Supporting Information

for

Amine–borane complex-initiated SF$_5$Cl radical addition on alkenes and alkynes

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General information, synthetic procedures, additional optimization results, NMR spectra for known compounds ($^1$H, $^{19}$F) and full characterization of all new compounds
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General information
All reactions were carried out under an argon atmosphere. Et₂O, dichloromethane, THF, and toluene were purified using a Vacuum Atmospheres Inc. Solvent Purification System. All other commercially available compounds were used as received. Thin-layer chromatography (TLC) analyses of reaction mixtures were performed using Silicycle silica gel 60 Å F254 TLC plates and visualized under UV light or by staining with potassium permanganate. Flash column chromatography was carried out on Silicycle silica gel 60 Å, 230–400 mesh. ¹H, ¹³C and ¹⁹F spectra were respectively recorded at 500, 126, and 470 MHz using CDCl₃ as the solvent at ambient temperature on an Agilent Technologies 500/54 Premium Shielded spectrometer. The internal standard used was: for ¹H NMR tetramethylsilane (δ = 0 ppm), for ¹³C NMR tetramethylsilane (δ = 0 ppm). For ¹⁹F spectra, calibration was performed using a unified scale [1]. Coupling constants (J) are measured in hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, h = sextet, M = multiplet, br = broad resonance. Low-resolution mass spectra were obtained on a GC–MS using chemical ionization (CI). Infrared spectra were recorded using an ABB MB300 FT-IR spectrometer.

[1] Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. Pure Appl. Chem. 2001, 73, 1795–1818.
Synthesis of dec-9-en-1-yl acetate

Dec-9-en-1-yl acetate: Following a procedure described by Schmalz et al. [2], dec-9-en-1-ol (1 equiv, 200 mg, 1.28 mmol) and pyridine (10 mL, 0.13 M) were charged in a round-bottomed flask at 0 °C. The solution was degassed with argon before a solution of acetic anhydride in pyridine (0.25 M, 1.2 equiv, 1.54 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by the addition of water, before pyridine was evaporated under reduced pressure. The crude mixture was then dissolved in Et₂O and successively washed with a 10% HCl solution in water and brine. The organic phase was dried over MgSO₄, filtered, and evaporated under reduce pressure. The crude product was purified by flash chromatography on silica gel using hexane/EtOAc 90:10 as the eluent to yield the title compound as colorless oil (71%, 179.3 mg). ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.00 (dq, J = 17.1, 1.7 Hz, 1H), 4.94 (ddt, J = 10.2, 2.3, 1.2 Hz, 1H), 4.06 (t, J = 6.8 Hz, 2H), 2.08 – 2.01 (m, 5H), 1.67 – 1.56 (m, 2H), 1.45 – 1.20 (m, 10H). Analytical data were identical to those previously reported [3].

General procedures for the SF₅Cl additions

Method A: A microwave vial under inert atmosphere was successively charged with the unsaturated compound (1.0 equiv) and degassed hexanes (0.25 M) at −40 °C. A solution of SF₅Cl in hexanes (1.5 equiv) was added, followed by a

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[2] Hirschhäuser, C.; Velcicky, J.; Schlawe, D.; Hessler, E.; Majdalani, A.; Neudörfl, J.-M.; Prokop, A.; Wieder, T.; Schmalz, H.-G. Chem. Eur. J. 2013, 19, 13017-13029.
[3] Winter, R.; Nixon, P. G.; Gard, G. L.; Radford, D. H.; Holcomb, N. R.; Grainger, D. W. J. Fluorine Chem. 2001, 107, 23-30.
solution of Et$_3$B (1 M in THF, 0.1 equiv). The mixture was stirred for 3 h at $-40^\circ$C.
The reaction mixture was then allowed to warm to room temperature, and a saturated solution of NaHCO$_3$ was added to quench the reaction. The phases were separated and the organic phase was dried over MgSO$_4$. The crude product was concentrated under reduced pressure and purified by flash chromatography on silica gel.

**Method B:** A microwave vial under inert atmosphere was successively charged with the unsaturated compound (1.0 equiv) and degassed MTBE (0.33 M) at $-40^\circ$C. The vial was hermetically sealed, before a solution of SF$_5$Cl in hexanes (3 equiv) was added. A solution of DICAB (0.10 M in MTBE, 0.1 equiv) was then added and the mixture was stirred for 3 h at 60 $^\circ$C. The reaction mixture was then allowed to cool to room temperature and a saturated solution of NaHCO$_3$ was added to quench the reaction. The phases were separated and the organic phase was dried over MgSO$_4$. The crude product was concentrated under reduced pressure and purified by flash chromatography on silica gel.

