Supporting Information

A Mild and Fast Photoredox-Catalyzed

Trifluoromethylation of Thiols in Batch and Microflow

Natan J.W. Straathof, Bart Tegelbeckers,

Volker Hessel, Xiao Wang* and Timothy Noël*.

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General considerations

All components and reagents were all used as received, unless stated otherwise. Reagents and anhydrous solvents (Sure/SealTM) were bought from Sigma-Aldrich, used as received and kept under an argon atmosphere using standard Schlenk-Line techniques. Technical solvents were bought from VWR-International and used as received. Product isolation was performed using silica (60, F254, Merck[™]), and TLC analysis was performed using Silica on Al foils TLC plates (F254, Supelco Sigma-Aldrich[™]) in combination with UV quenching or appropriate TLC staining. Microfluidic accessories were purchased from IDEX Health and Science (distributed by Inacom Instruments). ¹H, ¹³C and ¹⁹F NMR analysis were performed on a Bruker-Avance 400 (400 MHz) in solvent CDCl₃ with TMS unless stated otherwise. ¹H NMR spectra are reported in parts per million (ppm) downfield relative to TMS (0.00 ppm). All ¹³C NMR spectra are reported in ppm relative to CDCl₃ (77.16 ppm) and all ¹⁹F NMR spectra are reported in ppm relative to α, α, α -trifluorotoluene (-63.72 ppm). NMR spectra uses the following abbreviations to describe the multiplicity; s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet & b = broad. Melting points were recorded on a Büchi melting point B-540. GC analyses were performed on a GC-FID (Varian 430-GC) in combination with an auto sampler (Varian CP-8400) or GC-MS combination (Shimadzu GC-2010 Plus coupled to a Mass Spectrometer; Shimadzu GCMS-QP 2010 Ultra) with an auto sampler unit (AOC-20i, Shimadzu). IR analyses were recorded on a Shimadzu (MIRacle 10 ATR) infrared spectrometer.

Continuous Microfluidic Setup

Setup for the trifluoromethylation in continuous microflow: All capillary tubing and microfluidic fittings are purchased from IDEX Health and Science (Figure 1, page S4, setup overview). The combination of syringe pump (1) (Fusion 200 Classic) and disposable syringes (BD Discardit II or NORM-JECT, 2 - 10 mL) are available from VWR International. The syringes are connected to the capillary (2) using ¹/₄-28 flat-bottom flangeless fittings. The capillary tubing (3) was of high purity PFA (1/16" • 500 µm ID). The gas/liquid mixing was carried out in a Cross Tefzel Micromixer (4) (500 µm ID, P-729 PEEK Cross or similar cross-mixer).

Reactor Setup. The reactor (5 - 7) was made out of a high purity PFA capillary tubing $(1/16'' \cdot 500 \ \mu\text{m ID} \cdot 2.5 \ \text{m})$, with 90% of the capillary length wrapped around a 100 mL disposable syringe (Figure A) and fixated with an elastic rubber. The *reactor-syringe-tip* was connected to a rubber hose which supplied a constant flow of air to maintain room-temperature. The reactor was positioned inside a beaker, supporting a coiled visible-light blue LED array (3.12 W, 78 lm, 39 LED (97 cm length), Paulmann Lighting GmbH). Tin foil was used to refract the excess light back to the capillary reactor. The reactor outlet was connected to a back-pressure-regulator (5 or 40 psi (0.3 or 2.8 bar), P-790 or P785 PEEK BPR Assembly, respectively) and followed through a rubber septum (8); accordingly the reaction mixture can be collected in a sealed environment under desired atmosphere (for example; Argon).

Gas-inlet. A single-gauge gas-regulator (9) (stainless steel, 0 - 30 psi, ¹/₄" NPFT inlet, Sigma-Aldrich) was connected to the CF₃I gas container. A closing valve (10a) (stainless steel, 1/8" connections, Swagelok) was situated between the gas-regulator and the gas/mass flow controller (MFC) (11), and connected with stainless steel tubing and fittings (Swagelok). The gas flow-rate was controlled by a pre-calibrated MFC for CF₃I gas (11a) (stainless steel, F-

201CV Digital MFC, EL-FLOW Select, $0.1 - 5.0 \text{ mLn} \cdot \text{min}^{-1}$, 1/8'' connections, Bronkhorst BV Netherlands) combined with a digital display (11b) (B2 Bright R/C module, IP-40, 1.8'' colour TFT with four buttons, Bronkhorst BV Netherlands). An emergency closing valve (12) (500 µm ID) was connected to the MFC with a stainless steel connector (1/8'' connections) prior to the gas carrier capillary (3a). Close-up photographs are shown below of the microfluidic setup (Pictures A1 – A4, page S5).



Figure S1. Schematic representation of the Microflow Setup.

Picture A1 - A4. Microflow Setup Overview and Close-ups.









General Procedure for the Trifluoromethylation of Aromatic Thiols

(compounds; 1b - 26b) Method A

An oven-dried vial was charged with Ru(bpy)₃Cl₂•6H₂O (1.0 mol%), thiol (1 mmol, 1 equiv.) and dissolved in MeCN (4 mL) (mixture A). The mixture was degassed by the freeze-pump-thaw method, using standard Schlenk-Techniques. A second mixture (mixture B) was prepared with, TEA (1.1 mmol, 1.1 eq.) in degassed MeCN (1 mL). Thereafter a gas-tight syringe was filled with gaseous trifluoroiodomethane (50 mL, 200 psi, 0.78 g, ~4 mmol, ~4 equiv.; Calculated with Ideal-Gas-Law, eq. 1),¹ and subsequently added to the reaction mixture A (bubbled through the reaction mixture in 10 min, see *Gaseous CF₃I Addition Method* below), followed with the dropwise addition of mixture B. The reaction mixture was placed approximately 5 cm away from a 24 W Compact Fluorescent Lightbulb.² The reaction mixture was followed by TLC, GC-MS and/or ¹⁹F-NMR analysis until completion. After completion, the reaction mixture was diluted with Et₂O (5 mL) and washed with aqueous HCl (1 M in H₂O, three times), and washed with aqueous NaHCO₃ (sat. in H₂O, one time). The combined water layers were collected and extracted with Et₂O (one time), followed by concentrating the combined Et₂O layers *in vacuo*. The crude mixture was purified with flash chromatography.

$$P * V = n * R * T \tag{eq. 1}$$

¹ Calculated moles were in close agreement with obtained empirical data.

² E-27 240V Calex Daylight Lamb, 24 Watt, 1460 Lumen, 3.8 mg Hg.

General Procedure for the trifluoromethylation of other thiols

(compounds; 27b – 29b) Method B

In addition to Method A, a portion of triphenylphosphine (1 mmol, 1 equiv.) and H_2O (1 mmol, 1 equiv.) was added to the reaction mixture prior to the addition of gaseous CF_3I and Mixture B. Analysis, workup and purification according to Method A.

Gaseous Trifluoroiodomethane Addition Method for Batch Protocol.



