Supporting Information

Four-Component Photoredox-Mediated
Azidoalkoxy-trifluoromethylation of Alkenes

Guillaume Levitre,‡ Guillaume Dagousset,‡ Elsa Anselmi,† Béatrice Tuccio,§ Emmanuel Magnier‡ and Géraldine Masson‡*  

‡ Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Université Paris-Sud, Université Paris-Saclay, 1, av. de la Terrasse, 91198 Gif-sur-Yvette Cedex, France.  
† Institut Lavoisier de Versailles, UMR 8180, Université de Versailles-Saint-Quentin 78035 Versailles Cedex, France.  
§ Aix-Marseille Université-CNRS, Institut de Chimie Radicalaire (UMR 7273), F-13397 Marseille Cedex 20, France.
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I. General Information

All reactions were carried out under argon atmosphere in oven dried glassware with magnetic stirring. Reagents were obtained from commercial suppliers and used without further purification.

Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization was accomplished by irradiation with a UV light at 254 nm. Flash column chromatography was carried out using kieselgel 35-70 µm particle sized silica gel (200-400 mesh).

Chromatography was performed using silica gel 60 (0.040-0.063 mm) from Merck.

Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl₃, δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ¹³C chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl₃, δ 77.0 ppm).

Mass spectra were determined on a Waters XevoQTof spectrometer using an electrospray ionization coupled with a time of flight analyser (ESI-TOF).

Infrared spectra were recorded on an IR spectrometer (Perkin Elmer BX FT-IR), and absorption frequencies were reported in reciprocal centimeters (cm⁻¹).

Melting points were recorded on a Reichert apparatus and were uncorrected.

Ru(bpy)₃(PF₆)₂ was synthesized according to literature procedure.¹

Visible light irradiations were performed with a Flexled INSPIRE LED lamp (3.6 W; λ = 465 nm).

II. General Procedure

General Procedure A: Typical procedure for four-component trifluoromethylation of alkenes in presence of carbonyl compound and TMSN₃.

A flame tube under argon atmosphere was charged with the corresponding alkene 8 (0.1 mmol), Umemoto’s reagent 3 (51.0 mg, 0.15 mmol, 1.5 equiv), [Ru(bpy)]₃(PF₆)₂ 4a (4.4 mg, 0.005 mmol, 0.05 equiv). Then, it was dissolved in 2 mL of distilled DCM and the corresponding carbonyl compound 7 (0.6 mmol, 6 equiv) and TMSN₃ 2 (0.15 or 0.5 mmol, 1.5 or 5 equiv) were added successively. The solution was then irradiated with blue LEDs at rt for 2.5 h under inert atmosphere. The solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (Hept/AcOEt, 98:2 to 80:20) to afford the corresponding pure trifluoromethylated product.

General Procedure A’: Typical procedure for a 1 mmol scale of four-component trifluoromethylation of alkenes in presence of carbonyl compound and TMSN₃.

A flame tube under argon atmosphere was charged with the corresponding alkene 8a (1.0 mmol, 154.2 mg), Umemoto’s reagent 3 (510.1 mg, 1.5 mmol, 1.5 equiv), [Ru(bpy)]₃(PF₆)₂ 4a (44 mg, 0.005 mmol, 0.05 equiv). Then, it was dissolved in 20 mL of distilled DCM and acetone 7j (6.0 mmol, 0.44 mL, 6 equiv) and TMSN₃ 2 (1.5 mmol, 0.2 mL, 1.5 equiv) were added successively. The solution was then irradiated with blue LEDs at rt for 2.5 h under inert atmosphere. The solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (Hept/AcOEt, 98:2 to 80:20) to afford 198.1 mg of the corresponding pure 9j product with 61% yield.

General Procedure A’’: Typical procedure for four-component trifluoromethylation of alkenes in presence of carbonyl compound and TMSCN.

A flame tube under argon atmosphere was charged with the corresponding alkene 8 (0.1 mmol), Umemoto’s reagent 3 (51.0 mg, 0.15 mmol, 1.5 equiv), [Ru(bpy)]₃(PF₆)₂ 4a (4.4 mg, 0.005 mmol, 0.05 equiv). Then, it was dissolved in 2 mL of distilled DCM and the corresponding carbonyl compound 7 (0.6 mmol, 6 equiv) and TMSCN (19 µL, 0.15 equiv) were added successively. The solution was then irradiated with blue LEDs at rt for 2.5 h under inert atmosphere. The solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (Hept/AcOEt, 98:2 to 80:20) to afford the corresponding pure trifluoromethylated product.
III. Experimental Data of Compounds 9a to 9v

2-(1-(1-azido-3-phenylpropoxy)-3,3,3-trifluoropropyl)naphthalene 9a

According to the Procedure A, m = 24.3 mg, 61% yield, colorless oil, mixture of 2 diastereomers (dia 1: dia 2 = 56:44).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.94-7.80 (m, 4H), 7.59-7.46 (m, 3H), 7.36-7.33 (m, 1H), 7.27-7.11 (m, 3H), 7.03-7.00 (m, 1H), 5.24 (dd, $J = 8.5$ Hz and $4.1$ Hz, 1H, dia 1), 4.97 (dd, $J = 9.1$ Hz and $3.3$ Hz, 1H, dia 2), 4.55 (t, $J = 5.8$ Hz, 1H, dia 2), 4.17 (t, $J = 5.8$ Hz, 1H, dia 1), 2.95-2.51 (m, 4H), 2.21-2.04 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 140.7 (dia 2), 140.5 (dia 1), 137.8 (dia 2), 135.8 (dia 1), 133.6 (dia 1), 133.4 (dia 2), 133.2 (dia 2), 133.1 (dia 1), 129.3 (dia 1), 129.0 (dia 2), 128.6 (dia 1 or dia 2), 128.4 (dia 1 or dia 2), 128.2 (dia 1 or dia 2), 128.1 (dia 1 or dia 2), 128.0 (dia 1 or dia 2), 127.8 (dia 1 or dia 2), 127.8 (dia 1 or dia 2), 127.1 (dia 1 or dia 2), 126.7 (dia 1 or dia 2), 126.7 (dia 1 or dia 2), 126.5 (dia 1 or dia 2), 126.4 (dia 1 or dia 2), 126.2 (dia 1 or dia 2), 126.1 (dia 1 or dia 2), 125.6 (q, $J = 277.7$ Hz, dia 2), 125.5 (q, $J = 277.7$ Hz, dia 1), 125.5 (q, $J = 277.7$ Hz, dia 1), 125.4 (dia 1 or dia 2), 123.7 (dia 1), 123.5 (dia 2), 92.4 (dia 2), 88.1 (dia 1), 76.8 (dia 2), 73.3 (dia 1), 42.1 (q, $J = 27.5$ Hz, dia 2), 41.5 (q, $J = 28.4$ Hz, dia 1), 36.1 (dia 2), 35.9 (dia 1), 30.8 (dia 1), 30.7 (dia 2).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ (ppm): -63.44 (t, $J = 10.3$ Hz, dia 2), -63.54 (t, $J = 10.3$ Hz, dia 1).

IR (neat) $\nu$ (cm$^{-1}$): 3028, 2928, 2104, 1361, 1250, 1118, 818, 746.

