Photoinitiated Stereoselective Direct C(sp²)-H

Perfluoroalkylation and Difluoroacetylation of Enamides

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General Information

All photoredox-catalyzed reactions in Table 1-4 were carried out in oven-dried Schlenk tubes under nitrogen atmosphere using anhydrous solvent purchased from Energy Chemical. All enamides or enecarbamates were prepared using existing methods.¹⁻² Perfluoroalkyl iodides and ethyl bromodifluoroacetate were purchased from Energy Chemical. ¹H, ¹⁹F, ¹³C NMR spectra were recorded in CDCl₃ or (CD₃)₂SO on Bruker Avance 400 MHz spectrometers. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet); coupling constants (J) are in Hertz (Hz). NMR spectra were taken using TMS (¹H, δ = 0), CDCl₃ (¹H, δ = 7.26), and CDCl₃ (¹³C, CPD δ = 77.16) as the internal standards, respectively. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

The photoredox-catalyzed transformations were carried out in a customized dark cassette equipped with three 60 W (or 15 W) blue LEDs lamp from different directions for irradiation along with an electronic cooling fan for heat dissipation (Figure S1). A Heidolph magnetic hotplate stirrer was placed in the dark cassette for stirring. The reaction vessel was placed in the center of the stirrer so that the average distance from the lamp to the reaction medium was 10 cm.



Figure S1 The customized dark cassette equipped with blue LEDs lamps Abbreviations: Bn = benzyl, Ac = acetyl, EtOAc = Ethyl acetateDMF = N,Ndimethylformamide, DCM = dichloromethane, Boc = t-butoxycarbonyl, TEMPO = 2,2,6,6-tetramethylpiperidinooxy, TBPB = *tert*-butyl peroxybenzoate, THF = Tetrahydrofuran.

General Procedures for the Synthesis of β -perfluoroalkylated Enamides



To a Schlenk tube equipped with a magnetic stir bar was charged with enamides **1** (0.3 mmol), perfluoroalkyl iodide **2** (0.9 mmol), Eosin Y (9.7 mg, 5 mol%), and DABCO (134.6 mg, 1.2 mmol). The tube was sealed with a septum, evacuated and backfilled with nitrogen three times. 1.0 mL acetonitrile was added *via* syringe with gentle stirring. The tube was sealed and stirred under 60 W blue LEDs for 12 h. The resulting mixture was extracted with ethyl acetate. The combined organic phase was dried over anhydrous sodium sulfate, and the solvent was then removed under vacuum. The residue was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:10~1:3 v/v), to give compound **3**.

Gram-Scale Synthesis of β -perfluoroalkylated Enamide 3aa



To a Schlenk tube equipped with a magnetic stir bar was charged with enamides **1a** (5 mmol, 1.26 g), perfluoroalkyl iodide **2a** (15 mmol, 5.19 g), Eosin Y (0.18 g, 5 mol%), and DABCO (2.24 g, 20 mmol). The tube was sealed with a septum, evacuated and backfilled with nitrogen three times. 17.0 mL acetonitrile was added via syringe with gentle stirring. The tube was sealed and stirred under 60 W blue LEDs for 12 h. The resulting mixture was extracted with ethyl acetate. The combined organic phase was dried over anhydrous sodium sulfate, and the solvent was then removed under vacuum. The residue was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:10~1:3 v/v), to give compound **3aa** in 72% yield (1.69 g).

General Procedures for the Synthesis of β -difluoroacetylated Enamides



To a Schlenk tube equipped with a magnetic stir bar was charged with enamides 1 (0.3 mmol), ethyl bromodifluoroacetate 4 (121.8 mg, 0.6 mmol, 76.9 μ m), *fac*-Ir(ppy)₃ (2.0 mg, 1.0 mol%), and NaHCO₃ (75.6 mg, 0.9 mmol). The tube was sealed with a septum, evacuated and backfilled with nitrogen three times. 2.0 mL DMF was added via syringe with gentle stirring. The tube was sealed and stirred under 15 W blue LEDs for 12 h. The resulting mixture was extracted with ethyl acetate. The combined organic phase was dried over anhydrous sodium sulfate, and the solvent was then removed under vacuum. The residue was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:10~1:3 ν/ν), to give compound **5**.

Gram-Scale Synthesis of β -difluoroacetylated Enamide 5a



To a Schlenk tube equipped with a magnetic stir bar was charged with enamides 1a (5 mmol, 1.26 g), ethyl bromodifluoroacetate 4 (10 mmol, 2.03 g, 1.28 mL), Ir(ppy)₃ (33.3 mg, 1 mol%), and NaHCO₃ (1.26 g, 15 mmol). The tube was sealed with a septum, evacuated and backfilled with nitrogen three times. 34 mL DMF was added via syringe with gentle stirring. The tube was sealed and stirred under 15 W blue LEDs for 12 h. The resulting mixture was extracted with ethyl acetate. The combined organic phase was dried over anhydrous sodium sulfate, and the solvent was then removed under vacuum. The residue was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:10~1:3 v/v), to give compound 5a in 58% yield (1.08 g).

Stern-Volmer Experiment for the β -perfluoroalkylation of Enamides

The Stern-Volmer fluorescence quenching experiments was conducted by the following procedures. Firstly, the emission and excitation spectra of the photocatalyst Eosin Y was investigated. The luminescence quenching experiment was taken using an F97 pro Fluorescence spectrophotometer (Shanghai, China). A solution of Eosin Y (E) (1.0 mM) in DMSO was chosen as the model. The excitation wavelength was 451 nm and the emission intensity was collected at 565 nm.



a) The fluorescence emission spectra of Eosin Y with different concentration of added quencher (DABCO) excited at 451 nm



c) The fluorescence emission spectra of Eosin Y with different concentration of added quencher (*n*-C₄F₉I) excited at 451 nm.



b) Eosin Y emission quenching by DABCO. Linear quenching is observed.



d) Eosin Y emission quenching by C₄F₉I. No quenching was observed.

Figure S2 Stern-Volmer experiments for the β -perfluoroalkylation of enamides

Next, the fluorescence quenching experiment of Eosin Y with DABCO was conducted: In a typical experiment, 1.0 mL of solution of Eosin Y (1.0 mM) in DMSO was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette, 1 M solution of the quencher (DABCO) was added into the cuvette by 5 μ L, and the emission of the sample was collected (**Figure S2a**). The solution was excited at $\lambda = 451$ nm (excitation maximum of Eosin Y) and the emission intensity at 565 nm (emission

maximum of Eosin Y) was observed (Figure S2b).

Subsequently, another Stern–Volmer fluorescence quenching experiment to investigate the influence of *n*-C₄F₉I was performed. In a typical experiment, 1.0 mL of solution of Eosin Y (1.0 mM) in DMSO was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette, 1 M solution of the quencher (*n*-C₄F₉I) was added into the cuvette by 5 μ L, and the emission of the sample was collected (**Figure S2c**). The solution was excited at $\lambda = 451$ nm (excitation maximum of Eosin Y) and the emission intensity at 565 nm (emission maximum of Eosin Y) was observed (**Figure S2d**).

