

Stereoselective Synthesis of Trisubstituted Alkenylboranes by Palladium-Catalysed Reaction of Alkynyltriarylborates with Aryl Halides

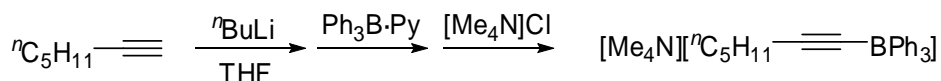
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Katsura, Kyoto 615-8510, Japan*

General. NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300 MHz and ^{13}C at 75 MHz) or Varian Mercury-400 (^1H at 400 MHz and ^{11}B at 128 MHz) spectrometers. Unless otherwise noted, CDCl_3 was used as a solvent. Me_4Si (^1H , $\delta=0.00$), residual H of CD_3CN (^1H in CD_3CN , $\delta=1.94$), CDCl_3 (^{13}C , $\delta=77.0$), CD_3CN (^{13}C , $\delta=1.32$), and $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B , $\delta=0.00$) were used as standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. UV-vis spectra were recorded on a JASCO V-550S. All reactions were carried out under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF₂₅₄ (Merck). Gel permeation chromatography (GPC) was carried out with Japan Analytical Industry LC-908.

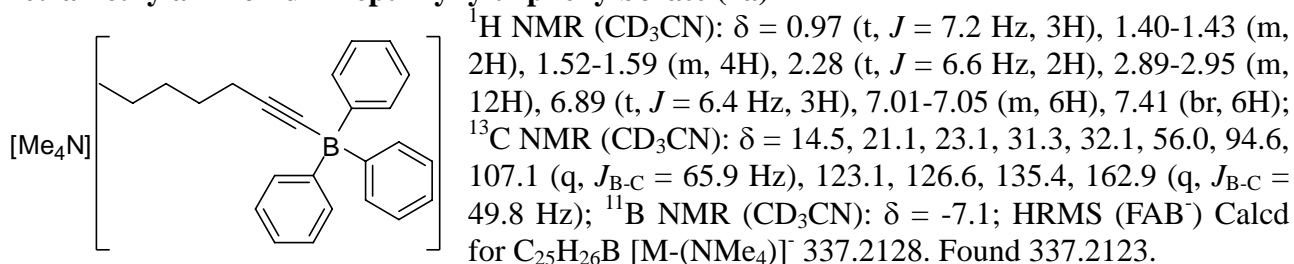
Materials. Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. CH_2Cl_2 was purchased from Kanto chemicals. $(\text{CH}_2\text{Cl})_2$ was dried over CaH_2 . $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$ was prepared according to the reported procedures.¹ AcOH and AcOD were degassed by sonication. $\text{Ar}_3\text{B}\cdot\text{Py}$ were prepared from thermolysis of $\text{Ar}_4\text{B}\cdot\text{HPy}$, which is prepared from ArLi and $\text{BF}_3\cdot\text{OEt}_2$ ² or ArMgBr and $\text{B}(\text{OMe})_3$,³ followed by cation exchange with $\text{Py}\cdot\text{HCl}$ in water. Aryl iodide **4** was prepared according to reported procedures.⁴

Preparation of alkynyltriarylborate 1a. A typical procedure for the preparation of alkynyltriarylborates.

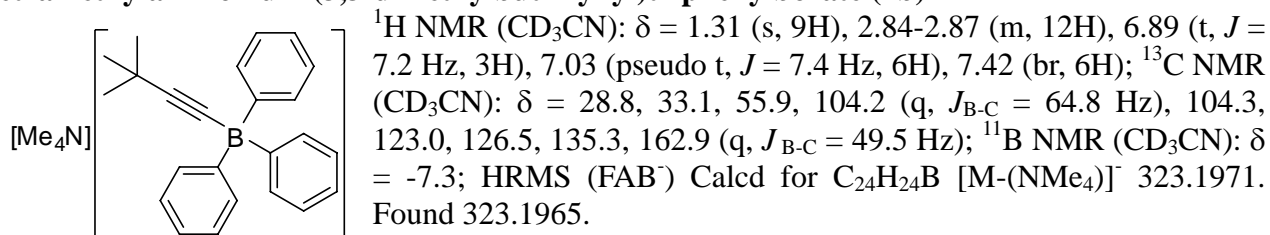


To a stirred solution of hept-1-yne (580 mg, 6.0 mmol) in THF (20 ml) at $-78\text{ }^\circ\text{C}$ was added $n\text{-BuLi}$ (1.6M in hexane, 3.4 ml, 5.5 mmol). After 30 minutes at this temperature, $\text{Ph}_3\text{B}\cdot\text{Py}$ (1.61 g, 5.0 mmol) was added and the cooling bath was removed. After being stirred for 1 h at room temperature, the reaction was quenched by adding a small amount of MeOH . Volatile materials were removed under reduced pressure and the residue was dissolved in MeOH . Me_4NCl (1.1g, 10 mmol) was added with stirring, resulting white solid. It was collected by filtration and was washed with cold MeOH to give alkynyltriarylborate **1a** (1.95 g, 4.7 mmol, 95% yield).

