Trifluoromethylation of Unactivated Alkenes with Me₃SiCF₃ and N-Iodosuccinimide

Xinkan Yang and Gavin Chit Tsui*

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General Experimental. Unless otherwise noted, reactions were carried out under argon in a 25mL round-bottom flask with magnetic stirring. Analytical thin layer chromatography (TLC) was performed with EM Science silica gel 60 F254 aluminum plates. Visualization was done under a UV lamp (254 nm) and by immersion in ethanolic phosphomolybdic acid (PMA) or potassium permanganate (KMnO₄), followed by heating using a heat gun. Organic solutions were concentrated by rotary evaporation at 23–35 °C. Purification of reaction products were generally done by flash column chromatography with Grace Materials Technologies 230–400 mesh silica gel.

Materials. Anhydrous DMSO was purchased from J&K Scientific. NIS was purchased from Dieckmann then recrystallized from hexane : dioxane (2 : 1), then filtration and dried under reduced pressure for overnight,. AgOAc was purchased from Acros. DMF was dried over Solvent Purification System then bubbled with argon for 24 h. Other chemicals for substrates preparation were purchased from Acros, J&K Scientific, Aldrich and Dikemann.

Instrumentation. Proton nuclear magnetic resonance spectra (¹H NMR) spectra, carbon nuclear magnetic resonance spectra (¹³C NMR) and fluorine nuclear magnetic resonance spectra (¹⁹F NMR) were recorded at 23 °C on a Bruker 400 spectrometer in CDCl₃ (400 MHz for ¹H, 101 MHz for ¹³C and 376 MHz for ¹⁹F) and Bruker 500 spectrometer in CDCl₃ (500 MHz for ¹H, 126 MHz for ¹³C and 470 MHz for ¹⁹F). Chemical shifts for protons were reported as parts per million in δ scale using solvent residual peak (CHCl₃: 7.26 ppm) or tetramethylsilane (0.00 ppm) as internal standards. Chemical shifts of ¹³C NMR spectra were reported in ppm from the central peak of CDCl₃ (77.16 ppm) on the δ scale. Chemical shifts of ¹⁹F NMR are reported as parts per million in δ scale using benzotrifluoride (-63.72 ppm) as internal standards. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintuplet, sx = sextet, sp = septuplet, m = multiplet, br = broad), and coupling constant (J, Hz). High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95XL GC Mass Spectrometer or a Thermo Scientific Q Exactive Focus Mass Spectrometer or Bruker 9.4T FTICR Mass Spectrometer. The control experiment results were obtained on a Shimadzu GCMS-QP2010 SE GC MS Spectrometer.
Experimental Procedures:

General procedure (cf. Scheme 2):

To a glass tube equipped with a magnetic stir bar were added alkene 1 (0.3 mmol), NIS (0.6 mmol), NaOAc (1.2 mmol) and AgOAc (0.36 mmol). The tube was then sealed with a septum, evacuated and refilled with argon for three times. Anhydrous DMSO (3.0 mL) was added via a syringe and the solution was further evacuated and refilled with argon for three times. Finally, Me₃SiCF₃ (180 μL, 0.4 mmol) was added dropwise to the solution. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h (see picture below). The E/Z ratio was determined by ¹⁹F NMR of the crude mixture. The reaction was quenched with H₂O, extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product.
Substrates:

Alkenes 1a-1c, 1e, 1g-1s, 1u-1y, 1ab, 1ae-1ah were synthesized according to the literature procedures.1 1z, 1aa, 1ac, 1ad were commercially available. It was synthesized from 1s, 1d and 1f were synthesized by esterification from corresponding benzoyl chloride and 5-hexene-1-ol. 3 was synthesized according to the literature reported procedure.2

1 (a) Zhu, L.; Wang, L. S.; Li, B.; Fu, B.; Zhang, C. P.; Li, W. Chem. Commun. 2016, 52, 6371. (b) Lin, Q.-Y.; Xu, X.-H.; Zhang, K.; Qing, F.-L. Angew. Chem., Int. Ed. 2016, 55, 1479. (c) Liu, Z.-Q.; Liu, D. J. Org. Chem. 2017, 82, 1649. (d) Braun, M.-G.; Doyle, A. G. J. Am. Chem. Soc. 2013, 135, 12990. (e) Wu, X.; Chu, L.; Qing, F.-L. Angew. Chem., Int. Ed. 2013, 52, 2198. (f) Ren, Y.; Zheng, X.; Zhang, X. Synlett 2018, 29, 1028. (g) Ma, G.; Wan, W.; Hu, Q.; Jiang, H.; Wang, J.; Zhu, S.; Hao, J. Chem. Commun. 2014, 50, 7527.
2 Shaw, M. H.; Croft, R. A.; Whittingham, W. G.; Bower, J. F. J. Am. Chem. Soc. 2015, 137, 8054.
Preparation of hex-5-en-1-yl 3-methoxybenzoate (1d):

To a solution of 5-hexene-1-ol (0.48 mL, 4.0 mmol), Et₃N (1.11 mL, 8.0 mmol), DMAP (49.0 mg, 0.4 mmol) in CH₂Cl₂ (10 mL) was added dropwise with a solution of 3-Methoxybenzoyl chloride (0.89 mL, 6.0 mmol) in CH₂Cl₂ (4.0 mL) at 0 °C, the resulting mixture was vigorously stirred at room temperature and monitored the reaction by TLC. After completion, treated with sat. NaHCO₃ aq. then stirred at room temperature for another 20 mins. Et₂O was added, the organic layer was separated, washed with water, the combined extracts were washed with brine, dried over anhydrous Na₂SO₄, Filtered and evaporated the solvent, the residue was directly purified by flash chromatography to deliver the desired product 1d as a colorless oil (930 mg, 4.0 mmol, 100% yield), Rₜ = 0.60 (hexane : EtOAc = 5 : 1). ^1H NMR (400 MHz, CDCl₃): δ 7.63 (d, J = 7.6 Hz, 1H), 7.56 (s, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.09 (dd, J = 8.4 Hz, J = 2.8 Hz, 1H), 5.87-5.77 (m, 1H), 5.06-4.96 (m, 2H), 4.32 (t, J = 6.6 Hz, 2H), 3.85 (s, 3H), 2.16-2.10 (m, 2H), 1.82-1.75 (m, 2H), 1.59-1.51 (m, 2H) ppm. ^13C NMR (101 MHz, CDCl₃): δ 166.6, 159.6, 138.4, 131.9, 129.5, 122.0, 119.4, 115.0, 114.2, 65.1, 55.5, 33.4, 28.3, 25.4 ppm. HRMS m/z (APCI): calcd. for C₁₆H₁₀O₃ [M+H]+: 235.1329; found: 235.1324.

Preparation of hex-5-en-1-yl 4-(trifluoromethyl)benzoate (1f):

To a solution of 5-hexene-1-ol (0.24 mL, 2.0 mmol), Et₃N (0.56 mL, 4.0 mmol), DMAP (24.4 mg, 0.2 mmol) in CH₂Cl₂ (5.0 mL) was added dropwise with a solution of 4-trifluoromethylbenzoyl chloride (626 mg, 3.0 mmol) in CH₂Cl₂ (2.0 mL) at 0 °C, the resulting mixture was vigorously stirred at room temperature and monitored the reaction by TLC. After completion, treated with sat. NaHCO₃ aq. then stirred at room temperature for another 20 mins. Et₂O was added, the organic layer was separated, washed with water, the combined extracts were washed with brine, dried over anhydrous Na₂SO₄. Filtered and evaporated the solvent, the residue was directly purified by flash chromatography to deliver the desired product 1f as a colorless oil (510 mg, 1.88 mmol, 94% yield), Rₜ = 0.70 (hexane : EtOAc = 5 : 1). ^1H NMR (400 MHz, CDCl₃): δ 8.15 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 5.87-5.77 (m, 1H), 5.06-4.97 (m, 2H), 4.36 (t, J = 6.6 Hz, 2H), 2.16-2.11 (m, 2H), 1.84-1.77 (m, 2H), 1.59-1.52 (m, 2H) ppm. ^13C NMR (101 MHz, CDCl₃): δ 165.6, 138.3, 134.5 (q, J_C,F = 32.6 Hz), 133.8, 130.1, 125.5 (q, J_C,F = 3.7 Hz), 123.8 (q, J_C,F = 273.6 Hz), 115.1, 65.6, 33.4, 28.2, 25.4 ppm. ^19F NMR (376 MHz, CDCl₃): δ: -64.11 (s, 3F). HRMS m/z (APCI): calcd. for C₁₄H₁₀F₃O₂ [M+H]+: 273.1097; found: 273.1098.
Preparation of 2-(hex-5-en-1-yl)-3-oxoisoindolin-1-yl acetate (1t):

A solution of 1s (190 mg, 0.83 mmol), Zn (124 mg, 1.91 mmol) dust in acetic acid (4.2 mL) was heated to reflux for 4 hours, then cool down to room temperature. Most of acetic acid was removed under reduced pressure, then the residue was directly purified by column chromatography to afford the product 1t (153 mg, 0.56 mmol, 68% yield) as a yellow oil. \( R_f = 0.20 \) (hexane : EtOAc = 5 : 1). \( ^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.78-7.76 (m, 1H), 7.55-7.47 (m, 3H), 6.98 (s, 1H), 5.80-5.69 (m, 1H), 5.00-4.90 (m, 2H), 3.76-3.69 (m, 1H), 3.28-3.21 (m, 1H), 2.14 (s, 3H), 2.09-2.03 (m, 2H), 1.70-1.54 (m, 2H), 1.45-1.37 (m, 2H) ppm. \( ^{13}C\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 171.2, 167.8, 140.9, 138.4, 132.3, 132.1, 130.3, 123.8, 123.5, 114.9, 81.2, 40.2, 33.3, 27.7, 26.1, 21.1 ppm. HRMS m/z (APCI): calcd. for C\(_{16}\)H\(_{20}\)NO\(_3\) [M+H]\(^+\) : 274.1438; found: 274.1437.