EI-HRMS (positive ion) $C_{22}H_{21}F_3N_3O$ [M+H]$^+$: requires 400.1631; found 400.1632.
2-(1-(azidoethoxy)-3,3-trifluoropropyl)naphthalene 9b

According to the Procedure A, m = 22.9 mg, 74% yield, colorless oil, mixture of 2 diatereomers (dia 1: dia 2 = 56:44).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.82-7.70 (m, 4H), 7.47-7.34 (m, 3H), 5.12 (dd, $J = 8.7$ Hz and 3.9 Hz, 1H, dia 2), 4.89 (d, $J = 9.5$ Hz, 1H, dia 1), 4.60 (q, $J = 5.5$ Hz, 1H, dia 1), 4.18 (q, $J = 5.5$ Hz, 1H, dia 2), 2.77-2.66 (m, 1H), 2.46-2.35 (m, 1H), 1.43 (d, $J = 5.7$ Hz, 3H, dia 1), 1.37 (d, $J = 5.7$ Hz, 3H, dia 2).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 138.0 (dia 1), 136.1 (dia 2), 133.5 (dia 2), 133.3 (dia 1), 133.2 (dia 1), 133.1 (dia 2), 129.2 (dia 2), 128.9 (dia 1), 128.1 (dia 1), 128.0 (dia 2), 127.8, 126.7 (dia 2), 126.7, 126.5 (dia 1), 126.4 (dia 2), 125.6 (q, $J = 276.8$ Hz, dia 2), 125.4 (q, $J = 276.8$ Hz, dia 1), 125.2 (dia 2), 123.6 (dia 2), 123.5 (dia 1), 89.6 (dia 1), 85.3 (dia 2), 76.4 (dia 1), 73.1 (dia 2), 42.3 (q, $J = 27.5$ Hz, dia 1), 41.7 (q, $J = 27.5$ Hz, dia 2), 20.3 (dia 1), 20.0 (dia 2).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ (ppm): -63.64 (t, $J = 10.3$ Hz, dia 2), -63.79 (t, $J = 10.3$ Hz, dia 1).

IR (neat) $\nu$ (cm$^{-1}$): 2987, 2108, 1381, 1249, 1091, 747.

EI-HRMS (positive ion) $^{13}$C$_{15}$H$_{14}$F$_3$N$_3$ONa [M+Na]$^+$: requires 332.0981; found 332.0986.
2-(1-(1-azidopropoxy)-3,3,3-trifluoropropyl)naphthalene 9c

According to the Procedure A, m = 22.5 mg, 70% yield, colorless oil mixture of 2 diastereomers (dia 1: dia 2 = 58:42).

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \] \( \delta \) (ppm): 7.92-7.80 (m, 4H), 7.56-7.44 (m, 3H), 5.22 (dd, \( J = 8.5 \) Hz and 4.4 Hz, 1H, dia 2), 4.97 (dd, \( J = 9.3 \) Hz and 3.3 Hz, 1H, dia 1), 4.46 (t, \( J = 6.0 \) Hz, 1H, dia 1), 4.03 (t, \( J = 6.0 \) Hz, 1H, dia 2), 2.89-2.78 (m, 1H), 2.57-2.45 (m, 1H), 1.91-1.76 (m, 2H), 1.03 (t, \( J = 7.4 \) Hz, 3H, dia 1), 0.91 (t, \( J = 7.4 \) Hz, 3H, dia 2).

\[ ^{13}C \text{ NMR (125 MHz, CDCl}_3 \] \( \delta \) (ppm): 138.1 (dia 1), 136.0 (dia 2), 133.5 (dia 2), 133.3 (dia 2), 133.2 (dia 1), 133.1 (dia 2), 129.2 (dia 2), 128.9 (dia 1), 128.0 (dia 1), 128.0 (dia 2), 127.8 (dia 1), 127.8 (dia 2), 126.9 (dia 2), 126.7 (dia 1), 126.7 (dia 2), 126.5 (dia 1), 126.4 (dia 1), 125.6 (q, \( J = 277.7 \) Hz, dia 2), 125.5 (q, \( J = 277.7 \) Hz, dia 1), 125.3 (dia 2), 123.7 (dia 2), 123.5 (dia 1), 94.4 (dia 1), 89.9 (dia 2), 76.7 (dia 1), 73.1 (dia 2), 42.2 (q, \( J = 27.5 \) Hz, dia 2), 41.6 (q, \( J = 27.5 \) Hz, dia 2), 27.8 (dia 1), 27.5 (dia 2), 9.1 (dia 2), 8.9 (dia 1).

\[ ^{19}F \text{ NMR (282 MHz, CDCl}_3 \] \( \delta \) (ppm): -63.57 (t, \( J = 10.3 \) Hz, dia 1), -63.58 (t, \( J = 10.3 \) Hz, dia 2).

IR (neat) \( \nu \) (cm\(^{-1}\)): 2973, 2940, 2103, 1249, 1382, 1118, 817, 746.

EI-HRMS (positive ion) \( \text{C}_{16}\text{H}_{16}\text{F}_{3}\text{N}_{3}\text{ONa} \) [M+Na]^+: requires 346.1138; found 346.1129.
According to the Procedure A, m = 21.3 mg, 63% yield, colorless oil mixture of 2 diatereomers (dia 1: dia 2 = 60:40).

$^{1}H$ NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.91-7.78 (m, 4H), 7.56-7.43 (m, 3H), 5.22 (dd, $J = 8.5$ Hz and $4.4$ Hz, 1H, dia 2), 4.96 (dd, $J = 9.3$ Hz and $3.3$ Hz, 1H, dia 1), 4.51 (t, $J = 6.1$ Hz, 1H, dia 1), 4.08 (t, $J = 6.1$ Hz, 1H, dia 2), 2.88-2.77 (m, 1H), 2.56-2.45 (m, 1H), 1.87-1.69 (m, 2H), 1.50-1.27 (m, 2H), 0.98 (t, $J = 7.4$ Hz, 3H, dia 1), 0.84 (t, $J = 7.4$ Hz, 3H, dia 2).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 138.1 (dia 1), 136.0 (dia 2), 133.5 (dia 2), 133.3 (dia 2), 133.2 (dia 1), 133.1 (dia 2), 129.2 (dia 2), 128.9 (dia 1), 128.0 (dia 1), 128.0 (dia 2), 127.8 (dia 1), 127.8 (dia 2), 126.9 (dia 2), 126.7 (dia 1), 126.7 (dia 2), 126.5 (dia 1), 126.4 (dia 1), 125.6 (q, $J = 277.7$ Hz, dia 2), 125.5 (q, $J = 277.7$ Hz, dia 1), 125.2 (dia 2), 123.7 (dia 2), 123.5 (dia 1), 93.1 (dia 1), 88.5 (dia 2), 76.8 (dia 1), 73.1 (dia 2), 4.22 (q, $J = 27.5$ Hz, dia 2), 4.16 (q, $J = 27.5$ Hz, dia 1), 36.5 (dia 1), 36.2 (dia 2), 18.0 (dia 2), 17.8 (dia 1), 13.7 (dia 1), 13.6 (dia 2).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ (ppm): -63.59 (t, $J = 10.3$ Hz).

IR (neat) $\nu$ (cm$^{-1}$): 2964, 2107, 1380, 1249, 1111, 1079, 817, 747.

EI-HRMS (positive ion) C$_{17}$H$_{19}$F$_{3}$N$_{3}$O [M+H]$^+$: requires 338.1475; found 338.1474.
2-(1-((1-azidooctyl)oxy)-3,3,3-trifluoropropyl)naphthalene 9e

According to the Procedure A, m = 30.3 mg, 77% yield, colorless oil, mixture of 2 diatereomers (dia 1: dia 2 = 52:48).

**$^1$H NMR (500 MHz, CDCl$_3$) δ (ppm):** 7.94-7.79 (m, 4H), 7.57-7.43 (m, 3H), 5.21 (dd, $J = 8.5$ Hz and 4.4 Hz, 1H, dia 2), 4.96 (dd, $J = 8.7$ Hz and 3.5 Hz, 1H, dia 1), 4.50 (t, $J = 6.0$ Hz, 1H, dia 1), 4.08 (t, $J = 6.1$ Hz, 1H, dia 2), 2.88-2.70 (m, 1H), 2.65-2.45 (m, 1H), 1.89-1.64 (m, 2H), 1.48-1.14 (m, 10H), 0.91 (t, $J = 7.1$ Hz, 3H, dia 1), 0.86 (t, $J = 7.1$ Hz, 3H, dia 2).