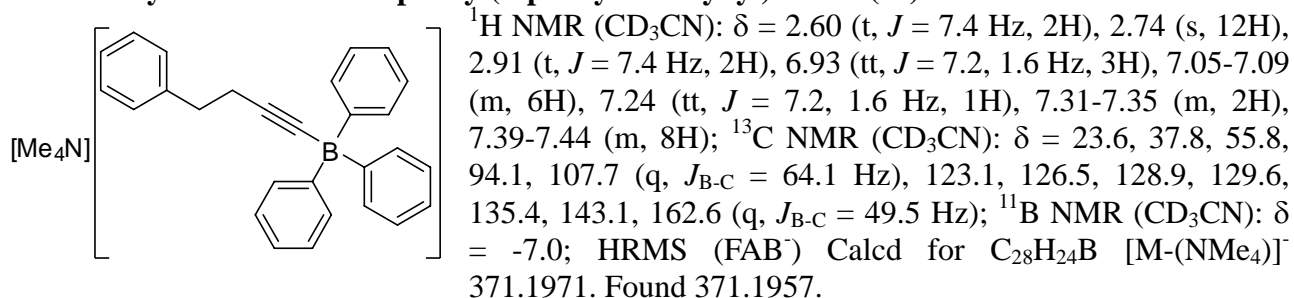
Tetramethylammonium hept-1-ynyltriphenylborate (1a)



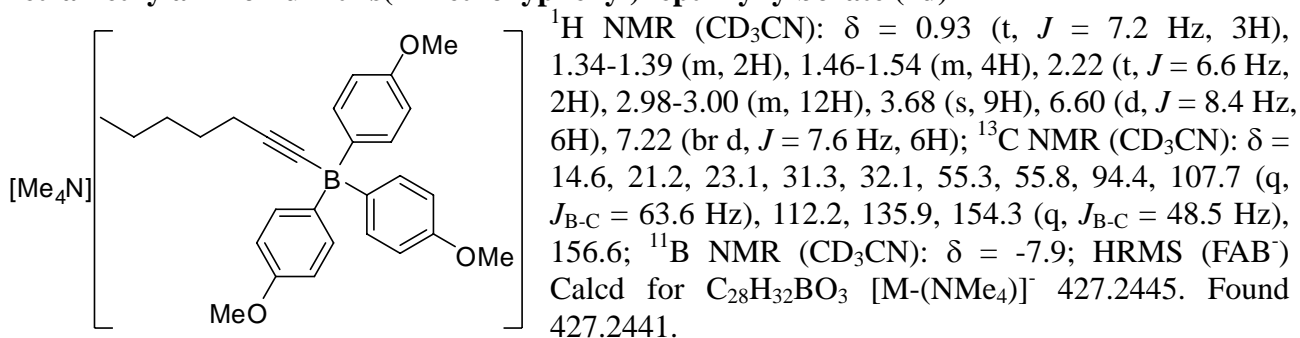
Tetramethylammonium (3,3-dimethylbut-1-ynyl)triphenylborate (1b)



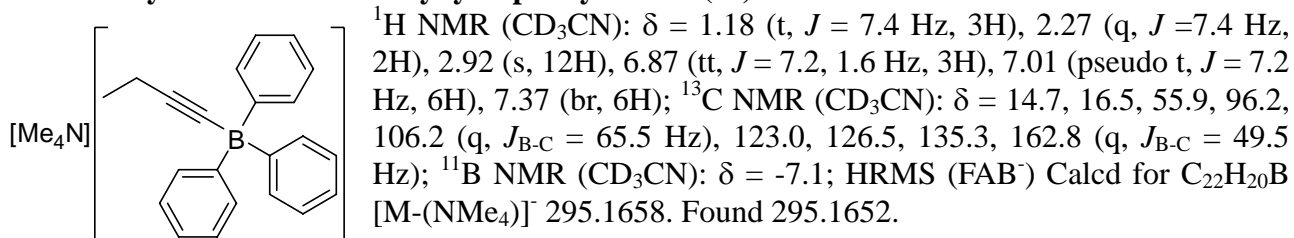
Tetramethylammonium triphenyl(4-phenylbut-1-ynyl)borate (1c)



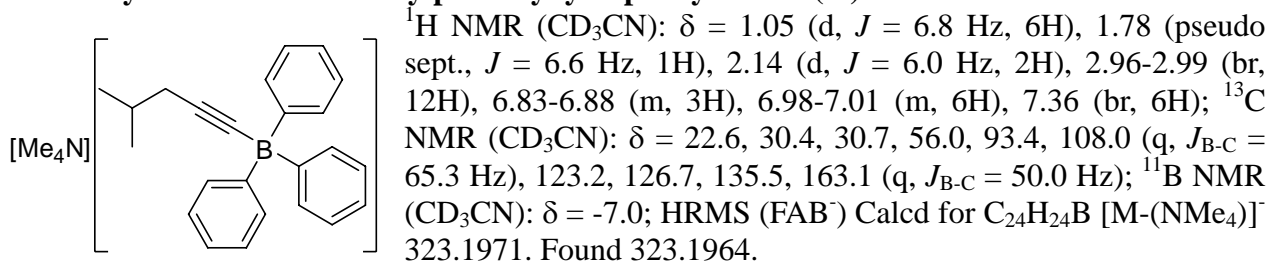
Tetramethylammonium tris(4-methoxyphenyl)hept-1-ynylborate (1d)



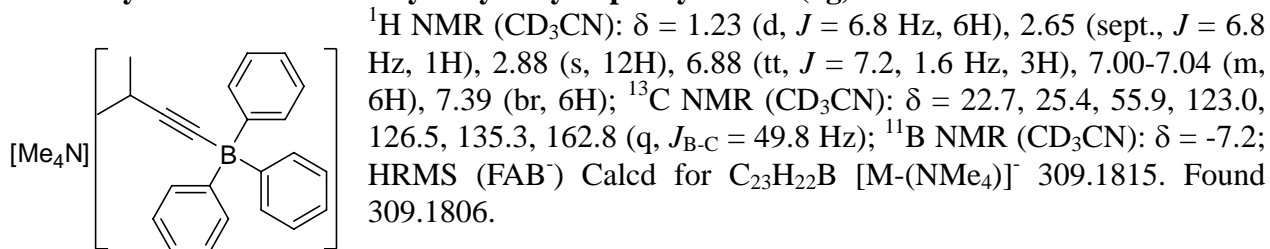
Tetramethylammonium but-1-ynyltriphenylborate (1e)



