Substrate-controlled divergent synthesis with ortho-vinyl-functionalised 1,3-enynes and imines via palladium catalysis

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1. General methods

Unless otherwise noted, the reactions were carried out under ambient atmosphere; when the reactions required heating, the heat source was oil bath. $^1$H NMR (400 MHz or 600 MHz), $^{13}$C NMR (100 MHz or 150 MHz) and $^{19}$F NMR (375 MHz) spectra were recorded on Varian INOVA 400/54, Agilent DD2 600/54 or Bruker AscendTM 400 instruments (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl$_3$ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet doublet, td = triple doublet, dt = double triplet, brs = broad singlet, m = multiplet, and coupling constants ($J$) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2, Agilent G1969-85000 or Shimadzu LCMS-IT-TOF using a time-of-flight mass spectrometer equipped with electrospray ionization (ESI) source. X-ray diffraction experiments were carried out on Bruker D8 venture diffractometer, and the data obtained were deposited at the Cambridge Crystallographic Data Centre (CCDC 2249982–2249984). In each case, enantiomeric excess was determined by HPLC analysis on a chiral stationary phase in comparison with the authentic racemate, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm), Chiralpak IB Column (250 × 4.6 mm), Chiralpak IC Column (250 × 4.6 mm), Chiralpak IE Column (250 × 4.6 mm), Chiralpak IF Column (250 × 4.6 mm). UV detection was monitored at 254 nm. Column chromatography was performed on silica gel (200–300 mesh) eluting with redistilled EtOAc and petroleum ether. TLC was performed on glass-backed silica plates. UV light (monitored at 254 nm), I$_2$ and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. THF was freshly distilled from sodium/benzophenone before use. Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes.
2. Substrate preparation and characterization

2.1 Preparation of 1,3-enyne substrates 1a–1o

1,3-Enynes 1a–1j, 1m–1o were prepared according to the literature procedures, which are known compounds and the spectroscopic data are consistent with the literature reports. The characterizations of new substrates are as follows:

1k, obtained as a yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.23 (d, \(J = 15.9\) Hz, 1H), 8.09–7.93 (m, 2H), 7.79–7.69 (m, 1H), 7.67–7.55 (m, 2H), 7.55–7.43 (m, 3H), 7.42–7.30 (m, 2H), 6.07 (dd, \(J = 17.5, 11.2\) Hz, 1H), 5.77 (dd, \(J = 17.5, 2.0\) Hz, 1H), 5.60 (dd, \(J = 11.1, 2.0\) Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm) 191.0, 142.9, 138.2, 136.2, 133.1, 132.7, 129.9, 128.61, 128.58, 127.8, 126.7, 124.3, 124.1, 116.9, 94.4, 87.6; HRMS (ESI-TOF) m/z: [M + Na]\(^+\) Calcd for C\(_{19}\)H\(_{14}\)O\(_2\)Na\(^+\) 281.0937; Found 281.0930.

1l, obtained as a white solid, mp = 193–195 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.05 (d, \(J = 15.5\) Hz, 1H), 7.63–7.53 (m, 1H), 7.53–7.43 (m, 1H), 7.36–7.26 (m, 2H), 7.05 (d, \(J = 15.5\) Hz, 1H), 6.07 (dd, \(J = 17.5, 11.2\) Hz, 1H), 5.79 (dd, \(J = 17.6, 2.0\) Hz, 1H), 5.58 (dd, \(J = 11.1, 2.0\) Hz, 1H), 3.17 (s, 3H), 3.07 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 166.7, 140.1, 136.7, 133.1, 128.9, 128.5, 127.6, 126.6, 123.3, 119.6, 117.0, 93.8, 87.9, 37.5, 35.9; HRMS (ESI-TOF) m/z: [M + Na]\(^+\) Calcd for C\(_{15}\)H\(_{15}\)N\(_2\)Na\(^+\) 248.1046; Found 248.1053.

2.2 Preparation of 1,3-enyne substrates 1p–1x

Substrates S1 were prepared according to the literature procedures and the spectroscopic data of these compounds are consistent with the reports. 1,3-Enyne derivatives 1p–1x were prepared according to the following procedures:
**Step 1.** To an oven-dried 50 mL flask was charged with PdCl₂(PPh₃)₂ (140.0 mg, 0.2000 mmol), CuI (95.0 mg, 0.500 mmol) and S¹ (10.0 mmol). After evacuating and refilling the flask with argon three times, Et₃N (20.0 mL) and ethynyltrimethylsilane (1.82 mL, 13.0 mmol, 1.3 equiv) were added sequentially. The mixture was stirred at room temperature until full consumption of S¹. The mixture was filtered, and the filtrate was concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 to 20/1) to afford S².

**Step 2.** S² (8.0 mmol, 1.0 equiv) was dissolved in anhydrous MeOH (10 mL) at room temperature. K₂CO₃ (110.4 mg, 0.8 mmol, 10 mol%) was added and the mixture was stirred for 10 minutes until complete conversion of S². The reaction was quenched by H₂O and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄. After concentration, the crude product S³ was used for the next step directly without further purification.

**Step 3.** To an over-dried flask equipped with a stirring bar were added CuI (76 mg, 0.4 mmol, 5 mol%) and Pd(PPh₃)₄ (184.8 mg, 0.1600 mmol, 2 mol%). After evacuating and refilling the flask with argon three times, Et₃N (20 mL), crude S³ (8.0 mmol, 1.0 equiv) and vinyl bromide (1.0 M in THF, 9.6 mL, 9.6 mmol, 1.2 equiv) were added via syringe sequentially. The resulting mixture was stirred at room temperature until complete conversion of S³. The mixture was filtered, and the filtrate was concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 to 20/1) to afford S⁴.

**Step 4.** NaH (300 mg, 7.50 mmol, 1.5 equiv) was suspended in anhydrous THF (15 mL) under atmosphere of argon. tert-Butyl diethylphosphonoacetate (1.64 mL, 7.00 mmol, 1.4 equiv) was then added slowly to the suspension over 15 minutes at 0 °C. The mixture was stirred about 30 minutes, and S⁴ (6 mmol, 1.0 equiv) was added. Then the reaction was stirred at 70 °C until full consumption of S⁴. After cooled to room temperature, the mixture was quenched with H₂O and extracted with EtOAc (20 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 to 20/1) to afford 1,3-enedyne derivatives.

![1q](image)

**1q**, obtained as a colorless oil; 43% yield for four steps; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.36–7.25 (m, 6H), 7.17–7.11 (m, 1H), 7.02 (d, J = 7.9 Hz, 1H), 6.35 (s, 1H), 5.81 (dd, J = 17.5, 11.1 Hz, 1H), 5.48 (dd, J = 17.5, 2.2 Hz, 1H), 2.53 (s, 3H), 2.53 (s, 3H).

S3
1H), 5.39 (dd, J = 11.1, 2.2 Hz, 1H), 2.36 (s, 3H), 1.29 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 165.3, 152.9, 140.7, 139.4, 137.3, 132.5, 129.0, 128.9, 128.3, 127.8, 126.6, 122.3, 121.3, 117.3, 90.8, 89.0, 80.1, 27.8, 21.1; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{24}$H$_{24}$O$_2$Na$^+$ 367.1669; Found 367.1677.

1r, obtained as a colorless oil; 21% yield for four steps; E/Z = 11:1, E-1r: $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.77 (s, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.40–7.26 (m, 4H), 7.25–7.19 (m, 2H), 6.42 (s, 1H), 5.82 (dd, J = 17.5, 11.1 Hz, 1H), 5.59–5.51 (dd, J = 17.5, 2.4 Hz, 1H), 5.51–5.43 (dd, J = 11.1, 2.3 Hz, 1H), 1.26 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm) 165.3, 152.4, 149.1, 148.2, 140.5, 135.5, 129.0, 128.3, 127.8, 126.1, 121.4, 117.3, 115.2, 114.8, 114.2, 112.9, 112.1, 89.9, 89.0, 80.1, 55.9, 27.9; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{23}$H$_{23}$F$_3$O$_2$Na$^+$ 421.1386; Found 421.1378.

1s, obtained as a colorless oil; 37% yield for four steps; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.42 (d, J = 8.3 Hz, 1H), 7.36–7.25 (m, 6H), 7.15 (d, J = 2.2 Hz, 1H), 6.37 (s, 1H), 5.80 (dd, J = 17.6, 11.1 Hz, 1H), 5.49 (dd, J = 17.6, 2.2 Hz, 1H), 5.42 (dd, J = 11.2, 2.2 Hz, 1H), 1.31 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 165.0, 151.3, 143.9, 139.6, 133.9, 133.0, 129.2, 129.1, 128.5, 127.8, 127.7, 127.3, 122.0, 121.2, 116.9, 92.1, 87.6, 80.5, 27.8; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{25}$H$_{26}$ClO$_2$Na$^+$ 387.1122; Found 387.1115; Calcd for C$_{23}$H$_{23}$ClO$_2$Na$^+$ 389.1093; Found 389.1090.

1t, obtained as a colorless oil; 23% yield for four steps; E/Z = 2.5:1, E-1t: $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.36–7.27 (m, 5H), 6.99 (s, 1H), 6.61 (s, 1H), 6.36 (s, 1H), 5.81 (m, 1H), 5.55–5.34 (m, 2H), 3.91 (s, 3H), 3.81 (s, 3H), 1.32 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm) 165.3, 152.4, 149.1, 148.2, 140.5, 135.5, 129.0, 128.3, 127.8, 126.1, 121.4, 117.3, 115.2, 114.8, 114.2, 112.9, 112.1, 89.9, 89.0, 80.1, 55.9, 27.9; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{25}$H$_{26}$O$_4$Na$^+$ 413.1723; Found 413.1721.
**1u**, obtained as a colorless oil; 19% yield for four steps; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.57–7.48 (m, 1H), 7.36–7.29 (m, 2H), 7.30–7.25 (m, 2H), 7.20–7.11 (m, 1H), 7.04–6.93 (m, 2H), 6.35 (s, 1H), 5.85 (dd, $J = 17.5, 11.1$ Hz, 1H), 5.53 (dd, $J = 17.5, 2.2$ Hz, 1H), 5.45 (dd, $J = 11.0, 2.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 165.1, 163.2 (d, $^1$J$_{FC} = 247.9$ Hz), 151.6, 142.1, 136.5 (d, $^3$J$_{FC} = 3.2$ Hz), 132.0, 129.5 (d, $^3$J$_{FC} = 8.3$ Hz), 129.0, 127.8 (d, $^3$J$_{FC} = 32.0$ Hz), 126.9, 122.5, 121.2, 117.1, 115.3 (d, $^2$J$_{FC} = 21.5$ Hz), 91.4, 88.5, 80.3, 27.7; $^{19}$F NMR (375 MHz, CDCl$_3$) δ (ppm) –112.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{23}$H$_{21}$FO$_2$Na$^+$ 371.1418; Found 371.1419.

**1v**, obtained as a colorless oil; 29% yield for four steps; $E/Z = 3.1:1$, $E$-$1v$: $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.52–7.45 (m, 1H), 7.33–7.25 (m, 2H), 7.23–7.17 (m, 2H), 7.17–7.10 (m, 1H), 6.87–6.75 (m, 2H), 6.31 (s, 1H), 5.83 (dd, $J = 17.5, 11.1$ Hz, 1H), 5.58–5.46 (m, 1H), 5.46–5.36 (m, 1H), 3.78 (s, 3H), 1.24 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm) 165.5, 160.4, 152.3, 142.6, 132.7, 131.9, 131.1, 129.1, 129.0, 127.9, 127.4, 126.7, 122.5, 121.9, 119.4, 117.2, 113.7, 91.1, 88.7, 79.9, 55.3, 27.8; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{24}$H$_{24}$O$_3$Na$^+$ 383.1618; Found 383.1626.

**1w**, obtained as a colorless oil; 16% yield for four steps; $E/Z = 3.1:1$, $E$-$1w$: $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.46–7.36 (m, 2H), 7.25 (m, 2H), 7.17–7.12 (m, 1H), 6.44 (s, 1H), 6.32–6.24 (m, 1H), 5.90 (d, $J = 3.4$ Hz, 1H), 5.85–5.75 (m, 1H), 5.54–5.42 (m, 1H), 5.41–5.31 (m, 1H), 1.16 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm) 165.3, 153.5, 144.0, 131.9, 128.8, 127.70, 127.67, 126.9, 117.0, 113.7, 112.0, 91.2, 88.3, 79.9, 27.7; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{21}$H$_{20}$O$_3$Na$^+$ 343.1305; Found 343.1307.

**1x**, obtained as a colorless oil; 35% yield for four steps; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.57–7.49 (m, 1H), 7.42–7.31 (m, 3H), 7.28–7.22 (m, 1H), 6.97 (dd, $J = 5.1, 3.7$ Hz, 1H), 6.77 (dd, $J = 3.8, 1.2$ Hz, 1H), 6.43 (s, 1H), 5.88 (dd, $J = 17.5, 11.1$ Hz, 1H), 5.56 (dd, $J = 17.5, 2.2$ Hz, 1H), 5.46 (dd, $J = 11.1, 2.2$ Hz, 1H), 1.26 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 165.0, 146.2, 144.6, 141.5, 131.9, 129.1, 128.7, 127.82, 127.81, 127.7, 127.4, 127.0, 122.4, 118.6, 117.2, 91.4, 88.3, 80.1, 27.8; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{21}$H$_{20}$O$_2$SNa$^+$ 359.1076; Found 359.1075.
Substrate imines 2 were synthesized according to the literature procedures, and the spectroscopic data were consistent with the literature reports.  

**References:**


**3. Detailed condition optimization**

**3.1 Detailed screening conditions for asymmetric synthesis of benzofulvene 3a**

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<td>EtOH</td>
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<td>A1</td>
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*Unless noted otherwise, reactions were performed with 1a (0.05 mmol), 2a (0.1 mmol), Pd$_2$(dba)$_3$ (5 mol%), L (12 mol%), base (x mol%), acid (20 mol%) and 4 Å MS (30 mg) in degassed dry solvent (0.5 mL) under Ar. b Yield of the isolated product. c Determined by HPLC analysis using a chiral stationary phase. d With Pd[(PPh)$_3$]$_4$ (10 mol%). e L5 (20 mol%). f Pd$_2$(dba)$_3$ (2.5 mol%), L5 (6 mol%)

3.2 Detailed screening conditions for asymmetric synthesis of indene derivative 4

3.3 Detailed screening conditions for asymmetric synthesis of naphthalene 5*
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<th>Entry</th>
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<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>ee (%)&lt;sup&gt;c&lt;/sup&gt;</th>
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<sup>a</sup> Unless noted otherwise, when R is tert butyl, the substrate is a single E-configuration. The reactions were performed with <sup>1</sup> (0.05 mmol), <sup>2</sup>a (0.1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5 mol%), <sup>L</sup>5 (12 mol%), Et<sub>3</sub>N (1.0 equiv) and 4 Å MS (30 mg) in solvent (0.5 mL) at 80 °C under Ar. <sup>b</sup> Yield of the isolated product. <sup>c</sup> Determined by HPLC analysis using a chiral stationary phase. <sup>d</sup> The structure of racemic 5r has been determined by X-ray analysis. <sup>e</sup> E/Z = 3:1. <sup>f</sup> Without Et<sub>3</sub>N.

