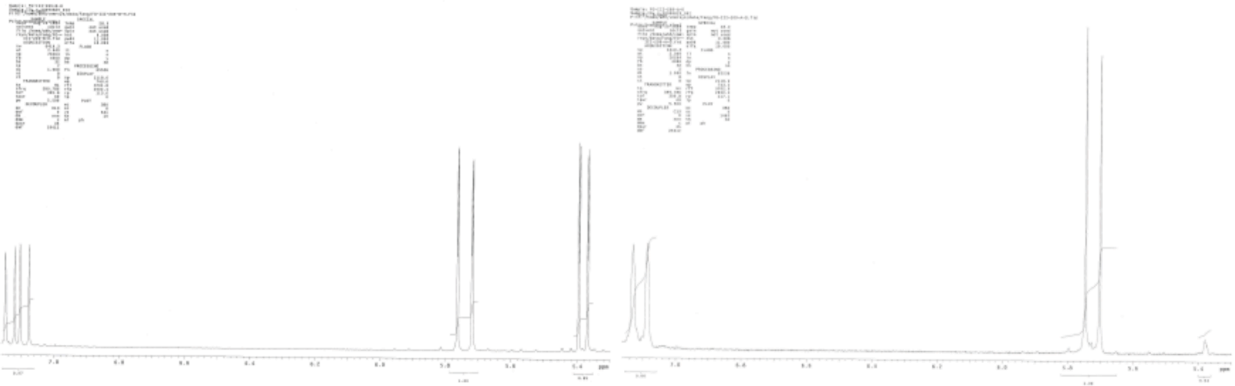
Site selectivity (8:92 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.67	0.96	47.9	1	6.66	0.95	92.2
3	5.21	1.01	52.1	3	5.19	0.08	7.8

(*E*)-β-Deuterio-1-chloro-2-vinylbenzene (Table S1, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (1H, dd, *J* = 7.6, 2.0 Hz), 7.35 (1H, dd, *J* = 7.6, 2.0 Hz), 7.26-7.17 (2H, m), 7.11 (1H, bd, *J* = 17.6 Hz), 5.72 (1H, d, *J* = 18.0 Hz). The spectroscopic data match those reported previously.[9]

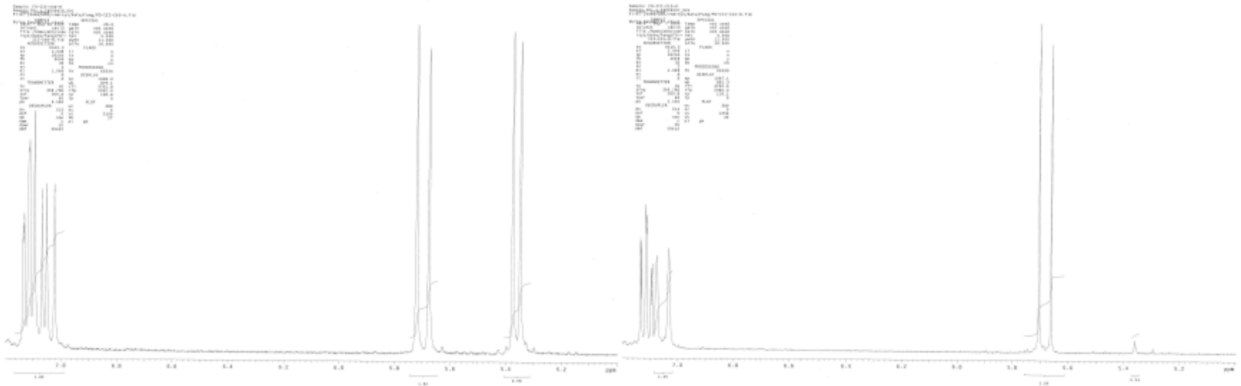
Site selectivity (4.5:95.5 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	7.11	0.97	49.5	1	7.11	0.86	95.5
3	5.38	0.99	50.5	3	5.38	0.04	4.5

