Nickel-catalyzed regio- and enantioselective Markovnikov hydromonofluoroalkylation of 1,3-dienes

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1. General information

Reactions were monitored by thin layer chromatography (TLC) using UV light or KMnO₄ to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. The optical rotation [α]₀ was measured using Anton Paar MCP 5500. Infrared (IR) spectra were obtained using a SHIMADZU TRT racer-100. The HRMS spectra were measured on Waters GCT Premier™ or Bruker maXis impact spectrometer using electron spray ionization (ESI) method. Chiral HPLC analysis was performed on a Shimadzu LC-20AD instrument using Daicel chiral columns at 25 °C and a mixture of HPLC-grade hexanes and isopropanol as eluent. ¹H, ¹³C, and ¹⁹F NMR were recorded using a Bruker DPX-400 and 500 MHz spectrometer. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Unless mentioned, all reactions were performed under N₂ atmosphere. Anhydrous CH₂Cl₂, and THF were prepared by Innovative Technology PS-MD-5. Anhydrous toluene was prepared by distillation over sodium-benzenophenone ketyl prior to use. Absolute MeOH, EtOH and PrOH were prepared by first dried over anhydrous Na₂SO₄, then treated by Mg chips, distilled and stored under N₂ atmosphere. Ni(COD)₂ was purchased from Sigma-Aldrich and used as received. The (E)-1,3-dienes 1a-1ad were prepared according to the corresponding literatures.¹,² FBSM 2 were prepared following the reported methods.³ Diethyl fluoromalonate 5 was commercially available and distillation before use.

List of abbreviation:

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<tr>
<th>Entry</th>
<th>Chemical name</th>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>1</td>
<td>Petroleum ether</td>
<td>PE</td>
</tr>
<tr>
<td>2</td>
<td>Ethyl acetate</td>
<td>EtOAc</td>
</tr>
<tr>
<td>3</td>
<td>Tetrahydrofuran</td>
<td>THF</td>
</tr>
<tr>
<td>4</td>
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<td>5</td>
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<td>MeOH</td>
</tr>
<tr>
<td>6</td>
<td>Dichloromethane</td>
<td>CH₂Cl₂</td>
</tr>
</tbody>
</table>

¹ For synthesis of 1a-1c, 1i-1j, 1n-1o and 1u-1v: J. S. Marcum, T. N. Cervarich, R. S. Manan, C. C. Roberts, S. J. Meek, ACS Catal. 2019, 9, 5881. For synthesis of 1d-1h, 1k, 1m, 1p-1t, and 1ab: A. Bhownik, R. A. Fernandes, Org. Lett. 2019, 21, 9203.
2. Selected conditions for reaction optimization

Table S1: Further optimization of chiral ligands for hydromonofluoromethylation.\[[a]\]

![Chemical structures and reaction conditions](image)

- **1a (0.15 mmol)**
- **2a (0.1 mmol)**
- **Ni(COD)$_2$ (10 mol%)**
- **Ligand (11 mol%)**
- **EtOH, 25 °C, time**

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<th>Ligand</th>
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<td>22 h</td>
<td>90%</td>
<td>67% ee</td>
</tr>
<tr>
<td>L6b</td>
<td>22 h</td>
<td>50%</td>
<td>64% ee</td>
</tr>
<tr>
<td>L6c</td>
<td>22 h</td>
<td>86%</td>
<td>56% ee</td>
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<tr>
<td>L6d</td>
<td>22 h</td>
<td>49%</td>
<td>10% ee</td>
</tr>
<tr>
<td>L7</td>
<td>22 h</td>
<td>50%</td>
<td>78% ee</td>
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<td>L9</td>
<td>30 h</td>
<td>40%</td>
<td>60% ee</td>
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<tr>
<td>L10</td>
<td>24 h</td>
<td>6%</td>
<td>40% ee</td>
</tr>
</tbody>
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\[[a]\] Determined by $^1$H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as internal standard. Ee was determined by chiral HPLC analysis.
Table S2: Selected conditions for optimization of hydromonofluoroalkylation.\textsuperscript{[a]}

![Chemical structures]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>Ee (%)</th>
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<tr>
<td>9\textsuperscript{[c]}</td>
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<td>EtOH</td>
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<td>96</td>
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<td>THF</td>
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<td>L8</td>
<td>EtOH</td>
<td>72</td>
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</table>

\textsuperscript{[a]} Reaction conditions: 1\textsubscript{a} (0.15 mmol), 2 (0.1 mmol), Ni(COD)\textsubscript{2} (10 mol\%), ligand (11 mol\%), and DIPEA (20 mol\%), run at 100 °C in EtOH (1 mL), unless otherwise noted; isolated yield is reported; ee was determined by chiral HPLC analysis. \textsuperscript{[b]} No reaction. \textsuperscript{[c]} At rt. \textsuperscript{[d]} Without the use of DIPEA, at rt. \textsuperscript{[e]} Run on a 0.25 mmol scale using Ni(COD)\textsubscript{2} (5 mol\%) and L8 (5.5 mol\%) at 50 °C in EtOH (1.5 mL), without DIPEA.
3. The correction of serial number of 1,3-dienes 1 and their structures
4. Enantioselective Markovnikov hydromonofluoromethylation of 1,3-dienes with FBSM 2

4.1 General procedure for enantioselective hydromonofluoromethylation of 1,3-dienes with 2

To an oven-dried Schlenk tube equipped with a stirring bar were successively added Ni(COD)$_2$ (3.5 mg, 5 mol%), (S,S)-QuinoxP* L8 (4.6 mg, 5.5 mol%) (or Ni(COD)$_2$ (7.0 mg, 10 mol%), (S,S)-QuinoxP* L8 (9.2 mg, 11 mol%)), 1,3-dienes 1 (0.375 mmol, 1.5 equivs), and FBSM 2 (0.25 mmol), followed by the addition of absolute EtOH (2.5 mL) in a glove box. After it take out from the glove box, the resulting mixture was stirred at 25 °C until full conversion. The reaction was monitored by TLC and GC-MS analysis. After full consumption of 2, the reaction mixture was concentrated under vacuum to give the crude residue, which was purified by silica gel column chromatography using PE/EtOAc (8:1, v/v) as the eluent to afford the products 3. (Note: 5 mol% Ni catalyst was used in the cases of product 3a, 3c, 3o, and 3s; 10 mol% of Ni was used in other cases.) Racemic products 3k, 3m and 3z were prepared using 10 mol% of Ni(COD)$_2$ with a mixed ligand consisting of (R,R)-quinoxp* and (S,S)-quinoxp* as the catalyst, and all other racemates 3 were prepared using 10 mol% Ni(COD)$_2$ and 11 mol% dppb.

Product 3a was obtained in 86% yield as a white solid (3 days). m.p. = 136-138 °C; HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; 
$t_r$ (major) = 17.12 min, $t_r$ (minor) = 19.18 min gave the isomeric composition of the product: 96% ee; $[\alpha]_D^{20} = -56.0$ (c = 0.04, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.93 (d, $J = 7.6$ Hz, 2H), 7.81 (d, $J = 7.2$ Hz, 2H), 7.70 (t, $J = 7.6$ Hz, 1H), 7.60-7.57 (m, 1H), 7.55-7.51 (m, 2H), 7.44-7.40 (m, 2H), 7.30-7.21 (m, 5H), 6.31-6.22 (m, 2H), 3.53-3.45 (m, 1H), 1.68 (d, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 136.5, 136.4, 136.0, 135.0, 134.8, 133.7 (d, $J = 2.0$ Hz), 131.0 (d, $J = 2.0$ Hz), 130.8 (d, $J = 2.0$ Hz), 128.8, 128.7, 128.4, 127.8, 126.5, 125.5 (d, $J = 5.0$ Hz), 116.2 (d, $J = 264.0$ Hz), 41.5 (d, $J = 18.0$ Hz), 15.0 (d, $J = 5.0$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -130.17 (s, 1F); IR (neat): 1448, 1344, 1169, 1151, 1076, 970, 752, 723, 685, 588, 572 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{23}$H$_{21}$FNaO$_4$S$_2$ [M+Na]$^+$: 467.0758, Found: 467.0769.
Product 3b was obtained in 99% yield as a white solid (4 days). m.p. = 118-120 °C; HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t_r (major) = 18.43 min, t_r (minor) = 20.76 min gave the isomeric composition of the product: 94% ee. [α]_D^{20} = -70.9 (c = 0.04, CHCl_3); 1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.69 (t, J = 7.2 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.14-7.07 (m, 4H), 6.21-6.20 (m, 2H), 3.51-3.43 (m, 1H), 2.32 (s, 3H), 1.67 (d, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl_3): δ 137.6, 136.5, 136.0, 135.0, 134.8, 133.62, 133.60, 131.0 (d, J = 1.8 Hz), 130.7 (d, J = 1.8 Hz), 129.1, 128.8, 128.7, 126.4, 124.4 (d, J = 5.6 Hz), 116.2 (d, J = 264.5 Hz), 41.5 (d, J = 17.8 Hz), 21.1, 15.0 (d, J = 5.0 Hz); 19F NMR (376 MHz, CDCl_3): δ -129.94 (s, 1F); IR (neat): 1448, 1339, 1149, 1072, 970, 800, 723, 683, 580, 571 cm⁻¹; HRMS (ESI): Exact mass calcd for C_{24}H_{23}FNaO_4S_2 [M+Na]^+ : 481.0914, Found: 481.0919.

Product 3c was obtained in 97% yield as a yellow oil (3 days). HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t_r (major) = 30.87 min, t_r (minor) = 33.36 min gave the isomeric composition of the product: 97% ee. [α]_D^{20} = -161.8 (c = 0.1, CHCl_3); 1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.69 (t, J = 7.2 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 6.19 (d, J = 15.6 Hz, 1H), 6.09 (dd, J = 15.6, 7.6 Hz, 1H), 3.80 (s, 3H), 3.52-3.43 (m, 1H), 1.67 (d, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl_3): δ 159.3, 136.5, 135.9, 135.0, 134.7, 133.1 (d, J = 1.4 Hz), 131.0 (d, J = 1.8 Hz), 130.69 (d, J = 1.8 Hz), 129.1, 128.8, 128.6, 127.6, 123.1 (d, J = 5.7 Hz), 116.2 (d, J = 264.3 Hz), 113.8, 55.2, 41.5 (d, J = 17.8 Hz), 15.0 (d, J = 5.0 Hz); 19F NMR (376 MHz, CDCl_3): δ -129.95 (s, 1F); IR (neat): 1510, 1448, 1339, 1252, 1167, 1149, 1076, 970, 910, 754, 723, 683, 553 cm⁻¹; HRMS (ESI): Exact mass calcd for C_{24}H_{23}FNaO_5S_2 [M+Na]^+ : 497.0863, Found: 497.0871.

The reaction was carried out at 50 °C for 3 days. Product 3d was obtained in 86% yield as a white solid. m.p. = 104-106 °C; HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t_r (major) = 26.92 min, t_r (minor) = 30.99 min gave the isomeric composition of the product: 98% ee. [α]_D^{20} = -35.2 (c = 0.04, CHCl_3); 1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.20 (t, J = 7.6
Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 6.80-6.78 (m, 2H), 3.81 (s, 3H), 3.53-3.44 (m, 1H), 1.69 (dd, J = 6.8, 0.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.6, 137.8, 136.4, 135.9, 135.0, 134.8, 133.6 (d, J = 1.5 Hz), 131.0 (d, J = 1.9 Hz), 130.7 (d, J = 1.9 Hz), 129.4, 128.8, 128.7, 125.8 (d, J = 5.5 Hz), 119.1, 116.1 (d, J = 264.5 Hz), 113.4, 111.8, 55.2, 41.5 (d, J = 17.8 Hz), 14.9 (d, J = 5.0 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -130.21 (s, 1F); IR (neat): 1583, 1448, 1352, 1167, 999, 817, 754, 682, 553 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{24}$H$_{23}$FNaO$_5$S$_2$ [M+Na]$^+$: 497.0863, Found: 497.0868. 

The reaction was carried out at 50 °C for 3 days. Product 3e was obtained in 93% yield as a colorless oil. HPLC analysis (Chiralcel OX-H, $^t$PrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t$_r$ (major) = 28.10 min, t$_r$ (minor) = 31.99 min gave the isomeric composition of the product: 98% ee. [α]$_D^{20}$ = -51.4 (c = 0.05, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.94 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H), 7.41 (t, J = 8.4 Hz, 2H), 7.29 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 6.89 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.62 (d, J = 16.0 Hz, 1H), 6.28 (dd, J = 16.0, 8.0 Hz, 1H), 3.81 (s, 3H), 3.54-3.45 (m, 1H), 1.67 (d, J = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.5, 136.6, 136.1, 135.0, 134.7, 131.0 (d, J = 1.8 Hz), 130.8 (d, J = 1.9 Hz), 128.9, 128.8, 128.7, 128.3, 126.9, 125.8 (d, J = 5.5 Hz), 125.5, 120.6, 116.3 (d, J = 264.7 Hz), 110.7, 55.4, 41.9 (d, J = 17.9 Hz), 15.0 (d, J = 5.1 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -130.12 (s, 1F); IR (neat): 1489, 1448, 1340, 1244, 1167, 1151, 1074, 976, 752, 685, 594 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{24}$H$_{23}$FNaO$_5$S$_2$ [M+Na]$^+$: 497.0863, Found: 497.0873. 

Product 3f was obtained in 98% yield as a colorless oil (3 days). HPLC analysis (Chiralcel OX-H, $^t$PrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t$_r$ (major) = 35.41 min, t$_r$ (minor) = 41.05 min gave the isomeric composition of the product: 99% ee. [α]$_D^{20}$ = -148.8 (c = 0.1, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, J = 7.6 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.70 (t, J = 7.2 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 8.4 Hz, 2H), 6.40 (d, J = 1.2 Hz, 2H), 6.37 (s, 1H), 6.27-6.16 (m, 2H), 3.78 (s, 6H), 3.53-3.44 (m, 1H), 1.68 (d, J = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 160.8, 138.4, 136.4, 135.9, 135.0, 134.8, 133.7 (d, J = 1.4 Hz), 131.0 (d, J = 1.8 Hz), 130.7 (d, J = 2.0 Hz), 128.8, 128.7, 126.0 (d, J = 5.7 Hz), 116.1 (d, J = 264.4 Hz), 104.6, 110.0, 55.3, 41.4 (d, J = 17.8 Hz), 14.9 (d, J = 5.1 Hz); $^{19}$F
NMR (376 MHz, CDCl$_3$): $\delta$ -130.15 (s, 1F); IR (neat): 1589, 1448, 1340, 1203, 1149, 1070, 968, 727, 682, 569 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{25}$H$_{25}$FNaO$_6$S$_2$ [M+Na]$^+$: 527.0969, Found: 527.0971.

The reaction was carried out at 50 °C for 4 days. Product 3g was obtained in 48% yield as a yellow oil. HPLC analysis (Chiralcel OX-H, $^t$PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; $t_r$ (major) = 34.39 min, $t_r$ (minor) = 37.16 min gave the isomeric composition of the product: 93% ee. $[\alpha]_D^{20} = -148.9$ (c = 0.03, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J$ = 8.3 Hz, 2H), 7.80 (d, $J$ = 8.3 Hz, 2H), 7.69 (t, $J$ = 7.5 Hz, 1H), 7.58 (t, $J$ = 7.5 Hz, 1H), 7.53 (t, $J$ = 7.9 Hz, 2H), 7.40 (t, $J$ = 7.9 Hz, 2H), 7.10 (d, $J$ = 8.8 Hz, 2H), 6.62 (d, $J$ = 8.8 Hz, 2H), 6.12 (d, $J$ = 15.8 Hz, 1H), 5.95 (dd, $J$ = 15.8, 7.8 Hz, 1H), 3.49-3.40 (m, 1H), 2.95 (s, 6H), 1.67 (d, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.2, 136.7, 136.1, 134.9, 134.6, 133.7, 131.1 (d, $J$ = 1.8 Hz), 130.7 (d, $J$ = 1.8 Hz), 128.7, 128.6, 127.5, 124.9, 120.8 (d, $J$ = 5.5 Hz), 116.5 (d, $J$ = 265.6 Hz), 112.2, 41.6 (d, $J$ = 17.9 Hz), 40.4, 15.1 (d, $J$ = 4.8 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -129.38 (s, 1F); IR (neat): 1448, 1348, 1166, 1151, 1078, 754, 684, 582, 570 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{25}$H$_{27}$FNO$_4$S$_2$ [M+H]$^+$: 488.1360, Found: 488.1351.

Product 3h was obtained in 68% yield as a colorless oil (3 days). HPLC analysis (Chiralcel OX-H, $^t$PrOH/hexane = 20/80, 1.0 mL/min, 254 nm; $t_r$ (major) = 14.15 min, $t_r$ (minor) = 15.92 min gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{20} = -110.4$ (c = 0.07, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J$ = 8.5 Hz, 2H), 7.80 (d, $J$ = 8.5 Hz, 2H), 7.69 (t, $J$ = 7.5 Hz, 1H), 7.58 (t, $J$ = 7.5 Hz, 1H), 7.52 (t, $J$ = 7.9 Hz, 2H), 7.41 (t, $J$ = 7.9 Hz, 2H), 7.20-7.05 (m, 4H), 6.22 (d, $J$ = 3.4 Hz, 2H), 5.89-5.79 (m, 1H), 5.06-5.00 (m, 1H), 4.99-4.96 (m, 1H), 3.52-3.45 (m, 1H), 2.71-2.67 (m, 2H), 2.38-2.20 (m, 2H), 1.67 (dd, $J$ = 7.1, 1.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.6, 137.89, 136.6, 136.0, 135.0, 134.7, 134.1, 133.6 (d, $J$ = 1.5 Hz), 131.0 (d, $J$ = 1.8 Hz), 130.7 (d, $J$ = 2.0 Hz), 128.8, 128.7, 128.5, 126.5, 124.6 (d, $J$ = 5.5 Hz), 116.2 (d, $J$ = 266.1 Hz), 115.0, 41.6 (d, $J$ = 17.9 Hz), 35.4, 35.0, 15.0 (d, $J$ = 5.1 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -130.00 (s, 1F); IR (neat): 1639, 1583, 1448, 1338, 1151, 1080, 972, 752, 723, 684, 584, 572 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{27}$H$_{28}$FO$_4$S$_2$ [M+H]$^+$: 499.1408, Found: 499.1408.
Product 3i was obtained in 94% yield as a white solid (4 days). m.p. = 102-104 °C; HPLC analysis (Chiralcel OX-H, tPrOH/hexane = 15/85, 1.0 mL/min, 254 nm; t_r (major) = 15.36 min, t_r (minor) = 17.13 min gave the isomeric composition of the product: 97% ee. [α]_D^20 = -104.6 (c = 0.08, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, J = 7.6 Hz, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.55-7.51 (m, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.46 (dd, J = 16, 7.6 Hz, 1H), 6.32 (d, J = 15.6 Hz, 1H), 3.58-3.49 (m, 1H), 1.68 (d, J = 6.8 Hz, 3H); ^13C NMR (100 MHz, CDCl_3): δ 139.9, 136.3, 135.8, 135.1, 134.9, 132.3, 131.0 (d, J = 1.8 Hz), 130.7 (d, J = 1.9 Hz), 129.6 (q, J = 24.0 Hz), 128.9, 128.8, 128.4 (d, J = 5.9 Hz), 126.7, 125.4 (q, J = 3.8 Hz), 124.1(q, J = 270.1 Hz) 115.9 (d, J = 265.1 Hz), 41.5 (d, J = 17.9 Hz), 14.8 (d, J = 5.2 Hz); ^19F NMR (376 MHz, CDCl_3): δ -62.47 (s, 3F), -130.79 (s, 1F); IR (neat): 1614, 1448, 1325, 1167, 1066, 974, 816, 754, 685, 574 cm⁻¹; HRMS (ESI): Exact mass calcd for C_{24}H_{20}F_4NaO_4S_2 [M+Na]^+: 535.0631, Found: 535.0639.

Product 3j was obtained in 82% yield as a colorless oil (3 days). HPLC analysis (Chiralcel AD-H, tPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t_r (major) = 25.55 min, t_r (minor) = 23.69 min gave the isomeric composition of the product: 96% ee; [α]_D^20 = -261.9 (c = 0.05, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.97-7.91 (m, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 6.41 (dd, J = 15.9, 7.5 Hz, 1H), 6.31 (d, J = 15.9 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 3.58-3.50 (m, 1H), 1.69 (d, J = 6.9 Hz, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^13C NMR (100 MHz, CDCl_3): 166.3, 140.7, 136.4, 135.9, 135.1, 134.9, 132.7 (d, J = 1.5 Hz), 131.0 (d, J = 1.8 Hz), 130.7 (d, J = 2.0 Hz), 129.7, 129.6, 128.8, 128.7, 128.2 (d, J = 5.7 Hz), 126.3, 116.0 (d, J = 266.5 Hz), 60.9, 41.4 (d, J = 18.0 Hz), 14.8 (d, J = 5.3 Hz), 14.3; ^19F NMR (376 MHz, CDCl_3): δ -130.59 (s, 1F); IR (neat): 1448, 1367, 1168, 1153, 1020, 974, 754, 725, 684, 586, 576 cm⁻¹; HRMS (ESI): Exact mass calcd for C_{26}H_{26}FO_6S_2 [M+Na]^+: 517.1149, Found: 517.1151.

Product 3k was obtained in 90% yield as a colorless oil (3 days). HPLC analysis (Chiralcel OD-H, tPrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 24.09 min, t_r (minor) = 27.25 min gave the isomeric composition of the product: 98% ee; [α]_D^20 = -277.1 (c = 0.03, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.63-7.56 (m, 3H), 7.52 (t, J = 7.8 Hz, 2H), 7.44 (t, J = 7.9 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 6.55 (dd, J = 15.9, 7.7 Hz, 1H), 6.34 (d, J = 15.9
Hz, 1H), 3.60-3.51 (m, 1H), 1.68-1.66 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.9, 136.0, 135.7, 135.1, 134.9, 132.2, 131.9 (d, $J = 1.5$ Hz), 130.8 (d, $J = 1.8$ Hz), 130.7 (d, $J = 2.0$ Hz), 129.7 (d, $J = 5.9$ Hz), 128.9, 128.7, 127.0, 118.8, 115.8 (d, $J = 267.0$ Hz), 110.9, 41.4 (d, $J = 18.1$ Hz), 14.8 (d, $J = 5.3$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -131.00 (s, 1F); IR (neat): 1448, 1313, 1168, 1153, 1078, 974, 754, 723, 684, 586, 569 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{24}$H$_{21}$FNO$_4$S$_2$ [M+H]$^+$: 470.0891, Found: 470.0889.

Product 3l was obtained in 90% yield as a yellow oil (3 days). HPLC analysis (Chiralcel OX-H, $^4$PrOH/hexane = 40/60, 1.0 mL/min, 254 nm; $t_r$ (major) = 29.43 min, $t_r$ (minor) = 26.82 min gave the isomeric composition of the product: 98% ee; [$\alpha$]$^20_D = -192.4$ (c = 0.04, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92-7.87 (m, 4H), 7.80 (d, $J = 8.5$ Hz, 2H), 7.70 (t, $J = 7.5$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.53 (t, $J = 7.9$ Hz, 2H), 7.43 (t, $J = 7.9$ Hz, 2H), 7.34 (d, $J = 8.3$ Hz, 2H), 6.47 (dd, $J = 15.9$, 7.7 Hz, 1H), 6.33 (d, $J = 15.9$ Hz, 1H), 3.59-3.50 (m, 1H), 2.59 (s, 3H), 1.69 (dd, $J = 7.1$, 1.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.4, 141.0, 136.3, 136.2, 135.8, 135.1, 134.9, 132.6 (d, $J = 1.6$ Hz), 130.9 (d, $J = 1.8$ Hz), 130.7 (d, $J = 2.0$ Hz), 128.8, 128.7, 128.6, 126.5, 116.0 (d, $J = 266.6$ Hz), 41.4 (d, $J = 18.0$ Hz), 26.5, 14.8 (d, $J = 5.3$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -130.64 (s, 1F); IR (neat): 1448, 1313, 1168, 1153, 1078, 972, 754, 725, 684, 584, 574 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{25}$H$_{24}$FO$_5$S$_2$ [M+H]$^+$: 487.1044, Found: 487.1041.

