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Synthesis of Aryl Triflones through the Trifluoromethanesulfonylation of Benzynes

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The direct synthesis of aryl triflones, that is, trifluoromethanesulfonyl arenes, was achieved through the trifluoromethanesulfonylation of benzynes. The trifluoromethanesulfonyl group, one of the fluorinated functional groups, is a highly electronnegative and mild lipophilic substituent. Aryl triflones have high potential in the synthesis of bioactive compounds and specialty materials. The treatment of 2-(trimethylsilyl)aryl trifluoromethanesulfonates with cesium fluoride in the presence of 15-crown-5 generated benzynes, which reacted with sodium trifluoromethanesulfinate followed by protonation with *t*BuOH under heating conditions, provided aryl triflones in moderated to good yields. Both symmetrical and unsymmetrical triflones were nicely accessed under the same reaction conditions. Interestingly, the trifluoromethanesulfonylation of unsymmetrical benzyne precursors proceeded smoothly to furnish corresponding aryl triflones in good yields with good to high regioselectivities. The balance of polarization of electric charge as well as steric hindrance of the benzyne intermediates are central factors to control the outcome of regioselectivity.

1. Introduction

Fluorinated aromatics are prevalent in specialty materials, pharmaceuticals, and agrochemicals.[1] Aryl fluorides (Ar–F) and benzotrifluorides (Ar–CF_3) have served as two major contributors in the last half century. In recent years, arenes with heteroatom-linked trifluoromethyl modifications, such as trifluoromethoxy arenes (Ar–OCF_3),[2] trifluoromethylthio arenes (Ar–SCF_3),[3] and trifluoromethanesulfonyl arenes (aryl triflones, Ar–SO_2CF_3)[3d,4–16] have been considerably targeted. Our group is interested in aryl triflones.[3d,5] Aryl triflones have a functional group, trifluoromethanesulfonyl (SO_2CF_3), which is a stronger electron-withdrawing group than trifluoromethyl (CF_3) (SO_2CF_3, $\sigma_m = 0.79$, $\sigma_p = 0.93$; CF_3, $\sigma_m = 0.43$, $\sigma_p = 0.54$), whereas its lipophilicity is milder than that of CF_3 (SO_2CF_3, $\pi = 0.55$; CF_3, $\pi = 0.88$).[3d,17] Thus, the replacement of CF_3–arene moieties in existing biologically active molecules and functional materials with CF_3SO_2–arenes is a potential strategy to improve and/or alter the stability and log *P* values of the original compounds. In fact, aryl triflones have been successfully used as central structural motifs in biologically active molecules,[6] functional materials,[7] and chiral catalysts.[8] The synthesis of aryl triflones has been explored over the last two decades, leading to its categorization into three methodologies: trifluoromethanesulfonylation of arenes,[5a,9] oxidation of aryl trifluoromethyl sulfides,[10] and trifluoromethylation of aryl sulfonyl fluorides or aryl sulfonates.[11] From the viewpoint of late-stage functionalization in pharmaceuticals, the direct trifluoromethanesulfonylation of arenes is particularly attractive.[12] In this context, we envisaged the use of benzynes for the direct synthesis of aryl triflones. Benzynes have a strained triple bond, which is highly reactive towards a wide variety of addition reactions.[18] We, thus, started the investigation of the preparation of aryl triflones using benzynes. During our investigation,[13] the only example of the synthesis of trifluoromethanesulfonyl benzene from benzyne was reported (Scheme 1 a).[14] However, it focused exclusively on the phenylsulfonylation of benzynes, and thus a general preparation of aryl triflones has not yet been established. Later, Li and co-workers[15] and Zhao et al.,[16] in this order, reported the synthesis of aryl triflones from benzynes (Schemes 1 b and 1 c), but their methods were limited to the preparation of *ortho*-substituted triflones. Finally, the direct mono-functionalization of benzynes to triflones continues to have limitations except for the single example by Singh and co-workers.[14] Herein, we disclose a full account of our work for the synthesis of aryl triflones through the trifluoromethanesulfonylation of benzynes (Scheme 1 d).[13]

A wide variety of aryl triflones can be nicely accessed in moderated to good yields through the reaction of sodium trifluoromethanesulfinate ($NaSO_2CF_3$; Langlois reagent)[19] with benzynes followed by the addition of *t*BuOH for protonation. Highly reactive benzyne derivatives were generated in situ

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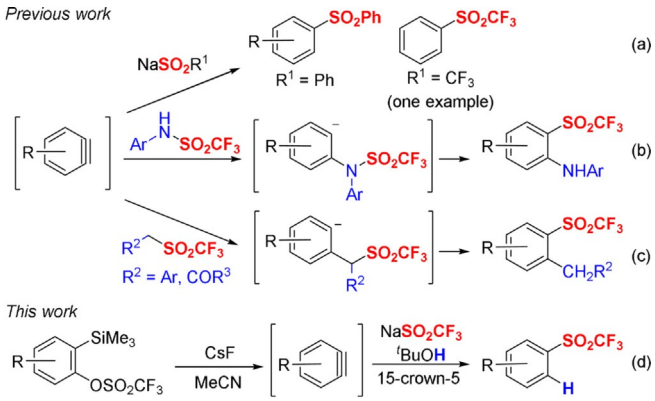


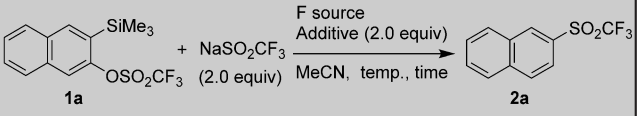
Scheme 1. Synthesis of aryl triflones from benzynes: a) by Singh and co-workers;[14] b) by Li and co-workers;[15] c) by Xu and co-workers;[16] d) this work.