Stern–Volmer fluorescence quenching experiments demonstrated that the emission intensity of Eosin Y diminished in the presence of DABCO rather than n-C₄F₉I, indicating that the excited Eosin Y* might be reductively quenched by DABCO, instead of the oxidative quenching of the photocatalyst by n-C₄F₉I.

References

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For the synthesis of *N*-2-bromophenyl protected enamide 1v, two synthetic steps were involved. Firstly, (*Z*)-2-bromo-*N*-(1-phenylethylidene)aniline was synthesis through a palladium-catalyzed cross-coupling of 2-bromoaniline with 1-bromostyrene, see: (a) J. Barluenga, M. A. Fernandez, F. Aznar, C. Valdes, *Chem. Eur. J.*, 2004, 35, 494. Secondly, enamide 1v was synthesis *via* the reaction of (*Z*)-2-bromo-*N*-(1phenylethylidene)aniline with benzoyl chloride, see: (b) H. Okamoto, S. Kato, M. Ogasawara, M. Konnai, T. Takematsu, *Agric. Biol. Chem.* 2014, 55, 2733.

Determination of Stereochemistry-NOESY Experiment of E-3aa and E-5a

NOESY-experiments of *E*-3aa and *E*-5a were performed to further testify the stereochemistry. It was shown that for both *E*-3aa and *E*-5a, a NOE effect between the olefinic hydrogen and the methyl of acetyl group was observed, indicating the *E*-configuration of those compounds.



Analytical Data for β -perfluoroalkylated Enamides



(E)-N-benzyl-N-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)acetamide

(**3aa**) was obtained in 81% yield (114.4 mg) as a colorless oil. The compound **3aa** was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.39 (m, 3H), 7.34-7.25 (m, 5H), 7.18-7.14 (m, 2H), 5.44 (t, *J* = 14.3 Hz, 1H), 4.51 (s, 2H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 151.7 (t, *J* = 3.5 Hz), 136.6, 133.2, 130.8, 129.2, 128.7, 128.6, 128.6, 127.8, 114.2 (t, *J* = 21.9 Hz), 49.5, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.02 – -81.10 (m), -103.94 (q, *J* = 12.7 Hz), -123.22 (q, *J* = 8.8 Hz), -125.69 – -125.81 (m); HRMS (ESI) calcd for C₂₁H₁₆F₉NNaO⁺ (M + Na)⁺ 492.0980, found 492.0981.



(E)-N-benzyl-N-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-fluorophenyl)hex-1-en-1-

yl)acetamide (3ba) was obtained in 88% yield (128.3 mg) as a colorless oil. The compound **3ba** was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.25 (m, 5H), 7.16-7.07 (m, 4H), 5.47 (t, *J* = 14.3 Hz, 1H), 4.53 (s, 2H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 164.1 (d, *J* = 252.0 Hz), 150.7, 136.4, 131.3 (d, *J* = 8.6 Hz), 129.3 (d, *J* = 3.4 Hz), 128.7, 128.6, 127.8, 115.8 (d, *J* = 22.0 Hz), 114.2 (t, *J* = 21.8 Hz), 49.5, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.20 (t, *J* = 9.6 Hz), -103.96 (q, *J* = 13.1 Hz), -108.80 (s), -123.30 (q, *J* = 8.5 Hz), -125.85 (h, *J* = 9.2 Hz); HRMS (ESI) calcd for C₂₁H₁₅F₁₀NNaO⁺ (M + Na)⁺ 510.0886, found 510.0890.

(E)-N-benzyl-N-(1-(4-chlorophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-

yl)acetamide (3ca) was obtained in 74% yield (111.6 mg) as a colorless oil. The compound 3ca was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1).¹H NMR (400 MHz, CDCl₃) δ 7.41-7.38 (m, 2H), 7.32-7.23 (m, 5H), 7.14 (dd, *J* = 7.7, 1.6 Hz, 2H), 5.47 (t, *J* = 14.3 Hz, 1H), 4.52 (s, 2H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 150.6 (d, *J* = 3.7 Hz), 137.1, 136.3, 131.7, 130.5, 128.9, 128.7, 128.6, 127.9, 114.6 (t, *J* = 21.9 Hz), 49.6, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.08 (t, *J* = 9.6 Hz), -103.97 (q, *J* = 13.1 Hz), -123.16 - -123.28 (m), -125.76 (h, *J* = 9.3 Hz); HRMS (ESI) calcd for C₂₁H₁₅F₉ClNNaO⁺ (M + Na)⁺ 526.0591, found 526.0594.

(*E*)-*N*-benzyl-*N*-(1-(4-bromophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-

yl)acetamide (3da) was obtained in 81% yield (133.6 mg) as a colorless oil. The compound 3da was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.54 (m, 2H), 7.31-7.26 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.13 (dd, *J* = 7.6, 1.7 Hz, 2H), 5.47 (t, *J* = 14.3 Hz, 1H), 4.51 (s, 2H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 150.6 (t, *J* = 3.6 Hz), 136.3, 132.2, 131.9, 130.7, 128.7, 128.6, 127.9, 125.4, 114.6 (t, *J* = 21.9 Hz), 49.6, 22.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.04 (t, *J* = 9.6 Hz), -103.96 (q, *J* = 13.0 Hz), -123.20 (q, *J* = 8.8 Hz), -125.68 – -125.81 (m); HRMS (ESI) calcd for C₂₁H₁₆BrF₉NO⁺ (M + H)⁺ 548.0266, found 548.0271.

(E)-N-Benzyl-N-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(2-fluorophenyl)hex-1-en-1-

yl)acetamide (3ea) was obtained in 73% yield (106.6 mg) as a colorless oil. The compound 3ea was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.42 (tdd, *J* = 7.5, 5.3, 2.5 Hz, 1H), 7.31-7.23 (m, 3H), 7.21-7.13 (m, 4H), 7.12-7.06 (m, 1H), 5.61 (t, *J* = 13.9 Hz, 1H), 4.53 (s, 2H), 2.33 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.2, 160.1 (d, *J* = 250.6 Hz), 146.4 (t, *J* = 4.8 Hz), 136.6, 132.5 (d, *J* = 8.5 Hz), 131.8 (d, *J* = 2.4 Hz), 128.6, 128.3, 127.7, 124.0 (d, *J* = 3.6 Hz), 121.1 (d, *J* = 13.9 Hz), 116.3 (t, *J* = 22.3 Hz), 116.0 (d, *J* = 21.6 Hz), 49.2, 22.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.27 (tt, *J* = 10.0, 3.1 Hz), -106.94 (t, *J* = 12.8 Hz), -112.73, -123.30 - -123.45 (m), -125.87 - -126.04 (m); HRMS (ESI) calcd for C₂₁H₁₆F₁₀NO⁺ (M + H)⁺ 488.1067, found 488.1062.