**SF$_5$Cl additions reactions**

**(2-Chloro-2-phenethoxyethyl)pentafluoro-\(\lambda^6\)-sulfane (2a):**

**Method A:** ((Allyloxy)methyl)benzene (1, 100 mg, 0.67 mmol), SF$_5$Cl (1.37 M in hexanes, 0.74 mL, 1.01 mmol), and Et$_3$B (1 M in THF, 67 μL, 0.067 mmol) were engaged in general procedure, Method A, to afford the title compound 2a as colorless oil (185.5 mg, 0.60 mmol, 88%) after purification by flash chromatography using hexanes/EtOAc 95:5 as the eluent. **Method B:**
((Allyloxy)methyl)benzene (1, 100 mg, 0.67 mmol), SF₅Cl (1.32 M in hexanes, 1.53 mL, 2.02 mmol), and DICAB (13.17 mg, 0.067 mmol) were engaged in general procedure, Method B, to afford the title compound 2a as colorless oil (161.0 mg, 0.52 mmol, 77%) after purification by flash chromatography using hexanes/EtOAc 95:5 as the eluent. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.41 – 7.34 (m, 2H), 7.36 – 7.30 (m, 3H), 4.59 (s, 2H), 4.51 – 4.43 (m, 1H), 4.34 – 4.20 (m, 1H), 3.95 – 3.80 (m, 1H), 3.76 (dd, J = 10.4, 4.6 Hz, 1H), 3.60 (dd, J = 10.4, 6.7 Hz, 1H); ¹⁹F NMR (470 MHz, CDCl₃): δ (ppm) = 83.9 – 82.4 (m, 1F), 66.6 (dt, J = 146.7, 8.0 Hz, 4F). Analytical data were identical to those previously reported [4].

(2-Chloro-4-phenylbutyl)pentafluoro-λ⁶-sulfane (2b): Method A: 4-Phenyl-1-butene (100 mg, 0.76 mmol), SF₅Cl (1.32 M in hexanes, 0.86 mL, 1.13 mmol), and Et₃B (1 M in THF, 76 μL, 0.076 mmol) were engaged in general procedure, Method A, to afford the title compound 2b as colorless oil (201.4 mg, 0.68 mmol, 90%) after purification by flash chromatography using 100% hexanes as the eluent. Method B: 4-Phenyl-1-butene (100 mg, 0.67 mmol), SF₅Cl (1.37 M in hexanes, 1.66 mL, 2.27 mmol), and DICAB (14.75 mg, 0.076 mmol) were engaged in general procedure, Method B, to afford the title compound 2b as colorless oil (191.2 mg, 0.65 mmol, 85%) after purification by flash chromatography using 100% hexanes as the eluent. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.32 (t, J = 7.3 Hz, 2H), 7.27 – 7.17 (m, 3H), 4.34 – 4.26 (m, 1H), 4.03 (td, J = 14.4, 8.4 Hz, 1H), 3.91 (td, J =

[4] Gilbert, A.; Paquin, J.-F. *J. Fluorine Chem.* **2019**, *221*, 70-74.
14.3, 7.9 Hz, 1H), 2.98 – 2.89 (m, 1H), 2.83 – 2.74 (m, 1H), 2.32 – 2.21 (m, 1H), 2.04 (td, \( J = 14.2, 9.3 \) Hz, 1H); \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 83.9 – 82.4 (m, 1F), 66.5 (dt, \( J = 146.6, 8.2 \) Hz, 4F). Analytical data were identical to those previously reported [5].

(2-Chloro-2-phenylethyl)pentafluoro-\( \lambda^6 \)-sulfane (2c): Method A: Styrene (100 mg, 0.38 mmol), SF\(_5\)Cl (1.32 M in hexanes, 0.43 mL, 0.56 mmol), and Et\(_3\)B (1 M in THF, 38 \( \mu \)L, 0.038 mmol) were engaged in general procedure, Method A, to afford the title compound 2c which could not be isolated. The yield was estimated using NMR analysis and 2-fluoro-4-nitrotoluene as the reference; yield: 8%.