Product 3m was obtained in 71% yield as a colorless oil (3 days). HPLC analysis (Chiralcel OD-H, $^4$PrOH/hexane = 20/80, 1.0 mL/min, 254 nm; $t_r$ (major) = 26.84 min, $t_r$ (minor) = 24.33 min gave the isomeric composition of the product: 90% ee; [$\alpha$]$^20_D = -72.9676$ (c = 0.02, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.98 (s, 1H), 7.91 (d, $J = 8.5$ Hz, 2H), 7.82-7.80 (m, 4H), 7.73-7.68 (m, 1H), 7.63-7.58 (m, 1H), 7.53 (t, $J = 7.9$ Hz, 2H), 7.46-7.42 (m, 4H), 6.54 (dd, $J = 15.9$, 7.8 Hz, 1H), 6.36 (d, $J = 15.9$ Hz, 1H), 3.60-3.51 (m, 1H), 1.69 (dd, $J = 8.0$, 0.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.6, 142.5, 136.3, 135.9, 135.6, 135.1, 134.9, 132.5 (d, $J = 1.5$ Hz), 131.0 (d, $J = 1.8$ Hz), 130.8 (d, $J = 1.9$ Hz), 130.0, 129.4 (d, $J = 5.9$ Hz), 128.9, 128.8, 127.0, 116.0 (d, $J = 266.7$ Hz), 41.5 (d, $J = 18.1$ Hz), 14.8 (d, $J = 5.3$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -130.86 (s, 1F); IR (neat): 1448, 1313, 1168, 1153, 1080, 974, 754, 725, 684, 576, 561 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{24}$H$_{22}$FO$_5$S$_2$ [M+H]$^+$: 473.0887, Found: 473.0886.
Product 3n was obtained in 87% yield as a white solid (4 days). m.p. = 99-102 °C; HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t_r (major) = 17.47 min, t_r (minor) = 20.04 min gave the isomeric composition of the product: 97% ee. [α]_D^{20} = -90.7 (c = 0.06, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.32-6.20 (m, 2H), 3.54-3.46 (m, 1H), 1.67 (d, J = 7.2 Hz, 3H); ^13C NMR (100 MHz, CDCl_3): δ 136.3, 135.8, 135.1, 134.90, 134.86, 133.4, 132.4 (d, J = 1.5 Hz), 130.9 (d, J = 1.8 Hz), 130.7 (d, J = 1.9 Hz), 128.8, 128.7, 128.5, 127.7, 126.2 (d, J = 5.7 Hz), 116.0 (d, J = 264.7 Hz), 41.4 (d, J = 17.9 Hz), 14.8 (d, J = 5.1 Hz); ^19F NMR (376 MHz, CDCl_3): δ -113.95 (s, 1F), -130.40 (s, 1F); IR (neat): 1497, 1448, 1337, 1167, 1088, 972, 752, 586, 532 cm^{-1}; HRMS (ESI): Exact mass calcd for C_{23}H_{20}ClFNaO_4S_2 [M+Na]^+: 501.0368, Found: 501.0365.

Product 3o was obtained in 74% yield as a white solid (4 days). m.p. = 76-79 °C; HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 205 nm; t_r (major) = 19.55 min, t_r (minor) = 22.49 min gave the isomeric composition of the product: 99% ee. [α]_D^{20} = -38.5 (c = 0.03, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.27-7.21 (m, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.94-6.91 (m, 2H), 6.33-6.21 (m, 2H), 3.55-3.47 (m, 1H), 1.68 (d, J = 7.2 Hz, 3H); ^13C NMR (100 MHz, CDCl_3): δ 162.3 (d, J = 245.7 Hz), 135.3, 135.8, 135.0, 134.8, 132.5 (d, J = 3.3 Hz), 132.4, 130.9 (d, J = 1.8 Hz), 130.7 (d, J = 2.0 Hz), 128.7 (d, J = 12.3 Hz), 128.0 (d, J = 8.0 Hz), 125.24 (d, J = 2.3 Hz), 125.18 (d, J = 2.3 Hz), 116.0 (d, J = 264.5 Hz), 115.3 (d, J = 21.5 Hz), 41.4 (d, J = 17.9 Hz), 14.9 (d, J = 5.1 Hz); ^19F NMR (376 MHz, CDCl_3): δ -113.95 (s, 1F), -130.40 (s, 1F); IR (neat): 1508, 1448, 1344, 1229, 1151, 1078, 1074, 972, 754, 723, 684, 638, 582 cm^{-1}; HRMS (ESI): Exact mass calcd for C_{23}H_{20}F_2NaO_4S_2 [M+Na]^+: 485.0663, Found: 485.0672.

The reaction was carried out at 60 °C for 4 days. Product 3p was obtained in 92% yield as a colorless oil. HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t_r (major) = 16.41 min, t_r (minor) = 18.48 min gave the isomeric composition of the product: 96% ee. [α]_D^{20} = -78.8 (c = 0.06, CHCl_3); ^1H NMR (400 MHz,
The reaction was carried out at 60 °C for 4 days. Product 3q was obtained in 99% yield as a colorless oil. HPLC analysis (Chiralcel OX-H, 1PrOH/hexane = 20/80, 1.0 mL/min, 254 nm; tr (major) = 16.33 min, tr (minor) = 18.71 min gave the isomeric composition of the product: 94% ee. [α]_D^2^0 = -33.55 (c = 0.07, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.27-7.21 (m, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.94-6.91 (m, 2H), 6.33-6.21 (m, 2H), 3.55-3.47 (m, 1H), 1.68 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.9 (d, J = 243.9 Hz), 138.7 (d, J = 7.6 Hz), 136.4, 135.9, 135.1, 134.9, 132.6 (dd, J = 4.2, 2.0 Hz), 131.0 (d, J = 2.1 Hz), 130.7 (d, J = 2.1 Hz), 130.0, 129.9 (d, J = 8.4 Hz), 128.8 (d, J = 9.8), 127.0 (d, J = 5.8 Hz), 122.4 (d, J = 2.8 Hz), 116.1 (d, J = 264.9 Hz), 114.6 (d, J = 21.2 Hz), 112.9 (d, J = 21.7 Hz), 41.4 (d, J = 17.8 Hz), 14.9 (d, J = 5.1 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ -113.54 (s, 1F), -130.54 (s, 1F); IR (neat): 1583, 1448, 1346, 1167, 1151, 1078, 974, 754, 571 cm⁻¹; HRMS (ESI): Exact mass calcd for C₂₆H₂₂F₂Na₄O₄S₂ [M+Na]⁺: 485.0663, Found: 485.0662.

Product 3r was obtained in 49% yield as a colorless oil (3 days). HPLC analysis (Chiralcel OX-H, 1PrOH/hexane = 20/80, 1.0 mL/min, 254 nm; tr (major) = 6.86 min, tr (minor) = 7.28 min gave the isomeric composition of the product: 95% ee. [α]_D^2^0 = -10.5 (c = 0.02, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.93 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.73-7.68 (m, 2H), 7.65-7.59 (m, 3H), 7.57-7.52 (m, 2H), 7.47-7.42 (m, 2H), 6.41 (d, J = 16.0 Hz, 1H), 6.32 (dd, J = 15.9, 6.9 Hz, 1H), 3.68-3.56 (m, 1H), 1.72 (d, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.5, 136.4, 135.9, 135.2, 135.0, 131.9 (q, J = 33.3 Hz), 127.9, 127.8, 127.7, 127.3 (d, J = 3.5 Hz), 125.8 (d, J = 4.0 Hz), 124.2, 124.1, 124.0 (d, J = 3.4 Hz), 115.9 (d, J = 264.9 Hz), 115.4 (d, J = 21.8 Hz), 41.7 (d, J = 17.8 Hz), 14.8 (d, J = 5.3 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ -118.40 (s, 1F), -130.50 (s, 1F); IR (neat): 1487, 1448, 1340, 1230, 1167, 1151, 1080, 972, 752, 685, 592 cm⁻¹; HRMS (ESI): Exact mass calcd for C₂₃H₂₀F₃Na₄O₄S₂ [M+Na]⁺: 485.0663, Found: 485.0674.
131.0 (d, J = 2.0 Hz), 130.8 (d, J = 2.0 Hz), 129.9 (d, J = 5.8 Hz), 129.5, 128.9 (d, J = 5.0 Hz), 126.3 (d, J = 2.6 Hz), 123.22 (q, J = 272.8 Hz), 121.3-121.1 (m), 115.9 (d, J = 266.6 Hz), 41.19 (d, J = 18.0 Hz), 14.78 (d, J = 5.4 Hz); 19F NMR (376 MHz, CDCl3): δ -62.95 (s, 6F), -131.11 (s, 1F); IR (neat): 1379, 1308, 1278, 11539, 1080, 970, 896, 759, 725, 682 cm⁻¹; HRMS (ESI): Exact mass calcd for C25H19F7O4S2Na [M+Na]⁺: 603.0505, Found: 603.0508.

Product 3s was obtained in 97% yield as a white solid (3 days). m.p. = 124-127 °C; HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t_r (major) = 24.44 min, t_r (minor) = 27.99 min gave the isomeric composition of the product: 99% ee. [α]D²⁰ = -81.7 (c = 0.04, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.95 (d, J = 7.6 Hz, 2H), 7.83-7.73 (m, 5H), 7.69 (t, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.57-7.51 (m, 3H), 7.47-7.37 (m, 5H), 6.44-6.34 (m, 2H), 3.61-3.52 (m, 1H), 1.73 (d, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 136.6, 136.1, 135.0, 134.8, 133.9, 133.8 (d, J = 2.0 Hz), 133.4, 133.1, 131.1 (d, J = 2.0 Hz), 130.8 (d, J = 2.0 Hz), 128.8, 128.7, 128.1, 127.9, 127.6, 126.4, 126.3, 125.96, 125.89 (d, J = 5.0 Hz), 123.7, 116.3 (d, J = 264.0 Hz), 41.6 (d, J = 18.0 Hz), 15.0 (d, J = 5.0 Hz); 19F NMR (376 MHz, CDCl3): δ -130.09 (s, 1F); IR (neat): 1448, 1346, 1169, 1151, 1078, 812, 752, 571, 546 cm⁻¹; HRMS (ESI): Exact mass calcd for C27H23FNaO4S2 [M+Na]⁺: 517.0914, Found: 517.0927.

The reaction was carried out at 60 °C for 3 days. Product 3t was obtained in 98% yield as a colorless oil (3 days). HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 205 nm; t_r (major) = 21.39 min, t_r (minor) = 25.11 min gave the isomeric composition of the product: 91% ee. [α]D²⁰ = -63.4 (c = 0.07, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.95 (d, J = 8.0 Hz, 3H), 7.85-7.77 (m, 4H), 7.70 (t, J = 7.6 Hz, 1H), 7.55-7.46 (m, 6H), 7.42 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 15.6 Hz, 1H), 6.38-6.32 (m, 1H), 3.69-3.60 (m, 1H), 1.75 (d, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 136.4, 136.0, 135.0, 134.7, 134.2, 133.4, 131.2, 131.0 (d, J = 1.7 Hz), 130.9, 130.7 (d, J = 2.0 Hz), 128.8, 128.696 (d, J = 5.3 Hz), 128.695, 128.5, 128.1, 126.0, 125.7, 125.6, 124.2, 123.6, 116.2 (d, J = 265.0 Hz), 41.8 (d, J = 17.9 Hz), 15.1 (d, J = 5.0 Hz); 19F NMR (376 MHz, CDCl3): δ -130.16 (s, 1F); IR (neat): 1448, 1346, 1313, 1167, 1078, 972, 798, 777, 721, 684, 575, 553 cm⁻¹; HRMS (ESI): Exact mass calcd for C27H23FNaO4S2 [M+Na]⁺: 517.0914, Found: 517.0915.
The reaction was carried out at 50 °C for 3 days. Product 3u was obtained in 85% yield as a yellow solid. m.p. = 100-103 °C; HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t_r (major) = 21.03 min, t_r (minor) = 24.41 min gave the isomeric composition of the product: 93% ee. \([\alpha]_D^{20} = -84.2 (c = 0.07, \text{CHCl}_3); \) ^1H NMR (400 MHz, CDCl₃): δ 7.94 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.70 (t, J = 7.2 Hz, 1H), 7.60-7.51 (m, 3H) 7.39 (t, J = 8.0 Hz, 2H), 7.29 (s, 1H), 6.33-6.32 (m, 1H), 6.15 (d, J = 3.2 Hz, 1H), 6.08 (d, J = 3.2 Hz, 2H), 3.52-3.45 (m, 1H), 1.69 (d, J = 7.2 Hz, 3H); \(^1^3^C\) NMR (100 MHz, CDCl₃): δ 151.9, 142.0, 136.5, 136.0, 135.0, 134.6, 131.1 (d, J = 2.0 Hz), 130.7 (d, J = 2.0 Hz), 128.8, 128.6, 124.0 (d, J = 5.8 Hz), 121.9 (d, J = 1.5 Hz), 116.2 (d, J = 264.2 Hz), 111.2, 108.3, 40.9 (d, J = 17.6 Hz), 14.5 (d, J = 5.3 Hz); ^1^9^F\ NMR (376 MHz, CDCl₃): δ -130.13 (s, 1F); IR (neat): 1448, 1339, 1169, 1151, 1078, 966, 754, 685, 690, 576 cm⁻¹; HRMS (ESI): Exact mass calcd for C₂₁H₁₉FNaO₅S₂ [M+Na]^+: 457.0550, Found: 457.0553.

The reaction was carried out at 50 °C for 3 days. Product 3v was obtained in 98% yield as a yellow solid. m.p. = 111-114 °C; HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t_r (major) = 22.49 min, t_r (minor) = 25.71 min gave the isomeric composition of the product: 98% ee. \([\alpha]_D^{20} = -59.1 (c = 0.07, \text{CHCl}_3); \) ^1H NMR (400 MHz, CDCl₃): δ 7.94 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.70 (t, J = 7.2 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.14 (d, J = 5.2 Hz, 1H), 6.92 (t, J = 3.6 Hz, 1H), 6.86 (d, J = 3.6 Hz, 1H), 6.36 (d, J = 7.6 Hz, 1H), 5.98 (dd, J = 15.6, 7.6 Hz, 1H), 3.54-3.45 (m, 1H), 1.69 (d, J = 7.2 Hz, 3H); ^1^3^C\ NMR (100 MHz, CDCl₃): δ 141.3, 136.4, 135.8, 135.0, 134.8, 131.1 (d, J = 1.8 Hz), 130.6 (d, J = 1.9 Hz), 128.8, 128.7, 127.2, 126.9 (d, J = 1.5 Hz), 125.9, 124.8 (d, J = 5.6 Hz), 124.6, 116.1 (d, J = 264.3 Hz), 41.1 (d, J = 17.5 Hz), 14.7 (d, J = 5.0 Hz); ^1^9^F\ NMR (376 MHz, CDCl₃): δ -129.83 (s, 1F); IR (neat): 1583, 1448, 1339, 1169, 1151, 1078, 966, 754, 685, 690, 576 cm⁻¹; HRMS (ESI): Exact mass calcd for C₂₁H₁₉FNaO₄S₂ [M+Na]^+: 473.0322, Found: 473.0321.

Product 3w was obtained in 99% yield as a colorless oil (3 days). HPLC analysis (Chiralcel AD-H, iPrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t_r (major) = 19.29 min, t_r (minor) = 22.40 min gave the isomeric composition of the product: 97% ee. \([\alpha]_D^{20} = -69.7 (c = 0.06, \text{CHCl}_3); \) ^1H NMR (400 MHz, CDCl₃): δ 7.91 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 7.6 Hz, 2H), 7.69 (t, J = 7.2 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.53 (t, J = 8.0
Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.37-7.29 (m, 4H), 7.24-7.21 (m, 1H), 6.63 (dd, J = 15.6, 10.4 Hz, 1H), 6.45 (d, J = 15.6 Hz, 1H), 6.07 (dd, J = 15.6, 10.4 Hz, 1H), 5.90 (dd, J = 14.8, 8.0 Hz, 1H), 3.46-3.37 (m, 1H), 1.64 (d, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 136.9, 136.4, 135.9, 135.0, 134.8, 134.2, 132.8, 131.0 (d, J = 1.8 Hz), 130.8 (d, J = 2.0 Hz), 129.3 (d, J = 5.7 Hz), 128.8, 128.7, 128.6, 128.1, 127.6, 126.3, 116.1 (d, J = 264.6 Hz), 41.3 (d, J = 17.9 Hz), 14.9 (d, J = 4.9 Hz); 19F NMR (376 MHz, CDCl3): δ -130.18 (s, 1F); IR (neat): 1448, 1340, 1169, 1151, 1080, 991, 750, 685, 580, 569 cm−1; HRMS (ESI): Exact mass calcd for C25H23FNaO4S2 [M+Na]+: 493.0914, Found: 493.0916.

The reaction was carried out at 70 °C for 3 days. Product 3x was obtained in 67% yield as a yellow oil. HPLC analysis (Chiralcel OD-H, iPrOH/hexane = 10/90, 1.0 mL/min, 230 nm; tR (major) = 10.72 min, tR (minor) = 11.41 min gave the isomeric composition of the product: 93% ee. [α]D20 = -7.2 (c = 0.06, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.90 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.71-7.64 (m, 2H), 7.54-7.47 (m, 4H), 5.54-5.48 (m, 1H), 5.39-5.32 (m, 1H), 3.31-3.22 (m, 1H), 1.93-1.87 (m, 2H), 1.56 (d, J = 6.4 Hz, 3H), 1.30-1.22 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 136.7, 136.0, 135.7 (d, J = 1.4 Hz), 134.9, 134.7, 130.9 (d, J = 1.9 Hz), 130.7 (d, J = 2.1 Hz), 128.7, 128.6, 125.4 (d, J = 5.6 Hz), 116.2 (d, J = 263.9 Hz), 41.3 (d, J = 17.8 Hz), 32.3, 31.2, 28.5, 22.4, 15.2 (d, J = 5.1 Hz), 14.0; 19F NMR (376 MHz, CDCl3): δ -129.78 (s, 1F); IR (neat): 2922, 1583, 1448, 1336, 1151, 972, 754, 723, 682, 570 cm−1; HRMS (ESI): Exact mass calcd for C22H27FNaO4S2 [M+Na]+: 461.1227, Found: 461.1236.

The reaction was carried out at 70 °C for 5 days. Product 3y was obtained in 81% yield as a white solid. m.p. = 110-113 °C; HPLC analysis (Chiralcel OD-H, iPrOH/hexane = 20/80, 1.0 mL/min, 205 nm; tR (major) = 15.14 min, tR (minor) = 17.59 min gave the isomeric composition of the product: 90% ee. [α]D20 = -19.9 (c = 0.1, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.89 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.70-7.63 (m, 2H), 7.53-7.45 (m, 4H), 7.29-7.25 (m, 2H), 7.20-7.12 (m, 3H), 5.57 (dd, J = 15.6, 8.0 Hz, 1H), 5.41 (dt, J = 15.2, 6.4 Hz, 1H), 3.30-3.21 (m, 1H), 2.59 (t, J = 7.6 Hz, 2H), 2.26-2.20 (m, 2H), 1.54 (d, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 141.5, 136.6, 136.0, 134.9, 134.9, 134.5 (d, J = 1.5 Hz), 130.9 (d, J = 1.9 Hz), 130.7 (d, J = 2.0 Hz), 128.7, 128.6, 128.4, 128.2, 126.3 (d, J = 5.6 Hz), 125.8, 116.1 (d, J = 264.2 Hz), 41.3 (d, J = 17.9 Hz), 35.3, 34.0, 15.2 (d, J = 5.2 Hz); 19F NMR (376 MHz, CDCl3): δ -
129.93 (s, 1F); IR (neat): 1448, 1339, 1166, 1149, 1078, 752, 683, 576, 561 cm⁻¹; HRMS (ESI): Exact mass calcd for C_{25}H_{25}FNaO_{4}S_{2} [M+Na]⁺: 495.1071, Found: 495.1072.

The reaction was carried out at 70 °C for 4 days. Product 3z was obtained in 69% yield as a colorless oil. HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 40/60, 1.0 mL/min, 205 nm; tᵣ (major) = 16.88 min, tᵣ (minor) = 13.81 min gave the isomeric composition of the product: 94% ee; [α]_D^{20} = -10.7 (c = 0.01, CHCl₃); ^¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.72-7.61 (m, 2H), 7.54-7.48 (m, 4H), 5.67-5.61 (m, 1H), 5.46-5.40 (m, 1H), 3.29-3.20 (m, 1H), 2.51-2.40 (m, 2H), 2.25-2.18 (m, 2H), 2.14 (s, 3H), 1.52 (dd, J = 7.1, 1.3 Hz, 3H); ^¹³C NMR (100 MHz, CDCl₃): δ 207.9, 136.4, 136.0, 134.9, 134.8, 133.4 (d, J = 1.4 Hz), 130.8 (d, J = 1.8 Hz), 130.7 (d, J = 2.1 Hz), 128.8, 128.7, 126.5 (d, J = 5.9 Hz), 116.1 (d, J = 266.4 Hz), 42.6, 41.2 (d, J = 18.0 Hz), 29.9, 26.3, 15.1 (d, J = 5.4 Hz); ^¹⁹F NMR (376 MHz, CDCl₃): δ -130.28 (s, 1F); IR (neat): 1448, 1339, 1166, 1149, 1078, 752, 683, 576, 561 cm⁻¹; HRMS (ESI): Exact mass calcd for C_{21}H_{24}FO_{5}S_{2} [M+H]⁺: 439.1044, Found: 439.1040.

The reaction was carried out at 50 °C for 5 days. Product 3aa was obtained in 94% yield as a yellow solid. m.p. = 135-137 °C; HPLC analysis (Chiralcel AD-H, iPrOH/hexane = 15/85, 1.0 mL/min, 254 nm; tᵣ (major) = 18.17 min, tᵣ (minor) = 18.95 min gave the isomeric composition of the product: 97% ee. [α]_D^{20} = -45.5 (c = 0.04, CHCl₃); ^¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.33-7.29 (m, 2H), 7.26-7.25 (m, 1H), 7.22-7.20 (m, 2H), 6.27 (d, J = 16.0 Hz, 1H), 6.13 (dd, J = 16.0, 7.6 Hz, 1H), 3.54-3.45 (m, 1H), 1.68 (d, J = 7.2 Hz, 3H); ^¹³C NMR (100 MHz, CDCl₃): δ 142.3, 142.2, 136.1, 134.8, 134.3, 133.9 (d, J = 1.5 Hz), 132.5 (d, J = 1.9 Hz), 132.1 (d, J = 2.1 Hz), 129.2, 129.1, 128.6, 128.0, 126.4, 124.9 (d, J = 5.4 Hz), 116.3 (d, J = 264.1 Hz), 41.2 (d, J = 17.5 Hz), 14.7 (d, J = 5.2 Hz); ^¹⁹F NMR (376 MHz, CDCl₃): δ -130.52 (s, 1F); IR (neat): 2361, 2341, 1576, 1475, 1344, 1168, 1153, 1091, 974, 754, 725, 686, 576, 563 cm⁻¹; HRMS (ESI): Exact mass calcd for C_{23}H_{19}Cl_{2}FNaO_{4}S_{2} [M+Na]⁺: 534.9978, Found: 534.9973.
The reaction was carried out at 50 °C for 5 days. Product 3ab was obtained in 99% yield as a yellow solid. HPLC analysis (Chiralcel AD-H, iPrOH/hexane = 40/60, 1.0 mL/min, 254 nm; t_r (major) = 19.23 min, t_r (minor) = 27.98 min gave the isomeric composition of the product: 95% ee. [α]D 20 = -52.2 (c = 0.05, CHCl3); 1H NMR (400 MHz, CDCl3): δ 8.42 (s, 1H), 8.24 (s, 1H), 7.82-7.76 (m, 4H), 7.72 (d, J = 8.0 Hz, 1H), 7.67-7.53 (m, 6H), 7.47 (t, J = 7.6 Hz, 1H), 7.21-7.16 (m, 5H), 6.40-6.30 (m, 2H), 3.75-3.67 (m, 1H), 1.79 (d, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 136.4, 135.7, 135.6, 133.7, 133.4, 133.2, 133.0, 132.8, 131.6, 131.5, 129.9, 129.8, 129.6, 129.5, 128.7 (d, J = 5.6 Hz), 128.4, 127.8, 127.7, 127.6, 127.5, 126.4, 125.7 (d, J = 5.6 Hz), 124.7 (d, J = 2.6 Hz), 124.4 (d, J = 3.2 Hz), 116.6 (d, J = 264.2 Hz), 41.5 (d, J = 17.8 Hz), 15.2 (d, J = 5.0 Hz); 19F NMR (376 MHz, CDCl3): δ -130.00 (s, 1F); IR (neat): 1340, 1167, 1130, 1067, 968, 864, 815, 748, 636, 571 cm⁻¹; HRMS (ESI): Exact mass calcd for C31H25FNaO4S2 [M+Na]+: 567.1071, Found: 567.1065.

