Electronic Supplementary Information

Visible-light-induced oxidative difunctionalization of styrenes: synthesis of α -trifluoromethylthio-substituted ketones

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I. Biologically active α -SCF₃-substituted ketones



II. Control experiments^{*a*}

	green LED $\frac{1}{\lambda} = 535 \text{ nm}$ $\frac{1}{\lambda}$ eosin Y 2 mol%	O SCF3
1a	air (O ₂) CF ₃ SO ₂ Na CS ₂	2a

Entry	Visible light	Eosin Y	Air	CS ₂	Yield (%) ^b
					2a
1	_	+	+	+	Zero
2	+	-	+	+	Zero
3	+	+	-	+	Zero ^c
4	+	+	+	_	Zero
5	+	+	+	+	67 ^d
6	+	+	+	+	67 ^e
7	+	+	O ₂	+	76 ^f
8	+	+	+	+	Zero ^g
9	+	+	+	+	76 ^{<i>h</i>}

^{*a*} Reaction conditions: **1** (1.0 mmol), CF₃SO₂Na (3.0 equiv.), CS₂ (3.0 equiv.), eosin Y (2 mol%) in DMSO (3 mL) irradiated using Luxeon Rebel high power green LED [2.50 W, λ = 535 nm] in open air at rt for 10 h, (+) sign indicates the presence & (–) sign indicates the absence. ^{*b*} Isolated product yield. ^{*c*} Reaction under N₂ atmosphere. ^{*d*} Reaction using white LED (7 W). ^{*e*} Reaction using green LED (3.0 W). ^{*f*} Reaction under O₂ (balloon). ^{*g*} Reaction quenched by TEMPO (3.0 equiv.). ^{*h*} Reaction conducted with DABCO (3.0 equiv.).

- **III. General Information:** All commercially available reagents were used without further purification unless otherwise specified by a reference. Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glassware. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates. Melting points (m. p.) were determined by open glass capillaries and are uncorrected. ¹H (500 MHz), ¹³C (125.7 MHz) & ¹⁹F (470 MHz) NMR spectra were recorded on a Bruker AVII spectrometer in CDCl₃ using TMS as internal reference. All chemical shifts are reported in δ /ppm and coupling constants (*J*) in Hertz (Hz). Green LED (2.50 W, λ = 535 nm) Rebel LED, mounted on a 25 mm cool base was purchased from commercial supplier Luxeon Star LEDs Quadica Developments Inc. 47 6th Concession Rd. Brantford, Ontario N 32 5L7 Canada. The quantum yield of the reaction was determined using Shimadzu UV-1601 and Perkin Elmer LS 55 Fluorescence spectrophotometer in EtOH solvent.
- **IV.** General procedure for the synthesis of the products **2**: To a mixture of CF_3SO_2Na (3.0 equiv.), CS_2 (3.0 equiv.), eosin Y (2.0 mol %), and styrene **1** (1.0 mmol) in DMSO (3mL) stirred under open air, irradiated with Luxeon Rebel high power green LED [2.50 W, $\lambda = 535$ nm] at room temperature for 10-12 h. After the completion of reaction (as indicated by TLC), it was quenched with water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The organic phase was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography using a mixture of EtOAc-Hexane (1:50) to give the pure product **2** in high yields.

The structure of the products was confirmed by the comparison of ${}^{1}H$, ${}^{13}C$ & ${}^{19}F$ NMR data with those reported in the literature.

Spectral data of compounds **2** are summarised below with relevant references:¹

- V. Spectral data of the products 2:
- (i) 1-Phenyl-2-((trifluoromethyl)thio)ethanone (2a):¹



Isolated as a yellow oily liquid. ¹H NMR (500 MHz, CDCl₃): δ = 7.95 (d, *J* = 8.5 Hz, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.53 (q, *J* = 8.0 Hz, 3H), 3.83 (q, ⁴*J*_{H-F} = 9.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ = 189.7 (s), 135.8 (s), 134.2 (s), 129.0 (s), 128.4 (s), 127.3 (q, ¹*J*_{C-F} = 276.6 Hz), 42.5 (q, ³*J*_{C-F} = 27.2 Hz). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.9 (s, 3F).