(E)-N-benzyl-N-(1-(3-chlorophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-

yl)acetamide (3fa) was obtained in 83% yield (125.8 mg) as a colorless oil. The compound 3fa was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.6 Hz, 1H), 7.37-7.26 (m, 5H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.17-7.13 (m, 2H), 5.51 (t, *J* = 14.3 Hz, 1H), 4.52 (s, 2H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.8, 150.2, 136.3, 135.1, 134.7, 130.9, 129.8, 128.9, 128.7, 128.6, 127.9, 127.6, 115.04 (t, *J* = 21.9 Hz), 49.6, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.12 (t, *J* = 9.6 Hz), -104.11 (q, *J* = 12.8 Hz), -123.16 - -123.32 (m), -125.70 - -125.87 (m); HRMS (ESI) calcd for C₂₁H₁₆F₉CINO⁺ (M + H)⁺ 504.0771, found 504.0767.

(*E*)-*N*-benzyl-*N*-(1-(3-bromo-4-fluorophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1en-1-yl)acetamide (3ga) was obtained in 69% yield (117.6 mg) as a colorless oil. The compound 3ga was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, *J* = 6.3, 2.0 Hz, 1H), 7.33-7.22 (m, 4H), 7.17-7.10 (m, 3H), 5.52 (s, 1H), 4.54 (s, 2H), 2.28 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 169.8, 160.4 (d, *J* = 253.0 Hz), 149.4 (t, *J* = 4.0 Hz), 136.2, 134.2, 130.8 (d, *J* = 4.1 Hz), 130.3 (dt, *J* = 7.0, 2.9 Hz), 128.8, 128.5, 128.0, 116.6 (d, *J* = 22.9 Hz), 115.0 (t, *J* = 21.9 Hz), 109.6 (d, *J* = 21.7 Hz), 49.8, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.10 – -81.29 (m), -102.97, -104.10 (t, *J* = 14.8 Hz), -123.33 (q, *J* = 9.3 Hz), -125.86 (dt, *J* = 13.1, 7.6 Hz); HRMS (ESI) calcd for C₂₁H₁₄BrF₁₀NNaO⁺ (M + Na)⁺ 587.9991, found 587.9998.

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-(trifluoromethyl)phenyl)hex-1en-1-yl)acetamide (3ha) was obtained in 44% yield (70.4 mg) as a colorless oil. The compound 3ha was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.34-7.24 (m, 3H), 7.13 (dd, *J* = 7.5, 1.7 Hz, 2H), 5.57 (t, *J* = 14.3 Hz, 1H), 4.52 (s, 2H), 2.30 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 169.9, 150.3 (t, *J* = 4.1 Hz), 137.0, 136.2, 132.7 (q, *J* = 32.9 Hz), 129.7 (t, *J* = 2.7 Hz), 128.8, 128.6, 128.0, 125.6 (q, *J* = 3.7 Hz), 123.7 (d, *J* = 272.5 Hz), 115.6 (t, *J* = 22.0 Hz), 49.8, 22.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -63.09, -81.16 (tt, *J* = 10.1, 3.1 Hz), -104.18 - -104.30 (m), -

123.22 - 123.41 (m), -125.75 - 125.94 (m); HRMS (ESI) calcd for $C_{22}H_{16}F_{12}NO^+$ (M + H)⁺ 538.1035, found 538.1039.

Ethyl-(E)-4-(1-(N-benzylacetamido)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-

yl)benzoate (3ia) was obtained in 54% yield (87.8 mg) as a colorless oil. The compound **3ia** was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.33-7.26 (m, 3H), 7.16-7.12 (m, 2H), 5.54 (t, J = 14.3 Hz, 1H), 4.51 (s, 2H), 4.41 (g, J = 7.1 Hz, 2H), 2.30 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 169.9, 165.7, 150.7 (t, *J* = 3.9 Hz), 137.6, 136.3, 132.6, 129.7, 129.2 (t, *J* = 2.5 Hz), 128.7, 128.6, 127.9, 115.2 (t, J = 22.0 Hz), 61.5, 49.6, 22.7, 14.3; ¹⁹F NMR $(376 \text{ MHz}, \text{CDCl}_3) \delta - 81.16 \text{ (tt}, J = 10.1, 3.0 \text{ Hz}), -104.10 - -104.24 \text{ (m)}, -123.26 \text{ (q}, J)$ = 9.5 Hz), -125.84 (td, J = 13.1, 3.7 Hz); HRMS (ESI) calcd for $C_{24}H_{21}F_9NO_3^+$ (M + H)⁺ 542.1372, found 542.1369.

(E)-N-benzyl-N-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-(methylsulfonyl)phenyl)hex-1en-1-yl)acetamide (3ja) was obtained in 65% yield (106.9 mg) as a colorless oil (E/Z = 93:7). The compound **3ja** was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). For major (*E*)-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.35-7.26 (m, 3H), 7.15-7.10 (m, 2H), 5.63 $(t, J = 14.3 \text{ Hz}, 1\text{H}), 4.53 (s, 2\text{H}), 3.11 (s, 3\text{H}), 2.31 (s, 3\text{H}); {}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{CDCl}_3)$ δ 169.8, 149.8 (t, J = 4.3 Hz), 142.4, 138.9, 136.0, 130.1, 128.8, 128.4, 128.0, 127.5,

116.0 (t, J = 22.0 Hz), 50.0, 44.4, 22.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.09 (t, J = 8.9 Hz), -104.18 (t, J = 11.9 Hz), -123.18 - -123.35 (m), -125.74 - -125.88 (m); HRMS (ESI) calcd for C₂₂H₁₉F₉NO₃S⁺ (M + H)⁺ 548.0936, found 548.0933.

(E)-N-benzyl-N-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-nitrophenyl)hex-1-en-1-

yl)acetamide (3ka) was obtained in 56% yield (86.4mg) as a colorless oil (E/Z = 80:20). The compound 3ka was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 3:1).For major (E)-isomer: ¹H NMR (400 MHz, CDCl₃) δ 8.28-8.24 (m, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.34-7.29 (m, 3H), 7.14-7.10 (m, 2H), 5.63 (t, J = 14.2 Hz, 1H), 4.55 (s, 2H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 149.5, 149.0, 139.8, 135.9, 130.3, 129.0, 128.4, 128.2, 123.7, 116.1 (t, J = 22.3 Hz), 50.1, 22.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (t, J = 9.6 Hz), -104.1 (q, J = 13.1 Hz), -123.06 – -123.20 (m), -125.61 – -125.78 (m). For minor (Z)-isomer: ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.23 – 7.12 (m, 5H), 6.10 (dd, J = 15.8, 11.7 Hz, 1H), 4.72 (q, J = 14.2 Hz, 2H), 2.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.6, 149.4, 149.2, 141.7, 135.6, 130.1, 128.6, 128.3, 128.3, 124.4, 114.5 (t, J = 19.8 Hz), 52.0, 21.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.83 (t, J = 9.6 Hz), -108.21 (q, J = 12.2 Hz), -108.96 (q, J = 12.2 Hz), -113.04 (q, J = 14.0 Hz), -113.79 (q, J = 13.0 Hz), - 123.17 – -123.37 (m), -125.52 – -125.66 (m); HRMS (ESI) calcd for C₂₁H₁₅F₉N₂NaO₃⁺ (M + Na)⁺ 537.0831, found 537.0826.