The reaction was carried out at 50 °C for 5 days. Product 3ac was obtained in 42% yield as a colorless oil. HPLC analysis (Chiralcel OX-H, iPrOH/hexane = 5/95, 1.0 mL/min, 205 nm; t_r(major) = 26.17 min, t_r(minor) = 28.82 min gave the isomeric composition of the product: 95% de. [α]D 20 = -6.4 (c = 0.03, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.91-7.88 (m, 2H), 7.83-7.80 (m, 2H), 7.71-7.63 (m, 2H), 7.54-7.46 (m, 4H), 5.56-5.51 (m, 1H), 5.38-5.30 (m, 1H), 5.10-5.06 (m, 1H), 3.31-3.23 (m, 1H), 1.98-1.89 (m, 3H), 1.81-1.74 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.58 (dd, J = 6.8, 0.8 Hz, 3H), 1.45-1.37 (m, 1H), 1.30-1.23 (m, 1H), 1.14-1.05 (m, 1H), 0.82 (d, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 136.7, 135.9, 134.9, 134.7, 134.2 (d, J = 1.4 Hz), 131.1, 130.9 (d, J = 1.9 Hz), 130.8 (d, J = 2.0 Hz), 128.8, 128.6, 126.8 (d, J = 5.5 Hz), 124.7, 116.1 (d, J = 264.0 Hz), 41.6 (d, J = 17.9 Hz), 39.7, 36.5, 32.4, 25.7, 25.5, 19.3, 17.6, 15.4 (d, J = 5.0 Hz); 19F NMR (376 MHz, CDCl3): δ -129.60 (s, 1F); IR (neat): 2962, 1448, 1348, 1217, 1168, 1080, 754, 725, 648, 578 cm⁻¹; HRMS (ESI): Exact mass calcd for C26H33FNaO4S2 [M+Na]+: 515.1697, Found: 515.1708.
4.2 Transformations of product 3a

To a solution of product 3a (44.4 mg, 0.1 mmol) in absolute MeOH (1.0 mL) was added activated Mg (20 equivs) in one portion at 0 °C under N₂ atmosphere. The reaction was stirred at 0 °C until full consumption of 3a monitored by TLC and GC-MS analysis (about 12 h). After adding water (3 mL) and dilute HCl (3 mL, 2 N), the reaction mixture was extracted with CH₂Cl₂ (5 mL × 3). The combined organic layers were dried over Na₂SO₄, and concentrated under reduced pressure to afford the crude residue, which was purified by flash chromatography with PE as the eluent) to provide the desired product 4a in 98% yield as a colorless oil. HPLC analysis (Chiralcel OD-H, iPrOH/hexane = 0/100, 1.0 mL/min, 254 nm; tᵣ (major) = 17.71 min, tᵣ (minor) = 13.90 min gave the isomeric composition of the product: 96% ee; [α]D²⁰ = -1.3 (c = 0.02, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.35 (m, 2H), 7.32-7.28 (m, 2H), 7.25-7.20 (m, 1H), 6.58 (d, J = 16.0 Hz, 1H), 6.13 (dd, J = 16.0, 7.6 Hz, 1H), 4.46-4.44 (m, 1H), 4.34-4.24 (m, 1H), 2.81-2.67 (m, 1H), 1.16 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.2, 130.7, 130.5 (d, J = 6.6 Hz), 128.5, 127.3, 126.1, 87.3 (d, J = 171.3 Hz), 37.9 (d, J = 18.9 Hz), 15.8 (d, J = 6.1 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ -219.64 (s, 1F); IR (neat): 2966, 1490, 1215, 1047, 966, 752, 721, 692, 678, 669 cm⁻¹; HRMS (EI): Exact mass calcd for C₁₁H₁₃F [M⁺]: 164.0998, Found: 164.0996.

To a solution of product 3a (44.4 mg, 0.1 mmol) in absolute CD₃OD (1.0 mL) was added activated Mg (48.6 mg, 20 equivs) in one portion at 0 °C under N₂ atmosphere. The reaction was stirred at 0 °C until full consumption of 3a monitored by TLC and GC-MS analysis (about 12 h). After adding water (3 mL) and dilute HCl (3 mL), the reaction mixture was extracted with CH₂Cl₂ (5 mL × 3). The combined organic layers were dried over Na₂SO₄, and concentrated under reduced pressure to afford the crude residue, which was purified by flash chromatography with PE as the eluent) to provide the desired product D-4a in 91% yield as a colorless oil. HPLC analysis (Chiralcel OD-H, iPrOH/hexane = 0/100, 1.0 mL/min, 254 nm; tᵣ (major) = 12.31 min, tᵣ (minor) = 15.24 min gave the
isomeric composition of the product: 98% ee; $[\alpha]_D^{20} = -2.8\ (c = 0.02,\ \text{CHCl}_3)$; $^1\text{H NMR (400 MHz, CDCl}_3)$: $\delta$ 7.37-7.34 (m, 2H), 7.32-7.28 (m, 2H), 7.24-7.20 (m, 1H), 6.47 (d, $J = 14.8\ Hz$, 1H), 6.13 (dd, $J = 16.0,\ 8.4\ Hz$, 1H), 2.78-2.67 (m, 1H), 1.16 (dd, $J = 6.8\ Hz,\ 5.6\ Hz$, 3H); $^{13}\text{C NMR (100 MHz, CDCl}_3)$: $\delta$ 137.2, 130.7, 130.5 (d, $J = 7.0\ Hz$), 128.5, 127.3, 126.1, 86.6 (dt, $J = 169\ Hz,\ 22.0\ Hz$), 37.7 (d, $J = 20.0\ Hz$), 15.8 (d, $J = 6.0\ Hz$); $^{19}\text{F NMR (376 MHz, CDCl}_3)$: $\delta$ -220.94~-221.01 (m, 1F); IR (neat): 1494, 1448, 1078, 958, 744, 721, 692 cm$^{-1}$; HRMS (EI): Exact mass calcd for $\text{C}_{11}\text{H}_{11}\text{D}_2\text{F}$ [M]$^+$: 166.1126, Found: 166.1121.

4.3 General procedure for the tandem synthesis of $\alpha$-monofluoromethyl allylic compounds

To an oven-dried Schlenk tube equipped with a stirring bar were successively added Ni(COD)$_2$ (7.0 mg, 10 mol%), (S,S)-QuinoxP$^*$ L8 (9.2 mg, 11 mol%), 1,3-dienes 1 (0.375 mmol, 1.5 equivs), and FBSM 2a (78.6 mg, 0.25 mmol), followed by the addition of absolute EtOH (2.5 mL) in a glove box. After it take out from the glove box, the resulting mixture was stirred at 25 °C until full conversion of 2 indicated by TLC or GC-MS analysis. The reaction mixture was concentrated under vacuum, and the residue was filtrated over a short pad of silica gel to give the crude product 3, which was used for the next reductive desulfonylation step.

To a solution of above crude products 3 in absolute MeOH (2.5 mL) or CD$_3$OD (2.5 mL) was added activated Mg (48.6 mg, 20 equivs) in one portion at 0 °C under N$_2$ atmosphere. The reaction was stirred at 0 °C ($4a$, $4d$ and $D$-$4a$) or rt ($4b$, $4c$, $D$-$4b$, $D$-$4c$ and $D$-$4d$) until full consumption of 3 monitored by TLC and GC-MS analysis (about 12 h). After adding water (3 mL) and dilute HCl (3 mL, 2 N), the reaction mixture was extracted with CH$_2$Cl$_2$ (10 mL $\times$ 2). The combined organic layers were dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The crude residue was purified by flash chromatography with PE as the eluent (in the case of $4b$ and $D$-$4b$, PE/CH$_2$Cl$_2$ (10:1, v/v) was used as the eluent) to provide the desired CH$_2$F- or CD$_2$F-containing products 4 or D-$4$. 
Product 4a was obtained in 86% yield from 1a as a colorless oil. HPLC analysis (Chiralcel OD-H, iPrOH/hexane = 0/100, 1.0 mL/min, 254 nm; t\textsubscript{r} (major) = 17.71 min, t\textsubscript{r} (minor) = 13.90 min gave the isomeric composition of the product: 96% ee. The NMR spectra of 4a is consistent with that of the product obtained via one-step desulfonylation reaction in Section 4.2.

Product 4b was obtained in 88% yield from 1c as a colorless oil. HPLC analysis (Chiralcel OD-H, iPrOH/hexane = 0.1/99.9, 1.0 mL/min, 254 nm; \(t\textsubscript{r}\) (major) = 18.29 min, \(t\textsubscript{r}\) (minor) = 17.22 min) gave the isomeric composition of the product: 96% ee. \([\alpha]_D^{20} = -8.3\) (c = 0.06, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.31-7.24 (m, 2H), 6.86-6.82 (m, 2H), 6.41 (d, \(J = 16.0\) Hz, 1H), 5.97 (dd, \(J = 16.0, 7.2\) Hz, 1H), 4.44-4.34 (m, 1H), 4.32-4.22 (m, 1H), 3.79 (s, 3H), 2.78-2.63 (m, 1H), 1.15 (dd, \(J = 6.8, 1.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 158.9, 130.1, 130.0, 128.2 (d, \(J = 6.7\) Hz), 127.2, 113.9, 87.4 (d, \(J = 171.1\) Hz), 55.2, 37.8 (d, \(J = 18.9\) Hz), 15.9 (d, \(J = 5.9\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -219.34 (s, 1F); IR (neat): 2964, 1606, 1510 1246, 1033, 966, 910, 806, 750, 669, 532 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{12}\)H\(_{16}\)OF \([M+H]^+\): 195.1185, Found: 195.1179.

Product 4c was obtained in 39% yield from 1n as a colorless oil. HPLC analysis (Chiralcel OD-H, iPrOH/hexane = 0/100, 1.0 mL/min, 254 nm; \(t\textsubscript{r}\) (major) = 8.96 min, \(t\textsubscript{r}\) (minor) = 8.36 min) gave the isomeric composition of the product: 96% ee. \([\alpha]_D^{20} = -3.2\) (c = 0.03, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.32 (d, \(J = 2.0\) Hz, 1H), 6.36-6.35 (m, 1H), 6.32-6.28 (m, 1H), 6.19 (d, \(J = 3.2\) Hz, 1H), 6.08 (dd, \(J = 16.0, 0.8\) Hz, 1H), 4.44-4.22 (m, 2H), 2.76-2.65 (m, 1H), 1.69 (dd, \(J = 6.8, 0.8\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 152.7, 141.6, 129.3 (d, \(J = 7.0\) Hz), 119.3, 111.2, 107.1, 84.1 (d, \(J = 117.0\) Hz), 37.6 (d, \(J = 19.0\) Hz), 15.7 (d, \(J = 6.0\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -219.35 (s, 1F); IR (neat): 2933, 1215, 1115, 981, 962, 883, 796, 667, 594 \(cm^{-1}\); HRMS (ESI): Exact mass calcd for C\(_9\)H\(_{12}\)F \([M+H]^+\): 155.0872, Found: 155.0866.

Product 4d was obtained in 86% yield from 1r as a colorless oil. HPLC analysis (Chiralcel OD-H + OD-H, iPrOH/hexane = 0/100, 1.0 mL/min, 205 nm; \(t\textsubscript{r}\) (major) = 18.81 min, \(t\textsubscript{r}\) (minor) = 20.60 min gave the isomeric composition of the product: 93% ee. \([\alpha]_D^{20} = -4.4\) (c = 0.06, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.30-7.26 (m, 2H), 7.20-7.16 (m, 3H), 5.60-5.52 (m, 1H), 5.36-5.29 (m, 1H), 4.32-4.09 (m, 2H), 2.69-2.65 (m, 2H), 2.56-
2.45 (m, 1H), 2.35-2.29 (m, 2H), 1.01 (dd, J = 6.8, 1.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 141.8, 131.0 (d, J = 6.9 Hz), 130.7, 128.5, 128.2, 125.7, 87.6 (d, J = 170.5 Hz), 37.4 (d, J = 18.8 Hz), 35.9, 34.5, 15.9 (d, J = 5.9 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -219.30 (s, 1F); IR (neat): 2927, 1454, 1388, 1215, 1006, 970, 908, 750, 698, 667, 650 cm$^{-1}$; HRMS (EI): Exact mass calced for C$_{13}$H$_{17}$F [M$^+$]: 192.1306, Found: 192.1309.

Product D-4a was obtained in 94% yield from 1a as a colorless oil. HPLC analysis (Chiralcel OD-H, $^t$PrOH/hexane = 0/100, 1.0 mL/min, 254 nm; $t_r$ (major) = 12.31 min, $t_r$ (minor) = 15.24 min gave the isomeric composition of the product: 98% ee. The NMR spectra of D-4a is consistent with that of the product obtained via one-step desulfonylation reaction in Section 4.2.

Product D-4b was obtained in 68% yield from 1c as a colorless oil. HPLC analysis (Chiralcel IC, $^t$PrOH/hexane = 1/100, 1.0 mL/min, 254 nm; $t_r$ (major) = 5.71 min, $t_r$ (minor) = 5.14 min) gave the isomeric composition of the product: 98% ee. [α]$_D^{20}$ = -0.4 (c = 0.02, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.30-7.28 (m, 2H), 6.85-6.83 (m, 2H), 6.44-6.40 (m, 1H), 5.98 (dd, J = 16.0, 7.6 Hz, 1H), 3.80 (s, 3H), 2.76-2.65 (m, 1H), 1.15 (dd, J = 6.8, 1.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.0, 130.1, 130.0, 128.2 (d, J = 7.0 Hz), 127.3, 113.9, 87.4 (m), 55.3, 37.6 (d, J = 19.0 Hz), 15.9 (d, J = 5.0 Hz) (Note: the peak for CD$_2$F is missed in the $^{13}$C NMR spectrum, possibly due to low intensity); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -220.69--220.77 (m, 1F); IR (neat): 1681, 1660, 1463, 1246, 1174, 1033, 964, 904, 804, 727, 650, 530 cm$^{-1}$; HRMS (EI): Exact mass calced for C$_{12}$H$_{13}$D$_2$OF [M$^+$]: 196.1230, Found: 196.1227.

Product D-4c was obtained in 54% yield from 1n as a colorless oil. HPLC analysis (Chiralcel OD-H, $^t$PrOH/hexane = 0/100, 1.0 mL/min, 254 nm; $t_r$ (major) = 8.51 min, $t_r$ (minor) = 9.12 min) gave the isomeric composition of the product: 97% ee. [α]$_D^{20}$ = -1.3 (c = 0.03, CHCl$_3$; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.32 (s, 1H), 6.36-6.34 (m, 1H), 6.30 (d, J = 15.6 Hz, 1H), 6.19 (d, J = 3.2 Hz, 1H), 6.08 (dd, J = 16.4, 8.8 Hz, 1H), 2.72-2.65 (m, 1H), 1.14 (d, J = 6.8Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 152.7, 141.6, 129.2 (d, J = 7.0 Hz), 119.3, 111.2, 107.1, 86.4 (dt, J = 169 Hz, 29 Hz), 37.4 (d, J = 19.0 Hz), 15.6 (d, J = 6.0 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): δ -220.68--220.75 (m, 1F); IR (neat): 1681, 1660, 1460, 1275, 952, 883, 800, 734, 665, 594 cm$^{-1}$; HRMS (EI): Exact mass calced for C$_5$H$_9$D$_2$FO [M$^+$]: 156.0916, Found: 156.0914.
Product **D-4d** was obtained in 66% yield from **1r** as a colorless oil. HPLC analysis (Chiralcel OD-H+OD-H, 1PrOH/hexane = 0/100, 1.0 mL/min, 220 nm; \( t_r \) (major) = 16.54 min, \( t_r \) (minor) = 17.63 min gave the isomeric composition of the product: 94% ee. \([\alpha]_D^{20} = -0.9 \) (c = 0.04, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.29-7.24 (m, 2H), 7.19-7.16 (m, 3H), 5.60-5.52 (m, 1H), 5.36-5.29 (m, 1H), 2.67 (t, \( J = 7.2 \) Hz, 2H), 2.54-2.43 (m, 1H), 2.35-2.29 (m, 2H), 1.01 (dd, \( J = 5.6, 1.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 141.8, 131.0 (d, \( J = 7.0 \) Hz), 130.7, 128.5, 128.2, 125.7, 86.8 (dt, \( J = 169, 23 \) Hz), 37.2 (d, \( J = 18.0 \) Hz), 35.9, 34.5, 15.9 (d, \( J = 6.0 \) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -220.59~220.67 (m, 1F); IR (neat): 1496, 1454, 1062, 952, 906, 731 698 cm\(^{-1}\); HRMS (El): Exact mass calcd for C\(_{13}\)H\(_{15}\)D\(_2\)F [M]+: 194.1437, Found: 194.1434.
5. Enantioselective Markovnikov hydromonofluoroalkylation of 1,3-dienes 1 with 5

To an oven-dried Schlenk tube equipped with a stirring bar were successively added Ni(COD)$_2$ (3.5 mg, 0.0125 mmol, 5 mol%), (S,S)-QuinoxP* L8 (4.6 mg, 0.01375 mmol, 5.5 mol%), 1,3-dienes 1 (0.375 mmol, 1.5 equivs), and diethyl fluoromalonate 5 (44.5 mg, 0.25 mmol), followed by the addition of absolute EtOH (1.5 mL) in a glove box. After it take out from the glove box, the resulting mixture was stirred at room temperature for 5 min, and then stirred at 50 °C until full conversion. The reaction was monitored by TLC and GC-MS analysis. After full consumption of 5, the mixture was concentrated under vacuum to give the crude residue, which was purified by silica gel column chromatography (PE/EA = 10:1, v/v) to afford products 6. Racemic products 6h, 6x and 6ab were prepared using 10 mol% of Ni(COD)$_2$ with a mixed ligand consisting of (R,R)-quinoxp* and (S,S)-quinoxp* as the catalyst, and all other racemates 6 were prepared using 10 mol% Ni(COD)$_2$ and 11 mol% dppb.

Product 6a was obtained in 97% yield as colorless oil (3 days). HPLC analysis (Chiralcel AD-H, iPrOH/hexane = 2/98, 1.0 mL/min, 254 nm; t$_r$(minor) = 10.97 min, t$_r$(major) = 12.50 min) gave the isomeric composition of the product: 96% ee; [α]$_D^{20}$ = -84.7 (c = 0.51, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.29-7.17 (m, 5H), 6.46 (d, J = 16.0 Hz, 1H), 6.07 (dd, J = 15.6, 9.2 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 4.20-4.15 (m, 2H), 3.42-3.29 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H), 1.19-1.15 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.56 (d, J = 25.3 Hz), 165.55 (d, J = 25.7 Hz), 163.67, 133.09, 128.51, 127.67, 126.85 (d, J = 2.7 Hz), 126.36, 97.08 (d, J = 203.9 Hz), 62.65, 62.48, 42.73 (d, J = 20.4 Hz), 14.70 (d, J = 4.4 Hz), 14.06, 14.03; $^{19}$F NMR (376 MHz, CDCl$_3$): δ -178.21 (s, 1F). IR (ATR): 1747, 1369, 1232, 1097, 968, 858, 746, 694 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{17}$H$_{21}$FNaO$_4$ [M+Na]$^+$: 331.1316, Found: 331.1309.

Product 6b was obtained in 82% yield as colorless oil (3 days). HPLC analysis (Chiralcel AD-H, iPrOH/hexane = 2/98, 1.0 mL/min, 254 nm; t$_r$(minor) = 14.32 min, t$_r$(major) = 18.78 min) gave the isomeric composition of the product: 97% ee; [α]$_D^{20}$ = -28.4 (c = 0.50, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.31–7.28 (m, 2H), 7.00–6.96 (m,
2H) 6.47 (d, J = 15.6 Hz, 1H), 6.04 (dd, J = 16.4, 9.2 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H), 3.44–3.30 (m, 1H), 1.33 (t, J = 7.2 Hz, 3H), 1.24-1.20 (m, 6H); 13C NMR (100 MHz, CDCl3): δ 165.54 (d, J = 25.5 Hz, 2C), 162.37 (d, J = 245.5 Hz), 132.82 (d, J = 3.3 Hz), 131.87, 127.85 (d, J = 7.9 Hz), 126.64 (t, J = 2.4 Hz), 97.03 (d, J = 204.1 Hz), 62.66, 62.47, 42.65 (d, J = 20.3 Hz), 14.66 (d, J = 4.3 Hz), 14.06, 14.02; 19F NMR (376 MHz, CDCl3): δ -178.21 (s, 1F), -114.33 (s, 1F); IR (ATR): 1747, 1369, 1232, 1163, 1093, 1039, 970, 810 cm⁻¹; HRMS (ESI): Exact mass calcd for C17H20F2NaO4 [M+Na]+: 349.1222, Found: 349.1219

Product 6c was obtained in 83% yield as colorless oil (3 days). HPLC analysis (Chiralcel AD-H, 4PrOH/hexane = 2/98, 1.0 mL/min, 254 nm; t_r (minor) = 12.05 min, t_r (major) = 15.76 min) gave the isomeric composition of the product: 95% ee; [α]D²⁰ = -40.0 (c = 0.52, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.26 (s, 4H), 6.45 (d, J = 16.0 Hz, 1H), 6.10 (dd, J = 16.0, 9.2 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H), 3.45–3.32 (m, 1H), 1.33 (t, J = 7.2 Hz, 3H), 1.23-1.20 (m, 6H); 13C NMR: (100 MHz, CDCl3): δ 165.51 (d, J = 25.6 Hz), 165.49 (d, J = 25.3 Hz), 135.14, 133.35, 131.87, 128.69, 127.60 (d, J = 1.8 Hz), 127.56, 96.96 (d, J = 204.2 Hz), 62.71, 62.51, 42.66 (d, J = 20.3 Hz), 14.61 (d, J = 4.3 Hz), 14.07, 14.03; 19F NMR (376 MHz, CDCl3): δ -178.19 (s, 1F); IR (ATR): 1747, 1369, 1232, 1163, 1093, 1039, 970, 810 cm⁻¹; HRMS (ESI): Exact mass calcd for C17H20ClFNaO4 [M+Na]+: 365.0926, Found: 365.0920.

Product 6d was obtained in 96% yield as colorless oil (4 days). HPLC analysis (Chiralcel AD-H, 4PrOH/hexane = 2/98, 1.0 mL/min, 254 nm; t_r(minor) = 10.68 min, t_r(major) = 13.89 min) gave the isomeric composition of the product: 93% ee; [α]D²⁰ = -47.4 (c = 0.71, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.55 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 15.6 Hz, 1H), 6.23 (dd, J = 16.0, 9.2 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 4.23 (q, J = 7.2 Hz, 2H), 3.49–3.34 (m, 1H), 1.33 (t, J = 7.2 Hz, 3H), 1.24-1.20 (m, 6H); 13C NMR (100 MHz, CDCl3): δ 165.40 (d, J = 25.8 Hz), 165.35 (d, J = 25.4 Hz), 140.08, 131.73, 129.72 (d, J = 2.6 Hz), 129.45 (q, J = 32.1 Hz), 126.48, 125.44 (q, J = 3.5 Hz), 124.07 (q, J = 270.1 Hz), 96.78 (d, J = 204.2 Hz), 62.69, 62.50, 42.55 (d, J = 20.5 Hz), 14.47 (d, J = 3.7 Hz), 13.99, 13.94; 19F NMR (376 MHz, CDCl3): δ -177.95 (s, 1F), -62.55 (s, 3F); IR (ATR): 1749, 1616, 1323, 1234, 1163, 1066, 824, 737 cm⁻¹; HRMS (ESI): Exact mass calcd for C18H20F4NaO4 [M+Na]+: 399.1190, Found: 399.1181.
Product 6e was obtained in 99% yield as colorless oil (3 days). HPLC analysis (Chiralcel OJ-H, 1PrOH/hexane = 15/85, 0.5 mL/min, 230 nm; t(minor) = 24.88 min, t(major) = 25.40 min) gave the isomeric composition of the product: 99% ee; [α]D20 = -65.45 (c = 0.91, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.96 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 6.54 (d, J = 16.0 Hz, 1H), 6.24 (dd, J = 16.0, 9.2 Hz, 1H), 4.39-4.30 (m, 4H), 4.22 (q, J = 6.8 Hz, 2H), 3.48–3.34 (m, 1H), 1.39 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H) 1.23-1.19 (m, 6H); 13C NMR (100 MHz, CDCl3): δ 166.32, 165.48 (d, J = 25.6 Hz), 165.44 (d, J = 25.2 Hz), 140.96, 132.27, 129.85, 129.60 (d, J = 2.6 Hz), 129.54, 126.19, 96.87 (d, J = 204.4 Hz), 62.73, 62.54, 60.91, 42.70 (d, J = 20.4 Hz), 14.54 (d, J = 4.3 Hz), 14.30, 14.05, 14.02; 19F NMR (376 MHz, CDCl3): δ -177.93 (s, 1F); IR (ATR): 1751, 1716, 1608, 1367, 1276, 1234, 1178, 765 cm⁻¹; HRMS (ESI): Exact mass calcd for C20H26FO6 [M+H]^+: 381.1708, Found: 381.1703.

Product 6f was obtained in 98% yield as colorless oil (4 days). HPLC analysis (Chiralcel OJ-H, 1PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; t(minor) = 37.15 min, t(major) = 42.76 min) gave the isomeric composition of the product: 98% ee; [α]D20 = -69.5 (c = 0.91, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.57 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 6.52 (d, J = 15.6 Hz, 1H), 6.26 (dd, J = 15.6, 8.8 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.25-4.20 (m, 2H), 3.46–3.36 (m, 1H), 1.32 (t, J = 7.2 Hz, 3H), 1.23-1.19 (m, 6H); 13C NMR (100 MHz, CDCl3): δ 165.37 (d, J = 25.6 Hz), 165.29 (d, J = 25.3 Hz), 141.07, 132.38, 131.49, 131.12 (d, J = 2.8 Hz), 126.83, 118.78, 111.01, 96.66 (d, J = 204.5 Hz), 62.77, 62.57, 42.50 (d, J = 20.4 Hz), 14.45 (d, J = 4.3 Hz), 14.04, 14.00; 19F NMR (376 MHz, CDCl3): δ -177.60 (s, 1F); IR (ATR): 2225, 1749, 1604, 1369, 1097, 1041, 858, 819 cm⁻¹; HRMS (ESI): Exact mass calcd for C18H21FNO4 [M+H]^+: 334.1449, Found: 334.1450.