(*E*)-β-Deuterio-1-bromo-2-vinylbenzene (Table S1, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (2H, d, *J* = 8.0 Hz), 7.28 (1H, dd, *J* = 8.0, 8.0 Hz), 7.11 (1H, ddd, *J* = 7.6, 7.6, 1.6 Hz), 7.05 (1H, bd, *J* = 17.6 Hz), 5.68 (1H, d, *J* = 17.6 Hz). The spectroscopic data match those reported previously.[10]

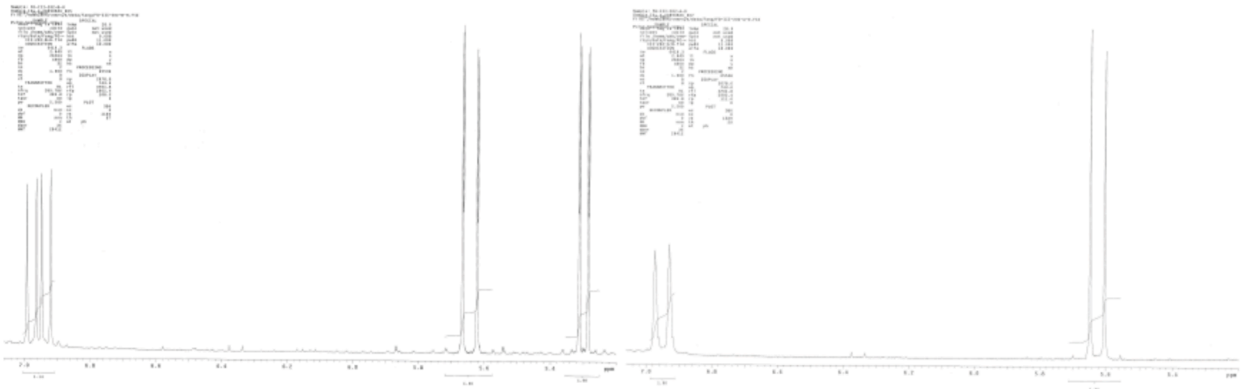
Site selectivity (4:96 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
2	7.05	0.93	48.7	2	7.05	1.05	96.3
4	5.36	0.98	51.3	4	5.36	0.04	3.7

(*E*)-*β*-Deuterio-1-methyl-2-vinylbenzene (Table S1, entry 9): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (1H, m), 7.19-7.15 (3H, m), 6.95 (1H, bd, *J* = 17.6 Hz), 5.63 (1H, d, *J* = 17.2 Hz), 2.36 (3H, s). The spectroscopic data match those reported previously.[11]

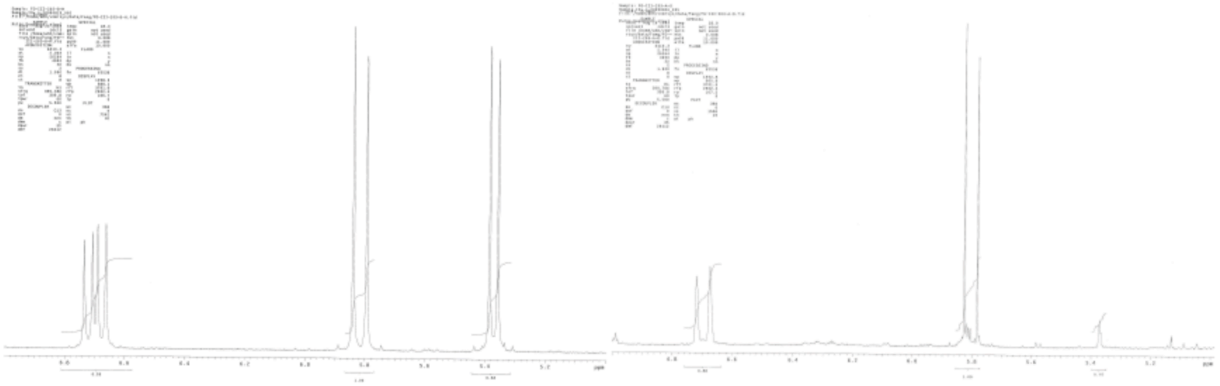
Site selectivity (<2:>98 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.96	1.14	53.3	1	6.95	1.06	>98.0
3	5.30	1.00	46.7	3	5.29	<0.02	<2.0

