Supporting Information

of

Efficient Cross-Coupling of Aryl/Alkenyl Triflates with Acyclic Secondary Alkylboronic acids

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1. General Considerations.

All reactions were carried out under nitrogen atmosphere unless otherwise specified. Unless otherwise noted, commercialized reagents were used without further purifications. Toluene was purchased from Sigma-Aldrich Chemical Co. All other solvents were purified and dried according to standard methods prior to use.

$^1$H NMR, $^{31}$P NMR, $^{19}$F NMR and $^{13}$C NMR data were recorded on a Bruker-Ultrashield PLUS400 NMR or a 500 MHz Agilent spectrometer with CDCl$_3$ as the solvent. $^1$H chemical shifts were referenced to CDCl$_3$ at 7.26 ppm. $^{13}$C chemical shifts were referenced to CDCl$_3$ at 77.14 ppm and obtained with $^1$H decoupling. $^{31}$P chemical shifts were referenced to 85% H$_3$PO$_4$ in D$_2$O at 0.0 ppm as external standard and obtained with $^1$H decoupling. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), triplet - doublet (td), quintet (quint), sextet (sextet), septet (septet), multiplet (m), and broad (br). MS was measured on Agilent 7890A/5975C Series GC/MSD mass spectrometer. HPLC yield were determined on Agilent 1200 Infinity Series.

2. Synthesis of substrates

2.1 Synthesis of aryl triflates

Phenol substrate (1.0 eq) and triethylamine (3.0 eq) were dissolved in dry DCM to give a saturated solution. The solution was then cooled to $-78$ $^\circ$C. Trifluoromethanesulfonic anhydride (1.1 eq) was added dropwise. After 2 h, the solution was allowed to warm to room temperature and stirred for 12 hours. Water (50 mL) was added and the organic layer was separated, washed with saturated brine and dried over anhydrous Na$_2$SO$_4$. The solution was concentrated under reduced pressure and the residue was directly subjected to flash column chromatography to give the pure triflate product.

2.1.1 Synthesis of 2-methoxynaphthalen-1-yl trifluoromethanesulfonate(3q)
3-Chloroperbenzoic acid (4.4 g, 21.5 mmol, 2.0 equiv) was added to a solution of 2-methoxynaphthaldehyde (2 g, 10.7 mmol, 1.0 equiv) and ethyl-acetate (20 mL) at 0°C. The reaction mixture was stirred at room temperature for 40 h. The progress of the reaction was monitored by $^1$H NMR analysis observing the disappearance of the aldehyde signal. At the end of the reaction ethyl acetate was evaporated under vacuum. The residue was diluted with dichloromethane, filtrated, and washed sequentially with saturated sodium bicarbonate solution and with water. The organic phase was dried and concentrated to give a (2.1 g, 95%) as violet oil. LiAlH$_4$ (0.4 g, 10.7 mmol, 1.0 equiv) was suspended in anhydrous THF (20 mL) under nitrogen and a solution of a in THF was added dropwise. After 4 h, the reaction was quenched by pouring into cold 10% HCl solution (10 mL) and the mixture was extracted with dichloromethane (20 mL). The organic phase was separated, washed with water, dried over sodium sulfate, and concentrated. The residue was purified by silica gel chromatography to afford b (1.0 g, 55%) as green solid.$^2$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J$ = 6.8 Hz, 1H), 7.75 (d, $J$ = 7.3 Hz,1H), 7.39–7.43 (m, 3H), 7.27 (d, $J$ = 6.3 Hz, 1H), 6. 05 (s, 1H), 4.00 (s, 3H).

Compound b (1.0 g, 5.7 mmol, 1.0 equiv) and triethylamine (2.4 mL, 17.3 mmol, 3.0 equiv) were dissolved in dry DCM (10 mL). The solution was then cooled to -78°C. Trifluoromethanesulfonic anhydride (1.1 ml, 6.3 mmol, 1.1 equiv) was added dropwise. After 2 h, the solution was allowed to warm to room temperature and stirred for 12 h. Thereafter, H$_2$O (10 mL) was added and the organic layer was separated, washed with brine, and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure and the residue was directly subjected to purification by flash column chromatography to give 3q (1.7 g, 95 %) as yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J$ = 8.6 Hz, 1H), 7.82 (dd, $J$ = 9.1, 3.4 Hz, 2H), 7.59–7.62 (m, 1H), 7.42–7.46 (m, 1H), 7.33 (d, $J$ = 9.1 Hz, 1H), 4.02 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 148.4, 132.3, 129.3, 129.0, 128.2, 127.9, 127.4, 124.8, 119.6, 118.8 (q, $J$ = 318.7 Hz), 113.6, 56.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -73.2(d, $J$ = 6.9 Hz); EI-MS: m/z 306.0 [M]$^+$; HRMS (EI) m/z calcd for C$_{12}$H$_9$F$_3$O$_4$S (M): 306.0174, found: 306.0181.
2.2 Synthesis of alkenyl triflates

\[
\text{Ketone A (1.0 eq.) and Na}_2\text{CO}_3 (3.0 eq.) were added to dry DCM. The solution was then cooled to 0 °C. Trifluoromethanesulfonic anhydride (1.1 eq.) was added dropwise. After 1 h, the solution was allowed to warm to room temperature and stirred for 5 h. Thereafter, H}_2\text{O (50 mL} was added, the organic layer was separated, washed with brine, and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure and the residue was directly subjected to purification by flash column chromatography to give alkenyl triflate.}
\]