from 2-(trimethylsilyl)aryl trifluoromethanesulfonates with cesium fluoride in the presence of 15-crown-5. This method is useful not only for the synthesis of symmetrical aryl triflones, but also unsymmetrical aryl triflones. More importantly, regioselective trifluoromethanesulfonylation of unsymmetrical benzyne precursors was also achieved, depending on both the steric hindrance and polarization of electric charge of benzynes. An ionic pathway, rather than a radical pathway, for the introduction of the SO_2CF_3 moiety to reactive benzynes was suggested by the use of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) experiments. The regioselectivity observed was analyzed based on the computations.

2. Results and Discussion

We first investigated the trifluoromethanesulfonylation of benzynes by using 2-(trimethylsilyl)naphthalen-3-yl trifluoromethanesulfonate (**1a**) as a benzyne precursor. Under conventional conditions[14,18] with KSO_2CF_3 (2.0 equiv)[20] and KF (4.0 equiv) in tetrahydrofuran (THF) at room temperature, no desired trifluoromethanesulfonylated product **2a** was observed (Table 1, entry 1). We next attempted the reaction by using $NaSO_2CF_3$ and CsF in MeCN at room temperature. Desired **2a**[5g,11f] was obtained in a low yield of 15% (entry 2). Screening the fluorides did not improve this transformation (entries 3–5), whereas the addition of 15-crown-5 increased the yield slightly to 19% (entry 6). The amount of CsF affected the conversion to **2a**, increasing the yield to 44% (entry 7). Heating the reaction shortened the reaction time without affecting significantly the yield (entries 8, 9). We further examined the proton source. The use of H_2O was not effective (entry 10), but the addition of 1.0 equivalent of *t*BuOH improved the yield to 50% (entry 11). The reaction was not inhibited in the presence of TEMPO, thus an ionic reaction was suggested (entry 12). We also attempted the reaction using sodium methanesulfinate ($NaSO_2CH_3$) instead of $NaSO_2CF_3$, but no desired SO_2CH_3-containing product, 2-methanesulfonyl naphthalene, was obtained (entry 13). The structure of product **2a** was confirmed by spectroscopic analysis [^{19}F NMR δ: −78.69 ppm (triflone, SO_2CF_3)] and also by a comparison with an authentic sample of **2a**, which was prepared by the oxidation of 2-trifluoromethylthio-naphthalene (see the Supporting Information).

Table 1. Optimization of reaction conditions.[a]



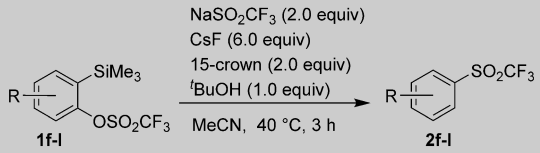
Entry	F source [equiv]	Additive	Temp. [°C]	Time [h]	Yield [%]
1[b]	KF (4.0)	18-crown-6	RT	24	NR
2	CsF (4.0)	-	RT	24	15
3	TMAF (4.0)	-	RT	24	9
4	TBAF·3 H_2O (4.0)	-	RT	24	trace
5	TBAT(4.0)	-	RT	24	trace
6	CsF (4.0)	15-crown-5	RT	24	19
7	CsF (6.0)	15-crown-5	RT	24	44
8	CsF (6.0)	15-crown-5	40	4	45
9	CsF (6.0)	15-crown-5	50	4	42
10[c]	CsF (6.0)	15-crown-5	40	3	42
11[d]	CsF (6.0)	15-crown-5	40	3	50
12[e]	CsF (6.0)	15-crown-5	40	3	49
13[f]	CsF (6.0)	15-crown-5	40	3	NR[g]

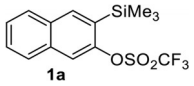
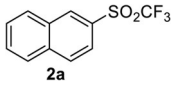
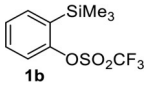
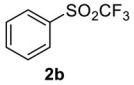
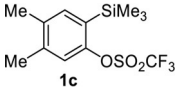
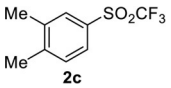
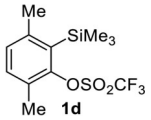
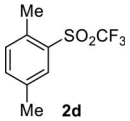
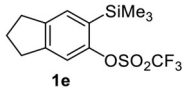
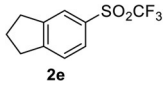
[a] Reaction was carried out with **1a**, $NaSO_2CF_3$ (2.0 equiv), an F source, and an additive (2.0 equiv) in MeCN (1.0 mL). [b] KSO_2CF_3 was used instead of $NaSO_2CF_3$, 18-crown-6 (6.0 equiv), with THF as the solvent. [c] H_2O (1.0 equiv) was added. [d] *t*BuOH (1.0 equiv) was added. [e] TEMPO (2.0 equiv) was added. [f] Reaction was carried out using $NaSO_2CH_3$ instead of $NaSO_2CF_3$. [g] No desired product, 2-methanesulfonyl naphthalene, was obtained.

