Synthesis and Characterization of β -Haloalkenyl- λ^3 -bromanes: Stereoselective Markownikoff Addition of Difluoro(aryl)- λ^3 -bromane to Terminal Acetylenes

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General Procedure for the Synthesis of β -Fluoro-1-alkenyl(aryl)- λ^3 -bromanes 2. A Typical Example (Table 1, Entry 7): (*E*)-(2-Fluoro-1-decenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (2a**).** To a white solid of difluoro[4-(trifluoromethyl)phenyl]- λ^3 -bromane (**1**) (80 mg, 0.3 mmol) in a PFA tube was added dropwise a solution of 1-decyne (21 mg, 0.15 mmol) in chloroform (1 mL) and then a solution of $\text{BF}_3 \cdot i\text{-Pr}_2\text{O}$ (39 mg, 0.23 mmol) in chloroform (0.5 mL) at -60°C with stirring under argon. The solution was gradually warmed to room temperature over 3.5 h. After the addition of a saturated aqueous solution of NaBF_4 , the mixture was extracted with dichloromethane four times. After separation and filtration of the organic phase, the solvent was evaporated under an aspirator vacuum to give an oil, which was washed several times with hexane by decantation at room temperature to give the λ^3 -bromane **2a** (54 mg, 74%, *E*:*Z* = 94:6) as an oil. (**E**)-**2a**: IR (neat) 3106, 2929, 2858, 1647, 1406, 1324, 1185-994, 840, 771 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.16 (d, $^3J_{\text{HF}}$ = 9.5 Hz, 1H), 2.79 (dt, $^3J_{\text{HF}}$ = 22.4 Hz, J = 7.5 Hz, 2H), 1.60-1.51 (m, 2H), 1.33-1.16 (m, 10H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.6 (d, $^1J_{\text{CF}}$ = 285.9 Hz), 135.5, 135.0 (q, $^2J_{\text{CF}}$ = 33.6 Hz), 130.2, 129.5 (q, $^3J_{\text{CF}}$ = 3.7 Hz), 122.7 (q, $^1J_{\text{CF}}$ = 273.4 Hz), 101.9 (d, $^2J_{\text{CF}}$ = 63.5 Hz), 31.7, 30.4 (d, $^2J_{\text{CF}}$ = 22.4 Hz), 29.2, 29.0, 28.9, 25.3, 22.6, 14.0; FAB MS m/z 381 [(M-BF₄)⁺]: HRMS (FAB) calcd for C₁₇H₂₂BrF₄ [(M-BF₄)⁺] 381.0841, found 381.0831. A vinylic proton of (*Z*)-**2a** appears as a doublet ($^3J_{\text{HF}}$ = 25.4 Hz) at δ 7.02 ppm.

(*E*)-(2-Fluoro-1-hexenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (**2b**): an oil; IR (neat) 3106, 2965, 2938, 2877, 1646, 1405, 1324, 1188-990, 839, 772 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 8.7 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.18 (d, $^3J_{\text{HF}}$ = 9.8 Hz, 1H), 2.79 (dt, $^3J_{\text{HF}}$ = 22.5 Hz, J = 7.6 Hz, 2H), 1.54 (quint, J = 7.6 Hz, 2H), 1.32 (sext, J = 7.6 Hz, 2H), 0.88 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.3 (d, $^1J_{\text{CF}}$ = 285.9 Hz), 135.4, 135.1 (q, $^2J_{\text{CF}}$ = 33.6 Hz), 130.2, 129.6 (q, $^3J_{\text{CF}}$ = 3.7 Hz), 122.6 (q, $^1J_{\text{CF}}$ = 273.4 Hz), 101.8 (d, $^2J_{\text{CF}}$ = 63.5 Hz), 30.1 (d, $^2J_{\text{CF}}$ = 22.4 Hz), 27.3, 22.0, 13.5; FAB MS m/z 325 [(M-BF₄)⁺]: HRMS (FAB) calcd for C₁₃H₁₄BrF₄ [(M-BF₄)⁺] 325.0215, found 325.0206. A vinylic proton of (*Z*)-**2b** appears as a doublet ($^3J_{\text{HF}}$ = 25.3 Hz) at δ 7.04 ppm.