### 3.4 Selected molecules embedding a benzofulvene or 1-naphthylated amine skeleton

Benzofulvenes, as a class of important skeleton, are widely existed in various natural products and bioactive molecules. As briefly exemplified in the above scheme, Zhang’s group disclosed that K-8008 and K-8012 are able to induce tumor apoptosis. Anmindenol A, separated from a marine-derived bacterium Streptomyces sp. in 2014, is a potential nitric oxide synthase inhibitor. In addition, Sulindac is widely used as a non-steroidal anti-inflammatory drug. In addition, the ortho-vinylated 1-naphthylated amines can be used as ligands in asymmetric transition-metal catalysis.
4. General procedure for asymmetric synthesis of benzofulvenes 3

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ortho-vinyl-functionalized 1,3-ynene 1 (0.100 mmol), imine 2 (0.200 mmol), Pd\(_2\)(dba)\(_3\) (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et\(_3\)N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give benzofulvene 3.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-((2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzenesulfonyamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd\(_2\)(dba)\(_3\) (4.6 mg, 0.0050 mmol, 5 mol%), L5 (7.9 mg, 0.012 mmol, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et\(_3\)N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give product 3a: 42.0 mg (0.0866 mmol), as a yellow solid; 87% yield; mp = 123–125 °C; [α]\(_\text{D}^25\) = +131.1 (c = 0.33 in CHCl\(_3\)); 91% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: t\(_k\) = 6.19 min (minor), t\(_R\) = 7.61 min (major); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ (ppm) 8.43–8.38 (m, 1H), 7.47–7.36 (m, 4H), 7.34–7.25 (m, 3H), 7.16–7.02 (m, 2H), 6.91 (d, J = 8.1 Hz, 2H), 6.78 (dd, J = 7.0, 1.3 Hz, 1H), 6.32 (dd, J = 17.8, 11.5 Hz, 1H), 6.24 (s, 1H), 5.92 (d, J = 9.0 Hz, 1H), 5.54 (dd, J = 8.9, 3.0 Hz, 1H), 5.46 (dd, J = 11.5, 1.6 Hz, 1H), 5.19 (dd, J = 17.8, 1.6 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ (ppm) 166.0, 149.8, 143.3, 141.6, 140.6, 138.5, 138.1, 136.6, 133.2, 129.8, 128.92, 128.85, 128.0,
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(2-methoxybenzylidene)-4-methylbenzenesulfonamide 2b (59.8 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product 3b: 45.7 mg (0.0886 mmol), as a yellow solid, 89% yield; mp = 57–59 °C; [α]_{25}^{D} = +13.1 (c = 0.52 in CHCl3); 90% ee, determined by HPLC analysis [Daicel Chiralpak IC, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, λ = 254 nm]: t_{R} = 9.56 min (minor), t_{R} = 13.55 min (major); 1H NMR (400 MHz, CDCl3) δ (ppm) 8.45–8.34 (m, 1H), 7.56–7.47 (m, 2H), 7.32–7.27 (m, 1H), 7.26–7.18 (m, 2H), 7.15–7.06 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.86–6.77 (m, 2H), 6.49 (dd, J = 17.8, 11.5 Hz, 1H), 6.33 (s, 1H), 5.99 (d, J = 5.4 Hz, 1H), 5.45 (dd, J = 11.5, 1.8 Hz, 1H), 5.33–5.25 (m, 1H), 5.10 (dd, J = 17.8, 1.8 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 3.70 (s, 3H), 2.28 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ (ppm) 166.3, 156.7, 150.0, 143.1, 142.7, 141.1, 137.7, 136.5, 133.0, 129.64, 129.55, 128.9, 128.6, 128.2, 127.4, 126.6, 126.5, 125.9, 122.3, 121.3, 120.6, 119.1, 110.8, 60.9, 55.3, 51.1, 21.4, 14.3; HRMS (ESI-TOF) m/z: [M + Na]^+ Calcd for C30H29NO5SNa^+ 538.1659; Found 538.1666.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), (E)-4-methyl-N-(3-methylbenzylidene)benzenesulfonamide 2c (54.6 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 0.0050 mmol, 5 mol%), L5 (7.9 mg, 0.012 mmol, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The
residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3c: 35.8 mg (0.0717 mmol), as a yellow solid, 72% yield; mp = 135–137 °C; $[\alpha]_D^{25} = +152.3$ (c = 0.26 in CHCl$_3$); 88% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R = 5.41$ min (minor), $t_R = 6.13$ min (major); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.44–8.37 (m, 1H), 7.40 (d, $J = 8.3$ Hz, 2H), 7.25–7.23 (m, 1H), 7.18–7.03 (m, 5H), 6.91 (d, $J = 9.2$ Hz, 1H), 5.52–5.42 (m, 2H), 5.20 (dd, $J = 17.7$, 1.6 Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 2.29 (s, 3H), 2.25 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 166.0, 149.9, 143.3, 141.7, 140.7, 138.4, 138.0, 136.6, 133.2, 129.8, 128.9, 128.7, 127.6, 127.3, 127.0, 126.9, 123.7, 122.6, 120.4, 119.0, 60.9, 53.9, 21.5, 21.3, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{30}$H$_{29}$NO$_4$SNa$^+$ 522.1710; Found 522.1718.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), (E)-4-methyl-N-(4-methylbenzylidene)benzenesulfonamide 2d (54.6 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 0.0050 mmol, 5 mol%), L5 (7.9 mg, 0.012 mmol, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3d: 44.7 mg (0.0896 mmol), as a yellow solid, 90% yield; mp = 140–142 °C; $[\alpha]_D^{25} = +104.3$ (c = 0.40 in CHCl$_3$); 91% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R = 6.75$ min (minor), $t_R = 8.43$ min (major); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.33–8.27 (m, 1H), 7.45–7.37 (m, 2H), 7.31–7.27 (m, 2H), 7.16–7.06 (m, 4H), 6.92 (d, $J = 8.1$ Hz, 2H), 6.80–6.74 (m, 1H), 6.31 (dd, $J = 17.7$, 11.5 Hz, 1H), 6.23 (s, 1H), 5.87 (d, $J = 8.9$ Hz, 1H), 5.46 (dd, $J = 11.5$, 1.6 Hz, 1H), 5.36–5.27 (m, 1H), 5.18 (dd, $J = 17.7$, 1.6 Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 2.31 (s, 3H), 2.25 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 166.0, 149.9, 143.3, 141.7, 140.7, 138.4, 137.9, 136.6, 135.1, 133.2, 129.7, 129.5, 128.9, 127.6, 127.1, 126.89, 126.87, 126.7, 122.5, 120.5, 119.0, 60.9, 53.8, 21.4, 21.1,
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), (E)-N-((1,1'-biphenyl)-4-ylmethylene)-4-methylbenzenesulfonamide 2e (67.0 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 0.0050 mmol, 5 mol%), L5 (7.9 mg, 0.012 mmol, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3e: 48.3 mg (0.0861 mmol), as a yellow solid, 86% yield; mp = 71–73 °C; [α]D25 = +66.7 (c = 0.17 in CHCl3); 92% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: tR = 8.64 min (minor), tR = 10.94 min (major); 1H NMR (400 MHz, CDCl3) δ (ppm) 8.45–8.38 (m, 1H), 7.58–7.46 (m, 6H), 7.46–7.38 (m, 4H), 7.36–7.30 (m, 1H), 7.17–7.06 (m, 2H), 6.93 (dd, J = 8.0 Hz, 2H), 6.83 (dd, J = 7.3, 1.3 Hz, 1H), 6.34 (dd, J = 17.7, 11.5 Hz, 1H), 6.26 (s, 1H), 5.96 (d, J = 9.0 Hz, 1H), 5.59–5.52 (m, 1H), 5.48 (dd, J = 11.5, 1.6 Hz, 1H), 5.22 (dd, J = 17.7, 1.6 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ (ppm) 166.0, 149.8, 143.4, 141.6, 141.0, 140.5, 140.4, 138.6, 137.1, 136.6, 133.2, 129.8, 129.0, 128.8, 127.6, 127.54, 127.51, 127.21, 127.16, 127.1, 127.0, 126.9, 122.7, 120.5, 119.2, 61.0, 53.8, 21.4, 14.3; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C35H31NO4SNa+ 584.1866; Found 584.1875.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(3-fluorobenzylidene)-4-methylbenzenesulfonamide 2f (55.4 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography.
chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3f: 37.8 mg (0.0751 mmol), as a yellow solid, 75% yield; mp = 114-116 °C; [α]_D^25 = +123.6 (c = 0.39 in CHCl₃); 83% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm]: tᵣ = 9.78 min (minor), tᵣ = 11.62 min (major); ^1H NMR (400 MHz, CDCl₃) δ (ppm) 8.41 (dd, J = 7.4, 1.4 Hz, 1H), 7.45–7.39 (m, 2H), 7.31–7.24 (m, 1H), 7.22–7.05 (m, 4H), 7.00–6.91 (m, 3H), 6.75 (dd, J = 7.0, 1.4 Hz, 1H), 6.27 (dd, J = 17.8, 11.5 Hz, 1H), 6.25 (s, 1H), 5.88 (d, J = 9.1 Hz, 1H), 5.61–5.54 (m, 1H), 5.48 (dd, J = 11.5, 1.5 Hz, 1H), 5.19 (dd, J = 17.8, 1.5 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.26 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^13C NMR (100 MHz, CDCl₃) δ (ppm) 165.9, 163.1 (d, ^1J_C=FC = 245.4 Hz), 149.6, 143.5, 141.2, 141.0 (d, ^3J_C=FC = 7.0 Hz), 139.9, 138.7, 136.5, 133.1, 130.4 (d, ^3J_C=FC = 8.2 Hz), 129.8, 129.0, 127.5, 127.3, 127.1, 126.9, 122.8, 122.3, 120.2, 119.6, 115.1 (d, ^2J_C=FC = 21.0 Hz), 113.9 (d, ^2J_C=FC = 23.0 Hz), 61.0, 53.5 (d, ^4J_C=FC = 2.0 Hz), 21.4, 14.3; ^19F NMR (375 MHz, CDCl₃) δ (ppm) –111.8; HRMS (ESI-TOF) m/z: [M + Na]^+ Calcd for C₂₉H₂₆FNO₄SNa⁺ 526.1459; Found 526.1467.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(3-chlorobenzylidene)-4-methylbenzensulfonylamine 2g (58.6 mg, 0.200 mmol, 2.0 equiv), Pd₂(dba)₃ (4.6 mg, 5 mol%), L₅ (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et₃N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3g: 39.9 mg (0.0767 mmol), as a yellow solid, 77% yield; mp = 128–130 °C; [α]_D^25 = +112.1 (c = 0.38 in CHCl₃); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm]: tᵣ = 9.77 min (minor), tᵣ = 11.60 min (major); ^1H NMR (400 MHz, CDCl₃) δ (ppm) 8.48–8.36 (m, 1H), 7.49–7.36 (m, 3H), 7.32–7.20 (m, 3H), 7.20–7.07 (m, 2H), 7.00–6.91 (m, 2H), 6.80–6.70 (m, 1H), 6.28 (dd, J = 17.8, 11.5 Hz, 1H), 6.25 (s, 1H), 5.86 (d, J = 9.1 Hz, 1H), 5.54–5.43 (m, 2H), 5.19 (dd, J = 17.7, 1.5 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 2.27 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^13C NMR (100 MHz, CDCl₃) δ (ppm) 165.9, 149.5, 143.5, 141.2, 140.4, 139.7, 138.8, 136.5, 133.1, 130.4 (d, ^3J_C=FC = 8.2 Hz), 129.8, 129.0, 127.5, 127.3, 127.1, 126.9, 122.8, 122.3, 120.2, 119.6, 115.1 (d, ^2J_C=FC = 21.0 Hz), 113.9 (d, ^2J_C=FC = 23.0 Hz), 61.0, 53.5 (d, ^4J_C=FC = 2.0 Hz), 21.4, 14.3.
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(4-chlorobenzylidene)-4-methylbenzenesulfonamide 2h (58.6 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 0.0050 mmol, 5 mol%), L5 (7.9 mg, 0.012 mmol, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3h: 44.4 mg (0.0853 mmol), as a yellow solid, 85% yield; mp = 145–147 °C; [α]D = +124.1 (c = 0.54 in CHCl3); 91% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm]: tR = 6.77 min (minor), tR = 8.46 min (major); 1H NMR (400 MHz, CDCl3) δ (ppm) 8.44–8.36 (m, 1H), 7.44–7.39 (m, 2H), 7.39–7.33 (m, 2H), 7.30–7.24 (m, 2H), 7.05–7.17 (m, 2H), 6.98–6.89 (m, 2H), 6.78–6.70 (m, 1H), 6.32–6.24 (dd, J = 17.7, 11.5 Hz, 1H), 6.24 (s, 1H), 5.85 (d, J = 9.2 Hz, 1H), 5.57–5.50 (m, 1H), 5.47 (dd, J = 11.5, 1.6 Hz, 1H), 5.16 (dd, J = 17.7, 1.6 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.26 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ (ppm) 165.9, 149.5, 143.5, 141.2, 139.9, 138.7, 136.8, 136.5, 134.0, 133.1, 129.8, 129.01, 128.99, 128.96, 128.2, 127.5, 127.2, 127.1, 126.9, 122.8, 120.2, 119.5, 61.0, 53.4, 21.3, 14.3; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C29H26NO4S35ClNa+ 542.1163; Found 542.1158; Calcd for C29H2637ClNO4SNa+ 544.1134; Found 544.1133.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), imine (E)-4-methyl-N-(naphthalen-2-ylmethylene)benzenesulfonamide 2i (61.8 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 μL, 0.10 mmol, 1.0 equiv) and
degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3i: 43.0 mg (0.0802 mmol), as a yellow solid, 80% yield; mp = 149–151 °C; [α]$_{D}^{25}$ = +127.9 (c = 0.43 in CHCl$_3$); 92% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: t$_R$ = 7.18 min (minor), t$_R$ = 9.49 min (major); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.42 (d, J = 7.6 Hz, 1H), 7.86–7.75 (m, 3H), 7.76–7.67 (m, 1H), 7.54 (dd, J = 8.6, 1.9 Hz, 1H), 7.48–7.39 (m, 4H), 7.15–7.09 (m, 1H), 7.08–7.01 (m, 1H), 6.92 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 7.4 Hz, 1H), 6.35 (dd, J = 17.7, 11.5 Hz, 1H), 6.27 (s, 1H), 6.07 (d, J = 9.2 Hz, 1H), 5.62 (d, J = 9.2 Hz, 1H), 5.47 (dd, J = 11.5, 1.6 Hz, 1H), 5.22 (dd, J = 17.7, 1.6 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 2.25 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 166.0, 149.8, 143.4, 141.7, 140.4, 138.7, 136.6, 135.6, 133.22, 133.18, 133.0, 129.8, 129.0, 128.8, 128.0, 127.6, 127.1, 127.0, 126.9, 126.41, 126.38, 125.5, 124.7, 122.8, 120.4, 119.2, 61.0, 54.2, 21.4, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{33}$H$_{29}$NO$_4$SNa$^+$ 558.1870; Found 558.1868.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide 2j (49.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3j: 35.4 mg (0.0744 mmol), as a yellow solid, 74% yield; mp = 76–78 °C; [α]$_{D}^{25}$ = +115.9 (c = 0.29 in CHCl$_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: t$_R$ = 8.29 min (minor), t$_R$ = 9.44 min (major); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.43–8.36 (m, 1H), 7.48–7.41 (m, 2H), 7.36–7.30 (m, 1H), 7.18–7.06 (m, 3H), 6.96–6.90 (m, 2H), 6.41 (dd, J = 17.7, 11.5 Hz, 1H), 6.31–6.21 (m, 3H), 5.92 (dd, J = 7.2, 1.1 Hz, 1H), 5.56 (dd, J = 11.5, 1.7 Hz, 1H), 5.44–5.36 (m, 1H), 5.33 (dd, J = 17.7, 1.7 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.25
(s, 3H), 1.37 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm) 165.9, 150.4, 149.8, 143.3, 142.8, 141.5, 138.8, 138.5, 136.4, 132.9, 129.7, 128.9, 127.5, 127.00, 126.96, 126.8, 123.2, 120.5, 119.4, 110.6, 108.2, 60.9, 49.4, 21.3, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{27}$H$_{25}$NO$_4$SNa$^+$ 498.1346; Found 498.1353.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1a (22.6 mg, 0.0999 mmol, 1.0 equiv), (E)-4-methyl-N-(thiophen-2-ylmethylene)benzenesulfonamide 2k (53.0 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3k: 40.2 mg (0.0817 mmol), as a yellow solid, 82% yield; mp = 147–149 °C; $[α]_D^{25} = +110.4$ (c = 0.48 in CHCl$_3$); 88% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, t = 254 nm]: t$_R$ = 7.31 min (minor), t$_R$ = 8.58 min (major); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.45–8.34 (m, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.25–7.22 (m, 1H), 7.17–7.06 (m, 2H), 6.98–6.85 (m, 5H), 6.36 (dd, J = 17.7, 11.4 Hz, 1H), 6.25 (s, 1H), 6.04 (d, J = 8.9 Hz, 1H), 5.63 (d, J = 8.8 Hz, 1H), 5.53 (dd, J = 11.4, 1.6 Hz, 1H), 5.30 (dd, J = 17.7, 1.6 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 165.9, 149.8, 143.5, 142.1, 141.3, 139.9, 138.5, 136.4, 133.1, 129.8, 128.9, 127.4, 127.19, 127.17, 127.0, 126.9, 125.9, 125.6, 122.9, 120.4, 119.5, 61.0, 51.2, 21.4, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{27}$H$_{25}$NO$_4$S$_2$Na$^+$ 514.1117; Found 514.1120.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)-4-methylphenyl)acrylate 1b (24.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzenesulfonamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were
added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3l: 42.7 mg (0.0854 mmol), as a yellow thick oil, 85% yield; [α]D^25 = +100.0 (c = 0.57 in CHCl₃); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm]: t_R = 8.73 min (minor), t_R = 10.09 min (major); ^1H NMR (400 MHz, CDCl₃) δ (ppm) 8.32 (d, J = 7.9 Hz, 1H), 7.46–7.38 (m, 4H), 7.35–7.26 (m, 3H), 7.00–6.86 (m, 3H), 6.58 (s, 1H), 6.26 (dd, J = 17.7, 11.5 Hz, 1H), 6.17 (s, 1H), 5.88 (d, J = 9.0 Hz, 1H), 5.58–5.46 (m, 1H), 5.43 (dd, J = 11.5, 1.6 Hz, 1H), 5.15 (dd, J = 17.8, 1.6 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 2.21 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^13C NMR (100 MHz, CDCl₃) δ (ppm) 166.1, 150.0, 143.3, 142.1, 140.6, 140.2, 138.8, 138.3, 136.6, 130.5, 128.9, 128.8, 128.0, 127.7, 127.5, 127.1, 126.9, 126.8, 122.4, 121.28, 121.26, 118.1, 60.8, 53.9, 21.7, 21.3, 14.3; HRMS (ESI-TOF) m/z: [M + Na]^+ Calcd for C₃₀H₂₉NO₄SNa^+ 522.1710; Found 522.1720.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)-4-methoxyphenyl)acrylate 1c (25.6 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzenesulfonylamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd₂(dba)₃ (4.6 mg, 5 mol%), L₅ (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et₃N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product 3m: 44.6 mg (0.0865 mmol), as a yellow solid, 87% yield; mp = 59–61 °C; [α]D^25 = +117.2 (c = 0.57 in CHCl₃); 91% ee, determined by HPLC analysis [Daicel Chiralpak IB, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: t_R = 6.08 min (major), t_R = 11.50 min (minor); ^1H NMR (400 MHz, CDCl₃) δ (ppm) 8.44 (d, J = 8.6 Hz, 1H), 7.51–7.36 (m, 4H), 7.36–7.22 (m, 3H), 6.96 (d, J = 8.0 Hz, 2H), 6.59 (dd, J = 8.6, 2.4 Hz, 1H), 6.35–6.21 (m, 2H), 6.12 (s, 1H), 5.88 (d, J = 8.8 Hz, 1H), 5.50–5.40 (m, 2H), 5.17 (dd, J = 17.8, 1.6 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.71 (s, 3H), 2.26 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^13C NMR (100 MHz, CDCl₃) δ (ppm) 166.2, 161.1, 149.9, 143.9, 143.3, 140.1, 139.9, 138.2,
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl \((E)-3-(2-(\text{but-3-en-1-yn-1-yl})-3\text{-fluorophenyl})\text{acrylate} \ 1d\) (24.4 mg, 0.0999 mmol, 1.0 equiv), \((E)-N\text{-benzylidene-4-methylbenzenesulfonamide} \ 2a\) (51.8 mg, 0.200 mmol, 2.0 equiv), \(\text{Pd}_2(\text{dba})_3\) (4.6 mg, 5 mol%), \(\text{L}5\) (7.9 mg, 12 mol%), \(\text{BzOH}\) (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then \(\text{Et}_3\text{N}\) (14 \(\mu\text{L}, 0.10 \text{mmol}, 1.0 \text{equiv}) and degassed dry \(\text{EtOH}\) (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/\(\text{EtOAc}=8/1\) to 5/1) to give product \(3n\): 32.9 mg (0.0655 mmol), as a yellow solid, 66% yield; mp = 108–110 °C; \([\alpha]_{D}^{25}=+141.4\ (c = 0.35\ \text{in} \ \text{CHCl}_3); 92\% \text{ee, determined by HPLC analysis} [\text{Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min,} l = 254 \text{nm}]: t_R = 9.58 \text{min (minor),} t_R = 10.86 \text{min (major);} ^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta\) (ppm) 8.24 (d, \(J = 7.6 \text{ Hz,} 1\text{H}), 7.48–7.20 (m, 7\text{H}), 7.17–7.06 (m, 1\text{H}), 6.87–6.76 (m, 3\text{H}), 6.47 (dd, \(J = 17.7, 11.5 \text{ Hz,} 1\text{H}), 6.36 (s, 1\text{H}), 6.04 (d, \(J = 10.4 \text{ Hz,} 1\text{H}), 5.66–5.44 (m, 2\text{H}), 5.28 (dd, \(J = 17.7, 1.5 \text{ Hz,} 1\text{H}), 4.34 (q, \(J = 7.1 \text{ Hz,} 2\text{H}), 2.19 (s, 3\text{H}), 1.39 (t, \(J = 7.1 \text{ Hz,} 3\text{H}); ^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta\) (ppm) 165.8, 154.5 (d, \(J_{\text{FC}} = 243.8 \text{ Hz}), 148.9, 148.8, 139.5, 138.4 (d, \(J_{\text{FC}} = 5.8 \text{ Hz}), 138.1, 137.0, 135.9 (d, \(J_{\text{FC}} = 6.1 \text{ Hz}), 128.8, 128.7, 128.7, 127.8, 127.9, 127.2 (d, \(J_{\text{FC}} = 14.2 \text{ Hz}), 127.0, 126.5, 126.4, 123.6, 123.3 (d, \(J_{\text{FC}} = 2.4 \text{ Hz}), 120.6 (d, \(J_{\text{FC}} = 1.9 \text{ Hz}), 117.7 (d, \(J_{\text{FC}} = 21.6 \text{ Hz}), 61.1, 53.7, 21.2, 14.3; ^{19}\text{F NMR (375 MHz, CDCl}_3\) \(\delta\) (ppm) –111.8; HRMS (ESI-TOF) m/z: [M + Na]^{+} \text{Calcd for C}_{29}\text{H}_{26}\text{FNO}_4\text{SNa}^{+} 526.1459; \text{Found 526.1468.}

