Palladium-catalyzed asymmetric 1,6-addition of diarylphosphines to \(\alpha,\beta,\gamma,\delta\)-unsaturated sulfonic esters: controlling regioselectivity by rational selection of electron-withdrawing groups

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Supporting Information

Table of Contents

General Methods S2
Experimental Details and Characterization Data S2-S19
Reference S19
NMR Spectra S20-S55
HPLC Chart S56-S74
X-Ray Data S75-S76
General Methods

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on a Varian instrument (300 MHz, 75 MHz and 121Hz; 400 MHz, 100 MHz and 162 MHz, respectively). $^1$H, $^{13}$C NMR chemical shifts are reported vs tetramethylsilane signal or residual protio solvent signals.

Toluene and THF were distilled over sodium benzophenone ketyl under nitrogen. Dichloromethane and tert-amyl alcohol was distilled over CaH$_2$ under nitrogen.

The pincer-PdOAc catalysts$^1$, diarylphosphine$^2$ and $\alpha$,$\beta$-unsaturated sulfonic esters$^3$ were synthesized following the literature procedures. All other chemicals and solvents were purchased from commercial company and used as received.

Experimental Details and Characterization Data

General Experimental Procedures for Table 2.

Diarylphosphine (0.20 mmol) was added to a solution of (S,S)-Pd catalyst (6.7 mg, 10 $\mu$mol Pd) and $\alpha$,$\beta$,$\gamma$,$\delta$-unsaturated sulfonic ester 1 (0.21 mmol) in toluene (4.0 mL) at $-60$ °C (realized with a refrigerated bath circulator), then the resulting solution was stirred for 24 h at the same temperature. The reaction was quenched with 30% H$_2$O$_2$ aqueous solution (0.1 mL) and concentrated under vacuum. The residue was purified by silica gel chromatography with CH$_2$Cl$_2$/MeOH = 100/1 to afford the 1,6-adduct.

Entry 1. White solid. (80.2 mg; 81% yield). The ee was determined on a Daicel Chiralcel OD column with hexane/2-propanol = 70/30, flow = 0.7 mL/min. Retention times: 12.2 min [(R)-enantiomer], 14.1 min [(S)-enantiomer]. 94% ee. $[\alpha]^{20}_D = -12.1$
(c 0.500, CH₂Cl₂), The absolute configuration was assigned by analogy with Table 2, entry 4.

$^1$H NMR (400 MHz, CDCl₃): $\delta$ 7.89-7.83 (m, 2H, Ar), 7.61-7.45 (m, 5H, Ar), 7.40-7.35 (m, 1H, Ar), 7.29-7.18 (m, 7H, Ar), 6.36-6.16 (m, 1H, olefin), 5.58-5.48 (m, 1H, olefin), 4.33-4.21 (m, 3H), 3.89-3.76 (m, 2H, CH₂S). $^{13}$C NMR (100 MHz, CDCl₃): $\delta$ 136.7 (d, $J_{CP} = 6.4$ Hz), 134.5 (d, $J_{CP} = 5.7$ Hz), 132.3 (d, $J_{CP} = 2.7$ Hz), 131.8 (d, $J_{CP} = 3.0$ Hz), 131.6 (d, $J_{CP} = 8.7$ Hz), 131.19 (d, $J_{CP} = 8.8$ Hz), 131.16 (d, $J_{CP} = 96.1$ Hz), 131.0 (d, $J_{CP} = 97.2$ Hz), 129.4 (d, $J_{CP} = 5.7$ Hz), 128.9 (d, $J_{CP} = 10.3$ Hz), 128.85, 128.4 (d, $J_{CP} = 11.8$ Hz), 127.7 (d, $J_{CP} = 2.3$ Hz), 121.9 (q, $J_{CF} = 277.8$ Hz), 119.8 (d, $J_{CP} = 11.0$ Hz), 65.1 (q, $J_{CF} = 37.8$ Hz), 55.0 (d, $J_{CP} = 1.9$ Hz), 51.6 (d, $J_{CP} = 64.5$ Hz). $^{31}$P{$^1$H} NMR (161 MHz, CDCl₃): $\delta$ 28.2 (s). HRMS (ESI) calcd for C₂₄H₂₃F₃O₄PS (M+H)$^+$: 495.1001, found: 495.1002.

**Entry 2.** White solid. (79.1 mg; 78% yield). The ee was determined on a Daicel Chiralpak AD column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 86.7 min ([R]-enantiomer), 98.5 min ([S]-enantiomer). 94% ee. $\lbrack \alpha \rbrack_{D}^{20} = -5.2$ (c 0.50, CH₂Cl₂), The absolute configuration was assigned by analogy with Table 2, entry 4.

$^1$H NMR (400 MHz, CDCl₃): $\delta$ 7.86-7.82 (m, 2H, Ar), 7.56-7.48 (m, 5H, Ar), 7.40-7.35 (m, 1H, Ar), 7.31-7.25 (m, 2H, Ar), 7.15 (d, $J = 7.6$ Hz, 2H, Ar), 7.02 (d, $J = 7.6$ Hz, 2H, Ar), 6.36-6.16 (m, 1H, olefin), 5.55-5.46 (m, 1H, olefin), 4.33-4.15 (m, 3H), 3.89-3.75 (m, 2H, CH₂S), 2.26 (s, 3H, Me). $^{13}$C NMR (100 MHz, CDCl₃): $\delta$ 137.5 (d, $J_{CP} = 2.3$ Hz), 137.0 (d, $J_{CP} = 6.0$ Hz), 132.2 (d, $J_{CP} = 3.0$ Hz), 131.8 (d, $J_{CP} = 2.7$ Hz), 131.6 (d, $J_{CP} = 8.8$ Hz), 131.4 (d, $J_{CP} = 6.1$ Hz), 131.31 (d, $J_{CP} = 89.0$ Hz), 131.29 (d, $J_{CP} = 9.1$ Hz), 130.21 (d, $J_{CP} = 96.9$ Hz), 129.6 (d, $J_{CP} = 1.5$ Hz), 129.3 (d, $J_{CP} = 5.7$ Hz), 128.9 (d, $J_{CP} = 11.4$ Hz), 128.4 (d, $J_{CP} = 11.8$ Hz), 121.9 (q, $J_{CF} = 277.7$ Hz), 119.6 (d, $J_{CP} = 11.0$ Hz), 65.1 (q, $J_{CF} = 38.2$ Hz), 55.0 (d, $J_{CP} = 1.9$ Hz), 51.2 (d,
\(J_{CP} = 64.8\, \text{Hz}\). \(^{31}\text{P}\{^1\text{H}\}\) NMR (161 MHz, CDCl\(_3\)): \(\delta 28.2\) (s). HRMS (ESI) calcd for C\(_{25}\)H\(_{25}\)F\(_3\)O\(_5\)PS (M+H\(^+\)): 509.1158, found: 509.1156.