(4-Chloro-2,4-diphenylbutyl)pentafluoro-\( \lambda^6 \)-sulfane (2d): Method B: Styrene (200 mg, 1.92 mmol), SF\(_5\)Cl (1.37 M in hexanes, 4.21 mL, 5.76 mmol), and DICAB (37.5 mg, 0.19 mmol) were engaged in general procedure, Method B, to afford the title compound 2d as colorless oil (113.0 mg, 0.30 mmol, 15%) after purification by flash chromatography using 100% hexane as the eluent. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 7.44 – 7.39 (m, 10H), 5.39 (t, \( J = 6.8 \) Hz, 1H), 5.03 (dd, \( J = 7.9, 6.6 \) Hz, 1H), 4.37 – 4.27 (m, 2H), 4.02 (dd, \( J = 11.3, 6.6 \) Hz, 1H), 3.95 (dd, \( J = 11.4, 7.9 \) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 138.5, 138.0, 129.4, 129.2, 129.1, 128.8, 127.4, 126.9, 76.9 (p, \( J = 13.3 \) Hz), 61.8, 56.4 (p, \( J = 4.7 \) Hz), 48.4; \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 83.2 – 80.8 (m, 1F), 66.4 (dt, \( J = 147.1, 2906-3912.

[5] Ponomarenko, M. V.; Serguchev, Y. A.; Röschenthaler, G.-V. Synthesis 2010, 22, 3906-3912.
7.8 Hz, 4F); GC-MS (Cl): m/z calcd for C\textsubscript{16}H\textsubscript{15}ClF\textsubscript{5}S [M-H]+ 369.05 found 369.07 (under all conditions tested for high-resolution mass spectra [ESI(+), ESI(−), APPI], no significant ion was detected); IR (ATR, Diamond): ν (cm\textsuperscript{-1}) = 3032, 1495, 1456, 1310, 1198, 878, 824, 696.

**9-Chloro-10-(pentafluoro-\textlambda\textsuperscript{6}-sulfanyl)decan-1-ol (2e): Method A:** Dec-9-en-1-ol (50 mg, 0.32 mmol), SF\textsubscript{5}Cl (0.96 M in hexanes, 0.50 mL, 0.48 mmol), and Et\textsubscript{3}B (1 M in THF, 32 μL, 0.032 mmol) were engaged in general procedure, Method A, to afford the title compound 2e as colorless oil (15.1 mg, 0.047 mmol, 15%) after purification by flash chromatography using hexanes/EtOAc 95:5 as the eluent.

**Method B:** Dec-9-en-1-ol (50 mg, 0.32 mmol), SF\textsubscript{5}Cl (0.96 M in hexanes, 0.99 mL, 0.96 mmol), and DICAB (6.2 mg, 0.032 mmol) were engaged in general procedure, Method B, to afford the title compound 2e which could not be isolated. The yield was estimated using NMR analysis and 2-fluoro-4-nitrotoluene as the reference; yield: 43%. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ (ppm) = 4.40 – 4.30 (m, 1H), 4.06 – 3.96 (m, 1H), 3.95 – 3.85 (m, 1H), 3.40 (t, J = 6.7 Hz, 2H), 1.97 – 1.87 (m, 1H), 1.82 – 1.67 (m, 1H), 1.67 – 1.25 (m, 13H); \textsuperscript{19}F NMR (470 MHz, CDCl\textsubscript{3}): δ (ppm) = 88.17 – 78.75 (m), 66.19 (dt, J = 146.5, 8.3 Hz). Analytical data were identical to those previously reported [3, 6].

[6] Dolbier Jr., W. R.; Aït-Mohand, S.; Schertz, T. D.; Sergeeva, T. A.; Cradlebaugh, J. A.; Mitani, A.; Gard, G. L.; Winter, R. W.; Thrasher, J. S. *J. Fluorine Chem.* 2006, 127, 1302-1310.
**9-Chloro-10-(pentafluoro-\(\lambda^6\)-sulfanyl)decyl acetate (2f): Method A:** Dec-9-en-1-yl acetate (50 mg, 0.25 mmol), SF\(_5\)Cl (0.96 M in hexanes, 0.39 mL, 0.38 mmol), and Et\(_3\)B (1 M in THF, 25 \(\mu\)L, 0.032 mmol) were engaged in general procedure, Method A, to afford the title compound \(2f\) as colorless oil (84.0 mg, 0.23 mmol, 92%) after purification by flash chromatography using hexanes/EtOAc 95:5 as the eluent. **Method B:** Dec-9-en-1-yl acetate (33.7 mg, 0.17 mmol), SF\(_5\)Cl (0.96 M in hexanes, 0.53 mL, 0.51 mmol), and DICAB (3.3 mg, 0.017 mmol) were engaged in general procedure, Method B, to afford the title compound \(2f\) which could not be isolated. The yield was estimated using NMR analysis and 2-fluoro-4-nitrotoluene as the reference; yield: 3%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 4.39 – 4.27 (m, 1H), 4.05 (t, \(J = 6.7\) Hz, 2H), 4.03 – 3.96 (m, 1H), 3.95 – 3.85 (m, 1H), 2.05 (s, 3H), 1.98 – 1.84 (m, 1H), 1.80 – 1.68 (m, 1H), 1.65 – 1.53 (m, 3H), 1.50 – 1.42 (m, 1H), 1.38 – 1.28 (m, 8H); \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 84.29 – 81.36 (m, 1F), 66.16 (dt, \(J = 146.3, 8.2\) Hz, 4F). Analytical data were identical to those previously reported [3, 6].

