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Benchmark and Solvent-Free Preparation of Sulfonium Salt Based Electrophilic Trifluoromethylating Reagents

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Dedicated to Prof. Yves Langlois on the occasion of his 70th birthday

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Here we describe work devoted to the one-pot preparation of electrophilic trifluoromethylating reagents. The first part describes a reappraisal of our earlier experimental conditions and leads to an improved protocol that avoids the use of solvent and allows better yields. The second part carefully studies the behavior of biaryl substrates, whose structures can drive the reaction through the formation of original noncyclic or tricyclic dibenzothiophenium salts. New compounds were tested, in a standard reaction with aniline, for their trifluoromethylating power and revealed equivalent or improved reactivity relative to that of existing reagents. Furthermore, contrary to common knowledge, the presence of electron-donating methyl groups gave reagents with very high activity.

Introduction

The trifluoromethyl group enjoys a special interest amongst fluorinated substituents. Starting from a status of "me to" group for replacing chlorine in crop treatment and pesticide chemistry,[1] it gains importance in the domain of materials[2] and now emerges as a choice substituent in medicinal chemistry.[3] Earlier[4] or new methods[5] for its direct elaboration are best suited for the preparation of small trifluoromethyl-bearing synthons. In the case of more elaborate substrates it is usually more convenient to introduce this substituent as a whole in a later stage of the synthesis. For this purpose, thanks to recent progress in organofluorine chemistry, radical, nucleophilic, and electrophilic trifluoromethylating tools are now available.[6] Amongst these tools, electrophilic trifluoromethylating reagents were the last to come into the arsenal of chemicals and so are scarcely used in laboratories. They suffer indeed from major drawbacks: their poor availability and their reactivity, which is often limited to particular substrates and/or experimental conditions. There is a high demand for new reagents and the intensive research devoted to that field is nicely illustrated by two recent discoveries. Togni et al. reported efficient two-step syntheses of hypervalent iodine(III)–CF_3 reagents **1** (Figure 1).[7] The key step was the displacement of an acetoxy group attached to iodine with (trifluoromethyl)trimethylsilane (Ruppert's reagent) through a formal umpolung sequence of the CF_3 group. Iodo derivative **1** possesses good activity for the trifluoromethylation of carbon or heteroatom (P and S) nucleophiles. Very recently, Shibata and coworkers published fluorinated analogue **2** of a Johnson-type methyl-transfer reagent.[8] They demonstrated the great potential of this new molecule for the electrophilic trifluoromethylation of β-keto esters and also realized the first vinylogous trifluoromethylation of dicyanoalkylidenes. The first series of sulfur-based trifluoromethylating compounds **1** were described earlier by Yagupolskii et al. in 1984.[9] Alternative routes for the preparation of these reagents were proposed by Shreeve and coworkers[10] and very recently again by Yagupolskii.[11] During this time, great improvements have been made by Umemoto et al. with the design of numerous dibenzothiophenium salts **4**.[12] This constrained aromatic skeleton associated with electron-withdrawing groups (R^1 and R^2) insured enhanced reactivity for the trifluoromethylation of carbon nucleophiles (for A = S, Se, Te)[13] and hetero (O and N) nucleophiles (for A = O).[14] Nevertheless, only one Umemoto-type reagent is currently commercially available ($R^1 = R^2 = H$, A = S) and sometimes displays disappointing reactivity, espe-

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cially for carbon trifluoromethylation. Although this problem can be partially solved thanks to the protocol of Cahard,[15] the development of an easy protocol for the production of new trifluoromethylating reagents is still a tricky challenge.

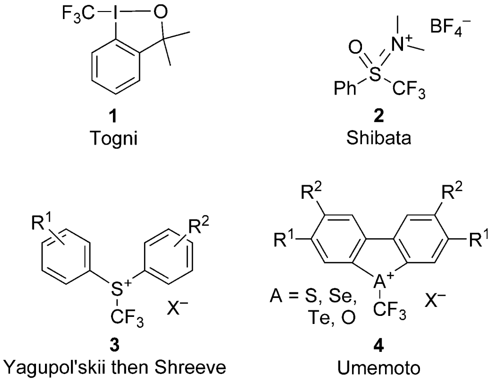
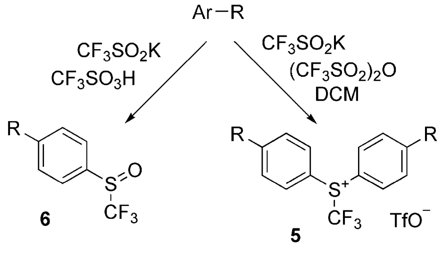


Figure 1. Electrophilic trifluoromethylating reagents.

Yagupol'skii or Shreeve reagents were usually prepared by activation of a preformed aryltrifluoromethyl sulfoxide with trifluoromethanesulfonic anhydride followed by Friedel–Crafts-like condensation with an aromatic ring. In this area, we first described the one-pot preparation of aryl trifluoromethyl sulfoxides **6**, involving treatment of an aromatic compound with potassium trifluoromethanesulfinate in the presence of trifluoromethanesulfonic acid.[16] In a further improvement, we showed that the simple replacement of the acid by trifluoromethanesulfonic anhydride gave rise directly to sulfonium salts **5** instead of sulfoxides **6** (Scheme 1).[17]



Scheme 1. Sulfonium salts vs. sulfoxides synthesis.

This procedure emerged as a powerful tool, accessible to all chemists, for the one-pot preparation, from commercially available compounds, of a wide range of new or known trifluoromethylating reagents **3**.

In efforts to extend this methodology to the preparation of more elaborate tricyclic sulfonium salts of type **4** (Umemoto-type reagents), we first envisaged a reappraisal, and subsequent updating, of the reaction conditions used earlier for the preparation of noncyclic sulfonium salts **3**. We finally describe a comparison of the trifluoromethylating power of the new reagents obtained.

Results and Discussion

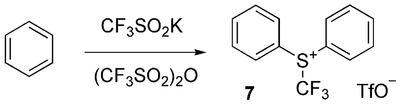
Improvement in the Formation of Sulfonium Salts

The main parameters susceptible to influence the course of the process were deduced to be the stoichiometry, the solvent, and finally the purity of the reagents. This study was conducted with a model reaction by using benzene as the substrate.

Stoichiometry

In our previous communication, we disclosed reaction conditions involving equivalent amounts of each reagent (aromatic substrate, potassium trifluoromethanesulfinate, and trifluoromethanesulfonic anhydride; Table 1, Entry 1). This appeared in opposition with the stoichiometry inferred from the mechanism proposed where two aromatic nuclei are theoretically needed for one mole of triflinate (Scheme 2).

