

Supporting Information for DOI: 10.1055/s-0036-1589044 © Georg Thieme Verlag KG Stuttgart · New York 2017



Supporting Information

Catalytic Radical Intramolecular Aminoperfluoroalkylation and

Aminodifluoromethylation of Unactivated Alkenes with

Fluoroalkylsulfonyl Chlorides

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General Information

All reagents were obtained from commercial sources and used without further purification, unless otherwise stated. Ethyl acetate (EA) was purchased from Adamas-beta®. CuBr and Ag₂CO₃ were purchased from Sigmaaldrich. Methyl 2-(chlorosulfonyl)-2,2-difluoroacetate difluoromethylsulfonyl and chloride were purchased from 9dingchem (China). Petroleum ether (bp 60-80 °C) and EtOAc were used for column chromatography. Silica Gel 200–300F (Tsingdao silica gel). ¹H NMR spectra were recorded in CDCl₃ at ambient temperature on Bruker DRX-500 and DPX 400 spectrometer at 400 or 500 MHz. ¹³C NMR spectra were recorded in CDC13 at ambient temperature on Bruker DRX-500 and DPX 400 spectrometer at 100 or 126 MHz. ¹⁹F NMR spectra were recorded in CDCl₃ at ambient temperature on Bruker DPX 400 spectrometer at 376 MHz. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz, respectively. Data for 1 H NMR are indicated as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet; br, broad), coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (δ , ppm). Mass spectrometric data were recorded using Bruker Apex IV RTMS.

Typical procedure

1) Direct radical aminoperfluoroalkylation of alkenes

An oven-dried Schlenk tube with a magnetic stir was charged with urea substrate **1a** (0.2 mmol, 1.0 equiv), phosphoric acid **PA1** (7.5 mg, 0.03 mmol, 15 mol%), CuBr (2.86 mg, 0.02 mmol, 10 mol%), Ag₂CO₃ (33.12 mg, 0.12 mmol, 0.6 equiv), n-C₄F₉SO₂Cl (**2a**) (76.3 mg, 0.24 mmol, 1.2 equiv) and EtOAc (2.0 mL) under an atmosphere of dry argon, the sealed tube was then stirred at 25 °C. Upon completion (monitored by TLC), the reaction mixture was directly purified by a silica gel chromatography [eluent: petroleum ether/EtOAc = 100/0-5/1, using petroleum ether (100%) to remove the solvent (EtOAc) at first] to afford the desired product **3A**.

2) Direct radical aminodifluoro(methoxycarbonyl)methylation of alkenes

An oven-dried Schlenk tube with a magnetic stir was charged with urea substrate **1a** (0.2 mmol, 1.0 equiv), phosphoric acid **PA1** (15 mg, 0.03 mmol, 30 mol%), CuBr (2.86 mg, 0.02 mmol, 10 mol%), Ag₂CO₃ (33.12 mg, 0.12 mmol, 0.6 equiv), MeO₂CCF₂SO₂Cl (**2b**) (50 mg, 0.24 mmol, 1.2 equiv) and EtOAc (2.0 mL) under an atmosphere of dry argon, the sealed tube was then stirred at 60 °C for 12 h. Upon completion (monitored by TLC), the reaction mixture was cooled to room tempreture, and directly purified by a silica gel chromatography [eluent: petroleum ether/EtOAc = 100/0-5/1, using petroleum ether (100%) to remove the solvent (EtOAc) at first] to afford the desired product **4A**.

3) Direct radical aminodifluoromethylation of alkenes

An oven-dried Schlenk tube with a magnetic stir was charged with urea substrate **1a** (0.2 mmol, 1.0 equiv), phosphoric acid **PA1** (15 mg, 0.03 mmol, 30 mol%), CuBr (2.86 mg, 0.02 mmol, 10 mol%), Ag₂CO₃ (33.12 mg, 0.12 mmol, 0.6 equiv), HCF₂SO₂Cl (**2c**) (36.0 mg, 0.24 mmol, 1.2 equiv) and EtOAc (2.0 mL) under an atmosphere of dry argon, the sealed tube was then stirred at 60 °C for 12 h. Upon completion (monitored by TLC), the reaction mixture was cooled to room tempreture, and directly purified by a silica gel chromatography [eluent: petroleum ether/EtOAc = 100/0-5/1, using petroleum ether (100%) to remove the solvent (EtOAc) at first] to afford the desired product **4B**.

4) Direct radical aminotrifluoromethylation of alkenes

An oven-dried Schlenk tube with a magnetic stir was charged with urea substrate **1a** (0.2 mmol, 1.0 equiv), phosphoric acid **PA1** (15 mg, 0.03 mmol, 30 mol%), CuBr (2.86 mg, 0.02 mmol, 10 mol%), Ag₂CO₃ (33.12 mg, 0.12 mmol, 0.6 equiv), CF₃SO₂Cl (**2d**) (40.32 mg, 0.24 mmol, 1.2 equiv) and EtOAc (2.0 mL) under an atmosphere of dry argon, the sealed tube was then stirred at 40 °C for 40 h. Upon completion (monitored by TLC), the reaction mixture was cooled to room tempreture, and directly purified by a silica gel chromatography [eluent: petroleum ether/EtOAc = 100/0-5/1, using petroleum ether (100%) to remove the solvent (EtOAc) at first] to afford the desired product **4C**.

NMR Spectra of new compounds

























-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 f1 (ppm)



















The spectra of **4C** matches previously reported spectra.¹

References:

(1) Lin, J.-S.; Dong, X.-Y.; Li, T.-T.; Jiang, N.-C.; Tan, B.; Liu, X.-Y. J. Am. Chem. Soc. **2016**, *138*, 9357.