**Entry 3.** White solid. (66.3 mg; 63\% yield). The ee was determined on a Daicel Chiralcel OD column with hexane/2-propanol = 85/15, flow = 1.0 mL/min. Retention times: 15.4 min [(R)-enantiomer], 26.6 min [(S)-enantiomer]. 96\% ee. \([\alpha]^{20}_D = -18.4\) (c 0.50, CH\(_2\)Cl\(_2\)). The absolute configuration was assigned by analogy with Table 2, entry 4.

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.86-7.82\) (m, 2H, Ar), 7.56-7.46 (m, 5H, Ar), 7.40-7.35 (m, 1H, Ar), 7.31-7.25 (m, 2H, Ar), 7.15 (dd, \(J = 6.8\) and 1.6 Hz, 2H, Ar), 6.75 (d, \(J = 8.8\) Hz, 2H, Ar), 6.32-6.22 (m, 1H, olefin), 5.55-5.46 (m, 1H, olefin), 4.31-4.15 (m, 3H), 3.87-3.75 (m, 2H, CH\(_2\)S), 3.75 (s, 3H, OMe). \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta 159.0\) (d, \(J_{CP} = 2.3\) Hz), 136.8 (d, \(J_{CP} = 6.1\) Hz), 132.2 (d, \(J_{CP} = 2.7\) Hz), 131.8 (d, \(J_{CP} = 3.0\) Hz), 131.6 (d, \(J_{CP} = 8.3\) Hz), 131.21 (d, \(J_{CP} = 9.1\) Hz), 131.18 (d, \(J_{CP} = 99.1\) Hz), 131.0 (d, \(J_{CP} = 96.5\) Hz), 130.5 (d, \(J_{CP} = 5.7\) Hz), 128.9 (d, \(J_{CP} = 11.3\) Hz), 128.4 (d, \(J_{CP} = 11.7\) Hz), 126.5 (d, \(J_{CP} = 6.1\) Hz), 121.9 (q, \(J_{CF} = 278.1\) Hz), 119.6 (d, \(J_{CP} = 11.0\) Hz), 114.3 (d, \(J_{CP} = 1.9\) Hz), 65.1 (q, \(J_{CF} = 37.8\) Hz), 55.2, 54.9 (d, \(J_{CP} = 1.2\) Hz), 50.6 (d, \(J_{CP} = 65.2\) Hz). \(^{31}\text{P}\{^1\text{H}\}\) NMR (161 MHz, CDCl\(_3\)): \(\delta 28.2\) (s). HRMS (ESI) calcd for C\(_{25}\)H\(_{25}\)F\(_3\)O\(_3\)PS (M+H\(^+\)): 525.1107, found: 525.1106.

**Entry 4.** White solid. (88.3 mg; 87\% yield). The ee was determined on a Daicel Chiralpak AD column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 15.4 min [(R)-enantiomer], 26.6 min [(S)-enantiomer].
times: 18.7 min [(R)-enantiomer], 20.8 min [(S)-enantiomer]. 93% ee. \( \alpha \)^{20}_D = -11.9 (c 0.500, CH₂Cl₂). The absolute configuration was determined as S according to the X-ray crystal diffraction analysis of the product.

\(^1\)H NMR (400 MHz, CDCl₃): δ 7.87-7.82 (m, 2H, Ar), 7.55-7.46 (m, 5H, Ar), 7.40-7.35 (m, 1H, Ar), 7.31-7.25 (m, 2H, Ar), 7.10-7.00 (m, 3H, Ar), 7.00 (d, \( J = 7.2 \) Hz, 1H, Ar), 6.35-6.28 (m, 1H, olefin), 5.57-5.48 (m, 1H, olefin), 4.32-4.15 (m, 3H), 3.88-3.75 (m, 2H, CH₂S), 2.23 (s, 3H, Me). \(^{13}\)C NMR (100 MHz, CDCl₃): δ 138.5 (d, \( J_{\text{CP}} = 1.9 \) Hz), 136.7 (d, \( J_{\text{CP}} = 6.3 \) Hz), 134.3 (d, \( J_{\text{CP}} = 5.9 \) Hz), 132.2 (d, \( J_{\text{CP}} = 3.0 \) Hz), 131.8 (d, \( J_{\text{CP}} = 3.0 \) Hz), 131.6 (d, \( J_{\text{CP}} = 8.2 \) Hz), 131.3 (d, \( J_{\text{CP}} = 9.0 \) Hz), 131.2 (d, \( J_{\text{CP}} = 99.1 \) Hz), 131.0 (d, \( J_{\text{CP}} = 96.9 \) Hz), 130.0 (d, \( J_{\text{CP}} = 5.6 \) Hz), 128.9 (d, \( J_{\text{CP}} = 11.5 \) Hz), 128.7 (d, \( J_{\text{CP}} = 1.5 \) Hz), 128.4 (d, \( J_{\text{CF}} = 2.3 \) Hz), 128.3 (d, \( J_{\text{CP}} = 11.9 \) Hz), 126.4 (d, \( J_{\text{CP}} = 6.0 \) Hz), 121.9 (q, \( J_{\text{CF}} = 278.3 \) Hz), 119.7 (d, \( J_{\text{CP}} = 11.2 \) Hz), 65.1 (q, \( J_{\text{CP}} = 38.1 \) Hz), 55.0 (d, \( J_{\text{CP}} = 1.5 \) Hz), 51.6 (d, \( J_{\text{CP}} = 64.3 \) Hz), 21.4. \(^{31}\)P\(^{1}\)H NMR (161 MHz, CDCl₃): δ 28.1 (s). HRMS (ESI) calcd for C\(_{25}\)H\(_{25}\)F\(_3\)O\(_4\)PS (M+H\(^+\)): 509.1158, found: 509.1162.

**Entry 5.** White solid. (82.1 mg; 78% yield). The ee was determined on a Daicel Chiralpak AD column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 24.8 min [(R)-enantiomer], 30.7 min [(S)-enantiomer]. 95% ee. The absolute configuration was assigned by analogy with Table 2, entry 4.