With the optimal reaction conditions in hand, we examined the substrate scope for the trifluoromethanesulfonylation of symmetrical benzynes derived from corresponding precursors, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate derivatives **1a–e** (Table 2). The simple benzyne generated from **1b** provided the trifluoromethanesulfonyl benzene (**2b**) in a moderate yield of 43% (entry 2). The alkyl-substituted benzyne derived from 4,5-dimethyl-substituted **1c** gave **2c** in 63% yield. It should be noted that the sterically demanding 3,6-dimethyl benzyne precursor **1d** was nicely converted to the dimethylphenyl-triflone **2d** in 76% yield (entry 4). The 5-trimethylsilyl-6-trifluoromethanesulfonyloxy indane **1e** also provided the corresponding 5-trifluoromethanesulfonylated indane **2e** in 74% yield (entry 5).

We next investigated the trifluoromethanesulfonylation of unsymmetrical benzynes generated from 4- or 6-substituted 1-trimethylsilyl-2-trifluoromethanesulfonate arenes **1f–n** (Table 3). 4-Methyl benzyne precursor **1f** gave a mixture of aryl triflones **2f** and **2f'** in a 48:52 regioisomeric ratio in a combined yield of 58% (entry 1). The bulky *t*Bu-substituted benzyne precursor **1g** gave the corresponding regioisomeric aryl triflones **2g** and **2g'** in 47% yield in a ratio of 33:67 (entry 2). 4-Methoxy-substituted benzyne precursor **1h** provided regioisomeric products **2h** and **2h'** in 57% yield (ratio, 74:26) selectively (entry 3). High regioselectivities were observed by the reaction of halogen-substituted benzyne precursors **1i** and **1j** to furnish the aryl triflones **2i** and **2i'** in 63% yield (ratio, 81:19) and **2j** and **2j'** in 41% yield (ratio, 85:15), respectively (en-

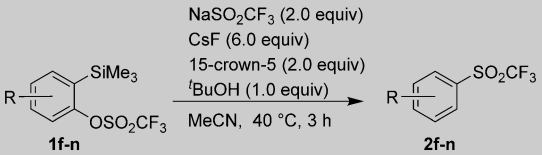
Table 2. Trifluoromethanesulfonylation of symmetrical benzyne precursors **1 a–e**.[a]

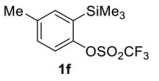
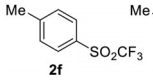
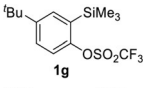
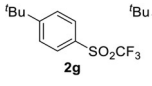
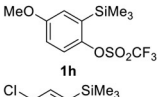
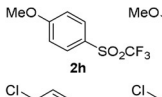
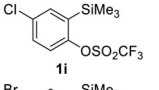
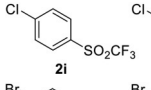
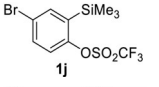
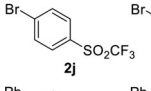
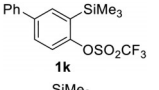
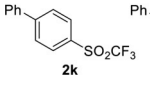
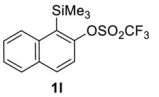
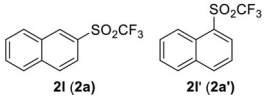
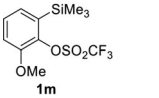
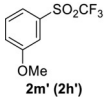
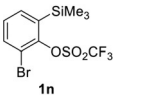
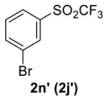


Entry	Substrate	Product	Yield [%]
1	 **1a**	 **2a**	50
2	 **1b**	 **2b**	43
3	 **1c**	 **2c**	63
4	 **1d**	 **2d**	76
5	 **1e**	 **2e**	74

[a] Reaction was carried out with **1**, $NaSO_2CF_3$ (2.0 equiv), CsF (6.0 equiv), 15-crown-5 (2.0 equiv), and *t*BuOH (1.0 equiv) in MeCN (1.0 mL) at 40 °C for 3 h.

Table 3. Trifluoromethanesulfonylation of unsymmetrical benzyne precursors **1 f–n**.[a]

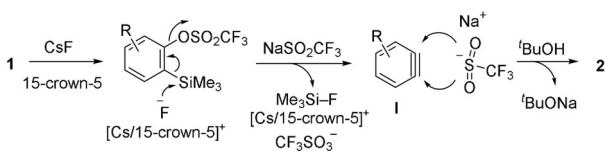


Entry	Substrate	Product	Yield[b] [%]
1	 **1f**	 **2f** **2f'**	58 (48:52)
2	 **1g**	 **2g** **2g'**	47 (33:67)
3	 **1h**	 **2h** **2h'**	57 (74:26)
4	 **1i**	 **2i** **2i'**	63 (81:19)
5	 **1j**	 **2j** **2j'**	41 (85:15)
6[c]	 **1k**	 **2k** **2k'**	77 (48:52)
7	 **1l**	 **2l (2a)** **2l' (2a')**	64 (67:33)
8	 **1m**	 **2m' (2h')**	42 (100:0)
9	 **1n**	 **2n' (2j')**	27 (100:0)

[a] Reaction was carried out with **1 a**, $NaSO_2CF_3$ (2.0 equiv), CsF (6.0 equiv), 15-crown-5 (2.0 equiv), *t*BuOH (1.0 equiv) in MeCN (1.0 mL) at 40 °C for 3 h. [b] The ratios of regioisomers are shown in parentheses and were determined by crude products of ^{19}F NMR spectroscopy. [c] Carried out at 50 °C.

tries 4 and 5). On the other hand, phenyl-substituted benzyne precursor **1 k** gave the aryl triflones **2 k** and **2 k'** in 77% yield in a ratio of 48:52 at a higher reaction temperature (50 °C) (entry 6). The unsymmetrical naphthalene-containing aryne precursor **1 l** provided the trifluoromethanesulfonylated naphthalenes **2 l** (**2 a**) and **2 l'** (**2 a'**) in 64% yield in a ratio of 67:33 (entry 7). It should be pointed out that 6-substituted 1-trimethylsilyl-2-trifluoromethanesulfonate benzyne precursors **1 m** and **1 n** solely provided the 3-substituted phenyl triflones **2 m'** (**2 h'**) and **2 n'** (**2 j'**) in moderate yields, 42 and 27%, respectively (entries 8 and 9).

