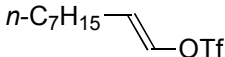


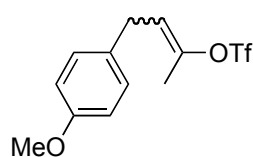
Supporting Information for Ruthenium-Catalyzed Transformation of Alkenyl Triflates to Alkenyl Halides

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General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL JNM LA500 (^1H , 500 MHz; ^{13}C , 125 MHz) spectrometer. High-resolution mass spectra (ESI or APCI) were obtained with a Bruker Daltonics microTOF-Q spectrometer. Low-resolution mass spectra (EI) were obtained with a Shimadzu GCMS-QP5050A. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-908 equipped with JAIGEL-1H and -2H using chloroform as an eluent. Unless otherwise noted, reagents were commercially available and used without further purification. Tetrahydrofuran was purified by passing through a alumina/catalyst column system (GlassContour Co.). 1,2-Dimethoxyethane was distilled from CaH_2 .

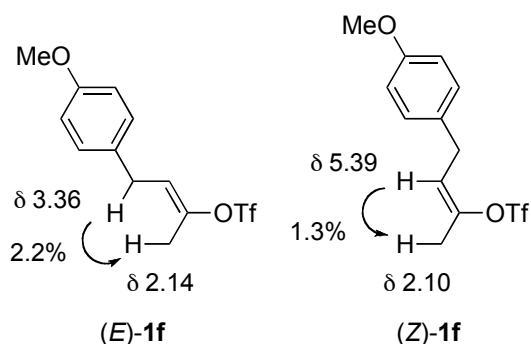
Synthesis of Alkenyl Triflates. All the alkenyl triflates but **1e**, **1f**, **1l** and **1a-d₁** are known compounds¹ and prepared by the reaction of the corresponding enolates with 2-[bis(trifluoromethanesulfonyl)amino]pyridine. 1-Alken-2-yl triflates **1a** and **1c** were contaminated with 5% and 9% of the corresponding (*E*)- and (*Z*)-alk-2-en-2-yl isomers, respectively.

 **(E)-1-Nonen-1-yl Triflate (1e).** To an oven-dried 100 mL Schlenk flask, MeLi (1.09 M ether solution, 15.9 mL, 17.3 mmol) was added, and most of ether was removed under reduced pressure. It was diluted with 1,2-dimethoxyethane (40 mL) and 1-nonen-1-yl trimethylsilyl ether² (3.37 g, 15.7 mmol, *E/Z* = 95/5) was added at $-78\text{ }^\circ\text{C}$. The mixture was allowed to warm up to $0\text{ }^\circ\text{C}$ before Tf_2O (4.88 g, 17.3 mmol) was added dropwise at $-78\text{ }^\circ\text{C}$ and stirring was continued for 1 h. The reaction mixture was allowed to warm up to room temperature and stirred overnight, and it was poured into 20% NaHCO_3 aq. (20 mL). It was extracted with hexane (3 x 20 mL), and the combined organic layer was dried over MgSO_4 . Evaporation of the solvent followed by purification by silica gel column chromatography (hexane/ AcOEt = 9/1) and GPC gave (*E*)-1-nonen-1-yl triflate (**1e**) as a colorless oil (1.29 g, 30% yield, *E/Z* = 97/3). ^1H NMR (500 MHz, CDCl_3) δ 0.89 (t, J = 6.9 Hz, 3 H), 1.20–1.35 (m, 8 H), 1.41 (quint, J = 7.1 Hz, 2 H), 2.04 (qd, J = 7.4, 1.3 Hz, 2 H), 5.77 (dt, J = 11.8, 7.7 Hz, 1 H), 6.49 (d, J = 11.8 Hz, 1 H). ^{13}C NMR (125 MHz, CDCl_3) δ 14.2, 22.7, 26.7, 28.8, 29.0, 29.1, 31.9, 118.8 (q, $^1J_{\text{P,F}}$ = 320.1 Hz), 123.1, 136.0. HRMS (APCI) Calcd for $\text{C}_{10}\text{H}_{16}\text{F}_3\text{O}_3\text{S}$: $[\text{M}-\text{H}]^-$, 273.0778. Found m/z 273.0770.