The reaction was carried out using 10 mol% of chiral Ni catalyst. Product 6g was obtained in 98% yield as colorless oil (4 days). HPLC analysis (Chiralcel AD-H, 1PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; t(minor) = 21.54 min, t(major) = 19.75 min) gave the isomeric composition of the product: 99% ee; [α]D20 = -72.41 (c = 0.93, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.88 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 6.54 (d, J = 15.6 Hz, 1H), 6.26 (dd, J = 16.0, 9.2 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.25-4.20 (m, 2H), 3.48–3.36 (m, 1H), 2.58 (s, 3H), 1.33 (t, J = 7.8 Hz, 3H), 1.23-1.20 (m, 6H); 13C NMR (100 MHz, CDCl3): δ 197.45, 165.46 (d, J = 25.5 Hz), 165.41 (d, J = 25.4 Hz), 141.26, 136.21, 132.13, 130.00 (d,
Product 6h was obtained in 77% yield as colorless oil (4 days). HPLC analysis (Chiralcel OJ-H, \textsuperscript{t}PrOH/hexane = 25/75, 1.0 mL/min, 230 nm; t(\text{minor}) = 11.95 min, t(\text{major}) = 15.43 min) gave the isomeric composition of the product: 97% ee; [\alpha]_{D}^{20} = -102.11 (c = 0.75, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 9.97 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 6.57 (d, J = 16.0 Hz, 1H), 6.31 (dd, J = 15.6, 8.8 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 4.26-4.21 (m, 2H), 3.48-3.37 (m, 1H), 1.33 (t, J = 7.2 Hz, 3H), 1.24-1.20 (m, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 191.59, 165.44 (d, J = 25.6 Hz), 165.38 (d, J = 25.4 Hz), 142.64, 135.56, 132.07, 130.81 (d, J = 2.7 Hz), 130.09, 126.86, 96.78 (d, J = 204.4 Hz), 62.77, 62.57, 42.66 (d, J = 20.5 Hz), 14.51 (d, J = 4.2 Hz), 14.06, 14.02; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \delta -177.71 (s, 1F); IR (ATR): 1749, 1697, 1602, 1271, 1166, 1041, 858, 738 cm\textsuperscript{-1}; HRMS (ESI): Exact mass calcd for C\textsubscript{19}H\textsubscript{24}F\textsubscript{3}O\textsubscript{5} [M+H]\textsuperscript{+}: 351.1602, Found: 351.1598.

The reaction was carried out using 10 mol% of chiral Ni catalyst. Product 6i was obtained in 97% yield as colorless oil (4 days). HPLC analysis (Chiralcel AD-H, \textsuperscript{t}PrOH/hexane = 2/98, 1.0 mL/min, 254 nm; t(\text{minor}) = 10.41 min, t(\text{major}) = 15.91 min) gave the isomeric composition of the product: 97% ee; [\alpha]_{D}^{20} = -101.9 (c = 0.71, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 7.28-7.22 (m, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 10.0 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.47 (d, J = 15.6 Hz, 1H), 6.13 (dd, J = 16.0, 9.2 Hz, 1H), 4.32 (q, J = 6.8 Hz, 2H), 4.23 (q, J = 6.8 Hz, 2H), 3.44-3.33 (m, 1H), 1.33 (t, J = 6.8 Hz, 3H), 1.24-1.20 (m, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 165.47 (d, J = 25.6 Hz, 2C), 163.04 (d, J = 243.9 Hz), 138.99 (d, J = 7.6 Hz), 132.00 (d, J = 2.6 Hz), 129.97 (d, J = 8.4 Hz), 128.37 (d, J = 2.8 Hz), 122.21 (d, J = 2.8 Hz), 114.48 (d, J = 21.2 Hz), 112.82 (d, J = 21.7 Hz), 96.90 (d, J = 204.2 Hz), 62.70, 62.52, 42.56 (d, J = 20.3 Hz), 14.57 (d, J = 4.2 Hz), 14.05, 14.01; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \delta -178.08 (s, 1F), -113.52 (s, 1F); IR (ATR): 1747, 1583, 1446, 1230, 1097, 941, 779, 686 cm\textsuperscript{-1}; HRMS (ESI): Exact mass calcd for C\textsubscript{17}H\textsubscript{20}F\textsubscript{2}Na\textsubscript{4} [M+Na]\textsuperscript{+}: 349.1222, Found: 349.1214.
Product 6j was obtained in 83% yield as colorless oil (4 days). HPLC analysis (Chiralcel AD-H, \textsuperscript{1}PrOH/hexane = 2/98, 1.0 mL/min, 230 nm; \( t_m \) (minor) = 11.63 min, \( t_M \) (major) = 12.27 min) gave the isomeric composition of the product: 95% ee; [\( \alpha \)]\textsubscript{D}\textsuperscript{20} = -66.2 (c = 0.49, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.42 (t, \( J = 8.0 \) Hz, 1H), 7.22-7.17 (m, 1H), 7.09-6.98 (m, 2H), 6.69 (d, \( J = 16.4 \) Hz, 1H), 6.19 (dd, \( J = 16.0, 9.2 \) Hz, 1H), 4.33 (q, \( J = 7.2 \) Hz, 2H), 4.24 (q, \( J = 7.2 \) Hz, 2H), 3.47-3.36 (m, 1H), 1.33 (t, \( J = 6.4 \) Hz, 3H), 1.26-1.21 (m, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 165.49 (d, \( J = 25.3 \) Hz), 165.45 (d, \( J = 26.0 \) Hz), 160.07 (d, \( J = 247.6 \) Hz), 129.47 (dd, \( J = 25.3, 3.0 \) Hz), 128.99 (d, \( J = 8.4 \) Hz), 127.23 (d, \( J = 3.6 \) Hz), 125.44 (d, \( J = 3.8 \) Hz), 124.41 (d, \( J = 12.3 \) Hz), 124.06 (d, \( J = 3.6 \) Hz), 115.59 (d, \( J = 21.9 \) Hz), 96.95 (d, \( J = 203.5 \) Hz), 62.67, 62.54, 43.00 (d, \( J = 20.4 \) Hz), 14.57 (d, \( J = 4.0 \) Hz), 14.00, 13.97; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \( \delta \) -178.11 (s, 1F), -118.54 (s, 1F); IR (ATR): 1749, 1487, 1456, 1271, 1230, 1041, 972, 756 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\textsubscript{17}H\textsubscript{20}F\textsubscript{2}NaO\textsubscript{4} [M+Na\textsuperscript{+}]: 349.1222, Found: 349.1213.

Product 6k was obtained in 73% yield as colorless oil (4 days). HPLC analysis (Chiralcel AD-H, \textsuperscript{1}PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; \( t_m \) (minor) = 3.97 min, \( t_M \) (major) = 7.34 min) gave the isomeric composition of the product: 97% ee; [\( \alpha \)]\textsubscript{D}\textsuperscript{20} = -30.66 (c = 0.99, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.74 (s, 3H), 6.58 (d, \( J = 16.0 \) Hz, 1H), 6.31 (dd, \( J = 15.6, 8.8 \) Hz, 1H), 4.34 (q, \( J = 7.2 \) Hz, 2H), 4.25 (q, \( J = 6.8 \) Hz, 2H), 3.49-3.39 (m, 1H), 1.34 (t, \( J = 7.2 \) Hz, 3H), 1.26-1.22 (m, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 165.40 (d, \( J = 25.5 \) Hz), 165.28 (d, \( J = 25.3 \) Hz), 138.72, 131.68 (q, \( J = 33.1 \) Hz), 131.40 (d, \( J = 2.8 \) Hz), 130.43, 126.15, 123.23 (q, \( J = 271.1 \) Hz), 121.18-121.14 (m), 96.68 (d, \( J = 204.7 \) Hz), 62.85, 62.67, 42.41 (d, \( J = 20.5 \) Hz), 14.48 (d, \( J = 4.2 \) Hz), 14.03; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \( \delta \) -177.44 (s, 1F), -63.04 (s, 6F); IR (ATR): 1753, 1381, 1278, 1178, 1134, 1043, 970, 682 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\textsubscript{19}H\textsubscript{20}F\textsubscript{7}O\textsubscript{4} [M+H\textsuperscript{+}]: 445.1244, Found: 445.1241.

Product 6l was obtained in 86% yield as colorless oil (3 days). HPLC analysis (Chiralcel AD-H, \textsuperscript{1}PrOH/hexane = 2/98, 1.0 mL/min, 254 nm; \( t_m \) (minor) = 9.67 min, \( t_M \) (major) = 11.08 min) gave the isomeric composition of the product: 97% ee; [\( \alpha \)]\textsubscript{D}\textsuperscript{20} = -121.1 (c = 0.84, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.22 (d, \( J = 7.6 \) Hz, 2H), 7.09 (d, \( J = 7.6 \) Hz, 2H), 6.47 (d, \( J = 16.0 \) Hz, 1H), 6.06 (dd, \( J = 16.0, 9.2 \) Hz, 1H), 4.32 (q, \( J = 7.2 \) Hz, 2H), 4.21 (q, \( J = 6.8 \) Hz, 2H), 3.44-3.30 (m, 1H), 2.32 (s, 3H), 1.33 (t, \( J = 8.8 \) Hz, 3H), 1.23-1.19 (m, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 165.57 (d, \( J = 25.4 \) Hz), 165.52 (d, \( J = 25.7 \) Hz), 137.43,
The reaction was carried out at 70 °C using 10 mol% of chiral Ni catalyst. Product 6m was obtained in 68% yield as colorless oil (4 days). HPLC analysis (Chiralcel OJ-H, 1PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; t_r (minor) = 58.72 min, t_r (major) = 44.60 min) gave the isomeric composition of the product: 96% ee; [α]_D^{20} = -22.49 (c = 0.61, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.22 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 6.41 (d, J = 15.6 Hz, 1H), 5.90 (dd, J = 15.6, 9.2 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 4.24-4.19 (m, 2H), 3.39-3.31 (m, 1H), 2.94 (s, 6H), 1.33 (t, J = 7.2 Hz, 3H), 1.24-1.18 (m, 6H); ^13C NMR (100 MHz, CDCl_3): δ 165.78 (d, J = 25.5 Hz), 165.66 (d, J = 25.8 Hz), 150.14, 132.94, 127.32, 125.21, 122.27 (d, J = 2.5 Hz), 112.31, 97.39 (d, J = 203.5 Hz), 62.54, 62.38, 42.96 (d, J = 20.3 Hz), 40.46, 14.93 (d, J = 4.4 Hz), 14.09, 14.03; ^19F NMR (376 MHz, CDCl_3): δ -178.54 (s, 1F); IR (ATR): 2980, 1749, 1608, 1521, 1446, 1355, 1039 cm^{-1}; HRMS (ESI): Exact mass calcd for C_{18}H_{23}FNaO_4 [M+Na]^+: 345.1473; Found: 345.1475.

The reaction was carried out using 10 mol% of chiral Ni catalyst. Product 6n was obtained in 99% yield as colorless oil (4 days). HPLC analysis (Chiralcel IF, 1PrOH/hexane = 5/95, 0.5 mL/min, 230 nm; t_r (minor) = 13.14 min, t_r(major) = 14.44 min) gave the isomeric composition of the product: 96% ee; [α]_D^{20} = -60.07 (c = 0.84, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.25 (d, J = 6.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.47 (d, J = 16.0 Hz, 1H), 6.07 (q, J = 6.4 Hz, 1H), 5.87-5.80 (m, 1H), 5.05-4.96 (m, 2H), 4.32 (q, J = 7.2 Hz, 2H), 4.25-4.19 (m, 2H), 3.43-3.32 (m, 1H), 2.68 (t, J = 7.2 Hz, 2H), 2.38-2.32 (m, 2H), 1.33 (t, J = 7.6 Hz, 3H), 1.24-1.19 (m, 6H); ^13C NMR (100 MHz, CDCl_3): δ 165.62 (d, J = 25.4 Hz), 165.56 (d, J = 25.7 Hz), 141.50, 137.92, 134.37, 132.92, 128.59, 126.32, 126.01 (d, J = 2.7 Hz), 114.96, 97.12 (d, J = 203.8 Hz), 62.60, 62.43, 42.73 (d, J = 20.3 Hz), 35.34, 35.04, 14.73 (d, J = 4.3 Hz), 14.05, 14.01; ^19F NMR (376 MHz, CDCl_3): δ -178.22 (s, 1F); IR (ATR): 2980, 1749, 1514, 1369, 1232, 1041, 970, 860 cm^{-1}; HRMS (ESI): Exact mass calcd for C_{21}H_{28}FO_4 [M+H]^+: 363.1966; Found: 363.1963.
Product 6o was obtained in 95% yield as colorless oil (50-70 °C, 6 days). HPLC analysis (Chiralcel OX-H, PrOH/hexane = 1/99, 1.0 mL/min, 254 nm; tₘ(major) = 22.39 min, tₘ(minor) = 20.38 min) gave the isomeric composition of the product: 97% ee; [α]ᵢ²⁰ = -77.9 (c = 0.50, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.27 (d, J = 7.2 Hz, 2H), 6.84-6.82 (m, 2H), 6.44 (d, J = 16.0 Hz, 1H), 5.97 (dd, J = 16.0, 9.2 Hz, 1H), 4.32 (q, J = 6.8 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H), 3.80 (s, 3H), 3.43-3.29 (m, 1H), 1.33 (t, J = 6.8 Hz, 3H), 1.24-1.19 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 166.15 (d, J = 25.5 Hz), 165.60 (d, J = 26.0 Hz), 159.27, 132.48, 129.47, 127.53, 124.56 (d, J = 2.7 Hz), 113.92, 97.21 (d, J = 203.9 Hz), 62.60, 62.42, 55.25, 42.79 (d, J = 20.3 Hz), 14.78 (d, J = 4.3 Hz), 14.07, 14.02; ¹⁹F NMR (376 MHz, CDCl₃): δ -178.47 (s, 1F); IR (ATR): 1747, 1512, 1246, 1174, 1032, 968, 856, 820 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₈H₂₃FNaO₅ [M+Na]⁺: 361.1422, Found: 361.1419.

Product 6p was obtained in 72% yield as colorless oil (3 days). HPLC analysis (Chiralcel OJ-H, PrOH/hexane = 2/98, 1.0 mL/min, 254 nm; tₘ(minor) = 54.85 min, tₘ(major) = 39.30 min) gave the isomeric composition of the product: 97% ee; [α]ᵢ²⁰ = -66.2 (c = 0.49, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.23-7.19 (m, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.86 (s, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.48 (d, J = 16.0 Hz, 1H), 6.11 (dd, J = 15.6, 9.2 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 4.23 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 3.46-3.31 (m, 1H), 1.33 (t, J = 7.2 Hz, 3H), 1.25-1.20 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 165.57 (d, J = 25.4 Hz), 165.53 (d, J = 25.7 Hz), 159.78, 138.12, 133.02, 129.48, 127.16 (d, J = 2.7 Hz), 119.06, 113.36, 111.64, 97.01 (d, J = 204.1 Hz), 62.65, 62.48, 55.21, 42.43 (d, J = 20.3 Hz), 14.68 (d, J = 4.3 Hz), 14.06, 14.02; ¹⁹F NMR (376 MHz, CDCl₃): δ -178.24 (s, 1F); IR (ATR): 1747, 1580, 1230, 1157, 1039, 775, 734, 690 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₈H₂₃FNaO₅ [M+Na]⁺: 361.1422, Found: 361.1419.

Product 6q was obtained in 80% yield as colorless oil (3 days). HPLC analysis (Chiralcel OX-H, PrOH/hexane = 2/98, 1.0 mL/min, 254 nm; tₘ(minor) = 13.1 min, tₘ(major) = 12.1 min) gave the isomeric composition of the product: 99% ee; [α]ᵢ²⁰ = -15.3 (c = 0.3, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, J = 7.6 Hz, 1H), 7.23-7.19 (m, 1H), 6.91-6.83 (m, 3H), 6.08 (dd, J = 16.0, 8.8 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.23 (q, J = 11.2 Hz, 2H), 3.82 (s, 3H), 3.46-3.35 (m, 1H), 1.33 (t, J = 6.8 Hz, 3H), 1.26-1.20 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 165.63 (d, J = 25.4 Hz), 165.53 (d, J = 26.0 Hz), 156.54, 128.67, 127.86, 127.17 (d, J = 2.6 Hz), 126.68, 125.74, 120.55, 110.71, 97.19 (d, J = 203.1 Hz), 62.52, 62.40, 55.30, 43.10 (d, J = 20.3 Hz)
Product 6r was obtained in 96% yield as colorless oil (4 days). HPLC analysis (Chiralcel AD-H, \(^1\)PrOH/hexane = 2/98, 1.0 mL/min, 254 nm; \(t_r\) (minor) = 17.24 min, \(t_r\) (major) = 35.06 min) gave the isomeric composition of the product: 97% ee; \([\alpha]_D^{20} = -55.8 (c = 0.50, CHCl_3)\); \(^1\)H NMR (400 MHz, CDCl_3): \(\delta\) 6.48 (s, 2H), 6.43 (d, \(J = 15.6\) Hz, 1H), 6.36 (s, 1H), 6.09 (dd, \(J = 15.6, 9.2\) Hz, 1H), 4.32 (q, \(J = 6.8\) Hz, 2H), 4.22 (q, \(J = 7.2\) Hz, 2H), 3.79 (s, 1H), 3.45-3.30 (m, 1H), 1.33 (t, \(J = 6.8\) Hz, 3H), 1.25-1.20 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl_3): \(\delta\) 165.55 (d, \(J = 25.3\) Hz), 165.51 (d, \(J = 25.8\) Hz), 160.87, 138.67, 133.13, 127.31 (d, \(J = 2.6\) Hz), 104.45, 99.99, 97.05 (d, \(J = 204.0\) Hz), 62.67, 62.51, 55.33, 42.68 (d, \(J = 20.4\) Hz), 14.68 (d, \(J = 4.3\) Hz), 14.08, 14.02; \(^19\)F NMR (376 MHz, CDCl_3): \(\delta\) -178.30 (s, 1F); IR (ATR): 1747, 1591, 1018, 1265, 608, 1153, 968, 734, 702 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C_{19}H_{23}FNaO_6 [M+Na]^+: 391.1527, Found: 391.1534.

The reaction was carried out using 10 mol% of chiral Ni catalyst. Product 6s was obtained in 81% yield as colorless oil (6 days). HPLC analysis (Chiralcel AD-H, \(^1\)PrOH/hexane = 2/98, 1.0 mL/min, 254 nm; \(t_r\) (minor) = 20.39 min, \(t_r\) (major) = 24.24 min) gave the isomeric composition of the product: 95% ee; \([\alpha]_D^{20} = -64.0 (c = 0.52, CHCl_3)\); \(^1\)H NMR (400 MHz, CDCl_3): \(\delta\) 6.87 (s, 1H), 6.76-6.70 (m, 2H), 6.40 (d, \(J = 15.6\) Hz, 1H), 5.96-5.90 (m, 3H), 4.31 (q, \(J = 6.8\) Hz, 2H), 4.21 (q, \(J = 8.0\) Hz, 2H), 3.39-3.28 (m, 1H), 1.31 (t, \(J = 6.8\) Hz, 3H), 1.23-1.17 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl_3): \(\delta\) 165.56 (d, \(J = 25.2\) Hz), 165.52 (d, \(J = 25.7\) Hz), 147.95, 147.24, 132.62, 131.07, 124.92 (d, \(J = 2.6\) Hz), 120.98, 108.16, 105.61, 101.03, 97.11 (d, \(J = 204.1\) Hz), 62.63, 62.45, 42.68 (d, \(J = 20.3\) Hz), 14.71 (d, \(J = 4.4\) Hz), 14.07, 14.00; \(^19\)F NMR (376 MHz, CDCl_3): \(\delta\) -178.58 (s, 1F); IR (ATR): 1745, 1489, 1444, 1247, 1093, 927, 858, 792 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C_{18}H_{21}FNaO_6 [M+Na]^+: 375.1214, Found: 375.1216.

Product 6t was obtained in 81% yield as a white solid (3 days), m.p. = 58-60 °C; HPLC analysis (Chiralcel AD-H, \(^1\)PrOH/hexane = 2/98, 1.0 mL/min, 230 nm; \(t_r\) (minor) = 14.34 min, \(t_r\) (major) = 17.98 min) gave the isomeric composition of the product: 97% ee; \([\alpha]_D^{20} = -66.7 (c = 0.26, CHCl_3)\); \(^1\)H NMR (400 MHz, CDCl_3): \(\delta\)
7.80-7.76 (m, 3H), 7.69 (s, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.48-7.41 (m, 2H), 6.67 (d, J = 16.0 Hz, 1H), 6.26 (dd, J = 15.6, 6.8 Hz, 1H), 4.34 (q, J = 6.8 Hz, 2H), 4.28 (q, J = 6.8 Hz, 2H), 3.53-3.38 (m, 1H), 1.34 (t, J = 7.2 Hz, 3H), 1.26-1.20 (m, 6H); 13C NMR (100 MHz, CDCl3): δ 165.56 (d, J = 25.4 Hz, 2C), 134.09, 133.48, 133.17, 132.99, 128.14, 127.90, 127.60, 127.21 (d, J = 2.6 Hz), 126.23 (d, J = 1.4 Hz), 125.86, 123.48, 97.09 (d, J = 204.1 Hz), 62.63, 62.46, 42.85 (d, J = 20.4 Hz), 14.71 (d, J = 4.4 Hz), 14.03, 13.99; 19F NMR (376 MHz, CDCl3): δ -178.20 (s, 1F). IR (ATR): 1747, 1367, 1265, 1230, 1095, 966, 813, 734 cm⁻¹; HRMS (ESI): Exact mass calcd for C21H23FNaO4 [M+Na⁺]: 381.1473, Found: 381.1474.

Product 6u was obtained in 98% yield as colorless oil (3 days). HPLC analysis (Chiralcel AD-H, 4PrOH/hexane = 2/98, 1.0 mL/min, 230 nm; tₘ(minor) = 11.51 min, tₘ(major) = 13.05 min) gave the isomeric composition of the product: 93% ee; [α]D²⁰ = -26.3 (c = 0.71, CHCl₃); 1H NMR (400 MHz, CDCl3): δ 8.06 (d, J = 8.0 Hz, 1H), 7.85-7.83 (m, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.55-7.41 (m, 4H), 7.28 (d, J = 16.4 Hz, 1H), 6.16 (dd, J = 15.6, 9.2 Hz, 1H), 4.35 (q, J = 10.8 Hz, 2H), 4.27-4.21 (m, 2H), 3.61-3.48 (m, 1H), 1.36 (t, J = 7.2 Hz, 3H), 1.29 (d, J = 6.8 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 165.69 (d, J = 25.7 Hz), 165.62 (d, J = 25.5 Hz), 134.46, 133.53, 131.06, 130.54, 130.23 (d, J = 2.6 Hz), 128.51, 128.03, 126.02, 125.74, 125.59, 124.04, 123.65, 97.19 (d, J = 204.2 Hz), 62.70, 62.57, 43.01 (d, J = 20.3 Hz), 14.72 (d, J = 4.3 Hz), 14.05 (s, 2C); 19F NMR (376 MHz, CDCl3): δ -178.35 (s, 1F); IR (ATR): 1745, 1456, 1367, 1228, 1099, 968, 858, 771 cm⁻¹; HRMS (ESI): Exact mass calcd for C21H23FNaO4 [M+Na⁺]: 381.1473, Found: 381.1479.

The reaction was carried out using 10 mol% of chiral Ni catalyst. Product 6v was obtained in 93% yield as colorless oil (5 days). HPLC analysis (Chiralcel AD-H, 4PrOH/hexane = 2/98, 1.0 mL/min, 254 nm; tₘ(minor) = 11.37 min, tₘ(major) = 13.60 min) gave the isomeric composition of the product: 94% ee; [α]D²⁰ = -73.06 (c = 0.99, CHCl₃); 1H NMR (400 MHz, CDCl3): δ 7.32 (s, 1H), 6.34-6.29 (m, 2H), 6.20 (s, 1H), 6.06 (dd, J = 16.0, 9.2 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.24 (q, J = 6.8 Hz, 2H), 3.40-3.29 (m, 1H), 1.32 (t, J = 6.8 Hz, 3H), 1.26-1.18 (m, 6H); 13C NMR (100 MHz, CDCl3): δ 165.54 (d, J = 25.5 Hz), 165.49 (d, J = 25.6 Hz), 152.13, 141.98, 125.43 (d, J = 2.8 Hz), 121.38, 111.14, 107.87, 96.90 (d, J = 204.4 Hz), 62.64, 62.49, 42.29 (d, J = 20.4 Hz), 14.51 (d, J = 4.4 Hz), 13.99, 13.96; 19F NMR (376 MHz, CDCl3): δ -178.14 (s, 1F); IR (ATR): 1747, 1232, 1095, 1037, 962, 929, 738, 596 cm⁻¹; HRMS (ESI): Exact mass calcd for C9H12F
The reaction was carried out using 10 mol% of chiral Ni catalyst. Product 6w was obtained in 98% yield as yellowish liquid (4 days); HPLC analysis (Chiralcel AD-H, \textsuperscript{1}PrOH/hexane = 2/98, 1.0 mL/min, 230 nm; t\textsubscript{r} (minor) = 13.51 min, t\textsubscript{r} (major) = 16.71 min) gave the isomeric composition of the product: 97% ee; [\alpha]_D^{20} = -5.23 (c = 0.15, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 7.14 (d, J = 5.2 Hz, 1H), 6.95-6.92 (m, 2H), 6.62 (d, J = 15.6 Hz, 1H), 5.95 (dd, J = 16.0, 9.2 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.24 (q, J = 7.2 Hz, 2H), 3.42–3.27 (m, 1H), 1.32 (t, J = 7.2 Hz, 3H), 1.26–1.19 (m, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 165.53 (d, J = 25.3 Hz, 2C), 141.67, 127.25, 126.38 (d, J = 2.6 Hz), 126.22, 125.69, 124.38, 96.95 (d, J = 204.4 Hz), 62.68, 62.53, 42.56 (d, J = 20.6 Hz), 14.58 (d, J = 4.4 Hz), 14.05, 14.02; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \delta -178.11 (s, 1F); IR (ATR): 1749, 1463, 1269, 1165, 1095, 958, 856, 698 cm\textsuperscript{-1}; HRMS (ESI): Exact mass calcd for C\textsubscript{15}H\textsubscript{10}FNaO\textsubscript{4}S [M+Na]\textsuperscript{+}: 337.0880, Found: 337.0877.