According to previous studies of regioselectivity of substituted benzynes,[14,21] the regioselectivity observed in Table 2 could be rationally explained by both the balance of polarization of the electric charge and steric hindrance of the benzyne intermediates **I** (Scheme 2). Initially, Cs^+ is captured by 15-crown-5 to generate naked fluoride anion, which attacks the silicon atom of **1** to generate highly reactive benzynes **I**. Then, SO_2CF_3 anion attacks benzynes **I** followed by protonation with *t*BuOH to provide desired aryl triflones **2** (Scheme 2). The formation of



Scheme 2. Proposed reaction mechanism for the reaction of **1** to **2**.

the major *meta*-isomer **2 g'** (R = *t*Bu) can be explained by the preferential attack of the SO_2CF_3 anion to C3, as C4 is more negative because of the electron-donating effect of the *t*Bu substituent (positive inductive effect, Figure 1 a).[21,22] On the other hand, for the MeO-, Cl- and Br-substituted benzynes, the major products are *para*-substituted regioisomers **2 h**, **2 i**, and **2 j**, indicating that the developing positive charge at the C4 position by the strong electron negativity of O(Me), Cl, and Br (negative inductive effect) should be the main factor controlling regioselectivity (Figure 1 b).[18h,21] In contrast, no selectivity in the reaction of **1 f** and **1 k** (R = Me, Ph) suggests that there is no significant difference between steric and electronic factors on C3 and C4 (Figure 1 c).[22] Complete regioselective formation of *meta*-substituted isomers **2 m'** (**2 h'**) and **2 n'** (**2 j'**) from **1 m** and **1 n** should be explained by both the steric effect and polarization of the electric charge on C2 and C3 (Figure 1 d).[21,22]

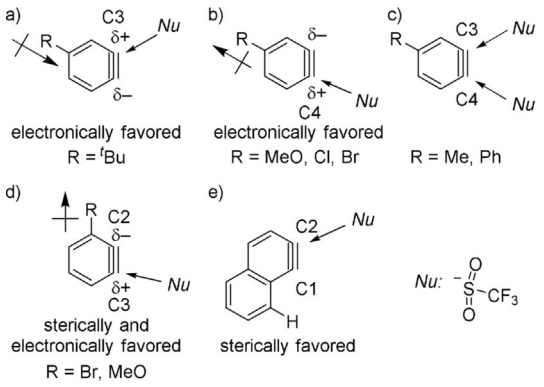


Figure 1. Proposed explanation of regioselectivity.

The preferred formation of 2-SO_2CF_3 naphthalene **2l** (**2a**) is the result of sterically favored attack on C2, owing to the steric repulsion by *peri*-hydrogen in the 1,2-naphthalyne (Figure 1e).[22]

Finally, the regioselectivity was analyzed by computations. The structures of benzynes were initially optimized by density functional theory (DFT) [B3LYP/6-31G(d)],[23] and then the electron densities of their reacting π orbitals were calculated by using a natural bond orbital (NBO) 6.0.[24,25] The differences of the electron densities in the π orbital at the triple bond are shown in Figure 2 and they are in good agreement with the experimental observations of the selectivity. In the case of 1-*t*Bu substitution of 3,4-benzyne, the electron density in the π orbital at C3 (0.9103) was lower than that at C4 (0.9576) (Figure 2a). On the other hand, the electron densities in the π orbitals at C4 of 1-Cl- and Br-substituted 3,4-benzynes were lower than those at C3 (Figure 2b). For 1-OMe-substituted 3,4-benzyne, the direction of the Me group against the triple bond strongly affected the bias of the electron density, and the electron densities in the *cis*-configuration of 1-OMe 3,4-benzyne are in good agreement with the experimental observation, whereas those of *trans*-configuration are not. In the case of Me- and Ph-substituted 3,4-benzyne, the difference between the electron densities are small, resulting in low regioselectivities (Figure 2c). Excellent regioselectivity was observed for MeO- and Br-substituted 2,3-benzynes, which could be well explained based on the large difference of electron densities in the π orbital at C3 and C2 (Figure 2d). The preferred formation of 2-SO_2CF_3 naphthalene is also in good agreement with the calculations (Figure 2e).