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(o-tolyl)hex-1-en-1-yl)acetamide S-13

(31a) was obtained in 90% yield (130.9 mg) as a colorless oil. The compound 31a was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.16 (m, 6H), 7.10-7.04 (t, *J* = 6.5 Hz, 3H), 5.67 (t, *J* = 13.9 Hz, 1H), 4.49 (d, br, 2H), 2.39 (s, 3H), 2.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 151.5 (t, *J* = 4.0 Hz), 137.0, 136.8, 132.5, 131.0 (t, *J* = 2.7 Hz), 130.7, 130.2, 128.6, 127.6, 127.5, 125.6, 112.2 (t, *J* = 22.1 Hz), 49.2, 23.1, 19.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.24 (ddd, *J* = 13.3, 10.1, 3.0 Hz), -123.26 (ddt, *J* = 15.3, 9.9, 5.0 Hz), -125.83 (dp, *J* = 20.7, 7.0 Hz); HRMS (ESI) calcd for C₂₂H₁₈F₉NNaO⁺ (M + Na)⁺ 506.1137, found 506.1141.

(*E*)-*N*-(1-([1,1'-biphenyl]-4-yl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)-*N*benzylacetamide (3ma) was obtained in 86% yield (140.7 mg) as a colorless oil. The compound 3ma was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.61 (m, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.44-7.34 (m, 3H), 7.32-7.26 (m, 3H), 7.21-7.17 (m, 2H), 5.46 (t, *J* = 14.4 Hz, 1H), 4.56 (s, 2H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 151.5, 143.6, 139.9, 136.6, 132.0, 129.7, 129.0, 128.8, 128.6, 128.2, 127.8, 127.2, 127.2, 114.1 (t, *J* = 21.8 Hz), 49.6, 22.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 (t, *J* = 9.6 Hz), -103.8 (q, *J* = 12.6 Hz), -123.07 - -123.20 (m), -125.7 (h, *J* = 9.5 Hz); HRMS (ESI) calcd for C₂₇H₂₁F₉NO⁺ (M + H)⁺ 546.1474, found 546.1479.

(*E*)-*N*-benzyl-*N*-(1-(4-(benzyloxy)phenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1yl)acetamide (3na) was obtained in 53% yield (91.6 mg) as a colorless oil (*E*/*Z* = 93:7). The compound 3na was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). For major (*E*)-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.33 (m, 5H), 7.30-7.24 (m, 5H), 7.16 (t, *J* = 7.0 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 5.34 (t, *J* = 14.5 Hz, 1H), 5.09 (s, 2H), 4.52 (s, 2H), 2.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 160.9, 151.5, 136.6, 136.4, 130.9, 128.8, 128.6, 128.4, 127.8, 127.7, 125.5, 114.9, 112.9 (t, *J* = 21.5 Hz), 70.3, 49.6, 22.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.98 (t, *J* = 9.6 Hz), -103.61 (q, *J* = 11.9 Hz),-123.19 (q, *J* = 7.2 Hz), -125.57 - -125.72 (m); HRMS (ESI) calcd for C₂₈H₂₃F₉NO₂⁺ (M + H)⁺ 576.1580, found 576.1576.

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1yl)acetamide (3oa) was obtained in 82% yield (123.0 mg) as a colorless oil (*E*/*Z* = 91:9). The compound 3oa was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). For major (*E*)-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.25 (m, 5H), 7.18-7.14 (m, 2H), 6.95-6.91 (m, 2H), 5.34 (t, *J* = 14.5 Hz, 1H), 4.52 (s, 2H), 3.85 (s, 3H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 161.7, 151.6, 136.7, 130.9, 128.8, 128.6, 127.8, 125.3, 114.0, 112.8 (t, *J* = 21.6 Hz), 55.4, 49.6, 22.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.92 – -81.06 (m), -103.7 (q, *J* = 12.6 Hz), -123.2 (q, *J* = 8.6 Hz), -125.62 – -125.77 (m); HRMS (ESI) calcd for C₂₂H₁₉F₉NO₂⁺ (M + H)⁺ 500.1267, found 500.1265.

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-(methylthio)phenyl)hex-1-en-1yl)acetamide (3pa) was obtained in 78% yield (120.9 mg) as a colorless oil (*E*/*Z* = 96:4). The compound **3pa** was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). For major (*E*)-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.22 (m, 7H), 7.15 (d, *J* = 6.2 Hz, 2H), 5.39 (t, *J* = 14.4 Hz, 1H), 4.52 (s, 2H), 2.50 (s, 3H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 151.3, 142.9, 136.5, 129.5, 129.2, 128.7, 128.6, 127.8, 113.6 (t, *J* = 21.6 Hz), 49.6, 22.6, 14. 9; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.97 – -81.11 (m), -103.77 (q, *J* = 12.2 Hz), -123.22 (q, *J* = 8.9, 8.5 Hz), -125.63 – -125.79 (m); HRMS (ESI) calcd for C₂₂H₁₉F₉NOS⁺ (M + H)⁺ 516.1038, found 516.1043.

(*E*)-*N*-(1-(benzo[d][1,3]dioxol-5-yl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)-*N*benzylacetamide (3qa) was obtained in 74% yield (114.3 mg) as a colorless oil (*E*/*Z* = 92:8). The compound 3qa was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). For major (*E*)-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.23 (m, 3H), 7.19-7.14 (m, 2H), 6.90-6.80 (m, 2H), 6.77 (s, 1H), 6.03 (s, 2H), 5.35 (t, *J* = 14.4 Hz, 1H), 4.53 (s, 2H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 151.3 (d, *J* = 3.8 Hz), 149.9, 148.1, 136.6, 128.7, 128.6, 127.8, 126.8, 124.2 (t, *J* = 3.0 Hz), 113.2 (t, *J* = 21.6 Hz), 109.1 (t, *J* = 2.6 Hz), 108.4, 101.9, 49.6, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.17 (tt, *J* = 10.0, 3.2 Hz), -103.73 (t, *J* = 14.9 Hz), -123.28 - -123.43 (m), -125.81 (td, *J* = 13.2, 5.1 Hz); HRMS (ESI) calcd for C₂₂H₁₆F₉NNaO₃⁺ (M + Na)⁺ 536.0879, found 536.0883.

(E)-N-benzyl-N-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(naphthalen-2-yl)hex-1-en-1-

yl)acetamide (3ra) was obtained in 55% yield (85.7 mg) as a colorless oil. The compound 3ra was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.91-7.81 (m, 3H), 7.81 (s, 1H), 7.60-7.52 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.34-7.24 (m, 3H), 7.20-7.14 (m, 2H), 5.54 (t, *J* = 14.4 Hz, 1H), 4.61-4.47 (m, 2H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 151.8 (t, *J* = 4.0 Hz), 136.6, 134.2, 132.7, 130.6, 129.8 (t, *J* = 2.8 Hz), 128.8, 128.8, 128.7, 128.5, 127.9, 127.9, 127.8, 127.1, 125.6 (t, *J* = 2.3 Hz), 114.4 (t, *J* = 21.8 Hz), 49.8, 22.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.09 (tt, *J* = 10.1, 3.0 Hz), -103.67 – 103.87 (m), -123.12 – -123.28 (m), -125.68 – -125.83 (m); HRMS (ESI) calcd for C₂₅H₁₉F₉NO⁺ (M + H)⁺ 520.1317, found 520.1318.

