SUPPORTING INFORMATION

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1. General information.

Unless otherwise noted, all reactions were heated on hot plates with oil baths calibrated to an external thermometer. Prior to starting experiments, the hot plate was turned on, and the oil bath was allowed to equilibrate to the desired temperature over 30 minutes.

¹H and ¹⁹F NMR (CFCl₃ as outside standard and low field is positive) spectra were recorded on a Bruker AM 400 spectrometer. ¹³C NMR spectra were recorded on a Bruker AM 400 spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The NMR yield was determined by ¹⁹F NMR using fluorobenzene as an internal standard before working up the reaction. High resolution mass spectra (HRMS) were performed using an LC/MS TOF high-resolution mass spectrometer equipped with a liquid chromatography system.

Materials: Unless otherwise noted, all reagents were obtained commercially and used without further purification. DMSO was distilled from CaH_2 and stored with 4 Å molecular sieves. Reactions were performed under an atmosphere of Ar using glassware that was flame-dried under vacuum. Tertbutylperoxybenzoate was purchased from Alfa and stored in refrigerated. AgSCF₃ was prepared following the literature¹.

2. Preparation of Substrates.

Substrates **1e** and **1f** were purchased from commercial source, and used without further purification. Other substrates were prepared according to the literature.

General Procedure for Preparation of Substrates 1a~1d²



To a solution of hex-5-en-1-ol (5.0 mmol), Et₃N (18.0 mmol) in CH₂Cl₂ (25 mL) was added dropwise with the corresponding sulfochloride (6 mmol) or acyl chloride (6 mmol) dissolved in CH₂Cl₂ at 0 °C. The resulted mixture was vigorously stirred at room temperature overnight. Then the reaction mixture was treated with saturated aqueous NaHCO₃ (20 mL). After stirring at room temperature for 20 min, the organic layer was separated. Then the aqueous layer was extracted with CH₂Cl₂ (2 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to provide the corresponding products.

hex-5-enyl 4-fluorobenzoate (1b)



1b was obtained as a colorless oil in 87% yield (Rf = 0.6 in hexane/ethyl acetate = 15:1). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 8.04 (dd, J = 8.7, 5.5 Hz, 2H), 7.09 (t, J = 8.5 Hz, 2H), 5.81 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.00 (ddd, J = 13.6, 11.0, 1.2 Hz, 2H), 4.30 (t, J = 6.6 Hz, 2H), 2.12 (q, J = 7.2 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.57 – 1.497 (m, 2H). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 166.30 (d, J = 133.1 Hz), 164.44, 138.27, 132.05 (d, J = 9.3 Hz), 126.72 (d, J = 3.0 Hz), 115.43 (d, J = 22.0 Hz), 114.90, 65.00, 33.29, 28.15, 25.29. IR (ATR): v_{max} 3077, 2937, 2860, 1719, 1603, 1273, 1114, 912, 854, 767 cm⁻¹. MS (EI): m/z (%) 123(100), [M]⁺, 222. HRMS: Calculated for C₁₃H₁₅FO₂: 222.1056; Found: [M]⁺, 222.1055.

General Procedure for Preparation of Substrates³ 1g-1r



To a solution of aromatic alcohol (5.0 mmol, 1.0 eq.) and K_2CO_3 (15.0 mmol, 2.5 eq.) in CH₃CN (10.0 mL) was added 5-bromopent-1-ene/6-bromohex-1-ene (10.0 mmol, 2.0 eq.), and the mixture was refluxed for 12 h. It was then cooled to 25 °C and the solvent was removed in vacuo. The residue was partitioned between ethyl acetate (EtOAc) and water, and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄

and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to provide the corresponding alkenes.

1-tert-butyl-4-(pent-4-enyloxy)benzene (1g)



Known compound⁴. **1g** was obtained as a colorless oil in 91% yield (Rf = 0.6 in hexane). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm δ 7.32 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.94 – 5.83 (m, 1H), 5.12 – 5.01 m, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 2.27 (q, *J* = 7.3 Hz, 2H), 2.01 – 1.84 (m, 2H), 1.34 (s, 9H). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 156.97, 143.26, 138.01, 126.27, 115.24, 114.11, 67.18, 34.14, 31.68, 30.29, 28.67. **IR** (ATR): *v*_{max} 3078, 2941, 2880, 1610, 1511, 1469, 1295, 1245, 1184, 1027, 914, 825 cm⁻¹. **MS** (EI): m/z (%) 203 (100), [M] ⁺, 218. **HRMS**: Calculated for C₁₅H₂₂O: 218.1671; Found: [M] ⁺, 218.1675.

1-methoxy-4-(pent-4-enyloxy) benzene(1h)



Known compound⁵. **1h** was obtained as a colorless oil in 92% yield (Rf = 0.6 in hexane). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 6.85 (s, 4H), 5.92 – 5.82 (m, 1H), 5.1 (m, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.78 (s, 3H), 2.25 (q, *J* = 6.5 Hz, 2H), 2.00 – 1.79 (m, 2H). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 153.86, 153.33, 137.98, 115.52, 115.15, 114.67, 67.85, 55.65, 30.22, 28.65. IR (ATR): *v*_{max} 3071, 2941, 2880, 1508, 1465, 1231, 1043, 826 cm⁻¹. MS (EI): m/z (%) 124 (100), [M] +, 192. HRMS: Calculated for C₁₂H₁₆O₂: 192.1150; Found: [M] +, 192.1153.