Preparation of (2-(2-vinylcyclopropyl)ethyl)benzene (9):

To a stirred solution of S1 (670 mg, 5.0 mmol) in CH\(_2\)Cl\(_2\) (20.0 mL), Wittig ylide (2.0 g, 6.0 mmol) was added at room temperature under argon atmosphere, then stirred at room temperature for 24 h. the solvent was evaporated and the residue was directly purified by column chromatography to afford S2 as a colorless oil (840 mg, 4.8 mmol, 96% yield, E / Z = 91 : 9). \( R_f = 0.60 \) (hexane : EtOAc = 8 : 1). The spectral data are in full accordance with the literature report.\(^3\)

To a stirred solution of S2 (840 mg, 4.78 mmol) in Et\(_2\)O (48.0 mL), DIBAL-H (1.0 M in hexane, 9.6 mL, 9.6 mmol) was added at -78 °C under argon atmosphere, then stirred at -78 °C for 2 h. Carefully quenched with saturated aqueous solution of sodium/potassium tartrate, then stirred for extra 1 h at room temperature. Extracted with Et\(_2\)O for three times, then the organic layers were combined and washed with brine, dried over anhydrous Na\(_2\)SO\(_4\). Filtered and evaporated the solvent, the residue was directly purified by flash chromatography to deliver the desired product S3 as a light yellow oil (435 mg, 4.4 mmol, 91% yield, E / Z = 91 : 9). \( R_f = 0.20 \) (hexane : EtOAc = 5 : 1). The spectral data are in full accordance with the literature report.\(^3\)

Under argon, S3 (405 mg, 2.5 mmol) in dry CH\(_2\)Cl\(_2\) (7.5 mL) was treated with Et\(_2\)Zn (1.0 M in hexane, 3.1 mmol, 3.1 mmol) at 0 °C, the suspension was stirred at 0 °C for 30 mins. In a second flask, Et\(_2\)Zn (1.0 M in hexane, 3.1 mmol, 3.1 mmol) was added to CH\(_2\)I\(_2\) (0.4 mL, 5.0 mmol) in dry CH\(_2\)Cl\(_2\)

\(^3\) Sanz-Marco, A.; Blay, G.; Muñoz, M. C.; Pedro, J. R. Chem. Commun. 2015, 51, 8958–8961.
(15.0 mL) and stirred for 30 min at 0 °C. The contents of the first flask were transferred into the second flask at 0 °C and the mixture was stirred at room temperature until the substrate was completely consumed. Slowly quenched with sat. NH₄Cl aq., when an emulsion formed, 2 M HCl aq. was added slowly until the solution became clear. Extracted with CH₂Cl₂ for three times, then the organic layers were combined and washed with brine, dried over anhydrous Na₂SO₄. Filtered and evaporated the solvent, the residue was directly purified by flash chromatography to deliver the desired product S4 as a light yellow oil. (350 mg, 2.0 mmol, 80% yield, dr (anti : syn) = 95 : 5). Rₜ= 0.22 (hexane : EtOAc = 5 : 1). ¹H NMR (400 MHz, CDCl₃): δ 7.32-7.28 (m, 2H), 7.21-7.18 (m, 3H), 3.44-3.36 (m, 2H), 2.79-5.67 (m, 2H), 1.66 (s, 1H), 1.69-1.51 (m, 2H), 0.88-0.80 (m, 1H), 0.67-0.59 (m, 1H), 0.42-0.32 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 142.3, 128.5, 128.4, 125.8, 67.0, 35.9, 35.4, 21.4, 16.9, 9.0 ppm.

To a stirred solution of S4 (350 mg, 2.0 mmol) in CH₂Cl₂ (10.0 mL) was added PCC (650 mg, 3.0 mmol) and silica gel (1.0 g) at room temperature under argon atmosphere, then stirred at room temperature and monitored by TLC. After completion, the solvent was evaporated and the residue was directly purified by column chromatography to afford the desired product S5 as a colorless oil: (334 mg, 1.9 mmol, 93% yield, dr (anti : syn) = 95 : 5). Rₜ= 0.4 (hexane : EtOAc = 2 : 1). ¹H NMR (400 MHz, CDCl₃): δ 8.97 (d, J = 5.6 Hz, 1H), 7.31-7.28 (m, 2H), 7.22-7.16 (m, 3H), 2.73 (d, J = 7.4 Hz, 2H), 1.76-1.59 (m, 3H), 1.51-1.46 (m, 1H), 1.31-1.27 (m, 1H), 0.95-0.90 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 201.0, 141.4, 128.5, 128.5, 126.1, 35.4, 34.5, 30.5, 22.3, 14.8 ppm.

Under argon, to a suspension of Wittig ylide (1.37 g, 3.84 mmol) in THF (2.0 mL) was quickly added t-ButOK (430 mg, 3.84 mmol), then stirred at room temperature for 30 mins, after that, the reaction system was cooled to 0 °C, a THF (2.0 mL) solution of S5 (334 mg, 1.92 mmol) was added dropwise, then warmed to room temperature and stirred for overnight. Quenched with water, extracted with Et₂O for three times, then the organic layers were combined and washed with brine, dried over anhydrous Na₂SO₄. Filtered and evaporated the solvent, the residue was directly purified by flash chromatography to deliver the desired product 9 as a colorless oil. (270 mg, 1.55 mmol, 81% yield, dr (anti : syn) = 95 : 5). Rₜ= 0.90 (hexane : EtOAc = 5 : 1). ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.32 (m, 2H), 7.26-7.24 (m, 3H), 5.48-5.39 (m, 1H), 5.08 (d, J = 16.8 Hz, 1H), 4.90 (d, J = 10.0 Hz, 1H), 2.79-2.76 (m, 2H), 1.69-1.63 (m, 2H), 1.26-1.21 (m, 1H), 0.88-0.85 (m, 1H), 0.67-0.57 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 142.4, 142.1, 128.6, 128.4, 125.8, 111.3, 35.9, 35.8, 22.7, 20.8, 14.0 ppm. HRMS m/z (APCI): calcd. for C₁₃H₁₇ [M+H]⁺ : 173.1325; found: 173.1324.
Gram scale synthesis:

Under argon, to a 50 mL round bottom flask equipped with a magnetic stir bar was added alkene \( \text{1q} \) (1.51 g, 5.0 mmol), NIS (2.25 g, 10.0 mmol), NaOAc (1.64 g, 20.0 mmol) and AgOAc (1.0 g, 6.0 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (25 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then Me3SiCF\(_3\) (3.0 mL, 20.0 mmol) was added dropwise to the above solution. The flask was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The E/Z ratio (94:6) was determined by \(^{19}\)F NMR of the crude mixture. Then quenched with H\(_2\)O, extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product \( \text{2q} \) as a colorless oil (1.25 g, 3.38 mmol, 68%, \( E/Z = 93:7 \), 398 mg \( \text{1q} \) was recovered, 94% brsm yield). \( R_t = 0.40 \) (hexane).
Mechanistic Studies:

NMR experiments:

Under argon, to an NMR tube charged with AgOAc (10.0 mg, 0.06 mmol), NIS (22.5 mg, 0.1 mmol), DMSO-d_6 (0.5 mL) was added, then sealed with a septum. The mixture was evacuated and refilled with argon for three times, sealed and sonicated for 5 mins, then directly run the $^1$H NMR and $^{13}$C NMR experiments on the set time.
UV-Vis absorption spectra (recorded on a Varian CARY 1E UV-vis spectrophotometer):

Note: ^NIS/AgOAc (1:0.6) in DMSO (0.0025 M) under argon atmosphere. ^NIS in DMSO (0.0025 M) under argon atmosphere.
[AgCF₃] experiment (cf. eq 1):

$$\text{AgF} + \text{TMSCF}_3 \xrightarrow{\text{CH}_3\text{CN, rt. 30 mins}} [\text{AgCF}_3]$$

The preparation of [AgCF₃] was according to literature reported procedure. To an oven-dried glass tube equipped with a stir bar was added AgF (63.5 mg, 0.5 mmol), CH₃CN (3.0 mL) and TMS CF₃ (71 mg, 0.5 mmol). After the mixture was stirred at rt for 30 min, a dark brown suspension [AgCF₃] was formed. This suspension was immediately used without further purification. The preparation should be avoided from the light due to the photosensitivity of [AgCF₃].

Labeling experiment (cf. eq 2):

Under argon, to a glass tube equipped with a magnetic stir bar was added alkene 1a (20.4 mg, 0.1 mmol), NIS (45.0 mg, 0.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and AgOAc (60.2 mg, 0.36 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (3.0 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then Me₃SiCF₃ (180 μL, 0.4 mmol) was added dropwise to the above solution. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The yield and E/Z ratio (91:9) were determined by ¹⁹F NMR of the crude mixture with benzotrifluoride as the internal standard. Then quenched with H₂O, extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product 4 as a colorless oil (56% ¹⁹F NMR yield, E/Z = 93:7). R₉ = 0.60 (hexane). Major isomer: ¹H NMR (500 MHz, CDCl₃): δ 7.32 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 7.5 Hz, 2H), 6.44-6.40 (m, 1H), 2.77 (t, J = 7.8 Hz, 2H), 2.51-2.48 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ 140.6, 139.7 (q, J_C-F = 6.6 Hz), 128.7, 128.5, 126.5, 123.1 (q, J_C-F = 269.6 Hz), 119.0 (m), 34.5, 33.3 ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ E isomer: -65.00 (s, 3F), Z isomer: -59.23 (s, 3F) ppm. HRMS m/z (EI): calcd. for C₁₁H₁₁DF₃ [M]+: 201.0870; found: 201.0872. The isotopic purity of 4 and succinimide 5 was determined by Shimadzu GCMS-QP2010 SE GC MS Spectrometer.

4 Zeng, Y.; Zhang, L.; Zhao, Y.; Ni, C.; Zhao, J.; Hu, J. J. Am. Chem. Soc. 2013, 135, 2955.
The EI-MS spectrum of succinimide 5 obtained from the labeling experiment:

The relative intensity of m/z 99 (93.5% isotopic purity) and m/z 100 are 12280 and 858 respectively.

The EI-MS spectrum of succinimide 4 obtained from the labeling experiment:

The relative intensity of m/z 200 and m/z 201 (95.3% isotopic purity) are 37049 and 1826 respectively.

Cyclohexene experiment (cf. eq3):

Under argon, to a glass tube equipped with a magnetic stir bar was added NIS (135 mg, 0.6 mmol), NaOAc (98.4 mg, 1.2 mmol) and AgOAc (60.2 mg, 0.36 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (3.0 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then cyclohexene (31 μL, 0.3 mmol) and Me$_3$SiCF$_3$ (180 μL, 0.4 mmol) was added dropwise to the above solution sequentially. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The result was analyzed by $^{19}$F NMR using benzotrifluoride as the internal standard. Then quenched with H$_2$O,
extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product.

6a: 27% $^{19}$F NMR yield, $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -70.67 (s, 3F) ppm.

6b: 21% $^{19}$F NMR yield, R$_f$ = 0.70 (hexane). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.40-4.35 (m, 1H), 2.58-2.50 (m, 1H), 2.32-2.27 (m, 1H), 2.11-1.96 (m, 2H), 1.80-1.73 (m, 1H), 1.68-1.57 (m, 2H), 1.50-1.38 (m, 2H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -69.40 (d, $J = 7.5$ Hz, 3F) ppm. The spectral data are in full accordance with the literature report.

Radical clock cyclization experiment (cf. eq 4):

Under argon, to a glass tube equipped with a magnetic stir bar was added alkene 7 (72 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), NaOAc (98.4 mg, 1.2 mmol) and AgOAc (60.2 mg, 0.36 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (3.0 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then Me$_3$SiCF$_3$ (180 $\mu$L, 0.4 mmol) was added dropwise to the above solution sequentially. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The result was analyzed by $^{19}$F NMR using benzotrifluoride as the internal standard. Then quenched with H$_2$O, extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product.

8a: (18 mg, 0.044 mmol, 15% yield, dr = 3 : 1), R$_f$ = 0.30 (hexane : EtOAc = 1 : 1). Major isomer:

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.19-4.14 (m, 4H), 3.48-3.38 (m, 2H), 2.70 (s, 4H), 2.56-2.51 (m, 1H), 2.46-2.39 (m, 1H), 2.38-2.32 (m, 2H), 2.16-2.08 (m, 1H), 1.98-1.92 (m, 1H), 1.23 (t, $J = 7.5$ Hz, 6H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 177.4, 172.2, 172.2, 127.1 (q, $J_{C-F} = 278.2$ Hz), 62.0, 61.9, 58.4, 43.9, 40.5, 38.9, 36.8, 35.4, 33.1 (q, $J_{C-F} = 28.1$ Hz), 28.2, 14.1 ppm.

$^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -65.32 (t, $J = 10.6$ Hz, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{18}$H$_{25}$F$_3$N$_6$O$_6$ [M+H]$^+$: 408.1629; found: 408.1628.