**$^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm):** 138.1 (dia 1 or dia 2), 136.0 (dia 1 or dia 2), 133.5 (dia 1 or dia 2), 133.3 (dia 1 or dia 2), 133.2 (dia 1 or dia 2), 129.2 (dia 1 or dia 2), 128.9 (dia 1 or dia 2), 128.1 (dia 1 or dia 2), 128.0 (dia 1 or dia 2), 127.8, 127.0 (dia 1 or dia 2), 126.8 (dia 1 or dia 2), 126.7 (dia 1 or dia 2), 126.5 (dia 1 or dia 2), 126.3 (dia 1 or dia 2), 125.6 (q, $J = 277.7$ Hz, dia 1 or dia 2), 125.5 (q, $J = 277.7$ Hz, dia 1 or dia 2), 125.3 (dia 1 or dia 2), 123.6 (dia 1 or dia 2), 123.5 (dia 1 or dia 2), 93.3 (dia 1 or dia 2), 88.8 (dia 1 or dia 2), 76.7 (dia 1 or dia 2), 73.1 (dia 1 or dia 2), 42.3 (q, $J = 27.5$ Hz, dia 1 or dia 2), 41.8 (q, $J = 27.5$ Hz, dia 1 or dia 2), 34.5 (dia 1 or dia 2), 34.1 (dia 1 or dia 2), 31.7 (dia 1 or dia 2), 29.2 (dia 1 or dia 2), 29.1 (dia 1 or dia 2), 29.1 (dia 1 or dia 2), 29.0 (dia 1 or dia 2), 24.6 (dia 1 or dia 2), 24.5 (dia 1 or dia 2), 22.6 (dia 1 or dia 2), 22.6 (dia 1 or dia 2), 14.1.

**$^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm):** -63.56 (t, $J = 10.3$ Hz, dia 1), -64.00 (t, $J = 10.3$ Hz, dia 2).

**IR (neat) ν (cm$^{-1}$):** 2927, 2106, 1379, 1249, 1116, 817, 746.

**EI-HRMS (positive ion) C$_{21}$H$_{30}$F$_3$N$_4$O [M+NH$_4$]$^+$:** requires 411.2366; found 411.2368.
According to the Procedure A, m = 24.9 mg, 52% yield, colorless oil, mixture of 2 diatereomers (dia 1: dia 2 = 50:50).

$^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.84-7.71 (m, 4H), 7.48-7.38 (m, 3H), 5.14 (dd, $J = 8.4$ Hz and 4.4 Hz, 1H, dia 1), 4.89 (dd, $J = 9.1$ Hz and 3.2 Hz, 1H, dia 2), 4.44 (t, $J = 6.0$ Hz, 1H, dia 2), 4.00 (t, $J = 6.0$ Hz, 1H, dia 1), 3.57 (t, $J = 6.0$ Hz, 2H, dia 1 or dia 2), 3.48 (t, $J = 5.8$ Hz, 2H, dia 1 or dia 2), 2.80-2.69 (m, 1H), 2.49-2.38 (m, 1H), 1.84-1.65 (m, 2H), 1.52-1.35 (m, 3H), 1.27-1.18 (m, 2H), 0.85 (s, 9H, dia 1 or dia 2), 0.81 (s, 9H, dia 1 or dia 2), 0.00 (s, 6H, dia 1 or dia 2), -0.04 (s, 3H dia 1 or dia 2), -0.05 (s, 3H dia 1 or dia 2).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): 138.1 (dia 1 or dia 2), 135.9 (dia 1 or dia 2), 133.5 (dia 1 or dia 2), 133.3 (dia 1 or dia 2), 133.2 (dia 1 or dia 2), 133.1 (dia 1 or dia 2), 129.2 (dia 1 or dia 2), 128.9 (dia 1 or dia 2), 128.0, 127.8, 127.0 (dia 1 or dia 2), 126.7 (dia 1 or dia 2), 126.7 (dia 1 or dia 2), 126.5 (dia 1 or dia 2), 126.4 (dia 1 or dia 2), 125.6 (q, $J = 277.7$ Hz, dia 1 or dia 2), 125.5 (q, $J = 277.7$ Hz, dia 1 or dia 2), 125.3 (dia 1 or dia 2), 123.6 (dia 1 or dia 2), 123.5 (dia 1 or dia 2), 93.2 (dia 1 or dia 2), 88.7 (dia 1 or dia 2), 76.8 (dia 1 or dia 2), 73.1 (dia 1 or dia 2), 62.8 (dia 1 or dia 2), 62.7 (dia 1 or dia 2), 42.2 (q, $J = 27.5$ Hz, dia 1 or dia 2), 41.6 (q, $J = 27.5$ Hz, dia 1 or dia 2), 34.3 (dia 1 or dia 2), 33.9 (dia 1 or dia 2), 32.3 (dia 1 or dia 2), 32.2 (dia 1 or dia 2), 29.7 (dia 1 or dia 2), 29.5 (dia 1 or dia 2), 26.0, 21.1 (dia 1 or dia 2), 21.0 (dia 1 or dia 2), -5.3.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm): -63.55 (t, $J = 10.3$ Hz, dia 1), -63.58 (t, $J = 10.3$ Hz, dia 2).

IR (neat) ν (cm$^{-1}$): 2929, 2106, 1250, 1097, 834, 774, 746.

EI-HRMS (positive ion) $^{13}$C$_{24}$H$_{35}$F$_3$N$_3$O$_2$Si [M+H]$^+$: requires 482.2445; found 482.2448.
2-(1-(1-azido-2-(4-bromophenyl)ethoxy)-3,3,3-trifluoropropyl)naphthalene 9g

According to the Procedure A, $m = 23.6 \text{ mg}$, 51% yield, colorless oil, mixture of 2 diastereomers (dia 1: dia 2 = 66:34).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.95-7.66 (m, 4H), 7.58-7.37 (m, 5H), 7.15-6.99 (m, 2H), 5.21 (dd, $J = 8.8$ Hz and $3.9$ Hz, 1H, dia 2), 4.99 (dd, $J = 8.4$ Hz and $5.2$ Hz, 1H, dia 1), 4.84 (t, $J = 6.5$ Hz, 1H, dia 1), 4.99 (dd, $J = 7.9$ Hz and $4.6$ Hz, 1H, dia 2), 3.06 (dd, $J = 13.7$ Hz and $8.0$ Hz, 1H, dia 2), 2.99 (dd, $J = 13.7$ Hz and $4.4$ Hz, 1H, dia 2), 2.95 (d, $J = 6.6$ Hz, 2H, dia 1), 2.80-2.71 (m, 1H), 2.67-2.44 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 135.2 (dia 2), 135.0 (dia 1), 134.5 (dia 2), 133.6 (dia 1), 133.5 (dia 1), 133.4 (dia 2), 133.2 (dia 1), 133.0 (dia 2), 131.9, 131.6 (dia 2), 131.5 (dia 2), 131.2, 129.4 (dia 1), 129.0 (dia 2), 128.1 (dia 1), 128.1 (dia 2), 127.8 (dia 1), 127.7 (dia 2), 126.8 (dia 1), 126.6 (dia 2), 126.4 (dia 2), 126.3 (dia 1), 125.6 (q, $J = 276.8$ Hz, dia 2), 125.5 (q, $J = 276.8$ Hz, dia 1), 123.7 (dia 1), 123.5 (dia 2), 121.7 (dia 2), 121.6 (dia 1), 88.8 (dia 2), 78.2 (dia 1), 73.4 (dia 2), 60.2 (dia 1), 41.8 (q, $J = 27.5$ Hz, dia 2), 40.4 (q, $J = 28.4$ Hz, dia 2), 40.3 (dia 2), 40.1 (dia 1).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ (ppm): -63.55 (t, $J = 10.3$ Hz, dia 2), -63.99 (t, $J = 10.3$ Hz, dia 1).

IR (neat) $\nu$ (cm$^{-1}$): 2928, 2101, 1249, 1117, 817, 747.