1-bromo-2-chloro-4-(hex-5-enyloxy)benzene (1i)



Known compound⁶. **1i** was obtained as a colorless oil in 87% yield (Rf = 0.6 in hexane). ¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.49 – 7.48 (m, 1H), 7.29 (ddd, J = 8.8, 2.2, 1.5 Hz, 1H),, 6.77 (dd, J = 8.8, 1.6 Hz, 1H), 5.82 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.01 (ddd, J = 13.7, 11.0, 5.4 Hz, 2H), 3.99 (td, J = 6.4, 1.4 Hz, 2H), 2.14 (q, J = 7.1 Hz, 2H), 1.87 – 1.80 (m, 2H), 1.63– 1.55 (m, 2H). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 153.95, 138.39, 132.63, 130.45, 124.1, 114.89, 114.49, 112.32, 69.20, 33.35, 28.47, 25.2. IR (ATR): v_{max} 3076, 2936, 2868, 1475, 1385, 1254, 1072, 1000, 802, 723 cm⁻¹. **MS** (EI): m/z (%) 208 (100), [M]⁺, 290. **HRMS**: Calculated for C₁₂H₁₄BrClO: 287.9917; Found: [M]⁺, 287.9914.

1-(hex-5-enyloxy)-4-iodobenzene (1j)



Known compound⁷. **1j** was obtained as a colorless oil in 86% yield (Rf = 0.6 in hexane).¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.53 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05 – 4.96 (m, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H), 1.82 – 1.74 (m, 2H), 1.60 – 1.52 (m, 2H). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 159.01, 138.46, 138.20, 116.98, 114.92, 82.57, 67.91, 33.46, 28.66, 25.34. **IR** (ATR): *v*_{max} 3071, 2934, 2866, 1581, 1479, 1285, 1240, 1175, 998, 912, 816, 628, 505 cm⁻¹. **MS** (EI): m/z (%) 220(100), [M]⁺, 302. **HRMS**: Calculated for C₁₂H₁₅IO: 302.0168; Found: [M]⁺, 302.0170.

1-nitro-4-(pent-4-enyloxy) benzene (1k)



Known compound⁸. **1k** was obtained as a colorless oil in 81% yield (Rf = 0.6 in hexane/ethyl acetate = 15:1).¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 8.33 – 8.00 (td, J = 9.1, 1.8 Hz, 2H), 6.93 (td, J = 9.1, 1.8 Hz, 2H), 5.89 – 5.78 (m, 1H), 5.08–4.99 (m, 2H), 4.05 (td, J = 6.3, 1.8 Hz, 2H), 2.24 (q, J = 7.1 Hz, 2H), 1.92 (m, 2H). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 164.18, 141.33, 137.33, 125.85, 115.55, 114.41, 68.02, 29.89, 28.07. **IR** (ATR): v_{max} 3071, 2941, 2880, 1598, 1509, 1338, 1260, 1110, 1007, 918, 850 cm⁻¹. **MS** (EI): m/z (%) 41(100), [M] +, 207. **HRMS**: Calculated for C₁₁H₁₃NO₃: 207.0895; Found: [M] +, 207.0898.

4-(hex-5-enyloxy)benzonitrile (11)



New compound. **11** was obtained as a colorless oil in 91% yield (Rf = 0.6 in hexane).¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.55 (dd, J = 8.9, 1.9 Hz, 2H), 6.92 (dd, J = 8.9, 1.9 Hz, 2H), 5.86 – 5.75 (m, 1H), 5.01 (ddd, J = 17.9, 9.7, 5.8 Hz, 2H), 3.99 (td, J = 6.4, 1.0 Hz, 2H), 2.12 (td, J = 7.6, 1.2 Hz, 2H), 1.84 – 1.73 (m, 2H), 1.60 – 1.52 (m, 2H). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 162.42, 138.25, 133.93, 119.28, 115.19, 114.94, 103.67, 68.19, 33.31, 28.39, 25.17. **IR** (ATR): v_{max} 3076, 2941, 2872, 2224, 1606, 1508, 1301, 1258, 1171, 996, 912, 835 cm⁻¹. **MS** (EI): m/z (%) 55 (100), [M]⁺, 210. **HRMS**: Calculated for C₁₃H₁₅NO: 201.1154; Found: [M]⁺, 201.1153.

4-(pent-4-enyloxy)benzaldehyde (1m)



Known compound⁹. **1m** was obtained as a colorless oil in 91% yield (Rf = 0.6 in hexane).¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 9.87 (s, 1H), 7.81 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 5.84 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.09 – 4.99 (m, 2H), 4.04 (t, J = 6.4 Hz, 2H), 2.24 (q, J = 7.1 Hz, 2H), 2.04 – 1.78 (m, 2H). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 190.71, 164.14, 137.42, 131.92, 129.79, 115.44, 114.73, 67.50, 29.93, 28.13. **IR** (ATR): v_{max} 3076, 2975, 2943, 2876, 2846, 2736, 1689, 1640, 1602, 1509, 1256, 1160, 1015, 915, 832 cm⁻¹. **MS** (EI): m/z (%) 121 (100), [M]⁺,190. **HRMS**: Calculated for C₁₂H₁₄O₂: 190.0994; Found: [M]⁺, 190.0995.

1-(4-(hex-5-enyloxy)phenyl)ethanone (1n)



New compound. **1n** was obtained as a colorless oil in 92% yield (Rf = 0.8 in hexane/ethyl acetate = 20:1).¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.91 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.00 (ddd, *J* = 13.6, 10.9, 1.1 Hz, 1H), 4.02 (t, *J* = 6.4 Hz, 2H), 2.54 (s, 3H), 2.13 (q, *J* = 7.2 Hz, 2H), 1.86 – 1.76 (m, 2H), 1.61 – 1.53 (m, 2H). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 196.69, 163.05, 138.33, 130.56, 130.15, 114.87, 114.12, 68.00, 33.35, 28.51, 26.28, 25.22. IR (ATR): *v*_{max} 3072, 2937, 2869, 1676, 1601, 1259, 1172, 1004, 955, 913, 834 cm⁻¹. **MS** (EI): m/z (%) 121(100), [M] +, 218. **HRMS**: Calculated for C₁₄H₁₈O₂: 218.1307; Found: [M] +, 218.1304.