(*E*)-*β*-Deuterio-3-vinylpyridine (Table S1, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (1H, s), 8.48 (1H, d, *J* = 3.2 Hz), 7.72 (1H, d, *J* = 7.6 Hz), 7.24 (1H, dd, *J* = 7.6, 2.0 Hz), 6.70 (1H, bd, *J* = 17.6 Hz), 5.80 (1H, d, *J* = 17.6 Hz). The spectroscopic data match those reported previously.[12]

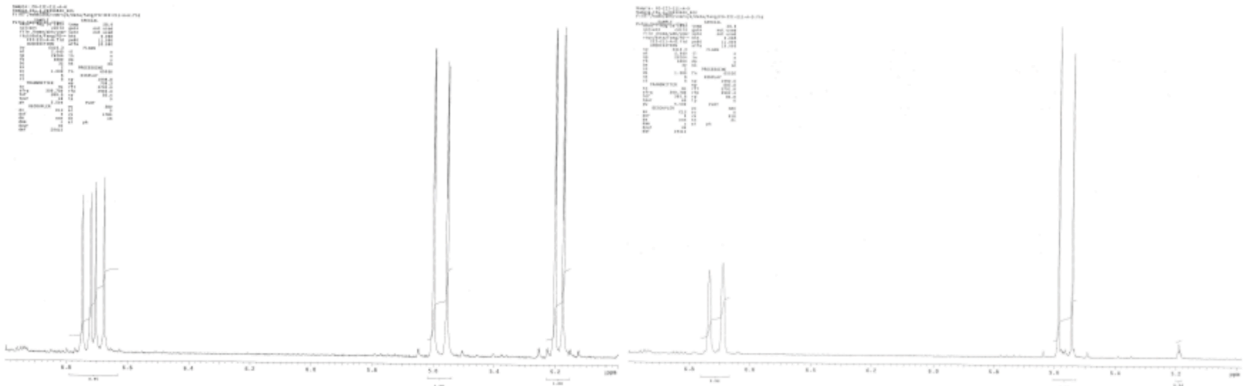
Site selectivity (14.5:85.5 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.70	0.99	50.3	1	6.70	0.88	85.4
3	5.37	0.98	49.7	3	5.38	0.15	14.6

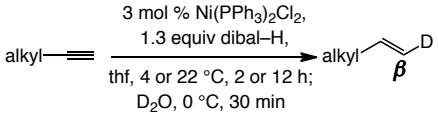
(*E*)-β-Deuterio-3-vinylthiophene (Table S1, entry 11): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.23 (2H, m), 7.18-7.17 (1H, m), 6.71 (1H, bd, *J* = 17.6 Hz), 5.56 (1H, d, *J* = 17.6 Hz). The spectroscopic data match those reported previously.[13]

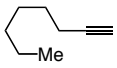
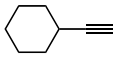
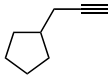
Site selectivity (4:96 α:β) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	6.71	0.95	48.7	1	6.71	0.96	96.0
3	5.19	1.00	51.3	3	5.19	0.04	4.0

Table S2. *β*-Selective Ni-Catalyzed Hydroalumination of Alkylacetylenes[a]