**1-Chloro-2-(pentafluoro-\(\lambda^6\)-sulfanyl)ethyl benzoate (2g): Method A:** Vinyl benzoate (100 mg, 0.68 mmol), SF\(_5\)Cl (1.32 M in hexanes, 0.77 mL, 1.01 mmol), and Et\(_3\)B (1 M in THF, 68 \(\mu\)L, 0.068 mmol) were engaged in general procedure, Method A, to afford the title compound \(2g\) as colorless oil (156.7 mg, 0.50 mmol, 75%) after purification by flash chromatography using hexanes/Et\(_2\)O 98:2 as the eluent. **Method B:** Vinyl benzoate (100 mg, 0.68 mmol), SF\(_5\)Cl (1.32 M in hexanes, 1.53 mL, 2.03 mmol), and DICAB (13.17 mg, 0.068 mmol) were
engaged in general procedure, Method B, to afford the title compound 2g as colorless oil (175.5 mg, 0.57 mmol, 84%) after purification by flash chromatography using hexanes/Et₂O 98:2 as the eluent. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.10 – 8.05 (m, 2H), 7.69 – 7.62 (m, 1H), 7.53 – 7.46 (m, 2H), 7.14 (dd, J = 9.8, 2.1 Hz, 1H), 4.49 – 4.37 (m, 1H), 4.26 – 4.16 (m, 1H); ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 163.4, 134.5, 130.2, 128.8, 127.9, 77.6 (p, J = 5.4 Hz), 73.4 (p, J = 14.7 Hz); ¹⁹F NMR (470 MHz, CDCl₃): δ (ppm) = 81.5 – 80.1 (m, 1F), 66.8 (dt, J = 147.2, 8.1 Hz, 4F); GC-MS (CI): m/z calcd for C₉H₉ClF₅O₂S [M+H]+ 310.99 found 311.00 (under all conditions tested for high-resolution mass spectra [ESI (+), ESI (−), APPI], no significant ion was detected); IR (ATR, Diamond): ν (cm⁻¹) = 3040, 1744, 1603, 1452, 1244, 1103, 1061, 837.

**Ethyl 4-chloro-2-methyl-5-(pentafluoro-λ₆-sulfanyl)pentanoate (2h): Method A:** Ethyl 2-methylpent-4-enoate (50 mg, 0.35 mmol), SF₅Cl (0.96 M in hexanes, 0.55 mL, 0.52 mmol), and Et₃B (1 M in THF, 35 μL, 0.035 mmol) were engaged in general procedure, Method A, to afford the title compound 2h as colorless oil (86.8 mg, 0.28 mmol, 81%) in a 63:37 mixture of diastereoisomers after purification by flash chromatography using hexanes/EtOAc 90:10 as the eluent. **Method B:** Ethyl 2-methylpent-4-enoate (50 mg, 0.35 mmol), SF₅Cl (0.96 M in hexanes, 1.10 mL, 1.05 mmol), and DICAB (6.9 mg, 0.035 mmol) were engaged in general procedure, Method B, to afford the title compound 2h as colorless oil (74.7 mg, 0.25 mmol, 70%) in a 57:43 mixture of diastereoisomers after purification by flash chromatography using hexanes/EtOAc 95:5 as the eluent. ¹H NMR (500 MHz,
CDCl₃): δ (ppm) = 4.50 – 4.44 (m, 1H), 4.42 – 4.35 (m, 0.6H), 4.17 (app. p, J = 7.1 Hz, 3.2H), 4.07 – 3.97 (m, 1.6H), 3.96 – 3.82 (m, 1.6H), 2.90 – 2.81 (m, 1H), 2.81 – 2.71 (m, 0.6H), 2.35 (ddd, J = 13.8, 10.7, 2.7 Hz, 1H), 2.18 (ddd, J = 15.4, 10.5, 5.1 Hz, 0.6H), 2.01 (ddd, J = 14.4, 8.9, 3.5 Hz, 0.6H), 1.68 (ddd, J = 14.3, 11.0, 3.2 Hz, 1H), 1.31 – 1.24 (m, 4.8H), 1.24 (d, J = 7.2 Hz, 3H), 1.22 (d, J = 7.0 Hz, 1.8H); ¹⁹F NMR (470 MHz, CDCl₃): δ (ppm) = 83.6 – 82.0 (m, 1.6F), 66.6 (dt, J = 146.6, 8.1 Hz, 4F), 66.4 (dt, J = 146.5, 8.3 Hz, 2.4F). Analytical data were identical to those previously reported [7].