(ii) 1-(*p*-Tolyl)-2-((trifluoromethyl)thio)ethanone (2b):¹



Isolated as a yellow oily liquid. ¹H NMR (500 MHz, CDCl₃): δ = 7.84 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.79 (q, ⁴*J*_{H-F} = 9.5 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ = 189.3 (s), 143.3 (s), 133.4 (s), 129.6 (s), 129.6 (s), 129.2 (q, ¹*J*_{C-F} = 289.6 Hz), 128.5(s), 42.3 (q, ³*J*_{C-F} = 28.1 Hz), 21.7 (s). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.9 (s, 3F).

(iii) 1-(4-Ethoxyphenyl)-2-(trifluoromethylthio)ethanone (2c):



Isolated as a yellow solid (m. p. 58–60 °C). ¹H NMR (500 MHz, CDCl₃): δ = 7.90 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.12 (q, ⁴*J*_{H-F} = 9.5 Hz, 2H), 3.76 (q, *J* = 9.5 Hz, 2H), 1.46 (t, *J* = 9.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ = 190.9 (s), 163.8 (s), 132.0 (s), 130.8 (q, ¹*J*_{C-F} = 276.7 Hz), 120.9, 114.5 (s), 64.0 (s), 42.2 (q, ³*J*_{C-F} = 27.1 Hz), 14.6 (s). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.9 (s, 3F).

(iv) 1-(4-*tert*-Butylphenyl)-2-(trifluoromethylthio)ethanone (2d):¹



Isolated as a yellow oily liquid. ¹H NMR (500 MHz, CDCl₃): δ = 7.88 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H) 7.55 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 3.80 (q, ⁴*J*_{H-F} = 9.5 Hz, 2H), 1.34 (s, 9H). ¹³C NMR (126 MHz, CDCl₃): δ = 192.1 (s), 158.2 (s), 129.7, 128.4 (s), 127.4 (q, ¹*J*_{C-F} = 276.4 Hz), 125.9(s), 42.3 (q, ³*J*_{C-F} = 27.9 Hz), 35.3 (s), 31.0 (s). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.8 (s, 3F).

(v) 1-*m*-Tolyl-2-(trifluoromethylthio)ethanone (2e):¹



Isolated as a yellow oily liquid. ¹H NMR (500 MHz, CDCl₃): δ = 7.67 (s, 1H), 7.33 (dd, J = 8.0 Hz, 11.0 Hz, 1H), 7.37 (ddd, J = 8.0 Hz, 2.1 Hz, 1.1 Hz, 1H), 7. 33 (t, J = 7.9 Hz, 1H), 3.73 (q, ⁴J_H. _F = 9.5 Hz, 2H), 2.35 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ = 193.3 (s), 139.6 (s), 136.0 (s), 135.7 (s), 134.3 (s), 130.7 (s), 129.6 (s), 129.5 (q, ${}^{1}J_{C-F}$ = 276.4 Hz), 43.2 (q, ${}^{3}J_{C-F}$ = 27.9 Hz), 22.0 (s). ${}^{19}F$ NMR (470 MHz, CDCl₃): δ = -61.9 (s, 3F).

(vi) 1-(4-Chlorophenyl)-2-((trifluoromethyl)thio)ethanone (2f):¹



Isolated as a yellow solid (m. p. 56–57 °C). ¹H NMR (500 MHz, CDCl₃): δ = 7.87 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 2H), 3.81 (q, ⁴*J*_{H-F} = 9.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ = 188.6 (s), 140.9 (s), 134.1 (s), 129.7 (s), 129.3 (s), 127.2 (q, ¹*J*_{C-F} = 276.7 Hz), 42.4 (q, ³*J*_{C-F} = 29.0 Hz). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.9 (s, 3F).

(vii) 1-(4-Bromophenyl)-2-(trifluoromethylthio)ethanone (2g):¹



Isolated as a reddish solid (m. p. 80–82 °C). ¹H NMR (500 MHz, CDCl₃): δ = 7.80 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 3.79 (q, ⁴*J*_{H-F} = 9.4 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ = 187.7 (s), 133.4 (s), 131.3 (s), 131.0 (q, ¹*J*_{C-F} = 279.3 Hz), 128.6 (s), 121.6 (s), 41.4 (q, ³*J*_{C-F} = 29.0 Hz). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.8 (s, 3F).