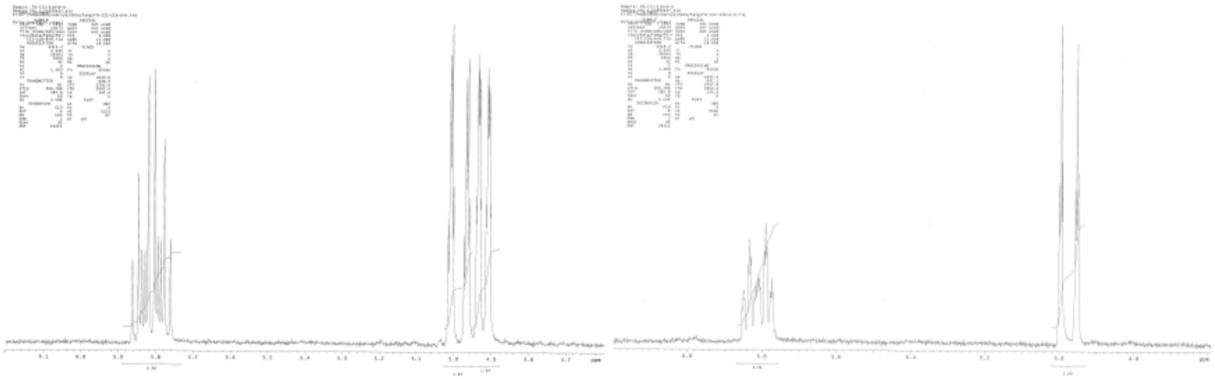


entry	substrate	temp (°C); time (h)[b]	conv (%)[c]	β:α[c]
1		22; 2	95	>98:2
2		4; 12	94	>98:2
3		22; 2	>98	>98:2
4		22; 2	>98	>98:2
5		22; 2	>98	>98:2

[a] Reactions under N_2 atm. [b] Reaction times correspond to hydroalumination portion of the process (not including D_2O quench). [c] By analysis of 400 MHz ^{1}H NMR spectra of unpurified mixtures (after D_2O).

(*E*)-1-Deuterio-oct-1-ene (Table S2, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85-5.77 (1H, m), 4.98 (1H, dt, *J* = 17.2, 1.6 Hz), 2.04 (2H, dtt, *J* = 7.6, 7.6, 1.2 Hz), 1.39-1.24 (8H, m), 0.88 (3H, t, *J* = 6.4 Hz). The spectroscopic data match those reported previously.[14]

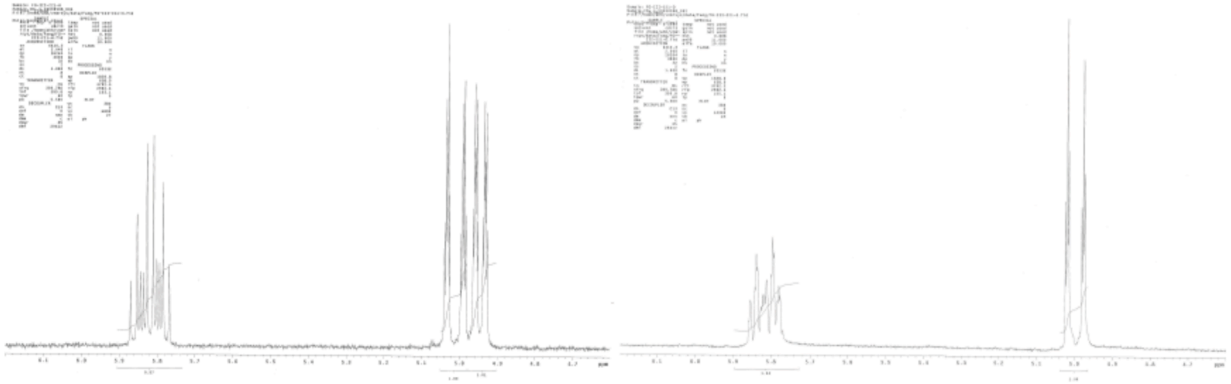
Site selectivity (<2:>98 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.81	0.98	48.5	1	5.81	0.98	>98.0
3	4.92	1.04	51.5	3	4.92	<0.02	<2.0