4-(4-Methoxyphenyl)-2-buten-2-yl Triflate (1f). To a THF solution of *p*-methoxyphenylmagnesium bromide (80.0 mL, 20.0 mmol) placed in a 300 mL three-neck flask, CuBr (115 mg, 0.80 mmol) and hexamethylphosphoramide (6.7 mL) was added and stirred for 30 min at

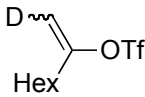
-78 °C. After addition of 3-buten-2-one (1.30 mL, 16.0 mmol) and chloro(trimethyl)silane (4.11 mL, 32.0 mmol), the stirring was continued for 3 h at -78 °C. The reaction was quenched by addition of hexane (80 mL), Et₃N (6 mL) and water (6 mL). The resulting mixture was extracted with hexane (2 x 20 mL). The combined organic layer was washed with water and brine, and was dried over MgSO₄. Evaporation of the solvent gave crude [4-(4-methoxyphenyl)-2-buten-2-yloxy]trimethylsilane (4.46 g). To an oven-dried 100 mL Schlenk flask, MeLi (1.09 M ether solution, 16.1 mL, 17.6 mmol) was added, and most of ether was removed under reduced pressure. After dilution of the resulting solution with 1,2-dimethoxyethane (40 mL), the silyl enolate was added at -78 °C. The mixture was allowed to warm up to 0 °C before Tf₂O (4.95 g, 17.6 mmol) was added dropwise at -78 °C. After stirring for 1 h, the reaction mixture was allowed to warm up to room temperature and stirred overnight. Addition of 20% NaHCO₃ aq. (20 mL) was followed by extraction with hexane (3 x 20 mL), and the combined organic layer was dried over MgSO₄. Evaporation of the solvent followed by purification by silica gel column chromatography (hexane/AcOEt = 9/1) and GPC gave 4-(4-methoxyphenyl)-2-buten-2-yl triflate (**1f**) as a colorless oil (301 mg, 6% yield, *E/Z* = 60/40). ¹H NMR (500 MHz, CDCl₃) (*E*)-**1f**: δ 2.14 (d, *J* = 0.8 Hz, 3 H), 3.36 (d, *J* = 8.0 Hz, 2 H), 3.80 (s, 3 H), 5.72 (td, *J* = 8.0, 0.8 Hz, 1 H), 6.82–6.88 (m, 2 H), 7.05–7.13 (m, 2 H). (*Z*)-**1f**: δ 2.10 (d, *J* = 1.0 Hz, 3 H), 3.45 (d, *J* = 7.4 Hz, 2 H), 3.79 (s, 3 H), 5.39 (td, *J* = 7.4, 1.0 Hz, 1 H), 6.82–6.88 (m, 2 H), 7.05–7.13 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 16.2, 19.8, 31.3, 31.9, 55.39, 55.40, 114.2, 114.3, 118.5 (q, ¹*J*_{P,F} = 319 Hz), 118.7 (q, ¹*J*_{P,F} = 320 Hz), 121.2, 121.3, 129.2, 130.6, 145.1, 147.0, 158.5, 158.6. HRMS (APCI) Calcd for C₁₂H₁₂F₃O₄S: [M-H]⁻, 309.0414. Found *m/z* 309.0414.