The reaction was carried out by using 10 mol% of chiral Ni catalyst. Product 6x was obtained in 98% yield as colorless oil (5 days). HPLC analysis (Chiralcel AD-H, \textsuperscript{1}PrOH/hexane = 1/99, 1.0 mL/min, 254 nm; t\textsubscript{r} (minor) = 30.74 min, t\textsubscript{r} (major) = 36.71 min) gave the isomeric composition of the product: 91% ee; [\alpha]_D^{20} = -57.1 (c = 0.50, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 7.38-7.29 (m, 4H), 7.24-7.20 (m, 1H), 6.71 (dd, J = 16.0, 10.8 Hz, 1H), 6.50 (d, J = 3.9 Hz, 1H), 6.31 (dd, J = 15.2, 10.9 Hz, 1H), 5.71 (dd, J = 15.2, 9.2 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.29-4.23 (m, 2H), 3.38-3.27 (m, 1H), 1.33 (t, J = 7.2 Hz, 3H), 1.27 (t, J = 7.2 Hz, 3H), 1.17 (d, J = 6.8 Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 165.56 (d, J = 25.5 Hz), 165.53 (d, J = 25.7 Hz), 137.05, 133.54, 132.54, 130.83 (d, J = 2.8 Hz), 128.59, 128.27, 127.59, 126.32, 96.99 (d, J = 203.9 Hz), 62.65, 62.51, 42.43 (d, J = 20.5 Hz), 14.58 (d, J = 4.3 Hz), 14.11, 14.03; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \delta -178.43 (s, 1F); IR (ATR): 1747, 1265, 1236, 1161, 989, 858, 734, 692 cm\textsuperscript{-1}; HRMS (ESI): Exact mass calcd for C\textsubscript{19}H\textsubscript{23}FNaO\textsubscript{4}S [M+Na]\textsuperscript{+}: 357.1473, Found: 357.1475.

The reaction was carried out at 60 °C using 10 mol% of chiral Ni catalyst. Product 6y was obtained in 94% yield as colorless oil (6 days). The \textsuperscript{19}F NMR analysis of the crude mixture revealed that the regioselective ratio was 7:1. HPLC analysis (Chiralcel AD-H, \textsuperscript{1}PrOH/hexane = 1/99, 1.0 mL/min, 210 nm; t\textsubscript{r} (minor) = 12.90 min, t\textsubscript{r} (major) = 13.93 min) gave the isomeric composition of the product: 97% ee; [\alpha]_D^{20} = -34.9 (c = 0.90, CHCl\textsubscript{3}); \textsuperscript{1}H NMR
(400 MHz, CDCl3): δ 7.29-7.26 (m, 2H), 7.19-7.14 (m, 3H), 5.67-5.59 (m, 1H), 5.41 (dd, J = 15.6 Hz, 8.8 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 4.21 (q, J = 7.2 Hz, 2H), 3.24-3.10 (m, 1H), 2.64 (t, J = 8.0 Hz, 2H), 2.33-2.27 (m, 2H), 1.33-1.25 (m, 6H), 1.08 (d, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl3): 165.66 (d, J = 25.4 Hz), 165.58 (d, J = 26.0 Hz), 141.53, 133.36, 128.32, 128.24, 127.75 (d, J = 2.6 Hz), 125.78, 97.17 (d, J = 203.2 Hz), 62.47, 62.27, 42.18 (d, J = 20.4 Hz), 35.61, 34.12, 14.64 (d, J = 4.3 Hz), 14.02, 13.97; 19F NMR (376 MHz, CDCl3): δ -178.92 (s, 1F); IR (ATR): 1747, 1454, 1234, 1163, 1028, 970, 798, 698 cm⁻¹; HRMS (ESI): Exact mass calcd for C19H25FNaO4 [M+Na]⁺: 359.1629, Found: 359.1625.

The reaction was carried out at 80 °C using 10 mol% of chiral Ni catalyst. Product 6z was obtained in 96% yield as colorless oil (5 days). The 19F NMR analysis of the crude mixture revealed that the regioselective ratio was 7:1. The isomeric composition of 6s was determined to be 95% ee by HPLC analysis of its derivative 6s'. [α]D²⁰ = -32.7 (c = 0.95, CHCl₃); ¹H NMR (400 MHz, CDCl3): 5.61-5.54 (m, 1 H), 5.34 (dd, J = 15.2, 8.8 Hz, 1H), 4.32-4.21 (m, 4 H), 3.24-3.09 (m, 1H), 1.98-1.93 (m, 2H), 1.33-1.24 (m, 12H), 1.08 (d, J = 6.8 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 165.77 (d, J = 25.5 Hz), 165.67 (d, J = 25.9 Hz), 134.55, 126.93 (d, J = 2.6 Hz), 97.4 (d, J = 203.2 Hz), 62.49, 62.28, 42.35 (d, J = 20.2 Hz), 32.39, 31.25, 28.87, 22.46, 14.77 (d, J = 4.3 Hz), 14.05, 14.01, 14.00; 19F NMR (376 MHz, CDCl3): δ -179.19 (s, 1F); IR (ATR): 1751, 1267, 1240, 1168, 1041, 974, 738, 704 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₆H₂₇FNaO₄ [M+Na]⁺: 325.1786, Found: 325.1778.

The reaction was carried out at 75 °C using 10 mol% of chiral Ni catalyst. Product 6aa was obtained in 97% yield as colorless oil (5 days). The 19F NMR analysis of the crude mixture revealed that the regioselective ratio was 10:1. The isomeric composition of 6t was determined to be 90% ee by HPLC analysis of its derivative 6t'; [α]D²⁰ = -25.5 (c = 0.49, CHCl₃); ¹H NMR (400 MHz, CDCl3): δ 5.51 (dd, J = 14.4, 6.8 Hz, 1H), 5.29 (dd, J = 15.6, 9.2 Hz, 1H), 4.29 (q, J = 7.2 Hz , 2H), 4.22 (q, J = 7.2 Hz , 2H), 3.20-3.05 (m, 1H), 1.90-1.87 (m, 1H), 1.70-1.61 (m, 5H), 1.33-1.25 (m, 9H), 1.10-1.02 (m, 5H); 13C NMR (100 MHz, CDCl3): δ 165.77 (d, J = 25.5 Hz), 165.63 (d, J = 26.3 Hz), 140.27, 124.60 (d, J = 2.7 Hz), 97.45 (d, J = 202.7 Hz), 62.48, 62.27, 42.45 (d, J = 20.2 Hz), 40.56, 32.85, 32.77, 26.06, 25.90, 25.88, 14.79 (d, J = 4.2 Hz), 14.07, 14.01; 19F NMR (376 MHz, CDCl3): δ -179.36 (s, 1F); IR (ATR): 2924, 2380, 2349, 1747, 1448, 1230, 1031, 970 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₁₇H₂₁₇FNaO₄ [M+Na]⁺: 337.1786, Found:
The reaction was carried out at 70 °C using 10 mol% of chiral Ni catalyst. Product 6ab was obtained in 79% yield as colorless oil (4 days). The $^{19}$F NMR analysis of the crude mixture revealed that the regioselective ratio was 22:1. HPLC analysis (Chiralcel IF, $^1$PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; $t_r$ (minor) = 7.87 min, $t_r$ (major) = 8.15 min) gave the isomeric composition of the product: 99% ee ($\lbrack \alpha \rbrack_{D}^{20}$ = -12.47 ($c$ = 0.51, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.61-5.54 (m, 1H), 5.38 (dd, $J$ = 15.6, 6.8 Hz, 1H), 4.31-4.20 (m, 4H), 3.22-3.08 (m, 1H), 2.46 (t, $J$ = 7.2 Hz, 2H), 2.24 (q, $J$ = 7.6 Hz, 2H), 2.12 (s, 3H), 1.32-1.26 (m, 6H), 1.07 (d, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 207.82, 165.61 (d, $J$ = 26.1 Hz), 165.55 (d, $J$ = 25.4 Hz), 132.40, 128.14 (d, $J$ = 2.7 Hz), 97.10 (d, $J$ = 203.0 Hz), 62.53, 62.33, 42.94, 42.06 (d, $J$ = 20.4 Hz), 29.87, 26.46, 14.59 (d, $J$ = 4.3 Hz), 14.05, 13.99; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -178.71 (s, 1F); IR (ATR): 2981, 1747, 1714, 1446, 1367, 1161, 1039, 858 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{15}$H$_{24}$FO$_5$ [M+H]$^+$: 303.1602, Found: 303.1600.

The reaction was carried out at 80 °C using 10 mol% of chiral Ni catalyst. Product 6ac was obtained in 96% yield as colorless oil (3 days). $^{19}$F NMR analysis of the crude reaction mixture revealed that dr value was 11:1; $[\alpha]_{D}^{20}$ = -13.6 ($c$ = 0.51, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): 5.60-5.53 (m, 1H), 5.34 (dd, $J$ = 15.2, 8.8 Hz, 1H ), 5.09-5.06 (m, 1H), 4.29 (q, $J$ = 7.2 Hz , 2H), 4.23 (q, $J$ = 7.2 Hz , 2H), 3.24-3.13 (m, 1H), 2.02-1.90 (m, 3H), 1.85-1.78 (m, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.46-1.42 (m, 1H), 1.33-1.26 (m, 8H), 1.8 (d, $J$ = 6.8 Hz, 3H), 0.83 (d, $J$ = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.77 (d, $J$ = 25.4 Hz), 165.68 (d, $J$ = 25.9 Hz), 132.94, 131.12, 128.23 (d, $J$ = 2.7 Hz), 124.72, 97.27 (d, $J$ = 203.4 Hz), 62.25, 62.30, 42.45 (d, $J$ = 1.0 Hz), 39.75, 36.57, 32.53, 25.68. 25.55, 19.18, 17.59, 14.85 (d, $J$ = 4.3 Hz), 14.03, 14.01; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -179.07 (s, 1F); IR (ATR): 1749, 1456, 1367, 1267, 1230, 1041, 972, 860 cm$^{-1}$; HRMS (ESI): Exact mass calcd for C$_{20}$H$_{33}$FNaO$_4$ [M+Na]$^+$: 379.2255, Found: 379.2249.

The reaction was carried out at 80 °C using 10 mol% of chiral Ni catalyst. Product 6ad was obtained in 82% yield as colorless oil (4 days). $^{19}$F NMR analysis of the crude reaction mixture revealed that dr value was 9:1; $[\alpha]_{D}^{20}$ = +67.0 ($c$ = 0.50, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.22 (d, $J$ = 8.0
7.12-7.08 (m, 2H), 6.45 (d, J = 16.0 Hz, 1H), 6.07 (dd, J = 15.6, 9.2 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.26-4.18 (m, 2H), 3.43-3.32 (m, 1H), 2.91-2.88 (m, 2H), 2.54-2.47 (m, 1H), 2.42-2.39 (m, 1H), 2.30-2.25 (m, 1H), 2.19-1.94 (m, 5H), 1.63-1.47 (m, 5H), 1.33 (t, J = 7.2 Hz, 3H), 1.25-1.18 (m, 6H), 0.91 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 220.80, 165.60 (d, \(J = 25.4\) Hz), 165.52 (d, \(J = 25.8\) Hz), 139.43, 136.59, 134.29, 132.78, 126.82, 126.20 (d, \(J = 2.7\) Hz), 125.50, 123.93, 97.10 (d, \(J = 203.7\) Hz), 62.63, 62.44, 50.46, 47.94, 44.40, 42.73 (d, \(J = 20.2\) Hz), 38.11, 35.82, 31.55, 29.31, 26.44, 25.68, 21.55, 14.77 (d, \(J = 4.3\) Hz), 14.10, 14.03, 13.81; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -178.53 (s, 1F); IR (ATR): 1737, 1454, 1267, 1234, 1039, 819, 734, 665 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{29}\)H\(_{37}\)FNaO\(_5\) \([\text{M+Na}]^+\): 507.2517, Found: 507.2524.

**General procedure for synthesizing the derivatives 6z’ and 6aa’ of product 6z and 6aa**

To a stirred solution of product 6z or 6aa (0.1 mmol) in a mixed solvent of anhydrous THF/MeOH (1.0 mL, 1:1, v/v) was added NaBH\(_4\) slowly at 0 °C, the resulting mixture was then stirred at rt for overnight. The reaction mixture was quenched with H\(_2\)O (5 mL) and extracted with CH\(_2\)Cl\(_2\) (10 mL \(\times\) 2). The combined organic layers were dried over Na\(_2\)SO\(_4\), the reaction mixture was concentrated under reduced pressure to give the residue, which was filtered over a short pad of silica gel eluting with PE/EtOAc (1/1, v/v) to afford the crude diols, which was used directly for next step.

To a solution of the above diol in CH\(_2\)Cl\(_2\) was added DMAP (0.4 equiv), Et\(_3\)N (3.0 equivs) and benzoyl chloride (2.4 equivs) at 0 °C. The reaction mixture was warmed to rt and stirred overnight. After quenching with H\(_2\)O (5 mL), the resulting mixture was extracted with CH\(_2\)Cl\(_2\) (10 mL \(\times\) 2). The combined organic layers were dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The obtained residue was purified by silica gel column chromatography using PE/EtOAc (20/1, v/v) as the elute to deliver the product 6z’ or 6aa’ as colorless oil.

Product 6z’ was obtained in 46% yield from 6z via the sequential NaBH\(_4\) reduction and benzoyl protection. HPLC analysis (Chiralpak IF, \(^{3}\)PrOH/hexane = 1/99, 0.5 mL/min, 230 nm; \(t_r\) (minor) = 22.54 min, \(t_r\) (major) = 24.25 min) gave the isomeric composition of the product: 95% ee; \([\alpha]\)\(_D^{20}\) = -108.3 (c = 0.48, CHCl\(_3\)); \(^{1}\)H NMR (400 Hz, 1H), 7.12-7.08 (m, 2H), 6.45 (d, J = 16.0 Hz, 1H), 6.07 (dd, J = 15.6, 9.2 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.26-4.18 (m, 2H), 3.43-3.32 (m, 1H), 2.91-2.88 (m, 2H), 2.54-2.47 (m, 1H), 2.42-2.39 (m, 1H), 2.30-2.25 (m, 1H), 2.19-1.94 (m, 5H), 1.63-1.47 (m, 5H), 1.33 (t, J = 7.2 Hz, 3H), 1.25-1.18 (m, 6H), 0.91 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 220.80, 165.60 (d, \(J = 25.4\) Hz), 165.52 (d, \(J = 25.8\) Hz), 139.43, 136.59, 134.29, 132.78, 126.82, 126.20 (d, \(J = 2.7\) Hz), 125.50, 123.93, 97.10 (d, \(J = 203.7\) Hz), 62.63, 62.44, 50.46, 47.94, 44.40, 42.73 (d, \(J = 20.2\) Hz), 38.11, 35.82, 31.55, 29.31, 26.44, 25.68, 21.55, 14.77 (d, \(J = 4.3\) Hz), 14.10, 14.03, 13.81; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -178.53 (s, 1F); IR (ATR): 1737, 1454, 1267, 1234, 1039, 819, 734, 665 cm\(^{-1}\); HRMS (ESI): Exact mass calcd for C\(_{29}\)H\(_{37}\)FNaO\(_5\) \([\text{M+Na}]^+\): 507.2517, Found: 507.2524.
MHz, CDCl₃): δ 8.04 (d, J = 8.4 Hz, 4H), 7.59-7.56 (m, 2H), 7.46-7.42 (m, 4H), 5.62-5.55 (m, 1H), 5.45 (dd, J = 15.6, 8.4 Hz, 1H), 4.68-4.51 (m, 4H), 2.92-2.80 (m, 1H), 2.02-1.97 (m, 2H), 1.32-1.21 (m, 9H), 0.86 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.92 (s, 2C), 134.00, 133.27, 129.69, 129.53 (d, J = 3.5 Hz), 128.47, 128.24 (d, J = 6.1 Hz), 96.01 (d, J = 179.8 Hz), 63.94 (d, J = 27.5 Hz), 63.78 (d, J = 27.9 Hz), 40.40 (d, J = 21.1 Hz), 32.51, 31.35, 28.86, 22.45, 14.48 (d, J = 4.7 Hz), 14.01; ¹⁹F NMR (376 MHz, CDCl₃): δ -172.54 (s, 1F); IR (ATR): 1724, 1452, 1265, 1176, 1070, 1028, 978, 707 cm⁻¹; HRMS (ESI): Exact mass calcd for C₂₆H₃₁FNaO₄ [M+Na]+: 449.2099, Found: 449.2108.

Product 6aa’ was obtained in 42% yield from 6aa via the sequential NaBH₄ reduction and benzoyl protection. HPLC analysis (Chiralcel OZ-H, ⁴PrOH/hexane = 1/99, 1.0 mL/min, 230 nm; tᵣ (minor) = 12.49 min, tᵣ (major) = 14.37 min) gave the isomeric composition of the product: 90% ee; [α]D²⁰ = -25.3 (c = 0.35, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.05-8.03 (m, 4H), 7.59-7.55 (m, 2H), 7.46-7.42 (m, 4H), 5.52 (dd, J = 15.6, 10.2 Hz, 1H), 5.40 (dd, J = 15.6, 8.4 Hz, 1H), 4.67-4.51 (m, 4H), 2.88-2.79 (m, 1H), 1.95-1.87 (m, 1H), 1.69-1.60 (m, 5H), 1.34-1.05 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ 165.91 (s, 2C), 139.73, 133.26 (d, J = 1.3 Hz), 129.70, 129.54 (d, J = 4.6 Hz), 128.46, 125.82 (d, J = 6.1 Hz), 96.03 (d, J = 179.8 Hz), 63.97 (d, J = 27.4 Hz), 63.71 (d, J = 28.2 Hz), 63.57, 40.64, 40.44 (d, J = 21.0 Hz), 32.84, 32.79, 26.06, 25.94, 14.47 (d, J = 4.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ -172.54 (s, 1F); IR (ATR): 1722, 1450, 1176, 1070, 1026, 974, 767, 686 cm⁻¹; HRMS (ESI): Exact mass calcd for C₂₇H₃₁FNaO₄ [M+Na]+: 461.2097, Found: 461.2097.

6. Synthetic utility

6.1 Gram-scale synthesis of monofluoroalkylated product 6a

To an oven-dried Schlenk tube equipped with a stirring bar were successively added Ni(COD)₂ (69.0 mg, 0.25 mmol, 5 mol%), (S,S)-QuinoxP* L₈ (91.9 mg, 0.275 mmol, 5.5 mol%), 1-phenyl-1,3-butadiene 1 (976.6 mg, 7.5 mmol), and diethyl fluoromalonate 5 (890.8 mg, 5.0 mmol), followed by the addition of absolute EtOH (30 mL) in a glove box. After it take out from the glove box, the resulting
mixture was stirred at room temperature for 5 min, and then stirred at 50 °C until full conversion. The reaction was monitored by TLC and GC-MS analysis. After full consumption of 5, the reaction mixture was concentrated under vacuum to remove the solvent EtOH. The crude residue was purified by silica gel column chromatography (PE/EA = 10:1, v/v) to afford product 6a as a colorless oil (1.47 g, 95% yield). HPLC analysis (Chiralcel AD-H, iPrOH/hexane = 2/98, 1.0 mL/min, 230 nm; t_r(minor) = 11.1 min, t_r(major) = 13.1 min) gave the isomeric composition of the product: 97% ee.

6.2 Transformations of product 6a

To a solution of 6a (308.5 mg, 1.0 mmol, 1.0 equiv) in a mixed solvent of phosphate buffer (20 mL, pH = 8) and DMSO (6 mL) was added pig liver esterase (PLE) (20 mg, 200 units), the reaction mixture was then stirred at 22 °C. After full conversion of 6a by TLC analysis, HCl (2 N) was added to make the pH of the solution to 3. The aqueous layers were extracted with CH_2Cl_2 (20 mL × 3). The combined organic phases were washed with brine (20 mL), dried over Na_2SO_4 and concentrated under the reduced pressure to afford the crude product. The ^1H and ^19F NMR analysis revealed that the dr value was 12:1. The crude residue was purified by flash column chromatography using CH_2Cl_2/MeOH (10:1 to 5:1, v/v) as the eluent to afford the desired product 7 (263.5 mg, 94% yield); [α]_D^20 = -60.9 (c = 0.51, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.21 (m, 5H), 6.52 (d, J = 16.0 Hz, 1H), 6.12 (dd, J = 16.0, 9.2 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.42-3.31 (m, 1H), 1.29 (t, J = 7.2 Hz, 3H), 1.19 (d, J = 6.8 Hz, 3H); ^13C NMR (100 MHz, CDCl_3): δ 168.67 (d, J = 28.7 Hz), 165.84 (d, J = 26.0 Hz), 136.62, 133.35, 128.50, 127.70, 126.44, 97.05 (d, J = 203.5 Hz), 63.03, 42.73 (d, J = 20.6 Hz), 14.63 (d, J = 3.9 Hz), 13.94; ^19F NMR (376 MHz, CDCl_3): δ -176.84 (s, 1F); IR (ATR): 1749, 1296, 1267, 1043, 1014, 750, 694 cm⁻¹; HRMS (ESI): Exact mass calcd for C_{15}H_{17}FNaO_4 [M+Na]^+: 303.1003, Found: 303.0989.

Compound 6a (61.6 mg, 0.2 mmol, 1.0 equiv) was dissolved in a mixed solvent of MeOH (0.2 mL)
and CH\textsubscript{2}Cl\textsubscript{2} (1.2 mL), followed by the addition of NaOH (17.6 mg, 0.44 mmol, 2.2 equivs). The reaction mixture was stirred at rt until full conversion of 3a (ca. 1 h). Then water and HCl (2 N) were added, the resulting mixture was extracted with EtOAc (10 mL × 3). The combined organic phases were successively washed with brine and water (10 mL, each), and then dried over Na\textsubscript{2}SO\textsubscript{4}, filtrated, and concentrated under vacuum to afford the analytically pure product 8 (49.9 mg, 99% yield) as white solid; m.p. = 151-154 °C; [α]\textsubscript{D}\textsuperscript{20} = -3.6 (c = 0.52, CHCl\textsubscript{3}). \textsuperscript{1}H NMR (400 MHz, MeOD-d\textsubscript{4}): δ 7.35 (d, J = 7.6 Hz, 2H), 7.28 (t, J = 7.2 Hz, 2H), 7.22-7.18 (m, 1H), 6.56 (d, J = 16.0 Hz, 1H), 6.15 (dd, J = 15.6, 8.8 Hz, 1H), 3.45-3.34 (m, 1H), 1.21 (d, J = 6.8 Hz, 3H); \textsuperscript{13}C NMR (100 MHz, MeOD-d\textsubscript{4}): δ 167.81 (d, J = 26.3 Hz), 167.65 (d, J = 25.8 Hz), 136.97, 132.73, 128.17, 127.24, 126.88 (d, J = 2.5 Hz), 125.97, 97.13 (d, J = 199.2 Hz), 42.13 (d, J = 20.4 Hz), 13.69 (d, J = 4.2 Hz); \textsuperscript{19}F NMR (376 MHz, MeOD-d\textsubscript{4}): δ -178.78 (s, 1F); IR (ATR): 1732, 1448, 1159, 1132, 1014, 970, 746, 694 cm\textsuperscript{-1}; HRMS (ESI): Exact mass calcd for C\textsubscript{13}H\textsubscript{13}FNaO\textsubscript{4} [M+Na]+: 275.0690, Found: 275.0686.