8b: (32.0 mg, 0.11 mmol, 35% yield), R$_f$ = 0.50 (hexane : EtOAc = 5 : 1). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.99 (s, 1H), 4.82 (s, 1H), 4.17 (q, $J = 6.0$ Hz, 4H), 3.02 (d, $J = 17.5$ Hz, 1H), 2.89 (d, $J = 17.0$ Hz, 1H), 2.82-2.76 (m, 1H), 2.69-2.64 (m, 1H), 2.50-2.40 (m, 1H), 2.07-1.99 (m, 1H), 1.91 (t, $J = 11.8$ Hz, 1H), 1.21 (t, $J = 7.0$ Hz, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 171.4, 150.0, 126.8 (q, $J_{C-F} = 278.2$ Hz), 107.2, 61.7, 58.4, 40.2, 39.8, 37.9 (q, $J_{C-F} = 28.1$ Hz), 36.3 (q, $J_{C-F} = 2.6$ Hz), 14.0 ppm. $^{19}$F

5 Beniazza, R.; Molton, F.; Duboc, C.; Tron, A.; McClenaghan, N. D.; Lastecoueres, D.; Vincent, J. M. Chem. Commun. 2015, 51, 9571–9574.
NMR (470 MHz, CDCl₃): δ -65.58 (t, J = 11.0 Hz, 3F) ppm. The spectral data are in full accordance with the literature report.⁶

Radical clock ring-opening experiment (cf. eq 5):

Under argon, to a glass tube equipped with a magnetic stir bar was added alkene 9 (51.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), NaOAc (98.4 mg, 1.2 mmol) and AgOAc (60.2 mg, 0.36 mmol). Then the tube was sealed with a septum, evacuated and refilled with argon for three times. Dry DMSO (3.0 mL) was added via syringe and the solution was again evacuated and refilled with argon for three times. Then Me₃SiCF₃ (180 μL, 0.4 mmol) was added dropwise to the above solution sequentially. The tube was sealed and placed under a 16 W blue LED light trip at room temperature and stirred for 24 h. The result was analyzed by ¹⁹F NMR using benzotrifluoride as the internal standard. Then quenched with H₂O, extracted with diethyl ether for three times. The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the desired product.

10a: (23.0 mg, 0.096 mmol, 32% yield), R_f = 0.40 (hexane). Major isomer: ¹H NMR (400 MHz, CDCl₃): δ 7.31 (t, J = 7.2 Hz, 2H), 7.23-7.19 (m, 3H), 6.23-6.20 (m, 1H), 6.13-6.06 (m, 1H), 5.81-5.73 (m, 1H), 5.53-5.45 (m, 1H), 2.89-2.79 (m, 2H), 2.73 (t, J = 7.8 Hz, 2H), 2.44 (t, J = 8.0 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ 141.7, 137.0, 135.1, 129.8, 128.5, 128.5, 126.1, 126.1 (q, J_C-F = 276.3 Hz), 118.5 (q, J_C-F = 3.5 Hz), 37.4 (q, J_C-F = 29.9 Hz), 35.7, 34.5 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ -67.41 (t, J = 10.7 Hz, 3F) ppm. HRMS m/z (APCI): calcd. for C₁₄H₁₅F₃[+H]⁺: 241.1199; found: 241.1198.

10b: (8.0 mg, 0.024 mmol, 8% yield), R_f = 0.30 (hexane : EtOAc = 2 : 1). Major isomer: ¹H NMR (400 MHz, CDCl₃): δ 7.26 (t, J = 7.4 Hz, 2H), 7.18-7.13 (m, 3H), 5.57-5.50 (m, 1H), 5.40-6.33 (m, 1H), 4.27-4.17 (m, 1H), 2.83-2.61 (m, 4H), 2.41-2.22 (m, 1H), 2.55-2.46 (m, 2H), 2.36 (s, 4H), 1.97-1.88 (m, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ 177.8, 144.1, 134.2, 128.5, 128.4, 126.2, 126.0 (q, J_C-F = 276.9 Hz), 121.4 (q, J_C-F = 3.5 Hz), 52.1, 37.3 (q, J_C-F = 29.6 Hz), 35.1, 33.5, 31.7, 27.8 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ -67.78 (t, J = 10.7 Hz, 3F) ppm. HRMS m/z (APCI): calcd. for C₁₃H₂₀F₃NO₂ [+H]⁺: 340.1519; found: 340.1518.

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⁶ Parsons, A. T.; Buchwald, S. L. Angew. Chem., Int. Ed. 2011, 50, 9120.
Optimization Studies:

Table S1. Optimization studies (part 1).

| entry | x     | additive (equiv) | yield (E/Z)¹ |
|-------|-------|------------------|--------------|
| 1     | 3.0   | none             | 2a 38% (94:6); 2a' 5% |
| 2b    | 3.0   | none             | 2a 0%; 2a' 0% |
| 3     | 3.0c  | none             | 2a 0%; 2a' 0% |
| 4     | 3.0d  | none             | 2a 0%; 2a' 0% |
| 5     | 3.0e  | none             | 2a 0%; 2a' 0% |
| 6     | 3.0f  | none             | 2a trace; 2a' 0% |
| 7     | 4.0   | none             | 2a 62% (92:8); 2a' 6% |
| 8g    | 4.0   | none             | 2a 0%; 2a' 0% |
| 9     | 5.0   | none             | 2a 42% (93:7); 2a' 4% |
| 10    | 3.0   | Ru(bpy)₃Cl₂·6H₂O (0.025) | 2a 53% (93:7); 2a' 5% |
| 11    | 3.0   | Ru(bpy)₃Cl₂·6H₂O (0.05) | 2a 45% (93:7); 2a' 5% |
| 12    | 3.0   | Ru(bpy)₃Cl₂·6H₂O (0.10) | 2a 15% (93:7); 2a' 1% |
| 13    | 3.0   | AgNO₃ (0.2)      | 2a 38% (93:7); 2a' 2% |
| 14    | 3.0   | AgNO₃ (0.4)      | 2a 39% (93:7); 2a' 2% |
| 15    | 3.0   | AgNO₃ (1.0)      | 2a 73% (93:7); 2a' 5% |
| 16g   | 3.0   | AgNO₃ (1.2)      | 2a 73% (93:7); 2a' 5% |
| 17    | 3.0   | AgNO₃ (2.0)      | 2a 74% (92:8); 2a' 5% |
| 18    | 3.0   | AgF (1.0)        | 2a 50% (94:6); 2a' 6% |
| 19    | 3.0   | Ag₂O (1.0)       | 2a 63% (93:7); 2a' 5% |
| 20    | 3.0   | AgOAc (1.0)      | 2a 73% (92:8); 2a' 6% |
| 21h   | 3.0   | AgOAc (1.2)      | 2a 73% (93:7); 2a' 5% |
| 22    | 3.0   | Ag₂CO₃ (1.0)     | 2a 49% (94:6); 2a' 1% |
| 23    | 3.0   | AgPF₆ (1.0)      | 2a 15% (94:6); 2a' 5% |
| 24    | 3.0   | AgOTf (1.0)      | 2a 18% (93:7); 2a' 2% |
| 25    | 3.0   | CuCl (1.0)       | 2a trace; 2a' 2% |
| 26    | 3.0   | FeCl₃ (1.0)      | 2a 0%; 2a' 0% |
| 27    | 3.0   | FeCl₂ (1.0)      | 2a 0%; 2a' 0% |
| 28i   | 3.0   | AgNO₃ (1.0)      | 2a 66% (92:8); 2a' 6% |
| 29j   | 3.0   | AgNO₃ (1.0)      | 2a 64% (91:9); 2a' 5% |
| 30k   | 3.0   | AgNO₃ (1.0)      | 2a 26% (92:8); 2a' 5% |

¹Yield and E/Z ratio were determined by ¹⁹F NMR analysis of the crude mixture using benzotrifluoride as the internal standard. ²Open to air. ³Used N-bromosuccinimide (NBS) instead. ⁴Used N-chlorosuccinimide (NCS) instead. ⁵Used iodine (I₂) instead. ⁶Used iodo-monooacetate (IOAc) instead.
\(^a\)Added TEMPO (2.0 equiv). \(^b\)Improved reproducibility. \(^c\)TMSCF\(_3\)/NaOAc (5.0/5.0 equiv). \(^d\)TMSCF\(_3\)/NaOAc (3.0/3.0 equiv). \(^e\)TMSCF\(_3\)/NaOAc (2.0/2.0 equiv).

Table S2. Optimization studies (part 2).

| Entry | x    | Initiator | Solvent | Yield (E/Z)\(^a\) |
|-------|------|-----------|---------|------------------|
| 1     | 3.0  | NaOAc     | DMF     | 2a 73% (93:7); 2a' 5% |
| 2     | 3.0  | NaOAc     | DMSO    | 2a 76% (93:7); 2a' 0% |
| 3     | 3.0  | NaOAc     | MeCN    | 2a 33% (96:4); 2a' 0% |
| 4     | 3.0  | NaOAc     | 1,4-dioxane | 2a 0%; 2a' 0% |
| 5     | 2.0  | NaOAc     | DMSO    | 2a 76% (93:7); 2a' 0% |
| 6     | 2.0  | Na\(_2\)CO\(_3\) | DMSO    | 2a 69% (93:7); 2a' 0% |
| 7     | 2.0  | NaHCO\(_3\) | DMSO    | 2a 56% (91:9); 2a' 0% |
| 8     | 2.0  | sodium phenoxide | DMSO    | 2a 0%; 2a' 0% |
| 9     | 2.0  | sodium benzoate | DMSO    | 2a 74% (93:7); 2a' 0% |
| 10    | 2.0  | NaH\(_2\)PO\(_4\) | DMSO    | 2a 44% (94:6); 2a' 0% |
| 11    | 2.0  | NaHPO\(_4\) | DMSO    | 2a trace; 2a' 0% |
| 12    | 2.0  | NaF       | DMSO    | 2a trace; 2a' 0% |
| 13    | 2.0  | NH\(_4\)OAc | DMSO    | 2a trace; 2a' 0% |
| 14    | 2.0  | Bu\(_4\)NOAc | DMSO    | 2a 49% (92:8); 2a' 0% |
| 15    | 2.0  | KOAc      | DMSO    | 2a 75% (92:8); 2a' 0% |
| 16    | 2.0  | LiOAc     | DMSO    | 2a 75% (92:8); 2a' 0% |
| 17    | 2.0  | K\(_2\)CO\(_3\) | DMSO    | 2a trace; 2a' 0% |
| 18    | 2.0  | Et\(_3\)N | DMSO    | 2a trace; 2a' 0% |
| 19\(^b\) | 2.0 | NaOAc     | DMSO    | 2a 61% (95:5); 2a' 0% |
| 20\(^c\) | 2.0 | NaOAc     | DMSO    | 2a 74% (93:7); 2a' 0% |
| 21\(^d\) | 2.0 | NaOAc     | DMSO    | 2a 68% (94:6); 2a' 0% |
| 22\(^e\) | 2.0 | NaOAc     | DMSO    | 2a 72% (92:8); 2a' 0% |

\(^a\)Yield and E/Z ratio were determined by \(^{19}\)F NMR analysis of the crude mixture using benzotrifluoride as the internal standard. \(^b\)Used 4 W blue LED instead. \(^c\)Used 24 W white CFL bulb instead. \(^d\)0.2 M in DMSO. \(^e\)0.05 M in DMSO.
Table S3. Control experiments.

| entry | change from the "standard conditions" | yield (E/Z)\(^a\) |
|-------|--------------------------------------|-------------------|
| 1     | none                                 | 2a 76\% (93:7); 2a' 0\% |
| 2\(^b\)| no NIS                               | 2a 0\%; 2a' 0\% |
| 3     | 1.0 equiv NIS                         | 2a 37\% (94:6); 2a' trace |
| 4     | no AgOAc                              | 2a 7\%; 2a' 3\% |
| 5     | no NaOAc                              | 2a 30\% (94:6); 2a' 0\% |
| 6     | no NaOAc, 5.2 equiv AgOAc             | 2a 15\% (93:7); 2a' 4\% |
| 7     | no irradiation                        | 2a 8\%; 2a' 0\% |
| 8     | no irradiation, 80 °C                 | 2a 13\% (92:8); 2a' 0\% |