(*E*)-(2-Fluoro-1-octenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (**2c**): an oil; IR (neat) 3106, 2959, 2935, 2863, 1645, 1595, 1468, 1406, 1324, 1104-1021, 839, 772 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 8.6 Hz, 2H), 7.20 (d, $^3J_{\text{HF}}$ = 9.7 Hz, 1H), 2.78 (dt, $^3J_{\text{HF}}$ = 22.4 Hz, J = 7.0 Hz, 2H), 1.53 (quint, J = 7.0 Hz, 2H), 1.32-1.16 (m, 6H), 0.91-0.79 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.4 (d, $^1J_{\text{CF}}$ = 285.9 Hz), 135.4, 135.1 (q, $^2J_{\text{CF}}$ = 33.6 Hz), 130.1, 129.5 (q, $^3J_{\text{CF}}$ = 3.7 Hz), 122.6 (q, $^1J_{\text{CF}}$ = 272.8 Hz), 101.7 (d, $^2J_{\text{CF}}$ = 63.5 Hz), 31.2, 30.4 (d, $^2J_{\text{CF}}$ = 21.8 Hz), 28.5, 25.2, 22.3, 13.9; FAB MS m/z 353 [(M-BF₄)⁺]: HRMS (FAB) calcd for C₁₅H₁₈BrF₄ [(M-BF₄)⁺] 353.0528, found 353.0536. A vinylic proton of (*Z*)-**2c** appears as a doublet ($^3J_{\text{HF}}$ = 25.6 Hz) at δ 7.03 ppm.

A Mixture of (*E*)-(2-Fluoro-4-methyl-1-pentenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (2d**) and (*E*)-(2,4-Difluoro-4-methyl-1-pentenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (**2k**):** a pale yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.21-8.13 (m, 2H), 7.88-7.81 (m, 2H), 7.31 (d, $^3J_{\text{HF}}$ = 9.9 Hz, 1H for **2k**), 7.23 (d, $^3J_{\text{HF}}$ = 9.9 Hz, 1H for **2d**), 3.18

(dd, $^3J_{\text{HF}} = 24.9, 21.3$ Hz, 2H for **2k**), 2.68 (dd, $^3J_{\text{HF}} = 23.1$ Hz, $J = 7.0$ Hz, 2H for **2d**), 2.04 (nonet, $J = 6.6$ Hz, 1H for **2d**), 1.48 (d, $^3J_{\text{HF}} = 21.3$ Hz, 6H for **2k**), 0.94 (d, $J = 6.6$ Hz, 6H for **2d**); ^{13}C NMR for **2d** (75 MHz, CDCl_3) δ 175.6 (d, $^1J_{\text{CF}} = 287.1$ Hz), 135.4, 135.1 (q, $^2J_{\text{CF}} = 34.9$ Hz), 130.1, 129.6 (q, $^3J_{\text{CF}} = 3.7$ Hz), 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 102.4 (d, $^2J_{\text{CF}} = 63.5$ Hz), 38.7 (d, $^2J_{\text{CF}} = 21.2$ Hz), 26.1, 21.8; FAB MS for **2d** m/z 325 $[(\text{M-BF}_4)^+]$: HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{14}\text{BrF}_4$ $[(\text{M-BF}_4)^+]$ 325.0215, found 325.0224; FAB MS for **2k** m/z 343 $[(\text{M-BF}_4)^+]$: HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{13}\text{BrF}_5$ $[(\text{M-BF}_4)^+]$ 343.0121, found 343.0125. A vinylic proton of (**Z**)-**2d** appears as a doublet ($^3J_{\text{HF}} = 25.3$ Hz) at δ 7.06 ppm.