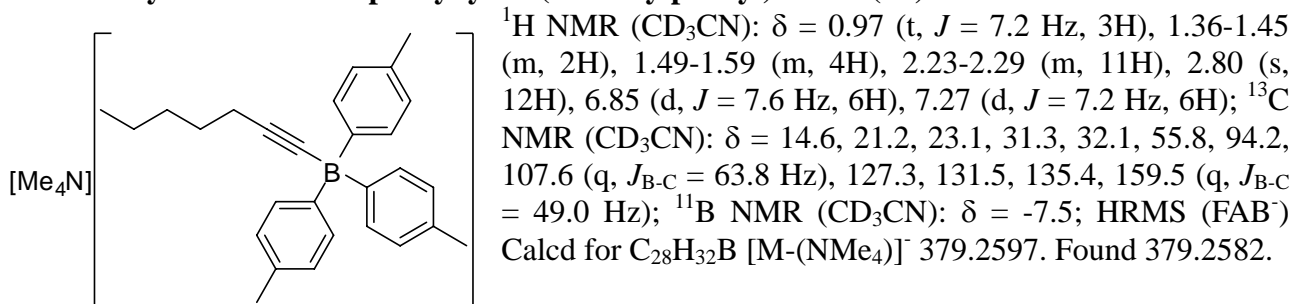
Tetramethylammonium 4-methylpent-1-ynyltriphenylborate (1f)



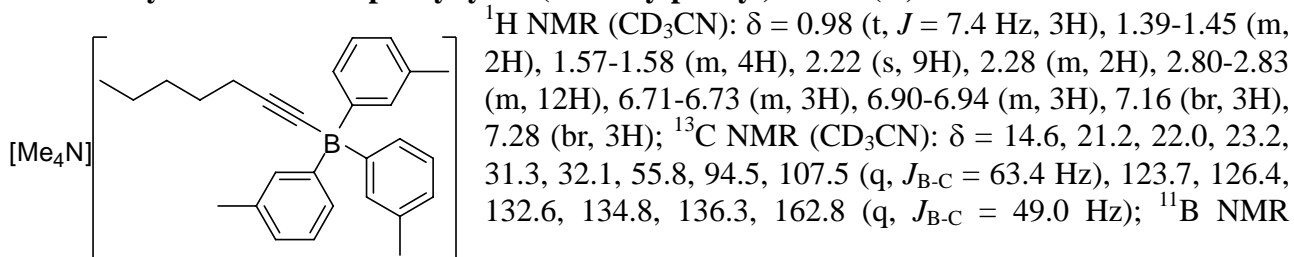
Tetramethylammonium 3-methylbutyn-1-yltriphenylborate (1g)



Tetramethylammonium hept-1-ynyltris(4-methylphenyl)borate (1h)

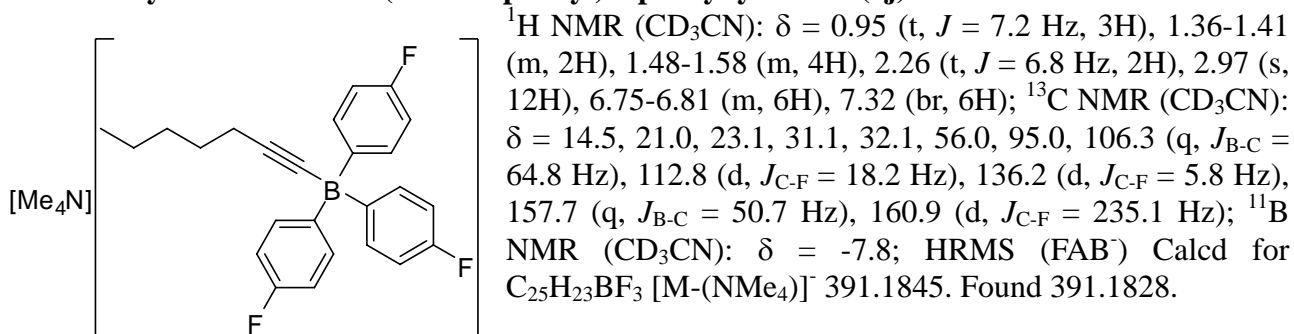


Tetramethylammonium hept-1-ynyltris(3-methylphenyl)borate (1i)

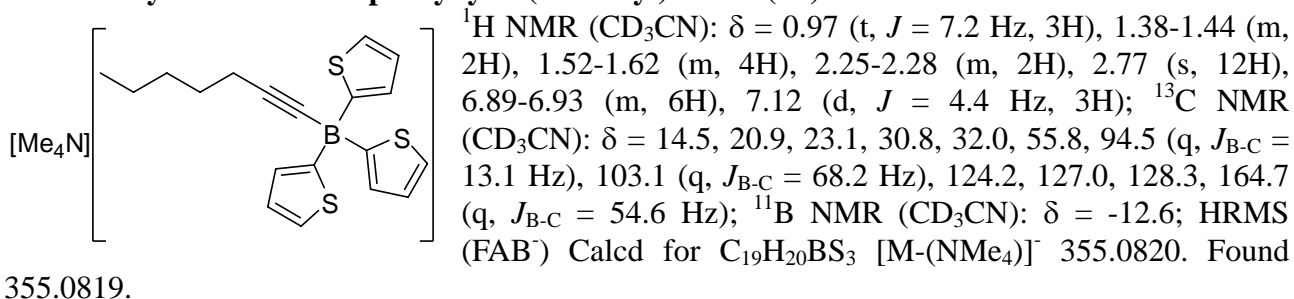


(CD₃CN): $\delta = -7.2$; HRMS (FAB⁻) Calcd for C₂₈H₃₂B [M-(NMe₄)]⁻ 379.2597. Found 379.2600.

