Supporting Information

Bismuth-Catalyzed Oxidative Coupling of Arylboronic Acids with Triflate and Nonaflate Salts

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1. General methods

1.1 Experimental methods

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under dry argon (Ar) in flame-dried glassware. Anhydrous solvents were distilled from appropriate drying agents and were transferred under Ar: tetrahydrofuran (Na/K), chloroform (CaH₂) and chloroform-d (MS), acetonitrile (SPS) and acetonitrile-d₃ (MS), acetone, toluene (Na/K), dichloromethane (CaH₂/P₄O₁₀) and dimethylformamide (MS). Commercially available xenon difluoride obtained from STREM, 1-fluoro-2,6-dichloropyridinium tetrafluoroborate, 1-fluoro-2,6-dichloropyridinium triflate, sodium nonaflate and all the arylboronic acids utilized in this work were obtained from Sigma-Aldrich. Molecular sieves were dried at 250 °C for 2 days before use. Flash chromatography: Merck silica gel 60 (40-63 µm). ESI-MS: ESQ 3000 (Bruker). Preparative TLC plates: PLC Silica gel 60 F₂₅₄, 1 mm, 20x20 cm (Sigma-Aldrich). High-resolution mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan). NMR spectra were recorded using 300 MHz Bruker Avance III and 500 MHz Bruker Avance III NMR spectrometers. ¹H NMR spectra (300.13 MHz, 500.1 Hz) were referenced to the residual protons of the deuterated solvent,¹ and are reported to tetramethylsilane (δTMS = 0 ppm), chloroform-d (δTMS = 7.26 ppm) or acetonitrile-d₃ (δTMS = 1.94 ppm). ¹³C{¹H} NMR spectra (75.47 MHz, 125 MHz) were referenced internally to the D-coupled ¹³C resonances of the NMR solvent and are reported to tetramethylsilane (δTMS = 0 ppm), chloroform-d (δTMS = 77.16 ppm) or acetonitrile-d₃ (δTMS = 1.32 ppm). ¹⁹F{¹H} NMR spectra (282 MHz, 471 MHz) are reported relative to the ¹⁹F resonances of CFCl₃. Chemical shifts (δ) are given in ppm, relative to deuterated solvent residual peak, and coupling constants (J) provided in Hz. For aryl nonaflates 5a-e and bismine nonaflate 4d, ¹³C NMR spectra were acquired with a Bruker BB-1H/19F TBO Probe with inverse gated decoupling. For ¹H NMR waltz16 was used for decoupling. For ¹⁹F the decoupling scheme bi_p5m4sp_4sp.2 with adiabatic chirp pulses was used to ensure the broadband decoupling on ¹⁹F. Sometime small artifacts can be seen in the spectra. ¹⁹F-HMQCs were acquired to show which ¹⁹F signals correlate with the corresponding ¹³C nuclei.
2. Synthesis of ligands

Figure S1. Ligands utilized in this study.

Ligand L1, L2, L3 and L4 were synthesized following previously reported protocols. Ligands L5 and L6 were synthesized by oxidation of the corresponding thioether with meta-chloroperbenzoic acid (mCPBA). Characterization and spectroscopic data for all of them matches those described in the literature. Ligand L7 was synthesized using the same protocol, which is described below.
2.1 Synthesis of diarylsulfone ligand L7

A round bottomed flask equipped with a stir bar was charged with bis(4-(trifluoromethyl)phenyl)sulfane\textsuperscript{7} (2.3 g, 7.1 mmol, 1.0 equiv.) and 20 mL of CH\textsubscript{2}Cl\textsubscript{2} under air. The reaction mixture was cooled to 0 °C, and \textit{m}CPBA (3.7 g, 21.4 mmol, 3.0 equiv.) was added in portions as a solid. The reaction is stirred overnight slowly warming to room temperature. Then, a solution of saturated Na\textsubscript{2}CO\textsubscript{3} was added slowly (vigorous CO\textsubscript{2} evolution) and the resulting mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 50 mL). The combined organics were dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated to give L7 as a white solid (2.245 g, 6.3 mmol, 89\%). The product obtained was used without further purification.

\textsuperscript{1}H NMR - (300 MHz, CDCl\textsubscript{3}): δ 8.09 (d, \textit{J} = 8.1 Hz, 4H), 7.80 (d, \textit{J} = 8.1 Hz, 4H).

\textsuperscript{13}C NMR - (75 MHz, CDCl\textsubscript{3}): δ 144.3, 135.6 (q, \textit{J} = 32.9 Hz), 128.6, 126.4 (q, \textit{J} = 3.6 Hz), 123.1 (q, \textit{J} = 272.9 Hz).

\textsuperscript{19}F NMR - (282 MHz, CDCl\textsubscript{3}): δ -63.4 (s, 6F).

HRMS (EI, \textit{m/z}): calc’d for C\textsubscript{14}H\textsubscript{8}O\textsubscript{2}S\textsubscript{1}F\textsubscript{6} [M]\textsuperscript{+} 354.0144; found 354.0146.

m.p. (°C): 141.5 – 142.3.
3. Synthesis of Bi(III) compounds

3.1 Synthesis of phenylbismines

Phenylbismines 9a-d were synthesized according to a previously reported protocol. Phenylbismines 9e, 9f and 6 were synthesized following the procedure described below.

**Figure S2.** Phenylbismines synthesized.
General procedure for the synthesis of phenylbismines.$^9$

![Chemical structure](image)

A Schlenk flask equipped with a stir bar was charged with BiBr$_3$ (0.66 equiv.), BiPh$_3$ (0.33 equiv.) and Et$_2$O (8 mL) under an Ar atmosphere and stirred at room temperature for 3 h. THF (10 mL) was added to completely dissolve the yellow precipitate, and this solution was added drop-wise to a $-78 \, ^\circ\text{C}$ dilithiated ligand solution. The dilithiated ligand was prepared in a separate Schlenk flask from the corresponding ligand (1 equiv.), dissolved in THF (30 mL), with n-butyllithium (2.6 M in hexanes, 2.1 equiv.) at $-78 \, ^\circ\text{C}$ for 1 h. Following the addition of the bismuth compound to the dilithiated ligand, the reaction was stirred overnight, slowly warming to room temperature. The reaction was quenched by the addition of brine (20 mL), extracted with EtOAc (40 mL), and re-extracted with CH$_2$Cl$_2$ ($2 \times 50$ mL). The combined organics were dried over Na$_2$SO$_4$, filtered and concentrated to give a thick yellow residue. The crude material was purified by flash chromatography (silica gel, hexanes/EtOAc) to give the corresponding phenylbismine as a white solid.
2-Methoxy-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (9e): Following the general procedure, using 2.2 g of L5 as ligand, 9e was obtained in 53% yield as a white solid (Eluent: hexanes/EtOAc = 4/1).

\[ \text{1H NMR} - (300 \text{ MHz, CDCl}_3): \delta 8.36-8.30 (m, 2H), 7.85 (dd, J = 7.1, 1.7 Hz, 1H), 7.86-7.80 (m, 2H), 7.46-7.29 (m, 6H), 6.85 (dd, J = 8.6, 2.4 Hz, 1H), 3.68 (s, 3H). \]

\[ \text{13C NMR} - (75 \text{ MHz, CDCl}_3): \delta 166.2, 163.6, 160.5, 158.4, 142.7, 138.8, 137.6, 133.3, 133.2, 131.0, 129.1, 128.7, 128.2, 126.7, 123.5, 112.9, 55.6. \]

HRMS (ESI, m/z): calc’d for C_{19}H_{15}BiSO_3Na^+ [M+Na]^+ 555.04379; found 555.04379.

m.p. (°C): 144.7 – 145.9.

10-Phenyl-2-(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (9f): Following the general procedure using 1.1 g of L6 as ligand, 9f was obtained in 50% yield as a white solid (Eluent: hexanes/EtOAc = 4/1).

\[ \text{1H NMR} - (300 \text{ MHz, CDCl}_3): \delta 8.47 (d, J = 8.2 \text{ Hz, 1H}), 8.40 (dd, J = 7.4, 1.2 \text{ Hz, 1H}), 8.09 (s, 1H), 7.77 (dd, J = 7.1, 1.5 \text{ Hz, 1H}), 7.76 (m, 2H), 7.68 (dd, J = 8.1, 1.8 \text{ Hz, 1H}), 7.50-7.36 (m, 5H). \]

\[ \text{13C NMR} - (75 \text{ MHz, CDCl}_3): \delta 166.6, 166.5, 159.6, 145.5, 141.1, 138.7, 137.8, 134.8 (q, J = 32.6 \text{ Hz}), 134.5 (q, J = 3.6 \text{ Hz}), 134.0, 131.3, 129.2, 128.6, 127.8, 127.2, 135.5 (q, J = 3.6 \text{ Hz}), 123.3 (q, J = 272.9 \text{ Hz}). \]

\[ \text{19F NMR} - (282 \text{ MHz, CDCl}_3): \delta -62.9 (s, 3F). \]

HRMS (ESI, m/z): calc’d for C_{19}H_{12}BiF_3SO_2Na^+ [M+Na]^+ 593.0206; found 593.0204.

m.p. (°C): 173.0–173.9.
10-Phenyl-2,8-bis(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (6): Following the general procedure, using 2.2 g of L7 as ligand, 6 was obtained in 22% yield as white solid (Eluent: hexanes/EtOAc = 4/1).

$^1$H NMR - (300 MHz, CDCl$_3$): $\delta$ 8.48 (d, $J = 8.0$ Hz, 2H), 8.12 (s, 2H), 7.76 (d, $J = 7.9$, 1.6 Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.54-7.41 (m, 3H).

$^{13}$C NMR - (101 MHz, CDCl$_3$): $\delta$ 167.2, 160.6, 144.7, 138.6, 135.4 (q, $J = 32.7$ Hz), 134.7 (q, $J = 3.7$ Hz), 131.7, 129.6, 127.7, 125.8 (q, $J = 3.8$ Hz), 123.2 (q, $J = 272.3$ Hz).

$^{19}$F NMR - (282 MHz, CDCl$_3$): $\delta$ -63.0 (s, 3F).