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl \((E)-3-(2-(\text{but-3-en-1-yn-1-yl})-4\text{-chlorophenyl})\text{acrylate} \ 1e\) (26.1 mg, 0.100 mmol, 1.0 equiv), \((E)-N\text{-benzylidene-4-methylbenzenesulfonamide} \ 2a\) (51.8 mg, 0.200 mmol, 2.0 equiv), \(\text{Pd}_2(\text{dba})_3\) (4.6 mg, 5 mol%), \(\text{L}5\) (7.9 mg, 12 mol%), \(\text{BzOH}\) (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then \(\text{Et}_3\text{N}\) (14 \(\mu\text{L, 0.10 mmol, 1.0 equiv}) and degassed dry \(\text{EtOH}\) (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After
completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3o: 32.7 mg (0.0628 mmol), as a yellow solid, 63% yield; mp = 72–74 °C; [α]$_{D}^{25}$ = +53.1 (c = 0.34 in CHCl$_3$); 84% ee, determined by HPLC analysis [Daicel Chiralpak IB, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm]: t$_R$ = 5.45 min (major), t$_R$ = 8.48 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.38 (d, J = 8.3 Hz, 1H), 7.47–7.40 (m, 2H), 7.38–7.28 (m, 5H), 7.08 (dd, J = 17.8, 11.5 Hz, 1H), 6.29 (s, 1H), 5.90 (d, J = 8.0 Hz, 1H), 5.53 (dd, J = 11.5, 1.5 Hz, 1H), 5.35–5.28 (m, 1H), 5.22 (dd, J = 17.8, 1.6 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 165.8, 148.8, 143.7, 143.4, 140.1, 139.7, 137.7, 136.5, 135.6, 131.3, 129.1, 129.0, 128.3, 128.1, 127.3, 127.0, 126.7, 126.4, 123.4, 120.8, 119.9, 61.1, 54.0, 21.3, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{29}$H$_{26}$ClNO$_4$SNa$^+$ 542.1163; Found 542.1170; Calcd for C$_{29}$H$_{26}$ClNO$_4$SNa$^+$ 544.1134; Found 544.1138.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(but-3-en-1-yn-1-yl)-4-(trifluoromethyl)phenyl)acrylate 1f (29.4 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzene-sulfonamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3p: 35.6 mg (0.0643 mmol), as a yellow solid, 64% yield; mp = 114–116 °C; [α]$_{D}^{25}$ = +57.0 (c = 0.17 in CHCl$_3$); 86% ee, determined by HPLC analysis [Daicel Chiralpak IB, n-hexane/i-PrOH = 0/10, flow rate = 1.0 mL/min, λ = 254 nm]: t$_R$ = 4.42 min (major), t$_R$ = 5.58 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.50 (d, J = 8.1 Hz, 1H), 7.44–7.27 (m, 8H), 7.03 (s, 1H), 6.91–6.82 (d, J = 8.0 Hz, 2H), 6.47 (dd, J = 17.8, 11.5 Hz, 1H), 6.41 (s, 1H), 5.98 (d, J = 7.5 Hz, 1H), 5.59 (dd, J = 11.5, 1.5 Hz, 1H), 5.33–5.28 (d, J = 8.0 Hz, 1H), 5.27 (dd, J = 17.8, 1.6 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 2.21 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 165.6, 148.3, 143.4, 142.4, 140.1, 139.9, 137.5, 136.4, 136.0, 131.2 (q, $^2$J$_{FC}$ = 31.9 Hz), 129.1, 128.9, 128.5, 127.2, 126.9, 126.8, 126.7, 126.5.
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(6-(but-3-en-1-yn-1-yl)-5-chlorophenyl)acrylate 1g (26.1 mg, 0.100 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzenesulfonamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3q: 37.5 mg (0.0721 mmol), as a yellow solid, 72% yield; mp = 121–123 °C; $[\alpha]_{25}^{25}$ = +122.2 ($c$ = 0.36 in CHCl$_3$); 91% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, $\lambda$ = 254 nm]: $t_R$ = 5.48 min (minor), $t_R$ = 7.25 min (major); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.46 (d, $J$ = 2.0 Hz, 1H), 7.44–7.27 (m, 7H), 7.07–7.00 (m, 1H), 6.94 (d, $J$ = 8.1 Hz, 2H), 6.71 (d, $J$ = 8.0 Hz, 1H), 6.35 (dd, $J$ = 17.8, 11.5 Hz, 1H), 6.30 (s, 1H), 5.92 (d, $J$ = 8.4 Hz, 1H), 5.51 (dd, $J$ = 11.5, 1.6 Hz, 1H), 5.48–5.36 (m, 1H), 5.21 (dd, $J$ = 17.7, 1.5 Hz, 1H), 4.34 (q, $J$ = 7.1 Hz, 2H), 2.28 (s, 3H), 1.39 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 165.7, 148.8, 143.5, 140.0, 139.0, 137.7, 136.5, 134.6, 132.9, 129.3, 128.98, 128.95, 128.3, 127.6, 127.3, 126.9, 126.6, 123.1, 121.2, 120.4, 61.2, 53.9, 21.4, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{30}$H$_{26}$F$_3$NO$_4$SNa$^+$ 576.1427; Found 576.1436.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(6-(but-3-en-1-yn-1-yl)benzo[d][1,3]dioxol-5-yl)acrylate 1h (27.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzenesulfonamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored
by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 3/1) to give product 3r: 42.4 mg (0.0800 mmol), as a yellow solid, 80% yield; mp = 58–60 °C; [α]_D^25 = +160.0 (c = 0.41 in CHCl₃); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: t_R = 10.00 min (minor), t_R = 14.54 min (major); _1H NMR (400 MHz, CDCl₃) δ (ppm) 8.10 (s, 1H), 7.51–7.44 (m, 2H), 7.42–7.35 (m, 2H), 7.34–7.26 (m, 3H), 7.00 (d, J = 8.0 Hz, 2H), 6.38–6.22 (m, 2H), 6.16 (s, 1H), 5.96–5.77 (m, 3H), 5.47–5.34 (m, 2H), 5.13 (dd, J = 17.7, 1.7 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 2.28 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); _13C NMR (100 MHz, CDCl₃) δ (ppm) 166.0, 149.7, 148.6, 146.7, 143.4, 139.8, 138.0, 137.7, 137.3, 136.7, 129.0, 128.9, 128.1, 127.5, 127.1, 127.0, 126.7, 121.9, 118.5, 109.2, 102.1, 101.5, 60.9, 53.9, 21.4, 14.3; HRMS (ESI-TOF) m/z: [M + Na]^+ Calcd for C₃₀H₂₇NO₆SNa⁺ 552.1451; Found 552.1458.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added methyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate 1i (21.2 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzenesulfonylamine 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd₂(dbcat)₅ (4.6 mg, 5 mol%), L₅ (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et₃N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3s: 31.3 mg (0.0663 mmol), as a yellow solid, 66% yield; mp = 145–147 °C; [α]_D^25 = +126.4 (c = 0.56 in CHCl₃); 87% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: t_R = 6.49 min (minor), t_R = 8.25 min (major); _1H NMR (400 MHz, CDCl₃) δ (ppm) 8.40 (d, J = 7.3, 1H), 7.44–7.38 (m, 4H), 7.34–7.26 (m, 3H), 7.17–7.04 (m, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.78 (dd, J = 7.3, 1.4 Hz, 1H), 6.31 (dd, J = 17.7, 11.5 Hz, 1H), 6.25 (s, 1H), 5.91 (d, J = 8.9 Hz, 1H), 5.51–5.39 (m, 2H), 5.19 (dd, J = 17.7, 1.6 Hz, 1H), 3.86 (s, 3H), 2.25 (s, 3H); _13C NMR (150 MHz, CDCl₃) δ (ppm) 166.3, 150.1, 143.3, 141.6, 140.7, 138.4, 138.1, 136.6, 133.1, 129.8, 128.9, 128.8, 128.0, 127.5, 127.1, 127.0, 126.9, 126.7, 122.6, 120.4, 118.5, 53.9, 51.9, 21.3; HRMS (ESI-TOF) m/z: [M +H]^+ Calcd for C₂₈H₂₆NO₄S⁺ 472.1577; Found 472.1586.
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added