(viii) 1-(4-Fluorophenyl)-2-((trifluoromethyl)thio)ethanone (2h):¹



Isolated as yellow oily liquid. ¹H NMR (500 MHz, CDCl₃): δ = 7.91 (dd, *J* = 6.0, 5.0 Hz, 2H), 7.19–7.08 (m, 2H), 3.73 (q, ⁴*J*_{H-F} = 10.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ = 188.1 (s), 167.4 (d, ¹*J*_{C-F} = 256.9 Hz), 132.3 (d, ³*J*_{C-F} = 146.9 Hz), 131.2 (s), 127.2 (q, ¹*J*_{C-F} = 276.7 Hz), 116.3 (d, ²*J*_{C-F} = 21.8 Hz), 42.5 (q, ³*J*_{C-F} = 28.6 Hz). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.9 (s, 3F), -102.7 (s, 1F).

(ix) 1-(3-Chlorophenyl)-2-[(trifluoromethyl)sulfanyl]ethan-1-one (3i):¹



Isolated as a yellow oily liquid. ¹H NMR (500 MHz, CDCl₃): δ = 7.84 (s, 1H), 7.74 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 3.73 (q, ⁴*J*_{H-F} = 9.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ = 193.0, 137.3, 135.5, 134.2 (s), 130.5 (q, ¹*J*_{C-F} = 276.8 Hz), 130.3 (s), 127.8 (s), 126.4 (s), 42.7 (q, ³*J*_{C-F} = 32.6 Hz). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.9 (s, 3F).

(x) 1-(3-Bromophenyl)-2-(trifluoromethylthio)ethanone (3j):¹



Isolated as a yellow oily liquid. ¹H NMR (500 MHz, CDCl₃): $\delta = 8.06$ (s, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.9 Hz, 1H), 3.80 (q, ⁴ $J_{H-F} = 9.5$ Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): $\delta = 188.5$ (s), 137.4 (s), 137.1 (s), 131.4 (s), 130.5 (s), 128.1 (s), 126.9 (s), 126.2 (q, ¹ $J_{C-F} = 283.1$ Hz), 42.6 (q, ³ $J_{C-F} = 27.7$ Hz). ¹⁹F NMR (470 MHz, CDCl₃): $\delta = -61.9$ (s, 3F).

(xi) 1-(2-Chlorophenyl)-2-(trifluoromethylthio)ethanone (3k):¹



Isolated as a yellow oily liquid. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.55$ (t, ² $J_{H-H} = 2.0$ Hz, 1H), 7.46 (dd, ² $J_{H-H} = 5.0$ Hz, 2.0 Hz, 2H), 7.39 (ddd, ³ $J_{H-H} = 1.1$ Hz, 2.1 Hz, 8.0 Hz, 1H), 3.89 (q, ⁴ $J_{H-F} = 9.5$ Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): $\delta = 192.4$ (s), 137.7 (s), 133.0 (s), 131.2 (s), 138.8 (s), 129.7 (s), 127.3 (s), 126.9 (q, ³ $J_{C-F} = 277.6$ Hz), 46.5 (q, ¹ $J_{C-F} = 26.7$ Hz). ¹⁹F NMR (470 MHz, CDCl₃): $\delta = -62.08$ (s, 3F).

(xii) 1-(4-Nitrophenyl)-2-(trifluoromethylthio)ethanone (3I):¹



Isolated as a yellow solid (m. p. 101–102 °C). ¹H NMR (500 MHz, CDCl₃): δ = 8.38 (d, *J* = 8.5 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 2H), 3.89 (q, ⁴*J*_{H-F} = 9.5, 2H). ¹³C NMR (126 MHz, CDCl₃): δ = 188.4 (s), 151.0 (s), 140.0 (s), 129.5 (s), 126.8 (q, ¹*J*_{C-F} = 277.2 Hz), 124.2 (s), 43.1 (q, ³*J*_{C-F} = 28.6 Hz). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.8 (s).