HRMS (ESI, m/z): calc’d for C$_{20}$H$_{11}$BiF$_6$SO$_2$Na$^+$ [M+Na]$^+$ 661.0080; found 661.0076.

m.p. (°C): 81.1 – 82.6.
3.2 Synthesis of bismine triflates

Bismine triflates were synthesized following a previously reported method.\textsuperscript{10}

\[
\begin{align*}
\text{Phenylbismine (1.0 equiv.)} & \text{ and trifluoromethanesulfonic acid (1.1 equiv.)} \\
\text{were mixed with CH}_2\text{Cl}_2 & \text{ and stirred for 1 h at room temperature.} \\
\text{Then, the solvent was removed under vacuum, and the remaining solid} & \text{ was washed with a CH}_2\text{Cl}_2/pentane (1:5) solution.} \\
\text{The white solid was dried under vacuum for 1 h.}
\end{align*}
\]

5,5-Dioxido-10H-dibenzo[b,e][1,4]thiabismin-10-yl trifluoromethanesulfonate (4a):

Following the general procedure, using 126 mg of 6, 4a was obtained in 91% yield as a white solid. Characterization was consistent with the previously reported data for this compound.\textsuperscript{10}

\[\text{1H NMR - (300 MHz, CDCl}_3\text{): } \delta 9.00 (\text{dd}, J = 7.6, 1.1 \text{ Hz}, 2H), 8.47 (\text{dd}, J = 7.7, 1.1 \text{ Hz}, 2H), 7.92 (\text{td}, J = 7.6, 1.2 \text{ Hz}, 2H), 7.56 (\text{td}, J = 7.6, 1.1 \text{ Hz}, 2H).\]

\[\text{13C NMR - (75 MHz, CDCl}_3\text{): } \delta 191.4, 139.0, 137.1, 135.3, 130.2, 129.6, 118.9 (\text{q}, J = 320.7 \text{ Hz}).\]

\[\text{19F NMR - (282 MHz, CDCl}_3\text{): } \delta 76.9 (\text{s}, 3F).\]

\[\text{HRMS (ESI, m/z): calc’d for C}_{13}\text{H}_8\text{BiF}_5\text{SO}_5\text{Na}^+ [M+Na]^+ 596.9461; found 596.9463.}\]
5,5-Dioxido-2-(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismen-10-yl

trifluoromethanesulfonate (4b): Following the general procedure starting from 114 mg of 9f, 4b was obtained in 94% yield as white solid.

$^1$H NMR - (300 MHz, CD$_3$CN): $\delta$ 9.35 (s, 1H), 9.13 (d, $J = 7.5$ Hz, 1H), 8.59 (d, $J = 7.5$ Hz, 1H), 8.53 (dd, $J = 7.7, 0.8$ Hz, 1H), 8.01 (td, $J = 7.7, 1.1$ Hz, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 7.63 (td, $J = 7.7, 1.2$ Hz, 1H)

$^{13}$C NMR - (75 MHz, CD$_3$CN): $\delta$ 201.2, 200.9, 144.8, 139.9, 138.4, 138.1 (q, $J = 32.6$ Hz), 136.5, 133.2 (q, $J = 3.8$ Hz), 131.3, 131.0, 130.4, 127.4 (q, $J = 3.8$ Hz), 124.8 (q, $J = 272.8$ Hz), 121.1 (q, $J = 242.7$ Hz)

$^{19}$F NMR - (282 MHz, CD$_3$CN): $\delta$ -63.5 (s, 3F), -78.6 (s, 3F).

HRMS (ESI, m/z): calc’d for C$_{14}$H$_7$BiO$_5$S$_2$F$_6$ [M]$^+$ 641.9443; found 641.9453.

m.p. (°C): 198.9 – 200.0.

5,5-Dioxido-2,8-bis(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismen-10-yl

trifluoromethanesulfonate (4c): Following the general procedure, using 120 mg of 6, 4a was obtained in 98% yield as white solid.

$^1$H NMR - (300 MHz, CD$_3$CN): $\delta$ 9.40 (s, 2H), 8.63 (d, $J = 8.1$ Hz, 2H), 7.91 (d, $J = 8.1$ Hz, 2H).

$^{13}$C NMR - (75 MHz, CD$_3$CN): $\delta$ 203.4, 144.2, 138.4 (q, $J = 32.7$ Hz), 133.5 (q, $J = 3.7$ Hz), 131.6, 127.5 (q, $J = 3.7$ Hz), 125.1 (q, $J = 272.7$ Hz), 121.1 (q, $J = 242.7$ Hz).

$^{19}$F NMR - (282 MHz, CD$_3$CN): $\delta$ -63.6 (s, 6F), 78.8 (s, 3F).

HRMS (ESI, m/z): calc’d for C$_{15}$H$_6$BiF$_9$S$_2$O$_3$Na$^+$ [M+Na]$^+$ 732.9205; found 732.9209.

m.p. (°C): 235.0 – 235.9.
3.3 Synthesis of bismine nonaflate 4d

Bismine nonaflate 4d was synthesized following the same method utilized for the synthesis of bismine triflates (see section 3.2). Phenylbismine 6 (191 mg, 0.3 mmol, 1.0 equiv.) was mixed with CH$_2$Cl$_2$ (2 mL) and nonafluorobutane-1-sulfonic acid (55 µL, 1.1 equiv.) and the reaction was stirred for 1h at room temperature. Then, the solvent was removed, and the remaining solid was washed with a CH$_2$Cl$_2$/pentane (1:5) solution. The white solid was dried under vacuum for 1 h, obtaining 235 mg of the title compound (91%).

$^1$H NMR - (300 MHz, CDCl$_3$): $\delta$ 9.34 (s, 2H), 8.61 (d, $J = 8.1$ Hz, 2H), 7.86 (dd, $J = 7.9$, 1.7 Hz, 2H).

$^{13}$C{$^{19}$F} NMR - (75 MHz, CDCl$_3$): $\delta$ 194.9, 142.0, 139.1, 132.9, 130.8, 127.2, 123.4, 117.3, 113.4, 110.4, 108.7.

$^{19}$F NMR - (282 MHz, CDCl$_3$): $\delta$ -63.3 (s, 6F), -80.9 (s, 3F), -112.5– -112.6 (m, 2F), -121.2– -121.3 (m, 2F), -126.0– -126.1 (m, 2F).

HRMS (ESI, m/z): calc’d for C$_{18}$H$_6$BiF$_{15}$S$_2$O$_5$Na$^+$ [M+Na]$^+$ 882.9113; found 882.9110.

m.p. (°C): 178.5 – 179.8.
4. Stoichiometric studies

4.1 Optimization of ligand backbone

The corresponding phenylbismine (0.025 mmol), 1-fluoro-2,6-pyridinium tetrafluoroborate (7.6 mg, 0.03 mmol) and sodium triflate (21.5 mg, 0.125 mmol) were mixed with CDCl$_3$ (1 mL) under an Ar atmosphere and the reaction was stirred for 16 h at 90 °C. Then, 1-fluoro-4-nitrobenzene was added as internal standard (0.025 mmol, addition by weight) and the crude reactions were analyzed by $^{19}$F NMR to determine the yield of aryl triflate.

**Table S1.** Optimization of the ligand backbone for the obtention of phenyl triflate 2a from phenylbismines and 1-fluoro-2,6-pyridinium tetrafluoroborate.

As shown in Table 1, bismine containing CF$_3$ groups furnished 2a in high yields after the oxidation-reductive elimination sequence. Although 9a also generated 2a in good yields, it was partially decomposed after reaction completion, and a significant amount of benzene was detected (>10%). On the other hand, when 6 was oxidized in presence of NaOTf at 90 °C, an excellent yield
of 2a was obtained, together with the corresponding Bi(III)-OTf (4c) and trace amounts of benzene (Figure S3). Similar results were obtained with 9f.

**Figure S3.** $^1$H NMR (top) and $^{19}$F NMR (bottom) analysis of the reaction crude after the oxidation-reductive elimination sequence with 6 using 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (1.0 equiv.) and NaOTf (5.0 equiv.) in CDCl$_3$ at 90 °C.

Based on these results, the corresponding triflates of 9f and 6 (4b and 4c, respectively) were synthesized to be tested in the catalytic reaction, together with the corresponding triflate of 9c (4a) as a control catalyst (see below).
4.2 Transmetallation to 4c

4.2.1 Influence of base and molecular sieves

This experiment corresponds to the data shown in Figure 2A in the manuscript.

In a culture tube, bismine triflate 4c (17.7 mg, 0.025 mmol), phenylboronic acid (1a, 3.1 mg, 0.025 mmol), Na₃PO₄ (8.2 mg, 0.05 mmol) and 20 mg of MS were mixed with anhydrous CDCl₃ under an Ar atmosphere and the reaction was stirred for 3 h at 60 °C. Then, 1,3,5-trimethoxybenzene was added as internal standard and the crude reactions were analyzed by ¹H NMR to determine the yield of 6 (see Table S2).

Table S2. Transmetalation to 4c with phenylboronic acid 1a. Yield calculated by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard.

| entry | [MS] | [Na₃PO₄] | 6, yield (%) | 3, yield (%) |
|-------|------|----------|--------------|--------------|
| 1     | 4Å MS| 2.0 equiv.| 82           | 14           |
| 2     | 4Å MS| -        | 65           | 21           |
| 3     | 5Å MS| 2.0 equiv.| 86           | 9            |
| 4     | 5Å MS| -        | 62           | 15           |
| 5     | -    | 2.0 equiv.| 21           | 73           |
| 6     | -    | -        | traces       | traces       |
4.2.2 Use of other phenylboron compounds

In a culture tube, bismine triflate $4c$ (17.7 mg, 0.025 mmol), phenylboronic acid derivative (0.025 mmol), Na$_3$PO$_4$ (8.2 mg, 0.05 mmol) and 20 mg of 5Å MS were mixed with anhydrous CDCl$_3$ under an Ar atmosphere and the reaction was stirred for 3 h at 60 °C. Then, 1,3,5-trimethoxybenzene was added as internal standard and the crude reactions were analyzed by $^1$H NMR to determine the yield of $6$ (see Table S3).

**Table S3.** Transmetalation to $4c$ with a variety of phenylboron compounds.

| Compound | Yield |
|----------|-------|
| $1a$    | 86%   |
| $10$    | 90%   |
| $11$    | 34%   |
| $12$    | 57%   |
| $13$    | <5%   |
4.3 Oxidation with XeF₂ and reductive elimination in presence of TMSOTf

4.3.1 One-pot oxidation-reductive elimination sequence

*This experiment corresponds to the data shown in Figure 2B in the manuscript.*

First, we performed a one-pot protocol consisting in a first oxidation with XeF₂ at 0 °C, followed by the addition of 1.0 equiv. of TMSOTf.

In a 10 mL Schlenk flask, phenyl bismine 6 (19.2 mg, 0.03 mmol) was mixed with anhydrous CDCl₃ (1 mL) under an Ar atmosphere and the reaction was cooled to 0 °C. Then, XeF₂ (5.1 mg, 0.03 mmol) were added at once as a solid, and the mixture was stirred for 1 h at 0 °C. Then, the reaction was warmed up to room temperature (ca. 22 °C) and TMSOTf was added with a micro syringe (5.4 μL, 0.03 mmol). After stirring for 5 min, 1-fluoro-4-nitrobenzene was added and the crude mixture was analyzed by ¹⁹F NMR. Full conversion to 2a was observed (>95%), together with the corresponding Me₃SiF byproduct (see Figure S4).
Figure S4. $^{19}$F NMR analysis of the reaction crude after the one-pot oxidation-reductive elimination sequence using XeF$_2$ (1.0 equiv.) and TMSOTf (1.0 equiv.) in CDCl$_3$ at 90 °C.
4.3.2 Synthesis and isolation of 14

The synthesis and isolation of the Bi(V) difluoride species 14 was attempted following the protocol described below.