EI-HRMS (positive ion) $C_{21}H_{18}F_3N_3OBr$ [M+H]$^+$: requires 464.0580; found 464.0592.
2-(1-(1-azido-3-methylbutoxy)-3,3,3-trifluoropropyl)naphthalene 9h

According to the Procedure A, m = 24.0 mg, 68% yield, colorless oil mixture of 2 diastereomers (dia 1: dia 2 = 50:50).

$^1\text{H NMR (500 MHz, CDCl}_3\text{)} \delta \text{ (ppm):}$ 7.95-7.80 (m, 4H), 7.58-4.45 (m, 3H), 5.24 (dd, $J = 8.5 \text{ Hz and } 4.3 \text{ Hz, 1H, dia 2}$), 4.98 (dd, $J = 9.2 \text{ Hz and } 3.4 \text{ Hz, 1H, dia 1}$), 4.56 (t, $J = 6.4 \text{ Hz, 1H, dia 1}$), 4.13 (t, $J = 6.4 \text{ Hz, 1H, dia 2}$), 2.87-2.73 (m, 1H), 2.62-2.49 (m, 1H), 1.87-1.74 (m, 2H), 1.68-1.59 (m, 1H), 0.98 (d, $J = 7.0 \text{ Hz, 3H, dia 1}$), 0.97 (d, $J = 7.0 \text{ Hz, 3H, dia 2}$), 0.86 (d, $J = 7.4 \text{ Hz, 3H, dia 1}$), 0.68 (d, $J = 7.0 \text{ Hz, 3H, dia 2}$).

$^{13}\text{C NMR (125 MHz, CDCl}_3\text{)} \delta \text{ (ppm):}$ 138.2 (dia 1 or dia 2), 135.9 (dia 1 or dia 2), 133.5 (dia 1 or dia 2), 133.3 (dia 1 or dia 2), 133.2 (dia 1 or dia 2), 129.2 (dia 1 or dia 2), 128.8 (dia 1 or dia 2), 128.0 (dia 1 or dia 2), 127.8 (dia 1 or dia 2), 127.0 (dia 1 or dia 2), 126.8 (dia 1 or dia 2), 126.7 (dia 1 or dia 2), 126.6 (dia 1 or dia 2), 126.5 (dia 1 or dia 2), 126.3 (dia 1 or dia 2), 126.3 (dia 1 or dia 2), 125.6 (q, $J = 277.7 \text{ Hz, dia 1 or dia 2}$), 125.5 (q, $J = 277.7 \text{ Hz, dia 1 or dia 2}$), 125.2 (dia 1 or dia 2), 123.7 (dia 1 or dia 2), 123.5 (dia 1 or dia 2), 92.1 (dia 1 or dia 2), 87.4 (dia 1 or dia 2), 76.8 (q, $J = 3.3 \text{ Hz, dia 1 or dia 2}$), 73.0 (q, $J = 3.3 \text{ Hz, dia 1 or dia 2}$), 43.2 (dia 1 or dia 2), 42.8 (dia 1 or dia 2), 42.2 (q, $J = 27.5 \text{ Hz, dia 1 or dia 2}$), 41.6 (q, $J = 27.5 \text{ Hz, dia 1 or dia 2}$), 24.2 (dia 1 or dia 2), 24.1 (dia 1 or dia 2), 22.8 (dia 1 or dia 2), 22.6 (dia 1 or dia 2), 22.3 (dia 1 or dia 2), 21.9 (dia 1 or dia 2).

$^{19}\text{F NMR (282 MHz, CDCl}_3\text{)} \delta \text{ (ppm):}$ -63.59 (t, $J = 10.3 \text{ Hz}$), -63.61 (t, $J = 10.3 \text{ Hz}$).

IR (neat) ν (cm$^{-1}$): 2960, 2106, 1368, 1249, 1126, 1116, 817, 747.

EI-HRMS (positive ion) $^{18}\text{C}_{18}\text{H}_{20}\text{F}_{3}\text{N}_{3}\text{ONa}$ [M+Na]$^+$: requires 374.1451; found 374.1463.
2-(1-(azido(cyclohexyl)methoxy)-3,3,3-trifluoropropyl)naphthalene 9i

According to the Procedure A, m = 14.2 mg, 37% yield, colorless oil, mixture of 2 diastereomers (dia 1: dia 2 = 65:35).

^1H NMR (500 MHz, CDCl\textsubscript{3}) δ (ppm): 7.93-7.81 (m, 4H), 7.58-7.46 (m, 3H), 5.22 (dd, \textit{J} = 8.4 Hz and 4.7 Hz, 1H, dia 1), 4.95 (dd, \textit{J} = 9.0 Hz and 3.6 Hz, 1H, dia 2), 4.29 (d, \textit{J} = 6.6 Hz, 1H, dia 2), 3.86 (d, \textit{J} = 6.8 Hz, 1H, dia 1), 2.93-2.81 (m, 1H), 2.61-2.48 (m, 1H), 1.97-1.92 (m, 1H), 1.86-1.70 (m, 4H), 1.70-1.62 (m, 1H), 1.35-1.18 (m, 3H), 1.16-1.05 (m, 1H), 1.00-0.86 (m, 1H).

^13C NMR (125 MHz, CDCl\textsubscript{3}) δ (ppm): 138.0 (dia 2), 135.7 (dia 1), 133.6 (dia 1), 133.3 (dia 2), 133.2 (dia 2), 133.1 (dia 1), 129.2 (dia 1), 128.9 (dia 2), 128.1, 127.8, 127.3 (dia 1 or dia 2), 126.7, 126.5 (dia 1 or dia 2), 126.4 (dia 1 or dia 2), 125.6 (q, \textit{J} = 276.8 Hz, dia 2), 125.4 (q, \textit{J} = 276.8 Hz, dia 1), 125.4 (dia 1 or dia 2), 123.8 (dia 1), 123.6 (dia 2), 97.1 (dia 2), 92.6 (dia 1), 77.0 (dia 1), 73.2 (dia 2), 42.7 (dia 2), 42.3 (dia 1), 42.1 (q, \textit{J} = 27.5 Hz, dia 2), 41.6 (q, \textit{J} = 28.4 Hz, dia 2), 28.2 (dia 1), 28.1 (dia 2), 28.1 (dia 1), 27.8 (dia 2), 26.2 (dia 2), 26.1 (dia 1), 25.7 (dia 2), 25.7 (dia 2), 25.6 (dia 1), 25.5 (dia 1).

^19F NMR (282 MHz, CDCl\textsubscript{3}) δ (ppm): -63.36 (t, \textit{J} = 10.3 Hz, dia 2), -63.47 (t, \textit{J} = 10.3 Hz, dia 1).

IR (neat) ν (cm\textsuperscript{-1}): 2930, 2856, 2105, 1264, 1251, 1129, 735.

EI-HRMS (positive ion) C\textsubscript{20}H\textsubscript{23}F\textsubscript{3}N\textsubscript{3}O [M+H]\textsuperscript{+}: requires 378.1788; found 378.1781.
2-(1-{[2-azidopropan-2-yl]oxy}-3,3-trifluoropropyl)naphthalene 9j

According to the Procedure A, m = 19.5 mg, 60% yield, colorless oil.
According to the Procedure A’, m = 198.1 mg, 61% yield, colorless oil.

\[ \text{1H NMR (500 MHz, CDCl}_3\text{)} \delta (\text{ppm}): 7.90-7.86 (m, 4H), 7.54-7.51 (m, 3H), 5.29 (dd, J = 8.8 Hz and 3.9 Hz), 2.78-2.71 (m, 1H), 2.48-2.42 (m, 1H), 1.59 (s, 3H), 1.30 (s, 3H). \]

\[ \text{13C NMR (125 MHz, CDCl}_3\text{)} \delta (\text{ppm}): 139.9, 133.3, 133.1, 128.8, 128.0, 127.8, 126.4, 126.2, 125.4 (q, J = 277.7 Hz), 125.0, 123.6, 93.5, 70.0, 43.0 (q, J = 27.5 Hz), 26.8, 26.0. \]

\[ \text{19F NMR (282 MHz, CDCl}_3\text{)} \delta (\text{ppm}): -63.55 (t, J = 10.3 Hz). \]

\[ \text{IR (neat) } \nu (\text{cm}^{-1}): 2991, 2107, 1383, 1246, 1126, 738. \]

\[ \text{EI-HRMS (positive ion) } C_{16}H_{17}F_3N_3O [M+H]^+: \text{ requires 324.1318; found 324.1308.} \]
2-(1-((3-azidopentan-3-yl)oxy)-3,3-trifluoropropyl)naphthalene 9k

According to the Procedure A, m = 7.9 mg, 22% yield, colorless oil (mixture of 2 rotamers rot 1:rot 2 = 81:19).