(*E*)-*tert*-Butyldimethyl(5-deuterio-pent-4-en-1-yloxy)silane (Table S2, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86-5.78 (1H, m), 5.00 (1H, dt, *J* = 16.8, 1.6 Hz), 3.61 (2H, t, *J* = 6.4 Hz), 2.10 (2H, dtt, *J* = 7.2, 7.2, 1.2 Hz), 1.64-1.57 (2H, m), 0.89 (9H, s), 0.04 (6H, s). The spectroscopic data match those reported previously.[16]

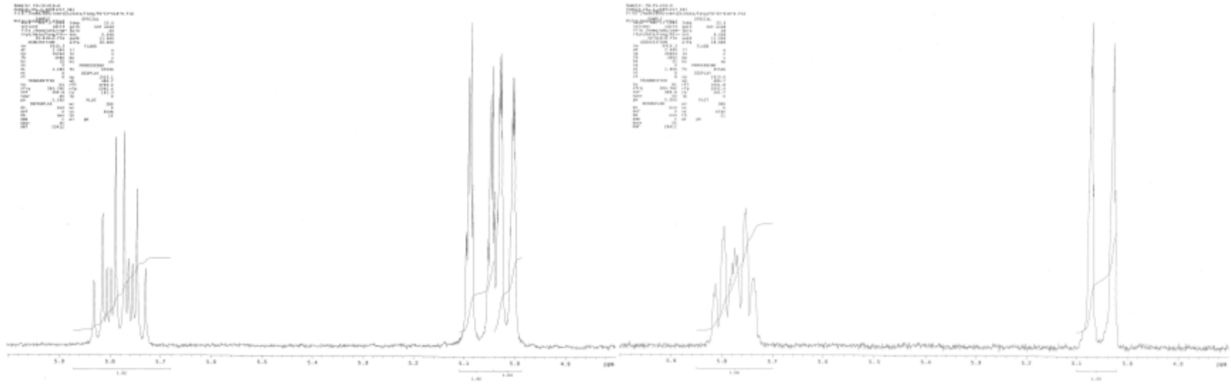
Site selectivity (<2:>98 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.82	0.97	48.5	1	5.82	1.04	>98.0
3	4.95	1.01	51.5	3	4.95	<0.02	<2.0

(*E*)-1-Deuterio-5-chloropent-1-ene (Table S2, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81-5.74 (1H, m), 5.05 (1H, dt, *J* = 17.2, 1.6 Hz), 3.55 (2H, t, *J* = 6.4 Hz), 2.21 (2H, dt, *J* = 6.8, 6.8 Hz), 1.89-1.84 (2H, m). The spectroscopic data match those reported previously.[17]

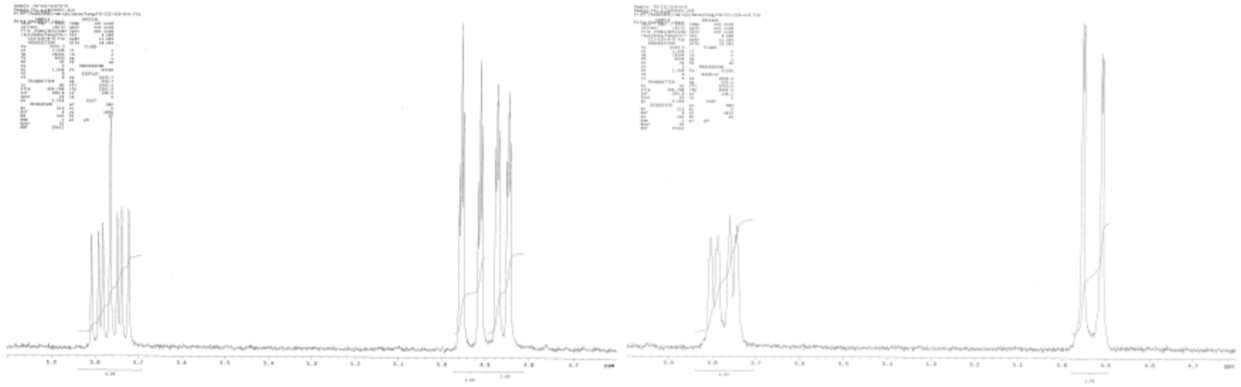
Site selectivity (<2:>98 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.78	1.02	49.5	1	5.78	1.08	>98.0
3	5.01	1.04	50.5	3	5.01	<0.02	<2.0