To a stirred solution of 6a (61.6 mg, 0.2 mmol, 1.0 equiv) in CH\textsubscript{2}Cl\textsubscript{2} (2 mL) was added \textit{m}-CPBA (69.0 mg, 0.4 mmol, 2.0 equivs) at 0 °C. After being stirred at rt for 24 h, the reaction mixture was quenched with saturated NH\textsubscript{4}Cl (aq., 5 mL) and extracted with CH\textsubscript{2}Cl\textsubscript{2} (10 mL × 2). The combined organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated under reduced pressure to give the residue, which was purified by flash column chromatography (PE/EtOAc, 9/1, v/v) to afford the fluorinated epoxide 9 in 73% yield as white solid (47.3 mg); m.p. = 130-133 °C; \textsuperscript{1}H NMR analysis of the crude residue revealed that the dr value was 1.4:1; HPLC analysis (Chiralcel AD-H, \textit{Pr}OH/hexane = 2/98, 1.0 mL/min, 230 nm; major diastereomer: t\textsubscript{R} (major) = 18.74 min, t\textsubscript{R} (minor) = 16.23 min) gave the isomeric composition of the major diastereomer: 96% ee; [α]\textsubscript{D}\textsuperscript{20} = -16.7 (c = 0.52, CHCl\textsubscript{3}); \textsuperscript{1}H NMR analysis for the mixture diastereomers (400 MHz, CDCl\textsubscript{3}): δ 7.35-7.21 (m, 5H), 4.37-4.19 (m, 4H), 3.79-3.66 (m, 1H), 3.11-3.00 (m, 1H), 2.66-2.50 (m, 1H), 1.35-1.25 (m, 6H), 1.18-1.14 (m, 3H); \textsuperscript{13}C NMR for mixture diastereomers (100 MHz, CDCl\textsubscript{3}): δ 165.51 (d, J = 14.6 Hz), 165.48 (d, J = 19.3 Hz), 165.24, 164.98, 136.67, 136.58, 128.47, 128.36, 128.34, 125.61, 125.53, 95.65 (d, J = 204.6 Hz), 95.47 (d, J = 203.1 Hz), 62.93, 62.92, 62.85, 62.80, 61.81 (d, J = 3.6 Hz), 61.17 (d, J = 3.2 Hz), 59.51, 57.58, 41.94 (d, J = 20.6 Hz), 41.38 (d, J = 19.7 Hz), 13.98 (d, J = 2.0 Hz), 13.73, 11.33 (d, J = 4.1 Hz), 10.88 (d, J = 3.6 Hz); \textsuperscript{19}F NMR for mixture diastereomers (376 MHz, CDCl\textsubscript{3}): δ -176.59 (s), -178.46 (s); IR
To a stirred solution of 6a (61.6 mg, 0.2 mmol, 1.0 equiv) in THF (2 mL) was added dropwise LiAl(OTBu)3 (1.0 M in THF, 900 μL) at -78 °C. The resulting mixture was then warmed to rt and stirred at rt for 2 days. After quenching with 10% KHSO4 (aq., 5 mL), the solution was extracted with CH2Cl2 (10 mL × 2). The combined organic layers were dried over Na2SO4, and concentrated under the reduced pressure. The residue was purified by flash column chromatography (PE/EtOAc, 1/1, v/v) to afford α-allylated α-fluoro-β-hydroxyl ester 10 in 67% yield as a light yellow liquid (34.5 mg); 19F NMR analysis of the crude mixture revealed that the dr value was 1.4:1; HPLC analysis (Chiralcel AD-H, iPrOH/hexane = 1/99, 1.0 mL/min, 254 nm; major diastereomer: tR(major) = 57.76 min, tR(minor) = 16.37 min; minor diastereomer: tR(major) = 35.26 min, tR(minor) = 42.96 min) gave the isomeric composition of major diastereomer: 96% ee, gave the isomeric composition of minor diastereomer: 95% ee; [α]D20 = -31.5 (c = 0.60, CHCl3); 1H NMR for the mixture diastereomers (400 MHz, CDCl3): δ 7.35-7.23 (m, 5H), 6.49-6.41 (m, 1H), 6.19-6.09 (m, 1H), 4.35-4.23 (m, 2H), 3.99-3.87 (m, 2H), 2.95-2.82 (m, 1H), 2.14 (br, 1H), 1.34 (t, J = 7.2 Hz, 1H), 1.26 (t, J = 7.2 Hz, 2H), 1.20-1.15 (m, 3H); 13C NMR for the mixture diastereomers (100 MHz, CDCl3): δ 169.88 (d, J = 25.8 Hz), 169.83 (d, J = 25.6 Hz), 136.75, 136.62, 132.47, 132.08, 128.58, 128.52, 128.28 (d, J = 5.1 Hz), 127.67, 127.63, 127.59, 126.30, 126.28, 99.79 (d, J = 190.9 Hz), 99.68 (d, J = 191.1 Hz), 66.07 (d, J = 23.3 Hz), 65.19 (d, J = 23.5 Hz), 61.89, 61.74, 41.70, 41.48, 41.27, 15.29 (d, J = 4.5Hz), 14.48 (d, J = 3.4 Hz), 14.23; 19F NMR for the mixture diastereomers (376 MHz, CDCl3): δ -183.59 (s), -179.11 (s); IR (ATR): 1747, 1367, 1238, 1095, 1037, 958, 856, 696 cm⁻¹; HRMS (ESI): Exact mass calcd for C15H19FNaO3 [M+Na]+: 289.1210, Found: 289.1219.

To a stirred solution of 6a (308.5 mg, 1.0 mmol, 1.0 equiv) in a mixed solvent of THF (5 mL) and
MeOH (5 mL) was slowly added NaBH₄ at 0 °C. The resulting suspension was stirred at rt for overnight. After quenching with H₂O (20 mL), the solution was extracted with CH₂Cl₂ (20 mL × 3). The combined organic layers were successively washed with saturated NH₄Cl (aq., 10 mL) and brine (10 mL), and then dried over Na₂SO₄ and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography using PE/EtOAc (1/1, v/v) as the eluent to afford fluorinated diol 11 (186.6 mg, 83% yield) as a white solid, m.p. = 97-100 °C; HPLC analysis (Chiralcel OJ-H, 1PrOH/hexane = 25/70, 1.0 mL/min, 254 nm; tᵣ (major) = 7.03 min, tᵣ (minor) = 7.76 min) gave the isomeric composition of the product: 97% ee; [α]D²⁰ = -13.6 (c = 0.42, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.31 (m, 4H), 7.23-7.21 (m, 1H), 6.47 (d, J = 16.0 Hz, 1H), 6.19 (dd, J = 16.0, 8.8 Hz, 1H), 3.96-3.80 (m, 4H), 2.90-2.82 (m, 1H), 1.94 (s, br, 2H), 1.20 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 136.92, 131.63, 129.33 (d, J = 5.9 Hz), 128.57, 127.50, 126.21, 98.64 (d, J = 175.5 Hz), 63.65 (d, J = 25.4 Hz, 2C), 40.05 (d, J = 20.9 Hz), 14.33 (d, J = 5.2 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ -177.69 (s, 1F); IR (ATR): 3334, 1448, 1265, 1055, 1024, 916, 748, 692 cm⁻¹; HRMS (ESI): Exact mass calcd forC₁₃H₁₇FNaO₂ [M+Na]⁺: 247.1105, Found: 247.1107.

To a stirred solution of 11 (22.4 mg, 0.1 mmol, 1.0 equiv) and 1-(dimethoxymethyl)-4-methoxybezene (27.3 mg, 0.15 mmol, 1.5 equivs) in CHCl₃ (1 mL) was added ZnCl₂ (21.8 mg, 0.16 mmol, 1.6 equivs). The reaction mixture was allowed to stir at room temperature until full conversion of 11. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (PE/EtOAc = 5:1, v/v) to afford 12 (19.8 mg, 58% yield) as a white solid, m.p. = 121-124 °C; HPLC analysis (Chiralcel OX-H, 1PrOH/hexane = 10/90, 1.0 mL/min, 254 nm; tᵣ (major) = 29.19 min, tᵣ (minor) = 16.45 min) gave the isomeric composition of the product: 97% ee; [α]D²⁰ = -13.9 (c = 0.49, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.44 (d, J = 8.8 Hz, 2H), 7.38-7.31 (m, 4H), 7.27-7.23 (m, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.44 (d, J = 15.6 Hz, 1H), 6.16 (dd, J = 15.6, 9.2 Hz, 1H), 5.40 (s, 1H), 4.35-4.22 (m, 2H), 4.01-3.82 (m, 2H), 3.79 (s, 3H), 2.50-2.40 (m, 1H), 1.19 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 160.09, 136.56, 132.19, 130.03, 128.62, 128.27 (d, J = 4.3 Hz), 127.70, 127.46, 126.25, 113.59, 100.76, 89.66 (d, J = 183.7 Hz), 71.56 (d, J = 22.4 Hz), 71.38 (d, J = 22.3 Hz), 55.27, 41.50 (d, J = 20.5Hz), 13.96 (d, J = 4.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ -177.35

To a stirred solution of 11 (22.4 mg, 0.1 mmol, 1.0 equiv) in CH₂Cl₂ (1 mL) was successively added Et₃N (20.2 mg, 0.2 mmol) and triphosgene (44.5 mg, 0.15 mmol) at -30 °C. The reaction mixture was naturally warmed to rt and stirred overnight. After full consumption of 11 by TLC analysis, the reaction mixture was directly purified by flash column chromatography using PE/EtOAc (2/1, v/v) as the eluent to afford 1,3-dioxan-2-one 13 (15.1 mg, 60% yield) as a white solid; m.p. = 115-118 °C; HPLC analysis (Chiralcel AD-H, iPrOH/hexane = 30/70, 1.0 mL/min, 254 nm; tᵣ(minor) = 7.41 min, tᵣ(major) = 8.38 min) gave the isomeric composition of the product: 97% ee; [α]D²⁰ = -4.3 (c = 0.34, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.26 (m, 5H), 6.49 (d, J = 15.6 Hz, 1H), 6.08 (dd, J = 15.6, 9.2 Hz, 1H), 4.55-4.34 (m, 4H), 2.69-2.60 (m, 1H), 1.24 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.40, 135.82, 133.70, 128.73, 128.24, 126.38, 125.97 (d, J = 4.2 Hz), 89.32 (d, J = 182.0 Hz), 72.05 (d, J = 21.4 Hz), 71.63 (d, J = 24.4 Hz), 41.01 (d, J = 20.9 Hz), 14.17 (d, J = 4.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ -175.22 (s, 1F); IR (ATR): 1753, 1456, 1184, 1087, 1020, 831, 752, 692 cm⁻¹; HRMS (ESI): Exact mass calcd for C₁₄H₁₅FNaO₃ [M+Na]^+: 273.0897, Found: 273.0895.

To a solution of 11 (56.1 mg, 0.25 mmol) in THF (1.0 mL) was added nBuLi (100 μL, 2.5 M in hexanes, 1.0 equiv.) at 0 °C. After being stirred at 0 °C for 30 min, a solution of p-toluenesulfonyl chloride (47.7 mg, 0.25 mmol, 1.0 equiv) in the THF (1.0 mL) was added. The resulting mixture was stirred at 0 °C for additional 1 h, and nBuLi (100 μL, 2.5 M in hexanes, 1.0 equiv) was then added. After being stirred at 60 °C for 6 h, the reaction mixture was cooled and diluted with Et₂O (10 mL) and H₂O (10 mL). The mixture was separated via a separating funnel, and the aqueous layer was extracted with Et₂O (2 x 10 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated. The obtained residue was purified by silica gel column chromatography (hexanes/EtOAc = 9:1, v/v) to yield

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\text{Ph} \quad \text{F} \quad \text{OH} \\
\text{11 (0.1 mmol, 97% ee)}
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\text{Ph} \quad \text{F} \quad \text{OH} \quad \text{11 (0.1 mmol, 97% ee)}
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\text{Ph} \quad \text{F} \quad \text{OH} \quad \text{11 (0.1 mmol, 97% ee)}
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\text{Ph} \quad \text{F} \quad \text{OH} \quad \text{11 (0.1 mmol, 97% ee)}
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\text{Ph} \quad \text{F} \quad \text{OH} \quad \text{11 (0.1 mmol, 97% ee)}
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fluorinated oxetane 14 as colorless oil. HPLC analysis (Chiralcel OD-H, iPrOH/hexane = 10/90, 1.0 mL/min, 254 nm; t_r(minor) = 6.59 min, t_r(major) = 9.01 min) gave the isomeric composition of the product: 98% ee; [α]_D^{20} = -1.5 (c = 0.31, CHCl₃); ¹H NMR (400 MHz, CDCl₃): 7.38-7.36 (m, 2H), 7.25-7.22 (m, 1H), 6.53 (d, J = 15.6 Hz, 1H), 6.15 (dd, J = 15.6, 8.4 Hz, 1H), 4.80-4.69 (m, 2H), 4.64-4.57 (m, 1H), 2.94-2.81 (m, 1H), 1.17 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.46, 133.07, 129.26, 128.46 (d, J = 3.8 Hz), 128.29, 126.96, 97.48 (d, J = 210.1 Hz), 80.31 (d, J = 24.3 Hz), 80.23 (d, J = 24.2 Hz), 42.95 (d, J = 22.3 Hz), 14.12 (d, J = 4.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ -158.95 (s, 1F); IR (ATR): 2924, 1494, 1450, 1249, 974, 881, 748, 692 cm⁻¹; HRMS (EI): Exact mass calcd for C₁₃H₁₅FO [M⁺]: 206.1101, Found: 206.1105

To a solution of 8 (11.2 mg, 0.05 mmol) and carboxylic acid-based drug (0.12 mmol, 2.4 equivs) in CH₂Cl₂ (0.6 mL) were added DMAP (6.1 mg, 0.02 mmol) and DIC (16.0 mg, 0.13 mmol). The resulting suspension was stirred at rt for overnight. After adding H₂O (5 mL), the reaction mixture was extracted with CH₂Cl₂ (10 mL × 3). The combined organic layers were dried over Na₂SO₄, and concentrated under reduced pressure to give the residue, which was purified by flash column chromatography (PE/EtOAc, 4/1, v/v) to afford the corresponding drug derivatives 15.

Product 15a was prepared by following the above procedure from S-naproxen, and isolated as a foamy solid (20.4 mg, 63% yield), ¹⁹F NMR analysis of the crude mixture revealed that the dr value was >20:1; [α]_D^{20} = -33.4 (c = 0.43, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.72-7.61 (m, 6H), 7.35-7.32 (m, 2H), 7.24-7.09 (m, 9H), 5.96-5.83 (m, 2H), 4.22-4.02 (m, 4H), 3.91 (s, 3H), 3.90 (s, 3H), 3.85-3.78 (m, 2H), 2.29-2.20 (m, 1H), 1.56-1.51 (m, 6H), 0.91 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.69, 173.64, 157.73, 157.66, 136.63, 135.16, 135.08, 133.77, 133.71, 132.04, 129.30, 129.24, 128.87 (d, J = 4.0 Hz), 128.43, 127.47, 127.25, 127.16, 126.17, 126.13, 126.06, 126.04, 125.96, 119.13, 119.02, 105.58, 95.79 (d, J = 180.0 Hz), 63.54 (d, J = 27.4 Hz), 63.39 (d, J = 30.4 Hz), 55.26, 45.34, 45.28, 40.00 (d, J = 20.5 Hz), 18.05, 17.84, 14.08 (d, J = 5.1 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ -174.68 (s, 1F); IR (ATR): 1737, 1606, 1392, 1265, 1031, 925, 812,
Product 15b was prepared by following the above procedure from oxaprozin, and isolated as a foamy solid (33.8 mg, 87% yield). HPLC analysis (Chiralcel AD-H, 4PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; t_r (major) = 63.73 min, t_r (minor) = 60.28 min) gave the isomeric composition of the product: 97% ee; [α]_D^{20} = -56.4 (c = 0.46, CHCl_3); [α]_D^{20} = -36.0 (c = 0.51, CHCl_3); 1H NMR (400 MHz, CDCl_3): δ 7.63-7.55 (m, 8H), 7.36-7.20 (m, 17H), 6.38 (d, J = 16.0 Hz, 1H), 6.11 (dd, J = 16.0, 8.8 Hz, 1H), 4.45-4.24 (m, 4H), 3.18-3.13 (m, 4H), 2.97-2.92 (m, 4H), 2.85-2.76 (m, 1H), 1.14 (d, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl_3): δ 171.24, 161.42, 145.47, 136.66, 135.12, 132.36, 128.91, 128.62, 128.52, 128.46, 128.04, 127.85, 127.58, 126.49, 126.26, 95.66 (d, J = 180.1 Hz), 63.41 (d, J = 27.5 Hz), 62.96 (d, J = 28.8 Hz), 40.14 (d, J = 20.9 Hz), 30.85, 23.35, 14.11 (d, J = 4.4 Hz); 19F NMR (376 MHz, CDCl_3): δ -173.90 (s, 1F); IR (ATR): 2382, 2349, 1743, 1219, 1155, 1026, 763, 692; HRMS (ESI): Exact mass calcd for C_{41}H_{41}FNaO_6 [M+Na]^+: 671.2779, Found: 671.2783.

Product 15c was prepared by following the above procedure from febuxostat, and isolated as a foamy solid (37.8 mg, 92% yield). HPLC analysis (Chiralcel AD-H, 4PrOH/hexane = 10/90, 1.0 mL/min, 254 nm; t_r (minor) = 45.49 min, t_r (major) = 52.32 min) gave the isomeric composition of the product: 97% ee; [α]_D^{20} = -130.3 (c = 0.48, CHCl_3); 1H NMR (400 MHz, CDCl_3): δ 8.11-8.01 (m, 4H), 7.36-7.34 (m, 2H), 7.31-7.23 (m, 3H), 7.01-6.97 (m, 2H), 6.54 (d, J = 16.0 Hz, 1H), 6.23 (dd, J = 15.6, 8.4 Hz, 1H), 4.67-4.52 (m, 4H), 3.90 (d, J = 6.4 Hz, 4H), 3.04-2.96 (m, 1H), 2.74 (s, 6H), 2.24-2.18 (m, 2H), 1.34 (d, J = 7.2 Hz, 3H), 1.10 (d, J = 8.4 Hz, 12H); 13C NMR (100 MHz, CDCl_3): δ 167.77, 162.61, 162.28, 161.24, 161.12, 161.08, 136.55, 132.60, 132.10, 132.07, 128.58, 127.80, 126.31, 125.68 (d, J = 2.7 Hz), 120.53, 120.44, 115.29, 115.27, 112.59, 112.56, 102.96, 95.50 (d, J = 180.7 Hz), 75.71, 64.16 (d, J = 28.4 Hz), 63.69 (d, J = 20.9 Hz), 41.11 (d, J = 20.8 Hz), 28.15, 19.03, 17.53, 14.34 (d, J = 4.8 Hz); 19F NMR (376 MHz, CDCl_3): δ -171.53 (s, 1F); IR (ATR): 1716, 1604, 1508, 1371, 1253, 1085, 1012, 754; HRMS (ESI): Exact mass calcd for C_{49}H_{43}FNaO_6S_2 [M+Na]^+: 843.2657, Found: 843.2666.
7. Mechanistic studies

To gain some insight into the reaction mechanism, we conducted the following experiments (Scheme S1A-B). First, (Z)-1-phenylbutadiene ((Z)-1a) was subjected to the current hydromonofluoromethylation condition (Scheme S1A). Although the reaction rate for the Z isomer was much slower than that of the E isomer, only (E)-product 3a was produced in 46% yield with 96% ee, suggesting a π-allylnickel species. The Z isomer did not appreciably generate the E isomer under the reaction conditions. Second, when EtOD was used as the solvent, the occurrence of H-D scrambling in diene 1a in the absence of 2a (eq 1, Scheme S1B), and 45% D (1.34 D) incorporation into the Me group of 3a under the model reaction (eq 2), revealed that a Ni-H intermediate was generated from the solvent EtOH and that insertion of the terminal double bond of the diene into the Ni-H bond was reversible. Third, the use of deuterated FBSM D-2a in this reaction led to the deuterium (0.7 D) incorporation at the C4 positions of product 3a in nonprotonic solvent THF, suggested that the hydrogen in the FBSM might be a partial source of the proton, though no D incorporation observed in protonic EtOH (eq 3). This result, together with 45% D incorporation at the methyl group using EtOD as the solvent (eq 2), demonstrated that the proton in the product mainly comes from both EtOH and FBSM.

Scheme S1. Preliminary mechanistic investigations and a proposed mechanism.

Based on our preliminary mechanistic investigations, and literature precedents,⁴ we propose a catalytic cycle shown in Scheme S1C. One of the possible pathway is that the oxidative addition of EtOH to Ni(0) species I forms Ni(II)-H intermediate II. The migration insertion of diene 1a into Ni(II)-H

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bond of II delivers π-allyl Ni(II) complex III, which might undergo a ligand exchange to give the species IV and EtOH. Subsequent reductive elimination of IV affords the target 3a and regenerates the Ni(0) species I. Another pathway to form π-allyl Ni(II) III involving a LLHT process was also possible.4a

7.1 Diene geometry study

To an oven-dried Schlenk tube equipped with a stirring bar were successively added Ni(COD)2 (2.8 mg, 10 mol%), (S,S)-QuinoxP* L8 (3.7 mg, 11 mol%), 1,3-diene (Z)-1a (Z:E = 10:1, 19.5 mg, 0.15 mmol, 1.5 equivs), and FBSM 2a (31.4 mg, 0.1 mmol), followed by the addition of absolute EtOH (1.0 mL) in a glove box. After it take out from the glove box, the resulting mixture was stirred at 25 °C for 16 h. The reaction mixture was concentrated under vacuum to give the crude residue, which was purified by silica gel column chromatography using PE/EtOAc (8:1 to 3:1, v/v) as the eluent to afford the product 3a with 46% yield (21.1 mg), recovery the 72% of 1,3-diene (Z)-1a (14.1 mg) with 20:1 Z/E and 50% of 2a (15.8 mg); HPLC analysis (Chiralcel OX-H, 1PrOH/hexane = 20/80, 1.0 mL/min, 254 nm; t(minor) = 17.88 min, t(major) = 20.30 min) gave the isomeric composition of 3a: 96% ee.

Figure S1. The 1H NMR spectrum of the recovered 1,3-diene (Z)-1a with 20:1 Z/E.
To an oven-dried Schlenk tube equipped with a stirring bar were successively added Ni(COD)$_2$ (2.8 mg, 10 mol%), (S,S)-QuinoxP* L8 (3.7 mg, 11 mol%) and 1,3-dienes 1a (19.5 mg, 0.15 mmol, 1.5 equivs) followed by the addition of absolute EtOD (1.0 mL) in a glove box. After it take out from the glove box, the resulting mixture was stirred at 25 °C for 16 h. The reaction mixture was concentrated under vacuum to give the crude residue, which was purified by silica gel column chromatography to recovery the deuterated 1,3-diene D-1a with 92% D incorporation (18.5 mg, 95% recovery).

**Figure S2.** The deuterium incorporation ratio of the recovered 1,3-diene (Z)-1a.
To an oven-dried Schlenk tube equipped with a stirring bar were successively added Ni(COD)$_2$ (2.8 mg, 10 mol%), (S,S)-QuinoxP* L8 (3.7 mg, 11 mol%), 1,3-diene 1a (19.5 mg, 0.15 mmol, 1.5 equivs), and FBSM 2 (31.4 mg, 0.1 mmol), followed by the addition of absolute EtOD (1.0 mL) in a glove box. After it take out from the glove box, the resulting mixture was stirred at 25 °C for 16 h. The reaction mixture was concentrated under vacuum to give the crude residue, which was purified by silica gel column chromatography using PE/EtOAc (8:1 to 6:1, v/v) as the eluent to afford the product D-3a in 96% yield (42.8 mg). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.95-7.92 (m, 2H), 7.82-7.80 (m, 2H), 7.72-7.68 (m, 1H), 7.61-7.57 (m, 1H), 7.56-7.51 (m, 2H), 7.44-7.39 (m, 2H), 7.31-7.21 (m, 5H), 6.31-6.22 (m, 2H), 3.52–3.45 (m, 1H), 1.69-1.64 (m, 1.66H).

Figure S3. The product 3a with 45% D (1.34 D) incorporation at the methyl group (in EtOD).
Figure S4. The recovered 1,3-diene 1a with 86% D incorporation.

To an oven-dried Schlenk tube equipped with a stirring bar were successively added Ni(COD)$_2$ (2.8 mg, 10 mol%), (S,S)-QuinoxP* L8 (3.7 mg, 11 mol%), 1,3-diene 1a (19.5 mg, 0.15 mmol, 1.5 equivs), and deuterated FBSM D-2a (31.4 mg, 0.1 mmol, 89% D), followed by the addition of absolute EtOH (1.0 mL) in a glove box. After it take out from the glove box, the resulting mixture was stirred at 25 °C for 16 h. The reaction mixture was concentrated under vacuum to give the crude residue, which was purified by silica gel column chromatography using PE/EtOAc (8:1 to 3:1, v/v) as the eluent to afford the product 3a in 92% yield (40.3 mg) without D incorporation, and recovery 41% of 1a (9.4 mg) without D incorporation.
Figure S5. The $^1$H NMR spectrum of the obtained product 3a with 0% D incorporation.

Figure S6. The $^1$H NMR spectrum of the deuterated FBSM D-2a with 89% D incorporation.
To an oven-dried Schlenk tube equipped with a stirring bar were successively added Ni(COD)$_2$ (2.8 mg, 10 mol%), (S,S)-QuinoxP$^\ast$ L8 (3.7 mg, 11 mol%), 1,3-diene 1a (19.5 mg, 0.15 mmol, 1.5 equivs), and deuterated FBSM D-2a (31.4 mg, 0.1 mmol), followed by the addition of anhydrous THF (1.0 mL) in a glove box. After it take out from the glove box, the resulting mixture was stirred at 25 °C for 16 h. The reaction mixture was concentrated under vacuum to give the crude residue, which was purified by silica gel column chromatography using PE/EtOAc (8:1 to 3:1, v/v) as the eluent to afford the product D-3a in 49% yield (21.6 mg) with 23% D incorporation, and recovery 68% of 1a (13.6 mg) and 50% of 2a (15.1 mg) without D incorporation. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95-7.92 (m, 2H), 7.82-7.80 (m, 2H), 7.72-7.68 (m, 1H), 7.61-7.57 (m, 1H), 7.56-7.51 (m, 2H), 7.44-7.40 (m, 2H), 7.31-7.21 (m, 5H), 6.31-6.22 (m, 2H), 3.52–3.45 (m, 1H), 1.70-1.66 (m, 2.3H).

**Figure S7.** The $^1$H NMR spectrum of the obtained D-3a with 23% D incorporation.
8. X-ray crystallographic data of 3a and 6t

Data intensity of 3a\(^5\) was collected using a 'Bruker APEX-II CCD' diffractometer at 150.00(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on \(F^2\) with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for 3a: C\(_{23}\)H\(_{21}\)FO\(_4\)S\(_2\), \(T = 173.00(10)\) K, trigonal, P\(_{21}\)2\(_1\)2\(_1\), \(a = 7.55430(10)\) Å, \(b = 10.05800(10)\) Å, \(c = 28.1125(2)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 90^\circ\), \(V = 2136.02(4)\) Å\(^3\). \(Z = 4\), \(\rho_{\text{calc}} = 1.382\) g/cm\(^3\). 46149 reflections collected, 3742 \([R_{\text{int}} = 0.0374, R_{\sigma} = 0.0133]\) independent reflections, \(R_1 = 0.0223\), \(wR_2 = 0.0585\) (I\(>=\)2\(\sigma\) (I)), \(R_1 = 0.0223\), \(wR_2 = 0.0586\) (all data), GOF = 1.097, and 0.010(3) parameters.

