Supporting Information

Efficient generation method and remarkable reactivities of 3-triflyloxybenzyne

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General Remarks

All reactions were performed in a dry glassware under atmosphere of argon otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F254, Cat. No. 1.05715). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60N, spherical neutral, particle size 40–50 μm, Cat. No. 37563-85 or particle size 63–210 μm, Cat. No. 37565-85). Preparative thin-layer chromatography (PTLC) was performed on silica-gel (Wako Pure Chemical Industries Ltd., Wakogel B5-F, Cat. No. 230-00043). Melting points (Mp) were measured on a YANACO MP-J3 instrument or an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. 1H and 13C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 or 126 MHz, respectively. 19F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. 31P NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 162 MHz. CDCl3 (Acros Organics, Cat. No. 368651000) or C6D6 (Kanto Chemical Co., Inc., Cat. No. 05081-43) was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from (CH3)4Si (δ 0.00 for 1H NMR in CDCl3) or the solvent peak (δ 77.0 for 13C NMR in CDCl3, and δ 7.15 for 1H NMR and δ 128.0 for 13C NMR in C6D6) as an internal reference, or α,α,α-trifluorotoluene (δ –63.0 ppm for 19F NMR in CDCl3) or phosphoric acid as (δ 0.00 ppm for 31P NMR in D2O) as an external standard with coupling constants (J) in hertz (Hz). The abbreviations s, d, t, q, m, and br signify singlet, doublet, triplet, quartet, multiplet, and broad, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm⁻¹. High-resolution mass spectra (HRMS) were measured on a Bruker microOTOF mass spectrometer under positive electrospray ionization (ESI) conditions. Elemental analyses were carried out at A Rabbit Science Japan Co., Ltd. X-ray crystallographic data was collected on a Rigaku R-AXIS RAPID diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54187 Å) at 23 K. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Tetrahydrofuran (THF) (Cat. No. 41001-84), diethyl ether (Et₂O) (Cat. No. 14547-84), tripotassium phosphate n-hydrate (Cat. No. 32380-30) and n-butyllithium (1.6 M, hexane solution, Cat. No. 04937-05) were purchased from Kanto Chemical Co. Inc. Magnesium turnings (19108-5000) was purchased from Acros Organics. Tetraphenylecyclopentadienone (10) (Cat. No. 326-46632), benzyl azide (12) (Cat. No. 327-79632), 4-methylphenylboronic acid (Cat. No. 321-63302), diphenyl sulfide (Cat. No. 162-12562), triphenylphosphine (Cat. No. 204-03061), isopropylmagnesium chloride lithium chloride complex (abt. 14%, THF solution, Cat. No. 095-06341) and 1,4-dioxane (Cat. No. 042-03766) were purchased from Wako Pure Chemical Industries Ltd. 1-Phenylpyrrole (8) (Cat. No. 131474), 1-((tert-butyl)dimethylsilyloxy)-1-
methoxyethene (4) (Cat. No. 519324), bromobenzene (Cat. No. 16350), ethylmagnesium bromide (3.0 M, Et₂O solution, Cat. No. 189871) and isopropylmagnesium chloride (2.0 M, THF solution, Cat. No. 230111) were purchased from Sigma–Aldrich Japan. N-tert-Butyl-α-phenylnitrore (16) (Cat. No. B1701), methyl 4-(bromomethyl)benzoate (Cat. No. B2053), 2,5-dimethylfuran (6) (Cat. No. D0725), dibenzyl sulfide (Cat. No. B0440) and trimethylsilylmethyl chloride (Cat. No. C0862) were purchased from Tokyo Chemical Industry Co., Ltd. Bis(di-tert-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II) (Pd(amphos)₂Cl₂) (Cat. No. 68 1844 5415) was purchased from Umicore AG & Co. KG.