\((E)-4-(2-(but-3-en-1-yn-1-yl)phenyl)but-3-en-2-one\) **1j** (19.6 mg, 0.0999 mmol, 1.0 equiv), \((E)-N\text{-benzyldiene-4-methylbenzenesulfonamide 2a} (51.8 mg, 0.200 mmol, 2.0 equiv), Pd\(_2\)(dba)\(_3\) (4.6 mg, 5 mol\%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et\(_3\)N (14 \(\mu\)L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3t**: 28.7 mg (0.0631 mmol), as a yellow solid, 63% yield; mp = 162–164 °C; \([\alpha]_{D}^{25} = +126.6 \ (c = 0.43 \text{ in CHCl}_3)\); 82% ee, determined by HPLC analysis \[[Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, \lambda = 254 \text{ nm}]: t_R = 7.90 \text{ min (minor), } t_R = 9.49 \text{ min (major); } 1^H \text{ NMR (400 MHz, CDCl}_3) \delta \text{ ppm) 8.29–8.09 (m, 1H), 7.47–7.36 (m, 4H), 7.35–7.26 (m, 3H), 7.14–7.01 (m, 2H), 6.92 (d, } J = 8.0 \text{ Hz, 2H), 6.81–6.73 (m, 1H), 6.53 (s, 1H), 6.34 (dd, } J = 17.8, 11.4 \text{ Hz, 1H), 5.92 (d, } J = 8.8 \text{ Hz, 1H), 5.58–5.41 (m, 2H), 5.19 (dd, } J = 17.8, 1.6 \text{ Hz, 1H), 2.43 (s, 3H), 2.26 (s, 3H); } 13^C \text{ NMR (100 MHz, CDCl}_3) \delta \text{ ppm) 199.3, 147.2, 143.3, 141.5, 141.4, 138.5, 138.1, 136.6, 133.2, 130.0, 128.92, 128.86, 128.1, 127.7, 127.2, 126.9, 126.7, 126.4, 126.3, 122.6, 120.5, 54.0, 32.1, 21.4; } \text{ HRMS (ESI-TOF) m/z: } [M + Na]^+ \text{ Calcd for C}_{28}H_{25}NO_3SNa}^{+} 478.1447; \text{ Found 478.1457.}

![Image](image_url)

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added

\((E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-1-phenylprop-2-en-1-one\) **1k** (25.8 mg, 0.0999 mmol, 1.0 equiv), \((E)-N\text{-benzyldiene-4-methylbenzenesulfonamide 2a} (51.8 mg, 0.200 mmol, 2.0 equiv), Pd\(_2\)(dba)\(_3\) (4.6 mg, 5 mol\%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et\(_3\)N (14 \(\mu\)L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3u**: 30.7 mg (0.0593 mmol), as a yellow solid, 59% yield; mp = 70–72 °C; \([\alpha]_{D}^{25} = +86.7 \ (c = 0.27 \text{ in CHCl}_3); 90% ee, determined by HPLC analysis \[[Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, \lambda = 254 \text{ nm}]: t_R = 7.90 \text{ min (minor), } t_R = 9.49 \text{ min (major); } 1^H \text{ NMR (400 MHz, CDCl}_3) \delta \text{ ppm) 8.29–8.09 (m, 1H), 7.47–7.36 (m, 4H), 7.35–7.26 (m, 3H), 7.14–7.01 (m, 2H), 6.92 (d, } J = 8.0 \text{ Hz, 2H), 6.81–6.73 (m, 1H), 6.53 (s, 1H), 6.34 (dd, } J = 17.8, 11.4 \text{ Hz, 1H), 5.92 (d, } J = 8.8 \text{ Hz, 1H), 5.58–5.41 (m, 2H), 5.19 (dd, } J = 17.8, 1.6 \text{ Hz, 1H), 2.43 (s, 3H), 2.26 (s, 3H); } 13^C \text{ NMR (100 MHz, CDCl}_3) \delta \text{ ppm) 199.3, 147.2, 143.3, 141.5, 141.4, 138.5, 138.1, 136.6, 133.2, 130.0, 128.92, 128.86, 128.1, 127.7, 127.2, 126.9, 126.7, 126.4, 126.3, 122.6, 120.5, 54.0, 32.1, 21.4; } \text{ HRMS (ESI-TOF) m/z: } [M + Na]^+ \text{ Calcd for C}_{28}H_{25}NO_3SNa}^{+} 478.1447; \text{ Found 478.1457.}

![Image](image_url)
nm]: $t_R = 9.98$ min (minor), $t_R = 11.78$ min (major); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.09–7.99 (m, 2H), 7.78 (dd, $J = 7.1$, 1.6 Hz, 1H), 7.66–7.59 (m, 1H), 7.57–7.49 (m, 2H), 7.49–7.40 (m, 4H), 7.36–7.27 (m, 3H), 7.10 (s, 1H), 7.08–6.98 (m, 2H), 6.95 (d, $J = 8.0$ Hz, 2H), 6.83–6.77 (m, 1H), 6.46 (dd, $J = 17.8$, 11.5 Hz, 1H), 5.97 (d, $J = 8.8$ Hz, 1H), 5.53 (dd, $J = 11.5$, 1.6 Hz, 1H), 5.45 (d, $J = 8.8$ Hz, 1H), 5.29 (dd, $J = 17.8$, 1.6 Hz, 1H), 2.24 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 193.0, 147.1, 143.5, 141.4, 140.5, 138.2, 137.9, 137.4, 136.6, 133.8, 133.5, 129.5, 129.0, 128.90, 128.87, 128.1, 127.8, 126.9, 126.8, 126.7, 125.7, 125.5, 122.7, 120.5, 54.0, 21.4; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{33}$H$_{27}$NO$_3$SNa$^+$ 544.1604; Found 544.1606.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-N,N-dimethylacrylamide 11 (22.5 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzenesulfonamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3v: 37.2 mg (0.0767 mmol), as a yellow solid, 77% yield; mp = 226–228 °C; [$\alpha$]$^D_{25} = +98.0$ (c = 0.26 in CHCl$_3$); 85% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, $\lambda = 254$ nm]: $t_R = 5.28$ min (minor), $t_R = 6.57$ min (major); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.55–7.35 (m, 5H), 7.33–7.26 (m, 3H), 7.12–6.92 (m, 4H), 6.88–6.79 (m, 1H), 6.52 (s, 1H), 6.39 (dd, $J = 17.8$, 11.5 Hz, 1H), 5.92 (d, $J = 8.5$ Hz, 1H), 5.45 (dd, $J = 11.5$, 1.6 Hz, 1H), 5.38 (d, $J = 8.5$ Hz, 1H), 5.24 (dd, $J = 17.8$, 1.7 Hz, 1H), 3.14 (s, 3H), 3.02 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 167.4, 143.4, 141.7, 140.9, 138.7, 138.4, 136.74, 136.67, 133.7, 129.1, 128.8, 128.7, 127.9, 127.8, 127.0, 126.7, 126.3, 123.30, 123.26, 122.2, 120.4, 53.9, 37.7, 34.6, 21.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{29}$H$_{28}$N$_2$O$_3$SNa$^+$ 507.1713; Found 507.1723.
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added 1-(but-3-en-1-yn-1-yl)-2-styrylbenzene 1m (23.0 mg, 0.0999 mmol, 1.0 equiv, E/Z = 2.7:1), (E)-N-benzylidene-4-methylbenzenesulfonylamine 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd₂dba₃ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et₃N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3w: 34.7 mg (0.0714 mmol), as a yellow solid, 71% yield; mp = 61–63 °C; [α]D²⁵ = +142.4 (c = 0.55 in CHCl₃); E/Z = 2.5:1, 84% ee/89% ee, determined by HPLC analysis [Daicel Chiralpak IF, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: tᵣ = 6.96 min (major), tᵣ = 8.11 min (minor); tᵣ = 7.63 min (minor), tᵣ = 9.51 min (major);

Reaction of 2-styrylbenzene substituted enyne 1m with N-Ts imine 2a under the standard conditions would deliver η¹-benzyl-Pd(II) intermediate III after vinylogous addition and 5-exo-trig migratory insertion, which underwent β-H elimination to form E-3w. As demonstrated in a previous
study (Tetrahedron Lett., 2013, 54, 5808), E-3w would feasibly undergo reversible hydropalladation and β-H elimination to form Z-3w. A base-mediated epimerization at the benzylic position of the intermediate III also might be possible for the formation of Z-3w isomer.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-3-(2-(3-methylbut-3-en-1-yn-1-yl)phenyl)acrylate 1n (24.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzenesulfonyamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3x: 38.9 mg (0.0778 mmol), as a yellow solid, 78% yield; mp = 51–53 °C; [α]25D = +61.0 (c = 0.32 in CHCl3); 91% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm]: tR = 5.38 min (minor), tR = 6.81 min (major); 1H NMR (400 MHz, CDCl3) δ (ppm) 8.46 (dd, J = 7.4, 1.4 Hz, 1H), 7.61–7.50 (m, 2H), 7.38–7.30 (m, 2H), 7.29–7.20 (m, 3H), 7.17–6.97 (m, 4H), 6.86 (d, J = 7.2, 1H), 6.19 (s, 1H), 5.79 (d, J = 7.9 Hz, 1H), 5.43 (d, J = 7.8 Hz, 1H), 5.37–5.28 (m, 1H), 4.78 (dd, J = 2.1, 1.1 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.29 (s, 3H), 1.83 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ (ppm) 166.1, 150.1, 143.4, 143.3, 141.8, 139.8, 138.5, 137.8, 137.1, 132.9, 129.7, 129.1, 128.7, 127.9, 127.2, 127.0, 126.9, 126.6, 120.6, 119.54, 119.48, 60.9, 54.5, 24.5, 21.4, 14.3; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C31H29NO4SNa+ 522.1710; Found 522.1716.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (E)-nona-2,8-dien-6-ynoate 1o (17.8 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzenesulfonyamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was
evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 3y: 26.1 mg (0.0597 mmol), as a white semisolid, 60% yield; \([\alpha]^2_{D} = +84.6 (c = 0.35 \text{ in CHCl}_3)\); 88% ee, determined by HPLC analysis [Daicel Chiralpak IF, *n*-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, \(l = 254 \text{ nm}\)]; \(t_R = 6.38 \text{ min (major), } t_R = 7.15 \text{ min (minor)}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta (ppm)\) 7.71–7.61 (m, 2H), 7.31–7.27 (m, 2H), 7.26–7.17 (m, 5H), 6.25–6.18 (m, 1H), 5.73 (t, \(J = 2.5 \text{ Hz, } 1H\)), 5.65 (d, \(J = 8.1 \text{ Hz, } 1H\)), 5.46 (dd, \(J = 11.6, 1.6 \text{ Hz, } 1H\)), 5.33 (dd, \(J = 8.2, 2.9 \text{ Hz, } 1H\)), 5.27 (dd, \(J = 17.9, 1.7 \text{ Hz, } 1H\)), 4.16 (q, \(J = 7.1 \text{ Hz, } 2H\)), 2.93–2.79 (m, 1H), 2.71–2.58 (m, 1H), 2.36 (s, 3H), 2.33–2.22 (m, 2H), 1.28 (t, \(J = 7.1 \text{ Hz, } 3H\)); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta (ppm)\) 167.6, 166.2, 153.2, 143.7, 140.3, 138.1, 137.1, 129.4, 128.9, 128.0, 127.1, 126.5, 121.7, 108.8, 59.6, 55.7, 30.3, 29.2, 21.4, 14.4; HRMS (ESI-TOF) m/z: \([M + Na]^+\) Calcd for C\(_{25}\)H\(_{27}\)NO\(_4\)SNa\(^+\) 460.1553; Found 460.1563.