\(^1\)H NMR (400 MHz, CDCl₃): δ 7.88-7.82 (m, 2H, Ar), 7.55-7.46 (m, 5H, Ar), 7.40-7.35 (m, 1H, Ar), 7.31-7.25 (m, 2H, Ar), 7.13 (t, \( J = 8.0 \) Hz, 1H, Ar), 6.86-6.79 (m, 2H, Ar), 6.73 (d, \( J = 8.4 \) Hz, 1H, Ar), 6.35-6.28 (m, 1H, olefin), 5.55-5.48 (m, 1H, olefin), 4.32-4.15 (m, 3H), 3.88-3.75 (m, 2H, CH₂S), 3.68 (s, 3H, OMe). \(^{13}\)C NMR (100 MHz, CDCl₃): δ 159.8 (d, \( J_{\text{CP}} = 1.6 \) Hz), 136.6 (d, \( J_{\text{CP}} = 6.5 \) Hz), 136.0 (d, \( J_{\text{CP}} = 5.6 \) Hz), 132.3 (d, \( J_{\text{CP}} = 2.6 \) Hz), 131.9 (d, \( J_{\text{CP}} = 3.1 \) Hz), 131.6 (d, \( J_{\text{CP}} = 8.4 \) Hz), 131.3 (d, \( J_{\text{CP}} = 9.1 \) Hz), 131.2 (d, \( J_{\text{CP}} = 99.2 \) Hz), 131.0 (d, \( J_{\text{CP}} = 96.9 \) Hz), 129.8 (d,
$J_{\text{CP}} = 1.6$ Hz), 128.9 (d, $J_{\text{CP}} = 11.7$ Hz), 128.4 (d, $J_{\text{CP}} = 11.7$ Hz), 121.9 (q, $J_{\text{CF}} = 278.1$ Hz), 121.8 (d, $J_{\text{CP}} = 6.0$ Hz), 119.8 (d, $J_{\text{CP}} = 11.0$ Hz), 114.7 (d, $J_{\text{CP}} = 5.7$ Hz), 113.6 (d, $J_{\text{CP}} = 2.3$ Hz), 65.1 (q, $J_{\text{CF}} = 38.3$ Hz), 55.3, 55.0 (d, $J_{\text{CP}} = 1.9$ Hz), 51.7 (d, $J_{\text{CP}} = 64.5$ Hz). $^{31}P\{^1H\}$ NMR (161 MHz, CDCl$_3$): $\delta$ 28.2 (s). HRMS (ESI) calcd for C$_{25}$H$_{25}$F$_3$O$_5$PS (M+H)$^+$: 525.1107, found: 525.1107.

Entry 6. White solid. (95.0 mg; 87% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 19.1 min [(R)-enantiomer], 25.2 min [(S)-enantiomer]. 90% ee. [$\alpha$]$^2$$_D = -6.4$ (c 0.50, CH$_2$Cl$_2$), The absolute configuration was assigned by analogy with Table 2, entry 4.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.91-7.83 (m, 2H, Ar), 7.75-7.68 (m, 4H, Ar), 7.60-7.35 (m, 5H, Ar), 7.45-7.37 (m, 3H, Ar), 7.31 (t, $J = 7.6$ Hz, 1H, Ar), 7.22 (dd, $J = 7.6$ and 2.8 Hz, 2H, Ar), 6.45-6.37 (m, 1H, olefin), 5.60-5.52 (m, 1H, olefin), 4.50 (t, $J = 9.2$ Hz, 1H, PCH), 4.32-4.17 (m, 2H, OCH$_2$), 3.87-3.75 (m, 2H, CH$_2$S). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 136.6 (d, $J_{\text{CP}} = 6.3$ Hz), 133.4 (d, $J_{\text{CP}} = 1.9$ Hz), 132.6 (d, $J_{\text{CP}} = 1.5$ Hz), 132.3 (d, $J_{\text{CP}} = 2.6$ Hz), 132.1 (d, $J_{\text{CP}} = 6.0$ Hz), 131.9 (d, $J_{\text{CP}} = 2.6$ Hz), 131.6 (d, $J_{\text{CP}} = 8.5$ Hz), 131.2 (d, $J_{\text{CP}} = 8.9$ Hz), 131.1 (d, $J_{\text{CP}} = 98.4$ Hz), 131.05 (d, $J_{\text{CP}} = 97.3$ Hz), 128.9 (d, $J_{\text{CP}} = 11.6$ Hz), 128.62 (d, $J_{\text{CP}} = 8.2$ Hz), 128.60, 128.4 (d, $J_{\text{CP}} = 11.9$ Hz), 127.9, 127.7, 127.1 (d, $J_{\text{CP}} = 4.8$ Hz), 126.4, 126.2, 121.9 (q, $J_{\text{CF}} = 277.9$ Hz), 120.0 (d, $J_{\text{CP}} = 11.2$ Hz), 65.0 (q, $J_{\text{CF}} = 38.1$ Hz), 55.9 (d, $J_{\text{CP}} = 1.4$ Hz), 51.7 (d, $J_{\text{CP}} = 64.4$ Hz). $^{31}P\{^1H\}$ NMR (161 MHz, CDCl$_3$): $\delta$ 32.1 (s). HRMS (ESI) calcd for C$_{28}$H$_{25}$F$_3$O$_4$PS (M+H)$^+$: 545.1158, found: 545.1161.
**Entry 7.** White solid. (89.7 mg; 85% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 13.2 min [(R)-enantiomer], 17.0 min [(S)-enantiomer]. 88% ee. \( \alpha^{20}_{\text{D}} = -20.7 \) (c 0.500, CH\(_2\)Cl\(_2\)). The absolute configuration was assigned by analogy with Table 2, entry 4.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.87-7.81 (m, 2H, Ar), 7.58-7.45 (m, 5H, Ar), 7.41-7.35 (m, 1H, Ar), 7.35-7.28 (m, 2H, Ar), 7.24-7.17 (m, 4H, Ar), 6.32-6.21 (m, 1H, olefin), 5.56-5.46 (m, 1H, olefin), 4.30-4.15 (m, 3H), 3.87-3.75 (m, 2H, CH\(_2\)S).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 136.2 (d, \( J_{\text{CP}} = 6.4 \) Hz), 133.7 (d, \( J_{\text{CP}} = 2.6 \) Hz), 133.1 (d, \( J_{\text{CP}} = 6.1 \) Hz), 132.4 (d, \( J_{\text{CP}} = 2.6 \) Hz), 132.1 (d, \( J_{\text{CP}} = 2.7 \) Hz), 131.6 (d, \( J_{\text{CP}} = 8.8 \) Hz), 131.1 (d, \( J_{\text{CP}} = 9.1 \) Hz), 130.9 (d, \( J_{\text{CP}} = 99.2 \) Hz), 130.7 (d, \( J_{\text{CP}} = 5.3 \) Hz), 130.67 (d, \( J_{\text{CP}} = 97.6 \) Hz), 129.04 (d, \( J_{\text{CP}} = 3.7 \) Hz), 128.99 (d, \( J_{\text{CP}} = 9.4 \) Hz), 121.9 (q, \( J_{\text{CF}} = 278.1 \) Hz), 120.2 (d, \( J_{\text{CP}} = 11.0 \) Hz), 64.9 (q, \( J_{\text{CF}} = 37.7 \) Hz), 54.9 (d, \( J_{\text{CP}} = 1.9 \) Hz), 51.9 (d, \( J_{\text{CP}} = 64.1 \) Hz). \(^{31}\)P\(^{1}\)H NMR (161 MHz, CDCl\(_3\)): \( \delta \) 27.9 (s). HRMS (ESI) calcd for C\(_{24}\)H\(_{22}\)ClF\(_3\)O\(_4\)PS (M+H): 529.0612, found: 529.0616.