(E)-(2-Fluoro-5-methyl-1-hexenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (2e): an oil; IR (neat) 3105, 2961, 2939, 2879, 1644, 1594, 1405, 1323, 1073-1010, 837, 771 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.4$ Hz, 2H), 7.84 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $^3J_{\text{HF}} = 9.2$ Hz, 1H), 2.77 (dt, $^3J_{\text{HF}} = 22.0$ Hz, $J = 7.8$ Hz, 2H), 1.58 (nonet, $J = 6.6$ Hz, 1H), 1.46-1.37 (m, 2H), 0.88 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.6 (d, $^1J_{\text{CF}} = 285.9$ Hz), 135.3, 135.1 (q, $^2J_{\text{CF}} = 34.3$ Hz), 130.1, 129.6 (q, $^3J_{\text{CF}} = 3.7$ Hz), 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 101.5 (d, $^2J_{\text{CF}} = 63.5$ Hz), 34.0, 28.5 (d, $^2J_{\text{CF}} = 21.8$ Hz), 27.7, 22.0; FAB MS m/z 339 $[(\text{M-BF}_4)^+]$: HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{16}\text{BrF}_4$ $[(\text{M-BF}_4)^+]$ 339.0371, found 339.0345. A vinylic proton of (**Z**)-**2e** appears as a doublet ($^3J_{\text{HF}} = 25.6$ Hz) at δ 7.04 ppm.

A Mixture of (E)-(3,3-Dimethyl-2-fluoro-1-butenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (2f) and (Z)-(2,3-Dimethyl-3-fluoro-1-butenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane: an oil; ^1H NMR (400 MHz, CDCl_3) δ 8.16-8.09 (m, 2H), 7.90-7.82 (m, 2H), 7.21 (s, 1H for β -methyl- λ^3 -bromane), 6.97 (d, $^3J_{\text{HF}} = 15.4$ Hz, 1H for **2f**), 2.23 (s, 3H for β -methyl- λ^3 -bromane), 1.56 (d, $^3J_{\text{HF}} = 22.0$ Hz, 6H for β -methyl- λ^3 -bromane), 1.39 (s, 9H for **2f**); ^{13}C NMR for **2f** (75 MHz, CDCl_3) δ 179.4 (d, $^1J_{\text{CF}} = 284.6$ Hz), 135.7, 135.0 (q, $^2J_{\text{CF}} = 33.6$ Hz), 129.8 (q, $^3J_{\text{CF}} = 3.7$ Hz), 129.5, 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 96.7 (d, $^2J_{\text{CF}} = 76.6$ Hz), 38.3 (d, $^2J_{\text{CF}} = 21.2$ Hz), 27.6 (d, $^3J_{\text{CF}} = 3.7$ Hz); FAB MS m/z 325 $[(\text{M-BF}_4)^+]$: HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{14}\text{BrF}_4$ $[(\text{M-BF}_4)^+]$ 325.0215, found 325.0204. A vinylic proton of (**Z**)-**2f** appears as a doublet ($^3J_{\text{HF}} = 26.4$ Hz) at δ 7.11 ppm.

(E)-(11-Acetoxy-2-fluoro-1-undecenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (2g): an oil; IR (neat) 3104, 2933, 2858, 1731, 1646, 1594, 1404, 1324, 1249, 1176, 1138, 1110-1021, 995, 840 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.8$ Hz, 2H), 7.84 (d, $J = 8.8$ Hz, 2H), 7.20 (d, $^3J_{\text{HF}} = 9.7$ Hz, 1H), 4.04 (t, $J = 6.6$ Hz, 2H), 2.78 (dt, $^3J_{\text{HF}} = 22.7$ Hz, $J = 7.4$ Hz, 2H), 2.04 (s, 3H), 1.60 (quint, $J = 6.6$ Hz, 2H), 1.57-1.50 (m, 2H), 1.36-1.16 (m, 10H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.3 (d, $^1J_{\text{CF}} = 286.5$ Hz), 171.4, 135.5, 135.1 (q, $^2J_{\text{CF}} = 33.6$ Hz), 130.1, 129.6 (q, $^3J_{\text{CF}} = 3.7$ Hz), 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 101.8 (d, $^2J_{\text{CF}} = 63.5$ Hz), 64.6, 53.5, 30.4 (d, $^2J_{\text{CF}} = 21.8$ Hz), 29.2, 29.1, 28.9, 28.5, 25.8, 25.3, 21.0; FAB MS m/z 453 $[(\text{M-BF}_4)^+]$: HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{26}\text{BrF}_4\text{O}_2$ $[(\text{M-BF}_4)^+]$ 453.1052, found 453.1038. A vinylic proton of (**Z**)-**2g** appears as a doublet ($^3J_{\text{HF}} = 25.6$ Hz) at δ 7.03 ppm.