Table 1. Influence of the stoichiometry and solvent.



Entry	Solvent	Equiv. of benzene[a]	Tf_2O	Yield of **7** [%][b]
1	CH_2Cl_2	1	1	60
2	CH_2Cl_2	2	1	18
3	none	5	1	3
4	none	2	10	12
5	none	1	4	77
6	none	1	3	71
7	none	1	2	69
8	none	1	1	20[c]

[a] Number of equivalents relative to potassium trifluoromethanesulfinate. [b] Isolated yield after purification by flash chromatography and calculated according to the number of moles of benzene. [c] In a mixture with 17% (*S*)-(trifluoromethyl)phenyl-2-trifluoromethylthiophenylsulfonium triflate.

$$CF_3SO_2K + Tf_2O + 2ArH \longrightarrow Ar_2S^+CF_3TfO^- + CF_3SO_3K + H_2O$$

Scheme 2. Global equation for synthesis of sulfonium salts.

The use of two equivalents of the aromatic compound (Table 1, Entry 2) was detrimental to the yield. This decrease was accentuated if benzene was introduced as a reagent and solvent (Table 1, Entry 3) even with increased quantities of trifluoromethanesulfonic anhydride (Table 1, Entry 4). These experiments clearly indicated that the aryl reagent should be introduced in a substoichiometric amount. The mechanism proposed earlier for this reaction is perhaps more complex than was originally thought and warrants further investigation, which is out of the scope of this manuscript.

Solvent

Dichloromethane, initially chosen for its inertness towards the reaction mixture and mainly used to increase the volume of the reaction medium, was not able to provide a homogeneous reaction mixture. When trifluoromethanesulfonic anhydride was used in its place as both the solvent and the reagent an enhancement in the yield was observed (Table 1, Entries 5–7). This result can be explained by better solubilization of the species, in particular potassium trifluoromethanesulfinate, and consequently by a better reactivity of the latter. Without solvent or an excess amount of reagent (Table 1, Entry 8), the yield was not significant due to extensive caking of the reaction mixture accompanied by the formation of a reduced sulfonium byproduct.

Purity of the Reagents

The nature of the trifluoromethanesulfinate reagent was studied next in order to detect any influence of the cation. Numerous synthetic methods for trifluoromethanesulfinates are described in the literature.[18] We tested four allowing the one-step preparation of the desired molecule (Table 2). We first noticed that the purity of the compounds obtained by using different methodologies was highly variable.[19] Moreover, it became evident that the yield of sulfonium salt was directly correlated with the purity of the reagent regardless of the nature of the cation. Various sources of trifluoromethanesulfinate are thus available for the procedure.

Table 2. Choice of the trifluoromethanesulfinate salt.

Entry	CF_3SO_2X		Purity[a]	Yield of **7**[b]
	X	Origin		[%]
1	Na	CF_3Br[20,21]	low	44
2	Na	CF_3CO_2Na[22]	high	72
3	Na	commercial	fair[c]	60
4	K	CF_3SO_2Cl[23]	low	34
5	K	CF_3CO_2K[22]	high	70
6	K	CF_3SiMe_3[24]	high	66
7	Cs	CF_3SiMe_3[25]	high	70

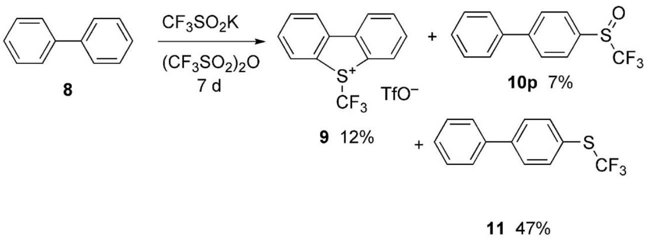
[a] Determined by ionic chromatography, NMR spectroscopy, and elemental analysis data. [b] Isolated yield after purification by flash chromatography of the diphenyl trifluoromethylsulfonium salt. [c] Variations of purity were observed between different batches.

In conclusion, the purity of the trifluoromethanesulfinate salt is an essential factor for the success of this reaction and the best compromise between the yield and the number of anhydride equivalents seems to be achieved by the stoichiometry depicted in Entry 7 (Table 1). These improved conditions, which gave a better yield and avoided the use of solvent, were used for the following work and constitute our standard procedure.

One-Pot Synthesis of Trifluoromethylating Agents Starting from Biphenyl Derivatives

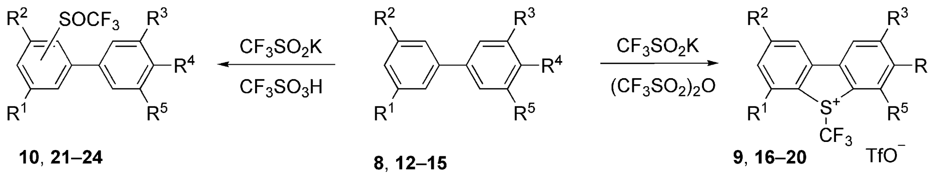
We then took advantage of these improvements to propose a one-step access to known and new dibenzothiophenium salts **4** through an extension of our methodology to biaryl molecules. On the basis of the probable occurrence of a trifluoromethyl sulfoxide intermediate, and depending on the substrate used, the success of this approach relied heavily on the first Friedel–Crafts-type trifluoromethanesulfinylation in the *ortho* position of the phenyl–phenyl link by the bis-protonated trifluoromethanesulfinate salt.[12b,17] We thus also undertook, for each aromatic substrate, the independent preparation of such sulfoxides in order to check the directing influence of the substituents located on the phenyl groups.

With biphenyl itself, Umemoto reagent **9** was isolated in pure form in 12% yield (Table 3, Entry 1). No other sulfonium compounds could be detected by NMR spectroscopy. This is the first one-step synthesis of this key reagent for electrophilic trifluoromethylation (Scheme 3).



Scheme 3. One-pot preparation of Umemoto's reagent.

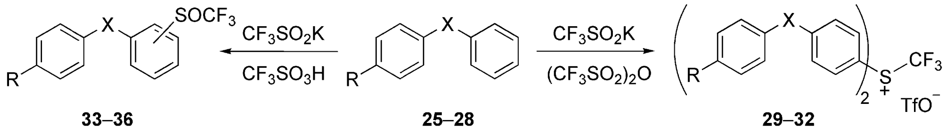
Table 3. Preparation of dibenzothiophenium salts.