The following setup was prepared from commercially available components (see Figures below) and used as a dedicated apparatus for addition of the CF₃I gas into the reaction mixtures (Batch Protocol). Gas-Container-Setup (Picture B1). A single-gauge gas-regulator (X) (stainless steel, 0 - 30 psi, $\frac{1}{4''}$ NPFT inlet, Sigma-Aldrich) was connected to the CF₃I gas container. A closing valve (1) (stainless steel, 1/8" connections) was situated between the gasregulator (2) and the outlet (3). The outlet was sealed with a rubber septum (Supelco, Thermogreen [™], LB-2 Septa for Shimadzu) and a 1/8" stainless steel connector. Gas-Syringe-Setup (Picture B2). A gas-tight-syringe (4) (Size/Type is application dependant; 100 mL Non-disposable Gas Tight Syringe (Borosilicate Glass, SGE Analytical Science, Part # 009760, 100MR-LL-GT), 50 mL Disposable Gas Tight Syringe (Terumo - Three part syringes, Part # BS-50LG with Luer Lock)) was fitted with PFA capillary tubing, microfluidic fittings and a microfluidic closing-valve (IDEX Health and Science, parts # 1508, XP-130x and P-721, respectively) and connected to a long needle (Sterican[®] Long Needle, VWR International) (see Figure for clarification). The gas-tight-syringes were loaded onto a syringe pump (Fusion 200 Classic). Gas-Loading-Procedure (Picture B3) & Gas-Addition-**Procedure (Picture B4).** The needle can be connected through the rubber septum, and filled with the appropriate amount. After loading of the syringe, the valves are closed and the needle is placed in the reaction medium as depicted below. Gas can be added to the reaction mixture over given time (regulated by the syringe-pump).

Picture B-1 – B4, Gaseous Trifluoroiodomethane Addition Setup.









General Procedure for the Trifluoromethylation in Continuous Microflow

An oven-dried volumetric flask was loaded with thiol (0.3 mol/L), an equimolar amount of trifluorotoluene as internal standard, Ru(bpy)₃Cl₂•6H₂O (0.5 mol%). The flask was closed with a rubber septum and degassed; evacuated and backfilled with argon (three times), and filled up to 5 mL with anhydrous MeCN (Solution A). A second oven-dried volumetric flask was prepared with TEA (1.1 equiv.), degassed (*vide supra*), and filled to 5 mL with anhydrous MeCN (Solution B). Subsequently, the mixtures (A & B) were transferred to corresponding syringes and mounted on the syringe pump (see picture). The CF₃I gas flow was established and maintained at a constant flow rate (1.1 equiv., 0.05 - 5.0 mL • min⁻¹) by means of a MFC and a stable outlet pressure (max. 40 psi). A series of syringe pumps delivered a constant liquid flow rate inside the microreactor (8.33 – 500 µL• min⁻¹). Collection was enabled after reaching steady state (2 reactor volumes). After collection of the reaction mixture it was quantified by GC/MS and ¹⁹F-NMR analysis.

Note: a slug flow regime was established at the reactor inlet. However, upon progress of the reaction, a homogeneous flow was obtained when most of the CF₃I was consumed.

Optimization of the Batch Conditions



Product Disulfide

| | Cat. | CF ₃ X | Additive (equiv.) |
|-----------------------|--------------------------------------|------------------------------------|-------------------|
| Entry 1 | Ru(bpy) ₃ Cl ₂ | CF ₃ SO ₂ Cl | none |
| Entry 2 | Ir(ppy) ₃ | CF ₃ SO ₂ Cl | none |
| Entry 3 | Ir(F-ppy) ₃ | CF ₃ SO ₂ Cl | none |
| Entry 4 | Ru(bpy) ₃ Cl ₂ | CF ₃ I | none |
| Entry 5 | Ir(ppy) ₃ | CF ₃ I | none |
| Entry 6 | Ir(F-ppy) ₃ | CF ₃ I | none |
| Entry 7 | Ru(bpy) ₃ Cl ₂ | CF ₃ I | Pyr (2) |
| Entry 8 | Ru(bpy) ₃ Cl ₂ | CF ₃ I | TEA (2) |
| Entry 9 | Ru(bpy) ₃ Cl ₂ | CF ₃ I | DIPEA (2) |
| Entry 10 | Ru(bpy) ₃ Cl ₂ | CF ₃ I | DBU (2) |
| Entry 11 | Ru(bpy) ₃ Cl ₂ | CF ₃ I | TMEDA (2) |
| Entry 12 | Ru(bpy) ₃ Cl ₂ | CF ₃ I | TEA (1.1) |
| Entry 13 | Ru(bpy) ₃ Cl ₂ | CF ₃ I | TEA (0.5) |
| Entry 14 | none | CF ₃ I | TEA (1) |
| Entry 15 ³ | Ru(bpy) ₃ Cl ₂ | CF ₃ I | TEA (1) |

³ Reaction carried out in absence of visible light.

Optimization of the Continuous Microflow Conditions⁴



Graph S1: Et₃N Concentration in Continuous Microflow (mmol, equiv.).

Graph S2: CF₃I:Substrate ratio (equiv.) and CF₃I flow (mmol • min⁻¹).



⁴ Reaction samples were prepared and analyzed according to General Procedure (S10).

Substrate Scope of the Continuous Microflow System

| | Residence time (min) | Flow speed $(\mu l \bullet min^{-1})$ | Note | Yield (% ¹⁹ F-NMR) |
|------------------|-------------------------|--|------|---|
| CF ₃ | 2,3 | 111 | | 93 |
| | 1,7 | 150 | | 93 |
| ~ | 1,4 | 175 | | 96 |
| | 1,0 | 250 | | 91 |
| | 0,7 | 375 | | 88 |
| <u> </u> | | | | |
| CF ₃ | 1,0 | 375 | | 95 |
| Moo | 1,5 | 250 | | 95 |
| MEO | 2,5 | 150 | | 96 |
| | 5,0 | 75 | | 97 |
| NC SCF3 | 30,0 | 7 | | 46 |
| S _{CE} | 10,0 | 50 | | 41 |
| | 30,0 | 17 | | 59 |
| \sim | 60,0 | 8 | | 54 |
| 0 | | | | |
| CI CI CI | 1,0 | 500 | | 96 |
| S_CF3 | 1,0 | 500 | | 91 |
| F | 1,5 | 333 | | 93 |
| S CF3 | 1,0 | 500 | | 91 |
| | 2,5 | 200 | | 92 |
| ~ | 5,0 | 100 | | 87 |
| ~ S | 0.0 | 500 | | 72 |
| CF ₃ | 0,9 | 250 | | 70 |
| H ₂ N | 1,0 | 230 | | 19 |
| 2 | 1,8 | 200 | | 70 |
| | 5,0 | 50 | | /0 |
| | 9,0 | 50 | | /3 |
| S CF | 0,6 | 500 | | 66 |
| | 1,1 | 333 | | 67 |
| HO | 1,7 | 200 | | 69 |
| | 3,0 | 100 | | 78 |
| | | | | |

Mechanistic investigations



Scheme S1. Competition experiment.