**Entry 8.** White solid. (99.5 mg; 87% yield). The ee was determined on a Daicel Chiralpak AD column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 40.3 min [(S)-enantiomer], 53.1 min [(R)-enantiomer]. 93% ee. \( \alpha^{20}_{\text{D}} = -25.9 \) (c 0.500, CH\(_2\)Cl\(_2\)). The absolute configuration was assigned by analogy with Table 2, entry 4.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.89-7.83 (m, 2H, Ar), 7.61-7.48 (m, 5H, Ar), 7.40-7.38 (m, 1H, Ar), 7.35-7.30 (m, 4H, Ar), 7.15 (d, \( J = 6.8 \) Hz, 2H, Ar), 6.30-6.22 (m, 1H, olefin), 5.58-5.46 (m, 1H, olefin), 4.33-4.24 (m, 3H), 3.89-3.76 (m, 2H, CH\(_2\)S). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 136.5 (d, \( J_{\text{CP}} = 6.8 \) Hz), 132.0 (d, \( J_{\text{CP}} = 2.7 \) Hz), 131.9 (d, \( J_{\text{CP}} = 2.6 \) Hz), 131.4 (d, \( J_{\text{CP}} = 97.7 \) Hz), 131.1 (d, \( J_{\text{CP}} = 8.7 \) Hz), 131.07 (d, \( J_{\text{CP}} = 8.8 \) Hz), 128.8 (d, \( J_{\text{CP}} = 13.3 \) Hz), 128.7 (d, \( J_{\text{CP}} = 12.9 \) Hz), 121.9 (q, \( J_{\text{CF}} = \))
277.7 Hz), 120.3 (d, $J_{CP} = 2.1$ Hz), 64.6 (q, $J_{CF} = 37.8$ Hz), 54.7, 45.9 (d, $J_{CP} = 68.0$ Hz), 20.7 (d, $J_{CP} = 2.6$ Hz), 12.4 (d, $J_{CP} = 13.3$ Hz). $^{31}$P{1H} NMR (161 MHz, CDCl$_3$): δ 27.9 (s). HRMS (ESI) calcd for C$_{24}$H$_{22}$BrF$_3$O$_4$PS (M+H)$^+$: 573.0106, found: 573.0114.

**Entry 9.** White solid. (86.9 mg; 86% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 12.1 min [(R)-enantiomer], 14.5 min [(S)-enantiomer]. 92% ee. [$\alpha$]$^{20}$D = $-15.4$ (c 0.500, CH$_2$Cl$_2$), The absolute configuration was assigned by analogy with Table 2, entry 4.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.89-7.83 (m, 2H, Ar), 7.60-7.46 (m, 5H, Ar), 7.40-7.38 (m, 1H, Ar), 7.35-7.28 (m, 2H, Ar), 7.19-7.15 (m, 1H, Ar), 7.04 (d, $J = 8.0$ Hz, 1H, Ar), 7.15 (dd, $J = 9.2$ and 1.6 Hz, 1H, Ar), 6.89 (t, $J = 8.0$ Hz, 1H, Ar), 6.30-6.22 (m, 1H, olefin), 5.54-5.46 (m, 1H, olefin), 4.33-4.21 (m, 3H), 3.89-3.76 (m, 2H, CH$_2$S). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 162.7 (dd, $J_{CF} = 246.9$ Hz, $J_{CP} = 1.9$ Hz), 137.0 (dd, $J = 7.4$ and 5.9 Hz), 136.0 (d, $J_{CP} = 6.3$ Hz), 132.4 (d, $J_{CP} = 2.6$ Hz), 132.0 (d, $J_{CP} = 2.6$ Hz), 131.5 (d, $J_{CP} = 8.6$ Hz), 131.1 (d, $J_{CP} = 9.0$ Hz), 130.8 (d, $J_{CP} = 99.5$ Hz), 130.6 (d, $J_{CP} = 96.9$ Hz), 130.3 (dd, $J = 9.3$ and 2.6 Hz), 129.0 (d, $J_{CP} = 11.5$ Hz), 128.5 (d, $J_{CP} = 11.9$ Hz), 125.1 (dd, $J = 6.0$ and 3.0 Hz), 121.9 (q, $J_{CF} = 277.9$ Hz), 120.2 (d, $J = 10.7$ Hz), 116.4 (dd, $J = 12.3$ and 5.9 Hz), 114.6 (dd, $J = 21.2$ and 1.2 Hz), 64.9 (hept, $J_{CF} = 38.2$ Hz), 54.8 (d, $J_{CP} = 1.4$ Hz), 51.3 (dd, $J_{CP} = 63.9$ Hz, $J_{CF} = 1.8$ Hz). $^{31}$P{1H} NMR (161 MHz, CDCl$_3$): δ 27.9 (s). HRMS (ESI) calcd for C$_{24}$H$_{22}$F$_4$O$_4$PS (M+H)$^+$: 513.0907, found: 513.0911.
**Entry 10.** White solid. (86.5 mg; 82% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 12.0 min [(R)-enantiomer], 14.1 min [(S)-enantiomer]. 89% ee. \( [\alpha]^{20}_{D} = -20.7 \) (c 0.500, CH\(_2\)Cl\(_2\)), The absolute configuration was assigned by analogy with Table 2, entry 4.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.88-7.83 (m, 2H, Ar), 7.61-7.46 (m, 5H, Ar), 7.43-7.38 (m, 1H, Ar), 7.34-7.28 (m, 2H, Ar), 7.23-7.12 (m, 4H, Ar), 6.32-6.22 (m, 1H, olefin), 5.58-5.48 (m, 1H, olefin), 4.35-4.24 (m, 3H), 3.89-3.77 (m, 2H, CH\(_2\)S).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 136.6 (d, \( J_{CP} = 5.9 \) Hz), 135.9 (d, \( J = 6.3 \) Hz), 134.5 (d, \( J_{CP} = 1.9 \) Hz), 132.4 (d, \( J_{CP} = 2.9 \) Hz), 132.1 (d, \( J_{CP} = 3.0 \) Hz), 131.6 (d, \( J_{CP} = 8.6 \) Hz), 131.1 (d, \( J_{CP} = 8.9 \) Hz), 130.8 (d, \( J_{CP} = 99.5 \) Hz), 130.5 (d, \( J_{CP} = 98.4 \) Hz), 130.0 (d, \( J = 1.5 \) Hz), 129.5 (d, \( J_{CP} = 5.5 \) Hz), 129.0 (d, \( J_{CP} = 11.9 \) Hz), 128.5 (d, \( J = 11.9 \) Hz), 127.8 (d, \( J = 2.3 \) Hz), 127.5 (d, \( J = 5.6 \) Hz), 121.9 (q, \( J_{CF} = 277.9 \) Hz), 120.3 (d, \( J = 10.8 \) Hz), 64.9 (hept, \( J_{CF} = 37.8 \) Hz), 54.8 (d, \( J_{CP} = 1.1 \) Hz), 51.3 (d, \( J_{CP} = 63.6 \) Hz).