(E)-(11-Chloro-2-fluoro-1-undecenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (2h): an oil; IR (neat) 3105, 2933, 2858, 1646, 1594, 1406, 1324, 1177, 1147-1042, 994, 839 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.4$ Hz, 2H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $^3J_{\text{HF}} = 9.5$ Hz, 1H), 3.53 (t, $J = 6.6$ Hz, 2H), 2.78 (dt, $^3J_{\text{HF}} = 22.4$ Hz, $J = 7.4$ Hz, 2H), 1.75 (quint, $J = 6.9$ Hz, 2H), 1.60-1.49 (m, 2H), 1.39 (quint, $J = 7.2$ Hz, 2H), 1.31-1.17 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.3 (d, $^1J_{\text{CF}} = 285.9$ Hz), 135.5, 135.0 (q, $^2J_{\text{CF}} = 33.6$ Hz), 130.2, 129.5 (q, $^3J_{\text{CF}} = 3.7$ Hz), 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 101.8 (d, $^2J_{\text{CF}} = 63.5$ Hz), 45.2, 32.5, 30.4 (d, $^2J_{\text{CF}} = 22.4$ Hz), 29.1, 29.0, 28.8, 28.7, 26.7, 25.3; FAB MS m/z 429 $[(\text{M-BF}_4)^+]$: HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{23}\text{BrClF}_4$ $[(\text{M-BF}_4)^+]$ 429.0608, found 429.0581. A vinylic proton of (**Z**)-**2h** appears as a doublet ($^3J_{\text{HF}} = 25.5$ Hz) at δ 7.02 ppm.

(E)-(2-Fluoro-10-methoxycarbonyl-1-decenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (2i): an oil; IR (neat) 3105, 2935, 2859, 1731, 1645, 1594, 1438, 1406, 1324, 1197-990, 840, 772 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.4$ Hz, 2H), 7.85 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $^3J_{\text{HF}} = 8.8$ Hz, 1H), 3.66 (s, 3H), 2.78 (dt, $^3J_{\text{HF}} = 22.4$ Hz, $J = 7.4$ Hz, 2H), 2.29 (t, $J = 7.4$ Hz, 2H), 1.64-1.50 (m, 4H), 1.33-1.19 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.3 (d, $^1J_{\text{CF}} = 286.5$ Hz), 174.4, 135.4, 135.1 (q, $^2J_{\text{CF}} = 33.6$ Hz), 130.1, 129.6 (q, $^3J_{\text{CF}} = 3.7$ Hz), 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 101.8 (d, $^2J_{\text{CF}} = 63.5$ Hz), 51.5, 34.0, 30.4 (d, $^2J_{\text{CF}} = 22.4$ Hz), 28.9, 28.9, 28.8, 25.2, 24.7; FAB MS m/z 439 [(M-BF₄)⁺]: HRMS (FAB) calcd for C₁₉H₂₄BrF₄O₂ [(M-BF₄)⁺] 439.0896, found 439.0887. A vinylic proton of (Z)-**2i** appears as a doublet ($^3J_{\text{HF}} = 25.6$ Hz) at δ 7.04 ppm.

(E)-(2-Fluoro-11-methoxy-1-undecenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (2j): an oil; IR (neat) 3104, 2932, 2858, 1647, 1594, 1405, 1324, 1176, 1138, 1111-1026, 995, 840 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.4$ Hz, 2H), 7.84 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $^3J_{\text{HF}} = 9.7$ Hz, 1H), 3.36 (t, $J = 6.6$ Hz, 2H), 3.34 (s, 3H), 2.77 (dt, $^3J_{\text{HF}} = 22.4$ Hz, $J = 7.4$ Hz, 2H), 1.60-1.45 (m, 4H), 1.35-1.14 (m, 10H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.3 (d, $^1J_{\text{CF}} = 285.3$ Hz), 135.4, 135.0 (q, $^2J_{\text{CF}} = 33.6$ Hz), 130.1, 129.5 (q, $^3J_{\text{CF}} = 3.7$ Hz), 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 101.8 (d, $^2J_{\text{CF}} = 63.5$ Hz), 72.8, 58.5, 30.4 (d, $^2J_{\text{CF}} = 21.8$ Hz), 29.6, 29.3, 29.2, 29.1, 28.9, 26.0, 25.3; FAB MS m/z 425 [(M-BF₄)⁺]: HRMS (FAB) calcd for C₁₉H₂₆BrF₄O [(M-BF₄)⁺] 425.1103, found 425.1082. A vinylic proton of (Z)-**2j** appears as a doublet ($^3J_{\text{HF}} = 25.6$ Hz) at δ 7.02 ppm.