$^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.77-7.66 (m, 4H), 7.40-7.35 (m, 3H), 5.14 (dd, $J$ = 8.0 Hz and 4.9 Hz, 1H), 2.66-2.57 (m, 1H), 2.37-2.31 (m, 1H), 1.77-1.67 (m, 2H), 1.45-1.35 (m, 2H), 0.85 (t, $J$ = 7.4 Hz, 3H), 0.59 (t, $J$ = 7.4 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): 139.9 (rot 1), 139.6 (rot 2), 133.2, 133.1, 128.9 (rot 2), 128.7 (rot 1), 128.0 (rot 2), 128.0 (rot 1), 127.8 (rot 1), 127.8 (rot 2), 126.5 (rot 2), 126.4 (rot 1), 126.4 (rot 2), 126.2 (rot 1), 125.4 (q, $J$ = 274.9 Hz), 125.2 (rot 1), 124.7 (rot 2), 123.9 (rot 1), 123.3 (rot 2), 98.8, 69.4 (rot 1), 69.0 (rot 2), 43.0 (q, $J$ = 28.4 Hz, rot 1), 42.9 (q, $J$ = 28.4 Hz, rot 2), 28.5, 27.4, 8.1.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm): -63.30 (t, $J$ = 10.3 Hz, rot 1), -63.70 (t, $J$ = 10.3 Hz, rot 2).

IR (neat) ν (cm$^{-1}$): 2976, 2945, 2104, 1380, 1248, 1111, 746.

EI-HRMS (positive ion) $^{12}$C$_{18}$H$_{20}$F$_3$N$_3$ONa [M+Na]$^+$: requires 374.1451; found 374.1544.
2-(1-(1-azidocyclobutoxy)-3,3,3-trifluoropropyl)naphthalene 9l

According to the Procedure A, m = 19.6 mg, 24% yield (determined by NMR), colorless oil (isolated with 60% of azido compound).

$^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.95-7.83 (m, 4H), 7.58-7.45 (m, 3H), 5.10 (dd, $J = 9.0$ Hz and $3.9$ Hz, 1H), 2.65-2.59 (m, 1H), 2.49-2.41 (m, 2H), 2.34-2.28 (m, 1H), 2.11-2.00 (m, 2H), 1.76-1.70 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): 138.9, 134.9, 133.2, 128.8, 128.0, 127.8, 126.8, 126.5, 125.5 (q, $J = 276.8$ Hz), 125.4, 123.7, 95.2, 71.0, 42.5 (q, $J = 27.5$ Hz), 34.2, 33.3, 12.2.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm): -63.55 (t, $J = 10.3$ Hz).

IR (neat) ν (cm$^{-1}$): 2955, 2106, 1382, 1247, 1113, 816, 747.

EI-HRMS (positive ion) C$_{17}$H$_{22}$F$_3$N$_3$O [M+H]$^+$: requires 336.1318; found 336.1309.
(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)benzene 9m

According to the Procedure A, m = 14.2 mg, 52% yield, colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.40-7.29 (m, 5H), 5.08 (dd, $J$ = 9.1 Hz and 4.0 Hz), 2.67-2.60 (m, 1H), 2.38-2.33 (m, 1H), 1.53 (s, 3H), 1.27 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 142.5, 128.6, 128.0, 125.9, 125.3 (q, $J$ = 276.8 Hz), 93.3, 69.9, 43.0 (q, $J$ = 27.5 Hz), 26.8, 25.7.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ (ppm): -63.63 (t, $J$ = 10.3 Hz).

IR (neat) \nu (cm$^{-1}$): 2923, 2111, 1383, 1266, 1094, 699.

EI-HRMS (positive ion) C$_{12}$H$_{15}$F$_3$N$_3$O [M+H]$^+$: requires 274.1162; found 274.1158.
1-(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)-2-bromobenzene 9n

According to the Procedure A, m = 21.1 mg, 60% yield, colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.58-7.52 (m, 2H), 7.37 (td, $J = 7.4$ Hz and 1.1 Hz, 1H), 7.17 (td, $J = 7.6$ Hz and 1.7 Hz, 1H), 5.52 (dd, $J = 9.5$ Hz and 2.6 Hz, 1H), 2.52-2.37 (m, 2H), 1.55 (s, 3H), 1.28 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 140.1, 132.9, 129.4, 128.0, 127.9, 125.3 (q, $J = 277.1$ Hz), 121.0, 93.3, 68.6, 41.2 (q, $J = 27.5$ Hz), 26.4, 25.5.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ (ppm): -63.73 (t, $J = 10.3$ Hz).

IR (neat) $\nu$ (cm$^{-1}$): 2985, 2109, 1249, 1067, 750.

EI-HRMS (positive ion) C$_{12}$H$_7$F$_3$N$_3$OBr [M+H]$^+$: requires 352.0267; found 352.0270.
1-(1-{(2-azidopropan-2-yl)oxy}-3,3,3-trifluoropropyl)-4-chlorobenzene 9o

According to the Procedure A, m = 17.2 mg, 56% yield, colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.35 (d, $J = 8.7$ Hz, 2H), 7.30 (d, $J = 8.7$ Hz, 2H), 5.05 (dd, $J = 8.7$ Hz, $J = 4.3$ Hz, 1H), 2.67-2.56 (m, 1H), 2.37-2.27 (m, 1H), 1.52 (s, 3H), 1.27 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): 141.0, 133.9, 129.0, 127.4, 125.2 (q, $J = 278.6$ Hz), 93.4, 69.2, 42.9 (q, $J = 27.5$ Hz), 26.8, 25.6.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm): -63.55 (t, $J = 10.3$ Hz).

IR (neat) ν (cm$^{-1}$): 2964, 2108, 1492, 1376, 1245, 1122, 1014, 817.

EI-HRMS (positive ion) C$_{12}$H$_{13}$F$_3$N$_3$OCl [M+H]$^+$: requires 308.0772; found 308.0770.
1-(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)-4-(tert-butyl)benzene 9p

According to the Procedure A, m = 22.0 mg, 67% yield, colorless oil.

^1H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.38 (d, $J = 8.5$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H), 5.06 (dd, $J = 9.0$ Hz, $J = 3.8$ Hz, 1H), 2.70-2.55 (m, 1H), 2.43-2.29 (m, 1H), 1.53 (s, 3H), 1.33 (s, 9H), 1.27 (s, 3H).

^13C NMR (125 MHz, CDCl$_3$) δ (ppm): 151.0, 139.4, 125.6, 125.6, 125.5 (q, $J = 277.7$ Hz), 93.3, 69.7, 43.0 (q, $J = 27.5$ Hz), 34.6, 31.3, 26.8, 25.7.

^19F NMR (282 MHz, CDCl$_3$) δ (ppm): -63.68 (t, $J = 10.3$ Hz).

IR (neat) ν (cm$^{-1}$): 2966, 2108, 1375, 1246, 1124, 1068, 818.