5. General procedure for asymmetric synthesis of indene derivative 4

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl \((E)-3-\)\((2\)-(but-3-en-1-yn-1-yl)phenyl)but-2-enoate 1y (24.0 mg, 0.0999 mmol, 1.0 equiv), \((E)-N\)-benzylidene-4-methylbenzenesulfonylamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd\(_2\)(dba)\(_3\) (4.6 mg, 5 mol%), L5 (12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et\(_3\)N (14 \(\mu\)L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 80 °C for 36 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 4: 30.1 mg (0.0598 mmol), as a colourless oil, 60% yield; 2:2:1 dr, determined by \(^1\)H NMR; 87% ee/70% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, \(l = 254 \text{ nm}\)]; \(t_R = 7.99 \text{ min (major), } t_R = 8.97 \text{ min (minor)}\); \(t_R = 10.23 \text{ min (minor), } t_R = 11.37 \text{ min (major)}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta (ppm)\) 7.61–7.56 (m, 2H), 7.53–7.46 (m, 2H), 7.32–7.28 (m, 3H), 7.17–7.05 (m, 5H), 6.82 (d, \(J = 7.5 \text{ Hz, } 1H\)), 6.30 (dd, \(J = 17.8, 11.6 \text{ Hz, } 1H\)), 5.90 (d, \(J = 8.3 \text{ Hz, } 1H\)), 5.36 (d, \(J =
6. General procedure for asymmetric synthesis of naphthalenes 5

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added 1,3-enyne derivative 1 (0.100 mmol), imine 2 (0.200 mmol), Pd₂(dbab)₃ (4.6 mg, 5 mol%), L₅ (12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et₃N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 48–60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give product 5.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate 1p (33.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-methylbenzenesulfonamide 2a (51.8 mg, 0.200 mmol, 2.0 equiv), Pd₂(dbab)₃ (4.6 mg, 5 mol%), L₅ (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et₃N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5a: 47.6 mg (0.0807 mmol), as a white solid, 81% yield; mp = 137–139 °C; [α]ᵢ²⁵ = +109.8 (c = 0.51 in CHCl₃); 82% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: tᵣ = 10.81 min (major), tᵣ = 12.59 min (minor); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.55–7.36 (m, 7H), 7.36–7.26 (m, 7H), 7.25–7.20 (m, 2H), 6.98–6.80 (m, 2H), 6.80–6.67 (m, 1H), 6.64 (d, J = 9.6 Hz, 1H), 5.33–5.26 (m, 2H), 3.79 (q, J = 7.1 Hz, 2H), 2.84 (d, J = 14.2 Hz, 1H), 2.67 (d, J = 14.2 Hz, 1H), 2.33 (s, 3H), 1.13 (s, 3H), 0.82 (t, J = 7.1 Hz, 3H).
Hz, 1H), 5.91 (s, 1H), 5.45 (dd, J = 11.4, 1.6 Hz, 1H), 5.33 (dd, J = 17.9, 1.7 Hz, 1H), 2.27 (s, 3H), 1.16 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 167.5, 142.6, 140.5, 137.4, 137.2, 137.0, 134.1, 130.7, 130.4, 128.8, 128.7, 128.0, 127.9, 127.8, 127.5, 127.1, 126.6, 126.4, 125.9, 124.6, 122.2, 81.8, 27.6, 21.5; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C37H35N2O6SNa+ 612.2179; Found 612.2170.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate \textbf{1p} (33.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-4-nitrobenzenesulfonamide \textbf{2o} (58.1 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), \textbf{L5} (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product \textbf{5b}: 40.1 mg (0.0647 mmol), as a white solid, 65% yield; mp = 145–147 °C; [α]D25 = +120.3 (c = 0.48 in CHCl3); 82% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm]: tR = 7.96 min (major), tR = 9.59 min (minor); 1H NMR (600 MHz, CDCl3) δ (ppm) 7.86–7.78 (d, J = 8.3 Hz, 2H), 7.55–7.26 (m, 14H), 7.23–7.14 (m, 2H), 6.96–6.68 (m, 2H), 6.16 (brs, 1H), 5.52 (d, J = 11.6 Hz, 1H), 5.36 (d, J = 17.8 Hz, 1H), 1.16 (s, 9H); 13C NMR (150MHz, CDCl3) δ (ppm) 167.2, 149.1, 145.4, 139.2, 137.7, 136.6, 130.5, 130.0, 128.9, 128.6, 128.3, 128.2, 128.13, 128.09, 128.0, 127.94, 127.89, 127.7, 127.3, 126.5, 126.2, 123.0, 122.9, 122.7, 82.2, 27.5; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C36H32N2O6SNa+ 643.1873; Found 643.1875.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate \textbf{1p} (33.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(2-fluorobenzylidene)-4-methylbenzenesulfonamide \textbf{21} (55.4 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), \textbf{L5} (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography

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on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5c: 49.8 mg (0.0819 mmol), as a white solid, 82% yield; mp = 187–189 °C; [α]_D sup25 = +24.0 (c = 0.38 in CHCl₃); 86% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm]: t_R = 14.00 min (major), t_R = 19.90 min (minor); ^1H NMR (400 MHz, CDCl₃) δ (ppm) 7.97 (d, J = 8.5 Hz, 1H), 7.54–7.48 (m, 1H), 7.47–7.38 (m, 4H), 7.37–7.26 (m, 6H), 7.25–7.22 (m, 1H), 7.11–7.04 (m, 1H), 7.02–6.95 (m, 1H), 6.91 (d, J = 8.0 Hz, 2H), 6.86–6.75 (m, 2H), 5.72 (d, J = 6.8 Hz, 1H), 5.43 (dd, J = 11.5, 1.7 Hz, 1H), 5.26 (dd, J = 17.9, 1.7 Hz, 1H), 2.28 (s, 3H), 1.14 (s, 9H); ^13C NMR (100 MHz, CDCl₃) δ (ppm) 167.6, 160.4 (d, J FC = 247.3 Hz), 142.8, 137.5, 136.9, 134.4, 133.5, 133.3, 132.1, 131.2, 130.7, 130.4, 130.3, 129.7 (d, J FC = 3.1 Hz), 129.6, 129.5, 128.9, 127.9, 127.81 (d, J FC = 24.5 Hz), 127.77, 126.9, 126.8, 125.8, 124.6, 123.8 (d, J FC = 3.5 Hz), 122.2, 116.1 (d, J FC = 21.6 Hz), 81.7, 53.0, 27.6, 21.5; ^19F NMR (375 MHz, CDCl₃) δ (ppm) –111.9; HRMS (ESI-TOF) m/z: [M + Na]^+ Calcd for C_{37}H_{34}FNO_{5}SNa^+ 630.2085; Found 630.2088.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-((but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate 1p (33.0 mg, 0.0999 mmol, 1.0 equiv), (E)-4-methyl-N-(3-methylbenzyldiene)benzenesulfonamide 2c (54.6 mg, 0.200 mmol, 2.0 equiv), Pd_2(dba)_3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et_3N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5d: 47.2 mg (0.0782 mmol), as a white solid, 78% yield; mp = 99–101 °C; [α]_D sup25 = +40.8 (c = 0.26 in CHCl₃); 81% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm]: t_R = 9.69 min (major), t_R = 11.06 min (minor); ^1H NMR (400 MHz, CDCl₃) δ (ppm) 7.44–7.33 (m, 4H), 7.36–7.25 (m, 5H), 7.25–7.03 (m, 6H), 6.91–6.81 (m, 2H), 6.81–6.68 (m, 1H), 6.62 (d, J = 9.6 Hz, 1H), 5.91 (brs, 1H), 5.46 (dd, J = 11.4, 1.6 Hz, 1H), 5.35 (dd, J = 17.9, 1.7 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H), 1.17 (s, 9H); ^13C NMR (100 MHz, CDCl₃) δ (ppm) 167.6, 142.5, 140.4, 138.5, 137.4, 137.1, 137.0, 130.7, 130.4, 128.8, 128.5, 128.3, 128.0, 127.9, 127.8, 127.1, 126.4, 125.8, 123.7, 122.1, 81.8, 27.6, 21.6, 21.5; HRMS (ESI-TOF) m/z: [M + Na]^+ Calcd for C_{38}H_{37}NO_{5}SNa^+ 626.2336;
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate 1p (33.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(4-methoxybenzylidene)-4-methylbenzenesulfonamide 2m (57.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5f: 55.2 mg (0.0829 mmol), as a white solid, 83% yield; mp = 118–120 °C; [α]$_{D}^{25}$ = +50.0
(c = 0.54 in CHCl₃); 82% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: tᵣ = 15.23 min (major), tᵣ = 19.23 min (minor); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.52–7.45 (m, 4H), 7.44–7.31 (m, 8H), 7.30–7.10 (m, 8H), 6.81 (s, 2H), 6.75–6.55 (m, 2H), 5.89 (br s, 1H), 5.40 (dd, J = 11.5, 1.6 Hz, 1H), 5.329 (d, J = 17.9 Hz, 1H), 2.20 (s, 3H), 1.09 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 167.5, 142.7, 140.5, 140.3, 137.4, 137.3, 137.0, 130.7, 130.4, 128.9, 128.8, 128.0, 127.93, 127.86, 127.42, 127.36, 127.1, 126.5, 81.8, 27.6, 21.6; HRMS (ESI-TOF) m/z: [M + Na]⁺ Calcd for C₄₃H₉₃NO₄SNa⁺ 688.2492; Found 688.2496.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate 1p (33.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(3-chlorobenzylidene)-4-methylbenzenesulfonamide 2g (58.6 mg, 0.200 mmol, 2.0 equiv), Pd₂(dba)₃ (4.6 mg, 5 mol%), L₅ (7.9 mg, 12 mol%), and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et₃N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5g: 46.7 mg (0.0748 mmol), as a white solid, 75% yield; mp = 164–166 °C; [α]D²⁵ = +63.7 (c = 0.63 in CHCl₃); 83% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: tᵣ = 9.19 min (major), tᵣ = 10.40 min (minor); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.43–7.33 (m, 5H), 7.30–2.24 (m, 2H), 7.24–7.11 (m, 8H), 6.93–6.73 (m, 2H), 6.69–6.55 (m, 1H), 6.55–6.40 (m, 1H), 5.84 (br s, 1H), 5.39 (dd, J = 11.4, 1.5 Hz, 1H), 5.26 (dd, J = 17.8, 1.5 Hz, 1H), 2.22 (s, 3H), 1.09 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 167.4, 142.9, 137.5, 137.3, 136.8, 134.8, 130.7, 130.3, 129.9, 129.0, 128.0, 127.93, 127.90, 127.7, 127.4, 126.6, 126.4, 126.0, 124.9, 81.9, 27.6, 21.6; HRMS (ESI-TOF) m/z: [M + Na]⁺ Calcd for C₃₇H₃₉ClNO₄SNa⁺ 646.1789; Found 646.1790; Calcd for C₃₇H₃₉ClNO₄SNa⁺ 647.1812; Found 647.1816.
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yln-1-yl)phenyl)-3-phenylacrylate 1p (33.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(4-chlorobenzylidene)-4-methylbenzenesulfonamide 2h (58.6 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5h: 50.0 mg (0.0801 mmol), as a white solid, 80% yield; mp = 99–101 °C; [α]25D = +64.9 (c = 0.25 in CHCl3); 81% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm]: tR = 9.23 min (major), tR = 11.48 min (minor); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.51–7.44 (m, 5H), 7.43–7.34 (m, 2H), 7.34–7.18 (m, 8H), 7.03–6.76 (m, 2H), 6.78–6.60 (m, 1H), 6.60–6.43 (m, 1H), 5.91 (brs, 1H), 5.45 (dd, J = 11.4, 1.5 Hz, 1H), 5.30 (d, J = 17.8 Hz, 1H), 2.29 (s, 3H), 1.16 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 167.4, 142.9, 137.5, 137.3, 136.8, 133.4, 130.7, 130.3, 128.9, 128.8, 128.1, 128.0, 127.93, 127.90, 127.3, 126.5, 126.0, 81.9, 27.6, 21.6; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C37H3435ClNO4SNa+ 646.1789; Found 646.1795; Calcd for C37H3437ClNO4SNa+ 647.1823; Found 647.1823.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yln-1-yl)phenyl)-3-phenylacrylate 1p (33.0 mg, 0.0999 mmol, 1.0 equiv), (E)-4-methyl-N-(thiophen-2-ylmethylene)benzenesulfonamide 2k (53.0 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5i: 36.9 mg (0.0619 mmol), as a white solid, 62% yield; [α]25D = +40.8 (c = 0.51 in CHCl3); 73% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm]: tR = 12.16 min.
(major), $t_R = 14.64 \text{ min (minor)}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.06–7.55 (m, 1H), 7.54–7.39 (m 4H), 7.39–7.26 (m, 5H), 7.26–7.21 (m, 2H), 7.02–6.56 (m, 6H), 6.00 (brs, 1H), 5.51 (d, $J = 11.4$ Hz, 1H), 5.40 (d, $J = 17.8$ Hz, 1H), 2.27 (s, 3H), 1.17 (s, 9H); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 167.4, 145.3, 142.8, 137.5, 137.3, 136.7, 130.7, 130.3, 128.8, 128.0, 127.90, 127.85, 127.2, 126.5, 125.9, 125.5, 125.4, 122.4, 81.8, 27.6, 21.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{35}$H$_{33}$NO$_4$S$_2$Na$^+$ 618.1743; Found 618.1736.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)-4-methylphenyl)-3-phenylacrylate 1q (34.4 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(2-fluorobenzylidene)-4-methylbenzenesulfonylamide 2l (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5j: 45.7 mg (0.0734 mmol), as a white solid, 73% yield; mp = 125–127 °C; $[\alpha]^{25}_D = +19.6$ (c = 0.25 in CHCl$_3$); 89% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, $l = 254$ nm]; $t_R = 12.03$ min (major), $t_R = 21.50$ min (minor); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.72 (s, 1H), 7.61–7.54 (m, 1H), 7.50–7.40 (m, 3H), 7.39–7.33 (m, 2H), 7.32–7.25 (m, 4H), 7.14–7.06 (m, 2H), 7.03–6.89 (m, 3H), 6.82–6.69 (m, 2H), 5.81–5.69 (m, 1H), 5.40 (dd, $J = 11.4$, 1.7 Hz, 1H), 5.25 (dd, $J = 17.9$, 1.7 Hz, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 1.13 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 167.7, 160.4 (d, $^1$J$_{CF} = 247.3$ Hz), 142.8, 137.7, 137.4, 136.9, 136.7, 134.6, 133.4, 132.5, 130.7, 130.6, 130.4, 130.3, 129.7 (d, $^3$J$_{CF} = 3.1$ Hz), 129.5 (d, $^3$J$_{CF} = 8.2$ Hz), 128.9, 128.0, 127.81, 127.80 (d, $^2$J$_{CF} = 21.9$ Hz), 127.5, 127.1, 127.0 (d, $^3$J$_{CF} = 11.9$ Hz), 126.8, 123.8, 123.6, 122.0, 116.0 (d, $^2$J$_{CF} = 21.5$ Hz), 115.9, 52.9, 27.6, 22.1, 21.5; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ (ppm) –112.0; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{38}$H$_{38}$FNO$_4$SNa$^+$ 644.2234; Found 644.2234.
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl 3-(2-(but-3-en-1-yln-1-yl)-4-(trifluoromethyl)phenyl)-3-phenylacrylate 1r (39.8 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(2-fluorobenzylidene)-4-methylbenzenesulfonamide 2l (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5k: 43.8 mg (0.0648 mmol), as a white solid, 65% yield; mp = 62–64 °C; [α]$_D$$^5$ = +9.4 (c = 0.43 in CHCl$_3$); 87% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 8.38 min (major), $t_S$ = 9.85 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.32 (s, 1H), 7.44–7.30 (m, 6H), 7.27 (d, $J$ = 8.1 Hz, 2H), 7.25–7.18 (m, 3H), 7.05–6.99 (m, 1H), 6.99–6.90 (m, 1H), 6.87–6.75 (m, 3H), 6.72 (d, $J$ = 5.8 Hz, 1H), 5.56 (d, $J$ = 5.8 Hz, 1H), 5.43 (dd, $J$ = 11.5, 1.6 Hz, 1H), 5.27 (dd, $J$ = 17.9, 1.6 Hz, 1H), 2.15 (s, 3H), 1.08 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 167.0, 160.2 (d, $^1$J$_{FC}$ = 246.6 Hz), 142.9, 137.6, 136.7, 136.5, 135.4, 135.2, 133.9, 133.4, 132.2, 130.6, 130.2, 130.0, 129.9 (d, $^1$J$_{FC}$ = 8.3 Hz), 129.4 (d, $^3$J$_{FC}$ = 3.1 Hz), 129.0 (q, $^1$J$_{FC}$ = 252.1 Hz), 128.8, 128.7 (d, $^2$J$_{FC}$ = 21.6 Hz), 128.23, 128.18, 128.1, 127.9, 126.9, 126.1 (d, $^2$J$_{FC}$ = 12.1 Hz), 125.4, 124.1, 122.73, 122.6 (q, $^3$J$_{FC}$ = 3.1 Hz), 121.3 (q, $^3$J$_{FC}$ = 3.2 Hz), 116.2 (d, $^3$J$_{FC}$ = 21.5 Hz), 82.3, 52.8, 27.6, 21.4; $^{19}$F NMR (375 MHz, CDCl$_3$) δ (ppm) –112.4, –62.6; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{38}$H$_{33}$F$_3$NO$_4$SNa$^+$ 698.1959; Found 698.1957.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yln-1-yl)-5-chlorophenyl)-3-phenylacrylate 1s (36.4 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(2-fluorobenzylidene)-4-methylbenzenesulfonamide 2l (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was
purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5l: 46.3 mg (0.0721 mmol), as a white solid, 72% yield; mp = 174–176 °C; [α]D25 = +23.2 (c = 0.41 in CHCl3); 83% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: tR = 9.34 min (major), tR = 10.37 min (minor); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.96 (d, J = 9.2 Hz, 1H), 7.53–7.38 (m, 4H), 7.38–7.32 (m, 3H), 7.31–7.26 (m, 3H), 7.26–7.23 (m, 1H), 7.11–6.98 (m, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.85–6.69 (m, 2H), 5.67 (d, J = 6.5 Hz, 1H), 5.45 (dd, J = 11.5, 1.6 Hz, 1H), 5.27 (dd, J = 17.8, 1.7 Hz, 1H), 2.28 (s, 3H), 1.14 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 167.2, 160.4 (d, JFC = 247.3 Hz), 143.0, 136.8, 136.72, 136.70, 134.4, 134.0, 133.9, 133.1, 132.1, 131.4, 130.6, 130.3, 129.9, 129.8 (d, JFC = 8.2 Hz), 129.7 (d, JFC = 3.1 Hz), 128.9, 128.8, 128.2, 128.10, 127.5, 126.8, 126.6, 126.4 (d, JFC = 11.9 Hz), 126.1, 124.0, 122.4, 116.2 (d, JFC = 21.5 Hz), 52.9, 27.6, 21.5. 19F NMR (375 MHz, CDCl3) δ (ppm) –112.1; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C37H33ClFNO4Na+ 664.1695; Found 664.1698; Calcd for C37H33ClFNO4Na+ 665.1729; Found 665.1728.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl-3-(2-(but-3-en-1-yl)-4,5-dimethoxyphenyl)-3-phenylacrylate 1t (39.0 mg, 0.0999 mmol, 1.0 equiv, E/Z = 2.5:1), (E)-N-(2-fluorobenzylidene)-4-methylbenzenesulfonamide 2l (51.8 mg, 0.200 mmol, 2.0 equiv), Pd2(dbac)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product 5m: 56.0 mg (0.0844 mmol), as a white solid, 84% yield; mp = 213–215 °C; [α]D25 = +108.8 (c = 0.68 in CHCl3); 85% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: tR = 9.75 min (major), tR = 20.01 min (minor); 1H NMR (400 MHz, CDCl3) δ (ppm) 7.83–7.69 (m, 2H), 7.48–7.41 (m, 4H), 7.36–7.28 (m, 2H), 7.26–7.20 (m, 2H), 7.13–7.09 (m, 1H), 7.07–7.00 (m, 2H), 6.98–6.92 (m, 1H), 6.69–6.66 (m, 1H), 6.61 (s, 1H), 5.94–5.76 (m, 1H), 5.34 (dd, J = 11.3, 1.8 Hz, 1H), 5.21 (dd, J = 17.9, 1.9 Hz, 1H), 5.05 (s, 1H), 3.78 (s, 3H), 3.57 (s, 3H), 2.32 (s, 3H), 1.13 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 168.0,
161.5 (d, $^1 J_{FC} = 247.3$ Hz), 149.6, 148.9, 143.4, 143.1, 137.0, 136.1, 134.5, 132.0, 131.9, 130.5, 130.1, 130.0 (d, $^2 J_{FC} = 20.3$ Hz), 129.7, 129.5, 129.4 (d, $^3 J_{FC} = 8.2$ Hz), 129.1, 128.1, 128.0, 127.7, 127.4 (d, $^3 J_{FC} = 11.9$ Hz), 127.0, 126.4, 126.3, 123.7, 121.7, 116.1 (d, $^2 J_{FC} = 21.5$ Hz), 106.0, 104.1, 81.5, 56.0, 55.4, 53.3, 27.6, 21.5. 