\(^a\)Yield and E/Z ratio were determined by \(^{19}\)F NMR analysis of the crude mixture using benzotrifluoride as the internal standard. \(^b\)Detected the formation of AgCF\(_3\) mainly.
Characterization Data:

2a: 7,7,7-trifluorohept-5-en-1-yl benzoate. Prepared according to the general procedure. Reaction was run using 1a (61.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (94:6) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 76.1 mg, 84 %, E/Z = 92:8), R$_f$= 0.60 (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ 7.98 (d, $J$ = 8.8 Hz, 2H), 6.90 (d, $J$ = 8.8 Hz, 2H), 6.39-6.35 (m, 1H), 5.67-5.58 (m, 1H), 4.29 (t, $J$ = 6.4 Hz, 2H), 2.28-2.15 (m, 2H), 1.80-1.73 (m, 2H), 1.62-1.55 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): δ 166.7, 140.1 (q, $J_{C,F}$ = 6.5 Hz), 133.1, 130.4, 129.6, 128.5, 123.1 (q, $J_{C,F}$ = 270.0 Hz), 119.0 (q, $J_{C,F}$ = 33.4 Hz), 64.6, 31.1, 28.2, 24.6 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ E isomer: -64.86 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. The spectral data are in full accordance with the literature report.\(^7\)

2b: 7,7,7-trifluorohept-5-en-1-yl 4-methoxybenzoate. Prepared according to the general procedure. Reaction was run using 1b (70.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (94:6) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.26 mmol, 77.0 mg, 85 %, E/Z = 92:8), R$_f$= 0.40 (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ 7.98 (d, $J$ = 8.8 Hz, 2H), 6.90 (d, $J$ = 8.8 Hz, 2H), 6.39-6.35 (m, 1H), 5.67-5.58 (m, 1H), 4.29 (t, $J$ = 6.4 Hz, 2H), 3.83 (s, 3H), 2.28-2.15 (m, 2H), 1.80-1.73 (m, 2H), 1.62-1.55 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): δ 166.4, 163.4, 140.2 (q, $J_{C,F}$ = 6.6 Hz), 131.6, 123.1 (q, $J_{C,F}$ = 270.0 Hz), 122.8, 118.9 (q, $J_{C,F}$ = 33.4 Hz), 113.7, 64.2, 55.4, 31.1, 28.3, 24.6 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ E isomer: -64.84 (s, 3F), Z isomer: -58.93 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{15}$H$_{13}$F$_3$O$_3$ [M+H]$^+$ : 303.1203; found: 303.1202.

2c: 7,7,7-trifluorohept-5-en-1-yl 2-methoxybenzoate. Prepared according to the general procedure. Reaction was run using 1c (70.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 76.1 mg, 84 %, E/Z = 92:8), R$_f$= 0.40 (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ 7.76 (d, $J$ = 8.0 Hz, 2H), 7.44 (d, $J$ = 8.0 Hz, 2H), 6.97-6.94 (m, 2H), 6.40-

\(^7\) Jacquet, J.; Blanchard, S.; Derat, E.; Desage-El Murr, M.; Fensterbank, L. Chem. Sci. 2016, 7, 2030.
6.33 (m, 1H), 5.66-5.59 (m, 1H), 4.29 (t, J = 6.4 Hz, 2H), 3.86 (s, 3H), 2.28-2.15 (m, 2H), 1.79-1.72 (m, 2H), 1.62-1.55 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 166.3, 159.1, 140.2 (q, $J_{C,F} = 6.5$ Hz), 133.5, 131.5, 123.1 (q, $J_{C,F} = 270.0$ Hz), 120.2, 120.1, 118.7 (q, $J_{C,F} = 33.3$ Hz), 112.0, 64.3, 55.8, 30.9, 28.1, 24.5 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\Delta$ E isomer: -64.86 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{15}$H$_{18}$F$_3$O$_3$ [M+H]$^+$ : 303.1203; found: 303.1202.

2d: 7,7,7-trifluorohept-5-en-1-yl 3-methoxybenzoate. Prepared according to the general procedure. Reaction was run using 1d (70.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 $\mu$L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.2 mmol, 60.0 mg, 66 %, E/Z = 91:9), R$_f$ = 0.40 (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.63 (d, $J = 7.6$ Hz, 2H), 7.56 (s, 1H), 7.34 (t, $J = 8.0$ Hz, 1H), 7.34 (dd, $J = 8.4$ Hz, $J = 2.0$ Hz, 1H), 6.42-6.34 (m, 1H), 5.68-5.61 (m, 1H), 4.33 (t, $J = 6.4$ Hz, 2H), 3.84 (s, 3H), 2.26-2.20 (m, 2H), 1.83-1.76 (m, 2H), 1.64-1.57 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 166.6, 159.7, 140.1 (q, $J_{C,F} = 6.5$ Hz), 131.7, 129.5, 123.1 (q, $J_{C,F} = 270.1$ Hz), 122.0, 119.4, 119.0 (q, $J_{C,F} = 33.3$ Hz), 114.3, 64.7, 55.5, 31.1, 28.2, 24.6 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\Delta$ E isomer: -64.85 (s, 3F), Z isomer: -58.93 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{15}$H$_{18}$F$_3$O$_3$ [M+H]$^+$ : 303.1203; found: 303.1203.

2e: 7,7,7-trifluorohept-5-en-1-yl 4-methylbenzoate. Prepared according to the general procedure. Reaction was run using 1e (65.4 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 $\mu$L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (96:4) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 70.4 mg, 82 %, E/Z = 93:7), R$_f$ = 0.60 (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.32-6.25 (m, 1H), 5.86-5.50 (m, 1H), 4.22 (t, $J = 6.4$ Hz, 2H), 2.30 (s, 3H), 2.12-2.10 (m, 2H), 1.73-1.66 (m, 2H), 1.54-1.47 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 166.7, 143.7, 140.2 (q, $J_{C,F} = 6.6$ Hz), 129.6, 129.2, 127.6, 123.1 (q, $J_{C,F} = 270.0$ Hz), 118.9 (q, $J_{C,F} = 33.4$ Hz), 64.3, 31.1, 28.2, 24.6, 21.7 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\Delta$ E isomer: -64.85 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{15}$H$_{18}$F$_3$O$_3$ [M+H]$^+$ : 287.1253; found: 287.1253.

2f: 7,7,7-trifluorohept-5-en-1-yl 4-(trifluoromethyl)benzoate. Prepared according to the general procedure. Reaction was run using 1f (81.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 $\mu$L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z
ratio (96:4) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.20 mmol, 69.4 mg, 68 %, $E/Z = 93:7$), $R_f = 0.60$ (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCI$_3$): $\delta$ 8.14 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 6.42-6.34 (m, 1H), 5.69-5.60 (m, 1H), 4.37 (t, $J = 6.4$ Hz, 2H), 2.27-2.21 (m, 2H), 1.86-1.78 (m, 2H), 1.65-1.58 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCI$_3$): $\delta$ 165.5, 140.0 (q, $J_{C:F} = 6.6$ Hz), 134.6 (q, $J_{C:F} = 32.7$ Hz), 133.6, 130.1, 125.5 (q, $J_{C:F} = 3.8$ Hz), 123.8 (q, $J_{C:F} = 273.7$ Hz), 123.1 (q, $J_{C:F} = 270.1$ Hz), 119.1 (q, $J_{C:F} = 33.4$ Hz), 65.2, 31.1, 28.2, 24.6 ppm. $^{19}$F NMR (376 MHz, CDCI$_3$): $\delta$ E isomer: -63.98 (s, 3F), -64.86 (s, 3F), Z isomer: -63.96 (s, 3F), -58.91 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{12}$H$_7$F$_3$O$_2$ [M+H]$^+$: 291.0971; found: 291.0970.

2g: 7,7,7-trifluorohept-5-en-1-yl 4-cyanobenzoate. Prepared according to the general procedure. Reaction was run using 1g (68.7 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The $E/Z$ ratio (96:4) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.17 mmol, 51.7 mg, 58 %, $E/Z = 93:7$), $R_f = 0.20$ (hexane : EtOAc = 8 : 1). Major isomer: $^1$H NMR (400 MHz, CDCI$_3$): $\delta$ 8.11 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 6.40-6.33 (m, 1H), 5.67-5.60 (m, 1H), 4.35 (t, $J = 6.4$ Hz, 2H), 2.23-2.20 (m, 2H), 1.84-1.77 (m, 2H), 1.63-1.56 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCI$_3$): $\delta$ 165.0, 139.9 (q, $J_{C:F} = 6.5$ Hz), 134.1, 132.3, 130.1, 123.0 (q, $J_{C:F} = 270.1$ Hz), 119.0 (q, $J_{C:F} = 33.4$ Hz), 118.0, 116.4, 65.4, 31.0, 28.1, 24.5 ppm. $^{19}$F NMR (376 MHz, CDCI$_3$): $\delta$ E isomer: -64.85 (s, 3F), Z isomer: -58.91 (s, 3F) ppm. The spectral data are in full accordance with the literature report.8

2h: 7,7,7-trifluorohept-5-en-1-yl 4-fluorobenzoate. Prepared according to the general procedure. Reaction was run using 1h (66.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The $E/Z$ ratio (95:5) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 71.3 mg, 82 %, $E/Z = 92:8$), $R_f = 0.60$ (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCI$_3$): $\delta$ 8.06-8.02 (m, 2H), 7.10 (t, $J = 8.6$ Hz, 2H), 6.40-6.35 (m, 1H), 5.68-5.59 (m, 1H), 4.32 (t, $J = 6.4$ Hz, 2H), 2.25-2.21 (m, 2H), 1.82-1.75 (m, 2H), 1.63-1.56 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCI$_3$): $\delta$ 165.8 (d, $J_{C:F} = 254.7$ Hz), 165.7, 140.1 (q, $J_{C:F} = 6.6$ Hz), 132.2 (d, $J_{C:F} = 9.3$ Hz), 126.6, 123.1 (q, $J_{C:F} = 270.1$ Hz), 119.0 (q, $J_{C:F} = 33.3$ Hz), 115.6 (d, $J_{C:F} = 22.1$ Hz), 64.7, 31.1, 28.2, 24.6 ppm. $^{19}$F NMR (376 MHz, CDCI$_3$): $\delta$ E isomer: -106.65 (s, 1F), -64.85 (s, 3F), Z isomer: -106.74 (s, 1F), -58.93 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{12}$H$_7$F$_3$O$_2$ [M+H]$^+$: 291.1003; found: 291.1007.

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8 Ren, Y.; Zheng, X.; Zhang, X. Synlett 2018, 29, 1028.
2i: 7,7,7-trifluorohept-5-en-1-yl 4-chlorobenzoate. Prepared according to the general procedure. Reaction was run using 1i (71.4 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (92:8) was determined by $^1$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.24 mmol, 73.4 mg, 80 %, E/Z = 92:8), R$_f$ = 0.60 (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ 7.96 (d, $J$ = 8.8 Hz, 2H), 7.40 (d, $J$ = 8.8 Hz, 2H), 6.42-6.34 (m, 1H), 5.68-5.59 (m, 1H), 4.32 (t, $J$ = 6.4 Hz, 2H), 2.26-2.20 (m, 2H), 1.83-1.74 (m, 2H), 1.63-1.56 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): δ 165.8, 140.0 (q, $J_{C-F}$ = 6.6 Hz), 139.5, 131.0, 128.8, 128.8, 123.1 (q, $J_{C-F}$ = 270.1 Hz), 119.0 (q, $J_{C-F}$ = 33.4 Hz), 64.8, 31.1, 28.2, 24.6 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ E isomer: -64.85 (s, 3F), Z isomer: -58.92 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{14}$H$_{12}$ClF$_3$O$_2$ [M+H]$^+$ : 307.0707; found: 307.0707.