Entry	Product / Yield [%][a]	*o*/*p*[b]	Substrate	R^1	R^2	R^3	R^4	R^5	Product / Yield [%][a]
1	**10**[c] / 60	10:90	**8**	H	H	H	H	H	**9** / 12
2	**21** / 69	30:70	**12**	H	Me	H	H	Me	**16**,**17**[d] / 15
3	**22** / 47	97:3	**13**	Me	Me	H	H	H	**18** / 36
4	**23** / 50	90:10	**14**	Me	Me	Me	H	Me	**19** / 46
5	**24** / 54	70:30	**15**	Me	Me	H	NO_2	H	**20** / 27

[a] Isolated yield after purification by flash chromatography. [b] Related to the aryl–aryl bond. [c] In case of a mixture of isomers, they are distinguished by indexation of their numbers in the text with *o* and *p*, including the Experimental Section. [d] As a 70 (R^3 = Me, R^5 = H):30 (R^3 = H, R^5 = Me) mixture of isomers.

Table 4. Preparation of biaryl sulfonium salts.



33–36 **25–28** **29–32**

Entry	Sulfoxide	Yield [%][a]	*o*/*p*[b]	Substrate	X	R	Sulfonium	Yield [%][a]
1	**33**	37	4:96	**25**	none	NO_2	**29**	30
2	**34**	56	4:96	**26**	CH_2	H	**30**	48
3	**35**	52	0:100	**27**	$C(Me)_2$	H	**31**	48
4	**36**	64	20:80	**28**	O	H	**32**	36

[a] Isolated yield after purification by flash chromatography. [b] Related to the aryl–aryl link.

In addition to Umemoto's reagent, other compounds were also isolated by column chromatography: 1,1′-biphenyl-4-yl trifluoromethyl sulfoxide (**10p**; 7% yield), its reduced form 1,1′-biphenyl-4-yl trifluoromethyl sulfide (**11**; 47% yield) and other unidentified molecules bearing the SCF_3 group as proven by the ^{19}F NMR spectra of the nonpolar fractions. This correlates very well with sulfoxide formation where the *para* isomer is largely predominant (Table 3, Entry 1). During formation of the sulfonium salt, only the *ortho* sulfoxide cyclizes into the sulfonium, whereas the *para* sulfoxide is not transformed into a Yagupol'skii–Shreeve-type sulfonium salt; instead it is subjected to a competitive reducing process. This reduction pathway has already been observed in previous work.[26]

We believed that the yields for the formation of Umemoto-type reagents could be improved with the use of biphenyl skeletons that are well equipped with electron-donating substituents that are able to drive the reaction at the *ortho* position of the biphenyl junction. Attempted use of methoxy substituents for this purpose was met by partial demethylation of the ether functionalities in the acidic medium. We thus restricted our study to methyl substitution.

With 3,3′-dimethyl-1,1′-biphenyl (**12**), we noticed a small increase in yield (15%) for dibenzothiophenium salts **16** and **17**, which is still rationalized by the ratio of isomers **21** in favor of the *para* isomer (Table 3, Entry 2). Better results were obtained with aromatic molecules **13**–**15**.[27] Aromatic **13** (3,5-disubstituted) was converted into sulfoxide **22** as almost a single isomer in favor of the desired *ortho* compound (Table 3, Entry 3). The presence of the two methyl groups is thus efficient for the activation of the first ring and their position allows high selectivity. As a consequence, dibenzothiophenium salt **18** could now be prepared with an acceptable yield (36%), slightly below the theoretical maximum yield (47%) defined here by the rate of preparation of the *ortho* sulfoxide. If the second ring also contained two methyl groups like in **14** (3,3′,5,5′ substitution pattern), sulfonium **19** was obtained in better yield (46%), fully equivalent to the conversion of biphenyl **14** into sulfoxide **23** (Table 3, Entry 4).

The introduction of a nitro group ($R^4 = NO_2$) in **12** (compound **15**) is slightly detrimental for the *ortho*/*para* selectivity of formation of **24** but gives rise again in one step, with a somewhat decreased yield, to sulfonium **20** possessing a powerful electron-withdrawing group (Table 3, Entry 5).

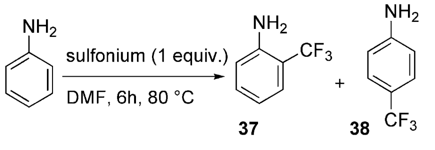
By contrast, with the nitro group as the unique substituent [4-nitro-1,1′-biphenyl (**25**)], only Yagupolskii–Shreeve-type sulfonium **29** was obtained, in accordance with single *para* sulfoxide **33** formation (Table 4, Entry 1).

Similar behavior was observed when a bridge was present between the two aromatic rings. With a carbon bridge, sulfonium salts **30** and **31** were isolated (Table 4, Entries 2 and 3) as expected, considering the exclusive formation of *para* isomers **34** and **35**. With an oxygen atom as the linker, again single sulfonium **32** was produced although an *ortho*/*para* mixture of isomers of sulfoxide **36** was formed (Table 4, Entry 4). The presence of numerous reduced compounds in the crude mixture and no trace amounts of the *ortho* sulfoxide suggested that this intermediate does not cyclize rapidly enough and secondary products are evolved. The failure of the production of tricyclic sulfonium salts in these cases can be explained by an inappropriate relative conformation of the two aromatic rings. Umemoto observed a very slow reaction and a low yield for the intramolecular condensation of 1-phenoxy-2-[(trifluoromethyl)sulfonyl]benzene and attributed this result to an important stabilization of the transition state by the oxygen atom.[12b]

Evaluation of the Trifluoromethylating Power

The trifluoromethylating power of our reagents was then tested with a model reaction. Amongst the numerous possibilities, we selected the aromatic trifluoromethylation of aniline. This reaction was chosen for its efficiency and its easiness to run. In order to possess confident data to reinforce the results and the discussion, the yields presented in Table 5 come from isolated compounds. We have optimized the treatment of the reaction in order to avoid cumbersome purification steps (the mixture of *ortho*/*para* trifluoromethylaniline **37** and **38** is so isolated by a simple procedure). The results are detailed in Table 5. This table does not include sulfonium salts **30**, **31**, and **32** because of the very-low yield achieved after a reasonable reaction time (6 h). Entry 1 (Table 5) can be considered as a reference point, as **9** is Umemoto's reagent (we used either our own preparation or the commercially available reagent after exchange of the tetrafluoroborate counteranion for a trifluoromethanesulfonate). Nitro derivative **29** revealed a trifluoromethylating power equivalent to that of Umemoto's reagent (Table 5, Entry 2) in accordance with the proposed enhanced reactivity of electron-poor sulfonium salts.[12b] By contrast, in the dibenzothiophenium series (Table 5, Entries 2–6), the results were much more surprising. Unexpectedly, the presence of electron-donating methyl groups did not affect the yield of trifluoromethylated compound. Indeed, even with four alkyl groups, the activity of **19** was comparable to that of **29** and slightly better than that of reagent **9** (Table 5,Entry 3). If the number of methyl groups was limited to two, the yields still increased by an amount deeply dependant on the position of these groups on the aromatic system (Table 5, Entries 4 and 5). The 1,3 relative position of these substituents as in **18** seems to be the most appropriate with a nine unit increased yield relative to that obtained with the mixture of isomers **16** and **17**. An additional nitro group, as in **20**, is however beneficial to the yield. Although current knowledge considers that electron-withdrawing groups attached to the aromatic part of sulfonium derivatives are essential to increase their trifluoromethylating power, the results presented here show that electron-donating groups are not detrimental to the reactivity. In fact, methylated dibenzothiophenium salts like **18** possess better activity than Umemoto's reagent. Results presented by Umemoto concerning the trifluoromethylation of aniline suggested that **16** is more stable than its non-methylated analogue. Our own experiences seem to confirm that alkyl groups are able to increase the stability of the reagents. Moreover, alkyl substitution should also disfavor the trifluoromethylation of dibenzothiophene, a byproduct of the reaction, which may act as a potential competitor for the trifluoromethylation process.