\(^{31}\)P\(^{1}\)H NMR (161 MHz, CDCl\(_3\)): \( \delta \) 28.0 (s). HRMS (ESI) calcd for C\(_{24}\)H\(_{22}\)ClF\(_3\)O\(_4\)PS (M+H\(^+\)): 529.0612, found: 529.0615.

**Entry 11.** White solid. (74.8 mg; 84% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 18.2 min [(R)-enantiomer], 19.9 min [(S)-enantiomer]. 71% ee. \( [\alpha]^{20}_{D} = -12.7 \) (c 0.500, CH\(_2\)Cl\(_2\)), The absolute configuration was assigned by analogy with Table 2, entry 4.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.82-7.50 (m, 4H, Ar), 7.52-7.45 (m, 6H, Ar), 5.89-5.82 (m, 1H, olefin), 5.56-5.48 (m, 1H, olefin), 4.40-4.33 (m, 2H, OCH\(_2\)), 3.91-3.77 (m, 2H, CH\(_2\)S), 3.08-2.95 (m, 1H, PCH), 1.79-1.65 (m, 2H), 0.92 (t, \( J_{CH} = 7.2 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 136.6 (d, \( J_{CP} = 5.9 \) Hz), 135.9 (d, \( J = 6.3 \) Hz), 134.5 (d, \( J_{CP} = 1.9 \) Hz), 132.4 (d, \( J_{CP} = 2.9 \) Hz), 132.1 (d, \( J_{CP} = 3.0 \) Hz), 131.6 (d, \( J_{CP} = 8.6 \) Hz), 131.1 (d, \( J_{CP} = 8.9 \) Hz), 130.8 (d, \( J_{CP} = 99.5 \) Hz), 130.5 (d, \( J_{CP} = 98.4 \) Hz), 130.0 (d, \( J = 11.9 \) Hz), 127.8 (d, \( J = 2.3 \) Hz), 127.5 (d, \( J = 5.6 \) Hz), 121.9 (q, \( J_{CF} = 277.9 \) Hz), 120.3 (d, \( J = 10.8 \) Hz), 64.9 (hept, \( J_{CF} = 37.8 \) Hz), 54.8 (d, \( J_{CP} = 1.1 \) Hz), 51.3 (d, \( J_{CP} = 63.6 \) Hz).
Hz), 130.0 (d, J = 1.5 Hz), 129.5 (d, JCP = 5.5 Hz), 129.0 (d, JCP = 11.9 Hz), 128.5 (d, J = 11.9 Hz), 127.8 (d, J = 2.3 Hz), 127.5 (d, J = 5.6 Hz), 121.9 (q, JCF = 277.9 Hz), 120.3 (d, J = 10.8 Hz), 64.9 (hept, JCF = 37.8 Hz), 54.8 (d, JCP = 1.1 Hz), 51.3 (d, JCP = 63.6 Hz). 31P {1H} NMR (161 MHz, CDCl3): δ 28.0 (s). HRMS (ESI) calcd for C20H23F3O4PS (M+H)+: 447.1001, found: 447.0999.

Entry 12. White solid. (95.5 mg; 87% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 85/15, flow = 1.0 mL/min. Retention times: 12.7 min [(R)-enantiomer], 16.6 min [(S)-enantiomer]. 86% ee. [α]20 D = −14.5 (c 0.50, CH2Cl2). The absolute configuration was assigned by analogy with Table 2, entry 4.

1H NMR (400 MHz, CDCl3): δ 7.45 (d, J = 11.2 Hz, 2H, Ar), 7.28-7.18 (m, 6H, Ar), 7.04 (d, J = 11.2 Hz, 2H, Ar), 6.97 (s, 1H, Ar), 6.34-6.26 (m, 1H, olefin), 5.58-5.47 (m, 1H, olefin), 4.32-4.15 (m, 3H), 3.87-3.77 (m, 2H, CH2S), 2.73 (s, 6H, Me), 2.17 (s, 6H, Me). 13C NMR (100 MHz, CDCl3): δ 138.6 (d, JCP = 11.9 Hz), 137.9 (d, J = 12.3 Hz), 137.0 (d, JCP = 6.3 Hz), 134.8 (d, JCP = 6.0 Hz), 133.9 (d, JCP = 3.0 Hz), 133.4 (d, JCP = 3.0 Hz), 131.1 (d, JCP = 98.8 Hz), 130.8 (d, JCP = 96.2 Hz), 129.5 (d, JCP = 5.6 Hz), 129.1 (d, J = 8.2 Hz), 128.8 (d, JCP = 8.9 Hz), 128.7 (d, JCP = 2.8 Hz), 127.5 (d, JCP = 2.2 Hz), 121.9 (q, JCF = 277.9 Hz), 119.6 (d, J = 11.1 Hz), 65.2 (q, JCF = 38.1 Hz), 55.0 (d, JCP = 1.1 Hz), 51.4 (d, JCP = 63.6 Hz), 21.4 (d, JCP = 0.8 Hz), 21.2 (d, JCP = 0.7 Hz). 31P {1H} NMR (161 MHz, CDCl3): δ 28.8 (s). HRMS (ESI) calcd for C28H31F3O4PS (M+H)+: 551.1627, found: 551.1626.
**Entry 13.** White solid. (95.0 mg; 86% yield). The ee was determined on a Daicel Chiralpak AS column with hexane/2-propanol = 85/15, flow = 1.0 mL/min. Retention times: 41.8 min [(R)-enantiomer], 54.8 min [(S)-enantiomer]. 76% ee. $\alpha_{20}^D = -8.6$ (c 0.50, CH$_2$Cl$_2$). The absolute configuration was assigned by analogy with Table 2, entry 4.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.73 (t, $J = 8.8$ Hz, 2H, Ar), 7.36 (dd, $J = 10.4$ and 8.8 Hz, 2H, Ar), 7.26-7.20 (m, 5H, Ar), 7.02 (d, $J = 6.8$ Hz, 2H, Ar), 6.78 (d, $J = 6.8$ Hz, 2H, Ar), 6.36-6.28 (m, 1H, olefin), 5.55-5.47 (m, 1H, olefin), 4.30-4.19 (m, 3H), 3.86 (s, 3H, OMe), 3.84-3.78 (m, 2H, CH$_2$S), 3.76 (s, 3H, OMe).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.6 (d, $J_{CP} = 2.6$ Hz), 162.2 (d, $J = 3.0$ Hz), 137.2 (d, $J_{CP} = 6.3$ Hz), 135.0 (d, $J_{CP} = 6.0$ Hz), 133.4 (d, $J_{CP} = 10.0$ Hz), 133.1 (d, $J_{CP} = 10.0$ Hz), 129.5 (d, $J_{CP} = 5.6$ Hz), 128.8 (d, $J_{CP} = 1.8$ Hz), 127.5 (d, $J_{CP} = 2.3$ Hz), 122.7 (d, $J = 105.4$ Hz), 122.1 (d, $J_{CP} = 104.3$ Hz), 121.9 (q, $J_{CF} = 277.9$ Hz), 119.4 (d, $J = 10.4$ Hz), 114.4 (d, $J = 12.2$ Hz), 113.9 (d, $J = 12.6$ Hz), 65.1 (q, $J_{CF} = 38.1$ Hz), 55.4, 55.3, 55.0 (d, $J_{CP} = 1.1$ Hz), 52.3 (d, $J_{CP} = 65.1$ Hz).