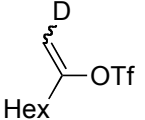


7-Phenyl-1-hepten-6-yn-2-yl Triflate (1f). To a NEt₃ solution (15 mL) of Pd(PPh₃)₄ (57.8 mg, 50 μmol) and CuI (47.6 mg, 250 μmol) placed in a 30 mL Schlenk flask were added iodobenzene (1.12 g, 5.50 mmol) and 6-heptyn-2-one³ (551 mg, 5.00 mmol) at room temperature. After stirring for 5 h at 60 °C, the reaction mixture was passed through a pad of silica gel with AcOEt. Purification by silica gel column chromatography (hexane/AcOEt = 9/1) gave 7-phenyl-6-heptyn-2-one as a colorless oil (702 mg, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ 1.88 (quint, *J* = 7.1 Hz, 2 H), 2.18 (s, 3 H), 2.46 (t, *J* = 6.8 Hz, 2 H), 2.64 (t, *J* = 7.3 Hz, 2 H), 7.25–7.31 (m, 3 H), 7.36–7.41 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 18.9, 22.8, 30.2, 42.4, 81.5, 89.2, 123.9, 127.8, 128.4, 131.7, 208.5. HRMS (ESI) Calcd for C₁₃H₁₄OLi: [M+Li]⁺, 193.1199. Found *m/z* 193.1207.

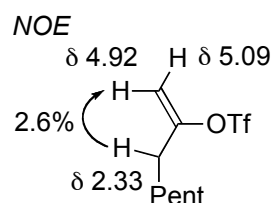
To a THF solution of diisopropylamine (408 mg, 4.03 mmol) placed in a 20 mL Schlenk flask was added dropwise *n*-BuLi (1.59 M hexane solution, 2.53 mL, 4.03 mmol) at -40 °C. The reaction mixture was allowed to warm up to 0 °C with stirring for 30 min. 7-Phenyl-6-heptyn-2-one was added dropwise at -78 °C and stirring was continued for 2 h.

After addition of a THF solution of 2-[bis(trifluoromethanesulfonyl)amino]pyridine (1.44 g, 4.03 mmol) at $-78\text{ }^{\circ}\text{C}$, stirring was continued for 1 h. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The resulting mixture was diluted with hexane and passed through a pad of silica gel with hexane. Evaporation of the solvent followed by purification by silica gel column chromatography (hexane) gave 7-phenyl-1-hepten-6-yn-2-yl triflate (**1l**), and (*E*)- and (*Z*)-7-phenyl-2-hepten-6-yn-2-yl triflates as a colorless oil (498 mg, 42% yield, **1l**:regioisomers = 81:19). ^1H NMR of **1k** (500 MHz, CDCl_3) δ 1.87 (quint, $J = 7.2$ Hz, 2 H), 2.51 (t, $J = 6.8$ Hz, 2 H), 2.56 (t, $J = 7.5$ Hz, 2 H), 5.02 (dt, $J = 3.5, 0.9$ Hz, 1 H), 5.16 (d, $J = 3.5$ Hz, 1 H), 7.26–7.33 (m, 3 H), 7.38–7.43 (m, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ 18.5, 25.1, 33.0, 81.9, 88.3, 105.0, 118.7 (q, $^1J_{\text{P-F}} = 318.6$ Hz), 123.7, 127.9, 128.4, 131.7, 156.1. HRMS (APCI) Calcd for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{O}_3\text{S}$: $[\text{M-H}]^-$, 317.0465. Found m/z 317.0453.

 **1-Deuterio-1-octen-2-yl Triflate (1a-d₁, *E/Z* = 71/29).** To a pentane solution (7.0 mL) of 1-deuterio-1-octyne (1.30 g, 11.7 mmol) was added dropwise trifluoromethanesulfonic acid (962 mg, 6.41 mmol) at $-20\text{ }^{\circ}\text{C}$ over 15 min. The mixture was warmed to $0\text{ }^{\circ}\text{C}$, and sat. NaHCO_3 aq. (5 mL) was added. After stirring for 5 min, the aqueous layer was removed. The organic layer was washed with sat. NaHCO_3 aq. (2 x 5 mL) and dried over MgSO_4 . Evaporation of the solvent followed by purification by silica gel column chromatography (hexane) gave 1-deuterio-1-octen-2-yl triflate as a colorless oil (897 mg, 39% yield, *E/Z* = 71/29).