(E)-N-benzyl-N-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(thiophen-3-yl)hex-1-en-1-

yl)acetamide (3sa) was obtained in 72% yield (102.9 mg) as a colorless oil. The compound 3sa was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 2.4 Hz, 1H), 7.35 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.32-7.25 (m, 3H), 7.19 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.10-7.06 (m, 1H), 5.37 (t, *J* = 14.6 Hz, 1H), 4.60 (s, 2H), 2.18 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 169.8, 146.5 (t, *J* = 4.1 Hz), 136.6, 134.3, 129.1 (t, *J* = 3.9 Hz), 128.9, 128.6, 127.9, 127.7 (t, *J* = 3.1 Hz), 126.6, 114.1 (t, *J* = 22.0 Hz), 50.2, 22.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.18 (td, *J* = 11.6, 10.0, 3.2 Hz), -104.58 – -104.70 (m), -123.59 – -123.78

(m), -125.73 - -125.91 (m); HRMS (ESI) calcd for $C_{19}H_{15}F_9NOS^+$ (M + H)⁺ 476.0725, found 476.0729.

(*E*)-*N*-methyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)acetamide (3ta) was obtained in 79% yield (93.8 mg) as a colorless oil (E/Z = 97:3). The compound 3ta was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). For major (*E*)-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.34 (m, 5H), 5.68 (t, J = 14.3, 1H), 2.91 (s, 3H), 2.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 153.6, 133.5, 130.8, 129.0, 128.6, 111.8 (t, J = 21.9 Hz), 35.2, 22.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.07 (t, J = 9.7 Hz), -103.55 (q, J = 13.3 Hz), -123.34 (q, J = 8.9 Hz), -125.64 - -125.78 (m); HRMS (ESI) calcd for C₁₅H₁₃F₉NO⁺ (M + H)⁺ 394.0848, found 394.0853.

(*E*)-*N*-(cyclohexylmethyl)-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1yl)acetamide (3ua) was obtained in 71% yield (101.5 mg) as a colorless oil. The compound **3ua** was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.39 (m, 3H), 7.35 (d, *J* = 7.2 Hz, 2H), 5.69 (t, *J* = 14.3 Hz, 1H), 3.09 (d, *J* = 6.9 Hz, 2H), 2.31 (s, 3H), 1.72-1.51 (m, 6H), 1.26-1.08 (m, 3H), 0.89 (q, *J* = 10.8, 9.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 152.8, 133.2, 130.6, 129.0 (t, *J* = 2.6 Hz), 128.5, 113.3 (t, *J* = 21.9 Hz), 51.4, 37.0, 30.8, 26.4, 25.8, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.23 (tt, *J* = 10.1, 3.1 Hz), -103.74 (t, J = 14.6 Hz), -123.20 - -123.39 (m), -125.77 - -125.97 (m); HRMS (ESI) calcd for $C_{21}H_{22}F_9NNaO^+$ (M + Na)⁺ 498.1450, found 498.1445.

Benzyl-(*E*)-benzyl(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)carbamate (3va) was obtained in 72% yield (121.3 mg) as a colorless oil. The compound 3va was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.25 (m, 10H), 7.22-7.16 (m, 5H), 5.67 (t, *J* = 14.5 Hz, 1H), 5.12 (s, 2H), 4.58 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 155.1, 150.8 (t, *J* = 4.0 Hz), 137.1, 135.6, 134.5, 129.8, 129.1, 128.8, 128.6, 128.4, 128.1, 128.0, 127.8, 112.0 (t, *J* = 21.9 Hz), 68.4, 52.4; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.01 (t, *J* = 9.7 Hz), -103.28 (q, *J* = 13.1 Hz), -123.60 (q, *J* = 8.9 Hz), -125.58 - -125.73 (m); HRMS (ESI) calcd for C₂₇H₂₁F₉NO₂⁺ (M + H)⁺ 562.1423, found 562.1423.

tert-Butyl (*E*)-benzyl(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)carbamate (3wa) was obtained in 65% yield (102.9 mg) as a colorless oil. The compound 3wa was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.22 (m, 10H), 5.57 (t, *J* = 14.5 Hz, 1H), 4.68 (s, 2H), 1.28 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 154.1, 152.4, 137.8, 135.7, 129.7, 129.0, 128.8, 127.9, 127.7, 127.7, 109.1 (t, *J* = 21.7 Hz), 82.0, 53.1, 28.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.14 (tt, *J* = 10.1, 3.2 Hz), -102.37 - -102.51 (m), -123.46 - -123.59 (m), -125.64 - -125.79 (m); HRMS (ESI) calcd for C₂₄H₂₃F₉NO₂⁺ (M + H)⁺ 528.1580, found 528.1585.

(*Z*)-*N*-benzyl-*N*-(5,5,6,6,7,7,8,8,8-nonafluoro-2,2-dimethyloct-3-en-3-yl)acetamide (**3xa**) was obtained in 36% yield (48.8 mg) as a colorless oil (*E*/*Z* = 8:92). The compound **3xa** was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). For major (*Z*)-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.23 (m, 5H), 5.18 (d, *J* = 15.3 Hz, 1H), 4.16 (d, *J* = 15.3 Hz, 1H), 2.08 (s, 3H), 1.13 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 164.2, 137.3, 128.7, 128.4, 127.5, 112.4 (t, *J* = 19.3 Hz), 54.6, 39.2, 30.3, 22.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.53 (t, *J* = 9.8 Hz), -111.48 (q, *J* = 12.8 Hz), -111.91 (q, *J* = 13.0 Hz), -124.48 - -124.64 (m), -126.30 (t, *J* = 12.9 Hz); HRMS (ESI) calcd for C₁₉H₂₁F₉NO⁺ (M + H)⁺ 450.1474, found 450.1479.

(*E*)-*N*-benzyl-*N*-(3,3,4,4,4-pentafluoro-1-phenylbut-1-en-1-yl)acetamide (3ab) was obtained in 53% yield (58.5 mg) as a colorless oil. The compound 3ab was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.40 (m, 3H), 7.34-7.26 (m, 5H), 7.17-7.12 (m, 2H), 5.37 (t, *J* = 14.1 Hz, 1H), 4.50 (s, 2H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 151.7 (t, *J* = 3.8 Hz), 136.6, 133.2, 130.9, 129.3 (t, *J* = 2.7 Hz), 128.8, 128. 7, 128.6, 127.8, 114.1 (t, *J* = 22.0 Hz), 49.5, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -85.27 – -85.30 (m), -107.81 – -107.86 (m); HRMS (ESI) calcd for C19H16F5NNaO⁺ (M + Na)⁺ 392.1044, found 392.1049.