This experiment demonstrates that the photocatalytic trifluoromethylation method is highly selective for thiophenols (Scheme S1). Phenol or aniline are completely unreactive. In the absence of a photocatalyst and light, no reaction is observed.



Scheme S2. Effect of the addition of an inorganic base instead of a nitrogen base. Reagents and conditions: thiophenol (1 mmol), CF₃I (4 mmol), Ru(bpy)₃Cl₂ (1 mol%), K₂HPO₄ (1.1 mmol) in MeCN (0.2 M, 5 mL), irradiated by 24W CFL for 1 hour, and analyzed by GC-MS.

The addition of inorganic base leads exclusively to the formation of the disulfide product. This observation indicates that the nitrogen base functions as a reductive quencher (Scheme S2).^[1] Inorganic bases cannot and probably are involved in a so-called proton-coupled electron transfer (PCET) to form a thiyl radical, which is in accordance with literature.^[2] This thiyl radical can subsequently react with thiophenol to give the observed disulfide product.^[3]



Scheme S3. Radical scavenging experiment. Reagents and conditions: thiophenol (0.5 mmol), *N*-methyl-1H-pyrrole (0.5 mmol), CF_3I (4 mmol), $Ru(bpy)_3Cl_2$ (1 mol%), Et_3N or K_2HPO_4 (1.1 mmol) in MeCN (0.2 M, 5 mL), irradiated by 24W CFL for 1 hour, and analyzed by GC-MS.

The formation of CF_3 radicals starting from CF_3I has been demonstrated by us as well as others in the past and has been conclusively demonstrated by TEMPO trapping experiments.^[4] The use of TEMPO is not possible under our reaction conditions given the reaction between TEMPO and thiols as shown in literature.^[5] Therefore, a competition experiment was carried out where N-methyl-1H-pyrrole was added together with thiophenol. Both N-methyl-1H-pyrrole and thiophenol were trifluoromethylated under the given reaction conditions indicating that indeed a CF_3 radical is formed. No direct reaction between N-methyl-1H-pyrrole and thiophenol was seen which indicates that a thiyl radical is not formed.

Table S1. Control experiments for the photocatalyzed trifluoromethylation of thiophenol with CF₃I. Reagents and conditions (unless stated otherwise): thiophenol (1 mmol), CF_3I (4 mmol), $Ru(bpy)_3Cl_2$ (1 mol%), Et_3N or K_2HPO_4 (1.1 mmol) in MeCN (0.2 M, 5 mL), irradiated by 24W CFL for 1 hour, and analyzed by GC-MS and NMR.

| \bigcirc | SH + CF ₃ I - | Catalyst, Additive | S-CF3 | + | s |
|------------|--------------------------------------|--------------------|---------------------------------------|--------------------|----------------------|
| Entry | Catalyst (1 mol%) | Light source | Additive (equiv) | Product (yield) | Disulfide (yield) |
| 1 | Ru(bpy) ₃ Cl ₂ | 24W CFL | TEA (1.1) | 100% | - |
| 2 | Ru(bpy) ₃ Cl ₂ | 24W CFL | - | <1% | 33% |
| 3 | Ru(bpy) ₃ Cl ₂ | - | TEA (1.1) | no rea | action |
| 4 | - | 24W CFL | TEA (1.1) | 55% | 45% |
| 5 | Ru(bpy) ₃ Cl ₂ | 24W CFL | K ₂ HPO ₄ (1.1) | <1% | 99% |
| 6 | - | 24W CFL | K ₂ HPO ₄ (1.1) | <1% | 45% |
| 7 | - | - | TEA (5.0) | no rea | action |

Emission spectra of light sources

The emission of the used light sources was recorded using an integrating sphere equipped with a Labsphere LPS 100-0260 light detector array. The results are shown in Figure S2 (white CFL light bulb) and Figure S3 (Blue LED).



Figure S2. Emission spectrum of the 24W Compact Fluorescent Light-bulb (CFL)



Figure S3. Emission spectrum of the 3.12W Blue LED array.



Phenyl(trifluoromethyl)sulfane (1b).⁶ Thiophenol (1a) was subjected to Method A and obtained in 95% yield as judged by NMR analysis (volatile product). TLC Rf.: 0.65 (100% PE). GC-MS: found m/z: 187.1 [M*], 109.0 [C6H5S*], 77.1 [C6H5*], 69.1 [CF3*]. 19F-NMR: δ -44.12



p-tolyl(trifluoromethyl)sulfane (2b).^{6,7} 4-methylthiophenol (**2a**) was subjected to Method A and obtained in 92% yield as judged by NMR analysis (volatile product). **TLC Rf.:** 0.78 (100% PE). **GC-MS:** found (m/z): 192.1 [M*], 91.0 [C7H7S*], 76.1 [C6H4*], 69.1 [CF3*]. **1H-NMR:** δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H). **13C-NMR:** δ 141.52, 136.50, 130.37, 129.85 (q, *J* = 307.6 Hz), 121.02 (q, *J* = 1.9 Hz), 21.35. **19F-NMR:** δ -44.76. **IR (neat):** v_{max} 2957, 2924, 2854, 1457, 1311, 1171, 1156, 1116, 1087, 1039, 1031, 1018, 822, 810, 771, 755, 685 cm⁻¹.



(**3-methylphenyl**)(**trifluoromethyl**)**sulfane** (**3b**).⁸ 3-methylthiophenol (**3a**) was subjected to Method A and obtained in 88% yield as judged by NMR analysis (volatile product). **TLC Rf.:** 0.75 (100% PE) **GC-MS:** found (m/z): 192.1 [M*], 91.0 [C7H7S*], 76.1 [C6H4*], 69.1 [CF3*] **19F-NMR:** δ -44.12.



(4-*tert*-Butylphenyl)(trifluoromethyl)sulfane (4b).⁹ 4-*tert*-butyl thiophenol (4a) was subjected to Method A and obtained in 85% yield (199 mg, white oil) after column chromatography (100% PE). TLC Rf.: 0.90 (100% PE), 0.82 (100% n-heptane) GC-MS: found (m/z): 234.1 [M*], 165.1 [C10H13S*], 133.1 [C10H13*], 69.1 [CF3*]. 1H-NMR: δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 1.31 (s, 9H). 13C-NMR: δ 154.27, 136.06 , 129.62 (q, *J* = 307.7 Hz), 126.47 , 120.77 , 79.65 – 73.76 (m), 30.98. 19F-NMR: δ -43.16. IR (neat): v_{max} 2965, 2908, 2872, 1596, 1490, 1464, 1395, 1365, 1268 cm⁻¹.