Tetramethylammonium tris(4-fluorophenyl)hept-1-ynylborate (1j)



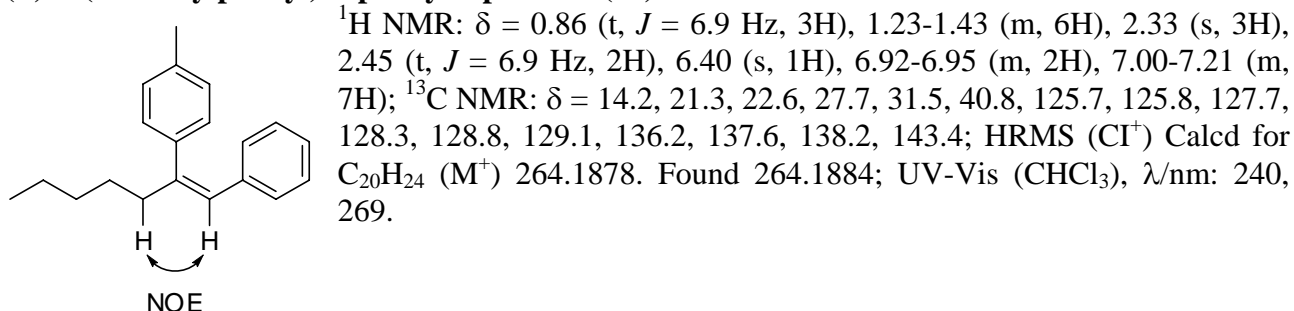
Tetramethylammonium hept-1-ynyltri(2-thienyl)borate (1k)



Palladium-catalysed reaction of alkynyltriarylborate 1a with 4-bromotoluene. A typical procedure for the palladium-catalysed reaction of alkynyltriarylborates with aryl halides.

Under an argon atmosphere, a CH₂Cl₂ solution (0.5 ml) of alkynyltriarylborate **1a** (82.2 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (5.2 mg, 2.5 μ mol), and P(*o*-tol)₃ (3.6 mg, 6.0 μ mol) was stirred for 30 minutes at room temperature. To the solution was added 4-bromotoluene (34.2 mg, 0.20 mmol) in CH₂Cl₂ (0.5 ml). After being stirred for 3 h, AcOH (1 ml) was added. After 3 h, the reaction mixture was neutralized with Na₂CO₃ solution. The aqueous layer was extracted with Et₂O (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane) to afford the trisubstituted alkene **3a** with a small amount of impurities. Further purification was performed by GPC, affording the alkene **3a** (46.9 mg, 0.18 mmol, 89% yield, *E/Z* = 7/93).

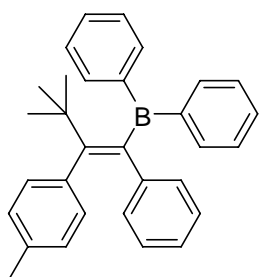
(Z)-2-(4-Methylphenyl)-1-phenylhept-1-ene (3a)



Preparation of trisubstituted alkenylborane **2b**

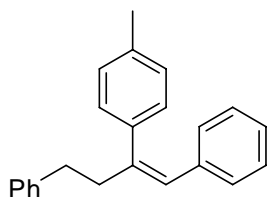
Under an argon atmosphere, a (CH₂Cl)₂ solution (0.5 ml) of alkynyltriarylborate **1b** (79.5 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (5.1 mg, 2.5 μmol), and P(*o*-tol)₃ (3.7 mg, 6.0 μmol) was stirred for 30 minutes at room temperature. To the solution was added 4-bromotoluene (35.0 mg, 0.20 mmol) in (CH₂Cl)₂ (0.5 ml). After being stirred at reflux for 3 h, water was added. The aqueous later was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane) to afford the trisubstituted alkenylborane **2b** (76.0 mg, 0.18 mmol, 92% yield).

(*Z*)-3,3-Dimethyl-2-(4-methylphenyl)-1-phenyl-1-diphenylborylbut-1-ene (**2b**)



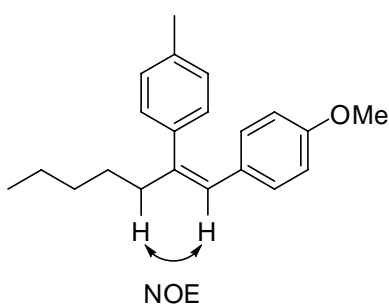
¹H NMR (CD₃CN): δ = 1.13 (s, 9H), 2.18 (s, 3H), 6.74-6.81 (m, 5H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 7.43-7.49 (m, 6H) 7.95 (d, *J* = 7.8 Hz, 4H); ¹³C NMR: δ = 21.1, 31.8, 37.8, 124.7, 127.1, 127.2, 127.5, 130.9, 131.1, 131.4, 134.4, 138.1, 139.0, 140.2, 141.2, 152.7; ¹¹B NMR: δ = 63.7; HRMS (CI⁺) Calcd for C₃₁H₃₁B (M⁺) 414.2519. Found 414.2526; UV-Vis (CHCl₃), λ/nm: 244, 275.