2.2.1 Synthesis of tert-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2H)-carboxylate (1ue)

\[
\text{1-Boc-4-piperidone in THF (10 mL) was cooled to -78 °C. After 20 min, a solution of 1,1,1-trifluoro-N-phenyl-N-(trifluoromethylsulfonyl)methane sulfonamide (1.8g, 5.02 mmol) in THF (10 mL) was slowly added to the mixture. The reaction mixture was allowed to warm to rt and stirred at rt for 3 h, then quenched with saturated NH}_4\text{Cl solution and extracted with EtOAc (20 mL). The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography with petroleum ether/ethyl acetate (10/1, v/v) to obtain the desired alkenyl triflate (1ue)(80% yield); }^{1}\text{H NMR (500 MHz, CDCl}_3\text{) }\delta 5.76 (s, 1H), 4.04 (d, J = 2.0 Hz, 2H), 3.63 (t, J = 5.4 Hz, 2H), 2.44 (d, J = 1.1, 2H ), 1.47 (s, 9H ); }^{13}\text{C NMR (125 MHz, CDCl}_3\text{) }\delta 154.3, 146.9, 119.7, 117.2, 80.6, 41.8, 39.8, 28.3, 28.0; }^{19}\text{F NMR (376 MHz, CDCl}_3\text{) }\delta -73.9 ; \text{ EI-MS: } m/z 331.0 [M]^+; \text{ HRMS (EI) } m/z \text{ calcd for C}_{11}\text{H}_{16}\text{F}_3\text{NO}_5\text{S (M): 330.9997, found: 331.0003.}
\]
3. Synthetic procedures of ligands L1-2

3.1 Synthesis of L1


**Synthesis of L1:** To a solution of compound c (0.38 g, 1.00 mmol, 1.0 equiv) in toluene (5 mL) at rt was added HSiCl₃ (0.51 mL, 5.00 mmol, 5.0 equiv) and TEA (1.40 mL, 10.00 mmol, 10.0 equiv). The mixture was stirred at 80 °C for 12 h and then concentrated under vacuum to remove most toluene. To the residue was added carefully 30% aqueous NaOH solution (20 mL). Gas was generated during addition. The resulting mixture was further stirred at 60 °C for 0.5 h. To the mixture at rt was added EA (20 mL). The EA layer was separated and the aqueous layer was washed with EA under nitrogen. The combined EA solution was dried, concentrated, and purified by passing through a neutral alumina plug to afford the desired product L₁ (0.35 g, 0.91 mmol, 96%) as white solid. **L₁:** ¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, J = 8.1 Hz, 1H), 6.44–6.48 (m, 2H), 5.47 (dd, J = 7.6, 3.2 Hz, 1H), 3.82 (s, 3H), 1.42 (d, J = 13.1 Hz, 9H), 1.20 (d, J = 13.6 Hz, 9H), 1.02 (d, J = 12.4 Hz, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 164.7 (d, J = 8.0 Hz), 161.7 (d, J = 12.7 Hz), 132.4, 110.7 (d, J = 17.9 Hz), 104.4, 103.2 (d, J = 1.3 Hz), 80.5 (dd, J = 61.7, 47.0 Hz), 55.5, 36.9 (d, J = 4.0 Hz), 36.5 (d, J = 5.3 Hz), 33.0 (dd, J = 25.0, 7.5 Hz), 27.4 (d, J = 5.5 Hz), 27.1 (d, J = 4.8 Hz), 27.1 (d, J = 10.0 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 57.1 (d, J = 40.1 Hz), 2.3 (d, J = 40.3 Hz); EI-MS: m/z 384.0 [M]+; HRMS (EI) m/z calcd for C₂₀H₃₄O₃P₂(M): 384.1983, found: 384.1986.

3.2 Synthesis of L2

SI-5
The syntheses of \( \mathbf{d} \) were followed according to procedures described in our previous report: Li, C.; Chen, T.; Li, B.; Xiao, G.; Tang, W. Angew. Chem. Int. Ed. 2015, 54, 3792.

**Synthesis of \( \mathbf{L2} \):** To a solution of compound \( \mathbf{d} \) (0.40 g, 1.74 mmol, 1.0 equiv) in THF (4 mL) at -78 °C was added LDA (0.95 mL, 2.0 M in THF, 1.1 equiv) over 5 min. The resulting mixture was stirred at -78 °C for 1 h followed by the addition of di-tert-butylchlorophosphane (0.36 mL, 1.90 mmol, 1.1 equiv). After stirred at -78 °C for 1 h, the mixture was allowed to warm to rt over 1 h and kept stirring at rt overnight. To the mixture at 0 °C was charged 30% \( \text{H}_2\text{O}_2 \) (5.0 mL) and the resulting mixture was stirred at rt for 0.5 h. Dichloromethane (10 mL) were added and the organic layer was separated and the aqueous layer was further extracted with dichloromethane (10 mL X 3). The combined dichloromethane was washed with brine, dried over magnesium sulfate, concentrated, and purified by silica gel column chromatography to give the desired product \( \mathbf{e} \) (0.60 g, 1.45 mmol, 92%) as white solid. Compound \( \mathbf{e} \): \( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.32 (t, \( J = 8.0 \) Hz, 1H), 6.53 (dd, \( J = 8.1, 4.5 \) Hz, 1H), 6.46 (dd, \( J = 8.2, 2.4 \) Hz, 1H), 4.90 (dd, \( J = 10.0, 5.7 \) Hz, 1H), 2.95 (s, 6H), 1.42 (d, \( J = 13.4 \) Hz, 9H), 1.40 (d, \( J = 14.3 \) Hz, 9H), 1.25 (d, \( J = 16.3 \) Hz, 9H); \( ^{13}\text{C} \) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 164.3, 157.6 (d, \( J = 2.3 \) Hz), 135.5, 110.9 (d, \( J = 6.7 \) Hz), 106.4 (d, \( J = 5.2 \) Hz), 70.1 (dd, \( J = 45.2, 5.1 \) Hz), 45.0, 38.0 (d, \( J = 57.2 \) Hz), 37.1 (dd, \( J = 54.5, 6.7 \) Hz), 36.3 (d, \( J = 77.3 \) Hz), 27.6, 26.8, 25.4; \( ^{31}\text{P} \) NMR (162 MHz, CDCl\(_3\)) \( \delta \) 62.0 (d, \( J = 8.5 \) Hz, 1P), 61.7 (d, \( J = 8.4 \) Hz, 1P); EI-MS: m/z 413.0 [M]+; HRMS (EI) m/z calcd for C\(_{21}\)H\(_{37}\)NO\(_3\)P\(_2\)(M\(+\)): 413.2246, found: 413.2245.