Table 5. Evaluation of the trifluoromethylating activity of the sulfonium salts.



Entry	Sulfonium	Yield [%][a]	*o*/*p* ratio
1	**9**	53	84:16
2	**29**	57	76:24
3	**19**	60	74:26
4	**16/17**	65	78:22
5	**18**	74	74:26
6	**20**	78	84:16

[a] Isolated yield; tests were repeated two or three times.

Conclusions

In summary, we have improved our methodology concerning the preparation of trifluoromethylsulfonium compounds and extended it to the synthesis of new trifluoromethyl dibenzothiophenium salts. Careful selection of biphenylic derivatives as substrates for this reaction permitted us to undertake the one-pot preparation of Umemoto-type reagents with reactivity comparable or better than that of the existing reagents. An easy route to a wide range of electrophilic trifluoromethylating reagents is therefore provided to the community of chemists, offering the opportunity to finetune the power of the trifluoromethylating reagent. Further studies concerning the potential of our reagents and the mechanism of electrophilic trifluoromethylation are currently under development in our laboratory.

Experimental Section

General: Each reaction was carried out under an argon atmosphere in freshly distilled solvent, unless otherwise noted. All chemicals were purchased from Sigma–Aldrich, ABCR, or Acros Organics and were used without further purification. Trifluoromethanesulfonic anhydride and sodium trifluoromethanesulfinate were purchased from Apollo. Organic solvents were purchased from Merck and Carlo Erba. Reactions were monitored by thin-layer chromatography on silica gel 60 F_{254}, or by ^{19}F NMR spectroscopy. Unless otherwise noted, yields refer to materials purified by column chromatography. NMR spectra were recorded with a Bruker AC-300 spectrometer. Reported coupling constants and chemicals shifts were based on first-order analysis. Internal reference was the residual peak of $CHCl_3$ (δ = 7.27 ppm) for ^1H (300 MHz), central peak of $CDCl_3$ (δ = 77 ppm) for ^{13}C (75 MHz) spectra and internal $CFCl_3$ (δ = 0 ppm) for ^{19}F (282 MHz) NMR spectra. Low-resolution mass spectra were recorded with an HPMS engine 5989B. High-resolution electrospray mass spectra in the positive ion mode were obtained with a Q-TOF Ultima Global hybrid quadrupole/time-of-flight instrument (Waters-Micromass, Manchester, U.K.), equipped with a pneumatically assisted electrospray (Z-spray) ion source and an additional sprayer (Lock Spray) for the reference compound. Melting points were determined with a Mettler FP61 melting point apparatus. Elemental analyses were carried out at ICSN (Gif-sur-Yvette).

3,3′,5,5′-Tetramethyl-1,1′-biphenyl (14): A DMSO solution (115 mL) of 1,3-bis(diphenylphosphanyl)propane (619 mg, 1.5 mmol) and $Pd(OAc)_2$ (225 mg, 1 mmol) was degassed through two freeze–thaw cycles, and the reaction flask was charged with oxygen. To this solution was added 3,5-dimethylbenzene boronic acid (5 g, 33.3 mmol), and the resulting mixture was stirred at 80 °C. After 24 h, the mixture was diluted with diethyl ether, washed with water, and dried with magnesium sulfate. Evaporation of the solvent followed by silica-gel column chromatography (pentane/diethyl ether, 90:10) gave **14** as a white solid (2.73 g, 13 mmol, 78%). M.p. 53.1 ± 0.2 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.10 (s, 4 H), 6.86 (s, 2 H), 2.26 (s, 12 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.1, 138.4, 129.2, 125.6, 21.8 ppm. MS (ESI+): *m/z* = 210 [M^+], 195 [$M^+ - CH_3$], 180 [$M^+ - 2CH_3$], 165 [$M^+ - 3CH_3$]. $C_{16}H_{18}$ (210.14): calcd. C 91.37, H 8.63; found C 90.81, H 8.82.

General Procedure for the Preparation of Dissymmetrical Diaryls: A mixture of Na_2CO_3 (4.7 g, 44.2 mmol), $Pd(OAc)_2$ (25 mg, 0.5 mol-%), 1-iodoaryl (22 mmol), 3,5-dimethylbenzene boronic acid (5 g, 33.3 mmol), distilled water (77 mL), and acetone (66 mL) was stirred for 30 min at 35 °C. The reaction solution was then extracted with diethyl ether (4 × 100 mL). The organic layer was dried with magnesium sulfate and concentrated, and the residue was purified by silica-gel chromatography (pentane/diethyl ether, 97:3).

3,5-Dimethyl-4′-nitro-1,1′-biphenyl (15): Yield: 4.86 g (21.4 mmol, 97%). Yellow powder. M.p. 120.0 ± 0.2 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.15 (d, J = 9.0 Hz, 2 H), 7.59 (d, J = 9.0 Hz, 2 H), 7.12 (s, 2 H), 6.98 (s, 1 H), 2.30 (s, 6 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 148.0, 147.0, 138.8, 130.6, 127.8, 125.3, 124.0, 21.4 ppm. MS (ESI+): m/z = 227 [M$^+$], 212 [M$^+$ – CH$_3$], 197 [M$^+$ – 2CH$_3$], 181 [M$^+$ – NO$_2$], 166 [M$^+$ – CH$_3$ – NO$_2$], 151 [M$^+$ – 2CH$_3$ – NO$_2$]. $C_{14}H_{13}NO_2$ (227.26): calcd. C 73.99, H 5.77, N 6.16; found C 73.78, H 5.94, N 5.94.