(E)-(2-Ethoxy-1-decenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (3a): ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.8$ Hz, 2H), 7.82 (d, $J = 8.8$ Hz, 2H), 6.55 (s, 1H), 4.06 (q, $J = 6.9$ Hz, 2H), 2.54 (t, $J = 7.7$ Hz, 2H), 1.51-1.43 (m, 2H), 1.39 (t, $J = 6.9$ Hz, 3H), 1.35-1.15 (m, 10H), 0.87 (t, $J = 6.6$ Hz, 3H). Ethoxyvinyl- λ^3 -bromane **3a** is highly labile.

(E)-(2-Chloro-1-decenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (3b): ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.8$ Hz, 2H), 7.86 (d, $J = 8.8$ Hz, 2H), 7.33 (s, 1H), 2.83 (t, $J = 7.7$ Hz, 2H), 1.60-1.50 (m, 2H), 1.30-1.15 (m, 10H), 0.87 (t, $J = 6.8$ Hz, 3H); FAB MS m/z 397 [(M-BF₄)⁺]: HRMS (FAB) calcd for C₁₇H₂₂BrClF₃ [(M-BF₄)⁺] 397.0545, found 397.0553.

Reaction of Difluoro[4-(trifluoromethyl)phenyl]- λ^3 -bromane (1) with 1-Decyne in 1,2-Dichloroethane (Table 1, Entry 9). To a white solid of difluoro- λ^3 -bromane **1** (69 mg, 0.26 mmol) in a PFA tube was added dropwise a solution of 1-decyne (24 mg, 0.17 mmol) in 1,2-dichloroethane (1 mL) and then a solution of BF₃-*i*-Pr₂O (44 mg, 0.26 mmol) in 1,2-dichloroethane (0.5 mL) at -30 °C with stirring under argon. The solution was gradually warmed to room temperature over 3.5 h. After the addition of a saturated aqueous solution of NaBF₄, the mixture was extracted with dichloromethane four times. After separation and filtration of the organic phase, the solvent was evaporated under an aspirator vacuum to give an oil, which was washed several times with hexane by decantation at room temperature to give a 66:6:28 mixture (53.8 mg) of (E)- (43%) and (Z)-2-fluoro-1-decenyl- λ^3 -bromane **2a** (4%) and (E)-2-chloro-1-decenyl- λ^3 -bromane **3b** (19%).

Synthesis of (E)-(2-Chloro-5-fluoro-1-pentenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (4a). To a stirred solution of difluoro[4-(trifluoromethyl)phenyl]- λ^3 -bromane (**1**) (80 mg, 0.3 mmol) and commercially available 5-chloro-1-pentyne (13 mg, 0.12 mmol) in chloroform (1 mL) in a PFA tube was added dropwise a solution of BF₃-*i*-Pr₂O (31 mg, 0.18 mmol) in chloroform (0.5 mL) at -60 °C under argon and then the solution was gradually warmed to room temperature over 3.5 h. After the addition of a saturated aqueous solution of NaBF₄, the mixture was extracted with dichloromethane four times. After separation and filtration of the organic phase, the solvent was evaporated under an aspirator vacuum to give an yellow oil, which was washed several times with hexane by decantation at room temperature to give the λ^3 -bromane **4a** (39 mg, 73%) as an oil. IR (neat) 3104, 2976, 1595, 1406, 1324, 1206-975, 839 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J =$