(*Z*)-2-(4-Methylphenyl)-1,4-diphenylbut-1-ene (**3c**)



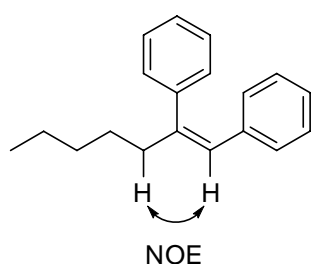
¹H NMR: δ = 2.35 (s, 3H), 2.68-2.79 (m, 4H), 6.37 (s, 1H), 6.90-6.92 (m, 2H), 7.01-7.30 (m, 12H); ¹³C NMR: δ = 21.3, 34.6, 42.6, 125.7, 126.0, 126.4, 127.7, 128.2, 128.38, 128.45, 128.9, 129.2, 136.5, 137.4, 137.7, 141.8, 142.1; HRMS (CI⁺) Calcd for C₂₃H₂₂ (M⁺) 298.1721. Found 298.1720.

(*Z*)-1-(4-Methoxyphenyl)-2-(4-methylphenyl)hept-1-ene (**3d**)



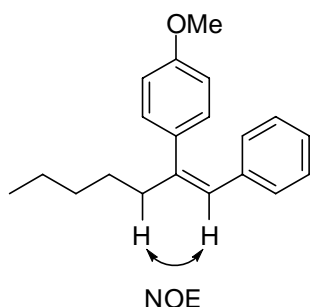
¹H NMR: δ = 0.86 (t, *J* = 6.9 Hz, 3H), 1.26-1.40 (m, 6H), 2.34 (s, 3H), 2.43 (t, *J* = 7.1 Hz, 2H), 3.71 (s, 3H), 6.33 (s, 1H), 6.63 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H); ¹³C NMR: δ = 14.2, 21.3, 22.6, 27.7, 31.5, 40.8, 55.1, 113.1, 125.1, 128.3, 129.1, 129.9, 130.2, 136.1, 138.4, 141.4, 157.6; HRMS (CI⁺) Calcd for C₂₁H₂₆O (M⁺) 294.1984. Found 294.1988; UV-Vis (CHCl₃), λ/nm: 240, 276.

(*Z*)-1,2-Diphenylhept-1-ene (**3e**)



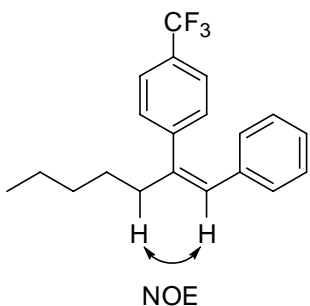
¹H NMR: δ = 0.87 (t, *J* = 7.1 Hz, 3H), 1.26-1.45 (m, 6H), 2.48 (t, *J* = 7.1 Hz, 2H), 6.42 (s, 1H), 6.89-6.92 (m, 2H), 7.03-7.32 (m, 8H); ¹³C NMR: δ = 14.2, 22.6, 27.6, 31.5, 40.7, 125.92, 125.95, 126.7, 127.7, 128.35, 128.43, 128.9, 137.4, 141.3, 143.4; HRMS (CI⁺) Calcd for C₁₉H₂₂ (M⁺) 250.1721. Found 250.1722.

(Z)-2-(4-Methoxyphenyl)-1-phenylhept-1-ene (3f)



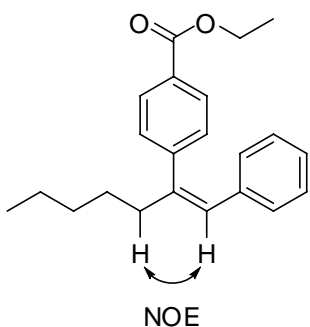
$^1\text{H NMR}$: δ = 0.87 (t, J = 7.2 Hz, 3H), 1.26-1.41 (m, 6H), 2.45 (t, J = 6.9 Hz, 2H), 3.80 (s, 3H), 6.39 (s, 1H), 6.81-6.84 (m, 2H), 6.92-6.96 (m, 2H), 7.03-7.09 (m, 5H); $^{13}\text{C NMR}$: δ = 14.2, 22.6, 27.7, 31.5, 40.7, 55.1, 113.7, 125.7, 125.8, 127.7, 128.8, 129.5, 133.3, 137.7, 143.0, 158.3; HRMS (CI^+) Calcd for $\text{C}_{20}\text{H}_{24}\text{O}$ (M^+) 280.1827. Found 280.1823; UV-Vis (CHCl_3), λ/nm : 240, 274.

(Z)-2-(4-Trifluoromethylphenyl)-1-phenylhept-1-ene (3g)



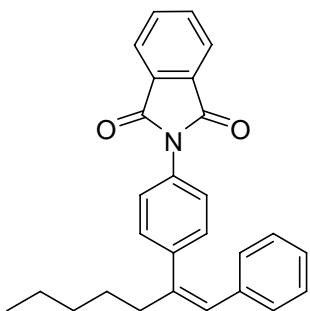
$^1\text{H NMR}$: δ = 0.87 (t, J = 7.1 Hz, 3H), 1.26-1.43 (m, 6H), 2.49 (t, J = 6.9 Hz, 2H), 6.51 (s, 1H), 6.84-6.93 (m, 2H), 7.06-7.14 (m, 3H), 7.26 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H); $^{13}\text{C NMR}$: δ = 14.2, 22.6, 27.6, 31.4, 40.3, 124.1 (q, $J_{\text{C-F}}$ = 270.2 Hz), 125.3 (q, $J_{\text{C-F}}$ = 3.7 Hz), 126.4, 127.2, 127.9, 128.4 (q, $J_{\text{C-F}}$ = 24.1 Hz), 128.91, 128.93, 136.8, 141.9, 145.2; HRMS (CI^+) Calcd for $\text{C}_{20}\text{H}_{21}\text{F}_3$ (M^+) 318.1595. Found 318.1597; UV-Vis (CHCl_3), λ/nm : 240.