In a 10 mL Schlenk flask, phenyl bismine 6 (128 mg, 0.2 mmol) was mixed with anhydrous CHCl₃ (5 mL) under an Ar atmosphere and the reaction was cooled to 0 °C. Then, XeF₂ (34 mg, 0.2 mmol) was added at once as a solid, and the mixture was stirred for 1 h at 0 °C. Then, pentane was added to the suspension (3 mL), and the solid was separated by decantation. The pale-yellow solid was washed with pentane (2 × 2mL), and dried under vacuum for a period of 2 h. The title compound was obtained in >95% yield.

¹H NMR - (500 MHz, CDCl₃): δ 8.68 (s, 2H), 8.40 (d, J = 8.1 Hz, 2H), 8.08 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 7.3 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H).

¹⁹F NMR - (471 MHz, CDCl₃): δ -63.0 (s, 6F), -107.7 (bs, 2F).

HRMS (ESI, m/z): calc’d for C₂₀H₁₁S₁F₉Bi⁺ [M+F]⁺ 695.0135; found 695.0144.

Due to the low solubility of 14 and the appearance of broad bands, ¹³C NMR could not be obtained.
Figure S5. $^1$H NMR of 14 in CDCl$_3$ at room temperature.

Figure S6. $^1$H NMR of 14 in CDCl$_3$ at room temperature.
4.3.3 Reductive elimination from 7a – HRMS studies

*This experiment corresponds to the data shown in Figure 2B in the manuscript.*

In a 10 mL Schlenk flask, difluoro bismine 14 (20.3 mg, 0.03 mmol) was mixed with anhydrous CDCl₃ (1 mL) under an Ar atmosphere and the reaction was cooled to -41 °C in a MeCN/N₂ cooling bath. Then TMSOTf (5.4 μL, 0.03 mmol) was added and the reaction was stirred for 15 min. Afterwards, an aliquot of the reaction was analyzed by HRMS (See Figure S7). 7a was detected as a sodium adduct by ESI-HRMS analysis (C₂₁H₁₁F₁₀O₅S₂BiNa⁺, *expt. m/z* = 828.9576; *calcd. m/z* = 828.9584; Figures S7 and S8). The crude reaction was warmed to room temperature (ca. 22 °C) and stirred for 5 min. Then, 1-fluoro-4-nitrobenzene was added and the crude mixture was analyzed by ¹⁹F NMR. Full conversion to 2a was observed (>95%), with traces of some byproducts.
**Figure S7.** High-Resolution Mass Spectrum of the crude reaction of 14 and TMSOTf (top), showing a peak corresponding to \([7a+Na]^+\); theoretical \(m/z\) of the peak corresponding to \([7a+Na]^+\) (bottom).

**Figure S8.** Detection of \([7a+Na]^+\) by ESI-HRMS analysis of the reaction of 14 with TMSOTf.
When the reaction was performed with TIPSOTf (8.1 µL, 0.03 mmol) instead of TMSOTf, 7a was also detected as a sodium adduct by ESI-HRMS analysis (C_{21}H_{11}F_{10}O_{5}S_{2}BiNa^+, \text{expt. } m/z = 828.9577; \text{calcd. } m/z = 828.9584; \text{Figures S9 and S10}).

**Figure S9.** High-Resolution Mass Spectrum of the crude reaction of 14 and TIPSOTf (up), showing a peak corresponding to [7a+Na]^+; theoretical m/z of the peak corresponding to [7a+Na]^+ (bottom).
Figure S10. Detection of [7a+Na]⁺ by ESI-HRMS analysis of the reaction of 14 with TIPSOTf.
4.4 Oxidation-reductive elimination sequence

This experiment corresponds to the data shown in Figure 2B in the manuscript.

In a 10 mL Schlenk flask, phenyl bismine 6 (15.9 mg, 0.025 mmol), N-fluoro-2,6-dichloropyridinium tetrafluoroborate (6.3 mg, 0.025 mmol) and sodium triflate (4.3 mg, 0.025 mmol) were mixed with anhydrous CHCl₃ (1 mL) under an Ar atmosphere and the reaction was stirred at 60 °C for 1 h. Then, 1-fluoro-4-nitrobenzene was added and the crude mixture was analyzed by ¹⁹F NMR, showing 92% yield of phenyl triflate 2a.

When the reaction was performed with N-fluoro-2,6-dichloropyridinium trifluoromethanesulfonate ([Cl₂pyrF]OTf) as oxidant, the yield of 2a decreased substantially. The triflate salt is not fully soluble in CDCl₃ at 60 °C and after 1 h stirring at this temperature, it became a sticky insoluble solid.
5. Catalytic studies

5.1 Optimization for the Bi-catalyzed coupling of arylboronic acids and NaOTf

**General Procedure:** A culture tube equipped with a stir bar was charged with phenylboronic acid (3.1 mg, 0.025 mmol). A teflon cap was fitted, and the tube was evacuated and refilled with Ar (3 cycles). The tube was transferred to a glove box, *bismine catalyst* (X mol%), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (7.0 mg, 1.1 equiv.), NaOTf (4.7 mg, 1.1 equiv.), *base* (Y equiv.) and additive (Z mg) were added. The tube was removed from the glove box and subjected to a positive pressure of Ar. CDCl₃ (0.5 mL) was added and the reaction was then stirred 16 h at the indicated temperature. Then, the yield was calculated by ¹⁹F NMR using 1-fluoro-4-nitrobenzene as internal standard (addition by weight).
Table S4. Optimization of reaction conditions for the Bi-catalyzed formation of phenyl triflate 2a. Yields calculated by $^{19}$F NMR using 1-flouro-4-nitrobenzene as internal standard.

![Chemical Structure]

| entry | base (Y equiv.) | catalyst (X mol%) | Additive (Z mg) | T (°C) | 2a, yield (%) | 3, yield (%)<sup>a</sup> |
|-------|----------------|-------------------|-----------------|--------|---------------|-----------------|
| 1     | K$_2$CO$_3$ (2) | 4c (10)           | -               | 60     | 31            | 5               |
| 2<sup>b</sup> | K$_2$CO$_3$ (2) | 4c (10)           | -               | 60     | 4             | <5              |
| 3     | NaOAc (2)       | 4c (10)           | -               | 60     | 15            | <5              |
| 4     | NaO'Bu (2)      | 4c (10)           | -               | 60     | <5            | <5              |
| 5     | KOTMS (2)       | 4c (10)           | -               | 60     | <5            | <5              |
| 6     | LiOMe (2)       | 4c (10)           | -               | 60     | 15            | <5              |
| 7     | CsF (2)         | 4c (10)           | -               | 60     | <5            | 80              |
| 8     | NaF (2)         | 4c (10)           | -               | 60     | 31            | 60              |
| 9     | -               | 4c (10)           | -               | 60     | 12            | <5              |
| 10    | K$_2$CO$_3$ (2) | 4a (10)           | -               | 60     | 6             | <5              |
| 11    | K$_2$CO$_3$ (2) | 4b (10)           | -               | 60     | 11            | <5              |
| 12    | K$_2$CO$_3$ (2) | 4c (10)           | 4Å MS (20)      | 60     | 54            | 5               |
| 13    | NaF (2)         | 4c (10)           | 4Å MS (20)      | 60     | 84            | 15              |
| 14    | Na$_2$CO$_3$ (2)| 4c (10)           | 4Å MS (20)      | 60     | 64            | <5              |
| 15    | NaHCO$_3$ (2)   | 4c (10)           | 4Å MS (20)      | 60     | 86            | 13              |
| 16    | Na$_3$PO$_4$ (2)| 4c (10)           | 4Å MS (20)      | 60     | 93            | 6               |
| 17    | -               | 4c (10)           | 4Å MS (20)      | 60     | 71            | 18              |
| 18    | Na$_3$PO$_4$ (4)| 4c (10)           | 4Å MS (20)      | 60     | >95           | <5              |
| 19    | Na$_3$PO$_4$ (2)| 4c (10)           | 5Å MS (10)      | 60     | >95           | <5              |
| 20    | Na$_3$PO$_4$ (2)| 4c (10)           | 5Å MS (5)       | 60     | 63            | <5              |
| 21    | Na$_3$PO$_4$ (2)| 4c (5)            | 5Å MS (10)      | 60     | 21            | <5              |
| 22    | Na$_3$PO$_4$ (2)| 4c (2.5)          | 5Å MS (10)      | 60     | <5            | <5              |
| 23    | Na$_3$PO$_4$ (2)| 4c (10)           | 5Å MS (10)      | 40     | 46            | <5              |
| 24    | Na$_3$PO$_4$ (2)| -                 | 5Å MS (10)      | 60     | <5            | <5              |
| 25    | Na$_3$PO$_4$ (2)| BiPh$_3$ (10)     | 5Å MS (10)      | 60     | <5            | <5              |
| 26    | Na$_3$PO$_4$ (2)| BiCl$_3$ (10)     | 5Å MS (10)      | 60     | <5            | <5              |
| 27    | Na$_3$PO$_4$ (2)| L7 (10)           | 5Å MS (10)      | 60     | <5            | <5              |

<sup>a</sup> $^1$H NMR yield using 1-flouro-4-nitrobenzene as internal standard; <sup>b</sup> Reaction run with PhBpin (11) instead of PhB(OH)$_2$ (1a).
Figure S11. **Left**: Influence of the amount of 5 Å MS. Reaction run in presence of 1a (0.025 mmol), [Cl$_2$pyrF]BF$_4$ (0.03 mmol), NaOTf (0.03 mmol), Na$_3$PO$_4$ (0.06 mmol), 5 Å MS (x mg) in CDCl$_3$ (0.5 mL) at 60 °C for 16 h. **Right**: Influence of the amount of NaOTf. Reaction run in presence of 1a (0.025 mmol), [Cl$_2$pyrF]BF$_4$ (0.03 mmol), NaOTf (x mmol), Na$_3$PO$_4$ (0.06 mmol), 5 Å MS (10 mg) in CDCl$_3$ (0.5 mL) at 60 °C for 16 h.