To a solution of compound \( \mathbf{e} \) (0.36 g, 0.87 mmol, 1.0 equiv) in toluene (3 mL) at rt was added HSiCl\(_3\) (0.44 ml, 4.35 mmol, 5.0 equiv) and TEA (1.20 mL, 8.70 mmol, 10.0 equiv). The mixture was stirred at 80 °C for 12 h and then concentrated under vacuum to remove most toluene. To the residue was added carefully 30% aqueous NaOH solution (20 mL). Gas was generated during addition. The resulting mixture was further stirred at 60 °C for 0.5 h. To the mixture at rt was added EA (20 mL). The EA layer was separated and the aqueous layer was washed with EA under nitrogen. The combined EA solution was dried, concentrated, and purified by passing through a neutral alumina plug to afford the desired product \( \mathbf{L2} \) (0.26 g, 0.65 mmol, 75%) as white solid. \( \mathbf{L2} \): \( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.15 (t, \( J = 8.0 \) Hz, 1H), 6.44 (dd, \( J = 8.0, 3.7 \) Hz, 1H), 6.40 (d, \( J = 8.0 \) Hz,
1H), 5.39 (dd, J = 7.7, 3.4 Hz, 1H), 2.93 (s, 6H), 1.43 (d, J = 13.0, 9H), 1.23 (d, J = 13.6 Hz, 9H), 0.98 (d, J = 12.3 Hz, 9H); 13C NMR (100 MHz, CDCl3) δ 164.9 (d, J = 1.35 Hz), 155.8 (d, J = 12.0 Hz), 132.0, 113.1 (dd, J = 21.7, 1.6 Hz), 109.5, (d, J = 6.5 Hz), 103.9, 79.2 (dd, J = 61.7, 45.9 Hz), 43.0, 42.9, 37.0 (dd, J = 13.8, 1.4 Hz), 36.5 (dd, J = 13.6, 1.4 Hz), 34.2 (dd, J = 24.9, 8.2 Hz), 27.5 (d, J = 4.7 Hz), 27.2, 26.9 (d, J = 14.5 Hz); 31P NMR (162 MHz, CDCl3) δ 57.4 (d, J = 39.9 Hz), 5.1 (d, J = 39.9 Hz); EI-MS: m/z 397.1 [M]+; HRMS (EI) m/z calcd for C21H37NO3P2(M): 397.2300, found: 397.2305.


To a mixture of aryl/alkenyl triflates (0.25 mmol), alkylboronic acid (0.5 mmol), potassium phosphate tribasic monohydrate (0.75 mmol), [Pd(cinnamyl)Cl]2 (0.0013 mmol, 2.0 mol % Pd), phosphorus ligand (L1 or L2, 5.4.0 mol %, Pd : L = 1 : 2) was charged dry toluene (2 mL). The mixture was pumped and refilled with nitrogen for three times. The resulting mixture was stirred at 110°C under nitrogen for 12 h, and then cooled to room temperature, partitioned with water (2 mL) and dichloromethane (3 mL). The organic layer was separated, dried over sodium sulfate, concentrated, and purified by silica gel column chromatography (hexanes/EtOAc as eluent) to provide the coupling product. The iPr/nPr ratios were determined by HPLC on a C18 reversed phase HPLC column or by 1H NMR.

5. Optimization table
Table 1. Cross-coupling between aryl trflate 1 and isopropylboronic acid 2

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*The reactions were performed under nitrogen in toluene (2 mL) at 110 °C for 12 h in the presence of 1 mol % [Pd(cinnamyl)Cl]₂ and 4 mol % L1 with 1 (0.25 mmol), 2 (0.5 mmol), and K₃PO₄·H₂O (0.75 mmol). Conversions were analyzed by reversed phase HPLC on a C-18 column. Isolated yields. *Pr/InPr ratios were determined by ¹H NMR spectroscopy.

6. Gram scale synthesis of 4-isopropyl-3,5-dimethylbenzaldehyde (3p)

![Chemical structure of 1p](image)

\[
\text{OHC-} \quad 1p \quad \overset{[\text{Pd(cinnamyl)Cl}]_2(1 \text{ mol %})}{\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}, \text{toluene}}} \quad \text{OHC-} \quad 3p \\
(1.0 \text{ g}) \quad \text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}, \text{toluene} \quad 110^\circ\text{C}, 8\text{h}
\]