Phenylmagnesium bromide (1.01 M in Et₂O or 1.05 M in THF) was prepared from bromobenzene and magnesium in the conventional way. (Trimethylsilyl)methylmagnesium chloride (1.07 M in Et₂O or 0.968 M in THF) was prepared from trimethylsilylmethyl chloride and magnesium in the conventional way. Phenylmagnesium bromide (1.05 M, THF solution), (trimethylsilyl)methylmagnesium chloride (1.07 M, Et₂O or THF solution) and commercial Grignard reagents were used after titrimetric determination of the concentration by the 1,10-phenanthroline method. ³¹

1,3-Bis(triflyloxy)-2-iodobenzene⁵² (1), methyl 4-(azidomethyl)benzoate⁵³ (14) and 2-iodo-3-methoxyphenyl triflate⁵⁴ (18) were prepared according to the reported methods.

**Experimental Procedures**

*A typical procedure for the cycloaddition of 3-triflyloxybenzene*

\[
\begin{align*}
\text{OTf} & \quad \text{MeO} \quad \text{OTf} \\
\text{MeO} & \quad \text{OMe} \\
\text{OMe} & \quad \text{MeO} \\
\end{align*}
\]

To a mixture of 1,3-bis(triflyloxy)-2-iodobenzene (1) (100 mg, 0.200 mmol) and 1,1-dimethoxyethylene (2) (37.9 µL, 0.400 mmol, 2.00 equiv) dissolved in Et₂O (3.0 mL) was slowly added (trimethylsilyl)-methylmagnesium chloride (1.07 M, Et₂O solution, 0.206 mL, 0.220 mmol, 1.10 equiv) at –30 °C. After stirring for 1 h at the same temperature, the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL x 3), and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 600 mg, n-hexane/EtOAc = 20/1) to give 8,8-dimethoxy-2-triflyloxybicyclo[4.2.0]octa-1,3,5-triene (3) (57.9 mg, 0.185 mmol, 92.5%) as a colorless oil.

**Palladium catalyzed cross-coupling reaction of cycloadduct 13**

\[
\begin{align*}
\text{OTf} & \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{N} & \quad \text{N} \quad \text{N} \\
\text{N} & \quad \text{N} \quad \text{N} \\
\end{align*}
\]

To a mixture of 1-benzyl-4-triflyloxy-1H-benzo[d][1,2,3]triazole (13) (71.5 mg, 0.200 mmol), 4-methylphenylboronic acid (32.6 mg, 0.240 mmol, 1.20 equiv), Pd(amphos)₂Cl₂ (2.8 mg, 4.0 µmol, 2.0 mol %), and tripotassium phosphate n-hydrate (106 mg, ca. 0.40 mmol, ca. 2.0 equiv) were added 1,4-dioxane (2.0 mL) and H₂O (0.20 mL) at room temperature and the mixture was heated at 100 °C with stirring for 10 h. After cooling to room temperature, to the mixture was added water (10 mL). The mixture was extracted with EtOAc (50 mL x 3), and the combined organic extract was washed with aqueous saturated solution of sodium bicarbonate, brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/EtOAc = 5/1) to give 1-benzyl-4-((4-tolyl)-1H-benzo[d][1,2,3]triazole (20) (51.5 mg, 0.172 mmol, 86.0%) as a colorless oil.
A typical procedure for the synthesis of aryl triflone via nucleophilic addition of tetrahydrofuran to 3-triflyloxybenzyne followed by thia-Fries rearrangement

To a solution of 1,3-bis(triflyloxy)-2-iodobenzene (1) (100 mg, 0.200 mmol) in THF (3.0 mL) was slowly added isopropylmagnesium chloride lithium chloride complex (1.10 equiv) at −78 °C. After stirring for 10 min at the same temperature, to the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na2SO4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/EtOAc = 5/1) to give 3-(4-chlorobutoxy)-2-triflylphenol (23) (54.0 mg, 0.162 mmol, 81.0%) as a colorless solid.