Figure S12. Yield of 2a at different time intervals. Reaction run in presence of 1a (0.025 mmol), [Cl$_2$pyrF]BF$_4$ (0.03 mmol), NaOTf (1.1 mmol), Na$_3$PO$_4$ (0.06 mmol), 5 Å MS (10 mg) in CDCl$_3$ (0.5 mL) at 60 °C for x h.
Figure S13. $^1$H NMR (top) and $^{19}$F NMR (bottom) analysis of the reaction crude after the Bi-catalyzed oxidative coupling of phenylboronic acid and sodium triflate with the reaction conditions described in Table S4, entry 19.
5.2 Scope of Bi-catalyzed coupling of arylboronic acids and NaOTf

5.2.1 General procedure for the NMR scale synthesis of aryl triflates

A culture tube equipped with a stirring bar was charged with aryl boronic acid (0.025 mmol, 1.0 equiv.), bismine 4c (1.78 mg, 0.0025 mmol, 0.1 equiv.), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (6.98 mg, 0.0275 mmol, 1.1 equiv.), sodium triflate (4.73 mg, 0.0275 mmol, 1.1 equiv.), sodium phosphate (8.20 mg, 0.050 mmol, 2.0 equiv.), 5Å molecular sieves (10 mg) and dry CDCl₃ (1 mL) under an Ar atmosphere and stirred at 60 ºC for 16 h. After this time, the yield was calculated by ¹⁹F NMR using 1-fluoro-4-nitrobenzene (added by weight) as internal standard. Yield was determined by integration of the CF₃ group on the Ar–OTf moiety at a chemical shift ca. δ = 73.0 ppm.
Table S5. Scope of the Bi-catalyzed coupling of arylboronic acids and NaOTf. Yields calculated by $^{19}$F NMR using 1-fluoro-4-nitrobenzene as internal standard.

![Chemical structures and yields](image)

- Reaction run at 90 °C with 4 equiv. of Na$_3$PO$_4$ and 20 mg of 5Å MS.
- Reaction run with 2.0 equiv. NaF and 40 mg of 5Å MS.

Spectroscopic data for compounds 2a-r was confirmed by isolation of the corresponding aryl triflates. Spectroscopic data for compounds 2s-w was compared with previously reported characterization data.\textsuperscript{11-13}
5.2.2 General procedure for synthesis of aryl triflates

A culture tube equipped with a stirring bar was charged with aryl boronic acid (0.30 mmol, 1.0 equiv.), bismine 4c (21.3 mg, 0.03 mmol, 0.1 equiv.), 2,6-dichloro-1-fluoropyridinium tetrafluoroborate (83.8 mg, 0.33 mmol, 1.1 equiv.), sodium triflate (56.8 mg, 0.33 mmol, 1.1 equiv.), sodium phosphate (98.4 mg, 0.60 mmol, 2.0 equiv.), activated 5Å molecular sieves (120 mg) and dry CHCl₃ (4 mL) under an Ar atmosphere and stirred at 60 ºC for 16 h. After filtration, the crude material was purified by preparative TLC (hexanes/CH₂Cl₂) to give the corresponding aryl triflate as colorless liquid or a white solid.
Phenyl trifluoromethanesulfonate (2a): Following the general procedure, using 0.30 mmol of respective aryl boronic acid, 2a was obtained in 90% yield as colorless liquid (Eluent: hexanes).

\[
\text{H NMR - (300 MHz, CDCl}_3\text{): } \delta 7.49-7.34 (m, 3H), 7.31-7.24 (m, 2H).
\]

\[
\text{C NMR - (75 MHz, CDCl}_3\text{): } \delta 149.8, 130.4, 128.6, 121.5, 118.9 (q, J = 320.1 Hz).
\]

\[
\text{F NMR - (282 MHz, CDCl}_3\text{): } \delta -73.0 (s, 3F).
\]

HRMS (EI, m/z): calc'd for C\text{7}H\text{5}F\text{3}O\text{3}S [M]^+ 225.9906; found 225.9906.

\[
\text{p-Tolyl trifluoromethanesulfonate (2b): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2b was obtained in 81% yield as colorless liquid (Eluent: hexanes)}
\]

\[
\text{H NMR - (300 MHz, CDCl}_3\text{): } \delta 7.23-7.18 (m, 2H), 7.16-7.10 (m, 2H), 2.34 (s, 3H).
\]

\[
\text{C NMR - (75 MHz, CDCl}_3\text{): } \delta 147.8, 138.7, 130.8, 121.1, 119.0 (q, J = 320.3 Hz), 20.9.
\]

\[
\text{F NMR - (282 MHz, CDCl}_3\text{): } \delta -73.1 (s, 3F).
\]

HRMS (EI, m/z): calc’d for C\text{8}H\text{7}F\text{3}O\text{3}S [M]^+ 240.0063; found 240.0065.

\[
\text{o-Tolyl trifluoromethanesulfonate (2c): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2c was obtained in 93% yield as colorless liquid (Eluent: hexanes)}
\]

\[
\text{H NMR - (300 MHz, CDCl}_3\text{): } \delta 7.33-7.20 (m, 4H), 2.38 (s, 3H).
\]

\[
\text{C NMR - (75 MHz, CDCl}_3\text{): } \delta 148.7, 132.3, 131.0, 128.4, 127.8 121.4, 118.8 (q, J = 320.1 Hz), 16.4.
\]

\[
\text{F NMR - (282 MHz, CDCl}_3\text{): } \delta -74.0 (s, 3F).
\]

HRMS (EI, m/z): calc’d for C\text{8}H\text{7}F\text{3}O\text{3}S [M]^+ 240.0063; found 240.0066.
2-Isopropylphenyl trifluoromethanesulfonate (2d): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2d was obtained in 87% yield as colorless liquid (Eluent: hexanes).

**1H NMR** (300 MHz, CDCl3): δ 7.43-7.21 (m, 4H), 3.30 (m, J = 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 6H).

**13C NMR** (75 MHz, CDCl3): δ 147.3, 141.4, 128.7, 128.0, 127.6, 121.3, 118.5 (q, J = 320.2 Hz), 27.3, 23.3.

**19F NMR** (282 MHz, CDCl3): δ -74.0 (s, 3F).

**HRMS (EI, m/z):** calc’d for C10H11F3O3S [M]+ 268.0376; found 268.0376.

2,6-Dimethylphenyl trifluoromethanesulfonate (2e): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2e was obtained in 70% yield as colorless liquid (Eluent: hexanes).

**1H NMR** (300 MHz, CDCl3): δ 7.18-7.07 (m, 3H), 2.40 (s, 6H).

**13C NMR** (75 MHz, CDCl3): δ 147.1, 131.7, 130.0, 128.1, 118.8 (q, J = 319.9 Hz), 17.2.

**19F NMR** (282 MHz, CDCl3): δ -73.6 (s, 3F).

**HRMS (EI, m/z):** calc’d for C9H9F3O3S [M]+ 254.0219; found 254.0219.

5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl trifluoromethanesulfonate (2f): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2f was obtained in 85% yield as colorless liquid (Eluent: hexanes).

**1H NMR** (300 MHz, CDCl3): δ 7.35 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 2.7 Hz, 1H), 7.01 (dd, J = 8.8, 2.7 Hz, 1H), 1.70 (s, 4H), 1.28 (s, 12H).

**13C NMR** (75 MHz, CDCl3): δ 147.9, 147.8, 145.5 128.6, 119.1, 119.0 (q, J = 320.4 Hz), 118.4, 34.9, 34.9, 34.8, 34.4, 31.9, 31.8.

**19F NMR** (282 MHz, CDCl3): δ -73.0 (s, 3F).

**HRMS (EI, m/z):** calc’d for C15H10F3O3S [M]+ 336.1002; found 336.1002.
4-(Tert-butyl)phenyl trifluoromethanesulfonate (2g): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2g was obtained in 93% yield as colorless liquid (Eluent: hexanes).

\[ \text{1H NMR - (300 MHz, CDCl}_3\text{)}: \delta 7.48-7.42 \text{ (m, 2H), 7.22-7.16 (m, 2H), 1.33 (s, 9H).} \]

\[ \text{13C NMR - (75 MHz, CDCl}_3\text{)}: \delta 151.8, 147.6, 127.3, 120.8, 118.9 (q, J = 320.6 Hz), 34.9, 31.4. \]

\[ \text{19F NMR - (282 MHz, CDCl}_3\text{)}: \delta -73.0 \text{ (s, 3F).} \]

\[ \text{HRMS (EI, m/z): calc’d for C}_{11}\text{H}_{13}\text{F}_3\text{O}_3\text{S} [M]^+ 282.0532; found 282.0532.} \]

3-Methoxyphenyl trifluoromethanesulfonate (2h): Following the general procedure at 90 °C and using 4.0 equivalents of Na\(_3\)PO\(_4\), 240 mg of dry 5Å molecular sieves and 0.3 mmol of respective aryl boronic acid, 2h was obtained in 51% yield as colorless liquid (Eluent: hexanes/CH\(_2\)Cl\(_2\) 4:1).

\[ \text{1H NMR - (300 MHz, CDCl}_3\text{)}: \delta 7.34 \text{ (t, } J = 8.4 \text{ Hz, 1H), 6.93 (ddd, } J = 8.4, 2.4, 0.9 \text{ Hz, 1H), 6.87 (ddd, } J = 8.4, 2.4, 0.9 \text{ Hz, 1H), 6.81 (t, } J = 2.4 \text{ Hz, 1H), 3.83 (s, 3H).} \]

\[ \text{13C NMR - (75 MHz, CDCl}_3\text{)}: \delta 161.0, 150.4, 130.7, 118.9 (q, J = 320.0 Hz), 114.3, 113.4, 107.6, 55.8. \]

\[ \text{19F NMR - (282 MHz, CDCl}_3\text{)}: \delta -72.9 \text{ (s, 3F).} \]

\[ \text{HRMS (EI, m/z): calc’d for C}_8\text{H}_7\text{F}_3\text{O}_4\text{S} [M]^+ 256.0012; found 256.0013.} \]

4-(Trifluoromethoxy)phenyl trifluoromethanesulfonate (2i): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2i was obtained in 50% yield as colorless liquid (Eluent: hexanes/CH\(_2\)Cl\(_2\) 4:1).

\[ \text{1H NMR - (300 MHz, CDCl}_3\text{)}: \delta 7.36-7.28 \text{ (m, 4H).} \]

\[ \text{13C NMR - (75 MHz, CDCl}_3\text{)}: \delta 148.7 \text{ (q, } J = 2.0 \text{ Hz), 147.5, 123.1, 122.9, 120.5 (q, } J = 258.4 \text{ Hz), 118.9 (q, } J = 320.6 \text{ Hz).} \]

\[ \text{19F NMR - (282 MHz, CDCl}_3\text{)}: \delta -58.3(s, 3F), -72.8 \text{ (s, 3F).} \]

\[ \text{HRMS (EI, m/z): calc’d for C}_8\text{H}_4\text{F}_6\text{O}_4\text{S} [M]^+ 309.9729; found 309.9730.} \]
4-Fluorophenyl trifluoromethanesulfonate (2j): Following the general procedure at 90 °C and using 4.0 equivalents of Na3PO4, 240 mg of dry 5Å molecular sieves and 0.3 mmol of respective aryl boronic acid, 2j was obtained in 60% yield as colorless liquid (Eluent: hexanes).

1H NMR - (300 MHz, CDCl3): δ 7.31-7.23 (m, 2H), 7.19-7.09 (m, 2H).

13C NMR - (75 MHz, CDCl3): δ 161.8 (q, J = 248.8 Hz), 145.4 3 (q, J = 3.93 Hz), 123.3 (d, J = 8.9 Hz), 118.9 (d, J = 320.7 Hz), 117.3 (d, J = 24.3 Hz).