(Z)-2-(4-Ethoxycarbonylphenyl)-1-phenylhept-1-ene (3h)



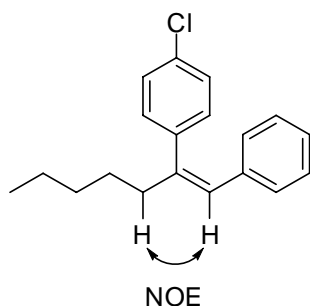
$^1\text{H NMR}$: δ = 0.86 (t, J = 7.1 Hz, 3H), 1.27-1.43 (m, 9H), 2.49 (t, J = 7.1 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 6.49 (s, 1H), 6.88-6.91 (m, 2H), 7.05-7.12 (m, 3H), 7.22 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 8.1 Hz, 2H); $^{13}\text{C NMR}$: δ = 14.1, 14.4, 22.5, 27.6, 31.4, 40.3, 60.9, 126.2, 126.9, 127.8, 128.6, 128.7, 128.9, 129.6, 136.9, 142.4, 146.3, 166.4; HRMS (CI^+) Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_2$ (M^+) 322.1933. Found 322.1925.

(Z)-1-Phenyl-2-(4-phthalimidophenyl)hept-1-ene (3i)



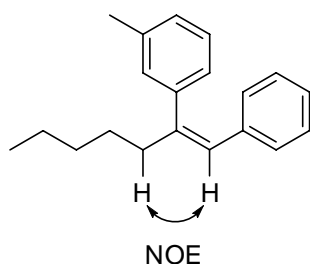
$^1\text{H NMR}$: δ = 0.89 (t, J = 6.9 Hz, 3H), 1.26-1.47 (m, 6H), 2.50 (t, J = 7.4 Hz, 2H), 6.48 (s, 1H), 6.96-6.99 (m, 2H), 7.04-7.15 (m, 3H), 7.27-7.31 (m, 2H), 7.38-7.42 (m, 2H), 7.75-7.81 (m, 2H), 7.92-7.98 (m, 2H); $^{13}\text{C NMR}$: δ = 14.2, 22.5, 27.7, 31.5, 40.5, 123.6, 126.1, 126.7, 127.8, 128.9, 129.1, 130.2, 131.6, 134.3, 137.1, 141.0, 142.3, 167.1; HRMS (CI^+) Calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_2$ (M^+) 395.1885. Found 395.1884; UV-Vis (CHCl_3), λ/nm : 241.

(Z)-2-(4-Chlorophenyl)-1-phenylhept-1-ene (3j)



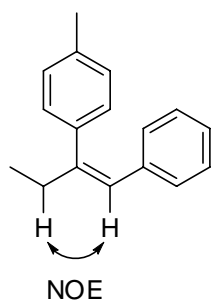
$^1\text{H NMR}$: δ = 0.87 (t, J = 7.1 Hz, 3H), 1.25-1.39 (m, 6H), 2.45 (t, J = 7.4 Hz, 2H), 6.44 (s, 1H), 6.91 (m, 2H), 7.07-7.11 (m, 5H), 7.25 (m, 2H); $^{13}\text{C NMR}$: δ = 14.2, 22.6, 27.6, 31.4, 40.4, 126.2, 126.6, 127.8, 128.6, 128.9, 129.9, 132.4, 137.1, 139.6, 142.0; HRMS (CI^+) Calcd for $\text{C}_{19}\text{H}_{21}\text{Cl}$ (M^+) 284.1332. Found 284.1328.

(Z)-2-(3-Methylphenyl)-1-phenylhept-1-ene (3k)



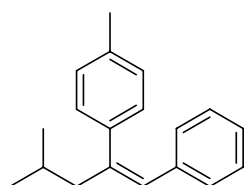
$^1\text{H NMR}$: δ = 0.87 (t, J = 7.1 Hz, 3H), 1.26-1.42 (m, 6H), 2.30 (s, 3H), 2.45 (t, J = 7.4 Hz, 2H), 6.39 (s, 1H), 6.90-7.08 (m, 8H), 7.17 (t, J = 7.5 Hz, 1H); $^{13}\text{C NMR}$: δ = 14.2, 21.6, 22.6, 27.7, 31.5, 40.9, 125.5, 125.7, 125.9, 127.4, 127.7, 128.2, 128.8, 137.4, 137.9, 141.3, 143.6; HRMS (CI^+) Calcd for $\text{C}_{20}\text{H}_{24}$ (M^+) 264.1878. Found 264.1879.

(Z)-2-(4-Methylphenyl)-1-phenylbut-1-ene (3l)



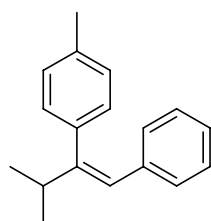
$^1\text{H NMR}$: δ = 1.06 (t, J = 7.5 Hz, 3H), 2.34 (s, 3H), 2.50 (q, J = 7.4 Hz, 2H), 6.40 (s, 1H), 6.91-6.96 (m, 2H), 7.01-7.11 (m, 7H); $^{13}\text{C NMR}$: δ = 13.0, 21.3, 33.6, 124.7, 125.8, 127.7, 128.3, 128.9, 129.1, 136.3, 137.6, 138.3, 144.8; HRMS (CI^+) Calcd for $\text{C}_{17}\text{H}_{18}$ (M^+) 222.1409. Found 222.1406.