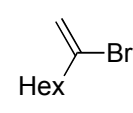
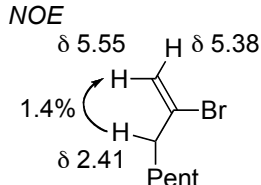
 **1-Deuterio-1-octen-2-yl Triflate (1a-d₁, *E/Z* = 20/80).** The reaction of 1-octyne (3.0 g, 36 mmol) with TfOD (3.0 g, 20 mmol) in a similar manner gave 1-deuterio-1-octen-2-yl triflate (*E/Z* = 20/80) as a colorless oil (4.01 g, 77% yield, 26% of 1-octen-2-yl triflate, **1a**, was contaminated).

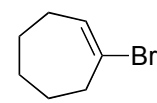
The *E/Z* ratios of **1a-d₁** were determined by comparison of ^1H NMR spectra with that of 1-octen-2-yl triflate (**1a**). ^1H NMR of **1a** (500 MHz, CDCl_3) δ 0.89 (t, $J = 6.8$ Hz, 3 H), 1.25–1.44 (m, 6 H), 1.48–1.58 (m, 2 H), 2.33 (t, $J = 7.5$ Hz, 2 H), 4.92 (d, $J = 3.4$ Hz, 1 H), 5.09 (d, $J = 3.4$ Hz, 1 H).

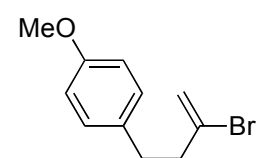


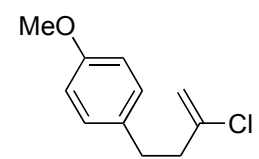
Ruthenium-Catalyzed Halogenation of Alkenyl Triflates: A Representative Procedure (entry 1 of Table 2). To a THF solution (0.97 mL) of $\text{Ru}(\text{acac})_3$ (3.0 mg, 7.5 μmol) and LiBr (26 mg, 0.30 mmol) placed in an oven-dried 20 mL Schlenk tube was added ethylmagnesium bromide (1.0 M THF solution, 0.030 mL, 30 μmol). After stirring for 10 min at room temperature, 4-(4-methoxyphenyl)-1-buten-2-yl triflate (**1c**, containing 9% of (*E*)- and (*Z*)-1-(4-methoxyphenyl)-2-buten-3-yl triflates, 77.5 mg, 0.250 mmol) was added at $20\text{ }^{\circ}\text{C}$ and stirring was continued for 1 h. Purification by passing through a pad of silica gel using hexane/ AcOEt (10/1) as an eluent gave 2-bromo-4-(4-methoxyphenyl)-1-butene as a

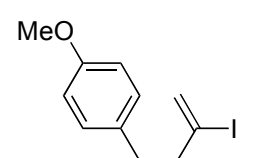
colorless oil (containing (*E*)- and (*Z*)-3-bromo-1-(4-methoxyphenyl)-2-butenes, 58.3 mg, 97% yield).

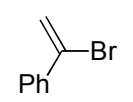
 **2-Bromo-1-octene (2a).**⁴ A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 0.89 (t, *J* = 6.9 Hz, 3 H), 1.23–1.37 (m, 6 H), 1.55 (quint, *J* = 7.3 Hz, 2 H), 2.41 (td, *J* = 7.6, 1.1 Hz, 2 H), 5.38 (d, *J* = 1.6 Hz, 1 H), 5.55 (dd, *J* = 1.6, 1.1 Hz, 1 H). ^{NOE} 

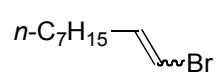
 **1-Bromocycloheptene (2b).**⁵ A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.53–1.66 (m, 4 H), 1.68–1.75 (m, 2 H), 2.04–2.11 (m, 2 H), 2.65–2.71 (m, 2 H), 6.20 (tt, *J* = 6.6, 0.7 Hz, 1 H). GC-MS (EI) *m/z* (%) M⁺ 174 (10), 175 (0.8), 176 (10), 177 (0.9), 95 (100).