19F NMR - (282 MHz, CDCl3): δ -72.8 (s, 3F), -112.4 (s, 1F).

HRMS (EI, m/z): calc’d for C7H4F4O3S [M]+ 243.9812; found 243.9814.

4-Bromophenyl trifluoromethanesulfonate (2k): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2k was obtained in 49% yield as colorless liquid (Eluent: hexanes/CH2Cl2 4:1).

1H NMR - (300 MHz, CDCl3): δ 7.62-7.55 (m, 2H), 7.20-7.13 (m, 2H).

13C NMR - (75 MHz, CDCl3): δ 148.6, 133.6, 125.2, 122.2, 118.8 (q, J = 320.5 Hz).

19F NMR - (282 MHz, CDCl3): δ -72.7 (s, 3F).

HRMS (EI, m/z): calc’d for C7H4BrF3O3S [M]+ 303.9011; found 303.9013.

2-Bromophenyl trifluoromethanesulfonate (2l): Following the general procedure at 90 °C and using 4.0 equivalents of Na3PO4, 240 mg of dry 5Å molecular sieves and 0.3 mmol of respective aryl boronic acid, 2l was obtained in 61% yield as colorless liquid (Eluent: hexanes/CH2Cl2 4:1).

1H NMR - (300 MHz, CDCl3): δ 7.72-7.66 (m, 1H), 7.43-7.33 (m, 2H), 7.30-7.22 (m, 1H).

13C NMR - (75 MHz, CDCl3): δ 147.2, 134.6, 129.6, 129.2, 123.1, 118.8 (q, J = 320.2 Hz), 116.2.

19F NMR - (282 MHz, CDCl3): δ -73.4 (s, 3F).

HRMS (EI, m/z): calc’d for C7H4BrF3O3S [M]+ 303.9011; found 303.9013.
4-(Trimethylsilyl)phenyl trifluoromethanesulfonate (2m): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2m was obtained in 96% yield as colorless liquid (Eluent: hexanes).

\[^{1}H\text{ NMR}\] - (300 MHz, CDCl\(_3\)): δ 7.62-7.55 (m, 2H), 7.28-7.21 (m, 2H), 0.28 (s, 9H).

\[^{13}C\text{ NMR}\] - (75 MHz, CDCl\(_3\)): δ 150.4, 141.8, 135.4, 120.6, 118.9 (q, \(J = 320.6\) Hz), -1.1.

\[^{19}F\text{ NMR}\] - (282 MHz, CDCl\(_3\)): δ -73.0 (s, 3F).

**HRMS (EI, m/z):** calc’d for C\(_{10}\)H\(_{13}\)F\(_3\)O\(_3\)SSi [M]\(^+\) 298.0301; found 298.0298.

[1,1'-Biphenyl]-4-yl trifluoromethanesulfonate (2n): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2n was obtained in 63% yield as a white solid (Eluent: hexanes/CH\(_2\)Cl\(_2\) 4:1).

\[^{1}H\text{ NMR}\] - (300 MHz, CDCl\(_3\)): δ 7.69-7.62 (m, 2H), 7.60-7.54 (m, 2H), 7.52-7.39 (m, 3H), 7.39-7.33 (m, 2H).

\[^{13}C\text{ NMR}\] - (75 MHz, CDCl\(_3\)): δ 149.1, 141.8, 139.4, 129.1, 129.0, 128.2, 127.3, 121.8, 119.0 (q, \(J = 320.5\) Hz).

\[^{19}F\text{ NMR}\] - (282 MHz, CDCl\(_3\)): δ -72.8 (s, 3F).

**HRMS (EI, m/z):** calc’d for C\(_{13}\)H\(_{9}\)F\(_3\)O\(_3\)S [M]\(^+\) 302.0219; found 302.0222.

Ethyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate (2o): Following the general procedure at 90 ºC and using 4.0 equivalents of Na\(_3\)PO\(_4\), 240 mg of dry 5Å molecular sieves and 0.3 mmol of respective aryl boronic acid, 2o was obtained in 42% yield as colorless liquid (Eluent: hexanes/CH\(_2\)Cl\(_2\) 3:1).

\[^{1}H\text{ NMR}\] - (300 MHz, CDCl\(_3\)): δ 8.18-8.11 (m, 2H), 7.38-7.31 (m, 2H), 4.40 (q, \(J = 7.1\) Hz, 2H), 1.40 (t, \(J = 7.1\) Hz, 3H).

\[^{13}C\text{ NMR}\] - (75 MHz, CDCl\(_3\)): δ 165.1, 152.6, 132.0, 130.9, 121.5, 118.9 (q, \(J = 320.7\) Hz), 61.7, 14.4.

\[^{19}F\text{ NMR}\] - (282 MHz, CDCl\(_3\)): δ -72.8 (s, 3F).

**HRMS (EI, m/z):** calc’d for C\(_{10}\)H\(_{9}\)F\(_3\)O\(_3\)S [M]\(^+\) 298.0117; found 298.0116.
4-(Phenylethynyl)phenyl trifluoromethanesulfonate (2p): Following the general procedure at 90 °C and using 4.0 equivalents of Na3PO4, 240 mg of dry 5Å molecular sieves and 0.3 mmol of respective aryl boronic acid, 2p was obtained in 86% yield as white solid (Eluent: hexanes/CH2Cl2 3:1).

1H NMR - (300 MHz, CDCl3): δ 7.63-7.56 (m, 2H), 7.56-7.48 (m, 2H), 7.40-7.32 (m, 3H), 7.29-7.21 (m, 2H).

13C NMR - (75 MHz, CDCl3): δ 149.1, 133.5, 131.8, 128.9, 128.6, 124.2, 122.7, 121.6, 118.9 (q, J = 320.8 Hz), 91.4, 87.5.

19F NMR - (282 MHz, CDCl3): δ -72.8 (s, 3F).

HRMS (EI, m/z): calc’d for C15H9F3O3S [M]+ 326.0219; found 326.0225.

4-Vinylphenyl trifluoromethanesulfonate (2q): Following the general procedure at 90 °C and using 4.0 equivalents of Na3PO4, 240 mg of dry 5Å molecular sieves and 0.3 mmol of respective aryl boronic acid, 2q was obtained in 78% yield as colorless liquid (Eluent: hexanes).

1H NMR - (300 MHz, CDCl3): δ 7.50-7.41 (m, 2H), 7.27-7.18 (m, 2H), 6.70 (dd, J = 17.6, 10.8 Hz, 1H), 5.76 (dd, J = 17.6, 0.7 Hz, 1H), 5.34 (dd, J = 10.8, 0.7 Hz, 1H).

13C NMR - (75 MHz, CDCl3): δ 149.0, 138.1, 135.2, 128.0, 121.6, 118.7 (q, J = 320.5 Hz), 116.1.

19F NMR - (282 MHz, CDCl3): δ -72.8 (s, 3F).

HRMS (EI, m/z): calc’d for C9H7F3O3S [M]+ 252.0063; found 252.0064.

9,9-Dimethyl-9H-fluoren-2-yl trifluoromethanesulfonate (2r): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 2r was obtained in 38% yields as colorless liquid (Eluent: hexanes).

1H NMR - (300 MHz, CDCl3): δ 7.76-7.66 (m, 2H), 7.47-7.40 (m, 1H), 7.39-7.32 (m, 2H), 7.32-7.28 (m, 1H), 7.26-7.19 (m, 1H), 1.49 (s, 6H).

13C NMR - (75 MHz, CDCl3): δ 156.1, 153.9, 149.0, 139.6, 137.5, 128.2, 127.5, 122.9, 121.2, 120.5, 120.3, 119.0 (q, J = 320.9 Hz), 116.2, 47.5, 27.0.

19F NMR - (282 MHz, CDCl3): δ -72.8 (s, 3F).

HRMS (EI, m/z): calc’d for C16H13F3O3S [M]+ 342.0532; found 342.0531.
5.3 Optimization for the Bi-catalyzed coupling of arylboronic acids and KONf

General Procedure: A culture tube equipped with a stir bar was charged with phenylboronic acid (3.1 mg, 0.025 mmol). A teflon cap was fitted, and the tube was evacuated and refilled with Ar (3 cycles). The tube was transferred to a glove box, *bismine catalyst* (X mol%), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (7.0 mg, 1.1 equiv.), KONf (9.3 mg, 1.1 equiv.), Na3PO4 (Y equiv.) and 5Å molecular sieves (Z mg) were added. The tube was removed from the glove box and subjected to a positive pressure of Ar. CDCl3 (0.5 mL) was added and the reaction was then stirred 16 h at the corresponding temperature. After the indicated time, the yield was calculated by 19F NMR using 1-fluoro-4-nitrobenzene as internal standard (addition by weight).

Table S6. Optimization of reaction conditions for the Bi-catalyzed formation of phenyl nonaflate 5a. Yields calculated by 19F NMR using 1-fluoro-4-nitrobenzene as internal standard.

| entry | Na3PO4 (Y equiv.) | catalyst (X mol%) | 5Å MS (Z mg) | 5a, yield (%) | 3, yield (%)a |
|-------|-------------------|-------------------|--------------|---------------|--------------|
| 1b    | 2                 | 4c (10)           | 10           | 56            | <5           |
| 2     | 2                 | 4d (5)            | 10           | 36            | <5           |
| 3     | 2                 | 4d (10)           | 10           | 83            | <5           |
| 4     | 2                 | 4d (15)           | 10           | >95           | <5           |
| 5c    | 2                 | 4d (10)           | 10           | 86            | <5           |
| 6d    | 2                 | 4d (10)           | 10           | >95           | <5           |
| 7     | 4                 | 4d (10)           | 20           | >95           | <5           |

a 1H NMR yield using 1-fluoro-4-nitrobenzene as internal standard; b Phenyltriflate 2a was also detected in 9% yield. c Reaction run for 24 h. d Reaction run at 80 °C.
5.4 Scope of Bi-catalyzed coupling of arylboronic acids and KONf

5.4.1 General procedure for the NMR scale synthesis of aryl nonaflates

A culture tube equipped with a stir bar was charged with aryl boronic acid (0.025 mmol, 1.0 equiv.), bismine 4d (2.15 mg, 0.0025 mmol, 0.1 equiv.), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (6.98 mg, 0.0275 mmol, 1.1 equiv.), potassium nonaflate (9.30 mg, 0.0275 mmol, 1.1 equiv.), sodium phosphate (16.39 mg, 0.10 mmol, 4.0 equiv.), 5Å molecular sieves (20 mg) and dry CDCl₃ (1 mL) under an Ar atmosphere and stirred at 60 ºC for 16 h. After the indicated time, the yield was calculated by ¹⁹F NMR using 1-fluoro-4-nitrobenzene as internal standard. Yield was determined by integration of the –CF₂– group on the Ar–ONf moiety at a chemical shift ca. δ = -109.0 ppm.