ethyl 4-(pent-4-enyloxy)benzoate (10)



Known compound¹⁰. **10** was obtained as a colorless oil in 93% yield (Rf = 0.7 in hexane/ethyl acetate = 15:1).¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm δ 7.98 (dd, J = 8.9, 2.4 Hz, 2H), 6.90 (dd, J = 8.8, 2.2 Hz, 2H), 5.88 – 5.79 (m, 1H), 5.08 – 4.99 (m, 2H), 4.34 (qd, J = 7.0, 2.5 Hz, 2H), 4.01 (td, J = 6.2, 1.5 Hz, 1H), 2.38 – 2.04 (m, 2H), 2.04 – 1.78 (m, 2H), 1.37 (td, J = 6.9, 2.4 Hz, 3H). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 166.39, 162.78, 137.57, 131.51, 122.80, 115.36, 114.02, 67.29, 60.56, 30.00, 28.26, 14.37. **IR** (ATR): v_{max} 3074, 2981, 2941, 1713, 1607, 1509, 1464, 1254, 1168, 1109, 1022, 917, 850, 770, 696 cm⁻¹. **MS** (EI): m/z (%) 121(100), [M] ⁺, 234. **HRMS**: Calculated for C₁₄H₁₈O₃: 234.1256; Found: [M] ⁺, 234.1253.

1-(hex-5-enyloxy)-4-(trifluoromethyl)benzene (1p)



New compound. **1p** was obtained as a colorless oil in 87% yield (Rf = 0.6 in hexane). **¹H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.53 (d, J = 8.6 Hz, 2H), 6.94 (d, J= 8.6 Hz, 2H), 5.83 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.02 (ddd, J = 13.7, 11.0, 1.3 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 2.14 (q, J = 7.2 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.62 – 1.54 (m, 2H). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 161.65, 138.35, 126.82 (q, J = 3.7 Hz), 124.60 (q, J = 270.6 Hz), 122.66 (q, J = 32.6 Hz), 114.82, 114.43, 67.98, 33.39, 28.54, 25.26. **IR** (ATR): v_{max} 3079, 2941, 2873, 1616, 1519, 1331, 1258, 1161, 1111, 1068, 913, 836, 673 cm⁻¹. **MS** (EI): m/z (%) 55 (100), [M]⁺, 244. **HRMS**: Calculated for C₁₃H₁₅F₃O: 244.1075; Found: [M]⁺, 244.1077.

2-(hex-5-enyloxy)naphthalene (1q)



New compound. **1q** was obtained as a colorless oil in 87% yield (Rf = 0.6 in hexane). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.77 – 7.71 (m, 3H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.15 (dd, *J* = 10.9, 1.9 Hz, 2H), 5.86 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 (ddd, *J* = 13.6, 11.0, 1.2 Hz, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 2.16 (q, *J* = 7.2 Hz, 2H), 1.91 – 1.83 (m, 2H), 1.67 – 1.58 (m, 2H). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 157.25, 138.68, 134.83, 129.48, 129.09, 127.81, 126.87, 126.45, 123.63, 119.18, 114.94, 106.71, 67.86, 33.64, 28.87, 25.57. IR (ATR): *v*_{max} 3058, 2938, 2868, 1629, 1600, 1440, 1356, 1216, 1180, 1119, 1030, 910, 837, 745, 623 cm⁻¹. MS (EI): m/z (%) 144 (100), [M] +, 226. HRMS: Calculated for C₁₆H₁₈O: 226.1358; Found: [M] +, 226.1356.

General Procedure for Preparation of 1s



A solution of 2-(Hydroxymethyl) pyridine (546 mg, 5.0 mmol) in 20mL DMF was cooled to 0 °C under an N₂ atmosphere and then NaH (144mg, 6.0mmol) was added. The mixture was stirred at 0 °C for 30 min. And then 5-Bromo-1-pentene (895mg, 6.0 mmol) was added dropwise over a period of 10 min. and the mixture was allowed to warm to room temperature over 1h. Ater stirring for 18h, the mixture was quenched with water and extracted with diethyl ether (2 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to provide1t (583mg) as a yellow oil with 66% yield. ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 8.53 (d, *J* = 4.8 Hz, 1H), 7.67 (td, *J* = 7.7, 1.3 Hz, 1H), 7.43 (d, *J* = 7.8

Hz, 1H), 7.18 – 7.14 (m, 1H), 5.81 (ddt, J = 17.0, 10.1, 6.7 Hz, 1H), 4.98 (ddd, J = 13.7, 11.3, 1.3 Hz, 2H), 4.61 (s, 2H), 3.56 (t, J = 6.5 Hz, 2H), 2.16 (q, J = 7.2 Hz, 2H), 1.78 – 1.71 (m, 2H). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 158.81, 148.93, 138.13, 136.59, 122.23, 121.23, 114.77, 73.68, 70.39, 30.26, 28.89. **IR** (ATR): v_{max} 3070, 2931, 2860, 1640, 1586, 1471, 1439, 1358, 1119, 994, 913, 759 cm⁻¹. **MS** (ESI): m/z (%) 178 (100). **HRMS**: Calculated for C₁₁H₁₆NO⁺: 178.1226; Found: [M+H]⁺, 178.1225.