Naphthalene-2-yl(trifluoromethyl)sulfane (5b).⁶ naphthalene-2-thiol (5a) was subjected to Method A and obtained in 73% yield (166 mg, oil) after column chromatography (100% PE). TLC Rf.: 0.77 (100% PE). GC-MS: found (m/z): 228.1 [M*], 159.1 [C10H7S*], 127.1 [C10H7*], 69.2 [CF3*]. 1H-NMR: δ 8.23 (s, 1H), 7.89 (d, J = 8.2 Hz, 3H), 7.71 (d, J = 8.2Hz, 1H), 7.60 (ddd, J = 7.1, 5.3, 1.6 Hz, 2H).13C-NMR: δ 137.01 , 133.86 , 133.37 , 131.74 , 129.81 (q, J = 308.2 Hz), 129.19 , 128.13 , 127.90 , 127.74 , 126.97 , 121.45 (d, J = 2.1 Hz). 19F-NMR: δ -42.52. IR (neat): v_{max} 3059, 2982, 1593, 1502, 1311, 1151, 1100, 1074, 945, 896, 858 cm⁻¹.



(4-trifluoromethylphenyl)(trifluoromethyl)sulfane (6b).¹⁰ 4-(trifluoromethyl)thiophenol (6a) was subjected to Method A and obtained in 96% yield as observed by NMR analysis (volatile product). TLC Rf.: >0.90 (100% PE) GC-MS: found (m/z): 246.2 [M*], 177.1

[C7H4F3S*], 157.1 [C7H3F2S*], 145.0 [C7H4F3*], 68.9 [CF3*]. **19F-NMR:** δ -42.24, -62.86.



Biphenyl-4-yl(trifluoromethyl)sulfane (**7b**).⁷ biphenyl-4-thiol (**7a**) was subjected to Method A and obtained in 77% yield (196 mg, transparent solid) after column chromatography (100% PE). **TLC Rf.:** 0.84 (100% PE), 0.53 (100% n-pentane). **M.p.:** 39 - 42 °C (Lit.: 40 - 42 °C).⁷ **GC-MS:** found (m/z): 254.2 [M*], 185.1 [C12H9S*], 153.1 [C12H9*], 77.1 [C6H5*], 69.1 [CF3*]. **1H-NMR:** δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.49 (m, 3H), 7.41 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.38 – 7.32 (m, 2H). **13C-NMR:** δ 143.89 , 139.67 , 136.77 , 129.78 (q, *J* = 308.1 Hz), 129.01 , 128.21 , 128.16 , 127.24 , 123.12 (d, *J* = 2.2 Hz). **19F-NMR:** δ -43.91. **IR (neat):** v_{max} 1477, 1395, 1142, 1105, 1082, 1039, 1015, 1003, 970, 952, 913, 837, 759, 715, 690, 660 cm⁻¹.



(4-nitrophenyl)(trifluoromethyl)sulfane (8b).¹¹ 4-nitrothiophenol (8a) was subjected to Method A and obtained in 80% yield (178 mg, white solid) after column chromatography (2% EtOAc in PE).. TLC Rf.: 0.48 (2% EtOAc in PE). M.p.: 37 - 42 °C (Lit.: 42 °C).¹¹ GC-MS: found (m/z): 223.1 [M*], 154.1 [C6H4NO2S*], 76.1 [C6H4*], 69.1 [CF3*]. 1H-NMR: δ 8.28 (d, J = 8.9 Hz, 2H), 7.84 (d, J = 8.9 Hz, 2H). 13C-NMR: δ 149.11, 136.05, 132.49 (d, J = 1.8 Hz), 128.91 (q, J = 308.7 Hz), 124.31. 19F-NMR: δ -41.45. IR (neat): v_{max} 2982, 2957, 2923, 2872, 2853, 1730, 1480, 1463, 1459, 1399, 1288, 1277, 1260, 1152, 1134, 1109, 1080, 1055, 1009, 963, 911, 840, 798, 754, 740, 668 cm⁻¹.



4-(trifluoromethylthio)benzoic acid (9b).¹² 4-mercaptobenzoic acid (**9a**) was subjected to Method A and obtained in 90% yield (200 mg, white sold) after column chromatography (10% EtOAc in PE + 1% AcOH). **TLC Rf.:** 0.29 (10% EtOAc in PE + 1% AcOH). **M.p.:** 150 – 152 °C (Lit.: 161 – 163 °C).¹² **GC-MS:** found (m/z): 222.1 [M*], 153.1 [C7H5O2S*], 120.9 [C7H5O2*], 68.9 [CF3*]. **1H-NMR:** δ 11.11 (bs, 1H), 8.13 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H). **13C-NMR:** δ 177.88 , 175.07 , 170.99 , 135.42 , 130.92 , 129.22 (q, J = 308.8 Hz). **19F-NMR:** δ -45.73. **IR (neat):** v_{max} 2982, 2962, 2929, 2925, 2854, 1595, 1424, 1400, 1180, 1035, 934, 912, 818, 805 cm⁻¹.



(4-fluorophenyl)(trifluoromethyl)sulfane (10b).¹³ 4-fluorothiophenol (10a) was subjected to Method A and obtained in 65% yield as observed by NMR analysis (volatile product). TLC Rf.: >0.90 (100% PE). GC-MS: found (m/z): 196.1 [M*], 127.1 [C6H4SF*], 95.1 [C6H4F*], 69.1 [CF3*]. 19F-NMR: δ -43.37, -117.2.



(4-chlorophenyl)(trifluoromethyl)sulfane (11b).^{6,7} 4-chlorothiophenol (11a) was subjected to Method A and obtained in 78% yield (165 mg, volatile liquid) after column chromatography (100% PE). TLC Rf.: >0.90 (100% PE), 0.71 (n-heptane). GC-MS: found (m/z): 212.5 [M*], 143.2 [C6H4SCI*], 111.2 [C6H4CI*], 69.0 [CF3*]. 1H-NMR: δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H). 13C-NMR: δ 143.33 , 137.59 , 129.80 , 129.35 (q, *J* = 308.2 Hz), 122.83 (d, *J* = 2.2 Hz). 19F-NMR: δ -43.26.



(4-bromophenyl)(trifluoromethyl)sulfane (12b).^{6,7} 4-bromothiophenol (12a) was subjected to Method A and obtained in 82% yield (210 mg, transparent oil) after column chromatography (100% PE). TLC Rf.: 0.85 (100% PE). GC-MS: found (m/z): 257.1 [M*], 187.1 [C6H4SBr*], 155.2 [C6H4Br*], 69.1 [CF3*]. 1H-NMR: δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H). 13C-NMR: δ 137.89 , 132.93 , 129.33 (q, *J* = 308.4 Hz), 126.14 , 123.54. 19F-NMR: δ -42.81. IR (neat): ν_{max} 1474, 1387, 1158, 1113, 1081, 1066, 1009, 817, 756, 732 cm⁻¹.



methyl(4-(trifluoromethylthio)phenyl)sulfane (13b).⁷ 4-(methylthio)benzenethiol (13a) was subjected to Method A and obtained in 78% yield (174 mg, yellow oil) after column chromatography (1% EtOAc in PE). TLC Rf.: 0.79 (20% EtOAc in PE). GC-MS: found (m/z): 224.3 [M*], 155.1 [C7H7S2*]. 1H-NMR: δ 7.53 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 2.48 (s, 3H). 13C-NMR: δ 143.31 , 136.67 , 129.51 (q, J = 308.3 Hz), 126.33 , 119.69 (d, J = 2.1 Hz), 14.97. 19F-NMR: δ -43.88. IR (neat): v_{max} 1576, 1479, 1437, 1391, 1151, 1114, 1089, 1041, 1011, 968, 956, 812, 755, 748 cm⁻¹.