Table S3. Crystal data and structure refinement for 3a.

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\(^5\) Supplementary crystallographic data have been deposited at Cambridge Crystallographic Data Center (CCDC number: 2130034).
Volume/Å³ 2136.02(4)
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μ /mm⁻¹ 2.572
F(000) 928.0
Crystal size/mm³ 0.36 × 0.28 × 0.12
Radiation CuKα (λ = 1.54184)
2Θ range for data collection/° 6.288 to 134.128
Index ranges -9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -33 ≤ l ≤ 33
Reflections collected 46149
Independent reflections 3742 [R_int = 0.0374, R_sigma = 0.0133]
Data/restraints/parameters 3742/0/272
Goodness-of-fit on F² 1.097
Final R indexes [I>=2σ (I)] R₁ = 0.0223, wR₂ = 0.0585
Final R indexes [all data] R₁ = 0.0223, wR₂ = 0.0586
Largest diff. peak/hole / e Å⁻³ 0.20/-0.26
Flack parameter 0.010(3)

Table S4. Fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for 3a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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Table S5. Anisotropic Displacement Parameters ($\text{Å}^2 \times 10^{3}$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[a^2U_{11}+2ha*b*U_{12}+...]$.

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Table S5. Anisotropic Displacement Parameters ($\text{Å}^2 \times 10^{3}$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[a^2U_{11}+2ha*b*U_{12}+...]$. 

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Table S6. Bond Lengths for 3a
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**Table S8.** Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 3a.

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Data intensity of 6t was collected using a 'Bruker APEX-II CCD' diffractometer at 150.00(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically. Crystal data for 6t: C$_{21}$H$_{23}$FO$_4$, $T = 173.00(10)$ K, trigonal, $P2_1$, $a = 8.0920(2)$ Å, $b = 5.94840(10)$ Å, $c = 19.5057(4)$ Å, $\alpha = 90^\circ$, $\beta = 98.051(2)^\circ$, $\gamma = 90^\circ$, $V = 929.64(3)$ Å$^3$. $Z = 2$, $\rho_{calc} = 1.280$ g/cm$^3$. 18308 reflections collected, 3278 [R(int) = 0.0550, R(sigma) = 0.0357] independent reflections, $R_1 = 0.0289$, wR$_2 = 0.0721$ ($I = 2\sigma(I)$, final), $R_1 = 0.0312$, wR$_2 = 0.0733$ (all data), GOF = 1.044, and 0.03(9) parameters.

Table S9. Crystal data and structure refinement for 6t.

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$^6$ Supplementary crystallographic data have been deposited at Cambridge Crystallographic Data Center (CCDC number: 2130032).
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<tr>
<td>Independent reflections</td>
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<tr>
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<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R₁ = 0.0289, wR₂ = 0.0721</td>
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<tr>
<td>Final R indexes [all data]</td>
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<td>Flack parameter</td>
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Table S10. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 6t. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized Uij tensor.

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<th>y</th>
<th>z</th>
<th>U(eq)</th>
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<td>7999.6(7)</td>
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<tr>
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<td>8582(4)</td>
<td>3607.3(11)</td>
<td>32.4(5)</td>
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<td>4041.7(10)</td>
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Table S11. Anisotropic Displacement Parameters (Å$^2 \times 10^3$) for 6t. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[a^2U_{11}+2hka*b*U_{12}+…]$. 

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<tr>
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### Table S12. Bond Lengths for 6t.

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### Table S13. Bond Angles for 6t.

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Table S14. Torsion angles for 6t.
Table S15. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6t.

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<td>7678.19</td>
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<tr>
<td>H20A</td>
<td>11538.32</td>
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<td>H20B</td>
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</tr>
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<td>H21B</td>
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<td>7450.75</td>
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9. NMR spectra
162
10. HPLC traces

**Analysis Report**

**Sample Information**
- Sample Name: Zhy-zb-91-rac-oxh-60-20-1.3-254-2
- Sample ID: 200
- Date Processed: 2021/7/9 16:23:53
- Method Filename: 1.0.kmc
- Batch Filename: 1.0.kmc
- Vial #: 1
- Injection Volume: 20 μL
- Date Acquired: 2021/7/9 16:23:53
- Acquired by: System Administrator
- Sample Type: Unknown

**Chromatogram**

**Peak Table**

<table>
<thead>
<tr>
<th>Peak Seq No.</th>
<th>Ret. Time (min)</th>
<th>Area</th>
<th>Height</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.2</td>
<td>15,517</td>
<td>49,640</td>
<td>0.53</td>
</tr>
<tr>
<td>2</td>
<td>6.8</td>
<td>18,717</td>
<td>67,900</td>
<td>0.50</td>
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<td>3</td>
<td>7.4</td>
<td>20,900</td>
<td>78,400</td>
<td>0.49</td>
</tr>
<tr>
<td>4</td>
<td>8.0</td>
<td>23,000</td>
<td>91,600</td>
<td>0.48</td>
</tr>
<tr>
<td>Total</td>
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<td>74,534</td>
<td>313,900</td>
<td>0.48</td>
</tr>
</tbody>
</table>

**Analysis Report**

**Sample Information**
- Sample Name: Zhy-zb-110-1-asox-60-20-254-2
- Sample ID: 200
- Date Processed: 2021/7/9 16:48:01
- Method Filename: 1.0.kmc
- Batch Filename: 1.0.kmc
- Vial #: 1
- Injection Volume: 20 μL
- Date Acquired: 2021/7/9 16:48:01
- Acquired by: System Administrator
- Sample Type: Unknown

**Chromatogram**

**Peak Table**

<table>
<thead>
<tr>
<th>Peak Seq No.</th>
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<th>Area</th>
<th>Height</th>
<th>Conc.</th>
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</thead>
<tbody>
<tr>
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<td>15,460</td>
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<td>2</td>
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<tr>
<td>3</td>
<td>7.4</td>
<td>20,900</td>
<td>78,400</td>
<td>0.49</td>
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<tr>
<td>4</td>
<td>8.0</td>
<td>23,000</td>
<td>91,600</td>
<td>0.48</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>74,534</td>
<td>313,900</td>
<td>0.48</td>
</tr>
</tbody>
</table>

**rac-3a**

**3a**
Analysis Report

Sample Name: zhy-zc-96-rac-osh-60-20-1.0-254-205-1
Sample ID: zhy-zc-96-rac-osh-60-20-1.0-254-205-1.lcd
Method Filename: 1.0.licm
Batch Filename: 1.1
Vial #: 1-1
Injection Volume: 20 uL
Date Acquired: 2021/10/29 16:08:10
Acquired by: System Administrator

Analysis Report

Sample Name: zhy-zc-96-rac-osh-60-20-1.0-254-205-1
Sample ID: zhy-zc-96-rac-osh-60-20-1.0-254-205-1.lcd
Method Filename: 1.0.licm
Batch Filename: 1.1
Vial #: 1-1
Injection Volume: 20 uL
Date Acquired: 2021/10/29 14:27:28
Acquired by: System Administrator

<Peak Table>

Detector A Channel 2 254nm

Peak Ref. Time Area Height Conc.
1 20.628 419248 69224 50.368

Total 8303802 193930

<Peak Table>

Detector A Channel 2 254nm

Peak Ref. Time Area Height Conc.
1 20.755 405561 89762 3.165

Total 14390218 347414

rac-3b

3b

SO₂Ph

SO₂Ph

SO₂Ph

SO₂Ph
Analysis Report

Sample Information
Sample Name: zhy-dl-65-rac-oxih-80-20-1.0-254-205-5
Sample ID: zhy-dl-65-rac-oxih-80-20-1.0-254-205-5.ld
Method Filename: 1.0.icm
Batch Filename: 1.1.icm
Val #: 1.1
Sample Type: Unknown
Injection Volume: 20.0 µL
Date Acquired: 2022/06/29 10:50:21
Acquired by: System Administrator
Date Processed: 2022/06/29 14:21:43
Processed by: System Administrator

Chromatogram

Peak Table
<table>
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<tr>
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<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>3212665</td>
<td>3212665</td>
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<tr>
<td>2</td>
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<td>521654</td>
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<tr>
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</table>

Analysis Report

Sample Information
Sample Name: zhy-dl-67-1-rac-oxih-80-20-1.0-254-205-5
Sample ID: zhy-dl-67-1-rac-oxih-80-20-1.0-254-205-5.ld
Method Filename: 1.0.icm
Batch Filename: 1.1.icm
Val #: 1.1
Sample Type: Unknown
Injection Volume: 20.0 µL
Date Acquired: 2022/06/29 11:22:30
Acquired by: System Administrator
Date Processed: 2022/06/29 15:22:51
Processed by: System Administrator

Chromatogram

Peak Table
<table>
<thead>
<tr>
<th>Peak</th>
<th>Area</th>
<th>Height</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>743222</td>
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<td>743222</td>
</tr>
<tr>
<td>2</td>
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<tr>
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<td>1314222</td>
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</table>

rac-3g

3g
Analysis Report

Sample Information
Sample Name: chy-dl-65-6-rac-adt-80-20-1.0-254-1
Sample ID: chy-dl-65-6-rac-adt-80-20-1.0-254-1
Method Filename: chy-dl-65-6-rac-adt-80-20-1.0-254-1.lod
Batch Filename: 1.0.1mm
Vial #: 1-1
Sample Type: Unknown
Injection Volume: 20 μL
Date Acquired: 2022/06/29 0:14:41
Date Processed: 2022/06/29 0:26:05

Chromatogram

Peak Table
<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>2871.8</td>
<td>0.050</td>
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<tr>
<td>2</td>
<td>25.520</td>
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</table>

rac-3j

3j
Analysis Report

Sample Name: ZHY-ZF-67-5-RAC-OEH-60-20-1.0-254-230-7
Sample ID: 1660
Method Filename: 1000m
Batch Filename: 
Vial #: 1
Sample Type: Unknown
Injection Volume: 20.0 µl
Date Acquired: 23/08/20 11:15:07
Acquired by: System Administrator
Date Processed: 2023/08/26 12:32:13
Processed by: System Administrator

<Peak Table>

Detector A Channel 1 254nm
Peak Type | Ret Time | Area | Height | Conc |
--- | --- | --- | --- | --- |
1 | 24.213 | 1977693 | 33000 | 56.295 |
2 | 28.798 | 1574530 | 11048 | 49.706 |
Total | | | | |

314
Analysis Report

Sample Information:
- Sample Name: ZHY-ZF-65-1-ASY-ODH-80-20-1.0-254-230-1
- Sample ID: ZHY-ZF-65-1-ASY-ODH-80-20-1.0-254-230-1
- Method Filename: 1.0km
- Batch Filename: 1.0km
- Volume: 20uL
- Sample Type: Unknown
- Acquired by: System Administrator
- Processed by: System Administrator

Chromatogram:

Peak Table:

<table>
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<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Area</th>
<th>Height</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.625</td>
<td>52759</td>
<td>192776</td>
<td>45.263</td>
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<td>57930</td>
<td>159884</td>
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<td>1077569</td>
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rac-3m

3m

Analysis Report

Sample Information:
- Sample Name: ZHY-ZF-65-1-ASY-ODH-80-20-1.0-254-230-1
- Sample ID: ZHY-ZF-65-1-ASY-ODH-80-20-1.0-254-230-1
- Method Filename: 1.0km
- Batch Filename: 1.0km
- Volume: 20uL
- Sample Type: Unknown
- Acquired by: System Administrator
- Processed by: System Administrator

Chromatogram:

Peak Table:

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<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Area</th>
<th>Height</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
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<td>65027</td>
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<td>26.641</td>
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rac-3m

3m

D:\Data\ZHY-ZF-65-1-ASY-ODH-80-20-1.0-254-230-1.txt

D:\Data\ZHY-ZF-65-1-ASY-ODH-80-20-1.0-254-230-1.txt

316
### 267 ZHY-Zd-21-2-RAC-OXH-80-20-1.0-205-1

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU·min)</th>
<th>Rel. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.57</td>
<td>n.a.</td>
<td>296.777</td>
<td>281.422</td>
<td>49.56</td>
<td>n.a.</td>
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<tr>
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<td>0.000</td>
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### 264 ZHY-Zd-21-2-ASY-OXH-80-20-1.0-254-1

<table>
<thead>
<tr>
<th>No.</th>
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<th>Height (mAU)</th>
<th>Area (mAU·min)</th>
<th>Rel. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
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### 275 ZHY-Zd-17-rac-OXH-95-5-1.0-205-3

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<th>Ret. Time (min)</th>
<th>Peak Name</th>
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<th>Area (mAU min)</th>
<th>Ret. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
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<td>n.a.</td>
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<tr>
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<td>n.a.</td>
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<td>604.343</td>
<td>45.73</td>
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<tr>
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<td>22.14</td>
<td>n.a.</td>
<td>51.278</td>
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### 276 ZHY-Zd-17-asy-OXH-95-5-1.0-205-3

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<th>Area (mAU min)</th>
<th>Ret. Area (%)</th>
<th>Amount</th>
<th>Type</th>
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<tr>
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rac-3q

3q
Analysis Report

<Sample Information>
Sample Name: zhy-zB-141-2-rac-oXH-80-20-1.254mm-1
Sample ID: Z2B-141-2-rac-oXH-80-20-1.254mm-1
Date Filename: 2021-09-17 10:53:56
Method Filename: 1.0_1kcm
Batch Filename: 1.1
Vial #: 1-1
Sample Type: Unknown
Injection Volume: 20 µL
Date Acquired: 2021/10/1 15:05:39
Acquired by: System Administrator
Date Processed: 2022/1/10 15:50:01
Processed by: System Administrator

<Chromatogram>

<Peak Table>

Detector A Channel 2 254nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.446</td>
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<td>44137</td>
<td>49.934</td>
</tr>
<tr>
<td>2</td>
<td>27.784</td>
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<tr>
<td>Total</td>
<td>4550548</td>
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</table>

rac-3s

D:/Data/ZHY/ZB/zhy-zB-141-2-rac-oXH-80-20-1.254mm-1.png

Analysis Report

<Sample Information>
Sample Name: zhy-zB-141-2-rac-oXH-80-20-1.254mm-1
Sample ID: Z2B-141-2-rac-oXH-80-20-1.254mm-1
Date Filename: 2021-09-17 10:53:56
Method Filename: 1.0_1kcm
Batch Filename: 1.1
Vial #: 1-1
Sample Type: Unknown
Injection Volume: 20 µL
Date Acquired: 2021/10/1 15:05:39
Acquired by: System Administrator
Date Processed: 2022/1/10 15:50:01
Processed by: System Administrator

<Chromatogram>

<Peak Table>

Detector A Channel 2 254nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<tr>
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<tr>
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<td>91312</td>
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</tr>
</tbody>
</table>

3s

D:/Data/ZHY/ZC/zhy-zB-25-1-asx-oXh-80-20-1.254mm-1.png
Analysis Report

Sample Information
Sample Name: zhi-zc-103-rac-oxh-80-20-1.0-254-230-1
Sample ID: 20402
Method Filename: zhi-zc-103-rac-oxh-80-20-1.0-254-230-1.lcd
Vial #: 1-1
Injection Volume: 20.0 µL
Date Processed: 2022/1/10 16:27:45

Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram

Peak Table

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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Analysis Report

Sample Information
Sample Name: zhi-zc-114-asy-oxh-80-20-1.0-254-205-1
Sample ID: 20402
Method Filename: zhi-zc-114-asy-oxh-80-20-1.0-254-205-1.lcd
Vial #: 1-1
Injection Volume: 20.0 µL
Date Processed: 2022/11/12 20:32:19

Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram

Peak Table

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
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<th>Height</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>59</td>
</tr>
<tr>
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<td>59236</td>
<td>1446</td>
<td>0.93</td>
</tr>
<tr>
<td>Total</td>
<td>59742.67</td>
<td>163556</td>
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<td></td>
</tr>
</tbody>
</table>

rac-3v

3v
**279 zhy-zc-135-rac-odh-80-20-1.0-205-1**

- **Sample Name:** zhy-zc-135-rac-odh-80-20-1.0-205-1
- **Injection Volume:** 20.0
- **Vial Number:** 377
- **Channel:** UV_VIS_1
- **Sample Type:** standard
- **Wavelength:** 205
- **Control Program:** Zhang Xuexin
- **Bandwidth:** n.a.
- **Quant. Method:** Zhang Xuexin
- **Dilution Factor:** 1.0000
- **Run Time (min):** 23.95
- **Sample Amount:** 1.0000

---

**278 zhy-zc-135-asy-odh-80-20-1.0-205-1**

- **Sample Name:** zhy-zc-135-asy-odh-80-20-1.0-205-1
- **Injection Volume:** 20.0
- **Vial Number:** 376
- **Channel:** UV_VIS_1
- **Sample Type:** standard
- **Wavelength:** 205
- **Control Program:** Zhang Xuexin
- **Bandwidth:** n.a.
- **Quant. Method:** Zhang Xuexin
- **Dilution Factor:** 1.0000
- **Run Time (min):** 33.78
- **Sample Amount:** 1.0000

---

**Chemical Structures:**

**rac-3y**

**3y**
Analysis Report

Sample Information
Sample ID: Unknown
Method Filename: 1.0.lcm
Vial #: 1-1
Injection Volume: 20.0 µL
Date Acquired: 2023/10/10 16:30:49
Date Processed: 2023/11/14 21:07:01
Sample Type: System Administrator

Chromatogram

Peak Table
Detector Channel 2 254nm
Peak Ret. Time Area Height Conc. 1 16.172 694521 201395 49.737 2 15.945 146538 5574 1.643 Total 0085079 288615

rac-3aa

3aa

Analysis Report

Sample Information
Sample ID: Unknown
Method Filename: 1.0.lcm
Vial #: 1-1
Injection Volume: 20.0 µL
Date Acquired: 2023/10/10 21:08:07
Date Processed: 2023/10/10 21:30:32
Sample Type: System Administrator

Chromatogram

Peak Table
Detector Channel 2 254nm
Peak Ret. Time Area Height Conc. 1 16.172 694521 201395 49.737 2 15.945 146538 5574 1.643 Total 0085079 288615
Analysis Report

Sample Information:
Sample Name: zhy-zc-61-rac-adh-60-40-1.0-254-230-1
Sample ID:
Data Filename: zhy-zc-61-rac-adh-60-40-1.0-254-230-1.lcd
Method Filename: rac-254-230-1.lcm
Vial #: 1-1
Injection Volume: 2.0 µL
Date Acquired: 2021/10/19 16:19:43
Date Processed: 2022/11/12 21:37:41
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

<Peak Table>

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.327</td>
<td>196762</td>
<td>51156</td>
<td>59.245</td>
</tr>
<tr>
<td>2</td>
<td>27.856</td>
<td>194959</td>
<td>34405</td>
<td>49.755</td>
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<td>391662</td>
<td>85561</td>
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<Chromatogram>

Detector A Channel 2 254nm

Analysis Report

Sample Information:
Sample Name: zhy-zc-146-as-str-60-40-1.0-254-230-1
Sample ID:
Data Filename: zhy-zc-146-as-str-60-40-1.0-254-230-1.lcd
Method Filename: 1.0.lcm
Vial #: 1-1
Injection Volume: 2.0 µL
Date Acquired: 2022/11/26 16:43:38
Date Processed: 2022/11/10 21:00:17
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

<Peak Table>

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.372</td>
<td>89060</td>
<td>20408</td>
<td>7.504</td>
</tr>
<tr>
<td>2</td>
<td>27.977</td>
<td>31450334</td>
<td>557446</td>
<td>97.406</td>
</tr>
<tr>
<td>Total</td>
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<td>34309335</td>
<td>577520</td>
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<Chromatogram>

Detector A Channel 2 254nm

rac-3ab

3ab

D:\Date\ZH\Y2\Z\zhy-zc-61-rac-adh-60-40-1.0-254-230-1.lcd
D:\Date\ZH\Y2\Z\zhy-zc-146-as-str-60-40-1.0-254-230-1.lcd
Analysis Report

Sample Name: zhy-zd-23-RAC-odh-100-0-254-205-1.0-1
Sample ID: 
Method Filename: zhy-zd-23-RAC-odh-100-0-254-205-1.0-1.lcd
Data Filename: 
Vial #: 1-1
Injection Volume: 20.0 μL
Date Processed: 2022/1/12 16:43:56
Sample Type: Unknown

Assay: rac-4a

<Peak Table>

<table>
<thead>
<tr>
<th>Peak Ref.</th>
<th>Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.86</td>
<td>138055</td>
<td>23070</td>
<td>40.2</td>
</tr>
<tr>
<td>2</td>
<td>17.85</td>
<td>60461713</td>
<td>1817770</td>
<td>50.749</td>
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<td>Total</td>
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<td>59471991</td>
<td>4192810</td>
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</tr>
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<Chromatogram>

D:/Data/ZHY/ZD/zhy-zd-23-RAC-odh-100-0-254-205-1.0-1.lcd

Analysis Report

Sample Name: zhy-zd-23-ASY-odh-100-0-254-205-1.0-1
Sample ID: 
Method Filename: zhy-zd-23-ASY-odh-100-0-254-205-1.0-1.lcd
Data Filename: 
Vial #: 1-1
Injection Volume: 20.0 μL
Date Processed: 2022/1/12 16:43:56
Sample Type: Unknown

Assay: 4a

<Peak Table>

<table>
<thead>
<tr>
<th>Peak Ref.</th>
<th>Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.69</td>
<td>1450028</td>
<td>9634</td>
<td>261</td>
</tr>
<tr>
<td>2</td>
<td>17.71</td>
<td>11434501</td>
<td>547523</td>
<td>98.738</td>
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<td>Total</td>
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</tr>
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<Chromatogram>

D:/Data/ZHY/ZD/zhy-zd-23-ASY-odh-100-0-254-205-1.0-1.lcd
Analysis Report

Sample Information
Sample Name: zhy-zl-45-rac-odh-100-0-1.0-205-254-1
Sample ID: zhy-zl-45-rac-odh-100-0-1.0-205-254-1
Method Filename: 1.0 cm
Batch Filename: 1-1
Volume: 10 µL
Injection Volume: 10 µL
Date Acquired: 2022/11/15 15:20:57
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram

Peak Table

<table>
<thead>
<tr>
<th>Peak Ref.</th>
<th>Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.49</td>
<td>747904</td>
<td>694617</td>
<td>50.430</td>
</tr>
<tr>
<td>2</td>
<td>8.66</td>
<td>336186</td>
<td>267705</td>
<td>97.951</td>
</tr>
<tr>
<td>Total</td>
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<td>1523938</td>
<td>1395102</td>
<td></td>
</tr>
</tbody>
</table>

rac-4c

Analysis Report

Sample Information
Sample Name: zhy-zl-45-rac-odh-100-0-1.0-205-254-1
Sample ID: zhy-zl-45-rac-odh-100-0-1.0-205-254-1
Method Filename: 1.0 cm
Batch Filename: 1-1
Volume: 10 µL
Injection Volume: 10 µL
Date Acquired: 2022/11/15 15:34:51
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram

Peak Table

<table>
<thead>
<tr>
<th>Peak Ref.</th>
<th>Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.85</td>
<td>753687</td>
<td>79057</td>
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</tr>
<tr>
<td>2</td>
<td>8.66</td>
<td>336186</td>
<td>267705</td>
<td>97.951</td>
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<td>Total</td>
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<td>3427258</td>
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</table>

4c
Analysis Report

Sample Information
Sample Name: ZHY-ZD-48-rac-2odh-100-0-1-0-254-205-2
Sample ID: 2400.00
Method Filename: ZHY-ZD-48-rac-2odh-100-0-1-0-254-205-2.lcd
Batch Filename: 1-1
Vial: 1
Injection Volume: 10.0 uL
Date Acquired: 2022/01/10 21:40:54
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram

Peak Table
Peak Ret. Time | Area  | Height | Conc. |
---------------|-------|--------|-------|
1             | 18.842| 1167693| 67906 | 50.466 |
2             | 20.834| 1167514| 594844| 40.531 |
Total         | 2336043| 1182350|       |

rac-4d

Analysis Report

Sample Information
Sample Name: ZHY-ZD-48-rac-2odh-100-0-1-0-254-205-2
Sample ID: 2400.00
Method Filename: ZHY-ZD-48-rac-2odh-100-0-1-0-254-205-2.lcd
Batch Filename: 1-1
Vial: 1
Injection Volume: 10.0 uL
Date Acquired: 2022/01/10 21:40:54
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram

Peak Table
Peak Ret. Time | Area  | Height | Conc. |
---------------|-------|--------|-------|
1             | 18.814| 2332872| 117737| 98.306 |
2             | 20.858| 804830 | 44587 | 3.654 |
Total         | 2423232| 1222463|       |

4d

D:\Data\ZHYZD\ZHY-ZD-48-rac-2odh-100-0-1-0-254-205-2.lcd
D:\Data\ZHYZD\ZHY-ZD-48-rac-2odh-100-0-1-0-254-205-2.lcd
Analysis Report

<Sample Information>
Sample Name: ZHY-ZD-120-FUNAN-RAC-OHH-100-0-1.0-254-205-1
Sample Lot: 20505
Data Filename: ZHY-ZD-120-FUNAN-RAC-OHH-100-0-1.0-254-205-11d
Method Filename: 1.0kim
Batch Filename: 2051d
Vol #: 1-1
Sample Type: Unknown
Injection Volume: 20 ul
Date Acquired: 2023/03/12 22:25:43
Acquired by: System Administrator
Processed by: System Administrator
Date Processed: 2023/03/12 22:29:40