(Z)-(2-Chloro-3-phenylprop-1-en-1-yl)pentafluoro-λ⁶-sulfane (2i): Method A:
4-Phenyl-1-butyne (50 mg, 0.38 mmol), SF₅Cl (0.96 M in hexanes, 0.60 mL, 0.58 mmol), and Et₃B (1 M in THF, 38 μL, 0.038 mmol) were engaged in general procedure, Method A, to afford the title compound 2i as colorless oil (89 mg, 0.30 mmol, 79%) after purification by flash chromatography using 100% hexanes as the eluent. Method B: 4-Phenyl-1-butyne (100 mg, 0.77 mmol), SF₅Cl (1.37 M in hexanes, 1.68 mL, 2.30 mmol), and DICAB (14.99 mg, 0.077 mmol) were engaged in general procedure, Method B, to afford the title compound 2i as colorless oil (196.8 mg, 0.67 mmol, 88%) after purification by flash chromatography using 100% hexanes as the eluent. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.35 – 7.28 (m, 2H), 7.26 – 7.17 (m, 3H), 6.64 (p, J = 8.2 Hz, 1H), 3.00 – 2.89 (m, 4H); ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 146.4 (p, J = 6.4 Hz), 139.5, 137.3 (p, J = 21.8 Hz), 128.7, 128.5, 126.7, 38.3, 33.5; ¹⁹F NMR (470 MHz, CDCl₃):

[7] Lim, D. S.; Ngo, S. C.; Lal, S. G.; Minnich, K. E.; Welch, J. T. Tetrahedron Lett. 2008, 49, 5662-5663.
δ (ppm) = 83.4 – 82.0 (m, 1F), 67.3 (dd, J = 151.4, 8.3 Hz, 4F); GC-MS (Cl): m/z calcd for C₁₀H₉ClF₅S [M-H]⁺ 291.00 found 291.00 (under all conditions tested for high-resolution mass spectra [ESI (+), ESI (−), APPI], no significant ion was detected); IR (ATR, Diamond): ν (cm⁻¹) = 3090, 3030, 1639, 1456, 1178, 1040, 989, 833.

(Z)-(2-Chloro-2-phenylvinyl)pentafluoro-λ⁶-sulfane (2j):

**Method A:** Ethynylbenzene (50 mg, 0.49 mmol), SF₅Cl (0.96 M in hexanes, 0.76 mL, 0.73 mmol), and Et₃B (1 M in THF, 49 μL, 0.049 mmol) were engaged in general procedure, Method A, to afford the title compound 2j as colorless oil (23.6 mg, 0.089 mmol, 18%) after purification by flash chromatography using 100% pentane as the eluent. **Method B:** Ethynylbenzene (50 mg, 0.49 mmol), SF₅Cl (0.96 M in hexanes, 1.53 mL, 1.47 mmol), and DICAB (9.6 mg, 0.049 mmol) were engaged in general procedure, Method B, to afford the title compound 2j as colorless oil (30.2 mg, 0.11 mmol, 23%) after purification by flash chromatography using 100% pentane as the eluent. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.44 – 7.38 (m, 3H), 7.38 – 7.33 (m, 2H), 6.94 (p, J = 7.7 Hz, 1H); ¹⁹F NMR (470 MHz, CDCl₃): δ (ppm) = 82.22 – 80.33 (m, 1F), 69.00 (dd, J = 152.8, 7.5 Hz, 4F). Analytical data were identical to those previously reported [6,8].