3,5-Dimethyl-1,1′-biphenyl (13): Yield: 4.05 g (22.2 mmol, 99%). Colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.47 (d, J = 7.0 Hz, 2 H), 7.31 (t, J = 7.0 Hz, 2 H), 7.22 (t, J = 7.0 Hz, 1 H), 7.11 (s, 2 H), 6.89 (s, 1 H), 2.28 (s, 6 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 141.6, 141.4, 138.3, 129.0, 128.7, 127.3, 127.2, 125.2, 21.5 ppm. MS (ESI+): m/z = 182 [M$^+$], 167 [M$^+$ – CH$_3$], 152 [M$^+$ – 2CH$_3$]. $C_{14}H_{14}$ (182.26): calcd. C 92.26, H 7.74; found C 91.71, H 7.93.

General Procedure for the Preparation of Sulfoxides: Under an atmosphere of argon, a round-bottomed flask was charged with potassium trifluoromethanesulfinate (1 g, 5.8 mmol) and trifluoromethanesulfonic acid (3.1 mL, 35.1 mmol). After stirring for 5 min, the substrate (6 mmol) was added, and the resulting mixture was stirred at room temperature. After consumption of the starting material, the resulting mixture was hydrolyzed with ice water and extracted with dichloromethane (3 × 25 mL). The combined organic phase was neutralized with NaHCO$_3$ until pH 7–8, dried with MgSO$_4$ and concentrated under reduced pressure. The residue was purified by silica-gel chromatography (pentane/ether, 9:1).

1,1′-Biphenyl-4-yl Trifluoromethyl Sulfoxide (10p) and 1,1′-Biphenyl-2-yl Trifluoromethyl Sulfoxide (10o): 1,1′-Biphenyl (0.5 g, 3.24 mmol) gave isomers **10o/10p** (10:90; 0.52 g, 1.93 mmol, 60%). ^{13}C NMR (50 MHz, CDCl$_3$): δ = 146.7, 139.2, 134.2, 134.1, 131.4 (q, J = 284 Hz, SOCF$_3$), 131.2, 129.2, 128.7, 128.6, 128.6, 128.3, 127.4, 126.5, 126.5, 124.9 (q, J = 335 Hz, SOCF$_3$) ppm. Data for **10p**: ^{19}F NMR (188 MHz, CDCl$_3$): δ = –74.9 (s, 3 F) ppm. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.93–7.78 (m, 4 H), 7.68–7.58 (m, 2 H), 7.56–7.42 (m, 3 H) ppm. Data for **10o**:[12b] ^{19}F NMR (188 MHz, CDCl$_3$): δ = –73.1 (s, 3 F) ppm. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 8.28–8.20 (m, 1 H), 7.56–7.51 (m, 3 H), 7.39–7.31 (m, 5 H) ppm.

3,3′-Dimethyl-1,1′-biphenyl-4-yl Trifluoromethyl Sulfoxide (21p) and 3,3′-Dimethyl-1,1′-biphenyl-2-yl Trifluoromethyl Sulfoxide (21o): 3,3′-Dimethyl-1,1′-biphenyl (1.06 g, 5.8 mmol) gave isomers **21o/21p** (30:70; 1.2 g 4.01 mmol, 69%). MS (EI): m/z = 298 [M$^+$], 229 [M – CF$_3^+$]. $C_{15}H_{13}F_3OS$ (298.32): calcd. C 60.39, H 4.39; found C 60.48, H 4.37. Data for **21p**: ^{19}F NMR (188 MHz, CDCl$_3$): δ = –74.0 (s, 3 F) ppm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.69 (d, J = 8.3 Hz, 1 H), 7.51 (s, 1 H), 7.50–7.30 (m, 4 H), 7.26 (s, 1 H), 2.55 (s, 3 H), 1.45 (s, 3 H) ppm. ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 146.1, 139.0, 138.4, 138.1, 132.5, 129.7, 129.1, 128.7, 127.8, 126.2, 125.7, 125.2 (q, J = 334 Hz, SOCF$_3$), 124.2, 21.1, 18.1 ppm. Data for **21o**:[12b] ^{19}F NMR (188 MHz, CDCl$_3$): δ = –73.5 (s, 3 F) ppm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.08 (d, J = 8.3 Hz, 1 H), 7.45 (d, 1 H), 7.33 (t, J = 7.9 Hz, 1 H), 7.24 (d, 1 H), 7.22 (s, 1 H), 7.14 (s, 1 H), 7.12 (d, 1 H), 2.49 (s, 3 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 144.1, 143.4, 138.2, 137.1, 131.7, 131.4, 130.1, 129.3, 129.1, 128.3, 126.5, 126.3, 125.0 (q, J = 335 Hz, SOCF$_3$), 21.5, 21.3 ppm.

3,5-Dimethyl-1,1′-biphenyl-4-yl Trifluoromethyl Sulfoxide (22p) and 3,5-Dimethyl-1,1′-biphenyl-2-yl Trifluoromethyl Sulfoxide (22o): 3,5-Dimethyl-1,1′-biphenyl (0.5 g, 2.7 mmol) gave isomers **22o/22p** (97:3; 0.38 g, 1.28 mmol, 47%). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 145.7, 143.4, 139.2, 136.1 (q, J = 337 Hz, SOCF$_3$), 129.0, 128.5, 128.2, 128.1, 127.3, 126.6 (q, J = 339 Hz, SOCF$_3$), 21.3, 19.6, 18.9 ppm. MS (DCi): m/z = 299 [M + H$^+$], 229 [M – CF$_3$]$^+$. $C_{15}H_{13}F_3OS$ (298.32): calcd. C 60.39, H 4.39; found C 60.36, H 4.33. Data for **22p**: ^{19}F NMR (188 MHz, CDCl$_3$): δ = –68.2 (s, 3 F) ppm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.26–7.22 (m, 3 H), 7.16 (m, 2 H), 7.00 (m, 2 H), 2.41 (s, 6 H) ppm. Data for **22o**: ^{19}F NMR (188 MHz, CDCl$_3$): δ = –70.3 (s, 3 F) ppm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.63–7.58 (m, 2 H), 7.52–7.39 (m, 3 H), 7.35 (s, 2 H), 2.79 (s, 3 H), 2.66 (s, 3 H) ppm.