$^{31}$P{1H} NMR (161 MHz, CDCl$_3$): $\delta$ 28.6 (s). HRMS (ESI) calcd for C$_{26}$H$_{27}$F$_3$O$_6$PS (M+H)$^+$: 555.1213, found: 555.1212.

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**Table 1, Entry 1.** White solid. (81.0 mg; 93% yield). The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 14.3 min [(S)-enantiomer], 17.2 min [(R)-enantiomer]. 93% ee. The absolute configuration was assigned by analogy with the literature example (Pincer Pd-catalyzed asymmetric 1,4-addition of diarylphosphines to $\alpha,\beta$-unsaturated enones).$^1$
Table 1, Entry 2. (CAS: 1334387-70-0). White solid. (76.2 mg; 90% yield). The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 25.3 min [(S)-enantiomer], 33.1 min [(R)-enantiomer]. 96% ee. The absolute configuration was assigned by analogy with the literature example (Pincer Pd-catalyzed asymmetric 1,4-addition of diarylphosphines to α,β-unsaturated N-acylpyrroles).4

Table 1, Entry 3. White solid. (64.1 mg; 61% combined yield). 1.4-adduct : 1.6-adduct = 1 : 2.

The ee of 1,4-adduct was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 6.6 min [(S)-enantiomer], 11.0 min [(R)-enantiomer]. 61% ee. The absolute configuration was
assigned by analogy with the literature examples (Pincer Pd-catalyzed asymmetric 1,4-addition of diarylphosphines to α,β-unsaturated carboxylic esters).^5

1H NMR (400 MHz, CDCl3) for 1,4-adduct: δ 6.35 (dd, J = 16.0 and 4.4 Hz, 1H, olefin), 6.02 (ddd, J = 16.0, 8.8 and 6.4 Hz, 1H, olefin), 3.83-3.74 (m, 1H), 3.07 (ddd, J = 16.4 and 8.8 and 3.6 Hz, 1H), 2.94 (ddd, J = 16.4, 11.2 and 5.2 Hz, 1H). 31P{1H} NMR (161 MHz, CDCl₃): δ 33.5 (s). HRMS (ESI) calcd for C₂₆H₂₂F₆O₃P (M+H)+: 527.1205, found: 527.1201.

The ee of 1,6-adduct was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 8.6 min [(R)-enantiomer], 9.6 min [(S)-enantiomer]. 71% ee. The absolute configuration was assigned by analogy with Table 2, entry 4.

1H NMR (400 MHz, CDCl₃) for 1,6-adduct: δ 6.15-6.06 (m, 1H, olefin), 5.71-5.63 (m, 1H), 5.60-5.48 (m, 1H), 4.26 (t, J = 9.6 Hz, 1H), 3.24-3.10 (m, 2H). 31P{1H} NMR (161 MHz, CDCl₃): δ 33.0 (s). HRMS (ESI) calcd for C₂₆H₂₂F₆O₃P (M+H)+: 527.1205, found: 527.1201.

**Experimental Procedures for the 1,6-Addition Reaction in Eq. 2**

Diphenylphosphine (18.6 mg, 0.10 mmol) was added to a solution of (S,S)-Pd catalyst (1.4 mg, 2 μmol Pd) and [(2E)-3-phenyl-2-propenylidene]- diethyl ester (32.9 mg, 0.12 mmol) in toluene (2.0 mL) at room temperature, then the resulting solution was stirred for 17 h. The reaction was quenched with Me₂SBH₃ (0.15 mL; 2 M in THF) and concentrated under vacuum. The residue was purified by silica gel chromatography with hexane/EtOAc = 10/1 to afford the 1,6-adduct as a white solid.
White solid. (32.0 mg; 68% yield). The ee was determined on a Daicel Chiralpak AD column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 7.8 min [major enantiomer], 8.7 min [minor enantiomer]. 43% ee. $[\alpha]^{20}_D = 7.3$ (c 1.00, CH$_2$Cl$_2$),

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (t, $J$ = 8.8 Hz, 2H, Ar), 7.52-7.32 (m, 6H, Ar), 7.30-7.26 (m, 2H, Ar), 7.20-7.10 (m, 5H, Ar), 6.17 (ddd, $J$ = 15.2, 9.6 and 6.4 Hz, 1H, olefin), 5.71 (ddd, $J$ = 15.2, 9.6 and 3.2 Hz, 1H, olefin), 4.44 (dd, $J$ = 15.2 and 9.6 Hz, 1H), 4.12 (q, $J$ = 7.2 Hz, 2H), 4.10-4.00 (m, 2H), 3.96 (d, $J$ = 9.2 Hz, 1H), 1.19 (t, $J$ = 7.2 Hz, 3H), 1.18 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.5 (d, $J_{CP}$ = 1.9 Hz), 167.3 (d, $J_{CP}$ = 2.2 Hz), 135.3 (d, $J_{CP}$ = 1.5 Hz), 133.5 (d, $J_{CP}$ = 8.4 Hz), 132.9 (d, $J_{CP}$ = 8.4 Hz), 131.4 (d, $J_{CP}$ = 2.2 Hz), 131.3, 131.0 (d, $J_{CP}$ = 2.6 Hz), 129.4 (d, $J_{CP}$ = 4.9 Hz), 128.6 (d, $J_{CP}$ = 9.8 Hz), 128.3 (d, $J_{CP}$ = 9.8 Hz), 128.1 (d, $J_{CP}$ = 2.3 Hz), 127.8 (d, $J_{CP}$ = 52.6 Hz), 127.3 (d, $J_{CP}$ = 2.7 Hz), 127.1 (q, $J_{CP}$ = 52.7 Hz), 126.1 (d, $J$ = 11.0 Hz), 61.7, 52.2 (q, $J_{CP}$ = 1.5 Hz), 48.0 (d, $J_{CP}$ = 29.9 Hz), 13.94, 13.93. $^{31}$P{${^1}$H}} NMR (161 MHz, CDCl$_3$): $\delta$ 24.7 (m). HRMS (ESI) calcd for C$_{28}$H$_{36}$BNO$_4$P (M+NH$_4$)$^+$: 491.2506, found: 491.2511.

