**Electronic supplementary information**

**Catalyzed [2+2]-CYCLOADDITION REACTIONS OF HEXAFLUOROISOPROPYL 4-CHLORO-2-OXOBUT-3-  
YNOATE WITH SIMPLE ALKENES**

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**Experimental section**

**General methods**

The 1H, 13C, and 19F{1H} NMR spectra were recorded on a Bruker AMX 400 spectrometer in CDCl3 at 400, 100, and 376.5 MHz, respectively. The chemical shifts are reported in ppm relative to TMS (1H, 13C). The FTIR spectra were recorded on a Bruker IFS 25 spectrometer and are reported in terms of frequency of absorption (cm–1). The mass spectra were recorded on a Finnigan Polaris Q instrument (EI, 70 eV, ion trap). Compound **2** was synthesized according to the described procedure [S1]. Tributyltin chloride was distilled prior to use. All operations with organolithium compounds were performed under an argon atmosphere; the cycloaddition reactions of **4** with volatile alkenes were performed in screw vials.

**Synthesis of crude *bis*(tributylstannyl)acetylene (1).** A strong flow of acetylene was introduced into a vigorously stirred solution of BuLi (1.0 N) in hexane (200 mL, totally 0.2 mol) at –35 °C until the absorption of the gas has ceased (detected with a gas counter at the system output). The reaction mixture was refluxed for 1 h. After cooling to 20 °C, a solution of Bu3SnCl (66.65 g, 0.21 mol) in 100 mL of hexane was added in one portion. The stirred reaction mixture was refluxed for 4 h and left under an argon atmosphere overnight. The most part of the clear solution was carefully decanted from lithium chloride. The remaining precipitate was diluted with hexane and filtered off. The combined hexane solutions were concentrated under vacuum to give crude product **1**, which was used at the next stage.

**One-pot synthesis of hexafluoroisopropyl 4-chloro-2-oxobut-3-ynoate (4)** **and the recycling of Bu3SnCl.** Crude compound **1**, obtained by the above-mentioned procedure, was dissolved in 100 mL of CH2Cl2. Then chloride **2** (64.50 g, 0.25 mol) was added to the resulting stirred solution in one portion. The reaction mixture was kept at 25 °C for 24 h and concentrated under vacuum. The residue containing compound **3** and Bu3SnCl was diluted with 200 mL of CH2Cl2. The stirred solution was cooled to –30 °C and a weak stream of chlorine gas from a measuring tube with condensed liquid chlorine (17.75 g, 0.25 mol, 11.2 mL) was passed through this solution using a cannula beneath the surface of the solution. During the exothermic reaction, the internal temperature of the reaction mixture was maintained at –20 to –25 °C, and the rate of the chlorine stream was controlled by the occasional immersing of a measuring tube to a dry ice–acetone base. After the absorption of chlorine, the resulting solution was allowed to warm to 20 °C. The solvent was concentrated, and the residue obtained was distilled under vacuum to give 43.43 g (77%) of compound **4**. Bp: 52–53 °C (10 Torr). The spectral and physical data of **4** were in agreement with those previously described [S1]. The distillation of a high-boiling fraction afforded 59.90 g (90%) of recovered Bu3SnCl, bp: 144–146 °C (8 Torr).

**General procedure for the cycloaddition of 4** **with alkenes in HFIP (Path B) (synthesis of adducts 5a–d).** A mixture of alkyne **4** (1.13 g, 4 mmol), the corresponding alkene (8 mmol), and **HFIP** (1.35 g, 8 mmol) was kept in a screw vial at 20 °C for the mentioned time (Scheme 2, Path **B**). The reaction mixture was concentrated, and the residue obtained was distilled under vacuum to give compounds **5a**–**d**. The spectral and physical data of **5a**–**d** were in good agreement with the reported data [S1].

**(8-Chloro-bicyclo[4.2.0]oct-7-en-7-yl)-oxo-acetic acid 2,2,2-trifluoro-1-trifluoromethyl-ethyl ester (5a)** was obtained as a yellowish oil from **4** and cyclohexene. Bp: 83–84 °C (0.3 Torr). Yield: 1.28 g (88%). IR (film): *ν* 3011, 2998, 1779, 1677, 1590, 1447, 1383, 1366, 1292, 1200. 1H NMR (400 MHz, CDCl3): *δ* 1.53 (4H, m), 1.83 (4H, m) (totally 8H, (CH2)4), 3.18 (1H, dd, Ј=10.3, 5.0 Hz, CH–CH), 3.30 (1H, dd, *Ј* = 10.3, 5.0 Hz, CH–CH), 5.87 (1H, hept, *Ј*HF = 5.8 Hz, СН–(CF3)2). 13C NMR (100 MHz, CDCl3): *δ* 18.0, 18.1, 21.9, 22.6 (CH2)4), 67.4 (hept, *Ј*СF = 35.0 Hz, СН-CF3)2), 120.3 (q, *Ј*СF = 284.0 Hz, CF3), 138.5 (C=C–C=O), 151.4 (Cl–C=), 158.6 (C=O), 173.8 (O–C=O). 19F NMR (CDCl3, 376.5 MHz): *δ* –73.1 (s, 2CF3). ESI-MS (m/z): 365.0 (44, [M+H]+), 329.0 (59, [M–Cl]+), 169.0 (73, [M–COOCH(CF3)2]+). Anal. Calcd. for C13H11ClF6O**3**: C, 42.82; H, 3.04; Cl, 9.72; F, 31.26. Found: C, 43.17; H, 3.07; Cl, 9.44; F, 31.21%.