<Chromatogram>

<Peak Table>
Peak No. Ret. Time Area Height Conc.
1 8.700 1140570 100350 49.368
2 8.354 1192730 106511 66.845
Total 2331340 216861

rac-D-4c

Analysis Report

<Sample Information>
Sample Name: ZHY-ZD-120-FUNAN-ASY-OHH-100-0-1.0-254-205-1
Sample Lot: 20505
Data Filename: ZHY-ZD-120-FUNAN-ASY-OHH-100-0-1.0-254-205-11d
Method Filename: 1.0kim
Batch Filename: 2051d
Vol #: 1-1
Sample Type: Unknown
Injection Volume: 20 ul
Date Acquired: 2023/03/12 22:24:18
Acquired by: System Administrator
Processed by: System Administrator
Date Processed: 2023/03/12 22:34:48

<Chromatogram>

<Peak Table>
Peak No. Ret. Time Area Height Conc.
1 6.707 60764 57357 1.699
2 9.118 5019713 446766 98.391
Total 605549 466524

D-4c
Analysis Report

Sample Information
Sample Name: NLLb-122-dppf-rac-adh-h-98-2-1.0-230nm-01
Sample ID: NLLb-122-dppf-rac-adh-h-98-2-1.0-230nm-01
Data Filename: NLLb-122-dppf-rac-adh-h-98-2-1.0-230nm-01.lcd
Method Filename: xal-230-254-1.0.lcm
Batch Filename: xal-230-254-1.0.lcm
Val # : 1-1
Sample Type: Unknown
Injection Volume: 20 ul
Date Acquired: 2021/7/20 15:06:50
Acquired by: System Administrator
Date Processed: 2021/7/20 15:21:09
Processed by: System Administrator

Chromatogram

Peak Table
<table>
<thead>
<tr>
<th>Peak Ref. Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc.</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>10.731</td>
<td>7582076</td>
<td>514069</td>
</tr>
<tr>
<td>2</td>
<td>12.207</td>
<td>7613970</td>
<td>460166</td>
</tr>
</tbody>
</table>
Total          | 1519564| 974224 |

Analysis Report

Sample Information
Sample Name: NLLb-13-5mol-50-nasy-adh-98-2-254-1.0
Sample ID: NLLb-13-5mol-50-nasy-adh-98-2-254-1.0
Data Filename: NLLb-13-5mol-50-nasy-adh-98-2-254-1.0.lcd
Method Filename: xal-230-254-1.0.lcm
Batch Filename: xal-230-254-1.0.lcm
Val # : 1-1
Sample Type: Unknown
Injection Volume: 20 ul
Date Acquired: 2021/9/30 12:21:47
Acquired by: System Administrator
Date Processed: 2021/9/30 12:46:42
Processed by: System Administrator

Chromatogram

Peak Table
<table>
<thead>
<tr>
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<th>Height</th>
<th>Conc.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>10.901</td>
<td>223304</td>
<td>14401</td>
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<tr>
<td>2</td>
<td>12.436</td>
<td>13383782</td>
<td>757750</td>
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</table>
Total          | 13000088| 772156 |

rac-6a

6a
90  ili-iloet-rac-ojh-85-15-230-0.5-2

Sample Name: ili-iloet-rac-ojh-85-15-230-0.5-2  Injection Volume: 20.0
Vial Number: 482  Channel: UV_VIS_1
Sample Type: standard  Wavelength: 230
Control Program: XSL  Bandwidth: n.a.
Quantif. Method: XSL  Dilution Factor: 1.0000
Run Time (min): 29.18  Sample Amount: 1.0000

104 ili-II-COOET-ASI-OJH-230-1.0-3

Sample Name: ili-II-COOET-ASI-OJH-230-1.0-3  Injection Volume: 20.0
Vial Number: 468  Channel: UV_VIS_1
Sample Type: standard  Wavelength: 230
Control Program: XSL  Bandwidth: n.a.
Quantif. Method: XSL  Dilution Factor: 1.0000
Run Time (min): 31.49  Sample Amount: 1.0000
83 lll-ii-cho-rac-ojh-75-25--230-1.0-2

Sample Name: lll-ii-cho-rac-ojh-75-25--230-1.0-2
Injection Volume: 20.0 μl
Vial Number: 444
Channel: UV_VIS_1
Sample Type: standard
Wavelength: 230 nm
Control Program: XSL
Bandwidth: n.a.
Quantif. Method: XSL
Dilution Factor: 1.0000
Run Time (min): 31.95
Sample Amount: 1.0000

84 lll-ii-cho-asy-ojh-95-5--230-1.0-2

Sample Name: lll-ii-cho-asy-ojh-95-5--230-1.0-2
Injection Volume: 20.0 μl
Vial Number: 445
Channel: UV_VIS_1
Sample Type: standard
Wavelength: 230 nm
Control Program: XSL
Bandwidth: n.a.
Quantif. Method: XSL
Dilution Factor: 1.0000
Run Time (min): 17.50
Sample Amount: 1.0000

---

No.  Ret.Time  Peak Name  Height  Area  Rel.Area  Amount  Type
      min      (mAU)  (mAU/min)   %
1  12.27    n.a.  344.902  143.496  54.77 n.a.  BMB*
2  16.20    n.a.  194.040  116.479  45.23 n.a.  BMB*
Total:                                            538.942 261.976 100.00 0.000

---

No.  Ret.Time  Peak Name  Height  Area  Rel.Area  Amount  Type
      min      (mAU)  (mAU/min)   %
1  11.95    n.a.  10.524  3.450  1.64 n.a.  BMB*
2  15.43    n.a.  341.140  207.471  0.86 n.a.  BMB*
Total:                                            351.664 210.921 100.00 0.000

---

rac-6h

---

6h

---

MulIntegration  Version 6.80 SR8a Build 2643 (158225)
Analysis Report

Sample Information
Sample Name: Ili-ltd-95-rac-adh-98-2-1.0-254-230-1
Sample ID: 1
Data Filename: Ili-ltd-95-rac-adh-98-2-1.0-254-230-1.lcd
Method Filename: gya-1.0-254-1.lcm
Batch Filename: Ili-ltd-95-rac-adh-98-2-1.0-254-230-1.lcm
Injection Volume: 25.1 µL
Sample Type: Unknown
Date Acquired: 2021/11/5 23:16:59
Acquired by: Systems Administrator
Date Processed: 2021/11/5 23:33:47
Processed by: Systems Administrator

Chromatogram

<Peak Table>

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.373</td>
<td>646595</td>
<td>386188</td>
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</tr>
<tr>
<td>2</td>
<td>12.312</td>
<td>6466442</td>
<td>341863</td>
<td>50.605</td>
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<tr>
<td>Total</td>
<td>1291403</td>
<td>756681</td>
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</tr>
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</table>

Detector A Channel 2 230nm

Analysis Report

Sample Information
Sample Name: Ili-ltd-95-rac-adh-98-2-1.0-254-230-1
Sample ID: 1
Data Filename: Ili-ltd-95-rac-adh-98-2-1.0-254-230-1.lcd
Method Filename: gya-1.0-254-1.lcm
Batch Filename: Ili-ltd-95-rac-adh-98-2-1.0-254-230-1.lcm
Injection Volume: 25.1 µL
Sample Type: Unknown
Date Acquired: 2021/11/5 22:25:21
Acquired by: Systems Administrator
Date Processed: 2021/11/5 23:10:05
Processed by: Systems Administrator

Chromatogram

<Peak Table>

<table>
<thead>
<tr>
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<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc.</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>11.628</td>
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<td>20162</td>
<td>2.276</td>
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<tr>
<td>2</td>
<td>12.274</td>
<td>14755955</td>
<td>816637</td>
<td>97.724</td>
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<tr>
<td>Total</td>
<td>15999440</td>
<td>836699</td>
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Detector A Channel 2 230nm

rac-6j

CO₂Et

CO₂Et

6j

CO₂Et

CO₂Et

D:\Datei\Löhi\Ili-ltd-95-rac-adh-98-2-1.0-254-230-1.lcd

D:\Datei\Löhi\Ili-ltd-95-rac-adh-98-2-1.0-254-230-1.lcd
Analysis Report

Sample Information:
- Sample Name: 8l-li-rac-ch3-adh-98-2-1.0-230-254mm-2
- Sample ID: 8l-li-rac-ch3-adh-98-2-1.0-230-254mm-2.ldc
- Method Filename: ZKK-xcitrus.icm
- Batch Filename: 1.t
- Injection Volume: 20 µL
- Date Acquired: 2021/10/09 20:34:01
- Processed by: System Administrator

Chromatogram:

Peak Table:

<table>
<thead>
<tr>
<th>Detector A Channel 1</th>
<th>254nm</th>
<th>Area</th>
<th>Height</th>
<th>Conc.</th>
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<tbody>
<tr>
<td>1</td>
<td>9.541</td>
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<td>15983</td>
<td>49.081</td>
</tr>
<tr>
<td>2</td>
<td>10.910</td>
<td>2551222</td>
<td>161486</td>
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<tr>
<td>Total</td>
<td>5010373</td>
<td>314139</td>
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<td></td>
</tr>
</tbody>
</table>

Analysis Report

Sample Information:
- Sample Name: 8l-li-25-3-ch3-adh-99-2-1.0-230-254mm-2
- Sample ID: 8l-li-25-3-ch3-adh-99-2-1.0-230-254mm-2.ldc
- Method Filename: ZKK-xcitrus.icm
- Batch Filename: 1.t
- Injection Volume: 20 µL
- Date Acquired: 2021/10/09 19:49:01
- Processed by: System Administrator

Chromatogram:

Peak Table:

<table>
<thead>
<tr>
<th>Detector A Channel 1</th>
<th>254nm</th>
<th>Area</th>
<th>Height</th>
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<tbody>
<tr>
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<td>24052</td>
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<td>Total</td>
<td>2236686</td>
<td>1457755</td>
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<td></td>
</tr>
</tbody>
</table>
189 iii-Il-ENE-IF-RAC-97-3--230-0.5-2

Sample Name: iii-Il-ENE-IF-RAC-97-3--230-0.5-2  Injection Volume: 20.0
Vial Number: 416  Channel: UV_VIS_1
Sample Type: standard  Wavelength: 230
Control Program: XSL  Bandwidth: n.a.
Quantif. Method: XSL  Dilution Factor: 1.0000
Run Time (min): 17.17  Sample Amount: 1.0000

62 iii-Il-20-1-ene-if-asy-95-5--230-0.5-2

Sample Name: iii-Il-20-1-ene-if-asy-95-5--230-0.5-2  Injection Volume: 20.0
Vial Number: 423  Channel: UV_VIS_1
Sample Type: standard  Wavelength: 230
Control Program: XSL  Bandwidth: n.a.
Quantif. Method: XSL  Dilution Factor: 1.0000
Run Time (min): 15.81  Sample Amount: 1.0000

---

**Diagram 1:**
- Column: XSL
- Wavelength: 230 nm
- Peak 1: Ret.Time = 13.03, Height = 75.324 mAU, Area = 33.157 mAU*min, Rel.Area = 50.25%, Amount = n.a., Type = BMB*
- Peak 2: Ret.Time = 14.29, Height = 59.390 mAU, Area = 32.623 mAU*min, Rel.Area = 49.75%, Amount = n.a., Type = BMB*
- Total: 128.615 mAU, 65.080 mAU*min, 100.00%, 0.000

**Diagram 2:**
- Column: XSL
- Wavelength: 230 nm
- Peak 1: Ret.Time = 13.14, Height = 4.415 mAU, Area = 1.479 mAU*min, Rel.Area = 3.12%, Amount = n.a., Type = BMB*
- Peak 2: Ret.Time = 14.44, Height = 151.062 mAU, Area = 68.417 mAU*min, Rel.Area = 97.86%, Amount = n.a., Type = BMB
- Total: 155.477 mAU, 69.896 mAU*min, 100.00%, 0.000

---

**Chemical Structures:**
- **rac-6n:**
  - Chemical structure of rac-6n with substituents
- **6n:**
  - Chemical structure of 6n with substituents.

---

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Version 6.80 SR8a Build 2643 (158225)

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Version 6.80 SR8a Build 2643 (158225)
Analysis Report

Sample Information
Sample Name: LIL-D-O-OME-RAC-OXH-08-2-254-230-1
Sample ID: LIL-D-O-OME-RAC-OXH-08-2-254-230-1
Method Filename: gase-1.0-254-1.lcm
Batch Filename: gase-1.0-254-1.lcm

Vial #: 1.1
Sample Type: Unknown
Injection Volume: 10 μL
Date Acquired: 2022/1/10 9:35:54
Acquired by: System Administrator
Date Processed: 2022/1/10 9:52:24
Processed by: System Administrator

Chromatogram

<Peak Table>
Detector A Channel 1 254nm

<table>
<thead>
<tr>
<th>Peak Ref. Time</th>
<th>Area</th>
<th>Height</th>
<th>Concentration</th>
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<tbody>
<tr>
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</tr>
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rac-6q

Ome

CO₂Et

CO₂Et

D:/Data/WLF/LIL-D-O-OME-RAC-OXH-08-2-254-230-1.lcd

6q

Ome

CO₂Et

CO₂Et

D:/Data/WLF/LIL-D-O-OME-ASY-ADH-08-2-254-230-1.lcd
Analysis Report

Sample Information
Sample Name: 8463-43-4-RAC-00-10-1.0-230-254nm-1
Sample ID: 8463-43-4-RAC-00-10-1.0-230-254nm-1.lcd
Method Filename: xl2-230-254-1.0.lcm
Batch Filename: 1-1
Injection Volume: 20 μL
Date Acquired: 2021/10/12 19:57:05
Date Processed: 2021/10/12 20:37:22
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram

Peak Table
Detector Channel 1 230nm
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<thead>
<tr>
<th>Peak</th>
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<th>Area</th>
<th>Height</th>
<th>Conc.</th>
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</thead>
<tbody>
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Detector Channel 2 254nm
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<th>Area</th>
<th>Height</th>
<th>Conc.</th>
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</thead>
<tbody>
<tr>
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<td>2</td>
<td>35.060</td>
<td>5745790</td>
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<tr>
<td>Total</td>
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<td>5840937</td>
<td>61717</td>
<td></td>
</tr>
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</table>

Analysis Report

Sample Information
Sample Name: 8463-43-4-aee-00-10-1.0-230-254nm-1
Sample ID: 8463-43-4-aee-00-10-1.0-230-254nm-1.lcd
Method Filename: xl2-230-254-1.0.lcm
Batch Filename: 1-1
Injection Volume: 20 μL
Date Acquired: 2021/10/12 18:42:17
Date Processed: 2021/10/12 19:27:35
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram

Peak Table
Detector Channel 2 254nm
<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Conc.</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>17.340</td>
<td>80548</td>
<td>2502</td>
<td>1.627</td>
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<tr>
<td>2</td>
<td>35.060</td>
<td>5745790</td>
<td>59215</td>
<td>98.373</td>
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<tr>
<td>Total</td>
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<td>5840937</td>
<td>61717</td>
<td></td>
</tr>
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D:\Data\ILD\06-8463-43-4-RAC-00-10-1.0-230-254nm-1.lcd  D:\Data\ILD\06-8463-43-4-aee-00-10-1.0-230-254nm-1.lcd
Analysis Report

Sample Information
Sample Name: IJ-67-rac-adi-99-1-1.0-190-210-2
Sample ID: 84-67-rac-adi-99-1-1.0-190-210-2
Data Filename: x:239-254-1.0-icm
Method Filename: x:239-254-1.0-icm
Batch Filename: x:239-254-1.0-icm
Injection Volume: 20 µL
Date Acquired: 2021/11/18 10:22:32
Acquired by: System Administrator
Date Processed: 2021/11/18 10:21:31
Processed by: System Administrator

<Chromatogram>

<Peak Table>
Detector A Channel 2 210nm
Peak Ret. Time Area Height Conc.
1 12.730 3411504 10002 49.598
2 13.906 3466826 17968 50.402
Total 6876330 279800

rac-6y

Ph
H
CO₂Et
CO₂Et

Analysis Report

Sample Information
Sample Name: IJ-67-ass-adh-99-1-1.0-190-210-2
Sample ID: 84-67-ass-adh-99-1-1.0-190-210-2
Data Filename: x:239-254-1.0-icm
Method Filename: x:239-254-1.0-icm
Batch Filename: x:239-254-1.0-icm
Injection Volume: 20 µL
Date Acquired: 2021/11/18 10:22:32
Acquired by: System Administrator
Date Processed: 2021/11/18 10:21:31
Processed by: System Administrator

<Chromatogram>

<Peak Table>
Detector A Channel 2 210nm
Peak Ret. Time Area Height Conc.
1 12.950 3491597 10961 1.410
2 13.934 34378035 1136912 98.590
Total 34896902 1146731

6y

Ph
H
CO₂Et
CO₂Et

D:\Dat\ii\LD\ii\id-67-rac-adi-99-1-1.0-190-210-1.lcd
D:\Dat\ii\LD\ii\id-67-ass-adh-99-1-1.0-190-210-2.lcd

365
103 ill-II-wanji-RAC-IF-230-1.0-3

Sample Name: ill-II-wanji-RAC-IF-230-1.0-3  
Injection Volume: 20.0

Vial Number: 465  
Channel: UV_VIS_1

Sample Type: standard  
Wavelength: 230

Control Program: XSL  
Bandwidth: n.a.

Quantif. Method: XSL  
Dilution Factor: 1.0000

Run Time (min): 9.91  
Sample Amount: 1.0000

---

101 ill-II-wanji-ASY-IF-230-1.0-2

Sample Name: ill-II-wanji-ASY-IF-230-1.0-2  
Injection Volume: 20.0

Vial Number: 463  
Channel: UV_VIS_1

Sample Type: standard  
Wavelength: 230

Control Program: XSL  
Bandwidth: n.a.

Quantif. Method: XSL  
Dilution Factor: 1.0000

Run Time (min): 10.87  
Sample Amount: 1.0000

---

**rac-6ab**

\[
\begin{align*}
\text{rac-6ab} & = \begin{cases} 
\text{COOEt} & \text{O} \\
\text{COOEt} & \text{O} \\
\end{cases} \\
\end{align*}
\]

**6ab**

\[
\begin{align*}
\text{6ab} & = \begin{cases} 
\text{COOEt} & \text{O} \\
\text{COOEt} & \text{O} \\
\end{cases} \\
\end{align*}
\]
Analysis Report

Sample Information:
- Sample Name: LIL-LEMPBAS-ADH-98-2-254-230-1.0-2
- Data Filename: LIL-LEMPBAS-ADH-98-2-254-230-1.0-2.lcd
- Batch Filename: xil-230-254-1.0.lcm
- Vial #: 1-1
- Sample Type: Unknown
- Injection Volume: 20 µL
- Date Acquired: 2021/12/01 13:25:40
- Acquired by: System Administrator
- Date Processed: 2021/12/01 21:07:30
- Processed by: System Administrator

Chromatogram:

Peak Table:

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<th>Conc</th>
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<tbody>
<tr>
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<td>6049</td>
<td>45.655</td>
</tr>
<tr>
<td>2</td>
<td>14928</td>
<td>53800</td>
<td>46.126</td>
</tr>
<tr>
<td>3</td>
<td>16176</td>
<td>4565</td>
<td>3.796</td>
</tr>
<tr>
<td>4</td>
<td>16754</td>
<td>4261</td>
<td>4.433</td>
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<td>Total</td>
<td>225372</td>
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Detector A Channel 2 230nm

Analysis Report

Sample Information:
- Sample Name: LIL-LEMPBAS-ASV-ADH-98-2-254-230-1.0-2
- Data Filename: LIL-LEMPBAS-ASV-ADH-98-2-254-230-1.0-2.lcd
- Batch Filename: xil-230-254-1.0.lcm
- Vial #: 1-1
- Sample Type: Unknown
- Injection Volume: 20 µL
- Date Acquired: 2021/12/01 13:53:16
- Acquired by: System Administrator
- Date Processed: 2021/12/01 14:14:47
- Processed by: System Administrator

Chromatogram:

Peak Table:

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<th>Area</th>
<th>Height</th>
<th>Conc</th>
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<tr>
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<tr>
<td>2</td>
<td>14928</td>
<td>53800</td>
<td>46.126</td>
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<td>16176</td>
<td>4565</td>
<td>3.796</td>
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<tr>
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<td>16754</td>
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<tr>
<td>Total</td>
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Detector A Channel 2 230nm
Analysis Report

<Sample Information>
Sample Name: LIL-LE-103-RAC-ODH-98-2-254-230-1
Sample ID: 
Data Filename: LIL-LE-103-RAC-ODH-98-2-254-230-1.lcd
Method Filename: xil-230-254-1.0.in
Batch Filename: 
Vial #: 1:1
Injection Volume: 20 µL
Date Acquired: 2021/12/20 9:49:03
Date Processed: 2021/12/20 10:57:27
Sample Type: Unknown

<Chromatogram>

<Peak Table>

D:/Dropbox/LIL-LE-103-RAC-ODH-98-2-254-230-1.lcd
D:/Dropbox/LIL-LE-103-ASY-ODH-98-2-254-230-1.lcd

370
Analysis Report

Sample Information:
Sample Name: LIL-LF-17-RAC-OJH-75-25-1.0-254-230-1
Sample ID: LIL-LF-17-RAC-OJH-75-25-1.0-254-230-1
Data Filename: LIL-LF-17-RAC-OJH-75-25-1.0-254-230-1.ldc
Method Filename: gax-1.0-254-1.1cm
Batch Filename: gax-1.0-254-1.1cm
Vial #: 1:1
Sample Type: Unknown
Injection Volume: 10.0 µL
Date Acquired: 2022/1/11 11:43:06
Acquired by: System Administrator
Date Processed: 2022/1/11 12:11:20
Processed by: System Administrator

Chromatogram:

Peak Table:

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<th>Area</th>
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<tbody>
<tr>
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D:\Data\LIL-LF-17-RAC-OJH-75-25-1.0-254-230-1.ldc

Analysis Report

Sample Information:
Sample Name: LIL-LF-17-ASY-OJH-75-25-1.0-254-230-1
Sample ID: LIL-LF-17-ASY-OJH-75-25-1.0-254-230-1
Data Filename: LIL-LF-17-ASY-OJH-75-25-1.0-254-230-1.ldc
Method Filename: gax-1.0-254-1.1cm
Batch Filename: gax-1.0-254-1.1cm
Vial #: 1:1
Sample Type: Unknown
Injection Volume: 10.0 µL
Date Acquired: 2022/1/11 12:14:49
Acquired by: System Administrator
Date Processed: 2022/1/11 12:25:34
Processed by: System Administrator

Chromatogram:

Peak Table:

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<tr>
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D:\Data\LIL-LF-17-ASY-OJH-75-25-1.0-254-230-1.ldc

Ph
rac-11

Ph
11
Analysis Report

Sample Information
Sample Name: IL-LF-12-RAC-0XH-95-5-254-230-1
Sample ID: 
Data Filename: IL-LF-12-RAC-0XH-95-5-254-230-1.lcd
Method Filename: 1.5.lcm
Batch Filename: 
Vial #: 1:1
Injection Volume: 10.5 µL
Date Acquired: 2022/1/1 19:12:05
Data Processed: 2022/1/1 19:48:21
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram

Peak Table

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<tr>
<th>Peak Ref. Time</th>
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<th>Height</th>
<th>Conc.</th>
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<tbody>
<tr>
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<td>28.988</td>
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<td>35485</td>
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</table>

Analysis Report

Sample Information
Sample Name: IL-LF-28-ASY-0XH-90-10-1.0-254-230-1
Sample ID: 
Data Filename: IL-LF-28-ASY-0XH-90-10-1.0-254-230-1.lcd
Method Filename: 1.5.lcm
Batch Filename: 
Vial #: 1:1
Injection Volume: 10.5 µL
Date Acquired: 2022/1/1 19:12:05
Data Processed: 2022/1/1 19:48:21
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram

Peak Table

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<tr>
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<th>Conc.</th>
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<tbody>
<tr>
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Analysis Report

Sample Information:
Sample Name: LIL-LF-25-RCY-OHD-90-10-0.10-54-230-1
Sample ID: 1.1
Data Filename: LIL-LF-25-RCY-OHD-90-10-0.10-54-230-1.lcd
Method Filename: gey-1.0-54-1.1cm
Batch Filename: gey-1.0-54-1.1cm
Vial #: 1.1
Injection Volume: 10 µL
Date Acquired: 2022/11/14 21:12
Date Processed: 2022/11/14 21:25
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram:

Peak Table:

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D:/Data/LIL-LF/LIL-LF-25-RCY-OHD-90-10-0.10-54-230-1.lcd

Analysis Report

Sample Information:
Sample Name: LIL-LF-26-ASY-OHD-90-10-0.254-230-1
Sample ID: 1.1
Data Filename: LIL-LF-26-ASY-OHD-90-10-0.254-230-1.lcd
Method Filename: gey-1.0-254-1.1cm
Batch Filename: gey-1.0-254-1.1cm
Vial #: 1.1
Injection Volume: 10 µL
Date Acquired: 2022/11/15 11:27:42
Date Processed: 2022/11/15 11:42:17
Sample Type: Unknown
Acquired by: System Administrator
Processed by: System Administrator

Chromatogram:

Peak Table:

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</tr>
</tbody>
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D:/Data/LIL-LF/LIL-LF-26-ASY-OHD-90-10-0.254-230-1.lcd

Ph 14 F O