**Experimental Procedure for Rhodium-Catalyzed 1,4-Addition of Phenylboronic Acid to Cyclohexenone**

A mixture of [RhCl(C$_2$H$_4$)$_2$]$_2$ (1.2 mg, 6 μmol Rh) and the allylic phosphine (2.9 mg, 6 μmol; Table 2, Entry 1) in dioxane (2 mL) was stirred at room temperature for 20 min. Then, 0.50 M aqueous KOH (0.20 mL, 0.10 mmol) was added into it, followed by the
addition of cyclohexenone (119.2 mg, 0.20 mmol) and PhB(OH)₂ (73.2 mg, 0.60 mmol). The solution was stirred for 4.5 h at 50 °C, and was then passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane to afford the 1,4-adduct. (CAS 57344-86-2). (22.0 mg; 63% yield). ¹H NMR data of the product are identical with the reported data of the product in literature. The ee was determined on a Daicel Chiralcel OD column with hexane/2-propanol = 98/2, flow = 1.0 mL/min. Retention times: 12.8 min [(S)-enantiomer], 13.6 min [(R)-enantiomer]. 27% ee.

**General Procedures for the Preparation of α,β,γ,δ-Unsaturated Sulfonic Esters**

n-BuLi (1.92 mmol; 2.5 M in hexane) was added to a solution of 2,2,2-trifluoroethyl (diethoxyphosphoryl)methanesulfonate (0.6 g, 1.92 mmol) in THF at −78 °C and stirred for 20 min. Aldehyde (1.6 mmol) was added to it, and the resulting solution was allowed to warm to room temperature slowly and stirred at room temperature for 20 h. After quenching with AcOH (0.2 mL), the mixture was extracted with EtOAc, dried over MgSO₄, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with hexane/EtOAc = 30/1 to afford product as a white solid. (0.42 g; 89% yield). ¹H NMR (300MHz, CDCl₃): δ 7.50-7.46 (m, 2H), 7.42-7.36 (m, 4H), 7.03 (d, J_HH = 15.0 Hz, 1H, olefin), 6.87-6.78 (m, 1H, olefin), 6.35 (d, J_HH = 15.0 Hz, 1H, olefin).
Hz, 1H, olefin), 4.42 (q, $J_{HF} = 7.8$ Hz, 2H, OCH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 146.7, 145.0, 135.0, 130.3, 129.1, 127.8, 122.7, 122.1 (q, $J_{CF} = 277.8$ Hz), 120.3, 64.6 (q, $J_{CF} = 38.0$ Hz). HRMS (ESI) calcd for C$_{12}$H$_{15}$F$_3$NO$_3$S (M+NH$_4$)$^+$: 310.0719, found: 310.0726.

(0.38 g; 77% yield). $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 7.36-7.28 (m, 3H), 7.12-7.09 (m, 2H), 6.92 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 6.74-6.65 (m, 1H, olefin), 6.22 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 4.32 (q, $J_{HF} = 8.1$ Hz, 2H, OCH$_2$), 2.28 (s, 3H, Me). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 147.0, 145.1, 140.8, 132.3, 129.8, 127.8, 122.1 (q, $J_{CF} = 277.8$ Hz), 121.8, 120.5, 64.6 (q, $J_{CF} = 38.0$ Hz), 21.5. HRMS (ESI) calcd for C$_{13}$H$_{13}$F$_3$NaO$_3$S (M+Na)$^+$: 329.0430, found: 329.0417.

(0.39 g; 76% yield). $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 7.46-7.37 (m, 3H), 7.01 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 6.93-6.90 (m, 2H, Ar), 6.77-6.68 (m, 1H, olefin), 6.28 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 4.41 (q, $J_{HF} = 8.1$ Hz, 2H, OCH$_2$), 3.85 (s, 3H, OMe). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 161.5, 147.3, 144.9, 129.5, 127.8, 122.3 (q, $J_{CF} = 277.8$ Hz), 120.6, 119.5, 114.6, 64.6 (q, $J_{CF} = 38.0$ Hz), 55.5. HRMS (ESI) calcd for C$_{13}$H$_{17}$F$_3$NO$_4$S (M+NH$_4$)$^+$: 340.0825, found: 340.0817.

(0.37 g; 76% yield). $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 7.46-7.38 (m, 1H), 7.30-7.25 (m, 3H), 7.20-7.18 (m, 1H), 7.02 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 6.88-6.79 (m, 1H, olefin), 6.33 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 4.42 (q, $J_{HF} = 7.8$ Hz, 2H, OCH$_2$), 2.37 (s, 3H, Me).
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 146.8, 145.3, 138.9, 135.0, 131.2, 129.0, 128.5, 125.1, 122.6, 122.1 (q, $J_{CF} = 277.8$ Hz), 121.0, 64.6 (q, $J_{CF} = 37.5$ Hz), 21.4. HRMS (ESI) cale for C$_{13}$H$_{17}$F$_3$NO$_3$S (M+NH$_4$)$^+$: 324.0876, found: 324.0879.

![Structure](image1)

(0.38 g; 76% yield). $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 7.45-7.29 (m, 2H), 7.09-6.78 (m, 5H), 6.35 (d, $J_{HH} = 14.7$ Hz, 1H, olefin), 4.42 (q, $J_{HF} = 7.2$ Hz, 2H, OCH$_2$), 3.83 (s, 3H, OMe). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 160.1, 146.5, 144.9, 136.4, 130.1, 123.1, 122.3 (q, $J_{CF} = 277.8$ Hz), 121.4, 120.5, 110.0, 112.9, 64.6 (q, $J_{CF} = 38.6$ Hz), 55.4. HRMS (ESI) cale for C$_{13}$H$_{17}$F$_3$NO$_4$S (M+NH$_4$)$^+$: 340.0825, found: 340.0829.

![Structure](image2)

(0.27 g; 50% yield). $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 7.74-7.71 (m, 4H), 7.51-7.31 (m, 4H), 7.03 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 6.84-6.75 (m, 1H, olefin), 6.25 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 4.34 (q, $J_{HF} = 7.8$ Hz, 2H, OCH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 146.7, 145.1, 134.2, 133.4, 132.5, 129.6, 128.9, 128.6, 127.9, 127.5, 127.0, 123.3, 123.0, 122.2, 122.3 (q, $J_{CF} = 277.8$ Hz), 64.6 (q, $J_{CF} = 37.4$ Hz). HRMS (ESI) cale for C$_{16}$H$_{17}$F$_3$NO$_3$S (M+NH$_4$)$^+$: 360.0876, found: 360.0879.