2j: 7,7,7-trifluorohept-5-en-1-yl 4-bromobenzoate. Prepared according to the general procedure. Reaction was run using 1j (84.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (95:5) was determined by $^1$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.26 mmol, 90.3 mg, 86 %, E/Z = 92:8), R$_f$ = 0.60 (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ 7.88 (d, $J$ = 8.4 Hz, 2H), 7.55 (d, $J$ = 8.4 Hz, 2H), 6.41-6.33 (m, 1H), 5.67-5.59 (m, 1H), 4.31 (t, $J$ = 6.4 Hz, 2H), 2.23-2.21 (m, 2H), 1.82-1.75 (m, 2H), 1.62-1.55 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): δ 165.9, 140.0 (q, $J_{C-F}$ = 6.6 Hz), 131.8, 131.1, 129.3, 128.1, 123.1 (q, $J_{C-F}$ = 270.2 Hz), 119.0 (q, $J_{C-F}$ = 33.4 Hz), 64.8, 31.1, 28.2, 24.6 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ E isomer: -64.86 (s, 3F), Z isomer: -58.93 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{14}$H$_{12}$BrF$_3$O$_2$ [M+H]$^+$ : 351.0209; found: 351.0209.

2k: 7,7,7-trifluorohept-5-en-1-yl 4-iodobenzoate. Prepared according to the general procedure. Reaction was run using 1k (99.0 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by $^1$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 99.1 mg, 83 %, E/Z = 92:8), R$_f$ = 0.60 (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ 7.79 (d, $J$ = 8.8 Hz, 2H), 7.72 (d, $J$ = 8.8 Hz, 2H), 6.41-6.33 (m, 1H), 5.67-5.59 (m, 1H), 4.31 (t, $J$ = 6.4 Hz, 2H), 2.24-2.19 (m, 2H), 1.82-1.75 (m, 2H), 1.62-1.55 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): δ 166.1, 140.0 (q, $J_{C-F}$ = 6.5 Hz), 137.8, 131.1, 129.8, 123.1 (q, $J_{C-F}$ = 270.1 Hz), 119.0 (q, $J_{C-F}$ = 33.3 Hz), 100.8, 64.8, 31.1, 28.2, 24.6 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ
2l: 7,7,7-trifluorohept-5-en-1-yl furan-2-carboxylate. Prepared according to the general procedure. Reaction was run using $\text{I}1$ (58.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 $\mu$L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by $^1$H NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.13 mmol, 33.0 mg, 42 %, $E/Z = 92:8$), $R_f$ = 0.70 (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56 (s, 1H), 7.16 (d, $J = 3.2$ Hz, 1H), 7.72 (dd, $J = 2.0$ Hz, 1H), 6.40-6.32 (m, 1H), 5.67-5.58 (m, 1H), 4.30 (t, $J = 6.4$ Hz, 2H), 2.24-2.18 (m, 2H), 1.80-1.73 (m, 2H), 1.61-1.53 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 158.8, 146.4, 144.8, 140.1 (q, $J_{C,F} = 6.6$ Hz), 123.1 (q, $J_{C,F} = 270.1$ Hz), 119.0 (q, $J_{C,F} = 33.4$ Hz), 118.0, 111.9, 64.5, 31.0, 28.2, 24.5 ppm. $^1$F NMR (376 MHz, CDCl$_3$): $\delta$ E isomer: -64.86 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. The spectral data are in full accordance with the literature report.

2m: 7,7,7-trifluorohept-5-en-1-yl picolinate. Prepared according to the general procedure. Reaction was run using $\text{I}1$m (61.5 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 $\mu$L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by $^1$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.14 mmol, 37.7 mg, 46 %, $E/Z = 93:7$), $R_f$ = 0.30 (hexane : EtOAc = 2 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.72 (d, $J = 4.0$ Hz, 1H), 8.08 (d, $J = 7.6$ Hz, 1H), 7.81 (t, $J = 7.8$ Hz, 1H), 7.44 (t, $J = 6.2$ Hz, 1H), 6.37-6.29 (m, 1H), 5.64-5.57 (m, 1H), 4.39 (t, $J = 6.6$ Hz, 2H), 2.18-2.15 (m, 2H), 1.85-1.78 (m, 2H), 1.60-1.53 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 165.3, 149.9, 148.1, 140.0 (q, $J_{C,F} = 6.5$ Hz), 137.1, 127.0, 125.2, 123.0 (q, $J_{C,F} = 270.2$ Hz), 118.9 (q, $J_{C,F} = 33.4$ Hz), 65.5, 31.0, 28.1, 24.4 ppm. $^1$F NMR (376 MHz, CDCl$_3$): $\delta$ E isomer: -64.84 (s, 3F), Z isomer: -58.92 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{15}$H$_{15}$F$_{3}$O$_2$ [M+H]$^+$: 274.1049; found: 274.1047.

2n: 7,7,7-trifluorohept-5-en-1-yl thiophene-2-carboxylate. Prepared according to the general procedure. Reaction was run using $\text{I}1$n (63.0 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 $\mu$L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by $^1$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.25 mmol, 68.4 mg, 82 %, $E/Z = 91:9$), $R_f$ = 0.60 (hexane : EtOAc = 5 : 1). E

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9 Parsons, A. T.; Senechal, T. D.; Buchwald, S. L. Angew. Chem., Int. Ed. 2012, 51, 2947.
isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (dd, $J = 3.6$ Hz, $J = 1.2$ Hz, 1H), 7.56 (dd, $J = 4.8$ Hz, $J = 1.2$ Hz, 1H), 7.11 (t, $J = 4.4$ Hz, 1H), 6.42-6.35 (m, 1H), 5.69-5.60 (m, 1H), 4.31 (t, $J = 6.4$ Hz, 2H), 2.24-2.21 (m, 2H), 1.82-1.75 (m, 2H), 1.64-1.56 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 162.3, 140.1 (q, $J_{C,F} = 6.6$ Hz), 133.9, 133.5, 132.4, 127.8, 123.1 (q, $J_{C,F} = 270.2$ Hz), 118.9 (q, $J_{C,F} = 33.3$ Hz), 64.7, 31.0, 28.2, 24.5 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ E isomer: -64.85 (s, 3F), Z isomer: -58.93 (s, 3F) ppm. HRMS m/z (APCI): calcld. for C$_{13}$H$_{12}$F$_3$S [M+H]$^+$: 279.0661; found: 279.0664.

2o: 1-(4-((7,7,7-trifluorohept-5-en-1-yl)oxy)phenyl)ethan-1-one. Prepared according to the general procedure. Reaction was run using 1o (65.4 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (92:8) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.20 mmol, 57.5 mg, 67 %, E/Z = 93:7, $R_f = 0.30$ (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J = 8.5$ Hz, 2H), 6.91 (d, $J = 8.5$ Hz, 2H), 6.41-6.39 (m, 1H), 5.67-5.63 (m, 1H), 4.03 (t, $J = 6.0$ Hz, 2H), 2.55 (s, 3H), 2.26-2.23 (m, 2H), 1.85-1.81 (m, 2H), 1.68-1.64 (m, 2H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 196.9, 163.0, 140.2 (q, $J_{C,F} = 6.4$ Hz), 130.7, 130.4, 123.1 (q, $J_{C,F} = 269.6$ Hz), 119.0 (q, $J_{C,F} = 33.3$ Hz), 114.2, 67.8, 31.2, 28.6, 26.5, 24.7 ppm. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ E isomer: -64.84 (m, 3F), Z isomer: -58.91 (d, $J = 8.3$, 3F) ppm. HRMS m/z (APCI): calcld. for C$_{15}$H$_{10}$F$_3$O$_2$ [M+H]$^+$: 287.1253; found: 287.1254.

2p: 4-((7,7,7-trifluorohept-5-en-1-yl)oxy)benzaldehyde. Prepared according to the general procedure. Reaction was run using 1p (61.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.18 mmol, 49.0 mg, 60 %, E/Z = 92:8), $R_f = 0.30$ (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.86 (s, 1H), 7.81 (d, $J = 8.8$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 6.42-6.35 (m, 1H), 5.68-5.60 (m, 1H), 4.04 (t, $J = 6.2$ Hz, 2H), 2.30-2.23 (m, 2H), 1.87-1.80 (m, 2H), 1.68-1.60 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 190.9, 164.1, 140.1 (q, $J_{C,F} = 6.6$ Hz), 132.1, 130.0, 123.1 (q, $J_{C,F} = 270.1$ Hz), 118.9 (q, $J_{C,F} = 33.3$ Hz), 114.8, 67.9, 31.1, 28.5, 24.6 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ E isomer: -64.84 (s, 3F), Z isomer: -58.90 (s, 3F) ppm. HRMS m/z (APCI): calcld. for C$_{14}$H$_{10}$F$_3$O$_2$ [M+H]$^+$: 273.1097; found: 273.1097.

2q: 1-iodo-4-((7,7,7-trifluorohept-5-en-1-yl)oxy)benzene. Prepared according to the general procedure. Reaction was run using 1q (90.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (94:6) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a
colorless oil (0.26 mmol, 96.6 mg, 87 %, E/Z = 92:8), Rf = 0.60 (hexane : EtOAc = 5 : 1). E isomer: 1H NMR (400 MHz, CDCl3): δ 7.55 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 6.45-6.37 (m, 1H), 5.70-5.61 (m, 1H), 3.93 (t, J = 6.2 Hz, 2H), 2.26-2.21 (m, 2H), 1.84-1.77 (m, 2H), 1.67-1.58 (m, 2H) ppm. 13C NMR (101 MHz, CDCl3): δ 158.9, 140.3 (q, JCF = 6.6 Hz), 138.3, 123.1 (q, JCF = 270.1 Hz), 118.9 (q, JCF = 33.3 Hz), 117.0, 82.7, 67.6, 31.2, 28.6, 24.6 ppm. 19F NMR (376 MHz, CDCl3): δ E isomer: -64.83 (s, 3F), Z isomer: -58.92 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C13H14F3O4 [M]+: 370.0036; found: 370.0034.

2r: 4,4,5,5-tetramethyl-2-(4-((7,7,7-trifluorohept-5-en-1-yl)oxy)phenyl)-1,3,2-dioxaborolane. Prepared according to the general procedure. Reaction was run using 1r (90.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me3SiCF3 (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (96:4) was determined by 19F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by preparative TLC (hexane/EtOAc) and obtained a colorless oil (0.17 mmol, 61.05 mg, 55 %, E/Z = 93:7), Rf = 0.30 (hexane : EtOAc = 10 : 1). E isomer: 1H NMR (400 MHz, CDCl3): δ 7.75 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.44-6.36 (m, 1H), 5.68-5.60 (m, 1H), 4.00 (t, J = 6.2 Hz, 2H), 2.26-2.21 (m, 2H), 1.85-1.78 (m, 2H), 1.68-1.61 (m, 2H), 1.34 (s, 12H) ppm. 13C NMR (101 MHz, CDCl3): δ 161.6, 140.3 (q, JCF = 6.5 Hz), 136.7, 123.2 (q, JCF = 270.1 Hz), 118.9 (q, JCF = 33.4 Hz), 113.9, 83.7, 67.3, 31.2, 28.7, 25.0, 24.7 ppm. 19F NMR (376 MHz, CDCl3): δ E isomer: -64.84 (s, 3F), Z isomer: -58.93 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C19H21F5O3 [M]+: 371.0203; found: 371.0203.