Table S7. Scope of the Bi-catalyzed coupling of arylboronic acids and NaOTf. Yields calculated by ¹⁹F NMR using 1-fluoro-4-nitrobenzene as internal standard.
5.4.2 General procedure for synthesis of aryl nonaflates

A culture tube equipped with a stir bar was charged with aryl boronic acid (0.30 mmol, 1.0 equiv.), bismine 4d (25.8 mg, 0.03 mmol, 0.1 equiv.), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (83.8 mg, 0.33 mmol, 1.1 equiv.), potassium nonaflate (111.6 mg, 0.33 mmol, 1.1 equiv.), sodium phosphate (196.8 mg, 1.20 mmol, 4.0 equiv.), 5Å molecular sieves (240 mg) and dry CHCl₃ (4 mL) under an Ar atmosphere and stirred vigorously at 60 ºC for 16 h. After filtration, the crude material was purified by preparative TLC (hexanes/CH₂Cl₂) to give the corresponding aryl nonaflate as colourless liquid or a white solid.
Phenyl nonafluorobutane-1-sulfonate (5a): Following the general procedure, using 0.30 mmol of respective aryl boronic acid, 5a was obtained in 97% yield as colorless liquid (Eluent: hexanes).

**H NMR** - (500 MHz, CDCl₃): δ 7.49-7.43 (m, 2H), 7.42-7.37 (m, 1H), 7.32-7.27 (m, 2H).

**C {¹⁹F} NMR** - (126 MHz, CDCl₃): δ 150.0, 130.4, 128.5, 121.5, 117.2, 114.9, 110.0, 108.6.

**F NMR** - (471 MHz, CDCl₃): δ -80.7--80.8 (m, 3F), -109.0--109.1 (m, 2F), -120.8--121.0 (m, 2F), -125.8--126.0 (m, 2F).

**HRMS (EI, m/z):** calc’d for C₁₀H₅F₉O₃S [M⁺] 375.9810; found 375.9817.

2-Bromophenyl nonafluorobutane-1-sulfonate (5b): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 5b was obtained in 82% yield as colorless liquid (Eluent: hexanes/CH₂Cl₂ 5:1).

**H NMR** - (500 MHz, CDCl₃): δ 7.69 (dd, J = 8.0, 1.5 Hz, 1H), 7.43-7.34 (m, 2H), 7.28-7.23 (m, 1H).

**C {¹⁹F} NMR** - (126 MHz, CDCl₃): δ 147.4, 134.7, 129.6, 129.2, 123.1, 117.2, 116.4, 114.8, 110.0, 108.6.

**F NMR** - (471 MHz, CDCl₃): δ -80.7--80.8 (m, 3F), -109.1--109.3 (m, 2F), -120.6--120.8 (m, 2F), -125.7--125.9 (m, 2F).

**HRMS (EI, m/z):** calc’d for C₁₀H₄BrF₉O₃S [M⁺] 453.8915; found 453.8918.

-o-Tolyl nonafluorobutane-1-sulfonate (5c): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 5c was obtained in 93% yield as colorless liquid (Eluent: hexanes).

**H NMR** - (500 MHz, CDCl₃): δ 7.32-7.23 (m, 4H), 2.39 (s, 3H).

**C {¹⁹F} NMR** - (126 MHz, CDCl₃): 148.9, 132.4, 131.2, 128.4, 127.8, 121.5, 117.3, 114.6, 110.1, 108.7, 16.6.

**F NMR** - (471 MHz, CDCl₃): δ -80.7--80.8 (m, 3F), -109.8--110.0 (m, 2F), -120.8--120.9 (m, 2F), -125.8--125.9 (m, 2F).

**HRMS (EI, m/z):** calc’d for C₁₁H₇F₉O₃S [M⁺] 389.9967; found 389.9974.
4-(Trimethylsilyl)phenyl nonafluorobutane-1-sulfonate (5d): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 5d was obtained in 96% yield as a colorless liquid (Eluent: hexanes).

$^1$H NMR - (500 MHz, CDCl$_3$): δ 7.60-7.56 (m, 2H), 7.27-7.23 (m, 2H), 0.28 (s, 9H).

$^{13}$C {$^{19}$F} NMR - (126 MHz, CDCl$_3$): 150.7, 141.8, 135.4, 120.7, 117.2, 114.9, 110.0, 108.6, -1.1.

$^{19}$F NMR - (471 MHz, CDCl$_3$): δ -80.7– -80.8 (m, 3F), -109.0– -109.1 (m, 2F), -120.8– -121.0 (m, 2F), -125.8– -126.0 (m, 2F).

HRMS (ESI, m/z): calc’d for C$_{13}$H$_{13}$F$_9$O$_3$Si [M]$^+$ 448.0206; found 448.0206.

4-(Phenylethynyl)phenyl nonafluorobutane-1-sulfonate (5e): Following the general procedure, using 0.3 mmol of respective aryl boronic acid, 5e was obtained in 92% yield as a white solid (Eluent: hexanes/CH$_2$Cl$_2$ 3:1).

$^1$H NMR - (500 MHz, CDCl$_3$): δ 7.63-7.58 (m, 2H), 7.57-7.52 (m, 2H), 7.40-7.35 (m, 3H), 7.30-7.26 (m, 2H).

$^{13}$C {$^{19}$F} NMR - (126 MHz, CDCl$_3$): 149.3, 133.5, 131.8, 128.9, 128.6, 124.1, 122.7, 121.7, 117.2, 115.0, 110.0, 108.6, 91.4, 87.5.

$^{19}$F NMR - (471 MHz, CDCl$_3$): δ -80.6– -80.7 (m, 3F), -108.7– -108.9 (m, 2F), -120.6 – -121.0 (m, 2F). -125.7– -125.9 (m, 2F).

HRMS (ESI, m/z): calc’d for C$_{18}$H$_9$F$_9$O$_3$S [M]$^+$ 476.0123; found 476.0123.

m.p. (°C): 68.1 – 68.5.
5.5 Catalytic studies using 6 and 14 as catalysts

Phenylbismine 6 and difluoro bismine 14 were tested as catalysts to see if they could be on-cycle intermediates of the Bi-catalyzed coupling of arylboronic acids and NaOTf.

A culture tube equipped with a stir bar was charged with aryl boronic acid (0.025 mmol, 1.0 equiv.), bismine (0.0025 mmol, 0.1 equiv.), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (6.98 mg, 0.0275 mmol, 1.1 equiv.), sodium triflate (4.73 mg, 0.0275 mmol, 1.1 equiv.), sodium phosphate (8.20 mg, 0.050 mmol, 2.0 equiv.), 5Å molecular sieves (10 mg) and dry CDCl₃ (1 mL) under an Ar atmosphere and stirred at 60 °C for 16 h. After the indicated time, the yield was calculated by ¹⁹F NMR using 1-fluoro-4-nitrobenzene (added by weight) as internal standard. Yield was determined by integration of the CF₃ group on the Ar‒OTf moiety at a chemical shift ca. δ = 73.0 ppm.

These results suggests that 6 and 14 could be used as catalysts. Indeed, phenylbismine 6 is a necessary intermediate after transmetalation to 4c with phenylboronic acid 2a, and therefore is proposed to be an on-cycle intermediate. Regarding difluorobismine 14, this high-valent species could enter the catalytic cycle via ligand exchange with NaOTf, generating the proposed intermediate 7a (see Figure 3, main text).
6. Computational details

All calculations were performed using the development version of ORCA 4.2. Geometries were optimized using the hybrid Perdew-Burke-Errzerhof functional (PBE0) in conjunction with the def2-TZVP basis set, the auxiliary def2/J basis set and the default effective core potential (ECP) for Bi. Fine integration grids (grid6) were applied. The dispersion correction by Grimme with Becke-Johnson damping (D3BJ) as well as the chain of spheres approximation (RIJCOSX) were employed. Subsequent frequency calculations were performed to evaluate enthalpy and entropy corrections at 298.15 K and ensured that all local minima had only real frequencies while a single imaginary frequency confirmed the presence of transition states. Natural bond orbital (NBO) analysis was performed at the PBE0-D3BJ/def2-TZVP level of theory. The Chemcraft software was used to display molecular geometries.
6.1 Energy profiles for the reductive elimination step

As stated in the manuscript, DFT studies on the reaction profile starting from 7a show that two reductive elimination pathways are possible to furnish 2a together with the corresponding bismine fluoride 8 (Figure S14). However, 7a could also undergo isomerization to 7a-trans through a kinetic barrier of $\Delta G^\ddagger = 5.8$ kcal/mol (TSra). The trans isomer 7a-trans is computed to be 2.7 kcal/mol higher in energy than 7a, being the latter the most stable species. This extra stabilization of the cis form is suggested to be a result of the coordination of the $\text{--SO}_2\text{--}$ moiety in 7a, thus providing electronic density to the highly electrophilic BiV center.

**Figure S14.** Gibbs energy profile of the reaction from 7a. Relative Gibbs energy values are given in kcal mol$^{-1}$. Other isomers were also evaluated (see Figure S15), but 7a resulted to be the most stable conformer. Bismines locating two phenyl groups in apical were not considered, as they are predicted to be highly energetic and therefore unlikely to be formed according to the polarity rule in pentavalent main-group compounds.$^{38}$
Figure S15. Isomers of 7a evaluated in this study. In parenthesis, relative energies given in kcal mol\(^{-1}\).

Then, 7a can undergo reductive elimination either through a 3-membered ring transition state (TS1a, \(\Delta G^\ddagger = 24.7\) kcal/mol) or through a 5-membered ring transition state (TS2a, \(\Delta G^\ddagger = 21.2\) kcal/mol). As shown in Figure S13, the 5-membered TS2a is slightly favored over the 3-membered TS1a (\(\Delta \Delta G^\ddagger = 3.5\) kcal/mol), pointing towards TS2a as the preferable pathway for the C–O bond forming event. Furthermore, the reductive elimination from 7a, which was detected by HRMS (see section 3.3.3), proceeds in less than 10 minutes at room temperature (ca. 22 °C). This result agrees with the theoretical results depicted in Figure S14.

Similar results were obtained when the DFT profile of the reaction starting from ditriflate bismine 7b was studied (Figure S16). Similarly to 7a, 7b can also undergo isomerization via turnstile pseudo-rotation to furnish 7b-trans (\(\Delta G = 2.8\) kcal/mol) through a kinetic barrier of \(\Delta G^\ddagger = 6.1\) kcal/mol (TSrb). In this case, the cis isomer is also the most stable form probably due to coordination of the –SO\(_2–\) moiety to the electrophilic Bi(V) center.
In line with the reactivity observed with 7a, 7b could also undergo reductive elimination through two different cyclic transition states. Indeed, a 3-membered ring transition state (TS1b) would yield 4c and 2a through a kinetic barrier of $\Delta G^\ddagger = 24.5$ kcal/mol, while a 5-membered transition state (TS2b) would yield the same products through a pathway with a lower activation barrier ($\Delta G^\ddagger = 22.9$ kcal/mol). In this case, although TS2b it is slightly favored over TS1b, the energetic difference between both routes ($\Delta \Delta G^\ddagger = 1.6$ kcal/mol) is not sufficient to fully rule out TS1b. Also, it is important to note than in both profiles the reaction is highly exergonic (Figures S14 and S16, $\Delta G = -40.8$ and -43.2 kcal/mol, respectively), showing that this reductive elimination is thermodynamically favored independently of the anions bonded to 7.