(xiii) 4-(2-(Trifluoromethylthio)acetyl)benzonitrile (2m):¹



Isolated as a white solid (m. p. 130–132 °C). ¹H NMR (500 MHz, CDCl₃): δ = 7.79 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.5 Hz, 2H), 3.78 (q, ⁴J_{H-F} = 10.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ =

188.6 (s), 138.5 (s), 132.8 (s), 132.5 (s), 128.8 (s), 126.9 (q, ${}^{1}J_{C-F} = 277.2 \text{ Hz}$), 116.8 (s), 42.8 (q, ${}^{3}J_{C-F} = 28.9 \text{ Hz}$). ${}^{19}\text{F}$ NMR (470 MHz, CDCl₃): $\delta = -61.8$ (s, 3F).

(xiv) Acetic acid 4-(2-trifluoromethylsulfanyl-acetyl)-phenyl ester (2n):



Isolated as a white solid (m. p. 81–82 °C). ¹H NMR (500 MHz, CDCl₃): δ = 7.98 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.80 (q, ⁴*J*_{H-F} = 10.0, 2H), 2.33 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ = 188.4 (s), 168.6 (s), 155.1 (s), 133.3 (s), 130.0 (s), 127.4 (q, ¹*J*_{C-F} = 276.7 Hz), 122.2 (s), 42.4 (q, ³*J*_{C-F} = 28.5 Hz), 21.1 (s). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.8 (s).

(xv) 1-(Naphthalen-2-yl)-2-((trifluoromethyl)thio)ethanone (2o):¹



Isolated as a yellow solid (m. p. 87–88 °C). ¹H NMR (500 MHz, CDCl₃): δ = 8.34 (s, 1H), 7.94-7.90 (m, 2H), 7.86–7.81 (m, 2H), 7.59 (dq, *J* = 1.5 Hz, 1.5 Hz, 7.0 Hz, 2H), 4.67 (q, ⁴*J*_{H-F} = 10.0, 2H). ¹³C NMR (126 MHz, CDCl₃): δ = 189.6 (s), 136.0 (s), 133.2 (s), 132.3 (s), 130.6 (q, ¹*J*_{C-F} = 276.8 Hz), 127.9 (s), 127.2 (s), 126.7 (s), 125.2 (s), 123.5 (s), 123.2 (s), 123.0 (s), 42.5 (q, ³*J*_{C-F} = 28.1 Hz). ¹⁹F NMR (470 MHz, CDCl₃): δ = -61.8 (s, 3F).

(xvi) 1,2-Diphenyl-2-(trifluoromethylthio)ethanone (2p):



Isolated as a yellow solid (m. p. 128–130 °C). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.90$ (s, 1H), 7.42–7.40 (m, 2H), 7.36–7.32 (m, 5H), 7.17–7.15 (m, 2H), 4.54 (q, ⁴J_{H-F} = 9.5 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃): $\delta = 197.1$ (s), 153.3 (s), 140.7 (s), 131.3 (s), 130.2 (q, ¹J_{C-F} = 272.6 Hz), 129.3 (s), 128.8 (s), 128.4 (s), 128.3 (s), 127.7 (s), 56.0 (q, ³J_{C-F} = 27.9 Hz). ¹⁹F NMR (470 MHz, CDCl₃): $\delta = -65.4$ (s, 3F).

(xvii) 1-(3-Methoxyphenyl)-2-((trifluoromethyl)thio)ethanone (2q):¹



Isolated as a yellow oily liquid. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.49$ (d, J = 7.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 1H), 7.18 (d, J = 9.0 Hz, 1H), 3.87 (s, 3H), 3.81 (q, J = 10.0 Hz 2H). ¹³C NMR (126 MHz, CDCl₃): $\delta = 189.5$ (s), 160.0 (s), 137.1 (s), 129.9 (q, J = 263.2 Hz), 127.1 (s), 120.9 (s), 120.7 (s), 112.4 (s), 55.5 (s), 42.5 (q, J = 28.0 Hz). ¹⁹F NMR (470 MHz, CDCl₃): $\delta = -61.9$ (s, 3F).

VI. References: 1 (a) S. Alazet, E. Ismalaj, Q. Glenadel, D. L. Bars and T. Billard, Eur. J. Org. Chem. 2015, 4607; (b) Y. Huang, X. He, X. Lin, M. Rong and Z. Weng, Org. Lett. 2014, 16, 3284.