- Yield: 85%
- *Pr/InPr: 30 : 1

SI-8
Synthesis of compound 3p: To a mixture of compound 1p (1.0 g, 3.54 mmol, 1.0 equiv), isopropylboronic acid (0.69 g, 7.09 mmol, 2.0 equiv), potassium phosphate tribasic monohydrate (2.44 g, 10.62 mmol, 3.0 equiv), [Pd(cinnamyl)Cl]₂ (18.1 mg, 0.035 mmol, 2 mol % Pd), and L1 (54.4 mg, 0.14 mmol, 4 mol %) was charged dry toluene (10 mL). The mixture was stirred at 110 °C under nitrogen for 12 h and then cooled to room temperature, passed through a celite plug, washed with copious dichloromethane, concentrated, and purified by column chromatography to provide compound 3p (85% iPr:nPr = 30:1, determined by ¹H NMR analysis). Compound 3p: ¹H NMR (500 MHz, CDCl₃) δ 9.88 (d, J = 0.4 Hz, 1H), 7.46 (s, 2H), 3.49 (septet, J = 7.3 Hz, 1H), 2.45 (s, 6H), 1.40 (dd, J = 7.3, 0.4 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 192.3, 151.6, 137.0, 133.7, 127.5, 29.9, 21.4, 20.3; EI-MS: m/z 176.0 [M⁺]; HRMS (EI) m/z calcd for C₁₂H₁₆O (M): 176.1201, found: 176.1194.

7. Synthetic procedures of gossypol intermediate 11

![Diagram of reaction](image)

Synthesis of diene 7: To a solution of methyl 3-methylbut-2-enoate (g, 5.0 g, 43.8 mmol, 1.0 equiv) in THF (50 mL) at -78 °C was added dropwise LDA (2.0 M in THF, 24 mL, 48.21 mmol, 1.1 equiv) over 10 min. The mixture was stirred at -78 °C for 1 h and then TMSCl (6.75 mL, 52.6 mmol, 1.2 equiv) was added over 1 h. The resulting mixture was stirred at -78 °C for 20 min and then allowed to warm to rt over 1 h. The solvent was removed under reduced pressure and the slurry was retreated with pentane (60 mL). The resulting slurry was filtered through celite and concentrated under reduced pressure to afford the crude product 7 (6.76 g, 36.3 mmol, 83%) as yellow liquid and used directly for next step without further purification. Compound 7: ¹H NMR (300 MHz, C₆D₆) δ 5.13 (d, J = 2.0 Hz, 1H), 4.86 (d, J = 1.2 Hz, 1H), 4.36 (s, 1H), 3.03 (s, 3H), 2.17 (s, 3H), 0.18 (s, 9H); ¹³C NMR (101 MHz, C₆D₆) δ 157.60, 140.26, 108.44, 81.84, 54.67, 23.90, 0.43.
Synthesis of compound 8: To a 3-necked flask charged with a solution of 2,3,4-trimethoxybenzaldehyde (h, 5.0 g, 25.5 mmol, 1.0 equiv) was charged H$_2$O$_2$ (3.5 mL, 33.2 mmol, 1.3 equiv) and MeOH (50 mL) under nitrogen. Concentrated H$_2$SO$_4$ (0.5 mL) was added at 0 °C over 5 min and the resulting mixture was warmed to rt and further stirred for 1 h. 10% NaHCO$_3$ solution (50 mL) and DCM (50 mL) was added. The DCM layer was separated, washed with brine (50 mL), dried over sodium sulfate, concentrated, and purified by flash chromatography (eluent: hexanes/EtOAc = 5/1) to afford 2,3,4-trimethoxyphenol (i, 4.5 g, 24.5 mmol, 96%) as yellow liquid. Compound 8: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.61 (d, J = 9.0 Hz, 1H), 6.54 (d, J = 9.0 Hz, 1H), 5.57 (s, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.79 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 147.0, 143.5, 142.4, 140.6, 108.7, 107.8, 61.3, 61.0, 56.6; EI-MS: m/z 184.1 [M]$^+$; HRMS (EI) m/z calcd for C$_9$H$_{12}$O$_4$ (M): 184.0736, found: 184.0734.

To a mixture of 2,3,4-trimethoxyphenol (i, 3.0 g, 16.3 mmol, 1.0 equiv), CuCl$_2$ (2.19 g, 16.3 mmol, 1.0 equiv), EtOAc (35 mL) and H$_2$O (17.5 mL) in a three-necked flask under oxygen atmosphere was stirred at 70 °C for 3 h. The organic layer was separated and the aqueous layer was further washed with DCM (40 mL X 3). The combined organic layer was dried over sodium sulfate, concentrated, and purified by flash chromatography (eluent: Hexanes/EtOAc = 10/1) to afford compound 8 (1.7 g, 10.1 mmol, 62%) as orange solid. Compound 8: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.60 (s, 2H), 4.02 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 184.1, 145.1, 134.6, 61.3; EI-MS: m/z 168.2 [M]$^+$; HRMS (EI) m/z calcd for C$_8$H$_8$O$_4$(M): 168.0423, found: 168.0428.

Synthesis of compound 9: To a solution of compound 8 (1.62 g, 9.25 mmol, 2.0 equiv) in DCM (22 mL) was added 7 (0.90 g, 4.84 mmol, 1.0 equiv) over 5 min at room temperature. The mixture was stirred at rt for 20 h and then HOAc (0.57 mL, 10.65 mmol,
2.2 equiv) was added. The resulting mixture was further stirred at room temperature for 30 min and then concentrated. The residue was purified by flash chromatography (eluent: hexanes/EtOAc = 10/1) to afford 9 (960 mg, 3.66 mmol, 76%) as yellow solid. Compound 9: ¹H NMR (500 MHz, CDCl₃) δ 7.53 (s, 1H), 7.03 (s, 1H), 4.07 (s, 3H), 4.03 (s, 3H), 3.96 (s, 3H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 182.4, 180.8, 159.9, 148.3, 146.3, 145.8, 133.1, 120.1, 118.4, 116.3, 61.5, 61.2, 56.6, 22.3; EI-MS: m/z 262.0 [M⁺]; HRMS (EI) m/z calcd for C₁₄H₁₄O₅(M): 262.0841, found: 262.0845.