3,3′,5,5′-Tetramethyl-1,1′-biphenyl-4-yl Trifluoromethyl Sulfoxide (23p) and 3,3′,5,5′-Tetramethyl-1,1′-biphenyl-2-yl Trifluoromethyl Sulfoxide (23o): 3,3′,5,5′-Tetramethyl-1,1′-biphenyl (0.21 g, 1.0 mmol) gave isomers **23o/23p** (9:1; 0.16 g, 0.5 mmol, 50%). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 146.0, 139.2, 138.6, 130.2, 127.0 (q, J = 338 Hz, SOCF$_3$), 125.2, 21.4, 21.3, 19.6 ppm. MS (EI): m/z = 326 [M$^+$], 257 [M – CF$_3^+$]. HRMS: calcd. for $C_{17}H_{17}F_3NaO^{32}S$ 349.0849; found 349.0850 (δ = –0.2 ppm). Data for **23p**: ^{19}F NMR (188 MHz, CDCl$_3$): δ = –67.8 (s, 3 F) ppm. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.14 (s, 2 H), 7.00 (s, 1 H), 6.85 (s, 2 H), 2.77 (s, 6 H), 2.35 (s, 6 H) ppm. Data for **23o**: ^{19}F NMR (188 MHz, CDCl$_3$): δ = –70.2 (s, 3 F) ppm. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.33 (s, 2 H), 7.21 (s, 2 H), 7.07 (s, 1 H), 2.67 (s, 6 H), 2.40 (s, 6 H) ppm.

3,5-Dimethyl-4′-nitro-1,1′-biphenyl-4-yl Trifluoromethyl Sulfoxide (24p) and 3,5-Dimethyl-4′-nitro-1,1′-biphenyl-2-yl Trifluoromethyl Sulfoxide (24o): 3,5-Dimethyl-4′-nitro-1,1′-biphenyl (0.66 g, 2.9 mmol) gave isomers **24o/24p** (70:30; 0.54 g, 1.57 mmol, 54%). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 147.8, 147.6, 145.5, 145.0, 144.0, 143.1, 143.0, 134.7, 130.6, 128.2, 126.1 (q, J = 339 Hz, SOCF$_3$), 124.3, 123.3, 21.3, 19.6, 19.0, 18.9 ppm. MS (DCi): m/z = 344 [M + H$^+$], 274 [M – CF$_3$]$^+$. $C_{15}H_{12}F_3NO_3S$ (315.27): calcd. C 52.48, H 3.52, N 4.08; found C 52.74, H 3.69, N 3.93. Data for **24p**: ^{19}F NMR (188 MHz, CDCl$_3$): δ = –68.9 (s, 3 F) ppm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.33 (d, J = 9.0 Hz, 2 H), 7.76 (d, J = 9.0 Hz, 2 H), 7.38 (s, 2 H), 2.43 (s, 6 H) ppm. Data for **24o**: ^{19}F NMR (188 MHz, CDCl$_3$): δ = –70.2 (s, 3 F) ppm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.26 (d, J = 8.9 Hz, 2 H), 7.44 (d, J = 8.5 Hz, 2 H), 7.24 (s, 1 H), 6.98 (s, 1 H), 2.76 (s, 3 H), 2.71 (s, 3 H) ppm.

4′-Nitro-1,1′-biphenyl-4-yl Trifluoromethyl Sulfoxide (33): Compound **25** (0.58 g, 2.9 mmol) gave **33** (0.34 g, 1.06 mmol, 37%). ^{19}F NMR (188 MHz, CDCl$_3$): δ = –74.7 (s, 3 F) ppm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.36 (d, J = 8.9 Hz, 2 H), 7.94 (d, J = 8.3 Hz, 2 H), 7.87 (d, J = 8.3 Hz, 2 H), 7.80 (d, J = 8.9 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 147.8, 145.4, 144.0, 136.1, 128.6, 128.3, 126.7, 124.7 (q, J = 335 Hz, SOCF$_3$), 124.2 ppm. MS (EI): m/z = 315 [M$^+$], 246 [M – CF$_3^+$]. $C_{13}H_8F_3NO_3S$ (315.27): calcd. C 49.53, H 2.56, N 4.44; found C 49.31, H 2.55, N 4.24.

1-Benzyl-4-[(trifluoromethyl)sulfinyl]benzene (34): Compound **26** (1.0 g, 2.9 mmol) gave **34** (0.47 g, 1.65 mmol, 56%). ^{19}F NMR (188 MHz, CDCl$_3$): δ = –75.1 (s, 3 F) ppm. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.55 (d, J = 8.3 Hz, 2 H), 7.25 (d, J = 8.3 Hz, 2 H), 7.19–7.13 (m, 2 H), 7.11–7.06 (m, 1 H), 7.05–7.02 (m, 2 H), 3.90 (s, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 147.8, 139.6, 133.3, 130.2, 129.1, 128.9, 126.8, 126.3, 124.9 (q, J = 333 Hz, SOCF$_3$), 41.9 ppm. MS (ESI+): m/z = 323 [M + K$^+$], 307 [M + Na$^+$]. HRMS: calcd. for $C_{14}H_{11}{}^{19}F_3Na^{32}OS$ 307.0379; found 307.0380 (δ = –0.6 ppm).

1-(1-Methyl-1-phenylethyl)-4-[(trifluoromethyl)sulfinyl]benzene (35): Compound **27** (0.39 g, 2.0 mmol) gave **35** (0.33 g, 1.06 mmol, 52%). ^{19}F NMR (188 MHz, CDCl$_3$): δ = –75.0 (s, 3 F) ppm. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.72 (d, J = 8.3 Hz, 2 H), 7.50 (d, J = 8.8 Hz, 2 H), 7.35–7.20 (m, 5 H), 1.75 (s, 6 H) ppm. ^{13}C NMR

(75 MHz, $CDCl_3$): δ = 157.3, 149.2, 128.4, 128.2, 126.8, 126.2, 125.9, 125.9, 124.8 (q, J = 335 Hz, $SOCF_3$), 43.5, 30.6 ppm. MS (EI): *m*/*z* = 312 [M^+], 243 [M – CF_3^+]. HRMS: calcd. for $C_{16}H_{15}F_3NaO^{32}S$ 335.0693; found 335.0695 (δ = –0.5 ppm).