2s: 2-(7,7,7-trifluorohept-5-en-1-yl)isoindoline-1,3-dione. Prepared according to the general procedure. Reaction was run using 1q (68.7 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me3SiCF3 (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by 19F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.13 mmol, 38.4 mg, 43 %, E/Z = 93:7), Rf = 0.40 (hexane : EtOAc = 5 : 1). E isomer: 1H NMR (500 MHz, CDCl3): δ 7.83-7.82 (m, 2H), 7.71-7.69 (m, 2H), 6.36-6.31 (m, 1H), 5.62-5.58 (m, 1H), 3.69 (t, J = 7.0 Hz, 2H), 2.20-2.18 (m, 2H), 1.73-1.67 (m, 2H), 1.51-1.47 (m, 2H) ppm. 13C NMR (126 MHz, CDCl3): δ 168.5, 140.0 (q, JCF = 6.6 Hz), 134.1, 132.2, 123.3 123.2 (q, JCF = 269.8 Hz), 118.9 (q, JCF = 33.3 Hz), 37.6, 31.0, 28.1, 25.3 ppm. 19F NMR (470 MHz, CDCl3): δ E isomer: -64.84 (m, 3F), Z isomer: -58.91 (d, J = 8.5, 3F) ppm. The spectral data are in full accordance with the literature report.7

2t: 3-oxo-2-(7,7,7-trifluorohept-5-en-1-yl)isoindolin-1-yl acetate. Prepared according to the general procedure. Reaction was run using 1t (81.9 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me3SiCF3 (180 μL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (94:6) was determined by 19F NMR of the crude mixture with benzotrifluoride as the internal

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7. Literature reference number.
standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.22 mmol, 75.7 mg, 74 %, \( E/Z = 92:8 \), \( R_t = 0.30 \) (hexane : EtOAc = 5 : 1). E isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.79-7.77 (m, 1H), 7.56-7.49 (m, 3H), 6.98 (s, 1H), 6.36-6.29 (m, 1H), 5.64-5.55 (m, 1H), 3.76-3.68 (m, 1H), 3.33-3.26 (m, 1H), 2.20-2.17 (m, 2H), 2.14 (s, 3H), 1.71-1.60 (m, 2H), 1.53-1.44 (m, 2H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 171.2, 168.0, 140.9, 140.1 (q, \( J_C\_F = 6.6 \) Hz), 132.5, 132.0, 130.4, 123.9, 123.6, 123.1 (q, \( J_{C\_F} = 270.1 \) Hz), 118.9 (q, \( J_{C\_F} = 33.3 \) Hz), 81.2, 40.0, 31.0, 27.8, 25.2, 21.1 ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) E isomer: -64.82 (s, 3F), Z isomer: -58.87 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C\(_{17}\)H\(_{19}\)F\(_3\)N\(_3\)O\(_3\) [M+H\(^+\)]: 342.1312; found: 342.1317.

2u: ((7,7,7-trifluorohept-5-en-1-yl)oxy)methylbenzene. Prepared according to the general procedure. Reaction was run using 1u (57.0 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me\(_3\)SiCF\(_3\) (180 \( \mu \)L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (94:6) was determined by \(^{19}\)F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.19 mmol, 49.5 mg, 64 %, \( E/Z = 92:8 \), \( R_t = 0.60 \) (hexane : EtOAc = 8 : 1). E isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.39-7.26 (m, 5H), 6.43-6.35 (m, 1H), 5.67-5.58 (m, 1H), 4.52 (s, 2H), 3.50 (t, \( J = 6.2 \) Hz, 2H), 2.22-2.15 (m, 2H), 1.70-1.63 (m, 2H), 1.60-1.54 (m, 2H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 140.6 (q, \( J_{C\_F} = 6.6 \) Hz), 138.6, 128.5, 127.8, 127.7, 123.2 (q, \( J_{C\_F} = 270.0 \) Hz), 118.7 (q, \( J_{C\_F} = 33.2 \) Hz), 73.1, 70.0, 31.3, 29.3, 24.8 ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) E isomer: -64.83 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. The spectral data are in full accordance with the literature report.\(^7\)

2v: tert-butylidimethyl((7,7,7-trifluorohept-5-en-1-yl)oxy)silane. Prepared according to the general procedure. Reaction was run using 1v (64.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me\(_3\)SiCF\(_3\) (180 \( \mu \)L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (92:8) was determined by \(^{19}\)F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.19 mmol, 52.3 mg, 62 %, \( E/Z = 93.7 \), \( R_t = 0.30 \) (hexane). E isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 6.41-6.34 (m, 1H), 5.65-5.57 (m, 1H), 3.62 (t, \( J = 6.0 \) Hz, 2H), 2.19-2.17 (m, 2H), 1.54-1.49 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 140.7 (q, \( J_{C\_F} = 6.6 \) Hz), 123.3 (q, \( J_{C\_F} = 270.0 \) Hz), 118.6 (q, \( J_{C\_F} = 33.3 \) Hz), 62.9, 32.2, 31.4, 26.1, 24.5, 18.5, -5.2 ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) E isomer: -64.85 (s, 3F), Z isomer: -58.98 (s, 3F) ppm. The spectral data are in full accordance with the literature report.\(^7\)

2w: 1-(7,7,7-trifluorohept-5-en-1-yl)pyrrolidine-2,5-dione. Prepared according to the general procedure. Reaction was run using 1w (76.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me\(_3\)SiCF\(_3\) (180 \( \mu \)L, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (92:8) was determined by \(^{19}\)F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and

10 Cheng, Y.; Yu, S. Org. Lett. 2016, 18, 2962.
obtained a colorless oil (0.18 mmol, 44.8 mg, 60 %, $E/Z = 93:7$), $R_f = 0.30$ (hexane : EtOAc = 2 : 1). $E$ isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.35-6.27 (m, 1H), 5.63-5.54 (m, 1H), 3.48 (t, $J = 7.2$ Hz, 2H), 2.68 (s, 4H), 2.17-2.14 (m, 2H), 1.60-1.53 (m, 2H), 1.45-1.36 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 177.4, 140.0 (q, $J_{C,F} = 6.6$ Hz), 123.0 (q, $J_{C,F} = 270.2$ Hz), 118.9 (q, $J_{C,F} = 33.4$ Hz), 38.4, 30.9, 28.2, 27.2, 25.2 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ E isomer: -64.84 (s, 3F), Z isomer: -58.90 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{19}$H$_{15}$F$_3$NO$_2$ [M+H]$^+$: 250.1049; found: 250.1046.

$2w$: (E)-7,7,7-trifluorohept-5-en-1-yl 4-methylbenzenesulfonate. Prepared according to the general procedure. Reaction was run using $1w$ (76.2 mg, 0.3 mmol), NIS (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The $E/Z$ ratio (91:9) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.045 mmol, 14.5 mg, 15 %, $E/Z = 90:10$), $R_f = 0.40$ (hexane : EtOAc = 8 : 1). $E$ isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 6.32-6.24 (m, 1H), 5.60-5.53 (m, 1H), 4.03 (t, $J = 6.2$ Hz, 2H), 2.44 (s, 3H), 2.13-2.08 (m, 2H), 1.69-1.62 (m, 2H), 1.51-1.43 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 145.0, 139.7 (q, $J_{C,F} = 6.6$ Hz), 133.1, 130.0, 128.0, 123.0 (q, $J_{C,F} = 270.1$ Hz), 119.1 (q, $J_{C,F} = 33.4$ Hz), 70.1, 30.7, 28.3, 24.0, 21.7 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ E isomer: -64.90 (s, 3F), Z isomer: -58.95 (s, 3F) ppm. The spectral data are in full accordance with the literature report.11

$2x$: 7,7,7-trifluorohept-5-en-1-yl 6-(2,5-dioxopyrrolidin-1-yl)hexanoate. Prepared according to the general procedure. Reaction was run using $1x$ (82.8 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The $E/Z$ ratio (91:9) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.23 mmol, 85.0 mg, 78 %, $E/Z = 92:8$), $R_f = 0.30$ (hexane : EtOAc = 2 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.63-6.26 (m, 1H), 5.59-5.53 (m, 1H), 3.99 (t, $J = 6.6$ Hz, 2H), 3.41 (t, $J = 7.4$ Hz, 2H), 2.62 (s, 4H), 2.22 (t, $J = 7.4$ Hz, 2H), 2.15-2.12 (m, 2H), 1.60-1.42 (m, 8H), 1.28-1.22 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 177.3, 173.4, 140.1 (q, $J_{C,F} = 6.5$ Hz), 123.0 (q, $J_{C,F} = 270.1$ Hz), 118.7 (q, $J_{C,F} = 33.4$ Hz), 63.8, 38.5, 33.9, 30.9, 28.1, 28.1, 28.0, 27.3, 26.3, 24.4 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ E isomer: -64.85 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{19}$H$_{15}$F$_3$NO$_3$ [M+H]$^+$: 364.1730; found: 364.1735.

$2y$: 5,5,5-trifluoropent-3-en-1-yl benzoate. Prepared according to the general procedure. Reaction was run using $1y$ (52.8 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me$_3$SiCF$_3$ (180 µL, 1.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The $E/Z$ ratio (90:10) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product

11 Xu, J.; Fu, Y.; Luo, D.-F.; Jiang, Y.-Y.; Xiao, B.; Liu, Z.-J.; Gong, T.-J.; Liu, L. J. Am. Chem. Soc. 2011, 133, 15300.
was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.19 mmol, 46.8 mg, 64 %, E/Z = 90:10), Rf = 0.40 (hexane : EtOAc = 8 : 1). E isomer: 1H NMR (400 MHz, CDCl3): δ 8.02 (d, J = 8.4 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 6.50-6.42 (m, 1H), 5.83-5.74 (m, 1H), 4.43 (t, J = 6.4 Hz, 2H), 2.67-2.61 (m, 2H) ppm. 13C NMR (101 MHz, CDCl3): δ 166.5, 136.3 (q, JCF = 6.7 Hz), 133.3, 129.7, 128.6, 128.5, 125.5 (q, JCF = 270.3 Hz), 121.1 (q, JCF = 33.7 Hz), 62.7, 31.1 ppm. 19F NMR (376 MHz, CDCl3): δ E isomer: -65.23 (s, 3F), Z isomer: -59.18 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C13H23F3O2 [M+H]+ : 245.0784; found: 245.0781.