Synthesis of compound 10: To a solution of compound 9 (1.0 g, 3.8 mmol, 1.0 equiv) in DCM (40 mL) at rt was added BF₃·Et₂O (5 mL) and Et₃SiH (1.8 mL, 11.4 mmol, 3.0 equiv) under nitrogen. The mixture was stirred at rt for 6 h and then water (20 mL) was added. The organic phase was separated and the aqueous layer was extracted with DCM (40 mL X 3). The combined organic solution was dried over sodium sulfate, concentrated, and purified by flash chromatography (eluent: hexanes/EtOAc = 15/1), then to dissolve in DCM (10 mL) and TEA (1.6 mL, 11.5 mmol, 3 equiv) was added. The mixture was then cooled to -78 °C. Trifluoromethanesulfonic anhydride (0.7 mL, 4.2 mmol, 1.1 equiv) was added dropwise. After 2 h, the solution was allowed to warm to room temperature and stirred for 12 h. Thereafter, water (50 mL) was added, the organic layer was evaporated, washed with saturated brine and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure and the residue was directly subjected to purification by flash column chromatography to give the pure product 10 (1.01 g, 2.7 mmol, 60%) as white solid. Compound 10: ¹H NMR (500 MHz, CDCl₃) δ 7.56 (s, 1H), 7.23 (s, 1H), 6.66 (s, 1H), 4.02 (s, 3H), 4.00 (s, 3H), 3.99 (s, 3H), 2.50 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 154.2, 150.8, 141.9, 136.8, 136.0, 123.4, 120.4, 118.7 (q, J = 318.7 Hz), 111.5, 106.8, 102.1, 61.4, 56.1, 55.6, 22.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -73.2 (q, J = 3.9 Hz); EI-MS: m/z 380.0 [M⁺]; HRMS (EI) m/z calcd for C₁₅H₁₅F₃O₆S (M): 380.0541, found: 380.0538.
Synthesis of compound 11: To a mixture of compound 10 (38 mg, 0.10 mmol, 1.0 equiv), isopropylboronic acid (17 mg, 0.20 mmol, 2.0 equiv), potassium phosphate tribasic monohydrate (70 mg, 0.30 mmol, 3.0 equiv), [Pd(cinnamyl)Cl]$_2$ (0.38 mg, 0.001 mmol, 2 mol % Pd), and L2 (1.53 mg, 0.004 mmol, 4 mol %) was charged dry toluene (2 mL). The mixture was stirred at 110 °C under nitrogen for 8 h and then cooled to room temperature, passed through a celite plug, washed with copious dichloromethane, concentrated, and purified by column chromatography to provide compound 11 (mixture, 62% $i$Pr:nPr = 5.5:1, determined by $^1$H NMR analysis).

8. Analytical data of substrates

2-Methylnaphthalen-1-y1 trifluoromethanesulfonate(1a): The title product was obtained after column chromatography (hexane/EA=50/1) as a colourless oil with 61% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J$ = 8.6 Hz, 1H), 7.86 (d, $J$ = 8.2 Hz, 1H), 7.77 (d, $J$ = 8.4 Hz, 1H), 7.60~7.64 (m, 1H), 7.51~7.55 (m, 1H), 7.36 (d, $J$ = 8.4 Hz, 1H), 2.58 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 142.8, 133.5, 129.0, 128.5, 128.2, 127.8, 127.6, 127.1, 126.3, 120.9, 118.7(q, $J$ = 318.2 Hz), 17.2; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -73.2(t, $J$ = 4.2 Hz); EI-MS: m/z 290.0 [M]; HRMS (EI) m/z calcd for C$_{12}$H$_9$F$_3$O$_3$S (M): 290.0225, found: 290.0228.
2-methylnaphthalen-1-yl methanesulfonate: The title product was obtained after column chromatography (hexane/EtOAc=10/1) as a white solid with 86% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 1H), 3.36 (d, $J = 0.4$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.2, 133.6, 129.2, 128.9, 128.1, 127.9, 127.2 (d, $J = 4.7$ Hz), 126.0, 121.8, 39.4, 17.8; EI-MS: $m/z$ 236.0 [M]; HRMS (EI) $m/z$ calcd for C$_{12}$H$_{12}$O$_3$S (M): 236.0566, found: 290.0565.

2-methylnaphthalen-1-yl 4-methylbenzenesulfonate: The title product was obtained after column chromatography (hexane/EtOAc=50/1) as a white solid with 95% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.85 (td, $J = 8.6$, 2.1 Hz, 2H), 7.78 (d, $J = 8.2$ Hz, 1H), 7.73 (d, $J = 8.6$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.42~7.39 (m, 1H), 7.36~7.32 (m, 3H), 2.48 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 145.4, 143.9, 134.2, 133.5, 130.0, 129.1 (d, $J = 12.1$ Hz), 128.5, 128.2, 127.6, 126.9, 126.5, 125.8, 122.3, 21.9, 17.5; EI-MS: $m/z$ 312.0 [M]; HRMS (EI) $m/z$ calcd for C$_{18}$H$_{16}$O$_3$S (M): 312.0853, found: 290.0832.

4-Formylphenyl trifluoromethanesulfonate(1b): The title product was obtained after column chromatography (hexane/EtOAc=50/1) as a white solid with 81% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.04 (s, 1H), 7.98~8.01 (m, 2H), 7.45~7.47 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 190.1, 153.2, 135.9, 131.7, 22.2, 119.0 (q, $J = 319.0$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -73.4; EI-MS: $m/z$ 254.0 [M$^+$]; HRMS (EI) $m/z$ calcd for C$_8$H$_5$F$_3$O$_4$S (M): 253.9861, found: 253.9858.