EI-HRMS (positive ion) C$_{16}$H$_{23}$F$_3$N$_3$O [M+H]$^+$: requires 330.1788; found 330.1778.
1-(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)-3-methylbenzene 9q

According to the Procedure A, m = 19.2 mg, 67% yield, colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.28-7.22 (m, 1H), 7.16-7.10 (m, 3H), 5.04 (dd, $J = 9.0$ Hz, $J = 3.8$ Hz, 1H), 2.68-2.56 (m, 1H), 2.39-2.28 (m, 1H), 2.37 (s, 3H), 1.52 (s, 3H), 1.28 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): 142.5, 138.4, 128.8, 128.6, 126.5, 125.4 (q, $J = 277.7$ Hz), 123.0, 93.3, 69.9, 43.0 (q, $J = 27.5$ Hz), 26.8, 25.7, 21.4.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm): -63.68 (t, $J = 10.3$ Hz).

IR (neat) ν (cm$^{-1}$): 2990, 2107, 1380, 1251, 1113, 746.

EI-HRMS (positive ion) $C_{13}H_{16}F_3N_3ONa$ [M+Na]$^+$: requires 310.1138; found 310.1146.
4-{1-[(2-azidopropan-2-yl)oxy]-3,3-trifluoropropyl}phenyl acetate 9r

According to the Procedure A, m = 20.1 mg, 61% yield, colorless oil.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.38 (d, \(J = 8.6\) Hz, 2H), 7.11 (d, \(J = 8.6\) Hz, 2H), 5.09 (dd, \(J = 8.9\) Hz and 4.1 Hz), 2.68-2.57 (m, 1H), 2.39-2.29 (m, 1H), 2.31 (s, 3H), 1.53 (s, 3H), 1.27 (s, 3H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) (ppm): 169.3, 150.3, 140.0, 127.0, 125.3 (q, \(J = 277.7\) Hz), 121.9, 93.4, 69.3, 43.0 (q, \(J = 27.5\) Hz), 26.8, 25.7, 21.1.

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) (ppm): -63.63 (t, \(J = 10.3\) Hz).

IR (neat) \(\nu\) (cm\(^{-1}\)): 2993, 2925, 2108, 1760, 1507, 1372, 1246, 1189, 1120, 911, 817.

El-HRMS (positive ion) \(\text{C}_{14}\text{H}_{18}\text{F}_{3}\text{N}_{3}\text{O}_{3}\text{Na} [\text{M+Na}]^+\): requires 354.1036; found 354.1044.
1-(2-((2-azidopropan-2-yl)oxy)-4,4,4-trifluorobutan-2-yl)-4-chlorobenzene 9s

According to the Procedure A, m = 14.3 mg, 44% yield, colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.44-7.34 (m, 4H), 2.74-2.62 (m, 1H), 2.50-2.38 (m, 1H), 2.05 (s, 3H), 1.58 (s, 3H), 0.99 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 144.6, 133.3, 128.6, 126.0, 125.6 (q, $J = 278.6$ Hz), 93.2, 71.7, 46.5 (q, $J = 25.7$ Hz), 29.8, 27.0, 22.4.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ (ppm): -59.82 (t, $J = 10.3$ Hz).

IR (neat) $\nu$ (cm$^{-1}$): 2925, 2109, 1492, 1369, 1259, 1118, 1013, 739.

EI-HRMS (positive ion) C$_{13}$H$_{16}$F$_3$N$_3$OCl [M+H]$^+$: requires 322.0929; found 322.0919.
(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoro-2-methylpropyl)benzene 9t

According to the Procedure A, m = 15.3 mg, 58% yield, colorless oil, mixture of diastereomers, dr = 68:32.

$^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.39-7.28 (m, 5H), 5.16 (d, $J = 3.0$ Hz, 1H, dia 2), 4.89 (d, $J = 7.3$ Hz, 1H, dia 1), 2.69-2.56 (m, 1H, dia 1), 2.39-2.27 (m, 1H, dia 2), 1.54 (s, 3H, dia 2), 1.51 (s, 3H, dia 1), 1.26 (s, 3H, dia 2), 1.24 (s, 3H, dia 1), 1.13 (d, $J = 7.2$ Hz, 3H, dia 2), 0.89 (d, $J = 7.2$ Hz, 3H, dia 1).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): (CF$_3$ was not assigned) 141.8 (dia 2), 140.5 (dia 1), 128.3, 128.0 (dia 1), 127.6 (dia 2), 127.4 (dia 1), 126.3 (dia 2), 93.4 (dia 1), 93.2 (dia 2), 74.1 (dia 1), 71.8 (dia 2), 45.7 (q, $J = 27.5$ Hz, dia 2), 44.8 (q, $J = 27.5$ Hz, dia 1), 26.8, 25.7, 10 (dia 1), 6.7 (dia 2).

$^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm): -68.44 (d, $J = 8.2$ Hz), -69.92 (d, $J = 8.2$ Hz).

IR (neat) ν (cm$^{-1}$): 2991, 2109, 1388, 1259, 1118, 702.

EI-HRMS (positive ion) C$_{13}$H$_{16}$F$_3$N$_3$ONa [M+Na]$^+$: requires 310.1138; found 310.1135.
(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropane-1,2-diyl)dibenzene 9u

According to the Procedure A, m = 17.3 mg, 50% yield, colorless oil, mixture of diastereomers, dr = 92:8.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.23-7.13 (m, 6H), 7.05-7.00 (m, 4H), 5.40 (d, $J = 4.9$ Hz, 1H, dia 2), 5.25 (d, $J = 9.3$ Hz, 1H, dia 1), 3.71-3.63 (quint., $J = 9.3$ Hz, 1H, dia 1), 3.47-3.40 (dq, $J = 9.6$ Hz and 4.9 Hz, 1H, dia 2), 1.62 (s, 3H, dia 2), 1.58 (s, 3H, dia 1), 1.27 (s, 3H, dia 1), 1.22 (s, 3H, dia 2).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 140.6 (dia 1), 139.8 (dia 2), 132.6, 129.5, 128.3, 128.2, 127.9, 127.7, 127.4, 126.1 (q, $J = 277.1$ Hz), 93.8 (dia 2), 93.5 (dia 1), 75.2, 57.5 (q, $J = 25.7$ Hz), 27.0 (dia 1), 26.9 (dia 2), 25.9 (dia 2), 25.6 (dia 1).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ (ppm): -62.99 (d, $J = 8.2$ Hz), -65.03 (d, $J = 10.3$ Hz).

IR (neat) $\nu$ (cm$^{-1}$): 3036, 2994, 2111, 1265, 1251, 1115, 734.

EI-HRMS (positive ion) C$_{18}$H$_{19}$F$_3$N$_3$O [M+H]$^+$: requires 350.1475; found 350.1466.
1-((2-azidopropan-2-yl)oxy)-2-(trifluoromethyl)-2,3-dihydro-1H-indene 9v

According to the Procedure A, m = 14.9 mg, 51% yield, colorless oil, mixture of diastereomers, cis/trans = 52:48.

$^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.47-7.44 (m, 1H), 7.35-7.26 (m, 3H), 5.50 (d, $J = 2.7$ Hz, 1H, cis), 5.50 (d, $J = 6.4$ Hz, 1H, trans), 3.44-3.33 (m, 2H), 3.16-3.04 (m, 2H), 1.64 (s, 3H, cis or trans), 1.61 (s, 3H, cis or trans), 1.59 (s, 3H, cis or trans), 1.58 (s, 3H, cis or trans).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): (CF$_3$ was not assigned) 141.2 (cis or trans), 141.1 (cis or trans), 140.9 (cis or trans), 140.3 (cis or trans), 129.2 (cis or trans), 128.8 (cis or trans), 127.6 (cis or trans), 127.3 (cis or trans), 125.5 (cis or trans), 124.9 (cis or trans), 124.6 (cis or trans), 124.6 (cis or trans), 93.3 (cis or trans), 93.2 (cis or trans), 75.0, 50.7 (q, $J = 25.7$ Hz, cis), 48.0 (q, $J = 25.7$ Hz, trans), 31.0 (cis or trans), 30.9 (cis or trans), 27.0, 25.8 (cis or trans), 24.9 (cis or trans).