A typical procedure for the synthesis of aryl triflone via nucleophilic addition of nucleophiles to 3-triflyloxybenzyne followed by thia-Fries rearrangement

To a mixture of 1,3-bis(triflyloxy)-2-iodobenzene (1) (100 mg, 0.200 mmol) and triphenylphosphine (262 mg, 1.00 mmol, 5.00 equiv) dissolved in Et2O (3.0 mL) was slowly added (trimethylsilyl)methylmagnesium chloride (1.07 M, THF solution, 0.206 mL, 0.220 mmol, 1.10 equiv) at −30 °C. After stirring for 1 h at the same temperature, to the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na2SO4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (dichloromethane/methanol = 10/1) to give 2-triflyl-3-(triphenylphosphonio)phenolate (25) (74.7 mg, 0.154 mmol, 77.0%) as a pale yellow solid.

Characterization Data of New Compounds

8,8-Dimethoxy-2-triflyloxybicyclo[4.2.0]octa-1,3,5-triene (3)

Colorless oil; TLC Rf 0.37 (n-hexane/EtOAc = 10/1); 1H NMR (CDCl3, 500 MHz) δ 3.40 (s, 2H, CH2), 3.46 (s, 6H, 2CH3), 7.16 (d, 1H, J = 8.5 Hz, aromatic), 7.25 (d, 1H, J = 7.5 Hz, aromatic), 7.41 (dd, 1H, J = 7.5, 8.5 Hz, aromatic); 13C NMR (CDCl3, 126 MHz) δ 43.5 (1C), 51.9 (2C), 105.1 (1C), 118.5 (q, 1C, J′C,F = 321 Hz), 119.5 (1C), 124.2 (1C), 132.1 (1C), 136.4 (1C), 140.6 (1C), 144.9 (1C); 19F NMR (CDCl3, 376 MHz) δ −73.9 (s); IR (KBr, cm−1) 840, 913, 992, 1065, 1142, 1217, 1245, 1424, 2942; HRMS (ESI+) m/z 335.0183 ([M+Na]+, C13H11F3NaOS2) requires 335.0171.

The regiochemistry was determined by HMBC analysis (500 MHz 1H NMR/126 MHz 13C NMR in CDCl3).
8-(tert-Butyldimethylsilyl)oxy-8-methoxy-2-triflyloxybicyclo[4.2.0]octa-1,3,5-triene (5)

Colorless oil; TLC Rf 0.52 (n-hexane/EtOAc = 10/1); 1H NMR (CDCl3, 500 MHz) δ 0.17 (s, 3H, SiCH3), 0.19 (s, 3H, SiCH3), 0.91 (s, 9H, 3CH3), 3.45 (d, 1H, J = 13.5 Hz, methylene CH), 3.49 (s, 3H, OCH3), 3.50 (d, 1H, J = 13.5 Hz, methylene CH), 7.13 (d, 1H, J = 8.5 Hz, aromatic), 7.22 (d, 1H, J = 7.0 Hz, aromatic), 7.38 (dd, 1H, J = 7.0, 8.5 Hz, aromatic); 13C NMR (CDCl3, 126 MHz) δ –3.9 (1C), –3.5 (1C), 17.9 (1C), 25.5 (3C), 48.9 (1C), 53.2 (1C), 102.8 (1C), 118.6 (q, 1C, J_{C,F} = 321 Hz), 119.3 (1C), 121.4 (1C), 131.8 (1C), 138.8 (1C), 140.3 (1C), 144.4 (1C); 19F NMR (CDCl3, 376 MHz) δ –74.1 (s); IR (KBr, cm⁻¹) 840, 1000, 1065, 1144, 1216, 1245, 1426, 2934; HRMS (ESI⁺) m/z 435.0867 ([M+Na]⁺, C16H13F3NaO5SSi⁺ requires 435.0880).

The regiochemistry was determined by HMBC analysis (500 MHz 1H NMR/126 MHz 13C NMR in C6D6).