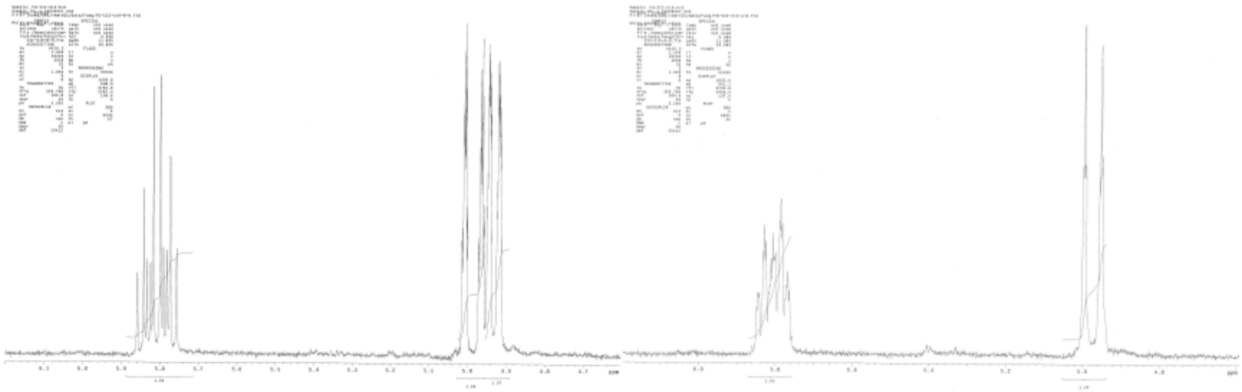
(*E*)-(2-Deuteriovinyl)cyclohexane (Table S2, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (1H, dd, *J* = 17.2, 6.0 Hz), 4.93 (1H, dd, *J* = 17.6, 1.6Hz), 1.97-1.89 (1H, m), 1.73-1.58 (4H, m), 1.31-1.02 (6H, m). The spectroscopic data match those reported previously.[18]

Site selectivity (<2:>98 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



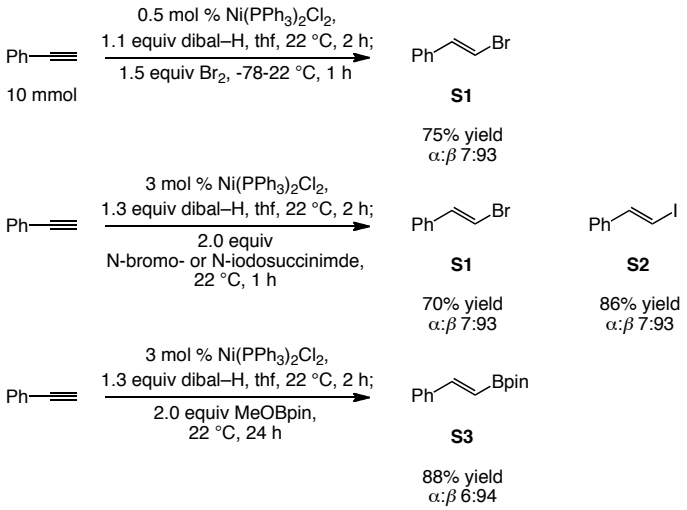
Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.77	0.98	48.3	1	5.78	1.01	>98.0
3	4.86	1.05	51.7	3	4.87	<0.02	<2.0