**(7-Chloro-bicyclo[3.2.0]hept-6-en-6-yl)-oxo-acetic acid 2,2,2-trifluoro-1-trifluoromethyl-ethyl ester (5b)** was obtained as a yellowish oil from **4** and cyclopentene. Bp: 68–69 °C (0.3 Torr). Yield: 1.30 g (92%). IR (film): *ν* 2968, 2868, 1781, 1674, 1594, 1447, 1384, 1362, 1290, 1204. 1H NMR (400 MHz, CDCl3): *δ* 1.44 (m), 1.61 (m), 1.87 (m) (totally 6H, (CH2)3), 3.46(1H, dd, *Ј* = 6.9, 3.5 Hz, CH–CH), 3.58 (1H, dd, *Ј* = 6.9, 3.5 Hz, CH–CH), 5.86 (1H, hept, *Ј*HF = 5.8 Hz, СН-(CF3)2). 13C NMR (100 MHz, CDCl3): *δ* 22.4, 24.1, 25.7 ((CH2)3), 44.9, 53.4 (CH–CH), 67.7 (hept, *Ј*СF = 35.1 Hz, СН–(CF3)2), 120.2 (q, *Ј*СF = 282.0 Hz, CF3), 135.6 (C=C–C=O), 149.1 (Cl–C=), 158.4 (C=O), 173.7 (O–C=O). 19F NMR (CDCl3, 376.5 MHz): *δ* –72.9 (s, 2CF3). ESI-MS (m/z): 317.0 (74, [M–Cl]+), 157.0 (100, [M–COOCH(CF3)2]+). Anal. Calcd. for C12H9ClF6O**3**: C, 41.11, H, 2.59, Cl, 10.11, F, 32.51. Found: C, 40.84; H, 2.70; Cl, 9.90; F, 32.44%.

(2-Chloro-4,4-dimethyl-cyclobut-1-enyl)-oxo-acetic acid 2,2,2-trifluoro-1-trifluoromethyl-ethyl ester (5c) was obtained as a yellowish oil from 4 and isobutene. Bp: 49–51 °C (0.3 Torr). Yield: 1.22 g (90%). IR (film): *ν* 2971, 1779, 1669, 1602, 1457, 1384, 1362, 1291, 1203. 1H NMR (400 MHz, CDCl3): *δ* 1.40 (6H, s, 2CH3), 2.69 (2H, s, CH2), 5.88 (1H, hept, *Ј*HF = 5.8 Hz, СН–(CF3)2). 13C NMR (100 MHz, CDCl3): *δ* 23.9 (2CH3), 42.9 (C–CH3), 51.2 (CH2), 35.4 (hept, *Ј*СF = 60.0 Hz, СН–(CF3)2), 120.0 (q, *Ј*СF = 283.0 Hz, CF3), 143.1 (C=C–C=O), 146.0 (Cl–C=), 158.7 (C=O), 174.1 (O–C=O). 19F NMR (CDCl3, 376.5 MHz): *δ* –73.3 (s, 2CF3). ESI-MS (m/z): 339.0 (17, [M+H]+), 171.0 (33, [M–OCH(CF3)2]+], 143.0 (100, [M–COOCH(CF3)2]+). Anal. Calcd. for C11H9ClF6O3: C, 39.02, H, 2.68, Cl, 10.47, F, 33.66. Found: C, 39.27; H, 2.70; Cl, 10.25; F, 33.50%.

**(2-Chloro-cis-3,4-dimethyl-cyclobut-1-enyl)-oxo-acetic acid 2,2,2-trifluoro-1-trifluoromethyl-ethyl ester (5d)** was obtained as a yellowish oil from **4** and *trans****-***butene-2. Bp: 54–56 °C (0.3 Torr). Yield: 1.22 g (90%). IR (film): *ν* 2976, 2938, 2887, 1776, 1673, 1595, 1464, 1384, 1290, 1205. 1H NMR (400 MHz, CDCl3): *δ* 1.18 (3H, d, *Ј* = 7.2 Hz, CH3), 1.21 (3H, d, *Ј* = 7.2 Hz, CH3), 3.22 (1H, m, *Ј* = 7.2, 4.8 Hz, CH–CH), 3.32(1H, m, *Ј* = 7.2, 4.8 Hz, CH–CH), 5.85 (1H, hept, *Ј*HF = 5.8 Hz, СН–(CF3)2). 13C NMR (100 MHz, CDCl3): *δ* 10.6 (CH3), 12.5 (CH3), 37.9 (CH), 46.2 (CH), 67.6 (hept, *Ј*СF = 35.4 Hz, СН–(CF3)2), 120.0 (q, *Ј*СF = 283.0 Hz, CF3), 138.8 (C=C–C=O), 151.5 (Cl–C=), 158.6 (C=O), 174.1 (O–C=O). 19F NMR (CDCl3, 376.5 MHz): *δ* –72.5 (s, 2CF3). ESI-MS (m/z): 339.0 (58, [M+H]+), 171.0 (71, [M–OCH(CF3)2]+], 143.0 (85, [M–COOCH(CF3)2]+). Anal. Calcd. for C11H9ClF6O3: C, 39.02, H, 2.68, Cl, 10.47, F, 33.66. Found: C, 39.11; H, 2.55; Cl, 10.14; F, 33.38%.

**References**

S1. A. B. Koldobskii, E. V. Solodova, I. A. Godovikov, P. V. Verteletskii, V. N. Kalinin, *J. Fluorine Chem*., **2010**, *131*, 873–878. DOI: 10.1016/j.jfluchem.2010.05.015