![Structure](image3)

(0.38 g; 72% yield). $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 7.35-7.46 (m, 5H), 7.01 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 6.78-6.86 (m, 1H, olefin), 6.38 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 4.43 (q, $J_{HF} = 7.8$ Hz, 2H, OCH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 146.2, 143.5, 136.2, 133.5, 129.4, 129.0, 123.3, 122.1 (q, $J_{CF} = 277.9$ Hz), 121.9, 64.7 (q, $J_{CF} = 38.0$ Hz). HRMS (ESI) cale for C$_{12}$H$_{14}$ClF$_3$NO$_3$S (M+NH$_4$)$^+$: 344.0330, found: 344.0331.
(0.36 g; 61% yield). $^1$H NMR (300MHz, CDCl$_3$): δ 7.54-7.51 (m, 2H), 7.45-7.34 (m, 3H), 6.99 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 6.88-6.79 (m, 1H, olefin), 6.38 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 4.43 (q, $J_{HF} = 7.8$ Hz, 2H, OCH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 146.1, 143.5, 133.9, 132.4, 129.2, 124.6, 123.4, 122.1 (q, $J_{CF} = 277.9$ Hz), 122.1, 64.7 (q, $J_{CF} = 38.0$ Hz). HRMS (ESI) calcd for C$_{12}$H$_{10}$BrF$_3$NaO$_3$S (M+Na)$^+$: 392.9378, found: 392.9362.

(0.35 g; 77% yield). $^1$H NMR (300MHz, CDCl$_3$): δ 7.46-7.33 (m, 2H), 7.27-7.17 (m, 2H), 7.10-6.98 (m, 2H), 6.88-6.79 (m, 1H, olefin), 6.40 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 4.44 (q, $J_{HF} = 7.8$ Hz, 2H, OCH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 163.1 (d, $J_{CF} = 247.1$ Hz), 145.9, 143.4 (d, $J_{CF} = 2.9$ Hz), 137.2 (d, $J_{CF} = 8.0$ Hz), 130.7 (d, $J_{CF} = 8.4$ Hz), 124.0, 123.8 (d, $J_{CF} = 2.8$ Hz), 122.4, 122.1 (q, $J_{CF} = 278.3$ Hz), 117.1 (d, $J_{CF} = 21.2$ Hz), 114.0 (d, $J_{CF} = 22.4$ Hz), 64.7 (q, $J_{CF} = 38.0$ Hz). HRMS (ESI) calcd for C$_{12}$H$_{14}$F$_4$NO$_3$S (M+NH$_4$)$^+$: 328.0625, found: 328.0631.

(0.6 g; 69% yield). $^1$H NMR (300MHz, CDCl$_3$): δ 7.47-7.34 (m, 5H), 6.98 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 6.88-6.80 (m, 1H, olefin), 6.40 (d, $J_{HH} = 15.0$ Hz, 1H, olefin), 4.40 (q, $J_{HF} = 8.1$ Hz, 2H, OCH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 145.9, 143.1, 136.8, 135.1, 130.4, 130.1, 127.5, 126.0, 124.1, 122.5, 122.1 (q, $J_{CF} = 277.9$ Hz), 64.7 (q, $J_{CF} = 38.0$ Hz). HRMS (ESI) calcd for C$_{12}$H$_{14}$ClF$_3$NO$_3$S (M+NH$_4$)$^+$: 344.0330, found: 344.0333.
(0.23 g; 60% yield). $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 7.30-7.22 (m, 1H, olefin), 6.45-6.35 (m, 1H, olefin), 6.24-6.16 (m, 2H, olefin), 4.39 (q, $J_{HF} = 7.8$ Hz, 2H, OCH$_2$), 2.31-2.22 (m, 2H, =CCH$_2$), 1.08 (t, $J_{HH} = 7.5$ Hz, 3H, Me). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 151.4, 147.3, 124.5, 120.8, 122.1 (q, $J_{CF} = 208.5$ Hz), 64.4 (q, $J_{CF} = 28.3$ Hz), 26.1, 12.3. HRMS (ESI) calcd for C$_8$H$_{12}$F$_3$O$_3$S (M+H)$^+$: 245.0454, found: 245.0452.

The substrate 1f was prepared from the corresponding acyl chloride with hexafluoroisopropanol in the presence of Et$_3$N following the literature procedure.

71% yield. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 7.66 (dd, $J_{HH} = 15.3$ and 10.2 Hz, 1H, olefin), 7.53-7.50 (m, 2H, Ar), 7.46-7.40 (m, 3H, Ar), 7.02-6.85 (m, 2H, olefin), 6.06 (q, $J_{HH} = 15.3$ Hz, 1H, olefin), 6.08-5.98 (m, 1H, OCH). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 163.5, 149.1, 143.4, 135.7, 129.9, 129.0, 127.7, 125.7, 122.7, 120.9 (q, $J_{CF} = 282.9$ Hz), 116.9, 66.6 (sept, $J_{CF} = 34.7$ Hz). MS (ESI): 324.8 (M$^+$).

References:
HPLC Chart

### 198 CjZ-5-6-+ OD-H 73 214 0.7

- **Sample Name:** CjZ-5-6-+ OD-H 73 214 0.7
- **Injection Volume:** 8.9
- **Vial Number:** RA2
- **Channel:** UV_VIS_2
- **Sample Type:** unknown
- **Wavelength:** 214.0
- **Control Program:** test_dsd
- **Bandwidth:** 4
- **Quantif. Method:** WXL
- **Dilution Factor:** 1.0000
- **Recording Time:** 2013-3-25 10:13
- **Run Time (min):** 21.00
- **Sample Weight:** 1.0000
- **Sample Amount:** 1.0000

### 199 CjZ-6-9-2 OD-H 73 214 0.7

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- **Injection Volume:** 4.0
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- **Run Time (min):** 23.44
- **Sample Weight:** 1.0000
- **Sample Amount:** 1.0000
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

== Shimadzu LCsolution Analysis Report ==

Sample Name : 1p0704-e08515  Date:
Column: The Inhibitor phase
Velocity: The detection wavelength:

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== Shimadzu LCsolution Analysis Report ==

Sample Name : 1p0704-e08515  Date:
Column: The Inhibitor phase
Velocity: The detection wavelength:

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== Shimadzu LCsolution Analysis Report ==

Sample Name: D(phenyl)acetic acid
Date: 
Column: The mobile phase
Wavelength: The detection wavelength

**Chromatogram**

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== Shimadzu LCsolution Analysis Report ==

Sample Name: D(phenyl)acetic acid
Date: 
Column: The mobile phase
Wavelength: The detection wavelength

**Chromatogram**

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Table 1. Crystal data and structure refinement for mo.dm13397_0m.

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<td></td>
<td>c = 13.304(3) Å</td>
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<tr>
<td></td>
<td>β = 99.518(4)°.</td>
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1.6-adduct in Table 2, Entry 4
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>R indices (all data)</td>
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<td>Absolute structure parameter</td>
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