((1Z,3Z)-4-Chloro-2,4-diphenylbuta-1,3-dien-1-yl)pentafluoro-λ⁶-sulfane (2k):

**Method B:** Ethynylbenzene (50 mg, 0.49 mmol), SF₅Cl (0.96 M in hexanes,
1.53 mL, 1.47 mmol) and DICAB (9.6 mg, 0.049 mmol) were engaged in general procedure, Method B, to afford the title compound 2k as colorless oil (9.1 mg, 0.025 mmol, 5%) after purification by flash chromatography using 100% pentane as the eluent. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 7.36 – 7.30 (m, 5H), 7.30 – 7.26 (m, 3H), 7.18 – 7.13 (m, 2H), 6.54 – 6.48 (m, 1H), 6.24 (p, $J = 8.7$ Hz, 1H); $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ (ppm) = 84.44 – 82.31 (m, 1F), 68.45 (dd, $J = 152.4, 8.6$ Hz, 4F). Analytical data were identical to those previously reported. [6,8]

$(E)$-(7-Chlorododec-6-en-6-yl)pentafluoro-$\lambda^6$-sulfane (2l): Method A: Dodec-6-yne (50 mg, 0.30 mmol), SF$_5$Cl (0.96 M in hexanes, 0.47 mL, 0.46 mmol), and Et$_3$B (1 M in THF, 30 $\mu$L, 0.030 mmol) were engaged in general procedure, Method A, to afford the title compound 2l as colorless oil (63.3 mg, 0.19 mmol, 65%) after purification by flash chromatography using 100% hexanes as the eluent. **Method B:** Dodec-6-yne (50 mg, 0.30 mmol), SF$_5$Cl (0.96 M in hexanes, 0.94 mL, 0.90 mmol), and DICAB (5.9 mg, 0.030 mmol) were engaged in general procedure, Method B, to afford the title compound 2l which could not be isolated. The yield was estimated using NMR analysis and 2-fluoro-4-nitrotoluene as the reference; yield: 17%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 2.73 – 2.66 (m, 2H), 2.62 – 2.51 (m, 2H), 1.66 – 1.55 (m, 4H), 1.40 – 1.18 (m, 8H), 0.90 (t, $J = 7.0$ Hz, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ (ppm) = 152.9 (p, $J = 12.0$ Hz), 146.1 (p, $J = 3.9$ Hz), 38.5 (t, $J = 3.2$ Hz), 33.7 (t, $J = 3.1$ Hz), 31.9, 31.3, 27.8, 27.2, 22.4, 22.2, 14.0, 13.9; $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ (ppm) = 87.1 (p, $J = 148.1$ Hz, 1F), 64.5 (d, $J = 148.1$ Hz, 4F); GC-MS (Cl): m/z calcd for C$_{12}$H$_{22}$ClF$_5$S [M]$^+$ 328.11 found
328.00 (under all conditions tested for high-resolution mass spectra [ESI (+), ESI (−), APPI], no significant ion was detected); IR (ATR, Diamond): ν (cm⁻¹) = 2959, 2864, 1618, 1460, 1040, 824, 766, 648.

**Full optimization results**

1. **Evaluation of the amino-borane complexes**

\[
\begin{align*}
\text{Product 1} & \quad \text{SF}_5\text{Cl (3 equiv.), DIPAB (0.1 equiv.)} \\
\text{solvent (0.25 M), } -40 \, ^\circ\text{C to } x \, ^\circ\text{C, 3 h} & \quad \text{Product 2a}
\end{align*}
\]