1,4-Dihydro-1,4-dimethyl-5-triflyloxy-1,4-epoxynaphthalene (7)

Colorless oil; TLC Rf 0.37 (n-hexane/EtOAc = 10/1); 1H NMR (CDCl3, 500 MHz) δ 1.91 (s, 3H, CH3), 2.03 (s, 3H, CH3), 5.79 (d, 1H, J = 5.0 Hz, alkenic), 6.83 (d, 1H, J = 8.0 Hz, aromatic), 6.88 (d, 1H, J = 5.0 Hz, alkenic), 7.05 (dd, 1H, J = 7.0, 8.0 Hz, aromatic), 7.11 (d, 1H, J = 7.0 Hz, aromatic); 13C NMR (CDCl3, 126 MHz) δ 15.1 (1C), 16.4 (1C), 88.8 (1C), 89.3 (1C), 118.1 (1C), 118.4 (1C), 118.6 (q, 1C, J_{C,F} = 321 Hz), 127.7 (1C), 142.3 (1C), 144.1 (1C), 146.4 (1C), 146.8 (1C), 157.5 (1C); 19F NMR (CDCl3, 376 MHz) δ –73.3 (s); IR (KBr, cm⁻¹) 932, 1141, 1221, 1423, 2936, 2984; HRMS (ESI⁺) m/z 343.0209 ([M+Na]⁺, C11H11F3NaO5S⁺ requires 343.0222).

1,4-Dihydro-9-phenyl-5-triflyloxyphthalen-1,4-imine (9)

Pale brown solid; Mp 60–62 °C; TLC Rf 0.44 (n-hexane/EtOAc = 5/1); 1H NMR (CDCl3, 500 MHz) δ 5.50 (s, 1H), 5.65 (s, 1H), 6.77–6.83 (m, 3H), 6.86 (dd, 1H, J = 7.5, 7.5 Hz), 6.97–7.03 (m, 3H), 7.15–7.20 (AA’BB’, 2H), 7.25 (d, 1H, J = 7.5 Hz); 13C NMR (CDCl3, 126 MHz) δ 67.0 (1C), 69.6 (1C), 117.8 (2C), 118.1 (1C), 118.7 (q, 1C, J_{C,F} = 321 Hz), 121.3 (1C), 121.4 (1C), 127.6 (1C), 129.0 (2C), 140.8 (1C), 141.5 (1C), 142.1 (1C), 143.9 (1C), 145.9 (1C), 152.9 (1C); 19F NMR (CDCl3, 376 MHz) δ –73.1 (s); IR (KBr, cm⁻¹) 866, 1119, 1142, 1213, 1422, 1495, 1601; HRMS (ESI⁺) m/z 390.0395 ([M+Na]⁺, C17H12F3NNaO5S⁺ requires 390.0382).
1-Benzyl-4-triflyloxy-1H-benzo[d][1,2,3]triazole (13)

![Chemical structure image]

Colorless solid; Mp 84–85 °C; TLC $R_f$ 0.29 ($n$-hexane/EtOAc = 5/1); $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 5.88 (s, 2H, CH$_2$), 7.25–7.32 (m, 3H, aromatic), 7.32–7.40 (m, 4H, aromatic), 7.43 (dd, 1H, $J = 8.5$, 8.5 Hz, aromatic); $^{13}$C NMR (CDCl$_3$, 126 MHz) $\delta$ 52.8 (1C), 110.4 (1C), 116.2 (1C), 118.8 (q, 1C, $J_{C,F} = 321$ Hz), 127.70 (2C), 127.74 (1C), 128.9 (1C), 133.8 (1C), 135.3 (1C), 139.1 (1C), 139.6 (1C); $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$ –72.9 (s); IR (KBr, cm$^{-1}$) 822, 1015, 1139, 1168, 1219, 1428, 1505, 3035; Anal. calcd. for C$_{14}$H$_{10}$F$_3$N$_3$O$_3$S: C, 47.06; N, 11.76; H, 2.82%; Found: C, 47.09; N, 11.96; H, 2.79%.