(4-methoxyphenyl)(trifluoromethyl)sulfane (14b).^{6,7} 4-methoxybenzenethiol (14a) was subjected to Method A and obtained in 87% yield (180 mg, volatile liquid) after column chromatography (2% EtOAc in PE). TLC Rf.: 0.70 (2% EtOAC in PE). GC-MS: found (m/z): 208.4 [M*], 139.1 [C7HSO*], 107.1 [C7H7O*], 69.2 [CF3*]. 1H-NMR: δ 7.57 (d, J =

8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H). **13C-NMR:** δ 161.84 , 138.26 , 129.62 (q, *J* = 308.2 Hz), 114.98 , 114.82 (d, *J* = 2.2 Hz), 55.37. **19F-NMR:** δ -43.88. **IR (neat):** v_{max} 1593, 1575, 1494, 1464, 1294, 1252, 1175, 1151, 1111, 1105, 1086, 1030, 1007, 929, 799, 755 cm⁻¹.



4-(trifluoromethylthio)aniline (**15b**).¹⁴ 4-aminobenzenethiol (**15a**) was subjected to Method A and obtained in 88% yield (170 mg, yellow oil) after column chromatography (20% EtOAc in PE + 1% TEA). **TLC Rf.:** 0.28 (20% EtOAc in PE + 1% TEA). **GC-MS:** found (m/z): 193.5 [M*], 124.0 [C6H6SN*], 92.1 [C6H6N*], 68.9 [CF3*]. **1H-NMR:** δ 7.61 (d, J = 1.6 Hz, 2H), 7.44 (dd, J = 8.5, 1.6 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H). **13C-NMR:** δ 146.05 , 140.12 , 123.13 (q, J = 272.2 Hz), 116.77 , 109.74 . **19F-NMR:** δ -65.76. **IR (neat):** v_{max} 2959, 2924, 2873, 2855, 1724, 1718, 1653, 1507, 1495, 1490, 1465, 1457, 1448, 1379, 1270, 1118, 1072, 1039, 962, 740, 705 cm⁻¹.



N,N-dimethyl-4-(trifluoromethylthio)aniline (16b).⁸ 4-(N,N-dimethylamino)benzenethiol (16a) was subjected to Method A and obtained in 85% yield (199 mg, oil) after column chromatography (100% PE). **TLC Rf.:** 0.39 (100% PE). **GC-MS:** found (m/z): 221.3 [M*], 152.2 [C8H10SN*], 120.1 [C8H10N*], 76.1 [C6H4*], 69.1 [CF3*]. **1H-NMR:** δ 7.46 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 2.98 (s, 6H). **13C-NMR:** δ 151.92 , 137.95 , 129.84 (q, *J* = 308.6 Hz), 112.35 , 108.33 , 40.06. **19F-NMR:** δ -44.70. **IR (neat):** v_{max} 2925, 2856, 1737, 1734, 1594, 1510, 1445, 1363, 1227, 1197, 1147, 1110, 1092, 1065, 1048, 999, 946, 812, 753 cm⁻¹.



N-(4-(trifluoromethylthio)phenyl)acetamide (17b).¹⁵ N-(4-mercaptophenyl)acetamide (17a) was subjected to Method A and obtained in 95% yield (223 mg, white solid) after column chromatography (50% EtOAc in PE). **TLC Rf.:** 0.24 – 0.32 (50% EtOAc in PE). **M.p.:** 185 – 186 °C (Lit.: 183 °C). **GC-MS:** (found (m/z): 235.4 [M*], 166.1 [C8H8NOS*], 134.1 C8H8NO*], 69.1 [CF*]. **1H-NMR (D6-DMSO)** δ 10.19 (bs, 1H), 7.68 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 2.03 (s, 3H).**13C-NMR (D6-DMSO):** δ 168.82 , 142.25 , 137.17 , 129.53 (q, J = 308.2 Hz), 119.72 , 115.52 , 109.54. **19F-NMR (D6-DMSO):** δ -42.99. **IR (neat):** v_{max} 1665, 1650, 1607, 1589, 1492, 1468, 1399, 1372, 1317, 1298, 1262, 1183, 1119, 1107, 1088, 1040, 1014, 968, 960, 949, 836, 827, 796, 761, 753, 716, 706 cm⁻¹.



4-(trifluoromethylthio)benzonitrile (18b).⁷ 4-mercaptobenzonitrile (18a) was subjected to Method A and obtained in 67% yield (136 mg, oil) after column chromatography (10% EtOAc in PE). TLC Rf.: 0.71 (10% EtOAc in PE). GC-MS: found (m/z): 203.2 [M*], 134.2 [C7H4SN*], 102.1 [C7H4N*], 69.1 [CF3*]. 1H-NMR: δ 7.71 (dd, J = 5.7, 3.3 Hz, 2H), 7.53 (dd, J = 5.7, 3.3 Hz, 2H). 13C-NMR: δ 167.73 , 132.42 , 130.85 , 129.91 (q, J = 308.5 Hz), 128.78 , 109.99. 19F-NMR: δ -42.60. IR (neat): v_{max} 2957, 2924, 2873, 2855, 1729, 1458, 1437, 1379, 1363, 1270, 1120, 1071, 1039, 961, 771, 740, 704 cm⁻¹.



4-(trifluoromethylthio)phenol (19b).⁸ 4-hydroxythiophenol (**19a**) was subjected to Method A and obtained in 92% yield (178 mg, yellow oil) after column chromatography (5% EtOAc in PE + 1% AcOH). **TLC Rf.:** 0.38 (5% EtOAc in PE + 1% AcOH). **GC-MS:** found (m/z): 194.1 [M*], 125.1 [C6H5SO*], 93.1 [C6H5O*], 69.1 [CF3*]. **1H-NMR:** δ 7.51 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.22 (bs, 1H). **13C-NMR:** δ 158.01 , 138.72 , 129.72 (q, *J* = 308.0 Hz), 116.67 , 115.39 (d, *J* = 2.2 Hz). **19F-NMR:** δ -45.75. **IR (neat):** v_{max} 3241, 1601, 1584, 1494, 1437, 1248, 1226, 1172, 1110, 1099, 1087, 1011, 828, 755, 651 cm⁻¹.