(*E*)-(3-deuterioallyl)cyclopentane (Table S2, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85-5.77 (1H, m), 4.97 (1H, dt, *J* = 17.2, 1.2 Hz), 2.05 (2H, dd, *J* = 6.8, 6.8 Hz), 1.77-1.69 (1H, m), 1.63-1.48 (6H, m), 1.17-1.09 (2H, m). The spectroscopic data match those reported previously.[20] Site selectivity (<2:>98 α*:β*) was determined by analysis of 400 MHz ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



Peak #	Chemical shift (ppm)	Area	Area (%)	Peak #	Chemical shift (ppm)	Area	Area (%)
1	5.81	1.00	48.3	1	5.81	1.05	>98.0
3	4.93	1.07	51.7	3	4.93	<0.02	<2.0

Scheme S1. *Functionalization of Terminal Vinylaluminum Reagents*



■ **Representative Procedure for Catalytic Hydroalumination of Terminal Alkynes with $Ni(PPh_3)_2Cl_2$ and Functionalization of the Resulting *Terminal* Vinylaluminum Reagent with Bromine**: Commercial grade bis(triphenylphosphine)nickel dichloride ($Ni(PPh_3)_2Cl_2$, 32.7 mg, 0.0500 mmol) is placed in a flame-dried 50 mL round bottom flask equipped with a stir bar. The flask is sealed with a septum and purged with N_2 for approximately ten minutes. Tetrahydrofuran (thf, 10.0 mL) is added through a syringe, followed by dropwise addition of dibal–H (1.96 mL, 11.0 mmol) at 22 °C (gas evolution occurs as dibal–H is added). The resulting black solution is allowed to cool to 0 °C (ice bath) before phenylacetylene (1.10 mL, 10.0 mmol) is added slowly over five minutes (reaction is exothermic). The resulting black solution is allowed to warm to 22 °C and stir for additional six hours. The solution is allowed to cool to –78 °C (dry ice-acetone bath), and bromine (Br_2; 0.771 mL, 15.0 mmol) is added through a syringe slowly in a dropwise manner (vigorous reaction occurs) over a period of approximately ten minutes. Tetrahydrofuran (thf, 5.0 mL) is used to wash off the residue on the sidewall of the flask. The resulting light brown solution is allowed to warm to 22 °C and kept at this temperature for one hour before the reaction is quenched at 0 °C through dropwise addition of a saturated solution of Rochelle's salt (sodium potassium tartrate; 10.0 mL) over ten minutes. The mixture is allowed to stir at 22 °C for 30 minutes and the layers are separated. The aqueous layer is washed with Et_2O (20.0 mL x 3) and the combined organic layers are dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum to furnish yellow oil, which is purified through silica gel chromatography (100% hexanes) to afford **S1** as light yellow oil in 75% yield (1.37g, 7.48 mmol) and as a 93:7 mixture (**S1**:**12**). **(*E*)-(2-bromovinyl)benzene (S1, Scheme S1):** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.27 (5H, m), 7.11 (1H, d, J = 13.6 Hz), 6.77 (1H, d, J = 14.0 Hz); The spectroscopic data match those reported previously.[25]

(*E*)-(2-iodovinyl)benzene (S2, Scheme S1): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (1H, d, J = 14.8 Hz), 7.35-7.26 (5H, m), 6.83 (1H, d, J = 14.8 Hz); HRMS (ESI$^+$): Calcd for $C_8H_8I_1$ $[M+H]^+$:

(25) Bull, J. A.; Mousseau, J. J.; Charette, A. B. *Org. Lett.* **2008**, *10*, 5485–5488.

230.9671; Found: 230.9672. The spectroscopic data match those reported previously.[3]

(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (S3, Scheme S1): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.47 (2H, m), 7.40 (1H, d, J = 18.4 Hz), 7.36-7.29 (3H, m), 6.17 (1H, d, J = 18.4 Hz), 1.32 (12H, s); HRMS (ESI$^+$): Calcd for $C_{14}H_{20}B_1O_2$ $[M+H]^+$: 231.1556; Found: 231.1549. The spectroscopic data match those reported previously.[26]

(26) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482–3485.