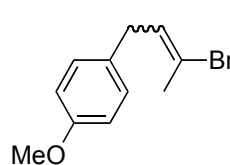
 **2-Bromo-4-(4-methoxyphenyl)-1-butene (entry 1 of Table 2).** A colorless oil. Containing 9% of the double bond regioisomers, starting with **1c** containing 9% of the isomers. ¹H NMR (500 MHz, CDCl₃) δ 2.68 (t, *J* = 7.6 Hz, 2 H), 2.82 (t, *J* = 7.6 Hz, 2 H), 3.79 (s, 3 H), 5.38 (s, 1 H), 5.50 (s, 1 H), 6.83 (d, *J* = 8.3 Hz, 2 H), 7.11 (d, *J* = 8.3 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 33.6, 43.7, 55.4, 114.0, 117.2, 129.6, 132.6, 133.8, 158.2. HRMS (APCI) Calcd for C₁₁H₁₃BrO: [M]⁺, 240.0144. Found *m/z* 240.0143.

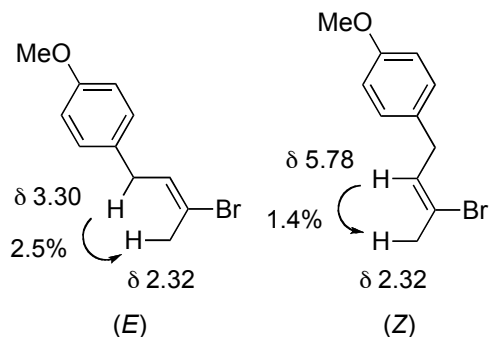
 **2-Chloro-4-(4-methoxyphenyl)-1-butene (entry 2 of Table 2).** A colorless oil. Containing 9% of the double bond regioisomers, starting with **1c** containing 9% of the isomers. ¹H NMR (500 MHz, CDCl₃) δ 2.60 (t, *J* = 7.6 Hz, 2 H), 2.83 (t, *J* = 7.6 Hz, 2 H), 3.79 (s, 3 H), 5.06 (s, 1 H), 5.14 (s, 1 H), 6.83 (d, *J* = 8.4 Hz, 2 H), 7.11 (d, *J* = 8.4 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 32.9, 41.4, 55.4, 112.7, 114.0, 129.5, 132.8, 142.2, 158.2. HRMS (APCI) Calcd for C₁₁H₁₃ClO: [M]⁺, 196.0649. Found *m/z* 196.0650.

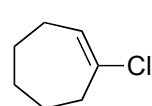
 **2-Iodo-4-(4-methoxyphenyl)-1-butene (entry 3 of Table 2).** A colorless oil. Containing 8% of the double bond regioisomers, starting with **1c** containing 9% of the isomers. ¹H NMR (500 MHz, CDCl₃) δ 2.65 (t, *J* = 7.6 Hz, 2 H), 2.78 (t, *J* = 7.6 Hz, 2 H), 3.79 (s, 3 H), 5.68 (d, *J* = 1.4 Hz, 1 H), 5.94 (d, *J* = 1.4 Hz, 1 H), 6.83 (d, *J* = 8.6 Hz, 2 H), 7.11 (d, *J* = 8.6 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 34.7, 47.6, 55.4, 111.3, 113.9, 126.1, 129.6, 132.4, 158.2. HRMS (APCI) Calcd for C₁₁H₁₃IO: [M]⁺, 288.0006. Found *m/z* 287.9993.

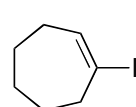
 **α-Bromostyrene (entry 4 of Table 2).**⁶ A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 5.78 (d, *J* = 2.1 Hz, 1 H), 6.12 (d, *J* = 2.1 Hz, 1 H), 7.30–7.38 (m, 3 H), 7.57–7.62 (m, 2 H).