$^{19}$F NMR (375 MHz, CDCl$_3$) δ (ppm) –112.2; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{39}$H$_{38}$FNO$_5$SNa$^+$ 690.2296; Found 690.2293.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-(4-fluorophenyl)acrylate 1u (34.8 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(2-fluorobenzylidene)-4-methylbenzenesulfonamide 21 (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5n: 39.2 mg (0.0627 mmol), as a white solid, 63% yield; mp = 176–178 °C; [α]$^D_25 = +30.3$ (c = 0.37 in CHCl$_3$); 82% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, 1 = 254 nm]: t$_R$ = 6.87 min (major), t$_R$ = 8.29 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.04–7.93 (m, 1H), 7.55–7.47 (m, 1H), 7.42–7.32 (m, 4H), 7.32–7.26 (m, 3H), 7.25–7.21 (m, 1H), 7.20–7.12 (m, 2H), 7.11–7.04 (m, 1H), 7.02–6.95 (m, 1H), 6.93 (d, J = 8.0 Hz, 2H), 6.83–6.72 (m, 2H), 5.68 (d, J = 7.2 Hz, 1H), 5.43 (dd, J = 11.5, 1.7 Hz, 1H), 5.26 (dd, J = 17.8, 1.7 Hz, 1H), 2.28 (s, 3H), 1.18 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm) 167.5, 162.3 (d, $^1 J_{FC} = 325.9$ Hz), 160.6 (d, $^1 J_{FC} = 327.6$ Hz), 142.8, 136.9, 136.3, 134.2, 133.6, 133.4, 133.3, 132.4 (d, $^1 J_{FC} = 8.5$ Hz), 132.14, 132.06, 132.0, 131.6, 130.3, 129.6, 129.62, 129.60, 129.5, 128.9, 127.4, 126.9, 126.83, 126.76, 125.9, 124.7, 123.8 (d, $^3 J_{FC} = 3.6$ Hz), 122.3, 116.1 (d, $^2 J_{FC} = 21.5$ Hz), 115.0 (d, $^3 J_{FC} = 4.5$ Hz), 114.8 (d, $^3 J_{FC} = 4.4$ Hz), 81.9, 53.0, 27.6, 21.5; $^{19}$F NMR (375 MHz, CDCl$_3$) δ (ppm) –114.2, –112.0; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{37}$H$_{33}$F$_2$NO$_5$SNa$^+$ 648.1991; Found 648.1994.
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-(4-methoxyphenyl)acrylate 1v (36.0 mg, 0.0999 mmol, 1.0 equiv, E/Z = 3.1:1), (E)-N-(2-fluorobenzylidene)-4-methyl-benzenesulfonamide 2l (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product 5o: 48.3 mg (0.0757 mmol), as a white solid, 76% yield; mp = 177–179 °C; [α]$^\circ_{D}^2$ = +27.4 (c = 0.38 in CHCl$_3$); 86% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 8.23 min (major), $t_R$ = 10.40 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.96 (d, $J = 8.5$ Hz, 1H), 7.55–7.47 (m, 1H), 7.46–7.41 (m, 3H), 7.30–7.26 (m, 1H), 7.25–7.17 (m, 3H), 7.11–7.04 (m, 1H), 7.03–6.95 (m, 3H), 6.91 (d, $J = 8.0$ Hz, 2H), 6.85–6.74 (m, 2H), 5.70 (d, $J = 7.2$ Hz, 1H), 5.43 (dd, $J = 11.4$, 1.7 Hz, 1H), 5.25 (dd, $J = 17.8$, 1.7 Hz, 1H), 3.88 (s, 3H), 2.27 (s, 3H), 1.19 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm) 167.7, 160.4 (d, $^1$J$_{FC} = 247.8$ Hz), 159.3, 142.7, 137.2, 136.9, 134.3, 133.6, 133.5, 132.5, 131.8, 131.5, 131.0, 130.3, 129.7 (d, $^2$J$_{FC} = 3.0$ Hz), 129.6, 129.5, 128.8, 126.9(d, $^2$J$_{FC} = 12.0$ Hz), 126.8, 126.7, 125.7, 124.6, 123.8, 122.1, 116.1 (d, $^2$J$_{FC} = 21.5$ Hz), 113.4, 113.3, 81.7, 55.4, 53.0, 27.7, 21.5; $^{19}$F NMR (375 MHz, CDCl$_3$) δ (ppm) −111.9; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{38}$H$_{36}$FNO$_5$SNa$^+$ 660.2190; Found 660.2188.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-(fur an-2-yl)acrylate 1w (32.0 mg, 0.0999 mmol, 1.0 equiv, E/Z = 3.1:1), (E)-N-(2-fluorobenzylidene)-4-methyl-benzenesulfonamide 2l (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 48 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product 5p: 48.3 mg (0.0757 mmol), as a white solid, 76% yield; mp = 177–179 °C; [α]$^\circ_{D}^2$ = +27.4 (c = 0.38 in CHCl$_3$); 86% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 8.23 min (major), $t_R$ = 10.40 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.96 (d, $J = 8.5$ Hz, 1H), 7.55–7.47 (m, 1H), 7.46–7.41 (m, 3H), 7.30–7.26 (m, 1H), 7.25–7.17 (m, 3H), 7.11–7.04 (m, 1H), 7.03–6.95 (m, 3H), 6.91 (d, $J = 8.0$ Hz, 2H), 6.85–6.74 (m, 2H), 5.70 (d, $J = 7.2$ Hz, 1H), 5.43 (dd, $J = 11.4$, 1.7 Hz, 1H), 5.25 (dd, $J = 17.8$, 1.7 Hz, 1H), 3.88 (s, 3H), 2.27 (s, 3H), 1.19 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm) 167.7, 160.4 (d, $^1$J$_{FC} = 247.8$ Hz), 159.3, 142.7, 137.2, 136.9, 134.3, 133.6, 133.5, 132.5, 131.8, 131.5, 131.0, 130.3, 129.7 (d, $^2$J$_{FC} = 3.0$ Hz), 129.6, 129.5, 128.8, 126.9(d, $^2$J$_{FC} = 12.0$ Hz), 126.8, 126.7, 125.7, 124.6, 123.8, 122.1, 116.1 (d, $^2$J$_{FC} = 21.5$ Hz), 113.4, 113.3, 81.7, 55.4, 53.0, 27.7, 21.5; $^{19}$F NMR (375 MHz, CDCl$_3$) δ (ppm) −111.9; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{38}$H$_{36}$FNO$_5$SNa$^+$ 660.2190; Found 660.2188.
vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5p: 41.5 mg (0.0695 mmol), as a white solid, 70% yield; mp = 104–106 °C; [α]_{D}^{25} = +14.4 (c = 0.20 in CHCl₃); 88% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: t_R = 7.63 min (major), t_R = 9.09 min (minor); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.97–7.86 (m, 1H), 7.70–7.57 (m, 2H), 7.49–7.31 (m, 3H), 7.30–7.26 (m, 1H), 7.24–7.18 (m, 2H), 7.10–6.95 (m, 2H), 6.90–6.70 (m, 4H), 6.62–6.47 (m, 2H), 5.66 (d, J = 7.2 Hz, 1H), 5.45 (dd, J = 11.4, 1.6 Hz, 1H), 5.23 (dd, J = 17.8, 1.7 Hz, 1H), 2.22 (s, 3H), 1.38 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 167.3, 160.4 (d, ¹J_CF = 247.3 Hz), 149.4, 142.9, 142.8, 136.4, 134.7, 134.0, 132.2, 130.4, 129.8, 129.7, 129.7, 128.7, 127.1, 127.0, 126.8, 126.5 (d, ³J_CF = 8.2 Hz), 126.4, 126.3, 124.8, 123.9 (d, ³J_CF = 3.5 Hz), 122.4, 116.2 (d, ²J_CF = 21.8 Hz), 112.0, 111.0, 82.1, 53.3, 27.9, 21.3; ¹⁹F NMR (375 MHz, CDCl₃) δ (ppm) –111.7; HRMS (ESI-TOF) m/z: [M + Na]^+ Calcd for C₃₅H₃₂FNO₂SNa⁺ 620.1887; Found 620.1883.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (Z)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-(thiophen-2-yl)acrylate 1x (33.6 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(2-fluorobenzylidene)-4-methyl-benzenesulfonylamide 21 (51.8 mg, 0.200 mmol, 2.0 equiv), Pd₂(dba)₃ (4.6 mg, 5 mol%), L₅ (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et₃N (14 µL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 48 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product 5q: 51.2 mg (0.0835 mmol), as a white solid, 84% yield; mp = 107–109 °C; [α]_{D}^{25} = +15.2 (c = 0.33 in CHCl₃); 87% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: t_R = 7.36 min (major), t_R = 9.34 min (minor); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.00–7.89 (m, 1H), 7.65–7.56 (m, 1H), 7.53–7.48 (m, 1H), 7.48–7.41 (m, 1H), 7.38–7.25 (m, 5H), 7.17–7.11 (m, 1H), 7.11–6.96 (m, 3H), 6.92–6.72 (m, 4H), 5.70 (d, J = 7.1 Hz, 1H), 5.46 (dd, J = 11.4, 1.7 Hz, 1H), 5.28 (dd, J = 17.2, 1.7 Hz, 1H), 2.27 (s, 3H), 1.25 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 167.2, 160.4 (d, ¹J_CF = 247.3 Hz), 142.8, 137.1, 136.6, 135.2, 134.0, 133.1, 130.2, 129.9, 129.7 (d, ³J_CF = 8.1 Hz), 128.7, 127.3, 126.9, 126.74, 126.73, 126.6, 126.5
(d, $^3J_{FC} = 7.8$ Hz), 126.1, 124.6, 123.9, 122.5, 116.1 (d, $^2J_{FC} = 21.5$ Hz), 82.0, 53.1, 27.7, 21.6; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ (ppm) –111.8; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{35}$H$_{32}$FNO$_4$S$_2$Na$^+$ 636.1649; Found 636.1643.