8.4 Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H), 7.31 (s, 1H), 4.54 (br d, $^2J_{\text{HF}} = 45.8$ Hz, 2H), 3.09 (t, $J = 6.6$ Hz, 2H), 2.12 (br d, $^3J_{\text{HF}} = 28.4$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.2, 135.2 (q, $^2J_{\text{CF}} = 33.6$ Hz), 134.3, 131.0, 129.7 (q, $^3J_{\text{CF}} = 3.7$ Hz), 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 111.8, 82.4 (d, $^1J_{\text{CF}} = 165.1$ Hz), 32.9 (d, $^3J_{\text{CF}} = 5.0$ Hz), 27.3 (d, $^2J_{\text{CF}} = 19.9$ Hz); FAB MS m/z 345 [(M-BF₄)⁺]; HRMS (FAB) calcd for C₁₂H₁₁BrClF₄ [(M-BF₄)⁺] 344.9669, found 344.9687.

(E)-(2-Chloro-5-fluoro-4-methyl-1-pentenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (4b): colorless needles (recrystallized from dichloromethane-hexane); mp 104-105 °C (decomp.); IR (neat) 3105, 2974, 1643, 1595, 1464, 1406, 1325, 1178, 1147-989, 839 cm⁻¹; ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.8$ Hz, 2H), 7.87 (d, $J = 8.8$ Hz, 2H), 7.35 (s, 1H), 4.38 (ddd, $^2J_{\text{HF}} = 47.2$ Hz, $J = 9.5, 5.2$ Hz, 1H), 4.34 (ddd, $^2J_{\text{HF}} = 47.2$ Hz, $J = 9.5, 5.2$ Hz, 1H), 3.10 (dd, $J = 14.7, 7.1$ Hz, 1H), 2.82 (dd, $J = 14.7, 7.1$ Hz, 1H), 2.53-2.36 (m, 1H), 1.03 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 152.6, 135.2 (q, $^2J_{\text{CF}} = 33.6$ Hz), 134.4, 131.0, 129.7 (q, $^3J_{\text{CF}} = 3.7$ Hz), 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 112.1, 86.6 (d, $^1J_{\text{CF}} = 169.4$ Hz), 39.6 (d, $^3J_{\text{CF}} = 4.4$ Hz), 32.5 (d, $^2J_{\text{CF}} = 18.1$ Hz), 14.9 (d, $^3J_{\text{CF}} = 6.9$ Hz); FAB MS m/z 359 [(M-BF₄)⁺]; HRMS (FAB) calcd for C₁₃H₁₃BrClF₄ [(M-BF₄)⁺] 358.9825, found 358.9844. Anal. Calcd for C₁₃H₁₃BBBrClF₈: C, 34.90; H, 2.93. Found: C, 34.61; H, 2.88.

(E)-(2-Chloro-4-fluoro-4-methyl-1-hexenyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (5): colorless needles (recrystallized from dichloromethane-hexane); mp 101-102 °C (decomp.); IR (neat) 3103, 2983, 1595, 1464, 1406, 1178, 1144-1021, 993, 839 cm⁻¹; ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.8$ Hz, 2H), 7.88 (d, $J = 8.8$ Hz, 2H), 7.32 (s, 1H), 3.41 (dd, $^3J_{\text{HF}} = 18.7$ Hz, $J = 15.4$ Hz, 1H), 3.15 (dd, $^3J_{\text{HF}} = 24.9$ Hz, $J = 15.4$ Hz, 1H), 1.91-1.73 (m, 2H), 1.47 (d, $^3J_{\text{HF}} = 22.0$ Hz, 3H), 1.02 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.9, 135.4 (q, $^2J_{\text{CF}} = 33.6$ Hz), 133.4, 131.4 (q, $^4J_{\text{CF}} = 3.1$ Hz), 129.6 (q, $^3J_{\text{CF}} = 3.7$ Hz), 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 114.3, 98.0 (d, $^1J_{\text{CF}} = 174.4$ Hz), 46.2 (d, $^2J_{\text{CF}} = 21.8$ Hz), 32.8 (d, $^2J_{\text{CF}} = 23.0$ Hz), 23.4 (d, $^2J_{\text{CF}} = 24.9$ Hz), 8.0 (d, $^3J_{\text{CF}} = 7.5$ Hz); FAB MS m/z 373 [(M-BF₄)⁺]; HRMS (FAB) calcd for C₁₄H₁₅BrClF₄ [(M-BF₄)⁺] 372.9982, found 372.9977. Anal. Calcd for C₁₄H₁₅BBBrClF₈: C, 36.44; H, 3.28. Found: C, 36.20; H, 3.12.