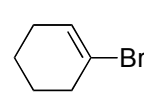
 **1-Bromo-1-nonene (entry 5 of Table 2).**⁷ A colorless oil. ¹H NMR (500 MHz, CDCl₃) (*E*)-1-Bromo-1-nonene: δ 0.88 (t, *J* = 7.0 Hz, 3 H), 1.20–1.35 (m, 8 H), 1.35–1.45 (m, 2 H), 2.03 (qd, *J* = 7.3, 1.4 Hz, 2 H), 6.01 (dt, *J* = 13.6, 1.4 Hz, 1 H), 6.17 (dt, *J* = 13.6, 7.2 Hz, 1 H). (*Z*)-1-Bromo-1-nonene: δ 0.88 (t, *J* = 7.0 Hz, 3 H), 1.20–1.35 (m, 8 H), 1.35–1.45 (m, 2 H), 2.19 (qd, *J* = 7.2, 1.1 Hz, 2 H), 6.08 (q, *J* = 6.8 Hz, 1 H), 6.13 (dt, *J* = 6.8, 1.3 Hz, 1 H).

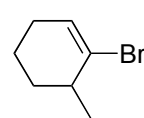
 **3-Bromo-1-(4-methoxyphenyl)-2-butene (entry 6 of Table 2).** A colorless oil, *E/Z* = 64/36. ¹H NMR (500 MHz, CDCl₃) (*E*): δ 2.32 (s, 3 H), 3.30 (d, *J* = 7.8 Hz, 2 H), 3.79 (s, 3 H), 6.02 (tq, *J* = 7.8, 1.3 Hz, 1 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 7.08 (d, *J* = 8.6 Hz, 2 H); (*Z*): δ 2.32 (s, 3 H), 3.43 (d, *J* = 6.9 Hz, 2 H), 3.79 (s, 3 H), 5.78 (tq, *J* = 7.1, 1.3 Hz, 1 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 7.13 (d, *J* = 8.8 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 23.4, 28.9, 34.9, 37.1, 55.41, 55.43, 114.1, 114.2, 120.2, 123.0, 128.3, 129.3, 129.5, 131.1, 131.4, 131.7, 158.26, 158.32. HRMS (APCI) Calcd for C₁₁H₁₃BrO: [M]⁺, 240.0144. Found *m/z* 240.0136.

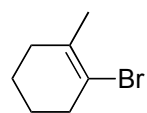
 (*E*) δ 3.30 (2.5%), δ 2.32; (*Z*) δ 5.78 (1.4%), δ 2.32

 **1-Chlorocycloheptene (entry 7 of Table 2).**⁸ A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.54–1.60 (m, 2 H), 1.61–1.67 (m, 2 H), 1.68–1.75 (m, 2 H), 2.07–2.13 (m, 2 H), 2.52–2.57 (m, 2 H), 5.95 (t, *J* = 6.6 Hz, 1 H). GC-MS (EI) *m/z* (%) M⁺ 130 (32), 131 (3), 132 (10), 133 (0.8), 95 (100).

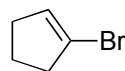
 **1-Iodocycloheptene (entry 8 of Table 2).**⁸ A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.50–1.58 (m, 4 H), 1.68–1.76 (m, 2 H), 2.02–2.08 (m, 2 H), 2.73–2.78 (m, 2 H), 6.51 (tt, *J* = 6.6, 0.8 Hz, 1 H). GC-MS (EI) *m/z* (%) M⁺ 222 (29), 223 (2), 95 (100).

 **1-Bromocyclohexene (entry 9 of Table 2).**⁵ A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.55–1.64 (m, 2 H), 1.69–1.78 (m, 2 H), 2.02–2.11 (m, 2 H), 2.36–2.46 (m, 2 H), 6.01–6.07 (m, 1 H). GC-MS (EI) *m/z* (%) M⁺ 160 (8), 161 (0.3), 162 (8), 163 (0.6), 81 (100).

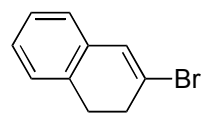
 **1-Bromo-6-methylcyclohexene (entry 10 of Table 2).**⁶ A colorless oil. Containing 2% of 1-bromo-2-methylcyclohexene, starting with **1g** containing 2% of **1h**. ¹H NMR (500 MHz, CDCl₃) δ 1.17 (d, *J* = 6.9 Hz, 3 H), 1.50–1.70 (m, 3 H), 1.85–1.94 (m, 1 H), 2.01–2.07 (m, 2 H), 2.41–2.49 (m, 1 H), 6.03 (td, *J* = 4.1, 1.3 Hz, 1 H).