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,5-heptafluoro-1-phenylpent-1-en-1-yl)acetamide (3ac) was obtained in 74% yield (93.1 mg) as a colorless oil. The compound **3ac** was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.37 (m, 3H), 7.34-7.25 (m, 5H), 7.17-7.14 (m, 2H), 5.43 (t, *J* = 14.3 Hz, 1H), 4.51 (s, 2H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 151.8 (t, *J* = 4.1 Hz), 136.6, 133.3, 130.8, 129.2 (t, *J* = 2.7 Hz), 128.7, 128.7, 128.6, 127.8, 114.1 (t, *J* = 21.8 Hz), 49.5, 22.7; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -80.16 – -80.28 (m), -104.71 (q, *J* = 10.2 Hz), -126.76; HRMS (ESI) calcd for C₂₀H₁₇F₇NO⁺ (M + H)⁺ 420.1193, found 420.1198.

(E)-N-benzyl-N-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyloct-1-en-1-

yl)acetamide (3ad) was obtained in 65% yield (110.8 mg) as a colorless oil. The compound 3ad was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.39 (m, 3H), 7.35-7.26 (m, 5H), 7.20-7.12 (m, 2H), 5.44 (t, *J* = 14.4 Hz, 1H), 4.51 (s, 2H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 151.6, 136.6, 133.3, 130.8, 129.2, 128.8, 128.7, 128.6, 127.8, 114.4 (t, *J* = 21.8 Hz), 49.5, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.89 (t, *J* = 9.9 Hz), -103.86 (q, *J* = 14.0 Hz), -121.65, -122.28 - -122.46 (m), -122.87, -126.09 - -126.27 (m); HRMS (ESI) calcd for C₂₃H₁₇F₁₃NO⁺ (M + H)⁺ 570.1097, found 570.1103.

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-phenyldec-1-en-1-yl)acetamide (3ae) was obtained in 75% yield (150.6 mg) as a colorless oil. The compound 3ae was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.39 (m, 3H), 7.35-7.25 (m, 5H), 7.19-7.15 (m, 2H), 5.45 (t, *J* = 14.4 Hz, 1H), 4.51 (s, 2H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 151.6, 136.6, 133.2, 130.7, 129.2, 128.7, 128.6, 128.5, 127.7, 114.4 (t, *J* = 21.8 Hz), 49.4, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -80.98 (t, *J* = 10.1 Hz), -103.90 (q, *J* = 13.9 Hz), -121.49, -122.00, -122.30 – -122.44 (m), -122.83, - 126.18 – -126.37 (m); HRMS (ESI) calcd for C₂₅H₁₇F₁₇NO⁺ (M + H)⁺ 670.1033, found 670.1030.

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluoro-1phenyldodec-1-en-1-yl)acetamide (3af) was obtained in 48% yield (110.6 mg) as a colorless oil. The compound 3af was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.39 (m, 3H), 7.35-7.25 (m, 5H), 7.18-7.15 (m, 2H), 5.44 (t, *J* = 14.3 Hz, 1H), 4.51 (s, 2H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 151.7 (t, *J* = 3.9 Hz), 136.6, 133.3, 130.8, 129.2, 128.8, 128.7, 128.6, 127.8, 114.5 (t, *J* = 21.8 Hz), 49.6, 22.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -81.03 – -81.15 (m), -104.00 (t, *J* = 15.2 Hz), -121.55, -121.97, -122.49, -122.93, -126.26 – -126.47 (m); HRMS (ESI) calcd for C₂₇H₁₇F₂₁NO⁺ (M + H)⁺ 770.0969, found 770.0967.

Analytical Data for β -difluoroacetylated Enamides

Ethyl (*E*)-4-(*N*-benzylacetamido)-2,2-difluoro-4-phenylbut-3-enoate (5a) was obtained in 60% yield (67.2 mg) as a colorless oil. The compound **5a** was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1).¹H NMR (400 MHz, CDCl₃) δ 7.48-7.37 (m, 3H), 7.33-7.25 (m, 5H), 7.16 (d, *J* = 6.4 Hz, 2H), 5.56 (t, *J* = 11.7 Hz, 1H), 4.50 (s, 2H), 3.83 (q, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 162.6 (t, *J* = 33.4 Hz), 148.4 (t, *J* = 10.0 Hz), 136.7, 133.1, 130.8, 129.2, 128.8, 128.8, 128.5, 127.6, 121.2 (t, *J* = 29.8 Hz), 111.6 (t, *J* = 243.1 Hz), 63.1, 49.4, 22.5, 13.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -90.82 (d, *J* = 11.6 Hz); HRMS (ESI) calcd for C₂₁H₂₂F₂NO₃⁺ (M + H)⁺ 374.1562, found 374.1568.

Ethyl (*E*)-4-(*N*-benzylacetamido)-2,2-difluoro-4-(o-tolyl)but-3-enoate (5b) was obtained in 78% yield (90.8 mg) as a colorless oil. The compound 5b was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.19 (m, 1H), 7.18-7.05 (m, 5H), 6.97 (d, J = 7.0 Hz, 3H), 5.63 (t, J = 11.1 Hz, 1H), 4.35 (s, br, 2H), 3.71 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 2.09 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 162.7 (t, J = 33.4 Hz), 148.5 (t, J = 9.9 Hz), 137.3, 136.9, 132.0, 131.8, 130.7, 130.4, 128.4, 127.8, 127.2, 125.7, 119.4 (t, J = 29.6 Hz), 111.8 (t, J = 245.4 Hz), 62.9, 48.8, 22.9, 19.6, 13.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -65.54, -90.76, -94.24; HRMS (ESI) calcd for C₂₂H₂₄F₂NO₃⁺ (M + H)⁺ 388.1719, found 388.1721.

Ethyl (*E*)-4-(*N*-benzylacetamido)-2,2-difluoro-4-(2-methoxyphenyl)but-3-enoate (5c) was obtained in 57% yield (68.8 mg) as a colorless oil. The compound 5c was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (ddd, J = 8.3, 7.5, 1.8 Hz, 1H), 7.26-7.17 (m, 3H), 7.12-7.06 (m, 3H), 6.94 (td, J = 7.5, 0.9 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 5.65 (t, J = 11.6 Hz, 1H), 4.45 (s, 2H), 3.88 (q, J = 7.2 Hz, 2H), 3.71 (s, 3H), 2.39 (s, 3H), 1.14 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 162.6 (t, J = 33.8 Hz), 157.4, 146.2 (t, J = 9.7 Hz), 137.2, 132.6, 132.1, 128.4, 128.2, 127.2, 121.8 (t, J = 28.8 Hz), 111.6 (t, J = 243.3 Hz), 110.6, 62.8, 55.3, 48.6, 22.5, 13.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -94.19 (d, J = 11.1 Hz); HRMS (ESI) calcd for C₂₂H₂₃F₂NNaO₄⁺ (M + Na)⁺ 426.1487, found 426.1494.