2-(trifluoromethylthio)pyridine (20b).⁶ 2-mercaptopyridine (**20a**) was subjected to Method A and obtained in 91% yield (163 mg, mild volatile fluid) after column chromatography (20% EtOAc in PE). **TLC Rf.:** 0.38 (20% EtOAc in PE). **GC-MS:** found (m/z): 179.2 [M*], 110.2 [C5H4SN*], 78.1 [C5H4N*], 69.1 [CF3*]. **1H-NMR:** δ 8.61 (ddd, *J* = 4.7, 1.9, 0.7 Hz, 1H), 7.72 (td, *J* = 7.9, 1.9 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.31 (ddd, *J* = 7.9, 4.7, 0.7 Hz, 1H). **13C-NMR:** δ 150.64 , 149.37 (d, *J* = 2.9 Hz), 137.68 , 129.35 (q, *J* = 308.2 Hz), 128.21 , 123.82. **19F-NMR:** δ -40.23.



4-(trifluoromethylthio)pyridine (21b).⁷ 2-mercaptopyridine (**21a**) was subjected to Method A and obtained in 73% yield (131 mg, volatile liquid) after column chromatography (20% EtOAc in PE). **TLC Rf.:** 0.40 (20% EtOAc in PE). **GC-MS:** (found (m/z): 179.1 [M*], 110.1 [C5H4SN*], 78.1 [C5H4N*], 69.1 [CF3*]. **1H-NMR:** δ 8.67 (d, *J* = 5.8 Hz, 2H), 7.51 (d, *J* =

5.8 Hz, 2H). **13C-NMR:** δ 150.42 , 135.91 , 128.90 (q, *J* = 308.3 Hz), 127.78. **19F-NMR:** δ - 40.56.



2-(trifluoromethylthio)pyrimidine (25b).¹⁶ 2-mercaptopyrimidine (25a) was subjected to Method A and obtained in 91% yield (163 mg, oil) after column chromatography (1% EtOAc in PE). **TLC Rf.:** 0.25 (1% EtOAc in PE). **GC-MS:** found (m/z): 180.2 [M*], 111.2 [C4H3N2S*], 79.1 [C4H3N2*], 69.2 [CF3*].**1H-NMR:** δ 8.56 (dd, *J* = 4.7, 1.7 Hz, 2H), 7.12 (td, *J* = 4.7, 1.7 Hz, 1H).. **13C-NMR:** δ 165.74 (q, *J* = 3.1 Hz), 158.02 , 128.32 (q, *J* = 307.6 Hz), 119.03 .. **19F-NMR:** δ -40.56.



2-(trifluoromethylthio)benzo[*d*]oxazole (22b).¹⁷ 2-mercaptobenzo[*d*]oxazole (22a) was subjected to Method A and obtained in 77% yield (169 mg, oil) after column chromatography (1% EtOAc in PE). **TLC Rf.:** 0.37 (1% EtOAc in PE). **GC-MS:** (found (m/z): 219.2 [M*], 150.1 [C7H4SNO*], 118.1 [C7H4NO*], 69.1 [CF3*]. **1H-NMR:** δ 7.78 (dd, *J* = 6.8, 2.1 Hz, 1H), 7.62 (dd, *J* = 6.8, 3.3 Hz, 1H), 7.59 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.42 (dd, *J* = 7.3, 1.3 Hz, 1H). **13C-NMR:** δ 152.51 , 141.49 , 131.02 , 129.35 (q, *J* = 312.2 Hz), 126.61 , 125.42 , 120.62 , 110.98. **19F-NMR:** δ -41.35. **IR (neat):** v_{max} 2957, 2924, 2873, 2855, 1730, 1718, 1653, 1507, 1490, 1465, 1458, 1448, 1379, 1362, 1270, 1121, 1071, 1039, 958, 741, 705 cm⁻¹.



2-(trifluoromethylthio)benzo[*d*]thiazole (23b).¹⁸ 2-mercaptobenzo[*d*]thiazole (23a) was subjected to Method A and obtained in 79% yield (186 mg, oil) after column chromatography (100% PE). TLC Rf.: 0.50 (100% PE). GC-MS: found (m/z): 235.2 [M*], 166.0 [C7H4S2N*], 134.0 [C7H4SN*], 68.9 [CF3*]. 1H-NMR: δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.50 (dt, *J* = 26.8, 8.1 Hz, 2H).13C-NMR: δ 153.18, 151.78 (d, *J* = 2.9 Hz), 137.96, 128.30 (q, *J* = 311.1 Hz), 127.05, 126.75, 124.20, 121.37. 19F-NMR: δ -42.56. IR (neat): v_{max} 1456, 1419, 1410, 1405, 1313, 1140, 1125, 1101, 1076, 989, 945, 756, 727, 707, 682 cm⁻¹.



2-(trifluoromethylthio)-1H-benzo[*d*]imidazole (24b).⁶ 2-mercapto-1H-benzo[*d*]imidazole (24a) was subjected to Method A (with solvent system 1:5 DMF/MeCN, instead) and obtained in 50% yield (110 mg, transparent oil) after column chromatography (2% EtOAc in PE). **TLC Rf.:** 0.65 (1% EtOAc in PE). **GC-MS:** found (m/z): 218.1 [M*], 149.1 [C7H5N2S*], 117.1 [C7H5N2*], 69.0 [CF3*]. **1H-NMR:** δ 13.55 (s, 1H), 7.65 (s, 1H), 7.31 (dd, *J* = 6.1, 3.1 Hz, 3H). **13C-NMR:** δ 148.90 , 140.64 , 133.66 (q, *J* = 310.2 Hz), 129.50 , 127.77 , 124.78 , 117.09 , 100.54. **19F-NMR:** δ -44.56. **IR (neat):** v_{max} 2980, 2960, 2930, 2873, 2680, 1723, 1717, 1458, 1407, 1395, 1352, 1330, 1301, 1275, 1162, 1144, 1102, 1075, 1052, 1008, 979, 966, 932, 762, 756, 743 cm⁻¹.



1-methyl-2-(trifluoromethylthio)-1H-benzo[d]imidazole (**26b).** 1-methyl-2-mercapto-1Hbenzo[*d*]imidazole (**26a**) was subjected to Method A (with solvent system 1:5 DMF/MeCN, instead) and obtained in 75% yield (175 mg, oil) after column chromatography (10% EtOAc in PE). **TLC Rf.:** 0.38 (10% EtOAc in PE). **GC-MS:** found (m/z): 232.2 [M*], 163.2 [C8H7N2S*], 131.2 [C8H7N2*], 116.1 [C7H4N2*], 69.1 [CF3*]. **1H-NMR:** δ 7.86 (dt, J =8.3, 0.8 Hz, 1H), 7.41 (dd, J = 3.8, 0.8 Hz, 2H), 7.36 (dq, J = 8.3, 3.8 Hz, 1H), 3.95 (s, 3H). **13C-NMR:** δ 143.39, 136.80, 132.85, 128.31 (q, J = 311.5 Hz), 125.07, 123.53, 121.13, 110.45, 31.46 .**19F-NMR:** δ -40.23. **IR (neat):** v_{max} 2925, 1465, 1447, 1412, 1337, 1327, 1282, 1160, 1145, 1117, 1100, 1088, 1004, 969, 818, 764, 746, 727 cm⁻¹.