1-[4-(Methoxycarbonyl)benzyl]-4-triflyloxy-1H-benzo[d][1,2,3]triazole (15)

![Chemical structure image]

Colorless solid; Mp 111–112 °C; TLC $R_f$ 0.46 ($n$-hexane/EtOAc = 1/1); $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 3.91 (s, 3H, CH$_3$), 5.94 (s, 2H, CH$_2$), 7.30 (d, 1H, $J = 8.0$ Hz, aromatic), 7.32–7.37 (m, 3H, aromatic), 7.46 (dd, 1H, $J = 8.0$, 8.0 Hz, aromatic), 8.01–8.05 (AA’BB’, 2H, aromatic); $^{13}$C NMR (CDCl$_3$, 126 MHz) $\delta$ 52.3 (1C+1C, two signals overlapped), 110.1 (1C), 116.4 (1C), 118.8 (q, 1C, $J_{C,F} = 321$ Hz), 127.5 (2C), 128.1 (1C), 130.5 (2C), 130.7 (1C), 135.2 (1C), 138.6 (1C), 139.2 (1C), 139.7 (1C), 166.3 (1C); $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$ –72.9 (s); IR (KBr, cm$^{-1}$) 827, 1018, 1139, 1216, 1283, 1424, 1505, 1728; Anal. calcd. for C$_{16}$H$_{12}$F$_3$N$_3$O$_5$S: C, 46.27; N, 10.12; H, 2.91%; Found: C, 46.07; N, 10.41; H, 2.84%.

The regiochemistry was determined by the NOESY experiment (500 MHz $^1$H NMR in C$_6$D$_6$).

2-tert-Butyl-2,3-dihydro-3-phenyl-4-triflyloxy-1,2-benzoisoxazole (17)

![Chemical structure image]

Colorless solid; Mp 48–49 °C; TLC $R_f$ 0.40 ($n$-hexane/EtOAc = 20/1); $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.19 (s, 9H, CH$_3$), 5.79 (s, 1H, sp$^3$CH), 6.72 (d, 1H, $J = 8.5$ Hz, aromatic), 6.88 (d, 1H, $J = 8.0$ Hz, aromatic), 7.22–7.36 (m, 6H, aromatic); $^{13}$C NMR (CDCl$_3$, 126 MHz) $\delta$ 25.2 (3C), 61.9 (1C), 65.5 (1C), 107.2 (1C), 113.3 (1C), 118.5 (q, 1C, $J_{C,F} = 321$ Hz), 122.8 (1C), 127.5 (2C), 128.0 (1C), 128.7 (2C), 130.8 (1C), 141.1 (1C), 144.4 (1C), 159.6 (1C); $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$ –73.4 (s); IR (KBr, cm$^{-1}$) 855, 1009, 1140, 1215, 1249, 1423, 1457, 2976; Anal. calcd. C$_{18}$H$_{18}$F$_3$N$_2$O$_4$S: C, 53.86; N, 3.49; H, 4.52%; Found: C, 53.86; N, 3.50;
H, 4.56%.
The regiochemistry was determined by HMBC analysis (500 MHz $^1$H NMR/126 MHz $^{13}$C NMR in CDCl$_3$).

![HMBC](https://example.com/hmbc.png)

1-Benzyl-4-(4-tolyl)-1H-benzo[d][1,2,3]triazole (20)

![NMR Spectrum](https://example.com/nmr.png)