7. General procedure for catalytic cascade reaction

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added $\beta$-aryl-acrylate derived 1,3-enyne 1 (0.100 mmol), 2-furfural derived imine 2n (49.8 mg, 0.200 mmol, 0.200 mmol), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give product 6.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate 1p (33.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-2-methylbenzene-sulfonamide 2n (49.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 4/1 to 5/1) to give product 6a: 39.3 mg (0.0679 mmol), as a white solid, 68% yield, >19:1 dr, determined by $^1$H NMR; mp = 119–121 °C; $[^1]D = -68.3$ (c = 0.36 in CHCl$_3$); 75% ee, determined by HPLC analysis [Daicel Chiralpak IB, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm]: t$_R$ = 8.08 min (minor), t$_R$ = 10.33 min (major); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.20 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.58–7.54 (m, 1H), 7.51–7.39 (m, 5H), 7.38–7.27 (m, 3H), 7.23–
7.15 (m, 2H), 7.02 (d, J = 8.2 Hz, 1H), 6.63 (d, J = 6.0 Hz, 1H), 6.33 (dd, J = 6.0, 1.6 Hz, 1H), 5.34 (d, J = 7.5 Hz, 1H), 5.08 (dd, J = 4.5, 1.7 Hz, 1H), 5.05–4.97 (m, 1H), 3.70 (dd, J = 8.4, 3.8 Hz, 1H), 2.51 (s, 3H), 2.01–1.94 (m, 1H), 1.83–1.76 (m, 1H), 1.14 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 167.8, 141.7, 140.3, 140.9, 138.2, 137.4, 136.1, 134.0, 132.6, 132.3, 130.9, 130.4, 130.1, 129.5, 128.3, 128.0, 127.7, 127.6, 126.59, 126.1, 123.1, 98.0, 81.9, 80.6, 56.5, 49.2, 30.8, 27.5, 20.6; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C35H33NO5SNa+ 602.1972; Found 602.1981.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)-4-methylphenyl)-3-phenylacrylate 1q (34.4 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-2-methylbenzenesulfonamide 2n (49.8 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product 6b: 42.8 mg (0.0722 mmol), as a white solid, 72% yield, >19:1 dr, determined by 1H NMR; mp = 133–135 °C; [α]D = −79.7 (c = 0.71 in CHCl3); 76% ee, determined by HPLC analysis [Daicel Chiralpak IB, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm]: tR = 5.98 min (minor), tR = 7.34 min (major); 1H NMR (400 MHz, CDCl3) δ (ppm) 8.19 (dd, J = 7.9, 1.5 Hz, 1H), 7.55–7.50 (m, 1H), 7.49–7.36 (m, 5H), 7.35–7.31 (m, 2H), 7.23–7.17 (m, 1H), 7.11 (dd, J = 8.7, 1.7 Hz, 1H), 6.98 (s, 1H), 6.70 (d, J = 6.0 Hz, 1H), 6.33 (dd, J = 6.0, 1.6 Hz, 1H), 5.35 (d, J = 7.6 Hz, 1H), 5.07 (dd, J = 4.5, 1.7 Hz, 1H), 5.00 (d, J = 7.6 Hz, 1H), 3.71 (dd, J = 8.4, 3.8 Hz, 1H), 2.54 (s, 3H), 2.20 (s, 3H), 2.00–1.92 (m, 1H), 1.79 (dd, J = 11.5, 8.4 Hz, 1H), 1.15 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 167.9, 141.9, 140.2, 138.5, 137.7, 137.1, 135.3, 134.5, 134.2, 133.1, 132.7, 130.9, 130.5, 130.0, 129.5, 129.4, 128.34, 128.26, 127.8, 127.6, 127.5, 126.5, 122.1, 98.1, 81.7, 80.6, 56.6, 49.2, 30.9, 27.5, 21.8, 20.5; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C36H35NO5SNa+ 616.2128; Found 616.2124.
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)-5-chlorophenyl)-3-phenylacrylate 1s (39.8 mg, 0.0999 mmol, 1.0 equiv), (E)-N-benzylidene-2-methylbenzenesulfonamide 2n (49.8 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product 6c: 36.9 mg (0.0602 mmol), as a white solid, 60% yield, >19:1 dr, determined by 1H NMR; mp = 163–165 °C; [α]D25 = −78.0 (c = 0.40 in CHCl3); 75% ee, determined by HPLC analysis [Daicel Chiralpak IB, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: tr = 5.37 min (minor), tm = 6.59 min (major); 1H NMR (400 MHz, CDCl3) δ (ppm) 8.16 (dd, J = 7.9, 1.4 Hz, 1H), 7.60–7.53 (m, 1H), 7.52–7.28 (m, 7H), 7.19–7.15 (m, 1H), 7.13 (dd, J = 8.9, 2.1 Hz, 1H), 7.01 (d, J = 8.9 Hz, 1H), 6.58 (d, J = 5.9 Hz, 1H), 6.32 (dd, J = 6.0, 1.6 Hz, 1H), 5.30 (d, J = 7.7 Hz, 1H), 5.11 (d, J = 7.8 Hz, 1H), 5.07 (dd, J = 4.4, 1.6 Hz, 1H), 3.67 (dd, J = 8.4, 3.8 Hz, 1H), 2.52 (s, 3H), 2.01–1.91 (m, 1H), 1.77 (dd, J = 11.5, 8.5 Hz, 1H), 1.14 (s, 9H); 13C NMR (100 MHz, CDCl3) δ (ppm) 167.4, 142.1, 139.4, 138.2, 137.5, 137.4, 136.4, 134.9, 133.7, 133.23, 133.19, 132.7, 132.2, 131.5, 130.8, 130.1, 129.4, 128.49, 128.45, 128.4, 128.0, 127.9, 126.74, 126.67, 124.8, 98.0, 82.2, 80.6, 56.4, 49.2, 30.7, 27.5, 20.6; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for C35H3235ClNO5SNa+ 636.1582; Found 636.1591; Calcd for C35H3237ClNO5SNa+ 637.1615; Found 637.1625.

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added tert-butyl (E)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate 1p (33.0 mg, 0.0999 mmol, 1.0 equiv), (E)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide 2j (49.8 mg, 0.200 mmol, 2.0 equiv), Pd2(dba)3 (4.6 mg, 5 mol%), L5 (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et3N (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel.
(petroleum ether/EtOAc = 8/1 to 4/1) to give product 6d: 42.7 mg (0.0742 mmol), 74% yield, 6:1 dr, determined by $^1$H NMR analysis; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.91 (d, $J = 8.0$ Hz, 2H), 7.50–7.41 (m, 2H), 7.41–7.32 (m, 3H), 7.26 (s, 1H), 7.30–7.26 (m, 2H), 7.25–7.20 (m, 1H), 7.06–6.98 (m, 1H), 6.96–6.84 (m, 1H), 6.72–6.57 (m, 2H), 6.35 (dd, $J = 6.0$, 1.6 Hz, 1H), 5.90–5.63 (m, 1H), 5.28 (d, $J = 6.4$ Hz, 1H), 5.07 (dd, $J = 4.2$, 1.7 Hz, 1H), 3.63 (dd, $J = 8.2$, 4.2 Hz, 1H), 2.53 (s, 3H), 1.98–1.79 (m, 2H), 1.11 (s, 1H), 1.06 (s, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 167.5, 143.9, 142.2, 139.4, 137.5, 137.3, 136.3, 134.4, 134.1, 132.0, 130.6, 129.9, 129.5, 128.4, 128.3, 127.9, 127.8, 127.7, 126.7, 125.2, 98.1, 82.4, 80.6, 56.5, 49.6, 30.6, 27.3, 21.7.

8. Transformations of the products

To an oven-dried 10 mL tube equipped with a magnetic stir bar were added product 3a (48.5 mg, 0.0999 mmol, 1.0 equiv), PdCl$_2$ (8.9 mg, 0.050 mmol, 0.5 equiv), CuCl (9.9 mg, 0.10 mmol, 1.0 equiv), and K$_2$CO$_3$ (27.6 mg, 0.200 mmol, 2.0 equiv). The tube was evacuated and back-filled three times with O$_2$. Then THF (1.0 mL) were added via syringe. The mixture was stirred at 40 $^\circ$C for 3 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1 to 6/1) to give product 7: 40.2 mg (0.0832 mmol), as a brown thick oil, 83% yield; [$\alpha$]$^D_{25}$ = −65.5 (c = 0.60 in CHCl$_3$); 89% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, 1 = 254 nm]; $t_R$ = 7.08 min (major), $t_R$ = 7.82 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.57–8.50 (m, 1H), 7.52–7.47 (m, 2H), 7.44–7.38 (m, 2H), 7.24–7.19 (m, 3H), 7.17–7.06 (m, 4H), 6.91 (d, $J = 7.0$, 1H), 6.77 (d, $J = 7.7$ Hz, 1H), 6.31 (d, $J = 4.0$ Hz, 2H), 5.87 (d, $J = 7.7$ Hz, 1H), 4.31 (q, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 165.8, 146.9, 143.9, 141.8, 138.7, 136.4, 135.8, 133.8, 130.3, 130.2, 129.6, 128.7, 128.6, 127.8, 127.5, 127.0, 126.6, 125.5, 118.5, 117.2, 102.1, 61.0, 57.3, 21.5, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{29}$H$_{25}$NO$_4$SNa$^+$ 506.1397; Found 506.1393.
To a solution of product 3a (48.5 mg, 0.0999 mmol, 1.0 equiv) in acetone (1.0 mL) was added Cs₂CO₃ (65.0 mg, 0.200 mmol, 2.0 equiv). The resultant mixture was stirred at room temperature for 10 min, and allyl bromide (17.2 μL, 0.200 mmol, 2.0 equiv) was added slowly. After complete consumption of 3a (monitored by TLC), the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether / EtOAc = 10/1) to give the N-allylation product.

To the solution of N-allylation product in DCM (1.0 mL) was added Hoveyda-Grubbs 2nd Generation Catalyst (6.3 mg, 0.010 mmol, 0.1 equiv). Then the mixture was degassed and charged with argon balloon and stirred at 40 ºC for 24 h. After completion monitored by TLC, the mixture was concentrated and purified by flash chromatography on silica gel (EtOAc/petroleum ether = 7/1) to give product 8: 35.8 mg (0.0720 mmol), as a yellow oil, 72% yield; [α]₂⁵ᵣ = +91.0 (c = 0.29 in CHCl₃); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: tᵣ = 6.06 min (major), tᵣ = 6.99 min (minor); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.53–8.43 (m, 1H), 7.50–7.43 (m, 2H), 7.36–7.27 (m, 5H), 7.23–7.16 (m, 2H), 7.02–6.94 (m, 1H), 6.89 (d, J = 8.0 Hz, 2H), 6.47 (s, 1H), 6.10 (s, 1H), 5.99 (dd, J = 12.0, 2.9 Hz, 1H), 5.73–5.64 (m, 1H), 4.54–4.43 (m, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.64–3.52 (m, 1H), 2.24 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 166.1, 149.4, 143.6, 143.5, 143.3, 137.3, 136.7, 133.2, 132.4, 130.5, 130.3, 129.1, 128.8, 128.62, 128.60, 128.60, 127.5, 127.4, 126.9, 119.9, 119.0, 116.3, 61.0, 58.6, 44.7, 21.3, 14.3; HRMS (ESI-TOF) m/z: [M + Na]⁺ Calcd for C₃₀H₂₇NO₄SNa⁺ 520.1553; Found 520.1547.

To an oven-dried 10 mL tube equipped with a magnetic stir bar were added product 5b (62.0 mg, 0.0999 mmol, 1.0 equiv), K₂CO₃ (138 mg, 1.00 mmol, 10.0 equiv). The tube was evacuated and back-
filled with argon for three times. Then dry MeCN (1.0 mL) and PhSH (41 µL, 0.40 mmol, 4.0 equiv) were added via syringe sequentially. The mixture was stirred at 35 °C for 6 h, and monitored by TLC. After completion, the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5/1 to 3/1) to give product 9: 41.8 mg (0.0960 mmol), as a colourless oil, 96% yield; [α]_D^{25} = +143.0 (c = 0.59 in CHCl₃); 82% ee, determined by HPLC analysis [Daicel Chiralpak IE, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, 1 = 254 nm]: t_R = 8.30 min (minor), t_R = 12.74 min (major); ^1H NMR (400 MHz, CDCl₃) δ (ppm) 7.96–7.89 (m, 1H), 7.52–7.37 (m, 8H), 7.34–7.29 (m, 2H), 7.27–7.26 (m, 1H), 7.24–7.18 (m, 2H), 7.12 (dd, J = 17.3, 11.8 Hz, 1H), 6.11 (s, 1H), 5.55 (s, 1H), 5.54–5.49 (m, 1H), 2.08–1.99 (m, 2H), 1.18 (s, 9H); ^13C NMR (150 MHz, CDCl₃) δ (ppm) 168.2, 145.0, 138.4, 137.9, 136.6, 135.0, 133.2, 132.9, 132.7, 130.7, 130.6, 130.4, 128.3, 127.9, 127.7, 127.6, 126.3, 126.2, 126.0, 125.7, 121.3, 81.7, 54.4, 27.6; HRMS (ESI-TOF) m/z: [M + H]^+ Calcd for C₃₀H₃₀N₂O₂^+ 436.2271; Found 436.2275.

9. More substrates and transformation exploration

To further expand the substrate scope, several imines and alkene-tethered enynes were investigated under the optimal conditions. Unfortunately, these substrates generally showed low reactivity, and no apparent transformations were observed.
Treatment of 3j in toluene at high temperature, the expected Diels–Alder adduct could be detected but only in a very low yield.

We tried several methods to remove the Ts group of racemic products 3a, 5a and 7, but no obvious conversions or complex reaction profiles were uniformly observed, probably due to the effect of existence of olefinic groups. Nevertheless, the N-Ns protected imines could be similarly applied, which could be easily removed.
10. Proposed mechanism

As illustrated in the above scheme, Pd\(^0\) coordinated with the double-bond of 1,3-ene 1 chemoseletively, and the resultant highest occupied molecular orbital (HOMO) energy raised \(\eta^2\)-complex A underwent vinylogous addition to imine 2 to produce \(\eta^1-\pi\)-allyl palladium B. With the assistance of triethylamine, the complex B would first be protonated by EtOH to deliver syn-alkenyl palladium C, which readily isomerized to thermodynamically more stable trans-alkenyl palladium species D through a three-membered ring-type transition state (TS-1) (ACS Catal., 2020, 10, 10516). The trans-alkenyl palladium species D might undergo 5-exo migratory addition, and the resultant species E would readily undertake \(\beta\)-H elimination to afford benzofulvene derivative 3 (for \(R^1 = H\)). In addition, for intermediate E bearing a quaternary carbon, a reduction process might be conducted to provide densely substituted indene 4. Nevertheless, when 1'-aryl substituted enyne was used, a 6-endo intramolecular migratory insertion to produce F might be favoured, because of steric hindrance and the formation of more stable benzyl palladium complex (Acc. Chem. Res., 1979, 12, 146; J. Am.