2-Isopropylphenyl trifluoromethanesulfonate(1c): The title product was obtained after column chromatography (hexane/EtOAc=50/1) as a colourless oil with 90% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41 (dd, $J = 7.8$, 1.5 Hz, 1H), 7.37~7.33 (m, 1H), 7.27~7.22 (m, 2H), 3.30 (septet, $J = 6.9$ Hz, 1H), 1.27 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 147.1, 141.2, 128.6, 127.8, 127.4, 121.2, 118.6 (q, $J = 318.2$ Hz), 27.1, 23.1; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -74.0; EI-MS: $m/z$ 268.0 [M$^+$]; HRMS (EI) $m/z$ calcd for C$_{10}$H$_{11}$F$_3$O$_3$S (M): 268.0374, found: 268.0374.
4-Cyano-2-[(trifluoromethyl)phenyl] trifluoromethanesulfonate (1d): The title product was obtained after column chromatography (hexane/EA=50/1) as a yellow solid with 85% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.08 (d, J = 1.9 Hz, 1H), 7.99 (dd, J = 8.7, 2.1 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H); ^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 148.8, 137.8, 132.2(q, J = 5.0 Hz), 125.0, 123.7, 120.9 (q, J = 321.1 Hz), 119.9, 116.0, 113.1; ^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -61.5 (d, J = 2.2 Hz), -73.2 (t, J = 5.0 Hz); EI-MS: m/z 319.0 [M]; HRMS (EI) m/z calcd for C\(_{19}\)H\(_{13}\)F\(_6\)NO\(_3\)S (M): 318.9738, found: 318.9741.

5-Formyl-2-methoxyphenyl trifluoromethanesulfonate (1e): The title product was obtained after column chromatography (hexane/EA=20/1) as a white solid with 99% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 9.87 (s, 1H), 7.87 (dd, J = 8.5, 2.0 Hz, 1H), 7.74 (d, J = 2.0 Hz, 1H), 7.17 (d, J = 8.5 Hz, 1H), 4.00 (s, 3H); ^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 189.0, 156.2, 139.1, 132.0, 129.9, 122.8, 118.6 (q, J = 318.7 Hz), 112.9, 56.7; ^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -73.3;\) EI-MS: m/z 284.0 [M]; HRMS (EI) m/z calcd for C\(_{9}\)H\(_{7}\)F\(_3\)O\(_5\)S (M): 283.9966, found: 283.9968.

Naphthalen-1-yl trifluoromethanesulfonate (1f): The title product was obtained after column chromatography (hexane) as a colourless oil with 84% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.10 (d, J = 8.4 Hz, 1H), 7.92(d, J = 8.2 Hz, 1H), 7.88 (dd, J = 6.8, 2.3 Hz, 1H), 7.64~7.68 (m, 1H), 7.59~7.62 (m, 1H), 7.47~7.51 (m, 2H); ^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 145.7, 134.9, 128.5, 128.1, 127.8, 127.4, 126.4, 125.1, 120.8, 118.8 (q, J = 318.4 Hz), 117.8; ^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -73.4;\) EI-MS: m/z 276.0 [M]; HRMS (EI) m/z calcd for C\(_{11}\)H\(_{7}\)F\(_3\)O\(_3\)S (M): 276.0068, found: 276.0070.

Tert-butyl 4-[(trifluoromethyl)sulfonyl]oxy)-1H-indole-1-carboxylate (1g): The title product was obtained after column chromatography (hexane/EA=10/1) as a colourless oil with 75% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.21 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 2.7 Hz, 1H), 7.17~7.34 (m, 1H), 7.18 (d, J = 8.1 Hz, 1H), 6.69 (d, J = 3.1 Hz, 1H), 1.69 (d, J = 3.1 Hz, 9H); ^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 149.1, 141.9, 137.1, 127.5, 124.6, 123.7, 118.8 (q, J = 318.8 Hz), 115.4, 114.8, 102.9, 84.7, 28.1; ^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -73.3 (q, J = 2.5 Hz);\) EI-MS: m/z 365.0 [M]; HRMS (EI) m/z calcd for C\(_{14}\)H\(_{14}\)F\(_3\)NO\(_3\)S (M): 365.0545, found: 365.05544.
2-Methoxy-4-methylphenyl trifluoromethanesulfonate (1h): The title product was obtained after column chromatography (hexane/EA=50/1) as a colourless oil with 99% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.08 (d, $J$ = 8.3 Hz, 1H), 6.83 (d, $J$ = 1.3 Hz, 1H), 6.76 (dd, $J$ = 8.2, 1.2 Hz, 1H), 3.89 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.0, 139.7, 136.7, 121.9, 121.3, 118.7 (q, $J$ = 318.7 Hz), 113.9, 56.0, 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -74.0 (d); EI-MS: m/z 270.0 [M]$^+$; HRMS (EI) m/z calcd for C$_9$H$_9$F$_3$O$_4$S (M): 270.0174, found: 270.0164.

4-Cyano-2-methoxyphenyl trifluoromethanesulfonate (1i): The title product was obtained after column chromatography (hexane/EA=20/1) as a yellow solid with 98.4% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.12 (d, $J$ = 1.6 Hz, 2H), 7.30 (s, 1H), 3.97 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 152.0, 141.6, 125.3, 123.7, 118.6 (q, $J$ = 318.8 Hz), 117.3, 116.5, 113.3, 56.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -73.7; EI-MS: m/z 281.0 [M]$^+$; HRMS (EI) m/z calcd for C$_9$H$_6$F$_3$NO$_4$S (M): 280.9970, found: 280.9976.