2z: 2-(9,9,9-trifluoronon-7-en-1-yl)oxirane. Prepared according to the general procedure. Reaction was run using 1z (46.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me3SiCF3 (180 μL, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (93:7) was determined by 19F NMR of the crude mixture with benzotri fluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.22 mmol, 48.0 mg, 72 %, E/Z = 93:7), Rf = 0.70 (hexane : EtOAc = 5 : 1). E isomer: 1H NMR (400 MHz, CDCl3): δ 6.40-6.31 (m, 1H), 5.63-5.54 (m, 1H), 2.90-2.86 (m, 1H), 2.72 (t, J = 4.6 Hz, 1H), 2.45-2.43 (m, 1H), 2.14-2.10 (m, 2H), 1.53-1.39 (m, 6H), 1.36-1.31 (m, 4H) ppm. 13C NMR (101 MHz, CDCl3): δ 140.8 (q, JCF = 6.6 Hz), 123.2 (q, JCF = 270.1 Hz), 118.4 (q, JCF = 33.2 Hz), 52.4, 47.1, 32.5, 31.5, 29.2, 29.0, 27.9, 26.0 ppm. 19F NMR (376 MHz, CDCl3): δ E isomer: -64.88 (s, 3F), Z isomer: -58.99 (s, 3F) ppm. The spectral data are in full accordance with the literature report.12

2aa: methyl-12,12,12-trifluorododec-10-enoate. Prepared according to the general procedure. Reaction was run using 1aa (59.4 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me3SiCF3 (180 μL, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (94:6) was determined by 19F NMR of the crude mixture with benzotri fluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.23 mmol, 60.6 mg, 76 %, E/Z = 92:8), Rf = 0.70 (hexane : EtOAc = 5 : 1). E isomer: 1H NMR (400 MHz, CDCl3): δ 6.40-6.32 (m, 1H), 5.63-5.56 (m, 1H), 3.66 (s, 3H), 2.30 (t, J = 7.6 Hz, 2H), 2.15-2.12 (m, 2H), 1.63-1.59 (m, 2H), 1.44-1.40 (m, 2H), 1.33-1.25 (m, 8H) ppm. 13C NMR (101 MHz, CDCl3): δ 174.4, 140.9 (q, JCF = 6.6 Hz), 123.3 (q, JCF = 270.0 Hz), 118.4 (q, JCF = 33.2 Hz), 32.6, 34.2, 31.5, 29.3, 29.2, 29.2, 29.1, 28.0, 25.0 ppm. 19F NMR (376 MHz, CDCl3): δ E isomer: -64.82 (s, 3F), Z isomer: -58.96 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C13H23F3O2 [M+H]+ : 267.1566; found: 267.1570.

2ab: 12,12,12-trifluoro-1-morpholinododec-10-en-1-one. Prepared according to the general procedure. Reaction was run using 1ab (75.9 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me3SiCF3 (180 μL, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (92:8) was determined by 19F NMR of the crude mixture with benzotri fluoride as the internal standard.

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12 Bazhin, D. N.; Gorbunova, T. I.; Zapevalov, A. Y.; Saloutin, V. I. Russ. J. Org. Chem. 2009, 45, 491–495.
The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.20 mmol, 64.5 mg, 67 %, E/Z = 92:8), Rf = 0.30 (hexane : EtOAc = 1 : 1). E isomer: \(^1^H\) NMR (500 MHz, CDCl\(_3\)): δ 6.36-6.31 (m, 1H), 5.59-5.54 (m, 1H), 3.64-3.62 (m, 4H), 3.59-3.57 (m, 2H), 3.45-3.40 (m, 2H), 2.27 (t, J = 7.5 Hz, 2H), 2.14-2.10 (m, 2H), 1.63-1.59 (m, 2H), 1.52-1.48 (m, 2H), 1.13-1.21 (m, 8H) ppm. \(^{13}C\) NMR (126 MHz, CDCl\(_3\)): δ 171.9, 140.9 (q, \(J_{C,F} = 6.6\) Hz), 123.2 (q, \(J_{C,F} = 269.5\) Hz), 118.3 (q, \(J_{C,F} = 33.1\) Hz), 76.0, 66.7, 46.1, 41.9, 33.1, 31.5, 29.4, 29.3, 29.2, 29.0, 28.0, 25.2 ppm. \(^{19}F\) NMR (470 MHz, CDCl\(_3\)): δ E isomer: -64.80 (m, 3F), Z isomer: -58.95 (d, \(J = 8.5, 3F\) ppm). HRMS m/z (APCI): calcd. for C\(_{16}H_{27}F_3NO\;[M+H]^+: 322.1988; found: 322.1983.

2ac: 12,12,12-trifluorododec-10-en-1-ol. Prepared according to the general procedure. Reaction was run using 1ac (51.0 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me\(_2\)SiCF\(_3\) (180 \(\mu\)L, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (92:8) was determined by \(^{19}F\) NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.24 mmol, 57.0 mg, 80 %, E/Z = 92:8), Rf = 0.40 (hexane : EtOAc = 2 : 1). E isomer: \(^1^H\) NMR (400 MHz, CDCl\(_3\)): δ 6.35-6.31 (m, 1H), 5.62-5.53 (m, 1H), 3.61 (t, \(J = 6.6\) Hz, 2H), 2.14-2.10 (m, 2H), 1.79 (s, 1H), 1.58-1.51 (m, 2H), 1.43-1.37 (m, 2H), 1.34-1.24 (m, 10H) ppm. \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): δ 140.9 (q, \(J_{C,F} = 6.6\) Hz), 123.2 (q, \(J_{C,F} = 269.9\) Hz), 118.4 (q, \(J_{C,F} = 33.2\) Hz), 63.1, 32.8, 31.5, 29.6, 29.5, 29.4, 29.1, 28.0, 25.8 ppm. \(^{19}F\) NMR (376 MHz, CDCl\(_3\)): δ E isomer: -64.81 (s, 3F), Z isomer: -58.95 (s, 3F) ppm. The spectral data are in full accordance with the literature report.\(^ {13}\)

2ad: 12,12,12-trifluorododec-10-enoic acid. Prepared according to the general procedure. Reaction was run using 1ad (55.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (60.1 mg, 0.36 mmol), Me\(_2\)SiCF\(_3\) (180 \(\mu\)L, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (92:8) was determined by \(^{19}F\) NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.21 mmol, 53.7 mg, 71 %, E/Z = 92:8), Rf = 0.40 (hexane : EtOAc = 2 : 1). E isomer: \(^1^H\) NMR (500 MHz, CDCl\(_3\)): δ 6.40-6.34 (m, 1H), 5.63-5.56 (m, 1H), 2.35 (t, \(J = 7.5\) Hz, 2H), 2.14-2.12 (m, 2H), 1.66-1.60 (m, 2H), 1.45-1.40 (m, 2H), 1.39-1.26 (m, 8H) ppm. \(^{13}C\) NMR (126 MHz, CDCl\(_3\)): δ 180.5, 140.9 (q, \(J_{C,F} = 6.6\) Hz), 123.3 (q, \(J_{C,F} = 269.4\) Hz), 118.5 (q, \(J_{C,F} = 33.3\) Hz), 34.2, 31.6, 29.3, 29.2, 29.1, 29.0, 28.0, 24.7 ppm. \(^{19}F\) NMR (470 MHz, CDCl\(_3\)): δ E isomer: -64.81 (m, 3F), Z isomer: -58.90 (d, \(J = 8.5, 3F\) ppm). HRMS m/z (APCI): calcd. for C\(_{16}H_{27}F_3O_2\;[M+H]^+: 253.1410; found: 253.1409.

2ae: (8R,9S,13S,14S)-13-methyl-3-((7,7,7-trifluorohept-5-en-1-yl)oxy)6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one. Prepared according to the general procedure. Reaction was run using 1ae (105.6 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me\(_2\)SiCF\(_3\) (180 \(\mu\)L, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio

\(^{13}\) Wu, X.; Chu, L.; Qing, F.-L. Angew. Chem., Int. Ed. 2013, 52, 2198.
(94:6) was determined by $^{19}$F NMR of the crude mixture with benzo trifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.14 mmol, 58.0 mg, 46 %, $E/Z = 92.8$, 51.0 mg 1ae was recovered, 94 % brsm yield), $R_f = 0.30$ (hexane : EtOAc = 8 : 1). E isomer: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.20 (d, $J = 8.5$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 1H), 6.65 (s, 1H), 6.42-6.39 (m, 1H), 5.67-5.62 (m, 1H), 3.96 (t, $J = 6.0$ Hz, 2H), 2.92-2.89 (m, 2H), 2.51 (d, $J = 9.3$ Hz, 2H), 2.41-2.38 (m, 1H), 2.30-2.21 (m, 2H), 2.18-2.11 (m, 1H), 2.09-2.00 (m, 2H), 1.96 (d, $J = 10.5$ Hz, 1H), 1.83-1.78 (m, 2H), 1.68-1.56 (m, 4H), 1.54-1.40 (m, 4H), 0.91 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 221.0, 157.0, 140.4 (q, $J_{C,F} = 6.6$ Hz), 137.8, 132.1, 126.4, 123.1 (q, $J_{C,F} = 270.3$ Hz), 118.8 (q, $J_{C,F} = 33.2$ Hz), 114.6, 112.1, 67.4, 50.5, 48.1, 44.1, 38.4, 35.9, 31.7, 31.2, 29.7, 28.7, 26.6, 26.0, 24.7, 21.7, 13.9 ppm. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ E isomer: -64.84 (m, 3F), Z isomer: -58.95 (d, $J = 8.5$, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{35}$H$_{32}$F$_3$O$_2$ [M+H]$^+$ : 421.2349; found: 421.2347.

2af: 4-methyl-7-((7,7,7-trifluorohept-5-en-1-yl)oxy)-2H-chromen-2-one. Prepared according to the general procedure. Reaction was run using 1af (77.4 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me$_3$SiCF$_3$ (180 $\mu$L, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The $E/Z$ ratio (93:7) was determined by $^{19}$F NMR of the crude mixture with benzo trifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.21 mmol, 68.5 mg, 70 %, $E/Z = 94.6$), $R_f = 0.30$ (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.45 (d, $J = 8.5$ Hz, 1H), 6.81 (d, $J = 8.5$ Hz, 1H), 6.74 (s, 1H), 6.39-6.36 (m, 1H), 6.08 (s, 1H), 5.67-5.61 (m, 1H), 3.99 (t, $J = 6.3$ Hz, 2H), 2.35 (s, 3H), 2.25-2.20 (m, 2H), 1.85-1.79 (m, 2H), 1.66-1.60 (m, 2H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 162.0, 161.3, 155.3, 152.7, 140.1 (q, $J_{C,F} = 6.6$ Hz), 125.6, 123.1 (q, $J_{C,F} = 269.5$ Hz), 118.9 (q, $J_{C,F} = 33.3$ Hz), 113.6, 112.6, 111.9, 101.3, 68.1, 31.1, 28.4, 24.5, 18.7 (q, $J_{C,F} = 2.4$ Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ E isomer: -64.84 (s, 3F), Z isomer: -58.91 (s, 3F) ppm. HRMS m/z (APCI): calcd. for C$_{19}$H$_{13}$F$_3$O$_2$ [M+H]$^+$ : 327.1201; found: 327.1203.

2ag: 4-methyl-7-((7,7,7-trifluorohept-5-en-1-yl)oxy)-2H-chromen-2-one. Prepared according to the general procedure. Reaction was run using 1ag (96.0 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me$_3$SiCF$_3$ (180 $\mu$L, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The $E/Z$ ratio (93:7) was determined by $^{19}$F NMR of the crude mixture with benzo trifluoride as the internal standard. The product was purified by flash column chromatography on silica gel (hexane/EtOAc) and obtained a colorless oil (0.28 mmol, 107.1 mg, 92 %, $E/Z = 92.8$), $R_f = 0.60$ (hexane : EtOAc = 5 : 1). E isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.23 (d, $J = 8.0$ Hz, 1H), 8.06-8.03 (m, 2H), 7.63 (t, $J = 7.8$ Hz, 1H), 7.50-7.47 (m, 4H), 7.35 (t, $J = 7.4$ Hz, 1H), 6.33-6.25 (m, 1H), 5.58-5.49 (m, 1H), 4.04 (t, $J = 6.2$ Hz, 2H), 2.13-2.07 (m, 2H), 1.72-1.65 (m, 2H), 1.54-1.47 (m, 2H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 175.2, 156.0, 155.3, 140.5, 140.4 (q, $J_{C,F} = 6.4$ Hz), 133.5, 131.0, 130.7, 128.7, 128.4, 125.8, 124.7, 124.2, 123.1 (q, $J_{C,F} = 269.5$ Hz), 118.5 (q, $J_{C,F} = 33.3$ Hz), 118.0, 72.1, 30.9, 29.3, 24.3 ppm. $^{19}$F NMR
(376 MHz, CDCl$_3$): $\delta$ E isomer: -64.82 (s, 3F), Z isomer: -58.94 (s, 3F) ppm. **HRMS** m/z (APCI): calcd. for C$_2$H$_{30}$F$_3$O$_2$ [M+H]$^+$ : 389.1357; found: 389.1359.