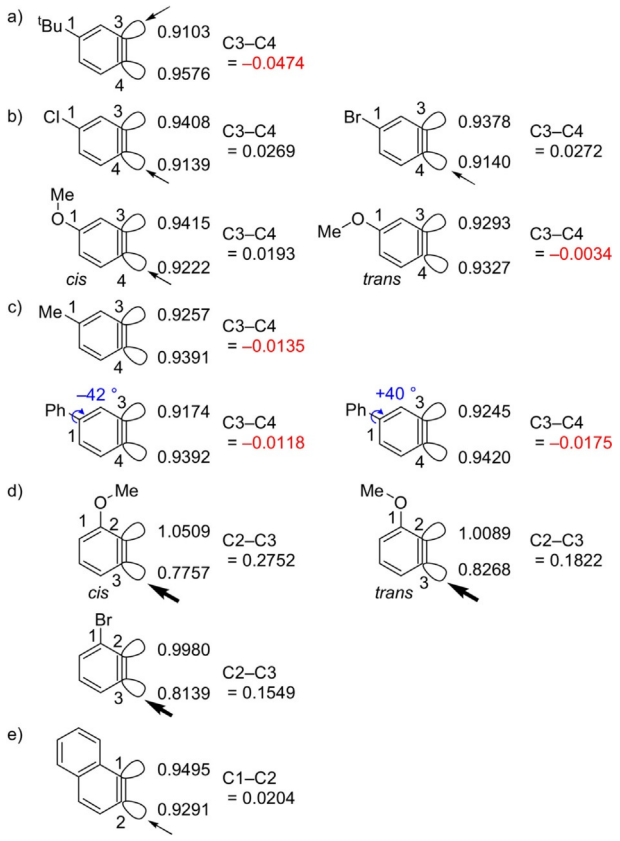


Figure 2. NBO analysis of substituted benzynes. Optimized structures of benzynes were calculated by using DFT [B3LYP6/31G(d)]. The electron densities of the reacting p orbitals were determined by NBO analysis. The arrow indicates the preferred direction of selectivity.

3. Conclusions

We have succeeded in synthesizing aryl triflones through the direct trifluoromethanesulfonylation of benzynes. A wide variety of 1-trimethylsilyl-2-trifluoromethanesulfonate arenes are feasible as precursors to generate highly reactive benzynes upon treatment with CsF and 5-crown-15 followed by the reaction with $NaSO_2CF_3$ to furnish a variety of aryl triflones in moderate to good yields. Regioselective trifluoromethanesulfonylation was achieved, depending on the substrate structures and selectivity, by balancing the polarization of electric charge and steric hindrance of the benzyne intermediates. All aryl triflones are expected to serve as building blocks for biologically active molecules and materials. As excess amounts of the reagents are necessary in the present method, further improvement of the reaction conditions are required. Applications of this methodology, including the synthesis of heteroaryl triflones,[4] are also under investigation.

Experimental Section

General Procedure of Trifluoromethanesulfonylation

To a stirred solution of 2-(trimethylsilyl)aryl trifluoromethanesulfonates **1**[26] (0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv) in acetonitrile (1.0 mL) was added with 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) at room temperature under a nitrogen atmosphere. After the reaction mixture was stirred at 40 °C for 3 h, it was cooled to room temperature, water was added, and the whole mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give the crude product. The residue was purified by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel to give trifluoromethanesulfonyl benzenes **2**.

2-(Trifluoromethylsulfonyl)naphthalene (2a)[5g,11f]

A reaction of 2-(trimethylsilyl)naphthalen-3-yl trifluoromethanesulfonate **1a** (34.8 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave 2-(trifluoromethylsulfonyl)naphthalene **2a** (13.1 mg, 50 %) as a yellow solid.

2a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.69–7.81 (m, 2H), 7.94–8.01 (m, 2H), 8.06–8.11 (m, 2H), 8.67 (s, 1H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.7 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 119.9 (q, J = 325.9 Hz), 123.7, 128.0, 128.1, 128.3, 129.8, 130.2, 130.8, 132.0, 134.0 (m), 136.5 ppm; IR (KBr): 3422, 3057, 2928, 2367, 1922, 1822, 1736, 1624, 1588, 1503, 1454, 1363, 1271, 1213, 1124, 1064, 1019, 955, 911, 857, 812, 746, 664, 578, 469 cm^{-1}; mp ($CHCl_3$): 61.0–62.0 °C; MS (EI, *m/z*): 260 (M+); HRMS (EI): calcd for $C_{11}H_7F_3O_2S$: 260.0119, found: 260.0135.

1-(Trifluoromethylsulfonyl)benzene (2b)[11f,27]

A reaction of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** (29.8 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave 1-(trifluoromethylsulfonyl)benzene **2b** (9.0 mg, 43 %) as a colorless oil.

2b: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.67–7.72 (m, 2H), 7.83–7.88 (m, 1H), 8.06 (d, J = 8.1 Hz, 2H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.9 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 119.8 (q, J = 325.9 Hz), 129.9, 130.8, 131.3, 136.6 ppm; IR (NaCl): 2360, 1844, 1793, 1771, 1734, 1716, 1699, 1684, 1653, 1635, 1616, 1576, 1558, 1541, 1521, 1507, 1473, 1456, 1437, 1418, 1373, 1074 cm^{-1}; MS (EI, *m/z*): 141 (M-CF_3^+); HRMS (EI): calcd for $C_6H_5O_2S$: 141.0010, found: 141.0055.

1,2-Dimethyl-4-(trifluoromethylsulfonyl)benzene (2c)

A reaction of 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1c** (32.6 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave 1,2-dimethyl-4-(trifluoromethylsulfonyl)benzene **2c** (15.1 mg, 63 %) as a white solid.

2c: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.39 (s, 3H), 2.41 (s, 3H), 7.42 (d, J = 7.5 Hz, 1H), 7.76–7.78 (m, 2H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −79.2 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 19.8, 20.3, 119.8 (q, J = 325.9 Hz), 128.1, 128.3, 131.0, 131.2, 139.0, 147.1 ppm; IR (KBr): 3083, 2952, 2877, 2609, 2375, 1930, 1790, 1654, 1596, 1483, 1451, 1362, 1304, 1216, 1125, 1082, 1024, 893, 826, 763, 705, 672, 608, 509 cm^{-1}; mp ($CHCl_3$): 50.5–51.5 °C; MS (EI, *m/z*): 238 (M^+); HRMS (EI): calcd for $C_9H_9F_3O_2S$: 238.0275, found: 238.0296.