3. General Procedure for Cu-Mediated Oxidative Trifluoromethylthiolation of Terminal Alkenes.

 $R \xrightarrow{\qquad + AgSCF_3} \xrightarrow{\qquad Cu(OAc)_2, K_2S_2O_8} R \xrightarrow{\qquad SCF_3} K_3PO_4, DMSO, 60 °C, 6 h$

A 25 ml Schlenk flask equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (37 mg, 0.2 mmol, 1.0 eq.), AgSCF₃ (83 mg, 0.4 mmol, 2.0 eq.), K₂S₂O₈(108 mg, 0.4 mmol, 2.0 eq.), K₃PO₄(85 mg, 0.4 mmol, 2.0 eq.). The tube was sealed with a septum, evacuated, and backfilled with argon (repeated three times). Then 1 mL anhydrous DMSO and terminal Alkenes **1a**(0.2 mmol, 1.0 eq.) were added. Then the flask was stirred at 60°C for 6 h. The mixture was cooled to room temperature. Then, Benzotrifluoride (25uL, 0.2 mmol) was added as an internal standard, the yield of the crude reaction was measured by ¹⁹F NMR analysis before working up. After that, 5 mL saturated Ammonium chloride aqueous solution was added. The resulting mixture was filtered by Celite, eluted with diethyl ether. Separated the layers and the water phase was extracted with diethyl ether for 2 times. The combined organic phase was washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel column chromatography to provide pure product **2a**.

(E)-6-(trifluoromethylthio)hex-4-enyl benzoate (2a)



2a was obtained as a light yellow oil in 61% yield (Rf = 0.6 in hexane/ethyl acetate = 20:1).¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 8.05 – 8.03 (m, 2H), 7.58 – 7.54 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.78 – 5.71(m, 1H), 5.61 – 5.53 (m, 1H), 4.32 (t, *J* = 6.5 Hz, 2H), 3.54 (d, *J* = 7.4 Hz, 2H), 2.22 (q, *J* = 7.0 Hz, 2H), 1.91 – 1.82 (m, 2H). ¹⁹**F NMR** (376 MHz, CDCl₃): δ ppm -41.00 (s, 3F). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 166.54, 134.55, 132.90, 130.83 (q, *J* = 306.3 Hz), 130.35, 129.54, 128.36, 124.60, 64.14, 32.16 (q, J = 2.2 Hz), 28.72, 28.62. IR (ATR): *v*_{max} 3064, 2954, 2853, 1719, 1451, 1275, 1111, 966, 711 cm⁻¹. **MS** (EI): m/z (%) 105 (100), [M]⁺, 304. **HRMS**: Calculated for C₁₄H₁₅F₃O₂S: 304.0745; Found: [M]⁺, 304.0748.

(E)-6-(trifluoromethylthio)hex-4-enyl 4-fluorobenzoate (2b)



2b was obtained as a light yellow oil in 63% yield (Rf = 0.6 in hexane/ethyl acetate = 20:1). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 8.04 (dd, J = 8.7, 5.5 Hz, 2H), 7.10 (t, J = 8.7 Hz, 2H), 5.77 – 5.70 (m, 1H), 5.60 – 5.52 (m, 1H), 4.31 (t, J = 6.5 Hz, 2H), 3.49 (d, J = 7.1 Hz, 2H), 2.20 (q, J = 7.1 Hz, 2H), 1.91 – 1.81 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -40.99 (s, 3F). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 165.76 (d, J = 253.5 Hz), 165.59, 135.38, 132.11, 132.01, 130.80 (q, J = 306.3 Hz), 124.67, 115.60, 115.38, 64.28, 32.15(q, J = 2.2 Hz), 28.68, 27.99. IR (ATR): v_{max} 2951, 2856, 1721, 1603, 1506, 1274, 1114, 968, 854, 765 cm⁻¹. MS (EI): m/z (%) 123 (100), [M]⁺, 322. HRMS: Calculated for C₁₄H₁₄F₄O₂S: 322.0651; Found: [M]⁺, 322.0647.

(E)-6-(trifluoromethylthio) hex-4-enyl 4-bromobenzoate (2c)



2c was obtained as a light yellow oil in 61% yield (Rf = 0.6 in hexane/ethyl acetate = 20:1).¹**H** NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.88 (dd, J = 8.2Hz, 1.2 Hz, 2H), 7.57 (dd, J = 8.2Hz, 1.2 Hz, 2H), 5.77 – 5.70(m, 1H), 5.60 – 5.53 (m, 1H), 4.31 (t, J = 6.5 Hz, 2H), 3.53 (d, J = 7.3 Hz, 2H), 2.20 (q, J = 7.1 Hz, 2H), 1.91 – 1.74 (m, 2H). ¹⁹**F** NMR (376 MHz, CDCl₃): δ ppm -40.98 (s, 3F). ¹³**C** NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 165.81, 134.38, 131.71, 131.08, 130.83, (q, J = 306.3 Hz), 129.22, 128.03, 124.72, 64.22, 32.15 (q, J = 2.2 Hz), 28.66, 27.96. **IR** (ATR): v_{max} 2951, 2855, 1721, 1590, 1475, 1274, 1109, 698, 846, 756 cm⁻¹. **MS** (ESI): m/z (%) 278 (100), [M+H₂O]⁺, 402. **HRMS**: Calculated for C₁₄H₁₅BrF₃O₂S⁺, [M+H]⁺: 382.9923; Found: [M+H]⁺, 382.9922.

(E)-6-(trifluoromethylthio) hex-4-enyl 4-methylbenzenesulfonate (2d)



2d was obtained as a light yellow oil in 54% yield (Rf = 0.5 in hexane /ethyl acetate = 15:1).¹**H** NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.78 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.60 – 5.49 (m, 1H), 5.48 – 5.35 (m, 1H), 4.00 (t, *J* = 6.3 Hz, 2H), 3.43 (d, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 2.08 (q, *J* = 7.0 Hz, 2H), 1.81 – 1.66 (m, 2H). ¹⁹**F** NMR (376 MHz, CDCl₃): δ ppm -40.91 (s, 3F). ¹³**C** NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 144.80, 135.33, 133.63, 130.76 (*J* = 306.3 Hz), 129.86, 127.89, 125.18, 69.45, 32.04 (q, *J* = 2.2 Hz), 28.04, 21.60. **IR** (ATR): *v*_{max} 3034, 2931, 2859, 1599, 1453, 1359, 1177, 966, 820, 747, 666, 563 cm⁻¹. **MS** (ESI): m/z (%) 371.9 (100), [M+NH₄]⁺, 371.9. **HRMS**: Calculated for C₁₄H₂₁F₃NO₃S₂⁺: 372.0909; Found: [M+NH₄]⁺, 372.0903.