Ethyl (*E*)-4-(benzo[d][1,3]dioxol-5-yl)-4-(*N*-benzylacetamido)-2,2-difluorobut-3enoate (5d) was obtained in 67% yield (83.9 mg) as a colorless oil. The compound 5d was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃ δ 7.32-7.25 (m, 3H), 7.19-7.15 (m, 2H), 6.84-6.79 (m, 2H), 6.72 (d, J = 1.4 Hz, 1H), 6.01 (s, 2H), 5.47 (t, J = 11.7 Hz, 1H), 4.51 (s, 2H), 3.95 (q, J = 7.2 Hz, 2H), 2.28 (s, 3H), 1.13 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 162.7 (t, J = 33.5 Hz), 149.8, 148.1, 148.0 (t, J = 10.0 Hz), 136.7, 128.8, 128.5, 127.6, 126.8, 124.4, 120.2 (t, J = 29.7 Hz), 111.7 (t, J = 243.4 Hz), 108.8, 108.4, 101.8, 63.1, 49.4, 22.4, 13.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -90.64 (d, J = 11.7 Hz); HRMS (ESI) calcd for C₂₂H₂₁F₂NNaO₅⁺ (M + Na)⁺ 440.1280, found 440.1285.

Ethyl (*E*)-4-(*N*-benzylacetamido)-2,2-difluoro-4-(4-fluorophenyl)but-3-enoate (5e) was obtained in 68% yield (79.8 mg) as a colorless oil. The compound 5e was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.24 (m, 5H), 7.16-7.07 (m, 4H), 5.55 (t, *J* = 11.9 Hz, 1H), 4.50 (s, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 164.1 (d, *J* = 252.3 Hz), 162.7 (t, *J* = 33.4 Hz),147.4 (t, *J* = 9.5 Hz), 136.6, 131.5 (dt, *J* = 8.6, 2.1 Hz), 129.3 (d, *J* = 3.3 Hz), 128.9, 128.7, 127.8, 121.2 (t, *J* = 29.2 Hz), 116.0 (d, *J* = 21.9 Hz), 111.6 (t, *J* = 245.9 Hz), 63.3, 49.5, 22.6, 13.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -91.73, -108.52; HRMS (ESI) calcd for $C_{21}H_{20}F_3NNaO_3^+$ (M + Na)⁺ 414.1287, found 414.1292.

Ethyl (*E***)-4-(***N***-benzylacetamido)-4-(4-chlorophenyl)-2,2-difluorobut-3-enoate (5f) was obtained in 66% yield (80.8 mg) as a colorless oil. The compound 5f was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.4 Hz, 2H), 7.32-7.25 (m, 3H), 7.22 (d, J = 8.4 Hz, 2H), 7.16-7.11 (m, 2H), 5.57 (t, J = 12.0 Hz, 1H), 4.50 (s, 2H), 3.95 (q, J = 7.1 Hz, 2H), 2.29 (s, 3H), 1.12 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 162.7 (t, J = 33.5 Hz), 147.3 (t, J = 9.2 Hz), 137.0, 136.5, 131.6, 130.6 (t, J = 2.1 Hz), 129.1, 128.8, 128.6, 127.8, 121.5 (t, J = 29.1 Hz), 111.4 (t, J = 246.2 Hz), 63.3, 49.5, 22.6, 13.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -92.05; HRMS (ESI) calcd for C₂₁H₂₀ClF₂NNaO₃⁺ (M + Na)⁺ 430.0992, found 430.0994.**

Ethyl (*E***)-4-(***N***-benzylacetamido)-2,2-difluoro-4-(2-fluorophenyl)but-3-enoate (5g) was obtained in 84% yield (98.6 mg) as a colorless oil. The compound 5g was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.38 (m, 1H), 7.29-7.22 (m, 3H), 7.21-7.12 (m, 4H), 7.10-7.04 (m, 1H), 5.72 (t, J = 12.0 Hz, 1H), 4.50 (s, 2H), 4.00 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 162.4 (t, J = 33.8 Hz), 160.0 (d, J = 251.0 Hz), 143.1 (t, J = 8.8 Hz), 136.7, 132.5 (d, J = 8.6 Hz), 132.3 (d, J = 2.1 Hz), 128.4, 128.4, 127.5, 124.2 (d, J = 3.6 Hz), 123.0 (t, J = 28.2 Hz), 120.9 (d, J = 13.4 Hz), 115.9 (d, J = 21.4 Hz), 111.2 (t, J = 246.9 Hz), 63.1, 48.8, 22.3, 13.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -95.45, -112.39; HRMS (ESI) calcd for C₂₁H₂₀F₃NNaO₃⁺ (M + Na)⁺ 414.1287, found 414.1292.**

Ethyl (*E*)-4-(*N*-benzylacetamido)-4-(3-bromo-4-fluorophenyl)-2,2-difluorobut-3enoate (5h) was obtained in 90% yield (127.1mg) as a colorless oil. The compound 5h was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (dd, J = 6.4, 2.2 Hz, 1H), 7.32-7.22 (m, 4H), 7.17-7.11 (m, 3H), 5.59 (t, J = 12.1 Hz, 1H), 4.52 (s, 2H), 4.01 (q, J = 7.2 Hz, 2H), 2.29 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 162.6 (t, J = 33.4Hz), 160.3 (d, J = 253.1 Hz), 146.1 (t, J = 8.9 Hz), 136.3, 134.2, 130.8 (d, J = 3.7 Hz), 130.4 (d, J = 7.8 Hz), 128.8, 128.6, 127.9, 121.7 (t, J = 28.7 Hz), 116.8 (d, J = 22.8 Hz), 111.3 (t, J = 245.8 Hz), 109.7 (d, J = 21.6 Hz), 63.4, 49.6, 22.5, 13.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -92.67 (d, J = 12.2 Hz), -102.81; HRMS (ESI) calcd for $C_{21}H_{19}BrF_3NNaO_3^+$ (M + Na)⁺ 492.0393, found 492.0399.

Ethyl (*E*)-4-(*N*-benzylacetamido)-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate (5i) was obtained in 96% yield (127.1 mg) as a colorless oil. The compound 5i was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.31-7.25 (m, 3H), 7.14 (dd, J = 7.6, 1.8 Hz, 2H), 5.67 (t, J = 12.2 Hz, 1H), 4.51 (s, 2H), 3.95 (q, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.11 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 162.5 (t, J = 33.4 Hz), 146.9 (t, J = 8.8 Hz), 136.9, 136.3, 132.4 (q, J= 32.9 Hz), 129.7 (d, J = 2.4 Hz), 128.7 (d, J = 11.3 Hz), 127. 8, 125.6 (q, J = 3.6 Hz), 123.6 (q, J = 270.5 Hz), 122.3 (t, J = 28.7 Hz), 111.3 (t, J = 247.2 Hz), 63.3, 49.5, 22.4, 13.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.91, -92.79; HRMS (ESI) calcd for C₂₂H₂₀F₅NNaO₃⁺ (M + Na)⁺ 464.1256, found 464.1261.