1,4-Dimethyl-2-(trifluoromethylsulfonyl)benzene (2d)

A reaction of 3,6-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1d** (32.6 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave 1,4-dimethyl-2-(trifluoromethylsulfonyl)benzene **2d** (18.0 mg, 76 %) as a colorless oil.

2d: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.43 (s, 3H), 2.68 (s, 3H), 7.32 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H) 7.88 (s, 1H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.8 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 20.1, 20.6, 120.1 (q, J = 326.4 Hz), 129.3, 133.3, 133.5, 137.2, 137.4, 139.0 ppm; IR (NaCl): 2932, 2372, 2351, 2326, 1653, 1558, 1495, 1456, 1393, 1361, 1283, 1215, 1125, 1059, 885, 826, 764, 701, 615, 588, 530, 481, 425, 412 cm^{-1}; MS (EI, *m/z*): 238 (M^+); HRMS (EI): calcd for $C_9H_9F_3O_2S$: 238.0275, found: 238.0298.

2,3-Dihydro-5-(trifluoromethylsulfonyl)-1*H*-indene (2e)

A reaction of 2,3-dihydro-5-(trimethylsilyl)-1*H*-inden-6-yl trifluoromethanesulfonate **1e** (33.8 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave 2,3-dihydro-5-(trifluoromethylsulfonyl)-1*H*-indene **2e** (18.5 mg, 50 %) as a white solid.

2e: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.14–2.24 (m, 2H), 3.02–3.07 (m, 4H), 7.49 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.85 (s, 1H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −79.1 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 25.2, 32.5, 33.2, 119.9 (q, J = 325.9 Hz), 125.6, 126.4, 128.7, 129.2, 146.5, 154.8 ppm; IR (KBr): 3066, 2969, 1931, 1814, 1598, 1573, 1437, 1413, 1363, 1216, 1063, 886, 828, 763, 686, 607, 518, 460, 417 cm^{-1}; mp: 58.0–59.0 °C ($CHCl_3$); MS (EI, *m/z*): 250 (M^+); HRMS (EI): calcd for $C_{10}H_9F_3O_2S$: 250.0275, found: 250.0302.

1-Methyl-4-(trifluoromethylsulfonyl)benzene (2f)[28] and 1-Methyl-3-(trifluoromethylsulfonyl)benzene (2f')[28]

A reaction of 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1f** (31.2 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave inseparable mixture of 1-methyl-4-(trifluoromethylsulfonyl)benzene **2f** and 1-methyl-3-(trifluoromethylsulfonyl)benzene **2f'** (12.8 mg, 57 %, 48:52) as a colorless oil.

Mixture of **2f** and **2f'**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.50 (s, 3H), 2.52 (s, 3H), 7.47 (d, J = 7.8 Hz, 2H), 7.53–7.58 (m, 1H), 7.63–7.65 (m, 1H), 7.82–7.86 (m, 2H), 7.93 (d, J = 8.4 Hz, 2H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −79.1(minor, s, 3F, **2f**), −79.0 (major, s, 3F, **2f'**) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 21.2, 21.9, 119.77 (q, J = 325.9 Hz), 119.80 (q, J = 325.9 Hz), 127.9, 128.1, 129.7, 130.5, 130.7, 130.8, 131.1, 137.4, 140.4, 148.4 ppm; IR (NaCl): 3070, 2930, 2372, 2322, 1596, 1477, 1365, 1310, 1210, 1140, 1078, 866, 816, 791, 763,

698, 683, 664, 613, 590, 561, 530, 518 cm^{-1}; MS (EI, *m/z*): 224 (M^+); HRMS (EI): calcd for $C_8H_7F_3O_2S$: 224.0119, found: 224.0134.

1-*tert*Butyl-4-(trifluoromethylsulfonyl)benzene (2 g)[11f,5g] and 1-*tert*Butyl-3-(trifluoromethylsulfonyl)benzene (2 g')

A reaction of 4-*tert*-butyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1 k** (35.4 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave a mixture of 1-*tert*-butyl-4-(trifluoromethylsulfonyl)benzene **2 g** and 1-*tert*-butyl-3-(trifluoromethylsulfonyl)benzene **2 g'** (16.1 mg, 77 %, 33:67) as a colorless oil.

Mixture of **2 g** and **2 g'**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.38 (s, 9 H), 7.60 (t, J = 8.0 Hz, 0.66 H), 7.74 (d, J = 8.7 Hz, 0.66 H), 7.87 (d, J = 7.8 Hz, 1.33 H), 7.94 (d, J = 8.4 Hz, 0.66 H), 8.02 (s, 0.66 H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −79.1 (minor, s, 3F, **2 g**), −79.0 (major, s, 3F, **2 g'**) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 30.8, 30.9, 35.2, 35.6, 119.79 (q, J = 325.9 Hz), 119.82 (q, J = 325.4 Hz), 127.0, 127.4, 127.9, 128.0, 129.6, 130.6, 130.9, 133.9, 153.7, 161.2 ppm; IR (NaCl): 2968, 2309, 1593, 1482, 1368, 1217, 1146, 1079, 840, 781, 692, 678, 631, 591, 497, 467, 457, 439 cm^{-1}; MS (EI, *m/z*): 266 (M^+), HRMS (EI): calcd for $C_{11}H_{13}F_3O_2S$: 266.0588, found: 266.0631.