benzyl(trifluoromethyl)sulfane (27b).¹⁹ Benzylthiol (**27a**) was subjected to Method B and obtained in 45% yield as observed by NMR analysis (volatile product). **GC-MS:** found (m/z): 192.1 [M*], 123.1 [C7H7S*], 77.1 [C6H5*], 69.1 [CF3*]. **19F-NMR:** δ -41.73.



cyclohexyl(trifluoromethyl)sulfane (28b).²⁰ Cyclohexanethiol (28a) was subjected to Method B and obtained in 41% yield as observed by NMR analysis (volatile product). **GC-MS:** found (m/z): 184.2 [M*], 115.1 [C6H11S*], 69.1 [CF3*]. **19F-NMR:** δ -39.30.



phenethyl(trifluoromethyl)sulfane (29b).²¹ 2-phenylethanethiol (29a) was subjected to Method B and obtained in 55% yield as observed by NMR analysis (volatile product). GC-MS: found (m/z): 206.1 [M*], 137.1 [C8H9S*], 91.1 [C7H7*], 69.1 [CF3*]. 19F-NMR: δ - 41.25.



ethyl 2,2-difluoro-2-(phenylthio)acetate (30b).²² An oven-dried vial was charged with Ru(bpy)₃Cl₂•6H₂O (1.0 mol%), thiophenol (1 mmol, 1 equiv.), ethyl 2-bromo-2,2difluoroacetate (2 mmol, 2 equiv.) and dissolved in MeCN (4 mL) (mixture A). The mixture was degassed by the freeze-pump-thaw method, using standard Schlenk-Techniques. A second mixture was prepared with amino base TEA (1.1 mmol, 1.1 eq.) in degassed MeCN (1 mL) and added drop wise to mixture A. The reaction mixture was placed approximately 5 cm away from a Compact Fluorescent Lightbulb (24 W, 1480 lm). The reaction mixture was followed by TLC, GC-MS and/or ¹⁹F-NMR analysis until completion. After completion; the reaction mixture was diluted with Et_2O (5 mL) and washed with aqueous HCl (1 M in H_2O). three times), and washed with aqueous $NaHCO_3$ (sat. in H₂O, one time). The combined water layers were collected and extracted with Et₂O (one time), followed by concentrating the combined Et₂O layers *in vacuo*. The crude mixture was purified with flash chromatography (2% EtOAc in PE) to yield 87% (200 mg, oil) product. **TLC Rf.:** 0.38 (2% EtOAc in PE). GC-MS: found (m/z): 232.1 [M*], 159.1 [C7H5F2S*], 109.1 [C6H5S*], 77.1 [C6H5*]. 1H-**NMR:** δ 7.64 – 7.56 (m, 2H), 7.47 – 7.41 (m, 1H), 7.41 – 7.34 (m, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). **13C-NMR:** δ 161.62 (t, J = 32.4), 136.74, 130.66, 129.34, 124.86 (t, J = 2.5 Hz), 120.15 (t, J = 286.9 Hz), 63.60 , 13.78. **19F-NMR:** δ -82.17. **IR** (neat): v_{max} 1763, 1728, 1475, 1442, 1392, 1371, 1287, 1173, 1102, 1086, 1068, 1014, 975, 856, 834, 784, 751, 721, 701, 689 cm⁻¹.



phenyl(perfluorohexyl)sulfane (31b).¹⁵ An oven-dried vial was charged with Ru(bpy)₃Cl₂•6H₂O (1.0 mol%), thiophenol (1 mmol, 1 equiv.), 1,1,1,2,2,3,3,4,4,5,5,6,6tridecafluoro-6-iodohexane (2 mmol, 2 equiv.) and dissolved in MeCN (4 mL) (mixture A). The mixture was degassed by the freeze-pump-thaw method, using standard Schlenk-Techniques. A second mixture was prepared with amino base TEA (1.1 mmol, 1.1 eq.) in degassed MeCN (1 mL) and added drop wise to mixture A. The reaction mixture was placed approximately 5 cm away from a Compact Fluorescent Lightbulb (24 W, 1480 lm). The reaction mixture was followed by TLC, GC-MS and/or ¹⁹F-NMR analysis until completion. After completion; the reaction mixture was diluted with Et₂O (5 mL) and washed with aqueous HCl (1 M in H₂O, three times), and washed with aqueous NaHCO₃ (sat. in H₂O, one time). The combined water layers were collected and extracted with Et₂O (one time), followed by concentrating the combined Et₂O layers *in vacuo*. The crude mixture was purified with flash chromatography (100% PE) to yield 75% (378 mg, yellow oil) product. TLC Rf.: 0.5 (100% PE). **GC-MS:** found (m/z): 428.1 [M*]. **1H-NMR:** δ 7.38 (t, J = 7.2 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.25 (d, J = 7.2 Hz, 2H). **13C-NMR:** δ 139.05 , 128.91 , 128.67 , 127.15 , 126.25 - 122.08 (m), 119.90 - 118.06 (m), 116.03 (t, J = 33.1 Hz), 113.82 (d, J = 33.1 Hz), 111.12 (d, J = 33.1 Hz), 109.81 – 107.50 (m). **19F-NMR:** δ -80.16 – -82.56 (m), -87.50 (ddt, J = 13.7, 6.5, 3.2 Hz), -119.97 (ddt, J = 18.5, 10.2, 3.2 Hz), -121.55 (dt, J = 13.0, 6.5 Hz), -122.83 - -123.10 (m), -126.38 (ddd, J = 18.5, 9.3, 3.9 Hz). **IR** (neat): v_{max} 1362, 1284, 1235, 1195, 1144, 1122, 1093, 1044, 1020, 1009, 742, 735, 720, 707, 696, 690, 668 cm⁻¹.