1-Phenoxy-4-[(trifluoromethyl)sulfinyl]benzene (36p) and 1-Phenoxy-2-[(trifluoromethyl)sulfinyl]benzene (36o): Diphenyl ether (0.99 g, 5.8 mmol) gave isomers **36o/36p** (20:80; 1.07 g, 3.74 mmol, 64%). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7, 156.2, 155.0, 154.7, 134.7, 130.2, 128.4, 128.1, 127.0, 125.3, 125.3 (q, J = 337 Hz), 125.1, 124.8 (q, J = 335 Hz), 123.6, 120.3, 120.0, 118.3, 116.6 ppm. MS (EI): *m*/*z* = 286 [M^+], 217 [M – CF_3^+]. $C_{13}H_9F_3O_2S$ (286.27): calcd. C 54.54, H 3.17; found C 54.41, H 3.15. Data for **36p**: ^{19}F NMR (188 MHz, $CDCl_3$): δ = –75.6 (s, 3 F) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, J = 8.5 Hz, 2 H), 7.36 (t, J = 7.5 Hz, 2 H), 7.18 (t, J = 7.5 Hz, 1 H), 7.10 (d, J = 9.0 Hz, 2 H), 7.04 (d, J = 7.5 Hz, 2 H) ppm. Data for **36o**: ^{19}F NMR (188 MHz, $CDCl_3$): δ = –74.3 (s, 3 F) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.00 (dd, J = 7.8, 1.5 Hz, 1 H), 7.44 (t, J = 7.4 Hz, 1 H), 7.36 (t, J = 7.5 Hz, 2 H), 7.25 (t, J = 7.4 Hz, 1 H), 7.18 (t, J = 7.4 Hz, 1 H), 7.04 (d, J = 7.5 Hz, 2 H), 6.81 (dd, J = 8.3, 0.8 Hz, 1 H) ppm.

General Procedure for the Preparation of Sulfonium Salts: Under an atmosphere of argon, a round-bottomed flask was charged with pure potassium trifluoromethanesulfinate (0.5 g, 3 mmol) dried under high vacuum and trifluoromethanesulfonic anhydride (1 mL, 6 mmol). After stirring for 5 min, the substrate (3 mmol) was added, and the resulting mixture was stirred at room temperature. After consumption of the starting material (monitored by TLC), the reaction mixture was filtered, diluted with CH_2Cl_2 (10 mL), washed with brine (10 mL) and then a solution of $NaHCO_3$ (10 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (dichloromethane/methanol, 95:5)to give a slightly off-white powder.

5-(Trifluoromethyl)dibenzo[*b*,*d*]thiophenium Trifluoromethanesulfonate (9): 1,1′-Biphenyl (0.5 g, 3.24 mmol) gave **9** (0.15 g, 0.37 mmol, 12%). M.p. 133 ± 0.2 °C. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –53.7 (s, 3 F), –79.0 (s, 3 F) ppm. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.43 (d, J = 7.9 Hz, 2 H), 8.16 (d, J = 8.1 Hz, 2 H), 8.00 (t, J = 7.7 Hz, 2 H), 7.80 (t, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.8, 136.0, 131.7, 129.2, 124.8, 124.0, 120.3 (q, J = 318 Hz, CF_3) ppm. MS (CI): *m*/*z* = 253 [M + H^+], 184 [M + H – CF_3^+].

1,1′-Biphenyl-4-yl Trifluoromethyl Sulfide (11): 1,1′-Biphenyl (0.5 g, 3.24 mmol) gave **11** (0.39 g, 1.54 mmol, 47%). M.p. 40.7 ± 0.2 °C. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –43.2 (s, 3 F) ppm. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.82–7.58 (m, 6 H), 7.56–7.37 (m, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.8, 139.6, 136.6, 129.6 (q, J = 308 Hz, SCF_3), 128.9, 128.1, 127.2, 123.0 ppm. MS (CI): *m*/*z* = 255 [M + H^+]. $C_{13}H_9F_3S$ (254.27): calcd. C 61.41, H 3.57; found C 61.13, H 3.46.

2,8-Dimethyl-5-(trifluoromethyl)dibenzo[*b*,*d*]thiophenium Trifluoromethanesulfonate (16) and 2,6-Dimethyl-5-(trifluoromethyl)dibenzo[*b*,*d*]thiophenium Trifluoromethanesulfonate (17): 3,3′-Dimethyl-1,1′-biphenyl (2.12 g, 11.66 mmol) gave isomers **16**/**17** (70:30; 0.76 g, 1.77 mmol, 15%). M.p. 135.6 ± 0.2 °C. ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 148.4, 141.4, 136.2, 132.8, 132.6, 129.4, 129.3, 125.5 (q, J = 224.0 Hz, CF_3), 125.0, 124.9, 122.0, 119.4 (q, J = 225.0 Hz, CF_3), 118.4, 21.4, 20.2 ppm. MS (ESI+): *m*/*z* = 281 [M^+], 212 [M – CF_3^+]. $C_{16}H_{12}F_6O_3S_2$ (430.39): calcd. C 44.65, H 2.81, found C 45.03, H 3.22. Data for **16**:[12b] ^{19}F NMR (188 MHz, $CDCl_3$): δ = –54.8 (s, 3 F), –79.0 (s, 3 F) ppm. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.26 (d, J = 8.1 Hz, 2 H), 8.01 (s, 2 H), 7.55 (d, J = 8.1 Hz, 2 H), 2.60 (s, 6 H) ppm. Data for **17**: ^{19}F NMR (188 MHz, $CDCl_3$): δ = –52.8 (s, 3 F), –79.0 (s, 3 F) ppm. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.32 (d, J = 8.3 Hz, 1 H), 7.97 (m, 1 H), 7.92 (s, 1 H), 7.85 (t, J = 7.5 Hz, 1 H), 7.75 (d, J = 7.5 Hz, 1 H), 7.70 (d, J = 8.3 Hz, 1 H), 2.78 (s, 3 H), 2.54 (s, 3 H) ppm.

2,4-Dimethyl-5-(trifluoromethyl)dibenzo[*b*,*d*]thiophenium Trifluoromethanesulfonate (18): Compound **13** (0.85 g, 4.7 mmol) **18** gave (0.7 g, 1.63 mmol, 36%). M.p. 138.6 ± 0.2 °C. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –52.8 (s, 3 F), –78.8 (s, 3 F) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.43 (d, J = 8.0 Hz, 1 H), 8.11 (d, J = 7.7 Hz, 1 H), 7.93 (t, J = 7.6 Hz, 1 H), 7.89 (s, 1 H), 7.73 (t, J = 7.7 Hz, 1 H), 7.37 (s, 1 H), 2.74 (s, 3 H), 2.55 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.9, 142.3, 142.0, 141.0, 136.3, 134.1, 131.9, 130.5, 124.8, 124.3 (q, J = 220 Hz, CF_3), 123.5 (q, J = 256 Hz, CF_3), 123.5, 122.9, 118.4, 21.9, 20.7 ppm. MS (ESI+): *m*/*z* = 281 [M + H^+], 212 [M + H – CF_3^+]. $C_{16}H_{12}F_6O_3S_2$ (430.39): calcd. C 44.65, H, 2.81; found C 44.79, H 3.17.