$^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm): -65.53 (d, $J = 10.3$ Hz, dia 2), -70.12 (d, $J = 10.3$ Hz, dia 1).

IR (neat) ν (cm$^{-1}$): 2995, 2963, 2109, 1264, 1105, 749.

EI-HRMS (positive ion) C$_{13}$H$_{15}$F$_3$N$_3$O [M+H]$^+$: requires 286.1162; found 286.1169.
2-((2-azidopropan-2-yl)oxy)-3-(trifluoromethyl)tetrahydro-2H-pyran 9w

![Chemical Structure](image)

m = 5.1 mg, 60% yield, colourless oil, mixture of diastereomers, cis/trans = 64:36

**1H NMR (500 MHz, CDCl₃) δ (ppm):** 5.46 (d, J = 2.8 Hz, 1H, cis), 5.05 (d, J = 6.3 Hz, 1H, trans), 4.02-3.99 (m, 1H, trans), 3.95-3.90 (m, 1H, cis), 3.66-3.63 (m, 1H, cis), 3.58-3.53 (m, 1H, trans), 2.51-2.44 (m, 1H, cis), 2.32-2.25 (m, 1H, trans), 2.15-2.11 (m, 1H, trans), 2.02-1.95 (m, 1H, cis), 1.85-1.69 (m, 3H), 1.54 (s, 3H, trans), 1.53 (s, 3H, cis), 1.52 (s, 3H, cis), 1.51 (s, 3H, trans).

**13C NMR (125 MHz, CDCl₃) δ (ppm):** 126.0 (q, J = 277.7 Hz, trans), 125.6 (q, J = 277.7 Hz, cis), 93.0 (cis), 92.7 (trans), 88.8 (cis), 88.8 (trans), 63.7 (trans), 59.3 (cis), 44.6 (q, J = 26.6 Hz, cis), 44.2 (q, J = 26.6 Hz, trans), 26.8 (trans), 26.7 (cis), 25.9 (trans), 25.5 (cis), 24.1 (cis), 22.7 (trans), 20.9 (trans), 17.4 (cis).

**19F NMR (282 MHz, CDCl₃) δ (ppm):** -68.25 (d, J = 8.8 Hz, trans), -70.08 (d, J = 8.2 Hz, cis).

**IR (neat) ν (cm⁻¹):** 2928, 2111, 1264, 1120, 896, 747.

**EI-HRMS (positive ion) C₉H₁₄F₃N₃O₂Na [M+Na]⁺:** requires 276.0930; found 276.0930.
2-methyl-2-(3,3,3-trifluoro-1-(naphthalen-2-yl)propoxy)propanenitrile 9x

According to the Procedure A**, m = 18.0 mg, 59% yield, colourless oil.

$^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.91-7.84 (m, 4H), 7.56-7.49 (m, 3H), 5.24 (dd, $J = 9.0$ Hz and 3.8 Hz), 2.83-2.72 (m, 1H), 2.55-2.38 (m, 1H), 1.70 (s, 3H), 1.36 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm): 138.2, 133.4, 133.2, 129.0, 128.0, 127.8, 126.6, 126.5, 125.5, 125.3 (q, $J = 283.6$ Hz), 123.5, 120.2, 73.5 (q, $J = 3.3$ Hz), 71.3, 43.0 (q, $J = 28.0$ Hz), 28.2, 27.9.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm): -63.38 (t, $J = 10.3$ Hz).

IR (neat) ν (cm$^{-1}$): 2993, 2943, 2100, 1383, 1251, 1130, 747.

EI-HRMS (positive ion) C$_{17}$H$_{17}$F$_3$NO [M+H]$^+$: requires 308.1257; found 308.1246.
IV. NMR Spectra of Compounds 9a to 9v

2-(1-(1-azido-3-phenylpropoxy)-3,3,3-trifluoropropyl)naphthalene 9a
2-(1-(1-azidoethoxy)-3,3,3-trifluoropropyl)naphthalene 9b
2-(1-azidopropoxy)-3,3,3-trifluoropropyl)naphthalene 9c
2-(1-(azidobutoxy)-3,3,3-trifluoropropyl)naphthalene 9d
2-((1-azidoctyl)oxy)-3,3,3-trifluoropropyl)naphthalene 9e
((5-azido-5-(3,3,3-trifluoro-1-(naphthalen-2-yl)propoxy)pentyl)oxy)(tert-butyl)dimethylsilane 9f
2-(1-azido-2-(4-bromophenyl)ethoxy)-3,3,3-trifluoropropyl)naphthalene 9g
2-(1-(1-azido-3-methylbutoxy)-3,3,3-trifluoropropyl)naphthalene 9h
2-(1-(azido(cyclohexyl)methoxy)-3,3,3-trifluoropropyl)naphthalene 9i
2-(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)naphthalene 9j
(1-((3-azidopentan-3-yl)oxy)-3,3,3-trifluoropropyl)naphthalene 9k
2-(1-(1-azidocyclobutoxy)-3,3,3-trifluoropropyl)naphthalene 9l
(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)benzene 9m
(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)-2-bromobenzene 9n
1-(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)-4-chlorobenzene 9o
1-((1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)-4-(tert-butyl)benzene

"1-((1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)-4-(tert-butyl)benzene"
1-(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)-3-methylbenzene 9q
4-(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropyl)phenyl acetate 9r
1-(2-((2-azidopropan-2-yl)oxy)-4,4-trifluorobutan-2-yl)-4-chlorobenzene 9s
(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoro-2-methylpropyl)benzene 9t
(1-((2-azidopropan-2-yl)oxy)-3,3,3-trifluoropropane-1,2-diyl)dibenzene 9u
1-((2-azidopropan-2-yl)oxy)-2-(trifluoromethyl)-2,3-dihydro-1H-indene 9v
2-((2-azidopropan-2-yl)oxy)-3-(trifluoromethyl)tetrahydro-2H-pyran 9w
2-methyl-2-(3,3,3-trifluoro-1-(naphthalen-2-yl)propoxy)propanenitrile 9x
V. Luminescence Quenching Experiments

Rates of quenching ($k_q$) were determined using Stern-Volmer kinetics:

$$\frac{I_0}{I} = k_q \tau_0 [\text{quencher}] + 1$$

Where $I_0$ is the luminescence intensity without the quencher, $I$ is the intensity with the quencher, and $\tau_0$ is the excited state lifetime of the photocatalyst (8.55 x 10^{-7} s for Ru(bpy)$_3^{2+}$ in MeCN at 25°C).

The following stock solutions were prepared in distilled CH$_2$Cl$_2$ and degassed by three freeze-pump-thaw cycles.

General procedure: A stock solution of 4a was prepared by dissolving Ru(bpy)$_3$(PF$_6$)$_2$ (21.4 mg, 25 µmol) in 10 mL of CH$_2$Cl$_2$. Of this solution, 0.1 mL were further diluted with CH$_2$Cl$_2$ to give a total volume of 10 mL. Concentration of [4a] = 2.5 x 10^{-5} M.

A stock solution of Umemoto’s reagent 3 was prepared by dissolving 3 (10.2 mg, 30 µmol) in 10 mL of CH$_2$Cl$_2$. Concentration of [3] = 3 x 10^{-3} M.

A stock solution of alcene 8a was prepared by dissolving 8a (4.6 mg, 30 µmol) in 10 mL of CH$_2$Cl$_2$. TMSN$_3$ (17.3 mg, 5 equiv) and 7a (24.2 mg, 6 equiv) were added. Concentration of [8a] = 3 x 10^{-3} M.

For each experiment, 6 samples were prepared in the dark. Quartz cuvettes (3.5 mL) were filled with photocatalyst stock solution (0.3 mL), reagent stock solution (0 mL, 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL, 1.0 mL) and CH$_2$Cl$_2$ (2.7 mL, 2.5 mL, 2.3 mL, 2.1 mL, 1.9 mL, 1.7 mL) to obtain a total volume of 3 mL. The final concentrations were [4a] = 2.5 x 10^{-6} M and [quencher] = 2 x 10^{-4} M, 4 x 10^{-4} M, 6 x 10^{-4} M, 8 x 10^{-4} M, 12 x 10^{-3} M. For each sample, emission spectra were acquired between 520 nm and 750 nm (excitation at 452 nm).