The most relevant structures of the reductive elimination profiles from species 7a and 7b are shown in Figures S17 and S18, together with selected structural parameters.
Figure S17. Relevant structures of the reductive elimination profile from species 7a.
Figure S18. Relevant structures of the reductive elimination profile from species 7b.
6.2 NBO analysis: Natural charges and Wiberg bond indices of selected species

NBO analysis was performed on the most relevant species involved in the reductive elimination from 7a, revealing interesting electronic and bonding features of these compounds (Figure S19). As reported in the main text, the natural charge on the Bi center decreased from 2.179 in 7a, to 1.849 and 1.884 in TS1a and TS2a, respectively, to finally 1.499 in 8. This progressive change of charge at the Bi center points out to a concerted reductive elimination. In addition, the C atom directly attached to the Bi center (C1) also experienced a substantial change, becoming positively charged at the transition state (see Figure S19 and Table S8). This buildup of positive charge on the C atom directly bound to the Bi center was also observed experimentally in previous reductive elimination studies from BiV species.8

![Diagram showing natural charges and Wiberg bond indices for species 7a, TS1a, TS2a, and 8](image)

**Figure S19.** Natural charges (C1, O1, O1’ and Bi atoms) and Wiberg bond indices (WBI) of selected bonds of species 7a, TS1a, TS2a and 8.

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Table S8. Relevant Wiberg Bond Indices (WBI) and NPA atomic charges ($q$) for Bi species 7a, TS1a, TS2a and 8.

| Compound | WBI$_{Bi-C1}$ | WBI$_{C1-O1}$ | WBI$_{C1-O1'}$ | $q$$_{Bi}$ | $q$$_{C1}$ | $q$$_{O1}$ | $q$$_{O1'}$ |
|----------|---------------|---------------|---------------|-----------|-----------|-----------|-----------|
| 7a       | 0.826         | -             | -             | 2.179     | -0.266    | -0.969    | -0.998    |
| TS1a     | 0.447         | 0.130         | -             | 1.849     | 0.217     | -0.917    | -0.997    |
| TS2a     | 0.454         | -             | 0.153         | 1.884     | 0.202     | -0.975    | -0.883    |
| 8        | -             | -             | -             | 1.499     | -         | -         | -         |

Furthermore, Wiberg bond indices revealed a decrease of bond order for the C1-Bi bond from 7a to TS1a and TS2a (See Figure S19 and Table S8). This result, together with the WBI > 0 for the respective C-O bonds being formed in TS1a and TS2a (see Figure S19 and Table S9) indicate that the C1-Bi cleavage happens simultaneously with the O1(’)-C1 bond forming event, as expected in a concerted reductive elimination step.
Similar results were obtained when NBO analysis was performed on the most relevant species involved in the reductive elimination from 7b (see Figure S20 and Table S9).

Table S9. Relevant Wiberg Bond Indices (WBI) and NPA atomic charges ($q$) for Bi species 7b, TS1b, TS2b and 4c.

| Compound | WBI$_{\text{Bi-C1}}$ | WBI$_{\text{C1-O1}}$ | WBI$_{\text{C1-O1'}}$ | $q_{\text{Bi}}$ | $q_{\text{C1}}$ | $q_{\text{O1}}$ | $q_{\text{O1'}}$ |
|----------|----------------------|-----------------------|-----------------------|----------------|-------------|-------------|-------------|
| 7b       | 0.824                | -                     | -                     | 2.139          | -0.269      | -0.995      | -0.998      |
| TS1b     | 0.466                | 0.121                 | -                     | 1.823          | 0.210       | -0.909      | -0.972      |
| TS2b     | 0.461                | -                     | 0.135                 | 1.877          | 0.187       | -0.925      | -0.892      |
| 4c       | -                    | -                     | -                     | 1.476          | -           | -1.036      | -           |

Figure S20. Natural charges (C1, O1, O1’ and Bi atoms) and Wiberg bond indices (WBI) of selected bonds of species 7b, TS1b, TS2b and 4c.
6.3 XYZ coordinates of DFT optimized structures

| Coordinates for 7a | Coordinates for 7a-trans |
|-------------------|--------------------------|
| Bi 3.823104       | Bi 3.648464              |
| S 6.755348        | S 6.372482               |
| O 6.396986        | O 6.722617               |
| C 5.083947        | C 5.278204               |
| C 6.313151        | C 6.165658               |
| C 7.144787        | H 7.094644               |
| H 8.094756        | C 6.987949               |
| C 6.728730        | C 2.543328               |
| H 7.356044        | H 7.665646               |
| C 5.496033        | C 6.120120               |
| C 4.666318        | C 4.768689               |
| H 3.694792        | H 4.535857               |
| C 4.228623        | C 3.633148               |
| C 5.543496        | C 4.766760               |
| C 5.892030        | H 4.711803               |
| H 6.942752        | H 5.998828               |
| C 4.900507        | C 3.536684               |
| H 5.150118        | H 3.498105               |
| C 3.586081        | C 2.415343               |
| C 3.232703        | C 2.449767               |
| H 2.208544        | H 1.559372               |
| C 3.746112        | C 2.736560               |
| C 4.816991        | C 3.353144               |
| C 5.698971        | H 4.225867               |
| C 4.696532        | C 2.798937               |
| H 5.510565        | H 3.261214               |
| C 3.539740        | C 1.665887               |
| H 3.454328        | H 1.241655               |
| C 2.485067        | C 1.073542               |
| H 1.577464        | H 0.188195               |
| C 2.574960        | C 1.610651               |
| H 1.750718        | H 1.173325               |
| O 8.067947        | F 2.228732               |
| C 5.063994        | F 7.223540               |
| F 5.452331        | C 6.16805                |
| F 5.595182        | F 6.797231               |
| F 3.737505        | F 6.675799               |
| C 2.536837        | F 4.873673               |
| F 1.307238        | F 1.123574               |
| F 2.727512        | F 0.454767               |
| F 2.581739        | F 0.317086               |
| S 2.665388        | F 1.329845               |
| F 2.644804        | F 4.694976               |
| F 0.804020        | S 4.660386               |
| F 2.532146        | O 4.693224               |
| O 2.045772        | S 5.607877               |
| O 4.107188        | C 2.996660               |
| O 2.142341        | F 2.697967               |
| O 2.125597        | F 2.923934               |
| F 2.180117        | F 2.068742               |

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Coordinates for TSra

| Atom | Bi   | S    | O    | C    | O    | C    | F    | F    | F    | F    | F    | H    |
|------|------|------|------|------|------|------|------|------|------|------|------|------|
|      | 3.32187 | 4.15542 | 6.49075 |      |      |      |      |      |      |      |      |      |

Coordinates for TS1a

| Atom | Bi   | S    | O    | C    | O    | C    | F    | F    | F    | F    | F    | H    |
|------|------|------|------|------|------|------|------|------|------|------|------|------|
|      | 3.597016 | 4.891890 | 5.395243 |      |      |      |      |      |      |      |      |      |

Coordinates for TS2a

| Atom | Bi   | S    | O    | C    | O    | C    | F    | F    | F    | F    | F    | H    |
|------|------|------|------|------|------|------|------|------|------|------|------|------|
|      | 3.816367 | 4.154540 | 6.438287 |      |      |      |      |      |      |      |      |      |

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| Coordinates for 7b | Coordinates for 8 |
|-------------------|-------------------|
| Bi                | Bi                |
| S                 | S                 |
| O                 | O                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| H                 | H                 |
| Bi                | Bi                |
| S                 | S                 |
| O                 | O                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| H                 | H                 |
| Bi                | Bi                |
| S                 | S                 |
| O                 | O                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| H                 | H                 |

| Coordinates for 7b | Coordinates for 8 |
|-------------------|-------------------|
| Bi                | Bi                |
| S                 | S                 |
| O                 | O                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| H                 | H                 |
| Bi                | Bi                |
| S                 | S                 |
| O                 | O                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| H                 | H                 |

| Coordinates for 7b | Coordinates for 8 |
|-------------------|-------------------|
| Bi                | Bi                |
| S                 | S                 |
| O                 | O                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| H                 | H                 |
| Bi                | Bi                |
| S                 | S                 |
| O                 | O                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| H                 | H                 |

| Coordinates for 7b | Coordinates for 8 |
|-------------------|-------------------|
| Bi                | Bi                |
| S                 | S                 |
| O                 | O                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| H                 | H                 |
| Bi                | Bi                |
| S                 | S                 |
| O                 | O                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| F                 | F                 |
| C                 | C                 |
| H                 | H                 |
Coordinates for 7b-trans

Bi  3.301499  4.007716  6.519554
S  6.255429  2.338434  6.023109
O  6.432619  3.067291  7.244496
C  4.828238  4.479609  5.027630
C  5.853673  3.568210  4.807265
C  6.665603  3.684984  3.694653
H  7.454777  2.961024  3.536579
C  6.456347  4.731973  2.809824
H  7.085997  4.830302  1.934732
C  5.436187  5.641714  3.035194
H  4.602180  5.511581  4.139917
C  3.779102  6.203068  4.275072
C  3.590461  1.840534  6.686078
C  4.804257  1.330624  6.247171
C  4.937168  -0.037231  6.065668
H  5.885514  -0.429735  5.721814
C  3.863374  -0.871192  6.325664
H  3.962997  -1.939764  6.180372
C  2.657330  -0.342521  6.758487
C  2.506618  1.025518  6.933465
H  1.547802  1.424795  7.234771
H  1.823520  5.604961  6.849672
C  2.248801  6.692755  7.593239
H  3.225360  6.719358  8.055932
C  1.368913  7.755909  7.742362