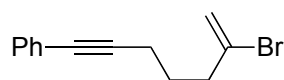
1-Bromo-2-methylcyclohexene (entry 11 of Table 2).⁶ A colorless oil. Containing 2% of 1-bromo-6-methylcyclohexene, starting with **1h** containing 2% of **1g**. ¹H NMR (500 MHz, CDCl₃) δ 1.61–1.71 (m, 4 H), 1.77–1.81 (m, 3 H), 2.05–2.11 (m, 2 H), 2.43–2.50 (m, 2 H).



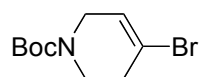
1-Bromocyclopentene (entry 12 of Table 2).⁵ A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.94–2.02 (m, 2 H), 2.29–2.36 (m, 2 H), 2.55–2.61 (m, 2 H), 5.83 (quint, *J* = 2.3 Hz, 1 H). GC-MS (EI) *m/z* (%) M⁺ 146 (100), 147 (13), 148 (95), 149 (5).



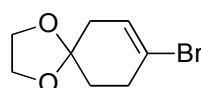
3-Bromo-1,2-dihydronaphthalene (entry 13 of Table 2).⁶ A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 2.77 (t, *J* = 8.3 Hz, 2 H), 2.95 (t, *J* = 8.3 Hz, 2 H), 6.79 (s, 1 H), 6.94–7.00 (m, 1 H), 7.07–7.11 (m, 1 H), 7.12–7.18 (m, 2 H).



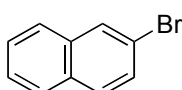
2-Bromo-6-phenyl-1-buten-5-yne (entry 14 of Table 2). A colorless oil. Containing 9% of the double bond regioisomers, starting with **1k** containing 19% of the isomers. ¹H NMR (500 MHz, CDCl₃) δ 1.88 (quint, *J* = 7.1 Hz, 2 H), 2.45 (t, *J* = 7.0 Hz, 2 H), 2.62 (t, *J* = 7.2 Hz, 2 H), 5.46 (d, *J* = 1.7 Hz, 1 H), 5.65 (d, *J* = 1.7 Hz, 1 H), 7.26–7.32 (m, 3 H), 7.37–7.43 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 18.2, 26.9, 40.4, 81.5, 89.2, 117.5, 123.9, 127.8, 128.4, 131.7, 133.6. HRMS (APCI) Calcd for C₁₃H₁₄Br: [M+H]⁺, 249.0273. Found *m/z* 249.0270.



tert-Butyl 4-bromo-5,6-dihydropyridine-1(2H)-carboxylate (entry 15 of Table 2). A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.46 (s, 9 H), 2.47–2.55 (m, 2 H), 3.50–3.63 (m, 2 H), 3.85–3.95 (m, 2 H), 5.95–6.10 (m, 1 H). ¹³C NMR (125 MHz, CDCl₃) δ 28.4, 35.0, 40.3–43.5, 44.9, 80.1, 119.3, 125.6, 154.5. HRMS (ESI) Calcd for C₁₀H₁₆BrNO₂Na: [M+Na]⁺, 284.0257. Found *m/z* 284.0247.



8-Bromo-1,4-dioxaspiro[4.5]dec-7-ene (entry 16 of Table 2). A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.86 (t, *J* = 6.6 Hz, 2 H), 2.28–2.32 (m, 2 H), 2.61–2.67 (m, 2 H), 3.95–4.01 (m, 4 H), 5.91 (tt, *J* = 8.0, 1.6 Hz, 1 H). ¹³C NMR (125 MHz, CDCl₃) δ 32.8, 34.3, 37.8, 64.7, 106.5, 121.3, 126.2. HRMS (APCI) Calcd for C₈H₁₁BrO₂: [M]⁺, 217.9937. Found *m/z* 217.9934.