Figure S1. Stern-Volmer plots ($I_0/I = f([\text{quencher}])$) for 3 and 8a+7a+2. For Umemoto’s reagent 3, $k_q$ = 4.11 x 10^{5} M^{-1}.s^{-1}$.
VI. ST/EPR Studies

The method of spin trapping (ST) followed by an electron paramagnetic resonance (EPR) detection was employed to characterize radical intermediates formed during the reaction. In this technique, a short-lived free radical adds to a diamagnetic spin trap (typically an aldonitrone or a nitroso compound) thereby yielding a much more stable paramagnetic spin adduct (a nitroxide radical) detectable by conventional EPR spectroscopy. Analyzing the spin adduct EPR spectrum provides structural information about the addend.

In a standard experiment, the medium was prepared in microtubes and deoxygenated. An aliquot (ca. 50µL) was then transferred in a capillary tube and irradiated directly into the EPR cavity with a blue LED. All the experiments were performed in triplicate. EPR assays were carried out at room temperature on a Bruker EMX spectrometer operating at X-band with 100 kHz modulation frequency and equipped with an NMR gaussmeter for magnetic field calibration. The following conditions were used: non-saturating microwave power, 10 mW; modulation amplitude, 1 G; receiver gain, 5x10⁵; 4 scans. For all the paramagnetic species detected, the hyperfine coupling constant values were determined after standard simulations of the experimental EPR signals using the WinSim software.

Our goal was to detect the radicals formed after irradiating with blue LED light a solution containing Umemoto’s reagent and the photocatalyst Ru(bpy)₃(PF₆)₂ in DCM, both in the absence and in the presence of 2-vinylnaphtalene. For this purpose, the following ST/EPR experiments were performed using the commercially available 2-methyl-2-nitrosopropane (MNP, Sigma-Aldrich) as spin trap. The spin adduct EPR spectra obtained always show at least 3 lines, due to hyperfine coupling of the unpaired electron with the nitrogen nucleus, eventually split by couplings with nonzero spin nuclei in α- or β-position towards the nitroxide group.

![Scheme S1: Spin trapping of a radical •R by the nitroso compound MNP](image)

In a first step, a deoxygenated DCM solution containing Umemoto’s reagent (75 mmol.L⁻¹), Ru(bpy)₃(PF₆)₂ (2.5 mmol.L⁻¹) and MNP (50 mmol.L⁻¹) was EPR analyzed. No spin adduct was ever detected in the absence of light. Under blue LED irradiation, the intense EPR spectrum shown in figure x1 was recorded. It shows six lines with 1-4-7-7-4-1 relative intensities, due to hyperfine couplings with the nitroxide nitrogen (I=1, a_N = 12.2 G) and three equivalent fluorine nuclei (I=1/2, a_F = 12.3 G, 3F) in β-position towards this nitrogen, and could be undoubtedly assigned to the MNP/•CF₃ spin adduct. Blank tests performed in the absence of one of the components (i.e. Umemoto’s reagent or Ru(bpy)₃(PF₆)₂ or MNP) never yielded any EPR signal.
In a second step, we aimed at detecting the radical formed after addition of the radical •CF_3 on 2-vinylnaphtalene. Our first attempts performed under standard conditions (75 mmol.L^-1 Umemoto’s reagent, 2.5 mmol.L^-1 Ru(bpy)_3(PF_6)_2, 50 mmol.L^-1 MNP and 50 mmol.L^-1 2-vinylnaphtalene) only yielded the spin adduct MNP/•CF_3. To overcome this issue, the MNP concentration was decreased to 20 mmol.L^-1 while 2-vinylnaphtalene and Umemoto’s reagent concentrations were raised to 100 mmol.L^-1 and 120 mmol.L^-1, respectively. Blue LED irradiation of this new medium led us to record the spectrum given in figure S2. It shows 6 lines of equal intensity due to hyperfine couplings with the nitrogen (a_N = 14.8 G) and a β-hydrogen nuclei (a_H = 2.9 G), and obviously correspond to a spin adduct obtained after trapping a radical centered on a secondary carbon. It could thus reasonably be assigned to the nitroxide generated after trapping the radical intermediate 13 (see scheme 5, with R_1 = 2-naphtalene and R^2=R^3=H), formed by addition of •CF_3 on 2-vinylnaphtalene. Blank tests performed in the absence of one of the components (i.e. Umemoto’s reagent or Ru(bpy)_3(PF_6)_2 or MNP) or before blue LED irradiation never yielded any EPR signal.
Figure S3: Experimental EPR spectrum of the spin adduct formed after trapping a radical intermediate centered on a secondary carbon atom (black lines) and its superimposed simulation (red dotted lines): $a_N = 14.8$ G and $a_H = 2.9$ G.

In conclusion, the ST/EPR experiments allowed us to characterize the two radical intermediates described in scheme 5 and support the mechanism postulated.
VII. Procedures for Control Experiments

Procedure B: Typical procedure for the formation of trimethylsilylated azohydrin 12a in presence of aldehyde 7a and TMSN₃.

A NMR tube was charged with hydrocinnamaldehyde 7a (80 µL, 0.6 mmol, 1.2 equiv), TMSN₃ 2 (66 µL, 0.5 mmol, 5 equiv) and Umemoto’s reagent 3 (51.0 mg, 0.15 mmol, 1.5 equiv). Finally, it was dissolved in 0.5 mL of CDCl₃. The solution was stirring at RT for 24 h. A crude ¹H NMR was perform to observed the formation of the trimethylsilylated azohydrin 12a.

Procedure C: Typical procedure for the formation of trimethylsilylated azohydrin 12b.

A mixture of butyraldehyde 7b (1.25 mL, 13.9 mmol, 1 equiv), TMSN₃ 2 (3.7 mL, 27.8 mmol, 2 equiv), NaN₃ (90.4 mg, 1.39 mmol, 0.1 equiv) and 15-crown-5 (154.2 mg, 0.7 mmol, 0.05 equiv) was stirred without solvent at RT during 24 h. After evaporation of unreacted TMSN₃, aqueous NaHCO₃ is added and the solution was extracted with CH₂Cl₂ and the combined organicphase was dried with MgSO₄. The solvent was evaporated under vaccum and the residu was purify by flash chromatography on silica gel (Heptane) to afford the corresponding pure trimethylsilylated azohydrin 12b in 50% yield (1.3 g).

Procedure D: Typical procedure for the trifluoromethylation of alkenes 8a from the trimethylsilylated azohydrin 12b.

A flame tube under argon atmosphere was charged with the vinylnaphtalene 8a (15.4 mg, 0.1 mmol, 1 equiv), Umemoto’s reagent 3 (51.0 mg, 0.15 mmol, 1.5 equiv), Ru(bpy)₃(PF₆)₂ 4a (4.4 mg, 0.005 mmol, 0.05 equiv). Then, it was dissolved in 2 mL of distilled DCM and the trimethylsilylated azohydrin 12b (0.15 or 0.5 mmol, 1.5 or 5 equiv) was added. The solution was then irradiated with blue LEDs at RT for 2.5 h under inert atmosphere. The solvent was removed in vacuo. The crude ¹H NMR revealed only a complex mixture without formation of the product 9d.
VIII. NMR Data and Spectra of Compound 12b

(1-azidobutoxy)trimethylsilane 12b

According to the Procedure C, m = 13.1 mg, 50% yield, colorless oil.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): \(4.73\) (t, \(J = 5.9\) Hz, 1H), 1.72 – 1.54 (m, 2H), 1.48 – 1.31 (m, 2H), 0.93 (t, \(J = 7.3\) Hz, 3H), 0.25 – 0.06 (m, 9H).