Coordinates for TSrb

Bi  3.240192  4.137819  6.437532
S  6.199487  2.967460  6.235491
O  5.780033  3.919404  7.253705
C  4.657455  4.571129  4.766349
C  5.818887  3.815546  4.738503
C  6.658504  3.809061  3.638913
H  7.565139  3.216889  3.648435
C  6.319361  4.598334  2.551025
H  6.961165  4.622033  1.678815
C  5.163948  5.368835  2.579827
C  4.321050  5.355783  3.683812
H  3.414994  5.947300  3.674096
C  3.681157  1.983859  6.556440
C  5.016560  1.661536  6.365480
C  5.426305  0.342393  6.407792
H  6.473748  0.102218  6.275138
C  4.484739  -0.640546  6.671544
H  4.791856  -1.675373  6.744192
C  3.156223  -0.301780  6.870964
C  2.731752  1.021948  6.799069
H  1.688890  1.266942  6.950978
Coordinates for TS1b

| Bi | 3.598214 | 4.834985 | 5.379389 |
| S  | 6.600760 | 4.159365 | 4.730082 |
| O  | 6.061687 | 4.720938 | 5.975731 |
| C  | 4.738434 | 5.748506 | 3.643885 |
| C  | 6.034778 | 5.277321 | 3.491185 |
| C  | 6.839094 | 5.647102 | 2.427910 |
| H  | 7.845505 | 5.256266 | 2.341133 |
| C  | 6.325227 | 6.540935 | 1.500863 |
| C  | 6.931802 | 6.866177 | 0.665790 |
| C  | 5.033461 | 7.025762 | 1.647710 |
| C  | 4.229267 | 6.628507 | 2.712194 |
| C  | 3.215973 | 7.002511 | 2.788711 |
| C  | 4.283993 | 2.793044 | 4.782045 |
| C  | 5.636305 | 2.707144 | 4.476364 |
| C  | 6.212584 | 1.533546 | 4.025520 |
| H  | 7.271241 | 1.495394 | 3.800617 |
| C  | 5.401475 | 0.416566 | 3.897388 |

Coordinates for TS2b

| Bi | 3.917148 | 4.029160 | 6.572899 |
| S  | 6.655329 | 2.531810 | 6.120196 |
| O  | 6.307381 | 3.442121 | 7.216702 |
| C  | 5.189661 | 4.266671 | 4.707280 |
| C  | 6.332924 | 3.477384 | 4.669584 |
| C  | 7.165806 | 3.413234 | 3.567825 |
| H  | 8.043361 | 2.778541 | 3.579251 |
| C  | 6.850453 | 4.195528 | 2.466640 |
| H  | 7.483389 | 4.180933 | 1.589427 |
| C  | 5.716791 | 4.993573 | 2.488749 |
| C  | 4.877446 | 5.028664 | 3.599881 |
| H  | 3.979694 | 5.634860 | 3.574959 |
| C  | 4.075400 | 1.797772 | 6.390630 |
| S  | 6.647742  | 3.226642  | 5.683471  |
| O  | 6.363523  | 4.293266  | 6.627079  |
| C  | 4.748872  | 4.443224  | 4.18524   |
| C  | 5.990467  | 3.816624  | 4.15557   |
| C  | 6.746632  | 3.742712  | 2.99687   |
| C  | 7.712523  | 3.252993  | 3.014513  |
| C  | 6.250929  | 4.328646  | 1.84376   |
| H  | 6.826135  | 4.295775  | 0.926708  |
| C  | 5.022957  | 4.975014  | 1.87005   |
| C  | 4.266063  | 5.032389  | 3.034434  |
| H  | 3.308179  | 5.311322  | 3.031786  |
| C  | 4.271489  | 2.250417  | 6.524412  |
| C  | 5.572598  | 1.919969  | 6.167497  |
| H  | 5.034624  | 0.618339  | 6.25801   |
| H  | 7.057234  | 0.389348  | 5.985164  |
| C  | 5.17126   | -0.35898  | 6.72788   |
| H  | 5.509269  | -1.38318  | 6.817619  |
| C  | 3.871333  | -0.02684  | 7.097814  |
| C  | 3.402911  | 1.27898   | 6.972416  |
| H  | 2.381144  | 1.532938  | 7.221498  |
| C  | 3.795182  | 6.212779  | 7.196083  |
| C  | 2.790807  | 6.574598  | 8.083577  |
| H  | 1.950768  | 5.924002  | 8.257609  |
| C  | 2.927457  | 7.792681  | 8.737937  |
| H  | 2.16263  | 8.102613  | 9.439945  |
| C  | 4.025566  | 8.605035  | 8.495882  |
| H  | 4.119105  | 9.551912  | 9.014483  |
| C  | 5.006096  | 8.215822  | 7.594762  |
| H  | 5.863879  | 8.851613  | 7.41066   |
| C  | 4.896634  | 7.004988  | 6.925802  |
| H  | 6.666228  | 6.865664  | 6.234601  |
| O  | 7.97744   | 2.733203  | 5.497303  |
| C  | 4.496368  | 5.59151   | 0.600211  |
| F  | 5.439893  | 6.321364  | -0.00912  |
| F  | 4.106937  | 4.65173   | -0.26932  |
| F  | 3.451143  | 3.868602  | 0.826374  |
| C  | 2.951687  | -1.08732  | 7.626869  |
| F  | 1.684826  | -0.87378  | 7.27764   |
| F  | 3.295947  | -2.30546  | 7.195905  |
| F  | 2.999848  | -1.1124   | 8.96649   |
| O  | 1.845921  | 4.786526  | 4.808244  |
| O  | 1.70233   | 2.393519  | 4.538014  |
| O  | -0.34     | 3.695467  | 5.088471  |
| C  | 0.625104  | 3.923359  | 2.681304  |
| S  | 0.939591  | 3.611893  | 4.477769  |
| F  | -0.24511  | 3.032076  | 2.235522  |
| F  | 0.132147  | 5.140812  | 2.503542  |
| F  | 1.745519  | 3.812437  | 1.971957  |
| F  | 1.955914  | 3.817637  | 7.297378  |

Coordinates for 7a-4

| Bi  | 3.916942  | 4.157179  | 6.447265  |
| S  | 6.899189  | 2.775792  | 5.762352  |
| O  | 6.851381  | 3.74212   | 6.830174  |
| C  | 5.059901  | 4.326599  | 4.51708   |
| C  | 6.229457  | 3.594197  | 4.346314  |
| C  | 6.888214  | 3.542879  | 3.130176  |
| H  | 7.801155  | 2.967872  | 3.036116  |

Coordinates for 7a-3

| Bi  | 3.969463  | 4.259301  | 6.543536  |
| S  | 6.791579  | 2.561449  | 6.002279  |
| O  | 6.72359   | 3.432624  | 7.149813  |
| C  | 5.307763  | 4.483132  | 4.771317  |
| Atomic Number | Atomic Symbol | Atomic Mass | Atomic Number | Atomic Symbol | Atomic Mass | Atomic Number | Atomic Symbol | Atomic Mass |
|---------------|---------------|-------------|---------------|---------------|-------------|---------------|---------------|-------------|
| 21            | Bi            | 209.02      | 87            | Fr            | 237.05      | 88            | Fr            | 229.00      |
| 9             | F             | 19.00        | 17            | Cl            | 35.45       | 16            | S             | 32.06       |
| 15            | P             | 30.97       | 12            | Mg            | 24.31       | 1             | H             | 1.01        |
| 20            | Ca            | 40.08       | 8             | O             | 16.00       | 16            | S             | 32.06       |

**Coordinates for 7a-trans-2**

| Atomic Number | Atomic Symbol | Atomic Mass | Atomic Number | Atomic Symbol | Atomic Mass | Atomic Number | Atomic Symbol | Atomic Mass |
|---------------|---------------|-------------|---------------|---------------|-------------|---------------|---------------|-------------|
| 87            | Fr            | 237.05      | 88            | Fr            | 229.00      | 8             | O             | 16.00       |
| 12            | Mg            | 24.31       | 1             | H             | 1.01        | 16            | S             | 32.06       |
| 30.97       | P             | 30.97       | 40.08         | Ca            | 40.08       | 16            | S             | 32.06       |
| 16.00       | O             | 16.00       | 1.01          | H             | 1.01        | 16            | S             | 32.06       |

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7. References

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8. NMR characterization of L7

L7, $^1$H NMR, CDCl$_3$
9. NMR characterization of Bi(III) compounds
9f, $^1$H NMR, CDCl$_3$
9f, $^{13}$C NMR, CDCl$_3$
6, $^{19}$F NMR, CDCl$_3$
$4b$, $^{13}$C NMR, CD$_3$CN
$^{19}$F NMR, CD$_3$CN
10. $^{19}$F NMR yields of the Bi-catalyzed coupling of arylboronic acids with NaOTf
2c, >95%, CDCl₃
2e, 71%, CDCl₃
2g, >95%, CDCl₃
2j, 60%, CDCl₃
Me$_3$SiOTf
2m, >95%, CDCl$_3$
EtO$_2$C-OTf

2o, 45%, CDCl$_3$
Ph\[\text{OTf}\]

2p, 92%, CDCl₃

-62.85
-72.75
-102.03

0.63
2.75
1.10

f1 (ppm)
2q, 90%, CDCl₃
S100
$2w$, 11%, CDCl$_3$
11. NMR characterization of isolated aryl triflates 2
2a, $^{19}$F NMR, CDCl$_3$
2a, $^{13}$C NMR, CDCl$_3$
2b, $^1$H NMR, CDCl$_3$
$2b, ^{13}\text{C NMR, CDCl}_3$
2c, $^1$H NMR, CDCl$_3$
$^2c, {^19F \text{ NMR, CDCl}_3}^{\text{OTf}}$
2c, $^{13}$C NMR, CDCl$_3$
$^{19}$F NMR, CDCl$_3$
$2f, \text{ }^1H \text{ NMR, CDCl}_3$
$^{19}$F NMR, CDCl$_3$
$^1$H NMR, CDCl$_3$
$^{19}$F NMR, CDCl$_3$
$2g, ^{13}C$ NMR, CDCl$_3$
$2h, ^{19}\text{F NMR, CDCl}_3$
2h, $^{13}$C NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
$^{19}$F NMR, CDCl$_3$
$^1$H, $^{13}$C NMR, CDCl$_3$
$2k$, $^1H$ NMR, CDCl$_3$
$2k, {^{19}\text{F}}\text{ NMR, CDCl}_3$
Br

\[ \text{OTf} \]

\[ \text{2k, } ^{13}\text{C NMR, CDCl}_3 \]
2l, $^{19}\text{F} NMR, \text{CDCl}_3$
21, $^{13}$C NMR, CDCl$_3$
Ph\(\text{OTf}\)

2H, ¹H NMR, CDCl₃
$^{13}$C NMR, CDCl$_3$
$^1\text{H}$ NMR, CDCl$_3$
Chemical shifts for compound 2ο, $^{13}$C NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
$2r,^{13}\text{C NMR, CDCl}_3$
12. $^{19}\text{F}$ NMR yields of the Bi-catalyzed coupling of arylboronic acids with KONf

![NMR Spectrum](image)

5a, >95%, CDCl$_3$
SNf

5c, >95%, CDCl₃
13. NMR characterization of isolated aryl nonaflates 5
5a, $^{13}$C ($^{19}$F) NMR, CDCl$_3$
$5b, ^{13}C\left(^{19}F\right)$ NMR, CDCl$_3$
$5c$, $^1H$ NMR, CDCl$_3$
5c, $^{13}$C ($^1$H) NMR, CDCl$_3$
Me$_3$Si
5d, $^{13}$C $^{19}$F NMR, CDCl$_3$
$5e$, $^1H$ NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$