1-Methoxy-4-(trifluoromethylsulfonyl)benzene (2 h)[11f,27,28] and 1-Methoxy-3-(trifluoromethylsulfonyl)benzene (2 h' (2 m'))

Synthesis from **1 h**: A reaction of 4-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1 h** (32.8 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave 1-methoxy-4-(trifluoromethylsulfonyl)benzene **2 h** and 1-methoxy-3-(trifluoromethylsulfonyl)benzene **2 h'** (15.1 mg, 63 %, 74:26) as a colorless oil.

Synthesis from **1 m**: A reaction of 6-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1 m** (32.8 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave 1-methoxy-3-(trifluoromethylsulfonyl)benzene **2 m'** (**2 h'**) (10.0 mg, 42 %) as a colorless oil.

2 h: Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.94 (s, 3 H), 7.11 (d, J = 9.0 Hz, 2 H), 7.97 (d, J = 9.3 Hz, 2 H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −79.4 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 55.9, 115.2, 119.8 (q, J = 325.4 Hz), 121.7, 133.1, 166.2 ppm; IR (NaCl): 3103, 2951, 2847, 2593, 2345, 1594, 1577, 1498, 1464, 1442, 1362, 1318, 1275, 1216, 1191, 1141, 1075, 1022, 837, 805, 805, 763, 673, 590 cm^{-1}; MS (EI, *m/z*): 240 (M^+); HRMS (EI) calcd for $C_8H_7F_3O_3S$: 240.0068, found: 240.0093.

2 h': Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.91 (s, 3 H), 7.35 (d, J = 8.1 Hz, 1 H), 7.50 (s, 1 H), 7.55–7.66 (m, 2 H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.8 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 55.9, 114.6, 119.8 (q, J = 325.9 Hz), 122.9, 123.2, 130.9, 132.3, 160.4 ppm; IR (NaCl): 3084, 3016, 2946, 2844, 1732, 1600, 1483, 1436, 1368, 1329, 1292, 1249, 1216, 1134, 1089, 1072, 1038, 857, 790, 763, 695, 623, 587, 469 cm^{-1}; MS (EI, *m/z*): 240 (M^+); HRMS (EI): calcd for $C_8H_7F_3O_3S$: 240.0068, found: 240.0089.

1-Chloro-4-(trifluoromethylsulfonyl)benzene (2 i)[5g,28] and 1-Chloro-3-(trifluoromethylsulfonyl)benzene (2 i')[28]

A reaction of 4-chloro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1 i** (33.3 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave a mixture of 1-chloro-4-(trifluoromethylsulfonyl)benzene **2 i** and 1-chloro-3-(trifluoromethylsulfonyl)benzene **2 i'** (10.0 mg, 41 %, 81:19) as a white semisolid.

2 i: White solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.67 (d, J = 6.9 Hz, 2 H), 7.99 (d, J = 7.2 Hz, 2 H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.8 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 119.6 (q, J = 325.4 Hz), 129.7, 130.4, 132.1, 144.0 ppm; IR (KBr): 3421, 3099, 2963, 2367, 1719, 1580, 1475, 1397, 1373, 1327, 1261, 1220, 1142, 1092, 1073, 1014, 804, 770, 702, 631, 580, 472 cm^{-1}; mp: 49.0–50.0 °C ($CHCl_3$); MS (EI, *m/z*): 111 (M-$SO_2CF_3^+$), HRMS (EI): calcd for C_6H_4Cl: 111.0002, found: 110.9991.

2 i': Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.64 (t, J = 8.0 Hz, 1 H), 7.82 (d, J = 8.1 Hz, 1 H), 7.95 (d, J = 8.1 Hz, 1 H), 8.03 (s, 1 H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.5 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 119.6 (q, J = 325.9 Hz), 128.9, 130.6, 131.1, 133.1, 136.4, 136.8 ppm; IR (NaCl): 3075, 2920, 2850, 2352, 1725, 1578, 1462, 1411, 1373, 1305, 1215, 1146, 1103, 1074, 889, 793, 760, 672, 612, 582, 534, 521, 499, 488 cm^{-1}; MS (EI, *m/z*): 111 (M-$SO_2CF_3^+$), HRMS (EI): calcd for C_6H_4Cl: 111.0002 Found: 111.0009.

1-Bromo-4-(trifluoromethylsulfonyl)benzene (2 j)[5g,27,28] and 1-Bromo-3-(trifluoromethylsulfonyl)benzene (2 j' (2 n'))[5g]

Synthesis from **1 j**: A reaction of 4-bromo-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1 j** (37.7 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave 1-bromo-4-(trifluoromethylsulfonyl)benzene **2 j** and 1-bromo-3-(trifluoromethylsulfonyl)benzene **2 j'** (13.5 mg, 47 %, 85:15) as a white semisolid.

Synthesis from **1 n**: A reaction of 6-bromo-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1 n** (37.7 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown 5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) acetonitrile (1.0 mL) proceeded at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave 1-bromo-3-(trifluoromethylsulfonyl)benzene **2 n'** (**2 j'**) (7.9 mg, 27 %) as a white solid.

2j: White solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.83 (d, J=8.4 Hz, 2H), 7.90 (d, J=8.7 Hz, 2H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.8 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 119.6 (q, J=325.9 Hz), 130.2, 132.0, 132.8, 133.4 ppm; IR (KBr): 3098, 2957, 2562, 2370, 2344, 1719, 1573, 1469, 1373, 1218, 1139, 1070, 1011, 826, 767, 699, 617, 578, 524, 474, 418 cm^{-1}; mp: 63.5–64.5 °C ($CHCl_3$); MS (EI, m/z): 219 (M-CF_3^+), HRMS (EI): calcd for $C_6H_4BrO_2S$: 218.9115, found: 218.9143.