Colorless oil; TLC $R_f$ 0.38 (n-hexane/EtOAc = 5/1); $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 2.46 (s, 3H, CH$_3$), 5.91 (s, 2H, CH$_2$), 7.29–7.39 (m, 8H, aromatic), 7.46 (dd, 1H, $J = 7.5$, 8.0 Hz, aromatic), 7.50 (d, 1H, $J = 7.5$ Hz, aromatic), 8.04–8.08 (AA'BB', 2H, aromatic); $^{13}$C NMR (CDCl$_3$, 126 MHz) $\delta$ 21.3 (1C), 52.2 (1C), 108.1 (1C), 122.0 (1C), 127.5 (2C), 127.6 (1C), 128.4 (1C), 128.9 (2C), 129.0 (2C), 129.4 (2C), 133.4 (1C), 133.5 (1C), 133.8 (1C), 134.8 (1C), 138.1 (1C), 144.4 (1C); IR (KBr, cm$^{-1}$) 824, 1097, 1159, 1245, 1257, 1455, 1496, 1506, 2921, 3032; HRMS (ESI$^+$) $m/z$ 322.1313 ([M+Na]$^+$, C$_{20}$H$_{17}$N$_3$Na$^+$ requires 322.1315).

3-Ethoxy-2-triflylphenol (22)

![NMR Spectrum](https://example.com/nmr.png)

Colorless oil; TLC $R_f$ 0.44 (n-hexane/EtOAc = 5/1); $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.45 (t, 3H, J = 7.0 Hz, CH$_3$), 4.14 (q, 2H, J = 7.0 Hz, CH$_2$), 6.48 (dd, 1H, J = 0.50, 8.5 Hz, aromatic), 6.63 (dd, 1H, J = 0.50, 8.5 Hz, aromatic), 9.55 (1H, OH); $^{13}$C NMR (CDCl$_3$, 126 MHz) $\delta$ 14.0 (1C), 65.6 (1C), 103.7 (1C), 103.8 (q, 1C, $J_{C-F} = 4.9$ Hz), 111.4 (1C), 119.9 (q, 1C, $J_{C-F} = 328$ Hz), 139.3 (1C), 159.9 (1C), 160.7 (1C); $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$ −76.5 (s); IR (KBr, cm$^{-1}$) 824, 1097, 1222, 1218, 1334, 1495, 1580, 1607, 3340; Anal. calcd. for C$_{20}$H$_{17}$F$_3$O$_4$: C, 40.00; H, 3.36%; Found: C, 40.10; H, 3.38%.

Regiochemistry was determined by the NOESY experiment (500 MHz $^1$H NMR in CDCl$_3$).
3-(4-Chlorobutoxy)-2-triflylphenol (23)

![Chemical structure](image)

Colorless solid; Mp 31–32 °C; TLC Rf 0.38 (n-hexane/EtOAc = 5/1); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 1.94–2.08 (m, 4H, CH\(_2\)), 3.63 (t, 2H, \(J = 6.0\) Hz, CH\(_2\)), 4.10 (t, 2H, \(J = 5.5\) Hz, CH\(_2\)), 6.49 (dd, 1H, \(J = 0.8, 8.5\) Hz, aromatic), 6.66 (dd, 1H, \(J = 8.5, 8.5\) Hz, aromatic), 7.53 (dd, 1H, \(J = 8.5, 8.5\) Hz, aromatic), 9.55 (s, 1H, OH); \(^13\)C NMR (CDCl\(_3\), 126 MHz) \(\delta\) 26.0 (1C), 28.6 (1C), 44.6 (1C), 68.9 (1C), 103.3 (1C), 103.5 (1C), 111.6 (1C), 119.9 (q, 1C, \(J_{\text{C-F}} = 328\) Hz), 139.4 (1C), 159.8 (1C), 160.9 (1C); \(^19\)F NMR (CDCl\(_3\), 376 MHz) \(\delta\) –77.0 (s); IR (KBr, cm\(^{-1}\)) 1039, 1220, 1335, 1495, 1568, 1575, 1606, 2956, 3314; Anal. calcd. for C\(_{11}\)H\(_{12}\)Cl\(_3\)F\(_3\)O\(_4\)S: C, 39.71; H, 3.64%; Found: C, 39.84; H, 3.59%.

Regiochemistry was determined by the NOESY experiment (500 MHz \(^1\)H NMR in CDCl\(_3\)).