(E)-[2-Chloro-3-(1-fluorocycloheptyl)-1-propenyl][4-(trifluoromethyl)phenyl](tetrafluoroborato)- λ^3 -bromane (6): colorless needles (recrystallized from dichloromethane-diethyl ether); mp 101-102.5 °C (decomp.); IR (KBr) 3095, 2933, 2861, 1665, 1595, 1460, 1404, 1325, 1183-994, 841 cm⁻¹; ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.7$ Hz, 2H), 7.86 (d, $J = 8.7$ Hz, 2H), 7.33 (s, 1H), 3.28 (d, $^3J_{\text{HF}} = 22.1$ Hz, 2H), 2.11-1.98 (m, 2H), 1.96-1.81 (m, 2H), 1.74-1.60 (m, 4H), 1.59-1.50 (m, 2H), 1.49-1.38 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.6, 135.2 (q, $^2J_{\text{CF}} = 33.6$ Hz), 133.6, 131.5 (q, $^4J_{\text{CF}} = 2.5$ Hz), 129.6 (q, $^3J_{\text{CF}} = 3.7$ Hz), 122.7 (q, $^1J_{\text{CF}} = 273.4$ Hz), 114.6, 101.0 (d, $^1J_{\text{CF}} = 174.4$ Hz), 47.5 (d, $^2J_{\text{CF}} = 22.4$ Hz), 38.5 (d, $^2J_{\text{CF}} = 23.7$ Hz), 29.3, 21.8 (d, $^3J_{\text{CF}} = 5.6$ Hz); FAB MS m/z 413 [(M-BF₄)⁺]; HRMS (FAB) calcd for C₁₇H₁₉BrClF₄ [(M-BF₄)⁺] 413.0295, found 413.0292. Anal. Calcd for C₁₇H₁₉BBBrClF₈: C, 40.72; H, 3.82. Found: C, 40.48; H, 3.72.

5-Chloro-4-methyl-1-pentyne: a colorless oil; IR (CHCl_3) 3306, 2969, 2933, 2118, 1458, 643 cm⁻¹; ^1H NMR (400 MHz, CDCl_3) δ 3.56 (d, $J = 6.2$ Hz, 2H), 2.38-2.26 (m, 2H), 2.08 (octet, $J = 6.2$ Hz, 1H), 2.0 (t, $J = 2.5$ Hz, 1H), 1.11 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 81.6, 70.0, 49.3, 34.9, 23.0, 17.3; MS m/z 116 (M⁺); HRMS calcd for C₆H₉Cl (M⁺) 116.0393, found 116.0323. This chloroalkyne was prepared from the known alcohol as shown in Scheme S1.

Scheme S1

5-Chloro-4,4-dimethyl-1-pentyne: a colorless oil; IR (CHCl₃) 3307, 2968, 2875, 2117, 1469, 644 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.47 (s, 2H), 2.24 (d, *J* = 2.4 Hz, 2H), 2.02 (t, *J* = 2.4 Hz, 1H), 1.08 (s, 6H); MS *m/z* 130 (M⁺): HRMS calcd for C₇H₁₁Cl (M⁺) 130.0549, found 130.0553. This chloroalkyne was prepared from the known alcohol as shown in Scheme S2.

Scheme S2

3-[1-(Chloromethyl)cyclohexyl]-1-propyne: a colorless oil; IR (CHCl₃) 3306, 2933, 2856, 2116, 1455, 1304, 644 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.59 (s, 2H), 2.32 (d, *J* = 2.7 Hz, 2H), 2.0 (t, *J* = 2.7 Hz, 1H), 1.56-1.39 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 80.9, 70.6, 52.0, 37.5, 32.8, 25.9, 25.6, 21.5; MS *m/z* (relative intensity) 135 (M⁺-Cl, 12), 131 (46), 95 (100); HRMS calcd for C₁₀H₁₅Cl (M⁺) 170.0862, found 170.0876. This chloroalkyne was prepared from the known ester as shown in Scheme S3.

Scheme S3