(Z)-4-Methyl-2-(4-methylphenyl)-1-phenylpent-1-ene (3m)



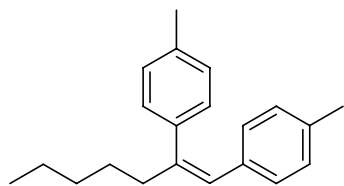
$^1\text{H NMR}$: δ = 0.90 (d, J = 6.3 Hz, 6H), 1.56 (pseudo sept., J = 6.8 Hz, 1H), 2.33-2.36 (m, 5H), 6.38 (s, 1H), 6.93-6.95 (m, 2H), 7.02-7.11 (m, 7H); $^{13}\text{C NMR}$: δ = 21.3, 22.4, 25.9, 50.5, 125.9, 127.0, 127.7, 128.4, 128.9, 129.1, 136.3, 137.6, 138.0, 142.3; HRMS (CI^+) Calcd for $\text{C}_{19}\text{H}_{22}$ (M^+) 250.1721. Found 250.1728.

(Z)-3-Methyl-2-(4-methylphenyl)-1-phenylbut-1-ene (3n)



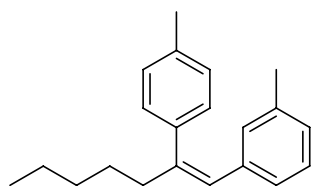
$^1\text{H NMR}$: δ = 1.10 (d, J = 6.9 Hz, 6H), 2.35 (s, 3H), 2.69 (sept., J = 6.8 Hz, 1H), 6.37 (s, 1H), 6.87 (dd, J = 8.8, 1.4 Hz, 2H), 7.01-7.12 (m, 7H); $^{13}\text{C NMR}$: δ = 21.3, 21.9, 37.5, 123.9, 125.8, 127.6, 128.7, 128.9, 129.0, 136.1, 137.6, 138.0, 149.3; HRMS (CI^+) Calcd for $\text{C}_{18}\text{H}_{20}$ (M^+) 236.1565. Found 236.1562; UV-Vis (CHCl_3), λ/nm : 240, 260.

(Z)-1,2-Bis(4-methylphenyl)hept-1-ene (3o)



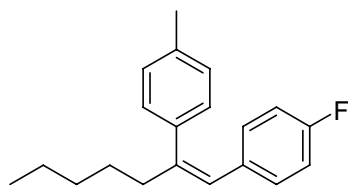
$^1\text{H NMR}$: δ = 0.86 (t, J = 7.2 Hz, 3H), 1.26-1.43 (m, 6H), 2.22 (s, 3H), 2.34 (s, 3H), 2.44 (t, J = 6.8 Hz, 2H), 6.36 (s, 1H), 6.82 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H); $^{13}\text{C NMR}$: δ = 14.2, 21.1, 21.3, 22.6, 27.7, 31.5, 40.8, 125.6, 128.3, 128.4, 128.7, 129.1, 134.7, 135.4, 136.1, 138.4, 142.5; HRMS (CI^+) Calcd for $\text{C}_{21}\text{H}_{26}$ (M^+) 278.2034. Found 278.2035.

(Z)-1-(3-Methylphenyl)-2-(4-methylphenyl)hept-1-ene (3p)



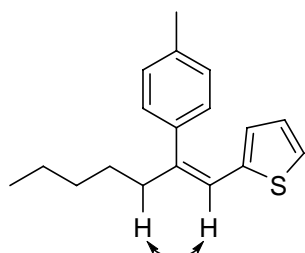
$^1\text{H NMR}$: δ = 0.87 (t, J = 6.9 Hz, 3H), 1.28-1.43 (m, 6H), 2.12 (s, 3H), 2.33 (s, 3H), 2.45 (t, J = 7.4 Hz, 2H), 6.36 (s, 1H), 6.68 (d, J = 7.5 Hz, 1H), 6.79 (s, 1H), 6.85 (d, J = 7.5 Hz, 1H), 6.94 (dd, J = 7.8, 7.2 Hz, 1H), 7.03 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H); $^{13}\text{C NMR}$: δ = 14.2, 21.3, 21.4, 22.6, 27.7, 31.5, 40.8, 125.77, 125.82, 126.6, 127.5, 128.3, 129.0, 129.8, 136.1, 137.1, 137.5, 138.3, 143.2; HRMS (CI^+) Calcd for $\text{C}_{21}\text{H}_{26}$ (M^+) 278.2034. Found 278.2042.

(Z)-1-(4-Fluorophenyl)-2-(4-methylphenyl)hept-1-ene (3q)



$^1\text{H NMR}$: δ = 0.86 (t, J = 7.1 Hz, 3H), 1.26-1.43 (m, 6H), 2.34 (s, 3H), 2.44 (t, J = 7.2 Hz, 2H), 6.35 (s, 1H), 6.72-6.80 (m, 2H), 6.85-6.91 (m, 2H), 7.01 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 7.5 Hz, 2H); $^{13}\text{C NMR}$: δ = 14.2, 21.3, 22.6, 27.7, 31.5, 40.7, 114.5 (d, $J_{\text{C-F}}$ = 21.2 Hz), 124.5, 128.3, 129.2, 130.3 (d, $J_{\text{C-F}}$ = 7.3 Hz), 133.6 (d, $J_{\text{C-F}}$ = 2.9 Hz), 136.4, 137.9, 143.2, 160.9 (d, $J_{\text{C-F}}$ = 243.2 Hz); HRMS (CI^+) Calcd for $\text{C}_{20}\text{H}_{23}\text{F}$ (M^+) 282.1784. Found 282.1776; UV-Vis (CHCl_3), λ/nm : 239, 266.