(E)- (8-bromooct-2-enyl) (trifluoromethyl) sulfane (2e)



2e was obtained as a light yellow oil in 51% yield (Rf = 0.8 in hexane). ¹**H** NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 5.69 (dt, J = 14.8, 6.8 Hz, 1H), 5.58 – 5.41 (m, 1H), 3.54 (d, J = 7.4 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 2.06 (q, J = 6.7 Hz, 2H), 1.93-1.80 (m, 2H), 1.42 (m, 4H). ¹⁹**F** NMR (376 MHz, CDCl₃): δ ppm -41.00 (s, 3F). ¹³**C** NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 135.65, 130.84 (q, J = 306.3 Hz), 123.82, 33.7, 32.57, 32.30 (q, J = 2.2 Hz), 31.94, 28.02, 27.54. IR (ATR): v_{max} 2932, 2857, 1446, 1241, 1115, 966 cm⁻¹. MS (EI): m/z (%) 109 (100), [M]⁺, 290. HRMS: Calculated for C₉H₁₄BrF₃S: 289.9952; Found: [M]⁺, 289.9951.

(E)-methyl 11-(trifluoromethylthio)undec-9-enoate (2f)



2f was obtained as a light yellow oil in 54% yield (Rf = 0.6 in hexane /ethyl acetate = 20:1).¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 5.68 (dt, *J* = 14.9, 6.8 Hz, 1H), 5.47 (dt, *J* = 14.6, 7.2 Hz, 1H), 3.65 (s, 3H), 3.52 (d *J* = 7.5 Hz, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.01 (q, *J* = 7.0 Hz, 2H), 1.69 – 1.54 (m, 2H), 1.43 – 1.21 (m, 8H). ¹⁹**F NMR** (376 MHz, CDCl₃): δ ppm -41.06 (s, 3F). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 174.25, 136.19, 130.85 (q, *J* = 306.3 Hz), 123.34, 51.39, 34.04, 32.32 (q, J = 2.2 Hz), 32.12, 29.02, 29.00, 28.97, 28.79, 24.88. **IR** (ATR): *v*_{max} 2930, 2857, 1446, 1738, 1437, 1116, 966, 755 cm⁻¹. **MS** (ESI): m/z (%) 196.9 (100), [M+H]⁺, 298.9. **HRMS**: Calculated for C₁₃H₂₂F₃O₂S⁺: 299.1287; Found: [M+H]⁺, 299.1285.

(E)-(5-(4-tert-butylphenoxy)pent-2-enyl)(trifluoromethyl)sulfane (2g)



2g was obtained as a light yellow oil in 60% yield (Rf = 0.7 in hexane /ethyl acetate = 20:1).¹**H** NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.31 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 5.87 – 5.77 (m, 1H), 5.71 – 5.60 (m, 1H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.53 (d, *J* = 7.1 Hz, 2H), 2.53 (q, *J* = 6.5 Hz, 2H), 1.31 (s, 9H). ¹⁹**F** NMR (376 MHz, CDCl₃): δ ppm -40.98 (s, 3F). ¹³**C** NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 152.52, 143.52, 131.73, 130.82 (q, *J* = 306.3 Hz), 126.24, 126.01, 114.04, 66.92, 34.07, 32.24, 32.19 (q, *J* = 2.2 Hz), 31.52. **IR** (ATR): *v*_{max} 2960, 2871, 1511, 1471, 1245, 1113, 1036, 965, 827 cm⁻¹. **MS** (ESI): m/z (%) 318.2. **HRMS**: Calculated for C₁₆H₂₂F₃OS⁺: 319.1338; Found: [M+H]⁺, 319.1334.

(E)-(5-(4-methoxyphenoxy)pent-2-enyl)(trifluoromethyl)sulfane (2h)



2h was obtained as a light yellow oil in 46% yield (Rf = 0.7 in hexane /ethyl acetate = 20:1).¹**H** NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 6.83 (s, 4H), 5.85 – 5.77(m, 1H), 5.69 – 5.61 (m, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 3.77 (s, 3H), 3.53 (d, *J* = 7.1 Hz, 2H), 2.51 (q, *J* = 6.6 Hz, 2H). ¹⁹**F** NMR (376 MHz, CDCl₃): δ ppm -40.99 (s, 3F). ¹³**C** NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 153.95, 152.93, 131.69, 130.82 (q, *J* = 306.3 Hz), 126.04, 115.62, 114.67, 67.67, 55.72, 32.27, 32.21 (q, J = 2.2 Hz), 31.85. IR (ATR): *v*_{max} 2943, 2865, 1508, 1226, 1109, 1034, 825, 741 cm⁻¹. MS (EI): m/z (%) 124 (100), [M]⁺, 292. HRMS: Calculated for C₁₃H₁₅F₃O₂S: 292.0745; Found: [M]⁺, 292.0742.