3-(4-Bromobutoxy)-2-triflylphenol (24)

![Chemical structure](image)

Colorless solid; Mp 32–33 °C; TLC Rf 0.35 (n-hexane/EtOAc = 5/1); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 2.00 (tt, 2H, \(J = 6.5, 6.5\) Hz, CH\(_2\)), 2.10 (tt, 2H, \(J = 6.5, 6.5\) Hz, CH\(_2\)), 3.49 (t, 2H, \(J = 6.5\) Hz, CH\(_2\)), 4.10 (t, 2H, \(J = 6.5\) Hz, CH\(_2\)), 6.49 (dd, 1H, \(J = 8.5\) Hz, aromatic), 6.66 (d, 1H, \(J = 8.5\) Hz, aromatic), 7.53 (dd, 1H, \(J = 8.5, 8.5\) Hz, aromatic), 9.55 (s, 1H, OH); \(^13\)C NMR (CDCl\(_3\), 126 MHz) \(\delta\) 27.2 (1C), 28.7 (1C), 33.3 (1C), 68.7 (1C), 103.3 (1C), 103.5 (1C), 111.7 (1C), 119.9 (q, 1C, \(J_{\text{C-F}} = 328\) Hz), 139.4 (1C), 159.8 (1C), 160.9 (1C); \(^19\)F NMR (CDCl\(_3\), 376 MHz) \(\delta\) –77.0 (s); IR (KBr, cm\(^{-1}\)) 1072, 1121, 1208, 1335, 1450, 1492, 1578, 1607, 2925, 3335; Anal. calcd. for C\(_{11}\)H\(_{12}\)BrF\(_3\)O\(_4\)S: C, 35.03; H, 3.21%; Found: C, 35.23; H, 3.15%.

Regiochemistry was determined by the NOESY experiment (500 MHz \(^1\)H NMR in CDCl\(_3\)).
2-Triflyl-3-(triphenylphosphonio)phenolate (25)

Pale yellow solid; Mp 261–262 °C; TLC Rf 0.56 (CH₂Cl₂/MeOH = 5/1); ¹H NMR (CDCl₃, 500 MHz) δ 5.86 (dd, 1H, J = 6.5 Hz, J₃₅ = 19.0 Hz, aromatic), 7.08 (d, 1H, J = 8.5 Hz, aromatic), 7.11–7.18 (m, 1H, aromatic), 7.40–7.90 (m, 15H, aromatic); ¹³C NMR (CDCl₃, 126 MHz) δ 116.0 (br s, 1C), 116.6 (d, 1C, J₃₋₅ = 38.4 Hz), 120.1 (q, 1C, J₁₋₃₋₅ = 330 Hz), 127.2–123.2 (br, 1C), 123.7 (br s, 1C), 129.5 (d, 6C, J₃₋₅ = 13.2 Hz), 133.6 (br, d, 3C, J₅₋₇ = 8.1 Hz), 133.7 (d, 6C, J₃₋₅ = 3.0 Hz), 134.1 (d, 3C, J₅₋₇ = 19.3 Hz), 135.1 (1C), 175.7 (d, 1C, J₅₋₇ = 4.8 Hz); ¹⁹F NMR (CDCl₃, 376 MHz) δ −72.3 (s); ³¹P NMR (CDCl₃, 162 MHz) δ 27.1 Hz (s); IR (KBr, cm⁻¹) 1109, 1174, 1185, 1211, 1328, 1437, 1524, 1595, 3061; HRMS (ESI⁺) m/z 487.0728 ([M+H]⁺, C₂⁵H₁₉F₃O₃Ps⁺ requires 487.0739).