(4-methoxyphenyl)(perfluorobutyl)sulfane (34b). An oven-dried vial was charged with Ru(bpy)₃Cl₂•6H₂O (1.0 mol%), 4-methoxythiophenol (1 mmol, 1 equiv.), 1,1,1,2,2,3,3,4,4nonafluoro-4-iodobutane (2 mmol, 2 equiv.) and dissolved in MeCN (4 mL) (mixture A). The mixture was degassed by the freeze-pump-thaw method, using standard Schlenk-Techniques. A second mixture was prepared with amino base TEA (1.1 mmol, 1.1 eq.) in degassed MeCN (1 mL) and added drop wise to mixture A. The reaction mixture was placed approximately 5 cm away from a Compact Fluorescent Lightbulb (24 W, 1480 lm). The reaction mixture was followed by TLC, GC-MS and/or ¹⁹F-NMR analysis until completion. After completion; the reaction mixture was diluted with Et_2O (5 mL) and washed with aqueous HCl (1 M in H_2O , three times), and washed with aqueous NaHCO₃ (sat. in H₂O, one time). The combined water layers were collected and extracted with Et_2O (one time), followed by concentrating the combined Et₂O layers *in vacuo*. The crude mixture was purified with flash chromatography (10% EtOAc in PE) to yield 91% (325 mg, yellow oil) product. TLC Rf.: 0.45 (10% EtOAc in PE). GC-MS: found (m/z): 358.1 [M*], 139.1 [C7H7OS*], 69.1 [CF3*]. 1H-NMR: δ 7.55 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H). **13C-NMR:** δ 162.32, 139.32, 122.94 (t, J = 33.4 Hz), 119.08 (t, J = 33.4 Hz), 116.21 (t, J = 33.4 Hz), 115.15, 113.22, 110.83 (t, J = 33.4 Hz), 55.41. **19F-NMR:** δ -81.32 (tt, J = 9.8, 2.8 Hz), -88.19 (ddd, J = 15.6, 9.8, 2.8 Hz), -120.37 (ddd, J = 14.9, 7.3, 2.8 Hz), -125.77 (tt, J = 12.3, 6.1 Hz). IR (neat): v_{max} 1593, 1573, 1495, 1465, 1349, 1294, 1231, 1199, 1183, 1174, 1133, 1101, 1086, 1031, 982, 864, 828, 792, 745, 729, 693 cm⁻¹.



4-(trifluoromethylsulfinyl)biphenyl (35).²³ In an oven-dried vial was loaded; biphenyl-4yl(trifluoromethyl)sulfane (7b) (0.1 mmol, prepared as mentioned above, after pH neutralisation of the reaction medium) dissolved in MeCN (0.5 mL, 0.2 M) and stirred at room temperature. Hydrogenperoxide (30% w/w. in H₂O, 0.5 mL,) was added drop wise to this solution at room temperature and stirred for 3 hours. After this; the reaction mixture was diluted with Et₂O and washed with aqueous HCl (1 M in H₂O, three times), and washed with aqueous NaHCO₃ (sat. in H₂O, one time). The combined water layers were collected and extracted with Et₂O, followed by concentrating the combined organic layers. The crude mixture was purified with flash chromatography (100% PE, transparent oil) to afford **35** in 60% yield over 2 steps. **GC-MS:** found (m/z): 298.1 [M*]. **1H-NMR:** δ 7.69 – 7.64 (m, 2H), 7.58 – 7.50 (m, 4H), 7.44 – 7.31 (m, 3H). **13C-NMR:** δ 143.97, 139.75, 136.86, 129.86 (q, *J* = 333.0 Hz), 129.10, 128.29, 128.25, 127.33, 123.20. **19F-NMR:** δ -72.4. **IR (neat):** v_{max} 1477, 1396, 1142, 1105, 1084, 1015, 1003, 970, 914, 838 cm⁻¹.



N-phenyl-4-(trifluoromethylthio)aniline (36).²⁴ An oven-dried vial was charged with Pd(OAc)₂ (1 mol%), JohnPhos ligand (2 mol%), NaOMe (1.4 mmol, 1.4 equiv) and (4-bromophenyl)(trifluoromethyl)sulfane (**12b**, as prepared above) (1 mmol). The vial was sealed and degassed with argon, using standard Schlenk-Techniques. Toluene (5 mL) was added and the mixture was stirred. Aniline (1.2 mmol, 1.2 equiv) was added and the reaction was stirred at 60 °C. The reaction mixture was followed by TLC, GC-MS and/or ¹⁹F-NMR analysis until completion. After all starting material had been consumed, the mixture was cooled to room temperature and diluted with ether.) and washed with aqueous HCl (1 M in H₂O, three times), and washed with aqueous NaHCO₃ (sat. in H₂O, one time). The combined water layers were collected and extracted with Et₂O (one time), followed by concentrating the combined Et₂O layers *in vacuo*. The crude mixture was purified with silica flash chromatography (Et₂O and PE) to yield 75% product. **1H-NMR:** δ 8.23 (s, 1H), 7.94 – 7.84 (m, 5H), 7.74 – 7.54 (m, 4H). **13C-NMR:** δ 137.97, 136.33, 132.78, 131.11, 130.18, 129.09, 127.59 (q, *J* = 308.2), 127.51, 127.12. **19F-NMR:** δ -42.78. **IR (neat):** v_{max} 2959, 2924, 2873, 2855, 1724, 1718, 1653, 1507, 1495, 1490, 1465, 1448, 1379, 1270, 1118, 1072, 1039 cm⁻¹.

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NMR Spectra





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-90 -100 -110 -120 -130 -140 f1 (ppm) -2 -10 -20 -30 -70 -40 -50 -60 -80 -150 -180 -190 -160 -170























50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 (f1 (ppm)



-90 -100 -110 f1 (ppm) 0 -10 -20 -30 -120 -130 . -40 -50 -60 -70 -80 -140 -150 -160 -170 -180 -190 -2

















50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 (f1 (ppm)











50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 i f1 (ppm)



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|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------------------|------|------|------|------|------|------|------|------|------|----|
| 0 | -10 | -20 | -30 | -40 | -50 | -60 | -70 | -80 | -90 | -100 f1 (ppm) | -110 | -120 | -130 | -140 | -150 | -160 | -170 | -180 | -190 | -2 |







-90 -100 -110 -120 -130 f1 (ppm) -2 0 -20 -10 -30 -40 -50 -60 -70 -80 -140 -150 -180 -190 -160 -170





























60 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 f1 (ppm)







80 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 6 fi (ppm)



| | | | | | · · | | | | · · | · · · | · · · | | | · I | | | | | | |
|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----------------|------------|------|------|------|------|------|------|------|------|----|
| 0 | -10 | -20 | -30 | -40 | -50 | -60 | -70 | -80 | -90 | -100 f1 (ppm | -110 1) | -120 | -130 | -140 | -150 | -160 | -170 | -180 | -190 | -2 |





















0 -90 -100 -110 -120 -130 f1 (ppm) -2 -10 -20 -30 -50 -60 -70 -80 -190 -40 -140 -150 -160 -170 -180













154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102 100 98 96 94 92 9 f1 (ppm)



0 -90 -100 -110 -120 -130 f1 (ppm) -10 -20 -30 -70 -80 -160 -40 -50 -60 -140 -150 -170 -180 -190 -2





































0 -100 -110 f1 (ppm) -10 -20 -50 -90 -120 -180 -190 -2 -30 -40 -60 -70 -80 -130 -140 -150 -160 -170














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|----|----|----|---|-----|-----|-----|-----|-----|-----|-----|-------------|-------------|------|------|------|-------|------|------|------|------|------|------|------|
| 30 | 20 | 10 | 0 | -10 | -20 | -30 | -40 | -50 | -60 | -70 | -80 f1 (| -90 ppm) | -100 | -110 | -120 | -130 | -140 | -150 | -160 | -170 | -180 | -190 | -200 |