(E)- (6-(4-bromo-3-chlorophenoxy)hex-2-enyl)(trifluoromethyl)sulfane (2i)

Cl O SCF₃ Br 2i

2i was obtained as a light yellow oil in 66% yield (Rf = 0.7 in hexane /ethyl acetate = 20:1).¹**H** NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.49 (d, *J* = 2.3 Hz, 1H), 7.29 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 5.78 – 5.65 (m, 1H), 5.65 – 5.52 (m, 1H), 3.98 (t, *J* = 6.2 Hz, 2H), 3.50 (d, *J* = 7.1 Hz, 2H), 2.27 (q, *J* = 7.1 Hz, 2H), 1.97 – 1.86 (m, 2H). ¹⁹**F** NMR (376 MHz, CDCl₃): δ ppm -40.94 (s, 3F). ¹³**C** NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 153.81, 135.41, 132.67, 130.83 (q, *J* = 306.3 Hz), 130.49, 124.69, 124.10, 114.53, 112.49, 68.31, 32.21 (q, *J* = 2.2 Hz), 28.55, 28.26. **IR** (ATR): *v*_{max} 2943, 2878, 151, 1484, 1289, 1249, 1116, 802 cm⁻¹. MS (EI): m/z (%) 81 (100), [M]⁺, 388. HRMS:Calculated for C₁₃H₁₄BrClF₃OS⁺: 388.9584; Found: [M+H]⁺, 388.9578.

(E)-(6-(4-iodophenoxy)hex-2-enyl)(trifluoromethyl)sulfane (2j)



2j was obtained as a light yellow oil in 65% yield (Rf = 0.7 in hexane /ethyl acetate = 20:1).¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.54 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 5.77 – 5.69 (m, 1H), 5.59 – 5.51 (m, 1H), 3.91 (t, *J* = 6.2 Hz, 2H), 3.53 (d, *J* = 7.3 Hz, 2H), 2.22 (q, *J* = 7.1 Hz, 2H), 1.93 – 1.76 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -40.91 (s, 3F). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 158.89 (d, *J* = 4.6 Hz), 138.26, 134.79, 130.89 (q, *J* = 306.3 Hz), 124.61, 116.96, 82.69, 67.11, 32.27, 28.61, 28.44. IR (ATR): *v*_{max} 2955, 2863, 1581, 1480, 1111, 812 cm⁻¹. MS (EI): m/z (%) 220 (100), [M]⁺, 402. HRMS: Calculated for C₁₃H₁₄F₃IOS: 401.9762; Found: [M]⁺, 401.9759.

(E)-(5-(4-nitrophenoxy)pent-2-enyl)(trifluoromethyl)sulfane (2k)



2k was obtained as a light yellow oil in 57% yield (Rf = 0.6 in hexane /ethyl acetate = 15:1). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 8.19 (d, *J* = 9.2 Hz, 2H), 6.93 (d, *J* = 9.2 Hz, 2H), 5.86 – 5.74 (m, 1H), 5.74 – 5.63 (m, 1H), 4.08 (t, *J* = 6.4 Hz, 2H), 3.53 (d, *J* = 6.9 Hz, 2H), 2.58 (q, *J* = 6.4 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -40.90 (s, 3F). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 163.82, 141.57, 130.81 (q, *J* = 306.3 Hz), 130.57, 127.01, 125.92, 114.44, 67.68, 32.09 (q, J = 2.2 Hz), 31.85. IR (ATR): v_{max} 3084, 2973, 1598, 1510, 1339, 1262, 1161, 850 cm⁻¹. MS (EI): m/z (%) 67 (100), [M] +, 307. HRMS: Calculated for C₁₂H₁₂F₃NO₃S: 307.0490; Found: [M]⁺, 307.0495.

(E)-4-(6-(trifluoromethylthio) hex-4-enyloxy)benzonitrile (2l)



21 was obtained as a light yellow oil in 64% yield (Rf = 0.6 in hexane /ethyl acetate = 20:1).¹**H** NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.55 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.76 – 5.68 (m, 1H), 5.62 – 5.51 (m, 1H), 3.98 (t, *J* = 6.3 Hz, 2H), 3.49 (d, *J* = 7.1 Hz, 2H), 2.23 (q, *J* = 7.1 Hz, 2H), 1.97 – 1.78 (m, 2H). ¹⁹**F** NMR (376 MHz, CDCl₃): δ ppm -40.91 (s, 3F). ¹³**C** NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 162.28, 134.40, 133.97, 130.82 (q, *J* = 306.3 Hz), 124.85, 115.1686, 103.84, 67.31, 32.17 (d, *J* = 1.8 Hz), 28.48, 28.19. **IR** (ATR): *v*_{max} 3035, 2943, 2874, 2559, 2223, 1605, 1507, 1257, 1110, 835 cm⁻¹. **MS** (EI): m/z (%) 81 (100), [M]⁺, 301. **HRMS**: Calculated for C₁₄H₁₄F₃NOS: 301.0748; Found: [M]⁺, 301.0745.

(E)-4-(5-(trifluoromethylthio) pent-3-enyloxy)benzaldehyde (2m)



2m was obtained as a light yellow oil in 54% yield (Rf = 0.7 in hexane /ethyl acetate = 20:1). ¹**H** NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 9.88 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 5.83 – 5.76 (m, 1H), 5.71 – 5.64 (m, 1H), 4.07 (t, *J* = 6.3 Hz, 2H), 3.53 (d, *J* = 6.9 Hz, 2H), 2.57 (q, *J* = 6.3 Hz, 2H). ¹⁹**F** NMR (376 MHz, CDCl₃): δ ppm -40.92 (s, 3F). ¹³**C** NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 190.76, 163.82, 131.98, 130.85, 130. 76 (q, *J* = 306.3 Hz), 130.04, 126.76, 114.77, 76.24, 32.12 (q, J = 2.2 Hz), 31.94. **IR** (ATR): *v*_{max} 3366, 3039, 2933, 2830, 2793, 1695, 1578, 1471, 1312, 1253, 1204, 967, 832 cm⁻¹. **MS** (EI): m/z (%) 127 (100), [M]⁺, 290. **HRMS**: Calculated for C₁₃H₁₃F₃O₂S: 290.0588; Found: [M]⁺, 290.0591.