1ah: (1S,4S,5S)-2-((R)-(benzyl)oxy)(6-methoxyquinolin-4-yl)methyl)-5-(-3,3,3-trifluoroprop-1-en-1-yl)quinuclidine. Prepared according to the general procedure. Reaction was run using 1ah (124.2 mg, 0.3 mmol), NIS (135 mg, 0.6 mmol), AgOAc (75.2 mg, 0.45 mmol), Me$_2$SiCF$_3$ (180 $\mu$L, 1.2 mol), NaOAc (98.4 mg, 1.2 mmol) and DMSO (3.0 mL). The E/Z ratio (63:37) was determined by $^{19}$F NMR of the crude mixture with benzotrifluoride as the internal standard. The product was purified by preparative TLC and obtained a yellow oil (0.16 mmol, 78.1 mg, 54%, E/Z isomer can be separated by preparative TLC to afford pure compound respectively), R$_t$ = 0.50 (CH$_2$Cl$_2$ : MeOH = 20 : 1).

E isomer: **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ 8.78 (d, $J = 4.4$ Hz, 1H), 8.06 (d, $J = 9.2$ Hz, 1H), 7.60 (s, 1H), 7.52 (d, $J = 4.0$ Hz, 1H), 7.43 (d, $J = 2.4$ Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 1H), 7.39-7.32 (m, 4H), 6.23-6.17 (m, 1H), 5.67-5.59 (m, 1H), 4.58-4.49 (m, 2H), 4.07 (s, 3H), 3.82 (s, 1H), 3.41-3.32 (m, 2H), 3.08-2.82 (m, 2H), 2.74-2.57 (m, 2H), 2.24-1.90 (m, 3H), 1.82-1.67 (m, 1H), 1.57 (t, $J = 10.8$ Hz, 1H) ppm. **$^{13}$C NMR** (101 MHz, CDCl$_3$): $\delta$ 158.9, 147.3, 144.9, 142.3 (m), 140.2 (m), 137.2, 132.0, 128.8, 128.3, 127.9, 127.2, 123.0, 122.5 (q, $J_{C,F} = 6.4$ Hz), 120.5 (m), 118.7, 101.1, 71.6, 60.1, 57.1, 55.1, 43.3, 36.9, 29.8, 27.2, 25.7, 20.5 ppm. **$^{19}$F NMR** (376 MHz, CDCl$_3$): $\delta$ -64.53 (s, 3F) ppm. **HRMS** m/z (APCI): calcd. for C$_{28}$H$_{30}$F$_3$N$_2$O$_2$ [M+H]$^+$ : 483.2254; found: 483.2252.

Z isomer: **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ 8.76 (d, $J = 4.0$ Hz, 1H), 8.05 (d, $J = 9.2$ Hz, 1H), 7.52 (d, $J = 3.6$ Hz, 2H), 7.41-7.28 (m, 6H), 5.87 (t, $J = 10.8$ Hz, 1H), 5.58-5.53 (m, 1H), 4.55-4.48 (m, 2H), 4.01 (s, 3H), 3.71-3.58 (m, 2H), 3.34-3.25 (m, 2H), 3.02-2.80 (m, 2H), 2.74-2.62 (m, 1H), 2.10-1.81 (m, 3H), 1.66-1.59 (m, 2H) ppm. **$^{13}$C NMR** (101 MHz, CDCl$_3$): $\delta$ 158.6, 147.5, 144.8, 143.6 (m), 142.9 (m), 137.4, 132.0, 128.7, 128.1, 127.8, 127.3, 122.8 (q, $J_{C,F} = 270.7$ Hz), 122.6, 119.8 (m), 118.6, 101.1, 71.5, 60.3, 56.8, 56.7, 43.2, 34.0, 29.8, 27.2, 26.2, 20.8 ppm. **$^{19}$F NMR** (376 MHz, CDCl$_3$): $\delta$ -58.73 (s, 3F) ppm. **HRMS** m/z (APCI): calcd. for C$_{28}$H$_{30}$F$_3$N$_2$O$_2$ [M+H]$^+$ : 483.2254; found: 483.2253.
Spectrum:

1d (CDCl₃, 400 MHz)

1d (CDCl₃, 101 MHz)
S4 (CDCl₃, 101 MHz)

S5 (CDCl₃, 400 MHz)
S5 (CDCl₃, 101 MHz)

9 (CDCl₃, 400 MHz)
9 (CDCl₃, 101 MHz)

2a (CDCl₃, 400 MHz)
2a (CDCl₃, 376 MHz)

2a (CDCl₃, 101 MHz)
2b (CDCl₃, 400 MHz)

2b (CDCl₃, 376 MHz)
2b (CDCl₃, 101 MHz)

[Chemical structure image]

2c (CDCl₃, 400 MHz)

[Chemical structure image]
$\text{Me}$

$\text{O}$

$\text{O}$

$\text{CF}_3$

$2e$ (CDCl$_3$, 376 MHz)

$\text{Me}$

$\text{O}$

$\text{O}$

$\text{CF}_3$

$2e$ (CDCl$_3$, 101 MHz)
$^{13}C$ (CDCl$_3$, 400 MHz)

2f (CDCl$_3$, 400 MHz)

$^{13}C$ (CDCl$_3$, 376 MHz)

2f (CDCl$_3$, 376 MHz)
$\text{O} \quad \text{O} \quad \text{CF}_3$

$2f (\text{CDCl}_3, 101 \text{ MHz})$

$\text{NC}$

$2g (\text{CDCl}_3, 400 \text{ MHz})$
$2g$ (CDCl$_3$, 376 MHz)

$2g$ (CDCl$_3$, 101 MHz)
$2h$ (CDCl$_3$, 400 MHz)

$2h$ (CDCl$_3$, 376 MHz)
2h (CDCl₃, 101 MHz)

2l (CDCl₃, 400 MHz)
2J (CDCl₃, 400 MHz)

2J (CDCl₃, 376 MHz)
2k (CDCl₃, 376 MHz)

2k (CDCl₃, 101 MHz)
$^{13}C$ NMR spectra of \( \text{21 (CDCl}_3, \text{400 MHz)} \) and \( \text{21 (CDCl}_3, \text{376 MHz)} \)
$^{13}C$ NMR (CDCl$_3$, 101 MHz)

$^1H$ NMR (CDCl$_3$, 400 MHz)

$^{13}C$ NMR (CDCl$_3$, 101 MHz)

$^1H$ NMR (CDCl$_3$, 400 MHz)
$^{13}C$ NMR Spectra

2m (CDCl$_3$, 376 MHz)

2m (CDCl$_3$, 101 MHz)
$2n$ (CDCl$_3$, 400 MHz)

\[ \text{S} \]

$2n$ (CDCl$_3$, 376 MHz)

\[ \text{CF}_3 \]
$\text{2n (CDCl}_3, 101 \text{ MHz)}$

$\text{2ø (CDCl}_3, 500 \text{ MHz)}$
$^{13}C$ (CDCl$_3$, 470 MHz)

$^{13}C$ (CDCl$_3$, 126 MHz)

$^{13}C$ (CDCl$_3$, 126 MHz)
$2p$ (CDCl$_3$, 400 MHz)

$2p$ (CDCl$_3$, 376 MHz)
$2p$ (CDCl$_3$, 101 MHz)

$2q$ (CDCl$_3$, 400 MHz)
$2q$ \((CDCl_3, 376 MHz)\)

$2q$ \((CDCl_3, 101 MHz)\)
$\text{PinB}$

$2r$ (CDCl$_3$, 400 MHz)

$\text{PinB}$

$2r$ (CDCl$_3$, 376 MHz)
$2r$ (CDCl$_3$, 101 MHz)

$2s$ (CDCl$_3$, 500 MHz)
2t (CDCl$_3$, 400 MHz)

2t (CDCl$_3$, 376 MHz)
$2t$ (CDCl$_3$, 101 MHz)

$2u$ (CDCl$_3$, 400 MHz)
$^2$u (CDCl$_3$, 376 MHz)

$^2$u (CDCl$_3$, 101 MHz)
$2v$ (CDCl$_3$, 400 MHz)

$2v$ (CDCl$_3$, 376 MHz)
$2v \text{ (CDCl}_3, 101 \text{ MHz)}$

$2w \text{ (CDCl}_3, 400 \text{ MHz)}$
2w' (CDCl₃, 400 MHz)

2w' (CDCl₃, 376 MHz)
$\text{2y (CDCl}_3, \text{ 400 MHz)}$

![NMR Spectrum 1](image1)

$\text{2y (CDCl}_3, \text{ 376 MHz)}$

![NMR Spectrum 2](image2)
$2y \text{ (CDCl}_3, 101 \text{ MHz)}$

$2z \text{ (CDCl}_3, 400 \text{ MHz)}$
$^{2z}$ (CDCl$_3$, 376 MHz)

$^{2z}$ (CDCl$_3$, 101 MHz)
2aa (CDCl₃, 400 MHz)

2aa (CDCl₃, 376 MHz)
2aa (CDCl₃, 101 MHz)

2ab (CDCl₃, 500 MHz)
2ab (CDCl₃, 470 MHz)

2ab (CDCl₃, 126 MHz)
2ac (CDCl₃, 400 MHz)

2ac (CDCl₃, 376 MHz)
2ac (CDCl$_3$, 101 MHz)

2ad (CDCl$_3$, 500 MHz)
2ad (CDCl₃, 470 MHz)

2ad (CDCl₃, 126 MHz)
2ae (CDCl$_3$, 500 MHz)

2ae (CDCl$_3$, 470 MHz)
2ag (CDCl$_3$, 400 MHz)

2ag (CDCl$_3$, 376 MHz)
2ah (E isomer, CDCl₃, 376 MHz)

2ah (E isomer, CDCl₃, 101 MHz)
2ah (Z isomer, CDCl$_3$, 400 MHz)

2ah (Z isomer, CDCl$_3$, 376 MHz)
2ah (Z isomer, CDCl$_3$, 101 MHz)

3 (CDCl$_3$, 400 MHz)
$4 \text{ (CDCl}_3, 500 \text{ MHz)}$

$4 \text{ (CDCl}_3, 470 \text{ MHz)}$
4 (CDCl₃, 126 MHz)

6a: 27% + 6b: 21% (crude ^19F NMR, 376 MHz)
6b (contain 10% cyclohexen) (CDCl₃, 126 MHz)

Et₂O

dr = 3 : 1

8a (CDCl₃, 500 MHz)
8a (CDCl$_3$, 470 MHz)

dr = 3 : 1

8a (CDCl$_3$, 101 MHz)
$8b : 7 = 1 : 1.3$ (CDCl$_3$, 500 MHz)

$8b : 7 = 1 : 1.3$ (CDCl$_3$, 470 MHz)
$8b : 7 = 1 : 1.3$ (CDCl$_3$, 101 MHz)

mixture of E/Z isomers

$10a$ (CDCl$_3$, 400 MHz)
mixture of E/Z isomers

10a (CDCl₃, 376 MHz)

mixture of E/Z isomers

10a (CDCl₃, 126 MHz)
10b (CDCl$_3$, 400 MHz)

E/Z = 85 : 15

10b (CDCl$_3$, 376 MHz)
$^{10b} (\text{CDCl}_3, 126 \text{ MHz})$

$E/Z = 85:15$

$^{10b} (\text{CDCl}_3, 126 \text{ MHz})$