| Entry | Solvent | x (°C) | Conversion (%) | Yield (%) |
|-------|---------|--------|---------------|-----------|
| 1     | hexane  | 30     | 28            | 2         |
| 2     | hexane  | 40     | 32            | 6         |
| 3     | hexane  | 50     | 33            | 7         |
| 4     | hexane  | 60     | 55            | 5         |
| 5     | EtOAc   | 30     | 100           | 72        |
| 6     | EtOAc   | 40     | 100           | 64        |
| 7     | EtOAc   | 50     | 100           | 5         |
| 8     | EtOAc   | 60     | 100           | 29        |
| 9     | MTBE    | 30     | 77            | 40        |
| 10    | MTBE    | 40     | 69            | 6         |
| 11    | MTBE    | 50     | 79            | 41        |
| 12    | MTBE    | 60     | 92            | 26        |
| 13    | THF     | 30     | 100           | 28        |
| 14    | THF     | 40     | 100           | 33        |
| 15    | THF     | 50     | 100           | 28        |
| 16    | THF     | 60     | 100           | 30        |
| 17    | toluene | 30     | 39            | 14        |
| 18    | toluene | 40     | 41            | 5         |
| 19    | toluene | 50     | 46            | 8         |
| 20    | toluene | 60     | 83            | 41        |
| 21    | MeOH    | 30     | 100           | 0         |
| 22    | MeOH    | 40     | 100           | traces    |
| 23    | MeOH    | 50     | 100           | traces    |
| 24    | MeOH    | 60     | 100           | 0         |
| 25    | acetone | 30     | 100           | traces    |
| 26    | acetone | 40     | 100           | 0         |
| 27    | acetone | 50     | 100           | 9         |
| 28    | CH₂Cl₂  | 30     | 15            | traces    |

aDisappearance of the starting material, estimated by ¹H NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard. bYield estimated by ¹⁹F NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.
| Entry | Solvent | x (°C) | Conversion (%)$^a$ | Yield (%)$^b$ |
|-------|---------|--------|-------------------|--------------|
| 1     | hexane  | 30     | 25                | 1            |
| 2     | hexane  | 40     | 17                | 2            |
| 3     | hexane  | 50     | 82                | 72           |
| 4     | hexane  | 60     | 75                | 32           |
| 5     | EtOAc   | 30     | 100               | traces       |
| 6     | EtOAc   | 40     | 100               | 4            |
| 7     | EtOAc   | 50     | 100               | 62           |
| 8     | EtOAc   | 60     | 100               | 56           |
| 9     | MTBE    | 30     | 49                | 3            |
| 10    | MTBE    | 40     | 100               | 65           |
| 11    | MTBE    | 50     | 94                | 21           |
| 12    | MTBE    | 60     | 100               | 86           |
| 13    | THF     | 30     | 100               | 43           |
| 14    | THF     | 40     | 100               | 27           |
| 15    | THF     | 50     | 100               | 38           |
| 16    | THF     | 60     | 100               | 20           |
| 17    | toluene | 30     | 58                | 37           |
| 18    | toluene | 40     | 53                | 39           |
| 19    | toluene | 50     | 50                | 23           |
| 20    | toluene | 60     | 71                | 33           |
| 21    | MeOH    | 30     | 100               | traces       |
| 22    | MeOH    | 40     | 100               | traces       |
| 23    | MeOH    | 50     | 100               | traces       |
| 24    | MeOH    | 60     | 100               | traces       |
| 25    | acetone | 30     | 100               | 1            |
| 26    | acetone | 40     | 100               | 0            |
| 27    | acetone | 50     | 100               | traces       |
| 28    | CH₂Cl₂  | 30     | 24                | traces       |

$^a$Disappearance of the starting material, estimated by $^1$H NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard. $^b$Yield estimated by $^{19}$F NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.
Entry | solvent | x (°C) | Conversion (%)<sup>a</sup> | Yield (%)<sup>b</sup>
--- | --- | --- | --- | ---
1 | hexane | 30 | 32 | traces
2 | hexane | 40 | 41 | 8
3 | hexane | 50 | 47 | 10
4 | hexane | 60 | 58 | 10
5 | EtOAc | 30 | 100 | 18
6 | EtOAc | 40 | 100 | 58
7 | EtOAc | 50 | 100 | 8
8 | EtOAc | 60 | 100 | 4
9 | THF | 30 | 100 | 6
10 | THF | 40 | 100 | 19
11 | THF | 50 | 100 | 24
12 | THF | 60 | 100 | 32
13 | toluene | 30 | 71 | 23
14 | toluene | 40 | 78 | 44
15 | toluene | 50 | 53 | 10
16 | toluene | 60 | 53 | 1

<sup>a</sup>Disappearance of the starting material, estimated by <sup>1</sup>H NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.  
<sup>b</sup>Yield estimated by <sup>19</sup>F NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.