(E)-1-(4-(6-(trifluoromethylthio)hex-4-enyloxy)phenyl)ethanone (2n)



2n was obtained as a light yellow oil in 75% yield (Rf = 0.5 in hexane /ethyl acetate = 20:1). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.91 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.77 – 5.69 (m, 1H), 5.60 – 5.51 (m, 1H), 4.00 (t, *J* = 6.3 Hz, 2H), 3.49 (d, *J* = 7.1 Hz, 2H), 2.53 (s, 3H), 2.23 (q, *J* = 7.1 Hz, 2H), 1.91 – 1.84 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -40.93 (s, 3F). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 196.75, 162.92, 134.59, 130.82 (q, *J* = 306.3 Hz), 130.58, 130.27, 124.68, 114.12, 67.16, 32.19(q, *J* = 2.2 Hz), 28.54, 28.32, 26.28. IR (ATR): *v*_{max} 2941, 2872, 1676, 1601, 1260, 1110, 960, 835 cm⁻¹. MS (EI): m/z (%) 67 (100), [M]⁺, 318. HRMS: Calculated for C₁₅H₁₇F₃O₂S: 318.0901; Found: [M]⁺, 318.0900.

(E)-ethyl 4-(5-(trifluoromethylthio) pent-3-enyloxy)benzoate (20)



20 was obtained as a light yellow oil in 65% yield (Rf = 0.7 in hexane /ethyl acetate = 15:1).¹**H** NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.98 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.84 – 5.76 (m, 1H), 5.72 – 5.62 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 3.52 (d, *J* = 7.0 Hz, 2H), 2.55 (q, *J* = 6.5 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ¹⁹**F** NMR (376 MHz, CDCl₃): δ ppm -40.96 (s, 3F). ¹³**C** NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 166.35, 162.46, 131.54, 131.08, 130.78 (q, *J* = 306.3 Hz), 126.54, 123.06, 114.03, 67.02, 60.62, 31.99(q, J = 2.2 Hz), 14.36. **IR** (ATR): *v*_{max} 2982, 2941, 1714, 1607, 1274, 1164, 850, 766 cm⁻¹. **MS** (EI): m/z (%) 67 (100), [M]⁺, 334. **HRMS**: Calculated for C₁₅H₁₇F₃O₃S: 334.0850; Found: [M]⁺, 334.0852.

(E)-(trifluoromethyl)(6-(4-(trifluoromethyl)phenoxy)hex-2-enyl)sulfane (2p)



2p was obtained as a light yellow oil in 50% yield (Rf = 0.7 in hexane /ethyl acetate = 20:1). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): 7.53 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2H), 5.76 – 5.71 (m, 1H), 5.61 – 5.53 (m, 1H), 3.99 (t, J = 5.8 Hz, 2H), 3.51 (d, J = 7.0 Hz, 2H), 2.27 (q, J = 7.3 Hz, 2H), 1.88 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -40.96 (s, 3F). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 161.44, 134.59, 130.83 (q, J = 306.3 Hz), 126.86 (q, J = 3.7 Hz), 124.70, 124.48 (q, J = 270.6 Hz), 122.80 (q, J = 32.6 Hz), 114.41, 67.14, 32.19 (q, J = 2.2 Hz), 28.55, 28.32. **IR** (ATR): v_{max} 2944, 2872, 1617, 1520, 1325, 1255, 1112, 836 cm⁻¹. **MS** (EI): m/z (%) 81 (100), [M]⁺, 344. **HRMS**: Calculated for C₁₄H₁₄F₆OS: 344.0670; Found: [M]⁺, 344.0667.

(E)-(6-(naphthalen-2-yloxy)hex-2-enyl)(trifluoromethyl)sulfane (2q)



2q was obtained as a white solid in 51% yield (Rf = 0.7 in hexane /ethyl acetate = 20:1, mp. 45~48 °C). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.75 (dd, *J* = 16.7, 7.9 Hz, 3H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.21 – 7.09 (m, 2H), 5.82– 5.74 (m, 1H), 5.63 – 5.55 (m, 1H), 4.08 (t, *J* = 6.3 Hz, 2H), 3.53 (d, *J* = 7.1 Hz, 2H), 2.30 (q, *J* = 7.1 Hz, 2H), 2.00 – 1.87 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -40.91 (s, 3F). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 156.95, 134.95, 134.62, 130.87 (q, *J* = 306.3 Hz), 129.39, 128.98, 127.66, 126.72, 126.36, 124.44, 123.57, 118.94, 106.65, 66.99, 32.26 (q, *J* = 2.2 Hz), 28.76, 28.53. IR (ATR): *v*_{max} 3055, 2939, 2863, 1929, 1464, 1391, 1261, 1113, 838, 749 cm⁻¹. MS (EI): m/z (%) 144 (100), [M]⁺, 326. HRMS: Calculated for C₁₇H₁₇F₃OS: 326.0952; Found: [M]⁺, 326.0955.

(E)-4-methyl-7-(5-(trifluoromethylthio) pent-3-enyloxy)-2H-chromen-2-one (2r)



2r was obtained as a light yellow oil in 76% yield (Rf = 0.5 in hexane /ethyl acetate = 20:1).¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.48 (d, *J* = 8.8 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.79 (d, *J* = 2.1 Hz, 1H), 6.13 (s, 1H), 5.84 – 5.74 (m, 1H), 5.73 – 5.63 (m, 1H), 4.04 (t, *J* = 6.5 Hz, 2H), 3.52 (d, *J* = 6.8 Hz, 2H), 2.57 (q, *J* = 6.5 Hz, 2H), 2.39 (s, 3H). ¹⁹**F NMR** (376 MHz, CDCl₃): δ ppm -40.92 (s, 3F). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 161.81, 161.27, 155.25, 154.54, 130.84, 130.77 (q, *J* = 306.3 Hz), 126.77, 125.56, 113.66, 112.59, 111.99, 101.42, 67.42, 32.12 (q, *J* = 2.2 Hz), 31.86, 18.64. **IR** (ATR): *v*_{max} 3076, 2928, 2879, 1730, 1614, 1104, 949 cm⁻¹. **MS** (EI): m/z (%) 67 (100), [M]⁺, 344. **HRMS**: Calculated for C₁₆H₁₅F₃O₃S: 344.0694; Found: [M]⁺, 344.0699.