Ethyl (*E*)-4-(*N*-benzylacetamido)-2,2-difluoro-4-(naphthalen-2-yl)but-3-enoate (5j) was obtained in 81% yield (102.9 mg) as a colorless oil. The compound 5j was purified with chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (dd, *J* = 8.9, 6.6 Hz, 3H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.60-7.54 (m, 2H), 7.33-7.26 (m, 4H), 7.18 (dd, *J* = 7.6, 1.7 Hz, 2H), 5.65 (t, *J* = 11.4 Hz, 1H), 4.54 (s, 2H), 3.62 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 162.7 (t, *J* = 33.1 Hz), 148.6 (t, *J* = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (d, *J* = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, *J* = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (d, *J* = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, *J* = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (d, *J* = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, *J* = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (d, *J* = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, *J* = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (d, *J* = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, *J* = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (d, *J* = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, J) = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (d, J = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, J) = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (d, J = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, J) = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (d, J = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, J) = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (t, J = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, J) = 10.2 Hz), 136.7, 134.1, 132.6, 130.5 (t, J = 4.4 Hz), 128.9, 128.8, 128.6, 128.0, 127.8, 127.7, 127.2, 124.9, 121.6 (t, J = 10.2 Hz), 136.7, 134.1, 130.8, 140.5 (t, J = 10

J= 30.0 Hz), 111.9 (t, J= 244.9 Hz), 63.0, 49.6, 22.6, 13.4; ¹⁹F NMR (376 MHz, CDCl₃) δ -90.16 (d, J= 11.4 Hz); HRMS (ESI) calcd for C₂₅H₂₃F₂NNaO₃⁺ (M + Na)⁺ 446.1538, found 446.1536.

Copies of ¹H NMR, ¹³C NMR and ¹⁹F NMR Spectra

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)acetamide (3aa)

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -30

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-fluorophenyl)hex-1-en-1-yl)acetamide (3ba)

100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 fil (ppm)

(*E*)-*N*-benzyl-*N*-(1-(4-chlorophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-

yl)acetamide (3ca)

(*E*)-*N*-benzyl-*N*-(1-(4-bromophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1yl)acetamide (3da)

¹³C NMR(100MHz, CDCl₃)

Ac_{\N}Bn Ċ₄F₉ Br 3da ¹⁹F NMR(376MHz, CDCl₃)

100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 f1 (ppm)

(E)-N-Benzyl-N-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(2-fluorophenyl)hex-1-en-1-

yl)acetamide (3ea)

(*E*)-*N*-benzyl-*N*-(1-(3-chlorophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)acetamide (3fa)





00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -30 fi (ppm)

(*E*)-*N*-benzyl-*N*-(1-(3-bromo-4-fluorophenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)acetamide (3ga)





(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-(trifluoromethyl)phenyl)hex-1en-1-yl)acetamide (3ha)





Ethyl-(*E*)-4-(1-(*N*-benzylacetamido)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1yl)benzoate (3ia)



(*112) (*



(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-(methylsulfonyl)phenyl)hex-1-en-1-yl)acetamide (3ja)





(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-nitrophenyl)hex-1-en-1-yl)acetamide (3ka)





100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 fit (ppm)

(*Z*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-nitrophenyl)hex-1-en-1-yl)acetamide (*Z*-3ka)





100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 fil (ppm)

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(o-tolyl)hex-1-en-1-yl)acetamide (3la)





(*E*)-*N*-(1-([1,1'-biphenyl]-4-yl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)-*N*-benzylacetamide (3ma)



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100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 fil (ppm)

(*E*)-*N*-benzyl-*N*-(1-(4-(benzyloxy)phenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1yl)acetamide (3na)





100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 fi (ppm)

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hex-1-en-1-yl)acetamide (30a)





(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-(methylthio)phenyl)hex-1-en-1-yl)acetamide (3pa)



81.019 81.017 81.037 81.037 81.037 81.037 81.037 81.037 81.077



00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -30 fl (ppm)

(*E*)-*N*-(1-(benzo[d][1,3]dioxol-5-yl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)-*N*-benzylacetamide (3qa)







(E)-N-benzyl-N-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(naphthalen-2-yl)hex-1-en-1-

yl)acetamide (3ra)



All 055 All 075 All



(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(thiophen-3-yl)hex-1-en-1-yl)acetamide (3sa)





(*E*)-*N*-methyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)acetamide (3ta)





100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 fi (ppm)

(*E*)-*N*-(cyclohexylmethyl)-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1yl)acetamide (3ua)



S-60



Benzyl-(*E*)-benzyl(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)carbamate (3va)





100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 fl (ppm)

tert-Butyl (*E*)-benzyl(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)carbamate (3wa)





S-64

(*Z*)-*N*-benzyl-*N*-(5,5,6,6,7,7,8,8,8-nonafluoro-2,2-dimethyloct-3-en-3-yl)acetamide (3xa)





100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 fil (ppm)

(E)-N-benzyl-N-(3,3,4,4,4-pentafluoro-1-phenylbut-1-en-1-yl)acetamide (3ab)





(E)-N-benzyl-N-(3,3,4,4,5,5,5-heptafluoro-1-phenylpent-1-en-1-yl)acetamide (3ac)





(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyloct-1-en-1-yl)acetamide (3ad)





100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -11 (ppm)

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-phenyldec-1-en-1-yl)acetamide (3ae)





100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -11 (ppm)

(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluoro-1-phenyldodec-1-en-1-yl)acetamide (3af)






Ethyl (E)-4-(N-benzylacetamido)-2,2-difluoro-4-phenylbut-3-enoate (5a)



 $<^{-90.801}_{-90.832}$

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -30 fl (ppm)

Ethyl (E)-4-(N-benzylacetamido)-2,2-difluoro-4-(o-tolyl)but-3-enoate (5b)





10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 fl(ppm)

Ethyl (*E*)-4-(*N*-benzylacetamido)-2,2-difluoro-4-(2-methoxyphenyl)but-3-enoate (5c)





00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -30 fl (ppm)





-170.309 -170.309 -170.309 -170.301 -149.786 -143.162 -143.063 -143.063 -143.063 -123.6306 -123.6306 -123.6306 -123.6306 -123.6306 -123.6306 -13.610 -23.160 -77.160 -77.160 -77.160 -77.160 -13.676 -13.676



100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 fil (ppm)

Ethyl (E)-4-(N-benzylacetamido)-2,2-difluoro-4-(4-fluorophenyl)but-3-enoate (5e)







3.5

2.5

2.0

3.0

1.5 1.0 0.5 0.0 -0

6.5 6.0

7.0

0.0

9.5 9.0 8.5 8.0







Ethyl (E)-4-(N-benzylacetamido)-2,2-difluoro-4-(2-fluorophenyl)but-3-enoate (5g)



Ethyl (*E*)-4-(*N*-benzylacetamido)-4-(3-bromo-4-fluorophenyl)-2,2-difluorobut-3-enoate (5h)







100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 fil (ppm)

Ethyl (*E*)-4-(*N*-benzylacetamido)-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate (5i)





 $Ethyl\,(E)-4-(N-benzylacetamido)-2, 2-difluoro-4-(naphthalen-2-yl) but-3-enoate\,(5j)$







00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -30 fl (ppm)