(Z)-2-(4-Methylphenyl)-1-(2-thienyl)hept-1-ene (3r)



$^1\text{H NMR}$: δ = 0.87 (t, J = 6.9 Hz, 3H), 1.28-1.45 (m, 6H), 2.36-2.42 (m, 5H), 6.58 (s, 1H), 6.73 (d, J = 3.3 Hz, 1H), 6.80 (dd, J = 5.1, 3.6 Hz, 1H), 6.92 (d, J = 5.1 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.5 Hz, 2H); $^{13}\text{C NMR}$: δ = 14.2, 21.4, 22.6, 27.5, 31.5, 40.9, 119.5, 124.5, 125.8, 126.6, 128.4, 129.5, 137.0, 137.8, 141.1, 142.2; HRMS (CI^+) Calcd for $\text{C}_{18}\text{H}_{22}\text{S}$ (M^+) 270.1442. Found 270.1445; UV-Vis (CHCl_3), λ/nm : 241, 290.

Preparation of (E)-Tamoxifen (5)

Under an argon atmosphere, a CH_2Cl_2 solution (0.5 ml) of alkynyltriarylborate **1e** (75.5 mg, 0.20 mmol), $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$ (5.2 mg, 2.5 μmol), and $\text{P}(o\text{-tol})_3$ (3.6 mg, 6.0 μmol) was stirred for 30 minutes at room temperature. To the solution was added bromobenzene (33.0 mg, 0.20 mmol) in CH_2Cl_2 (0.5 ml). After being stirred for 3 h, 4-($\text{Me}_2\text{NCH}_2\text{CH}_2\text{O}$) $\text{C}_6\text{H}_4\text{I}$ (**4**, 178 mg, 0.60 mmol) in CH_2Cl_2 (0.5 ml), powdered NaOH (78 mg, 1.8 mmol), and water (100 μl) were added. After 24 h, water was added to the reaction mixture. The aqueous later was extracted with CH_2Cl_2 (3 times),

washed with water (once), brine (once), dried over Na₂SO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (benzene:AcOEt:NEt₃ = 100:40:1) to afford Tamoxifen (**5**, 58.4 mg, 0.16 mmol, 79% yield, *E/Z* = 97/3). The spectral data was identical to that reported.⁵

Preparation of alkenyl iodide **6**

Under an argon atmosphere, a CH₂Cl₂ solution (0.5 ml) of alkynyltriarylborate **1e** (75.9 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (5.2 mg, 2.5 μmol), and P(*o*-tol)₃ (3.6 mg, 6.0 μmol) was stirred for 30 minutes at room temperature. To the solution was added bromobenzene (33.2 mg, 0.20 mmol) in CH₂Cl₂ (0.5 ml). After being stirred for 3 h, aqueous ammonia (1 ml) was added. The aqueous later was extracted with Et₂O (3 times), washed with water (once), brine (once), dried over Na₂SO₄ and concentrated. The residue was dissolved in acetone and treated with NIS (225 mg, 1.0 mmol) at 0 °C for 1 h. The reaction mixture was purified by preparative thin-layer chromatography on silica gel (hexane), followed by GPC to afford alkenyl iodide **6** (39.2 mg, 0.12 mmol, 59% yield, *E/Z* = 96/4). The spectral data was identical to that reported.⁶

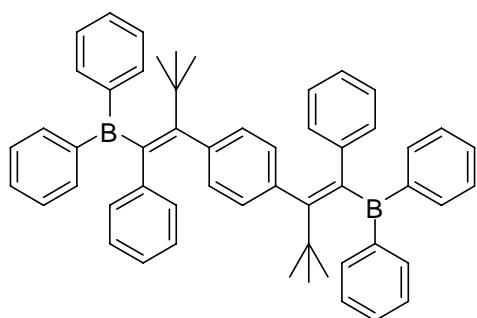
Preparation of ketone **7**

Under an argon atmosphere, a CH₂Cl₂ solution (0.5 ml) of alkynyltriarylborate **1e** (75.9 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (5.2 mg, 2.5 μmol), and P(*o*-tol)₃ (3.6 mg, 6.0 μmol) was stirred for 30 minutes at room temperature. To the solution was added bromobenzene (33.2 mg, 0.20 mmol) in CH₂Cl₂ (0.5 ml). After being stirred for 3 h, trimethylamine-*N*-oxide (75.1 mg, 1.0 mmol) was added. After 3 h, water was added to the reaction mixture. The aqueous later was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 50:1) to afford ketone **7** (40.8 mg, 0.18 mmol, 91% yield). The spectral data was identical to that reported.⁷

Preparation of diboranyl compound **8**

Under an argon atmosphere, a (CH₂Cl)₂ solution (0.5 ml) of alkynyltriarylborate **1b** (79.5 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (2.5 mg, 1.2 μmol), and P(*o*-tol)₃ (2.9 mg, 3.0 μmol) was stirred for 30 minutes at room temperature. To the solution was added 1,4-dibromobenzene (23.7 mg, 0.10 mmol) in (CH₂Cl)₂ (0.5 ml). After being stirred at reflux for 1 h, water was added. The aqueous later was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 10:1) to afford the diboranyl compound **8** (44.9 mg, 0.062 mmol, 62% yield).

1,4-Bis[(*Z*)-1-*tert*-butyl-2-phenyl-2-(diphenylboryl)ethenyl]benzene (**8**)



¹H NMR: δ = 0.98 (s, 18H), 6.71-6.76 (m, 14H), 7.40-7.48 (m, 12H), 7.91 (d, *J* = 6.8 Hz, 8H); ¹³C NMR: δ = 31.7, 37.6, 124.6, 127.0, 127.5, 129.5, 130.9, 131.3, 138.1, 139.1, 140.5, 141.3, 143.9, 153.3; ¹¹B NMR: δ = 59.6; HRMS (CI⁺) Calcd for C₅₄H₅₂B₂ (M⁺) 722.4255. Found 722.4252; UV-Vis (CHCl₃), λ/nm: 248.

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