4-Formyl-2-methoxyphenyl trifluoromethanesulfonate (1j): The title product was obtained after column chromatography (hexane/EA=10/1) as a white solid with 93% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.96 (s, 1H), 7.55 (d, $J$ = 1.8 Hz, 1H), 7.49 (dd, $J$ = 8.2, 1.9 Hz, 1H), 7.39 (d, $J$ = 8.2 Hz, 1H), 3.97 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 190.3, 152.2, 142.6, 136.8, 124.0, 123.1, 118.6 (q, $J$ = 318.6 Hz), 111.8, 56.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -73.9 (d, $J$ = 6.2 Hz); EI-MS: m/z 284.0 [M]$^+$; HRMS (EI) m/z calcd for C$_9$H$_7$F$_3$O$_5$S (M): 283.9966, found: 283.9958.

2-Formyl-4-methoxyphenyl trifluoromethanesulfonate (1k): The title product was obtained after column chromatography (hexane/EA=50/1) as a colourless oil with 90% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.87 (s, 1H), 7.87 (dd, $J$ = 8.5, 2.0 Hz, 1H), 7.74 (d, $J$ = 2.0 Hz, 1H), 7.17 (d, $J$ = 8.5 Hz, 1H), 4.00 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 189.0, 156.2, 139.1, 132.0, 129.98, 122.8, 118.6 (q, $J$ = 318.6 Hz), 112.9, 56.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -73.8; EI-MS: m/z 284.0 [M]$^+$; HRMS (EI) m/z calcd for C$_9$H$_7$F$_3$O$_5$S (M): 283.9966, found: 283.9970.
4-Formyl-2-methylphenyl trifluoromethanesulfonate (1l): The title product was obtained after column chromatography (hexane/EtOAc=50/1) as a white solid with 81% yield. \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 10.01 (s, 1H), 7.86 (d, \( J = 1.2 \) Hz, 1H), 7.79–7.82 (m, 1H), 7.44 (d, \( J = 8.4 \) Hz, 1H), 2.47 (s, 3H); \(^1^C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 190.4, 152.1, 135.7, 133.3, 132.2, 129.2, 122.2, 118.6 (q, \( J = 318.5 \) Hz), 16.4; \(^1^F\) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -73.6 (d, \( J = 2.5 \) Hz); EI-MS: m/z 268.0 [M]; HRMS (EI) m/z calcd for C\(_9\)H\(_7\)F\(_3\)O\(_4\)S (M): 268.0017, found: 268.0013.

2,6-Dimethylphenyl trifluoromethanesulfonate (1m): The title product was obtained after column chromatography (hexane) as a colourless oil with 90% yield. \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.11–7.17 (m, 3H), 2.39 (s, 6H); \(^1^C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 146.9, 131.5, 129.9, 128.0, 118.6 (q, \( J = 317.9 \) Hz), 17.1; \(^1^F\) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -73.6 (d, \( J = 9.0 \) Hz); EI-MS: m/z 254.0 [M]; HRMS (EI) m/z calcd for C\(_9\)H\(_9\)F\(_3\)O\(_3\)S (M): 254.0225, found: 254.0217.

Mesityl trifluoromethanesulfonate (1n): The title product was obtained after column chromatography (hexane) as a colourless oil with 91% yield. \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 6.92 (s, 2H), 2.34 (s, 6H), 2.28 (s, 3H); \(^1^C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 144.8, 137.8, 131.0, 130.4, 118.6 (q, \( J = 317.9 \) Hz), 20.6, 17.0; \(^1^F\) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -73.64 (t, \( J = 4.6 \) Hz); EI-MS: m/z 268.0[M]; HRMS (EI) m/z calcd for C\(_{10}\)H\(_{11}\)F\(_3\)O\(_3\)S (M): 268.0367, found: 268.0368.

4-Cyano-2,6-dimethylphenyl trifluoromethanesulfonate (1o): The title product was obtained after column chromatography (hexane/EtOAc=40/1) as a yellow solid with 72% yield. \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.45 (s, 2H), 2.43 (s, 6H); \(^1^C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 149.3, 133.6, 133.5, 118.5 (q, \( J = 318.2 \) Hz), 117.4, 112.3, 17.1; \(^1^F\) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -73.1; EI-MS: m/z 279.0 [M]; HRMS (EI) m/z calcd for C\(_{10}\)H\(_8\)F\(_3\)NO\(_3\)S (M): 279.0177, found:279.0174.
4-Formyl-2,6-dimethylphenyl trifluoromethanesulphonate (1p): The title product was obtained after column chromatography (hexane/EtOAc = 50/1) as a white solid with 55% yield. °H NMR (500 MHz, CDCl₃) δ 9.96 (s, 1H), 7.66 (s, 2H), 2.47 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 190.8, 150.6, 135.3, 133.0, 131.0, 118.5 (q, J = 318.2 Hz), 17.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -73.8; EI-MS: m/z 282.0 [M]+; HRMS (EI) m/z calcd for C₁₀H₉F₃O₄S (M): 282.1074, found: 282.1065.

1H-Inden-2-yl trifluoromethanesulphonate (1ua): The title product was obtained after column chromatography (hexane) as a colourless oil with 76% yield. °H NMR (500 MHz, CDCl₃) δ 7.36~7.40 (m, 2H), 7.29~7.33 (m, 1H), 7.27 (td, J = 7.4, 1.4 Hz, 1H), 7.69 (s, 1H), 3.67 (t, J = 0.6, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 153.3, 140.3, 137.5, 127.4, 126.3, 123.9, 122.3, 119.6, 118.8 (q, J = 319.3 Hz), 37.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -72.9 (t, J = 2.0); EI-MS: m/z 264.0 [M]+; HRMS (EI) m/z calcd for C₁₀H₇F₃O₃S (M): 264.0068, found: 264.0065.