2j': Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ:7.55–7.61 (m, 1H), 7.97–8.00 (m, 2H), 8.19 (s, 1H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.5 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 119.6 (q, J= 325.9 Hz), 123.9, 129.3, 131.3, 133.2, 133.4, 139.7 ppm; IR (NaCl): 3088, 2929, 2352, 1717, 1572, 1460, 1406, 1373, 1302, 1215, 1145, 1073, 782, 674, 658, 610, 580, 523, 498, 480, 452, 436, 425, 407 cm^{-1}; MS (EI, m/z): 288 (M^+), HRMS (EI): calcd for $C_7H_4BrF_3O_2S$: 287.9067, found: 287.9132.

4-(Trifluoromethylsulfonyl)biphenyl (2k) [5g,11f] and 3-(Trifluoromethylsulfonyl)biphenyl (2k')

A reaction of 4-phenyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1k** (29.8 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceeded at 50 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave 4-(trifluoromethylsulfonyl)biphenyl **2k** and 3-(trifluoromethylsulfonyl)biphenyl **2k'** (18.3 mg, 64%, 48:52) as a white solid.

2k: White solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.45–7.54 (m, 3H), 7.62–7.65 (m, 2H), 7.86 (d, J=7.8 Hz, 2H), 8.09 (d, J=8.4 Hz, 2H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.9 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 119.8 (q, J=325.4 Hz), 127.5, 128.4, 129.25, 129.33, 129.5, 131.3, 138.4, 149.6 ppm; IR (KBr): 3071, 2567, 2347, 1937, 1814, 1686, 1593, 1561, 1479, 1449, 1401, 1359, 1318, 1293, 1212, 1139, 1071, 1005, 847, 767, 677, 608, 580, 526 cm^{-1}; mp ($CHCl_3$): 76.5–77.5 °C; MS (EI, m/z): 286 (M^+), HRMS (EI): calcd for $C_{13}H_9F_3O_2S$: 286.0275, found: 286.0271.

2k': Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.43–7.53 (m, 3H), 7.60–7.62 (m, 2H), 7.71–7.76 (m, 1H), 8.00–8.05 (m, 2H), 8.23 (s, 1H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.8 (s, 3F) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 119.8 (q, J=325.9 Hz), 127.2, 128.8, 129.0, 129.2, 129.3, 130.3, 131.9, 135.1, 138.2, 143.4 ppm; IR (NaCl): 3068, 3035, 1595, 1471, 1453, 1411, 1367, 1311, 1283, 1216, 1138, 1080, 1047, 1022, 994, 901, 811, 756, 698, 627, 587, 548, 523 cm^{-1}; MS (EI, m/z): 286 (M^+), HRMS (EI): calcd for $C_{13}H_9F_3O_2S$: 286.0275, found: 286.0255.

2-(Trifluoromethylsulfonyl)naphthalene (2l (2a)) and 1-(Trifluoromethylsulfonyl)naphthalene (2l' (2a'))[5g]

A reaction of 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate **1l** (34.8 mg, 0.1 mmol), sodium trifluoromethanesulfinate (31.2 mg, 0.2 mmol, 2.0 equiv), 15-crown-5 (39.7 μL, 0.2 mmol, 2.0 equiv), *tert*-butyl alcohol (9.5 μL, 0.1 mmol, 1.0 equiv), and cesium fluoride (91.2 mg, 0.6 mmol, 6.0 equiv) in acetonitrile (1.0 mL) proceed at 40 °C for 3 h. Subsequent purification by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel gave inseparable mixture of 2-(trifluoromethylsulfonyl)naphthalene **2l** (**2a**) and 1-(trifluoromethylsulfonyl)naphthalene **2l'** (**2a'**) (15.8 mg, 58%, 67:33) as a yellow semisolid.

Mixture of **2l** (**2a**) and **2l'** (**2a'**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.67–7.82 (m, 2.32H), 7.94–8.01 (m, 1.33H), 8.06–8.11 (m, 1.66H), 8.31 (d, J=8.4 Hz, 0.33H), 8.47 (d, J=7.8 Hz, 0.33H), 8.67 (s, 0.66H), 8.82 (d, J=9 Hz, 0.33H) ppm; ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.7 (major, s, 3F, **2l** (**2a**)), −78.3 (minor, s, 3F, **2l'** (**2a'**)) ppm; ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ: 119.9 (q, J=325.9 Hz), 120.2 (q, J=327.0 Hz), 123.6, 124.3, 124.4, 126.7, 127.7, 127.9, 128.1, 128.3, 129.2, 129.6, 129.8, 130.0, 130.1, 130.8, 132.0, 134.0 (m), 134.2, 135.1, 136.5, 138.4 ppm IR (KBr): 3057, 2963, 2318, 1717, 1624, 1588, 1506, 1456, 1362, 1261, 1213, 1114, 1065, 1020, 972, 857, 812, 747, 663, 578, 513, 470 cm^{-1}; MS (EI, m/z): 260 (M^+); HRMS (EI): calcd for $C_{11}H_7F_3O_2S$: 260.0119, found: 260.0133.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: benzynes · fluorine · pharmaceuticals · trifluoromethanesulfonyl group · trifluoromethanesulfonylation

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