VII. Copies of ¹H, ¹³C & ¹⁹F NMR spectra.

Compound 2a. ¹H NMR Spectrum (CDCl₃).





Compound 2a. ¹³C NMR Spectrum (CDCl₃).



Compound 2a.¹⁹F NMR Spectrum (CDCl₃).





Compound 2b. ¹H NMR Spectrum (CDCl₃).





Page 14 **Compound 2b.** ¹³C NMR Spectrum (CDCl₃).





Compound 2b. ¹³F NMR Spectrum (CDCl₃).





Compound 2c. ¹H NMR Spectrum (CDCl₃).





Compound 2c. ¹³C NMR Spectrum (CDCl₃).





Compound 2c. ¹⁹F NMR Spectrum (CDCl₃).





Compound 2d. ¹H NMR Spectrum (CDCl₃).





Compound 2d. ¹³C NMR Spectrum (CDCl₃).



Compound 2d. ¹⁹F NMR Spectrum (CDCl₃).





Compound 2e. ¹H NMR Spectrum (CDCl₃).





Page 23 **Compound 2e.** ¹³C NMR Spectrum (CDCl₃).





Compound 2e.¹⁹F NMR Spectrum (CDCl₃).





Page 25 **Compound 2f.** ¹H NMR Spectrum (CDCl₃).





Compound 2f.¹³C NMR Spectrum (CDCl₃).





Compound 2f.¹⁹F NMR Spectrum (CDCl₃).







Compound 2g. ¹H NMR Spectrum (CDCl₃).





Compound 2g. ¹³C NMR Spectrum (CDCl₃).





Compound 2g.¹⁹F NMR Spectrum (CDCl₃).





Page 31 **Compound 2h.** ¹H NMR Spectrum (CDCl₃).





Compound 2h. ¹³C NMR Spectrum (CDCl₃).





Compound 2h.¹⁹F NMR Spectrum (CDCl₃).





Compound 2i.¹³C NMR Spectrum (CDCl₃).





Compound 2i.¹³C NMR Spectrum (CDCl₃).



Compound 2i.¹⁹F NMR Spectrum (CDCl₃).





Compound 2j. ¹H NMR Spectrum (CDCl₃).





Compound 2j.¹³C NMR Spectrum (CDCl₃).





Compound 2j. ¹⁹F NMR Spectrum (CDCl₃).





Page 40 **Compound 2k.** ¹H NMR Spectrum (CDCl₃).





Page 41 **Compound 2k.** ¹³C NMR Spectrum (CDCl₃).





Compound 2k. ¹⁹F NMR Spectrum (CDCl₃).





Compound 2I. ¹H NMR Spectrum (CDCl₃).





Compound 21. ¹³C NMR Spectrum (CDCl₃).





Compound 2I. ¹⁹F NMR Spectrum (CDCl₃).





Compound 2m. ¹H NMR Spectrum (CDCl₃).





Compound 2m.¹³C NMR Spectrum (CDCl₃).



Compound 2m. ¹⁹F NMR Spectrum (CDCl₃).





Compound 2n. ¹H NMR Spectrum (CDCl₃).







Compound 2n. ¹³C NMR Spectrum (CDCl₃).





Compound 2n.¹⁹F NMR Spectrum (CDCl₃).





Compound 20. ¹H NMR Spectrum (CDCl₃).





Compound 20. ¹³C NMR Spectrum (CDCl₃).



Compound 20. ¹⁹F NMR Spectrum (CDCl₃).





Compound 2p. ¹H NMR Spectrum (CDCl₃).







Compound 2p. ¹³C NMR Spectrum (CDCl₃).





Compound 2p. ¹⁹F NMR Spectrum (CDCl₃).





Compound 2q. ¹H NMR Spectrum (CDCl₃).





Compound 2q. ¹³C NMR Spectrum (CDCl₃).





Compound 2q.¹⁹F NMR Spectrum (CDCl₃).





VIII. UV-Vis and Fluorescence spectra of the representative reaction 1a to 2a:





$$\phi_s = 0.67 \times \frac{15776.89}{22552.88} \times \frac{105.85}{429.04} \left(\frac{1.35}{1.32}\right)^2$$