3,4-Dihydronaphthalen-1-yl trifluoromethanesulphonate (1ub): The title product was obtained after column chromatography (hexane/EtOAc = 50/1) as a colourless oil with 63% yield. °H NMR (500 MHz, CDCl₃) δ 7.34~7.37 (m, 1H), 7.24~7.29 (m, 2H), 7.17~7.19 (m, 1H), 6.02 (t, J = 4.8, 1H), 2.88 (t, J = 8.1, 1H), 2.49~2.54 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 146.3, 136.2, 129.2, 128.6, 127.7, 126.9, 121.2 118.6 (q, J = 318.4 Hz), 117.7, 26.8, 22.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -73.7 ; EI-MS: m/z 278.0 [M]+; HRMS (EI) m/z calcd for C₁₁H₉F₃O₃S (M): 278.0225, found: 278.0216.

6,7-Dihydro-5H-benzo[7]annulen-9-yl trifluoromethanesulphonate (1uc): The title product was obtained after column chromatography (hexane) as a colourless oil with 77% yield. °H NMR (500 MHz, CDCl₃) δ 7.51~7.54 (m, 1H), 7.29~7.32 (m, 2H), 7.22~7.24 (m, 1H), 6.23 (t, J = 6.3, 1H ), 2.79 (m, 2H), 2.24 (q, J = 7.0, 2H), 2.05~2.11 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 146.2, 141.7, 132.1, 129.6, 129.4, 126.6, 126.5, 123.5, 118.7 (q, J = 318.6 Hz), 33.6, 30.7, 25.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.0 (t, J = 4.7 Hz); EI-MS: m/z 292.0 [M]+; HRMS (EI) m/z calcd for C₁₂H₁₁F₃O₃S (M): 292.0381, found: 292.0376.
2H-Chromen-4-yl trifluoromethanesulfonate (1ud): The title product was obtained after column chromatography (hexane) as a colourless oil with 43% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.22–7.27 (m, 2H), 6.98 (dt, $J = 7.7$, 1.1 Hz, 1H), 6.85 (dd, $J = 8.5$, 1.0 Hz, 1H), 5.76 (t, $J = 3.9$, 1H), 4.99 (d, $J = 3.9$, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 155.0, 143.1, 131.5, 121.8, 121.7, 118.5(q, $J = 318.6$ Hz), 117.3, 116.3, 110.0, 65.0; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -73.5; EI-MS: $m/z$ 280.0 [M]$^+$; HRMS (EI) $m/z$ calcd for C$_{10}$H$_7$F$_3$O$_4$S (M): 280.0017, found: 280.0010.

2-Methyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (1uf): The title product was obtained after column chromatography (hexane) as a colourless oil with 48% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31 (d, $J = 7.6$ Hz, 1H), 7.18–7.27 (m, 2H), 7.14 (d, $J = 7.3$ Hz, 1H), 2.85 (t, $J = 7.9$, 2H), 2.43 (t, $J = 8.1$, 2H), 2.00 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 140.9, 135.1, 129.7, 129.5, 128.0, 127.3, 126.7, 120.8, 118.5(q, $J = 318.0$ Hz), 29.8, 27.1, 17.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -73.8; EI-MS: $m/z$ 292.0 [M]$^+$; HRMS (EI) $m/z$ calcd for C$_{12}$H$_{11}$F$_3$O$_3$S (M): 292.0356, found: 292.0312.

9. X-ray structure of naphthol 10a
CCDC 1567308 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
Crystal data and structure refinement for naphthol 10a.

Identification code          cd214576
Empirical formula           C14 H16 O4
Formula weight              248.27
Temperature                 293(2) K
Wavelength                  0.71073 Å
Crystal system              Monoclinic
Space group                 P 21/c
Unit cell dimensions
a = 13.9254(13) Å           a = 90°.
b = 17.3264(16) Å           b = 100.865(2)°.
c = 11.0023(10) Å           g = 90°.
Volume                      2607.0(4) Å³
Z                            8
Density (calculated)        1.265 Mg/m³
Absorption coefficient      0.092 mm⁻¹
F(000)                      1056
Crystal size                0.211 x 0.165 x 0.123 mm³
Theta range for data collection  1.897 to 25.996°.
Index ranges                -10<=h<=17, -21<=k<=21, -13<=l<=13
Reflections collected       15679
Independent reflections    5117 [R(int) = 0.0366]
Completeness to theta       25.242° 100.0 %
Absorption correction       Semi-empirical from equivalents
Max. and min. transmission 0.7457 and 0.6067
Refinement method Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters 5117 / 0 / 342
Goodness-of-fit on \( F^2 \) 1.029
Final R indices [I>2\( \sigma(I) \)] R1 = 0.0454, wR2 = 0.1172
R indices (all data) R1 = 0.0728, wR2 = 0.1323
Extinction coefficient 0.0051(8)
Largest diff. peak and hole 0.194 and -0.147 e.Å\(^{-3}\)

10. References

11. NMR spectra of substrates
$^{13}$C NMR of

$^{19}$F NMR of
\( ^{13}\text{C NMR of} \)

\( ^{19}\text{F NMR of} \)
SI-34
**SI-48**

**1H NMR of**

![1H NMR spectrum](image)

**13C NMR of**

![13C NMR spectrum](image)
$^{19}$F NMR of

$^1$H NMR of
12. NMR spectra of products
$^1$H NMR of

$^{13}$C NMR of

SI-62
$^{13}$C NMR of

$^1$H NMR of
\[ ^{13}C \text{ NMR of } \]

\[ ^{1}H \text{ NMR of } \]