2-Bromonaphthalene (4 in Scheme 2). A white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.46–7.52 (m, 2 H), 7.55 (dd, *J* = 8.6, 1.9 Hz, 1 H), 7.72 (d, *J* = 8.9 Hz, 1 H), 7.74–7.83 (m, 2 H), 8.01 (d, *J* = 1.9 Hz, 1 H).

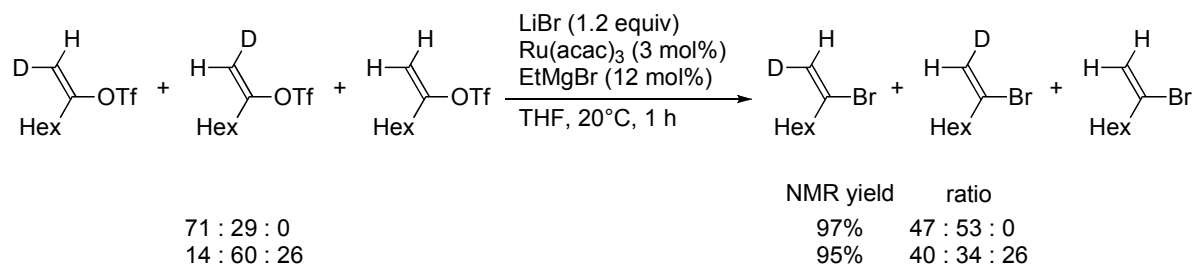
Bromination of Alkenyl Triflate 1a Followed by Lithiation and Addition to Benzaldehyde (Scheme 1). To a THF solution (0.97 mL) of Ru(acac)₃ (3.0 mg, 7.5 μmol) and LiBr (26 mg, 0.30 mmol) placed in an oven-dried 20 mL Schlenk tube was added ethylmagnesium bromide (1.0 M THF solution, 0.030 mL, 30 μmol). Stirring for 10 min at

room temperature was followed by addition of 1-cycloheptenyl triflate (**1b**, 61 mg, 0.25 mmol) at 60 °C and stirring was continued for 3 h. After addition of hexane (3.0 mL) at room temperature, *t*-BuLi (1.59 M pentane solution, 0.31 mL, 0.50 mmol) was added dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 1 h, and benzaldehyde (32 mg, 0.30 mmol) was added. The reaction mixture was stirred further for 1 h, quenched with water and extracted with Et₂O (3 x 5 mL). The combined organic layer was washed with brine and dried over MgSO₄. Evaporation followed by PTLC (hexane/EtOAc = 9/1) gave (1-cycloheptenyl)phenylmethanol (**3**, 39.0 mg, 77% yield) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.31 (quint, *J* = 5.8 Hz, 2 H), 1.43–1.55 (m, 2 H), 1.62–1.78 (m, 2 H), 1.79 (d, *J* = 3.4 Hz, 1 H), 1.93–2.06 (m, 2 H), 2.13–2.26 (m, 2 H), 5.12 (d, *J* = 2.4 Hz, 1 H), 6.05 (t, *J* = 6.5 Hz, 1 H), 7.25 (t, *J* = 7.1 Hz, 1 H), 7.33 (t, *J* = 7.7 Hz, 2 H), 7.37 (t, *J* = 7.5 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 27.07, 27.15, 28.4, 28.8, 32.6, 79.3, 126.5, 127.3, 128.3, 128.7, 142.4, 145.8. HRMS (APCI) Calcd for C₁₄H₁₈OLi: [M+Li]⁺, 209.1513. Found *m/z* 209.1522.

Ruthenium-Catalyzed Bromination of 1-Deuterio-1-octen-2-yl Triflate (Footnote 9).

Stereoisomeric mixtures of 1-deuterio-1-octen-2-yl triflate (**1a-d**₁) of different compositions were treated with LiBr under the conditions of entry 1 of Table 1. The result is shown in Scheme S1, where the configurations of the products were determined by comparison of ¹H NMR spectra with that of **2a**.

Scheme S1



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