2. Evaluation of the increase in the amount of DICAB and the reaction time

| Solvent | DICAB equiv. | Time (h) | Conversion (%)<sup>a</sup> | Yield (%)<sup>b</sup>
--- | --- | --- | --- | ---
EtOAc | 0.2 | 3 | 100 | 80
EtOAc | 0.1 | 6 | 100 | 86
hexane | 0.2 | 3 | 61 | 37
hexane | 0.1 | 6 | 94 | 89
hexane | 0 | 6 | 20 | traces

<sup>a</sup>Disappearance of the starting material, estimated by <sup>1</sup>H NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.  
<sup>b</sup>Yield estimated by <sup>19</sup>F NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.
3. Evaluation of the decreased in the amount of amino-borane complex

![Reaction Scheme]

| Entry | Solvent | Amino-borane Complex | Temp (°C) | Conversion (%)<sup>a</sup> | Yield (%)<sup>b</sup> |
|-------|---------|----------------------|----------|--------------------------|----------------------|
| 1     | hexane  | DIPAB                | 30       | 17                       | traces               |
| 2     | hexane  | DIPAB                | 40       | 19                       | traces               |
| 3     | hexane  | DIPAB                | 50       | 25                       | 2                    |
| 4     | hexane  | DIPAB                | 60       | 65                       | 41                   |
| 5     | hexane  | DICAB                | 30       | 14                       | traces               |
| 6     | hexane  | DICAB                | 40       | 17                       | 2                    |
| 7     | hexane  | DICAB                | 50       | 93                       | 86                   |
| 8     | hexane  | DICAB                | 60       | 30                       | 22                   |
| 9     | EtOAc   | DIPAB                | 30       | 21                       | traces               |
| 10    | EtOAc   | DIPAB                | 40       | 70                       | traces               |
| 11    | EtOAc   | DIPAB                | 50       | 54                       | 9                    |
| 12    | EtOAc   | DIPAB                | 60       | 100                      | 6                    |
| 13    | EtOAc   | DICAB                | 30       | 38                       | 1                    |
| 14    | EtOAc   | DICAB                | 40       | 100                      | 1                    |
| 15    | EtOAc   | DICAB                | 50       | 66                       | 2                    |
| 16    | EtOAc   | DICAB                | 60       | 100                      | 37                   |
| 17    | MTBE    | DIPAB                | 30       | 30                       | 1                    |
| 18    | MTBE    | DIPAB                | 40       | 78                       | 33                   |
| 19    | MTBE    | DIPAB                | 50       | 67                       | 20                   |
| 20    | MTBE    | DIPAB                | 60       | 67                       | 24                   |
| 21    | MTBE    | DICAB                | 30       | 58                       | 27                   |
| 22    | MTBE    | DICAB                | 40       | 100                      | 77                   |
| 23    | MTBE    | DICAB                | 50       | 100                      | 73                   |
| 24    | MTBE    | DICAB                | 60       | 100                      | 75                   |

<sup>a</sup>Disappearance of the starting material, estimated by <sup>1</sup>H NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.  
<sup>b</sup>Yield estimated by <sup>19</sup>F NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.
4. Evaluation of the initial temperature

\[
\begin{align*}
1 & \quad \text{SF}_5\text{Cl (3 equiv.), DICAB (0.1 equiv.)} \\
& \quad \text{solvent (0.25 M), x °C to 50 °C, 3 h} \\
& \quad \text{2a}
\end{align*}
\]

| Solvent | x °C | Conversion (%)<sup>a</sup> | Yield (%)<sup>b</sup> |
|---------|------|---------------------------|----------------------|
| EtOAc   | 0    | 100                       | 93                   |
| EtOAc   | rt   | 100                       | 71                   |
| hexane  | 0    | 40                        | 2                    |
| hexane  | rt   | 100                       | 81                   |
| MTBE    | 0    | 100                       | 75                   |
| MTBE    | rt   | 100                       | 79                   |

<sup>a</sup>Disappearance of the starting material, estimated by <sup>1</sup>H NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.  
<sup>b</sup>Yield estimated by <sup>19</sup>F NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.

NMR spectra
$\text{DICAB}$

$^{11}$B NMR (160 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
\[
\text{Cl} \quad \text{Ph} \quad \text{SF}_5
\]

\(2d\)

\(^{13}\text{C NMR (126 MHz, CDCl}_3)\)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$\text{OCl} \cdot \text{SF}_5$

$^1\text{H NMR (500 MHz, CDCl}_3\text{)}$

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$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)

2h
$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$^{19}\text{F NMR (470 MHz, CDCl$_3$)}$
$^{1}H$ NMR (500 MHz, CDCl$_3$)
$^{13}\text{C NMR (126 MHz, CDCl}_3\text{)}$

![S44]
$^{19}$F NMR (470 MHz, CDCl$_3$)