(E)-2-((5-(trifluoromethylthio) pent-3-enyloxy) methyl) pyridine (2s)



2s was obtained as a yellow oil in 73% yield (Rf = 0.5 in hexane /ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 8.53 (d, *J* = 4.2 Hz, 1H), 7.68 (td, *J* = 7.7, 1.7 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.12 (m, 1H), 5.80 – 5.67 (m, 1H), 5.67 – 5.55 (m, 1H), 4.61 (s, 2H), 3.58 (t, *J* = 6.6 Hz, 2H), 3.50 (d, *J* = 7.0 Hz, 2H), 2.39 (q, *J* = 6.7 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -41.05 (s, 3F). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 154.54, 149.03, 136.65, 132.24, 130.81 (q, *J* = 306.3 Hz), 125.58, 122.35, 121.31, 73.76, 70.76, 32.65, 32.20 (q, *J* = 2.2 Hz). IR (ATR): *v*_{max} 3015, 2914, 2862, 1586, 1434, 1115, 967, 759 cm⁻¹. MS (ESI): m/z (%) 278. HRMS: Calculated for C₁₂H₁₅F₃NOS⁺: 278.0821; Found: [M+H]⁺, 278.0818. (E)-2-(5-(trifluoromethylthio) pent-3-enyl)isoindoline-1,3-dione (2t)



2t was obtained as a light yellow oil in 66% yield (Rf = 0.6 in hexane /ethyl acetate = 15:1). ¹**H NMR** (400 MHz, CDCl₃, 293K, TMS): δ ppm 7.82 – 7.79 (m, 2H), 7.69 – 7.67 (m, 2H), 5.66 (m, 1H), 5.60 – 5.47 (m, 1H), 3.73 (t, *J* = 7.0 Hz, 2H), 3.41 (d, *J* = 7.0 Hz, 2H), 2.43 (q, *J* = 6.9 Hz, 2H). ¹⁹**F NMR** (376 MHz, CDCl₃): δ ppm -41.14 (s, 3F). ¹³**C NMR** (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 168.25, 133.92, 132.02, 131.45, 130.67 (*J* = 306.3 Hz), 126.78, 123.20, 37.06, 31.90 (q, *J* = 2.2 Hz), 31.34. **IR** (ATR): *v*_{max} 3035, 2940, 2860, 1771, 1717, 1398, 1362, 1113, 718 cm⁻¹. **MS** (EI): m/z (%) 160 (100). [M–SCF₃]⁺, 214. **HRMS**: Calculated for C₁₄H₁₃F₃NO₂S⁺: 316.0614; Found: [M+H]⁺, 316.0614.

5-(2,5-dihydroxyphenyl)-6-(trifluoromethylthio)hexyl benzoate (2a')



2a' was obtained as a brown thick liquid in 65% yield (Rf = 0.7 in hexane /ethyl acetate = 20:1). ¹H NMR (400 MHz, CDCl₃, 293K, TMS): δ ppm 8.00 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 6.78 – 6.71 (m, 2H), 6.56 (s, 1H), 4.29 (t, J = 6.4 Hz, 2H), 3.20 – 3.00 (m, 3H), 1.81– 1.69 (m, 4H), 1.45 – 1.38 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -41.04 (s, 3F). ¹³C NMR (100.5 MHz, CDCl₃, 293K, TMS): δ ppm 187.02, 186.67, 166.55, 148.38, 137.04, 136.15, 133.87, 132.96, 130.68 (q, J = 306.3 Hz), 130.22, 128.38, 64.29, 39.40, 33.20 (q, J = 1.9 Hz, 9H), 32.42, 28.43, 23.77. IR (ATR): v_{max} 3419,3312, 3063, 2947, 2865, 1715, 1660, 1600, 1452, 1284, 1099, 911, 836, 712 cm⁻¹. MS (ESI): m/z (%) 435 (100), [M + Na] +, 414. HRMS: Calculated for C₂₀H₁₉F₃O₄SNa⁺: 435.0848; Found: [M+Na]⁺, 435.0836.

4. References:

- 1. G. Teverovskiy, D. S. Surry and S. L. Buchwald, *Angew. Chem., Int. Ed.,* 2011, **50**, 7312.
- J. Xu, Y. Fu, D.-F. Luo, Y.-Y. Jiang, B. Xiao, Z.-J. Liu, T.-J. Gong and L. Liu, J. Am. Chem. Soc., 2011, 133, 15300.
- 3. B. H. Lipshutz, S. Ghorai and W. W. Y. Leong, J. Org. Chem., 2009, 74, 2854.
- 4. Berger, M. Frank, Jr. DeGraw, I. Joseph and H. L. Johnson, U.S. Patent 4451474 A, 1984.
- 5. J. Huang, Y. Chen, J. Chan, M. L. Ronk, R. D. Larsen and M. M. Faul, *Synlett*, 2011, 1419.
- 6. X. Wu, L. Chu and F.-L. Qing, Angew. Chem., Int. Ed., 2013, 52, 2198.
- 7. S. Ogi, K. Sugiyasu, and M. Takeuchi, Bull. Chem. Soc. Jpn., 2011, 84, 40.
- 8. A. M. Whittaker and G. Lalic, Org. Lett., 2013, 15, 1112.

- 9. B. Kang, J. W. Kurutz, K.-T. Youm, R. K. Totten, J. T. Hupp and S. T. Nguyen, *Chem. Sci.*, 2012, **3**, 1938.
- 10. M. Qaddoura, K. Belfield, Materials, 2010, 3, 827.

5. ¹H NMR, ¹⁹F NMR and ¹³C NMR spectra or all Compounds



























