2,4,6,8-Tetramethyl-5-(trifluoromethyl)dibenzo[*b*,*d*]thiophenium Trifluoromethanesulfonate (19): Compound **14** (0.21 g, 1.0 mmol) gave **19** (0.21 g, 0.46 mmol, 46%). M.p. 170.1 ± 0.2 °C. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –52.8 (s, 3 F), –78.9 (s, 3 F) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.70 (s, 2 H), 7.32 (s, 2 H), 2.77 (s, 6 H), 2.52 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.2, 142.7, 140.9, 133.9, 129.3 (q, J = 349 Hz, CF_3), 124.9 (q, J = 332 Hz, CF_3), 123.4, 119.7, 21.9, 20.7 ppm. MS (ESI+): *m*/*z* = 309 [M + H^+], 240 [M + H – CF_3^+]. $C_{18}H_{16}F_6O_3S_2$ (458.44): calcd. C 47.16, H 3.52; found C 47.31, H 3.81.

2,4-Dimethyl-7-nitro-5-(trifluoromethyl)dibenzo[*b*,*d*]thiophenium Trifluoromethanesulfonate (20): Compound **15** (0.1 g, 0.44 mmol) gave **20** (0.06 g, 0.11 mmol, 27%). M.p. 146.0 ± 0.2 °C. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –52.0 (s, 3 F), –79.5 (s, 3 F) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.18 (s, 1 H), 8.74 (d, J = 8.3 Hz, 1 H), 8.28 (d, J = 8.9 Hz, 1 H), 7.91 (s, 1 H), 7.50 (s, 1 H), 2.80 (s, 3 H), 2.60 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.2, 149.1, 147.2, 140.7, 139.9, 135.2, 131.0, 125.7, 125.3, 124.9, 124.8, 123.8 (q, J = 332 Hz, CF_3), 121.7, 120.3 (q, J = 319 Hz, CF_3), 20.4, 19.2 ppm. MS (ESI+): *m*/*z* = 326 [M + H^+], 257 [M + H – CF_3^+]. HRMS: calcd. for $C_{15}H_{11}{}^{19}F_3NO_2{}^{32}S$ 326.0472; found 326.0463 (δ = 3.0 ppm).

Bis(4′-nitro-1,1′-biphenyl-4-yl)(trifluoromethyl)sulfonium Trifluoromethanesulfonate (29): Compound **25** (0.58 g, 2.9 mmol) gave (0.28 g, 0.43 mmol, 30%). M.p. 100.4 ± 0.2 °C. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –50.3 (s, 3 F), –78.9 (s, 3 F) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.29 (m, 8 H), 8.00 (m, 4 H), 7.73 (m, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.6, 147.5, 143.5, 133.6, 130.9, 129.6 (q, J = 301.0 Hz, CF_3), 128.6, 126.2 (q, J = 298.0 Hz, CF_3), 124.6, 116.8 ppm. MS (ESI+): *m*/*z* = 497 [M + H^+], 428 [M + H – CF_3^+]. HRMS: calcd. for $C_{25}H_{16}{}^{19}F_3N_2O_4{}^{32}S$ 497.0782; found 497.0783 (δ = –0.1 ppm).

Bis(4-benzylphenyl)(trifluoromethyl)sulfonium Trifluoromethanesulfonate (30): Compound **26** (0.98 g, 5.8 mmol) gave **30** (0.83 g, 1.43 mmol, 48%). ^{19}F NMR (188 MHz, $CDCl_3$): δ = –51.3 (s, 3 F), –78.9 (s, 3 F) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.5 Hz, 4 H), 7.51 (d, J = 8.5 Hz, 4 H), 7.29–7.18 (m, 6 H), 7.09 (d, J = 8.2 Hz, 4 H), 4.03 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.1, 138.1, 133.0, 132.6, 129.1, 129.0, 128.8 (q, J = 336.0 Hz, CF_3), 127.1, 126.2 (q, J = 324.0 Hz, CF_3), 114.2, 41.8 ppm. MS (ESI+): *m*/*z* = 435 [M + H^+], 366 [M + H – CF_3^+]. $C_{28}H_{22}F_6O_3S_2$ (584.59): calcd. C 57.53, H 3.79; found C 57.22, H 3.57.

Bis[4-(1-methyl-1-phenylethyl)phenyl](trifluoromethyl)sulfonium Trifluoromethanesulfonate (31): Compound **27** (0.57 g, 2.9 mmol) gave **31** (0.45 g, 0.71 mmol, 48%). M.p. 173 ± 0.2 °C. ^{19}F NMR

(188 MHz, $CDCl_3$): δ = –51.3 (s, 3 F), –78.9 (s, 3 F) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.6 Hz, 4 H), 7.56 (d, J = 8.6 Hz, 4 H), 7.26–7.08 (m, 10 H), 1.64 (s, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5, 147.9, 132.7, 130.7, 128.6, 126.7, 113.7, 44.0, 30.2 ppm. MS (ESI+): m/z = 491 [M + H^+]. $C_{32}H_{30}F_6O_3S_2$ (640.70): calcd. C 59.99, H 4.72; found C 59.87, H 4.97.

Bis(4-phenoxyphenyl)(trifluoromethyl)sulfonium Trifluoromethanesulfonate (32): Compound **28** (1.98 g, 11.66 mmol) gave **32** (1.25 g, 2.13 mmol, 36%). M.p. 178.1 ± 0.2 °C. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –52.7 (s, 3 F), –78.9 (s, 3 F) ppm. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.22 (d, J = 8.8 Hz, 4 H), 7.40–7.00 (m, 10 H), 6.93 (d, J = 7.7 Hz, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.5, 153.5, 135.3, 130.6, 129.3 (q, J = 296.0 Hz, CF_3), 126.3, 122.0 (q, J = 494.0 Hz, CF_3), 120.8, 119.9, 108.0 ppm. MS (ESI+): m/z = 439 [M^+], 370 [M – SCF_3^+]. HRMS: calcd. for $C_{25}H_{18}{}^{19}F_3O_2{}^{32}S$ 439.0980; found 439.0980 (δ = 0.1 ppm).

General Procedure for the Trifluoromethylation of Aniline: Under an argon atmosphere, trifluoromethylsulfonium salt (1 mmol) was added to a stirred solution of aniline (2 mmol, 180 µL) in dry DMF (3 mL). The mixture was stirred for 6 h at 80 °C. The reaction solution was then extracted with HCl (1 M, 3 × 25 mL). The aqueous layer was neutralized with $NaHCO_3$ until pH 7–8, and then extracted with dichloromethane (3 × 50mL). The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The resulting red oil was diluted in ethyl ether (25 mL) and washed with 5% $NaHCO_3$ (3 × 25 mL). The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure to give pure trifluoromethylaniline as a mixture of *ortho* **37** and *para* **38** isomers.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H, ^{19}F, and ^{13}C NMR spectra for compounds **9**–**11**, **13**–**15**, **16**–**20**, **21**–**24**, **29**–**32**, and **33**–**36**.

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