Crystallographic analysis

![ORTEP drawing of phosphonium salt 25 (ellipsoids set at 40% probability level).](image)

Selected crystal data: Crystal System; monoclinic, Space Group; P₂₁/n (No. 14), a = 9.528(2) Å, b = 17.804(3) Å, c = 13.794(2) Å, β = 104.385(9)°, V = 2266.6(6) Å³, Z = 4, R₁ = 0.0316, wR₂ = 0.0836. CCDC 1014336 contains the supplementary crystallographic data for this compound. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3-(Diphenylsulfonio)-2-triflylphenolate (26)

Pale yellow solid; Mp 176–177 °C; TLC Rf 0.59 (CH₂Cl₂/MeOH = 5/1); ¹H NMR (CDCl₃, 500 MHz) δ 5.63 (d, 1H, J = 7.5 Hz, aromatic), 6.87 (d, 1H, J = 9.0 Hz, aromatic), 7.10 (dd, 1H, J = 7.5, 9.0 Hz, aromatic), 7.48 (d, 4H, J = 8.0 Hz, aromatic), 7.66 (dd, 4H, J = 7.5, 8.0 Hz, aromatic), 7.74 (t, 2H, J = 7.5 Hz, aromatic); ¹³C NMR (CDCl₃, 126 MHz) δ 110.2 (1C), 114.6 (1C), 120.3 (q, 1C, J₁₋₃₋₅ = 329 Hz), 123.2 (1C), 125.7 (1C), 130.7 (4C), 131.2 (4C), 133.3 (1C), 133.9 (1C), 134.1 (2C), 175.8 (1C); ¹⁹F NMR (CDCl₃, 376 MHz) δ −75.4 (s); IR (KBr, cm⁻¹) 1011, 1108, 1196, 1333, 1447, 1484, 1535, 1600, 3060; HRMS (ESI⁺) m/z 411.0325 ([M+H]⁺, C₁₉H₁₄F₃O₃S⁺ requires 411.0331).
3-Benzylthio-2-triflylphenol (27)

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\begin{array}{c}
\text{OH} \\
\text{S} \\
\text{CF}_3 \\
\text{Ph}
\end{array}
\]

Colorless solid; Mp 112–113 °C; TLC \( R_f \) 0.41 (\( n \)-hexane/EtOAc = 5/1); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 4.18 (s, 2H, CH\(_2\)), 6.85 (d, 1H, \( J = 8.0 \) Hz, aromatic), 6.94 (d, 1H, \( J = 8.0 \) Hz, aromatic), 7.26–7.43 (m, 5H, aromatic), 7.44 (dd, 1H, \( J \approx 8.0 \) Hz, aromatic), 9.43 (s, 1H, OH); \(^{13}\)C NMR (CDCl\(_3\), 126 MHz) \( \delta \) 38.9 (1C), 110.6 (1C), 116.6 (1C), 120.2 (q, 1C, \( J^{1C-F} = 329 \) Hz), 120.4 (1C), 127.8 (1C), 128.8 (2C), 129.0 (2C), 134.8 (1C), 137.8 (1C), 144.5 (1C), 161.3 (1C); \(^{19}\)F NMR (CDCl\(_3\), 376 MHz) \( \delta \) −77.3 (s); IR (KBr, cm\(^{-1}\)) 1033, 1095, 1137, 1206, 1221, 1357, 1464, 1585, 3370; Anal. calcd. for C\(_{14}\)H\(_{11}\)F\(_3\)O\(_3\)S\(_2\): C, 48.27%; H, 3.18%; Found: C, 48.27; H, 3.25%. Regiochemistry was determined by the NOESY experiment (500 MHz \(^1\)H NMR in C\(_6\)D\(_6\)).

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\begin{array}{c}
\text{OH} \\
\text{S} \\
\text{CF}_3 \\
\text{Ph}
\end{array}
\]

\text{NOESY}

References for Supporting Information
$^{1}H$ and $^{13}C$ NMR Spectra of Compounds

$^{1}H$ NMR (500 MHz) and $^{13}C$ NMR (126 MHz) spectra of 3 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 5 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 7 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 9 (CDCl$_3$)
$^{1}H$ NMR (500 MHz) and $^{13}C$ NMR (126 MHz) spectra of 13 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 15 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 17 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 20 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 22 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 23 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 24 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 25 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 26 (CDCl$_3$)
$^1$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) spectra of 27 (CDCl$_3$)