11. Crystal data and structural refinement

Procedure for the recrystallization of chiral 3a: To a 10 mL tube containing 3a (45 mg) were added petroleum ether (2.5 mL) and EtOAc (1.0 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of enantiopure 3a. The data were collected by Bruker D8 venture CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 273.15 K. CCDC 2249982 (3a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

(ellipsoid contour probability 50%)

Identification code 3a
Empirical formula C29H27NO4S
Formula weight 485.07
Temperature/K 273.15
Crystal system monoclinic
Space group P2₁
a/Å 9.7229(12)
b/Å 26.817(4)
c/Å 9.7328(16)
α/° 90
β/° 90.021(5)
γ/° 90
Volume/Å³ 2537.8(7)
Z 4
ρcalcg/cm³ 1.270
μ/mm⁻¹ 0.163
Procedure for the recrystallization of racemic 5r: To a 10 mL tube containing 5r (50 mg) were added petroleum ether (3.5 mL) and EtOAc (1.0 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the relative configuration of 5r. The data were collected by Bruker D8 venture CCD equipped with a Mo radiation source ($\lambda = 0.71073 \, \text{Å}$) at 302.0 K. CCDC 2249983 (rac-5r) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The absolute configuration of chiral 5r was assigned by similar vinylogous addition reaction with regard to enantiopure product 3a.
Procedure for the recrystallization of racemic 6d: To a 10 mL tube containing 6d (40 mg) were added petroleum ether (2.5 mL) and CHCl₃ (1.0 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the relative configuration of product 6d. The data were collected by Bruker D8 venture CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 240.0 K. CCDC 2249984 (rac-6d) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The absolute configuration of chiral 6d was assigned by similar vinylogous addition reaction with regard to enantiopure product 3a.
(ellipsoid contour probability 50%)

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12. NMR, HRMS spectra and HPLC chromatograms

\[ 1^H \text{NMR (400 MHz, CDCl}_3) \]

\[ 13^C \text{NMR (150 MHz, CDCl}_3) \]
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{19}H_{16}ONa^+ 281.0937
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{18}H_{18}NONa^+ 248.1046
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{24}H_{24}O_{2}Na^+ 367.1669
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (150 MHz, CDCl$_3$)
$^{19}$F NMR (375 MHz, CDCl$_3$)

$\text{CF}_3$–$\text{Ph}$

$\text{CO}_2$-$\text{Bu}$

$1r$ E/Z = 11:1

(ESI-TOF) m/z: [M + Na]$^+$

Calcd for C$_{24}$H$_{21}$F$_3$O$_2$Na$^+$ 421.1386
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{23}H_{21}^{35}ClO_2Na^+ 387.1122
Calcd for C_{23}H_{21}^{37}ClO_2Na^+ 389.1093
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)

$^{1}t$ E/Z = 2.5:1

$^{(Z)}$-$t$

$^{(Z)}$-$t$
1t E/Z = 2.5:1
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{25}H_{25}O_4Na^+ 413.1723
$1^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (375 MHz, CDCl₃)

1u

$^1$H NMR (375 MHz, CDCl₃)

1u

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for C$_{23}$H$_{21}$FO$_2$Na$^+$ 371.1418
$^{1}$H NMR (400 MHz, CDCl$_3$)

1v E/Z = 3.1:1

$^{13}$C NMR (150 MHz, CDCl$_3$)

1v E/Z = 3.1:1
$1v$ E/Z = 3.1:1

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for $C_{24}H_{24}O_4Na^+$ 383.1618
$1^w$ $E/Z = 4.6:1$

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$^1_6$ E/Z = 4.6:1

(ESI-TOF) m/z: [M + Na]$^+$

Calcd for $C_{21}H_{29}O_3Na^+$ 343.1305
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(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{21}H_{20}O_{2}SNa^+ 359.1076
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$^{13}$C NMR (100 MHz, CDCl₃)
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Calcd for C₂₉H₂₇NO₄SNa⁺ 508.1553
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$^{13}$C NMR (100 MHz, CDCl$_3$)
3b

(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{30}H_{29}NO_{5}SNa^+ 538.1659

538.1666

539.1700
$^1$H NMR (400 MHz, CDCl$_3$)

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(ESI-TOF) m/z: [M + Na]⁺
Calcd for C₃₀H₂₉NO₅SNa⁺ 522.1710
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3d
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{30}H_{28}NO_4SNa^+ 522.1710

\[
\begin{align*}
\text{Me} & \quad \text{NHTs} \\
\text{EtO}_2C & \quad \text{Me} \\
\end{align*}
\]
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$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (375 MHz, CDCl$_3$)

(ESI-TOF) m/z: [M + Na]$^+$
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3g

(ESI-TOF) m/z: [M + Na]−
Calcd for C_{29}H_{36}^{35}CINO_{4}SNa^+ 542.1163
Calcd for C_{29}H_{36}^{37}CINO_{4}SNa^+ 544.1134
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(ESI-TOF) m/z: [M + Na]⁺
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3h

(ESI-TOF) m/z: [M + Na]⁺
Calcd for C₂₉H₂₈ClO₅Na⁺ 544.1134
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
### Retention Time Table

<table>
<thead>
<tr>
<th>Ret Time [min]</th>
<th>Peak Type</th>
<th>Width [min]</th>
<th>Height [mAU]</th>
<th>Area [mAU*s]</th>
<th>Area [%]</th>
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**Totals:** 15382.9038 100.0000

### Retention Time Table

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**Totals:** 24023.7507 100.0000
31
(ESI-TOF) m/z: [M + Na]⁺
Calcld for C₃₃H₂₉NO₄SNa⁺ 558.1870
$3j$

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{27}H_{28}NO_5SNa^+$ 498.1346
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3k

(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{27}H_{25}NO_{2}S_{2}Na^+ 514.1117
$\text{Me}$

$\text{Ph}$

$\text{NHTs}$

$\text{EtO}_2\text{C}$

$3\text{I}$

$^1\text{H NMR (400 MHz, CDCl}_3\text{)}$

$\text{Me}$

$\text{Ph}$

$\text{NHTs}$

$\text{EtO}_2\text{C}$

$3\text{I}$

$^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}$
**(ESI-TOF) m/z: [M + Na]⁺
Calcd for C_{30}H_{29}NO_2SNa⁺ 522.1710

31

$\text{Me}$ $\text{Ph}$
$\text{NHTs}$
$\text{EtO}_2\text{C}$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3m
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{30}H_{29}NO_5SNa^+ 538.1659
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (375 MHz, CDCl$_3$)

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for C$_{23}$H$_{28}$FNO$_3$SNa$^+$ 526.1459
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3o
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{29}H_{28}CINO_2SNa^+ 542.1163

3o
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{29}H_{28}^{37}CINO_2SNa^+ 544.1134
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}\text{F NMR (375 MHz, CDCl}_3\text{)}$.

$3p$

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for C$_{30}$H$_{28}$F$_3$NO$_4$SNa$^+$ 576.1427
### Retention Time (min) | Peak Type | Width (min) | Height [mAU] | Area [mAU*] | Area [%]
--- | --- | --- | --- | --- | ---
5.560 | BBA | 0.26 | 203.4204 | 3787.6702 | 50.0238
7.291 | BBA | 0.28 | 204.6914 | 3784.0591 | 49.9762
**Totals:** | | | | 7571.7292 | **100.0000**

### Retention Time (min) | Peak Type | Width (min) | Height [mAU] | Area [mAU*] | Area [%]
--- | --- | --- | --- | --- | ---
5.483 | BBA | 0.19 | 61.6714 | 752.2999 | 4.7230
7.246 | BBA | 0.24 | 977.9205 | 15176.1416 | 95.2770
**Totals:** | | | | 15928.4415 | **100.0000**
**3q**

(ESI-TOF) $m/z$: [M + Na]$^+$

Calcd for $C_{29}H_{26}^{35}ClNO_3SNa^+$ 542.1163

---

**3q**

(ESI-TOF) $m/z$: [M + Na]$^+$

Calcd for $C_{29}H_{26}^{37}ClNO_3SNa^+$ 544.1134
3r

(ESI-TOF) m/z: [M + Na]^+

Calcd for C_{30}H_{27}NO_6SNa^+ 552.1451
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (150 MHz, CDCl$_3$)
$^{3s}$

(ESI-TOF) m/z: [M +H]$^+$
Calcd for $C_{29}H_{28}NO_4S$: 472.1577
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
3t

(ESI-TOF) m/z: [M + Na]^+
Calc for C_{28}H_{32}N_{2}O_{3}SNa^+ 478.1447
$3u$

$^1H$ NMR (400 MHz, CDCl$_3$)

$^13C$ NMR (100 MHz, CDCl$_3$)

S131
3u

(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{33}H_{27}NO_{3}SNa^+ 544.1604
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
### Table 1: Retention Time and Peak Area Analysis

<table>
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<tr>
<th>Ret Time [min]</th>
<th>Peak Type</th>
<th>Width [min]</th>
<th>Height [mAU]</th>
<th>Area [mAU*sec]</th>
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### Table 2: Retention Time and Peak Area Analysis

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S135
$3v$

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for $C_{28}H_{28}N_2O_3Na^+$ 507.1713
$3w \ E/Z = 2.5:1$

$^1H$ NMR (400 MHz, CDCl$_3$)

$3w \ E/Z = 2.5:1$

$^{13}C$ NMR (100 MHz, CDCl$_3$)
3w E/Z = 2.5:1
HRMS (ESI-TOF) m/z: [M + Na]^+
Calcld for C_{32}H_{27}NO_{2}SNa^+ 512.1655
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(ESI-TOF) m/z: [M + Na]^+
Calcld for C_{39}H_{28}NO_{4}SNa^+ 522.1710
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
### Table 1: Retention Time and Peak Analysis

<table>
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<th>Ret Time [min]</th>
<th>Peak Type</th>
<th>Width [min]</th>
<th>Height [mAU]</th>
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### Table 2: Retention Time and Peak Analysis

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$3y$

(ESI-TOF) m/z: [$M + Na]^+$
Calc'd for $C_{20}H_{27}NO_3SNa^+$ 460.1553
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{32}H_{41}NO_2SNa^+ 524.1866
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{37}H_{35}NO_2SNa^+ 612.2179
$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
Spectrum from 20230510.will2 (sample 2) - 2, +TOF MS (300 - 800) from 0.050 to 0.101 min, Recalibrated, centroided

(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{39}H_{24}N_2O_6SNa^+ 643.1873

5b

\[ \text{Formula Image} \]
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{32}H_{34}FNO_{4}SNa^+ 630.2085
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
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<tr>
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<th>Peak Type</th>
<th>Width [min]</th>
<th>Height [mAU]</th>
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(ESI-TOF) m/z: [M + Na]⁺
Calcd for C₃₉H₃₇NO₂SNa⁺ 626.2336
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(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{39}H_{37}NO_{5}SNa^+ 642.2285
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(ESI-TOF) m/z: [M + Na]\(^+\)
Calcd for C\(_{43}\)H\(_{39}\)NO\(_2\)SNa\(^+\) 688.2492
\( \text{(ESI-TOF) m/z: [M + Na]}^+ \)

Calcd for C\(_{37}\)H\(_{38}\)\(^{35}\)C/NO\(_2\)SNa\(^+\) 646.1789

Calcd for C\(_{37}\)H\(_{38}\)\(^{37}\)C/NO\(_2\)SNa\(^+\) 647.1823
$^1\text{H NMR (400 MHz, CDCl}_3\text{)}$

$^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}$
### Chart 1: Retention Time vs. Absorbance

- **Molecule:** Rac-5h

<table>
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<th>Ret Time [min]</th>
<th>Peak Type</th>
<th>Width [min]</th>
<th>Height [mAU]</th>
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### Chart 2: Retention Time vs. Absorbance

- **Molecule:** 5h

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<th>Height [mAU]</th>
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</table>
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{37}H_{34}^{35}CINO_{4}SNa^+ 646.1789
Calcd for C_{37}H_{34}^{37}CINO_{4}SNa^+ 647.1823
<table>
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<th>Ret Time [min]</th>
<th>Peak Type</th>
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<th>Height [mAU]</th>
<th>Area [mAU*s]</th>
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<th>Height [mAU]</th>
<th>Area [mAU*s]</th>
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</table>
5i

(ESI-TOF) m/z: [M + Na]⁺
Calcd for C₃₆H₃₃NO₅S₂Na⁺ 618.1743
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
\[ \text{\(^{19}\text{F NMR}\ (375 \text{ MHz, CDCl}_3)\)} \]

\[ 5j \]

\[ \text{(ESI-TOF) m/z: [M + Na]\(^+\)} \]

Calcd for C\(_{38}\)H\(_{36}\)FNO\(_4\)SNa\(^+\) 644.2234
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (375 MHz, CDCl$_3$)

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for C$_{36}$H$_{30}$F$_4$NO$_2$SNa$^+$ 698.1959
### Table 1: Retention Time and Peak Analysis

<table>
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<tr>
<th>Ret Time [min]</th>
<th>Peak Type</th>
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<th>Height [mAU]</th>
<th>Area [mAU^2]</th>
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### Table 2: Retention Time and Peak Analysis

<table>
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<tr>
<th>Ret Time [min]</th>
<th>Peak Type</th>
<th>Width [min]</th>
<th>Height [mAU]</th>
<th>Area [mAU^2]</th>
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$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

5I
$^{19}$F NMR (375 MHz, CDCl$_3$)

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for C$_{37}$H$_{33}^{35}$ClFNO$_2$SNa$^+$ 664.1695
Calcd for C$_{37}$H$_{33}^{37}$ClFNO$_2$SNa$^+$ 665.1729
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (375 MHz, CDCl$_3$)

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for C$_{39}$H$_{38}$FNO$_5$SNa$^+$ 690.2296
$^{19}\text{F NMR (375 MHz, CDCl}_{3}\text{)}$

(ESI-TOF) m/z: $[\text{M + Na}]^{+}$
Calcd for $C_{37}H_{33}F_3NO_3SNa^+$ 648.1991
### Retention Time and Peak Properties

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### Retention Time and Peak Properties

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S190
$^{19}$F NMR (375 MHz, CDCl$_3$)

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for C$_{38}$H$_{36}$FNO$_2$SNa$^+$ 660.2190
### Retention Time Details

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$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$\text{S195}$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
$^{19}$F NMR (375 MHz, CDCl$_3$)

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for C$_{35}$H$_{12}$FNO$_4$S$_2$Na$^+$ 636.1649
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{36}H_{33}NO_{6}SNa^+ 602.1972

6a
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (400 MHz, CDCl$_3$)
6b

(ESI-TOF) m/z: [M + Na]^+
Calcld for C_{38}H_{36}NO_{5}SNa^+ 616.2128
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(ESI-TOF) m/z: [M + Na]$^+$
Calcd for C$_{33}$H$_{32}$$^{35}$ClNO$_2$SNa$^+$ 636.1582
Calcd for C$_{33}$H$_{32}$$^{37}$ClNO$_2$SNa$^+$ 637.1615
**$^1$H NMR (400 MHz, CDCl$_3$)**

**$^{13}$C NMR (100 MHz, CDCl$_3$)**
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(ESI-TOF) m/z: [M + Na]^+
Calcd for C_{28}H_{26}NO_{3}SNa^+ 506.1397
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
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(ESI-TOF) m/z: [M + Na]⁺
Calcd for C₃₀H₂₇NO₄SNa⁺ 520.1553
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
Spectrum from 20230510.wfit2 (sample 1) - 1, +TOF MS (300 - 800) from 0.019 to 0.069 min, Recalibrated, centroided

(ESI-TOF) m/z: [M +H]^+
Calcd for C_{30}H_{30}NO_2 436.2271

\[ \text{Formula: } \text{C}_{30}\text{H}_{30}\text{NO}_2 \]

Mass/Charge, Da

Intensity, cps

435.9 436.0 436.1 436.2 436.3 436.4 436.5 436.6 436.7

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400 500 600

100